STEREOSELECTIVE FUNCTIONALIZATIONS ON ARENE CHROMIUM TEMPLATE

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STEREOSELECTIVE FUNCTIONALIZATIONS

ON ARENE CHROMIUM TEMPLATE

A THESIS

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T. SURESH KUMAR

DIVISION OF ORGANIC CHEMISTRY (SYNTHESIS)

NATIONAL CHEMICAL LABORATORY

PUNE - 411 008

To

My Parents

And

the power which created you

and me and….curiosity!

CERTIFICATE

This is to certify that the work incorporated in the thesis entitled ***"Steroeselective Functionalizations on Arene Chromium Template"*** submitted by Mr. T. Suresh Kumar was carried out by him under my supervision at National Chemical Laboratory. Such material as has been obtained from other sources has been duly acknowledged in the thesis.

Date: 18-8-2003

National Chemical Laboratory
Pune 411008

Prof. Amitabha Sarkar
(Research Guide)

Acknowledgments

"First comes the thought; then organization of that thought, into ideas and plans; then transformation of those plans into reality. The beginning, as you see, is in imagination". It is precisely this gift of imagination and clarity of thought that Prof. Sarkar has bestowed on me. He has been a continuous source of inspiration and was ever alert to put me back on the course whenever I went astray. The most befitting tribute to Prof. Sarkar's training would only come through the practice of chemistry of highest quality and I would sincerely look forward to achieve this task.

This thesis would not have been possible without the kind care and encouragement of Dr. Deshmukh. His unparalleled earnestness towards chemistry is something I wish to carry with me as an ideal. Dr. Bhawal's encouragement constantly propelled me through the course of my work.

I acknowledge the timely help rendered by Dr. (Mrs) Puranik, Dr. Panse, Dr. Kulkarni and Dr. (Mrs) Joshi. I thank Dr. Sanjayan and Dr. Argade for their encouragement. Special thanks are due to my seniors Sunilda, Surojitda, Debasisda, Bikasda for their assistance and guidance. Swamy has been immensely helpful with his wise counsel from time to time.

If there was not a single day that I was tired of working in the lab, it was due to my explosive combination with Dr. Gumaste. His joyful nature not only kept the lab lively but also served as a pressure-vent to one and all. The warm memories of my days in lab-194 will haunt me forever.

Thyagu's calmness even amidst tempests, Krishnaswamy's spontaneity and Govande's forbearance make them unique individuals and I cherished their company all the time. Friendly attitude of my colleagues Bidhan, Annyt, Aarif and Neelesh helped me to have cheerful atmosphere in the laboratory. I thank Jadhav and Pawar for helping me through administrative hurdles.

I'm grateful to my group members Tarun, Dilip, SAM and Anuradha for their cooperation. I thank Subramanium, Dumre, Prabal, Pasu, Sh(B)iju, Easwer, Subbu, Nagendra and all my friends at NCL for their help and cooperation. All the Tamil makkal deserve special thanks for bearing with me and treating me never separately. I enjoyed weekly seminars among Tamil and Telugu gangs in the hostel; they were very lively and educative.

I'm gifted with the blessings of my grand parents and a small but intimate group of well-wishers outside NCL in the form of Mrs. Koushik, Ganga, Reddy, Srinu, Chakri, KK, Jaspreet and Vidya. I would like to thank all my relatives for their constant encouragement.

My short acquaintance has grown into a strong bond of love and affection during my stay with Indra and Chandrima at Kolkata. Their hospitality had a profound influence on my perception of friendship and love. The motherly affection of Indra's parents created for me 'a home away from home'.

I'm greatly indebted to my brothers Sairam and Raghuram for their goodwill and encouragement. Jayanthi was patience personified to put up with all my chemistry blabber, childish pranks and teasing. I'm grateful to her for her love and care. She is no less dear to me than my own family.

It is my parent's prayers, constant struggle and relentless hard work to overcome the odds of life that has challenged me to pursue life with greater optimism. The ideals I have inculcated from them made me a different individual and have put me far ahead of my fellow men in taking life head-on. My successes are dedicated to them- now and always.

I'm thankful to Dr. K. N. Ganesh for his constant encouragement and support. I thank the Director, NCL, for providing infrastructural facilities. CSIR, New Delhi is acknowledged for the financial assistance.

-Suresh

CONTENTS

GENERAL REMARKS

1. All melting points (recorded on a Thermonik Campbell melting point apparatus) are uncorrected and are recorded on the Celsius scale.
2. IR spectra were recorded as nujol mull or chloroform, on a Perkin-Elmer Infrared Spectrometer Model 599-B, Model 1600 FT-IR and ATI Mattson, UK, Model-RS-1 FT-IR, using sodium chloride optics. IR bands are expressed in frequency (cm^{-1}).
3. Proton NMR spectra were recorded using tetramethylsilane as internal reference on Bruker MSL-300 and Bruker AC-200. Chemical shifts were recorded in parts per million (δ). Abbreviations, *viz.*, s = singlet, d = doublet, t = triplet, dd = doublet of doublet, brs = broad singlet, br = broad peak, dt=doublet of triplet and m = multiplet have been used to describe spectral data. $CDCl_3$ was used as the solvent unless otherwise mentioned.
4. ^{13}C NMR spectra were recorded on Bruker MSL-300 and Bruker AC-200 instrument operating at 75.2 MHz and 50.3 MHz respectively.
5. Elemental analyses (C, H, N) were obtained on a Carlo-Erba 1100 automatic analyzer by Dr. S. Y. Kulkarni and his group at NCL.
6. Circular Dichroism data was collected on Jasco J-15 spectrophotometer in a cell of path length 1 cm and scanned from a range 250 nm to 400 nm.
7. The progress of the reaction was monitored by analytical thin layer chromatography plates pre-coated with silica gel 60 F_{254}(Merck). Column chromatography of chromium complexes were carried out with silica gel obtained from Merck (230-400 mesh, 9385 grade) under argon or nitrogen pressure.
8. Known compounds were characterized by IR and proton NMR spectroscopy.
9. Pet-ether refers to the fraction boiling between 60-80 °C.
10 All the reactions were performed under argon atmosphere.

ABBREVIATIONS

n-BuLi or butyllithium	*n*- Butyl Lithium in hexane
DMF	Dimethylformamide
Et_2O or ether	Diethyl ether
h	Hour
LDA	Lithium diisopropyl amide
o	Ortho
m	Meta
p	Para
mnts	Minutes
rt	Room temperature
tert	Tertiary
THF	Tetrahydrofuran
TLC	Thin layer chromatography

Synopsis of the thesis

Compound numbers in the synopsis are not related to the numbers in the chapters

Name of student: **T. Suresh Kumar**

Name of Research Guide: **Prof. Amitabha Sarkar**

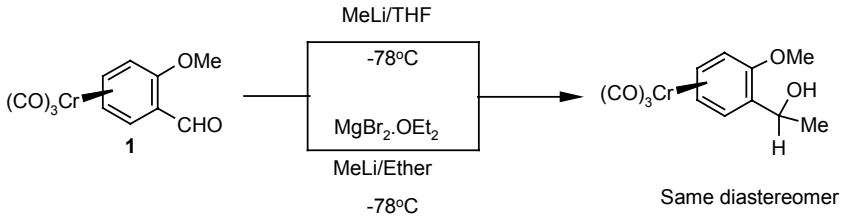
Synopsis of thesis entitled: **"Stereoselective Functionalizations on Arene Chromium Template"**

Part A

Chelation-control in nucleophilic addition to $Cr(CO)_3$-complexed aryl aldehydes

Asymmetric synthesis of chiral alpha substituted benzyl alchohols *via* stereoselective chelation-controlled addition of nucleophiles to *ortho* substituted arene tricarbonylchromium complexes was studied. Failure of *o*-OMe-benzaldehyde-$Cr(CO)_3$ complex **1** to act as bidentate ligand to Lewis acidic metals and induce stereodivergence in nucleophilic addition (Scheme-1) indicated that non-bonding electrons on oxygen strongly interact with the π-system of the complexed aromatic ring and thus impede binding of the oxygen atom with Lewis acids.

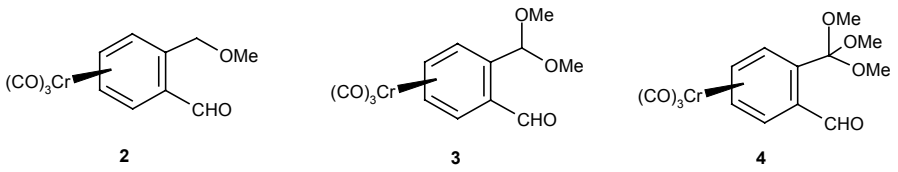
Scheme – 1



Insertion of an extra carbon between the aromatic ring and the alkoxy group was expected to restore the Lewis basicity of the oxygen and facilitate chelation. To this end, aldehyde complexes **2**, **3** and **4** featuring one, two and three methoxy groups respectively at the benzylic center were synthesized. Incremental methoxy

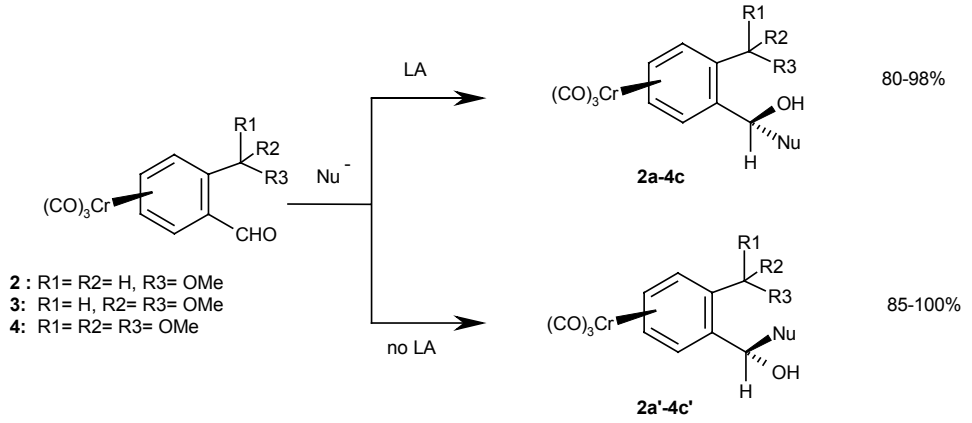
substitution was expected to favor the entropy of chelation with Lewis acid (Scheme-2).

Scheme – 2



Nucleophilic additions to the above substrates were studied using MeLi, n-BuLi and PhLi – *without* Lewis acid in ether or THF, and *with* Lewis acids in dichloromethane at –90 °C. Results indicated that Lewis acid additives indeed reverse the diastereoselectivity (Scheme-3).

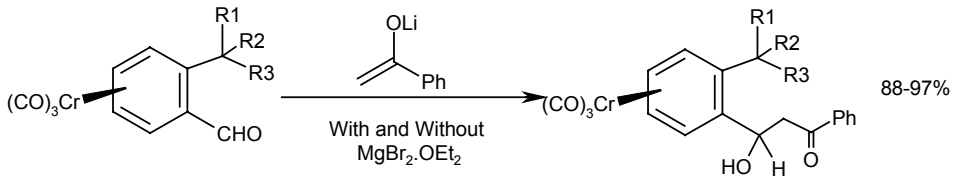
Scheme – 3



Diastereoselectivity improved on going from substrates **2** to **4** – as the number of methoxy group on adjacent carbon increased, but in absence of a Lewis acid additive the selectivity remained moderate. In presence of Lewis acid, diastereoselectivity was consistently very high. Use of $ZnCl_2.OEt_2$ or $Sc(OTf)_3$ as Lewis acid resulted in a chelation controlled addition, but diastereomeric excess and yields were inferior to those obtained with $MgBr_2.OEt_2$.

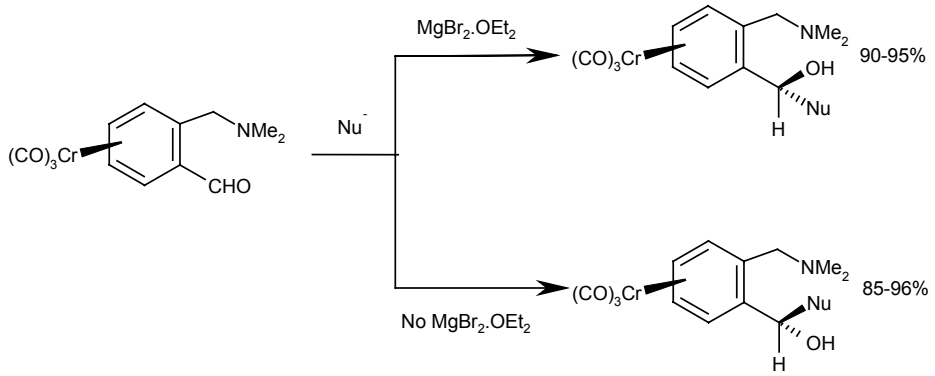
Chelation-controlled addition of nucleophiles to *ortho* substituted tricarbonylchromium benzaldehyde complexes was extended to asymmetric aldol reaction. However, addition of lithium enolate of acetophenone did not result in any stereodivergence in the presence of $MgBr_2.OEt_2$ (Scheme-4).

Scheme – 4



Addition of alkyl lithium reagents to *o*-N,N-dimethylamino-benzaldehyde tricarbonylchromium gave amino alchohols with respectable stereodivergence in the presence of $MgBr_2.OEt_2$ as Lewis acid (Scheme-5).

Scheme – 5



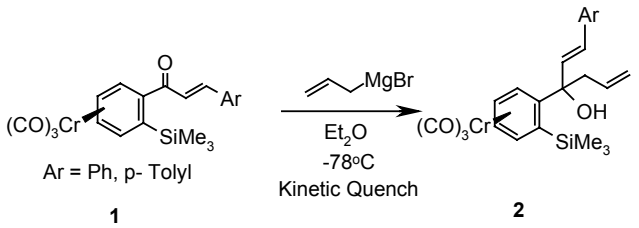
In summary, this part of the thesis describes the first definitive example of diastereoselective nucleophilic addition under chelation-control on arene-chromium complexes, and demonstrates its use in devising stereodivergent routes to products with predictable stereochemistry. Presumably these findings should be equally applicable for any planar chiral moiety and find their utility in the preparation of novel chiral bidentate ligands for asymmetric catalysis.

Part B

Counterion Dependent Cleavage of Si-Ar bond *vs* Si-Me bond

In course of our studies on stereoselectivity of nucleophilic additions on acyclic arene-tricarbonylchromium complexes, allylmagnesium bromide was added to the enone **1**. The carbinol **2** was subsequently treated with KH or NaH to effect an anionic oxy-Cope rearrangement (Scheme 1).

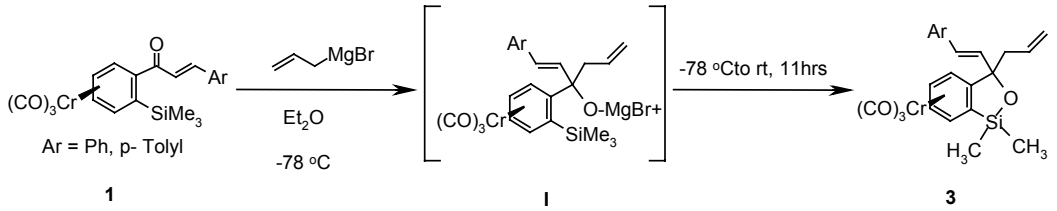
Scheme – 1



During this study it was recognized that the alkoxide derived from the carbinol **2** followed diverse reaction pathways depending on counterion, temperature and additives. This part of the thesis is an account of the experiments carried out to understand and identify such factors conclusively.

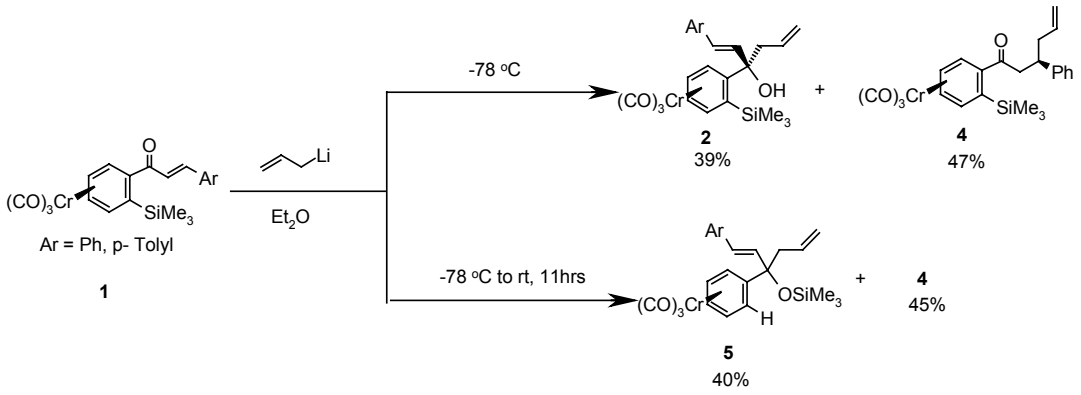
When the above reaction mixture was allowed to slowly attain room temperature over several hours, an unusual cyclic siloxane **3** was obtained. Significantly, in this instance, the alkoxide **I** undergoes an Si-Me bond cleavage in preference to an Si-Ar bond cleavage under mild condition even when the Si-Ar bond is evidently activated by complexation with tricarbonylchromium (Scheme-2). The anionic nature of the methyl group lost from the trimethyl silane in **3** was confirmed by quantitatively trapping it with benzophenone and isolating the corresponding carbinol.

Scheme – 2



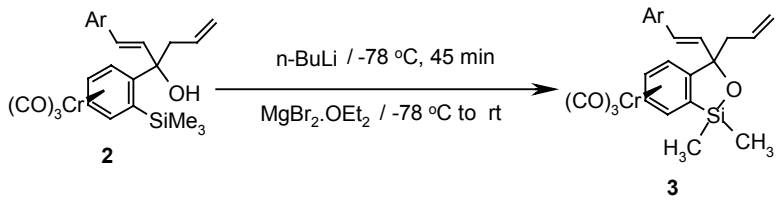
Addition of allyl lithium to **1** on the other hand showed a different reaction profile. Carbinol **2** and conjugate addition product **4** were isolated if the reaction was quenched at –78 ^{o}C, but when the same reaction was allowed to warm up to room temperature and stirred for several hours compound **5** was obtained as the product, presumably resulting from a 1,4- Brook rearrangement (Scheme-3).

Scheme – 3



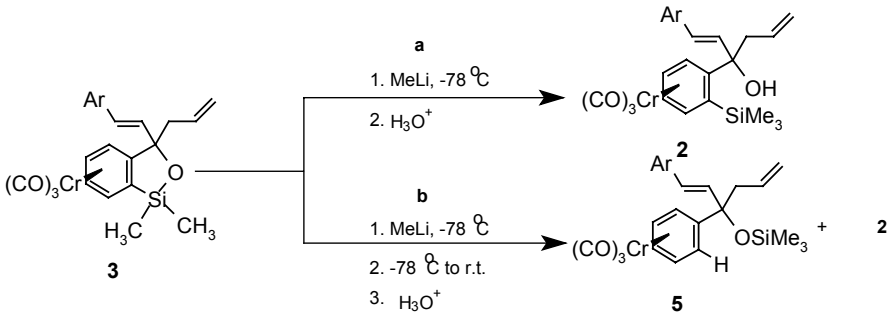
That the cyclization was indeed dictated by magnesium counterion was readily ascertained by treatment of lithium alkoxide of **I** with a three-fold excess of $MgBr_2.OEt_2$ prior to warming up, which yielded **3** exclusively (Scheme-4).

Scheme – 4



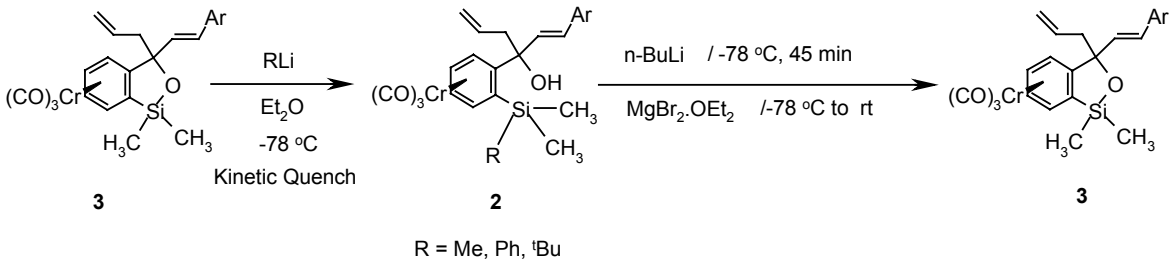
When methyllithium was added to **2** at a low temperature, and the reaction was quenched shortly thereafter, the carbinol **2** was isolated in 85% yield. Brook rearrangement accounted for 60% of the product when the same reaction mixture was allowed to attain room temperature and stirred for an extended period of time (*path b*, Scheme 5). This experiment indicated that the Si-O cyclization step was reversible and products resulted from a thermodynamic control.

Scheme – 5



The reversibility of the cyclised product to the carbinol by the addition of an alkyl lithium at low temperature was effectively employed in preparing the carbinols **2** with a hetero substitution on Si by treating the cyclized product with phenyl and t-butyl lithium reagents at –78 ^{o}C. Subjecting these carbinols to cyclization according to the protocol used in scheme-4 resulted only in **3** revealing greater leaving group abilities of phenyl and *tert*-Butyl groups over the methyl group (Scheme-6).

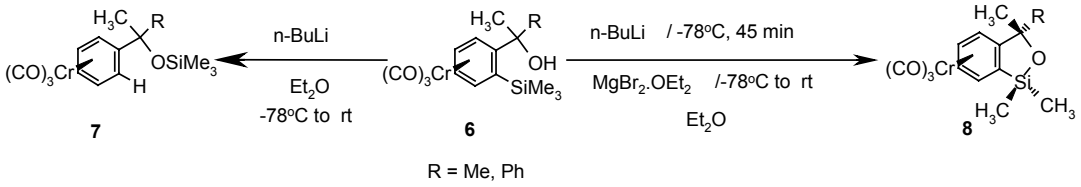
Scheme – 6



Failure of carbinols derived from *o*-TMS benzaldehyde complex under identical conditions to provide cyclic products as above, but a facile switch over of

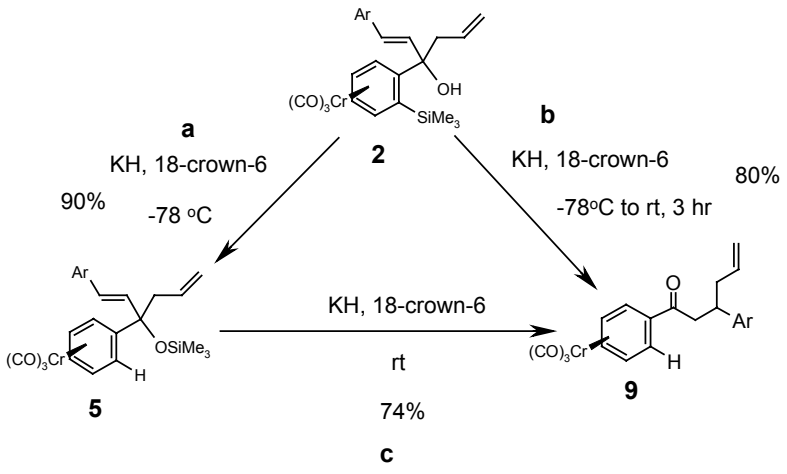
reaction pathways by change of counterion on carbinols **6** to Brook and cyclised products (**7** and **8** respectively) establishes the importance of a *gem*-disubstitution at the bezylic position in favor of cyclization (Scheme-7).

Scheme – 7



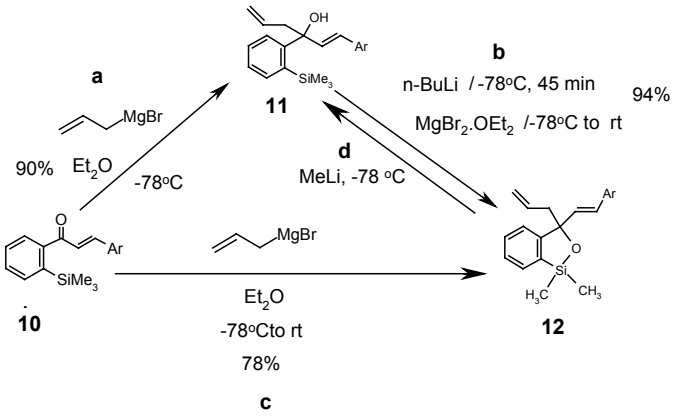
The carbinol **2** possesses structural features ideally suited to study the competition between Brook rearrangement and anionic oxy-Cope rearrangement. When it was treated with KH and a catalytic amount of 18-crown-6 in ether at –78 °C, Brook product **5** formed almost quantitatively (90%) within 20 min at that temperature (*path a*, Scheme-8); with lithium as counterion, this rearrangement proceeded only after warming up to room temperature. With potassium as counterion, the anionic oxy-Cope rearrangement is complete in three hours at room temperature (*path b*, Scheme-8). The intermediacy of complex **5** in the anionic oxy-Cope rearrangement was established by the clean conversion of **5** to **9** at room temperature (*path c*, Scheme-8).

Scheme – 8



That the tricarbonylchromium plays no role in cyclization was ascertained by subjecting the above reaction sequences on an uncomplexed substrate. Reaction of **10** with allylmagnesium bromide at –78 ^{o}C afforded the carbinol **11** in 90% yield (*path a*, Scheme-9). This has undergone a facile cyclization when treated with n- BuLi/$MgBr_2$.OEt_2 (*path b*, Scheme-9). The cyclized product **12** could be directly obtained by warming the reaction mixture of allylmagnesium bromide and enone **10** to room temperature and prolonged stirring (*path c*, Scheme-9). Additon of MeLi to **12** resulted in the carbinol as in the case of tricarbonylchromium complexed substrates (*path d*, Scheme-9).

Scheme – 9



In summary, this part of the thesis describes an interesting example of counterion dependence of reaction pathways involving arguably the same intermediate alkoxide. Factors that precisely tune the energetics of different mechanistic possibilities have been systematically studied.

Publications :

1. Chelation-control in nucleophilic addition to $Cr(CO)_3$-complexed aryl aldehydes-Suresh Kumar Tipparaju, Vedavati G. Puranik and Amitabha Sarkar **Org. Biomol.Chem.** *2003* **1** 1720.

2. Cleavage of Si-Ar bond *vs* Si-Me bond: a remarkable counterion effect on reactivity Suresh Kumar Tipparaju, Sunil K. Mandal, Surojit Sur, Vedavati G. Puranik and Amitabha Sarkar **Chem. Commun.** *2002* 1924.

3. Contraintuitive Stereocontrol: *endo*-Selective Nucleophilic Addition on Arene-Tricarbonylchromium Template Amitabha Sarkar, Sambasivam Ganesh, Surojit Sur, Sunil K. Mandal, Vishwanath M. Swamy, Bikash C. Maity and T. Suresh Kumar **J. Organomet. Chem**. *2001* **624** 18.

Part A

Chelation-control in nucleophilic addition to $Cr(CO)_3$-complexed aryl aldehydes

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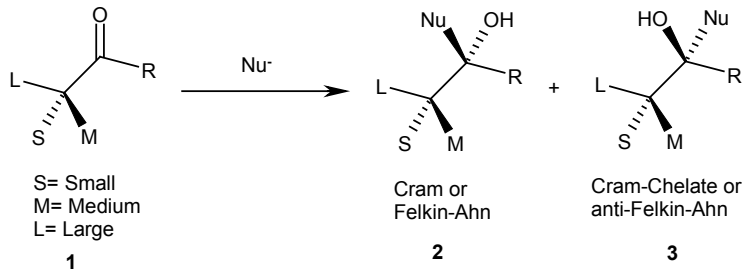
Part of this work was published in *Org. Biomol. Chem.***2003**, *1*, 1720.

Experiments are the only means of knowledge at our disposal,
rest is poetry and imagination.

-Enrico Fermi

Introduction

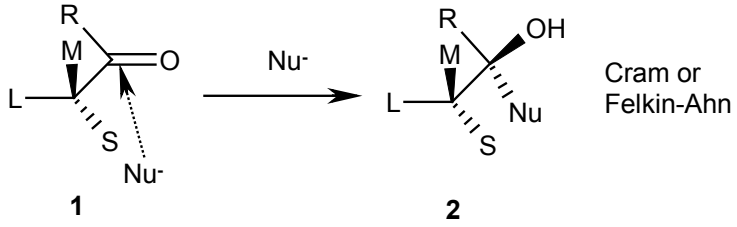
Carbon-carbon bond formation resulting from nucleophilic attack on carbonyl compounds has played a prominent role in the evolution of organic synthesis. The means by which the stereochemical outcome of these condensations may be predictably controlled has been the focus of considerable research.[1] Several models have been developed to rationalize the addition of nucleophiles to the carbonyl group of chiral aldehydes or ketones in which a stereogenic center is adjacent to the carbonyl group. Though there have been subsequent modifications,[2] the seminal contribution by Cram[3] sustained it's credibility over the years in explaining the favored trajectory of the attacking nucleophile and preferential formation of **2** or **3** (Scheme-1).



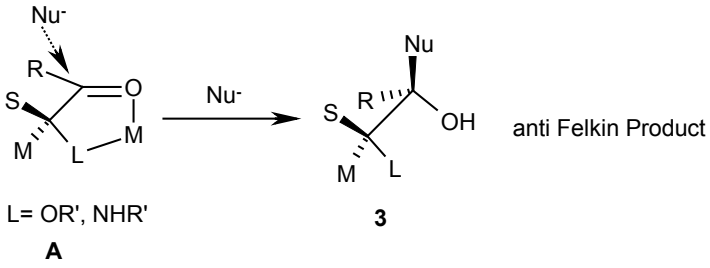
Scheme 1. 1,2-induction in α-chiral carbonyls

In Cram's model, steric interaction between the large substituent **L** and the carbonyl group was sought to be avoided. Consequently, **L** is oriented *anti* with respect to the carbonyl group that is flanked by the small group **S** and the medium group **M** on two sides. A nucleophile will now preferentially attack from the side of the small substituent **S**, leading to **2** as the major product (the 'Cram product' or the 'Felkin-Anh product') as shown in Scheme-2.[3b]

Scheme 2. Cram- Model



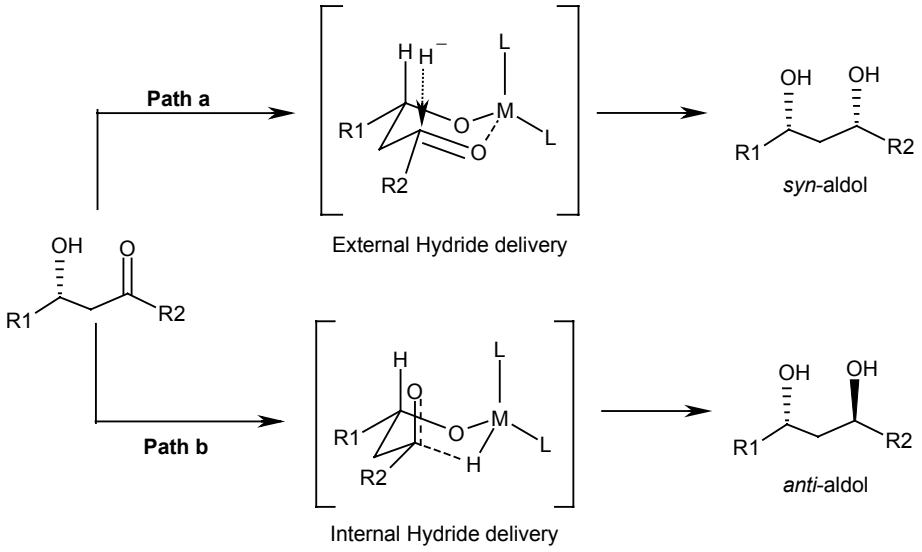
However, when the α-stereocenter contains a donor heteroatom capable of coordination with a metal cation forming a chelate, the substrate is locked into the conformation **A** (Scheme-3). This will place the remaining two substituents, here **S** and **M**, on two sides of the carbonyl group. A nucleophile will now preferentially attack the carbonyl group from the side of the smaller substituent **S** leading to **3** as the major product. This is generally referred to as the Cram-chelate product. The Cram-chelate rule has been shown to be most reliable in its predictive power for numerous examples in organic synthesis; no amendments were thus necessary to correct the basic assumptions. Oliver Reiser has recently contributed an excellent review on the evolution of various models based on Cram's rule and their application to disatereoselective synthesis.[4]



Scheme 3. Cram-Chelate Model

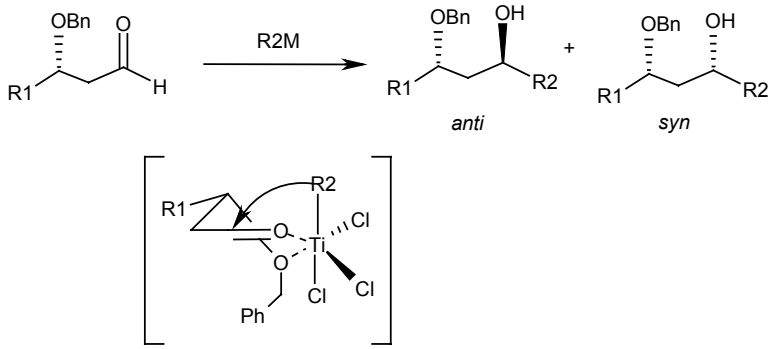
The close proximity of a chiral center to a prochiral reaction center as in the above Schemes is expected to exhibit a strong and predictable influence over the stereochemical outcome of the reactions and could be more reliably predicted. Consequently, there are numerous examples and models for such 1,2-induction.[5] However, moving the chiral center to the β-position with respect to the carbonyl group would diminish its influence unless the reactive conformation of the molecule is locked by chelation in such a manner that the steric factors are clearly defined.[6] Thus, examples of 1,3-inductions with non chelation-controlled process are very scarce.[7]

Two complementary modes for chelation-controlled reaction that provides 1,3-induction have been described.[8] Either the reaction center and the chiral center are locked together when the nucleophile is delivered externally (*path a*, Scheme-4) or the nucleophile becomes part of the chelate itself and could be delivered internally (*path b*, Scheme-4).[8]



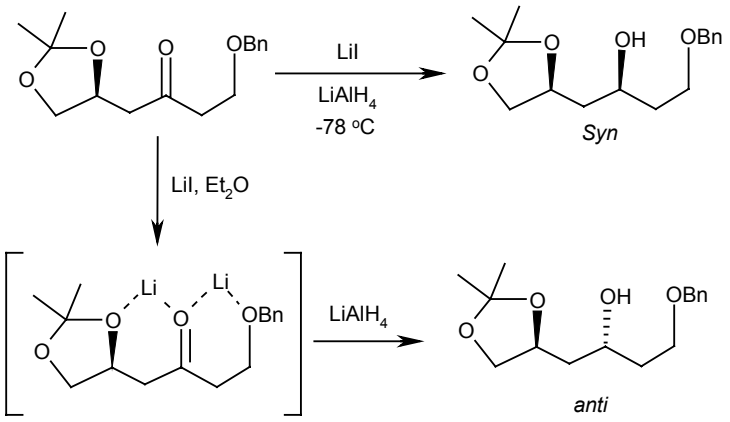
Scheme 4. Chelation-controlled 1,3-induction by internal and external hydride delivery. Evans Model

Reetz successfully applied Cram-chelate model to β-Hydroxy aldehydes, where he proposed that attack of the nucleophile should occur from the sterically less hindered side, i.e., *anti* to the substituent R1, predicting *anti* isomer as the major product (Scheme-5).[9]



Scheme 5. Chelation-controlled 1,3-induction. Reetz Model

Such 1,3–asymmetric induction would be even more interesting when there is a competing β-oxygen functionality which could also participate in chelation. A variety of functionalized optically active *syn*-1,3-diols were synthesized by chelation-controlled reduction of chiral β-alkoxy ketones using Mori and Suzuki's $LiAlH_4$-LiI protocol (Scheme-6).[10]



Scheme 6. Competitive chelation

An essential requirement to form such chelate is of course that the metal center must have at least two free coordination sites[11] and the proximal group containing a donor heteroatom like aliphatic –OR or $–NR_2$ must permit effective bidentate complexation of the Lewis acid.[12, 13]

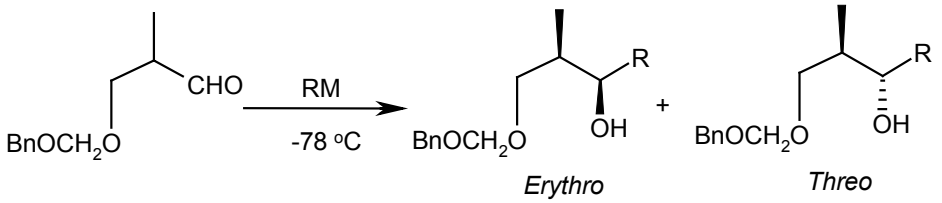
There have been a very few reports of organized γ or 1,4-induction in nucleophilic additions to carbonyl groups,[14] understandably due to difficulty in formation of such chelates. This chapter describes one such 'uncommonly-effective' seven membered chelation that induces stereodivergence in nucleophilic addition in presence of a Lewis acid.

Chelation-Control in Organic Synthesis

There are numerous examples wherein chelation-control was incorporated as a key element of stereocontrol in diastereoselective and enantioselective carbonyl additions.[15] It was employed as a cornerstone in designing the synthesis of many complex natural products[16] and in development of several new synthetic strategies.[17] Next few paragraphs present an overview of recent use of chelation-control strategy in organic syntheses.

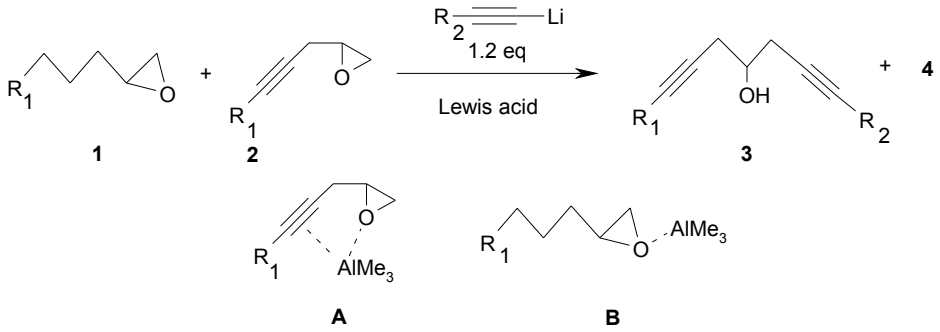
In course of their investigations on the use of chiral silyl ethers as auxiliaries for the asymmetric nucleophilic additions to α and β siloxy carbonyl compounds,[18] Bienz *et al*. have studied the addition of Grignard reagents in a chelation-controlled manner employing Lewis acids such as $MgBr_2$.[19]

Still described an optimum reaction condition for the highly stereoselective addition of carbanionic nucleophiles to chiral α-alkoxyketones. A number of oxygen protecting groups were screened to allow chelation-controlled α-asymmetric induction with diastereomeric product ratios ranging from 50->200:1.[20] Organocuprates were found to be highly stereoselective reagents for the addition of carbanionic nucleophiles to α-asymmetric aldehydes bearing β-oxygen substituents. The major products could be predicted by a chelation-controlled transition state and diastereomeric purities ranging from 15-30:1 were obtained (Scheme-7).[21]



Scheme 7. 1,3-asymmetric induction in Organocuprate addition

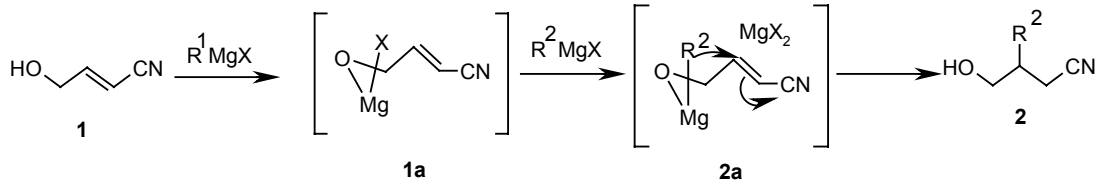
Recently Yamamoto described an unusual σ-π chelation-control in chemo-selective ring opening of epoxides.[22] While ring opening of alkynyl epoxides **2** is almost quantitative in the presence of Lewis acids, the alkyl epoxide **1** fails to react with alkynyllithium reagents. This chemoselectivity was ascribed to an interesting bidentate complexation of the Lewis acid with a non-bonding electron pair of the oxygen atom of the epoxide and π-electrons of the C-C triple bond, (as shown in **A**) which is feasible only with substrate **2** (Scheme-8).



Scheme 8. π-Chelation

Over the past few years, interest in transition metal catalyzed activation of C-H and C-C bonds has seen a steady increase. Chelation-assistance utilizing cyclometalation proved to be one of the most promising ways for such activations.[23]

Chelation-controlled conjugate additions to γ-hydroxy-α,β–alkenenitriles by sequential deprotonation and addition of a modest excess of a second Grignard reagent provide substituted nitriles, installing up to two new stereocenters in a single synthetic operation. The exploratory addition of excess methylmagnesium chloride to 4-hydroxybutenenitrile **1** triggered an efficient chelation-controlled conjugate addition resulting in **2** (Scheme-9).

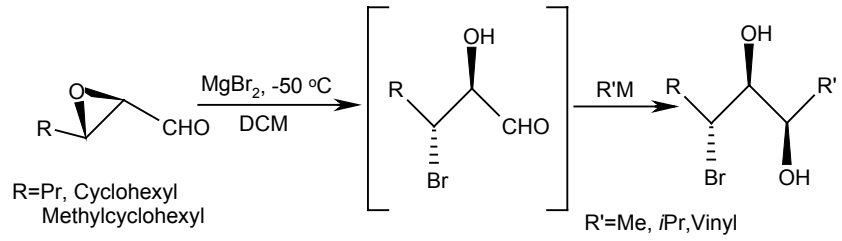


Scheme 9. Chelation assisted conjugate addition

Mechanistically, deprotonation by the first Grignard R^1MgX at low temperature generates the halomagnesium alkoxide **1a** that rapidly engages in a halogen-alkyl exchange with the second Grignard reagent R^2MgX. The resulting alkylmagnesium alkoxide **2a** initiates a smooth conjugate addition upon warming to room temperature, ultimately generating the conjugate adduct **2**.[24] The substantial rate difference between deprotonation and conjugate addition at -78 °C allows *t*-BuMgCl or PhMgCl to be employed as sacrificial bases.

