SYNTHESIS, RELATED MECHANISTIC AND STRUCTURAL STUDIES OF CYCLITOLS AND THEIR DERIVATIVES

THESIS

SUBMITTED TO THE

UNIVERSITY OF PUNE

FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN

CHEMISTRY

BY

BHARAT P. GURALE

DR. M. S. SHASHIDHAR

RESEARCH SUPERVISOR

DIVISION OF ORGANIC CHEMISTRY

NATIONAL CHEMICAL LABORATORY

PUNE 411 008, INDIA

February 2012

Dedicated to my Beloved Parents and Brother...

NATIONAL CHEMICAL LABORATORY

(Council of Scientific and Industrial Research)

Dr. Homibhabha Road, Pune – 411008, INDIA.

CERTIFICATE

This is to certify that the work incorporated in the thesis entitled "**Synthesis, Related Mechanistic and Structural Studies of Cyclitols and their Derivatives**" submitted by **Bharat P. Gurale** was carried out by him under my supervision at the National Chemical Laboratory, Pune, India. Such materials, obtained from other sources have been duly acknowledged in the thesis.

Date: 2011

Division of Organic Chemistry

National Chemical Laboratory

Pune-411 008, India

(Dr. M. S. SHASHIDHAR)

Research Supervisor

Communication Channels:

☎ FAX

NCL Level DID : 2590

NCL Board No : +91-20-25902000

EPABX : +91-20-25893300

+91-20-25893400

Director's Office : +91-20-25902601

COA's Office : +91-20-25902660

COS&P's Office : +91-20-25902664

Website: www.ncl-india.org

National Chemical Laboratory, Pune (India)

DECLARATION

I hereby declare that the thesis entitled **"Synthesis**, **Related Mechanistic and Structural Studies of Cyclitols and their Derivatives"** submitted for Ph.D. degree to the University of Pune has been carried out at National Chemical Laboratory, under the supervision of **Dr. M. S. Shashidhar**. This work is original and has not been submitted in part or full by me for any degree or diploma to any university.

Date:

Division of Organic Chemistry,
National Chemical Laboratory,
Pune-411 008

(BHARTA P. GURALE)

Acknowledgements

I wish to express my deep sense of gratitude and profound thanks to my research supervisor ***Dr. M. S. Shashidhar*** *for introducing me to the fascinating field of inositol chemistry. His systematic working style, logical way of thinking and humanitarianism is an attribute that I wish to take forward with me along with the chemistry that I learnt from him.*

I would like to thank X-ray crystallography group Dr. M. M. Bhadbhade, Dr. R. G. Gonnade, Dr. K. Manoj and Dr. Shobhana K. for their great help in determining the x-ray structures.

I wish to express my gratitude to Dr. Kumar Vanka for teaching me theoretical (DFT) calculations.

I would like to thank Dr. S. P. Chavan and Prof. D. D. Dhawale for their valuable suggestions and scientific discussion during assessment of my Ph.D. work.

My sincere thanks to scientists of the division; Dr. G. Pandey (HOD), Dr. N. N. Joshi, Dr. P. K. Tripathi, Dr. R. A. Joshi, Dr.(Mrs.) V. A. Kumar, Dr. N. P. Argade, Dr. G. J. Sanjayan, Dr. H. V. Thulasiram, Dr. C. V. Ramana, Dr. Reddy, Dr. R. P. Singh, Dr. Santosh Mhaske, Dr. S. Iyer, Dr. (Mrs.) A. P. Likhithe, Dr. (Mrs.) S. P. Maybhate, Dr. Muthukrishnan, Dr. A. T. Biju and others. I wish to thank Dr. A. Sudalai and Dr. Gurunath (CEPD Division), Dr. P. A. Joy, Mrs. Puranik and Mrs. Kolhe (SAC office) for their help.

Help from analytical units for characterization of compounds is gratefully acknowledged. I thank Dr. Rajmohanan for NMR, Dr. U. R. Kalkote for analytical facilities, Mrs. S. P. Kunte, and Dr. Sonawane for HPLC, Mrs. Mane for LC-MS, Dr. P. L. Joshi (and Mrs. Sawant, Mrs. Sanas) for microanalysis. I express my thanks to the office staff, Library members and administrative staff for their timely help.

I wish to thank Dr. Gurav - Dr. Vibhute - Dr. Kuberkar (Bramha-Vishnu-Mahesh of Chemistry Department), Dr. P. A. Kulkarni, Dr. Dawane of Yeshwant Mahavidyalaya, Nanded, Dr. Umatale, Dr. T. M. Patil, Dr. Mule, Dr. Gupta, Dr. Sabbanwad (Shivaji Mahavidyalaya, Udgir), Mr. N. D. Biradar, Mr. M. S. Bolegave, Mrs. Padkonde, Mr. Banate (Nrusinha Vidyalaya, Ankulga (Rani) for excellent teaching and time encouragement.

It gives me immense pleasure to express my sincere thanks to my senior colleagues; Dr. M. Sarmah, Dr. S. Devaraj, Dr. S. Deshpande, Dr. C. Murali, Mrs. Madhuri Patil, Dr. Rajendra and especially Dr. Shailesh Dixit for their friendly nature, giving excellent training, valuable discussion and support. I am thankful to my labmates Alson, Tamboli, Richa, Jayendra, Niharika and Rohit for maintaining cheerful atmosphere in the lab. I would like to thank Moreji for help and lab maintenance.

I would like to thank Dr. (Mrs.) Vidya Shashidhar, Mrs. Vaishali Gonnade, Dr. (Mrs.) Vedavati Puranik and Mrs. Nandini Dixit for their advices and help.

I thank all my friends at NCL: Dr. Nagendra, Dr. Kulbhushan, Dr. Kotkar, Dr. Sharad, Dr. Pandurang, Dr. Haval, Dr. Abasaheb, Dr. Manmath, Dr. Suleman, Dr. Bande, Dr. Vishwas, Dr.

Korbad, Dr. Sachin, Dr. Amol, Dr. Sachin, Dr. Deepak, Dr. Sudhir, Dr. Namdev, Dr. Bapu, Dr. Nilkanth, Dr. Swaroop, Dr. Prasanna, Dr. Prasad, Dr. Umesh, Dr. Giri, Dr. Nilkant, Dr. Purude, Dr. Moneesha, Dr. Nishant, Dr. Puspesh, Dr. Abhishekh, Dr. Madhuri, Dr. Ravindra, Dr. Rajender, Dr. Sharan, Dr. Namrata, Dr. Tanveer, Dr. Ramesh, Dr. Arun, Dr. Victor, Dr. Shyla, Dr. Emanual, Dr. Nagesh, Dr. Ajay Kale, Dr. Bhaskar, DeepakBhau, Satish, Ravi, Sutar, Kishor, Seema, Venu, Kiran, Manoj, Namrata, Mahesh, Amrut, Debashish, Sujit, Deepak, Rajesh, Tukaram, Sangram, Ramesh, Arup, Sangram, Vijay, Sachin, Vijayadas, Ganesh, Gauri, Roshna, Sanjeev, Prashant, Mandeep, Ramesh, Pankaj, Swati, Ashish, Harshal, Kishor, Lalit, Nilesh, Pradeep, Prakash, Sumanta, Kailash, Harshali, Sunil, Shijo, Krishanu, Partha, Rahul, Divya, Kiran, Menka, Shruti, Pronoy, Rohan, Pitambar, Rahul Patil, Sachin, Chandrababu, Yadagiri, Atul, Pankaj, Mangesh, Sangmesh, Anand, Rupesh, Pranaya, Mangesh, Dhanu, Nagesh, Chinmay, Anil, Manik, Maroti, Shivaji, Sarpanch, Gopi, Tavade, Sane, Pathan, Amol, Ajay, Narayan and others. I will cherish their company in NCL for long time.

I wish to thank my College friends: Rayewar, Pawar², Shivpuje, Shrimant, Sawargave, Padre, Khallal, Yogesh, Harish, Nitin Jagtap, Mate, Ankush, Abbas, Chivde, Kokane guruji, Kalme, Sudhir, Amol Deshmukh, Anantwad, Mahesh, Modani, Lalpotu, Vijay, Ramu, Satish, Sandy, Sunil, Pravin², Harshal, Huple, Manju, Veena, Kirti, Akanksha, Trupti, Kalpana, Marakwad, Chaudhari; my PG senior's Selukar, Shrikar, Todewale, Omprakash, Avinash, Ningdale, Kedar, Gound, Komple, Sachin, Jyoti, Satish Biradar, Krishna, for their company in my college days and in NCL for long time.

A lots of thanks goes to my friends Avinash (Balu), Manoj, Sarpanch (Ramesh), Kumar, Hariom, Madhav, Rambhau, Balaji, Sada Patil, Raju,Viju (Innova), Vijay (guruji), Ranjan Pandey, Sambha, Kishor, Paka, Rameshwar, Ganesh, Vishu, Vilas, Shivdarshan, Bhauji (upper), Waghambar, Pintu, Eaknath, Pavan, Anil, Deepak, Balaji, (uncles: Pitaji and Nana), Sarnikar Sir who directly or indirectly helped me during my doctoral research.

I would like to express a deep sense of gratitude to my Brother (and Vahini, Nikita, Neha, Nilesh), and my parents for their blessing, love, care and constant encouragement throughout my life. I would like extend my thanks to my wife Priya for her endless support, love and affection.

I would like to thank the Council of Scientific and Industrial Research (CSIR), New Delhi for the award of fellowship. I am thankful to Dr. Ganesh Pandey, Head of organic chemistry division and Dr. S. Pal, Director, NCL for opportunity to work in this prestigious research institute and providing all necessary infrastructure and facilities.

29 th February 2012 *Bharat*

CONTENTS

Abbreviations

Ac	Acetyl
Ac_2O	Acetic anhydride
AcCl	Acetyl chloride
AIBN	Azobisisobutyronitrile
All	Allyl
Anhd.	Anhydrous
aq.	Aqueous
Bn	Benzyl
BnBr	Benzyl bromide
Boc	*tert*-Butyloxycarbonyl
BuLi	Butyl lithium
Bz	Benzoyl
BzCl	Benzoyl chloride
Calcd	Calculated
Cat.	Catalytic
Concd	Concentration
CSA	Camphorsulfonic acid
COSY	Correlation Spectroscopy
DCC	N,N'-Dicyclohexylcarbodiimide
D_2O	Deuterium Oxide
DCM	Dichloromethane
DDQ	2,3-Dichloro-5,6-dicyano-1,4-benzoquinone
DFT	Density Functional Theory
DIBAL-H	Diisobutyl aluminium Hydride
dil.	Dilute
DIPEA	Di-isopropyl ethyl amine
DMAP	*N, N*-dimethylamino pyridine
DMF	*N, N*-Dimethylformamide
DMM	Dimethoxymethane
DMSO	Dimethyl sulfoxide
eq.	Equivalent

EDC·HCl	1-Ethyl-3-(3-dimethyllaminopropyl)carbodiimide hydrochloride
Et_3N	Triethylamine
g	Gram
GPI	Glycophosphatidylinositol
HOBt	1-Hydroxybenzotriazole
h	Hour (s)
Hz	Hertz
i$BuNH_2$	*iso*-Butyl amine
IBX	2-Iodoxybenzoic acid
IR	Infrared
KOAc	Potassium acetate
KOBz	Potassium benzoate
LC-MS	Liquid chromatography-mass spectrometry
LDA	Lithium diisopropylamide
L-selectride	Lithium tri-*sec*-butylborohydride
*m*CPBA	3-Chloroperbenzoic acid
Mp	Melting point
Me	Methyl
MeOH	Methanol
MeI	Methyliodide
Mes	Mesityl
mg	Milli gram
min.	Minute(s)
mL	Milliliter
mmol	Milli moles
MsCl	Methane sulfonyl chloride
$NiCl_2$(dppp)	[1,3-bis(diphenylphosphino)propane]dichloronickel(II)
NaOMe	Sodium methoxide
NMR	Nuclear magnetic Resonance
NMO	N-Methylmorpholine-N-oxide

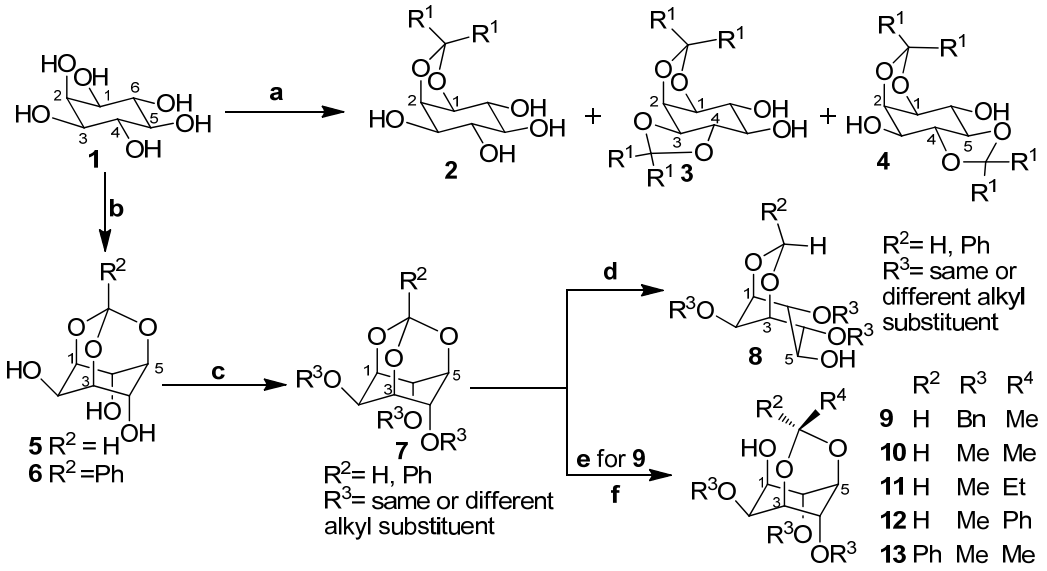
nOe	Nuclear Overhauser Effect
NOESY	Nuclear Overhauser Effect Spectroscopy
ORTEP	Oak Ridge Thermal Ellipsoid Plot Program
$Pd(dba)_2$	Bis(dibenzylideneacetone) palladium(0)
Ph	Phenyl
PI-PLC	Phosphatidylinositol-specific phospholipase C
PMB	4-Methoxy benzyl
PCB	4-Chloro benzyl
PBB	4-Bromo benzyl
PPTS	Pyridinium para toluene sulfonate
PIP_3	Phosphatidylinositol-3,4,5-tris-phosphate
Py	Pyridine
rac-	Racemic
rt	Room temperature (23–30 ^oC)
TBS	*tert*-Butyldimethylsilyl
TMS	Trimethylsilyl
TFA	Trifluoroacetic acid
TFAA	Trifluroacetic anhydride
Tf_2O	Trifluoromethanesulfonic anhydride
THF	Tetrahydrofuran
TLC	Thin layer chromatography
TsCl	4-Toluene sulfonyl chloride
TsOH	4-Toluene sulfonic acid

Synopsis of the thesis

The thesis entitled '**Synthesis**, **Related Mechanistic and Structural Studies of Cyclitols and their Derivatives**' consists of four chapters. Chapter 1 is a review on the utility of *myo*-inositol 1,3-acetals for the synthesis of biologically or medicinally relevant natural products, natural and unnatural inositol derivatives such as phosphoinositols and their analogs etc. Chapter 2 presents the synthesis of deoxy- and dideoxy inositol derivatives, and related mechanistic study of dideoxygenation involving intramolecular abstraction of the benzylidene hydrogen by radical generated (under Barton – McCombie conditions) from a monoxanthate derivative of *myo*-inositol. Three sections in Chapter 3, describe (a) the synthesis of inosamine and aminocyclitol moiety present in Hygromycin A and Methoxyhygromycin from *myo*-inositol; (b) preparation of 2-*C*-alkyl/aryl derivatives of *neo*-inositol from *myo*-inositol; and (c) the synthesis of differentially protected tetrahydroxy benzenes starting from *myo*-inositol. Chapter 4 presents a conformational study of bicyclic inositol derivatives by using 2D NMR spectroscopy, X-ray crystallography and DFT calculations. Most of these bicyclic derivatives were synthesized in previous chapters and data on others were obtained from the literature. Chapters 2 and 3 have detailed experimental procedures, spectroscopic, crystallographic and analytical data relevant to the results described in the respective chapter.

Chapter 1. A review on the synthetic utility of inositol 1,3-acetals.

myo-Inositol and its derivatives / analogs have become conspicuous in the literature related to chemistry and biology due to the involvement of phosphoinositols in cellular signal transduction mechanisms and anchoring of certain proteins to cell membranes.[1] However, the intricacies and biological implications of the *myo*-inositol cycle are not yet unraveled completely. Many synthetic methodologies and techniques have been developed in the recent past for the synthesis of inositol derivatives useful in the study of the inositol cycle. Some of these methods have also been used for the synthesis of natural products (other than inositol derivatives) and their analogs.[2]



Scheme 1. (a) DMF, R^1COR^1, TsOH; (b) DMF, $R^2C(OEt)_3$ or $R^2C(OMe)_3$, TsOH, 110-140 °C; (c) DMF, NaH or LiH, alkyl halide; (d) DCM, DIBAL-H (2.2 eq), rt; (e) DCM, Me_3Al, rt; (f) benzene, R^4MgX (2 eq), reflux.

1,2 acetal derivatives **2**–**4** (scheme 1) of *myo*-inositol have been frequently used as early intermediates for the synthesis of various classes of compounds mentioned above, although the acetalization of *myo*-inositol **1** often leads to the formation of all possible isomeric acetals, which have to be separated. In contrast, the 1,3-bridged acetals **8**–**13** of *myo*-inositol on the other hand can be prepared as single products in good yields. The differentially protected *myo*-inositol 1,3-acetals as well as 1(3),5-acetals can be obtained *via* selective Lewis acid-mediated reductive or alkylative cleavage of *O*-protected orthoester derivatives of *myo*-inositol. The 1,3-acetals can be obtained by reduction[3] with DIBAL-H while 1(3),5-acetals can be obtained by cleavage with trimethylaluminium[3a] or alkyl magnesium halides.[4] There does not appear to be any report on the preparation of such 1,3-acetals from the corresponding 1,3-diols by classical acid catalyzed ketalization reactions.

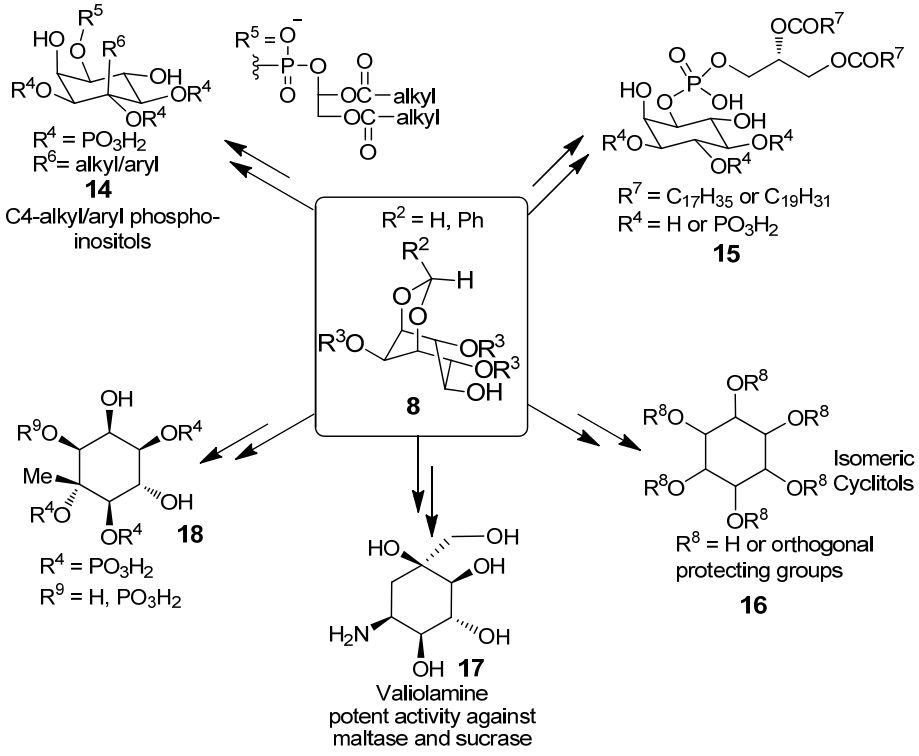
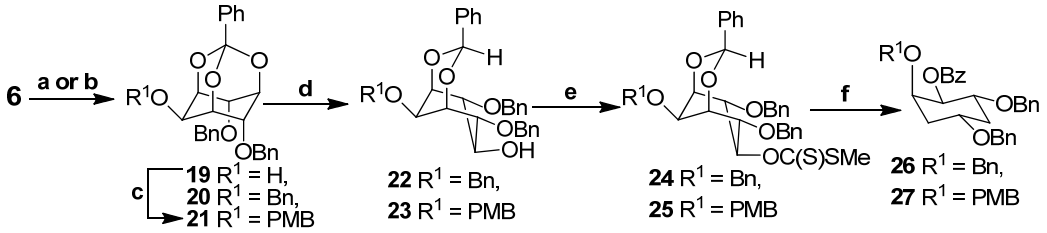


Figure 1.

These bridged acetals provide opportunities for new selective reactions (of the inositol hydroxyl groups) since conformation of the two six membered rings deviate from the normal chair conformation. Hence, 1,3-acetals of *myo*-inositol derivatives have the potential to emerge as useful intermediates for the preparation of many biologically relevant inositol derivatives (Figure 1).[5] The results described in the present thesis is an attempt to exploit the synthetic utility of *myo*-inositol 1,3-acetals.

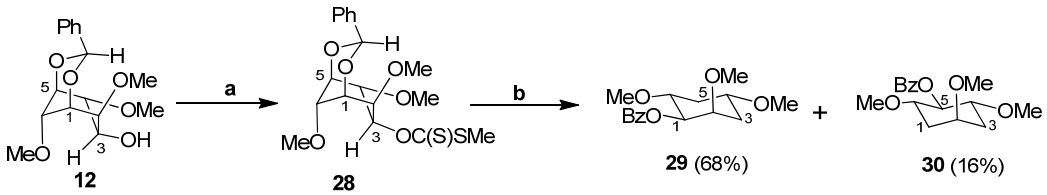
Chapter 2. **Synthesis of deoxy and dideoxy cyclitol derivatives and related mechanistic studies.**

Cyclohexane pentols or mono-deoxy inositols are referred to, using the generic term, 'Quercitols'. Among the sixteen isomers reported in the literature, (+)-*proto*-, (-)-*proto*- and (-)-*vibo*- quercitols occur in nature.[6] The biological activity shown by some of these quercitols against glycosidases led to an interest in the synthesis of natural and unnatural quercitols as well as their derivatives / analogs. This chapter describes the detailed mechanistic study of the radical mediated (Barton – McCombie deoxygenation conditions) dideoxygenation of monoxanthates **24** and **25** (Scheme 2). This deoxygenation reaction provides novel routes for the synthesis of 5-deoxy, 1,3-dideoxy and 3, 5-dideoxy *myo*-inositols.[7]



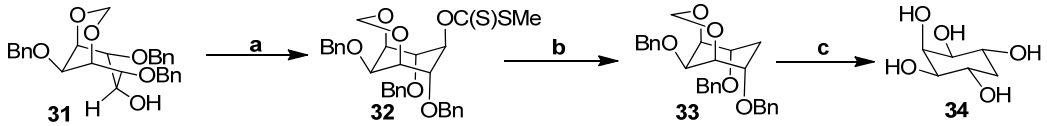
Scheme 2. (a) DMF, LiH, BnBr, rt, 12 h, 81% (for **19**); (b) DMF, NaH, BnBr, rt, 3 h, 98% (for **20**); (c) DMF, NaH, PMBCl, rt, 3 h, 96%; (d) DCM, DIBAL-H, 0 °C, 80–94%; (e) THF, NaH, CS_2, MeI, rt, 16 h, 96-98%; (f) toluene, *n*-Bu_3SnH, AIBN, reflux, 1 h, 92%.

To examine the versatility of the newly discovered dideoxygenation of the inositol derived monoxanthates,[7] we prepared the C3-xanthate **28** (with 1,5-benzylidene acetal, scheme 3). Deoxygenation of the xanthate **28** led to the formation of two isomeric dideoxy inositols. The 3,5-dideoxyinositol derivative **29** was obtained as the major product.



Scheme 3. (a) NaH, THF, CS_2, MeI, rt, 16 h, 94%; (b) toluene, *n*-Bu_3SnH, AIBN, reflux, 1 h.

We also carried out the deoxygenation reaction on the xanthate **32** (Scheme 4), which has a methylidene acetal instead of the benzylidene acetal. This reaction gave the monodeoxygenated product **33** and hence this provided a route for the synthesis of *neo*-quercitol (**34**, 6 steps, 77% overall yield).

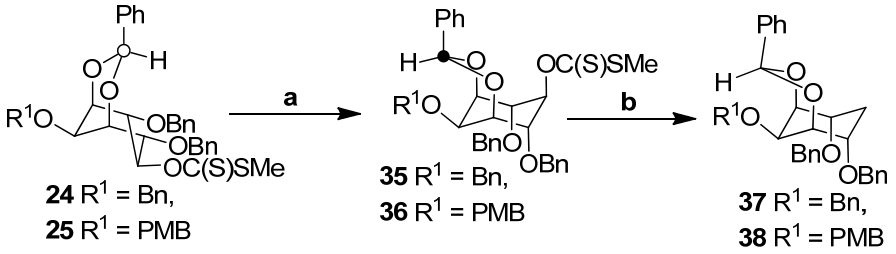


Scheme 4. (a) NaH, CS_2, MeI, rt, 16 h, 99%; (b) toluene, *n*-Bu_3SnH, AIBN, reflux, 1 h, 95%; (c) i) THF:H_2O, HCl, reflux, 2 h; ii) MeOH, 10% $Pd(OH)_2$/C, H_2 (60 psi), rt, 10 h, 92% (for 2 steps).

Various aspects related to the deoxygenation reaction shown in Scheme 2, investigated, are mentioned below.

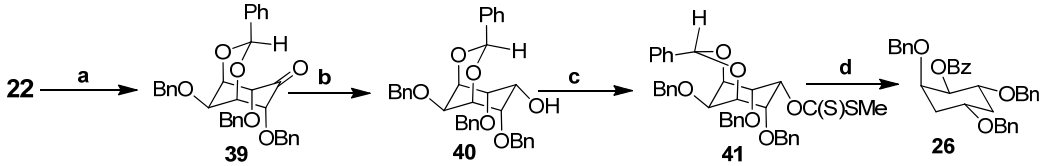
(a) Whether cleavage of the benzylidene acetal takes place by intermolecular or intramolecular hydrogen abstraction was examined by (i) deoxygenation of the xanthate **24** in the presence of the alcohol **22**; (ii) deoxygenation of epimers (**35**, **36**, Scheme 5) of xanthates **24** and **25**. Results of both these experiments revealed that the cleavage of the benzylidene acetal was due to intramolecular abstraction of the corresponding acetal hydrogen atom, in the radical initially produced. The

xanthates **35** and **36** when subjected to radical deoxygenation conditions provided the monodeoxy derivatives since intramolecular hydrogen abstraction is sterically forbidden in these molecules.



Scheme 5. (a) Heat, 120°C (12 h for **24**, 30 h for **25**), 70-72%; (b) toluene, *n*-Bu_3SnH, AIBN, reflux, 1 h, 80-92%.

(b) To understand whether the relative orientation of the xanthate or the conformation of the inositol ring affects the reaction, we carried out deoxygenation of the *neo*-xanthate (**41**, Scheme 6) but there was no difference in product formation. Although the configuration of the carbon carrying the xanthate and conformation of both the six memebered rings in xanthates **24** and **41** are different, deoxygenation reaction gave the same result (Scheme 6). This suggested that the deoxygenation reaction perhaps proceeds through the same radical intermediate. Conformation of the *myo*- and *neo*- xanthates **24**, **25** and **41** was established by single crystal X-ray diffraction methods.



Scheme 6. (a) EtOAc, IBX, reflux, 3 h, 95%; (b) EtOH, $NaBH_4$, rt, 3 h, 98%; (c) THF, NaH, CS_2, MeI, rt, 16 h, 98%; (d) toluene, *n*-Bu_3SnH, AIBN, reflux, 1 h, 94%.

In principle, the two six membered rings in xanthates **24** and **41**, can exist either in the chair or in the boat conformation giving rise to four distinct conformers. 2D-NMR spectroscopy of the *myo*-xanthate **24** and **25** suggested that the molecular conformation in the crystal is conserved in the solution state as well; but for the *neo*-xanthate **41** (in which the benzylidene acetal ring has the boat conformation in the crystalline state), nOe spectroscopy suggested that the benzylidene acetal ring is in the chair conformation in the solution state. We also carried out geometrical optimization studies (DFT calculations) results of which suggested that either the xanthates or the radicals produced from them undergo conformational change prior to intramolecular

proton abstraction. Results of the geometrical optimization studies for the *neo*-xanthate **41** are shown in Figure 2 for illustration.

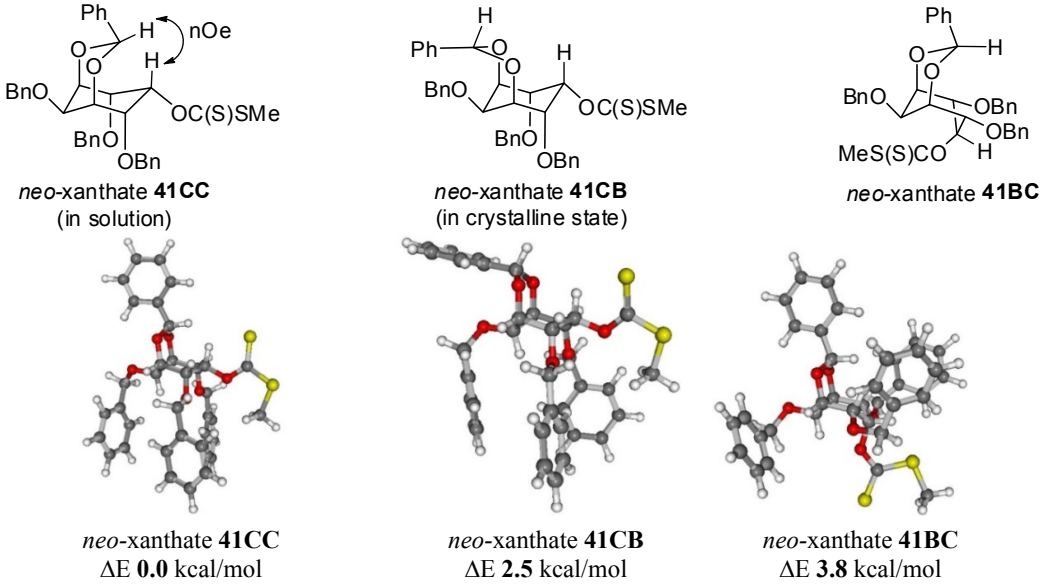
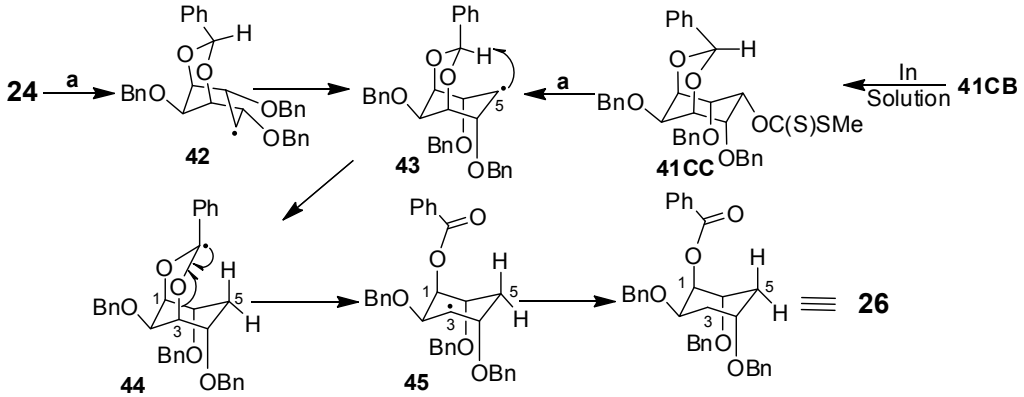


Figure 2.

Hence based on the experimental observations and DFT calculations, the plausible mechanism for the deoxygenation of the xanthates is shown in Scheme 7.



Scheme 7. (a) toluene, *n*-Bu_3SnH, AIBN, reflux.

Chapter 3, *myo*-Inositol-1,3-acetals as early intermediates for the synthesis of polyphenols and analogs of inositols.

Section A. Synthesis of aminocyclitols

Interest in the synthesis of aminocyclitols and their derivatives is because of their presence in antibiotics and their ability to function as glycosidase inhibitors. This section presents the synthesis of the aminocyclitol cores of Hygromycin A (HMA, **46**, Figure 3) and methoxyhygromycin (MHM, **47**).

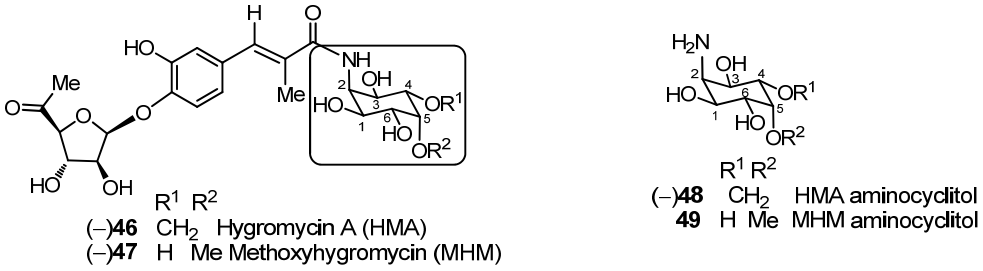
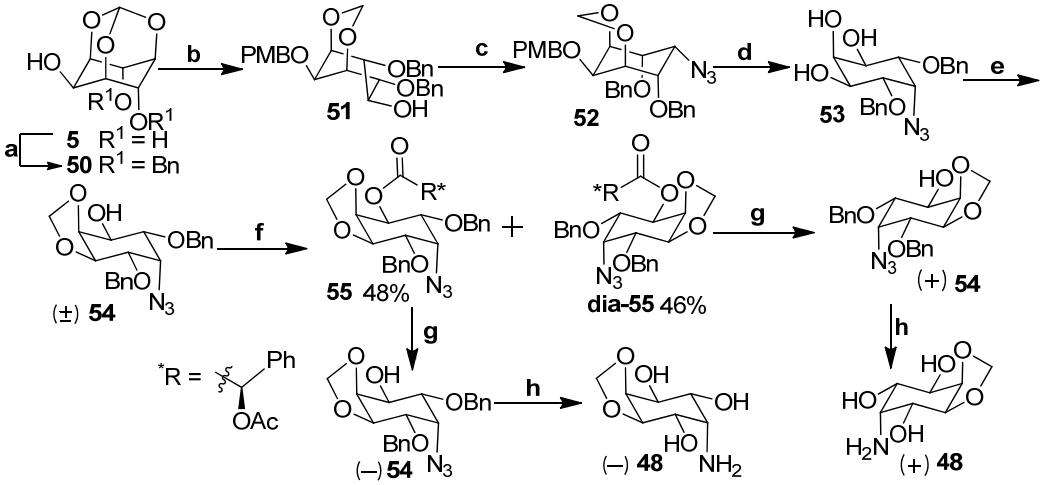


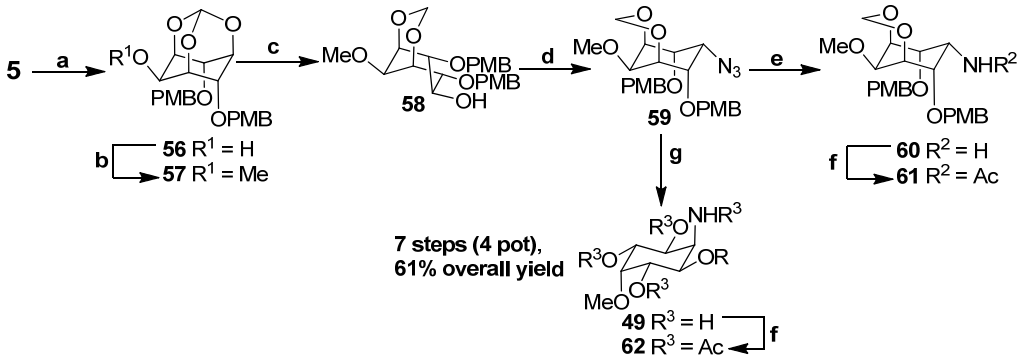
Figure 3.

Our planned synthetic approach (Schemes 8 and 9) involved (i) lithium hydride mediated selective benzylation of the C4- and C6-hydroxyl groups of *myo*-inositol orthoformate (**5**); (ii) regioselective cleavage of orthoformate by DIBAL-H and (iii) stereospecific introduction of the azido group, as a precursor for the amine. The key aminocyclitol portion of Hygromycin A was synthesized in 12 steps and 30% overall yield (with only five coloumn chromatography purifications).

The aminocyclitol unit of MHM was synthesized in 7 steps with 61% overall yield (without column chromatographic purification); these procedures represent the highest yielding routes reported for these compounds. Structures of the compounds **52**, **58**, **59**, **61** and **62** were confirmed by single crystal X-ray diffraction analysis. To date two total synthesis of HMA[8] and one total synthesis of MHM is reported.[9] The aminocyclitol unit **48** has also been synthesized by Trost[10] and Donohoe[8] (13 steps with 10% yield and 14 steps with 20% yield respectively). Aminocyclitol unit of **49** was synthesized from *myo*-inositol by Chida *et al*,[9] in 12 steps with <1% yield.



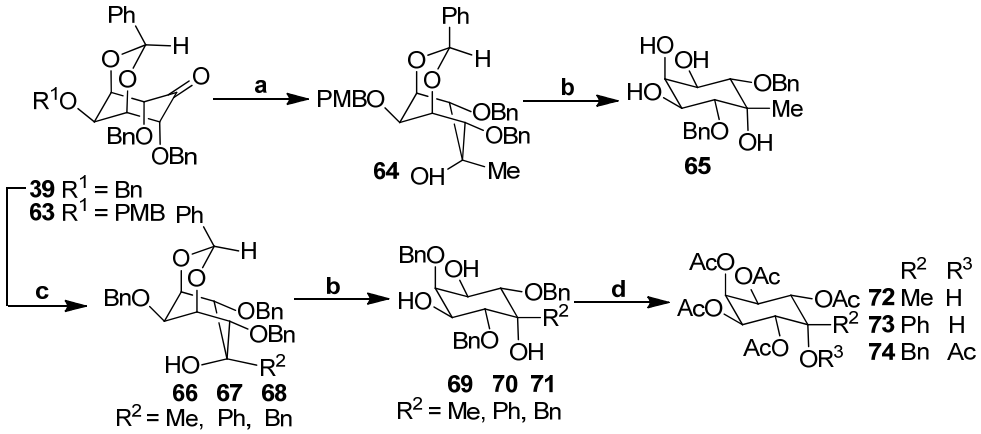
Scheme 8. (a) DMF, LiH, BnBr, rt, 4 h, 84%; (b) i) DMF, NaH, PMBCl, rt, 3 h; ii) DCM, DIBAL-H, 0 °C-rt; (c) i) pyridine:DCM (1:1), Tf_2O, –30 °C-rt , 30 min; ii) HMPA, NaN_3, rt, 10 h, 91% (4 steps); (d) THF**:**MeOH, concd HCl, reflux, 2 h, 98%; (e) i) $H_2C(OMe)_2$, TMSOTf, 2,6-Lutidine, 0 °C-rt; ii) MeOH, TsOH, reflux, 12 h, 94% (2 steps); (f) DCM, R (–)-*O*-acetyl mandelic acid, DCC, DMAP, rt, 3 h; (g) MeOH, KOH, rt, 6 h, 98-99%; (h) MeOH, 10% Pd/C, H_2 (400 psi), rt, 36 h, 91-92%.



Scheme 9. (a) DMF, LiH, PMBCl, rt, 12 h, 84%; (b) DMF, NaH, MeI, rt, 3 h; (c) DCM, DIBAL-H, rt, 3 h; (d) i) pyridine:DCM (1:1), Tf_2O, –10 °C-rt, 1 h; ii) HMPA, NaN_3, rt, 10 h, 88% (4 steps); (e) DCM, H_2O, PPh_3, rt, 2 h; (f) pyridine, Ac_2O, 40 h, 82-84%; (g) MeOH, Pd/C, H_2 (400 psi), concd HCl, 55 °C, 12 h.

Section B. Synthesis of 5-*C*-alkyl/aryl *neo*-inositol derivatives

In this section, synthesis of 5-*C*-alkyl/aryl *neo*-inositols *via* stereoselective addition of alkyl/aryl magnesium halides to *myo*-5-inosose is reported (Scheme 10). The observed selectivity during the nucleophilic addition appears to be due to the conformation of the inositol ring forced by the 1,3-benzylidene acetal ring as well as steric hindrance due to 4,6-*O*-protected benzyl groups in **39** and **63**. Stereochemistry of the products **63**, **67**, **69**, **72**−**74** was established by X-ray crystallography. 5-*C*-alkyl/aryl *neo*-inositol (7 to 8 steps from *myo*-inositol) were obtained in an overall yield of >60%.

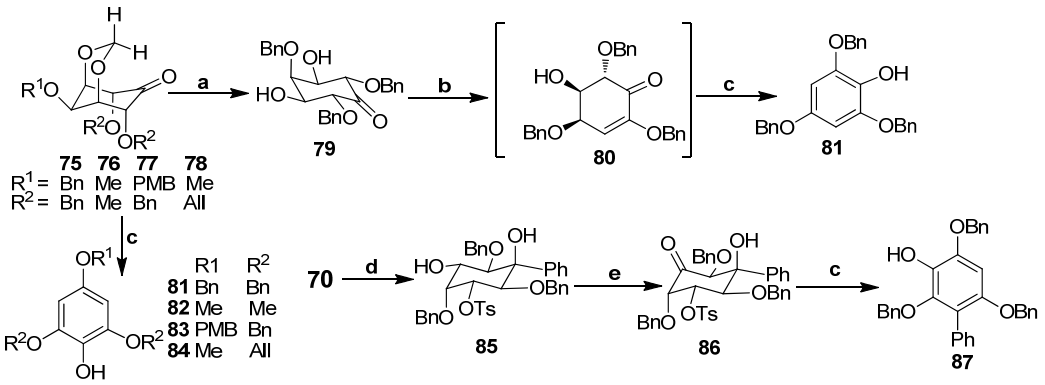


Scheme 10. (a) Et_2O, MeMgI, 0 °C, 2 h, 96%; (b) THF:H_2O, TFA, reflux, 2 h, 88–92%; (c) Et_2O, R^2MgX, 0 °C, 2 h, 90–94%; (d) i) MeOH, 10% Pd/C, H_2 (400 psi), 12 h; ii) pyridine, Ac_2O, DMAP, rt, 24 h, 80–85% (2 steps).

Section C. Inositols to aromatics (benzene free synthesis of tetra hydroxyl benzene derivatives)

This section delineates a novel route to the synthesis of polyhydroxy benzene and biaryl derivatives starting from readily available *myo*-inositol (5 to 6 steps, 55 to 80%

overall yield). We found that the ketones **75**–**79** aromatize to form tetra hydroxyl benzene (THB) derivatives (Scheme 11) in the presence of a base (Et_3N or NaH) at room temperature. We could establish the intermediacy of the α,β-unsaturated ketone **80** in this process by carrying out the reaction under controlled conditions. We have also synthesized the polyhydroxy biaryls from *neo*-2-inosose. Triol **70** on tosylation afforded **85**, which on oxidation with IBX followed by treatment with NaH gave the biaryl **87** in 85% yield.



Scheme 11. (a) THF:MeOH, concd HCl, reflux, 1 h, 91%; (b) THF, Et_3N, –10 °C, 1 h, 94%; (c) THF, NaH, 0 °C, 5 min, 85-98%; (d) pyridine, TsCl, rt, 2 h, 85%; (e) EtOAc, IBX, reflux, 3 h.

Polyphenol moieties such as **81** are present in a variety of organic molecules and natural products (Figure 4) which possess interesting chemical and biological properties.[11] It has recently been reported that baicalein (5,6,7-trihydroxy flavone) and related 6-hydroxy flavones are a new class of glucosidase inhibitors.[12] Besides, their physiological role in plants, these different flavonoids have also been reported to possess a wide range of biological activities such as anxiolytic, anti-inflammatory, antiviral, antioxidant, cardiovascular and anti-carcinogenic properties.[12] It is of relevance to mention that the derivatives (**81**–**84**) can be converted to the baicaleins (5,6,7-trihydroxy flavones) in 3 to 4 steps.[12a]

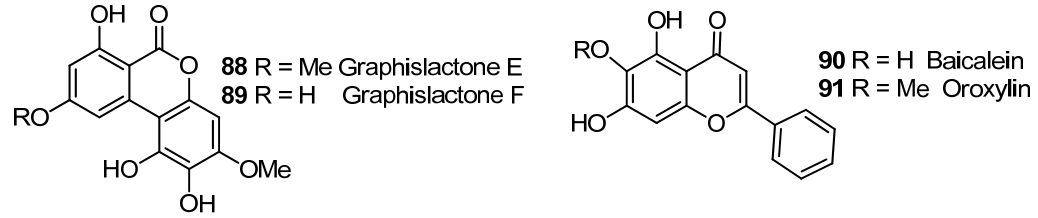


Figure 4

Chapter 4. **Structural studies of bicyclic 1,3-acetal derivatives of inositols**.

The purpose of this study was to gain insight into the conformational flexibility of bicyclic inositol derivatives that we have encountered in the previous chapters as well

as their analogs. In principle bicyclic inositol derivatives shown in figure **5** can exist in any of the four different conformations **CC**, **CB**, **BC**, **BB**. Hence the structures of these molecules were investigated using NMR spectroscopy, single crystal X-ray diffraction and DFT calculations. These investigations showed that the conformations of most of the bicyclic compounds are conserved in the solid state and in solution. An interesting feature that emerged from this study was that in all the bicyclic *myo*-inositol derivatives, the inositol ring has the boat conformation while the acetal ring has the chair conformation, except in the derivatives which are epimerized at the acetal carbon (**35** and **36**). Among the bicyclic *neo*-inositol derivatives, in four derivatives (**40**, **100–102)** both the rings are in the chair conformation, but in one derivative (**41**) the conformation of the acetal ring varied depending on the phase in which the molecules are present. However, in all the ring substituted derivatives (**64**, **66–68**), the inositol ring has the boat conformation. Interestingly, in the derivatives which are epimerized at the acetal carbon, in all the compounds the acetal ring is in the boat conformation and the insoitol ring is in the chair conformation, irrespective of whether it has the *myo*- or the *neo* configuration. The conformation predicted by geometrical optimization studies is in agreement with the experimental results. The difference in energy (ΔE) between the conformers varied from 2.0 kcal/mole to 12.5 kcal/mole.

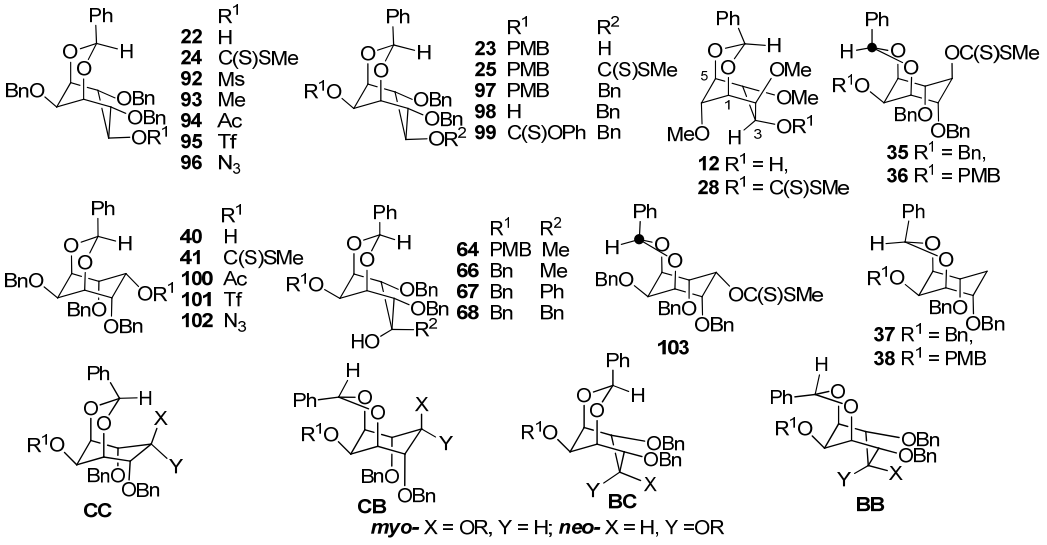


Figure 5.

References

1. a) B. V. L. Potter, *Comprehensive Medicinal Chemistry*, Vol 4, Pergamon Press 1990; b) D. C. Billington, *The Inositol Phosphates: Chemical synthesis and*

biological significance. VCH, New York, N.Y. 1993; c) K. Hinchliffe, R. Irvine, *Nature*, **1997**, *390*, 123; d) M. A. J. Ferguson, A. F. Williams, *Annu. Rev. Biochem.* **1988**, *57*, 285; e) *Phosphoinositides: chemistry, biochemistry and biochemical applications*, K. S. Bruzik, Ed.; ACS symposium series 718. American chemical society, Washington D.C. USA, 1999.

2. a) J. Duchek, D. R. Adams, T. Hudlicky, *Chem. Rev.* **2011**, *111*, 4223 and references cited there in; b) S. Pilgrim, G. Kociok-K€ohn, M. D. Lloyd, S. E. Lewis, *Chem. Commun.* **2011**, *47*, 4799.
3. a) I. H. Gilbert, A. B. Holmes, M. J. Pestchanker, R. C. Young, *Carbohydr. Res.* **1992**, *234*, 117; b) C. Murali, M. S. Shashidhar, C. S. Gopinath, *Tetrahedron,* **2007**, *63*, 4149.
4. S-M. Yeh, G. H. Lee, Y. Wang, T-Y. Luh, *J. Org. Chem.* **1997**, *62*, 8315.
5. a) R. C. Jagdhane, M. S. Shashidhar, *Eur. J. Org. Chem.* **2010**, 2945; b) J. M. Swarbrick, P. R. J. Gaffney, *J. Org. Chem.* **2010**, *75,* 4376; c) R. C. Jagdhane, M. S. Shashidhar, *Tetrahedron*, **2011**, *67*, 7963.
6. a) G. E. McCasland, S. Furuta, L. F. Johnson, J. N. Shoolery, *J. Am. Chem. Soc.* **1961**, *83*, 2335; b) A. Maras, H. Secen, Y. Sütbeyaz, M. Balci, *J. Org. Chem.* **1998**, *63*, 2039.
7. C. Murali, B. P. Gurale, M. S. Shashidhar, *Eur. J. Org. Chem.* **2010**, 755.
8. a) N. Chida, M. Ohtsuka, K. Nakazawa, S. Ogawa, *J. Org. Chem.* **1991**, *56*, 2976; b) T. J. Donohoe, P. D. Johnson, R. J. Pye, M. Keenan, *Org. Lett.* **2005**, 7, 1275; c) T. J. Donohoe, A. Flores, C. J. R. Battaille, F. Churruca, *Angew. Chem. Int. Ed*. **2009**, *48*, 6507.
9. N. Chida, N. Nakazawa, M. Ohtsuka, M. Suzuki, S. Ogawa, *Chem. Lett.* **1990**, 423.
10. B. M. Trost, J. Dudash, *Chem. Eur. J.* **2001**, *7*, 1619.
11. a) H.-W. Zhang, W.-Y. Huang, Y.-C. Song, J.-R. Chen, R.-X. Tan, *Helv. Chim. Acta* **2005**, *88*, 2861; b) M. Altemöller, T. Gehring, J. Cudaj, J. Podlech, H. Goesmann, C. Feldmann, A. Rothenberger, *Eur. J. Org. Chem.* **2009**, 2130.
12. a) Y. Lee, H. Yeo, S. Liu, Z. Jiang, R. M. Savizky, D. J. Austin, Y. Cheng, *J. Med. Chem.* **2004**, *47,* 5555; b) T. Hari Babu, V. R. Subba Rao, A. K. Tiwari, K. Suresh Babu, P. V. Srinivas, A. Z. Ali, J. Madhusudana Rao, *Bioorg. Med. Chem. Lett.* **2008**, *18*, 1659; c) F. Orallo, F. Ortuso, S. Alcaro, R. Cirilli, R. Ferretti, M. L. Sanna, *Bioorg. & Med. Chem.* **2010**, *18,* 1273 and references cited there in.

List of Publications

1. Murali, C.; **Gurale**, **B. P.**; Shashidhar, M. S. 'Intramolecular hydrogen abstraction in benzylidene acetals: efficient access to cyclitols' *Eur. J. Org. Chem*., **2010**, 755–766.

2. **Gurale**, **B. P.**; Vanka, K.; Krishnaswamy, S.; Shashidhar, M. S. 'Thermal Epimerization of inositol inositol 1,3-benzylidene acetals in the molten state' *Tetrahedron,* **2011**, *67*, 7280–7288.

3. **Gurale, B. P.**; Vanka, K.; Shashidhar, M. S. 'Radical mediated deoxygneation of inositol benzylidene acetals: conformational analysis, DFT calculations and mechanism' *Carbohydrate Res.* **2012**, DOI: 10.1016/j.carres.2012.01.00.

4. **Gurale**, **B. P.**; Gonnade, R. G.; Shashidhar, M. S. 'Chiral crystals from an achiral molecule - 1,3-*O*-Benzylidene-4,6-di-*O*-benzyl-2-*O*-(4-methoxybenzyl)-*myo*-5-inososе' *Acta Crystallogr. Sect C.* Accepted.

5. **Gurale, B. P.**; Gonnade, R. G. and Shashidhar, M. S. 'Synthesis of aminocyclitol units of (–)hygromycin A and methoxyhygromycin from *myo*-inositol' *Communicated.*

6. **Gurale**, **B. P.**; Shashidhar, M. S. 'Stereoselective addition of Grignard reagents to *myo*-5-inososе: efficient synthesis of 5-*C*-alkyl/aryl *neo*-inositol' *to be Communicated.*

7. **Gurale**, **B. P.**; Shashidhar, M. S. 'Inositols to aromatics: benzene free synthesis of polydroxy benzene derivatives and biaryls from *myo*-Inositol' *to be Communicated.*

8. **Gurale**, **B. P.**; Gonnade, R. G., Vanka, K.; Shashidhar, M. S. 'Conformational Study of inositol 1,3-acetals by using X-ray crystallography, NMR spectroscopy and DFT calculations' *manuscript under preparation.*

9. **Gurale**, **B. P.**; Shashidhar, M. S. 'A review on the synthetic utility of inositol-1,3-acetals' *manuscript under preparation.*

Poster presentations

5. Bharat P. Gurale, Mysore S. Shashidhar, Poster presentation, 'Intramolecular abstraction of hydrogen by radical derived from 1,3-acetals: efficient access to cyclitols' *5th J-NOST symposium held at IIT, Kanpur Nov 2009 and for National Science Day at NCL, 2011.*

Chapter 1

A review on the synthetic utility of *myo*-inositol 1,3-acetals

1.1. Introduction

myo-Inositol and its derivatives / analogs have become conspicuous in the literature related to chemistry and biology due to the involvement of phosphoinositols in cellular signal transduction mechanisms and anchoring of certain proteins to cell membranes.[1] Derivatives of inositols other than phosphoinositols are also important since several of them occur in nature and some are essential constituents of our diet. Amino derivatives of inositols are present in antibiotics[2] and some of them act as glycosidase inhibitors.[3] Key intermediates for the synthesis of biologically important derivatives of inositols are the corresponding hydroxyl group protected derivatives. Many of these intermediates have been synthesized from benzene, quinic acid, carbohydrates and naturally occurring inositols.[4]

The revival in interest in the chemistry of inositols led to efforts to use naturally occurring inositols and their derivatives for the synthesis of a variety of organic compounds and natural products.[5] Examples of some natural products and biologically active compounds containing cyclitol moiety as the main core are shown in Chart 1.1. (–)Quinic acid (**1.2**), a constituent of cinchona bark, is a chiral building block for organic synthesis and has been used as a convenient starting material, most notably in the Gilead synthesis of oseltamivir.[6] (+)Pancratistatin (**1.3**), an Amaryllidaceae constituent, is a potent antineoplastic agent, exhibits cancer cell growth inhibitory activity and antiviral activity;[7] it has been the subject of several biological and synthetic studies.[8,5b] Tamiflu (**1.4**) has become extremely important for protecting humans against a lethal flu caused due to avian influenza (H5N1).[9] (–)Hygromycin A (**1.5**), an antibiotic, shows hemagglutination inactivation activity, high antitreponemal activity and is also an effective agent for the control of swine dysentery.[10] Methoxyhygromycin (**1.6**) shows herbicidal activity and hence is a potential selective bioherbicidal agent.[11] Tetrodotoxin (**1.7**), one of the best-known marine toxins, was originally isolated from the puffer fish.[12,5e] (+)Valiolamine (**1.8**) and (+)validamine (**1.9**), obtained from chemical or microbial degradation of validamycin, have been shown to be α-glucosidase inhibitors.[13] Fortimicin A (**1.10**) is a deoxyaminoglycoside antibiotic and is active against gram +ve and gram –ve bacteria including most aminoglycoside resistant bacteria.[14]

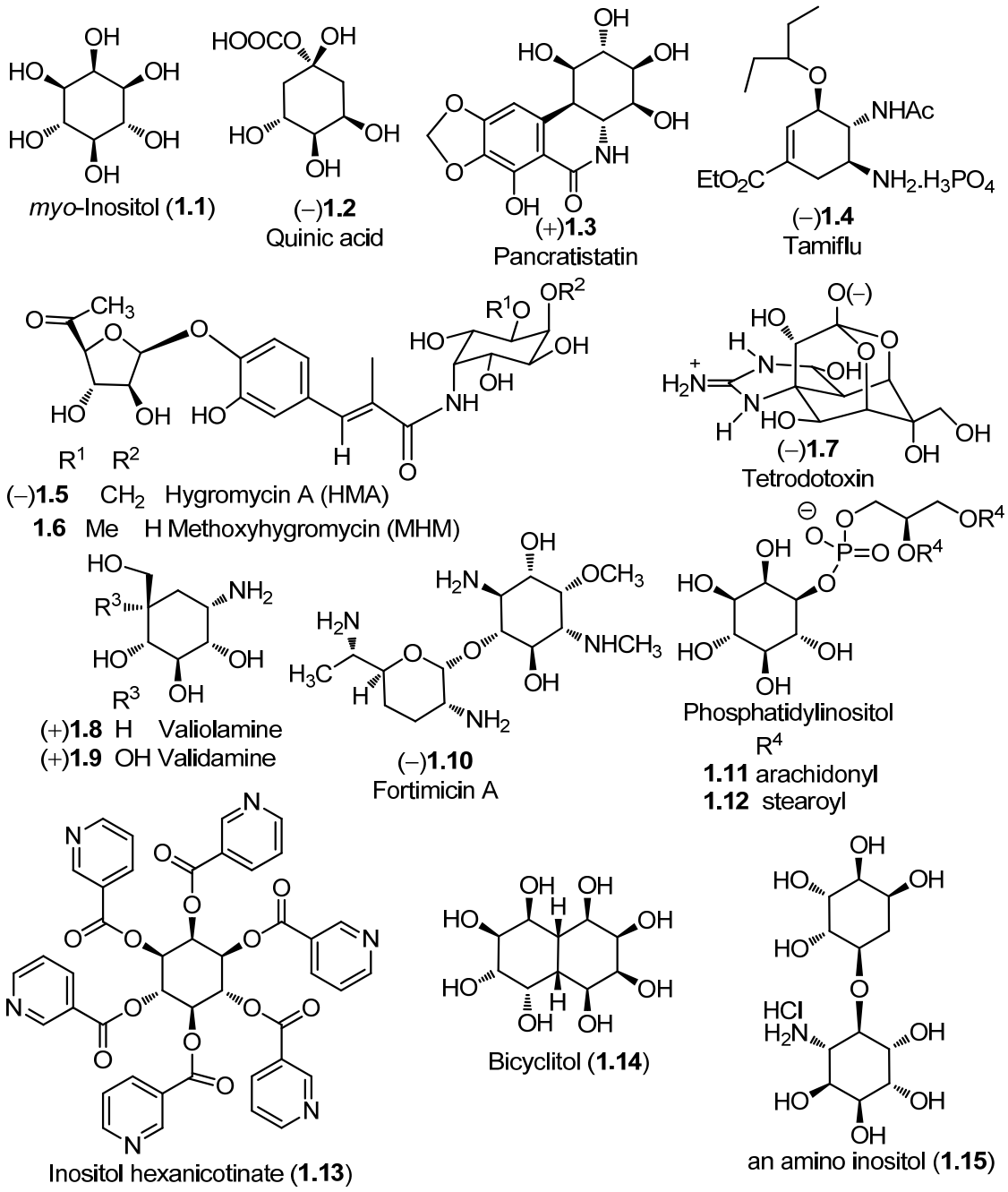


Chart 1.1: Structure of natural products (**1.1**–**1.11**) and unnatural cyclitol derivatives (**1.12**–**1.15**).

Phosphatidylinositol (**1.11**) is a component of mammalian cell membranes. Phosphorylated derivatives of **1.11** play fundamental role in a multitude of cellular processes.[15] Inositol hexanicotinate (**1.13**) is used as a food supplement since it functions as a source of nicotinic acid (niacin, vitamin B3). Bicyclitol **1.14** and amino inositol **1.15** are examples of un-natural cyclitol derivatives. The bicyclitol **1.14** displayed a strong α-glucosidase (from yeast) inhibitory activity.[16] The chemistry of these compounds (Chart 1.1) has a long

history from the perspectives of both their syntheses and the biological activities that some of these compounds and their derivatives exhibit.[17]

Although, the chemistry of *myo*-inositol (**1.1**), the most abundantly available cyclitol (Chart 1.2) in nature, was studied extensively in the last two decades[4e–j,18] reports on the utility of *myo*-inositol as a starting material for the synthesis of natural products containing cyclitol moiety are scarce. We are interested in investigating the potential of *myo*-inositol as a starting material for the synthesis of the cyclitol core of natural products (and their analogs), using inositol derived 1,3-acetals as early intermediates.

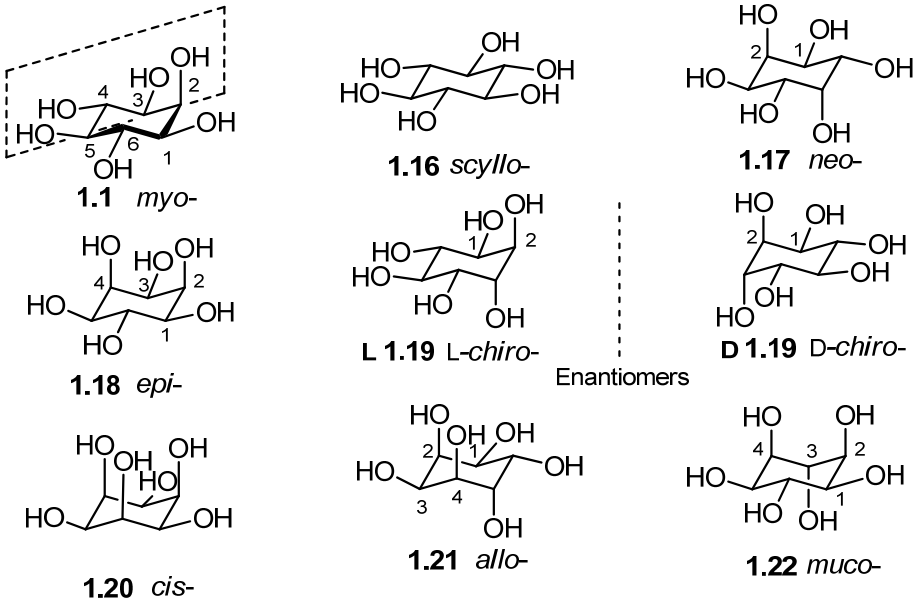


Chart 1.2: Nine isomeric inositols reported in the literature.

myo-Inositol, a hexahydroxy cyclohexane, is a *meso* isomer with five equatorial hydroxyl groups and an axial hydroxyl group. There is a plane of symmetry passing through two carbon atoms (**1.1**, as shown in Chart 1.2). The carbon bearing the axial hydroxyl group is designated as C2 and the other ring carbons can be numbered from C1 to C6 starting from a C1 atom and proceeding around the ring in anticlockwise (**1.23**) or clockwise (**1.24**) fashion. According to convention,[19] anti-clockwise numbering in an unsymmetrically substituted *myo*-inositol leads to the configurational D-prefix and clockwise numbering gives the substituted *myo*-inositol an L-prefix. An IUBAC recommendation allowing all biologically relevant compounds to be denoted as D-isomers has also been proposed (Chart 1.3).[20]

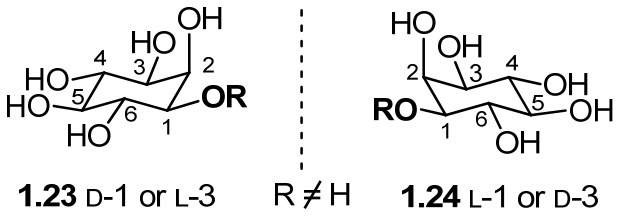
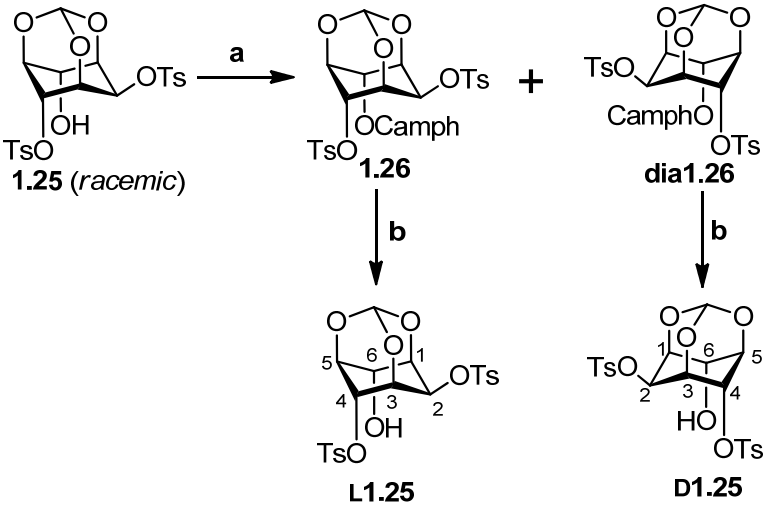


Chart 1.3: Numbering in unsymmetrical *myo*-inositol derivatives.

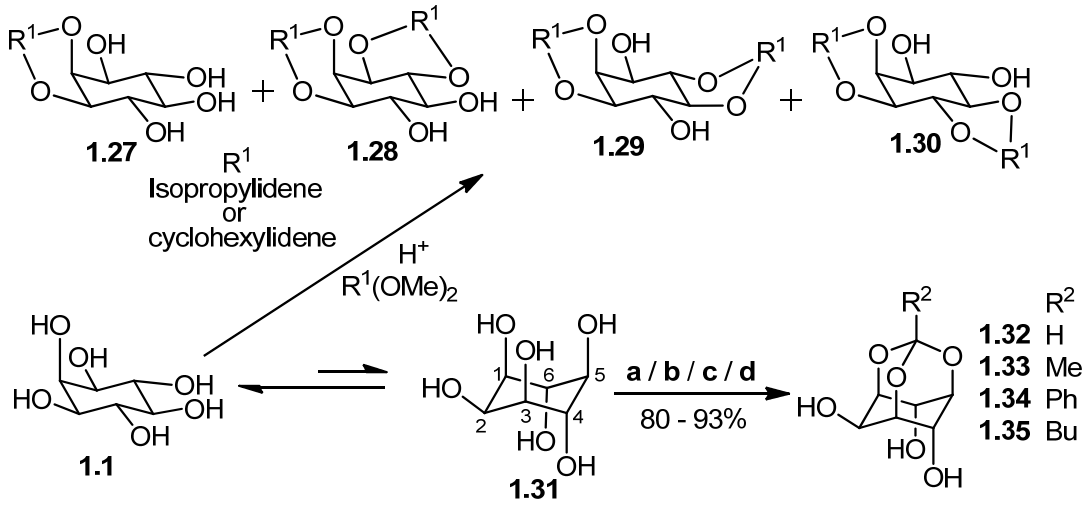
Although, many of the unsymmetrically substituted *myo*-inositol derivatives reported in this thesis are racemic, for clarity and simplicity they are represented in schemes by only one enantiomer. Optically inactive (*racemic*, *meso*) synthetic derivatives of inositol (other than phosphates) are numbered without prefixes, while optically active derivatives are numbered with a suitable prefix (**D**, **L**). Convention for numbering of structures in schemes in this thesis is shown in Scheme 1.1 using the tosylate derivative of *myo*-inositol orthoformate as an example;[5f] racemic 2,4-di-*O*-tosyl-*myo*-inositol 1,3,5-orthoformate – **1.25**; D-2,4-di-*O*-tosyl-*myo*-inositol orthoformate – **D1.25** and its enantiomer L-2,4-di-*O*-tosyl-*myo*-inositol 1,3,5-orthoformate – **L1.25**. Diasteroisomers are numbered with same number with a prefix **dia** to one of the diastereomer. For example: *racemic* alcohol **1.25** on esterification with 1*S*-(–)camphanoyl chloride forms diastereomeric mixture of corresponding camphanate ester which are numbered as **1.26** and **dia1.26**.



Scheme 1.1: (a) py., DMAP, 1*S*-(–) camphanoyl chloride; (b) DCM-MeOH, *i*-$BuNH_2$.

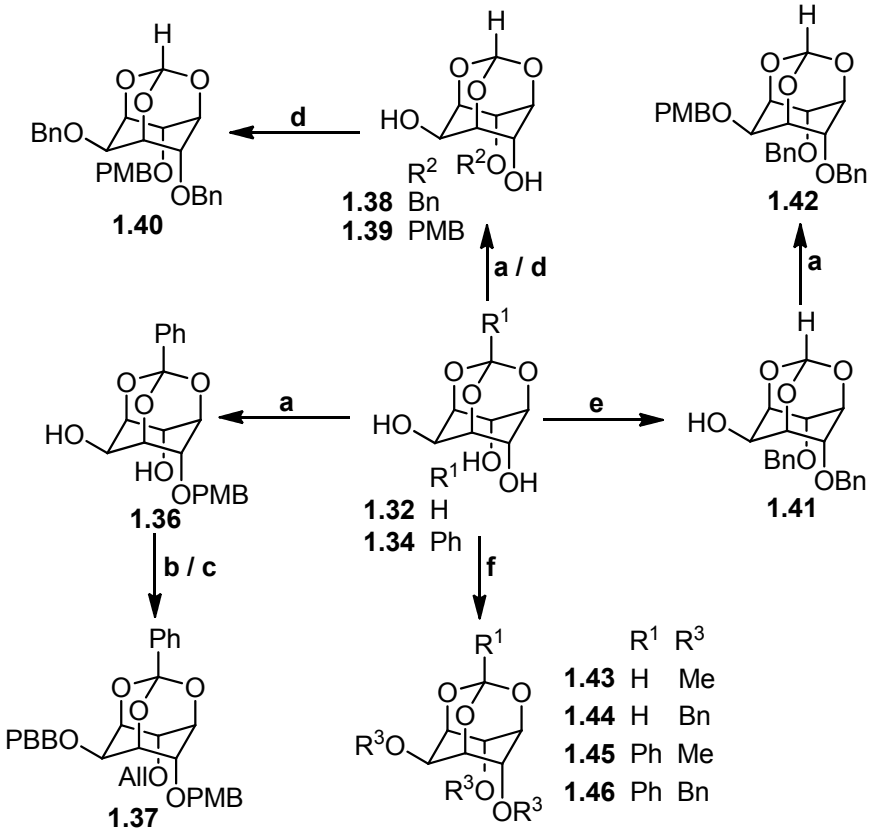
1.2. Preparation of *myo*-inositol-1,3-acetals by cleavage of orthoesters

Regioselective protection of *myo*-inositol hydroxyl groups is a difficult and elaborate task since all the hydroxyl groups are secondary and the reactivity differences between them is subtle. Hence, reaction of inositols with most reagents leads to the formation of a mixture of products; formation of acetals (**1.27**–**1.30**) of *myo*-inositol is shown in Scheme 1.2 as an example. All these methods result in the formation of acetals of the vicinal hydroxyl groups (1,2-diol) and there is no report on the formation of inositol-1,3-bridged acetals (from 1,3-diols) in any of these reactions. The latter acetals can only be obtained by the partial cleavage of *myo*-inositol-1,3,5-orthoesters.



Scheme 1.2: (a) DMF, $HC(OEt)_3$, TsOH, 110 °C, 4 h; (b) DMF, $MeC(OEt)_3$, TsOH, 90–100 °C, 4 h; (c) DMSO, $PhC(OMe)_3$, CSA, 85 °C, 5 h; (d) DMSO, *n*-$BuC(OMe)_3$, CSA, 60 °C.

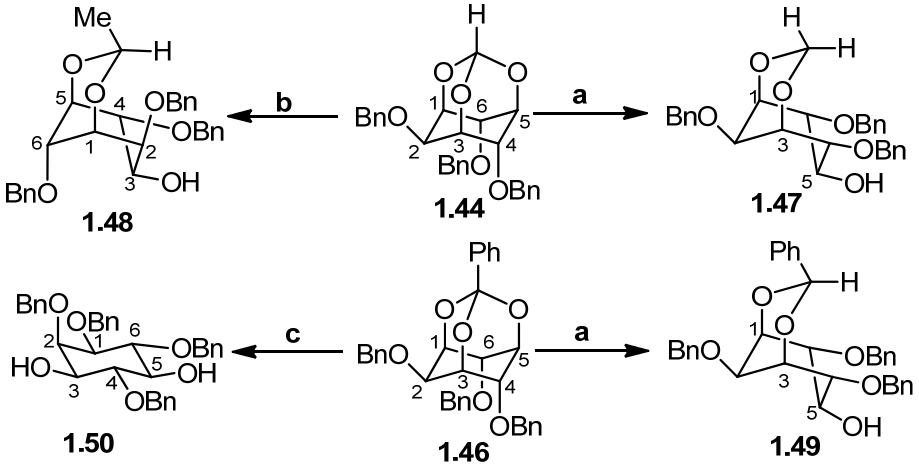
Reaction of *myo*-inositol with trialkyl-orthoesters results in the formation of *myo*-inositol-1,3,5-orthoester as the sole product in high yield (Scheme 1.2), wherein three hydroxyl groups are protected simultaneously.[4c,21] Due to strong intramolecular hydrogen bonding between the C4- and C6-hydroxyl groups of *myo*-inositol orthoesters, and differences in the ability of these hydroxyl groups to form chelates with metal ions, reaction of the three hydroxyl groups of these orthoesters with alkyl halides can be controlled to obtain mono-, di- or triethers exclusively (Scheme 1.3).[22]



Scheme 1.3: (a) DMF, NaH, PMBCl, 90–95%; (b) THF, *n*-BuLi, AllBr in DMF, 80%; (c) DMF, NaH, PBBBr, 95%; (d) DMF, NaH, BnBr; (e) DMF, LiH, BnBr, 84%; (f) DMF, NaH, R^3X (X = I, Br).

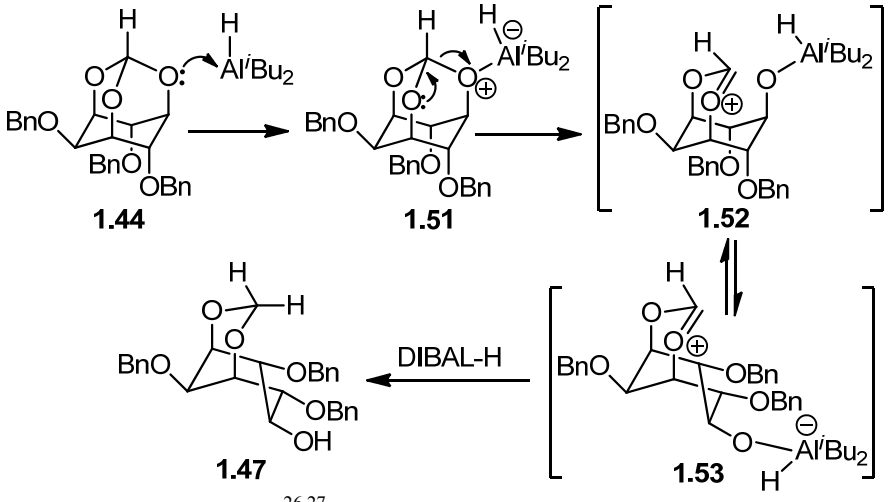
Reductive cleavage of these orthoesters in the presence of Lewis acids affords the corresponding *myo*-inositol-1,3-acetal. Some aspects of these reactions which are useful in generating *myo*-inositol-1,3-acetals are elaborated below.

It was observed that, change in selectivity in the Lewis acid-mediated reductive or alkylative C–O bond cleavage of *O*-protected orthoester derivatives of *myo*-inositol, was dependent on the size of the organometallic reagent (scheme 1.4).[23] Reduction of the orthoester **1.44** and **1.46** with DIBAL-H at room temperature resulted in a highly stereoselective cleavage of the C5–O bond of the orthoester moiety to produce the 1,3-acetal **1.47** and **1.49** respectively.[24] The C1 (or C3)-hydroxyl group could be released selectively in the orthoester **1.44** by cleavage with trimethylaluminium[24a] to produce the acetal **1.48**. Complete cleavage of the orthobenzoate **1.46** could also be effected to obtain the diol **1.50**.[24b]



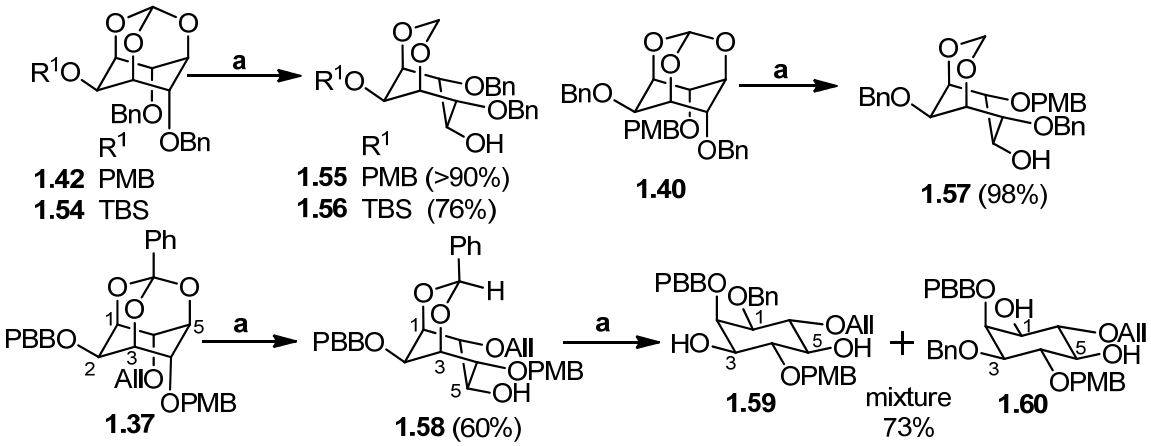
Scheme 1.4: (a) DCM, DIBAL-H (2.2 eq.), 93–100%; (b) DCM, $AlMe_3$ (2.5 eq.), 84%; (c) DCM, DIBAL-H (excess).

The stereoselectivity of these Lewis acid-mediated reductive and alkylative cleavages of the orthoformate **1.44** have been investigated and the mechanisms proposed (Scheme 1.5).[24a,25] In the DIBAL-H reduction of **1.44** to **1.47** (and **1.46** to **1.49)**, it was determined that at least 2 molar equivalents of DIBAL-H are required for the reaction to proceed to completion (Scheme 1.5). It was proposed that the first equivalent of DIBAL-H acts as a Lewis acid, coordinating to the C-5 oxygen, perhaps the most sterically accessible oxygen in **1.44**. Subsequent cleavage of the orthoformate affords the oxocarbenium ion **1.52**, the unfavourable 1,3-steric interactions in which can be accommodated by a ring-flip to the boat conformation **1.53**. Reduction of this oxocarbenium ion by a second equivalent of DIBAL-H from the less hindered face produces the 1,3-acetal **1.47** exclusively.



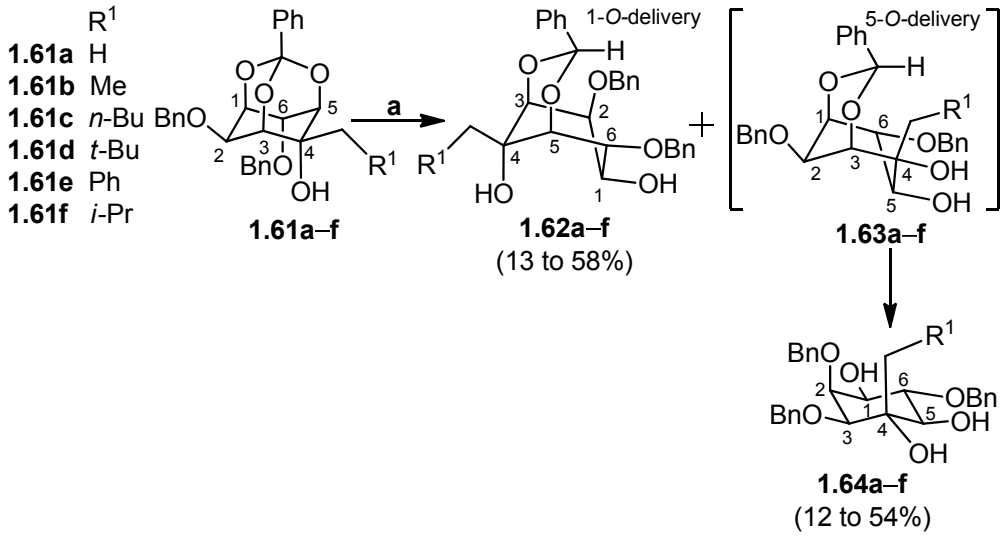
Scheme 1.5: Proposed mechanisms[26,27] for the cleavage of symmetrically substituted *myo*-inositol orthoformates by DIBAL-H: (a) DCM, DIBAL-H.

Regioselectivity during the DIBAL-H cleavage of symmetrically substituted orthoformate **1.42** and **1.54** was same as that observed in **1.44** (Scheme 1.6).[22c,26] However, regioselectivity of the cleavage of *myo*-inositol orthoesters with DIBAL-H carrying unsymmetrical substituents could not be ascertained clearly . Reduction of unsymmetrically O-substituted orthoformate **1.40** gave the C5-alcohol **1.57** as a single product [27] while, reduction of the orthobenzoate moiety in **1.37** resulted in the formation of a mixture of products from which the benzylidene acetal **1.58** (Scheme 1.6) was isolated in 60% yield.[22c] Reduction of **1.37** with an excess of DIBAL-H gave a mixture of isomeric diols **1.59** and **1.60**, but this result is not sufficient to conclude the sole intermediacy of the 1,3-acetal **1.58**. This is because no data on the regioselectivity of the cleavage of 1,3-acetals or relative reactivities for the reduction of the C1,C3- and C1,C5-acetals are available.



Scheme 1.6: (a) DCM, DIBAL-H.

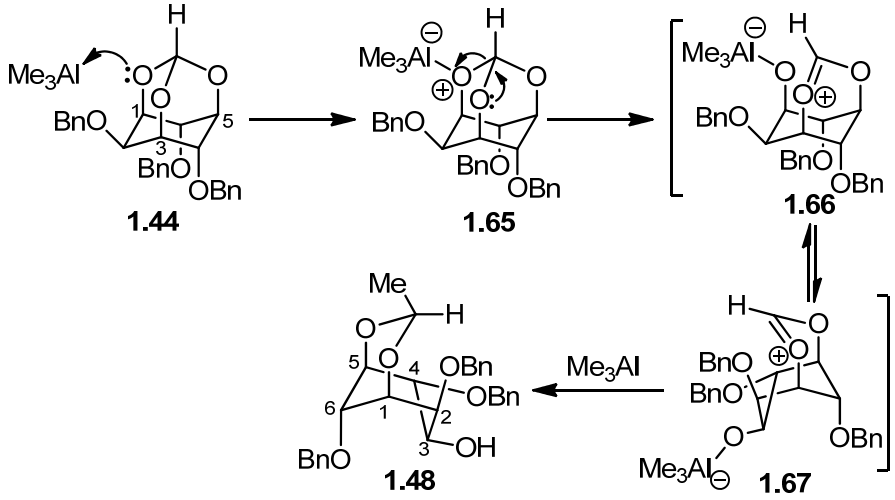
Results on the cleavage of the orthoesters of ring C-substituted *myo*-inositol (Scheme 1.7) showed that the nature of the product formed was dependent on the inositol ring C-substituent. Most of these orthoesters yielded a mixture of the C3,C5-acetal (**1.62a**–**f**) and the triol (**1.64a**–**f**) on reaction with DIBAL-H. Generation of the 3,5-*O*-benzylidene acetal shows that the initial attack of DIBAL-H need not necessarily occur at the 5-O as reported for normal inositol orthoesters.[28]



Scheme 1.7: (a) DCM, DIBAL-H.

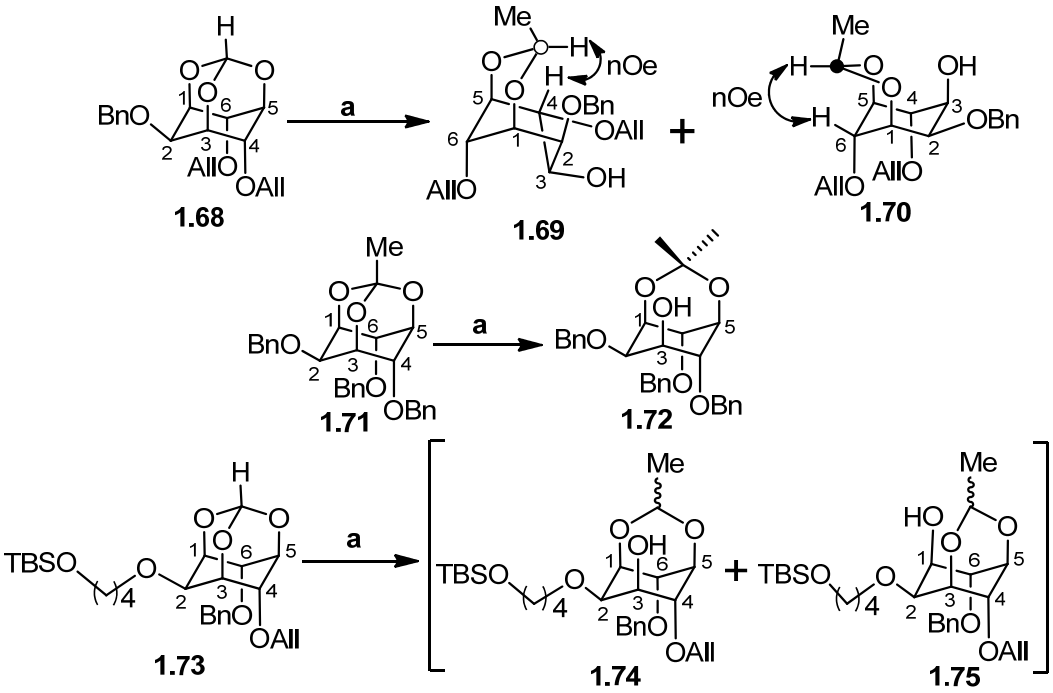
1.3. Trimethylaluminium mediated cleavage of inositol orthoesters

In contrast to the DIBAL-H cleavage of inositol orthoesters, the trimethylaluminium-mediated cleavage of the orthoformate **1.44** exclusively affords the acetal **1.48** (Scheme 1.4, 1.8), which results from the cleavage of either the C1-O or the C3-O bonds in the orthoformate **1.44**.[24a] This outcome indicates that trimethylaluminium is presumably sufficiently small to coordinate to one or both of the equivalent oxygens at the C1- or C3-positions, allowing an alternative cleavage pathway resulting in the oxocarbenium ion **1.66**. Delivery of a methyl group to the *exo* face of the oxocarbenium **1.67** affords the C1,C5-acetal **1.48** (Scheme 1.8).



Scheme 1.8: Proposed mechanisms[24a] for the regioselective cleavage of the orthoformate **1.44** by Me_3Al.

The orthoformate derivative **1.68** on reaction with trimethylaluminium led to the formation of a mixture of epimeric acetals **1.69** and **1.70** (Scheme 1.9)[29] However, only one of these epimers (**1.69**) was expected according to the mechanism proposed in the literature.[24a] Similarly, the orthoacetate **1.71** could be regioselectively cleaved by trimethylaluminium to obtain C1(3),C5-acetal **1.72** exclusively.[21c] Trimethylaluminium mediated cleavage of orthogonally protected orthoformate **1.73** led to the formation of a mixture of acetals **1.74** and **1.75** (Scheme 1.9) both of which were utilized in the synthesis of purinyl analog of Ins(1,4,5)P_3.[30]

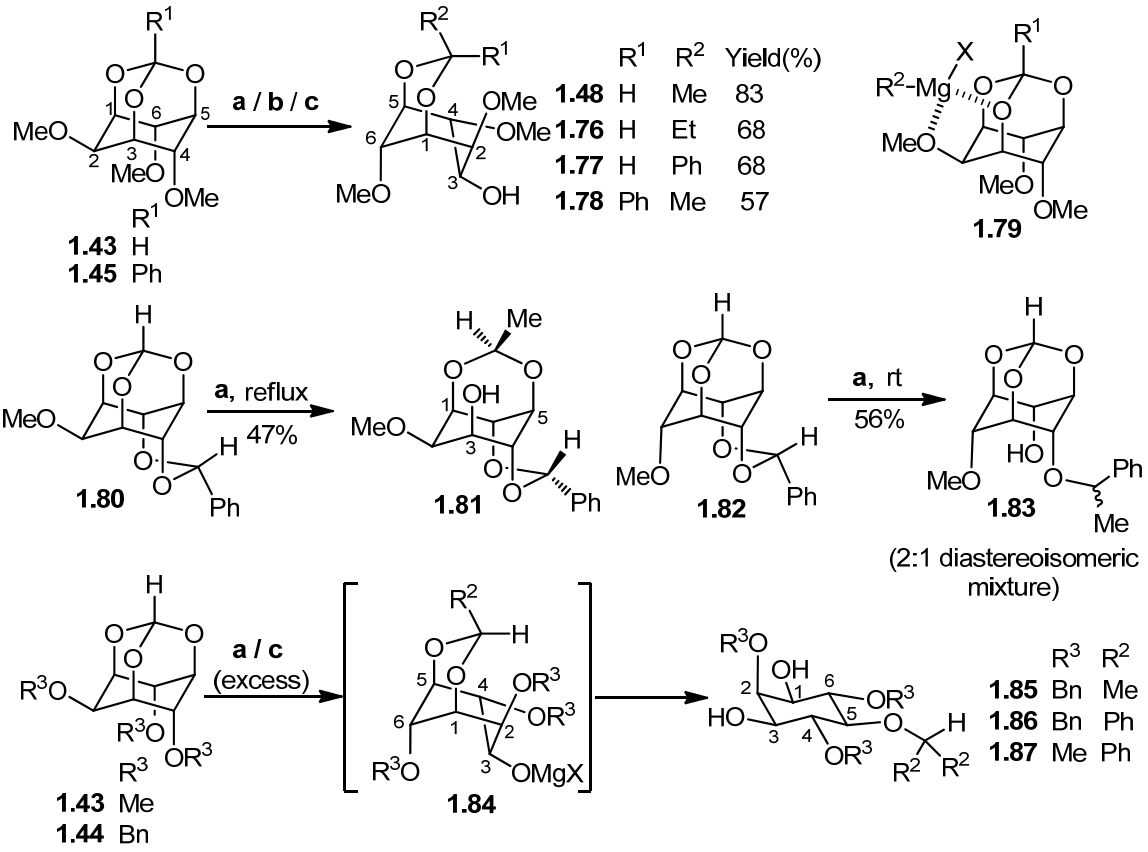


Scheme 1.9: (a) DCM, $AlMe_3$, –78 °C to 0 °C.

1.4. Cleavage of inositol orthoesters by Grignard reagent

Selective cleavage of the orthoester moiety in *myo*-inositol orthoesters at C1–O bond could also be effected with Grignard reagents (Scheme 1.10).[31] The regioselectivity for the cleavage of the orthoester was rationalized owing to the presence of the equatorial oxygen at the C2 position which could serve as an auxiliary to form a chelate such as **1.79** (Scheme 1.10). This mechanism is supported by the reaction of MeMgI with **1.80** which resulted in cleavage of the orthoester moiety; whereas in the reaction of the analogous *scyllo*-inositol orthoester derivative **1.82** with MeMgI, a diastereomeric mixture of **1.83**

(2:1) was obtained in 56% yield. No C–O bond cleavage at the orthoester moiety in **1.82** was observed. The methoxy group in **1.80** apparently directs the selectivity of the ring opening reaction at the benzylidene moiety. As observed with the reduction of DIBAL-H (Scheme 1.4), inositol 1,3-acetals initially produced (C1,C5-acetals, **1.84**) are cleaved with excess of Grignard reagent (Scheme 1.10) to the corresponding diols (**1.85**–**1.87**).



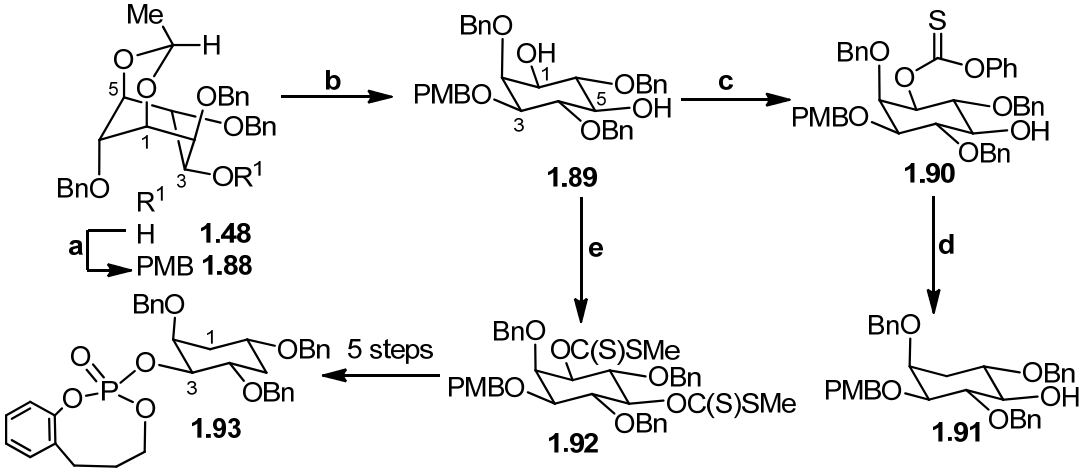
Scheme 1.10: (a) benzene, MeMgI in ether, rt-reflux, 16 h; (b) benzene, EtMgBr in ether; (c) benzene, PhMgBr in ether.

The remaining part of this chapter showcases the utility of *myo*-inositol 1,3-acetals for the synthesis of natural and unnatural derivatives or analogs of inositols.

1.5. Synthetic utility of inositol-1,3-acetals

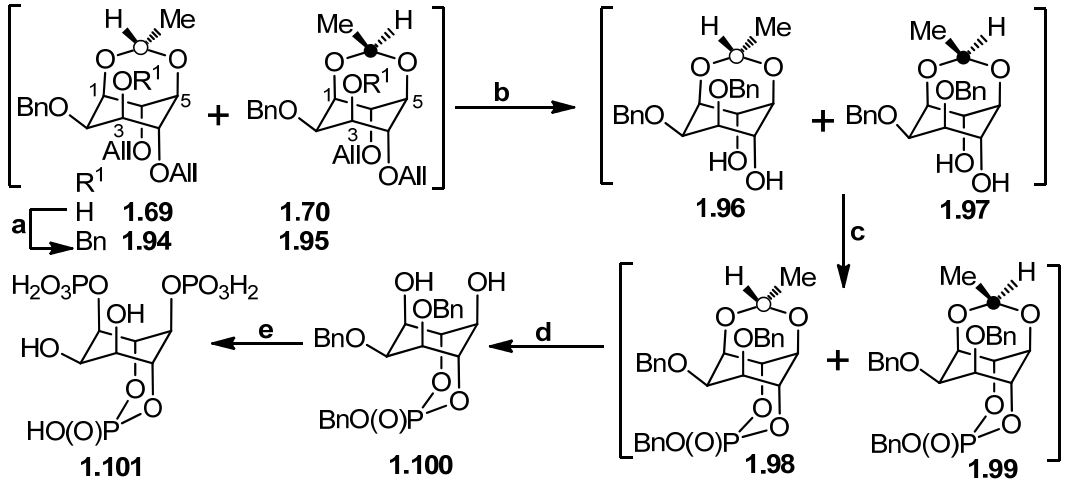
1.5.1. Synthesis of phosphorylated inositol derivatives

The inositol derivative **1.93** (Scheme 1.11) was prepared by using *myo*-inositol C1,C5-acetal **1.48** as a key intermediate; the phosphate **1.93** was tested as an inhibitor toward human inositol monophosphatase.[32]



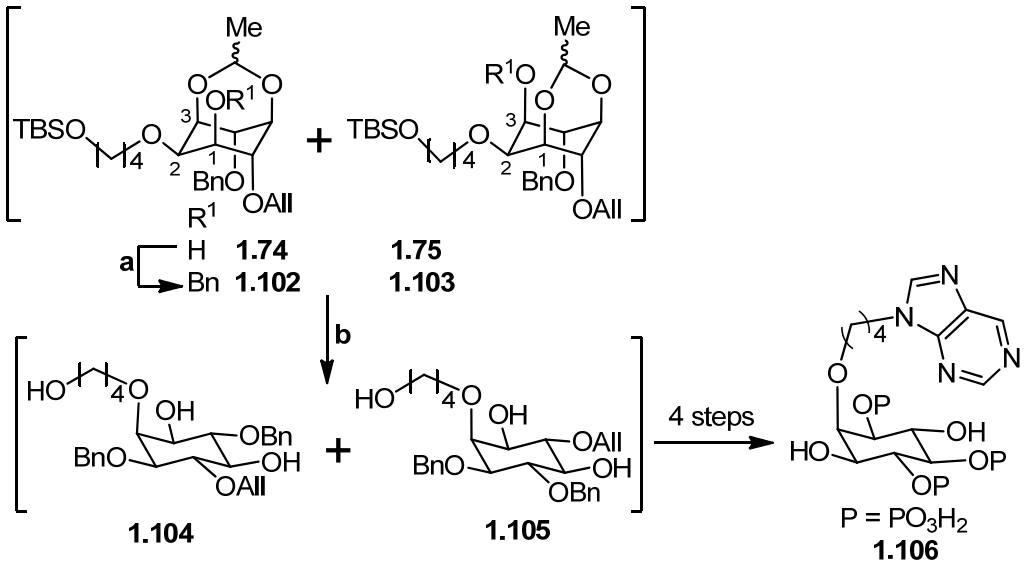
Scheme 1.11: (a) DMF, NaH, PMBCl; (b) aq. TFA; (c) MeCN, DMAP, PhOCSCl; (d) toluene, *n*-Bu_3SnH, AIBN; (e) THF, NaH, CS_2, MeI.

The cyclic phosphate **1.101** was prepared (Scheme 1.12)[29] from a diastereomeric mixture of the acetals **1.69** and **1.70**. The trisphosphate **1.101** was used to study the structure activity relationship on the interaction of the second-messenger, D-Ins(1,4,5)P_3 with its receptor.



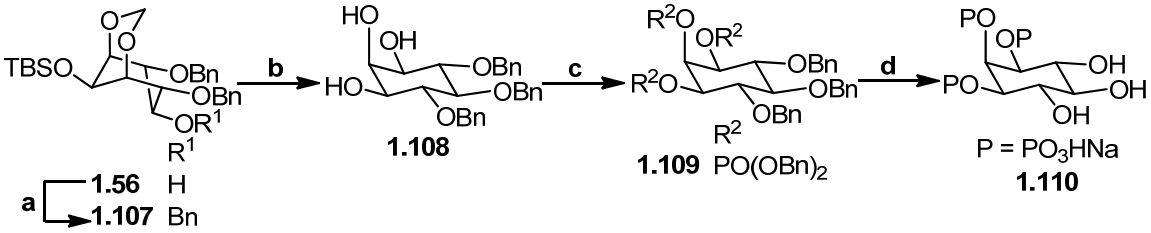
Scheme 1.12: (a) DMF, NaH, BnBr; (b) $RhCl(PPh_3)_3$, DABCO, then $Hg(OAc)_2$; (c) DCM, $(Et_2N)_2POBn$, 1*H*-tetrazole, then *m*-CPBA; (d) TFA, THF-EtOH-H_2O; (e) i) DCM, *o*-xylene *N*,*N*-diethylphosphoramidite, 1*H*-tetrazole, then *m*-CPBA; ii) MeOH, H_2, Pd/C.

The purinyl derivative *racemic*-**1.106** was synthesized[30] from the diastereomeric mixture of acetals **1.74** and **1.75** (Scheme 1.13). The purinyl analog **1.106** of Ins(1,4,5)P_3 behaved as a potent full agonist at the Ins(1,4,5)P_3-receptor.



Scheme 1.13: (a) DMF, NaH, BnBr; (b) MeOH, TsOH.

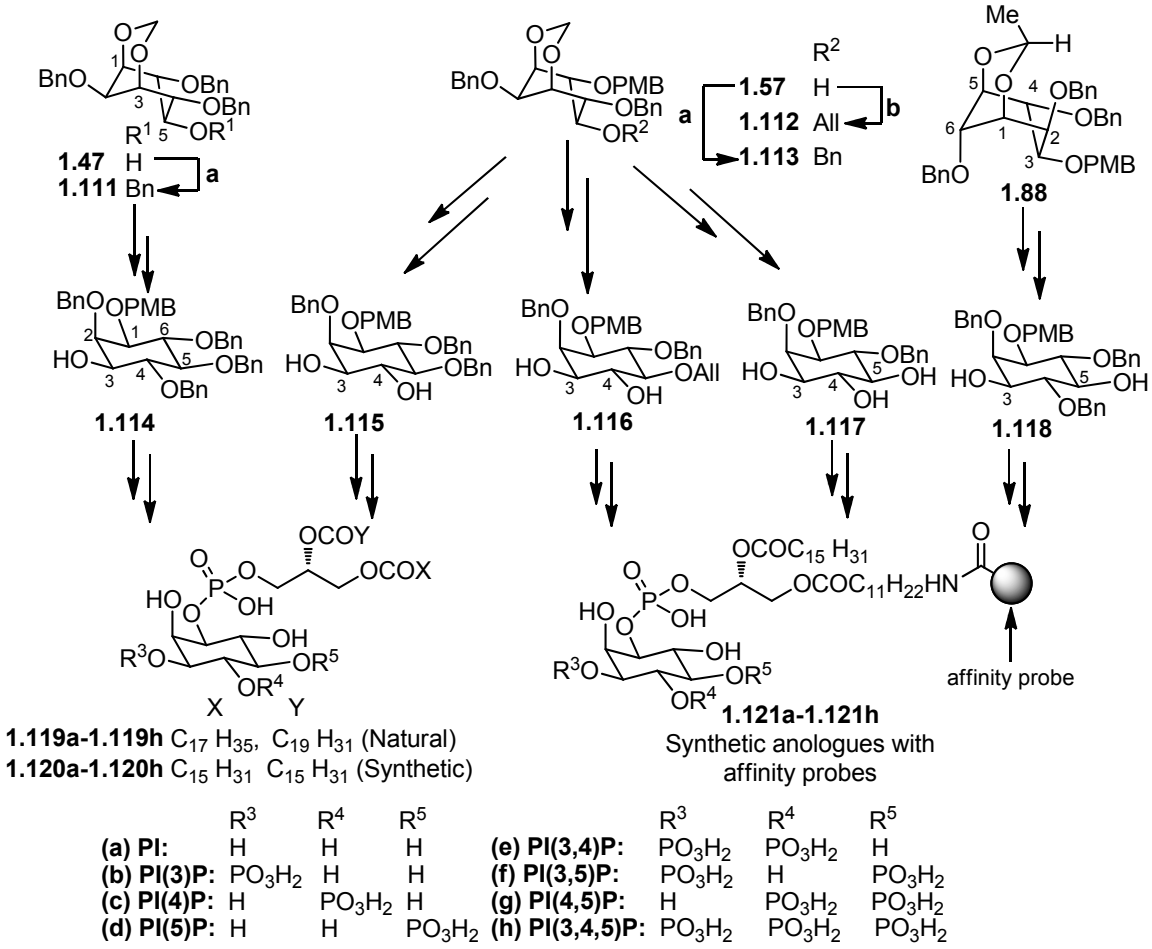
myo-Inositol-1,2,3-tris-dihydrogenphosphate (**1.110)** was synthesized by using the 1,3-acetal **1.56** as a key intermediate (Scheme 1.14).[26] The trisphosphate **1.110** was obtained from the acetal **1.107** by deprotection of the C1, C2, and C3- hydroxyl groups followed by phosphorylation.



Scheme 1.14: (a) DMF, BnBr, NaH, *n*-Bu_4NI; (b) MeOH, HCl; (c) DCM, $(BnO)_2P$-N(*i*-Pr)$_2$, 1*H*-tetrazole; (d) i) DCM, *m*-CPBA; ii) MeOH, H_2, Pd/C; then ion exchange.

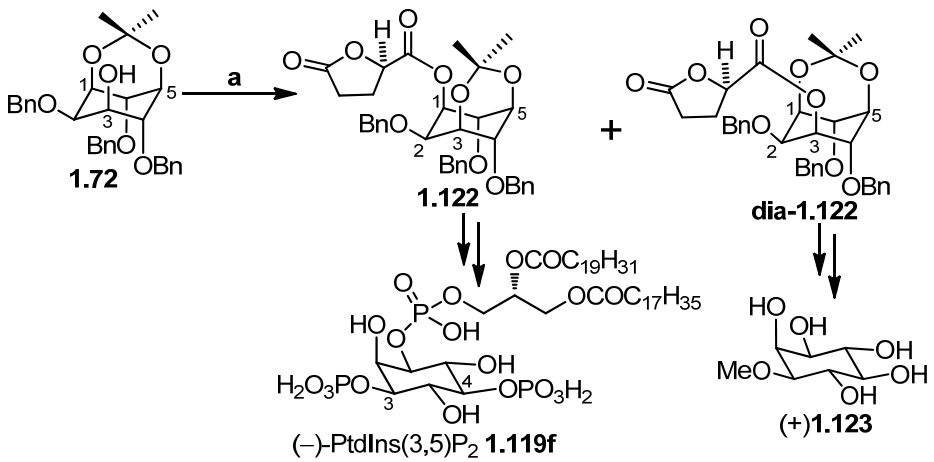
The D-3-phosphorylated *myo*-inositol phospholipids PtdIns(3)P, PtdIns(3,4)P_2, PtdIns(3,4,5)P_3 and PtdIns(3,5)P_2 were synthesized[27,33] from *myo*-inositol 1,3-acetal **1.47**, **1.57** and **1.88** with divergent strategy (Scheme 1.15). The 1,3-acetals **1.47**, **1.57** and **1.88** were also used for the synthesis of phosphatidylinositol phosphate analogues containing affinity probes (**121a-121h**) which were useful in the identification of proteins in the PI3K

signalling pathway.[25b] The key transformation included resolution–protection protocol of intermediates **1.114** to **1.118**.



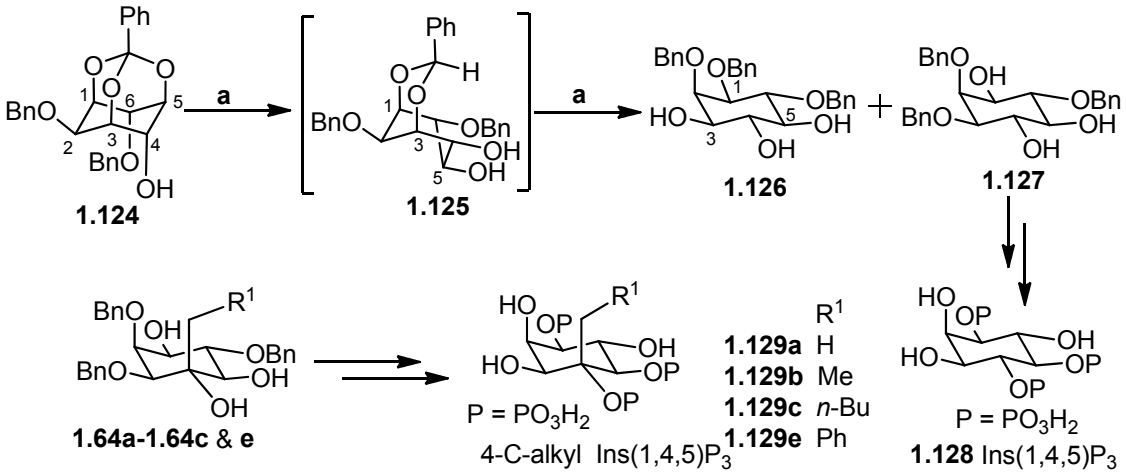
Scheme 1.15: (a) DMF, NaH, BnBr; (b) DMF, NaH, AllBr.

The *racemic* acetal **1.72** was resolved as its diastereomeric esters of (R)-(–)-5-oxo-2-tetrahydro-furancarboxylic acid (Scheme 1.16). The diastereomers **1.122** and **dia-1.122** were used for the synthesis of Ptdlns(3,5)P_2 (**1.119f**) and (+)-bornisitol (**1.123**)[21c] respectively.



Scheme 1.16: (a) DCM, (*R*)-(–)-5-oxo-2-tetrahydro-furancarboxylic acid, DCC, DMAP.

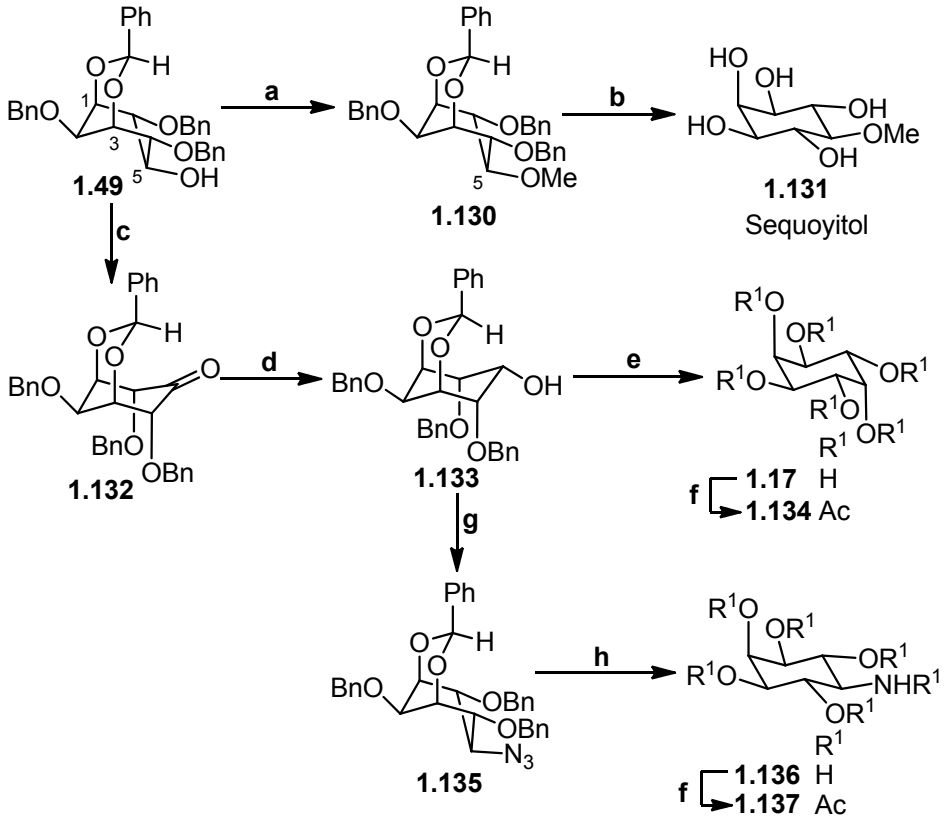
Regioselective cleavage of *O*-protected inositol orthobenzoate was utilized[28] for the synthesis of natural and unnatural inositol phosphates (Scheme 1.17). Natural inositol phosphates [Ins(1,3,4,5)P_3] and unnatural 4-C-alkyl inositol phosphates **1.129a-c** & **e** were synthesized from the triol **1.127** and **1.64a-c** & **e** (Scheme 1.17). The triols **1.127** and **1.64a-c** & **e** were obtained from the corresponding orthobenzoate *via* 1,3-acetal **1.125** and **1.63a-c** & **e** as shown in scheme 1.7 and 1.17. Although all the inositol 1,3-acetals were not isolated in these reactions, their intermediacy was crucial for the planned synthesis.



Scheme 1.17: (a) DCM, DIBAL-H.

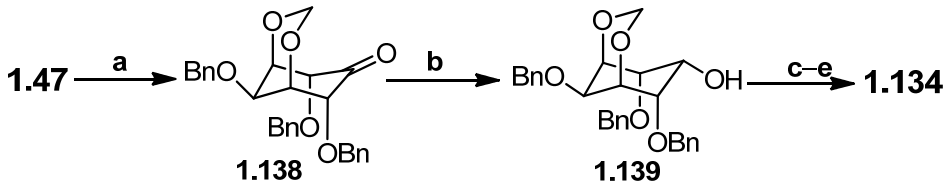
1.5.2. Synthesis of isomeric inositols and their analogs

Synthesis of sequoyitol **1.131**, *neo*-inositol **1.17** and *myo*-inosamine **1.136** was reported by Murali *et al*[24b,34] from *myo*-inositol (5 to 7 steps) by using 1,3-*O*-benzylidene acetal **1.49** as a key intermediate (Scheme 1.18).



Scheme 1.18: (a) DMF, NaH, MeI; (b) MeOH, 20% $Pd(OH)_2/C$, reflux, 20 h; (c) DCM, PDC (1.5 eq), MS (3Å), rt, 22 h; (d) THF-MeOH, $NaBH_4$, rt, 1 h, 94% (for 2 steps); (e) EtOH, 20% $Pd(OH)_2/C$, H_2 (50 Psi), 6 h; (f) pyridine, excess Ac_2O, rt, 40 h; (g) (i) DCM, py., Tf_2O; (ii) DMF, NaN_3, 100 °C; (h) EtOH, AcOH, 20% $Pd(OH)_2/C$, H_2 (50 Psi).

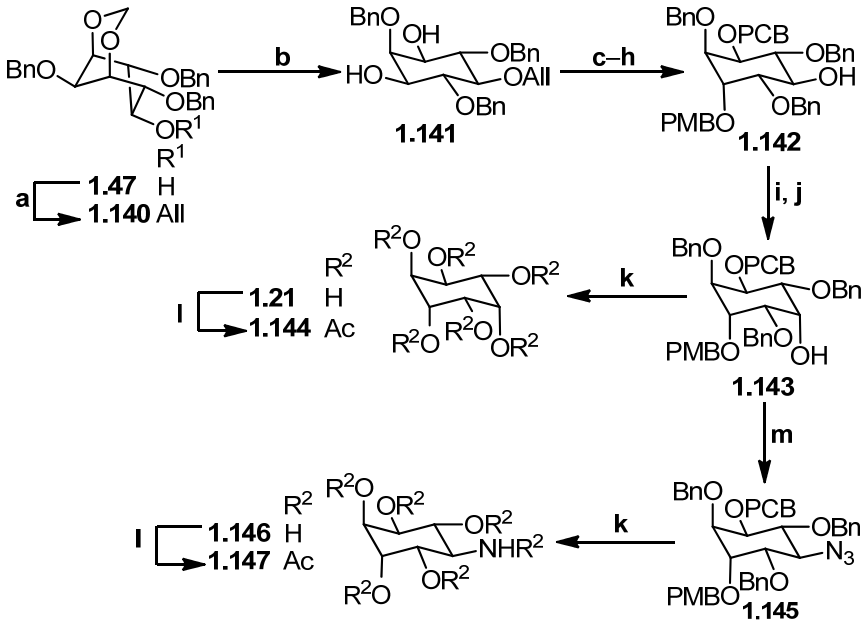
Wessig and co-workers also synthesized *neo*-inositol[35] by using a similar procedure where 1,3-formaldehyde acetal **1.47** was an intermediate (Scheme 1.19). The key steps of the sequence were oxidation of the hydroxy group at C-5 to the corresponding ketone, followed by a highly (dr = 7.8:1) stereoselective reduction.



Scheme 1.19: (a) DCM, DMP; (b) THF-MeOH, $NaBH_4$, rt, 1 h, 94% (for 2 steps); (c) MeOH, HCl; (d) MeOH, $Pd(OH)_2/C$, H_2 (50 Psi); (e) py., Ac_2O.

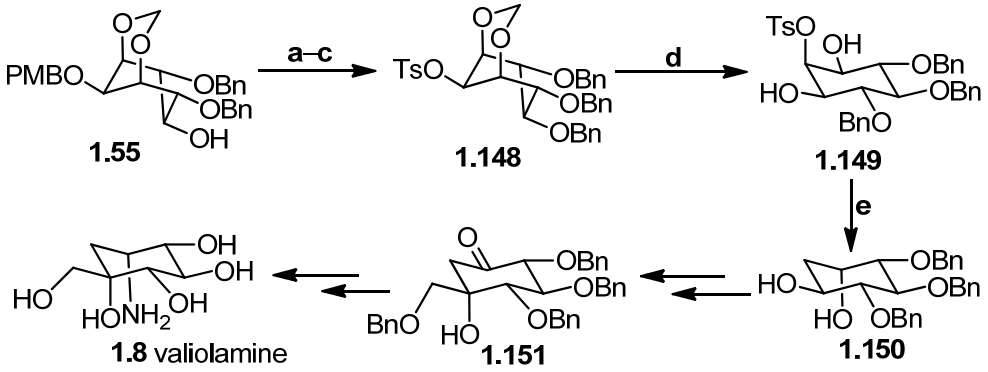
allo-Inositol **1.21** and the *racemic chiro*-inosamine **1.146** were prepared[22c] by using inositol 1,3-acetal **1.47** as a key intermediate (Scheme 1.20). The synthesis involved use of

different protecting groups for the orthogonal protection of inositol hydroxyl groups and hence these derivatives are of utility to prepare diastereomeric inositol derivatives.



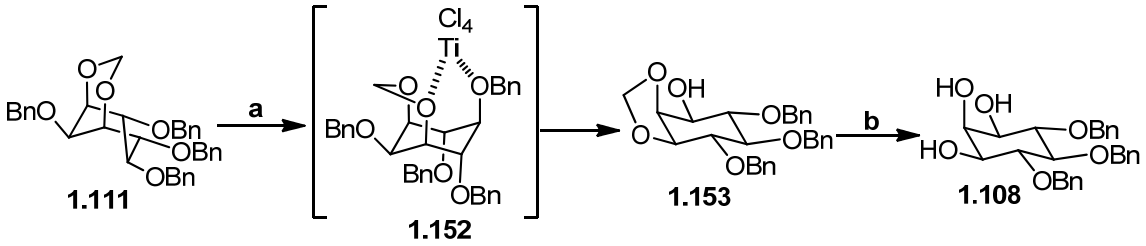
Scheme 1.20: (a) DMF, NaH, AllBr; (b) MeOH, concd. HCl, reflux; (c) DMF, NaH, PCBBr, 48%; (d) DCM, pyridine, Tf_2O, –15 °C–rt; (e) benzene, CsOAc, 18-crown-6, reflux; (f) MeOH, *i*$BuNH_2$, reflux; (g) DMF, NaH, PMBCl, 0 °C–rt; (h) toluene, $NiCl_2$(dppp), DIBAL-H; (i) DCM, $(COCl)_2$, DMSO, Et_3N, –78 °C–rt; (j) THF, MeOH, $NaBH_4$; (k) EtOH, THF, TFA, $Pd(OH)_2/C$, H_2, rt; (l) py., Ac_2O, 80 °C; (m) i) DCM, py., Tf_2O; ii) DMF, NaN_3, rt, 3 h.

A formal synthesis of *racemic* valiolamine (±)**1.8** is reported[5h] by using inositol 1,3-acetal **1.55** as an early intermediate (Scheme 1.21).



Scheme 1.21: (a) DMF, NaH, BnBr; (b) DCM:H_2O, DDQ; (c) py., TsCl, DMAP; (d) DCM, TFAA, AcOH; (e) THF, $LiEt_3BH$.

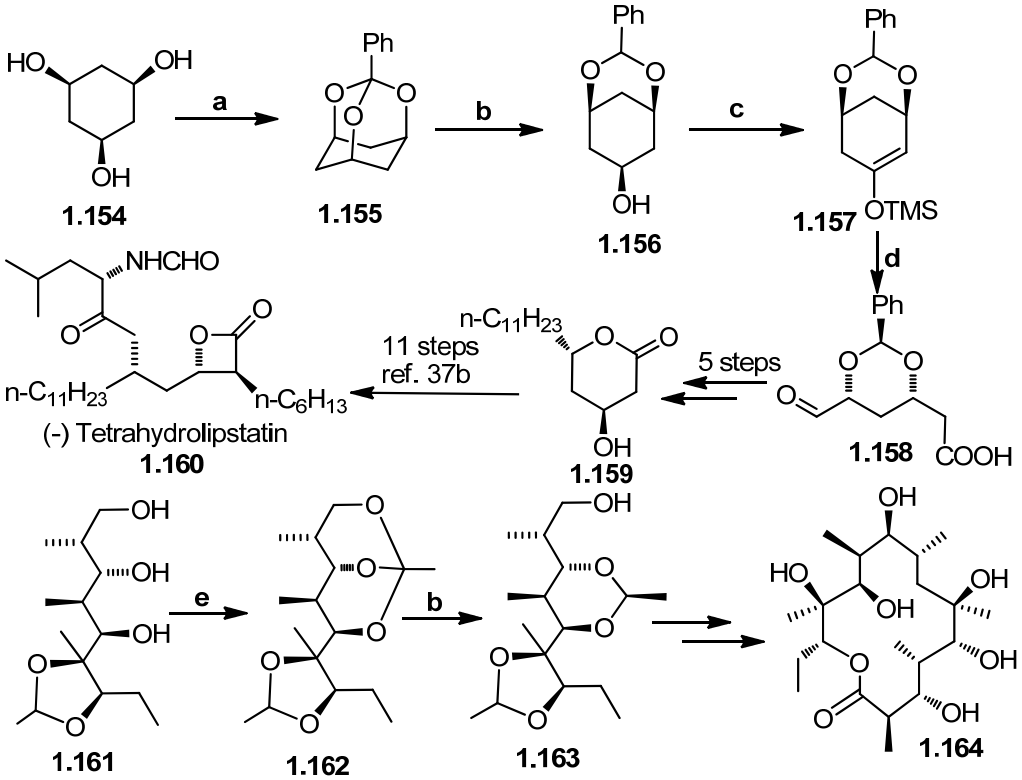
The isomerization of 1,3-acetal **1.111** to the corresponding 1,2-acetal **1.153** in the presence of titanium tetrachloride was reported (Scheme 1.22).[24a,36] The 1,2-acetal **1.153** and the triol **1.108** can be utilized for the synthesis of isomeric cyclitols and their analogs.



Scheme 1.22: (a) DCM, $TiCl_4$, –78 °C, 1 h, 85%; (b) MeOH, HBr, rt, 36 h, 95%.

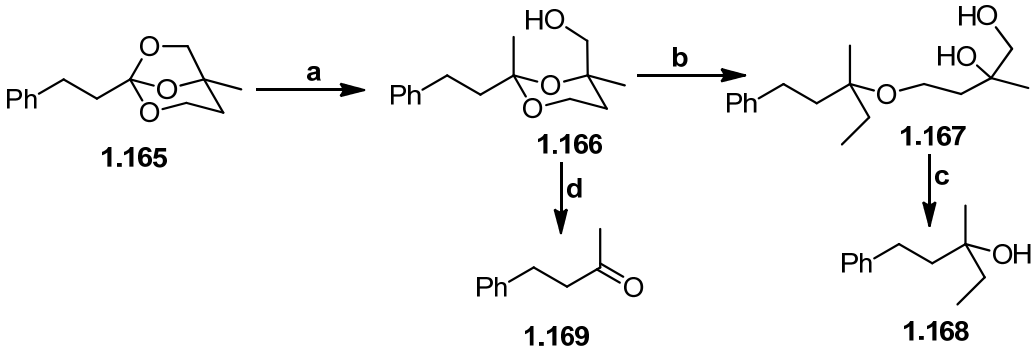
1.5.3. 1,3-acetals from polyols other than inositols

Although almost all of the 1,3-acetals mentioned in the previous pages are derivatives of *myo*-inositol, there are reports in the literature, on the utility of such acetals derived from other polyols. Few such instances are presented below. Synthesis of an antiobesity agent, (–) tetrahydrolipstatin (**1.160**, Scheme 1.23)[37] using the 1,3-acetal **1.156** of cyclohexane triol **1.154** and a natural product, (+)-(9s)-dihydroerythronolide A (**1.164**)[38] from the 1,3-acetal **1.163** are reported. Both these acetals were obtained by the regioselective reduction of the corresponding orthoester derivatives **1.155** and **1.162** using borane-THF complex.



Scheme 1.23: (a) HMPA-THF, $PhC(OEt)_3$, BF_3•OEt_2; (b) BH_3•THF; (c) i) periodinane; ii) lithium (S,S')-α,α-dimethylidinebenzylamide, TMSCl; (d) MeOH-DCM, O_3, –78 ^oC; then PPh_3; (e) $MeC(OEt)_3$, PPTS.

Tertiary alcohols can be obtained from 1,3-acetals by cleavage with Grignard reagent in the presence of Lewis acids. An example of such a conversion is shown in scheme 1.24. Acidic hydrolysis of the acetal **1.166** resulted in the formation of corresponding ketone **1.169**.[39]



Scheme 1.24: (a) benzene/THF, MeMgCl, 60 °C, 12 h, 72%; (b) THF, TMSCl, $TiCl_4$/DCM, EtMgBr, –78 °C, 56%; (c) AcOH/piperidine, PCC, 80%; (d) acetone, H_2O, TsOH, reflux.

1.6. Conclusions

Although the chemistry of inositols has been investigated for the past several decades, their use in synthesis has been restricted to the last one or two decades. Perusal of the literature reports on the utility of *myo*-inositol 1,3-acetals, reveal that it has been used as an intermediate during the synthesis of isomeric inositols and their analogs, natural and unnatural inositol phosphates as well as a natural product. However the utility of these 1,3-acetals has not been exploited to the full extent possible. Hence we have investigated the synthetic utility and structure of *myo*-inositol-1,3-acetals for the synthesis of inositol derivatives and natural products. Some of these bicyclic derivatives of the 1,3-acetals have shown interesting conformational changes in the solid and solution states. During the course of these investigations, we also discovered an interesting epimerization of 1,3-benzylidene acetals in the molten state. Results pertaining to these aspects are described in the subsequent chapters of this thesis.

1.7. References

1. (a) Ferguson, M. A. J.; Williams, A. F. *Annu. Rev. Biochem.* **1988**, *57*, 285–320; (b) Schmittberger, T.; Waldmann, H., *Synlett*. **1988**, 574–584; (c) Hinchliffe, K; Irvine, R. *Nature*, **1997**, *390*, 123–124; (d) *Phosphoinositides: Chemistry, Biochemistry and Biomedical Applications*; Bruzik, K. S., Ed.; ACS Symposium Series 718; American Chemical Society: Washington, DC, 1999; (e) *Cell Signalling*, Hancock, J. T., Oxford University Press, 2005.
2. (a) Walker, J. B. *Appl. Environ. Microbiol.* **2002**, *68*, 2404–2410; (b) Busscher, G. F.; Rutjes, F. P. J. T.; van Delft, F. L. *Chem. Rev.* **2005**, *105*, 775–791 and references cited therein; (c) Delgado, A. *Eur. J. Org. Chem.* **2008**, 3893–3906; (d) Diaz, L.; Casas, J.; Bujons, J.; Llebaria, A.; Deglado, A. *J. Med. Chem*. **2011**, *54*, 2069–2079.
3. (a) Asano, N. *J. Enzyme Inhib*. **2000**, *15*, 215–234; (b) Egido-Gabás, M.; Serrano, P.; Casas, J.; Llebaria, A.; Delgado, A. *Org. Biomol. Chem.* **2005**, *3*, 1195–1201.
4. (a) Billington, D. C. *The Inositol Phosphates: Chemical synthesis and biological significance*. VCH, New York, N.Y. **1993**; (b) Potter, B. V. L.; Lampe, D. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1933–1972; (c) Garrett, S. W.; Liu, C.; Riley, A. M.; Potter, B. V. L. *J. Chem. Soc. Perkin Trans 1*, **1998**, 1367–1368; (d) Chida, N.; Sakata, N.; Murai, K.; Tobe, T.; Nagase, T.; Ogawa, S. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 259–272; (e) Sureshan, K. M.; Shashidhar, M. S.; Praveen, T.; Das, T. *Chem. Rev*. **2003**, *103*, 4477–4503; (f) Podeschwa, M. A. L.; Plettenburg, O.; Altenbach, H. J. *Org. Biomol. Chem.* **2003**, *1*, 1919–1929; (g) Busscher, G. F.; Groothuys, S.; Gelder, R.; Rutjes, F. P. J. T.; van Delft, F. L. *J. Org. Chem.* **2004**, *69*, 4477–4481; (h) Sureshan, K. M.; Ikeda, K.; Asano, N.; Watanabe, Y. *Tetrahedron*, **2008**, *64*, 4072–4080; (i) Kılbas, B.; Balci, M. *Tetrahedron*, **2011**, *67*, 2355–2389; (j) Duchek, J.; Adams, D. R.; Hudlicky, T. *Chem. Rev.* **2011**, *111*, 4223–4258 and references cited therein.
5. (a) Tse, B.; Kishi, Y. *J. Am. Chem. Soc.* **1993**, *115*, 7892–7893; (b) Gauthier, D. R.; Bender, S. L. *Tetrahedron Lett.* **1996**, *37*, 13–16; (c) Chida, N.; Ogawa, S. *Chem. Commun.* **1997**, 807–813; (d) Suzuki, T.; Suzuki, S. T.; Yamada, I.; Koashi, Y.; Yamada, K.; Chida, N. *J. Org. Chem.* **2002**, *67*, 2874–2880; (e) Sato, K.; Akai, S.;

Sugita, N.; Ohsawa, T.; Kogure, T.; Shoji, H.; Yoshimura, J. *J. Org. Chem.* **2005**, *70*, 7496–7504; (f) Sarmah, M. P.; Shashidhar, M. S.; Sureshan, K. M.; Gonnade, R. G.; Bhadbhade, M. M. *Tetrahedron* **2005**, *61*, 4437–4446; (g) Li, M.; Wu, A.; Zhou, P. *Tetrahedron Lett.* **2006**, *47*, 3707–3710; (h) Jagdhane, R. C.; Shashidhar, M. S. *Tetrahedron*, **2011**, *67*, 7963–7970.

6. Rohloff, J. C.; Kent, K. M.; Postich, M. J.; Becker, M. W.; Chapman, H. H.; Kelly, D. E.; Lew, W.; Louie, M. S.; McGee, L. R.; Prisbe, E. J.; Schultze, L. M.; Yu, R. H.; Zhang, L. *J. Org. Chem.* **1998**, *63*, 4545–4550.
7. Gabrielsen, B.; Monath, T. P.; Huggins, J. W.; Kirsi, J. J.; Holingshead, M.; Shannon, W. M.; Pettit, G. R. *In Natural Products as Antiviral Agents*; Chu, C. K., Culter, H. G., Eds.; Plenum: New York, 1992; pp 121–135.
8. (a) Evidente, A.; Kornienko, A. *Phytochem. Rev.* **2009**, *8*, 449–459; (b) Kornienko, A.; Evidente, A. *Chem. Rev.* **2008**, *108*, 1982–2014.
9. Kim, C. U.; Lew, W.; Williams, M. A.; Liu, H.; Zhang, L.; Swaminathan, S.; Bischofberger, N.; Chen, M. S.; Mendel, D. B.; Tai, C. Y.; Laver, W. G.; Stevens, R. C. *J. Am. Chem. Soc.* **1997**, *119*, 681–690.
10. (a) Omura, S.; Hakagawa, A.; Fujimoto, T.; Saito, K.; Otoguro, K. *J. Antibiot.* **1987**, *40*, 1619–1626; (b) Cooper, C. B.; Blair, K. T.; Jones, C. S.; Minich, M. L. *Bioorg. Med. Chem. Lett*. **1997**, *7*, 1747–1752.
11. Palaniappan, N.; Ayers, S.; Gupta, S.; Habib el, S. E.; Reynolds, K. A. *Chemistry & Biology* **2006**, *13*, 753–764.
12. Tahara, Y. *Biochem. Z.* **1911**, *30*, 255–275.
13. (a) Iwasa, T.; Yamamoto, H.; Shibata, M. J. *J. Antibiot.* **1970**, *23*, 595–602. (b) Iwasa, T.; Higashide, E.; Yamamoto, H.; Shibata, M. *J. Antibiot.* **1971**, *24*, 107–113.
14. Nara, T.; Yamamoto, M.; Kawamoto, I.; Takayama, K.; Okachi, R.; Takasawa, R.; Sato, T.; Sato, S. *J. Antibiot.* **1977**, *30*, 533–540.
15. Di Paolo, G.; De Camilli, P. *Nature* **2006**, *443*, 651–657.
16. Mehta, G.; Ramesh, S. S. *Can. J. Chem.* **2005**, 83, 581–594.
17. (a) See the thematic issue of *Biochem. Soc. Symp.* **2007**, 74; (b) Michell, R. H. *Nat. Rev. Mol. Cell Biol*. **2008**, *9*, 151–161.

18. (a) Potter, B. V. L.; Lampe, D. *Angew. Chem., Int. Ed.* **1995**, *34*, 1933–1972; (b) Shashidhar, M. S. *ARKIVOC* (Gainesville, FL, USA), **2002**, *7*, 63–75.
19. Parthasarathy, R.; Eisenberg, F. *Biochem. J.* **1986**, *235*, 313–322.
20. Nomenclature committee – IUB, *Biochem. J.* **1989**, *258*, 1–2.
21. (a) Lee, H. W.; Kishi, Y. *J. Org. Chem.* **1985**, *50*, 4402–4404; (b) Biomonte, M. A. ; Vasella, A. *Helv. Chim. Acta.* **1998**, *81*, 688–694; (c) Riley, A. M.; Potter, B. V. L. *Tetrahedron Lett.* **1998**, *39*, 6769–6772; (d) Praveen, T.; Shashidhar, M. S. *Carbohydr. Res*. **2001**, *330*, 409–411; (e) Bhosekar, G.; Murali, C.; Gonnade, R. G.; Shashidhar, M. S.; Bhadbhade, M. M. *Cryst. Growth. Design* **2005**, *5*, 1977–1982.
22. (a) Billington, D. C.; Baker, R.; Kulagowski, J. J.; Mawer, I. M.; Vacca, J. P.; de Solms, S. J.; Huff, J. R. *J. Chem. Soc. Perkin Trans. 1* **1989**, 1423–1429; (b) Devaraj, S.; Shashidhar, M. S.; Dixit, S. S. *Tetrahedron* **2005**, *61*, 529–536; (c) Jagdhane, R. C.; Shashidhar, M. S. *Eur. J. Org. Chem.* **2010**, 2945–2953.
23. Gilbert, I. H.; Holmes, A. B.; Young, R. C. *Tetrahedron Lett.* 1**990**, *31*, 2633–2634.
24. (a) Gilbert, I. H.; Holmes, A. B.; Pestchanker, M. J.; Young R. C. *Carbohydr. Res.* **1992**, *234*, 117–130; (b) Murali, C.; Shashidhar, M. S.; Gopinath, C. S. *Tetrahedron,* **2007**, *63*, 4149–4155.
25. (a) Eisch, J. J.; Rhee, S. G. *J. Am. Chem. Soc.*, **1974**, *96*, 7276–7284; (b) Conway, S. J.; Gardiner, J.; Grove, S. J. A.; Johns, M. K.; Lim, Z.-Y.; Painter, G. F.; Robinson, D. E. J. E.; Schieber, C.; Thuring, J. W.; Wong, L. S. M.; Yin, M.-X.; Burgess, A. W.; Catimel, B.; Hawkins, P. T.; Ktistakis, N. T.; Stephens, L. R.; Holmes, A. B. *Org. Biomol. Chem*. **2010**, *8*, 66–74 and references cited therein.
26. Šala, M.; Kolar, J.; Strlič, M.; Kočevarb, M. *Carbohydr. Res.* **2006**, *341*, 897–902.
27. Painter, G. F.; Grove S. J. A.; Gilbert, I. H.; Holmes, A. B.; Raithby, P. R.; Hill, M. L.; Hawkins, P. T.; Stephens, L. R. *J. Chem. Soc., Perkin Trans. 1*, **1999**, 923–935.
28. (a) Swarbrick, J. M.; Cooper, S.; Bultynck, G.; Gaffney, P. R. J. *Org. Biomol. Chem.* **2009**, *7*, 1709–1715; (b) Swarbrick, J. M.; Gaffney, P. R. J. *J. Org. Chem.* **2010**, *75,* 4376–4386.
29. Ballereau, S.; Poirier, S. N.; Guillemette, G.; Spiess, B.; Schlewer, G. *J. Chem. Soc., Perkin Trans. 1*, **1998**, 1859–1864.

30. Moris, M. A.; Caron, A. Z.; Guillemette, G.; Rognan, D.; Schmitt, M.; Schlewer, G. *J. Med. Chem.* **2005**, *48*, 1251–1255.
31. Yeh, S. M.; Lee, G. H.; Wang, Y.; Luh, T. Y. *J. Org. Chem.* **1997**, *62*, 8315–8318.
32. Schmitt, L.; Spiess, B.; Schlewer, G. *Tetrahedron Lett.* **1998**, *39*, 4817–4820.
33. Grove, S. J. A.; Gilbert, I. H.; Holmes, A. B.; Painter, G. F.; Hill, M. L. *Chem. Commun*. **1997**, 1633–1634.
34. Murali, C.; Gurale, B. P.; Shashidhar, M. S. *Eur. J. Org. Chem.* **2010**, 755–766.
35. Wessig, P.; Möllnitz, K.; Hübner, S. *Synlett* **2010**, 1497–1500.
36. Yue, Z, Z.; Li, Y. C. *Chin. Chem. Lett.* **2005**, *16*, 171–174.
37. (a) Honda, T.; Endo, K.; Ono, S. *Chem. Pharm. Bull.* **2000**, *48*, 1545–1548; (b) Ghosh, A. K.; Liu, C. *Chem. Commun.* **1999**, 1743–1744.
38. Stork, G.; Rychnovsky, S. D. *J. Am. Chem. Soc.* **1987**, *109,* 1565–1567.
39. Wipf, P.; Tsuchimoto, T.; Takahashi, H. *Pure Appl. Chem.* **1990**, *71,* 415–421 and references cited therein.

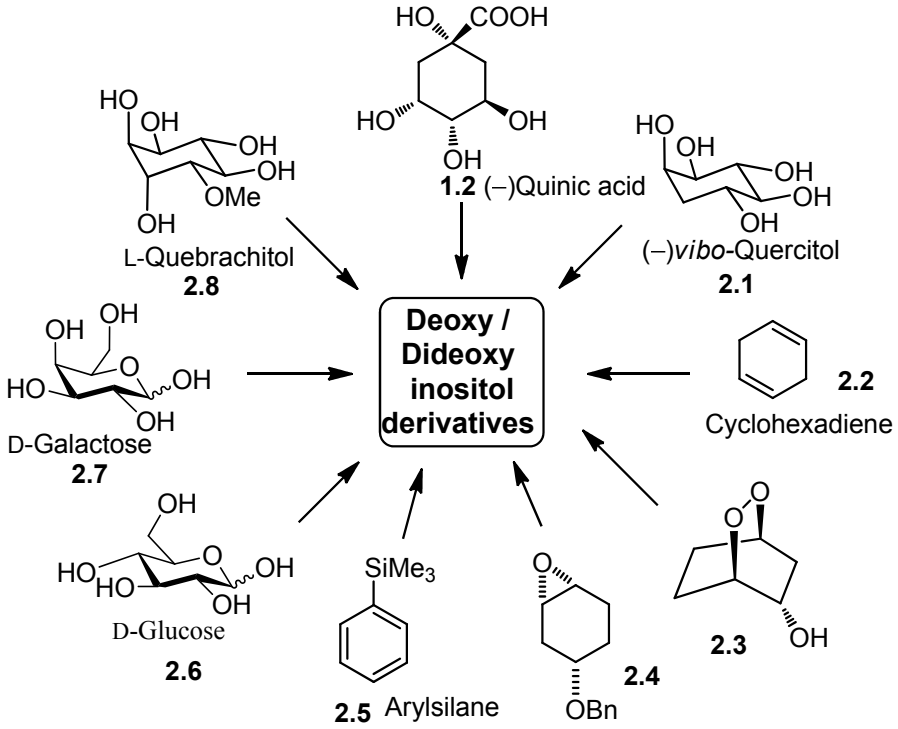
Chapter 2

Synthesis of deoxy and dideoxy cyclitol derivatives and related mechanistic studies

2.1. Introduction

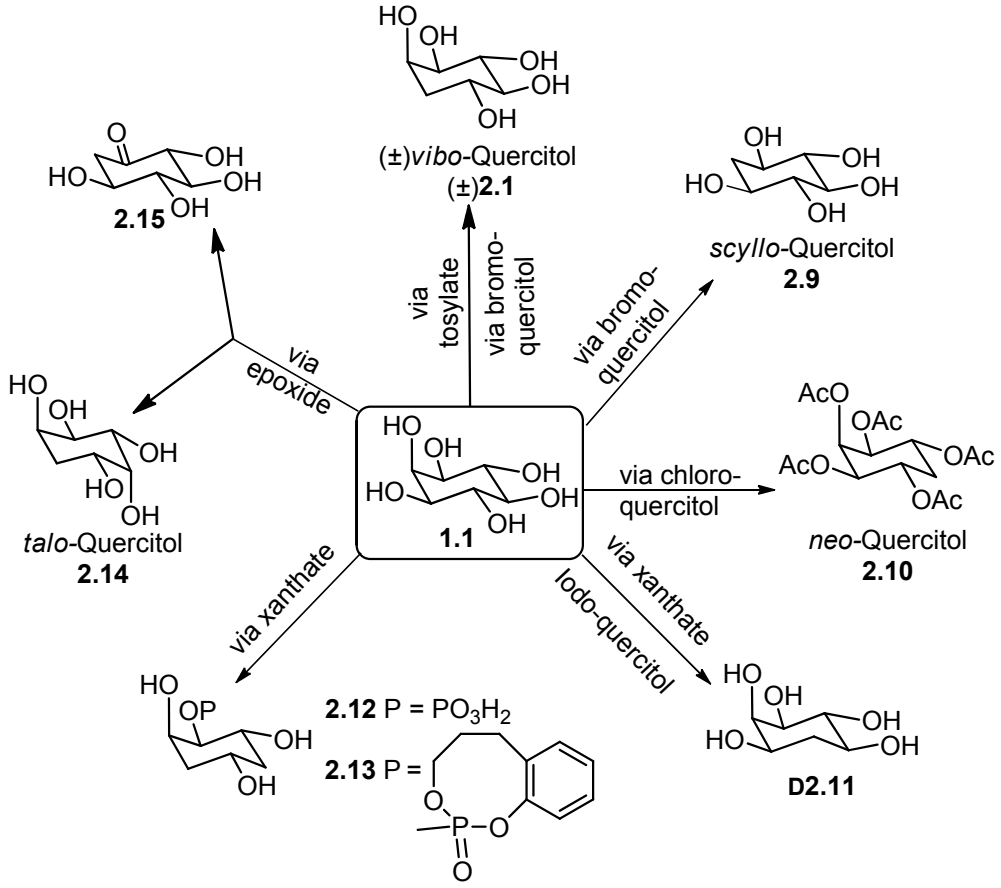
Deoxy inositols (quercitols) and dideoxy inositols (cyclohexane tetrols)

Cyclitols (polyhydroxy-substituted cycloalkanes), their alkylated and aminated analogs constitute a class of natural and synthetic compounds that are of interest to a wide cross section of chemists due to their biological activity.[1] The developments in chemical biology related to cyclitols, especially the phosphoinositol based signal transduction pathways and the associated *myo*-inositol cycle, in the last two decades, revived the interest of chemists in cyclitols and their derivatives. Cyclohexane pentols or mono-deoxy inositols are called using a generic term, 'quercitols'. Among the sixteen stereoisomers reported in the literature,[2] (+)*proto*-, (–)*proto*- and (–)*vibo*- quercitols occur in nature.[3] The biological activity shown by some of these quercitols against glycosidases led to an interest in the synthesis of natural and unnatural quercitols as well as their derivatives / analogs. Six 1,2-dideoxy inositols (two meso, four chiral) can exist and all are known; three 1,3- dideoxy inositols (one meso, two chiral) are reported and all possible five diastereomeric (three meso, two chiral) 1,4-dideoxy inositols have been prepared and characterized.[4] Deoxy and dideoxy inositols have been synthesized from various starting materials such as D-glucose,[5] D-galactopyranose,[6] L-quebrachitol,[7] quinic acid,[8] (–)*vibo*-quercitol,[9] 1,4-cyclohexadiene,[10] the peroxide **2.3**,[11] epoxide **2.4**[12] and arylsilane **2.5** (Scheme 2.1).[13]



Scheme 2.1: Starting materials used for the synthesis of deoxy and dideoxy inositol derivatives.

Although *myo*-inositol has been used as a starting material for the synthesis of inositol derivatives and analogs,[14] there are relatively few reports on the deoxygenation of these derivatives (Scheme 2.2).[2,15] D-6-Deoxy-Ins(1,3,4,5)P_4 (tetraphosphate of **2.11**) and its enantiomer were used as tools to unravel the enigmatic role of Ins(1,3,4,5)P_4 in the polyphosphoinositide pathway of signal transduction.[15i] Mono phosphorylated 3,5-dideoxy *myo*-inositol **2.12** is an inhibitor of *myo*-inositol monophosphatase.[15g] The phosphate **2.13** was used to test the role of hydroxyl groups in binding of the substrate with mammalian IMPase.[15g,j]

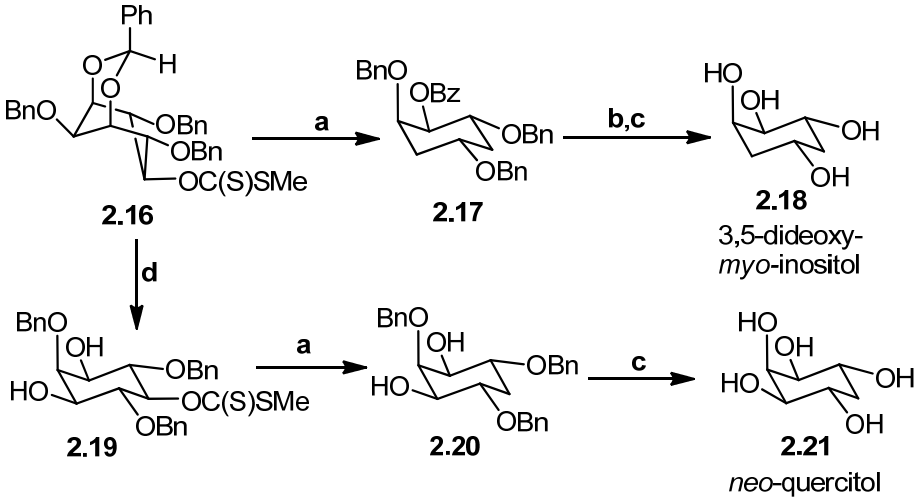


Scheme 2.2: Deoxy and dideoxy inositol derivatives synthesized from *myo*-inositol.

2.2. Present work

2.2.1. Deoxygenation of *myo*-xanthates with 1,3-*O*-benzylidene acetal

A novel route for the dideoxygenation of *myo*-inositol *via* its 1,3-*O*-benzylidene derivative was discovered in our laboratory.[16] The radical mediated deoxygenation of the xanthate **2.16** led to the formation of the dideoxy inositol derivative **2.17** (Scheme 2.3). The same xanthate **2.16** could also be used to generate the monodeoxy derivative **2.20** by deprotecting the acetal prior to deoxygenation under Barton – McCombie conditions.[17]



Scheme 2.3: (a) toluene, *n*-Bu_3SnH, AIBN, 100 ºC, 1 h, 91–92%; (b) MeOH, *i*-$BuNH_2$; (c) MeOH, H_2, $Pd(OH)_2/C$, rt, 24 h; (d) THF/MeOH, TFA.

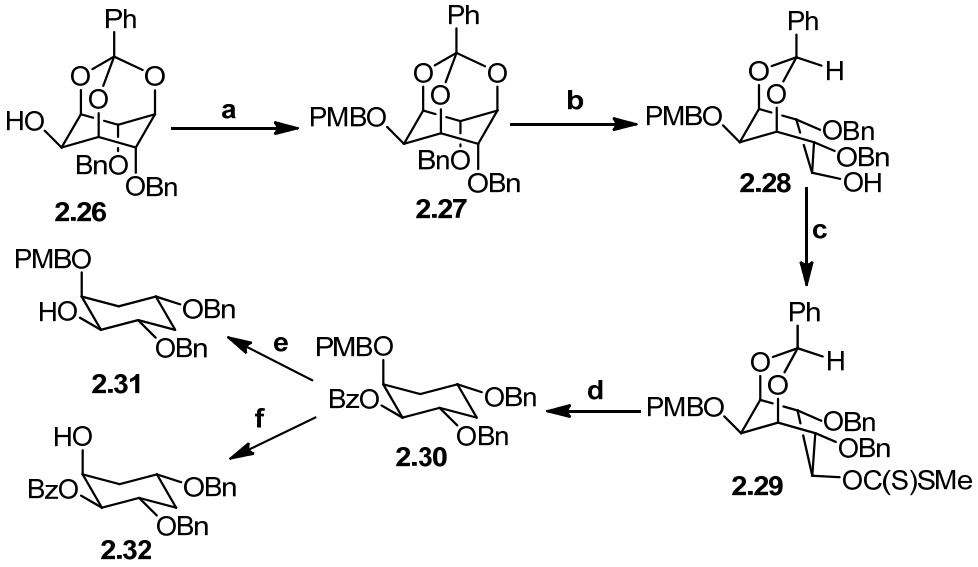
Comparison of these two reactions clearly showed that the dideoxyinositol derivative is produced due to the cleavage of the benzylidene acetal, eventually leading to the formation of a benzoate. Radical initiated cleavage of benzylidene acetals of 1,3-diols leading to the formation of benzoates has earlier been reported (Scheme 2.4).[18]

Radical Source: (*t*-BuO)$_3$SiSH or *i*-Pr_3SiSH and 2,2- bis (*t*-butyl peroxy) butane

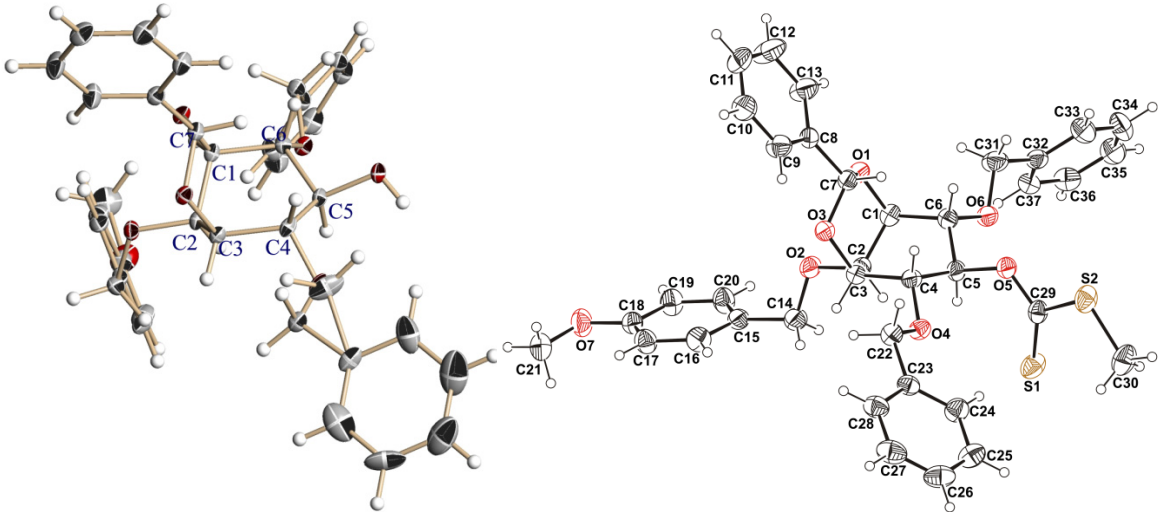
Scheme 2.4: Radical initiated cleavage of benzylidene acetals.

We deoxygenated the C5-hydroxyl group in **2.28** *via* its xanthate **2.29**; the dideoxy inositol derivative **2.30** obtained has orthogonal protecting groups on two of its hydroxyl groups. Hence this derivative is amenable to further manipulation to generate other cyclitol

derivatives (Scheme 2.5). The structure of **2.29** was established by single crystal X-ray diffraction analysis (Figure 2.1).



Scheme 2.5: (a) DMF, NaH, PMBCl, rt, 3 h, 96%; (b) DCM, DIBAL-H, 0 °C, 2.5 h, 86–95%; (c) THF, NaH, CS_2, reflux, 1 h, MeI, rt, 16 h, 94%; (d) toluene, *n*-Bu_3SnH, AIBN, reflux, 1 h, 93%; (e) MeOH, KOH, rt, 3 h, 98%; (f) DCM:water (95:5), DDQ, rt, 2 h, 92%.



(a) (b)

Figure 2.1: ORTEP of (a) **2.28** (methylene carbon of the benzyl ether at C4-position showing orientational disorder at two positions with equal occupancies) and (b) **2.29**. Thermal ellipsoids are drawn at 30% probability and hydrogen atoms are depicted as small spheres of arbitrary radii.

The following aspects of this novel deoxygenation reaction (of **2.16** and **2.29**) have been investigated and the results are reported below: (a) Deoxygenation reaction of the xanthate of a regioisomeric (C1,C5-) *O*-benzylidene acetal; (b) Deoxygenation reaction of regioisomeric C2-xanthate of a benzylidene acetal; (c) Deoxygenation reaction of the xanthate of a 1,3-acetal, other than the benzylidene acetal; (d) Experiments to see whether the relative orientation of the xanthate or the conformation of the inositol ring affects the outcome of deoxygenation reaction; (e) Experiments to see whether cleavage of the benzylidene acetal takes place by intermolecular or intramolecular hydrogen abstraction; (f) Experiments and calculations to understand if the bicyclic inositol derivatives undergo conformational changes during the deoxygenation reaction.

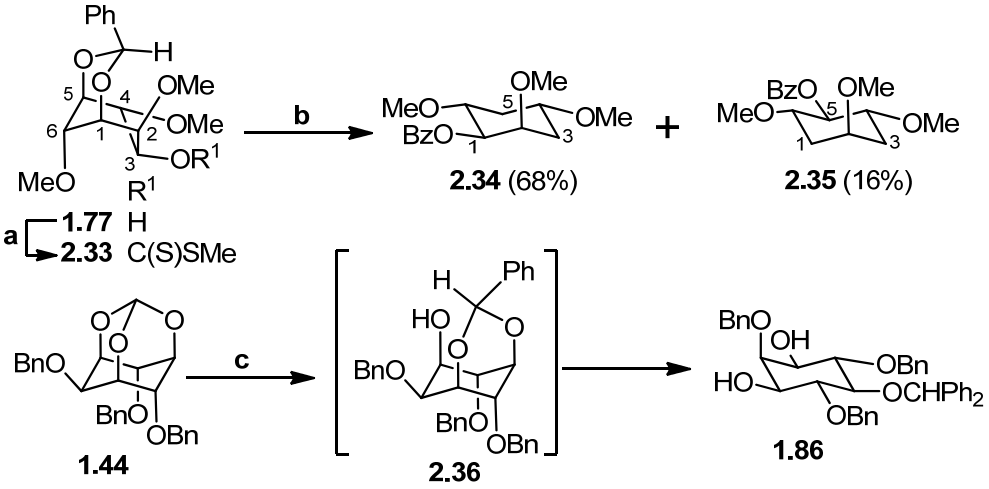
Investigations of the mechanistic aspects of the deoxygenation reaction

2.2.2. Deoxygenation reaction of the xanthate of a regioisomeric (C1,C5-) *O*-benzylidene acetal

In order to gauge the possibility of synthesis of other cyclitol derivatives *via* the deoxygenation of inositol derivatives, the regioisomeric xanthate **2.33** carrying the xanthate at the C3-position and the benzylidene acetal at the C1,C5-position was prepared and subjected to deoxygenation conditions as earlier. This was especially since the C1- and C5-positions of *myo*-inositol are not equivalent (unlike C1- and C3-positions) and hence dideoxygenation of the xanthate **2.33** is expected to yield two different products (Scheme 2.6). This is of significance since, (i) selective deoxygenation at any of the two positions would be of potential synthetic utility and (ii) plasma radiation-induced generation of hydroxyl alkyl radicals in solid *myo*-inositol led to preferential formation of radical at the C5-position (over the C1-positon), but the C1-radical was relatively more stable than the C5-radical produced.[19] Hence it was of interest to see the trend in stability of the radicals generated during the dideoxygenation of the xanthate carrying the unsymmetrical benzylidene acetal moiety.

Deoxygenation of the xanthate **2.33** led to the formation of two isomeric dideoxy inositols (Scheme 2.6). The 3,5-dideoxyinositol derivative **2.34** was obtained as the major product. The C-3 alcohol with C1,C5-*O*-benzylidene acetal **1.77** could be prepared by a reported

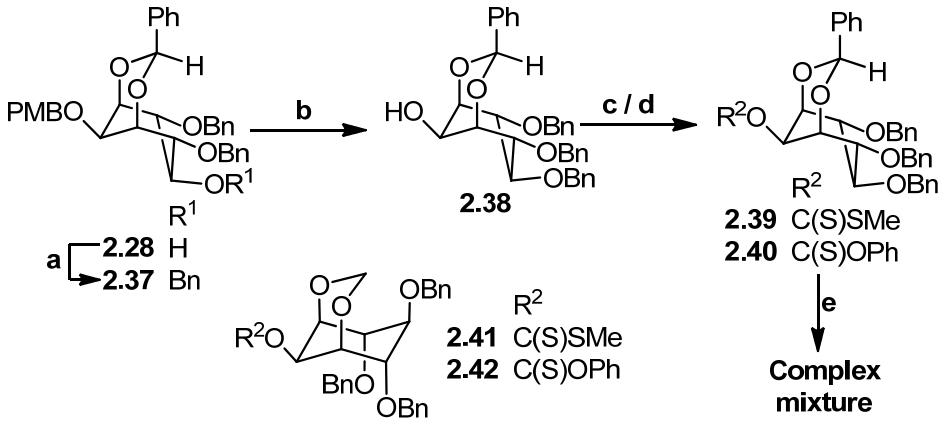
procedure[20] and converted to the corresponding xanthate **2.33**. Our attempts to prepare the *racemic* alcohol **2.36** by the cleavage of the orthoformate moiety in the tribenzylether **1.44** with phenyl magnesium bromide, provided the corresponding 1,3-diol **1.86** exclusively and we could not isolate the acetal intermediate **2.36** consistently in several trials. The reasons for this observed difference in product formation by change of methyl groups to benzyl groups is not clear.



Scheme 2.6: (a) THF, NaH, CS_2, reflux, 1 h, MeI, rt, 16 h, 94%; (b) toluene, *n*-Bu_3SnH, AIBN, reflux, 1 h, 84%; (c) benzene, PhMgBr, rt–reflux, 3 h.

2.2.3. Deoxygenation reaction of regioisomeric C2-xanthate of a benzylidene acetal

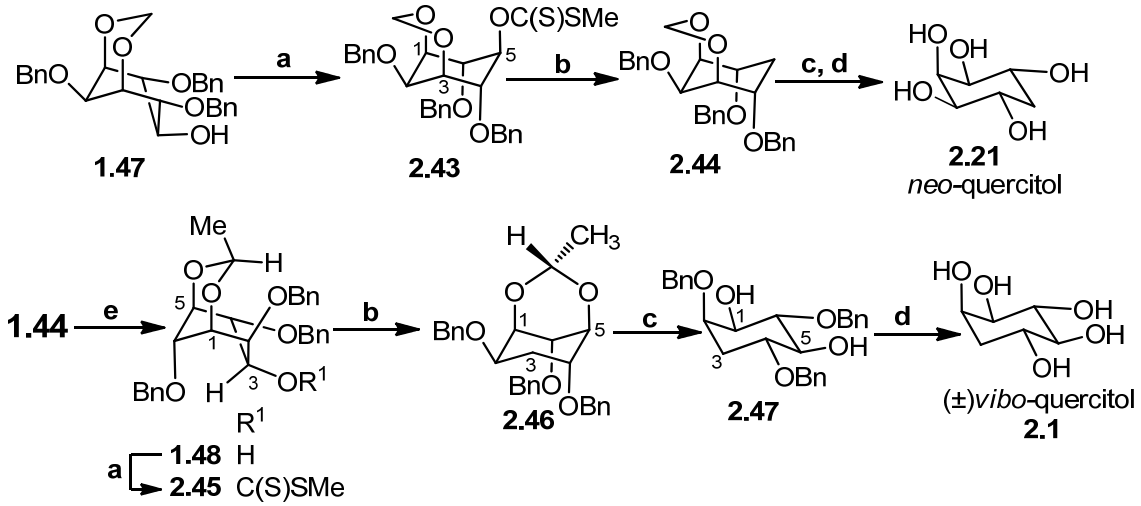
We also attempted to carry out the deoxygenation of the C2-xanthate derivative **2.39**, hoping to widen the synthetic scope of the reaction under discussion (Scheme 2.7). The Barton-McCombie deoxygenation of **2.39** with tributyltinhydride in the presence of AIBN led to a mixture of products which were inseparable by column chromatography. Similar was the outcome of the reaction of the more reactive phenyl thionoformate derivative **2.40** with tributyltinhydride. We had made similar observations earlier in our laboratory[21] while attempting to deoxygenate the C2-hydroxyl group (*via* its xanthate) in the *myo*-inositol derivative **2.41** and **2.42**. The xanthate **2.39** was prepared from alcohol **2.28** as shown in Scheme 2.7.



Scheme 2.7: (a) DMF, NaH, BnBr, rt, 3 h, 96%; (b) DCM:H_2O (95:5), DDQ, rt, 2.5 h, 92%; (c) THF, NaH, CS_2 , reflux, 1 h, MeI, rt, 16 h; (d) THF, py., PhOC(S)Cl, rt, 2 h, 88%; (e) toluene, *n*-Bu_3SnH, AIBN, reflux, 1 h.

2.2.4. Deoxygenation reaction of the xanthate of a 1,3-acetal, other than the benzylidene acetal (deoxygenation of the 1,3-acetals 2.43 and 2.45)

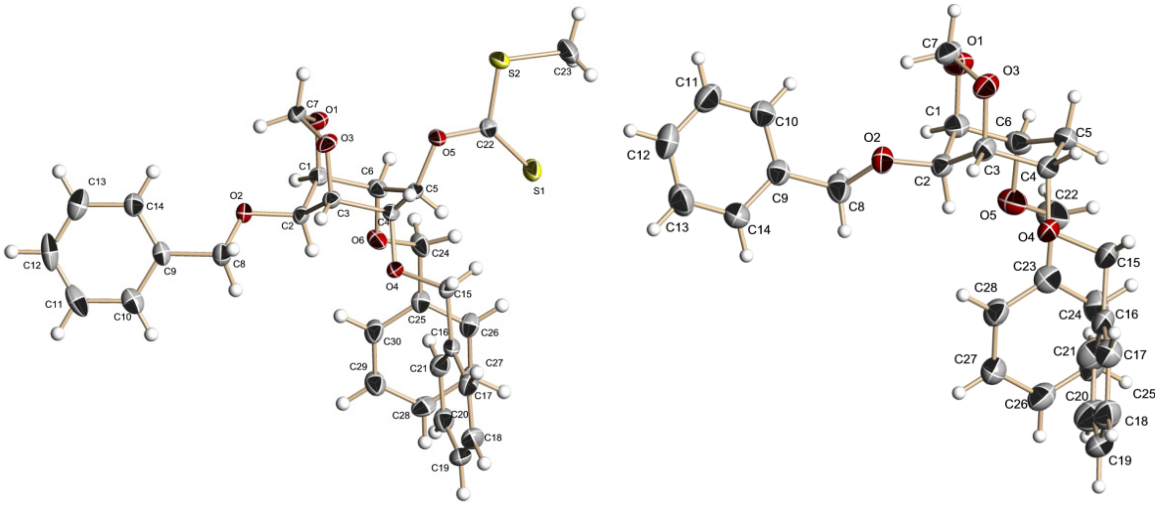
To check whether the dideoxygenation occurs in the C5-xanthates with acetals other than the benzylidene acetal, xanthates **2.43** and **2.45** were prepared and subjected to radical deoxygenation conditions. In both the experiments the corresponding monodeoxy product was obtained exclusively (Scheme 2.8).



Scheme 2.8: (a) THF, NaH, CS_2, reflux, 1 h, then MeI, rt, 16 h, 98%; (b) toluene, *n*-Bu_3SnH, AIBN, reflux, 1 h, 92–94%; (c) THF:H_2O, HCl, reflux, 2 h; (d) MeOH, H_2 (60 psi), 20% $Pd(OH)_2/C$, rt, 10 h, 88–92% (for 2 steps); (e) benzene, MeMgI, , rt, 15 h, 84%.

The xanthate **2.43** was prepared from the acetal **1.47**; the structure and conformation of **2.43** and the deoxygenated derivative **2.44** was established by single crystal X-ray

diffraction methods (Figure 2.2). Hydrolysis of the acetal in **2.44** and hydrogenolysis of all the benzyl ethers gave *neo*-quercitol **2.21** (77% overall yield in 6 steps from *myo*-inositol). Deoxygenation of the xanthate **2.45** having C1,C5-*O*-ethylidene acetal gave the monodeoxy derivative **2.46** exclusively. The deoxygenated derivative **2.46** was converted to *racemic vibo*-quercitol (**2.1**, 64% yield in 7 steps from *myo*-inositol, Scheme 2.8) by global deprotection of the hydroxyl groups. *Racemic vibo*-quercitol has been prepared earlier[2,5] from D-glucose with <5% overall yield in 8 steps.

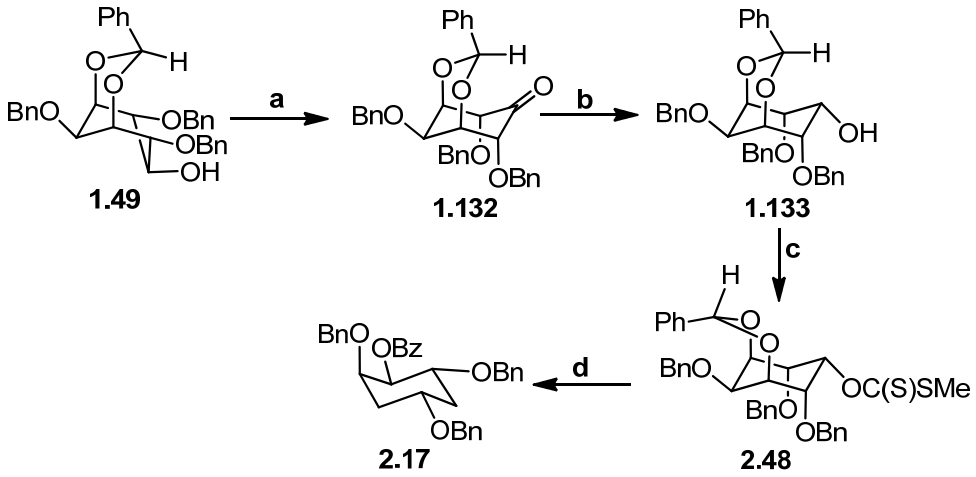


(a) (b)

Figure 2.2: ORTEP of (a) **2.43** and (b) **2.44**. Thermal ellipsoids are drawn at 30% probability and hydrogen atoms are depicted as small spheres of arbitrary radii.

2.2.5. Experiments to see whether the relative orientation of the xanthate or the conformation of the inositol ring affect the outcome of the deoxygenation reaction

To investigate whether the relative orientation of the xanthate or the conformation of the acetal and inositol ring affects the reaction, we carried out deoxygenation of the *neo*-xanthate (**2.48**). The *myo*-inositol derivative **1.49** (Scheme 2.9) was oxidized by IBX to the corresponding ketone **1.132** which was reduced by sodium borohydride to obtain the *neo*-alcohol **1.133**. The xanthate **2.48** of the *neo*-alcohol **1.133** on deoxygenation under Barton – McCombie conditions gave the dideoxygenated inositol derivative **2.17**. A comparison of the results of deoxygenation of the xanthates **2.16** and **2.48** (which have different configuration and ring conformation) suggests that the deoxygenation reaction proceeds through the same radical intermediate. Conformation of the *neo*-xanthate **2.48** was established by single crystal X-ray diffraction methods (Figure 2.3).



Scheme 2.9: (a) EtOAc, IBX, reflux, 3 h, 94%; (b) EtOH, $NaBH_4$, 0 °C, 94%; (c) THF, NaH, CS_2, reflux, 1 h, MeI, rt, 16 h, 98%; (d) toluene, *n*-Bu_3SnH, AIBN, 100 ºC, 1 h, 91%.

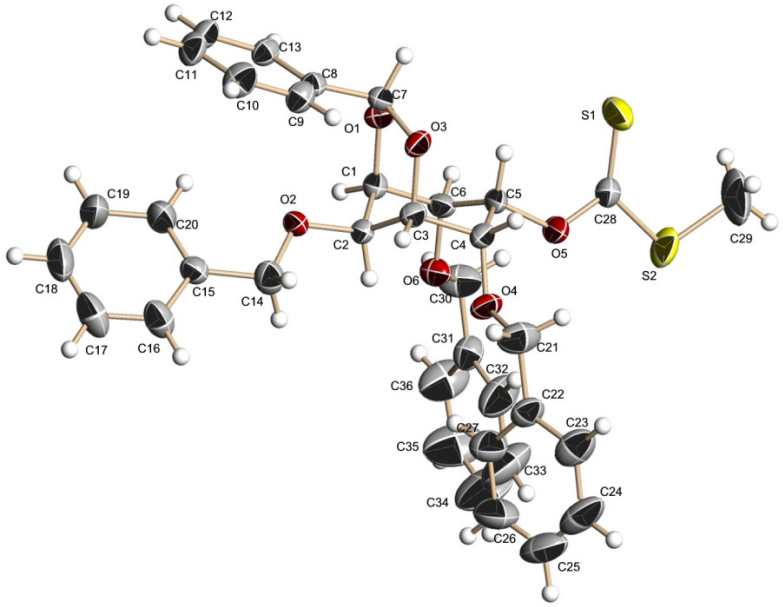
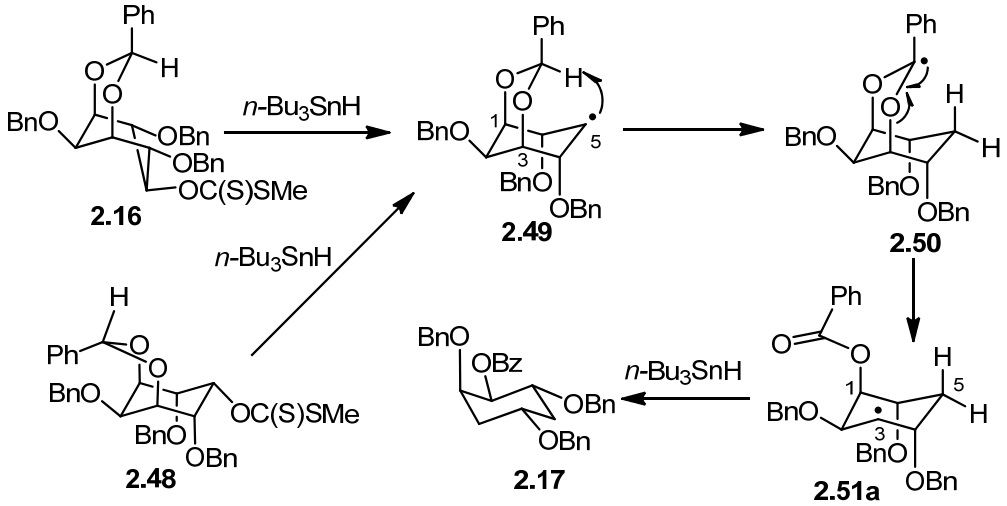


Figure 2.3: ORTEP of *neo*-xanthate **2.48**. Thermal ellipsoids are drawn at 30% probability and hydrogen atoms are depicted as small spheres of arbitrary radii.

2.2.6. Experiments to confirm that the cleavage of the benzylidene acetal (in 2.16, 2.29 and 2.48) is by intramolecular hydrogen abstraction

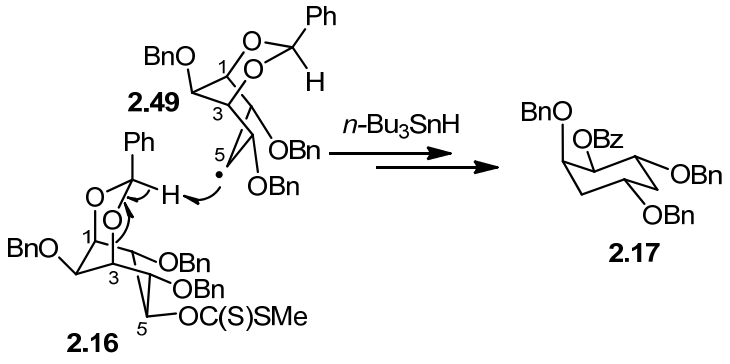
A perusal of the structure and conformation of the xanthates **2.16**, **2.29** and **2.48** shows that intramolecular abstraction of the benzylic hydrogen is not feasible in the radicals generated from these molecules under Barton-McCombie conditions, if their conformation is maintained as depicted in Schemes 2.3 and 2.9. However, a comparison of the results of deoxygenation of the three xanthates suggests the involvement of a common radical

intermediate. We can postulate this common radical intermediate to be **2.49** (Scheme 2.10) as this can be obtained by boat-chair inter-conversion of one of the two six membered rings in these xanthates. As is clear from the conformation of the two rings in the radical **2.49**, this intermediate allows facile intramolecular abstraction of the benzylic hydrogen which leads to the formation of the dideoxygenated product, isolated in all the experiments.



Scheme 2.10: Intramolecular hydrogen abstraction in benzylidene acetals.

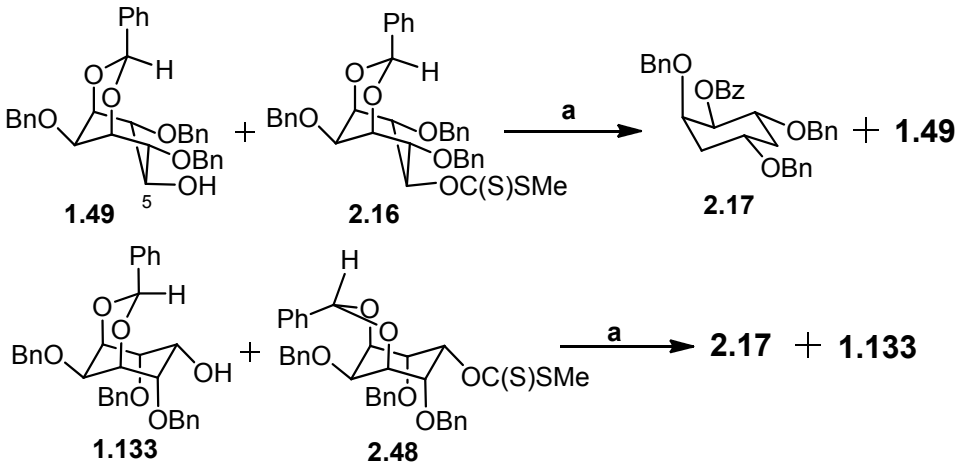
Although cleavage of the benzylidene acetal **2.16** *via* an intramolecular hydrogen abstraction is shown in the Scheme 2.10, other route shown in the Scheme 2.11 is in principle possible by intermolecular hydrogen abstraction. Hence we carried out a few experiments to rule out this possibility, unambiguously.



Scheme 2.11: Intermolecular hydrogen abstraction in benzylidene acetals.

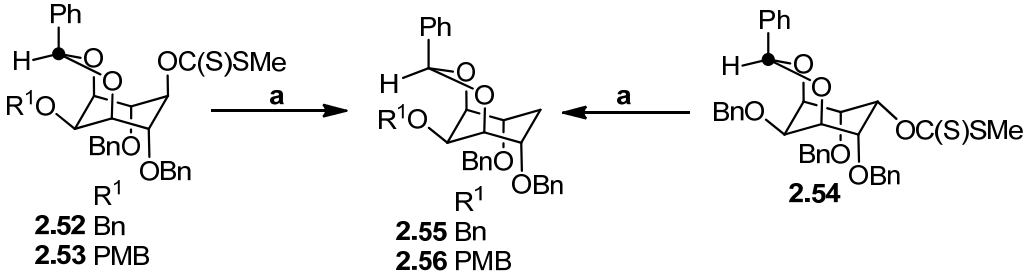
Deoxygenation of the xanthates **2.16** and **2.48** in the presence of **1.49** and **1.133** respectively yielded the dideoxygenated product **2.17** exclusively (Scheme 2.12) and the benzylidene acetals **1.49** and **1.133** were recovered almost quantitatively. If cleavage of the

benzylidene acetals was proceeding by intermolecular hydrogen abstraction, we should have isolated products arising from the cleavage of the acetals in **1.49** and **1.133** along with **2.17**.



Scheme 2.12: (a) toluene, *n*-Bu_3SnH, AIBN, reflux, 1 h.

In another set of experiments, deoxygenation of epimers (**2.52**, **2.53** and **2.54**, Scheme 2.13) of xanthates **2.16**, **2.29** and **2.48** under radical deoxygenation conditions were carried out. All these experiments yielded the corresponding monodeoxy derivative exclusively, since intramolecular benzylic hydrogen abstraction is sterically forbidden in these molecules. The structure of the mono-deoxy derivative **2.56** was established by single crystal X-ray diffraction analysis (Figure 2.4).



Scheme 2.13: (a) toluene, *n*-Bu_3SnH, AIBN, reflux, 1 h, 80-92%.

Non formation of the dideoxy derivatives in these experiments also rules out the intermolecular hydrogen abstraction pathway depicted in Scheme 2.11. For details on the epimerization of inositol 1,3-benzylidene acetals in **2.16**, **2.29** and **2.48** please see section 2.2.9, page No. 48. Results of both these experiments (Schemes 2.12 and 2.13) ruled out

the cleavage of the benzylidene acetal by intermolecular abstraction of the corresponding acetal hydrogen atom in the radical initially produced, which is shown in scheme 2.11.

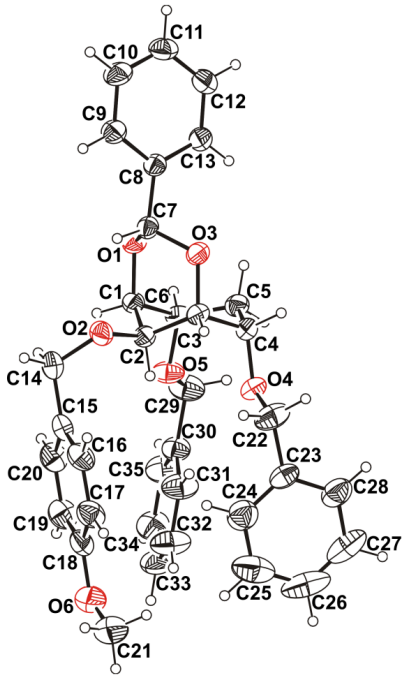


Figure 2.4: ORTEP of **2.56**. Thermal ellipsoids are drawn at 30% probability and hydrogen atoms are depicted as small spheres of arbitrary radii.

2.2.7. Experiments and calculations performed to understand if the bicyclic inositol derivatives undergo conformational changes during the deoxygenation reaction

A comparison of the structure of the xanthates **2.16**, **2.29** and **2.48** shows that the relative conformation of the inositol and the acetal rings can vary among these bicyclic inositol derivatives. Such variations could have implications on the course and mechanism of these deoxygenation reactions. Although the conformations of the xanthates shown in Schemes 2.3, 2.5 and 2.9 were established by X-ray crystallography, it does not imply that these are the reactive conformations nor minimum energy conformations nor does it imply that these conformations exist in solution, exclusively. In order to gain insight into these possibilities and the associated reaction mechanism, we have examined the conformation of the xanthates by DFT calculations and computed the geometry of the transition state for the intramolecular hydrogen transfer.

Conformation of the molecules of *myo*-xanthates **2.16**[16] and **2.29** and the *neo*-xanthate **2.48** in their crystals are as shown in Figures 2.5, 2.1 and 2.3 respectively. NMR spectroscopy of the same compounds (Chart 2.1) revealed that solution state conformation of the *myo*-xanthates **2.16** and **2.29** is perhaps same as that in their crystals but the conformation of the *neo*-xanthate **2.48** is not same in the crystalline and solution states.

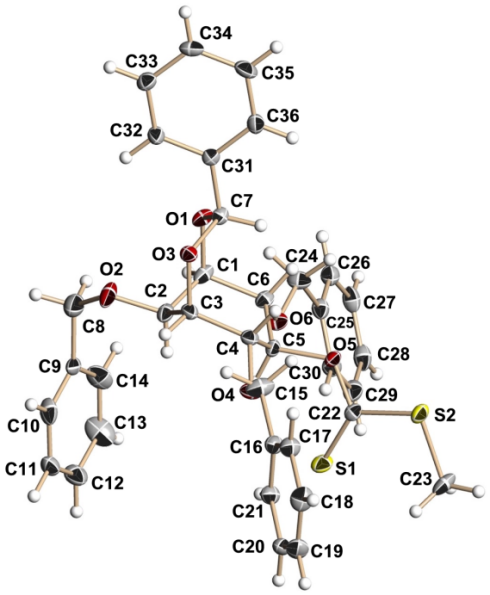


Figure 2.5: ORTEP of *myo*-xanthate **2.16**.[16] Thermal ellipsoids are drawn at 30% probability and hydrogen atoms are depicted as small spheres of arbitrary radii.

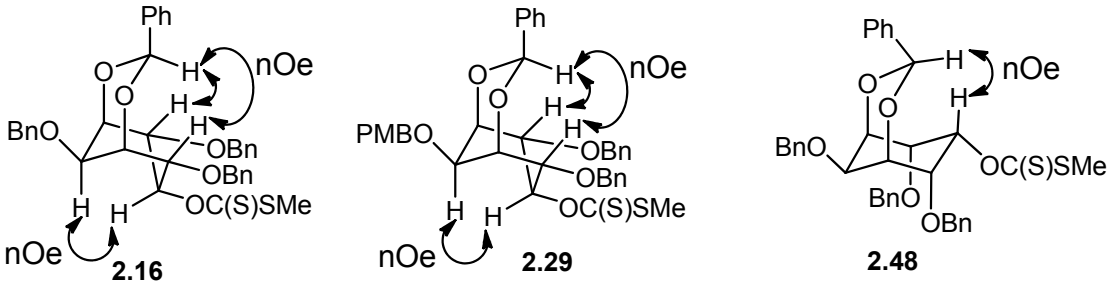


Chart 2.1: Conformation of the two rings in the xanthates as suggested by results of 2D NMR spectroscopy.

Hence the possibility that these xanthates exist in more than one conformation in solution cannot be ruled out. Four possible conformations of the xanthates and conformation of the radicals generated from them are shown in Chart 2.2 (same radical – **2.49**, is generated from xanthates **2.16** and **2.48**).

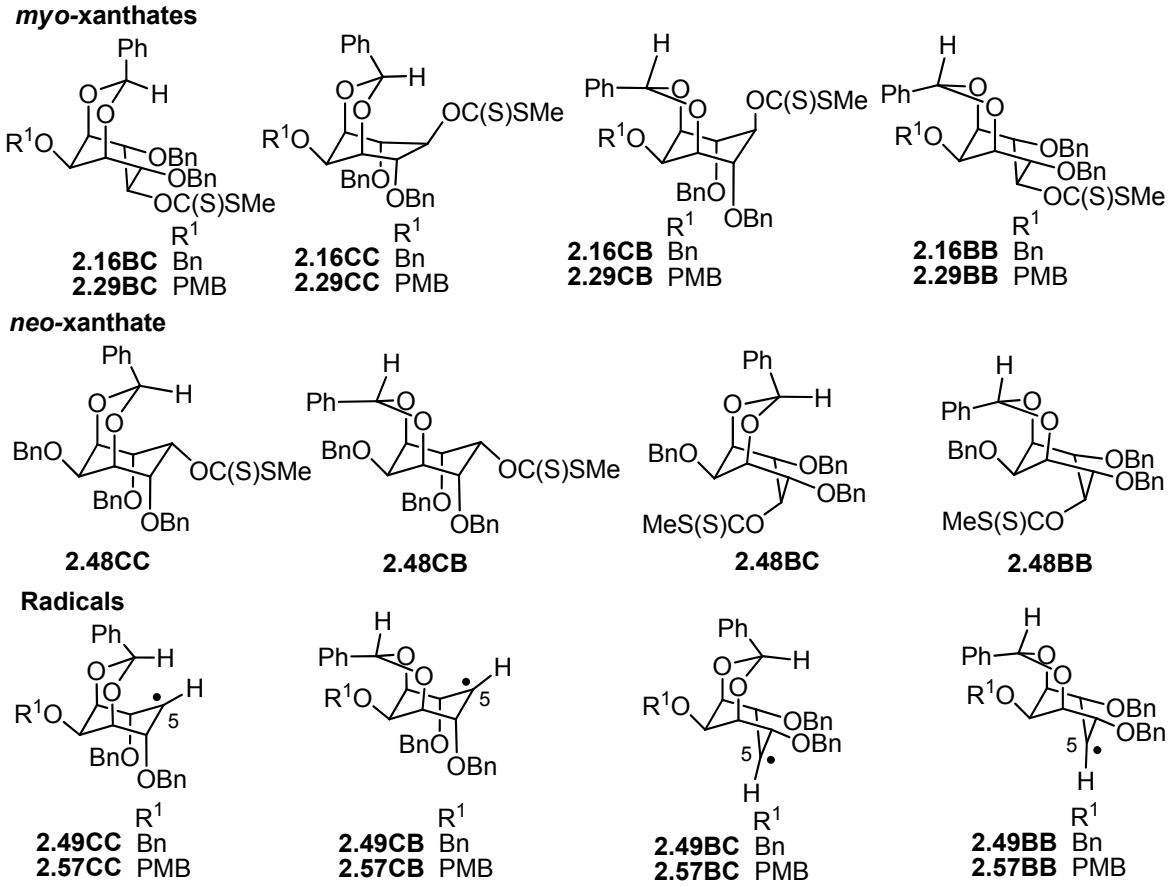
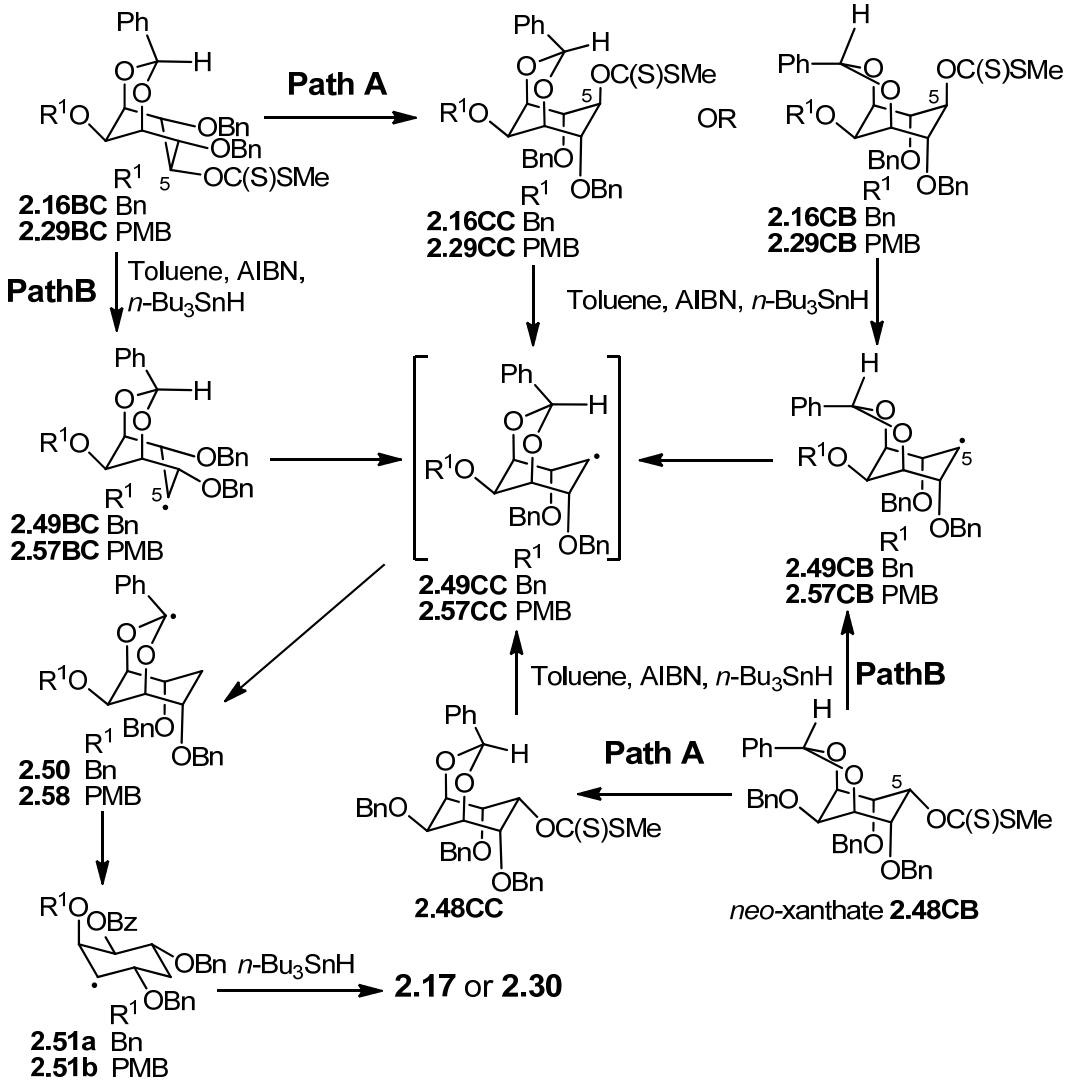


Chart 2.2: Possible conformations of the *myo*- and *neo*-xanthates and the radicals generated from them. The suffixes to compound numbers indicate the Chair (**C**) or Boat (**B**) conformation of the inositol and the acetal rings respectively.

Intramolecular abstraction of the acetal hydrogen in the radicals generated at the C5-carbon from the xanthates appears likely only in one of the conformations (**2.49CC** / **2.57CC**) depicted for the radical **2.49** and **2.57** in Chart 2.2. However, since experimentally we obtain the dideoxy inositol derivative **2.17** (or **2.30**) as the only product, on treatment of the xanthates **2.16**, **2.29** and **2.48** with tributyltinhydride, either the starting xanthates or the intermediate radicals must be undergoing conformational change prior to intramolecular abstraction of the benzylidene acetal hydrogen, leading to the formation of the same radical (in which intramolecular hydrogen abstraction is facile). Hence, one can visualize two different paths for the deoxygenation reaction (Scheme 2.14), leading to the formation of the dideoxy inositols **2.17** and **2.30**. Path A, in which conformational change of the xanthate precedes formation of the radical (in which intramolecular hydrogen abstraction is facile) and Path B, in which the initially generated radicals from *myo*- and

neo-xanthates undergo a change in conformation before intramolecular hydrogen abstraction. Since all the three xanthates **2.16**, **2.29** and **2.48** give the same dideoxy derivative in high yield, the reaction must be proceeding *via* a common radical intermediate. Since experiments cannot distinguish between Path A and Path B, we performed DFT calculations to see the relative facilities of the two paths leading to the formation of the dideoxy derivatives **2.17** and **2.30**.



Scheme 2.14: Plausible pathways for the intramolecular abstraction of hydrogen by the radical initially generated from xanthates **2.16**, **2.29** and **2.48**.

Results obtained from geometrical optimization studies (DFT calculations), showed that the relative stabilities of the conformations of the *myo*-xanthates are in the order **2.16BC** > **2.16CC** > **2.16CB** and **2.29BC** > **2.29CB** > **2.29CC** (Figure 2.6). Although the relative

order of stability for the conformers of **2.16** and **2.29** are different, the most stable conformer for both the xanthates has the boat-chair conformation. For the *neo*-xanthate **2.48** the order of relative stabilities for the three different conformations was **2.48CC** > **2.48CB** > **2.48BC**.

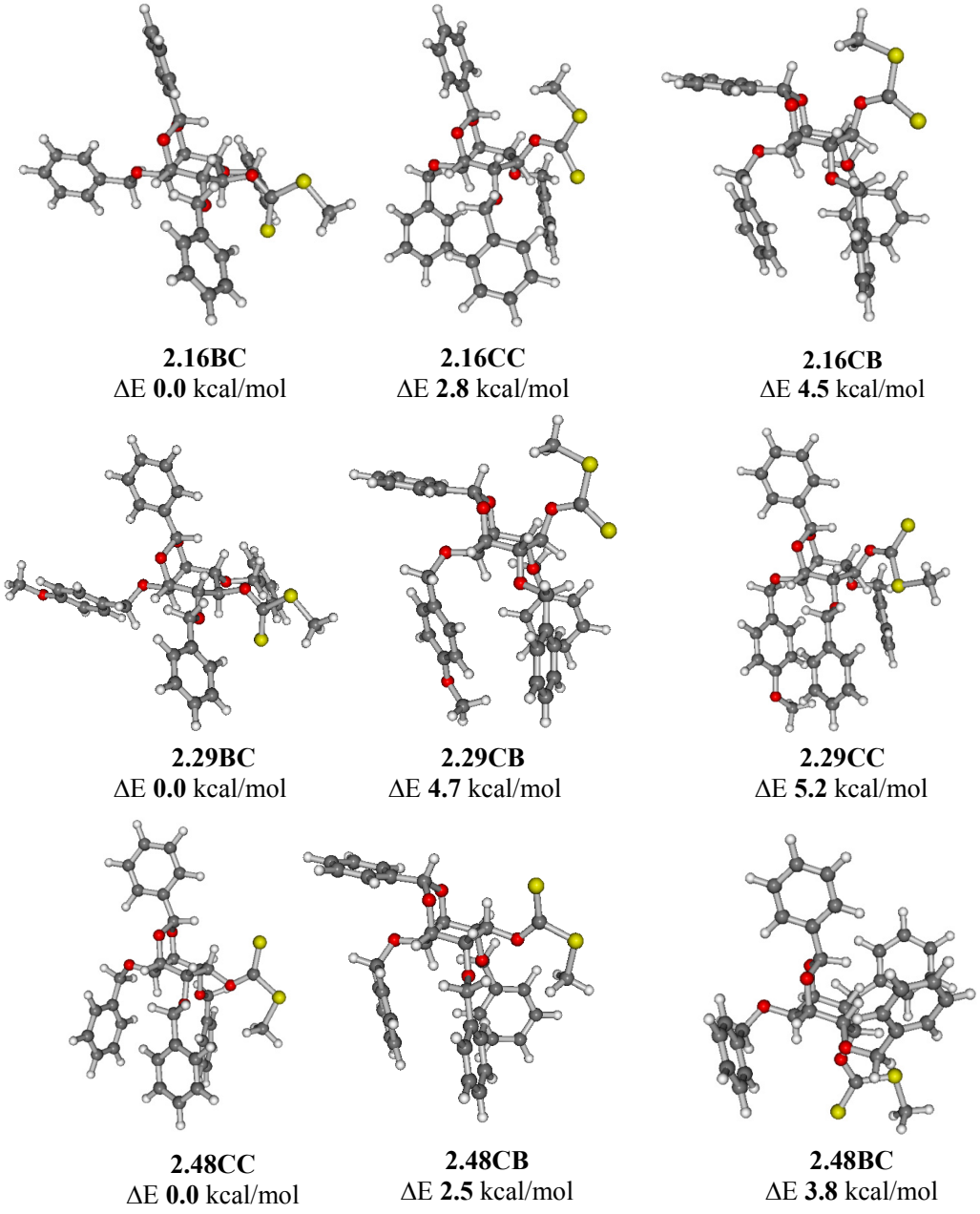


Figure 2.6: Results of geometrical optimization for xanthates **2.16**, **2.29** and **2.48**.

During these DFT calculations we found that for all the xanthates the conformation in which both the rings are in the boat form are least stable and inherently flip over to one of the three conformations in which at least one ring has the chair conformation. It is

interesting to note that while the conformation of the *myo*-xanthate in its crystals is **2.16BC** (most stable conformation according to DFT calculations) the conformation of the *neo*-xanthate in its crystals is **2.48CB** (which is not the most stable conformation according to DFT calculations). This difference in the conformation of the *neo*-xanthate between the crystalline state and that predicted by geometrical optimization could be due to lattice interactions in the crystal, since the difference in stability between **2.48CB** and **2.48CC** is not large. It is interesting to note that **2.48CC** is the conformation (or one of the conformations present in solution) suggested by NMR spectroscopy in chloroform solution. The change in conformation of the xanthate **2.48** on going from crystalline state to the solution state at ambient temperature also suggests that these conformational changes do not involve high energy barriers.

The order of relative stabilities (predicted by DFT calculations) for the three different conformations for the radical generated from **2.16** or **2.48** is in the order **2.49CC** > **2.49BC** > **2.49CB** and for the radical generated from **2.29** is in the order **2.57CC** > **2.57BC** > **2.57CB** (Figure 2.7). The geometry of the inositol ring in the radical **2.49BC** (and **2.57BC**) deviates from 'boat' implying that the boat form of the radical (as depicted in Chart 2.2) is unstable.

The change in energy necessary for the *myo*-xanthate **2.16** to undergo deoxygenation *via* Path A is 2.8 kcal/mol while that through Path B is 0.6 kcal/mol and the corresponding values for the xanthate **2.29** are 5.2 kcal/mol and 0.6 kcal/mol. Since Path B requires lesser change in energy, the conversion of the *myo*-xanthates to the dideoxy inositol proceeds *via* Path B. Similarly, the change in energy necessary for the *neo*-xanthate **2.48** to undergo deoxygenation *via* Path A is 2.5 kcal/mol while that through Path B is 6.3 kcal/mol. Since in this conversion, Path A requires lesser change in energy, the conversion of the *neo*-xanthate to the dideoxy inositol proceeds *via* Path A. Hence although both the *myo* and *neo*-xanthates lead to the formation of the same product by radical deoxygenation, the product appears to be forming by two different pathways. However both the pathways lead to the formation of the relatively stable radical **2.49CC** where the radical center and the benzylidene hydrogen are in close proximity to allow the intramolecular abstraction of hydrogen and generate the benzylidene radical (which rearranges to form the dideoxy product).

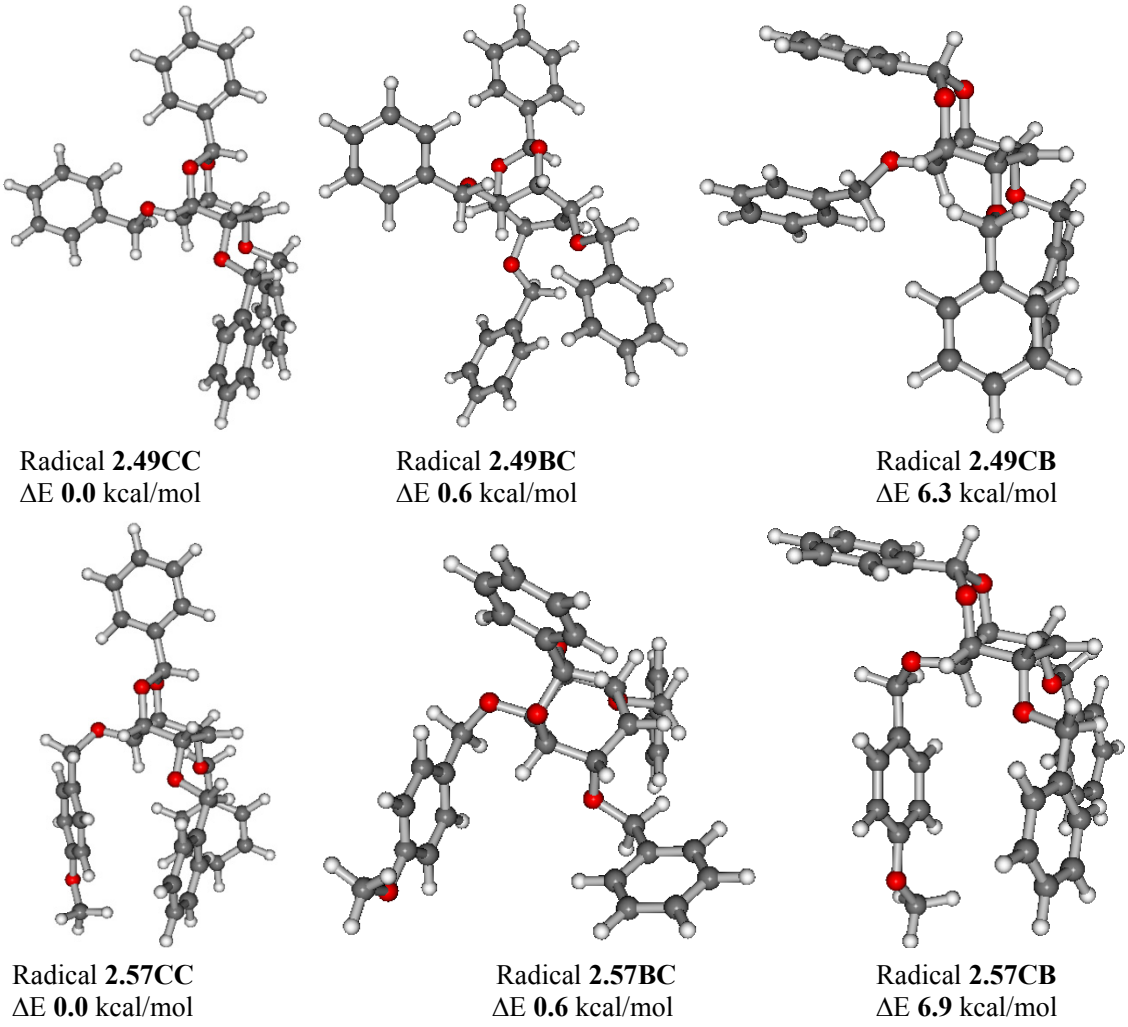


Figure 2.7: Results of geometrical optimization for radicals derived from xanthates **2.16**, **2.48** and **2.29**.

We have also determined the geometry and energy of the transition state for the intramolecular abstraction of the benzylidene hydrogen in the radical **2.49CC**, as well as the energy of the radicals formed subsequent to intramolecular hydrogen transfer (Chart 2.3 and Figure 2.8). These values reveal that the barrier for the intramolecular hydrogen transfer in **2.49CC** is quite low (4.2 kcal/mol), which is in agreement with the experimentally observed extreme facility with which the di-deoxygenation reaction occurs. A comparison of the energies of the radicals formed subsequent to intramolecular hydrogen transfer also supports the ease of cleavage of the benzylidene acetal. The results of the DFT calculations therefore support the sequence of events depicted (in Scheme 2.14) during the dideoxygenation reaction shown in Scheme 2.3.

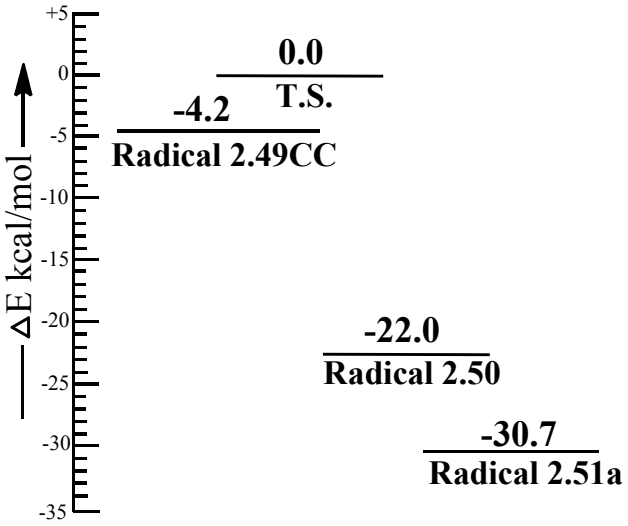


Chart 2.3: A comparison of the energies of the transition state and radicals **2.49**, **2.50** and **2.51a**.

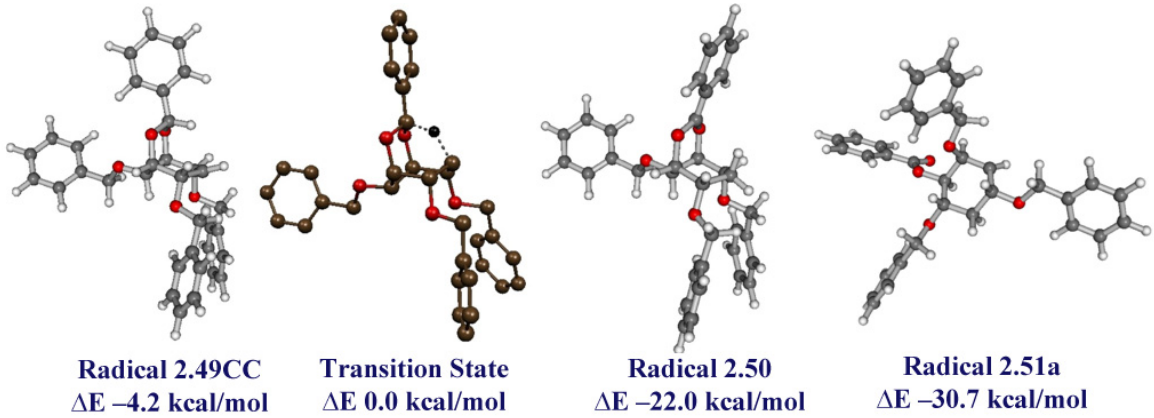


Figure 2.8: Results of the geometrical optimization of the transition state during the intramolecular abstraction of hydrogen in **2.49** and conformation of the radicals **2.50** and **2.51a**. Only the migrating hydrogen atom is shown in the transition state, for clarity.

2.2.8. DFT calculations on the deoxygenation of the (C1,C5)-*O*-benzylidene acetal 2.33

As mentioned earlier (Scheme 2.6, page No. 31), deoxygenation of the xanthate **2.33** yielded the 1,5-dideoxy derivative **2.34** as the major product and 1,3-dideoxy derivative **2.35** as the minor product. 2D NMR spectrum of **2.33** suggests that the xanthate **2.33** exists in the conformation **2.33BC** (Chart 2.4) in solution. We could not obtain crystals of **2.33** as it is a gummy solid and hence its molecular conformation in its crystals is not known. Intramolecular benzylic hydrogen abstraction does not appear to be facile in the radical generated from **2.33BC**, if it maintains the same conformation. Hence as observed in the

case of the C5-xanthates, **2.33** or the radical generated from this xanthate must be undergoing conformational change during the deoxygenation reaction. In order to gain insight into the conformational aspects of **2.33**, we performed DFT calculations on the four different conformations of the xanthates **2.33** and conformation of the radical generated from **2.33** (Chart 2.4).

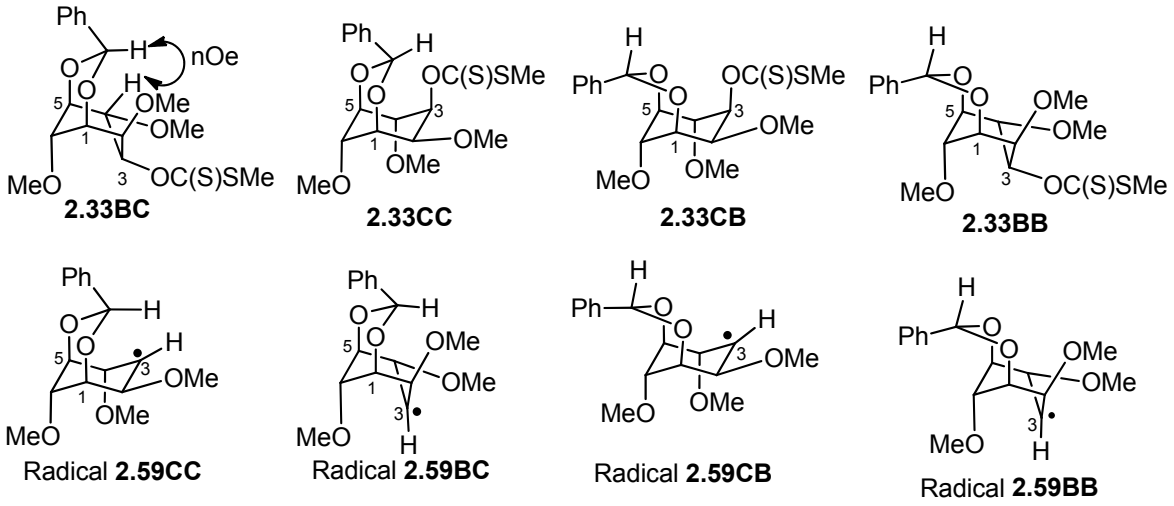
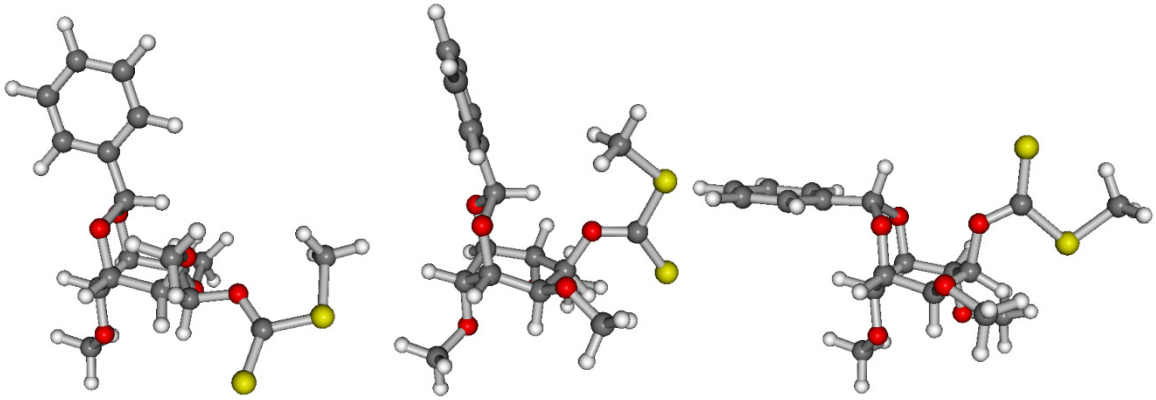


Chart 2.4: Possible conformations of the xanthate **2.33** and the radicals generated from them.

Results of the geometrical optimization of the possible conformations of the xanthate **2.33** reveal a decreasing order of stability of the three conformers, **2.33BC** > **2.33CC** > **2.33CB** (Figure 2.9). As observed for the xanthates **2.16** and **2.29**, the conformation in which both the rings are in the boat form is least stable and inherently flip over to one of the three conformations in which at least one ring has the chair conformation. Results on the geometrical optimization of the radicals generated from the four possible conformers of **2.33** (Figure 2.10) reveal the order of stability to be **2.59CC** > **2.59BC** > **2.59CB**. DFT calculations also indicate that conformation **2.59BB** is very unstable and flips over to one of the other three conformations and energy minimization of **2.59BC** results in a conformation similar to **2.59CC**.

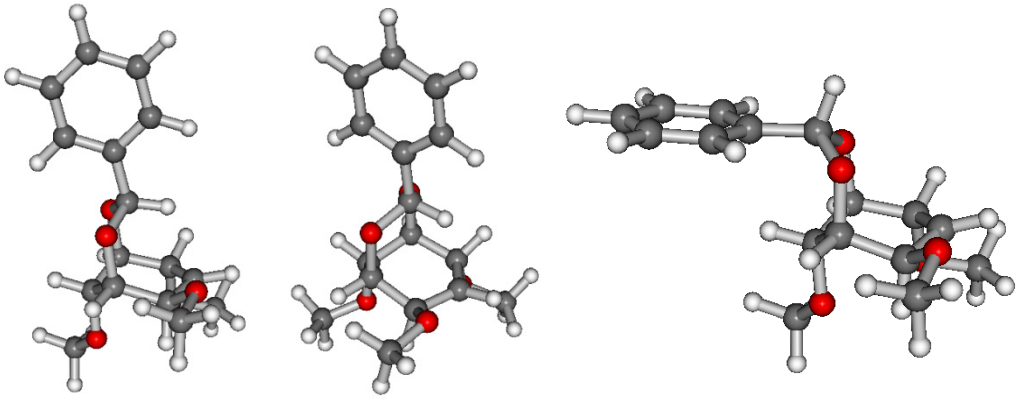


2.33BC
ΔE **0.0** kcal/mol

2.33CC
ΔE **4.3** kcal/mol

2.33CB
ΔE **10.8** kcal/mol

Figure 2.9: Results of geometrical optimization of possible conformations of the xanthate **2.33**.



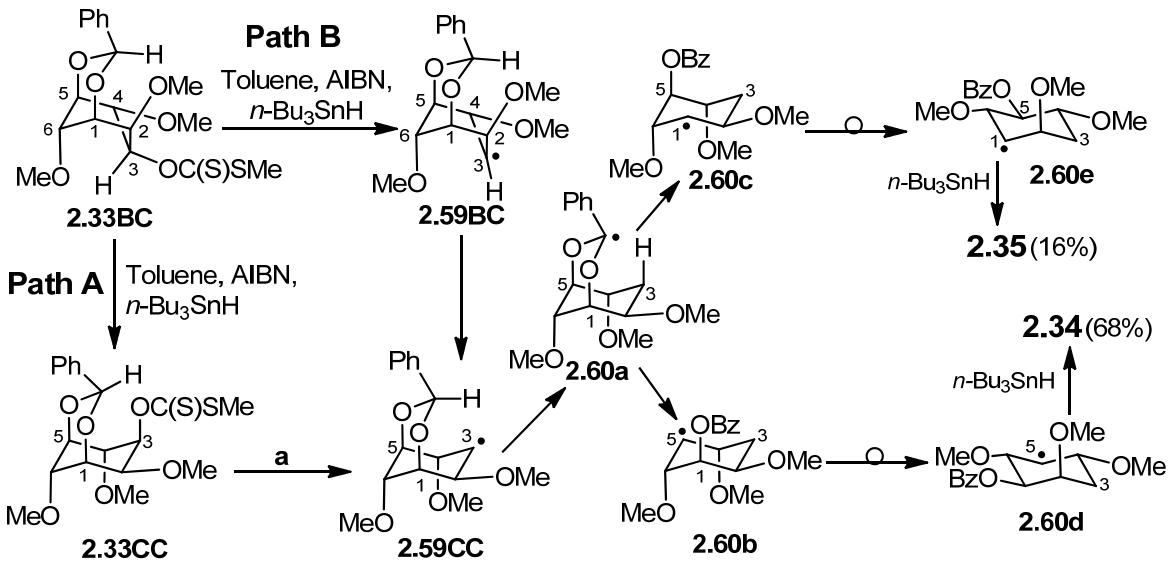
Radical **2.59CC**
ΔE **0.0** kcal/mol

Radical **2.59BC**
ΔE **2.2** kcal/mol

Radical **2.59CB**
ΔE **6.6** kcal/mol

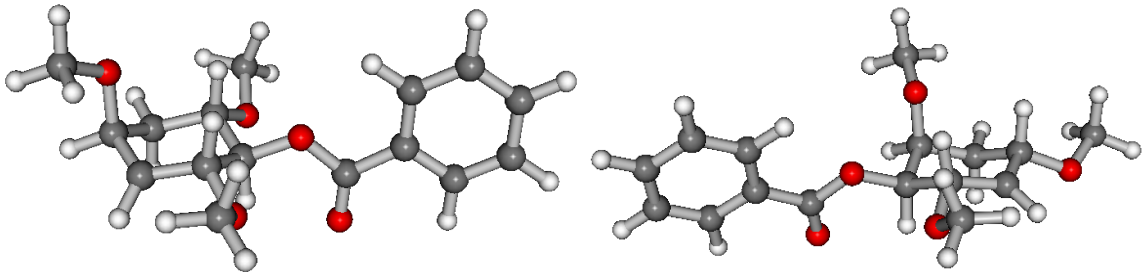
Figure 2.10: Results of the geometrical optimization of possible conformations of the radical **2.59**.

A comparison of the two possible Paths (Scheme 2.15) for the formation of the dideoxy inositol derivatives **2.34** and **2.35** from the xanthate **2.33** supports the deoxygenation of **2.33** *via* Path B, since the change in energy is lesser in Path B. We have assumed that **2.60b** and **2.60c** flip over to **2.60d** and **2.60e** respectively, since the former 'axial rich' conformations would be expected to be far less stable than the latter 'equatorial rich' conformations.



Scheme 2.15: Plausible mechanism for the deoxygenation of the xanthate **2.33**.

It is interesting to note that the radical formation (by cleavage of the benzylidene acetal moiety) at the C5-position is preferred over that at the C1-position of the inositol ring, as revealed by the formation of larger proportion of the C5-deoxy derivative relative to the C1-deoxy derivative. This is similar to the observation during the plasma radiation-induced generation of hydroxyl alkyl radicals in solid *myo*-inositol wherein the formation of the C5-radical was preferred over the formation of the radical at C1- and C4-positions.[19] However, estimation of the relative stabilities of the two regioisomeric radicals **2.60d** and **2.60e** generated by the cleavage of the benzylidene acetal, suggested negligible difference between them (Figure 2.11).



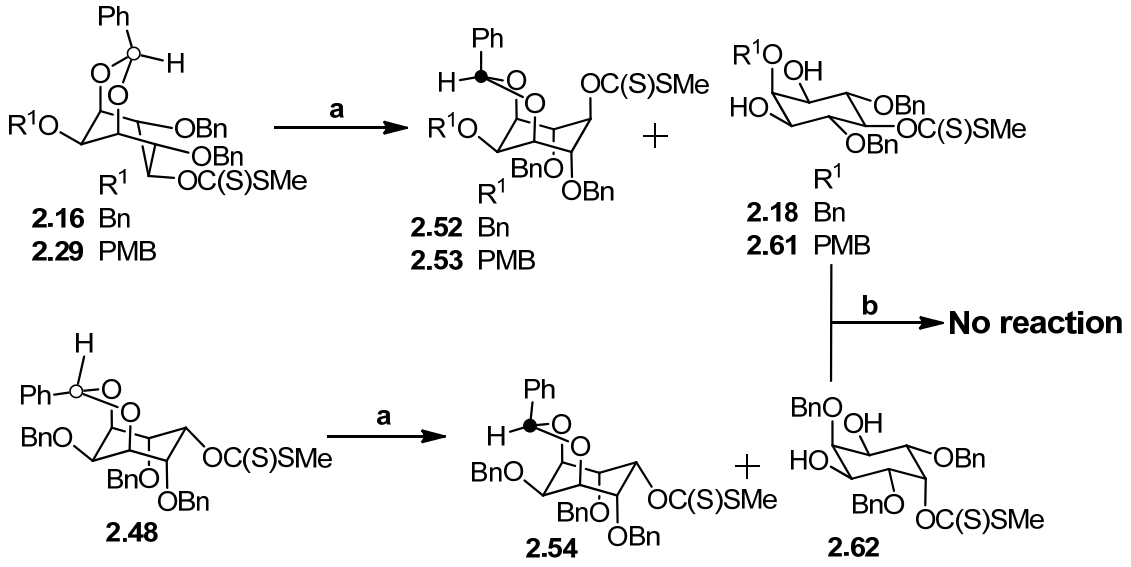
2.60e
ΔE **0.0** kcal/mol

2.60d
ΔE **0.8** kcal/mol

Figure 2.11: Results of the geometrical optimization of the radicals **2.60e** and **2.60d**.

2.2.9. Thermal epimerization of inositol (C1,C3)-*O*-benzylidene acetals in the molten state

During the course of the investigations described in previous sections, we observed that the xanthate **2.29** was stable in the solid state (see below) but produced minor amounts of another organic compound while isolation from its solution (by evaporation of the solvent) or storage (as a gum) at ambient temperature. Isolation of this product and the scrutiny of its spectral characteristics showed it to be an isomer of the starting PMB ether **2.29**. We were intrigued to see that refluxing a toluene solution or heating a DMF solution (obtained by dissolving crystals of **2.29**) at 130 ºC however did not produce the isomer of **2.29** that we had observed earlier. Hence we wondered whether the isomerization could be occurring in the solid state. But, heating crystals of **2.29** just below their melting point did not result in isomerization of **2.29**. Continued heating of the xanthate **2.29** beyond its melting point resulted in its isomerization to **2.53** (Scheme 2.16, about 50% conversion) with concomitant formation of the corresponding diol **2.61**.



Scheme 2.16: (a) 120 °C, 12 h for **2.16** and **2.48**, 30 h for **2.29**; (b) PhCHO, 120 °C, 24 h.

We could improve the yield of the isomeric product to about 70% by heating molten **2.29** in an inert (argon) atmosphere. This isomer of **2.29** could be crystallized from a mixture of ethyl acetate and hexanes; single crystal X-ray diffraction studies of these crystals established the structure of the isomer of **2.29** as **2.53** (Figure 2.12 and Scheme 2.16; carbon atom undergoing a change in configuration is marked in **2.53**).

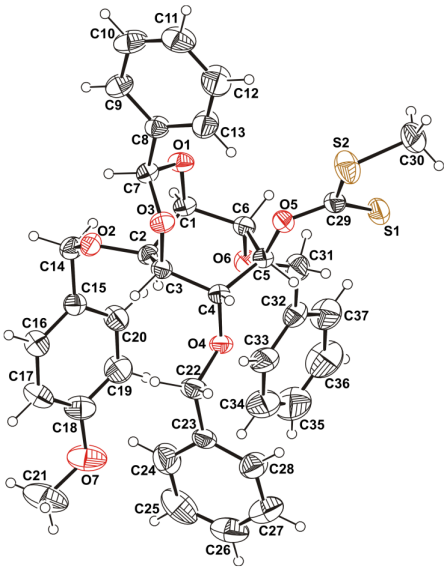


Figure 2.12: ORTEP of epimeric xanthate **2.53**. Thermal ellipsoids are drawn at 30% probability and hydrogen atoms are depicted as small spheres of arbitrary radii.

We carried out the epimerization (in the molten state) of two other 1,3-acetals **2.16** and **2.48** having the *myo*- and the *neo*- configurations which gave the epimerized products **2.52** and **2.54** respectively (Figures 2.13–2.15). All these epimerization reactions were not feasible in the crystalline state as well as in solution (DMF, 130 °C). It is interesting to note that epimerization of the acetals **2.16** and **2.29** having the *myo*-configuration leads to a change in the conformation of the inositol as well as the acetal ring, while in the acetal **2.48** with *neo*-configuration, the conformation of the two rings are retained.

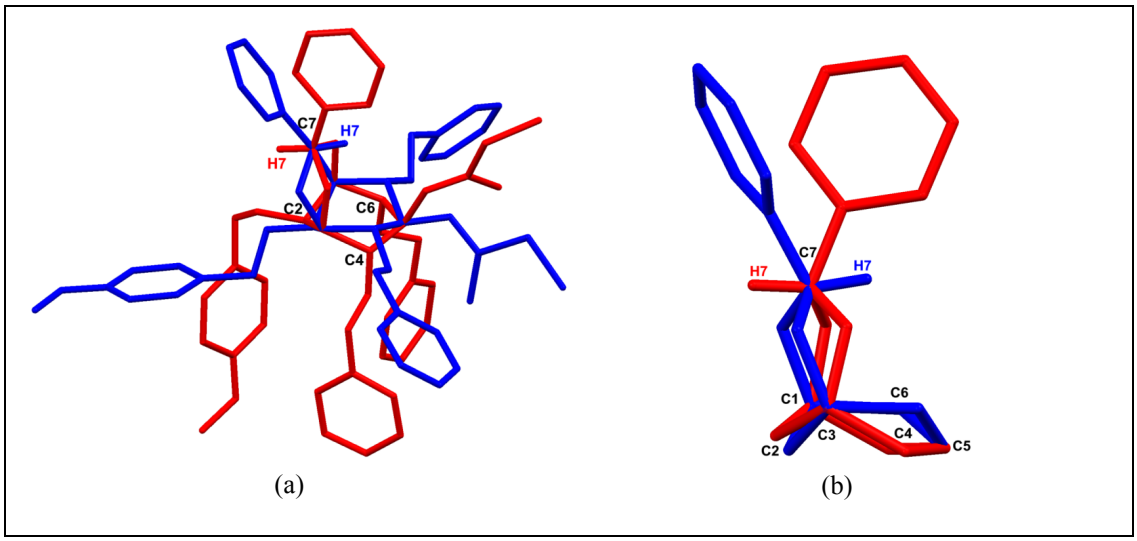


Figure 2.13: (a) Molecular overlap of the xanthate **2.29** (blue) with its epimer, **2.53** (red). (b) Parts of the molecules are not shown to highlight the carbon atom that underwent epimerization.

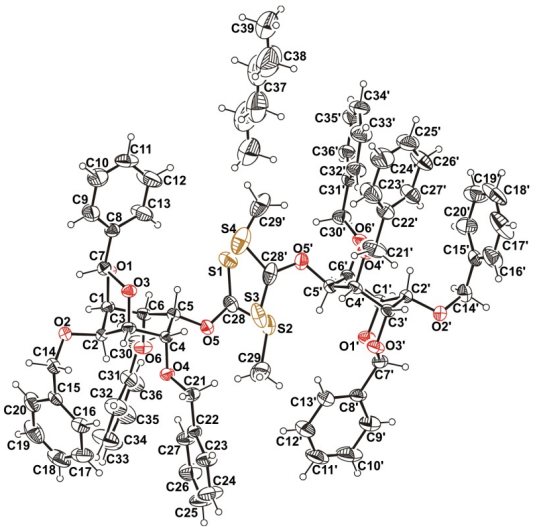


Figure 2.14: ORTEP of hexane solvate of *neo*-xanthate **2.54** (epimer of **2.48**). Thermal ellipsoids are drawn at 30% probability and hydrogen atoms are depicted as small spheres of arbitrary radii.

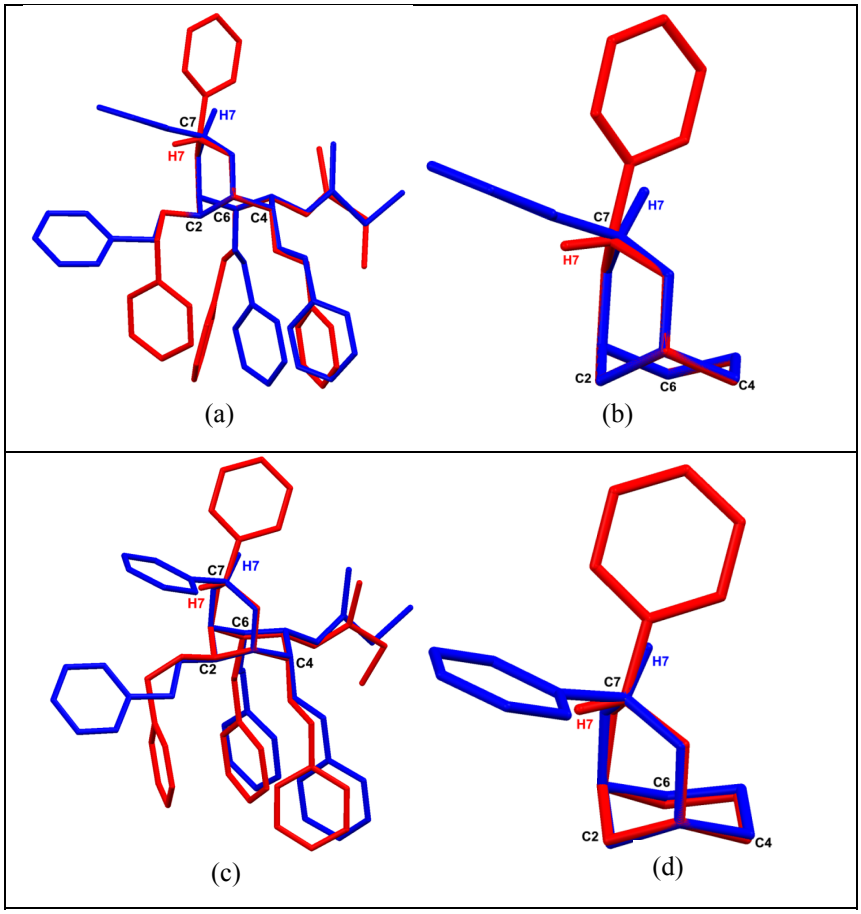


Figure 2.15: Molecular overlap of the xanthate **2.48** (blue) with its epimer, **2.54** (red). Two different overlap figures shown (a, b and c, d) correspond to the two molecules in the asymmetric unit of **2.54**. In the figures on the right (b and d), parts of the molecules are not shown to highlight the carbon atom that underwent epimerization.

Comparison of the results of deoxygenation of the xanthates **2.16**, **2.29** and **2.48** with that of their epimers **2.52**, **2.53** and **2.54**, provide additional support for the nonoccurrence of epimerization of the acetals **2.16**, **2.29** and **2.48** in solution. As discussed earlier (Schemes 2.3, 2.5 and 2.9; page No. 28, 29 and 34 respectively), the xanthates **2.16**, **2.29** and **2.48** resulted in the formation of the corresponding dideoxy derivative, while the epimeric xanthates **2.52**, **2.53** and **2.54** under identical conditions resulted in the formation of the corresponding monodeoxy derivative exclusively (**2.55**, **2.56**; Scheme 2.13), since intramolecular (acetal) hydrogen abstraction is sterically forbidden in these molecules. The contrasting results of these deoxygenation reactions with the two epimers supports our observation that the epimerization of the xanthates **2.16**, **2.29** and **2.48** does not occur in the solution phase. If it did, we would have observed formation of a mixture of the mono and the dideoxy derivatives during the deoxygenation of the epimeric xanthates.

Since we noticed the formation of 1,3-diols (**2.18**, **2.61** and **2.62**) during the epimerization of the acetals **2.16**, **2.29** and **2.48** we wondered whether they were intermediates during the process of epimerization. That is, whether epimerization of the acetals **2.16**, **2.29** and **2.48** was occurring in two steps: (a) formation of the corresponding diol followed by (b) its reaction *in situ* with benzaldehyde produced. However, heating of the diols **2.18**, **2.61** and **2.62** with benzaldehyde under the conditions of epimerization did not result in the formation of the corresponding 1,3 acetal. This ruled out the epimerization of the acetal *via* the corresponding diol and suggested that the diols **2.18**, **2.61** and **2.62** were formed only as a biproducts during epimerization of the acetals **2.16**, **2.29** and **2.48**, but did not function as intermediates. These experiments also led to an interesting observation. Although both the epimeric acetals (**2.16**, **2.52** or **2.29**, **2.53**, or **2.48**, **2.54**) cannot be prepared from the parent diol (**2.18** or **2.61** or **2.62**), they can be accessed *via* the orthobenzoates (**1.46** and **2.27**) and the relatively more stable acetal (**2.52** or **2.53**, or **2.54**) can only be obtained by isomerization of its less stable epimer (see below), since reduction of the orthobenzoate (**1.46** or **2.27**) is stereoselective to yield **2.16**, **2.29** and **2.48** exclusively!

We also estimated the relative stability of the epimeric acetals (**2.16** *vs* **2.52**, **2.29** *vs* **2.53**, **2.48** *vs* **2.54**) by DFT calculations. Geometry optimization for all the acetals was carried out with the input structures taken from the conformation of the two rings (inositol

and the acetal) as observed in their crystals. The ^{1}H NMR spectra of these xanthates suggested that the conformations observed in their crystals are retained in their solution. Estimation of the relative energies (Figure 2.16) suggested that the acetals **2.52**, **2.53** and **2.54** are relatively more stable compared to their epimers **2.16**, **2.29** and **2.48** respectively. The relative difference in stability (3.9 kcal/mole) is slightly higher for the pair of acetals (**2.48**, **2.54**) with the *neo*-configuration as compared to those having the *myo*-configuration (**2.16**, **2.52** and **2.29**, **2.53**, <1.4 kcal/mole). The differences in the stability of these 1,3-acetals could explain the facility of epimerization under thermal conditions.

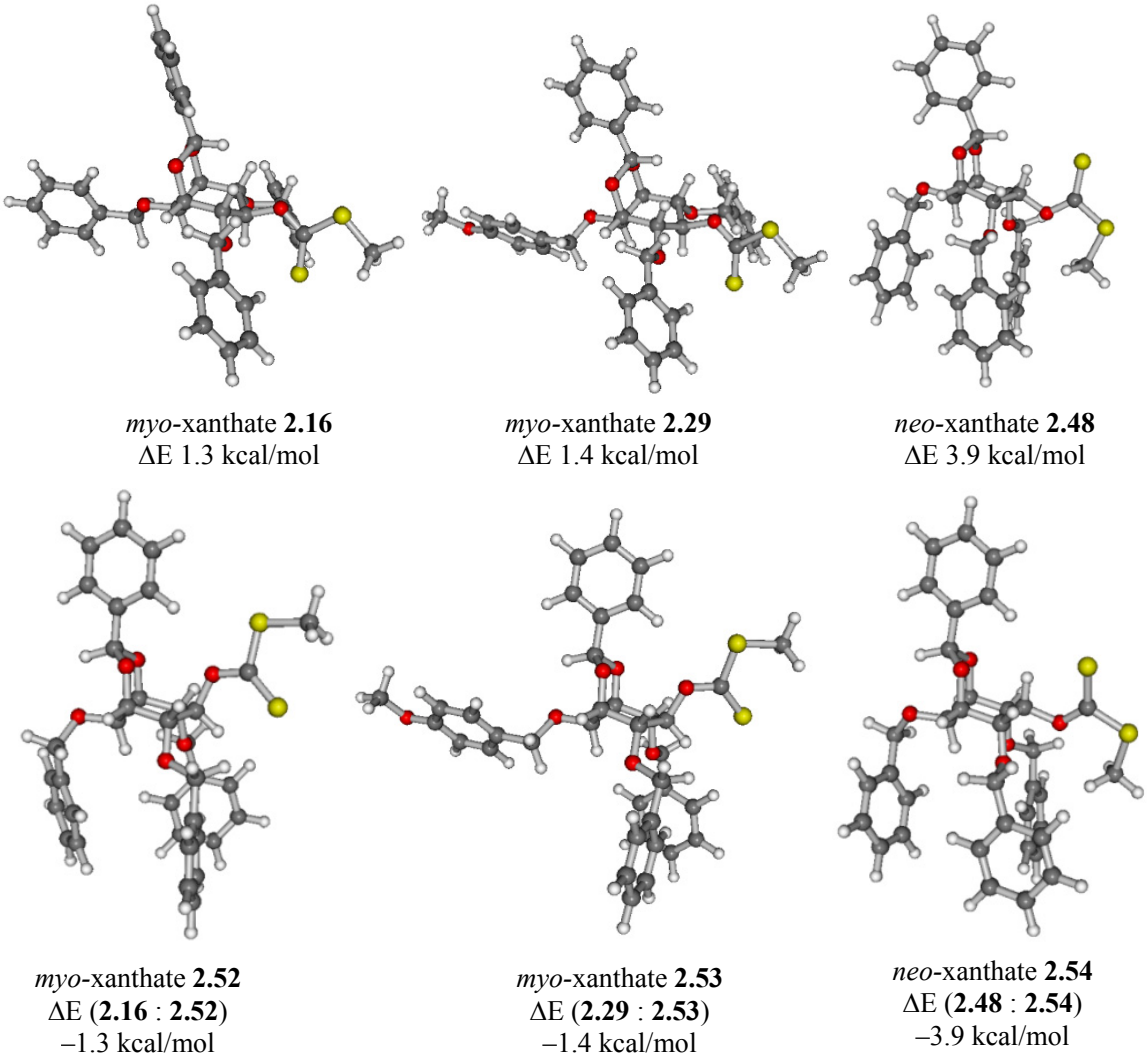
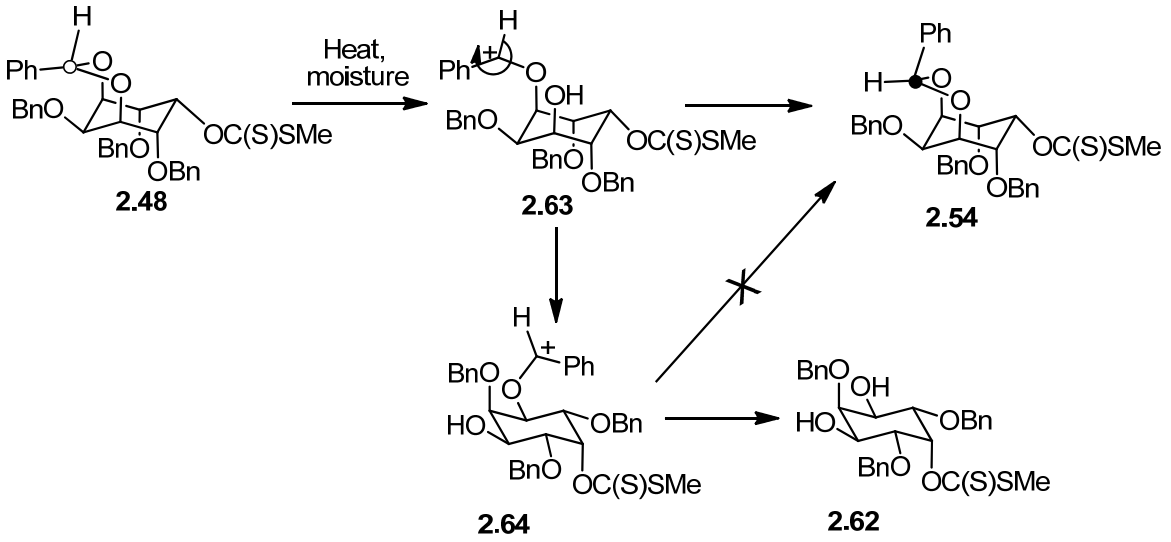


Figure 2.16: Geometry optimized structures of xanthates **2.16**, **2.29**, **2.48** and their epimers **2.52**, **2.53** and **2.54**.

Although the mechanism of epimerization of acetals **2.16**, **2.29**, and **2.48** is not clear, we can postulate that the reaction proceeds by cleavage of one of the acetal C-O bonds, rotation of the other C-O bond and re-formation of the broken C–O bond (Scheme 2.17).



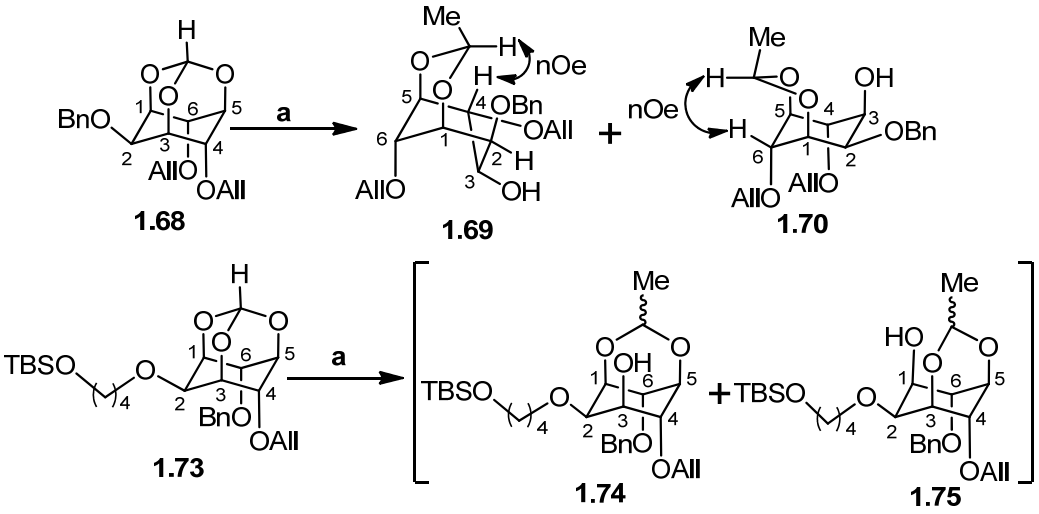
Scheme 2.17: Plausible mechanism for the epimerization of 1,3-acetals in the molten state.

It is not unlikely that the diol **2.62** is formed as a result of flipping of the inositol ring (**2.63→2.64**), since in this 'equatorial rich' conformation (**2.64**), re-establishment of the broken C–O bond is not feasible. Since the major product obtained is the epimer of the starting acetal, it is plausible that re-formation of the broken acetal C–O bond is faster than flipping of the inositol ring. The relatively sluggish flipping of the inositol ring could be a result of closely packed molecules in the melt just above the melting point of the crystals. This is supported by the fact that epimerization of the acetals at higher temperatures resulted in increased yield of the corresponding diol, perhaps due to loosening of the molecules in the melt, resulting in faster ring flipping. These possibilities are schematically represented for the epimerization of the acetal **2.48** (for illustration) in Scheme 2.17.

The process of epimerization of the acetals (**2.16** and **2.29**) having the *myo*-configuration involve a change in conformation of the acetal ring as well as the inositol ring. The data available to us is not sufficient to figure out whether these conformational changes precede or succeed epimerization of the acetal carbon. Perusal of the crystal structures of the acetals **2.16**, **2.29** and **2.48** as well as their epimers **2.52**, **2.53** and **2.54** shows that the close packing of molecules in the crystal lattice does not allow major conformational changes required for the epimerization reaction under discussion (see appendix I).

A measurement of the unit cell parameters of the reactant crystals (of **2.16**, **2.29** and **2.48**) at (a) ambient temperature, (b) when heated up to 90 ºC and then (c) cooled down to ambient temperature did not show significant variation, indicating that the reaction does not occur in the crystal. This is in line with our experimental observations that the epimerization of **2.16**, **2.29** and **2.48** sets in, subsequent to melting of the crystals. That the nonoccurrence of epimerization in the crystalline state is not due to differences in temperature between the molten state and the crystalline state alone, is suggested by the fact that the epimerization in solution at temperatures higher than the melting point of **2.16**, **2.29** and **2.48** also did not occur.

Formation of epimeric acetals **1.69** and **1.70** (Scheme 2.18) was reported[22] in the trimethylalumnium mediated cleavage of orthoformate derivative **1.68**. Only one of these epimers (**1.69**) was expected according to the mechanism proposed in the literature.[23] Although it was not studied in detail, the possibility of epimerization of **1.69** to yield the epimer **1.70** cannot be ruled out. Similarly, trimethylaluminium mediated cleavage of the orthogonally protected orthoformate **1.73** leads to the formation of diastereomeric mixture of acetals **1.74** and **1.75**;[24] but it is not clear whether these diastereomers are interconvertible or not.



Scheme 2.18: (a) DCM, $AlMe_3$, –78 °C to 0 °C.

2.3. Conclusion

The benzylidene acetals derived from *myo*-inositol-1,3,5-orthobenzoate can be cleaved *via* intramolecular radical reactions to obtain inositol derivatives deoxygenated at specific positions. Similar acetal cleavage reactions do not occur in other analogous acetals and hence these acetals provide the corresponding mono-deoxy cyclitol. Analysis of the structure and conformation of inositol derived xanthates and the radicals generated from them under Barton-McCombie conditions reveal that *myo*-inositol derived xanthates and their *neo*-inositol analogs undergo deoxygenation by two different pathways. During this reaction, conformational changes occur in radicals derived from *myo*-inositol derivatives while conformational changes occur in *neo*-inositol derived xanthate prior to the formation of the radical. Although the difference in stability predicted between the conformers is not very large, the observed trend in stability allows us to arrive at these interesting conclusions.

Thermal epimerization of inositol derived 1,3-benzylidene acetals occur only in the molten state wherein the molecules are free enough to go through the bond scission and conformational changes to result in the formation of the relatively stable epimer. Interestingly, results presented here suggest that in the molten state (just above the melting point of crystals), molecules are not very free to undergo flipping of the inositol ring, which would sterically forbid the formation of the cyclic 1,3-acetal. Hence it is likely that in the molten state, aggregated molecules achieve the fine balance between the rigidity of the matrix, and the molecular motion needed for their reaction to realize their epimerization. This process of epimerization is perhaps augmented by the relative stabilities of the two epimers. In the solution state which allows complete freedom of movement for the molecules, the acetal molecules may not achieve the required aggregation and rigidity necessary for fruitful epimerization. Encountering such unusual facile reactions in the molten state makes one wonder whether organic chemists should consider carrying out reactions in melt routinely, just as they carry out reactions in different solvents, to maximize the yield and selectivity. This is especially significant since reactions in melt are easy to carry out, do not need any specialized equipment, and are far less hazardous (in terms of generating waste) to our environment as compared to solution state reactions. The results presented here reiterates the importance of the phase (in which the reaction is carried out) on the facility and selectivity of a reaction, whether or not the phase of a substance can be defined and characterized by conventional methods and stresses the need for investigations aimed at deeper understanding of the phases other than solids, liquids and vapour.

2.4. Experimental

2.4.1. X-ray Data (Collection, Structure Solution and Refinement)

Single crystal X-ray studies were carried out on a Bruker SMART APEX single crystal X-ray CCD diffractometer with graphite-monochromatized (Mo K_α= 0.71073Å) radiation. The X-ray generator was operated at 50 kV and 30 mA. Diffraction data were collected with ω scan width of 0.3° at different settings of φ (0°, 90°, 180° and 270°) keeping the sample-to-detector distance fixed at 6.145 cm and the detector position (2θ) fixed at -28°. The X-ray data acquisition was monitored by SMART program (Bruker, 2003).[25] All the data were corrected for Lorentzian and polarization effects using SAINT programs (Bruker, 2003).[25] A semi-empirical absorption correction (multiscan) based on symmetry equivalent reflections was applied by using the SADABS program (Bruker, 2003).[25] Lattice parameters were determined from least squares analysis of all reflections. The structure was solved by direct method and refined by full matrix least-squares, based on F^2, using SHELX-97 software package.[26] Molecular diagrams were generated using SHELXTL and ORTEP-32.[27]

2.4.2. Computational details

All the density functional theory calculations were carried out using the Turbomole suite of programs.[28] The strategy adopted for the geometry optimizations is as follows: for a given geometry, a conformational search was first done using Molecular Mechanics (MM+ force field) methods as implemented in the Hyperchem[29] software. The best five geometries obtained from the conformational analysis were then used as input structures for the DFT calculations. The conformation obtained with the lowest energy (i.e. the most stable conformation) has then been considered for the relative (ΔE) analysis. The DFT Geometry optimizations were performed using the B-P 86 functional.[30] The electronic configuration of the atoms was described by a triple-zeta basis set augmented by a polarization function (TURBOMOLE basis set TZVP).[31] The resolution of identity (RI),[32] along with the multipole accelerated resolution of identity (marij)[33] approximations were employed for an accurate and efficient treatment of the electronic Coulomb term in the density functional calculations. Solvent effects have been incorporated using the COSMO model, 44 with toluene (epsilon = 2.38)[34] as the solvent.

In the case of the radical structures, care was taken to ensure that the geometry optimization of the structures, done with UHF, did not lead to spin contamination. A perusal of the total spin quantum number values from the geometry optimization outputs indicated that their value was different by only about 1% from the exact value in every case, indicating the absence of spin contamination. Also, all the radical structures considered were assumed to be in the doublet state. For certain cases, the quartet spin state calculations were also done, and they showed that the resultant quartet geometries were significantly higher in energy than their doublet counterparts, thus indicating that the doublet is the stable spin state for the radicals that have been considered in this study. The transition state obtained for the intramolecular hydrogen transfer was confirmed to have only one negative frequency corresponding to the proper normal mode.

2.4.3. General Experimental Methods

All the solvents were purified according to the literature procedure[35] before use. All air or moisture sensitive reactions were carried out in an atmosphere of argon or nitrogen. Dry DMF and dry THF were used as solvents in all the experiments involving metal hydrides. Sodium hydride used in experiments was 60% suspension in mineral oil. Thin layer chromatography was performed on E. Merck pre-coated 60 F_{254} plates and the spots were rendered visible either by shining UV light or by charring the plates with chromic acid solution. Column chromatographic separations (silica gel, 100–200 mesh) and flash column chromatographic separations (silica gel, 230–400 mesh) were carried out with light petroleum–ethyl acetate mixtures as eluent. 'Usual work-up' implies washing of the organic layer with water followed by brine, drying over anhydrous sodium sulfate, and removal of the solvent under reduced pressure using a rotary evaporator. IR spectra were recorded (in $CHCl_3$ solution, or as a Nujol mull or as a neat film) with a Shimadzu FTIR-8400 or Perkin–Elmer spectrophotometer. NMR spectra (200 MHz for ^1H and 50.3 MHz for ^{13}C) were recorded with a Bruker ACF 200 spectrometer unless otherwise mentioned. Chemical shifts (δ, ppm) reported are referred to internal tetramethylsilane (0 ppm) for ^1H NMR and $CDCl_3$ (77 ppm) for ^{13}C NMR. Microanalytical data were obtained using a Carlo-Erba CHNS-0 EA 1108 elemental analyzer. All the melting points reported are uncorrected and were recorded using a Büchi B-540 electro-thermal melting point apparatus. Yields refer to chromatographically and spectroscopically pure compounds. All

the asymmetrically substituted *myo*-inositol derivatives reported are racemic; however only one of the enantiomers is shown in all the schemes for convenience and clarity. Compounds previously reported in the literature were characterized by comparison of their melting points and/or ^{1}H NMR spectra with the reported data.

General procedure for the preparation of xanthates (**Procedure A**): To a cooled (0 °C) solution of the required alcohol (2 to 5 mmol) in dry THF (5 to 30 mL), sodium hydride (10 to 25 mmol) was added and stirred at ambient temperature for 30 min. Carbon disulfide (30 to 75 mmol) was added to the reaction mixture and refluxed for 1 h. The reaction mixture was allowed to cool to room temperature; methyl iodide (10 to 25 mmol) was added and stirred for 16 h. The reaction mixture was diluted with ethanol (4 to 10 mL), water (8 to 20 mL) and extracted with ethyl acetate. The organic layer was washed with saturated ammonium chloride solution followed by brine and dried over anhd sodium sulfate. The residue obtained after evaporation of the solvent was purified by column chromatography to obtain the xanthate.

General procedure for the deoxygenation of xanthates (Procedure B): To a solution of the required xanthate (0.14 to 3 mmol) in dry toluene (4 to 20 mL), tri-*n*-butyltin hydride (0.5 to 13 mmol) and AIBN (0.001 to 0.08 g) were added and heated at 100 ^{o}C for 1 h. The solvents were removed under reduced pressure and the residue obtained was purified by column chromatography (eluent: ethyl acetate in light petroleum).

2-*O*-(4-Methoxybenzyl)-4,6-di-*O*-benzyl-*myo*-inositol-1,3,5-orthobenzoate (2.27): To a solution of **2.26**[16] (8.93 g, 20.00 mmol) in dry DMF (100 mL) sodium hydride (0.96 g, 24.00 mmol) was added and stirred for 10 min. *p*-Methoxybenzyl chloride (3.00 mL, 22.00 mmol) was then added drop wise and the reaction mixture stirred for 4 h. Excess of sodium hydride was quenched by the addition of cold water. The reaction mixture was concentrated under reduced pressure to get a gum which was worked up with ethyl acetate; the organic extract was dried over anhd sodium sulfate. The solvent was removed under reduced pressure to afford a gummy residue which was purified by column chromatography (eluent: 20% ethyl acetate/light petroleum) to obtain **2.27** as a colorless solid (10.92 g, 96%). TLC *Rf* = 0.5 (20% ethyl acetate/light petroleum); **mp** 89.4–92.0 °C; **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 7.60-7.68 (m, 2H, Ar H), 7.17–7.38 (m, 15H, Ar H), 6.79–6.86 (m, 2H, Ar H), 4.40–4.70 (m, 11H, 3 × CH_2 and 5 Ins H), 4.10 (t, 1H, *J* = 1.5 Hz),

3.76 (s, 3H, CH_3) ppm; **^{13}C NMR** ($CDCl_3$, 50.3 MHz): δ 159.2 (C_{arom}), 137.6 (C_{arom}), 137.2 (C_{arom}), 130.0 (C_{arom}), 129.7 (C_{arom}), 129.3 (C_{arom}), 128.3 (C_{arom}), 127.9 (C_{arom}), 127.7 (C_{arom}), 127.5 (C_{arom}), 125.4 (C_{arom}), 113.7 (C_{arom}), 107.8 ($PhCO_3$), 74.0 (Ins C), 71.9 (Ins C), 71.5 (CH_2), 70.7 (CH_2), 69.0 (Ins C), 65.5 (Ins C), 55.1 (CH_3) ppm; elemental analysis calcd (%) for $C_{35}H_{34}O_7$ (566.64): C 74.19, H 6.05; found: C 74.11, H 6.43 %.

1,3-*O*-Benzylidene-2-*O*-(4-methoxybenzyl)-4,6-di-*O*-benzyl-*myo*-inositol (2.28): 1 M solution of DIBAL-H in toluene (15.40 mL, 15.40 mmol) was added drop-wise over a period of 15 min. to a solution of **2.27** (3.96 g, 7.00 mmol) in dry dichloromethane (60 mL) at 0 °C and stirred at room temperature for 2.5 h. The reaction mixture was poured into a stirred solution of sodium potassium tartrate (42 g in 70 mL water) and saturated ammonium chloride (70 mL) and stirred for 12 h. The mixture was extracted with dichloromethane (2 × 100 mL), washed with brine and dried over anhd sodium sulfate. The solvent was removed under reduced pressure to obtain a gummy residue which was purified by column chromatography (eluent: 25% ethyl acetate/light petroleum) to afford **2.28** as a colorless solid (3.78 g, 95%). TLC *Rf* = 0.4 (25% ethyl acetate/light petroleum); **mp** 122.8–124.6 °C; **IR** (neat): $\bar{\nu}$ 3330–3510 cm^{-1}; **^{1}H NMR** (CD_2Cl_2, 200 MHz): δ 7.42–7.51 (m, 2H, Ar H), 7.24–7.45 (m, 15H, Ar H), 6.83–6.91 (m, 2H, Ar H), 5.68 (s, 1H, $PhCHO_2$), 4.66 (q, 4H, 2 × CH_2, *J* = 11.6 Hz), 4.59 (s, 2H, CH_2), 4.33 (d, 2H, Ins H, *J* = 2.4 Hz), 3.94 (d, 2H, Ins H, *J* = 8.2 Hz), 3.72–3.80 (m, 1H, Ins H), 3.75 (s, 3H, CH_3), 3.57 (t, 1H, *J* = 2.4 Hz, Ins H), 2.54 (d, 1H, *J* = 2.9 Hz, OH) ppm; **^{13}C NMR** ($CDCl_3$, 50.3 MHz): δ 159.7 (C_{arom}), 138.8 (C_{arom}), 138.1 (C_{arom}), 130.4 (C_{arom}), 129.7 (C_{arom}), 128.8 (C_{arom}), 128.4 (C_{arom}), 126.8 (C_{arom}), 114.1 (C_{arom}), 92.8 ($PhCHO_2$), 82.1 (Ins C), 73.9 (Ins C), 72.0 (CH_2), 70.8 (CH_2), 68.5 (Ins C), 55.5 (CH_3) ppm; elemental analysis calcd (%) for $C_{35}H_{36}O_7$ (568.66): C 73.92, H 6.38; found: C 73.94, H 6.12 %.

1,3-*O*-Benzylidene-2-*O*-(4-methoxybenzyl)-4,6-di-*O*-benzyl-5-*O*-[(methylthio)thiocarbonyl]-*myo*-inositol (2.29): The alcohol **2.28** (1.14 g, 2.00 mmol), dry THF (10 mL), sodium hydride (0.40 g, 10.00 mmol), carbon disulfide (1.80 mL, 30.00 mmol) and methyl iodide (0.60 mL, 10.00 mmol) were used (Procedure A) to obtain the xanthate **2.29** as a colorless solid (1.24 g, 94%) after column chromatography (eluent: 15% ethyl acetate/light petroleum). TLC *Rf* = 0.4 (15% ethyl acetate/light petroleum); **mp** 93–93.8 °C; **IR** ($CHCl_3$): $\bar{\nu}$ 1455, 1377 cm^{-1}; **^{1}H NMR** (CD_2Cl_2, 200 MHz) δ 7.20–7.48 (m, 17H, Ar H),

6.82–6.89 (m, 2H, Ar H), 6.20 (t, 1H, Ins H, J = 7.5 Hz), 5.75 (s, 1H, $PhCHO_2$), 4.60 (s, 2H, CH_2), 4.58 (q, 4H, 2 × CH_2, J = 11.9 Hz), 4.38 (d, 2H, Ins H, J = 2.3 Hz), 4.10 (d, 2H, Ins H, J = 7.5 Hz), 3.76 (s, 3H, OCH_3) 3.72–3.74 (m, 1H, Ins H), 2.51 (s, 3H, SCH_3) ppm; **^{13}C NMR** (CD_2Cl_2, 50.3 MHz): δ 216.0 (C=S), 159.7 (C_{arom}), 138.7 (C_{arom}), 137.6 (C_{arom}), 130.4 (C_{arom}), 129.7 (C_{arom}), 128.7 (C_{arom}), 128.3 (C_{arom}), 128.2 (C_{arom}), 126.7 (C_{arom}), 114.1 (C_{arom}), 92.9 ($PhCHO_2$), 82.4 (Ins C), 79.7 (Ins C), 73.8 (Ins C), 71.8 (CH_2), 70.9 (CH_2), 68.4 (Ins C), 55.5 (OCH_3), 19.5 (SCH_3) ppm; elemental analysis calcd (%) for $C_{37}H_{38}O_7S_2$ (658.82): C 67.45, H 5.81, S 9.73; found C 67.51, H 5.98, S 9.67 %.

***Racemic*-1-*O*-benzoyl-2-*O*-(4-methoxybenzyl)-3,5-dideoxy-4,6-di-*O*-benzyl-*myo*-inositol (2.30):** The xanthate **2.29** (1.05 g, 1.60 mmol), dry toluene (10 mL), tri-*n*-butyltin hydride (0.70 mL, 2.50 mmol) and AIBN (0.02 g, 0.15 mmol) were used (Procedure B) to obtain **2.30** as a gum (0.82 g, 93%) after column chromatography (eluent: 15% ethyl acetate in light petroleum). TLC Rf = 0.4 (15% ethyl acetate/light petroleum); **IR** (neat): $\bar{\nu}$ 1716 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 8.0–8.01 (m, 2H, Ar H), 7.09–7.63 (m, 15H, Ar H), 6.67–6.75 (m, 2H, Ar H), 5.11 (dd, 1H, Ins H, J = 9.4, 3.0 Hz), 4.61–4.65 (m, 2H, CH_2), 4.52–4.56 (m, 2H, CH_2), 4.44 (s, 2H, CH_2), 3.95–4.13 (m, 2H, Ins H), 3.79–3.90 (m, 1H, Ins H), 3.74 (s, 3H, CH_3), 2.49–2.64 (m, 1H, Ins H), 2.27–2.43 (m, 1H, Ins H), 1.45–1.7 (m, 2H, Ins H) ppm; **^{13}C NMR** ($CDCl_3$, 50.3 MHz): δ 165.9 (C=O), 159.0 (C_{arom}), 138.5 (C_{arom}), 132.9 (C_{arom}), 130.3 (C_{arom}), 129.7 (C_{arom}), 129.1 (C_{arom}), 128.4 (C_{arom}), 128.3 (C_{arom}), 128.2 (C_{arom}), 127.6 (C_{arom}), 127.5 (C_{arom}), 127.4 (C_{arom}), 113.6 (C_{arom}), 77.4 (Ins C), 74.0 (Ins C), 73.7 (Ins C), 71.9 (CH_2), 71.7 (CH_2), 71.4 (Ins C), 70.6 (CH_2), 55.1 (CH_3), 36.0 (Ins CH_2), 34.2 (Ins CH_2) ppm; elemental analysis calcd (%) for $C_{35}H_{36}O_6$ (552.66): C 76.06, H 6.57; found: C 75.66, H 6.48 %.

***Racemic*-2-*O*-(4-methoxybenzyl)-3,5-dideoxy-4,6-di-*O*-benzyl-*myo*-inositol (2.31):** To a solution of **2.30** (0.13 g, 0.23 mmol) in methanol (5 mL), added KOH (0.05 g, 0.90 mmol) and stirred for 2 hrs at room temperature. The solvents were removed under reduced pressure and the residue worked up with ethyl acetate and dried over anhd sodium sulfate. The gummy residue obtained after evaporation of the solvent was purified by column chromatography (eluent: 25% ethyl acetate/light petroleum) to obtain **2.31** as a gum (0.10 g, 98%). TLC Rf = 0.3 (25% ethyl acetate/light petroleum); **IR** (neat): $\bar{\nu}$ 3250-3350 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 7.19-7.50 (m, 12H, Ar H), 6.85-6.89 (m, 2H, Ar H), 4.43-

4.71 (m, 6H, 3 × CH_2), 3.95-3.97 (m, 1H, Ins H), 3.81 (s, 1H, CH_3), 3.55-3.73 (m, 3H, Ins H), 2.33-2.54 (m, 3H, OH and Ins H), 1.37-1.47 (m, 2H, Ins H) ppm; **^{13}C NMR** ($CDCl_3$, 50.3 MHz): δ 159.2 (C_{arom}), 138.5 (C_{arom}), 130.4 (C_{arom}), 129.2 (C_{arom}), 128.3 (C_{arom}), 127.7 (C_{arom}), 127.5 (C_{arom}), 113.7 (C_{arom}), 76.9 (Ins C), 75.8 (Ins C), 75.4 (Ins C), 71.6 (CH_2), 71.54 (Ins C), 71.49 (CH_2), 70.5 (CH_2), 55.2 (CH_3), 35.3 (Ins CH_2), 33.8 (Ins CH_2) ppm; elemental analysis calcd (%) for $C_{28}H_{32}O_5$ (448.55): C 74.97, H 7.19; found: C 74.98, H 6.91 %.

***Racemic*-1-*O*-benzoyl-3,5-dideoxy-4,6-di-*O*-benzyl-*myo*-inositol (2.32):** To a solution of **2.30** (0.30 g, 0.54 mmol) in dichloromethane:water (10 mL, 95:5), DDQ (0.19 g, 0.81 mmol) was added and stirred for 2 h. The reaction mixture was diluted with dichloromethane (100 mL) and washed with sat. $NaHCO_3$ solution and water followed by brine and dried over anhd sodium sulfate. The solvent was evaporated under reduced pressure to obtain a gum which was purified by column chromatography (eluent: 20% ethyl acetate in light petroleum) to afford **2.32** (0.21 g, 92%) as a gum. TLC *Rf* = 0.3 (25% ethyl acetate/light petroleum); **IR** (neat): $\bar{\nu}$ 3200-3550, 1716 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 7.97-8.12 (m, 2H, Ar H), 7.22-7.64 (m, 13H, Ar H), 5.17 (dd, 1H, Ins H, *J* = 9.4, 3.0 Hz), 4.52-4.70 (m, 4H, 2 × CH_2), 4.31-4.38 (m, 1H, Ins H), 3.84-4.05 (m, 2H, Ins H), 2.50-2.65 (m, 1H, Ins H), 2.31-2.41 (m, 1H, Ins H), 2.04 (brs, 1H, OH), 1.49-1.75 (m, 2H, Ins H) ppm; **^{13}C NMR** ($CDCl_3$, 50.3 MHz): δ 165.7 (C=O), 138.4 (C_{arom}), 138.2 (C_{arom}), 133.2 (C_{arom}), 129.9 (C_{arom}), 129.7 (C_{arom}), 128.40 (C_{arom}), 128.36 (C_{arom}), 128.2 (C_{arom}), 127.5 (C_{arom}), 77.8 (Ins C), 73.4 (Ins C), 71.5 (CH_2), 71.1 (Ins C), 70.7 (CH_2), 67.5 (Ins C), 36.2 (Ins CH_2), 35.9 (Ins CH_2) ppm; elemental analysis calcd (%) for $C_{27}H_{28}O_5$ (432.51): C 74.98, H 6.53; found: C 74.85, H 6.36 %.

***Racemic*-3-*O*-[(methylthio)thiocarbonyl]-2,4,6-tri-*O*-methyl-1,5-*O*-benzylidene-*myo*-inositol (2.33):** The alcohol **1.77**[20] (1.15 g, 3.7 mmol), dry THF (20 mL), sodium hydride (0.74 g, 18.50 mmol), carbon disulfide (3.5 mL, 58.33 mmol) and methyl iodide (1.1 mL, 17.67 mmol) were used (Procedure A) to obtain the xanthate **2.33** as a gum (1.39 g, 94%) after column chromatography (eluent: 7% ethyl acetate/light petroleum): TLC *Rf* = 0.3 (10% ethyl acetate in light petroleum); **IR** ($CHCl_3$): $\bar{\nu}$ 1062, 1213, cm^{-1}; **^{1}H NMR** (CD_2Cl_2, 400 MHz): δ 7.41-7.49 (m, 2H, Ar H), 7.28-7.38 (m, 3H, Ar H), 5.98 (t, 1H, Ins H, *J* = 8.3 Hz), 5.95 (s, 1H, $PhCHO_2$), 4.61-4.67 (m, 1H, Ins H), 4.40-4.44 (m, 1H, Ins H),

4.38 (t, 1H, Ins H, J = 7.5 Hz), 4.07 (d, 1H, Ins H, J = 8.3 Hz), 3.91 (t, 1H, Ins H, J = 3.4 Hz), 3.44 (s, 3H, OCH_3), 3.41 (s, 3H, OCH_3), 3.40 (s, 3H, OCH_3), 2.58 (s, 3H, CH_3) ppm; **^{13}C NMR** (CD_2Cl_2, 125.4 MHz): δ 216.1 (C=S), 138.6 (C_{arom}), 129.3 (C_{arom}), 128.5 (C_{arom}), 126.6 (C_{arom}), 93.5 ($PhCO_2$), 81.1 (Ins C), 81.0 (Ins C), 74.9 (Ins C), 73.3 (Ins C), 71.8 (Ins C), 68.6 (Ins C), 59.2 (OCH_3), 58.3 (OCH_3), 57.3 (OCH_3), 19.5 (SCH_3) ppm; elemental analysis calcd (%) for $C_{18}H_{24}O_6S_2$ (400.51): C 53.98, H 6.04, S 16.01; found: C 53.90, H 5.72, S 16.11 %.

Deoxygenation of 2.33: The xanthate **2.33** (1.00 g, 2.50 mmol), dry toluene (15 mL), tri-*n*-butyltin hydride (3.40 mL, 12.50 mmol) and AIBN (0.06 g) were used (Procedure B) to obtain **2.34** (colorless solid, 0.51 g, 68%) and **2.35** (gum, 0.12 g, 16%),) after column chromatography (eluent: 12-17% ethyl acetate in light petroleum). Data for **2.34**: TLC *Rf* = 0.3 (15% ethyl acetate/light petroleum); **mp** 54–55 °C; **IR** ($CHCl_3$): $\bar{\nu}$ 1710 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.10 (d, 2H, Ar H, J = 7.3 Hz), 7.57 (t, 1H, Ar H, J = 7.3 Hz), 7.46 (t, 2H, Ar H, J = 7.8 Hz), 5.07 (dd, 1H, Ins H, J_1 = 3.9, J_2 = 6.3 Hz), 3.85-3.89 (m, 1H, Ins H), 3.71-3.78 (m, 1H, Ins H), 3.53-3.61 (m, 1H, Ins H), 3.42 (s, 3H, OCH_3), 3.39 (s, 3H, OCH_3), 3.38 (s, 3H, OCH_3), 2.44-2.52 (m, 1H, Ins H), 2.30-2.39 (m, 1H, Ins H), 1.32-1.52 (m, 2H, Ins H) ppm; **^{13}C NMR** ($CDCl_3$, 50.3 MHz): δ 166.0 (C=O), 132.9 (C_{arom}), 130.1 (C_{arom}), 129.7 (C_{arom}), 128.2 (C_{arom}), 76.8 (Ins C), 76.0 (Ins C), 75.6 (Ins C), 73.1 (Ins C), 58.0 (CH_3), 57.1 (CH_3), 56.1 (CH_3), 34.6 (Ins CH_2), 33.1 (Ins CH_2) ppm; elemental analysis calcd (%) for $C_{16}H_{22}O_5$ (294.34): C 65.29, H 7.53; found: C 65.13, H 7.90 %.

Data for **2.35:** TLC *Rf* = 0.3 (20% ethyl acetate/light petroleum); **IR** ($CHCl_3$): $\bar{\nu}$ 1722 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.06 (d, 2H, Ar H, J = 7.3 Hz), 7.56-7.59 (m, 1H, Ar H), 7.42-7.49 (m, 2H, Ar H), 5.20 (t, 1H, Ins H, J = 9 Hz), 3.68-3.74 (m, 1H, Ins H), 3.58-3.67 (m, 2H, Ins H), 3.37 (s, 3H, CH_3), 3.34 (s, 6H, 2 × CH_3), 2.33-2.41 (m, 2H, Ins H), 1.46-1.55 (m, 2H, Ins H) ppm; **^{13}C NMR** ($CDCl_3$, 50.3 MHz): δ 166.0 (C=O), 132.7 (C_{arom}), 130.6 (C_{arom}), 129.7 (C_{arom}), 128.3 (C_{arom}), 78.1 (Ins C), 73.6 (Ins C), 57.7 (CH_3), 56.1 (CH_3), 32.9 (Ins CH_2) ppm; elemental analysis calcd (%) for $C_{16}H_{22}O_5$ (294.34): C 65.29, H 7.53; found: C, 65.66; H, 7.70 %.

1,3-*O*-Benzylidene-4,5,6-tri-*O*-benzyl-2-*O*-(4-methoxybenzyl)-*myo*-inositol (2.37): To a solution of **2.28** (2.27 g, 4.00 mmol) in dry DMF (20 mL) sodium hydride (0.20 g, 5.00

mmol) was added and stirred for 10 min. Benzyl bromide (0.60 mL, 5.00 mmol) was then added drop wise and the reaction mixture stirred for 4 h. Excess of sodium hydride was quenched by the addition of cold water. The reaction mixture was concentrated under reduced pressure to get a gum which was worked up with ethyl acetate; the organic extract was dried over anhd sodium sulfate. The solvent was removed under reduced pressure to afford a gummy residue which was purified by column chromatography (eluent: 20% ethyl acetate/light petroleum) to obtain **2.37** as a colorless solid (2.52 g, 96%). TLC *Rf* = 0.40 (20% ethyl acetate/light petroleum); **^{1}H NMR** (CD_2Cl_2, 200 MHz): δ 7.45-7.50 (m, 2H, Ar H), 7.27-7.38 (m, 20H, Ar H), 6.86-6.87 (m, 2H, ArH), 5.77 (s, 1H, $PhCHO_2$), 4.74 (s, 2H, $PhCH_2$), 4.65 (q, 4H, 2 × CH_2Ph, *J* = 11.5 Hz), 4.61 (s, 2H, $PhCH_2$), 4.33 (d, 2H, Ins H, *J* = 2.5 Hz), 4.09 (d, 2H, Ins H, *J* = 7.2 Hz), 3.76 (s, 3H, OCH_3) 3.66 (t, 1H, Ins H, *J* = 6.9 Hz), 3.59 (t, 1H, Ins H, *J* = 2.2 Hz) ppm; **^{13}C NMR** (CD_2Cl_2, 50.3 MHz): δ 159.7 (C_{arom}), 138.9 (C_{arom}), 138.1 (C_{arom}), 130.5 (C_{arom}), 129.8 (C_{arom}), 129.4 (C_{arom}), 128.7 (C_{arom}), 128.6 (C_{arom}), 128.5 (C_{arom}), 128.4 (C_{arom}), 128.3 (C_{arom}), 128.2 (C_{arom}), 128.0 (C_{arom}), 127.2 (C_{arom}), 126.7 (C_{arom}), 114.1 (C_{arom}), 92.9 ($PhCHO_2$), 82.8 (Ins C), 82.1 (Ins C), 74.4 (CH_2), 73.7 (Ins C), 71.9 (CH_2), 70.8 (CH_2), 68.6 (Ins C), 55.5 (CH_3) ppm; elemental analysis calcd (%) for $C_{42}H_{42}O_7$ (658.78): C 76.57, H 6.43; found: C 76.40, H 6.12 %.

1,3-*O*-Benzylidene-4,5,6-tri-*O*-benzyl-*myo*-inositol (2.38): To a solution of **2.37** (2.30 g, 3.5 mmol) in dichloromethane:water (20 mL, 95:5), DDQ (1.20 g, 5.25 mmol) was added and stirred for 1.5 h. The reaction mixture was diluted with dichloromethane (100 mL) and washed with sat. $NaHCO_3$ solution and water followed by brine and dried over anhd sodium sulfate. The solvent was evaporated under reduced pressure to obtain a gum which was purified by column chromatography (eluent: 20% ethyl acetate in light petroleum) to afford **2.38** (1.73 g, 92%) as a gum. TLC *Rf* = 0.3 (20% ethyl acetate/light petroleum); **IR** ($CHCl_3$): $\bar{\nu}$ 3445 cm^{-1}; **^{1}H NMR** (CD_2Cl_2, 200 MHz): δ 7.24-7.46 (m, 20H, Ar H), 5.7 (s, 1H, $PhCHO_2$), 4.76 (s, 2H, $PhCH_2$), 4.66 (q, 4H, 2 × CH_2Ph, *J* = 11.5 Hz), 4.20 (d, 2H, Ins H, *J* = 2.2 Hz), 4.08 (d, 2H, Ins H, *J* = 7.4 Hz), 3.82 (d, 1H, Ins H, *J* = 11.3 Hz), 3.69 (t, 1H, Ins H, *J* = 7.5 Hz) 3.08 (d, 1H, OH, *J* = 11.3 Hz) ppm; **^{13}C NMR** (CD_2Cl_2, 50.3 MHz): δ 138.9 (C_{arom}), 138.2 (C_{arom}), 138.0 (C_{arom}), 128.7 (C_{arom}), 128.63 (C_{arom}), 128.61 (C_{arom}), 128.5 (C_{arom}), 128.4 (C_{arom}), 128.2 (C_{arom}), 128.0 (C_{arom}), 126.4 (C_{arom}), 93.0 ($PhCO_2$), 82.1

(Ins C), 81.8 (Ins C), 76.9 (Ins C), 74.8 (CH_2), 71.9 (CH_2), 62.6 (Ins C) ppm; elemental analysis calcd (%) for $C_{34}H_{34}O_6$ (538.63): C 75.82, H 6.36; found: C 76.21, H 5.98 %.

1,3-*O*-Benzylidene-2-[(methylthio)thiocarbonyl]-4,5,6-tri-*O*-benzyl-*myo*-inositol (2.39): The alcohol **2.38** (1.07 g, 2.00 mmol), dry THF (10 mL), sodium hydride (0.40 g, 10.00 mmol), carbon disulfide (1.80 mL, 30.00 mmol) and methyl iodide (0.60 mL, 10.00 mmol) were used (Procedure A) to obtain the xanthate **2.39** as a gummy liquid (1.29 g; TLC *Rf* = 0.4 in 15% ethyl acetate/light petroleum) which was used for next reaction without purification.

Deoxygenation of 2.39: To a solution of the xanthate **2.39** (1.29 g) in dry toluene (10 mL), tri-*n*-butyltin hydride (0.1 mL, 3.7 mmol) and AIBN (0.02 g, 0.15 mmol) were added and heated at 100 °C for 1 h. The solvents were removed under reduced pressure to obtain residue which shows mixture of products on TLC which were inseparable by column chromatography.

1,3-*O*-Benzylidene-2-[(*O*-phenyl)-thiocarbonyl]-4,5,6-tri-*O*-benzyl-*myo*-inositol (2.40): To a cooled (0 °C) solution of the alcohol **2.38** (0.81 g, 1.5 mmol) in dry THF (10 mL), pyridine (1 mL) and phenylchlorothionoformate (0.52 g, 3.00 mmol) was added and stirred at ambient temperature for 2 h. Solvent were removed under reduced pressure to obtain gummy residue which was diluted with ethyl acetate and washed with saturated ammonium chloride solution followed by brine and dried over anhd sodium sulfate. The gummy residue obtained after evaporation of the solvent was purified by column chromatography (eluent: 10% ethyl acetate/light petroleum) to obtain **2.40** as a colorless solid (1.18 g, 88%). TLC *Rf* = 0.3 (10% ethyl acetate/light petroleum); **mp** 110–115 °C; **^{1}H NMR** (CD_2Cl_2, 200 MHz): δ 7.14-7.51 (m, 25H, Ar H), 5.89 (s, 1H, $PhCHO_2$), 5.43 (t, 1H, Ins H, *J* = 2.4 Hz), 4.74 (s, 2H, $PhCH_2$), 4.67 (q, 4H, 2 × CH_2Ph, *J* = 11.5 Hz), 4.63 (s, 2H, Ins H), 4.17 (d, 2H, Ins H, *J* = 6.4 Hz), 3.81 (t, 1H, *J* = 4.0 Hz) ppm; **^{13}C NMR** (CD_2Cl_2, 50.3 MHz): δ 194.6 (C=S), 153.7 (C_{arom}), 138.6 (C_{arom}), 137.8 (C_{arom}), 130.0 (C_{arom}), 129.7 (C_{arom}), 128.8 (C_{arom}), 128.6 (C_{arom}), 128.5 (C_{arom}), 128.4 (C_{arom}), 128.3 (C_{arom}), 128.1 (C_{arom}), 127.0 (C_{arom}), 126.7 (C_{arom}), 122.3 (C_{arom}), 93.1 ($PhCHO_2$), 82.4 (Ins C), 81.8 (Ins C), 74.5 (CH_2), 73.9 (Ins C) 72.9 (Ins C), 72.0 (CH_2) ppm; elemental analysis calcd (%) for $C_{41}H_{38}O_7S_2$ (674.80): C 72.98, H 5.68, S 4.75; found: C 73.24, H 5.98 %.

Deoxygenation of 2.40: To a solution of **2.40** (1.01 g, 1.5 mmol) in dry toluene (10 mL), tri-*n*-butyltin hydride (0.70 mL, 2.50 mmol) and AIBN (0.02 g, 0.15 mmol) were added and heated at 100 °C for 1 h. The solvents were removed under reduced pressure to obtain residue which Shows mixture of products on TLC which were inseparable by column chromatography.

1,3-*O*-Methylidene-2,4,6-tri-*O*-benzyl-5-*O*-[(methylthio)thiocarbonyl]-*myo*-inositol (2.43): The alcohol **1.47** (2.31 g, 5.0 mmol), dry THF (30 mL), sodium hydride (1.0 g, 25 mmol), carbon disulfide (4.5 mL, 75.0 mmol) and methyl iodide (1.50 mL, 24.19 mmol) were used (Procedure A) to obtain the xanthate **2.43** as a colorless solid (2.71 g, 98%) after column chromatography (eluent: 7% ethyl acetate in light petroleum). TLC *Rf* = 0.4 (10% ethyl acetate/light petroleum); **mp** 86–87 °C; **IR** ($CHCl_3$): $\bar{\nu}$ 1377 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 7.27-7.45 (m, 15H, Ar H), 6.07 (s, 1H, Ins H), 5.55 (d, 1H, H_2CO_2, *J* = 4.5 Hz), 4.80 (d, 2H, CH_2, *J* = 12 Hz), 4.6-4.71 (m, 5H), 4.32-4.4 (m, 3H, Ins H), 4.0 (q, 2H, Ins H, *J* = 1.7 Hz), 2.52 (s, 3H, CH_3) ppm; **^{13}C NMR** ($CDCl_3$, 50.3 MHz): δ 214.1 (C=S), 137.5 (C_{arom}), 128.4 (C_{arom}), 128.3 (C_{arom}), 127.8 (C_{arom}), 127.7 (C_{arom}), 127.6 (C_{arom}), 85.3 (H_2CO_2), 78.7 (Ins C), 76.4 (Ins C), 72.1 (CH_2), 70.8 (Ins C), 70.6 (CH_2), 70.0 (Ins C), 18.3 (CH_3) ppm; elemental analysis calcd (%) for $C_{30}H_{32}O_6S_2$ (552.70): C 65.19, H 5.84; found: C 64.79, H 5.74 %.

1,3-*O*-Methylidene-2,4,6-tri-*O*-benzyl-5-deoxy-*myo*-inositol (2.44): The xanthate **2.43** (1.66 g, 3.0 mmol), dry toluene (20 mL), tri-*n*-butyltin hydride (3.0 mL, 11.13 mmol) and AIBN (0.08 g) were used (Procedure B) to obtain deoxy inositol derivative **2.44** as a colorless solid (1.26 g, 94%) after column chromatography (eluent: 10% ethyl acetate in light petroleum). TLC *Rf* = 0.4 (10% ethyl acetate/light petroleum); **mp** 60–62 °C; **IR** ($CHCl_3$): $\bar{\nu}$ 1454 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 7.2-7.4 (m, 15H, Ar H), 5.6 (d, 1H, HCO_2 *J* = 4.3 Hz), 4.55- 4.71 (m, 5H, H_2CO_2 and 2 × CH_2), 4.32-4.51 (m, 5H), 3.90 (br s, 2H, Ins H), 2.16-2.32 (m, 1H, CH_2), 1.95-2.10 (m, 1H, CH_2) ppm; **^{13}C NMR** $CDCl_3$, 50.3 MHz): δ 138.4 (C_{arom}), 137.8 (C_{arom}), 128.2 (C_{arom}), 128.1 (C_{arom}), 127.7 (C_{arom}), 127.5 (C_{arom}), 127.3 (C_{arom}), 85.4 (H_2CO_2), 77.4 (Ins C), 71.3, (Ins C), 71.0 (CH_2), 70.2 (CH_2), 70.1 (Ins C), 23.2 (CH_2) ppm; elemental analysis calcd (%) for $C_{28}H_{30}O_5$ (446.53): C 75.31, H 6.77; found: C 75.32, H 6.82 %.

***neo*-Quercitol (2.21):** A mixture of **2.44** (0.89 g, 2.00 mmol), THF-water mixture (10 mL + 0.5 mL), and conc. HCl (1 mL) was refluxed for 2 h. The solvents were removed under reduced pressure to obtain a gummy residue which was dissolved in ethyl acetate (100 mL). The solution was washed with saturated sodium bicarbonate solution followed by brine and dried over anhd sodium sulfate. The crude product (0.86 g) obtained after evaporation of the solvent was used in the next step.

The crude tribenzyl ether (0.86 g) was debenzylated in the presence of Pearlmann's catalyst (20% $Pd(OH)_2/C$, 0.03 g) in ethanol by hydrogenolysis (60 psi) at rt for 12 h. The catalyst was allowed to settle and the supernatant liquid was removed using a pipette. The catalyst was repeatedly washed with warm (50 °C) aqueous ethanol (1:1, 3 × 150 mL). Combined washings were filtered over a short column of Celite. The filtrate was evaporated under reduced pressure to obtain a white solid which was crystallized from hot methanol to afford *neo*-quercitol **2.21** colorless crystals (0.30 g, 92%). **Mp** 235–238 °C (Lit.[10c] **mp** 237–241 °C).

***Racemic*-2,4,6-tri-*O*-benzyl-1,5-*O*-ethylidene-*myo*-inositol (1.48):** To a cooled (0 °C) solution of **1.44** (2.76 g, 6.0 mmol) in dry benzene (30 mL) was added methylmagnesium iodide (1 M solution in diethyl ether, 12.0 mL, 12 mmol) and stirred for 15 h at room temperature. The reaction mixture was then diluted with ether (100 mL) and washed with saturated solution of NH_4Cl. The organic layer was washed with brine and dried over anhd sodium sulfate. The gummy residue obtained after evaporation of the solvent was purified by column chromatography (eluent: 10% ethyl acetate in light petroleum) to obtain the alcohol **1.48**[20] as a syrupy liquid (2.40 g, 84%).

***Racemic*-3-*O*-[(methylthio)thiocarbonyl]-2,4,6-tri-*O*-benzyl-1,5-*O*-ethylidene-*myo*-inositol (2.45):** The alcohol **1.48** (1.43 g, 3.0 mmol), dry THF (20 mL), sodium hydride (0.60 g, 15 mmol), carbon disulfide (2.70 mL, 45.0 mmol) and methyl iodide (0.93 mL, 15.0 mmol) were used (Procedure A) to obtain the xanthate **2.45** (1.66 g, 98%) as a thick oil after column chromatography (eluent: 10% ethyl acetate in light petroleum). TLC *Rf* = 0.3 (10% ethyl acetate/light petroleum); **IR** ($CHCl_3$): $\bar{\nu}$ 1359 cm^{-1}; ^{1}**H NMR** ($CDCl_3$, 200 MHz): δ 7.2-7.4 (m, 15H, Ar H), 6.27 (t, 1H, Ins H, *J* = 8.2 Hz), 5.20 (q, 1H, CO_2, *J* = 4.8 Hz), 4.5-4.8 (m, 6H), 4.16-4.46 (m, 4H, Ins H), 3.98 (t, 1H, Ins H, *J* = 3.8 Hz), 2.51 (s, 3H, SCH_3), 1.22 (d, 3H, CH_3, *J* = 4.8 Hz) ppm; ^{13}**C NMR** ($CDCl_3$, 50.3 MHz): δ 215.3

(C=S), 137.7 (C_{arom}), 137.4 (C_{arom}), 128.4 (C_{arom}), 128.3 (C_{arom}), 128.1 (C_{arom}), 128 (C_{arom}), 127.9 (C_{arom}), 127.8 (C_{arom}), 127.64 (C_{arom}), 127.59 (C_{arom}), 90.7 (HCO_2), 80.6 (Ins C), 77.8 (Ins C), 73.3 (Ins C), 72.9 (CH_2), 71.5 (CH_2), 71.4 (CH_2), 69.1 (Ins C), 68.1 (Ins C), 20.7 (CH_3), 19.0 (CH_3) ppm; elemental analysis calcd (%) for $C_{31}H_{34}O_6S_2$ (566.73): C 65.70, H 6.05; found: C 65.42, H 5.97 %.

***Racemic*-3-deoxy-2,4,6-tri-*O*-benzyl-1,5-*O*-ethylidene-*myo*-inositol (2.46):** The xanthate **2.45** (1.50 g, 2.65 mmol), dry toluene (20 mL), tri-*n*-butyltin hydride (3.50 mL , 13.01 mmol) and AIBN (0.07 g) were used (Procedure B) to obtain the deoxy inositol derivative **2.46** as a gum (1.12 g, 92%) after column chromatography (eluent: 15% ethyl acetate in light petroleum). TLC *Rf* = 0.3 (15% ethyl acetate/light petroleum); **IR** ($CHCl_3$): $\bar{\nu}$ 1514 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.2-7.4 (m, 15H, Ar H), 5.44 (q, 1H, HCO_2, J = 4.8 Hz), 4.64 (d, 1H, CH_2, J = 11.8 Hz), 4.61 (t, 1H, Ins H, J = 4.1 Hz), 4.55-4.58 (m, 3H), 4.47-4.52 (m, 2H, Ins H), 4.42 (d, 1H, CH_2, J = 11.8 Hz), 4.35 (brs, 1H, Ins H), 4.09-4.13 (dd, 1H, Ins H, J_1 = 11.2 Hz, J_2 = 4.3 Hz), 3.75-3.82 (m, 1H, Ins H), 2.24-2.42 (m, 1H, Ins H), 2.05-2.17 (m, 1H, Ins H), 1.25 (d, 3H, CH_3, J = 4.8 Hz) ppm; **^{13}C NMR** ($CDCl_3$, 50.3 MHz): δ 138.6 (C_{arom}), 138.5 (C_{arom}), 137.6 (C_{arom}), 128.2 (C_{arom}), 127.6 (C_{arom}), 127.4 (C_{arom}), 127.3 (C_{arom}), 89.6 (HCO_2), 77.3 (Ins C), 71.7 (Ins C), 71.4 (CH_2), 71.2 (Ins C), 71.2 (CH_2), 70.9 (CH_2), 69.3 (Ins H), 67.3 (Ins C), 26.8 (CH_2), 21.4 (CH_3) ppm; elemental analysis calcd (%) for $C_{29}H_{32}O_5$ (460.56): C 75.63, H 7.00; found: C 75.52, H 7.24 %.

***Racemic-vibo*-quercitol (2.1):** A mixture of **2.46** (0.92 g, 2.00 mmol), THF-water mixture (10 mL + 0.5 mL), and conc. HCl (1 mL) was refluxed for 2 h. The solvents were removed under reduced pressure to obtain a gummy residue which was dissolved in ethyl acetate (100 mL). The solution was washed with saturated sodium bicarbonate solution followed by brine and dried over anhd sodium sulfate. The crude product **2.47** (0.90 g) obtained after evaporation of the solvent was used in the next step without purification.

The crude tribenzyl ether **2.47** (0.90 g) was debenzylated in the presence of Pearlmann's catalyst (20% $Pd(OH)_2$/C, 0.03 g) in ethanol by hydrogenolysis (60 psi) at rt for 12 h. The catalyst was allowed to settle and the supernatant liquid was removed using a pipette. The catalyst was repeatedly washed with warm (50 °C) aqueous methanol (1:1, 3 × 150 mL). Combined washings were filtered over a short column of Celite. The filtrate was evaporated under reduced pressure to obtain a colorless solid which was crystallized from

hot methanol to afford colorless crystals (0.29 g, 88%) of *racemic* **2.1**. **Mp** 158-160 °C (lit[2] mp 163 °C); **IR** (nujol): $\bar{\nu}$ 3540, 1445 cm^{-1}; **H^1 NMR** (D_2O, 200 MHz): δ 4.0-4.07 (m, 1H), 3.66-3.82 (m, 1H), 3.42-3.6 (m, 2H), 3.17-3.32 (m, 1H), 2.0-2.14 (m, 1H), 1.46-1.60 (m, 1H) ppm.

1,3-*O*-Benzylidine-2,4,6-tri-*O*-benzyl-*myo*-5-inososе (1.132): To a solution of the alcohol **1.49**[16] (2.69 g, 5.00 mmol) in ethyl acetate (25 mL) was added 2-iodoxybenzoic acid (2.80 g, 10.00 mmol) and refluxed for 3 h. The reaction mixture was filtered through sintered glass funnel, and the residue washed with ethyl acetate (2 × 15 mL). The combined filtrate and washings was evaporated under reduced pressure to get the ketone **1.132** (2.61 g) as a colorless solid. Crystals of the pure ketone **1.132** could be obtained by crystallization from hot methanol. **Mp** 107–109 °C (Lit.[16] **mp** 106–108 °C).

1,3-*O*-benzylidene-2,4,6-tri-*O*-benzyl-*neo*-inositol (1.133): The crude ketone **1.132** (2.61 g) was dissolved in a mixture of THF (5 mL) and methanol (20 mL) and cooled to 0 °C. To this solution, sodium borohydride (0.57 g, 15.07 mmol) was added in one lot and stirred for 1 h at ambient temperature. TLC analysis of the reaction mixture showed the absence of the starting material. The solvents were removed under reduced pressure and the gummy residue obtained was worked up with dichloromethane. The product was purified by column chromatography [eluent: ethyl acetate : dichloromethane : light petroleum (1:1:8)] to afford the alcohol **1.133** as a colorless solid (2.52 g, 94%). **Mp** 98–102 °C (Lit.[16] **mp** 101–103 °C).

1,3-*O*-Benzylidene-2,4,6-tri-*O*-benzyl-5-*O*-[(methylthio)thiocarbonyl]-*neo*-inositol (2.48): The alcohol **1.133** (1.50 g, 2.80 mmol), dry THF (20 mL), sodium hydride (0.56 g, 14.0 mmol), carbon disulfide (2.5 mL, 41.70 mmol) and methyl iodide (0.90 mL, 14.46 mmol) were used (Procedure A) to obtain the xanthate **2.48** as a colorless solid (1.68 g, 98%) after column chromatography (eluent: 10% ethyl acetate in light petroleum). TLC *Rf* = 0.35 (10% ethyl acetate/light petroleum); **mp** 100–102 °C; **IR** ($CHCl_3$): $\bar{\nu}$ 1377 cm^{-1}; **^{1}H NMR** (CD_2Cl_2, 400 MHz): δ 7.50-7.60 (m, 2H, Ar H), 7.27-7.47 (m, 18H, Ar H), 6.49 (t, 1H, Ins H, *J* = 4.4 Hz), 5.93 (s, 1H, $PhCHO_2$), 4.72-4.78 (d, 2H, CH_2, *J* = 12.1 Hz), 4.65 (s, 2H, CH_2), 4.54-4.61 (d, 2H, CH_2, *J* = 12.1 Hz), 4.34-4.36 (m, 4H, Ins H), 4.27 (t, 1H, Ins H, *J* = 2.1 Hz), 2.58 (s, 3H, CH_3) ppm; **^{13}C NMR** ($CDCl_3$, 50.3 MHz): δ 215.8 (C=S), 139.5 (C_{arom}), 137.7 (C_{arom}), 129.3 (C_{arom}), 128.3 (C_{arom}), 127.8 (C_{arom}), 126.6 (C_{arom}), 95.4

($PhCO_2$), 77.8 (Ins C), 76.2 (Ins C), 73.9 (Ins C), 71.8 (CH_2), 70.6 (CH_2), 65.7 (Ins C), 19.3 (CH_3) ppm; elemental analysis calcd (%) for $C_{36}H_{36}O_6S_2$ (628.80): C 68.76, H 5.77, S 10.20; found: C 68.65, H 5.57, S 9.95 %.

***Racemic*-1-*O*-benzoyl-2,4,6-tri-*O*-benzyl-3,5-dideoxy-*myo*-inositol (2.17):** The xanthate **2.48** (1.25 g, 2.00 mmol), dry toluene (15 mL), tri-*n*-butyltin hydride (2.0 mL, 7.43 mmol) and AIBN (0.04 g) were used (Procedure B) to obtain **2.17** as a gum (0.95 g, 91%) after column chromatography (eluent: 10% ethyl acetate in light petroleum). **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 8.01-8.12 (m, 2H, Ar H), 7.13-7.66 (m, 18H, Ar H), 5.14 (dd, 1H, Ins H, J = 9.5, 2.9 Hz), 4.45-4.76 (m, 6H, 3 × CH_2), 3.97-4.17 (m, 2H, Ins H), 3.71-3.95 (m, 1H, Ins H), 2.48-2.64 (m, 1H, CH_2), 2.27-2.46 (m, 1H, CH_2), 1.48-1.71 (m, 2H, CH_2) ppm.

1,3-*O*-Benzylidene-2,4,6-tri-*O*-benzyl-5-*O*-[(methylthio)thiocarbonyl]-*myo*-inositol (2.52, epimer of 2.16): The solid xanthate **2.16** (0.20 g, 0.32 mmol) was heated at 120 °C (mp of **2.16** is 112–114 °C lit[16]) under argon for 12 h and the products were separated by column chromatography (eluent: 5 to 7% ethyl acetate in light petroleum) to afford **2.52** (0.14 g, 70%; TLC *Rf* = 0.4 in 10% ethyl acetate/light petroleum) and **2.18**[16] as gums (0.04 g, 25%; TLC *Rf* = 0.3 in 40% ethyl acetate/light petroleum). Data for **2.52**: **^{1}H NMR** (CD_2Cl_2, 200 MHz): δ 7.45–7.58 (m, 2H, Ar H), 7.10–7.40 (m, 18 H, Ar H), 6.45 (s, 1H, $PhCHO_2$), 6.06 (brs, 1H, Ins H), 4.69 (s, 2H, CH_2), 4.69 (q, 4H, 2 × CH_2, J = 12.1 Hz), 4.50–4.64 (m, 2H, Ins H), 4.39 (t, 1H, Ins H, J = 1.4 Hz), 4.05 (dd, 2H, Ins H, J_1 = 1.3 Hz and J_2 = 3.5 Hz), 2.41 (s, 3H, CH_3) ppm; **^{13}C NMR** (CD_2Cl_2, 125.76 MHz): δ 216.2 (C=S), 139.2 (C_{arom}), 138.3 (C_{arom}), 138.2 (C_{arom}), 129.1 (C_{arom}), 128.8 (C_{arom}), 128.7 (C_{arom}), 128.31 (C_{arom}), 128.29 (C_{arom}), 128.2 (C_{arom}), 128.1 (C_{arom}), 128.0 (C_{arom}), 127.4 (C_{arom}), 92.7 ($PhCO_2$), 80.0 (Ins C), 78.6 (Ins C), 72.8 (CH_2), 72.4 (Ins C), 71.0 (CH_2), 70.5 (Ins C), 19.7 (CH_3) ppm; elemental analysis calcd (%) for $C_{36}H_{36}O_6S_2$ (628.80): C 68.76, H 5.77; found: C 68.51, H 6.03 %.

1,3-*O*-Benzylidene-2-*O*-(4-methoxybenzyl)-4,6-di-*O*-benzyl-5-*O*-[(methylthio)thiocarbonyl]-*myo*-inositol (2.53, epimer of 2.29): The solid xanthate **2.29** (0.20 g, 0.30 mmol) was heated at 120 °C (mp of **2.29** is 93–93.8 °C) under argon for 30 h and the products separated by column chromatography (eluent: 10% ethyl acetate in light petroleum) to afford **2.53** as gum (0.14 g, 72%; TLC *Rf* = 0.6 in 20% ethyl acetate/light petroleum) and **2.61** as a solid (0.04 g, 24%; TLC *Rf* = 0.3 in 40% ethyl acetate/light petroleum). The

gummy xanthate **2.53** was stored under *n*-pentane at –20 °C for 12 h when it turned into a colorless solid.

Data for **2.53: Mp** 77–79.2 °C (crystallized from a hot mixture of 10% ethyl acetate in light petroleum); **^{1}H NMR** (CD_2Cl_2, 200 MHz): δ 7.45–7.60 (m, 2H, Ar H), 7.16–7.43 (m, 15H, Ar H), 6.75–6.88 (m, 2H, Ar H), 6.44 (s, 1H, $PhCHO_2$), 6.06 (br s, 1H, Ins H), 4.69 (q, 4H, 2 × CH_2, J = 11.9 Hz), 4.63 (s, 2H, CH_2), 4.49–4.55 (m, 2H, Ins H), 4.38 (t, 1H, Ins H, J = 1.3 Hz), 4.01–4.09 (m, 2H, Ins H), 3.75 (s, 3H, OCH_3), 2.42 (s, 3H, SCH_3) ppm; **^{13}C NMR** (CD_2Cl_2, 125.76 MHz): δ 216.2 (C=S), 159.8 (C_{arom}), 139.2 (C_{arom}), 138.3 (C_{arom}), 130.2 (C_{arom}), 130.0 (C_{arom}), 129.1 (C_{arom}), 128.7 (C_{arom}), 128.3 (C_{arom}), 128.1 (C_{arom}), 128.0 (C_{arom}), 127.4 (C_{arom}), 114.1 (C_{arom}), 92.7 ($PhCHO_2$), 80.0 (Ins C), 78.5 (Ins C), 72.7 (CH_2), 72.4 (Ins C), 70.5 (CH_2), 69.9 (Ins C), 55.5 (OCH_3); 19.6 (SCH_3) ppm; elemental analysis calcd (%) for $C_{37}H_{38}O_7S_2$ (658.82): C 67.45, H 5.81; found: C 67.51, H 5.98 %.

Data for **2.61: Mp** 83.3 to 83.6 °C; **IR** ($CHCl_3$): $\bar{\nu}$ 3300–3500 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 7.24–7.40 (m, 12H, Ar H), 6.87–6.95 (m, 2H, Ar H), 6.15 (t, 1H, Ins H, J = 9.3 Hz), 4.75 (s, 2H, CH_2), 4.67 (q, 4H, 2 × CH_2, J = 11.2 Hz), 4.01 (t, 1H, Ins H, J = 2.7 Hz), 3.87–3.97 (m, 2H, Ins H), 3.83 (s, 3H, OCH_3), 3.65 (dd, 2H, Ins H, J_1 = 9.6 Hz, J_2 = 2.6 Hz), 2.60 (s, 3H, SCH_3), 2.36 (brs, 2H, 2 × OH) ppm; **^{13}C NMR** ($CDCl_3$, 50.3 MHz): δ 215.7 (C=S), 159.2 (C_{arom}), 137.7 (C_{arom}), 130.4 (C_{arom}), 129.6 (C_{arom}), 128.3 (C_{arom}), 128.1 (C_{arom}), 127.8 (C_{arom}), 113.7 (C_{arom}), 83.6 (Ins C), 80.0 (Ins C), 78.3 (Ins C), 74.9 (CH_2), 74.8 (CH_2), 71.8 (Ins C), 55.1 (CH_3); 19.3 (CH_3) ppm; elemental analysis calcd (%) for $C_{30}H_{34}O_7S_2$ (570.72): C 63.13, H 6.00; found: C 63.09, H 6.11 %.

1,3-*O*-Benzylidene-2,4,6-tri-*O*-benzyl-5-*O*-[(methylthio)thiocarbonyl]-*neo*-inositol (2.54, epimer of 2.48): The solid xanthate **2.48** (0.20 g, 0.32 mmol) was heated at 110 °C (mp of **2.48** is 100–102 °C) under argon for 12 h and the products separated by column chromatography (eluent: 5 to 7% ethyl acetate in light petroleum) to afford **2.54** (0.14 g, 72%; TLC Rf = 0.4 in 10% ethyl acetate/light petroleum) and **2.62** (0.04 g, 24%; TLC Rf = 0.3 in 40% ethyl acetate/light petroleum) as a gums. Solid **2.54** could be obtained by storing the gummy **2.54** in *n*-pentane at –20 °C for 12 h.

Data for **2.54: Mp** 68.8–69.4 °C (crystallized from a hot mixture of 5% ethyl acetate in light petroleum); **^{1}H NMR** (CD_2Cl_2, 200 MHz): δ 7.40-7.52 (m, 2H, Ar H), 7.22–7.40 (m, 18H, Ar H), 6.66 (t, 1H, Ins H, J = 4.2 Hz), 6.42 (s, 1H, $PhCHO_2$), 4.66 (s, 2H, CH_2), 4.63

(q, 4H, 2 × CH_2, J = 11.9 Hz), 4.48-4.55 (m, 3H, Ins H), 4.30 (t, 2H, Ins H, J = 4.2 Hz), 2.56 (s, 3H, CH_3) ppm; **^{13}C NMR** (CD_2Cl_2, 125.76 MHz): δ 216.0 (C=S), 139.1 (C_{arom}), 138.8 (C_{arom}), 138.3 (C_{arom}), 129.5 (C_{arom}), 128.8 (C_{arom}), 128.65 (C_{arom}), 128.61 (C_{arom}), 128.3 (C_{arom}), 128.2 (C_{arom}), 128.1 (C_{arom}), 128.0 (C_{arom}), 127.2 (C_{arom}), 93.3 ($PhCHO_2$), 78.2 (Ins C), 77.6 (Ins C), 74.1 (CH_2), 72.9 (Ins C), 71.3 (CH_2), 69.9 (Ins C), 19.5 (CH_3) ppm; elemental analysis calcd (%) for $C_{36}H_{36}O_6S_2$ (628.80): C 68.76, H 5.77; found: C 68.78, H 6.11 %.

Data for **2.62: IR** ($CHCl_3$): $\bar{\nu}$ 3360–3550 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 200 MHz) δ 7.25–7.45 (m, 15H, ArH), 6.88 (t, 1H, Ins H, J = 2.65 Hz), 4.84 (s, 2H, CH_2), 4.68 (q, 4H, 2 × CH_2, J = 11.0 Hz), 4.12–4.20 (m, 1H, Ins H), 3.98 (dd, 2H, Ins H, J_1 = 2.7 Hz, J_2 = 10.1 Hz), 3.85 (dd, 2H, Ins H, J_1 = 2.8 Hz, J_2 = 10.1 Hz), 2.57 (s, 3H, SCH_3), 2.20–2.48 (brs, 2H, 2 × OH) ppm; **^{13}C NMR** ($CDCl_3$, 125.76 MHz): δ 216.7 (C=S), 138.6 (C_{arom}), 137.3 (C_{arom}), 128.5 (C_{arom}), 128.4 (C_{arom}), 128.2 (C_{arom}), 128.0 (C_{arom}), 127.73 (C_{arom}), 127.68 (C_{arom}), 78.4 (Ins C), 77.4 (Ins C), 75.5 (CH_2), 74.9 (Ins C), 72.5 (CH_2), 70.8 (Ins C), 19.0 (CH_3) ppm; elemental analysis calcd (%) for $C_{29}H_{32}O_6S_2$ (540.69): C 64.42, H 5.97; found: C 64.84, H 6.30 %.

1,3-*O*-Benzylidene-2,4,6-tri-*O*-benzyl-5-deoxy-*myo*-inositol (2.55): The xanthate **2.52** (0.09 g, 0.14 mmol), tri-*n*-butyltin hydride (0.20 mL, 0.50 mmol), AIBN (0.01 g) and dry toluene (4 mL) were used (Procedure B) to obtain **2.55** as a gum (0.06 g, 82%) after column chromatography (eluent: 7% ethyl acetate in light petroleum). The gummy compound **2.55** was stored under *n*-pentane at –20 °C for 12 h to afford a colorless solid. TLC *Rf* = 0.4 (10% ethyl acetate/light petroleum); **mp** 69.5-72.2 °C (crystallized from a hot mixture of 5% ethyl acetate in light petroleum); **^{1}H NMR** (CD_2Cl_2, 500 MHz): δ 7.20–7.50 (m, 20H, Ar H), 6.47 (s, 1H, $PhCHO_2$), 4.66 (s, 2H, CH_2), 4.55 (q, 4H, 2 × CH_2, J = 11.9 Hz), 4.52 (d, 2H, Ins H, J = 3.3 Hz), 4.46–4.48 (m, 1H, Ins H), 3.91–3.97 (m, 2H, Ins H), 2.27–2.38 (m, 1H, Ins H), 2.05–2.11 (m, 1H, Ins H) ppm; **^{13}C NMR** (CD_2Cl_2, 125.76 MHz): δ 139.8 (C_{arom}), 139.1 (C_{arom}), 138.6 (C_{arom}), 129.1 (C_{arom}), 128.7 (C_{arom}), 128.6 (C_{arom}), 128.5 (C_{arom}), 128.3 (C_{arom}), 128.0 (C_{arom}), 127.9 (C_{arom}), 127.8 (C_{arom}), 126.9 (C_{arom}), 92.8 ($PhCHO_2$), 78.1 (Ins C), 72.9 (Ins C), 71.7 (CH_2), 70.8 (CH_2), 70.6 (Ins C), 24.2 (Ins CH_2) ppm; elemental analysis calcd (%) for $C_{34}H_{34}O_5$ (522.63): C 78.14, H 6.56; found: C 77.83, H 6.71 %.

Deoxygenation of 2.54: The xanthate **2.54** (0.10 g, 0.14 mmol), tri-*n*-butyltin hydride (0.20 mL, 0.50 mmol), AIBN (0.01 g) and dry toluene (4 mL) were used (Procedure B) to obtain **2.55** as a gum (0.07 g, 84%) after column chromatography (eluent: 7% ethyl acetate in light petroleum).

1,3-*O*-Benzylidene-2-*O*-(4-methoxybenzyl)-4,6-di-*O*-benzyl-5-deoxy-*myo*-inositol (2.56): The xanthate **2.53** (0.10 g, 0.15 mmol), dry toluene (4 mL), tri-*n*-butyltin hydride (0.20 mL, 0.50 mmol) and AIBN (0.01 g) were used (Procedure B) to obtain **2.56** as a colorless solid (0.07 g, 85%) after column chromatography (eluent: 10% ethyl acetate in light petroleum). TLC R_f = 0.6 (20% ethyl acetate/light petroleum); **mp** 99.5–101.2 °C (crystallized from a hot mixture of 10% ethyl acetate in light petroleum); **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 7.24–7.50 (m, 17H, Ar H), 6.80–6.90 (m, 2H, Ar H), 6.52 (s, 1H, $PhCHO_2$), 4.61 (s, 2H, CH_2), 4.55 (q, 4H, 2 × CH_2, J = 11.9 Hz), 4.51–4.58 (m, 3H, Ins H), 3.95–4.01 (m, 2H, Ins H), 3.78 (s, 3H, OCH_3), 2.30–3.42 (m, 1H, Ins H), 2.03–2.30 (m, 1H, Ins H) ppm; **^{13}C NMR** ($CDCl_3$, 50.3 MHz): δ 159.2 (C_{arom}), 139.0 (C_{arom}), 138.5 (C_{arom}), 130.0 (C_{arom}), 129.6 (C_{arom}), 128.9 (C_{arom}), 128.3 (C_{arom}), 128.2 (C_{arom}), 127.4 (C_{arom}), 126.5 (C_{arom}), 113.8 (C_{arom}), 92.5 ($PhCHO_2$), 77.4 (Ins C), 72.7 (Ins C), 71.1 (CH_2), 70.0 (CH_2), 69.5 (Ins C), 55.2 (CH_3), 23.8 (Ins CH_2) ppm; elemental analysis calcd (%) for $C_{35}H_{36}O_6$ (552.66): C 76.06, H 6.57; found: C 75.73, H 6.34 %.

2.5. References

1. (a) Mehta, G.; Narinder, M.; Lakshminath, S. *Tetrahedron Lett.* **2000**, *41*, 3505–3508; (b) Gathergood, N.; Knudsen, K. R.; Jørgensen, K. A. *J. Org. Chem.* **2001**, *66*, 1014–1017; (c) Walker, J. B. *Appl. Environ. Microbiol.* **2002**, *68*, 2404–2410; (d) Egido-Gabas, M.; Serrano, P.; Casas, J.; Llebaria, A.; Delgado, A. *Org. Biomol. Chem.* **2005**, *3*, 1195–1201; (e) Busscher, G. F.; Rutjes, F. P. J. T.; van Delft, F. L. *Chem. Rev.* **2005**, *105*, 775-791; (f) Arjona, O.; Gimez, A. M.; Lipez, J. C.; Plumet, J. *Chem. Rev*. **2007**, *107*, 1919–2036; (g) Beniazza, R.; Desvergnes, V.; Landais, Y. *Org. Lett.* **2008**, *10*, 4195–4198 and references cited therein.
2. McCasland, G. E.; Furuta, S.; Johnson, L. F.; Shoolery, J. N. *J. Am. Chem. Soc.* **1961**, *83*, 2335–2343.
3. Maras, A.; Secen, H.; Sütbeyaz, Y.; Balci, M. *J. Org. Chem.* **1998**, *63*, 2039–2041 and references cited therein.
4. McCasland, G. E.; Furuta, S.; Johnson, L. F.; Shoolery, J. N. *J. Org. Chem.* **1963**, *28*, 894–900 and references cited therein.
5. Posternak, Th. *Helvetica Chimica Acta* **1950**, *33*, 1597–1605.
6. (a) Dubreuil, D.; Cleophax, J.; Vieira de Almeda, M.; VerreSbri, C.; Pipelier, M.; Vass, G.; Gero, S. D. *Tetrahedron* **1999**, *55*, 7573–7582; (b) Hyldtoft, L.; Madsen, R. *J. Am. Chem. Soc.* **2000**, *122,* 8444–8452; (c) Benício, A. A. A.; Silva, A. D.; Almeida, M. V.; Silva, M. M.; Gero, S. D. *Tetrahedron* **2001**, *57*, 1161–1167 and references cited therein.
7. Kozikowski, A. P.; Powis, G.; Fauq, A. H.; Tuckmantel, W.; Gallegos, A. *J. Org. Chem.* **1994**, *59*, 963–971.
8. (a) Schulz, J.; Beaton, M. W.; Gani, D. *J. Chem. Soc., Perkin Trans. 1* **2000**, 943–954; (b) Surfraz, M. B.; Miller, D. J.; Gani, D.; Allemann, R. K. *Tetrahedron Lett.* **2003**, *44*, 7677–7679.
9. (a) McCasland, G. E.; Naumann, M. O.; Durham, L. J. *Carbohyd. Res.* **1967**, *4*, 516–518; (b) Ogawa, S.; Tezuka, Y. *Bioorg. Med. Chem. Lett.* **2006**, *16*, 5238–5243.
10. (a) Kee, A.; O'Brien, P.; Pilgram, C. D.; Watson, S. T. *Chem. Commun.* **2000**, 1521–1522; (b) Gultekin, M. S.; Salamci, E.; Balci, M. *Carbhydr. Res.* **2003**, *338*, 1615–

1619; (c) Shih, T. L.; Lin, Y. L. Kuo, W. S. *Tetrahedron* **2005**, *61*, 1919–1924 and references cited therein.

11. Gultekin, M. S.; Celik, M.; Turkut, E.; Tanyeli, C.; Balci, M. *Tetrahedron: Asymmetry* **2004**, *15*, 1959–1960.
12. Baker, R.; Carrick, C.; Leeson, P. D.; Lennon, I. C.; Liverton, N. J. *J. Chem. Soc. Chem. Commun.* **1991**, 298–300.
13. Angelaud, R.; Landais, Y. *J. Org. Chem.* **1996**, *61*, 5202–5203.
14. (a) Sureshan, K. M.; Shashidhar, M. S.; Praveen, T.; Das, T. *Chem. Rev*. **2003**, *103*, 4477–4503; (b) Jagdhane, R. C.; Shashidhar, M. S. *Eur. J. Org. Chem.* **2010**, 2945–2953; (c) Kılbas, B.; Balci, M. *Tetrahedron*, **2011**, *67*, 2355–2389 and references cited therein.
15. *Via* halo-quercitol: (a) Ogawa, S.; Hongo, Y.; Fujimori, H.; Iwata, K.; Kasuga, A; Suami, T. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2957–2963; (b) McCasland, G. E.; Horswill, E. C. *J. Am. Chem. Soc.* **1953**, *75*, 4020–4026; (c) McCasland, G. E.; Horswill, E. C. *J. Am. Chem. Soc.* **1954**, *76*, 2373–2379; (d) Baker, R.; Kulagowski, J. J.; Billington, D. C.; Leeson, P. D.; Lennon, I. C.; Liverton, N. *J. Chem. Soc., Chem. Commun.* **1989**, 1383–1385; *via* tosylate: (e) Yu, J.; Spencer, J. B. *J. Org. Chem*. **1996**, *61*, 3234–3235; via xanthate (f) Angyal, S. J.; Odier, L. *Carbohyd. Res.* **1982**, *101*, 209–219; (g) Schmidtt, L.; Spiess, B.; Schlewer, G. *Tetrahedron Lett.* **1998**, *39*, 4817–4820; (h) Ballereau, S.; Guédat, P.; Poirier, S. N.; Guillemette, G.; Spiess, B.; Schlewer, G. *J. Med. Chem*. **1999**, *42*, 4824–4835; (i) Horne, G.; Potter, B. V. L. *Chem. Eur. J.* **2001**, *7*, 80–87; (j) Morgan, A. J.; Wang, Y. K.; Roberts, M. F.; Miller, S. J. *J. Am. Chem. Soc.* **2004**, *126*, 15370–15371; (k) Xu, Y.; Sculimbrene, B. R.; Miller, S. J. *J. Org. Chem.* **2006**, *71*, 4919–4928
16. Murali, C. Ph.D thesis, University of Pune, India, **2008**.
17. (a) Barton, D. H. R.; McCombie, S. W. *J. Chem. Soc. Perkin Trans 1* **1975**, *16*, 1574–1585; (b) Wang, Z. *Barton Deoxygenation. Comprehensive Organic Name Reactions and Reagents*, John Wiley & Sons, Inc. 2010.
18. Dang, H. S.; Roberts, B. P.; Sekhon, J.; Smits, T. M. *Org. Biol. Chem.* **2003**, *1*, 1330–1341.
19. Kuzuya, M.; Noda, N.; Kondo, S-i.; Washino, K.; Noguchi, A. *J. Am. Chem. Soc*. **1992**, *114,* 6505–6512.

20. Yeh, S. M.; Lee, G. H.; Wang, Y.; Luh, T. Y. *J. Org. Chem.* **1997**, *62*, 8315-8318.
21. Jagdhane, R. C. Ph.D thesis, University of Pune, India, 2010.
22. Ballereau, S.; Poirier, S. N.; Guillemette, G.; Spiess, B.; Schlewer, G. *J. Chem. Soc., Perkin Trans. 1*, **1998**, 1859–1864.
23. Gilbert, I. H.; Holmes, A. B.; Pestchanker, M. J.; Young R. C. *Carbohydr. Res.* **1992**, *234*, 117–130.
24. Moris, M. A.; Caron, A. Z.; Guillemette, G.; Rognan, D.; Schmitt, M.; Schlewer, G. *J. Med. Chem.* **2005**, *48*, 1251–1255.
25. Bruker (2003). *SADABS* (Version 2.05), *SMART* (Version 5.631), *SAINT* (Version 6.45) and *SHELXTL* (Version 6.14). Bruker AXS Inc., Madison, Wisconsin, USA.
26. Sheldrick, G. M. *Acta Cryst.* **2008,** *A64*, 112–122.
27. Farrugia, L. J. *J. Appl. Cryst.* **1997**, *30*, 565–565.
28. (a) Ahlrichs, R.; Bär, M.; Baron, H.-P.; Bauernschmitt, R.; Böcker, S.; Ehrig, M.; Eichkorn, K.; Elliott, S.; Furche, F.; Haase, F.; Häser, M.; Horn, H.; Huber, C.; Huniar, U.; Kattannek, M.; Kölmel, C.; Kollwitz, M.; May, K.; Ochsenfeld, C.; Öhm, H.; Schäfer, A.; Schneider, U.; Treutler, O.; von Arnim, M.; Weigend, F.; Weis, P.; Weiss, H. TURBOMOLE (Version 5.3); Universität Karlsruhe, Karlsruhe, Germany, **2000**; (b) Schäfer, A.; Huber, C.; Ahlrichs, R. *J. Chem. Phys.* **1994**, *100*, 5829–5835; (c) Andrae, D.; Haeussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1990**, *77*, 123–141.
29. *Hyperchem (version 5)*; Hypercube Inc., Gainesville, FL, 32601.
30. (a) Becke, A. D. *Phys. Rev. A*: *At., Mol., Opt. Phys.* **1988**, *38*, 3098–3100; (b) Perdew, J. P. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1986**, *33*, 8822–8824.
31. Schäfer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys*. **1992**, *97*, 2571–2577.
32. Eichkorn, K.; Treutler, O.; Öhm, H.; Häser, M.; Ahlrichs, R. *Chem. Phys. Lett.* **1995**, *240*, 283–290.
33. Sierka, M.; Hogekamp, A.; Ahlrichs, R. *J. Chem. Phys.* **2003***, 118,* 9136–9148.
34. Klamt, A. *J. Phy. Chem.* **1995**, *99*, 2224–2235.
35. Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 2nd edition, Pergamon Press, Oxford, U.K., 1988.

Appendix I

Appendix I Index

Crystal Data Table

Compound No.	**2.28**	**2.29**	**2.43**	**2.44**
Chemical formula	$C_{35}H_{36}O_7$	$C_{37}H_{38}O_7S_2$	$C_{30}H_{32}O_6S_2$	$C_{28}H_{30}O_5$
M_r	568.66	658.79	552.28	446.52
Temperature/K	173(2)	297(2) K	133(2) K	297(2) K
Morphology	Plate	Plate	Plate	Plate
Crystal size	0.48×0.33 ×0.17	0.41×0.22 ×0.08	0.18×0.15 ×0.12	0.34×0.21 ×0.17
Crystal system, Space group	monoclinic, $P2_1/n$	triclinic, P-1	monoclinic, Cc	monoclinic, $P2_1/c$
a (Å) b (Å) c (Å) α (°) β (°) γ (°)	19.019(2) 7.4121(8) 20.821(2) 90 95.963(5) 90	12.1038(12) 12.1371(12) 12.8640(13) 82.429(2) 77.934(2) 64.037(2)	19.461(3) 6.9523(9) 21.753(3) 90 110.245(4) 90	12.747(15) 13.603(16) 14.423(17) 90 106.708(2) 90
Volume V (Å^3)	2919.3(5)	1659.8(3)	2761.3 (6)	2395.4(5)
Z	6	2	4	4
D_{calc} (g cm^{-3})	1.294	0.210	1.329	1.238
μ (mm^{-1})	0.089	0.210	0.235	0.084
F(000)	1208	696	1168	952
Absorption correction T_{min} / T_{max}	multi-scan 0.9587 / 0.9850	multi-scan 0.9199 / 0.9828	multi-scan 0.9595/ 0.9732	multi-scan 0.9720/ 0.9859
θ_{max} (°)	25.50	25.00	26.00	26.00
h, k, l (min, max)	(-21,23), (-8,8), (-25,23)	(-14,14), (-14,14), (-15,15)	(-24,24), (-8,8), (-26,26)	(-15,15), (-16,16), (-17,17)
Reflns collected	26116	16279	10115	18470
Unique reflns, Observed reflns	5416, 4525	5833, 4564	5214, 4923	4694, 3540
R_{int}	0.0309	0.0246	0.0558	0.0223
No. of parameters	378	417	344	298
(GoF)	1.049	1.020	1.036	1.036
$R1$ [$I > 2\sigma(I)$] $wR2$ [$I > 2\sigma(I)$]	0.0791 0.2121	0.0415 0.0965	0.0393 0.0990	0.0458 0.1169
$R1$ (all data) $wR2$ (all data)	0.0910 0.2240	0.0558 0.1065	0.0410 0.1004	0.0613 0.1273
$\Delta\rho_{max}$,$\Delta\rho_{min}$(eÅ^{-3})	1.346,-1.081	0.23,-0.22	0.33,-0.21	0.24,-0.14
CCDC		817427	747073	747074

Crystal Data Table

Compound No.	**2.48**	**2.53**	**2.54**	**2.56**
Chemical formula	$C_{36}H_{36}O_6S_2$	$C_{37}H_{38}O_7S_2$	$2(C_{36}H_{36}O_6S_2)$ $0.5(C_6H_{14})$	$C_{35}H_{36}O_6$
M_r	628.77	658.79	628.77	552.64
Temperature/K	297(2) K	297(2) K	297(2) K	297(2)
Morphology	plate	plate	plate	plate
Crystal size	0.16×0.12× 0.07	0.16×0.12× 0.11	0.21×0.17× 0.08	0.47×0.17× 0.07
Crystal system, Space group	monoclinic, $P2_1/c$	monoclinic, $P2_1/c$	triclinic, P-1	triclinic, P-1
a (Å) b (Å) c (Å) α (°) β (°) γ (°)	19.296 (9) 9.177 (4) 19.258 (9) 90 105.841(10) 90	15.220 (2) 26.472(4) 8.8065(13) 90 104.498(10) 90	13.968(8) 15.223(9) 18.645(11) 79.963(11) 71.362(10) 67.525(9)	10.3094(12) 10.3163(12) 14.0511(16) 94.350(2) 92.309(2) 97.547(2)
Volume V (Å^3)	3281.0(3)	3435.2(9)	3465(4) Å^3	1475.3(3)
Z	4	4	2	2
D_{calc} (g cm^{-3})	1.273	1.274	1.247	1.244
μ (mm^{-1})	0.207	0.203	0.198	0.084
F(000)	1328	1392	1378	588
Absorption correction T_{min}, T_{max}	multi-scan 0.9857, 0.9683	multi-scan 0.9685, 0.9775	multi-scan 0.9604, 0.9841	multi-scan 0.9617, 0.9946
θ_{max} (°)	25.00	25.00	25.00	25.00
h, k, l (min, max)	(-22,22), (-10,10), (-22,22)	(-18,18), (-31,31), (-10,10)	(-16,16), (-18,18), (-22,22)	(-12,12), (-12,12), (-16,16)
Reflns collected	23089	32897	33588	14376
Unique reflns, Observed reflns	5771, 3341	6045, 4898	12169, 8454	5181, 3672
R_{int}	0.0751	0.0282	0.0428	0.0293
No. of parameters	398	417	823	371
(GoF)	1.122	1.041	1.156	1.019
$R1$ [$I > 2\sigma(I)$] $wR2$ [$I > 2\sigma(I)$]	0.0969 0.1838	0.0614 0.1270	0.0927 0.2014	0.0523 0.1175
$R1$ (all data) $wR2$ (all data)	0.1633 0.2133	0.0614 0.1270	0.1301 0.2178	0.0785 0.1297
$\Delta\rho_{max}$,$\Delta\rho_{min}$(eÅ^{-3})	0.33,-0.21	0.28,-0.18	0.47,-0.50	0.28, -0.19
CCDC	747072	817424	817425	817426

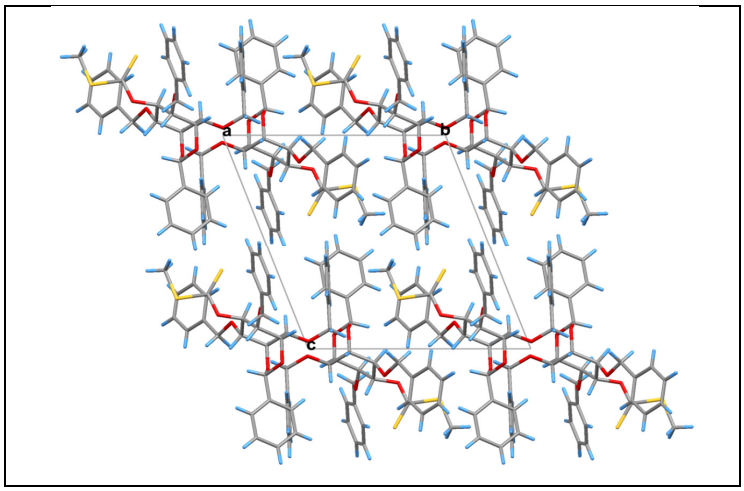


Figure A1: Close packing of molecules in the crystals of **2.16**, viewed down the *c*-axis.

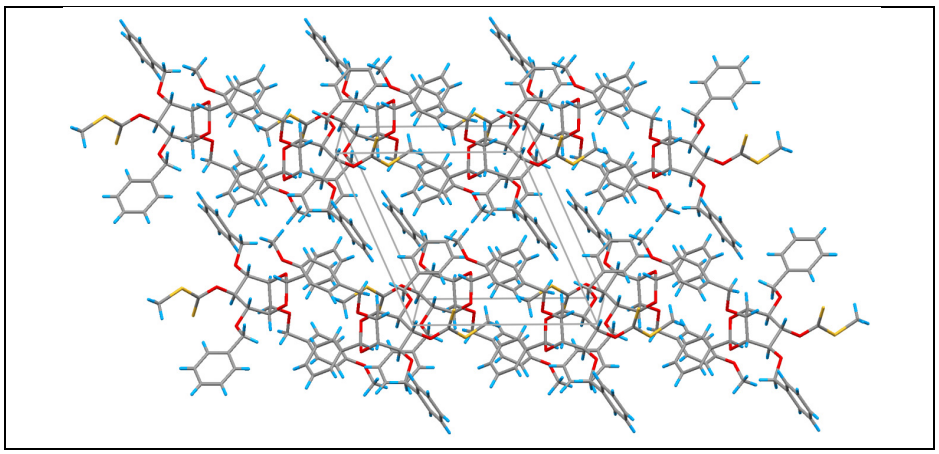


Figure A2: Close packing of molecules in the crystals of **2.29**, viewed down the *c*-axis.

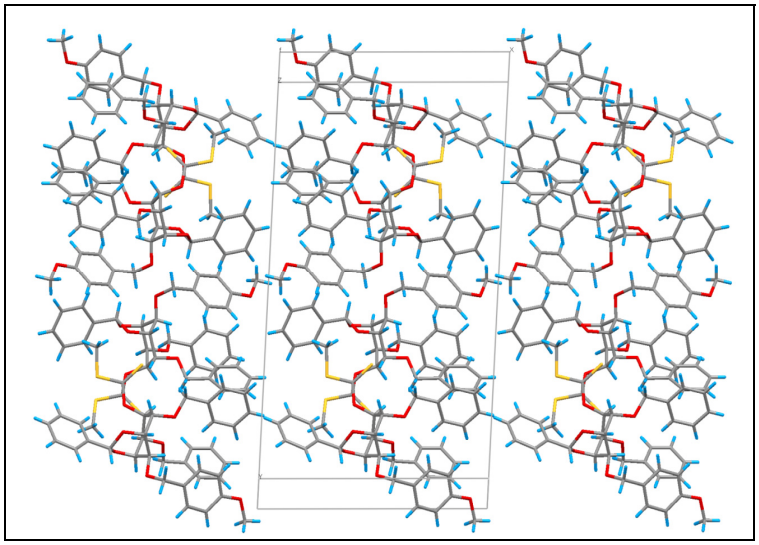


Figure A3: Close packing of molecules in the crystals of **2.53** (epimer of **2.29**) viewed down the *c*-axis.

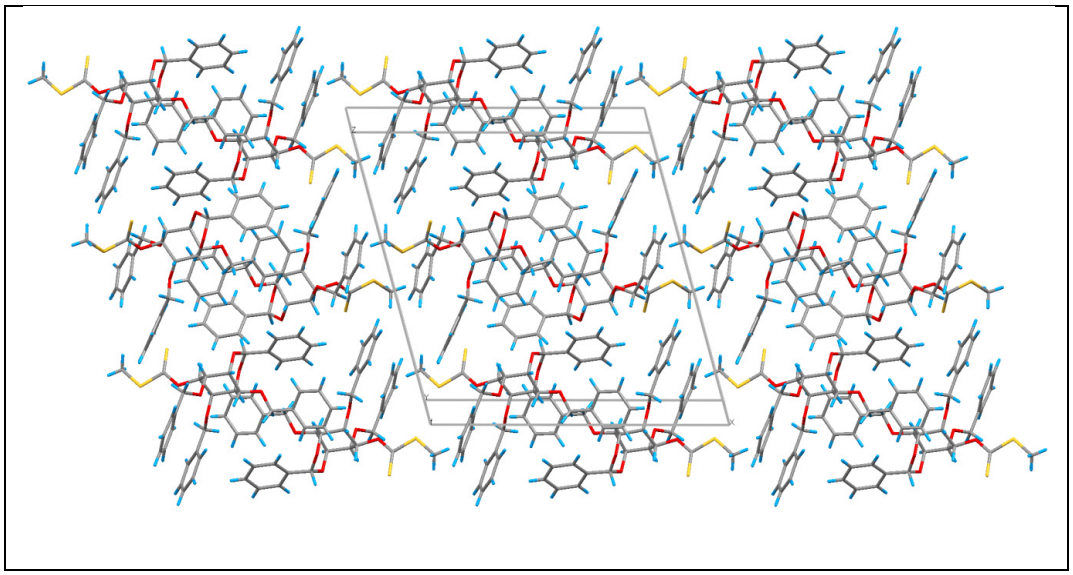


Figure A4: Close packing of molecules in the crystals of **2.48**, viewed down the *b*-axis.

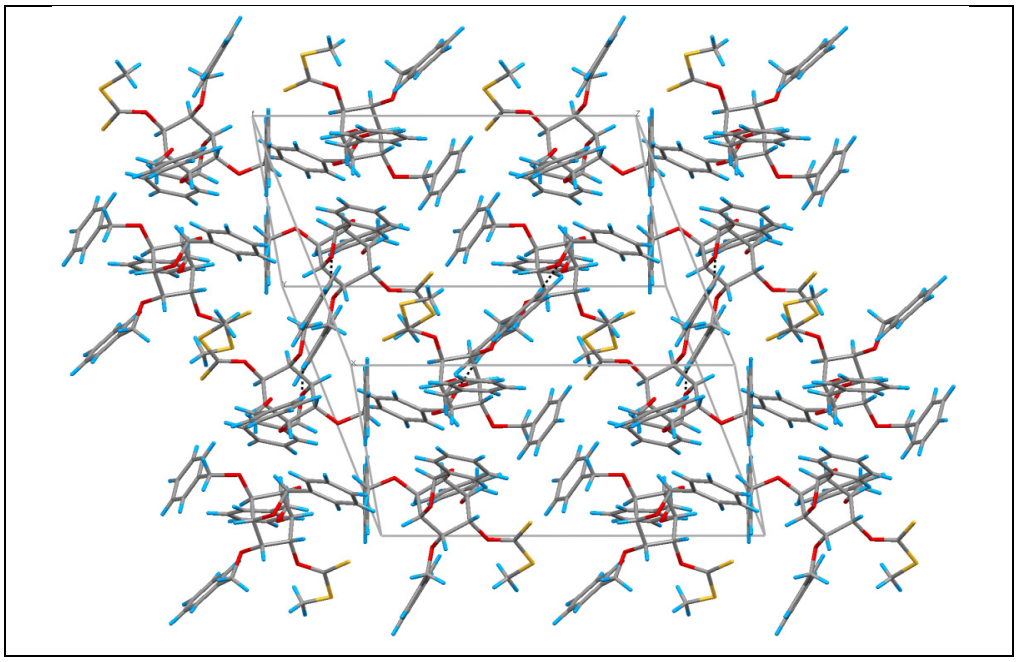
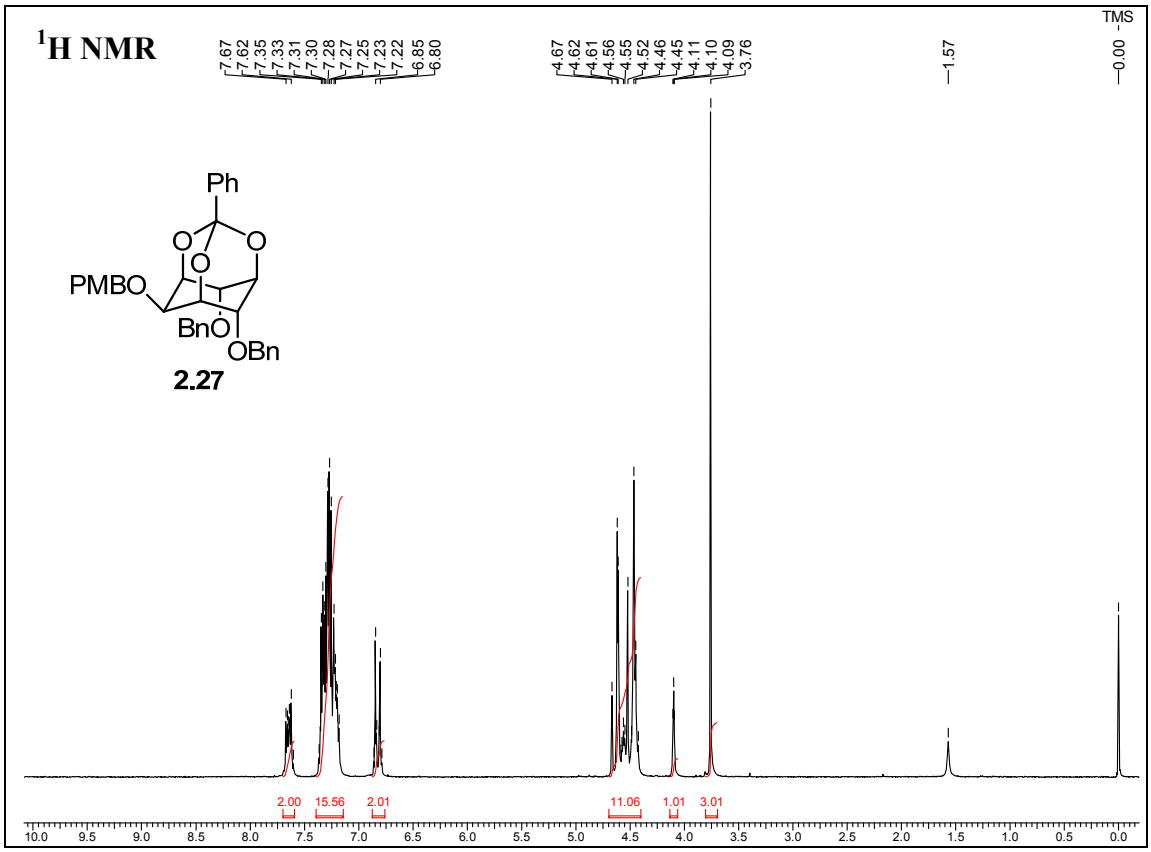
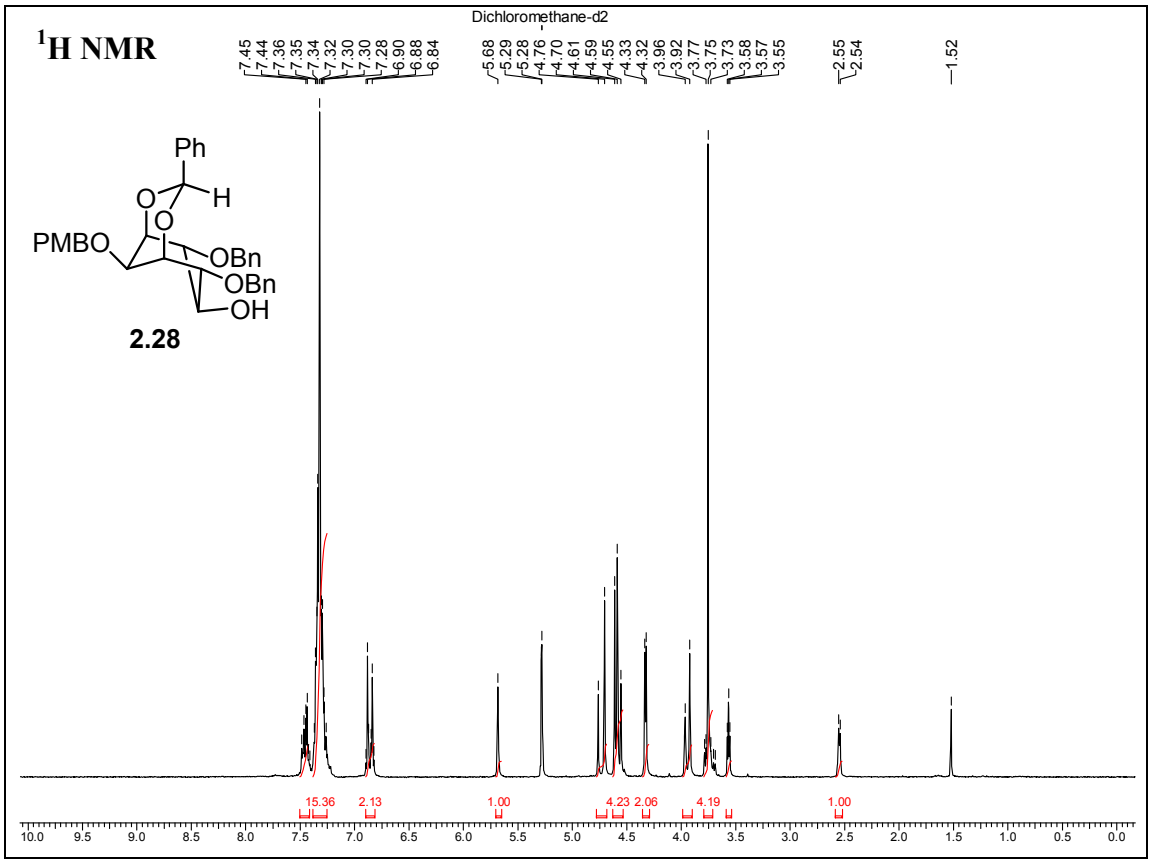
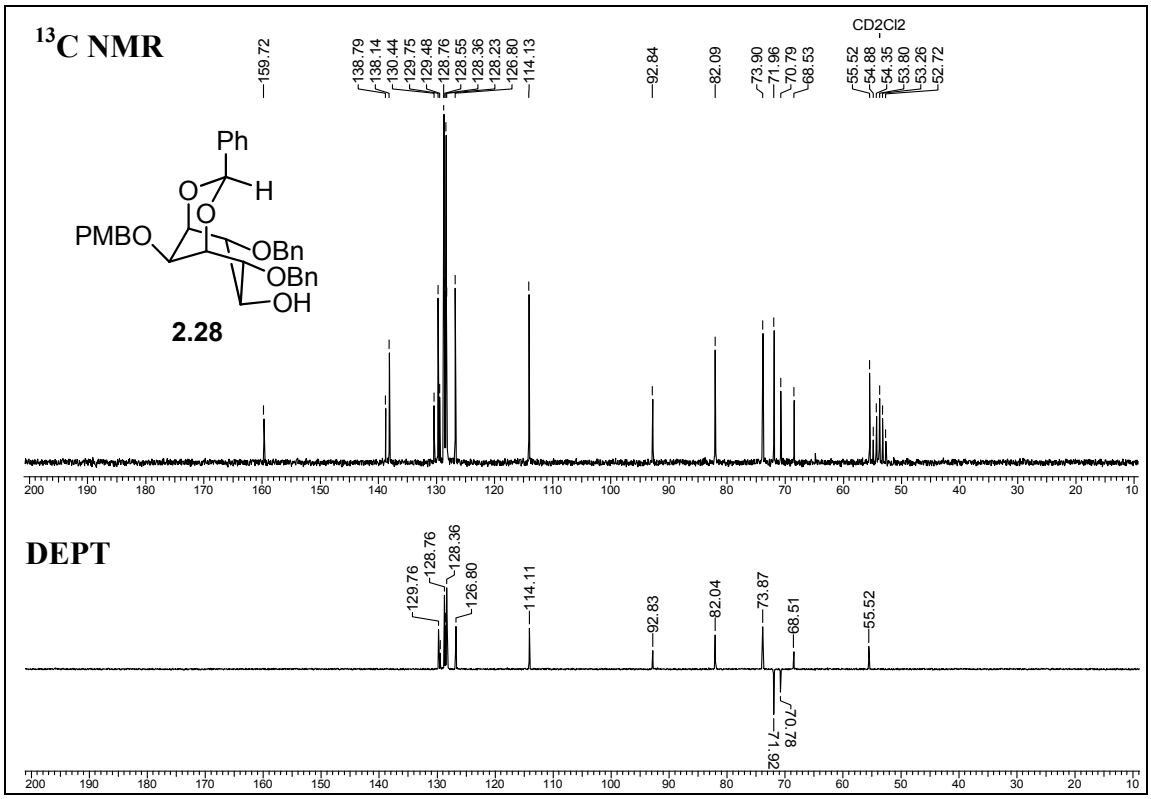


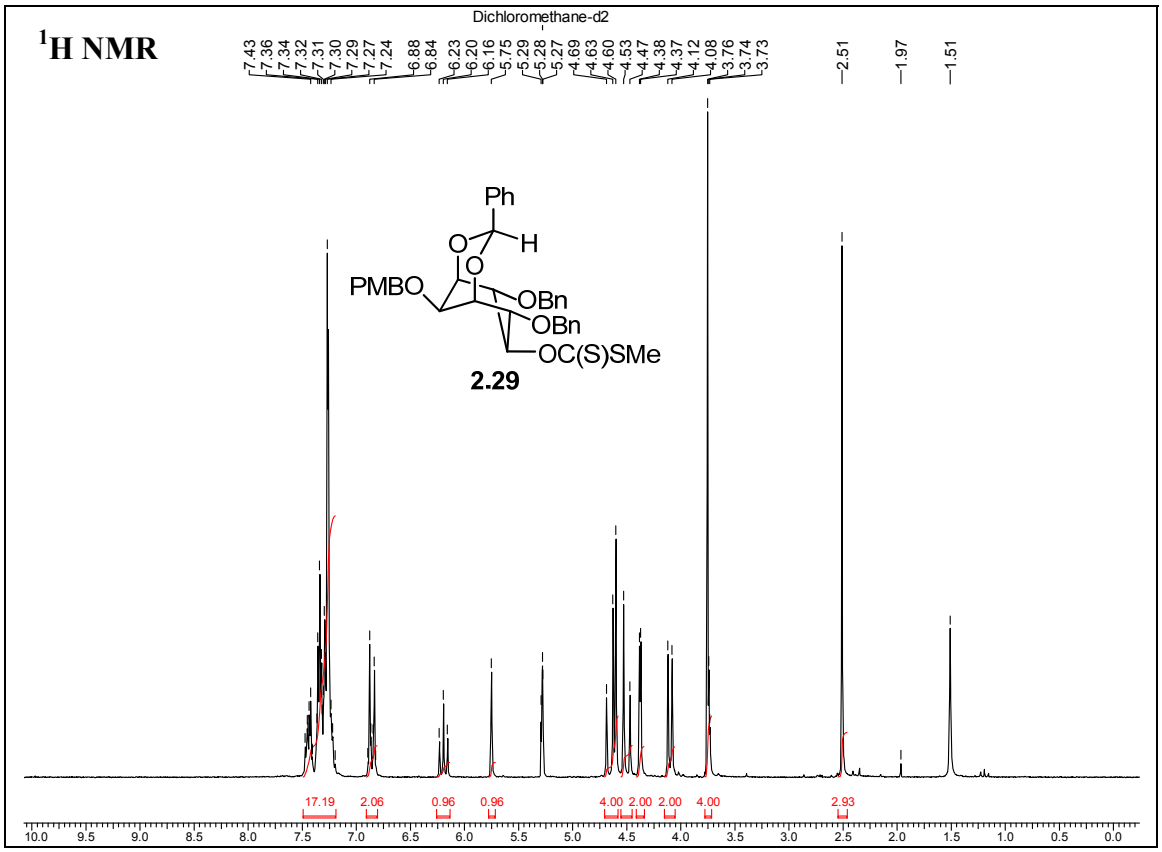
Figure A5: Close packing of molecules in the crystals of **2.54** (epimer of **2.48**), viewed down the *b*-axis.

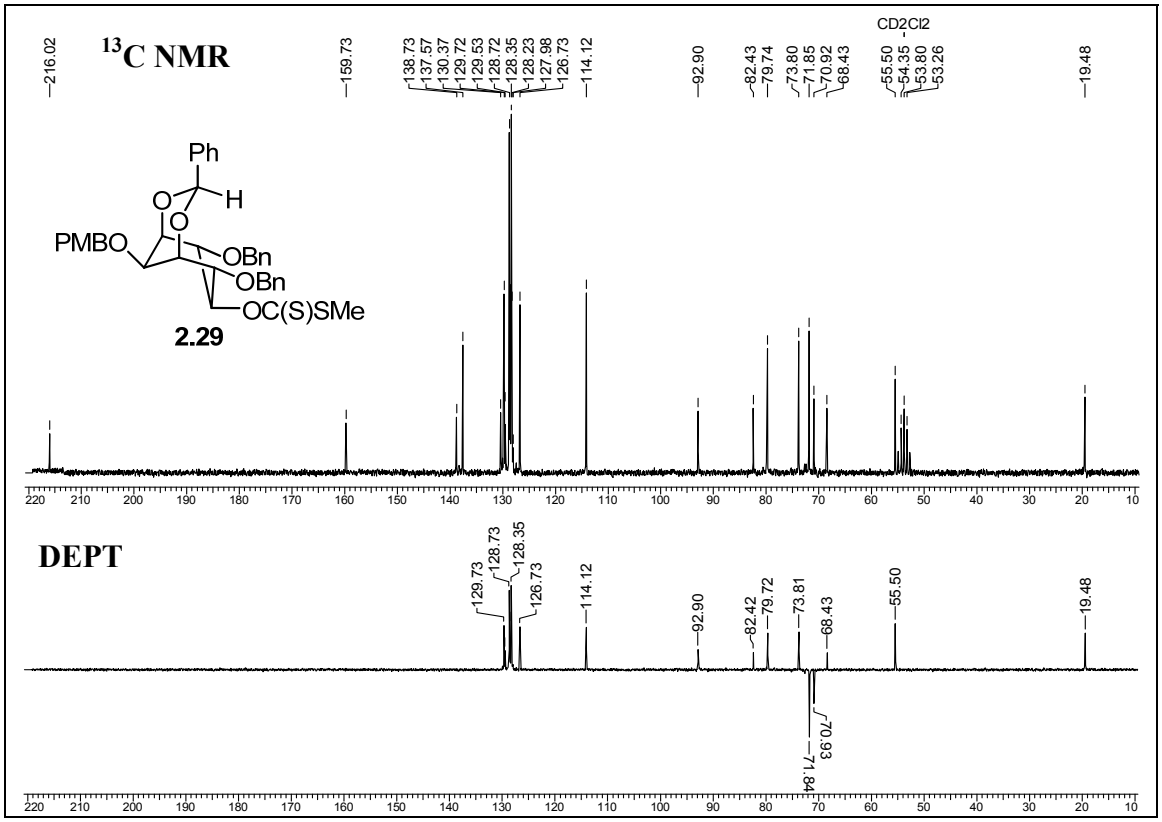

^{1}H NMR
TMS
Ph
PMBO
BnO
OBn
2.27
Chloroform-d
^{13}C NMR
DEPT



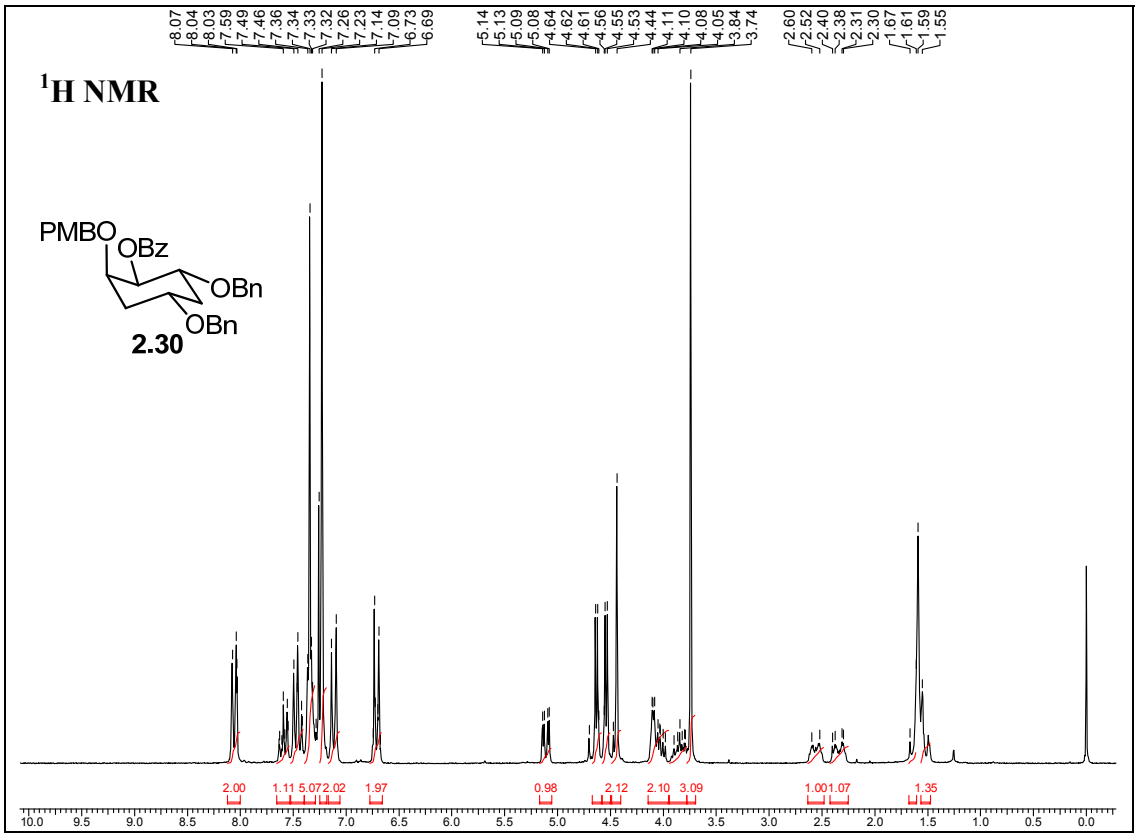


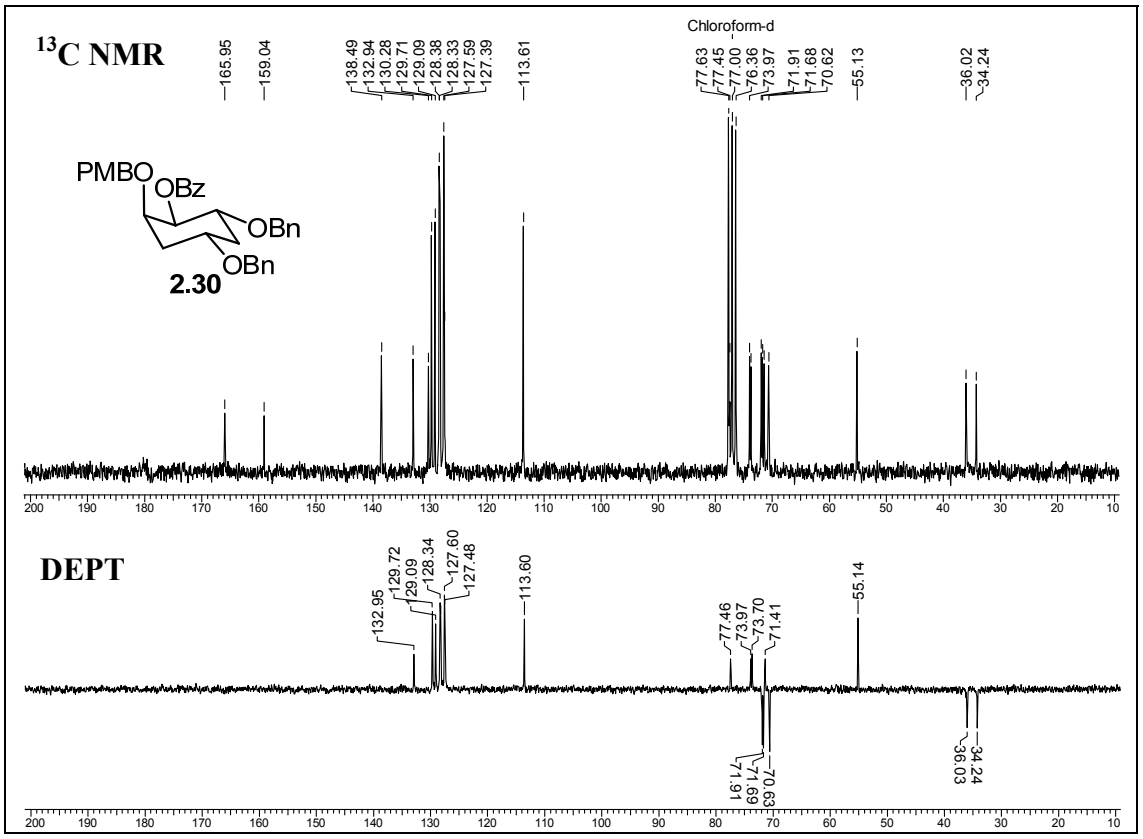
For 2D NMR see appendix III

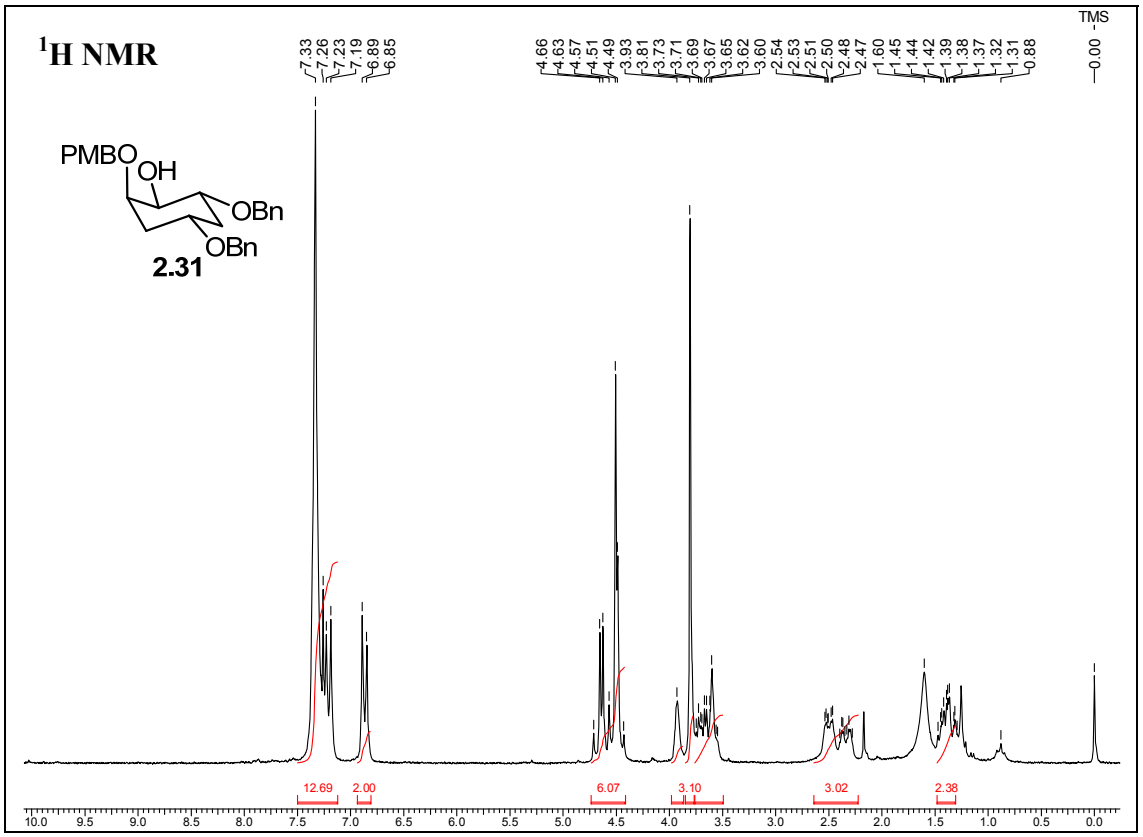


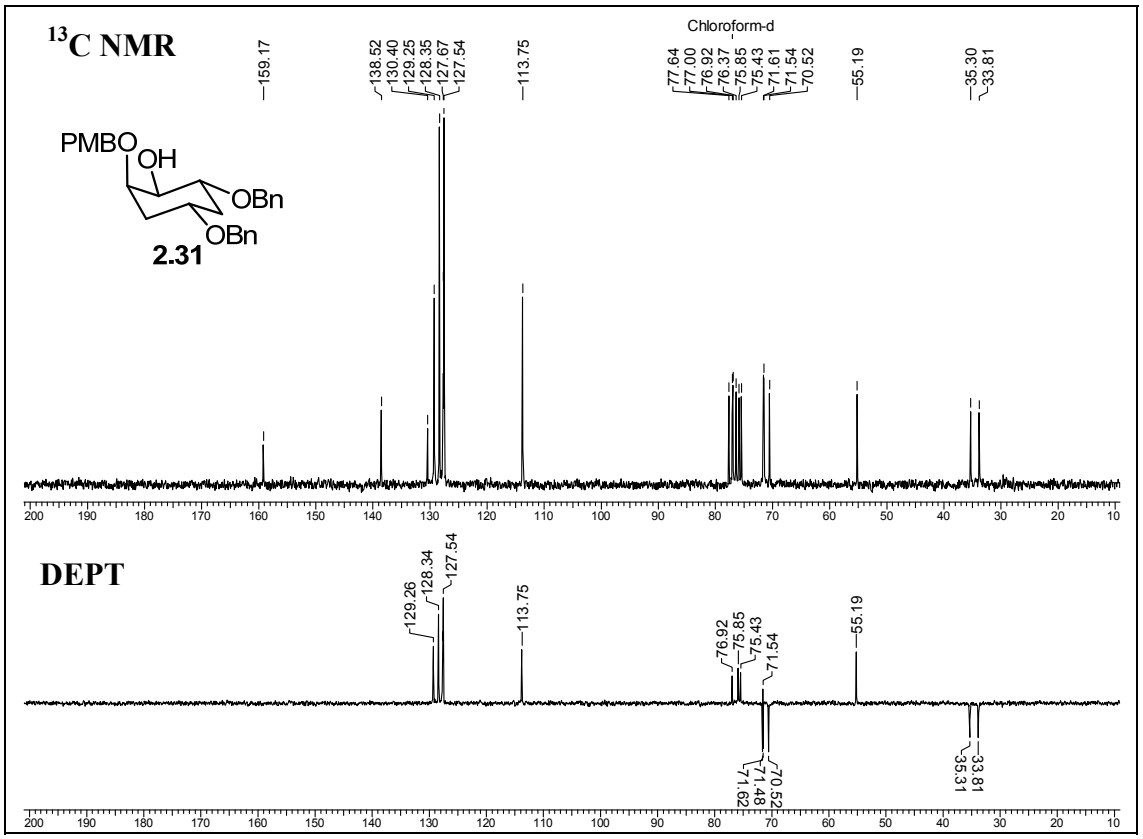


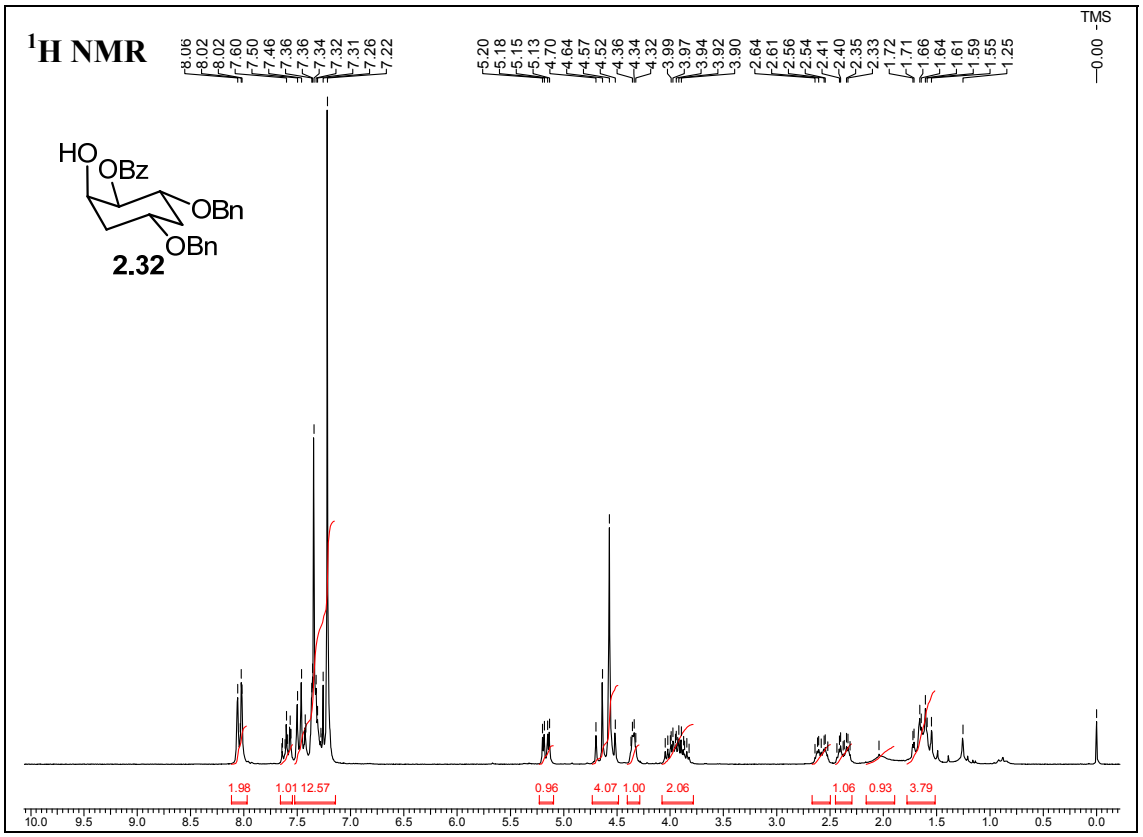
For 2D NMR see appendix III

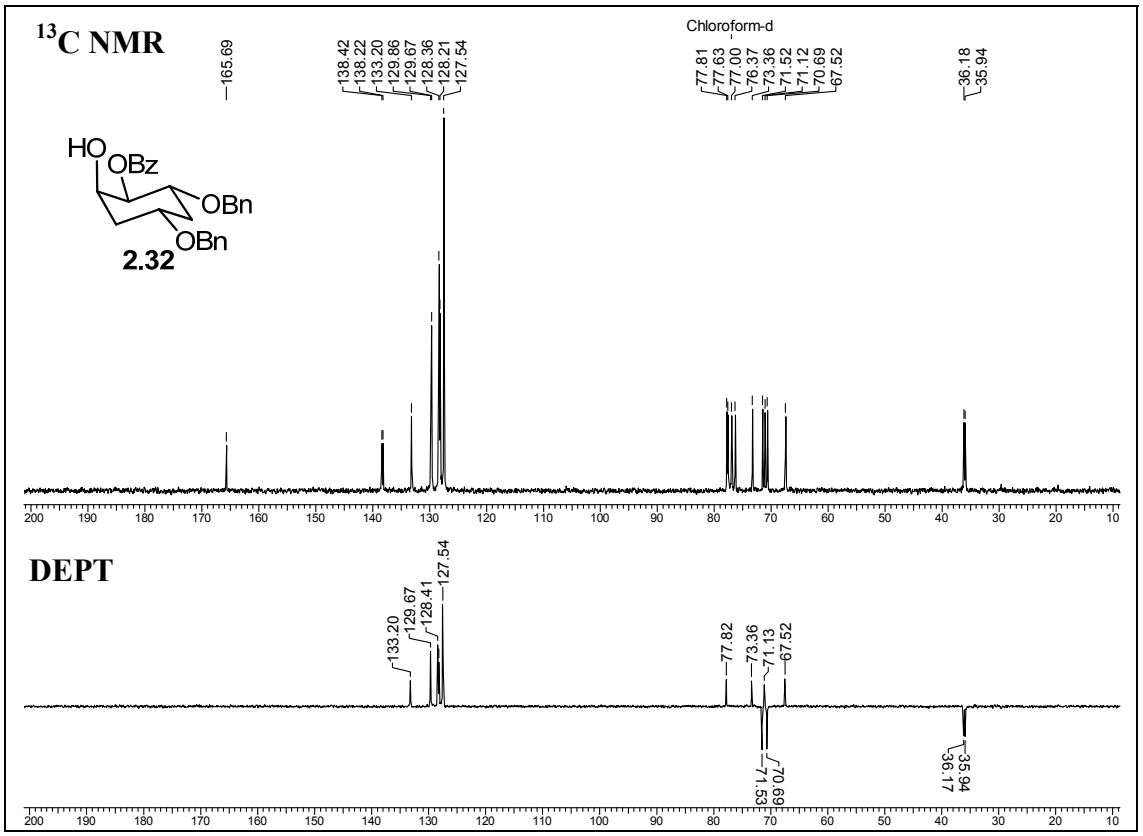

^{1}H NMR
PMBO
OBz
OBn
OBn
2.30

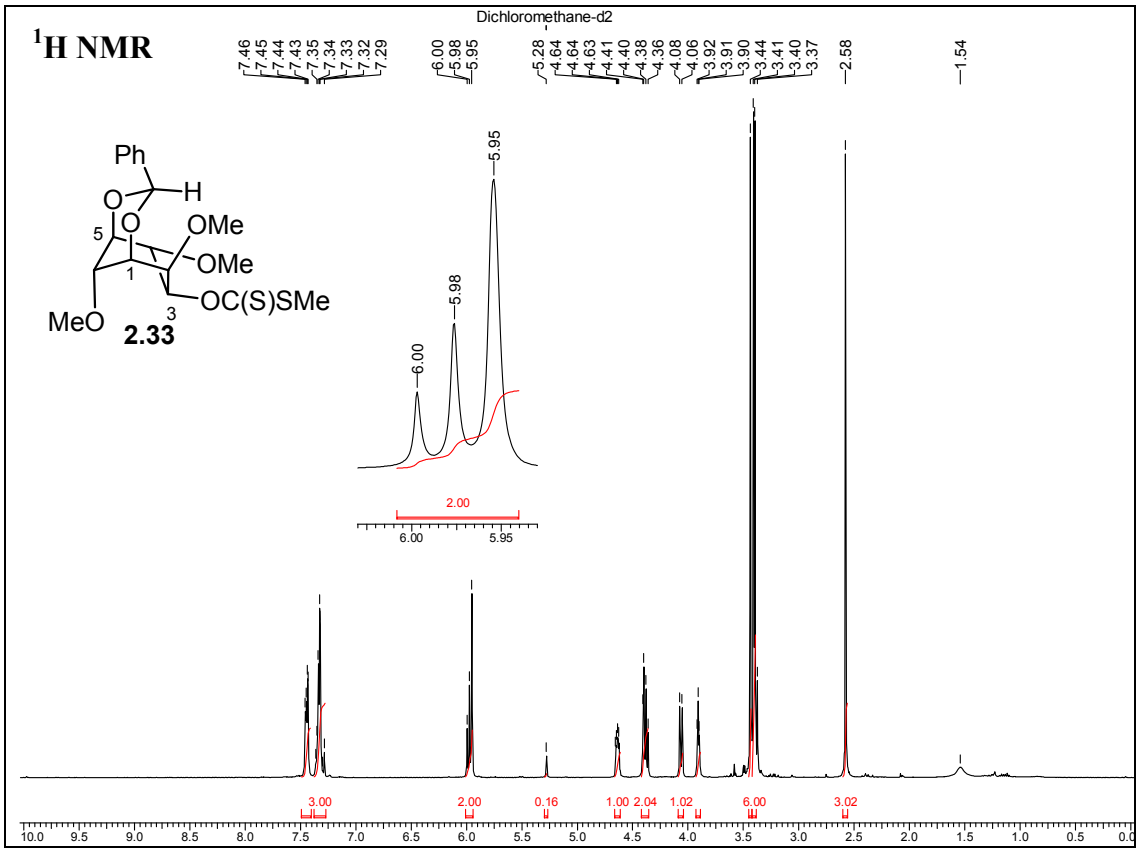

^{13}C NMR
Chloroform-d
PMBO
OBz
OBn
OBn
2.30
DEPT

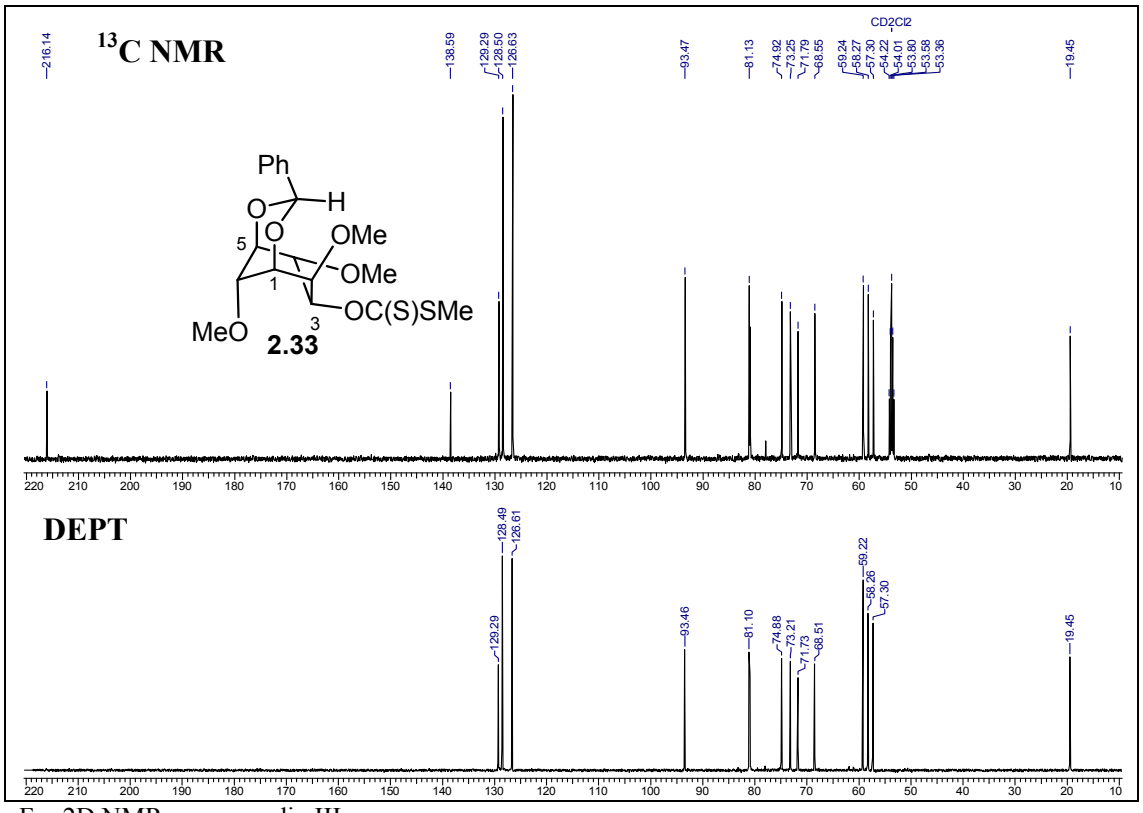

^{1}H NMR
PMBO
OH
OBn
OBn
2.31
TMS
12.69
2.00
6.07
3.10
3.02
2.38


^{13}C NMR
Chloroform-d
PMBO
OH
OBn
OBn
2.31
DEPT

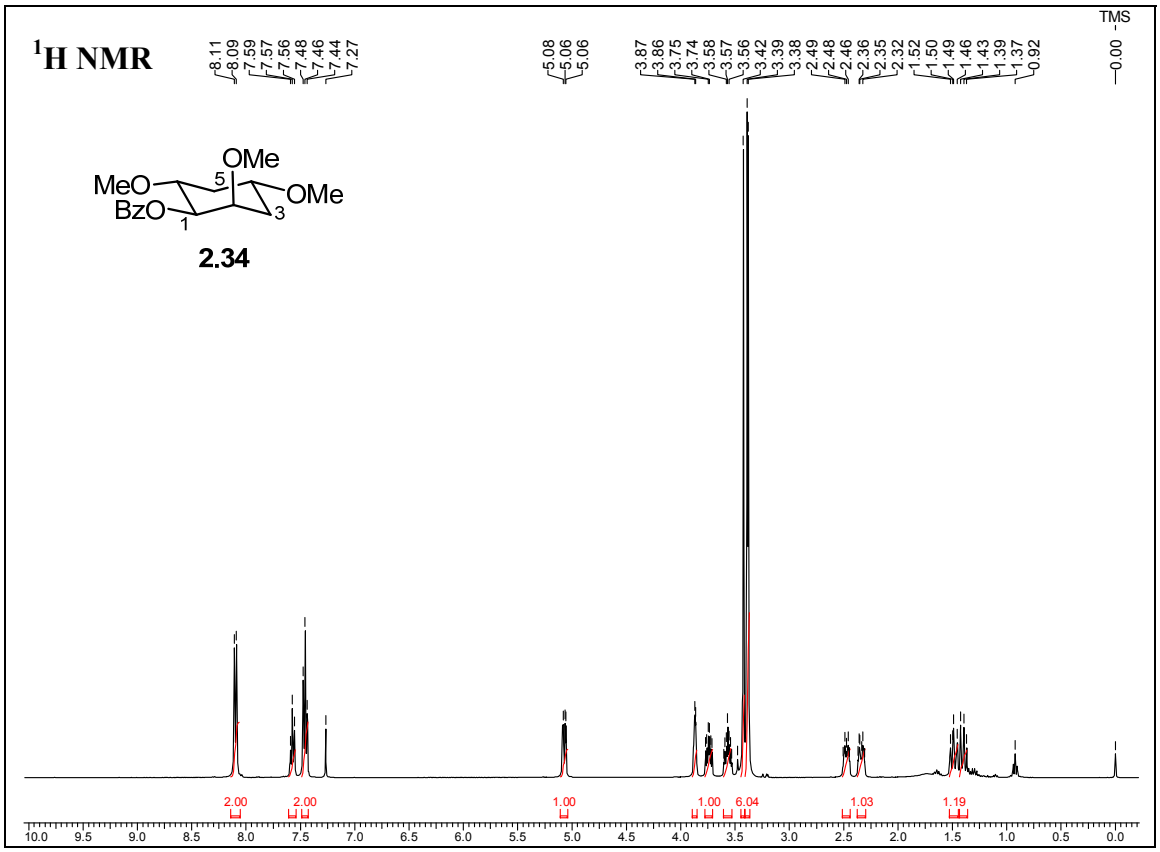

^{1}H NMR
TMS
HO
OBz
OBn
OBn
2.32
8.06 8.02 8.02 7.60 7.50 7.46 7.36 7.36 7.34 7.32 7.31 7.26 7.22
5.20 5.18 5.15 5.13 4.70 4.64 4.57 4.52 4.36 4.34 4.32 3.99 3.97 3.94 3.92 3.90 2.64 2.61 2.56 2.54 2.41 2.40 2.35 2.33 1.72 1.71 1.66 1.64 1.61 1.59 1.55 1.25 0.00
1.98 1.01 12.57 0.96 4.07 1.00 2.06 1.06 0.93 3.79

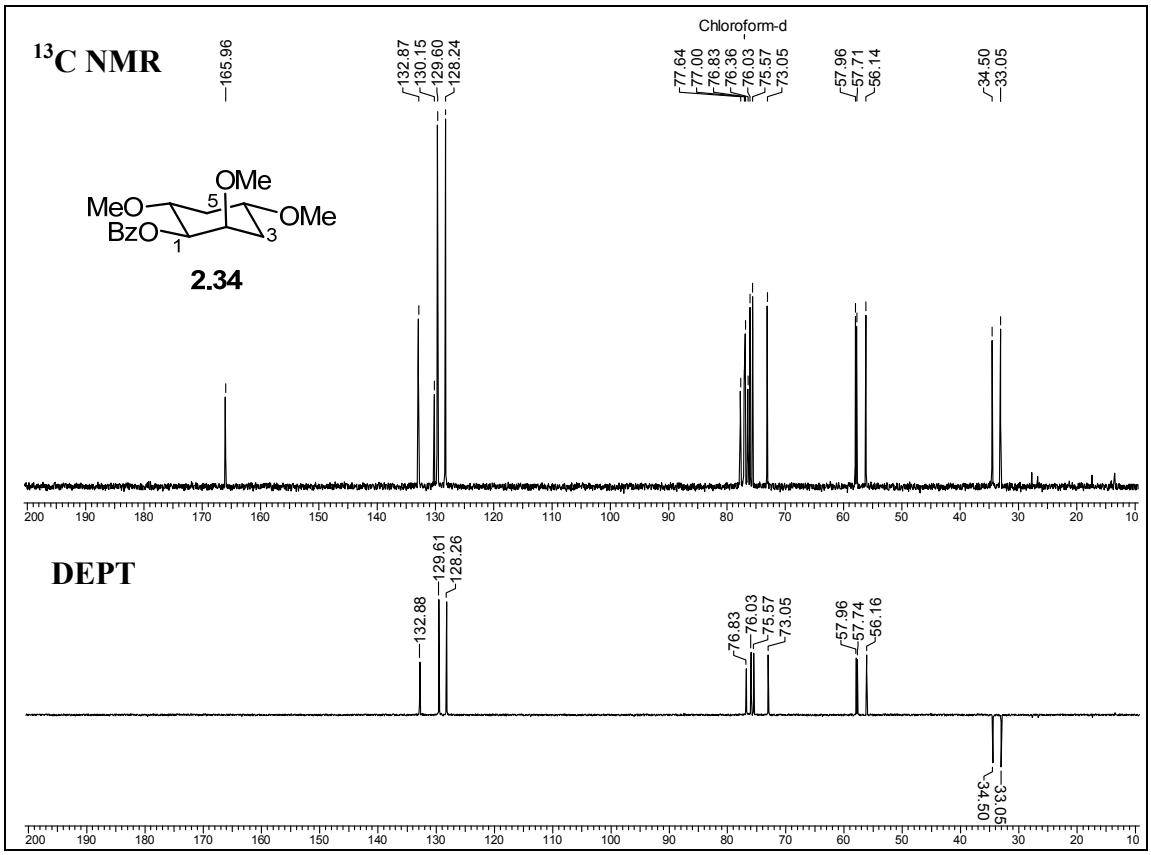

^{13}C NMR
Chloroform-d
HO
OBz
OBn
OBn
2.32
165.69
138.42 138.22 133.20 129.86 129.67 128.36 128.21 127.54
77.81 77.63 77.00 76.37 73.36 71.52 71.12 70.69 67.52
36.18 35.94
DEPT
133.20 129.67 128.41 127.54
77.82 73.36 71.13 67.52
71.53 70.69
36.17 35.94

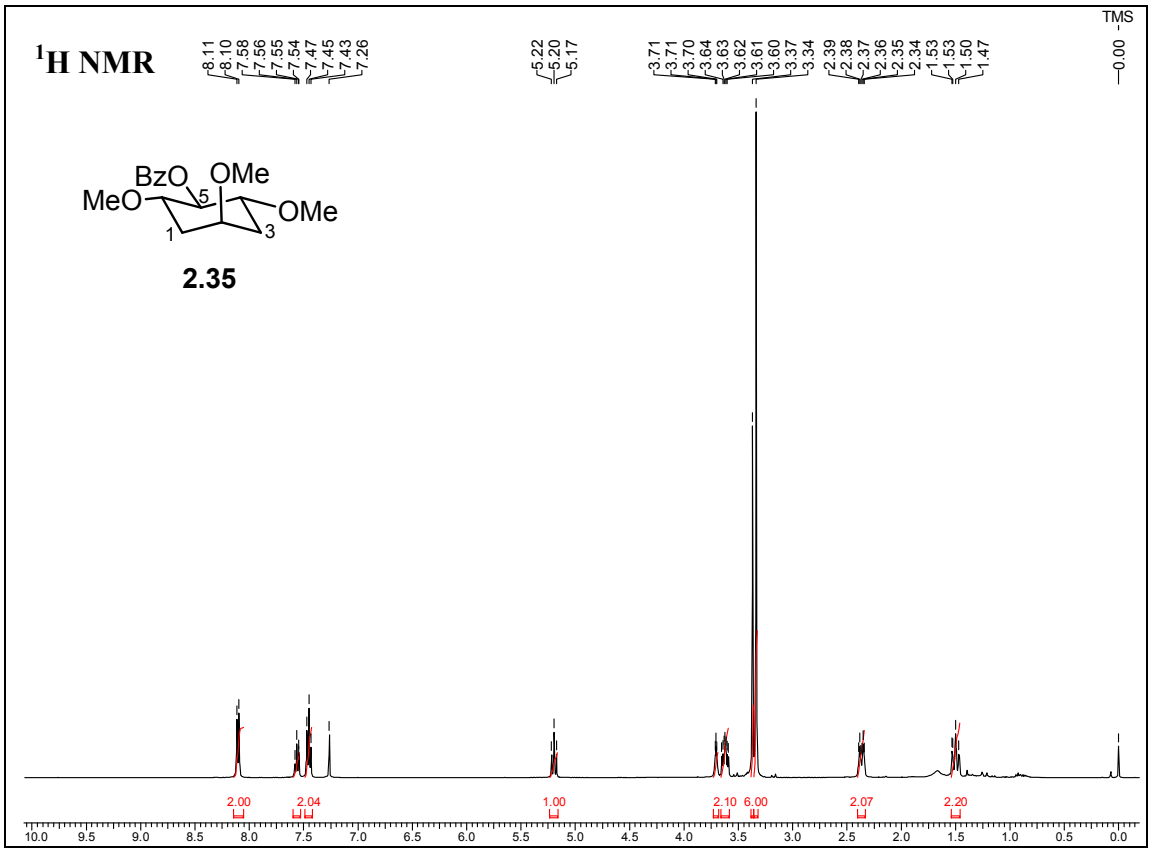


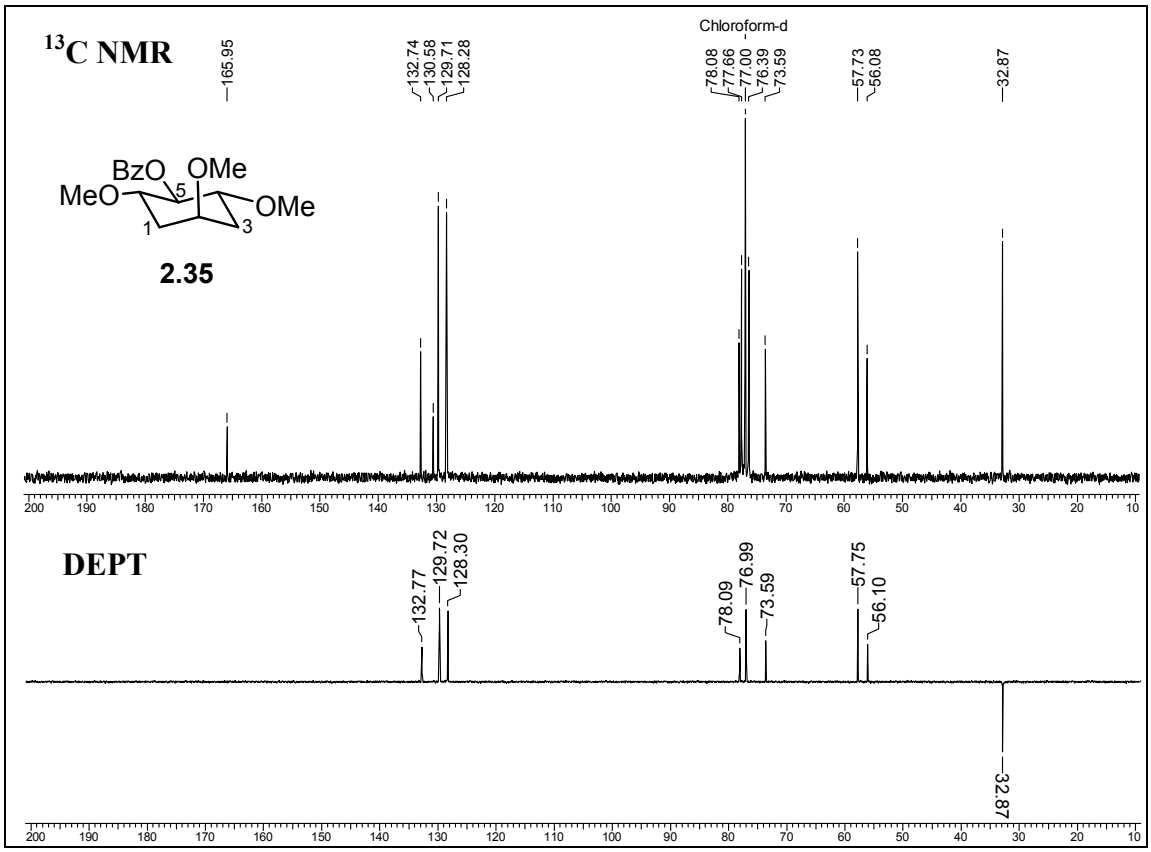


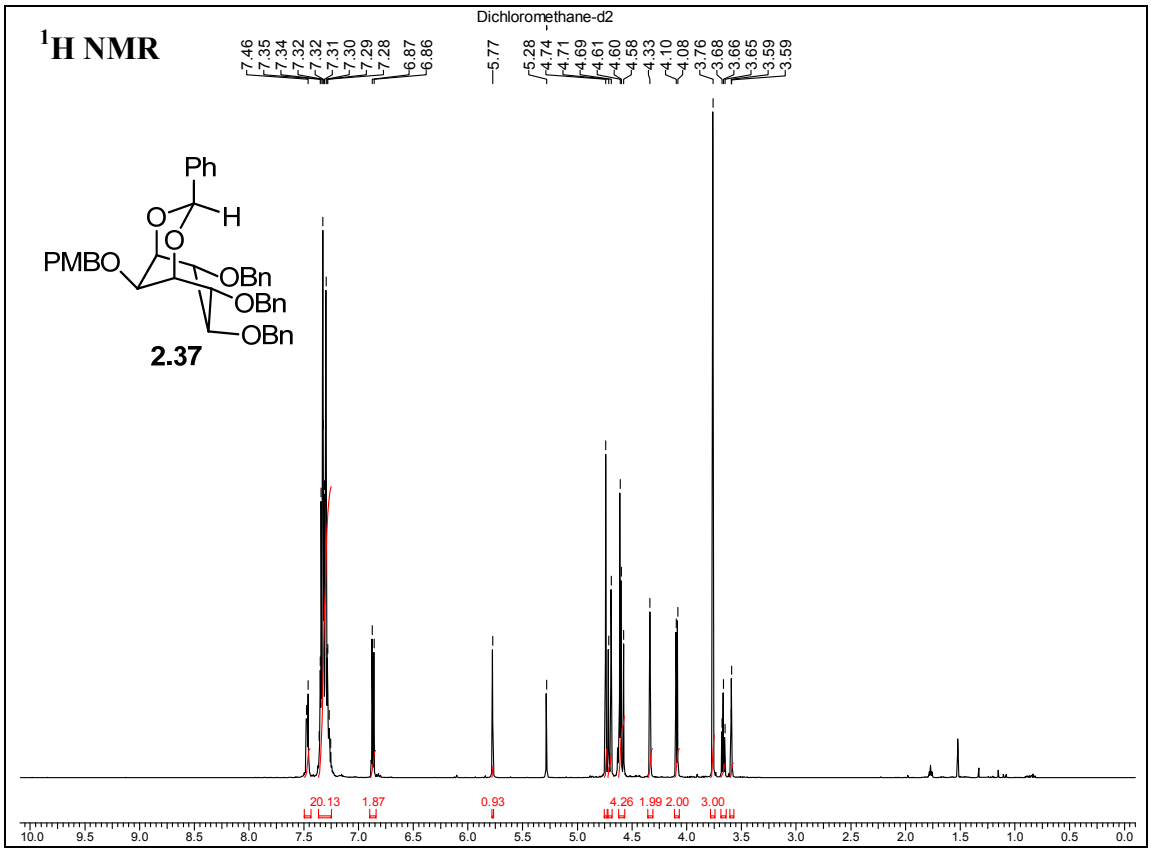
For 2D NMR see appendix III

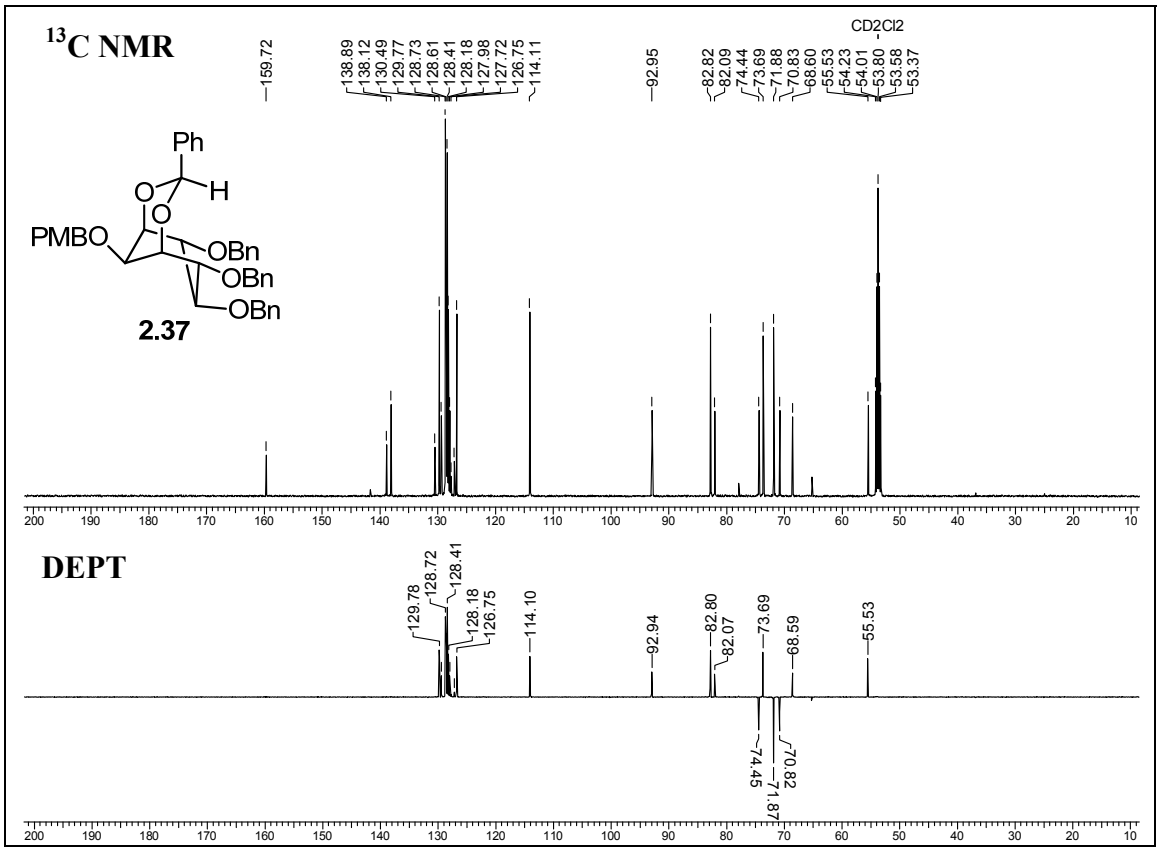

^{1}H NMR
TMS
OMe
MeO
BzO
OMe
5
1
3
2.34

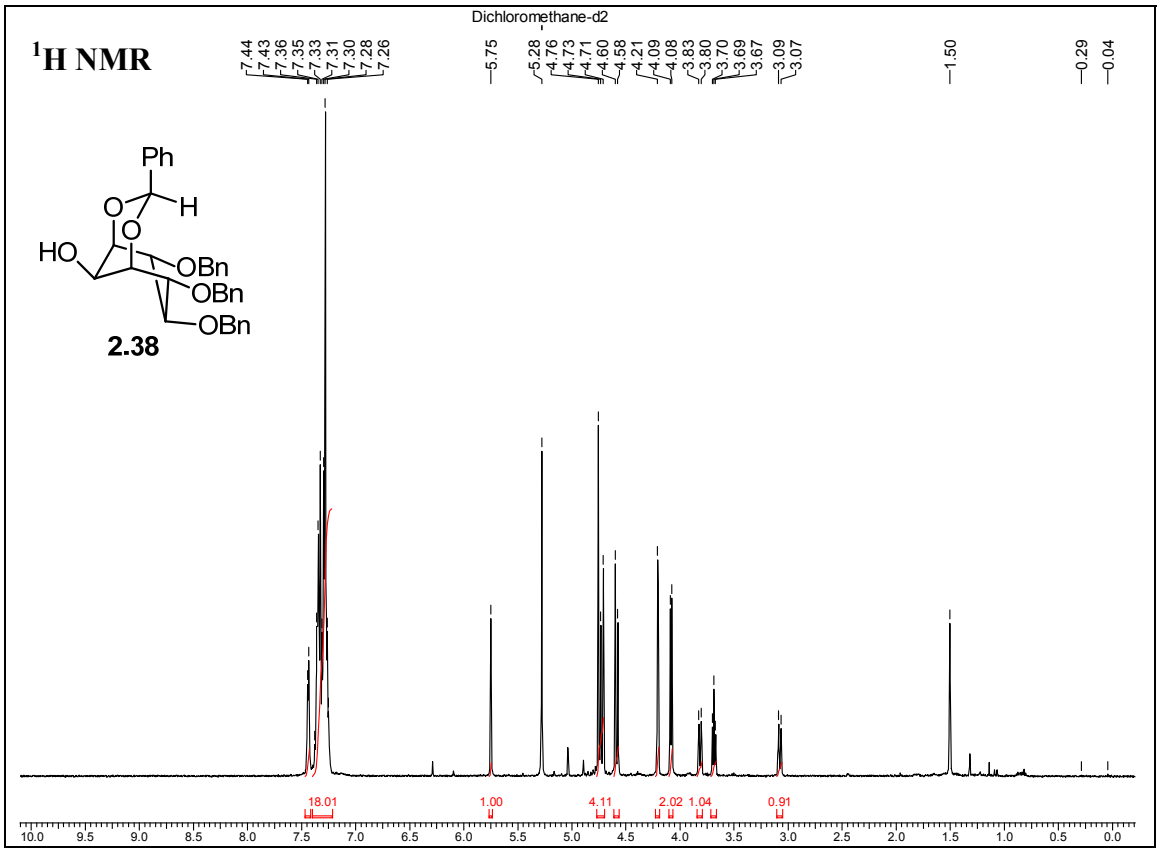

^{13}C NMR
Chloroform-d
OMe
MeO
BzO
OMe
5
1
3
2.34
DEPT

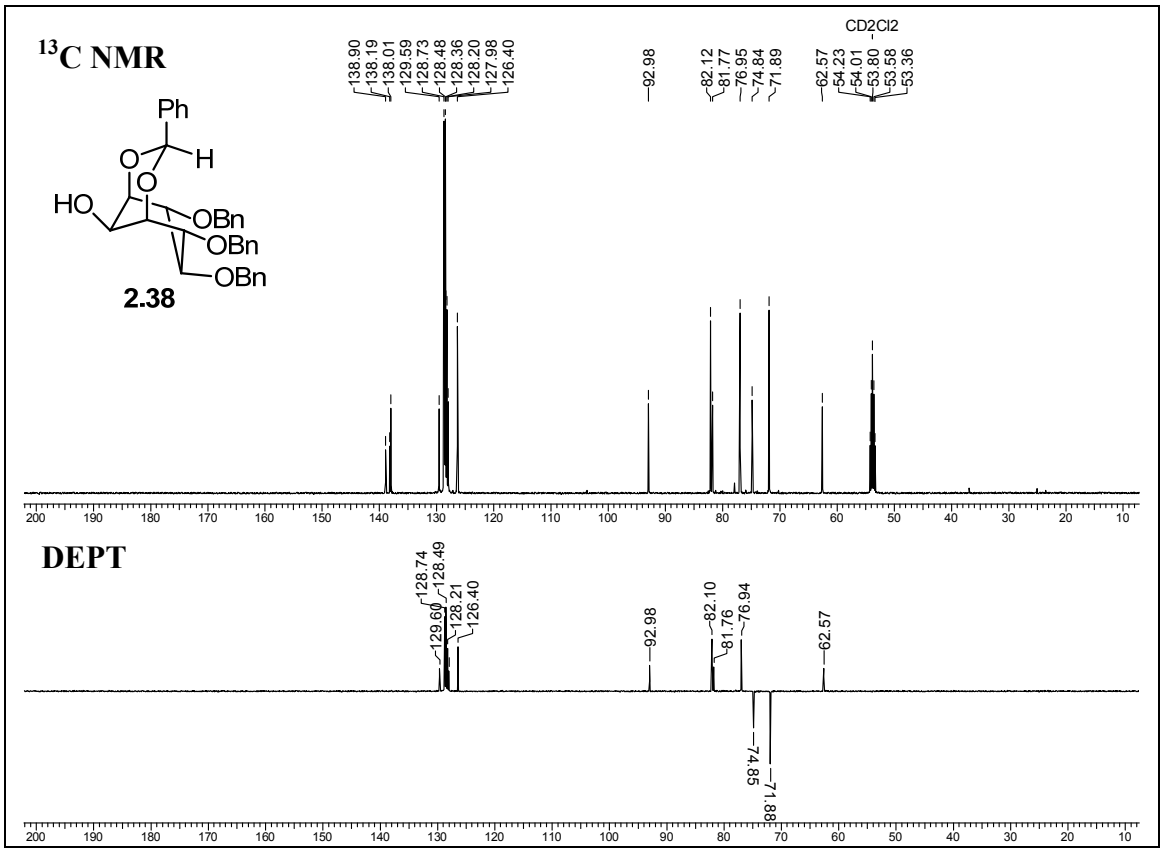

^{1}H NMR
TMS
BzO
OMe
MeO
OMe
2.35

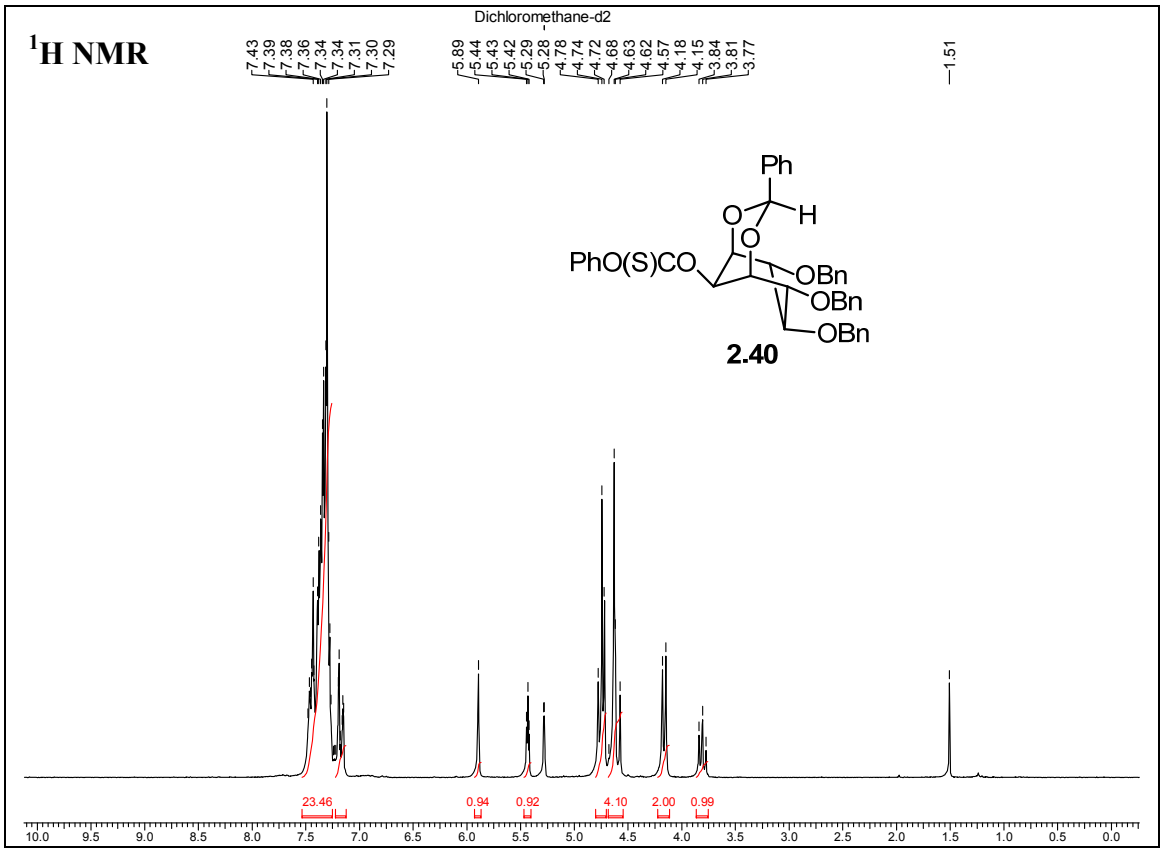

^{13}C NMR
Chloroform-d
BzO
OMe
MeO
OMe
2.35
DEPT

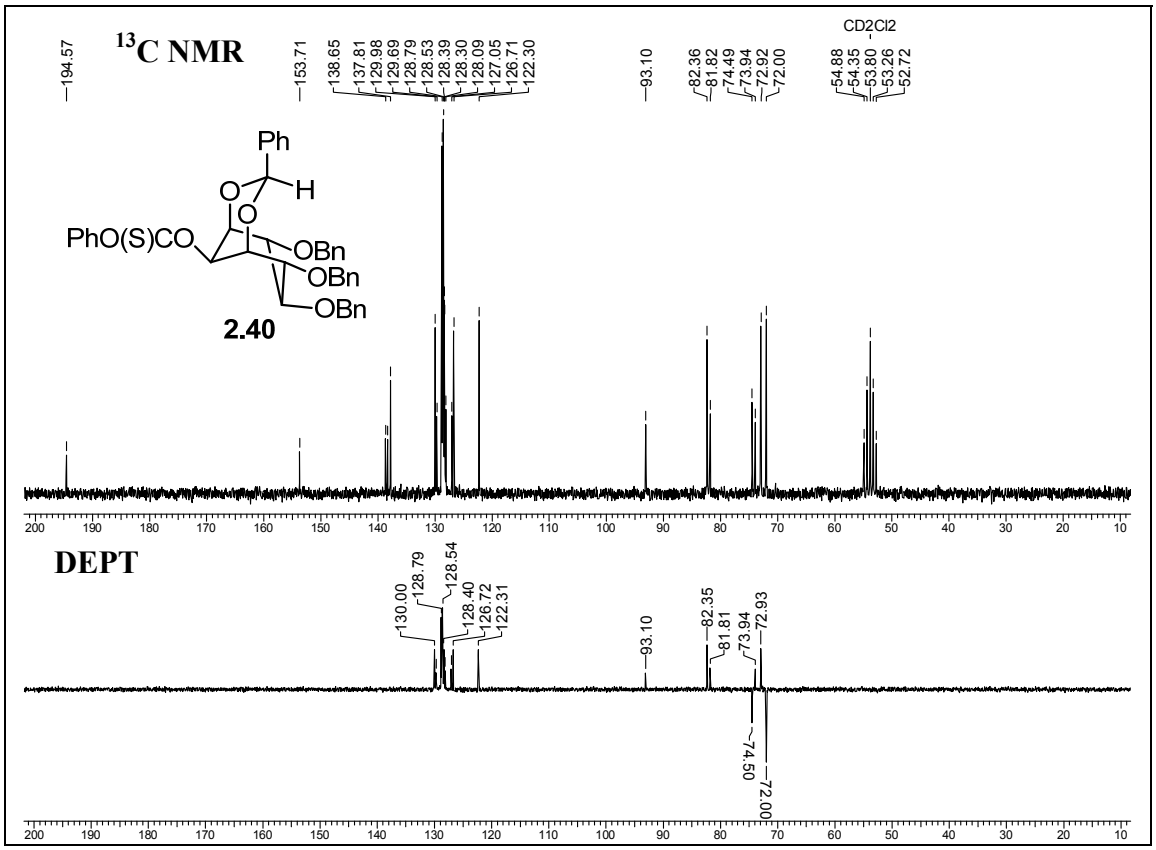

^{1}H NMR
Dichloromethane-d2
7.46
7.35
7.34
7.32
7.32
7.31
7.30
7.29
7.28
6.87
6.86
5.77
5.28
4.74
4.71
4.69
4.61
4.60
4.58
4.33
4.10
4.08
3.76
3.68
3.66
3.65
3.59
3.59
Ph
O
H
O
PMBO
OBn
OBn
OBn
2.37
20.13
1.87
0.93
4.26
1.99
2.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

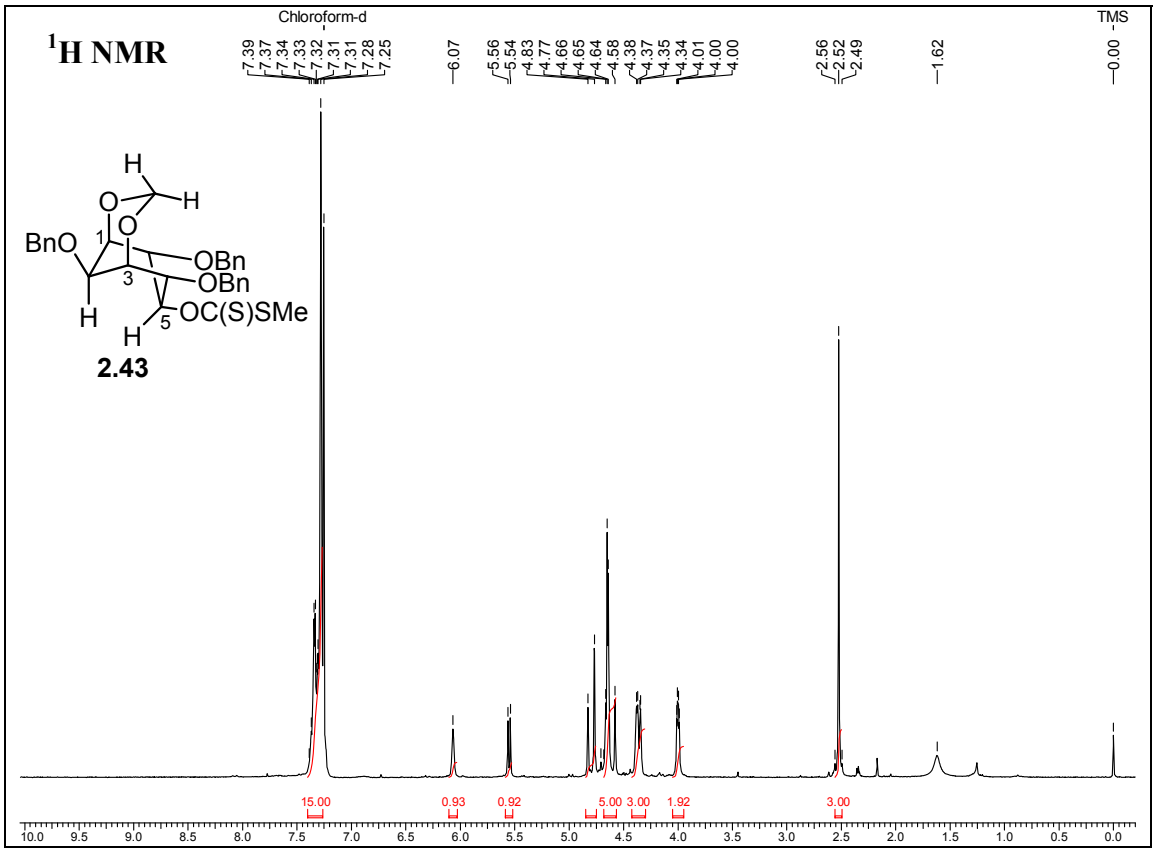

^{13}C NMR
CD2Cl2
159.72
138.89
138.12
130.49
129.77
128.73
128.61
128.41
128.18
127.98
127.72
126.75
114.11
92.95
82.82
82.09
74.44
73.69
71.88
70.83
68.60
55.53
54.23
54.01
53.80
53.58
53.37
Ph
O
H
O
PMBO
OBn
OBn
OBn
2.37
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
DEPT
129.78
128.72
128.41
128.18
126.75
114.10
92.94
82.80
82.07
73.69
68.59
55.53
74.45
71.87
70.82

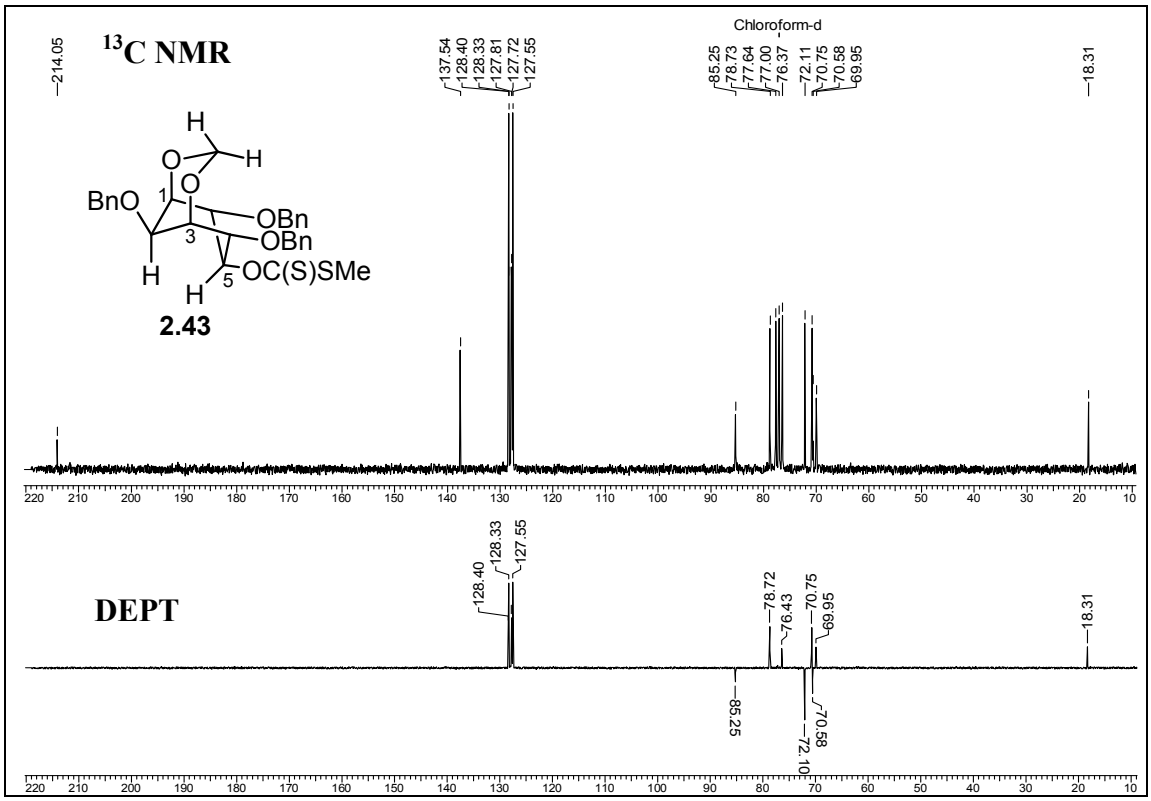

^{1}H NMR
Dichloromethane-d2
7.44
7.43
7.36
7.35
7.33
7.31
7.30
7.28
7.26
5.75
5.28
4.76
4.73
4.71
4.60
4.58
4.21
4.09
4.08
3.83
3.80
3.70
3.69
3.67
3.09
3.07
1.50
0.29
0.04
Ph
O
H
O
HO
OBn
OBn
OBn
2.38
18.01
1.00
4.11
2.02
1.04
0.91
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


^{13}C NMR
CD2Cl2
138.90
138.19
138.01
129.59
128.73
128.48
128.36
128.20
127.98
126.40
92.98
82.12
81.77
76.95
74.84
71.89
62.57
54.23
54.01
53.80
53.58
53.36
Ph
O
H
O
HO
OBn
OBn
OBn
2.38
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
DEPT
128.74
128.49
129.60
128.21
126.40
92.98
82.10
81.76
76.94
62.57
74.85
71.88

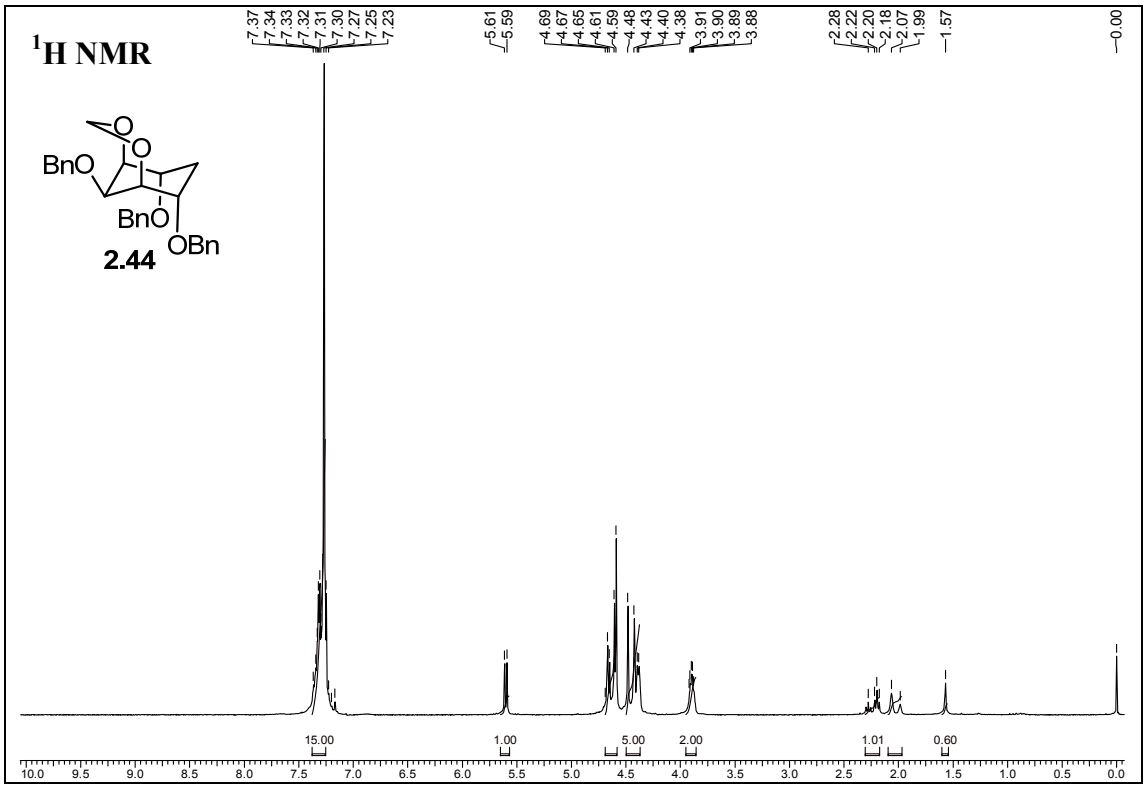

^{1}H NMR
Dichloromethane-d2
7.43
7.39
7.38
7.36
7.34
7.34
7.31
7.30
7.29
5.89
5.44
5.43
5.42
5.29
5.28
4.78
4.74
4.72
4.68
4.63
4.62
4.57
4.18
4.15
3.84
3.81
3.77
1.51
Ph
O
H
O
PhO(S)CO
OBn
OBn
OBn
2.40
23.46
0.94
0.92
4.10
2.00
0.99
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

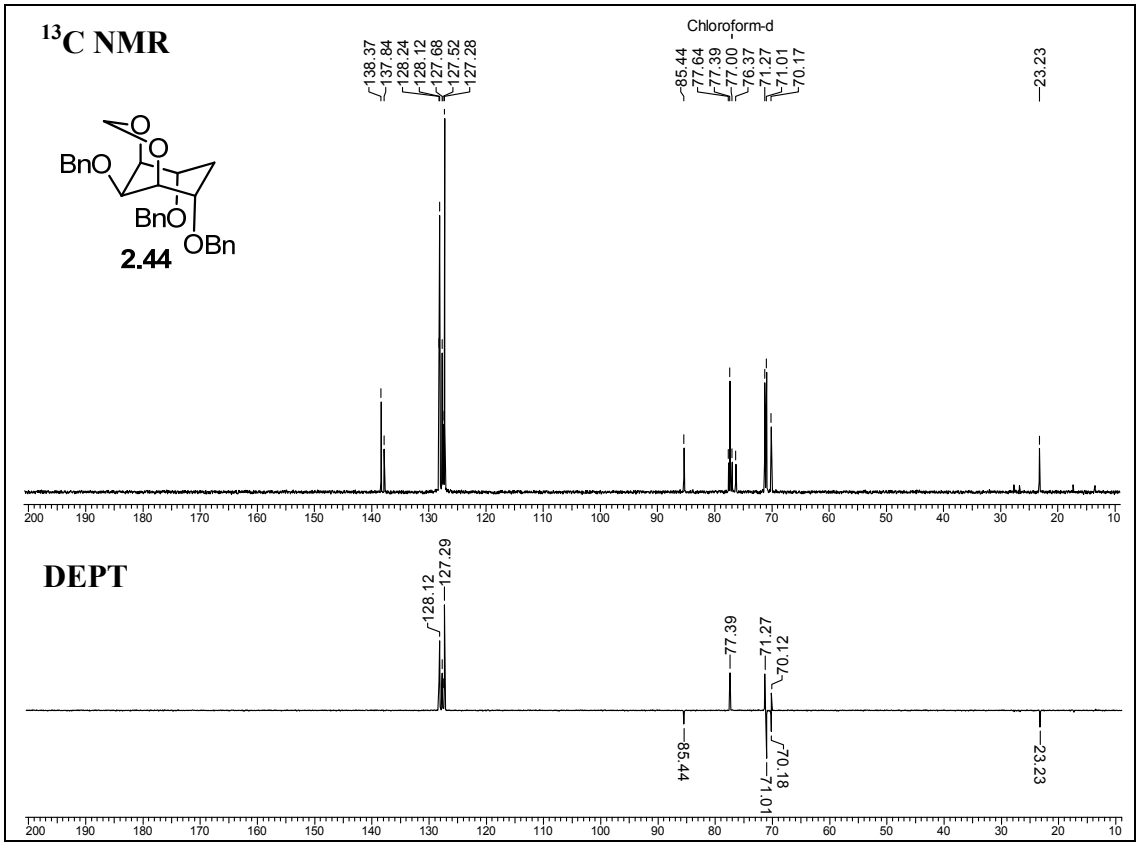

^{13}C NMR
CD2Cl2
194.57
153.71
138.65
137.81
129.98
129.69
128.79
128.53
128.39
128.30
128.09
127.05
126.71
122.30
93.10
82.36
81.82
74.49
73.94
72.92
72.00
54.88
54.35
53.80
53.26
52.72
Ph
O
H
O
PhO(S)CO
OBn
OBn
OBn
2.40
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
DEPT
130.00
128.79
128.54
128.40
126.72
122.31
93.10
82.35
81.81
73.94
72.93
74.50
72.00

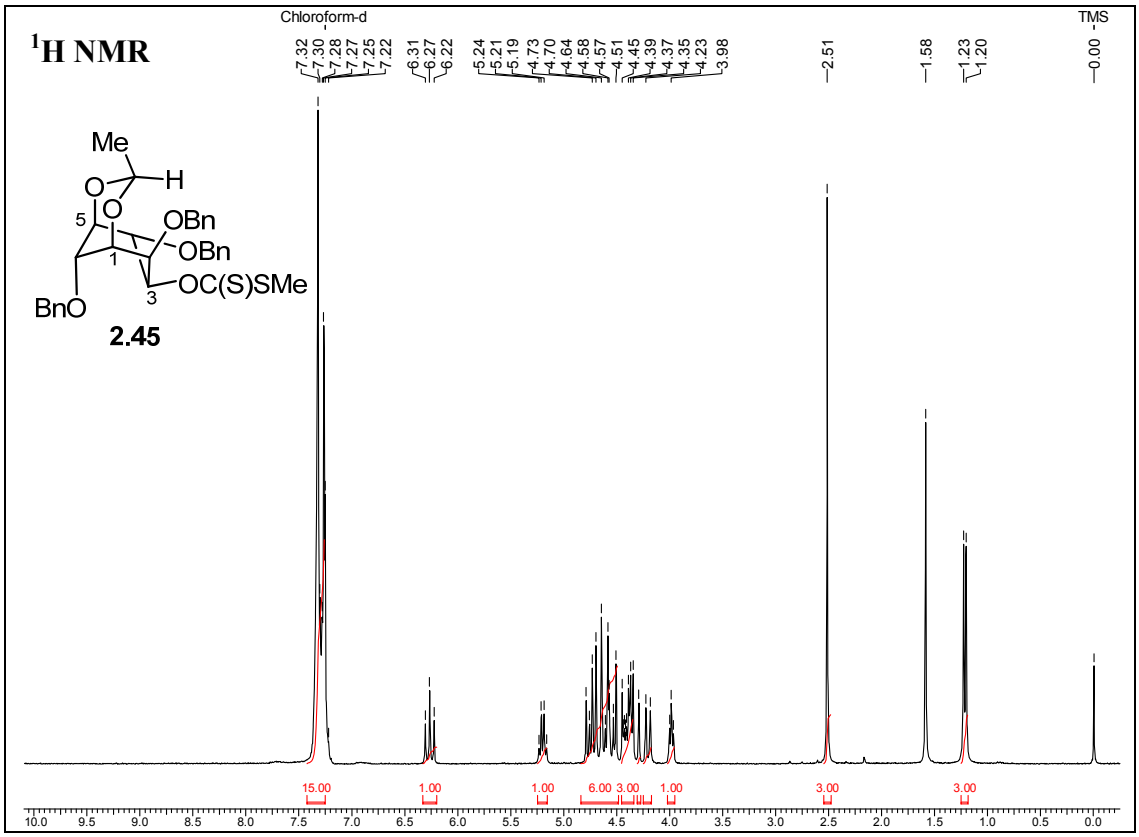


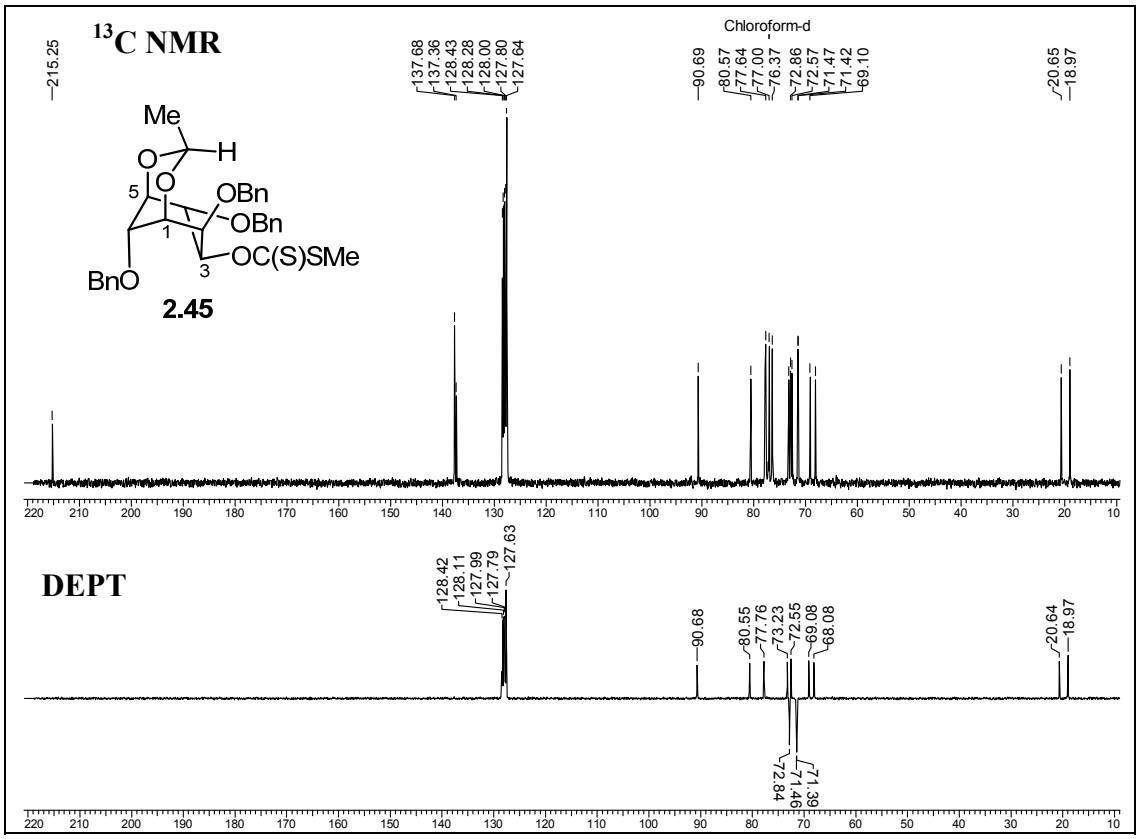


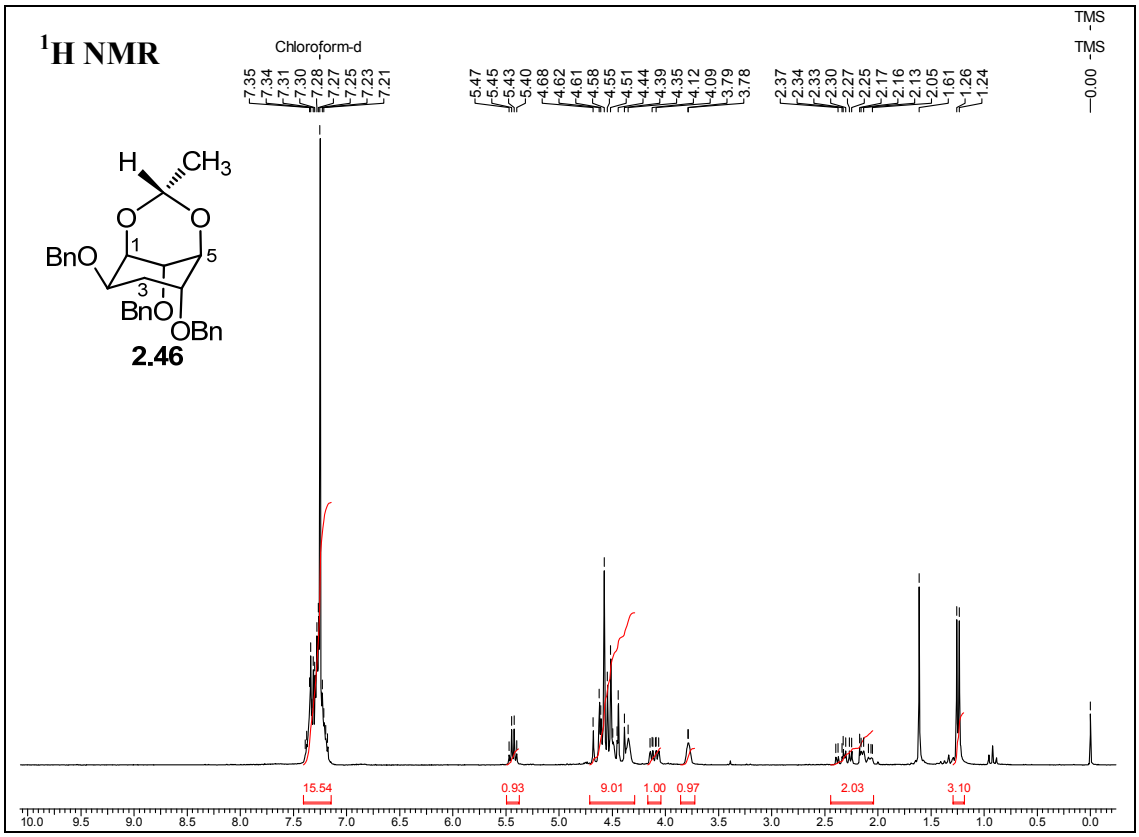
For 2D NMR see appendix III

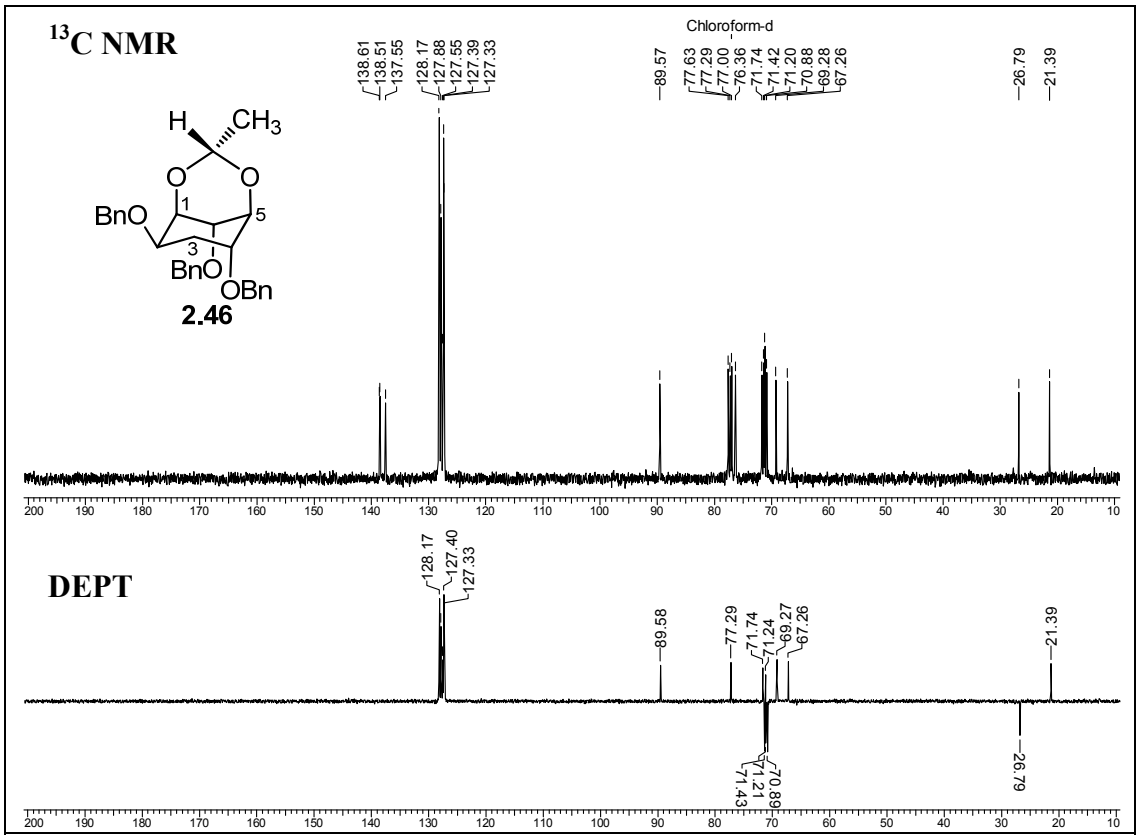

^{1}H NMR
BnO
BnO
OBn
2.44
7.37
7.34
7.33
7.32
7.31
7.30
7.27
7.25
7.23
5.61
5.59
4.69
4.67
4.65
4.61
4.59
4.48
4.43
4.40
4.38
3.91
3.90
3.89
3.88
2.28
2.22
2.20
2.18
2.07
1.99
1.57
0.00
15.00
1.00
5.00
2.00
1.01
0.60

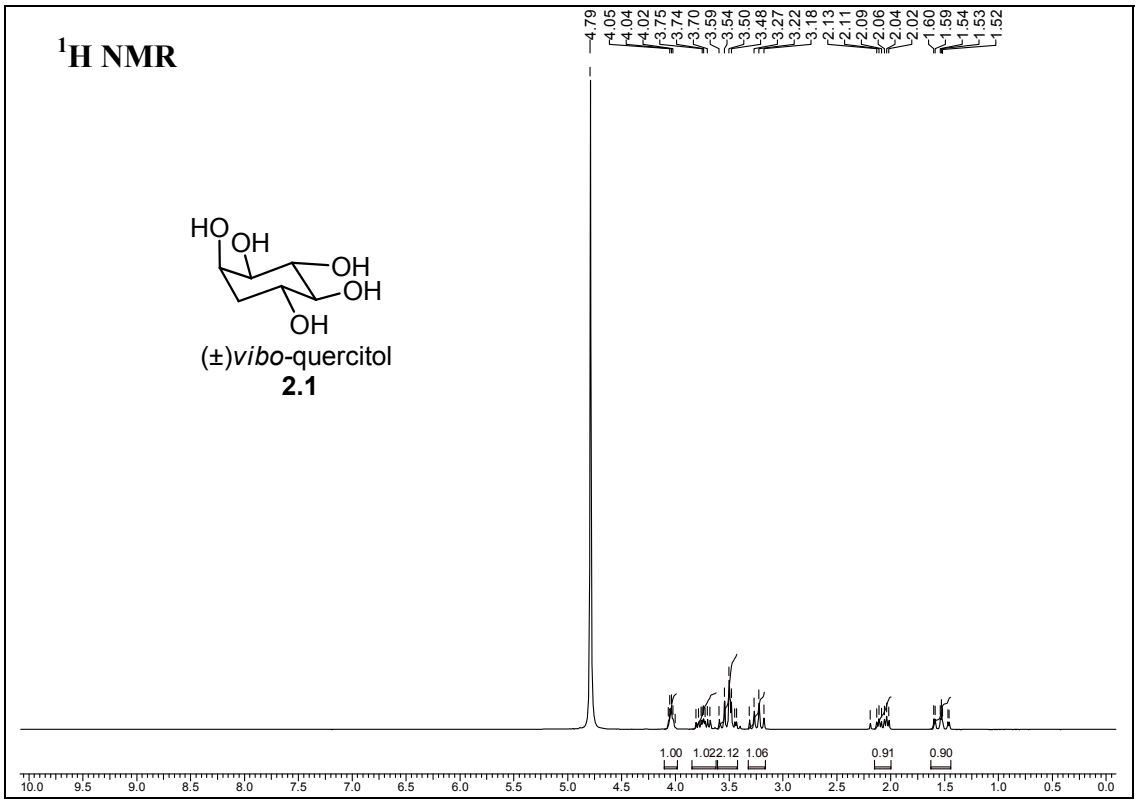

^{13}C NMR
BnO
BnO
OBn
2.44
Chloroform-d
138.37
137.84
128.24
128.12
127.68
127.52
127.28
85.44
77.64
77.39
77.00
76.37
71.27
71.01
70.17
23.23
DEPT
128.12
127.29
77.39
71.27
70.12
85.44
70.18
71.01
23.23

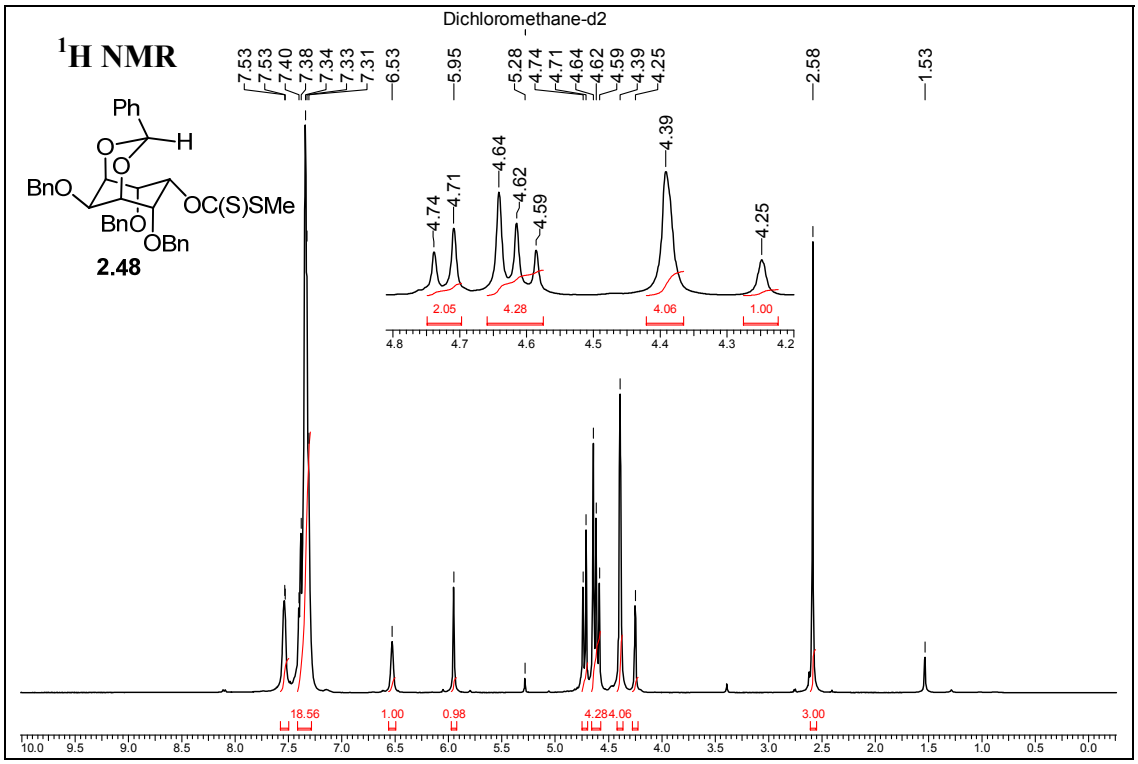

^{1}H NMR
Chloroform-d
TMS
7.32
7.30
7.28
7.27
7.25
7.22
6.31
6.27
6.22
5.24
5.21
5.19
4.73
4.70
4.64
4.58
4.57
4.51
4.45
4.39
4.37
4.35
4.23
3.98
2.51
1.58
1.23
1.20
0.00
Me
H
O
O
5
1
3
OBn
OBn
OC(S)SMe
BnO
2.45
15.00
1.00
1.00
6.00
3.00
1.00
3.00
3.00

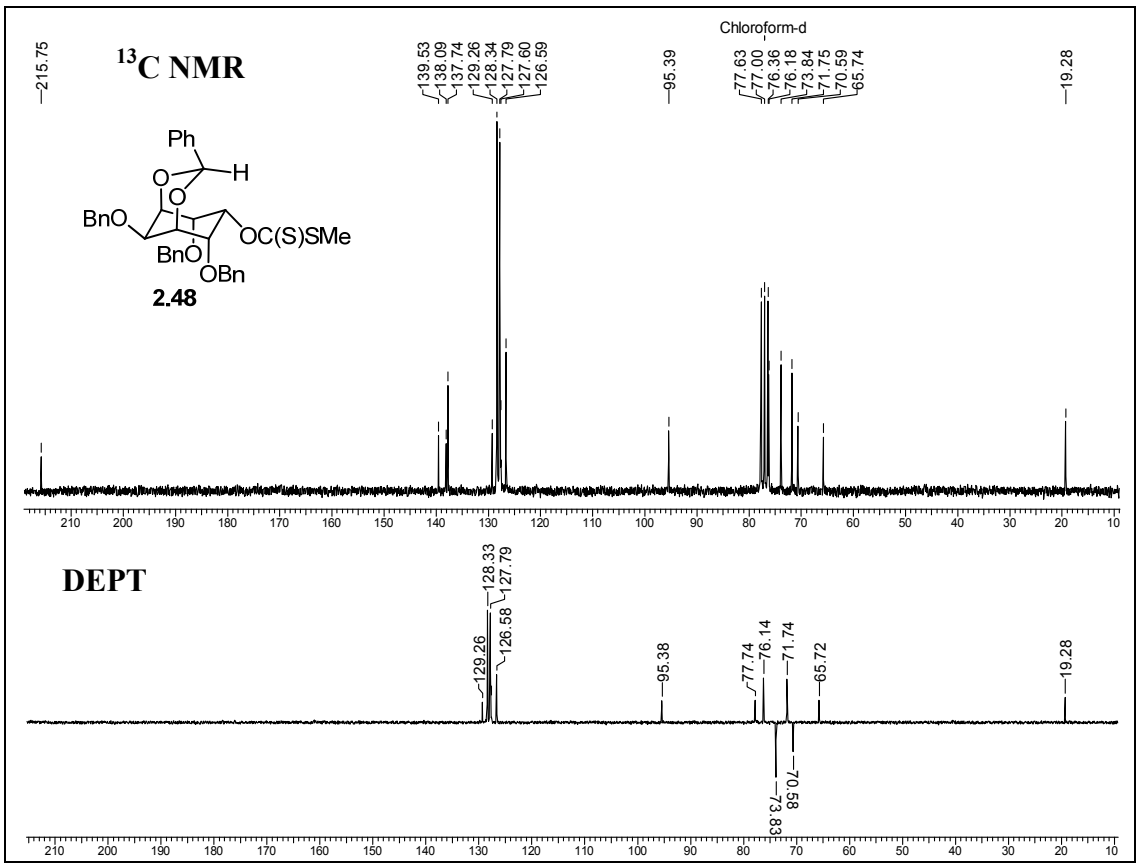

^{13}C NMR
215.25
137.68
137.36
128.43
128.28
128.00
127.80
127.64
Chloroform-d
90.69
80.57
77.64
77.00
76.37
72.86
72.57
71.47
71.42
69.10
20.65
18.97
Me
H
O
O
5
1
3
OBn
OBn
OC(S)SMe
BnO
2.45
DEPT
128.42
128.11
127.99
127.79
127.63
90.68
80.55
77.76
73.23
72.55
69.08
68.08
20.64
18.97
72.84
71.46
71.39


^{1}H NMR
Chloroform-d
TMS
TMS
7.35
7.34
7.31
7.30
7.28
7.27
7.25
7.23
7.21
5.47
5.45
5.43
5.40
4.68
4.62
4.61
4.58
4.55
4.51
4.44
4.39
4.35
4.12
4.09
3.79
3.78
2.37
2.34
2.33
2.30
2.27
2.25
2.17
2.16
2.13
2.05
1.61
1.26
1.24
0.00
H
CH3
O
O
BnO
1
5
3
BnO
OBn
2.46
15.54
0.93
9.01
1.00
0.97
2.03
3.10
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

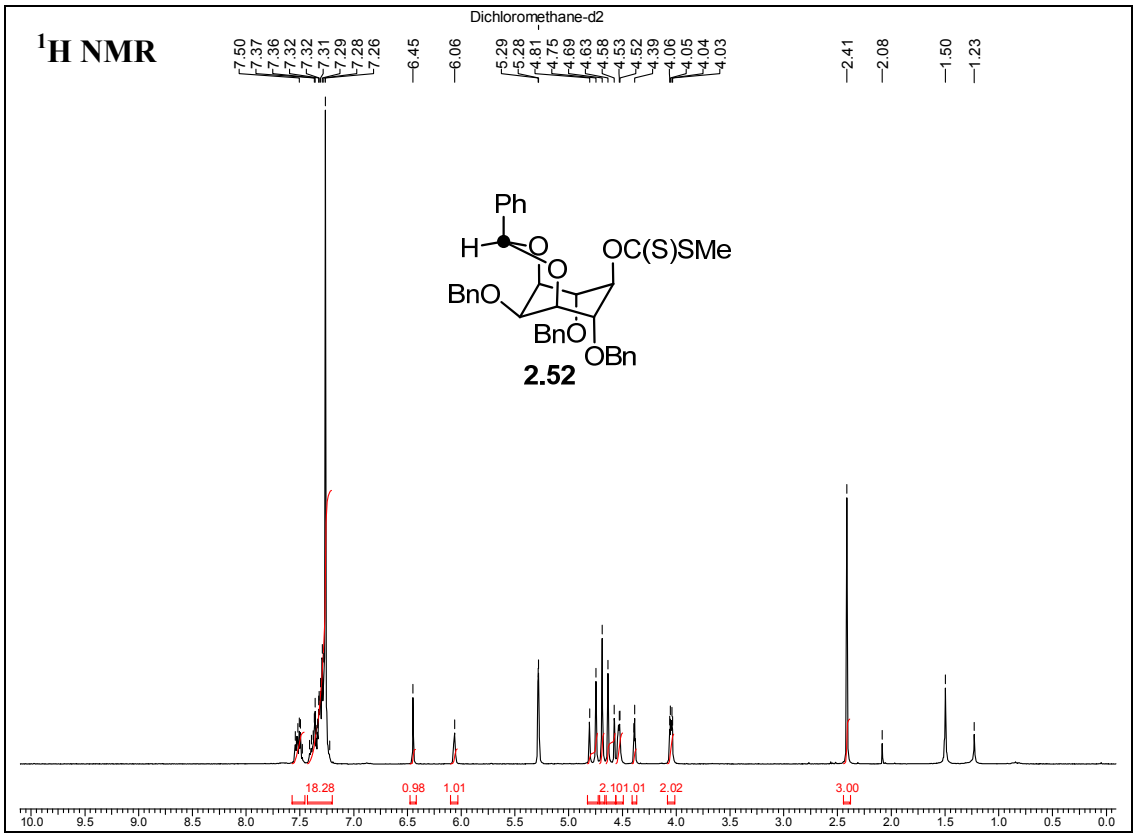

^{13}C NMR
Chloroform-d
138.61
138.51
137.55
128.17
127.88
127.55
127.39
127.33
89.57
77.63
77.29
77.00
76.36
71.74
71.42
71.20
70.88
69.28
67.26
26.79
21.39
H
CH3
O
O
BnO
1
5
3
BnO
OBn
2.46
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
DEPT
128.17
127.40
127.33
89.58
77.29
71.74
71.24
69.27
67.26
21.39
71.43
71.21
70.88
26.79

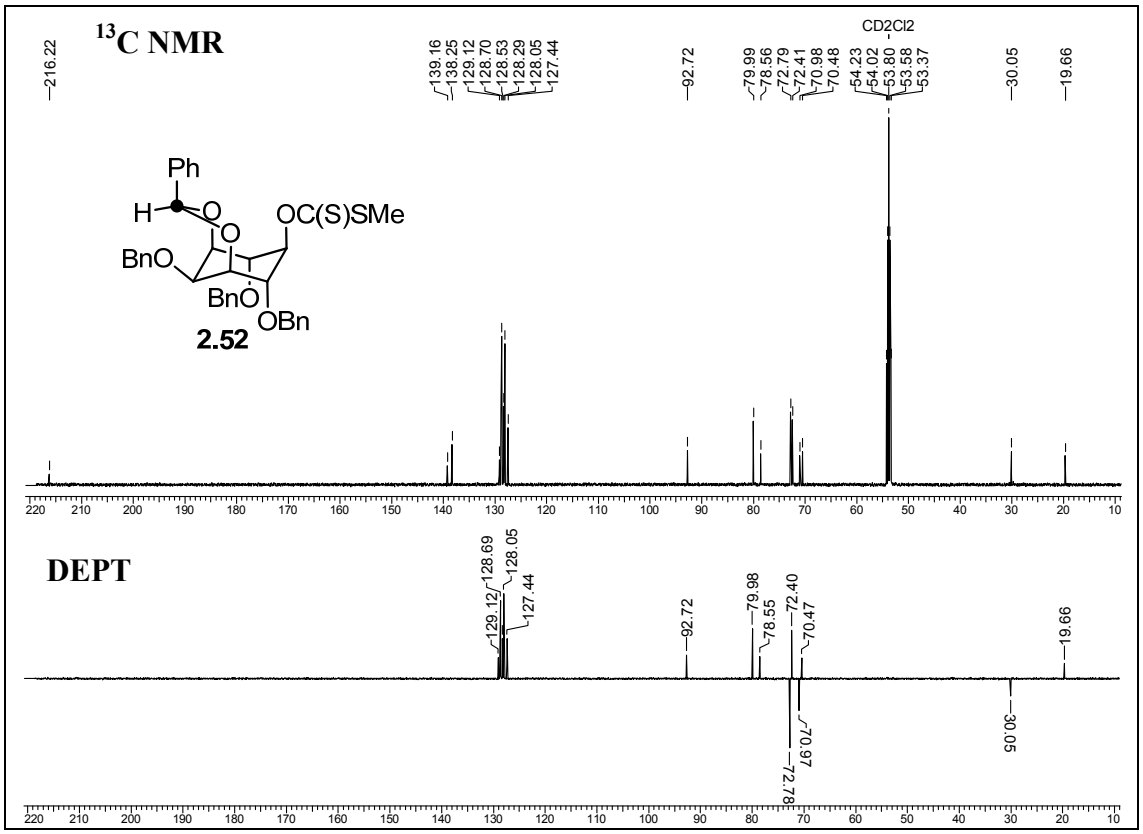

^{1}H NMR
HO
OH
OH
OH
OH
(±)*vibo*-quercitol
2.1
4.79
4.05
4.04
4.02
3.75
3.74
3.70
3.59
3.54
3.50
3.48
3.27
3.22
3.18
2.13
2.11
2.09
2.06
2.04
2.02
1.60
1.59
1.54
1.53
1.52
1.00
1.02
2.12
1.06
0.91
0.90
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0



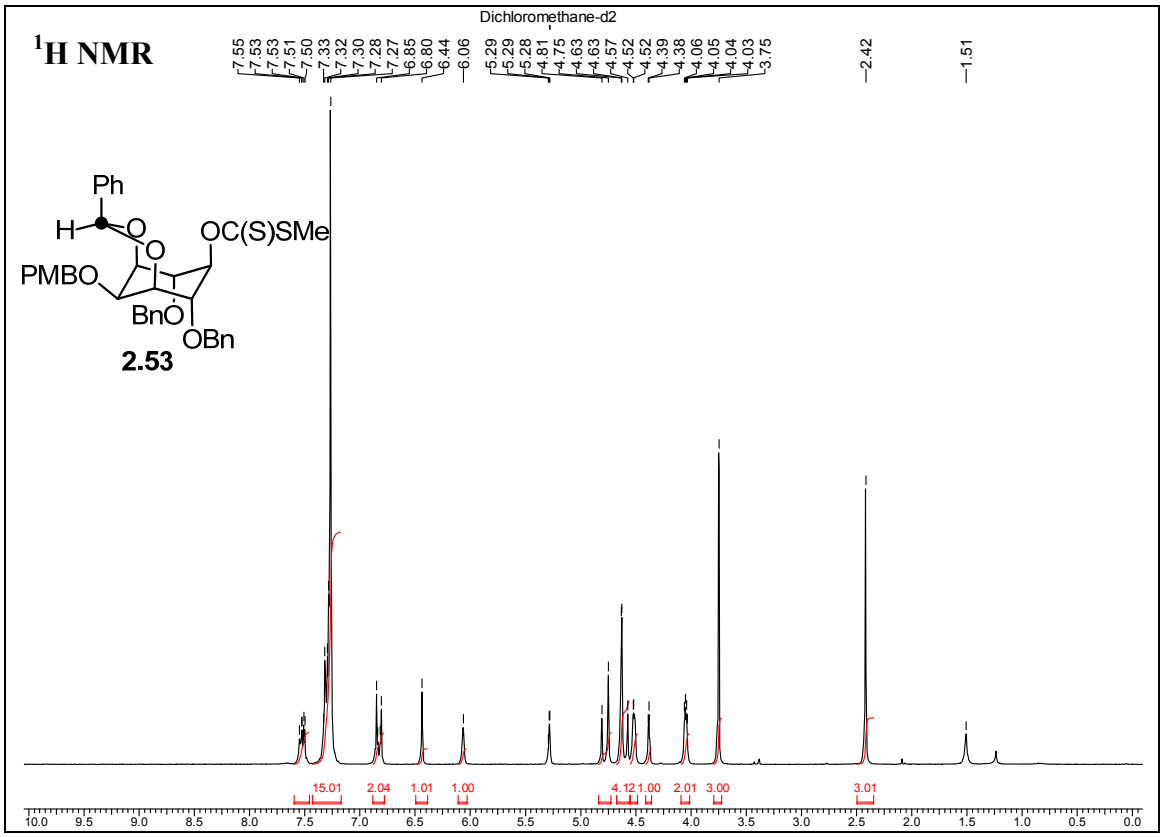


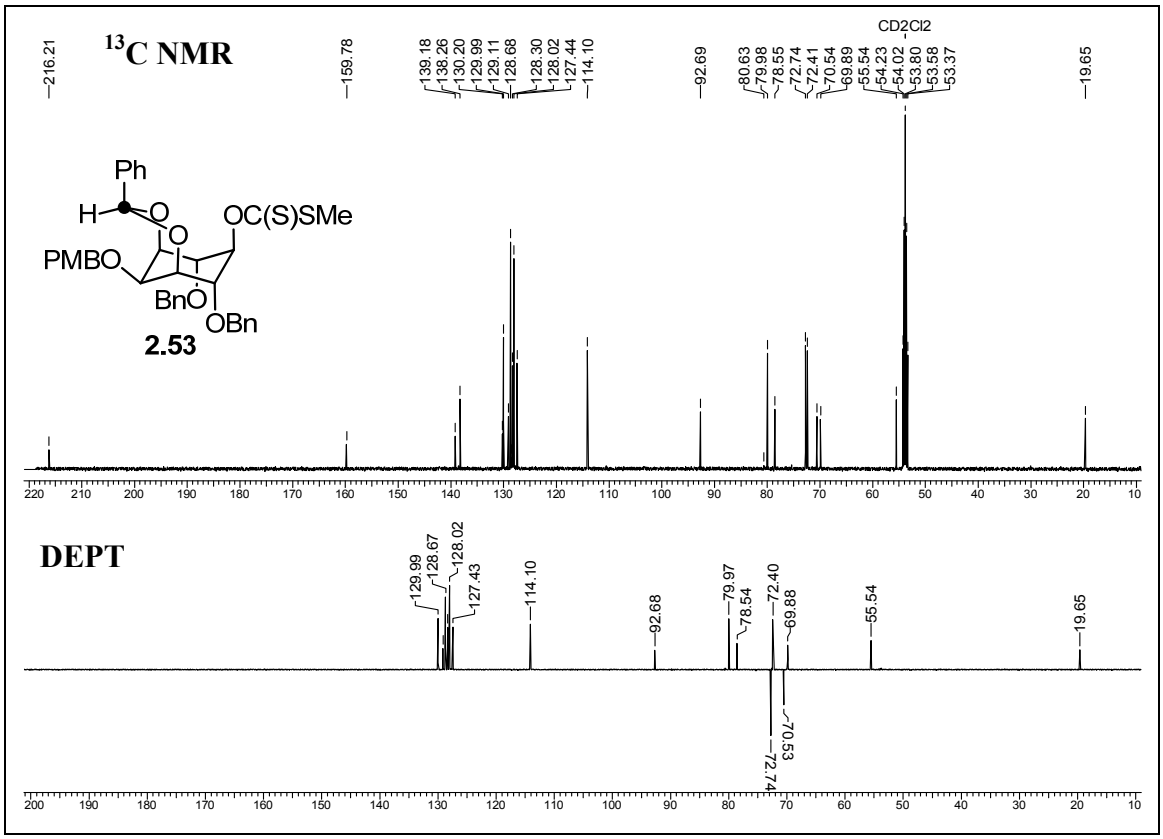
For 2D NMR see appendix III



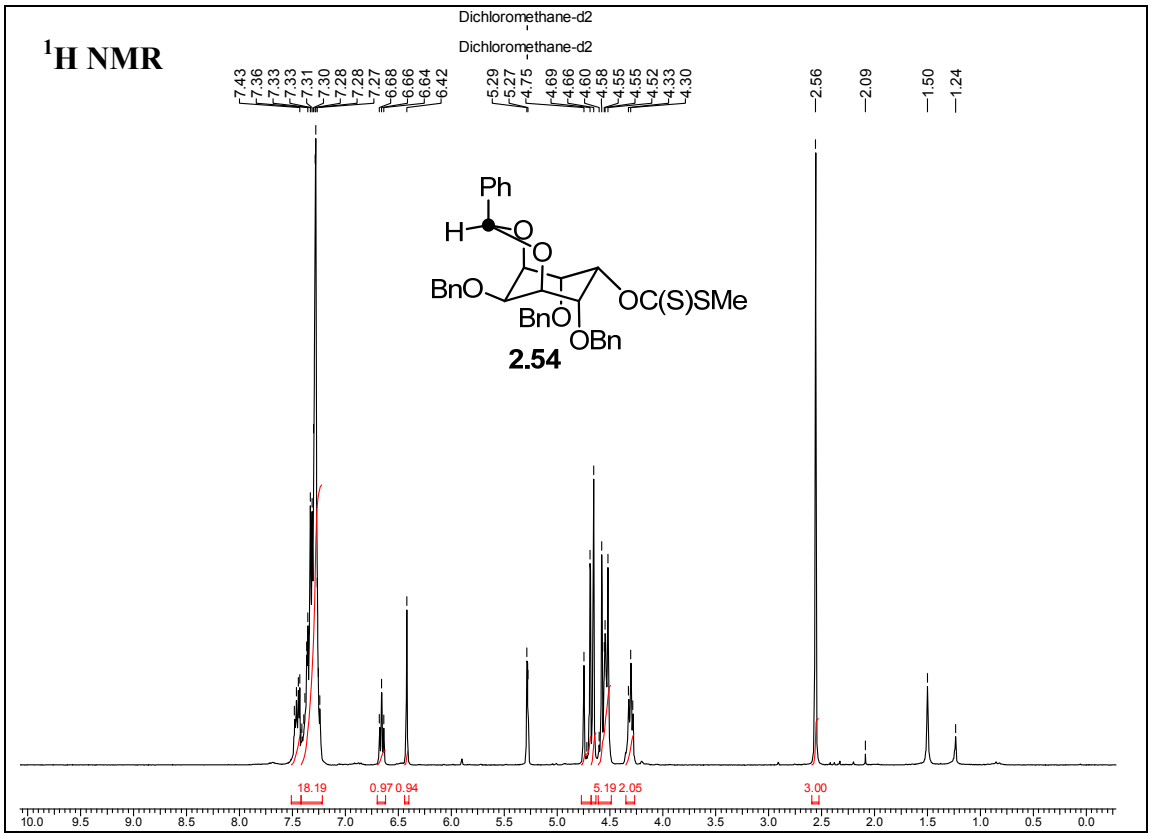


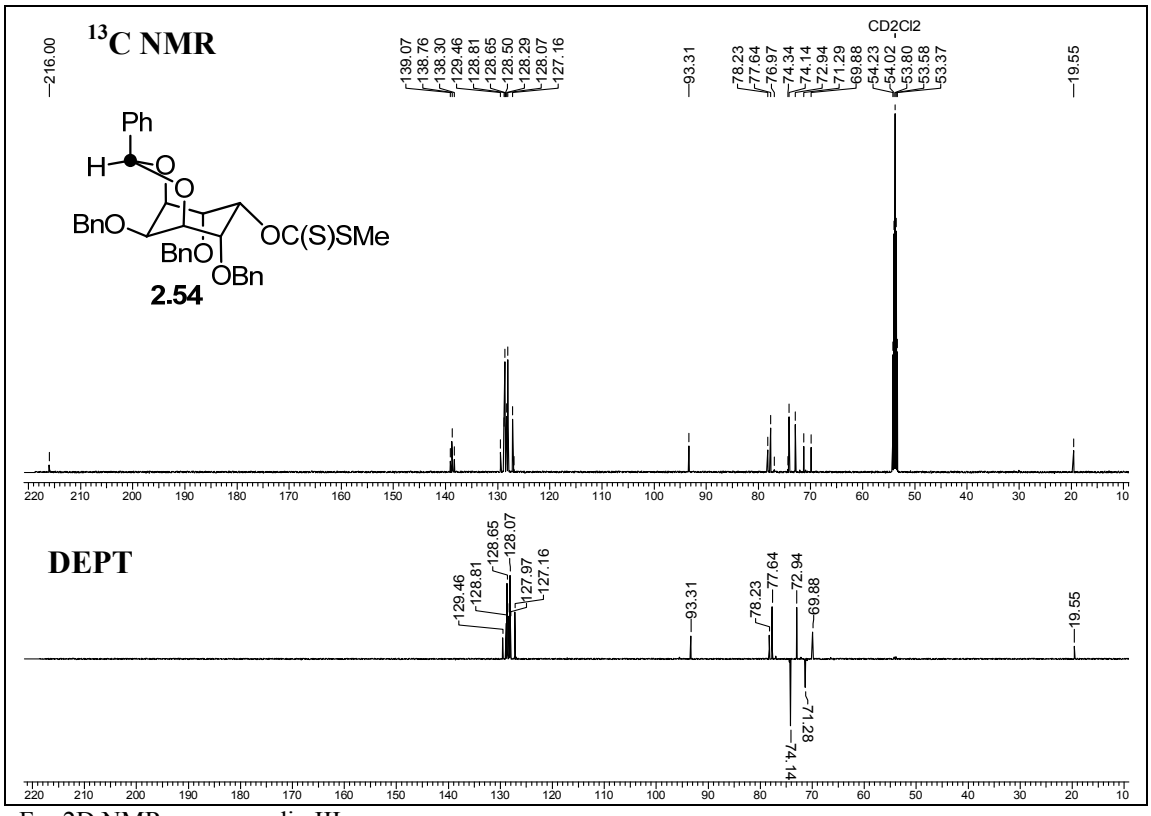
For 2D NMR see appendix III



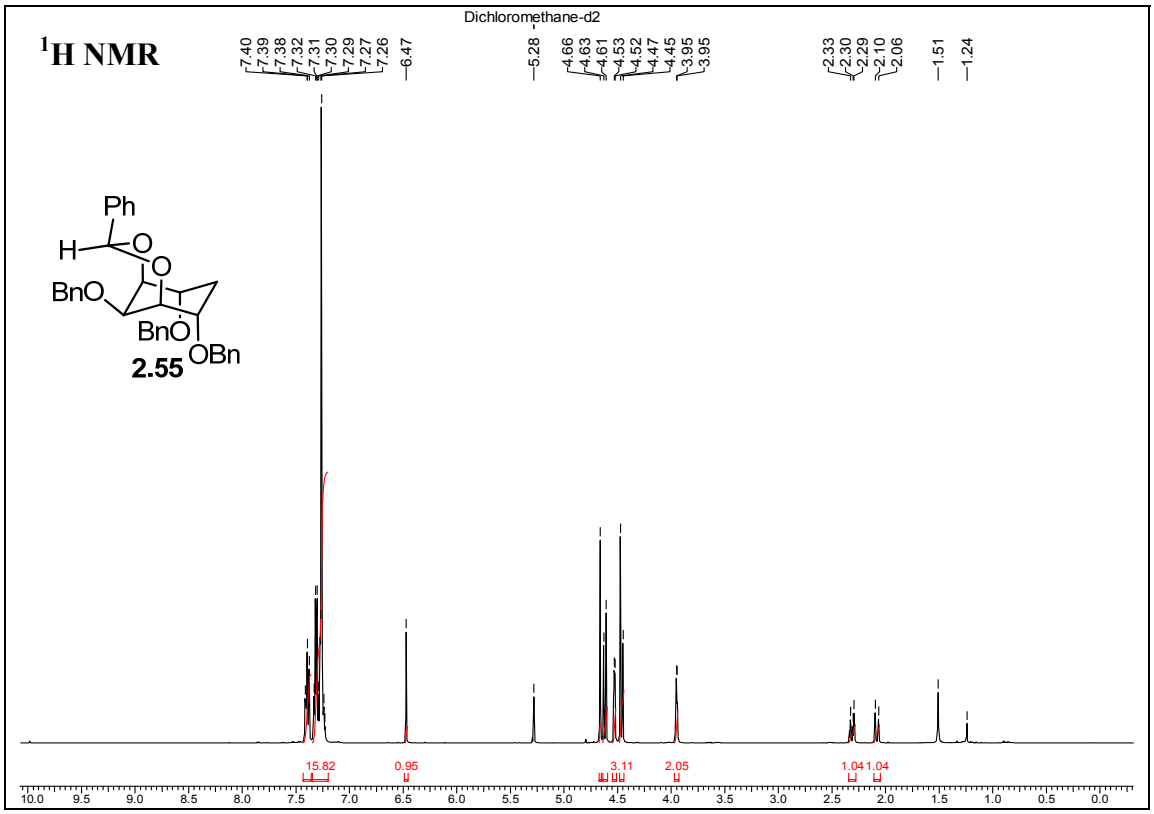


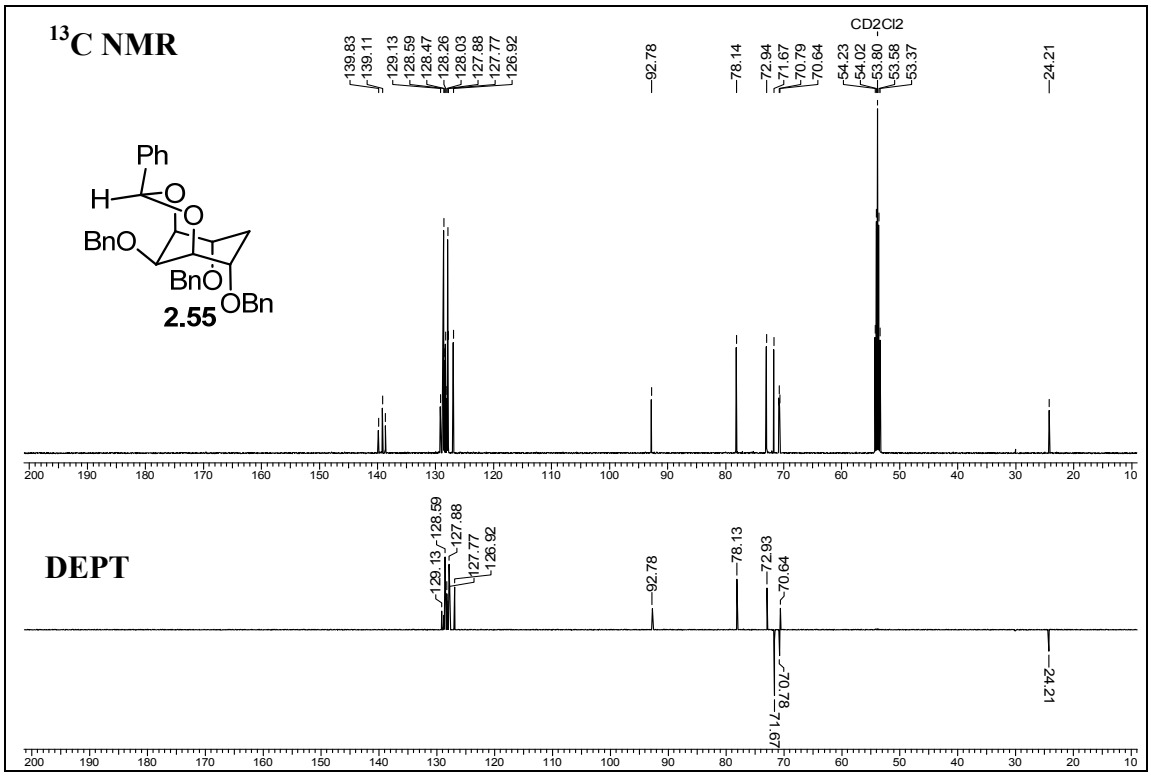
For 2D NMR see appendix III



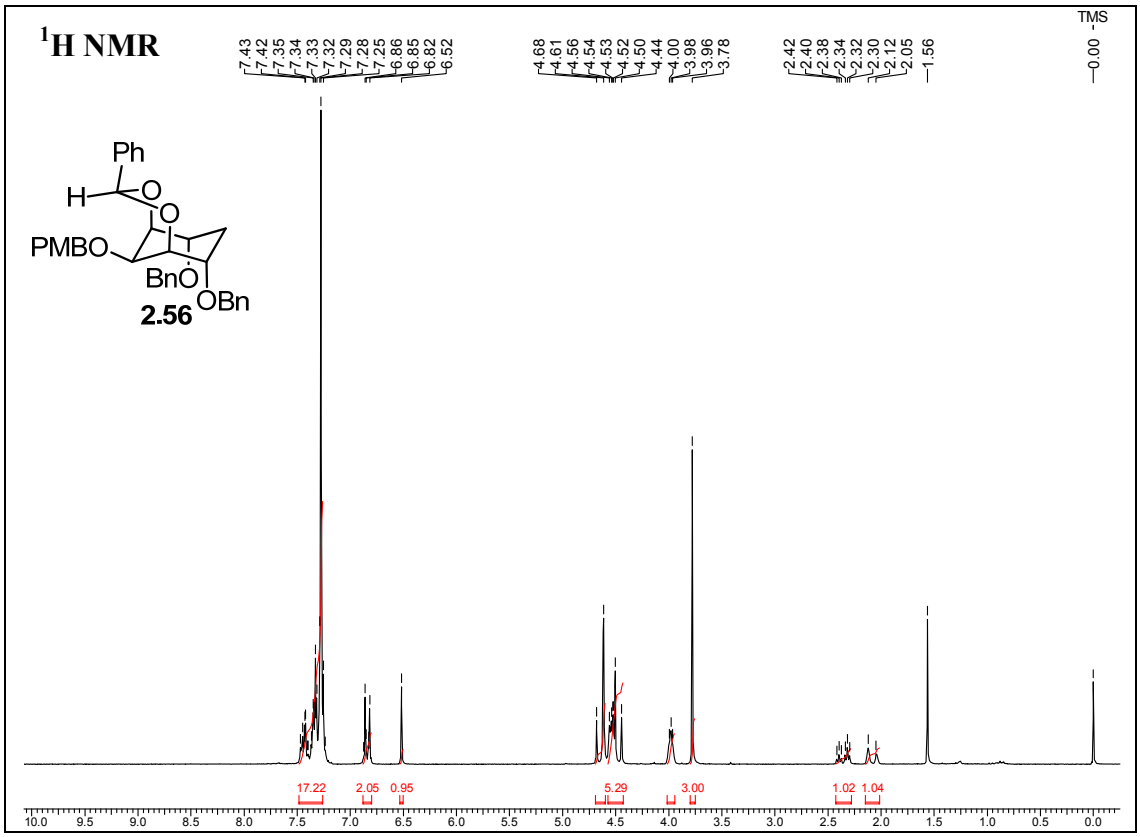


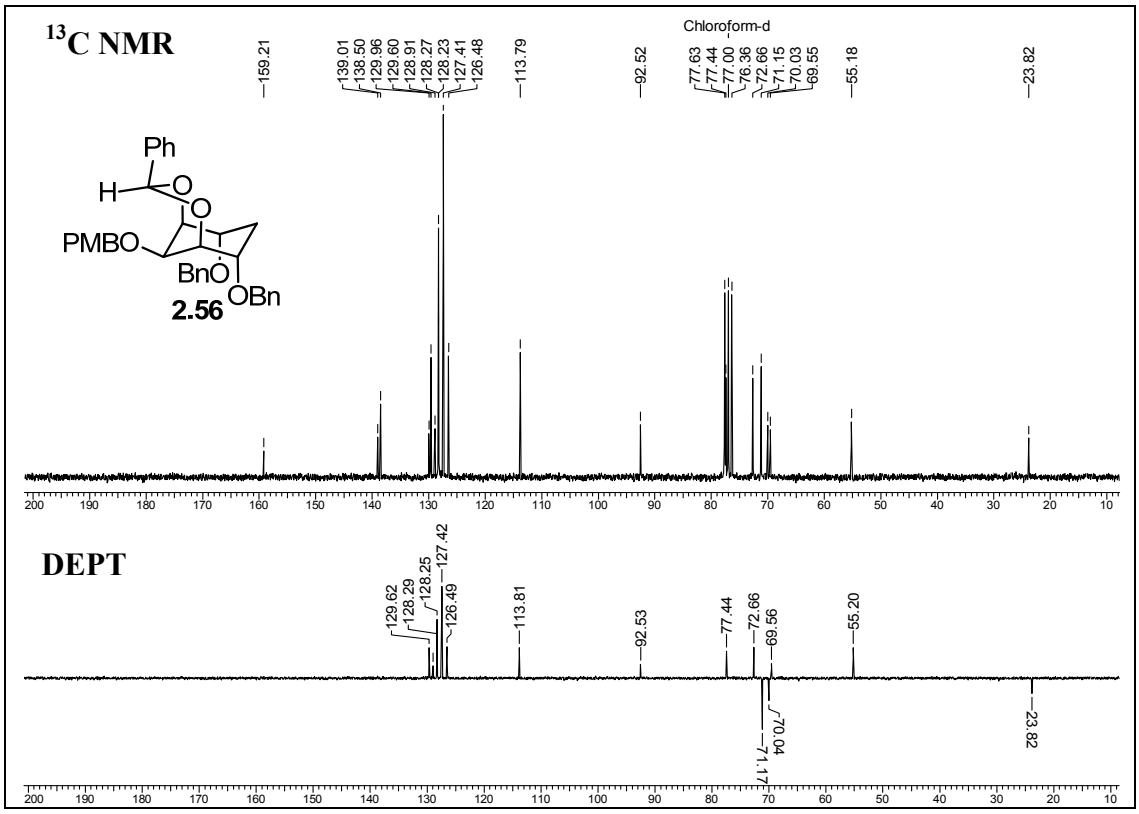
For 2D NMR see appendix III



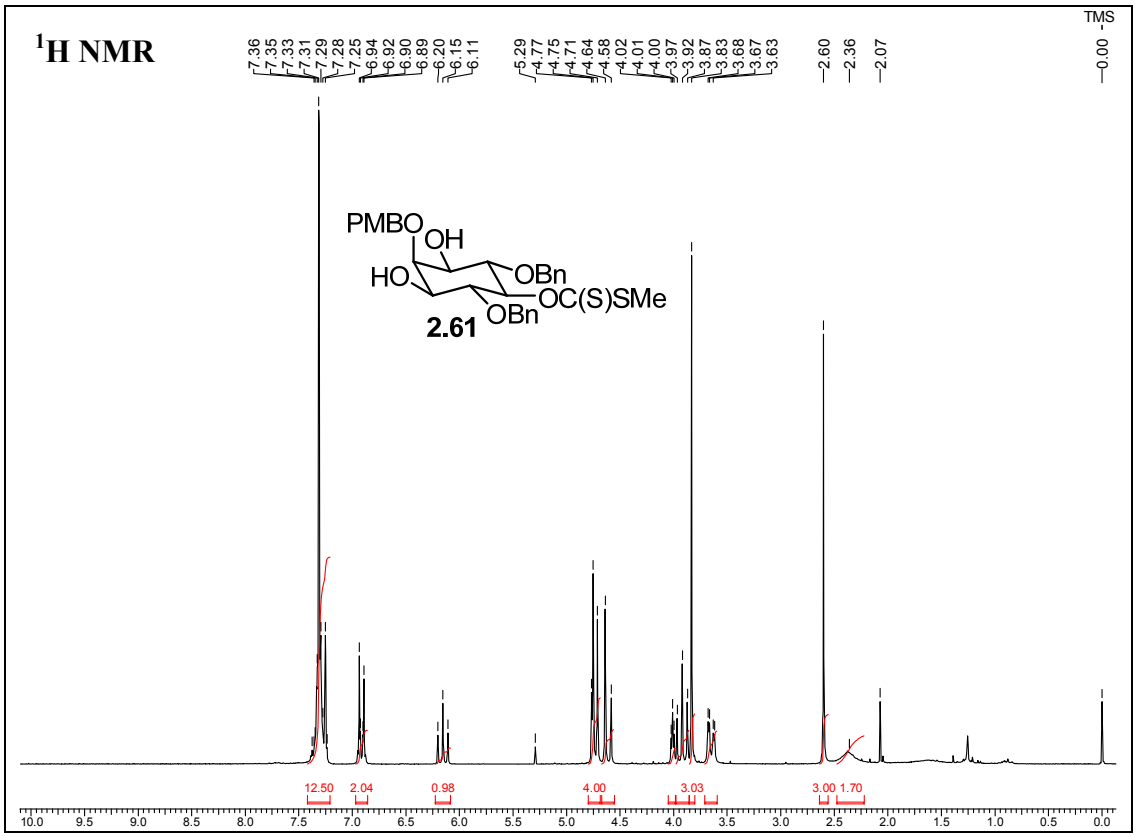


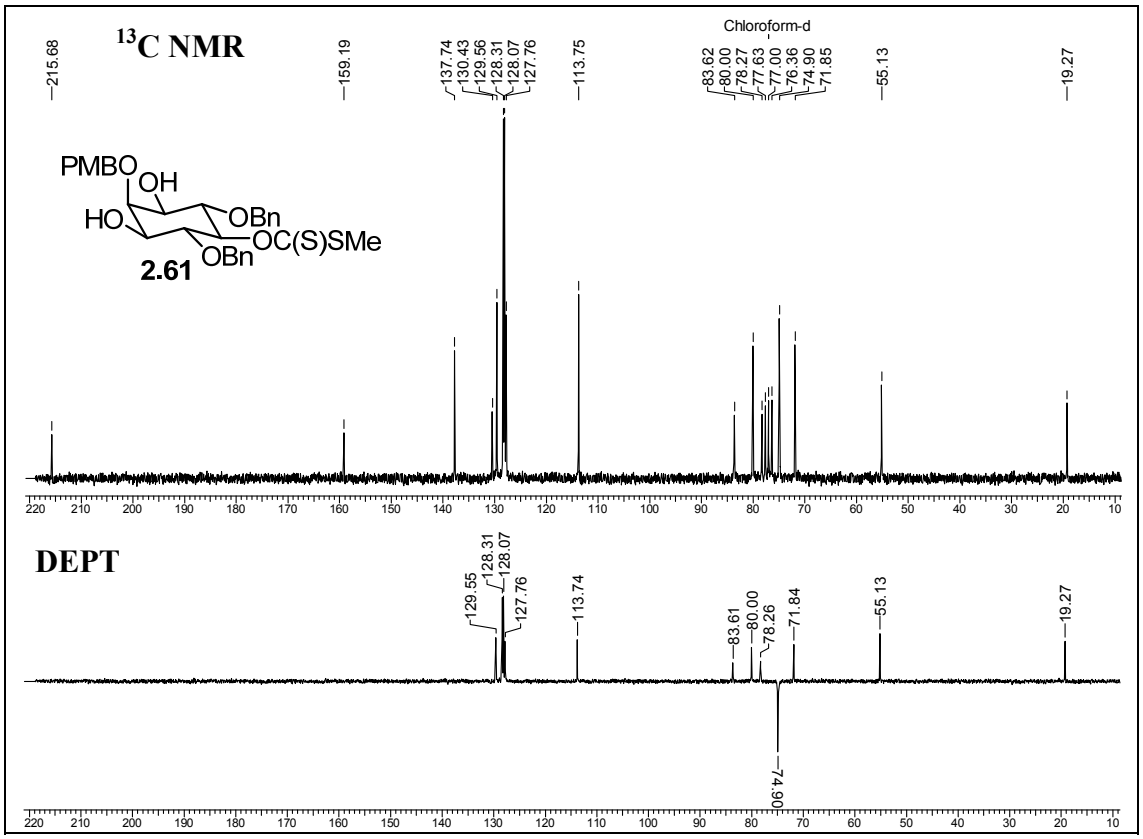
For 2D NMR see appendix III

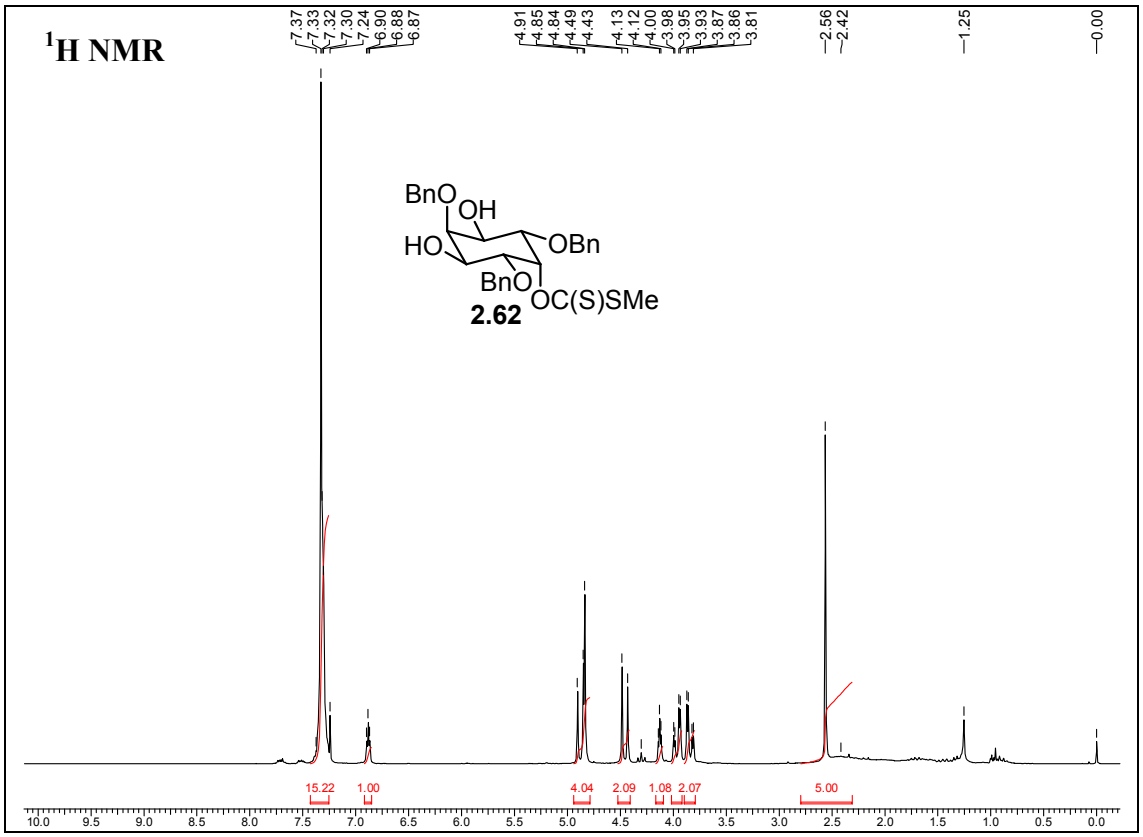


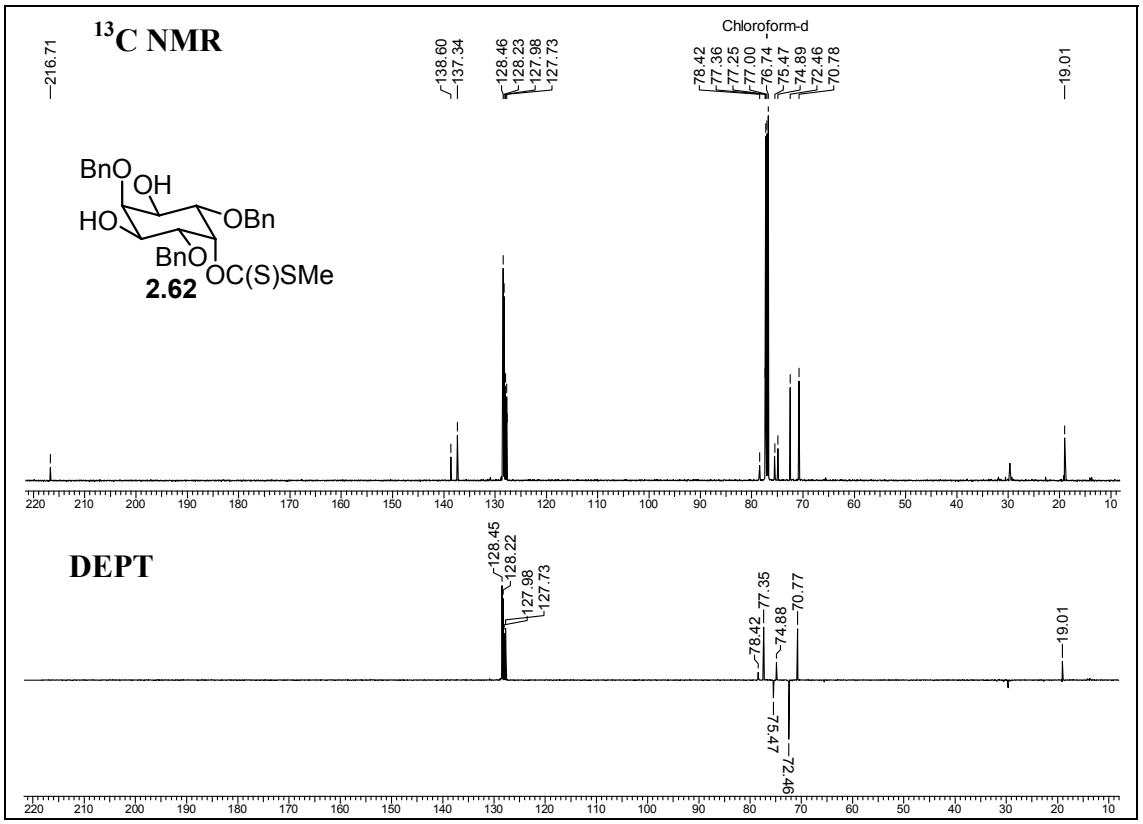


For 2D NMR see appendix III


^{1}H NMR
TMS
PMBO
OH
HO
OBn
OC(S)SMe
OBn
2.61


^{13}C NMR
Chloroform-d
PMBO
OH
HO
OBn
OC(S)SMe
OBn
2.61
DEPT


^{1}H NMR
BnO
OH
HO
OBn
BnO
OC(S)SMe
2.62


^{13}C NMR
Chloroform-d
BnO
OH
HO
OBn
BnO
OC(S)SMe
2.62
DEPT

Chapter 3

myo-Inositol 1,3-acetals as early intermediates for the synthesis of polyphenols and analogs of inositols

Section 3A. Synthesis of aminocyclitols

Section 3B. Synthesis of 5-*C*-alkyl/aryl *neo*-inositol derivatives

Section 3C. Inositols to aromatics (benzene free synthesis of tetra hydroxyl benzene derivatives)

The previous chapter presented results on a novel deoxygenation reaction of inositol-1,3-acetals *via* their xanthates. The present chapter attempts to investigate the advantages of using inositol-1,3-acetals to generate other types of inositol derivatives. The starting point of this work was the hope that inositol 1,3-bridged acetals could provide opportunities for new selective reactions since conformation of the two six membered rings in these acetals can deviate from the normal chair conformation found in most O-protected inositol derivatives. The present chapter delineates the synthesis of aminocyclitols, 5-C-alkyl/aryl *neo*-inositols and polyhydroxy benzene derivatives from *myo*-inositol *via* its 1,3-bridged acetals. Section A describes the synthesis of (i) *neo*-inosamine, (ii) aminocyclitol moiety of (–)hygromycin A (HMA) and its unnatural enantiomer and (iii) aminocyclitol moiety of (–)methoxyhygromycin (MHM), from *myo*-inositol *via* its 1,3-bridged acetals. These synthetic sequences represent the highest yielding procedures documented in the literature, due to the formation of exclusively one product in most of the synthetic steps. This work illustrates the flexibility and adaptability of the 1,3-bridged acetals to prepare biologically important inositol derivatives. Section B reports stereoselective introduction of alkyl and aryl substituent at the C5-position of the inositol ring *via myo*-5-inosose carrying 1,3-acetal bridge. Subsequent cleavage of 1,3-acetal gives the corresponding 5-*C*-alkyl/aryl *neo*-inositol. Section C reports a novel route to the synthesis of differentially protected tetrahydroxyl benzene derivatives which are important in the synthesis of differentially protected Baicalein (5,6,7-trihydroxy flavones) and biaryl derivatives starting from readily available *myo*-inositol. This provides a route for the synthesis of benzene derivatives from non-aromatic precursors.