On addition of organometallic reagents, α,β-epoxy aldehydes predominantly give *anti* adducts *via* Felkin-Ahn model (Scheme-10). Recently, Righi *et al.* reported a general "one pot" ring-opening-organometallic addition to *trans* α, β-epoxy aldehydes to afford *anti* or *syn* 3-bromo-1,2-diols with a high stereoselectivity and chemical yield using $MgBr_2$ and then adding R'MgBr in the same reaction vessel (Scheme-10).[25]

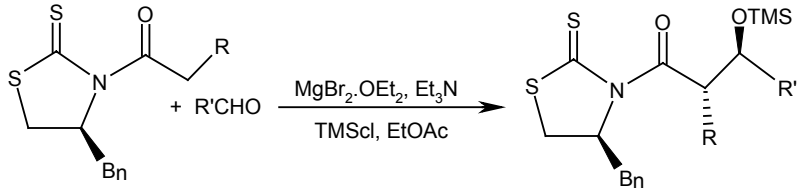
It seems probable that Mg^{2+} ion initially controls the regiochemistry of the attack by chelation between the carbonyl and the epoxide oxygen and, subsequently dictates *syn* stereochemistry of the Grignard addition (Scheme-10).[25]



Scheme 10. Chelation controlled opening of epoxides

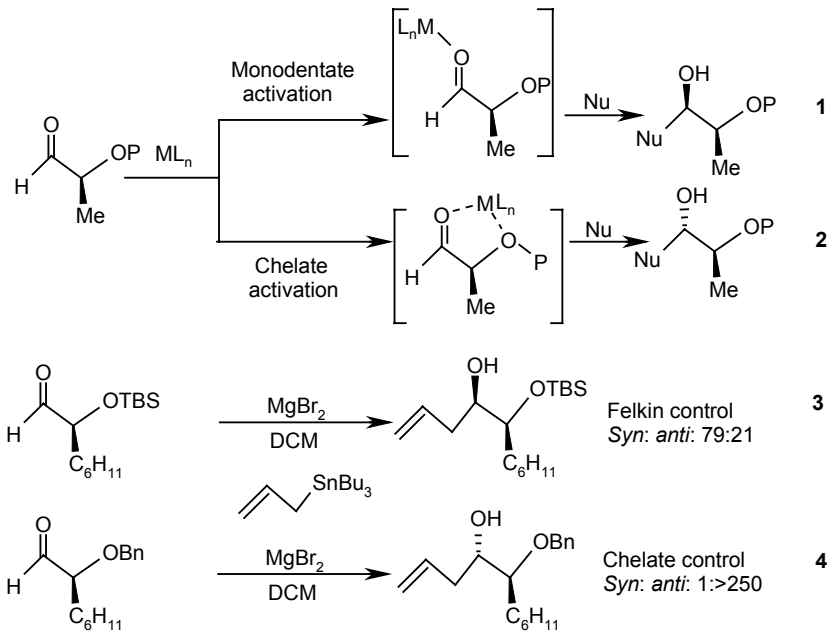
During synthesis of (-)- Azaspirene Hayashi *et al*. have studied the effect of various Lewis acids on Mukaiyama aldol in which $MgBr_2.OEt_2$ gave most impressive results.[26] Many reports exist wherein $MgBr_2.OEt_2$ was elegantly used as an effective bidentate chelating Lewis acid.[27]

Evans employed $MgBr_2.OEt_2$ as a Lewis acid catalyst in inducing a chelation-controlled addition of chiral enolates of *N*-acylthiazolidinethiones to aldehydes resulting in a disatereoselective *anti*-aldol reaction (Scheme-11).[28]



Scheme 11. $MgBr_2.OEt_2$ as a Lewis acid and a chelating agent

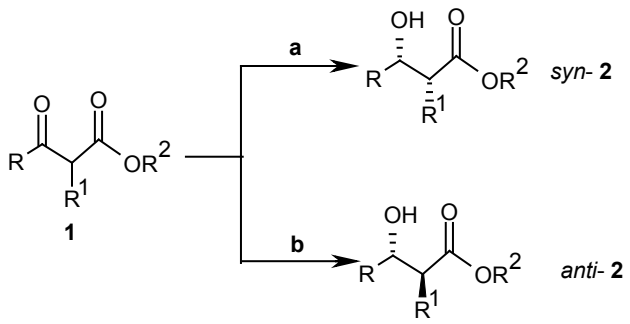
In substrates such as R-alkoxy carbonyl derivatives, operation of either Felkin-type monodentate activation (eq 1) or chelation control (eq 2) is directly reflected on the stereochemical outcome of the reaction. In otherwords, the stereochemical outcome of this reaction provides strong circumstantial evidence of the mode of carbonyl activation (Scheme-12). [29]



Scheme 12. Monodentate *vs* Bidentate chelation

Marcantoni has elegantly exploited the difference in the mode of coordination of two metal ions to effect stereodivergent addition to carbonyl group.[30] Whereas titanium (IV) compounds have a strong ability to engage in bidentate chelation, $CeCl_3$ though apparently a good Lewis acid, cannot participate in such chelation and can activate the carbonyl only by monodentate activation.

In Lewis acid-mediated reduction of α-alkyl-β-keto esters, **1**, strongly chelating $TiCl_4$ led to the *syn* isomer in high diastereomeric excess in non-coordinating solvents (CH_2Cl_2) at -78 °C with BH_3.py as reducing agent. The non-chelating $CeCl_3$ afforded a high excess of the *anti* isomer in coordinating solvents (THF) at the same temperature with lithium triethylborohydride ($LiEt_3BH$) as reducing agent. The methodology was successfully utilized for obtaining important *syn* and *anti*-α-alkyl-β-hydroxy esters with high diastereoselectivity (Scheme-13). [30]

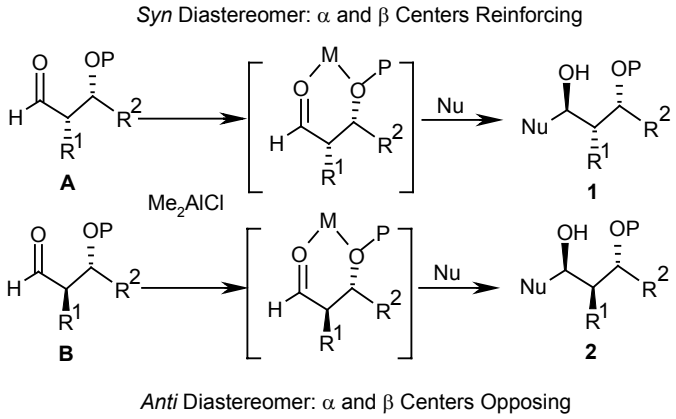


Scheme 13. a) $TiCl_4$/DCM at -78 ^oC, then BH_3.py**;** b) $CeCl_3$/THF at -78 ^oC, then $LiEt_3BH$

A number of factors are responsible for determining as to which mode of Lewis acid-substrate activation might be anticipated. Such factors include the nature of the coordinating Lewis acid with respect to its binding to the substrate, its concentration,[31] the nature of the oxygen protecting group[32, 33] and the reaction solvent (Coordinating *vs* non-coordinating).[34]

The impact of many such variables like the oxygen protecting group on the mode of substrate activation has been highlighted by Keck in his study of the catalyzed addition of allylstannanes to α-alkoxy aldehydes (eqs 3 and 4 in Scheme-12).[33d] This and related instances provide direct evidence that hindered silyl ethers do not generally participate in chelate organization.[35]

Dimethylaluminium chloride and Methylaluminium chloride have shown exceptional chelating abilities with chiral β-hydroxy aldehydes. Good stereocontrol in Lewis acid-promoted Mukaiyama aldol reactions was achieved for enolsilane aldol reactions of β-alkoxy and β-silyloxy aldehydes bearing only an α- or a β-stereogenic center. The *syn* aldehyde possesses an arrangement of stereocenters wherein α and β-substituents impart a reinforcing facial bias of the aldehyde carbonyl towards the nucleophilic attack. Aldol reactions of *syn* aldehydes were thus observed to proceed with uniformly excellent diastereofacial selectivity (Scheme-14).[36]



Scheme 14. Chelation in β-Hydroxy aldehydes

Background for present work

The present research concerns exploration of chelation control in nucleophilic addition to carbonyl group anchored on an arene tricarbonylchromium template. To place the work in perspective, it is appropriate that stereochemical aspects of such complexes be briefly reviewed, as presented in the following paragraphs.

Arenes are achiral since the molecular plane itself is their plane of symmetry. Tricarbonylchromium complexation occurs from one □-face of the arene and hence destroys the molecular plane of symmetry. If the arene ring is unsymmetrically substituted, *i.e.* it features non-equivalent substituents in *ortho* or *meta* positions, such complexation would afford a pair of enantiomers, **1** and **ent-1** (Chart-1)**.**

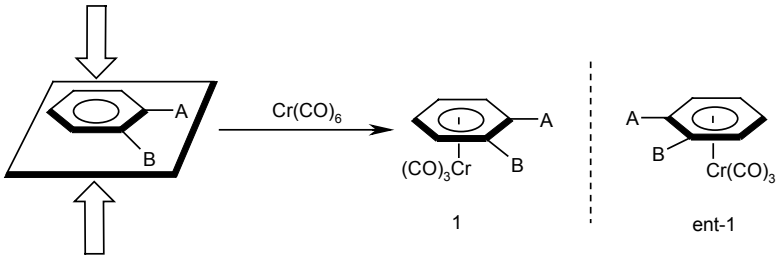


Chart 1. Enantiotopic π faces of an arene ring

These complexes are referred to as 'planar-chiral' complexes.[37] The planar-chirality associated with appropriately substituted arene-tricarbonylchromium complexes has been extensively investigated to provide useful synthons for a variety of targets ranging from biologically relevant molecules to chiral chelating ligands for metals in asymmetric catalysis.[38]

Similarly, appropriately-disubstituted ferrocenes can be planar chiral. Several optically pure, planar chiral ferrocene derivatives have been used in asymmetric catalysis.[39]

When one of the groups, A or B in Chart-1 is a carbonyl function, nucleophilic addition would create a new stereogenic center. The stereochemical outcome of such additions is extensively studied in reactions of chiral *ortho*-substituted benzaldehyde complexes.

Diastereoselective nucleophilic additions to *ortho*-substituted aryl aldehyde[40] and imine[41] complexes has been an important route for the synthesis of a number of ligands for asymmetric synthesis based on arene tricarbonylchromium complexes. A wide range of nucleophiles are known to add to the aryl aldehyde complexes. These include alkyl, aryl and alkynyl metals[42], enolates and their equivalents,[43] nitronate anions,[44] Reformatsky reagents,[43b,45] α-halo carbonyl enolates[46] and active methylene compounds.[47]

In most cases the addition is highly disatereoselective and invariably takes place from the face opposite to the bulky $Cr(CO)_3$ group at the benzylic site. However, rotation around Ar-CO bond exposes two different π faces of the carbonyl for the attack of nucleophile. For instance, chiral *o*-methoxy-benzaldehyde-$Cr(CO)_3$ complex, **1**, can adopt two possible conformations involving the carbonyl group: it is turned either towards (*syn*) or away from (*anti*) the *ortho*-substituent. Since nucleophilic addition is always *exo*-selective, configuration of the stereogenic center resulting from nucleophilic addition will then be governed by conformation of the carbonyl group (Chart-2).

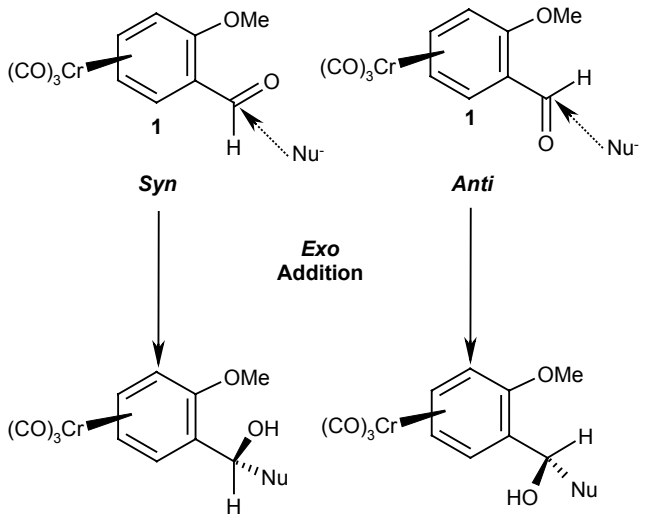


Chart 2. Conformations of carbonyl group with respect to *ortho* substituent and stereodivergent nucleophilic attack

An *o*-OMe group would normally force the carbonyl group to adopt an *anti* orientation that minimizes repulsion between non-bonded electron pair on two oxygen atoms (see A, Chart-3). However, if the methoxy group participates in chelation with a Lewis acidic metal ion, the carbonyl group would necessarily adopt the *syn* conformation (see B, Chart-3). In this case, one would clearly envisage a stereodivergent addition to the same molecule. Such a situation cannot exist in absence of a metal coordination (see C, Chart-3).

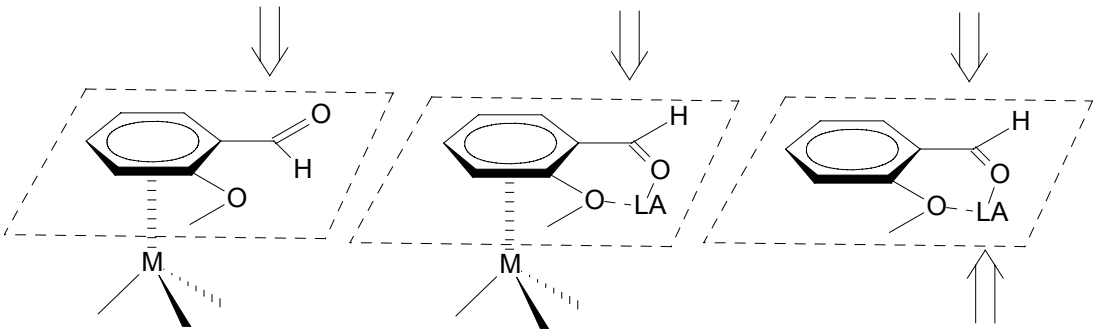
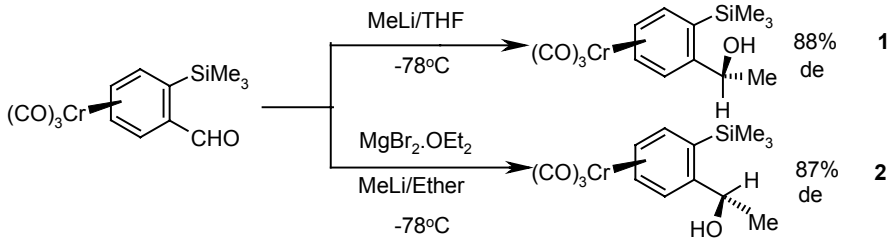


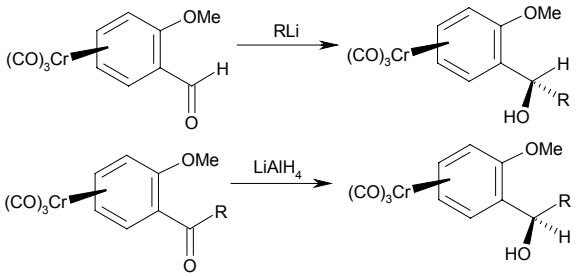
Chart 3. Diastereotopic and enantiotopic π faces of a carbonyl

The conformation of the carbonyl group depends largely on the nature of the *ortho* substituent and is *anti* in the majority of the cases. Davies *et al.* have studied the influence of an *ortho* substituent in directing the incoming nucleophile in some detail (Scheme-15).[48] The diastereomeric excess in case of addition of MeLi (eq 1) was attributed to a stabilizing Si-O non-bonding interaction which holds the conformation of the carbonyl in *syn* orientation, while the presence of Lewis acid (eq 2) forces it to *anti* conformation *via* monodentate activation previously depicted in Scheme-12.



Scheme 15. Stereodivergence in presence of Lewis acid

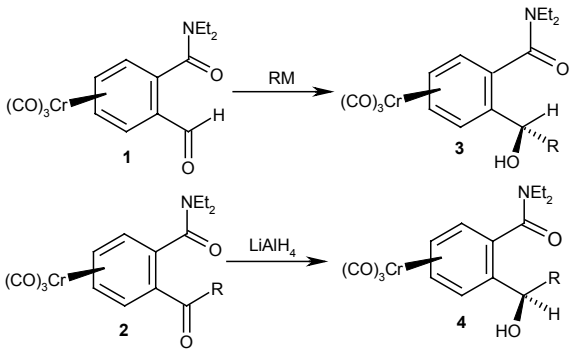
Asymmetric synthesis of α-subsbstituted benzyl alcohols *via* stereoselective addition of nucleophiles to chromium complexes of *ortho*-substituted benzaldehyde or acetophenone, followed by decomplexation of the products has been studied by several groups.[49] Often diastereomeric secondary benzylic alcohols have been prepared by the complementary routes of addition of alkyllithium reagents to the chiral complexed aldehydes and hydride reduction of corresponding chiral ketones (Scheme-16).[50]



Scheme 16. Synthesis of complementary diastereomers

These diastereomeric alcohols have also been prepared by direct complexation of the optically pure benzyl alcohol derivatives in which the sterically bulky and easily removable trimethylsilyl group was temporarily introduced at the *ortho* position.[51]

Uemura *et al.* have employed the same strategy as described in the above Scheme to prepare enantiomerically pure N,N-diethyl-2-methyl-6-α-hydroxyalkylbenzamides complexes, **3** and **4** by nucleophilic additions to planar chiral $Cr(CO)_3$ complexed 2-acyl and formyl-6-methylbenzamides, **1** and **2** respectively (Scheme-17).[40a]



Scheme 17. Synthesis of axially chiral benzamides

It is evident from the above illustrations that, desired configuration of the benzylic alcohol could be obtained by efficient control of the conformation of the carbonyl with respect to the *ortho* substituent. The *syn* conformer could be enforced if a Lewis acidic metal center forms a chelate involving the two oxygenated functions (Chart-4).

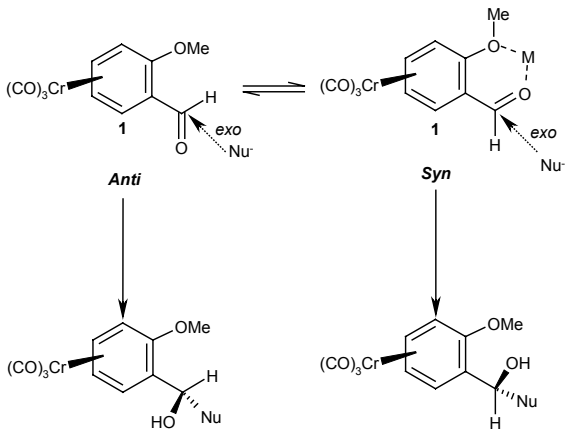
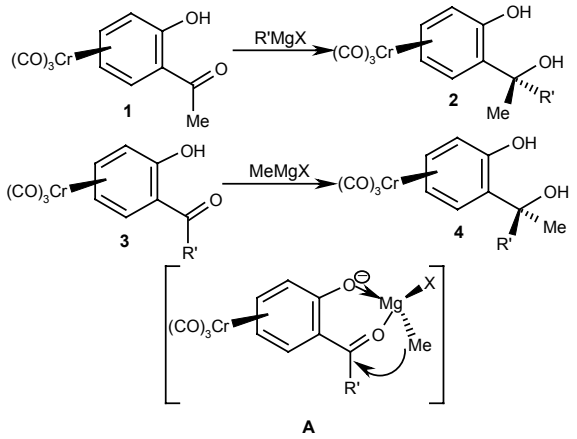


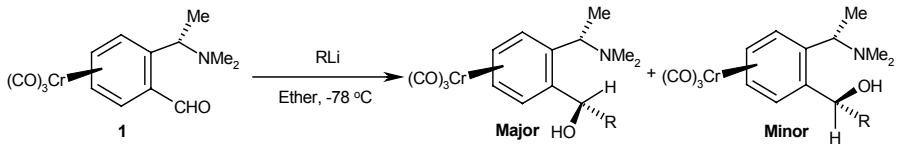
Chart 4. Stereodivergence *via* Lewis acid chelation

As early as 1969, Beasancon and Tirouflet have demonstrated that the *syn* conformer could indeed be enforced *via* chelation involving an *ortho*-OH and neighboring carbonyl functionality. Addition of R'MgX to the *ortho* hydroxy acetophenone complex **1** gives the tertiary carbinol **2,** while addition of MeMgX to **3** results in the complementary diastereomeric carbinol **4**. Both additions occur presumably through a chelation-controlled internal addition of the nucleophile as depicted in **A** (Scheme-18).[52]



Scheme 18. Chelation-controlled internal delivery of nucleophile

Uemura *et al*. described stereoselective synthesis of planar chiral (1,2-disubstituted arene) chromium complexes possessing amino and hydroxyl groups, both at benzylic positions.[40b] These chiral amino alcohols have proved to be efficient ligands in the asymmetric catalysis.[53] The synthesis of these amino alcohols was achieved by a highly diastereoselective addition of alkyllithium reagents to the aldehyde **1**, major diastereomer being the one obtained from an *exo* attack of carbanions to the carbonyl group in *anti*-conformation with respect to the *ortho* dimethylaminoethyl substituent (Scheme-19).



Scheme 19. Synthesis of chiral ligands for asymmetric synthesis

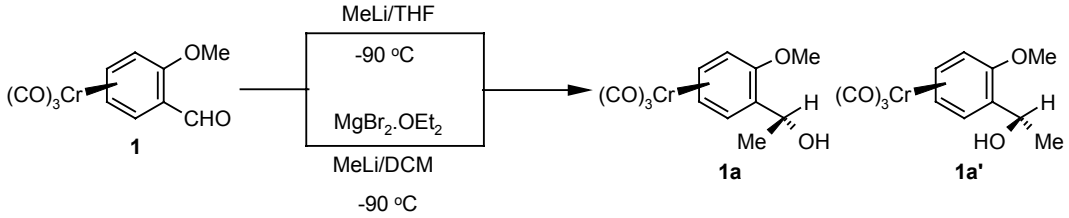
In order to convert the minor diastereomer into major diastereomer, the authors have employed decomplexation and a chiral face-selective re-complexation protocol. It appears, however, that a chelation-controlled addition would have provided the same result in a more direct way.

The examples cited above clearly indicate absence of a definitive study on application of chelation-control in nucleophilic addition to arene chromium complexes featuring a carbonyl function, and examine efficacy as well as advantages of such an approach in devising stereodivergent routes.

Present work

We wished to explore the general adaptability of chelation-control as a strategy to induce stereodivergence in the addition of nucleophiles to *ortho*-substituted benzaldehyde complexes. If one could engineer formation of a configurationally pure product in this manner, synthesis of α-substituted benzyl alcohols would become extremely convenient and straightforward.

Preliminary investigation concerned an observation that addition of MeLi to *o*-anisaldehyde complex **1** gives the same diastereomer irrespective of the presence of Lewis acid in the reaction medium (Table-1). In a typical attempt for chelation-controlled addition, $MgBr_2.OEt_2$ was added as solid to a cold solution (-78 ^oC) of the aldehyde complex **1** in dichloromethane and the mixture was stirred for 30 minutes during which time the color of the reaction mixture turned dark purple. The temperature was further lowered (–90 ^oC) and dropwise addition of MeLi resulted in an instant color change from purple to greenish yellow. The product **1a'** was the same as the major product obtained from addition of MeLi in THF without any Lewis acid additive (Scheme-20).[54]



Scheme 20. No stereodivergence in *o*-anisaldehyde complex

Table-1

Entry	Aldehyde	Reagent / Solvent	Yield (%)	Product (ratio)
1	**1**	MeLi/ THF	100[54]	**1a**:**1a'**= 1:15.7
2		$MeLi/MgBr_2.OEt_2/DCM$	98	**1a'**

$MgBr_2.OEt_2$ was used as Lewis acid since it is mild, easy to handle and can be weighed accurately. It is also well known that Mg^{2+} can effectively participate in bidentate chelation.[26,27] Non-coordinating dichloromethane was used as solvent for the reactions to maximize the coordinating ability of $MgBr_2.OEt_2$. [55]

It was reported in literature that the crystal structures of anisole-$Cr(CO)_3$ complex[56a] and 4-fluoroanisole-$Cr(CO)_3$ complex[56b] reveal a near co-planarity of OMe group with aromatic ring and a shortening of (*Ar*)C-O bond. This indicates that non-bonding electrons on oxygen strongly interact with the π-system of the electron-depleted aromatic ring, which would account for its inefficient coordination to metal ions (Fig. 1). This was also evident in lack of regioselectivity during directed lithiation.[56b]

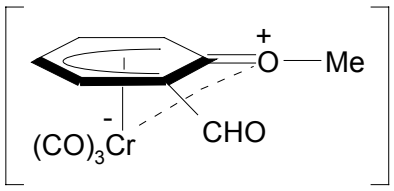
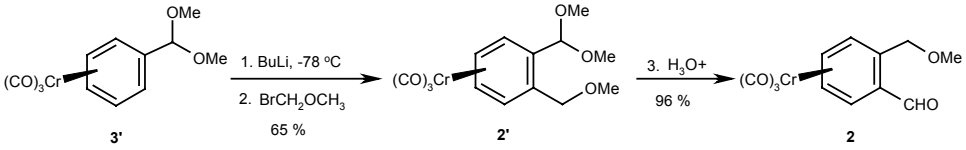


Fig 1. Delocalization in *o*-anisaldehyde complex

The failure of *o*-OMe-acetophenone-$Cr(CO)_3$ complex to act as bidentate ligand to Lewis acidic metal ions and thus induce stereodivergence in nucleophilic addition is consistent with the above result.[57]

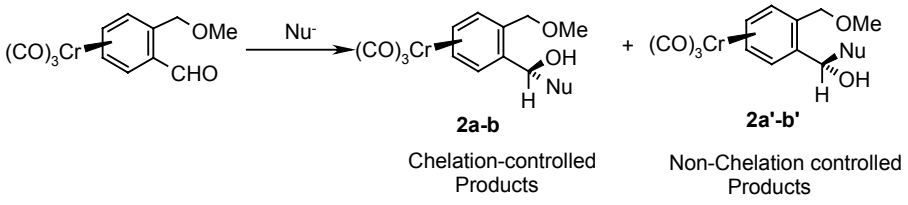
We envisioned that the insertion of an extra carbon between the aromatic ring and the alkoxy group would prevent the non-bonding electrons on oxygen from delocalizing to the arene ring and should restore the Lewis basicity of the oxygen. If chelation can thus be enforced, one can perform nucleophilic addition in a stereodivergent manner in presence or absence of a Lewis acidic metal cation.[52]

To this end, *ortho* formyl complex **2** was thought to be the most appropriate substrate to test our hypothesis. This was prepared from **3'** by lithiation,[48] followed by treatment with bromomethyl methyl ether and acid hydrolysis of acetal **2'** to aldehyde (Scheme-21).



Scheme 21. Preparation of complex **2**

Complex **2'** was a greenish yellow oily liquid showing characteristic methylene doublets at δ 4.24 and 4.84 ppm with a *gem* coupling of 13 Hz in the ^{1}H NMR spectrum. The OCH_3 signals of acetal appeared at δ 3.50 and 3.58 ppm, while OCH_3 signal of CH_2OCH_3 appeared at δ 3.24 ppm. Complex **2** also was an oily red liquid in which acetal OCH_3 signals have disappeared and a characteristic singlet of the aldehydic proton appeared at δ 9.67 ppm. The IR spectrum of **2** showed absorption at 1691 cm^{-1}corresponding to the carbonyl function.



Scheme 22. Nucleophilic addition on complex **2**

Addition of MeLi to substrate **2** in ether at –90 °C gave a diastereomeric mixture of **2a** and **2a'** in the ratio of 1:1.4 in an overall isolated yield of 91 %. The two diastereomers could be easily separated by flash column chromatography. Chelation-Controlled addition of MeLi to substrate **2**, pretreated with $MgBr_2.Et_2O$, however, gave only **2a** as a single diastereomer in 95 % isolated yield (entries 1 and 2 of Table-2).

The proton NMR of **2a** and **2a'** spectra were distinctly different and the diastereomers could be easily recognized. The most striking feature was chemical shift difference between the diastereotopic Ar-CH_2-O protons. For **2a** these appeared at δ 3.87 and 4.76 ppm, whereas for **2a'** these appeared at δ 3.98 and 4.41 ppm, the difference in the former being 0.89 ppm and the later 0.43 ppm. The pattern of proton splitting on the complexed aromatic ring was also different. The O*H* signal appeared at δ 3.80 ppm for **2a** whereas it appeared at δ 1.95 ppm for **2a'**.

The product stereochemistry in 'chelation-controlled' addition could be explained by invoking a model similar to Cram-chelate model. While chelation 'holds' the carbonyl conformation in *syn* orientation, nucleophile attacks the carbonyl carbon from the face *anti* to $Cr(CO)_3$ at a 109 ^{o} trajectory (Fig. 2).[48]

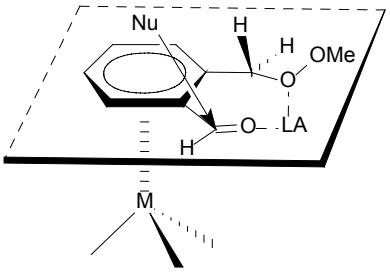


Fig 2. Cram-chelate model

It is important to mention here that this serves as a rare example of a 1,4 or γ-asymmetric stereocontrol reaction where a seven membered chelate controls the configuration of a newly formed stereogenic center.

With success in chelation-controlled addition of MeLi, addition of n-BuLi under same set of conditions was examined. Addition of n-BuLi in ether at –90 ^{o}C resulted in a diastereomeric mixture of **2b** and **2b'** in the ratio of 1:1.6 in an overall isolated yield of 98 %. Chelation-controlled addition, however, was not completely disatereoselective and yielded 8:1 ratio of the above diastereomers (entries 3 and 4 of Table-2). Nevertheless, respectable stereodivergence was

effected and major diastereomers became minor isomers when Lewis acids were present in the reaction medium.

Table-2

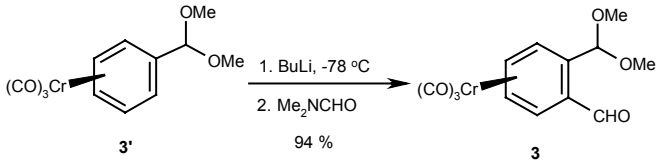
Entry	Aldehyde	Reagent / Solvent	Yield (%)	Product (ratio)
1	**2**	MeLi/ Ether	91	**2a**:**2a'** = 1:1.4
2		$MeLi/MgBr_2.OEt_2/DCM$	95	**2a**
3		n-BuLi/ Ether	98	**2b**:**2b'**= 1:1.6
4		$n\text{-}BuLi/MgBr_2.OEt_2/DCM$	96	**2b**:**2b'** = 8:1

The proton NMR of **2b** and **2b'** showed a similar trend to what was observed in the case of **2a** and **2a'**. The chemical shift difference between diastereotopic Ar-CH_2-O protons was 0.88 ppm for **2b** and 0.39 ppm for **2b'**. Whereas the signals on complexed aromatic ring of **2b** appeared as four proton multiplet, those in **2b'** appeared as two signals of three proton multiplet and a one proton doublet.

Encouraged by the success with our first model substrate, we wished to examine the influence of *ortho* substitution in inducing stereodivergence. It was anticipated that increasing the number of methoxy groups on the *ortho* position would be helpful in both ways: in absence of Lewis acid, greater electronic repulsions would force the carbonyl function to adopt *anti* conformation while in presence of a Lewis acid, bidentate coordination would force the carbonyl function into *syn* conformation.

Complex **3** was easily prepared in 94% isolated yield by lithiation of complex **3'** and quenching it with DMF (Scheme-23). It has one methoxy group more than substrate **2**. Complex **3** is a red crystalline solid showing characteristic NMR signals for OCH_3 groups of acetal at δ 3.29 and 3.60 ppm. The benzylic proton appeared as a singlet at δ 5.77 and the aldehydic proton appeared at δ 9.84

ppm. Carbonyl stretching frequency at 1688 cm^{-1} in IR spectrum corroborated the presence of a –CHO function.



Scheme 23. Preparation of complex **3**

With **3** in hand, MeLi was added both under 'chelation-controlled' and 'non-chelation controlled' conditions (entries 1, 2 and 3 of Table-3). While addition in ether gave diastereomeric mixture of carbinols **3a** and **3a'** in the ratio of 1:1.2 in an overall isolated yield of 90%, addition in THF gave a better ratio of 1:1.6 in excellent yield. Addition in presence of $MgBr_2.Et_2O$ resulted in the reversal of the above stereoselectivity and gave the diastereomers in 11:1 ratio in an overall isolated yield of 91%. It is notable here that the increased number of methoxy groups has indeed enhanced selectivity and accentuated the stereodivergence.

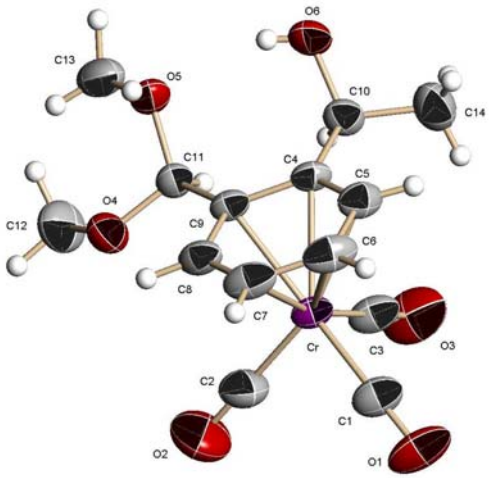
The diastereomers **3a** and **3a'** could be easily separated by flash column chromatography and like in the earlier cases showed distinct proton NMR spectra. Complex **3a** showed a doublet at δ 1.52 with a coupling of 6 Hz; for **3a'** the corresponding signal shifted upfield to δ 1.47 ppm. Singlets corresponding to the benzylic protons appeared at δ 5.5 and 5.30 ppm respectively. Here too, as in the previous cases, the OH signal for non-chelation product **3a'** appear at high field at δ 2.0 ppm as compared to that of **3a**, which appears at δ 3.85 ppm.

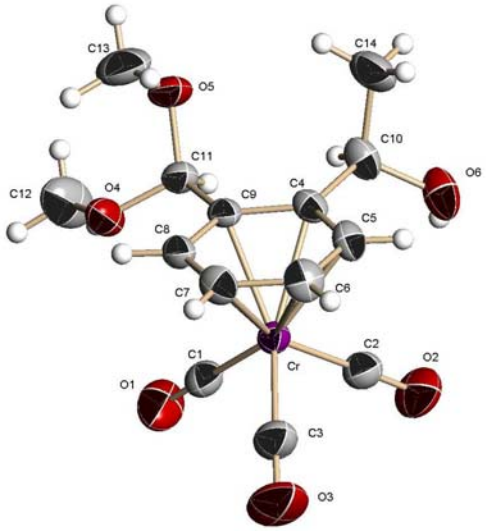
Table-3

Entry	Aldehyde	Reagent / Solvent	Yield (%)	Product (ratio)
1	**3**	MeLi/ Ether	90	**3a**:**3a'**= 1:1.2
2		MeLi/ THF	98	**3a**:**3a'**= 1:1.6
3		MeLi/$MgBr_2$.OEt_2/DCM	91	**3a**:**3a'**= 11:1
4		n-BuLi/ Ether	80	**3b**:**3b'**= 1:1.2
5		n-BuLi/ THF	98	**3b**:**3b'**= 1:4.4
6		n-BuLi/$MgBr_2$.OEt_2/DCM	94	**3b**
7		PhLi/ Ether	92	**3c**:**3c'**= 1:1.3
8		PhLi/ THF	90	**3c**:**3c'**= 1:2.7
9		PhLi/ $MgBr_2$.OEt_2/DCM	77	**3c**

At this stage we wished to unambiguously confirm that the diastereomers obtained as major products in 'chelation-controlled' additions indeed resulted from an *exo* attack of the nucleophile on the *syn* conformer of the aldehyde and that the major products in 'non-chelation controlled' reactions resulted from the *anti* conformer of the aldehyde. Complexes **3a** and **3a'** gave crystals suitable for the X-Ray crystal analysis. Crystal structures vindicated above observations and inferences (Fig 3).

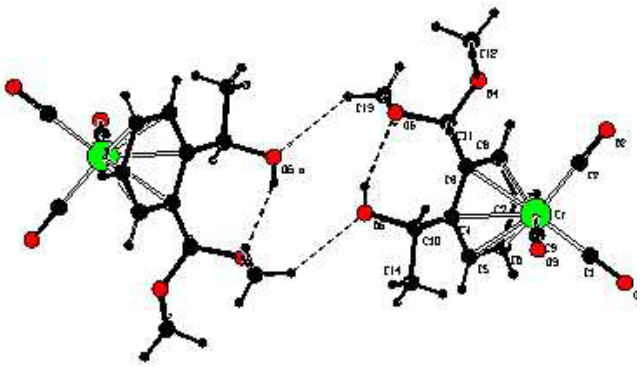
The crystal lattice structures of both the complexes were centrosymmetric and showed interesting features. For complex **3a'**, four molecules are held together by intermolecular O—H—O type hydrogen bond, while for complex **3a** two molecules are held together by two intramolecular O—H—O type hydrogen bonds and two intermolecular C—H—O type interactions[58] (Fig. 4). The average O-H[C] bond distance was 2.5 Å while average O-H(O) distance was 2.1 Å (Fig. 4).

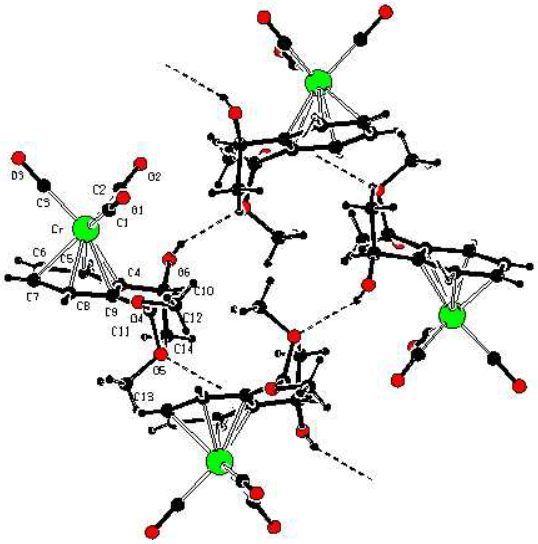




(a) ORTEP diagram of complex **3a** (b) ORTEP diagram of complex **3a'**

Fig 3





(a) C-H-O interaction in complex **3a** (b) C-H-O interaction in complex **3a'**

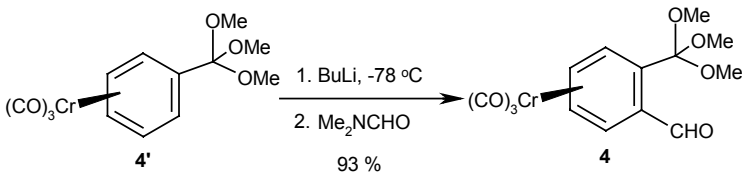
Fig 4

Addition of n-BuLi to substrate **3** also showed similar trends in stereoselectivity. THF as solvent provided 98 % overall yield and a product ratio of 1:4.4 as against 1:1.2 in ether. But chelation-controlled addition of n-BuLi in presence of $MgBr_2.Et_2O$ gave exclusively **3b** (entries 4, 5 and 6 of Table-3). Marked difference of pattern in the signals of protons on complexed aromatic ring was observed in **3b** and **3b'**. The OH signals also appeared in accord with the above trend i.e upfield for **3b'** at δ 1.91 ppm and downfield for **3b** at δ 3.72.

Addition of PhLi gave same product ratio and isolated yields irrespective of whether ether or THF was used as solvent for the non-chelation controlled protocol. In presence of $MgBr_2.Et_2O$, the addition was highly stereoselective (entries 7, 8, and 9 of Table-3). Here too, complexed arene ring protons showed distinctly different patterns in ^1H NMR. While two triplets at δ 5.14 and 5.45 ppm were observed for **3c** and two doublets at δ 5.62 and 5.87, complex multiplets were observed for **3c'**. Signals of OH protons also appeared in line with the above trend.

A close look at the results in Table-2 and Table-3 clearly demonstrates that, though the selectivity remained moderate in the absence of Lewis acid, it was very high in its presence. As a step further in this direction, we designed substrate **4** has three methoxy groups on the benzylic position *ortho* to the aldehyde group.

Complex **4'** was prepared in 91 % yield by refluxing of trimethyl orthobenzoate and hexacarbonylchromium for 20 hours in Bu_2O-THF mixture at 140 ^oC under inert atmosphere. The proton NMR showed aromatic signals as two triplets and a doublet. Characteristic nine-proton singlet was seen at 3.40 for the three methoxy groups on the benzylic position. *Ortho* lithiation of **4'** with n-BuLi in THF at –78 ^oC followed by DMF quench afforded substrate **4** as a crystalline red solid in 93 % yield (Scheme-24).



Scheme 24. Preparation of complex **4**

The ^{1}H NMR spectrum of complex **4** showed characteristic aldehyde signal at δ 10.3 ppm and a nine-proton singlet for three methoxy groups at δ 3.40 ppm. Aromatic protons appeared as two doublets at δ 5.67 and 5.87 ppm and a one-proton multiplet at δ 5.48 ppm. Carbonyl stretching absorption was observed at 1676 cm^{-1} in the IR spectrum.

Whereas addition of MeLi to **4** in ether gave a high selectivity ratio of 1:18 in favor of the non-chelation product **4a'**, a 'chelation-controlled' addition in presence of $MgBr_2.Et_2O$ gave **4a** exclusively in 91% isolated yield. Addition of n-BuLi was found to be highly stereodivergent: in absence of Lewis acid, **4b'** was exclusively obtained while in the of Lewis acid, **4b** is the only product (entries 1, 2, 3, and 4 of Table-4).

The proton NMR spectra in this series too have shown exactly the same trends as those of previous ones. The most striking feature in the entire set of compounds is the consistency in the chemical shift trend of OH signal, which normally is rather unpredictable. There was also a comparable pattern in the other signals in ^{1}H NMR spectra of the major products within the same series (**2a, 2b, 3a-3c** and **4a-4c vis-à-vis 2a', 2b', 3a'-3c'** and **4a'-4c'**).

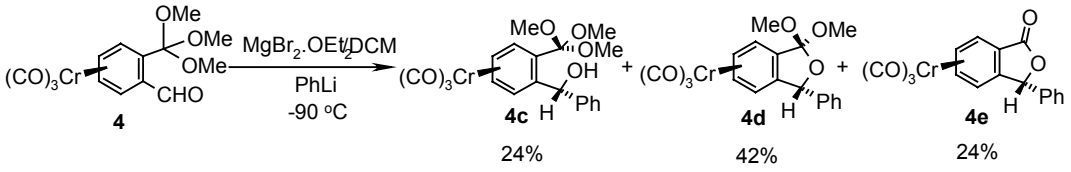
Table-4

Entry	Aldehyde	Reagent / Solvent	Yield (%)	Product (ratio)
1	**4**	MeLi/ Ether	94	**4a**:**4a'**= 1:18
2		MeLi/$MgBr_2.OEt_2$/DCM	91	**4a**
3		n-BuLi/ Ether	86	**4b'**
4		n-BuLi/$MgBr_2.OEt_2$/DCM	95	**4b**
5		PhLi/ Ether	96	**4c'**
6		PhLi/ $MgBr_2.OEt_2$/DCM	93[a]	**4c**:**4c'**= 7.2:1

a: 2 equiv. of $MgBr_2.OEt_2$ was used instead of 4 equiv. to avoid side reactions

Addition of PhLi in ether gave exclusively **4c'** in 96 % yield. The reaction between complex **4** and PhLi in the presence of four equivalents of $MgBr_2.OEt_2$, however, gave a mixture of three products. The proton NMR of the major product, **4d,** showed two singlets of three protons each instead of a nine proton singlet for the three methoxy groups on the benzylic position. Also, the OH signal was absent. One of the minor products, **4e**, did not show any methoxy signals and showed a strong carbonyl stretching frequency at 1753 cm^{-1} that could correspond to a cyclic lactone. The proton spectra of other minor product **4c** had the expected signals of the carbinol, a nine-proton singlet at δ 3.51 ppm, alcoholic proton signal at δ 4.62 ppm (As against δ 2.53 ppm for **4c'**). Interestingly, one of the complexed aromatic protons appeared to have been considerably shielded by the phenyl ring. This signal appeared at δ 4.49 ppm.

Based on the products obtained we presumed that the reaction went beyond the first step of nucleophilic addition. In the presence of excess of $MgBr_2.OEt_2$, the methoxy groups must have coordinated with the Lewis acid and intramolecular nucleophilic attack by the newly formed alkoxide *in situ* has resulted in a facile expulsion of the methoxy group *anti* to the $Cr(CO)_3$ moiety (Fig. 5).[59] This would result in an ortho ester **4d**, the hydrolysis of which during aqueous work up could furnish the lactone **4e** (Scheme-25).