Section 3A. Synthesis of aminocyclitols

3A.1. Introduction

Aminocyclitols are a wide class of compounds with interesting biological properties.[1] There have been continuous efforts in the recent past to obtain naturally occurring aminocyclitols as well as their synthetic analogues with enhanced or more selective biological profiles that could be useful in the intervention of cellular processes.[2] For instance, certain aminocyclitol derivatives (Chart 1.1 of chapter 1) have been shown to be potential candidates for the development of therapeutic agents,[3] enzyme inhibitors with

diverse biomedical applications[4] and also as molecular tools for the investigation of the *myo*-inositol cycle and related cellular processes.[5] Hygromycin A ((–)**1.5**, Chart 3.1) in addition to being a broad spectrum antibiotic,[6] functions as peptidyl transferase inhibitor,[7] hemagglutination inactivator, and as an effective agent for the control of swine dysentery.[8] A series of synthetic modifications and structure activity relationship studies to (–)**1.5** revealed that the aminocyclitol moiety in hygromycin A is critical for the antibacterial activity, while the fucofuranose moiety can be replaced with an allyl group or hydrogen.[8c,9] Methoxyhygromycin (MHM) (–)**1.6** is an analog of hygromycin A; it has been shown to have herbicidal activity.[8a,9b,10] *neo*-Inosamine (**3.3**) was isolated by hydrolysis of hygromycin A[11] and there is no reported synthesis of *neo*-inosamine **3.3**.

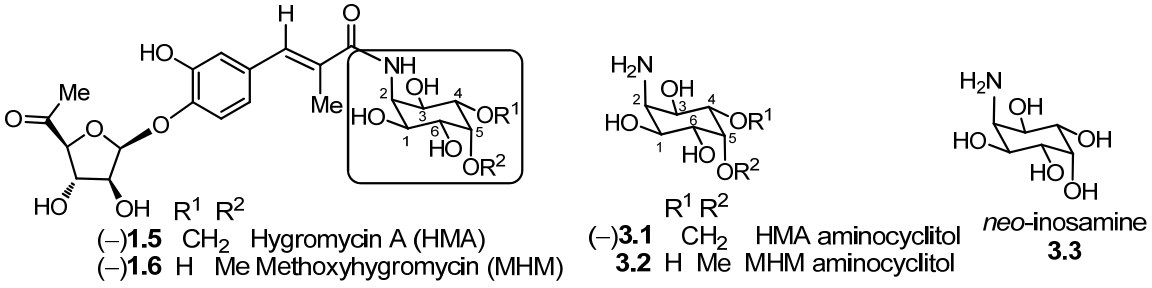


Chart 3.1: Structure of hygromycin A (HMA), methoxyhygromycin (MHM), their aminocyclitol units and *neo*-inosamine.

The aminocyclitol unit of (–)**1.5** has earlier been synthesized by Trost[12] from 1,4-benzoquinone (**3.4**) and Donohoe[13] from the Diels–Alder *endo*-adduct **3.5** of 1,4-benzoquinone and cyclopentadiene (Chart 3.2).

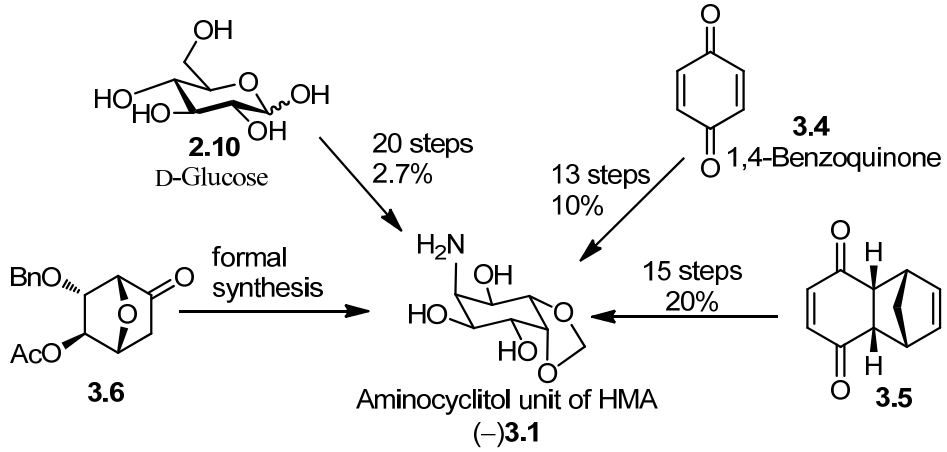


Chart 3.2: Summary of literature reported syntheses of aminocyclitol unit of HMA. Numbers on the arrow indicate total number of steps and overall yield.

A formal synthesis of (–)**3.1** was reported by Arjona[14] starting from **3.6**. The aminocyclitol **3.2** was synthesized from *myo*-inositol by Chida *et al*.[15] The complete synthesis of (–)**1.5** (from D-glucose) was reported by Ogawa *et al*[16] and Donohoe *et al* (from (–)**3.1** and D-Arabinose).[17] Biosynthesis of the aminocyclitol unit of (–)**1.5** has also been investigated.[18]

We envisioned a route to these aminocyclitols from abundantly available *myo*-inositol *via* its 1,3-bridged acetals. *myo*-Inositol has earlier been used as a starting material for the synthesis of natural products (Chart 3.3) other than (–)**3.1**.[19] However, its potential to be a starting material for the synthesis of natural products and their analogs has not been fully exploited.

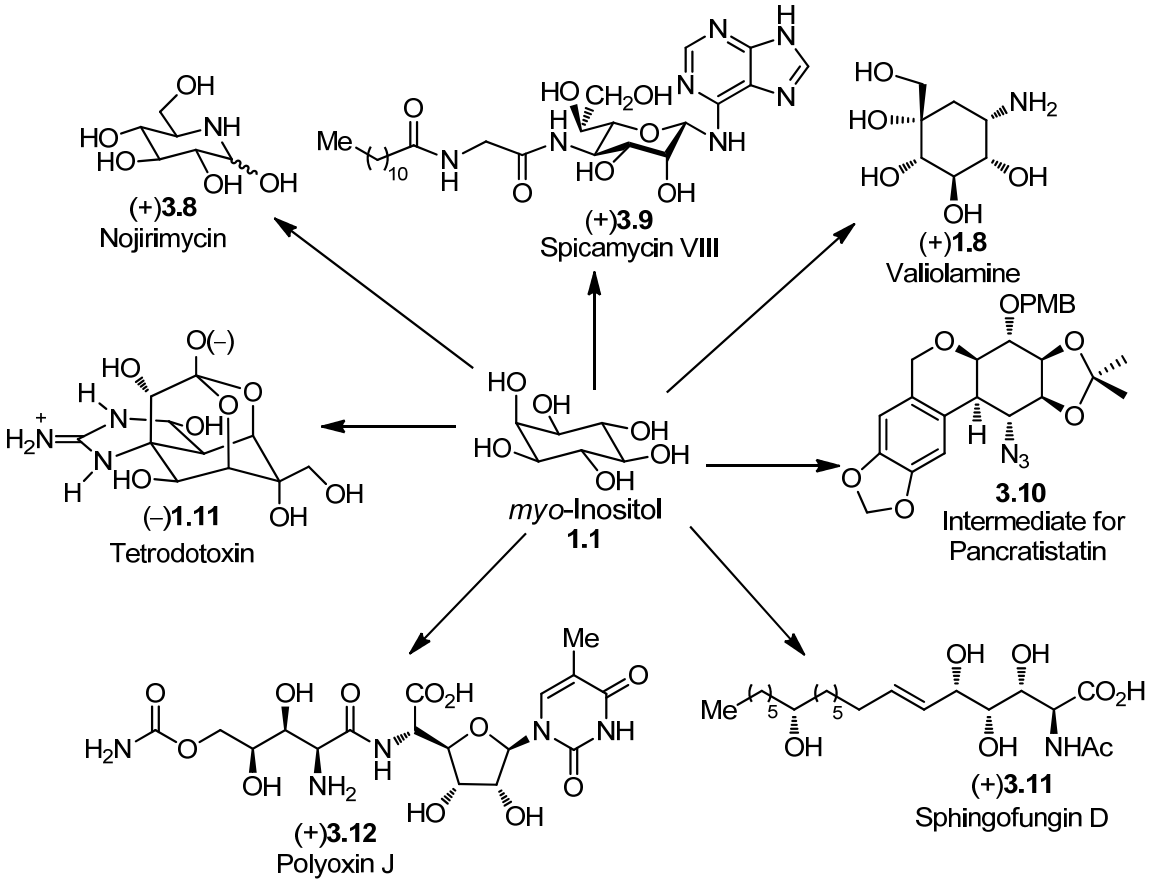
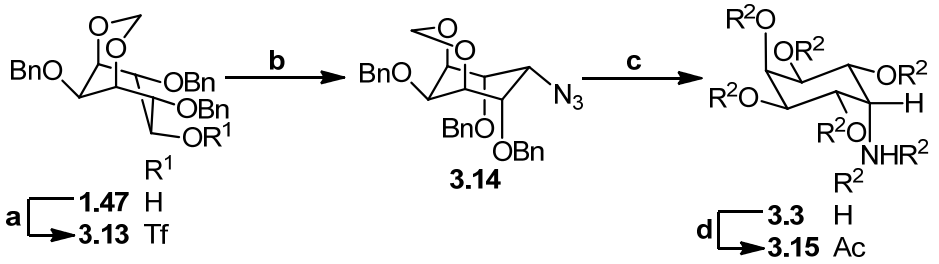


Chart 3.3: Natural products synthesized from *myo*-inositol.

3A.2. Results and discussion

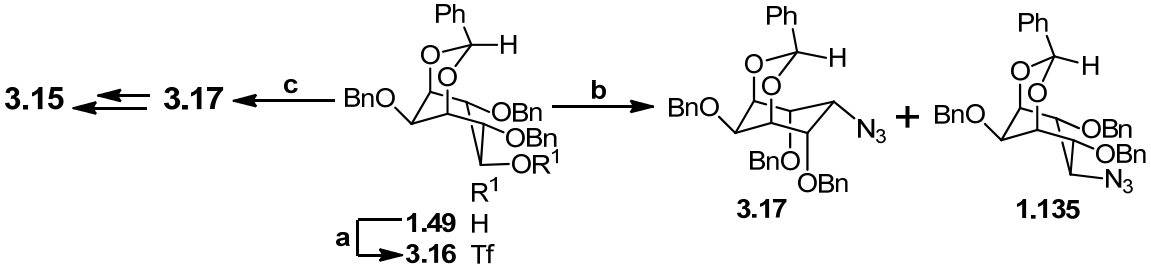
3A.2.1. Synthesis of 2-amino-2-deoxy-*neo*-inositol (3.3)

neo-Inosamine (**3.3**) was prepared from the protected *neo*-alcohol **1.47** (Scheme 3.1). Reaction of the triflate **3.13** with sodium azide in HMPA at room temperature (12 h) provided the *neo*-azide **3.14**. Reduction of the azide **3.14** as well as deprotection of the hydroxyl groups was achieved by hydrogenation in the presence of Pd/C. The crude 2-amino-2-deoxy-*neo*-inositol (**3.3**) obtained was isolated and characterized as its hexaacetate (**3.15**) in a good overall yield of 70% (7 steps from *myo*-inositol).



Scheme 3.1: (a) DCM, py., Tf_2O, 0 °C, 30 min; (b) HMPA, NaN_3, rt, 12 h, 92% (for 2 steps); (c) EtOH/HCl, H_2 (400 Psi), 20% Pd/C, rt, 32 h; (d) py., Ac_2O, DMAP, rt, 48 h, 84%.

Earlier work in our laboratory had shown that the reaction of the triflate **3.16** with sodium azide in DMF (100 °C), gives a mixture of *neo*- and *myo*-azides (Scheme 3.2).[20] Hence we carried out the reaction of triflate **3.16** with sodium azide in HMPA at room temperature which provided *neo*-azide **3.17** exclusively. The structure of **3.17** was established by single crystal X-ray diffraction analysis (Figure 3.1).



Scheme 3.2: (a) DCM, py., Tf_2O, 0 °C, 30 min; (b) DMF, NaN_3, 100 °C; (c) HMPA, NaN_3, rt, 12 h, 94%.

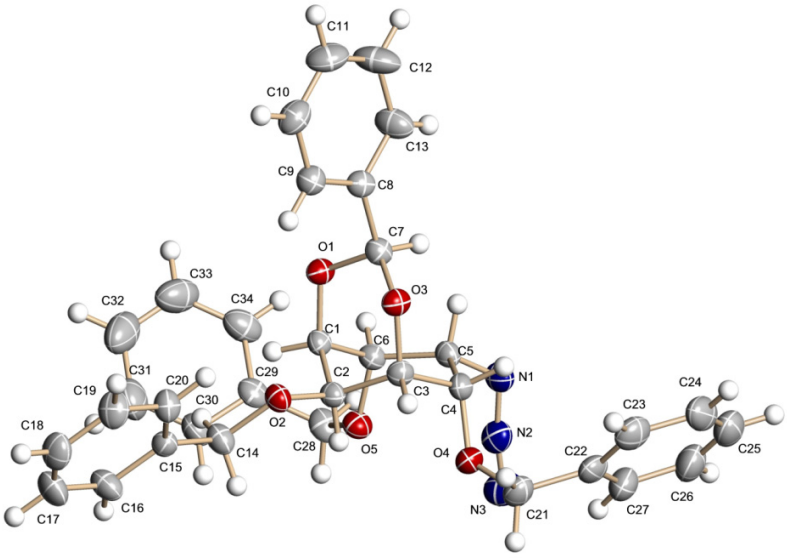


Figure 3.1: ORTEP of **3.17**. Thermal ellipsoids are drawn at 30% probability and hydrogen atoms are depicted as small spheres of arbitrary radii.

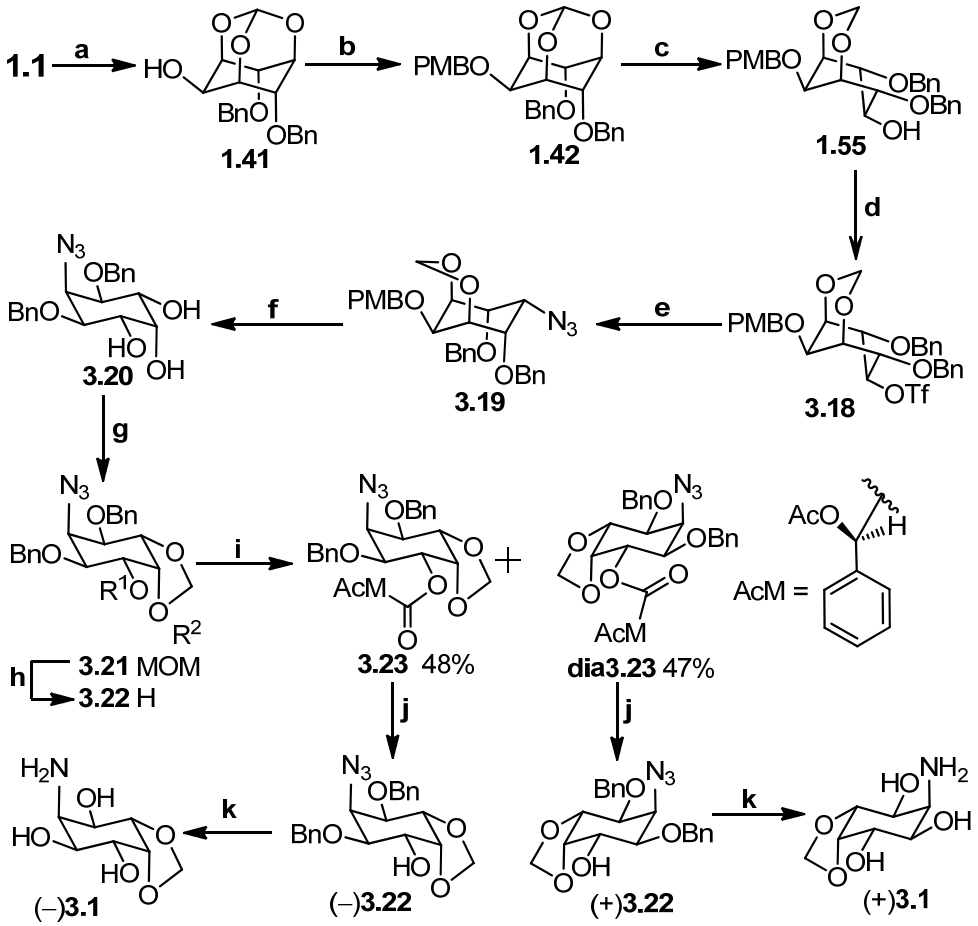
Since we were able to arive at experimetnal conditions (Scheme 3.2, c) for the selective substitution of the triflate (in **3.16**) by the azide ion, we proceeded to synthesize the aminocyclitol unit of HMA from *myo*-inositol.

3A.2.2. Synthesis of aminocyclitol unit of (–)hygromycin A (HMA)

A comparison of the structure of aminocyclitol unit of HMA ((–)**3.1**) and *myo*-inositol reveals that the relative orientation of all the substituents on the carbocylic ring, except the C5- substitutent is same in both the molecules. To convert *myo*-inositol (**1.1**) to (–)**3.1**, (a) C5-hydroxyl group must be converted to an amino group with inversion of configuration at the C5-carbon; (b) the C2 and C3-hydroxyl groups must be converted to the corresponding methylidene acetal and (c) *myo*-inositol derivative must be resolved or desymmetrized to obtain one enantiomer of the aminocyclitol unit of HMA. Key reactions in our synthetic approach to achieve these changes in *myo*-inositol were (i) one pot conversion of *myo*-inositol to 4,6-di-*O*-benzyl orthoformate **1.41**, (ii) regioselective cleavage of the orthoformate in **1.42**, (iii) stereospecific introduction of the azido group at C5 and (iv) the resolution of the *racemic*-alcohol **3.22** as its mandelate esters.

Our synthesis began with a one pot conversion of commercially available *myo*-inositol (**1.1**) to the dibenzyl ether **1.41** (Scheme 3.3).[21] The C-2 hydroxyl group in **1.41** was protected as the PMB ether (**1.42**) and the crude **1.42** was subjected to regioselective

cleavage by DIBAL-H[22] to obtain the alcohol **1.55**. The free hydroxyl group in **1.55** was converted to the corresponding triflate **3.18** by treating with triflic anhydride in dichloromethane/pyridine at –10 °C. Nucleophilic displacement of the triflate in **3.18** by azide in HMPA[20] gave the desired azide **3.19** in 94% yield (over 4 steps, **1.41** to **3.19**). The azide **3.19** was isolated by crystallization from hot 20% ethyl acetate in light petroleum. The PMB group and the 4,6-methylidene acetal in **3.19** were cleaved with concd HCl to obtain the triol **3.20**. Treatment of the triol **3.20** with TMSOTf/lutidine in dimethoxymethane gave *racemic* **3.21**; the MOM ether in **3.21** could be cleaved in refluxing methanol in the presence of catalytic amount of TsOH[12,23] without disturbing the *cis*-acetal to obtain the *racemic* alcohol **3.22** exclusively.



Scheme 3.3: (a) DMF, $HC(OEt)_3$, TsOH, 110 °C, 4 h then DMF, LiH, BnBr, rt, 12 h 84% (for 2 steps); (b) DMF, NaH, PMBCl, rt, 3 h; (c) DCM, DIBAL-H in toluene, rt, 3 h; (d) DCM, py., Tf_2O, 0 °C, 30 min; (e) HMPA, NaN_3, rt, 12 h, 94% (for 4 steps); (f) THF:MeOH, HCl, reflux, 1 h, 98%; (g) $H_2C(OMe)_2$, TMSOTf, 2,6-Lutidine, 0 °C–rt; (h) MeOH, TsOH (cat), reflux, 12 h, 94% (for 2 steps); (i) DCM, R(–)-*O*-acetylmandelic acid, DCC, rt, 3 h; (j) MeOH, KOH, rt, 2 h, 98–99%; (k) MeOH, AcOH, H_2 (400 psi), 20% Pd/C, rt, 40 h, 92–94%.

To synthesize the enantiomeric aminocyclitol of HMA, the *racemic*-alcohol **3.22** was *O*-acylated with R(−)-*O*-acetylmandelic acid in the presence of DCC. The diasteriomeric esters (1:1) were seperated by flash coloumn chromatography to isolate **3.23** (48%) and **dia3.23** (47%). The structure and relative configuration of **3.23** was confirmed by single crystal X-ray diffraction analysis (Figure 3.2).

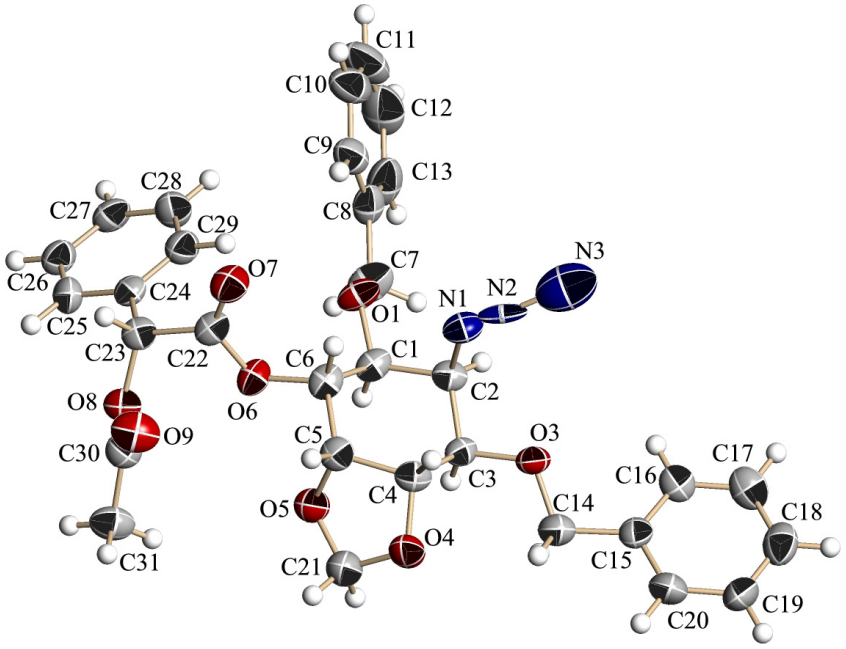
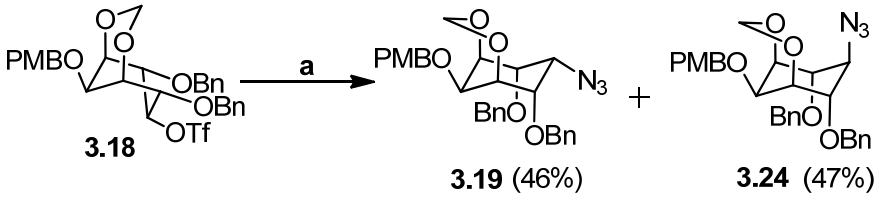


Figure 3.2. ORTEP of **3.23**. Thermal ellipsoids are drawn at 50% probability and hydrogen atoms are depicted as small spheres of arbitrary radii.

The mandelate ester in **3.23** was hydrolyzed in methanolic KOH at room temperature to obtain (−)**3.22**. Finally, cleavage of the two *O*-benzyl ethers and reduction of the azide to amine was carried out by catalytic hydrogenolysis in the presence of Pd/C, in methanol-AcOH to afford the amino cyclitol (−)**3.1**. Similarly we also converted **dia3.23** to the unnatural isomer (+)**3.1**. All in all, the aminocyclitol unit of **1.5** as well as its enantiomer were obtained in 11 steps from *myo*-inositol, with 31% overall yield. It is pertinent to note that none of the synthetic steps during the conversion of **1.1** to **3.19** involved chromatography and the latter six steps (except the separation of **3.23** and **dia3.23**) resulted in the formation of a single product, which were isolated by chromatography. We also prepared *racemic* amino cyclitol unit of HMA by reduction of the azide and cleavage of the benzyl ethers in *racemic* **3.22**. This was done in order to optimize the reaction conditions before the resolution of **3.22** and preparation of the

enantiomeric aminocyclitol **3.1**. While carrying out these experiments we observed that **3.20** could be converted to the desired 1,2-methylidene acetal **3.22** by using $POCl_3$ and DMSO,[24] but the yield obtained was very low (20%). Hence we opted for the conversion of **3.20** to **3.22** *via* the MOM ether **3.21**.

The hurdles we faced during the synthesis shown in Scheme 3.3 and their circumvention are briefly described below. We initialy used DMF as a solvent for the substitution of the triflate in **3.18** by the azide ion. This reaction gave a mixture of isomeric azides **3.19** and **3.24** (1:1), separable by chromatography (Scheme 3.4). Configuration of the *neo*-azide **3.19** and *myo*-azide **3.24** was established unambiguously by single crystal X-ray diffraction analysis (Figure 3.3). Perhaps this nucleophilic substitution reaction proceeds by an S_N1 like mechanism in DMF resulting in the formation of both the possible isomeric azides. It is likely that the intermediate carbocation at the C-5 position is stabilized by two neighboring benzyloxy groups at C-4 and C-6 positions.



Scheme 3.4: (a) DMF, NaN_3, 100 °C, 1 h.

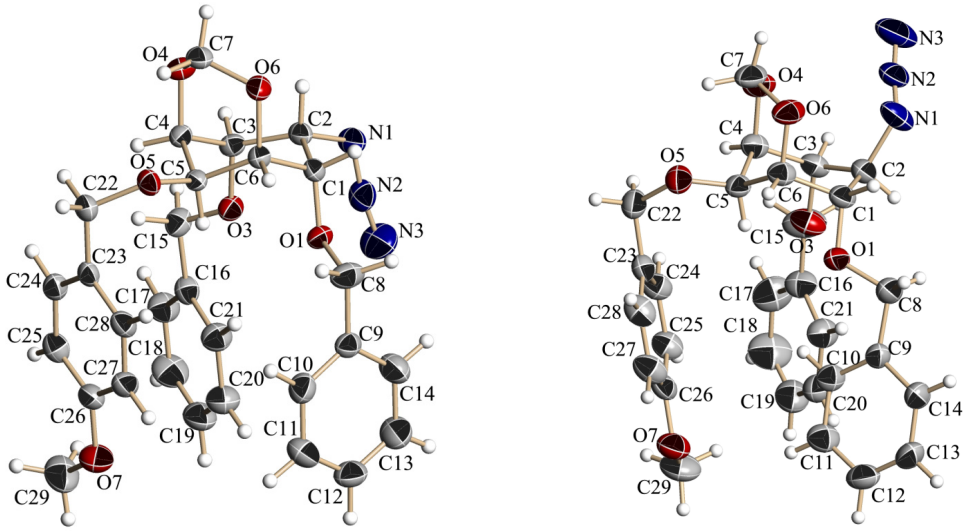
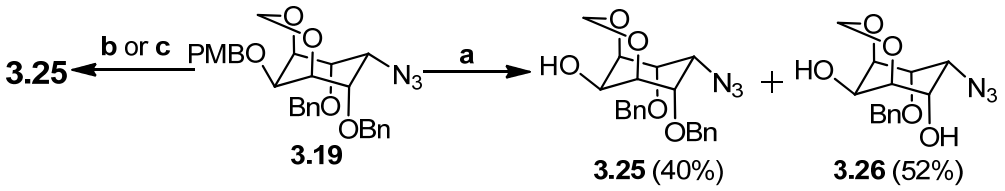


Figure 3.3: ORTEP of (a) **3.19** and (b) **3.24**. Thermal ellipsoids are drawn at 50% probability and hydrogen atoms are depicted as small spheres of arbitrary radii.

Our initial attempts to cleave the PMB ether in **3.19** with DDQ resulted in the concomitant cleavage of one of the benzyl ethers as well.[25] However we could achieve the exclusive cleavage of the PMB ether by carrying out the reaction of **3.19** with DDQ under controlled conditions (Scheme 3.5). The structures of the mono and the dibenzyl ethers **3.25** and **3.26** were established by single crystal X-ray diffraction analysis (Figure 3.4).



Scheme 3.5: (a) DCM:H_2O (95:5), DDQ (2 eq), rt, 3–12 h; (b) DCM:H_2O (95:5), DDQ (1.5 eq), rt, 1.5 h, 88%; (c) DCM, $MgBr_2$, 0 ^oC–rt, 10 h, 65%.

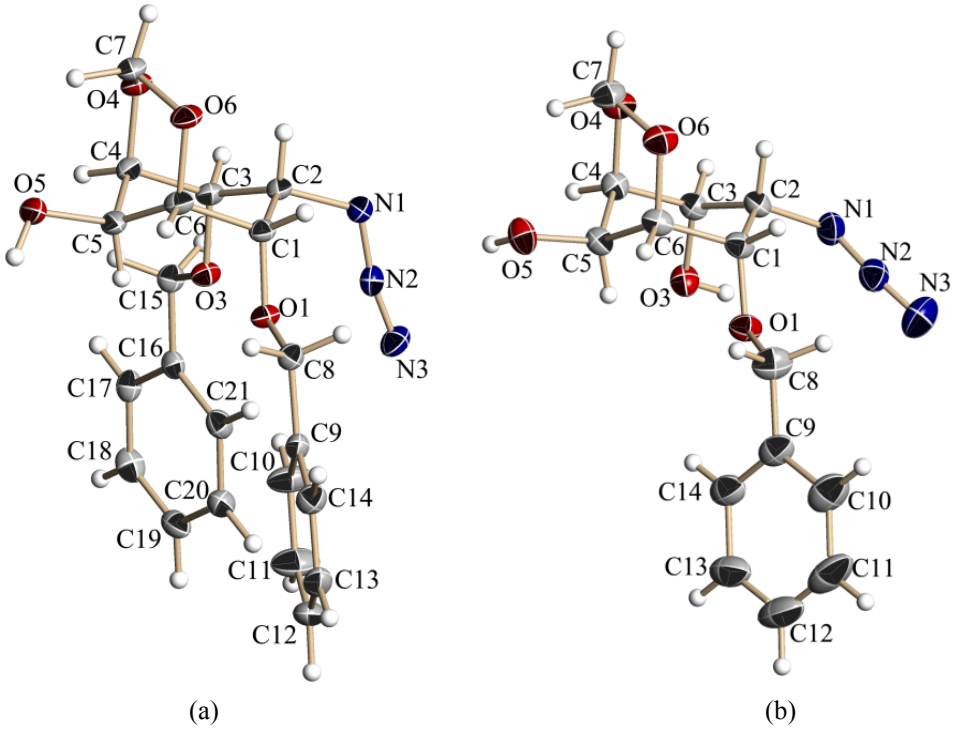
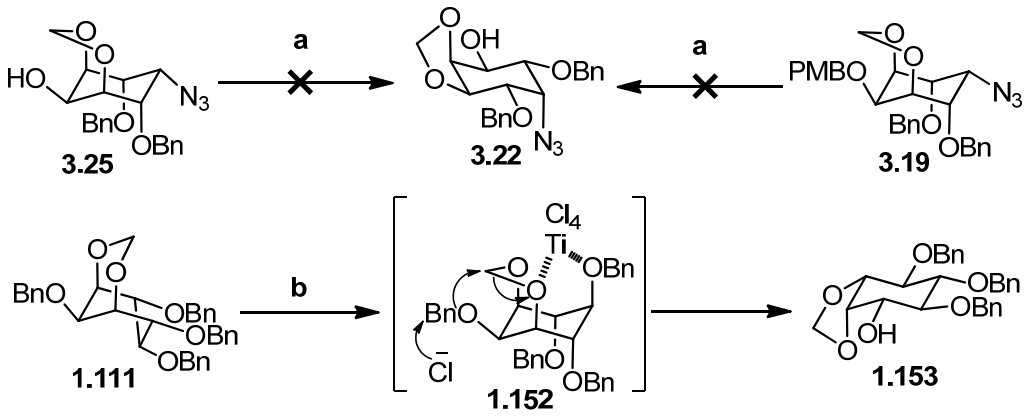


Figure 3.4: ORTEP of (a) **3.25** and (b) **3.26**. Thermal ellipsoids are drawn at 50% and 30% probability respectively and hydrogen atoms are depicted as small spheres of arbitrary radii.

Our attempts to isomerize the 1,3-methylidene acetal in **3.19** and **3.25** (which appears to be less stable due to bicyclic system with four axial substituents) in the presence of Lewis acids ($TiCl_4$, $ZnCl_2$, $MgBr_2$, $BF_3.OEt_2$)[22a,26] to the corresponding 1,2-methylidene acetal **3.22** (which would result in the flipping of the inositol ring), failed (Scheme 3.6). We attempted this isomerization since the 1,3-acetal **1.111** on treatment with

stoichiometric quantity of titanium tetrachloride is known to give the 1,2-acetal **1.153** (Scheme 3.6).[22a,27]

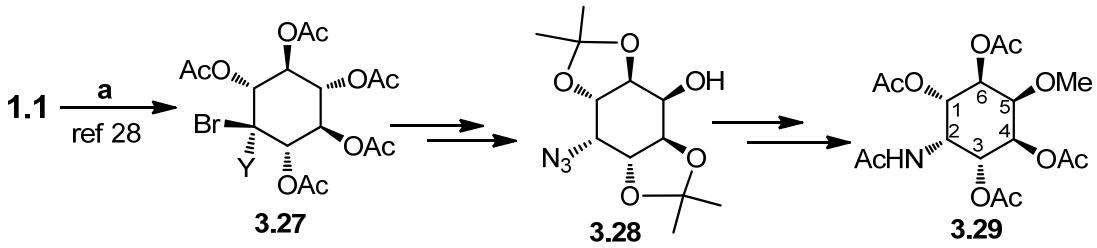


Scheme 3.6: (a) DCM, Lewis ($TiCl_4$, $ZnCl_2$, $MgBr_2$, $BF_3{\cdot}OEt_2$), –78 °C–rt, 5–12 h; (b) DCM, $TiCl_4$, –78 °C.

The mechanism proposed for the conversion of **1.111** to **1.153** requires chelation of titanium with three axially oriented oxygen atoms of the cyclitol. Perhaps, the isomerization of **3.19** or **3.25** to the corresponding 1,2-acetal did not proceed due to the absence of a suitably oriented oxygen atom at the C5-position of the inositol ring in **3.19** and **3.25**, to aid the chelation of the Lewis acid.

3A.2.3. Synthesis of aminocyclitol unit of methoxyhygromycin

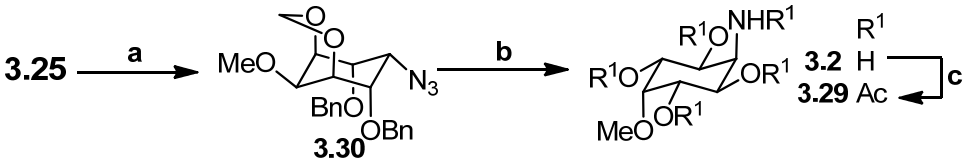
Methoxyhygromycin has been synthesized from *myo*-inositol; this sequence of reactions yielded the aminocyclitol unit in <1% overall yield in 12 steps (Scheme 3.7). [15]



Scheme 3.7: (a) AcBr, Ac_2O, 120 °C, 11%.[28]

In the present work the aminocyclitol unit of methoxyhygromycin was synthesized from the alcohol **3.25** by (a) methylation of C2-hydroxyl group in **3.25** (Scheme 3.8); (b) deprotection of all the hydroxyl groups as well as reduction of the azide to the amine in a single step. The aminocyclitol unit **3.2** of MHM was isolated as its pentaacetate **3.29**. The structure of **3.29** was established by single crystal X-ray diffraction analysis (Figure 3.5).

This synthetic sequence involved 9 steps from *myo*-inositol, in 4 pots, and the overall yield of **3.29** was 56%.



Scheme 3.8: (a) DMF, NaH, MeI, rt, 3 h; (b) MeOH, concd HCl, H_2 (400 psi), 20% Pd/C, 55 °C, 12 h; (c) py., Ac_2O, 40 h, 81% (for 3 steps).

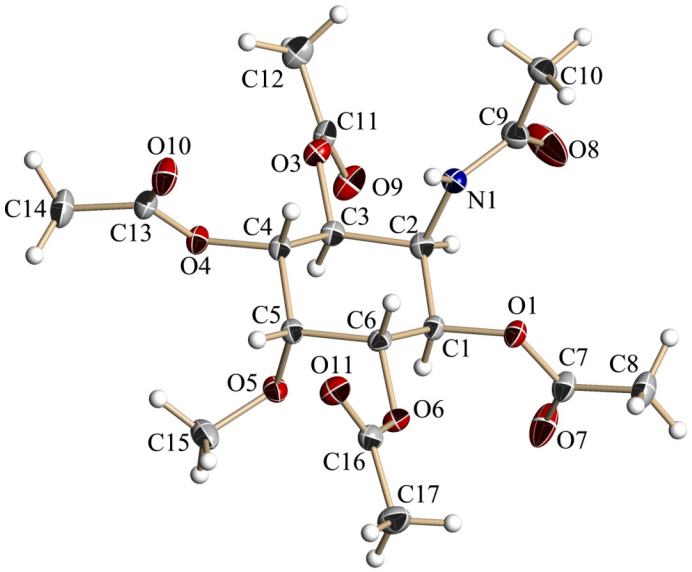
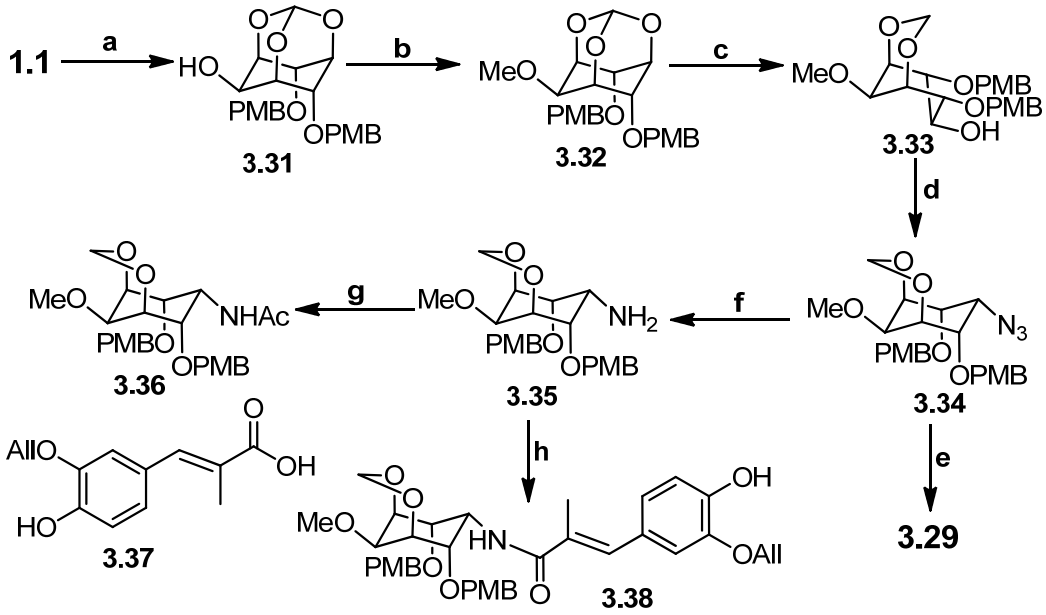


Figure 3.5: ORTEP of **3.29**. Thermal ellipsoids are drawn at 30% probability and hydrogen atoms are depicted as small spheres of arbitrary radii.

3A.2.4. Synthesis of an intermediate for the synthesis of MHM (an approach towards the total synthesis of MHM)

An intermediate **3.38** for the synthesis of MHM ((–)**1.6**) was synthesized from *myo*-inositol (**1.1**) *via* its 1,3-acetal as shown in Scheme 3.9. This synthetic sequence is similar to that shown in Scheme 3.3, except that the C4- and C6-hydroxyl groups of *myo*-inositol were protected as the corresponding PMB ethers since we planned to adopt the sequence of reactions in Scheme 3.9 for the synthesis of MHM. This would allow the deprotection of C4- and C6- hydroxyl groups in the end, without hydrogenolysis (as MHM has a C-C double bond). The azide was introduced at the C5-positiion as described in section 3A.2.2. The structure of **3.34** was established by single crystal X-ray diffraction analysis (Figure 3.6). The azide in **3.34** was reduced to the corresponding amine by Staudinger reaction and

the amine **3.35** was characterized as its acetate **3.36** (Scheme 3.9). The structure of **3.36** was established by single crystal X-ray diffraction analysis (Figure 3.7). The amine **3.34** was coupled with acid **3.37**[17] in EDC·HCl, to obtain the amide **3.38** which can be converted to MHM or its analogs by glycosylation and global deprotection.



Scheme 3.9: (a) DMF, $HC(OEt)_3$, TsOH, 110 °C, 4 h then DMF, LiH, PMBCl, rt, 3 h, 82%; (b) DMF, NaH, MeI, rt, 3 h; (c) DCM, DIBAL-H in toluene, rt, 3 h; (d) i) DCM, py., Tf_2O, 0 °C, 30 min; ii) HMPA, NaN_3, rt, 12 h, 88% (for 4 steps); (e) i) MeOH, concd HCl, H_2 (400 psi), 20% Pd/C, 60 °C, 12 h; ii) py., Ac_2O, 40 h, 84% (for 2 steps); (f) DCM, PPh_3, H_2O; (g) py., Ac_2O, rt, 12 h, 82%; (h) **3.37**, DCM, EDC·HCl, HOBt, DIEPA, rt, 5 h, 85%.

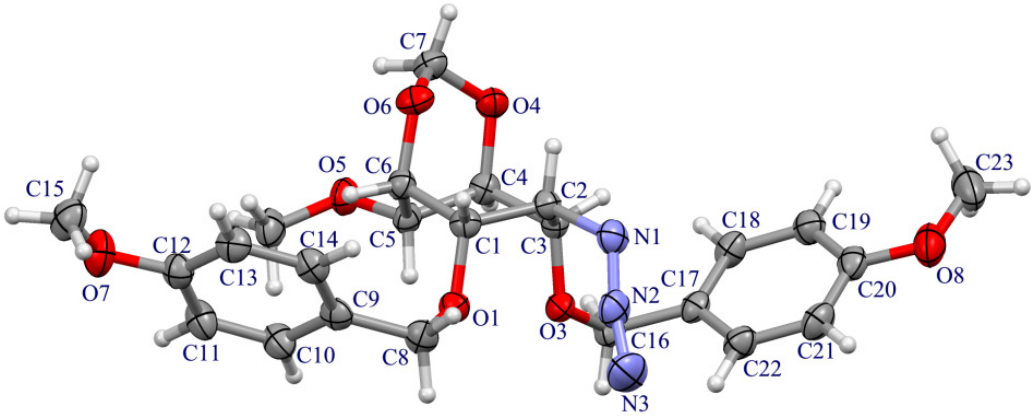


Figure 3.6: ORTEP of **3.34**. Thermal ellipsoids are drawn at 30% probability and hydrogen atoms are depicted as small spheres of arbitrary radii.

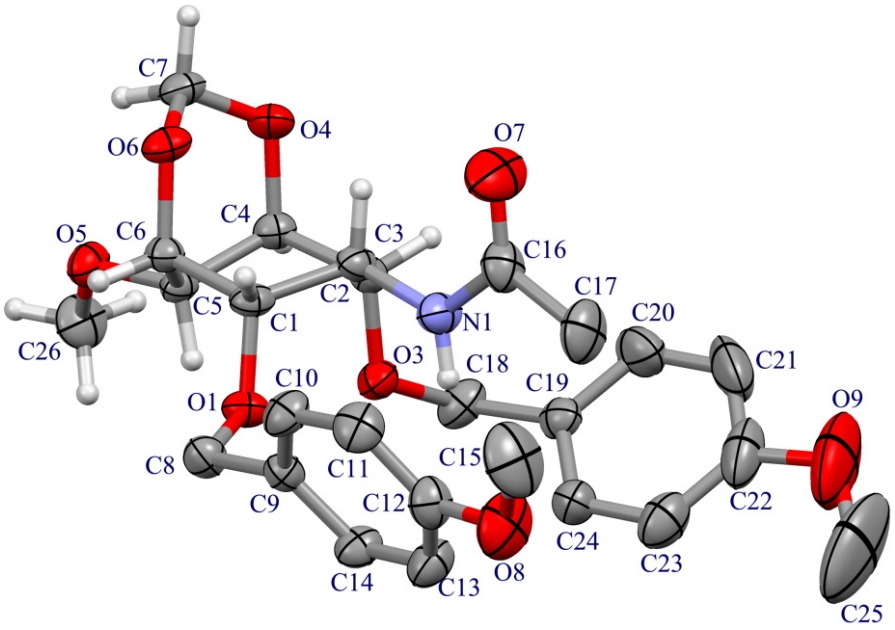
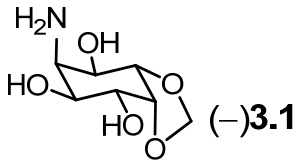
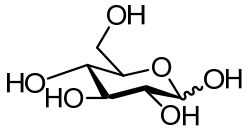
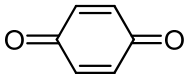
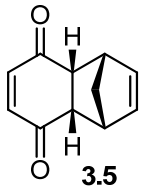
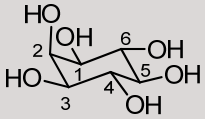
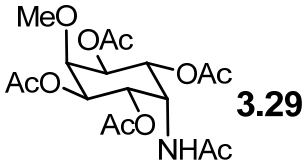


Figure 3.7: ORTEP of **3.36**. Thermal ellipsoids are drawn at 30% probability and hydrogen atoms are depicted as small spheres of arbitrary radii.

Deprotection of all the hydroxyl groups as well as reduction of the azide in **3.34** to the amine in a single step gave the aminocyclitol unit of MHM which was isolated as its pentaacetate **3.29**. This synthetic sequence involved 7 steps, in 4 pots, and the overall yield of **3.29** was 61%; all the products were isolated / purified by crystallization. Incidently, this scheme of reactions provided a better route for the synthesis of the aminocyclitol unit of MHM.

Table 3.1 gives a comparison of the previously known methods of synthesis of aminocyclitols **3.1** and **3.2** with the methods described in this section. This comparison clearly establishes the advantages of the current methodology involving inositol 1,3-acetals as early intermediates.

Table 3.1: Synthesis of aminocyclitol unit of HMA and MHM; comparison with methods reported in the literature.

Sr. No.	Starting material	No. of steps	Overall yield[a] (%)	Reference
	 (−)**3.1**			
1	 D-Glucose (**2.10**)	20	2.7	16b
2	 1,4-benzoquinone (**3.4**)	13	10	12
3	 **3.5**	14	12	13
4		15	20	17
5	 *myo*-Inositol (**1.1**)	**12**	**31**	**Present work**
	 **3.29**			
6	*myo*-Inositol (**1.1**)	11	4	15
7	*myo*-Inositol (**1.1**)	**7 (4 pot)**	**61**	**Present work**

[a]Overall yield refers to aminocyclitol units of HMA/MHM

Section B. Synthesis of 5-*C*-alkyl/aryl *neo*-inositol derivatives

3B.1. Introduction

C-methyl inositols, laminitol ((–)**3.39**, Chart 3.4) and mytilitol (**3.40**), having *myo*- and *scyllo*-type configurations, respectively, occur in marine algae.[29] Carbaglycosylamines, such as valiolamine ((+)**1.8**) and validamine ((+)**1.9**), are of microbial origin, and their analogues, possess inhibitory activity toward certain glycosidases.[30] Among several analogues of validamine synthesized, **3.41** was demonstrated to be a very strong α-fucosidase inhibitor.[31] C-Aryl polyhydroxylated cyclohexane rings are found in the amaryllidaceae family of natural products, most notably pancratistatin, lycoricidine and narciclasine and their analogs (Chart 3.4).[32]

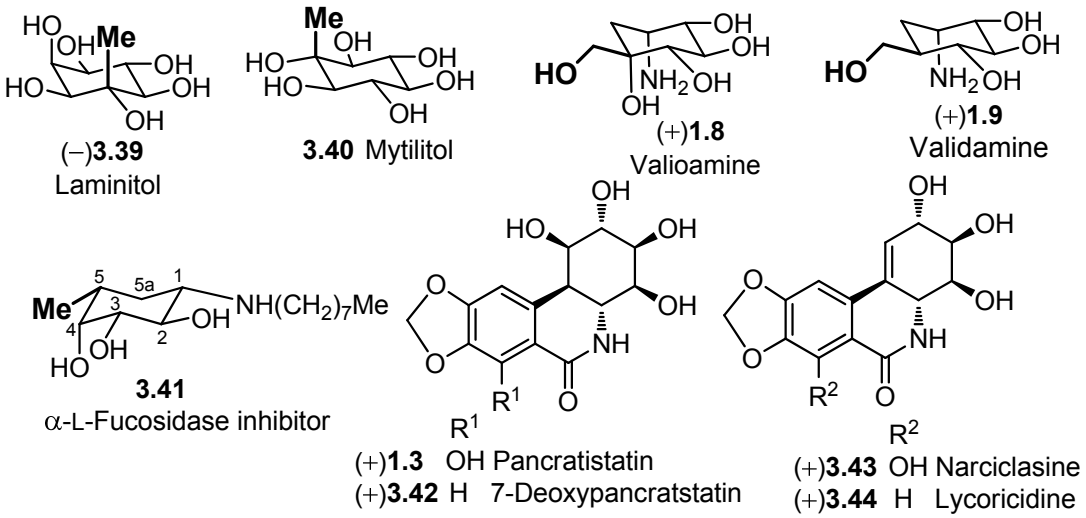
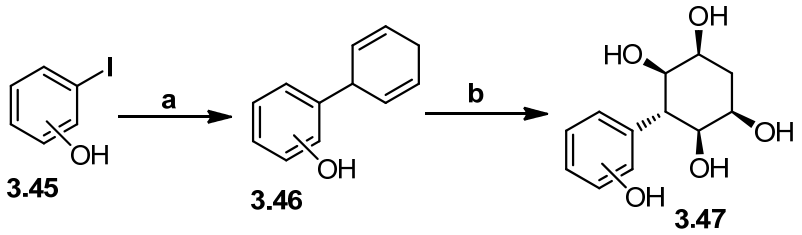


Chart 3.4: Natural and synthetic C-alkyl/aryl cyclitols.

C-alkyl and C-aryl polyhydroxylated cyclohexanes and their derivatives are widespread constituents of biologically important compounds, the most obvious instances being the carbasugars.[33] With their ability to function as glycosidase inhibitors, C-alkyl and C-aryl polyhydroxylated cyclohexanes have potential in many therapeutic areas. C-Linked glycosyl inositols are potentially valuable mechanistic probes, because of their greater hydrolytic stability and different conformational behavior compared with their parent O-glycosides.[34] Simple C-branched inositols are synthetic precursors to these and other groups of inositol mimetics. Due to the potential utility of C-alkyl/aryl

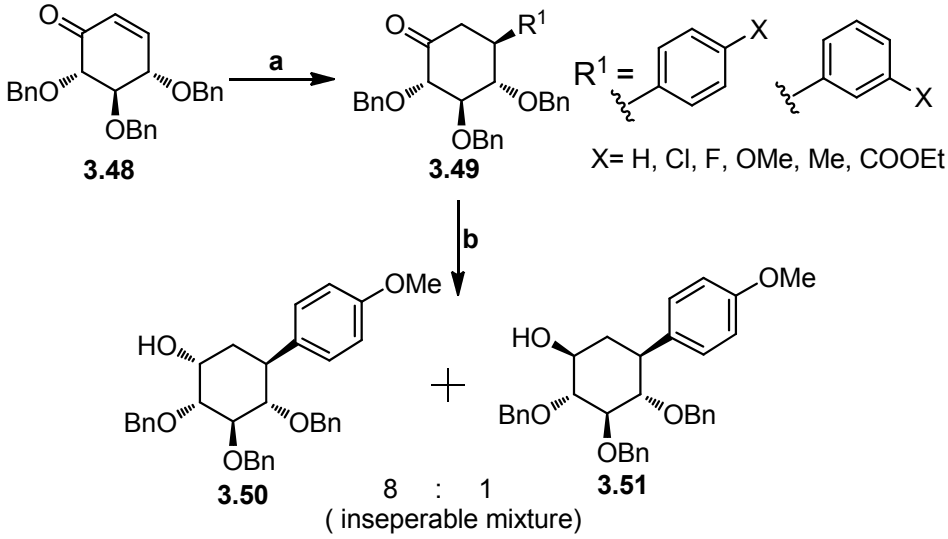
polyhydroxycyclohexanes, there have been studies directed towards their synthesis. Some of these pertinent and recent reports are mentioned below.

Synthesis of phenolic cyclitols was reported[35] by reductive radical arylation of benzene and subsequent hydroxylation with osmium tetroxide (Scheme 3.10).



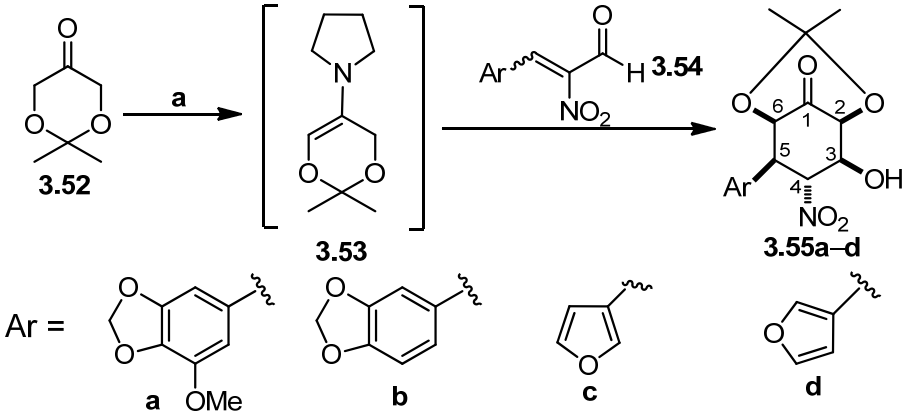
Scheme 3.10: (a) benzene, *n*-Bu_3SnH, PhSeH, 49%; (b) OsO_4, NMO, 65–78%.

Synthesis of triethereal cyclohexanones was reported[36] *via* copper (I) mediated 1,4-addition of organometallic reagents to glucose-derived triethereal cyclohexenone **3.48** (Scheme 3.11). The cyclohexanones generated were further reduced with modest stereoselectivity to afford a variety of substituted inositol derivatives.



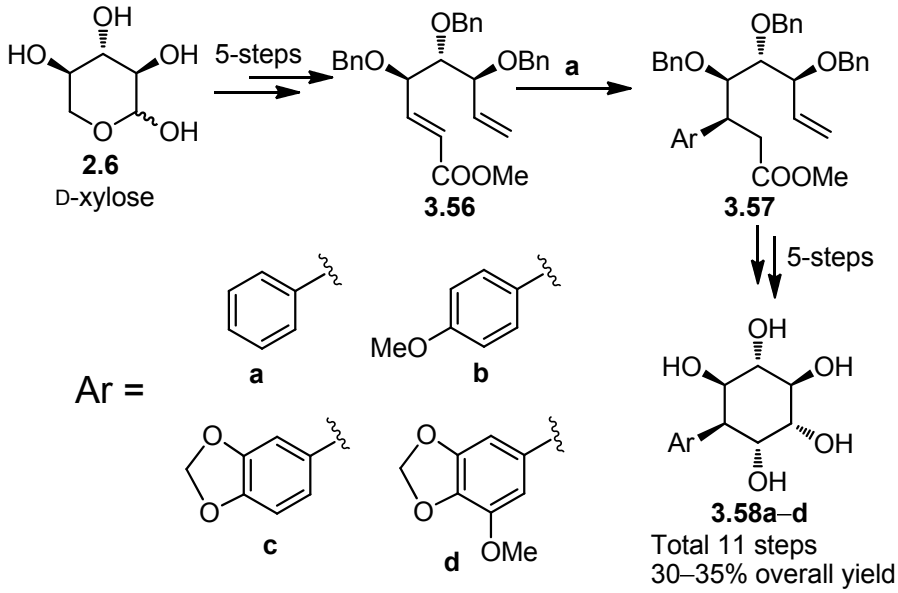
Scheme 3.11: (a) THF, R^1CuM, $BF_3{\cdot}OEt_2$, –78 °C, 70–83%; (b) THF, MeOH, $NaBH_4$, –10 °C.

A highly stereocontrolled formal [3 + 3] annulation of β-aryl-α-nitro-α,β-enals (**3.54**) with the enamine **3.53** derived from 2,2-dimethyl-1,3-dioxan-5-one (**3.52**) and pyrrolidine (Scheme 3.12) was reported.[37] This reaction created protected nitrocyclitols (**3.55a**–**d**) with five stereocentres and constituted the key step in a short, gram-scale synthesis of a pancratistatin analogs.



Scheme 3.12: (a) MeCN or DMF, pyrrolidine, PPTs (0.2 eq), 30–40%.

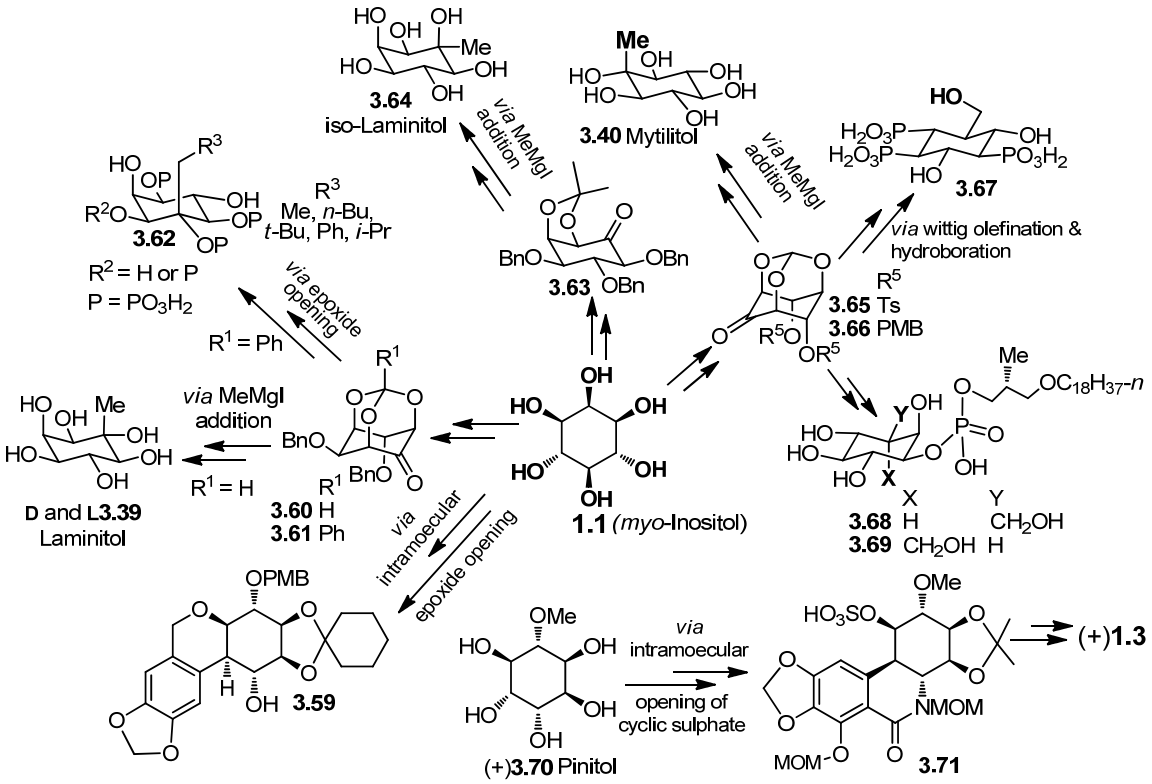
Aromatic analogues of conduritol and L-*chiro*-inositol (**3.58a**–**d**) synthesized from D-xylose (Scheme 3.13) were evaluated for anticancer activity.[38] The lack of activity of these compounds provided a further insight into pancratistatin's minimum structural requirements for cytotoxicity, particularly the criticality of the intact phenanthridone skeleton.[38]



Scheme 3.13: (a) $Ar_2CuMgBr$, Me_3SiCl, 85–97%.

There are few reports on the syntheses of C-branched cyclitols by modification of naturally occurring inositols. Some of the examples are shown in Scheme 3.14: (i) an advanced intermediate **3.59** for the synthesis of 7-deoxypancratistatin (**3.42**);[19a] (ii) (+)pancratistatin ((+)**1.3**);[39] (iii) laminitol (**3.39**) and *iso*-laminitol (**3.64**);[40] (iv) mytilitol (**3.40**) and D- and L-laminitol (**3.39**);[41] (v) *racemic* 6-deoxy-6-hydroxymethyl-*scyllo*-inositol-1,2,4-

trisphosphate (**3.67**);[39,42] (vi) 4-C-alkyl Ins(1,4,5)P_3 and Ins(1,3,4,5)P_4 (**3.62**);[43] (vii) PI analogs **3.68** and **3.69**.[44] All these compounds except **3.71** were sythesized from *myo*-inositol.



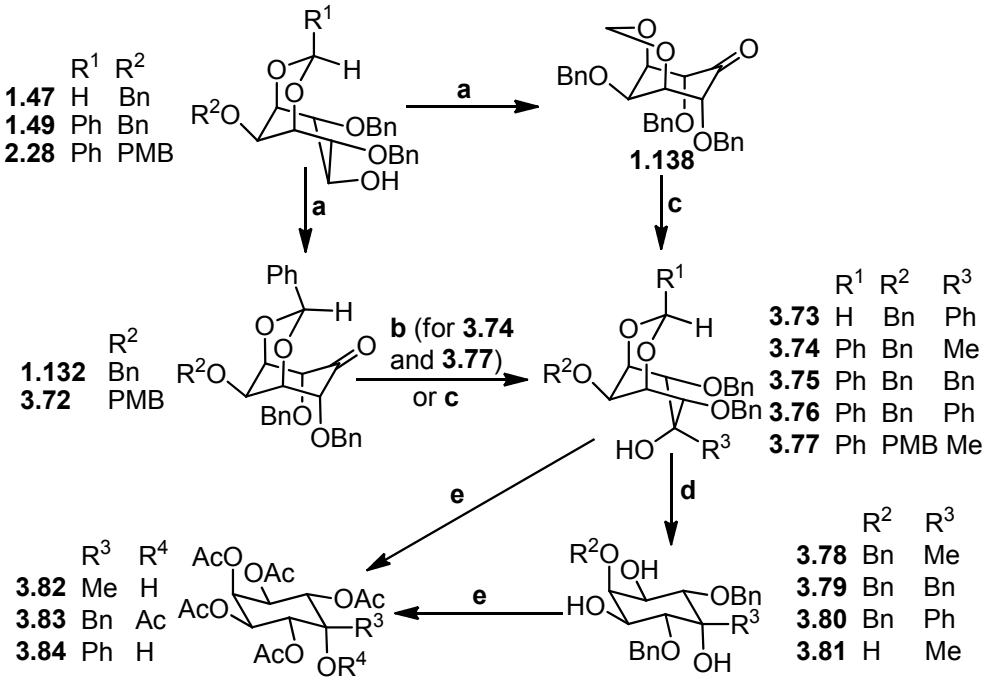
Scheme 3.14: C-branched cyclitols and natural products synthesized from naturally occurring inositols.

It was found that[43] the addition of MeMgI to the *myo*-4-inosose **3.61** (Scheme 3.14) resulted in the formation of axial alcohol with equatorial attack of methyl group. But the reaction of **3.61** with larger alkyl Grignard reagents resulted in the complete reduction of the inosose to get axial alcohol by β-hydride transfer, without any detectable alkyl addition. The reduction of inosose as well as addition of Grignard reagent to inosose favors the formation of the axial alcohol as a major product.[45] However, reactivity of a carbonyl group is susceptible to the presence of agents which can interact with the oxygen atom of the carbonyl group. For instance, the factors which facilitate the reaction of organometallic reagents with carbonyl compounds are the interaction of the carbonyl oxygen with metal ions and the steric factor where the conformation or the orientation of the molecule directs the nucleophilic addition. Such chelation effects and steric effects could gain prominence during nucleophilic addition to cyclohexanones derived from cyclitols and their derivatives

since they contain several hetero atoms. The focus in the present section however is to see if conformation of the inositol and acetal rings and orientation of the *O*-benzyl groups with respect to the carbonyl groups influence the product selectivity.

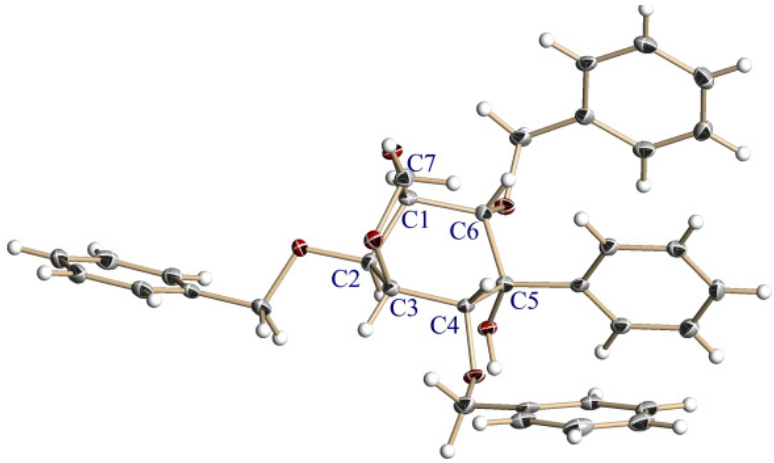
3B.2. Results and discussion

The *myo*-5-inosose **1.132** on reaction with alkyl and aryl Grignard reagents in diethyl ether at –10 °C gave 5-*C*-alkyl/aryl *neo*-inositol derivatives **3.74**–**3.76** quantitatively (Scheme 3.15). Similar result was obtained by the addition of phenyl magnesium bromide to the *myo*-5-inosose **1.138**. The 1,3-acetal in **3.73**–**3.77** and the PMB ether in **3.77** were deprotected by solvolysis (THF:MeOH) in acid (TFA or HCl) medium to obtain the triols **3.78**–**3.80** and the tetrol **3.81**. Global deprotection of **3.74**–**3.77** by hydrogenolysis afforded 5-*C*-alkyl/aryl *neo*-inositol (characterized as their corresponding acetates) with >70% overall yield in 7 steps from *myo*-inositol.

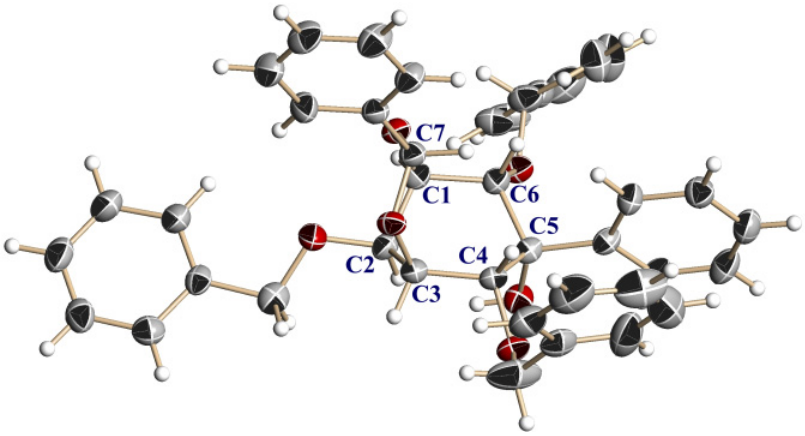


Scheme 3.15: (a) EtOAc, IBX, reflux, 3 h, 96-98%; (b) diethyl ether, MeMgI, –10 °C, 94–96%; (c) diethyl ether, R^3MgBr, –10 °C, 2 h, 90–94%; (d) THF:H_2O, H^+, reflux, 3 h, 88–92%; (e) i) MeOH, H_2, 20% Pd/C, 60 psi, 12 h; ii) py., Ac_2O, DMAP, rt (reflux for **3.83**), 24 h, 80–85% (for 2 steps).

The configuration of the products (**3.73** and **3.76**) was ascertained by single crystal X-ray diffraction analysis (Figure 3.8).



(a)



(b)

Figure 3.8: ORTEP of (a) **3.73** and (b) **3.76**. Thermal ellipsoids are drawn at 30% probability and hydrogen atoms are depicted as small spheres of arbitrary radii.

These results showed that the direction of approach of the nucleophile to the carbonyl group in these 1,3-acetal bridged inososes is from the acetal side of the molecule. The C-alkylated inositols were converted to their acetates **3.82**–**3.84**, and their structure was confirmed by single crystal X-ray diffraction analysis (Figure 3.9). It is interesting to note that the benzylic hydroxyl group in **3.80** remained unaffected during hydrogenolysis. Thus, the product selectivity observed during the Grignard reaction on these ketones is same as that observed during their hydride reduction.[46]

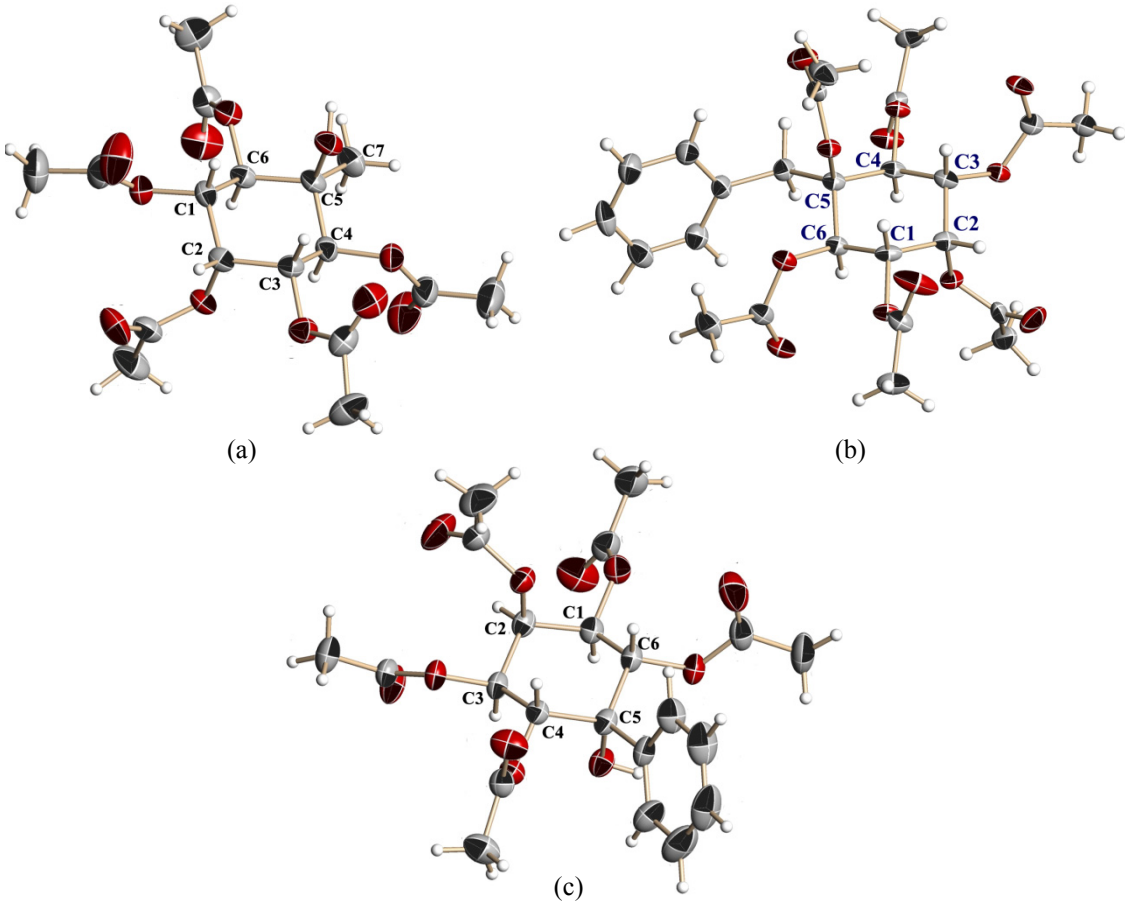


Figure 3.9: ORTEP of (a) **3.82**, (b) **3.83** and (c) **3.84**. Thermal ellipsoids are drawn at 30% probability and hydrogen atoms are depicted as small spheres of arbitrary radii.

Exclusive formation of *neo*-inositol derivative in reactions shown in Scheme 3.15 can be attributed to the following factors:

a) Single crystal X-ray diffraction analysis of the *myo*-5-inososes **1.132**,[20] and **3.72** revealed that the inositol ring is slightly distorted from the chair form (flattered chair, Figure 3.10).

The axial benzyl ether groups (at C4- and C6-positions) appear to flank the carbonyl group in such a way as to prevent the nucleophilic attack by the alkyl/aryl group from the same side of the molecule (in which C4 and C6-benzyl ethers are present). It is also likely that magnesium is chelated to the carbonyl oxygen and ether oxygen, which further blocks this face of the molecule for approach by the alkyl group of the Grignard reagent (Scheme 3.16). This is possible since more than one equivalent of the Grignard reagent was used in these C-alkylation reactions. Since the acetal ring in **1.132** and **3.72** is in the chair conformation and in **1.138** the same ring has the boat conformation, the outcome of

Grignard reaction of these ketones does not seem to depend on the conformation of the acetal ring. Geometrical optimization studies (DFT) for the *myo*-5-inososes **1.132** and **3.72** shows acetal ring in the chair and inositol ring in the flattered chair conformation. Geometrical optimization (DFT) and 2D NMR studies for the *myo*-5-inosose **1.138** have shown Chair-Boat conformation which is similar to the conformation observed in crystals of **1.138**. Details of the results of conformational analysis of the inososes are discussed in Chapter 4.

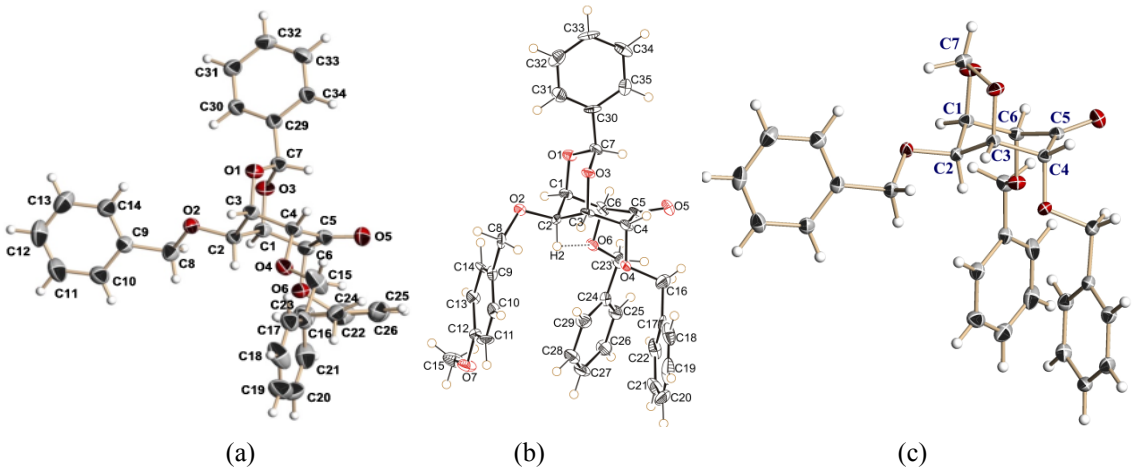
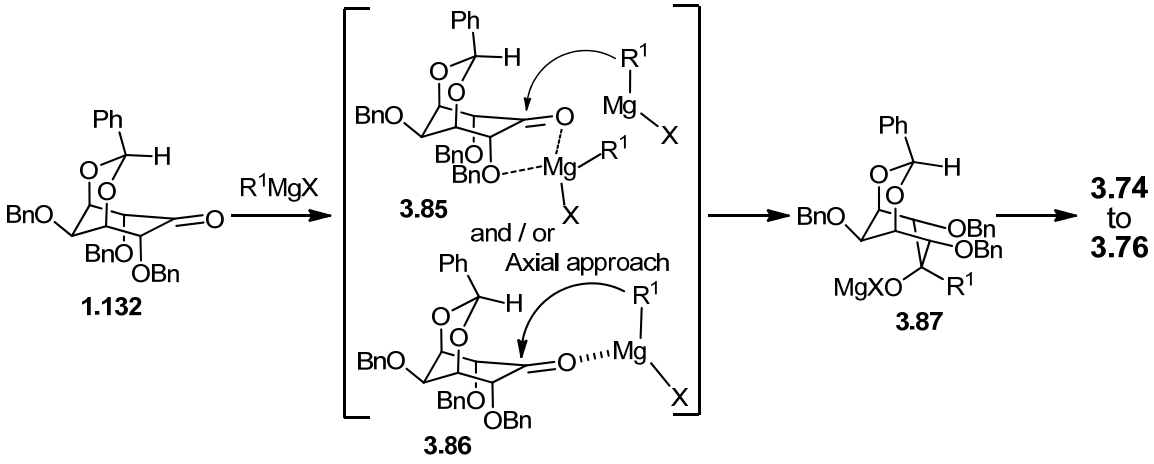


Figure 3.10: ORTEP of (a) **1.132**[20] and (b) **3.72** and (c) **1.138**. Thermal ellipsoids are drawn at 30% probability and hydrogen atoms are depicted as small spheres of arbitrary radii.

On the basis of the results mentioned above, a plausible mechanism for the reaction of Grignard reagents with *myo*-5-inososes is depicted in Scheme 3.16, using **1.132** as an example.



Scheme 3.16: Possible mechanism for the reaction of Grignard reagents with *myo*-5-inososes.

Section C. Inositols to aromatics - benzene free synthesis of tetra hydroxyl benzene derivatives

3C.1. Introduction

Polyhydroxy benzenes such as 1,2,3,5-tetrahydroxy benzene (**3.88**) are present in a variety of organic molecules and natural products (Chart 3.5) which possess interesting chemical and biological properties.[47]

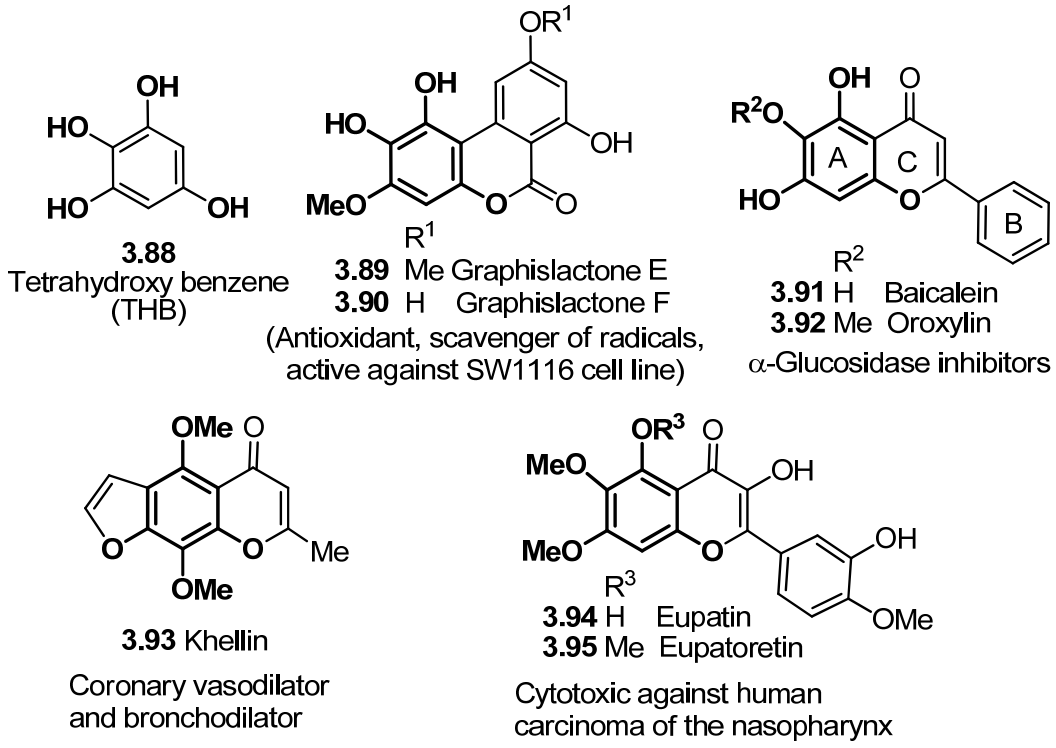
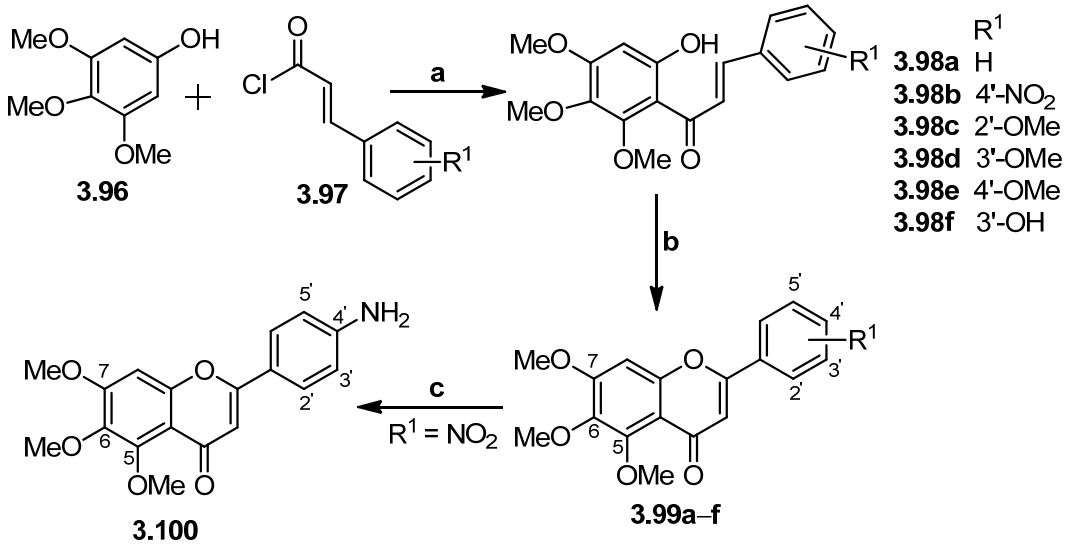


Chart 3.5: Natural products containing polyhydroxybenzene moieties.[47]

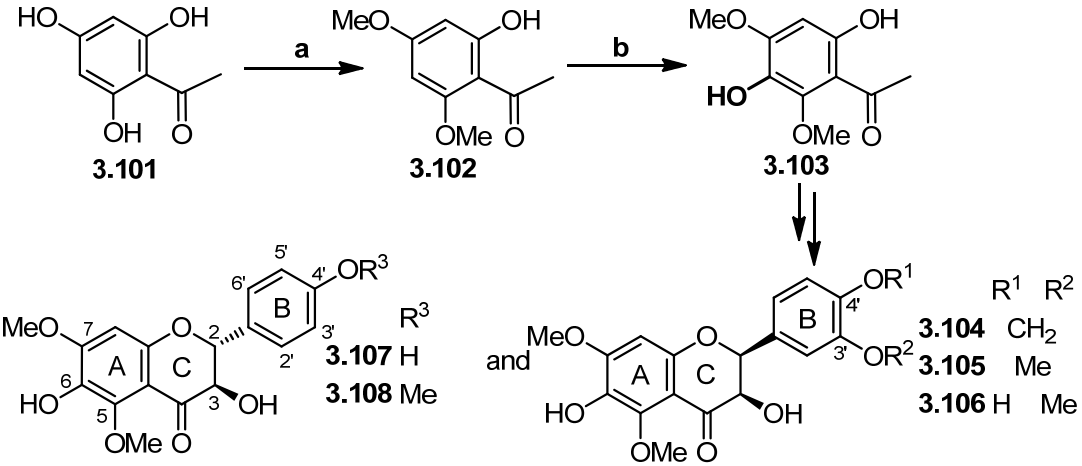
These flavonoids (polyphenolic compounds) are abundant in vegetables, plants, olive oil, and beverages like tea and wine[48] and are implicated to have anticarcinogenic,[49] antiviral,[50] anixiolytic,[51] antiprotozoal[52] and anti-inflammatory activities.[53] These biological activities could be partly due to their antioxidant property.[54]

Synthesis and anticancer activities of 5,6,7-trimethylbaicalein derivatives (**3.99a**–**f**) and **3.100** from THB derivative **3.96** was reported (Scheme 3.18).[55]



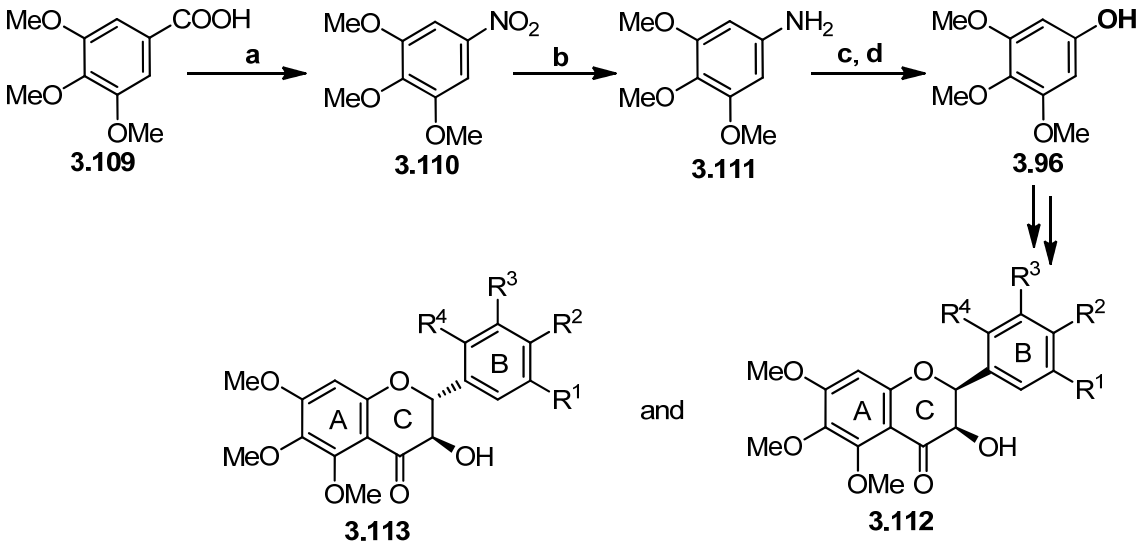
Scheme 3.18: (a) $BF_3{\cdot}Et_2O$, heat, 46–96%; (b) DMSO, I_2, heat, 65–98%; (c) EtOH, $SnCl_2{\cdot}2H_2O$.

Synthesis of two series of hybridized 5,6,7-trioxygenated dihydroflavonols (**3.104**–**3.108**, **3.112** and **3.113**) was reported[56] and their antioxidant properties were evaluated. This work showed that 6-hydroxy substitution on the A ring is important for the antioxidant activities. The dihydroflavonols having ortho-dihydroxy substitution pattern on the B ring exhibited strong free radical scavenging activity, which might be attributable to its polyphenolic character. Synthesis of **3.104**–**3.108** was achieved by the selective protection of hydroxyl groups in **3.101** as methyl ether followed by the introduction of hydroxyl group on the trihydroxy derivatives **3.102** with 44% yield (for **3.103**) as key step (Scheme 3.19).



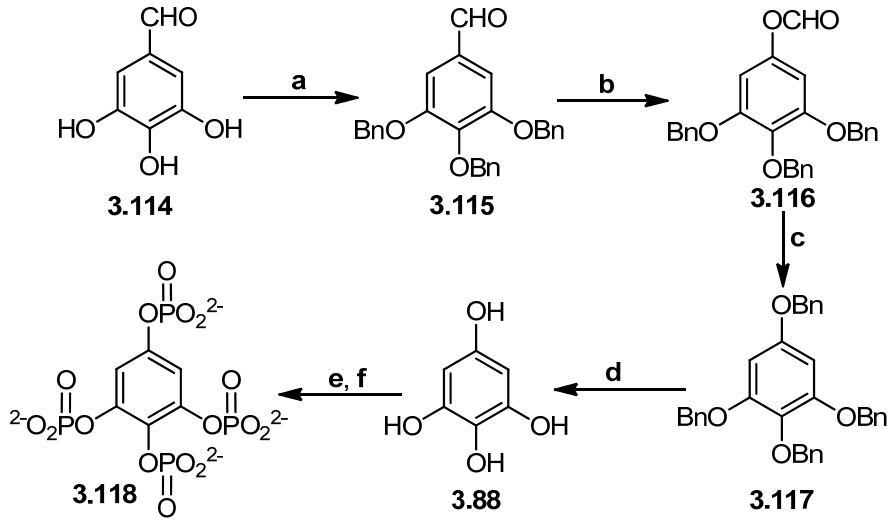
Scheme 3.19: (a) Me_2SO_4, K_2CO_3, acetone, rt, 78%; (b) $K_2S_2O_8$, KOH, H_2O, rt, 44%;

The intermediate **3.96** needed for the synthesis of **3.112** and **3.113** was synthesized from 3,4,5-trimethoxy benzoic acid (**3.109**) in 4 steps with 32% overall yield (Scheme 3.20).[56]



Scheme 3.20: (a) HNO_3, AcOH, rt, 69%; (b) EtOH, 10% Pd/C, N_2H_4, H_2O, reflux, 85%; (c) THF, 40% HBF_4, $NaNO_2$, H_2O, 0 °C, 80%; (d) H_2SO_4, H_2O, 70 °C, 70%.

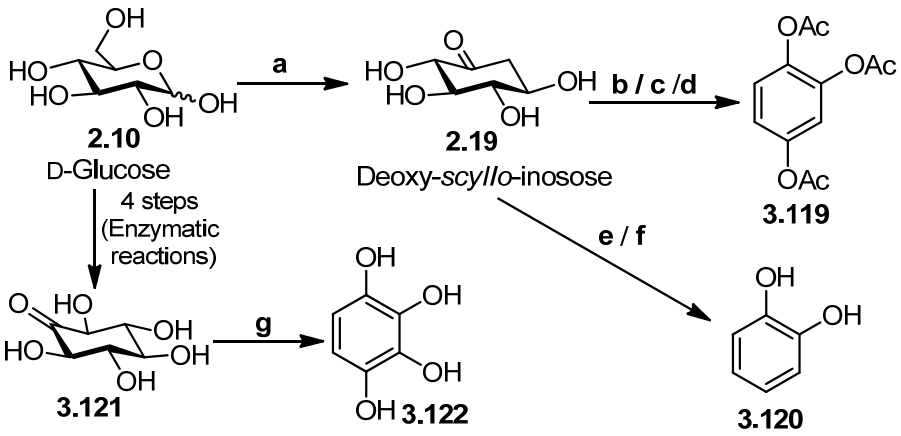
Phosphorylated derivatives of polyhydroxy benzenes (such as **3.118**; Scheme 3.21) have been tested as substitutes for inositol polyphosphates in the context of cellular signal trnasduction.[57] THB **3.88** needed for this work was synthesized from 3,4,5-trihydroxy benzaldehyde (**3.114**) in 5 steps with 45% overall yield. Hence biological / medicinal relevance of polyhydroxybenzenes has generated considerable synthetic interest.



Scheme 3.21: (a) DMF, BnBr, Cs_2CO_3, 80 °C, 17 h, 87%; (b) DCM, *m*CPBA; (c) i) DCM/MeOH (1:1, 100 mL), 1% Amberlyst, 85%; ii) DMF, BnBr, Cs_2CO_3, 18 h, 80 °C, 89%; (d) THF, $Pd(OH)_2/C$, H_2, 71%; (e) $CDCl_3$, N,N-di-isopropylethylamine, $(EtO)_2PCl$, 51%; (f) DCM, TMSBr, 17 h, then MeOH, 80%.

There are few reports on the synthesis of polyhydroxy benzene derivatives starting from aliphatic substrates. A two-step process to catechol from D-glucose *via* 2-deoxy-*scyllo*-

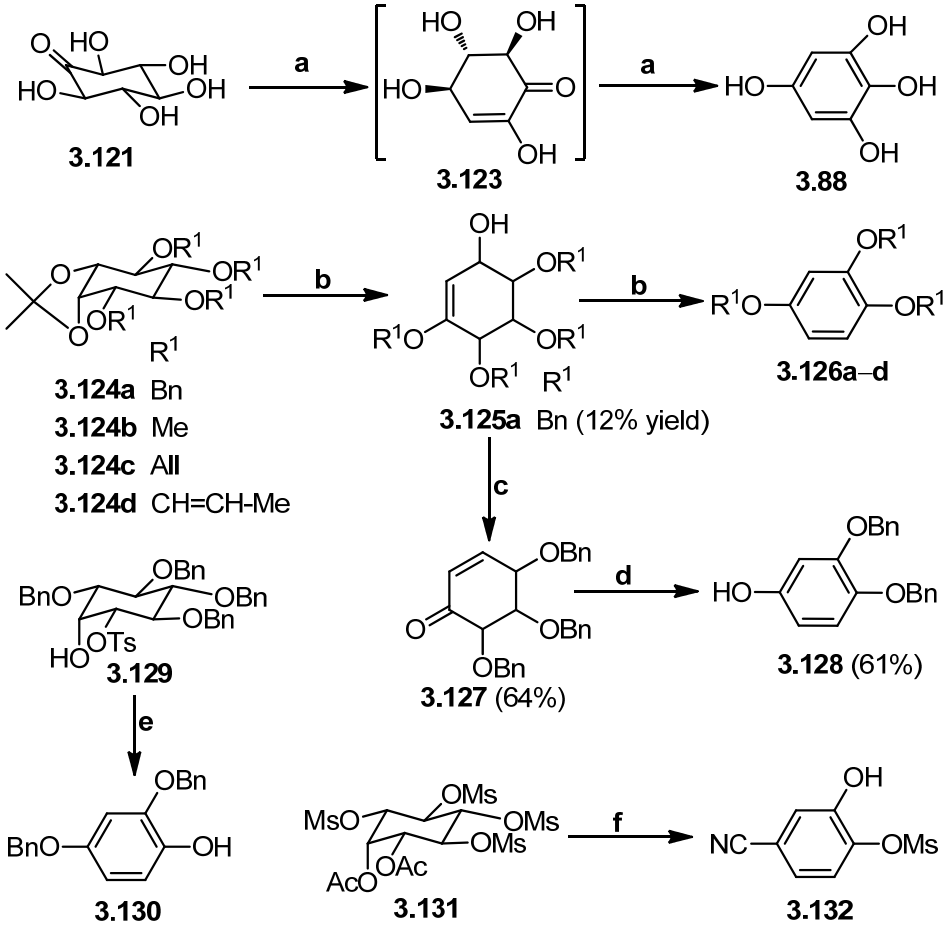
inosose **2.19** was reported (Scheme 3.22).[58] Frost and co-workers reported[59] synthesis of 1,2,3,4-tetrahydroxybenzene (**3.122**) from D-glucose, *via* *myo*-2-inosose (**3.121**).



Scheme 3.22: (a) BtrC, Hexokinase, ATP, Mg^{2+}; (b) Ac_2O, AcOH, conc. H_2SO_4, reflux, 20%; (c) Ac_2O, AcOH, reflux, 29%; (d) py., Ac_2O, rt, 26%; (e) Zn, AcOH, reflux, 18%; (f) AcOH, concd HI, 70 °C, 59%; (g) H_2O, 0.5 M H_2SO_4, reflux, 66%.

D-Glucose was converted to *myo*-2-inosose using the enzyme hexokinase. The 1,2,3,4-tetrahydroxybenzene (**3.122**) was converted to a coenzyme which is an essential antioxidant in humans, protecting low-density lipoproteins from atherosclerosis related oxidative modification. Frost and co-workers also reported the biochemical conversion of D-glucose to pro-catechuic acid, gallic acid, vanillin, and mono-, di-, and trihydroxy benzenes *via* 3-dehydroshikimic acid.[59,60]

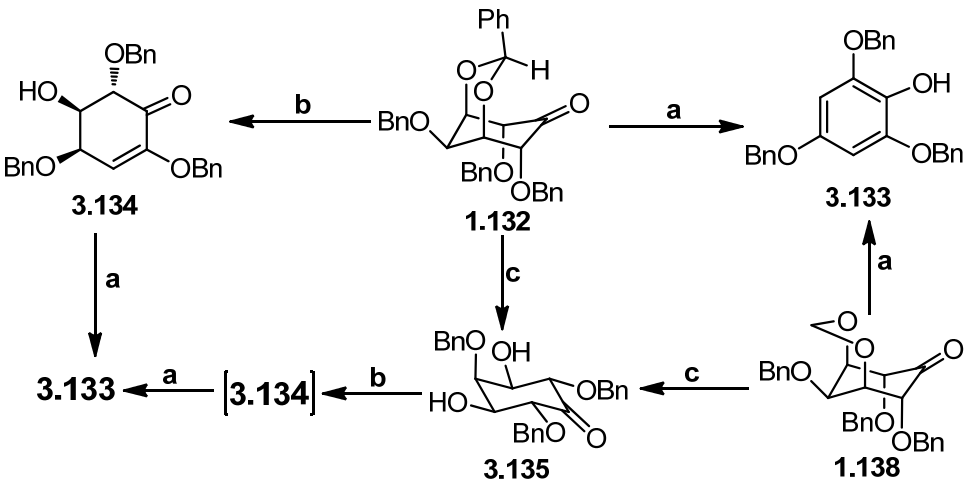
Although aromatization of *myo*-2-inosose **3.121** and 1,2-isopropylidene-*myo*-inositol derivatives **3.124a**–**d** in basic conditions[61] and aromatization of sulfonylated derivatives[62] of *myo*-inositol **1.129** and **3.131** are reported (Scheme 3.23) they have not been elaborated further for the synthesis of polyhydroxy benzenes and their derivatives. Here we report a preparative method for the conversion of *myo*-inositol to polyhydroxy benzene derivatives *via* 1,3-bridged acetals.



Scheme 3.22: (a) H_2O, $Ba(OH)_2$ or NaOH; (b) DMSO, *t*-BuOK, 80 °C, 1–8 h; (c) acetone, H_2SO_4; (d) MeOH, KOH, 20 min (74%, for 2 steps); (e) benzene, KOH, 71%; (f) MeOEtOH, KCN, 100 °C, 42%.

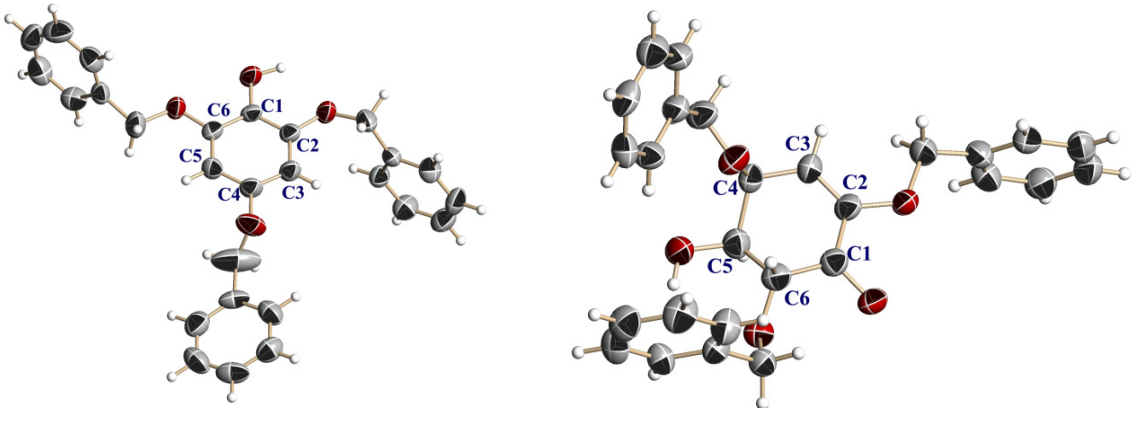
3C.2. Results and discussion

During the course of the synthesis of C-alkyl inositol derivatives described in section 3B, we attempted to prepare the hydroxymethyl derivative of *myo*-inositol from *myo*-5-inosose **1.132** by Wittig olefination followed by hydroboration. We then observed that **1.132** was converted (within 5 min) to another compound, in the presence of sodium hydride in THF, at 0 °C. Isolation of this product and its spectral characteristics showed it to be the benzene derivative **3.133**. The inosose **1.138** also aromatized under similar conditions to form tetra hydroxyl benzene (THB) derivative **3.133** (Scheme 3.24).



Scheme 3.24: (a) THF, NaH, 0 °C, 5 min., 96-98%; (b) THF, Et_3N, –10 °C, 1 h, 94%; (c) THF:MeOH, concd HCl, reflux, 1 h, 91%.

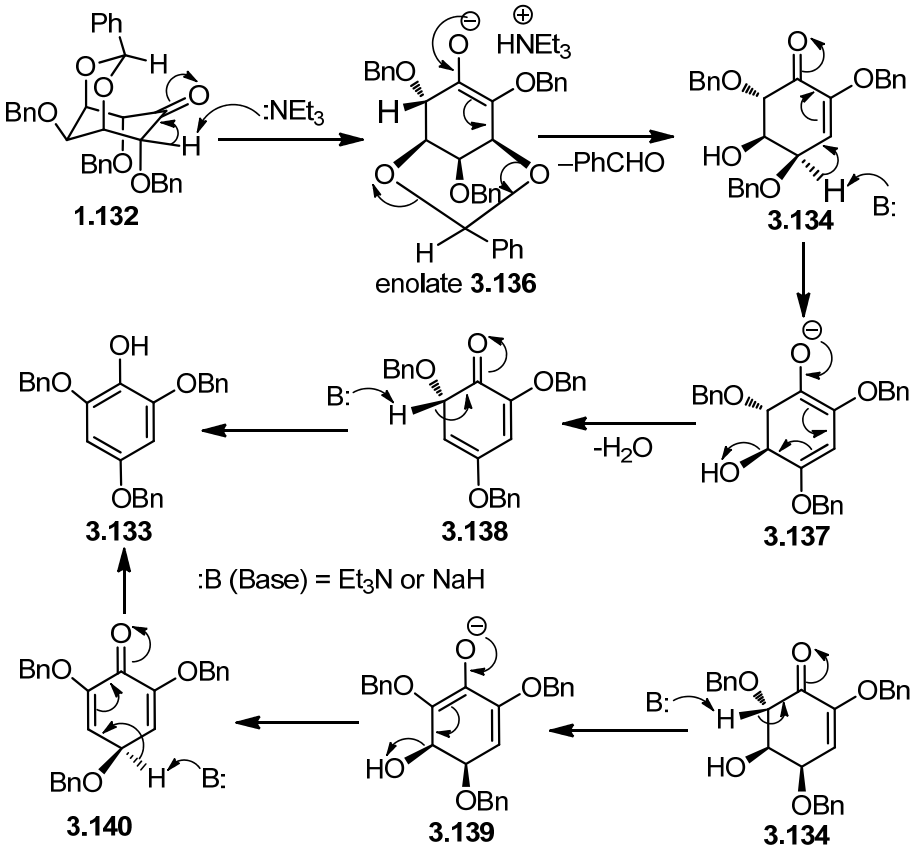
We could establish the intermediacy of the α,β-unsaturated ketone **3.134** in this process by exposing the inosose **1.132** (and **1.138**) to a milder base, triethylamine, at or below –10 °C and subsequent treatment of **3.134** with sodium hydride in THF to obtain **3.133**. The conversion of the acetals **1.132** and **1.138** to **3.133** and **3.134** is unusual, since we observed cleavage of acetals under basic conditions; perhaps this is unprecedented in the literature. The 1,3-bridged acetals **1.132** and **1.138** when exposed to acid underwent solvolysis to provide the corresponding diol **3.135** and no aromatization was observed. The diol **3.135** on exposure to triethylamine or sodium hydride behaved similar to the acetals **1.132** and **1.138** to give the unsaturated ketone **3.134** and the benzene derivative **3.133** respectively. The structure of **3.133** and **3.134** were established by single crystal X-ray diffraction analysis (Figure 3.11).



(a) (b)

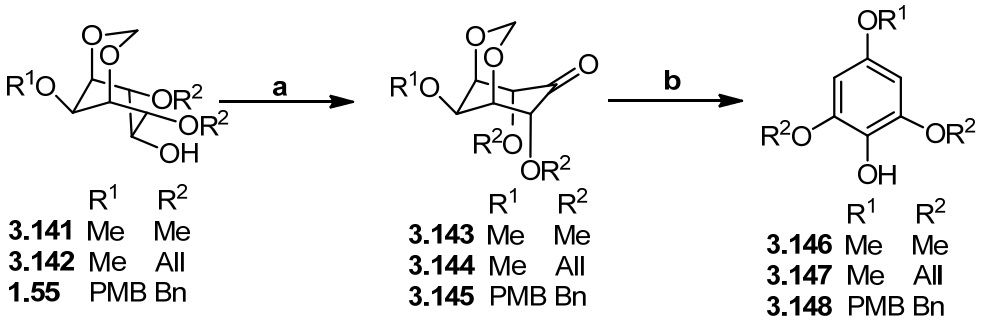
Figure 3.11: ORTEP of (a) **3.133** and (b) **3.134**. Thermal ellipsoids are drawn at 30% probability and hydrogen atoms are depicted as small spheres of arbitrary radii.

On the basis of the experimantal observations described so far, plausible mechanisms for the aromatization reaction are depicted in Scheme 3.25. We assume that formation of **3.133** from inososе (**1.138**) involves an enolization as the first step leading to the formation of enolate **3.136**, wherein loss of a benzaldehyde molecule from the enol species **3.136** afforded **3.134**, an immediate precursor to **3.133**. Again enolization of the **3.134** and successive β-elimination affords THB derivative **3.133**.



Scheme 3.25: Plausible mechanism for aromatization of inososе.

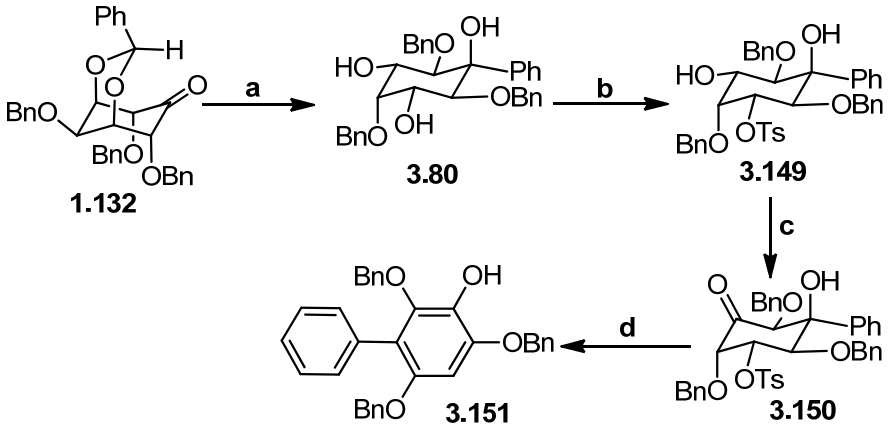
Since we had access to orthogonally protected inososе derivatives **3.143**–**3.145** we converted them to the corresponding orthogonally protected tetrahydroxy benzene derivatives **3.146**–**3.148** (Scheme 3.26).



Scheme 3.26: (a) EtOAc, IBX, reflux, 3 h; (b) THF, NaH, rt, 15 min.

It is of relevance to mention that the derivatives (**3.133**, **3.146**–**3.148**) can be converted to the baicaleins (5,6,7-trihydroxy flavones) in 3 to 4 steps by a reported method[55,63] as shown in Scheme 3.18.

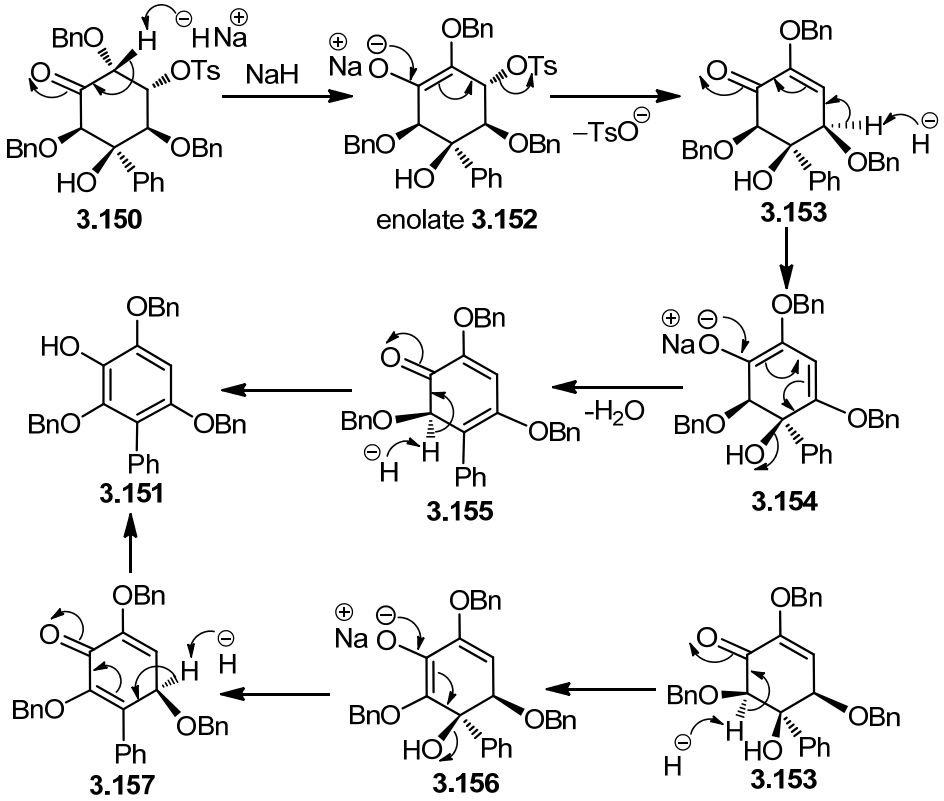
We were also able to develop a completely new route to the synthesis of polyhydroxy biaryls from *myo*-5-inososе. *myo*-5-Inososе **1.132** was converted to the 5-C-phenyl triol **3.80** (Scheme 3.27); one of the secondary hydroxyl groups in **3.80** was tosylated to afford **3.149**. Oxidation of the secondary hydroxyl group in **3.149** with IBX and exposure of the resulting ketone **3.150** to NaH in THF gave the biaryl **3.151**.



Scheme 3.27: (a) diethyl ether, PhMgBr, –10 °C, 1 h then aq. HCl; (b) py., TsCl, rt, 2 h, 85%; (c) EtOAc, IBX, reflux, 3 h; (d) THF, NaH, rt, 15 min., 85% (for 2 steps).

This reaction can also be adopted for the preparation of alkylated tetrahdroxy benzenes, by using different Grignard reagents. This sequence of reactions provides an alternative to reactions like Suzuki coupling, which result in the formation of biaryls.[64] Plausible mechanism for the aromatization reaction of inosose **3.150** is depicted in Scheme 3.28. We assume that formation of **3.151** from the inosose **3.150** involves an enolization as the first step leading to the formation of enolate **3.152**, which looses *p*-toluenesulfonic acid to give

the enone **3.153**. Again enolization of **3.153** and successive β-elimination affords the biaryl derivative **3.151**.



Scheme 3.28: Plausible mechanism for the formation of polyhydroxy biaryl.

3D.1. Conclusions

We have illustrated the utility and potential of 1,3-bridged acetals of *myo*-inositol to serve as early intermediates for the synthesis of cyclitols, their analogs, important moieties of natural products as well as structurally diverse aromatic compounds. The improvement in yields in most of the methods reported in this chapter is due to the fact that one product was obtained in most reactions, especially during the reactions of inositol hydroxyl groups. We are of the opinion that the formation of mixture of products during the reactions of inositols or their partially protected derivatives largely contribute to the inefficiency of most synthetic procedures reported in the literature. The synthetic methods involving inositol derived 1,3-acetals that we have developed do not suffer from this shortcoming. Hence our work raises the hope and possibility of utilizing naturally occurring inositols as starting materials for the synthesis of a variety of organic compounds.

3D.2. Experimental

X-ray Data (Collection, Structure Solution and Refinement): Same as in the sub-section 2.4.1 (Chapter 2).

General Experimental Methods: General experimental methods are same as in the sub-section 2.4.3 (Chapter 2).

Experimental Procedures for Section 3A

General procedure for the *O*-alkylation of C4,C6-hydroxyl group of *myo*-inositol orthoformate (Procedure A): To a solution of orthoformate triol (**1.32**) in dry DMF (300 to 500 mL), added lithium hydride (160 to 252 mmol) at ambient temperature and stirred for 1 h. To the above solution (thick slurry) alkyl halide (84 to 139 mmol) was added and stirred for 12 h. Ice was added to the reaction mixture and stirred for 2 h, solvents were removed under reduced pressure and the residue worked up with ethyl acetate and dried over anhd sodium sulphate. The solvent was removed under reduced pressure to obtain the crude 4,6-dialkyl ether.

General procedure for the *O*-alkylation of C2-hydroxyl (Procedure B): To a solution of the required inositol derivative (1.01 to 40.00 mmol) in dry DMF (5 to 100 mL), sodium hydride (1.25 to 48.00 mmol) was added and stirred for 10 min. Alkyl halide (1.6 to 44 mmol) was then added drop-wise and the reaction mixture was stirred for 3 h. Excess of sodium hydride was quenched by the addition of ice-cold water. The solvent was evaporated under reduced pressure and the residue was worked up with ethyl acetate and dried over anhd sodium sulfate. The solvent was removed under reduced pressure to afford the crude ether.

General procedure for the cleavage of orthoformate by DIBAL-H (Procedure C): 1 M solution of DIBAL-H in toluene (50 to 100 mmol) was added drop-wise over a period of 15 min to a solution of the crude orthoformate (20 to 40 mmol) in dry dichloromethane (150 to 250 mL) at 0 °C and then stirred at room temperature for 2.5 h. The reaction mixture was poured into a stirred solution of sodium potassium tartarate (120 to 240 g in 300 to 400 mL water) and saturated solution of ammonium chloride (200 to 400 mL) and stirred for 12 h. The mixture was extracted with dichloromethane (2 × 400 mL), washed with brine and dried over anhd sodium sulfate. The solvent was removed under reduced pressure to obtain the alcohol.

General procedure for the preparation of triflate (Procedure D): To a cooled (–10 °C) solution of the alcohol (10 to 25 mmol) in dry pyridine (5 to 15 mL) and dry dichloromethane (25 to 50 mL), triflic anhydride (15 to 35 mmol) was added drop-wise over a period of 15 min. The temperature of the reaction mixture was then allowed to rise to room temperature and stirring was continued for 1 h. The solvents were removed under reduced pressure and the residue was worked up with dichloromethane and dried over anhd sodium sulfate. The solvent was removed under reduced pressure to afford the crude triflate.

General procedure for the reaction of triflate with sodium azide (Procedure E): To a solution of crude triflate (10 to 24 mmol) in HMPA (15 to 30 mL) sodium azide (40 to 100 mmol) was added and the reaction mixture stirred for 12 h at room temperature. The reaction mixture was poured into cold water and extracted with diethyl ether (3 × 100 mL). The ether extract was washed with brine and dried over anhd sodium sulfate. Solvent was removed under reduced pressure to obtain a solid azide.

General procedure for ester hydrolysis (Procedure F): To a solution of *O*-acetyl mandeloyl ester (1.00 mmol) in methanol (10 mL) was added KOH (5.00 mmol) and stirred for 3 h at room temperature. The solvents were removed under reduced pressure and the residue dissolved in ethyl acetate, washed with water, brine and dried over anhd sodium sulfate. Solvent was removed under reduced pressure to obtain the corresponding alcohol.

General procedure for hydrogenolysis (Procedure G): The required azide (0.90 to 2 mmol) was hydrogenolyzed in a mixture of methanol and acetic acid (or aqueous HCl) in the presence of 20% Pd/C at 400 psi at rt (or 55 °C) for 12 to 40 h in a Parr Reactor. The catalyst was filtered using a short bed of Celite and the catalyst was washed with methanol (2 × 25 mL) and distilled water (2 × 10 mL) successively. The combined filtrate was evaporated under reduced pressure and the residue co-evaporated with triethyl amine (2 × 5 mL) to get the crude inosamine.

General procedure for acetylation by acetic anhydride (Procedure H): To a solution of the required alcohol or amine in dry pyridine (2 to 5 mL), acetic anhydride (2 to 5 mL) was added and the reaction mixture stirred at room temperature or 100 °C) for 12 to 24 h. The residue obtained was taken in dichloromethane, washed with water, saturated sodium

bicarbonate solution followed by brine and dried over anhd sodium sulfate. The solvent was removed under reduced pressure to afford the crude acetate.

1,3,5-Tri-*O*-benzyl-2-azido-2-deoxy-4,6-*O*-methylidine-*neo*-inositol (3.14): The alcohol **1.47** (4.62 g, 10.0 mmol), dry pyridine (5 mL), dry dichloromethane (25 mL) and triflic anhydride (1.2 mL, 15.30 mmol) were used (Procedure D) to obtain the crude triflate (5.96 g) as a gum which was used in the next step without purification.

The crude triflate (5.96 g), HMPA (15 mL) and sodium azide (2.6 g, 40.00 mmol) were used (Procedure E) to obtain the crude product which was purified by column chromatography (eluent: 10% ethyl acetate in light petroleum) to afford the azide **3.14** (4.48 g, 92% for 4 steps) as a colorless solid. TLC R_f = 0.3 (10% ethyl acetate/light petroleum); **mp** 74–76 $^{\circ}$C (crystals from hot 10% ethyl acetate in light petroleum); **IR** (nujol): $\bar{\nu}$ 2108 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 7.28-7.37 (m, 10H, Ar H), 7.28-7.42 (m, 15H, Ar H), 5.47 (d, 1H, J = 4.5 Hz, H_2CO_2), 4.68 (q, 4H, J = 11.8 Hz, CH_2), 4.58 (brs, 1H, H_2CO_2), 4.46 (s, 2H, CH_2), 4.38-4.40 (m, 1H, Ins H), 4.22-4.27 (m, 2H, Ins H), 4.06 (t, 2H, J = 4.2 Hz, Ins H), 3.73 (t, 1H, J = 4.0 Hz, Ins H) ppm; **^{13}C NMR** ($CDCl_3$, 50.3 MHz): δ 137.7 (C_{arom}), 137.5 (C_{arom}), 128.4 (C_{arom}), 128.3 (C_{arom}), 85.4 (CH_2), 80.2 (Ins C), 73.5 (CH_2), 70.6 (CH_2), 70.4 (Ins C), 69.4 (Ins C), 53.6 (Ins C) ppm; elemental analysis calcd (%) for $C_{28}H_{29}N_3O_5$ (487.54): C 68.98, H 6.00, N 8.62; found: C 69.15, H 6.31, N 9.05 %.

1,3,4,5,6-Penta-*O*-acetyl-2-acetylamino-2-deoxy-*neo*-inositol (3.15): The azide **3.14** (0.97 g, 2.0 mmol) was hydrogenolyzed (at 50 psi) in the presence of 20% Pd/C (0.08 g) in ethanol (6 mL) and concd hydrochloric acid (3 mL) at rt for 32 h (Procedure G) to obtain crude product which was co-evaporated with dry toluene (2 × 7 mL) to get the crude amine (0.41 g) as an off white solid. The crude product (0.41 g), dry pyridine (7 mL), acetic anhydride (3.0 mL) were used (Procedure H) to obtain the crude product which was purified by column chromatography (eluent: 1:1 dichloromethane:ethyl acetate) to afford the hexaacetate **3.15** as a colorless solid (0.72 g, 84% for 2 steps). TLC *Rf* = 0.3 (ethyl acetate:light petroleum (4:1)); **mp** 276–278 ^{o}C; **IR** ($CHCl_3$) 3385, 1751, 1690, 1686 cm $^{-1}$; **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 6.24-6.44 (m, 1H, NH), 5.61 (t, 1H, J = 2.6 Hz, Ins H), 5.21-5.43 (m, 4H, Ins H), 4.96-5.1 (m, 1H, (Ins H)), 2.18 (s, 3H, CH_3), 2.06 (s, 3H, CH_3), 2.04 (s, 6H, CH_3), 2.03 (s, 6H, CH_3) ppm; **^{13}C NMR** ($CDCl_3$, 50.3 MHz): δ 171.3 (C=O),

170.5 (C=O), 170.0 (C=O), 169.6 (C=O), 169.3 (C=O), 67.6 (Ins C), 66.9 (Ins C), 46.8 (Ins C), 22.8 (CH_3), 20.8 (CH_3), 20.6 (CH_3), 20.5 (CH_3) ppm; elemental analysis calcd (%) for $C_{18}H_{25}NO_{11}$ (431.39): C 50.12, H 5.84, N 3.25; found: C 49.80, H 6.12, N 3.06 %.

1,3,5-Tri-*O*-benzyl-2-azido-2-deoxy-4,6-*O*-benzylidine-*neo*-inositol (3.17): The alcohol **1.49** (2.15 g, 4.00 mmol), dry pyridine (8 mL), dry dichloromethane (8 mL) and triflic anhydride (1.00 mL, 5.94 mmol) were used (Procedure D) to obtain the crude triflate. The crude triflate, HMPA (10 mL) and sodium azide (1.62 g, 25 mmol) were used (Procedure E) to obtain the crude product which was purified by column chromatography (eluent: 10% ethyl acetate in light petroleum) to afford the *neo*-azide **3.17** (2.07 g, 92%) as a colorless solid. TLC *Rf* = 0.3 (10% ethyl acetate/light petroleum); **mp** 87–89 ^oC (crystals from hot 15% ethyl acetate in light petroleum); **IR** ($CHCl_3$) 2109 cm $^{-1}$; **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 7.44-7.52 (m, 2H, Ar H), 7.22-7.41 (m, 18H, Ar H), 5.78 (s, 1H, $PhCO_2$), 4.70 (q, 4H, *J* = 12 Hz, 2 × $PhCH_2$), 4.53 (s, 2H, $PhCH_2$), 4.18-4.32 (m, 5H, Ins H), 3.66 (t, 1H, Ins H, *J* = 5 Hz) ppm; **^{13}C NMR** ($CDCl_3$, 50.3 MHz): δ 139.7 (C_{arom}), 138.0 (C_{arom}), 137.2 (C_{arom}), 129.2 (C_{arom}), 128.4 (C_{arom}), 128.2 (C_{arom}), 128.0 (C_{arom}), 127.7 (C_{arom}), 127.6 (C_{arom}), 126.4 (C_{arom}), 94.8 ($PhCHO_2$), 79.2 (Ins C), 73.6 (CH_2), 70.8 (Ins C), 70.5 (CH_2), 65.8 (Ins C), 57.46 (Ins C) ppm; elemental analysis calcd (%) for $C_{34}H_{33}N_3O_5$ (563.64): C 72.45, H 5.90, N 7.46; found: C 72.10, H 6.19, N 7.42 %.

1,3,4,5,6-Penta-*O*-acetyl-2-acetylamino-2-deoxy-*neo*-inositol (3.15): The azide **3.17** (0.96 g, 1.65 mmol), 20% Pd/C (0.07 g), ethanol (6 mL) and trifluoroacetic acid (3 mL) were used (Procedure G) to obtain crude product (0.39 g) as an off white solid. The crude product (0.39 g), dry pyridine (7 mL), acetic anhydride (3.0 mL) were used (Procedure H) to obtain the crude product which was purified by column chromatography (eluent: 1:1 dichloromethane:ethyl acetate) to afford the hexaacetate **3.15** as a colorless solid (0.63 g, 86% for two steps). **Mp** 276–278 ^oC.

4,6-Di-*O*-benzyl-*myo*-inositol-1,3,5-orthoformate (1.41): *myo*-Inositol (**1.1**, 11.36 g, 63.10 mmol), triethyl orthoformate (16.00 mL, 96.78 mmol) and *p*-toluenesulfonic acid (1.08 g, 6.31 mmol) in dry DMF (100 mL) were heated at 110 ºC for 4 h. The clear solution obtained was allowed to cool to room temperature and dry triethylamine (1.2 mL) was added. The reaction mixture was concentrated under reduced pressure to afford a gummy solid (12.05 g). The gummy solid (12.05 g), dry DMF (500 mL), lithium hydride

(2.00 g, 252.4 mmol) and benzyl bromide (16.5 mL, 138.82 mmol) were used (Procedure A) to obtain crude product which was crystallized from hot 30% ethyl acetate in light petroleum to afford the crystalline dibenzyl ether **1.41** (19.63 g, 84%, for 2 steps). **Mp** 123–124 ^{o}C (lit.[21] mp 124–125 ^{o}C).

2-*O*-(4-Methoxybenzyl)-4,6-di-*O*-benzyl-*myo*-inositol-1,3,5-orthoformate (1.42): The dibenzyl ether **1.41** (14.81 g, 40.00 mmol), dry DMF (100 mL), sodium hydride (1.92 g, 48.00 mmol) and *p*-methoxy benzyl chloride (6.00 mL, 44.00 mmol) were used (Procedure B) to obtain **1.42** (19.60 g) as a gum, which was used for next reaction without purification. A small quantity of the crude **1.42** was purified by column chromatography (eluent: 15% ethyl acetate in light petroleum) to afford **1.42** as a gummy liquid. TLC R_f = 0.3 (15% ethyl acetate/light petroleum); ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.15-7.32 (m, 12H, Ar H), 6.80-6.85 (m, 2H, Ar H), 5.52 (d, 1H, J = 1.2 Hz, HCO_3), 4.59 (s, 2H, CH_2), 4.54 (q, 4H, J = 11.4 Hz, 2 × CH_2), 4.40-4.42 (m, 1H, Ins H), 4.29-4.37 (m, 2H, Ins H), 4.22-4.28 (m, 2H, Ins H), 4.01-4.06 (m, 1H, Ins H), 3.76 (s, 3H, CH_3) ppm; ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 159.2 (C_{arom}), 137.5 (C_{arom}), 129.7 (C_{arom}), 128.3 (C_{arom}), 127.7 (C_{arom}), 127.4 (C_{arom}), 113.7 (C_{arom}), 103.1 (HCO_3), 73.9 (Ins C), 71.4 (CH_2), 71.1 (CH_2), 70.5 (Ins C), 68.0 (Ins C), 66.5 (Ins C), 55.1 (CH_3); elemental analysis calcd (%) for $C_{29}H_{30}O_7$ (490.54): C 71.00, H 6.16; found: C 71.26, H 6.10 %.

1,3-*O*-Methylidene-2-*O*-(4-methoxybenzyl)-4,6-di-*O*-benzyl-*myo*-inositol (1.55): The crude orthoformate (**1.42**), 1 M solution of DIBAL-H in toluene (100.0 mL, 100.00 mmol), dry dichloromethane (250 mL), solution of sodium potassium tartarate (240 g in 400 mL water) and saturated solution of ammonium chloride (400 mL) were used (Procedure C) to obtain the alcohol **1.55** (19.73 g) as a gummy liquid which was used for next reaction without purification. A small quantity of the crude **1.55** was purified by column chromatography (eluent: 15% ethyl acetate in light petroleum). TLC R_f = 0.3 (15% ethyl acetate/light petroleum); **IR** (neat): $\bar{\nu}$ 3510–3570 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 7.15-7.35 (m, 12H, Ar H), 6.7-6.85 (m, 2H, Ar H), 5.55 (d, 1H, J = 4.9 Hz, H_2CO_2), 4.69 (d, 1H, J = 4.9 Hz, H_2CO_2), 4.50-4.66 (m, 6H), 4.39-4.46 (m, 2H, Ins H), 4.27-4.32 (m, 1H, Ins H), 3.90-4.07 (m, 3H, Ins H), 3.77 (s, 3H, CH_3), 3.00 (d, 1H, J = 9.9 Hz, OH) ppm; **^{13}C NMR** ($CDCl_3$, 50.3 MHz): δ 159.2 (C_{arom}), 137.8 (C_{arom}), 129.5 (C_{arom}), 128.2 (C_{arom}), 127.5 (C_{arom}), 127.3 (C_{arom}), 113.7 (C_{arom}), 85.5 (CH_2), 81.0 (Ins C), 72.5 (Ins C), 71.9

(CH_2), 70.1 (CH_2), 69.4 (Ins C), 69.3 (Ins C), 55.1 (CH_3); elemental analysis calcd (%) for $C_{29}H_{32}O_7$ (492.56): C 70.71, H 6.55, found: C 70.32, H 6.65 %.

1,3-Di-*O*-benzyl-2-azido-2-deoxy-4,6-*O*-methylidene-5-*O*-(4-methoxybenzyl)-*neo*-inositol (3.19): The crude alcohol **1.55** (12.40 g, ~25.0 mmol), dry pyridine (15 mL), dry dichloromethane (50 mL) and triflic anhydride (3.26 mL, 30.00 mmol) were used (Procedure D) to obtain the crude triflate **3.18** (15.7 g) as a gum which was used in the next step. The crude triflate **3.18** (15.0 g), HMPA (30 mL) and sodium azide (3.90 g, 60.00 mmol) were used (Procedure E) to obtain the crude product which was purified by crystallization (hot 10% ethyl acetate in light petroleum) to afford the azide **3.19** (11.67 g, 94% for 4 steps) as a colorless solid. TLC R_f = 0.5 (30% ethyl acetate/light petroleum); **mp** 81–82 °C (crystals from hot 20% ethyl acetate in light petroleum); IR (nujol): $\bar{\nu}$ 2110 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 7.28-7.37 (m, 10H, Ar H), 7.13-7.20 (m, 2H, Ar H), 6.72-6.82 (m, 2H, Ar H), 5.46 (d, 1H, J = 4.6 Hz, H_2CO_2), 4.67 (q, 4H, J = 11.9 Hz, CH_2), 4.52 (brs, 1H, H_2CO_2), 4.41 (s, 2H, CH_2), 4.37-4.39 (m, 1H, Ins H), 4.21-4.26 (m, 2H, Ins H), 4.05 (t, 2H, J = 4.2 Hz, Ins H), 3.74 (s, 3H, CH_3), 3.69-3.73 (m, 1H, Ins H) ppm; **^{13}C NMR** ($CDCl_3$, 50.3 MHz): δ 159.2 (C_{arom}), 137.7 (C_{arom}), 129.5 (C_{arom}), 129.4 (C_{arom}), 128.3 (C_{arom}), 127.7 (C_{arom}), 127.6 (C_{arom}), 113.8 (C_{arom}), 85.4 (CH_2), 80.2 (Ins C), 73.4 (CH_2), 70.4 (Ins C), 70.2 (CH_2), 68.8 (Ins C), 55.1 (CH_3), 53.7 (Ins C) ppm; elemental analysis calcd (%) for $C_{29}H_{31}N_3O_6$ (517.57): C 67.30, H 6.04, N 8.12; found: C 67.07, H 6.36, N 8.32 %.

1,3-Di-*O*-benzyl-2-azido-2-deoxy-*neo*-inositol (3.20): A mixture of **3.19** (9.31 g, 18.00 mmol), THF-Methanol (25 mL + 75 mL) and concd HCl (10 mL) was refluxed for 2 h. The solvents were removed under reduced pressure to obtain a solid which was purified by column chromatography (eluent: 50% ethyl acetate in light petroleum) to afford **3.20** (6.80 g, 98%) as a colorless solid. TLC R_f = 0.3 (50% ethyl acetate/light petroleum); **mp** 106–107.5 °C; **IR** (nujol): $\bar{\nu}$ 3350–3430, 2099 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 7.30-7.45 (m, 10H, Ar H), 4.63 (q, 4H, J = 11.6 Hz, CH_2), 4.14 (t, 1H, J = 2.9 Hz, Ins H), 4.00 (t, 1H, J = 3.0 Hz, Ins H), 3.84 (dd, 2H, J_1 = 3.0 Hz, J_2 = 9.7 Hz, Ins H), 3.67 (dd, 2H, J_1 = 3.2 Hz, J_2 = 9.6 Hz, Ins H), 2.56 (brs, 3H, OH) ppm; **^{13}C NMR** (CD_3OD, 50.3 MHz): δ 139.6 (C_{arom}), 129.4 (C_{arom}), 129.1 (C_{arom}), 128.8 (C_{arom}), 78.5 (Ins C), 73.7 (CH_2), 73.4 (Ins C),

71.0 (Ins C), 62.4 (Ins C) ppm; elemental analysis calcd (%) for $C_{20}H_{23}N_3O_5$ (385.41): C 62.33, H 6.01, N 10.90; found: C 62.22, H 6.42, N 11.18 %.

***Racemic*-1,3-di-*O*-benzyl-2-azido-2-deoxy-4,5-*O*-methylidene-6-*O*-(methoxymethyl)-*neo*-inositol** [**3.21**]: To a cooled (0 °C) solution of **3.20** (1.93 g, 5.00 mmol) in dimethoxy methane (20 mL), 2,6-lutidine (1.40 mL, 12.00 mmol) and trimethylsilyl trifluoromethanesulfonate (TMSOTf, 3.60 mL, 20.00 mmol) were added. The reaction mixture was allowed to warm to ambient temperature and stirring was continued for 1 h. The reaction mixture was quenched by solid sodium bicarbonate and the solvents were removed under reduced pressure. The crude reaction mixture was dissolved in ethyl acetate, washed successively with water, saturated sodium bicarbonate solution followed by brine and dried over anhd sodium sulfate. The solvent was removed under reduced pressure to afford a gum (2.20 g) which was used in the next step without purification. A small quantity of the crude **3.21** was purified by column chromatography (eluent: 15% ethyl acetate in light petroleum). TLC R_f = 0.3 in 15% ethyl acetate/light petroleum; **IR** (neat): $\bar{\nu}$ 2104 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 7.29-7.45 (m, 10H Ar H), 5.08 (s, 1H, H_2CO_2), 4.99 (s, 1H, H_2CO_2), 4.60-4.94 (m, 7H), 4.35 (dd, 1H, J_1 = 4.6 Hz, J_2 = 7.5 Hz, Ins H), 4.06-4.28 (m, 2H, Ins H), 3.92 (t, 1H, J_1 = 2.9 Hz), 3.74 (dd, 1H, J_1 = 2.7 Hz, J_2 = 9.2 Hz), 3.30-3.50 (m, 5H) ppm; **^{13}C NMR** ($CDCl_3$, 50.3 MHz): δ 137.7 (C_{arom}), 137.5 (C_{arom}), 128.5 (C_{arom}), 128.4 (C_{arom}), 127.9 (C_{arom}), 127.8 (C_{arom}), 127.6 (C_{arom}), 127.5 (C_{arom}), 97.3 (CH_2), 94.8 (CH_2), 77.2 (Ins C), 76.8 (Ins C), 76.5 (Ins C), 75.6 (Ins C), 73.6 (Ins C), 73.2 (CH_2), 71.9 (CH_2), 62.0 (Ins C), 55.6 (CH_3) ppm; elemental analysis calcd (%) for $C_{23}H_{27}N_3O_6$ (441.48): C 62.57, H 6.16, N 9.52; found: C 62.65, H 5.89, N 9.23 %.

***Racemic*-1,3-di-*O*-benzyl-2-azido-2-deoxy-4,5-*O*-methylidene-*neo*-inositol (3.22)**: To a solution of crude **3.21** (2.18 g) in dichloromethane (15 mL) was added methanol (25 mL), water (2 mL), *p*-toluenesulfonic acid (0.10 g, 0.53 mmol) and the mixture refluxed for 12 h. After neutralization with solid Na_2CO_3 and filtration, the residue was concentrated under reduced pressure. Purification of the residue by column chromatography (eluent: 40% ethyl acetate in light petroleum) gave *racemic* **3.22** (1.89 g, 95%, for 2 steps) as a gum. TLC R_f= 0.3 (40% ethyl acetate/light petroleum); **IR** (neat): $\bar{\nu}$ 3300-3600, 2102 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 7.27-7.45 (m, 10H, Ar H), 5.09 (s, 1H, H_2CO_2), 4.96 (s, 1H, H_2CO_2), 4.60-4.79 (m, 4H), 4.35 (dd, 1H, J_1 = 5.2 Hz, J_2 = 7.6 Hz, Ins H), 4.12-4.26 (m, 2H), 3.95

(t, 1H, J_1 = 3.0 Hz, Ins H), 3.62 (dd, 1H, J_1 = 2.7 Hz, J_2 = 9.0 Hz, Ins H), 3.40 (dd, 1H, J_1 = 3.0 Hz, J_2 = 7.7 Hz, Ins H), 2.57 (brs, 1H, OH) ppm; **^{13}C NMR** ($CDCl_3$, 50.3 MHz): δ 137.5 (C_{arom}), 137.3 (C_{arom}), 128.6 (C_{arom}), 128.4 (C_{arom}), 128.1 (C_{arom}), 127.9 (C_{arom}), 127.8 (C_{arom}), 127.76 (C_{arom}), 127.6 (C_{arom}), 94.8 (CH_2), 77.7 (Ins C), 77.2 (Ins C), 76.5 (Ins C), 76.0 (Ins C), 72.7 (CH_2), 72.0 (CH_2), 68.1 (Ins C), 61.1 (Ins C) ppm; elemental analysis calcd (%) for $C_{21}H_{23}N_3O_5$ (397.42): C 63.46, H 5.83, N 10.57; found: C 63.26, H 5.88, N, 10.38 %.

Reaction of the triol 3.20 with $POCl_3$ in DMSO:[24] To a solution of **3.20** (0.50 g, 1.3 mmol) in dry DMSO (7 mL), $POCl_3$ (0.2 mL, 2.2 mmol) was added and stirred at 65°C for 3 h. The reaction mixture was then diluted with water and extracted with dichloromethane (3 × 100 mL). After the usual work-up the crude **3.22** was purified by column chromatography (eluent: 40% ethyl acetate in light petroleum) to obtain *racemic* **3.22** (0.10 g, 20%) as a gum.

1L-1,3-Di-*O*-benzyl-2-azido-2-deoxy-4,5-*O*-methylidene-6-[(R)-(–)-*O*-(acetyl-mandeloyl)]-*neo*-inositol (3.23) and 1D-1,3-di-*O*-benzyl-2-azido-2-deoxy-4,5-*O*-methylidene-6-[(R)-(–)-*O*-(acetyl-mandeloyl)]-*neo*-inositol (dia3.23): To a solution of *racemic* **3.22** (0.84 g, 2.12 mmol) in dry dichloromethane (15 mL) was added R-(–)-*O*-acetyl mandelic acid (0.62 g, 3.18 mmol), DCC (0.52 g, 2.52 mmol), DMAP (0.02 g, 0.21 mmol) and the mixture was stirred at room temperature for 12 h. The solvent was removed under reduced pressure to obtain a gum which was purified by flash column chromatography to afford **3.23** (0.58 g, 48%; eluent: 10 to 15% ethyl acetate in light petroleum) as a solid and **dia3.23** (0.57 g, 47%; eluent: 15 to 20% ethyl acetate in light petroleum) as a gummy liquid. Data for **3.23**: TLC R_f = 0.5 (25% ethyl acetate/light petroleum); **mp** 106–107.5 °C (crystals from hot 10% chloroform in *n*-hexane); $[\alpha]_D^{25}$ –36° (c = 1.0, $CHCl_3$); **IR** ($CHCl_3$): $\bar{\nu}$ 2106, 1755, 1748 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 7.27-7.50 (m, 15H, Ar H), 5.98 (s, 1H, AcOC<u>H</u>PhCO$_2$), 5.49 (dd, 1H, J_1 = 4.3 Hz, J_2 = 9.4 Hz, Ins H), 4.88 (s, 1H, H_2CO_2), 4.75 (s, 1H, H_2CO_2), 4.48-4.70 (m, 4H, CH_2), 4.30 (dd, 1H, J_1 = 4.9 Hz, J_2 = 7.4 Hz, Ins H), 4.05 (t, 1H, J = 4.6 Hz), 3.85 (t, 1H, J = 3.0 Hz), 3.76 (dd, 1H, J_1 = 3.1 Hz, J_2 = 9.4 Hz, Ins H), 3.3 (dd, 1H, J_1 = 2.9 Hz, J_2 = 7.5 Hz, Ins H), 2.19 (s, 3H, CH_3) ppm; **^{13}C NMR** ($CDCl_3$, 50.3 MHz): δ 170.1 (C=O), 168.0

(C=O), 137.4, 133.2, 129.1, 128.6, 128.5, 128.4, 128.0, 127.9, 127.86, 127.7, 127.4, 94.8 (CH_2), 75.2 (Ins C), 74.9 (Ins C), 74.4 (Ins C), 74.2 (Ins C), 72.9 (CH_2), 71.9 (CH_2), 71.3 (Ins C), 61.8 (Ins C), 20.6 (CH_3) ppm; elemental analysis calcd (%) for $C_{31}H_{31}N_3O_8$ (573.59): C 64.91, H 5.45, N 7.33; found: C 65.01, H 5.68, N 7.00 %.

Data for **dia3.23:** TLC R_f = 0.45 (25% ethyl acetate/light petroleum); $[\alpha]_D^{25}$ +30° (c = 1.0, $CHCl_3$); **IR** ($CHCl_3$): $\bar{\nu}$ 2106, 1751, 1744 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 7.26-7.55 (m, 13H, Ar H), 6.97-7.07 (m, 2H, Ar H), 6.03 (s, 1H, $AcOCHCO_2$), 5.46 (dd, 1H, J_1 = 4.1 Hz, J_2 = 9.8 Hz, Ins H), 5.06 (s, 1H, H_2CO_2), 4.97 (s, 1H, H_2CO_2), 4.62 (q, 2H, J = 12.2 Hz, CH_2), 4.35 (dd, 1H, J_1 = 5.0 Hz, J_2 = 12.4 Hz, Ins H), 4.24 (t, 1H, J = 4.5 Hz, Ins H), 4.02 (q, 2H, J = 12.3 Hz, CH_2), 3.70 (t, 1H, J = 3.1 Hz, Ins H), 3.62 (dd, 1H, J_1 = 3.0 Hz, J_2 = 10.2 Hz, Ins H), 3.30 (dd, 1H, J_1 = 2.9 Hz, J_2 = 8.5 Hz, Ins H), 2.19 (s, 3H, CH_3) ppm; **^{13}C NMR** ($CDCl_3$, 50.3 MHz): δ 170.2 (C=O), 168.0 (C=O), 137.3, 137.2, 133.3, 129.3, 128.7, 128.5, 128.4, 128.0, 127.8, 127.7, 127.6, 127.5, 94.9 (CH_2), 77.0, 75.2, 74.6, 74.4, 74.2, 72.7 (CH_2), 71.8 (CH_2), 71.5, 61.9, 20.6 (CH_3) ppm; HRMS (ES^+) calcd for $C_{31}H_{31}N_3O_8Na$ $[M + Na]^+$ 596.2009; found 596.2047.

1L-1,3-Di-*O*-benzyl-2-azido-2-deoxy-4,5-*O*-methylidene-*neo*-inositol [(–)**3.22**]**:** The ester **3.23** (0.57 g, 1.00 mmol), methanol (10 mL) and KOH (0.28 g, 5.00 mmol) were used (Procedure F) and the product was purified by column chromatography (eluent: 40% ethyl acetate/light petroleum) to obtain (–)**3.22** as a gum (0.39 g, 98%). TLC R_f = 0.3 (40% ethyl acetate/light petroleum); $[\alpha]_D^{25}$ –32° (c = 1.0 in $CHCl_3$); **IR** (neat): $\bar{\nu}$ 3320-3600, 2103 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 7.27-7.45 (m, 10H, Ar H), 5.09 (s, 1H, H_2CO_2), 4.96 (s, 1H, H_2CO_2), 4.60-4.79 (m, 4H), 4.32-4.8 (dd, 1H, J_1 = 5.2 Hz, J_2 = 7.6 Hz, Ins H) 4.13-4.26 (m, 2H), 3.95 (t, 1H, J_1 = 3.0 Hz, Ins H), 3.59-3.365 (dd, 1H, J_1 = 2.7 Hz, J_2 = 9.0 Hz, Ins H), 3.37-3.42 (dd, 1H, J_1 = 3.0 Hz, J_2 = 7.7 Hz, Ins H), 2.57 (brs, 1H, OH) ppm; ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 137.5 (C_{arom}), 137.3 (C_{arom}), 128.6 (C_{arom}), 128.4 (C_{arom}), 128.1 (C_{arom}), 127.9 (C_{arom}), 127.8 (C_{arom}), 127.76 (C_{arom}), 127.6 (C_{arom}), 94.8 (CH_2), 77.7 (Ins C), 77.2 (Ins C), 76.5 (Ins C), 76.0 (Ins C), 72.7 (CH_2), 72.0 (CH_2), 68.1 (Ins C), 61.1 (Ins C) ppm; HRMS (ES^+) calcd for $C_{21}H_{24}N_3O_5$ $[M + H]^+$ 398.1716; found 398.1715.

1L-2-Amino-2-deoxy-4,5-*O*-methylidene-*neo*-inositol [(–)**3.1**]**:** The azide (–)**3.22** (0.36 g, 0.91 mmol), a mixture of methanol (6 mL) and acetic acid (0.1 mL), 20% Pd/C (0.09 g)

were used (Procedure G; at room temperature for 40 h) to obtain the crude amine which was purified by column chromatography [neutral alumina; eluent: MeOH:$CHCl_3$:NH_4OH (10:10:0.1)] to isolate (–)**3.1** as a colorless amorphous solid (0.163 g, 94%). $[\alpha]_D^{25}$ -29° (c = 1.1, H_2O), [lit.[65] $[\alpha]_D^{22}$ -33° (c = 1.97, H_2O)]; mp 150–157 °C, (lit.[16c] mp 151–156 °C).

1D-2-Amino-2-deoxy-4,5-*O*-methylidene-*neo*-inositol [(+)**3.1**]: The ester **dia3.23** (0.57 g, 1.00 mmol), methanol (10 mL) and KOH (0.28 g, 5.00 mmol) were used (Procedure F) to obtain the alcohol (+)**3.22** (0.40 g) as a gummy liquid which was used in the next reaction without purification.

The crude alcohol (+)**3.22** (0.40 g), a mixture of methanol (6 mL) and acetic acid (0.1 mL), 20% Pd/C (0.10 g) were used (Procedure G; at room temperature for 40 h) to obtain the crude amine which was purified by column chromatography [neutral alumina; eluent: MeOH:$CHCl_3$:NH_4OH (10:10:0.1)] to obtain (+)**3.1** as a colorless amorphous solid (0.176 g, 92%). $[\alpha]_D^{25}$ $+30^\circ$ (c = 1.2, H_2O). Mp 153–159 °C; **^{1}H NMR** (D_2O, 500 MHz; with acetone as internal standard at δ 2.08 ppm): 5.07 (s, 1H), 4.83 (s, 1H), 4.17 (dd, 1H, J_1 = 4.9 Hz, J_2 = 7.7 Hz), 4.06 (t, 1H, J = 4.6), 4.01 (dd, 1H, J_1 = 4.2 Hz, J_2 = 9.7 Hz), 3.73 (dd, 1H, J_1 = 3.7 Hz, J_2 = 9.8 Hz), 3.60 (dd, 1H, J_1 = 3.1 Hz, J_2 = 7.7 Hz), 3.26 (t, 1H, J = 3.1 Hz) ppm; **^{13}C NMR** (D_2O, 125.76 MHz): δ 95.5 (CH_2), 76.8, 76.2, 70.5, 67.74, 67.70, 50.9 ppm; HRMS (ES^+) calcd for $C_7H_{14}NO_5$ $[M + H]^+$ 192.0872; found 192.0881.

Reaction of the triflate of 3.18 with sodium azide in DMF: A mixture of the crude triflate **3.18** (0.62 g, ~1.0 mmol), sodium azide (0.33 g, 2.14 mmol) and DMF (10 mL) was stirred at 100 °C for 1 h in an atmosphere of argon. The solvent was evaporated under reduced pressure and the residue worked up with ethyl acetate and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the crude product was purified by column chromatography to obtain **3.19** (0.238 g, 46%; eluent: 10% ethyl acetate in light petroleum) and **3.24** (0.243 g, 47%; eluent: 15% ethyl acetate in light petroleum) as colorless solids.

Data for **3.24:** TLC R_f = 0.4 (30% ethyl acetate/light petroleum); **mp** 61–62 °C (crystals from hot 10% ethyl acetate in light petroleum); **IR** (neat): $\bar{\nu}$ 2104 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 7.28-7.45 (m, 12H, Ar H), 6.82-6.90 (m, 2H, Ar H), 5.23 (d, 1H, H_2CO_2, J =

5.2 Hz), 4.74 (d, 1H, H_2CO_2, J = 5.1 Hz), 4.60-4.71 (m, 4H, 2 × CH_2), 4.58 (s, 2H, CH_2), 4.25 (brs, 2H, Ins H), 3.87 (t, 1H, J = 1.8 Hz, Ins H), 3.78-3.83 (m, 2H, Ins H), 3.79 (s, 3H, CH_3), 3.56 (t, 1H, Ins H, J = 7.0 Hz) ppm; **^{13}C NMR** ($CDCl_3$, 50.3 MHz): δ 159.4 (C_{arom}), 137.1 (C_{arom}), 129.5 (C_{arom}), 128.4 (C_{arom}), 127.9 (C_{arom}), 113.9 (C_{arom}), 85.5 (CH_2), 81.1 (Ins C), 71.9 (CH_2), 71.7 (Ins C), 70.6 (CH_2), 69.6 (Ins C), 63.5 (Ins C), 55.2 (CH_3) ppm; elemental analysis calcd (%) for $C_{29}H_{31}N_3O_6$ (517.57): C 67.30, H 6.04, N 8.12; found: C 67.25, H 6.01, N 8.02 %.

1,3-Di-*O*-benzyl-2-azido-2-deoxy-4,6-*O*-methylidene-*neo*-inositol (3.25): To a solution of **3.19** (3.10 g, 6.00 mmol) in dichloromethane (40 mL) and water (2 mL), DDQ (3.40 g, 15.00 mmol) was added and stirred for 2.5 h at room temperature. The reaction mixture was diluted with dichloromethane (100 mL) and washed with sat. $NaHCO_3$ solution, water followed by brine and dried over anhd sodium sulfate. The solvent was evaporated under reduced pressure to obtain a gum which was purified by column chromatography (eluent: 20% ethyl acetate in light petroleum) to afford **3.25** (2.10 g, 88%) as a colorless solid. TLC R_f = 0.3 (20% ethyl acetate/light petroleum); **mp** 55.5–57 °C (crystals from hot 20% ethyl acetate in light petroleum); IR (nujol): $\bar{\nu}$ 3200-3650, 2108 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 7.27-7.43 (m, 10H, Ar H), 5.48 (d, 1H, J = 4.6 Hz, H_2CO_2), 4.83 (d, 2H, J = 11.8 Hz, CH_2), 4.56-4.69 (m, 4H), 4.14-4.21 (m, 2H, Ins H), 4.07 (t, 2H, Ins H, J = 4.2 Hz), 3.76 (t, 1H, J = Ins H, 3.9 Hz), 2.07 (s, 1H, OH) ppm; **^{13}C NMR** ($CDCl_3$, 50.3 MHz): δ 137.6 (C_{arom}), 128.3 (C_{arom}), 127.8 (C_{arom}), 127.7 (C_{arom}), 85.2 (CH_2), 79.9 (Ins C), 73.5 (CH_2), 72.6 (Ins C), 62.7 (Ins C), 53.7 (Ins C) ppm; elemental analysis calcd (%) for $C_{21}H_{23}N_3O_5$ (397.42): C, 63.46; H, 5.83; N, 10.57; found: C, 63.80; H, 5.45; N, 10.96 %.

***Racemic*-1-*O*-benzyl-2-azido-2-deoxy-4,6-*O*-methylidene-*neo*-inositol (3.26):** To a solution of **3.19** (1.03 g, 2.00 mmol) in dichloromethane (30 mL) and water (1.5 mL), DDQ (1.1 g, 5.00 mmol) was added and stirred for 12 h at room temperature. The reaction mixture was diluted with dichloromethane (50 mL) and washed with sat. $NaHCO_3$ solution, water followed by brine and dried over anhd sodium sulfate. The solvent was evaporated under reduced pressure to obtain a gum which was purified by column chromatography to afford **3.25** (0.32 g, 40%; eluent: 15% ethyl acetate in light petroleum) and **3.26** (0.41 g, 52%; eluent: 30% ethyl acetate in light petroleum) as a colorless solids. Data for **3.26**: TLC R_f = 0.3 (30% ethyl acetate/light petroleum); **mp** 107-108 °C (crystals from hot 50% ethyl

acetate in light petroleum); **IR** (nujol): $\bar{\nu}$ 3200-3500, 2109 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 7.27-7.45 (m, 5H, Ar H), 5.57 (d, 1H, H_2CO_2, *J* = 4.6 Hz), 4.79 (d, 1H, *J* = 11.5 Hz, CH_2), 4.51-4.68 (m, 3H), 4.16-4.33 (m, 4H), 4.04-4.12 (m, 1H), 2.89 (d, 1H, *J* = 6.6 Hz, OH), 2.39 (d, 1H, *J* = 4.2 Hz, OH) ppm; ^{13}C **NMR** ($CDCl_3$+CD_3OD, 50.3 MHz): δ 136.8 (C_{arom}), 128.3 (C_{arom}), 127.9 (C_{arom}), 85.0 (CH_2), 79.4 (Ins C), 74.7 (Ins C), 73.8 (CH_2), 72.3 (Ins C), 72.2 (Ins C), 60.9 (Ins C), 54.7 (Ins C) ppm; elemental analysis calcd (%) for $C_{14}H_{17}N_3O_5$ (307.30): C, 54.72; H, 5.58; N, 13.67; found: C, 54.84; H, 5.59; N, 13.30 %.

1,3-Di-*O*-benzyl-2-azido-2-deoxy-4,6-*O*-methylidene-5-*O*-methyl-*neo*-inositol (3.30): The alcohol **3.25** (0.40 g, 1.01 mmol), sodium hydride (0.05 g, 1.25 mmol), methyl iodide (0.1 mL, 1.6 mmol) and dry DMF (5 mL) were used (Procedure B) to obtain the corresponding methyl ether (0.405 g) as a gum which was used for the next reaction without purification. A small quantity of the crude product was purified by column chromatography (15% ethyl acetate in light petroleum) to obtain **3.30** as a gummy solid. TLC R_f = 0.3 (15% ethyl acetate/light petroleum); **IR** ($CHCI_3$): $\bar{\nu}$ 2112 cm^{-1}; **^{1}H NMR** ($CDCI_3$, 400 MHz): δ 7.29-7.41 (m, 10H, Ar H), 5.33 (d, 1H, *J* = 4.5 Hz, H_2CO_2), 4.75 (q, 4H, *J* = 12.0 Hz, 2 × CH_2), 4.52 (d, 1H, *J* = 4.5 Hz, H_2CO_2), 4.22 (d, 2H, *J* = 3.2 Hz, Ins H), 4.12 (brs, 1H, Ins H), 4.07 (t, 2H, *J* = 4.2 Hz, Ins H), 3.74 (t, 1H, *J* = 4.1 Hz, Ins H), 3.29 (s, 3H, CH_3) ppm; **^{13}C NMR** ($CDCl_3$, 100.6 MHz): δ 137.7 (C_{arom}), 128.4 (C_{arom}), 127.9 (C_{arom}), 85.2 (H_2CO_3), 80.1 (Ins C), 73.8 (CH_2), 73.3 (Ins C), 69.8 (Ins C), 55.9, 53.7 ppm; elemental analysis calcd (%) for $C_{22}H_{25}N_3O_5$ (411.45): C 64.22, H 6.12, N 10.21; found: C 63.99, H 6.26, N 10.10 %.

1,3,4,6-Tetra-*O*-acetyl-2-acetylamino-2-deoxy-5-*O*-methyl-*neo*-inositol (3.29): One pot deprotection of benzyl groups, 1,3-*O*-methylidene acetal and reduction of the azide in **3.30** (0.40 g, 1.01 mmol) was carried out by hydrogenation (Procedure G; 55 °C for 12 h) using 20% Pd/C (0.10 g), methanol (7 mL) and concd HCl (1 mL) to obtain crude amine (0.095 g) as a dirty white solid. The crude amine was acetylated with acetic anhydride (2.0 mL), DMAP (0.01 g) and dry pyridine (5 mL) at 60 °C for 12 h (Procedure H) to obtain the crude acetate which was purified by crystallization from a mixture of hot ethyl acetate/light petroleum (4:1) to obtain colorless crystals of **3.29** (0.33 g, 81% for 3 steps). TLC R_f = 0.3 in ethyl acetate; **mp** 159-162 °C; **IR** ($CHCI_3$): $\bar{\nu}$ 3379, 1747, 1720, 1684 cm^{-1}; ^{1}H NMR

($CDCI_3$, 400MHz): δ 6.47 (d, 1H, J = 9.8 Hz, NH), 5.44 (dd, 2H, J_1 = 5.5 Hz, J_2 = 11.0 Hz, Ins H), 5.17 (dd, 2H, J_1 = 2.5 Hz, J_2 = 11.0 Hz, Ins H), 4.95-5.04 (m, 1H, Ins H), 3.93 (t, 1H, J = 2.6 Hz, Ins H), 3.52 (s, 3H, CH_3), 2.12 (s, 6H, 2 × CH_3), 2.06 (s, 3H, CH_3), 2.01 (s, 6H, 2 × CH_3) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 170.9 (C=O), 169.5 (C=O), 76.5 (Ins C), 70.1 (Ins C), 67.1 (Ins C), 61.5 (Ins C), 47.0 (CH_3), 23.1 (CH_3), 20.9 (CH_3), 20.7 (CH_3) ppm; elemental analysis calcd (%) for $C_{17}H_{25}NO_{10}$ (403.38): C 50.62, H 6.25, N 3.47; found: C 51.01, H 6.26, N 3.19 %.

4,6-Di-*O*-(4-methoxybenzyl)-*myo*-inositol-1,3,5-orthoformate (3.31): *myo*-Inositol (**1.1**, 7.10 g, 39.43 mmol), triethyl orthoformate (10.0 mL, 60.48 mmol) and *p*-toluenesulfonic acid (0.68 g, 3.95 mmol) in dry DMF (100 mL) were heated at 110 ºC for 4 h. The clear solution obtained was allowed to cool to room temperature and dry triethylamine (1.0 mL) was added. The reaction mixture was concentrated under reduced pressure to afford a gummy solid (7.6 g). The gummy solid (7.6 g), dry DMF (300 mL), lithium hydride (1.25 g, 157.80 mmol) and *p*-methoxybenzyl chloride (11.70 mL, 86.79 mmol) were used (Procedure A) to obtain **3.31** (13.91 g, 82% yield) as colorless crystals. TLC R_f = 0.3 in 40% ethyl acetate/light petroleum; mp 120–122 °C (Lit[66] mp 120–121 °C).

2-*O*-Methyl-4,6-di-*O*-(4-methoxybenzyl)-*myo*-inositol-1,3,5-orthoformate (**3.32**): The alcohol **3.31** (8.61 g, 20.0 mmol), sodium hydride (0.96 g, 24.0 mmol), methyl iodide (1.50 mL, 24 mmol) and dry DMF (100 mL) were used (Procedure B) to obtain **3.32** as a colorless solid (8.9 g) which was used for the next reaction without purification. A small quantity of the crude solid was purified by crystallization (hot mixture of 20% ethyl acetate in light petroleum) to obtain colorless crystals of **3.32**. TLC R_f = 0.3 (20% ethyl acetate/light petroleum); **mp** 124.4-126 °C; **^{1}H NMR** ($CDCI_3$, 200 MHz): δ 7.13-7.25 (m, 4H, Ar H), 6.77-6.88 (m, 4H, Ar H), 5.49 (s, 1H, HCO_3), 4.56 (q, 4H, J = 11.3 Hz, 2 × CH_2), 4.26-4.43 (m, 5H, Ins H), 3.81 (s, 6H, 2 × CH_3), 3.75-3.79 (m, 1H, Ins H), 3.45 (s, 3H, CH_3) ppm. **^{13}C NMR** ($CDCl_3$, 50.3 MHz): δ 159.3 (C_{arom}), 129.6 (C_{arom}), 129.3 (C_{arom}), 113.7 (C_{arom}), 103.1 (HCO_3), 73.6 (Ins C), 71.4 (CH_2), 69.8 (Ins C), 69.3 (Ins C), 68.0 (Ins C), 56.6 (CH_3), 55.1 (CH_3) ppm; elemental analysis calcd (%) for $C_{24}H_{28}O_8$ (444.47): C 64.85, H 6.35; found: C 64.67, H 6.13 %.

1,3-*O*-Methylidene-2-*O*-methyl-4,6-di-*O*-(4-methoxybenzyl)-*myo*-inositol (3.33): The crude **3.32** (8.88 g), 1 M solution of DIBAL-H in toluene (50.0 mL, 50.0 mmol), dry

dichloromethane (150 mL), sodium potassium tartarate (102 g in 170 mL water) and saturated solution of ammonium chloride (170 mL) were used (Procedure C) to obtain a colorless solid (8.89 g). A small quantity of the solid was crystallized from hot mixture of 20% ethyl acetate in light petroleum to obtain **3.33** as a crystalline solid. TLC R_f = 0.3 (20% ethyl acetate/light petroleum); **mp** 114.2-115.4 °C; **IR** ($CHCl_3$): $\bar{\nu}$ 3490–3580 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.23-7.28 (m, 4H, Ar H), 6.85 (d, 4H, *J* = 8.0 Hz, Ar H), 5.38 (d, 1H, *J* = 5.0 Hz, H_2CO_2), 4.64 (d, 1H, *J* = 5.0 Hz, H_2CO_2), 4.59 (q, 4H, *J* = 11.6 Hz, 2 × CH_2), 4.35-4.38 (m, 2H, Ins H), 3.97 (t, 2H, *J* = 2.9 Hz), 3.87-3.96 (m, 2H, Ins H), 3.80 (s, 6H, 2 × CH_3), 3.41 (s, 3H, CH_3), 2.90 (d, 1H, *J* = 9.2 Hz, OH) ppm; ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 159.1 (C_{arom}), 129.8 (C_{arom}), 129.2 (C_{arom}), 113.6 (C_{arom}), 85.2 (CH_2), 80.6 (Ins C), 71.8 (Ins C), 71.6 (CH_2), 69.8 (Ins C), 55.8 (CH_3), 55.0 (CH_3) ppm; elemental analysis calcd (%) for $C_{24}H_{30}O_8$ (446.49): C 64.56, H 6.77; found: C 64.20, H 7.02 %.

1,3-Di-*O*-(4-methoxybenzyl)-2-azido-2-deoxy-4,6-*O*-methylidene-5-*O*-methyl-*neo*-inositol (3.34): The alcohol **3.33** (8.85 g), dry dichloromethane (40 mL), pyridine (10 mL) and triflic anhydride (5.0 mL, 30.0 mmol) were used (Procedure D) to obtain the crude triflate (11.5 g) as a gum, which was used in the next step, without purification. The crude triflate (11.5 g), HMPA (30 mL) and sodium azide (6.50 g, 100.0 mmol) were used (Procedure E) to obtain a solid which was crystallized from a hot mixture of 10% ethyl acetate in light petroleum (colorless crystals of **3.34**, 8.29 g, 88% yield, for 4 steps). TLC R_f= 0.5 (20% ethyl acetate/light petroleum; **mp** 126-128 °C; IR ($CHCl_3$): $\bar{\nu}$ 2108 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400MHz): δ 7.32 (d, 4H, *J* = 8.0 Hz, Ar H), 6.87 (d, 4H, *J* = 8.0 Hz, Ar H), 5.30 (d, 1H, *J* = 4.5 Hz, H_2CO_2), 4.67 (q, 4H, *J* = 11.8 Hz, 2 × CH_2), 4.49 (d, 1H, *J* = 4.5 Hz, H_2CO_2), 4.13 (d, 2H, *J* = 4.5 Hz, Ins H), 4.08 (s, 1H, Ins H), 4.02 (t, 2H, *J* = 3.9 Hz, Ins H), 3.81 (s, 6H, 2 × CH_3), 3.66 (t, 1H, *J* = 4.1 Hz, Ins H), 3.31 (s, 3H, CH_3) ppm; **^{13}C NMR** ($CDCl_3$, 100.6 MHz): δ 159.4 (C_{arom}), 129.7 (C_{arom}), 129.6 (C_{arom}), 113.8 (C_{arom}), 85.1 (CH_2), 79.6 (Ins C), 73.3 (CH_2), 71.3 (Ins C), 69.8 (Ins C), 55.8, 55.1, 53.5 ppm; elemental analysis calcd (%) for $C_{24}H_{29}N_3O_7$ (471.50): C 61.14, H 6.20, N 8.91; found: C 60.89, H 6.31, N 8.96 %.

1,3,4,6-Tetra-*O*-acetyl-2-acetylamino-2-deoxy-5-*O*-methyl-*neo*-inositol (3.29): The azide **3.34** (0.94 g, 2.00 mmol) was hydrogenolyzed in methanol (10 mL) and conc. HCl (2

mL) in the presence of 20% Pd/C (0.15 g) at 400 psi on a Parr reactor (Procedure G; 55 °C for 12 h) to obtain the crude product (0.19 g) as an off white solid. The crude product was acetylated with acetic anhydride (3.0 mL), DMAP (0.01 g) in dry pyridine (10 mL) at room temperature for 40 h (Procedure H) to obtain the crude product which was purified by crystallization from mixture of hot ethyl acetate/light petroleum (4:1) to obtain **3.29** as colorless crystals (0.68 g, 84% for two steps). TLC R_f = 0.3 in ethyl acetate. **Mp** 159–162 $^{\circ}$C.

1,3-Di-*O*-(4-methoxybenzyl)-2-acetylamino-2-deoxy-4,6-*O*-methylidene-5-*O*-methyl-*neo*-inositol (3.36): A solution of **3.34** (0.47 g, 1.0 mmol) in dichloromethane (10 mL), water (1 mL), and Ph_3P (0.53 g, 2.02 mmol) were mixed and stirred for 2 h at room temperature. The mixture was concentrated under reduced pressure to get the crude amine as a gum which was acetylated by acetic anhydride (2 mL) and DMAP (0.001 g) and pyridine (5 mL) (Procedure H: 12 h at room temperature) to obtain a solid which was purified by crystallization from a hot mixture of 30% ethyl acetate in light petroleum to obtain **3.36** (0.41 g, 84%, for 2 steps) as colorless crystals. TLC R_f = 0.3 (25% ethyl acetate/light petroleum); **mp** 149–150.5 $^{\circ}$C; **IR** (nujol): $\bar{\nu}$ 3438, 1668 cm^{-1}; **^{1}H NMR** ($CDCI_3$, 200 MHz): δ 7.20–7.27 (m, 4H, Ar H), 6.84–6.90 (m, 4H, Ar H), 5.76 (d, 1H, J = 9.4 Hz, NH), 5.37 (d, 1H, J = 4.4 Hz, H_2CO_2), 4.70-4.83 (m, 1H, Ins H), 4.61 (d, 1H, J = 4.5 Hz, H_2CO_2), 4.51 (q, 4H, J = 12.1 Hz, 2 × CH_2), 4.25 (d, 2H, J = 3.2 Hz, Ins H), 3.99 (t, 1H, J = 1.2 Hz, Ins H), 3.82-3.84 (m, 2H, Ins H), 3.81 (s, 6H, 2 × CH_3), 3.35 (s, 3H, CH_3), 1.73 (s, 3H, CH_3) ppm; **^{13}C NMR** ($CDCl_3$, 50.3 MHz): δ 169.1 (C=O), 159.4 (C_{arom}), 132.1 (C_{arom}), 131.9 (C_{arom}), 130.1 (C_{arom}), 129.4 (C_{arom}), 128.6 (C_{arom}), 128.4 (C_{arom}), 113.9 (C_{arom}), 85.1 (CH_2), 78.4 (Ins C), 73.2 (CH_2), 71.4 (Ins C), 69.2 (Ins C), 55.8 (Ins C), 55.2 (CH_3), 43.4 (CH_3), 23.0 (CH_3) ppm; elemental analysis calcd (%) for $C_{26}H_{33}NO_8$ (487.54): C 64.05, H 6.82, N 2.87; found: C 63.92, H 6.59, N 2.75 %.

l,3-Di-*O*-(4-methoxybenzyl)-(E)-2-[[3-(3-(propenyloxy)-4-hydroxyphenyl)-2-methyl-l-oxo-2-propenyl]-amino]-2-deoxy-4,6-*O*-methylidene-2-*O*-methyl-*neo*-inositol (3.38): A solution of **3.34** (0.47 g, 1.0 mmol) in ethyl acetate/methanol (5 + 10 mL) and 20% Pd/C (0.08 g), was stirred in an atmosphere of hydrogen (balloon pressure) for 1.5 h at room temperature. The reaction mixture was filtered through Celite, and the catalyst was washed

with methanol. The combined filtrate was concentrated to get the amine **3.35** (0.44 g) which was used for next step without purification.

A solution of the acid[17] **3.37** (0.35, 1.5 mmol) in dichloromethane (10 mL), EDC.HCl (0.28 g, 1.5 mmol), DIPEA (0.7 mL, 4.0 mmol) and HOBt (0.20 g, 1.5 mmol) were mixed and stirred for 10 min. To this mixture, a solution of the amine **3.35** (0.44 g, 1.0 mmol) in dichloromethane (10 mL) was added drop-wise (over a period of 15 min.) and the reaction mixture was stirred for 5 h at room temperature. The solvent was removed under reduced pressure, the residue was suspended in ethyl acetate and washed with water, brine, dried over anhd sodium sulphate and concentrated to obtain gum which was purified by column chromatography (eluent: 40% ethyl acetate in light petroleum) to afford **3.38** (0.61 g, 92%, for 2 steps). TLC R_f = 0.3 (40% ethyl acetate/light petroleum); **IR** ($CDCI_3$): $\bar{\nu}$ 3200–3480, 1652 cm^{-1}; **^{1}H NMR** ($CDCI_3$, 200MHz): δ 7.20-7.25 (m, 4H, Ar H), 7.02-7.08 (m, 1H, Ar H), 6.70-6.92 (m, 7H, Ar H), 6.36 (d, 1H, *J* = 9.3 Hz), 5.97-6.18 (m, 1H, olefinic H), 5.72 (brs, 1H, OH), 5.30-5.49 (m, 3H), 4.86-4.97 (m, 1H), 4.65-4.67 (m, 3H), 4.54 (q, 4H, *J* = 11.8 Hz, 2 × CH_2), 4.31 (d, 2H, *J* = 3.3 Hz), 4.03-4.05 (m, 1H), 3.93 (t, 2H, *J* = 4.1 Hz), 3.69-3.82 (m, 1H, Ins H), 3.74 (s, 6H, 2 × CH_3), 3.38 (s, 3H, CH_3), 1.93 (s, 3H, CH_3) ppm; **^{13}C NMR** ($CDCl_3$, 50.3 MHz): δ 168.5 (C=O), 159.3, 145.5, 145.2, 133.5, 132.6, 130.3, 130.0, 129.7, 129.2, 121.9, 118.5, 115.7, 113.9, 111.7, 85.0, (CH_2), 78.6, 73.3 (CH_2), 71.5, 69.8 (CH_2), 69.2, 55.8, 55.1, 44.0, 14.0 ppm; elemental analysis calcd (%) for $C_{37}H_{43}NO_{10}$ (661.74): C 67.16, H 6.55, N, 2.12; Found: C 67.46, H 6.71, N, 2.40 %.

Experimental Procedures for Section 3B

General procedure for the preparation of inososes (procedure I): To a solution of the alcohol (2.00 to 4.00 mmol) in ethyl acetate (20 to 40 mL) was added IBX (4.00 to 8.00 mmol) and refluxed for 3 h. Then the reaction mixture was filtered through sintered glass funnel and washed with ethyl acetate. The combined filtrate and washings were evaporated under reduced pressure to obtain a crude product.

General procedure for the reaction of inososes with Grignard reagents (**Procedure J**): To a cooled (–10 ^{o}C) solution of the inosose (2.00 to 4.00 mmol) in dry diethyl ether (20 to 40 mL) was added a solution of RMgX (3.00 to 6.00 mmol) in diethyl ether and stirred for 1 h. The reaction mixture was diluted with diethyl ether, washed with saturated solution of ammonium chloride, water, followed by brine and dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure and the residue obtained was purified by column chromatography.

General procedure for the solvolysis of 1,3-acetal (**Procedure K**): A mixture of the acetal (1 to 5 mmol), conc. HCl (1 to 4 mL) and THF:water mixture (10 to 20 mL; 9:1) was refluxed for 12 h. The solvents were removed under reduced pressure to obtain gummy residue which was dissolved in dichloromethane (100 to 200 mL). The organic extract was washed with saturated $NaHCO_3$ solution followed by brine and dried over anhd sodium sulfate. The solvent was removed under reduced pressure and the colorless solid obtained was purified by column chromatography.

General procedure for hydrogenolysis of benzyl ether and acetylation of corresponding hydroxyl groups (Procedure L): The tribenzyl ether (0.5 to 1.1 mmol) was hydrogenolyzed (60 psi) in the presence of 20% Pd/C (0.03 to 0.05 g) in ethanol (10 mL) at rt for 24 h. Catalyst was filtered by using a short bed of Celite and washed with distilled water (2 × 10 mL). The combined filtrate and washings were evaporated under reduced pressure and the residue was co-evaporated with dry toluene (2 × 5 mL) to obtain the crude product. The crude product was acetylated with acetic anhydride (1 to 2 mL) and DMAP (0.010 to 0.020 g) in dry pyridine (3 to 5 mL) at room temperature (or 100 °C) for 12 to 40 h. The reaction mixture was worked up with dichloromethane and purified by column chromatography to obtain the corresponding pentaacetate or hexaacetate.

1,3-*O*-benzylidene-2-*O*-(4-methoxybenzyl)-4,6-di-*O*-benzyl-*myo*-5-inososе (**3.72**): The alcohol **2.28** (1.80 g, 3.16 mmol), IBX (1.77 g, 6.32 mmol) and ethyl acetate (20 mL) were used (Procedure I) to obtain crude product which was crystallized from hot methanol to obtain the pure ketone **3.72** (1.70 g, 95%). TLC R_f = 0.5 (20% ethyl acetate/light petroleum); **mp** 75.8–77.5 °C; **IR** ($CHCl_3$): $\bar{\nu}$ 1716 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.41-7.49 (m, 2H, Ar H), 7.20-7.40 (m, 15H, Ar H), 6.83-6.88 (m, 2H, Ar H), 5.66 (s, 1H, HCO_2), 4.67 (s, 2H, CH_2), 4.63 (q, 4H, J = 11.8 Hz, 2 × CH_2), 4.49 (m, 2H, Ins H), 4.23 (t, 1H, J = 2.0 Hz, Ins H), 4.17 (d, 2H, J = 2.5 Hz, Ins H), 3.79 (s, 3H, CH_3) ppm; **^{13}C NMR** ($CDCl_3$, 100.6 MHz): δ 201.0 (C=O), 159.3 (C_{arom}), 137.7 (C_{arom}), 136.6 (C_{arom}), 129.9 (C_{arom}), 129.7 (C_{arom}), 129.4 (C_{arom}), 128.4 (C_{arom}), 128.3 (C_{arom}), 128.1 (C_{arom}), 127.9 (C_{arom}), 126.2 (C_{arom}), 113.8 (C_{arom}), 93.9 (HCO_2), 79.4 (Ins C), 73.7 (Ins C), 71.9 (CH_2), 70.7 (CH_2), 66.0 (Ins C), 55.2 (CH_3) ppm; elemental analysis calcd (%) for $C_{35}H_{34}O_7$ (566.64): C 74.19, H 6.05; found: C 74.36, H 6.04 %.

1,3-*O*-Methylidene-2,4,6-tri-*O*-benzyl-*myo*-5-inososе (**1.138**)[46b]: The alcohol **1.47** (3.24 g, 7.00 mmol), ethyl acetate (40 mL) and IBX (3.92 g, 14.00 mmol) were used (procedure I) to obtain the ketone **1.138** as a gummy liquid. The gummy alcohol **1.138** was stored under *n*-pentane at –20 °C for 12 h when it turned into a colorless solid which was crystallized from a hot methanol to obtain pure ketone **1.138** (3.10 g, 96%). TLC R_f = 0.45 (15% ethyl acetate/light petroleum); **mp** 55–57 °C; **IR** ($CHCl_3$): $\bar{\nu}$ 1719 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 7.15-7.40 (m, 15H, Ar H), 5.48 (d, 1H, J = 4.7 Hz, $HCHO_2$), 4.55-4.74 (m, 6H), 4.43-4.53 (m, 4H), 3.92 (d, 2H, J = 3.8 Hz, Ins H) ppm; **^{13}C NMR** ($CDCl_3$, 50.3 MHz): δ 202.7 (C=O), 137.3 (C_{arom}), 136.8 (C_{arom}), 128.5 (C_{arom}), 128.3 (C_{arom}), 127.8 (C_{arom}), 85.5 (H_2CO_2), 81.6 (Ins C), 72.34 (CH_2), 72.26 (Ins C), 71.1 (CH_2), 69.8 (Ins C) ppm; elemental analysis calcd (%) for $C_{28}H_{28}O_6$ (460.52): C 73.03, H 6.13; found: C 72.69, H 6.12 %.

1,3-*O*-Methylidene-2,4,6-tri-*O*-benzyl-5-*C*-phenyl-*neo*-inositol (**3.73**): The ketone **1.138** (0.92 g, 2.00 mmol), dry diethyl ether (20 mL) and 1M solution of PhMgBr in diethyl ether (6.00 mL, 6.00 mmol) were used (procedure J) to obtain the compound **3.73** as a colorless solid (2.20 g, 94%) after coloumn chromatography (eluent: 15% ethyl acetate in light petroleum). TLC R_f = 0.4 in 15% ethyl acetate/light petroleum); **mp** 90–93 °C; **IR** ($CHCl_3$): $\bar{\nu}$ 3420-3540 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.10-7.44 (m, 20H, Ar H),

5.41 (d, 1H, J = 4.5 Hz, H_2CO_2), 4.93 (t, 1H, J = 2.2 Hz, Ins H), 4.87 (d, 1H, J = 4.5 Hz, H_2CO_2), 4.71 (s, 2H, CH_2), 4.42 (q, 4H, J = 12.0 Hz, 2 × CH_2), 4.36 (brs, 2H, Ins H), 4.08 (brs, 2H, Ins H), 3.52 (s, 1H, OH) ppm; **^{13}C NMR** ($CDCl_3$, 100.6 MHz): δ 145.2 (C_{arom}), 137.9 (C_{arom}), 136.8 (C_{arom}), 128.5 (C_{arom}), 128.2 (C_{arom}), 128.0 (C_{arom}), 127.9 (C_{arom}), 127.8 (C_{arom}), 127.7 (C_{arom}), 126.9 (C_{arom}), 125.6 (C_{arom}), 86.5 (H_2CO_2), 84.2 (Ins C), 75.7 (Ins C quart.), 72.9 (Ins C), 72.3 (CH_2), 71.8 (CH_2), 71.1 (Ins C) ppm; elemental analysis calcd (%) for $C_{34}H_{34}O_6$ (538.63): C 75.82, H 6.36; found: C 75.56, H 6.51 %.

1,3-*O*-Benzylidene-2,4,6-tri-*O*-benzyl-5-*C*-methyl-*neo*-inositol (**3.74**): The ketone **1.132** (1.07 g, 2.00 mmol), dry diethyl ether (20 mL) and 3M solution of MeMgI in diethyl ether (1.00 mL, 3.00 mmol) were used (Procedure J) to obtain **3.74** as a gum (1.05 g, 95%) after coloumn chromatography (eluent: 15% ethyl acetate in light petroleum). TLC R_f = 0.3 (15% ethyl acetate/light petroleum); **IR** ($CHCl_3$): $\bar{\nu}$ 3480–3570 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 7.27-7.60 (m, 20H, Ar H), 5.57 (s, 1H, HCO_2), 4.75 (s, 2H, CH_2), 4.68 (q, 4H, J = 11.7 Hz, 2 × CH_2), 4.67 (t, 1H, J = 2.8 Hz, Ins H), 4.41 (d, 2H, J = 2.8 Hz, Ins H), 3.73 (brs, 2H, Ins H), 2.60 (s, 1H, OH), 1.23 (s, 3H, CH_3) ppm; **^{13}C NMR** ($CDCl_3$, 50.3 MHz): δ 138.4 (C_{arom}), 138.3 (C_{arom}), 136.5 (C_{arom}), 129.2 (C_{arom}), 128.8 (C_{arom}), 128.4 (C_{arom}), 128.32 (C_{arom}), 128.28 (C_{arom}), 128.2 (C_{arom}), 127.8 (C_{arom}), 127.5 (C_{arom}), 126.5 (C_{arom}), 92.2 (HCO_2), 79.8 (Ins C), 77.2 (Ins C quart.), 73.1 (Ins C), 71.5 (CH_2), 70.8 (CH_2), 69.0 (Ins C), 25.1 (CH_3) ppm; elemental analysis calcd (%) for $C_{35}H_{36}O_6$ (552.66): C 76.06, H 6.57; found: C 75.87, H 6.91 %.

1,3-*O*-Benzylidene-2,4,6-tri-*O*-benzyl-5-*C*-phenyl-*neo*-inositol (**3.76**): The ketone **1.132** (2.15 g, 4.00 mmol), dry diethyl ether (40 mL) and 1M solution of PhMgBr in diethyl ether (6.00 mL, 6.00 mmol) were used (Procedure J) to obtain the compound **3.76** as a colorless solid (2.20 g, 94%) after coloumn chromatography (eluent: 15% ethyl acetate in light petroleum). TLC R_f = 0.3 (15% ethyl acetate/light petroleum); **mp** 145-147 °C; **IR** ($CHCl_3$): $\bar{\nu}$ 3481-3550 cm^{-1}; **^{1}H NMR** (CD_2Cl_2, 400 MHz): δ 7.05-7.60 (m, 21H, Ar H), 6.84-6.89 (m, 4H, Ar H), 5.94 (s, 1H, HCO_2), 4.80 (t, 1H, J = 2.7 Hz, Ins H), 4.73 (s, 2H, CH_2 or Ins H), 4.43 (d, 2H, J = 2.8 Hz, Ins H), 4.36 (q, 4H, J = 11.5 Hz, 2 × CH_2), 4.33 (s, 2H, Ins H or CH_2), 3.32 (s, 1H, OH) ppm; **^{13}C NMR** ($CDCl_3$, 100.6 MHz): δ 145.4 (C_{arom}), 139.1 (C_{arom}), 137.1 (C_{arom}), 129.5 (C_{arom}), 128.7 (C_{arom}), 128.55 (C_{arom}), 128.52 (C_{arom}), 128.2 (C_{arom}), 128.1 (C_{arom}), 128.0 (C_{arom}), 127.6 (C_{arom}), 126.8 (C_{arom}), 125.7 (C_{arom}), 92.6

(HCO_2), 82.5 (Ins C), 75.5 (Ins C quart.), 74.4 (Ins C), 72.4 (CH_2), 71.3 (CH_2), 70.1 (Ins C) ppm; elemental analysis calcd (%) for $C_{40}H_{38}O_6$ (614.73): C 78.15, H 6.23; found: C 77.82, H 5.98 %.

1,**3**-***O*-Benzylidene-2-*O*-(4-methoxybenzyl)-4,6-di-*O*-benzyl-5-*C*-methyl-*neo*-inositol** (**3.77**): The ketone **3.72** (1.13 g, 2.00 mmol), dry diethyl ether (20 mL) and 3M solution of MeMgI in diethyl ether (1.00 mL, 3.00 mmol) were used (Procedure J) to obtain compound **3.77** as a gum (1.09 g, 94%) after coloumn chromatography (eluent: 20% ethyl acetate in light petroleum). TLC R_f = 0.3 (20% ethyl acetate/light petroleum); **IR** ($CHCl_3$): $\bar{\nu}$ 3510–3580 cm^{-1}; **^{1}H NMR** (CD_2Cl_2, 500 MHz): δ 7.45-7.50 (m, 2H, Ar H), 7.2-7.40 (m, 15H, Ar H), 6.85-6.90 (m, 2H, Ar H), 5.61 (s, 1H, HCO_2), 4.65 (q, 4H, J = 11.6 Hz, 2 × CH_2), 4.61 (s, 2H, CH_2), 4.58 (t, 1H, J = 2.9 Hz, Ins H), 4.32 (d, 2H, J = 3.3 Hz, Ins H), 3.76 (s, 3H, OCH_3), 3.73-3.75 (m, 2H, Ins H), 2.56 (s, 1H, OH), 1.28 (s, 3H, CH_3) ppm; **^{13}C NMR** (CD_2Cl_2, 125.76 MHz): δ 159.6 (C_{arom}), 139.2 (C_{arom}), 137.5 (C_{arom}), 131.0 (C_{arom}), 129.7 (C_{arom}), 129.4 (C_{arom}), 129.0 (C_{arom}), 128.7 (C_{arom}), 128.5 (C_{arom}), 128.4 (C_{arom}), 126.8 (C_{arom}), 114.0 (C_{arom}), 92.3 (HCO_2), 81.1 (Ins C), 73.7 (Ins C), 72.2 (CH_2), 71.5 (Ins C quart.), 70.9 (CH_2), 69.4 (Ins C), 55.5 (OCH_3), 25.5 (CH_3) ppm; elemental analysis calcd (%) for $C_{36}H_{38}O_7$ (582.68): C 74.21, H 6.57; found: C 73.89, H 7.06 %.

2,**4**,**6-Tri-*O*-benzyl-5-*C*-methyl-*neo*-inositol** (**3.78**): The acetal **3.74** (0.83 g, 1.5 mmol), concd HCl (1 mL) and THF-water mixture (9 mL + 1 mL) were used (Procedure K) to obtain a gummy residue which was purified by column chromatography [eluent: 60% ethyl acetate in light petroleum] to afford the triol **3.78** as a colorless solid (0.67 g, 96%). TLC R_f = 0.4 (50% ethyl acetate/light petroleum); **mp** 129.5–130.5 °C; **IR** ($CHCl_3$): $\bar{\nu}$ 3540-3568, 3430-3460 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 7.27-7.48 (m, 15H, Ar H), 4.82 (s, 2H, CH_2), 4.79 (q, 4H, J = 11.3 Hz, 2 × CH_2), 3.86-4.08 (m, 3H, Ins H), 3.43 (d, 2H, J = 9.3 Hz, Ins H), 2.03-2.25 (m, 3H, 3 × OH), 1.37 (s, 3H, CH_3) ppm; **^{13}C NMR** ($CDCl_3$, 50.3 MHz): δ 138.7 (C_{arom}), 138.0 (C_{arom}), 128.4 (C_{arom}), 128.2 (C_{arom}), 127.8 (C_{arom}), 127.7 (C_{arom}), 82.5 (Ins C), 79.6 (Ins C), 75.9 (CH_2), 75.1 (CH_2), 74.8 (Ins C quart.), 71.6 (Ins C), 23.3 (CH_3) ppm; elemental analysis calcd (%) for $C_{28}H_{32}O_6$ (464.55): C 72.39, H 6.94; found: C 72.45, H 7.09 %.

2,**4**,**6-Tri-*O*-benzyl-5-*C*-benzyl-*neo*-inositol** (**3.79**): The ketone **1.132** (1.07 g, 2.00 mmol), dry diethyl ether (20 mL) and 1M solution of BnMgBr in diethyl ether (3.00 mL,

3.00 mmol) were used (procedure J) to obtain compound **3.75** as colorless solid (1.25 g) which was used for next reaction without purification. A mixture of crude **3.75** (1.25 g), concd HCl (2 mL) and THF-water mixture (10 mL + 1 mL) were used (Procedure K) to obtain a solid residue which was purified by column chromatography [eluent: 30 % ethyl acetate in light petroleum] to afford the triol **3.79** (0.99 g, 92%, for two steps) as a colorless solid. TLC R_f = 0.3 (30% ethyl acetate/light petroleum); **mp** 119.4–119.8 °C; **IR** ($CHCl_3$): $\bar{\nu}$ 3502, 3430-3537 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.25-7.45 (m, 18H, Ar H), 7.12-7.19 (m, 2H, Ar H), 4.88 (q, 4H, *J* = 11.5 Hz, 2 × CH_2), 4.80 (s, 2H, CH_2), 4.10-4.17 (m, 2H, Ins H), 3.98 (t, 1H, *J* = 3.2 Hz, Ins H), 3.65 (d, 2H, *J* = 9.2 Hz, Ins H), 3.21 (s, 2H, CH_2), 2.65 (brs, 1H, OH), 2.20 (d, 2H, *J* = 6.0 Hz, OH) ppm; **^{13}C NMR** ($CDCl_3$, 100.6 MHz): δ 138.7 (C_{arom}), 138.5 (C_{arom}), 137.1 (C_{arom}), 130.4 (C_{arom}), 128.5 (C_{arom}), 128.4 (C_{arom}), 127.7 (C_{arom}), 127.5 (C_{arom}), 127.4 (C_{arom}), 126.5 (C_{arom}), 79.6 (Ins C), 79.2 (Ins C), 77.9 (Ins C quart.), 74.6 (CH_2), 73.4 (CH_2), 72.1 (Ins C), 42.0 (CH_2) ppm; elemental analysis calcd (%) for $C_{34}H_{36}O_6$ (540.65): C 75.53, H 6.51; found: C 75.52, H 6.87 %.

2,**4**,**6-Tri-*O*-benzyl-5-*C*-phenyl-*neo*-inositol** (**3.80**): A mixture of the compound **3.76** (2.15 g, 3.50 mmol), concd HCl (2 mL) and THF-water mixture (20 mL + 2 mL) was used (Procedure K) to obtain a gummy residue which was purified by column chromatography [eluent: 50% ethyl acetate in light petroleum] to afford the triol **3.80** as a colorless solid (1.75 g, 95%). TLC R_f = 0.3 (40% ethyl acetate/light petroleum); **mp** 125–129 °C; IR ($CHCl_3$): $\bar{\nu}$ 3542-3567 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 7.33-7.70 (m, 10H, Ar H), 7.15-7.25 (m, 6H, Ar H), 7.85-7.04 (m, 4H, Ar H), 4.88 (s, 2H, CH_2), 4.01-4.13 (m, 5H, Ins H), 4.07 (q, 4H, *J* = 11.0 Hz, 2 × CH_2), 2.99 (s, 1H, OH), 2.24 (brs, 2H, OH) ppm; **^{13}C NMR** ($CDCl_3$, 50.3 MHz): δ 143.3 (C_{arom}), 138.8 (C_{arom}), 137.6 (C_{arom}), 128.5 (C_{arom}), 128.4 (C_{arom}), 128.2 (C_{arom}), 127.8 (C_{arom}), 127.7 (C_{arom}), 127.4 (C_{arom}), 125.8 (C_{arom}), 83.6 (Ins C), 79.2 (Ins C), 78.0 (Ins C quart.), 75.4 (CH_2), 75.1 (CH_2), 71.9 (Ins C) ppm; elemental analysis calcd (%) for $C_{33}H_{34}O_6$ (526.62): C 75.26, H 6.51; found: C 74.88; H 6.60 %.

4,**6-Di-*O*-benzyl-5-*C*-methyl-*neo*-inositol** (**3.81**): A mixture of the compound **3.77** (0.58 g, 1.00 mmol), conc. HCl (2 mL) and THF-water mixture (10 mL + 1 mL) were used (Procedure K; refluxed for 12 h) to obtain obtain a gummy liquid which was purified by

column chromatography (eluent: 60–70% ethyl acetate in light petroleum) to afford the tetrol **3.81** as a colorless solid (0.33 g, 88%). TLC R_f = 0.3 in ethyl acetate; **mp** 175.5–177.5 °C; **IR** (nujol): $\bar{\nu}$ 3280–3550 cm^{-1}; **^{1}H NMR** (CD_3OD, 200 MHz): δ 7.15-7.60 (m, 10H, Ar H), 4.97 (d, 2H, J = 11.0 Hz, CH_2), 4.89 (s, 2H, Ins H), 4.63 (d, 2H, J = 11.0 Hz, CH_2), 3.97 (t, 1H, Ins H), 3.87 (dd, 2H, J_1 = 2.9 Hz, J_2 = 9.8 Hz, Ins H), 3.45 (d, 2H, J = 9.9 Hz, Ins H), 1.23 (s, 3H, CH_3) ppm; **^{13}C NMR** (DMSO-D6, 125.76 MHz): δ 139.7 (C_{arom}), 128.1 (C_{arom}), 128.0 (C_{arom}), 82.2 (Ins C), 74.7 (CH_2), 74.2 (Ins C quart.), 73.0 (Ins C), 70.9 (Ins C), 22.9 (CH_3) ppm; elemental analysis calcd (%) for $C_{21}H_{26}O_6$ (374.428): C 67.36, H 7.00; found: C 67.74, H 6.83 %.

1,2,3,4,6-Penta-*O*-acetyl-5-*C*-methyl-*neo*-inositol (**3.82**): The triol **3.78** (0.46 g, 1.0 mmol), was hydrogenolyzed in presence of 20% Pd/C (0.04 g), ethanol (10 mL) and the resulting product was acetylated by using acetic anhydride (2.0 mL), DMAP (0.020 g), dry pyridine (5 mL) (Procedure L) to obtain **3.82** as a white solid (0.36 g, 89% for 2 steps) after column chromatography (eluent: 40% ethyl acetate in light petroleum). TLC R_f = 0.50 (40% ethyl acetate/light petroleum); **mp** 124–126 °C; **IR** ($CHCl_3$): $\bar{\nu}$ 3461, 1753, 1728 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 5.64 (t, 1H, J = 3.1 Hz, Ins H), 5.40 (dd, 2H, J_1 = 2.9 Hz, J_2 = 10.5 Hz, Ins H), 5.30 (d, 2H, J = 10.5 Hz, Ins H), 2.20 (s, 3H, CH_3), 2.14 (s, 6H, 2 × CH_3), 1.99 (s, 6H, 2 × CH_3), 1.18 (s, 3H, CH_3) ppm; **^{13}C NMR** ($CDCl_3$, 125.76 MHz): δ 170.1 (C=O), 169.8 (C=O), 169.6 (C=O), 73.2 (Ins C quart.), 72.0 (Ins C), 68.4 (Ins C), 68.0 (Ins H), 22.4 (CH_3), 20.8 (CH_3), 20.6 (CH_3), 20.5 (CH_3) ppm; elemental analysis calcd (%) for $C_{17}H_{24}O_{11}$ (404.37): C 50.49, H 5.98; found: C 50.99, H 5.59 %.

1,2,3,4,5,6-Penta-*O*-acetyl-5-*C*-benzyl-*neo*-inositol (**3.83**): The triol **3.79** (0.27 g, 0.5 mmol), was hydrogenolyzed in the presence of 20% Pd/C (0.03 g) in ethanol (10 mL) and the corresponding product was acetylated by acetic anhydride (1.5 mL), DMAP (0.010 g) and dry pyridine (4 mL; at 100 °C for 12 h) (Procedure L) to obtain **3.83** as a colorless solid (0.24 g, 92% for two steps) after column chromatography (eluent: 40% ethyl acetate in light petroleum). TLC R_f = 0.4 (40% ethyl acetate/light petroleum); **mp** 181.3 °C; **IR** ($CHCl_3$): $\bar{\nu}$ 1760, 1755, 1750 cm^{-1}; **^{1}H NMR** (CD_2Cl_2, 500 MHz): δ 7.16-7.30 (m, 5H, Ar H), 5.51 (t, 1H, J = 2.9 Hz, Ins H), 5.33 (d, 2H, J = 10.0 Hz, Ins H), 5.24 (dd, 2H, J_1 = 3.0 Hz, J_2 = 10.4 Hz, Ins H), 3.56 (s, 2H, CH_2), 2.17 (s, 3H, CH_3), 2.01 (s, 3H, CH_3), 1.89 (s, 6H, 2 × CH_3), 1.88 (s, 6H, 2 × CH_3) ppm; **^{13}C NMR** (CD_2Cl_2, 125.76 MHz): δ 170.2

(C=O), 170.0 (C=O), 169.6 (C=O), 169.56 (C=O), 135.3 (C_{arom}), 130.6 (C_{arom}), 128.8 (C_{arom}), 127.4 (C_{arom}), 70.8 (Ins C), 69.5 (Ins C), 38.9 (CH_2), 22.9 (CH_3), 20.8 (CH_3), 20.7 (CH_3) ppm; elemental analysis calcd (%) for $C_{25}H_{30}O_{12}$ (522.50): C 57.47, H 5.79; found: C 57.07, H 5.89 %.

1,**2**,**3**,**4**,**6-Penta-*O*-acetyl-5-*C*-phenyl-*neo*-inositol** (**3.84**): The triol **3.80** (0.68 g, 1.1 mmol) was hydrogenolyzed in the presence of 20% Pd/C (0.05 g) in ethanol (10 mL) and the resulting product was acetylated by with acetic anhydride (2.5 mL), DMAP (0.015 g) in dry pyridine (7 mL) at ambient temperature for 40 h (procedure L) to obtain **3.84** as a colorless solid (0.46 g, 90% for two steps) after column chromatography (eluent: 40% ethyl acetate in light petroleum) TLC R_f = 0.4 (40% ethyl acetate/light petroleum); **mp** 241-242 °C; **IR** ($CHCl_3$): $\bar{\nu}$ 3479, 1749, 1737 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 7.24-7.50 (m, 5H, Ar H), 5.71-5.82 (m, 3H, Ins H), 5.56 (dd, 2H, J_1 = 2.9 Hz, J_2 = 10.3 Hz, Ins H), 2.80 (brs, 1H, OH), 2.28 (s, 3H, CH_3), 1.99 (s, 6H, 2 × CH_3), 1.77 (s, 6H, 2 × CH_3) ppm; **^{13}C NMR** ($CDCl_3$, 125.76 MHz): δ 170.1 (C=O), 169.7 (C=O), 168.7 (C=O), 138.1 (C_{arom}), 128.2 (C_{arom}), 125.4 (C_{arom}), 77.6 (Ins C quart.), 71.8 (Ins C), 68.9 (Ins C), 68.2 (Ins H), 20.9 (CH_3), 20.5 (CH_3), 20.1 (CH_3) ppm; elemental analysis calcd (%) for $C_{22}H_{26}O_{11}$ (466.44): C 56.65, H 5.62; found: C 56.40, H 5.41 %.

Experimental Procedures for Section 3C

General procedure for the aromatization of inososes (**Procedure M**): To a cooled (0 ^{o}C) solution of the inosose (1.00 to 3.00 mmol) in dry THF (5 to 15 mL) was added sodium hydride (1.00 to 3.00 mmol) and stirred for 5 min. The solvent was removed under reduced pressure and the crude reaction mixture was dissolved in ethyl acetate, washed successively with water, 2% aq. hydrochloric acid, saturated sodium bicarbonate solution followed by brine and dried over anhd sodium sulphate. The solvent was removed under reduced pressure and the crude product obtained was purified by column chromatography (eluent: ethyl acetate in light petroleum) to afford the tetrahydroxy benzene derivative.

2,**4**,**6-tris**(**benzyloxy**)**phenol** (**3.133**): The *myo*-inosose **1.132** (1.61 g, 3.00 mmol), dry THF (15 mL) and sodium hydride (0.12 g, 3.00 mmol) were used (procedure M) to obtain **3.133** as a colorless solid (1.21 g, 98%) after column chromatography (eluent: 15% ethyl acetate in light petroleum). TLC R_f = 0.3 (15% ethyl acetate/light petroleum); **mp** 103-105 °C; **IR** ($CHCl_3$): $\bar{\nu}$ 3340–3620, 1630 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 7.26-7.50 (m, 15H, Ar H), 6.30 (s, 2H, Ar H), 5.21 (s, 1H, OH), 5.09 (s, 4H, 2 × CH_2), 4.90 (s, 2H, CH_2) ppm; **^{13}C NMR** ($CDCl_3$, 50.3 MHz): 151.8, 146.4, 136.9, 136.6, 130.4, 128.54, 128.48, 128.0, 127.9, 127.53, 127.48, 95.4, 71.4 (CH_2), 70.7 (CH_2) ppm; elemental analysis calcd (%) for $C_{27}H_{24}O_4$ (412.48): C 78.62, H 5.86; found: C 78.40, H 5.62 %.

2,**4**,**6-Tris(benzyloxy)-5-hydroxycyclohex-2-enone (3.134)**: To a cooled (–10 ^{o}C) solution of the *myo*-inosose **1.132** (1.60 g, 3.00 mmol) in dry THF (15 mL) was added triethyl amine (0.50 mL, 3.50 mmol) and stirred for 1 h. The reaction mixture was diluted with ethyl acetate, washed with water, followed by brine and dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure and the brown solid obtained was purified by column chromatography (eluent: 30% ethyl acetate in light petroleum) to afford **3.134** as a colorless solid (1.15 g, 89%): TLC R_f = 0.3 (30% ethyl acetate/light petroleum); **mp** 86–88 °C; **IR** ($CHCl_3$): $\bar{\nu}$ 3497, 1705, 1626 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 7.27-7.50 (m, 15H, Ar H), 5.70 (d, 1H, J = 5.6 Hz), 5.00 (d, 1H, J = 11.2 Hz), 4.82 (s, 2H), 4.55-4.75 (m, 3H), 4.40-4.47 (m, 1H), 4.35 (d, 1H, J = 8.7 Hz), 4.05-4.17 (m, 1H), 2.72 (d, 1H, J = 4.5 Hz, OH) ppm; **^{13}C NMR** ($CDCl_3$, 50.3 MHz): δ 191.4 (C=O), 150.3 (C_{arom}), 137.8 (C_{arom}), 137.4 (C_{arom}), 135.4 (C_{arom}), 128.5 (C_{arom}), 128.4 (C_{arom}), 128.3 (C_{arom}), 128.2 (C_{arom}), 128.0 (C_{arom}), 127.9 (C_{arom}), 127.85 (C_{arom}), 127.81 (C_{arom}), 127.2

(C_{arom}), 112.2, 80.4, 73.6 (CH_2), 72.4 (Ins C), 72.1 (CH_2), 71.1 (Ins C), 69.8 (CH_2) ppm; elemental analysis calcd (%) for $C_{27}H_{26}O_5$ (430.49): C 75.33, H 6.09; found: C 75.52, H 6.42 %.

2,**4**,**6-Tri-*O*-benzyl-*myo*-5-inososе** (**3.135**): The *myo*-5-inosose **1.138**[46b] (2.30 g, 5.00 mmol), conc. HCl (4 mL) and THF-water mixture (25 mL + 2.5 mL) were used (Procedure K) to obtain the diol **3.135** as a colorless solid (2.04 g, 91%) after column chromatography (eluent: 30% ethyl acetate in light petroleum). TLC R_f = 0.3 (35% ethyl acetate/light petroleum); **mp** 124-127 °C; **IR** ($CHCl_3$): $\bar{\nu}$ 3325–3550, 1733 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 7.24-7.50 (m, 15H, Ar H), 4.92 (s, 2H, CH_2), 4.72 (q, 4H, J = 11.1 Hz, 2 × CH_2), 4.42 (d, 2H, J = 10.0 Hz, Ins H), 4.22 (t, 1H, J = 2.6 Hz, Ins H), 3.67-3.78 (dd, 2H, J_1 = 2.6, J_2 = 10.1 Hz, Ins H), 2.38-2.85 (brs, 2H, OH) ppm; **^{13}C NMR** ($CDCl_3$, 50.3 MHz): δ 203.0 (C=O), 138.3 (C_{arom}), 137.2 (C_{arom}), 128.45 (C_{arom}), 128.37 (C_{arom}), 128.2 (C_{arom}), 128.0 (C_{arom}), 127.9 (C_{arom}), 127.8 (C_{arom}), 82.7 (Ins C), 78.1 (Ins C), 75.6 (CH_2), 73.3 (CH_2), 72.2 (Ins C) ppm; elemental analysis calcd (%) for $C_{27}H_{28}O_6$ (448.50): C 72.30, H 6.29; found: C 72.52, H 6.02 %.

Reaction of inosose 1.138 and 3.135 with sodium hydride: The inosose **1.138** or **3.135** (2 mmol), dry THF (10 mL) and sodium hydride (1.0 to 1.5 mmol) were used (Procedure M) to obtain 2,4,6-tris(benzyloxy)phenol **3.133** as a colorless solid (94–96%) after column chromatography.

Reaction of inosose 1.138 and 3.135 with triethyl amine: To a cooled (–10 ^oC) solution of the inosose **1.138** or **3.135** (1.0 to 1.5 mmol) in dry THF (10 mL), added dry triethyl amine (1.0 to 1.5 mmol) and stirred for 1 h. The reaction mixture was worked up with ethyl acetate and the brown solid obtained was purified by column chromatography to obtain **3.134** as a colorless solid (88–90%).

1,**3-*O*-Methylidene-2**,**4**,**6-tri-*O*-methyl-*myo*-inositol (3.141)**: 1 M solution of DIBAL-H in toluene (12.50 mL, 12.50 mmol), **1.43** (1.16 g, g, 5.00 mmol), dry dichloromethane (50 mL), Na / K tartrate (30 g in 50 mL water) and saturated ammonium chloride solution (50 mL) were used (Procedure C) to obtain **3.141** as a colorless solid (1.17 g, 98%) after column chromatography (eluent: 25% ethyl acetate in light petroleum). TLC R_f= 0.3 (25% ethyl acetate/light petroleum); **mp** 70-71 ^oC; **IR** ($CHCl_3$): $\bar{\nu}$ 3250–3620 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 5.41 (d, 1H, J = 5.1 Hz, H_2CO_2), 4.70 (d, 1H, J = 5.1 Hz, HCO_2),

4.30-4.45 (m, 2H, Ins H), 3.75-3.90 (m, 4H, Ins H), 3.48 (s, 6H, CH_3), 3.46 (s, 3H, CH_3), 3.00 (d, 1H, J = 9.2 Hz, OH) ppm; **^{13}C NMR** ($CDCl_3$, 50.3 MHz): δ 85.3 (CH_2), 83.4 (Ins C), 71.8 (Ins C), 71.2 (Ins C), 69.6 (Ins C), 58.3 (CH_3), 56.1 (CH_3); elemental analysis calcd (%) for $C_{10}H_{18}O_6$ (234.25): C 51.27, H 7.75; found: C 51.13, H 7.68 %.

1,3-*O*-Methylidene-2,4,6-tri-*O*-methyl-*myo*-5-inosose (3.143): The alcohol **3.141** (0.80 g, 3.41 mmol), ethyl acetate (15 mL) and IBX (0.56 g, 6.00 mmol) were used (procedure I) to obtain the ketone **3.143** (0.74 g, 94%) as a crystalline solid (crystals from hot 15% ethyl acetate in light petroleum). TLC R_f = 0.5 (25% ethyl acetate/light petroleum); **mp** 45.8–47 ^{o}C; **IR** ($CHCl_3$): $\bar{\nu}$ 1725 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 5.30 (d, 1H, J = 4.9 Hz, H_2CO_2), 4.51 (d, 1H, J = 4.8 Hz, H_2CO_2), 4.37-4.40 (m, 2H, Ins H), 4.15 (t, 1H, J = 1.2 Hz, Ins H), 3.59 (d, 2H, J = 3.6 Hz, Ins H), 3.44 (s, 3H, CH_3), 3.35 (s, 6H, CH_3) ppm; **^{13}C NMR** ($CDCl_3$, 125.76 MHz): δ 202.9 (C=O), 85.7 (CH_2), 84.5 (Ins C), 72.0 (Ins C), 71.9 (Ins C), 58.9 (CH_3), 56.7 (CH_3); elemental analysis calcd (%) for $C_{10}H_{16}O_6$ (232.23): C 51.72, H 6.94; found: C 51.69, H 7.14 %.

1,3-*O*-Methylidene-2-*O*-methy-4,6-di-*O*-allyl-*myo*-5-inosose (3.144): The 4,6-di-*O*-allyl-1,3,5-orthoformate (5.00 g, 18.50 mmol,) dry DMF (100 mL), sodium hydride (0.96 g, 24.00 mmol) and methyl iodide (1.30 mL, 20.35 mmol) were used (Procedure B) to obtain the corresponding methyl ether (5.30 g; TLC R_f = 0.4 in 20% ethyl acetate/light petroleum) which was used in the next reaction without purification. The crude methyl ether (5.30 g), 1 M solution of DIBAL-H in toluene (46.00 mL, 46.00 mmol), dry dichloromethane (150 mL), Na / K tartrate (110 g in 180 mL water) and saturated ammonium chloride solution (180 mL) were used (procedure C) to obtain **3.142** (5.31 g; TLC R_f = 0.4 (25% ethyl acetate/light petroleum) as a gummy liquid, which was used in next reaction without purification.

The crude **3.142** (2.7 g), ethyl acetate (50 mL) and IBX (5.18 g, 18.50 mmol) were used (procedure I) to obtain the ketone **3.144** (2.45 g, 93%, over 3 steps) as a colorless gum, after column chromatography (eluent: 10% ethyl acetate in light petroleum). TLC R_f = 0.45 (15% ethyl acetate/light petroleum); **IR** ($CHCl_3$): $\bar{\nu}$ 1726 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 5.75-596 (m, 2H), 5.32-5.40 (m, 2H), 5.16-5.27 (m, 3H), 4.60 (d, 1H, J = 5.2 Hz), 4.42-4.50 (m, 2H), 4.32-4.35 (m, 1H), 3.93-4.16 (m, 4H), 3.86 (d, 2H, J = 3.2 Hz), 3.52 (s, 3H, CH_3) ppm; **^{13}C NMR** ($CDCl_3$, 125.76 MHz): δ 202.9 (C=O), 133.2 (CH), 118.0

(H_2CO_2), 85.3 (CH_2), 81.2 (Ins C), 71.7 (Ins C), 71.6 (Ins C), 71.2 (CH_2), 56.4 (CH_3); elemental analysis calcd (%) for $C_{14}H_{20}O_6$ (227.23): C 59.14, H 7.09; found: C 59.03, H 6.47 %.

1,3-*O*-Methylidene-2-*O*-(4-methoxybenzyl)-4,6-di-*O*-benzyl-*myo*-5-inosose (3.145): The alcohol **1.55** (1.48 g, 3.00 mmol), IBX (1.68 g, 6.00 mmol) and ethyl acetate (20 mL) were used (procedure I) to obtain the ketone **3.145** as a colorless gum (1.41 g, 95%) after column chromatography (eluent: 10% ethyl acetate in light petroleum). TLC R_f = 0.35 in 10% ethyl acetate/light petroleum; **IR** ($CHCl_3$): $\bar{\nu}$ 1719 cm $^{-1}$; **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 7.15-7.40 (m, 12H, Ar H), 6.80-6.91 (m, 2H, Ar H), 5.46 (d, 1H, H_2CO_2, J = 4.7 Hz), 4.71 (t, 1H, J = 1.4 Hz, Ins H), 4.57-4.67 (m, 5H), 4.42-4.51 (m, 4H), 3.91 (d, 2H, J = 3.6 Hz), 3.79 (s, 3H, CH_3) ppm; **^{13}C NMR** ($CDCl_3$, 50.3 MHz): δ 202.8 (C=O), 159.4 (C_{arom}), 136.9 (C_{arom}), 129.7 (C_{arom}), 128.3 (C_{arom}), 127.8 (C_{arom}), 113.9 (C_{arom}), 85.5 (H_2CO_2), 81.7 (Ins C), 72.32 (CH_2), 72.28 (Ins C), 70.7 (CH_2), 69.2 (Ins C), 55.2 (CH_3) ppm; elemental analysis calcd (%) for $C_{29}H_{30}O_7$ (490.54): C 71.00, H 6.16; found: C 70.93, H 5.93 %.