Scheme 25. Addition of PhLi to complex **4**

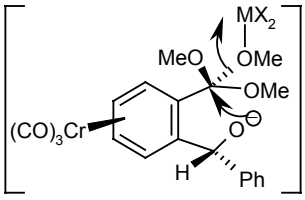
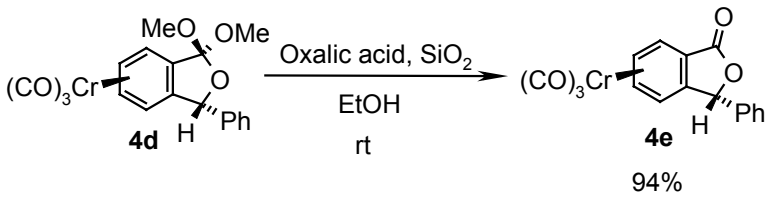


Fig. 5 Formation of the ortho ester

Though no signal corresponding to the carbinol **4c'** was detected in the proton NMR of the above reaction mixture, it was necessary to affirm that the addition of PhLi was indeed 100 % disatereoselective. Fortuitously, complex **4e** gave crystals suitable for X-Ray analysis and the crystal structure revealed that the nucleophilic attack took place indeed in a 'chelation-controlled' fashion (Fig. 6).

Fig. 6 ORTEP diagram of complex **4e**

Facile conversion of **4d** to **4e** by mild hydrolysis using silica gel, oxalic acid and ethanol, unambiguously proved that **4e** resulted from **4d** and that the sense of stereochemistry is same in both the compounds (Scheme-26).



Scheme 26. Hydrolysis of ortho ester **4d** to lactone **4e**

Using only 2 equivalents of the $MgBr_2.OEt_2$ circumvented formation of byproducts in the addition of PhLi to substrate **4** in 'chelation-controlled' fashion. The reaction however proceeded with lower diastereoselectivity and formation of non-chelation product **4c** was also observed (entry 6 of Table-4).

From the above results we could infer that selectivity improved on going from substrates **2** to **4** – as the number of methoxy group on adjacent carbon increased. Tendency for chelation seemed to peak when a *gem*-disubstitution was present.

Also, substrate **4** addressed the entropy factor–one out of three methoxy groups was always available for coordination irrespective of conformation of Ar-$C(OMe)_3$ moiety. This point was reflected in the results where exclusive products could be obtained only in the case of substrate **4** (with an exception of one or two entries in Tables 2 and 3).

When optically pure substrates were used, optically active products could be obtained.

There are reports where aryl aldehyde complexes were resolved by the chromatographic separation of imines prepared from L-valinol[54] or of diastereomeric aminals.[60] Three groups have employed successful enzymatic[61a-d] or nonenzymatic[61e] kinetic resolution for preparation of enantiomerically enriched complexes. In some cases, highly diastereoselective complexation of enantiomerically pure substrates was successful.[60,62] HPLC on chiral supports also is useful in the separation of racemic mixtures of these compounds.[63] However, enantioselective *ortho*-metallation[64] and subsequent quench with an electrophile

remains one of the most efficient methods for the generation of chiral tricarbonylchromium complexes.[65]

As a representative set, complex **2** was resolved following Solladie-Cavallo's method by the chromatographic separation of its diastereomeric semioxamazones prepared with (S)-(-)-5-(α-phenylethyl)semioxamazide.[66] Addition of n-BuLi to the resolved aldehyde furnished optically pure products **2b** and **2b'** whose CD spectra (displayed in Chart-5) are useful as additional means of characterization of analogous diastereomers.

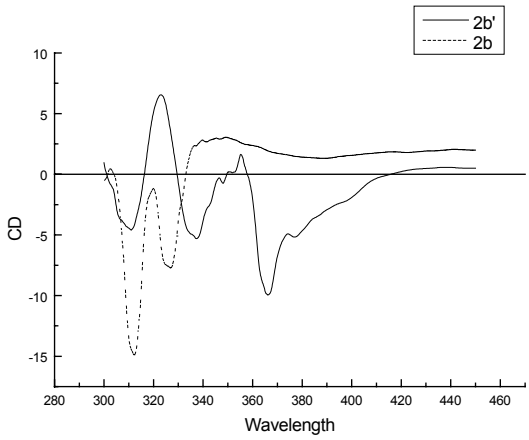


Chart 5. CD spectral pattern of **2b** and **2b'**

Our initial efforts to use $TiCl_4$ as a bidentate chelating Lewis acid proved deleterious to the complexes- especially the acetals, -and major decomposition of the substrates was observed. Choice of $MgBr_2.OEt_2$ as a mild chelating Lewis acid was in fact an outcome of the search for a better alternative. Having succeeded in inducing the desired stereodivergence in chelation-controlled nucleophilic additions, we looked at the possibilities of using other bidentate Lewis acids for this purpose.

Although use of $ZnCl_2.OEt_2$ as Lewis acid resulted in a chelation controlled addition, the yields and the diatereomeric excess of products were less compared to those of $MgBr_2.OEt_2$ (Table-5). A solution of $ZnCl_2.OEt_2$ *ca* 1.4M was prepared by dissolving fused $ZnCl_2$ first in minimum amount of dry DCM and making up the solution with dry ether according to the reported procedure.[67]

Table-5

Entry	Aldehyde	Reagent /Solvent	Yield (%)	Product (ratio)
1	**2**	MeLi/ $ZnCl_2.OEt_2$ /DCM	83	**2a**:**2a'** = 3.5:1
2	**3**	MeLi/ $ZnCl_2.OEt_2$ /DCM	88	**3a**:**3a'** = 5.5:1
3	**4**	MeLi/ $ZnCl_2.OEt_2$ /DCM	84	**4a**:**4a'** = 1:3.6

Surprisingly, addition of MeLi to **4** in presence of $ZnCl_2.OEt_2$ reversed the diastereoselectivity giving major diastereomer from *exo*-addition to *anti*-conformer (entry 3 of Table-5). Such reversal of diastereoselectivity though is not clearly understood, may be attributed to the preferred orientation **B** over **A** due to steric reasons (Fig. 7).

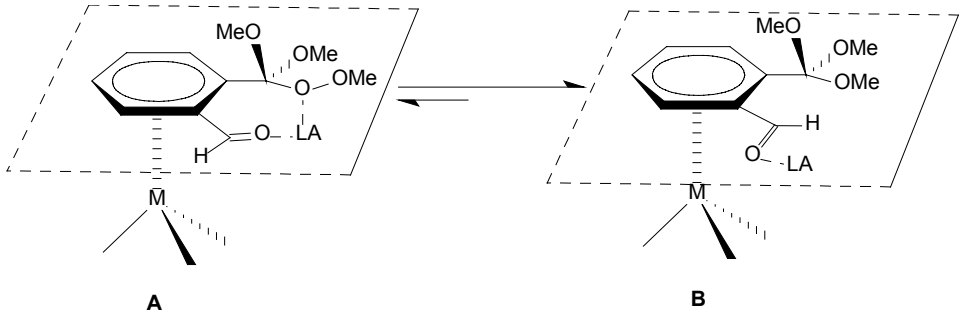


Fig 7. Preferred conformations of Lewis acid chelated **4**

The results reaffirm that Zn^{2+} too has a tendency for bidentate chelation like that of Mg^{2+} and Ti^{4+}.

There have been several reports of rare earth triflates being used as Lewis acids in nucleophilic addition and cycloaddition reactions.[68] However, there are no precedents for their use as bidentate chelating Lewis acids that define stereochemical outcome of nucleophilic additions to carbonyls. Encouraged by the success of $MgBr_2.OEt_2$ as a mild chelating Lewis acid, we investigated the use of scandium triflate for this purpose.

The procedure described for the 'chelation-controlled' additions in the above cases needed a minor modification in these reactions. Solid $Sc(OTf)_3$ was added to the aldehyde substrate in DCM at room temperature instead of low temperature in view of its poor solubility. After stirring for half an hour at room temperature, by which time, the color of the reaction mixture turned dark purple from red indicating the Lewis acid activation of the carbonyl, the reaction was cooled to –90 ^oC. Alkyllithiums were added at the same temperature.

Table-6

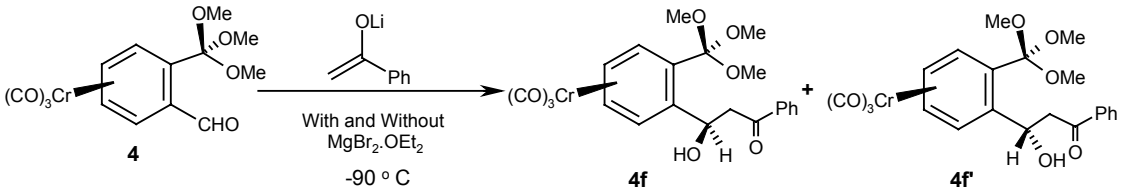
Entry	Aldehyde	Reagent /Solvent	Yield (%)	Product (ratio)
1	**3**	MeLi/ $Sc(OTf)_3$ /DCM	92	**3a**:**3a'** = 2.6:1
2		n-BuLi/ $Sc(OTf)_3$ /DCM	96	**3b**:**3b'** = 6:1
3		PhLi/ $Sc(OTf)_3$ /DCM	89	**3c**:**3c'** = 6.5:1

The reaction was studied on aldehyde **3,** whose electronic and steric attributes are intermediate between substrates **2** and **4**. Addition of MeLi to aldehyde **3** in the presence of $Sc(OTf)_3$ gave a diastereomeric mixture of products in which chelation-controlled product **3a** was obtained as a major isomer (entry 1, Table-6). However, the diastereomeric excess was lower than that obtained with either $MgBr_2.OEt_2$ (entry 3, Table-3) or $ZnCl_2.OEt_2$ (entry 2, Table-5). Addition of n-BuLi and PhLi were less stereoselective compared to the reaction when $MgBr_2.OEt_2$ was used as Lewis acid (entries 2 and 3 of Table-6 as compared to

entries 6 and 9 of Table-3). While the yield in n-BuLi addition was comparable, there was an improvement in the yield of PhLi reaction.

Having developed a reliable protocol to bring about stereodivergence in the addition of nucleophiles to benzaldehyde complexes, our interest in Lewis acid catalyzed aldol reactions[69] has prompted us to perform a chelation-controlled addition of a lithium enolate to the aldehyde substrate **4.** This was thought to be an immediate and a logical extension of the above results. However, to our disappointment addition of lithium enolate of acetophenone generated by LDA at 0 ^{o}C did not result in the expected stereoselectivity (Table-7).

Whereas addition in ether without any added Lewis acid gave the products **4f** and **4f'** in the ratio of 1:1.6, addition to substrate pretreated with $MgBr_2.OEt_2$ resulted in poor diastereoselectivity (ratio 1:2) and no stereodivergence could be detected (Scheme-27). The stereochemistry of **4f** and **4f'** was assigned based on the correlation of the proton spectra of a closely related compound reported by Brocard *et al.*[43a]



Scheme 27. Li Enolate addition to substrate **4**

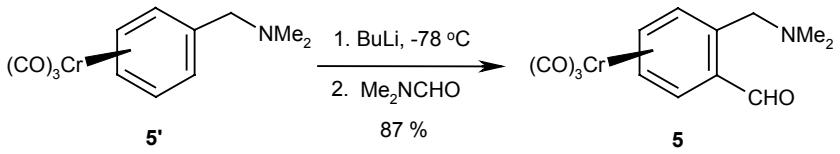
Table-7

Entry	Aldehyde	Reagent /Solvent	Yield (%)	Product (ratio)
1	**4**	H_2C=C(OLi)Ph/Ether	90	**4f**:**4f'** = 1:1.6
2		H_2C=C(OLi)Ph/$MgBr_2.OEt_2$/DCM	93	**4f**:**4f'** = 1:2

Transition state (TS) for the addition of alkyllithiums might involve a tight four-membered arrangement of the atoms, but enolates being larger and softer nucleophiles, they are known to add through the Zimmerman-Traxler type six membered cylic transition states. Steric requirements of such a TS may strongly counter chelation effect.

Since chelation is facilitated by the presence of a proximal donor hetero atom like nitrogen and since an $-NMe_2$ group is known to be a good chelating agent, we anticipated that replacing the methoxy group in aldehyde substrate **3** by an NMe_2 group would still facilitate chelation controlled additions on the aldehyde functionality eventually resulting in chiral amino alcohols.

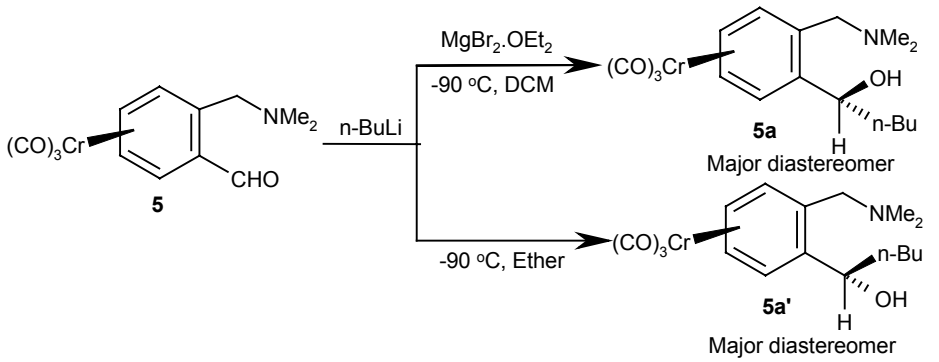
To this end, substrate **5** was easily prepared by *ortho* lithiation of N,N-Dimethylbenzyl amine tricarbonylchromium complex **5'** and quenching it with DMF. Complex **5'** was obtained by direct complexation of N,N-Dimethylbenzyl amine with hexacarbonylchromium(0) in refluxing dibutyl ether (Scheme-28). The complex **5** was a red solid that showed characteristic NMR signal of aldehydic proton at δ 9.84 ppm, diastereotopic benzylic protons appeared as two doublets at δ 2.93 and 4.07 ppm with a *gem* coupling of 13 Hz. The six NMe_2 protons appeared as a singlet at δ 2.29 ppm.



5' **5**

Scheme 28. Preparation of Complex **5**

Addition of n-BuLi to **5** in ether gave the diastereomeric amino alcohols **5a** and **5a'** in the ratio of 1: 4.6 (Scheme-29) whereas chelation-controlled addition in the presence of $MgBr_2.OEt_2$ resulted in a reversal of stereoselectivity giving **5a** as a major product (Table-8).



Scheme 29. Preparation of diastereomeric amino alcohols

Table-8

Entry	Aldehyde	Reagent / Solvent	Yield (%)	Product (ratio)
1	**5**	MeLi/ Ether	96	**5a**:**5a'** = 1:6.2
2		$MeLi/MgBr_2.OEt_2/DCM$	90	**5a**:**5a'** = 4:1
3		n-BuLi/ Ether	85	**5b**:**5b'**= 1:4.6
4		$n\text{-}BuLi/MgBr_2.OEt_2/DCM$	95	**5b**:**5b'**= 3.5:1

Summary

The experiments described in this part of the thesis presented the first definitive example of diastereoselective nucleophilic addition under chelation-control on arene-chromium complexes, and demonstrated its use in devising stereodivergent routes to products with predictable stereochemistry. Various factors that govern such disatereoselective additions like nature of solvent, mode of chelation of the Lewis acids, their chelating ability, steric and electronic factors were systematically studied. The 'chelation-control' protocol was successfully employed to synthesize amino alcohols based on arene tricarbonylchromium complexes. Presumably, these findings should be equally applicable for any planar chiral moiety and find their utility in the preparation of novel chiral bidentate ligands for asymmetric catalysis.

Experimental

All reactions were performed under an inert atmosphere of argon, using freshly distilled, degassed solvents. Diethyl ether and THF were freshly distilled over sodium benzophenone ketyl. Dichloromethane was stirred over calcium hydride for twelve hours and freshly distilled over P_2O_5. DMF was freshly distilled over calcium hydride. Scandium oxide was purchased from Strem Chemicals, Germany. Scandium triflate, $ZnCl_2.OEt_2$ and organolithium reagents were prepared following reported procedures.[67] $MgBr_2.OEt_2$ was purchased from Aldrich, USA, and used as received. Metal complexes were crystallized from dichloromethane-hexane/ dichloromethane-petroleum ether. Complexes **1**, **1a** and **1a'** are reported in ref. 54.

General Procedure for the ortho-lithiation of Tricarbonyl(η^6–arene)chromium(0) Complexes.

A solution of n-BuLi (1.6 M) was added dropwise to a cooled (-78 ^oC) THF solution of the complex and the mixture stirred (-78 ^oC, 2 h). The electrophile was added and stirring continued (-78 ^oC, 2 h), after completion (TLC) the reaction was quenched slowly by dropwise addition of saturated ammonium chloride solution and allowed to warm to room temperature (20 ^oC). The reaction mixture was extracted with ether (3 x 10 ml), dried over Na_2SO_4 and solvent was evaporated under reduced pressure to give a residue containing the crude product.

Preparation of Complex 2':

Complex **3'**[48] (2.0 g, 6.94 mmol) in THF (40 ml) was treated with n-BuLi (1.66 M, 4.6 ml, 7.63 mmol) and bromomethyl methyl ether (1.3 g, 10.4 mmol) under standard conditions. Work-up and purification by flash column chromatography using 5 % acetone and petroleum ether as eluent resulted in **2'** (1.5 g, 65 %).

Complex 2'

State	:	Yellow oil
IR ($CHCl_3$)	:	3094, 2935, 1963 and 1884 cm^{-1}
^1H NMR	:	(δ, $CDCl_3$)
(200 MHz)		3.24 (3 H, s, CH_2OCH_3), 3.50 (3 H, s, OCH_3), 3.58 (3 H, s, OCH_3), 4.24 (1 H, d, *J* 13, CH_2), 4.84 (1 H, d, *J* 13, CH_2), 5.24 (1 H, s, $CH(OMe)_2$), 5.31 (1 H, d, *J* 6, Ar*H*), 5.41 (1 H, t, *J* 6, Ar*H*), 5.54 (1 H, t, *J* 6, Ar*H*) and 5.78 (1 H, d, *J* 6, Ar*H*).
^{13}C NMR	:	(δ, $CDCl_3$)
(50.3 MHz)		50.9, 56.4, 59.1, 69.5, 90.4, 91.1, 91.2, 91.5, 92.7, 99.7, 104.1, 107.3, 159.6 and 232.5.
Analysis:	:	Calculated. : C, 50.61; H, 4.85
		Observed: C, 50.98; H, 4.62 %

Preparation of Complex 2:

Acetal complex **2'** (1.5 g, 4.52 mmol) dissolved in ethanol (15 ml) was hydrolyzed under mild conditions[70] by the addition of activated silica gel (5 g) and dropwise addition of saturated solution of oxalic acid at room temperature. Stirring for 20 minutes changed the color of the reaction mixture from yellow to deep red. Upon complete conversion (TLC) the reaction mixture was filtered and extracted with ether (3 x 5 ml). The combined organic fractions were dried over Na_2SO_4. Purification by flash column chromatography using 10 % acetone and petroleum ether as eluent resulted in **2** (1.2 g, 96 %).

Complex 2

State	:	Red oil
IR ($CHCl_3$)	:	3020, 1985, 1919, 1691cm^{-1}

^{1}H NMR	:	(δ, $CDCl_3$)
(200 MHz)		3.51 (3 H, s, OC*H*$_3$), 4.47 (1 H, d, *J* 13, *CH*$_2$), 4.84 (1 H, d, *J* 13, *CH*$_2$), 5.28 (1 H, dd, *J* 7 and 9, Ar*H*), 5.45 (1 H, d, *J* 7, Ar*H*), 5.76 (1 H, dd, *J* 6 and 5, Ar*H*), 6.0 (1 H, d, *J* 6, Ar*H*) and 9.66 (1 H, s, C*H*O).
^{13}C NMR	:	(δ, $CDCl_3$)
(50.3 MHz)		58.9, 70.0, 88.4, 88.9, 92.7, 95.0, 95.5, 111.0, 188.0 and 230.1.
Analysis:	:	Calculated. : 50.36; H, 3.52
		Observed: 50.20; H, 3.14 %

Preparation of Complex 3:

Complex **3'**[48] (2.5 g, 8.68 mmol) in THF (50 ml) was treated with n-BuLi (1.66 M, 6 ml, 9.98 mmol) and *N,N*-Dimethylformamide (0.95 g, 13.02 mmol) under standard conditions. Usual work-up and purification by flash column chromatography using 5 % acetone and petroleum ether as eluent resulted in **3** (2.57 g, 94 %).

Complex 3

State	:	Red solid
Mp	:	72 °C
IR ($CHCl_3$)	:	3020, 1988, 1923, 1688 cm^{-1}
^{1}H NMR	:	(δ, $CDCl_3$)
(200 MHz)		3.29 (3 H, s, OC*H*$_3$), 3.60 (3 H, s, OC*H*$_3$), 5.32 (1 H, t, *J* 6, Ar*H*), 5.61 (1 H, d, *J* 6, Ar*H*), 5.72 (1 H, d, *J* 6, Ar*H*), 5.77 (1 H, s, C*H* $(OCH_3)_2$), 6.04 (1 H, d, *J* 7, Ar*H*) and 9.84 (1 H, s, C*H*O).
^{13}C NMR	:	(δ, $CDCl_3$)
(50.3 MHz)		51.2, 56.3, 87.9, 89.1, 93.1, 93.4, 94.1, 99.3, 110.2,

		121.7, 187.1 and 230.1.
Analysis:	:	Calculated: C, 49.38; H, 3.83
		Observed: C, 49.91; H, 4.06 %

Preparation of Complex 4':

A deoxygenated mixture of Bu_2O-THF (10:1, 100 ml), trimethyl orthobenzoate (5 g, 27.4 mmol), and hexacarbonylchromium(0) (3 g, 13.6 mmol) was heated to reflux for about 20 hours until the first trace of green precipitate was observed. The cooled solution was then filtered through Celite and the solvent evaporated to give the crude complex. Purification by flash column chromatography using 5 % acetone and petroleum ether as eluent resulted in **4'** (3.5 g, 91 %, based on the recovered arene).

Complex 4'

State	:	Yellow solid
Mp	:	86-87 °C
IR ($CHCl_3$)	:	1973, 1894, 1892 cm^{-1}
^1H NMR	:	(δ, $CDCl_3$)
(200 MHz)		3.36 (9 H, s, 3xOC*H*$_3$), 5.21 (2 H, t, *J* 6, Ar*H*), 5.47 (1 H, t, *J* 6, Ar*H*) and 5.70 (2 H, d, *J* 6, Ar*H*)
^{13}C NMR	:	(δ, $CDCl_3$)
(50.3 MHz)		50.8, 89.0, 93.1, 94.3, 105.0, 112.5, 159.7 and 232.3.
Analysis:	:	Calculated. : 49.06; H, 4.43
		Observed: C, 48.99; H, 4.26 %

Preparation of Complex 4:

Complex **4'** (2.5 g, 7.86 mmol) in THF (60 ml) was treated with n-BuLi (1.66 M, 5.7 ml, 9.43 mmol) and *N,N*-Dimethylformamide (0.86 g, 11.79 mmol) under standard conditions. Usual work-up and purification by flash column chromatography using 5 % acetone and petroleum ether as eluent resulted in **4** (2.53 g, 93 %).

Complex 4

State	:	Red solid
Mp	:	78 °C
IR ($CHCl_3$)	:	1987, 1965, 1920, 1676 cm^{-1}
^1H NMR (200 MHz)	:	(δ, $CDCl_3$) 3.40 (9 H, s, 3xOC*H*$_3$), 5.44-5.54 (2 H, m, Ar*H*), 5.67 (1 H, d, *J* 6, Ar*H*), 5.87 (1 H, d, *J* 6, Ar*H*) and 10.30 (1 H, s, C*H*O)
^{13}C NMR (50.3 MHz)	:	(δ, $CDCl_3$) 51.0, 89.6, 90.7, 91.4, 92.1, 96.0, 108.6, 112.7, 191.2 and 230.7.
Analysis:	:	Calculated: C, 48.56; H, 4.08 Observed: C, 48.72; H, 3.78 %

General Procedure for the Chelation-Controlled nucleophilic additions to aldehyde Complexes 2-4:

To a solution of aldehyde (n mmol) in dichloromethane (10n ml) cooled to –78 ^{o}C Lewis acid (4n mmol) was added and the mixture was stirred for 30 minutes during which color of the reaction mixture turned to dark purple. The reaction mixture was further cooled to –90^{o} C (Methanol slush bath) and dropwise addition of alkyllithium (1.5n mmol) instantly resulted in a color change to yellow. After the reaction was complete (15-20 mnts, TLC) it was quenched slowly by dropwise addition of saturated ammonium chloride solution and warmed to room temperature. Crude product resulting after usual work-up was purified by flash column chromatography. The products were crystallized from dichloromethane and petroleum ether.

$MgBr_2.OEt_2$ and $Sc(OTf)_3$ were added as solids. Freshly prepared $ZnCl_2.OEt_2$ was added as a 1.41 M solution in ether. In the case of chelation-

controlled reactions using Scandium triflate, addition of Lewis acid was done at room temperature and stirred for 30 minutes. Addition of nucleophile and work up procedures are same as described above.

Complex 2a

State	:	Yellow solid
Mp	:	55 °C
IR ($CHCl_3$)	:	3383, 1969, 1892 cm^{-1}
^1H NMR (200 MHz)	:	(δ, $CDCl_3$) 1.52 (3 H, d, *J* 6, C*H*$_3$), 3.50 (3 H, s, OC*H*$_3$), 3.80 (1 H, d, *J* 2, O*H*), 3.87 (1 H, d, *J* 11, C*H*$_2$), 4.76 (1 H, d, *J* 11, C*H*$_2$), 4.85 (1 H, doublet of quartet, *J* 2 and 6, CH_3C*H*OH), 5.33-5.40 (2 H, m, Ar*H*) and 5.41-5.49 (2 H, m, Ar*H*).
^{13}C NMR (50.3 MHz)	:	(δ, $CDCl_3$) 19.0, 58.7, 65.3, 72.6, 90.1, 91.9, 94.5, 104.5, 113.5 and 232.0.
Analysis:	:	Calculated: C, 51.66; H, 4.67 Observed: C, 51.27; H, 4.36 %

Complex 2b

State	:	Yellow solid
Mp	:	55 °C
IR ($CHCl_3$)	:	3420, 1970, 1969, 1870 cm^{-1}
^1H NMR (300 MHz)	:	(δ, $CDCl_3$) 0.97 (3 H, t, *J* 7, C*H*$_3$), 1.41-1.83 (6 H, m, (C*H*$_2$)$_3$), 3.5 (3 H, s, OC*H*$_3$), 3.61 (1 H, s, O*H*), 3.89 (1 H, d, *J* 12, C*H*$_2$), 4.54 (1 H, d, *J* 9, n-BuC*H*OH), 4.77 (1 H, d, *J* 12, C*H*$_2$) and 5.32-5.47 (4 H, m, Ar*H*).

^{13}C NMR	:	(δ, $CDCl_3$)
(50.3 MHz)		13.9, 22.5, 28.7, 29.6, 33.3, 58.7, 69.7, 72.3, 91.0, 91.9, 94.3, 104.6, 113.7, 159.6 and 232.2.
Analysis:	:	Calculated: C, 55.81; H, 5.86
		Observed: C, 55.50; H, 5.89 %

Complex 3a

State	:	Yellow solid
Mp	:	101 °C
IR ($CHCl_3$)	:	3406, 1960, 1886, 1461 cm^{-1}
^{1}H NMR	:	(δ, $CDCl_3$)
(300 MHz)		1.52 (3 H, d, *J* 6, C*H*$_3$), 3.32 (3 H, s, OC*H*$_3$), 3.61 (3 H, s, OC*H*$_3$), 3.85 (1 H, s, O*H*), 4.86 (1 H, q, *J* 6, C*H*(CH_3)OH), 5.38 (1 H, d, *J* 3, Ar*H*), 5.41 (1 H, d, *J* 3, Ar*H*), 5.46 (1 H, t, *J* 3, Ar*H*), 5.5 (1 H, s, C*H*($OMe)_2$) and 5.72 (1 H, t, *J* 3, Ar*H*).
^{13}C NMR	:	(δ, $CDCl_3$)
(50.3 MHz)		19.1, 50.9, 57.2, 64.5, 89.5, 90.8, 91.2, 92.4, 100.1, 105.1, 111.4 and 232.1.
Analysis:	:	Calculated: 50.61; H, 4.85
		Observed: C, 50.84; H, 5.17 %

Complex 3b

State	:	Orange yellow solid
Mp	:	64-65 °C
IR ($CHCl_3$)	:	3475, 1973, 1886 cm^{-1}
^{1}H NMR	:	(δ, $CDCl_3$)
(300 MHz)		0.97 (3 H, t, *J* 6, C*H*$_3$), 1.38-1.89 (6 H, m, ($CH_2)_3$), 3.32

(3 H, s, OCH_3), 3.61 (3 H, s, OCH_3), 3.72 (1 H, d, *J* 3, O*H*), 4.51-4.58 (1 H, m, C*H*(n-Bu)OH), 5.36-5.41 (3H, m, Ar*H*), 5.54 (1 H, s, C*H*$(OMe)_2$) and 5.68-5.77 (1 H, m, Ar*H*).

^{13}C NMR (50.3 MHz) : (δ, $CDCl_3$)
14.0, 22.5, 28.9, 33.2, 50.8, 57.3, 68.8, 90.3, 90.9, 91.2, 92.6, 99.9, 104.9, 111.9, 121.8 and 232.2.

Analysis: : Calculated: C, 50.54; H, 5.92
Observed: C, 54.21; H, 5.90 %

Complex 3c

State : Yellow solid

Mp : 98 °C

IR ($CHCl_3$) : 3489, 1965, 1886, 1861 cm^{-1}

^{1}H NMR (300 MHz) : (δ, $CDCl_3$)
3.41 (3 H, s, OCH_3), 3.68 (3 H, s, OCH_3), 4.51 (1 H, d, , *J* 2, O*H*), 4.71 (1 H, d, *J* 6, Ar*H*), 5.14 (1 H, t, *J* 6, Ar*H*), 5.45 (1 H, t, *J* 6, Ar*H*), 5.62 (1 H, d, *J* 6, Ar*H*), 5.73 (1 H, s, C*H*$(OMe)_2$), 5.87 (1 H, d, *J* 2, Ar*H*), 7.34-7.46 (3 H, m, Ph) and 7.58 (2 H, d, *J* 7, Ph).

^{13}C NMR (50.3 MHz) : (δ, $CDCl_3$)
51.3, 57.4, 70.7, 88.8, 91.0, 92.8, 93.4, 100.5, 106.0, 111.5, 127.2, 128.2, 137.9 and 232.0.

Analysis: : Calculated: C, 57.87; H, 4.60
Observed: C, 58.10; H, 4.79 %

Complex 4a

State	:	Yellow solid
Mp	:	103-104 °C
IR ($CHCl_3$)	:	3385, 1961, 1907, 1894 cm^{-1}
^1H NMR	:	(δ, $CDCl_3$)
(300 MHz)		1.45 (3 H, d, *J* 6, C*H*$_3$), 3.40 (9 H, s, 3xOC*H*$_3$), 3.86 (1 H, d, *J* 3, O*H*), 5.24 (1 H, t, *J* 6, Ar*H*), 5.33 (1 H, d, *J* 6, Ar*H*), 5.41 (1 H, doublet of quartet, *J* 3, 6, CH_3C*H*OH), 5.59 (1 H, t, *J* 6, Ar*H*) and 5.76 (1 H, d, *J* 6, Ar*H*).
^{13}C NMR	:	(δ, $CDCl_3$)
(75.48 MHz)		19.4, 50.9, 64.2, 88.1, 94.5, 94.8, 112.9, 113.6 and 232.0.
Analysis:	:	Calculated: C, 49.73; H, 5.0
		Observed: C, 49.93; H, 4.76 %

Complex 4b

State	:	Yellow solid
Mp	:	99-100 °C
IR ($CHCl_3$)	:	3018, 1973, 1902 cm^{-1}
^1H NMR	:	(δ, $CDCl_3$)
(200 MHz)		0.96 (3 H, t, *J* 6, C*H*$_3$), 1.23-1.84 (6 H, m, (C*H*$_2$)$_3$), 3.40 (9 H, s, 3xOC*H*$_3$), 3.72 (1 H, d, *J* 3, O*H*), 5.10-5.18 (1 H, m, C*H*(n-Bu)OH), 5.23 (1 H, t, *J* 6, Ar*H*), 5.32 (1 H, d, *J* 6, Ar*H*), 5.56 (1 H, t, *J* 6, Ar*H*) and 5.75 (1 H, d, *J* 6, Ar*H*).
^{13}C NMR	:	(δ, $CDCl_3$)
(75.48 MHz)		13.8, 22.3, 28.8, 33.6, 50.8, 67.9, 88.3, 89.2, 94.2, 94.5, 102.9, 113.5 and 232.0.
Analysis:	:	Calculated: C, 55.08; H, 5.85

Observed: C, 54.6; H, 5.92 %

Complex 4c

State : Orange yellow solid

Mp : 131-132 °C

IR ($CHCl_3$) : 3474, 3018, 1973, 1900 cm^{-1}

^1H NMR : (δ, $CDCl_3$)

(200 MHz) 3.51 (9 H, s, 3xOC*H*$_3$), 4.49 (1 H, dd, *J* 2, 6, Ar*H*), 4.62 (1 H, d, *J* 2, O*H*), 5.26 (1 H, t, *J* 6, Ar*H*), 5.34 (1 H, t, *J* 6, Ar*H*), 5.58 (1 H, dd, *J* 6, 2 Ar*H*), 6.50 (1 H, d, *J* 2, PhC*H*OH) and 7.31-7.58 (5 H, m, Ph).

^{13}C NMR : (δ, $CDCl_3$)

(75.48 MHz) 51.5, 71.1, 90.2, 92.4, 92.7, 92.8, 103.6, 111.6, 113.9, 127.3, 127.9, 128.1, 138.7 and 231.8.

Analysis: : Calculated: C, 56.61; H, 4.75

Observed: C, 56.71; H, 4.83 %

Complex 4d

State : Yellow solid

Mp : 78 °C

IR ($CHCl_3$) : 1958, 1892, 1871 cm^{-1}

^1H NMR : (δ, $CDCl_3$)

(300 MHz) 3.43 (3 H, s, OC*H*$_3$), 3.61 (3 H, s, OC*H*$_3$), 5.10 (2 H, t, *J* 6, Ar*H*), 5.39 (1 H, t, *J* 6, Ar*H*), 5.84 (1 H, d, *J* 6, Ar*H*), 6.03 (1 H, s, ArC(Ph)*H*O-), 7.38 (5 H, m, Ph).

^{13}C NMR : (δ, $CDCl_3$)

(75.48 MHz) 50.6, 51.6, 83.0, 83.2, 87.6, 88.7, 93.9, 106.3, 114.3, 120.9, 127.2, 128.9, 129.0, 139.3 and 231.6

Analysis:	:	Calculated: C, 58.17; H, 4.11
		Observed: C, 57.66; H, 4.06 %

Preparation of Complex 4e from Complex 4d:

Acetal complex **4d** (0.1g, 0.255 mmol) dissolved in ethanol (5 ml) was hydrolyzed under mild conditions[70] by the addition of activated silica gel (1 g) and dropwise addition of saturated solution of oxalic acid at room temperature. Stirring for 20 minutes changed the color of the reaction mixture from yellow to orange red. Upon complete conversion (TLC) the reaction mixture was filtered and extracted with ether (3 x 5 ml). The combined organic fractions were dried over Na_2SO_4. Purification by flash column chromatography using 10 % acetone and petroleum ether as eluent resulted in **4e** (83 mg, 94 %).

Complex 4e

State	:	Red solid
Mp	:	115 °C
IR ($CHCl_3$)	:	1981, 1915, 1753 cm^{-1}
^1H NMR	:	(δ, $CDCl_3$)
(300 MHz)		5.24 (1 H, t, *J* 6, Ar*H*), 5.37 (1 H, d, *J* 6, Ar*H*), 5.60 (1 H, t, *J* 6, Ar*H*), 6.15 (1 H, d, *J* 6, Ar*H*), 6.25 (1 H, s, ArC(Ph)*H*O-), 7.27-7.44 (5 H, m, Ph).
^{13}C NMR	:	(δ, $CDCl_3$)
(75.48 MHz)		81.8, 83.2, 84.2, 88.5, 89.1, 94.1, 117.2, 126.4, 129.3, 130.0 and 229.1
Analysis:	:	Calculated: C, 57.96; H, 4.58
		Observed: C, 57.70; H, 4.80 %

General Procedure for the Non Chelation-Controlled nucleophilic additions to aldehyde complexes 2-4:

To a solution of aldehyde (n mmol) in ether or THF (10n ml) cooled to –90 ^{o}C alkyllithium (1.5n mmol) was added dropwise. The color of the reaction mixture instantly turned to yellow from dark red. After the reaction was complete (15-20 mnts, TLC) it was quenched slowly by dropwise addition of saturated ammonium chloride solution and warmed to room temperature. Crude product resulting after usual work-up was purified by flash column chromatography. The products were recrystallized from dichloromethane and petroleum ether.

Complex 2a'

State	:	Yellow solid
Mp	:	79 °C
IR ($CHCl_3$)	:	3379, 1974, 1880 cm^{-1}
^{1}H NMR (300 MHz)	:	(δ, $CDCl_3$) 1.50 (3 H, d, *J* 6, C*H*$_3$), 1.95 (1 H, d, *J* 2, O*H*), 3.45 (3 H, s, OC*H*$_3$), 3.98 (1 H, d, *J* 12, C*H*$_2$), 4.41 (1 H, d, *J* 12, C*H*$_2$), 4.82 (1 H, doublet of quartet, *J* 2, 6, C*H*(CH_3)OH), 5.29-5.50 (3 H, m, Ar*H*) and 5.72 (1 H, d, *J* 6, Ar*H*).
^{13}C NMR (75.48 MHz)	:	(δ, $CDCl_3$) 25.2, 58.7, 64.8, 71.0, 89.2, 92.1, 92.4, 93.6, 104.6, 117.5 and 232.7.
Analysis:	:	Calculated: C, 51.66; H, 4.67 Observed: C, 51.44; H, 4.41 %

Complex 2b'

State	:	Yellow solid
Mp	:	57 °C
IR ($CHCl_3$)	:	3414, 1963, 1973, 1874 cm^{-1}
^1H NMR	:	(δ, $CDCl_3$)
(300 MHz)		0.92 (3 H, t, *J* 7, C*H*$_3$), 1.33-1.74 (6 H, m, (C*H*$_2$)$_3$), 1.95 (1 H, s, O*H*), 3.45 (3 H, s, OC*H*$_3$), 3.99 (1 H, d, *J* 11, C*H*$_2$), 4.38 (1 H, d, *J* 11, C*H*$_2$), 4.58-4.65 (1 H ,m, n-BuC*H*OH), 5.36-5.43 (3 H, m, Ar*H*) and 5.69 (1 H, d, *J* 6, Ar*H*).
^{13}C NMR	:	(δ, $CDCl_3$)
(50 MHz)		13.9, 22.3, 28.2, 29.6, 38.9, 58.8, 68.3, 70.9, 89.5, 92.1, 92.4, 93.6, 104.6, 159.7 and 232.8.
Analysis:	:	Calculated: C, 55.81; H, 5.86
		Observed: C, 55.98; H, 5.48 %

Complex 3a'

State	:	Yellow solid
Mp	:	115-116 °C
IR ($CHCl_3$)	:	3461, 1973, 1880 cm^{-1}
^1H NMR	:	(δ, $CDCl_3$)
(200 MHz)		1.47 (3 H, d, *J* 6, C*H*$_3$), 2.0 (1 H, d, *J* 4, O*H*), 3.24 (3 H, s, OC*H*$_3$), 3.57 (3 H, s, OC*H*$_3$), 4.83 (1 H, doublet of quartet, *J* 4 and 6, C*H*(CH_3)OH), 5.30 (1 H, s, C*H*($OMe)_2$), 5.36-5.46 (2 H, m, Ar*H*) and 5.66-5.75 (2 H, m, Ar*H*).
^{13}C NMR	:	(δ, $CDCl_3$)

(50 MHz) 24.9, 50.6, 56.8, 64.3, 89.1, 90.6, 91.6, 93.0, 99.5, 105.1, 117.3 and 232.7.

Analysis: : Calculated: C, 50.77; H, 4.67
Observed: C, 50.61; H, 4.85 %

Complex 3b'

State : Yellow solid

Mp : 86 °C

IR ($CHCl_3$) : 3336, 1969, 1894 cm^{-1}

^1H NMR : (δ, $CDCl_3$)

(300 MHz) 0.92 (3 H, t, *J* 7, C*H*$_3$), 1.26-1.75 (6 H, m, (C*H*$_2$)$_3$), 1.91 (1 H, s, O*H*), 3.24 (3 H, s, OC*H*$_3$), 3.56 (3 H, s, OC*H*$_3$), 4.62 (1 H, d, *J* 9, C*H*(n-Bu)OH), 5.28 (1 H, s, C*H*(OMe)$_2$), 5.36 –5.45 (2H, m, Ar*H*), 5.64 (1 H, d, *J* 6, Ar*H*) and 5.74 (1 H, d, *J* 6, Ar*H*).

^{13}C NMR : (δ, $CDCl_3$)

(50 MHz) 14.0, 22.5, 28.6, 38.7, 50.8, 57.0, 68.1, 89.3, 90.8, 91.6, 92.9, 99.7, 117.0 and 232.7.

Analysis: : Calculated: C, 54.54; H, 5.92
Observed: C, 54.59; H, 5.76 %

Complex 3c'

State : Yellow solid

Mp : 68 °C

IR ($CHCl_3$) : 3369, 1975, 1894, 1880 cm^{-1}

^1H NMR : (δ, $CDCl_3$)

(300 MHz) 2.41 (1 H, d, *J* 3, O*H*), 2.90 (3 H, s, OC*H*$_3$), 3.55 (3 H, s, OC*H*$_3$), 5.37-5.45 (2 H, m, Ar*H*, C*H*(Ph)OH), 5.72 (1 H, dd, *J* 6, 3, Ar*H*), 5.76 (1 H, dd, *J* 6, 3, Ar*H*), 5.81 (1 H, d,

J 3, Ar*H*) and 7.33-7.41 (5H, m, Ph).

^{13}C NMR : (δ, $CDCl_3$)

(75.48 MHz) 50.7, 56.4, 70.1, 90.4, 91.2, 91.6, 92.0, 99.7, 106.1, 114.3, 127.2, 128.2, 128.4, 141.4 and 232.5.

Analysis: : Calculated: C, 57.87; H, 4.57

Observed: C, 57.65; H, 4.96 %

Complex 4a'

State : Orange yellow solid

Mp : 108 °C

IR ($CHCl_3$) : 3562, 1967, 1958, 1884 cm^{-1}

^{1}H NMR : (δ, $CDCl_3$)

(300 MHz) 1.42 (3 H, d, *J* 6, C*H*$_3$), 2.09 (1 H, s, O*H*), 3.35 (9 H, s, 3xOC*H*$_3$), 5.20 (1 H, t, *J* 6, Ar*H*), 5.41 (1 H, doublet of quartet, *J* 3, 6, CH_3C*H*OH), 5.56 (1 H, d, *J* 6, Ar*H*), 5.63 (1 H, t, *J* 6, Ar*H*) and 5.79 (1 H, d, *J* 6, Ar*H*).

^{13}C NMR : (δ, $CDCl_3$)

(75.48 MHz) 24.8, 50.5, 64.1, 87.5, 88.1, 94.5, 95.6, 103.0, 113.0, 119.6 and 232.6.