2,4,6-Tri-methoxyphenol (3.146): The *myo*-inosose **3.143** (0.23 g, 1.00 mmol), dry THF (5 mL) and sodium hydride (0.04 g, 1.00 mmol) were used (Procedure M) to obtain **3.146** (0.175 g, 95%) as a yellow crystalline solid after column chromatography (eluent: 10% ethyl acetate in light petroleum). TLC R_f = 0.3 (30% ethyl acetate/light petroleum); **mp** 58–61.2 °C; **IR** ($CHCl_3$): $\bar{\nu}$ 3440–3450, 1622 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 6.19 (s, 2H, Ar H), 5.12 (s, 1H, OH), 3.87 (s, 3H, CH_3), 3.77 (s, 6H, CH_3) ppm; **^{13}C NMR** ($CDCl_3$, 50.3 MHz): 153.0, 147.3, 129.0, 91.7, 56.2 (CH_3), 55.7 (CH_3) ppm; elemental analysis calcd (%) for $C_9H_{12}O_4$ (184.19): C 58.69, H 6.57; found: C 58.30, H 6.78 %.

2,6-Bis(allyloxy)-4-methoxyphenol (3.147): The *myo*-inosose **3.144** (0.85 g, 3.00 mmol), dry THF (15 mL) and sodium hydride (0.12 g, 3.00 mmol) were used (Procedure M) to obtain **3.147** (0.67 g, 95%) as a colorless solid, after column chromatography (eluent: 10% ethyl acetate in light petroleum). TLC R_f = 0.5 (20% ethyl acetate/light petroleum); **mp** 63.5–65 °C; **IR** ($CHCl_3$): $\bar{\nu}$ 3100–3400, 1622 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 6.19 (s, 2H, Ar H), 5.98-6.17 (m, 2H), 5.43-5.47 (m, 1H), 5.30-5.40 (m, 2H), 5.24-5.30 (m, 1H), 5.17 (s, 1H, OH), 4.55-4.59 (m, 4H), 3.73 (s, 3H, CH_3) ppm; **^{13}C NMR** ($CDCl_3$, 50.3

MHz): 152.6, 146.3, 133.1, 129.9, 118.0, 93.7, 70.2, 55.6, ppm; elemental analysis calcd (%) for $C_{13}H_{16}O_4$ (236.26): C 66.09, H 6.83; found: C 66.28, H 7.00 %.

2,6-Bis(benzyloxy)-4-(4-methoxybenzyloxy)phenol (3.148): The *myo*-inosose **3.145** (0.98 g, 2.00 mmol), dry THF (10 mL) and sodium hydride (0.80 g, 2.00 mmol) were used (procedure M) to obtain **3.148** as a colorless solid (0.85 g, 96%) after column chromatography (eluent: 10% ethyl acetate in light petroleum). TLC R_f = 0.3 in 10% ethyl acetate/light petroleum; **mp** 94.6-95.7 °C; **IR** ($CHCl_3$): $\bar{\nu}$ 3514 cm $^{-1}$; **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 7.27-7.49 (m, 12H, Ar H), 6.80-6.95 (m, 2H, Ar H) , 6.29 (s, 2H, Ar H), 5.21 (s, 1H, OH), 5.09 (s, 4H, 2 × CH_2), 4.82 (s, 2H, CH_2), 3.81 (s, 3H, CH_3) ppm; **^{13}C NMR** ($CDCl_3$, 50.3 MHz): 159.3, 151.8, 146.4, 136.7, 130.3, 129.2, 128.9, 128.5, 128.0, 127.5, 113.9, 95.4, 71.3 (CH_2), 70.4 (CH_2), 55.2 (CH_3) ppm; elemental analysis calcd (%) for $C_{28}H_{26}O_5$ (442.50): C 76.00, H 5.92; found: C 75.60, H 6.05 %.

***Racemic* 2,4,6-tri-*O*-benzyl-5-*C*-phenyl-1-*O*-tosyl-*neo*-inositol (3.149)**: To a cooled (0 °C) solution of the triol **3.80** (0.30 g, 0.57 mmol) in pyridine (3 mL), TsCl (0.11 g, 0.57 mmol) was added and stirred for 12 h. The reaction mixture was concentrated under reduced pressure to get a gum which was worked up with ethyl acetate; the organic extract was dried over anhd sodium sulfate. The solvent was removed under reduced pressure and the gummy compound obtained was purified by column chromatography (eluent: 20% ethyl acetate in light petroleum) to afford **3.149** as a gummy liquid (0.29 g, 72%). TLC R_f= 0.5 (30% ethyl acetate/light petroleum); **IR** ($CHCl_3$): $\bar{\nu}$ 3510-3550 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 7.70-7.87 (m, 2H, Ar H), 7.05-7.60 (m, 18H, Ar H), 6.85-7.00 (m, 2H, Ar H), 6.55-6.70 (m, 2H, Ar H), 4.74-5.01 (m, 3H), 3.88-4.15 (m, 7H), 3.72 (d, 1H, J = 10.4 Hz, Ins H), 2.96 (s, 1H, OH), 2.35 (m, 3H, CH_3), 2.05 (s, 1H, OH) ppm; **^{13}C NMR** ($CDCl_3$, 125.76 MHz): δ 144.8, 142.4, 138.5, 137.5, 137.0, 133.7, 129.8, 128.5, 128.3, 128.1, 127.9, 127.82, 127.77, 127.6, 127.5, 82.5 (Ins C), 82.1 (Ins C), 80.2 (Ins C), 78.6 (Ins C), 78.1 (Ins C), 75.7 (CH_2), 75.6 (Ins C), 75.3 (CH_2), 21.6 (CH_3); elemental analysis calcd (%) for $C_{40}H_{40}O_8S$ (680.81): C 70.57, H 5.92, S 4.71; found: C 70.88, H 5.80, S 4.92 %.

2,4,6-Tris(benzyloxy)-[1,1'-biphenyl]-3-ol (3.151): The alcohol **3.149** (0.068 g, 0.10 mmol), ethyl acetate (10 mL) and IBX (0.056 g, 0.2 mmol) were used (procedure I) to obtain the ketone **3.150** as a gummy liquid (0.066 g, TLC R_f = 0.3 in 20% ethyl acetate/light petroleum) which was used for the next reaction without purification. The

ketone **3.150** (0.066 g), dry THF (5 mL) and sodium hydride (0.01 g, 0.25 mmol) were used (procedure M) to obtain the 2,4,6-tris(benzyloxy)-[1,1'-biphenyl]-3-ol **3.151** as a gummy liquid (0.046 g, 94%) after column chromatography (eluent: 10% ethyl acetate in light petroleum). TLC R_f = 0.6 in 20% ethyl acetate/light petroleum; **IR** ($CHCl_3$): $\bar{\nu}$ 3525 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 7.0-7.50 (m, 20H, Ar H), 6.50 (s, 1H, Ar H), 5.37 (s, 1H, OH), 5.10 (s, 2H, CH_2), 4.79 (s, 2H, CH_2), 4.57 (s, 2H, CH_2) ppm; **^{13}C NMR** ($CDCl_3$, 125.76 MHz): 148.8, 145.6, 144.3, 137.2, 136.9, 136.6, 134.5, 133.8, 131.1, 128.7, 128.4, 128.3, 128.27, 128.2, 128.0, 127.8, 127.7, 127.6, 127.1, 126.9, 119.9, 98.8, 74.9 (CH_2), 72.3 (CH_2), 71.6 (CH_2) ppm; elemental analysis calcd (%) for $C_{33}H_{28}O_4$ (488.57): C 81.12, H 5.78, found: C 79.85, H 6.12 %.

3D.3. References.

1. (a) Chapleur, Y. *Carbohydrate Mimics*; Wiley-VCH: Weinheim, **1998**; (b) Asano, N. *J. Enzyme Inhib*. **2000**, *15*, 215–234; (c) Mahmud, T. *Nat. Prod. Rep.* **2003***, 20*, 137–166; (d) Busscher, G. F.; Rutjes, F. P. J. T.; van Delft, F. L. *Chem. Rev.* **2005**, *105*, 775–791; (e) Díaz, L.; Delgado, A., *Curr. Med. Chem.* **2010**, *17*, 2393–2418 and references cited therein.
2. (a) Diaz, L.; Casas, J.; Bujons, J.; Llebaria, A.; Deglado, A. *J. Med. Chem*. **2011**, *54*, 2069–2079; (b) Kilbas, B.; Balci, M. *Tetrahedron* **2011**, *67*, 2355–2389; (c) Duchek, J.; Adams, D. R.; Hudlicky, T. *Chem. Rev.* **2011**, *111*, 4223–4258; (d) Harrak, Y.; Barra, C. M.; Delgado, A.; Castaño, A. R.; Llebaria, A. *J. Am. Chem. Soc.* **2011**, *133,* 12079–12084 and references cited therein.
3. Zheng, Y. G.; Shentu, X. P.; Shen, Y. C. *J. Enzyme Inhib. Med. Chem.* **2005***, 20*, 49–53.
4. (a) Chang, Y.; Choi, G.; Bae, Y.; Burdett, M.; Moon, H.; Lee, J.; Gray, N.; Schultz, P.; Meijer, L.; Chung, S.; Choi, K.; Suh, P.; Ryu, S. *ChemBioChem* **2002**, *3*, 897–901; (b) Mills, S. J.; Potter, B. V. L. *Bioorg. Med. Chem.* **2003**, *11*, 4245–4253.
5. (a) Powis, G.; Aksoy, I. A.; Melder, D. C.; Aksoy, S.; Eichinger, H.; Fauq, A. H.; Kozikowski, A. P. *Cancer Chemother. Pharmacol.* **1991**, *29*, 95–104; (b) Brunn, G.; Fauq, A. H.; Chow, S.; Kozikowski, A. P.; Gallegos, A.; Powis, G. *Cancer Chemother. Pharmacol.* **1994**, *35*, 71–79; (c) Clarke, J. H. *Curr. Biol.* **2003**, *13*, R815- R817.
6. (a) Wakisaka, Y.; Koizumi, K.; Nishimoto, Y.; Kobayashi, M.; Tsuji, N. *J. Antibiot.* **1980**, *33*, 695–704; (b) Uyeda, M.; Mizukami, M.; Yokomizo, K.; Suzuki, K. *Biosci. Biotechnol. Biochem*. **2001**, 65, 1252–1254.
7. Guerrer, M. C.; Modolell, J. *Eur. J. Biochem.* **1980**, *107*, 409–414.
8. (a) Yoshida, M.; Takahashi, E.; Uozumi, T.; Beppu, T. *Agric. Biol. Chem*. **1986**, *50*, 143–149; (b) Nakagawa, A.; Fujimoto, T.; Omura, S.; Walsh, J. C.; Stoish, R. L.; George, B. *J. Antibiot.* **1987**, *40*, 1627–1635; (c) Cooper, C. B.; Blair, K. T.; Jones, C. S.; Minich, M. L. *Bioorg. Med. Chem. Lett*. **1997**, *7*, 1747–1752 and references cited therein.

9. (a) James, B. H.; Elliott, N. C.; Jefson, M. R.; Koss, D. A.; Schicho, D. L. *J. Org. Chem*. **1994**, *59*, 1224–1225; (b) Palaniappan, N.; Ayers, S.; Gupta, S.; Habib el, S. E.; Reynolds, K. A. *Chemistry & Biology* **2006**, *13*, 753–764; (c) Visser, M. S.; Freeman-Cook, K. D.; Brickner, S. J.; Brighty, K. E.; Le, P. T.; Wade, S. K.; Monahan, R.; Martinelli, G. J.; Blair, K. T.; Moore, D. E. *Bioorg. Med. Chem. Lett*. **2010**, *20*, 6730–6734.
10. Lee, H. B.; Kim, C. -J.; Kim, J. -S.; Hong, K. -S.; Cho, K. Y. *Lett. Appl. Microbiol*. **2003**, *36*, 387–391.
11. McCasland, G. E.; Furuta, S.; Johnson, L. F.; Shoolery, J. N. *J. Am. Chem. Soc.* **1961**, *83*, 2335–2343.
12. Trost, B. M.; Dudash, J. *Chem. Eur. J.* **2001**, *7*, 1619–1629.
13. Donohoe, T. J.; Johnson, P. D.; Pye, R. J.; Keenan, M. *Org. Lett.* **2005**, *7*, 1275–1277.
14. (a) Arjona, O.; deDios, A.; Plumet, J.; Saez, B. *J. Org. Chem.* **1995**, *60*, 4932–4935; (b) Arjona, O.; deDios, A.; Plumet, J.; Saez, B.; *Tetrahedron Lett.* **1995**, *36*, 1319–1320.
15. Chida, N.; Nakazawa, N.; Ohtsuka, M.; Suzuki, M.; Ogawa, S. *Chem. Lett.* **1990**, 423–426.
16. (a) Chida, N.; Ohtsuka, M.; Ogawa, S. *Chem. Lett.* **1988**, *17*, 969–972; (b) Chida, N.; Ohtsuka, M.; Nakazawa, K.; Ogawa, S. *J. Chem. Soc., Chem. Commun.* **1989**, *7*, 436–438; (c) Chida, N.; Ohtsuka, M.; Nakazawa, K.; Ogawa, S. *J. Org. Chem.* **1991**, *56*, 2976–2983.
17. Donohoe, T. J.; Flores, A.; Battaille, C. J. R.; Churruca, F. *Angew. Chem. Int. Ed*. **2009**, *48*, 6507–6510.
18. Palaniappan, N.; Dhote, V.; Ayers, S.; Starosta, A. L.; Wilson, D. N.; Reynolds, K. A. *Chemistry & Biology* **2009**, *16,* 1–10.
19. (a) Gauthier, D. R.; Bender, S. L. *Tetrahedron Lett.* **1996**, *37*, 13–16; (b) Chida, N.; Ogawa, S. *Chem. Commun.* **1997**, 807–813; (c) Suzuki, T.; Suzuki, S. T.; Yamada, I.; Koashi, Y.; Yamada, K.; Chida, N. *J. Org. Chem.* **2002**, *67*, 2874–2880; (d) Sato, K.-I,; Akai, S.; Sugita, N.; Ohsawa, T.; Kogure, T.; Shoji, H.; Yoshimura, J.

J. Org. Chem. **2005**, *70*, 7496–7504; (e) Jagdhane, R. C.; Shashidhar, M. S. *Tetrahedron*, **2011**, *67*, 7963–7970.

20. Murali, C. Ph.D thesis University of Pune **2008**.
21. (a) Lee, H. W.; Kishi, Y. J. *J. Org. Chem.* **1985**, *50*, 4402–4404; (b) Devaraj, S.; Shashidhar, M. S.; Dixit, S. S. *Tetrahedron* **2005**, *61*, 529–536.
22. (a) Gilbert, I. H.; Holmes, A. B.; Pestchanker, M. J.; Young, R. C. *Carbohydr. Res.* **1992**, *234*, 117–130; (b) Murali, C.; Shashidhar, M. S.; Gopinath, C. S. *Tetrahedron* **2007**, *63*, 4149–4155.
23. Robert Nouguier, R.; Mignon, V.; Gras, J. -L. *Carbohydr. Res.* **1995**, *277*, 339–345.
24. Guiso, M.; Procaccio, C.; Fizzano, M. R.; Piccioni, F. *Tetrahedron Lett.* **1997**, *38*, 4291–4294.
25. Crich, D; Vinogradova, O. *J. Org. Chem.* **2007**, *72*, 3581–3584.
26. (a) Mukaiyama, T.; Takeuchi, K.; Uchiro, H. *Chem. Lett.* **1997**, 625–626; (b) Onoda, T.; Shirai, R.; Iwasaki, S. *Tetrahedron Lett.* **1997**, *38*, 1443–1446; (c) Yang, Z.; Cao, H.; Hu, J.; Shan, R.; Yu, B. *Tetrahedron* **2003**, *59*, 249–254.
27. Yue, Z, Z.; Li, Y. C. *Chin. Chem. Lett.* **2005**, *16*, 171–174.
28. Mccasland, G. E.; Horswill, E. C. *J. Am. Chem. Soc.* **1953**, *75,* 4020–4026.
29. (a) Lindberg, B.; Mcpherson, J. *Acta Chem. Scand.* **1954**, *8*, 1875–1876; (b) Percival, E.; Young, M. *Carbohydr. Res*. **1974**, *32*, 195–201.
30. Ogawa, S. *Trends Glycosci. Glycotechnol*. **2004**, *16*, 33-53.
31. (a) Ogawa, S.; Fujieda, S.; Sakata, Y.; Ishizaki, M.; Hisamatsu, S.; Okazaki, K. *Bioorg. Med. Chem. Lett.* **2003**, *13*, 3461–3463; (b) Ogawa, S.; Kanto, M. *J. Nat. Prod.* **2007,** *70,* 493–497 and references cited therein.
32. (a) Martin, S. F. In *The Alkaloids*; Brossi, A., Ed.; Academic Press: San Diego, **1987**; Vol. 30, pp 252–376; (b) Polt, R. In *Organic Synthesis: Theory and Applications*; Hudlicky, T., Ed.; JAI Press: Greenwich, CT, **1996**; Vol. 3, pp 109–148; (c) Hoshino, O. In *The alkaloids*; Cordell, G. A., Ed.; Academic: New York, **1998**; Vol. 51, pp 323-424; (d) Jin, Z. *Nat. Prod. Rep.* **2003**, *20*, 606–614; (e) Rinner, U.; Hudlicky, T. *Synlett* **2005**, 365–405.

33. (a) Ferrier, R. J.; Middleton, S. *Chem. Rev.* **1993**, *93*, 2779–2831; (b) *Carbohydrate Mimics: Concepts and Methods*; Chapleur, Y., Ed.; Wiley-VCH: New York, 1998; (c) Kobayashi, Y. In *Glycosciene: Chemistry and Biology*; Fraser-Reid, B., Tatsuta, K., Thiem, J., Eds.; Springer: Berlin, **2001**; Vol. 3, pp 2595–2661; (d) Rassu, G.; Auzzas, L.; Pinna, L.; Battistini, L.; Curti, C. In *Bioactive Natural Products*. Atta-ur-Rahman, Ed.; Elsevier Science: New York, **2003**; Vol. 29, pp 449–520; (e) Arjona, O.; Gomez, A. M.; Lopez, J. C.; Plumet, J. *Chem. Rev.* **2007**, *107*, 1919–2036; (f) Shing, T. K. M.; Cheng, H. M. *Org. Biomol. Chem.* **2009**, *7*, 5098–5102.
34. For reviews of chemistry and applications of C-glycosides: (a) Postema, M. H. D. C-Glycoside Synthesis; CRC Press: Boca Raton, 1995; (b) Levy, D.; Tang, C. The Synthesis of C-Glycosides; Elsevier/Pergamon: Oxford, 1995; (c) Skrydstrup, T.; Vauzeilles, B.; Beau, J. M. Synthesis of C-Oligosaccharides. In *Carbohydrates in Chemistry and Biology*; Ernst, B., Hart, G. W., Sinay, P. Eds.; Wiley-VCH: Weinheim, **2000**; pp 495–530; (d) Jime´nez-Barbero, J.; Espinosa, J. F.; Asensio, J. L.; Canada, F. J. *Adv. Carbohydr. Chem. Biochem.* **2001**, *56*, 235–284.
35. Crich, D.; Grant, D.; Wink, D. J. *J. Org. Chem.* **2006**, *71*, 4521–4524.
36. Bian, J.; Schneider, S. R.; Maguire, R. J. *Tetrahedron Lett.* **2011**, *52*, 5417–5420.
37. Ortiz, J. C.; Ozores, L.; Cagide-Fagin, F.; Alonso, R. *Chem. Commun.,* **2006**, 4239–4241.
38. (a) Kireev, A. S.; Nadein, O. N.; Agustin, V. J.; Bush, N. E.; Evidente, A.; Manpadi, M.; Ogasawara, M. A.; Rastogi, S. K.; Rogelj, S.; Shors, S. T.; Kornienko, A. *J. Org. Chem.* **2006**, *71*, 5694–5707; (b) Manpadi, M.; Kireev, A. S.; Magedov, I. V.; Altig, J.; Tongwa, P.; Antipin, M. Y.; Evidente, A.; van Otterlo, W. A. L.; Kornienko, A. *J. Org. Chem.* **2009**, *74*, 7122–7131.
39. Li, M.; Wu, A.; Zhou, P. *Tetrahedron Lett.* **2006**, *47*, 3707–3710.
40. Gigg, J.; Gigg, R. *Carbohydr. Res.* **1997**, *299*, 77–83.
41. Sarmah, M. P.; Shashidhar, M. S.; Sureshan, K. M.; Gonnade, R. G.; Bhadbhade, M. M. *Tetrahedron* **2005**, 61, 4437–4446.
42. (a) Riley, A. M.; Murphy, C. T.; Lindley, C. J.; Westwick, J.; Potter, B. V. L. *Bioorg. Med. Chem. Lett*. **1996**, *6*, 2197–2200.

43. (a) Swarbrick, J. M.; Cooper, S.; Bultynck, G.; Gaffney, P. R. J. *Org. Biomol. Chem.* **2009**, *7*, 1709–1715; (b) Swarbrick, J. M.; Gaffney, P. R. J. *J. Org. Chem.* **2010**, *75,* 4376–4386.

44. (a) Hu, Y.; Qiao, L.; Wang, S.; Rong, S.; Meuillet, E. J.; Berggren, M.; Gallegos, A.; Powis, G.; Kozikowski, A. P. *J. Med. Chem.* **2000**, *43*, 3045–3051; (b) Sun, H.; Reddy, G. B.; George, C.; Meuillet, E. J.; Berggren, M.; Powis, G.; Kozikowski, A. P. *Tetrahedron Lett.* **2002**, *43*, 2835–2838.

45. (a) House, H. O. *'Modern Synthetic Reactions,'* W. A. Benjamin, Inc., Menlo Park, CA, 1972, pp. 55–70; (b) Espelie, K. E.; Anderson, L. *Carbohydr. Res*. **1976**, *46*, 53–66; (c) Gigg, J.; Gigg, R.; Payne, S.; Conant, R. *J. Chem. Soc., Perkin Trans. I,* **1987**, 1757–1762; (d) Takahashi, H.; Kittaka, H.; Ikegami, S. *J. Org. Chem.* **2001**, *6*, 2705–2716; (e) Patil, M. T.; Krishnaswamy, S.; Sarmah, M. P.; Shashidhar, M. S. *Tetrahedron Lett.* **2011**, *52*, 3756–3758 and references cited therein.

46. (a) Murali, C.; Gurale, B. P.; Shashidhar, M. S. *Eur. J. Org. Chem.* **2010**, 755–764; (b) Wessig, P.; Möllnitz, K.; Hübner, S. *Synlett* **2010**, 1497–1500.

47. (a) Song, Y. C.; Huang, W. Y.; Sun, C.; Wang, F. W.; Tan, R. X. *Biol. Pharm. Bull.* **2005**, *28*, 506–509; (b) Zhang, H. W.; Huang, W. Y.; Song, Y. C.; Chen, J. R.; Tan, R. X. *Helv. Chim. Acta* **2005**, *88*, 2861–2864; (c) Altemöller, M.; Gehring, T.; Cudaj, J.; Podlech, J.; Goesmann, H.; Feldmann, C.; Rothenberger, A. *Eur. J. Org. Chem.* **2009**, 2130–2140; (d) Yamashita, A.; Toy, A.; Scahill, T. A. *J. Org. Chem.* **1989**, *54*, 3625–3634; (e) Kupchan, S. M.; Sigel, C.W.; Knox, J. R.; Udayamurthy, M. S. *J. Org. Chem.* **1969**, *34*, 1460; (f) Gao, H.; Nishioka, T.; Kawabata, J.; Kasai, T. *Biosci. Biotechnol. Biochem.* **2004**, *68*, 369–375; (g) Gao, H.; Kawabata, J. *Bioorg. Med. Chem*. **2005**, *13*, 1661–1671; (h) Hari Babu, T.; Subba Rao, V. R.; Tiwari, A. K.; Suresh Babu, K.; Srinivas, P. V.; Ali, A. Z.; Madhusudana Rao, J. *Bioorg. Med. Chem. Lett.* **2008**, *18*, 1659–1662.

48. (a) Harborne, J. B.; Baxter, H. Eds.; The Handbook of Natural Flavonoids; **1999**; Vol. 2, pp 879–889; (b) Aherne, S. A.; O'Brien, N. M. *Nutrition* **2002**, *18*, 75–81; (c) Middleton, E.; Kandaswami, C.; Theoharides, T. C. *Pharmacol. Rev*. **2000**, *52*, 673–751.

49. (a) Akama, T.; Shida, Y.; Sugaya, T.; Ishida, H.; Gomi, K.; Kasai, M. J. *J. Med. Chem.* **1996**, *39*, 3461–3469; (b) Cardenas, M.; Marder, M.; Blank, V. C.; Roguin, L. P. *Bioorg. Med. Chem.* **2006**, *14*, 2966–2971; (c) Li, Y.; Fang, H.; Xu, W. *Mini Rev. Med. Chem*. **2007**, *7*, 663–678; (d) Shankar, S.; Ganapathy, S.; Srivastava, R. K. *Front Biosci.* **2007**, *12*, 4881–4899.
50. Manthey, J. A.; Grohmann, K.; Guthrie, N. *Curr. Med. Chem*. **2001**, *8*, 135–153.
51. Marder, M.; Paladini, A. C. *Curr. Top. Med. Chem*. **2002**, *2*, 853–867.
52. Fournet, A.; Munoz, V. *Curr. Top. Med. Chem.* **2002**, *2*, 1215–1237.
53. Chen, C. C.; Chow, M. P.; Huang, W. C.; Lin, Y. C.; Chang, Y. *J. Mol. Pharmacol.* **2004**, *66*, 683–693.
54. (a) Shieh, D. E.; Liu, L. T.; Lin, C. C. *Anticancer Res.* **2000**, *20*, 2861–2865; (b) Huang, W. H.; Lee, A. R.; Yang, C. H. *Biosci. Biotechnol. Biochem.* **2006**, *70*, 2371–2380.
55. Liao, H. -L.; Hu, M. -K. *Chem. Pharm. Bull.* **2004**, *52*, 1162–1165
56. Gong, J.; Huang, K.; Wang, F.; Yang, L.; Feng, Y.; Li, H.; Li, X.; Zeng, S.; Wu, X.; Stöckigt, J.; Zhao, Y.; Qu, J.; *Bioorg. Med. Chem*. **2009**, *17*, 3414–3425.
57. (a) Vandeput, F.; Combettes, L.; Mills, S. J.; Backers, K.; Wohlkonig, A.; Parys, J. B.; De Smedt, H.; Missiaen, L.; Dupont, G.; Potter, B. V. L.; Erneux, C. *FASEB J.* **2007**, *21*, 1481–1491; (b) Mills, S. J.; Vandeput, F.; Trusselle, M. N.; Safrany, S. T.; Erneux, C.; Potter, B. V. L. *ChemBioChem* **2008**, *9*, 1757–1766.
58. (a) Kakinuma, K.; Nango, E.; Kudo, F.; Matsushima, Y.; Eguchi, T. *Tetrahedron Lett.* **2000**, *41,* 1935–1938; (b) Hansen, C. A.; Frost, J. W. *J. Am. Chem. Soc.* **2002**, *124*, 5926–5927.
59. Li, K.; Frost, J. W. *J. Am. Chem. Soc.* **1998**, *120*, 10545–10546.
60. (a) Draths, K. M.; Frost, J. W. *J. Am. Chem. Soc*. **1995**, *117*, 2395–2400; (b) Hansen, C. A.; Dean, A. B.; Draths, K. M.; Frost, J. W. *J. Am. Chem. Soc.* **1999**, *121*, 3799–3800; (c) Gibson, J. M.; Thomas, P. S.; Thomas, J. D.; Barker, J. L.; Chandran, S. S.; Harrup, M. K.; Draths, K. M.; Frost, J. W. *Angew .Chem., Int. Ed.* **2001**, *40*, 1945–1946; (d) Achkar, J.; Xian, M.; Zhao, H.; Frost, J. W. *J. Am. Chem. Soc.* **2005**, *127*, 5332–5333; (e) Li, W.; Xie, D.; Frost, J. W. *J. Am. Chem. Soc.* **2005**, *127*, 2874–2882 and references cited therein.

61. (a) Posternak, T. *The Cyclitols*; Holden-Day: San Fransisco, 1965; Chapter 8; (b) Gent, P. A.; Gigg, R. *J. Chem. Soc.* **1970**, 2253–2255; (c) Angyal, S. J.; Range, D.; Defaye, J.; Gadelle, A. *Carbohydr. Res.* **1979**, *76*, 121–130.
62. (a) Angyal, S. J.; Tate, M. E. *J. Chem. Soc.***1965**, 6949–6955; (b) Mosfiting, J.; Gelpi, M. E.; Cadenas, R. A. *Carbohydr. Res.* **1981**, *98*, 51–56.
63. Lee, Y.; Yeo, H.; Liu, S. H.; Jiang, Z.; Savizky, R. M.; Austin, D. J.; Cheng, Y. C. *J. Med. Chem.* **2004**, *47,* 5555–5566.
64. (a) Suzuki, A. *Proc. Jpn. Acad.* **2004**, *80*, 359–371; (b) Barder, T. E.; Walker, S. D. Martinelli, J. R.; Buchwald, S. L. *J. Am. Chem. Soc.* **2005**, *127*, 4685–4696; (c) Alonso, F.; Beletskaya, I. P.; Yus, M. *Tetrahedron* **2008**, *64*, 3047–3101; (d) Martin, R.; Buchwald, S. L. *Acc. Chem. Res.* **2008**, *41*, 1461–1473.
65. Kakinuma, K. Sakagami, Y. *Agric. Biol. Chem.* **1978**, *42*, 279–286.
66. Riley, A. M.; Guedat, P.; Schlewer, G.; Spiess, B.; Potter, B. V. L. *J. Org. Chem.* **1998**, *63,* 295–305.

Appendix II

Appendix II Index

Crystal Data Table

Compound No.	**3.17**	**3.19**	**3.23**	**3.24**
Chemical formula	$C_{34}H_{33}N_3O_5$	$C_{29}H_{31}N_3O_6$	$C_{31}H_{31}N_3O_8$	$C_{29}H_{31}N_3O_6$
M_r	563.64	517.57	573.59	517.57
Temperature/K	297(2)	297(2)	100(2)	100(2)
Morphology	Plate	Plate	Prism	Needle
Crystal size	0.57×0.31×0.19	0.12×0.10×0.01	0.27×0.07×0.05	0.22×0.19×0.12
Crystal system, Space group	monoclinic, $P2_1/c$	monoclinic, $C2/c$	monoclinic, $P2_1$	triclinic, P-1
a (Å) b (Å) c (Å) α (°) β (°) γ (°)	11.750(5) 11.602(5) 21.622(9) 90 92.976(7) 90	33.130(5) 10.4844(17) 16.523(3) 90 111.386(3) 90	7.4388(5) 26.4633(17) 14.6237(10) 90 93.580(3) 90	9.3727(19) 10.020(2) 15.193(3) 102.788(4) 104.677(3) 99.305(4)
Volume V (Å^3)	2395.4(5)	5344.0(15)	2873.1(3)	1309.8(5)
Z	4	8	4	2
D_{calc} (g cm^{-3})	1.238	1.287	1.236	1.312
μ (mm^{-1})	0.084	0.091	0.097	0.093
F(000)	952	2192	1208	548
Absorption correction T_{min} / T_{max}	multi-scan 0.972 / 0.9859	multi-scan 0.989 / 0.993	multi-scan 0.975 / 0.995	multi-scan 0.980 / 0.989
θ_{max} (°)	26	25	25	25
h, k, l (min, max)	(-15,15), (-16,16), (-17,17)	(-34,39), (-12,12), (-19,19)	(-7,7), (-28,31), (-16,15)	(-11,11), (-11,11), (-18,18)
Reflns collected	18470	13185	16623	12730
Unique reflns, Observed reflns	4694, 3540	4681, 2867	6962, 5841	4585, 3474
R_{int}	0.0223	0.0341	0.0248	0.0253
No. of parameters	298	448	799	376
(GoF)	1.036	1.011	1.047	1.097
$R1$ [$I > 2\sigma(I)$] $wR2$ [$I > 2\sigma(I)$]	0.0458 0.1169	0.0437 $wR2$=0.0872	$R1$=0.0375 $wR2$=0.0752	$R1$=0.0673 $wR2$=0.1576
$R1$ (all data) $wR2$ (all data)	0.0613 0.1273	0.0859 0.1026	0.0527 0.0821	0.0865 0.1703
$\Delta\rho_{max}$,$\Delta\rho_{min}$(eÅ^{-3})	0.24,-0.14	0.131, -0.170	0.455, -0.251	0.392, -0.187
CCDC	747074			

Crystal Data Table

Compound No.	**3.25**	**3.26**	**3.29**	**3.34**
Chemical Formula	$C_{23}H_{26}N_4O_5$	$C_{14}H_{17}N_3O_5$	$C_{17}H_{25}N_1O_{10}$	$C_{24}H_{29}N_3O_7$
M_r	438.48	307.31	403.38	471.50
Temp/K	100(2)	297(2)	133(2)	297(2)
Morphology	Needle	Plate	Rhombic	Plate
Crystal size (mm)	0.37×0.02 ×0.04	0.29×0.14 ×0.11	0.57×0.36 ×0.30	0.52×0.38 ×0.18
Crystal system, Space group	orthorhombic $P2_12_12_1$	triclinic, P-1	monoclinic, Cc	triclinic, P-1
a (Å) b (Å) c (Å) α (°) β (°) γ (°)	7.564(3) 15.725(7) 18.913(8) 90 90 90	10.2239(8) 10.7231(9) 15.4953(13) 91.7140(10) 103.390(10) 90	15.345(2) 11.1876(18) 12.2187(19) 90 103.406(2) 90	9.609(3) 9.838(3) 13.731(4) 72.388(5) 71.558(5) 85.742(5)
Volume V (Å^3)	2249.7(16)	1443.5(2)	2040.5(6)	1173.4(6)
Z	4	4	4	2
D_{calc} (g cm^{-3})	1.295	1.414	1.313	1.334
μ (mm^{-1})	0.093	0.109	0.109	0.099
F(000)	928	648	856	500
Absorption correction T_{min} / T_{max}	multi-scan 0.967 / 0.997	multi-scan 0.969 / 0.988	multi-scan 0.941 / 0.968	multi-scan 0.9505 / 0.9826
θ_{max} (°)	25	25	25	25
h, k, l (min, max)	(-12,11), (-22,21), (-25,22)	(-12,12), (-12,12), (-18,18)	(-18,18), (-13,13), (-14,14)	(-11,11), (-12,12), (-16,16)
Reflns collected	16193	13362	7131	9903
Unique reflns, Observed reflns	3957, 3787	5061, 4416	3525, 3475	4559, 3942
R_{int}	0.0510	0.0136	0.0245	0.0146
No. of parameters	365	401	287	423
(GoF)	1.172	1.031	1.087	1.048
$R1$ [$I > 2\sigma(I)$] $wR2$ [$I > 2\sigma(I)$]	0.0420 0.0871	0.0374 0.0941	0.0351 0.0889	0.0430 0.1030
$R1$ (all data) $wR2$ (all data)	0.0447 0.0882	0.0430 0.0987	0.0355 0.0894	0.0497 0.1074
$\Delta\rho_{max}$,$\Delta\rho_{min}$(eÅ^{-3})	0.197,-0.162	0.188,-0.164	0.240,-0.165	0.179, -0.184

Crystal Data Table

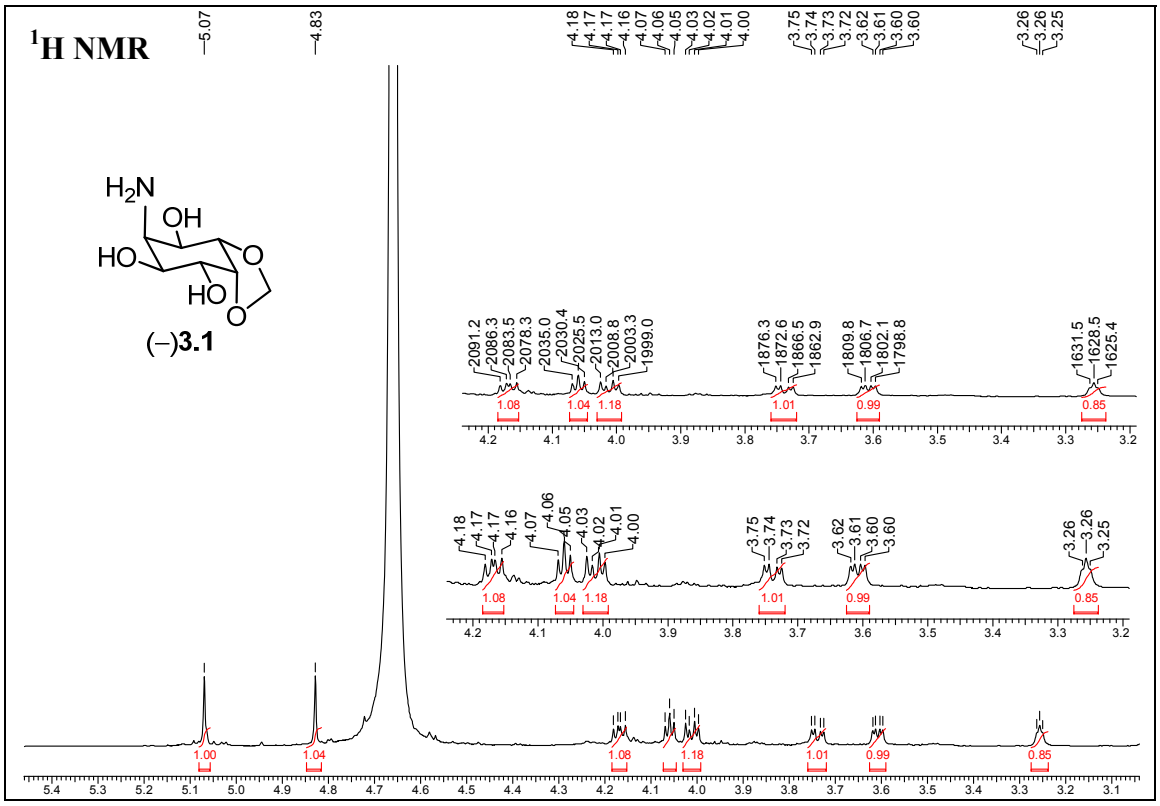
Compound No.	**3.36**	**1.138**	**3.72**	**3.73**
Chemical formula	$C_{26}H_{33}NO_8$	$C_{28}H_8O_6$	$C_{35}H_{34}O_7$	$C_{34}H_{34}O_6$
M_r	487.54	460.51	566.62	538.63
Temperature/K	297(2)	100(2)	133	100(2)
Morphology	Needle	Plate	Prism	Plate
Crystal size (mm)	0.34×0.02 ×0.14	0.65×0.03 ×0.31	0.18×0.01 ×0.09	0.58×0.08 ×0.05
Crystal system, Space group	monoclinic, $P2_1/n$	monoclinic, $C2/c$	monoclinic, $P2_1$	monoclinic, $P2_1/n$
a (Å) b (Å) c (Å) α (°) β (°) γ (°)	17.767(2) 7.0074(9) 21.189(3) 90 101.795(2) 90	31.6493(12) 6.8309(3100.2 21.5358(10) 90 24(2) 90	9.492 (8) 9.735 (8) 16.289 (13) 90 103.206 (12) 90	5.8478(15) 30.127(8) 15.291(4) 90 92.719(4) 90
Volume V (Å^3)	2582.4(6)	4582.0(3)	1465 (2)	2690.9(12)
Z	4	8	2	4
D_{calc} (g cm^{-3})	1.254	1.135	1.284	1.329
μ (mm^{-1})	0.093	0.093	0.009	0.090
F(000)	1040	1952	600	1144
Absorption correction T_{min} / T_{max}	multiscan 0.9691 / 0.9874	multiscan 0.9418 / 0.9716	multiscan 0.984 / 0.992	multiscan 0.9495 / 0.9951
θ_{max} (°)	25	25	25	25
h, k, l (min, max)	(-21,20), (-8,7), (-25,24)	(-42,40), (-9,9), (-28,22)	(-11,11), (-11,11), (-10,19)	(-6,6), (-18,35), (-18,17)
Reflns collected	12428	21621	7169	13005
Unique reflns, Observed reflns	4546, 3598	5639, 4672	2741, 2503	4711, 3934
R_{int}	0.0230	0.0222	0.047	0.0444
No. of parameters	320	419	380	365
(GoF)	1.084	1.029	1.219	1.097
R1 [$I > 2\sigma(I)$] *wR2* [$I > 2\sigma(I)$]	0.0420 0.1556	0.0378 0.0997	0.0772 0.1491	0.0508 0.1067
R1 (all data) *wR2* (all data)	0.0819 0.1470	0.0483 0.0936	0.0855 0.1523	0.0638 0.1124
$\Delta\rho_{max}$,$\Delta\rho_{min}$(eÅ^{-3})	0.214, -0.197	0.357, -0.204	0.29, -0.29	0.242, -0.234

Crystal Data Table

Compd No.	**3.76**	**3.82**	**3.83**
Chemical formula	$C_{40}H_{38}O_6$	$C_{17}H_{24}O_{11}$	$C_{25}H_{30}O_{12}$
M_r	614.73	404.36	522.50
Temp/K	273(2)	297(2)	297(2)
Morphology	Plate	Needle	Needle
Crystal size	0.14×0.01 ×0.13	0.34×0.02 ×0.09	0.18×0.02 ×0.11
Crystal system, Space group	monoclinic, *C*2/*c*	monoclinic, $P2_1/c$	monoclinic, *C*2/*c*
a (Å) *b* (Å) *c* (Å) α (°) *β* (°) γ (°)	34.476(14) 10.877(4) 23.479(9) 90 131.958(7) 90	9.409(6) 16.322 (11) 15.975(8) 90 121.58(3) 90	24.972(3) 11.8770(12) 18.2350(19) 90 107.056(2) 90
Volume *V* (Å^3)	6547(4)	2090(2)	5710.5
Z	8	4	16
D_{calc} (g cm^{-3})	1.247	1.285	1.342
μ (mm^{-1})	0.083	0.109	0.108
F(000)	2608	856	2208
Absorption correction T_{min} / T_{max}	multiscan 0.9885 / 0.9893	multiscan 0.9903 / 0.9640	multiscan 0.9809 / 0.9882
θ_{max} (°)	25	25	25
h, k, l (min, max)	(-40,40), (-12,12), (-27,27)	(-11,11), (-18,19), (-18,17)	(-29,29), (-14,14), (-21,21)
Reflns collected	22337	9850	24202
Unique reflns, Observed reflns	5736, 1859	3681, 3681	4556, 4326
R_{int}	0.1090	0.0590	0.0425
No. of parameters	419	259	368
(GoF)	0.809	1.186	1.285
R1 [$I > 2\sigma(I)$] *wR2* [$I > 2\sigma(I)$]	0.0602 0.1514	0.0710 0.1492	0.0.985 0.1837
R1 (all data) *wR2* (all data)	0.1932 0.1979	0.0950 0.1592	0.1039 0.1865
$\Delta\rho_{max}$,$\Delta\rho_{min}$(eÅ^{-3})	0.481,-0.286	0.234,-0.185	0.492,-0.289

Crystal Data Table

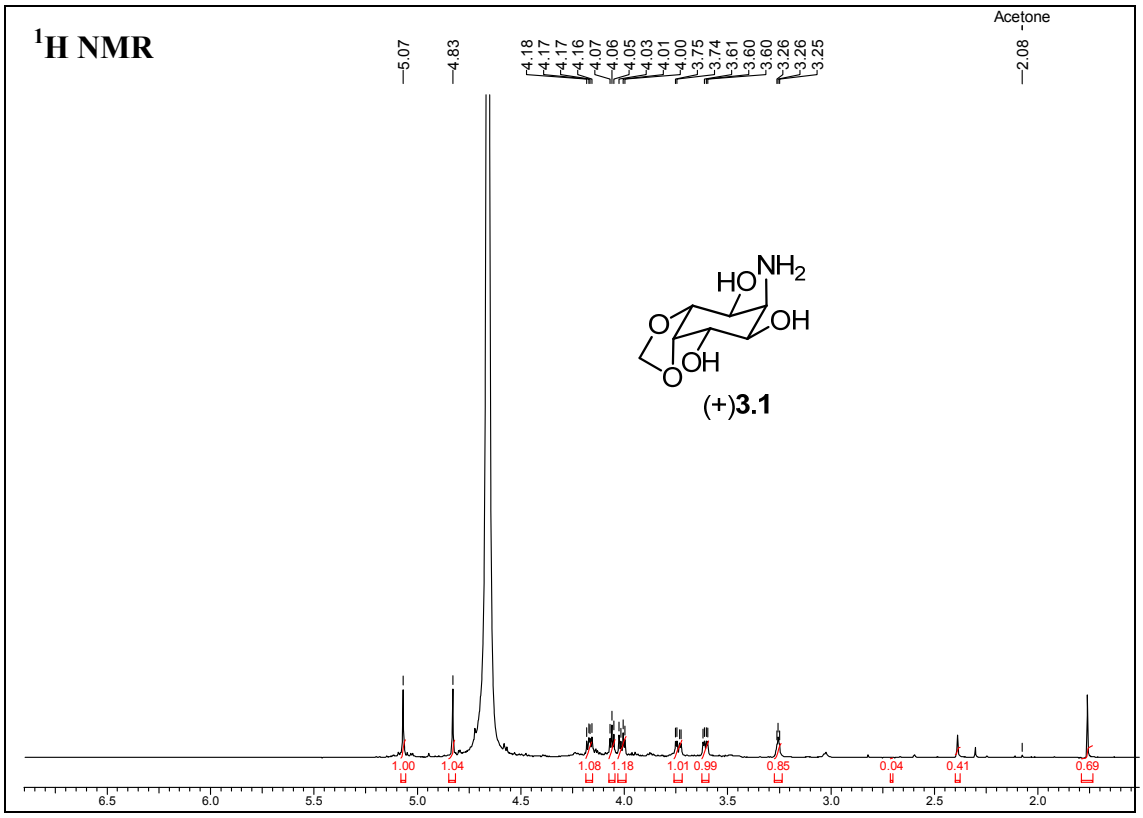
Compound No.	**3.84**	**3.133**	**3.134**
Chemical formula	$C_{22}H_{26}O_{11}$	$C_{27}H_{24}O_4$	$C_{27}H_{26}O_5$
M_r	466.43	412.46	430.48
Temperature/K	297(2)	297(2)	297(2)
Morphology	Needle	Plate	Plate
Crystal size	0.22×0.01 ×0.09	0.19×0.06 ×0.03	0.19×0.06 ×0.03
Crystal system, Space group	triclinic, *P*-1	monoclinic, $P2_1/c$	monoclinic, $P2_1/c$
a (Å) *b* (Å) *c* (Å) α (°) *β* (°) γ (°)	9.192(4) 11.256 (5) 12.809(6) 92.389(8) 106.345(8) 110.287(7)	18.320(4) 5.7385(13) 21.273(5) 90 108.402(4) 90	14.30(3) 17.31(4) 8.859(18) 90 90.03(2) 90
Volume *V* (Å^3)	1178.5(9)	2122.1(8)	2193(8)
Z	2	4	4
D_{calc} (g cm^{-3})	1.314	1.291	1.304
μ (mm^{-1})	0.106	0.086	0.089
F(000)	492	872	912
Absorption correction T_{min} / T_{max}	multi-scan 0.9908 / 0.9768	multi-scan 0.9839 / 0.9974	multi-scan 0.9737 / 0.9964
θ_{max} (°)	25	25	25
h, k, l (min, max)	(-10,10), (-13,13), (-15,15)	(-21,21), (-6,6), (-25,25)	(-16,15), (-19,19), (-10,7)
Reflns collected	11430	14613	8904
Unique reflns, Observed reflns	4125, 4125	3740, 2118	3263
R_{int}	0.0184	0.0679	1169
No. of parameters	306	284	255
(GoF)	1.043	1.042	1.728
R1 [$I > 2\sigma(I)$] *wR2* [$I > 2\sigma(I)$]	0.0434 0.1116	0.0719 0.1349	0.2634 0.5968
R1 (all data) *wR2* (all data)	0.0495 0.1165	0.1364 0.1648	0.3481 0.6231
$\Delta\rho_{max}$,$\Delta\rho_{min}$(eÅ^{-3})	0.226, -0.151	0.512, -0.314	0.858, -0.725

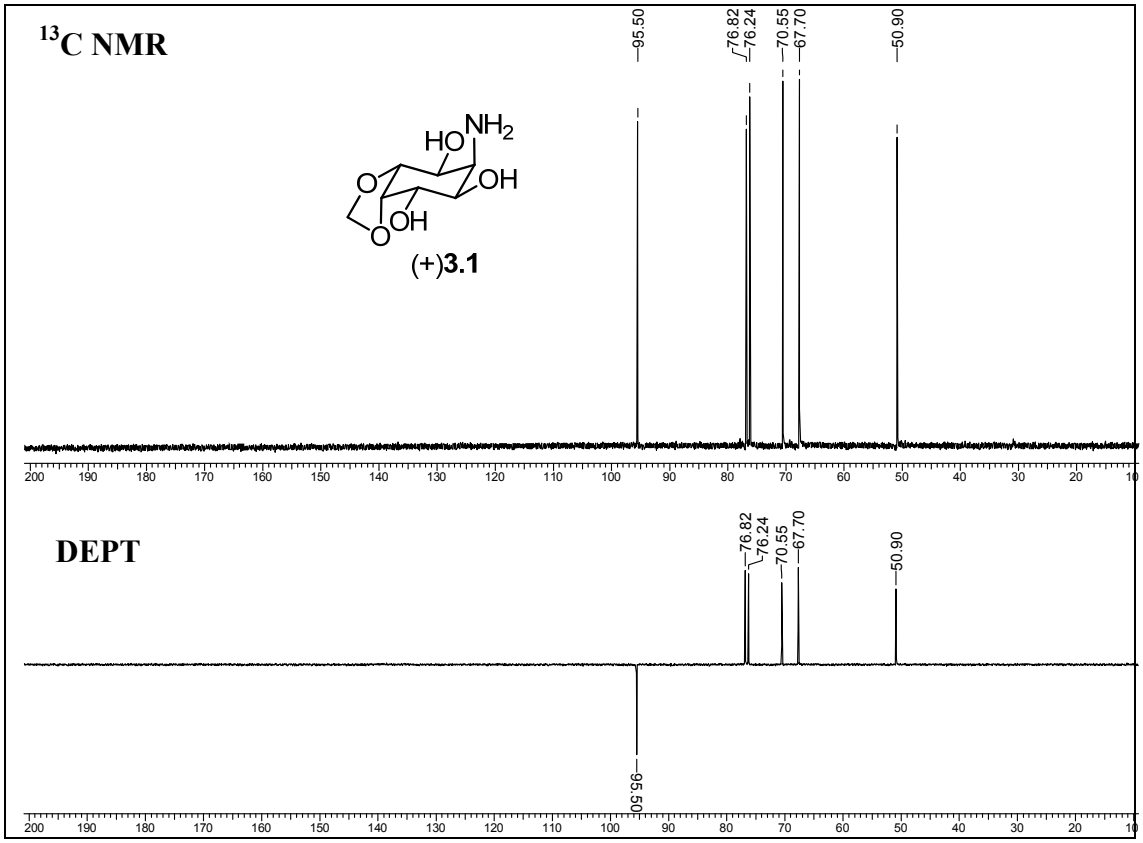


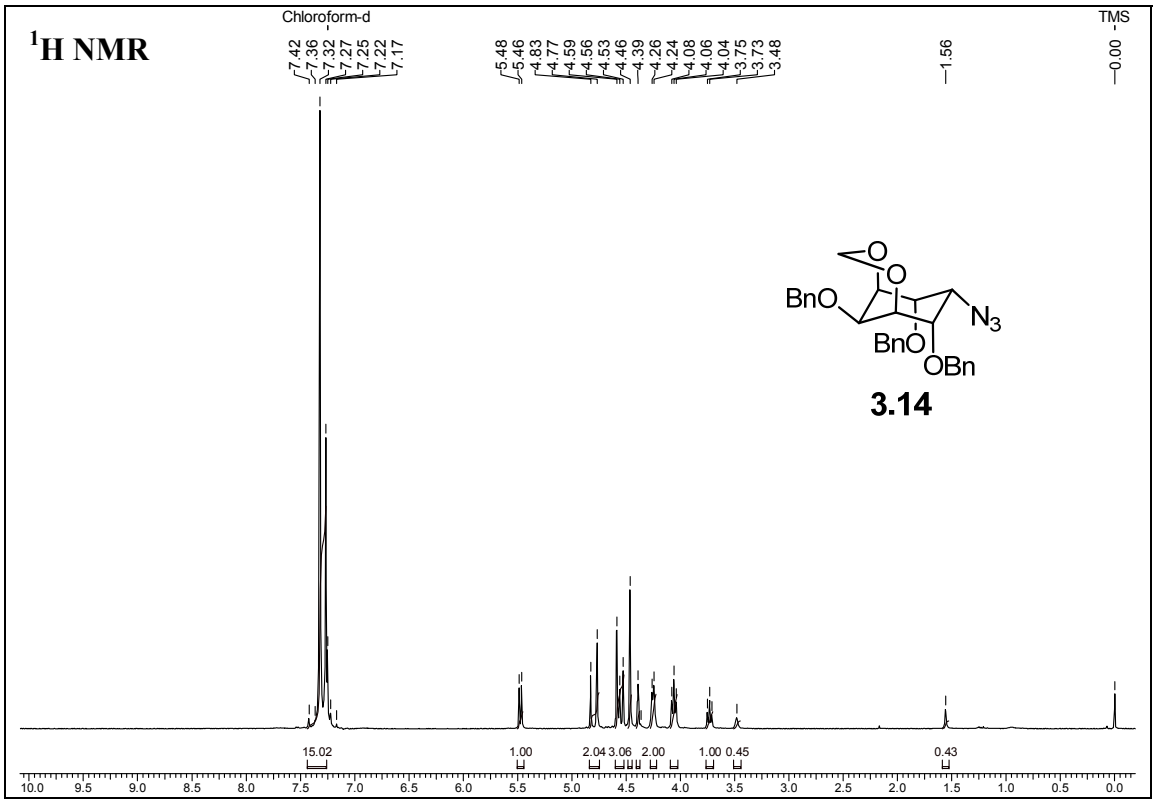
Comparison of the ^{1}H NMR spectroscopic data and specific rotation of (–)**3.1** with literature reports:

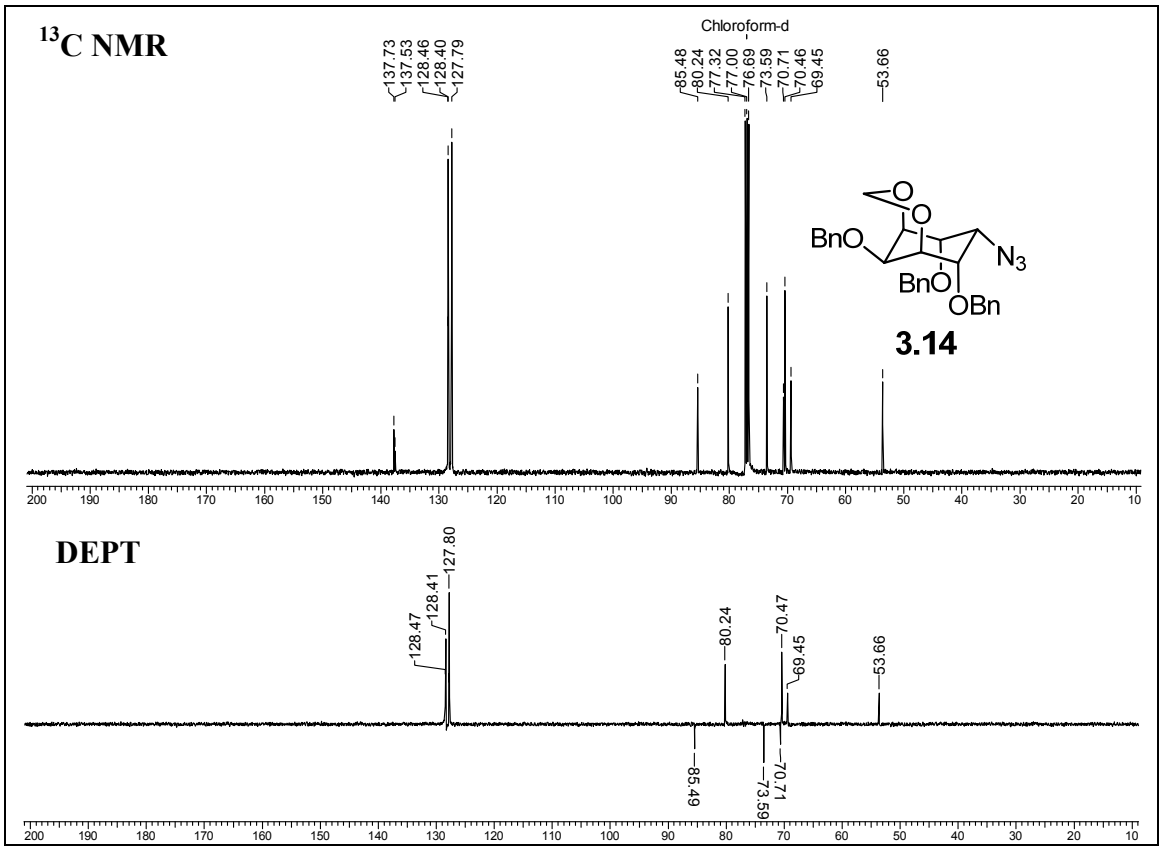
Trost[a] (300 MHz)	Donoho[b] (400 MHz)	**Present work** (500 MHz)
5.07 (s, 1H)	5.07 (s, 1H)	5.07 (s, 1H)
4.83 (s, 1H)	4.84 (s, 1H)	4.83 (s, 1H)
4.17 (dd, 1H, *J* 5.1,7.8)	4.17 (dd, 1H, *J* 4.8,7.6)	4.17 (dd, 1H, *J* 4.9,7.7)
4.03 (m, 2H)	4.07 (dd, 1H, *J* 4.4,4.4)	4.06 (t, 1H, *J* 4.6)
	4.01 (dd, 1H, *J* 4.0,10.0)	4.01 (dd, 1H, *J* 4.2,9.7)
3.74 (dd, 1H, *J* 3.7,9.8)	3.73 (dd, 1H, *J* 3.6,10.0)	3.73 (dd, 1H, *J* 3.7,9.8)
3.61 (dd, 1H, *J* 3.4,7.8)	3.60 (dd, 1H, *J* 3.2,8.0)	3.60 (dd, 1H, *J* 3.1,7.7)
3.26 (t, 1H, *J* 3.4)	3.25 (t, 1H, *J* 3.3)	3.26 (t, 1H, *J* 3.1)
$[\alpha]_D^{21}$ –28.9° (c = 0.85, H_2O)	$[\alpha]_D^{20}$ –27.2° (c = 0.45, H_2O)	$[\alpha]_D^{25}$ –29° (c = 1.1, H_2O)

[a]Trost, B. M.; Dudash, J. *Chem. Eur. J.* **2001**, *7*, 1619–1629; [b]Donohoe, T. J.; Johnson, P. D.; Pye, R. J.; Keenan, M. *Org. Lett.* **2005**, *7*, 1275–1277.

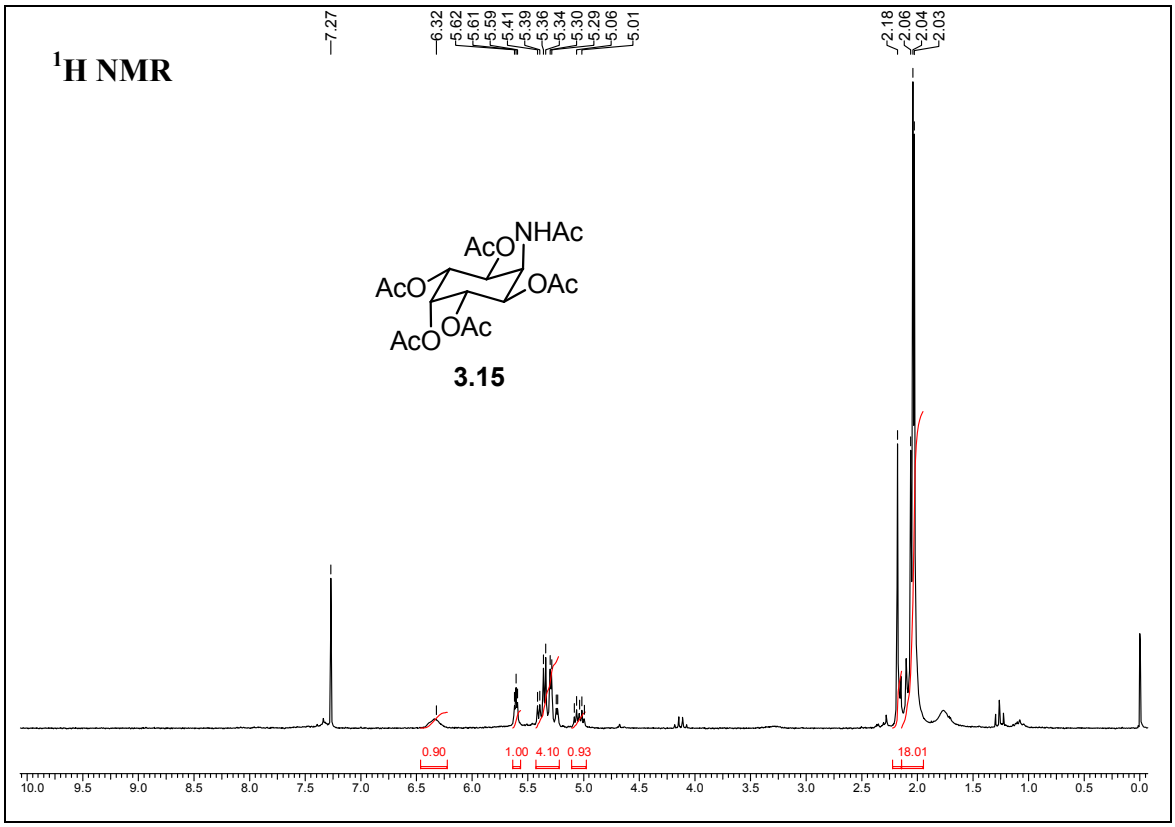

^{1}H NMR
5.07
4.83
4.18
4.17
4.17
4.16
4.07
4.06
4.05
4.03
4.01
4.00
3.75
3.74
3.61
3.60
3.60
3.26
3.26
3.25
Acetone
2.08
HO
NH2
O
OH
OH
O
(+)3.1
1.00
1.04
1.08
1.18
1.01
0.99
0.85
0.04
0.41
0.69
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0

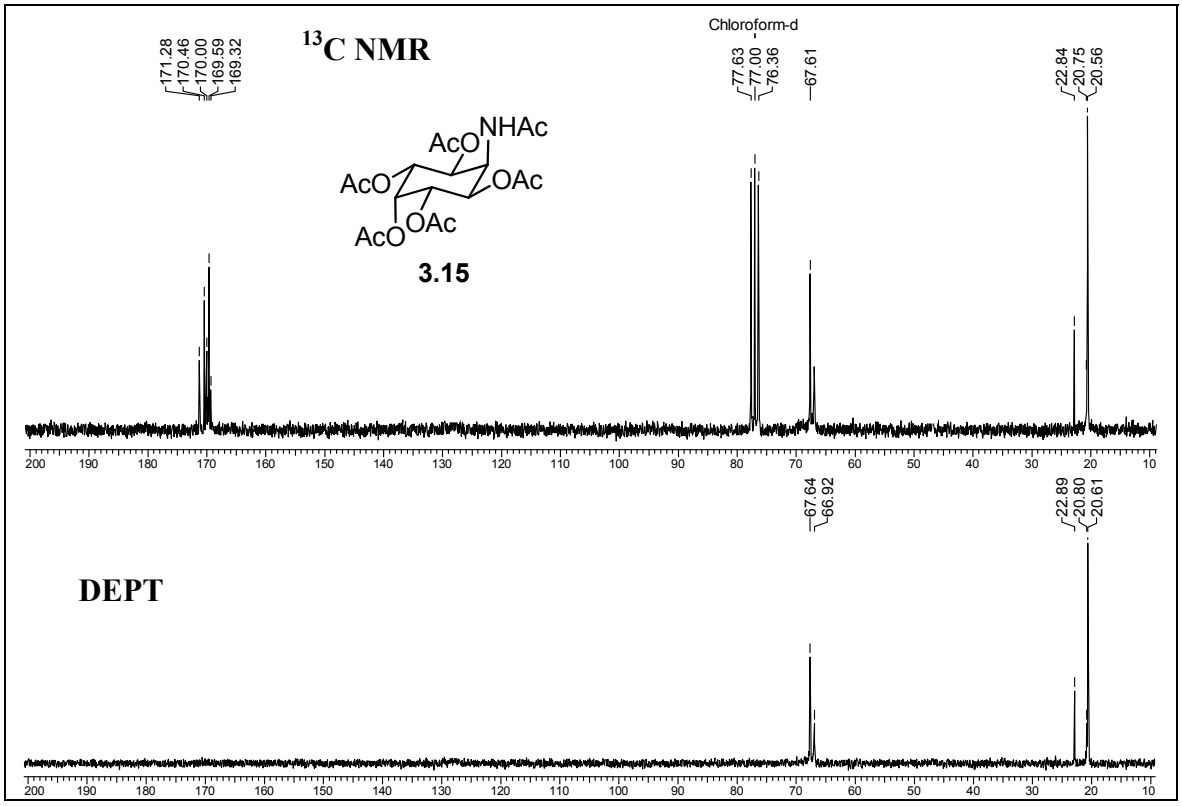

^{13}C NMR
95.50
76.82
76.24
70.55
67.70
50.90
HO
NH2
O
OH
OH
O
(+)3.1
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
DEPT
76.82
76.24
70.55
67.70
50.90
95.50

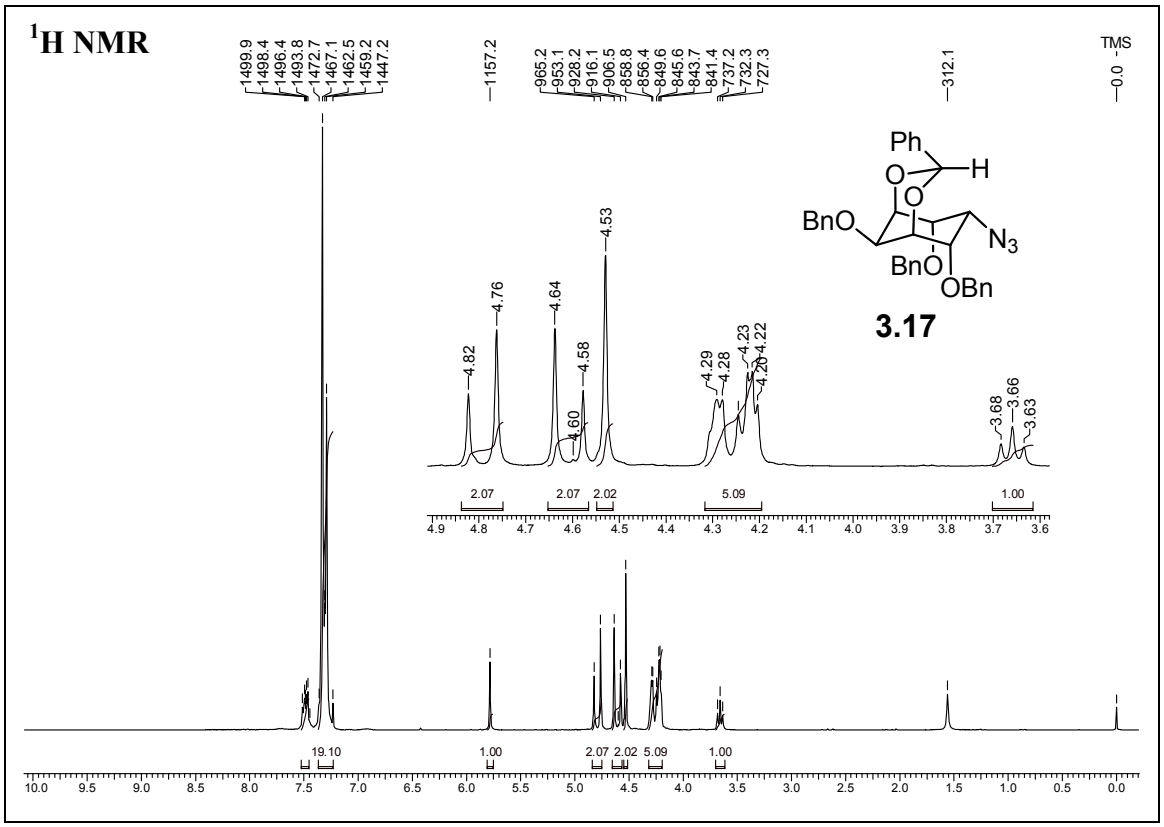


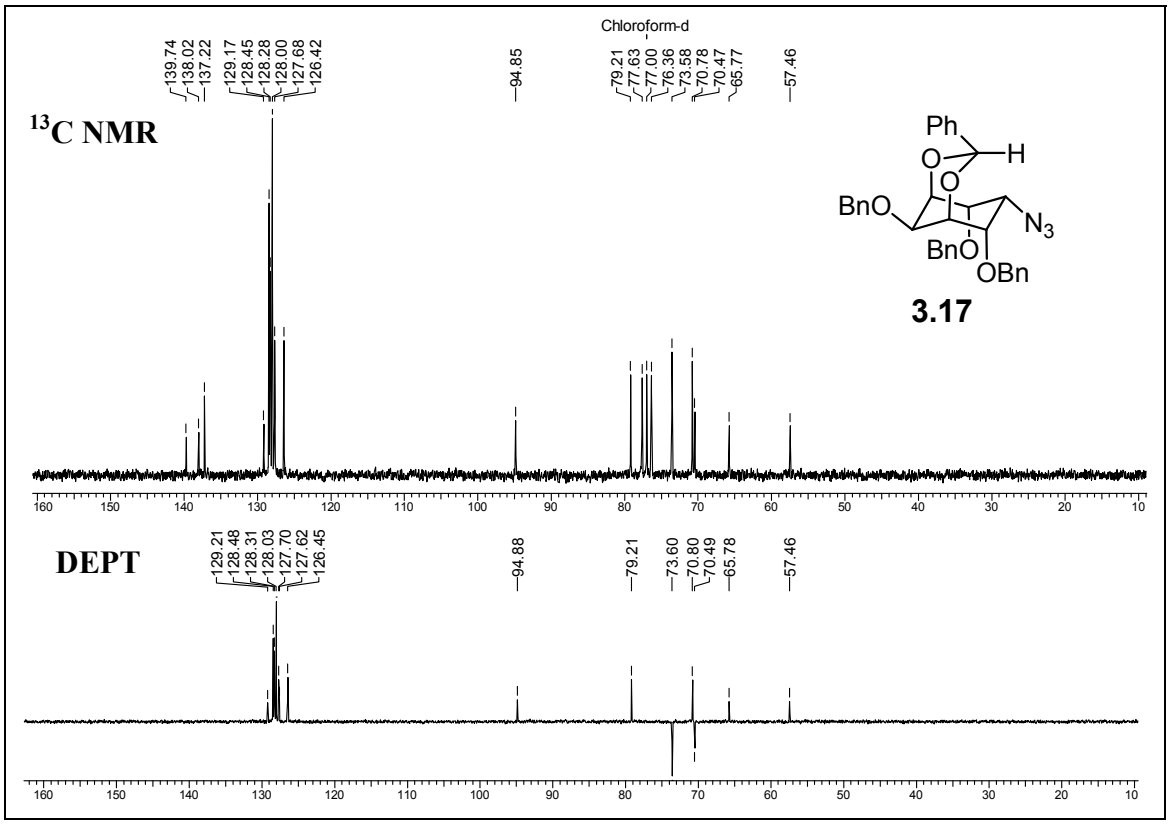


For 2D NMR see appendix III

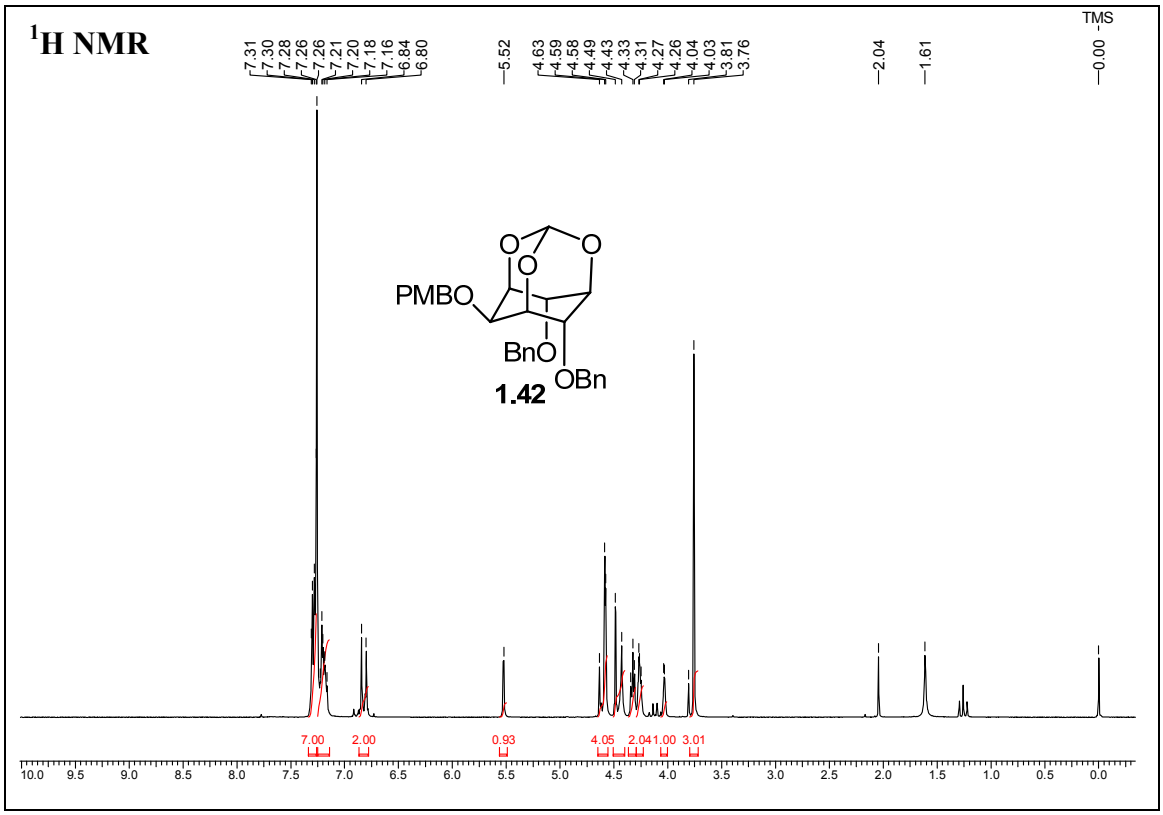

^{1}H NMR
7.27
6.32
5.62
5.61
5.59
5.41
5.39
5.36
5.34
5.30
5.29
5.06
5.01
2.18
2.06
2.04
2.03
AcO
NHAc
AcO
OAc
AcO
OAc
3.15
0.90
1.00
4.10
0.93
18.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

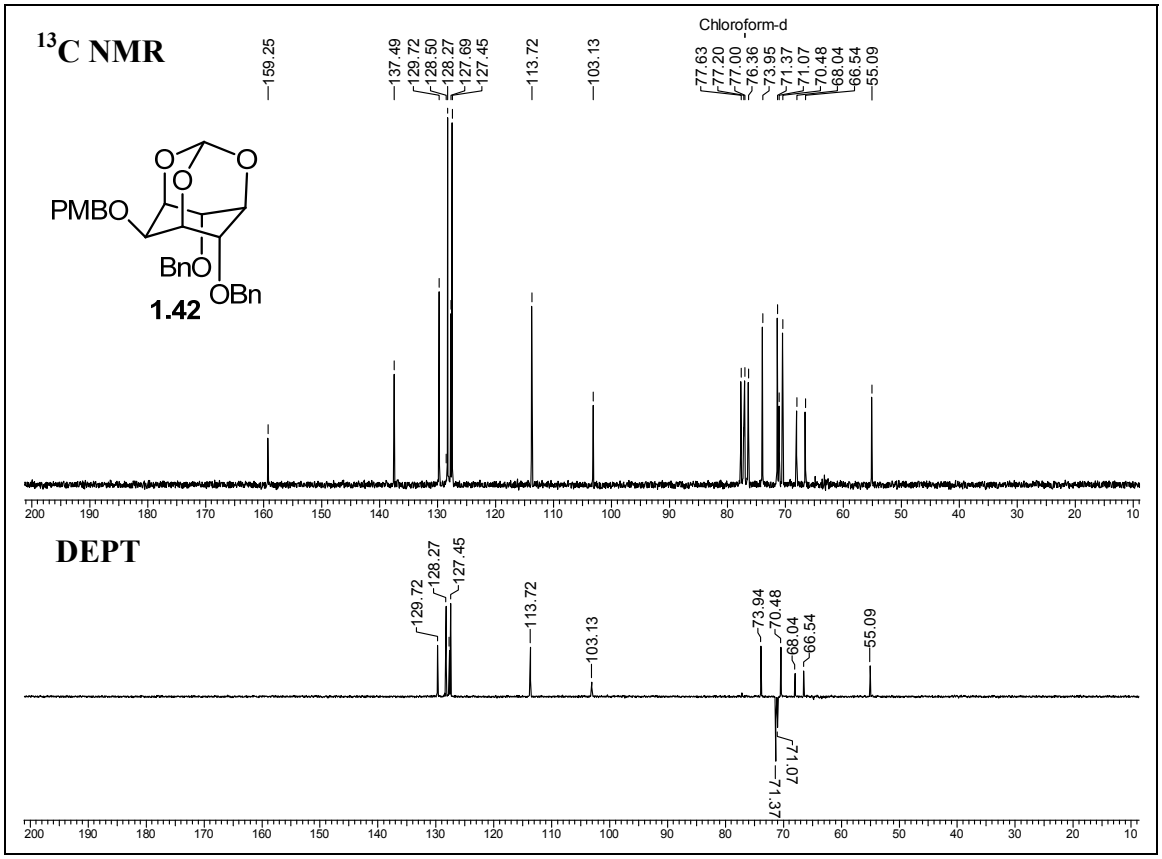

^{13}C NMR
171.28
170.46
170.00
169.59
169.32
Chloroform-d
77.63
77.00
76.36
67.61
22.84
20.75
20.56
AcO
NHAc
AcO
OAc
AcO
OAc
3.15
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
67.64
66.92
22.89
20.80
20.61
DEPT
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

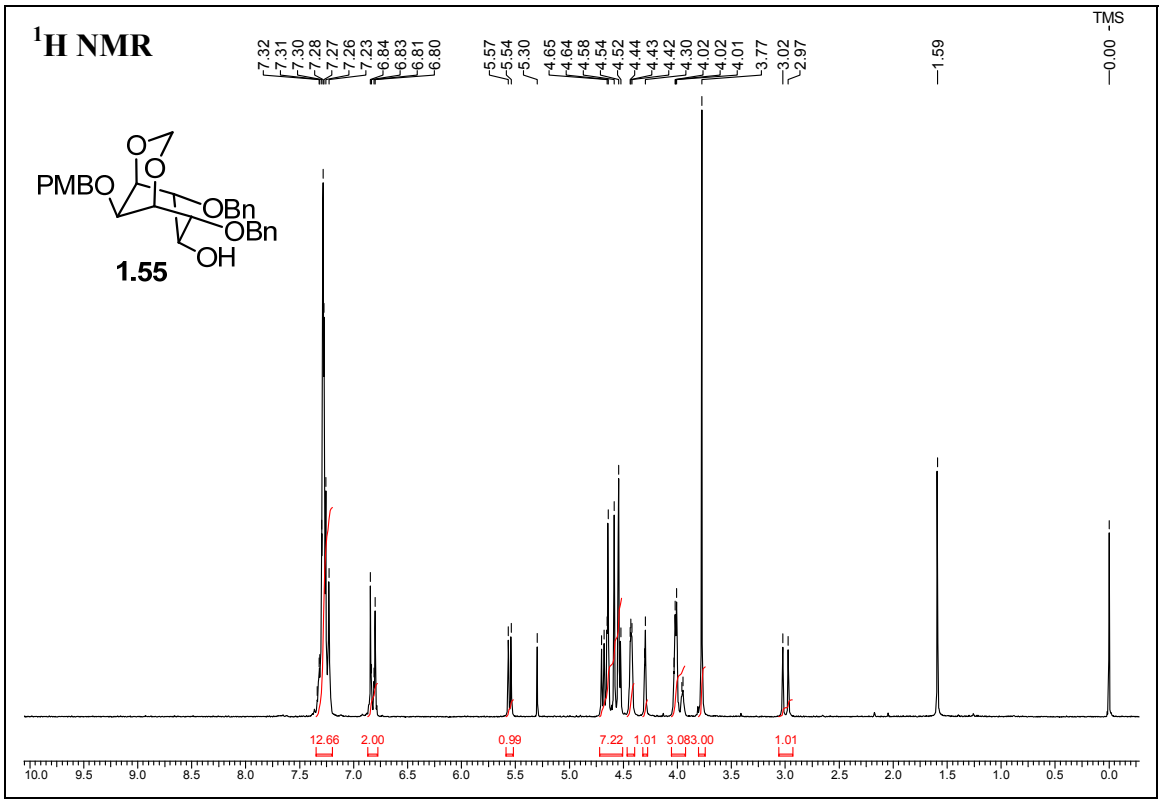


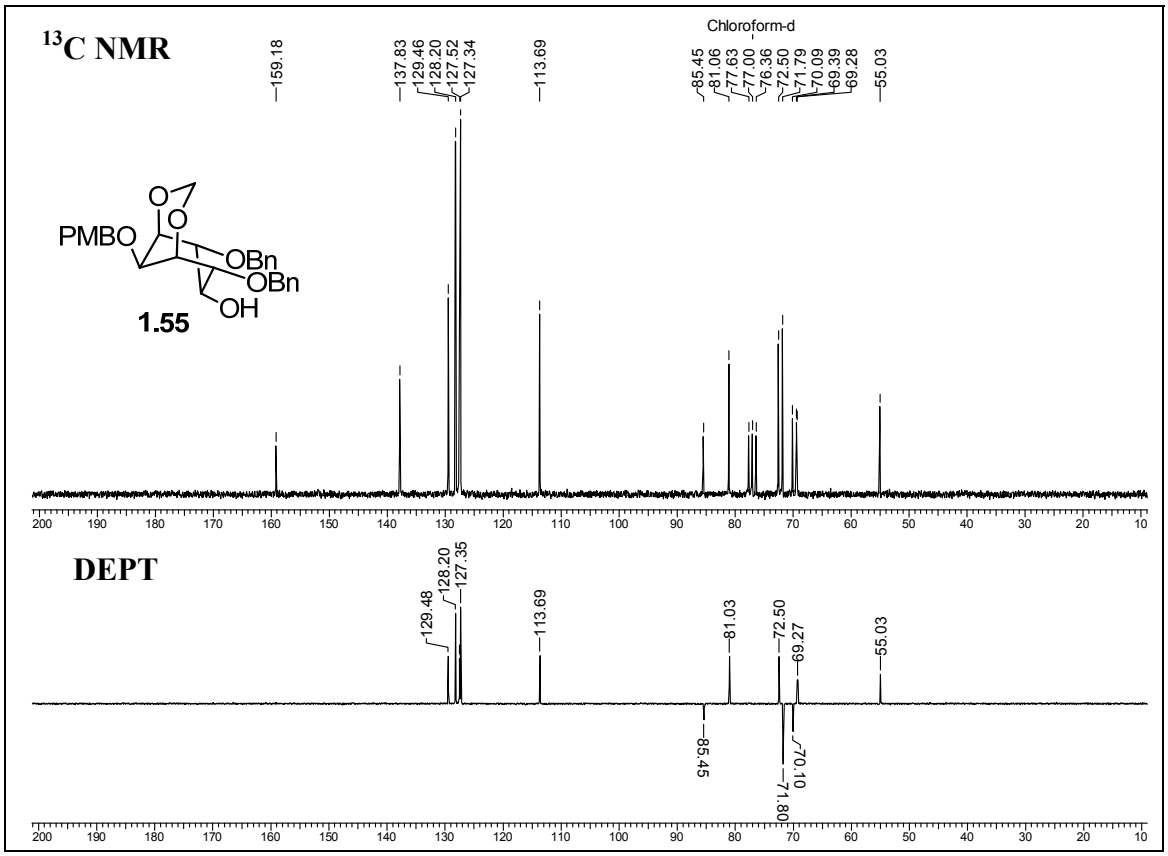


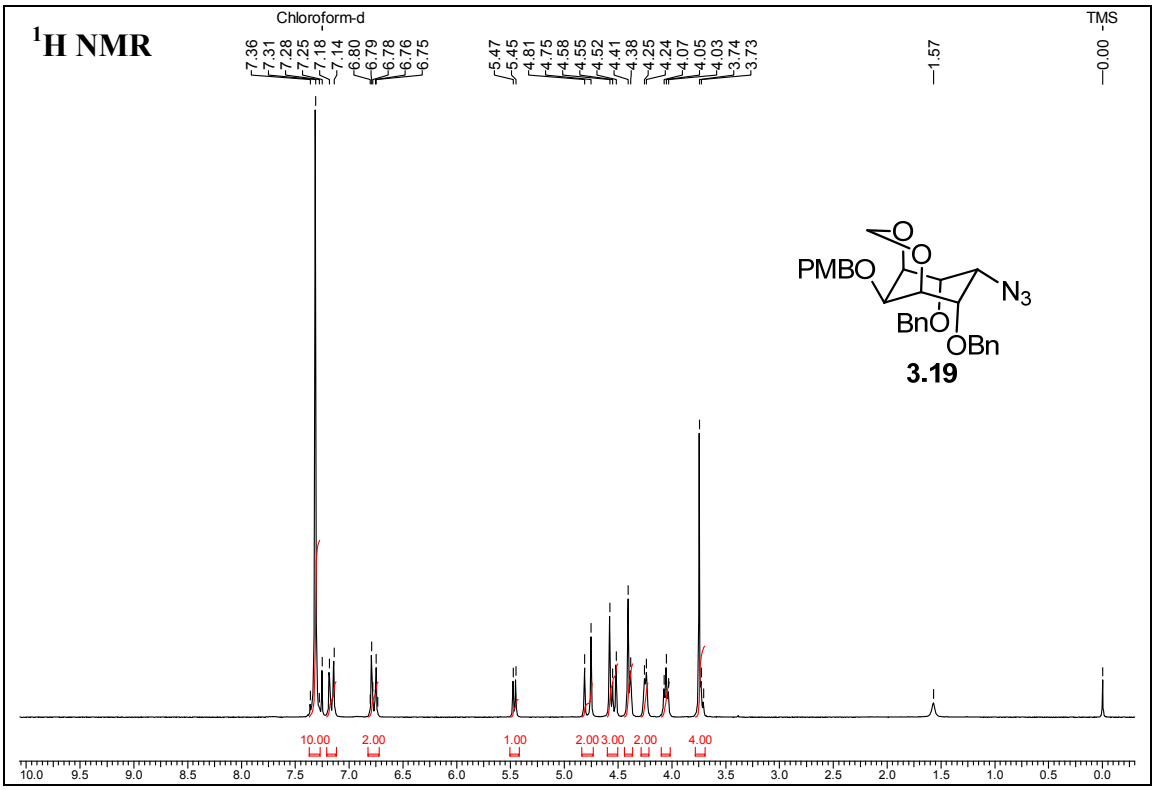
For 2D NMR see appendix III

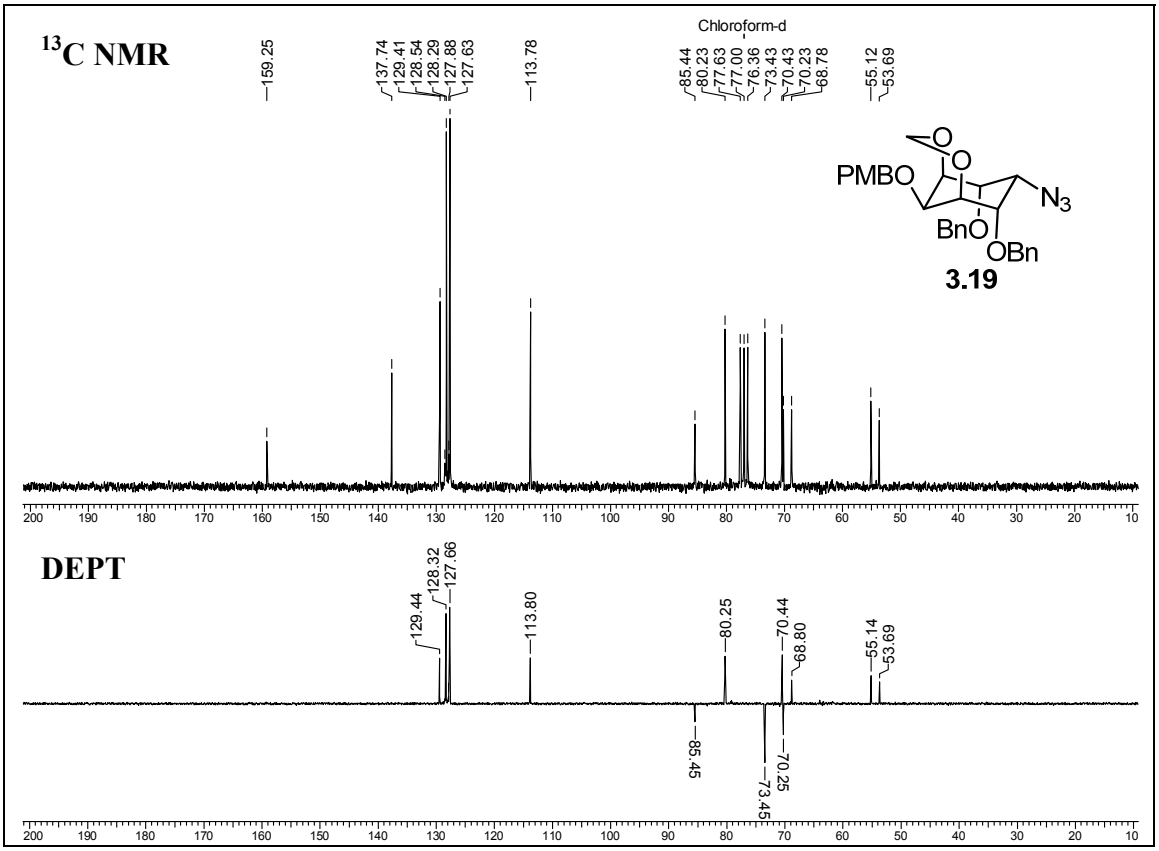

^{1}H NMR
TMS
PMBO
BnO
OBn
1.42


^{13}C NMR
Chloroform-d
PMBO
BnO
OBn
1.42
DEPT

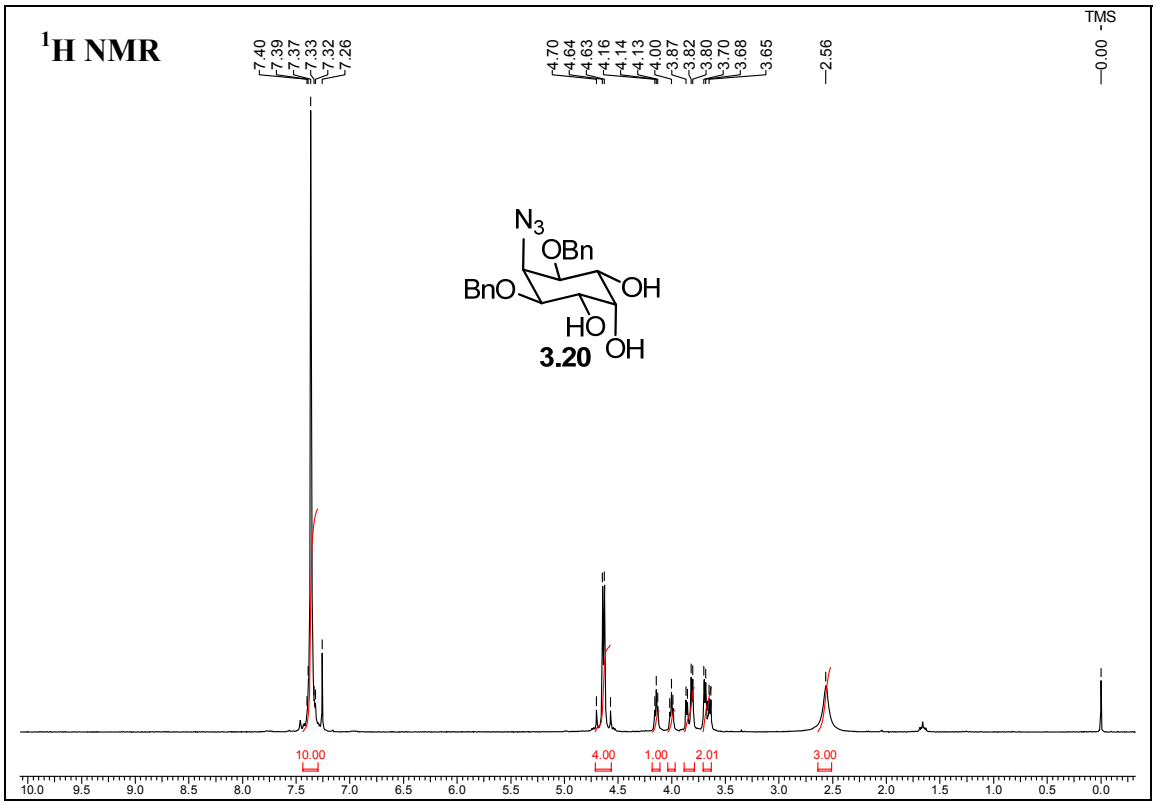

^{1}H NMR
TMS
PMBO
OBn
OBn
OH
1.55

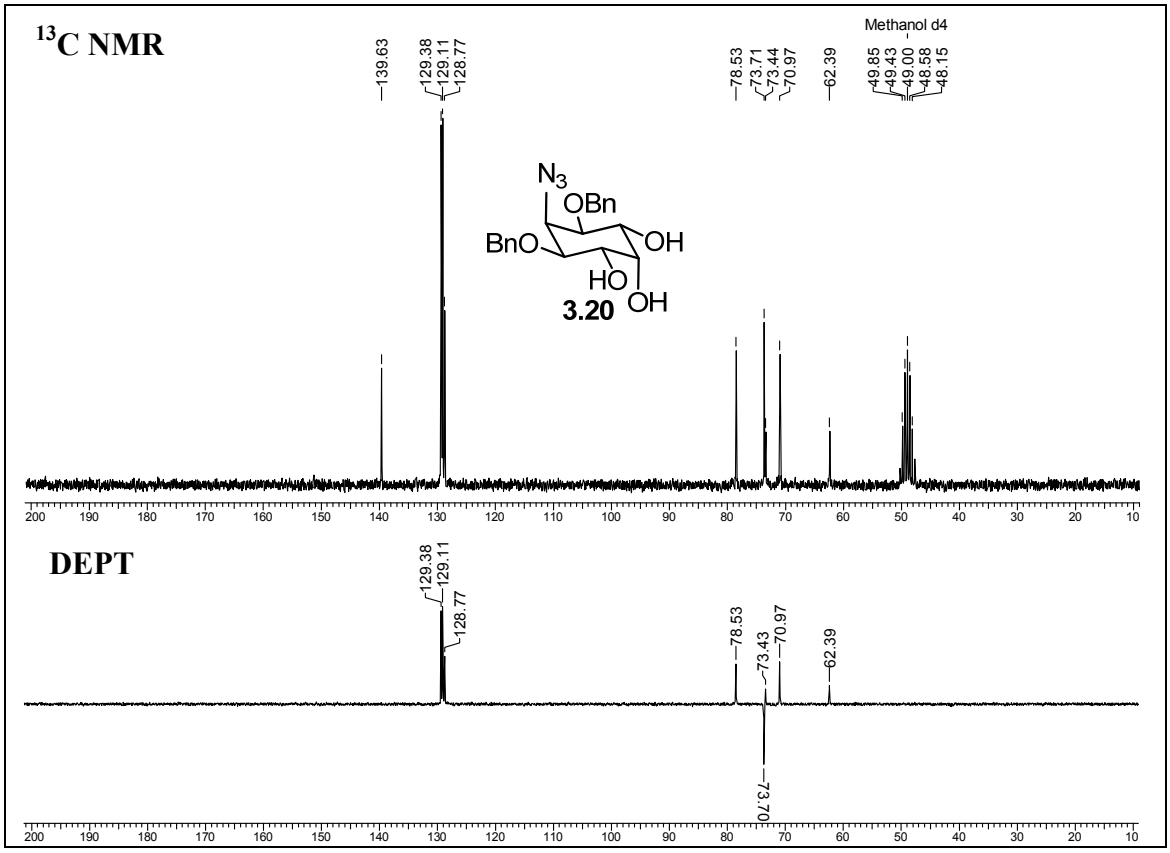

^{13}C NMR
Chloroform-d
PMBO
OBn
OBn
OH
1.55
DEPT

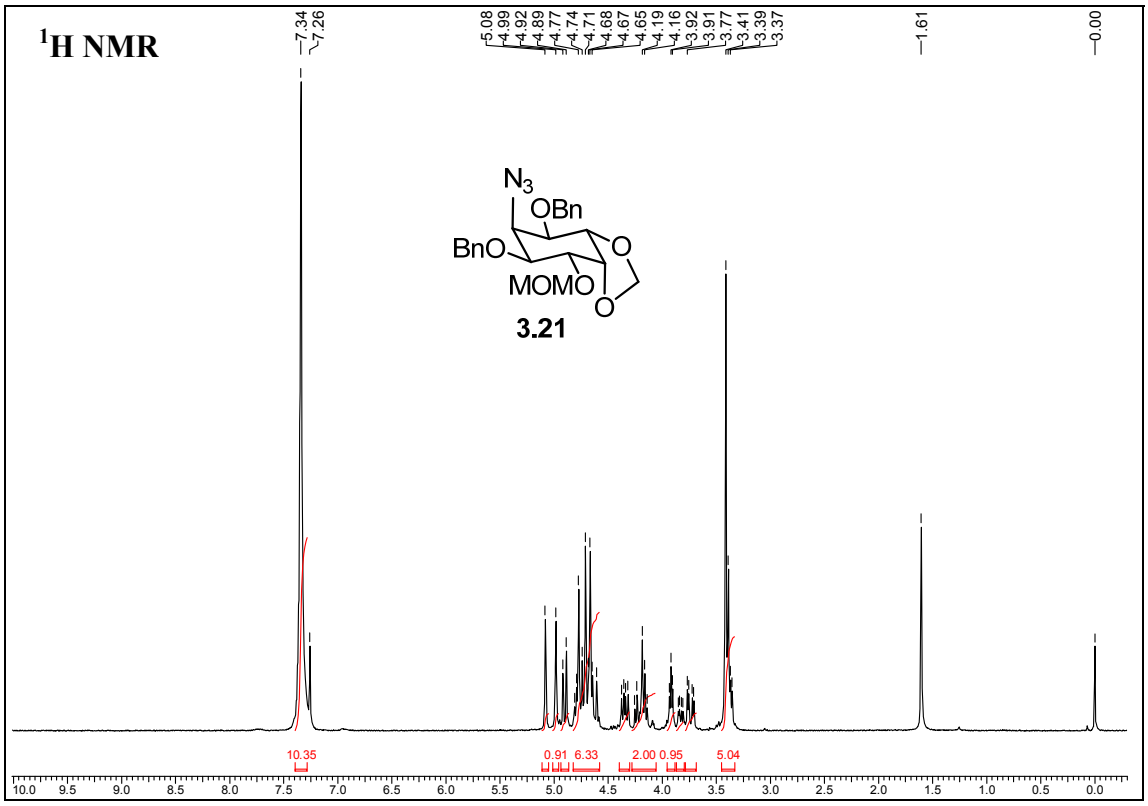


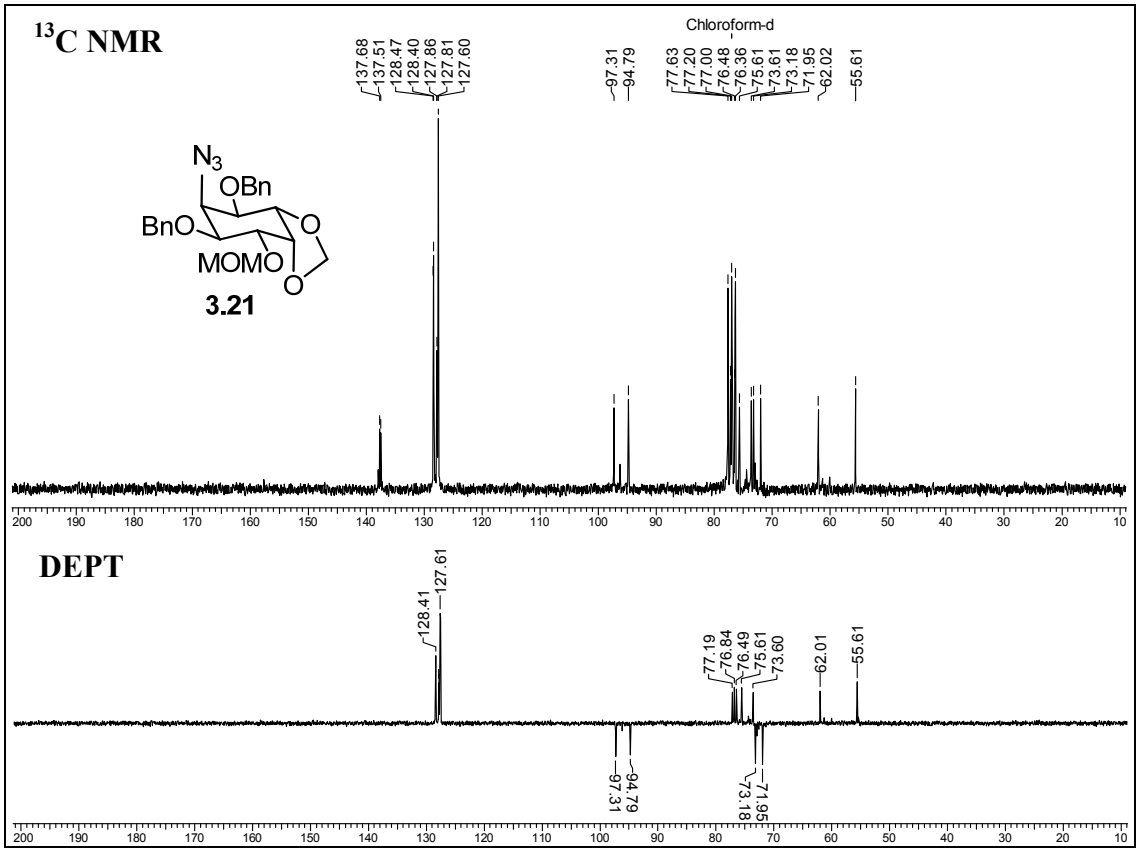


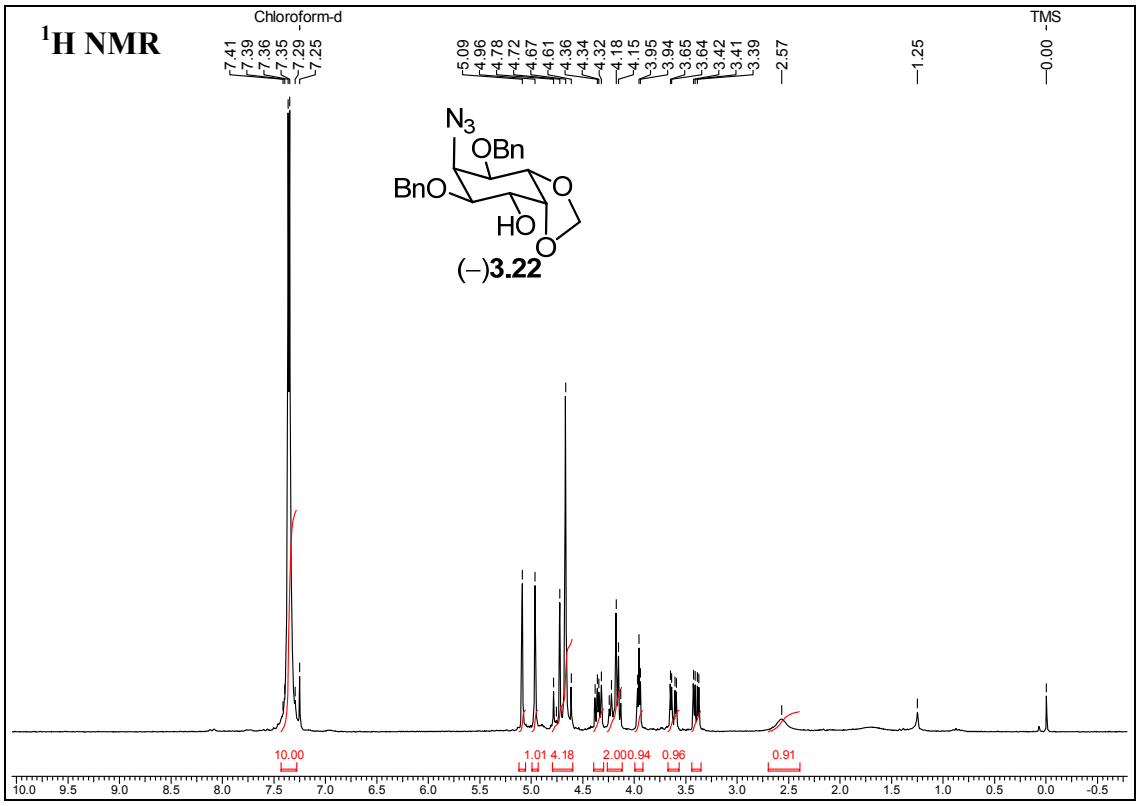
For 2D NMR see appendix III

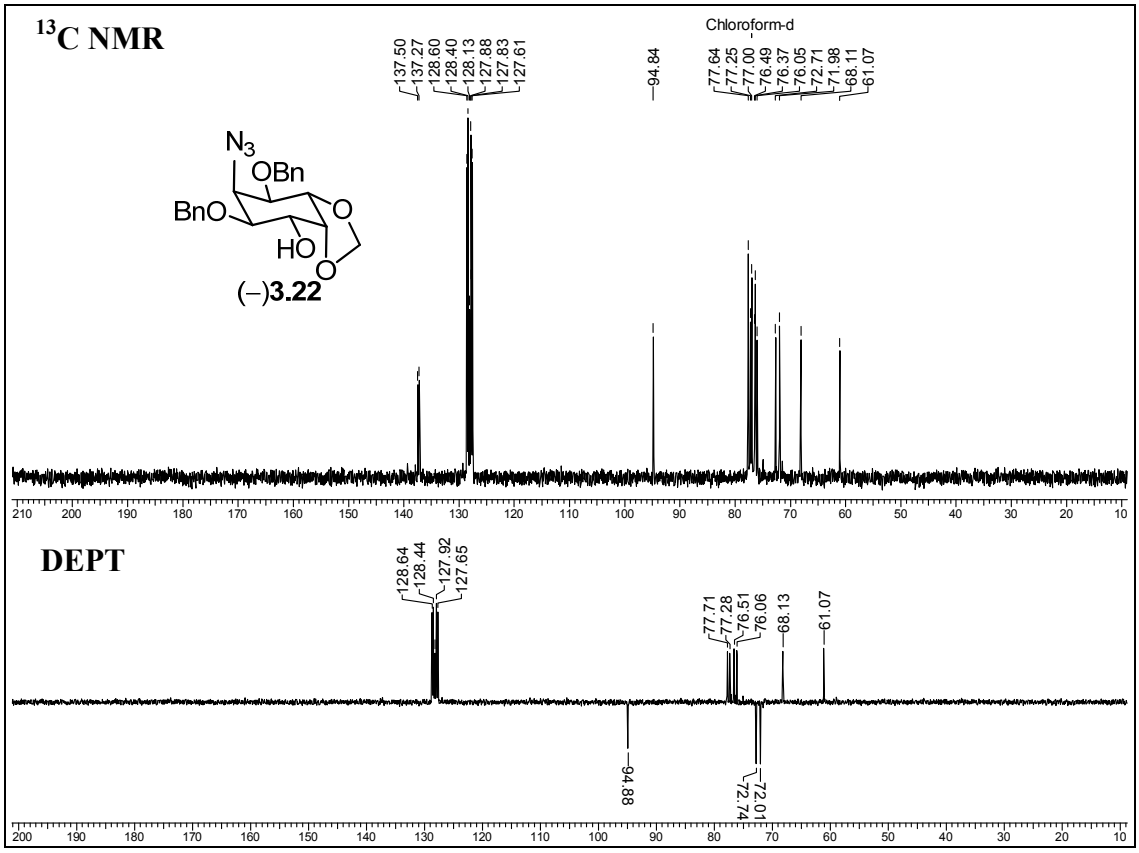

^{1}H NMR
TMS
7.40
7.39
7.37
7.33
7.32
7.26
4.70
4.64
4.63
4.16
4.14
4.13
4.00
3.87
3.82
3.80
3.70
3.68
3.65
2.56
0.00
N3
OBn
BnO
OH
HO
OH
3.20
10.00
4.00
1.00
2.01
3.00

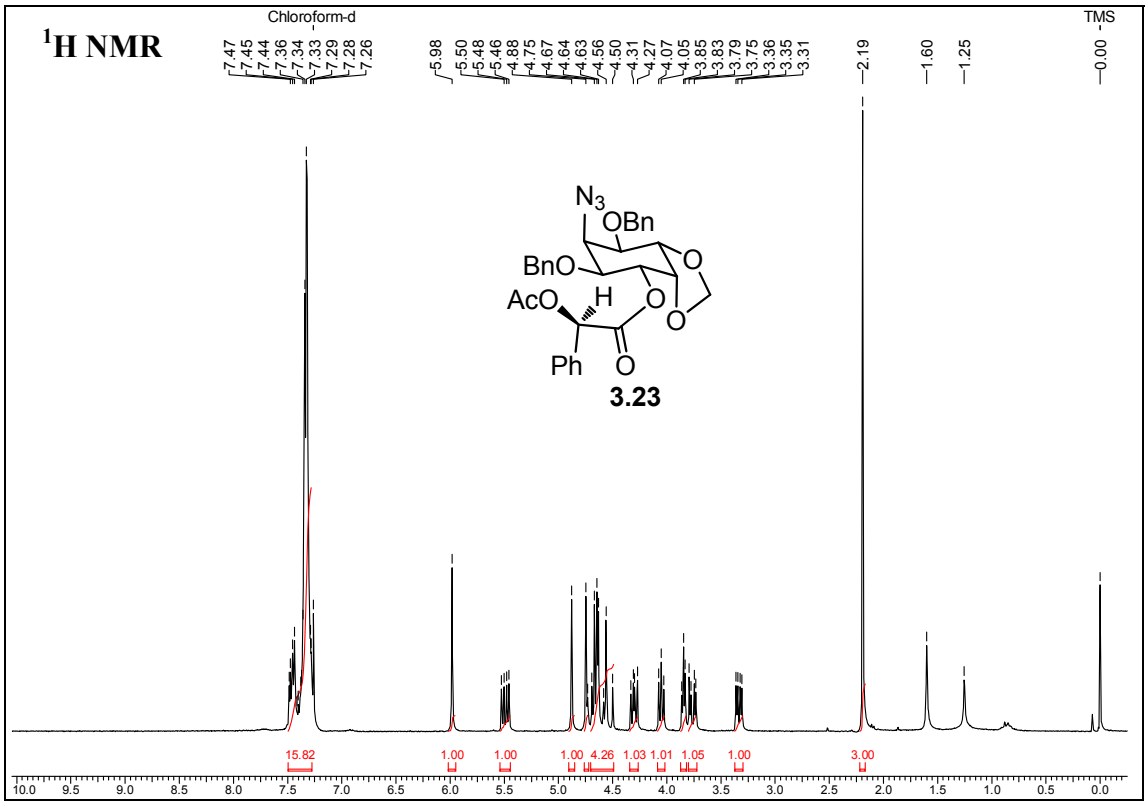

^{13}C NMR
Methanol d4
139.63
129.38
129.11
128.77
78.53
73.71
73.44
70.97
62.39
49.85
49.43
49.00
48.58
48.15
N3
OBn
BnO
OH
HO
OH
3.20
DEPT
129.38
129.11
128.77
78.53
73.43
70.97
62.39
73.70

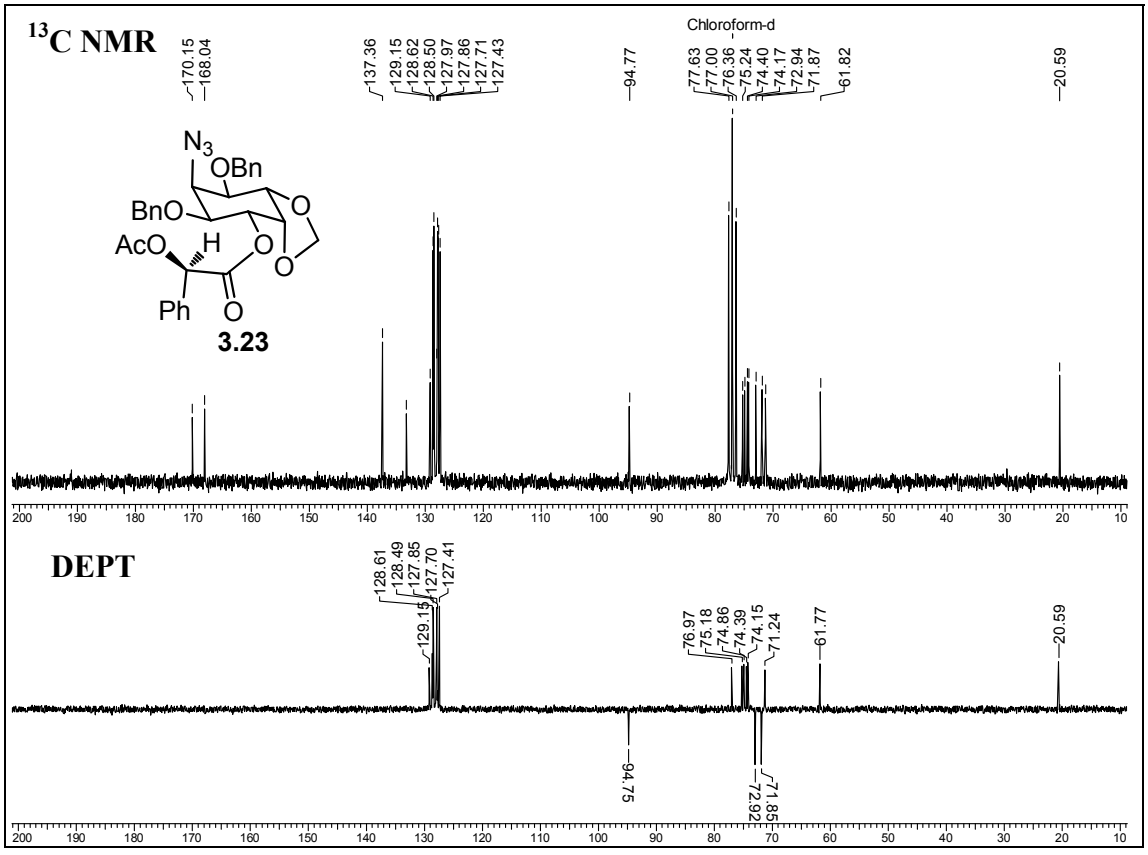

^{1}H NMR
7.34
7.26
5.08
4.99
4.92
4.89
4.77
4.74
4.71
4.68
4.67
4.65
4.19
4.16
3.92
3.91
3.77
3.41
3.39
3.37
1.61
0.00
N3
OBn
BnO
O
MOMO
O
3.21
10.35
0.91
6.33
2.00
0.95
5.04

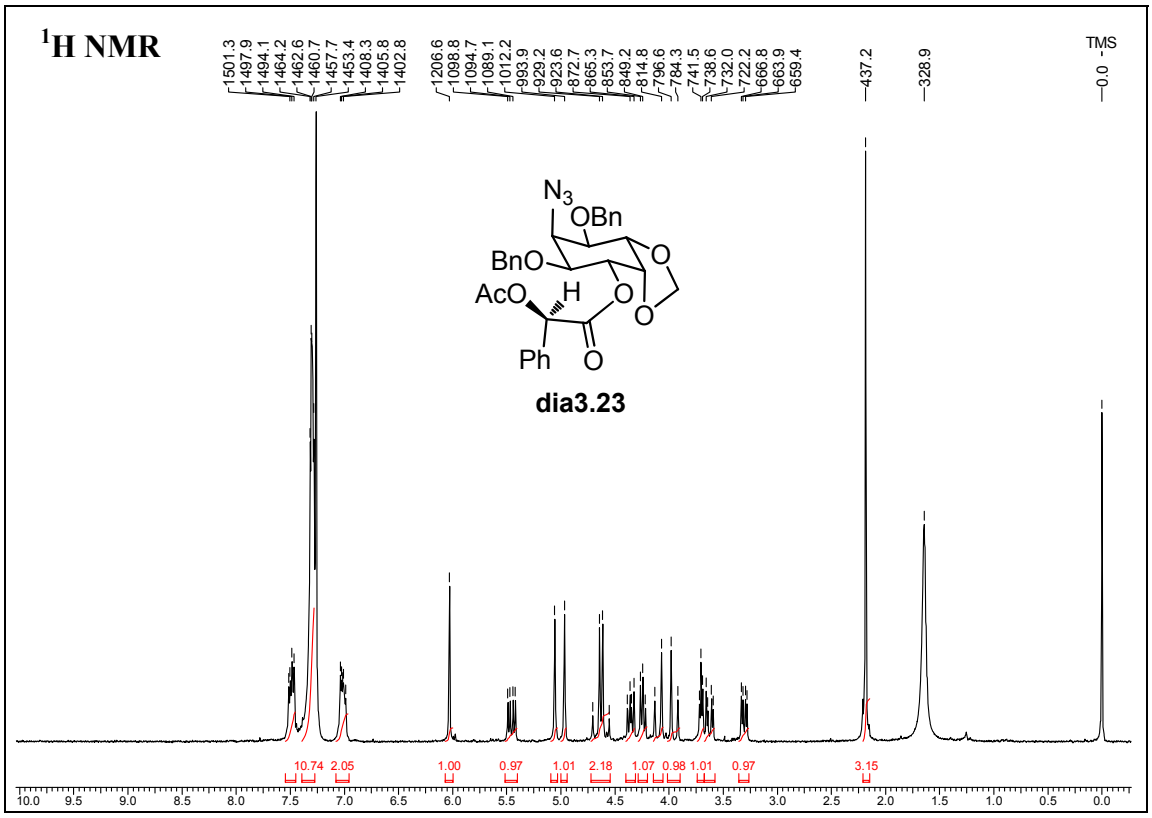

^{13}C NMR
Chloroform-d
137.68
137.51
128.47
128.40
127.86
127.81
127.60
97.31
94.79
77.63
77.20
77.00
76.48
76.36
75.61
73.61
73.18
71.95
62.02
55.61
N3
OBn
BnO
O
MOMO
O
3.21
DEPT
128.41
127.61
77.19
76.84
76.49
75.61
73.60
62.01
55.61
97.31
94.79
73.18
71.95

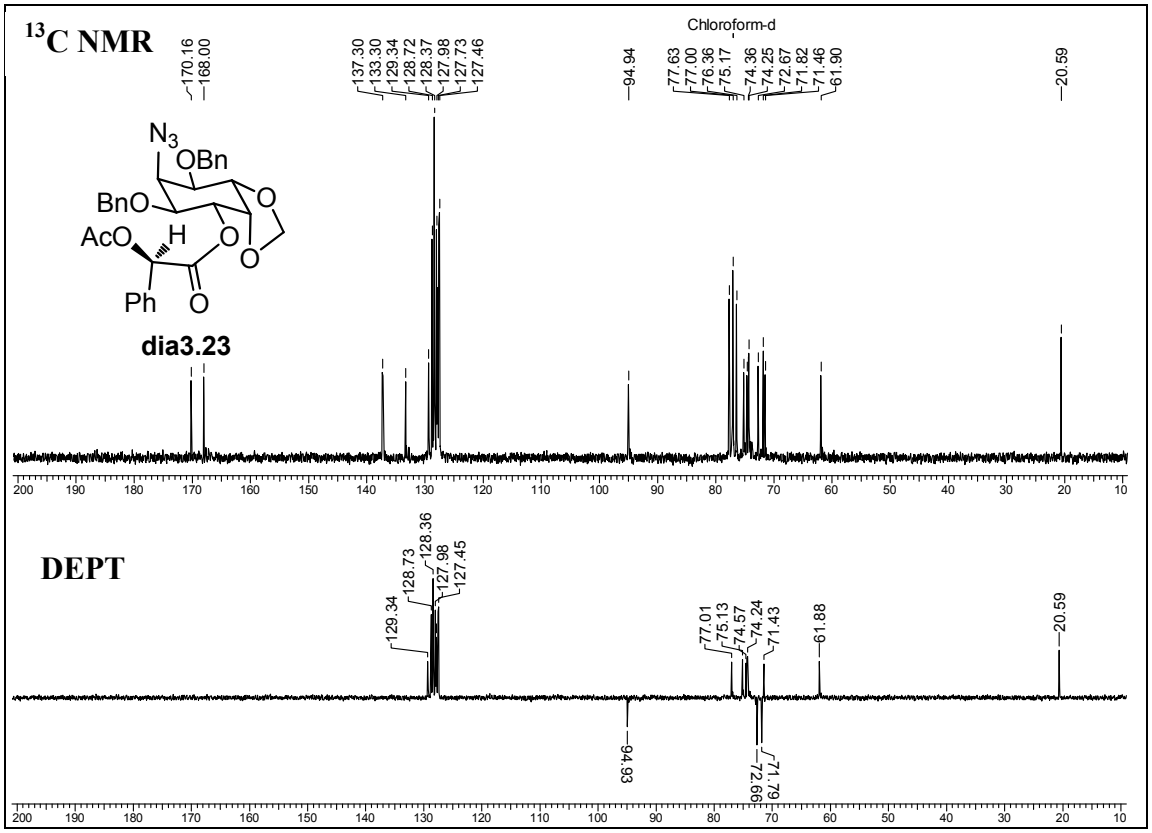

^{1}H NMR
Chloroform-d
TMS
7.41
7.39
7.36
7.35
7.29
7.25
5.09
4.96
4.78
4.72
4.67
4.61
4.36
4.34
4.32
4.18
4.15
3.95
3.94
3.65
3.64
3.42
3.41
3.39
2.57
1.25
0.00
N3
OBn
BnO
O
HO
O
(–)3.22
10.00
1.01
4.18
2.00
0.94
0.96
0.91

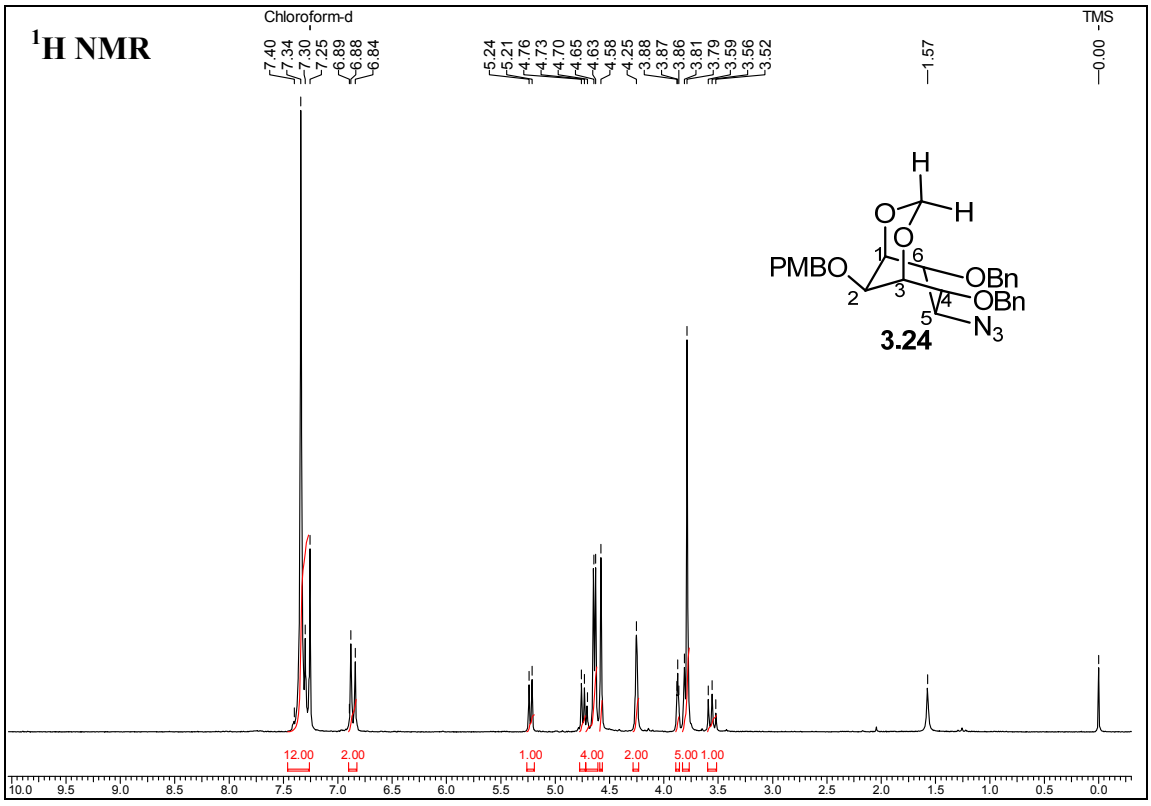

^{13}C NMR
137.50
137.27
128.60
128.40
128.13
127.88
127.83
127.61
94.84
Chloroform-d
77.64
77.25
77.00
76.49
76.37
76.05
72.71
71.98
68.11
61.07
N3
OBn
BnO
O
HO
O
(–)3.22
DEPT
128.64
128.44
127.92
127.65
77.71
77.28
76.51
76.06
68.13
61.07
94.88
72.74
72.10

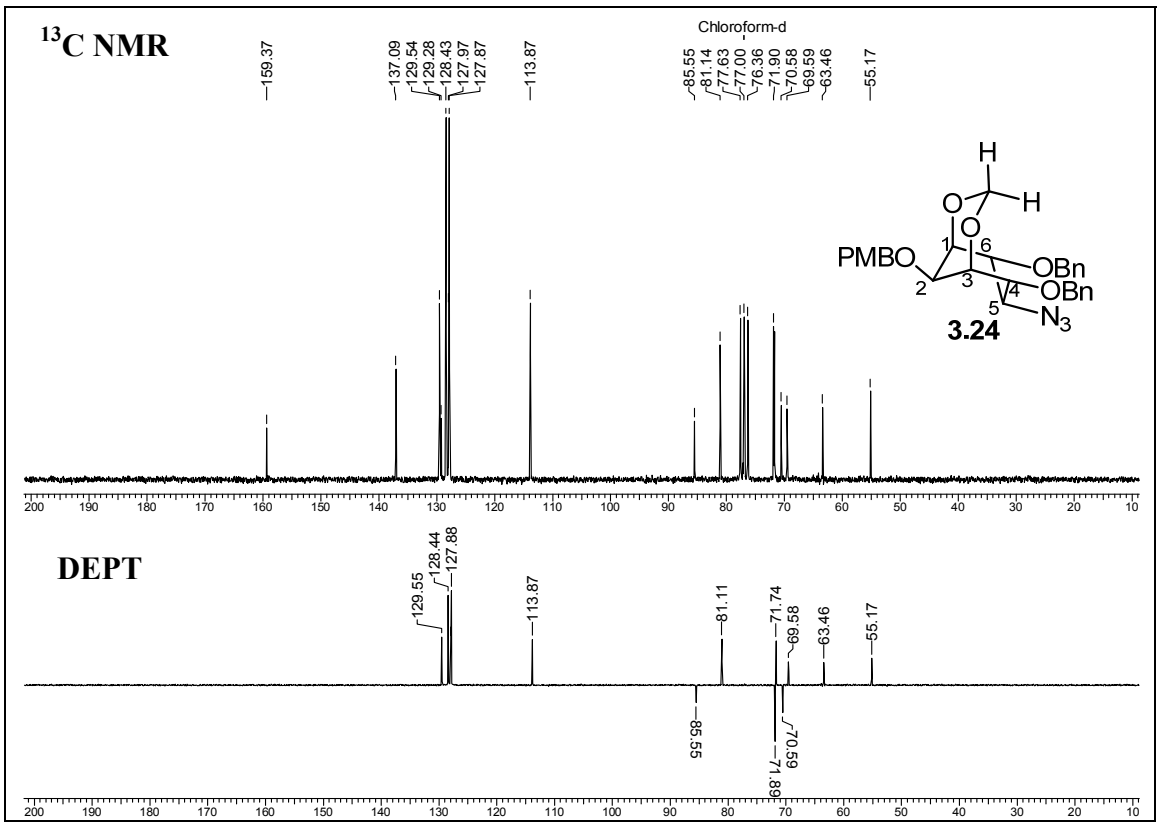

^{1}H NMR
Chloroform-d
TMS
7.47 7.45 7.44 7.36 7.34 7.33 7.29 7.28 7.26
5.98 5.50 5.48 5.46 4.88 4.75 4.67 4.64 4.63 4.56 4.50 4.31 4.27 4.07 4.05 3.85 3.83 3.79 3.75 3.36 3.35 3.31
2.19
1.60
1.25
0.00
N3
OBn
BnO
AcO
H
O
Ph
3.23
15.82 1.00 1.00 1.00 4.26 1.03 1.01 1.05 1.00 3.00


^{13}C NMR
Chloroform-d
170.15 168.04 137.36 129.15 128.62 128.50 127.97 127.86 127.71 127.43 94.77 77.63 77.00 76.36 75.24 74.40 74.17 72.94 71.87 61.82 20.59
N3
OBn
BnO
AcO
H
Ph
3.23
DEPT
128.61 128.49 127.85 127.70 127.41 129.15
76.97 75.18 74.86 74.39 74.15 71.24 61.77 20.59
94.75 72.92 71.85

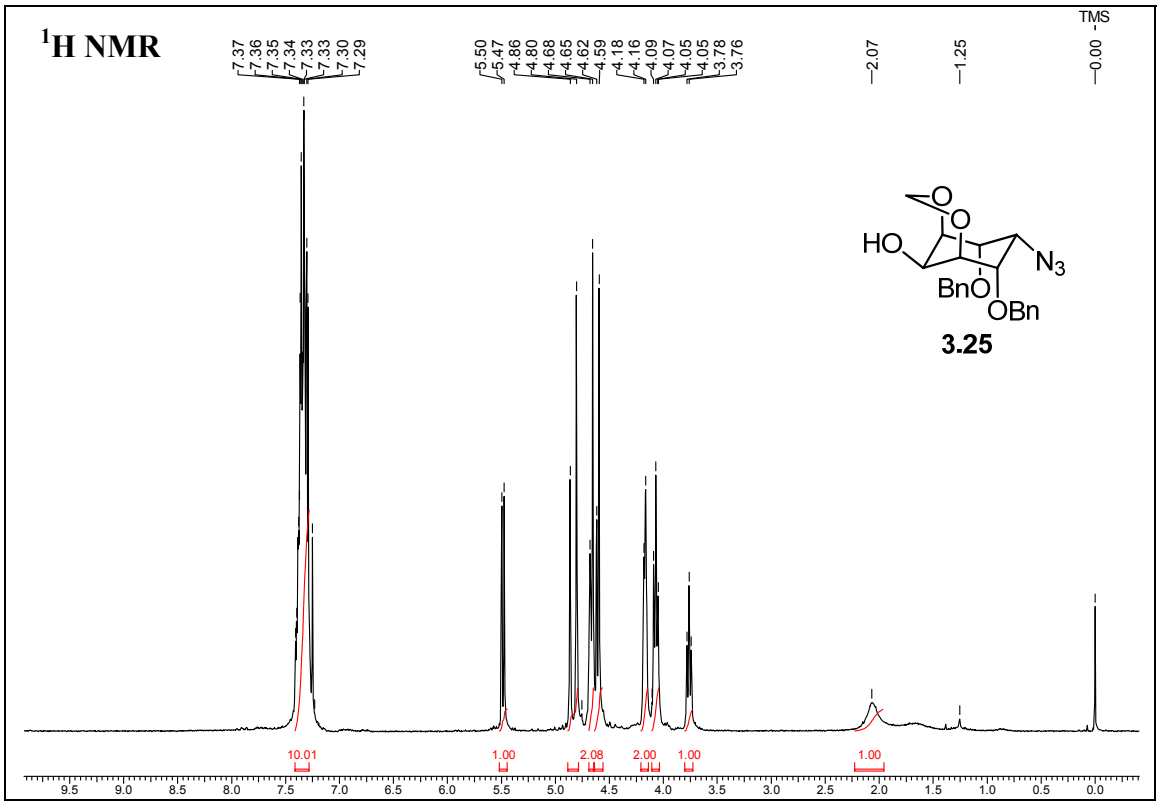

^{1}H NMR
TMS
dia3.23

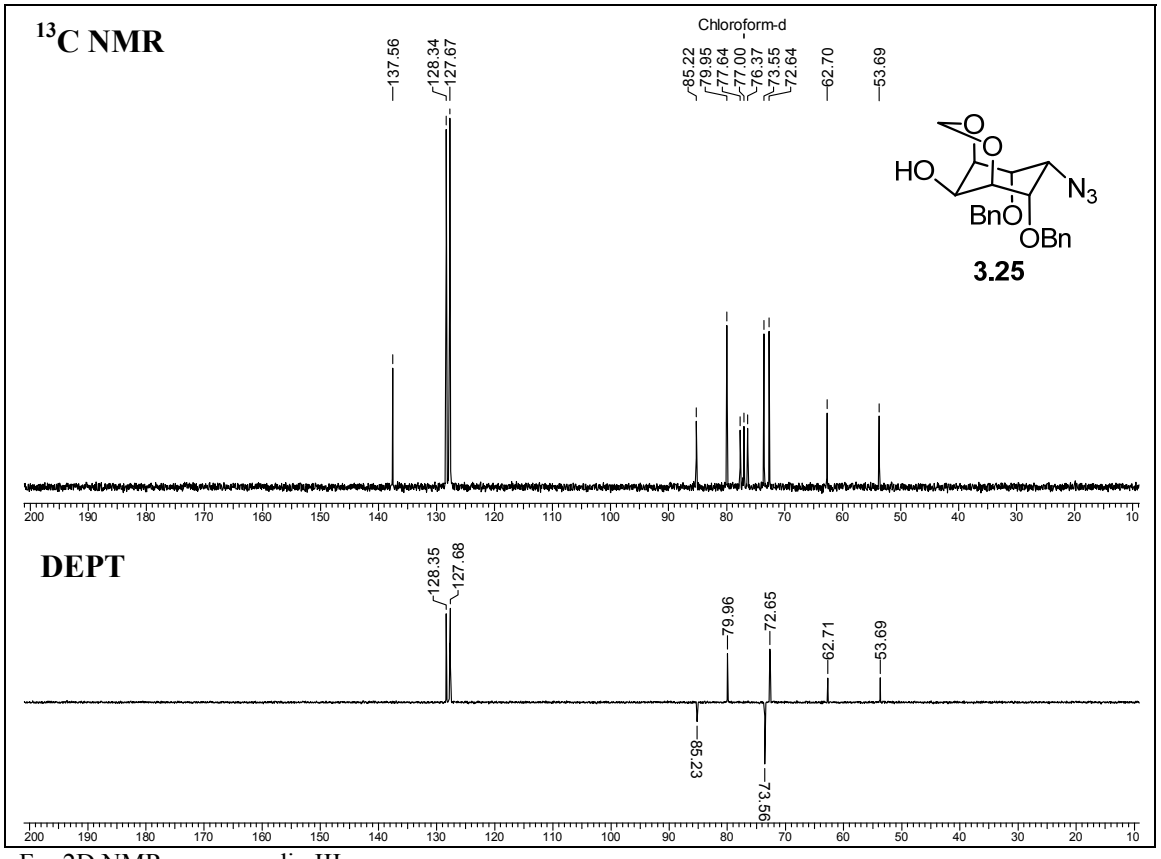

^{13}C NMR
Chloroform-d
dia3.23
DEPT



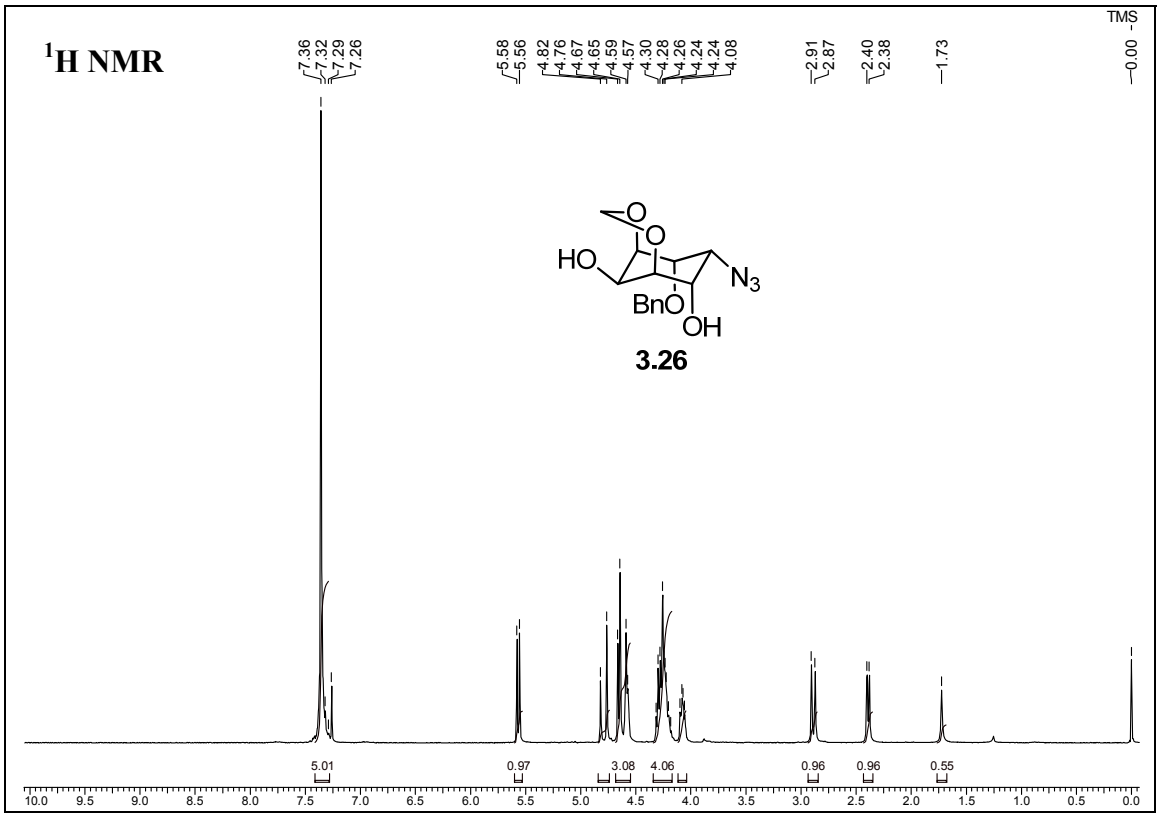


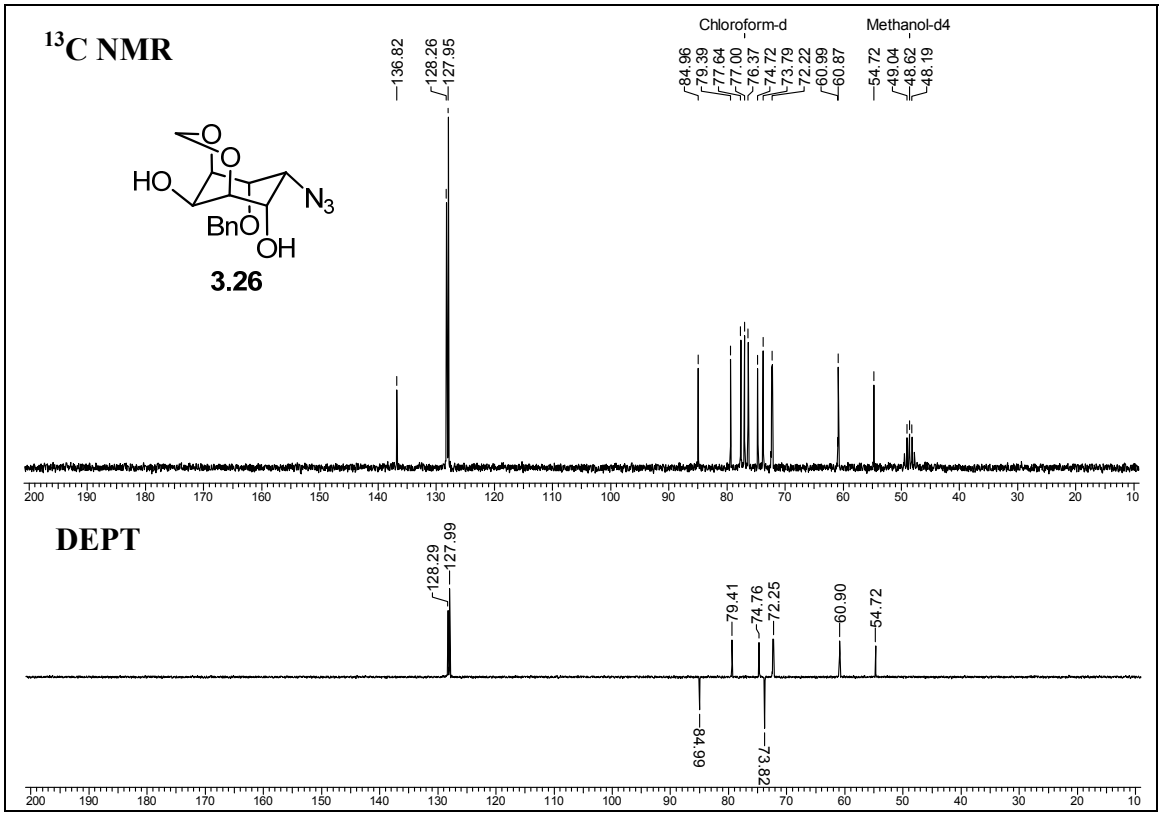
For 2D NMR see appendix III

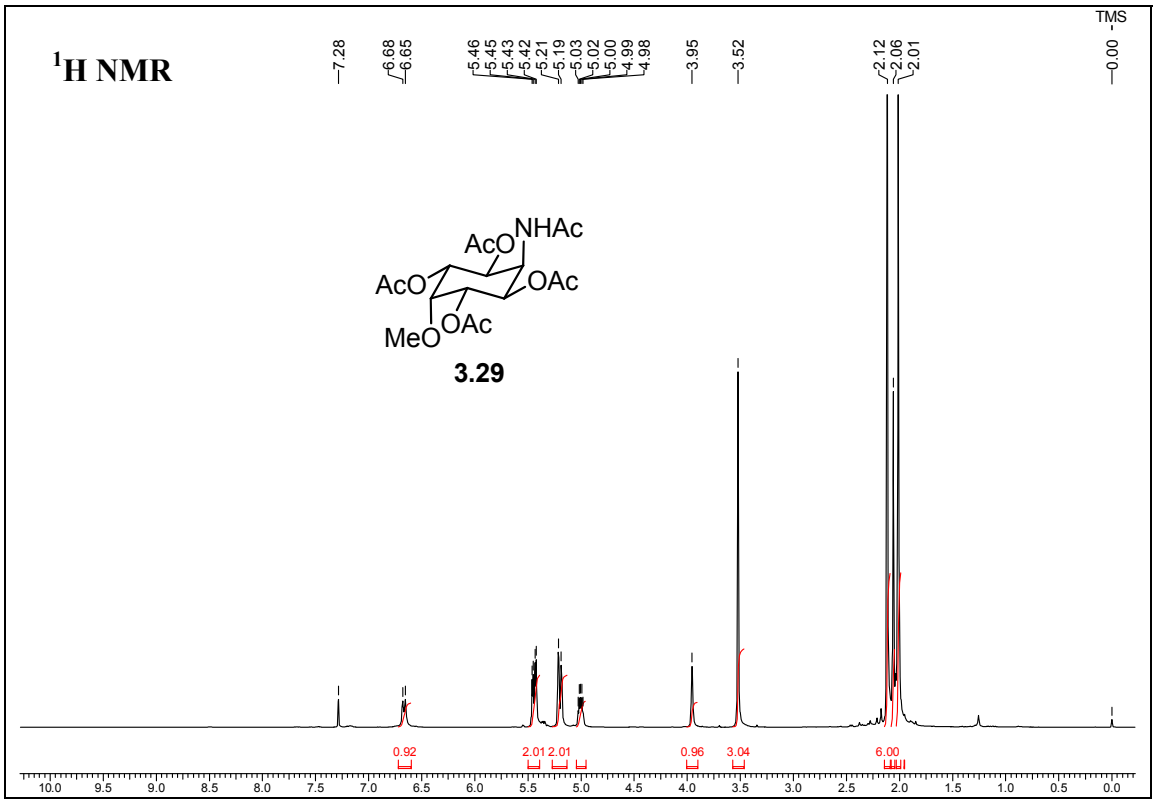


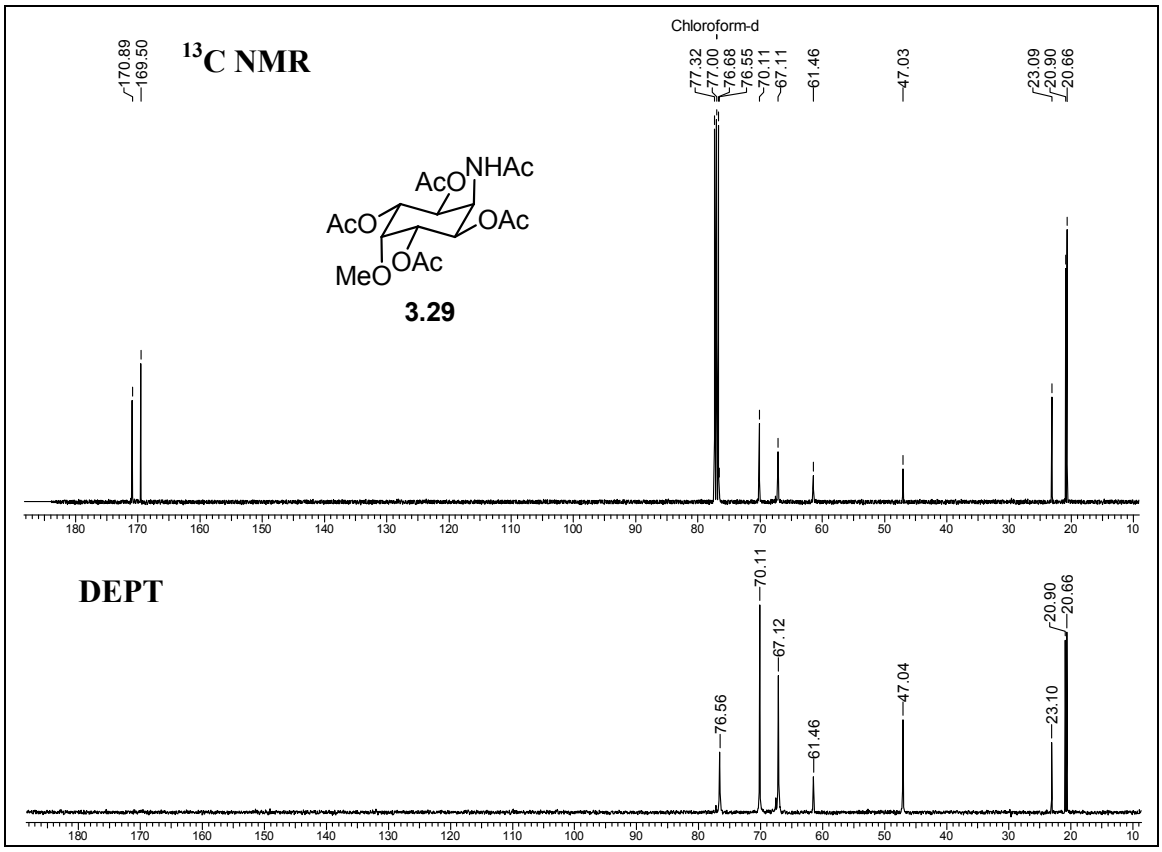


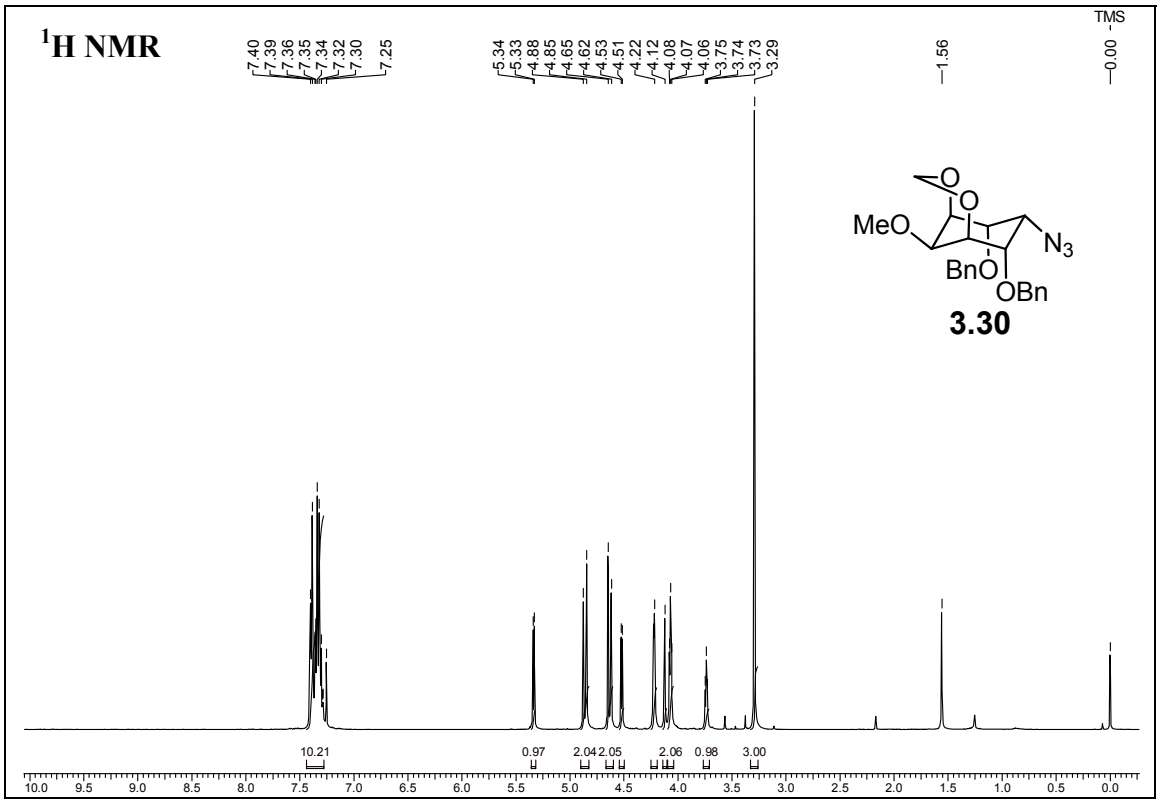
For 2D NMR see appendix III

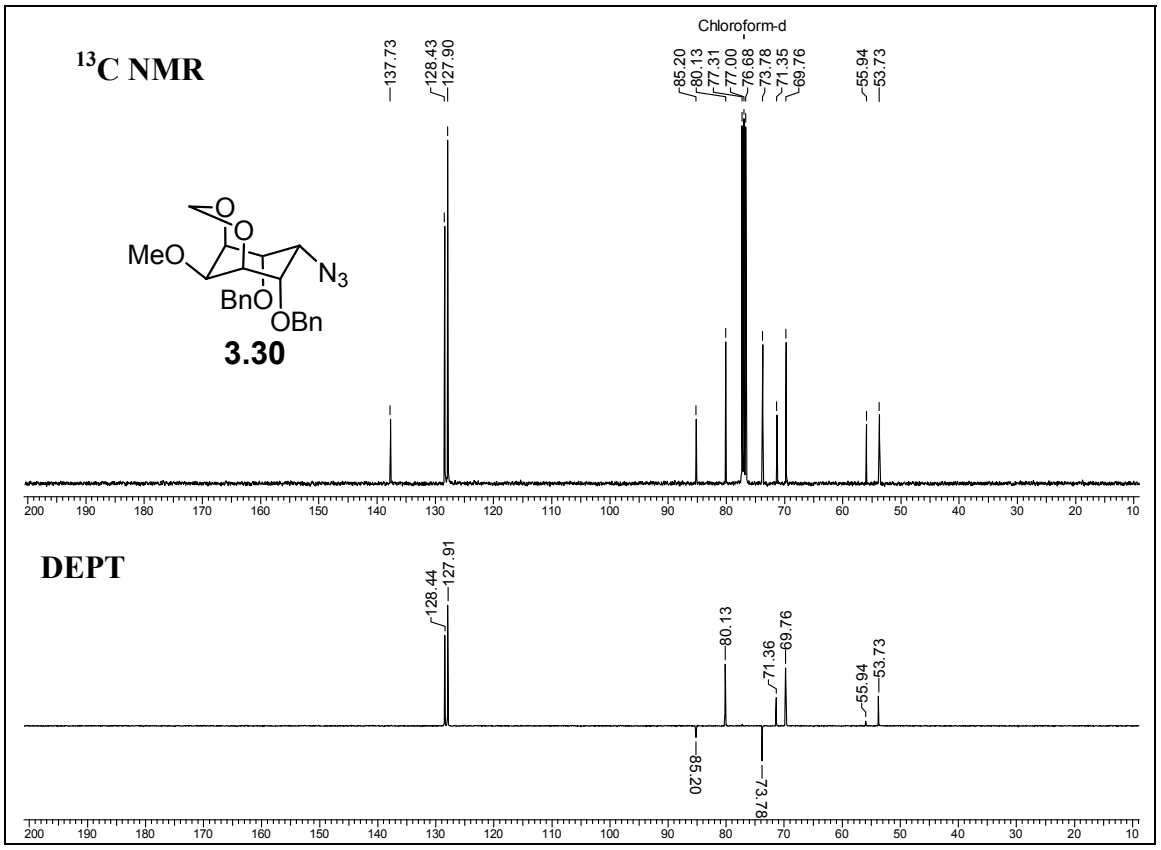

^{1}H NMR
TMS
7.36
7.32
7.29
7.26
5.58
5.56
4.82
4.76
4.67
4.65
4.59
4.57
4.30
4.28
4.26
4.24
4.08
2.91
2.87
2.40
2.38
1.73
0.00
HO
O
O
N3
BnO
OH
3.26
5.01
0.97
3.08
4.06
0.96
0.96
0.55

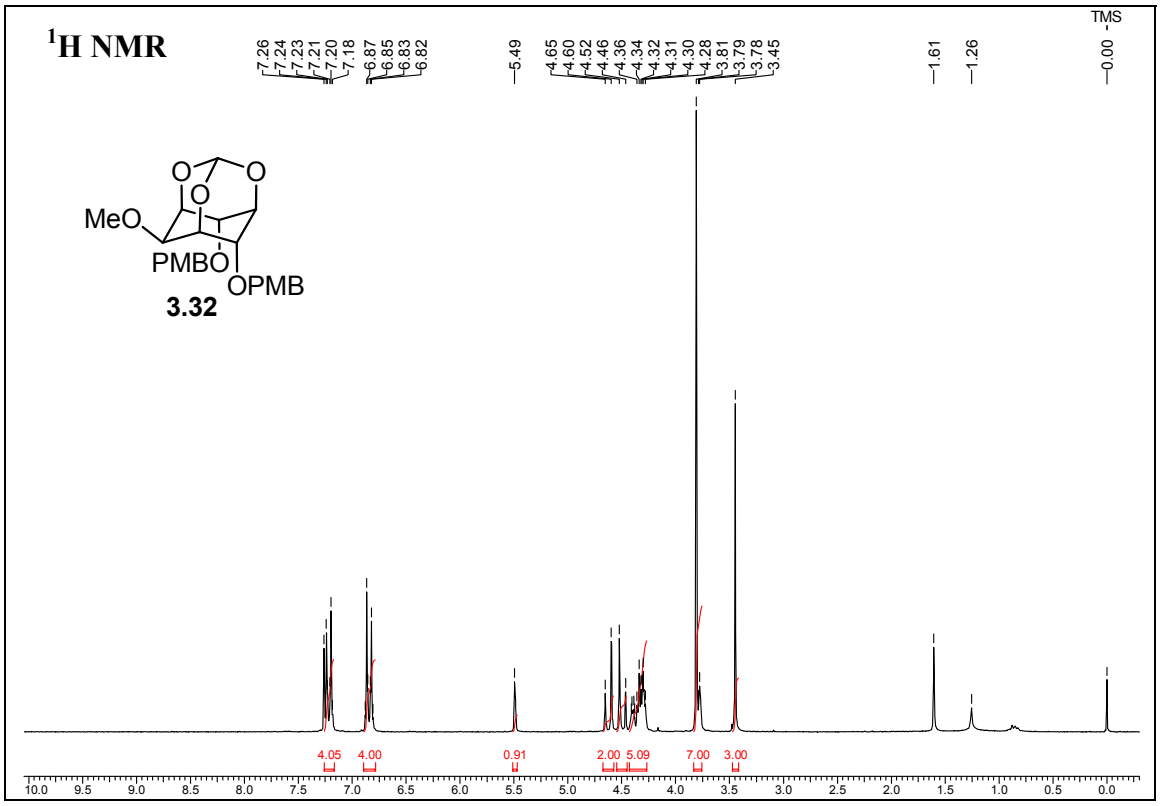

^{13}C NMR
136.82
128.26
127.95
Chloroform-d
Methanol-d4
84.96
79.39
77.64
77.00
76.37
74.72
73.79
72.22
60.99
60.87
54.72
49.04
48.62
48.19
HO
O
O
N3
BnO
OH
3.26
DEPT
128.29
127.99
79.41
74.76
72.25
60.90
54.72
84.39
73.82

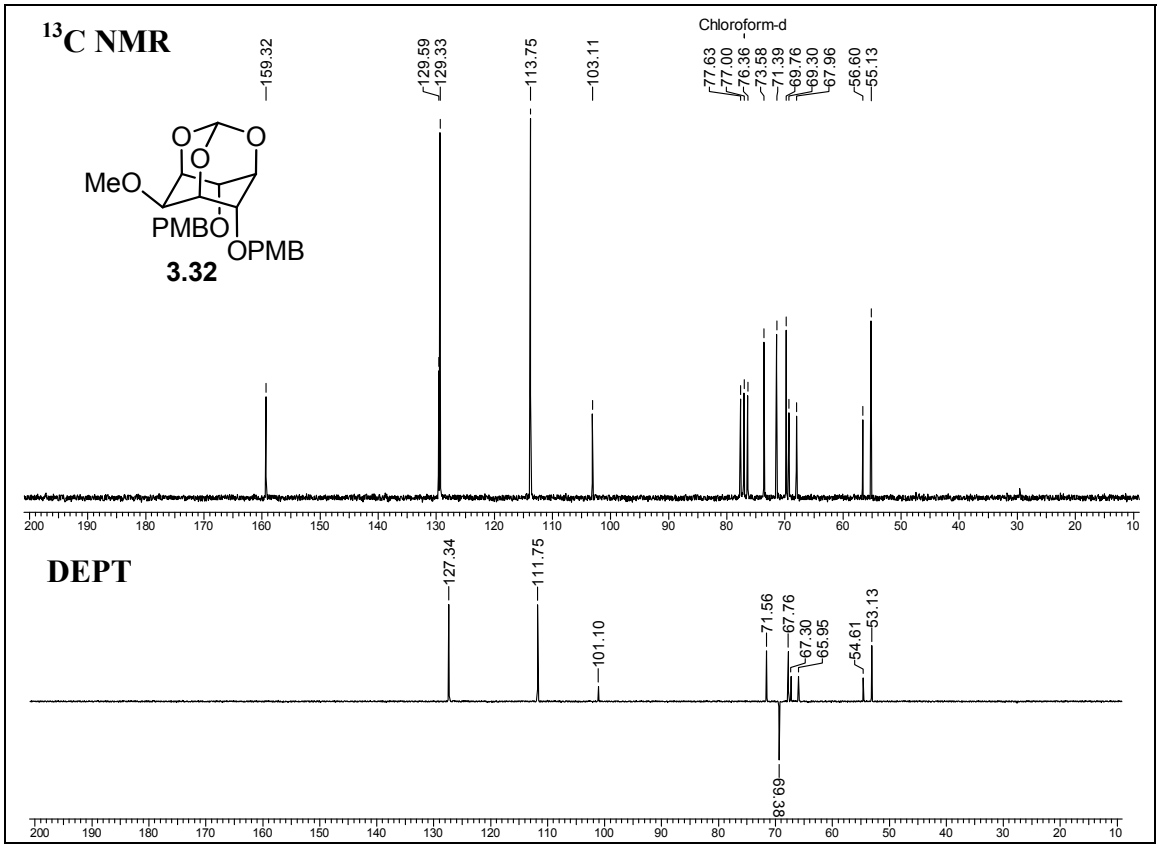

^{1}H NMR
TMS
7.28
6.68
6.65
5.46
5.45
5.43
5.42
5.21
5.19
5.03
5.02
5.00
4.99
4.98
3.95
3.52
2.12
2.06
2.01
0.00
AcO
NHAc
AcO
OAc
MeO
OAc
3.29
0.92
2.01
2.01
0.96
3.04
6.00

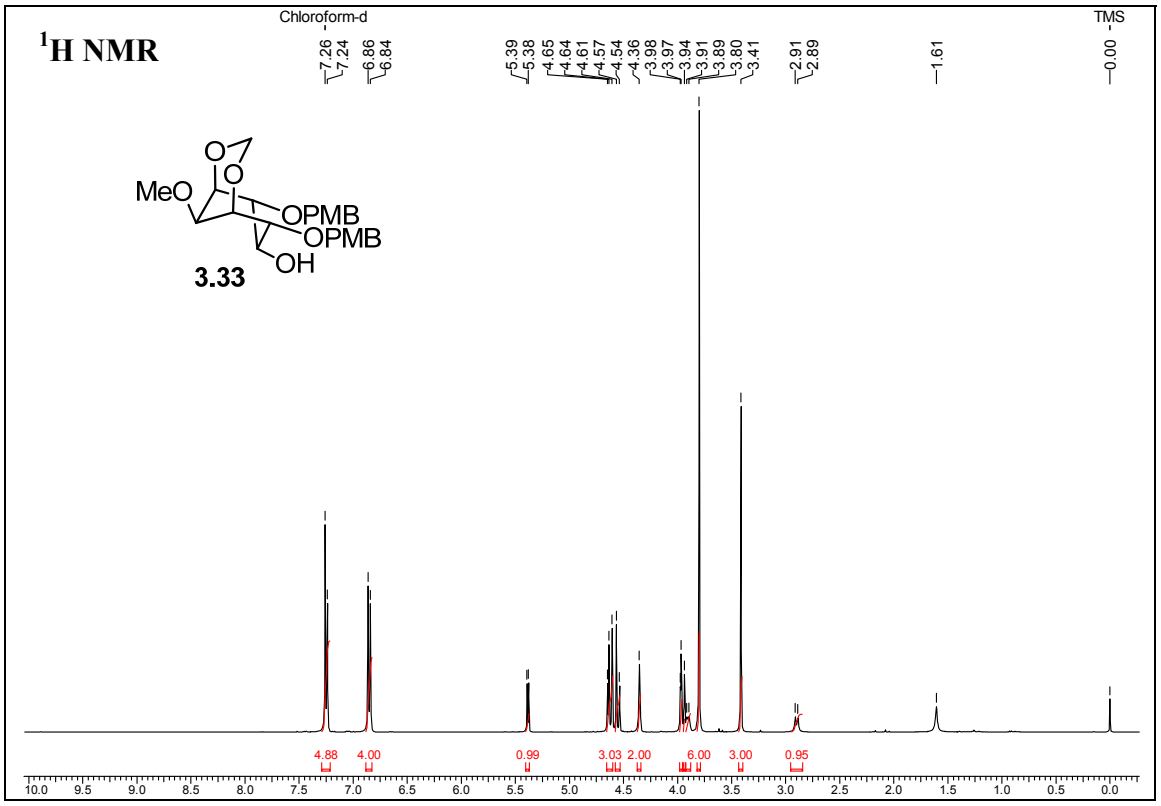

^{13}C NMR
Chloroform-d
170.89
169.50
77.32
77.00
76.68
76.55
70.11
67.11
61.46
47.03
23.09
20.90
20.66
AcO
NHAc
AcO
OAc
MeO
OAc
3.29
DEPT
70.11
67.12
20.90
20.66
76.56
61.46
47.04
23.10

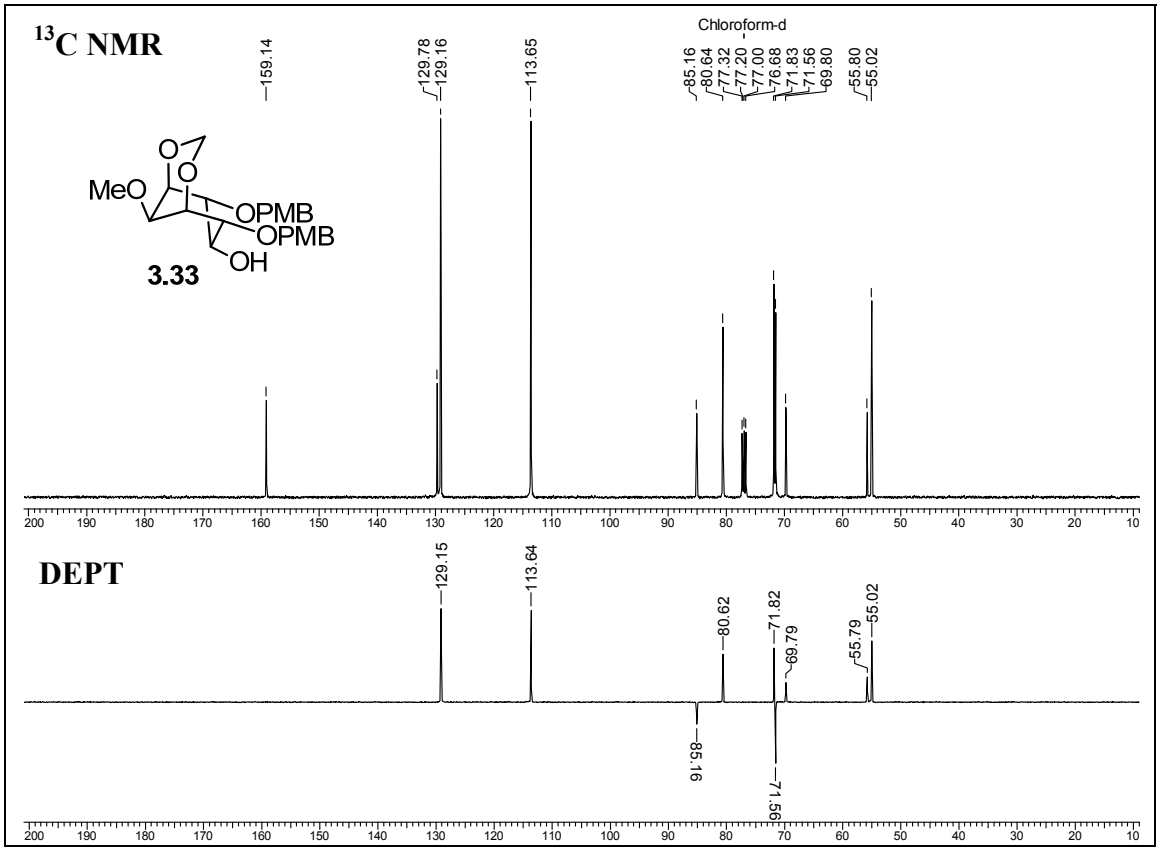

^{1}H NMR
TMS
7.40
7.39
7.36
7.35
7.34
7.32
7.30
7.25
5.34
5.33
4.88
4.85
4.65
4.62
4.53
4.51
4.22
4.12
4.08
4.07
4.06
3.75
3.74
3.73
3.29
1.56
0.00
MeO
N3
BnO
OBn
3.30
10.21
0.97
2.04
2.05
2.06
0.98
3.00

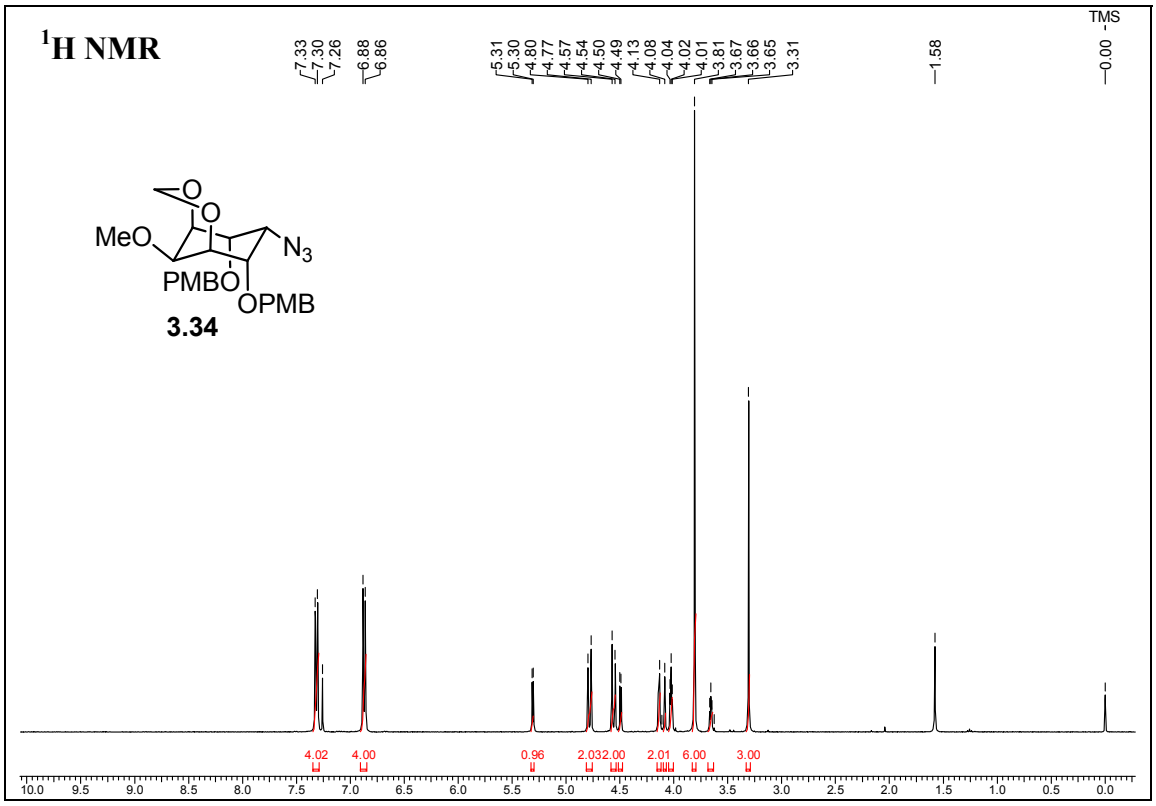

^{13}C NMR
Chloroform-d
137.73
128.43
127.90
85.20
80.13
77.31
77.00
76.68
73.78
71.35
69.76
55.94
53.73
MeO
N3
BnO
OBn
3.30
DEPT
128.44
127.91
80.13
71.36
69.76
55.94
53.73
65.20
73.78

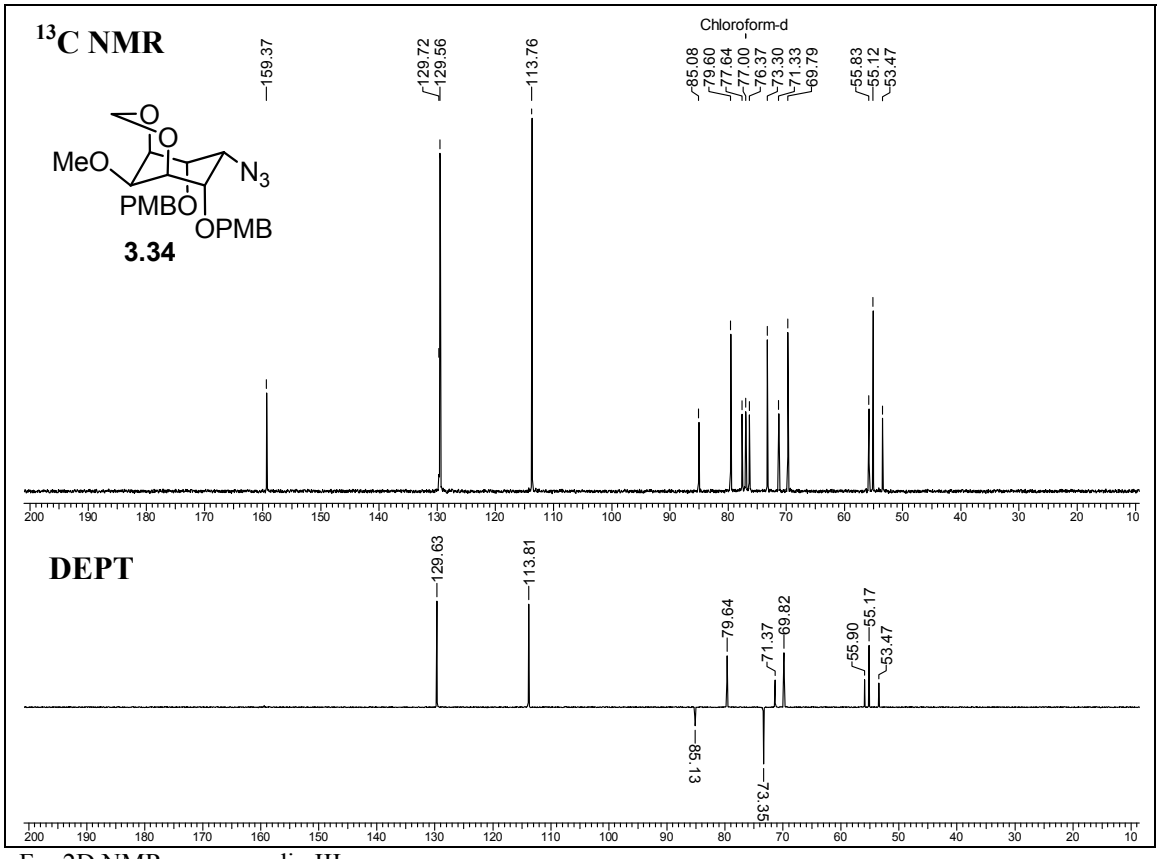

^{1}H NMR
TMS
MeO
PMBO
OPMB
3.32


^{13}C NMR
Chloroform-d
MeO
PMBO
OPMB
3.32
DEPT

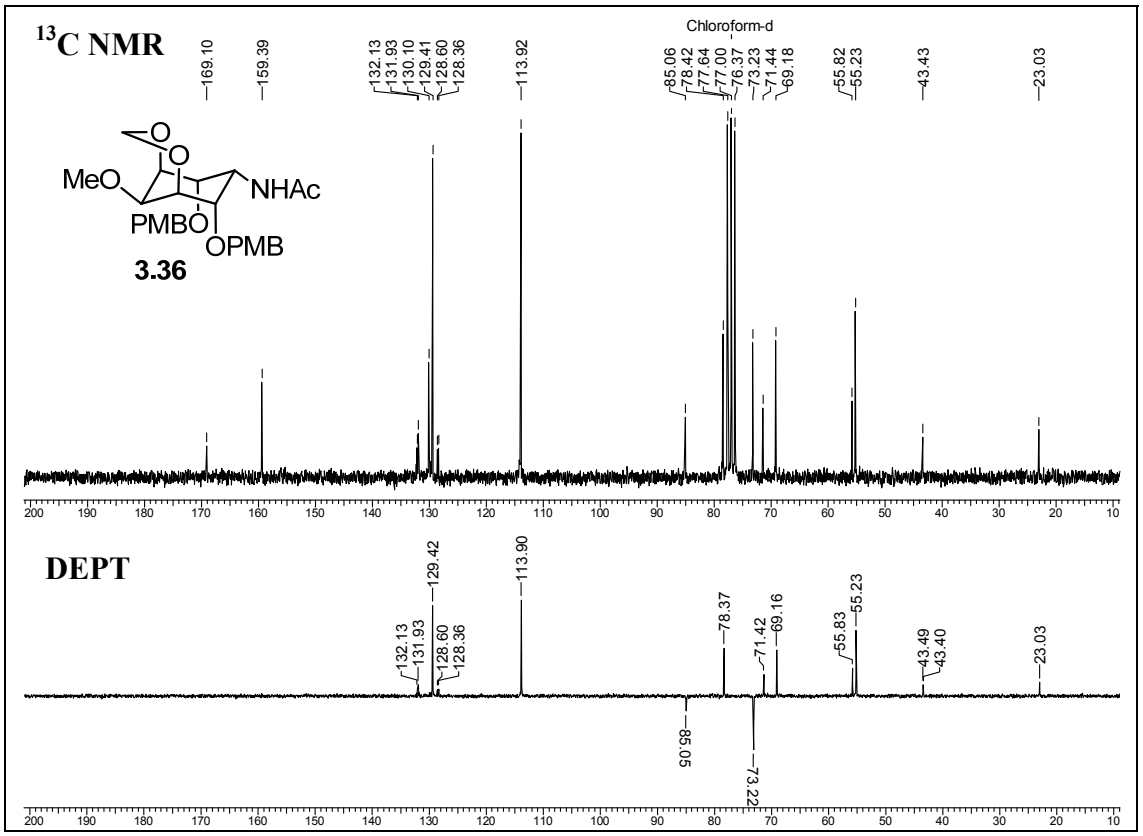

^{1}H NMR
Chloroform-d
TMS
7.26
7.24
6.86
6.84
5.39
5.38
4.65
4.64
4.61
4.57
4.54
4.36
3.98
3.97
3.94
3.91
3.89
3.80
3.41
2.91
2.89
1.61
0.00
MeO
OPMB
OPMB
OH
3.33
4.88
4.00
0.99
3.03
2.00
6.00
3.00
0.95


^{13}C NMR
Chloroform-d
159.14
129.78
129.16
113.65
85.16
80.64
77.32
77.20
77.00
76.68
71.83
71.56
69.80
55.80
55.02
MeO
OPMB
OPMB
OH
3.33
DEPT
129.15
113.64
80.62
71.82
69.79
55.79
55.02
-85.16
-71.56

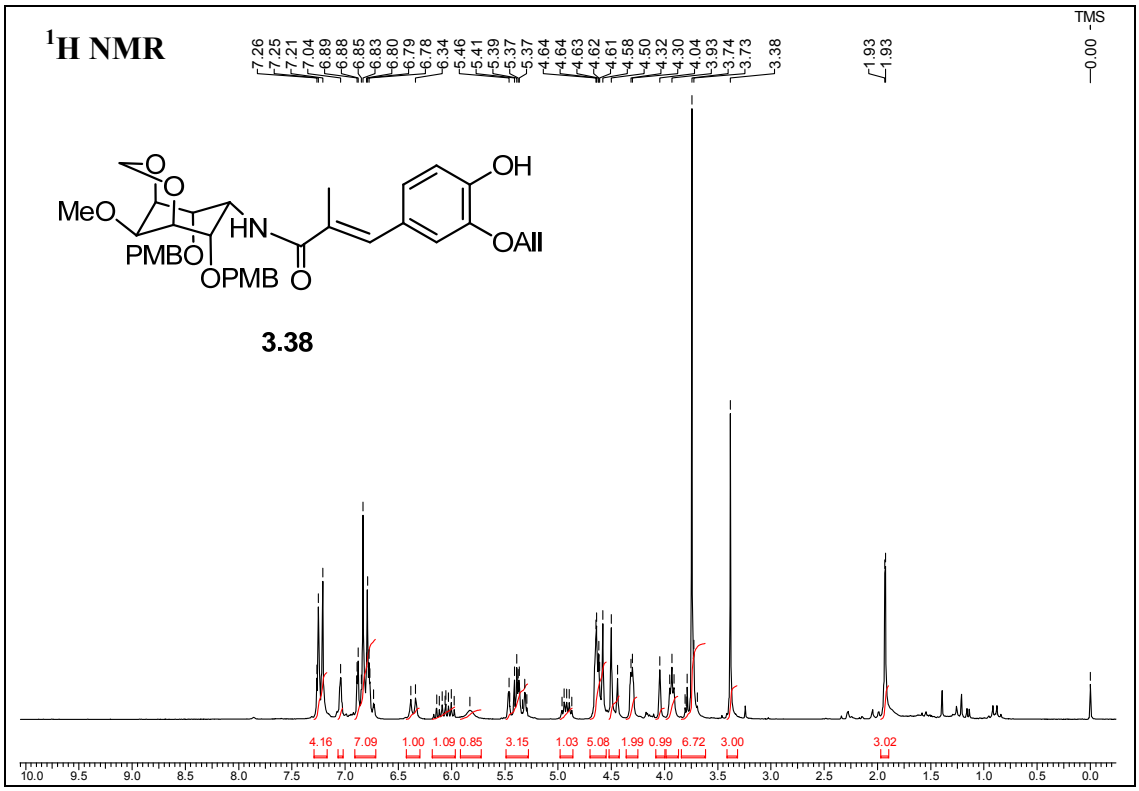


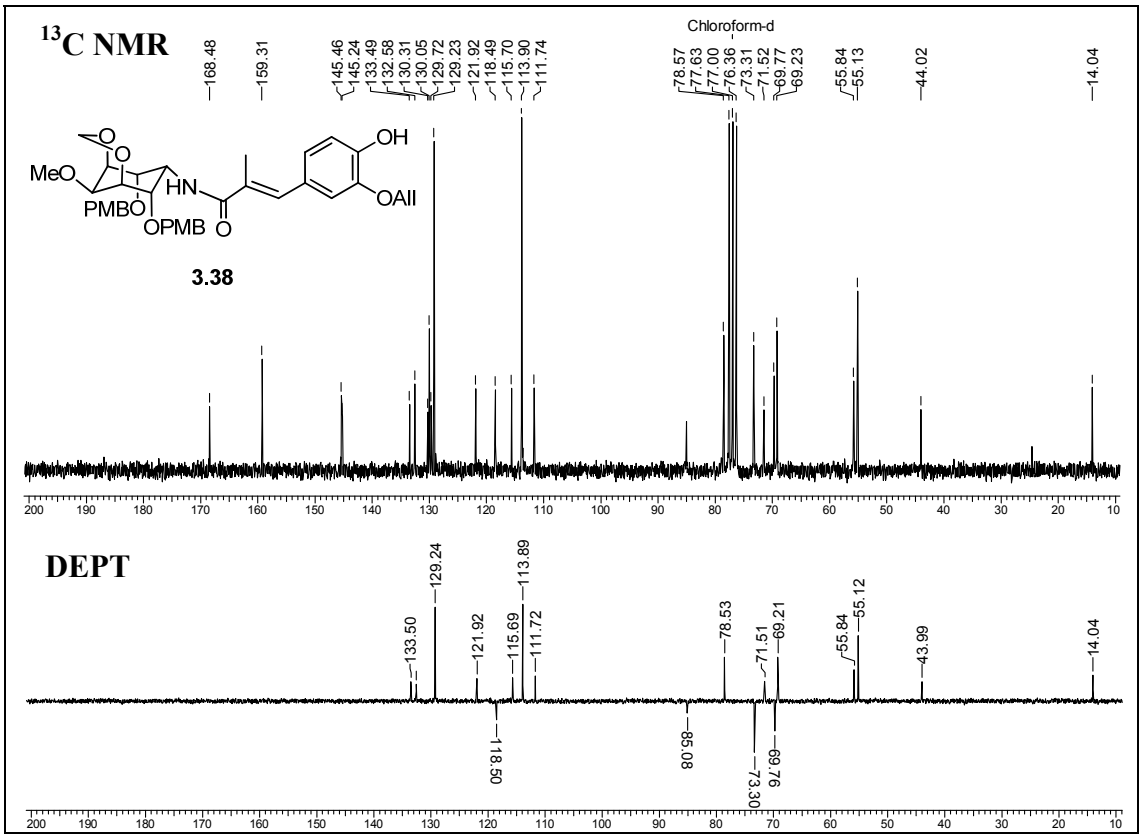


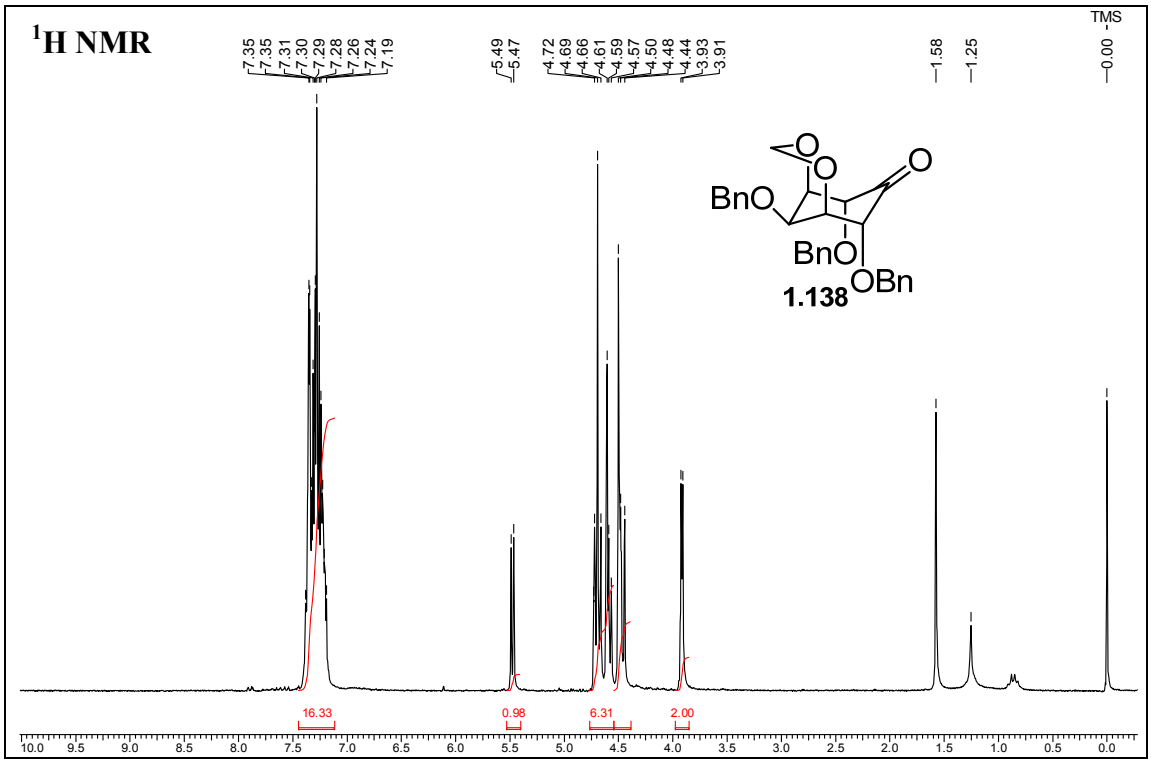
For 2D NMR see appendix III

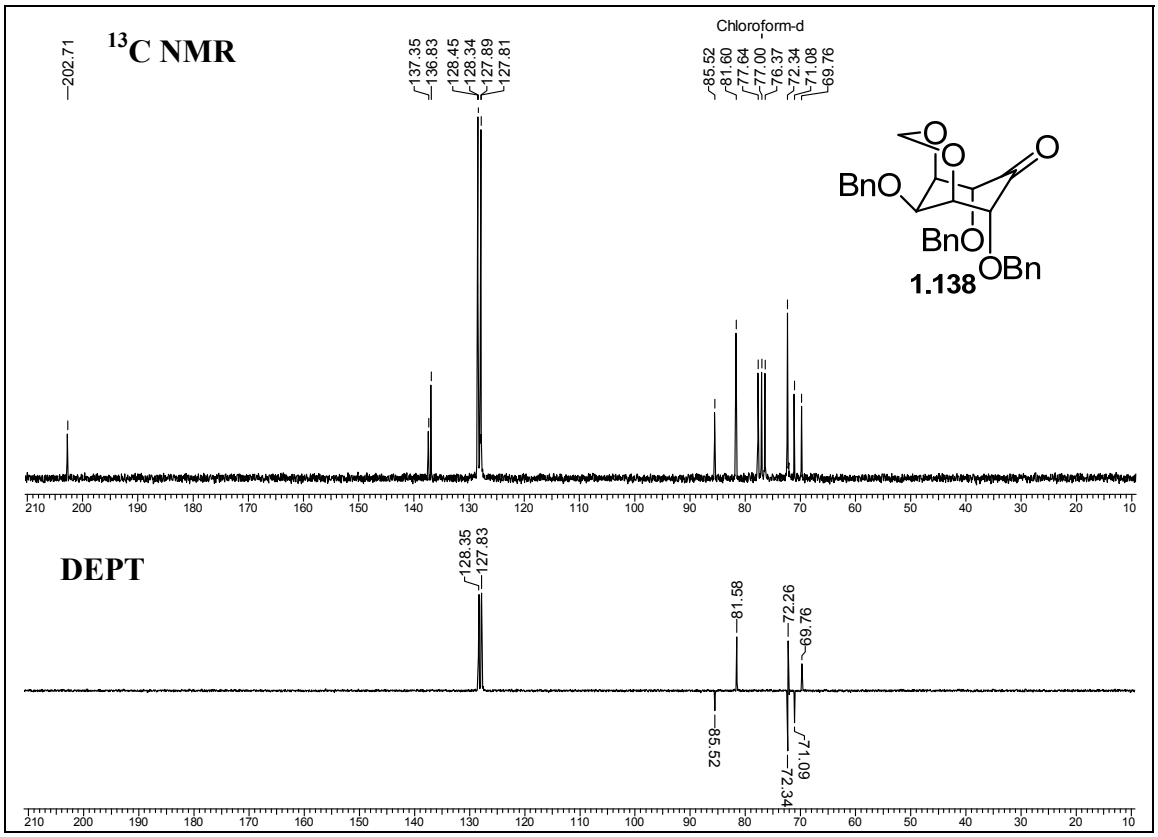


For 2D NMR see appendix III

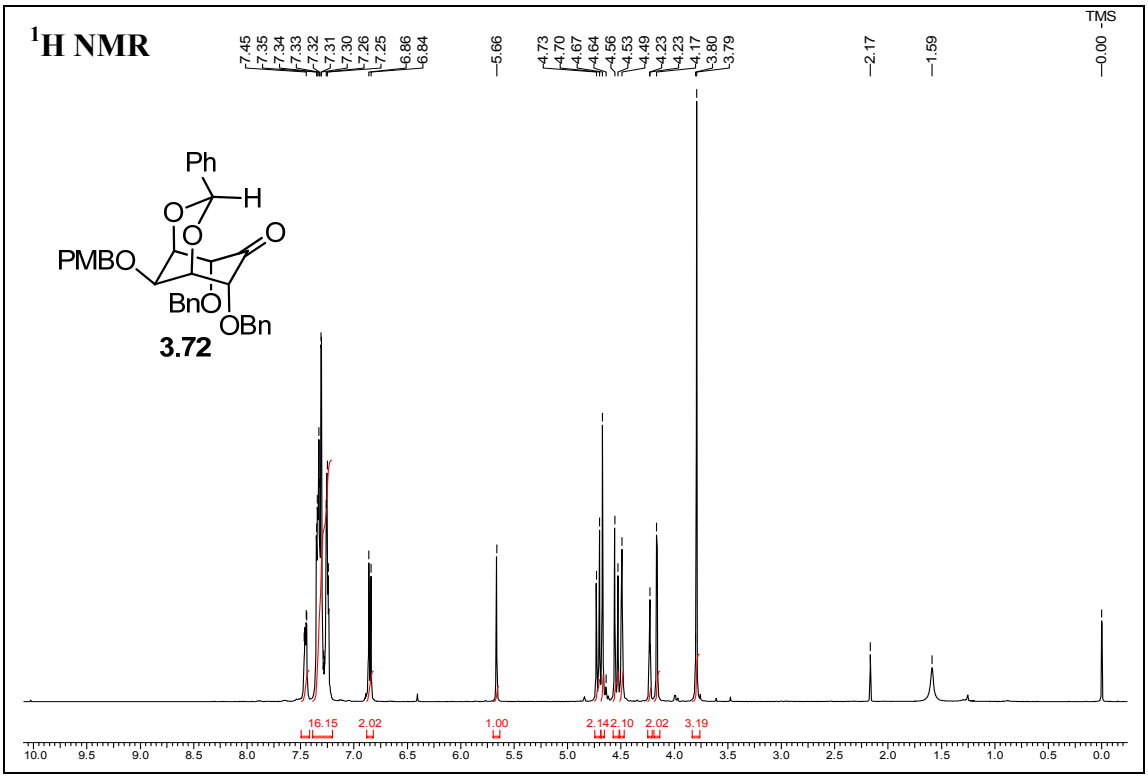

^{1}H NMR
TMS
MeO
HN
PMBO
OPMB
O
OH
OAll
3.38

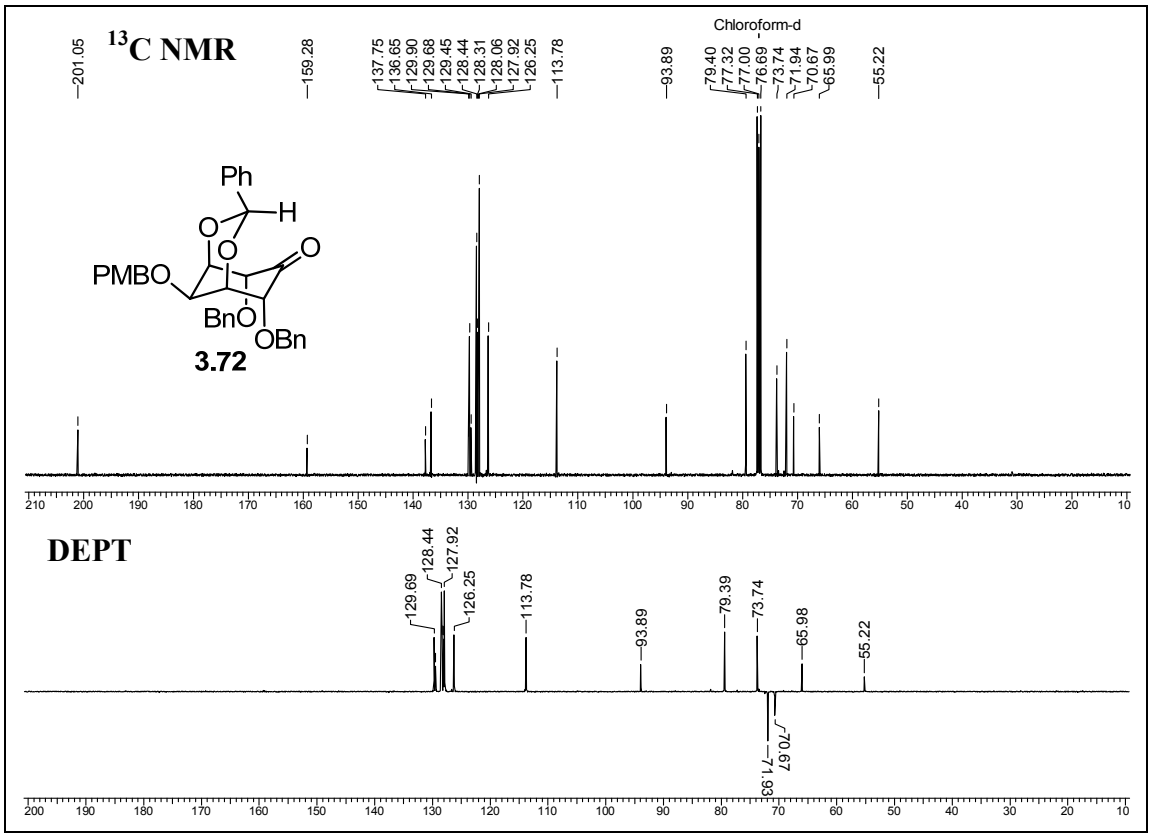

^{13}C NMR
Chloroform-d
MeO
HN
PMBO
OPMB
O
OH
OAll
3.38
DEPT



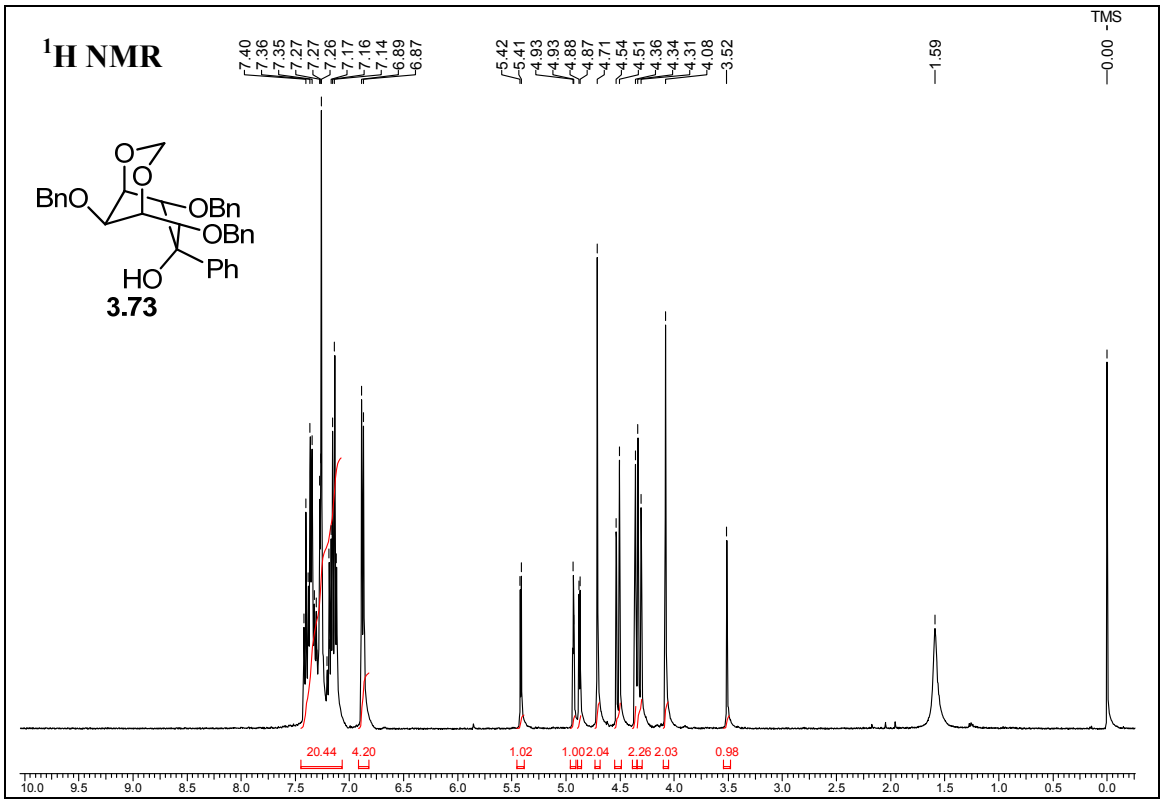


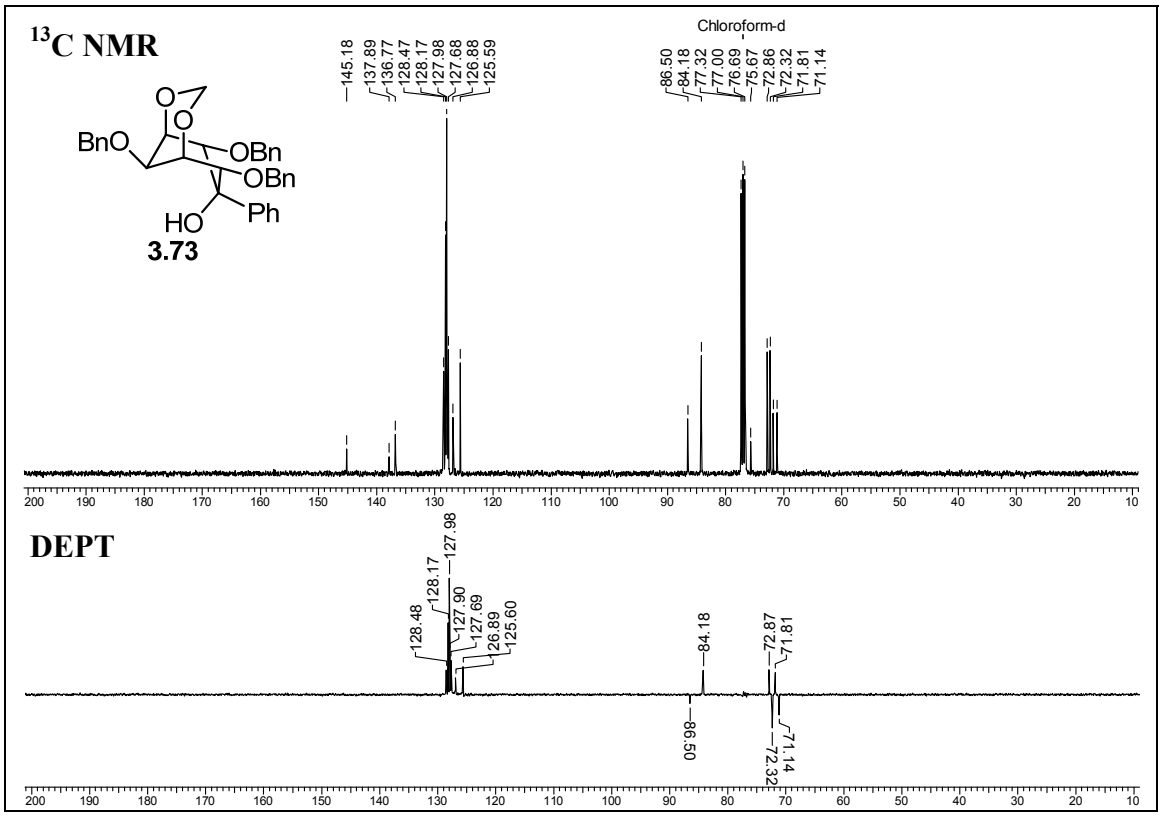
For 2D NMR see appendix III



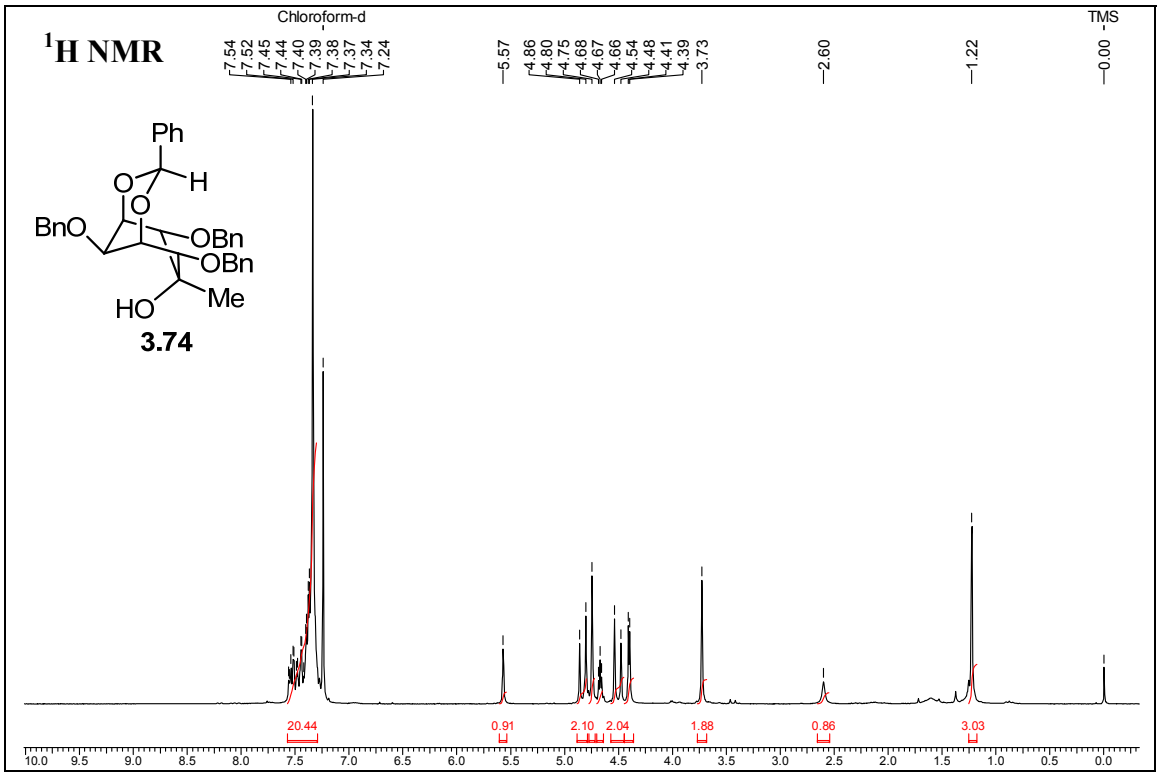


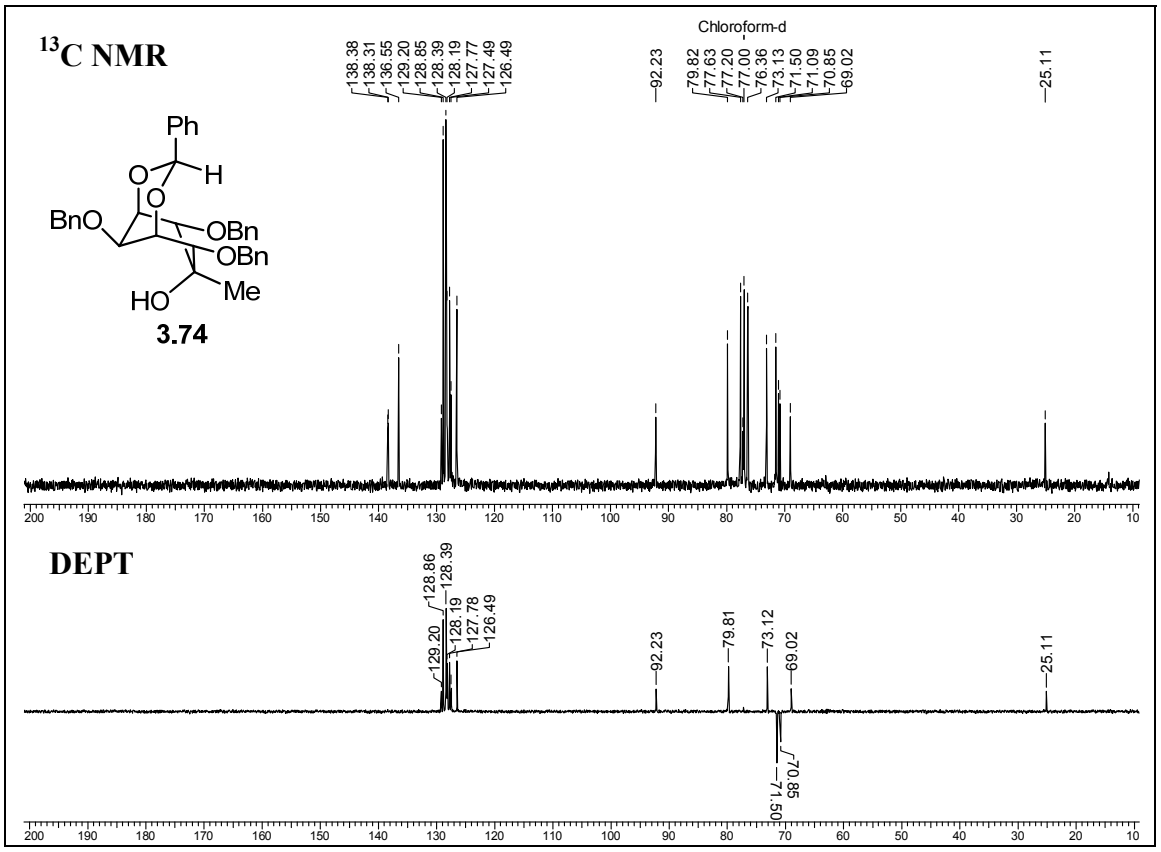
For 2D NMR see appendix III

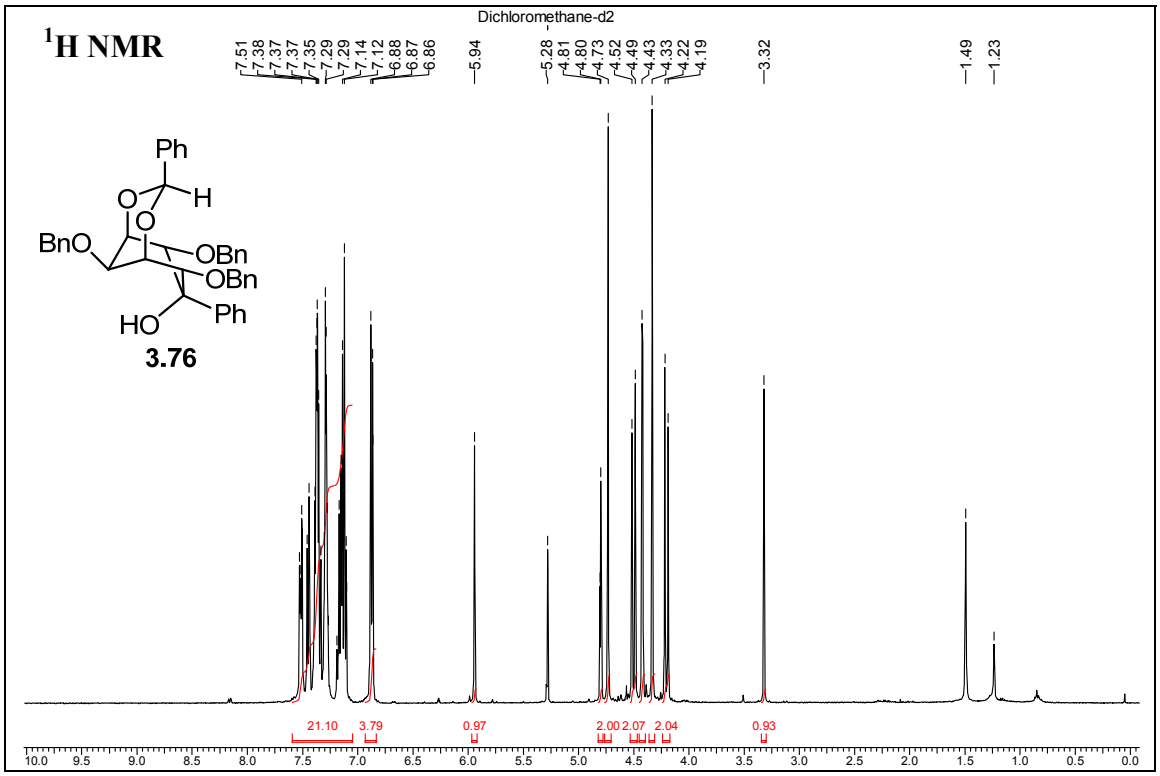


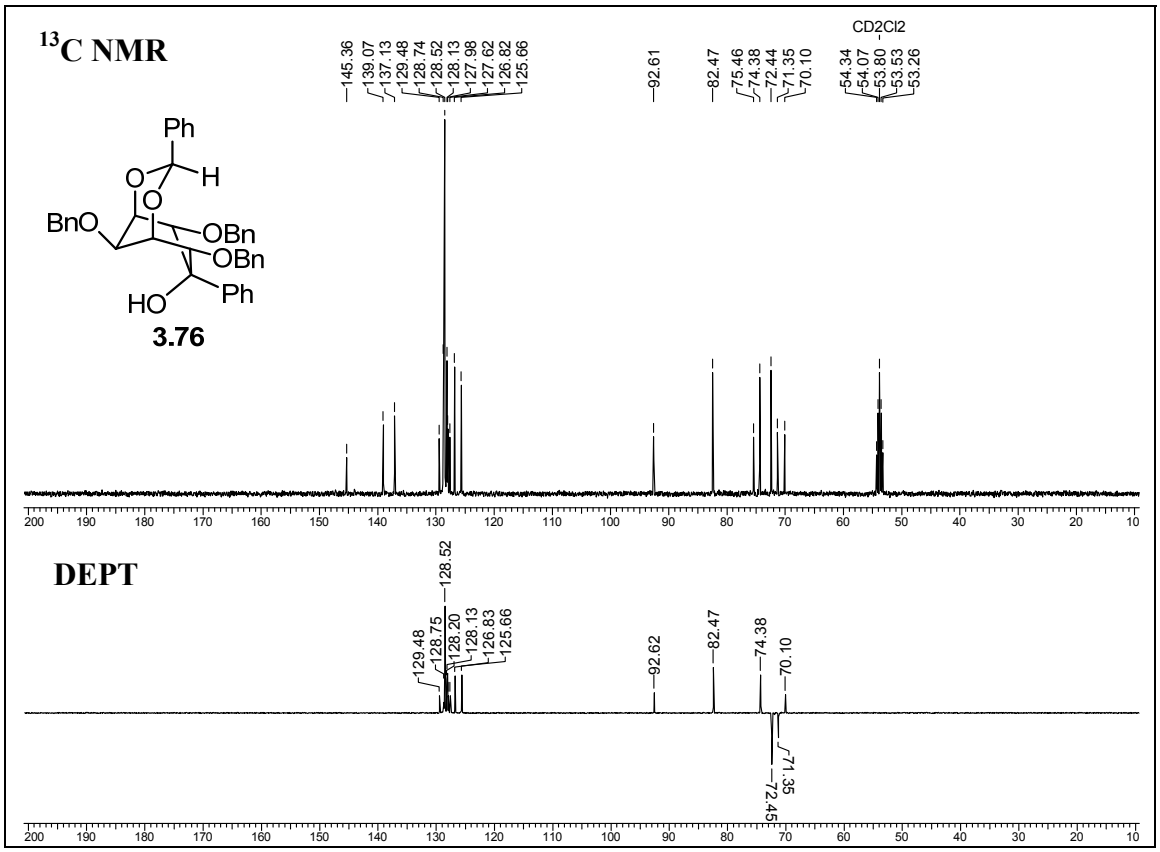


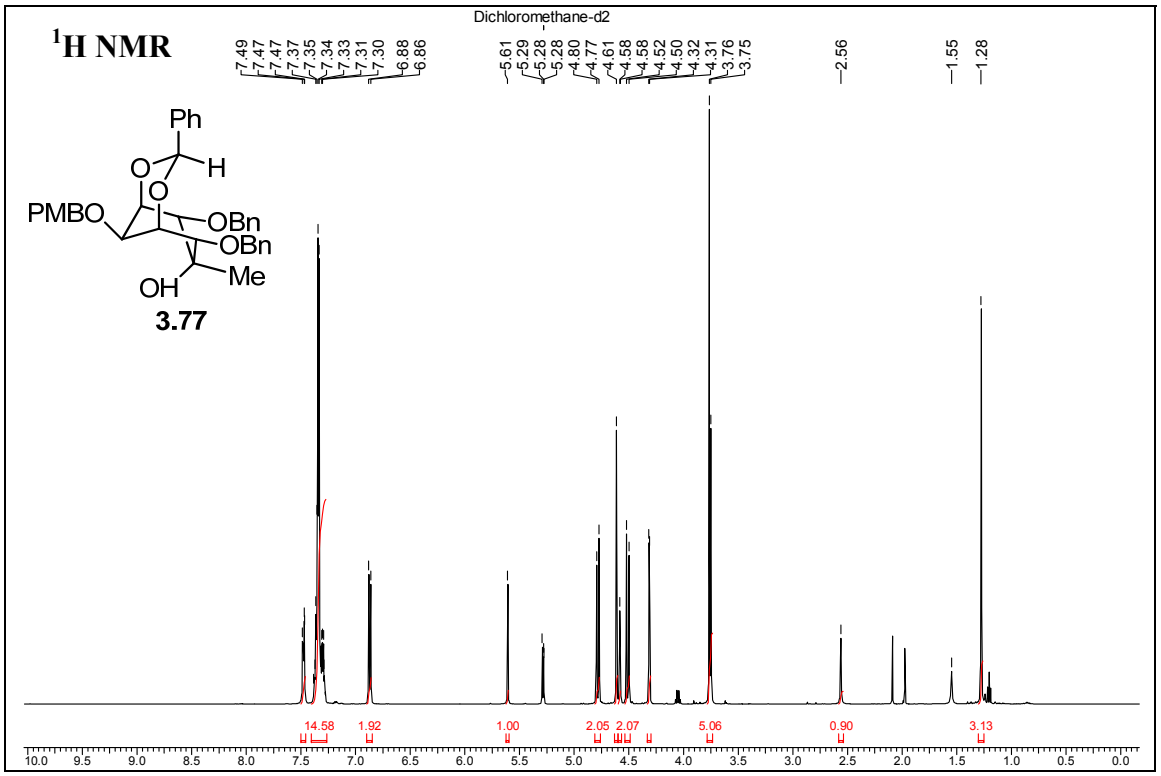
For 2D NMR see appendix III

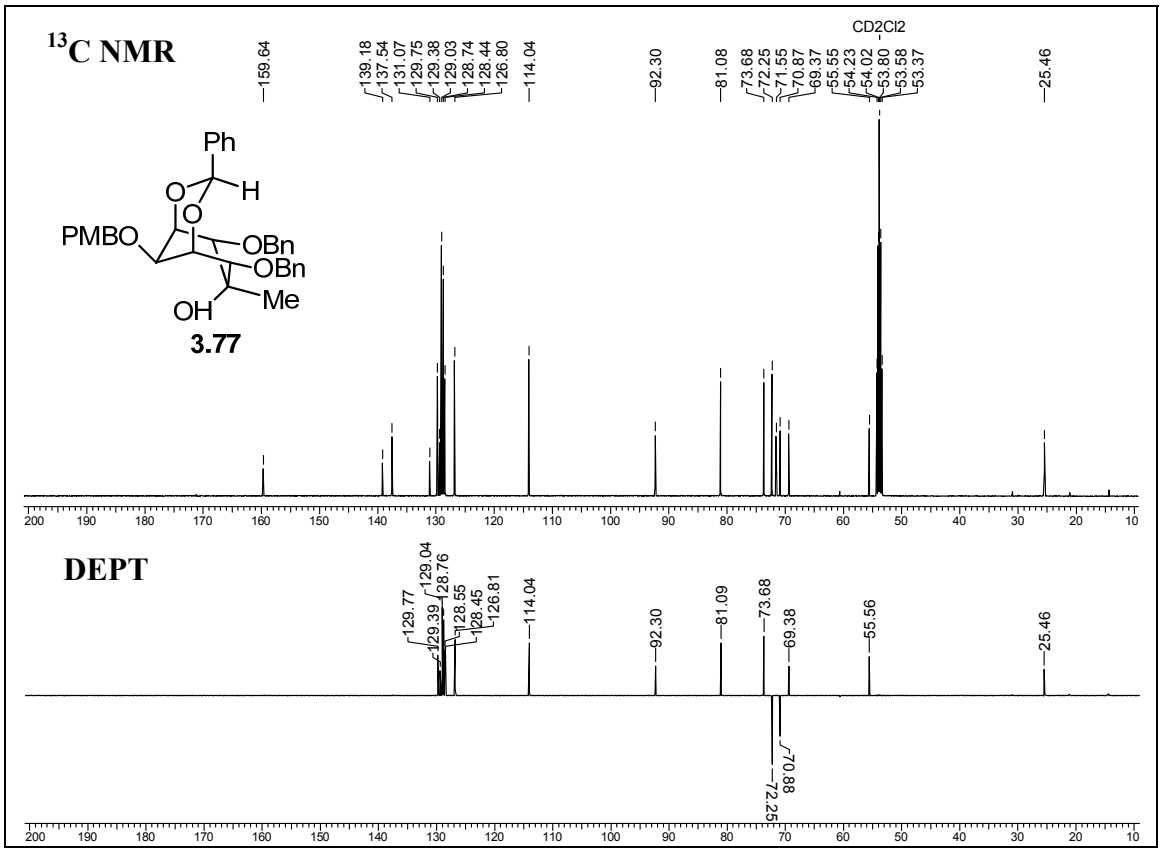

^{1}H NMR
Chloroform-d
TMS
7.54
7.52
7.45
7.44
7.40
7.39
7.38
7.37
7.34
7.24
5.57
4.86
4.80
4.75
4.68
4.67
4.66
4.54
4.48
4.41
4.39
3.73
2.60
1.22
0.00
Ph
O
H
O
BnO
OBn
OBn
HO
Me
3.74
20.44
0.91
2.10
2.04
1.88
0.86
3.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

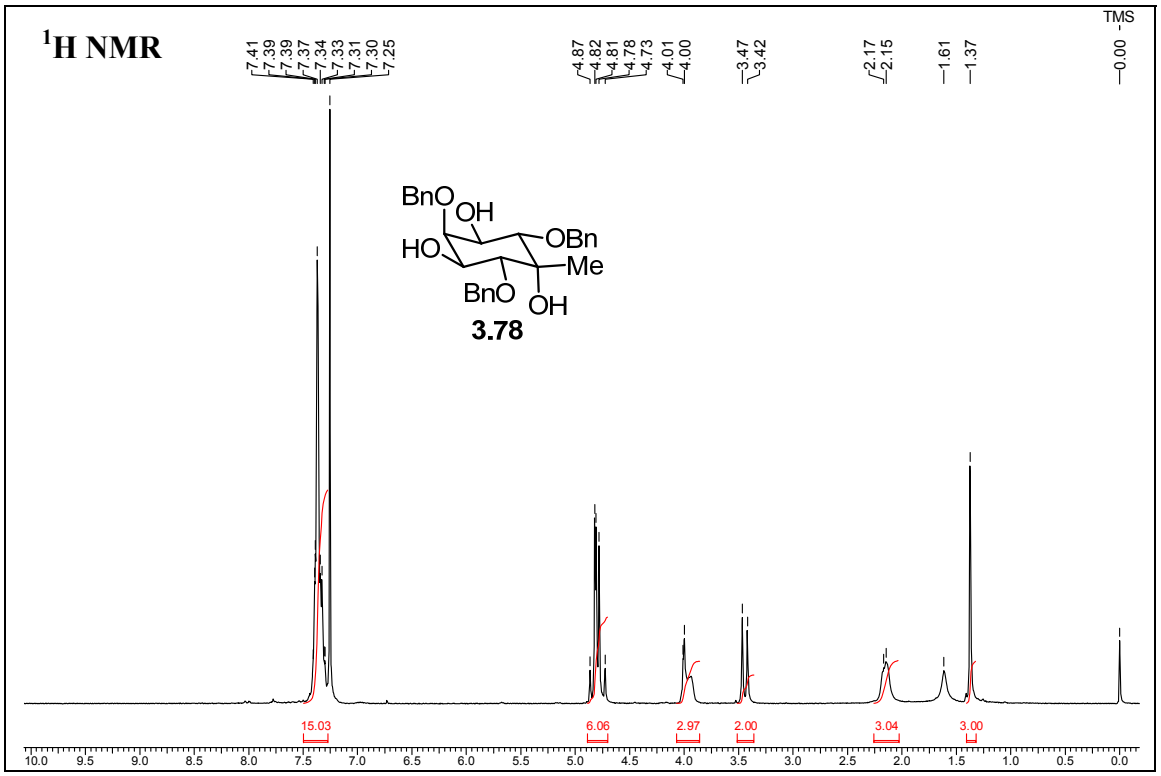

^{13}C NMR
Chloroform-d
138.38
138.31
136.55
129.20
128.85
128.39
128.19
127.77
127.49
126.49
92.23
79.82
77.63
77.20
77.00
76.36
73.13
71.50
71.09
70.85
69.02
25.11
Ph
O
H
O
BnO
OBn
OBn
HO
Me
3.74
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
DEPT
128.86
128.39
129.20
128.19
127.78
126.49
92.23
79.81
73.12
69.02
25.11
71.50
70.86

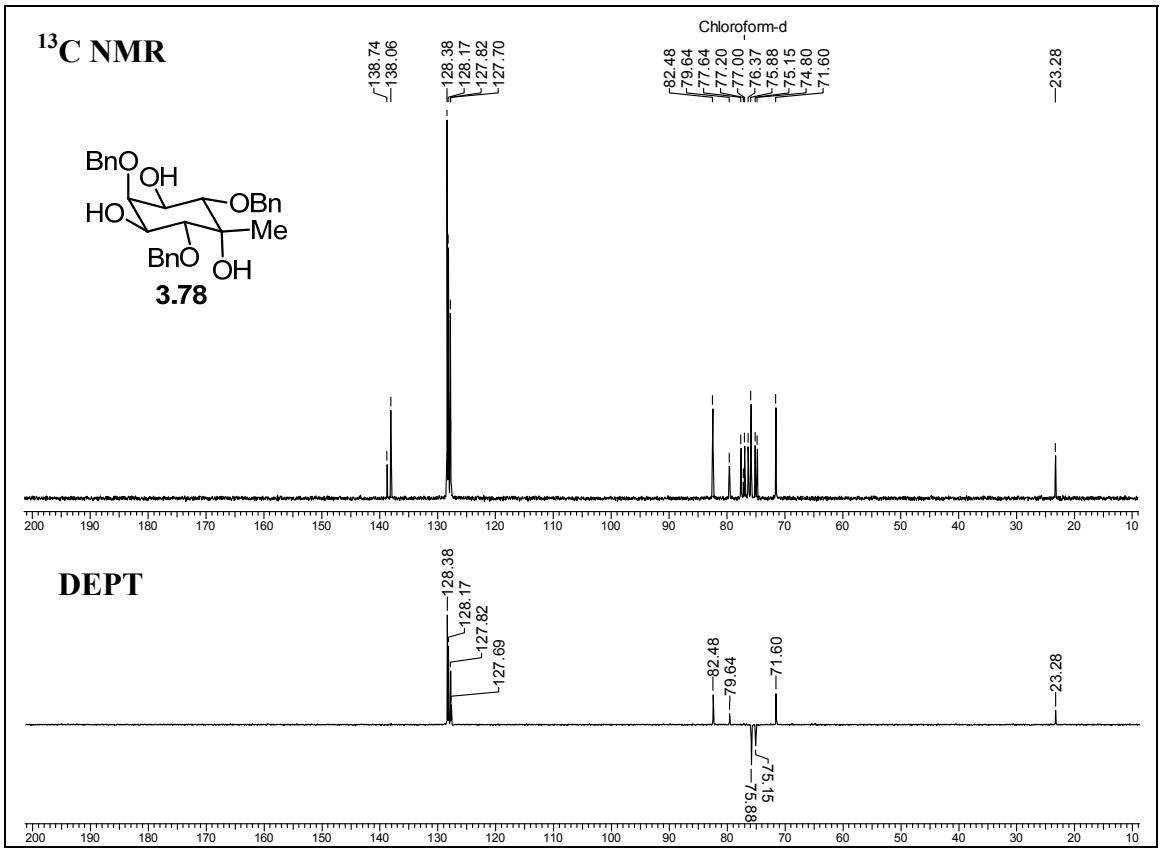

^{1}H NMR
Dichloromethane-d2
7.51
7.38
7.37
7.37
7.35
7.29
7.29
7.14
7.12
6.88
6.87
6.86
5.94
5.28
4.81
4.80
4.73
4.52
4.49
4.43
4.33
4.22
4.19
3.32
1.49
1.23
Ph
O
H
O
BnO
OBn
OBn
HO
Ph
3.76
21.10
3.79
0.97
2.00
2.07
2.04
0.93
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

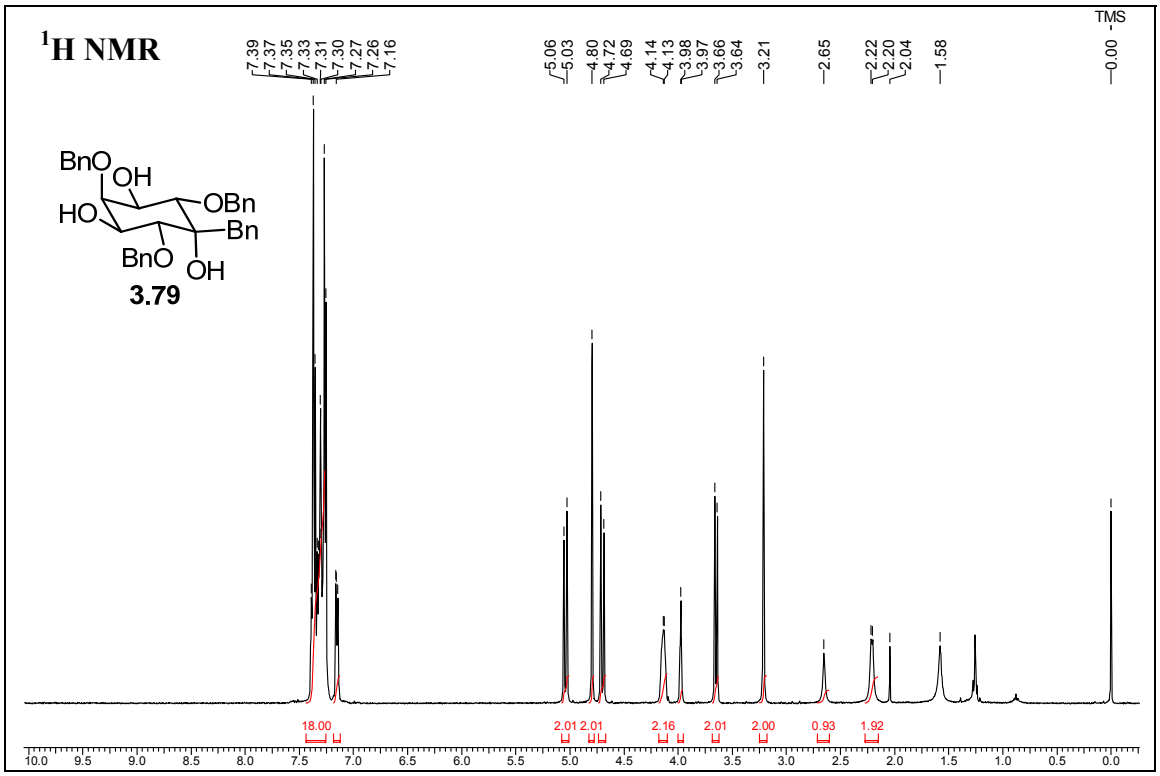

^{13}C NMR
CD2Cl2
145.36
139.07
137.13
129.48
128.74
128.52
128.13
127.98
127.62
126.82
125.66
92.61
82.47
75.46
74.38
72.44
71.35
70.10
54.34
54.07
53.80
53.53
53.26
Ph
O
H
O
BnO
OBn
OBn
HO
Ph
3.76
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
DEPT
128.52
129.48
128.75
128.20
128.13
126.83
125.66
92.62
82.47
74.38
70.10
71.35
72.45