Analysis: : Calculated: C, 49.73; H, 5.0

Observed: C, 48.89; H, 5.12 %

Complex 4b'

State : Yellow solid

Mp : 110 °C

IR ($CHCl_3$) : 3010, 1978, 1900 cm^{-1}

^{1}H NMR : (δ, $CDCl_3$)

(300 MHz) 0.91 (3 H, t, *J* 6, C*H*$_3$), 1.26-1.77 (6 H, m, (C*H*$_2$)$_3$), 1.94 (1 H, s, O*H*), 3.36 (9 H, s, 3xOC*H*$_3$), 5.20 (2 H, t, *J* 6,

Ar*H*, C*H*(n-Bu)OH), 5.54 (1 H, d, *J* 6, Ar*H*), 5.61 (1 H, t, *J* 6, Ar*H*) and 5.78 (1 H, d, *J* 6, Ar*H*).

^{13}C NMR : (δ, $CDCl_3$)

(75.48 MHz) 13.9, 22.4, 28.7, 38.5, 50.7, 67.9, 88.1, 88.3, 94.5, 95.2, 103.3, 113.1, 119.1 and 232.7.

Analysis: : Calculated: C, 55.08; H, 5.85

Observed: C, 54.87; H, 5.67 %

Complex 4c'

State : Yellow solid

Mp : 108-109 °C

IR ($CHCl_3$) : 3483, 3016, 1971, 1892 cm^{-1}

^{1}H NMR : (δ, $CDCl_3$)

(300 MHz) 2.55 (1 H, d, *J* 3, O*H*), 3.22 (9 H, s, 3xOCH_3), 5.21 (1 H, t, *J* 6, Ar*H*), 5.55 (1 H, t, *J* 6, Ar*H*), 5.64 (1 H, dd, *J* 6 and 1, Ar*H*), 5.75 (1 H, dd, *J* 6 and 1, Ar*H*), 6.29 (1 H, d, *J* 3, PhC*H*OH) and 7.22-7.39 (5 H, m, Ph).

^{13}C NMR : (δ, $CDCl_3$)

(75.48 MHz) 50.6, 69.6, 88.9, 90.0, 93.9, 104.1, 113.0, 116.9, 127.3, 127.6, 128.1, 142.0 and 232.4.

Analysis: : Calculated: 56.61; H, 4.75

Observed: C, 57.14; H, 4.54 %

Addition of enolate to substrate 4, preparation of complexes 4f and 4f':

LDA was generated from equimolar quantities of diisopropyl amine and n-BuLi at –78 °C. To this an equivalent quantity of acetophenone was added at the same temperature and stirred for 1 hr.

The lithium enolate (1.2 equivalents) was added by a cannula to the substrate at –90 °C in chelation and non-chelation controlled fashion according to the same conditions as described above. The color of the solution instantaneously changed from red to yellow. After completion of the reaction (TLC), degassed saturated ammonium chloride solution was added to the reaction at same temperature. The reaction was warmed gradually to room temperature, and extracted with dichloromethane. The organic layer was washed with brine, dried over sodium sulfate. Evaporation of the solvent gave the crude product, which was purified by flash column chromatography with 10 % acetone in petroleum ether as the eluent.

For chelation-controlled addition, the reaction of **4** (150 mg, 0.434 mmol) in 5 ml DCM at –90 ^{o}C pretreated with $MgBr_2.OEt_2$ (450 mg, 1.74 mmol) resulted in **4f** (63 mg, 31 %) and **4f'** (125 mg, 62 %).

For non chelation-controlled addition, the reaction of **4** (150 mg, 0.434 mmol) in 5 ml ether –90 ^{o}C resulted in **4f** (70 mg, 35 %) and **4f'** (112 mg, 55 %).

Complex 4f

State	:	Orange yellow solid
Mp	:	112 °C
IR ($CHCl_3$)	:	1974, 1892, 1685 cm^{-1}
^{1}H NMR	:	(δ, $CDCl_3$)
(300 MHz)		3.18 (1 H, dd, *J* 3, 17, Ph(CO)CH_2), 3.37 (9 H, s, 3xOCH_3), 3.81 (1 H, dd, *J* 2, 17, Ph(CO)CH_2), 3.95 (1 H, d, *J* 2, O*H*), 5.45 (2 H, doublet of quintet, *J* 2, 6, Ar*H*),

5.61-5.71 (2 H, m, Ar*H*), 5.91 (1 H, dd, *J* 2, 6, C(OH)*H*), 7.47-7.67 (3 H, m, Ph) and 8.03-8.11 (2 H, m, Ph).

^{13}C NMR (125.8 MHz) : (δ, $CDCl_3$) 47.4, 51.1, 65.0, 88.2, 89.2, 91.4, 91.8, 93.8, 113.1, 114.1, 128.3, 128.8, 133.6, 136.6, 200.0 and 232.6.

Analysis: : Calculated: C, 56.66; H, 4.75
Observed: C, 57.30; H, 4.28 %

Complex 4f'

State : Yellow solid

Mp : 117-118 °C

IR ($CHCl_3$) : 3018, 1971, 1896, 1680 cm^{-1}

^{1}H NMR (300 MHz) : (δ, $CDCl_3$) 3.11 (1 H, dd, *J* 9, 17, Ph(CO)CH_2), 3.28 (1 H, d, *J* 4, O*H*), 3.37 (9 H, s, 3xOCH_3), 3.65 (1 H, dd, , *J* 2, 17, Ph(CO)CH_2), 5.19 (1 H, quintet, *J* 4, Ar*H*), 5.63 (2 H, d, Ar*H*), 5.79 (1 H, d, , *J* 6, Ar*H*), 5.86 (1 H, ddd, *J* 2, 4, C(OH)*H*), 7.44-7.63 (3 H, m, Ph) and 7.94-7.99 (2 H, m, Ph).

^{13}C NMR (50 MHz) : (δ, $CDCl_3$) 46.9, 50.7, 64.6, 87.6, 87.7, 94.1, 95.1, 113.2, 115.2, 128.1, 128.6, 133.4, 136.7, 159.6, 199.0 and 232.4.

Analysis: : Calculated: C, 56.66; H, 4.75
Observed: C, 57.40; H, 4.35 %

Preparation of Complex 5:

N,N-Dimethylbenzyl amine tricarbonylchromium complex (2.5 g, 9.23 mmol) in THF (70 ml) was treated with n-BuLi (1.66 M, 6.7 ml, 11.1 mmol) and *N,N*-Dimethylformamide (1.0 g, 13.85 mmol) under standard conditions. Usual work-up and purification by flash column chromatography using 15 % acetone in petroleum ether as eluent resulted in **5** (2.4 g, 87 %).

Complex 5

State	:	Red solid
Mp	:	74 °C
IR ($CHCl_3$)	:	1985, 1917, 1686 cm^{-1}
^1H NMR (200 MHz)	:	(δ, $CDCl_3$) 2.29 (6 H, s, N(CH_3)$_2$), 2.93 (1 H, d, *J* 13, CH_2), 4.08 (1 H, d, *J* 13, CH_2), 5.15 (1 H, d, *J* 6, Ar*H*), 5.29 (1 H, t, *J* 6, Ar*H*), 5.72 (1 H, t, *J* 6, Ar*H*), 6.09 (1 H, d, *J* 6, Ar*H*) and 9.84 (1H, s, C*H*O)
^{13}C NMR (50.32 MHz)	:	(δ, $CDCl_3$) 45.0, 59.9, 88.6, 91.3, 93.7, 94.7, 112.3, 187.1 and 230.4.
Analysis:	:	Calculated: C, 52.18; H, 4.38; N, 4.68 Observed: C, 52.52; H, 4.73; N, 4.56 %

Addition of nucleophiles to Complex 5:

The same procedures described above for 'chelation' and 'non-chelation' controlled additions to the *ortho* substituted benzaldehydes were followed here.

Complex 5b

State	:	Yellow solid
Mp	:	84-85 °C
IR ($CHCl_3$)	:	3330, 1981, 1870 cm^{-1}

^{1}H NMR (300 MHz)	:	(δ, $CDCl_3$) 0.98 (3H, t, *J* 6, $(CH_2)_3CH_3$), 1.36-1.80 (7H, m, O*H*, $(CH_2)_3$), 2.32 (6 H, s, $N(CH_3)_2$), 2.59 (1 H, d, *J* 12, CH_2), 4.03 (1 H, d, *J* 12, CH_2), 4.55 (1H, d, *J* 9, C*H*(OH)n-Bu), 5.19 (1H, d, *J* 6, Ar*H*), 5.31-5.40 (2H, m, Ar*H*) and 5.46 (1H, d, *J* 6, Ar*H*).
^{13}C NMR (50.32 MHz)	:	(δ, $CDCl_3$) 14.0, 22.6, 28.8, 29.7, 31.9, 44.4, 61.9, 68.7, 90.4, 91.4, 92.3, 95.7, 106.0, 114.6, 159.7 and 232.4.
Analysis:	:	Calculated: C, 57.14; H, 6.49; N, 3.92 Observed: C, 56.60; H, 6.41; N, 3.78 %

Complex 5b'

State	:	Yellow solid
Mp	:	67 °C
IR ($CHCl_3$)	:	3385, 1969, 1892 cm^{-1}
^{1}H NMR (200 MHz)	:	(δ, $CDCl_3$) 0.93 (3H, t, *J* 6, $(CH_2)_3CH_3$), 1.25-1.87 (6H, m, $(CH_2)_3$), 2.26 (6 H, s, $N(CH_3)_2$), 2.72 (1 H, d, *J* 12, CH_2), 3.85 (1 H, d, *J* 12, CH_2), 4.10 (1H, bs, O*H*), 4.38 (1H, dd, *J* 2, 9, C*H*(OH)n-Bu), 5.17 (1H, d, *J* 6, Ar*H*), 5.27 (1H, t, *J* 6, Ar*H*), 5.42 (1H, t, *J* 6, Ar*H*) and 5.64 (1H, d, *J* 6, Ar*H*).
^{13}C NMR (50.32 MHz)	:	(δ, $CDCl_3$) 13.9, 22.3, 28.9, 39.1, 44.8, 61.3, 90.9, 92.8, 93.1, 93.8, 107.3, 117.6, 159.7 and 232.9.
Analysis:	:	Calculated: C, 57.14; H, 6.49; N, 3.92 Observed: C, 56.99; H, 6.55; N, 3.81 %

X-ray Crystal Structure Analysis For 3a', 3a and 4e:

Data for both the compounds were collected on *MACH-3* diffractometer using Mo K_α radiation with fine focus tube. All the data were corrected for Lorentzian, polarization and absorption effects. SHELX-97 (SHELXTL)[ref] was used for structure solution and full matrix least squares refinement on F^2.

Crystal Data for 3a': Rectangular pale yellow single crystals were grown by slow evaporation of solvent from a mixture of dichloromethane and petroleum ether. $C_{14}H_{16}CrO_6$, M = 332.27. Crystals belong to monoclinic, space group P21/n^o, a = 13.639(1), b = 8.994(1), c = 13.74(1) Å, β = 113.594 (7) °, V = 1544.6 (3) Å^3, Z = 4, D_c = 1.429 mg m^{-3}, μ (Mo–K□) = 0.763 mm^{-1}, T = 293(2) K, 2710 unique [I>2σ(I)], R_1 = 0.0289, wR_2 = 0.0838.

Crystal Data for 3a: Cubic yellow single crystals were grown by slow evaporation of solvent from a mixture of dichloromethane and petroleum ether. $C_{14}H_{16}CrO_6$, M = 332.27. Crystals belong to monoclinic, space group P21/c^o, a = 8.099(1), b = 8.084(6), c = 23.252(2) Å, β = 99.51(1) °, V = 1501.4(3) Å^3, Z = 4, D_c = 1.47 mg m^{-3}, μ (Mo–K□) = 0.785 mm^{-1}, T = 293(2) K, 2649 unique [I>2σ(I)], R_1 = 0.0350, wR_2 = 0.0889.

Crystal Data for 4e: Orange flake crystals were grown by slow evaporation of solvent from a mixture of dichloromethane and petroleum ether. $C_{17}H_{10}CrO_5$, M = 346.25. Crystals belong to monoclinic, space group P21/c^o, a = 12.14 (7), b = 13.20 (7), c = 10.32 (5) Å, β = 113.5 (1) °, V = 1515.9(14) Å^3, Z = 4, D_c = 1.52 mg m^{-3}, μ (Mo–K□) = 0.777 mm^{-1}, T = 293(2) K, 2653 unique [I>2σ(I)], R_1 = 0.0593, wR_2 = 0.4352.

Reference

G. M. Sheldrick, SHELX-97 program for crystal structure solution and refinement, University of Gottingen, Germany, 1997

Crystal data and structure refinement for 3a

Empirical formula	C14 H16 Cr O6
Formula weight	332.27
Temperature	293(2) K
Wavelength	0.70930 Å
Crystal system, space group	Monoclinic, P21/c^{o}
Unit cell dimensions	a = 8.099(1) Å b = 8.084(6)Å c = 23.252(2) Å β = 99.51(1) °
Volume	1501.4(3) Å ^{3}
Z, Calculated density	4, 1.470 Mg/m^{3}
Absorption coefficient	0.785 mm^{-1}
F(000)	688
Crystal size	0.25 x 0.20 x 0.20 mm
Theta range for data collection	1.77 to 24.91^{o}.
Limiting indices	-9<=h<=9, 0<=k<=9, 0<=l<=27
Reflections collected / unique	2649 / 2649 [R(int)= 0.0000]
Completeness to theta = 24.91	100.0 %
Refinement method	Full-matrix least-squares on F^{2}
Data / restraints / parameters	2649 / 0 / 254
Goodness-of-fit on F^{2}	1.022
Final R indices [I>2sigma(I)]	R1 = 0.0350, wR2 = 0.0889
R indices (all data)	R1 = 0.0527, wR2 = 0.0949
Largest diff. Peak and hole	0.365 and –0.269 e. Å $^{-3}$

Crystal data and structure refinement for 3a'

Empirical formula	C14 H16 Cr O6
Formula weight	332.27
Temperature	293(2) K
Wavelength	0.70930 Å
Crystal system, space group	Monoclinic, P21/n
Unit cell dimensions	a = 13.639(1) Å b = 8.994(1) Å c = 13.74(1)Å β = 113.594 (7) °
Volume	1544.6(3) A^3
Z, Calculated density	4, 1.429 Mg/m^3
Absorption coefficient	0.763 mm^{-1}
F(000)	688
Crystal size	0.4 x 0.35 x 0.30 mm
Theta range for data collection	1.77 to 24.90 ^{o}.
Limiting indices	-16<=h<=14, 0<=k<=10, 0<=l<=16
Reflections collected / unique	2710 / 2710 [R(int) = 0.0000]
Completeness to theta = 24.90	99.9 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2710 / 0 / 254
Goodness-of-fit on F^2	1.087
Final R indices [I>2sigma(I)]	R1 = 0.0289, wR2 = 0.0838
R indices (all data)	R1 = 0.0350, wR2 = 0.0861
Largest diff. Peak and hole	0.210 and –0.381 e. $Å^{-3}$

Crystal data and structure refinement for 4e

Empirical formula	C17 H10 Cr O5
Formula weight	346.25
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P21/c
Unit cell dimensions	a = 12.14 (7) Å b = 13.20 (7) Å c = 10.315(5) Å β = 113.47(1) °
Volume	1515.9(14) A ^{3}
Z, Calculated density	4, 1.517 Mg/m^3
Absorption coefficient	0.777 mm^{-1}
F(000)	704
Crystal size	0.30 x 0.04 x 0.02 mm
Theta range for data collection	1.83 to 25.00 ^{o}.
Limiting indices	-14<=h<=12, -15<=k<=14, -12<=l<=10
Reflections collected / unique	7168 / 2653 [R(int) = 0.1373]
Completeness to theta = 25.00	99.3 %
Max. and min. transmission	0.9816 and 0.8004
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2653 / 0 / 209
Goodness-of-fit on F^2	0.729
Final R indices [I>2sigma(I)]	R1 = 0.0593, wR2 = 0.4352
R indices (all data)	R1 = 0.2447, wR2 = 0.5443
Largest diff. Peak and hole	1.247 and –1.623 e. Å $^{-3}$

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Part B

Counterion dependence of selectivity in C-Si bond cleavage

Part of this work was published in *Chem. Commun.* **2002**, 1924.

If I have an idea and you have one, when we share them, each of us have two.

-George Bernard Shaw

Introduction and background

Complexation of an arene by tricarbonylchromium increases acidity of the ring protons. This is evident from greatly enhanced rates in the *ortho*-lithiation of chromium complexed anisole as compared to the free arene.[1]

Our earlier studies proved that such intermediate aryl-anionic species can be generated by desilylation of complexed aryl silanes by nucleophilic attack of a hydride on the silicon and could be easily trapped by different electrophiles to prepare metal complexed arenes with electron-withdrawing functional groups on the arene ring by an *ipso* substitution of the *SiMe*$_3$ group (Chart-1).[2a]

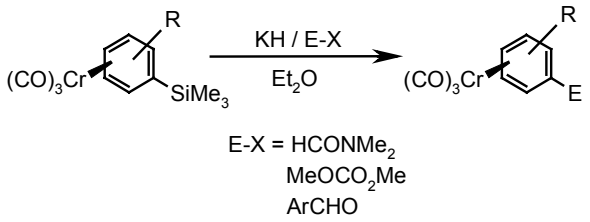


Chart 1. Desilylation of $(CO)_3Cr$- complexed aryl silanes

The protocol was further extended towards a convenient and general synthesis of diaryl ketones wherein one aromatic ring is predictably complexed with tricarbonylchromium.[2b]

Above studies stemmed from the observation of a facile cleavage of Ar-$SiMe_3$ bond while attempting standard organic transformations like aldol-dehydration (Chart-2) and anion assisted Cope rearrangement (Chart-3). In both instances, desilylation could be suppressed only at low temperatures.

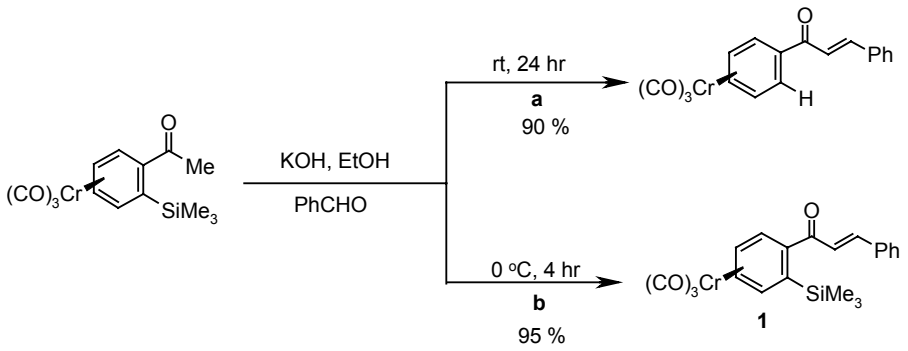


Chart 2. Desilylation during Claisen-Schmidt condensation

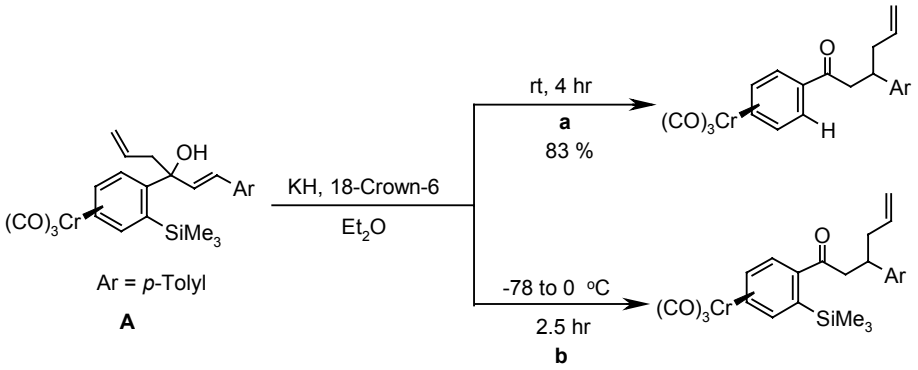


Chart 3. Desilylation during oxy-anionic Cope rearrangement

In course of preparation of the carbinol **A** above, it was noticed that the addition of allylmagnesium bromide to the enone **1** in THF gave an unusual cyclic product in low yields when the reaction mixture was warmed up before quenching. The product was identified by the two three-proton singlets in the H^1 NMR instead of a nine-proton singlet for the trimethyl silyl group (Chart-4) and appeared to be a single diastereomer.

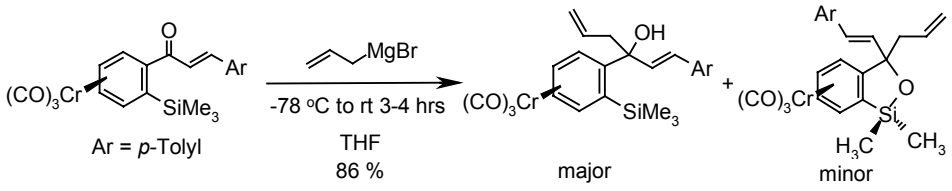


Chart 4. Inadvertent formation of cyclic product

In the above reaction, formation of a cyclic product attracted our attention as it involved a preferential cleavage of an Si-Me bond over the Ar-Si bond under exceptionally mild conditions. The following pages describe our efforts to understand this unusual reaction.

Present work

Although the attack of the nucleophile at the benzylic position of a chromium complexed arene is exclusively *anti* to the bulky $(CO)_3Cr$ moiety, stereochemical course of the reaction is difficult to predict. This is due to the free rotation of $(CO)_3CrAr$-CO bond that exposes different π-faces of the enone (*syn* and *anti* orientation with respect to the *ortho* substituent) randomizing the diastereoselectivity of the product formation (Chart-5).

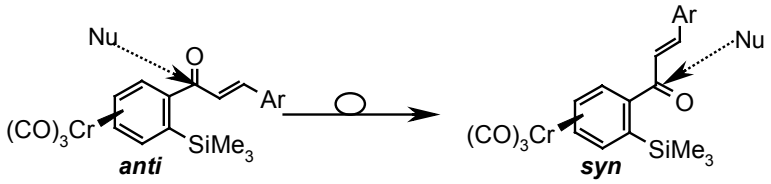
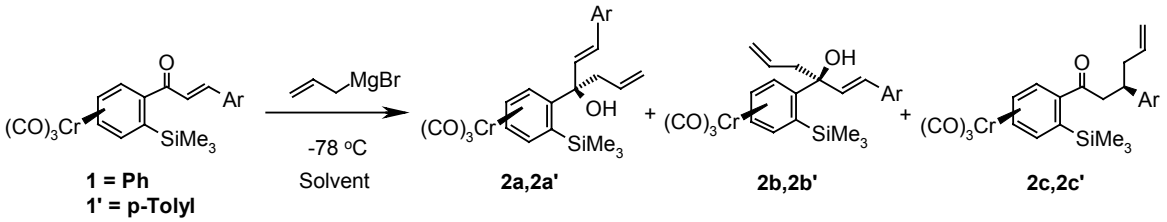


Chart 5. Randomization of diastereoselectivity

With an interest to explore the course of addition of nucleophiles to such flexible substrates, acyclic enone complex **1** was prepared by the Claisen-Schmidt condensation of *o*-$SiMe_3$-acetophenone-$Cr(CO)_3$ complex with benzaldehyde in aqueous ethanol in the presence of potassium hydroxide as a base. Complex **1** showed characteristic carbonyl absorption at 1666 cm^{-1} in infrared spectrum. Proton NMR spectrum showed signals due to olefinic protons at δ 7.20 and 7.88 ppm with a *trans* coupling of 16 Hz. Employing *p*-methoxybenzaldehyde for the Claisen-Schmidt reaction furnished complex **1'** reported earlier by our group.[3]

Addition of allylmagnesium bromide to these enone complexes showed different stereoselectivities depending on the solvent employed for the reaction. At -78 ^oC addition of allylmagnesium bromide to **1** in ether resulted in a 1:1 diastereomeric mixture of carbinols **2a** and **2b** in 96% yield. Addition to enone **1'** afforded carbinols **2a'** and **2b'** comparable yield and diastereomeric ratio (Scheme-1).



Scheme 1. Addition of allylMgBr (low temperature quench)

Table-1

Entry	Substrate	Reagent	Solvent	Yield (%)	Product (ratio)
1	**1**	AllylMgBr	Ether	96	**2a**:**2b** = 1:1.13
2			THF	92	**2a**:**2b**:**2c** = 8:1.2:1
3	**1'**		Ether	93	**2a'**:**2b'**= 1:1.1
4			THF	94	**2a'**:**2b'**:**2c'**=9:1.3:1

It is interesting to note here that no conjugate addition was observed with ether as solvent and the diastereoselectivity of addition was poor (entries 1 and 3, Table-1). On the other hand, use of THF as solvent afforded a minor amount of conjugate addition products **2c** and **2c'**. The diastereoselectivity was very high in favor of the product resulting from *anti* addition on the *syn* conformer in both cases (entries 2 and 4, Table-1). Though the stereochemical outcome of these reactions is not clearly understood, it is well known that the constitution of Grignard reagents varies dramatically with the solvent.[4]

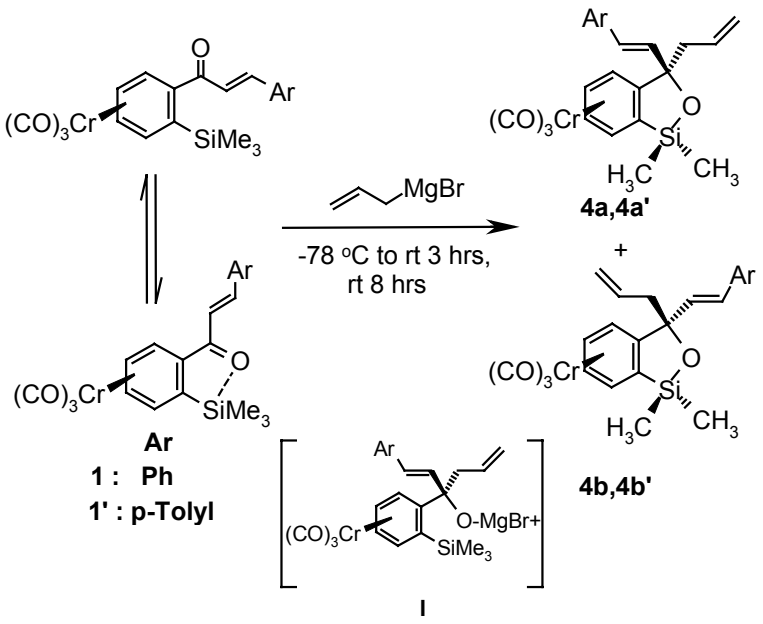
The diastereomers could be easily separated by flash-column chromatography. Yields given in the Table are isolated yields of the pure products. The compounds described in this part of the thesis are all racemic complexes. Only one enantiomer is depicted in the Schemes to illustrate the chemistry. The

relative stereochemistry of products is based on the crystal structure of complex **2a'** and a closely related compound to **2c'** reported earlier.[3]

The proton NMR spectra of **2a** and **2b** are distinctly different. The carbinol **2a** showed nine-proton singlet for trimethylsilyl group at δ 0.43 ppm, allylic protons appeared as a multiplet at δ 2.70 ppm and the olefinic protons of the styryl moiety appeared at δ 6.46 and 6.78 ppm with a characteristic *trans* coupling of 16 Hz. The splitting pattern of protons on the complexed aromatic ring was different in carbinol **2b**. Another characteristic feature is Δδ of the olefinic protons on the styryl moiety. Where as it is 0.32 ppm for **2a**, it is only 0.12 ppm for **2b**. It is also notable that the chemical shift values and the splitting patterns for **2a** and **2a'** as well as **2b** and **2b'** are almost same.

Reactions of allylmagnesium bromide to the above enones took a different course when the reaction mixture was allowed to warm up to room temperature before quenching.

When allylmagnesium bromide was added to the enone **1** at -78 ºC in ether and the reaction mixture was allowed to slowly attain room temperature and stirred for several hours, unusual isomeric five-membered heterocycles **4a** and **4b** were the only products obtained in 1:1.1 ratio (entry 1, Table-2). Though the products were not separable by flash-column chromatography, they could be readily separated by fractional crystallization in 96 % over-all yield. Complex **4a** crystallized from dichloromethane/petroleum ether at temperature < 5 ^{o}C. Further crystallization of mother liquor afforded **4b** (Scheme-2).



Scheme 2. Addition of allylMgBr- -78 ^{o}C to rt

Two distinct three-proton singlets corresponding to the two Si-Me groups at δ 0.50 and 0.66 ppm are the diagnostic proton NMR features for isomer **4a**. For **4b** these peaks appear at δ 0.45 and 0.68 ppm.

The bicyclic structure of cyclized product was further confirmed by crystal structure determination of complex **4a**, which also ascertained that the product was formed by an *exo*-selective addition of allymagnesium bromide to the *syn*-conformer (Fig-1).

Fig. 1ORTEP diagram of **4a**.

When the reaction was carried out on the enone **1'** in ether, the products **4a'** and **4b'** were obtained in 94 % yield (entry 3, Table-2). When THF was employed as solvent for the reaction, **4a** and **4a'** were the major products along with minor amounts of **4b**, **4b'** and **2c**, **2c'** (entries 2 and 4, Table-2).

Table-2

Entry	Substrate	Reagent	Solvent	Yield (%)	Product (ratio)
1	**1**	AllylMgBr	Ether	96	**4a**:**4b** = 1:1.1
2			THF	81	**4a**:**4b**:**2c** = 7.5:1.1:1
3	**1'**		Ether	94	**4a'**:**4b'** = 1:1.2
4			THF	75	**4a'**:**4b'**:**2c'**=8.5:1.2:1

It is pertinent to observe the following significant points:

When magnesium was counterion -

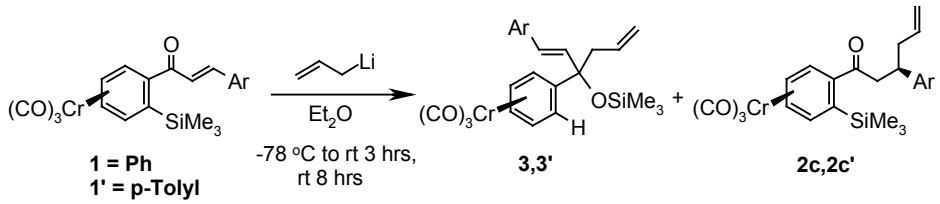
1) An Si-Me bond was cleaved under mild condition and in preference to an Si-Ar bond.[2c] This was quite unexpected since cleavage of Si-Ar bond is supposed to be facilitated by the stability of the aryl anion complexed to an electron withdrawing $Cr(CO)_3$ moiety, whereas the driving force for the cleavage of Si-Me bond is not clear.

2) No product from anionic oxy-Cope rearrangement of the intermediate magnesium alkoxide **I** was observed. Unusual cyclic products were obtained instead. The small amount of conjugate addition product obtained when THF was used as solvent, was the result of a direct – however limited – conjugate addition of organomagnesium reagent to enone.

3) Fate of the departed methyl group from TMS during the formation of Si-O heterocycle was unknown.

At this stage, it was of immediate interest to know if the reactions described above would yield the same results when allyllithium is employed as a nucleophile instead of allylmagnesium bromide under same reaction conditions.

Accordingly, addition of allyllithium to enone **1** at -78 ^{o}C in ether was allowed to warm up to room temperature slowly and stirred for further 8 hours. While the reaction did not afford any cyclization products as in the case of addition of allylmagnesium bromide, complex **3** and the conjugate addition product **2c** were the only isolable products in 40 and 45 % yield respectively (Scheme-3). Reaction of allyllithium with enone complex **1'** under the same conditions gave **3'** and **2c'** in 42 and 51 % respectively (Table-3).



Scheme 3. Addition of allylLi- -78 ^{o}C to rt

Table-3

Entry	Substrate	Reagent/ Solvent	Yield (%)	Product (ratio)
1	**1**	AllylLi/ Ether	85	**3**:**2c** = 1:1.13
2	**1'**		93	**3'**:**2c'** = 1:1.2

We were surprised as well as excited at this sudden turn in the course of reaction by a mere change in the metal counterion. When Li was the counterion- there was a facile Si-Ar bond cleavage resulting in the Brook rearrangement and

no cyclization product was observed, as was observed when Mg was the counterion. Although the postulated intermediate is the same alkoxide, it is interesting how pathways differ when counterion differs.

Ever since the first observation of *C*-to-*O* anionic migration of a silyl group,[5] the Brook rearrangement[6] has found numerous applications in organic synthesis. There were several interesting developments in tandem Brook rearrangement reactions after the subject has been thoroughly reviewed by Moser a few years ago.[7] It is pertinent to briefly summarize some of these recent applications in the following few paragraphs.

Moser *et al.* have demonstrated the usefulness of Brook rearrangement in preparing various functionalized tricarbonylchromium arenes **D**. The strategy involved initial addition of an organolithium reagent to an *o*-silyl-substituted benzaldehyde chromium tricarbonyl complex **A**, generating oxy-anion **B**. Subsequent 1,4 carbon-to-oxygen silyl migration was favored by the resultant aryl anion stabilized by the powerful electron-withdrawing nature of the $Cr(CO)_3$ moiety. A second bond-formation step was then accomplished by treatment of the aryllithium **C** with various electrophiles (Chart-6).[8a]

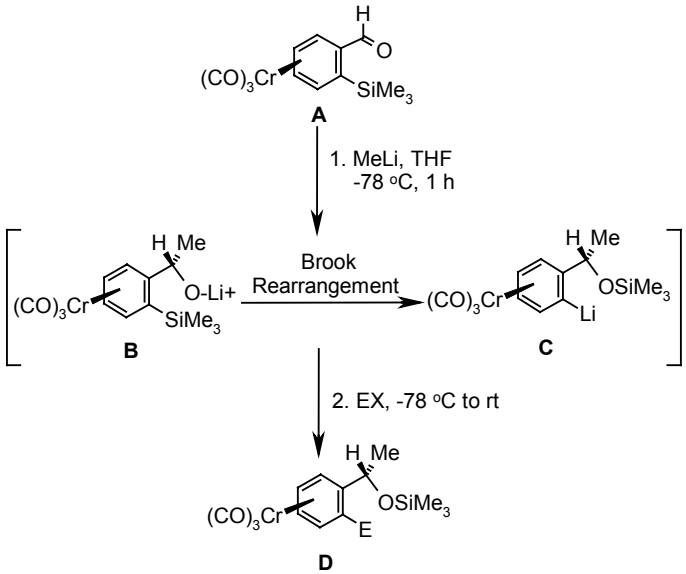


Chart 6. Brook rearrangement in arene chromium complexes

The facility of Ar-$SiMe_3$ bond cleavage by an intramolecular attack of lithium alkoxide was elegantly exploited by the same group for a [3+2] annulation of a lithium ester enolate with a tricarbonylchromium complexed aryl aldehyde **A** for stereocontrolled construction of polycyclic and spirocyclic compounds **E**, including the spirocyclic core of an antitumor agent Fredericamycin A.[8b] The strategy involved a one-pot aldol addition/Brook rearrangement/cyclization sequence beginning from arene chromiumtricarbonyl complexes (Chart-7).

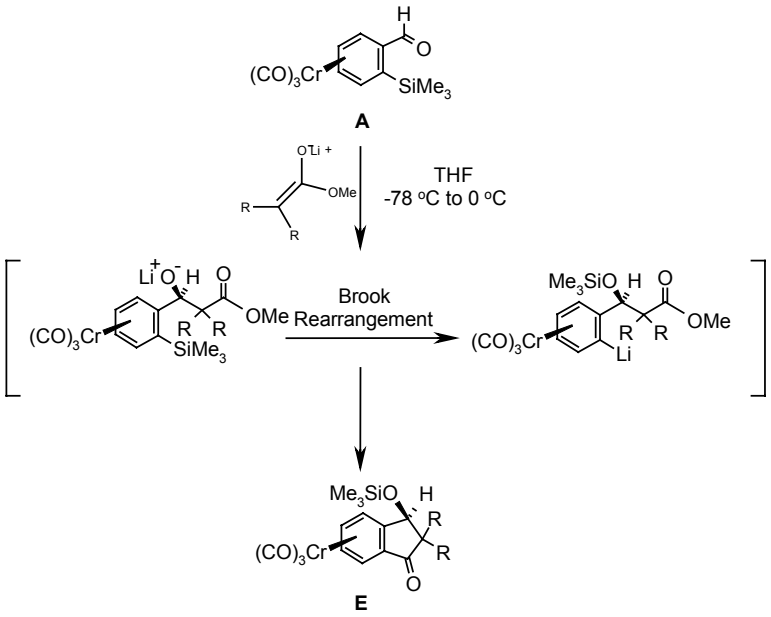


Chart 7. Synthesis of spirocyclic core of Fredericamycin A

Takeda's group has been active in developing several annulation protocols based on these silyl migrations. They have recently developed a novel Brook rearrangement mediated [3+4] annulation method for stereoselective synthesis of eight-membered carbocycles (Chart-8).[9] It has also been shown that this strategy is useful in the synthesis of highly functionalized five membered carbocycles.[10]

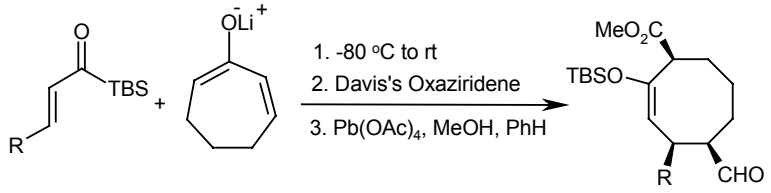


Chart 8. Synthesis of eight-membered carbocycles

It was observed by the same group that the metallated *O*-Silyl cyanohydrins of β-silyl-α, β-epoxyaldehyde could serve as functionalized homoenolate equivalents by a tandem sequence of a base-promoted ring opening of the epoxide-1, 2-Brook rearrangement and alkylation of the resulting allylic anion. Alkylations can be effected on this anion by an alkyl halide as an internal quench (Chart-9).[11]

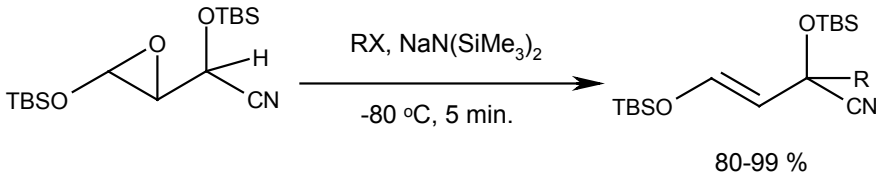


Chart 9. Tandem Brook rearrangement in *O*-Silyl cyanohydrins

Another recent application involves tandem C-C bond construction *via* Cyanation-Brook rearrangement and C-acylation reactions of acylsilanes. The reaction affords functionalized unsymmetric malonic acid derivatives (Chart-10).[12]

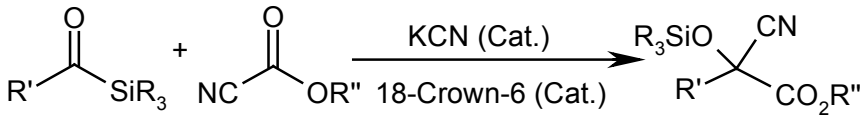
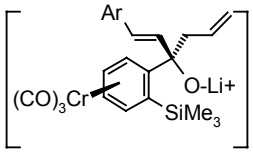


Chart 10. Tandem Brook rearrangement in acylsilanes

Brook rearrangement was also employed as a key reaction in the stereoselective synthesis of silyl enol ethers from carbonyl compounds[13] and a radical cyclization-β-fragmentation sequence in the preparation of acylsilanes with terminal α-stannyl bromides or xanthate functionalities.[14a] *O*-Silylated cinnamyl alcohols have been synthesized using silicon migration-rearrangement sequence from β-silyl sulfones.[14b]

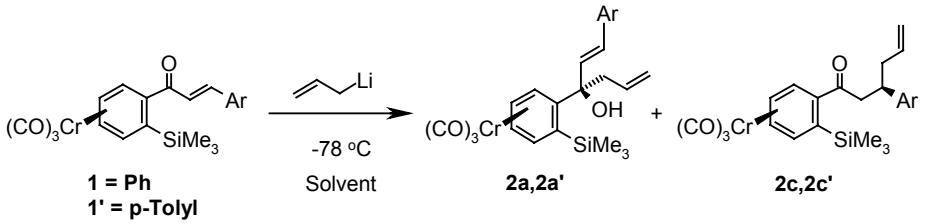
Based on the past precedents such as those of Moser *et al.* (Charts 6 and 7), we were prompted to presume that while complex **3** in Scheme-3 could have resulted from the alkoxide **II** (Fig. 2) through a Brook rearrangement consisting of 1,4: *C*-to-*O* silyl migration, product **2c** could result either by a competitive anionic oxy-Cope rearrangement of the intermediate lithium alkoxide **II** or by a direct 1,4-conjugate addition across the enone. We sought to further investigate the above result in order to get a better insight into the reaction pathway.



II

Fig 2. Intermediate Li alkoxide

Addition of allyllithium to enones **1** and **1'** in ether or THF at -78 ^{o}C resulted in 1,4-conjugate addition as a major product obtained as a single diastereomer (Scheme-4). 1,2-Addition to the enone was also highly disatereoselective resulting in only carbinols **2a** and **2a'** resulting from an *anti* attack of the reagent on the *syn* conformation of the enone (Table-4).



Scheme 4. Addition of allylLi (low temperature quench)

Table-4

Entry	Substrate	Reagent	Solvent	Yield (%)	Product (ratio)
1	**1**	AllylLi	Ether	86	**2a**:**2c** = 1:1.2
2			THF	77	**2a**:**2c** = 1:1.5
3	**1'**		Ether	94	**2a'**:**2c'** = 1:1.1
4			THF	82	**2a'**:**2c'** = 1:1

Significant observations collected in Table-4 are:

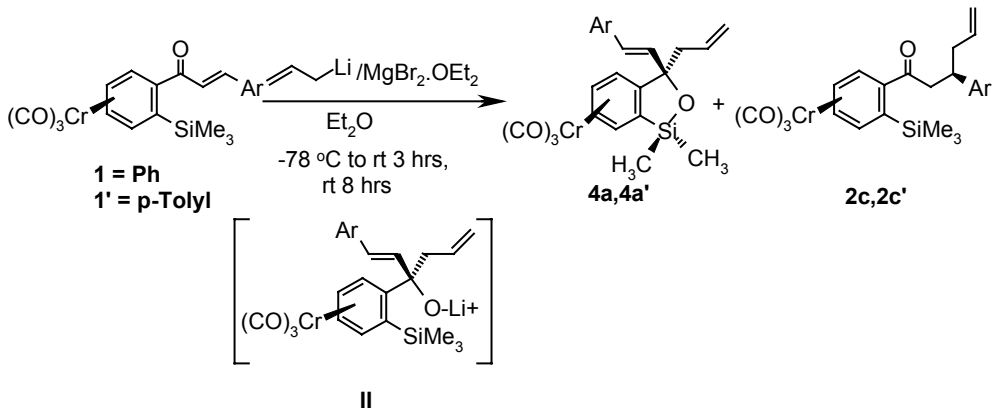
1) Conjugate addition product was formed in substantial amounts although organolithium reagents generally prefer 1,2-Addition to enones. No such conjugate addition product was observed in our earlier studies in reactions of analogous cyclic substrates like 2-arylidene-1-tetralone-$Cr(CO)_3$ complexes studied earlier.

2) The diastereoselectivity of addition was very high. Carbinols **2b** and **2b'** that result from the attack of the reagent on the *anti* conformation of the enone were not detected by 300 MHz NMR spectrometer.

3) Brook rearrangement products were not isolated under these conditions (low temperature quench).

The presumption that the heterocyclic product **4** was indeed formed by a pathway dictated by magnesium counterion was readily ascertained by exchanging Li counterion in the lithium alkoxide **II** with MgBr by adding a three-fold excess of $MgBr_2.Et_2O$ as described below.

After allyllithium had reacted with **1** at -78 °C (indicated by a rapid color change), a three-fold molar excess of anhydrous magnesium bromide was introduced with stirring. The reaction mixture was stirred for 30 minutes at this temperature in order to facilitate complete exchange of the Li counterion with that of MgBr. After the reaction mixture was allowed to slowly attain room temperature over 3 h, it was stirred for additional 8 h. Products isolated from this reaction were complexes **4a** (40 %) - not **3,** and **2c** (44 %) (Scheme-5).

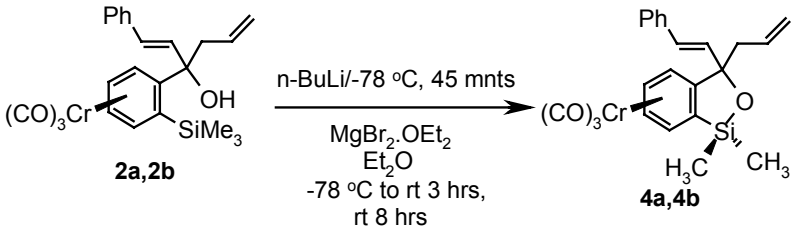


Scheme 5. *In situ* exchange of Li counterion with MgBr

We know that complex **2c** is formed independently during allyllithium addition. This experiment thus implied that the Brook rearrangement observed in Scheme-2 is facile only when lithium is the counterion and the cyclic product is produced when magnesium is the counterion. Reaction of enone **1'** resulted in **4a'** and **2c'** in 43 and 49 % yield respectively (Scheme-5).

The lithium alkoxide **II** could be generated directly by deprotonation of the corresponding carbinol using n-BuLi at -78 ^oC. Lithium counterion was exchanged by MgBr by adding excess $MgBr_2.OEt_2$ to the reaction mixture at the same

temperature. It was then allowed to warm up to room temperature slowly and stirred for further eight hours at room temperature. Cyclized products **4a** and **4b** were obtained in 98 and 96 % yields respectively when **2a** and **2b** were used as the starting carbinols (Scheme-6).



Scheme 6. Exchange of Li counterion with MgBr

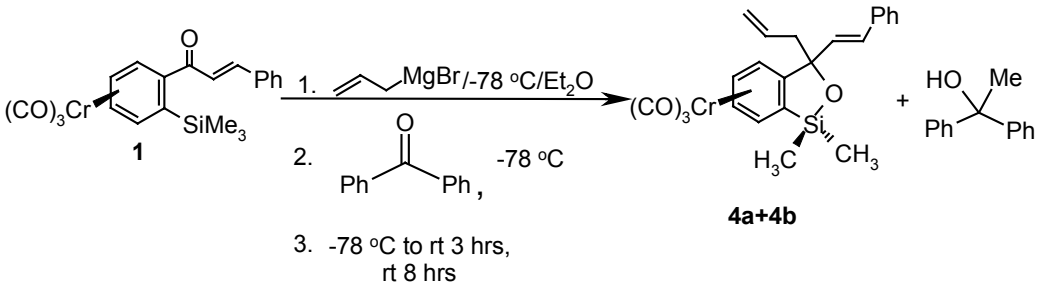
The high yields in the above reaction indicate the effectiveness of the counterion exchange and subsequent cyclization. The protocol also affords diastereomerically pure cyclized products when diastereomerically pure carbinols are employed as starting material (**2a** and **2b**).

It is important to mention here that the carbinol **2a''** (See Appendix-II for structure) corresponding to *ortho*-trimethyltin analogue of **2a'** failed to undergo either cyclization or the Brook rearrangement under same set of conditions. This indicates that the energetics involved in the C-Si and C-Sn bond cleavages are certainly different and cannot obviously be compared.[15]

Having thus established that the pathway for cyclization is indeed directed by a magnesium counterion, we sought to explore the fate of the Me group that is lost during the process.

As an attempt to verify the possibility of the methyl group leaving the silicon as an anionic species, 1.2 equivalents of benzophenone was added to reaction mixture after allylmagnesium bromide had consumed substrate **1** and prior to warming up. It was anticipated that the anionic methyl group could be trapped with electrophilic benzophenone moiety.

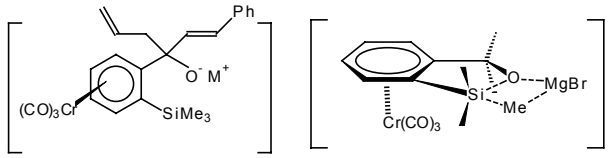
The reaction afforded diphenyl methyl carbinol in an yield that corresponded to 0.95 mol % of the amount of cyclized product obtained. While the total mass recovery of the reaction was 96 %, the yield of cyclized product was 82 % (**4a**: **4b** = 1:1.2) and the yield of diphenyl methyl carbinol was 65 % (Scheme-7). Also, a minor amount of diphenyl allyl carbinol was obtained in the reaction, which could have resulted from the addition of the excess Grignard reagent present in the reaction medium.



Scheme 7. Anionic nature of the departed Me group from $SiMe_3$

From the above reaction it is evident that the cyclized product resulted from an intramolecular nucleophilic attack of magnesium alkoxide on the silicon atom. This could occur in a stepwise manner or by a concerted, intramolecular, S_Ni type displacement at silicon by the alkoxide.[16]

The reaction pathways and transition states in the two reactions i.e. Brook rearrangement and Si-O cyclization seem to be distinctly different. It is possible that the reaction proceeds *via* a common alkoxide intermediate **II**, which can exist in equilibrium with a cyclic intermediate **III** featuring a pentacoordinated silicon (Fig. 3).[17]



II
When M = Li or MgBr at low temperature

III
When M = MgBr at ambient temperature

Fig 3. Possible intermediate alkoxides

At low temperature, the equilibrium favors **II.** When lithium is the counterion, and the temperature is raised, intramolecular nucleophilic attack of the alkoxide on the silicon would cleave Ar-Si bond to produce an aryl anionic species stabilized by tricarbonylchromium complexation with concomitant formation of O-Si bond, affording the Brook rearrangement product.

The intermediate **III** seems significant only when the counterion is magnesium and temperature is raised from -78 °C. Literature precedents suggest that a four-centered transition state would facilitate the siloxane formation.[18]

A facile expulsion of CH_3MgBr from a hypervalent penta coordinate silicon "ate" complex **III** could be the driving force behind the preferential rupture of a Si-Me bond in preference to Si-Ar bond in the reaction mediated by magnesium counterion.[18]

It is pertinent here to comment on the counterion dependence of the Brook and cyclization reactions that we encountered. Though there are several examples where the yields and stereoselectivity of the reactions were typical of the ionic species involved,[19] there are only a few scattered examples of counterion-dependent reaction pathways and systematic investigations of such phenomena are very rare.[20] For instance, product geometry and rates of Peterson elimination reaction are known to be dependent on the counterion.[20a] It is also known that the rate of reactions like oxy-Cope rearrangement is highly counterion dependent.[21]

Recently McIntosh *et al.* reported an unusual counterion-dependent reversal of diastereoselectivity in 1,2-Additions of hard carbon nucleophiles to C6-heterosubstituted cyclohexenones. Whereas the Grignard reagents preferentially added in a *syn* fashion to the C6-substituent, the Li reagents predominantly gave *anti* adducts (Chart-11).[22] The diastereoselectivity was also shown to vary with the solvents employed for the reaction.

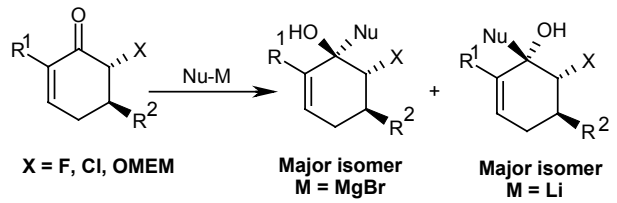


Chart 11. Counterion-dependence of diastereoselectivity

Five and six membered cyclic siloxanes are important intermediates in organic synthesis and have been employed in several C-C bond formation reactions.[23] The following few paragraphs aim to survey some of the general methods employed to synthesize such compounds.

In general, the cyclic siloxanes are prepared from a synthetic precursor that already has an Si-O linkage, for instance, *via* radical cyclization of α-(propargyloxy)silyl-α-diazoacetates,[24] or, cyclizations of the pendant radical precursors attached to the Si-O bond as a tether.[25,26] Other important methods involve cycloadditions,[27] aldehyde insertion into the C-Si bond of siliranes,[28] hydrosilylations,[29] and fluoride ion catalyzed intramolecular cyclizations,[30]

In course of their studies on disatereoselective chromium complexation of *m*-methoxybenzyl alcohol derivatives featuring a trimethylsilyl substituent *ortho* to the methoxy group,[31] Uemura *et al.* isolated cyclic siloxanes under thermal conditions. Reaction of **A** with $Cr(CO)_6$ in refluxing dibutylether at 130-140 ^oC for two days gave a mixture of *endo*- and *exo*-methyl chromium complexed siloxanes **C** and **D** in 88 % yield in the 3:2 diastereomeric ratio respectively (Chart-12).

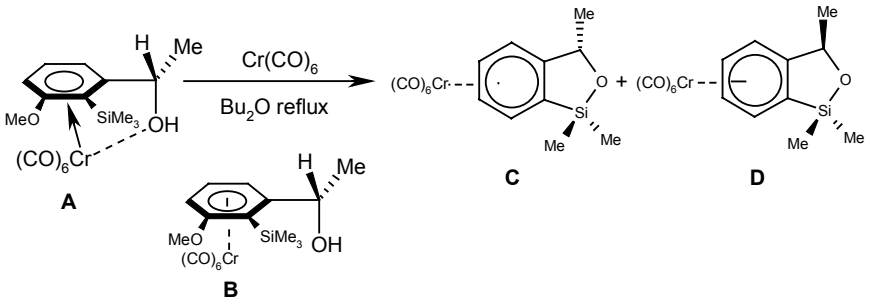


Chart 12. Formation of cyclic siloxanes during thermolysis

It was proposed that the initially formed complexation product **B** transforms to the *endo*-methyl complex **C** by an intramolecular attack of the benzylic alkoxide anion to the silyl group with an excess of $Cr(CO)_6$ and then this *endo*-methyl complex **C** equilibrates to the *exo*-methyl complex **D** under thermal conditions. It is interesting that the silicon-methyl bond was selectively cleaved over the Ar-Si bond.

Unlike the above reaction, *o*-silyl benzyl alcohols **E** cyclized to give cyclic siloxanes **G** in quantitative yields in aprotic polar solvents such as acetonitrile with elimination of hydrocarbons under very mild conditions.[32]The result is explained by concerted four-membered elimination of hydrocarbon from hypervalent silicon intermediate **F** (Chart-13).

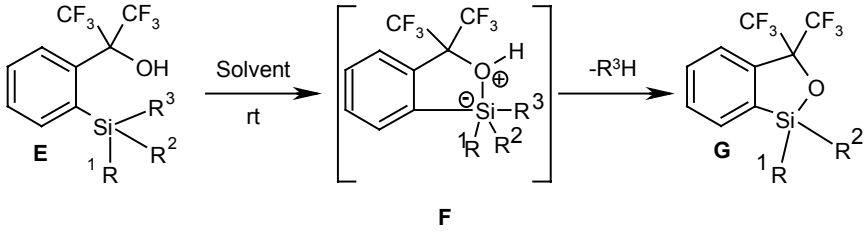


Chart 13. Cyclization by elimination of hydrocarbon

In our case however, prolonged stirring of carbinols **2a** and **2b** for two days using the above protocol in dry acetonitrile did not produce any cyclization products (by the loss of methane) either at room temperature or at elevated

temperature. An alkoxide intermediate thus seems to be imperative for the cyclization to occur.

Unlike the protocols described above, there are a very few reports on the formation of cyclic siloxanes through an intramolecular attack of an alkoxide on the silicon.

In course of their efforts towards the synthesis of C_{33}-C_{38} fragments of Amphotericin B and Nystatin, Brückner *et al.* effected a facile potassium alkoxide induced cyclization of the diol **H** with CsF and KOEt in EtOH/THF at 65 ^{o}C for almost two days to afford the cyclic siloxane **I** in 81 % yield (Chart-14).[33]

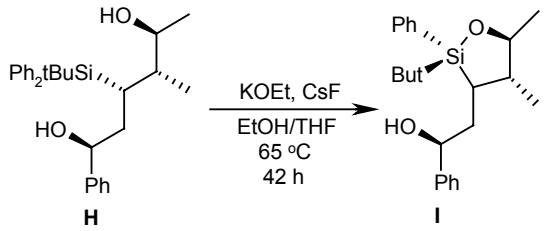


Chart 14. Cyclization by intramolecular attack of alkoxide

γ-Hydroxysilanes **J** are known to form alkoxides **K** on treatment with bases like KH, NaH and RLi in appropriate solvents. These alkoxides are shown to be in equilibrium with cyclic siloxanes **L** and anionic species R^-. Presence of an electrophilic reagent (E^+) results in **M** or E-R along with the cyclic siloxane **L** (Chart-15).[34]

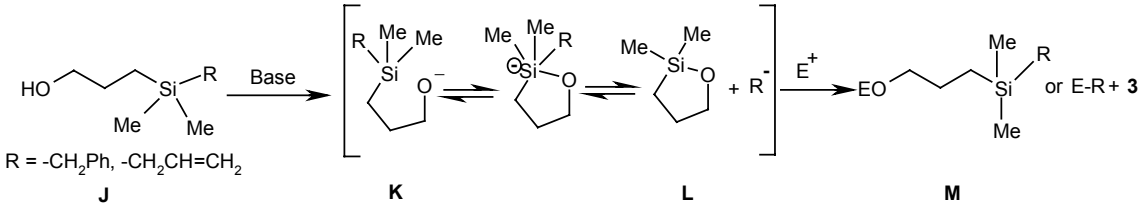


Chart 15. Cyclization of γ-hydroxysilanes by intramolecular attack of alkoxide

A similar cyclization by intramolecular nucleophilic attack of the alkoxide on Si resulting in cyclic siloxanes was recently reported by Takeda *et al*.[35] Lithium *tert*-butoxide was employed as a base in these reactions.

A novel and immensely useful protocol for a rapid and high yielding silicon-assisted cross-coupling of cycloalkenylsiloxane derivatives **O** with various aryl and alkenyl halides was recently described by Denmark (Chart-16).[36]

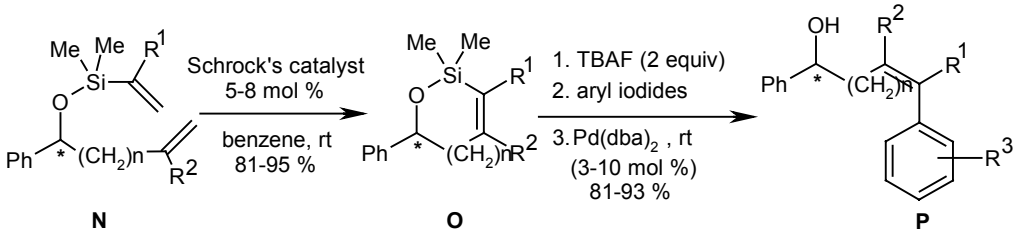
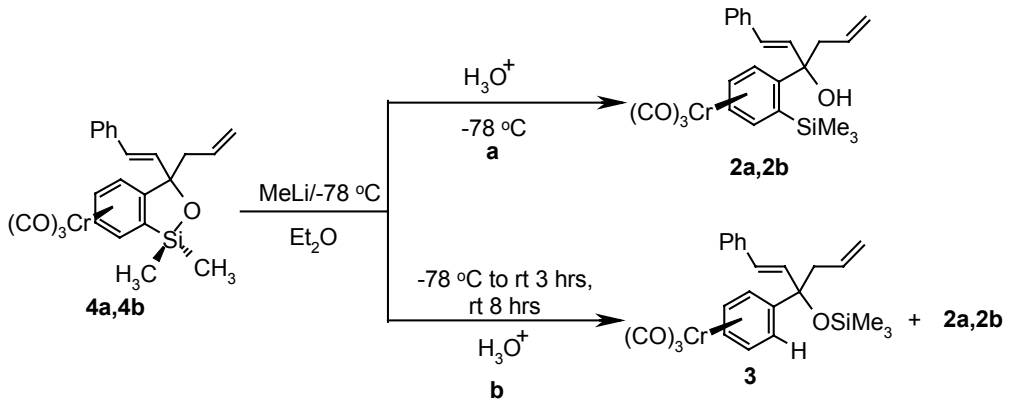


Chart 16. Silicon-assisted cross-coupling of cycloalkenyl siloxane

The required cyclic akenylsiloxanes are synthesized in good yield by RCM (Ring Closing Metathesis) of the corresponding vinylsiloxanes with a double bond tether (Chart-16). The product carbinols **P** consistently showed a Z-geometry of the resulting double bond.[37] An important advantage of the process is that the stereochemistry at the indicated carbon in **N** could be desirably controlled by asymmetric nucleophilic additions to the corresponding aldehyde.

It was thought that the presence of an anionic hypervalent silicon intermediate in the Si-O heterocyle formation could be proved by reversing the steps of cyclization. To this end, MeLi was added to the cyclized product **4a** in ether at -78 ^{o}C. The reaction cleanly resulted carbinol **2a** in 85 % yield (*path a*, Scheme-8). The same reaction mixture when allowed to warm up to room temperature (3 h) and stirred for further 8 hours gave **3** and **2a** in 1.5:1 ratio in an overall yield of 82 % (*path b*, Scheme-8).

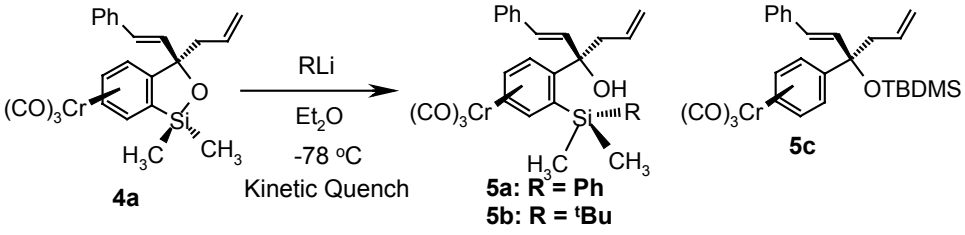


Scheme 8. Opening of the cyclic siloxane with MeLi leading to different products

The reaction of **4b** with MeLi under condition *a*, gave **2b** in 88 % yield, and under condition *b* afforded **3** and **2b** in the ratio 1.3:1 and 72 % overall yield.

Addition of methyllithium to **4** reversed the steps of heterocyclization as depicted in Scheme-8, to provide the lithium alkoxide **II** – eventually preferring Brook rearrangement as the kinetically favored pathway at warmer temperatures. This in turn implied that the pentacoordinated silicon intermediate with lithium counterion was not a low-energy species at room temperature. Corriu has earlier performed extensive studies on the attack of nucleophiles on a tetravalent silicon.[38]

The above reaction also hinted at an effective and useful way of preparing the carbinols **5** with a mixed substitution at the silicon by treating the cyclized product with phenyl and t-butyl lithium reagents at -78 ^{o}C (Scheme-9).



Scheme 9. Preparation of carbinols with mixed alkyl substituents on silicon

When the cyclized product **4a** in ether was treated with PhLi at -78 ^{o}C, carbinol **5a** was isolated in 93 % yield. Treatment of **4a** with *t*-BuLi at low temperature resulted in **5b** in 62 % yield. Surprisingly, a minor amount of Brook rearrangement product **5c** also was obtained in this reaction (16 %).

In contrast to the PhLi addition, addition of PhMgBr to **4a** in ether at -78 ^{o}C gave only 63 % of the carbinol **5a** while the rest of the starting material was recovered unreacted.

The experiment suggests that there exists an equilibrium between the intermediate alkoxides **II** and **III** (Fig. 3). While **II** is preferred at lower temperatures when MgBr is the counterion, **III** could be the intermediate at higher temperatures resulting eventually in the cyclization.

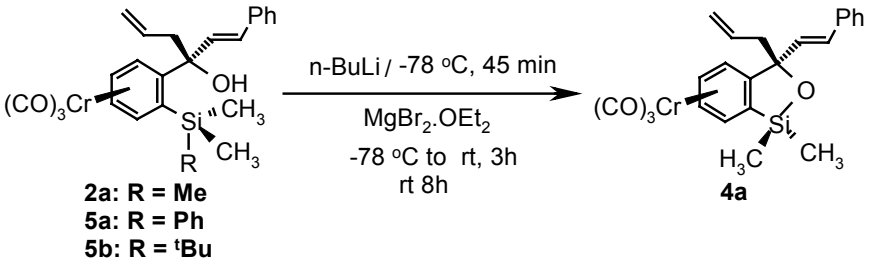
As for the structural features of these carbinols, the two *diastereotopic* Me groups on the Si have appeared as two separate singlets at δ 0.58 and 0.86 ppm in the proton NMR spectra of **5a**. The singlet that appeared at δ 2.32 ppm was assigned to the O*H* proton based on a deuterium exchange experiment.

It is notable that Δδ of the protons on the styryl moiety remained 0.34 ppm as in the case of carbinols **2a** and **2a'**. Since in the present case, there is no ambiguity in the stereochemistry of **5a**, Δδ can serve as a cue to the stereochemistry of other carbinols of this class prepared by other means.

The availability of carbinols **5a** and **5b** with Ph and ^{t}Bu groups respectively as hetero-substitutions on the Si as compared to the $SiMe_3$ moiety in carbinol **2a** presented us an opportunity to study the relative leaving group abilities of phenyl and *tert*-butyl groups over the methyl group from a hypervalent silicon.

This was made possible by subjecting these carbinols to cyclization by the counterion exchange protocol that was depicted in Scheme-6. Cyclization of both the carbinols afforded only **4a** and not the cyclic products resulting from the

expulsion of the Me group, the structures of which would carry a chiral silicon center (Scheme-10).



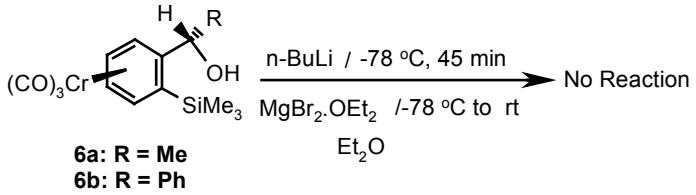
Scheme 10. Cyclization of the carbinols by counterion exchange

The experiment indicated that the leaving group abilities of phenyl and *tert*-butyl groups are much higher than that of the methyl group.[39] The result was in agreement with the gas-phase result by DePuy (Ph>> ^{t}Bu>Me),[40] it was slightly different from the one reported by Akiba in acetonitrile.[32]The results here have endorsed the fact that the structure of *ortho*-silylbenzyl alcohols dramatically affected the selectivity for the elimination of substituents.[32] It appears that the oxygen nucleophile approaches silicon from the least hindered side as in an S_N2 transition state and expels the larger alkyl group.

It was of immediate interest to examine the influence of substituents at the benzylic positions of these carbinols on their ability to cyclize. The presence of a styryl moiety at the benzylic position cannot specially influence the course of the reaction.

Also, unlike the ketones, the *ortho*-trimethylsilyl benzaldehyde arene tricarbonylchromium complexes can be easily resolved using the known protocols,[41] we envisioned that the cyclization of enantiomerically pure carbinols derived from these could result in optically active cyclic siloxanes.

In an attempt to realize this objective, the carbinols **6** derived from *o*-TMS benzaldehyde complex were subjected to the cyclization by both the counterion exchange protocol and Grignard-addition at low temperature followed up by warming up protocol.

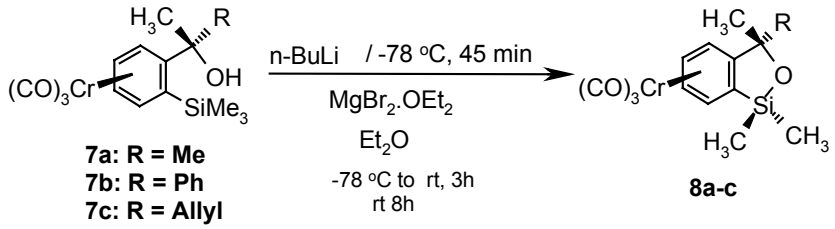


Scheme 11. Secondary benzylic alcohols failed to cyclize

Unfortunately, these carbinols failed to undergo the expected cyclization and the starting materials were recovered unreacted (Scheme-11). This has prompted us to suspect that a *geminal* disubstitution at the benzylic position could be essential for such cyclization.[32]

We prepared tertiary benzylic alcohols **7** from the *o*-TMS acetophenone complex in order to verify the above supposition. The relative stereochemistry of carbinols **7b** and **7c** depicted in Scheme-12 was based on the literature precedents.[41]

The carbinol **7a** when subjected to cyclization protocol by counterion exchange, gave the cyclized product **8a** in excellent yield (96 %). Cyclization of **7b** resulted in **8b** in 82 % yield (entry 2, Table-5). However, the reaction of **7c** was not very facile and resulted in only 60 % cyclized product **8c** (Scheme-12).

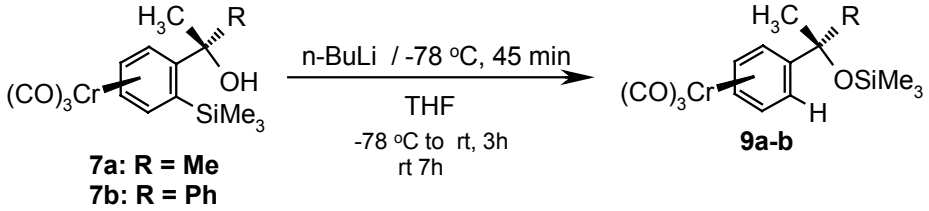


Scheme 12. Cyclization of tertiary benzylic alcohols

Table-5

Entry	Substrate	Product	Yield (%)
1	**7a**	**8a**	96
2	**7b**	**8b**	82
3	**7c**	**8c**	60

The Brook rearrangement too was facile with carbinols **7a** and **7b**. Carbinol **7a** when treated with n-BuLi in THF at -78 ^{o}C, allowed to warm up and stirred at room temperature for further seven hours, resulted **9a** in 89 % yield (entry 1, Table-6). Under same conditions, carbinol **7b** gave **9b** in 76 % yield (Scheme-13).



Scheme 13. Brook rearrangement of tertiary benzylic alcohols

Table-6

Entry	Substrate	Product	Yield (%)
1	**7a**	**9a**	89
2	**7b**	**9b**	76

Above experiments highlight the importance of a *gem*-disubstitution at the chiral center in formation of the cyclization product indicating that the Thorpe-Ingold effect is in play.[42]

Importance of *geminal* disubstitutions leading to a steric compression of trimethylsilyl groups in such cyclizations was elegantly demonstrated by Kirmse and Söllenböhmer. Where as **A** results in complete conversion to **C** with Bu^tOK in THF, the carbinol **B** failed to react (Chart-17).[43]

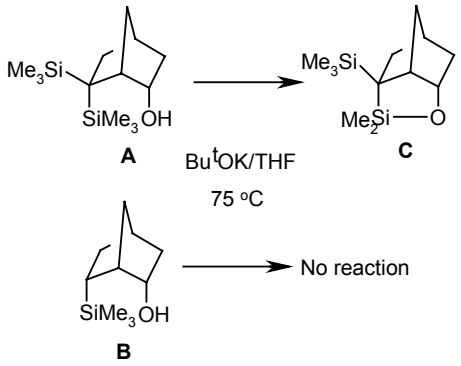


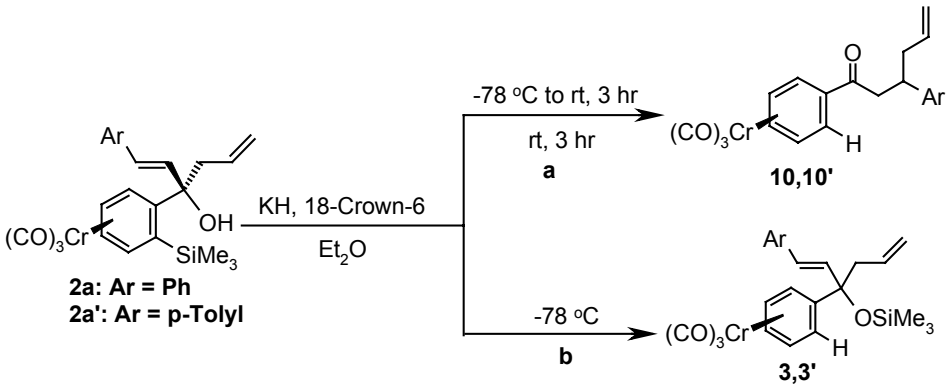
Chart 17. Importance of *gem*-disubstitution in cyclization

Complex **7d**, the $SnMe_3$ analogue of **7a**, underwent neither the cyclization nor the Brook rearrangement. This is in agreement with our earlier experiments indicating that C-Sn bond cleavage is not feasible under these reaction conditions.

Fortunately, the carbinols **2** upon which these interesting counterion dependent reaction pathways are manifested had structural features that presented us an opportunity to study the oxy-anionic Cope rearrangement reaction. Counterion dependence of this reaction is very well established and in general the rate of the reaction is accepted to be significantly dependent on the cation in the order K>>Li>Mg.[44]

When carbinol **2a** was treated with KH and a catalytic amount of 18-crown-6 in ether at -78 ^oC, allowed to warm-up to room temperature (3 h) and stirred for further three hours, product **10** was isolated in 79 % yield. A minor amount of desilylated starting carbinol was also obtained in this reaction (10 %).

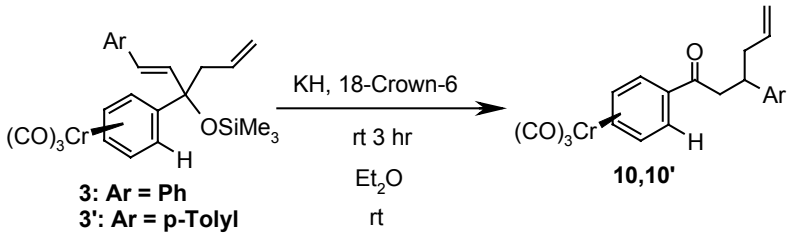
When **2a'** was employed as the starting carbinol, **10'** was obtained in 80 % yield and desilylated **2a'** was obtained in 14 % yield. The ketones **10** and **10'** though result from an anionic oxy-Cope rearrangement of the starting carbinols **2**, desilylation also seemed to have occurred in the process (*path a*, Scheme-14).



Scheme 14. Oxy-anionic Cope and Brook rearrangements of the same carbinol with KH, 18-Crown-6

Interestingly, when the above reaction was quenched at -78 ^{o}C, complex **3** resulting from a Brook rearrangement of the carbinol **2a** was the only product isolated in 90 % yield (*path b*, Scheme-14); with lithium as counterion, this rearrangement proceeded only after warming up to room temperature.

The finding indicated an intermediacy of complex **3** in the anionic oxy-Cope rearrangement of the carbinol **2a**. Facile conversion of **3** to **10** with KH and catalytic 18-Crown-6 in ether at room temperature in 74 % yield has supported this argument (Scheme-15). When **3'** was used as the substrate, **10'** was obtained in 79 % yield.

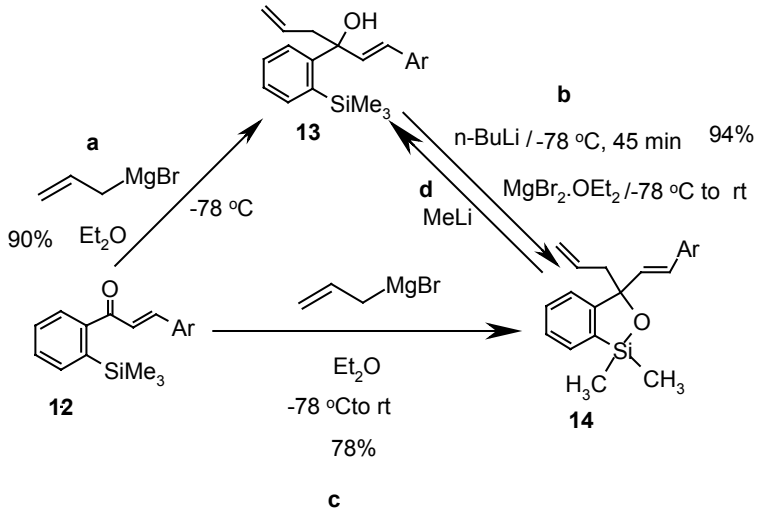


Scheme 15. Oxy Cope rearrangement of Brook rearrangement product

Apparently, initial formation of hypervalent silicon by the nucleophilic attack of the hydride on the $SiMe_3$ group and subsequent formation of an oxy-anion assists the formation of a Cope-rearrangement product.

Finally, we wanted to know whether presence of the tricarbonylchromium group is critical to this cyclization and other reactions described above. It was necessary therefore to subject an uncomplexed substrate to above reaction sequences.

Enone **12** was prepared by Claisen-Schmidt condensation of *o*-trimethylsilyl acetophenone **11** and benzaldehyde. Reaction of **12** with allylmagnesium bromide at –78 ^oC afforded the carbinol **13** in 90% yield (*path a*, Scheme-16). Carbinol **13** resulted in a facile cyclization when treated with n-BuLi/$MgBr_2.OEt_2$ (*path b*, Scheme-16).



Scheme 16. Reactions of uncomplexed substrates

The cyclized product **14** could be directly obtained by warming the reaction mixture of allylmagnesium bromide and enone **12** to room temperature and prolonged stirring (*path c*, Scheme-16). Additon of MeLi to **14** resulted in the carbinol in 93 % as in the case of tricarbonylchromium complexed substrates (*path d*, Scheme-16).

Brook rearrangement did not occur on the carbinol **13** under the same set of conditions employed for the complexed alcohol. The failure could be attributed to the reduced stability of an aryl anion in absence of metal complexation.

Taken together these reactions describe an unusual counterion dependence of selectivity in C-Si bond cleavage. These findings may be briefly summarized in the form of a Chart-18.

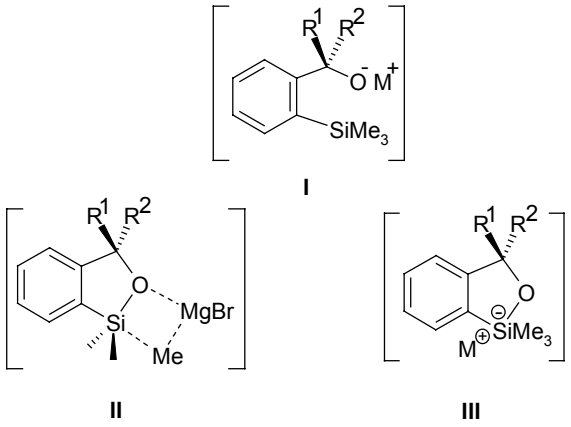


Chart 18. Possible intermediate alkoxides

Metal counterion	Temperature regime	Intermediate alkoxide	Reaction	Product
Li	-78 ^{o}C	**I**	Addition on enone	Carbinol+Conjugate
MgBr		**I**	Addition on enone	Carbinol
K		**III**	Brook Rearrangement	Brook Product
Li	-78 ^{o}C to rt	**III**	Brook Rearrangement	Brook Product
MgBr		**II**	Cyclization	Cyclic Siloxane
K		**III**	Oxy anionic-Cope	Oxy-Cope Product

Though the addition of allyllithium to complex **1** at low temperature resulted in conjugate addition as major product, this is considered a side reaction and the intermediate alkoxide that leads to the carbinols **2** is **I** and is essentially the same for both allylmagnesium bromide and allyllithium.

Formation of Brook rearrangement product with potassium as counterion at low temperature is however an interesting finding and could be possible only *via* **III**. The distinction of reaction pathways followed when Li and Mg are counterions is evident only at higher temperatures. Whereas Li prefers the intermediate alkoxide **III** leading to the Brook rearrangement, MgBr as counterion chooses to give the cyclization *via* **II**.

Anionic oxy-Cope rearrangement reaction with potassium as counterion seems to be an outcome of Cope-rearrangement of the Brook product that forms initially at low temperature *via* the alkoxide intermediate **III**.

Summary

This part of the thesis described an unusual reaction distinguished by interesting features: different counterions (Li, Mg, K) led to distinctly different pathways from presumably the same tertiary alkoxide intermediate in the same solvent and in practically the same temperature regime, to provide different products. It was a fortunate coincidence that carbinol under study had the structural features appropriate for all these reactions, and turned out to be a unique substrate upon which subtle yet decisive effects of alkali or alkaline earth metal cations are manifested. The thesis also reports one of the mildest methods to produce a Si-O heterocycle by reaction of a nucleophilic oxygen anion with silicon where an anionic methyl group is lost. Several questions regarding stability of pentacoordinated silicon, role of the tricarbonylchromium group, scope and generality of these transformations have been addressed.

Experimental

All reactions were performed under an inert atmosphere of argon, using freshly distilled, degassed solvents. Diethyl ether and THF were freshly distilled over sodium benzophenone ketyl. Organomagnesium and organolithium reagents were prepared following reported procedures.[45]Metal complexes were crystallized from dichloromethane-hexane/ dichloromethane-petroleum ether. Complexes **1'**, **2a'** and **2c'** are all reported in ref. 3.

Preparation of enone 1

A solution of benzaldehyde (280 mg, 2.64 mmol) and the *ortho*-trimethylsilyl acetophenone tricarbonylchromium complex (577 mg, 1.76 mmol) in ethanol (10 ml) was cooled in ice salt bath (0-5 ^{o}C). An ethanolic solution of KOH (99 mg, 1.76 mmol) in 10 ml ethanol was added dropwise *via* a syringe. Progress of the reaction was monitored by TLC. After complete disappearance of starting material (3 hours), ethanol was removed under reduced pressure and washed with water. The residue was extracted with dichloromethane. Removal of solvent provided the enone as red solid product. The crude solid product was washed with petroleum ether (3 x 20 ml) and recrystallized from dichloromethane-petroleum ether to afford analytically pure sample of **1** (695 mg, 95 %).

Complex 1

State	:	Red solid
Mp	:	96-97 °C
IR (Nujol)	:	1973, 1900, 1666 and 1607 cm^{-1}
^{1}H NMR	:	(δ, $CDCl_3$)
(200 MHz)		0.36 (9 H, s, Si*Me*$_3$), 5.46 (1 H, t, *J* 6, Ar*H*), 5.58 (2 H, t, *J* 6, Ar*H*), 5.75 (1 H, d, *J* 6, Ar*H*), 7.20 (1 H, d, *J* 15, PhCH=C*H*), 7.44 (3 H, m), 7.65 (2 H, m) and 7.88 (1 H, d, *J* 15 Hz, PhC*H*=CH).

^{13}C NMR	:	(δ, $CDCl_3$)
(50.3 MHz)		0.4, 92.6, 93.3, 98.8, 101.1, 107.7, 120.9, 128.7, 129.1, 131.1, 134.3, 145.8 and 231.8.
Analysis:	:	Calculated. : C, 60.56; H, 4.84.
		Observed: C, 60.62; H, 4.83 %

Reaction of enone 1 with Allylmagnesium Bromide: isolation of carbinols.

To a solution of **1** (175 mg, 0.42 mmol) in 5 ml ether cooled to -78 ^{o}C in a dry ice-acetone bath, freshly prepared allylmagnesium bromide (0.84 mmol, 0.84 ml from 1M ether solution) was added dropwise, during which, color of the reaction mixture turned from dark red to greenish yellow. The reaction was complete in 15 min (TLC). It was quenched at same temperature with saturated NH_4Cl and extracted with ether to furnish crude product. Purification by flash column chromatography (2 % acetone: petroleum ether) provided **2a** (77 mg, 45%) and **2b** (98 mg, 51%).

The reaction of **1'** (200 mg, 0.465 mmol) resulted in **2a'** (97 mg, 44%) and **2b'** (108 mg, 49%).

When THF was used as solvent, addition of allylmagnesium bromide to **1** afforded **2a**, **2b** and **2c** in 72, 11 and 9 % respectively. Addition to **1'** resulted in **2a'**, **2b'** and **2c'** in 75, 11 and 8 % respectively.

Reaction of enone 1 with AllylLithium: isolation of carbinols and conjugate addition products.

To a solution of **1** (183 mg, 0.44 mmol) in 5 ml ether cooled to -78 ^{o}C allyllithium (0.52 mmol, 1.04 ml from 0.5 M THF solution) was added dropwise, during which, the color of the reaction mixture turned from dark red to orange yellow. The reaction was complete in 15 min (TLC). It was quenched at same temperature with saturated NH_4Cl and extracted with ether followed by

evaporation of solvent gave the crude product. Purification by flash column chromatography (2 % acetone: petroleum ether) provided **2a** (78 mg, 39 %) and the conjugate addition product **2c** (95 mg, 47 %).

The reaction of **1'** (210 mg, 0.488 mmol) resulted in **2a'** (98 mg, 45 %) and **2c'** (119 mg, 49 %).

When THF was used as solvent, addition of allyllithium to **1** afforded **2a** and **2c** in 31 and 46 % respectively. Addition to **1'** resulted in **2a'** and **2c'** in 39 and 43 % respectively.

Complex 2a

State	:	Yellow solid
Mp	:	137-138 °C
IR (Nujol)	:	3535, 1961, 1894 and 1873 cm^{-1}
^{1}H NMR (300 MHz)	:	(δ, $CDCl_3$) 0.43 (9 H, s, Si*Me*$_3$), 2.46 (1 H, s, O*H*), 2.63-2.78 (2 H, m, C*H*$_2$), 5.07-5.19 (2 H, m, Ar*H*), 5.27 (2 H, d, *J* 9, Ar*H*), 5.58 (1 H, t, *J* 6, Ar*H*), 5.70 (1 H, d, *J* 6, CH=C*H*$_2$), 5.87-5.75 (1 H, m, C*H*=CH$_2$), 6.46 (1 H, d, *J* 16, PhC*H*=CH), 6.78 (1 H, d, *J* 16, PhCH=C*H*), 7.32-7.40 (3 H, m, Ph) and 7.47 (2 H, d, *J* 6, Ph).
^{13}C NMR (50.3 MHz)	:	(δ, $CDCl_3$) 3.5, 49.1, 76.5, 89.5, 89.7, 95.2, 96.5, 101.8, 120.9, 125.6, 126.8, 128.2, 128.7, 131.3, 132.2, 132.5, 136.2 and 233.1.
Analysis:	:	Calculated. : C, 62.86; H, 5.72. Observed: C, 62.39; H, 5.55 %

Complex 2b

State	:	Yellow solid
Mp	:	98-99 °C
IR (Nujol)	:	3547, 1960, 1877 and 1861 cm^{-1}
^{1}H NMR (300 MHz)	:	(δ, $CDCl_3$) 0.38 (9 H, s, Si*Me*$_3$), 2.62 (1 H, s, O*H*), 2.85-2.96 (2 H, m, C*H*$_2$), 5.27 (2 H, t, *J* 6, Ar*H*), 5.40 (2 H, d, *J* 6, Ar*H*), 5.63 (1 H, t, *J* 6, CH=C*H*$_2$), 5.70 (1 H, d, CH=C*H*$_2$), 5.88-6.02 (1 H, m, C*H*=CH$_2$), 6.31 (1 H, d, *J* 16, PhC*H*=CH), 6.43 (1 H, d, *J* 16, PhCH=C*H*) and 7.26-7.35 (5 H, m, Ph).
^{13}C NMR (75.48 MHz)	:	(δ, $CDCl_3$) 3.3, 46.9, 75.4, 89.5, 90.7, 94.6, 98.8, 101.5, 122.1, 126.2, 126.6, 128.0, 128.7, 130.0, 132.0, 135.6, 136.2 and 233.4.
Analysis:	:	Calculated. : C, 62.86; H, 5.72. Observed: C, 62.67; H, 5.85 %

Complex **2a'** is reported in ref. 3.