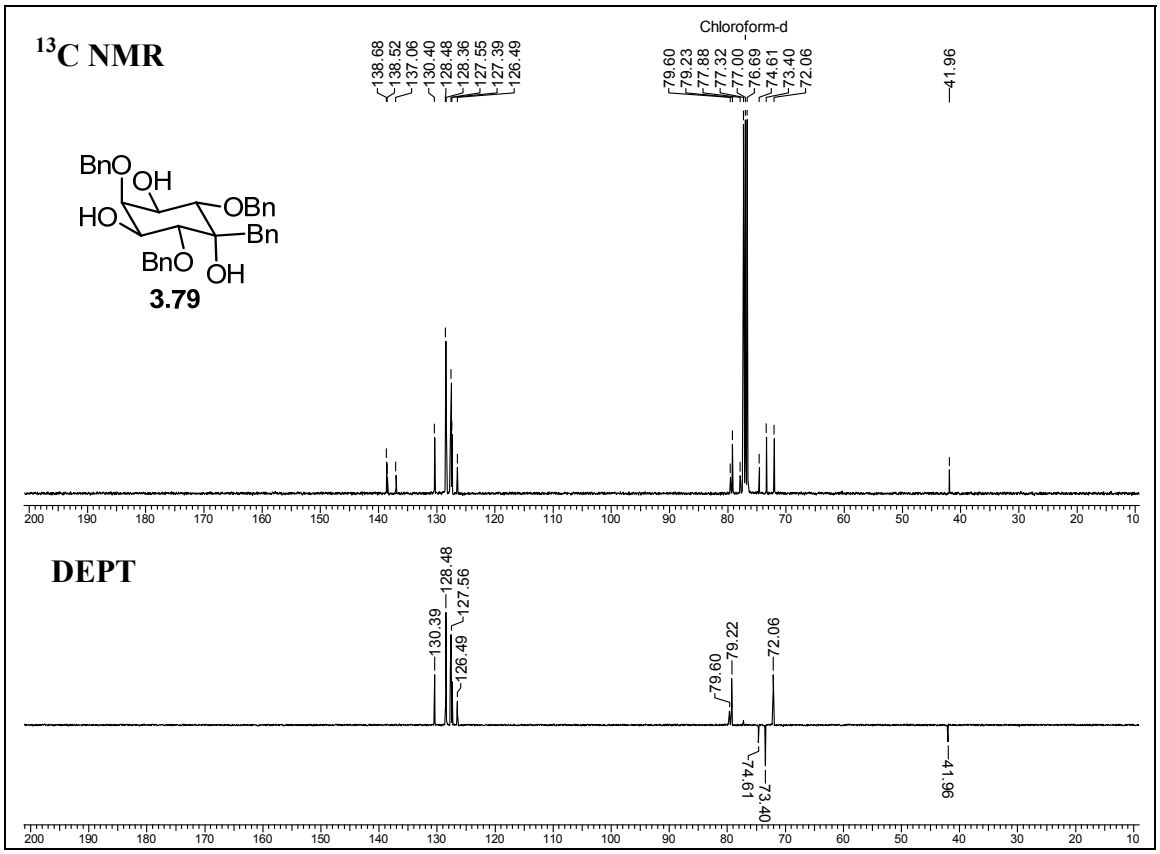

^{1}H NMR
Dichloromethane-d2
7.49 7.47 7.47 7.37 7.35 7.34 7.33 7.31 7.30 6.88 6.86
5.61 5.29 5.28 5.28 4.80 4.77 4.61 4.58 4.58 4.52 4.50 4.32 4.31 3.76 3.75
2.56
1.55
1.28
Ph
O
H
O
PMBO
OBn
OBn
Me
OH
3.77
14.58 1.92 1.00 2.05 2.07 5.06 0.90 3.13
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

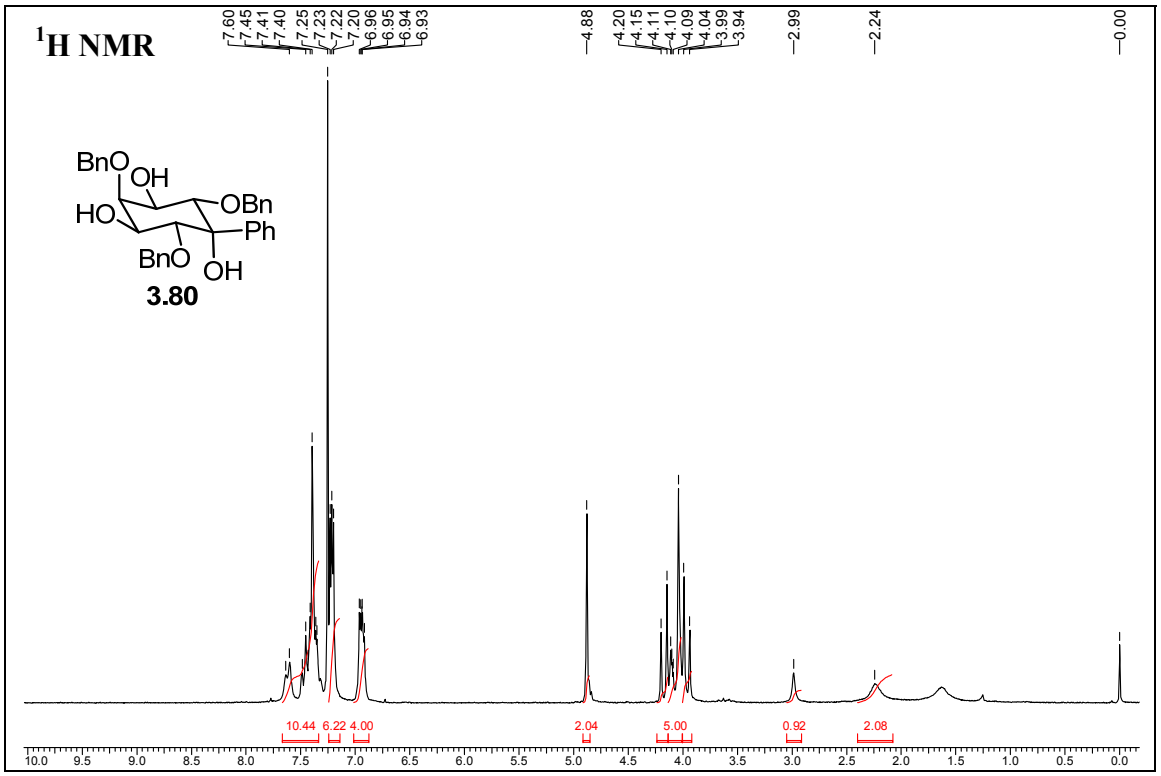

^{13}C NMR
CD2Cl2
159.64
139.18 137.54 131.07 129.75 129.38 129.03 128.74 128.44 126.80
114.04
92.30
81.08
73.68 72.25 71.55 70.87 69.37 55.55 54.23 54.02 53.80 53.58 53.37
25.46
Ph
O
H
O
PMBO
OBn
OBn
Me
OH
3.77
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
DEPT
129.77 129.39 129.04 128.76 128.55 128.45 126.81
114.04
92.30
81.09
73.68
69.38
55.56
25.46
72.25
70.88
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

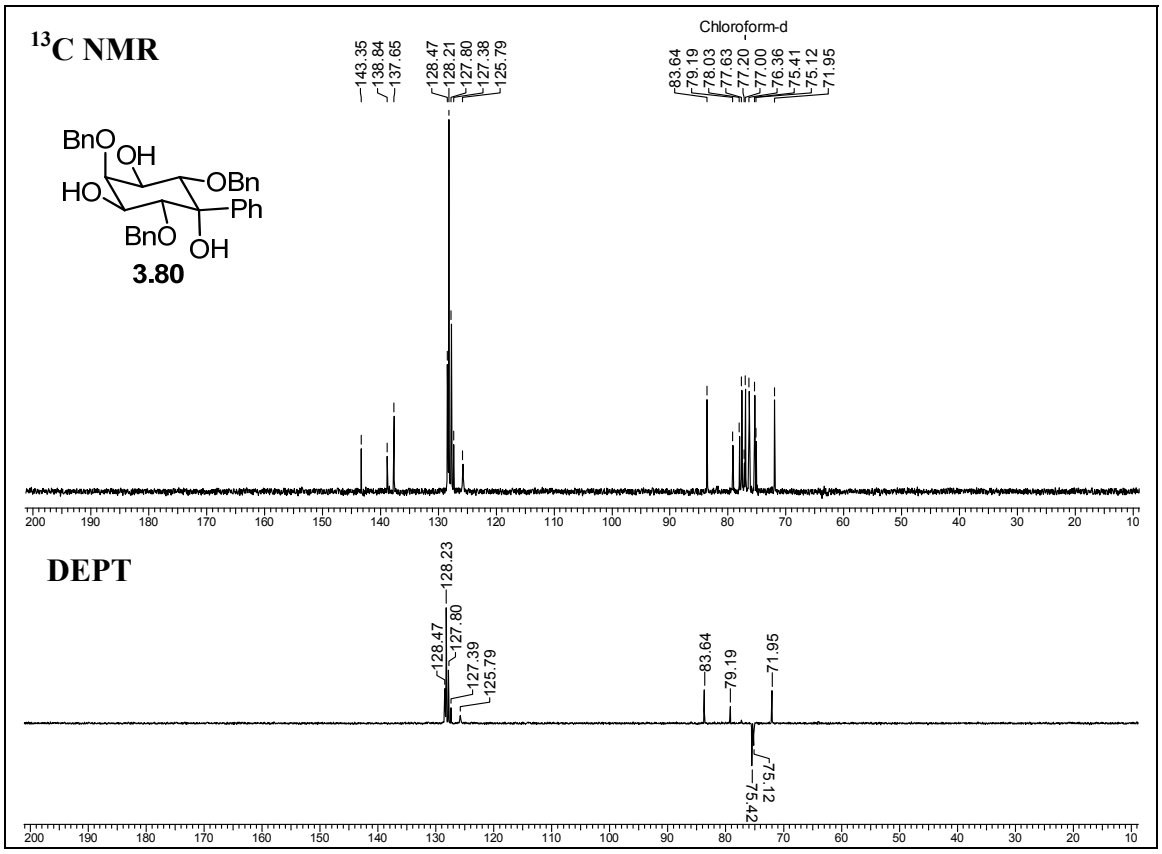

^{1}H NMR
TMS
7.41
7.39
7.39
7.37
7.34
7.33
7.31
7.30
7.25
4.87
4.82
4.81
4.78
4.73
4.01
4.00
3.47
3.42
2.17
2.15
1.61
1.37
0.00
BnO
OH
HO
OBn
Me
BnO
OH
3.78
15.03
6.06
2.97
2.00
3.04
3.00

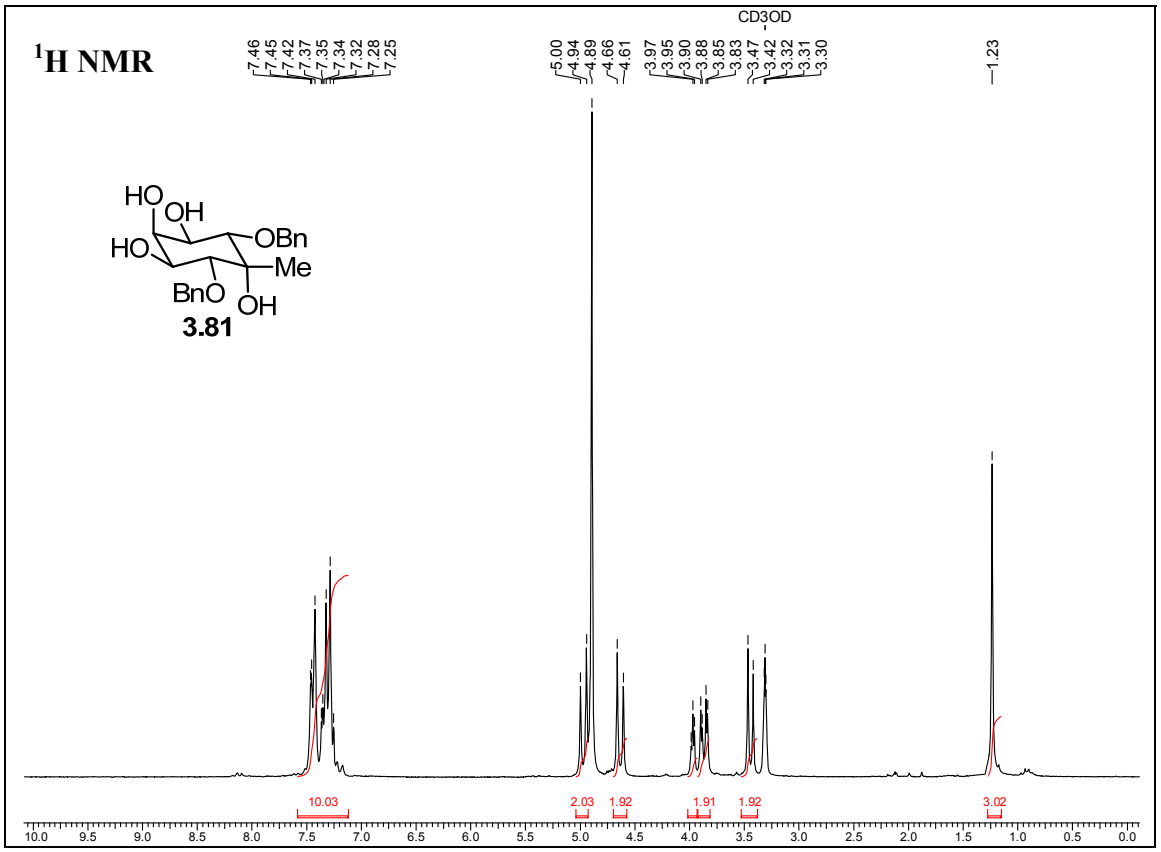

^{13}C NMR
Chloroform-d
138.74
138.06
128.38
128.17
127.82
127.70
82.48
79.64
77.64
77.20
77.00
76.37
75.88
75.15
74.80
71.60
23.28
BnO
OH
HO
OBn
Me
BnO
OH
3.78
DEPT
128.38
128.17
127.82
127.69
82.48
79.64
71.60
75.88
75.15
23.28

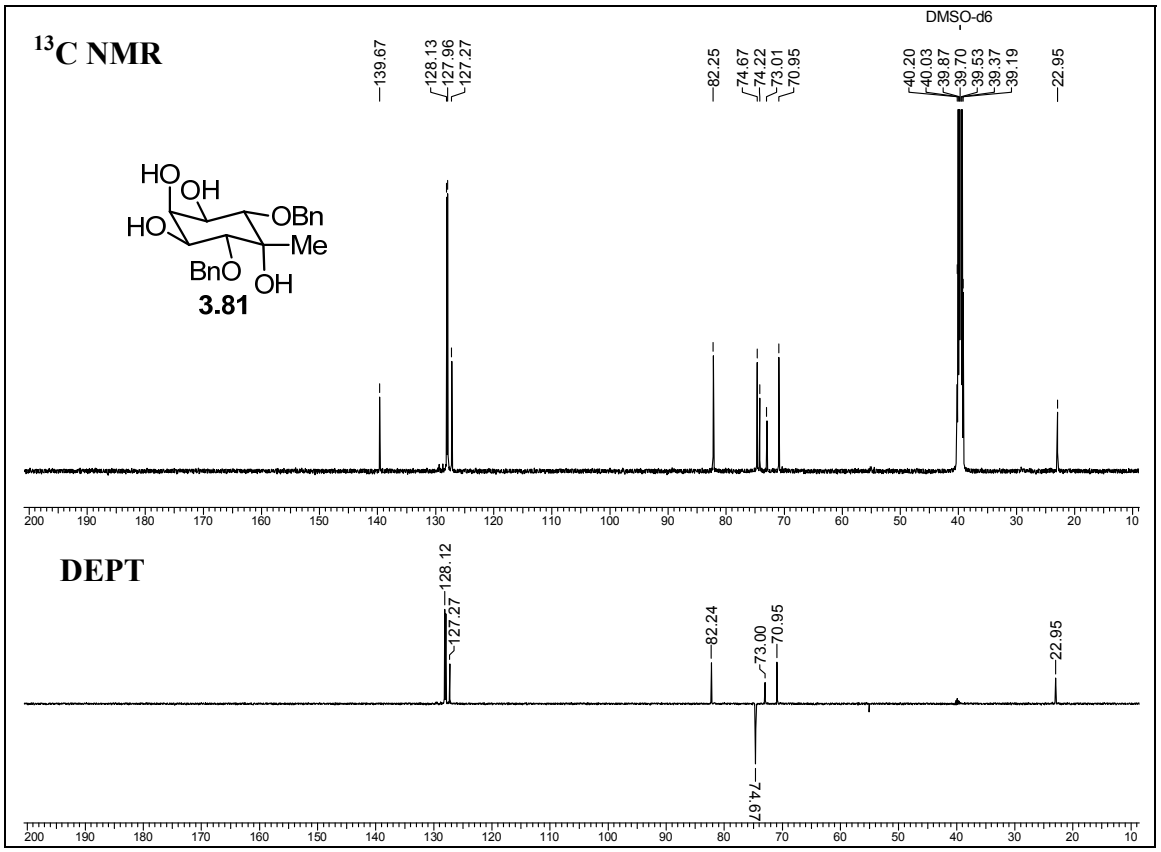

^{1}H NMR
TMS
7.39
7.37
7.35
7.33
7.31
7.30
7.27
7.26
7.16
5.06
5.03
4.80
4.72
4.69
4.14
4.13
3.98
3.97
3.66
3.64
3.21
2.65
2.22
2.20
2.04
1.58
0.00
BnO
OH
HO
OBn
Bn
BnO
OH
3.79
18.00
2.01
2.01
2.16
2.01
2.00
0.93
1.92

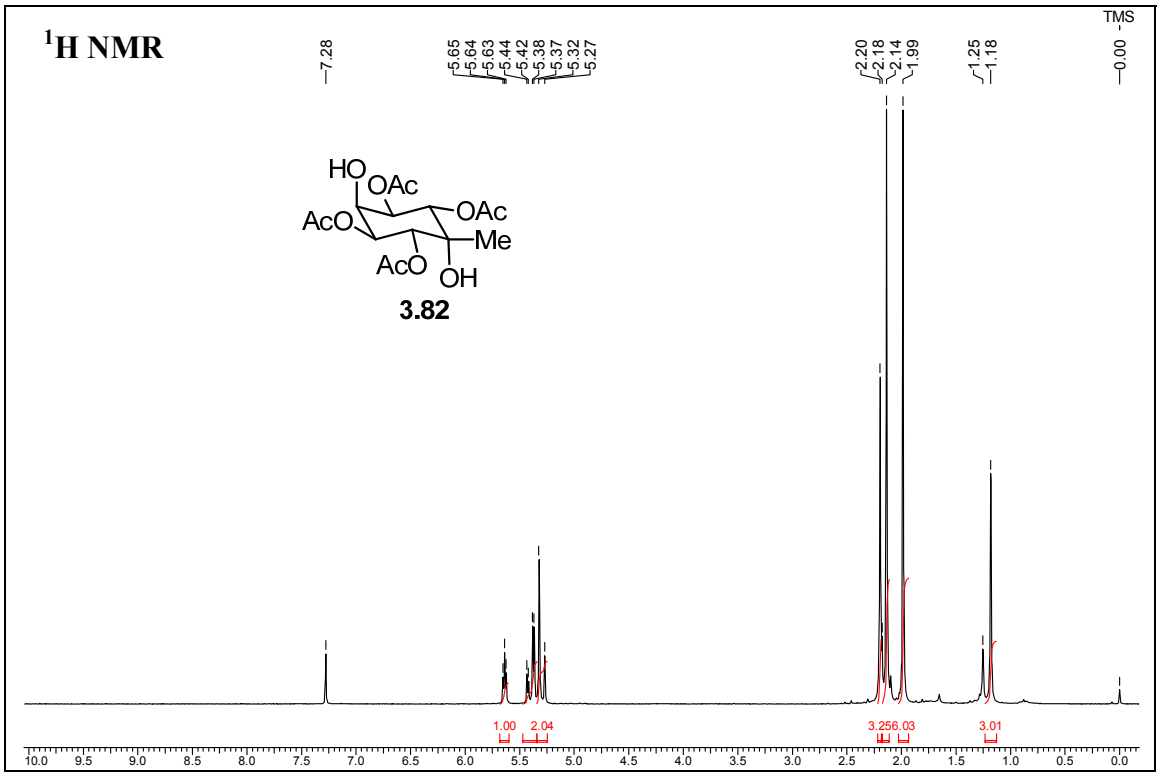

^{13}C NMR
Chloroform-d
138.68
138.52
137.06
130.40
128.48
128.36
127.55
127.39
126.49
79.60
79.23
77.88
77.32
77.00
76.69
74.61
73.40
72.06
41.96
BnO
OH
HO
OBn
Bn
BnO
OH
3.79
DEPT
130.39
128.48
127.56
126.49
79.60
79.22
72.06
74.61
73.40
41.96

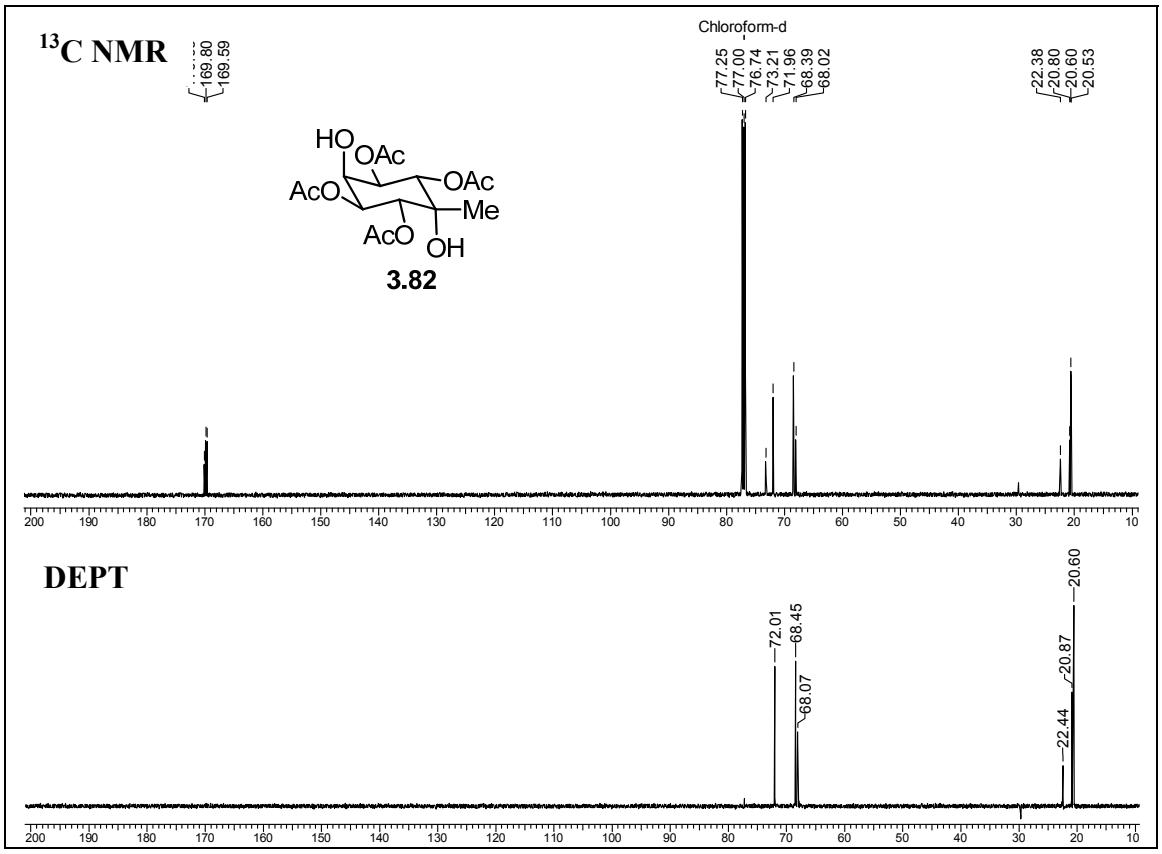

^{1}H NMR
BnO
OH
HO
OBn
Ph
BnO
OH
3.80
7.60
7.45
7.41
7.40
7.25
7.23
7.22
7.20
6.96
6.95
6.94
6.93
4.88
4.20
4.15
4.11
4.10
4.09
4.04
3.99
3.94
2.99
2.24
0.00
10.44
6.22
4.00
2.04
5.00
0.92
2.08

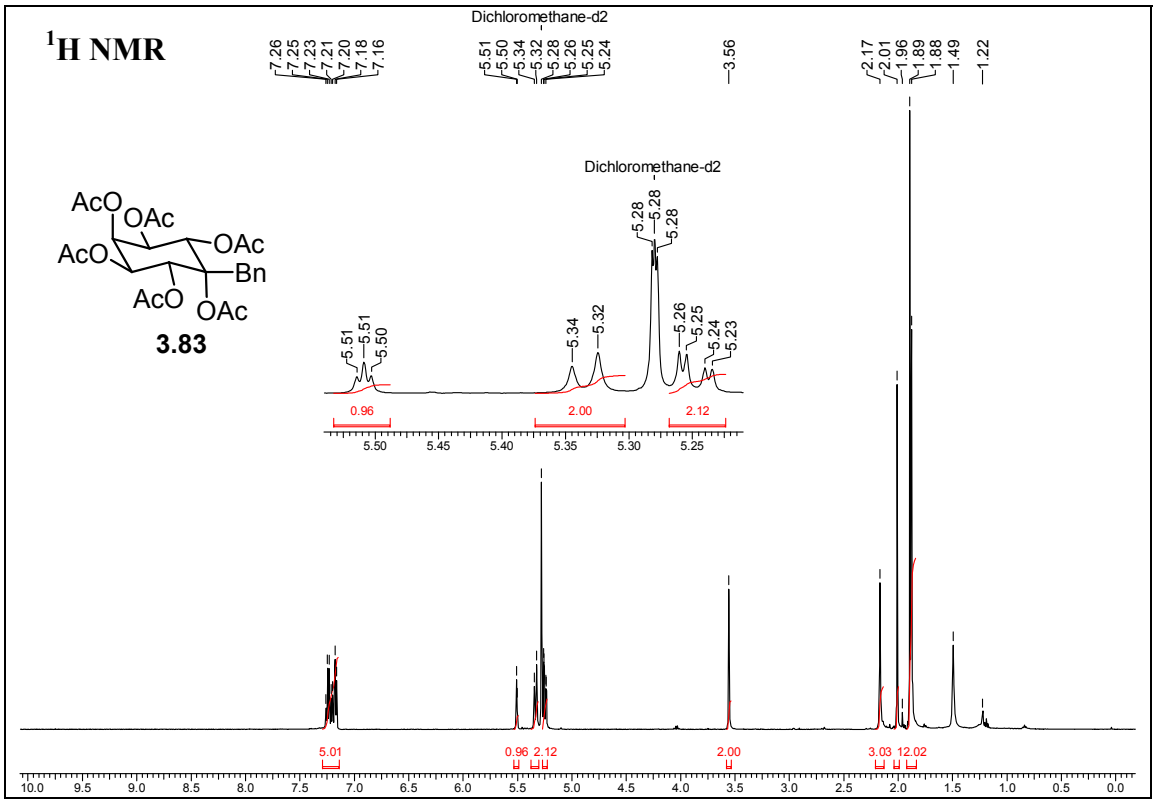

^{13}C NMR
BnO
OH
HO
OBn
Ph
BnO
OH
3.80
143.35
138.84
137.65
128.47
128.21
127.80
127.38
125.79
Chloroform-d
83.64
79.19
78.03
77.63
77.20
77.00
76.36
75.41
75.12
71.95
DEPT
128.23
128.47
127.80
127.39
125.79
83.64
79.19
71.95
75.42
75.12

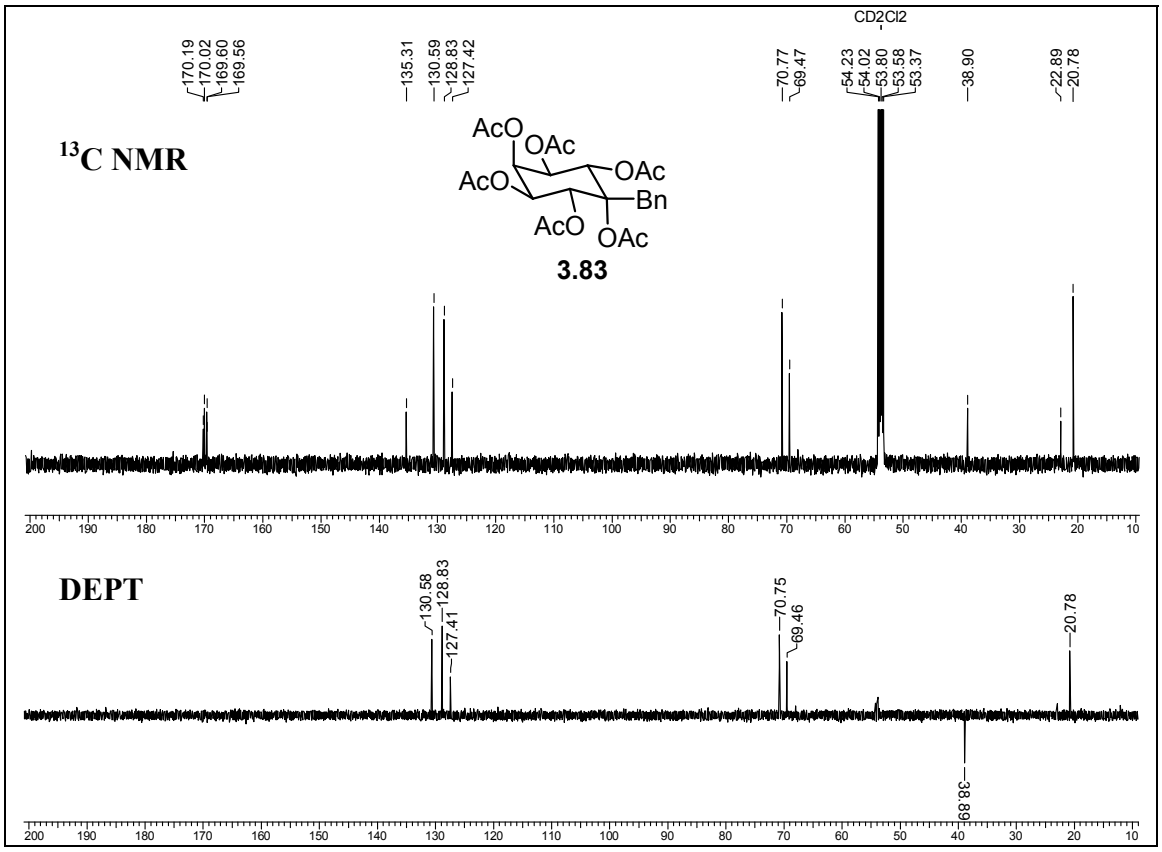

^{1}H NMR
CD3OD
7.46
7.45
7.42
7.37
7.35
7.34
7.32
7.28
7.25
5.00
4.94
4.89
4.66
4.61
3.97
3.95
3.90
3.88
3.85
3.83
3.47
3.42
3.32
3.31
3.30
1.23
HO
OH
HO
OBn
Me
BnO
OH
3.81
10.03
2.03
1.92
1.91
1.92
3.02

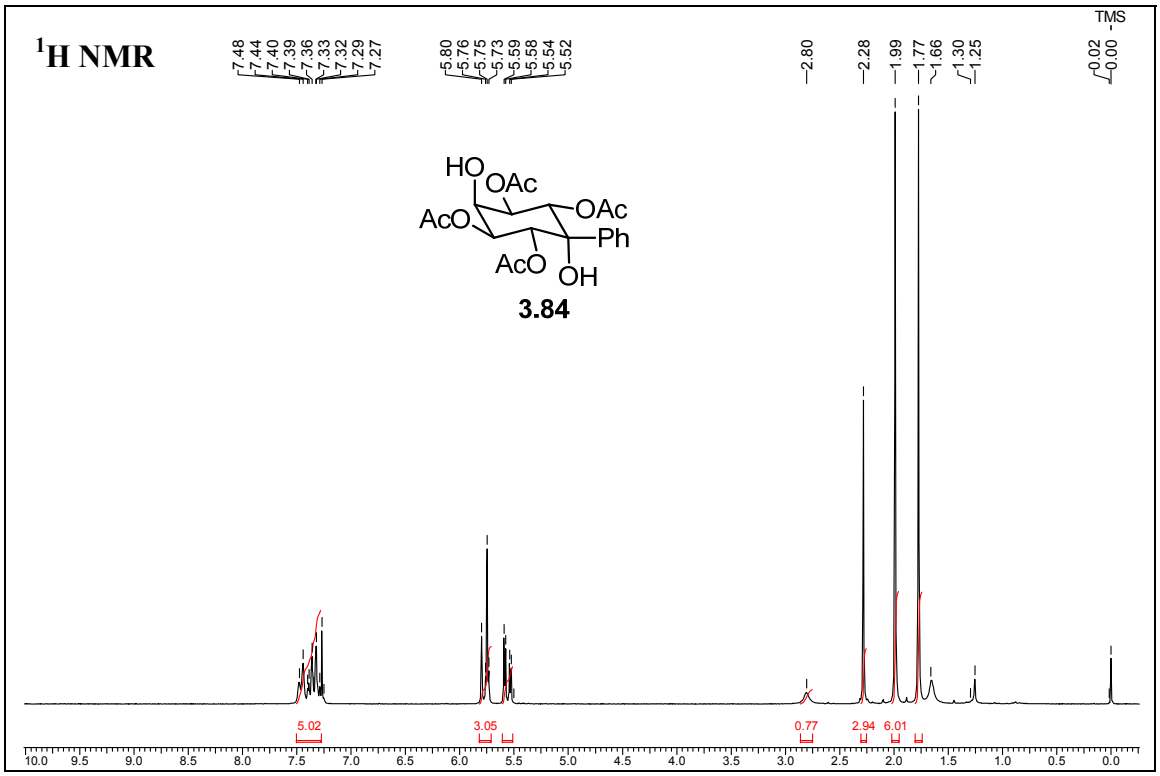

^{13}C NMR
DMSO-d6
139.67
128.13
127.96
127.27
82.25
74.67
74.22
73.01
70.95
40.20
40.03
39.87
39.70
39.53
39.37
39.19
22.95
HO
OH
HO
OBn
Me
BnO
OH
3.81
DEPT
128.12
127.27
82.24
73.00
70.95
22.95
74.67

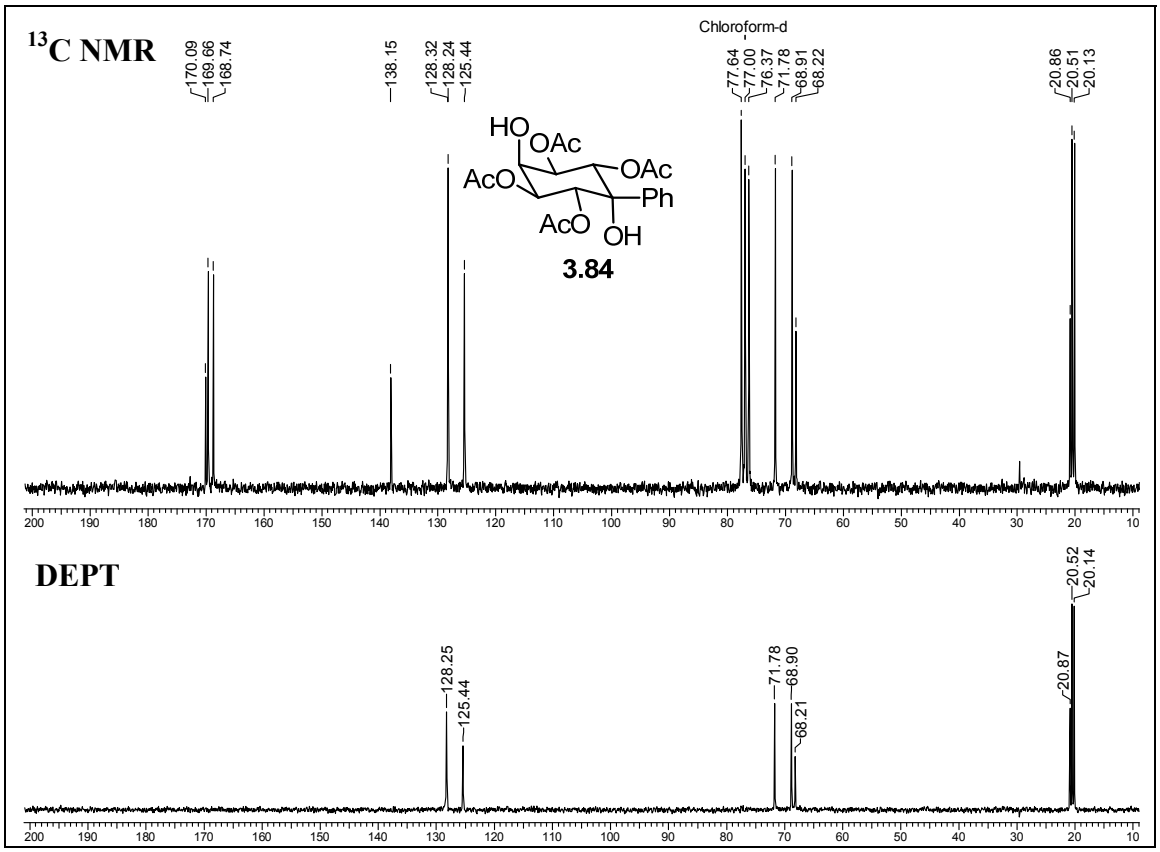

^{1}H NMR
TMS
7.28
5.65
5.64
5.63
5.44
5.42
5.38
5.37
5.32
5.27
2.20
2.18
2.14
1.99
1.25
1.18
0.00
HO
OAc
AcO
OAc
Me
AcO
OH
3.82
1.00
2.04
3.25
6.03
3.01

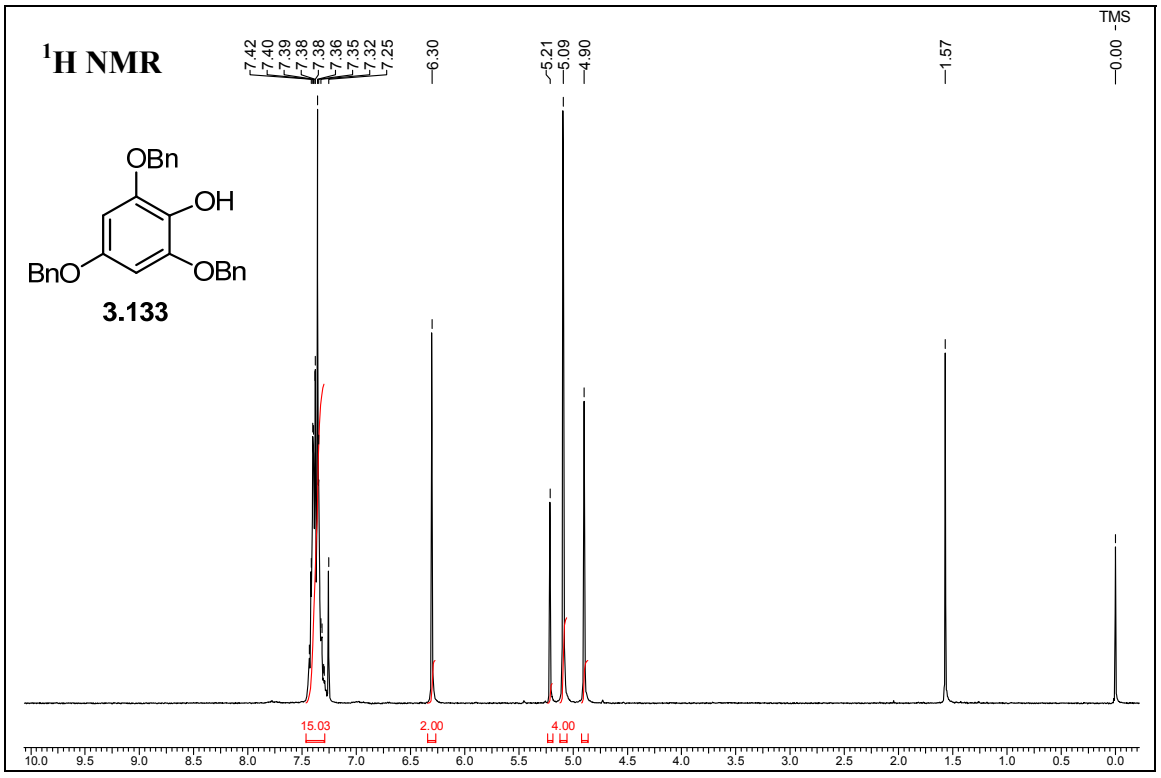

^{13}C NMR
169.80
169.59
Chloroform-d
77.25
77.00
76.74
73.21
71.96
68.39
68.02
22.38
20.80
20.60
20.53
HO
OAc
AcO
OAc
Me
AcO
OH
3.82
DEPT
72.01
68.45
68.07
20.60
20.87
22.44

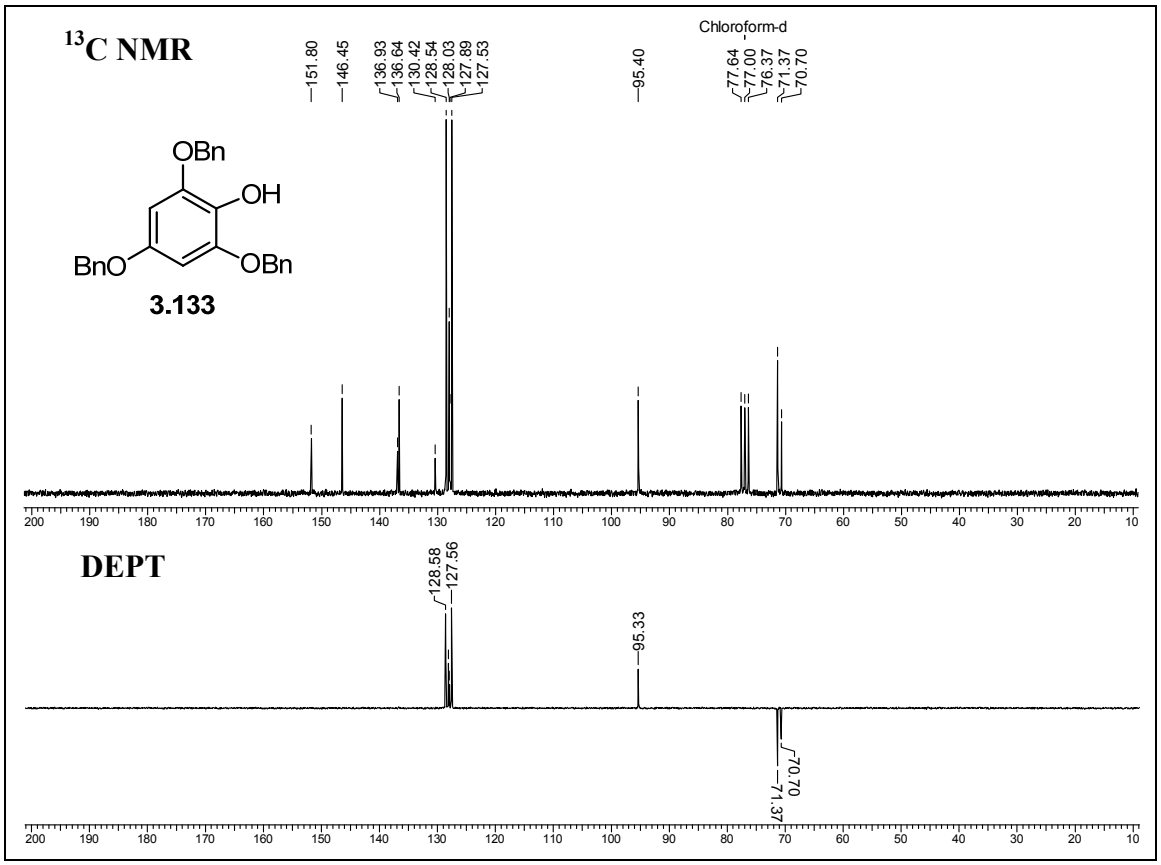

^{1}H NMR
Dichloromethane-d2
7.26 7.25 7.23 7.21 7.20 7.18 7.16
5.51 5.50 5.34 5.32 5.28 5.26 5.25 5.24
3.56
2.17 2.01 1.96 1.89 1.88 1.49 1.22
AcO OAc AcO OAc Bn AcO OAc
3.83
5.01 0.96 2.12 2.00 3.03 12.02

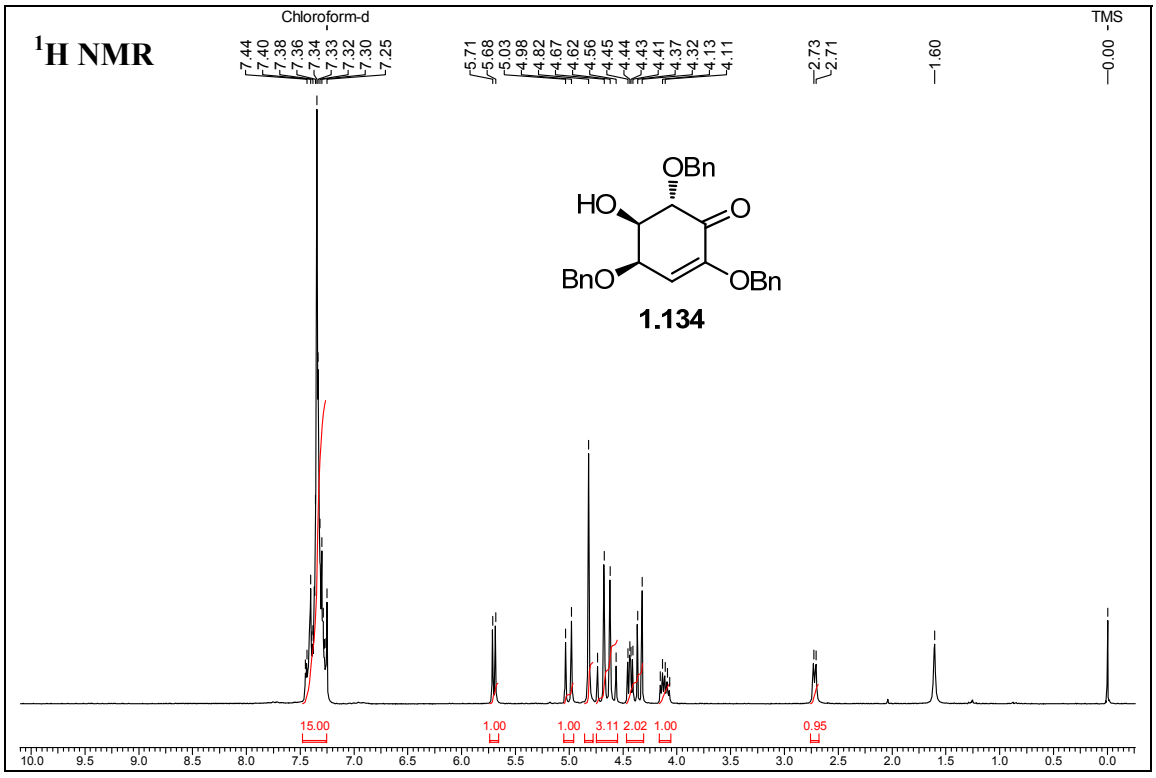

^{13}C NMR
CD2Cl2
170.19 170.02 169.60 169.56
135.31 130.59 128.83 127.42
70.77 69.47
54.23 54.02 53.80 53.58 53.37
38.90
22.89 20.78
AcO OAc AcO OAc Bn AcO OAc
3.83
DEPT
130.58 128.83 127.41
70.75 69.46
20.78
38.89

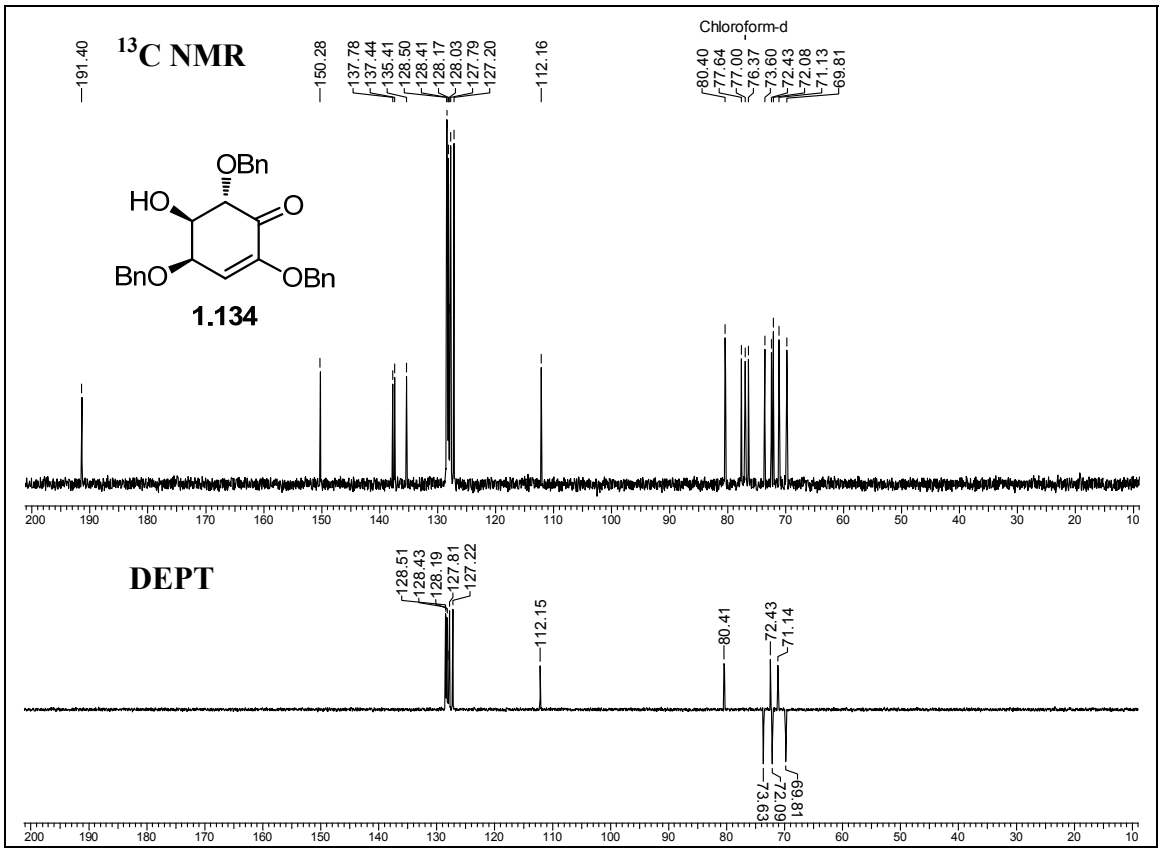

^{1}H NMR
TMS
7.48
7.44
7.40
7.39
7.36
7.33
7.32
7.29
7.27
5.80
5.76
5.75
5.73
5.59
5.58
5.54
5.52
2.80
2.28
1.99
1.77
1.66
1.30
1.25
0.02
0.00
HO
OAc
AcO
OAc
Ph
AcO
OH
3.84
5.02
3.05
0.77
2.94
6.01

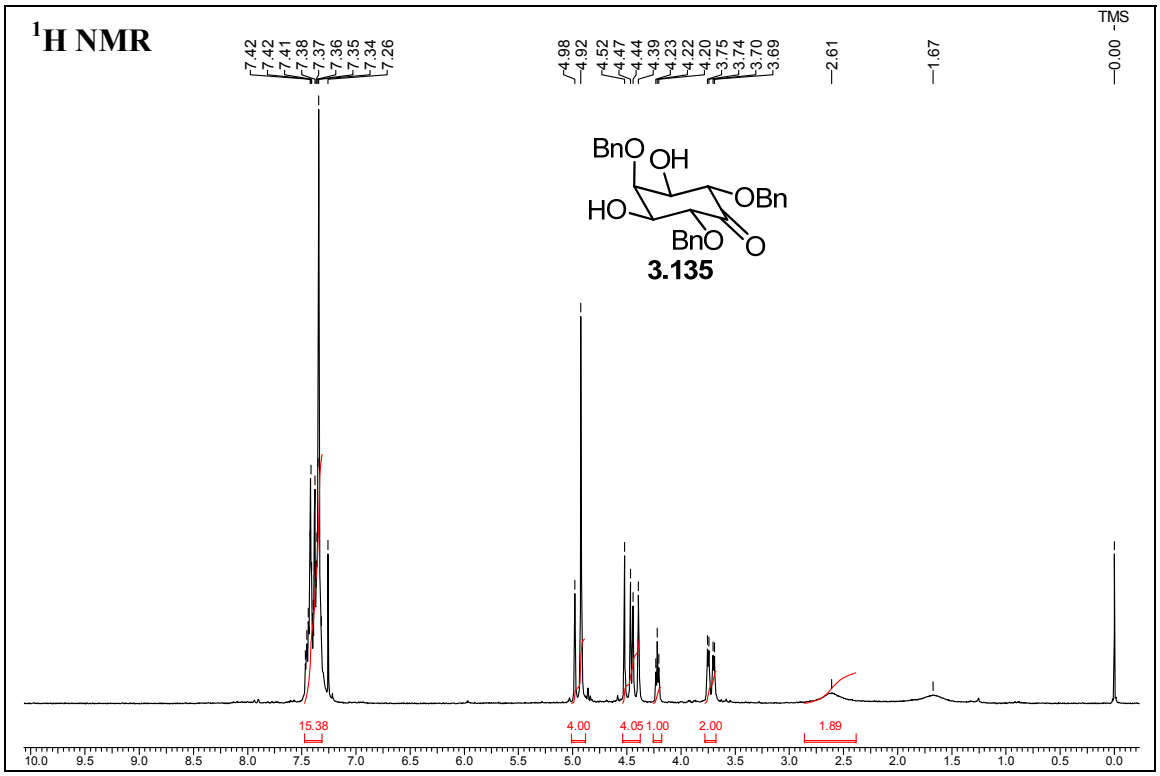

^{13}C NMR
Chloroform-d
170.09
169.66
168.74
138.15
128.32
128.24
125.44
77.64
77.00
76.37
71.78
68.91
68.22
20.86
20.51
20.13
HO
OAc
AcO
OAc
Ph
AcO
OH
3.84
DEPT
20.52
20.14
128.25
125.44
71.78
68.90
68.21
20.87

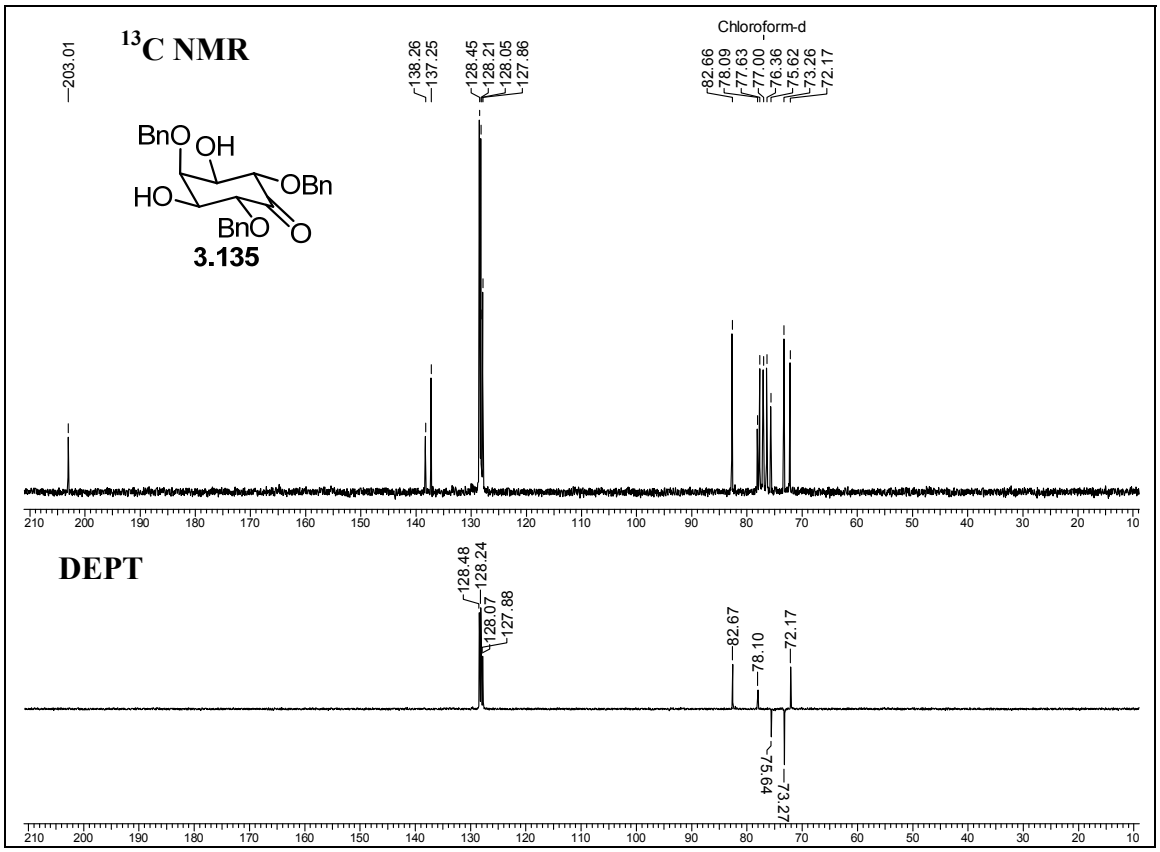

^{1}H NMR
OBn
OH
BnO
OBn
3.133
7.42
7.40
7.39
7.38
7.38
7.36
7.35
7.32
7.25
6.30
5.21
5.09
4.90
1.57
TMS
0.00
15.03
2.00
4.00

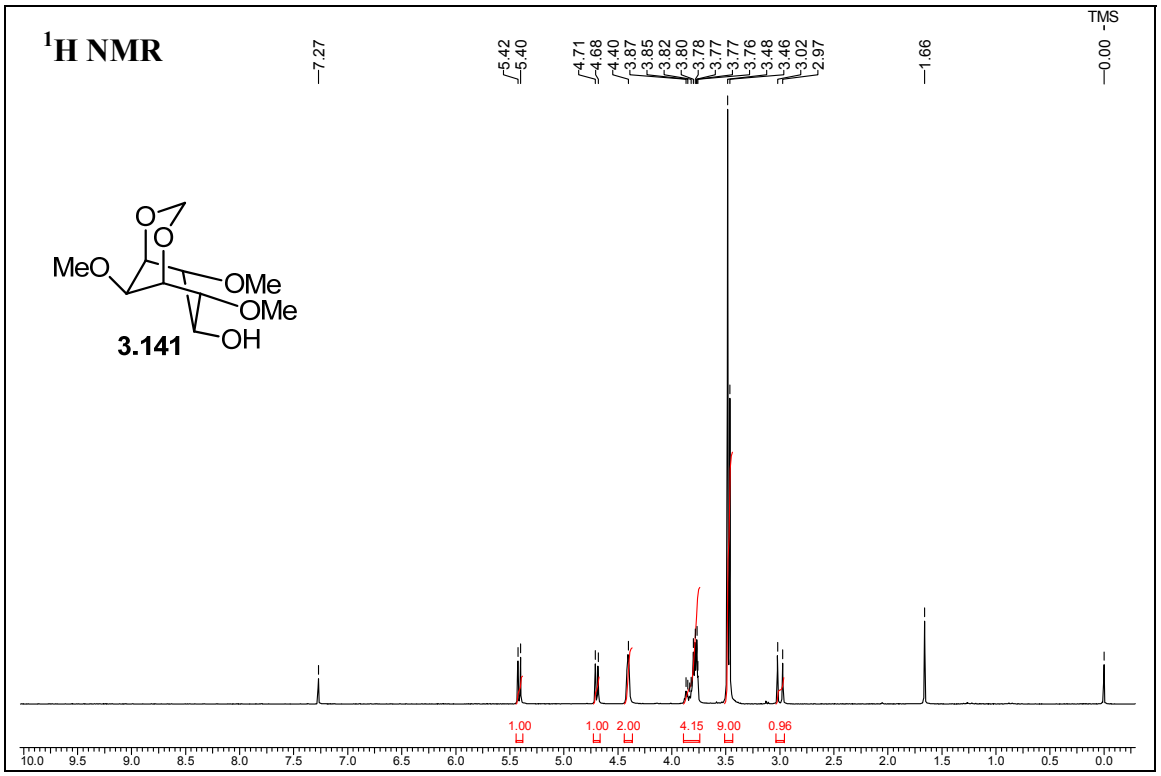

^{13}C NMR
OBn
OH
BnO
OBn
3.133
151.80
146.45
136.93
136.64
130.42
128.54
128.03
127.89
127.53
95.40
Chloroform-d
77.64
77.00
76.37
71.37
70.70
DEPT
128.58
127.56
95.33
71.37
70.70

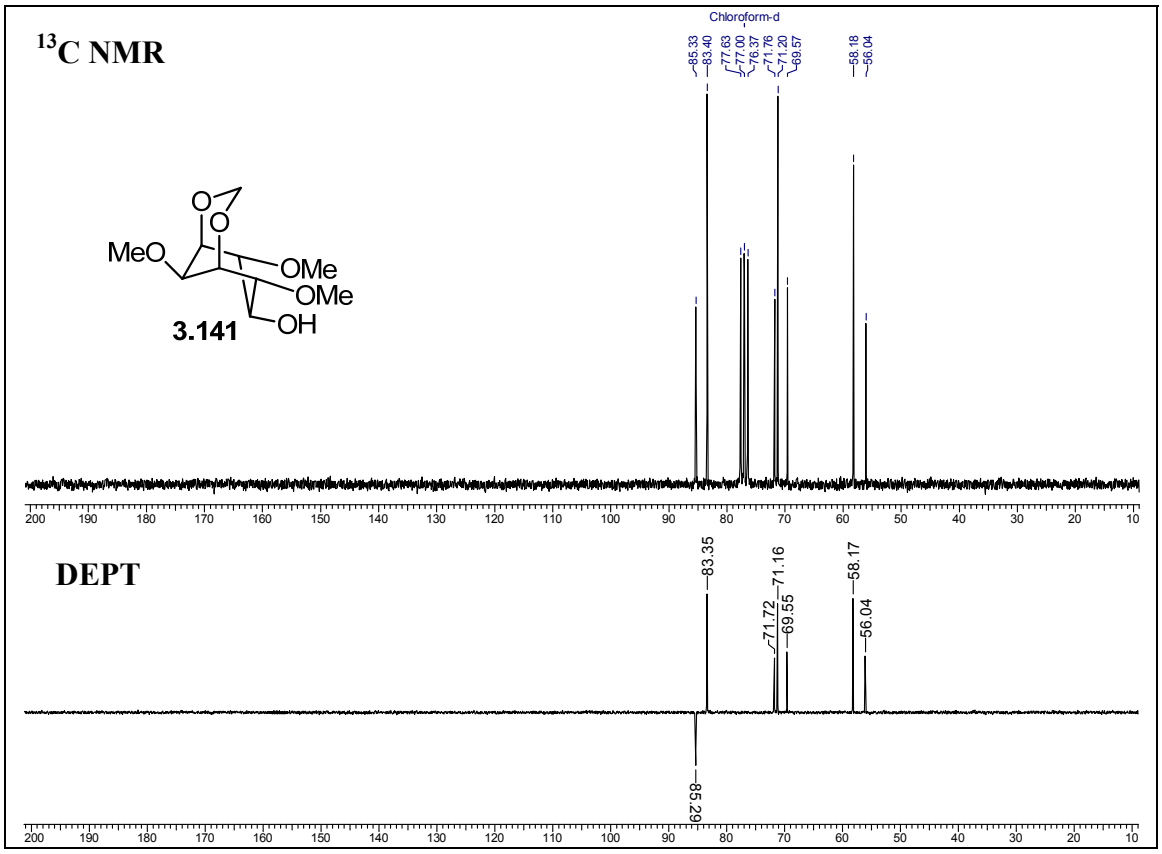

^{1}H NMR
Chloroform-d
TMS
7.44
7.40
7.38
7.36
7.34
7.33
7.32
7.30
7.25
5.71
5.68
5.03
4.98
4.82
4.67
4.62
4.56
4.45
4.44
4.43
4.41
4.37
4.32
4.13
4.11
2.73
2.71
1.60
0.00
OBn
HO
O
BnO
OBn
1.134
15.00
1.00
1.00
3.11
2.02
1.00
0.95

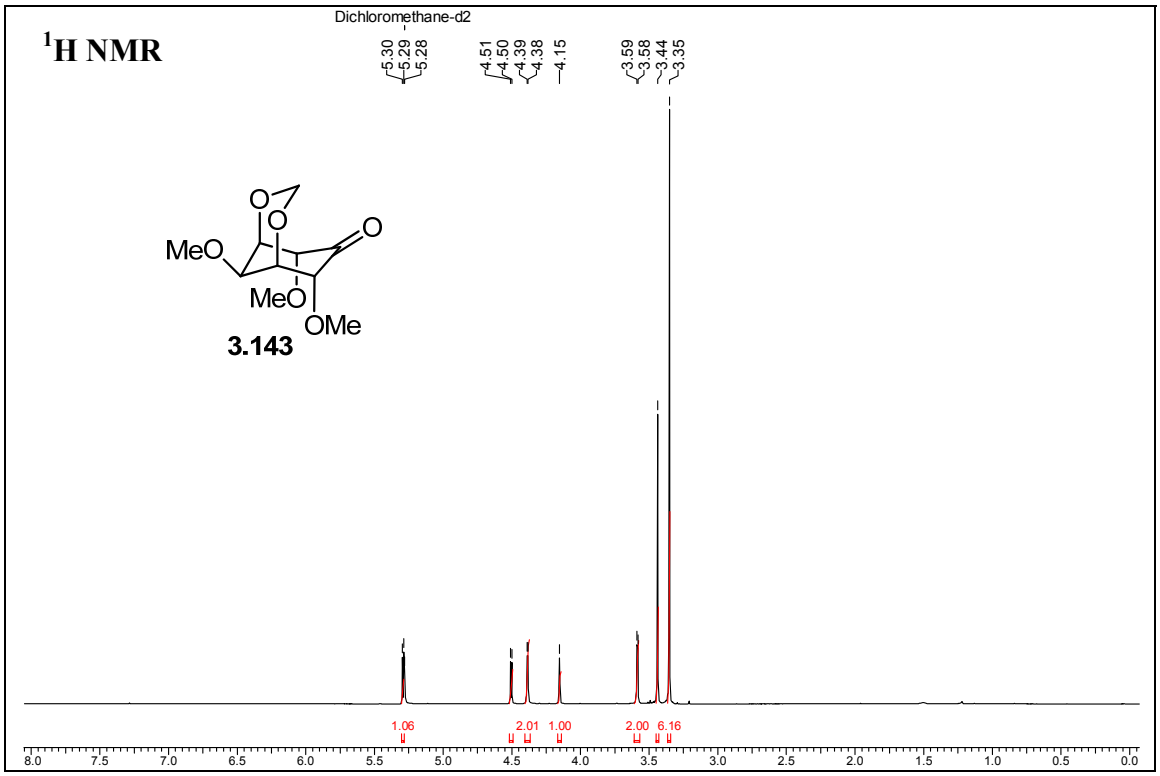

^{13}C NMR
191.40
150.28
137.78
137.44
135.41
128.50
128.41
128.17
128.03
127.79
127.20
112.16
Chloroform-d
80.40
77.64
77.00
76.37
73.60
72.43
72.08
71.13
69.81
OBn
HO
O
BnO
OBn
1.134
DEPT
128.51
128.43
128.19
127.81
127.22
112.15
80.41
72.43
71.14
73.60
72.08
69.81

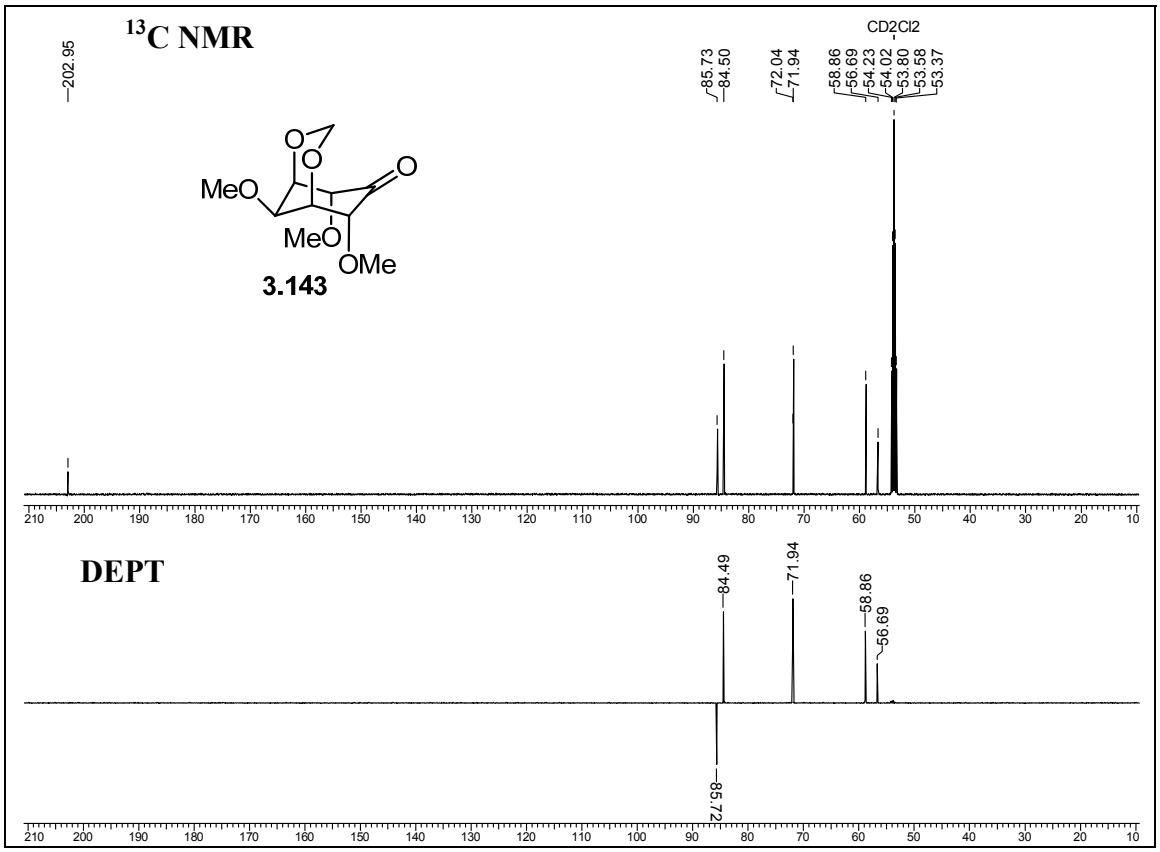

^{1}H NMR
TMS
BnO
OH
HO
OBn
BnO
O
3.135

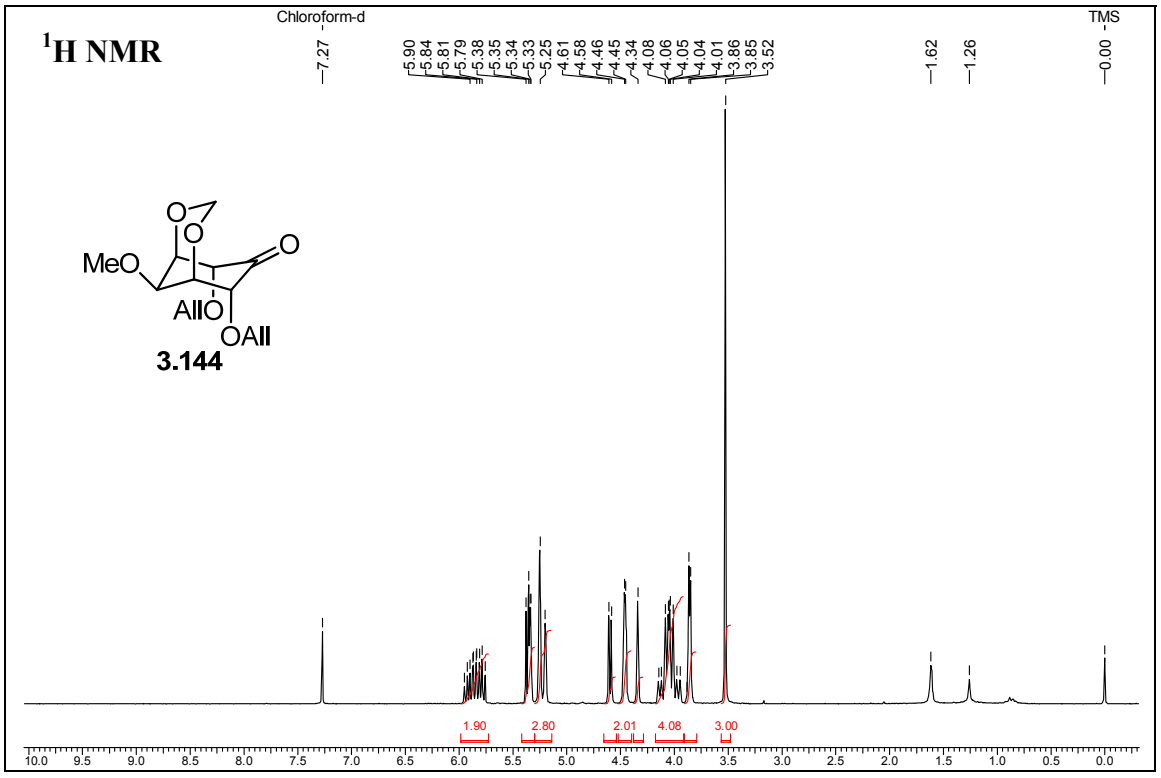

^{13}C NMR
Chloroform-d
BnO
OH
HO
OBn
BnO
O
3.135
DEPT

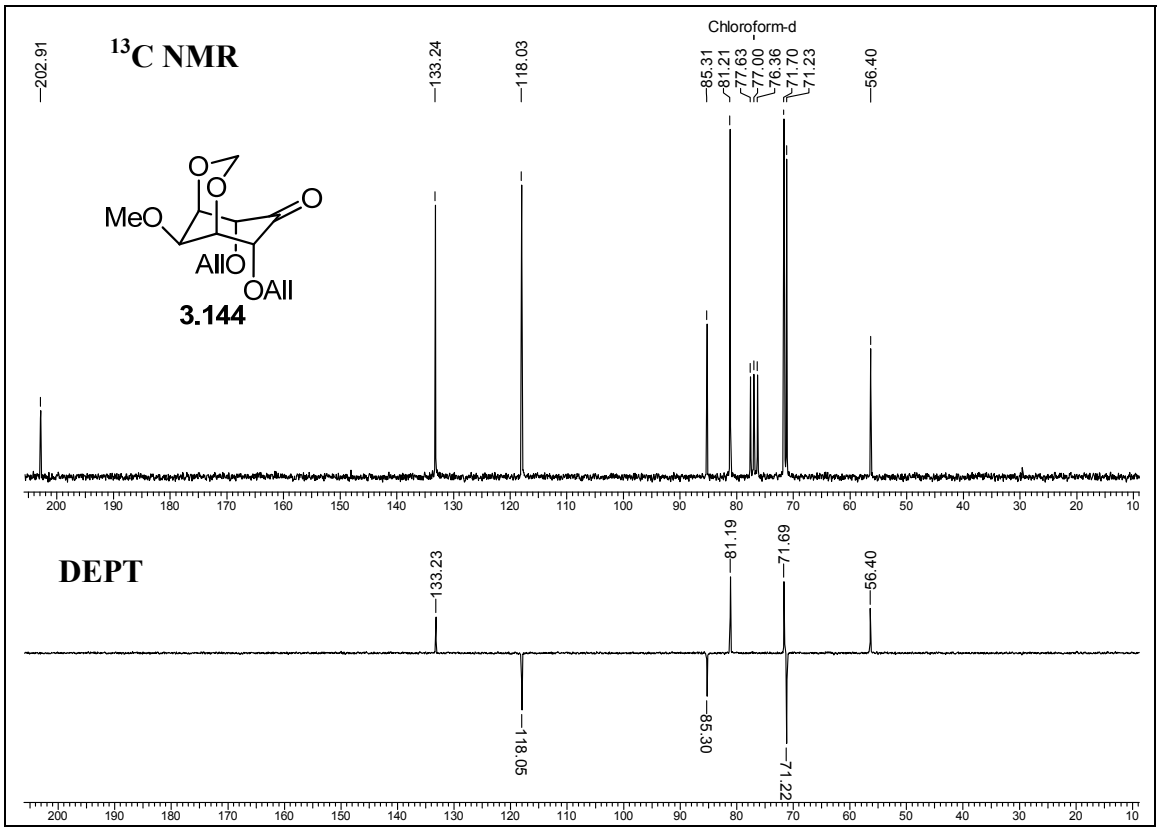

^{1}H NMR
TMS
7.27
5.42
5.40
4.71
4.68
4.40
3.87
3.85
3.82
3.80
3.78
3.77
3.77
3.76
3.48
3.46
3.02
2.97
1.66
0.00
MeO
OMe
OMe
OH
3.141
1.00
1.00
2.00
4.15
9.00
0.96

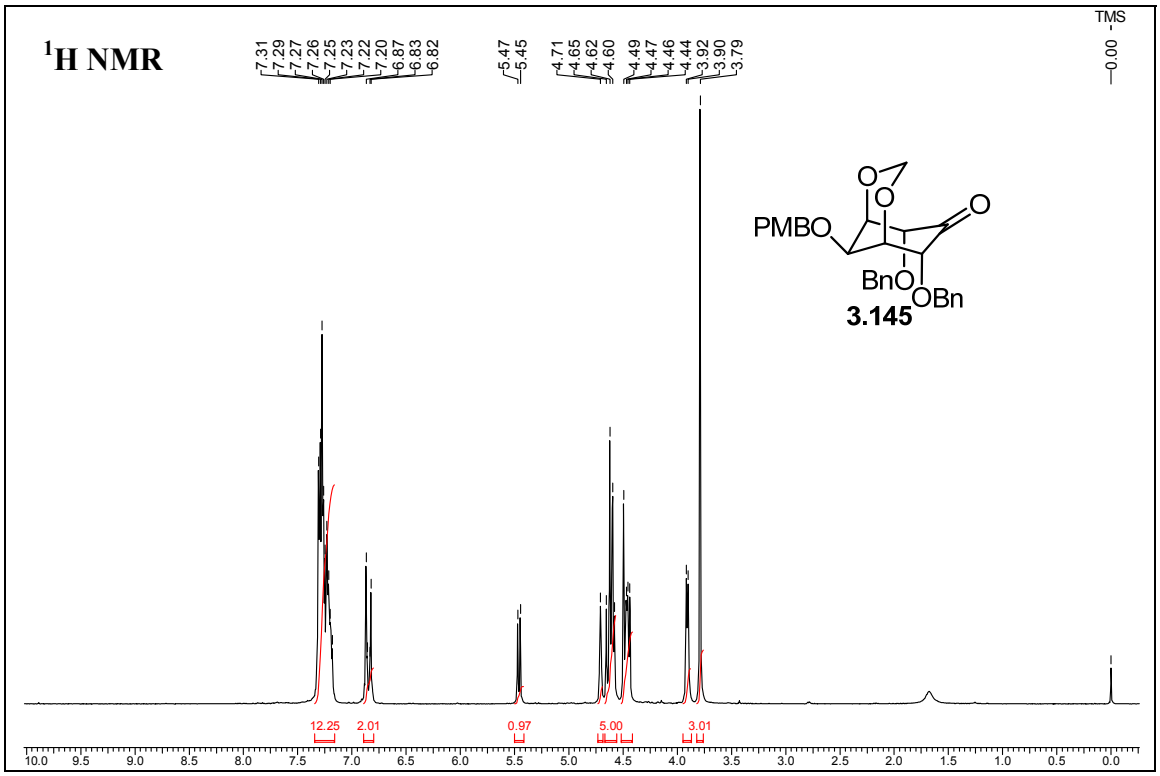

^{13}C NMR
Chloroform-d
85.33
83.40
77.63
77.00
76.37
71.76
71.20
69.57
58.18
56.04
MeO
OMe
OMe
OH
3.141
DEPT
83.35
71.16
58.17
71.72
69.55
56.04
86.29

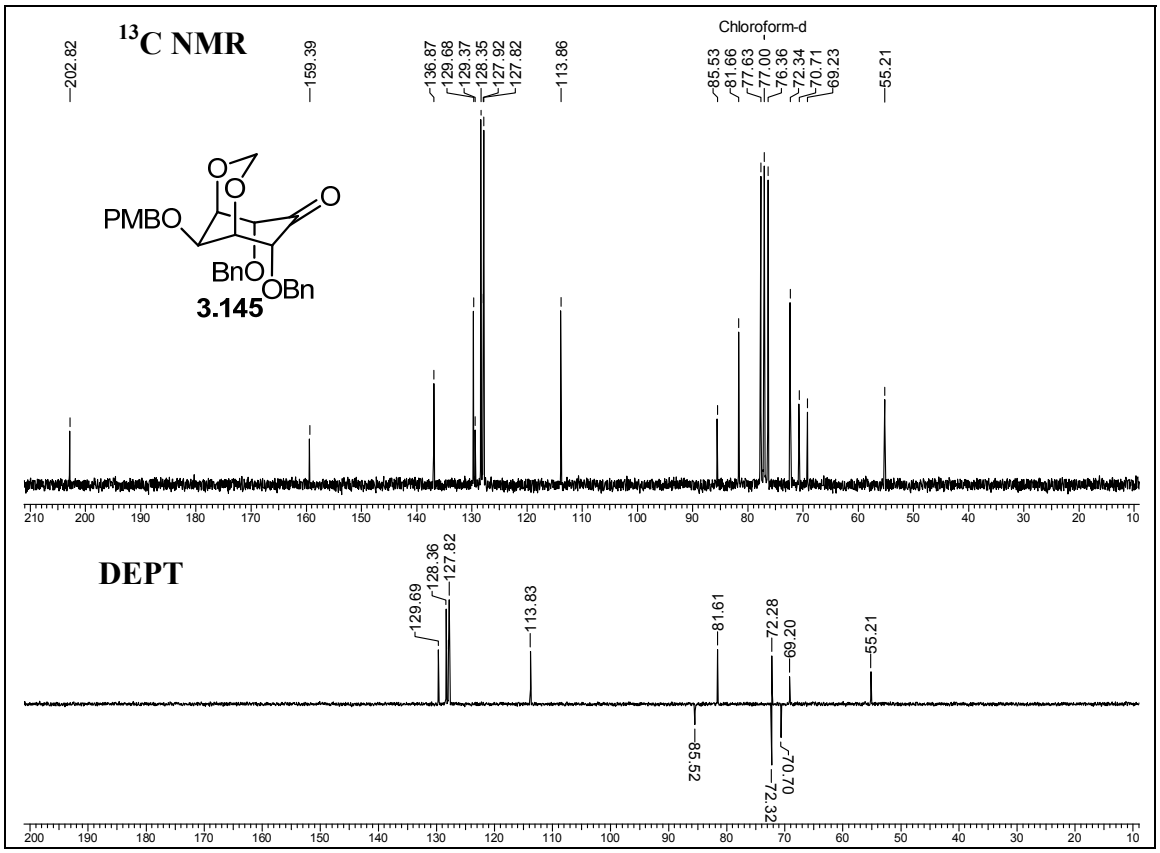

^{1}H NMR
Dichloromethane-d2
5.30
5.29
5.28
4.51
4.50
4.39
4.38
4.15
3.59
3.58
3.44
3.35
MeO
MeO
OMe
O
O
O
3.143
1.06
2.01
1.00
2.00
6.16

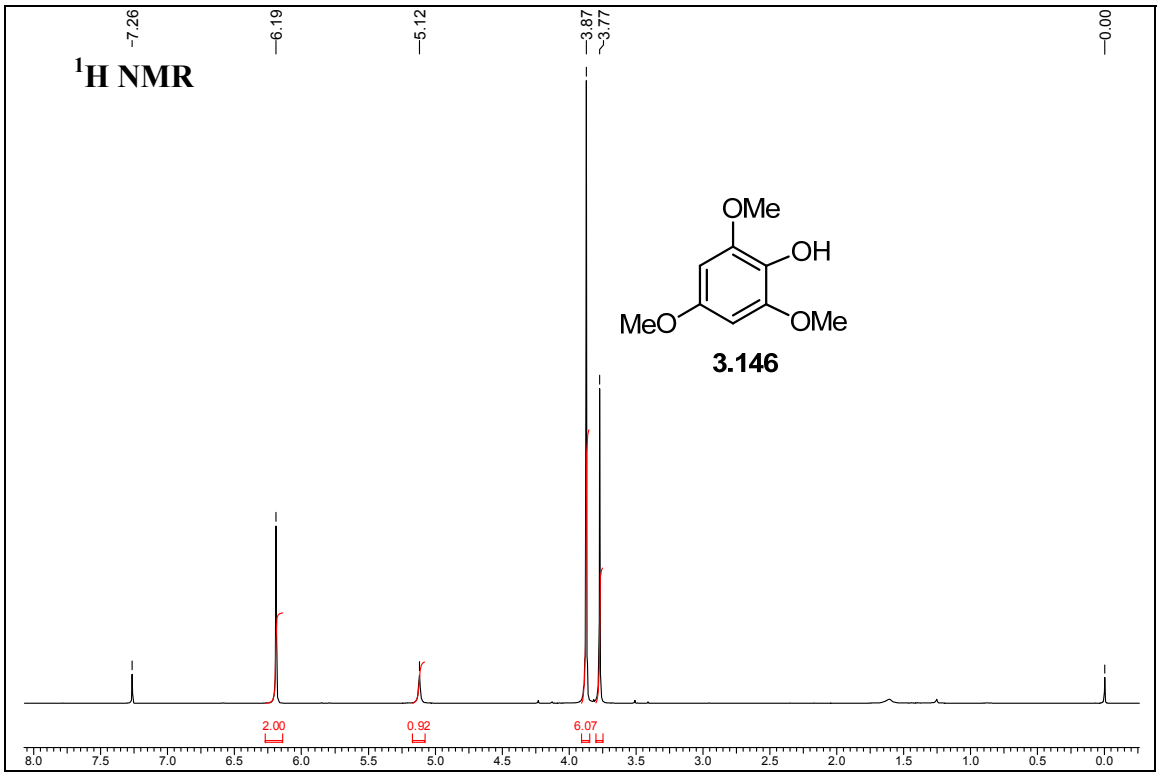

^{13}C NMR
202.95
85.73
84.50
72.04
71.94
58.86
56.69
54.23
54.02
53.80
53.58
53.37
CD2Cl2
MeO
MeO
OMe
O
O
O
3.143
DEPT
84.49
71.94
58.86
56.69
85.72

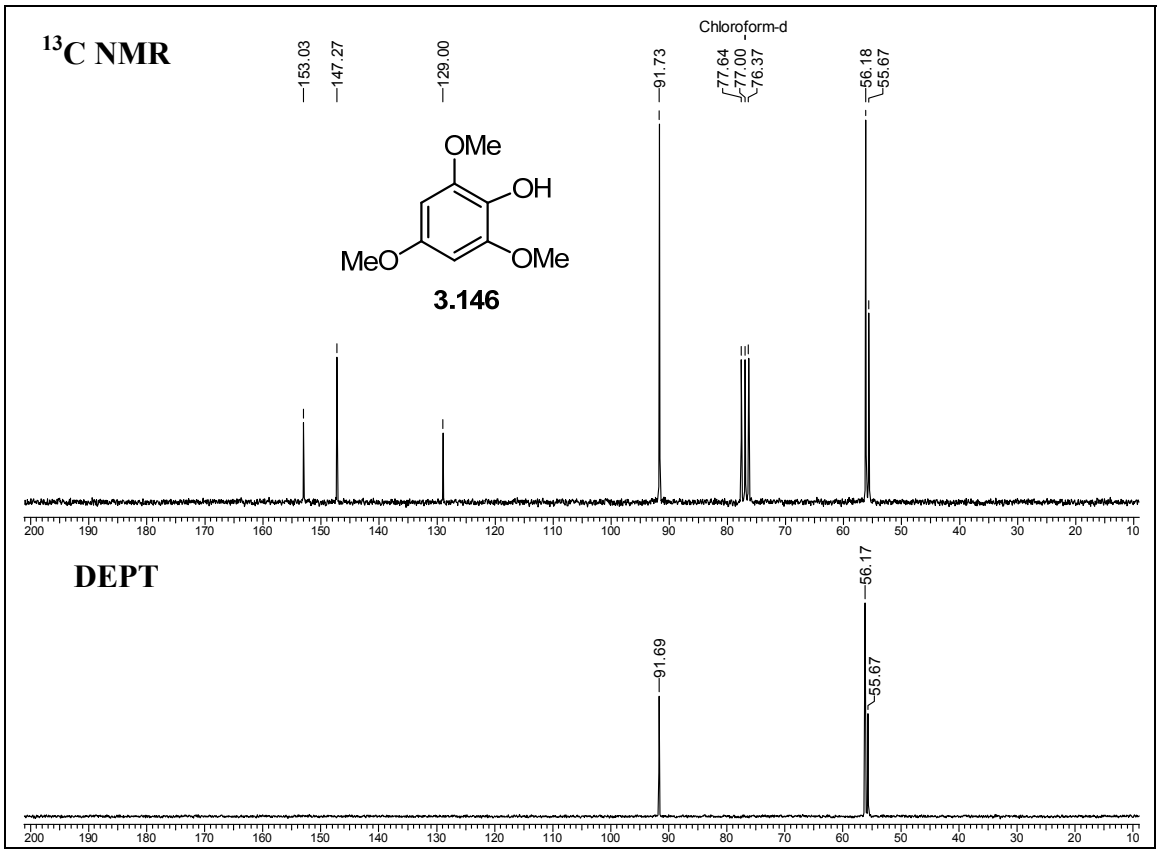

^{1}H NMR
Chloroform-d
TMS
7.27
5.90
5.84
5.81
5.79
5.38
5.35
5.34
5.33
5.25
4.61
4.58
4.46
4.45
4.34
4.08
4.06
4.05
4.04
4.01
3.86
3.85
3.52
1.62
1.26
0.00
MeO
AllO
OAll
3.144
1.90
2.80
2.01
4.08
3.00

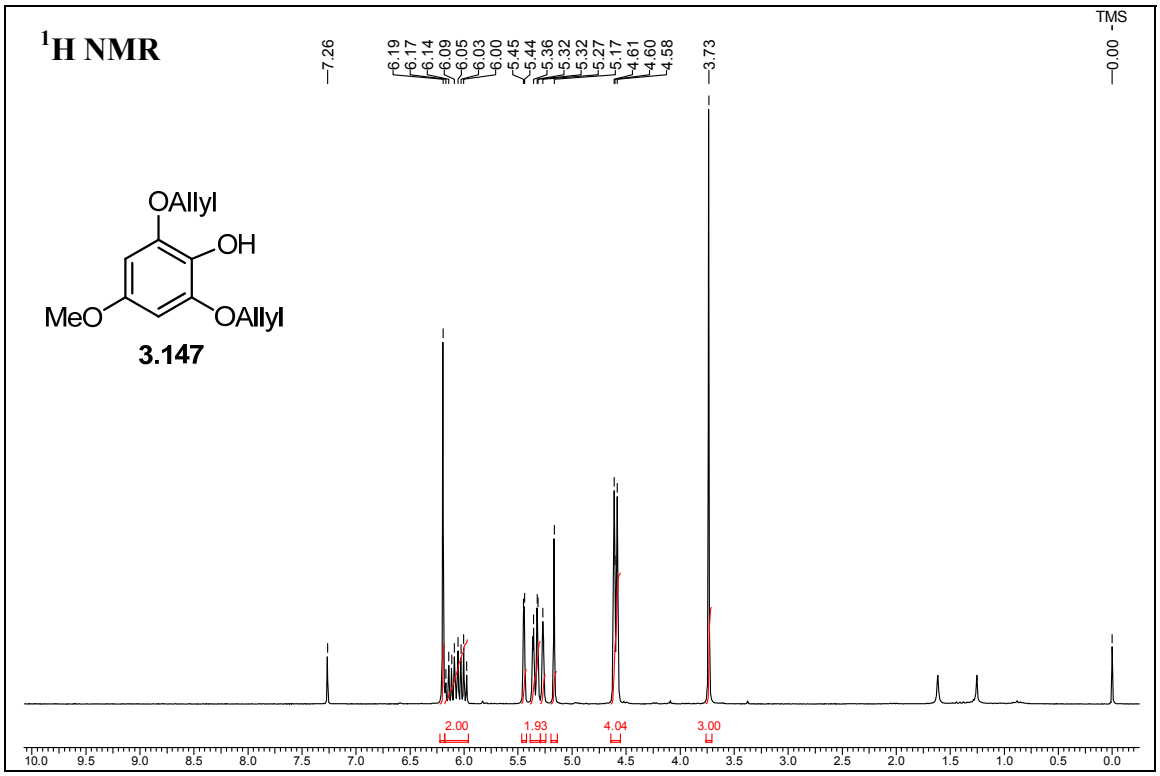

^{13}C NMR
Chloroform-d
202.91
133.24
118.03
85.31
81.21
77.63
77.00
76.36
71.70
71.23
56.40
MeO
AllO
OAll
3.144
DEPT
133.23
81.19
71.69
56.40
118.05
85.30
71.22

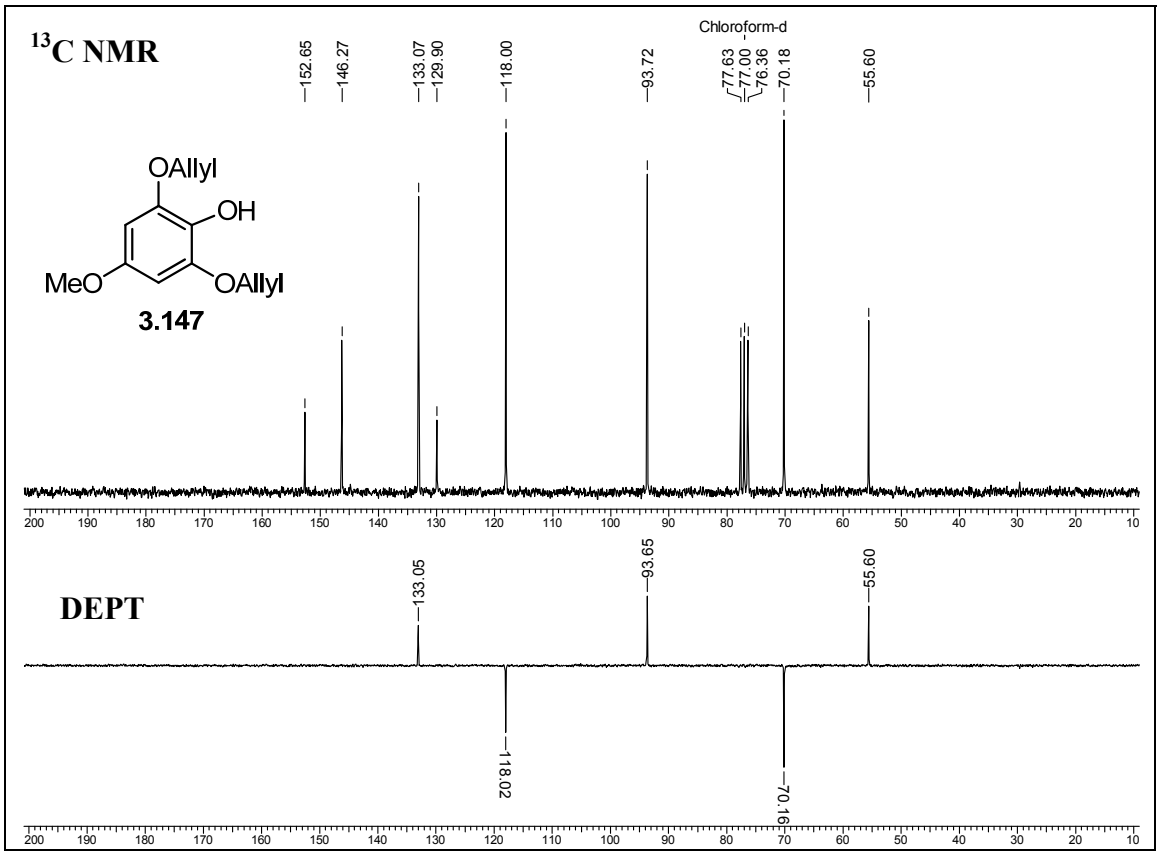

^{1}H NMR
TMS
PMBO
BnO
OBn
3.145
12.25
2.01
0.97
5.00
3.01

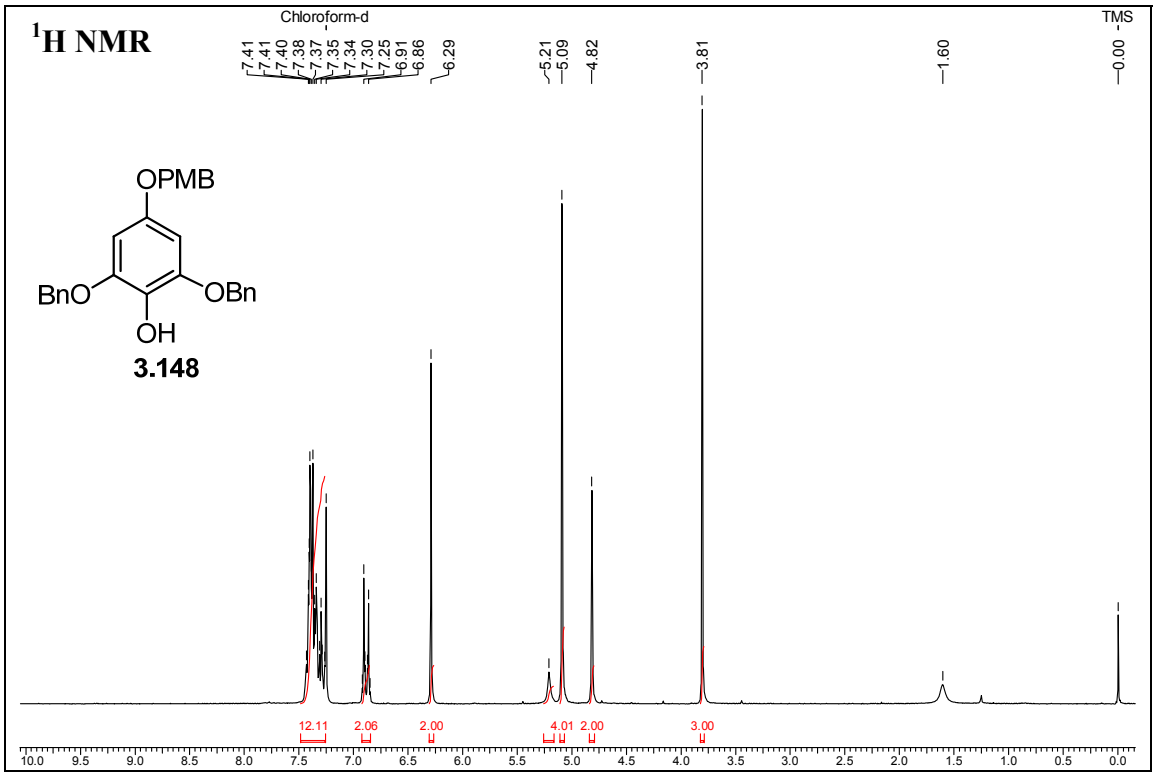

^{13}C NMR
Chloroform-d
PMBO
BnO
OBn
3.145
DEPT

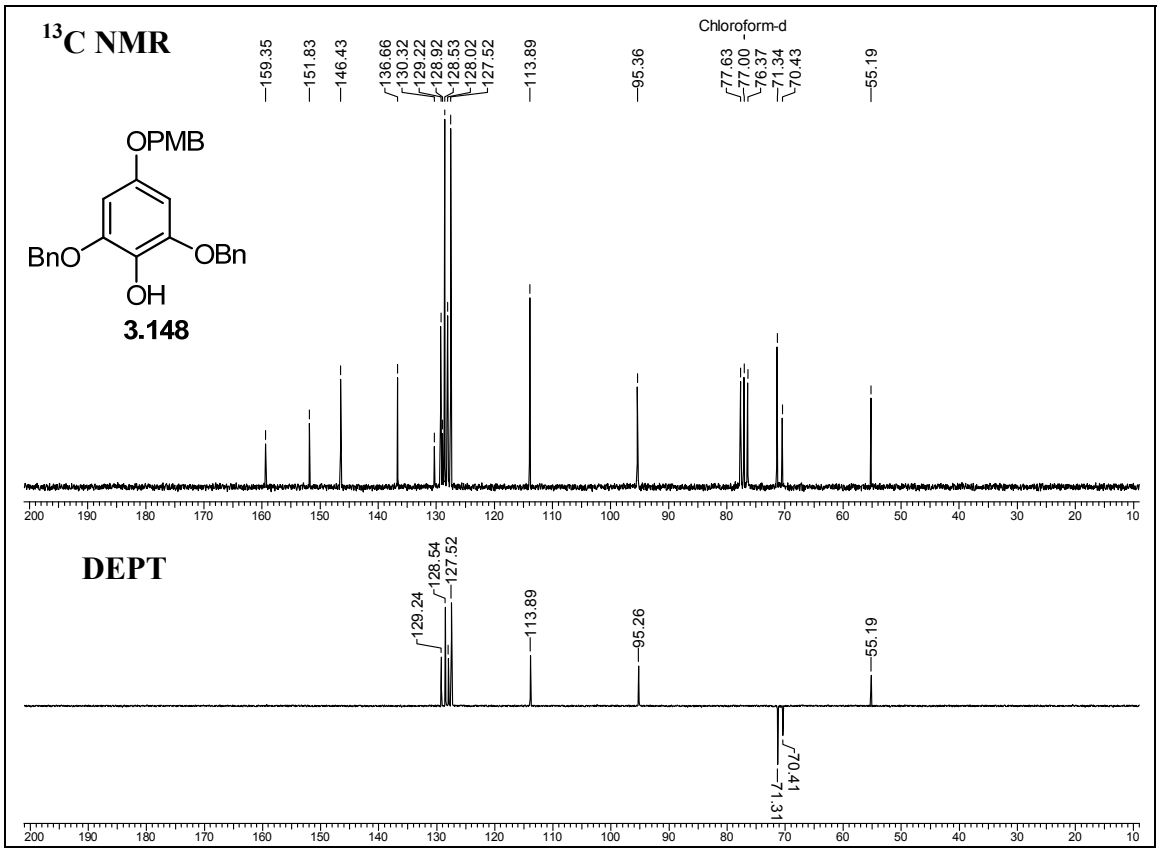

7.26
6.19
5.12
3.87
3.77
0.00
1H NMR
OMe
OH
MeO
OMe
3.146
2.00
0.92
6.07

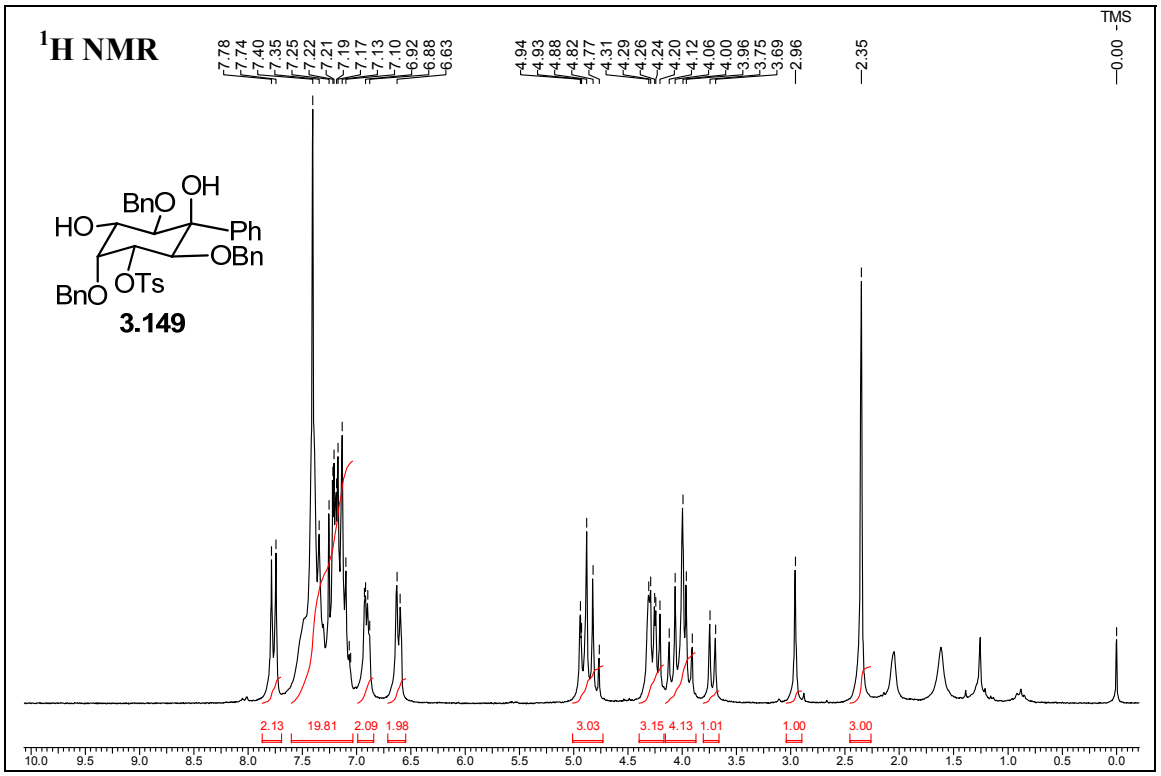

13C NMR
153.03
147.27
129.00
91.73
Chloroform-d
77.64
77.00
76.37
56.18
55.67
OMe
OH
MeO
OMe
3.146
DEPT
91.69
56.17
55.67

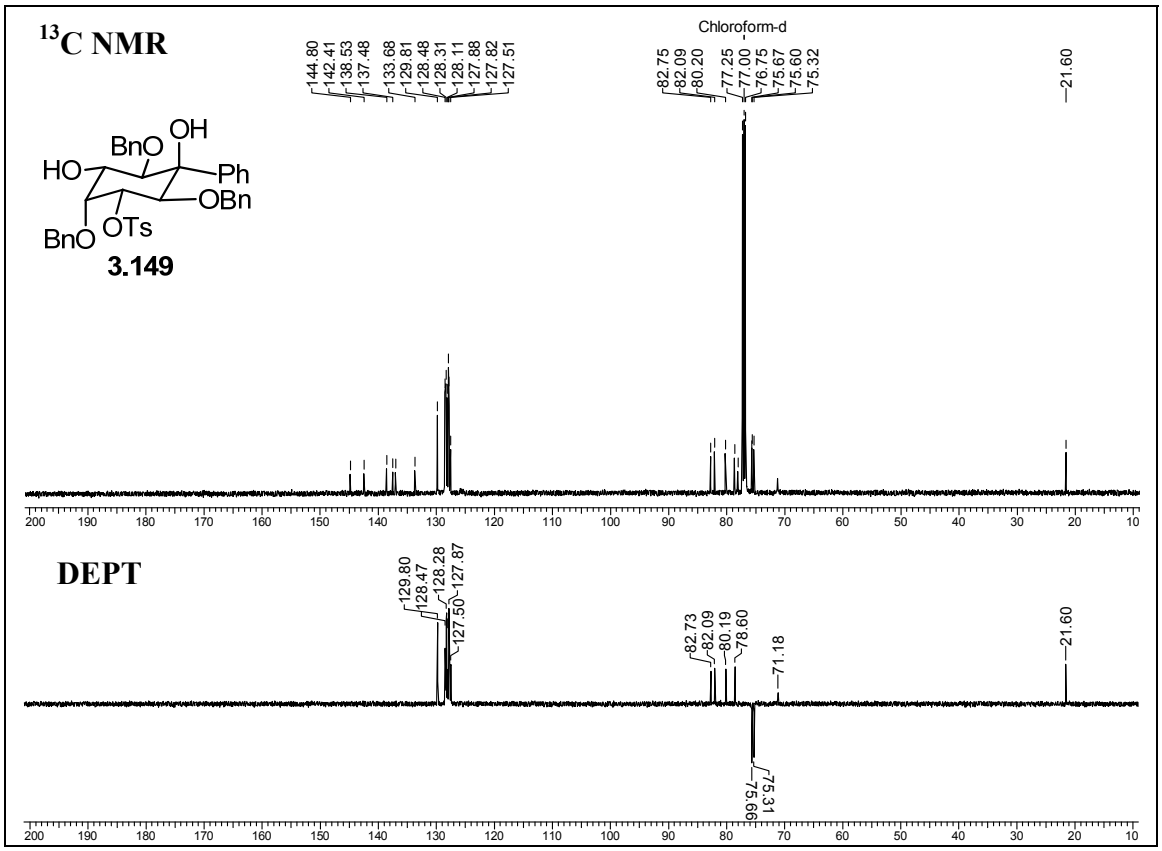

^{1}H NMR
TMS
7.26
6.19
6.17
6.14
6.09
6.05
6.03
6.00
5.45
5.44
5.36
5.32
5.27
5.17
4.61
4.60
4.58
3.73
0.00
OAllyl
OH
MeO
OAllyl
3.147
2.00
1.93
4.04
3.00

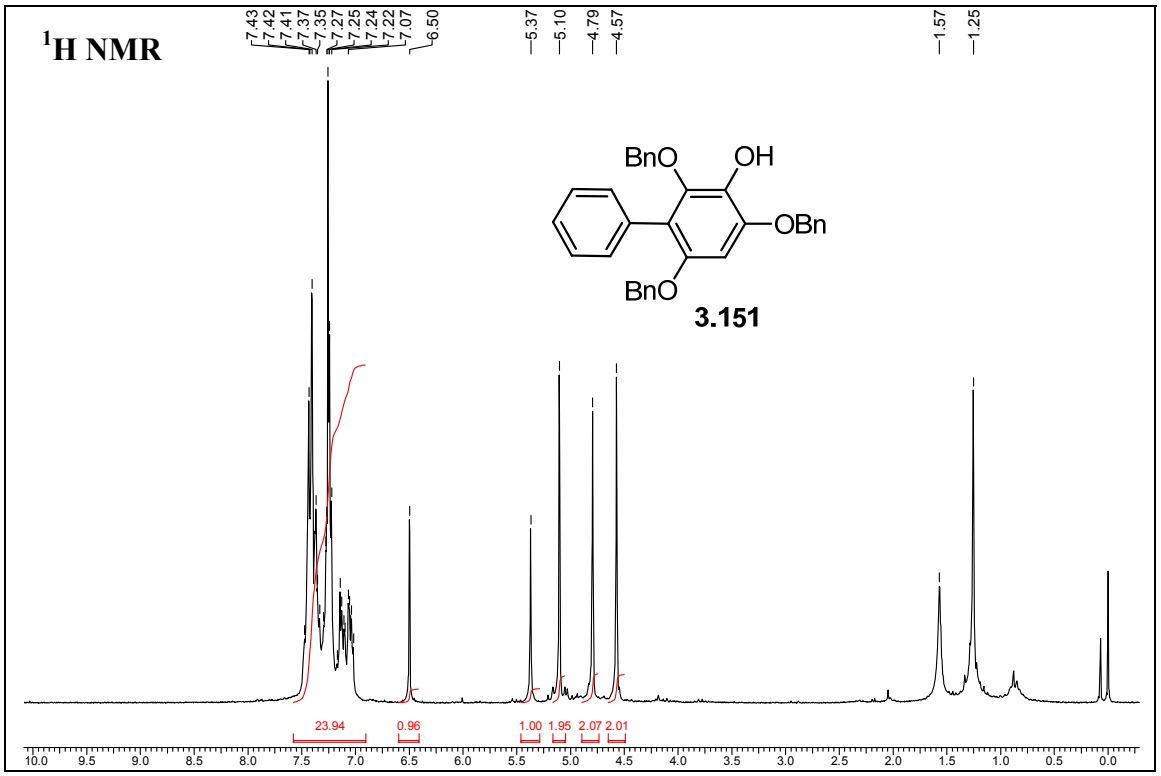

^{13}C NMR
Chloroform-d
152.65
146.27
133.07
129.90
118.00
93.72
77.63
77.00
76.36
70.18
55.60
OAllyl
OH
MeO
OAllyl
3.147
DEPT
133.05
93.65
55.60
118.02
70.16

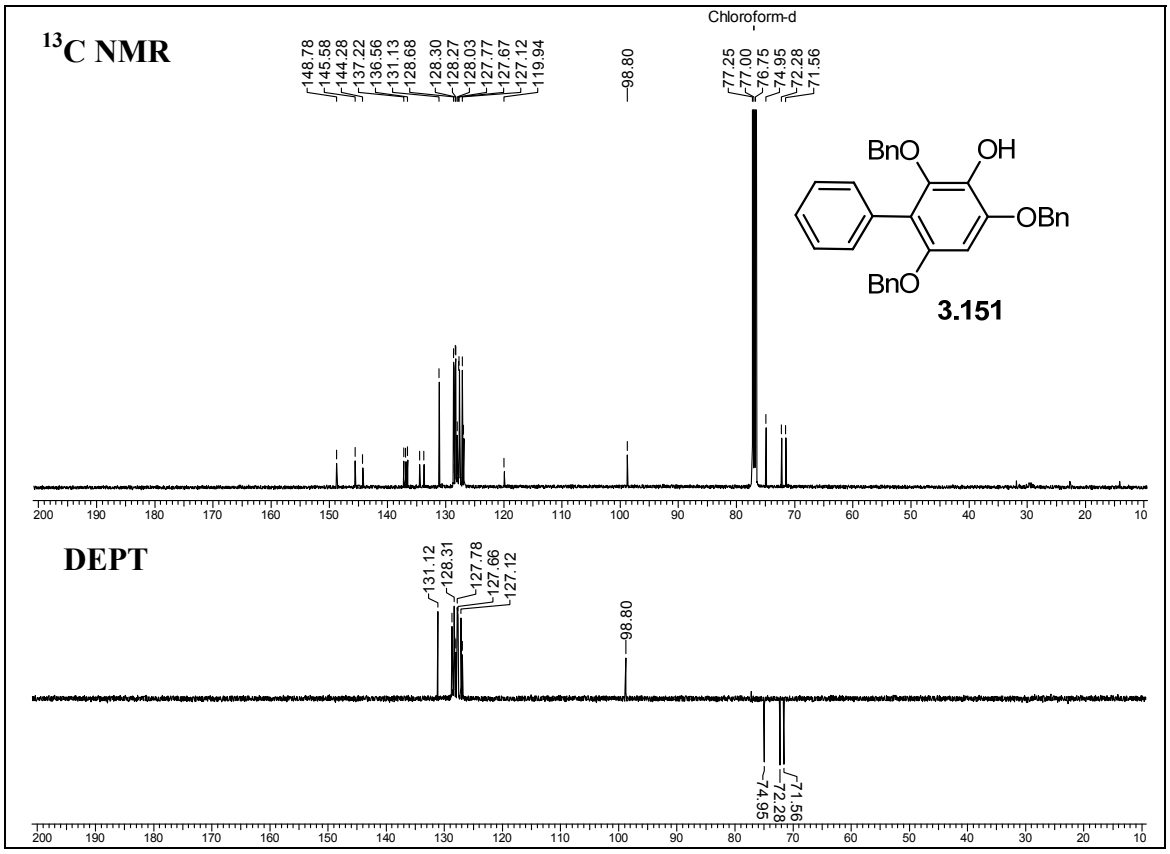

^{1}H NMR
Chloroform-d
TMS
7.41
7.41
7.40
7.38
7.37
7.35
7.34
7.30
7.25
6.91
6.86
6.29
5.21
5.09
4.82
3.81
1.60
0.00
OPMB
BnO
OBn
OH
3.148
12.11
2.06
2.00
4.01
2.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


^{13}C NMR
Chloroform-d
159.35
151.83
146.43
136.66
130.32
129.22
128.92
128.53
128.02
127.52
113.89
95.36
77.63
77.00
76.37
71.34
70.43
55.19
OPMB
BnO
OBn
OH
3.148
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
DEPT
129.24
128.54
127.52
113.89
95.26
55.19
70.41
71.31
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10


^{1}H NMR
TMS
BnO
OH
HO
Ph
OBn
BnO
OTs
3.149


^{13}C NMR
Chloroform-d
BnO
OH
HO
Ph
OBn
BnO
OTs
3.149
DEPT


^{1}H NMR
7.43
7.42
7.41
7.37
7.35
7.27
7.25
7.24
7.22
7.07
6.50
5.37
5.10
4.79
4.57
1.57
1.25
BnO
OH
OBn
BnO
3.151
23.94
0.96
1.00
1.95
2.07
2.01


^{13}C NMR
Chloroform-d
148.78
145.58
144.28
137.22
136.56
131.13
128.68
128.30
128.27
128.03
127.77
127.67
127.12
119.94
98.80
77.25
77.00
76.75
74.95
72.28
71.56
BnO
OH
OBn
BnO
3.151
DEPT
131.12
128.31
127.78
127.66
127.12
98.80
74.95
72.28
71.56

Chapter 4

Structural studies of bicyclic 1,3-acetal derivatives of inositol

4.1. Introduction

The previous chapters presented the utility of bicyclic 1,3-acetal derivatives of inositol for the synthesis of deoxy-, dideoxy inositols, aminocyclitol natural products, 5-C-alkyl inositol and polyhydroxy benzene derivatives. During the course of these investigations, we found that some of the 1,3-acetals showed interesting conformational changes on going from solid to solution states. Conformation of these 1,3-acetal derivatvies also appeared to be dependent on the configuration of the inositol ring as well as the substitutents present on the inositol oxygen atoms. Hence we compiled and compared the conformations of the inositol derived 1,3-acetals available to us in our laboratory as well as those reported in the literature. Relative energies of different conformers of several inositol 1,3-acetals were also computed by DFT calculations, to know the trend in their stability. Discussion of these aspects forms the subject of the present chapter.

Structure and conformation of diastereomeric inositols and their derivatives have earlier been investigated using spectroscopic, crystallographic and theoretical methods to gain insight into their relative stabilities.[1] Such investigations revealed that although the all-equatorial *scyllo*-inositol (**1.16**) is intrinsically expected to be the most stable isomer, the naturally abundant *myo*-inositol (**1.1**) with five equatorial and one axial hydroxyl groups, and the un-natural *neo*-inositol (**1.17**) with four equatorial and two axial hydroxyls, tend to be slightly lower in energy than *scyllo*-inositol (**1.16**).[2] This was attributed to the presence of intramolecular hydrogen bonding in *myo*- and *neo*-inositols. On the other hand, when all intramolecular hydrogen bonds in *scyllo*- and *myo*-inositols were removed by changing the orientation of the OH groups, as may occur in aqueous solution or crystals, *scyllo*-inositol turned out to be lower in energy than *myo*- inositol. Attempts have also been made to use these methods (as above) to rationalize the relative reactivities of the hydroxyl groups in certain inositol derivatives (Chart 4.1)[3] towards O-alkylation, O-acylation, O-silylation and *O*-sulfonylation.[4]

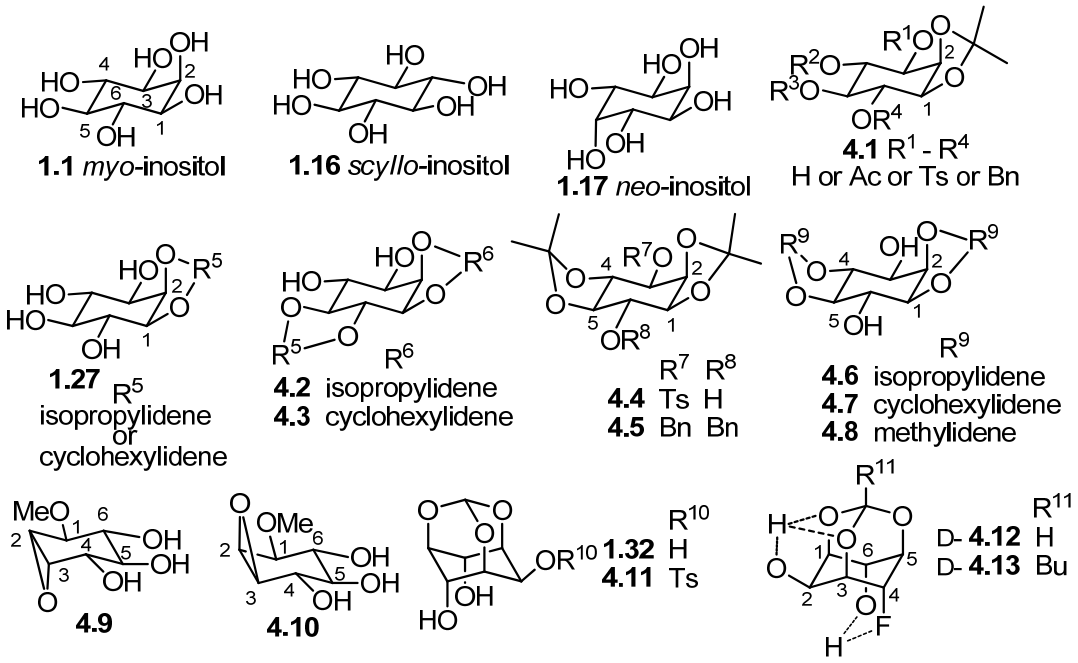


Chart 4.1

The ability of different metal ions to chelate with hydroxyl groups in orthoester of *myo*-inositol (**1.32**) has also been investigated.[4a,5] Conformational study of the natural iron chelator, *myo*-inositol 1,2,3-trisphosphate[6] provided evidence that Fe^{3+} binds tightly to the less stable penta-axial conformation of Ins(1,2,3)P_3 **4.14B** (Chart 4.2) using terminal and bridging phosphate ester oxygen atoms. The conformation of the Ins(1,2,3)P_3–Fe^{3+} complex, 4,6-carbonate **4.15** and 4,6-methylidene-*myo*-inositol-1,2,3,5-tetrakis- phosphate (**4.16**), which are locked in the unstable penta-axial chair conformation were analyzed by using high level density functional calculations.

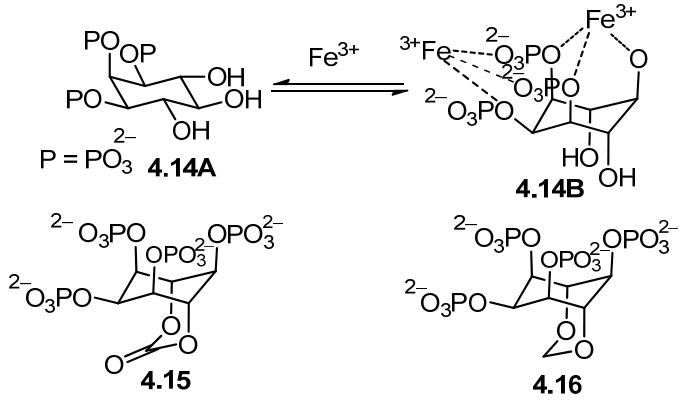


Chart 4.2: Conformational ring-flip of Ins(1,2,3)P_3 from the equatorial rich (**4.14A**) to the axial rich (**4.14B**) conformation upon association with Fe^{3+} and conformationally restricted analogs **4.15** and **4.16**, of Ins(1,2,3,5)P_4.

Sureshan *et al.*[7] recently reported that the effect of inter- or intramolecular CH···O bonding can bring about a change in conformation of the inositol ring on going from solid to solution state (Chart 4.3).

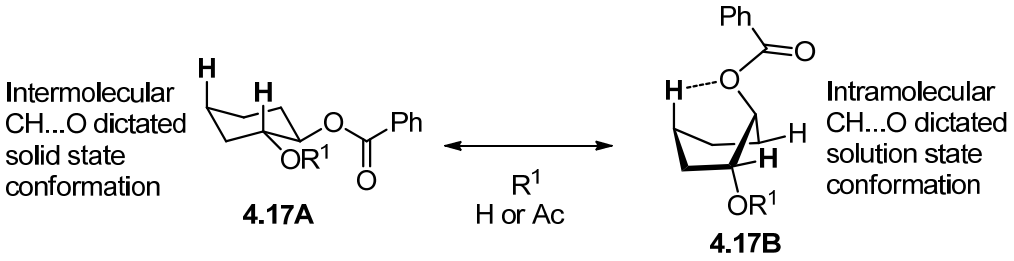


Chart 4.3: Change in conformation of the inositol ring on going from solid to solution state. Other substituents on the inositol ring have been omited for clarity.

4.2. Results and discussion

In principle bicyclic inositol 1,3-acetal derivatives can exist in any of the four different conformations **CC** (**C**hair-**C**hair), **CB** (**C**hair-**B**oat), **BC** (**B**oat-**C**hair), **BB** (**B**oat-**B**oat) shown in Chart 4.4. Hence the structures of these molecules were investigated using NMR spectroscopy, single crystal X-ray diffraction and DFT calculations. Results of NMR spectroscopy gave us information on the solution state conformation; conformation in the solid state was determined from single crystal X-ray diffraction analysis and geometry optimization studies (DFT calculations) on these bicyclic systems helped in gauging the relative stability of different conformers shown in Chart 4.4. Solution state conformation of the compounds for which 2D NMR was not available were arrived at by a comparison of the coupling constants with the coupling constants of anologous compounds for which 2D NMR was recorded.

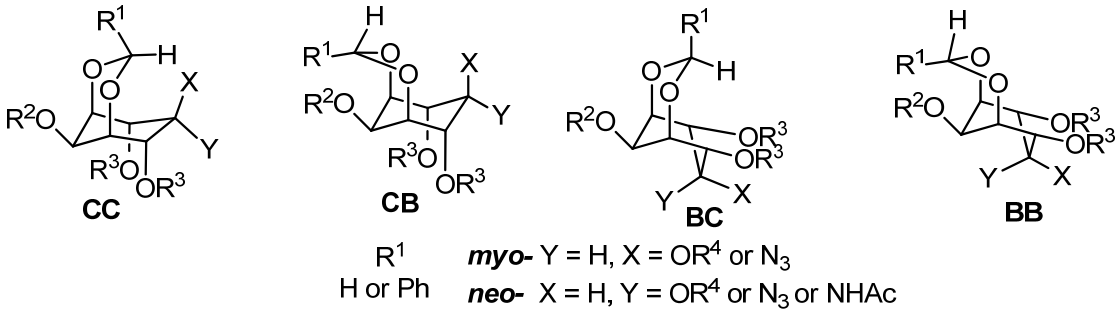
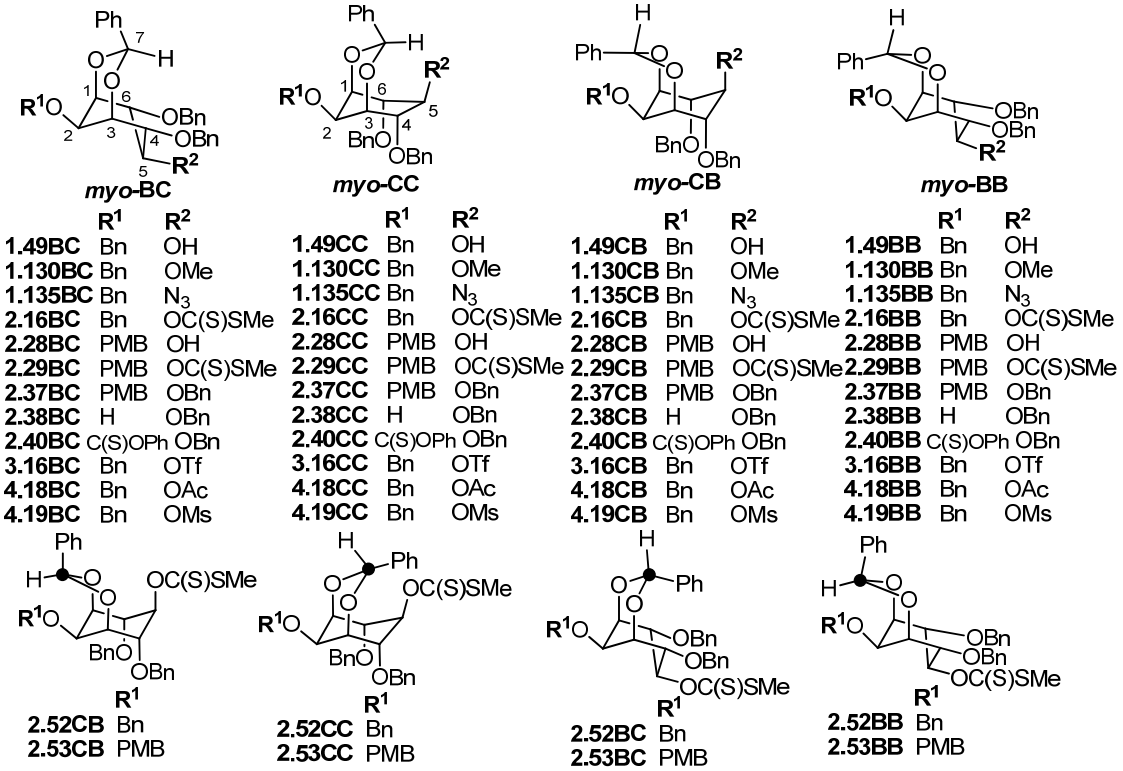


Chart 4.4. Possible conformations of the bicyclic *myo*- and *neo*- inositol derivatives. **C**hair and **B**oat conformation of the inositol and the acetal rings are denoted by **C** and **B** respectively, below each conformer.

The bridged acetal derivatives of insitols were divided into eight groups: C1,C3-*O*-benzylidene *myo*-inositol derivatives; C1,C3-*O*-methylidene *myo*-inositol derivatives; C1,C3-*O*-benzylidene *neo*-inositol derivatives; C1,C3-*O*-methylidene *neo*-inositol derivatives; C1,C3-acetal derivatives of 5-deoxy *myo*-inositol; C1,C3-acetal derivatives of *myo*-5-inosose; C1,C3-*O*-acetals of 5-*C*-alkyl/aryl *neo*-inositol derivatives and C1,C5-*O*-benzylidene *myo*-inositol derivatives, for convenience and comparison. The numbering used in these sub-titles ie., C1,C3 or C1,C5- refers to the numbering of the carbon atoms in the inositol ring; this is done to distinguish specific numbering of carbon atoms from the relative numbering of the carbon atoms (eg. as in, 1,3-*O*-benzylidene *myo*-inositol derivatives…) referred to in the text, throughout this thesis.

4.2.1. C1,C3-*O*-Benzylidene *myo*-inositol derivatives

The C1,C3-*O*-benzylidene *myo*-inositol derivatives can exist in four possible conformations as shown in Chart 4.5. All these bicyclic inositol derivatives have been mentioned in the previous chapters. Although some of the compounds (**1.49**, **1.130**, **1.135**, **2.16**, **3.16**, **4.18** and **4.19**) are reported in the literature,[8] their conformational aspects have not been investigated.



	myo-BC		*myo*-CC		*myo*-CB		*myo*-BB	
	R^1	R^2	R^1	R^2	R^1	R^2	R^1	R^2
1.49	Bn	OH	Bn	OH	Bn	OH	Bn	OH
1.130	Bn	OMe	Bn	OMe	Bn	OMe	Bn	OMe
1.135	Bn	N_3	Bn	N_3	Bn	N_3	Bn	N_3
2.16	Bn	OC(S)SMe	Bn	OC(S)SMe	Bn	OC(S)SMe	Bn	OC(S)SMe
2.28	PMB	OH	PMB	OH	PMB	OH	PMB	OH
2.29	PMB	OC(S)SMe	PMB	OC(S)SMe	PMB	OC(S)SMe	PMB	OC(S)SMe
2.37	PMB	OBn	PMB	OBn	PMB	OBn	PMB	OBn
2.38	H	OBn	H	OBn	H	OBn	H	OBn
2.40	C(S)OPh	OBn	C(S)OPh	OBn	C(S)OPh	OBn	C(S)OPh	OBn
3.16	Bn	OTf	Bn	OTf	Bn	OTf	Bn	OTf
4.18	Bn	OAc	Bn	OAc	Bn	OAc	Bn	OAc
4.19	Bn	OMs	Bn	OMs	Bn	OMs	Bn	OMs

	R^1	R^1	R^1	R^1
2.52	Bn	Bn	Bn	Bn
2.53	PMB	PMB	PMB	PMB

Chart 4.5: Possible conformations of the *myo*-inositol derivatives (with C1,C3-*O*-benzylidene acetal). Suffixes **B** and **C** to compound numbers indicate the conformation of the inositol and the acetal rings respectively.

Conformation of the bicyclic *myo*-inositol derivatvies (Chart 4.5) in solid, solution and the most stable conformation suggested by DFT calculations are listed in Table 4.1. From this table it is clear that in all the compounds except **2.52** and **2.53**, the inositol ring has the boat conformation while the acetal ring has the chair conformation. In compounds **2.52** and **2.53** inositol and the acetal rings flip over to the chair and the boat conformations respectively. Solution state conformation of the compounds **1.135**, **2.16**, **2.28**, **2.29**, **2.52**, **2.53** and **4.18** were arrived at, based on the reuslts of 2D NMR spectroscopy (Chart 4.6). Solution state conformation of the remaining compounds (**1.49**, **1.130**, **2.37**, **2.38**, **2.40**, **3.16** and **4.19**) were arrived at by a comparison of the coupling constants (Table 4.1) of these compounds with the coupling constants of compounds whose conformation was determined by 2D NMR spectroscopy. For instance, coupling constants for inositol ring hydrogen atoms in compounds **1.49**, **1.130**, **2.37**, **2.38**, **2.40**, **3.16** and **4.19** are closer to those observed in **1.135**, **2.16**, **2.28**, **2.29**, **2.52**, **2.53** and **4.18** than those observed in **2.52** and **2.53**. **Table 4.1:** Conformations of the *myo*-inositol derivatives shown in Chart 4.5 in different phases and coupling constants ($^3J_{HH}$) for inositol ring hydrogen atoms.

				$^3J_{HH}$ (Hz)			
Compound	**Solid**[a]	**Solution**	**DFT**[b]	**H1,H3**[c]	**H2**[c]	**H4,H6**[c]	**H5**[c]
1.49	**BC**	**BC**[d]	**BC**	2.4	2.4	8.4	[e]
1.130	**BC**	**BC**[d]	**BC**	2.3	2.2	6.9	7.1
1.135	**BC**	**BC**[f]	**BC**	2.4	2.5	9.1	9.1
2.16	**BC**	**BC**[f]	**BC**	2.3	2.3	7.2	7.2
2.28	**BC**	**BC**[f]	**BC**	2.4	2.4	8.2	[e]
2.29	**BC**	**BC**[f]	**BC**	2.4	[e]	7.5	7.5
2.37	[g]	**BC**[d]	**BC**	2.5	2.2	7.2	6.8
2.38	[g]	**BC**[d]	**BC**	2.2	[e]	7.4	7.8
2.40	[h]	**BC**[d]	**BC**	[e]	2.4	6.4	6.6
2.52	[h]	**CB**[f]	**CB**	1.3	1.3	2.4	[e]
2.53	**CB**	**CB**[f]	**CB**	1.3	1.2	1.4	[e]
3.16	[g]	**BC**[d]	**BC**	3.7	3.6	8.7	8.7
4.18	**BC**	**BC**[f]	**BC**	2.3	2.3	8.0	7.9
4.19	[g]	**BC**[d]	**BC**	2.3	2.3	8.6	[e]

[a]By X-ray crystallography, see figures 2.1, 2.2 and reference 8; [b]most stable conformation indicated by geometrical optimization; [c]range of chemical shift for H1(H3) - 4.37 to 4.68 (doublet), H2 - 3.6 to 5.4 (triplet), H4 (H6) - 3.9 to 4.2 (doublet), H5 - 3.6 to 6.3 (triplet); [d]conformation arrived at based on the results of 1D NMR (*J* values) spectroscopy; [e]broad singlet or multiplet; [f]conformation arrived at based on 2D NMR spectroscopy (Chart 4.6); [g]gummy solid; [h]X-ray diffraction data not available.

Hence the conformation of the compounds **1.49**, **1.130**, **2.37**, **2.38**, **2.40**, **3.16** and **4.19** must be similar to that of **1.135**, **2.16**, **2.28**, **2.29**, **2.52**, **2.53** and **4.18** (BC) rather than to

the conformation of **2.52** and **2.53** (CB). This argument is valid for arriving at the solution state conformation of the compounds (for wihch 2D NMR spectra were not available) mentioned in the following sections as well.

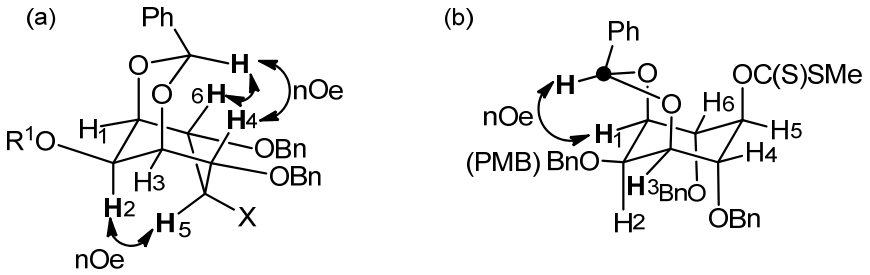


Chart 4.6: Summary of the results of 2D NMR spectroscopy: (a) For compounds **1.135**, **2.16**, **2.28**, **2.29** and **4.18**; (b) for compounds **2.52** and **2.53**.

The geometry optimization studies (DFT calculations) on compounds shown in Chart 4.5 (Table 4.2) showed that **BC** is preferred over **CC** by (ΔE) 0.6 to 5.2 kcal/mol and over **CB** by (ΔE) 3.8 to 12.5 kcal/mol. This data suggests that in all the *myo*-inositol derivatives shown in Chart 4.5 except **2.52** and **2.53**, the cyclitol ring adopts a slightly distorted boat conformation, whereas the acetal ring remains in the chair conformation.

Table 4.2: Relative energies (ΔE, kcal/mol) of the possible conformations of bicyclic *myo*-inositol derivatives obtained by geometrical optimization (for optimized figures see appendix III).

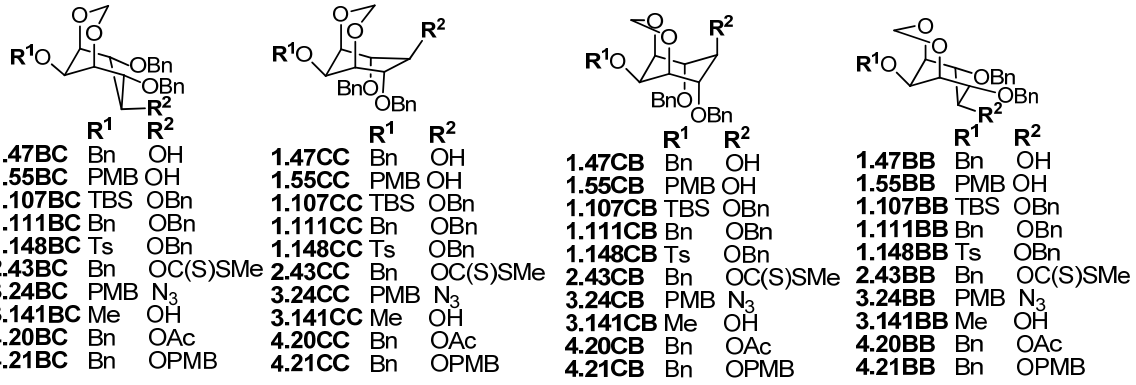
	1.49	**1.130**	**1.135**	**2.16**	**2.28**	**2.29**	**2.37**	**2.38**	**2.40**	**3.16**	**4.18**	**4.19**	**2.52**, **2.53**
BC	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	[a]
CC	4.4	1.2	0.2	2.8	3.1	5.2	2.5	4.4	1.9	0.6	0.6	3.1	[a]
CB	9.4	5.0	3.8	4.5	3.8	4.7	5.0	6.3	7.5	5.0	12.5	5.6	0.0
BB	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	6.3

[a]**BC** and **CC** are very unstable and flip over to **CB** and **BB** respectively during the process of optimization; [b]**BB** is least stable and inherently flips over to **BC** or **CC** or **CB**.

In contrast, *myo*-inositol ring in acetals epimerized at the acetal carbon (**2.52** and **2.53**) exists in the chair form and the acetal ring exists in the boat form. The geometry optimization studies (DFT calculations) for both these compounds (**2.52** and **2.53**) showed that **CB** is preferred over **BB** by (ΔE) 6.3 kcal/mol. The conformations predicted by geometrical optimization studies are in agreement with the experimental results as discussed in the Chapter 2. It is interesting to note that a change in configuration at the acetal carbon results in change in conformaion of both the rings in these 1,3-acetal derivatives of *myo*-inositol.

4.2.2. C1,C3-*O*-Methylidene *myo*-inositol derivatives

Conformations in which C1,C3-*O*-methylidene acetal derivatives of *myo*-inositol can exist are shown in Chart 4.7.



	R^1	R^2
1.47BC	Bn	OH
1.55BC	PMB	OH
1.107BC	TBS	OBn
1.111BC	Bn	OBn
1.148BC	Ts	OBn
2.43BC	Bn	OC(S)SMe
3.24BC	PMB	N_3
3.141BC	Me	OH
4.20BC	Bn	OAc
4.21BC	Bn	OPMB

	R^1	R^2
1.47CC	Bn	OH
1.55CC	PMB	OH
1.107CC	TBS	OBn
1.111CC	Bn	OBn
1.148CC	Ts	OBn
2.43CC	Bn	OC(S)SMe
3.24CC	PMB	N_3
3.141CC	Me	OH
4.20CC	Bn	OAc
4.21CC	Bn	OPMB

	R^1	R^2
1.47CB	Bn	OH
1.55CB	PMB	OH
1.107CB	TBS	OBn
1.111CB	Bn	OBn
1.148CB	Ts	OBn
2.43CB	Bn	OC(S)SMe
3.24CB	PMB	N_3
3.141CB	Me	OH
4.20CB	Bn	OAc
4.21CB	Bn	OPMB

	R^1	R^2
1.47BB	Bn	OH
1.55BB	PMB	OH
1.107BB	TBS	OBn
1.111BB	Bn	OBn
1.148BB	Ts	OBn
2.43BB	Bn	OC(S)SMe
3.24BB	PMB	N_3
3.141BB	Me	OH
4.20BB	Bn	OAc
4.21BB	Bn	OPMB

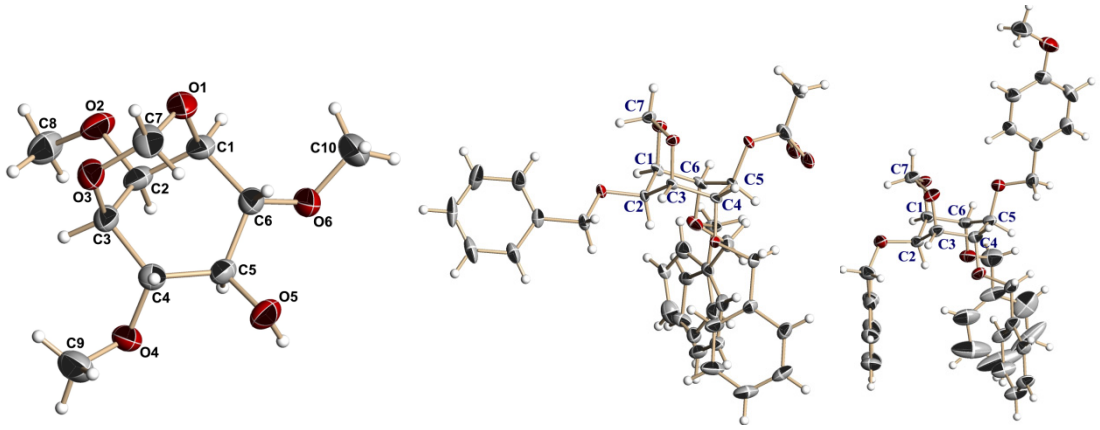
Chart 4.7: Possible conformations of C1,C3-*O*-methylidene acetal derivatives of *myo*-inositol.

Table 4.3: Conformations of the *myo*-inositol derivatives shown in Chart 4.7 in different phases and coupling constants ($^3J_{HH}$) for inositol ring hydrogen atoms.

				$^3J_{HH}$ (Hz)			
Compound	**Solid**[a]	**Solution**	**DFT**[b]	**H1,H3**[c]	**H2**[c]	**H4,H6**[c]	**H5**[c]
1.47[9]	[d]	[e]	**BC**				
1.55	[d]	[e]	**BC**				
1.107[10]	[d]	**BC**[f]	**BC**	1.8[g]	1.8[h]	4.6[h]	4.6[g]
1.111[11]	[d]	**BC**[f]	**BC**		1.8[h]	5.5[h]	5.5[g]
1.148[12]	[d]	**BC**[i]	**BC**			4.0[h]	4.5[g]
2.43	**CB**	**BC**[i]	**BC**				
3.24	**CB**	**BC**[i]	**BC**		2.0[h]	6.6[h]	7.1[g]
3.141	**BC**	[e]	**BC**				
4.20[9]	**CB**	**BC**[i]	**BC**				
4.21	**CB**	**BC**[i]	**BC**		1.8[h]	5.5[h]	5.5[g]

[a]By X-ray crystallography, see figures 2.2, 3.3 and 4.1; [b]most stable conformation indicated by geometrical optimization; [c]range of chemical shifts for H1(H3) - 4.08 to 4.38 (multiplet), H2 - 3.73 to 4.90 (broad singlet), H4(H6) 3.62 to 3.93 (multiplet), H5 - 3.56 to 6.03 (broad singlet); [d]gummy solid; [e]2D NMR data not available; [f]conformation arrived at based on the results of 1D NMR (*J* values) spectroscopy; [g]triplet; [h]doublet; [i]conformation arrived at based on 2D NMR spectroscopy (Chart 4.8).

From Table 4.3 and Figure 4.1, it is clear that at least four of these derivatives (**2.43**, **3.24**, **4.20** and **4.21**) undergo a change in conformation from **CB** to **BC** forms on going from crystalline state to solution state. Compounds **1.107**, **1.111** and **1.148** exist in the **BC** conformation in solution (Chart 4.8).



(a) (b) (c)

Figure 4.1: ORTEP′s of (a) **3.141**, (b) **4.20** and (c) **4.21**. Thermal ellipsoids are drawn at 30% (for **3.141**) and 50% (for **4.20** and **4.21**) probability and hydrogen atoms are depicted as small spheres of arbitrary radii.

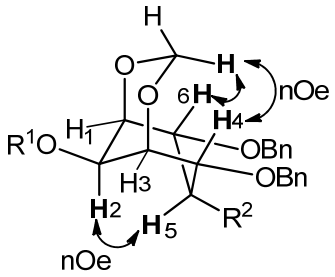


Chart 4.8: Summary of the results of 2D NMR spectroscopy for compounds **1.148**, **2.43**, **3.24**, **4.20** and **4.21**.

The DFT calculations showed that the relative stabilities of the conformations of the *myo*-inositol derivatives are in the order **BC** > **CC** > **CB** for compounds **1.47** and **1.107** and **BC** > **CB** > **CC** for remaining compounds (Table 4.4). Although the relative order of stability for the conformers of 1,3-*O*-methylidene acetal derivatives of *myo*-inositol are different, the **BC** conformation is prefferd over **CC** and **CB** conformation by (ΔE) 0.2 to 6.3 kcal/mol. The change in conformation of these compounds on going from solution state or the gaseous state (as predicted by DFT calulation) to crystalline state could be the result of lattice interactions.

Table 4.4: Relative energies (ΔE, kcal/mol) of the possible conformations of bicyclic *myo*-inositol derivatives obtained by geometrical optimization (for optimized figures see appendix III).

	1.47	**1.55**	**1.107**	**1.111**	**1.148**	**2.43**	**3.24**	**3.141**	**4.20**	**4.21**
BC	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CB	4.4	1.2	4.4	0.2	0.6	5.6	1.9	2.5	2.5	0.2
CC	3.8	5.0	2.5	1.9	1.9	6.3	4.4	4.4	5.6	2.1

4.2.3. C1,C3-*O*-Benzylidene *neo*-inositol derivatives

Four possible conformations of the *neo*-inositol derived benzylidene acetals are shown in Chart 4.9.

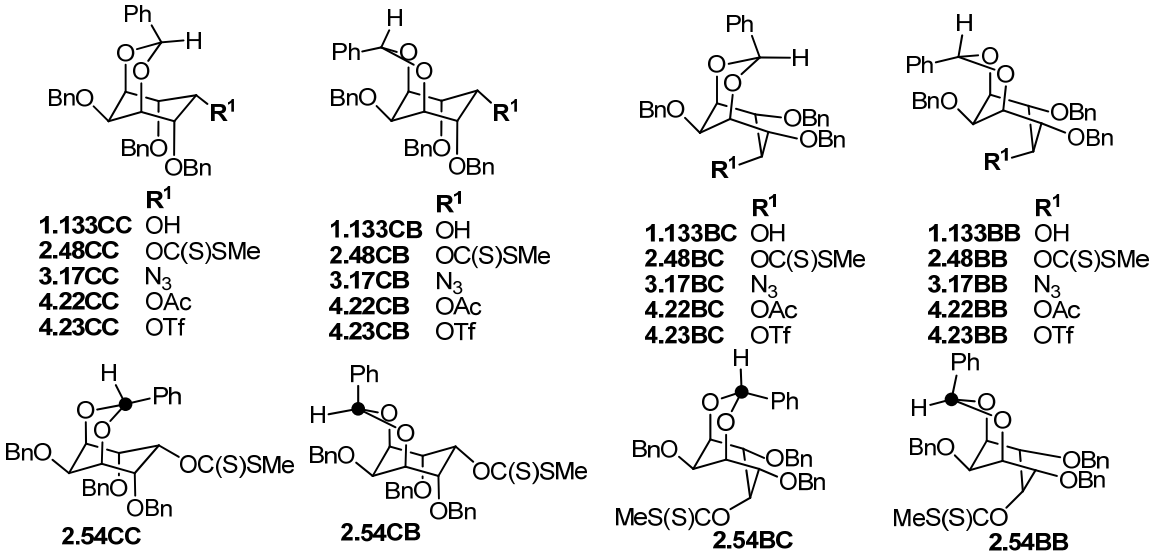


Chart 4.9: Possible conformations of the *neo*-inositol derivatives with C1,C3-*O*-benzylidene acetal.

The crystallographic, NMR spectroscopic data and DFT calculations (Tables 4.5, 4.6 and Chart 4.10) show that all the C1,C3-*O*-benzylidene acetals derived from *neo*-inositol maintain chair conformation for both the six memebered rings except the acetals **2.48** and **2.54**. The acetal ring in **2.48** has chair conformation in solution but boat conformation in the crystalline state, perhaps due to lattice interactions.

Table 4.5: Conformations of the *neo*-inositol derivatives shown in Chart 4.9 in different phases and coupling constants ($^3J_{HH}$) for inositol ring hydrogen atoms.

				$^3J_{HH}$ (Hz)			
Compound	**Solid**[a]	**Solution**[b]	**DFT**[c]	**H1,H3**[d]	**H2**[d]	**H4,H6**[d]	**H5**[d]
1.133[8]	**CC**	**CC**[e]	**CC**				[f]
2.48	**CB**	**CC**	**CC**				5.4
2.54	**CB**	**CB**	**CB**			4.2[g]	4.2
3.17	**CC**	**CC**	**CC**				5.0
4.22[8]	**CC**	**CC**	**CC**	2.2[g]	2.2[h]	4.8[g]	5.0
4.23[8]	[i]	[j]	**CC**		2.1[h]		4.6

[a]By X-ray crystallography, see figures 2.3, 2.14 and reference 8; [b]conformation arrived at based on 2D NMR spectroscopy (Chart 4.10); [c]most stable conformation indicated by geometrical optimization; [d]range of chemical shifts for H1(H3) - 4.27 to 4.52 (multiplet), H2 - 4.19 to 4.52 (broad singlet), H4(H6) - 4.0 to 4.4 (multiplet), H5 - 3.66 to 6.63 (triplet); [e]conformation arrived at based on the results of 1D NMR (*J* values) spectroscopy; [f]broad singlet; [g]doublet; [h]triplet; [i]gummy solid; [j]2D NMR data not available.

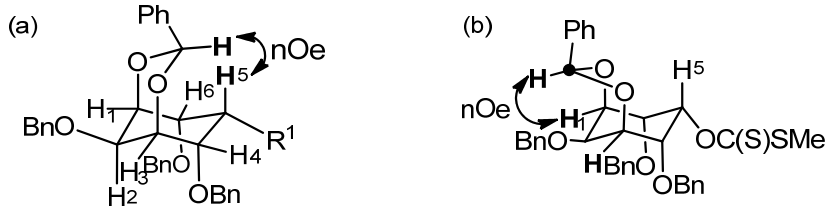


Chart 4.10: Summary of the results of 2D NMR spectroscopy for compounds (a) **2.48**, **3.17** and **4.22**; (b) **2.54**.

As observed in *myo*-inositol derivatives (section 4.2.1) epimerization at the acetal carbon (acetal **2.54**) results in change in conformation of the acetal ring from chair to boat, irrespetive of the phase in which these moleules are present. However, in contrast to *myo*-inositol derivatives (section 4.2.1) conformation of the inositol ring on epimerization of the acetal carbon in *neo*-inositol derivatives is manitained in the chair form. A comparison of the conformation of the two epimeric acetals **2.52** and **2.54** shows that a change in configuration of the inositol ring (*myo*- to *neo*-) in these epimeric acetals do not bring in any conformational change in these molecules.

Table 4.6: Relative energies (ΔE, kcal/mol) of the possible conformations of bicyclic *neo*-inositol derivatives obtained by geometrical optimization (for optimized figures see appendix III).

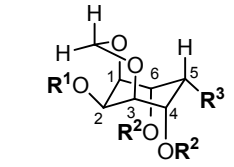
Compound	1.133	2.48	2.54	3.17	4.22	4.23
CC	0.0	0.0	[b]	0.0	0.0	0.0
BC	1.9	3.8	[b]	0.6	7.5	0.6
CB	3.1	2.5	0.0	2.5	2.5	1.9
BB	[a]	[a]	6.9	[a]	[a]	[a]

[a]**BB** is least stable and inherently flips over to **BC** or **CC** or **CB**; [b]**BC** and **CC** are unstable and flip over to **CB** and **BB** respectively during the process of optimization.

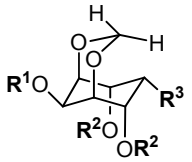
Results obtained from geometrical optimization studies (DFT calculations) for compounds shown in Chart 4.9, showed that the relative stabilities of the conformations of the *neo*-inositol derivatives are in the order **CC** > **BC** > **CB** for compounds **1.133**, **3.17** and **4.23** and **CC** > **CB** > **BC** for compounds **4.22** and **2.48** (Table 4.6). Although the relative order of stability for the conformers of these are different, **CC** conformation is most prefferd over **BC** and **CB** conformations. The difference in energy between the stable and unstable conformations is in the range 0.6 to 7.5 kcal/mol. Results of geometrical optimization studies (DFT calculations) for **2.54**, showed that **CB** conformation is preferred over **BB** conformation by 6.9 kcal/mol.

4.2.4. C1,C3-*O*-Methylidene-*neo*-inositol derivatives

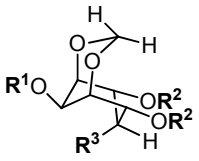
Four possible conformations of the *neo*-inositol derived methylidene acetals are shown in Chart 4.11.



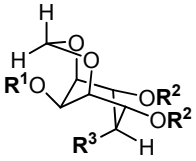
	R^1	R^2	R^3
3.14CB	Bn	Bn	N_3
3.19CB	PMB	Bn	N_3
3.25CB	H	Bn	N_3
3.34CB	Me	PMB	N_3
3.36CB	Me	PMB	NHAc
4.24CB	C(S)-SMe	Bn	N_3



	R^1	R^2	R^3
3.14CC	Bn	Bn	N_3
3.19CC	PMB	Bn	N_3
3.25CC	H	Bn	N_3
3.34CC	Me	PMB	N_3
3.36CC	Me	PMB	NHAc
4.24CC	C(S)-SMe	Bn	N_3



	R^1	R^2	R^3
3.14BC	Bn	Bn	N_3
3.19BC	PMB	Bn	N_3
3.25BC	H	Bn	N_3
3.34BC	Me	PMB	N_3
3.36BC	Me	PMB	NHAc
4.24BC	C(S)-SMe	Bn	N_3



	R^1	R^2	R^3
3.14BB	Bn	Bn	N_3
3.19BB	PMB	Bn	N_3
3.25BB	H	Bn	N_3
3.34BB	Me	PMB	N_3
3.36BB	Me	PMB	NHAc
4.24BB	C(S)-SMe	Bn	N_3

Chart 4.11: Possible conformations of the *neo*-inositol derivatives (with C1,C3-*O*-methylidene acetal).

Table 4.7: Conformations of the *neo*-inositol derivatives shown in Chart 4.11 in different phases and coupling constants ($^3J_{HH}$) for inositol ring hydrogen atoms.

				$^3J_{HH}$ (Hz)			
Compound	**Solid**[a]	**Solution**[b]	**DFT**[c]	**H1,H3**[d]	**H2**[d]	**H4,H6**[d]	**H5**[d]
3.14	[e]	**CB**	**CB**	3.5		4.3	4.0
3.19	**CB**	**CB**	**CB**	3.3		4.0	4.3
3.25	**CB**	**CB**	**CB**	3.0		4.2	4.1
3.34	**CB**	**CB**	**CB**	3.5		4.3	4.2
3.36	**CB**	**CB**	**CB**	3.5		[f]	5.3
4.24	**CB**	**CB**	**CB**	3.0		4.3	4.3

[a]By X-ray crystallography, see figures 3.3, 3.4, 3.6, 3.7 and 4.2; [b]conformation arrived at based on 2D NMR spectroscopy (Chart 4.12); [c]most stable conformation indicated by geometrical optimization; [d]range of chemical shifts for for H1(H3) - 4.17 to 4.53 (doublet), H2 - 4.08 to 6.64 (broad singlet), H4(H6) - 3.84 to 4.13 (doublet), H5 - 3.73 to 4.77 (triplet); [e]X-ray data not available; [f]multiplet.

The crystallographic and NMR spectroscopic data (Table 4.7 and Chart 4.12) show that all the 1,3-*O*-methylidene acetals derived from *neo*-inositol maintain chair conformation for the inositol ring but boat conformation for the acetal ring, in solution as well as in crystalline states. The same conformation is also the minimum energy conformation predicted by DFT calculations. A comparison of the conformation of the *myo*- and *neo*-inositol derivatives having the methylidene acetal bridge reveals that conformation of the *neo*-inositol derivatives shown in Chart 4.11 are not perturbed by change of state unlike in *myo*-inositol derivatives with 1,3-*O*-methylidene acetal (section 4.2.2). Comparison of the acetals **3.19** and **3.24** shows that a change in configuration of the inositol ring (*myo*- to *neo*-) in these methylidene acetals brings in a change in conformation of both the rings in

solution, but not necessarily in the solid state. This is similar to benzylidene acetals wherein conformational change was observed on going from *myo*- to *neo*-inositol derivatives.

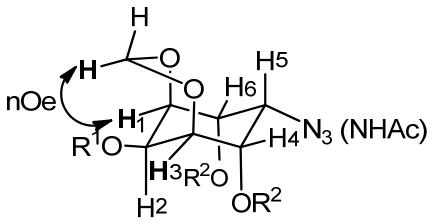


Chart 4.12: Summary of the results of 2D NMR spectroscopy for compounds **3.14**, **3.19**, **3.25**, **3.34**, **3.36** and **4.24**.

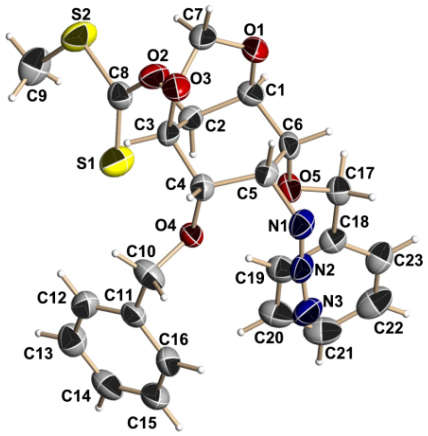


Figure 4.2: ORTEP of **4.24**. Thermal ellipsoids are drawn at 30% probability and hydrogen atoms are depicted as small spheres of arbitrary radii.

The geometry optimization studies (DFT calculations) on all these *neo*-inositol derivatives showed that the **CB** conformation is preferred over **BC** by (ΔE) 1.9 to 5.0 kcal/mol and **CC** by 1.2 to 6.9 kcal/mol (Table 4.8).

Table 4.8: Relative energies (ΔE, kcal/mol) of the possible conformations of bicyclic *neo*-inositol derivatives shown in Chart 4.11 obtained by geometrical optimization (for optimized figures see appendix III).

Compound	**3.14**	**3.19**	**3.25**	**3.34**	**3.36**	**4.24**
CB	0.0	0.0	0.0	0.0	0.0	0.0
BC	5.0	4.4	5.0	4.4	14.0	1.9
CC	5.0	5.6	5.6	5.0	1.2	6.9
BB	[a]	[a]	[a]	[a]	[a]	[a]

[a]**BB** is least stable and inherently flips over to **BC** or **CC** or **CB** during the process of optimization.

4.2.5. C1,C3-Acetals of C5-deoxy *myo*-inositol derivatives

Four possible conformations of the C1,C3-acetals of C5-deoxy-*myo*-inositol derivatives are shown in Chart 4.13.

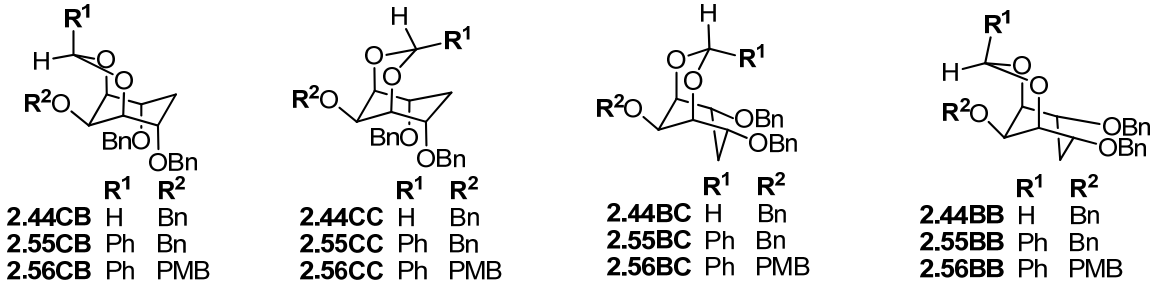


Chart 4.13: Possible conformations of the C5-deoxy *myo*-inositol derivatives (with 1,3-acetal).

Table 4.9: Conformations of C5-deoxy *myo*-inositol derivatives shown in Chart 4.13 in different phases and coupling constants ($^3J_{HH}$) for inositol ring hydrogen atoms.

				$^3J_{HH}$ (Hz)			
Compound	**Solid**[a]	**Solution**[b]	**DFT**[c]	**H1,H3**[d]	**H2**[d]	**H4,H6**[d]	**H5**[d]
2.44	**CB**	[e]	**CB**				
2.55	[f]	**CB**	**CB**	3.3[g]	2.6[h]		
2.56	**CB**	**CB**	**CB**			4.2[g]	

[a]By X-ray crystallography, see figures 2.4 and 2.2; [b]conformation arrived at based on 2D NMR spectroscopy (Chart 4.14); [c]most stable conformation indicated by geometrical optimization; [d]range of chemical shifts for H1(H3) - 4.39 to 4.55 (multiplet), H2 - 4.4 to 4.47 (broad singlet), H4(H6) - 3.8 to 3.9 (multiplet), H5 - 1.99 to 2.31 (multiplet); [e]2D NMR data not available; [f]X-ray data not available; [g]doublet; [h]triplet.

Results of NMR spectroscopy (Tables 4.9, Chart 4.14), X-ray crystallography and DFT calculations (Table 4.10) show that **2.56** exists in **CB** conformation, while the conformation of **2.55** in the solid state is not known. Conformation of **2.44** in solution state could not be ascertained clearly since coupling constants for all the hydrogen atoms could not be calculated.

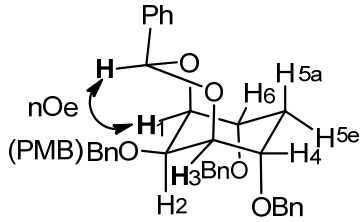


Chart 4.14: Summary of the results of 2D NMR spectroscopy for compounds **2.55** and **2.56**.

The geometry optimization studies (DFT calculations) for **2.55** and **2.56** showed that **CB** is preferred over **BC** by (ΔE) 10.7 to 11.3 kcal/mol (Table 4.10). The geometry optimization

studies (DFT calculations) for **2.44** showed that the **CB** conformation is preffered over **BC** and **CC** by 3.1 and 4.4 kcal/mol respectively.

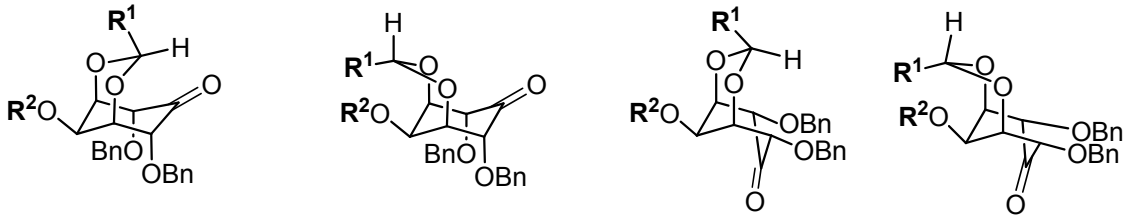
Table 4.10: Relative energies (ΔE, kcal/mol) of the possible conformations of bicyclic C5-deoxy *myo*-inositol derivatives shown in Chart 4.13 obtained by geometrical optimization (for optimized figures see appendix III).

Compound	CB	BC	CC	BB[a]
2.44	0.0	3.1	4.4	
2.55	0.0	10.7	[a]	
2.56	0.0	11.3	[a]	

[a]**BB** and **CC** are least stable and inherently flips over to **BC** and **CB** respectively during the process of optimization.

4.2.6. C1,C3-Acetal derivatives of *myo*-5-inosose

Four possible conformations of the C1,C3-acetals of *myo*-inosose derivatives are shown in Chart 4.15.



	R1	R2
1.132CC	Ph	Bn
1.138CC	H	Bn
3.72CC	Ph	PMB

	R1	R2
1.132CB	Ph	Bn
1.138CB	H	Bn
3.72CB	Ph	PMB

	R1	R2
1.132BC	Ph	Bn
1.138BC	H	Bn
3.72BC	Ph	PMB

	R1	R2
1.132BB	Ph	Bn
1.138BB	H	Bn
3.72BB	Ph	PMB

Chart 4.15: Possible conformations of C1,C3-acetal derivatives of *myo*-5-inosose.

Table 4.11: Conformations of C1,C3-acetal derivatives of *myo*-5-inosose in different phases and coupling constants ($^3J_{HH}$) for inositol ring hydrogen atoms.

				$^3J_{HH}$ (Hz)		
Compound	**Solid[a]**	**Solution[b]**	**DFT[c]**	**H1,H3[d]**	**H2[d]**	**H4,H6[d]**
1.132	**CC**	**CC**	**CC**		2.0	2.7
1.138	**CB**	**CB**	**CB**		[e]	3.8
3.72	**CC**	**CC**	**CC**		2.0	2.5

[a]By X-ray crystallography, see figure 3.10; [b]conformation arrived at based on 2D NMR spectroscopy (Chart 4.16); [c]most stable conformation indicated by geometrical optimization; [d]range of chemical shifts for H1(H3) - 4.44 to 4.52 (broad singlet), H2 - 4.23 to 4.42 (triplet), H4(H6) - 3.91 to 4.17 (doublet); [e]broad singlet.

Among the three inosose derivatives examined for conformational behavior, **1.132** and **3.72** maintained chair conformation for both the rings in solid as well as solution states (Tables 4.11; Chart 4.16). This was also the minimum energy conformation predicted by

DFT calculations (Table 4.12). The methylidene acetal **1.138** however prefered chair conformation for the inositol ring but boat conformation for the acetal ring.

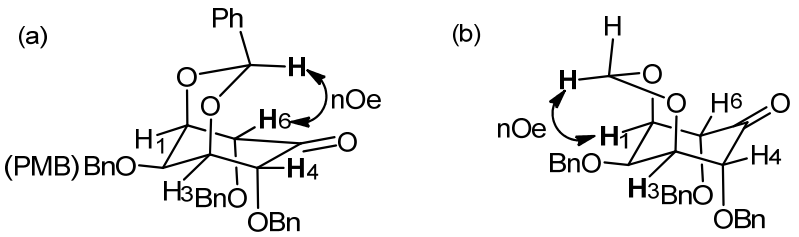


Chart 4.16: Summary of the results of 2D NMR spectroscopy for compounds (a) **1.132**, **3.72**; (b) **1.138**.

The geometry optimization studies (DFT calculations) for **1.132** and **3.72** showed that the **CC** conformation is preffered over **BC** by 1.3 to 2.5 kcal/mol and over **CB** by 4.4 to 5.0 kcal/mol (Table 4.12). However, for the inosose **1.138**, **CB** is preffered over **CC** by 0.6 kcal/mol and over **BC** by 1.9 kcal/mol. Comparison of the conformation of the inososes **1.132** and **3.72** with the corresponding alcohols **1.49** and **2.28** shows that conformation of the inositol ring changes from boat to chair on conversion of the carbon-C5 from planar sp3 to tetrahedral sp2. In the case of the methylidene acetals **1.138** and **1.47**, oxidation of the C5-OH to the corresponding ketone results in change in conformation of both the inositol and the acetal rings (**BC** to **CB**).

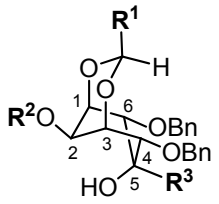
Table 4.12: Relative energies (ΔE, kcal/mol) of the possible conformations of bicyclic *myo*-5-inosose derivatives obtained by geometrical optimization (for optimized figures see appendix III).

Compound	CC	BC	CB	BB [a]
1.132	0.0	2.5	5.0	
1.138	0.6	1.9	0.0	
3.72	0.0	1.3	4.4	

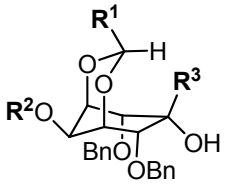
[a]**BB** is least stable and inherently flips over to **BC** or **CC** or **CB** during the process of optimization.

4.2.7. C1,C3-Acetals of 5-*C*-alkyl/aryl *neo*-inositol derivatives

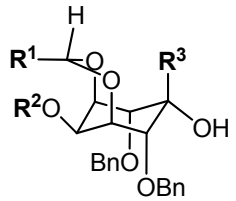
Four possible conformations of the C1,C3-acetals of C-alkylated-*neo*-inositol derivatives are shown in Chart 4.17.



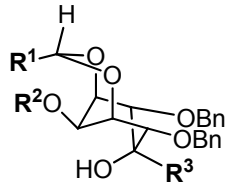
	R^1	R^2	R^3
3.73BC	H	Bn	Ph
3.74BC	Ph	Bn	Me
3.75BC	Ph	Bn	Bn
3.76BC	Ph	Bn	Ph
3.77BC	Ph	PMB	Me



	R^1	R^2	R^3
3.73CC	H	Bn	Ph
3.74CC	Ph	Bn	Me
3.75CC	Ph	Bn	Bn
3.76CC	Ph	Bn	Ph
3.77CC	Ph	PMB	Me



	R^1	R^2	R^3
3.73CC	H	Bn	Ph
3.74CC	Ph	Bn	Me
3.75CC	Ph	Bn	Bn
3.76CC	Ph	Bn	Ph
3.77CC	Ph	PMB	Me



	R^1	R^2	R^3
3.73BB	H	Bn	Ph
3.74BB	Ph	Bn	Me
3.75BB	Ph	Bn	Bn
3.76BB	Ph	Bn	Ph
3.77BB	Ph	PMB	Me

Chart 4.17: Possible conformations of C1,C3-acetals of 5-*C*-alkyl/aryl-*neo*-inositol derivatives.

Table 4.13: Conformations of C1,C3-acetals of 5-*C*-alkyl/aryl-*neo*-inositol derivatives in different phases and coupling constants ($^3J_{HH}$) for inositol ring hydrogen atoms.

				$^3J_{HH}$ (Hz)		
Compound	**Solid**[a]	**Solution**[b]	**DFT**[c]	**H1,H3**[d]	**H2**[d]	**H4,H6**[d]
3.73	**BC**	**BC**[e]	**CB**	2.2	2.2	
3.74	[f]		**BC**	2.8	2.9	
3.75[g]	-	-	**BC**	-	-	-
3.76	**BC**		**BC**	2.8	2.8	
3.77	[f]		**BC**	2.8	2.8	

[a]By X-ray crystallography, see figure 3.8; [b]2D NMR was not recorded; [c]most stable conformation indicated by geometrical optimization; [d]range of chemical shifts for H1(H3) - 4.31 to 4.40 (doublet), for H2 - 4.58 to 4.80 (triplet), H4(H6) - 3.73 to 4.33 (broad singlet); [e]conformation arrived at based on 2D NMR spectroscopy (Chart 4.18); [f]gummy solid; [g]could not be isolated and characterized due to its susceptibility to hydrolysis.

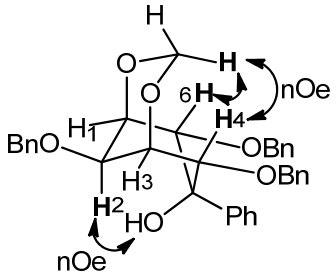


Chart 4.18: Summary of the results of 2D NMR spectroscopy for **3.73**.

From the results in Table 4.13, Chart 4.18, it is clear that all the compounds (except **3.75**) listed in Chart 4.17 maintain boat conformation for the inositol ring and chair conformation for the acetal ring, in solid and solution states, irrespective of the substituents present. The acetal **3.75** was susceptible to hydrolysis and hence could not be isolated as

mentioned in Chapter 3 (section 3B.2) and investigated by spectroscopy or crystallography for conformational behavior.

Geometry optimization studies (Table 4.14) suggested that, in the derivatives **3.74**–**3.77**, most stable conformation for the inositol ring is boat form and for acetal ring, the chair form. Geometry optimization studies for **3.73** showed that most stable conformation for the inositol ring is chair form and for the acetal ring, the boat form. It is interesting to note that the difference in energy between the CB and BC conformations for **3.73** is very less (as compared to other compounds listed in Table 4.12). This could account for the observed difference in conformation (of **3.73**) between the solution state and the minimum energy conformation predicted by DFT calculation.

Table 4.14: Relative energies (ΔE, kcal/mol) of the possible conformations of bicyclic 5-*C*-alkyl/aryl-*neo*-inositol derivatives (**3.73**–**3.77**) obtained by geometrical optimization (for optimized figures see appendix III).

Compound	BC	CC	CB	BB[a]
3.73	1.9	6.3	0.0	
3.74	0.0	1.2	4.4	
3.75	0.0	0.8	3.8	
3.76	0.0	5.0	10.0	
3.77	0.0	2.5	5.6	

[a]**BB** is least stable and inherently flips over to **BC** or **CC** or **CB** during the process of optimization.

4.2.8. C1,C5-*O*-Benzylidene *myo*-inositol derivatives

As discussed for the C1,C3-acetal derivatives of *myo*- and *neo*-inositols in previous sections, C1,C5-acetal derivatives **1.77** and **2.33**, of *myo*-inositol can exist in any of the four different conformations shown in Chart 4.19.

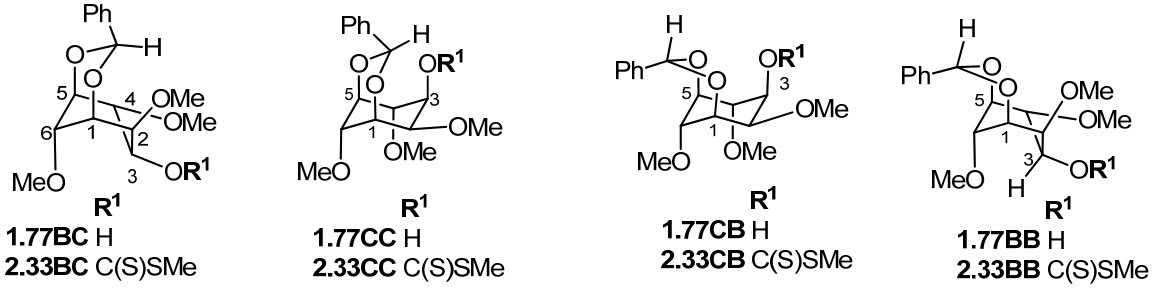


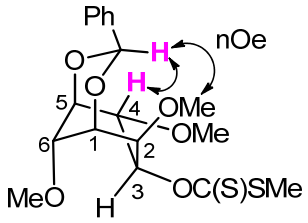
Chart 4.19: Possible conformations of the *myo*-inositol derivatives **1.77** and **2.33**.

Table 4.15: Conformation of the *myo*-inositol derivatives **1.77** and **2.33** in different phases and coupling constants ($^3J_{HH}$) for inositol ring hydrogen atoms.

				$^3J_{HH}$ (Hz)			
Compound	**Solid**[a]	**Solution**	**DFT**[b]	**H1,H2**[c]	**H3**	**H4**[c]	**H5,H6**[c]
1.77		[d]	**BC**		4.4,[e] 6.4	6.4	
2.33		**BC**[f]	**BC**		8.3[g]	8.3	

[a]Gummy solids; [b]most stable conformation indicated by geometrical optimization; [c]range of chemical shifts for H1,H2 - 4.31 to 4.40 (multiplet), H3 - 4.62 to 5.98, H4 - 3.69 to 4.07 (doublet), H5,H6 4.36 to 4.64 (multiplet); [d]2D NMR data not available; [e]doublet of doublet; [f]conformation arrived at based on 2D NMR spectroscopy (Chart 4.20); [g]doublet.

Results of NMR spectroscopy in solution (Table 4.15) suggested the conformation of the inositol and acetal rings in **1.77** and **2.33** to be boat and chair respectively. This was also the most stable conformation predicted by DFT calculations. We are of the opinion that **1.77** exists in BC conformation in solution since the differences in energy between the conformers is relatively high (as compared to those compounds which show conformational change depending on its physical state, see Table 4.17).



2.33

Chart 4.20: Conformation of the two rings in **2.33** as suggested by results of 2D NMR spectroscopy.

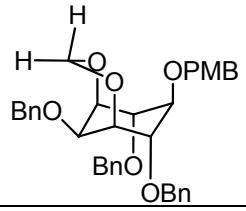
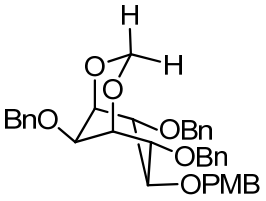
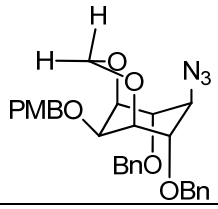
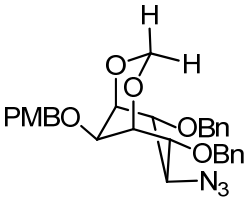
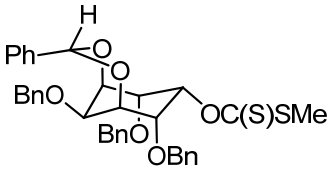
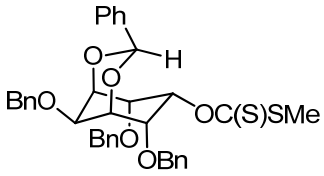
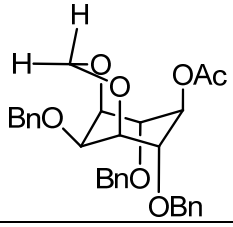
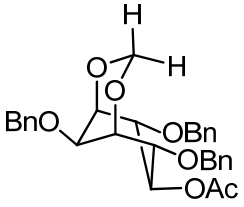
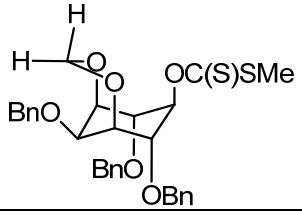
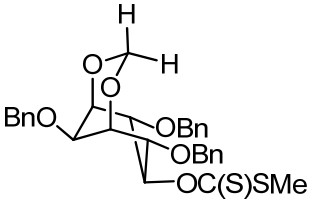
We could not obtain crystals of **1.77** and **2.33** as they are gummy solids and hence their molecular conformation in their crystals are not known. Results of the geometrical optimization for the possible conformations of **1.77** and **2.33** reveal a decreasing order of stability of the three conformers, **BC** > **CC** > **CB** (Table 4.16).

Table 4.16: Relative energies (ΔE, kcal/mol) of the possible conformations of *myo*-inositol derivatives **1.77** and **2.33** obtained by geometrical optimization (for optimized figures see appendix III).

Compound	**BC**	**CC**	**CB**	**BB**
1.77	0.0	8.1	11.0	[a]
2.33	0.0	4.3	10.8	[a]

Footnotes: [a]**BB** is least stable and inherently flips over to **BC** or **CC** or **CB** during the process of optimization.

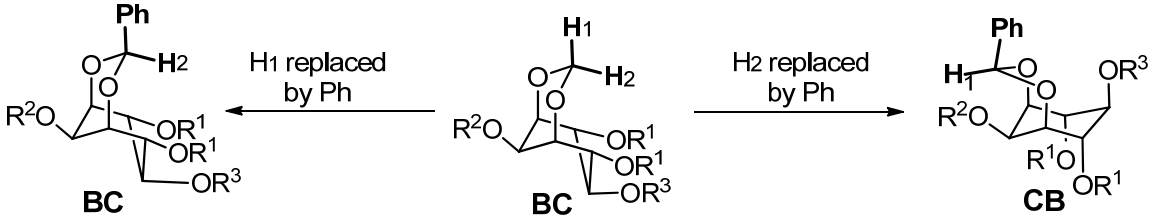
Table 4.17: List of compounds (with decreasing order of facility) which undergo conformational change from solid to solution state and comparison of difference in energy between the two forms as predicted by DFT.

Compound	Solid	Solution / DFT
4.21	**CB** 	**BC** 
	ΔE **0.2** kcal/mol	ΔE 0.0 kcal/mol
3.24	**CB** 	**BC** 
	ΔE **1.9** kcal/mol	ΔE 0.0 kcal/mol
2.48	**CB** 	**CC** 
	ΔE **2.5** kcal/mol	ΔE 0.0 kcal/mol
4.20	**CB** 	**BC** 
	ΔE **2.5** kcal/mol	ΔE 0.0 kcal/mol
2.43	**CB** 	**BC** 
	ΔE **5.6** kcal/mol	ΔE 0.0 kcal/mol

4.2.9. Possible causes for the variation in conformation among 1,3-acetals of inositols

This section makes an attempt to arrive at causes for the variation in conformation among the inositol 1,3-acetals encountered in this thesis. Table 4.17 lists compounds which undergo conformational change on change of state (from crystal to fluid – solution or as predicted by DFT). A comparison of the relative energies of the compounds which undergo conformational change in the crystalline state and those which do not undergo such a change show that these conformational changes cannot be correlated with the relative differences in energies between the conformers.

Table 4.18 compares the conformation of molecules (in the same physical state) which have a single variation in their molecular structure. This comparison reveals that *O*-substitution on the inositol hydroxyl groups do not result in a conformational change in insoitol 1,3-acetals. Conformational change in brought about by (a) change in configuration at C5 (*myo*- to *neo*-) and (b) change in configuration at the acetal carbon. The situation in (b) is schematically shown in Scheme 4.1.



Scheme 4.1

Table 4.18: Comparison of the conformation of compounds which differ in configuration at one carbon or carry different substitutent at one carbon.

Compounds which differ only in configuration at the C5 carbon		
Entry	**C5 configuration**	**Compound No. /Conformation**
1	*myo*	**1.49 / BC**
2	*neo*	**1.133 / CC**
3	*myo*	**1.135 / BC**
4	*neo*	**3.17 / CC**
5	*myo*	**2.16 / BC**
6	*neo*	**2.48 / CC**
7	*myo*	**3.16 / BC**
8	*neo*	**4.23 / CC**
9	*myo*	**4.18 / BC**
10	*neo*	**4.22 / CC**
11	*myo*	**3.24 / BC**
12	*neo*	**3.19 / CB**
Compounds which differ in configuration only at acetal carbon		
13	Benzylidene acetal	**2.16 / BC**
14	Epimer of **2.16**	**2.52 / CB**
15	Benzylidene acetal	**2.29 / BC**
16	Epimer of **2.29**	**2.53 / CB**
17	Benzylidene acetal	**2.48 / CC**
18	Epimer of **2.48**	**2.54 / CB**
Compounds which differ only in substituent at the acetal carbon		
19	Benzylidene	**1.49 / BC**
20	Methylidene	**1.47 / BC**
21	Benzylidene	**2.16 / BC**
22	Methylidene	**2.43 / BC**
23	Benzylidene	**4.18 / BC**
24	Methylidene	**4.20 / BC**
25	Benzylidene	**3.17 / CC**
26	Methylidene	**3.14 / CB**
27	Benzylidene	**1.132 / CC**
28	Methylidene	**1.138 / CB**

Table 4.18: contd.....

Compounds which differ only in substitutent at C5 or C2 (See chart 4.5)		
29	*myo*- with C1,C3-benzylidene acetal	No change in conformation
Compounds which differ only in substitutent at C5 (See chart 4.7)		
30	*myo*- with C1,C3-methylidene acetal	No change in conformation
Compounds which differ only in substitutent at C5 (See chart 4.9)		
31	*neo*- with C1,C3-benzylidene acetal	No change in conformation
Compounds which differ only in substitutent at C5 or C2 (See chart 4.11)		
32	*neo*- with C1,C3-methylidene acetal	No change in conformation
Compounds which differ only in substitutent at C2 or C4 or C6 (See chart 4.11)		
33	*neo*- with C1,C3-methylidene acetal	No change in conformation
Compounds which differ only in substitutent at C1 (See chart 4.19)		
34	*myo*- with C1,C5- benzylidene acetal	No change in conformation

4.3. Conclusions

A systematic study of the conformation of the 1,3-acetal derivatives of inositols encountered in this thesis revealed the perturbations in the bicyclic molecular framework that cause a change in conformation of the molecules. Estimation of the relative energies of the four different conformers by DFT calculations showed that the differences in energies are perhaps not high enough to freeze the conformation of these molecules in the fluid state. However, we have not computed the activation barriers between any two conformations, but it is unlikely that these are high enough to restrict the 1,3-acetal derivatives to one conformation. This is because, we do observe conformational change in some compounds on going from solid state to solution state. Hence it is likely that in solution, more than one conformer is present, although with the data available to us, their realtive ratios cannot be determined. In spite this, the conformational studies were useful in arriving at the mechanism of deoxygenation of xanthate derivatives discussed in Chapter 2.

4.4. Experimental

X-ray Data (Collection, **Structure Solution and Refinement):** Same as in the sub-section 2.4.1 (Chapter 2).

Computational details: Same as in the sub-section 2.4.2 (Chapter 2).

General Experimental Methods: Same as in the sub-section 2.4.3 (Chapter 2).

1,**3-*O*-Methylidene-2**,**4**,**6-tri-*O*-benzyl-5-*O*-(4-methoxybenzyl)-*myo*-inositol (4.21):** The alcohol **1.47** (4.62 g, 10.0 mmol), dry DMF (25 mL), sodium hydride (0.48 g, 12.0 mmol), *p*-methoxybenzyl chloride (1.6 mL, 12.0 mmol) were used (Procedure B of section 3D.2 of chapter 3) to obtain **4.21** as a colorless solid (5.59 g, 96%) after coloumn chromatography (eluent: 15% ethyl acetate in light petroleum). TLC R_f = 0.3 (10% ethyl acetate/light petroleum); **mp** 88–90 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.18-7.41 (m, 17H, Ar H), 6.82-6.86 (m, 2H, Ar H), 5.19 (d, 1H, H_2CO_2, J = 5.5 Hz), 4.84 (d, 1H, H_2CO_2, J = 5.5 Hz), 4.50-4.67 (m, 8H, 4 × CH_2), 4.27 (brs, 2H, Ins H), 3.94 (d, 2H, Ins H, J = 5.5 Hz), 3.84 (t, 1H, Ins H, J = 1.8 Hz), 3.79 (s, 3H, CH_3), 3.62 (t, 1H, Ins H, J = 5.5 Hz) ppm; **^{13}C NMR** ($CDCl_3$, 100.6 MHz): δ 159.2 (C_{arom}), 137.7 (C_{arom}), 130.4 (C_{arom}), 129.5 (C_{arom}), 128.5 (C_{arom}), 128.4 (C_{arom}), 127.9 (C_{arom}), 127.8 (C_{arom}), 113.7 (C_{arom}), 85.5 (H_2CO_2), 82.1 (Ins C), 79.6 (Ins C), 73.1 (CH_2), 72.0 (Ins C), 71.7 (CH_2), 71.0 (CH_2), 70.2 (Ins C), 55.3 (CH_3) ppm; elemental analysis calcd (%) for $C_{36}H_{38}O_7$ (582.68): C 74.21, H 6.57; found: C 74.47, H 6.75 %.

1,**3-*O*-Methylidene-2-*O*-[(methylthio)thiocarbonyl]-4**,**6-di-*O*-benzyl-5-azido-5-deoxy-*neo*-inositol (4.24):** The alcohol **3.25** (1.00 g, 2.51 mmol), dry THF (15 mL), sodium hydride (0.5 g, 12.5 mmol), carbon disulfide (2.2 mL, 37.0 mmol) and methyl iodide (0.8 mL, 24.19 mmol) were used (Procedure A of section 2.4. of chapter 2) to obtain the xanthate **4.24** as a yellow crystals (1.02 g, 84%) after crystallization from hot 20% ethyl acetate in light petroleum. TLC R_f = 0.3 (10% ethyl acetate/light petroleum); **mp** 118–119.5 °C; **IR** ($CHCl_3$): $\bar{\nu}$ 2116 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.27-7.42 (m, 10H, Ar H), 6.64 (brs, 1H, Ins H), 5.29 (d, 1H, H_2CO_2, J = 5.2 Hz), 4.74 (q, 4H, 2 × CH_2, J = 12 Hz), 4.69 (d, 1H, H_2CO_2, J = 5.2 Hz), 4.53 (d, 2H, Ins H, , J = 3.0 Hz), 4.13 (t, 2H, Ins H, J = 4.1 Hz), 3.74 (t, 1H, J = 4.3 Hz, Ins H), 2.59 (s, 3H, CH_3) ppm; **^{13}C NMR** ($CDCl_3$, 125.76 MHz): δ 214.0 (C=S), 137.3 (C_{arom}), 128.3 (C_{arom}), 127.9 (C_{arom}), 127.8 (C_{arom}), 85.7 (H_2CO_2), 79.9 (Ins C), 74.6 (Ins C), 73.5 (CH_2), 70.3 (Ins C), 53.2 (Ins C), 19.3 (CH_3) ppm; elemental analysis calcd (%) for $C_{23}H_{25}O_3N_5S_2$ (487.59): C 56.66, H 5.17; found: C 56.42, H 5.51 %.

4.5. References

1. Lee, S. J.; Cho, S. J.; Oh, K. S.; Cui, C.; Ryu, Y.; Chang, Y. T.; Kim, K. S.; Chung, S. K. *J. Phys. Chem.* **1996**, *100*, 10111–10115; (b) Salazar-Pereda, V.; Martinez-Martinez, F. J.; Contreras, R.; Flores-Parra, A. *J. Carbohydr. Chem.* **1997**, *16*, 1479–1507; (c) Husson, Ch.; Delangle, P.; Pecaut, J.; Vottero, Ph. J. A.; *Inorg. Chem.* **1999**, *38*, 2012–2019; (d) Sureshan, K. M.; Miyasou, T.; Watanabe, Y. *Carbohydr. Res.* **2004**, *339*, 1551–1555; (e) Sureshan, K. M.; Watanabe, Y. *Carbohydr. Res.* **2005**, *340*, 2311–2318 and references cited therein.
2. Liang, C.; Ewing, C. S.; Stouch, T. R.; Hagler, A. T. *J. Am. Chem. Soc.* **1994**, *116*, 3904–3911.
3. (a) Hancock, R. D.; Hegetschweiler, K. *J. Chem. Soc. Dalton Trans. I*, **1993**, 2137-2140; (b) Biamonte, M. A.; Vasella, A. *Helv. Chim. Acta*, **1998**, *81*, 695–717; (c) De Almeda, M. V.; Figueiredo, R. M.; Dos Santos, H. F.; Da Silva, A. D.; Almeida, W. B. *Tetrahedron Lett.* **2001**, *42*, 2767–2769; (d) Dos Santos, H. F.; De Almeida, M. V.; De Almeida, W. B. *Theor. Chem. Acc.* **2002**, *107*, 229–240; (e) Serrano, P.; Llebaria, A.; Vázquez, J.; Pablo, J. D.; Anglada, J. M.; Delgado, A. *Chem. Eur. J.* **2005**, *11*, 4465–4472; (f) For epoxide see ref: De Almeida, M. V.; De Assis, J. V.; Couri, M. R. C.; Anconi, C. P. A.; Guerreiro, M. C.; Dos Santos, H. F.; De Almeida, W. B. *Org. Lett.* **2010**, *12*, 5458–5461.
4. (a) Chung, S.-K.; Ryu, Y. *Carbohydr. Res.* **1994**, *258*, 145–167; (b) Kim, K. S.; Cho, S. J.; Oh, K. S.; Son, J. S.; Kim, J.; Lee, J. Y.; Lee, S. J.; Lee, S.; Chang, Y. T.; Chung, S. K.; Ha, T. K.; Lee, B. S.; Lee, I. *J. Phys. Chem.* **1997**, *101*, 3776–3783; (c) Vibhute, A. M.; Vidyasagar, A.; Sarala, S.; Sureshan, K. M. *Chem. Commun.*, **2012**, *48*, 2448–2450.
5. Uhlmann, P.; Vasella, A. *Helv. Chim. Acta*, **1992**, *75*, 1979–1994.
6. Mansell, D.; Veiga, N.; Torres, J.; Etchells, L. L.; Bryce, R. A.; Kremer, C.; Freeman, S. *Tetrahedron,* **2008**, *66*, 8949–8957.
7. Vibhute, A. M.; Gonnade, R. G.; Swathi, R. S.; Sureshan, K. M. *Chem. Commun.* **2012**, *48*, 717–719.
8. Murali, C. Ph.D thesis, University of Pune, India, **2008**.
9. Gilbert, I. H.; Holmes, A. B.; Pestchanker, M. J.; Young R. C. *Carbohydr. Res.* **1992**, *234*, 117–130.
10. Sala, M.; Kolar, J.; Strlič, M.; Kočevarb, M. *Carbohydr. Res.* **2006**, *341*, 897–902.
11. Grove, S. J. A.; Gilbert, I. H.; Holmes, A. B.; Painter, G. F.; Hill, M. L. *Chem. Commun*. **1997**, 1633–1634.
12. Jagdhane, R. C.; Shashidhar, M. S. *Tetrahedron*, **2011**, *67*, 7963–7970.

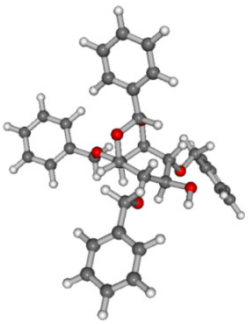
Appendix III

Appendix III Index

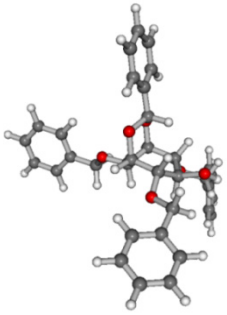
Crystal Data Table

Compound No.	**3.141**	**4.20**	**4.21**	**4.24**
Chemical formula	$C_{10}H_{18}O_6$	$C_{30}H_{32}O_7$	$C_{36}H_{38}O_7$	$C_{23}H_{25}N_3O_5S_2$
M_r	234.24	504.56	582.68	487.58
Temperature/K	297(2)	100(2)	100(2)	297(2)
Morphology	Plate	Needle	Needle	
Crystal size	0.34×0.16×0.09	0.88×0.07×0.05	0.27×0.18×0.13	0.55×0.44×0.11
Crystal system, Space group	triclinic, *P*-1	monoclinic *P*2/c	monoclinic $P2_1/c$	orthorhombic $P_{na}2/1$
a (Å) *b* (Å) *c* (Å) α (°) *β* (°) γ (°)	6.3888(10) 9.6401(15) 9.8673(16) 83.005(3) 79.552(3) 80.874(3)	32.819(3) 6.5670(8) 24.110(3) 90 99.107 (9) 90	10.0332(18) 20.599(3) 14.737(3) 90 93.011(9) 90	10.062(3) 16.545(4) 14.565(4) 90 90 90
Volume *V* (Å^3)	587.36(16)	5130.8(10)	3041.7(9)	2424.7(11)
Z	2	8	6	4
D_{calc} (g cm^{-3})	1.324	1.306	1.272	1.336
μ (mm^{-1})	0.109	0.092	0.087	0.258
F(000)	252	2144	1240	1024
Absorption correction T_{min} / T_{max}	multi-scan 0.9636 / 0.9908	multi-scan 0.9227 / 0.9950	multi-scan 0.9766 / 0.9885	multi-scan 0.8721 / 0.9721
θ_{max} (°)	25	25	25	25
h, k, l (min, max)	(-7,7), (-11,11), (-11,11)	(-39,39), (-7,7), (-28,28)	(-12,12), (-24,24), (-15,17)	(-11,11), (-17,19), (-17,10)
Reflns collected	5733	67609	28310	11718
Unique reflns, Observed reflns	2070, 1927	9030 7463	5504 3454	3768 3152
R_{int}	0.0157	0.0649	0.1019	0.0228
No. of parameters	152	780	390	299
(GoF)	1.122	1.190	1.092	1.024
*R*1 [$I > 2\sigma(I)$] *wR*2 [$I > 2\sigma(I)$]	0.0486 0.1141	0.0692 0.1223	0.0793 0.2135	0.0443 0.1021
*R*1 (all data) *wR*2 (all data)	0.0519 0.1161	0.0879 0.1296	0.1246 0.2620	0.0542 0.1079
$\Delta\rho_{max}$,$\Delta\rho_{min}$(eÅ^{-3})	0.197,-0.158	0.274,-0.251	0.977,- 0.425	0.373,-0.222

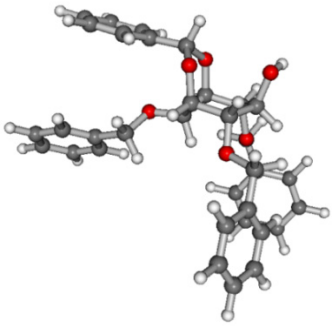
Figure A1: Results of geometrical optimization of possible conformations of bicyclic *myo*-inositol derivatives with 1,3-*O*-benzylidene acetal.



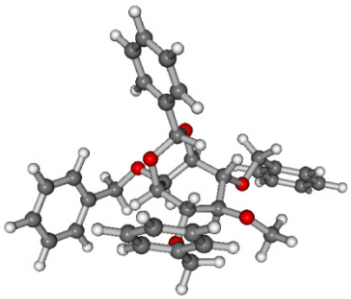
1.49BC
ΔE **0.0** kcal/mol



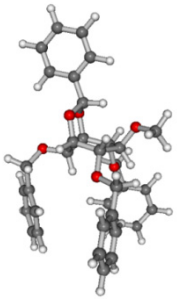
1.49CC
ΔE **4.4** kcal/mol



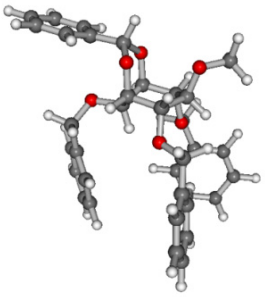
1.49CB
ΔE **9.4** kcal/mol



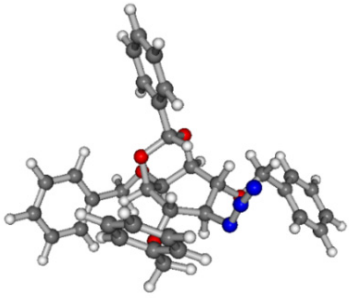
1.130BC
ΔE **0.0** kcal/mol



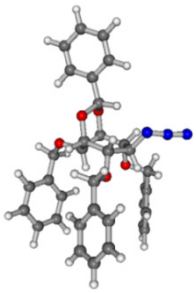
1.130CC
ΔE **1.2** kcal/mol



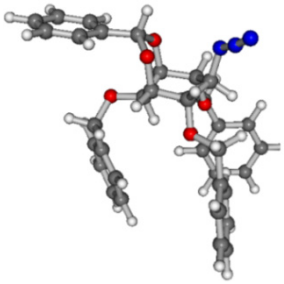
1.130CB
ΔE **5.0** kcal/mol



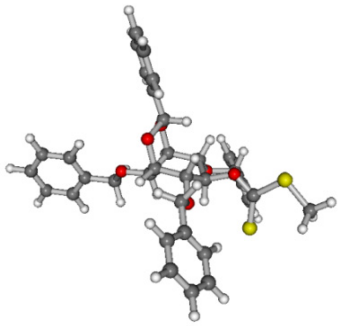
1.135BC
ΔE **0.0** kcal/mol



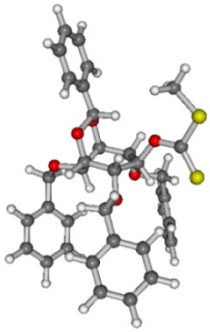
1.135CC
ΔE **0.2** kcal/mol



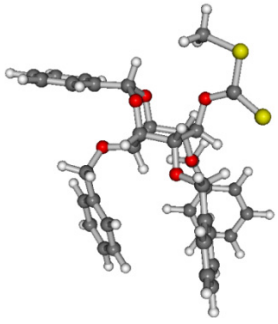
1.135CB
ΔE **3.8** kcal/mol



2.16BC
ΔE **0.0** kcal/mol

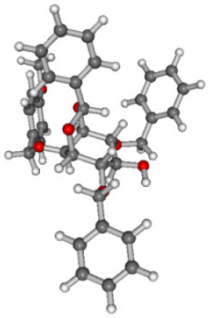


2.16CC
ΔE **2.8** kcal/mol

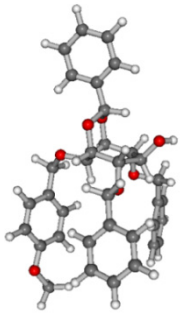


2.16CB
ΔE **4.5** kcal/mol

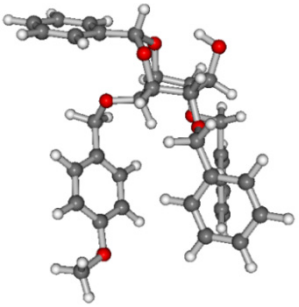
Figure A1: Contd...



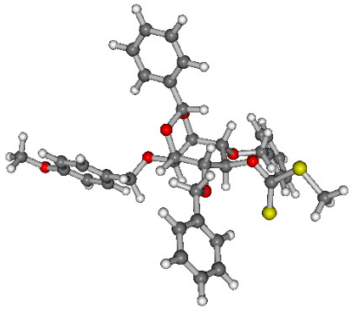
2.28BC
ΔE **0.0** kcal/mol



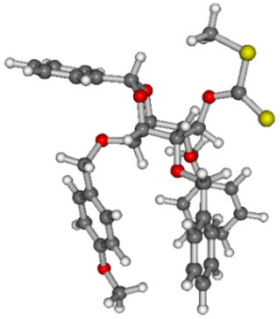
2.28CC
ΔE **3.1** kcal/mol



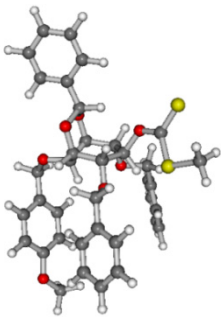
2.28CB
ΔE **3.8** kcal/mol



2.29BC
ΔE **0.0** kcal/mol

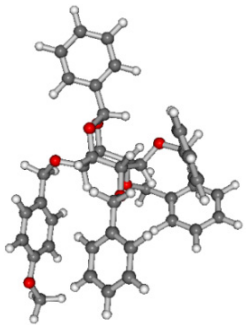


2.29CB
ΔE **4.7** kcal/mol

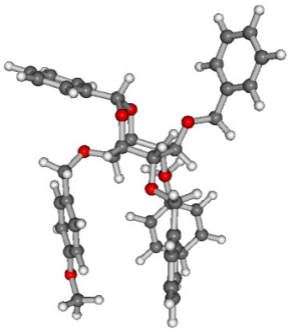


2.29CC
ΔE **5.2** kcal/mol

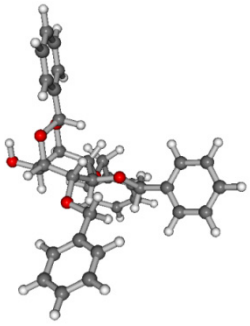
2.37BC
ΔE **0.0** kcal/mol



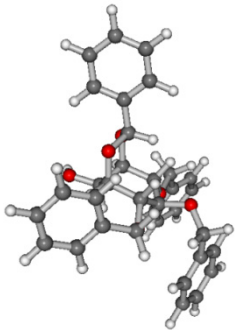
2.37CC
ΔE **2.5** kcal/mol



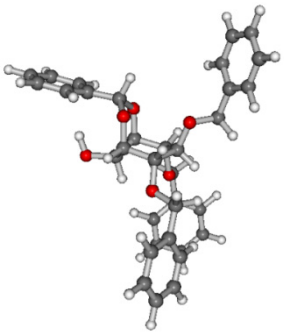
2.37CB
ΔE **5.0** kcal/mol



2.38BC
ΔE **0.0** kcal/mol

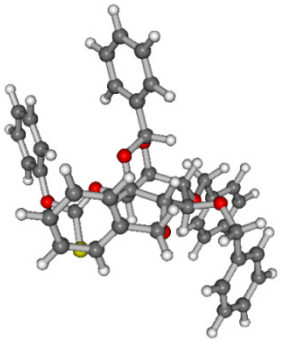


2.38CC
ΔE **4.4** kcal/mol

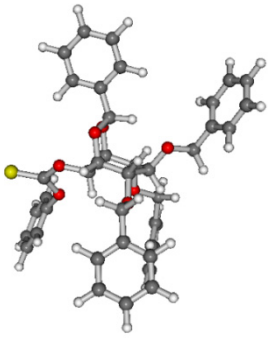


2.38CB
ΔE **6.3** kcal/mol

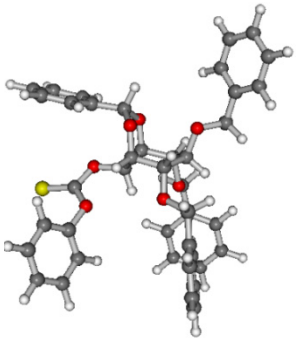
Figure A1: Contd...



2.40BC
ΔE **0.0** kcal/mol



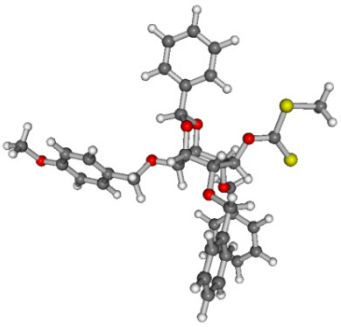
2.40CC
ΔE **1.9** kcal/mol



2.40CB
ΔE **7.5** kcal/mol

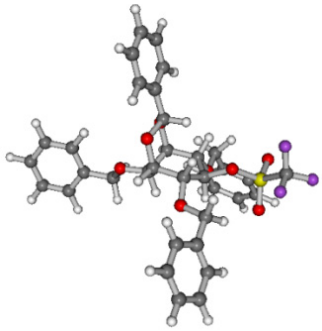
2.52CB
ΔE **0.0** kcal/mol

2.52BB
ΔE **6.3** kcal/mol

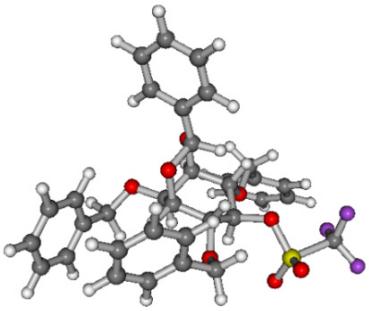


2.53CB
ΔE **0.0** kcal/mol

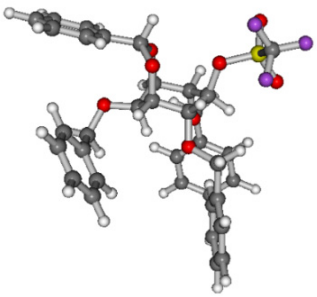
2.53BB
ΔE **6.3** kcal/mol



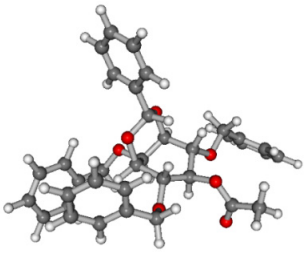
3.16BC
ΔE **0.0** kcal/mol



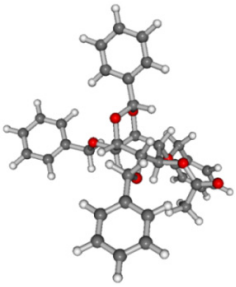
3.16CC
ΔE **0.6** kcal/mol



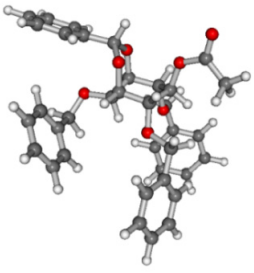
3.16CB
ΔE **5.0** kcal/mol



4.18BC
ΔE **0.0** kcal/mol

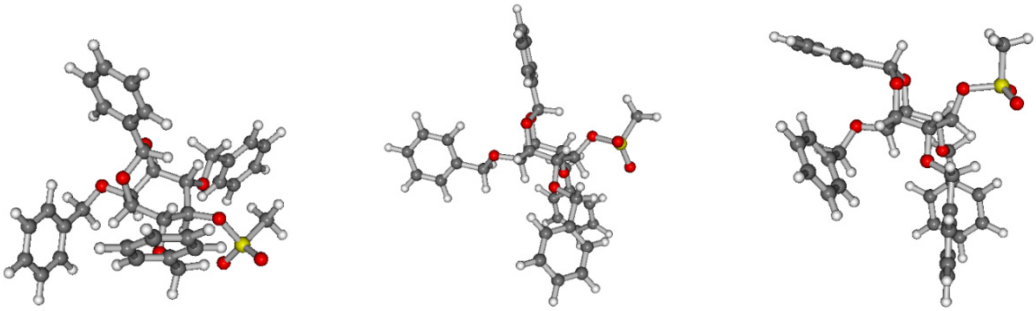


4.18CC
ΔE **0.6** kcal/mol



4.18CB
ΔE **12.5** kcal/mol

Figure A1: Contd...

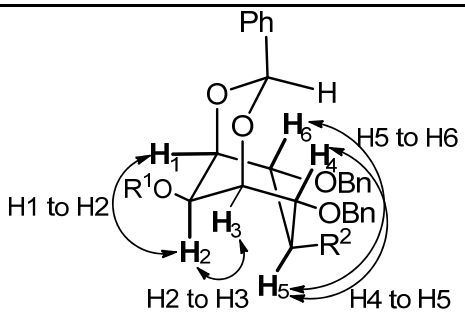


4.19BC
ΔE **0.0** kcal/mol

4.19CC
ΔE **3.1** kcal/mol

4.19CB
ΔE **5.6** kcal/mol

Table A1: Calculated dihedral angles from DFT structures and coupling constants ($^3J_{HH}$) for most stable conformation by Karplus equation (graphical tool MestRe-J)[a].

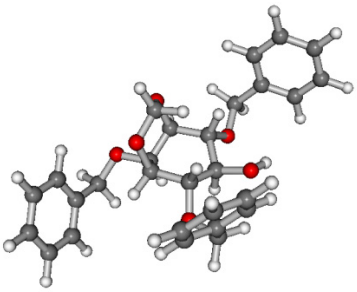


***myo*-BC**

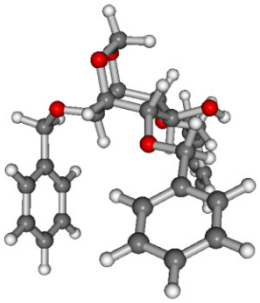
	1.49	**1.130**	**1.135**	**2.16**	**2.28**	**2.29**	**2.37**	**2.38**	**2.40**	**3.16**	**4.18**	**4.19**
H2 to H1	69	70	69	68	68	69	69	69	69	70	69	69
H2 to H3	69	69	69	68	68	68	72	71	66	69	68	68
Calculated *J* in Hz	**2.1–2.2 Hz**											
H1 to H6	103	103	101	105	103	103	97	102	101	102	106	107
H3 to H4	106	103	99	106	106	103	98	102	103	102	104	104
Calculated *J* in Hz	**1.8-2.03 Hz**											
H5 to H4	161	157	154	159	163	153	147	154	155	154	158	161
H5 to H6	158	157	156	158	161	152	147	153	153	152	158	159
Calculated *J* in Hz	**7.8-9.3 Hz**											

[a]Navarro-Vazquez, A.; Cobas, J. C.; Sardina, F. J.; Casanueva, J.; Diez, E. *J. Chem. Inf. Comput. Sci.* **2004**, *44*, 1680–1685.

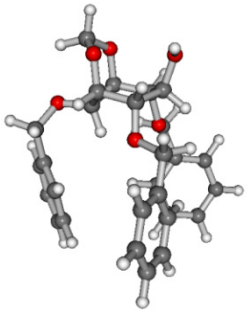
Figure A2: Results of geometrical optimization of *myo*-inositol derivatives with 1,3-*O*-methylidene acetal.



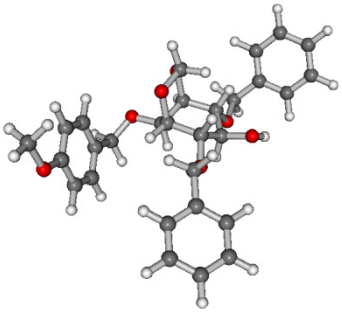
1.47BC
ΔE **0.0** kcal/mol



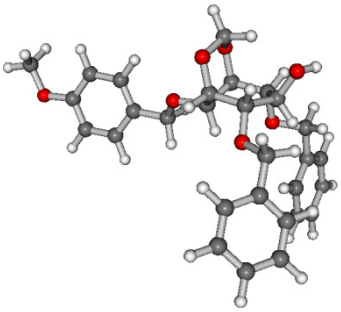
1.47CC
ΔE **3.8** kcal/mol



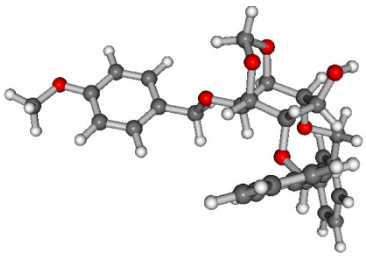
1.47CB
ΔE **4.4** kcal/mol



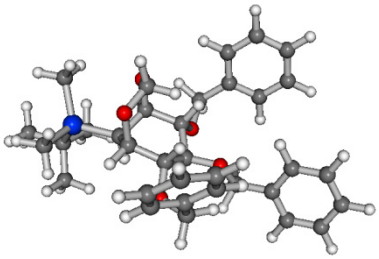
1.55BC
ΔE **0.0** kcal/mol



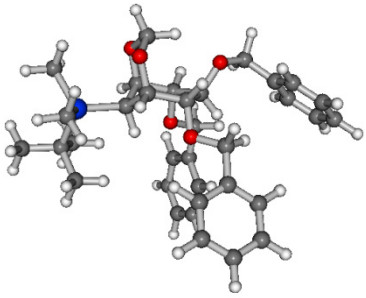
1.55CB
ΔE **1.2** kcal/mol



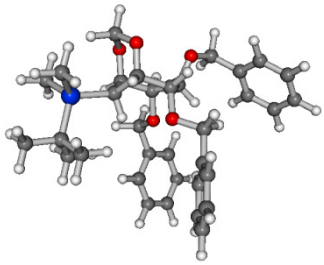
1.55CC
ΔE **5.0** kcal/mol



1.107BC
ΔE **0.0** kcal/mol

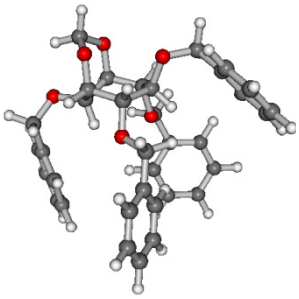


1.107CC
ΔE **2.5** kcal/mol

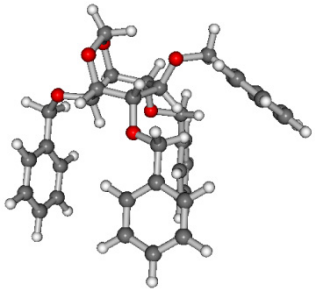


1.107CB
ΔE **4.4** kcal/mol

1.111BC
ΔE **0.0** kcal/mol

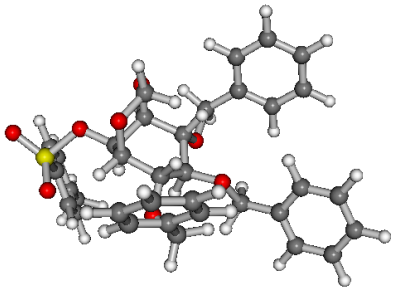


1.111CB
ΔE **0.2** kcal/mol

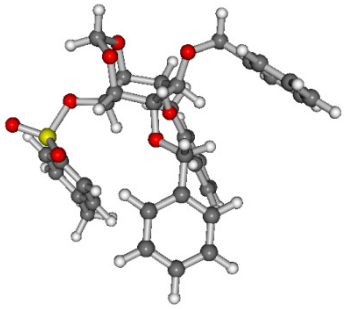


1.111CC
ΔE **1.9** kcal/mol

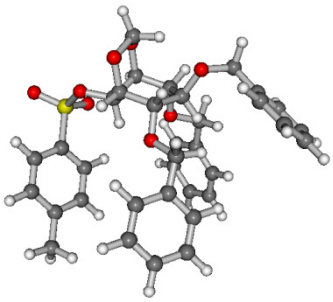
Figure A2: Contd....



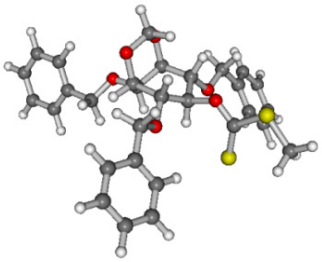
1.148BC
ΔE **0.0** kcal/mol



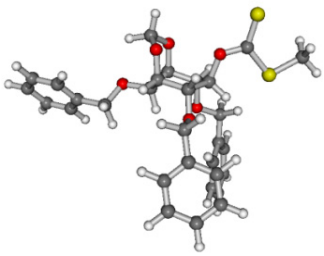
1.148CB
ΔE **0.6** kcal/mol



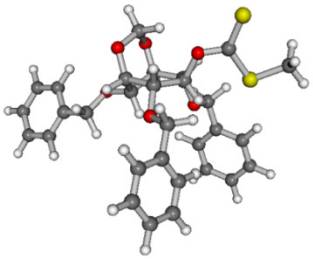
1.148CC
ΔE **1.9** kcal/mol



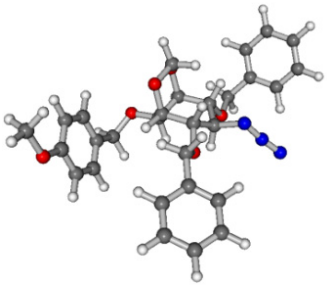
2.43BC
ΔE **0.0** kcal/mol



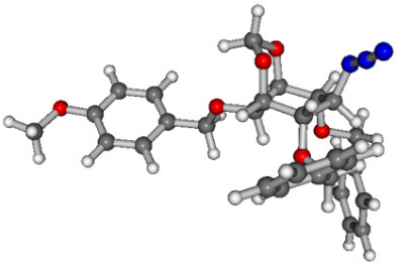
2.43CB
ΔE **5.6** kcal/mol



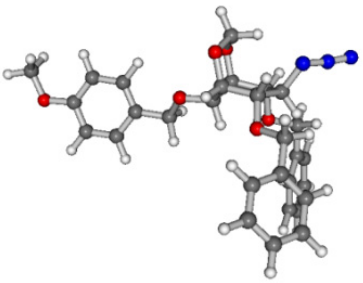
2.43CC
ΔE **6.3** kcal/mol



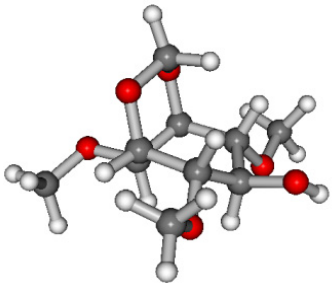
3.25BC
ΔE **0.0** kcal/mol



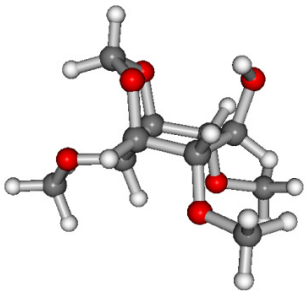
3.25CB
ΔE **1.9** kcal/mol



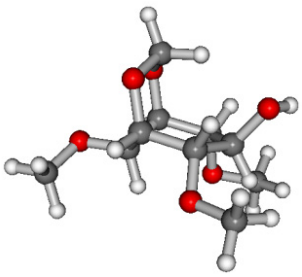
3.25CC
ΔE **4.4** kcal/mol



3.141BC
ΔE **0.0** kcal/mol

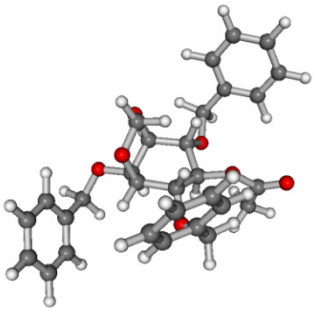


3.141CB
ΔE **2.5** kcal/mol

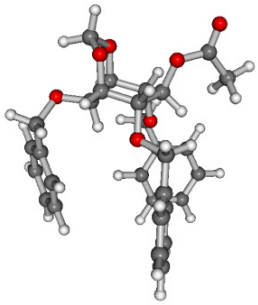


3.141CC
ΔE **4.4** kcal/mol

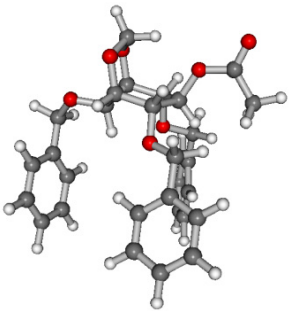
Figure A2: Contd....



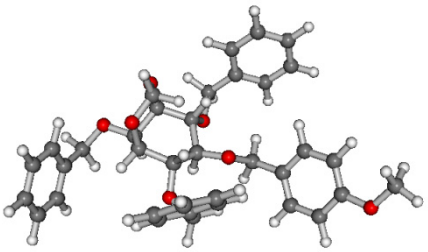
4.20BC
ΔE **0.0** kcal/mol



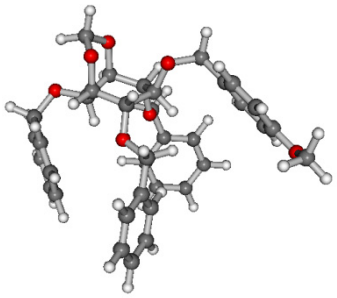
4.20CB
ΔE **2.5** kcal/mol



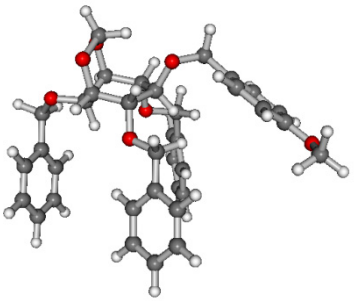
4.20CC
ΔE **5.6** kcal/mol



4.21BC
ΔE **0.0** kcal/mol

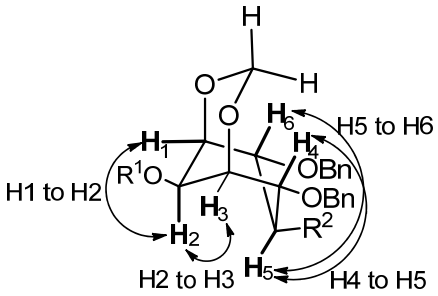


4.21CB
ΔE **0.2** kcal/mol



4.21CC
ΔE **2.1** kcal/mol

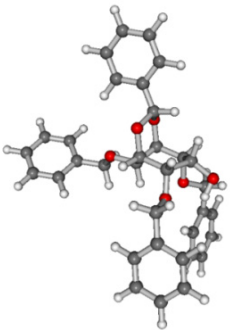
Table A2: Calculated dihedral angles from DFT structures and coupling constants ($^3J_{HH}$) by Karplus equation (graphical tool MestRe-J).



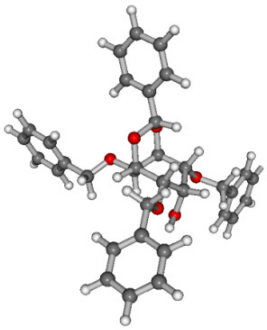
***myo*-BC**

Dihedral Angle and *J* in Hz	**H1 to H2,H3**	**H1 to H6 H3 to H4**	**H4 to H5 H6 to H5**
1.111 BC	69 (2.0 Hz)	105 (2.2 Hz)	159 (9.0 Hz)
4.21BC	70 (1.9 Hz)	101 (1.89 Hz)	153 (8.5 Hz)
Similar values for other derivatives			

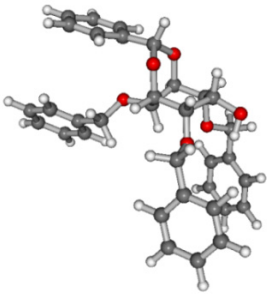
Figure A3: Results of geometrical optimization of possible conformations of bicyclic *neo*-inositol derivatives (with 1,3-*O*-benzylidene acetal).



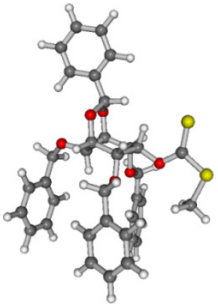
1.133CC
ΔE **0.0** kcal/mol



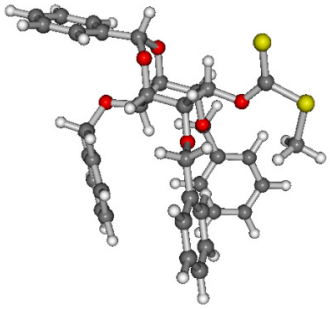
1.133BC
ΔE **1.9** kcal/mol



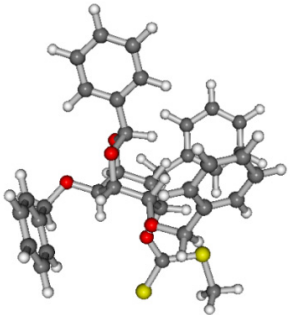
1.133CB
ΔE **3.1** kcal/mol



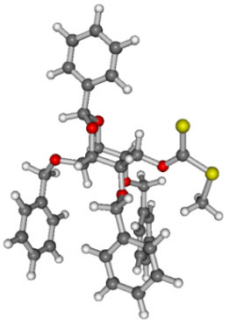
2.48CC
ΔE **0.0** kcal/mol



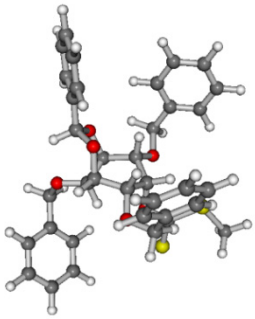
2.48CB
ΔE **2.5** kcal/mol



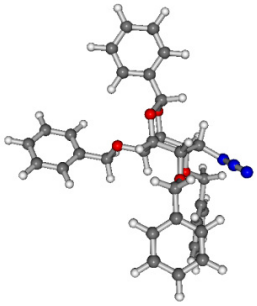
2.48BC
ΔE **3.8** kcal/mol



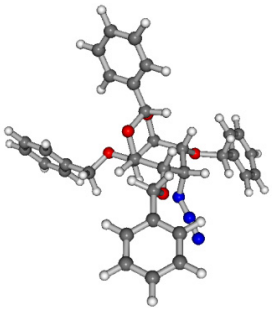
2.54CB
ΔE **0.0** kcal/mol



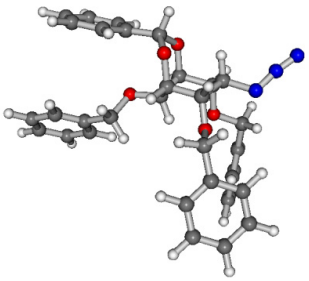
2.54BB
ΔE **6.9** kcal/mol



3.17CC
ΔE **0.0** kcal/mol

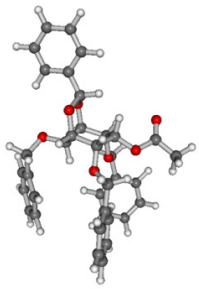


3.17BC
ΔE **0.6** kcal/mol

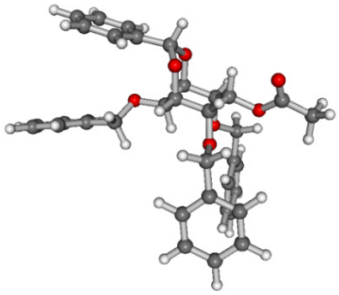


3.17CB
ΔE **2.5** kcal/mol

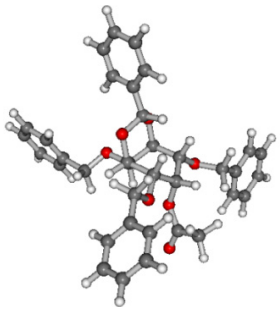
Figure A3: Contd....



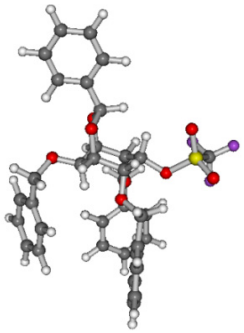
4.22CC
ΔE **0.0** kcal/mol



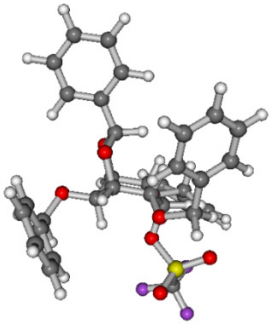
4.22CB
、ΔE **2.5** kcal/mol



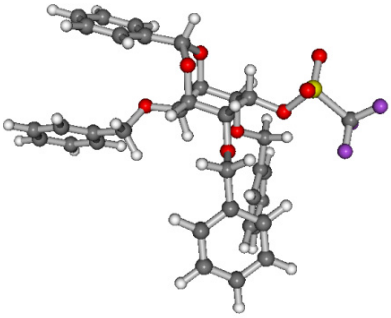
4.22BC
ΔE **7.5** kcal/mol



4.23CC
ΔE **0.0** kcal/mol

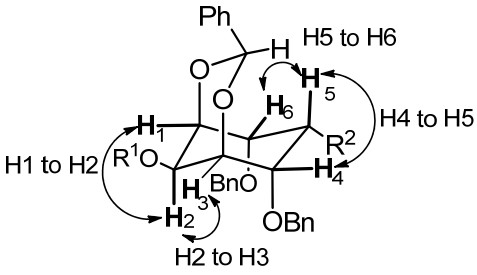


4.23BC
ΔE **0.6** kcal/mol



4.23CB
ΔE **1.9** kcal/mol

Table A3: Calculated dihedral angles from DFT structures and coupling constants ($^3J_{HH}$) for most stable conformation by Karplus equation (graphical tool MestRe-J).



***neo*-CC**

	H1 to H2,H3	**H1 to H6 H3 to H4**	**H4 to H5 H6 to H5**
Dihedral Angle and *J* in Hz for compounds shown in Chart 4.9	68-70 (1.9-2.1 Hz)	69-71 (1.8-2.0 Hz) 65-68 (2.0-2.3 Hz)	41–44 (4.6-5.0 Hz)

Figure A4: Results of geometrical optimization of *neo*-inositol derivatives with 1,3-*O*-methylidene acetal.