Complex 2b'

State	:	Yellow solid
Mp	:	116 °C
IR (Nujol)	:	3558, 1951, 1882 and 1874 cm^{-1}
^{1}H NMR (300 MHz)	:	(δ, $CDCl_3$) 0.36 (9 H, s, Si*Me*$_3$), 2.13 (3 H, s, C*H*$_3$), 2.34 (1 H, s, O*H*), 2.78-2.94 (2 H, m, C*H*$_2$), 5.24 (2 H, t, *J* 6, Ar*H*), 5.38 (2 H, d, *J* 12, Ar*H*), 5.62 (1 H, t, *J* 6, CH=C*H*$_2$), 5.69 (1 H, d, C*H*=CH$_2$), 5.86-6.02 (1 H, m, C*H*=CH$_2$),

6.25 (1 H, d, *J* 16, PhC*H*=CH), 6.37 (1 H, d, *J* 16, PhCH=C*H*), 7.13 (2 H, d, *J* 6, Ph) and 7.23 (2 H, d, *J* 6, Ph).

^{13}C NMR : (δ, $CDCl_3$)

(50.3 MHz) 3.3, 46.9, 75.3, 89.5, 90.7, 94.6, 98.7, 100.7, 122.4, 126.4, 129.3, 129.8, 132.0, 133.3, 134.5, 137.9 and 233.5.

Analysis: : Calculated. : C, 63.54; H, 5.97.

Observed: C, 63.34; H, 6.23 %

Complex 2a''

State : Yellow solid

Mp : 120 °C

IR (Nujol) : 3530, 1965, 1890 and 1878 cm^{-1}

^{1}H NMR : (δ, $CDCl_3$)

(200 MHz) 0.36 (9 H, s, Sn*Me*$_3$), 2.37 (3 H, s, C*H*$_3$), 2.46 (1 H, s, O*H*), 2.59 (1 H, dd, *J* 6, 14, C*H*$_2$), 2.74 (1 H, dd, *J* 6, 14, C*H*$_2$), 5.16-5.26 (4 H, m, 3xAr*H*, CH=C*H*$_2$), 5.46-5.54 (2 H, m, Ar*H*, CH=C*H*$_2$), 5.70-5.90 (1 H, m, C*H*=CH$_2$), 6.41 (1 H, d, *J* 16, PhC*H*=CH), 6.73 (1 H, d, *J* 16, PhCH=C*H*), 7.18 (2 H, d, *J* 8, Ph) and 7.37 (2 H, d, *J* 8, Ph).

^{13}C NMR : (δ, $CDCl_3$)

(50.3 MHz) 4.6, 21.2, 49.1, 91.0, 91.7, 93.8, 94.4, 96.4, 101.2, 120.7, 124.3, 126.7, 129.4, 130.4, 131.4, 132.4, 133.2 and 233.6.

Analysis: : Calculated. : C, 53.32; H, 5.01.

Observed: C, 53.05; H, 4.76%

Complex 2c

State	:	Red oil
IR (Nujol)	:	1973, 1900, 1879 and 1666 cm^{-1}
^1H NMR	:	(δ, $CDCl_3$)
(200 MHz)		0.18 (9 H, s, Si*Me*$_3$), 2.45 (2 H, t, *J* 6, CH_2=CHC*H*$_2$), 2.99-3.20 (2 H, m, COC*H*$_2$CHPh), 3.38-3.52 (1 H, m, CH_2C*H*Ph), 4.98-5.08 (2 H, m, Ar*H*), 5.45-5.49 (3 H, m, Ar*H*, CH_2=C*H*CH_2), 5.60-5.81 (2 H, m, C*H*$_2$=CH) and 7.19-7.34 (5 H, m, Ph).
^{13}C NMR	:	(δ, $CDCl_3$)
(50.3 MHz)		0.4, 40.5, 40.7, 43.5, 91.8, 93.4, 98.2, 102.0, 104.3, 117.0, 126.5, 127.5, 128.5, 136.1, 143.4, 199.4 and 231.4.
Analysis:	:	Calculated. : C, 62.86; H, 5.72.
		Observed: C, 63.52; H, 6.02 %

Complex **2c'** is reported in ref. 3.

Addition of allyllithium on 1: Formation of Brook rearrangement product and conjugate addition products.

To a solution of **1** (250 mg, 0.6 mmol) in 6 ml ether cooled to -78 ^oC allyllithium (0.72 mmol, 1.44 ml from 0.5 M THF solution) was added dropwise during which the color of reaction mixture turned from dark red to orange yellow. It was allowed to warm up to room temperature (3 h) and was stirred for further 8 h. At the end, the reaction mixture was blackish green in color**.** After usual workup, crude product obtained was purified by flash column chromatography (2 % acetone: petroleum ether) affording **3** (110 mg, 40 %) and the conjugate addition product **2c** (124 mg, 45 %).

The reaction of **1'** (200 mg, 0.465 mmol) resulted in **3'** (92 mg, 42 %) and **2c'** (112 mg, 51 %).

Reaction of carbinol 2a with n-BuLi: Brook rearrangement.

To a solution of **2a** (137 mg, 0.3 mmol) in 4 ml ether cooled to -78 ^{o}C, n-BuLi (0.45 mmol, 0.27 ml from 1.66 M n-hexane solution) was added dropwise. There was no change in the color. It was allowed to warm up to room temperature (3 h) and was stirred for further 8 h. At the end, the reaction mixture was blackish green in color**.** Usual workup gave the crude product, which was purified by flash column chromatography (2 % acetone: petroleum ether) affording **3** (126 mg, 92 %).

The reaction of **2a'** (150 mg, 0.318 mmol) gave **3'** (141 mg, 94 %).

The reaction of a 1:1 mixture of carbinols **2a** and **2b** (145 mg, 0.318 mmol) in 5 ml ether with n-BuLi under the same conditions as above resulted in **3** as a single product (113 mg, 78 %).

Complex 3

State	:	Yellow solid
Mp	:	108 °C
IR (Nujol)	:	1958, 1884 and 1867 cm^{-1}
^{1}H NMR (300 MHz)	:	(δ, $CDCl_3$) 0.21 (9 H, s, Si*Me*$_3$), 2.64 (1 H, dd, *J* 7, 14, C*H*$_2$), 2.93 (1 H, dd, *J* 7, 14, C*H*$_2$), 4.94-5.29 (5 H, m, 4xAr*H*, HC*H*=CH), 5.44 (1 H, t, *J* 6, Ar*H*), 5.77 (1 H, sextet, *J* 6, CH_2=C*H*), 5.91 (1 H, d, *J* 6, *H*CH=CH), 6.50 (1 H, d, *J* 15, PhC*H*=CH), 6.67 (1 H, d, *J* 15, PhCH=C*H*) and 7.27-7.54 (5 H, m, Ph).
^{13}C NMR (50.3 MHz)	:	(δ, $CDCl_3$) 2.2, 46.2, 76.7, 88.9, 89.2, 93.4, 94.1, 94.6, 116.8, 118.9,

126.8, 128.3, 128.6, 130.5, 132.6, 133.7, 136.0 and 233.2.

Analysis: : Calculated. : C, 62.86; H, 5.72.
Observed: C, 62.42; H, 5.84 %

Complex 3'

State : Yellow solid

Mp : 98 °C

IR (Nujol) : 1956, 1887 and 1862 cm^{-1}

^{1}H NMR : (δ, $CDCl_3$)

(300 MHz) 0.19 (9 H, s, Si*Me*$_3$), 2.37 3H, s, C*H*$_3$), 2.64 (1 H, dd, *J* 7, 14, C*H*$_2$), 2.93 (1 H, dd, *J* 7, 14, C*H*$_2$), 4.94-5.29 (5 H, m, Ar*H*, HC*H*=CH), 5.44 (1 H, t, *J* 6, Ar*H*), 5.77 (1 H, sextet, *J* 6, CH_2=C*H*), 5.91 (1 H, d, *J* 6, HC*H*=CH), 6.50 (1 H, d, *J* 15, PhC*H*=CH), 6.67 (1 H, d, *J* 15, PhCH=C*H*) and 7.27-7.54 (5 H, m, Ph).

^{13}C NMR : (δ, $CDCl_3$)

(50.3 MHz) 2.2, 21.2, 46.1, 76.6, 88.9, 89.2, 93.5, 94.2, 94.7, 116.9, 118.8, 126.7, 129.5, 130.2, 132.6, 133.1, 138.1 and 233.2.

Analysis: : Calculated. : C, 63.54; H, 5.97.
Observed: C, 63.20; H, 5.90 %

Allylmagnesium Bromide addition to 1: Formation of Si-O heterocycle.

To a solution of **1** (416 mg, 1 mmol) in 10 ml ether cooled to -78 ^{o}C freshly prepared allylmagnesium bromide (3 mmol, 3 ml from 1M ether solution) was added over 5 min during which period the color of the reaction mixture turned from dark red to greenish yellow. It was allowed to warm up to room temperature (3 h) and was stirred for further 8 h. At the end, the reaction mixture was orange in

color. Usual work up gave the crude product, which was filtered through a pad of neutral alumina. Evaporation of solvent followed by crystallization from ether/pentane at <5 ^{o}C afforded **4b** (234 mg, 53 %). Mother liquor was filtered through alumina and concentrated. Crystallization of the residue from DCM/petroleum ether provided **4a** (190 mg, 43 %).

The reaction of **1'** (430 mg, 1 mmol) in ether gave **4a'** (196 mg, 43 %) and **4b'** (233 mg, 51 %).

When THF was used as solvent, addition of allylmagnesium bromide to **1** afforded **4a**, **4b** and **2c** in 64, 9 and 8 % respectively. Addition to **1'** resulted in **4a'**, **4b'** and **2c'** in 60, 8 and 7 % respectively.

Exchange of Li with Magnesium Counterion:

Addition of allyllithium to enone followed by $MgBr_2.OEt_2$:

Dropwise addition of allyllithium (0.58 mmol, 1.2 ml from 0.5 M THF solution) to a solution of **1** (200 mg, 0.48 mmol) in 5 ml ether cooled to -78 ^{o}C resulted in a rapid change in the color of the reaction mixture from dark red to orange yellow. The reaction was complete in 15 min (TLC). At this point $MgBr_2.OEt_2$ (1.44 mmol dissolved in 3 ml of dry ether) was added dropwise through a syringe. The reaction mixture was then allowed to warm up to room temperature (3 h) and was stirred for further 8 h. At the end, the reaction mixture was greenish brown in color**.** Usual workup gave the crude product that was purified by flash column chromatography (3 % acetone: petroleum ether) to afford **4a** (85 mg, 40 %) and the conjugate addition product **2c** (97 mg, 44 %).

The reaction of **1'** (250 mg, 0.581 mmol) in ether gave **4a'** (114 mg, 43 %) and **2c'** (134 mg, 49 %).

Deprotonation of carbinol 2a with n-BuLi followed by $MgBr_2.OEt_2$:

To a solution of **2a** (220 mg, 0.48 mmol) in 6 ml ether cooled to -78 ^{o}C, n-BuLi (0.58 mmol, 0.41 ml from 1.41 M n-hexane solution) was added dropwise.

There was no change in the color. The reaction mixture was stirred at same temperature for 45 minutes after which $MgBr_2.OEt_2$ (300 mg, 1.16 mmol dissolved in 3 ml of dry ether) was added dropwise through a syringe. The reaction mixture was then allowed to warm up to room temperature (3 h) and stirred for further 8 h. At the end, the reaction mixture was blackish green to bottle green in color**.** Usual workup gave the crude product, which was purified by flash column chromatography (10 % acetone: petroleum ether) affording **4a** (208 mg, 98 %).

The reaction of **2b** (150 mg, 0.328 mmol) gave **4b** (203 mg, 96 %).

Cyclization in presence of benzophenone: Trapping the Methyl anion.

To a solution of **1** (832 mg, 2 mmol) in 20 ml ether cooled to -78 ^{o}C freshly prepared allylmagnesium bromide was added (6 mmol, 6 ml from 1M ether solution) over 6-8 min, during which, the color of the reaction mixture turned from dark red to greenish yellow. Benzophenone (437 mg, 2.4 mmol in 3 ml dry ether) was added dropwise through a syringe to this mixture at the same temperature. It was allowed to warm up to room temperature (3 h) and was stirred for further 8 h. At the end, the reaction mixture was orange in color. Usual workup gave the crude product that was filtered through a pad of neutral alumina. Purification by flash column chromatography (2 % acetone: petroleum ether) provided **4** (725 mg, 82 % as 1:1.2 mixture of **4a** and **4b**) and diphenyl methyl carbinol (309 mg, 65 % yield, 0.95 mol % w. r. to the yield of **4**). Also a minor amount of diphenyl allyl carbinol was obtained (22 mg, 10 %). Rest of the benzophenone was recovered unreacted (total mass recovery of benzophenone was 98 %).

Complex 4a

State : Yellow solid

Mp : 98 °C

IR (Nujol) : 1962, 1892 and 1871 cm^{-1}

^{1}H NMR (200 MHz)	:	(δ, $CDCl_3$) 0.50 (3 H, s, Si*Me*$_3$), 0.66 (3 H, s, Si*Me*$_3$), 2.60 (2 H, d of AB q, *J* 7, 14, C*H*$_2$), 4.99-5.13 (2 H, m, Ar*H*), 5.18 (1 H, d, *J* 6, C*H*$_2$=CH), 5.34 (1 H, d, *J* 6, C*H*$_2$=CH), 5.48-5.79 (3 H, m, Ar*H*, CH_2=C*H*), 6.37 (1 H, d, *J* 15, PhC*H*=CH), 6.79 (1 H, d, *J* 15, PhCH=C*H*) and 7.21-7.48 (5 H, m, Ph).
^{13}C NMR (50.3 MHz)	:	(δ, $CDCl_3$) 1.7, 49.4, 85.2, 86.5, 90.5, 93.5, 93.8, 96.0, 116.8, 119.2, 126.8, 127.5, 128.0, 128.4, 128.5, 131.8, 132.4, 136.5, 159.6 and 232.3.
Analysis:	:	Calculated. : C, 62.43; H, 5.01. Observed: C, 62.08; H, 5.11%

Complex 4b

State	:	Yellow solid
Mp	:	119 °C
IR (Nujol)	:	1965, 1887 and 1867 cm^{-1}
^{1}H NMR (300 MHz)	:	(δ, $CDCl_3$) 0.45 (3 H, s, Si*Me*$_3$), 0.68 (3 H, s, Si*Me*$_3$), 2.82 (2 H, d of AB q, *J* 7, 14, C*H*$_2$), 5.17-5.31 (3 H, m, 3xAr*H*), 5.45-5.48 (3 H, m, Ar*H*, C*H*$_2$=CH), 5.95 (1 H, d of t, *J* 6, 16, CH_2=C*H*), 6.23 (1 H, d, *J* 15, PhC*H*=CH), 6.53 (1 H, d, *J* 15, PhCH=C*H*) and 7.25-7.32 (5 H, m, Ph).
^{13}C NMR (50.3 MHz)	:	(δ, $CDCl_3$) 1.0, 1.9, 84.8, 88.1, 92.0, 92.4, 93.1, 118.7, 126.6, 127.9, 128.6, 129.1, 133.0, 134.2, 136.2 and 232.7
Analysis:	:	Calculated. : C, 62.43; H, 5.01.

Observed: C, 62.15; H, 4.81%

Complex 4a'

State	:	Yellow solid
Mp	:	109 °C
IR (Nujol)	:	1952, 1882 and 1867 cm^{-1}
^1H NMR	:	(δ, $CDCl_3$)
(200 MHz)		0.51 (3 H, s, Si*Me*$_3$), 0.66 (3 H, s, Si*Me*$_3$), 2.36 (3 H, s, C*H*$_3$), 2.60 (2 H, d of AB q, *J* 7, 14, C*H*$_2$), 4.99-5.12 (2 H, m, Ar*H*), 5.18 (1 H, d, *J* 6, C*H*$_2$=CH), 5.33 (1 H, d, *J* 6, C*H*$_2$=CH), 5.48-5.55 (2 H, m, Ar*H*), 5.62-5.79 (1 H, m, CH_2=C*H*), 6.34 (1 H, d, *J* 15, PhC*H*=CH), 6.76 (1 H, d, *J* 15, PhCH=C*H*), 7.16 (2 H, d, *J* 8, Ph) and 7.37 (2 H, d, *J* 8, Ph).
^{13}C NMR	:	(δ, $CDCl_3$)
(50.3 MHz)		1.7, 21.1, 49.5, 85.2, 86.5, 90.4, 93.5, 93.8, 95.9, 119.2, 126.7, 128.2, 129.2, 130.9, 132.5, 133.7, 136.5, 137.4 and 232.3.
Analysis:	:	Calculated. : C, 63.14; H, 5.30.
		Observed: C, 63.0; H, 4.85 %

Complex 4b'

State	:	Yellow solid
Mp	:	169 °C
IR (Nujol)	:	1954, 1890 and 1843 cm^{-1}
^1H NMR	:	(δ, $CDCl_3$)
(200 MHz)		0.45 (3 H, s, Si*Me*$_3$), 0.67 (3 H, s, Si*Me*$_3$), 2.33 (3 H, s, C*H*$_3$), 2.81 (2 H, d of AB q, *J* 7, 14, C*H*$_2$), 5.13-5.32 (3

H, m, Ar*H*, CH_2=CH), 5.44-5.49 (3 H, m, Ar*H*, CH_2=C*H*), 5.84-6.05 (1 H, m, C*H*=CH_2), 6.17 (1 H, d, *J* 15, PhC*H*=CH), 6.49(1 H, d, *J* 15, PhCH=C*H*), 7.11 (2 H, d, *J* 8, Ph) and 7.22 (2 H, d, *J* 8, Ph).

^{13}C NMR (50.3 MHz) : (δ, $CDCl_3$)
1.0, 1.8, 47.5, 84.8, 88.1, 91.9, 92.3, 93.1, 118.7, 126.5, 129.0, 129.3, 133.0, 133.2, 137.8, 159.7 and 232.8.

Analysis: : Calculated. : C, 63.14; H, 5.30.
Observed: C, 63.19; H, 5.33 %

General Procedure for opening the Si-O hetrocycle: Addition of RLi to 4 at low temperature.

To a solution of **4** (n mmol) in 10n ml ether cooled to -78 ^{o}C RLi (1.2-1.5n mmol) was added dropwise. There was no change in the color. The reaction was complete in 15 min (TLC). Quenching at same temperature with saturated NH_4Cl solution and extraction with ether gave the crude product. Purification by flash column chromatography provided the corresponding carbinols.

Addition of MeLi to **4a** (204 mg, 0.46 mmol) resulted in **2a** (180 mg, 85 %). The same reaction on the cyclized product **4b** (210 mg, 0.46 mmol) gave **2b** (191 mg, 88 %) exclusively.

Preparation of carbinols 5a and 5b:

Following the same procedure as above, addition of PhLi (2.2 ml of 0.3 M PhLi in ether, 0.66 mmol) to **4a** (196 mg, 0.443 mmol) resulted in **5a** (214 mg, 93 %).

Addition of *t*-BuLi (0.7 ml of 0.98 M *t*-BuLi, 0.68 mmol) to **4a** (200 mg, 0.45 mmol) resulted in **5b** (140 mg, 62 %). Also a minor amount of **5c** (36 mg, 16 %) was obtained in this reaction.

Addition of freshly prepared PhMgBr (0.53 ml of 1 M solution in ether, 0.53 mmol) to **4a** (194 mg, 0.44 mmol) in 5 ml ether gave **5a** (144 mg, 63 %), rest of the starting material was recovered unreacted.

Cyclization of the carbinols 5a and 5b:

Cyclization of the carbinols was carried out following the counterion exchange protocol by deprotonation described above with carbinol **2**. The carbinol **5a** (169 mg, 0.32 mmol) in 5 ml ether gave **4a** (128 mg, 89 %). Cyclization of the carbinol **5b** (180 mg, 0.36 mmol) resulted in **4a** (148 mg, 93 %).

Complex 5a

State	:	Yellow solid
Mp	:	105-106 °C
IR (Nujol)	:	3018, 1967and 1896 cm^{-1}
^{1}H NMR (200 MHz)	:	(δ, $CDCl_3$) 0.58 (3 H, s, Si*Me*$_3$), 0.86 (3 H, s, Si*Me*$_3$), 2.18-2.32 (1 H, m, C*H*$_2$), 2.32 (1 H, s, O*H*), 2.49-2.63 (1 H, m, C*H*$_2$), 4.38 (1 H, d, *J* 18, HC*H*=CH), 4.96 (1 H, d, *H*CH=CH), 5.07-5.14 (2 H, m, Ar*H*), 5.47-5.67 (3 H, m, 2xAr*H*, CH_2=C*H*), 6.37 (1 H, d, *J* 16, PhC*H*=CH), 6.71 (1 H, d, *J* 16, PhCH=C*H*) and 7.25-7.64 (10 H, m, 2xPh).
^{13}C NMR (50.3 MHz)	:	(δ, $CDCl_3$) 1.6, 2.7, 26.9, 48.8, 76.2, 89.2, 89.5, 95.4, 102.5, 121.3, 125.7, 126.7, 128.0, 128.6, 128.8, 130.7, 131.7, 133.6, 136.2, 141.4 and 232.9.
Analysis:	:	Calculated. : C, 66.91; H, 5.42. Observed: C, 67.11; H, 5.51 %

Complex 5b

State : Yellow solid

Mp : 119 °C

IR (Nujol) : 3020, 1971and 1886 cm^{-1}

^{1}H NMR : (δ, $CDCl_3$)

(200 MHz) 0.34 (3 H, s, Si*Me*$_3$), 0.57 (3 H, s, Si*Me*$_3$), 1.03 (9 H, s, 3xC*H*$_3$), 2.43 (1 H, s, O*H*), 2.60-2.79 (2 H, m, C*H*$_2$), 5.18-5.33 (4 H, m, Ar*H*, C*H*$_2$=CH), 5.47 (2 H, d, *J* 6, Ar*H*), 5.67-5.88 (1 H, m, CH_2=C*H*), 6.29 (1 H, d, *J* 16, PhC*H*=CH), 6.66 (1 H, d, *J* 16, PhCH=C*H*) and 7.24-7.49 (5 H, m, Ph).

^{13}C NMR : (δ, $CDCl_3$)

(50.3 MHz) 0.3, 18.9, 28.6, 49.4, 75.0, 91.7, 92.6, 93.2, 97.3, 100.2, 121.6, 126.8, 127.8, 128.6, 132.3, 133.6, 136.3 and 233.1.

Analysis: : Calculated. : C, 64.77; H, 6.44.

Observed: C, 64.77; H, 6.88 %

Complex 5c

State : Yellow solid

Mp : 104 °C

IR (Nujol) : 1956, 1892, 1875 and 1466 cm^{-1}

^{1}H NMR : (δ, $CDCl_3$)

(200 MHz) 0.11 (3 H, s, Si*Me*$_3$), 0.17 (3 H, s, Si*Me*$_3$), 0.99 (9 H, s, 3xC*H*$_3$), 2.63 (1 H, dd, *J* 8, 14, C*H*$_2$), 2.93 (1 H, dd, *J* 8, 14, C*H*$_2$), 4.93 (1 H, d, *J* 16, HC*H*=CH), 5.02-5.14 (2H, m, Ar*H*), 5.24 (2H, t, *J* 6, Ar*H*), 5.69-5.86 (1H, m, H_2C=C*H*), 5.93 (1 H, d, *J* 6, *H*CH=CH), 6.52 (1 H, d, *J*

16, PhC*H*=CH), 6.70 (1 H, d, *J* 16, PhC*H*=CH) and 7.31-7.54 (5 H, m, Ph).

^{13}C NMR : (δ, $CDCl_3$)

(50.3 MHz) -1.8, -2.2, 18.6, 26.2, 46.2, 89.2, 89.5, 92.9, 93.5, 94.4, 117.2, 119.0, 126.8, 128.4, 128.9, 130.4, 132.5, 133.6, 135.9 and 233.1.

Analysis: : Calculated. : C, 64.77; H, 6.44.

Observed: C, 64.76; H, 6.39 %

Preparation of carbinols 7a-d:

In general the carbinols **7a-c** were prepared in excellent yields (**7a**-96 %, **7b**-80 %, **7c**-90 % and **7d**-94 %) by the addition 1.5 equivalents of corresponding freshly prepared Grignard reagent in ether to the *ortho*-trimethylsilyl acetophenone tricarbonylchromium complex in THF at -78 ^{o}C. The color of the reaction mixture immediately turned to yellow from red. The reaction was complete in 15 minutes (TLC), it was quenched at same temperature with saturated NH_4Cl, allowed to warm up to room temperature and worked up in the usual manner. The yields are of chromatographically purified products.

Carbinols **6a** and **6b** are reported in ref. 41.

Complex 7a

State : Yellow solid

Mp : 107 °C

IR (Nujol) : 3560, 1958, 1892 and 1861 cm^{-1}

^{1}H NMR : (δ, $CDCl_3$)

(200 MHz) 0.37 (9 H, s, Si*Me*$_3$), 1.5 (3 H, s, C*H*$_3$), 1.68 (3 H, s, C*H*$_3$), 1.96 (1 H, s, O*H*), 5.03 (1 H, d, *J* 6, Ar*H*), 5.18 (1 H, t, *J* 6, Ar*H*), 5.63 (1 H, t, *J* 6, Ar*H*) and 5.76 (1 H, t, *J* 6, Ar*H*).

^{13}C NMR	:	(δ, $CDCl_3$)
(50.3 MHz)		3.3, 30.7, 34.1, 73.1, 88.1, 89.7, 96.3, 96.9, 103.0, 121.8, 129.3 and 233.7.
Analysis:	:	Calculated. : C, 52.31; H, 5.85.
		Observed: C, 52.21; H, 5.50 %

Complex 7b

State	:	Yellow solid
mp	:	96 °C
IR (Nujol)	:	3538, 1974, 1890 and 1856 cm^{-1}
^{1}H NMR	:	(δ, $CDCl_3$)
(200 MHz)		0.09 (9 H, s, Si*Me*$_3$), 1.91 (3 H, s, C*H*$_3$), 2.61 (1 H, s, O*H*), 5.27 (1 H, d, *J* 6, Ar*H*), 5.33 (1 H, t, *J* 6, Ar*H*), 5.72 (1 H, t, *J* 6, Ar*H*), 5.80 (1 H, t, *J* 6, Ar*H*) and 7.28 (5 H, m, Ph).
^{13}C NMR	:	(δ, $CDCl_3$)
(50.3 MHz)		2.6, 33.3, 90.4, 91.0, 95.0, 99.7, 102.4, 125.8, 127.2, 127.5, 128.1, 147.3 and 233.6.
Analysis:	:	Calculated. : C, 59.09; H, 5.46.
		Observed: C, 59.38; H, 5.28 %

Complex 7c

State	:	Yellow solid
mp	:	69 °C
IR (Nujol)	:	3020, 1965, 1890 and 1215 cm^{-1}
^{1}H NMR	:	(δ, $CDCl_3$)
(200 MHz)		0.38 (9 H, s, Si*Me*$_3$), 1.60 (3 H, s, C*H*$_3$), 2.08 (1 H, s, O*H*), 2.29 (1 H, dd, *J* 8, 14, C*H*$_2$), 2.57 (1 H, dd, *J* 8, 14,

		CH_2), 4.99 (1 H, d, *J* 6, Ar*H*), 5.08-5.23 (3 H, m, 2xAr*H*, H_2C=CH), 5.62 (1 H, t, *J* 6, Ar*H*) and 5.72-5.93 (3 H, m, Ar*H*, H_2C=CH, H_2C=C*H*).
^{13}C NMR	:	(δ, $CDCl_3$)
(50.3 MHz)		3.4, 27.7, 50.2, 74.6, 88.7, 89.8, 95.7, 102.7, 120.0, 121.7, 128.6, 132.7 and 233.6.
Analysis:	:	Calculated. : C, 55.12; H, 5.97.
		Observed: C, 55.56; H, 5.82 %

Complex 7d

State	:	Yellow solid
mp	:	115 °C
IR (Nujol)	:	3570, 1948, 1886 and 1875 cm^{-1}
^{1}H NMR	:	(δ, $CDCl_3$)
(200 MHz)		0.31 (9 H, s, Sn*Me*$_3$), 1.46 (3 H, s, CH_3), 1.67 (3 H, s, CH_3), 1.93 (1 H, s, O*H*), 5.14 (1 H, d, *J* 6, Ar*H*), 5.23 (1 H, t, *J* 6, Ar*H*), 5.55 (1 H, dd, *J* 2, 6, Ar*H*) and 5.61 (1 H, dd, *J* 2, 6, Ar*H*).
^{13}C NMR	:	(δ, $CDCl_3$)
(50.3 MHz)		-4.8, 29.4, 34.3, 72.9, 89.1, 91.3, 95.6, 97.0, 102.9, 128.0 and 234.2.
Analysis:	:	Calculated. : C, 41.42; H, 4.63.
		Observed: C, 41.49; H, 5.17 %

Cyclization of the carbinols 7a, 7b and 7c:

Cyclization of these carbinols was carried out following the counterion exchange protocol by deprotonation with n-BuLi followed by $MgBr_2.OEt_2$ as described above with carbinols **2** and **5**.

Carbinol **7a** (151 mg, 0.439 mmol) in 5 ml ether for 8 hours at room temperature gave **8a** (138 mg, 96 %). Complex **7b** (120 mg, 0.296 mmol) resulted in **8b** (94 mg, 82 %). Carbinol **7c** (140 mg, 0.378 mmol) yielded **8c** (80 mg, 60 %).

Complex 8a

State	:	Yellow solid
Mp	:	113 °C
IR (Nujol)	:	1950, 1877 and 1853 cm^{-1}
^{1}H NMR (200 MHz)	:	(δ, $CDCl_3$) 0.41 (3 H, s, Si*Me*$_3$), 0.59 (3 H, s, Si*Me*$_3$), 1.46 (3 H, s, C*H*$_3$), 1.65 (3 H, s, C*H*$_3$), 5.19-5.27 (2 H, m, Ar*H*) and 5.44-5.53 (2 H, m, Ar*H*).
^{13}C NMR (50.3 MHz)	:	(δ, $CDCl_3$) 0.9, 2.0, 30.2, 34.5, 81.5, 86.7, 91.2, 93.3, 93.9, 96.7, 131.3 and 232.9.
Analysis:	:	Calculated. : C, 51.21; H, 4.91. Observed: C, 51.70; H, 5.16 %

Complex 8b

State	:	Yellow solid
Mp	:	129 °C
IR (Nujol)	:	3018, 1969 and 1898 cm^{-1}
^{1}H NMR (200 MHz)	:	(δ, $CDCl_3$) 0.28 (3 H, s, Si*Me*$_3$), 0.68 (3 H, s, Si*Me*$_3$), 1.99 (3 H, s, C*H*$_3$), 5.22-5.30 (1 H, m, Ar*H*) and 5.50-5.57 (3 H, m, Ar*H*).
^{13}C NMR (50.3 MHz)	:	(δ, $CDCl_3$) 1.1, 31.6, 84.5, 88.2, 91.5, 92.6, 93.6, 97.1, 125.1, 127.4,

128.2, 130.4, 147.1 and 232.7.

Analysis: : Calculated. : C, 58.45; H, 4.65.
Observed: C, 58.41; H, 5.15 %

Complex 8c

State : Yellow solid

mp : 99 °C

IR (Nujol) : 3025, 1971 and 1884 cm^{-1}

^{1}H NMR : (δ, $CDCl_3$)

(200 MHz) 0.43 (3 H, s, Si*Me*$_3$), 0.59 (3 H, s, Si*Me*$_3$), 1.62 (3 H, s, C*H*$_3$), 2.38-2.41 (2 H, m, C*H*$_2$), 4.97-5.17 (3 H, m, 2xAr*H*, C*H*$_2$=CH), 5.21-5.26 (2 H, m, Ar*H*), 5.44-5.52 (1 H, m, C*H*$_2$=CH) and 5.61-5.76 (1 H, m, CH_2=C*H*).

^{13}C NMR : (δ, $CDCl_3$)

(50.3 MHz) 1.4, 1.9, 28.6, 48.5, 50.7, 83.6, 87.0, 91.3, 92.8, 93.5, 119.2, 124.8, 128.2, 132.9, 133.7 and 232.7.

Analysis: : Calculated. : C, 52.93; H, 4.74.
Observed: C, 52.70; H, 5.15 %

Brook rearrangement of the Carbinols 7a and 7b:

To a solution of **7a** (100 mg, 0.291 mmol) in 4 ml THF cooled to -78 ^{o}C, n-BuLi (0.35 mmol, 0.23 ml from 1.5 M n-hexane solution) was added dropwise. There was no change in the color. The reaction was allowed to stir at this temperature for 45 minutes and then was allowed to warm up to room temperature (3 h) and further stirred for 8 h. At the end, the reaction mixture was blackish green in color**.** Usual workup gave the crude product, which was purified by flash column chromatography (4 % acetone: petroleum ether) affording **9a** (89 mg, 89 %).

Complex **7b** (106 mg, 0.26 mmol) resulted in **9b** (80 mg, 76 %).

Complex 9a

State	:	Yellow solid
mp	:	108 °C
IR ($CHCl_3$)	:	3020, 1969 and 1894 cm^{-1}
^1H NMR	:	(δ, $CDCl_3$)
(200 MHz)		0.21 (9 H, s, Si*Me*$_3$), 1.54 (6 H, s, 2xC*H*$_3$), 5.20 (2 H, t, *J* 6, Ar*H*), 5.39 (1 H, t, *J* 6, Ar*H*) and 5.63 (2 H, d, *J* 6, Ar*H*).
^{13}C NMR	:	(δ, $CDCl_3$)
(50.3 MHz)		2.3, 32.3, 73.4, 89.8, 92.0, 93.6, 121.8, 159.7 and 233.2.
Analysis:	:	Calculated. : C, 52.31; H, 5.85.
		Observed: C, 51.68; H, 4.91 %

Complex 9b

State	:	Yellow solid
mp	:	75 °C
IR ($CHCl_3$)	:	3020, 1969 and 1892 cm^{-1}
^1H NMR	:	(δ, $CDCl_3$)
(200 MHz)		0.06 (9 H, s, Si*Me*$_3$), 1.99 (6 H, s, 2xC*H*$_3$), 5.08 (2 H, t, *J* 6, Ar*H*), 5.39 (1 H, t, *J* 6, Ar*H*), 5.57 (2 H, t, *J* 6, Ar*H*) and 7.23-7.51 (5 H, m, Ph*H*).
^{13}C NMR	:	(δ, $CDCl_3$)
(50.3 MHz)		1.9, 30.2, 88.8, 93.1, 93.4, 94.4, 121.7, 126.0, 127.7, 128.2 and 233.2.
Analysis:	:	Calculated. : C, 59.09; H, 5.46.
		Observed: C, 59.04; H, 4.93 %

Anionic oxy-Cope rearrangement of 2a with KH:

To a suspension of KH (13 mg, 0.31 mmol) in ether (2 ml) and 18-Crown-6 (10 mol %) at -78 ^{o}C, a solution of the complex **2a** (120 mg, 0.26 mmol) in ether (5 ml) was added dropwise with stirring. The reaction was allowed to warm up to room temperature (3 h) and stirred for further three hours. Quenching with saturated ammonium chloride solution at 0 ^{o}C followed by usual workup gave the crude product that was purified by flash column chromatography (5 % acetone: petroleum ether) affording **10** (79 %).

Complex **2a'** (130 mg, 0.28 mmol) resulted in **10'** (88 mg, 80 %). **10** and **10'** are reported in ref. 2a and 3 respectively.

Brook rearrangement of 2a with KH:

To a suspension of KH (10 mg, 0.26 mmol) in ether (2 ml) and 18-Crown-6 (10 mol %) at -78 ^{o}C, a solution of complex **2a** (100 mg, 0.22 mmol) in ether (5 ml) was added dropwise with stirring. There was no change in the color of the reaction mixture. TLC after 15 minutes showed the reaction to be complete. Quenching with saturated ammonium chloride solution at the same temperature followed by usual workup gave the crude product that was purified by flash column chromatography (5 % acetone: petroleum ether) affording **3** (90 mg, 90 %).

Reaction of Complex **2a'** (120 mg, 0.25 mmol) resulted in **3'** (114 mg, 95 %).

Desilylation and anionic oxy-Cope rearrangement of 3 with KH:

To a suspension of KH (14 mg, 0.36 mmol) in ether (2 ml) and 18-Crown-6 (10 mol %) at room temperature, a solution of the complex **3** (110 mg, 0.24 mmol) in ether (5 ml) was added dropwise with stirring. The reaction was complete in three hours (TLC) and the color of the reaction mixture turned to red from greenish yellow. Quenching with saturated ammonium chloride solution at 0 ^{o}C followed by usual workup gave the crude product that was purified by flash

column chromatography (5 % acetone: petroleum ether) affording **10** (69 mg, 74 %).

Reaction of Complex **3'** (120 mg, 0.25 mmol) afforded **10'** (81 mg, 79 %).

Preparation of uncomplexed enone 12 and carbinol 13:

Uncomplexed enone **12** was prepared (in 96 % yield) by Claisen-Schmidt condensation of benzaldehyde (244 mg, 2.3 mmol) and *ortho* trimethylsilyl acetophenone **11** (291 mg, 1.52 mmol) using ethanolic potassium hydroxide as base following the same conditions that were employed to prepare tricarbonylchromium complexed enone **1**. Compound **11** was prepared by decomplexation of the corresponding tricarbonylchromium complex by exposing its ethereal solution to air and sunlight.

Addition of freshly prepared allylmagnesium bromide (1.8 ml of *ca* 1M soln., 1.8 mmol) to enone **12** (250 mg, 0.89 mmol) in 9 ml THF at -78 ^{o}C showed the reaction to be complete in 20 minutes by TLC. Quenching with saturated ammonium chloride solution followed by usual work up and flash column chromatography using 2 % acetone: petroleum ether afforded the carbinol **13** (260 mg, 90 %).

Complex 11

State	:	Colorless liquid
IR ($CHCl_3$)	:	1969, 1894 and 1680 cm^{-1}
^{1}H NMR	:	(δ, $CDCl_3$)
(200 MHz)		0.30 (9 H, s, Si*Me*$_3$), 2.83 (3 H, s, C*H*$_3$) and 7.51-7.89 (4 H, m, Ph*H*).
^{13}C NMR	:	(δ, $CDCl_3$)
(50.3 MHz)		0.3, 27.2, 128.8, 129.5, 131.5, 135.9, 142.0, 142.6 and 200.1.
Analysis:	:	Calculated. : C, 68.69; H, 8.39.

Observed: C, 68.50; H, 8.32 %

Complex 12

State : Colorless oily liquid

IR ($CHCl_3$) : 1970, 1850 and 1640 cm^{-1}

^1H NMR : (δ, $CDCl_3$)

(200 MHz) 0.33 (9 H, s, Si*Me*$_3$) and 7.32-7.79 (11 H, m, 4xAr*H*, *H*C=C*H*, 5xPh*H*).

^{13}C NMR : (δ, $CDCl_3$)

(50.3 MHz) 0.3, 124.6, 128.1, 128.2, 128.8, 130.4, 134.6, 135.7, 141.4, 144.4, 145.2 and 194.8.

Analysis: : Calculated. : C, 77.09; H, 7.19.

Observed: C, 76.85; H, 7.32 %

Complex 13

State : Colorless liquid

IR ($CHCl_3$) : 3451, 1450 and 1220 cm^{-1}

^1H NMR : (δ, $CDCl_3$)

(200 MHz) 0.36 (9 H, s, Si*Me*$_3$), 2.52 (1 H, s, O*H*), 2.76 (1 H, dd, *J* 8, 14, C*H*$_2$), 2.93 (1 H, dd, *J* 8, 14, C*H*$_2$), 5.23 (1 H, s, CH=C*H*$_2$), 5.31 (1 H, d, *J* 6, CH=C*H*$_2$), 5.60-5.85 (1 H, m, C*H*=CH$_2$), 6.56 (2 H, d, *J* 2, PhC*H*=C*H*) and 7.24-7.39 (9 H, m, 4xAr*H*, 5xPh*H*).

^{13}C NMR : (δ, $CDCl_3$)

(50.3 MHz) 3.4, 48.4, 120.8, 126.0, 126.3, 126.5, 127.5, 128.5, 128.6, 128.8, 133.3, 136.2, 136.4, 136.9, 150.8 and 159.5.

Analysis: : Calculated. : C, 78.21; H, 8.13.

Observed: C, 77.80; H, 7.98 %

Cyclization of the uncomplexed substrates:

Same procedure that was described for tricarbonylchromium analogues was followed both for direct one-pot cyclization of the Magnesium alkoxide (generated by addition of allylmagnesium bromide to enone **12** at -78 ^{o}C and warming up to rt.) and Li/MgBr exchange by deprotonation of alcohol **13** by n-BuLi and exchange of Li with excess of $MgBr_2.OEt_2$.

Complex 14

State	:	Colorless oil
IR ($CHCl_3$)	:	3435, 1682 and 1442 cm^{-1}
^{1}H NMR	:	(δ, $CDCl_3$)
(200 MHz)		0.46 (6 H, s, Si*Me*$_2$), 2.73-2.78 (2 H, m, C*H*$_2$), 5.01-5.11 (2 H, m, CH=C*H*$_2$), 5.54-5.75 (1 H, m, C*H*=CH$_2$), 6.51 (1 H, d, *J* 16, PhC*H*=CH), 6.69 (1 H, d, *J* 16, PhCH=C*H*) and 7.21-7.59 (9 H, m, 4xAr*H*, 5xPh*H*).
^{13}C NMR	:	(δ, $CDCl_3$)
(50.3 MHz)		0.8, 1.1, 47.2, 87.2, 118.1, 122.9, 126.5, 127.0, 127.2, 128.4, 129.8, 130.9, 133.4, 135.1, 135.3, 137.1 and 153.9.
MS (m/z)		308.05 (M^{+}+2)
Analysis:	:	Calculated. : C, 78.38; H, 7.24.
		Observed: C, 78.80; H, 7.56 %

X-ray Crystal Structure Analysis For 4a:

Needle-like yellow single crystals were grown in a mixture of dichloromethane and petroleum ether. Data were collected on MACH-3 single crystal X-ray diffractometer using Mo Kα radiation. Crystal belongs to monoclinic space group P21/n with cell dimensions: a = 12.488 (2), b = 9.1030 (9), c = 20.682 (3) Å , β = 107.16 (1)°, V = 2246.4 (5) Å. The structure was solved and refined using *SHELXS* [Ref]. The refinement with number of refined parameters 265, converged to R_1 = 0.0341, wR_2 = 0.0814, for 3546 unique reflections ([I>2σ(I)]).

The initial solution yielded the coordinates of Cr, Si, Cl and few carbon atoms. Successive difference Fourier maps revealed the rest of the structure. Least squares refinement of scale, positional and anisotropic thermal parameters of all the atoms were carried out.

Crystal data and the data collection parameters are given in Table 1. The residual density in the difference map for peak and hole is 0.271 and -0.263 e. $Å^{-3}$ respectively.

Ref: Sheldrick, G. M SHELXS - 97 Program for crystal structure solution and refinement, University of Göttingen, Germany, 1997.

Crystal data and structure refinement for 4a

Empirical formula	C23 H22 Cr O4 Si
Formula weight	442.50
Temperature	293(2) K
Wavelength	0.70930 Å
Crystal system, space group	Monoclinic, P21/ n
Unit cell dimensions	a = 12.488 (2) Å b = 9.1030 (9) Å c = 20.682 (3) Å β = 107.16 (1)°
Volume	2246.4 (5) $Å^3$
Crystal size	0.40 x 0.40 x 0.25 mm
Z, Calculated density	4, 1.308 Mg/m^3
Absorption coefficient	0.587 mm^{-1}
F(000)	920

Theta range for data collection - 1.71 to 24.91 °.