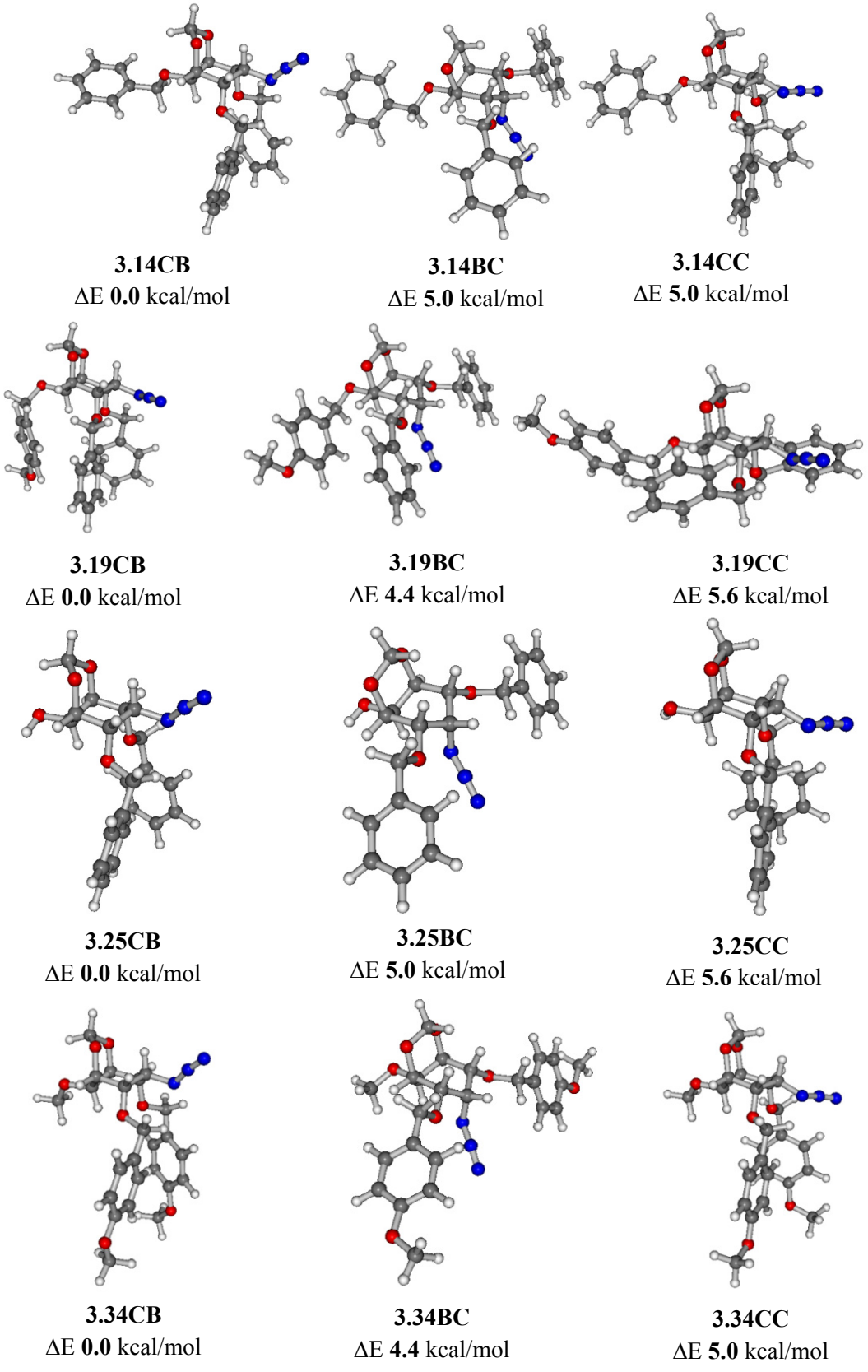
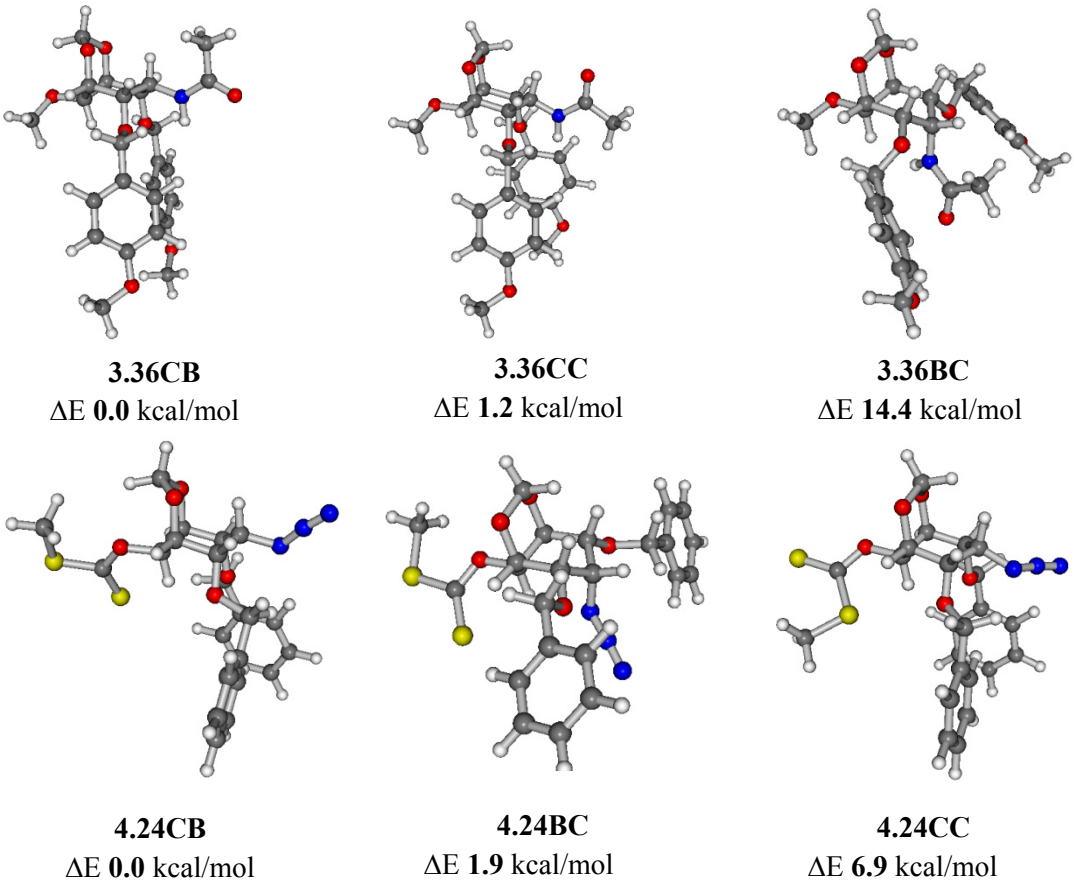


Figure A4: Contd.....



3.36CB
ΔE **0.0** kcal/mol

3.36CC
ΔE **1.2** kcal/mol

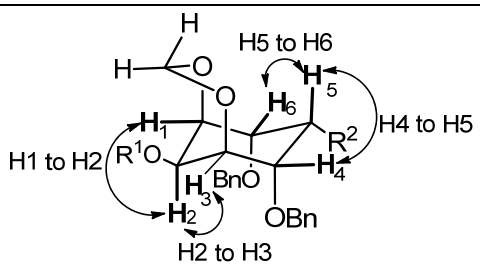
3.36BC
ΔE **14.4** kcal/mol

4.24CB
ΔE **0.0** kcal/mol

4.24BC
ΔE **1.9** kcal/mol

4.24CC
ΔE **6.9** kcal/mol

Table A4: Calculated dihedral angles from DFT structures and coupling constants ($^3J_{HH}$) for most stable conformation by Karplus equation (graphical tool MestRe-J)



***neo*-CC**

Dihedral Angle and *J* in Hz	**H1 to H2,H3**	**H1 to H6 H3 to H4**	**H4 to H5 H6 to H5**
3.14CB	66 (2.24 Hz)	111 (2.8 Hz)	45 (4.5 Hz)
Similar values for other derivatives			

Figure A5. Results of geometrical optimization of possible conformations of the C5-deoxy inositol derivatives.

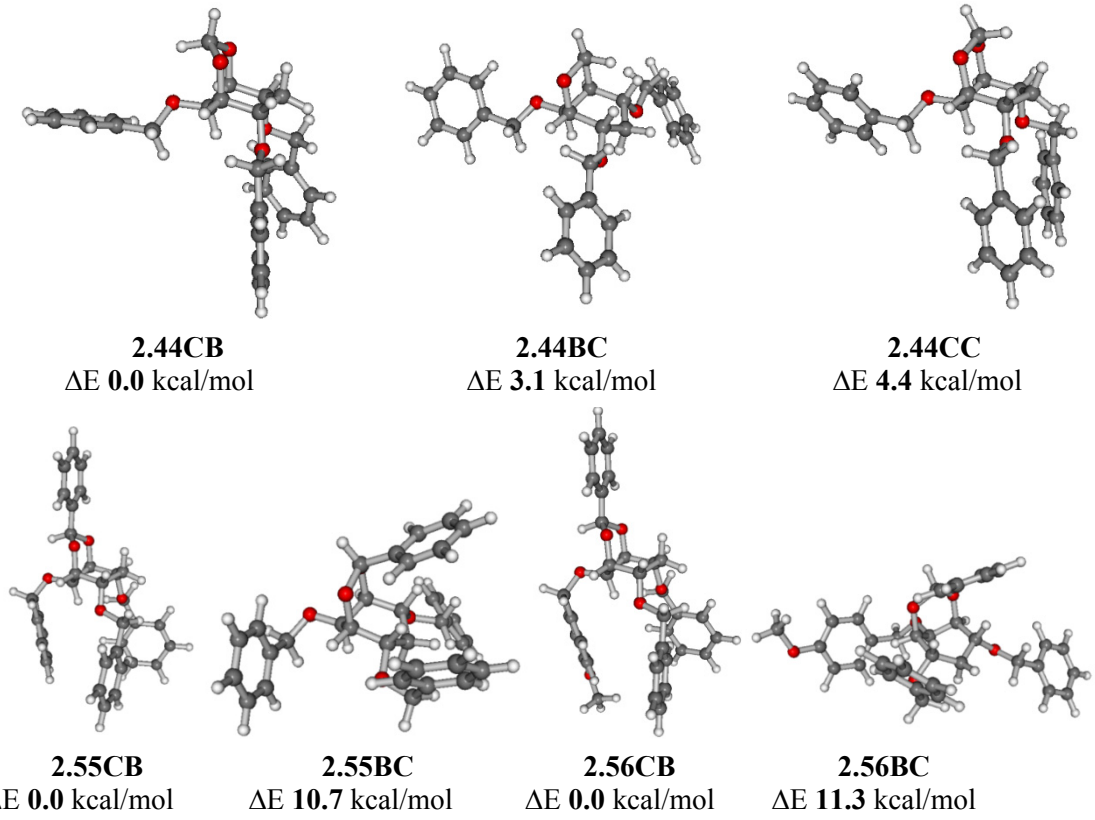


Figure A6: Results of geometrical optimization of possible conformations of the *myo*-5-inosose (with 1,3-acetal).

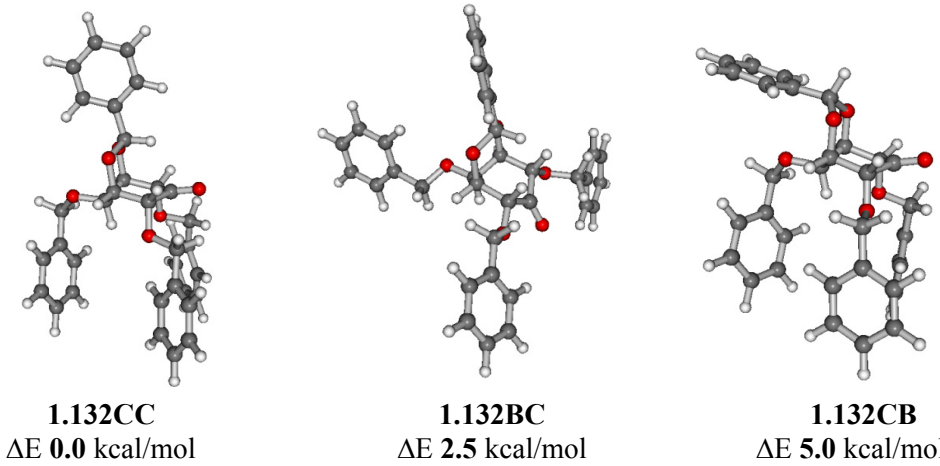
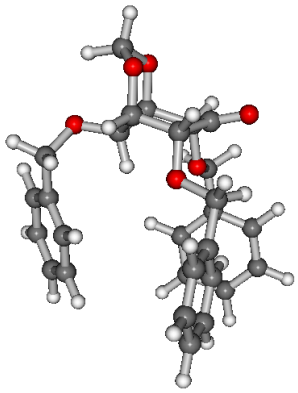
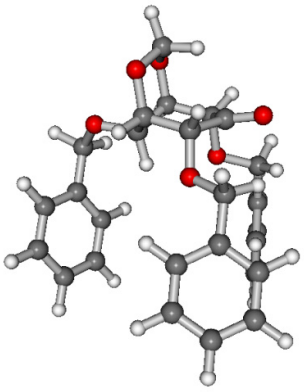


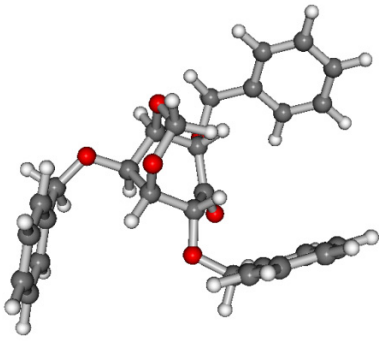
Figure A6: Contd.....



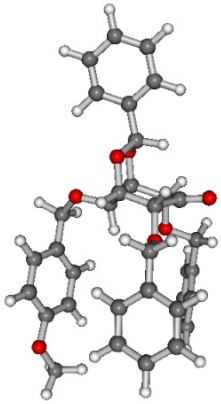
1.138CB
ΔE **0.0** kcal/mol



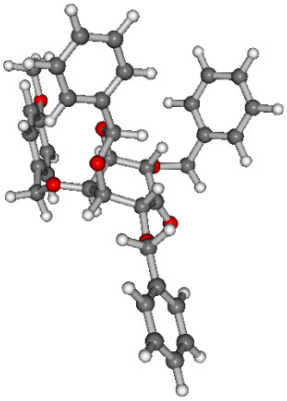
1.138CC
ΔE **0.6** kcal/mol



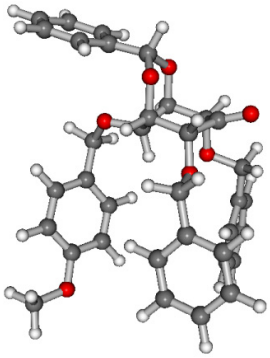
1.138BC
ΔE **1.9** kcal/mol



3.72CC
ΔE **0.0** kcal/mol



3.72BC
ΔE **1.3** kcal/mol

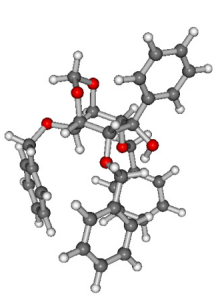


3.72CB
ΔE **4.4** kcal/mol

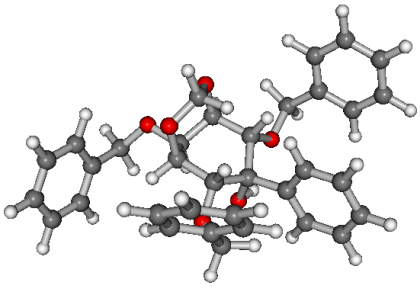
Table A5: Calculated dihedral angles from DFT structures and coupling constants ($^3J_{HH}$) for most stable conformation by Karplus equation (graphical tool MestRe-J).

Dihedral Angle and *J* in Hz	**H1 to H2,H3**	**H1 to H6 H3 to H4**
1.132	70 (2.0 Hz)	71 (1.9 Hz)
1.138	73 (1.7 Hz)	68 (2.3 Hz)
3.72	71 (1.9 Hz)	69 (2.2 Hz)

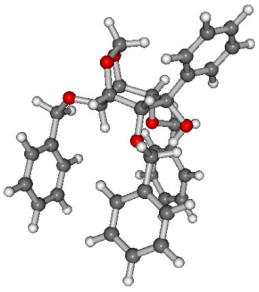
Figure A7: Results of geometrical optimization of possible conformations of 1,3- actals of 5-*C*-alkyl/aryl-*neo*-inositol derivatives (**3.73**–**3.77**).



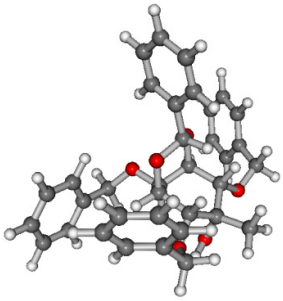
3.73CB
ΔE **0.0** kcal/mol



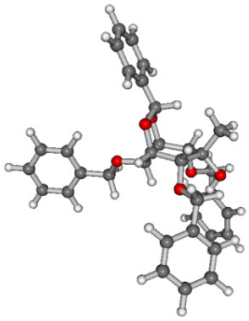
3.73BC
ΔE **1.9** kcal/mol



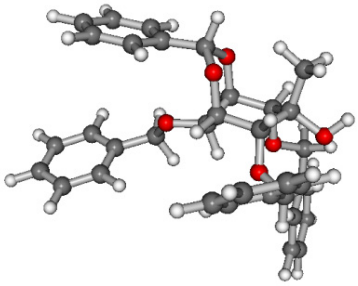
3.73CC
ΔE **6.3** kcal/mol



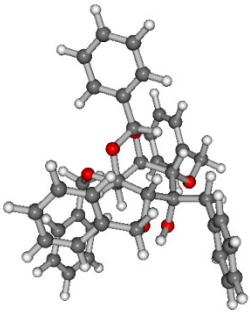
3.74BC
ΔE **0.0** kcal/mol



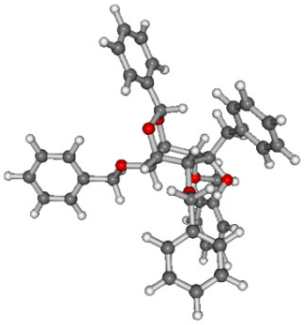
3.74CC
ΔE **1.2** kcal/mol



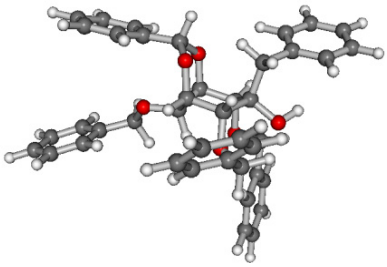
3.74CB
ΔE **4.4** kcal/mol



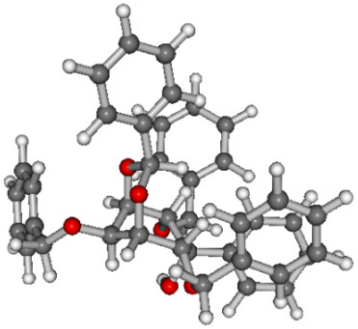
3.75BC
ΔE **0.0** kcal/mol



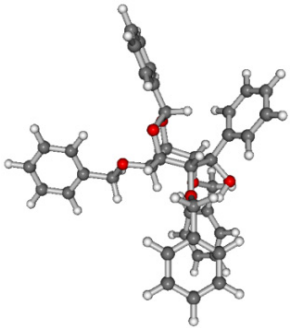
3.75CC
ΔE **0.8** kcal/mol



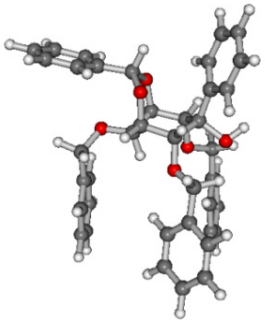
3.75CB
ΔE **3.8** kcal/mol



3.76BC
ΔE **0.0** kcal/mol



3.76CC
ΔE **5.0** kcal/mol



3.76CB
ΔE **10.0** kcal/mol

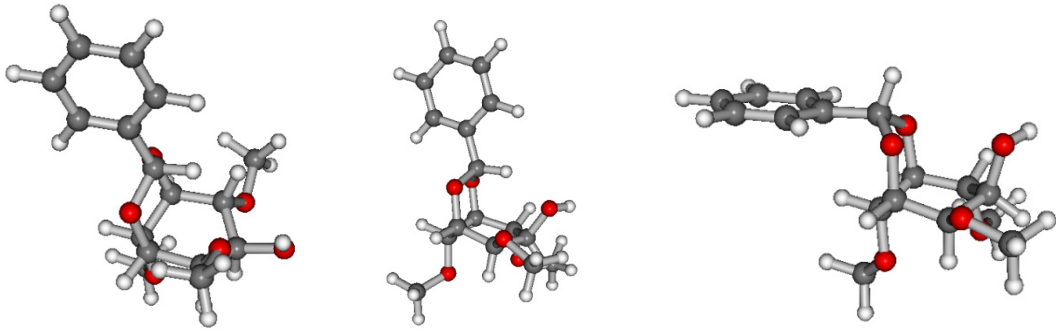
Figure A7: Contd.....

3.77BC
ΔE **0.0** kcal/mol

3.77CC
ΔE **2.5** kcal/mol

3.77CB
ΔE **5.6** kcal/mol

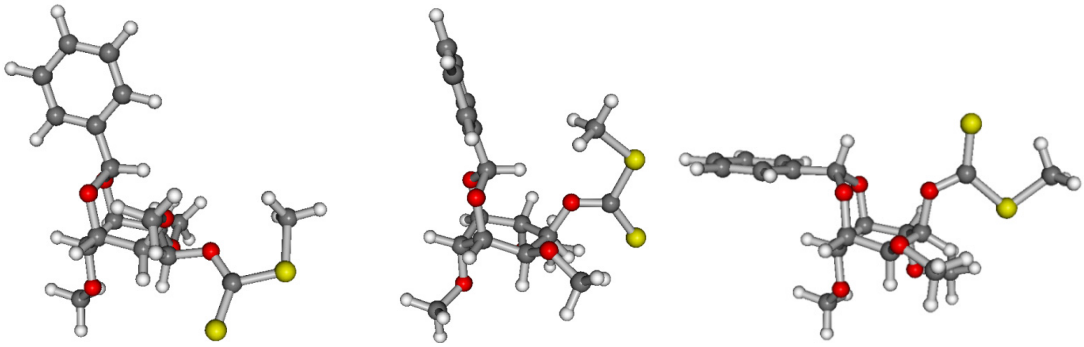
Figure A8: Results of geometrical optimization of possible conformations of **1.77** and **2.33**.



1.77BC
ΔE **0.0** kcal/mol

1.77CC
ΔE **8.1** kcal/mol

1.77CB
ΔE **11.0** kcal/mol



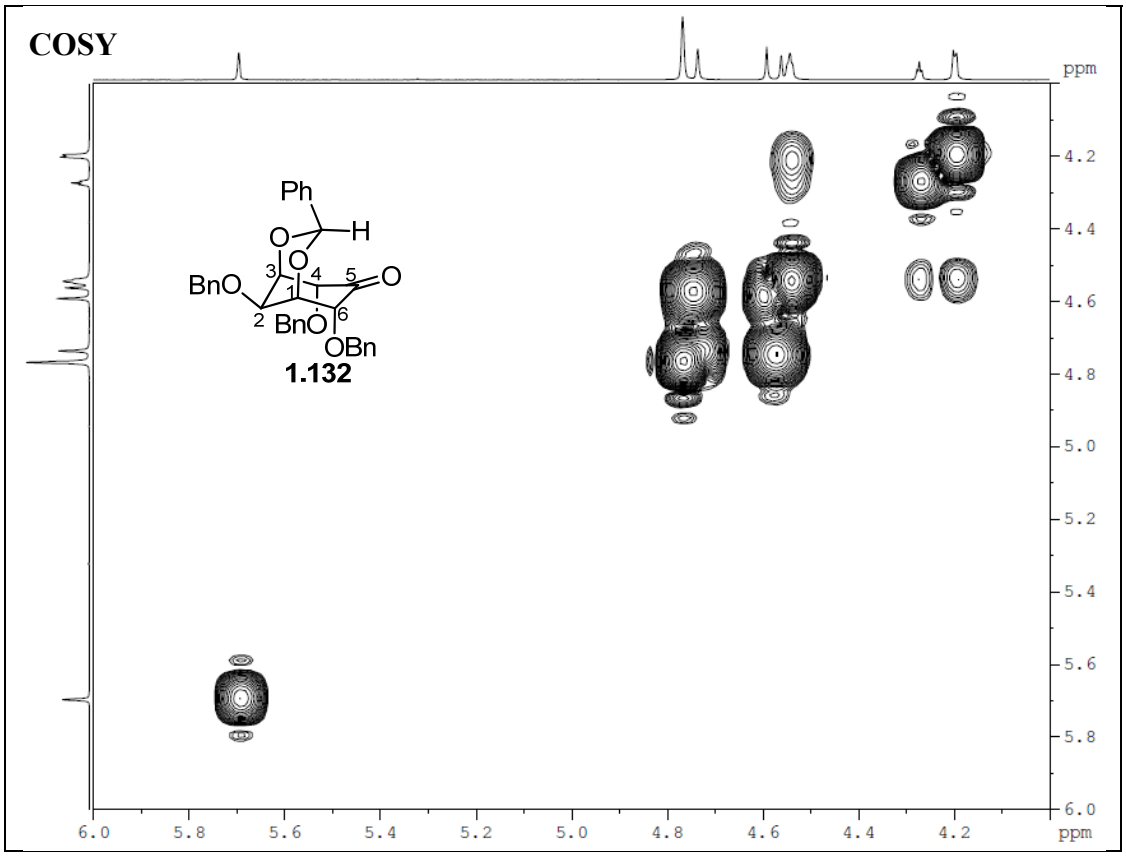
2.33BC
ΔE **0.0** kcal/mol

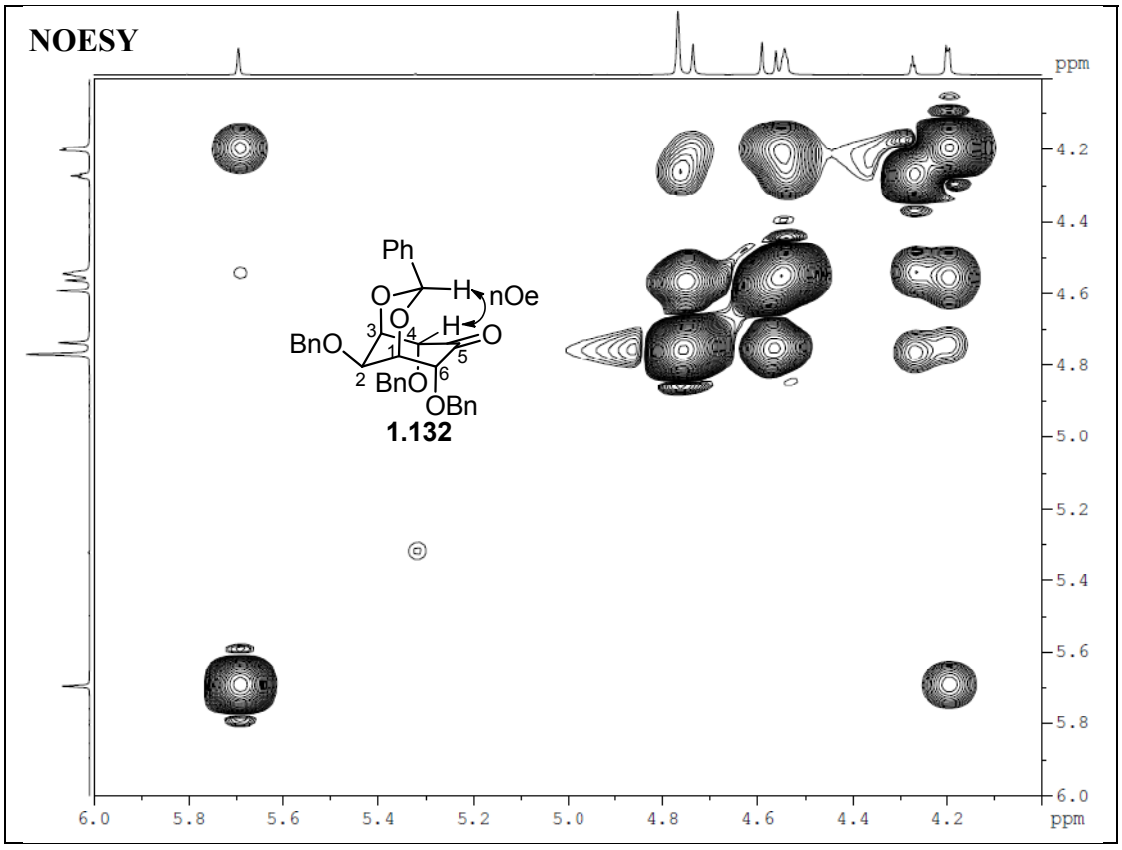
2.33CC
ΔE **4.3** kcal/mol

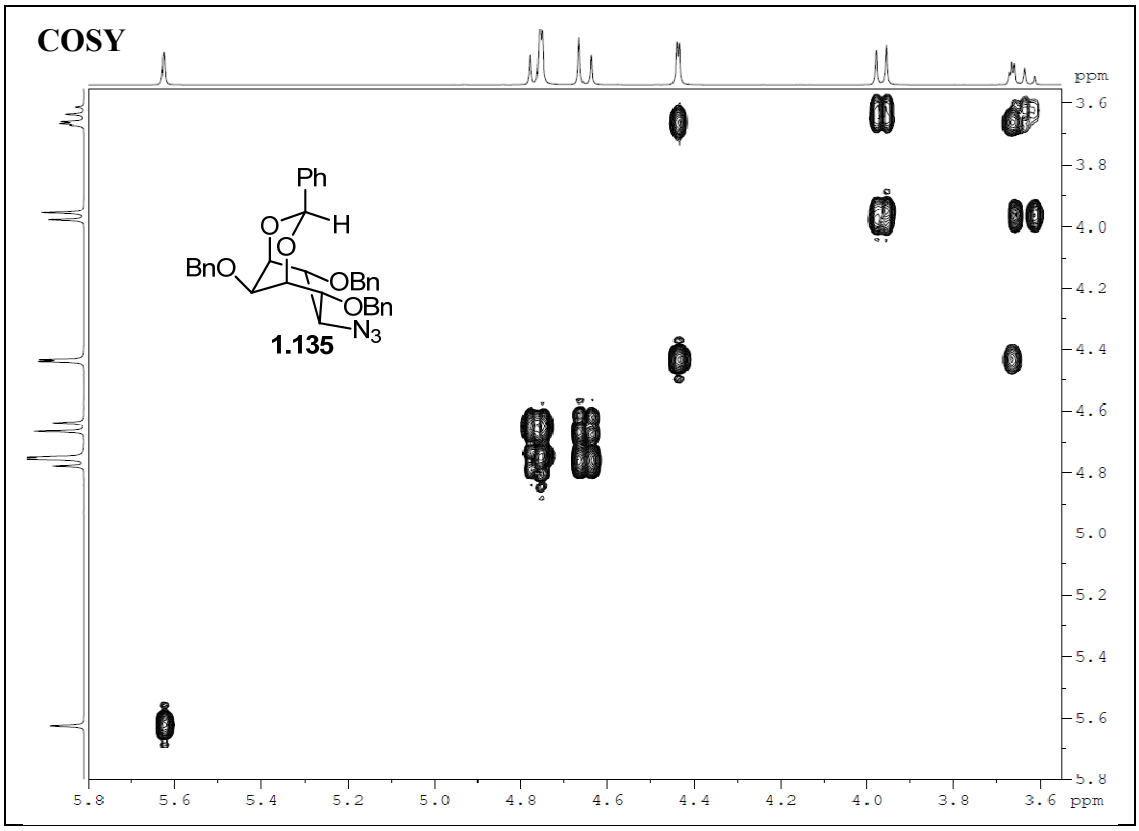
2.33CB
ΔE **10.8** kcal/mol

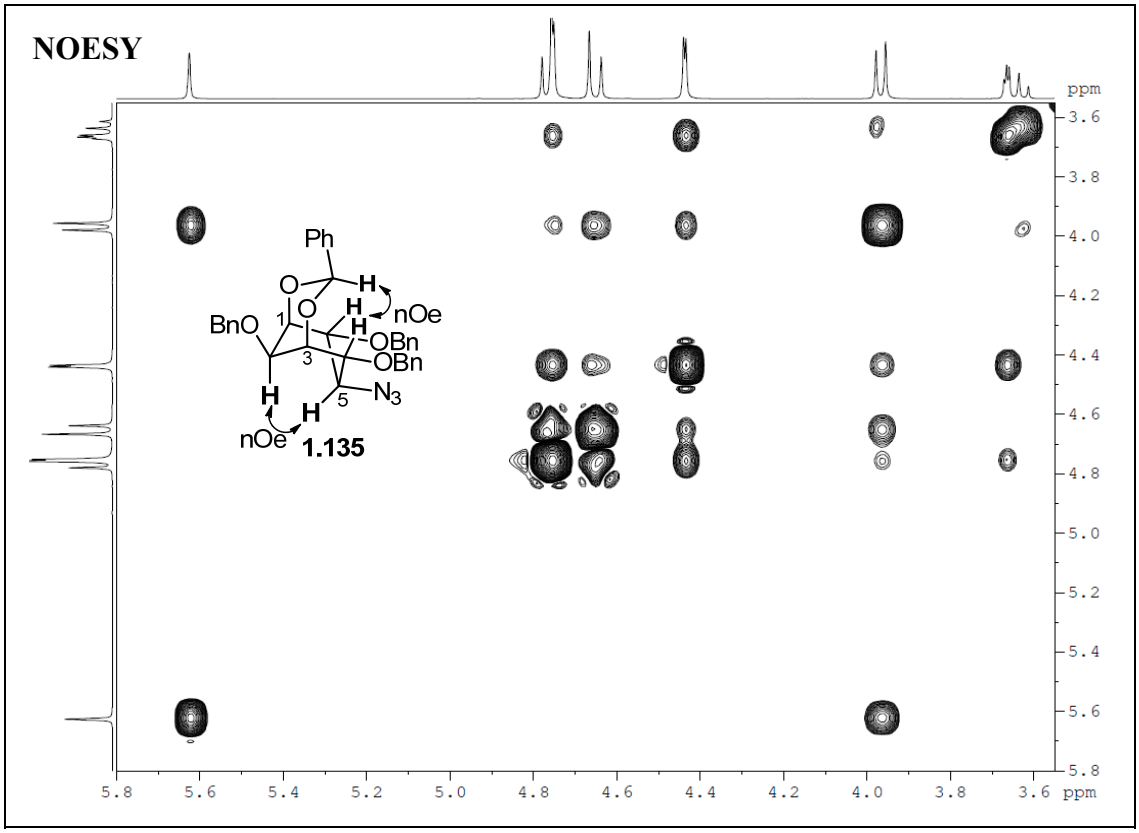
Table A6: Calculated dihedral angles from DFT structures and coupling constants ($^3J_{HH}$) for most stable conformation by Karplus equation (graphical tool MestRe-J).

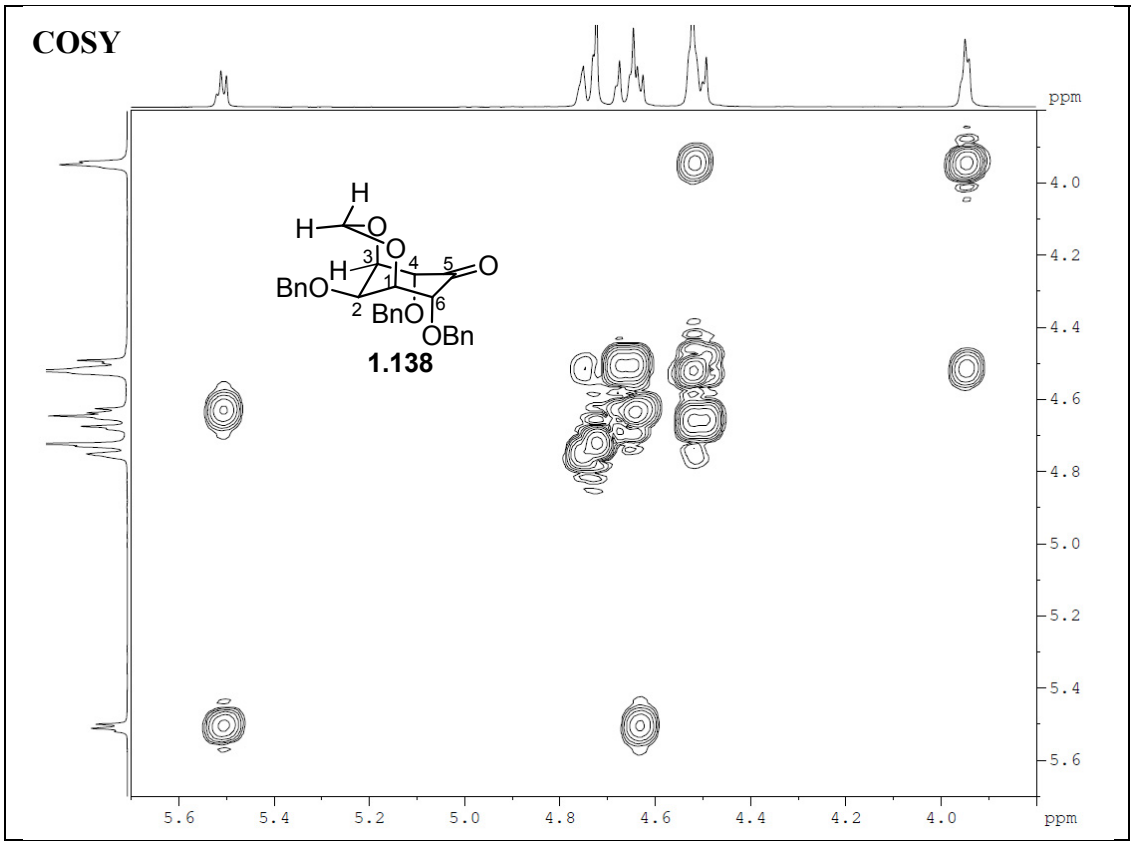
Dihedral angle H1 to		**H3 to**	**H4 to H5**
1.77	**H2** 20 (0.5-1 Hz) **H6** 58 (3 Hz)	**H2** 35 (1 Hz) **H4** 158 (9 Hz)	104 (2.2 Hz)
2.33	**H2** 21 **H6** 59 (2.89 Hz)	**H2** 33 **H4** 159 (9 Hz)	105 (2.2 Hz)

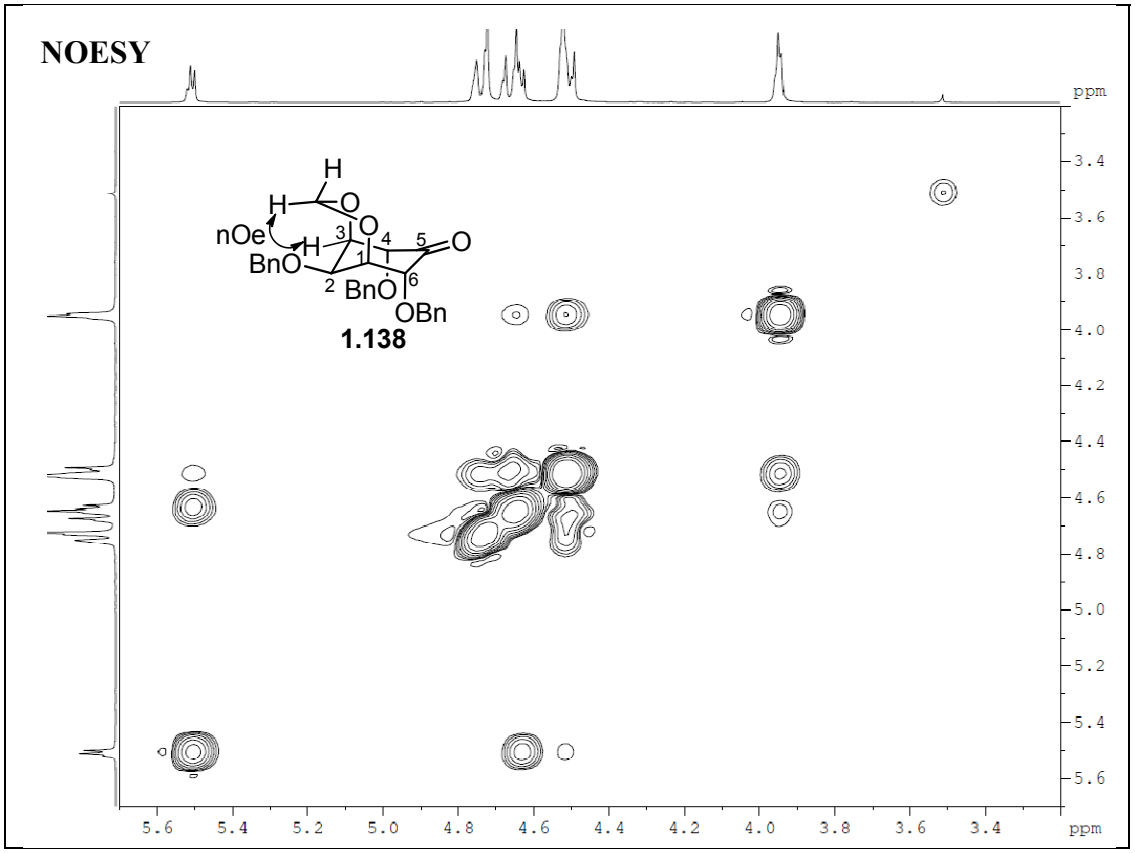

COSY
Ph
O
H
O
3
4
5
O
BnO
1
2
BnO
6
OBn
1.132
ppm
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
ppm

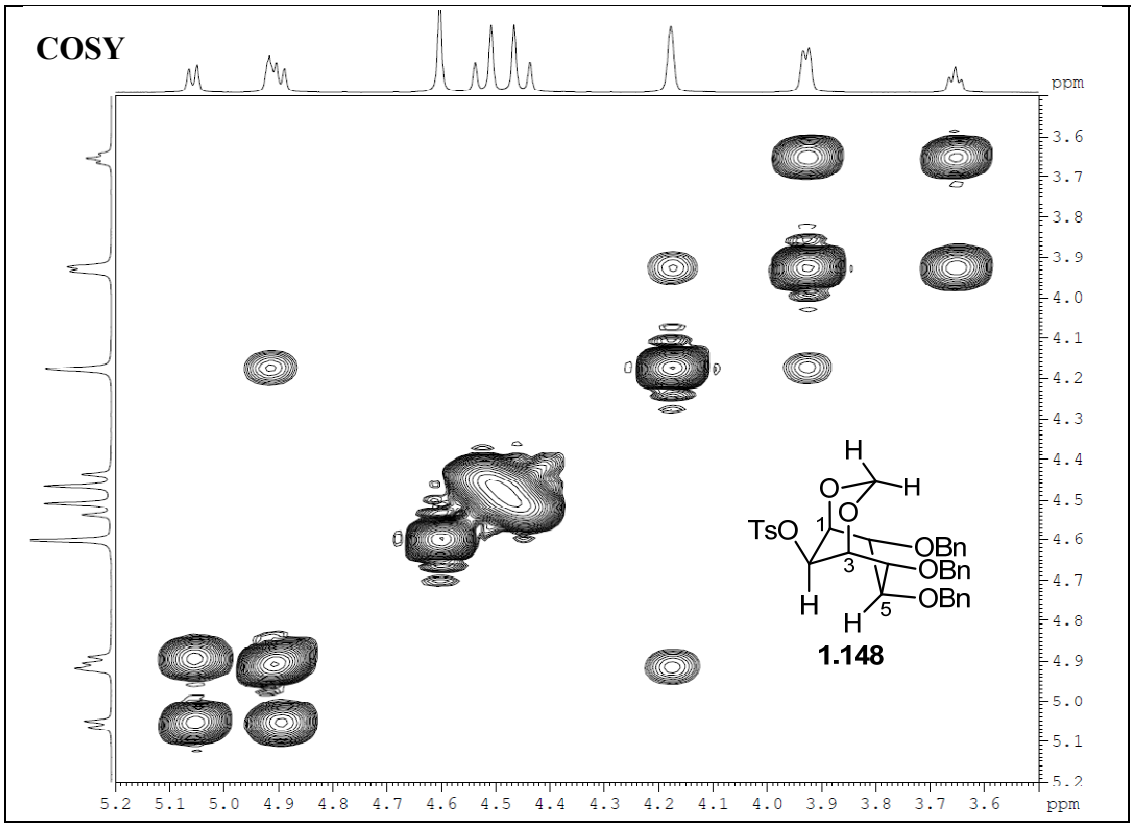

NOESY
Ph
O
H
nOe
O
3
4
H
O
BnO
1
5
2
BnO
6
OBn
1.132
ppm
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
ppm

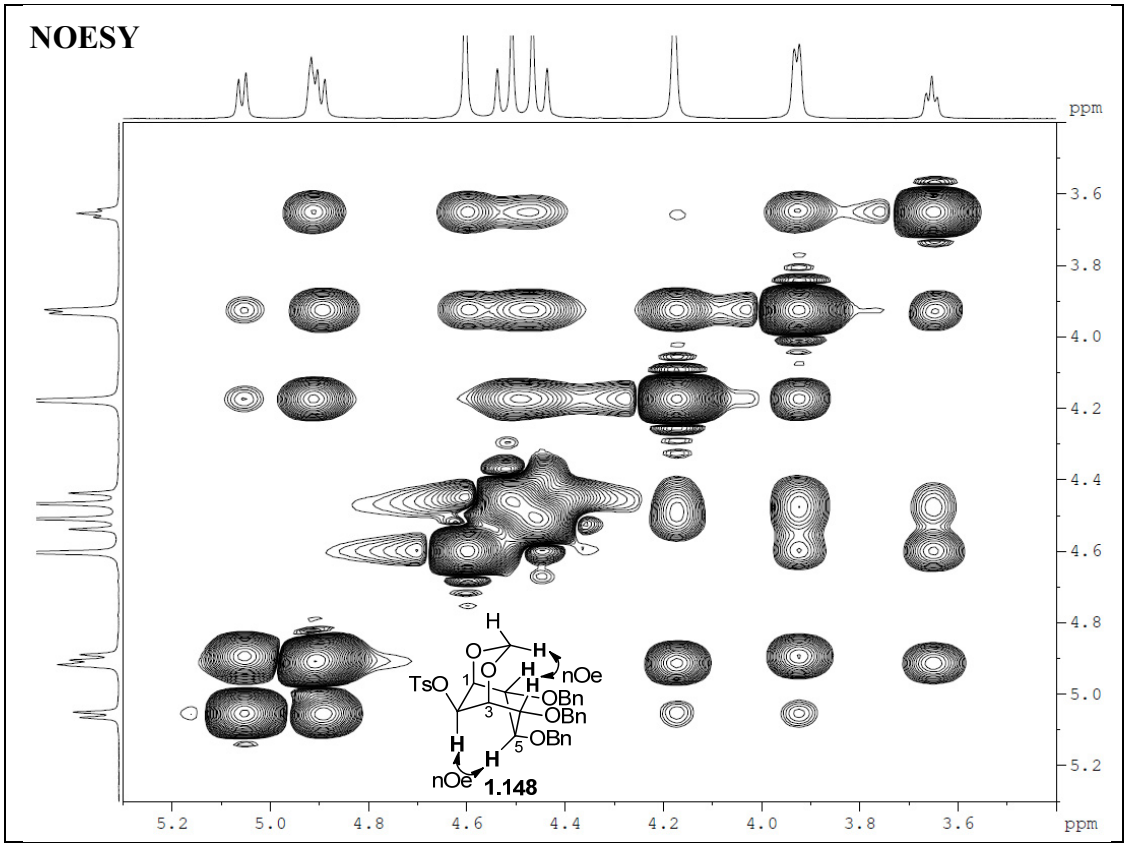

COSY
Ph
O
H
O
BnO
OBn
OBn
N3
1.135
ppm
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 ppm

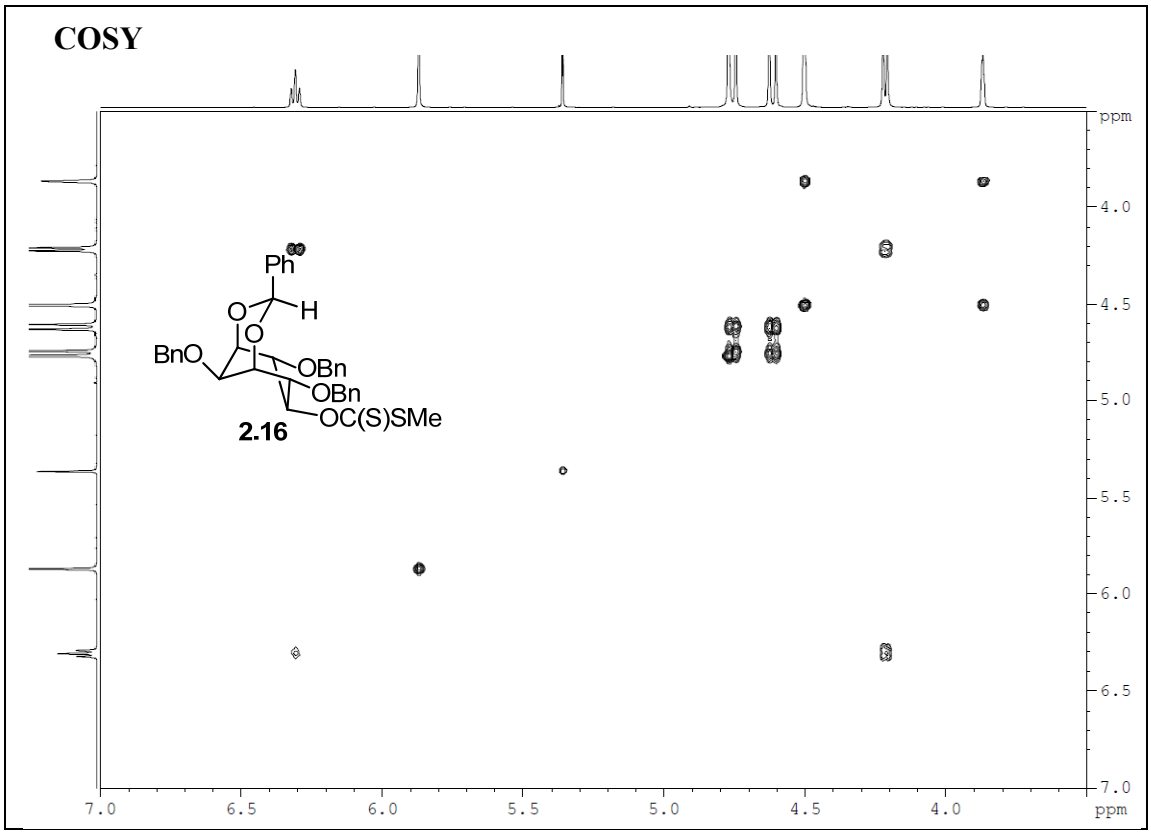

NOESY
Ph
O
H
nOe
1
O
H
BnO
OBn
3
OBn
H
5
N3
H
H
nOe
1.135
ppm
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 ppm

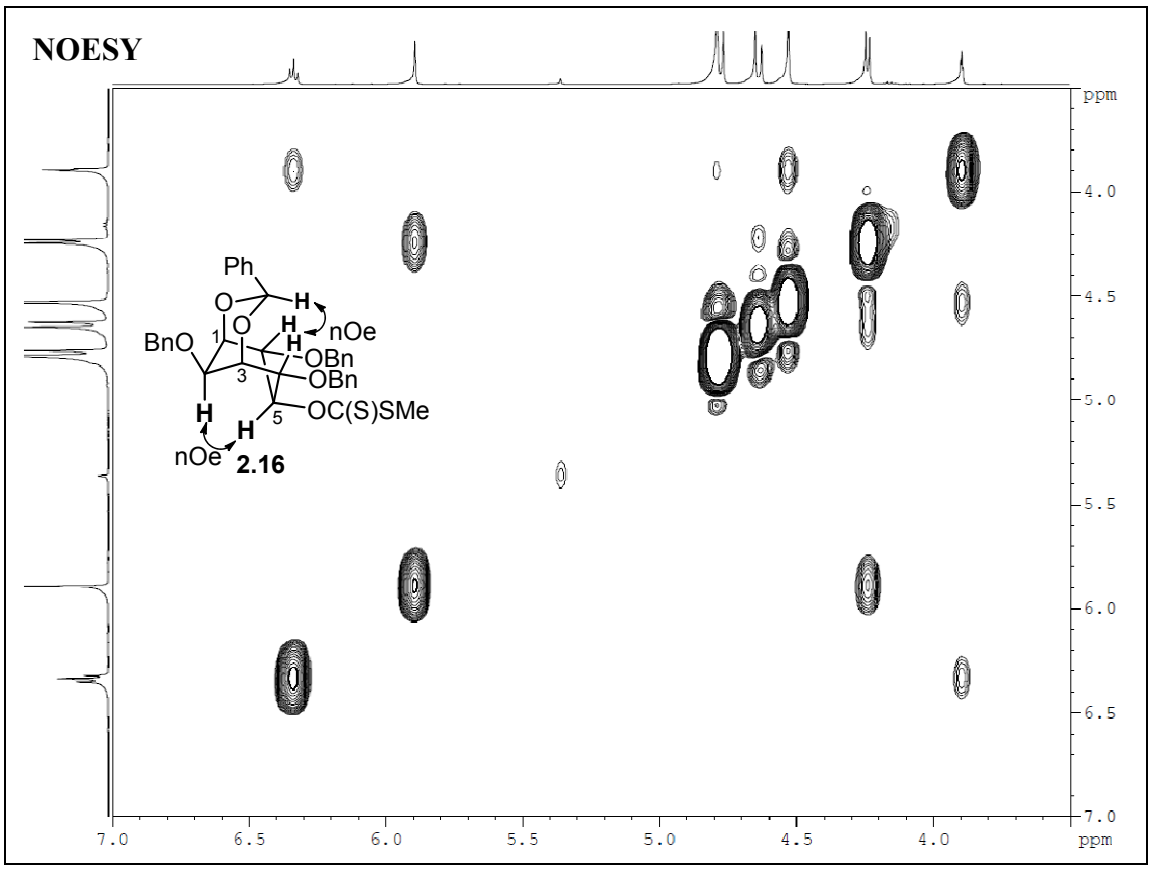

COSY
ppm
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 ppm
H
H
O
O
3
4
5
O
H
1
BnO
2
BnO
6
OBn
1.138

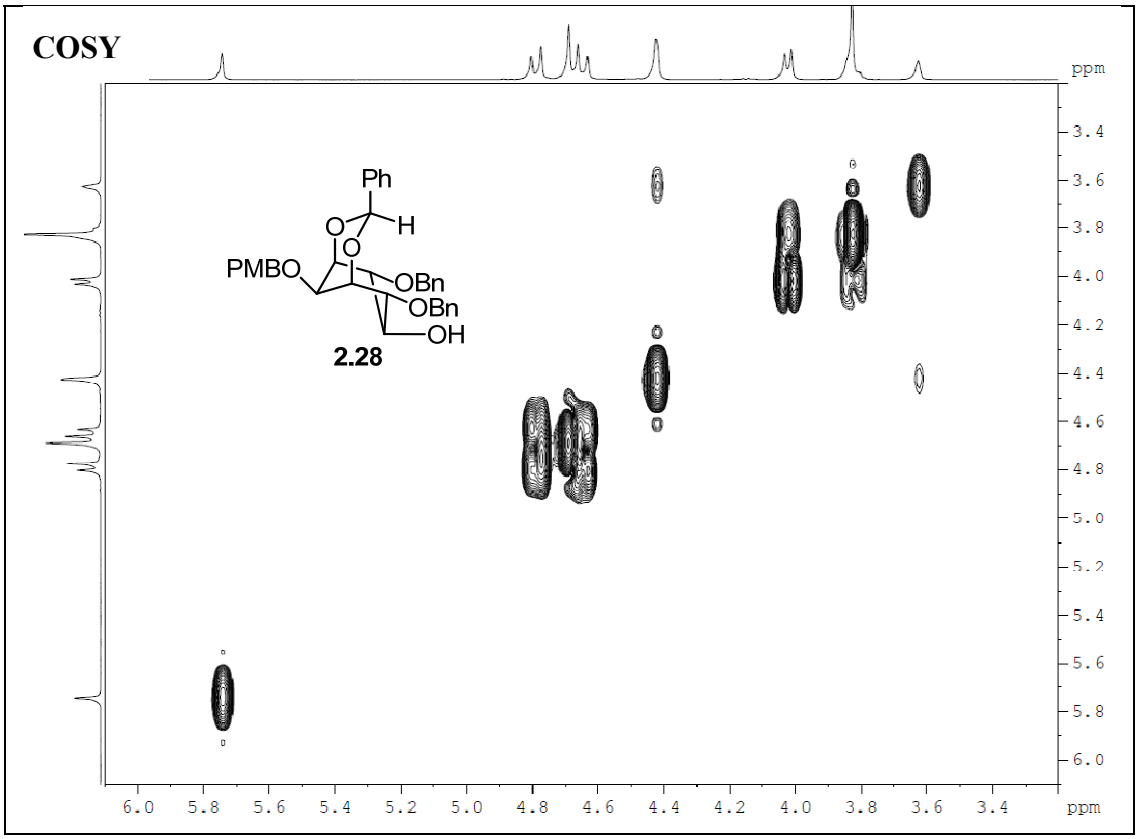

NOESY
ppm
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 ppm
H
H
O
nOe
O
3
4
5
O
H
1
BnO
2
BnO
6
OBn
1.138

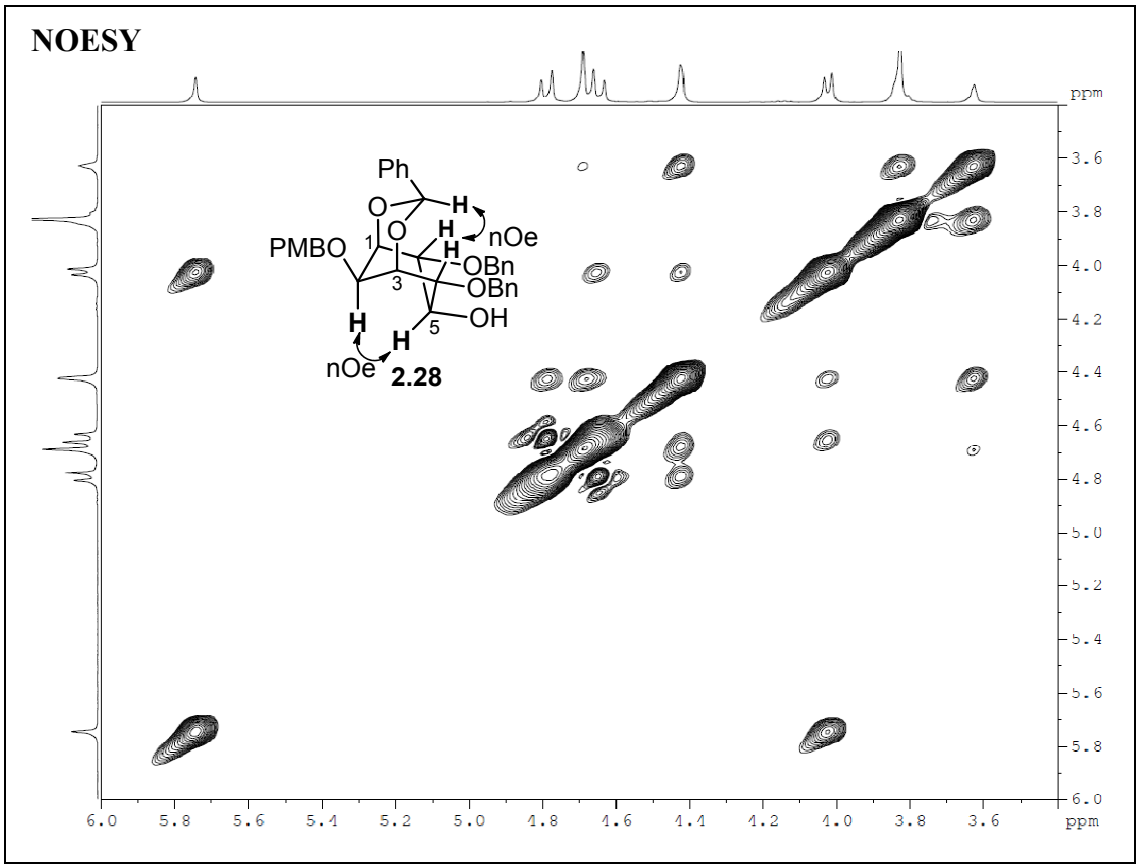

COSY
ppm
3.6
3.7
3.8
3.9
4.0
4.1
4.2
4.3
4.4
4.5
4.6
4.7
4.8
4.9
5.0
5.1
5.2
5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 ppm
H
O
H
O
TsO
1
OBn
3
OBn
H
5
OBn
H
1.148

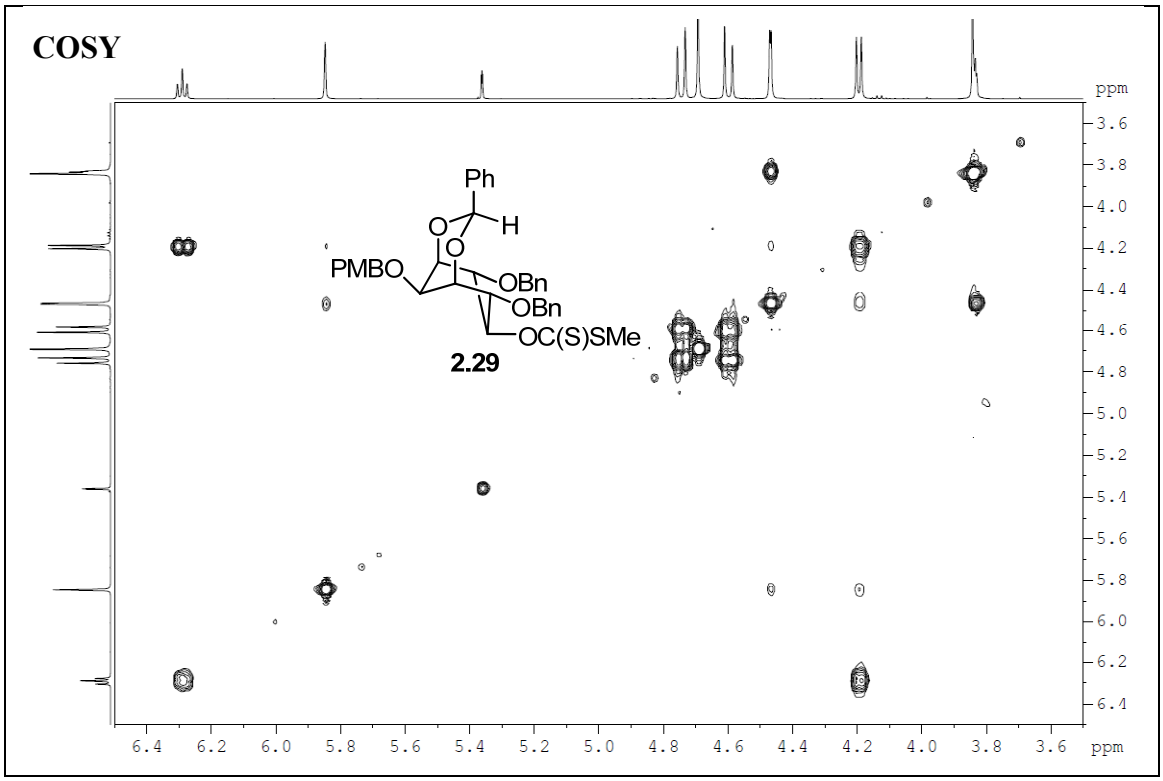

NOESY
ppm
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 ppm
H
O
H
O
H
nOe
TsO
1
H
OBn
3
OBn
5
OBn
H
H
nOe
1.148

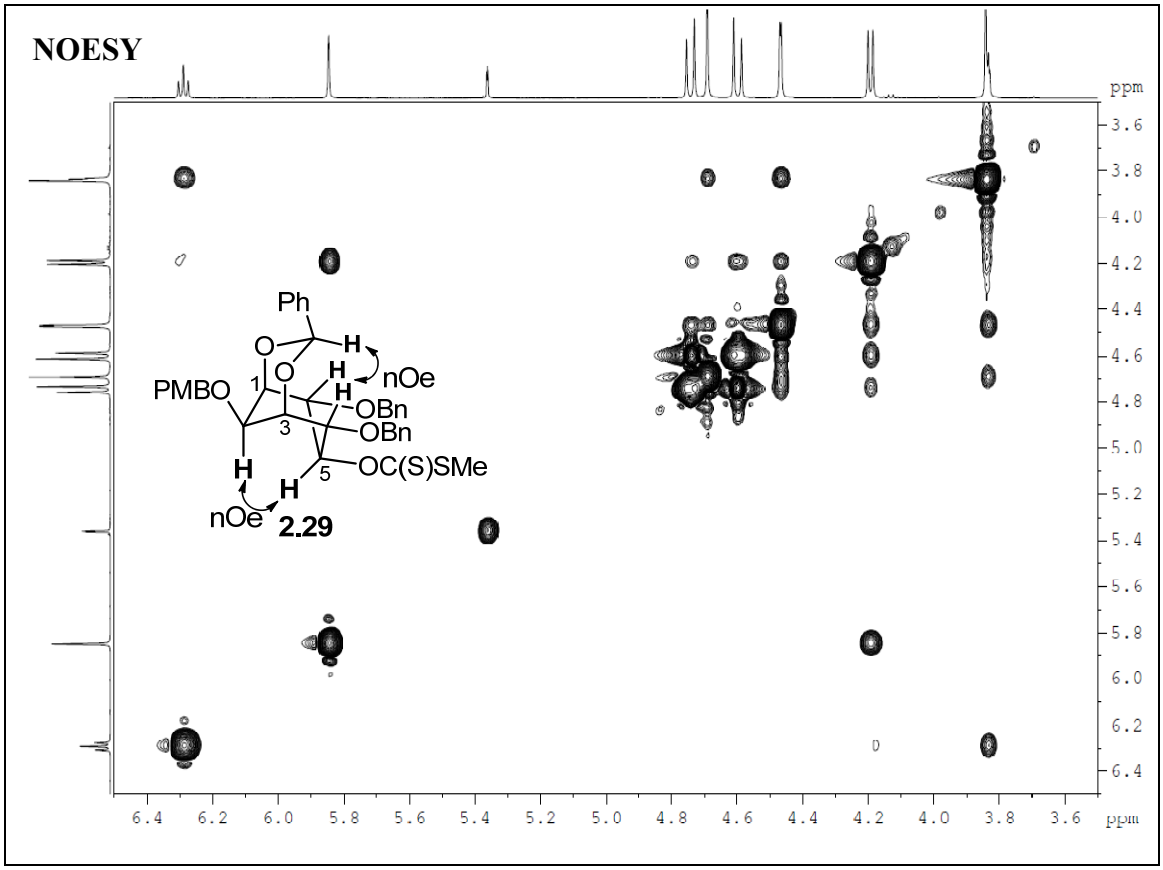

COSY
Ph
O
H
O
BnO
OBn
OBn
OC(S)SMe
2.16
ppm
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.0
6.5
6.0
5.5
5.0
4.5
4.0
ppm

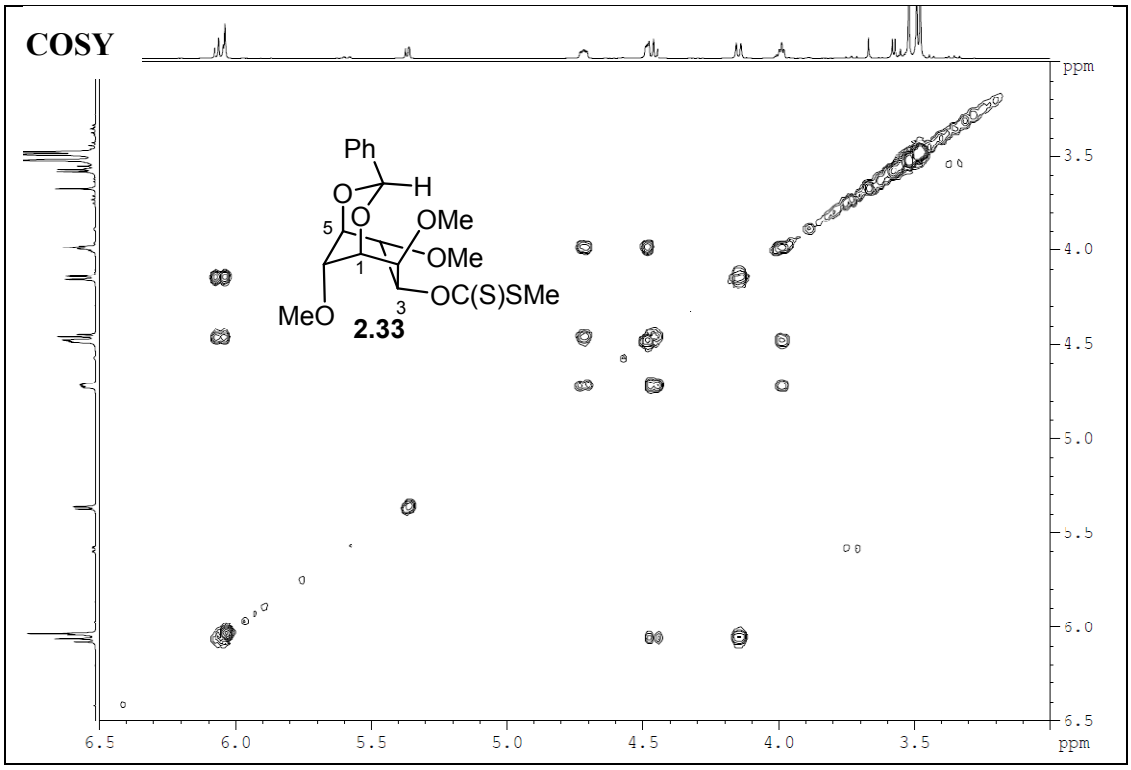

NOESY
Ph
O
H
O
H
nOe
BnO
1
H
OBn
3
OBn
H
5
OC(S)SMe
H
nOe
2.16
ppm
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.0
6.5
6.0
5.5
5.0
4.5
4.0
ppm

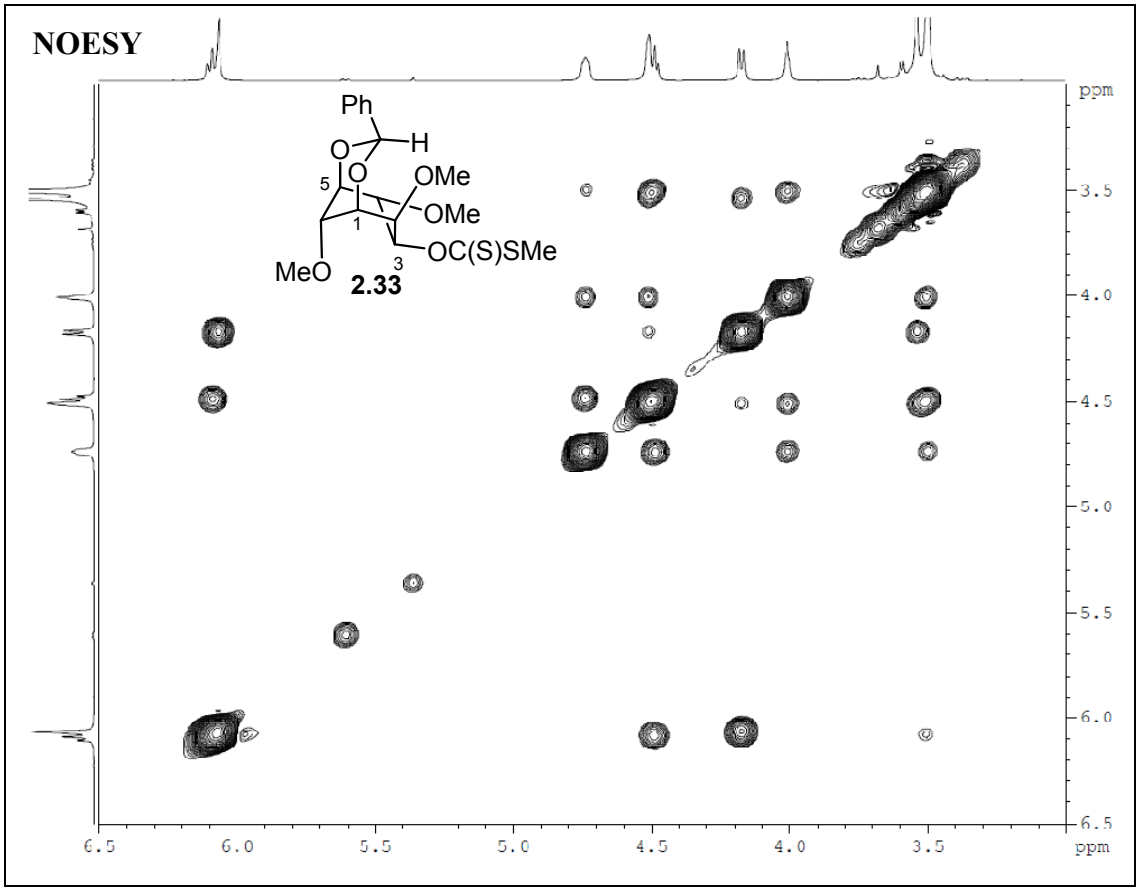

COSY
Ph
O
H
O
PMBO
OBn
OBn
OH
2.28
ppm
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 ppm

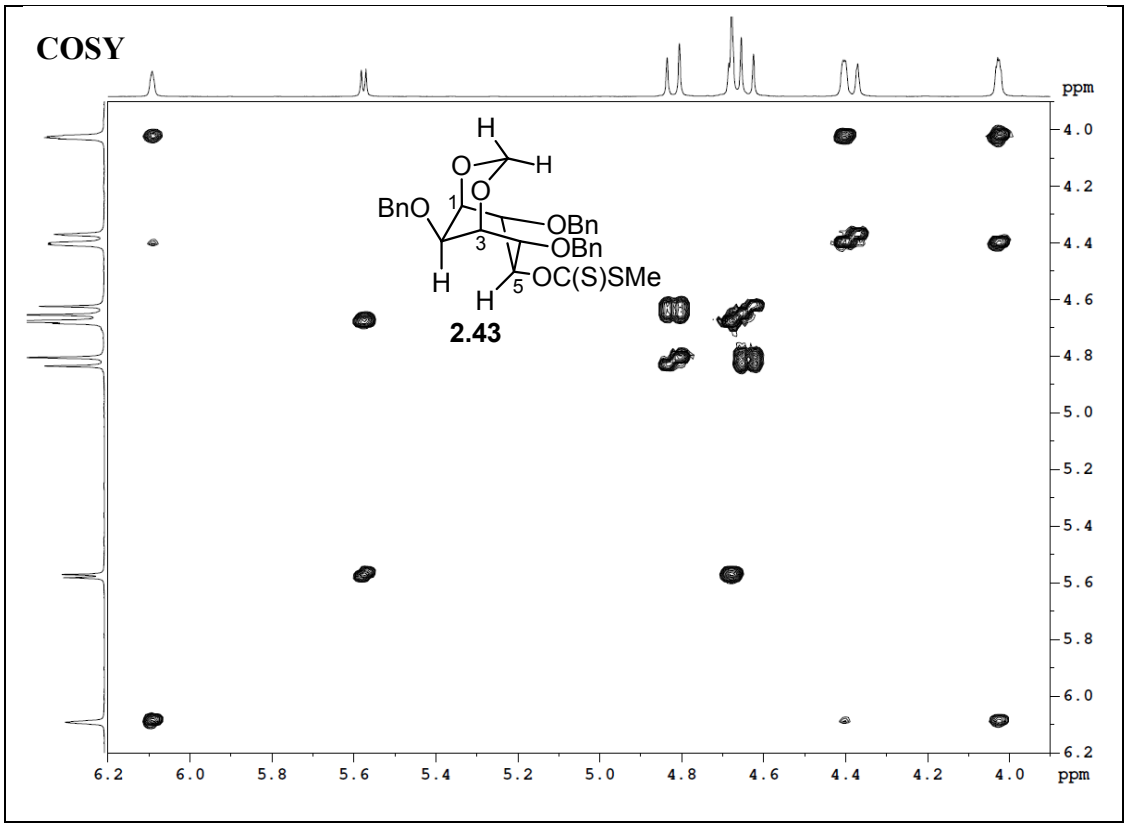

NOESY
Ph
O
H
O
H
nOe
PMBO
1
H
OBn
3
OBn
H
5
OH
H
nOe
2.28
ppm
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 ppm

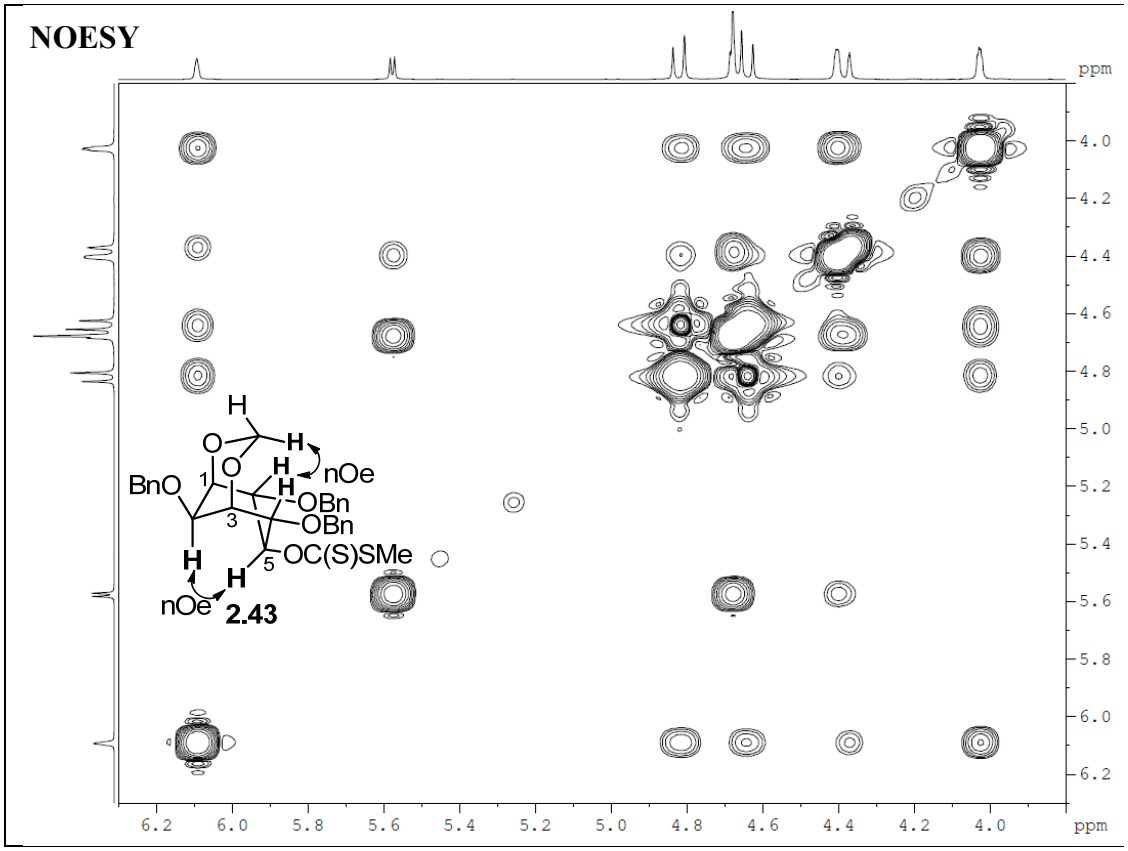

COSY
Ph
O
H
O
PMBO
OBn
OBn
OC(S)SMe
2.29
ppm
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
6.2
6.4
6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 ppm

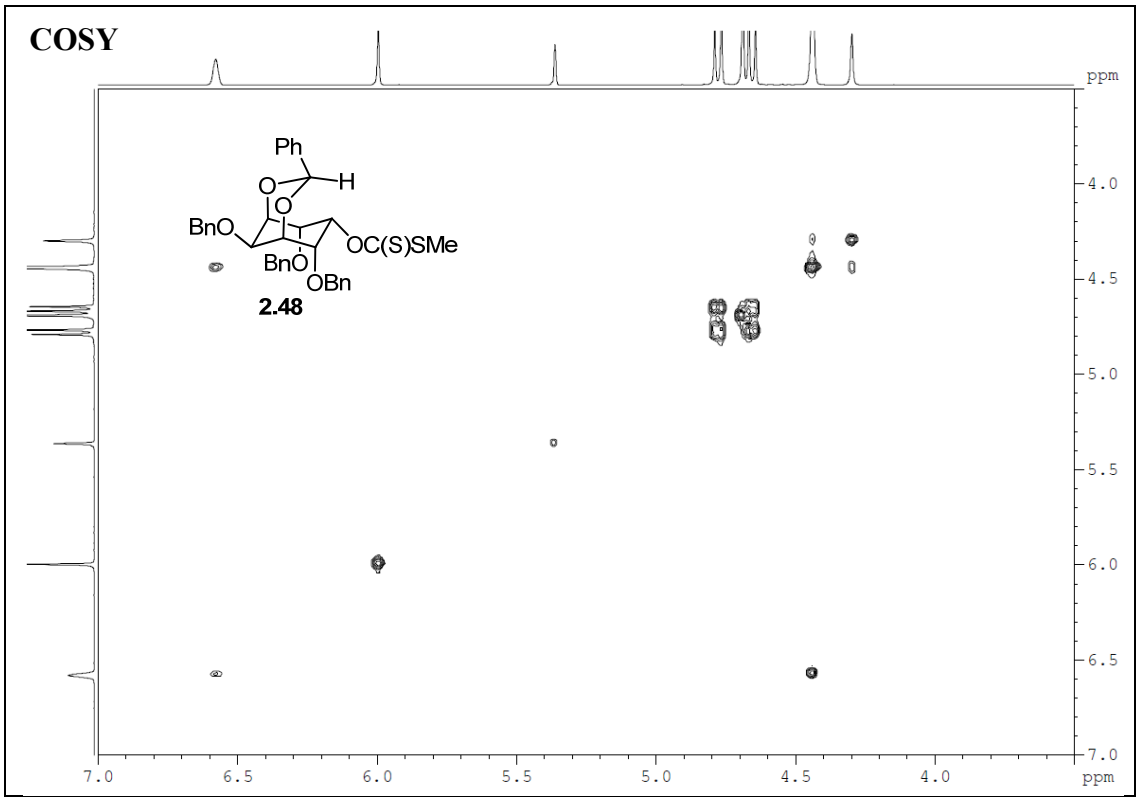

NOESY
Ph
O
H
O
H
nOe
1
PMBO
H
OBn
3
OBn
H
5
OC(S)SMe
H
nOe
2.29
ppm
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
6.2
6.4
6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 ppm

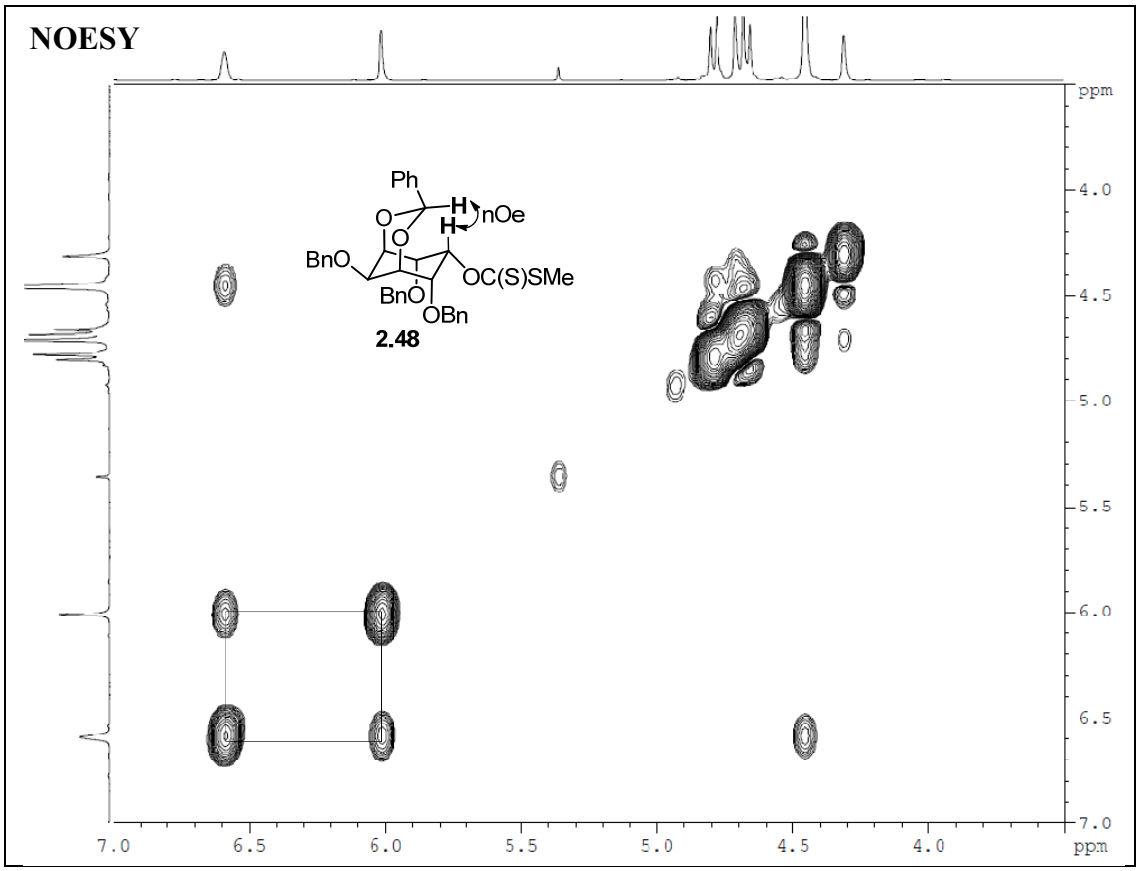

COSY
Ph
O
H
O
5
O
OMe
1
OMe
3
OC(S)SMe
MeO
2.33
ppm
3.5
4.0
4.5
5.0
5.5
6.0
6.5
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm

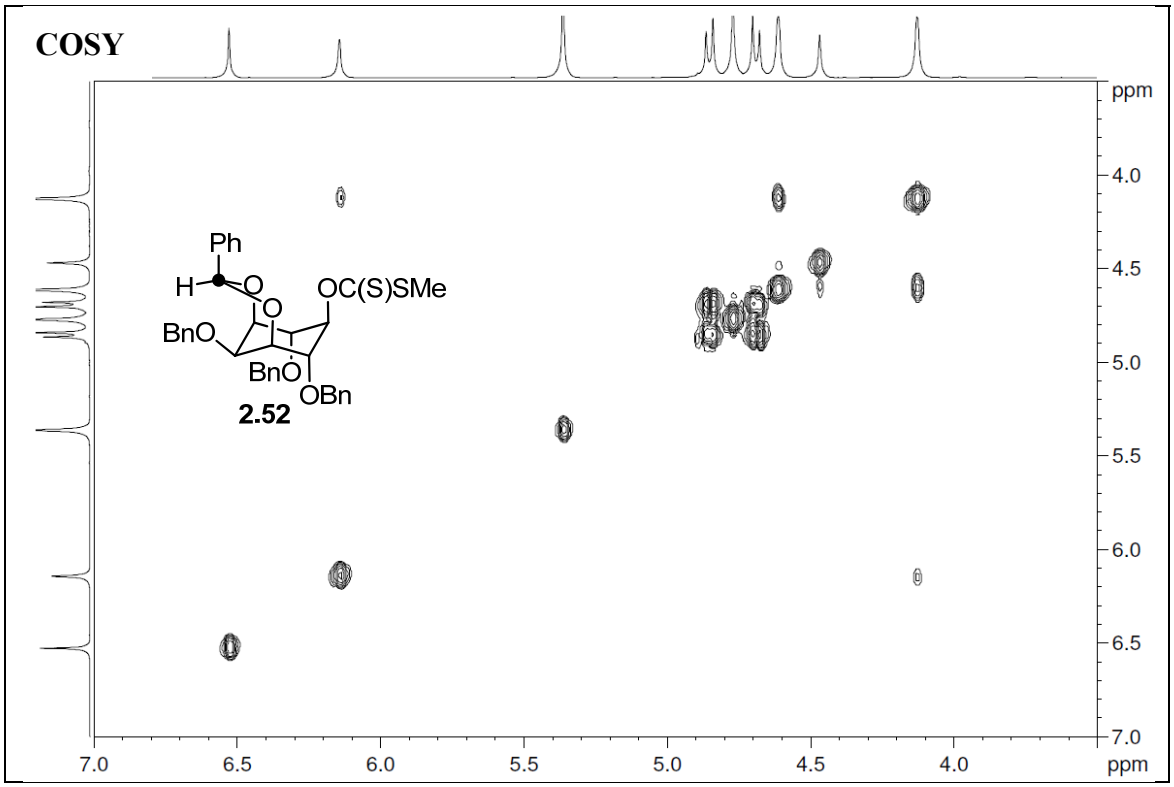

NOESY
Ph
O
H
O
5
O
OMe
1
OMe
3
OC(S)SMe
MeO
2.33
ppm
3.5
4.0
4.5
5.0
5.5
6.0
6.5
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm

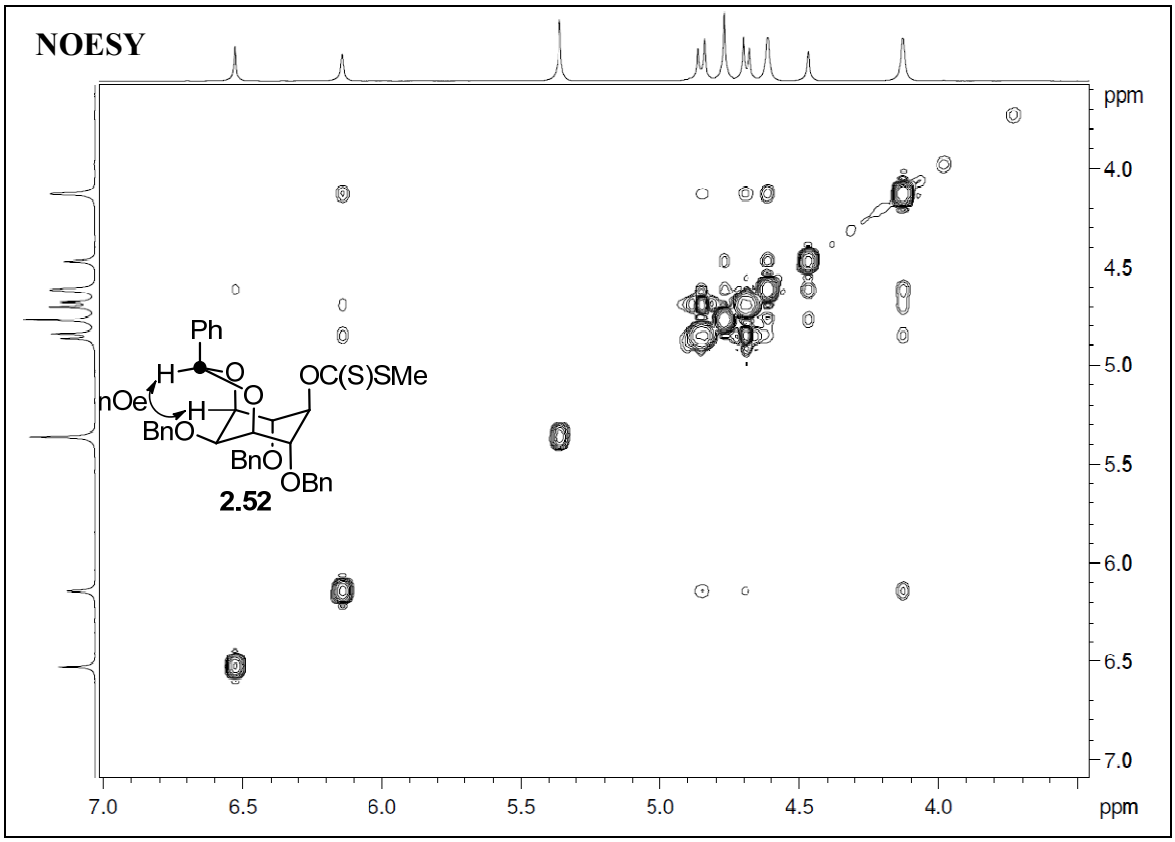

COSY
ppm
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
6.2
6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 ppm
H
O
H
O
BnO
1
OBn
3
OBn
H
5
OC(S)SMe
H
2.43

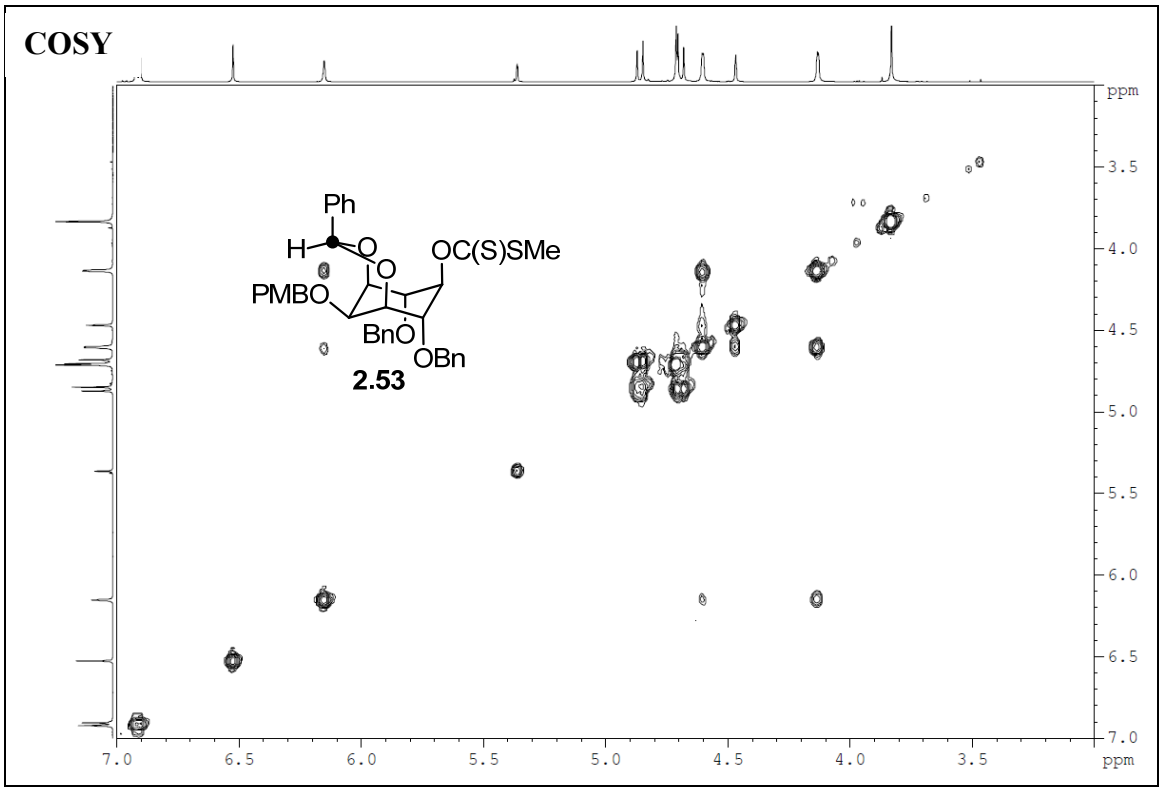

NOESY
ppm
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
6.2
6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 ppm
H
O
H
O
H
nOe
BnO
1
H
OBn
3
OBn
H
5
OC(S)SMe
H
nOe
2.43

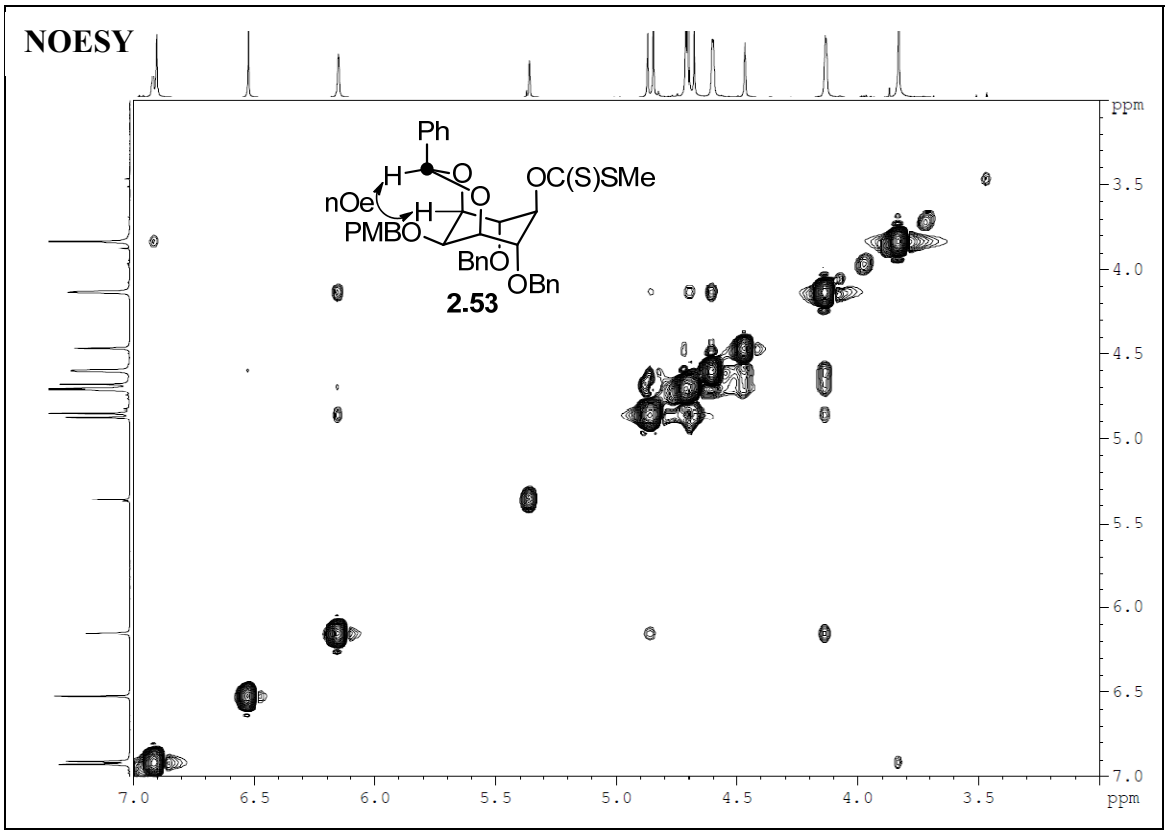

COSY
Ph
O
H
O
BnO
OC(S)SMe
BnO
OBn
2.48
ppm
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.0
6.5
6.0
5.5
5.0
4.5
4.0
ppm

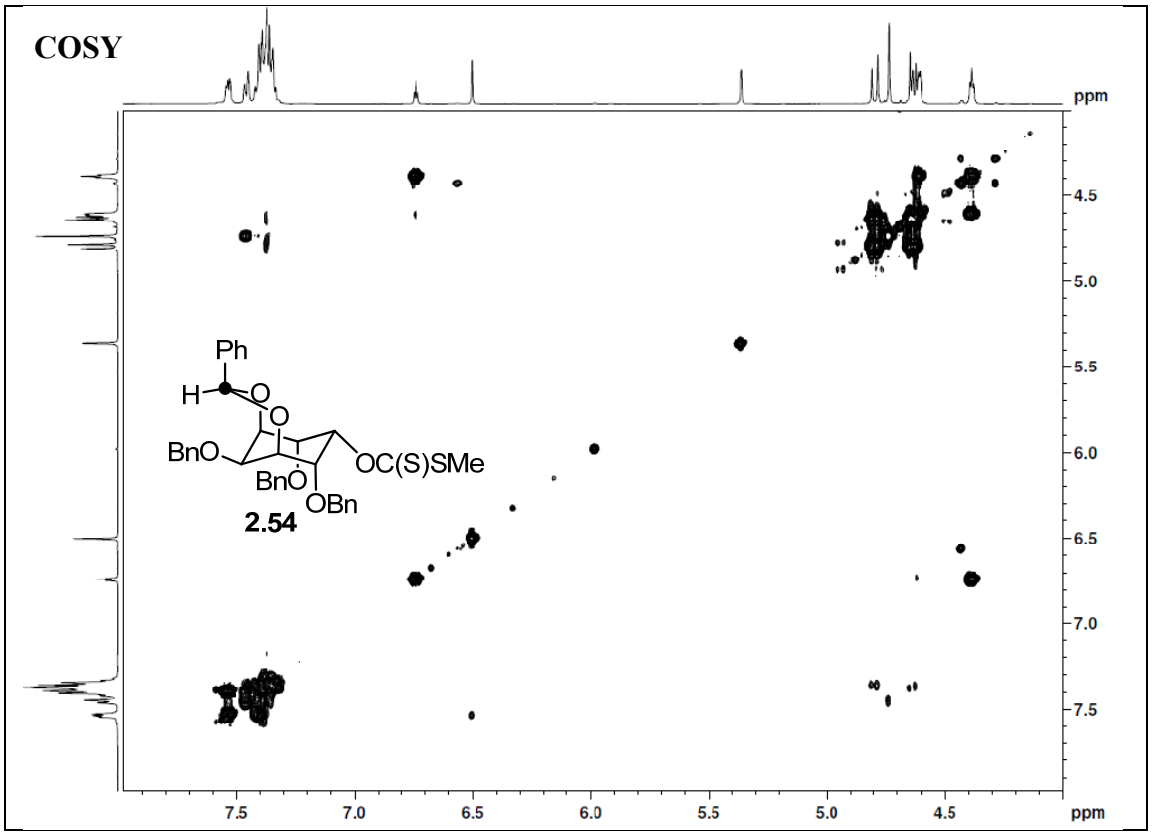

NOESY
Ph
O
H
nOe
H
O
BnO
OC(S)SMe
BnO
OBn
2.48
ppm
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.0
6.5
6.0
5.5
5.0
4.5
4.0
ppm

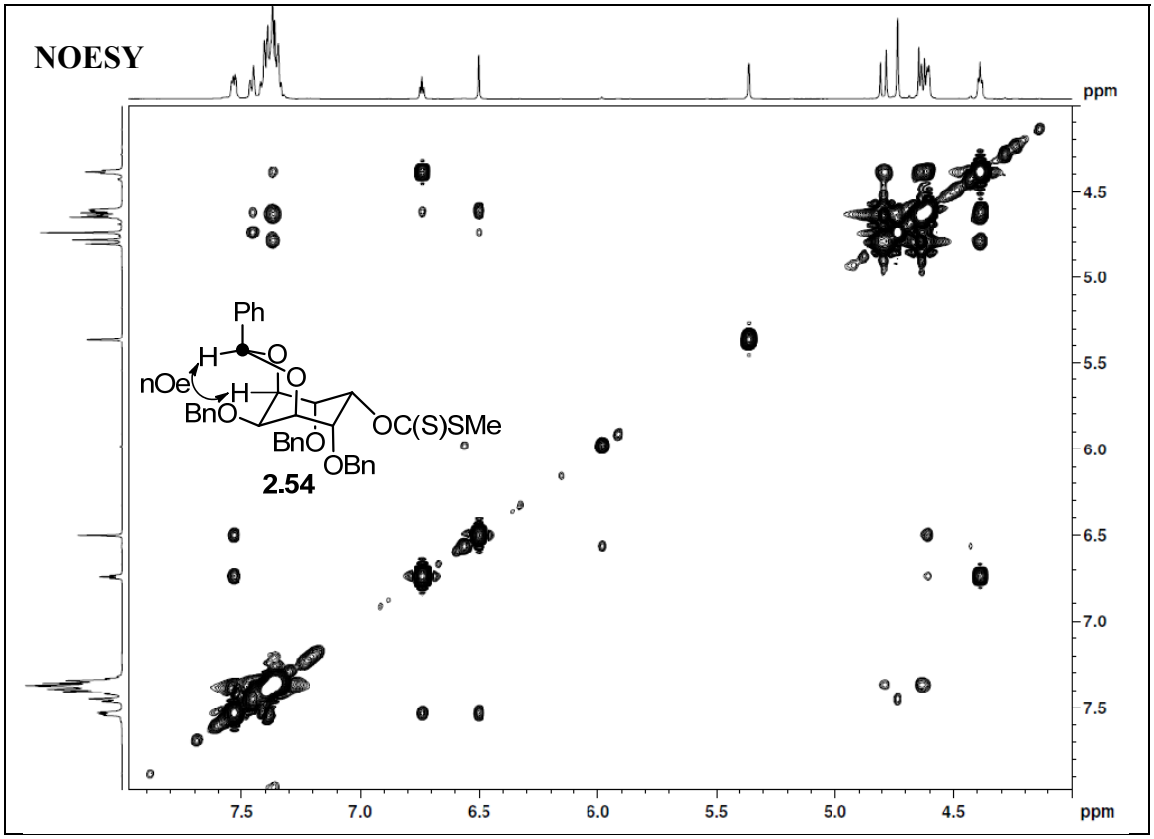

COSY
Ph
H
O
O
OC(S)SMe
BnO
BnO
OBn
2.52
ppm
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.0
6.5
6.0
5.5
5.0
4.5
4.0
ppm

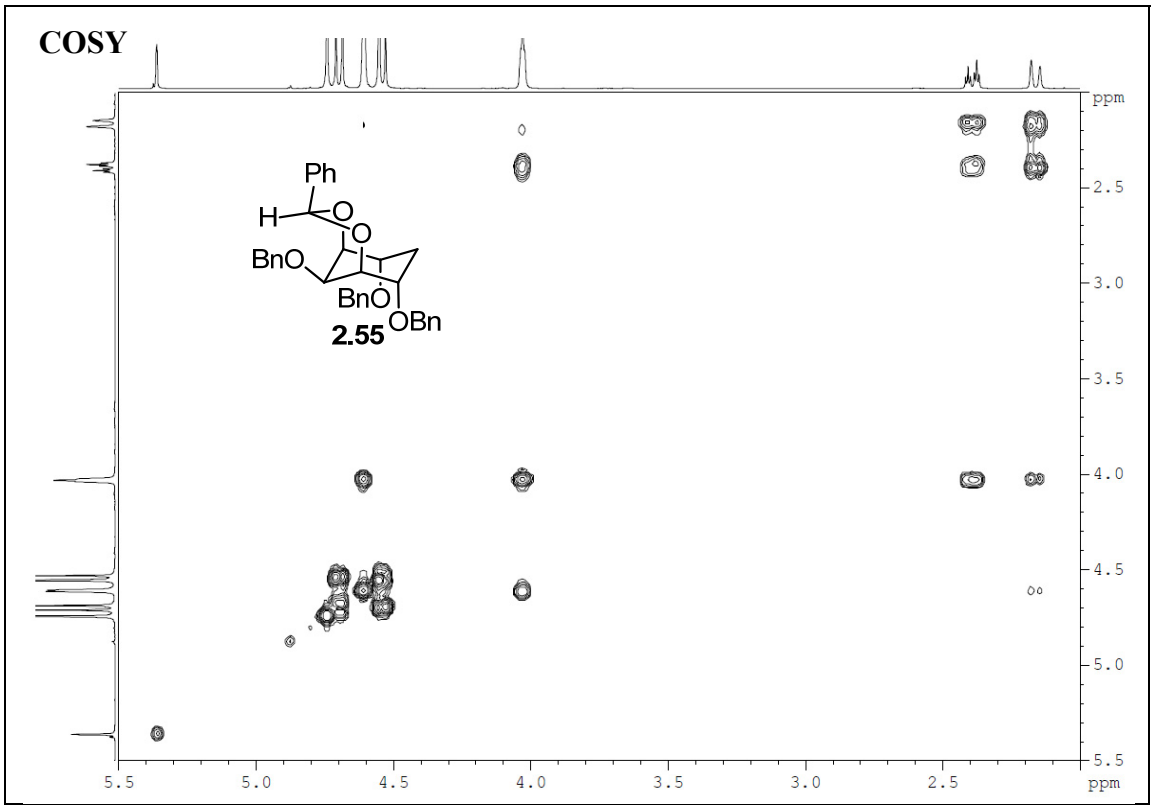

NOESY
Ph
H
O
O
OC(S)SMe
nOe
H
BnO
BnO
OBn
2.52
ppm
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.0
6.5
6.0
5.5
5.0
4.5
4.0
ppm

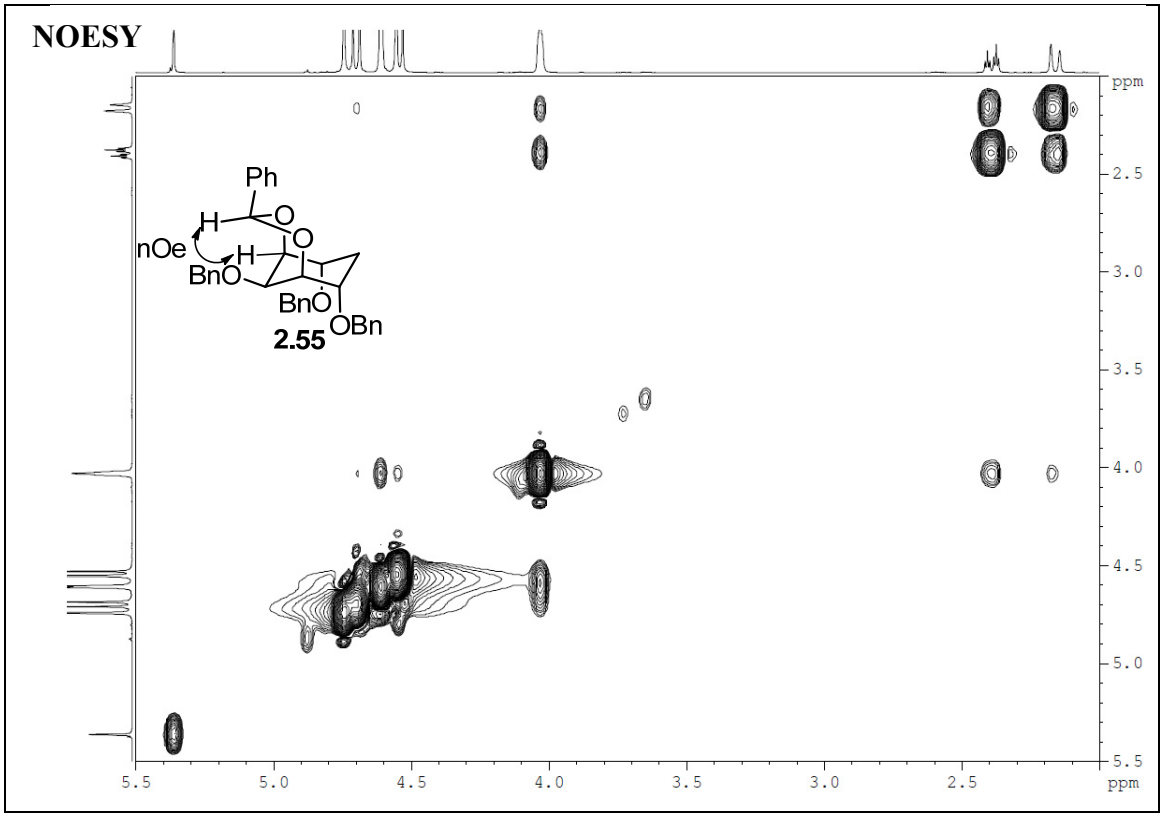

COSY
Ph
H
O
O
OC(S)SMe
PMBO
BnO
OBn
2.53
ppm
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm

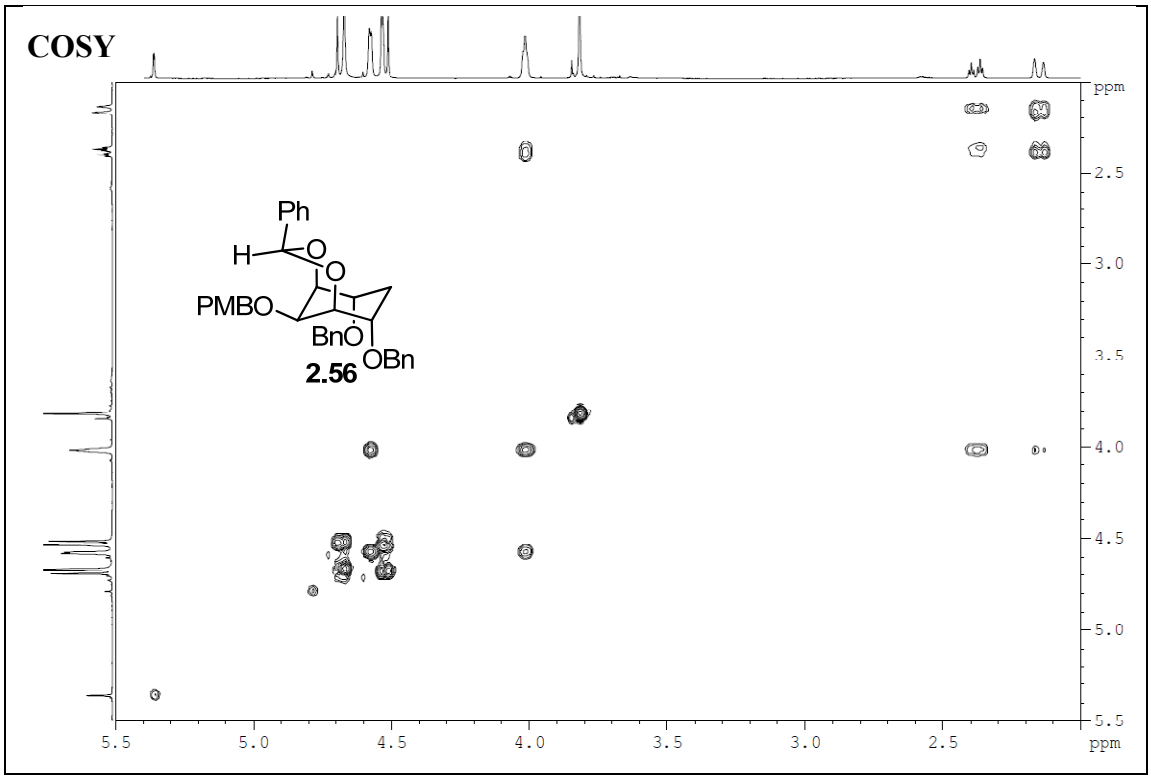

NOESY
Ph
H
O
O
OC(S)SMe
nOe
H
PMBO
BnO
OBn
2.53
ppm
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm

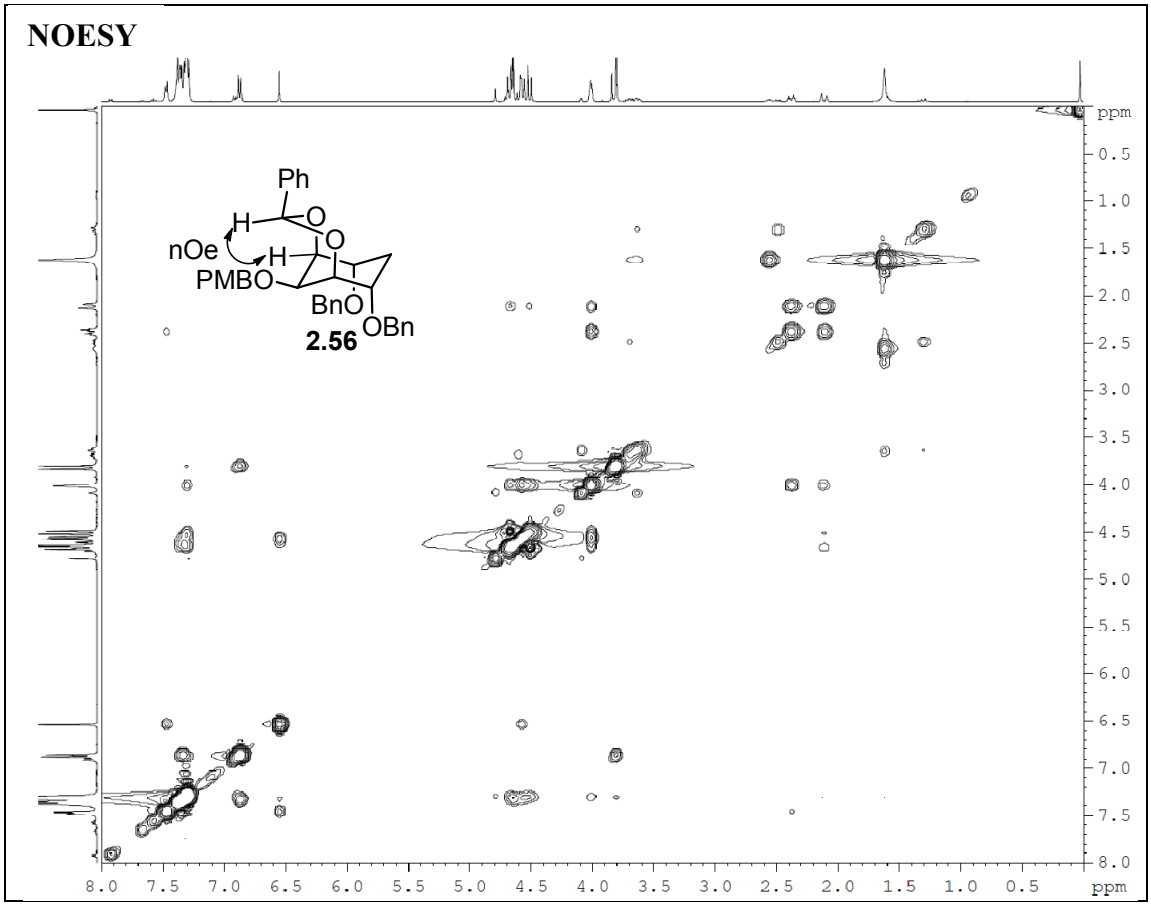

COSY
ppm
4.5
5.0
5.5
6.0
6.5
7.0
7.5
Ph
H
O
O
BnO
OC(S)SMe
BnO
OBn
2.54

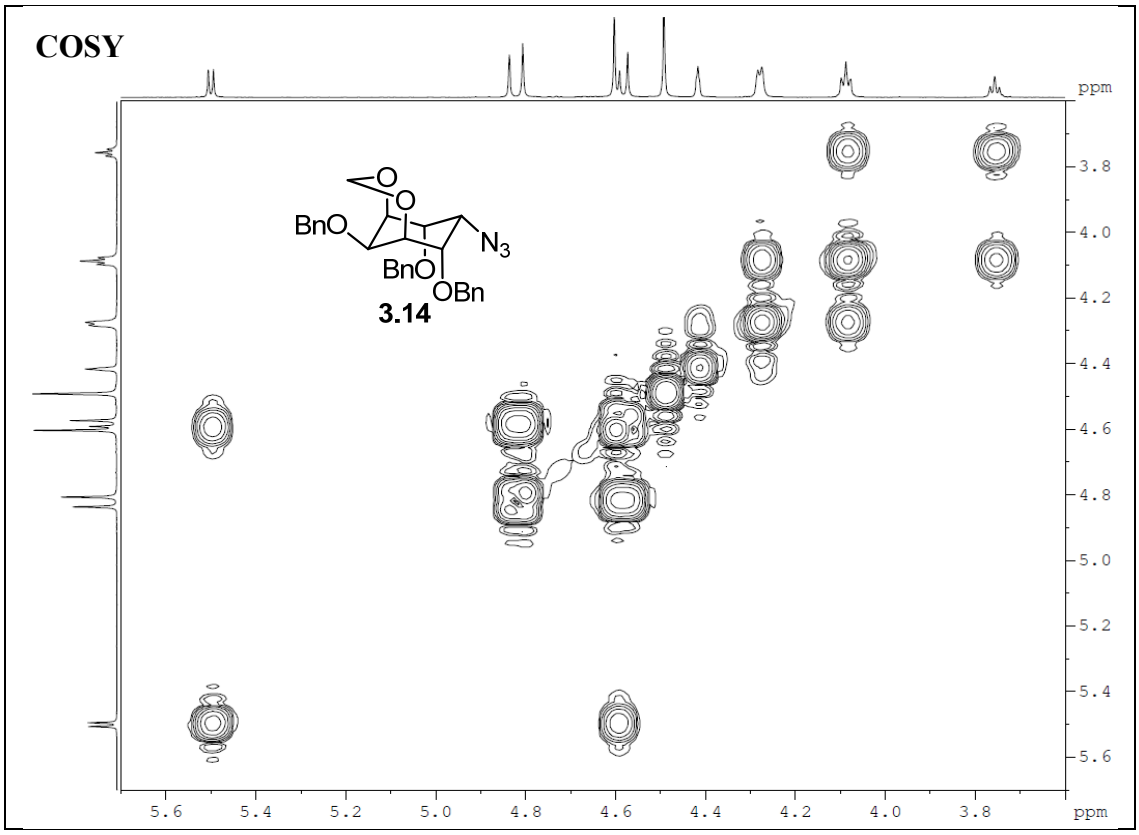

NOESY
ppm
4.5
5.0
5.5
6.0
6.5
7.0
7.5
Ph
H
O
O
nOe
H
BnO
OC(S)SMe
BnO
OBn
2.54

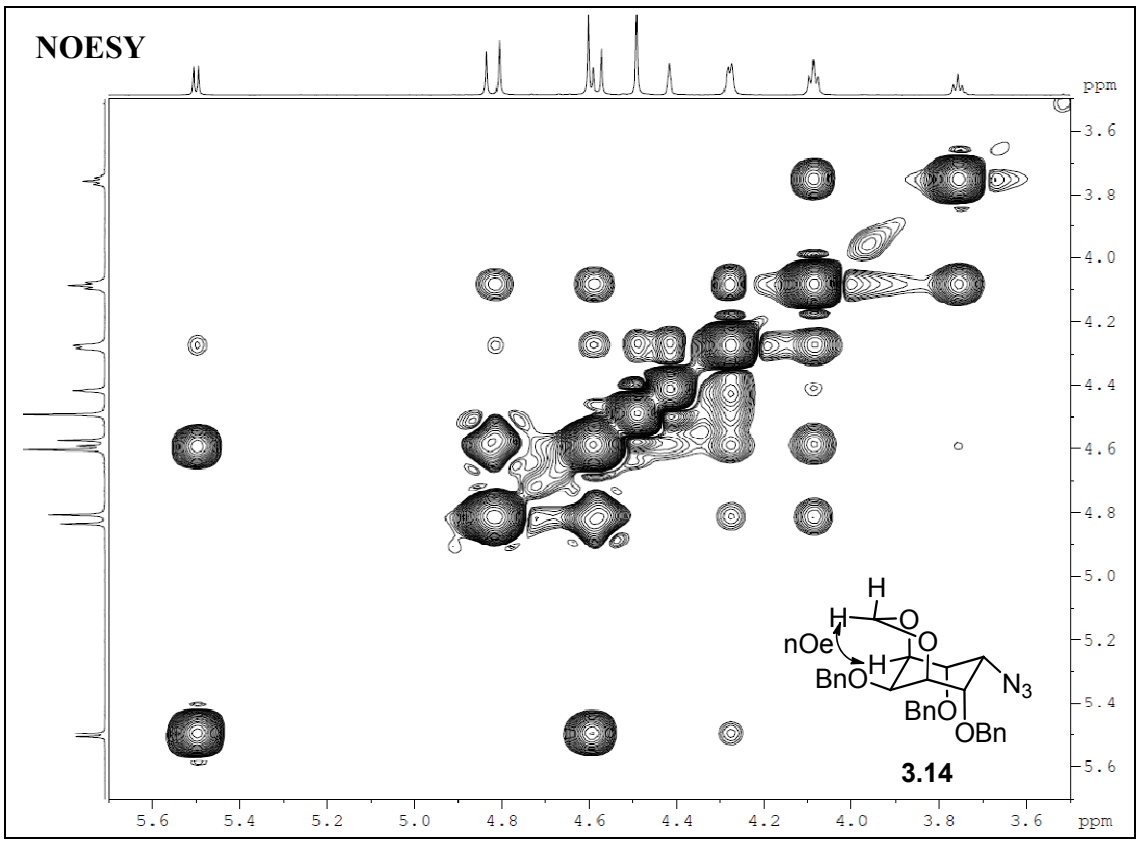

COSY
Ph
H
O
O
BnO
BnO
OBn
2.55
ppm
2.5
3.0
3.5
4.0
4.5
5.0
5.5
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm

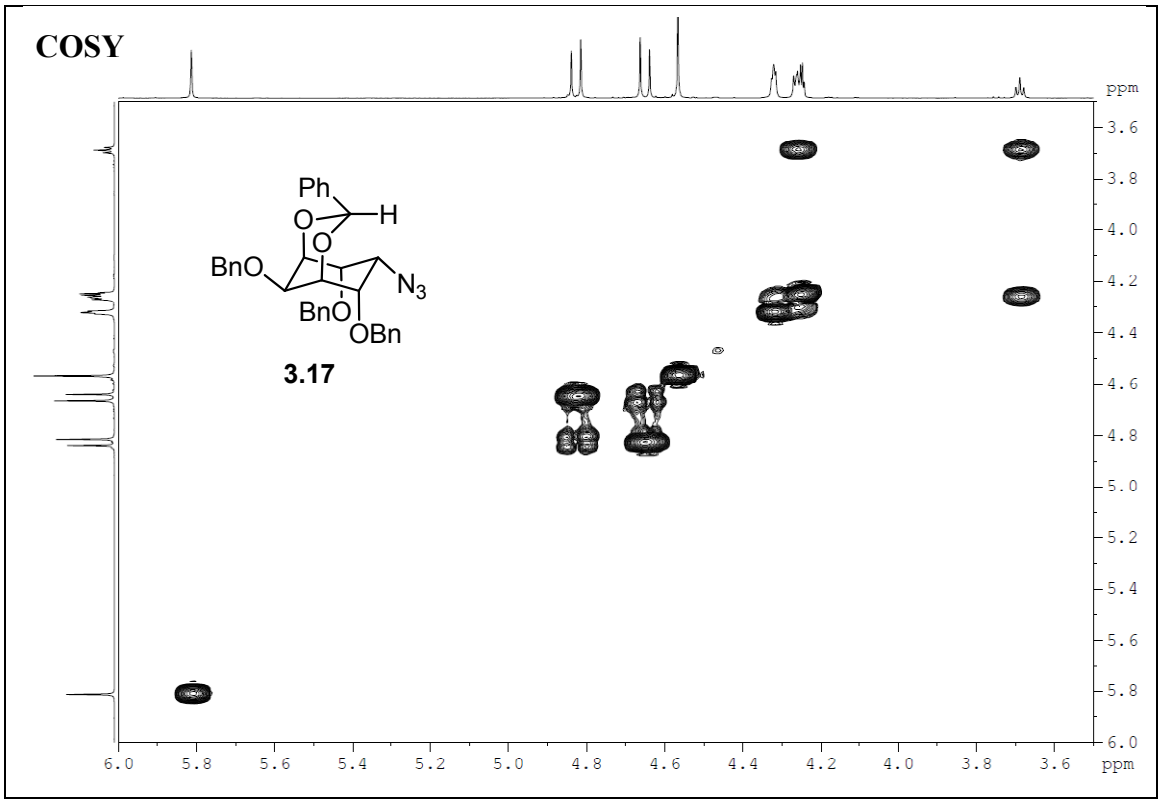

NOESY
Ph
H
O
O
nOe
H
BnO
BnO
OBn
2.55
ppm
2.5
3.0
3.5
4.0
4.5
5.0
5.5
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm

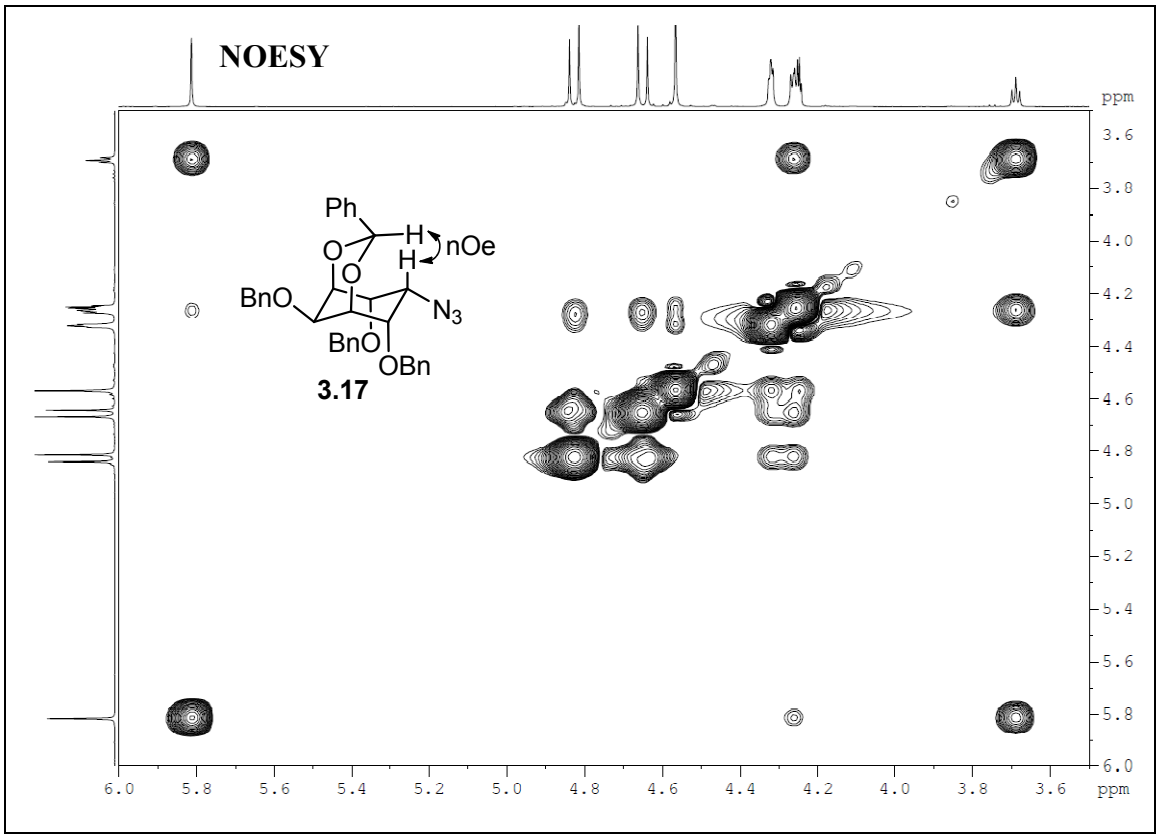

COSY
Ph
H
O
O
PMBO
BnO
OBn
2.56
ppm
2.5
3.0
3.5
4.0
4.5
5.0
5.5
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm

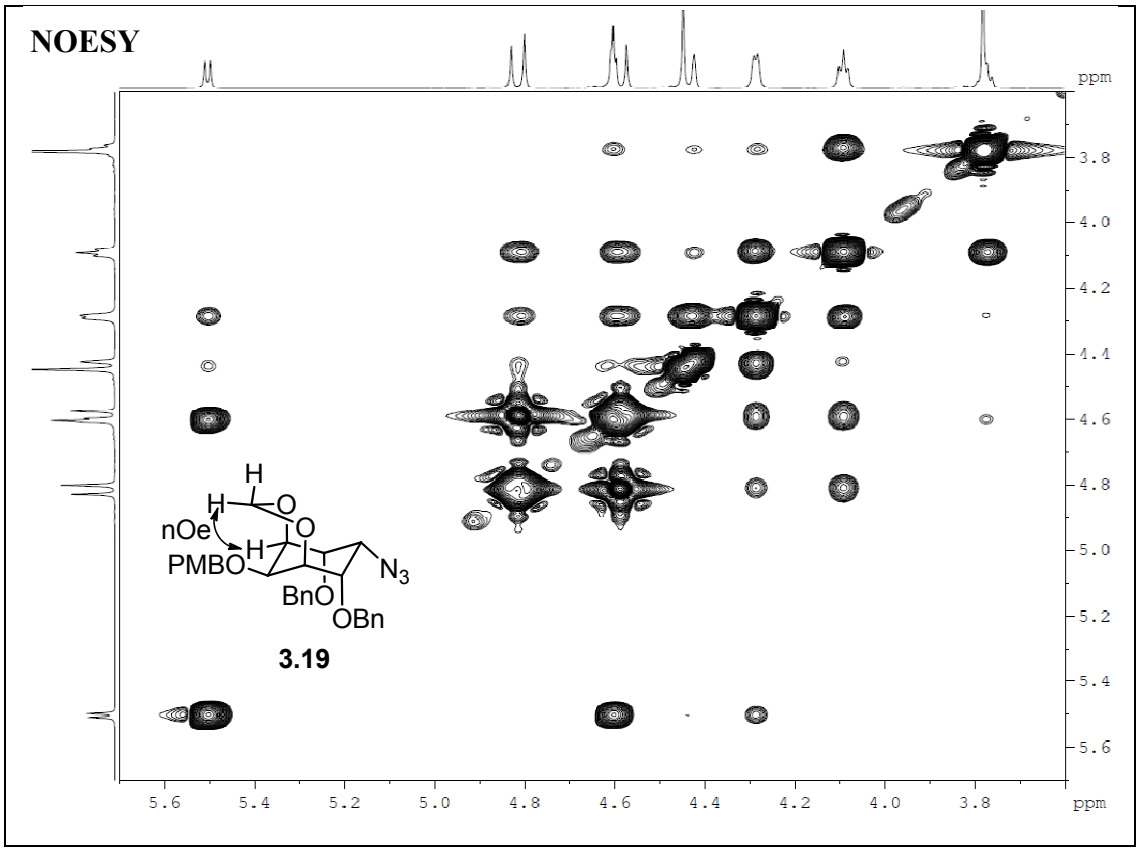

NOESY
Ph
H
O
O
nOe
H
PMBO
BnO
OBn
2.56
ppm
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

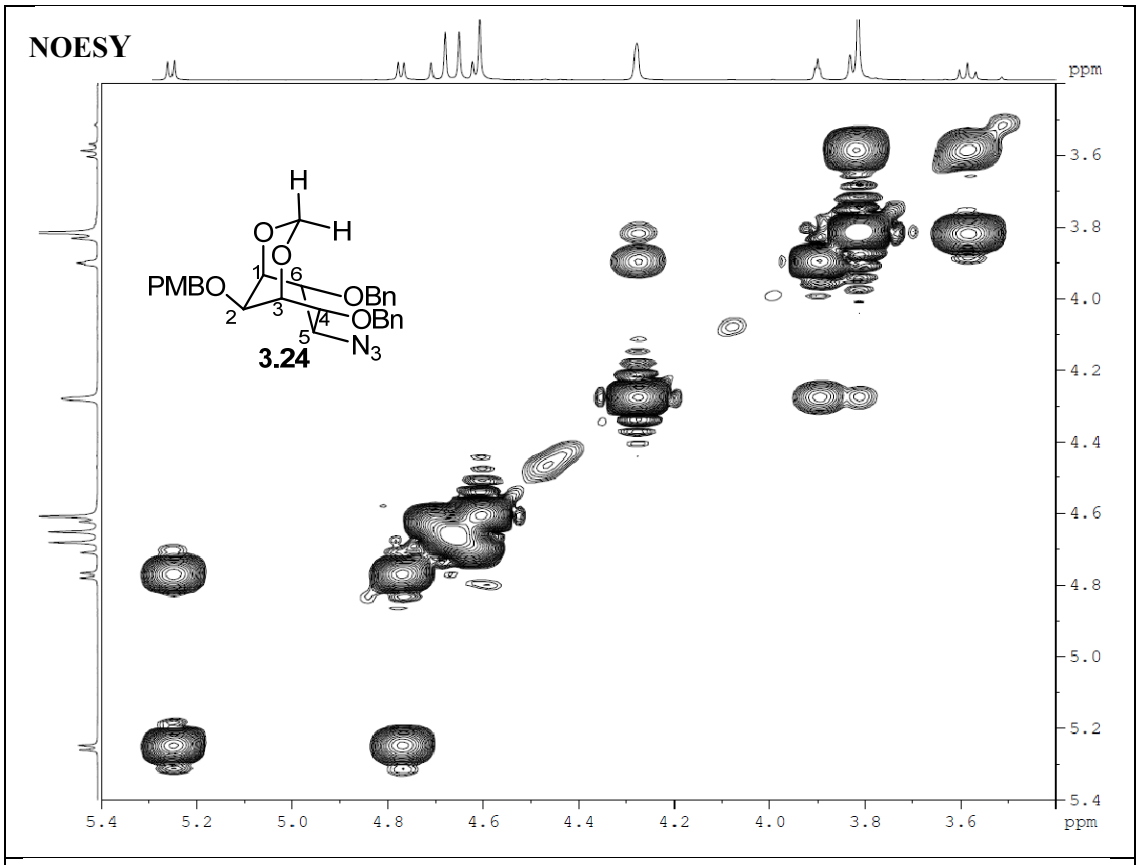

COSY
BnO
BnO
OBn
N3
3.14
ppm
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8

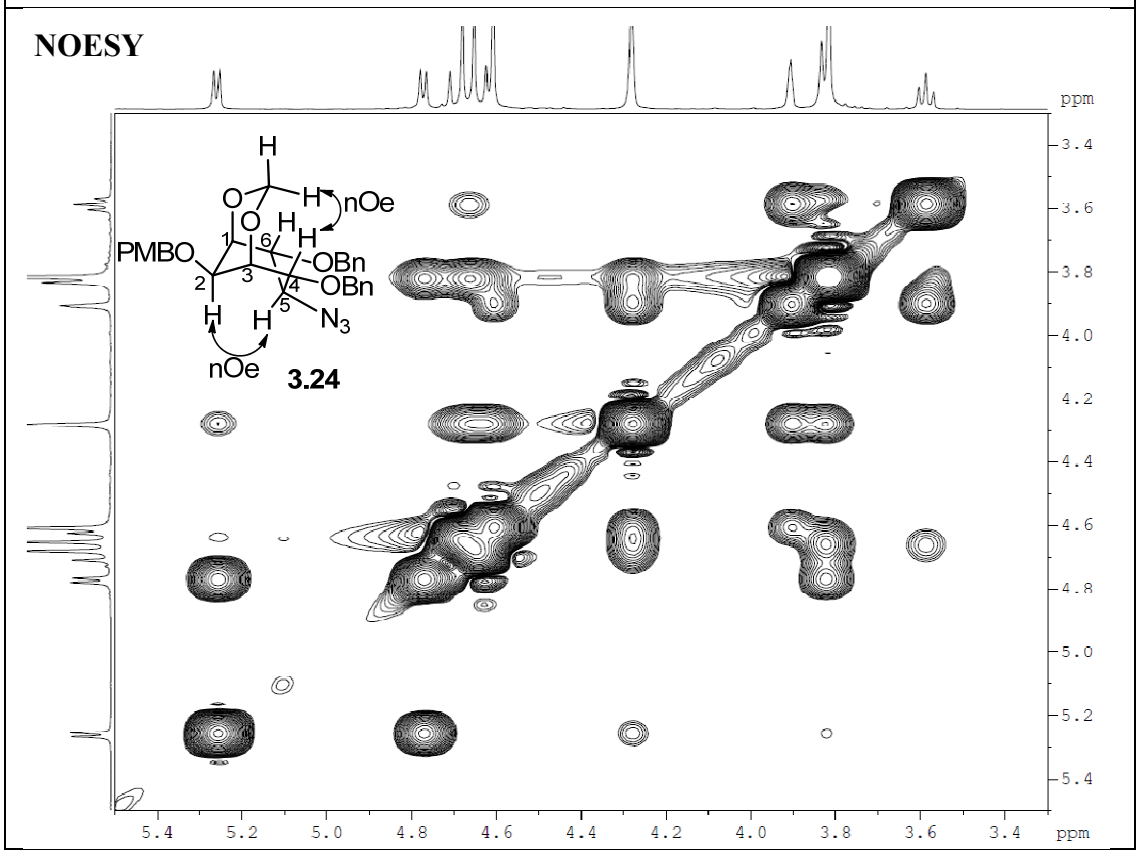

NOESY
nOe
H
BnO
BnO
OBn
N3
3.14
ppm
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6

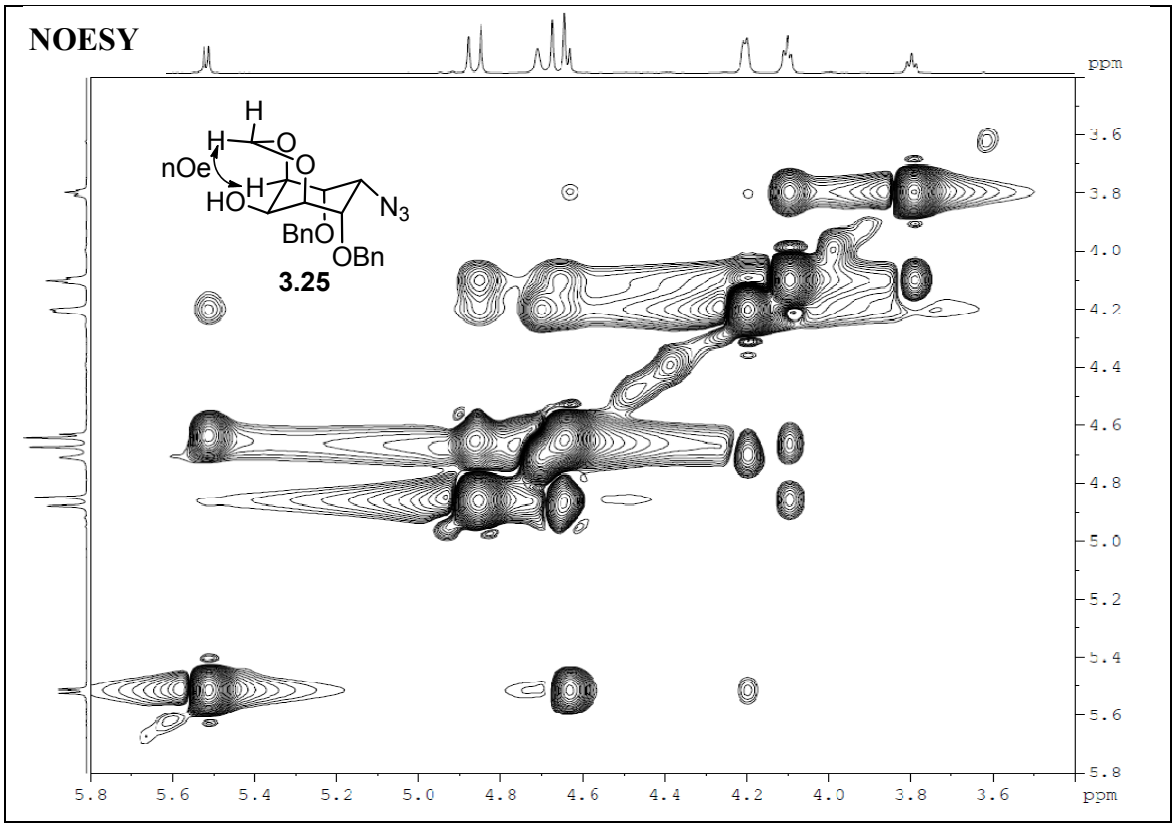

COSY
Ph
O
H
O
BnO
N3
BnO
OBn
3.17
ppm
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 ppm

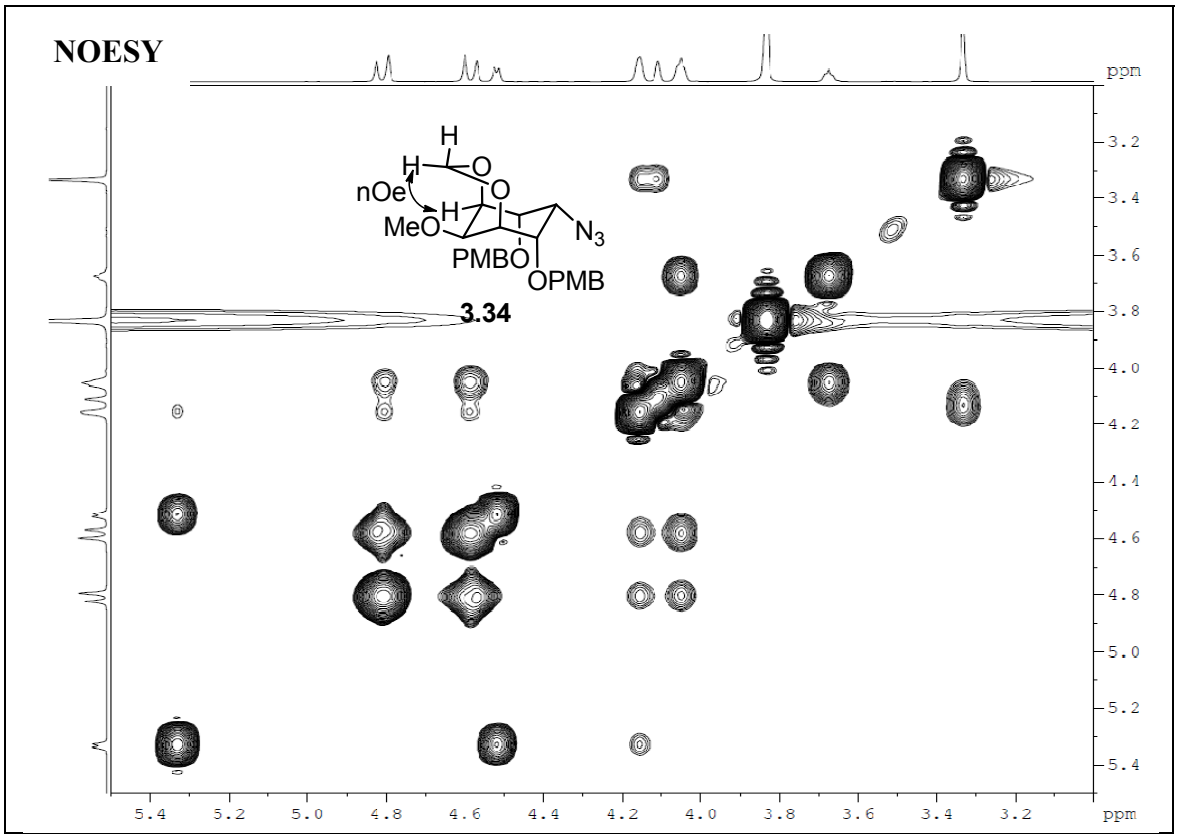

NOESY
Ph
H
nOe
O
H
O
BnO
N3
BnO
OBn
3.17
ppm
3.6
3.0
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 ppm

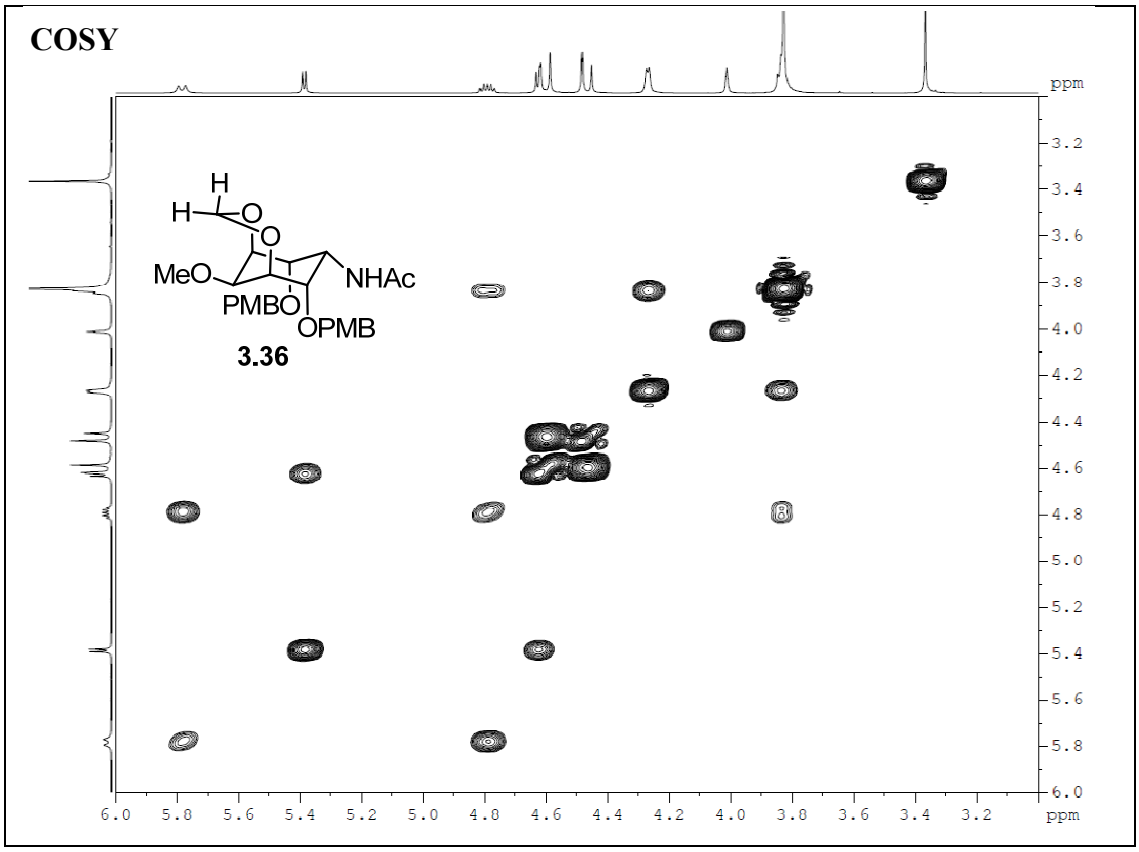

NOESY
ppm
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
ppm
H
H
O
nOe
O
H
PMBO
N3
BnO
OBn
3.19

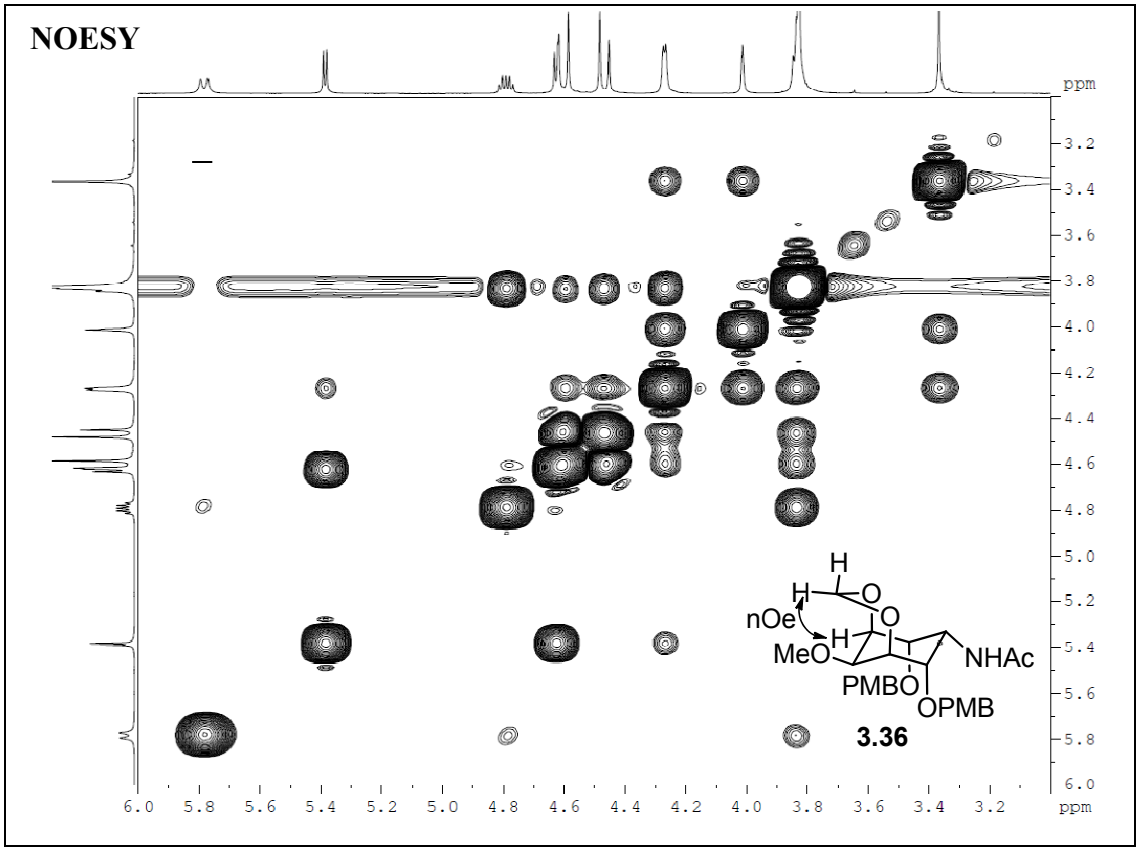

NOESY
ppm
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
PMBO
OBn
OBn
N3
3.24


NOESY
ppm
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
nOe
nOe
PMBO
OBn
OBn
N3
3.24

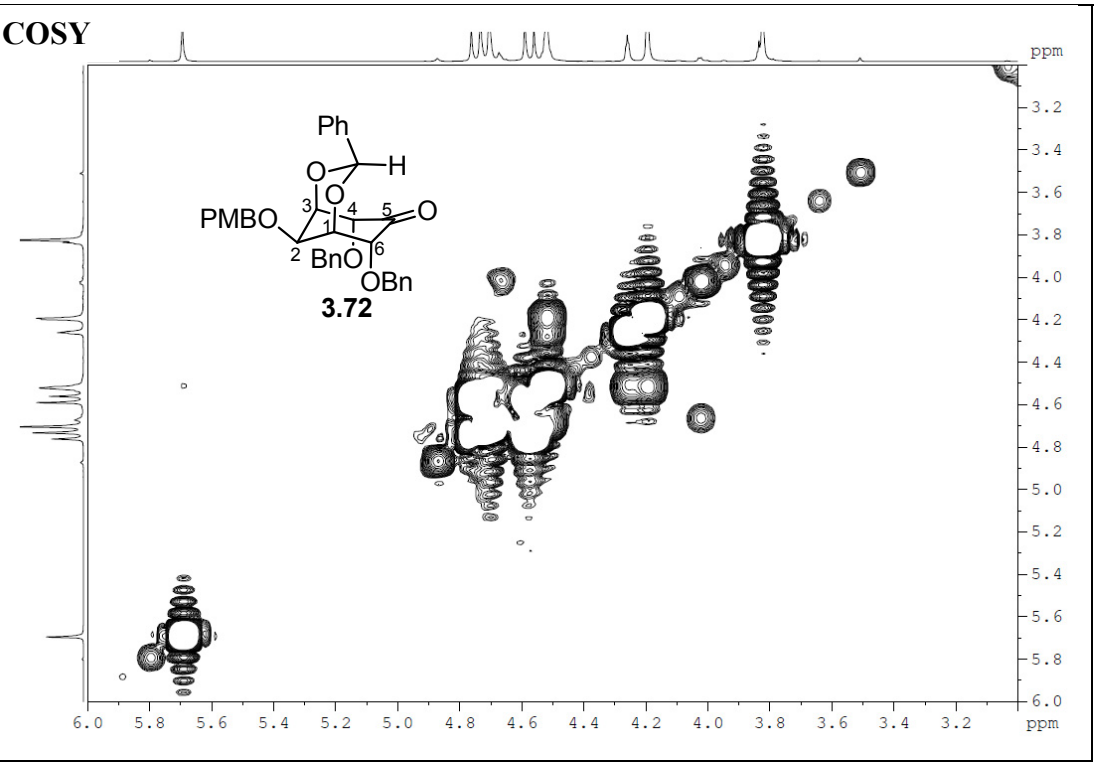

NOESY
nOe
HO
BnO
OBn
N3
3.25
ppm
5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 ppm


NOESY
nOe
MeO
PMBO
OPMB
N3
3.34
ppm
5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 ppm

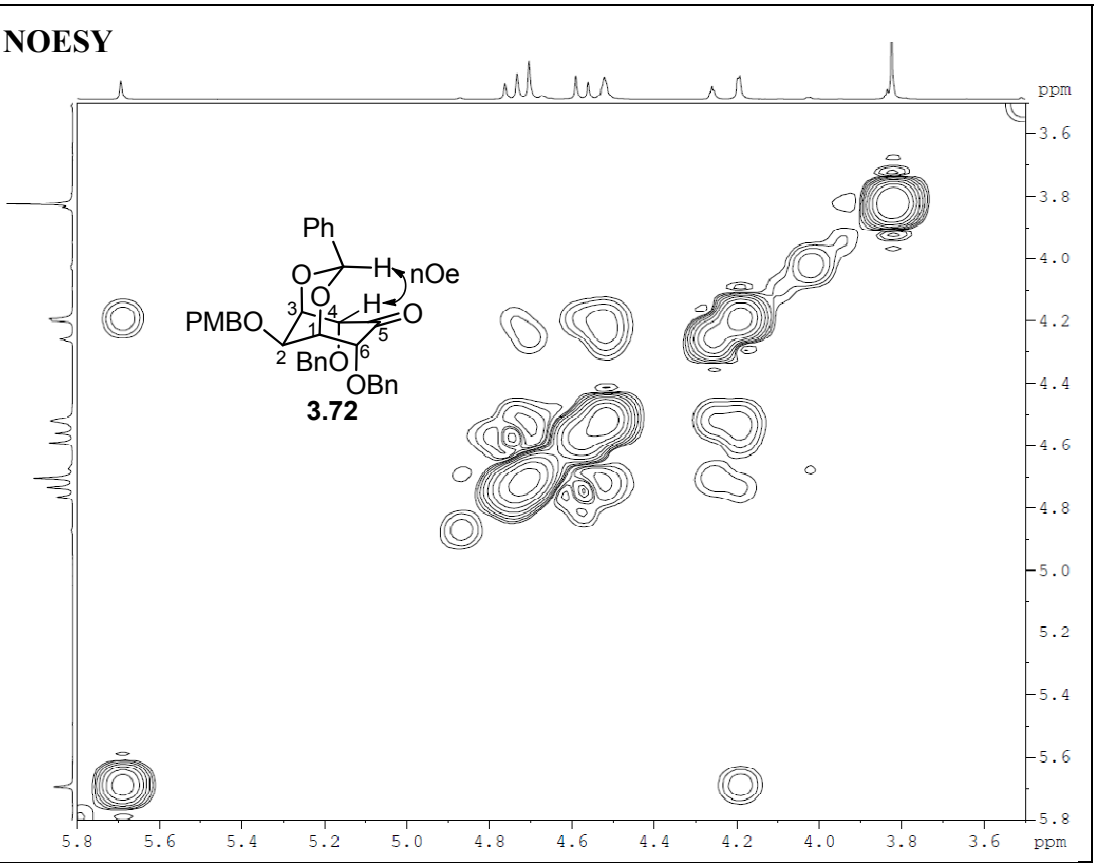

COSY
ppm
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2
ppm
H
H
O
O
MeO
NHAc
PMBO
OPMB
3.36

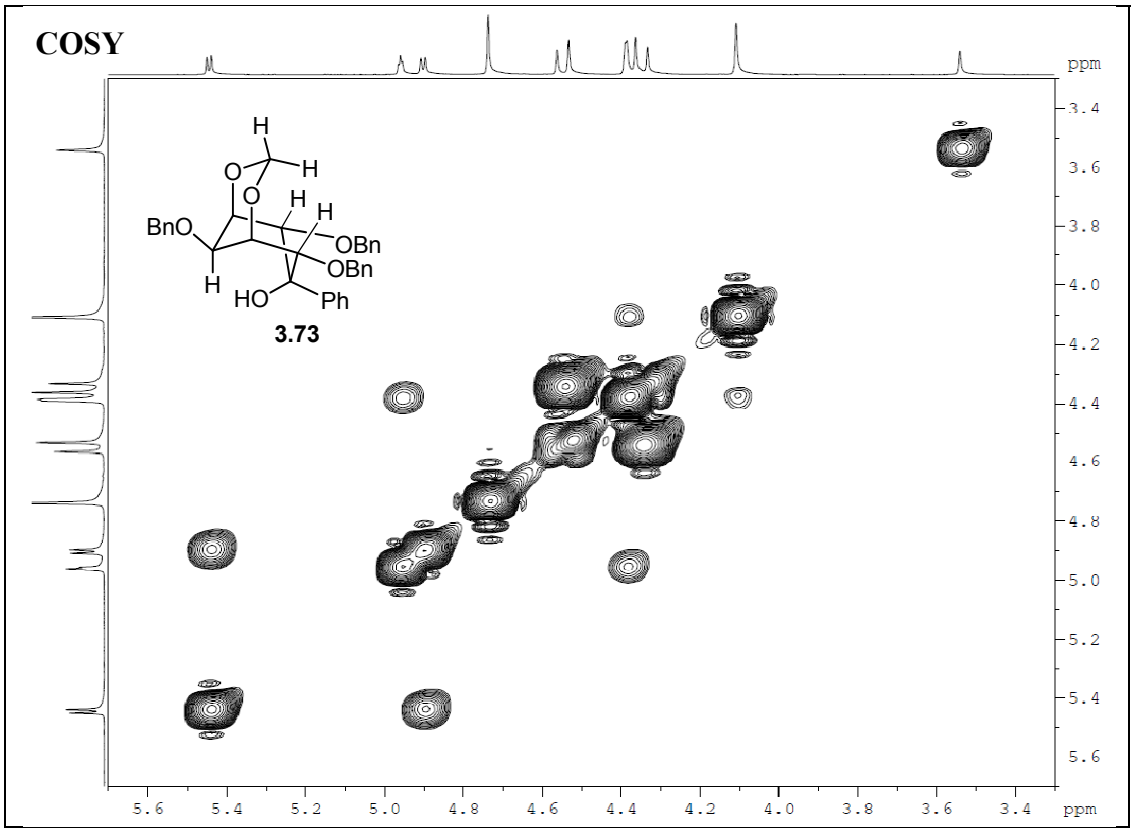

NOESY
ppm
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2
ppm
H
H
O
O
nOe
H
MeO
NHAc
PMBO
OPMB
3.36

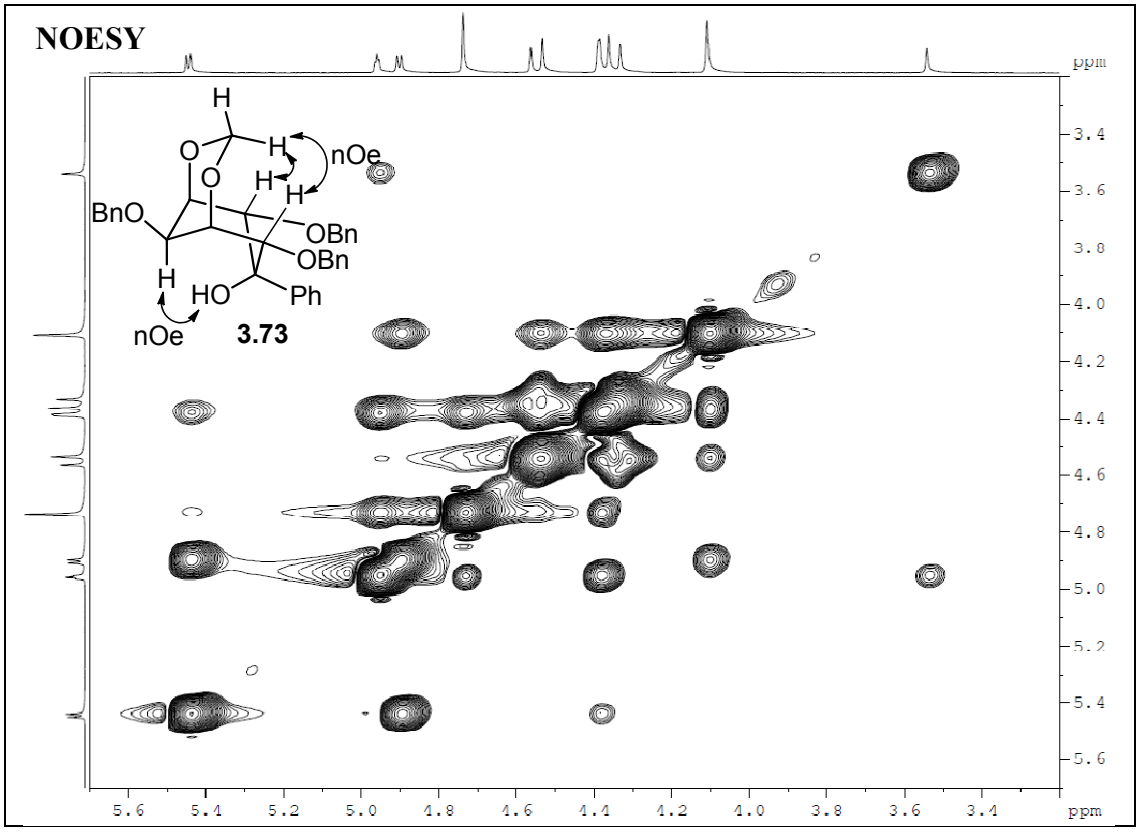
COSY

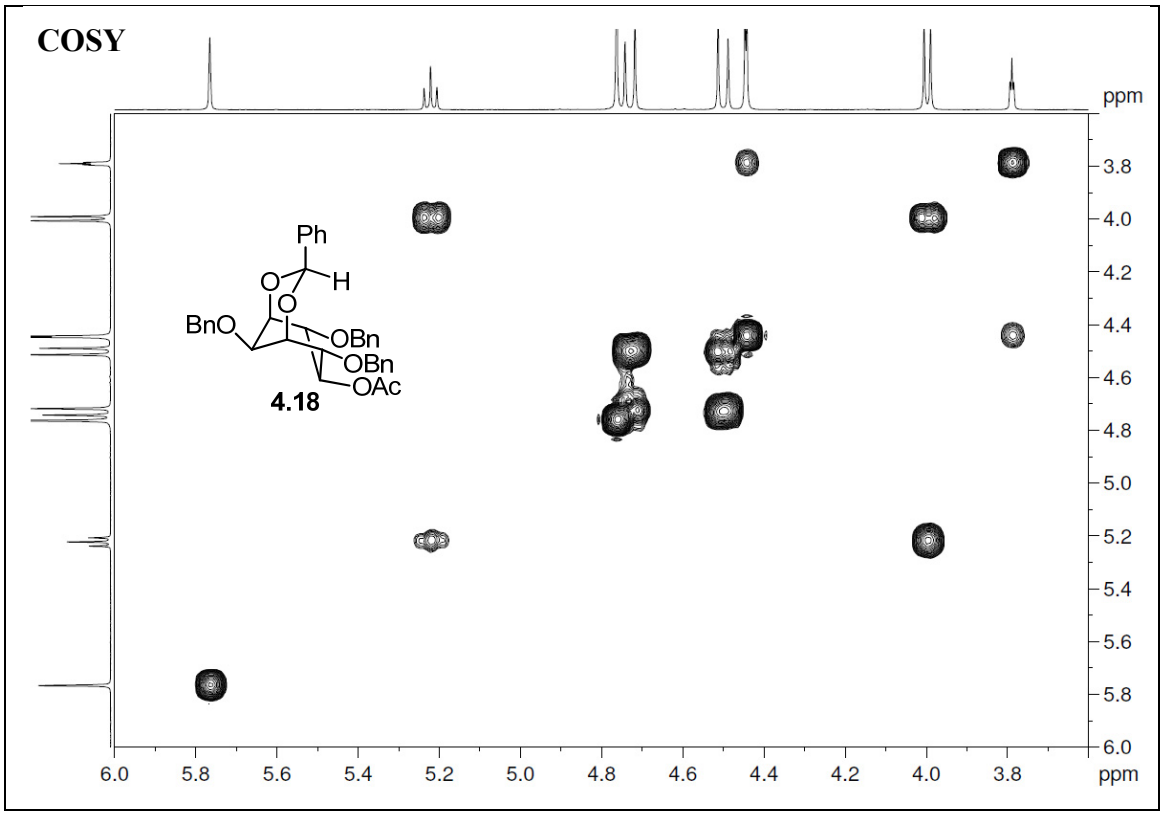

Ph
O
H
O
3
4
5
O
PMBO
1
2
BnO
6
OBn
3.72
ppm
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2
ppm

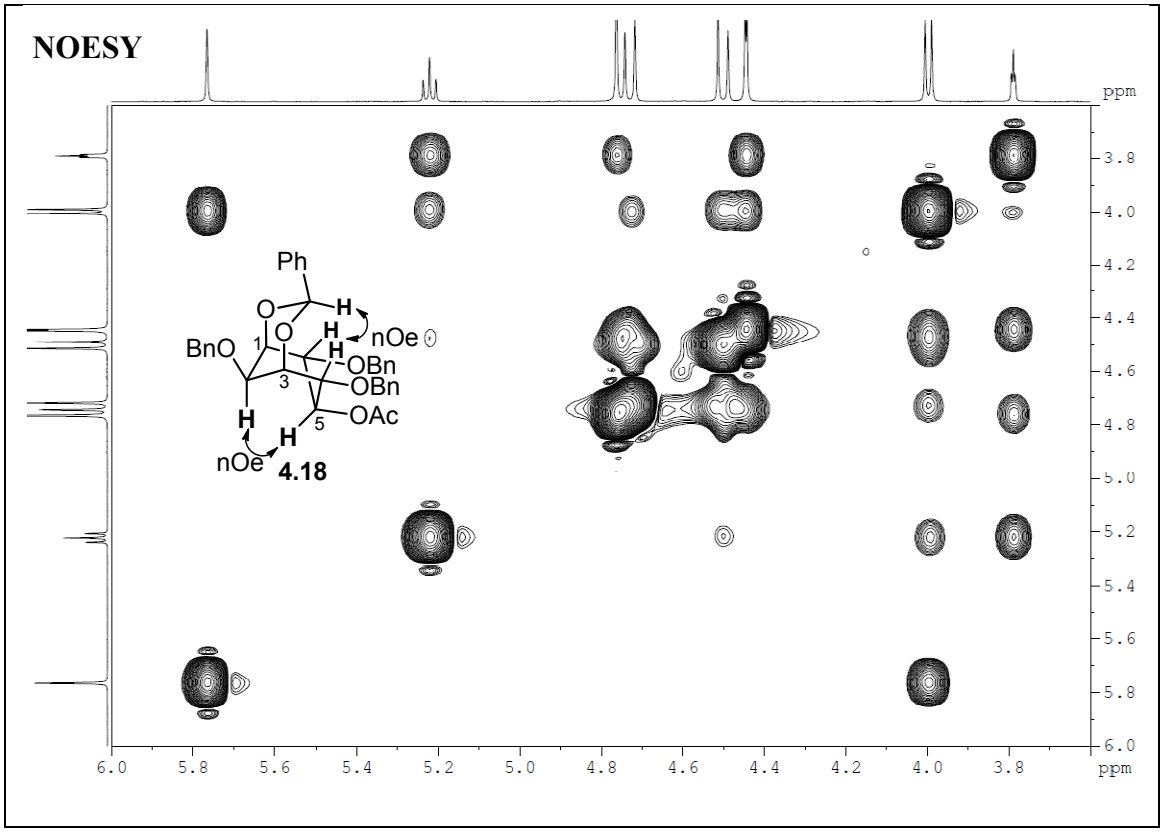
NOESY

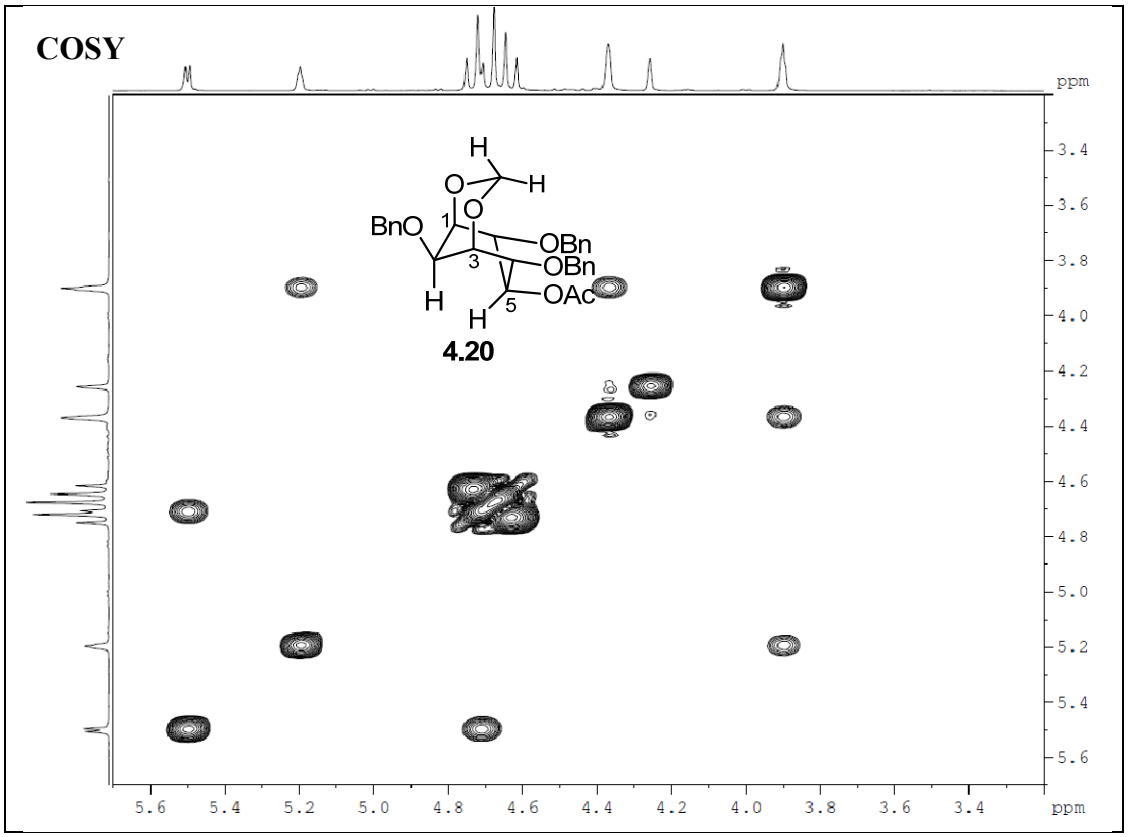

Ph
O
H
nOe
O
3
4
H
O
PMBO
1
5
2
BnO
6
OBn
3.72
ppm
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6
ppm

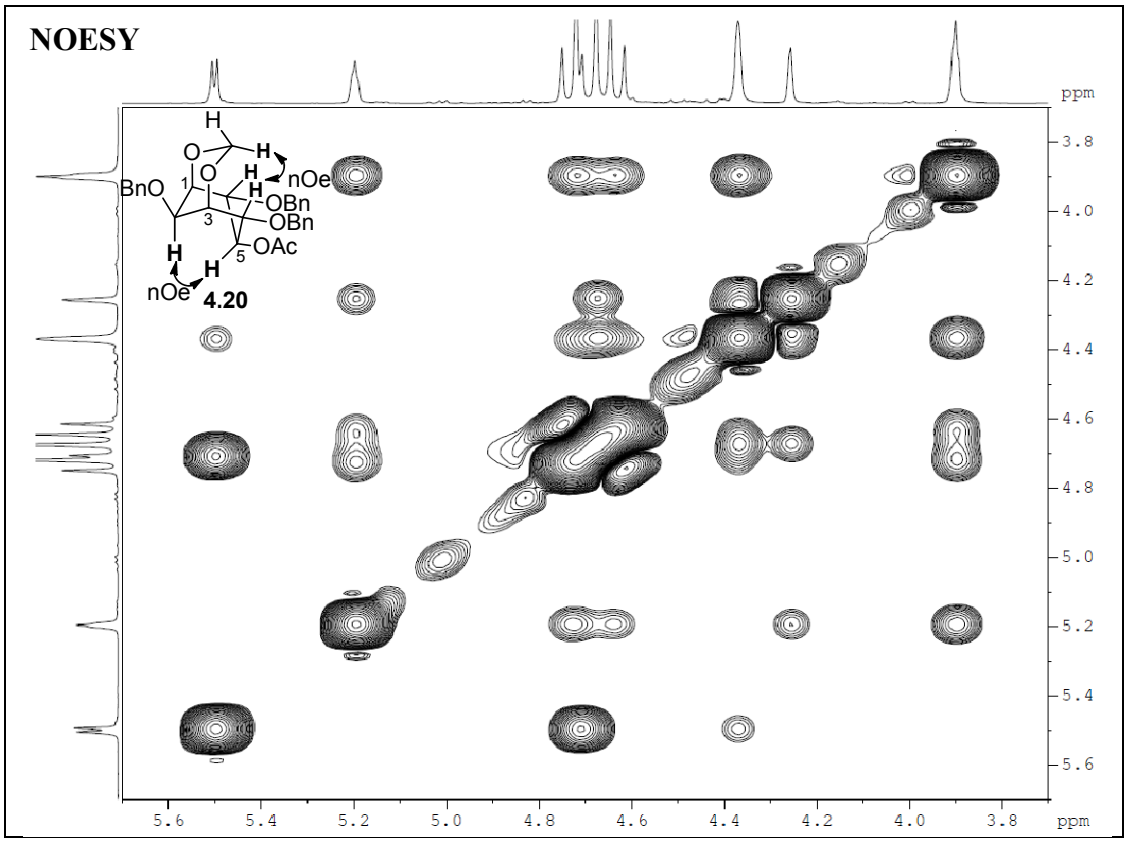

COSY
BnO
OBn
OBn
HO
Ph
3.73
ppm
5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 ppm

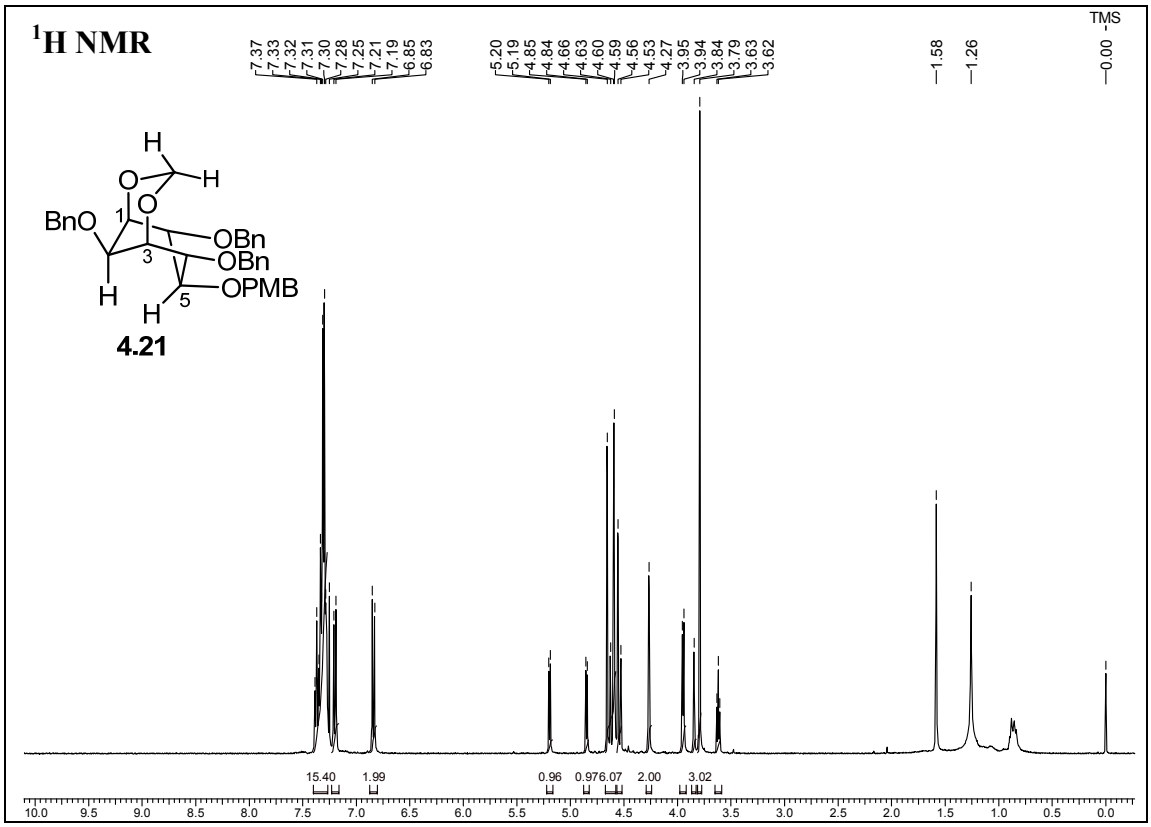

NOESY
nOe
nOe
BnO
OBn
OBn
HO
Ph
3.73
ppm
5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 ppm

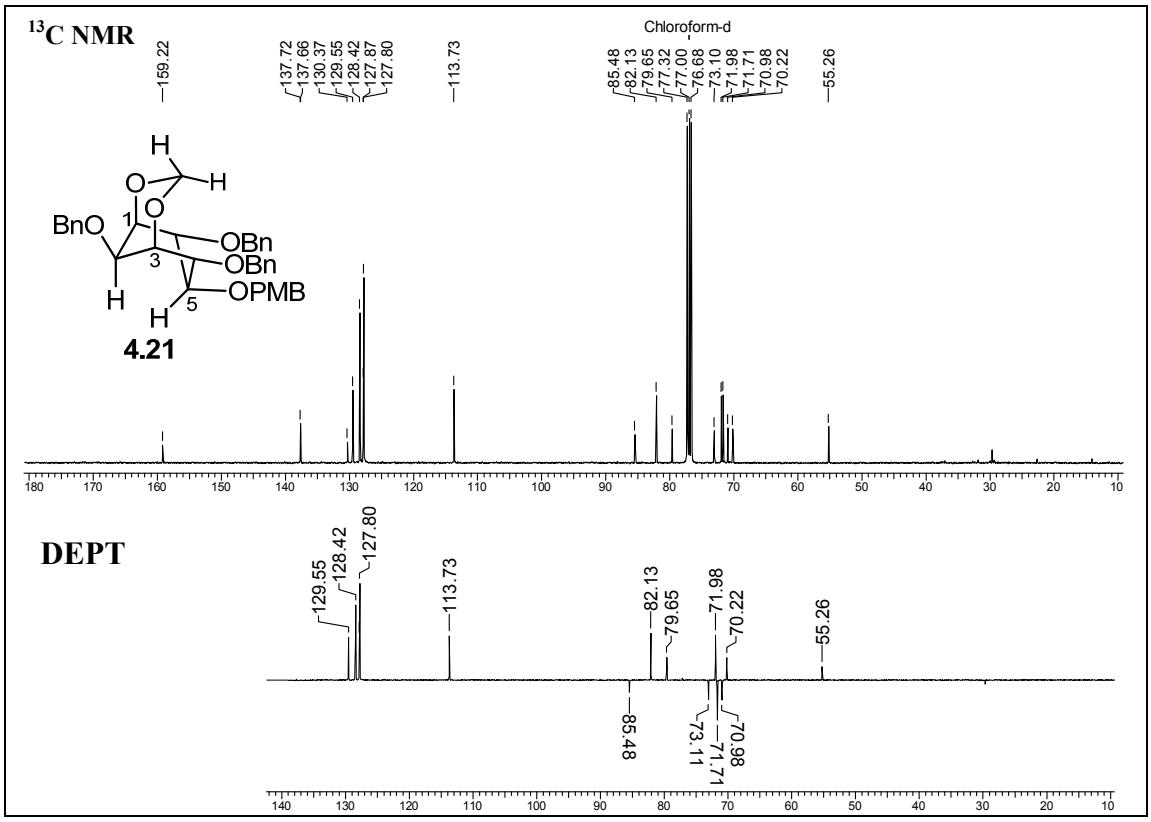

COSY
Ph
O
H
O
BnO
OBn
OBn
OAc
4.18
ppm
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 ppm

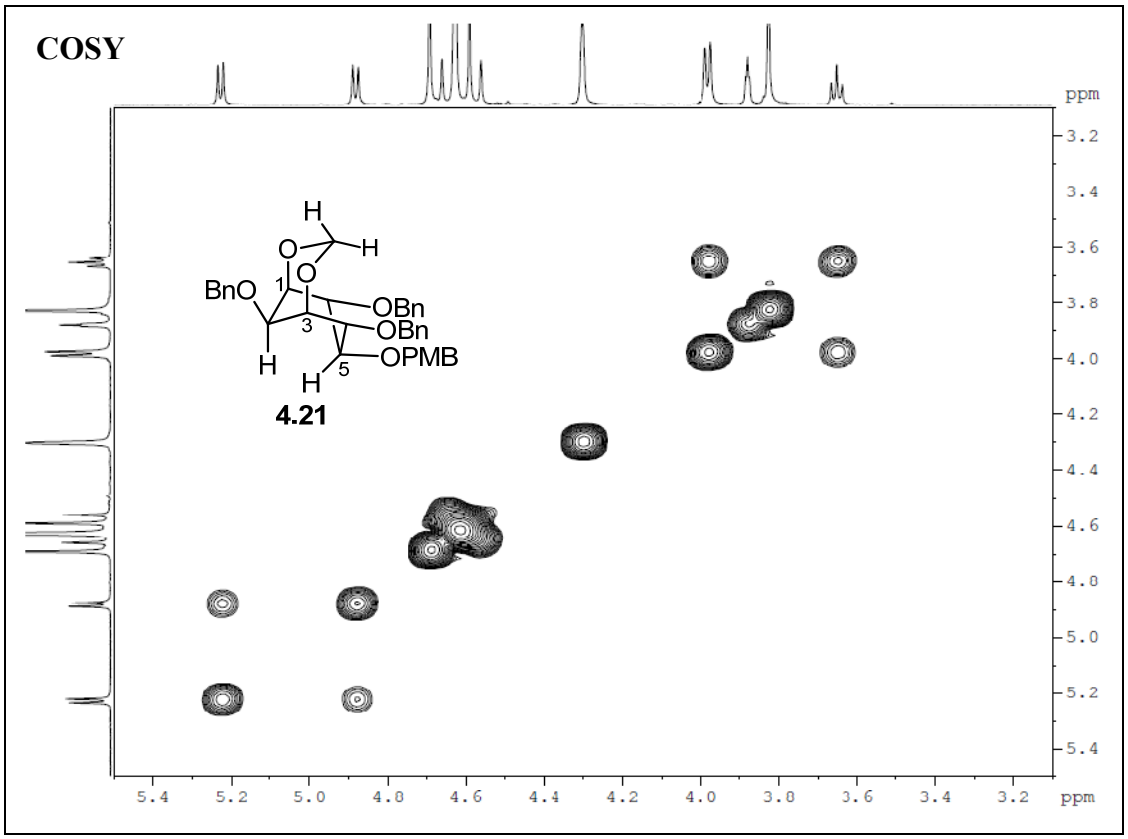

NOESY
Ph
O
H
O
H
nOe
BnO
1
H
OBn
3
OBn
H
5
OAc
nOe
H
4.18
ppm
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 ppm

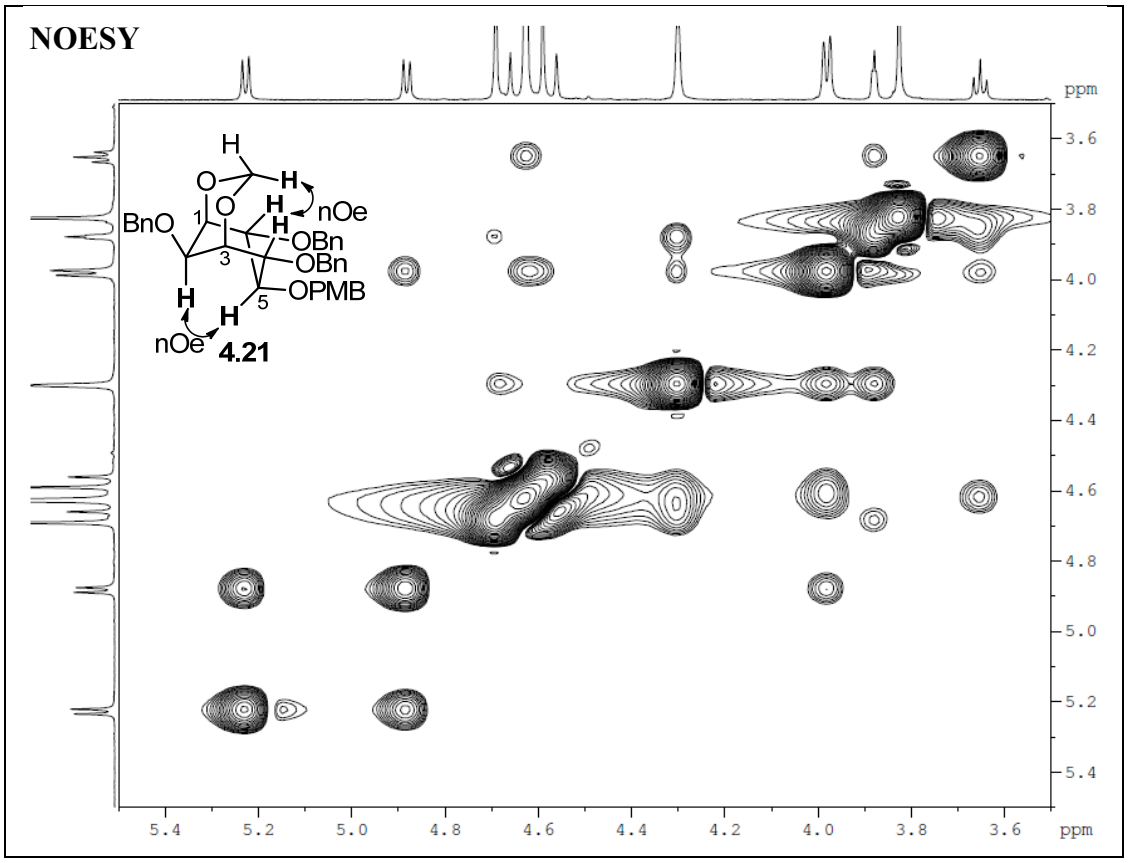

COSY
ppm
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 ppm
H
O
H
O
BnO
1
OBn
3
OBn
H
5
OAc
H
4.20

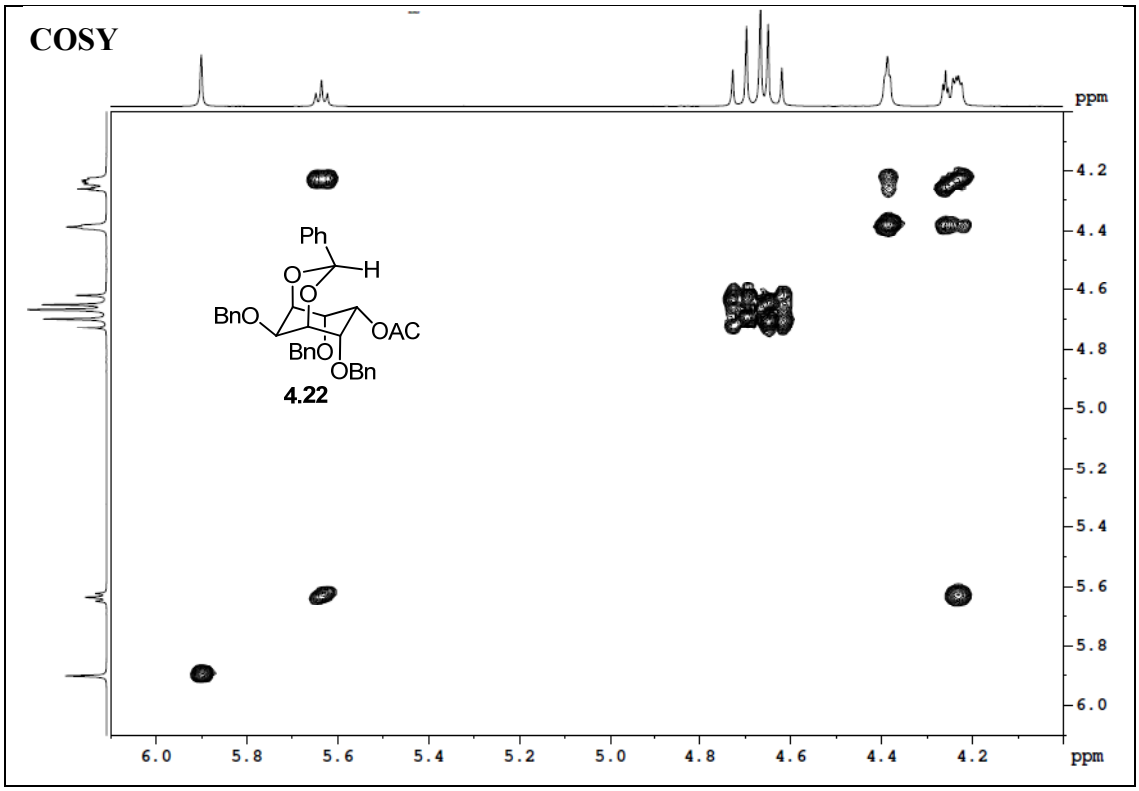

NOESY
ppm
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 ppm
H
O
H
O
H
nOe
BnO
1
H
OBn
3
OBn
H
5
OAc
H
nOe
4.20

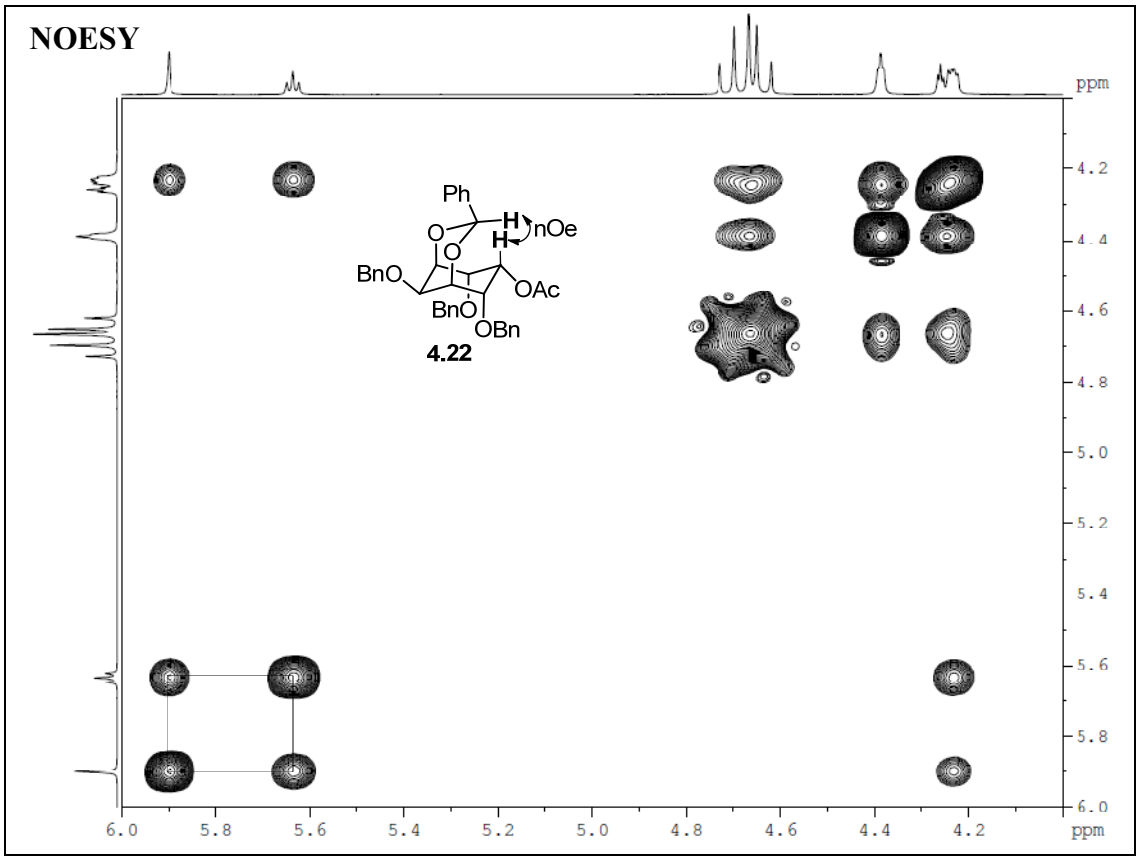

^{1}H NMR
TMS
7.37
7.33
7.32
7.31
7.30
7.28
7.25
7.21
7.19
6.85
6.83
5.20
5.19
4.85
4.84
4.66
4.63
4.60
4.59
4.56
4.53
4.27
3.95
3.94
3.84
3.79
3.63
3.62
1.58
1.26
0.00
15.40
1.99
0.96
0.97
6.07
2.00
3.02
BnO
OBn
OBn
OPMB
4.21


^{13}C NMR
Chloroform-d
159.22
137.72
137.66
130.37
129.55
128.42
127.87
127.80
113.73
85.48
82.13
79.65
77.32
77.00
76.88
73.10
71.98
71.71
70.98
70.22
55.26
BnO
OBn
OBn
OPMB
4.21
DEPT
129.55
128.42
127.80
113.73
82.13
79.65
71.98
70.22
55.26
85.48
73.11
71.71
70.98

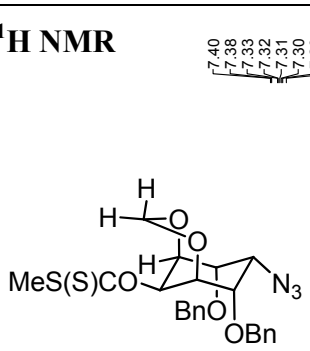

COSY
H
O
H
1
O
BnO
OBn
3
OBn
H
5
OPMB
H
4.21
ppm
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 ppm


NOESY
H
O
H
1
O
H
nOe
BnO
H
OBn
3
OBn
H
5
OPMB
H
H
nOe
4.21
ppm
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 ppm

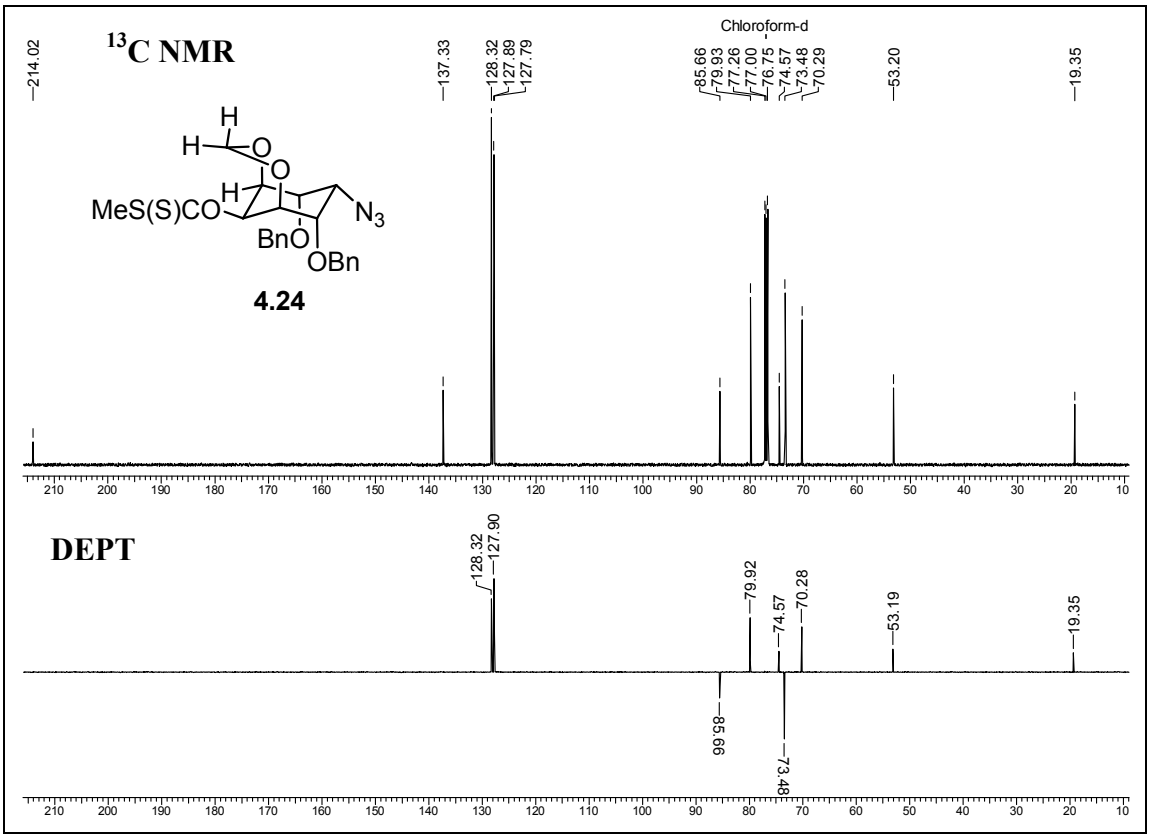

COSY
ppm
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
Ph
O
H
O
BnO
OAC
BnO
OBn
4.22


NOESY
ppm
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
Ph
O
H
nOe
H
O
BnO
OAc
BnO
OBn
4.22

^{1}H NMR



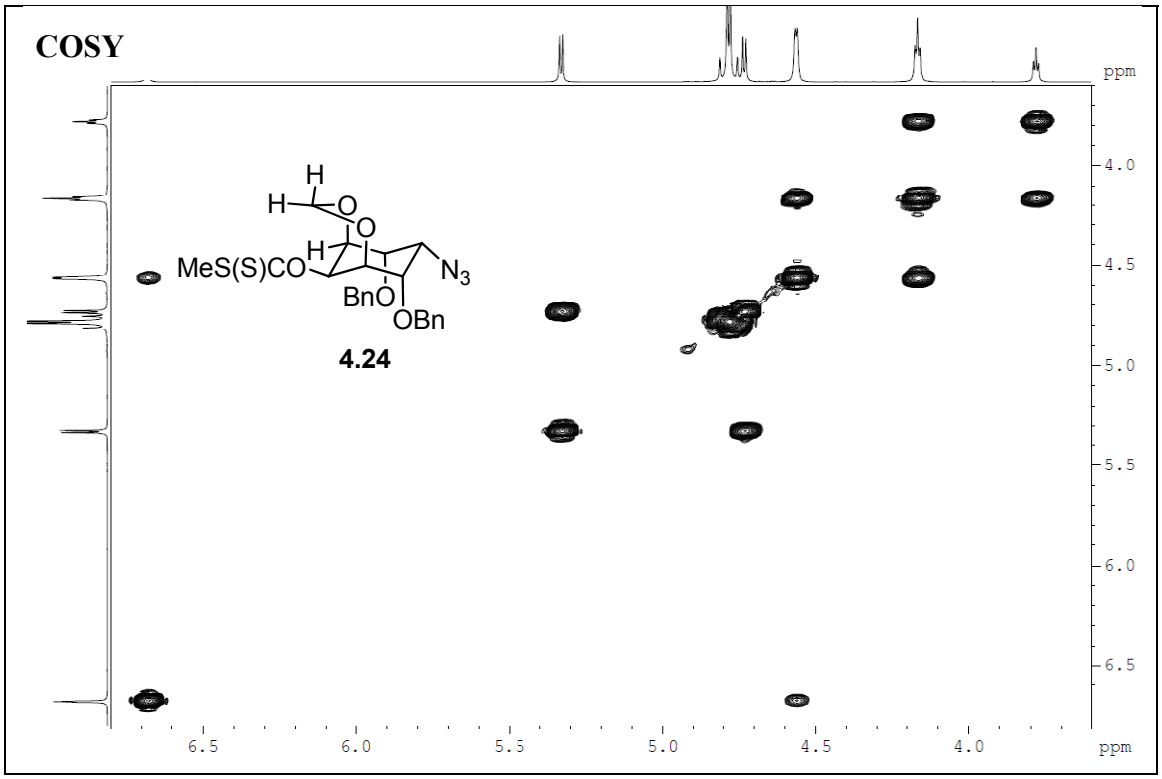
4.24

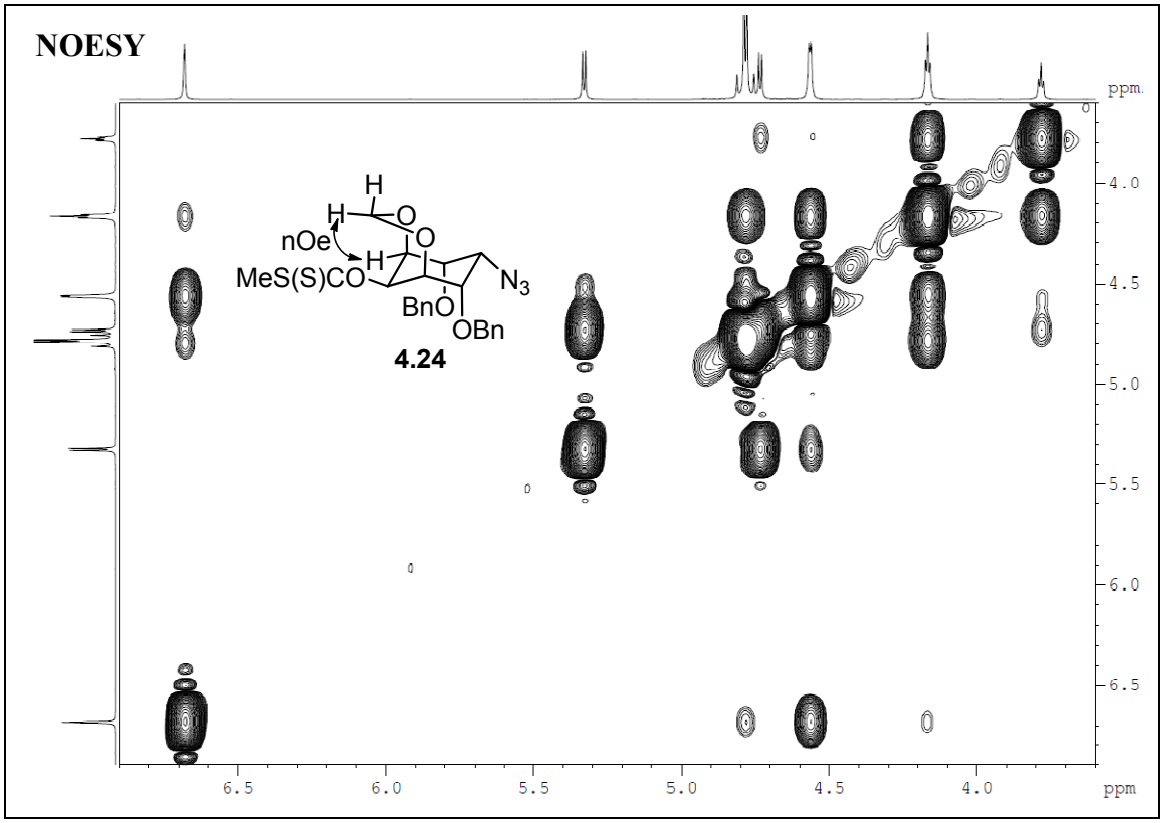


^{13}C NMR

4.24

DEPT





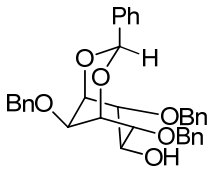
DFT data: For the atomic symbol and three (x, y, z) Cartesian coordinates in Å see Appendix IV (CD enclosed).

Appendix IV

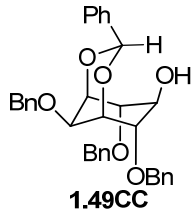
The optimized geometries for bicyclic inositol derivatives and the atomic symbol followed by the three Cartesian coordinates, in Å

Index

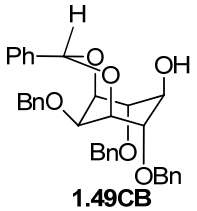
1). C1,C3-*O*-Benzylidene *myo*-inositol derivatives



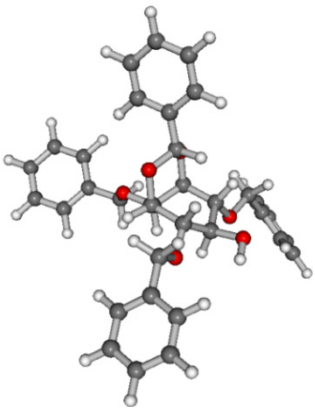
1.49BC



1.49CC

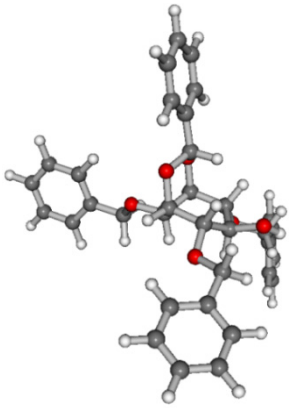


1.49CB



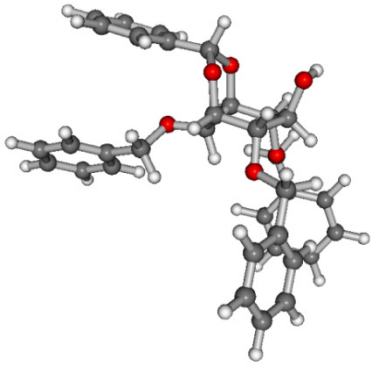
1.49BC

ΔE **0.0** kcal/mol



1.49CC

ΔE **4.4** kcal/mol



1.49CB

ΔE **9.4** kcal/mol

1.49BC

Final heat of formation = –1768.037

C	0.000	0.000	0.000
C	0.000	0.000	1.403
C	1.227	0.000	2.081
C	2.432	0.003	1.373
C	2.421	0.003	-0.024
C	1.202	-0.001	-0.711
C	-1.300	-0.023	2.163
O	-1.761	-1.384	2.250
C	-2.938	-1.532	3.038
C	-3.154	-3.020	3.319
C	-4.304	-3.215	4.348
C	-5.137	-1.950	4.617
C	-5.427	-1.112	3.368
C	-4.234	-1.055	2.360
O	-4.458	-1.810	1.152
C	-4.543	-3.220	1.381
O	-3.408	-3.723	2.083
O	-6.390	-2.291	5.223
O	-3.820	-3.617	5.642
C	-3.473	-5.018	5.713
C	-2.998	-5.328	7.107
C	-3.901	-5.761	8.089
C	-3.465	-6.025	9.390
C	-2.118	-5.856	9.724
C	-1.209	-5.425	8.752
C	-1.648	-5.164	7.452
O	-5.744	0.205	3.836
C	-6.618	0.926	2.952
C	-6.940	2.267	3.561
C	-7.511	2.342	4.841
C	-7.826	3.581	5.403
C	-7.581	4.760	4.690
C	-7.013	4.694	3.415
C	-6.691	3.452	2.858
C	-4.628	-3.912	0.045
C	-3.504	-3.959	-0.791
C	-3.588	-4.585	-2.036
C	-4.791	-5.165	-2.454
C	-5.913	-5.119	-1.622
C	-5.829	-4.494	-0.374
H	-6.169	-2.713	6.073
H	-4.553	-1.313	5.307
H	-4.979	-4.001	3.959
H	-2.230	-3.466	3.709
H	-2.813	-0.993	3.998
H	-4.145	-0.015	2.020
H	-6.303	-1.543	2.847
H	-5.461	-3.428	1.971
H	-2.571	-3.509	-0.452
H	-2.710	-4.623	-2.685
H	-4.853	-5.655	-3.428
H	-6.853	-5.571	-1.943
H	-6.704	-4.458	0.279
H	-6.153	1.065	1.958
H	-7.543	0.333	2.805
H	-7.694	1.421	5.398
H	-8.269	3.628	6.400
H	-7.831	5.728	5.129
H	-6.815	5.609	2.855
H	-6.239	3.403	1.864
H	-4.363	-5.624	5.458
H	-2.684	-5.251	4.977
H	-4.953	-5.896	7.828
H	-4.177	-6.366	10.144
H	-1.775	-6.066	10.739
H	-0.156	-5.297	9.007
H	-0.937	-4.829	6.694
H	-2.049	0.604	1.646
H	-1.158	0.386	3.182
H	1.235	-0.002	3.174
H	3.380	0.008	1.913
H	3.361	0.008	-0.579
H	1.189	0.001	-1.802
H	-0.952	-0.004	-0.535

1.49CC

Final heat of formation = –1768.030

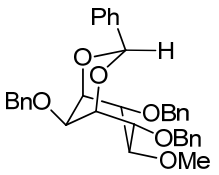
C	0.000	0.000	0.000
C	0.000	0.000	1.403
C	1.225	0.000	2.083
C	2.431	0.001	1.377
C	2.421	0.001	-0.020

C	1.203	-0.001	-0.708
C	-1.302	-0.028	2.161
O	-1.825	-1.366	2.136
C	-3.192	-1.497	2.573
C	-3.337	-1.192	4.094
C	-4.377	-2.032	4.880
C	-4.680	-3.428	4.279
C	-3.554	-3.879	3.349
C	-3.602	-2.929	2.141
O	-4.900	-2.977	1.521
C	-5.947	-2.637	2.428
O	-5.943	-3.461	3.584
O	-3.753	-5.250	3.032
C	-2.617	-5.872	2.423
C	-2.949	-7.302	2.070
C	-1.952	-8.285	2.122
C	-2.229	-9.601	1.739
C	-3.514	-9.949	1.311
C	-4.516	-8.974	1.268
C	-4.237	-7.657	1.642
O	-3.933	-2.274	6.222
C	-4.053	-1.152	7.110
C	-3.791	-1.597	8.529
C	-3.233	-0.694	9.447
C	-3.033	-1.063	10.780
C	-3.377	-2.348	11.209
C	-3.924	-3.257	10.298
C	-4.134	-2.884	8.968
O	-3.702	0.187	4.325
C	-7.279	-2.770	1.722
C	-8.437	-3.075	2.449
C	-9.673	-3.150	1.801
C	-9.763	-2.918	0.425
C	-8.608	-2.614	-0.302
C	-7.371	-2.538	0.342
H	-2.584	-3.745	3.870
H	-4.794	-4.134	5.109
H	-5.323	-1.458	4.904
H	-2.355	-1.410	4.555
H	-3.825	-0.775	2.020
H	-2.902	-3.232	1.353
H	-2.980	0.753	4.000
H	-5.803	-1.578	2.745
H	-2.326	-5.327	1.503
H	-1.749	-5.841	3.110
H	-0.950	-8.022	2.469
H	-1.443	-10.357	1.785
H	-3.734	-10.977	1.017
H	-5.523	-9.240	0.942
H	-5.017	-6.896	1.619
H	-8.361	-3.269	3.519
H	-10.569	-3.394	2.375
H	-10.729	-2.978	-0.079
H	-8.670	-2.439	-1.378
H	-6.466	-2.315	-0.224
H	-2.038	0.659	1.698
H	-1.119	0.305	3.203
H	-3.356	-0.345	6.830
H	-5.077	-0.735	7.021
H	-2.950	0.307	9.113
H	-2.598	-0.349	11.481
H	-3.214	-2.642	12.248
H	-4.189	-4.264	10.625
H	-4.555	-3.593	8.255
H	1.233	-0.004	3.176
H	3.379	0.002	1.918
H	3.362	0.003	-0.574
H	1.192	0.002	-1.800
H	-0.951	-0.003	-0.538

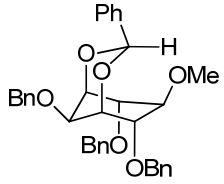
1.49CB

Final heat of formation = –1768.022

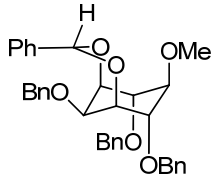
C	0.000	0.000	0.000
C	0.000	0.000	1.402
C	1.227	0.000	2.081
C	2.431	-0.003	1.373
C	2.420	-0.006	-0.025
C	1.202	-0.003	-0.712
C	-1.297	0.030	2.166
O	-1.662	1.402	2.407
C	-2.924	1.555	3.069
C	-3.450	2.948	2.643
C	-2.610	4.011	3.352
C	-2.964	3.932	4.829
C	-2.392	2.618	5.412
C	-2.803	1.356	4.602
O	-4.857	3.027	2.926
C	-5.275	3.885	3.988
O	-4.383	3.907	5.100
O	-0.961	2.631	5.478
C	-0.432	3.421	6.564
C	1.042	3.143	6.698
C	1.490	1.979	7.341
C	2.855	1.710	7.456
C	3.792	2.606	6.929
C	3.357	3.768	6.286
C	1.989	4.032	6.172
O	-2.774	5.358	2.907
C	-2.325	5.580	1.560
C	-2.072	7.051	1.343
C	-2.708	7.737	0.301
C	-2.442	9.090	0.069
C	-1.541	9.775	0.888
C	-0.908	9.101	1.939
C	-1.170	7.748	2.162
O	-4.062	0.816	5.031
C	-5.673	5.279	3.499
C	-6.198	5.445	2.211
C	-6.662	6.695	1.792
C	-6.615	7.790	2.660
C	-6.107	7.625	3.952
C	-5.645	6.375	4.372
H	-3.647	0.801	2.706
H	-2.805	2.513	6.437
H	-2.541	4.803	5.353
H	-0.595	4.499	6.382
H	-0.963	3.150	7.497
H	-1.188	-0.512	3.123
H	-2.101	-0.464	1.586
H	-0.681	7.223	2.985
H	-0.205	9.632	2.583
H	-1.334	10.832	0.712
H	-2.945	9.611	-0.747
H	-3.424	7.207	-0.332
H	1.235	0.010	3.173
H	3.380	-0.004	1.913
H	3.361	-0.011	-0.580
H	1.190	-0.006	-1.803
H	-0.952	0.002	-0.536
H	0.760	1.279	7.754
H	3.191	0.804	7.964
H	4.860	2.400	7.023
H	4.083	4.470	5.873
H	1.650	4.940	5.667
H	-3.332	3.015	1.551
H	-1.550	3.711	3.240
H	-1.393	5.003	1.389
H	-3.077	5.222	0.835
H	-5.247	6.242	5.379
H	-6.067	8.475	4.636
H	-6.976	8.767	2.332
H	-7.064	6.814	0.783
H	-6.235	4.587	1.538
H	-6.177	3.393	4.388
H	-1.992	0.624	4.779
H	-4.108	0.893	6.001



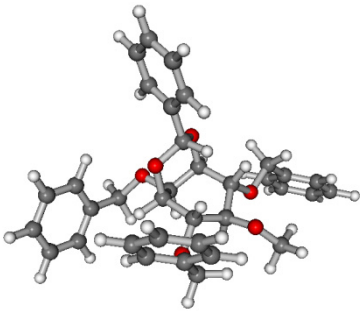
1.130BC



1.130CC

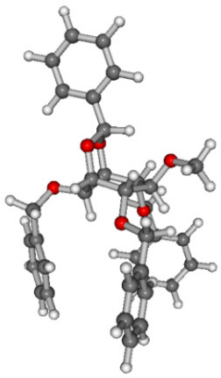


1.130CB



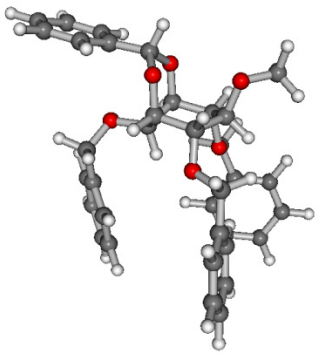
1.130BC

ΔE **0.0** kcal/mol



1.130CC

ΔE **1.2** kcal/mol



1.130CB

ΔE **5.0** kcal/mol

1.130BC

Final heat of formation = –1807.343

C	0.000	0.000	0.000
C	0.000	0.000	1.403
C	1.227	0.000	2.080
C	2.433	0.002	1.372
C	2.422	0.000	-0.026
C	1.202	-0.002	-0.711
C	-1.300	-0.014	2.164
O	-1.838	-1.353	2.147
C	-3.122	-1.451	2.789
C	-4.250	-0.941	1.843
C	-5.033	-2.119	1.261
C	-5.759	-2.757	2.456
C	-4.737	-3.378	3.451
C	-3.277	-2.925	3.224
O	-6.620	-1.775	3.074
C	-5.909	-0.626	3.535
O	-5.145	-0.016	2.495
C	-6.909	0.376	4.053
C	-7.105	0.525	5.431
C	-8.053	1.431	5.916
C	-8.808	2.195	5.022
C	-8.612	2.051	3.643
C	-7.667	1.144	3.159
O	-5.880	-1.631	0.222
C	-6.290	-2.609	-0.740
C	-7.503	-3.439	-0.359
C	-7.575	-4.791	-0.723
C	-8.716	-5.548	-0.437
C	-9.796	-4.959	0.227
C	-9.727	-3.613	0.603
C	-8.591	-2.856	0.308
O	-2.565	-3.191	4.443
C	-1.186	-3.541	4.274
O	-4.832	-4.807	3.301
C	-4.630	-5.573	4.506
C	-5.736	-5.409	5.530
C	-5.428	-5.148	6.873
C	-6.443	-5.035	7.830
C	-7.780	-5.173	7.449
C	-8.097	-5.424	6.109
C	-7.083	-5.545	5.158
H	-2.859	-3.553	2.415
H	-5.043	-3.092	4.472
H	-6.433	-3.559	2.136
H	-4.319	-2.853	0.837
H	-3.797	-0.359	1.030
H	-3.127	-0.820	3.699
H	-5.226	-0.933	4.355
H	-7.501	1.029	2.087
H	-9.198	2.650	2.944
H	-9.547	2.905	5.398
H	-8.201	1.540	6.992
H	-6.515	-0.075	6.128
H	-2.018	0.691	1.707
H	-1.142	0.304	3.212
H	1.238	0.001	3.173
H	3.382	0.007	1.912
H	3.361	0.004	-0.581
H	1.188	0.001	-1.802
H	-0.951	0.001	-0.537
H	-4.594	-6.614	4.151
H	-3.659	-5.328	4.963
H	-4.383	-5.026	7.168
H	-6.188	-4.830	8.872
H	-8.574	-5.079	8.192
H	-9.141	-5.527	5.806
H	-7.331	-5.734	4.112
H	-6.521	-2.024	-1.645
H	-5.445	-3.280	-0.989
H	-8.526	-1.812	0.620
H	-10.563	-3.149	1.131
H	-10.685	-5.548	0.457
H	-8.757	-6.600	-0.725
H	-6.728	-5.258	-1.232
H	-1.079	-4.423	3.617
H	-0.599	-2.714	3.848
H	-0.808	-3.789	5.274

1.130CC

Final heat of formation = –1807.341

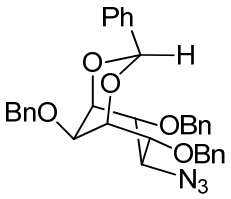
C	0.000	0.000	0.000
C	0.000	0.000	1.401
C	1.231	0.000	2.079
C	2.433	0.002	1.369
C	2.422	0.007	-0.032
C	1.203	0.004	-0.715
C	-1.296	0.004	2.186
O	-1.473	-1.167	3.004
C	-1.834	-2.338	2.267
C	-1.539	-3.566	3.119
O	-2.368	-3.585	4.298
C	-3.769	-3.566	4.010
O	-4.123	-2.485	3.133
C	-3.330	-2.408	1.937

C	-3.578	-3.568	0.943
C	-2.865	-4.919	1.278
C	-1.668	-4.858	2.270
C	-4.511	-3.371	5.308
C	-4.270	-2.233	6.090
C	-4.960	-2.051	7.290
C	-5.894	-3.003	7.717
C	-6.135	-4.139	6.940
C	-5.444	-4.321	5.737
O	-0.486	-5.060	1.473
C	0.631	-5.599	2.208
C	1.735	-5.920	1.235
C	1.940	-7.235	0.795
C	2.955	-7.531	-0.120
C	3.774	-6.509	-0.609
C	3.574	-5.192	-0.180
C	2.563	-4.901	0.738
O	-3.784	-5.895	1.811
C	-4.606	-6.515	0.828
O	-3.128	-3.050	-0.324
C	-3.758	-3.662	-1.461
C	-3.174	-3.083	-2.723
C	-1.849	-3.372	-3.086
C	-1.304	-2.841	-4.256
C	-2.078	-2.017	-5.081
C	-3.397	-1.721	-4.726
C	-3.939	-2.251	-3.551
H	-1.252	-2.408	1.331
H	-3.672	-1.492	1.438
H	-4.668	-3.751	0.912
H	-2.438	-5.306	0.335
H	-1.798	-5.704	2.970
H	-0.516	-3.502	3.513
H	-4.064	-4.522	3.542
H	-2.150	0.140	1.498
H	-1.309	0.840	2.900
H	1.239	-0.006	3.171
H	3.383	0.009	1.907
H	3.361	0.015	-0.587
H	1.186	0.002	-1.806
H	-0.951	-0.009	-0.538
H	-5.627	-5.208	5.127
H	-6.861	-4.885	7.270
H	-6.432	-2.859	8.656
H	-4.769	-1.164	7.898
H	-3.538	-1.500	5.748
H	0.988	-4.872	2.960
H	0.310	-6.512	2.744
H	-3.598	-4.757	-1.440
H	-4.849	-3.482	-1.424
H	-1.242	-4.011	-2.441
H	-0.273	-3.074	-4.529
H	-1.653	-1.606	-5.999
H	-4.005	-1.077	-5.364
H	-4.969	-2.016	-3.272
H	2.407	-3.872	1.071
H	4.211	-4.391	-0.558
H	4.568	-6.738	-1.322
H	3.107	-8.560	-0.450
H	1.299	-8.034	1.175
H	-5.219	-7.257	1.355
H	-5.280	-5.799	0.322
H	-3.995	-7.029	0.062

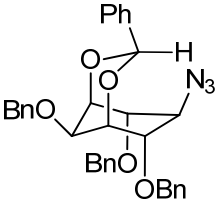
1.130CB

Final heat of formation = –1807.335

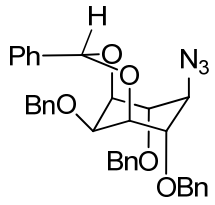
C	0.000	0.000	0.000
C	0.000	0.000	1.402
C	1.227	0.000	2.081
C	2.433	0.004	1.375
C	2.422	0.006	-0.023
C	1.204	0.001	-0.710
C	-1.297	-0.020	2.167
O	-1.701	-1.391	2.366
C	-2.775	-1.554	3.305
C	-4.139	-1.125	2.710
C	-4.573	-2.135	1.660
C	-4.900	-3.428	2.407
C	-3.585	-4.028	2.949
C	-2.732	-3.034	3.782
O	-5.059	-0.990	3.816
C	-6.140	-1.916	3.896
O	-5.793	-3.246	3.521
C	-7.415	-1.413	3.214
C	-7.653	-0.039	3.081
C	-8.861	0.422	2.551
C	-9.850	-0.486	2.160
C	-9.624	-1.858	2.307
C	-8.415	-2.318	2.837
O	-5.665	-1.602	0.905
C	-5.848	-2.223	-0.381
C	-4.835	-1.769	-1.411
C	-3.925	-2.671	-1.981
C	-2.999	-2.243	-2.939
C	-2.973	-0.903	-3.334
C	-3.873	0.008	-2.766
C	-4.796	-0.423	-1.812
O	-3.133	-3.178	5.149
C	-2.140	-2.773	6.083
O	-2.865	-4.500	1.800
C	-1.984	-5.596	2.090
C	-1.144	-5.900	0.876
C	-0.327	-4.905	0.317
C	0.475	-5.190	-0.789
C	0.474	-6.474	-1.349
C	-0.339	-7.469	-0.800
C	-1.147	-7.180	0.305
H	-3.846	-4.866	3.619
H	-2.597	-0.908	4.185
H	-4.049	-0.132	2.244
H	-2.072	0.534	1.608
H	-1.173	0.468	3.153
H	-1.327	-5.335	2.943
H	-2.573	-6.485	2.386
H	-5.498	0.286	-1.368
H	-3.858	1.055	-3.076
H	-2.256	-0.567	-4.086
H	-2.297	-2.957	-3.371
H	-3.938	-3.717	-1.667
H	-1.788	-7.957	0.728
H	-0.350	-8.470	-1.235
H	1.105	-6.696	-2.212
H	1.108	-4.409	-1.214
H	-0.333	-3.902	0.748
H	1.236	0.000	3.174
H	3.381	0.011	1.915
H	3.363	0.014	-0.577
H	1.191	0.005	-1.801
H	-0.951	-0.005	-0.538
H	-5.355	-4.170	1.732
H	-3.705	-2.325	1.005
H	-5.830	-3.324	-0.295
H	-6.863	-1.928	-0.682
H	-6.878	0.665	3.384
H	-9.031	1.495	2.443
H	-10.795	-0.126	1.748
H	-10.393	-2.574	2.010
H	-8.235	-3.388	2.954
H	-6.342	-1.993	4.977
H	-1.673	-3.344	3.677
H	-1.930	-1.689	6.039
H	-2.532	-3.010	7.080
H	-1.192	-3.322	5.924



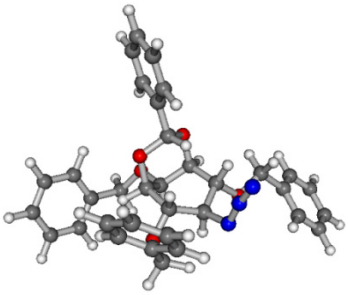
1.135BC



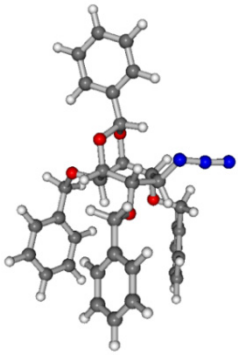
1.1354CC



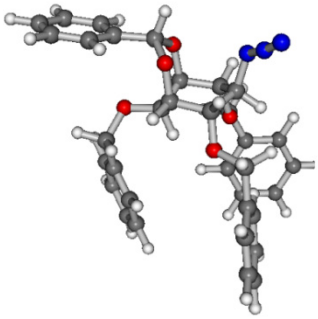
1.1354CB



1.135BC
ΔE **0.0** kcal/mol



1.135CC
ΔE **0.1** kcal/mol



1.135CB
ΔE **3.8** kcal/mol

1.135BC

Final heat of formation = –1856.443

C	0.000	0.000	0.000
C	0.000	0.000	1.401
C	1.227	0.000	2.083
C	2.429	0.001	1.372
C	2.421	0.012	-0.028
C	1.203	0.012	-0.713
C	-1.299	0.036	2.165
O	-1.274	-0.965	3.200
C	-2.447	-0.964	4.018
C	-3.620	-1.716	3.321
C	-3.812	-3.108	3.922
C	-4.285	-2.871	5.365
C	-3.154	-2.223	6.218
C	-2.015	-1.585	5.366
O	-5.499	-2.095	5.361
C	-5.357	-0.834	4.706
O	-4.855	-0.971	3.379
C	-6.712	-0.173	4.649
C	-7.031	0.845	5.555
C	-8.296	1.441	5.528
C	-9.244	1.021	4.591
C	-8.925	0.005	3.682
C	-7.664	-0.592	3.711
O	-4.725	-3.831	3.101
C	-4.600	-5.259	3.157
C	-5.285	-5.928	4.334
C	-6.581	-5.546	4.717
C	-7.226	-6.195	5.771
C	-6.591	-7.241	6.451
C	-5.301	-7.627	6.076
C	-4.653	-6.971	5.025
N	-1.190	-0.636	6.164
N	-1.664	0.475	6.414
N	-1.956	1.544	6.724
O	-2.639	-3.289	7.027
C	-1.931	-2.907	8.228
C	-2.797	-2.189	9.242
C	-4.041	-2.722	9.620
C	-4.830	-2.074	10.572
C	-4.384	-0.888	11.166
C	-3.148	-0.350	10.798
C	-2.362	-0.997	9.838
H	-1.311	-2.394	5.127
H	-3.619	-1.453	6.861
H	-4.553	-3.811	5.859
H	-2.836	-3.633	3.942
H	-3.395	-1.800	2.250
H	-2.787	0.079	4.176
H	-4.659	-0.202	5.296
H	-7.402	-1.380	3.004
H	-9.664	-0.320	2.947
H	-10.233	1.487	4.566
H	-8.539	2.235	6.237
H	-6.288	1.174	6.285
H	-2.146	-0.128	1.474
H	-1.447	1.029	2.635
H	1.233	-0.014	3.174
H	3.378	-0.002	1.912
H	3.362	0.017	-0.581
H	1.188	0.014	-1.804
H	-0.951	-0.011	-0.539
H	-1.583	-3.869	8.633
H	-1.046	-2.296	7.986
H	-4.392	-3.644	9.151
H	-5.796	-2.496	10.854
H	-5.001	-0.382	11.911
H	-2.796	0.578	11.252
H	-1.398	-0.572	9.547
H	-5.057	-5.608	2.218
H	-3.532	-5.550	3.133
H	-3.640	-7.269	4.741
H	-4.795	-8.436	6.608
H	-7.098	-7.748	7.274
H	-8.231	-5.884	6.064
H	-7.068	-4.718	4.199

1.135CC

Final heat of formation = –1856.443

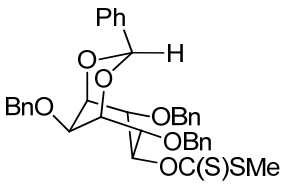
C	0.000	0.000	0.000
C	0.000	0.000	1.401
C	1.227	0.000	2.082
C	2.430	-0.002	1.372
C	2.421	0.005	-0.028
C	1.203	0.007	-0.713
C	-1.296	-0.004	2.169
O	-1.418	-1.261	2.865
C	-2.661	-1.415	3.573
C	-2.616	-0.659	4.927
C	-1.885	-1.484	5.979
C	-2.789	-2.688	6.270
C	-2.783	-3.642	5.053
C	-2.908	-2.951	3.650

O	-3.925	-0.276	5.389
C	-4.751	-1.390	5.732
O	-4.105	-2.268	6.665
O	-1.651	-0.666	7.126
C	-0.614	-1.160	7.994
C	0.782	-0.958	7.441
C	1.605	-2.050	7.132
C	2.896	-1.851	6.630
C	3.376	-0.554	6.431
C	2.559	0.543	6.730
C	1.273	0.342	7.232
C	-6.010	-0.870	6.377
C	-7.261	-1.186	5.837
C	-8.430	-0.711	6.440
C	-8.349	0.083	7.587
C	-7.097	0.401	8.129
C	-5.930	-0.073	7.528
N	-4.243	-3.200	3.024
N	-4.457	-4.338	2.598
N	-4.785	-5.345	2.155
O	-1.540	-4.353	5.152
C	-1.553	-5.643	4.505
C	-0.228	-6.317	4.742
C	0.855	-6.079	3.882
C	2.091	-6.686	4.115
C	2.257	-7.541	5.210
C	1.183	-7.784	6.072
C	-0.052	-7.174	5.838
H	-0.931	-1.841	5.549
H	-2.093	0.294	4.777
H	-3.486	-0.977	2.982
H	-2.128	-3.392	3.010
H	-3.629	-4.345	5.176
H	-2.416	-3.270	7.127
H	-0.745	-0.590	8.925
H	-0.772	-2.228	8.231
H	0.636	1.197	7.466
H	2.932	1.558	6.580
H	4.385	-0.397	6.044
H	3.524	-2.711	6.392
H	1.230	-3.065	7.281
H	-4.950	0.168	7.939
H	-7.033	1.022	9.025
H	-9.259	0.455	8.060
H	-9.403	-0.961	6.014
H	-7.320	-1.805	4.939
H	-2.379	-6.249	4.920
H	-1.730	-5.528	3.419
H	-2.153	0.121	1.481
H	-1.316	0.836	2.888
H	1.239	-0.007	3.173
H	3.378	-0.003	1.912
H	3.361	0.009	-0.582
H	1.188	0.011	-1.805
H	-0.951	-0.005	-0.538
H	-0.891	-7.364	6.511
H	1.306	-8.454	6.925
H	3.221	-8.020	5.389
H	2.926	-6.498	3.437
H	0.727	-5.412	3.027
H	-5.005	-1.958	4.815

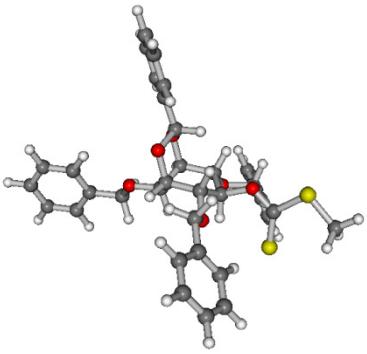
1.135CB

Final heat of formation = –1856.437

C	0.000	0.000	0.000
C	0.000	0.000	1.402
C	1.227	0.000	2.083
C	2.432	0.004	1.376
C	2.422	0.005	-0.022
C	1.204	0.001	-0.709
C	-1.298	-0.022	2.166
O	-1.704	-1.396	2.348
C	-2.785	-1.564	3.276
C	-4.147	-1.156	2.655
C	-4.547	-2.176	1.602
C	-4.850	-3.479	2.346
C	-3.526	-4.058	2.881
C	-2.726	-3.038	3.750
O	-5.097	-1.022	3.734
C	-6.138	-1.993	3.823
O	-5.719	-3.314	3.484
C	-7.426	-1.569	3.115
C	-7.729	-0.212	2.946
C	-8.952	0.175	2.391
C	-9.890	-0.790	2.010
C	-9.598	-2.145	2.193
C	-8.376	-2.532	2.749
O	-5.643	-1.670	0.836
C	-5.796	-2.292	-0.454
C	-4.784	-1.810	-1.473
C	-3.868	-2.694	-2.059
C	-2.948	-2.241	-3.012
C	-2.935	-0.895	-3.385
C	-3.840	-0.001	-2.798
C	-4.758	-0.457	-1.850
N	-3.139	-3.048	5.179
N	-3.071	-4.121	5.781
N	-3.059	-5.041	6.470
O	-2.771	-4.471	1.739
C	-1.852	-5.546	2.010
C	-1.030	-5.824	0.779
C	-0.207	-4.822	0.240
C	0.573	-5.082	-0.888
C	0.544	-6.347	-1.489
C	-0.275	-7.348	-0.960
C	-1.061	-7.084	0.167
H	-3.775	-4.936	3.506
H	-2.625	-0.928	4.165
H	-4.056	-0.165	2.188
H	-2.070	0.541	1.613
H	-1.173	0.452	3.158
H	-1.188	-5.270	2.852
H	-2.414	-6.451	2.311
H	-5.465	0.239	-1.393
H	-3.835	1.051	-3.090
H	-2.222	-0.540	-4.131
H	-2.241	-2.942	-3.459
H	-3.871	-3.746	-1.764
H	-1.705	-7.866	0.576
H	-0.306	-8.334	-1.426
H	1.158	-6.550	-2.368
H	1.210	-4.297	-1.298
H	-0.191	-3.833	0.702
H	1.235	0.001	3.175
H	3.380	0.011	1.917
H	3.363	0.013	-0.576
H	1.192	0.004	-1.800
H	-0.950	-0.006	-0.539
H	-5.305	-4.222	1.672
H	-3.669	-2.348	0.955
H	-5.750	-3.392	-0.370
H	-6.815	-2.023	-0.764
H	-6.993	0.537	3.241
H	-9.173	1.236	2.255
H	-10.845	-0.486	1.578
H	-10.327	-2.905	1.904
H	-8.147	-3.589	2.896
H	-6.349	-2.057	4.903
H	-1.661	-3.322	3.690



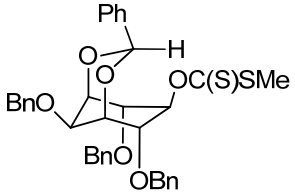
2.16BC



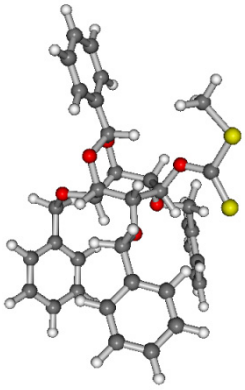
2.16BC
ΔE **0.0** kcal/mol

2.16BC
Final heat of formation =
–2641.969

C	1.856	-0.833	-5.337
C	2.665	-0.052	-4.500
C	3.919	0.371	-4.963
C	4.356	0.029	-6.246
C	3.546	-0.750	-7.077
C	2.298	-1.182	-6.616
C	2.188	0.382	-3.134
O	1.234	-0.557	-2.630
C	0.735	-0.232	-1.342
C	-0.026	-1.437	-0.793
C	-0.374	-1.221	0.710
C	-0.228	0.236	1.184
C	-0.612	1.325	0.153
C	-0.268	0.932	-1.315
O	-1.427	0.604	-2.100
C	-2.077	-0.576	-1.654
O	-1.195	-1.699	-1.598
O	-1.109	0.387	2.347
O	0.478	-1.996	1.557
C	0.078	-3.370	1.661
C	1.002	-4.105	2.602
C	1.191	-5.486	2.445
C	1.995	-6.200	3.338
C	2.632	-5.535	4.391
C	2.457	-4.156	4.543
C	1.644	-3.443	3.657
O	0.085	2.553	0.375
C	-0.380	3.350	1.489

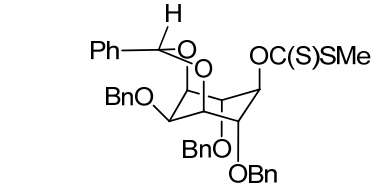


2.16CC

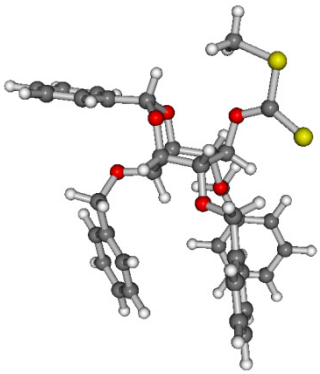


2.16CC
ΔE **2.8** kcal/mol

C	0.175	4.742	1.340
C	1.136	5.227	2.236
C	1.653	6.520	2.097
C	1.216	7.337	1.052
C	0.259	6.860	0.148
C	-0.258	5.572	0.293
C	-3.225	-0.915	-2.579
C	-3.944	-2.099	-2.360
C	-5.023	-2.429	-3.182
C	-5.396	-1.577	-4.226
C	-4.682	-0.396	-4.444
C	-3.599	-0.063	-3.623
C	-0.614	0.490	3.601
H	0.806	0.401	1.525
H	-1.426	-1.534	0.859
H	0.587	-2.342	-0.887
H	1.577	0.005	-0.659
H	0.141	1.836	-1.781
H	-1.704	1.499	0.215
H	-2.474	-0.391	-0.630
H	-3.645	-2.771	-1.553
H	-5.575	-3.355	-3.007
H	-6.241	-1.833	-4.868
H	-4.965	0.272	-5.260
H	-3.036	0.854	-3.791
H	-1.486	3.363	1.479
H	-0.046	2.914	2.445
H	1.483	4.584	3.049
H	2.401	6.885	2.803
H	1.620	8.345	0.940
H	-0.086	7.497	-0.668
H	-1.003	5.200	-0.413



2.16CB



2.16CB
ΔE **4.5** kcal/mol

H	-0.965	-3.410	2.037
H	0.086	-3.862	0.671
H	0.707	-6.008	1.615
H	2.134	-7.274	3.203
H	3.267	-6.089	5.084
H	2.959	-3.629	5.357
H	1.515	-2.366	3.770
H	1.734	1.389	-3.209
H	3.047	0.463	-2.438
H	4.562	0.971	-4.314
H	5.335	0.365	-6.593
H	3.887	-1.023	-8.077
H	1.662	-1.796	-7.257
H	0.886	-1.173	-4.972
S	0.967	0.694	4.052
S	-2.027	0.420	4.681
C	-1.256	0.648	6.319
H	-2.086	0.609	7.036
H	-0.541	-0.157	6.520
H	-0.751	1.619	6.373

2.16CC
Final heat of formation =
–2641.965

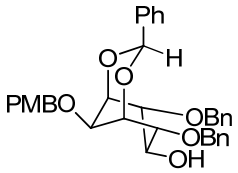
C	1.494	1.134	-5.225
C	1.388	-0.052	-4.484
C	1.623	-1.282	-5.115
C	1.961	-1.323	-6.471
C	2.064	-0.139	-7.208
C	1.833	1.088	-6.580
C	0.962	-0.004	-3.032
O	1.446	1.204	-2.448
C	1.202	1.295	-1.033

C	1.803	0.091	-0.296
C	1.190	-1.145	-0.946
O	1.442	-1.166	-2.365
C	-0.297	1.437	-0.670
C	-1.100	0.103	-0.583
C	-0.319	-1.240	-0.592
O	-0.306	2.114	0.592
C	-1.549	2.800	0.872
C	-1.432	3.480	2.210
C	-0.948	4.793	2.303
C	-0.821	5.418	3.546
C	-1.177	4.733	4.712
C	-1.659	3.422	4.630
C	-1.786	2.801	3.385
O	-2.053	0.091	-1.708
C	-3.372	-0.079	-1.475
S	-4.334	-0.055	-2.955
C	-3.109	0.183	-4.308
O	-0.482	-1.792	0.721
C	-0.387	-3.228	0.773
C	-0.853	-3.701	2.126
C	-2.171	-3.456	2.543
C	-2.613	-3.907	3.788
C	-1.744	-4.613	4.629
C	-0.431	-4.860	4.222
C	0.012	-4.401	2.977
O	3.222	0.010	-0.407
C	3.938	0.895	0.478
C	3.929	0.437	1.921
C	3.192	1.123	2.896
C	3.182	0.683	4.225
C	3.914	-0.449	4.591
C	4.654	-1.142	3.625
C	4.661	-0.701	2.301
S	-4.133	-0.286	-0.013
H	1.489	0.121	0.763
H	1.692	-2.045	-0.569
H	-0.795	-1.902	-1.340
H	-1.694	0.103	0.343
H	-0.775	2.066	-1.444
H	1.683	2.233	-0.729
H	-0.146	0.002	-2.981
H	4.962	0.900	0.081
H	3.545	1.925	0.408
H	2.617	2.008	2.614
H	2.599	1.225	4.971
H	3.909	-0.793	5.627
H	5.232	-2.023	3.909
H	5.237	-1.242	1.546
H	1.557	-2.201	-4.533
H	2.149	-2.285	-6.951
H	2.329	-0.174	-8.266
H	1.920	2.017	-7.146
H	1.329	2.090	-4.729
H	-1.736	3.540	0.072
H	-2.390	2.083	0.879
H	-1.025	-3.653	-0.027
H	0.649	-3.567	0.592
H	-2.844	-2.898	1.889
H	-3.639	-3.711	4.102
H	-2.092	-4.968	5.601
H	0.253	-5.404	4.876
H	1.042	-4.586	2.663
H	-2.163	1.778	3.321
H	-1.941	2.885	5.537
H	-1.082	5.221	5.684
H	-0.448	6.442	3.606
H	-0.671	5.328	1.392
H	-3.705	0.210	-5.229
H	-2.573	1.131	-4.191
H	-2.404	-0.654	-4.353

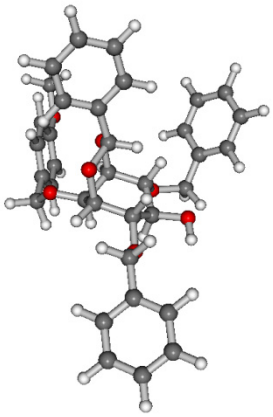
2.16CB

Final heat of formation = –2641.962

C	1.607	4.840	-1.222
C	1.228	4.320	0.022
C	1.983	4.641	1.157
C	3.120	5.445	1.045
C	3.506	5.948	-0.202
C	2.744	5.644	-1.335
C	-0.080	3.539	0.162
O	-0.482	2.874	-1.034
C	0.010	1.535	-1.253
C	0.995	1.053	-0.183
C	0.349	1.342	1.164
O	-0.128	2.700	1.313
C	-0.871	0.407	1.354
C	-1.836	0.383	0.147
C	-1.204	0.581	-1.258
O	-0.725	-0.660	-1.777
C	-1.741	-1.445	-2.439
C	-1.180	-2.802	-2.770
C	-0.673	-3.625	-1.751
C	-0.179	-4.896	-2.052
C	-0.191	-5.363	-3.372
C	-0.692	-4.549	-4.391
C	-1.179	-3.273	-4.090
O	2.281	1.669	-0.244
C	3.165	1.097	-1.231
C	3.770	-0.219	-0.794
C	3.431	-1.421	-1.430
C	3.997	-2.632	-1.017
C	4.910	-2.651	0.040
C	5.252	-1.457	0.687
C	4.686	-0.250	0.272
O	-0.468	-0.951	1.573
C	-0.024	-1.214	2.923
C	0.104	-2.703	3.112
C	-1.016	-3.471	3.463
C	-0.906	-4.854	3.629
C	0.330	-5.483	3.446
C	1.451	-4.726	3.092
C	1.337	-3.343	2.927
O	-2.839	1.429	0.366
C	-4.145	1.130	0.223
S	-5.189	2.535	0.463
C	-4.017	3.919	0.772
S	-4.827	-0.346	-0.123
H	-1.978	1.011	-1.921
H	-1.441	0.778	2.226
H	1.081	1.165	1.966
H	0.948	-0.725	3.113
H	-0.764	-0.796	3.631
H	-2.625	-1.540	-1.782
H	-2.066	-0.926	-3.360
H	4.953	0.681	0.775
H	5.970	-1.467	1.509
H	5.359	-3.594	0.359
H	3.721	-3.559	-1.522
H	2.713	-1.411	-2.254
H	-1.565	-2.635	-4.889
H	-0.700	-4.905	-5.423
H	0.191	-6.359	-3.604
H	0.212	-5.527	-1.252
H	-0.658	-3.259	-0.723
H	-1.982	-2.980	3.604
H	-1.783	-5.440	3.906
H	0.419	-6.563	3.582
H	2.417	-5.213	2.948
H	2.213	-2.753	2.645
H	0.467	1.503	-2.254
H	1.086	-0.044	-0.274
H	2.645	0.972	-2.197
H	3.946	1.859	-1.366
H	1.009	4.602	-2.103
H	3.035	6.038	-2.311
H	4.393	6.578	-0.289
H	3.706	5.682	1.934
H	1.679	4.245	2.127
H	-0.886	4.271	0.337
H	-2.360	-0.584	0.163
H	-4.650	4.799	0.9414
H	-3.406	3.721	1.659
H	-3.378	4.080	-0.102



2.28BC



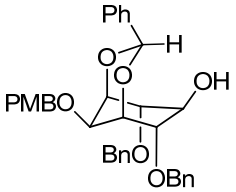
2.28BC

ΔE **0.0** kcal/mol

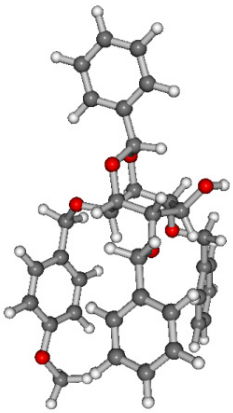
2.28BC

Final heat of formation = –1882.608

C	0.000	0.000	0.000
C	0.000	0.000	1.405
C	1.228	0.000	2.081
C	2.435	-0.011	1.371
C	2.423	-0.014	-0.026
C	1.202	-0.004	-0.710
C	-1.305	-0.016	2.172
O	-2.176	1.095	1.856
C	-1.703	2.392	2.255
C	-2.427	3.410	1.321
C	-3.509	4.191	2.090
C	-2.749	5.041	3.112
C	-2.018	4.131	4.139
C	-1.985	2.646	3.748
O	-1.526	4.343	0.689
C	-0.895	5.230	1.613
O	-1.833	5.926	2.431
C	-0.092	6.235	0.823
C	1.262	5.993	0.567
C	2.009	6.894	-0.197
C	1.402	8.046	-0.706
C	0.048	8.292	-0.450
C	-0.698	7.389	0.311
O	-4.310	5.062	1.294
C	-5.431	4.442	0.647
C	-5.119	3.711	-0.644
C	-5.686	2.455	-0.914
C	-5.444	1.797	-2.117
C	-4.613	2.387	-3.083
C	-4.031	3.638	-2.825
C	-4.293	4.288	-1.616
O	-1.001	1.953	4.537
O	-2.635	4.153	5.439
C	-2.323	5.339	6.204
C	-2.985	5.231	7.551
C	-4.303	5.675	7.734
C	-4.930	5.549	8.977
C	-4.241	4.979	10.053
C	-2.926	4.535	9.881
C	-2.304	4.661	8.636
O	-4.426	1.662	-4.233
C	-3.582	2.225	-5.241
H	-2.985	2.227	3.966
H	-0.975	4.492	4.233
H	-3.444	5.708	3.637
H	-4.164	3.475	2.623
H	-2.860	2.835	0.496
H	-0.617	2.466	2.073
H	-0.214	4.637	2.262
H	1.735	5.092	0.966
H	3.064	6.698	-0.393
H	1.984	8.754	-1.300
H	-0.427	9.192	-0.844
H	-1.752	7.572	0.522
H	-1.108	-0.058	3.254
H	-1.902	-0.897	1.891
H	-0.953	0.013	-0.534
H	1.188	-0.005	-1.802
H	3.362	-0.021	-0.582
H	3.383	-0.011	1.911
H	1.235	0.017	3.173
H	-1.225	5.423	6.311
H	-2.678	6.238	5.670
H	-1.275	4.319	8.504
H	-2.384	4.095	10.719
H	-4.728	4.884	11.025
H	-5.954	5.900	9.108
H	-4.841	6.121	6.895
H	-5.943	3.753	1.347
H	-6.119	5.279	0.447
H	-3.820	5.250	-1.412
H	-3.372	4.112	-3.552
H	-5.881	0.820	-2.327
H	-6.325	1.979	-0.166
H	-3.571	1.495	-6.058
H	-3.980	3.183	-5.613
H	-2.554	2.375	-4.872
H	-1.262	2.098	5.466



2.28CC



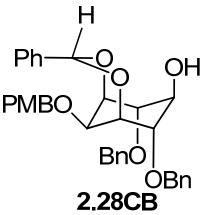
2.28CC

ΔE **3.1** kcal/mol

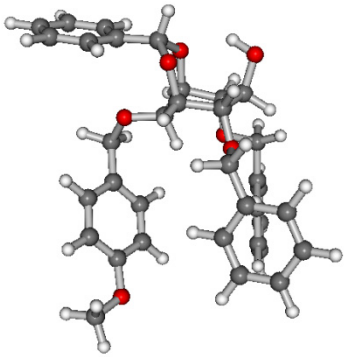
2.28CC

Final heat of formation = –1882.603

C	0.000	0.000	0.000
C	0.000	0.000	1.404
C	1.225	0.000	2.084
C	2.432	-0.009	1.377
C	2.423	-0.011	-0.020
C	1.204	-0.004	-0.707
C	-1.302	0.002	2.161
O	-1.937	1.283	2.015
C	-3.234	1.347	2.635



2.28CB



2.28CB

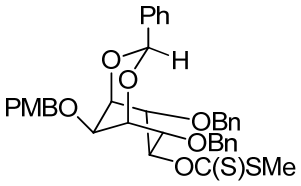
ΔE **3.8** kcal/mol

C	-3.479	2.851	2.895
C	-3.951	3.524	1.600
C	-5.358	2.996	1.344
C	-5.315	1.491	0.972
C	-4.302	0.614	1.758
O	-4.397	3.098	3.973
C	-5.747	2.701	3.690
O	-6.222	3.267	2.466
O	-4.983	1.330	-0.420
C	-6.101	1.525	-1.309
C	-5.656	1.220	-2.716
C	-5.866	-0.051	-3.269
C	-5.439	-0.341	-4.569
C	-4.792	0.640	-5.327
C	-4.574	1.909	-4.781
C	-5.006	2.197	-3.484
O	-4.001	4.948	1.694
C	-2.726	5.593	1.504
C	-2.258	5.601	0.066
C	-1.098	4.928	-0.330
C	-0.659	4.941	-1.661
C	-1.399	5.641	-2.622
C	-2.572	6.319	-2.241
C	-2.988	6.297	-0.916
O	-5.096	-0.309	2.536
C	-6.624	3.201	4.809
C	-6.712	4.576	5.070
C	-7.526	5.039	6.105
C	-8.257	4.134	6.885
C	-8.172	2.763	6.626
C	-7.356	2.299	5.589
O	-1.071	5.726	-3.952
C	0.123	5.069	-4.382
H	-3.299	3.209	0.765
H	-5.812	3.552	0.514
H	-6.318	1.071	1.169
H	-3.748	0.062	0.980
H	-3.199	0.847	3.624
H	-2.525	3.272	3.240
H	-5.796	1.598	3.630
H	-2.891	6.620	1.863
H	-1.952	5.136	2.147
H	-3.901	6.825	-0.630
H	-3.131	6.865	-3.003
H	0.248	4.402	-1.929
H	-0.518	4.373	0.412
H	-7.288	1.229	5.381
H	-8.741	2.055	7.231
H	-8.893	4.499	7.694
H	-7.593	6.109	6.306
H	-6.140	5.270	4.454
H	-1.125	-0.203	3.235
H	-1.962	-0.797	1.768
H	-6.926	0.852	-1.008
H	-6.471	2.564	-1.246
H	-4.833	3.188	-3.059
H	-4.072	2.679	-5.369
H	-4.462	0.416	-6.343
H	-5.615	-1.332	-4.991
H	-6.370	-0.818	-2.676
H	-0.950	0.010	-0.538
H	1.191	-0.007	-1.799
H	3.363	-0.020	-0.573
H	3.380	-0.012	1.919
H	1.233	0.006	3.176
H	0.200	5.268	-5.456
H	1.013	5.473	-3.871
H	0.069	3.980	-4.215
H	-4.485	-0.911	2.996

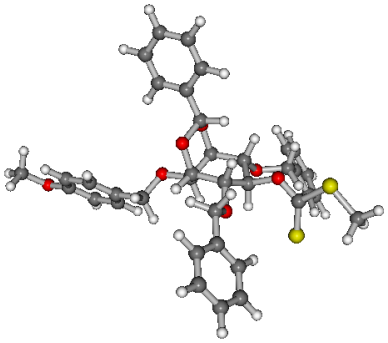
2.28CB

Final heat of formation = –1882.602

C	0.000	0.000	0.000
C	0.000	0.000	1.401
C	1.227	0.000	2.085
C	2.429	0.005	1.374
C	2.421	0.014	-0.026
C	1.204	0.011	-0.713
C	-1.295	0.024	2.171
O	-1.381	-1.155	2.993
C	-2.510	-1.155	3.873
C	-2.784	-2.627	4.229
C	-1.578	-3.162	5.011
C	-1.648	-2.537	6.396
C	-1.446	-1.001	6.267
C	-2.302	-0.311	5.164
O	-4.016	-2.596	5.016
C	-3.986	-3.248	6.292
O	-2.893	-2.805	7.090
C	-4.143	-4.766	6.218
C	-4.907	-5.336	5.189
C	-5.148	-6.712	5.170
C	-4.646	-7.529	6.188
C	-3.903	-6.958	7.228
C	-3.657	-5.583	7.245
O	-1.521	-4.584	5.114
C	-0.941	-5.235	3.957
C	0.565	-5.141	3.914
C	1.347	-5.914	4.782
C	2.743	-5.830	4.783
C	3.381	-4.952	3.892
C	2.613	-4.171	3.014
C	1.224	-4.269	3.029
O	-3.566	0.131	5.673
O	-0.071	-0.695	5.979
C	0.788	-0.717	7.137
C	2.132	-0.154	6.752
C	2.424	1.201	6.963
C	3.661	1.731	6.587
C	4.621	0.908	5.988
C	4.338	-0.445	5.769
C	3.102	-0.972	6.153
O	4.742	-4.793	3.798
C	5.565	-5.584	4.658
H	-1.747	-0.541	7.227
H	-3.397	-0.742	3.355
H	-2.966	-3.213	3.314
H	-2.157	0.060	1.477
H	-1.338	0.927	2.807
H	0.333	-0.110	7.941
H	0.903	-1.749	7.515
H	0.641	-3.658	2.337
H	3.121	-3.497	2.324
H	3.318	-6.455	5.464
H	0.857	-6.598	5.479
H	1.673	1.845	7.428
H	3.877	2.786	6.762
H	5.588	1.320	5.695
H	5.083	-1.092	5.304
H	2.883	-2.028	5.979
H	-0.951	-0.007	-0.538
H	1.190	0.012	-1.804
H	3.361	0.020	-0.580
H	3.377	0.009	1.916
H	1.233	-0.008	3.176
H	-0.852	-2.959	7.027
H	-0.667	-2.773	4.525
H	-1.266	-6.280	4.051
H	-1.375	-4.826	3.028
H	-3.072	-5.133	8.048
H	-3.512	-7.587	8.029
H	-4.838	-8.603	6.176
H	-5.732	-7.149	4.357
H	-5.303	-4.696	4.399
H	-4.880	-2.850	6.801
H	-1.748	0.602	4.899
H	5.359	-5.377	5.721
H	5.434	-6.662	4.464
H	6.597	-5.298	4.426
H	-4.144	-0.659	5.656



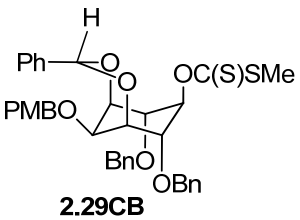
2.29BC



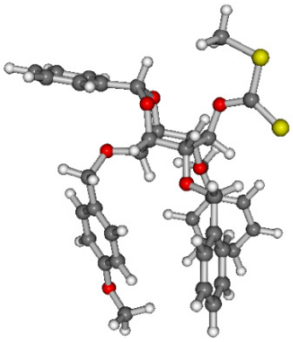
2.29BC
ΔE **0.0** kcal/mol

2.29BC
Final heat of formation =
–2756.542

C	0.000	0.000	0.000
C	0.000	0.000	1.402
C	1.225	0.000	2.085
C	2.432	0.014	1.382
C	2.427	0.014	-0.017
C	1.209	0.003	-0.703
C	-1.289	0.042	2.187
O	-2.354	-0.525	1.413
C	-3.613	-0.516	2.092
C	-3.728	-1.711	3.088
C	-4.663	-2.790	2.516
C	-6.047	-2.143	2.473
C	-6.093	-0.989	1.429
C	-4.687	-0.515	0.991
O	-4.179	-1.306	4.394
C	-5.521	-0.800	4.385
O	-6.437	-1.714	3.793
O	-6.853	-1.502	0.334
C	-7.432	-0.512	-0.546
C	-8.510	-1.172	-1.366
C	-9.708	-1.589	-0.764
C	-10.705	-2.205	-1.522
C	-10.518	-2.411	-2.894
C	-9.329	-2.000	-3.502
C	-8.330	-1.386	-2.739
O	-4.744	-3.982	3.284
C	-3.553	-4.795	3.219
C	-3.836	-6.133	3.841
C	-4.537	-7.123	3.129
C	-4.824	-8.355	3.702

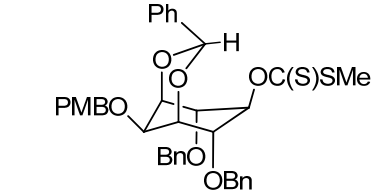


2.29CB

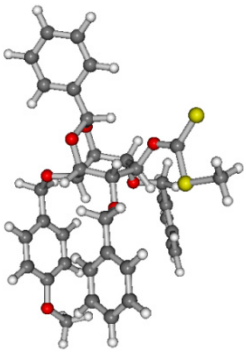


2.29CB
ΔE **4.7** kcal/mol

C	-4.410	-8.631	5.018
C	-3.712	-7.657	5.746
C	-3.436	-6.420	5.150
O	-4.798	0.871	0.522
C	-4.335	1.242	-0.692
S	-4.460	3.019	-0.730
C	-3.890	3.396	-2.422
C	-5.942	-0.552	5.811
C	-6.131	-1.636	6.680
C	-6.509	-1.409	8.004
C	-6.697	-0.102	8.470
C	-6.509	0.979	7.605
C	-6.132	0.752	6.278
O	-4.734	-9.876	5.493
C	-4.340	-10.201	6.827
S	-3.798	0.263	-1.917
H	-4.342	-1.127	0.144
H	-3.710	0.417	2.678
H	-2.716	-2.103	3.251
H	-4.340	-3.031	1.483
H	-6.806	-2.877	2.179
H	-6.628	-0.135	1.886
H	-5.537	0.155	3.817
H	-5.986	1.597	5.599
H	-6.657	2.000	7.963
H	-6.994	0.072	9.506
H	-6.659	-2.255	8.678
H	-5.987	-2.650	6.304
H	-7.853	0.308	0.067
H	-6.663	-0.088	-1.212
H	-7.397	-1.071	-3.211
H	-9.176	-2.160	-4.571
H	-11.299	-2.891	-3.487
H	-11.634	-2.524	-1.044



2.29CC



2.29CC
ΔE **5.2** kcal/mol

H	-9.853	-1.433	0.306
H	-1.550	1.089	2.443
H	-1.160	-0.501	3.143
H	1.236	-0.014	3.178
H	3.378	0.013	1.926
H	3.369	0.018	-0.568
H	1.197	-0.004	-1.794
H	-0.951	-0.015	-0.534
H	-3.255	-4.913	2.159
H	-2.721	-4.302	3.754
H	-2.897	-5.664	5.724
H	-3.382	-7.846	6.766
H	-5.363	-9.126	3.151
H	-4.866	-6.918	2.107
H	-3.945	4.489	-2.507
H	-2.859	3.056	-2.563
H	-4.545	2.923	-3.162
H	-4.696	-11.224	7.001
H	-3.244	-10.172	6.944
H	-4.804	-9.523	7.562

2.29CB
Final heat of formation =
–2756.535

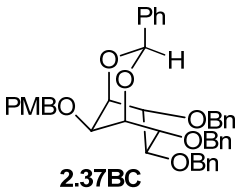
C	0.000	0.000	0.000
C	0.000	0.000	1.402
C	1.228	0.000	2.082
C	2.430	-0.006	1.372
C	2.420	-0.012	-0.028
C	1.203	-0.008	-0.714
C	-1.293	0.002	2.171
O	-1.487	1.310	2.757
C	-2.649	1.398	3.585
C	-3.101	2.872	3.535

C	-2.072	3.720	4.290
C	-2.234	3.391	5.766
C	-1.769	1.935	6.020
C	-2.345	0.900	5.025
O	-4.431	2.929	4.097
C	-4.618	3.706	5.277
O	-3.594	3.507	6.249
O	-0.341	1.826	5.940
C	0.335	2.228	7.151
C	1.796	1.884	7.034
C	2.725	2.846	6.614
C	4.081	2.524	6.500
C	4.520	1.232	6.805
C	3.600	0.263	7.220
C	2.246	0.589	7.334
O	-2.205	5.126	4.098
C	-1.660	5.613	2.848
C	-0.152	5.641	2.820
C	0.581	4.723	2.059
C	1.981	4.740	2.039
C	2.669	5.696	2.797
C	1.948	6.625	3.569
C	0.559	6.592	3.577
O	-3.581	0.372	5.609
C	-3.759	-0.961	5.686
S	-5.339	-1.393	6.348
C	-6.160	0.227	6.639
C	-4.925	5.180	4.999
C	-5.568	5.550	3.811
C	-5.944	6.880	3.596
C	-5.694	7.848	4.574
C	-5.070	7.477	5.769
C	-4.692	6.149	5.983
O	4.035	5.812	2.853
C	4.809	4.912	2.056
S	-2.695	-2.165	5.254
H	-3.464	0.773	3.178
H	-2.116	1.647	7.030
H	-1.620	4.082	6.363
H	0.216	3.313	7.320
H	-0.120	1.696	8.008
H	-1.278	-0.766	2.965
H	-2.143	-0.224	1.500
H	0.008	7.318	4.179
H	2.501	7.368	4.145
H	2.514	4.003	1.439
H	0.056	3.968	1.470
H	-0.952	0.002	-0.536
H	1.188	-0.014	-1.805
H	3.361	-0.024	-0.583
H	3.379	-0.012	1.912
H	1.237	0.010	3.173
H	1.528	-0.167	7.658
H	3.939	-0.746	7.461
H	5.579	0.980	6.723
H	4.794	3.284	6.177
H	2.383	3.855	6.372
H	-3.166	3.173	2.478
H	-1.065	3.381	3.985
H	-2.043	5.017	2.001
H	-2.075	6.626	2.760
H	-5.764	4.792	3.052
H	-6.436	7.160	2.663
H	-5.989	8.886	4.407
H	-4.874	8.226	6.539
H	-4.200	5.856	6.912
H	-5.514	3.263	5.743
H	-1.627	0.069	4.965
H	-6.273	0.773	5.697
H	-7.147	-0.021	7.050
H	-5.595	0.826	7.361
H	4.579	5.024	0.984
H	5.855	5.183	2.234
H	4.646	3.863	2.357

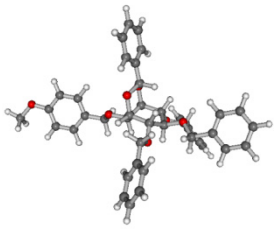
2.29CC

Final heat of formation = –2756.534

C	0.000	0.000	0.000
C	0.000	0.000	1.404
C	1.226	0.000	2.083
C	2.433	-0.007	1.376
C	2.423	-0.006	-0.021
C	1.203	0.001	-0.708
C	-1.299	-0.017	2.167
O	-2.040	1.182	1.866
C	-3.331	1.230	2.497
C	-4.360	0.456	1.632
C	-4.794	1.314	0.448
C	-5.644	2.444	1.040
C	-4.748	3.410	1.853
C	-3.635	2.740	2.718
O	-5.493	-0.016	2.383
C	-6.346	1.032	2.858
O	-6.743	1.916	1.802
O	-5.505	0.489	-0.475
C	-5.636	1.056	-1.794
C	-4.339	1.103	-2.569
C	-3.669	-0.088	-2.913
C	-2.478	-0.063	-3.627
C	-1.919	1.167	-4.022
C	-2.568	2.363	-3.688
C	-3.767	2.316	-2.965
O	-0.741	1.087	-4.722
C	-0.152	2.310	-5.169
C	-7.586	0.404	3.438
C	-8.410	-0.396	2.634
C	-9.559	-0.975	3.174
C	-9.893	-0.759	4.517
C	-9.073	0.038	5.319
C	-7.921	0.619	4.780
O	-4.032	2.983	4.115
C	-3.147	3.121	5.126
S	-1.421	3.022	4.643
C	-0.595	3.357	6.236
O	-4.166	4.297	0.889
C	-3.741	5.555	1.454
C	-3.193	6.423	0.353
C	-4.030	7.312	-0.337
C	-3.526	8.106	-1.372
C	-2.176	8.018	-1.726
C	-1.334	7.133	-1.045
C	-1.841	6.341	-0.011
S	-3.705	3.372	6.662
H	-3.893	1.745	-0.026
H	-3.878	-0.459	1.264
H	-3.291	0.743	3.489
H	-2.693	3.273	2.519
H	-5.403	3.972	2.543
H	-6.114	3.049	0.255
H	-5.819	1.611	3.639
H	-6.364	0.399	-2.291
H	-6.079	2.068	-1.747
H	-4.260	3.255	-2.701
H	-2.154	3.329	-3.974
H	-1.962	-0.984	-3.902
H	-4.094	-1.047	-2.610
H	-7.277	1.244	5.404
H	-9.329	0.209	6.366
H	-10.793	-1.213	4.936
H	-10.199	-1.598	2.546
H	-8.137	-0.558	1.591
H	-4.606	6.042	1.943
H	-2.966	5.389	2.226
H	-1.106	-0.065	3.255
H	-1.891	-0.909	1.888
H	1.235	0.004	3.175
H	3.380	-0.011	1.917
H	3.364	-0.011	-0.575
H	1.188	0.002	-1.799
H	-0.949	0.009	-0.540
H	-1.182	5.650	0.520
H	-0.279	7.064	-1.315
H	-1.780	8.641	-2.530
H	-4.187	8.797	-1.897
H	-5.084	7.382	-0.059
H	0.480	3.303	6.018
H	-0.866	4.354	6.601
H	-0.882	2.601	6.975
H	0.757	2.021	-5.709
H	-0.824	2.856	-5.851
H	0.118	2.963	-4.322



2.37BC



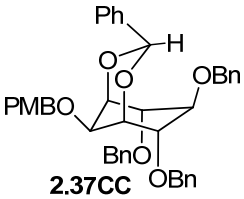
2.37BC

ΔE **0.0** kcal/mol

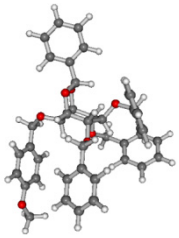
2.37BC

Final heat of formation = –2153.047

C	4.439	0.806	-2.509
C	4.600	1.410	-1.252
C	5.714	2.231	-1.031
C	6.660	2.438	-2.041
C	6.492	1.833	-3.290
C	5.377	1.020	-3.521
C	3.619	1.148	-0.137
O	2.277	1.209	-0.644
C	1.280	0.872	0.340
C	-0.024	1.564	-0.130
C	-1.354	0.847	0.225
C	-1.250	-0.689	0.406
C	0.011	-1.225	-0.288
C	1.188	-0.669	0.512
O	1.094	-1.067	1.895
C	-0.119	-0.640	2.499
O	-1.266	-1.096	1.788
O	-0.147	2.890	0.407
C	0.727	3.864	-0.176
C	0.400	5.238	0.359
C	-0.197	5.415	1.614
C	-0.444	6.701	2.105
C	-0.093	7.825	1.352
C	0.502	7.655	0.098
C	0.742	6.371	-0.395
O	-2.336	1.033	-0.802
C	-2.879	2.362	-0.899
C	-4.101	2.335	-1.784
C	-4.287	3.323	-2.761
C	-5.440	3.337	-3.552
C	-6.417	2.352	-3.382
C	-6.235	1.357	-2.415
C	-5.087	1.351	-1.619
O	0.129	-2.640	-0.329
C	-0.812	-3.280	-1.210



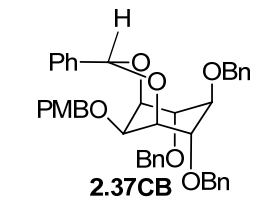
2.37CC



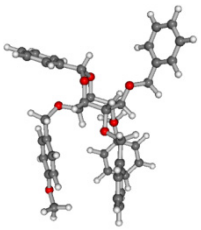
2.37CC

ΔE **2.5** kcal/mol

C	-0.549	-4.761	-1.215
C	-0.650	-5.507	-0.026
C	-0.422	-6.877	-0.020
C	-0.095	-7.544	-1.215
C	0.008	-6.817	-2.409
C	-0.212	-5.433	-2.392
C	-0.184	-1.151	3.921
C	-1.423	-1.253	4.569
C	-1.488	-1.678	5.899
C	-0.318	-2.003	6.592
C	0.917	-1.904	5.947
C	0.986	-1.478	4.617
O	0.103	-8.897	-1.105
C	0.435	-9.616	-2.293
H	0.032	1.617	-1.234
H	1.565	1.306	1.318
H	2.120	-1.126	0.156
H	0.046	-0.811	-1.317
H	-2.165	-1.114	-0.021
H	-1.725	1.283	1.173
H	-0.136	0.472	2.507
H	1.947	-1.412	4.107
H	1.834	-2.163	6.480
H	-0.370	-2.336	7.630
H	-2.458	-1.760	6.393
H	-2.335	-1.012	4.022
H	-3.140	2.717	0.116
H	-2.135	3.069	-1.304
H	-3.520	4.088	-2.904
H	-5.570	4.112	-4.309
H	-7.315	2.357	-4.002
H	-6.993	0.583	-2.279
H	-4.942	0.572	-0.869
H	3.750	1.894	0.670
H	3.814	0.153	0.307
H	5.843	2.716	-0.061
H	7.523	3.079	-1.853
H	7.226	1.997	-4.081
H	5.239	0.548	-4.496



2.37CB



2.37CB

ΔE **5.0** kcal/mol

H	3.567	0.178	-2.692
H	-1.844	-3.079	-0.866
H	-0.714	-2.868	-2.233
H	-0.119	-4.873	-3.325
H	0.266	-7.307	-3.346
H	-0.495	-7.459	0.899
H	-0.897	-4.996	0.906
H	1.780	3.614	0.043
H	0.625	3.848	-1.278
H	1.199	6.246	-1.380
H	0.772	8.526	-0.501
H	-0.287	8.827	1.737
H	-0.915	6.824	3.083
H	-0.476	4.538	2.199
H	0.543	-10.662	-1.986
H	-0.363	-9.538	-3.050
H	1.385	-9.263	-2.728

2.37CC

Final heat of formation = –2153.043

C	3.909	3.937	0.887
C	4.070	2.639	0.383
C	5.357	2.132	0.175
C	6.480	2.912	0.469
C	6.317	4.205	0.974
C	5.030	4.716	1.182
C	2.861	1.801	0.052
O	2.236	2.376	-1.105
C	0.941	1.831	-1.415
C	-0.003	1.941	-0.214
C	0.699	1.224	0.932
O	1.993	1.803	1.188
C	0.972	0.361	-1.903
C	1.135	-0.726	-0.794
C	0.753	-0.302	0.658
O	-0.265	0.188	-2.623
C	-0.166	-0.546	-3.852
C	-0.108	-2.055	-3.705

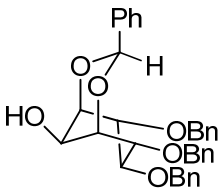
C	-1.111	-2.739	-2.998
C	-1.080	-4.131	-2.890
C	-0.049	-4.861	-3.495
C	0.952	-4.190	-4.202
C	0.921	-2.793	-4.302
O	2.492	-1.211	-0.877
C	2.651	-2.632	-0.710
C	2.626	-3.129	0.722
O	-0.540	-0.883	0.919
C	-0.779	-1.154	2.313
C	-2.176	-1.694	2.479
C	-3.289	-0.911	2.133
C	-4.584	-1.404	2.302
C	-4.785	-2.687	2.827
C	-3.684	-3.473	3.175
C	-2.388	-2.979	2.998
O	-0.271	3.288	0.184
C	-1.245	3.960	-0.632
C	-2.661	3.468	-0.426
C	-3.419	2.959	-1.484
C	-4.739	2.525	-1.303
C	-5.316	2.597	-0.029
C	-4.564	3.098	1.049
C	-3.259	3.529	0.846
H	-0.943	1.407	-0.442
H	0.143	1.392	1.864
H	1.504	-0.737	1.338
H	0.445	-1.544	-1.051
H	1.829	0.246	-2.589
H	0.587	2.434	-2.262
H	3.165	0.765	-0.179
H	-1.157	5.016	-0.338
H	-0.981	3.894	-1.703
H	-2.973	2.892	-2.480
H	-5.297	2.133	-2.152
O	-6.596	2.201	0.272
H	-5.032	3.151	2.033
H	-2.682	3.916	1.688
H	5.479	1.121	-0.221
H	7.482	2.510	0.304
H	7.192	4.816	1.206
H	4.902	5.725	1.577
H	2.901	4.321	1.048
H	-1.072	-0.265	-4.411
H	0.708	-0.196	-4.431
H	-0.036	-1.887	2.679
H	-0.661	-0.230	2.909
H	-3.137	0.089	1.723
H	-5.439	-0.782	2.032
H	-5.798	-3.070	2.964
H	-3.833	-4.475	3.583
H	-1.527	-3.596	3.266
H	1.709	-2.271	-4.851
H	1.760	-4.751	-4.673
H	-0.028	-5.949	-3.415
H	-1.866	-4.648	-2.337
H	-1.911	-2.171	-2.519
C	1.708	-4.108	1.122
C	1.711	-4.597	2.434
C	2.629	-4.102	3.363
C	3.547	-3.118	2.975
C	3.549	-2.641	1.663
H	0.984	-4.490	0.399
H	0.994	-5.366	2.728
H	2.632	-4.480	4.387
H	4.267	-2.728	3.696
H	4.267	-1.874	1.363
H	1.887	-3.163	-1.304
H	3.635	-2.845	-1.156
C	-7.407	1.712	-0.797
H	-8.377	1.472	-0.348
H	-7.546	2.476	-1.580
H	-6.978	0.801	-1.247

2.37CB

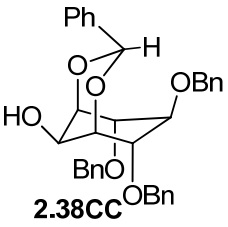
Final heat of formation =

– 2153.039

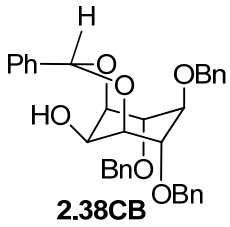
C	-1.883	1.094	-5.749
C	-2.744	0.393	-4.891
C	-3.700	-0.467	-5.446
C	-3.801	-0.623	-6.832
C	-2.938	0.079	-7.678
C	-1.977	0.938	-7.134
C	-2.622	0.550	-3.398
O	-1.508	-0.232	-2.939
C	-1.314	-0.174	-1.519
C	-0.623	1.146	-1.074
C	0.922	1.067	-1.062
C	1.365	-0.157	-0.279
C	0.955	-1.375	-1.109
C	-0.584	-1.480	-1.105
O	1.352	1.072	-2.442
C	1.974	-0.105	-2.951
O	1.391	-1.318	-2.479
C	3.500	-0.086	-2.825
C	4.224	-1.284	-2.880
C	5.622	-1.267	-2.866
C	6.310	-0.050	-2.811
C	5.591	1.147	-2.775
C	4.193	1.130	-2.788
O	2.766	-0.057	-0.015
C	3.252	-0.950	1.007
C	2.828	-0.562	2.405
C	3.274	0.644	2.977
C	2.904	1.009	4.266
C	2.071	0.165	5.025
C	1.612	-1.036	4.472
C	1.994	-1.383	3.169
O	-1.147	1.487	0.219
C	-1.050	2.893	0.527
C	-1.738	3.156	1.841
C	-3.066	3.607	1.874
C	-3.708	3.843	3.093
C	-3.027	3.625	4.295
C	-1.704	3.169	4.272
C	-1.064	2.937	3.052
O	-0.952	-1.884	0.222
C	-2.179	-2.628	0.268
C	-2.587	-2.843	1.703
C	-2.805	-4.136	2.198
C	-3.226	-4.332	3.517
C	-3.424	-3.233	4.357
C	-3.197	-1.939	3.873
C	-2.783	-1.744	2.554
H	-0.868	-2.253	-1.841
H	-0.896	1.931	-1.803
H	1.341	1.969	-0.590
H	0.008	3.203	0.589
H	-1.528	3.477	-0.281
H	-2.052	-3.598	-0.247
H	-2.976	-2.072	-0.264
H	1.622	-2.318	2.744
H	0.958	-1.702	5.032
O	1.767	0.611	6.287
H	3.257	1.938	4.716
H	3.922	1.304	2.397
H	-2.596	-0.736	2.179
H	-3.351	-1.077	4.524
H	-3.754	-3.383	5.387
H	-3.394	-5.345	3.889
H	-2.645	-4.997	1.544
H	-3.598	3.778	0.935
H	-4.740	4.200	3.105
H	-3.525	3.813	5.247
H	-1.166	3.001	5.206
H	-0.032	2.580	3.037
H	1.351	-2.306	-0.673
H	0.793	-0.178	0.664
H	2.945	-1.990	0.798
H	4.344	-0.899	0.900
H	3.683	-2.230	-2.925
H	6.176	-2.207	-2.902
H	7.402	-0.037	-2.803
H	6.121	2.101	-2.735
H	3.628	2.062	-2.756
H	1.722	-0.094	-4.024
H	-2.298	-0.175	-1.012
H	-3.548	0.208	-2.896
H	-2.476	1.617	-3.144
H	-4.372	-1.021	-4.785
H	-4.552	-1.295	-7.251
H	-3.015	-0.041	-8.760
H	-1.302	1.489	-7.791
H	-1.129	1.761	-5.324
C	0.962	-0.235	7.111
H	0.855	0.292	8.064
H	-0.034	-0.400	6.670
H	1.449	-1.209	7.284



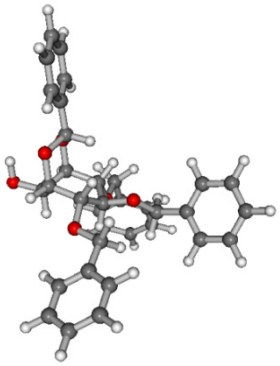
2.38BC



2.38CC

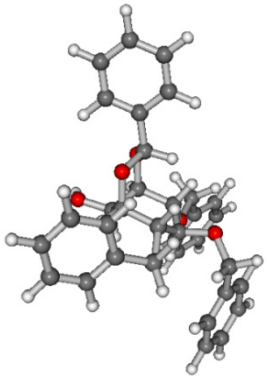


2.38CB



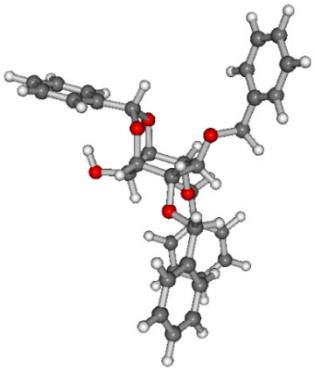
2.38BC

ΔE **0.0** kcal/mol



2.38CC

ΔE **4.4** kcal/mol



2.38CB

ΔE **6.3** kcal/mol

2.38BC

Final heat of formation =

– 1768.038

C	4.444	-2.590	1.169
C	4.426	-1.205	0.959
C	5.646	-0.512	0.898
C	6.859	-1.188	1.039
C	6.870	-2.572	1.247
C	5.660	-3.268	1.313
C	3.138	-0.437	0.768
O	2.020	-1.254	1.128
C	0.760	-0.573	1.185
C	0.220	-0.263	-0.235
C	-1.319	-0.288	-0.415
C	-2.084	-1.205	0.575
C	-1.161	-2.260	1.195
C	-0.151	-1.483	2.045
O	-0.881	-0.751	3.063
C	-1.804	0.175	2.497
O	-2.740	-0.470	1.638
O	0.778	1.014	-0.583
C	0.756	1.328	-1.993
C	1.555	2.587	-2.214
C	1.044	3.831	-1.814
C	1.786	4.999	-2.005
C	3.048	4.938	-2.606
C	3.565	3.704	-3.011
C	2.822	2.536	-2.811
O	-1.545	-0.728	-1.769
C	-2.815	-0.299	-2.304
C	-2.981	-0.879	-3.684
C	-3.411	-2.204	-3.848
C	-3.544	-2.755	-5.125
C	-3.252	-1.983	-6.254
C	-2.824	-0.661	-6.101
C	-2.689	-0.114	-4.822
O	-1.875	-3.233	1.948
C	-2.544	0.878	3.614
C	-3.876	1.279	3.445
C	-4.536	1.968	4.467
C	-3.872	2.264	5.660
C	-2.543	1.864	5.830
C	-1.880	1.175	4.812
H	-0.637	-2.811	0.399
H	0.495	-2.169	2.604
H	0.889	0.391	1.713
H	0.622	-1.041	-0.913
H	-1.698	0.745	-0.291
H	-2.904	-1.701	0.040
H	-1.234	0.920	1.901
H	-0.848	0.850	4.947
H	-2.019	2.087	6.761
H	-4.389	2.802	6.457
H	-5.576	2.272	4.329
H	-4.394	1.039	2.517
H	-3.640	-0.631	-1.648
H	-2.841	0.806	-2.340
H	3.053	-0.103	-0.281
H	3.144	0.477	1.389
H	5.645	0.570	0.742
H	7.798	-0.634	0.993
H	7.817	-3.103	1.361
H	5.659	-4.347	1.478
H	3.500	-3.131	1.225
H	-2.354	0.918	-4.704
H	-2.597	-0.053	-6.979
H	-3.359	-2.411	-7.252
H	-3.881	-3.787	-5.239
H	-3.641	-2.808	-2.968
H	3.229	1.572	-3.127
H	4.548	3.650	-3.482
H	3.626	5.851	-2.760
H	1.378	5.961	-1.689
H	0.059	3.882	-1.346
H	1.182	0.487	-2.568
H	-0.284	1.466	-2.332
H	-2.294	-2.751	2.687

2.38CC

Final heat of formation =

–1768.031

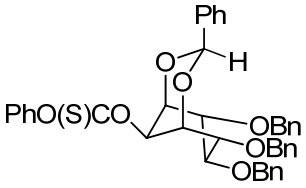
C	5.222	-2.944	-0.039
C	4.261	-2.081	0.506
C	4.616	-1.267	1.590
C	5.907	-1.324	2.123
C	6.857	-2.195	1.582
C	6.511	-3.006	0.497
C	2.857	-2.086	-0.050
O	2.221	-0.826	0.175
C	0.837	-0.827	-0.200
C	-0.034	-1.405	0.954
C	-0.751	-0.273	1.696

C	-1.745	0.307	0.693
C	-0.993	0.999	-0.483
C	0.501	0.618	-0.609
O	-0.987	-2.390	0.506
C	-1.982	-1.830	-0.362
O	-2.648	-0.722	0.231
C	-2.999	-2.901	-0.664
C	-3.089	-3.451	-1.947
C	-4.022	-4.457	-2.220
C	-4.868	-4.915	-1.207
C	-4.781	-4.365	0.077
C	-3.850	-3.361	0.350
O	-1.457	-0.688	2.863
O	-1.018	2.435	-0.368
C	-2.188	3.083	-0.914
C	-3.390	3.131	0.004
C	-4.571	2.447	-0.315
C	-5.680	2.503	0.534
C	-5.619	3.246	1.715
C	-4.445	3.934	2.044
C	-3.341	3.880	1.192
O	0.963	0.757	-1.961
C	1.403	2.077	-2.352
C	2.649	2.556	-1.638
C	3.859	1.855	-1.766
C	5.013	2.308	-1.127
C	4.976	3.474	-0.353
C	3.777	4.178	-0.215
C	2.620	3.717	-0.853
H	-0.009	0.506	1.953
H	-2.393	1.043	1.182
H	-1.502	0.706	-1.420
H	1.074	1.290	0.053
H	0.697	-1.469	-1.089
H	0.633	-1.958	1.632
H	-1.487	-1.504	-1.301
H	-2.426	-3.091	-2.737
H	-4.087	-4.882	-3.223
H	-5.597	-5.700	-1.417
H	-5.443	-4.721	0.869
H	-3.776	-2.920	1.344
H	2.277	-2.901	0.429
H	2.878	-2.305	-1.135
H	-1.850	4.107	-1.135
H	-2.465	2.600	-1.869
H	-2.424	4.415	1.451
H	-4.394	4.518	2.965
H	-6.483	3.289	2.380
H	-6.591	1.959	0.275
H	-4.618	1.855	-1.232
H	4.962	-3.573	-0.894
H	7.248	-3.683	0.061
H	7.865	-2.239	2.000
H	6.172	-0.680	2.964
H	3.878	-0.577	2.001
H	1.679	4.261	-0.739
H	3.740	5.085	0.391
H	5.881	3.830	0.144
H	5.947	1.753	-1.233
H	3.886	0.942	-2.363
H	1.599	1.972	-3.429
H	0.592	2.810	-2.216
H	-0.909	-1.342	3.331

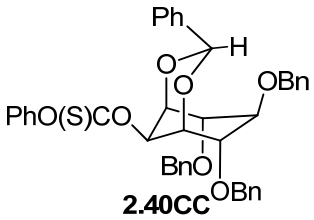
2.38CB

Final heat of formation = –1768.028

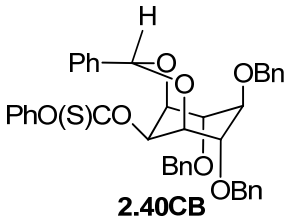
C	3.370	-3.659	-1.139
C	2.722	-3.378	0.074
C	3.373	-3.676	1.282
C	4.659	-4.225	1.275
C	5.303	-4.493	0.063
C	4.656	-4.207	-1.143
C	1.269	-2.873	0.082
O	0.937	-2.189	1.282
C	1.162	-0.759	1.332
C	1.877	-0.205	0.101
C	1.117	-0.732	-1.113
O	0.934	-2.171	-1.111
C	-0.218	-0.084	1.454
C	-1.079	-0.172	0.164
C	-0.289	-0.089	-1.172
O	0.048	1.274	1.823
C	-1.035	1.913	2.521
C	-0.594	3.287	2.950
C	-0.802	4.396	2.118
C	-0.370	5.667	2.506
C	0.274	5.842	3.735
C	0.488	4.742	4.571
C	0.056	3.473	4.179
O	-1.858	-1.373	0.257
C	-3.086	-1.320	-0.490
C	-3.839	-2.607	-0.279
C	-3.570	-3.727	-1.079
C	-4.249	-4.930	-0.871
C	-5.208	-5.026	0.142
C	-5.482	-3.915	0.946
C	-4.800	-2.714	0.735
O	-0.206	1.298	-1.536
C	-0.077	1.513	-2.955
C	0.010	2.992	-3.224
C	-1.060	3.681	-3.808
C	-0.973	5.054	-4.060
C	0.188	5.753	-3.722
C	1.260	5.075	-3.132
C	1.173	3.704	-2.887
O	3.289	-0.410	0.064
H	-0.784	-0.599	2.251
H	-0.866	-0.641	-1.937
H	1.675	-0.484	-2.030
H	0.826	1.006	-3.340
H	-0.953	1.080	-3.475
H	-1.312	1.301	3.401
H	-1.924	1.988	1.867
H	-1.297	4.258	1.154
H	-0.538	6.522	1.849
H	0.609	6.835	4.040
H	0.991	4.874	5.531
H	0.225	2.613	4.832
H	-1.971	3.136	-4.068
H	-1.813	5.577	-4.521
H	0.259	6.824	-3.919
H	2.170	5.617	-2.866
H	2.010	3.177	-2.426
H	1.743	-0.539	2.239
H	1.749	0.885	0.119
H	2.864	-3.465	2.223
H	5.159	-4.443	2.220
H	6.307	-4.920	0.058
H	5.154	-4.412	-2.092
H	2.860	-3.433	-2.076
H	0.604	-3.751	0.078
H	-1.754	0.704	0.159
H	-3.688	-0.456	-0.146
H	-2.878	-1.178	-1.567
H	-5.013	-1.848	1.366
H	-6.231	-3.985	1.738
H	-5.742	-5.964	0.303
H	-4.032	-5.793	-1.502
H	-2.818	-3.652	-1.868
H	3.470	-1.372	0.061



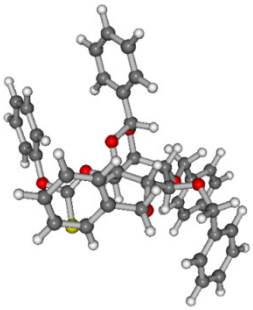
2.40BC



2.40CC

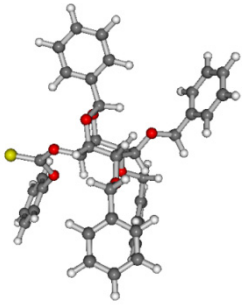


2.40CB



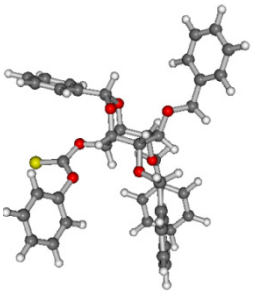
2.40BC

ΔE **0.0** kcal/mol



2.40CC

ΔE **1.9** kcal/mol



2.40CB

ΔE **7.5** kcal/mol

2.40BC

Final heat of formation =

–2510.775

C	4.163	-1.540	1.676
C	3.396	-2.624	2.104
C	3.549	-3.175	3.375
C	4.487	-2.616	4.248
C	5.263	-1.526	3.843
C	5.096	-0.993	2.560
O	2.528	-3.323	1.232
C	1.541	-2.729	0.528
S	0.687	-3.597	-0.598
O	1.362	-1.450	0.893
C	0.358	-0.660	0.198
C	-0.223	0.360	1.163
C	-1.446	1.054	0.487
C	-1.526	0.890	-1.042
C	-0.161	0.829	-1.770
C	0.973	0.126	-0.957
O	1.955	1.056	-0.450
C	1.399	1.973	0.500
O	0.787	1.296	1.590
O	-0.415	0.163	-3.018
C	0.420	0.569	-4.122
C	1.796	-0.064	-4.167
C	2.950	0.730	-4.180
C	4.219	0.146	-4.249
C	4.344	-1.243	-4.302
C	3.197	-2.047	-4.285
C	1.932	-1.461	-4.225
O	-2.318	1.990	-1.511
C	-3.119	1.746	-2.694
C	-4.212	0.718	-2.500
C	-4.176	-0.500	-3.192
C	-5.191	-1.448	-3.023
C	-6.253	-1.184	-2.154
C	-6.294	0.026	-1.453
C	-5.281	0.970	-1.626
O	-2.667	0.517	1.008
C	-3.050	1.110	2.253
C	-4.255	0.400	2.823
C	-4.468	-0.967	2.601
C	-5.561	-1.615	3.184
C	-6.450	-0.907	4.000
C	-6.244	0.457	4.223
C	-5.156	1.106	3.633
C	2.506	2.860	1.012
C	3.245	2.512	2.150
C	4.282	3.339	2.587
C	4.592	4.512	1.891
C	3.857	4.861	0.755
C	2.815	4.038	0.320
H	-2.049	-0.062	-1.240
H	0.170	1.864	-1.975
H	1.524	-0.538	-1.630
H	-0.413	-1.351	-0.175
H	-0.561	-0.125	2.086
H	-1.388	2.135	0.712
H	0.637	2.594	-0.014
H	2.234	4.313	-0.563
H	4.090	5.777	0.210
H	5.403	5.156	2.237
H	4.850	3.068	3.480
H	2.994	1.599	2.690
H	-2.213	1.053	2.979
H	-3.275	2.183	2.104
H	-3.784	-1.515	1.954
H	-5.720	-2.679	2.998
H	-7.302	-1.415	4.455
H	-6.937	1.020	4.850
H	-5.007	2.176	3.802
H	-0.153	0.272	-5.013
H	0.516	1.670	-4.130
H	1.039	-2.089	-4.202
H	3.290	-3.133	-4.321
H	5.333	-1.703	-4.351
H	5.109	0.778	-4.254
H	2.855	1.817	-4.127
H	-3.554	2.732	-2.913
H	-2.476	1.452	-3.538
H	-5.310	1.911	-1.073
H	-7.119	0.233	-0.769
H	-7.047	-1.922	-2.019
H	-5.150	-2.394	-3.567
H	-3.340	-0.709	-3.864
H	2.942	-4.034	3.662
H	4.614	-3.042	5.245
H	5.998	-1.095	4.523
H	5.700	-0.145	2.235
H	4.028	-1.122	0.679

2.40CC

Final heat of formation =

–2510.772

C	5.213	1.671	-0.134
C	4.113	2.213	0.524
C	4.242	2.934	1.707
C	5.520	3.131	2.237
C	6.642	2.602	1.590
C	6.486	1.874	0.406
O	2.818	1.927	0.038
C	2.249	2.765	-0.875
S	2.906	4.150	-1.489
O	1.042	2.327	-1.250

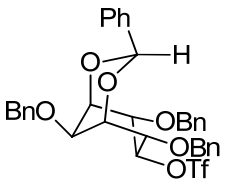
C	0.484	1.080	-0.724
C	-0.184	1.261	0.635
C	-0.582	-0.137	1.177
C	-1.277	-1.101	0.161
C	-1.070	-0.788	-1.347
C	-0.610	0.651	-1.692
O	-1.681	1.610	-1.713
C	-2.267	1.858	-0.427
O	-1.271	2.192	0.553
O	-2.701	-1.184	0.370
C	-3.082	-2.021	1.479
C	-4.585	-2.068	1.556
C	-5.285	-1.195	2.402
C	-6.681	-1.221	2.453
C	-7.393	-2.122	1.655
C	-6.704	-2.996	0.807
C	-5.309	-2.968	0.759
O	0.655	-0.700	1.646
C	0.494	-1.675	2.689
C	1.836	-2.269	3.027
C	2.402	-2.084	4.295
C	3.640	-2.651	4.613
C	4.329	-3.403	3.657
C	3.774	-3.586	2.385
C	2.535	-3.025	2.073
O	-0.099	-1.734	-1.833
C	-0.250	-2.049	-3.235
C	0.774	-3.089	-3.605
C	1.991	-2.716	-4.192
C	2.952	-3.679	-4.512
C	2.704	-5.029	-4.247
C	1.492	-5.412	-3.661
C	0.534	-4.446	-3.344
C	-3.202	3.032	-0.561
C	-2.709	4.284	-0.954
C	-3.580	5.368	-1.077
C	-4.946	5.208	-0.810
C	-5.439	3.960	-0.420
C	-4.567	2.874	-0.296
H	1.271	0.316	-0.661
H	-0.225	0.655	-2.720
H	-2.045	-0.954	-1.840
H	-0.832	-2.101	0.311
H	-1.272	0.032	2.025
H	0.512	1.694	1.362
H	-2.818	0.962	-0.094
H	-4.948	1.895	0.004
H	-6.503	3.831	-0.214
H	-5.624	6.058	-0.908
H	-3.194	6.342	-1.383
H	-1.645	4.398	-1.163
H	0.048	-1.196	3.582
H	-0.196	-2.475	2.358
H	-1.274	-2.428	-3.409
H	-0.112	-1.146	-3.856
H	2.186	-1.661	-4.401
H	3.894	-3.376	-4.972
H	3.452	-5.783	-4.499
H	1.292	-6.465	-3.457
H	-0.412	-4.746	-2.889
H	2.107	-3.162	1.078
H	4.310	-4.170	1.635
H	5.297	-3.844	3.901
H	4.070	-2.500	5.604
H	1.869	-1.488	5.040
H	-4.771	-3.650	0.097
H	-7.256	-3.703	0.185
H	-8.483	-2.146	1.696
H	-7.214	-0.539	3.118
H	-4.729	-0.490	3.025
H	-2.667	-3.036	1.323
H	-2.668	-1.627	2.425
H	3.356	3.339	2.195
H	5.637	3.696	3.163
H	7.637	2.757	2.008
H	7.358	1.458	-0.100
H	5.070	1.105	-1.054

2.40CB

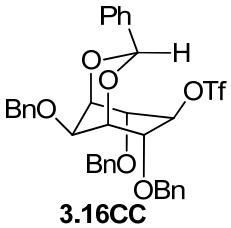
Final heat of formation =

– 2510.763

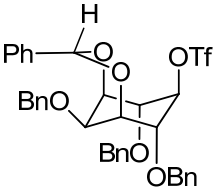
C	0.677	-0.742	-4.716
C	0.865	-1.790	-3.821
C	1.646	-2.901	-4.136
C	2.230	-2.968	-5.403
C	2.039	-1.935	-6.328
C	1.268	-0.822	-5.982
O	0.343	-1.636	-2.520
C	-0.660	-2.443	-2.073
S	-1.443	-3.626	-2.915
O	-0.974	-2.154	-0.801
C	-0.443	-0.960	-0.139
C	-1.367	-0.625	1.017
C	-1.064	0.822	1.478
C	0.445	1.093	1.746
C	1.428	0.340	0.808
C	0.966	-1.086	0.425
O	1.061	-1.897	1.609
C	-0.139	-2.416	2.171
O	-1.226	-1.485	2.163
O	1.605	1.046	-0.425
C	2.568	2.108	-0.348
C	2.478	2.964	-1.585
C	1.246	3.511	-1.978
C	1.167	4.334	-3.103
C	2.318	4.625	-3.846
C	3.546	4.080	-3.463
C	3.623	3.249	-2.341
O	0.815	0.789	3.096
C	0.462	1.826	4.027
C	0.867	1.402	5.415
C	1.937	2.025	6.071
C	2.309	1.631	7.361
C	1.615	0.602	8.004
C	0.550	-0.030	7.353
C	0.177	0.369	6.068
O	-1.515	1.774	0.502
C	-2.919	2.097	0.618
C	-3.262	3.150	-0.401
C	-3.024	4.506	-0.130
C	-3.319	5.484	-1.082
C	-3.860	5.116	-2.318
C	-4.102	3.767	-2.598
C	-3.802	2.791	-1.644
C	-0.520	-3.787	1.611
C	0.475	-4.651	1.136
C	0.148	-5.943	0.716
C	-1.175	-6.388	0.777
C	-2.169	-5.533	1.263
C	-1.843	-4.241	1.682
H	2.384	0.242	1.352
H	-1.606	0.975	2.430
H	-2.415	-0.692	0.684
H	-3.539	1.198	0.456
H	-3.118	2.467	1.642
H	3.585	1.685	-0.243
H	2.373	2.728	0.547
H	0.348	3.276	-1.404
H	0.204	4.754	-3.399
H	2.255	5.271	-4.724
H	4.446	4.295	-4.043
H	4.582	2.814	-2.051
H	-2.604	4.795	0.836
H	-3.134	6.536	-0.858
H	-4.098	5.880	-3.061
H	-4.528	3.475	-3.560
H	-3.993	1.738	-1.863
H	1.661	-1.483	-0.326
H	-0.451	-0.127	-0.856
H	1.508	-4.302	1.094
H	0.930	-6.605	0.338
H	-1.432	-7.395	0.445
H	-3.206	-5.871	1.308
H	-2.616	-3.570	2.057
H	0.100	-2.530	3.240
H	0.587	2.175	1.557
H	0.971	2.768	3.746
H	-0.628	2.014	3.996
H	-0.651	-0.126	5.558
H	0.006	-0.835	7.851
H	1.904	0.292	9.009
H	3.142	2.126	7.862
H	2.484	2.825	5.567
H	1.781	-3.699	-3.408
H	2.839	-3.834	-5.668
H	2.498	-1.996	-7.316
H	1.126	-0.007	-6.693
H	0.081	0.120	-4.417



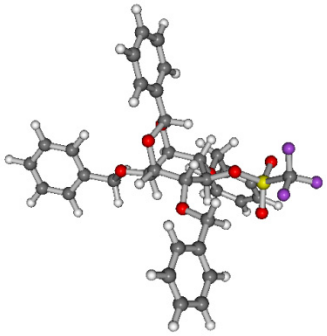
3.16BC



3.16CC

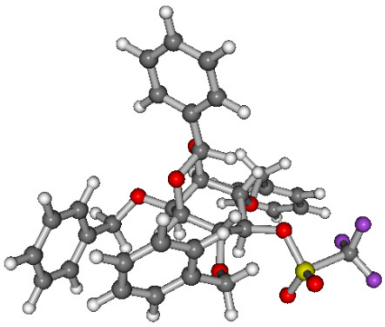


3.16CB



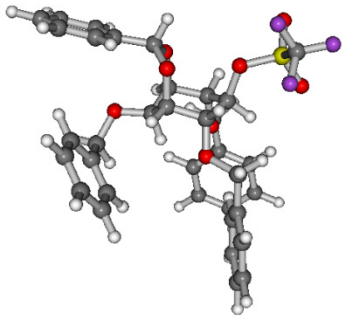
3.16BC

ΔE **0.0** kcal/mol



3.16CC

ΔE **0.6** kcal/mol



3.16CB

ΔE **5.0** kcal/mol

3.16BC

Final heat of formation =

– 2653.914

C	5.875	0.241	-1.109
C	5.046	-0.115	-2.183
C	5.604	-0.247	-3.461
C	6.971	-0.040	-3.666
C	7.793	0.314	-2.592
C	7.239	0.459	-1.315
C	3.581	-0.397	-1.961
O	3.046	0.552	-1.031
C	1.687	0.322	-0.696
C	1.460	-0.831	0.294
O	2.107	-0.545	1.548
C	1.631	0.666	2.134
O	1.775	1.776	1.261
C	1.135	1.571	-0.009
C	-0.412	1.499	0.104
C	-0.978	0.056	0.035
C	-0.062	-1.110	0.454
C	2.386	0.922	3.419
C	2.662	-0.147	4.281
C	3.315	0.078	5.495
C	3.694	1.375	5.858
C	3.421	2.442	4.999
C	2.767	2.220	3.783
O	-0.475	-2.215	-0.359
C	-0.225	-3.506	0.252
C	-0.636	-4.587	-0.710
C	0.319	-5.252	-1.489
C	-0.064	-6.246	-2.393
C	-1.415	-6.583	-2.527
C	-2.377	-5.923	-1.754
C	-1.990	-4.933	-0.849
O	-2.175	0.065	0.910
S	-3.396	-1.024	0.609
O	-3.177	-2.300	1.321
O	-0.900	2.304	-0.968
C	-2.289	2.696	-0.868
C	-2.554	3.774	-1.886
C	-3.377	3.526	-2.992
C	-3.622	4.528	-3.937
C	-3.039	5.789	-3.784
C	-2.212	6.045	-2.684
C	-1.974	5.044	-1.740
C	-4.689	-0.037	1.652
O	-3.796	-0.974	-0.810
H	1.092	0.130	-1.614
H	1.374	2.465	-0.598
H	-0.704	1.943	1.076
H	-1.309	-0.130	-0.997
H	-0.248	-1.335	1.521
H	1.931	-1.757	-0.057
H	0.549	0.539	2.365
H	3.459	-1.427	-1.569
H	3.030	-0.344	-2.920
H	4.962	-0.510	-4.306
H	7.392	-0.145	-4.668
H	8.859	0.483	-2.751
H	7.875	0.742	-0.474
H	5.439	0.362	-0.117
H	2.558	3.048	3.106
H	3.719	3.456	5.273
H	4.204	1.551	6.807
H	3.530	-0.760	6.159
H	2.376	-1.159	3.992
H	0.846	-3.607	0.500
H	-0.808	-3.566	1.188
H	-2.953	1.834	-1.049
H	-2.480	3.065	0.157
H	-3.829	2.538	-3.115
H	-4.265	4.322	-4.794
H	-3.228	6.572	-4.520
H	-1.755	7.028	-2.560
H	-1.328	5.244	-0.883
H	-2.738	-4.417	-0.244
H	-3.431	-6.185	-1.855
H	-1.717	-7.359	-3.232
H	0.689	-6.760	-2.991
H	1.375	-4.992	-1.384
F	-5.822	-0.752	1.651
F	-4.250	0.114	2.907
F	-4.913	1.162	1.099

3.16CC

Final heat of formation =

–2653.913

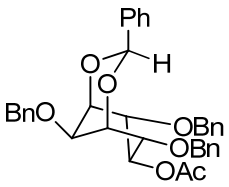
C	4.295	-1.301	-3.723
C	4.523	-0.368	-2.700
C	5.807	-0.267	-2.147
C	6.845	-1.083	-2.607
C	6.608	-2.010	-3.625
C	5.329	-2.120	-4.183
C	3.398	0.496	-2.197
O	2.642	-0.243	-1.212
C	1.443	0.425	-0.805
C	0.308	0.216	-1.855
C	-0.675	-0.859	-1.386
C	-1.393	-0.259	-0.164
C	-0.378	-0.060	1.009
C	1.093	-0.151	0.570

O	-2.044	0.972	-0.542
C	-1.139	1.944	-1.066
O	-0.388	1.437	-2.168
C	-1.932	3.139	-1.527
C	-2.707	3.064	-2.693
C	-3.455	4.168	-3.106
C	-3.436	5.352	-2.358
C	-2.664	5.429	-1.195
C	-1.913	4.324	-0.783
O	-1.517	-1.198	-2.483
C	-2.060	-2.523	-2.468
C	-3.446	-2.653	-1.862
C	-3.877	-3.899	-1.381
C	-5.185	-4.070	-0.919
C	-6.074	-2.990	-0.922
C	-5.644	-1.741	-1.382
C	-4.339	-1.573	-1.853
O	1.921	0.579	1.547
S	2.569	-0.250	2.839
O	1.886	0.161	4.081
O	-0.521	-1.057	2.026
C	-1.252	-0.652	3.211
C	-2.748	-0.531	3.034
C	-3.386	0.707	3.191
C	-4.774	0.818	3.061
C	-5.539	-0.312	2.766
C	-4.912	-1.554	2.604
C	-3.528	-1.662	2.742
C	4.254	0.692	2.813
O	2.826	-1.661	2.496
H	1.399	-1.208	0.587
H	-0.560	0.941	1.438
H	-2.201	-0.909	0.190
H	-0.105	-1.754	-1.068
H	0.766	-0.092	-2.802
H	1.625	1.512	-0.712
H	-0.437	2.253	-0.262
H	-1.306	4.384	0.122
H	-2.643	6.351	-0.611
H	-4.021	6.214	-2.684
H	-4.055	4.108	-4.016
H	-2.708	2.140	-3.272
H	2.742	0.791	-3.036
H	3.789	1.420	-1.732
H	5.993	0.454	-1.350
H	7.841	-0.993	-2.170
H	7.418	-2.646	-3.986
H	5.140	-2.839	-4.981
H	3.298	-1.385	-4.162
H	-1.012	-1.438	3.940
H	-0.833	0.294	3.589
H	-2.789	1.592	3.423
H	-5.256	1.788	3.186
H	-6.622	-0.228	2.662
H	-5.505	-2.439	2.371
H	-3.041	-2.633	2.620
H	-2.110	-2.820	-3.529
H	-1.362	-3.221	-1.969
H	-3.997	-0.599	-2.205
H	-6.328	-0.891	-1.375
H	-7.096	-3.121	-0.562
H	-5.508	-5.046	-0.552
H	-3.185	-4.746	-1.374
F	4.948	0.314	3.898
F	4.044	2.016	2.856
F	4.943	0.378	1.709

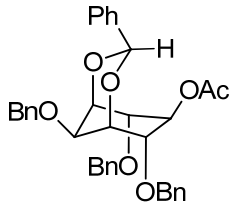
3.16CB

Final heat of formation =
– 2653.906

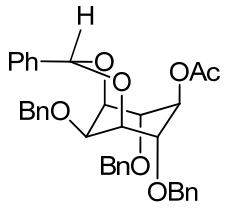
C	3.159	3.730	-2.285
C	3.285	3.222	-0.985
C	4.543	2.779	-0.547
C	5.652	2.843	-1.393
C	5.516	3.355	-2.688
C	4.268	3.799	-3.134
C	2.091	3.136	-0.073
O	1.594	1.777	-0.079
C	0.478	1.583	0.801
C	-0.853	1.874	0.064
C	-1.132	0.761	-0.939
C	-1.410	-0.504	-0.124
C	-0.086	-0.969	0.517
C	0.587	0.143	1.361
O	-1.885	2.042	1.054
C	-2.857	1.003	1.184
O	-2.332	-0.304	0.968
C	-4.139	1.279	0.397
C	-4.485	2.582	0.020
C	-5.711	2.836	-0.599
C	-6.611	1.792	-0.835
C	-6.277	0.491	-0.443
C	-5.049	0.237	0.172
O	-2.181	1.159	-1.823
C	-2.032	0.704	-3.182
C	-2.359	-0.757	-3.412
C	-3.659	-1.237	-3.181
C	-3.968	-2.580	-3.400
C	-2.983	-3.463	-3.862
C	-1.688	-2.994	-4.098
C	-1.380	-1.647	-3.873
O	-0.007	0.118	2.712
S	0.989	0.031	4.035
O	2.408	-0.053	3.621
O	0.775	-1.364	-0.550
C	1.775	-2.327	-0.169
C	2.737	-2.524	-1.312
C	3.394	-1.421	-1.881
C	4.308	-1.605	-2.921
C	4.583	-2.892	-3.398
C	3.933	-3.994	-2.836
C	3.010	-3.808	-1.801
C	0.470	-1.721	4.662
O	0.493	0.994	5.030
H	-0.306	-1.821	1.184
H	0.542	2.274	1.660
H	-0.762	2.834	-0.467
H	1.304	3.835	-0.412
H	2.369	3.410	0.961
H	2.323	-1.968	0.723
H	1.290	-3.283	0.099
H	-0.363	-1.287	-4.048
H	-0.914	-3.675	-4.454
H	-3.226	-4.512	-4.037
H	-4.981	-2.942	-3.217
H	-4.425	-0.551	-2.812
H	2.496	-4.670	-1.369
H	4.139	-5.000	-3.206
H	5.300	-3.035	-4.208
H	4.811	-0.741	-3.357
H	3.176	-0.417	-1.511
H	4.650	2.383	0.465
H	6.626	2.500	-1.040
H	6.384	3.411	-3.348
H	4.158	4.201	-4.143
H	2.184	4.079	-2.634
H	-1.797	-1.306	-0.767
H	-0.202	0.590	-1.510
H	-2.726	1.340	-3.751
H	-1.006	0.914	-3.535
H	-3.781	3.393	0.209
H	-5.966	3.855	-0.898
H	-7.571	1.992	-1.314
H	-6.978	-0.327	-0.616
H	-4.785	-0.776	0.478
H	-3.110	1.006	2.257
H	1.659	-0.078	1.451
F	1.213	-2.020	5.737
F	0.695	-2.631	3.697
F	-0.824	-1.725	4.990



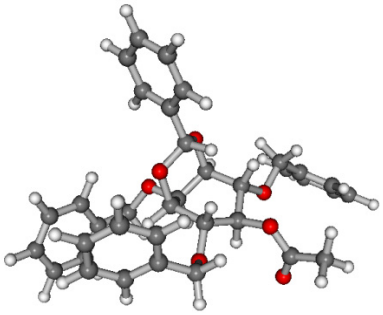
4.18BC



4.18CC

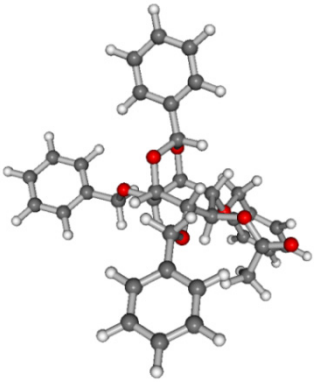


4.18CB



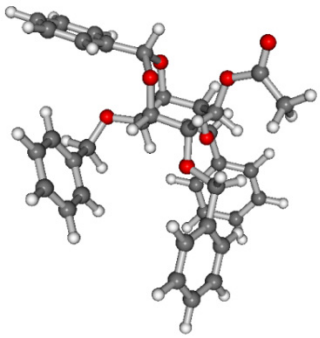
4.18BC

ΔE **0.0** kcal/mol



4.18CC

ΔE **0.6** kcal/mol



4.18CB

ΔE **12.5** kcal/mol

4.18BC

Final heat of formation =
–1920.755

C	0.000	0.000	0.000
C	0.000	0.000	1.402
C	1.215	0.000	2.094
C	2.427	0.002	1.395
C	2.424	0.002	-0.003
C	1.209	0.000	-0.698
C	-1.306	0.018	2.156
O	-2.143	-1.015	1.639
C	-3.476	-0.988	2.191
C	-4.132	0.368	1.919
C	-3.216	1.408	2.587
O	-1.892	1.313	2.015
C	-3.496	-1.320	3.715
C	-3.859	-0.111	4.585
C	-3.222	1.216	4.138
O	-4.290	0.519	0.509
C	-5.381	1.346	0.096
C	-5.059	2.820	-0.078
C	-6.084	3.772	0.033
C	-5.831	5.124	-0.216
C	-4.543	5.540	-0.571
C	-3.514	4.598	-0.668
C	-3.770	3.245	-0.429
O	-3.968	2.259	4.782
C	-3.186	3.213	5.529
C	-2.414	4.204	4.684
C	-1.013	4.220	4.694
C	-0.302	5.143	3.921
C	-0.990	6.062	3.125
C	-2.390	6.054	3.106
C	-3.096	5.135	3.882
O	-3.424	-0.379	5.948
C	-4.395	-0.447	6.921
C	-3.769	-0.710	8.271
O	-4.461	-2.335	4.012
C	-3.982	-3.665	3.718
C	-5.086	-4.651	3.994
C	-5.324	-5.107	5.299
C	-6.362	-6.004	5.561
C	-7.176	-6.458	4.517
C	-6.947	-6.010	3.212
C	-5.908	-5.112	2.955
O	-5.581	-0.297	6.721
H	-4.953	0.004	4.605
H	-2.173	1.243	4.481
H	-3.540	2.433	2.373
H	-5.126	0.392	2.405
H	-4.016	-1.777	1.652
H	-2.486	-1.676	3.998
H	-1.117	-0.174	3.234
H	1.215	-0.002	3.187
H	3.372	0.000	1.941
H	3.368	0.002	-0.551
H	1.205	-0.002	-1.790
H	-0.953	-0.010	-0.530
H	-3.665	-3.736	2.662
H	-3.099	-3.876	4.350
H	-4.690	-4.752	6.114
H	-6.537	-6.352	6.580
H	-7.985	-7.160	4.720
H	-7.577	-6.363	2.394
H	-5.730	-4.762	1.934
H	-3.929	3.736	6.148
H	-2.493	2.679	6.204
H	-0.473	3.503	5.318
H	0.790	5.141	3.938
H	-0.438	6.783	2.517
H	-2.932	6.770	2.485
H	-4.188	5.129	3.864
H	-5.692	0.934	-0.879
H	-6.238	1.228	0.787
H	-2.967	2.509	-0.490
H	-2.504	4.917	-0.932
H	-4.343	6.595	-0.766
H	-6.638	5.853	-0.128
H	-7.090	3.453	0.318
H	-2.746	-1.091	8.185
H	-3.751	0.233	8.838
H	-4.398	-1.417	8.825

4.18CC

Final heat of formation =
–1920.754

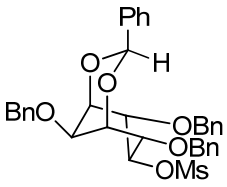
C	0.000	0.000	0.000
C	0.000	0.000	1.399
C	1.216	0.000	2.095
C	2.422	-0.000	1.390
C	2.420	0.002	-0.012
C	1.208	0.002	-0.705
C	-1.301	0.020	2.158
O	-1.440	1.305	2.778
C	-2.597	1.390	3.632

C	-2.516	0.314	4.730
C	-2.440	-1.020	3.986
O	-1.292	-1.038	3.113
C	-3.941	1.265	2.850
C	-4.671	-0.065	3.078
C	-3.772	-1.300	3.226
O	-4.874	2.279	3.250
C	-4.672	3.541	2.575
C	-5.731	4.507	3.035
C	-5.471	5.415	4.071
C	-6.464	6.293	4.515
C	-7.731	6.270	3.925
C	-8.000	5.368	2.888
C	-7.005	4.493	2.447
O	-5.561	-0.286	1.959
C	-6.932	-0.363	2.092
C	-7.537	-0.212	3.471
O	-4.577	-2.268	3.912
C	-4.180	-3.633	3.650
C	-5.144	-4.558	4.343
C	-6.365	-4.890	3.736
C	-7.274	-5.730	4.384
C	-6.972	-6.248	5.648
C	-5.758	-5.922	6.261
C	-4.851	-5.081	5.610
O	-1.387	0.420	5.589
C	-1.486	1.501	6.536
C	-0.293	1.449	7.453
C	-0.354	0.753	8.668
C	0.761	0.687	9.508
C	1.953	1.317	9.138
C	2.025	2.012	7.926
C	0.907	2.078	7.090
O	-7.578	-0.550	1.084
H	-3.447	0.343	5.332
H	-2.260	-1.834	4.699
H	-3.517	-1.679	2.219
H	-5.245	0.032	4.009
H	-3.720	1.369	1.771
H	-2.554	2.401	4.059
H	-2.148	-0.128	1.456
H	-1.513	2.472	6.010
H	-2.425	1.400	7.115
H	-1.284	0.258	8.957
H	0.700	0.145	10.453
H	2.825	1.268	9.793
H	2.953	2.506	7.633
H	0.964	2.618	6.143
H	1.205	-0.007	3.185
H	3.368	-0.003	1.934
H	3.364	0.001	-0.558
H	1.201	0.000	-1.797
H	-0.949	-0.003	-0.542
H	-3.665	3.940	2.800
H	-4.737	3.377	1.484
H	-4.190	-3.804	2.558
H	-3.151	-3.810	4.012
H	-6.602	-4.488	2.748
H	-8.219	-5.986	3.900
H	-7.679	-6.908	6.153
H	-5.516	-6.327	7.245
H	-3.902	-4.827	6.089
H	-7.215	3.791	1.637
H	-8.986	5.350	2.421
H	-8.507	6.956	4.266
H	-6.248	6.997	5.320
H	-4.481	5.435	4.533
H	-7.291	0.768	3.905
H	-8.622	-0.302	3.369
H	-7.168	-0.993	4.151

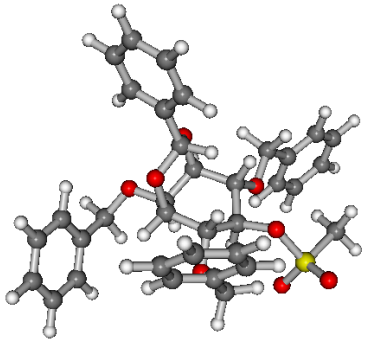
4.18CB

Final heat of formation = –1920.735

C	0.000	0.000	0.000
C	0.000	0.000	1.400
C	1.223	0.000	2.084
C	2.429	0.024	1.377
C	2.424	0.042	-0.022
C	1.205	0.029	-0.707
C	-1.304	-0.146	2.187
O	-1.250	0.484	3.467
C	-1.701	1.845	3.591
C	-2.084	2.496	2.259
C	-3.003	1.514	1.544
O	-2.457	0.188	1.415
C	-4.344	1.399	2.313
C	-4.178	1.138	3.830
C	-2.951	1.826	4.499
O	-3.221	3.193	4.827
C	-4.005	3.378	6.019
C	-4.013	4.839	6.385
C	-5.100	5.655	6.043
C	-5.105	7.012	6.379
C	-4.018	7.566	7.063
C	-2.927	6.760	7.405
C	-2.925	5.405	7.068
O	-0.988	2.832	1.406
C	-0.522	4.188	1.520
C	0.375	4.470	2.709
C	1.575	3.758	2.875
C	2.418	4.034	3.952
C	2.081	5.034	4.873
C	0.891	5.748	4.715
C	0.042	5.464	3.640
O	-5.131	2.594	2.180
C	-5.886	2.651	0.950
C	-6.786	3.858	0.993
C	-8.096	3.752	1.484
C	-8.926	4.874	1.546
C	-8.452	6.119	1.118
C	-7.148	6.235	0.627
C	-6.322	5.109	0.563
O	-4.096	-0.299	4.009
C	-4.784	-0.972	4.988
C	-5.729	-0.193	5.886
O	-4.616	-2.169	5.079
H	-2.702	1.254	5.412
H	-4.889	0.533	1.896
H	-3.200	1.877	0.524
H	-5.206	2.716	0.081
H	-6.482	1.725	0.846
H	-5.042	3.030	5.860
H	-3.562	2.778	6.837
H	-0.894	6.016	3.526
H	0.619	6.526	5.430
H	2.745	5.253	5.711
H	3.348	3.474	4.071
H	1.834	2.973	2.161
H	-2.073	4.776	7.334
H	-2.079	7.188	7.943
H	-4.023	8.624	7.331
H	-5.958	7.636	6.109
H	-5.946	5.224	5.503
H	-8.467	2.780	1.817
H	-9.946	4.777	1.924
H	-9.100	6.996	1.163
H	-6.776	7.203	0.288
H	-5.305	5.201	0.176
H	-0.914	2.423	4.095
H	-2.675	3.400	2.489
H	0.034	4.359	0.586
H	-1.384	4.882	1.535
H	-0.953	-0.016	-0.530
H	1.193	0.038	-1.799
H	3.365	0.060	-0.574
H	3.376	0.025	1.920
H	1.223	-0.011	3.175
H	-1.443	-1.212	2.428
H	-5.091	1.531	4.300
H	-6.159	-0.897	6.604
H	-5.210	0.606	6.433
H	-6.544	0.270	5.310



4.19BC



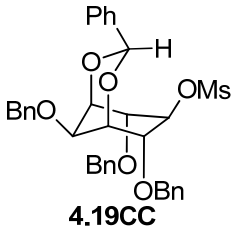
4.19BC

ΔE **0.0** kcal/mol

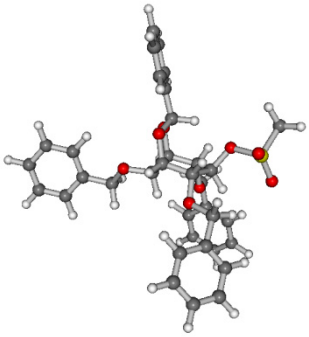
4.19BC

Final heat of formation = –2356.071

C	2.084	2.249	-3.584
C	2.427	1.819	-2.295
C	3.674	2.159	-1.760
C	4.576	2.925	-2.505
C	4.233	3.352	-3.791
C	2.986	3.012	-4.329
C	1.444	1.020	-1.477
O	0.900	-0.014	-2.299
C	-0.164	-0.741	-1.656
C	-1.287	0.217	-1.250
C	-0.630	1.230	-0.298
O	0.440	1.907	-0.987
C	0.340	-1.555	-0.425
C	-0.179	-1.011	0.911
C	-0.167	0.530	1.020
O	-1.847	0.775	-2.435
C	-3.206	1.220	-2.316
C	-3.396	2.587	-1.686
C	-4.422	2.802	-0.756
C	-4.641	4.073	-0.216
C	-3.827	5.143	-0.597
C	-2.793	4.935	-1.518
C	-2.582	3.667	-2.063
O	-1.060	0.956	2.055
C	-0.464	1.195	3.353
C	0.513	2.352	3.376
C	1.787	2.189	3.939
C	2.682	3.263	4.002
C	2.313	4.510	3.492



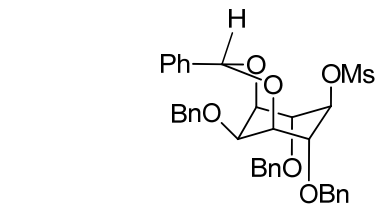
4.19CC



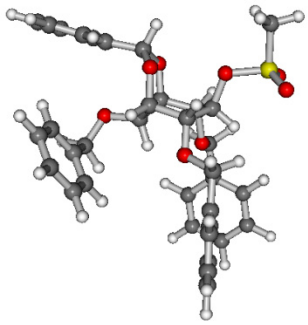
4.19CC

ΔE **3.1** kcal/mol

C	1.046	4.680	2.920
C	0.152	3.610	2.867
O	0.647	-1.548	1.989
S	-0.024	-2.657	3.082
C	0.655	-4.224	2.480
O	-0.072	-2.928	-0.491
C	0.695	-3.703	-1.426
C	0.207	-5.131	-1.429
C	1.117	-6.179	-1.627
C	0.677	-7.505	-1.683
C	-0.681	-7.798	-1.529
C	-1.593	-6.759	-1.321
C	-1.154	-5.433	-1.276
O	-1.499	-2.668	2.923
H	-1.213	-1.358	1.069
H	0.858	0.872	1.239
H	-1.327	2.024	-0.010
H	-2.068	-0.344	-0.702
H	-0.529	-1.437	-2.421
H	1.446	-1.511	-0.420
H	1.966	0.559	-0.612
H	3.940	1.827	-0.754
H	5.547	3.187	-2.082
H	4.936	3.947	-4.375
H	2.717	3.342	-5.334
H	1.112	1.973	-3.995
H	0.608	-3.270	-2.441
H	1.767	-3.666	-1.152
H	2.182	-5.957	-1.737
H	1.397	-8.310	-1.838
H	-1.026	-8.833	-1.565
H	-2.655	-6.981	-1.195
H	-1.866	-4.623	-1.107



4.19CB



4.19CB

ΔE **5.6** kcal/mol

H	-1.331	1.411	3.994
H	0.022	0.288	3.740
H	2.076	1.212	4.332
H	3.669	3.123	4.446
H	3.010	5.349	3.535
H	0.755	5.652	2.517
H	-0.834	3.742	2.418
H	-3.576	1.238	-3.353
H	-3.806	0.471	-1.763
H	-1.765	3.498	-2.767
H	-2.149	5.765	-1.814
H	-3.992	6.136	-0.174
H	-5.442	4.226	0.509
H	-5.053	1.965	-0.446
H	0.293	-4.997	3.168
H	0.282	-4.378	1.463
H	1.747	-4.146	2.513
O	0.615	-2.320	4.373

4.19CC

Final heat of formation = –2356.066

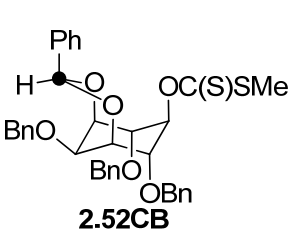
C	2.750	4.024	-1.545
C	2.710	3.290	-0.352
C	3.516	3.681	0.726
C	4.349	4.798	0.611
C	4.388	5.529	-0.579
C	3.585	5.140	-1.655
C	1.856	2.045	-0.245
O	0.742	2.165	-1.132
C	-0.192	1.077	-1.008
C	-0.713	0.972	0.431
C	0.520	0.802	1.311

O	1.456	1.875	1.111
C	0.382	-0.288	-1.466
C	1.212	-1.067	-0.407
C	1.116	-0.608	1.084
O	-0.693	-1.156	-1.859
C	-1.112	-0.975	-3.226
C	-2.159	-2.006	-3.557
C	-3.455	-1.619	-3.924
C	-4.422	-2.578	-4.242
C	-4.103	-3.936	-4.185
C	-2.812	-4.332	-3.813
C	-1.846	-3.373	-3.505
O	2.603	-1.024	-0.891
S	3.561	-2.378	-0.570
C	4.822	-2.015	-1.817
O	0.246	-1.484	1.810
C	0.865	-2.718	2.229
C	-0.082	-3.473	3.125
C	-0.354	-4.827	2.886
C	-1.198	-5.545	3.740
C	-1.788	-4.911	4.836
C	-1.529	-3.556	5.076
C	-0.678	-2.844	4.229
O	-1.438	2.118	0.865
C	-2.792	2.143	0.409
C	-3.451	3.434	0.830
C	-4.831	3.466	1.079
C	-5.466	4.666	1.412
C	-4.724	5.846	1.513
C	-3.346	5.818	1.277
C	-2.711	4.621	0.934
O	4.153	-2.258	0.783
H	-1.335	0.062	0.523
H	0.238	0.870	2.369
H	2.133	-0.629	1.516
H	0.864	-2.109	-0.465
H	1.050	-0.101	-2.327
H	-1.003	1.340	-1.701
H	2.456	1.166	-0.551
H	-2.829	2.057	-0.695
H	-3.350	1.278	0.819
H	-5.413	2.543	1.016
H	-6.541	4.675	1.605
H	-5.217	6.783	1.780
H	-2.758	6.734	1.362
H	-1.635	4.592	0.759
H	3.474	3.117	1.657
H	4.968	5.099	1.459
H	5.039	6.401	-0.667
H	3.604	5.710	-2.586
H	2.113	3.726	-2.377
H	-1.520	0.038	-3.387
H	-0.228	-1.088	-3.885
H	1.133	-3.343	1.358
H	1.805	-2.480	2.764
H	0.097	-5.322	2.024
H	-1.400	-6.600	3.543
H	-2.450	-5.468	5.501
H	-1.990	-3.055	5.929
H	-0.481	-1.786	4.413
H	-0.842	-3.684	-3.209
H	-2.559	-5.393	-3.766
H	-4.857	-4.687	-4.429
H	-5.427	-2.262	-4.528
H	-3.708	-0.557	-3.962
H	5.228	-1.020	-1.607
H	5.590	-2.788	-1.696
H	4.355	-2.068	-2.805
O	2.799	-3.598	-0.939

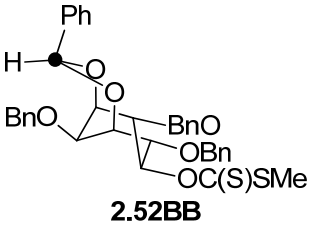
4.19CB

Final heat of formation = –2356.062

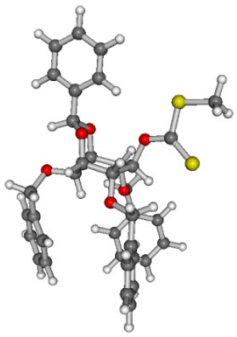
C	-1.501	-4.446	-1.926
C	-1.183	-4.120	-0.602
C	-0.438	-5.025	0.165
C	0.003	-6.228	-0.392
C	-0.300	-6.542	-1.721
C	-1.055	-5.647	-2.485
C	-1.766	-2.868	0.057
O	-0.953	-2.350	1.106
C	0.070	-1.387	0.765
C	0.166	-1.094	-0.734
C	-1.255	-0.838	-1.222
O	-2.192	-1.882	-0.881
C	-1.773	0.486	-0.611
C	-1.579	0.586	0.921
C	-0.299	-0.077	1.493
O	0.825	0.792	1.356
C	0.936	1.771	2.407
C	2.057	2.724	2.079
C	2.070	3.406	0.852
C	3.095	4.307	0.557
C	4.115	4.544	1.487
C	4.107	3.870	2.711
C	3.085	2.960	3.001
O	0.775	-2.120	-1.520
C	2.179	-1.930	-1.779
C	3.100	-2.263	-0.623
C	3.173	-3.579	-0.135
C	4.025	-3.896	0.923
C	4.824	-2.903	1.504
C	4.761	-1.593	1.023
C	3.902	-1.276	-0.034
O	-1.090	1.602	-1.204
C	-1.758	2.116	-2.380
C	-0.982	3.295	-2.902
C	-1.167	4.569	-2.343
C	-0.435	5.663	-2.810
C	0.490	5.496	-3.845
C	0.683	4.231	-4.409
C	-0.049	3.138	-3.938
O	-2.735	-0.006	1.602
S	-3.824	1.109	2.230
C	-4.960	-0.115	2.927
H	-0.491	-0.312	2.555
H	-2.857	0.554	-0.805
H	-1.255	-0.752	-2.320
H	-1.824	1.332	-3.156
H	-2.786	2.415	-2.105
H	-0.015	2.324	2.512
H	1.130	1.263	3.370
H	3.847	-0.248	-0.399
H	5.377	-0.812	1.474
H	5.493	-3.152	2.330
H	4.074	-4.922	1.294
H	2.544	-4.351	-0.583
H	3.086	2.427	3.955
H	4.901	4.046	3.439
H	4.914	5.251	1.256
H	3.097	4.829	-0.400
H	1.278	3.218	0.125
H	-1.892	4.700	-1.537
H	-0.592	6.650	-2.371
H	1.058	6.352	-4.215
H	1.402	4.096	-5.219
H	0.100	2.150	-4.379
H	1.030	-1.751	1.155
H	0.726	-0.149	-0.851
H	2.385	-2.598	-2.628
H	2.360	-0.890	-2.110
H	-2.091	-3.745	-2.518
H	-1.299	-5.885	-3.522
H	0.044	-7.482	-2.156
H	0.586	-6.925	0.214
H	-0.199	-4.775	1.200
H	-2.695	-3.165	0.573
H	-1.531	1.660	1.159
H	-5.764	0.458	3.399
H	-5.339	-0.730	2.106
H	-4.409	-0.709	3.663
O	-4.483	1.843	1.119
O	-3.164	1.876	3.317



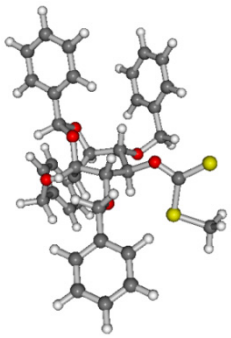
2.52CB



2.52BB



2.52CB
ΔE **0.0** kcal/mol



2.52BB
ΔE **6.3** kcal/mol

2.52CB

Final heat of formation
= -2641.971

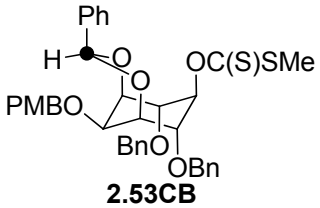
C	-4.514	-2.495	-0.107
C	-3.624	-2.138	-1.135
C	-2.773	-3.117	-1.665
C	-2.811	-4.431	-1.185
C	-3.703	-4.777	-0.167
C	-4.553	-3.804	0.374
C	-3.597	-0.716	-1.652
O	-3.146	0.243	-0.669
C	-1.728	0.217	-0.437
C	-0.923	1.036	-1.453
O	-1.078	2.460	-1.280
C	-1.967	2.826	-0.221
O	-1.578	2.226	1.013
C	-1.418	0.792	0.940
C	0.056	0.481	1.300
C	1.067	0.845	0.188
C	0.572	0.700	-1.278
C	-1.953	4.332	-0.070
C	-1.802	5.148	-1.199
C	-1.850	6.539	-1.074
C	-2.052	7.127	0.178
C	-2.205	6.314	1.306
C	-2.157	4.923	1.184
O	0.725	-0.648	-1.730
C	2.034	-0.938	-2.263
C	2.149	-2.417	-2.524
C	2.511	-2.892	-3.791
C	2.659	-4.264	-4.023
C	2.435	-5.175	-2.988
C	2.064	-4.708	-1.721
C	1.925	-3.338	-1.488
O	1.482	2.223	0.426
C	2.778	2.569	0.303
S	4.066	1.568	-0.020
O	0.252	-0.911	1.582
C	-0.166	-1.303	2.907
C	0.370	-2.680	3.200
C	1.728	-2.859	3.508
C	2.234	-4.133	3.773
C	1.385	-5.246	3.734
C	0.033	-5.078	3.425
C	-0.470	-3.801	3.157
S	2.846	4.326	0.573
C	4.636	4.650	0.430
H	-1.357	-0.822	-0.455
H	-2.086	0.337	1.689
H	0.315	1.088	2.187
H	1.948	0.200	0.320
H	1.158	1.393	-1.905
H	-1.208	0.776	-2.485
H	-4.611	-0.379	-1.910
H	-2.978	-0.658	-2.565
H	-2.070	-2.849	-2.457
H	-2.140	-5.181	-1.606
H	-3.737	-5.802	0.206
H	-5.255	-4.072	1.167
H	-5.177	-1.736	0.314
H	-2.267	4.286	2.062
H	-2.359	6.765	2.288
H	-2.090	8.213	0.276
H	-1.726	7.166	-1.959
H	-1.633	4.687	-2.173
H	2.186	-0.369	-3.200
H	2.809	-0.608	-1.546
H	0.227	-0.570	3.637
H	-1.268	-1.304	2.986
H	2.390	-1.991	3.538
H	3.291	-4.259	4.015
H	1.780	-6.241	3.945
H	-0.632	-5.943	3.391
H	-1.526	-3.671	2.908
H	1.631	-2.975	-0.502
H	1.889	-5.414	-0.907
H	2.548	-6.246	-3.166
H	2.943	-4.620	-5.015
H	2.679	-2.182	-4.605
H	4.745	5.732	0.582
H	5.190	4.102	1.200
H	5.000	4.367	-0.563
H	-2.981	2.472	-0.479

2.52BB

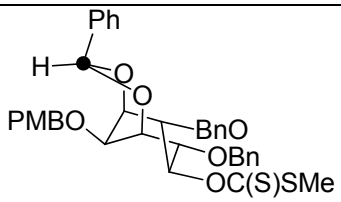
Final heat of formation
= -2641.961

C	0.000	0.000	0.000
C	0.000	0.000	1.403
C	1.227	0.000	2.082
C	2.432	-0.002	1.374
C	2.422	-0.002	-0.024
C	1.203	-0.001	-0.711
C	-1.298	-0.024	2.165
O	-1.737	-1.397	2.292
C	-2.953	-1.536	3.033
C	-2.688	-1.598	4.552
C	-2.391	-3.051	4.931
C	-3.771	-3.735	4.954
C	-4.499	-3.561	3.577
C	-3.629	-2.826	2.535

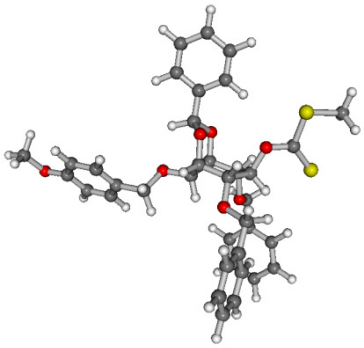
O	-3.904	-1.119	5.175	C	-2.912	-4.083	-1.961	H	-8.222	-3.372	1.956
C	-4.257	-1.839	6.354	C	-5.468	-1.209	6.999	H	-10.259	-3.070	3.357
O	-4.570	-3.211	6.030	C	-5.623	-1.303	8.388	H	-10.481	-4.300	5.514
O	-4.824	-4.871	3.092	C	-6.748	-0.758	9.014	H	-8.662	-5.834	6.258
C	-6.095	-5.006	2.415	C	-7.722	-0.105	8.252	H	-6.637	-6.142	4.847
C	-7.302	-4.788	3.302	C	-7.567	-0.003	6.865	H	-2.077	0.552	1.635
C	-7.437	-5.476	4.518	C	-6.447	-0.555	6.239	H	-1.159	0.427	3.165
C	-8.572	-5.299	5.311	S	-5.481	-2.582	-0.989	H	1.236	0.003	3.174
C	-9.594	-4.438	4.893	H	-2.852	-3.521	2.185	H	3.381	0.002	1.914
C	-9.469	-3.748	3.685	H	-3.629	-0.684	2.842	H	3.362	0.001	-0.578
C	-8.325	-3.919	2.897	H	-1.845	-0.944	4.828	H	1.190	0.004	-1.802
O	-1.681	-3.108	6.172	H	-1.761	-3.494	4.137	H	-0.952	-0.002	-0.536
C	-0.745	-4.195	6.288	H	-3.683	-4.813	5.136	H	-0.089	-4.218	5.397
C	-1.360	-5.563	6.501	H	-5.415	-2.980	3.764	H	-0.123	-3.919	7.153
C	-1.020	-6.635	5.665	H	-3.400	-1.837	7.051	H	-2.522	-4.957	8.219
C	-1.553	-7.910	5.884	H	-6.322	-0.473	5.160	H	-3.475	-7.219	8.615
C	-2.436	-8.123	6.946	H	-8.324	0.509	6.268	H	-2.858	-9.115	7.117
C	-2.783	-7.057	7.786	H	-8.598	0.327	8.738	H	-1.283	-8.734	5.222
C	-2.242	-5.789	7.571	H	-6.860	-0.837	10.096	H	-0.333	-6.470	4.831
O	-4.503	-2.476	1.408	H	-4.856	-1.807	8.981	H	-3.758	-4.770	-2.066
C	-4.287	-2.851	0.130	H	-6.153	-4.337	1.542	H	-3.072	-3.198	-2.585
S	-2.698	-3.598	-0.213	H	-6.075	-6.042	2.044	H	-1.972	-4.582	-2.232



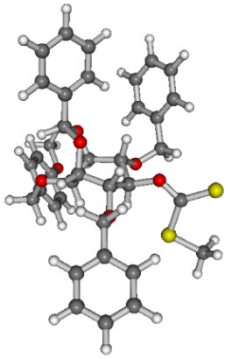
2.53CB



2.53BB



2.53CB
ΔE **0.00** kcal/mol



2.53BB
ΔE **6.27** kcal/mol

2.53CB
Final heat of formation =
–2756.545

C	0.000	0.000	0.000	C	-1.302	0.016	2.160	C	-4.902	2.7601	5.400
C	0.000	0.000	1.404	O	-1.856	1.349	2.100	O	-5.023	3.819	4.439
C	1.226	0.000	2.083	C	-3.160	1.447	2.689	C	-6.278	2.415	5.908
C	2.433	-0.003	1.376	C	-3.042	1.848	4.175	C	-6.587	2.610	7.259
C	2.422	-0.003	-0.022	C	-2.599	3.306	4.259	C	-7.861	2.301	7.745
C	1.203	-0.000	-0.709	C	-3.784	4.156	3.782	C	-8.833	1.791	6.878
				C	-3.956	3.938	2.263	C	-8.525	1.592	5.527
				C	-3.972	2.450	1.827	C	-7.254	1.903	5.042
				O	-4.327	1.602	4.793	O	-2.140	3.598	5.586

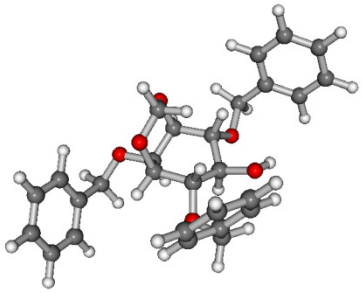
C	-1.303	4.777	5.651
C	-0.774	4.922	7.050
C	0.365	4.209	7.466
C	0.845	4.315	8.766
C	0.189	5.145	9.692
C	-0.948	5.865	9.296
C	-1.415	5.743	7.982
O	-5.379	2.048	1.763
C	-5.766	1.151	0.836
S	-4.804	0.358	-0.261
O	-2.859	4.630	1.653
C	-3.092	5.014	0.283
C	-1.879	5.749	-0.222
C	-1.892	7.144	-0.358
C	-0.759	7.826	-0.812
C	0.402	7.116	-1.130
C	0.426	5.724	-0.992
C	-0.709	5.044	-0.543
O	0.740	5.186	10.947
C	0.107	6.017	11.923
S	-7.533	0.993	1.004
C	-7.912	-0.279	-0.250
H	-4.919	4.388	1.959
H	-3.676	0.474	2.638
H	-2.293	1.206	4.666
H	-1.136	-0.286	3.210
H	-2.024	-0.688	1.706
H	-3.282	4.118	-0.337
H	-3.988	5.660	0.230
H	-2.302	6.306	7.682
H	-1.472	6.517	9.994
H	1.731	3.768	9.090
H	0.881	3.561	6.755
H	-2.799	7.700	-0.105
H	-0.784	8.912	-0.918
H	1.288	7.646	-1.484
H	1.331	5.165	-1.238
H	-0.687	3.959	-0.429
H	-0.953	0.001	-0.534
H	1.191	-0.004	-1.801
H	3.363	-0.007	-0.576
H	3.381	-0.006	1.916
H	1.234	0.001	3.175
H	-3.592	5.230	3.936
H	-1.770	3.445	3.541
H	-7.006	1.751	3.992
H	-9.281	1.193	4.848
H	-9.828	1.549	7.255
H	-8.095	2.456	8.800
H	-5.824	3.005	7.934
H	-4.253	3.096	6.225
H	-3.563	2.366	0.810
H	-8.997	-0.429	-0.189
H	-7.631	0.073	-1.248
H	-7.386	-1.212	-0.020
H	0.697	5.900	12.838
H	0.114	7.076	11.617
H	-0.931	5.697	12.114
H	-0.475	4.667	4.926
H	-1.882	5.674	5.368

2.53BB

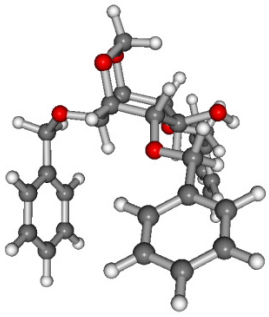
Final heat of formation = –2756.534

C	0.000	0.000	0.000
C	0.000	0.000	1.400
C	1.219	0.000	2.091
C	2.429	-0.009	1.392
C	2.425	-0.013	-0.007
C	1.210	-0.006	-0.699
C	-1.285	-0.048	2.190
O	-1.654	-1.424	2.374
C	-2.808	-1.594	3.236
C	-3.678	-0.335	3.265
C	-3.641	0.189	1.816
O	-2.318	0.655	1.490
C	-4.103	-0.923	0.812
C	-4.591	-2.196	1.535
C	-3.623	-2.740	2.598
O	-4.418	-3.436	3.562
C	-3.693	-4.475	4.258
C	-4.625	-5.153	5.225
C	-5.551	-6.103	4.767
C	-6.430	-6.724	5.657
C	-6.392	-6.403	7.018
C	-5.472	-5.459	7.485
C	-4.595	-4.838	6.590
O	-3.187	0.582	4.246
C	-4.188	1.428	4.850
C	-4.710	2.546	3.977
C	-6.080	2.662	3.691
C	-6.570	3.702	2.907
C	-5.686	4.658	2.381
C	-4.312	4.556	2.652
C	-3.841	3.509	3.447
O	-5.164	-0.379	0.017
C	-5.164	-0.754	-1.379
C	-4.006	-0.189	-2.174
C	-3.711	1.184	-2.141
C	-2.669	1.704	-2.910
C	-1.910	0.860	-3.730
C	-2.191	-0.507	-3.766
C	-3.232	-1.028	-2.988
O	-4.779	-3.235	0.515
C	-5.942	-3.880	0.290
S	-6.065	-4.854	-1.047
O	-6.258	5.644	1.620
C	-5.396	6.638	1.060
S	-7.237	-3.612	1.495
C	-8.625	-4.515	0.727
H	-5.560	-1.979	2.008
H	-2.909	-3.427	2.109
H	-2.482	-1.865	4.254
H	-4.710	-0.628	3.535
H	-4.307	1.048	1.677
H	-3.238	-1.177	0.182
H	-1.149	0.414	3.183
H	-0.949	0.023	-0.536
H	1.202	-0.004	-1.790
H	3.369	-0.016	-0.556
H	3.374	-0.007	1.938
H	1.219	0.006	3.183
H	-5.197	-1.848	-1.497
H	-6.115	-0.346	-1.753
H	-3.449	-2.099	-3.011
H	-1.599	-1.173	-4.397
H	-1.098	1.270	-4.334
H	-2.449	2.773	-2.875
H	-4.300	1.841	-1.498
H	-3.304	-5.196	3.516
H	-2.831	-4.046	4.800
H	-3.876	-4.101	6.955
H	-5.437	-5.207	8.546
H	-7.076	-6.890	7.715
H	-7.144	-7.463	5.290
H	-5.582	-6.352	3.704
H	-5.033	0.805	5.201
H	-3.680	1.835	5.737
H	-2.769	3.432	3.644
H	-3.606	5.283	2.252
H	-7.634	3.792	2.684
H	-6.778	1.922	4.092
H	-8.861	-4.089	-0.255
H	-8.375	-5.575	0.620
H	-9.468	-4.381	1.418
H	-6.050	7.313	0.498
H	-4.872	7.207	1.846
H	-4.656	6.193	0.375

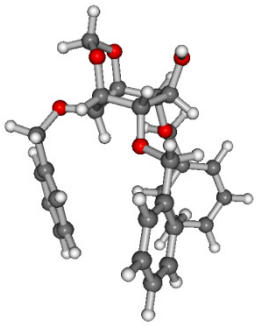
2). C1,C3-*O*-Methylidene *myo*-inositol derivatives



1.47BC
ΔE **0.0** kcal/mol



1.47CC
ΔE **3.8** kcal/mol



1.47CB
ΔE **4.4** kcal/mol

1.47BC
Final heat of formation
= –1536.904

C	4.165	2.195	-1.091
C	3.914	2.379	0.276
C	4.830	1.876	1.210
C	5.985	1.207	0.789
C	6.228	1.028	-0.575
C	5.313	1.520	-1.513
C	2.701	3.166	0.740
O	1.508	2.964	-0.025
C	0.701	1.864	0.391
C	1.174	0.478	-0.084
O	1.169	0.441	-1.527
C	-0.108	0.721	-2.065
O	-0.651	1.960	-1.633
C	-0.702	2.049	-0.192
C	-1.676	1.006	0.418
C	-0.988	-0.126	1.198
C	0.310	-0.650	0.554
O	-2.580	1.605	1.370
C	-3.685	2.322	0.772
C	-4.720	1.409	0.154
C	-4.890	1.344	-1.235
C	-5.836	0.480	-1.798
C	-6.623	-0.327	-0.973
C	-6.462	-0.269	0.415
C	-5.519	0.594	0.974
O	-1.897	-1.228	1.365
O	1.154	-1.277	1.534
C	0.803	-2.636	1.888
C	0.986	-3.620	0.751
C	-0.101	-4.355	0.257
C	0.072	-5.276	-0.781
C	1.337	-5.466	-1.342
C	2.428	-4.730	-0.862
C	2.253	-3.817	0.177
H	-0.718	0.278	2.192
H	0.052	-1.375	-0.237
H	2.215	0.287	0.200
H	0.636	1.860	1.497
H	-1.063	3.064	0.016
H	-2.259	0.554	-0.403
H	-2.710	-0.849	1.750
H	0.015	0.796	-3.151
H	-0.809	-0.105	-1.824
H	-4.117	2.894	1.605
H	-3.316	3.041	0.020
H	1.493	-2.872	2.711
H	-0.227	-2.683	2.268
H	2.911	4.244	0.645
H	2.511	2.961	1.811
H	-4.274	1.975	-1.881
H	-5.958	0.439	-2.882
H	-7.362	-1.000	-1.410
H	-7.082	-0.892	1.063
H	-5.401	0.646	2.059
H	-1.092	-4.193	0.688
H	-0.783	-5.841	-1.155
H	1.476	-6.182	-2.154
H	3.418	-4.876	-1.298
H	3.103	-3.239	0.548
H	4.637	2.004	2.278
H	6.687	0.818	1.527
H	7.125	0.501	-0.907
H	5.494	1.376	-2.580
H	3.440	2.561	-1.818

1.47CC
Final heat of formation
= –1536.898

C	3.276	-1.448	1.544
C	3.644	-0.438	0.645
C	4.178	-0.804	-0.601
C	4.339	-2.149	-0.938
C	3.973	-3.150	-0.030
C	3.441	-2.797	1.212
C	3.490	1.025	1.008
O	2.710	1.777	0.064
C	1.323	1.451	0.054
C	0.692	2.046	-1.204
C	-0.753	1.524	-1.400
C	-1.418	0.941	-0.125
C	-0.913	1.491	1.240
C	0.538	2.038	1.239
O	0.586	3.476	1.210
C	0.091	4.001	-0.011
O	0.746	3.487	-1.154
O	-0.677	0.539	-2.439
C	-1.915	0.269	-3.102
C	-1.686	-0.627	-4.297
C	-2.795	-1.044	-5.051
C	-2.630	-1.866	-6.167
C	-1.350	-2.289	-6.544
C	-0.243	-1.881	-5.795
C	-0.408	-1.053	-4.678
O	-0.918	0.469	2.256
C	-2.219	0.012	2.657
C	-2.088	-0.788	3.927
C	-1.854	-0.139	5.149
C	-1.716	-0.875	6.327
C	-1.811	-2.271	6.297
C	-2.043	-2.926	5.085
C	-2.178	-2.186	3.906
O	-2.837	1.167	-0.291
H	-1.200	-0.142	-0.132
H	-1.375	2.372	-1.744
H	1.272	1.769	-2.092
H	0.981	1.758	2.202
H	-1.589	2.313	1.545
H	0.286	5.079	0.008
H	-1.004	3.819	-0.082
H	-3.310	0.652	0.385
H	-2.637	-0.201	-2.412
H	-2.371	1.225	-3.430
H	-2.879	0.888	2.815
H	-2.671	-0.629	1.873
H	1.186	0.352	0.038
H	4.468	1.526	1.005

H	3.076	1.113	2.029
H	-3.799	-0.720	-4.763
H	-3.502	-2.179	-6.745
H	-1.218	-2.933	-7.415
H	0.758	-2.207	-6.080
H	0.452	-0.733	-4.094
H	-1.778	0.949	5.173
H	-1.537	-0.360	7.273
H	-1.706	-2.847	7.218
H	-2.117	-4.014	5.055
H	-2.355	-2.699	2.957
H	4.458	-0.022	-1.311
H	4.756	-2.420	-1.910
H	4.101	-4.201	-0.293
H	3.148	-3.572	1.923
H	2.851	-1.175	2.514

1.47CB

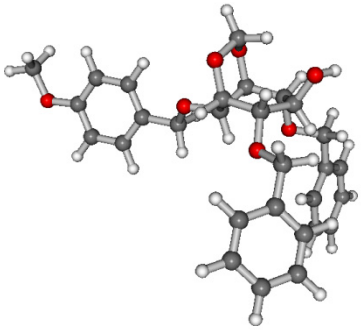
Final heat of formation =

–1536.897

C	-2.242	-1.338	-2.498
C	-3.020	-1.557	-1.350
C	-4.387	-1.239	-1.385
C	-4.968	-0.712	-2.543
C	-4.183	-0.497	-3.681
C	-2.820	-0.812	-3.657
C	-2.395	-2.107	-0.099
O	-1.689	-1.054	0.586
C	-1.186	-1.434	1.869
C	-1.075	-0.125	2.678
C	0.098	0.688	2.112
C	1.375	-0.068	2.466
C	1.428	-1.392	1.665
C	0.141	-2.243	1.785
O	1.453	-0.425	3.862
C	0.333	-0.029	4.626
O	-0.904	-0.463	4.067
O	0.190	2.027	2.620
C	-0.729	2.965	2.024
C	-0.394	3.304	0.586
C	-1.241	2.927	-0.465
C	-0.917	3.240	-1.791
C	0.262	3.934	-2.076
C	1.118	4.313	-1.033
C	0.790	4.000	0.287
O	1.659	-1.171	0.271
C	3.033	-0.906	-0.072
C	3.170	-0.902	-1.571
C	2.562	0.106	-2.337
C	2.678	0.104	-3.730
C	3.410	-0.901	-4.374
C	4.019	-1.909	-3.619
C	3.895	-1.909	-2.225
O	0.323	-3.118	2.904
H	0.097	-2.831	0.847
H	-1.939	-2.071	2.384
H	-2.028	0.418	2.569
H	2.252	0.556	2.220
H	2.246	-2.001	2.096
H	0.422	-0.533	5.596
H	0.321	1.068	4.740
H	-0.556	-3.394	3.217
H	-1.696	-2.927	-0.349
H	-3.177	-2.515	0.571
H	3.364	0.064	0.345
H	3.670	-1.696	0.368
H	0.006	0.701	1.012
H	-1.769	2.594	2.091
H	-0.650	3.858	2.661
H	-5.001	-1.412	-0.496
H	-6.035	-0.479	-2.561
H	-4.637	-0.092	-4.589
H	-2.203	-0.648	-4.543
H	-1.176	-1.575	-2.476
H	1.993	0.892	-1.836
H	2.205	0.896	-4.315
H	3.504	-0.899	-5.462
H	4.591	-2.696	-4.115
H	4.368	-2.699	-1.636
H	1.457	4.295	1.101
H	2.038	4.859	-1.252
H	0.515	4.182	-3.110
H	-1.584	2.934	-2.599
H	-2.161	2.379	-0.247

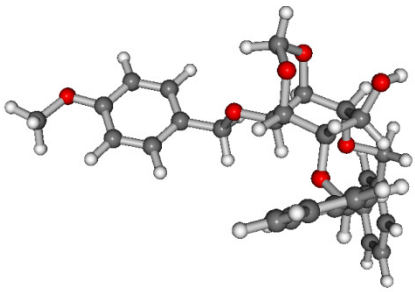
1.55BC

ΔE **0.0** kcal/mol



1.55CB

ΔE **1.2** kcal/mol



1.55CC

ΔE **5.0** kcal/mol

1.55BC

Final heat of formation =

–1651.476

C	1.790	4.436	0.504
C	2.424	3.183	0.539
C	3.730	3.071	0.043
C	4.393	4.188	-0.477
C	3.753	5.429	-0.510
C	2.448	5.552	-0.017
C	1.694	1.978	1.091
O	0.573	1.565	0.277
C	0.942	0.961	-0.980
C	1.417	-0.506	-0.799
C	0.344	-1.482	-1.293
C	0.223	-1.234	-2.808
C	-0.362	0.187	-3.077
C	-0.303	1.129	-1.867
O	2.663	-0.758	-1.490
C	2.517	-0.627	-2.895
O	1.502	-1.451	-3.442
O	-1.749	0.100	-3.432
C	-1.968	-0.222	-4.815
C	-3.442	-0.126	-5.114
C	-4.135	1.069	-4.868
C	-5.495	1.171	-5.164
C	-6.180	0.082	-5.715
C	-5.498	-1.111	-5.962
C	-4.136	-1.215	-5.658
O	0.730	-2.801	-0.919
C	-0.339	-3.758	-0.863
C	-0.746	-4.353	-2.196
C	-2.099	-4.449	-2.562
C	-2.481	-5.027	-3.770
C	-1.504	-5.520	-4.650
C	-0.147	-5.428	-4.303
C	0.216	-4.853	-3.082
O	-0.398	2.472	-2.357
O	-1.974	-6.063	-5.821
C	-1.015	-6.581	-6.745

H	-1.183	0.897	-1.238
H	0.206	0.644	-3.909
H	-0.443	-1.971	-3.269
H	1.637	-0.700	0.258
H	1.768	1.538	-1.432
H	3.464	-0.954	-3.340
H	2.325	0.434	-3.161
H	-1.399	0.492	-5.442
H	-1.601	-1.238	-5.051
H	1.245	2.208	2.067
H	2.401	1.141	1.230
H	-0.622	-1.231	-0.812
H	-1.224	-3.311	-0.371
H	0.044	-4.549	-0.200
H	4.231	2.100	0.065
H	5.411	4.086	-0.860
H	4.268	6.300	-0.916
H	1.947	6.521	-0.035
H	0.775	4.535	0.896
H	-3.607	-2.153	-5.840
H	-6.027	-1.967	-6.386
H	-7.243	0.164	-5.949
H	-6.025	2.106	-4.967
H	-3.600	1.914	-4.431
H	1.273	-4.765	-2.824
H	0.629	-5.797	-4.971
H	-3.531	-5.100	-4.056
H	-2.869	-4.057	-1.893
H	-1.597	-6.963	-7.591
H	-0.328	-5.795	-7.099
H	-0.431	-7.405	-6.302
H	-0.410	3.048	-1.571

1.55CB

Final heat of formation = –1651.474

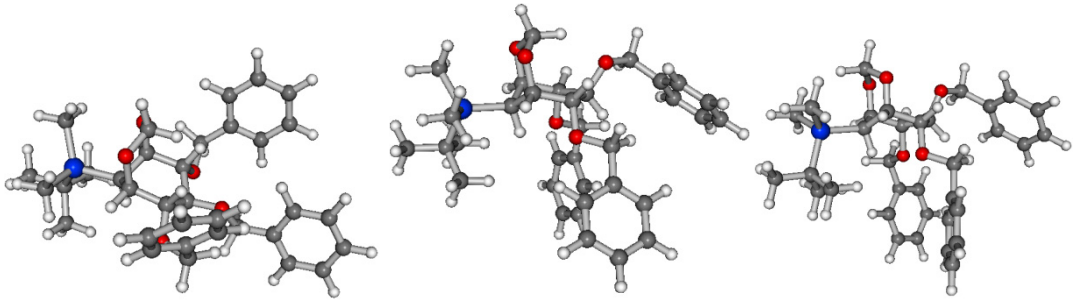
C	-3.414	1.282	-4.235
C	-2.631	1.762	-3.180
C	-3.266	2.500	-2.166
C	-4.630	2.766	-2.214
C	-5.402	2.278	-3.282
C	-4.789	1.531	-4.299
C	-1.159	1.470	-3.114
O	-0.954	0.221	-2.414
C	0.430	-0.136	-2.303
C	1.159	0.530	-1.126
C	2.671	0.300	-1.286
C	3.044	-1.200	-1.432
C	2.056	-2.031	-2.301
C	0.571	-1.645	-2.117
O	0.144	-2.092	-0.810
C	-0.219	-1.039	0.060
O	0.796	-0.037	0.158
O	2.350	-1.878	-3.701
C	3.291	-2.841	-4.207
C	2.713	-4.235	-4.344
C	3.286	-5.324	-3.675
C	2.756	-6.612	-3.821
C	1.645	-6.820	-4.642
C	1.054	-5.735	-5.301
C	1.584	-4.452	-5.152
O	3.177	-1.851	-0.160
O	3.088	1.090	-2.405
C	4.468	1.498	-2.341
C	4.769	2.394	-3.514
C	5.216	1.855	-4.729
C	5.496	2.686	-5.816
C	5.321	4.069	-5.703
C	4.851	4.615	-4.504
C	4.590	3.781	-3.413
O	-6.737	2.589	-3.241
C	-7.565	2.109	-4.302
H	4.025	-1.240	-1.940
H	2.160	-3.084	-1.990
H	-0.023	-2.178	-2.873
H	0.963	1.614	-1.101
H	3.167	0.678	-0.367
H	-0.312	-1.479	1.060
H	-1.165	-0.575	-0.265
H	3.584	-2.447	-5.191
H	4.198	-2.874	-3.575
H	4.644	2.036	-1.389
H	5.130	0.613	-2.358
H	0.965	0.138	-3.229
H	-0.631	2.289	-2.593
H	-0.730	1.385	-4.130
H	4.252	4.211	-2.467
H	4.678	5.689	-4.422
H	5.563	4.722	-6.543
H	5.853	2.255	-6.753
H	5.344	0.774	-4.820
H	1.108	-3.601	-5.643
H	0.180	-5.892	-5.935
H	1.241	-7.825	-4.773
H	3.201	-7.448	-3.279
H	4.140	-5.159	-3.013
H	-2.944	0.693	-5.027
H	-5.367	1.138	-5.134
H	-5.122	3.353	-1.437
H	-2.679	2.867	-1.320
H	-7.563	1.007	-4.349
H	-8.576	2.461	-4.071
H	-7.250	2.517	-5.278
H	2.863	-1.237	0.527

1.55CC

Final heat of formation = –1651.468

C	2.578	-4.311	-0.757
C	3.363	-3.229	-0.331
C	4.505	-2.887	-1.066
C	4.867	-3.618	-2.202
C	4.080	-4.694	-2.618
C	2.932	-5.037	-1.895
C	2.991	-2.461	0.910
O	1.652	-1.961	0.780
C	1.164	-1.312	1.965
C	0.060	-0.349	1.461
C	-1.229	-1.147	1.208
C	-1.747	-1.557	2.585
C	-0.803	-2.610	3.215
C	0.728	-2.368	3.037
O	-0.181	0.758	2.339
C	-0.770	0.371	3.578
O	-1.946	-0.405	3.423
O	-1.184	-3.865	2.628
C	-0.884	-4.996	3.464
C	-1.375	-6.253	2.793
C	-2.736	-6.405	2.485
C	-3.199	-7.571	1.873
C	-2.307	-8.606	1.566
C	-0.950	-8.464	1.869
C	-0.489	-7.290	2.475
O	-2.247	-0.414	0.536
C	-2.030	-0.305	-0.878
C	-3.124	0.530	-1.488
C	-3.760	0.130	-2.674
C	-4.741	0.919	-3.269
C	-5.119	2.133	-2.674
C	-4.503	2.542	-1.482
C	-3.511	1.742	-0.905
O	1.245	-2.062	4.349
O	-6.099	2.838	-3.328
C	-6.522	4.075	-2.751
H	1.145	-3.332	2.693
H	-0.998	-2.626	4.303
H	-2.738	-2.018	2.492
H	0.439	0.100	0.535
H	1.965	-0.684	2.408
H	-1.077	1.300	4.072
H	-0.030	-0.169	4.197
H	0.202	-5.071	3.654
H	-1.380	-4.856	4.445
H	3.692	-1.620	1.068
H	3.064	-3.127	1.795
H	-0.974	-2.063	0.641
H	-1.044	0.157	-1.077
H	-2.017	-1.312	-1.340
H	-3.485	-0.818	-3.140
H	-5.237	0.608	-4.189
H	-4.785	3.475	-0.996
H	-3.041	2.058	0.027
H	-7.296	4.466	-3.421
H	-6.951	3.928	-1.746
H	-5.692	4.799	-2.690
H	5.116	-2.037	-0.749
H	5.759	-3.341	-2.766
H	4.357	-5.264	-3.507
H	2.311	-5.874	-2.219
H	1.676	-4.573	-0.199

H	0.573	-7.179	2.705
H	-0.248	-9.265	1.630
H	-2.670	-9.519	1.091
H	-4.259	-7.677	1.637
H	-3.432	-5.597	2.721
H	2.202	-1.901	4.266



1.107BC
ΔE **0.0** kcal/mol

1.107CC
ΔE **2.5** kcal/mol

1.107CB
ΔE **4.4** kcal/mol

1.107BC
Final heat of formation = –1988.361

C	0.289	-0.457	0.037
C	0.278	-0.276	1.428
C	1.497	-0.075	2.095
C	2.704	-0.066	1.391
C	2.707	-0.247	0.004
C	1.496	-0.438	-0.668
C	-1.006	-0.339	2.217
O	-2.092	0.156	1.419
C	-3.368	0.158	2.081
C	-4.095	1.452	1.669
C	-5.616	1.436	2.000
C	-6.006	0.267	2.918
C	-5.692	-0.993	2.092
C	-4.166	-1.123	1.782
O	-6.483	-0.991	0.877
C	-6.244	0.169	0.094
O	-6.437	1.379	0.802
O	-3.523	2.571	2.374
C	-2.483	3.282	1.669
C	-2.984	4.065	0.472
C	-4.025	4.997	0.612
C	-4.474	5.731	-0.486
C	-3.885	5.548	-1.743
C	-2.850	4.622	-1.894
C	-2.405	3.883	-0.791
O	-3.569	-2.162	2.586
C	-3.882	-3.507	2.157
C	-3.274	-3.890	0.825
C	-4.081	-4.044	-0.312
C	-3.518	-4.398	-1.543
C	-2.140	-4.600	-1.649
C	-1.325	-4.448	-0.520
C	-1.890	-4.097	0.707
H	-3.210	0.209	3.174
H	-3.975	1.603	0.582
H	-5.846	2.411	2.446
H	-5.328	0.278	3.790
H	-6.006	-1.904	2.619
H	-4.041	-1.372	0.713
H	-6.978	0.156	-0.720
H	-5.218	0.135	-0.327
H	-3.483	-4.141	2.961
H	-4.975	-3.658	2.120
H	-2.073	3.966	2.427
H	-1.685	2.589	1.359
H	-5.158	-3.882	-0.231
H	-4.158	-4.515	-2.420
H	-1.698	-4.878	-2.608
H	-0.249	-4.608	-0.597
H	-1.253	-3.982	1.586
H	-1.598	3.156	-0.910
H	-2.389	4.470	-2.872
H	-4.236	6.123	-2.601
H	-5.284	6.453	-0.363
H	-4.487	5.137	1.591
H	-0.910	0.266	3.138
H	-1.218	-1.378	2.526
H	1.500	0.080	3.177
H	3.642	0.092	1.925
H	3.647	-0.231	-0.549
H	1.490	-0.575	-1.751
H	-0.655	-0.604	-0.484
Si	-7.797	0.388	3.666
C	-8.316	2.219	3.705
C	-7.721	-0.309	5.482
C	-9.086	-0.579	2.659
H	-9.300	2.333	4.183
H	-7.602	2.849	4.255
H	-8.395	2.611	2.680
H	-10.081	-0.485	3.118
H	-9.141	-0.180	1.637
H	-8.844	-1.648	2.581
C	-9.141	-0.332	6.086
C	-7.157	-1.744	5.482
C	-6.824	0.583	6.363
H	-6.775	0.178	7.390
H	-5.791	0.639	5.989
H	-7.211	1.610	6.436
H	-9.106	-0.701	7.126
H	-9.598	0.669	6.111
H	-9.816	-0.996	5.526
H	-7.148	-2.152	6.509
H	-7.765	-2.427	4.868
H	-6.121	-1.782	5.112

1.107CC
Final heat of formation = –1988.357

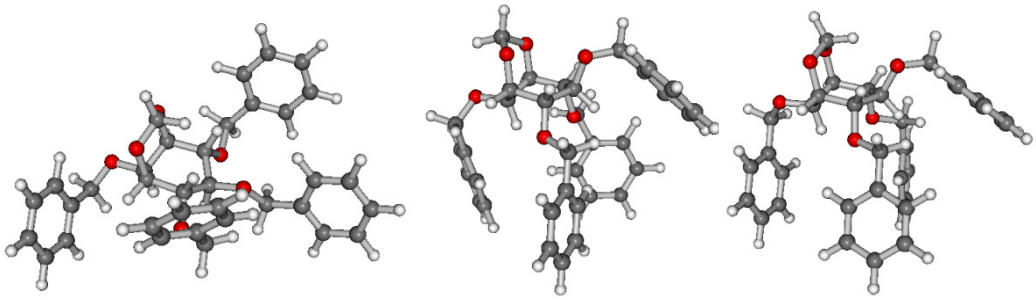
C	-2.522	2.089	-4.662
C	-1.529	1.424	-3.927
C	-0.263	1.247	-4.502
C	0.004	1.712	-5.793
C	-0.989	2.373	-6.520
C	-2.252	2.563	-5.948
C	-1.818	0.859	-2.557
O	-2.742	1.702	-1.863
C	-3.152	1.181	-0.587
C	-2.067	1.470	0.494
C	-2.349	2.691	1.427
C	-3.829	3.137	1.539
C	-4.471	3.239	0.146
C	-4.558	1.791	-0.352
O	-5.373	1.008	0.549
C	-4.860	0.992	1.875
O	-4.612	2.290	2.406
O	-1.888	0.248	1.249
C	-0.611	0.109	1.886
C	0.517	-0.254	0.937
C	0.337	-1.257	-0.029
C	1.390	-1.628	-0.869
C	2.639	-1.008	-0.749
C	2.829	-0.013	0.212
C	1.771	0.361	1.047
O	-1.667	3.866	0.949
C	-0.283	3.935	1.328
C	0.310	5.209	0.785
C	0.689	5.298	-0.562
C	1.219	6.485	-1.073

C	1.379	7.598	-0.239
C	1.004	7.519	1.104
C	0.471	6.330	1.612
Si	-6.134	4.236	0.048
C	-7.123	4.168	1.670
C	-5.699	6.083	-0.385
C	-7.209	3.491	-1.337
H	-1.133	1.691	-0.050
H	-3.260	0.082	-0.646
H	-5.075	1.721	-1.317
H	-3.810	4.106	2.052
H	-1.997	2.438	2.446
H	-5.645	0.553	2.503
H	-3.942	0.381	1.921
H	-0.873	0.749	-1.994
H	-2.258	-0.155	-2.650
H	-0.201	3.914	2.432
H	0.267	3.061	0.929
H	-3.759	3.773	-0.506
H	0.521	0.744	-3.932
H	0.995	1.567	-6.227
H	-0.780	2.742	-7.525
H	-3.031	3.084	-6.507
H	-3.503	2.243	-4.211
H	0.173	6.271	2.661
H	1.126	8.384	1.758
H	1.796	8.524	-0.638
H	1.510	6.543	-2.123
H	0.560	4.433	-1.215
H	-0.757	-0.695	2.622
H	-0.342	1.020	2.451
H	1.924	1.141	1.798
H	3.799	0.477	0.310
H	3.462	-1.302	-1.403
H	1.238	-2.410	-1.615
H	-0.637	-1.739	-0.120
H	-8.126	4.083	-1.478
H	-6.685	3.455	-2.304
H	-7.511	2.467	-1.075
H	-8.054	4.746	1.580
H	-7.386	3.128	1.906
H	-6.555	4.563	2.524
C	-6.984	6.937	-0.351
C	-4.694	6.653	0.635
C	-5.083	6.169	-1.796
H	-6.751	7.982	-0.628
H	-7.744	6.574	-1.060
H	-7.438	6.959	0.650
H	-4.823	7.216	-2.034
H	-4.158	5.579	-1.885
H	-5.782	5.822	-2.572
H	-4.481	7.713	0.408
H	-5.086	6.616	1.664
H	-3.733	6.118	0.615

1.107CB

Final heat of formation = –1988.353

C	-0.775	-1.229	0.302
C	0.044	-0.746	1.336
C	1.428	-0.954	1.252
C	1.986	-1.632	0.162
C	1.161	-2.108	-0.858
C	-0.222	-1.903	-0.787
C	-0.570	-0.010	2.510
O	-1.251	1.197	2.134
C	-0.371	2.266	1.742
C	0.188	3.015	2.982
C	-0.646	4.242	3.428
C	-0.996	5.145	2.234
C	-1.920	4.308	1.334
C	-1.131	3.140	0.713
O	-3.034	3.733	2.063
C	-3.038	4.035	3.442
O	-1.824	3.724	4.101
O	1.546	3.377	2.673
C	2.363	3.632	3.832
C	3.816	3.590	3.430
C	4.608	2.473	3.730
C	5.953	2.427	3.350
C	6.519	3.500	2.655
C	5.736	4.619	2.347
C	4.395	4.664	2.737
O	-0.227	3.749	-0.222
C	0.142	2.885	-1.312
C	1.124	3.609	-2.195
C	2.458	3.770	-1.789
C	3.368	4.452	-2.599
C	2.957	4.982	-3.827
C	1.630	4.829	-4.240
C	0.720	4.148	-3.425
H	0.508	1.850	1.221
H	-1.843	2.478	0.190
H	-2.332	4.902	0.503
H	-0.066	4.791	4.188
H	0.184	2.304	3.831
H	-3.810	3.402	3.898
H	-3.293	5.102	3.602
H	0.594	1.954	-0.923
H	-0.761	2.607	-1.886
H	2.120	4.618	4.268
H	2.160	2.864	4.602
H	-0.057	5.257	1.663
H	-0.317	4.031	-3.746
H	1.303	5.241	-5.196
H	3.670	5.512	-4.461
H	4.404	4.568	-2.273
H	2.778	3.361	-0.828
H	3.788	5.539	2.499
H	6.174	5.461	1.809
H	7.568	3.468	2.358
H	6.559	1.554	3.596
H	4.168	1.633	4.274
H	0.205	0.189	3.272
H	-1.348	-0.625	2.985
H	2.075	-0.578	2.048
H	3.066	-1.782	0.110
H	1.593	-2.637	-1.710
H	-0.870	-2.277	-1.582
H	-1.853	-1.063	0.355
Si	-1.523	6.983	2.604
C	-3.229	7.369	1.847
C	-1.581	7.301	4.483
C	-0.197	8.152	1.795
H	-3.526	8.400	2.089
H	-3.221	7.273	0.752
H	-4.012	6.699	2.229
H	-1.958	8.313	4.690
H	-2.242	6.588	4.996
H	-0.586	7.217	4.945
C	-0.555	9.624	2.082
C	1.197	7.856	2.382
C	-0.157	7.931	0.269
H	0.193	10.293	1.624
H	-1.535	9.901	1.664
H	-0.573	9.844	3.161
H	1.952	8.516	1.920
H	1.235	8.030	3.469
H	1.513	6.819	2.191
H	0.609	8.581	-0.187
H	0.093	6.894	-0.001
H	-1.119	8.179	-0.205



1.111BC
ΔE **0.0** kcal/mol

1.111BC
Final heat of formation =
–1807.341545

C	-0.266	-0.278	-0.362
C	-0.082	0.000	1.001
C	1.217	0.220	1.477
C	2.313	0.174	0.609
C	2.119	-0.102	-0.746
C	0.825	-0.332	-1.229
C	-1.269	0.087	1.939
O	-2.148	-1.055	1.875
C	-1.598	-2.289	2.369
C	-2.162	-3.429	1.470
C	-3.205	-4.256	2.243
C	-2.430	-4.948	3.368
C	-1.882	-3.900	4.383
C	-1.935	-2.446	3.869
O	-1.386	-5.777	2.813
C	-0.493	-5.027	2.004
O	-1.133	-4.308	0.967
O	-3.877	-5.256	1.480
C	-5.015	-4.798	0.742
C	-4.712	-4.178	-0.610
C	-3.732	-4.732	-1.448
C	-3.497	-4.188	-2.713
C	-4.244	-3.093	-3.161
C	-5.221	-2.536	-2.332
C	-5.449	-3.075	-1.061
O	-2.645	-3.918	5.605
C	-2.404	-5.069	6.450
C	-1.016	-5.120	7.048
C	-0.063	-6.032	6.568
C	1.221	-6.077	7.119
C	1.566	-5.209	8.158
C	0.624	-4.295	8.644
C	-0.657	-4.253	8.092
O	-1.031	-1.597	4.596
H	-2.969	-2.079	4.010
H	-0.500	-2.280	2.252
H	-2.597	-2.961	0.581
H	-3.953	-3.570	2.687
H	-3.094	-5.648	3.890
H	-0.828	-4.150	4.603

1.111CB
ΔE **0.2** kcal/mol

C	-1.616	-0.931	5.727
H	0.174	-5.750	1.521
H	0.099	-4.334	2.637
H	-3.164	-4.979	7.239
H	-2.603	-6.003	5.894
H	-1.918	0.930	1.656
H	-0.919	0.250	2.970
H	-5.630	-5.702	0.598
H	-5.608	-4.089	1.351
H	-0.332	-6.709	5.754
H	1.952	-6.791	6.737
H	2.567	-5.244	8.592
H	0.888	-3.617	9.458
H	-1.392	-3.542	8.476
H	1.369	0.427	2.539
H	3.320	0.347	0.994
H	2.973	-0.144	-1.425
H	0.669	-0.552	-2.287
H	-1.275	-0.464	-0.738
H	-6.207	-2.629	-0.411
H	-5.801	-1.675	-2.669
H	-4.059	-2.671	-4.151
H	-2.727	-4.622	-3.353
H	-3.139	-5.573	-1.087
C	-0.575	-0.083	6.416
H	-2.458	-0.294	5.393
H	-2.025	-1.681	6.426
C	-0.956	1.104	7.059
C	-0.019	1.872	7.755
C	1.318	1.468	7.805
C	1.708	0.292	7.158
C	0.768	-0.481	6.471
H	-1.997	1.432	7.011
H	-0.332	2.793	8.250
H	2.054	2.071	8.342
H	2.752	-0.026	7.188
H	1.071	-1.398	5.965

1.111CB
Final heat of formation =
–1807.341371

C	0.249	-0.256	0.295
C	0.284	-0.295	1.696
C	1.525	-0.404	2.341

1.111CC
ΔE **1.9** kcal/mol

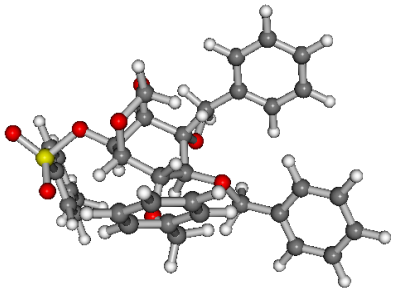
C	2.707	-0.468	1.598
C	2.661	-0.431	0.200
C	1.429	-0.327	-0.450
C	-0.987	-0.205	2.500
O	-1.131	1.140	2.996
C	-2.434	1.433	3.526
C	-2.674	0.753	4.896
C	-1.839	1.456	5.960
C	-2.438	2.855	6.147
C	-2.151	3.680	4.876
C	-2.567	2.983	3.552
O	-4.095	0.811	5.152
C	-4.428	1.529	6.331
O	-3.865	2.833	6.356
O	-0.742	3.956	4.908
C	-0.377	5.156	4.201
C	1.119	5.317	4.249
C	1.947	4.452	3.516
C	3.335	4.598	3.557
C	3.914	5.612	4.329
C	3.098	6.476	5.064
C	1.708	6.325	5.025
O	-1.815	0.669	7.163
C	-0.682	0.941	8.014
C	0.610	0.348	7.496
C	1.667	1.168	7.076
C	2.859	0.609	6.602
C	3.005	-0.779	6.542
C	1.953	-1.607	6.953
C	0.766	-1.046	7.427
O	-3.909	3.402	3.253
H	-1.879	3.350	2.770
H	-2.732	4.617	4.940
H	-1.971	3.376	6.998
H	-2.384	-0.308	4.845
H	-3.209	1.040	2.841
H	-5.515	1.665	6.313
H	-4.107	0.960	7.222
C	-4.226	3.402	1.851
H	-0.719	5.098	3.151
H	-0.874	6.027	4.668
H	-0.955	-0.925	3.338
H	-1.859	-0.459	1.868

H	-0.817	1.569	5.559
H	-0.562	2.028	8.170
H	-0.952	0.491	8.980
H	1.071	6.999	5.603
H	3.543	7.267	5.670
H	4.999	5.728	4.356
H	3.968	3.921	2.979
H	1.496	3.658	2.918
H	1.564	-0.434	3.432
H	3.666	-0.554	2.111
H	3.584	-0.489	-0.379
H	1.386	-0.302	-1.541
H	-0.713	-0.176	-0.215
H	-0.055	-1.692	7.746
H	2.064	-2.692	6.911
H	3.936	-1.217	6.178
H	3.672	1.261	6.278
H	1.554	2.253	7.114
H	-3.998	2.422	1.390
H	-5.317	3.534	1.820
C	-3.534	4.506	1.077
C	-2.632	4.214	0.044
C	-1.995	5.240	-0.662
C	-2.256	6.574	-0.339
C	-3.154	6.878	0.691
C	-3.788	5.851	1.392
H	-2.424	3.170	-0.206
H	-1.292	4.997	-1.460
H	-1.761	7.377	-0.888
H	-3.363	7.919	0.943
H	-4.485	6.087	2.200

1.111CC

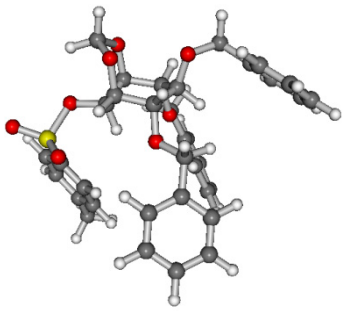
Final heat of formation = –1807.338

C	0.862	-0.434	1.477
C	-0.007	-1.033	2.401
C	0.418	-2.173	3.095
C	1.686	-2.716	2.865
C	2.545	-2.115	1.941
C	2.131	-0.970	1.250
C	-1.378	-0.457	2.641
O	-1.252	0.826	3.272
C	-2.511	1.463	3.552
C	-3.078	2.175	2.280
C	-2.763	3.699	2.160
C	-2.423	4.441	3.477
C	-1.435	3.618	4.298
C	-2.213	2.380	4.768
O	-3.376	2.763	5.517
C	-4.241	3.657	4.821
O	-3.577	4.783	4.262
O	-0.959	4.419	5.382
C	0.259	3.940	5.967
C	1.495	4.234	5.138
C	2.444	3.235	4.881
C	3.606	3.522	4.157
C	3.828	4.815	3.676
C	2.881	5.817	3.918
C	1.725	5.529	4.646
O	-1.629	3.909	1.305
C	-1.956	3.904	-0.084
C	-0.728	4.181	-0.919
C	-0.739	3.855	-2.284
C	0.360	4.145	-3.094
C	1.494	4.755	-2.545
C	1.515	5.070	-1.184
C	0.410	4.789	-0.373
O	-4.512	2.026	2.183
H	-2.609	1.694	1.404
H	-3.660	4.179	1.729
H	-1.975	5.404	3.200
H	-1.617	1.779	5.467
H	-3.252	0.710	3.882
H	-4.931	4.055	5.575
H	-4.793	3.111	4.036
C	-4.957	0.759	1.680
H	-2.398	2.935	-0.387
H	-2.726	4.679	-0.278
H	-1.967	-1.134	3.289
H	-1.919	-0.356	1.679
H	-0.603	3.302	3.646
H	0.321	4.461	6.935
H	0.204	2.857	6.180
H	-1.617	3.367	-2.716
H	0.336	3.887	-4.154
H	2.356	4.977	-3.175
H	2.398	5.539	-0.745
H	0.429	5.028	0.688
H	-0.249	-2.640	3.824
H	2.004	-3.606	3.410
H	3.535	-2.535	1.760
H	2.799	-0.496	0.529
H	0.544	0.461	0.941
H	0.983	6.308	4.834
H	3.049	6.829	3.544
H	4.733	5.042	3.110
H	4.335	2.733	3.963
H	2.268	2.220	5.246
H	-6.023	0.714	1.953
C	-4.800	0.607	0.178
H	-4.452	-0.077	2.196
C	-4.267	-0.566	-0.373
C	-4.169	-0.724	-1.760
C	-4.601	0.296	-2.611
C	-5.132	1.473	-2.069
C	-5.233	1.626	-0.685
H	-3.931	-1.368	0.288
H	-3.751	-1.643	-2.174
H	-4.525	0.176	-3.693
H	-5.476	2.271	-2.730
H	-5.646	2.543	-0.261



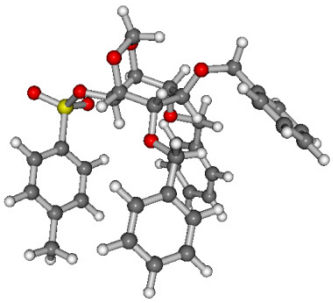
1.148BC

ΔE **0.0** kcal/mol



1.148CB

ΔE **0.6** kcal/mol



1.148CC

ΔE **1.9** kcal/mol

1.148BC

Final heat of formation = –2356.065

C	1.291	-0.370	6.519
C	0.034	0.238	6.393
C	-0.148	1.528	6.912
C	0.897	2.194	7.557
C	2.147	1.580	7.678
C	2.341	0.298	7.154
C	-1.125	-0.486	5.756
O	-0.648	-1.314	4.682
C	-1.672	-2.037	3.983

C	-1.301	-2.000	2.484
C	-2.035	-3.068	1.621
C	-3.196	-3.672	2.418
C	-2.571	-4.443	3.582
C	-1.862	-3.456	4.560
O	-1.680	-5.456	3.075
C	-0.663	-4.901	2.247
O	-1.165	-4.128	1.176
O	-1.637	-0.704	1.960
C	-0.534	0.220	1.855
C	0.456	-0.129	0.762
C	0.014	-0.419	-0.538
C	0.931	-0.713	-1.549
C	2.304	-0.713	-1.275
C	2.753	-0.426	0.015
C	1.832	-0.140	1.029
O	-3.987	-4.612	1.643
S	-5.255	-3.985	0.730
C	-6.517	-3.649	1.983
C	-6.778	-2.329	2.360
C	-7.763	-2.084	3.317
C	-8.490	-3.136	3.901
C	-8.206	-4.451	3.493
C	-7.226	-4.718	2.536
O	-2.624	-3.295	5.771
C	-2.583	-4.432	6.665
C	-1.223	-4.696	7.272
C	-0.463	-5.806	6.874
C	0.793	-6.048	7.436
C	1.304	-5.180	8.404
C	0.555	-4.068	8.808
C	-0.699	-3.830	8.246
H	-2.633	-1.502	4.092
H	-0.217	-2.177	2.381
H	-2.395	-2.580	0.710
H	-3.848	-2.872	2.810
H	-3.349	-4.996	4.123
H	-0.867	-3.871	4.801
H	-0.128	-5.748	1.803
H	0.032	-4.295	2.864
H	-3.315	-4.180	7.444
H	-2.940	-5.342	6.149
H	-1.020	1.182	1.633
H	-0.016	0.310	2.822
H	-0.860	-6.483	6.113
H	1.373	-6.916	7.118
H	2.284	-5.369	8.847
H	0.949	-3.389	9.566
H	-1.283	-2.964	8.565
H	2.183	0.076	2.040
H	3.822	-0.431	0.237
H	3.020	-0.942	-2.067
H	0.575	-0.940	-2.555
H	-1.056	-0.422	-0.751
H	-7.020	-5.738	2.212
H	-8.767	-5.280	3.928
C	-9.554	-2.854	4.932
H	-7.976	-1.054	3.612
H	-6.227	-1.512	1.892
H	-1.858	0.245	5.367
H	-1.646	-1.113	6.501
H	-1.119	2.019	6.807
H	0.739	3.198	7.954
H	2.969	2.101	8.174
H	3.316	-0.184	7.240
H	1.441	-1.368	6.107
H	-10.025	-3.779	5.287
H	-9.133	-2.331	5.803
H	-10.345	-2.209	4.518
O	-4.835	-2.690	0.138
O	-5.675	-5.136	-0.090

1.148CB

Final heat of formation = –2356.064

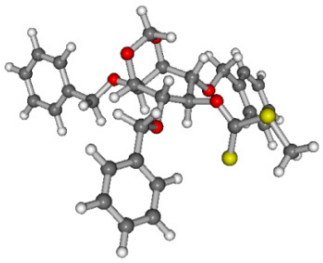
C	-4.192	5.790	1.271
C	-3.953	4.454	0.907
C	-3.227	4.192	-0.262
C	-2.751	5.239	-1.059
C	-2.994	6.564	-0.688
C	-3.713	6.837	0.481
C	-4.493	3.324	1.763
O	-4.087	3.397	3.138
C	-2.692	3.138	3.356
C	-2.385	1.612	3.341
C	-2.496	0.923	4.725
C	-1.708	1.741	5.743
C	-2.444	3.064	5.943
C	-2.274	3.888	4.648
O	-3.858	2.892	6.172
C	-4.275	1.539	6.211
O	-3.896	0.812	5.046
O	-1.071	1.444	2.787
C	-0.861	0.182	2.155
C	0.444	0.182	1.391
C	0.828	-0.978	0.700
C	2.018	-1.011	-0.028
C	2.845	0.117	-0.073
C	2.469	1.273	0.616
C	1.275	1.308	1.345
O	-1.577	0.951	6.966
S	-0.227	1.232	7.950
C	1.108	0.413	7.050
C	1.955	1.170	6.237
C	2.985	0.520	5.553
C	3.180	-0.864	5.676
C	2.311	-1.593	6.506
C	1.274	-0.966	7.197
O	-0.892	4.265	4.602
C	-0.646	5.505	3.927
C	0.797	5.902	4.111
C	1.520	6.455	3.045
C	2.842	6.876	3.222
C	3.459	6.736	4.468
C	2.747	6.175	5.534
C	1.423	5.764	5.360
H	-2.098	3.569	2.530
H	-2.919	4.781	4.727
H	-2.008	3.630	6.779
H	-2.079	-0.094	4.662
H	-3.131	1.125	2.687
H	-5.371	1.553	6.219
H	-3.878	1.039	7.111
H	-0.881	5.428	2.850
H	-1.313	6.282	4.353
H	-0.849	-0.637	2.899
H	-1.699	-0.026	1.460
H	-0.713	1.950	5.323
H	0.871	5.322	6.190
H	3.224	6.061	6.510
H	4.492	7.060	4.607
H	3.392	7.306	2.383
H	1.044	6.555	2.066
H	0.980	2.207	1.884
H	3.108	2.158	0.587
H	3.774	0.094	-0.644
H	2.301	-1.919	-0.563
H	0.187	-1.864	0.730
H	0.609	-1.531	7.850
H	2.451	-2.670	6.617
C	4.315	-1.546	4.953
H	3.647	1.104	4.911
H	1.817	2.248	6.151
H	-4.214	2.353	1.312
H	-5.591	3.362	1.803
H	-3.032	3.156	-0.552
H	-2.186	5.018	-1.967
H	-2.624	7.383	-1.307
H	-3.908	7.871	0.773
H	-4.751	6.001	2.184
O	0.049	2.689	7.981
O	-0.549	0.458	9.164
H	4.159	-2.631	4.892
H	4.430	-1.156	3.933
H	5.269	-1.377	5.478

1.148CC

Final heat of formation = –2356.062

C	-5.046	1.742	-0.801
C	-4.764	0.685	0.078
C	-4.309	-0.530	-0.449
C	-4.141	-0.693	-1.828
C	-4.421	0.365	-2.696
C	-4.872	1.585	-2.178
C	-5.005	0.841	1.568
O	-4.531	2.081	2.109
C	-3.099	2.169	2.278
C	-2.607	1.370	3.527
C	-2.351	2.199	4.813

C	-1.503	3.415	4.438
C	-2.407	4.340	3.626
C	-2.730	3.686	2.257
O	-3.536	2.596	5.514
C	-4.320	3.573	4.836
O	-3.569	4.697	4.386
O	-1.343	0.742	3.251
C	-1.451	-0.533	2.600
C	-0.079	-1.147	2.486
C	0.479	-1.426	1.232
C	1.745	-2.012	1.130
C	2.468	-2.316	2.287
C	1.920	-2.032	3.544
C	0.653	-1.454	3.643
O	-1.568	3.921	1.448
C	-1.853	3.960	0.040
C	-0.615	4.360	-0.720
C	-0.189	3.610	-1.825
C	0.928	4.004	-2.567
C	1.639	5.150	-2.203
C	1.227	5.898	-1.094
C	0.105	5.509	-0.360
O	-1.043	4.169	5.594
S	0.346	3.633	6.380
C	1.669	4.088	5.232
C	2.177	3.129	4.352
C	3.203	3.495	3.481
C	3.729	4.798	3.480
C	3.199	5.734	4.383
C	2.170	5.391	5.261
H	-2.608	1.715	1.399
H	-3.602	4.219	1.837
H	-1.898	5.289	3.419
H	-1.806	1.552	5.511
H	-3.366	0.606	3.777
H	-5.027	3.961	5.579
H	-4.855	3.109	3.989
H	-2.212	2.979	-0.321
H	-2.667	4.692	-0.137
H	-2.117	-1.185	3.200
H	-1.899	-0.427	1.594
H	-0.648	3.101	3.819
O	0.408	4.506	7.568
O	0.311	2.153	6.484
H	-0.739	2.709	-2.107
H	1.246	3.411	-3.426
H	2.513	5.459	-2.779
H	1.780	6.794	-0.805
H	-0.212	6.090	0.506
H	0.231	-1.226	4.623
H	2.482	-2.265	4.450
H	3.457	-2.772	2.211
H	2.169	-2.225	0.147
H	-0.079	-1.179	0.327
H	1.768	6.116	5.970
H	3.602	6.749	4.403
C	4.845	5.172	2.537
H	3.603	2.751	2.788
H	1.784	2.112	4.362
H	-6.086	0.847	1.776
H	-4.575	-0.022	2.107
H	-4.090	-1.362	0.225
H	-3.788	-1.647	-2.224
H	-4.290	0.241	-3.772
H	-5.097	2.414	-2.851
H	-5.400	2.692	-0.395
H	5.111	6.233	2.629
H	5.750	4.579	2.740
H	4.561	4.980	1.492



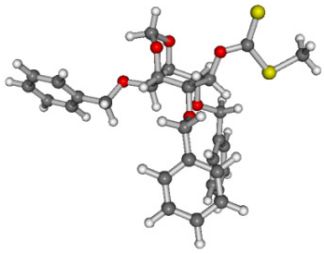
2.43BC

ΔE **0.0** kcal/mol

2.43BC

Final heat of formation = –2410.838

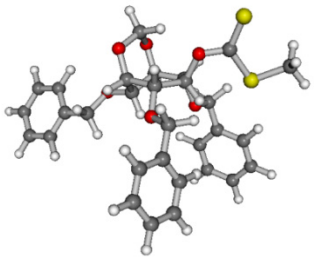
C	5.806	0.369	1.486
C	5.154	-0.793	1.052
C	5.817	-2.024	1.153
C	7.115	-2.094	1.667
C	7.760	-0.932	2.098
C	7.100	0.298	2.009
C	3.777	-0.723	0.439
O	2.988	0.247	1.139
C	1.670	0.384	0.629
C	1.565	1.185	-0.681
O	2.048	2.528	-0.477
C	1.334	3.197	0.549
O	1.328	2.504	1.784
C	0.829	1.157	1.648
C	-0.679	1.112	1.254
C	-0.921	0.651	-0.189



2.43CB

ΔE **5.6** kcal/mol

C	0.102	1.140	-1.223
O	-1.400	0.195	2.080
C	-1.772	0.742	3.352
C	-2.535	-0.288	4.148
C	-2.499	-0.248	5.549
C	-3.238	-1.160	6.307
C	-4.013	-2.134	5.668
C	-4.043	-2.186	4.271
C	-3.313	-1.266	3.513
O	-2.230	1.154	-0.598
C	-3.234	0.308	-0.922
S	-4.616	1.353	-1.338
C	-5.898	0.122	-1.755
O	-0.006	0.246	-2.333
C	0.388	0.831	-3.581
C	0.221	-0.177	-4.691
C	-0.794	-1.143	-4.644
C	-0.957	-2.043	-5.699
C	-0.118	-1.984	-6.817



2.43CC

ΔE **6.3** kcal/mol

C	0.895	-1.024	-6.869
C	1.068	-0.131	-5.808
S	-3.205	-1.346	-0.936
H	-0.965	-0.448	-0.216
H	-0.171	2.165	-1.541
H	2.218	0.766	-1.457
H	1.219	-0.617	0.476
H	0.946	0.710	2.643
H	-1.091	2.132	1.380
H	1.849	4.148	0.722
H	0.291	3.391	0.216
H	-0.880	1.067	3.921
H	-2.397	1.643	3.185
H	-0.241	1.724	-3.772
H	1.438	1.176	-3.545
H	3.288	-1.716	0.484
H	3.863	-0.447	-0.630
H	-6.786	0.710	-2.021
H	-5.578	-0.489	-2.605

H	-6.109	-0.517	-0.892
H	-1.883	0.500	6.054
H	-3.199	-1.118	7.397
H	-4.584	-2.853	6.257
H	-4.639	-2.948	3.766
H	-3.329	-1.311	2.423
H	-1.441	-1.195	-3.767
H	-1.746	-2.796	-5.648
H	-0.250	-2.689	-7.640
H	1.563	-0.977	-7.731
H	1.872	0.608	-5.848
H	5.311	-2.939	0.831
H	7.618	-3.060	1.741
H	8.771	-0.984	2.506
H	7.596	1.209	2.350
H	5.285	1.325	1.424

2.43CB

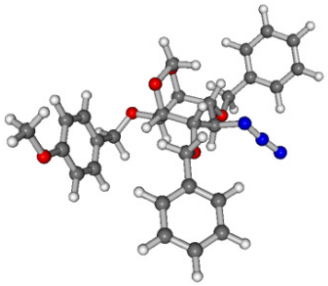
Final heat of formation = –2410.829

C	6.017	0.792	-0.656
C	5.175	0.080	0.210
C	5.698	-0.402	1.419
C	7.037	-0.180	1.754
C	7.868	0.529	0.882
C	7.355	1.017	-0.324
C	3.727	-0.137	-0.137
O	2.954	0.960	0.388
C	1.544	0.816	0.163
C	1.086	1.215	-1.244
O	1.204	2.627	-1.495
C	1.592	3.385	-0.351
O	0.798	3.097	0.788
C	0.778	1.701	1.145
C	-0.696	1.253	1.148
C	-1.329	1.245	-0.272
C	-0.398	0.809	-1.431
O	-0.713	-0.063	1.707
C	-1.905	-0.376	2.450
C	-1.896	-1.837	2.818
C	-2.164	-2.240	4.133
C	-2.207	-3.597	4.468
C	-1.969	-4.566	3.489
C	-1.688	-4.170	2.176
C	-1.657	-2.815	1.840
O	-1.807	2.586	-0.613
C	-3.077	2.990	-0.430
S	-4.219	1.717	0.142
C	-5.781	2.655	0.232
O	-0.521	-0.616	-1.561
C	-0.383	-1.074	-2.923
C	-0.641	-2.557	-2.969
C	-1.952	-3.050	-2.869
C	-2.198	-4.424	-2.900
C	-1.135	-5.324	-3.038
C	0.172	-4.843	-3.139
C	0.415	-3.467	-3.103
S	-3.495	4.556	-0.755
H	-2.170	0.535	-0.275
H	-0.767	1.311	-2.342
H	1.678	0.688	-2.011
H	1.188	1.579	2.160
H	-1.269	1.958	1.777
H	1.401	4.434	-0.602
H	2.657	3.206	-0.127
H	-1.110	-0.533	-3.558
H	0.628	-0.855	-3.308
H	-1.954	0.249	3.360
H	-2.799	-0.143	1.842
H	1.241	-0.229	0.343
H	3.358	-1.084	0.300
H	3.608	-0.201	-1.234
H	-2.338	-1.485	4.904
H	-2.417	-3.897	5.497
H	-1.996	-5.625	3.749
H	-1.496	-4.922	1.408
H	-1.430	-2.507	0.818
H	-2.782	-2.348	-2.765
H	-3.222	-4.794	-2.825
H	-1.328	-6.398	-3.069
H	1.005	-5.540	-3.247
H	1.439	-3.093	-3.181
H	5.048	-0.954	2.101
H	7.433	-0.564	2.695
H	8.914	0.701	1.141
H	8.000	1.571	-1.008
H	5.617	1.174	-1.598
H	-6.526	1.936	0.596
H	-5.677	3.494	0.929
H	-6.054	3.029	-0.759

2.43CC

Final heat of formation = –2410.828

C	-2.563	-2.407	3.347
C	-2.740	-1.165	2.720
C	-2.849	-0.013	3.513
C	-2.781	-0.099	4.906
C	-2.605	-1.343	5.521
C	-2.495	-2.497	4.739
C	-2.792	-1.069	1.219
O	-1.445	-0.910	0.718
C	-1.384	-0.746	-0.709
C	-0.015	-1.343	-1.149
C	1.117	-0.357	-1.570
C	0.679	1.103	-1.844
C	-0.331	1.536	-0.772
C	-1.608	0.748	-1.057
O	-2.070	0.965	-2.401
C	-1.087	0.661	-3.383
O	0.154	1.316	-3.162
O	-0.649	2.923	-0.774
C	0.388	3.751	-0.243
C	-0.075	5.187	-0.196
C	-1.031	5.672	-1.098
C	-1.413	7.017	-1.065
C	-0.842	7.892	-0.137
C	0.111	7.414	0.766
C	0.487	6.068	0.739
O	2.102	-0.258	-0.533
C	3.016	-1.376	-0.497
C	4.012	-1.150	0.608
C	3.683	-1.464	1.935
C	4.596	-1.234	2.966
C	5.853	-0.690	2.680
C	6.191	-0.375	1.361
C	5.273	-0.602	0.331
O	-0.194	-2.244	-2.298
C	-0.598	-3.527	-2.178
S	-0.861	-4.088	-0.493
C	-1.289	-5.840	-0.773
S	-0.795	-4.445	-3.539
H	0.353	-1.928	-0.293
H	1.569	-0.755	-2.496
H	1.595	1.706	-1.803
H	-2.420	1.128	-0.424
H	-2.184	-1.333	-1.196
H	-1.473	1.048	-4.333
H	-0.936	-0.431	-3.454
H	2.462	-2.318	-0.324
H	3.527	-1.458	-1.474
H	-3.419	-0.210	0.916
H	-3.228	-1.985	0.780
H	0.055	1.234	0.220
H	0.667	3.408	0.771
H	1.297	3.680	-0.872
H	2.701	-1.887	2.160
H	4.329	-1.483	3.995
H	6.569	-0.514	3.485
H	7.170	0.047	1.132
H	5.536	-0.354	-0.698
H	-2.988	0.958	3.033
H	-2.870	0.803	5.512
H	-2.556	-1.413	6.609
H	-2.361	-3.470	5.216
H	-2.478	-3.307	2.735
H	1.225	5.698	1.456
H	0.557	8.087	1.500
H	-1.142	8.942	-0.114
H	-2.162	7.382	-1.770
H	-1.479	4.985	-1.816
H	-1.474	-6.255	0.226
H	-2.186	-5.913	-1.397
H	-0.456	-6.360	-1.258



3.25BC

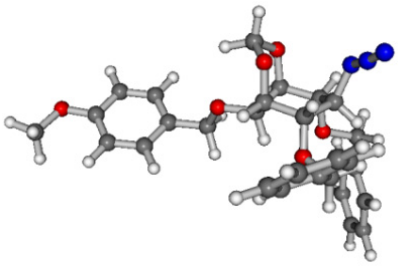
ΔE **0.0** kcal/mol

3.25BC

Final heat of formation =

–1739.888

C	1.818	4.388	0.373
C	2.437	3.143	0.565
C	3.797	3.006	0.260
C	4.532	4.094	-0.222
C	3.907	5.329	-0.413
C	2.546	5.473	-0.117
C	1.642	1.977	1.091
O	0.651	1.608	0.111
C	-0.216	0.556	0.548
C	0.449	-0.838	0.344
C	-0.141	-1.531	-0.897
C	-1.603	-1.824	-0.548
C	-2.406	-0.500	-0.377
C	-1.519	0.753	-0.246
O	-1.671	-2.660	0.626
C	-1.035	-2.055	1.739
O	0.314	-1.697	1.497
O	0.485	-2.754	-1.270
C	1.679	-2.614	-2.056
C	2.946	-2.345	-1.268
C	3.870	-1.378	-1.696
C	5.059	-1.159	-1.005
C	5.347	-1.907	0.147
C	4.429	-2.871	0.595
C	3.246	-3.084	-0.117
O	6.537	-1.617	0.765
C	6.875	-2.361	1.938
O	-3.238	-0.239	-1.518
C	-4.450	-1.023	-1.568
C	-5.444	-0.689	-0.476
C	-5.842	-1.661	0.452
C	-6.772	-1.355	1.452
C	-7.309	-0.068	1.535
C	-6.914	0.910	0.615
C	-5.991	0.601	-0.385
N	-2.279	1.853	0.402
N	-2.843	2.663	-0.334
N	-3.408	3.494	-0.887
H	-1.232	1.057	-1.266
H	-0.433	0.676	1.627
H	1.529	-0.690	0.230
H	-2.060	-2.423	-1.346
H	-3.033	-0.592	0.526
H	-1.024	-2.803	2.540
H	-1.610	-1.164	2.068
H	1.124	2.248	2.032
H	2.314	1.128	1.308
H	-4.869	-0.796	-2.559
H	-4.216	-2.102	-1.540
H	-0.105	-0.825	-1.750
H	1.542	-1.825	-2.820
H	1.764	-3.576	-2.586
H	-5.417	-2.666	0.393
H	-7.073	-2.122	2.167
H	-8.033	0.173	2.314
H	-7.331	1.917	0.676
H	-5.684	1.367	-1.100
H	4.285	2.038	0.401
H	5.592	3.975	-0.453
H	4.477	6.178	-0.794
H	2.055	6.437	-0.263
H	0.757	4.501	0.603
H	2.528	-3.823	0.243
H	4.626	-3.460	1.490
H	5.779	-0.411	-1.339
H	3.655	-0.782	-2.587
H	7.852	-1.981	2.258
H	6.140	-2.203	2.744
H	6.956	-3.440	1.723



3.25CB

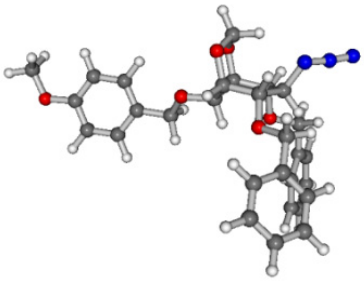
ΔE **1.9** kcal/mol

3.25CB

Final heat of formation =

–1739.885

C	-3.365	1.292	-4.238
C	-2.645	1.781	-3.139
C	-3.331	2.485	-2.136
C	-4.708	2.692	-2.232
C	-5.417	2.205	-3.337
C	-4.744	1.504	-4.340
C	-1.147	1.576	-3.035
O	-0.734	0.948	-1.807
C	-1.083	-0.438	-1.706
C	0.054	-1.322	-2.309
C	1.236	-1.633	-1.346
C	0.825	-1.807	0.133
C	-0.043	-0.614	0.553
C	-1.355	-0.730	-0.221
O	0.148	-3.071	0.275
C	-1.215	-2.950	0.666
O	-1.937	-2.051	-0.161
O	2.213	-0.586	-1.365
C	3.159	-0.697	-2.447
C	4.206	0.373	-2.290
C	4.069	1.609	-2.937
C	5.030	2.610	-2.772
C	6.142	2.384	-1.955
C	6.287	1.154	-1.304
C	5.325	0.156	-1.472
N	-0.421	-2.628	-2.840
N	-1.322	-2.609	-3.678
N	-2.149	-2.747	-4.465
O	-0.317	-0.539	1.957
C	0.773	0.027	2.718
C	0.356	0.147	4.156
C	0.605	-0.890	5.071
C	0.196	-0.797	6.397
C	-0.482	0.350	6.842
C	-0.740	1.397	5.945
C	-0.319	1.282	4.615
O	-0.842	0.351	8.165
C	-1.540	1.495	8.663
H	0.478	-0.745	-3.150
H	-2.021	-0.633	-2.256
H	-2.085	0.001	0.159
H	1.753	-1.848	0.723
H	1.685	-2.586	-1.680
H	-1.665	-3.938	0.517
H	-1.280	-2.629	1.719
H	-0.623	2.542	-3.034
H	-0.788	1.003	-3.911
H	3.622	-1.701	-2.421
H	2.647	-0.586	-3.421
H	0.463	0.310	0.221
H	1.670	-0.612	2.634
H	1.025	1.019	2.298
H	5.439	-0.803	-0.964
H	7.156	0.971	-0.668



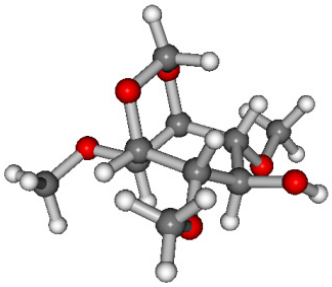
3.25CC

ΔE **4.4** kcal/mol

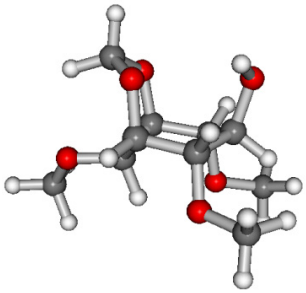
H	6.895	3.163	-1.827
H	4.913	3.567	-3.284
H	3.201	1.787	-3.576
H	-2.778	2.861	-1.273
H	-5.232	3.240	-1.446
H	-6.494	2.369	-3.411
H	-5.291	1.113	-5.199
H	-2.843	0.734	-5.019
H	-0.526	2.100	3.922
H	-1.260	2.298	6.267
H	0.391	-1.599	7.109
H	1.129	-1.788	4.735
H	-2.498	1.645	8.137
H	-1.735	1.286	9.720
H	-0.929	2.410	8.579

3.25CC
Final heat of formation =
–1739.881

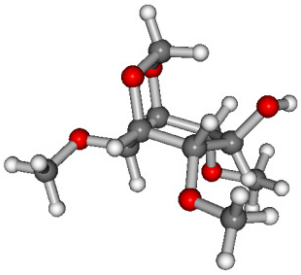
C	2.500	-4.329	-0.755
C	3.300	-3.251	-0.347
C	4.432	-2.921	-1.104
C	4.766	-3.657	-2.245
C	3.962	-4.728	-2.644
C	2.826	-5.060	-1.898
C	2.947	-2.469	0.890
O	1.661	-1.847	0.705
C	1.200	-1.135	1.862
C	-0.344	-1.160	1.775
C	-0.832	-0.101	0.790
C	-0.541	1.255	1.451
C	0.988	1.498	1.470
C	1.867	0.278	1.922
O	-1.157	1.344	2.744
C	-0.802	0.279	3.619
O	-0.984	-1.008	3.053
O	-2.210	-0.332	0.516
C	-2.675	0.343	-0.661
C	-4.153	0.103	-0.829
C	-4.695	-0.162	-2.097
C	-6.066	-0.332	-2.275
C	-6.931	-0.249	-1.172
C	-6.404	0.001	0.103
C	-5.025	0.180	0.262
O	1.315	1.871	0.123
C	2.484	2.700	0.019
C	2.772	2.981	-1.433
C	2.931	4.297	-1.884
C	3.234	4.559	-3.224
C	3.368	3.504	-4.129
C	3.201	2.186	-3.688
C	2.909	1.925	-2.348
N	2.408	0.447	3.306
N	3.244	1.339	3.473
N	4.032	2.123	3.764
O	-8.264	-0.436	-1.443
C	-9.179	-0.365	-0.349
H	2.716	0.242	1.220
H	1.490	-1.675	2.782
H	-0.635	-2.159	1.428
H	-0.976	2.082	0.875
H	1.180	2.345	2.155
H	-1.489	0.342	4.471
H	0.243	0.402	3.964
H	3.728	-1.713	1.090
H	2.896	-3.134	1.775
H	2.325	3.646	0.570
H	3.354	2.192	0.482
H	-0.235	-0.178	-0.137
H	-2.477	1.430	-0.578
H	-2.126	-0.021	-1.550
H	-4.033	-0.241	-2.962
H	-6.488	-0.539	-3.258
H	-7.052	0.060	0.977
H	-4.618	0.366	1.256
H	-10.171	-0.540	-0.780
H	-8.968	-1.141	0.406
H	-9.160	0.626	0.131
H	2.815	5.126	-1.181
H	3.356	5.590	-3.562
H	3.600	3.706	-5.176
H	3.301	1.357	-4.392
H	2.770	0.897	-2.008
H	5.060	-2.081	-0.797
H	5.652	-3.391	-2.824
H	4.219	-5.303	-3.536
H	2.195	-5.896	-2.206
H	1.612	-4.587	-0.175



3.141BC
ΔE **0.0** kcal/mol



3.141CB
ΔE **2.5** kcal/mol



3.141CC
ΔE **4.4** kcal/mol

3.141BC
Final heat of formation =
–843.509

C	-0.180	1.291	0.790
C	-0.203	-0.171	1.336
C	0.680	-1.079	0.461
C	-0.021	-1.149	-0.897
C	-0.038	0.251	-1.571
C	0.352	1.412	-0.640
O	-1.353	-1.687	-0.732
C	-2.128	-0.908	0.162
O	-1.529	-0.730	1.435
O	0.851	-2.403	0.948
C	1.661	-2.483	2.117
O	0.881	0.339	-2.672
C	0.407	-0.298	-3.859
O	-0.105	2.661	-1.173
O	0.673	2.109	1.600
C	0.028	2.611	2.768
H	1.455	1.419	-0.573
H	-1.213	1.688	0.818
H	0.161	-0.141	2.371
H	0.494	-1.868	-1.547
H	-1.063	0.437	-1.946
H	-3.062	-1.457	0.327
H	-2.351	0.083	-0.287
H	0.361	2.782	-2.019
H	0.771	3.220	3.298
H	-0.838	3.243	2.503
H	-0.314	1.804	3.442
H	1.178	-0.149	-4.625
H	0.251	-1.382	-3.716
H	-0.542	0.151	-4.202
H	1.671	-0.597	0.338
H	1.829	-3.551	2.305
H	2.637	-1.984	1.970
H	1.167	-2.045	3.002

3.141CB
Final heat of formation

–843.505

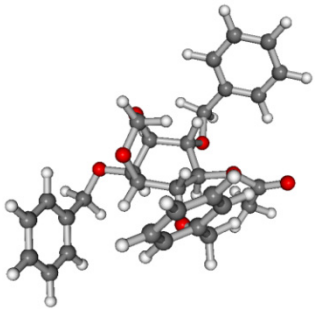
C	-0.171	-0.000	0.046
C	-0.185	-0.017	1.584
C	1.242	0.227	2.078
C	2.049	-1.034	1.740
C	2.184	-1.142	0.203
C	0.846	-0.993	-0.575
O	1.441	-2.240	2.244
C	0.155	-2.038	2.819
O	-0.710	-1.305	1.970
O	1.206	0.580	3.466
C	2.444	1.098	3.956
O	3.140	-0.140	-0.177
C	3.805	-0.434	-1.403
O	0.310	-2.311	-0.760
O	0.096	1.348	-0.347
C	-0.432	1.691	-1.627
H	1.103	-0.569	-1.564
H	-1.190	-0.286	-0.290
H	-0.854	0.775	1.953
H	3.070	-0.969	2.151
H	2.572	-2.151	-0.021
H	-0.286	-3.034	2.935
H	0.253	-1.529	3.793
H	-0.632	-2.300	-0.521
H	-0.193	2.748	-1.791
H	0.020	1.095	-2.439
H	-1.529	1.559	-1.652
H	4.512	0.385	-1.581
H	4.360	-1.388	-1.336
H	3.107	-0.490	-2.256
H	1.661	1.064	1.493
H	2.255	1.427	4.985
H	3.246	0.340	3.969
H	2.777	1.963	3.355

3.141CC

Final heat of formation =

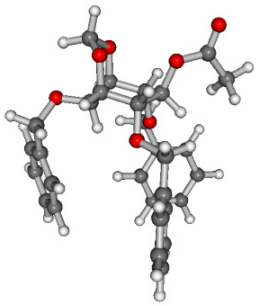
–843.502

O	-1.561	-1.553	0.710
C	-0.275	-0.981	0.996
C	0.691	-1.209	-0.174
C	0.020	-0.595	-1.401
O	-1.287	-1.151	-1.613
C	-2.135	-1.030	-0.478
C	0.005	0.943	-1.274
C	-0.335	1.521	0.142
C	-0.339	0.525	1.344
O	0.784	0.759	2.206
C	0.631	1.908	3.037
O	0.980	-2.572	-0.457
C	1.779	-3.207	0.535
O	1.309	1.372	-1.696
C	1.349	2.727	-2.127
O	-1.620	2.178	0.166
H	0.459	2.256	0.363
H	-1.281	0.700	1.896
H	0.067	-1.490	1.906
H	0.588	-0.847	-2.305
H	-0.756	1.318	-1.988
H	-3.019	-1.643	-0.691
H	-2.427	0.026	-0.327
H	-1.654	2.798	-0.583
H	1.533	1.968	3.658
H	0.540	2.842	2.453
H	-0.257	1.814	3.687
H	2.378	2.927	-2.450
H	0.662	2.896	-2.979
H	1.094	3.438	-1.318
H	1.630	-0.655	0.033
H	2.048	-4.192	0.134
H	2.704	-2.634	0.737
H	1.236	-3.351	1.485



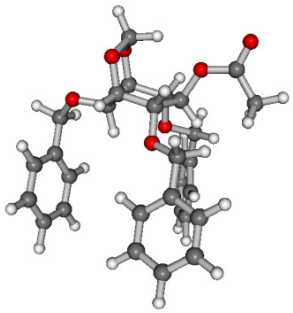
4.20BC

ΔE **0.0** kcal/mol



4.20CB

ΔE **2.5** kcal/mol



4.20CC

ΔE **5.6** kcal/mol

4.20BC

Final heat of formation =

–1689.617

C	0.204	3.162	-2.960
C	-0.174	3.384	-1.626
C	0.605	4.237	-0.833
C	1.740	4.863	-1.361
C	2.108	4.635	-2.689
C	1.339	3.779	-3.487
C	-1.416	2.731	-1.058
O	-1.425	1.287	-1.168
C	-0.427	0.605	-0.391
C	0.148	-0.558	-1.256
C	-0.319	-1.921	-0.711
C	0.319	-2.051	0.675
C	-0.254	-0.976	1.648
C	-1.057	0.116	0.927
O	1.755	-1.983	0.562
C	2.182	-0.777	-0.053
O	1.589	-0.541	-1.317
O	0.060	-3.052	-1.487
C	-0.778	-3.328	-2.615
C	-0.444	-2.559	-3.881
C	0.890	-2.363	-4.266
C	1.190	-1.705	-5.460
C	0.162	-1.243	-6.290
C	-1.169	-1.433	-5.913
C	-1.469	-2.085	-4.712
O	-1.157	-1.558	2.602
C	-0.508	-2.282	3.673
C	0.350	-1.421	4.574
C	1.723	-1.676	4.705
C	2.516	-0.889	5.547
C	1.943	0.166	6.260
C	0.575	0.432	6.130
C	-0.215	-0.359	5.296
O	-1.191	1.268	1.798
H	-2.051	-0.285	0.688
H	0.401	1.294	-0.161
H	-0.184	-0.397	-2.287
H	-1.422	-1.909	-0.604
H	0.116	-3.050	1.083
H	0.588	-0.502	2.180
C	-2.354	1.567	2.475
H	3.260	-0.877	-0.223
H	1.989	0.081	0.622
H	-1.344	-2.725	4.233
H	0.098	-3.111	3.265

H	-2.307	3.037	-1.626
H	-1.552	3.042	-0.010
H	-0.645	-4.406	-2.798
H	-1.841	-3.167	-2.351
H	2.174	-2.492	4.137
H	3.584	-1.098	5.639
H	2.560	0.784	6.914
H	0.123	1.260	6.679
H	-1.281	-0.144	5.195
H	0.321	4.410	0.207
H	2.338	5.525	-0.732
H	2.994	5.120	-3.103
H	1.623	3.598	-4.525
H	-0.392	2.490	-3.581
H	-2.512	-2.223	-4.415
H	-1.977	-1.068	-6.550
H	0.399	-0.731	-7.224
H	2.232	-1.552	-5.746
H	1.689	-2.708	-3.608
O	-2.341	2.532	3.209
C	-3.576	0.704	2.242
H	-4.380	1.085	2.880
H	-3.899	0.753	1.191
H	-3.369	-0.346	2.486

4.20CB

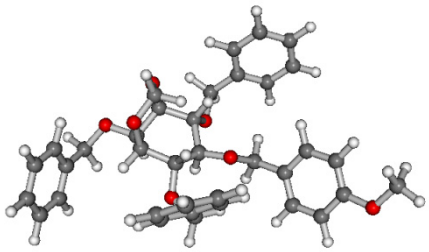
Final heat of formation = –1689.613

C	1.120	2.092	-3.860
C	1.282	0.911	-3.121
C	2.564	0.561	-2.671
C	3.661	1.380	-2.951
C	3.490	2.555	-3.690
C	2.216	2.911	-4.145
C	0.096	0.043	-2.794
O	-0.414	0.427	-1.497
C	-1.726	-0.078	-1.208
C	-1.745	-1.607	-0.973
C	-1.062	-1.922	0.352
C	-1.976	-1.390	1.463
C	-1.966	0.151	1.410
C	-2.242	0.747	0.002
O	-3.132	-2.006	-1.016
C	-3.580	-2.630	0.178
O	-3.339	-1.835	1.332
O	-0.676	0.554	1.891
C	-0.678	1.846	2.519
C	0.731	2.227	2.888
C	1.713	2.351	1.893
C	3.015	2.725	2.230
C	3.351	2.985	3.564
C	2.380	2.862	4.560
C	1.077	2.481	4.222
O	-0.808	-3.333	0.449
C	0.284	-3.668	1.329
C	1.643	-3.386	0.726
C	2.516	-2.457	1.307
C	3.775	-2.213	0.747
C	4.171	-2.896	-0.405
C	3.302	-3.821	-0.998
C	2.049	-4.065	-0.435
O	-3.671	0.968	-0.090
H	-1.707	1.707	-0.044
H	-2.765	0.516	2.080
H	-1.607	-1.690	2.457
H	-1.216	-2.122	-1.791
H	-2.400	0.116	-2.064
H	-4.668	-2.718	0.090
H	-3.100	-3.617	0.291
C	-4.193	2.018	-0.810
H	-1.101	2.601	1.827
H	-1.321	1.825	3.419
H	0.394	-1.019	-2.790
H	-0.699	0.174	-3.551
H	-0.113	-1.360	0.381
H	0.183	-3.144	2.296
H	0.161	-4.745	1.517
H	0.320	2.378	5.003
H	2.635	3.060	5.603
H	4.368	3.283	3.825
H	3.771	2.820	1.448
H	1.454	2.141	0.853
H	2.700	-0.356	-2.095
H	4.655	1.096	-2.599
H	4.348	3.191	-3.915
H	2.078	3.824	-4.726
H	0.126	2.369	-4.220
H	1.372	-4.787	-0.896
H	3.610	-4.361	-1.896
H	5.154	-2.712	-0.841
H	4.444	-1.486	1.211
H	2.207	-1.916	2.205
O	-5.399	2.114	-0.884
C	-3.236	3.017	-1.436
H	-2.449	2.539	-2.035
H	-3.823	3.690	-2.068
H	-2.737	3.613	-0.657

4.20CC

Final heat of formation = –1689.608

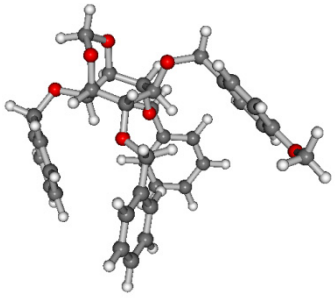
C	0.996	-3.354	1.537
C	0.055	-2.851	2.447
C	0.258	-3.056	3.819
C	1.378	-3.757	4.275
C	2.310	-4.255	3.360
C	2.119	-4.050	1.989
C	-1.146	-2.086	1.958
O	-0.756	-0.731	1.669
C	-1.848	0.138	1.334
C	-2.256	-0.028	-0.165
C	-1.639	1.002	-1.166
C	-1.140	2.338	-0.556
C	-0.337	2.058	0.711
C	-1.353	1.549	1.746
O	-2.397	2.510	1.948
C	-3.066	2.909	0.754
O	-2.187	3.285	-0.300
O	0.312	3.263	1.115
C	1.413	3.059	2.015
C	2.659	2.520	1.340
C	3.277	1.347	1.792
C	4.445	0.873	1.183
C	5.004	1.570	0.109
C	4.389	2.739	-0.356
C	3.226	3.211	0.256
O	-0.491	0.424	-1.808
C	-0.799	-0.293	-3.000
C	0.460	-0.828	-3.644
C	0.348	-1.775	-4.674
C	1.487	-2.262	-5.318
C	2.755	-1.813	-4.933
C	2.871	-0.875	-3.903
C	1.730	-0.382	-3.261
O	-3.707	0.050	-0.260
H	-1.914	-1.020	-0.487
H	-2.415	1.246	-1.913
H	-0.503	2.817	-1.310
H	-0.888	1.430	2.733
H	-2.736	-0.105	1.945
H	-3.630	3.812	1.014
H	-3.751	2.113	0.418
C	-4.530	-0.983	-0.651
H	-1.483	-1.140	-2.785
H	-1.332	0.375	-3.706
H	-1.942	-2.083	2.726
H	-1.552	-2.570	1.050
H	0.399	1.264	0.499
H	1.609	4.057	2.435
H	1.127	2.397	2.853
H	-0.638	-2.135	-4.977
H	1.385	-2.997	-6.118
H	3.647	-2.194	-5.433
H	3.857	-0.523	-3.593
H	1.822	0.345	-2.455
H	-0.469	-2.667	4.535
H	1.522	-3.916	5.345
H	3.184	-4.805	3.714
H	2.844	-4.437	1.271
H	0.850	-3.191	0.467
H	2.744	4.120	-0.107
H	4.823	3.287	-1.194
H	5.916	1.204	-0.365
H	4.914	-0.042	1.547
H	2.837	0.795	2.626
O	-5.722	-0.773	-0.671
C	-3.909	-2.311	-1.032
H	-3.209	-2.206	-1.874
H	-3.357	-2.757	-0.193
H	-4.719	-2.985	-1.324



4.21BC
ΔE **0.0** kcal/mol

4.21BC
Final heat of formation =
–1921.914

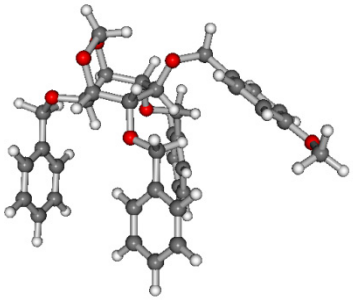
C	0.998	-0.673	6.893
C	-0.258	-0.309	6.395
C	-0.565	1.059	6.314
C	0.345	2.030	6.717
C	1.605	1.648	7.210
C	1.931	0.286	7.298
C	-1.235	-1.356	5.934
O	-0.904	-1.730	4.574
C	-1.891	-2.525	3.898
C	-1.640	-2.299	2.385
C	-2.184	-3.421	1.457
C	-3.200	-4.291	2.212
C	-2.402	-5.015	3.299
C	-1.883	-4.003	4.361
O	-1.337	-5.792	2.710
C	-0.468	-4.984	1.929
O	-1.136	-4.256	0.918
O	-2.274	-1.079	1.960
C	-1.473	0.116	2.091
C	-0.276	0.152	1.162
C	-0.443	-0.001	-0.223
C	0.657	0.048	-1.080
C	1.941	0.259	-0.563
C	2.118	0.411	0.813
C	1.013	0.354	1.671
O	-3.877	-5.270	1.425
C	-5.007	-4.787	0.691
C	-4.697	-4.184	-0.667
C	-3.702	-4.738	-1.487
C	-3.464	-4.213	-2.759
C	-4.223	-3.137	-3.233
C	-5.214	-2.579	-2.421
C	-5.445	-3.099	-1.143
O	-2.713	-4.046	5.541
C	-2.562	-5.232	6.355
C	-1.236	-5.325	7.077
C	-0.205	-6.141	6.583
C	1.023	-6.217	7.245
C	1.234	-5.482	8.416
C	0.211	-4.671	8.921



4.21CB
ΔE **0.2** kcal/mol

C	-1.013	-4.595	8.255
H	-2.899	-2.126	4.126
H	-0.550	-2.229	2.222
H	-2.636	-2.934	0.587
H	-3.946	-3.630	2.697
H	-3.048	-5.756	3.785
H	-0.845	-4.279	4.622
H	0.224	-5.666	1.424
H	0.098	-4.292	2.587
H	-3.388	-5.164	7.076
H	-2.718	-6.141	5.748
H	-2.174	0.926	1.842
H	-1.140	0.247	3.132
H	-5.647	-5.674	0.555
H	-5.578	-4.059	1.299
H	-0.370	-6.721	5.671
H	1.815	-6.856	6.850
H	2.190	-5.547	8.938
H	0.367	-4.104	9.841
H	-1.812	-3.967	8.656
H	1.151	0.461	2.750
H	3.117	0.569	1.224
H	2.801	0.299	-1.234
H	0.515	-0.074	-2.156
H	-1.444	-0.173	-0.626
H	-6.214	-2.652	-0.507
H	-5.804	-1.732	-2.778
H	-4.036	-2.729	-4.228
H	-2.682	-4.647	-3.385
H	-3.100	-5.564	-1.106
H	-2.268	-0.964	5.961
H	-1.194	-2.243	6.584
H	-1.541	1.370	5.934
H	0.106	3.093	6.661
O	2.434	2.675	7.583
H	2.899	-0.035	7.682
H	1.257	-1.731	6.968
C	3.726	2.334	8.090
H	4.215	3.287	8.318
H	3.654	1.732	9.011
H	4.323	1.787	7.342

4.21CB
Final heat of formation =



4.21CC
ΔE **2.1** kcal/mol

–1921.914

C	-3.379	5.759	1.134
C	-3.194	4.384	0.937
C	-2.247	3.975	-0.015
C	-1.512	4.902	-0.750
C	-1.710	6.276	-0.541
C	-2.650	6.706	0.410
C	-3.991	3.380	1.742
O	-3.716	3.419	3.155
C	-2.409	2.947	3.516
C	-2.346	1.392	3.535
C	-2.674	0.760	4.910
C	-1.851	1.454	5.990
C	-2.391	2.882	6.117
C	-2.015	3.659	4.839
O	-3.825	2.931	6.267
C	-4.447	1.654	6.251
O	-4.100	0.890	5.105
O	-1.037	1.024	3.070
C	-0.942	-0.333	2.598
C	0.374	-0.510	1.887
C	0.438	-0.507	0.486
C	1.662	-0.658	-0.172
C	2.839	-0.809	0.566
C	2.786	-0.810	1.965
C	1.561	-0.665	2.620
O	-1.916	0.699	7.214
C	-0.808	0.943	8.105
C	0.475	0.273	7.662
C	1.595	1.029	7.291
C	2.779	0.400	6.890
C	2.852	-0.994	6.854
C	1.736	-1.759	7.217
C	0.557	-1.128	7.619
O	-0.597	3.873	4.925
C	-0.147	5.033	4.201
C	1.347	5.147	4.339
C	2.190	4.261	3.650
C	3.577	4.358	3.779
C	4.140	5.345	4.598
C	3.308	6.230	5.289
C	1.919	6.127	5.161
H	-1.675	3.261	2.754

H	-2.554	4.622	4.855
H	-1.935	3.404	6.974
H	-2.431	-0.313	4.899
H	-3.109	1.015	2.827
H	-5.525	1.840	6.183
H	-4.191	1.095	7.168
H	-0.425	4.947	3.134
H	-0.642	5.936	4.606
H	-1.013	-1.043	3.441
H	-1.782	-0.542	1.908
H	-0.809	1.507	5.631
H	-0.642	2.027	8.235
H	-1.140	0.536	9.071
H	1.269	6.817	5.704
H	3.740	7.001	5.929
H	5.224	5.423	4.695
H	4.223	3.666	3.235
H	1.752	3.488	3.015
H	1.523	-0.668	3.712
H	3.701	-0.931	2.546
H	3.795	-0.928	0.054
H	1.696	-0.659	-1.263
H	-0.480	-0.390	-0.091
H	-0.313	-1.724	7.900
H	1.789	-2.849	7.193
H	3.776	-1.487	6.546
H	3.642	1.002	6.602
H	1.539	2.120	7.308
H	-3.828	2.364	1.335
H	-5.068	3.592	1.676
H	-2.082	2.909	-0.185
H	-0.775	4.585	-1.488
O	-0.943	7.113	-1.310
H	-2.824	7.766	0.586
H	-4.106	6.099	1.875
C	-1.104	8.521	-1.126
H	-0.405	8.993	-1.825
H	-2.131	8.845	-1.363
H	-0.853	8.826	-0.097

4.21CC

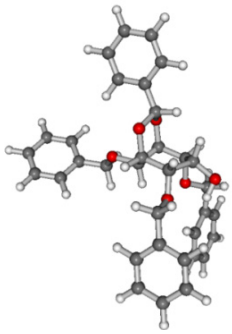
Final heat of formation =

–1921.910

C	-4.902	1.395	-0.773
C	-4.576	0.443	0.200
C	-4.046	-0.785	-0.228
C	-3.849	-1.057	-1.579
C	-4.176	-0.090	-2.543
C	-4.703	1.145	-2.134
C	-4.850	0.706	1.667
O	-4.435	2.004	2.120
C	-3.009	2.178	2.274
C	-2.477	1.494	3.577
C	-2.230	2.431	4.788
C	-1.460	3.675	4.324
C	-2.437	4.472	3.465
C	-2.725	3.708	2.148
O	-3.421	2.803	5.497
C	-4.281	3.670	4.761
O	-3.620	4.802	4.211
O	-1.201	0.867	3.346
C	-1.295	-0.431	2.736
C	0.088	-1.001	2.567
C	0.888	-0.614	1.482
C	2.175	-1.132	1.329
C	2.678	-2.047	2.260
C	1.890	-2.437	3.347
C	0.602	-1.914	3.498
O	-1.573	3.944	1.323
C	-1.854	3.901	-0.073
C	-0.604	4.176	-0.877
C	-0.711	4.336	-2.268
C	0.422	4.577	-3.046
C	1.681	4.663	-2.443
C	1.793	4.508	-1.059
C	0.657	4.265	-0.277
O	-1.022	4.499	5.407
C	0.182	4.041	6.034
C	1.437	4.307	5.223
C	2.388	3.299	5.016
C	3.565	3.562	4.308
C	3.800	4.840	3.793
C	2.850	5.851	3.985
C	1.680	5.587	4.698
H	-2.496	1.694	1.425

H	-3.622	4.162	1.689
H	-1.998	5.438	3.188
H	-1.645	1.849	5.512
H	-3.217	0.736	3.895
H	-5.004	4.062	5.486
H	-4.794	3.103	3.965
H	-2.267	2.913	-0.360
H	-2.630	4.654	-0.319
H	-1.906	-1.094	3.380
H	-1.795	-0.356	1.753
H	-0.606	3.363	3.697
H	0.222	4.593	6.985
H	0.123	2.965	6.282
H	-1.692	4.276	-2.746
H	0.322	4.702	-4.126
H	2.568	4.854	-3.049
H	2.770	4.578	-0.578
H	0.744	4.149	0.801
H	-0.013	-2.219	4.348
H	2.277	-3.151	4.076
H	3.682	-2.456	2.138
H	2.787	-0.825	0.479
H	0.498	0.100	0.754
H	0.935	6.372	4.846
H	3.028	6.850	3.582
H	4.718	5.048	3.239
H	4.295	2.766	4.152
H	2.201	2.296	5.406
H	-5.932	0.688	1.866
H	-4.395	-0.095	2.278
H	-3.788	-1.548	0.510
H	-3.436	-2.010	-1.911
O	-3.945	-0.446	-3.846
H	-4.970	1.909	-2.863
H	-5.316	2.356	-0.460
C	-4.261	0.506	-4.864
H	-4.001	0.022	-5.812
H	-5.335	0.757	-4.864
H	-3.668	1.429	-4.752

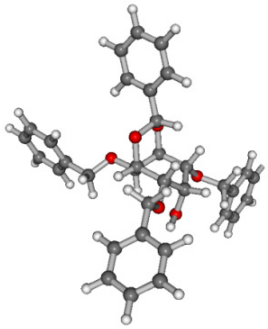
3). C1,C3-*O*-Benzylidene *neo*-inositol derivatives



1.133CC
ΔE **0.0** kcal/mol

1.133CC
Final heat of formation =
–1768.036

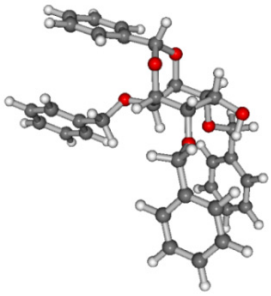
C	0.000	0.000	0.000
C	0.000	0.000	1.398
C	1.216	0.000	2.095
C	2.421	0.001	1.390
C	2.420	0.002	-0.010
C	1.208	0.003	-0.706
C	-1.303	0.009	2.161
O	-1.412	1.273	2.825
C	-2.387	1.355	3.882
C	-2.176	0.231	4.902
C	-2.275	-1.069	4.113
O	-1.298	-1.106	3.054
C	-3.866	1.330	3.410
C	-4.325	-0.054	2.862
C	-3.730	-1.275	3.618
O	-4.643	1.717	4.554
C	-5.668	2.681	4.265
C	-6.453	2.984	5.517
C	-6.948	4.277	5.737
C	-7.729	4.561	6.862
C	-8.014	3.554	7.788
C	-7.515	2.264	7.580
C	-6.742	1.978	6.452
O	-5.744	-0.153	2.804
O	-4.591	-1.537	4.746
C	-4.702	-2.942	5.076
C	-5.714	-3.103	6.178
C	-5.313	-3.118	7.521
C	-6.256	-3.246	8.544
C	-7.614	-3.363	8.232
C	-8.025	-3.349	6.895
C	-7.079	-3.221	5.875
O	-0.911	0.258	5.565
C	-0.809	1.298	6.555
C	0.479	1.116	7.315
C	1.602	1.901	7.021
C	2.801	1.719	7.717



1.133BC
ΔE **1.9** kcal/mol

C	2.889	0.744	8.715
C	1.774	-0.048	9.014
C	0.577	0.140	8.318
H	-2.999	0.267	5.639
H	-1.997	-1.915	4.756
H	-3.750	-2.145	2.937
H	-3.984	2.077	2.607
H	-2.215	2.343	4.331
H	-2.144	-0.096	1.447
H	-0.824	2.294	6.077
H	-1.677	1.238	7.239
H	1.534	2.660	6.239
H	3.667	2.339	7.480
H	3.823	0.601	9.260
H	1.837	-0.808	9.794
H	-0.292	-0.478	8.552
H	1.203	-0.006	3.185
H	3.368	-0.001	1.934
H	3.364	0.002	-0.558
H	1.202	0.002	-1.797
H	-0.950	-0.002	-0.541
H	-5.213	3.612	3.874
H	-6.337	2.278	3.482
H	-5.015	-3.498	4.173
H	-3.720	-3.332	5.397
H	-4.252	-3.029	7.765
H	-5.931	-3.260	9.586
H	-8.351	-3.468	9.030
H	-9.084	-3.445	6.647
H	-7.400	-3.216	4.831
H	-6.343	0.975	6.297
H	-7.728	1.473	8.302
H	-8.618	3.774	8.670
H	-8.105	5.574	7.019
H	-6.717	5.073	5.024
H	-6.004	-0.444	3.704
H	-3.982	-0.119	1.819

1.133BC
Final heat of formation =
–1768.033



1.133CB
ΔE **3.1** kcal/mol

C	0.000	0.000	0.000
C	0.000	0.000	1.401
C	1.228	0.000	2.080
C	2.431	-0.000	1.372
C	2.421	0.004	-0.027
C	1.203	0.004	-0.713
C	-1.294	-0.025	2.172
O	-1.533	-1.365	2.632
C	-2.753	-1.497	3.360
C	-2.651	-1.015	4.819
O	-1.614	-1.757	5.498
C	-1.831	-3.176	5.476
O	-2.067	-3.681	4.169
C	-3.108	-2.979	3.450
C	-4.510	-3.185	4.090
C	-5.105	-1.911	4.748
C	-4.029	-1.128	5.540
C	-0.598	-3.843	6.033
C	0.591	-3.835	5.291
C	1.739	-4.436	5.809
C	1.708	-5.048	7.069
C	0.523	-5.058	7.809
C	-0.628	-4.456	7.290
O	-4.616	0.162	5.784
C	-4.059	0.853	6.924
C	-4.746	2.184	7.067
C	-5.859	2.323	7.909
C	-6.513	3.553	8.027
C	-6.061	4.657	7.297
C	-4.953	4.528	6.453
C	-4.300	3.299	6.341
O	-5.695	-1.086	3.739
O	-5.338	-3.728	3.065
C	-6.642	-4.141	3.520
C	-7.333	-4.861	2.392
C	-7.993	-4.134	1.390
C	-8.612	-4.792	0.326
C	-8.583	-6.190	0.253
C	-7.928	-6.924	1.247
C	-7.304	-6.261	2.308

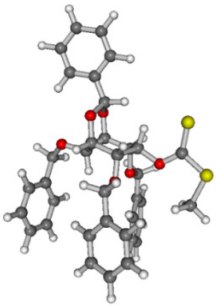
H	-3.121	-3.440	2.456
H	-4.397	-3.936	4.900
H	-5.887	-2.214	5.471
H	-3.860	-1.637	6.508
H	-2.132	0.306	1.530
H	-1.230	0.671	3.030
H	1.235	-0.007	3.172
H	3.380	0.000	1.912
H	3.361	0.007	-0.581
H	1.189	0.007	-1.804
H	-0.952	-0.006	-0.537
H	-2.705	-3.409	6.123
H	-1.557	-4.465	7.865
H	0.493	-5.536	8.790
H	2.607	-5.519	7.470
H	2.663	-4.432	5.228
H	0.599	-3.361	4.309
H	-3.574	-0.963	2.851
H	-6.532	-4.811	4.395
H	-7.229	-3.257	3.824
H	-8.011	-3.043	1.448
H	-9.123	-4.216	-0.448
H	-9.071	-6.705	-0.576
H	-7.902	-8.014	1.195
H	-6.788	-6.834	3.081
H	-4.209	0.236	7.829
H	-2.971	0.990	6.785
H	-3.433	3.200	5.685
H	-4.595	5.389	5.885
H	-6.570	5.619	7.389
H	-7.375	3.650	8.689
H	-6.213	1.461	8.479
H	-2.319	0.030	4.871
H	-5.845	-0.224	4.178

1.133CB

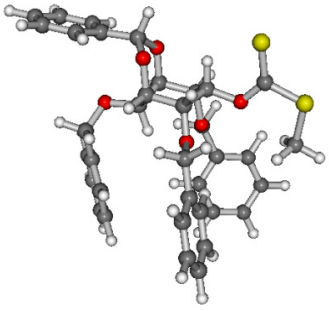
Final heat of formation =
–1768.031

C	0.000	0.000	0.000
C	0.000	0.000	1.401
C	1.221	0.000	2.086
C	2.426	-0.030	1.380
C	2.423	-0.045	-0.018
C	1.206	-0.027	-0.706
C	-1.316	0.159	2.164
O	-2.442	-0.370	1.456
C	-2.785	-1.752	1.707
C	-1.768	-2.509	2.566
C	-1.518	-1.662	3.805
O	-1.254	-0.264	3.522
C	-2.789	-1.706	4.680
C	-4.030	-1.204	3.894
C	-4.146	-1.752	2.449
O	-4.709	-3.073	2.515
C	-5.549	-3.401	1.386
C	-6.265	-4.695	1.668
C	-5.694	-5.924	1.309
C	-6.351	-7.124	1.591
C	-7.592	-7.107	2.236
C	-8.171	-5.886	2.598
C	-7.510	-4.689	2.315
O	-0.521	-2.827	1.948
C	-0.627	-3.809	0.903
C	0.722	-4.440	0.671
C	1.269	-5.307	1.631
C	2.513	-5.903	1.422
C	3.228	-5.640	0.247
C	2.693	-4.777	-0.712
C	1.447	-4.178	-0.497
O	-2.969	-3.053	5.143
C	-3.138	-3.156	6.575
C	-3.231	-4.611	6.949
C	-4.477	-5.214	7.169
C	-4.565	-6.570	7.499
C	-3.403	-7.338	7.610
C	-2.154	-6.747	7.391

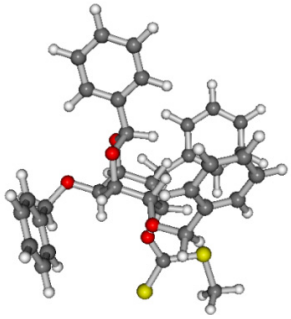
C	-2.071	-5.392	7.063
O	-5.233	-1.458	4.612
H	-4.835	-1.089	1.896
H	-2.640	-1.029	5.538
H	-0.661	-2.064	4.367
H	-2.272	-2.686	7.079
H	-4.050	-2.616	6.881
H	-6.276	-2.584	1.228
H	-4.935	-3.496	0.472
H	1.034	-3.494	-1.242
H	3.249	-4.564	-1.628
H	4.200	-6.108	0.082
H	2.927	-6.578	2.173
H	0.711	-5.512	2.547
H	-7.964	-3.735	2.595
H	-9.142	-5.867	3.097
H	-8.109	-8.043	2.454
H	-5.897	-8.074	1.306
H	-4.726	-5.939	0.803
H	-5.386	-4.614	7.082
H	-5.541	-7.026	7.671
H	-3.469	-8.397	7.870
H	-1.243	-7.342	7.482
H	-1.096	-4.930	6.893
H	-2.909	-2.237	0.725
H	-2.261	-3.442	2.898
H	-1.362	-4.580	1.206
H	-0.987	-3.342	-0.032
H	-0.952	0.020	-0.532
H	1.195	-0.028	-1.798
H	3.365	-0.067	-0.569
H	3.373	-0.045	1.924
H	1.220	0.014	3.176
H	-1.534	1.238	2.234
H	-3.935	-0.113	3.813
H	-5.417	-2.405	4.446



2.48CC
ΔE **0.0** kcal/mol



2.48CB
ΔE **2.5** kcal/mol



2.48BC
ΔE **3.8** kcal/mol

2.48CC

Final heat of formation =
–2641.965

C	6.007	-0.028	-0.542
C	5.010	-0.054	0.438
C	5.366	-0.085	1.793
C	6.712	-0.089	2.160

C	7.710	-0.062	1.177
C	7.357	-0.032	-0.175
C	3.554	-0.040	0.041
O	2.983	1.187	0.519

C	1.549	1.238	0.591
C	1.008	0.052	1.399
C	1.500	-1.199	0.683
O	2.936	-1.210	0.587
C	0.820	1.289	-0.786
C	0.923	-0.056	-1.526
C	0.759	-1.334	-0.685
O	-0.549	1.640	-0.559
C	-0.804	3.040	-0.685
C	-2.262	3.334	-0.414
C	-3.206	2.308	-0.275
C	-4.552	2.617	-0.049
C	-4.968	3.948	0.040
C	-4.028	4.976	-0.097
C	-2.684	4.669	-0.320
O	-0.014	-0.074	-2.636
O	-0.630	-1.602	-0.472
C	-0.914	-2.998	-0.238
C	-2.406	-3.199	-0.225
C	-3.171	-2.777	0.874
C	-4.556	-2.956	0.883
C	-5.193	-3.565	-0.204
C	-4.440	-3.990	-1.302
C	-3.054	-3.802	-1.312
O	1.494	0.032	2.745
C	0.750	0.871	3.642
C	-0.600	0.302	4.035
C	-1.767	1.069	3.925
C	-3.003	0.558	4.331
C	-3.082	-0.744	4.846
C	-1.922	-1.523	4.950
C	-0.690	-1.002	4.550
H	-0.094	0.063	1.374
H	1.279	-2.087	1.286
H	1.218	-2.170	-1.245
H	1.306	2.055	-1.417
H	1.342	2.190	1.101
H	3.482	-0.066	-1.064
H	1.395	0.964	4.529
H	0.619	1.887	3.225
H	-1.711	2.080	3.516
H	-3.903	1.162	4.239
H	-4.044	-1.150	5.166
H	-1.979	-2.536	5.354
H	0.215	-1.608	4.630
H	4.578	-0.108	2.547
H	6.989	-0.114	3.215
H	8.763	-0.066	1.466
H	8.131	-0.012	-0.944
H	5.726	-0.005	-1.598
H	-0.174	3.622	0.017
H	-0.537	3.373	-1.708
H	-0.453	-3.605	-1.040
H	-0.478	-3.323	0.725
H	-2.678	-2.303	1.725
H	-5.139	-2.625	1.744
H	-6.275	-3.712	-0.193
H	-4.931	-4.469	-2.151
H	-2.466	-4.135	-2.171
H	-1.955	5.478	-0.421
H	-4.342	6.019	-0.027
H	-6.019	4.186	0.215
H	-5.278	1.810	0.059
H	-2.878	1.271	-0.340
C	0.463	-0.101	-3.897
H	1.928	-0.095	-1.977
S	2.055	-0.115	-4.383
S	-0.829	-0.128	-5.096
C	-2.368	-0.090	-4.087
H	-3.187	-0.153	-4.816
H	-2.405	-0.944	-3.404
H	-2.440	0.844	-3.523

2.48CB

Final heat of formation = –2641.961

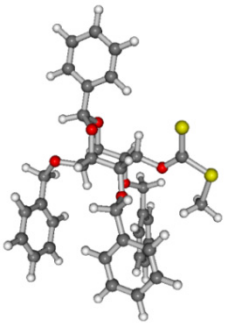
C	0.000	0.000	0.000
C	0.000	0.000	1.404
C	1.222	0.000	2.087
C	2.426	-0.006	1.373
C	2.422	-0.014	-0.024
C	1.202	-0.011	-0.711
C	-1.319	-0.030	2.141
O	-1.114	0.223	3.532
C	-2.316	0.176	4.302
C	-2.883	1.610	4.491
C	-1.902	2.401	5.362
C	-1.969	1.800	6.758
C	-1.328	0.382	6.714
C	-2.084	-0.465	5.680
O	-4.204	1.491	5.058
C	-4.396	1.963	6.394
O	-3.315	1.638	7.269
O	0.064	0.429	6.407
C	0.888	0.815	7.529
C	2.322	0.472	7.224
C	3.105	1.323	6.429
C	4.430	0.995	6.132
C	4.990	-0.186	6.631
C	4.219	-1.038	7.426
C	2.892	-0.710	7.718
O	-2.167	3.804	5.418
C	-1.626	4.547	4.312
C	-0.131	4.771	4.409
C	0.414	5.393	5.545
C	1.786	5.635	5.633
C	2.634	5.261	4.582
C	2.103	4.637	3.451
C	0.727	4.392	3.369
O	-1.405	-1.739	5.527
C	-2.117	-2.882	5.605
S	-3.740	-3.054	5.916
C	-4.823	3.430	6.464
C	-5.540	4.005	5.407
C	-6.022	5.313	5.509
C	-5.803	6.054	6.675
C	-5.104	5.476	7.739
C	-4.621	4.168	7.637
S	-1.109	-4.307	5.335
C	0.562	-3.614	4.997
H	-3.078	-0.434	3.784
H	-1.476	-0.086	7.706
H	-1.422	2.440	7.465
H	0.789	1.898	7.721
H	0.549	0.275	8.432
H	-1.798	-1.022	2.013
H	-2.008	0.717	1.698
H	0.318	3.897	2.485
H	2.758	4.335	2.632
H	3.705	5.457	4.648
H	2.196	6.126	6.517
H	-0.249	5.687	6.362
H	-0.949	0.007	-0.543
H	1.187	-0.013	-1.802
H	3.362	-0.020	-0.578
H	3.373	-0.005	1.916
H	1.222	0.011	3.177
H	2.291	-1.376	8.342
H	4.652	-1.958	7.824
H	6.028	-0.438	6.404
H	5.030	1.667	5.516
H	2.672	2.248	6.041
H	-2.991	2.079	3.499
H	-0.885	2.216	4.976
H	-1.869	4.060	3.350
H	-2.162	5.507	4.342
H	-5.712	3.422	4.501
H	-6.573	5.754	4.676
H	-6.182	7.075	6.756
H	-4.935	6.046	8.655
H	-4.077	3.714	8.466
H	-5.230	1.348	6.771
H	-3.083	-0.665	6.097
H	0.919	-3.025	5.847
H	1.208	-4.488	4.846
H	0.550	-2.996	4.094

2.48BC

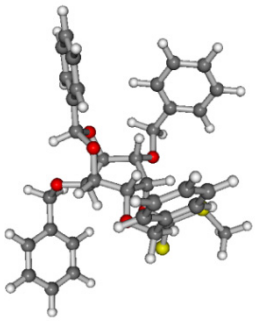
Final heat of formation = –2641.959

C	0.000	0.000	0.000
C	0.000	0.000	1.405
C	1.227	0.000	2.082
C	2.433	0.001	1.374
C	2.423	0.001	-0.023
C	1.202	-0.001	-0.709
C	-1.308	0.002	2.169
O	-2.134	-1.159	1.960

C	-1.672	-2.337	2.621
C	-0.867	-3.276	1.706
O	-1.688	-3.636	0.570
C	-2.916	-4.270	0.929
O	-3.662	-3.535	1.903
C	-2.884	-3.161	3.064
C	-2.453	-4.401	3.911
C	-0.933	-4.658	3.913
C	-0.355	-4.528	2.479
C	-3.759	-4.401	-0.314
C	-4.280	-3.253	-0.926
C	-5.048	-3.368	-2.086
C	-5.300	-4.629	-2.642
C	-4.781	-5.774	-2.033
C	-4.013	-5.659	-0.870
O	1.069	-4.480	2.455
C	1.733	-5.712	2.792
C	1.458	-6.850	1.829
C	1.141	-8.128	2.309
C	0.928	-9.191	1.424
C	1.020	-8.981	0.046
C	1.327	-7.705	-0.443
C	1.549	-6.649	0.441
O	-0.267	-3.677	4.769
C	0.263	-3.950	5.973
S	0.996	-2.736	6.827
O	-2.865	-4.294	5.273
C	-4.267	-4.570	5.479
C	-4.639	-6.020	5.251
C	-5.600	-6.373	4.293
C	-5.955	-7.713	4.099
C	-5.346	-8.714	4.861
C	-4.378	-8.371	5.814
C	-4.030	-7.034	6.009
S	0.128	-5.657	6.522
C	1.104	-5.610	8.065
H	-3.563	-2.540	3.663
H	-2.918	-5.294	3.452
H	-0.740	-5.665	4.309
H	-0.703	-5.423	1.929
H	-1.939	0.841	1.838
H	-1.107	0.133	3.248
H	1.238	-0.010	3.175
H	3.381	-0.003	1.915
H	3.362	0.001	-0.578
H	1.189	-0.001	-1.801
H	-0.952	-0.013	-0.535
H	-2.694	-5.281	1.334
H	-3.605	-6.553	-0.392
H	-4.975	-6.759	-2.462
H	-5.900	-4.716	-3.549
H	-5.453	-2.473	-2.560
H	-4.078	-2.278	-0.481
H	-1.069	-2.068	3.501
H	-4.441	-4.283	6.526
H	-4.890	-3.918	4.841
H	-6.069	-5.592	3.690
H	-6.705	-7.974	3.351
H	-5.621	-9.759	4.712
H	-3.902	-9.150	6.411
H	-3.272	-6.764	6.748
H	2.799	-5.443	2.774
H	1.492	-6.026	3.824
H	1.782	-5.652	0.061
H	1.396	-7.535	-1.519
H	0.850	-9.807	-0.647
H	0.684	-10.182	1.812
H	1.062	-8.293	3.386
H	0.003	-2.770	1.276
H	0.652	-4.906	8.771
H	1.066	-6.634	8.458
H	2.137	-5.314	7.855



2.54CB
ΔE **0.0** kcal/mol



2.54BB
ΔE **6.9** kcal/mol

2.54CB
Final heat of formation =
–2641.970

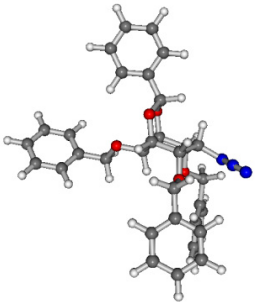
C	5.368	-0.177	-0.171
C	4.916	1.136	0.028
C	5.843	2.157	0.267
C	7.211	1.875	0.311
C	7.659	0.566	0.113
C	6.735	-0.457	-0.129
C	3.444	1.459	0.014
O	2.868	0.978	1.245
C	1.428	1.080	1.303
C	0.820	1.697	0.037
C	1.396	0.936	-1.152
O	2.839	0.823	-1.113
C	0.820	-0.508	-1.139
C	1.166	-1.168	0.206
C	0.853	-0.353	1.468
O	-0.551	-0.287	1.722
C	-0.884	-0.363	3.108
C	-2.384	-0.329	3.288
C	-2.917	-0.144	4.574
C	-4.298	-0.148	4.778
C	-5.166	-0.329	3.695
C	-4.640	-0.505	2.412
C	-3.256	-0.507	2.206
O	1.089	3.104	-0.096
C	0.133	3.947	0.575
C	-1.194	4.052	-0.147
C	-1.235	4.475	-1.487
C	-2.454	4.601	-2.154
C	-3.653	4.311	-1.490
C	-3.622	3.887	-0.159
C	-2.398	3.756	0.506
O	-0.590	-0.530	-1.357
C	-0.955	-0.426	-2.751
C	-2.409	-0.790	-2.904
C	-3.409	0.174	-2.713
C	-4.758	-0.169	-2.838
C	-5.121	-1.481	-3.161
C	-4.130	-2.449	-3.354
C	-2.782	-2.104	-3.224
O	0.515	-2.461	0.3340
C	1.150	-3.563	-0.104
S	0.150	-5.012	0.040
C	-1.442	-4.389	0.721
S	2.689	-3.676	-0.723
H	1.369	-0.841	2.314
H	1.334	-1.083	-1.931
H	1.121	1.442	-2.091

H	-0.782	0.603	-3.116
H	-0.323	-1.111	-3.345
H	-0.476	-1.303	3.533
H	-0.423	0.471	3.674
H	-2.379	3.415	1.544
H	-4.551	3.651	0.363
H	-4.606	4.417	-2.010
H	-2.474	4.935	-3.194
H	-0.300	4.699	-2.005
H	-2.245	0.004	5.424
H	-4.698	-0.005	5.783
H	-6.246	-0.329	3.852
H	-5.310	-0.641	1.561
H	-2.842	-0.637	1.207
H	-2.009	-2.860	-3.377
H	-4.408	-3.472	-3.611
H	-6.174	-1.747	-3.267
H	-5.528	0.590	-2.690
H	-3.129	1.200	-2.461
H	1.161	1.671	2.195
H	-0.267	1.515	0.049
H	-0.030	3.608	1.614
H	0.623	4.931	0.620
H	5.490	3.180	0.418
H	7.927	2.678	0.497
H	8.727	0.343	0.144
H	7.082	-1.480	-0.288
H	4.649	-0.971	-0.370
H	3.279	2.548	-0.049
H	2.253	-1.336	0.191
H	-1.853	-3.603	0.079
H	-2.111	-5.259	0.728
H	-1.311	-4.013	1.740

2.54CB

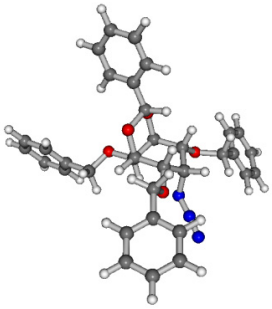
Final heat of formation = –2641.959

C	0.000	0.000	0.000
C	0.000	0.000	1.405
C	1.228	0.000	2.083
C	2.433	0.004	1.373
C	2.422	0.009	-0.024
C	1.201	0.005	-0.710
C	-1.308	-0.017	2.164
O	-2.019	-1.273	2.049
C	-1.415	-2.347	2.769
C	-1.692	-2.257	4.312
C	-2.218	-3.607	4.848
C	-1.174	-4.625	4.393
C	-1.362	-4.907	2.888
C	-1.901	-3.651	2.121
O	-0.488	-1.877	5.012
C	0.276	-3.023	5.452
O	0.175	-4.087	4.515
O	-2.356	-3.630	6.272
C	-3.590	-3.045	6.756
C	-4.781	-3.961	6.593
C	-4.947	-5.056	7.458
C	-6.028	-5.925	7.306
C	-6.960	-5.712	6.281
C	-6.803	-4.628	5.414
C	-5.721	-3.755	5.572
C	1.723	-2.615	5.615
C	2.032	-1.347	6.130
C	3.363	-0.977	6.339
C	4.397	-1.870	6.038
C	4.091	-3.134	5.525
C	2.760	-3.507	5.316
O	-3.366	-3.667	2.146
C	-4.145	-3.461	1.070
S	-3.288	-3.296	-0.502
C	-4.693	-3.234	-1.666
O	-2.205	-6.044	2.775
C	-2.228	-6.662	1.473
C	-0.898	-7.251	1.048
C	-0.342	-6.931	-0.198
C	0.872	-7.494	-0.605
C	1.547	-8.381	0.237
C	1.004	-8.702	1.487
C	-0.211	-8.144	1.888
S	-5.789	-3.409	1.257
H	-2.411	-1.444	4.481
H	-0.318	-2.328	2.647
H	-1.560	-3.676	1.077
H	-0.359	-5.122	2.476
H	-3.395	-2.848	7.819
H	-3.776	-2.077	6.260
H	-5.608	-2.913	4.887
H	-7.517	-4.461	4.606
H	-7.805	-6.392	6.162
H	-6.149	-6.769	7.988
H	-4.218	-5.225	8.253
H	2.518	-4.490	4.913
H	4.893	-3.835	5.285
H	5.437	-1.581	6.203
H	3.594	0.011	6.740
H	1.225	-0.651	6.360
H	-3.179	-3.858	4.373
H	-2.007	0.722	1.750
H	-1.134	0.229	3.225
H	1.238	-0.012	3.175
H	3.381	-0.001	1.914
H	3.362	0.015	-0.579
H	1.189	0.013	-1.802
H	-0.952	-0.007	-0.535
H	-2.986	-7.452	1.575
H	-2.586	-5.956	0.704
H	-0.635	-8.391	2.864
H	1.528	-9.395	2.148
H	2.496	-8.820	-0.076
H	1.294	-7.235	-1.579
H	-0.866	-6.232	-0.856
H	-1.256	-5.565	4.957
H	-5.328	-2.371	-1.439
H	-4.234	-3.129	-2.658
H	-5.282	-4.155	-1.607
H	-0.146	-3.354	6.418