Limiting indices	0<=h<=14, 0<=k<=10, -24<=l<=23
Completeness to theta = 24.91	90.0 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3546 / 0 / 265
Goodness-of-fit on F^2	1.061
Final R indices [I>2sigma(I)]	R1 = 0.0341, wR2 = 0.0814
R indices (all data)	R1 = 0.0439, wR2 = 0.0881

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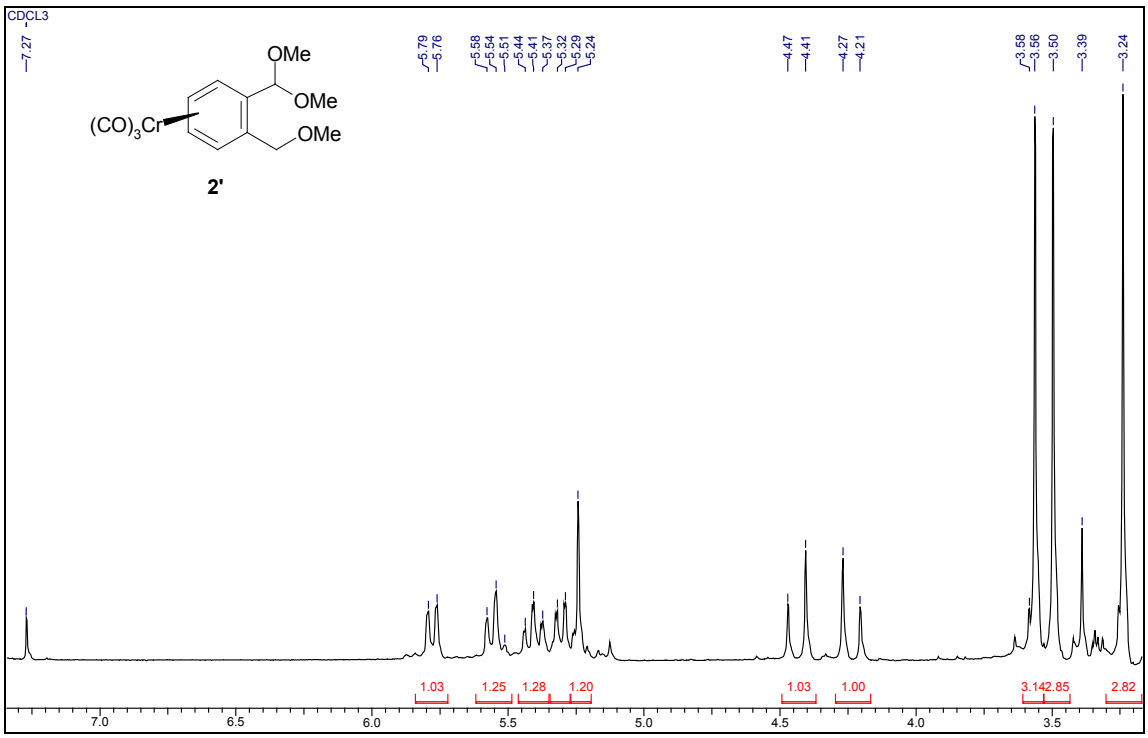
Appendix-I

Spectra of compounds - Part A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5.24
4.47
4.41
4.27
4.21
3.58
3.56
3.50
3.39
3.24
OMe
OMe
OMe
(CO)3Cr
2'
1.03
1.25
1.28
1.20
1.03
1.00
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6.5
6.0
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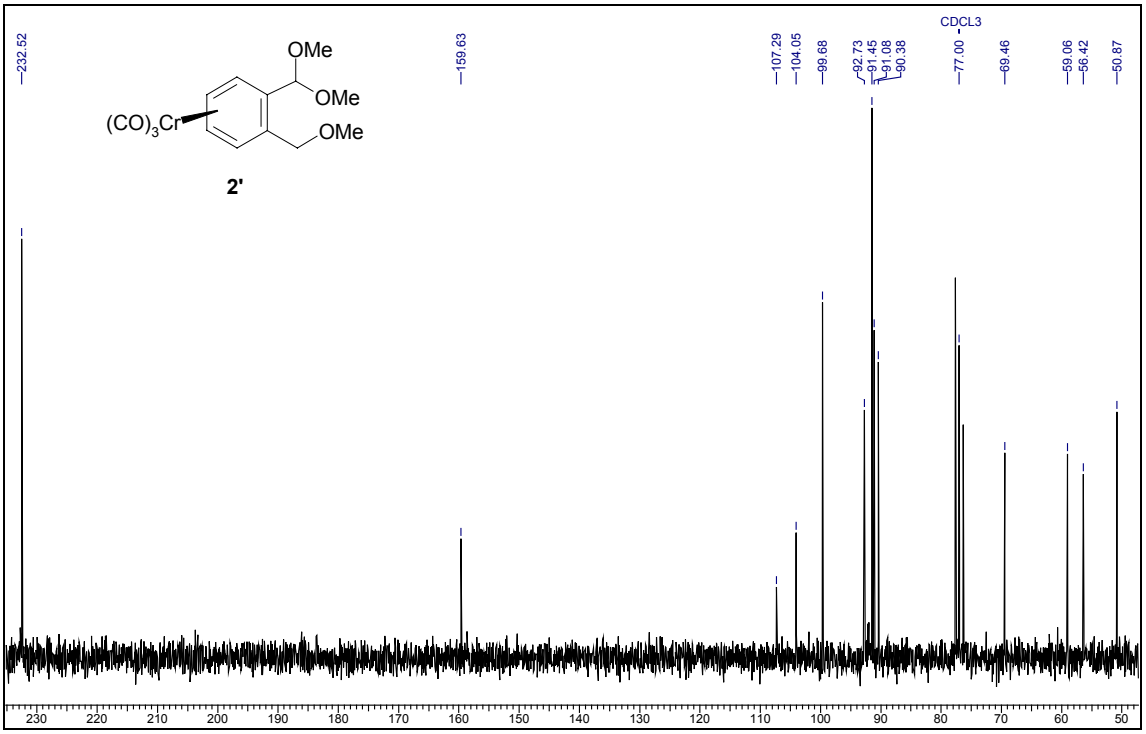
4.0
3.5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59.06
56.42
50.87
OMe
OMe
OMe
(CO)3Cr
2'
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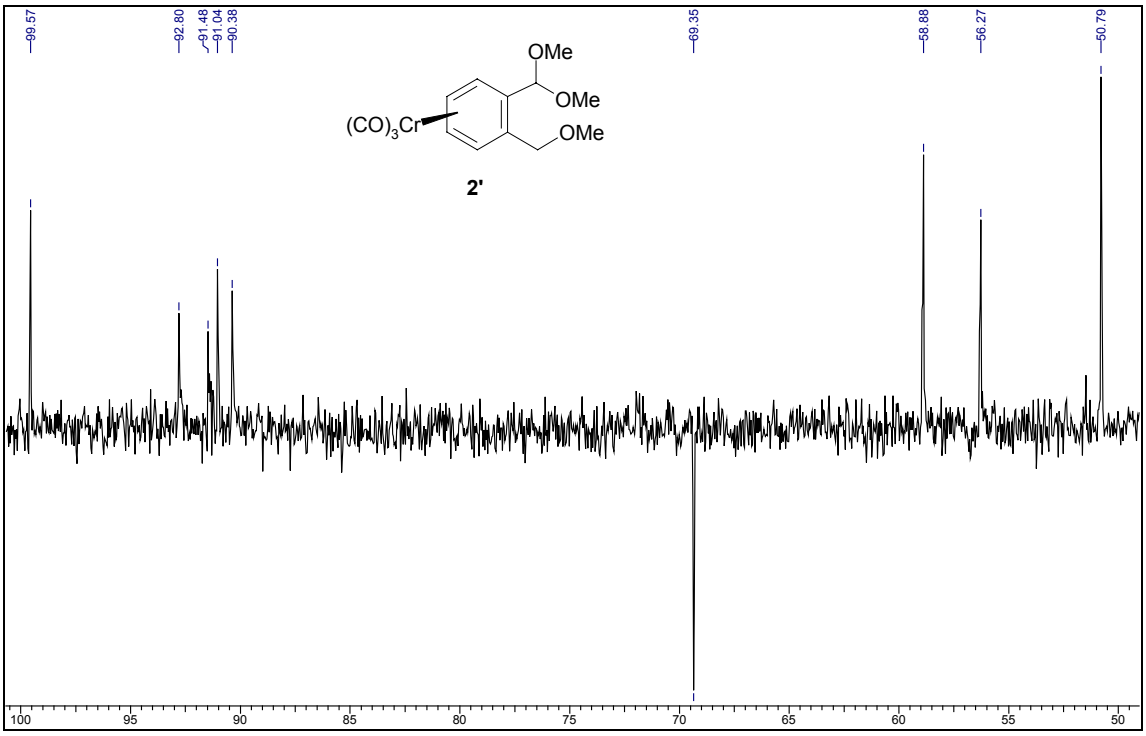
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55
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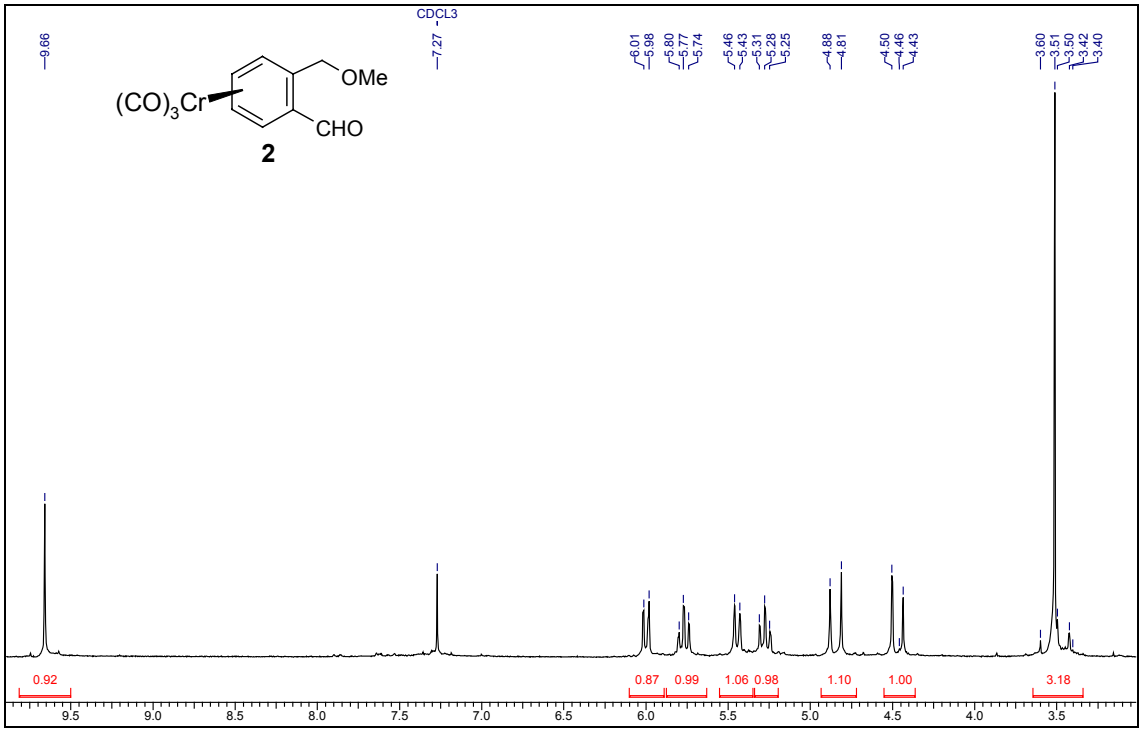
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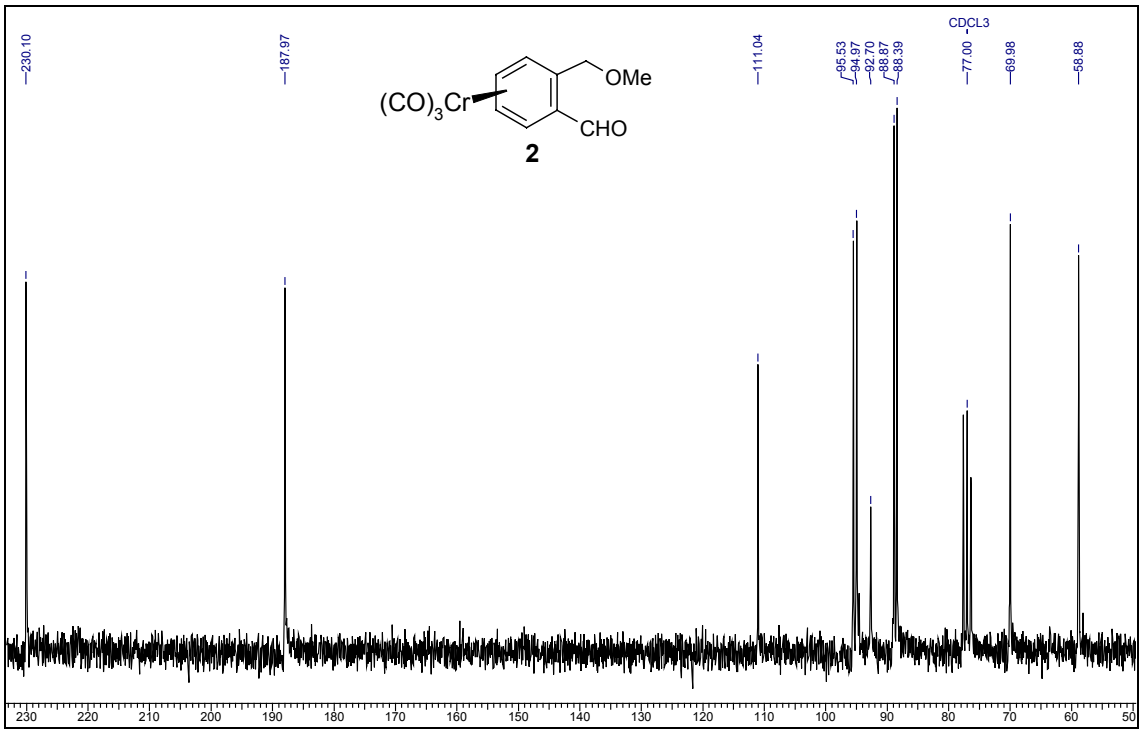
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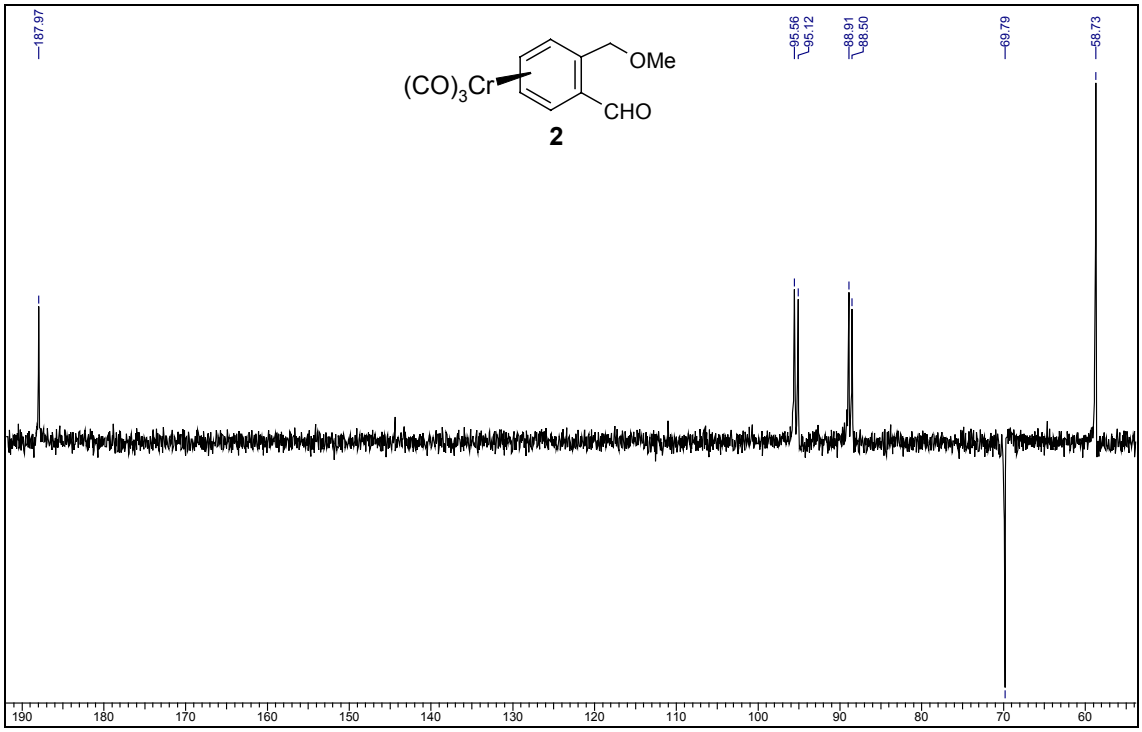
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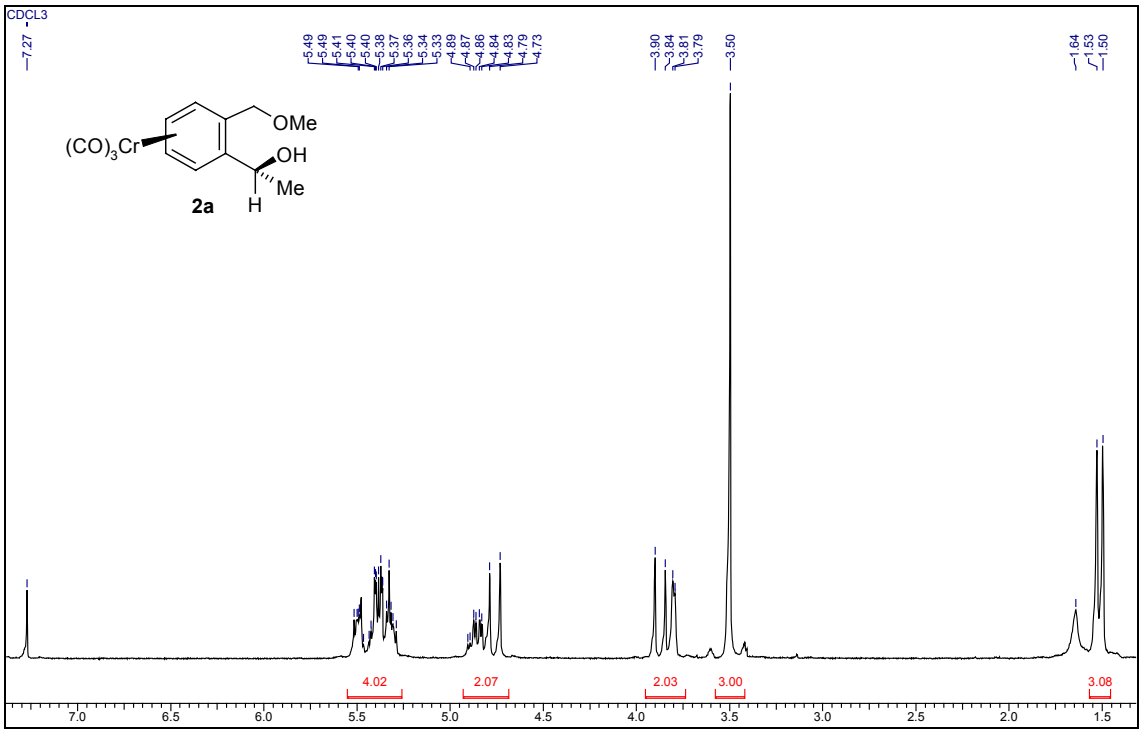
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3.81
3.79
3.50
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1.53
1.50
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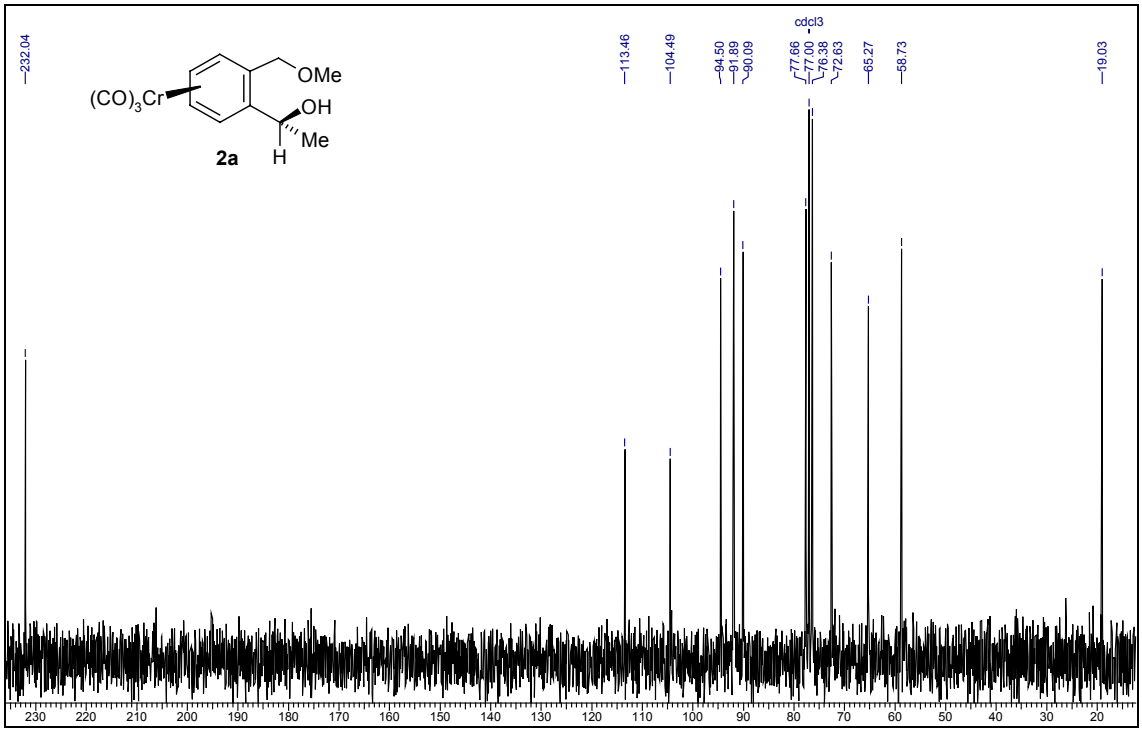
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2a
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230
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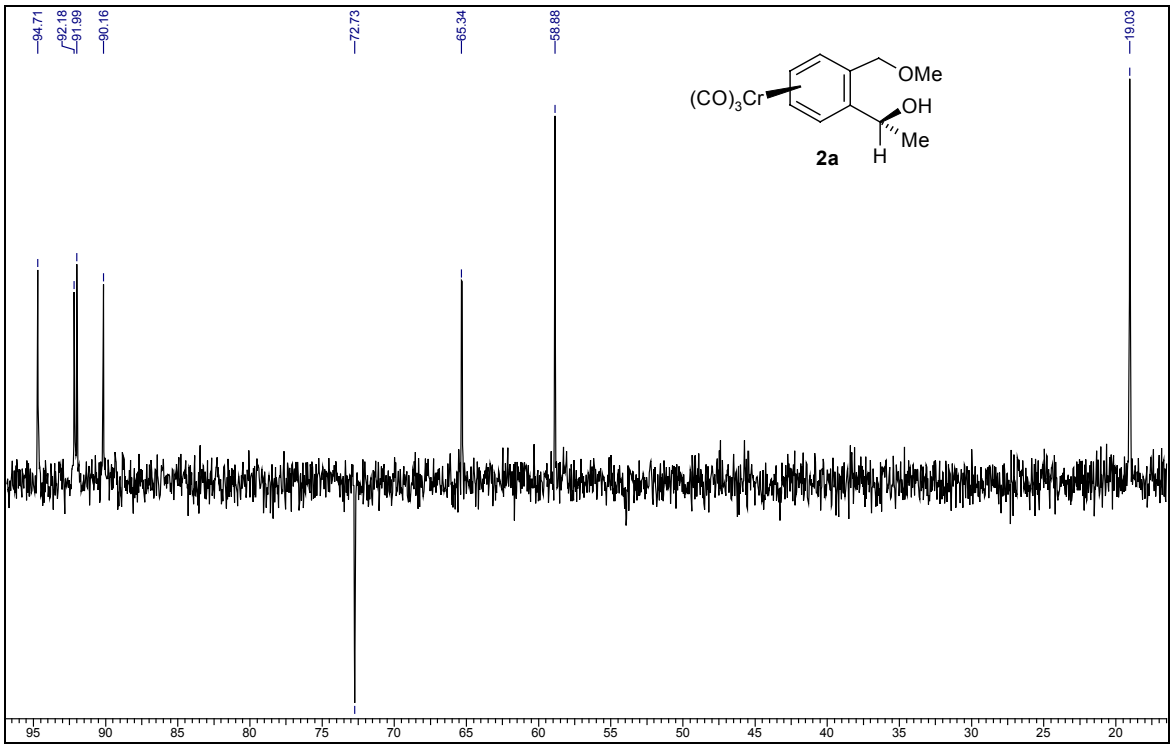
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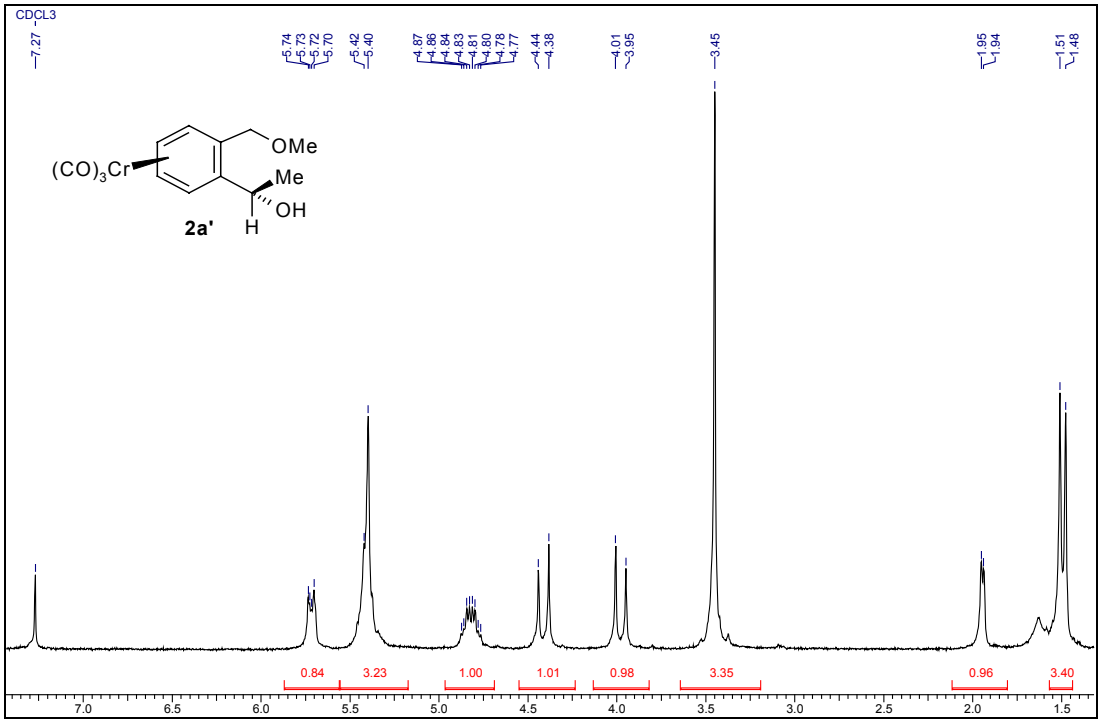
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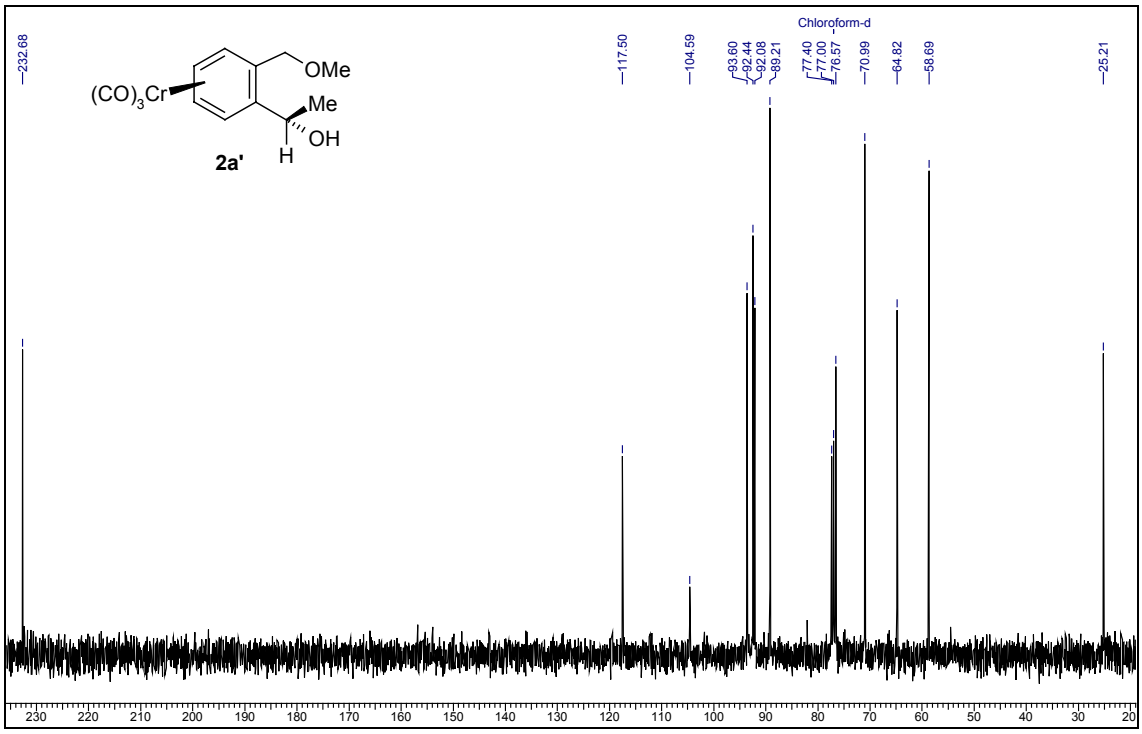
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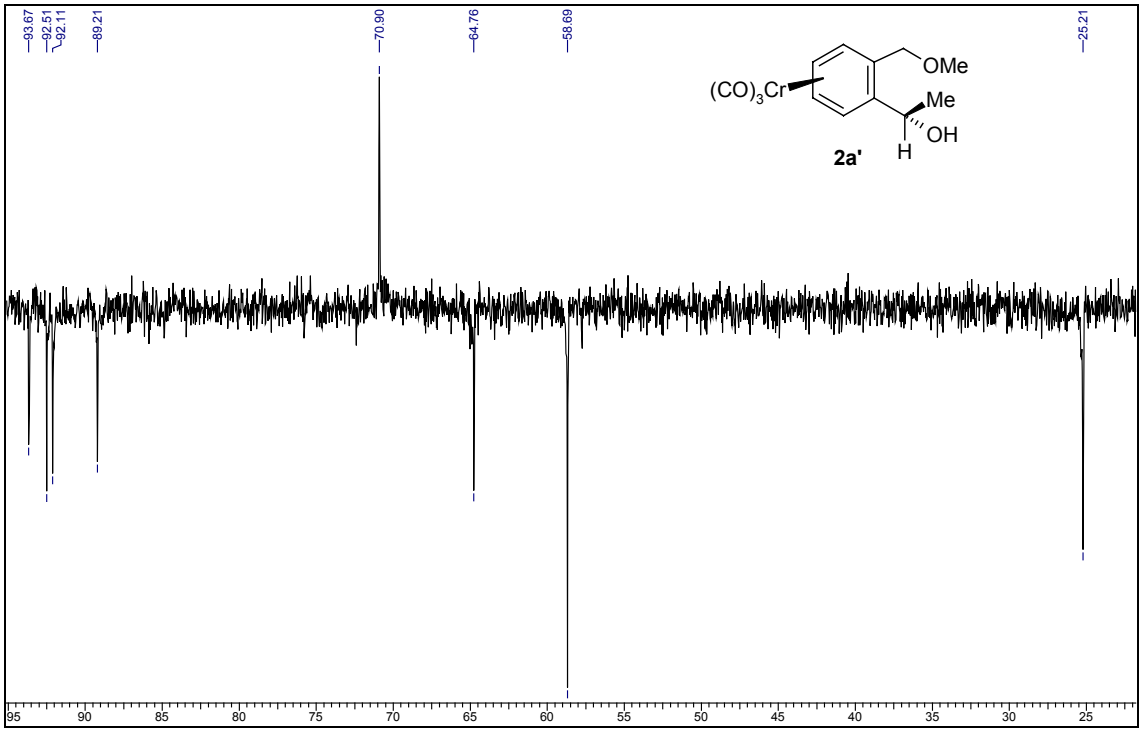
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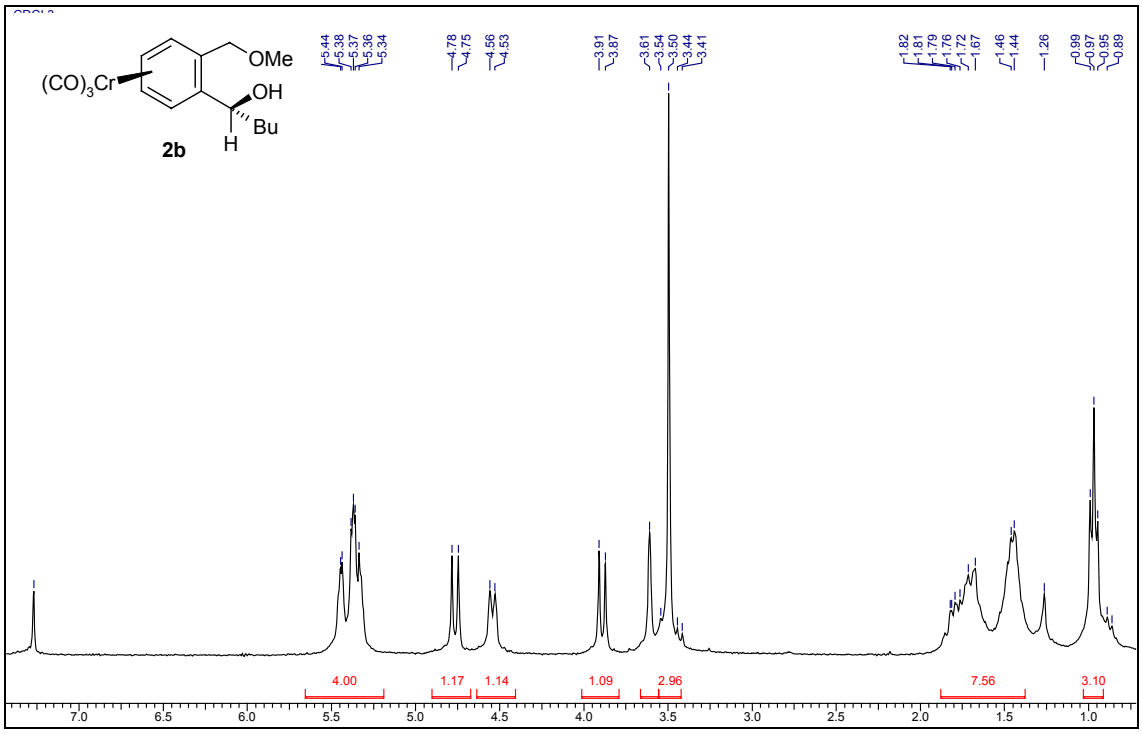
(CO)3Cr
2a'


(CO)3Cr
OMe
OH
Bu
H
2b
5.44
5.38
5.37
5.36
5.34
4.78
4.75
4.56
4.53
3.91
3.87
3.61
3.54
3.50
3.44
3.41
1.82
1.81
1.79
1.76
1.72
1.67
1.46
1.44
1.26
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0.95
0.89
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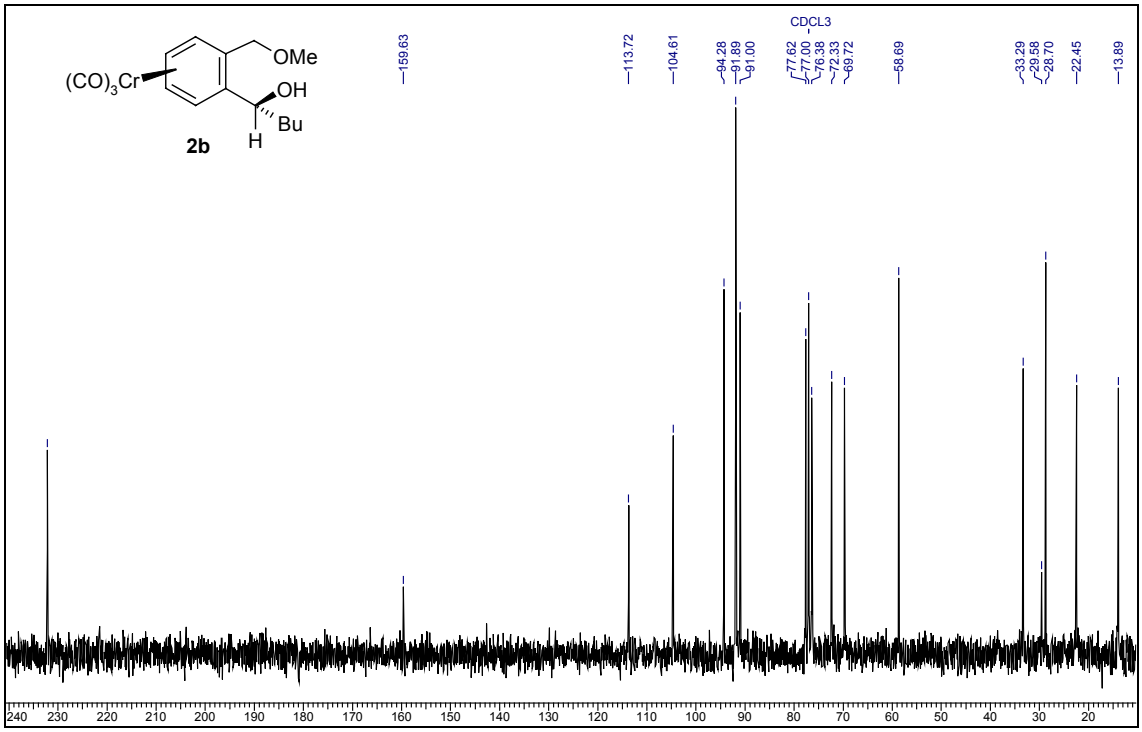
1.14
1.09
2.96
7.56
3.10


(CO)3Cr
OMe
OH
Bu
H
2b
CDCL3
159.63
113.72
104.61
94.28
91.89
91.00
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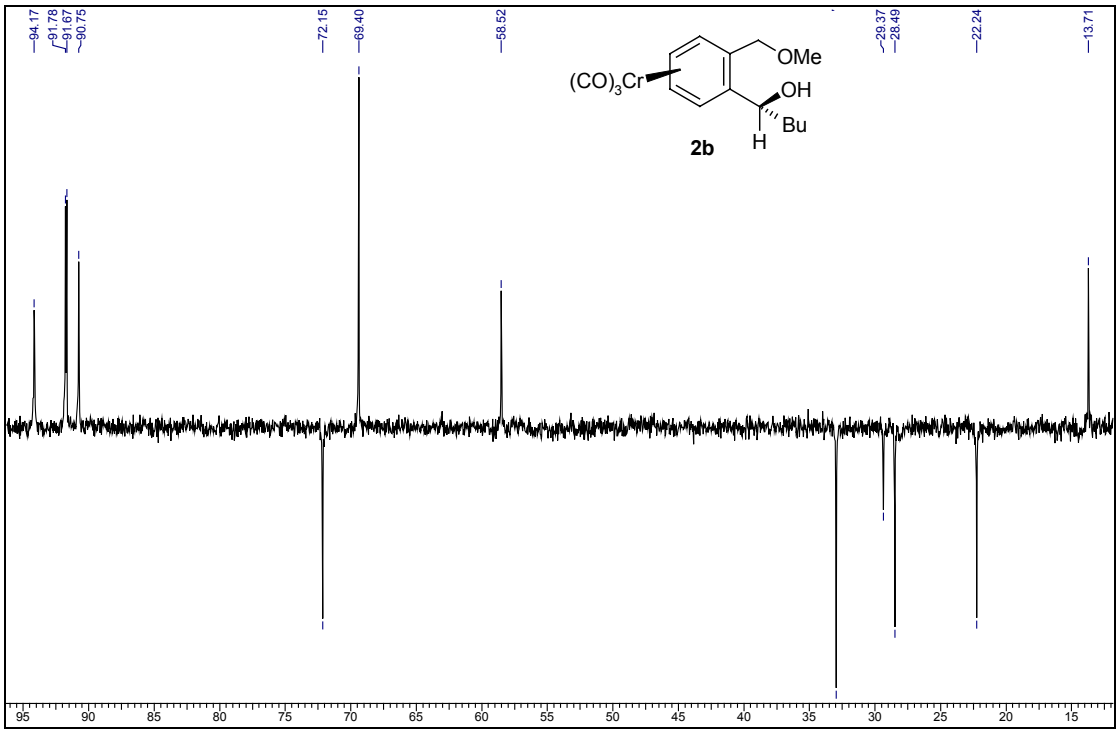
77.00
76.38
72.33
69.72
58.69
33.29
29.58
28.70
22.45
13.89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91.78
91.67
90.75
72.15
69.40
58.52
29.37
28.49
22.24
13.71
(CO)3Cr
OMe
OH
Bu
H
2b
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90
85
80
75
70
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50
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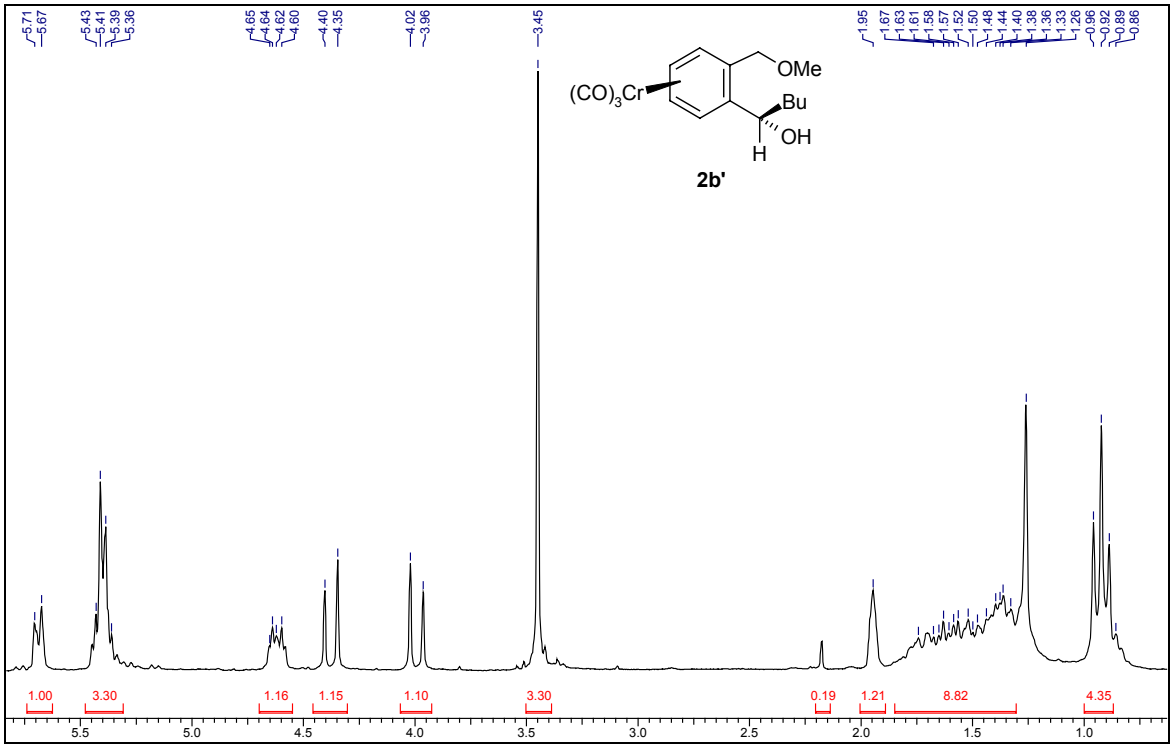
30
25
20
15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5.67
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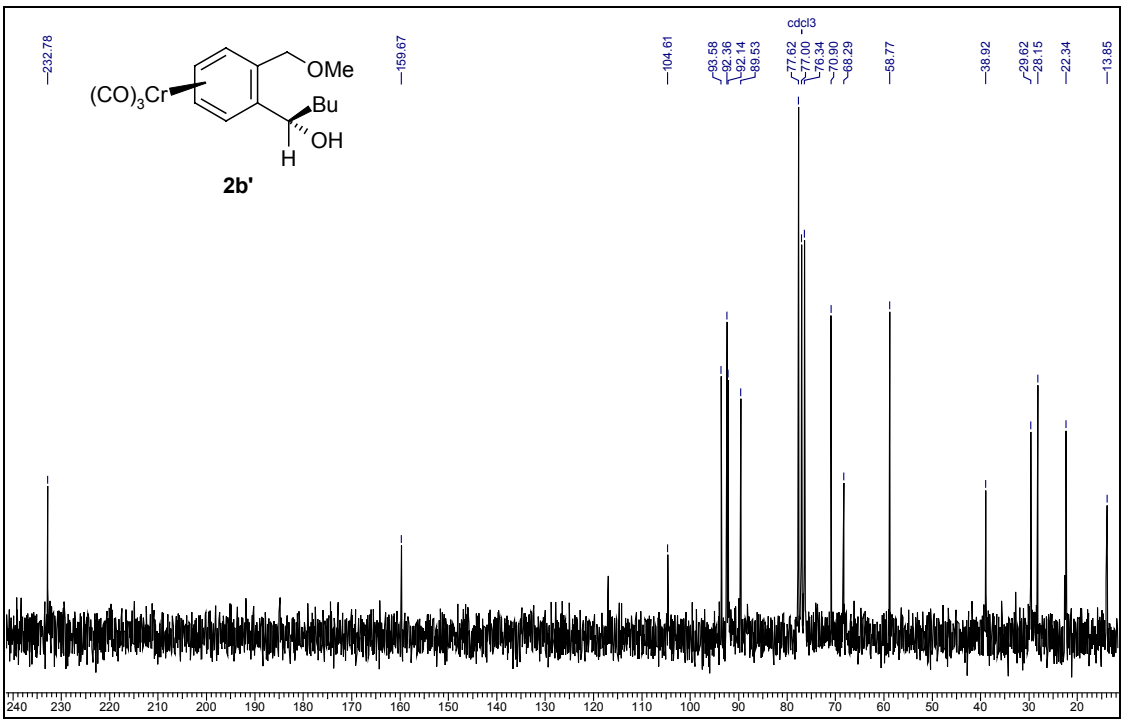
5.39
5.36
4.65
4.64
4.62
4.60
4.40
4.35
4.02
3.96
3.45
1.95
1.67
1.63
1.61
1.58
1.57
1.52
1.50
1.48
1.44
1.40
1.38
1.36
1.33
1.26
0.96
0.92
0.89
0.86
(CO)3Cr
OMe
Bu
OH
H
2b'
1.00
3.30
1.16
1.15
1.10
3.30
0.19
1.21
8.82
4.35
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0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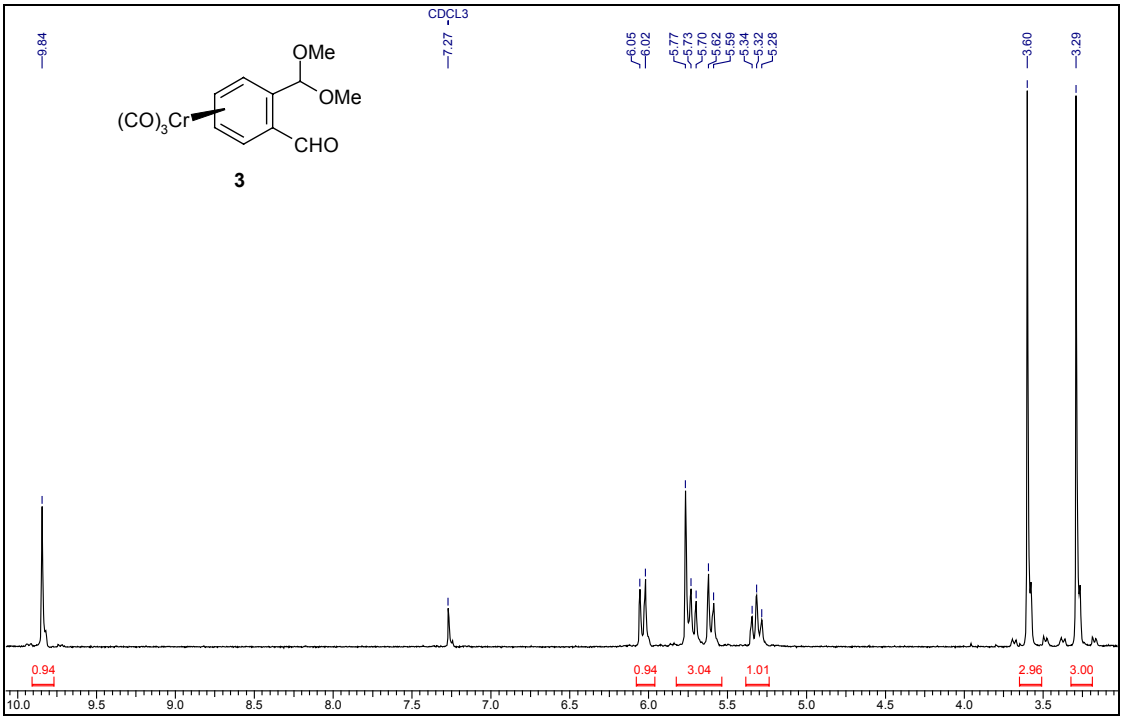
232.78
159.67
104.61
93.58
92.36
92.14
89.53
77.62
77.00
76.34
70.90
68.29
58.77
38.92
29.62
28.15
22.34
13.85
OMe
(CO)3Cr
Bu
OH
H
2b'