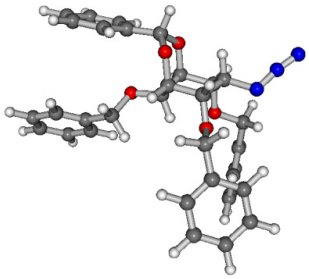
3.17CC

ΔE **0.0** kcal/mol



3.17BC

ΔE **0.6** kcal/mol



3.17CB

ΔE **2.5** kcal/mol

3.17CC

Final heat of formation = –1856.441

C	-0.069	-0.174	-0.051
C	-0.099	-0.100	1.349
C	1.110	-0.006	2.051
C	2.330	0.012	1.369
C	2.349	-0.061	-0.026
C	1.147	-0.156	-0.736
C	-1.412	-0.133	2.084
O	-1.846	-1.509	2.207
C	-3.120	-1.644	2.842
C	-2.948	-1.685	4.390
C	-2.255	-2.978	4.796
C	-3.266	-4.096	4.515
C	-3.425	-4.247	2.976
C	-3.838	-2.913	2.305
O	-4.173	-1.497	5.121
C	-5.101	-2.584	5.116
O	-4.488	-3.873	5.241
O	-1.863	-2.871	6.165
C	-0.911	-3.878	6.561
C	-0.492	-3.612	7.983
C	0.556	-2.722	8.262
C	0.931	-2.455	9.581
C	0.259	-3.076	10.639
C	-0.787	-3.963	10.372
C	-1.159	-4.228	9.051
C	-6.037	-2.404	6.288
C	-7.420	-2.381	6.088
C	-8.288	-2.229	7.175
C	-7.768	-2.100	8.466
C	-6.382	-2.123	8.667
C	-5.516	-2.275	7.583
N	-3.736	-3.093	0.839
N	-3.733	-2.093	0.123
O	-2.163	-4.732	2.514
C	-2.247	-5.764	1.511
C	-0.858	-6.103	1.033
C	-0.474	-7.440	0.862
C	0.794	-7.759	0.368
C	1.697	-6.741	0.052
C	1.324	-5.404	0.231
C	0.052	-5.085	0.713
H	-1.373	-3.129	4.149
H	-2.332	-0.825	4.687
H	-3.750	-0.766	2.600
H	-4.217	-4.991	2.779
H	-2.905	-5.065	4.884
H	-5.691	-2.556	4.177
H	-1.359	-4.885	6.485
H	-0.037	-3.843	5.884
H	-1.978	-4.920	8.843
H	-1.313	-4.452	11.194
H	0.554	-2.871	11.670
H	1.752	-1.764	9.784
H	1.081	-2.238	7.435
H	-4.435	-2.291	7.725
H	-5.976	-2.020	9.675
H	-8.442	-1.981	9.316
H	-9.367	-2.211	7.014
H	-7.823	-2.481	5.077
H	-2.734	-6.663	1.935
H	-2.863	-5.403	0.669
H	-2.183	0.434	1.530
H	-1.298	0.325	3.082
H	1.095	0.053	3.142
H	3.265	0.090	1.927
H	3.300	-0.042	-0.562
H	1.158	-0.211	-1.826
H	-1.008	-0.246	-0.605
H	-0.237	-4.044	0.860
H	2.026	-4.604	-0.009
H	2.690	-6.987	-0.327
H	1.080	-8.805	0.239
H	-1.172	-8.240	1.121
H	-4.908	-2.774	2.537
N	-3.720	-1.262	-0.669

3.17BC

Final heat of formation = –1856.440

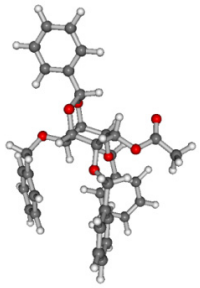
C	0.004	-0.768	0.054
C	0.011	-0.053	1.263
C	1.161	0.658	1.625
C	2.285	0.666	0.793
C	2.270	-0.048	-0.407
C	1.127	-0.768	-0.773
C	-1.205	-0.055	2.152
O	-1.449	-1.398	2.608
C	-2.708	-1.577	3.243
C	-2.949	-3.111	3.344
C	-3.031	-3.569	4.798
C	-4.275	-2.865	5.370
C	-4.095	-1.313	5.358
C	-2.832	-0.828	4.603
O	-4.146	-3.523	2.643
C	-5.350	-3.038	3.224
O	-5.442	-3.295	4.633
O	-3.106	-4.991	4.815
C	-2.930	-5.554	6.128
C	-2.847	-7.053	6.006
C	-1.616	-7.680	5.767
C	-1.539	-9.069	5.631
C	-2.697	-9.846	5.733
C	-3.931	-9.230	5.968
C	-4.003	-7.841	6.105
C	-6.516	-3.717	2.550
C	-6.537	-5.113	2.432
C	-7.623	-5.745	1.824
C	-8.695	-4.988	1.335
C	-8.677	-3.596	1.453
C	-7.587	-2.963	2.059
N	-1.595	-1.045	5.388
O	-4.030	-0.762	6.673
C	-5.327	-0.638	7.300
C	-5.152	-0.051	8.675
C	-4.913	1.322	8.834
C	-4.734	1.869	10.106
C	-4.796	1.047	11.237
C	-5.035	-0.322	11.089
C	-5.210	-0.866	9.813
H	-2.130	-3.616	2.820
H	-3.503	-1.161	2.590
H	-2.951	0.250	4.415
H	-4.972	-0.889	4.830
H	-2.003	-5.151	6.581
H	-3.777	-5.279	6.784
H	-4.966	-7.359	6.286
H	-4.837	-9.833	6.049
H	-2.639	-10.931	5.630
H	-0.574	-9.546	5.449
H	-0.711	-7.073	5.685
H	-5.417	-1.939	3.062
H	-7.569	-1.874	2.150
H	-9.509	-3.002	1.071
H	-9.543	-5.485	0.859
H	-7.635	-6.832	1.730
H	-5.693	-5.690	2.812
H	-2.134	-3.226	5.344
H	-2.095	0.300	1.594
H	-1.043	0.627	3.005
H	1.178	1.208	2.568
H	3.176	1.225	1.087
H	3.147	-0.046	-1.056
H	1.112	-1.329	-1.710
H	-0.884	-1.335	-0.228
H	-5.965	0.012	6.672
H	-5.817	-1.626	7.365
H	-5.395	-1.937	9.699
H	-5.085	-0.967	11.968
H	-4.660	1.474	12.231
H	-4.548	2.938	10.218
H	-4.864	1.964	7.952
H	-4.470	-3.175	6.405
N	-1.263	-0.158	6.178
N	-0.813	0.581	6.929

3.17CB

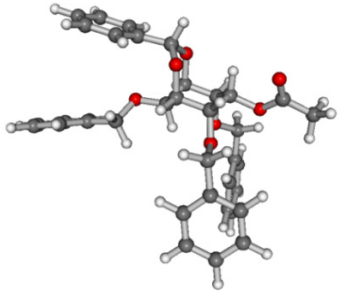
Final heat of formation = –1856.437

C	0.151	0.847	0.701
C	0.143	-0.211	1.619
C	1.183	-1.154	1.580
C	2.208	-1.037	0.638
C	2.210	0.026	-0.269
C	1.180	0.970	-0.236

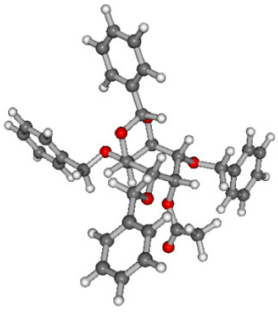
C	-0.968	-0.355	2.624
O	-1.860	-1.399	2.171
C	-3.113	-1.474	2.836
C	-4.045	-2.256	1.874
C	-3.500	-3.673	1.746
C	-3.751	-4.367	3.090
C	-2.839	-3.699	4.159
C	-3.128	-2.188	4.217
O	-5.387	-2.190	2.415
C	-5.998	-3.415	2.819
O	-5.115	-4.267	3.560
C	-6.739	-4.142	1.699
C	-7.055	-5.500	1.840
C	-7.829	-6.149	0.873
C	-8.302	-5.443	-0.236
C	-8.004	-4.084	-0.370
C	-7.233	-3.434	0.596
O	-4.063	-4.296	0.593
C	-3.429	-5.539	0.241
C	-3.685	-5.840	-1.213
C	-3.152	-5.008	-2.210
C	-3.369	-5.290	-3.560
C	-4.118	-6.414	-3.931
C	-4.653	-7.247	-2.945
C	-4.439	-6.957	-1.593
N	-2.221	-1.568	5.217
O	-1.462	-3.949	3.878
C	-0.924	-5.072	4.609
C	0.552	-5.169	4.337
C	1.066	-6.168	3.499
C	2.439	-6.250	3.246
C	3.312	-5.326	3.826
C	2.808	-4.322	4.662
C	1.437	-4.246	4.916
H	-3.107	-4.122	5.143
H	-3.530	-0.457	2.976
H	-4.045	-1.761	0.893
H	-1.531	0.593	2.712
H	-0.569	-0.618	3.616
H	-1.109	-4.917	5.688
H	-1.426	-6.010	4.307
H	-4.868	-7.601	-0.822
H	-5.244	-8.120	-3.227
H	-4.285	-6.637	-4.986
H	-2.949	-4.637	-4.326
H	-2.569	-4.131	-1.922
H	1.043	-3.462	5.566
H	3.487	-3.601	5.120
H	4.384	-5.389	3.632
H	2.826	-7.035	2.594
H	0.384	-6.890	3.043
H	1.180	-1.985	2.288
H	3.011	-1.776	0.616
H	3.015	0.119	-1.001
H	1.177	1.803	-0.941
H	-0.655	1.584	0.725
H	-3.500	-5.438	3.035
H	-2.404	-3.597	1.626
H	-2.340	-5.453	0.427
H	-3.818	-6.363	0.868
H	-6.688	-6.046	2.710
H	-8.066	-7.208	0.990
H	-8.905	-5.950	-0.993
H	-8.370	-3.527	-1.234
H	-6.997	-2.374	0.495
H	-6.744	-3.100	3.567
H	-4.168	-2.101	4.569
N	-2.684	-0.637	5.882
N	-2.975	0.234	6.571



4.22CC
ΔE **0.0** kcal/mol



4.22CB
ΔE **2.5** kcal/mol



4.22BC
ΔE **7.5** kcal/mol

4.22CC
Final heat of formation = –1920.754

C	6.001	-0.039	-1.166
C	5.049	-0.001	-0.143
C	5.465	0.083	1.193
C	6.826	0.130	1.497
C	7.779	0.090	0.471
C	7.366	0.006	-0.861
C	3.576	-0.059	-0.469
O	2.96	1.113	0.064
C	1.527	1.066	0.213
C	1.110	-0.147	1.032
C	1.634	-1.367	0.266
O	3.058	-1.283	0.073
C	0.743	1.092	-1.136
C	0.858	-0.252	-1.901
C	0.810	-1.530	-1.039
O	-0.637	1.389	-0.902
C	-0.897	2.803	-0.774
C	-2.385	3.025	-0.687
C	-3.093	2.660	0.468
C	-4.472	2.868	0.548
C	-5.158	3.451	-0.523
C	-4.462	3.819	-1.676
C	-3.082	3.602	-1.757
O	-0.159	-0.377	-2.930
O	-0.514	-1.872	-0.609
C	-1.156	-2.883	-1.406
C	-2.572	-3.071	-0.924
C	-3.091	-4.358	-0.727
C	-4.421	-4.537	-0.333
C	-5.242	-3.426	-0.121
C	-4.727	-2.138	-0.307
C	-3.402	-1.959	-0.709
O	1.666	-0.034	2.345
C	0.993	-0.838	3.331
C	-0.337	-0.262	3.771
C	-0.380	0.966	4.452
C	-1.598	1.505	4.871
C	-2.793	0.821	4.615
C	-2.763	-0.398	3.933
C	-1.540	-0.935	3.514
H	0.009	-0.187	1.068
H	1.495	-2.291	0.844
H	1.243	-2.361	-1.624
H	1.189	1.876	-1.774
H	1.292	1.986	0.763
H	3.450	-0.069	-1.570
H	0.852	-1.872	2.969
H	1.692	-0.875	4.179
H	0.552	1.500	4.650
H	-1.617	2.457	5.406
H	-3.744	1.239	4.948
H	-3.690	-0.934	3.724
H	-1.520	-1.886	2.977

H	4.711	0.117	1.980
H	7.148	0.198	2.538
H	8.843	0.126	0.712
H	8.106	-0.023	-1.663
H	5.675	-0.102	-2.207
H	-0.403	3.203	0.131
H	-0.480	3.334	-1.649
H	-1.155	-2.570	-2.465
H	-0.599	-3.837	-1.330
H	-2.449	-5.228	-0.880
H	-4.813	-5.545	-0.184
H	-6.280	-3.562	0.190
H	-5.362	-1.266	-0.142
H	-2.995	-0.956	-0.847
H	-2.538	3.888	-2.661
H	-4.991	4.275	-2.515
H	-6.235	3.620	-0.456
H	-5.011	2.581	1.453
H	-2.561	2.207	1.307
C	0.064	0.307	-4.092
H	1.830	-0.226	-2.414
O	1.057	0.977	-4.303
C	-1.084	0.107	-5.051
H	-2.008	0.508	-4.612
H	-0.865	0.619	-5.993
H	-1.248	-0.963	-5.235

4.22CB

Final heat of formation =
–1920.750

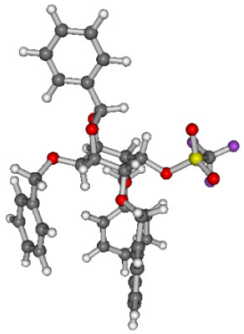
C	0.000	0.000	0.000
C	0.000	0.000	1.401
C	1.226	0.000	2.084
C	2.428	-0.000	1.373
C	2.421	0.011	-0.027
C	1.203	0.012	-0.713
C	-1.297	0.050	2.168
O	-1.250	-0.906	3.242
C	-2.369	-0.862	4.126
C	-2.674	-2.324	4.532
C	-1.480	-2.848	5.319
C	-1.490	-2.123	6.669
C	-1.155	-0.622	6.424
C	-2.145	-0.027	5.402
O	-3.913	-2.309	5.281
C	-3.869	-2.727	6.645
O	-2.753	-2.191	7.365
C	-4.042	-4.233	6.837
C	-3.620	-4.841	8.027
C	-3.872	-6.197	8.255
C	-4.557	-6.955	7.301
C	-4.996	-6.347	6.121
C	-4.746	-4.991	5.893
O	-1.530	-4.273	5.365
C	-0.334	-4.876	5.873
C	-0.258	-6.321	5.442
C	-0.575	-6.697	4.128
C	-0.449	-8.027	3.722
C	0.004	-8.999	4.621
C	0.321	-8.633	5.933
C	0.184	-7.302	6.340
O	-1.761	1.315	4.996
C	-2.106	2.337	5.838
C	-1.709	3.668	5.247
O	0.199	-0.465	5.988
C	1.121	-0.294	7.086
C	2.502	-0.0519	6.535
C	3.375	-1.123	6.297
C	4.650	-0.899	5.771
C	5.067	0.403	5.478
C	4.204	1.479	5.711
C	2.930	1.250	6.236
O	-2.674	2.177	6.901
H	-1.309	-0.085	7.376
H	-3.254	-0.458	3.603
H	-2.824	-2.927	3.625
H	-2.146	-0.178	1.495
H	-1.453	1.061	2.582
H	0.796	0.564	7.703
H	1.125	-1.192	7.731
H	0.417	-7.023	7.370
H	0.665	-9.386	6.644
H	0.104	-10.038	4.302
H	-0.704	-8.307	2.698
H	-0.936	-5.939	3.431
H	2.256	2.090	6.420
H	4.526	2.497	5.486
H	6.064	0.580	5.072
H	5.322	-1.741	5.594
H	3.053	-2.140	6.529
H	1.228	-0.016	3.175
H	3.375	-0.006	1.915
H	3.362	0.012	-0.581
H	1.189	0.011	-1.804
H	-0.950	-0.014	-0.540
H	-0.727	-2.542	7.345
H	-0.564	-2.528	4.787
H	0.544	-4.321	5.482
H	-0.301	-4.818	6.977
H	-3.090	-4.244	8.771
H	-3.532	-6.663	9.182
H	-4.751	-8.014	7.478
H	-5.533	-6.932	5.372
H	-5.086	-4.514	4.973
H	-4.739	-2.226	7.099
H	-3.109	0.035	5.926
H	-0.762	3.596	4.699
H	-2.486	3.989	4.537
H	-1.639	4.414	6.046

4.22BC

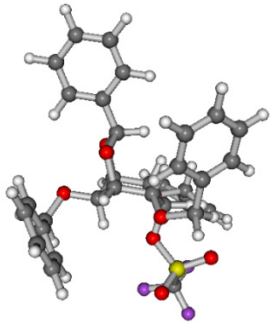
Final heat of formation =
–1920.742

C	0.000	0.000	0.000
C	0.000	0.000	1.401
C	1.226	0.000	2.083
C	2.429	0.001	1.375
C	2.420	0.008	-0.024
C	1.203	0.008	-0.711
C	-1.294	-0.024	2.170
O	-1.536	-1.368	2.626
C	-2.813	-1.563	3.222
C	-3.031	-3.102	3.318
C	-3.134	-3.563	4.769
C	-4.400	-2.876	5.316
C	-4.259	-1.319	5.291
C	-2.983	-0.817	4.580
O	-4.208	-3.535	2.595
C	-5.433	-3.079	3.153
O	-5.545	-3.333	4.562
O	-3.208	-4.987	4.784
C	-2.971	-5.551	6.086
C	-3.040	-7.053	5.983
C	-1.869	-7.821	5.911
C	-1.937	-9.213	5.802
C	-3.180	-9.851	5.759
C	-4.354	-9.092	5.824
C	-4.283	-7.702	5.938
C	-6.571	-3.788	2.462
C	-6.540	-5.181	2.316
C	-7.603	-5.839	1.696
C	-8.703	-5.113	1.223
C	-8.736	-3.724	1.369
C	-7.669	-3.064	1.987
O	-1.807	-1.059	5.382
C	-1.235	-0.112	6.208
C	-1.802	1.292	6.210
O	-4.282	-0.735	6.595
C	-5.604	-0.710	7.181
C	-5.526	-0.039	8.526
C	-5.914	1.300	8.679
C	-5.827	1.929	9.924
C	-5.347	1.223	11.031
C	-4.955	-0.112	10.889
C	-5.047	-0.739	9.644
O	-0.289	-0.460	6.878
H	-2.194	-3.591	2.807
H	-3.595	-1.158	2.547
H	-3.089	0.262	4.398
H	-5.118	-0.928	4.710
H	-1.978	-5.233	6.456
H	-3.732	-5.191	6.804
H	-5.198	-7.109	5.986
H	-5.327	-9.587	5.792
H	-3.235	-10.938	5.675
H	-1.018	-9.800	5.750
H	-0.898	-7.322	5.940
H	-5.524	-1.983	2.985

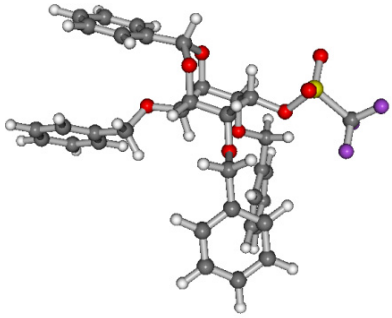
H	-7.691	-1.977	2.100
H	-9.591	-3.153	1.000
H	-9.533	-5.631	0.738
H	-7.575	-6.924	1.578
H	-5.675	-5.734	2.684
H	-2.250	-3.217	5.329
H	-2.134	0.305	1.527
H	-1.232	0.667	3.032
H	1.235	-0.011	3.175
H	3.378	0.001	1.916
H	3.361	0.015	-0.577
H	1.190	0.011	-1.803
H	-0.951	-0.008	-0.538
H	-6.290	-0.157	6.510
H	-5.992	-1.739	7.281
H	-4.740	-1.782	9.535
H	-4.580	-0.667	11.750
H	-5.279	1.712	12.004
H	-6.137	2.970	10.031
H	-6.291	1.852	7.814
H	-4.605	-3.184	6.349
H	-2.852	1.281	6.529
H	-1.208	1.889	6.908
H	-1.747	1.753	5.212



4.23CC
ΔE **0.0** kcal/mol



4.23BC
ΔE **0.6** kcal/mol



4.23CB
ΔE **1.9** kcal/mol

4.23CC

Final heat of formation = –2653.909

C	1.727	4.145	-0.934
C	0.575	4.436	-0.191
C	0.713	5.069	1.055
C	1.976	5.410	1.543
C	3.121	5.122	0.788
C	2.995	4.485	-0.448
C	-0.802	4.086	-0.715
O	-1.487	3.098	0.078
C	-0.996	1.768	-0.100
C	-1.456	0.919	1.078
O	-2.891	0.833	1.124
C	-3.555	0.428	-0.076
O	-2.993	0.987	-1.272
C	-1.561	1.085	-1.350
C	-0.820	-0.266	-1.565
C	-0.943	-1.160	-0.312
C	-0.730	-0.462	1.044
C	-4.994	0.876	0.012
C	-6.031	-0.049	-0.130
C	-7.364	0.369	-0.058
C	-7.659	1.717	0.158
C	-6.620	2.646	0.302
C	-5.291	2.229	0.228
O	0.665	-0.286	1.290
C	0.990	-0.268	2.698
C	2.474	-0.081	2.865
C	3.067	1.165	2.612
C	4.442	1.340	2.774
C	5.242	0.273	3.197
C	4.661	-0.972	3.450
C	3.285	-1.147	3.280
O	-0.005	-2.291	-0.432
S	-0.612	-3.813	-0.691
C	-0.076	-4.622	0.975
O	0.527	0.077	-1.877
C	1.129	-0.718	-2.921
C	2.585	-0.349	-3.045
C	3.157	-0.131	-4.305
C	4.522	0.148	-4.428
C	5.325	0.225	-3.287
C	4.756	0.021	-2.024
C	3.396	-0.269	-1.902
O	0.203	-4.436	-1.746
H	0.105	1.750	-0.141
H	-1.380	1.683	-2.252
H	-1.294	-0.790	-2.414
H	-1.173	-1.102	1.831
H	-1.193	1.418	2.020
H	-3.530	-0.678	-0.151
H	-0.731	3.764	-1.769
H	-1.459	4.966	-0.680
H	-0.179	5.295	1.642
H	2.070	5.910	2.508
H	4.107	5.396	1.165
H	3.882	4.250	-1.038
H	1.634	3.644	-1.900
H	-4.471	2.939	0.341
H	-6.851	3.699	0.472
H	-8.698	2.046	0.217
H	-8.171	-0.357	-0.169
H	-5.797	-1.104	-0.298
H	0.447	0.552	3.203
H	0.669	-1.220	3.160
H	1.033	-1.789	-2.674
H	0.606	-0.539	-3.879
H	2.531	-0.182	-5.199
H	4.956	0.312	-5.417
H	6.390	0.447	-3.380
H	5.377	0.083	-1.128
H	2.950	-0.424	-0.918
H	2.832	-2.123	3.473
H	5.280	-1.809	3.778
H	6.316	0.413	3.331
H	4.890	2.315	2.575
H	2.448	2.002	2.282
H	-1.959	-1.579	-0.309
O	-2.092	-3.793	-0.711
F	-0.460	-5.905	0.961
F	-0.679	-3.984	1.994
F	1.249	-4.546	1.118

4.23BC

Final heat of formation = –2653.908

C	4.422	-0.981	-3.298
C	4.405	0.150	-2.470
C	5.608	0.819	-2.205
C	6.809	0.372	-2.764
C	6.819	-0.756	-3.587
C	5.623	-1.434	-3.848
C	3.107	0.675	-1.908
O	2.302	-0.419	-1.437

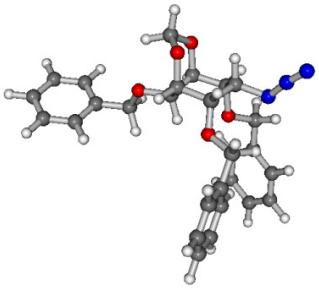
C	0.951	-0.068	-1.169
C	0.079	-1.356	-1.267
C	-0.618	-1.676	0.058
C	-1.548	-0.476	0.321
C	-0.743	0.852	0.480
C	0.761	0.703	0.158
O	-0.914	-1.249	-2.309
C	-1.924	-0.272	-2.047
O	-2.513	-0.406	-0.753
O	-1.310	-2.915	-0.085
C	-1.409	-3.690	1.122
C	-2.414	-3.178	2.136
C	-3.779	-3.117	1.811
C	-4.709	-2.651	2.742
C	-4.287	-2.243	4.014
C	-2.931	-2.300	4.346
C	-2.001	-2.765	3.410
C	-3.011	-0.431	-3.081
C	-3.591	-1.689	-3.293
C	-4.605	-1.837	-4.241
C	-5.046	-0.732	-4.980
C	-4.470	0.522	-4.767
C	-3.453	0.671	-3.818
O	1.436	-0.062	1.223
S	2.210	0.727	2.455
C	3.915	-0.159	2.264
O	-0.954	1.356	1.798
C	-0.902	2.796	1.918
C	-1.990	3.519	1.151
C	-3.326	3.095	1.228
C	-4.329	3.786	0.545
C	-4.011	4.916	-0.216
C	-2.684	5.347	-0.299
C	-1.680	4.646	0.377
O	1.661	0.273	3.742
H	0.728	-2.182	-1.579
H	0.596	0.623	-1.959
H	1.243	1.690	0.110
H	-1.153	1.569	-0.255
H	-1.701	-4.691	0.773
H	-0.414	-3.773	1.599
H	-0.941	-2.801	3.671
H	-2.594	-1.977	5.333
H	-5.015	-1.881	4.742
H	-5.767	-2.609	2.478
H	-4.107	-3.424	0.816
H	-1.477	0.742	-2.134
H	-3.002	1.652	-3.650
H	-4.811	1.386	-5.341
H	-5.838	-0.852	-5.722
H	-5.053	-2.818	-4.408
H	-3.233	-2.541	-2.715
H	0.129	-1.756	0.862
H	2.541	1.215	-2.695
H	3.317	1.394	-1.096
H	5.606	1.695	-1.551
H	7.738	0.901	-2.548
H	7.756	-1.111	-4.019
H	5.625	-2.320	-4.486
H	3.491	-1.514	-3.494
H	-1.008	2.965	2.999
H	0.089	3.180	1.624
H	-0.641	4.982	0.308
H	-2.429	6.225	-0.895
H	-4.796	5.457	-0.748
H	-5.363	3.442	0.607
H	-3.574	2.210	1.818
H	-2.143	-0.615	1.229
O	2.408	2.155	2.115
F	4.675	0.197	3.312
F	4.509	0.226	1.128
F	3.744	-1.486	2.264

4.23CC

Final heat of formation = –2653.906

C	2.694	2.136	-4.044
C	2.147	2.037	-2.757
C	2.996	2.149	-1.644
C	4.365	2.356	-1.821
C	4.903	2.464	-3.109
C	4.064	2.355	-4.221
C	0.665	1.845	-2.569
O	0.445	0.739	-1.668
C	-0.919	0.401	-1.462
C	-0.988	-1.143	-1.346
C	-0.223	-1.556	-0.095
C	-1.061	-1.100	1.106
C	-1.033	0.455	1.150
C	-1.554	1.002	-0.191
O	-2.387	-1.512	-1.329
C	-2.893	-2.140	-0.150
O	-2.446	-1.506	1.053
C	-2.730	-3.658	-0.132
C	-2.801	-4.353	1.082
C	-2.767	-5.750	1.098
C	-2.672	-6.465	-0.099
C	-2.619	-5.774	-1.314
C	-2.655	-4.378	-1.331
O	0.084	-2.946	-0.168
C	1.006	-3.388	0.843
C	1.669	-4.668	0.397
C	2.442	-4.694	-0.773
C	3.081	-5.867	-1.175
C	2.961	-7.031	-0.405
C	2.192	-7.015	0.760
C	1.547	-5.839	1.155
O	-1.406	2.468	-0.242
S	-2.761	3.339	0.155
C	-1.913	5.047	-0.155
O	0.282	0.931	1.428
C	0.485	1.240	2.826
C	1.878	1.779	3.010
C	2.893	0.976	3.550
C	4.187	1.479	3.716
C	4.479	2.792	3.339
C	3.474	3.601	2.797
C	2.182	3.097	2.636
O	-3.054	3.226	1.600
H	-1.732	0.786	1.937
H	-1.532	0.713	-2.326
H	-0.522	-1.587	-2.238
H	0.182	1.638	-3.542
H	0.209	2.758	-2.150
H	-0.266	1.987	3.140
H	0.346	0.335	3.445
H	0.935	-5.831	2.060
H	2.089	-7.921	1.360
H	3.465	-7.948	-0.717
H	3.680	-5.875	-2.087
H	2.533	-3.787	-1.374
H	1.397	3.729	2.216
H	3.697	4.629	2.505
H	5.488	3.188	3.471
H	4.967	0.845	4.142
H	2.665	-0.049	3.847
H	2.577	2.058	-0.641
H	5.016	2.436	-0.948
H	5.974	2.629	-3.244
H	4.477	2.431	-5.229
H	2.043	2.038	-4.916
H	-0.639	-1.481	2.049
H	0.714	-0.971	-0.069
H	1.768	-2.601	1.004
H	0.481	-3.554	1.801
H	-2.883	-3.791	2.014
H	-2.819	-6.283	2.050
H	-2.644	-7.555	-0.087
H	-2.547	-6.326	-2.253
H	-2.615	-3.836	-2.277
H	-3.971	-1.915	-0.178
H	-2.623	0.748	-0.246
O	-3.818	3.156	-0.859
F	-2.851	5.987	0.024
F	-1.442	5.115	-1.406
F	-0.916	5.231	0.718

4). C1,C3-*O*-Methylidene *neo*-inositol derivatives



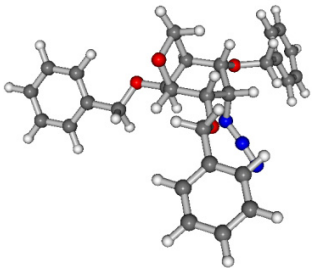
3.14CB

ΔE **0.0** kcal/mol

3.14CB

Final heat of formation = –1625.315

C	-1.157	-1.440	0.676
C	-0.521	-0.331	1.251
C	0.491	0.320	0.530
C	0.858	-0.128	-0.739
C	0.223	-1.241	-1.302
C	-0.784	-1.898	-0.591
C	-0.926	0.172	2.612
O	-1.638	1.417	2.444
C	-2.369	1.870	3.575
C	-3.478	2.794	3.013
C	-2.800	4.016	2.387
C	-2.205	4.838	3.540
C	-1.045	4.031	4.178
C	-1.565	2.656	4.649
O	-4.361	3.135	4.109
C	-4.449	4.535	4.340
O	-3.171	5.122	4.580
O	0.009	3.955	3.218
C	1.328	4.148	3.777
C	2.332	4.187	2.655
C	2.361	5.268	1.761
C	3.289	5.306	0.719
C	4.207	4.261	0.560
C	4.189	3.181	1.446
C	3.253	3.144	2.485
O	-3.742	4.727	1.571
N	-0.426	1.870	5.198
N	-0.648	1.195	6.207
N	-0.708	0.525	7.138
H	-0.705	4.586	5.071
H	-1.796	5.795	3.179
H	-1.966	3.649	1.764
H	-4.052	2.245	2.251
H	-2.857	1.013	4.080
H	1.342	5.103	4.339
H	1.564	3.332	4.478
H	-0.041	0.336	3.249
H	-1.582	-0.563	3.113



3.14BC

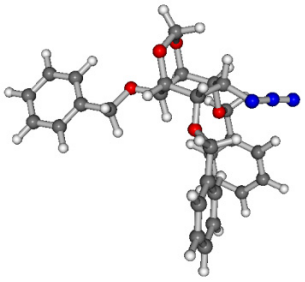
ΔE **5.0** kcal/mol

H	-5.023	4.662	5.265
H	-4.941	5.030	3.488
H	0.985	1.190	0.967
H	1.646	0.387	-1.290
H	-1.284	-2.766	-1.025
H	-1.949	-1.951	1.228
H	3.238	2.297	3.174
H	4.904	2.364	1.328
H	3.302	6.154	0.032
H	1.647	6.085	1.886
H	-2.286	2.867	5.455
H	0.514	-1.595	-2.293
H	4.937	4.293	-0.250
C	-3.112	5.564	0.578
C	-4.180	6.143	-0.311
H	-2.541	6.376	1.063
H	-2.402	4.953	-0.009
C	-4.660	7.444	-0.102
C	-5.665	7.972	-0.917
C	-6.202	7.201	-1.952
C	-5.731	5.901	-2.168
C	-4.726	5.377	-1.352
H	-4.241	8.046	0.707
H	-6.028	8.987	-0.745
H	-6.985	7.612	-2.591
H	-6.145	5.297	-2.977
H	-4.358	4.362	-1.520

3.14BC

Final heat of formation = –1625.307

C	-4.919	-7.779	2.321
C	-5.630	-6.706	2.876
C	-6.772	-6.973	3.646
C	-7.195	-8.286	3.857
C	-6.481	-9.351	3.295
C	-5.341	-9.095	2.527
C	-5.169	-5.288	2.666
O	-4.562	-4.812	3.883
C	-4.283	-3.418	3.885
C	-3.974	-3.023	5.359
C	-2.542	-2.510	5.509



3.14CC

ΔE **5.0** kcal/mol

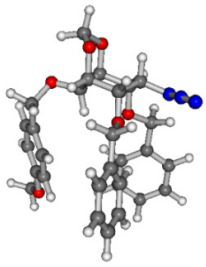
C	-2.478	-1.226	4.659
C	-2.725	-1.544	3.149
C	-3.171	-3.003	2.876
O	-4.891	-2.023	5.863
C	-4.751	-0.775	5.212
O	-3.424	-0.267	5.183
O	-1.572	-1.306	2.342
C	-1.362	0.094	2.050
C	-0.131	0.233	1.195
C	-0.202	0.025	-0.189
C	0.941	0.130	-0.983
C	2.172	0.448	-0.398
C	2.253	0.658	0.981
C	1.106	0.551	1.772
O	-2.284	-2.297	6.892
N	-2.043	-3.958	2.979
N	-1.371	-4.153	1.963
N	-0.676	-4.458	1.104
H	-4.141	-3.905	5.988
H	-3.549	-0.885	2.809
H	-1.841	-3.258	5.098
H	-5.348	-0.054	5.783
H	-1.501	-0.734	4.750
H	-5.195	-2.866	3.579
H	-5.148	-0.842	4.174
H	-6.025	-4.632	2.411
H	-4.448	-5.249	1.830
H	-2.253	0.487	1.524
H	-1.246	0.665	2.988
H	-1.162	-0.222	-0.647
H	0.874	-0.031	-2.060
H	3.210	0.907	1.441
H	1.170	0.714	2.850
H	-7.328	-6.142	4.087
H	-8.086	-8.482	4.456
H	-4.779	-9.922	2.089
H	-4.024	-7.580	1.726
H	-3.577	-3.039	1.852
H	3.066	0.532	-1.018
H	-6.813	-10.378	3.456
C	-0.900	-2.133	7.195

C	-0.712	-1.952	8.684
H	-0.325	-3.015	6.846
H	-0.489	-1.249	6.668
C	0.559	-2.139	9.245
C	0.771	-1.933	10.610
C	-0.291	-1.545	11.434
C	-1.561	-1.365	10.880
C	-1.773	-1.565	9.512
H	1.391	-2.453	8.610
H	1.766	-2.084	11.034
H	-0.128	-1.388	12.501
H	-2.397	-1.068	11.517
H	-2.763	-1.431	9.076

3.14CC

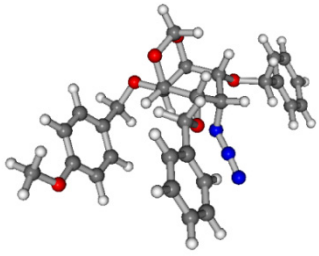
Final heat of formation = –1625.307284

C	-0.210	0.327	0.017
O	-0.019	-0.040	1.375
C	1.351	-0.092	1.812
C	2.076	1.211	1.495
C	1.967	1.393	-0.023
O	0.590	1.407	-0.439
C	2.161	-1.294	1.239
C	2.489	-1.116	-0.269
C	2.861	0.323	-0.711
O	4.200	0.680	-0.364
C	5.154	0.555	-1.439
C	6.532	0.862	-0.913
C	7.388	1.719	-1.618
C	8.686	1.966	-1.160
C	9.137	1.366	0.017
C	8.284	0.518	0.734
C	6.991	0.263	0.270
O	1.476	2.251	2.261
O	3.374	-1.462	1.975
C	3.212	-2.268	3.168
C	4.552	-2.438	3.831
C	5.457	-3.401	3.360
C	6.705	-3.556	3.967
C	7.061	-2.751	5.055
C	6.165	-1.789	5.531
C	4.918	-1.634	4.919
N	3.542	-2.029	-0.770
N	3.583	-3.174	-0.325
N	3.746	-4.267	-0.007
H	2.716	0.395	-1.803
H	2.356	2.369	-0.340
H	1.277	-0.219	2.900
H	1.534	-2.200	1.348
H	5.117	-0.472	-1.839
H	4.893	1.254	-2.256
H	2.504	-1.785	3.865
H	2.794	-3.250	2.878
H	3.142	1.099	1.760
H	4.219	-0.881	5.291
H	6.437	-1.160	6.381
H	7.400	-4.311	3.596
H	5.178	-4.031	2.512
H	7.034	2.200	-2.534
H	9.341	2.636	-1.720
H	8.628	0.050	1.657
H	6.323	-0.391	0.831
H	1.561	-1.369	-0.811
H	-1.251	0.666	-0.061
H	-0.067	-0.555	-0.639
H	10.147	1.561	0.380
H	8.033	-2.878	5.534
C	2.243	3.455	2.291
C	1.611	4.451	3.236
H	3.281	3.237	2.611
H	2.304	3.901	1.278
C	2.357	5.562	3.660
C	1.789	6.519	4.504
C	0.468	6.374	4.941
C	-0.276	5.267	4.526
C	0.289	4.310	3.676
H	3.392	5.678	3.329
H	2.382	7.377	4.827
H	0.024	7.119	5.604
H	-1.306	5.144	4.865
H	-0.286	3.443	3.353



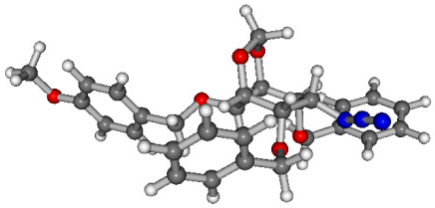
3.19CB

ΔE **0.0** kcal/mol



3.19BC

ΔE **4.4** kcal/mol



3.19CC

ΔE **5.6** kcal/mol

3.19CB

Final heat of formation = –1739.886

C	-0.601	1.445	-2.838
C	-1.576	2.313	-2.331
C	-1.710	3.594	-2.889
C	-0.891	3.998	-3.945
C	0.079	3.127	-4.451
C	0.222	1.854	-3.892
C	-2.508	1.897	-1.217
O	-2.035	0.697	-0.596
C	-2.838	0.279	0.506
C	-2.317	0.896	1.831
C	-0.943	0.291	2.158
C	-1.170	-1.185	2.480
C	-1.584	-1.908	1.177
C	-2.873	-1.263	0.620
O	-3.303	0.633	2.856
C	-2.811	-0.185	3.917
O	-2.235	-1.395	3.443
O	-0.472	-1.852	0.287
C	-0.281	-3.041	-0.494
C	0.989	-2.940	-1.303
C	1.128	-3.729	-2.455
C	2.311	-3.703	-3.199
C	3.366	-2.873	-2.807
C	3.229	-2.073	-1.668
C	2.049	-2.109	-0.917
O	-0.288	0.944	3.254
C	0.502	2.094	2.869
C	1.815	1.733	2.217
C	2.824	1.103	2.959
C	4.045	0.750	2.380
C	4.273	1.032	1.023
C	3.274	1.665	0.266
C	2.063	2.006	0.862
N	-3.227	-1.953	-0.640
N	-4.096	-1.453	-1.354
N	-4.882	-1.106	-2.117
O	5.429	0.727	0.350
C	6.488	0.113	1.089
H	-3.653	-1.481	1.368
H	-3.879	0.628	0.365
H	-2.240	1.990	1.708
H	-0.246	-1.637	2.869
H	-1.816	-2.959	1.429
H	-3.686	-0.470	4.513
H	-2.078	0.376	4.517

H	-3.525	1.722	-1.622
H	-2.590	2.717	-0.478
H	-0.220	-3.914	0.188
H	-1.144	-3.202	-1.161
H	-0.317	0.335	1.252
H	-0.079	2.759	2.207
H	0.669	2.629	3.816
H	0.301	-4.367	-2.777
H	2.403	-4.322	-4.093
H	4.288	-2.844	-3.391
H	4.042	-1.412	-1.361
H	1.940	-1.477	-0.035
H	-0.487	0.455	-2.398
H	0.980	1.169	-4.278
H	0.723	3.442	-5.274
H	-1.007	4.996	-4.371
H	-2.464	4.282	-2.496
H	2.652	0.877	4.014
H	4.806	0.264	2.989
H	3.465	1.875	-0.786
H	1.295	2.495	0.258
H	6.186	-0.867	1.491
H	7.307	-0.024	0.374
H	6.830	0.759	1.916

3.19BC

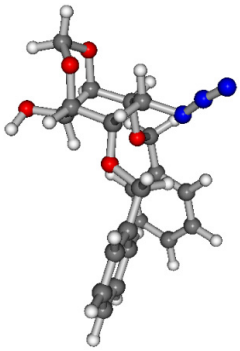
Final heat of formation = – 1739.879

C	2.378	-2.160	1.924
C	2.020	-1.198	2.884
C	3.017	-0.329	3.349
C	4.330	-0.407	2.878
C	4.669	-1.380	1.923
C	3.681	-2.256	1.445
C	0.605	-1.102	3.409
O	-0.072	0.132	3.113
C	-0.476	0.277	1.753
C	-1.843	0.967	1.713
C	-2.404	1.039	0.263
C	-1.376	0.619	-0.830
C	-0.006	1.285	-0.552
C	0.462	1.183	0.935
O	0.525	2.484	1.569
C	-0.752	3.087	1.702
O	-1.730	2.273	2.324
O	-3.597	0.265	0.245
C	-4.413	0.465	-0.924
C	-5.750	-0.192	-0.704
C	-6.631	0.304	0.267
C	-7.868	-0.304	0.479
C	-8.243	-1.417	-0.282
C	-7.372	-1.918	-1.252
C	-6.130	-1.309	-1.458
O	0.927	0.720	-1.470
C	2.062	1.561	-1.696
C	2.992	0.951	-2.719
C	4.256	1.530	-2.911
C	5.133	1.023	-3.872
C	4.759	-0.078	-4.649
C	3.505	-0.663	-4.456
C	2.623	-0.151	-3.499
N	-1.283	-0.859	-0.857
N	-0.969	-1.387	-1.924
N	-0.712	-2.020	-2.846
O	5.924	-1.553	1.400
C	6.962	-0.686	1.859
H	-1.725	0.971	-1.814
H	-0.126	2.363	-0.783
H	1.490	0.803	0.965
H	-2.571	0.428	2.329
H	-2.656	2.099	0.055
H	-0.617	3.962	2.349
H	-1.118	3.420	0.705
H	1.712	2.552	-2.050
H	2.610	1.734	-0.751
H	-4.536	1.554	-1.093
H	-3.928	0.035	-1.819
H	-0.553	-0.707	1.265
H	0.012	-1.958	3.034
H	0.600	-1.146	4.508
H	-5.447	-1.708	-2.212
H	-7.656	-2.788	-1.847
H	-9.211	-1.892	-0.117
H	-8.546	0.090	1.239
H	-6.337	1.170	0.865
H	1.648	-0.615	-3.350
H	3.207	-1.527	-5.053
H	5.444	-0.479	-5.398
H	6.112	1.485	-4.010
H	4.558	2.386	-2.301
H	1.618	-2.849	1.545
H	3.958	-3.002	0.699
H	5.080	0.282	3.265
H	2.759	0.433	4.086
H	7.130	-0.795	2.944
H	7.864	-0.993	1.320
H	6.741	0.368	1.628

3.19CC

Final heat of formation = – 1739.877

C	-0.205	-4.943	-0.404
C	0.852	-4.044	-0.210
C	1.665	-3.710	-1.307
C	1.418	-4.256	-2.568
C	0.355	-5.149	-2.750
C	-0.456	-5.493	-1.666
C	1.119	-3.439	1.150
O	0.859	-2.021	1.234
C	-0.522	-1.651	1.261
C	-0.794	-0.667	2.438
C	-0.431	0.811	2.179
C	-0.809	1.257	0.736
C	-0.169	0.309	-0.271
C	-0.902	-1.029	-0.115
O	-2.315	-0.865	-0.338
C	-2.947	0.167	0.405
O	-2.225	1.385	0.499
O	-0.272	0.891	-1.568
C	0.562	0.245	-2.549
C	0.488	1.014	-3.839
C	1.353	2.095	-4.085
C	1.276	2.826	-5.265
C	0.317	2.491	-6.237
C	-0.557	1.418	-6.009
C	-0.460	0.694	-4.814
O	0.320	3.267	-7.368
C	-0.638	2.965	-8.383
O	0.974	1.001	2.366
C	1.341	2.325	2.793
C	0.893	2.678	4.198
C	1.120	1.790	5.261
C	0.744	2.134	6.561
C	0.144	3.373	6.817
C	-0.086	4.262	5.764
C	0.282	3.911	4.461
N	-0.166	-1.084	3.713
N	-0.447	-2.204	4.138
N	-0.611	-3.219	4.654
H	-1.887	-0.680	2.587
H	-1.149	-2.548	1.415
H	-0.590	-1.751	-0.880
H	-0.424	2.273	0.580
H	-0.994	1.427	2.902
H	2.184	-3.527	1.408
H	0.537	-3.975	1.920
H	2.440	2.325	2.731
H	0.972	3.090	2.085
H	0.889	0.162	0.007
H	1.604	0.213	-2.176
H	0.230	-0.795	-2.712
H	-1.148	-0.136	-4.641
H	-1.307	1.138	-6.746
H	1.949	3.662	-5.461
H	2.100	2.366	-3.335
H	-0.466	3.696	-9.180
H	-0.497	1.947	-8.785
H	-1.670	3.069	-8.008
H	0.092	4.605	3.637
H	-0.562	5.225	5.955
H	-0.146	3.640	7.834
H	0.922	1.434	7.380
H	1.571	0.818	5.054
H	-0.837	-5.220	0.443
H	-1.284	-6.190	-1.801
H	0.163	-5.578	-3.735
H	2.059	-3.991	-3.411
H	2.495	-3.015	-1.165
H	-3.873	0.404	-0.133
H	-3.206	-0.201	1.419



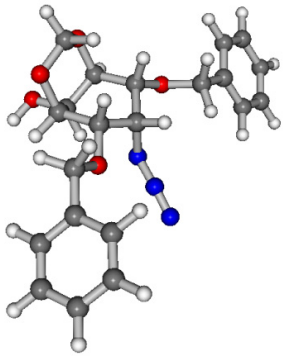
3.25CB

ΔE **0.0** kcal/mol

3.25CB

Final heat of formation = –1354.872

C	-0.632	-1.574	0.647
C	-0.146	-0.391	1.221
C	0.820	0.353	0.527
C	1.285	-0.075	-0.717
C	0.797	-1.260	-1.280
C	-0.161	-2.011	-0.595
C	-0.658	0.090	2.553
O	-1.558	1.197	2.320
C	-2.366	1.583	3.423
C	-3.517	2.420	2.805
C	-2.897	3.695	2.211
C	-2.432	4.557	3.381
C	-1.245	3.838	4.079
C	-1.686	2.436	4.531
O	-4.487	2.696	3.841
C	-4.680	4.089	4.075
O	-3.462	4.760	4.382
O	-0.113	3.764	3.213
C	0.811	4.857	3.389
C	2.005	4.633	2.499
C	2.181	5.383	1.329
C	3.289	5.166	0.502
C	4.231	4.190	0.839
C	4.061	3.432	2.004
C	2.957	3.654	2.829
O	-3.789	4.455	1.375
N	-0.533	1.759	5.178
N	-0.792	1.004	6.120
N	-0.876	0.276	7.004
H	-0.989	4.412	4.988
H	-2.107	5.544	3.017
H	-1.999	3.397	1.647
H	-4.001	1.816	2.020
H	-2.802	0.687	3.908
H	0.328	5.819	3.138
H	1.121	4.897	4.450
H	0.170	0.422	3.197
H	-1.201	-0.721	3.073



3.25BC

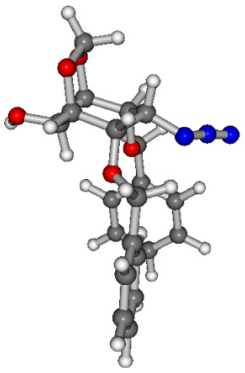
ΔE **5.0** kcal/mol

H	-5.307	4.165	4.971
H	-5.162	4.557	3.202
H	1.201	1.277	0.967
H	2.036	0.512	-1.247
H	-0.544	-2.937	-1.027
H	-1.384	-2.160	1.180
H	2.823	3.063	3.738
H	4.796	2.671	2.272
H	3.416	5.760	-0.403
H	1.444	6.144	1.063
H	-2.476	2.604	5.279
H	1.167	-1.598	-2.250
H	5.097	4.021	0.198
H	-3.910	3.953	0.550

3.25BC

Final heat of formation = –1354.864

C	-0.125	0.019	0.000
C	-0.051	0.155	1.394
C	1.196	0.394	1.987
C	2.349	0.495	1.204
C	2.264	0.356	-0.184
C	1.024	0.118	-0.785
C	-1.289	0.021	2.239
O	-1.538	-1.382	2.481
C	-2.708	-1.618	3.264
C	-2.474	-1.363	4.789
C	-2.579	-2.673	5.589
C	-4.022	-3.141	5.407
C	-4.320	-3.480	3.917
C	-3.189	-3.054	2.933
O	-3.397	-0.395	5.334
C	-4.738	-0.869	5.329
O	-4.921	-2.135	5.930
O	-4.628	-4.867	3.862
C	-5.229	-5.288	2.623
C	-5.726	-6.701	2.779
C	-6.877	-6.967	3.536
C	-7.335	-8.276	3.696
C	-6.646	-9.337	3.096
C	-5.498	-9.082	2.341



3.25CC

ΔE **5.6** kcal/mol

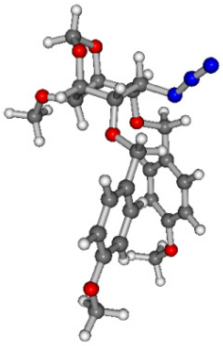
C	-5.040	-7.770	2.187
O	-2.333	-2.512	6.985
N	-2.087	-4.040	3.004
N	-1.417	-4.216	1.984
N	-0.726	-4.508	1.116
H	-4.222	-4.039	6.004
H	-3.509	-0.924	2.938
H	-1.900	-3.422	5.150
H	-5.321	-0.153	5.920
H	-1.481	-0.906	4.913
H	-5.217	-2.898	3.621
H	-5.123	-0.885	4.285
H	-6.067	-4.604	2.379
H	-4.497	-5.239	1.797
H	-2.166	0.457	1.724
H	-1.161	0.555	3.197
H	-1.093	-0.167	-0.470
H	0.953	0.011	-1.869
H	3.314	0.683	1.677
H	1.264	0.502	3.072
H	-7.413	-6.139	4.007
H	-8.232	-8.471	4.286
H	-4.955	-9.906	1.874
H	-4.139	-7.572	1.602
H	-3.589	-3.039	1.905
H	3.163	0.436	-0.797
H	-7.005	-10.360	3.218
H	-1.437	-2.146	7.088

3.25CC

Final heat of formation = –1354.863

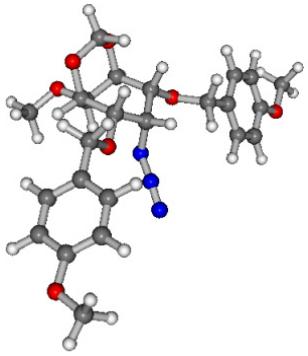
C	-0.145	0.522	0.131
O	0.090	0.207	1.498
C	1.475	0.105	1.866
C	2.238	1.372	1.465
C	2.074	1.497	-0.045
O	0.682	1.534	-0.414
C	2.205	-1.151	1.300
C	2.482	-1.033	-0.225
C	2.899	0.373	-0.727
O	4.266	0.674	-0.444

C	5.161	0.497	-1.561
C	6.577	0.735	-1.105
C	7.449	1.514	-1.878
C	8.781	1.692	-1.488
C	9.249	1.101	-0.312
C	8.380	0.333	0.470
C	7.054	0.146	0.076
O	1.733	2.561	2.075
O	3.435	-1.351	2.003
C	3.284	-2.158	3.196
C	4.633	-2.347	3.835
C	5.517	-3.321	3.345
C	6.774	-3.493	3.929
C	7.159	-2.697	5.012
C	6.285	-1.725	5.508
C	5.028	-1.553	4.920
N	3.474	-2.007	-0.735
N	3.492	-3.136	-0.249
N	3.628	-4.221	0.102
H	2.713	0.418	-1.815
H	2.477	2.457	-0.390
H	1.451	-0.001	2.961
H	1.542	-2.024	1.458
H	5.054	-0.529	-1.953
H	4.898	1.206	-2.369
H	2.594	-1.668	3.907
H	2.847	-3.134	2.912
H	3.309	1.228	1.684
H	4.345	-0.794	5.309
H	6.580	-1.103	6.355
H	7.452	-4.256	3.542
H	5.214	-3.945	2.501
H	7.083	1.988	-2.791
H	9.449	2.301	-2.100
H	8.739	-0.125	1.394
H	6.373	-0.445	0.689
H	1.523	-1.261	-0.722
H	-1.171	0.909	0.083
H	-0.079	-0.401	-0.480
H	10.286	1.244	-0.002
H	8.139	-2.836	5.473
H	1.838	2.468	3.038



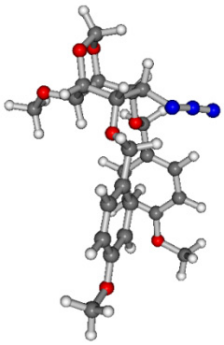
3.34CB

ΔE **0.0** kcal/mol



3.34BC

ΔE **4.4** kcal/mol



3.34CC

ΔE **5.0** kcal/mol

3.34CB

Final heat of formation = –1623.328

C	1.386	3.624	-0.395
C	0.931	2.881	0.699
C	1.889	2.285	1.538
C	3.251	2.429	1.294
C	3.691	3.177	0.189
C	2.750	3.780	-0.660
C	-0.536	2.702	0.958
O	-1.038	1.628	0.123
C	-2.436	1.384	0.287
C	-3.073	1.241	-1.118
C	-2.550	-0.047	-1.769
C	-3.119	-1.218	-0.964
C	-2.427	-1.216	0.421
C	-2.748	0.129	1.131
O	-4.512	1.238	-0.953
C	-5.127	0.021	-1.371
O	-4.547	-1.117	-0.747
O	-1.058	-1.491	0.159
C	-0.288	-2.010	1.270
C	0.987	-2.598	0.737
C	2.078	-1.777	0.430
C	3.264	-2.304	-0.092
C	3.368	-3.686	-0.314
C	2.280	-4.523	-0.012
C	1.108	-3.979	0.502
O	4.480	-4.312	-0.817
C	5.611	-3.500	-1.138
O	-2.898	-0.194	-3.153
C	-2.044	0.541	-4.027
N	-2.079	0.265	2.452
N	-2.671	-0.203	3.428
N	-3.104	-0.591	4.418
O	5.050	3.262	0.031
C	5.545	4.026	-1.070
H	-2.917	2.247	0.780
H	-2.797	2.128	-1.709
H	-1.454	-0.068	-1.654
H	-2.902	-2.169	-1.473
H	-2.867	-2.031	1.031
H	-1.089	3.630	0.718
H	-0.714	2.456	2.018
H	-0.080	-1.195	1.982
H	-0.882	-2.785	1.791
H	-2.128	1.632	-3.876
H	-0.987	0.245	-3.896
H	-6.166	0.068	-1.026
H	-5.068	-0.075	-2.467
H	2.003	-0.700	0.593
H	4.092	-1.634	-0.318
H	2.380	-5.595	-0.188
H	0.269	-4.639	0.731
H	1.557	1.703	2.400
H	3.996	1.974	1.949
H	3.066	4.371	-1.518
H	0.660	4.099	-1.059
H	-2.362	0.302	-5.049
H	6.372	-4.190	-1.519
H	5.368	-2.758	-1.917
H	6.002	-2.981	-0.248
H	6.637	3.966	-1.005
H	5.213	3.608	-2.035
H	5.233	5.082	-1.003
H	-3.840	0.125	1.275

3.34BC

Final heat of formation = –1623.321

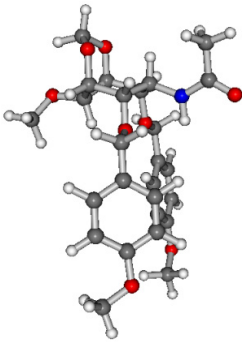
C	0.406	0.976	-5.495
C	1.125	0.630	-4.345
C	2.277	-0.159	-4.495
C	2.699	-0.587	-5.749
C	1.965	-0.235	-6.894
C	0.810	0.552	-6.764
C	0.658	1.067	-2.986
O	-0.438	0.223	-2.574
C	-1.100	0.666	-1.396

C	-2.440	-0.119	-1.310
C	-2.491	-1.000	-0.061
C	-2.449	-0.021	1.128
C	-1.103	0.772	1.149
C	-0.224	0.564	-0.110
O	-3.592	0.757	-1.319
C	-3.676	1.562	-0.159
O	-3.604	0.846	1.066
O	-0.293	0.443	2.278
C	-0.729	1.095	3.497
C	0.147	0.656	4.633
C	-0.193	-0.458	5.418
C	0.627	-0.887	6.454
C	1.824	-0.204	6.731
C	2.180	0.912	5.959
C	1.340	1.327	4.922
O	2.564	-0.700	7.771
C	3.796	-0.044	8.083
O	-3.669	-1.793	-0.121
C	-3.715	-2.816	0.867
N	0.464	-0.746	-0.098
N	1.560	-0.806	0.463
N	2.591	-1.013	0.920
O	2.456	-0.704	-8.084
C	1.735	-0.384	-9.276
H	-2.537	-0.724	-2.218
H	-1.362	1.849	1.187
H	-1.595	-1.646	-0.030
H	-4.661	2.042	-0.181
H	-4.592	-3.433	0.637
H	-2.809	-3.451	0.838
H	-3.832	-2.411	1.888
H	-2.547	-0.550	2.084
H	-1.354	1.740	-1.507
H	-2.884	2.343	-0.181
H	0.308	2.118	-3.008
H	1.491	0.999	-2.263
H	-0.671	2.191	3.353
H	-1.784	0.839	3.702
H	1.626	2.195	4.324
H	3.100	1.461	6.156
H	0.364	-1.750	7.066
H	-1.119	-0.999	5.211
H	-0.496	1.584	-5.402
H	0.225	0.841	-7.637
H	3.593	-1.200	-5.868
H	2.851	-0.447	-3.611
H	4.221	-0.600	8.925
H	4.496	-0.076	7.232
H	3.631	1.003	8.383
H	2.288	-0.859	-10.093
H	0.709	-0.786	-9.247
H	1.697	0.704	-9.445
H	0.533	1.365	-0.122

3.34CC

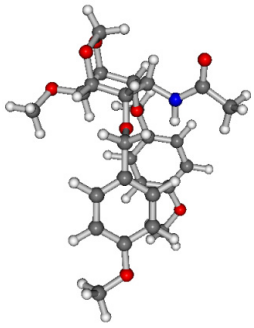
Final heat of formation = –1623.320

C	1.534	-4.229	0.544
C	1.060	-2.934	0.772
C	1.918	-1.852	0.500
C	3.203	-2.064	0.018
C	3.671	-3.373	-0.196
C	2.831	-4.462	0.070
C	-0.322	-2.696	1.313
O	-1.042	-1.841	0.395
C	-2.380	-1.537	0.787
C	-3.216	-1.610	-0.519
C	-2.764	-0.487	-1.447
C	-3.264	0.813	-0.806
C	-2.494	1.076	0.522
C	-2.514	-0.153	1.474
O	-1.141	1.439	0.235
C	-0.965	2.863	0.017
C	0.490	3.155	-0.201
C	1.351	3.350	0.885
C	2.713	3.604	0.699
C	3.234	3.667	-0.602
C	2.381	3.474	-1.703
C	1.030	3.221	-1.497
O	4.547	3.914	-0.904
C	5.455	4.108	0.182
O	-3.290	-0.732	-2.748
C	-2.694	0.071	-3.760
N	-1.511	-0.087	2.563
N	-1.272	1.004	3.076
N	-0.946	1.944	3.650
O	4.956	-3.475	-0.668
C	5.475	-4.786	-0.899
H	-2.758	-2.305	1.485
H	-3.017	-2.584	-0.983
H	-3.075	1.675	-1.461
H	-2.999	1.914	1.042
H	-0.280	-2.207	2.301
H	-0.857	-3.658	1.425
H	-1.554	3.190	-0.858
H	-1.343	3.405	0.904
H	-1.660	-0.474	-1.469
H	-1.593	-0.030	-3.762
H	-3.089	-0.289	-4.718
H	-2.953	1.141	-3.658
H	0.376	3.073	-2.360
H	2.802	3.530	-2.708
H	3.353	3.755	1.567
H	0.953	3.302	1.901
H	0.881	-5.084	0.737
H	3.166	-5.486	-0.093
H	3.869	-1.228	-0.201
H	1.559	-0.833	0.653
H	6.434	4.280	-0.277
H	5.178	4.986	0.789
H	5.507	3.217	0.829
H	6.498	-4.640	-1.264
H	5.499	-5.382	0.027
H	4.889	-5.324	-1.663
H	-3.507	-0.149	1.955
O	-4.697	0.789	-0.674
O	-4.645	-1.586	-0.328
C	-5.216	-0.334	0.020
H	-6.277	-0.398	-0.255
H	-5.138	-0.168	1.115



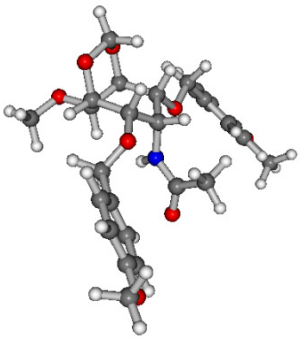
3.36CB

ΔE **0.0** kcal/mol



3.36CC

ΔE **1.2** kcal/mol



3.36BC

ΔE **14.4** kcal/mol

3.36CB
Final heat of formation =
– 1667.768

C	1.389	-0.118	-4.438
C	0.844	-0.068	-3.142
C	1.717	-0.079	-2.053
C	3.106	-0.136	-2.239
C	3.634	-0.184	-3.535
C	2.763	-0.176	-4.638
C	-0.655	-0.003	-2.975
O	-0.995	0.091	-1.588
C	-2.401	0.162	-1.342
C	-3.015	-1.251	-1.193
C	-2.420	-1.906	0.050
C	-2.963	-1.145	1.268
C	-2.351	0.276	1.260
C	-2.661	1.007	-0.072
O	-4.453	-1.077	-1.115
C	-5.008	-1.582	0.092
O	-4.405	-1.002	1.246
O	-0.937	0.208	1.476
C	-0.555	0.457	2.851
C	0.938	0.364	2.974
C	1.547	-0.758	3.541
C	2.939	-0.863	3.647
C	3.746	0.178	3.166
C	3.147	1.314	2.592
C	1.763	1.402	2.502
O	5.116	0.186	3.211
C	5.768	-0.931	3.815
O	-2.708	-3.311	0.042
C	-1.837	-4.069	0.881
N	-1.977	2.281	-0.153
O	4.973	-0.239	-3.834
C	5.895	-0.235	-2.743
H	-2.903	0.670	-2.186
H	-2.789	-1.865	-2.080
H	-1.328	-1.748	0.018
H	-2.686	-1.652	2.208
H	-2.826	0.860	2.069
H	-1.121	-0.901	-3.426
H	-1.060	0.877	-3.512
H	-0.911	1.464	3.139
H	-1.037	-0.278	3.521
H	-0.780	-3.921	0.597
H	-1.956	-3.816	1.950
H	-6.059	-1.270	0.105
H	-4.912	-2.679	0.125
H	1.311	2.291	2.060
H	3.789	2.119	2.232
H	3.378	-1.751	4.102
H	0.926	-1.575	3.916
H	0.727	-0.108	-5.308
H	3.187	-0.211	-5.642
H	3.756	-0.138	-1.365
H	1.312	-0.040	-1.042
H	-2.106	-5.123	0.739
H	6.841	-0.718	3.753
H	5.479	-1.044	4.873
H	5.551	-1.868	3.274
H	6.891	-0.277	-3.196
H	5.806	0.683	-2.140
H	5.752	-1.113	-2.090
H	-3.743	1.189	-0.063
C	-2.496	3.547	-0.017
H	-0.963	2.235	-0.244
O	-1.761	4.536	-0.028
C	-4.008	3.669	0.131
H	-4.375	3.150	1.029
H	-4.249	4.733	0.212
H	-4.537	3.247	-0.736

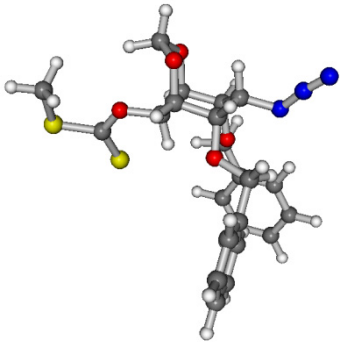
3.36CC
Final heat of formation =
–1667.766

C	1.837	2.964	-1.674
C	0.943	3.261	-0.641
C	1.465	3.763	0.564
C	2.831	3.959	0.732
C	3.718	3.652	-0.315
C	3.216	3.153	-1.526
C	-0.531	3.022	-0.796
O	-0.856	1.719	-0.258
C	-2.258	1.509	-0.029
C	-2.970	1.123	-1.354
C	-2.495	-0.255	-1.799
C	-3.082	-1.250	-0.788
C	-2.380	-1.043	0.582
C	-2.410	0.430	1.073
O	-4.409	1.180	-1.284
C	-5.023	0.152	-0.518
O	-4.518	-1.154	-0.758
O	-1.016	-1.483	0.458
C	-0.821	-2.853	0.875
C	0.618	-3.231	0.676
C	1.026	-3.959	-0.444
C	2.368	-4.299	-0.652
C	3.332	-3.895	0.283
C	2.938	-3.164	1.418
C	1.600	-2.842	1.606
O	4.672	-4.167	0.187
C	5.119	-4.919	-0.942
O	-2.910	-0.461	-3.148
C	-2.318	-1.603	-3.756
N	-1.465	0.653	2.149
O	5.044	3.881	-0.055
C	5.984	3.588	-1.091
H	-2.899	-1.653	1.342
H	-2.892	-2.287	-1.098
H	-2.716	1.866	-2.122
H	-2.710	2.447	0.345
H	-6.074	0.132	-0.831
H	-4.967	0.390	0.560
H	-1.109	-2.947	1.939
H	-1.473	-3.528	0.289
H	-0.818	3.080	-1.861
H	-1.110	3.788	-0.246
H	-1.393	-0.293	-1.724
H	-2.609	-1.580	-4.814
H	-1.214	-1.576	-3.683
H	-2.679	-2.551	-3.317
H	0.785	4.008	1.383
H	3.238	4.356	1.662
H	3.882	2.912	-2.354
H	1.455	2.573	-2.619
H	1.305	-2.277	2.492
H	3.701	-2.866	2.138
H	2.646	-4.872	-1.535
H	0.281	-4.276	-1.179
H	6.967	3.840	-0.678
H	5.965	2.519	-1.363
H	5.799	4.198	-1.990
H	6.203	-5.021	-0.821
H	4.659	-5.921	-0.969
H	4.905	-4.393	-1.888
H	-3.393	0.583	1.542
H	-0.483	0.688	1.893
C	-1.865	0.852	3.445
O	-3.049	0.837	3.789
C	-0.742	1.091	4.443
H	0.258	1.093	3.992
H	-0.915	2.053	4.943
H	-0.786	0.311	5.216

3.36BC
Final heat of formation =
–1667.745

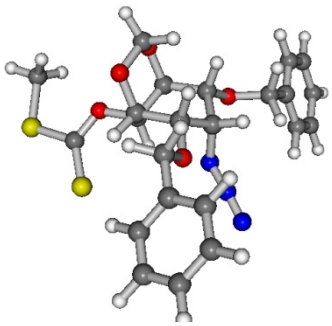
C	5.424	0.189	0.024
C	4.213	-0.404	-0.350
C	4.080	-0.873	-1.669
C	5.123	-0.749	-2.582
C	6.331	-0.147	-2.194
C	6.480	0.328	-0.881
C	3.084	-0.524	0.636
O	2.504	0.794	0.829
C	1.262	0.906	1.538
C	1.112	-0.016	2.790
C	-0.096	-0.956	2.640
C	-1.323	-0.042	2.587
C	-1.302	0.877	1.323
C	0.045	0.880	0.544
O	0.969	0.736	4.017
C	-0.236	1.481	4.060
O	-1.404	0.715	3.815
O	-2.334	0.523	0.403
C	-3.634	1.009	0.802
C	-4.667	0.557	-0.192
C	-4.489	0.769	-1.565
C	-5.453	0.366	-2.494
C	-6.632	-0.250	-2.048

C	-6.825	-0.465	-0.674
C	-5.848	-0.070	0.234
O	-7.644	-0.680	-2.867
C	-7.481	-0.501	-4.276
O	-0.279	-1.875	3.706
C	0.738	-2.868	3.794
N	0.105	-0.180	-0.450
O	7.299	-0.073	-3.162
C	8.541	0.542	-2.815
H	-2.237	-0.649	2.572
H	1.300	1.932	1.939
H	0.002	-1.517	1.690
H	-0.325	1.871	5.080
H	0.396	-3.597	4.539
H	0.885	-3.386	2.827
H	1.703	-2.451	4.130
H	2.038	-0.581	2.939
H	-1.476	1.909	1.686
H	-0.181	2.329	3.343
H	-3.899	0.642	1.810
H	-3.587	2.116	0.859
H	3.476	-0.895	1.600
H	2.327	-1.232	0.265
H	3.144	-1.337	-1.989
H	5.024	-1.116	-3.604
H	7.409	0.794	-0.554
H	5.547	0.562	1.043
H	-6.005	-0.257	1.299
H	-7.742	-0.954	-0.343
H	-5.275	0.537	-3.555
H	-3.572	1.240	-1.921
H	9.154	0.503	-3.722
H	8.402	1.593	-2.513
H	9.053	-0.005	-2.006
H	-8.387	-0.915	-4.733
H	-7.394	0.565	-4.541
H	-6.600	-1.046	-4.654
H	0.093	1.826	-0.010
C	0.498	-0.073	-1.768
H	-0.388	-1.052	-0.265
O	0.449	-1.059	-2.507
C	0.995	1.278	-2.250
H	1.856	1.622	-1.660
H	1.288	1.172	-3.299
H	0.205	2.042	-2.177



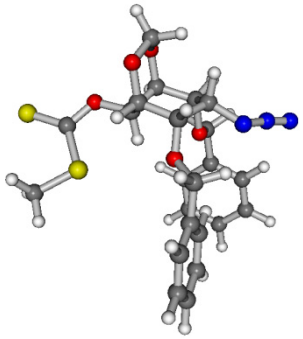
4.24CB

ΔE **0.0** kcal/mol



4.24BC

ΔE **1.9** kcal/mol



4.24CC

ΔE **6.9** kcal/mol

4.24CB

Final heat of formation = –2228.806

C	2.923	3.484	2.980
C	2.190	4.540	2.415
C	2.723	5.226	1.315
C	3.973	4.875	0.795
C	4.697	3.824	1.364
C	4.166	3.126	2.455
C	0.865	4.951	3.005
O	0.023	3.791	3.144
C	-1.054	3.959	4.050
C	-2.240	4.761	3.428
C	-2.808	3.929	2.280
C	-3.473	2.692	2.877
C	-2.335	1.789	3.425
C	-1.562	2.584	4.515
O	-3.202	4.997	4.487
C	-4.467	4.391	4.255
O	-4.370	3.000	3.971
O	-1.607	1.385	2.278
C	-0.717	0.256	2.453
C	-0.318	-0.243	1.091
C	-1.016	-1.295	0.479
C	-0.659	-1.740	-0.796
C	0.399	-1.130	-1.476
C	1.099	-0.078	-0.876
C	0.743	0.360	0.401
O	-3.800	4.650	1.474
N	-0.429	1.830	5.108
N	-0.700	1.073	6.044
N	-0.797	0.333	6.918
H	-0.717	4.518	4.944
H	-1.880	5.734	3.065
H	-1.982	3.625	1.621
H	-4.028	2.134	2.108
H	-2.799	0.909	3.916
H	0.384	5.705	2.357
H	1.015	5.403	4.006
H	0.164	0.573	3.031
H	-1.243	-0.535	3.019
H	-5.028	4.475	5.193
H	-4.992	4.910	3.436
H	1.287	1.183	0.870
H	1.927	0.399	-1.403
H	-1.206	-2.562	-1.259
H	-1.844	-1.771	1.010
H	2.502	2.937	3.826
H	4.726	2.302	2.901
H	4.377	5.418	-0.061
H	2.152	6.038	0.859
H	-2.307	2.792	5.298
H	0.680	-1.476	-2.473
H	5.671	3.545	0.957
C	-3.372	5.431	0.457
S	-1.806	5.749	0.012
S	-4.704	6.149	-0.455
C	-6.225	5.468	0.323
H	-7.054	5.859	-0.279
H	-6.225	4.373	0.284
H	-6.328	5.815	1.356

4.24BC

Final heat of formation = –2228.803

C	-0.207	0.363	-0.005
C	-0.027	0.118	1.363
C	1.274	-0.019	1.865
C	2.377	0.083	1.014
C	2.188	0.331	-0.349
C	0.894	0.471	-0.858
C	-1.214	-0.016	2.278
O	-1.518	-1.421	2.444
C	-2.637	-1.662	3.289
C	-2.314	-1.453	4.805
C	-2.412	-2.786	5.553

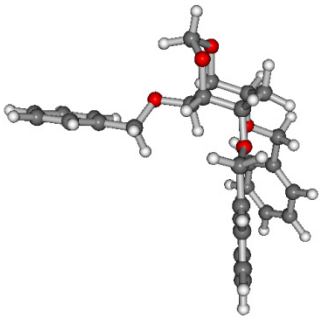
C	-3.868	-3.229	5.451
C	-4.249	-3.511	3.967
C	-3.154	-3.084	2.947
O	-3.197	-0.494	5.433
C	-4.544	-0.943	5.477
O	-4.714	-2.224	6.059
O	-4.599	-4.886	3.897
C	-5.241	-5.268	2.662
C	-5.774	-6.669	2.810
C	-7.029	-6.893	3.393
C	-7.516	-8.193	3.553
C	-6.749	-9.284	3.131
C	-5.495	-9.070	2.551
C	-5.012	-7.768	2.392
O	-2.104	-2.625	6.967
N	-2.074	-4.093	2.967
N	-1.385	-4.213	1.949
N	-0.683	-4.465	1.079
H	-4.052	-4.145	6.023
H	-3.448	-0.950	3.032
H	-1.723	-3.523	5.119
H	-5.089	-0.235	6.112
H	-1.306	-1.032	4.905
H	-5.144	-2.897	3.735
H	-4.979	-0.933	4.454
H	-6.065	-4.559	2.448
H	-4.521	-5.224	1.826
H	-2.096	0.496	1.852
H	-0.998	0.439	3.261
H	-1.218	0.471	-0.404
H	0.742	0.664	-1.922
H	3.385	-0.026	1.415
H	1.423	-0.215	2.930
H	-7.628	-6.042	3.726
H	-8.496	-8.355	4.005
H	-4.893	-9.918	2.220
H	-4.030	-7.602	1.941
H	-3.593	-3.040	1.936
H	3.049	0.415	-1.013
H	-7.130	-10.299	3.253
C	-0.816	-2.667	7.358
S	0.522	-2.914	6.408
S	-0.638	-2.432	9.100
C	-2.364	-2.204	9.700
H	-2.270	-2.021	10.778
H	-2.830	-1.343	9.212
H	-2.959	-3.106	9.526

4.24CC

Final heat of formation = –2228.795

C	-0.142	0.501	0.273
O	0.080	0.038	1.598
C	1.456	-0.099	1.983
C	2.232	1.184	1.711
C	2.078	1.477	0.218
O	0.691	1.574	-0.140
C	2.201	-1.292	1.311
C	2.475	-1.036	-0.197
C	2.901	0.409	-0.559
O	4.263	0.673	-0.228
C	5.177	0.612	-1.343
C	6.585	0.796	-0.838
C	7.461	1.680	-1.481
C	8.784	1.814	-1.048
C	9.239	1.071	0.043
C	8.366	0.194	0.697
C	7.049	0.052	0.258
O	1.644	2.220	2.547
O	3.435	-1.535	1.987
C	3.296	-2.410	3.136
C	4.653	-2.640	3.743
C	5.500	-3.633	3.228
C	6.765	-3.842	3.783
C	7.194	-3.061	4.861
C	6.356	-2.069	5.380
C	5.093	-1.861	4.822
N	3.468	-1.957	-0.795
N	3.481	-3.127	-0.417
N	3.612	-4.241	-0.169
H	2.727	0.562	-1.639
H	2.502	2.455	-0.037
H	1.414	-0.291	3.063
H	1.547	-2.181	1.396
H	5.073	-0.366	-1.841
H	4.929	1.404	-2.075
H	2.619	-1.957	3.883
H	2.851	-3.365	2.802
H	3.292	1.034	1.962
H	4.439	-1.086	5.229
H	6.686	-1.460	6.224
H	7.414	-4.620	3.377
H	5.163	-4.244	2.387
H	7.105	2.272	-2.328
H	9.456	2.507	-1.559
H	8.714	-0.384	1.555
H	6.365	-0.623	0.772
H	1.517	-1.216	-0.715
H	-1.167	0.892	0.258
H	-0.063	-0.341	-0.442
H	10.270	1.178	0.388
H	8.179	-3.229	5.300
C	2.329	3.321	2.928
S	1.581	4.456	3.869
S	4.027	3.394	2.352
C	4.583	4.965	3.095
H	5.625	5.083	2.768
H	3.965	5.793	2.731
H	4.524	4.910	4.187

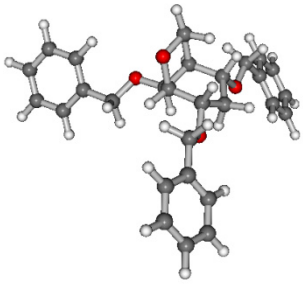
5). C1,C3-Acetals of C5-deoxy *myo*-inositol derivatives



2.44CB
ΔE **0.0** kcal/mol

2.44CB
Final heat of formation =
–1461.653

C	4.191	2.078	-1.014
C	3.982	1.497	0.246
C	4.969	1.638	1.229
C	6.142	2.353	0.966
C	6.342	2.928	-0.291
C	5.364	2.785	-1.283
C	2.705	0.751	0.536
O	2.566	-0.331	-0.399
C	1.292	-0.990	-0.323
C	1.167	-2.011	0.816
O	1.962	-3.200	0.596
C	2.647	-3.193	-0.654
O	1.773	-2.965	-1.749
C	1.017	-1.735	-1.629
C	-0.477	-2.121	-1.655
C	-0.838	-2.977	-0.426
C	-0.315	-2.459	0.919
O	-1.196	-0.884	-1.764
C	-2.580	-1.040	-2.093
C	-3.162	0.292	-2.498
C	-4.438	0.668	-2.055
C	-5.009	1.877	-2.465
C	-4.302	2.730	-3.316
C	-3.024	2.367	-3.755
C	-2.459	1.155	-3.352
O	-1.144	-1.375	1.373
C	-1.198	-1.255	2.793
C	-2.051	-0.072	3.194
C	-2.368	0.111	4.550
C	-3.134	1.204	4.959
C	-3.599	2.127	4.015
C	-3.290	1.947	2.665
C	-2.519	0.853	2.254
H	-1.926	-3.117	-0.353
H	-0.361	-3.286	1.652
H	1.485	-1.568	1.775
H	1.251	-1.090	-2.490
H	-0.658	-2.724	-2.566

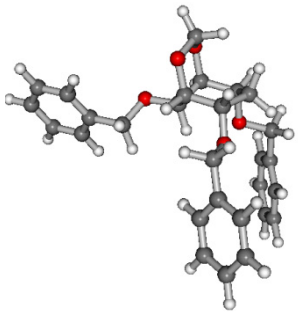


2.44BC
ΔE **3.1** kcal/mol

H	3.053	-4.203	-0.786
H	3.448	-2.435	-0.642
H	-1.615	-2.184	3.232
H	-0.181	-1.130	3.216
H	-2.674	-1.764	-2.929
H	-3.147	-1.446	-1.237
H	0.494	-0.239	-0.194
H	1.830	1.424	0.437
H	2.721	0.377	1.576
H	-2.013	-0.607	5.293
H	-3.372	1.334	6.016
H	-4.200	2.981	4.333
H	-3.649	2.660	1.921
H	-2.279	0.709	1.201
H	-4.988	0.011	-1.376
H	-6.003	2.156	-2.111
H	-4.742	3.677	-3.634
H	-2.465	3.032	-4.416
H	-1.460	0.874	-3.687
H	4.819	1.182	2.211
H	6.903	2.456	1.742
H	7.258	3.483	-0.500
H	5.517	3.231	-2.267
H	3.431	1.963	-1.789
H	-0.400	-3.971	-0.592

2.44BC
Final heat of formation =
–1461.648

C	3.802	3.649	-0.969
C	4.251	2.710	-0.030
C	5.624	2.432	0.051
C	6.534	3.090	-0.779
C	6.080	4.025	-1.713
C	4.712	4.299	-1.808
C	3.294	2.032	0.921
O	1.995	1.934	0.328
C	1.017	1.337	1.194
C	1.150	-0.218	1.197
C	0.004	-0.849	0.385
C	-1.276	-0.534	1.160
C	-1.550	1.002	1.155



2.44CC
ΔE **4.4** kcal/mol

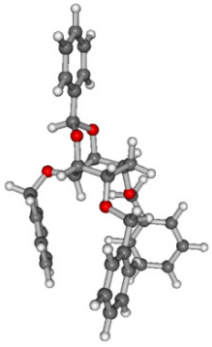
C	-0.346	1.838	0.696
O	-1.188	-1.080	2.497
C	-0.065	-0.584	3.202
O	1.169	-0.778	2.529
O	0.097	-2.258	0.219
C	1.085	-2.665	-0.729
C	1.049	-4.166	-0.891
C	0.679	-4.999	0.174
C	0.692	-6.388	0.019
C	1.081	-6.961	-1.195
C	1.450	-6.136	-2.261
C	1.429	-4.747	-2.110
O	-2.620	1.331	0.257
C	-3.917	1.072	0.803
C	-4.990	1.506	-0.167
C	-6.252	0.894	-0.122
C	-7.279	1.318	-0.969
C	-7.052	2.352	-1.883
C	-5.793	2.958	-1.941
C	-4.768	2.541	-1.085
H	-0.328	1.819	-0.403
H	1.202	1.680	2.230
H	2.128	-0.479	0.772
H	-0.044	-0.360	-0.606
H	-2.125	-1.056	0.701
H	-1.847	1.282	2.184
H	-0.004	-1.153	4.137
H	-0.204	0.494	3.429
H	-4.044	-0.001	1.040
H	-4.024	1.626	1.759
H	3.217	2.615	1.863
H	3.686	1.035	1.194
H	0.903	-2.174	-1.705
H	2.094	-2.357	-0.392
H	-6.431	0.076	0.579
H	-8.255	0.832	-0.923
H	-7.850	2.679	-2.551
H	-5.606	3.760	-2.657
H	-3.784	3.007	-1.133
H	5.983	1.692	0.771
H	7.599	2.863	-0.703

H	6.789	4.535	-2.368
H	4.350	5.023	-2.540
H	2.734	3.855	-1.046
H	1.705	-4.106	-2.952
H	1.745	-6.573	-3.217
H	1.089	-8.046	-1.312
H	0.395	-7.026	0.854
H	0.368	-4.547	1.116
H	-0.487	2.888	0.989

2.44CC

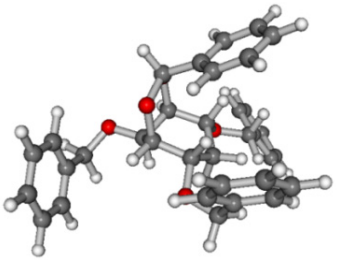
Final heat of formation = –1461.646

C	1.951	-2.816	-1.394
C	2.157	-3.300	-0.093
C	3.252	-4.139	0.151
C	4.122	-4.499	-0.883
C	3.909	-4.011	-2.175
C	2.823	-3.165	-2.427
C	1.206	-2.933	1.017
O	1.209	-1.506	1.193
C	0.369	-1.057	2.276
C	0.957	0.263	2.813
C	0.433	1.568	2.174
C	-1.052	1.499	1.745
C	-1.260	0.266	0.869
C	-1.104	-0.946	1.795
O	-1.977	1.510	2.851
C	-2.004	0.324	3.627
O	-2.057	-0.880	2.875
O	1.138	1.916	0.968
C	2.429	2.503	1.201
C	3.034	2.887	-0.123
C	2.712	4.114	-0.721
C	3.256	4.466	-1.959
C	4.130	3.591	-2.613
C	4.455	2.365	-2.025
C	3.908	2.016	-0.787
O	-2.539	0.366	0.245
C	-2.712	-0.541	-0.853
C	-4.051	-0.279	-1.492
C	-4.150	0.499	-2.653
C	-5.395	0.758	-3.234
C	-6.557	0.241	-2.653
C	-6.469	-0.532	-1.491
C	-5.223	-0.792	-0.916
H	2.049	0.208	2.691
H	0.396	-1.811	3.087
H	-1.364	-1.877	1.274
H	-1.287	2.407	1.177
H	0.535	2.394	2.904
H	-1.142	0.299	4.324
H	1.512	-3.427	1.958
H	0.187	-3.291	0.772
H	2.313	3.394	1.849
H	3.094	1.789	1.722
H	-0.458	0.240	0.108
H	-1.899	-0.394	-1.591
H	-2.664	-1.589	-0.501
H	3.426	-4.515	1.162
H	4.969	-5.155	-0.677
H	4.587	-4.288	-2.984
H	2.653	-2.781	-3.434
H	1.108	-2.152	-1.592
H	4.155	1.054	-0.332
H	5.136	1.678	-2.531
H	4.559	3.866	-3.578
H	3.001	5.425	-2.413
H	2.029	4.798	-0.211
H	-5.153	-1.392	-0.006
H	-7.374	-0.937	-1.034
H	-7.531	0.442	-3.104
H	-5.459	1.363	-4.140
H	-3.242	0.906	-3.105
H	-2.937	0.361	4.205
H	0.778	0.310	3.898



2.55CB

ΔE **0.0** kcal/mol



2.55BC

ΔE **10.7** kcal/mol

2.55CB

Final heat of formation = –1692.786

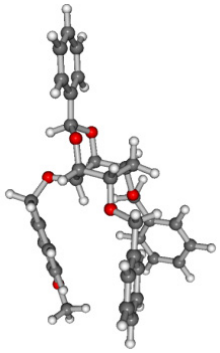
C	0.000	0.000	0.000
C	0.000	0.000	1.402
C	1.221	0.000	2.089
C	2.427	0.004	1.382
C	2.424	0.004	-0.016
C	1.207	0.003	-0.704
C	-1.306	-0.066	2.162
O	-2.317	0.60	1.401
C	-3.591	0.705	2.078
C	-3.571	0.080	3.480
C	-2.359	0.649	4.209
O	-1.131	0.540	3.443
C	-2.586	2.164	4.459
C	-2.894	2.897	3.148
C	-3.915	2.208	2.224
O	-5.281	2.254	2.659
C	-5.849	3.575	2.671
C	-7.337	3.463	2.879
C	-8.206	3.353	1.783
C	-9.585	3.234	1.976
C	-10.111	3.221	3.272
C	-9.252	3.327	4.371
C	-7.874	3.447	4.175
O	-3.512	-1.359	3.467
C	-4.803	-1.990	3.359
C	-5.597	-1.963	4.650
C	-6.891	-1.427	4.690
C	-7.630	-1.435	5.879
C	-7.076	-1.975	7.042
C	-5.779	-2.503	7.014
C	-5.047	-2.499	5.826
O	-3.654	2.415	5.386
C	-3.323	2.118	6.757
C	-4.344	2.767	7.656
C	-4.218	4.119	8.013
C	-5.168	4.730	8.833
C	-6.260	3.995	9.307
C	-6.396	2.649	8.955
C	-5.442	2.039	8.134
H	-3.840	2.674	1.221
H	-1.643	2.565	4.879
H	-2.208	0.113	5.159
H	-3.313	1.027	6.929
H	-2.311	2.508	6.978

H	-5.400	4.173	3.483
H	-5.633	4.077	1.707
H	-4.035	-2.909	5.803
H	-5.343	-2.928	7.921
H	-8.636	-1.012	5.894
H	-7.322	-0.992	3.786
H	-7.202	3.526	5.033
H	-9.658	3.320	5.385
H	-11.188	3.134	3.425
H	-10.251	3.155	1.114
H	-7.796	3.365	0.771
H	-3.365	4.693	7.644
H	-5.055	5.780	9.108
H	-7.001	4.470	9.952
H	-7.245	2.070	9.323
H	-5.552	0.989	7.856
H	-4.360	0.234	1.445
H	-4.471	0.420	4.018
H	-5.395	-1.538	2.544
H	-4.577	-3.027	3.071
H	-0.950	0.010	-0.533
H	1.196	0.007	-1.796
H	3.367	0.005	-0.567
H	3.373	0.008	1.927
H	1.220	0.008	3.179
H	-3.208	3.925	3.381
H	-1.956	2.973	2.580
H	-1.616	-1.116	2.312
H	-7.652	-1.985	7.970

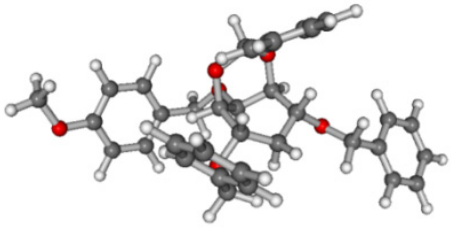
2.55BC

Final heat of formation =
–1692.769

C	0.000	0.000	0.000
C	0.000	0.000	1.402
C	1.227	0.000	2.082
C	2.431	0.041	1.373
C	2.423	0.068	-0.026
C	1.204	0.042	-0.710
C	-1.313	-0.159	2.186
O	-2.458	0.262	1.447
C	-2.943	1.605	1.652
C	-3.079	1.888	3.154
C	-1.677	1.708	3.732
O	-1.228	0.354	3.515
C	-0.706	2.788	3.181
C	-1.267	3.558	1.966
C	-2.082	2.705	0.970
O	-3.026	3.533	0.252
C	-2.443	4.407	-0.723
C	-1.871	3.696	-1.935
C	-0.643	4.091	-2.482
C	-0.141	3.475	-3.633
C	-0.861	2.446	-4.244
C	-2.084	2.036	-3.699
C	-2.587	2.659	-2.555
O	-3.973	1.023	3.853
C	-5.348	1.423	3.827
C	-6.123	1.017	2.586
C	-5.997	-0.278	2.060
C	-6.745	-0.664	0.946
C	-7.635	0.236	0.347
C	-7.766	1.527	0.865
C	-7.010	1.915	1.977
O	-0.453	3.679	4.285
C	0.644	4.576	4.066
C	1.008	5.253	5.365
C	1.207	6.639	5.411
C	1.586	7.267	6.602
C	1.759	6.513	7.765
C	1.551	5.129	7.730
C	1.182	4.503	6.538
H	-1.935	4.344	2.354
H	-1.413	2.208	0.250
H	-3.921	1.609	1.156
H	-3.395	2.939	3.294
H	-1.698	1.807	4.824
H	0.237	2.286	2.908
H	1.230	-0.029	3.172
H	3.379	0.048	1.915
H	3.364	0.099	-0.580
H	1.187	0.056	-1.801
H	-0.951	-0.032	-0.533
H	1.509	3.998	3.679
H	0.392	5.340	3.309
H	1.060	7.235	4.506
H	1.737	8.348	6.622
H	2.049	7.000	8.697
H	1.679	4.535	8.637
H	1.010	3.426	6.512
H	-3.275	5.060	-1.029
H	-1.670	5.056	-0.273
H	-0.073	4.891	-2.002
H	0.817	3.795	-4.048
H	-0.472	1.961	-5.141
H	-2.650	1.231	-4.171
H	-3.538	2.339	-2.125
H	-5.791	0.933	4.710
H	-5.433	2.516	3.978
H	-7.106	2.929	2.372
H	-8.452	2.238	0.399
H	-6.634	-1.672	0.542
H	-5.290	-0.971	2.518
H	-0.444	4.063	1.439
H	-1.478	-1.240	2.333
H	-8.220	-0.068	-0.523



2.56CB
ΔE **0.0** kcal/mol



2.56BC
ΔE **11.3** kcal/mol

2.56CB

Final heat of formation =
–1807.359

C	0.000	0.000	0.000
C	0.000	0.000	1.401
C	1.227	0.000	2.083
C	2.429	-0.004	1.372
C	2.421	-0.011	-0.028
C	1.203	-0.008	-0.714
C	-1.293	-0.003	2.175
O	-1.431	1.247	2.863
C	-2.629	1.346	3.648
C	-2.821	2.855	3.918
C	-1.704	3.324	4.860
C	-1.957	2.670	6.215
C	-1.738	1.140	6.085
C	-2.608	0.549	4.967

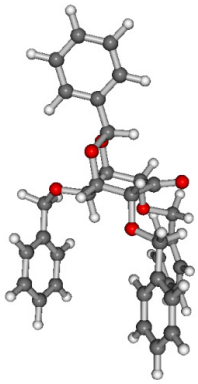
O	-4.141	3.028	4.484
C	-4.141	3.596	5.795
O	-3.316	2.848	6.689
O	-0.365	0.801	5.830
C	0.500	0.981	6.963
C	1.765	0.181	6.767
C	1.702	-1.196	6.500
C	2.872	-1.944	6.353
C	4.122	-1.327	6.479
C	4.194	0.043	6.743
C	3.020	0.792	6.880
O	-1.637	4.753	5.007
C	-0.869	5.412	3.975
C	0.623	5.228	4.124
C	1.377	4.554	3.159
C	2.762	4.390	3.292
C	3.411	4.909	4.420
C	2.666	5.584	5.404
C	1.294	5.740	5.252
C	-5.558	3.606	6.326
C	-5.795	3.570	7.707
C	-7.101	3.637	8.200
C	-8.182	3.744	7.319
C	-7.949	3.781	5.941
C	-6.644	3.713	5.445
O	4.758	4.810	4.660
C	5.561	4.161	3.670
H	-3.490	0.999	3.044
H	-2.045	0.688	7.049
H	-1.279	3.101	6.968
H	0.756	2.046	7.105
H	-0.027	0.639	7.877
H	-1.290	-0.838	2.901
H	-2.151	-0.153	1.491
H	0.724	6.265	6.022
H	3.190	5.987	6.272
H	3.311	3.852	2.520
H	0.879	4.134	2.282
H	1.232	0.010	3.175
H	3.377	-0.012	1.913
H	3.361	-0.021	-0.582
H	1.189	-0.012	-1.805
H	-0.951	0.006	-0.537
H	0.728	-1.677	6.399
H	2.890	-3.014	6.146
H	5.036	-1.914	6.370
H	5.165	0.533	6.837
H	3.080	1.866	7.075
H	-2.783	3.394	2.958
H	-0.746	2.934	4.478
H	-1.192	5.074	2.974
H	-1.144	6.472	4.075
H	-6.458	3.731	4.371
H	-8.787	3.860	5.246
H	-9.202	3.798	7.705
H	-7.275	3.604	9.277
H	-4.951	3.477	8.390
H	-2.295	-0.489	4.787
H	6.589	4.207	4.046
H	5.267	3.107	3.538
H	5.504	4.682	2.700
H	-3.642	0.510	5.336
H	-3.743	4.625	5.731

2.56BC

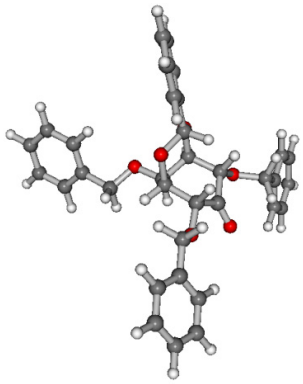
Final heat of formation = –1807.341

C	0.000	0.000	0.000
C	0.000	0.000	1.401
C	1.229	0.000	2.079
C	2.431	-0.001	1.368
C	2.421	-0.011	-0.032
C	1.202	-0.011	-0.715
C	-1.305	-0.052	2.176
O	-1.348	0.812	3.317
C	-1.367	2.227	3.018
C	-1.067	2.931	4.371
C	-2.344	3.562	4.940
C	-2.707	4.688	3.975
C	-3.085	4.125	2.577
C	-2.720	2.636	2.397
O	-0.018	3.920	4.299
C	-0.322	5.183	3.707
O	-1.645	5.663	3.944
O	-4.504	4.335	2.445
C	-4.996	4.147	1.111
C	-6.405	4.679	1.019
C	-7.446	3.869	0.547
C	-8.747	4.372	0.431
C	-9.020	5.692	0.798
C	-7.988	6.506	1.280
C	-6.690	6.004	1.387
O	-2.213	4.110	6.251
C	-2.456	3.188	7.324
C	-1.296	2.281	7.682
C	-0.008	2.800	7.860
C	1.061	1.980	8.234
C	0.844	0.609	8.446
C	-0.442	0.075	8.270
C	-1.492	0.907	7.890
C	0.081	5.263	2.225
C	-0.467	6.260	1.403
C	-0.034	6.409	0.083
C	0.961	5.570	-0.430
C	1.527	4.590	0.391
C	1.096	4.444	1.714
O	1.816	-0.285	8.820
C	3.141	0.215	9.010
H	-3.508	2.038	2.883
H	-0.542	2.462	2.327
H	-0.664	2.170	5.049
H	-3.151	2.806	4.933
H	-3.571	5.251	4.350
H	-2.565	4.733	1.816
H	-1.238	6.917	1.808
H	-0.473	7.184	-0.547
H	1.299	5.684	-1.461
H	2.308	3.933	0.003
H	1.546	3.688	2.358
H	-4.335	4.687	0.403
H	-4.985	3.079	0.827
H	-7.237	2.833	0.269
H	-9.547	3.729	0.061
H	-10.034	6.086	0.712
H	-8.197	7.537	1.571
H	-5.886	6.635	1.771
H	-1.450	-1.059	2.597
H	-2.151	0.139	1.491
H	-0.952	0.009	-0.538
H	1.186	-0.012	-1.807
H	3.361	-0.018	-0.587
H	3.380	-0.002	1.907
H	1.234	0.010	3.171
H	-2.704	3.836	8.179
H	-3.351	2.574	7.104
H	-2.487	0.477	7.748
H	-0.593	-0.993	8.430
H	2.052	2.417	8.357
H	0.169	3.862	7.681
H	3.745	-0.651	9.301
H	3.548	0.649	8.081
H	3.177	0.971	9.812
H	-2.733	2.380	1.327
H	0.317	5.892	4.260

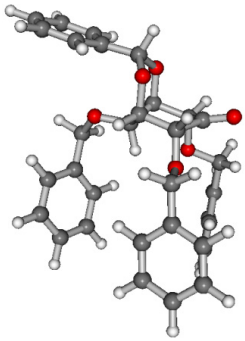
6). C1,C3-Acetal derivatives of *myo*-5-inosose



1.132CC
ΔE **0.0** kcal/mol



1.132BC
ΔE **2.5** kcal/mol



1.132CB
ΔE **5.0** kcal/mol

1.132CC
Final heat of formation =
–1766.826

C	3.291	-0.385	2.157
C	2.524	0.014	3.260
C	3.093	-0.037	4.541
C	4.410	-0.467	4.718
C	5.171	-0.865	3.615
C	4.605	-0.827	2.336
C	1.122	0.545	3.090
O	0.477	-0.132	1.996
C	-0.870	0.304	1.759
C	-1.576	-0.836	0.998
C	-1.069	-0.905	-0.441
C	-1.573	0.369	-1.137
C	-0.860	1.608	-0.557
C	-0.823	1.642	0.987
O	-3.010	-0.691	1.032
C	-3.485	0.442	0.310
O	-3.005	0.472	-1.037
O	-1.574	-2.102	-1.035
C	-0.891	-2.495	-2.238
C	0.508	-3.026	-2.003
C	1.613	-2.455	-2.649
C	2.900	-2.968	-2.450
C	3.093	-4.056	-1.595
C	1.996	-4.628	-0.939
C	0.713	-4.118	-1.144
C	-4.990	0.395	0.275
C	-5.639	-0.730	-0.251
C	-7.033	-0.773	-0.294
C	-7.787	0.304	0.185
C	-7.142	1.427	0.710
C	-5.745	1.470	0.754
O	-0.672	2.703	1.583
O	0.485	1.579	-1.060
C	1.153	2.866	-1.017
C	2.457	2.751	-1.760
C	3.667	2.617	-1.066
C	4.877	2.507	-1.758
C	4.887	2.528	-3.156
C	3.683	2.659	-3.859
C	2.477	2.770	-3.164
H	0.034	-0.905	-0.431
H	-1.370	-1.778	1.521
H	-1.396	0.482	2.715
H	-1.379	2.524	-0.897
H	-1.366	0.348	-2.215
H	-3.156	1.370	0.828
H	-1.532	-3.280	-2.665
H	-0.857	-1.665	-2.967
H	-0.142	-4.560	-0.630
H	2.143	-5.477	-0.269
H	4.095	-4.457	-1.436
H	3.751	-2.512	-2.958
H	1.466	-1.598	-3.310
H	-5.238	2.347	1.165
H	-7.725	2.269	1.086
H	-8.877	0.267	0.150
H	-7.537	-1.652	-0.702
H	-5.041	-1.564	-0.619
H	0.495	3.618	-1.491
H	1.321	3.175	0.026
H	1.143	1.633	2.897
H	0.537	0.391	4.016
H	2.498	0.258	5.409
H	4.839	-0.502	5.721
H	6.198	-1.209	3.751
H	5.189	-1.145	1.471
H	2.849	-0.365	1.161
H	1.539	2.878	-3.712
H	3.687	2.682	-4.950
H	5.830	2.447	-3.698
H	5.813	2.407	-1.205
H	3.662	2.599	0.025

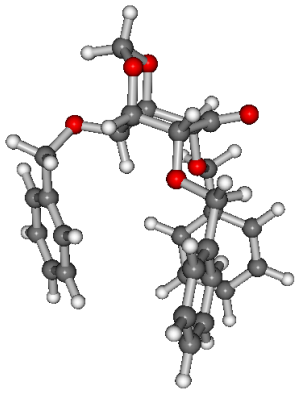
1.132BC
Final heat of formation =
–1766.822

C	2.261	-3.156	-3.188
C	3.085	-2.554	-2.225
C	4.475	-2.694	-2.331
C	5.038	-3.434	-3.376
C	4.212	-4.032	-4.332
C	2.824	-3.887	-4.237
C	2.482	-1.800	-1.066
O	1.429	-0.950	-1.545
C	0.773	-0.221	-0.524
C	-0.188	-1.050	0.348
C	-0.708	-0.161	1.538
C	-0.347	1.324	1.329
C	-0.625	1.852	-0.098
C	-0.091	0.858	-1.179
O	-1.138	0.244	-1.952
C	-1.966	-0.614	-1.190
O	-1.231	-1.610	-0.468
O	0.140	2.012	2.204
O	-0.186	-0.579	2.782
C	-0.876	-1.703	3.344
C	-0.319	-2.007	4.713
C	-0.376	-3.316	5.212
C	0.082	-3.606	6.500
C	0.616	-2.589	7.297
C	0.687	-1.284	6.799
C	0.219	-0.991	5.516
O	-0.033	3.110	-0.347
C	-0.743	4.228	0.248
C	-0.013	5.493	-0.107
C	1.036	5.952	0.700
C	1.737	7.112	0.362
C	1.394	7.827	-0.789
C	0.349	7.377	-1.602
C	-0.348	6.215	-1.262
C	-2.955	-1.315	-2.095

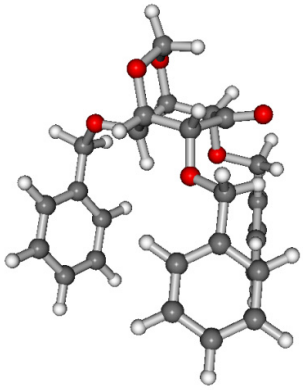
C	-3.847	-2.241	-1.535
C	-4.782	-2.893	-2.342
C	-4.834	-2.622	-3.714
C	-3.947	-1.699	-4.272
C	-3.008	-1.045	-3.467
H	-1.818	-0.228	1.539
H	0.316	-1.916	0.794
H	1.517	0.271	0.137
H	0.493	1.443	-1.898
H	-1.730	1.913	-0.217
H	-2.523	0.000	-0.446
H	-3.799	-2.460	-0.467
H	-5.470	-3.615	-1.899
H	-5.566	-3.131	-4.344
H	-3.981	-1.485	-5.342
H	-2.310	-0.328	-3.897
H	-1.774	4.245	-0.153
H	-0.785	4.099	1.340
H	1.304	5.389	1.597
H	2.552	7.461	1.000
H	1.939	8.735	-1.052
H	0.076	7.933	-2.500
H	-1.163	5.862	-1.898
H	-1.957	-1.461	3.414
H	-0.786	-2.594	2.694
H	-0.781	-4.117	4.588
H	0.032	-4.629	6.877
H	0.982	-2.815	8.301
H	1.112	-0.488	7.414
H	0.282	0.021	5.118
H	3.257	-1.196	-0.557
H	2.083	-2.520	-0.323
H	5.124	-2.216	-1.593
H	6.122	-3.536	-3.447
H	4.649	-4.606	-5.152
H	2.174	-4.347	-4.984
H	1.180	-3.034	-3.117

1.132CB
Final heat of formation = –1766.818

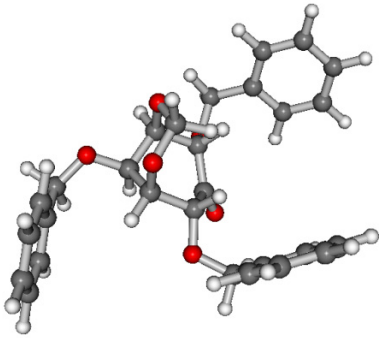
C	3.004	4.047	-1.209
C	2.900	2.997	-0.286
C	3.815	1.936	-0.355
C	4.817	1.927	-1.328
C	4.917	2.982	-2.242
C	4.008	4.043	-2.181
C	1.813	2.995	0.754
O	0.716	2.183	0.266
C	-0.438	2.194	1.115
C	-1.607	1.623	0.295
C	-1.356	0.130	0.041
C	-1.502	-0.582	1.379
C	-0.329	-0.181	2.299
C	-0.151	1.355	2.381
O	-2.804	1.898	1.057
C	-3.540	0.781	1.556
O	-2.702	-0.228	2.114
C	-4.586	0.248	0.577
C	-5.066	-1.061	0.701
C	-6.099	-1.516	-0.122
C	-6.669	-0.662	-1.071
C	-6.204	0.652	-1.186
C	-5.173	1.107	-0.360
O	-2.237	-0.456	-0.915
C	-1.878	-0.200	-2.289
C	-0.722	-1.048	-2.772
C	-0.884	-2.436	-2.920
C	0.171	-3.231	-3.368
C	1.407	-2.647	-3.674
C	1.581	-1.269	-3.525
C	0.520	-0.476	-3.076
O	0.286	1.876	3.393
O	0.924	-0.714	1.850
C	1.248	-1.982	2.469
C	2.586	-2.448	1.962
C	3.718	-2.395	2.788
C	4.962	-2.832	2.322
C	5.086	-3.319	1.018
C	3.963	-3.368	0.183
C	2.721	-2.938	0.654
H	-0.555	-0.520	3.324
H	-0.680	3.221	1.440
H	-1.674	2.178	-0.653
H	2.184	2.588	1.708
H	1.445	4.021	0.939
H	1.277	-1.856	3.566
H	0.465	-2.725	2.228
H	0.661	0.600	-2.956
H	2.543	-0.809	-3.755
H	2.231	-3.268	-4.033
H	0.031	-4.307	-3.488
H	-1.848	-2.891	-2.680
H	1.848	-2.974	-0.001
H	4.055	-3.747	-0.835
H	6.055	-3.662	0.651
H	5.834	-2.790	2.977
H	3.622	-2.009	3.806
H	3.735	1.111	0.355
H	5.526	1.099	-1.370
H	5.704	2.979	-2.998
H	4.083	4.870	-2.890
H	2.295	4.877	-1.160
H	-1.513	-1.671	1.217
H	-0.304	0.013	-0.276
H	-2.792	-0.433	-2.853
H	-1.652	0.869	-2.442
H	-4.619	-1.724	1.443
H	-6.460	-2.541	-0.023
H	-7.477	-1.016	-1.715
H	-6.649	1.327	-1.920
H	-4.810	2.132	-0.444
H	-4.073	1.190	2.430



1.138CB
ΔE **0.0** kcal/mol



1.138CC
ΔE **0.6** kcal/mol



1.138BC
ΔE **1.9** kcal/mol

1.138CB

Final heat of formation = –1535.694

C	0.304	0.803	0.165
C	0.083	0.197	1.411
C	1.160	-0.411	2.071
C	2.433	-0.419	1.496
C	2.642	0.181	0.250
C	1.576	0.795	-0.413
C	-1.285	0.216	2.034
O	-1.367	1.330	2.956
C	-2.667	1.466	3.548
C	-2.783	0.727	4.897
C	-1.926	1.441	5.941
C	-2.580	2.804	6.223
C	-2.444	3.694	4.978
C	-2.931	2.986	3.693
O	-4.198	0.742	5.216
C	-4.491	1.372	6.454
O	-3.994	2.704	6.507
O	-1.053	4.018	4.844
C	-0.790	5.115	3.934
C	0.679	5.430	3.986
C	1.592	4.676	3.232
C	2.959	4.958	3.287
C	3.429	6.000	4.094
C	2.528	6.755	4.850
C	1.161	6.469	4.796
O	-1.803	0.616	7.111
C	-0.651	0.921	7.929
C	0.650	0.419	7.343
C	1.626	1.311	6.879
C	2.829	0.837	6.343
C	3.065	-0.537	6.268
C	2.094	-1.437	6.724
C	0.895	-0.960	7.257
H	-3.052	4.608	5.107
H	-2.088	3.310	7.070
H	-2.454	-0.318	4.798
H	-3.448	1.082	2.871
H	-5.582	1.450	6.511
H	-4.082	0.779	7.289
H	-1.096	4.836	2.912
H	-1.391	5.990	4.244
H	-1.475	-0.730	2.573
H	-2.061	0.332	1.256
H	-0.935	1.618	5.489
H	-0.586	2.006	8.121
H	-0.861	0.422	8.886
H	0.456	7.061	5.385
H	2.889	7.571	5.479
H	4.497	6.225	4.131
H	3.658	4.368	2.692
H	1.224	3.862	2.605
H	1.000	-0.879	3.045
H	3.262	-0.899	2.018
H	3.635	0.169	-0.203
H	1.734	1.264	-1.386
H	-0.528	1.283	-0.352
H	0.138	-1.662	7.614
H	2.278	-2.512	6.671
H	4.006	-0.909	5.857
H	3.578	1.544	5.984
H	1.444	2.387	6.933
O	-3.426	3.620	2.777

1.138CC

Final heat of formation = –1535.693

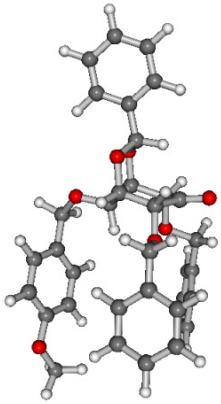
C	0.715	-0.230	0.791
C	-0.183	-0.769	1.723
C	0.203	-1.890	2.471
C	1.463	-2.467	2.289
C	2.351	-1.924	1.357
C	1.977	-0.802	0.609
C	-1.537	-0.144	1.927
O	-1.394	0.958	2.857
C	-2.641	1.547	3.259
C	-3.188	2.423	2.109
C	-2.807	3.920	2.072
C	-2.478	4.526	3.452
C	-1.536	3.602	4.226
C	-2.343	2.331	4.554
O	-3.543	2.666	5.276
C	-4.352	3.603	4.585
O	-3.674	4.790	4.213
O	-1.095	4.289	5.397
C	0.095	3.739	5.989
C	1.359	4.069	5.222
C	2.137	3.060	4.638
C	3.308	3.374	3.939
C	3.712	4.706	3.818
C	2.940	5.722	4.395
C	1.773	5.405	5.092
O	-1.632	4.057	1.255
C	-1.915	4.068	-0.157
C	-0.647	4.340	-0.926
C	-0.435	3.712	-2.162
C	0.702	4.001	-2.921
C	1.649	4.912	-2.444
C	1.450	5.532	-1.206
C	0.307	5.253	-0.454
H	-3.654	4.475	1.627
H	-2.008	5.506	3.301
H	-1.784	1.664	5.222
H	-3.392	0.761	3.465
H	-5.148	3.900	5.277
H	-4.802	3.124	3.687
H	-2.360	3.109	-0.474
H	-2.667	4.858	-0.357
H	-2.248	-0.878	2.349
H	-1.952	0.218	0.973
H	-0.686	3.336	3.574
H	0.128	4.185	6.993
H	0.007	2.645	6.112
H	-1.167	2.991	-2.533
H	0.852	3.506	-3.883
H	2.540	5.135	-3.033
H	2.189	6.239	-0.825
H	0.156	5.731	0.514
H	-0.490	-2.315	3.200
H	1.749	-3.344	2.873
H	3.334	-2.376	1.210
H	2.667	-0.375	-0.120
H	0.426	0.646	0.208
H	1.169	6.198	5.539
H	3.255	6.764	4.306
H	4.626	4.954	3.275
H	3.901	2.578	3.486
H	1.820	2.018	4.725
O	-3.835	1.923	1.197

1.138BC

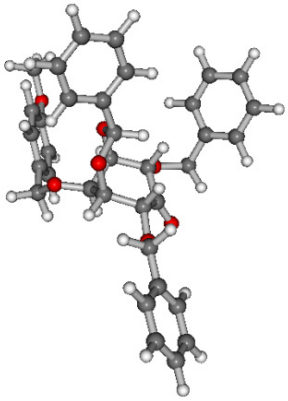
Final heat of formation = –-1535.691

C	0.420	-0.443	0.299
C	0.110	-0.161	1.640
C	1.159	0.046	2.547
C	2.492	-0.012	2.125
C	2.790	-0.293	0.789
C	1.750	-0.512	-0.121
C	-1.330	-0.064	2.097
O	-2.145	-1.184	1.680
C	-1.764	-2.438	2.221
C	-2.414	-3.550	1.332
C	-3.431	-4.356	2.164
C	-2.608	-5.087	3.230
C	-1.995	-4.044	4.232
C	-2.150	-2.604	3.707
O	-1.626	-5.933	2.602
C	-0.772	-5.216	1.726
O	-1.452	-4.449	0.750
O	-4.183	-5.318	1.436
C	-5.341	-4.805	0.760
C	-5.078	-4.166	-0.590
C	-4.202	-4.767	-1.507
C	-4.001	-4.200	-2.766
C	-4.679	-3.031	-3.131
C	-5.553	-2.426	-2.223
C	-5.747	-2.991	-0.958
O	-2.598	-4.128	5.512
C	-2.070	-5.190	6.328
C	-0.641	-4.954	6.773
C	0.326	-5.959	6.640
C	1.637	-5.750	7.084
C	1.991	-4.527	7.660
C	1.033	-3.514	7.787
C	-0.275	-3.727	7.350
H	-0.663	-2.566	2.156
H	-2.890	-3.043	0.486

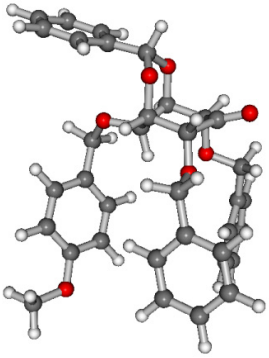
H	-4.118	-3.647	2.670
H	-3.250	-5.770	3.800
H	-0.905	-4.243	4.301
H	-0.180	-5.963	1.184
H	-0.095	-4.561	2.316
H	-2.746	-5.218	7.196
H	-2.146	-6.165	5.812
H	-1.825	0.798	1.629
H	-1.384	0.062	3.188
H	-5.990	-5.686	0.631
H	-5.877	-4.090	1.413
H	0.052	-6.912	6.180
H	2.381	-6.541	6.974
H	3.013	-4.361	8.005
H	1.307	-2.557	8.234
H	-1.022	-2.936	7.437
H	0.928	0.257	3.594
H	3.298	0.154	2.843
H	3.828	-0.345	0.458
H	1.977	-0.733	-1.166
H	-0.390	-0.619	-0.409
H	-6.423	-2.508	-0.247
H	-6.079	-1.509	-2.496
H	-4.521	-2.590	-4.116
H	-3.311	-4.672	-3.469
H	-3.661	-5.669	-1.214
O	-2.554	-1.687	4.395



3.72CC
ΔE **0.0** kcal/mol



3.72BC
ΔE **1.3** kcal/mol



3.72CB
ΔE **4.4** kcal/mol

3.72CC

Final heat of formation = –1881.397

C	2.880	-3.221	-0.141
C	1.767	-3.726	0.545
C	1.967	-4.426	1.744
C	3.257	-4.623	2.247
C	4.361	-4.118	1.553
C	4.170	-3.415	0.358
C	0.378	-3.504	0.010
O	-0.094	-2.224	0.503
C	-1.450	-1.920	0.128
C	-1.902	-0.785	1.070
C	-1.171	0.517	0.706
C	-1.714	0.948	-0.654
C	-1.258	-0.048	-1.748
C	-1.462	-1.534	-1.364
O	-3.329	-0.594	1.050
C	-3.821	-0.101	-0.198
O	-3.151	1.086	-0.617
O	0.140	0.105	-2.032
C	0.395	1.070	-3.080
C	1.881	1.201	-3.271
C	2.517	0.586	-4.358
C	3.899	0.707	-4.537
C	4.658	1.444	-3.623
C	4.033	2.056	-2.530
C	2.653	1.936	-2.357
O	-1.407	1.567	1.644

C	-0.565	1.510	2.815
C	0.873	1.886	2.547
C	1.908	0.957	2.687
C	3.243	1.302	2.443
C	3.554	2.609	2.045
C	2.523	3.555	1.894
C	1.205	3.193	2.145
C	-5.287	0.207	-0.042
C	-5.696	1.211	0.846
C	-7.054	1.498	0.995
C	-8.010	0.785	0.260
C	-7.604	-0.215	-0.625
C	-6.243	-0.502	-0.775
O	4.821	3.063	1.778
C	5.903	2.144	1.949
H	-0.091	0.312	0.603
H	-1.346	1.952	-0.902
H	-1.859	0.118	-2.660
H	-2.100	-2.804	0.261
H	-1.672	-1.097	2.098
H	-3.689	-0.888	-0.972
H	-1.032	2.223	3.510
H	-0.610	0.510	3.283
H	0.413	3.935	2.024
H	2.785	4.570	1.591
H	4.020	0.547	2.559
H	1.676	-0.067	2.989
H	-5.923	-1.284	-1.468
H	-8.345	-0.772	-1.200

H	-9.071	1.012	0.379
H	-7.370	2.280	1.687
H	-4.942	1.760	1.410
H	-0.310	-4.295	0.357
H	0.376	-3.508	-1.090
H	-0.086	0.728	-4.014
H	-0.043	2.047	-2.804
H	2.169	2.412	-1.502
H	4.620	2.633	-1.815
H	5.736	1.543	-3.763
H	4.381	0.229	-5.391
H	1.924	0.009	-5.071
H	2.731	-2.669	-1.071
H	5.029	-3.023	-0.188
H	5.369	-4.277	1.940
H	3.400	-5.176	3.177
H	1.105	-4.823	2.285
H	6.810	2.706	1.702
H	5.967	1.787	2.990
H	5.811	1.279	1.271
O	-1.574	-2.387	-2.231

3.72BC

Final heat of formation = –1881.395

C	2.240	-3.707	-1.363
C	0.962	-3.620	-1.941
C	0.041	-4.651	-1.703
C	0.390	-5.754	-0.915
C	1.664	-5.830	-0.346

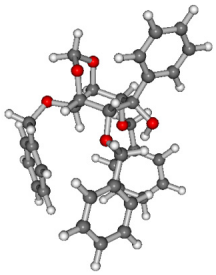
C	2.587	-4.801	-0.569
C	0.590	-2.447	-2.825
O	0.837	-1.159	-2.215
C	0.084	-0.887	-1.046
C	0.766	0.320	-0.320
C	-0.186	1.530	-0.304
C	-1.363	1.111	0.581
C	-2.171	-0.045	-0.111
C	-1.404	-0.599	-1.328
O	1.184	0.022	1.023
C	0.094	-0.249	1.907
O	-0.897	0.772	1.900
C	0.648	-0.394	3.303
C	1.081	-1.650	3.746
C	1.637	-1.795	5.020
C	1.758	-0.684	5.859
C	1.323	0.570	5.419
C	0.772	0.718	4.144
O	0.366	2.728	0.221
C	1.091	3.536	-0.723
C	2.502	3.078	-1.027
C	2.956	2.972	-2.351
C	4.265	2.593	-2.638
C	5.154	2.301	-1.592
C	4.715	2.394	-0.261
C	3.400	2.785	0.006
O	-3.449	0.375	-0.536
C	-4.415	0.416	0.521
C	-5.773	0.758	-0.042
C	-6.727	1.382	0.773
C	-8.008	1.655	0.288
C	-8.345	1.318	-1.026
C	-7.393	0.707	-1.849
C	-6.114	0.424	-1.361
O	6.420	1.933	-1.969
C	7.358	1.621	-0.936
H	-2.260	-0.873	0.624
H	-2.044	1.958	0.730
H	-0.560	1.705	-1.334
H	1.690	0.537	-0.869
H	0.122	-1.754	-0.352
H	-0.376	-1.207	1.594
H	0.986	-2.517	3.089
H	1.972	-2.777	5.359
H	2.187	-0.796	6.857
H	1.414	1.439	6.074
H	0.427	1.690	3.792
H	-0.458	-2.522	-3.147
H	1.222	-2.428	-3.724
H	2.958	-2.902	-1.535
H	3.584	-4.857	-0.127
H	1.939	-6.688	0.269
H	-0.335	-6.551	-0.742
H	-0.956	-4.590	-2.144
H	-4.446	-0.575	1.018
H	-4.130	1.156	1.293
H	-5.365	-0.041	-2.001
H	-7.647	0.449	-2.879
H	-9.343	1.537	-1.410
H	-8.742	2.142	0.934
H	-6.465	1.659	1.798
H	0.517	3.620	-1.666
H	1.108	4.532	-0.255
H	3.060	2.838	1.042
H	5.383	2.165	0.567
H	4.618	2.507	-3.666
H	2.271	3.186	-3.175
H	8.287	1.355	-1.451
H	7.540	2.488	-0.279
H	7.019	0.766	-0.327
O	-1.924	-0.766	-2.415

3.72CB

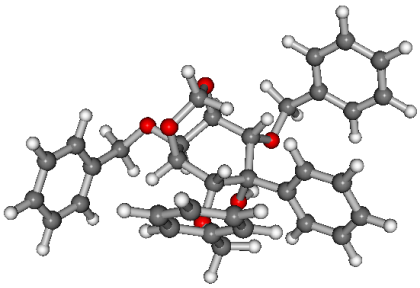
Final heat of formation = –1881.390

C	2.687	3.210	-3.219
C	2.498	2.798	-1.893
C	3.421	1.911	-1.317
C	4.511	1.447	-2.056
C	4.695	1.869	-3.378
C	3.781	2.752	-3.959
C	1.320	3.290	-1.096
O	0.324	2.238	-1.053
C	-0.897	2.623	-0.412
C	-1.939	1.541	-0.736
C	-1.544	0.234	-0.035
C	-1.731	0.452	1.460
C	-0.677	1.465	1.963
C	-0.674	2.760	1.112
O	-3.212	2.075	-0.306
C	-3.887	1.406	0.757
O	-3.014	1.023	1.819
C	-4.813	0.284	0.283
C	-5.396	0.346	-0.988
C	-6.325	-0.618	-1.387
C	-6.692	-1.646	-0.511
C	-6.125	-1.699	0.765
C	-5.194	-0.735	1.163
O	-2.294	-0.902	-0.456
C	-1.821	-1.504	-1.683
C	-0.578	-2.344	-1.499
C	-0.652	-3.580	-0.842
C	0.481	-4.377	-0.652
C	1.725	-3.933	-1.130
C	1.816	-2.695	-1.787
C	0.676	-1.917	-1.966
O	0.660	0.951	1.906
C	1.048	0.229	3.099
C	2.509	-0.115	2.995
C	3.482	0.748	3.519
C	4.841	0.443	3.405
C	5.241	-0.730	2.757
C	4.279	-1.594	2.224
C	2.921	-1.288	2.345
O	2.900	-4.630	-1.002
C	2.843	-5.926	-0.402
H	-0.939	1.766	2.992
H	-1.248	3.602	-0.785
H	-1.980	1.403	-1.829
H	0.878	4.188	-1.563
H	1.626	3.555	-0.070
H	0.863	0.865	3.983
H	0.442	-0.688	3.200
H	0.763	-0.957	-2.480
H	2.789	-2.362	-2.150
H	0.384	-5.335	-0.144
H	-1.616	-3.932	-0.469
H	3.169	1.666	4.021
H	5.588	1.120	3.822
H	6.302	-0.970	2.668
H	4.586	-2.506	1.711
H	2.171	-1.960	1.921
H	1.971	3.900	-3.675
H	3.921	3.086	-4.989
H	5.552	1.512	-3.952
H	5.224	0.760	-1.597
H	3.276	1.581	-0.286
H	-1.632	-0.508	1.988
H	-0.464	0.072	-0.204
H	-2.665	-2.122	-2.018
H	-1.644	-0.731	-2.451
H	-4.750	-0.773	2.159
H	-6.410	-2.494	1.457
H	-7.421	-2.397	-0.820
H	-6.768	-0.565	-2.383
H	-5.111	1.151	-1.667
H	-4.514	2.194	1.205
H	2.500	-5.875	0.644
H	2.184	-6.605	-0.969
H	3.868	-6.310	-0.428
O	-0.427	3.839	1.620

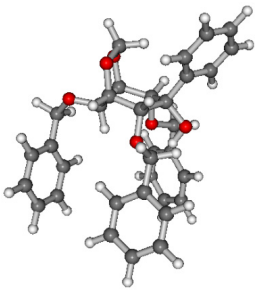
7). C1,C3-Acetals of 5-*C*-alkyl/aryl *neo*-inositol derivatives



3.73CB
ΔE **0.0** kcal/mol



3.73BC
ΔE **1.9** kcal/mol



3.73CC
ΔE **6.3** kcal/mol

3.73CB
Final heat of formation =
–1768.027

C	0.061	0.449	0.219
C	-0.059	-0.014	1.537
C	1.080	-0.504	2.193
C	2.315	-0.530	1.542
C	2.425	-0.070	0.226
C	1.296	0.420	-0.435
C	-1.388	0.029	2.240
O	-1.435	1.198	3.092
C	-2.736	1.459	3.657
C	-2.811	0.814	5.052
C	-1.840	1.535	5.982
C	-2.439	2.916	6.252
C	-2.390	3.741	4.936
C	-2.967	3.031	3.638
O	-4.189	0.903	5.484
C	-4.344	1.530	6.745
O	-3.783	2.842	6.772
O	-1.000	4.053	4.768
C	-0.753	5.417	4.351
C	0.733	5.651	4.322
C	1.466	5.430	3.148
C	2.850	5.628	3.123
C	3.517	6.050	4.278
C	2.796	6.274	5.455
C	1.413	6.074	5.475
O	-1.631	0.753	7.170
C	-0.410	1.071	7.873
C	0.826	0.500	7.215
C	1.791	1.337	6.636
C	2.937	0.799	6.040
C	3.128	-0.584	6.017
C	2.167	-1.430	6.585
C	1.025	-0.889	7.179
O	-2.266	3.539	2.496
C	-4.449	3.344	3.371
H	-2.959	4.672	5.095
H	-1.838	3.473	6.988
H	-2.534	-0.251	4.983
H	-3.511	1.004	3.019
H	-5.422	1.653	6.900
H	-3.889	0.914	7.539
H	-1.451	2.991	2.451
H	-1.199	5.581	3.357
H	-1.235	6.105	5.071
H	-1.533	-0.878	2.853
H	-2.212	0.082	1.505
H	-0.890	1.663	5.437
H	-0.304	2.163	7.994
H	-0.550	0.634	8.872
H	0.849	6.254	6.393
H	3.311	6.610	6.357
H	4.597	6.210	4.259
H	3.408	5.455	2.201
H	0.945	5.104	2.245
H	0.999	-0.859	3.223
H	3.194	-0.913	2.063
H	3.390	-0.097	-0.284
H	1.375	0.778	-1.463
H	-0.820	0.833	-0.297
H	0.275	-1.549	7.623
H	2.314	-2.511	6.573
H	4.026	-1.006	5.560
H	3.677	1.463	5.592
H	1.642	2.419	6.647
C	-4.936	3.115	2.071
C	-6.263	3.390	1.737
C	-7.136	3.912	2.697
C	-6.663	4.151	3.988
C	-5.333	3.871	4.323
H	-4.252	2.744	1.308
H	-6.613	3.206	0.720
H	-8.174	4.132	2.439
H	-7.331	4.561	4.748
H	-4.998	4.039	5.345

3.73BC
Final heat of formation =
–1768.024

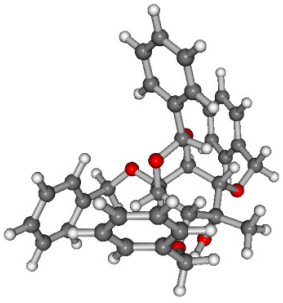
C	-0.105	-0.474	-0.247
C	0.074	-0.125	1.100
C	1.375	0.093	1.575
C	2.477	-0.021	0.720
C	2.287	-0.368	-0.619
C	0.992	-0.598	-1.100
C	-1.118	0.043	2.020
O	-2.059	-1.046	1.967
C	-1.594	-2.307	2.454
C	-2.207	-3.400	1.523
C	-3.230	-4.274	2.264
C	-2.427	-5.002	3.343
C	-1.842	-4.005	4.387
C	-1.920	-2.490	3.983
O	-1.397	-5.809	2.728
C	-0.529	-5.037	1.909
O	-1.194	-4.254	0.940
O	-3.876	-5.258	1.452
C	-5.036	-4.793	0.754
C	-4.764	-4.101	-0.569
C	-3.806	-4.614	-1.457
C	-3.595	-4.005	-2.696
C	-4.343	-2.882	-3.068
C	-5.298	-2.364	-2.188
C	-5.502	-2.970	-0.944
O	-2.569	-4.078	5.629
C	-2.301	-5.248	6.436
C	-0.896	-5.308	6.989
C	0.000	-6.294	6.552
C	1.296	-6.360	7.075
C	1.707	-5.437	8.040
C	0.821	-4.445	8.477
C	-0.471	-4.382	7.955
O	-3.269	-2.045	4.184
C	-0.947	-1.673	4.851
H	-0.498	-2.366	2.336
H	-2.664	-2.883	0.674
H	-3.978	-3.620	2.740
H	-3.072	-5.727	3.857
H	-0.790	-4.281	4.566
H	-3.545	-2.478	5.019
H	0.100	-5.750	1.364
H	0.109	-4.389	2.547

H	-3.038	-5.180	7.248
H	-2.515	-6.165	5.859
H	-1.717	0.914	1.712
H	-0.775	0.223	3.051
H	-5.632	-5.702	0.573
H	-5.636	-4.127	1.404
H	-0.318	-7.012	5.793
H	1.984	-7.133	6.728
H	2.716	-5.488	8.452
H	1.138	-3.722	9.230
H	-1.160	-3.605	8.293
H	1.523	0.354	2.626
H	3.484	0.152	1.104
H	3.145	-0.463	-1.287
H	0.839	-0.873	-2.145
H	-1.114	-0.659	-0.621
H	-6.241	-2.555	-0.252
H	-5.878	-1.482	-2.465
H	-4.178	-2.408	-4.037
H	-2.843	-4.409	-3.376
H	-3.210	-5.476	-1.155
C	0.426	-1.967	4.875
C	1.309	-1.213	5.652
C	0.834	-0.149	6.424
C	-0.529	0.151	6.409
C	-1.411	-0.603	5.630
H	0.824	-2.791	4.280
H	2.372	-1.462	5.655
H	1.523	0.440	7.032
H	-0.913	0.982	7.005
H	-2.472	-0.355	5.599

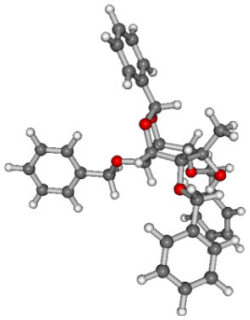
3.73CC

Final heat of formation = –1768.017

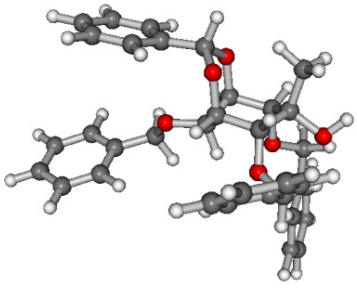
C	0.017	-1.035	0.770
C	-0.415	-1.023	2.104
C	0.423	-1.558	3.093
C	1.669	-2.093	2.758
C	2.092	-2.098	1.424
C	1.263	-1.567	0.430
C	-1.748	-0.428	2.469
O	-1.561	0.967	2.807
C	-2.762	1.626	3.250
C	-3.376	2.487	2.040
C	-2.864	3.984	2.071
C	-2.514	4.566	3.465
C	-1.516	3.638	4.150
C	-2.317	2.390	4.534
O	-3.369	2.746	5.441
C	-4.266	3.711	4.921
O	-3.647	4.842	4.310
O	-0.958	4.311	5.282
C	0.261	3.727	5.764
C	1.472	4.060	4.914
C	2.260	3.050	4.347
C	3.393	3.367	3.590
C	3.747	4.703	3.388
C	2.960	5.721	3.942
C	1.832	5.401	4.699
O	-1.644	4.081	1.312
C	-1.822	4.677	0.014
C	-0.498	4.767	-0.703
C	-0.466	4.690	-2.103
C	0.738	4.828	-2.798
C	1.930	5.030	-2.096
C	1.908	5.094	-0.699
C	0.701	4.968	-0.005
O	-2.932	1.893	0.810
C	-4.906	2.347	1.962
H	-3.620	4.634	1.606
H	-2.055	5.550	3.300
H	-1.702	1.679	5.101
H	-3.510	0.876	3.553
H	-4.828	4.105	5.778
H	-4.956	3.226	4.210
H	-1.953	1.941	0.858
H	-2.536	4.082	-0.580
H	-2.251	5.691	0.144
H	-2.180	-0.952	3.342
H	-2.453	-0.509	1.624
H	-0.731	3.369	3.425
H	0.382	4.143	6.776
H	0.167	2.631	5.866
H	-1.394	4.517	-2.655
H	0.746	4.767	-3.887
H	2.874	5.132	-2.636
H	2.835	5.242	-0.143
H	0.689	5.010	1.083
H	0.092	-1.559	4.134
H	2.310	-2.513	3.536
H	3.063	-2.519	1.159
H	1.587	-1.572	-0.611
H	-0.631	-0.627	-0.007
H	1.215	6.194	5.128
H	3.233	6.767	3.788
H	4.633	4.953	2.802
H	3.995	2.568	3.153
H	1.981	2.004	4.496
C	-5.431	1.056	1.775
C	-6.803	0.844	1.632
C	-7.689	1.925	1.672
C	-7.184	3.213	1.852
C	-5.808	3.423	1.991
H	-4.751	0.206	1.714
H	-7.180	-0.169	1.483
H	-8.763	1.763	1.561
H	-7.862	4.068	1.884
H	-5.455	4.442	2.148



3.74BC
ΔE **0.0** kcal/mol



3.74CC
ΔE **1.2** kcal/mol



3.74CB
ΔE **4.4** kcal/mol

3.74BC

Final heat of formation = –1807.355

C	0.000	0.000	0.000
C	1.217	0.000	2.092
C	2.422	-0.001	1.387
C	2.420	-0.003	-0.013
C	1.207	-0.002	-0.707
C	-1.303	-0.030	2.160
O	-1.242	0.933	3.203
C	-2.369	0.866	4.116
C	-2.443	-0.533	4.727
C	-2.634	-1.486	3.536

O	-1.504	-1.362	2.642
C	-3.700	1.260	3.401
C	-4.720	0.100	3.233
C	-3.993	-1.226	2.817
O	-1.241	-0.770	5.469
C	-1.392	-1.615	6.610
C	-1.310	-3.109	6.335
C	-0.456	-3.612	5.343
C	-0.336	-4.990	5.146
C	-1.062	-5.884	5.941
C	-1.919	-5.389	6.930
C	-2.044	-4.009	7.121
O	-4.904	-2.307	3.135
C	-5.407	-3.060	2.010
C	-4.380	-3.942	1.336
C	-3.671	-4.905	2.071
C	-2.743	-5.734	1.439
C	-2.518	-5.619	0.062
C	-3.219	-4.665	-0.678
C	-4.142	-3.829	-0.041
C	-5.791	0.489	2.204
O	-5.352	-0.121	4.509
O	-4.392	2.334	4.041
C	-3.908	3.653	3.734
C	-2.788	4.147	4.631
C	-2.982	4.223	6.020
C	-1.966	4.696	6.852
C	-0.744	5.107	6.306
C	-0.543	5.037	4.925
C	-1.560	4.557	4.094
H	-3.800	-1.222	1.732
H	-2.619	-2.534	3.854
H	-3.322	-0.583	5.389
H	-2.142	1.608	4.888
H	-3.418	1.587	2.380
H	-2.139	0.224	1.471
H	1.205	0.009	3.182
H	3.369	0.001	1.930
H	3.364	-0.003	-0.562
H	1.199	-0.002	-1.798
H	-0.950	-0.000	-0.540
H	-3.592	3.706	2.676
H	-4.789	4.302	3.857
H	-3.934	3.897	6.445
H	-2.128	4.749	7.931
H	0.049	5.479	6.957
H	0.410	5.348	4.494
H	-1.394	4.487	3.016
H	-6.215	-3.670	2.443
H	-5.860	-2.381	1.266
H	-3.841	-4.995	3.146
H	-2.194	-6.475	2.023
H	-1.793	-6.270	-0.430
H	-3.044	-4.567	-1.751
H	-4.689	-3.081	-0.621
H	-0.565	-1.330	7.281
H	-2.337	-1.388	7.139
H	-2.720	-3.628	7.890
H	-2.496	-6.079	7.550
H	-0.963	-6.960	5.790
H	0.330	-5.368	4.368
H	0.096	-2.912	4.713
H	-5.720	-1.027	4.430
H	-6.290	1.407	2.538
H	-5.356	0.661	1.207
H	-6.549	-0.302	2.124

3.74CC

Final heat of formation = –1807.353

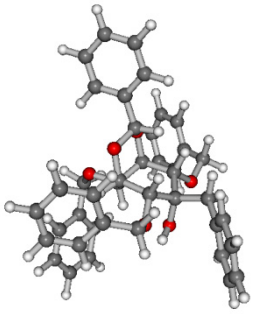
C	0.000	0.000	0.000
C	0.000	0.000	1.402
C	1.219	0.000	2.091
C	2.425	0.005	1.384
C	2.423	0.006	-0.013
C	1.207	0.005	-0.703
C	-1.317	-0.056	2.149
O	-2.268	0.745	1.456
C	-3.495	0.956	2.175
C	-3.208	1.606	3.531
C	-2.294	0.631	4.263
O	-1.107	0.346	3.497
C	-4.390	-0.303	2.375
C	-4.057	-1.278	3.599
C	-3.124	-0.606	4.700
O	-5.712	0.247	2.543
C	-6.737	-0.443	1.784
C	-8.058	0.230	2.039
C	-8.413	1.393	1.338
C	-9.628	2.033	1.590
C	-10.506	1.514	2.548
C	-10.163	0.355	3.251
C	-8.945	-0.281	2.996
C	-3.469	-2.616	3.133
O	-5.291	-1.667	4.211
O	-3.920	-0.112	5.790
C	-4.013	-1.021	6.910
C	-4.821	-0.367	8.000
C	-6.054	-0.904	8.395
C	-6.802	-0.302	9.412
C	-6.325	0.852	10.038
C	-5.098	1.400	9.646
C	-4.350	0.792	8.637
O	-2.562	2.873	3.453
C	-3.440	3.938	3.085
C	-2.668	5.234	3.008
C	-3.319	6.449	3.267
C	-2.637	7.663	3.145
C	-1.289	7.674	2.774
C	-0.631	6.464	2.526
C	-1.316	5.251	2.638
H	-4.153	1.692	4.098
H	-1.912	1.096	5.179
H	-2.419	-1.371	5.072
H	-4.350	-0.892	1.442
H	-4.071	1.624	1.523
H	-1.687	-1.098	2.144
H	-3.905	3.732	2.100
H	-4.262	4.028	3.821
H	-4.369	6.446	3.572
H	-3.156	8.601	3.351
H	-0.752	8.620	2.685
H	0.423	6.464	2.242
H	-0.807	4.305	2.452
H	1.215	0.011	3.181
H	3.371	0.011	1.930
H	3.366	0.010	-0.564
H	1.197	0.013	-1.795
H	-0.949	0.014	-0.537
H	-6.475	-0.394	0.710
H	-6.774	-1.501	2.092
H	-4.489	-1.963	6.591
H	-2.990	-1.248	7.267
H	-6.429	-1.803	7.901
H	-7.760	-0.732	9.711
H	-6.908	1.326	10.831
H	-4.723	2.302	10.133
H	-3.394	1.221	8.332
H	-8.679	-1.190	3.542
H	-10.846	-0.055	3.997
H	-11.458	2.011	2.743
H	-9.894	2.934	1.036
H	-7.729	1.797	0.589
H	-4.078	-3.038	2.321
H	-2.432	-2.544	2.789
H	-3.493	-3.317	3.978
H	-5.753	-0.832	4.428

3.74CB

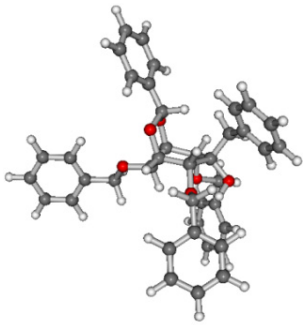
Final heat of formation = -1807.348

C	0.000	0.000	0.000
C	0.000	0.000	1.401
C	1.221	0.000	2.087
C	2.426	0.032	1.381
C	2.423	0.050	-0.018
C	1.206	0.032	-0.706
C	-1.314	-0.157	2.166
O	-1.259	0.290	3.518
C	-1.573	1.680	3.779
C	-1.790	2.504	2.520
C	-2.800	1.729	1.669
O	-2.449	0.345	1.456
C	-4.178	1.813	2.381
C	-4.150	1.303	3.867
C	-2.862	1.758	4.637
O	-2.938	3.120	5.075
C	-3.368	3.301	6.438

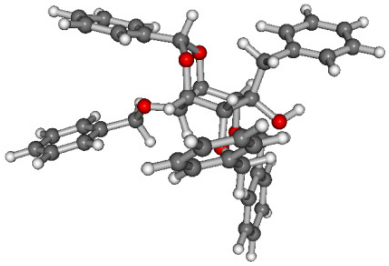
C	-2.366	2.816	7.467
C	-1.024	3.227	7.407
C	-0.106	2.799	8.369
C	-0.518	1.958	9.409
C	-1.850	1.544	9.479
C	-2.766	1.969	8.510
O	-0.531	2.791	1.914
C	-0.614	3.729	0.831
C	0.735	4.364	0.600
C	1.434	4.960	1.661
C	2.662	5.585	1.439
C	3.207	5.629	0.151
C	2.519	5.038	-0.911
C	1.293	4.404	-0.684
O	-4.562	3.185	2.268
C	-5.956	3.403	2.002
C	-6.221	4.885	1.929
C	-5.693	5.750	2.901
C	-5.971	7.117	2.855
C	-6.787	7.639	1.845
C	-7.316	6.785	0.874
C	-7.028	5.416	0.915
O	-5.283	1.886	4.564
C	-4.301	-0.221	3.917
H	-2.728	1.090	5.505
H	-4.887	1.178	1.817
H	-2.923	2.192	0.679
H	-6.240	2.920	1.047
H	-6.555	2.950	2.810
H	-3.508	4.389	6.529
H	-4.346	2.820	6.594
H	0.763	3.930	-1.513
H	2.941	5.060	-1.918
H	4.167	6.119	-0.022
H	3.197	6.043	2.273
H	1.012	4.920	2.667
H	-3.807	1.640	8.563
H	-2.177	0.884	10.285
H	0.200	1.624	10.161
H	0.934	3.126	8.311
H	-0.704	3.884	6.596
H	-5.053	5.338	3.683
H	-5.551	7.781	3.613
H	-7.005	8.708	1.812
H	-7.947	7.184	0.077
H	-7.433	4.754	0.145
H	-0.746	2.099	4.370
H	-2.279	3.449	2.816
H	-0.951	3.229	-0.095
H	-1.362	4.507	1.081
H	-0.952	-0.019	-0.533
H	1.195	0.039	-1.798
H	3.365	0.077	-0.568
H	3.372	0.046	1.925
H	1.219	-0.011	3.177
H	-1.516	-1.239	2.253
H	-5.906	1.162	4.745
H	-4.323	-0.557	4.966
H	-5.244	-0.517	3.427
H	-3.486	-0.744	3.411



3.75BC
ΔE **0.0** kcal/mol



3.75CC
ΔE **0.8** kcal/mol



3.75CB
ΔE **3.8** kcal/mol

3.75BC

Final heat of formation = –2038.483

C	0.000	0.000	0.000
C	0.000	0.000	1.405
C	1.241	0.000	2.067
C	2.438	0.035	1.346
C	2.421	0.052	-0.052
C	1.196	0.026	-0.725
C	-1.294	-0.052	2.180
C	-1.732	1.241	2.940
C	-3.009	0.875	3.756
C	-3.870	2.088	4.228
C	-3.150	3.422	3.998
C	-2.981	3.532	2.487
C	-2.006	2.436	1.955
O	-4.271	3.495	1.834
C	-5.040	2.338	2.148
O	-5.153	2.113	3.553
C	-6.428	2.520	1.585

C	-6.967	1.583	0.698
C	-8.258	1.754	0.187
C	-9.015	2.866	0.566
C	-8.478	3.805	1.456
C	-7.190	3.634	1.966
O	-3.900	4.551	4.457
C	-3.808	4.768	5.872
C	-2.455	5.281	6.331
C	-1.863	6.385	5.696
C	-0.633	6.880	6.133
C	0.022	6.281	7.217
C	-0.557	5.180	7.852
C	-1.787	4.683	7.407
O	-2.588	0.026	4.826
C	-3.593	-0.873	5.328
C	-4.419	-0.321	6.475
C	-3.781	0.163	7.629
C	-4.531	0.649	8.702
C	-5.930	0.652	8.639
C	-6.572	0.170	7.495

C	-5.819	-0.312	6.419
O	-0.721	1.642	3.869
O	-0.710	3.007	1.703
C	-0.458	3.488	0.364
C	-0.993	4.875	0.082
C	-0.391	5.998	0.675
C	-0.878	7.282	0.423
C	-1.971	7.461	-0.434
C	-2.573	6.352	-1.033
C	-2.084	5.068	-0.776
H	-2.422	2.046	1.009
H	-2.571	4.512	2.218
H	-2.156	3.389	4.472
H	-4.120	1.942	5.284
H	-3.662	0.285	3.084
H	-4.563	1.450	1.674
H	-6.758	4.359	2.656
H	-9.068	4.674	1.752
H	-10.023	3.002	0.170
H	-8.672	1.019	-0.506

H	-6.373	0.715	0.402
H	-4.260	-1.200	4.509
H	-3.029	-1.753	5.675
H	-2.690	0.165	7.675
H	-4.025	1.021	9.595
H	-6.516	1.031	9.477
H	-7.662	0.177	7.434
H	-6.324	-0.672	5.520
H	0.638	3.476	0.278
H	-0.862	2.765	-0.365
H	0.462	5.859	1.344
H	-0.400	8.146	0.887
H	-2.350	8.465	-0.632
H	-3.428	6.486	-1.698
H	-2.562	4.202	-1.241
H	-4.587	5.517	6.083
H	-4.070	3.855	6.436
H	-2.234	3.815	7.899
H	-0.048	4.702	8.691
H	0.982	6.670	7.559
H	-0.184	7.740	5.632
H	-2.373	6.847	4.847
H	-0.096	2.176	3.332
H	-1.226	-0.831	2.954
H	-2.112	-0.340	1.498
H	1.260	-0.032	3.158
H	3.391	0.037	1.880
H	3.356	0.069	-0.614
H	1.170	0.017	-1.816
H	-0.953	-0.038	-0.535

3.75CC

Final heat of formation = –2038.482

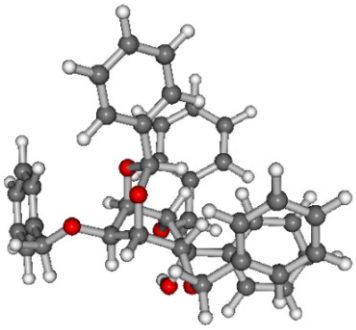
C	0.000	0.000	0.000
C	0.000	0.000	1.405
C	1.240	0.000	2.070
C	2.437	0.014	1.350
C	2.421	0.022	-0.049
C	1.197	0.011	-0.723
C	-1.300	-0.010	2.177
C	-1.672	1.307	2.927
C	-3.164	1.158	3.480
C	-4.262	1.984	2.750
C	-3.770	3.428	2.614
C	-2.698	3.390	1.535
C	-1.449	2.620	2.048
O	-3.245	2.909	0.294
C	-3.813	1.615	0.387
O	-4.714	1.461	1.486
C	-4.563	1.294	-0.889
C	-5.401	0.171	-0.930
C	-6.071	-0.164	-2.109
C	-5.907	0.616	-3.258
C	-5.071	1.736	-3.219
C	-4.399	2.075	-2.040
O	-4.766	4.372	2.233
C	-5.634	4.747	3.307
C	-6.633	5.769	2.821
C	-7.130	6.735	3.709
C	-8.095	7.656	3.291
C	-8.565	7.629	1.974
C	-8.065	6.675	1.082
C	-7.107	5.747	1.502
O	-3.273	1.604	4.835
C	-3.039	0.577	5.827
C	-3.306	1.163	7.188
C	-4.604	1.179	7.719
C	-4.856	1.746	8.971
C	-3.807	2.305	9.708
C	-2.509	2.296	9.188
C	-2.262	1.728	7.935
O	-0.763	1.351	4.026
O	-0.728	3.568	2.872
C	0.381	4.210	2.192
C	1.058	5.146	3.155
C	2.132	4.702	3.941
C	2.745	5.561	4.857
C	2.287	6.875	4.997
C	1.217	7.327	4.218
C	0.607	6.467	3.302
H	-3.303	3.727	3.571
H	-2.372	4.412	1.299
H	-0.827	2.350	1.179
H	-3.446	0.090	3.418
H	-5.151	1.925	3.390
H	-2.987	0.889	0.511
H	-6.173	3.859	3.693
H	-5.045	5.159	4.149
H	-6.757	6.769	4.735
H	-8.472	8.403	3.992
H	-9.313	8.352	1.643
H	-8.423	6.651	0.051
H	-6.709	5.007	0.808
H	-3.754	2.952	-2.002
H	-4.943	2.353	-4.110
H	-6.431	0.354	-4.178
H	-6.726	-1.037	-2.129
H	-5.541	-0.428	-0.029
H	-3.723	-0.271	5.631
H	-2.000	0.223	5.751
H	1.081	3.435	1.833
H	-0.003	4.765	1.317
H	2.491	3.677	3.828
H	3.582	5.206	5.461
H	2.767	7.549	5.709
H	0.859	8.353	4.322
H	-0.227	6.821	2.693
H	-1.249	1.720	7.528
H	-1.687	2.730	9.761
H	-4.001	2.746	10.688
H	-5.870	1.747	9.375
H	-5.423	0.741	7.144
H	-2.118	-0.323	1.513
H	-0.547	2.305	4.138
H	-1.251	-0.770	2.973
H	1.252	-0.008	3.161
H	3.390	0.008	1.884
H	3.357	0.027	-0.610
H	1.171	0.006	-1.814
H	-0.951	-0.017	-0.539

3.75CB

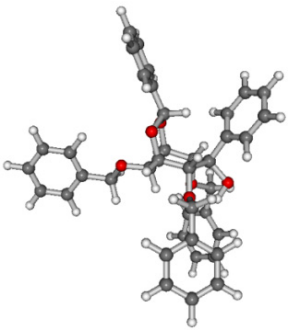
Final heat of formation = –2038.4771

C	0.000	0.000	0.000
C	0.000	0.000	1.408
C	1.242	0.000	2.070
C	2.439	0.019	1.350
C	2.422	0.041	-0.049
C	1.199	0.027	-0.723
C	-1.298	-0.003	2.182
C	-1.903	1.414	2.454
C	-0.969	2.293	3.365
C	-1.116	1.999	4.883
C	-2.593	2.185	5.244
C	-3.338	1.028	4.599
C	-3.339	1.245	3.064
O	-0.601	0.680	5.175
C	-1.542	-0.300	5.625
O	-2.767	-0.270	4.899
C	-1.714	-0.328	7.144
C	-0.657	0.060	7.978
C	-0.770	-0.067	9.365
C	-1.934	-0.596	9.930
C	-2.982	-1.002	9.099
C	-2.871	-0.875	7.712
O	-2.909	2.244	6.635
C	-2.411	3.416	7.289
C	-3.208	3.700	8.540
C	-4.590	3.468	8.587
C	-5.324	3.797	9.729
C	-4.689	4.366	10.837
C	-3.311	4.596	10.800
C	-2.576	4.258	9.659
O	-1.247	3.693	3.244
C	-0.390	4.409	2.346
C	-0.819	5.855	2.298
C	-2.180	6.191	2.238
C	-2.573	7.528	2.151
C	-1.613	8.546	2.113
C	-0.256	8.218	2.172
C	0.137	6.879	2.271
O	-2.089	2.073	1.187
O	-4.164	2.394	2.849
C	-5.036	2.319	1.701
C	-6.149	1.302	1.855
C	-7.037	1.376	2.942

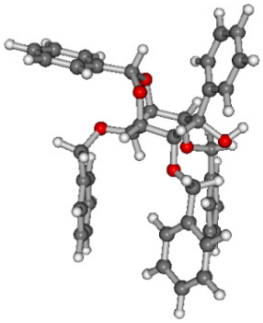
C	-8.069	0.448	3.082
C	-8.234	-0.569	2.134
C	-7.359	-0.652	1.048
C	-6.322	0.278	0.914
H	-3.804	0.357	2.601
H	0.079	2.097	3.078
H	-0.482	2.724	5.415
H	0.663	4.335	2.679
H	-0.458	3.967	1.336
H	-5.455	3.332	1.622
H	-4.448	2.118	0.793
H	-1.496	4.427	9.640
H	-2.803	5.030	11.663
H	-5.264	4.623	11.728
H	-6.400	3.607	9.754
H	-5.081	3.015	7.725
H	-5.636	0.210	0.065
H	-7.480	-1.445	0.307
H	-9.043	-1.294	2.243
H	-8.753	0.519	3.930
H	-6.908	2.170	3.681
H	-2.922	5.392	2.274
H	-3.634	7.779	2.110
H	-1.922	9.590	2.044
H	0.500	9.006	2.153
H	1.199	6.629	2.331
H	-4.384	1.014	4.936
H	-2.927	3.117	4.754
H	-1.343	3.294	7.551
H	-2.483	4.278	6.596
H	0.251	0.468	7.532
H	0.056	0.247	10.007
H	-2.023	-0.694	11.014
H	-3.894	-1.416	9.533
H	-3.688	-1.186	7.061
H	-1.083	-1.260	5.329
H	-1.315	1.842	0.634
H	-1.167	-0.533	3.130
H	-2.060	-0.551	1.607
H	1.260	-0.027	3.161
H	3.391	0.011	1.884
H	3.358	0.055	-0.610
H	1.174	0.022	-1.814
H	-0.951	-0.060	-0.537



3.76BC
ΔE **0.0** kcal/mol



3.76CC
ΔE **5.0** kcal/mol



3.76CB
ΔE **10.0** kcal/mol

3.76BC
Final heat of formation =
–1999.158

C	0.000	0.000	0.000
C	0.000	0.000	1.401
C	1.235	0.000	2.070
C	2.437	0.021	1.359
C	2.425	0.040	-0.039
C	1.202	0.024	-0.715
C	-1.328	-0.024	2.178
C	-1.409	1.164	3.214
C	-2.470	0.974	4.341
C	-3.432	-0.182	4.027
C	-2.557	-1.433	4.025
C	-1.472	-1.394	2.906
O	-1.965	-1.604	5.339
C	-1.173	-0.492	5.742
O	-1.870	0.752	5.638
C	-0.773	-0.683	7.185
C	0.542	-0.431	7.592
C	0.907	-0.578	8.934
C	-0.045	-0.981	9.874
C	-1.361	-1.235	9.470
C	-1.726	-1.085	8.131
O	-4.468	-0.352	5.001
C	-5.705	0.290	4.681
C	-5.766	1.779	4.979
C	-6.426	2.650	4.102
C	-6.541	4.013	4.399
C	-5.986	4.520	5.578
C	-5.316	3.657	6.455
C	-5.210	2.296	6.160
O	-1.789	2.355	2.488
C	-0.701	3.215	2.060
C	0.031	3.882	3.203
C	-0.675	4.580	4.197
C	0.008	5.220	5.232
C	1.406	5.182	5.283
C	2.117	4.492	4.298
C	1.431	3.841	3.267
O	-2.437	0.125	1.282
O	-1.715	-2.378	1.898
C	-1.430	-3.728	2.318
C	0.037	-4.011	2.562
C	0.958	-3.950	1.503
C	2.308	-4.229	1.720
C	2.757	-4.576	3.000
C	1.851	-4.634	4.062
C	0.498	-4.351	3.842
H	-0.503	-1.604	3.391
H	-3.183	-2.323	3.889
H	-3.865	-0.048	3.023
H	-3.006	1.923	4.446
H	-0.433	1.326	3.696
H	-0.262	-0.442	5.108
H	-2.746	-1.284	7.801
H	-2.105	-1.552	10.203
H	0.238	-1.099	10.922
H	1.934	-0.380	9.243
H	1.284	-0.116	6.855
H	0.007	2.659	1.427
H	-1.202	3.967	1.432
H	-1.766	4.609	4.160
H	-0.552	5.756	6.001
H	1.938	5.685	6.092
H	3.207	4.453	4.335
H	1.986	3.294	2.501
H	-2.009	-3.988	3.222
H	-1.809	-4.344	1.490
H	0.610	-3.671	0.506
H	3.013	-4.181	0.889
H	3.812	-4.799	3.168
H	2.195	-4.897	5.064
H	-0.209	-4.388	4.674
H	-5.969	0.114	3.621
H	-6.453	-0.234	5.297
H	-4.673	1.625	6.833

H	-4.875	4.047	7.374
H	-6.070	5.582	5.811
H	-7.057	4.679	3.706
H	-6.853	2.259	3.175
H	-2.544	1.101	1.210
H	1.272	-0.018	3.162
H	3.386	0.018	1.899
H	3.363	0.059	-0.597
H	1.181	0.025	-1.806
H	-0.957	-0.028	-0.520

3.76CC

Final heat of formation = –1999.150

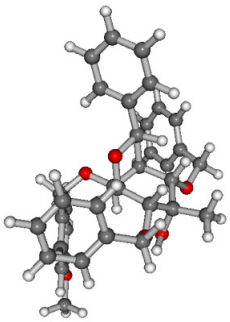
C	0.000	0.000	0.000
C	0.000	0.000	1.404
C	1.244	0.000	2.059
C	2.442	0.015	1.344
C	2.425	0.024	-0.055
C	1.200	0.015	-0.722
C	-1.264	-0.083	2.283
C	-2.598	-0.307	1.457
C	-3.439	0.966	1.161
C	-3.724	1.670	2.493
C	-2.403	2.303	2.906
C	-1.375	1.188	3.258
O	-1.981	3.258	1.922
C	-1.795	2.695	0.628
O	-2.888	1.879	0.193
C	-1.601	3.820	-0.368
C	-2.073	3.707	-1.682
C	-1.844	4.735	-2.602
C	-1.142	5.881	-2.218
C	-0.669	5.996	-0.907
C	-0.895	4.970	0.014
O	-4.716	2.691	2.426
C	-6.052	2.183	2.432
C	-7.035	3.326	2.342
C	-8.308	3.199	2.918
C	-9.249	4.225	2.800
C	-8.923	5.397	2.112
C	-7.652	5.534	1.545
C	-6.713	4.505	1.655
O	-3.505	-1.151	2.180
C	-3.432	-2.547	1.804
C	-4.480	-3.305	2.574
C	-5.817	-3.307	2.148
C	-6.795	-3.991	2.874
C	-6.446	-4.686	4.037
C	-5.116	-4.692	4.470
C	-4.141	-4.004	3.742
O	-1.028	-1.231	3.107
O	-1.788	0.691	4.552
C	-1.046	1.254	5.662
C	-1.561	0.653	6.942
C	-1.007	-0.535	7.441
C	-1.500	-1.110	8.616
C	-2.554	-0.500	9.304
C	-3.111	0.686	8.814
C	-2.616	1.258	7.640
H	-4.007	0.907	3.239
H	-2.547	2.905	3.814
H	-0.376	1.645	3.339
H	-2.348	-0.792	0.501
H	-4.368	0.616	0.693
H	-0.883	2.072	0.656
H	-6.207	1.497	1.574
H	-6.236	1.595	3.352
H	-8.563	2.289	3.469
H	-10.235	4.112	3.255
H	-9.654	6.203	2.024
H	-7.388	6.450	1.012
H	-5.718	4.611	1.222
H	-0.538	5.063	1.040
H	-0.125	6.890	-0.597
H	-0.965	6.684	-2.937
H	-2.221	4.641	-3.622
H	-2.632	2.819	-1.974
H	-3.616	-2.633	0.716
H	-2.426	-2.935	2.024
H	0.028	1.033	5.529
H	-1.176	2.351	5.670
H	-0.182	-1.011	6.906
H	-1.059	-2.032	8.997
H	-2.938	-0.946	10.223
H	-3.932	1.167	9.350
H	-3.053	2.184	7.258
H	-3.102	-4.008	4.079
H	-4.839	-5.234	5.375
H	-7.208	-5.224	4.602
H	-7.831	-3.988	2.529
H	-6.090	-2.767	1.239
H	-1.531	-1.045	3.933
H	1.270	-0.047	3.148
H	3.392	0.012	1.880
H	3.360	0.034	-0.618
H	1.168	0.021	-1.812
H	-0.936	0.011	-0.559

3.76CB

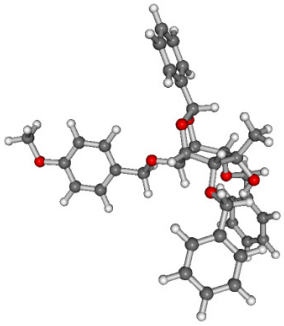
Final heat of formation = –1999.142

C	0.000	0.000	0.000
C	0.000	0.000	1.405
C	1.250	0.000	2.059
C	2.447	0.009	1.343
C	2.428	0.017	-0.055
C	1.201	0.011	-0.719
C	-1.261	-0.121	2.277
C	-2.603	-0.269	1.466
C	-3.264	1.069	1.032
C	-3.434	1.954	2.256
C	-2.020	2.320	2.709
C	-1.346	1.067	3.311
O	-2.515	1.707	-0.024
C	-1.708	2.839	0.321
O	-1.165	2.771	1.635
C	-2.382	4.174	0.006
C	-3.365	4.262	-0.987
C	-3.902	5.502	-1.341
C	-3.455	6.669	-0.713
C	-2.463	6.588	0.269
C	-1.925	5.347	0.622
O	-4.255	3.071	1.904
C	-4.764	3.817	3.016
C	-5.906	3.140	3.752
C	-6.020	3.257	5.144
C	-7.108	2.698	5.821
C	-8.089	1.999	5.112
C	-7.976	1.866	3.723
C	-6.895	2.438	3.048
O	-3.610	-0.927	2.238
C	-3.754	-2.329	1.955
C	-4.812	-2.919	2.850
C	-4.790	-2.676	4.233
C	-5.745	-3.262	5.066
C	-6.728	-4.104	4.533
C	-6.756	-4.351	3.158
C	-5.806	-3.755	2.322
O	-1.097	-1.327	3.077
O	-2.081	0.736	4.486
C	-1.271	0.315	5.587
C	-2.113	0.107	6.825
C	-3.485	0.383	6.852
C	-4.223	0.176	8.024
C	-3.601	-0.305	9.178
C	-2.229	-0.583	9.156
C	-1.493	-0.381	7.987
H	-0.315	1.348	3.587
H	-2.399	-0.858	0.554
H	-4.247	0.822	0.607
H	-4.033	-2.473	0.893
H	-2.789	-2.836	2.129
H	-0.747	-0.621	5.329
H	-0.501	1.088	5.792
H	-6.804	2.336	1.965
H	-8.735	1.316	3.164
H	-8.935	1.554	5.638
H	-7.185	2.801	6.905
H	-5.248	3.791	5.705
H	-0.423	-0.607	7.976
H	-1.732	-0.962	10.051
H	-4.178	-0.466	10.090
H	-5.293	0.391	8.028
H	-3.974	0.754	5.952
H	-4.027	-2.015	4.645
H	-5.720	-3.061	6.139
H	-7.471	-4.563	5.188

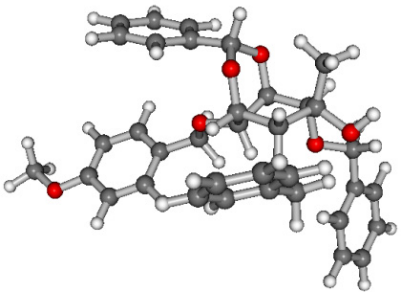
H	-7.523	-5.001	2.733
H	-5.838	-3.941	1.246
H	-2.037	3.103	3.483
H	-3.909	1.354	3.050
H	-3.961	4.072	3.731
H	-5.111	4.762	2.570
H	-3.716	3.348	-1.468
H	-4.675	5.558	-2.110
H	-3.875	7.638	-0.991
H	-2.105	7.494	0.762
H	-1.148	5.280	1.385
H	-0.819	2.747	-0.327
H	-0.404	-1.852	2.640
H	1.288	-0.021	3.150
H	3.397	0.013	1.880
H	3.362	0.026	-0.620
H	1.169	0.016	-1.810
H	-0.939	0.029	-0.549



3.77BC
ΔE **0.0** kcal/mol



3.77CC
ΔE **2.5** kcal/mol



3.77CB
ΔE **5.6** kcal/mol

3.77BC

Final heat of formation = –1921.929

C	0.000	0.000	0.000
C	0.000	0.000	1.401
C	1.229	0.000	2.081
C	2.431	-0.003	1.371
C	2.421	0.002	-0.029
C	1.203	0.003	-0.714
C	-1.299	0.033	2.183
O	-1.465	-1.039	3.129
C	-2.081	-2.219	2.615
C	-1.102	-3.138	1.815
C	-0.877	-4.475	2.514
C	-2.254	-5.156	2.538
C	-3.269	-4.349	3.405
C	-2.804	-2.909	3.805
O	-2.723	-5.344	1.182
C	-2.796	-4.130	0.429
O	-1.590	-3.378	0.467
C	-3.088	-4.489	-1.007
C	-4.311	-4.148	-1.593
C	-4.580	-4.495	-2.921
C	-3.622	-5.186	-3.667
C	-2.396	-5.528	-3.083
C	-2.128	-5.182	-1.758
O	0.097	-5.217	1.775
C	0.670	-6.315	2.505
C	1.593	-5.894	3.629
C	1.386	-6.324	4.942
C	2.252	-5.958	5.982
C	3.350	-5.135	5.703
C	3.569	-4.688	4.387
C	2.702	-5.067	3.370
C	-4.004	-2.065	4.256
O	-1.863	-3.015	4.889
O	-3.542	-5.007	4.657
C	-4.660	-5.922	4.673
C	-4.333	-7.324	4.205
C	-3.626	-8.198	5.047
C	-3.309	-9.490	4.626
C	-3.700	-9.928	3.355
C	-4.407	-9.067	2.511
C	-4.723	-7.774	2.936
O	4.264	-4.709	6.634
C	4.075	-5.126	7.987
H	-4.209	-4.275	2.830
H	-2.196	-6.172	2.946
H	-0.535	-4.286	3.544
H	-0.150	-2.616	1.673
H	-2.869	-1.915	1.898
H	-3.629	-3.512	0.832
H	-1.177	-5.437	-1.290
H	-1.646	-6.065	-3.666
H	-3.828	-5.457	-4.704
H	-5.537	-4.224	-3.373
H	-5.059	-3.606	-1.007
H	-2.156	0.061	1.485
H	-1.334	0.947	2.796
H	1.236	-0.013	3.173
H	3.381	-0.004	1.910
H	3.362	0.001	-0.584
H	1.188	-0.004	-1.805
H	-0.950	-0.018	-0.538
H	-4.980	-5.944	5.725
H	-5.485	-5.503	4.071
H	-3.325	-7.858	6.041
H	-2.763	-10.162	5.291
H	-3.455	-10.939	3.025
H	-4.711	-9.402	1.518
H	-5.265	-7.102	2.267
H	2.874	-4.708	2.353
H	4.430	-4.048	4.189
H	2.055	-6.311	6.994
H	0.528	-6.963	5.169
H	-2.262	-3.673	5.495
H	-3.648	-1.079	4.581
H	-4.735	-1.931	3.443
H	-4.510	-2.552	5.102
H	4.900	-4.681	8.553
H	3.116	-4.760	8.392
H	4.117	-6.224	8.082
H	-0.115	-6.985	2.900
H	1.226	-6.879	1.741

3.77CC

Final heat of formation = –1921.925

C	0.000	0.000	0.000
C	0.000	0.000	1.400
C	1.236	0.000	2.065
C	2.436	0.013	1.359
C	2.422	0.014	-0.044
C	1.195	0.001	-0.726
C	-1.294	0.037	2.172
O	-2.207	-0.920	1.616
C	-3.464	-0.964	2.283
C	-4.391	0.214	1.974
O	-4.648	0.274	0.561
C	-5.266	-0.899	0.048
O	-4.620	-2.106	0.441
C	-4.220	-2.205	1.823
C	-5.366	-2.489	2.828
C	-6.326	-1.269	3.170
C	-5.653	0.156	2.889
C	-5.287	-0.821	-1.466

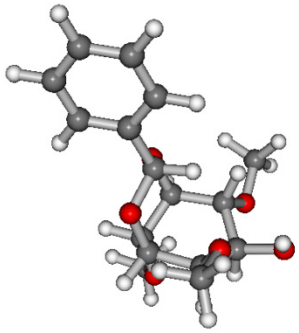
C	-5.494	0.415	-2.094
C	-5.568	0.493	-3.487
C	-5.442	-0.663	-4.264
C	-5.237	-1.896	-3.639
C	-5.161	-1.978	-2.246
O	-5.195	0.717	4.136
C	-6.093	1.710	4.697
C	-5.526	2.182	6.008
C	-4.533	3.173	6.042
C	-3.985	3.588	7.257
C	-4.427	3.017	8.456
C	-5.417	2.031	8.433
C	-5.962	1.616	7.215
C	-7.674	-1.440	2.457
O	-6.681	-1.327	4.555
O	-4.685	-2.939	4.009
C	-5.318	-4.057	4.667
C	-4.462	-4.492	5.829
C	-4.986	-4.520	7.128
C	-4.202	-4.944	8.206
C	-2.878	-5.335	7.994
C	-2.342	-5.302	6.701
C	-3.131	-4.888	5.626
O	3.654	0.023	-0.654
C	3.685	0.001	-2.082
H	-3.316	-1.031	3.377
H	-3.552	-3.075	1.843
H	-5.982	-3.311	2.420
H	-6.416	0.818	2.444
H	-3.912	1.175	2.198
H	-6.308	-0.916	0.417
H	-1.732	1.053	2.122
H	-1.108	-0.189	3.239
H	1.261	-0.015	3.158
H	3.397	0.010	1.875
H	1.158	-0.008	-1.814
H	-0.952	-0.019	-0.533
H	-4.988	-2.935	-1.755
H	-5.132	-2.802	-4.239
H	-5.501	-0.601	-5.352
H	-5.721	1.461	-3.967
H	-5.579	1.317	-1.487
H	-6.182	2.550	3.983
H	-7.090	1.263	4.844
H	-6.323	-3.771	5.015
H	-5.425	-4.883	3.936
H	-6.019	-4.205	7.296
H	-4.625	-4.962	9.212
H	-2.262	-5.663	8.833
H	-1.308	-5.605	6.530
H	-2.711	-4.858	4.618
H	-6.739	0.848	7.196
H	-5.767	1.584	9.366
H	-4.001	3.343	9.406
H	-3.215	4.362	7.272
H	-4.189	3.619	5.107
H	-8.289	-0.536	2.562
H	-7.579	-1.680	1.391
H	-8.206	-2.273	2.936
H	-5.878	-1.046	5.041
H	4.747	0.005	-2.354
H	3.209	-0.909	-2.484
H	3.195	0.890	-2.512

3.77CB

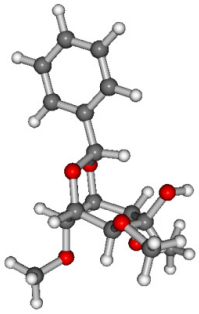
Final heat of formation = –1921.920

C	0.000	0.000	0.000
C	0.000	0.000	1.402
C	1.227	0.000	2.082
C	2.429	0.002	1.370
C	2.421	0.013	-0.029
C	1.203	0.013	-0.713
C	-1.300	0.048	2.164
O	-1.208	-0.798	3.319
C	-2.378	-0.826	4.139
C	-2.518	-2.310	4.578
C	-1.357	-2.628	5.526
C	-1.632	-1.862	6.809
C	-1.428	-0.353	6.526
C	-2.307	0.182	5.342
O	-3.824	-2.518	5.161
C	-3.874	-2.837	6.554
O	-2.966	-2.069	7.337
C	-3.832	-4.339	6.836
C	-4.360	-5.240	5.902
C	-4.441	-6.603	6.203
C	-4.003	-7.076	7.444
C	-3.489	-6.176	8.383
C	-3.410	-4.814	8.084
O	-1.134	-4.003	5.828
C	-0.649	-4.769	4.706
C	0.068	-5.994	5.204
C	1.328	-5.885	5.822
C	2.004	-7.007	6.282
C	1.433	-8.284	6.128
C	0.179	-8.414	5.517
C	-0.488	-7.268	5.066
O	-1.676	1.403	4.874
C	-3.716	0.540	5.829
O	-0.025	-0.203	6.274
C	0.579	0.973	6.843
C	0.642	0.956	8.357
C	1.198	-0.140	9.037
C	1.273	-0.149	10.431
C	0.799	0.944	11.168
C	0.246	2.040	10.503
C	0.166	2.042	9.106
O	2.181	-9.331	6.606
C	1.644	-10.647	6.467
H	-1.707	0.203	7.438
H	-3.267	-0.570	3.533
H	-2.465	-2.922	3.665
H	-2.133	-0.286	1.514
H	-1.509	1.083	2.486
H	1.595	0.980	6.420
H	0.059	1.876	6.487
H	-1.471	-7.375	4.601
H	-0.287	-9.390	5.391
H	2.983	-6.926	6.757
H	1.781	-4.898	5.945
H	-0.272	2.898	8.586
H	-0.130	2.893	11.071
H	0.860	0.937	12.258
H	1.708	-1.007	10.947
H	1.566	-0.992	8.463
H	1.226	-0.014	3.173
H	3.378	-0.004	1.910
H	3.362	0.016	-0.584
H	1.187	0.012	-1.805
H	-0.950	-0.014	-0.540
H	-0.918	-2.162	7.589
H	-0.447	-2.200	5.069
H	-1.490	-5.065	4.053
H	0.036	-4.136	4.110
H	-4.705	-4.865	4.937
H	-4.851	-7.297	5.466
H	-4.066	-8.140	7.680
H	-3.144	-6.538	9.354
H	-3.009	-4.110	8.813
H	-4.867	-2.475	6.871
H	-2.374	2.080	4.824
H	-3.651	1.268	6.652
H	-4.291	0.987	5.001
H	-4.273	-0.329	6.187
H	2.389	-11.319	6.906
H	0.691	-10.755	7.012
H	1.491	-10.912	5.408

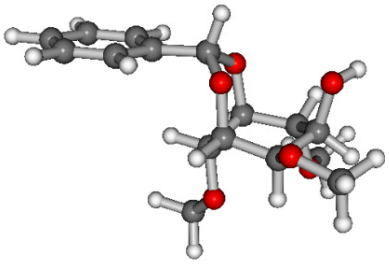
8). C1,C5-*O*-Benzylidene *myo*-inositol derivatives



1.77BC
ΔE **0.0** kcal/mol



1.77CC
ΔE **8.1** kcal/mol



1.77CB
ΔE **11.0** kcal/mol

1.77BC

Final heat of formation =
–1074.641

C	-1.040	-0.018	0.055
O	-0.731	1.220	-0.598
C	0.680	1.481	-0.704
C	1.271	1.481	0.709
C	1.011	0.069	1.276
O	-0.426	-0.095	1.343
C	1.723	-1.051	0.465
C	2.298	-0.590	-0.888
C	1.443	0.470	-1.639
O	2.575	-1.698	-1.742
O	0.551	-0.243	-2.505
C	0.029	0.546	-3.577
O	2.641	1.862	0.614
C	3.282	2.039	1.879
O	2.839	-1.568	1.207
C	2.470	-2.565	2.156
H	3.261	-0.118	-0.654
H	2.139	1.055	-2.266
H	0.740	2.490	-1.134
H	1.341	-0.000	2.322
H	0.997	-1.868	0.288
H	1.806	-1.746	-2.348
C	-2.535	-0.105	0.230
H	-0.679	-0.846	-0.579
H	2.002	-3.434	1.658
H	3.395	-2.887	2.651
H	1.770	-2.181	2.923
H	0.848	1.017	-4.150
H	-0.524	-0.137	-4.231
H	-0.657	1.322	-3.202
H	2.695	2.711	2.531
H	3.446	1.078	2.394
H	4.256	2.500	1.672
H	0.714	2.208	1.330
C	-3.241	-1.189	-0.303
C	-4.627	-1.281	-0.137
C	-5.312	-0.285	0.562
C	-4.609	0.801	1.096
C	-3.226	0.891	0.932
H	-2.702	-1.965	-0.852
H	-5.170	-2.131	-0.556
H	-6.394	-0.354	0.693
H	-5.144	1.580	1.643
H	-2.673	1.736	1.344

1.77CC

Final heat of formation =
–1074.628

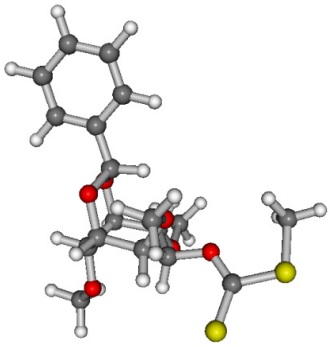
C	-0.970	1.658	-0.870
C	-1.412	0.710	0.258
C	-0.676	1.099	1.556
C	0.799	0.767	1.314
C	1.448	1.560	0.152
C	0.565	1.789	-1.123
O	0.891	-0.658	1.117
C	0.124	-1.132	-0.004
O	-1.239	-0.705	0.063
C	0.142	-2.640	0.014
C	-0.197	-3.346	1.176
C	-0.193	-4.742	1.175
C	0.150	-5.444	0.013
C	0.488	-4.744	-1.147
C	0.485	-3.345	-1.144
O	-0.807	2.471	1.918
C	-2.069	2.779	2.509
O	1.915	2.797	0.701
C	3.001	3.360	-0.025
O	0.935	0.911	-2.203
O	-1.719	1.338	-2.031
C	-1.692	2.352	-3.031
H	-2.500	0.827	0.354
H	-1.042	0.449	2.373
H	1.393	0.980	2.213
H	2.321	0.951	-0.168
H	0.749	2.831	-1.439
H	-1.272	2.658	-0.496
H	0.570	-0.755	-0.939
H	1.876	1.077	-2.393
H	-1.997	3.333	-2.619
H	-0.695	2.443	-3.495
H	-2.414	2.049	-3.800
H	2.723	3.639	-1.059
H	3.299	4.271	0.507
H	3.862	2.665	-0.064
H	-2.270	2.129	3.380
H	-2.011	3.821	2.845
H	-2.907	2.681	1.796
H	0.743	-2.794	-2.051
H	0.755	-5.286	-2.056
H	0.153	-6.535	0.015
H	-0.457	-5.287	2.083
H	-0.459	-2.793	2.078

1.77CB

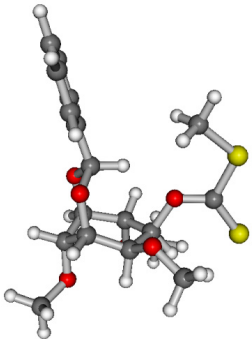
Final heat of formation =
–1074.623

C	0.385	-0.458	1.188
H	0.144	-0.456	2.264
C	1.873	-0.847	1.020
O	-0.420	-1.499	0.585
C	2.452	-0.637	-0.410
O	2.706	-0.138	1.949
H	1.933	-1.934	1.226
C	1.886	0.626	-1.103
H	3.537	-0.486	-0.259
O	2.225	-1.771	-1.254
C	0.368	0.777	-0.935
H	2.339	1.489	-0.576
O	2.171	0.710	-2.494
C	0.041	0.904	0.554
H	0.051	1.678	-1.483
O	-0.317	-0.361	-1.509
O	0.775	2.009	1.071
H	-1.038	1.090	0.686
C	-1.095	-1.150	-0.632
H	-1.204	-2.111	-1.159
C	-2.493	-0.571	-0.373
H	2.651	-2.534	-0.825
C	3.561	0.761	-2.793

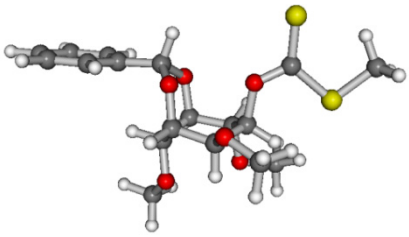
H	4.060	-0.203	-2.597
H	3.641	0.986	-3.863
H	4.072	1.557	-2.218
C	2.804	-0.772	3.221
H	3.488	-0.163	3.825
H	1.831	-0.832	3.742
H	3.216	-1.795	3.131
C	0.353	2.427	2.367
H	0.887	3.360	2.582
H	-0.735	2.617	2.392
H	0.609	1.688	3.146
C	-3.210	-0.923	0.779
C	-4.509	-0.445	0.976
C	-5.107	0.382	0.020
C	-4.401	0.723	-1.136
C	-3.103	0.244	-1.336
H	-2.739	-1.570	1.520
H	-5.057	-0.721	1.879
H	-6.121	0.755	0.176
H	-4.864	1.364	-1.890
H	-2.549	0.502	-2.239



2.33BC
ΔE **0.0** kcal/mol



2.33CC
ΔE **4.3** kcal/mol



2.33CB
ΔE **10.8** kcal/mol

2.33BC

Final heat of formation =
–1948.573

C	0.000	0.000	0.000
C	0.000	0.000	1.402
C	1.217	0.000	2.092
C	2.427	-0.002	1.392
C	2.423	-0.003	-0.006
C	1.207	-0.002	-0.700
C	-1.299	0.007	2.165
O	-2.055	-1.152	1.789
C	-3.366	-1.172	2.399
C	-4.121	0.080	1.904
C	-3.322	1.279	2.425
O	-2.004	1.214	1.849
C	-3.314	-1.278	3.951
C	-3.770	0.001	4.651
C	-3.323	1.337	4.003
O	-2.059	1.718	4.535
C	-1.777	3.109	4.358
O	-5.461	0.205	2.367
C	-6.361	-0.762	1.817
O	-4.174	-2.324	4.424
C	-3.582	-3.619	4.336
O	-3.283	-0.098	6.025
C	-3.968	0.511	7.005
S	-5.381	1.376	6.878
S	-3.205	0.310	8.588
C	-1.696	-0.682	8.235
H	-4.868	0.007	4.686
H	-4.077	2.085	4.304
H	-3.747	2.213	2.033
H	-3.833	-2.090	2.017
H	-2.271	-1.504	4.243
H	-1.108	-0.009	3.251
H	-4.319	-4.327	4.734
H	-3.339	-3.902	3.296
H	-2.658	-3.676	4.939
H	-1.617	3.361	3.297
H	-2.594	3.729	4.769
H	-0.856	3.313	4.917
H	-6.297	-0.781	0.714
H	-6.170	-1.773	2.213
H	-7.369	-0.450	2.115
H	-4.093	0.083	0.798
H	-0.950	0.001	-0.534
H	1.203	-0.002	-1.791
H	3.366	-0.004	-0.555
H	3.372	-0.002	1.937
H	1.216	0.003	3.185
H	-1.962	-1.684	7.882
H	-1.067	-0.172	7.498
H	-1.166	-0.754	9.193

2.33CC

Final heat of formation=
–1948.566

C	0.000	0.000	0.000
C	0.000	0.000	1.540
C	1.460	0.000	2.039
C	2.034	-1.367	1.651
C	2.054	-1.654	0.126
C	0.832	-1.123	-0.696
O	1.287	-2.352	2.396
C	-0.114	-2.348	2.092
O	-0.704	-1.056	2.219
C	-0.817	-3.300	3.036
C	-2.145	-3.069	3.419
C	-2.805	-3.978	4.251
C	-2.147	-5.126	4.704
C	-0.822	-5.359	4.323
C	-0.159	-4.452	3.491
O	2.260	1.039	1.484
C	2.056	2.304	2.115
O	3.277	-1.115	-0.370
C	3.774	-1.796	-1.526
O	-0.048	-2.249	-1.018
C	-0.247	-2.614	-2.300
S	-1.407	-3.931	-2.470
C	-2.016	-4.239	-0.762
O	-1.337	0.086	-0.464
C	-1.479	0.799	-1.698
S	0.463	-1.982	-3.668
H	-0.536	0.908	1.850
H	1.454	0.062	3.143
H	3.070	-1.461	1.999
H	2.055	-2.757	0.017
H	1.210	-0.747	-1.657
H	0.547	0.931	-0.249
H	-0.246	-2.693	1.052
H	-2.554	0.838	-1.911
H	-1.090	1.830	-1.605
H	-0.966	0.294	-2.535
H	3.980	-2.859	-1.299
H	3.074	-1.744	-2.378
H	4.711	-1.296	-1.798
H	1.044	2.710	1.936
H	2.221	2.236	3.206
H	2.793	2.991	1.681
H	0.879	-4.624	3.205
H	-0.299	-6.249	4.678
H	-2.664	-5.834	5.354
H	-3.837	-3.786	4.549
H	-2.650	-2.167	3.073

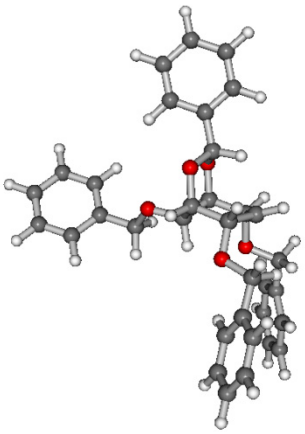
H	-2.827	-4.969	-0.876
H	-1.230	-4.664	-0.130
H	-2.408	-3.315	-0.324

2.33CB

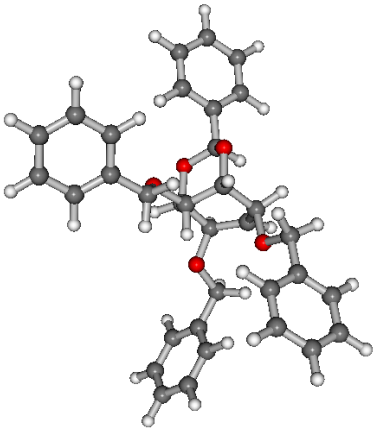
Final heat of formation = –1948.556

C	0.000	0.000	0.000
C	0.000	0.000	1.545
C	1.415	0.000	2.157
C	2.091	1.287	1.670
C	2.286	1.200	0.148
C	0.954	1.058	-0.625
O	-0.722	1.174	1.978
C	0.041	2.204	2.622
O	1.302	2.444	2.018
C	0.132	1.994	4.139
C	-0.879	1.307	4.825
C	-0.826	1.175	6.216
C	0.233	1.737	6.936
C	1.236	2.437	6.258
C	1.184	2.570	4.867
O	2.243	-1.091	1.776
C	1.855	-2.342	2.344
O	3.074	2.306	-0.267
C	3.674	2.138	-1.550
O	0.287	2.360	-0.646
C	-0.340	2.866	-1.715
S	-0.180	1.875	-3.230
C	-1.084	2.880	-4.458
O	0.341	-1.315	-0.444
C	-0.324	-1.707	-1.647
S	-1.163	4.295	-1.574
H	-0.575	-0.880	1.873
H	-1.028	0.256	-0.314
H	1.178	0.747	-1.656
H	2.831	0.253	-0.033
H	3.085	1.401	2.130
H	1.320	0.022	3.257
H	-0.533	3.121	2.421
H	2.931	2.150	-2.368
H	4.355	2.987	-1.686
H	4.252	1.197	-1.604
H	-1.421	-1.706	-1.514
H	-0.074	-1.050	-2.497
H	0.012	-2.727	-1.871
H	0.924	-2.723	1.894
H	2.667	-3.046	2.127
H	1.730	-2.262	3.440
H	-1.705	0.872	4.259
H	-1.616	0.632	6.739
H	0.274	1.634	8.022
H	2.062	2.884	6.814
H	1.961	3.119	4.333
H	-1.567	3.706	-3.913
H	-0.375	3.272	-5.195
H	-1.831	2.240	-4.941

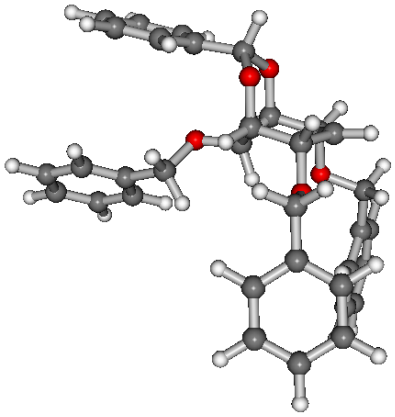
9). Radical 2.49 and 2.57



Radical **2.49CC**
ΔE **0.0** kcal/mol



Radical **2.49BC**
ΔE **0.6** kcal/mol



Radical **2.49CB**
ΔE **6.3** kcal/mol

Radical **2.49CC**
Final heat of formation = –1692.122

C	0.000	0.000	0.000
C	0.000	0.000	1.399
C	1.217	0.000	2.094
C	2.422	-0.001	1.390
C	2.420	-0.001	-0.010
C	1.208	0.000	-0.705
C	-1.301	0.021	2.160
O	-1.469	1.324	2.726
C	-2.591	1.427	3.622
C	-2.481	0.384	4.745
C	-2.384	-0.977	4.056
O	-1.273	-1.010	3.140
C	-3.727	-1.302	3.351
C	-4.207	-0.163	2.506
C	-3.948	1.261	2.888
O	-4.932	1.813	3.814
C	-6.212	2.047	3.201
C	-7.079	2.820	4.161
C	-6.772	4.155	4.472
C	-7.569	4.878	5.362
C	-8.689	4.276	5.948
C	-9.003	2.949	5.644
C	-8.198	2.225	4.758
O	-1.328	0.553	5.570
C	-1.486	1.588	6.556
C	-0.203	1.715	7.335
C	-0.105	1.224	8.644
C	1.091	1.337	9.361
C	2.206	1.937	8.769
C	2.120	2.425	7.460
C	0.922	2.316	6.750
O	-4.629	-1.652	4.440
C	-5.864	-2.215	3.984
C	-6.731	-2.556	5.170
C	-6.885	-1.647	6.228
C	-7.717	-1.954	7.308
C	-8.415	-3.167	7.339
C	-8.269	-4.075	6.287
C	-7.426	-3.773	5.213
H	-3.403	0.410	5.352
H	-2.176	-1.765	4.789
H	-3.576	-2.200	2.721
H	-3.933	1.896	1.981
H	-2.550	2.452	4.012
H	-2.157	-0.168	1.469

H	-1.724	2.551	6.067
H	-2.325	1.337	7.231
H	0.855	2.693	5.727
H	2.988	2.895	6.994
H	3.141	2.025	9.325
H	1.153	0.953	10.381
H	-0.974	0.750	9.105
H	-0.949	-0.001	-0.541
H	1.201	-0.001	-1.797
H	3.364	-0.003	-0.558
H	3.368	-0.005	1.934
H	1.205	-0.006	3.185
H	-6.064	2.623	2.265
H	-6.699	1.092	2.935
H	-6.387	-1.489	3.329
H	-5.672	-3.124	3.380
H	-7.302	-4.493	4.400
H	-8.803	-5.027	6.306
H	-9.065	-3.404	8.182
H	-7.823	-1.242	8.128
H	-6.338	-0.704	6.206
H	-5.899	4.625	4.015
H	-7.321	5.915	5.595
H	-9.315	4.842	6.640
H	-9.873	2.473	6.099
H	-8.440	1.185	4.528
H	-4.701	-0.375	1.555

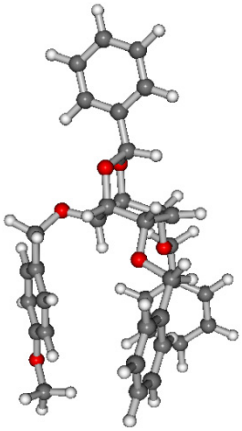
Radical **2.49BC**
Final heat of formation = –1692.121

C	0.000	0.000	0.000
C	0.000	0.000	1.402
C	1.215	0.000	2.095
C	2.426	0.001	1.397
C	2.424	0.000	-0.000
C	1.210	-0.001	-0.697
C	-1.306	0.021	2.155
O	-1.886	1.323	2.007
C	-3.219	1.420	2.552
C	-4.139	0.377	1.900
C	-3.490	-0.983	2.151
O	-2.141	-1.013	1.646
C	-3.564	-1.311	3.662
C	-3.086	-0.177	4.510
C	-3.232	1.248	4.095
O	-4.475	1.773	4.655
C	-4.420	3.191	4.924
C	-5.718	3.610	5.559
C	-6.862	3.815	4.772
C	-8.074	4.181	5.360
C	-8.156	4.354	6.746
C	-7.023	4.154	7.539
C	-5.813	3.781	6.947
O	-4.296	0.548	0.491
C	-5.223	1.590	0.144
C	-5.360	1.634	-1.356
C	-4.438	2.351	-2.134
C	-4.545	2.371	-3.527
C	-5.580	1.673	-4.159
C	-6.504	0.956	-3.393
C	-6.392	0.936	-2.000
O	-4.968	-1.649	3.877
C	-5.252	-2.098	5.216
C	-6.688	-2.545	5.271
C	-7.037	-3.871	4.975
C	-8.373	-4.280	5.007
C	-9.377	-3.364	5.336
C	-9.040	-2.038	5.629
C	-7.703	-1.632	5.595
H	-4.021	-1.766	1.597
H	-2.955	-2.215	3.860
H	-2.390	1.839	4.505
H	-6.203	1.387	0.615
H	-4.863	2.568	0.515
H	-7.111	0.372	-1.402
H	-7.314	0.410	-3.882
H	-5.667	1.691	-5.247
H	-3.8220	2.933	-4.120
H	-3.628	2.892	-1.640
H	-1.129	-0.163	3.239
H	-0.953	-0.006	-0.530
H	1.207	-0.004	-1.788
H	3.369	-0.001	-0.548
H	3.371	-0.001	1.944
H	1.213	-0.003	3.188
H	-5.122	0.395	2.406
H	-4.576	-2.937	5.474
H	-5.079	-1.279	5.935
H	-7.439	-0.597	5.821
H	-9.820	-1.320	5.887
H	-10.420	-3.683	5.365
H	-8.631	-5.316	4.779
H	-6.253	-4.587	4.718
H	-3.573	3.407	5.602
H	-4.253	3.754	3.986
H	-6.799	3.682	3.689
H	-8.956	4.339	4.736
H	-9.102	4.646	7.206
H	-7.081	4.290	8.621
H	-4.928	3.622	7.568
H	-3.538	2.443	2.309
H	-2.663	-0.383	5.495

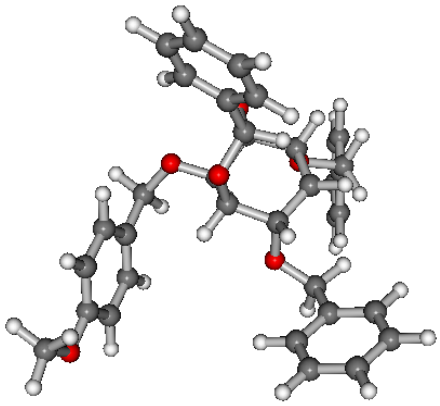
Radical **2.49CB**
Final heat of formation = –1692.112

C	0.000	0.000	0.000
C	0.000	0.000	1.401
C	1.222	0.000	2.085
C	2.427	-0.033	1.379
C	2.423	-0.051	-0.020
C	1.205	-0.031	-0.707
C	-1.318	0.153	2.164
O	-2.441	-0.376	1.455
C	-2.758	-1.769	1.668
C	-1.748	-2.519	2.543
C	-1.527	-1.673	3.791
O	-1.256	-0.278	3.519
C	-2.810	-1.727	4.645
C	-4.039	-1.474	3.831
C	-4.135	-1.806	2.378
O	-4.744	-3.125	2.244
C	-5.591	-3.243	1.079
C	-6.154	-4.638	1.035
C	-5.533	-5.638	0.272
C	-6.040	-6.940	0.255
C	-7.178	-7.257	1.004
C	-7.804	-6.267	1.769
C	-7.295	-4.967	1.783
O	-0.487	-2.820	1.948
C	-0.559	-3.792	0.894
C	0.791	-4.438	0.707
C	1.380	-5.161	1.755
C	2.617	-5.784	1.579
C	3.279	-5.697	0.348
C	2.700	-4.978	-0.700
C	1.464	-4.349	-0.517
O	-2.800	-3.054	5.251
C	-3.792	-3.233	6.277
C	-3.606	-4.598	6.886
C	-2.960	-4.754	8.120
C	-2.778	-6.025	8.674
C	-3.236	-7.156	7.992
C	-3.878	-7.011	6.756
C	-4.063	-5.740	6.209
H	-4.958	-1.173	4.337
H	-4.782	-1.064	1.875
H	-2.852	-2.243	0.678
H	-2.236	-3.460	2.860
H	-0.688	-2.079	4.375
H	-2.723	-0.972	5.449
H	-1.540	1.230	2.240
H	-3.675	-2.447	7.049
H	-4.804	-3.144	5.845
H	-6.405	-2.497	1.141
H	-5.012	-3.037	0.159
H	-7.785	-4.195	2.380
H	-8.695	-6.509	2.352
H	-7.577	-8.273	0.990
H	-5.549	-7.708	-0.346
H	-4.645	-5.392	-0.314
H	-4.561	-5.626	5.243
H	-4.238	-7.891	6.221
H	-3.096	-8.149	8.423
H	-2.276	-6.133	9.637
H	-2.597	-3.871	8.651
H	-1.313	-4.559	1.161
H	-0.878	-3.319	-0.052
H	0.867	-5.225	2.717

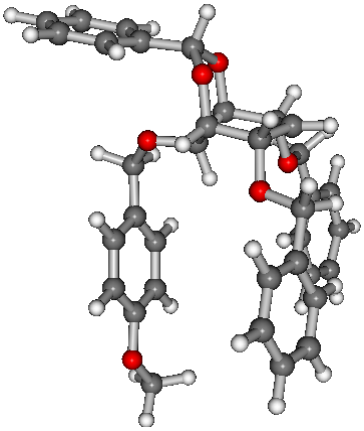
H	3.066	-6.343	2.402
H	4.245	-6.186	0.210
H	3.214	-4.899	-1.660
H	1.019	-3.775	-1.333
H	-0.952	0.021	-0.532
H	1.194	-0.037	-1.799
H	3.365	-0.077	-0.570
H	3.373	-0.048	1.922
H	1.221	0.012	3.176



Radical **2.57CC**
ΔE **0.0** kcal/mol



Radical **2.57BC**
ΔE **0.6** kcal/mol



Radical **2.57CB**
ΔE **6.9** kcal/mol

Radical **2.57CC**
Final heat of formation =
–1806.695

C	0.000	0.000	0.000
C	0.000	0.000	1.403
C	1.228	0.000	2.082
C	2.432	-0.005	1.372
C	2.421	-0.007	-0.026
C	1.202	-0.003	-0.712
C	-1.296	0.022	2.170
O	-1.720	1.391	2.311
C	-3.049	1.526	2.901
C	-3.342	3.044	2.813
C	-2.527	3.781	3.888
C	-3.119	3.367	5.231
C	-2.843	1.863	5.492
C	-3.141	1.013	4.301
O	-4.745	3.345	2.941
C	-5.281	3.059	4.234
O	-4.533	3.667	5.285
O	-1.448	1.658	5.867
C	-1.208	1.868	7.276
C	0.249	1.620	7.559
C	0.679	0.385	8.065
C	2.034	0.151	8.317
C	2.975	1.152	8.060
C	2.557	2.386	7.548
C	1.202	2.617	7.301
O	-2.608	5.203	3.776
C	-1.734	5.765	2.775
C	-0.272	5.743	3.159
C	0.652	4.953	2.469
C	2.009	4.935	2.819
C	2.455	5.722	3.889
C	1.536	6.518	4.598
C	0.196	6.525	4.233
C	-6.694	3.584	4.286
C	-6.927	4.965	4.239
C	-8.235	5.453	4.276
C	-9.316	4.566	4.357
C	-9.085	3.189	4.403
C	-7.775	2.700	4.368
O	3.755	5.787	4.323
C	4.730	5.023	3.609
H	-3.768	0.985	2.255
H	-3.482	1.546	6.339
H	-2.681	3.972	6.036
H	-1.480	2.900	7.562
H	-1.839	1.175	7.865
H	-1.159	-0.438	3.164
H	-2.075	-0.549	1.627
H	-0.509	7.147	4.790
H	1.903	7.130	5.423
H	2.696	4.302	2.259
H	0.314	4.329	1.639
H	1.235	0.007	3.174
H	3.380	-0.013	1.912
H	3.361	-0.017	-0.581
H	1.188	-0.008	-1.804
H	-0.952	0.001	-0.536
H	-0.056	-0.397	8.266
H	2.355	-0.812	8.718
H	4.033	0.973	8.260
H	3.287	3.172	7.346
H	0.879	3.579	6.898
H	-3.073	3.376	1.802
H	-1.478	3.439	3.845
H	-1.872	5.257	1.803
H	-2.090	6.799	2.663
H	-7.591	1.624	4.404
H	-9.925	2.494	4.467
H	-10.337	4.951	4.385
H	-8.414	6.529	4.240
H	-6.076	5.645	4.178
H	-5.276	1.955	4.380
H	5.686	5.227	4.103
H	4.515	3.942	3.661
H	4.790	5.332	2.552
H	-3.382	-0.038	4.472

Radical **2.57BC**
Final het of formation =
–1806.694

C	0.000	0.000	0.000
C	0.000	0.000	1.402
C	1.230	0.000	2.079
C	2.431	0.002	1.367
C	2.421	-0.006	-0.033
C	1.202	-0.008	-0.716
C	-1.303	-0.024	2.177
O	-1.385	0.952	3.225
C	-1.364	2.337	2.758
C	-1.232	3.169	4.062
C	-2.579	3.193	4.801
C	-3.538	3.990	3.916
C	-3.827	3.199	2.614
C	-2.569	2.723	1.959
O	-0.780	4.514	3.805
C	-1.715	5.301	3.067
O	-3.016	5.305	3.644
O	-4.716	2.124	3.041
C	-5.347	1.439	1.945

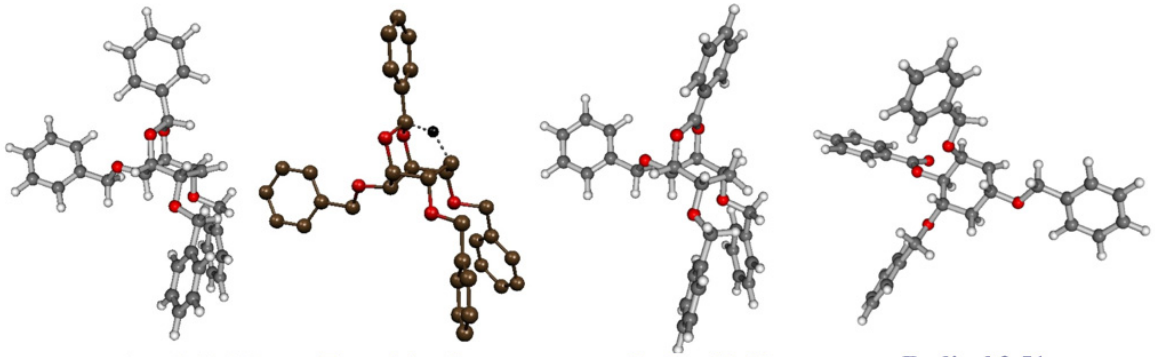
C	-6.378	0.495	2.505
C	-6.047	-0.835	2.798
C	-6.996	-1.702	3.346
C	-8.291	-1.245	3.608
C	-8.632	0.081	3.321
C	-7.680	0.944	2.773
O	-2.529	3.821	6.085
C	-2.275	2.935	7.184
C	-0.822	2.555	7.392
C	0.182	3.531	7.405
C	1.520	3.198	7.636
C	1.871	1.859	7.874
C	0.875	0.869	7.863
C	-0.451	1.220	7.621
C	-1.202	6.719	3.016
C	-0.560	7.193	1.867
C	-0.056	8.497	1.826
C	-0.196	9.333	2.938
C	-0.839	8.861	4.089
C	-1.340	7.559	4.130
O	3.148	1.420	8.119
C	4.193	2.394	8.133
H	-0.450	2.491	2.157
H	-0.446	2.716	4.677
H	-2.958	2.161	4.890
H	-4.488	4.161	4.437
H	-4.387	3.858	1.923
H	-1.786	4.879	2.036
H	-0.454	6.539	0.998
H	0.442	8.861	0.926
H	0.193	10.352	2.908
H	-0.951	9.513	4.957
H	-1.848	7.181	5.017
H	-5.825	2.180	1.274
H	-4.595	0.882	1.356
H	-5.034	-1.191	2.596
H	-6.725	-2.736	3.568
H	-9.034	-1.921	4.034
H	-9.642	0.441	3.522
H	-7.947	1.980	2.550
H	-1.416	-0.986	2.701
H	-2.152	0.078	1.476
H	-0.952	0.005	-0.537
H	1.186	-0.010	-1.808
H	3.360	-0.007	-0.588
H	3.381	0.004	1.905
H	1.238	0.011	3.171
H	-2.647	3.485	8.063
H	-2.885	2.018	7.082
H	-1.214	0.438	7.606
H	1.164	-0.167	8.041
H	2.274	3.984	7.631
H	-0.083	4.571	7.207
H	5.114	1.838	8.340
H	4.285	2.903	7.159
H	4.035	3.147	8.924
H	-2.504	2.723	0.868

Radical **2.57CB**

Final het of formation = –1806.684

C	0.000	0.000	0.000
C	0.000	0.000	1.403
C	1.227	0.000	2.081
C	2.432	-0.002	1.372
C	2.421	-0.002	-0.025
C	1.202	-0.000	-0.711
C	-1.297	0.022	2.166
O	-1.765	1.382	2.245
C	-3.114	1.500	2.792
C	-3.622	2.887	2.353
C	-2.965	3.957	3.216
C	-3.543	3.805	4.626
C	-3.057	2.468	5.238
C	-3.123	1.330	4.277
O	-5.066	2.853	2.465
C	-5.683	3.714	3.416
O	-4.987	3.781	4.661
O	-1.691	2.588	5.726
C	-1.617	3.026	7.084
C	-0.176	3.133	7.529
C	0.881	3.133	6.609
C	2.202	3.256	7.055
C	2.481	3.389	8.418
C	1.428	3.390	9.340
C	0.110	3.259	8.897
O	-3.189	5.234	2.618
C	-2.347	6.293	3.110
C	-0.907	6.195	2.657
C	-0.596	6.036	1.293
C	0.723	5.994	0.859
C	1.774	6.124	1.785
C	1.484	6.280	3.147
C	0.148	6.307	3.566
C	-6.050	5.091	2.854
C	-6.279	6.165	3.723
C	-6.716	7.396	3.226
C	-6.944	7.560	1.856
C	-6.734	6.483	0.988
C	-6.296	5.253	1.485
O	3.040	6.081	1.256
C	4.139	6.222	2.158
H	-3.752	0.737	2.308
H	-3.718	2.252	6.100
H	-3.217	4.633	5.276
H	-2.113	4.012	7.201
H	-2.157	2.317	7.741
H	-1.148	-0.393	3.178
H	-2.060	-0.594	1.650
H	-0.068	6.422	4.631
H	2.279	6.375	3.886
H	0.969	5.866	-0.195
H	-1.406	5.935	0.569
H	1.235	0.003	3.173
H	3.381	-0.006	1.912
H	3.361	-0.006	-0.580
H	1.189	-0.004	-1.803
H	-0.952	0.002	-0.536
H	0.661	3.024	5.548
H	3.017	3.247	6.329
H	3.512	3.486	8.762
H	1.635	3.486	10.407
H	-0.706	3.251	9.625
H	-3.366	3.047	1.297
H	-1.882	3.736	3.260
H	-2.821	7.204	2.714
H	-2.388	6.355	4.212
H	-6.128	4.412	0.812
H	-6.912	6.603	-0.082
H	-7.287	8.520	1.466
H	-6.883	8.230	3.911
H	-6.103	6.033	4.792
H	-6.623	3.197	3.668
H	5.040	6.170	1.537
H	4.111	7.193	2.680
H	4.160	5.407	2.901
H	-3.005	0.326	4.692

10). Radical 2.49, Transition state, Radical 2.50 and 2.51a



Radical 2.49CC
ΔE –4.2 kcal/mol

Transition State
ΔE 0.0 kcal/mol

Radical 2.50
ΔE –22.0 kcal/mol

Radical 2.51a
ΔE –30.7 kcal/mol

Radical **2.49CC**
Final heat of formation = –1692.122

C	0.000	0.000	0.000
C	0.000	0.000	1.399
C	1.217	0.000	2.094
C	2.422	-0.001	1.390
C	2.420	-0.001	-0.010
C	1.208	0.000	-0.705
C	-1.301	0.021	2.160
O	-1.469	1.324	2.726
C	-2.591	1.427	3.622
C	-2.481	0.384	4.745
C	-2.384	-0.977	4.056
O	-1.273	-1.010	3.140
C	-3.727	-1.302	3.351
C	-4.207	-0.163	2.506
C	-3.948	1.261	2.888
O	-4.932	1.813	3.814
C	-6.212	2.047	3.201
C	-7.079	2.820	4.161
C	-6.772	4.155	4.472
C	-7.569	4.878	5.362
C	-8.689	4.276	5.948
C	-9.003	2.949	5.644
C	-8.198	2.225	4.758
O	-1.328	0.553	5.570
C	-1.486	1.588	6.556
C	-0.203	1.715	7.335
C	-0.105	1.224	8.644
C	1.091	1.337	9.361
C	2.206	1.937	8.769
C	2.120	2.425	7.460
C	0.922	2.316	6.750
O	-4.629	-1.652	4.440
C	-5.864	-2.215	3.984
C	-6.731	-2.556	5.170
C	-6.885	-1.647	6.228
C	-7.717	-1.954	7.308
C	-8.415	-3.167	7.339
C	-8.269	-4.075	6.287
C	-7.426	-3.773	5.213
H	-3.403	0.410	5.352
H	-2.176	-1.765	4.789
H	-3.576	-2.200	2.721
H	-3.933	1.896	1.981
H	-2.550	2.452	4.012
H	-2.157	-0.168	1.469
H	-1.724	2.551	6.067
H	-2.325	1.337	7.231
H	0.855	2.693	5.727
H	2.988	2.895	6.994
H	3.141	2.025	9.325
H	1.153	0.953	10.381
H	-0.974	0.750	9.105
H	-0.949	-0.001	-0.541
H	1.201	-0.001	-1.797
H	3.364	-0.003	-0.558
H	3.368	-0.005	1.934
H	1.205	-0.006	3.185
H	-6.064	2.623	2.265
H	-6.699	1.092	2.935
H	-6.387	-1.489	3.329
H	-5.672	-3.124	3.380
H	-7.302	-4.493	4.400
H	-8.803	-5.027	6.306
H	-9.065	-3.404	8.182
H	-7.823	-1.242	8.128
H	-6.338	-0.704	6.206
H	-5.899	4.625	4.015
H	-7.321	5.915	5.595
H	-9.315	4.842	6.640
H	-9.873	2.473	6.099
H	-8.440	1.185	4.528
H	-4.701	-0.375	1.555

Radical **2.50**
Final heat of formation = –1692.151

C	0.102	0.941	0.233
C	0.650	1.105	1.498
C	1.227	-0.006	2.188
C	1.234	-1.273	1.525
C	0.680	-1.410	0.261
C	0.106	-0.311	-0.401
C	1.770	0.140	3.482
O	1.869	1.390	4.031
C	2.022	1.483	5.468
C	3.077	0.488	5.961
C	2.610	-0.885	5.499
O	2.420	-0.912	4.061
C	1.303	-1.283	6.217
C	0.202	-0.221	6.029
C	0.670	1.239	6.177
O	4.379	0.722	5.432
C	5.086	1.783	6.101
C	6.446	1.933	5.472
C	7.604	1.569	6.172
C	8.865	1.707	5.584
C	8.979	2.204	4.283
C	7.827	2.563	3.573
C	6.570	2.431	4.165
O	1.673	-1.502	7.586
C	0.780	-2.372	8.288
C	1.252	-2.552	9.710
C	1.763	-1.469	10.441
C	2.160	-1.640	11.769
C	2.044	-2.890	12.386
C	1.534	-3.973	11.664
C	1.147	-3.804	10.331
O	0.872	1.660	7.534
C	-0.345	1.987	8.225
C	-0.013	2.665	9.529
C	0.646	3.905	9.533
C	0.950	4.543	10.737
C	0.591	3.953	11.954
C	-0.067	2.721	11.960
C	-0.363	2.080	10.752

H	3.085	0.499	7.065
H	3.382	-1.639	5.691
H	0.960	-2.237	5.775
H	-0.080	1.900	5.703
H	2.325	2.521	5.645
H	4.523	2.732	6.013
H	5.183	1.548	7.177
H	5.671	2.704	3.609
H	7.910	2.949	2.555
H	9.962	2.310	3.820
H	9.760	1.422	6.141
H	7.516	1.173	7.186
H	-0.951	2.659	7.583
H	-0.946	1.079	8.418
H	-0.244	-1.948	8.286
H	0.728	-3.354	7.779
H	0.764	-4.658	9.766
H	1.449	-4.955	12.134
H	2.355	-3.022	13.424
H	2.563	-0.792	12.325
H	1.859	-0.496	9.957
H	0.926	4.366	8.584
H	1.462	5.507	10.727
H	0.824	4.454	12.895
H	-0.347	2.253	12.906
H	-0.869	1.112	10.761
H	-0.631	-0.419	6.719
H	-0.214	-0.341	5.015
H	1.684	-2.130	2.026
H	0.697	-2.388	-0.225
H	-0.325	-0.429	-1.396
H	-0.334	1.804	-0.273
H	0.646	2.084	1.977

Radical **2.51a**
Final heat of formation = –1692.165

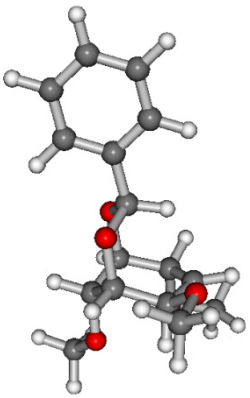
C	0.033	-0.065	0.128
C	-0.004	-0.074	1.675
C	1.401	-0.098	2.281
C	2.214	-1.279	1.718
C	2.254	-1.300	0.175
C	0.853	-1.222	-0.342
O	-0.689	1.096	2.179
C	-2.040	0.979	2.354
O	-2.669	-0.031	2.084
O	1.243	-0.229	3.699
C	2.323	0.315	4.452
O	2.935	-2.495	-0.216
C	3.347	-2.470	-1.581
O	0.612	1.199	-0.269
C	0.425	1.465	-1.658
C	-2.644	2.225	2.907
C	-4.024	2.223	3.171
C	-4.640	3.361	3.691
C	-3.883	4.510	3.949
C	-2.509	4.518	3.686
C	-1.888	3.380	3.168
H	1.899	0.860	2.050
H	-0.561	-0.968	1.994
H	-1.004	-0.131	-0.243
H	2.834	-0.416	-0.167
H	1.756	-2.217	2.067
H	0.867	0.654	-2.269
H	-0.660	1.484	-1.886
C	1.050	2.788	-2.037
C	2.061	0.175	5.935
H	3.275	-0.193	4.202
H	2.451	1.386	4.195
C	4.041	-3.760	-1.954
H	2.473	-2.314	-2.244
H	4.032	-1.612	-1.747
H	0.390	-2.107	-0.782
H	-0.818	3.378	2.961
H	-1.920	5.414	3.887
H	-4.366	5.401	4.356
H	-5.711	3.354	3.896
H	-4.594	1.317	2.961
H	3.245	-1.246	2.101
C	4.444	-3.958	-3.285
C	5.096	-5.132	-3.664
C	5.352	-6.130	-2.716
C	4.952	-5.940	-1.391
C	4.300	-4.761	-1.010
H	4.245	-3.185	-4.032
H	5.403	-5.271	-4.702
H	5.860	-7.050	-3.011
H	5.146	-6.713	-0.646
H	3.985	-4.611	0.021
C	1.125	3.142	-3.394
C	1.676	4.365	-3.781
C	2.168	5.250	-2.815
C	2.100	4.901	-1.464
C	1.542	3.678	-1.075
H	0.748	2.454	-4.155
H	1.726	4.626	-4.840
H	2.603	6.204	-3.116
H	2.482	5.586	-0.704
H	1.483	3.405	-0.022
C	3.065	0.549	6.841
C	2.854	0.451	8.218
C	1.634	-0.029	8.707
C	0.633	-0.407	7.809
C	0.842	-0.305	6.429
H	4.023	0.921	6.467
H	3.644	0.746	8.911
H	1.467	-0.109	9.783
H	-0.320	-0.785	8.182
H	0.064	-0.600	5.726

Transition state
Final heat of formation = –1692.116

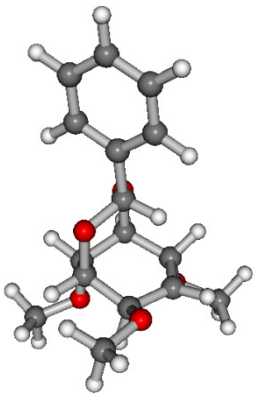
C	-4.157	-2.706	1.815
C	-3.598	-2.633	0.525
C	-4.144	-3.421	-0.505
C	-5.230	-4.259	-0.247
C	-5.783	-4.328	1.036
C	-5.243	-3.546	2.064
C	-2.408	-1.791	0.272
O	-2.297	-0.713	1.169
C	-1.017	-0.043	1.036
C	-0.820	0.433	-0.412
C	-0.977	-0.794	-1.313
O	-2.255	-1.438	-1.076
C	0.168	-1.797	-1.033
C	0.168	-2.140	0.436
C	0.116	-1.017	1.440
O	1.309	-0.202	1.573
C	2.347	-0.847	2.324
C	3.418	0.155	2.675
C	3.081	1.369	3.295
C	4.074	2.283	3.650
C	5.421	1.993	3.398
C	5.765	0.787	2.782
C	4.767	-0.122	2.418
O	-1.778	1.413	-0.811
C	-1.421	2.743	-0.422
C	-2.558	3.687	-0.725
C	-3.889	3.300	-0.506
C	-4.932	4.197	-0.743
C	-4.661	5.493	-1.196
C	-3.338	5.884	-1.419
C	-2.294	4.983	-1.190
O	1.358	-1.159	-1.556
C	2.491	-2.036	-1.606
C	3.667	-1.294	-2.186
C	4.102	-0.091	-1.607
C	5.202	0.588	-2.133
C	5.888	0.072	-3.239
C	5.462	-1.124	-3.820
C	4.354	-1.800	-3.298
H	0.208	0.815	-0.527
H	-0.985	-0.504	-2.369
H	-0.025	-2.715	-1.623
H	-0.128	-1.430	2.438
H	-1.055	0.794	1.742
H	-1.316	-2.415	0.494
H	-1.194	2.777	0.662
H	-0.505	3.065	-0.954
H	-1.262	5.288	-1.380
H	-3.117	6.890	-1.782
H	-5.478	6.193	-1.381
H	-5.964	3.883	-0.575
H	-4.097	2.285	-0.165
H	-3.742	-2.089	2.611
H	-5.673	-3.589	3.066
H	-6.631	-4.985	1.233
H	-5.651	-4.859	-1.056
H	-3.719	-3.358	-1.507

H	1.908	-1.275	3.250
H	2.787	-1.685	1.752
H	2.730	-2.395	-0.585
H	2.258	-2.926	-2.224
H	4.015	-2.729	-3.762
H	5.987	-1.531	-4.687
H	6.749	0.603	-3.647
H	5.529	1.524	-1.676
H	3.565	0.314	-0.747
H	2.031	1.597	3.486
H	3.799	3.224	4.129
H	6.197	2.707	3.679
H	6.811	0.556	2.575
H	5.040	-1.057	1.923
H	0.597	-3.096	0.749

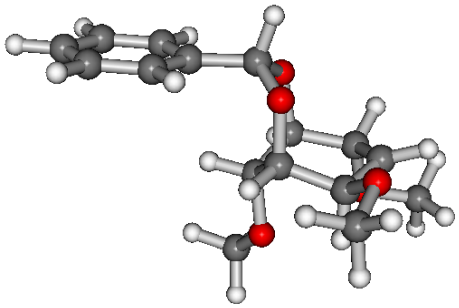
11). Radical 2.59, 2.60e and 2.60d



Radical **2.59CC**
ΔE **0.0** kcal/mol



Radical **2.59BC**
ΔE **2.2** kcal/mol



Radical **2.59CB**
ΔE **6.6** kcal/mol

Radical **2.59CC**
Final heat of formation =
–998.728

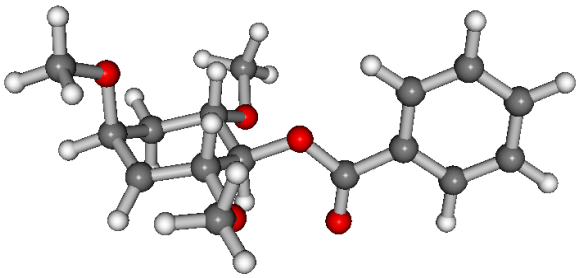
C	0.000	0.000	0.000
C	0.000	0.000	1.561
C	1.446	0.000	2.075
C	2.066	-1.345	1.633
C	2.147	-1.499	0.101
C	0.907	-1.027	-0.582
O	1.279	-2.399	2.236
C	-0.103	-2.369	1.854
O	-0.703	-1.108	2.148
C	-0.833	-3.443	2.620
C	-0.847	-3.429	4.021
C	-1.526	-4.425	4.724
C	-2.196	-5.442	4.034
C	-2.185	-5.458	2.637
C	-1.505	-4.460	1.933
O	2.074	1.173	1.574
C	3.385	1.397	2.096
O	3.366	-0.804	-0.298
C	3.733	-1.060	-1.651
O	-1.298	-0.211	-0.567
C	-2.223	0.841	-0.302
H	-0.525	0.893	1.925
H	1.431	0.014	3.182
H	3.077	-1.480	2.040
H	2.296	-2.576	-0.118
H	0.617	-1.443	-1.548
H	0.358	1.020	-0.274
H	-0.182	-2.549	0.762
H	-2.541	0.860	0.755
H	-1.801	1.828	-0.570
H	-3.102	0.646	-0.928
H	3.003	-0.646	-2.368
H	4.702	-0.572	-1.810
H	3.842	-2.146	-1.840
H	3.674	2.409	1.785
H	3.387	1.345	3.200
H	4.112	0.677	1.688
H	-1.498	-4.468	0.840
H	-2.707	-6.248	2.093
H	-2.726	-6.220	4.586
H	-1.534	-4.411	5.816
H	-0.322	-2.635	4.553

Radical **2.59BC**
Final heat of formation =
–998.724

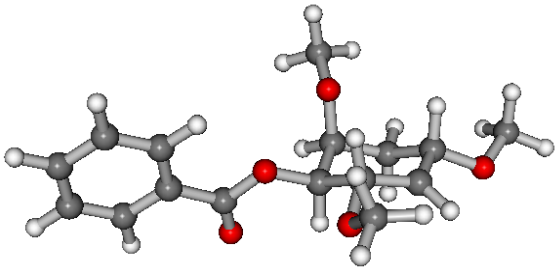
C	0.000	0.000	0.000
C	0.000	0.000	1.559
C	1.453	0.000	2.079
C	2.079	-1.327	1.626
C	2.144	-1.498	0.093
C	0.893	-1.039	-0.580
O	1.304	-2.389	2.235
C	-0.079	-2.373	1.861
O	-0.692	-1.115	2.151
C	-0.796	-3.449	2.636
C	-0.813	-3.421	4.037
C	-1.480	-4.419	4.749
C	-2.135	-5.452	4.067
C	-2.120	-5.482	2.670
C	-1.452	-4.482	1.958
O	2.223	1.102	1.608
C	2.003	2.299	2.350
O	3.348	-0.809	-0.343
C	3.695	-1.104	-1.692
O	-1.299	-0.188	-0.570
C	-2.206	0.881	-0.316
H	0.596	-1.456	-1.544
H	0.374	1.016	-0.277
H	-0.548	0.881	1.919
H	3.096	-1.433	2.025
H	2.288	-2.580	-0.107
H	-0.164	-2.559	0.770
H	3.804	-2.195	-1.854
H	2.956	-0.712	-2.413
H	4.661	-0.618	-1.877
H	-3.087	0.699	-0.945
H	-2.530	0.913	0.739
H	-1.766	1.859	-0.589
H	2.192	2.143	3.428
H	2.713	3.041	1.965
H	0.978	2.695	2.226
H	1.424	-0.004	3.184
H	-1.442	-4.501	0.866
H	-2.630	-6.285	2.134
H	-2.656	-6.231	4.626
H	-1.490	-4.394	5.841
H	-0.299	-2.615	4.562

Radical **2.59CB**
Final heat of formation =
–998.717

C	0.000	0.000	0.000
C	0.000	0.000	1.544
C	1.422	0.000	2.140
C	2.108	1.279	1.639
C	2.338	1.151	0.109
C	1.047	0.888	-0.586
O	1.276	2.442	1.868
C	0.063	2.220	2.567
O	-0.727	1.169	2.001
C	0.250	2.064	4.082
C	1.328	2.687	4.728
C	1.462	2.605	6.117
C	0.514	1.912	6.876
C	-0.572	1.305	6.238
C	-0.706	1.384	4.849
O	2.243	-1.093	1.746
C	1.836	-2.351	2.291
O	2.926	2.318	-0.474
C	4.311	2.470	-0.182
O	0.127	-1.402	-0.390
C	-0.126	-1.621	-1.774
H	-0.571	-0.879	1.878
H	-1.000	0.349	-0.322
H	0.895	1.363	-1.555
H	3.029	0.288	-0.023
H	3.067	1.426	2.160
H	1.341	0.017	3.242
H	-0.525	3.132	2.379
H	4.666	3.312	-0.788
H	4.497	2.702	0.882
H	4.884	1.562	-0.451
H	-0.111	-2.707	-1.928
H	-1.118	-1.230	-2.070
H	0.643	-1.159	-2.418
H	2.647	-3.057	2.077
H	1.694	-2.283	3.386
H	0.910	-2.716	1.819
H	-1.552	0.912	4.346
H	-1.320	0.768	6.825
H	0.619	1.850	7.961
H	2.310	3.087	6.608
H	2.061	3.233	4.131



2.60e
ΔE **0.0** kcal/mol



2.60d
ΔE **0.8** kcal/mol

C1-radical **2.60e**
Final heat of formation =
–998.772

C	0.000	0.000	0.000
C	0.000	0.000	1.404
C	1.222	0.000	2.098
C	2.426	0.001	1.391
C	2.420	-0.001	-0.008
C	1.205	-0.001	-0.702
C	-1.324	0.001	2.099
O	-2.398	0.012	1.526
O	-1.175	-0.012	3.461
C	-2.377	-0.017	4.266
C	-2.396	-1.331	5.083
C	-3.467	-1.278	6.125
C	-3.525	-0.087	7.025
C	-3.515	1.195	6.179
C	-2.354	1.219	5.172
O	-2.573	-2.404	4.160
C	-2.121	-3.654	4.671
O	-2.371	0.005	7.905
C	-2.346	-1.023	8.893
O	-2.438	2.362	4.313
C	-1.850	3.536	4.863
H	-1.394	-1.416	5.563
H	-4.285	-1.998	6.074
H	-4.440	-0.119	7.647
H	-4.462	1.268	5.623
H	-1.391	1.235	5.716
H	-3.249	0.013	3.596
H	-1.467	-0.834	9.522
O	-1.178	0.017	3.459
C	-2.398	0.067	4.238
C	-2.153	0.979	5.451
C	-3.326	0.906	6.376
C	-3.911	-0.407	6.760
C	-4.105	-1.291	5.502
C	-2.822	-1.346	4.661
O	-1.941	2.303	4.951
C	-1.250	3.141	5.871
O	-1.729	-1.928	5.393
C	-1.741	-3.351	5.398
H	-3.254	-0.996	9.525
H	-2.260	-2.029	8.445
H	-1.047	-3.618	4.932
H	-2.691	-3.969	5.564
H	-2.272	-4.393	3.874
H	-1.928	4.314	4.094
H	-2.373	3.885	5.773
H	-0.783	3.377	5.107
H	1.219	0.001	3.187
H	3.373	0.001	1.933
H	3.364	-0.001	-0.558
H	1.198	-0.002	-1.793
H	-0.959	0.000	-0.520
H	-3.449	2.065	6.850

C5-radical **2.60d**
Final heat of formation =
–998.771

C	0.000	0.000	0.000
C	0.000	0.000	1.404
C	1.220	0.000	2.100
C	2.425	-0.000	1.395
C	2.420	0.002	-0.004
C	1.206	0.002	-0.700
C	-1.320	-0.002	2.102
O	-2.400	-0.025	1.531
O	-5.143	-0.161	7.453
C	-5.607	-1.276	8.205
H	-1.222	0.621	5.947
H	-3.194	0.501	3.616
H	-3.001	-1.934	3.741
H	-4.923	-0.865	4.900
H	-3.218	-0.949	7.445
H	-3.776	1.820	6.760
H	-2.613	-3.767	5.934
H	-1.734	-3.755	4.368
H	-0.827	-3.672	5.913

H	-1.106	4.107	5.371	H	-6.476	-0.928	8.778	H	-4.404	-2.311	5.787
H	-1.823	3.303	6.802	H	-5.925	-2.119	7.565	H	1.214	-0.002	3.192
H	-0.262	2.718	6.134	H	-4.835	-1.639	8.910				