CDCL3
9.84
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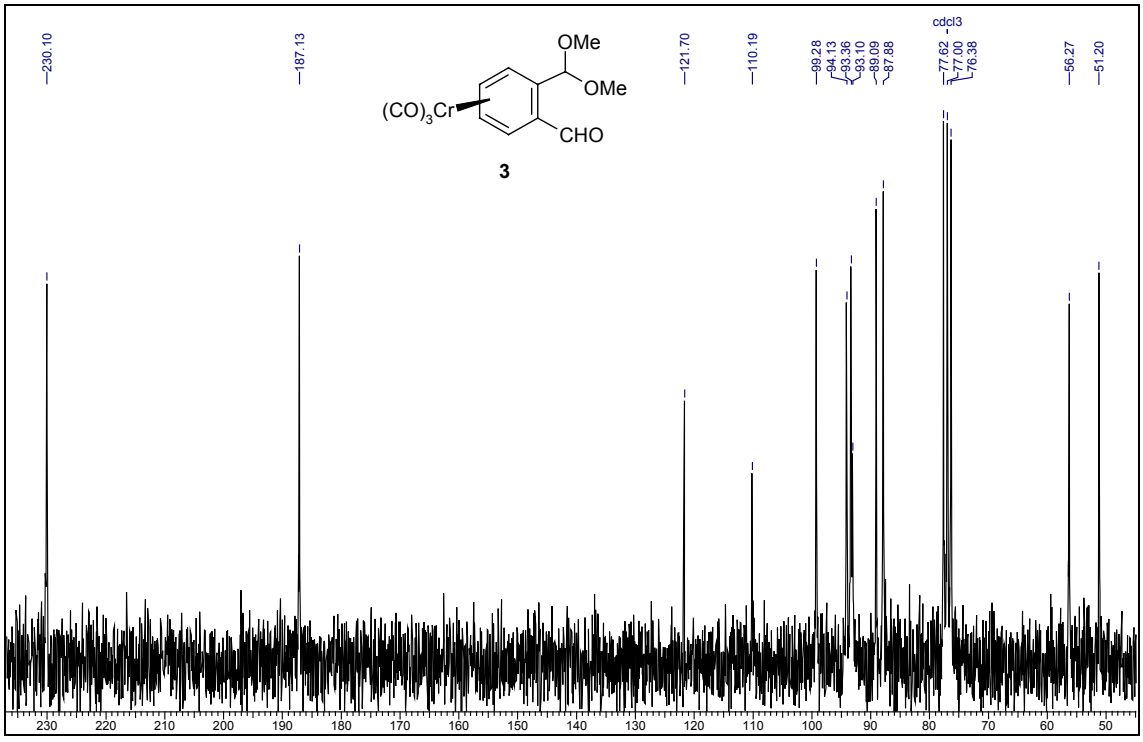
6.05
6.02
5.77
5.73
5.70
5.62
5.59
5.34
5.32
5.28
3.60
3.29
OMe
OMe
(CO)3Cr
CHO
3
0.94
0.94
3.04
1.01
2.96
3.00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94.13
93.36
93.10
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77.62
77.00
76.38
56.27
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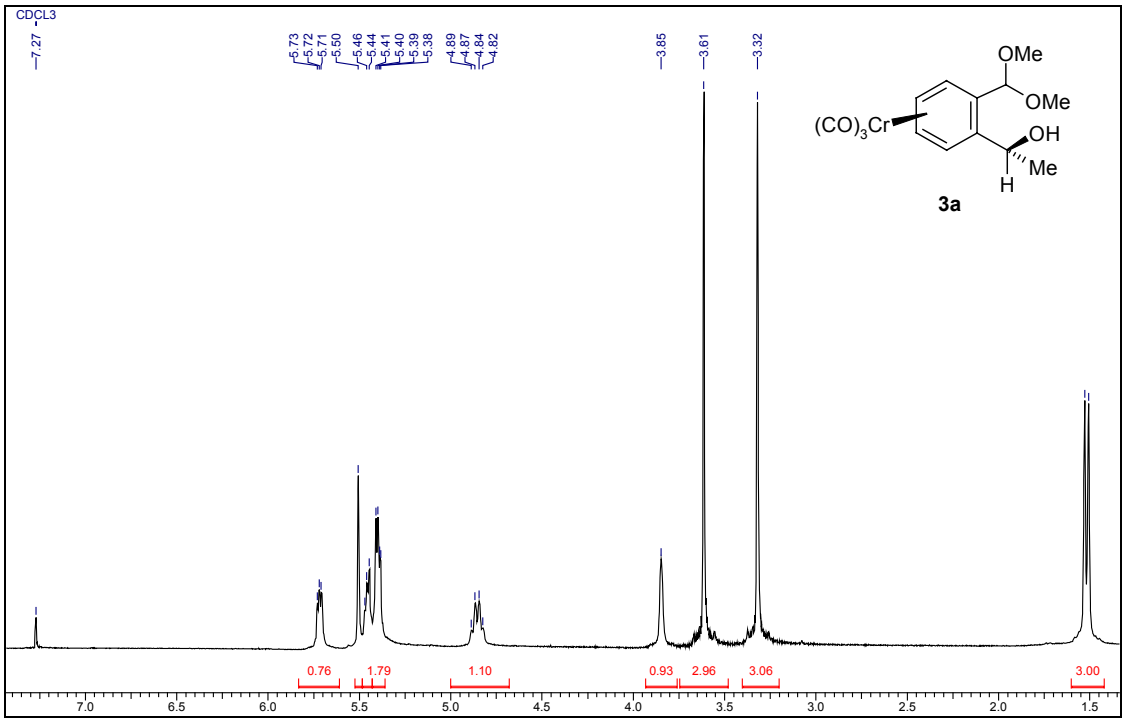
OMe
OMe
(CO)3Cr
CHO
3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5.71
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5.46
5.44
5.41
5.40
5.39
5.38
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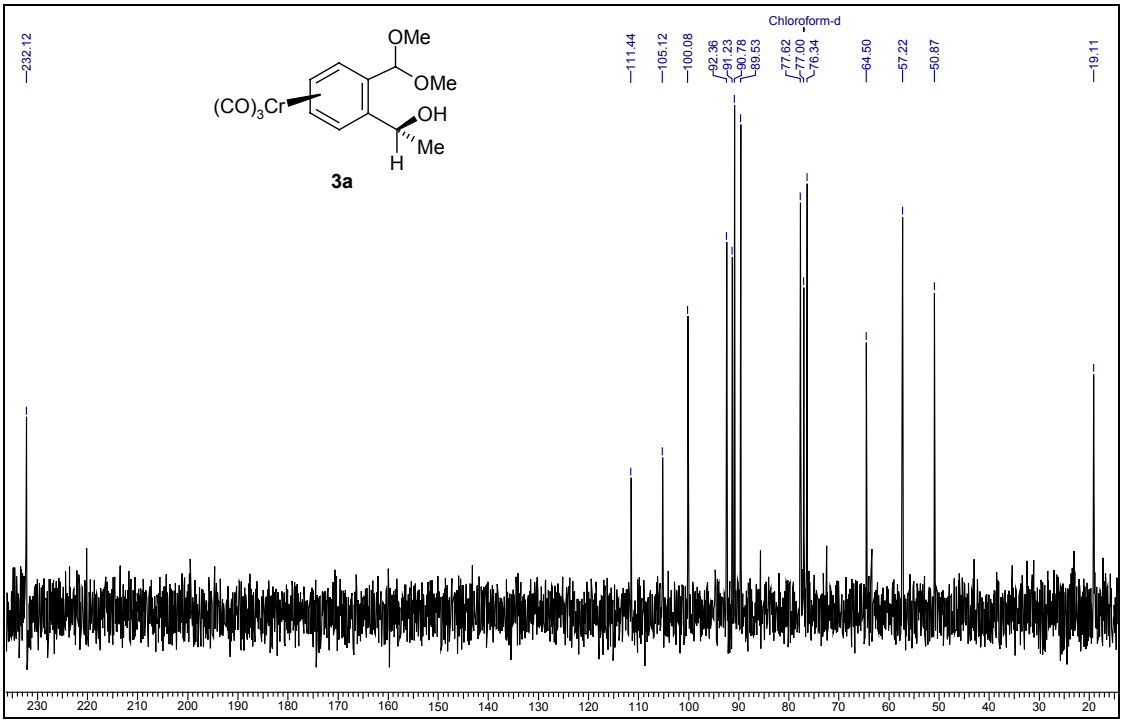
4.87
4.84
4.82
3.85
3.61
3.32
OMe
OMe
(CO)3Cr
OH
Me
H
3a
0.76
1.79
1.10
0.93
2.96
3.06
3.00


Chloroform-d
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105.12
100.08
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91.23
90.78
89.53
77.62
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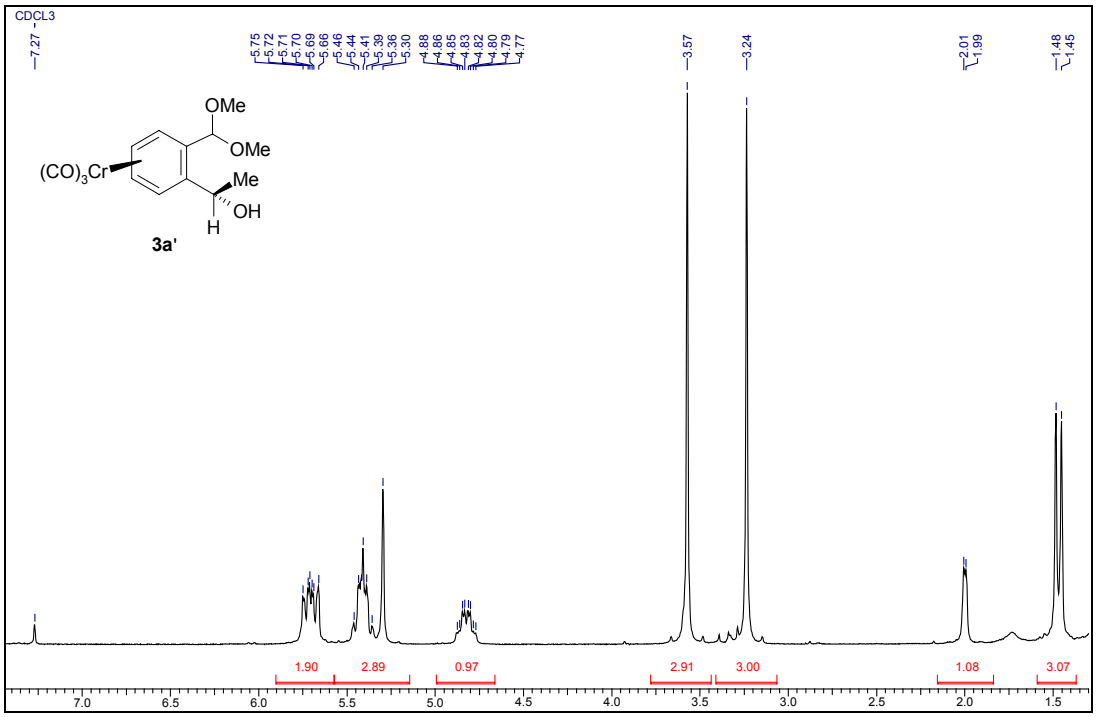
76.34
64.50
57.22
50.87
19.11
OMe
OMe
(CO)3Cr
OH
Me
H
3a


CDCL3
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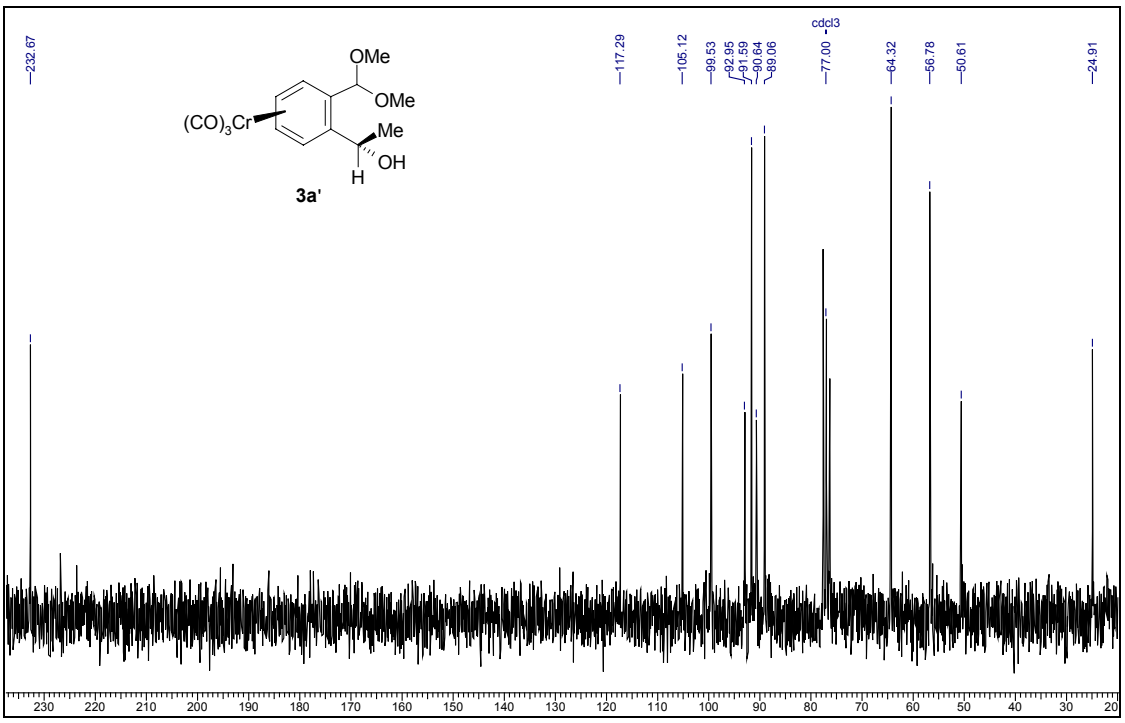
5.72
5.71
5.70
5.69
5.66
5.46
5.44
5.41
5.38
5.36
5.30
4.88
4.86
4.85
4.83
4.82
4.80
4.79
4.77
3.57
3.24
2.01
1.99
1.48
1.45
OMe
OMe
Me
(CO)3Cr
OH
H
3a'
1.90
2.89
0.97
2.91
3.00
1.08
3.07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91.59
90.64
89.06
cdcl3
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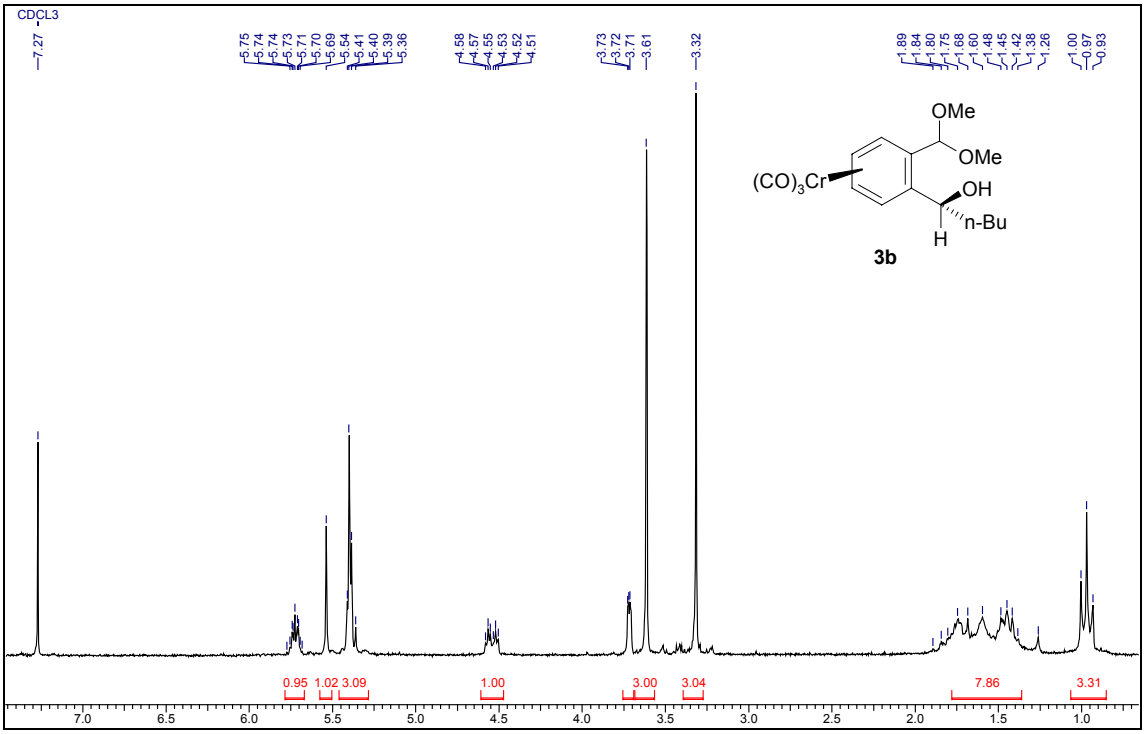
64.32
56.78
50.61
24.91
OMe
OMe
(CO)3Cr
Me
OH
H
3a'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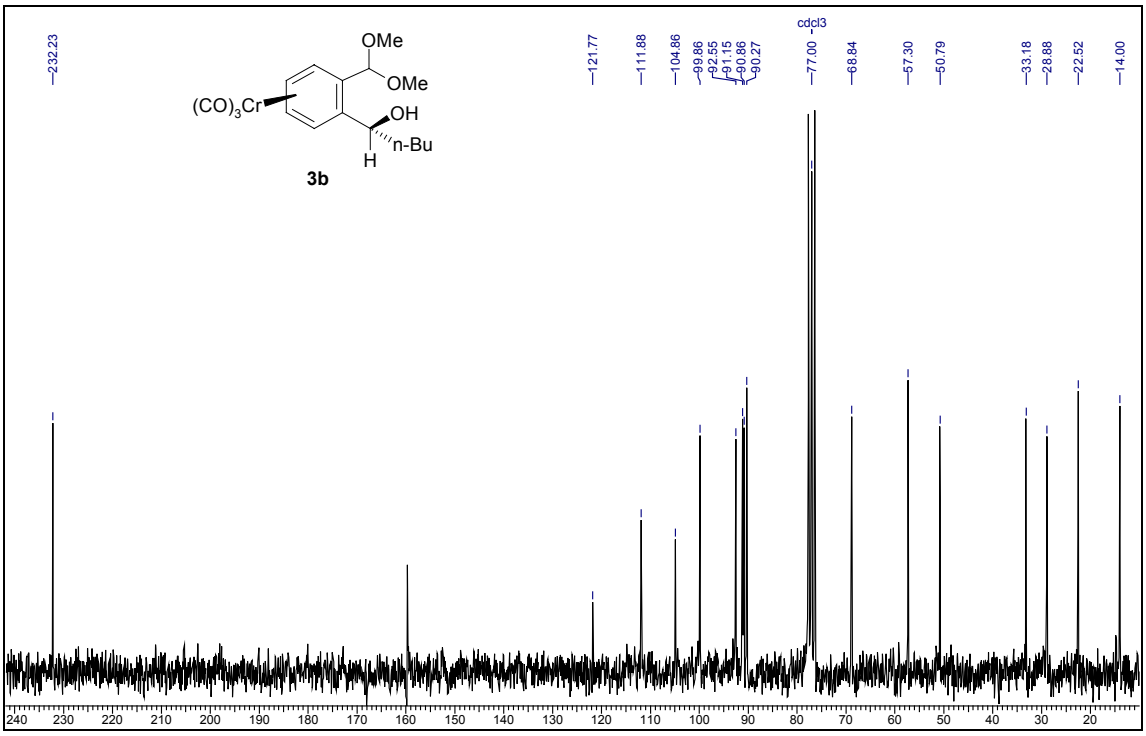
5.74
5.74
5.73
5.71
5.70
5.69
5.54
5.41
5.40
5.39
5.36
4.58
4.57
4.55
4.53
4.52
4.51
3.73
3.72
3.71
3.61
3.32
1.89
1.84
1.80
1.75
1.68
1.60
1.48
1.45
1.42
1.38
1.26
1.00
0.97
0.93
OMe
OMe
(CO)3Cr
OH
n-Bu
H
3b
0.95
1.02
3.09
1.00
3.00
3.04
7.86
3.31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92.55
91.15
90.86
90.27
cdcl3
77.00
68.84
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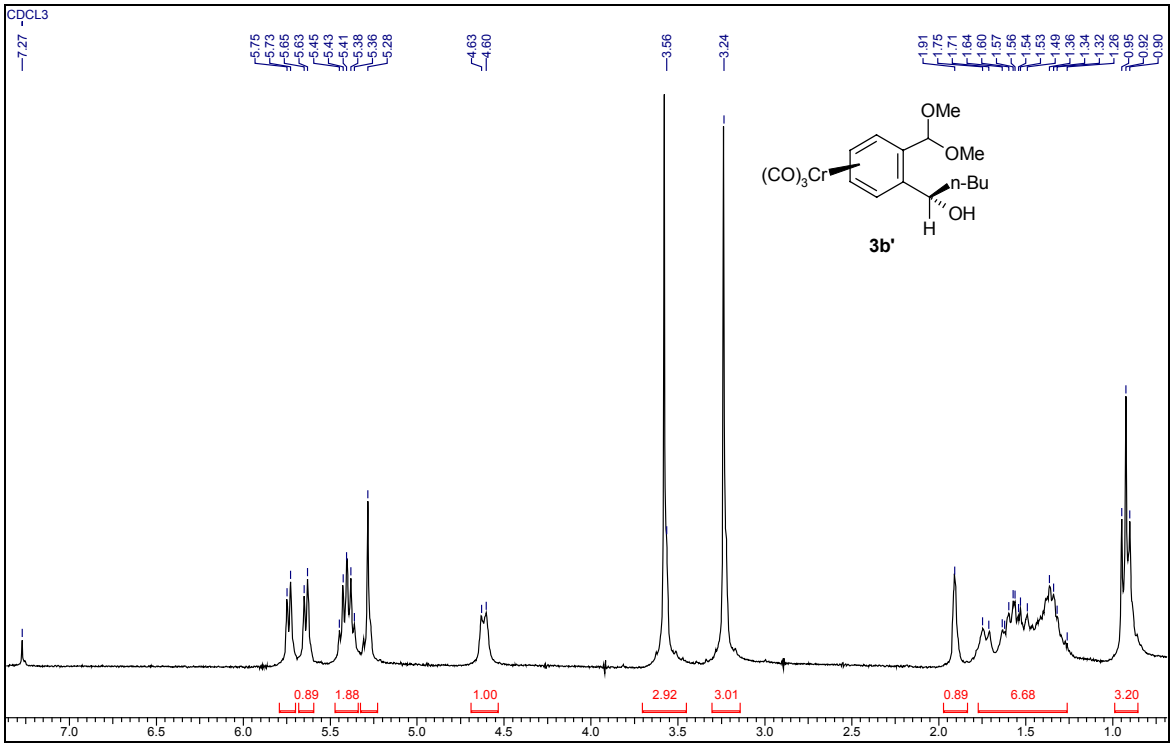
33.18
28.88
22.52
14.00
OMe
OMe
(CO)3Cr
OH
n-Bu
H
3b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5.73
5.65
5.63
5.45
5.43
5.41
5.38
5.36
5.28
4.63
4.60
3.56
3.24
1.91
1.75
1.71
1.64
1.60
1.57
1.56
1.54
1.53
1.49
1.36
1.34
1.32
1.26
0.95
0.92
0.90
OMe
OMe
(CO)3Cr
n-Bu
OH
H
3b'
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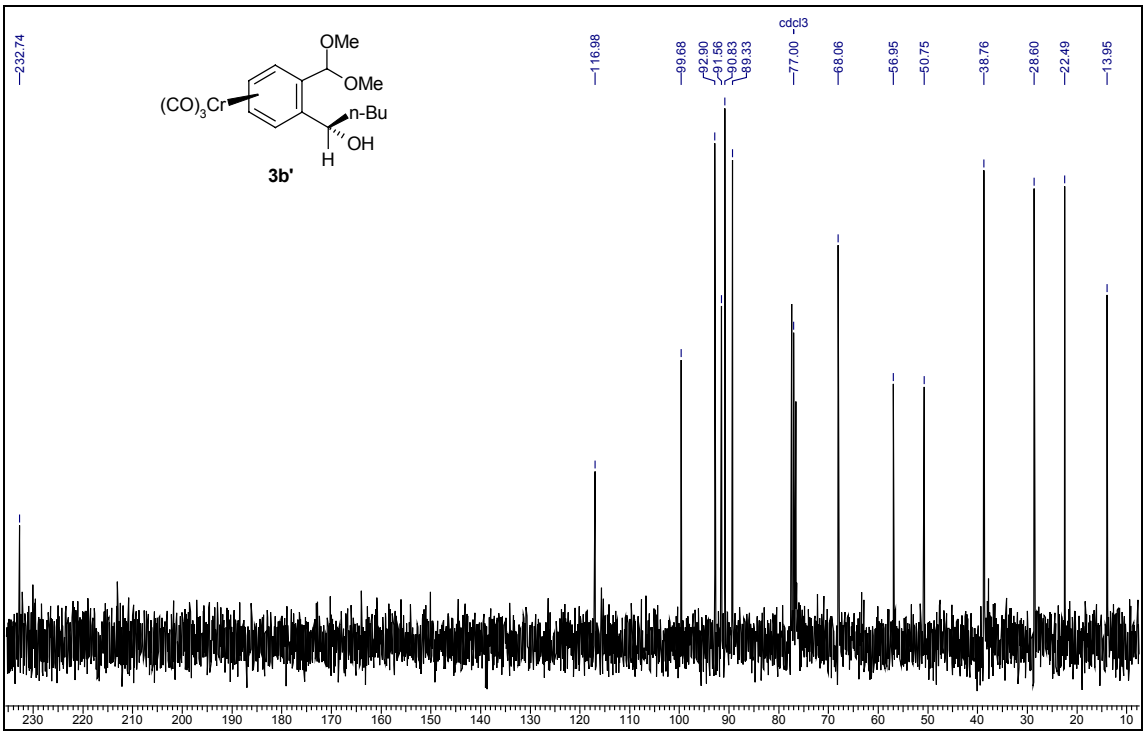
1.88
1.00
2.92
3.01
0.89
6.68
3.20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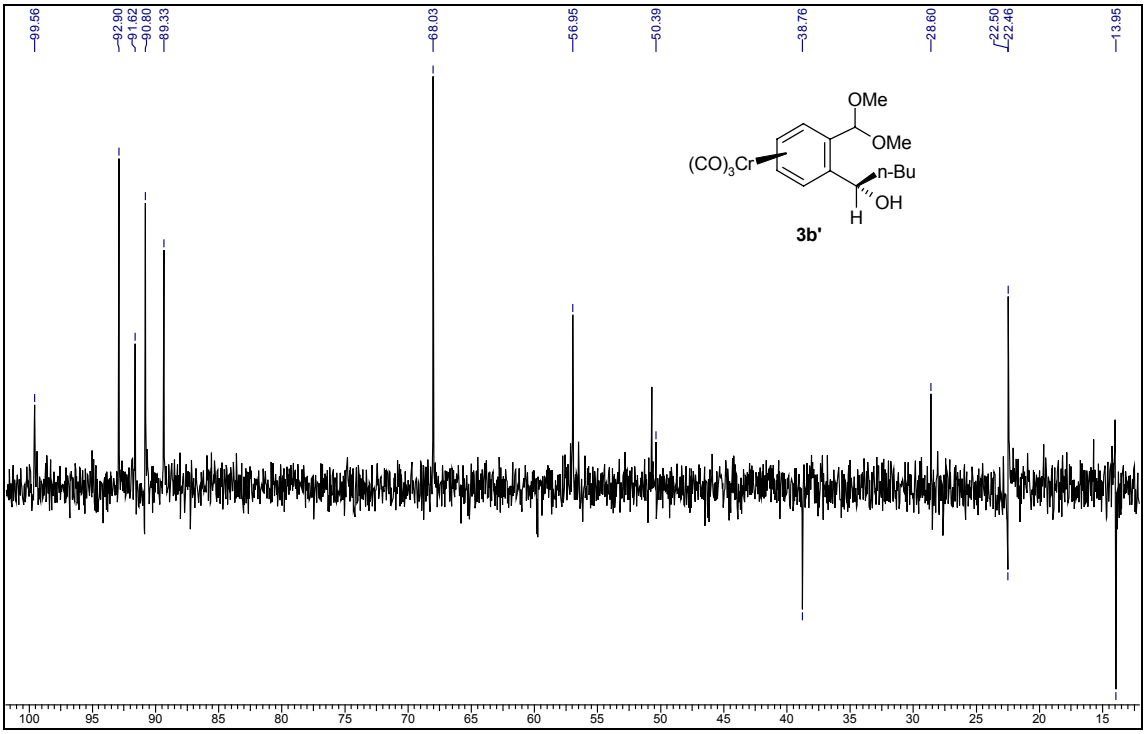
116.98
99.68
92.90
91.56
90.83
89.33
cdcl3
77.00
68.06
56.95
50.75
38.76
28.60
22.49
13.95
OMe
OMe
(CO)3Cr
n-Bu
OH
H
3b'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92.90
91.62
90.80
89.33
68.03
56.95
50.39
38.76
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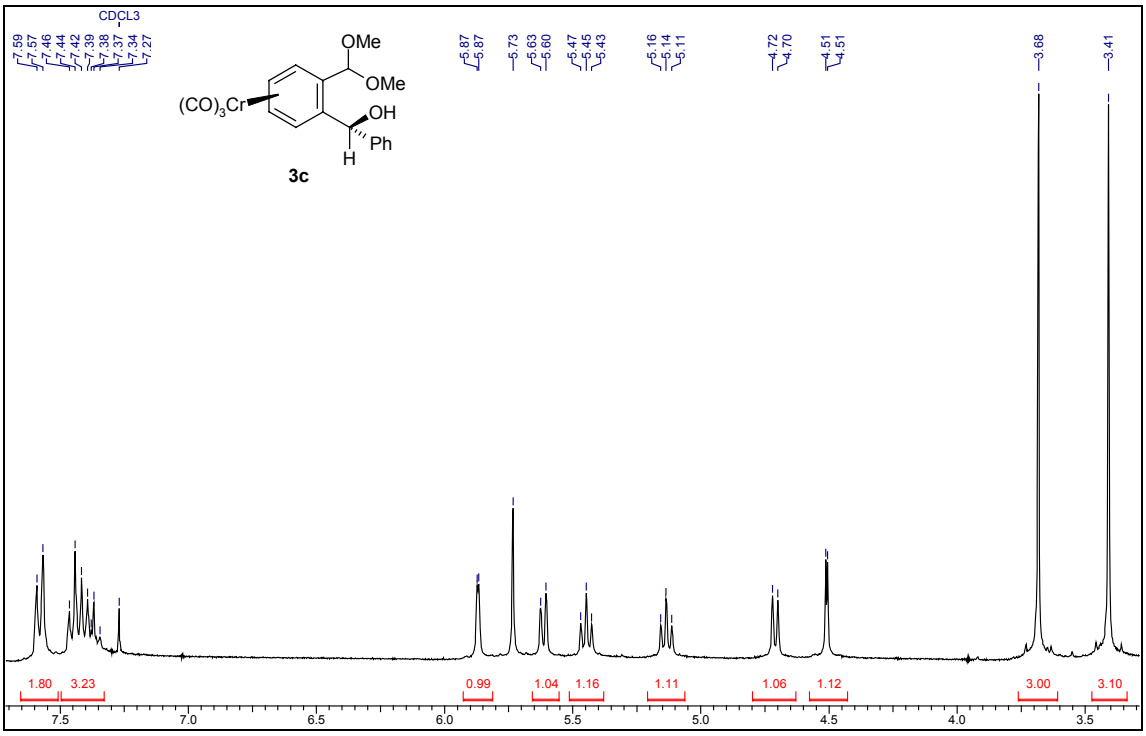
22.50
22.46
13.95
OMe
OMe
(CO)3Cr
n-Bu
OH
H
3b'


CDCL3
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7.57
7.46
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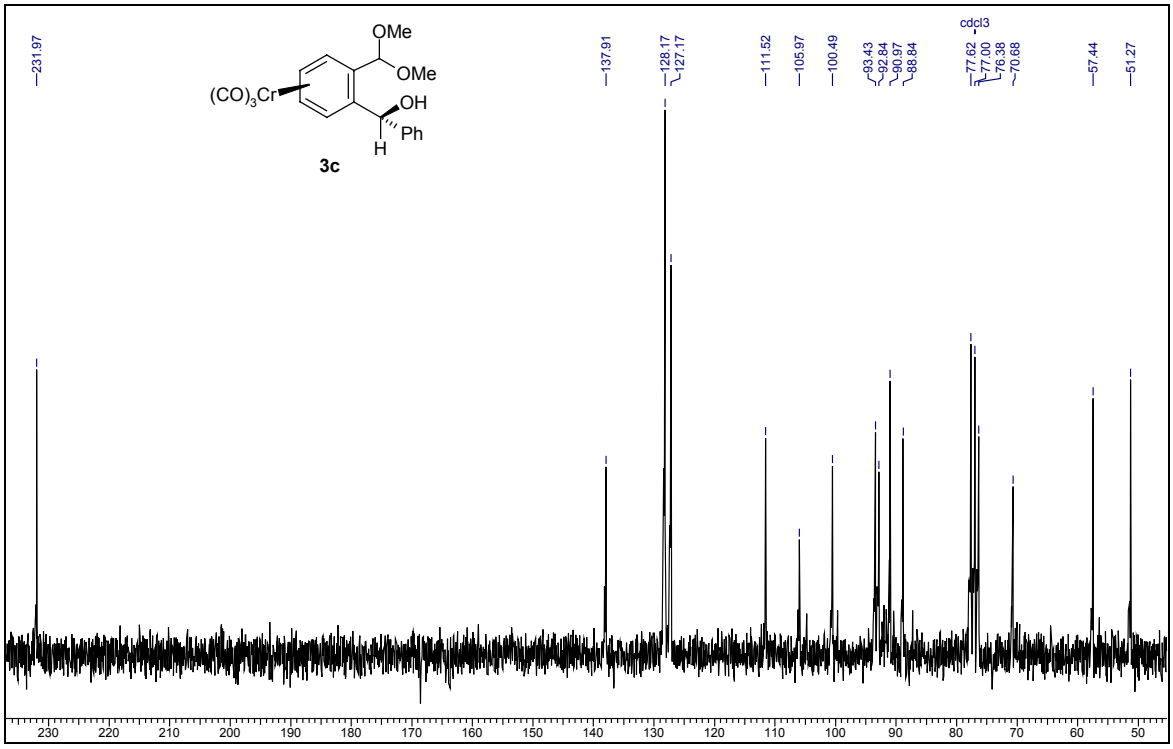
7.42
7.39
7.38
7.37
7.34
7.27
5.87
5.87
5.73
5.63
5.60
5.47
5.45
5.43
5.16
5.14
5.11
4.72
4.70
4.51
4.51
3.68
3.41
OMe
OMe
OH
Ph
H
(CO)3Cr
3c
1.80
3.23
0.99
1.04
1.16
1.11
1.06
1.12
3.00
3.10
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5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90.97
88.84
cdcl3
77.62
77.00
76.38
70.68
57.44
51.27
OMe
OMe
OH
Ph
H
(CO)3Cr
3c
230
220
210
200
190
180
170
160
150
140
130
120
110
100
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80
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60
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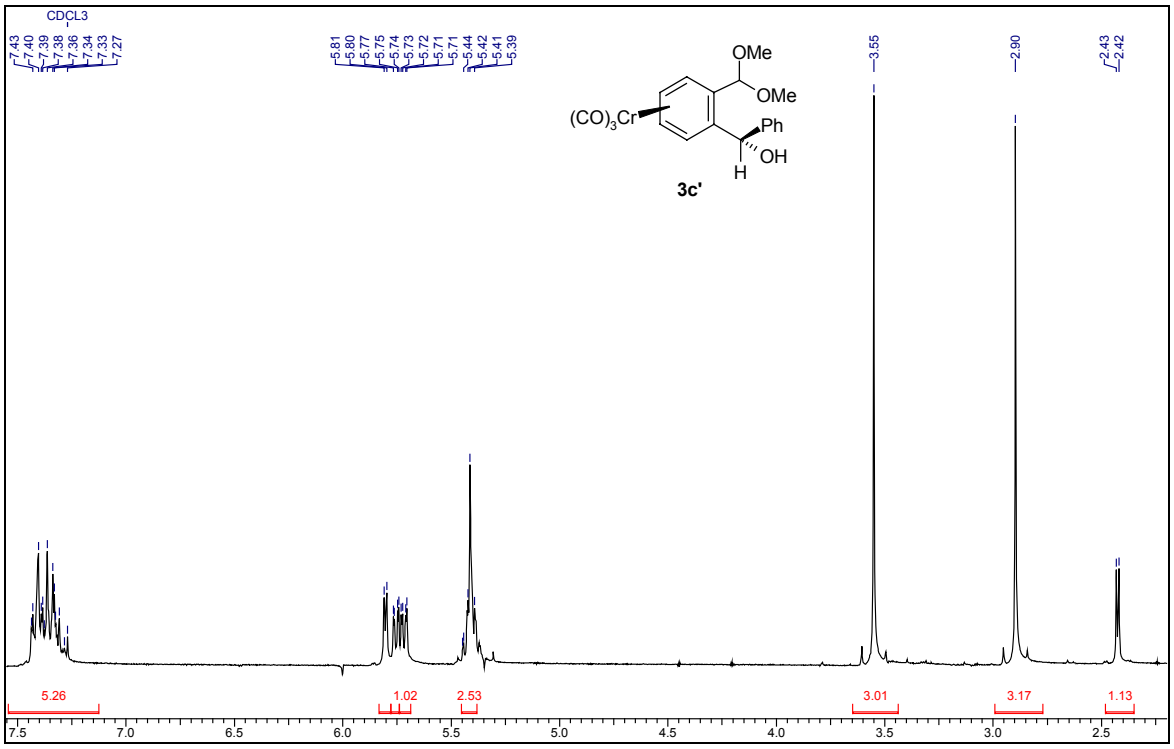
CDCL3
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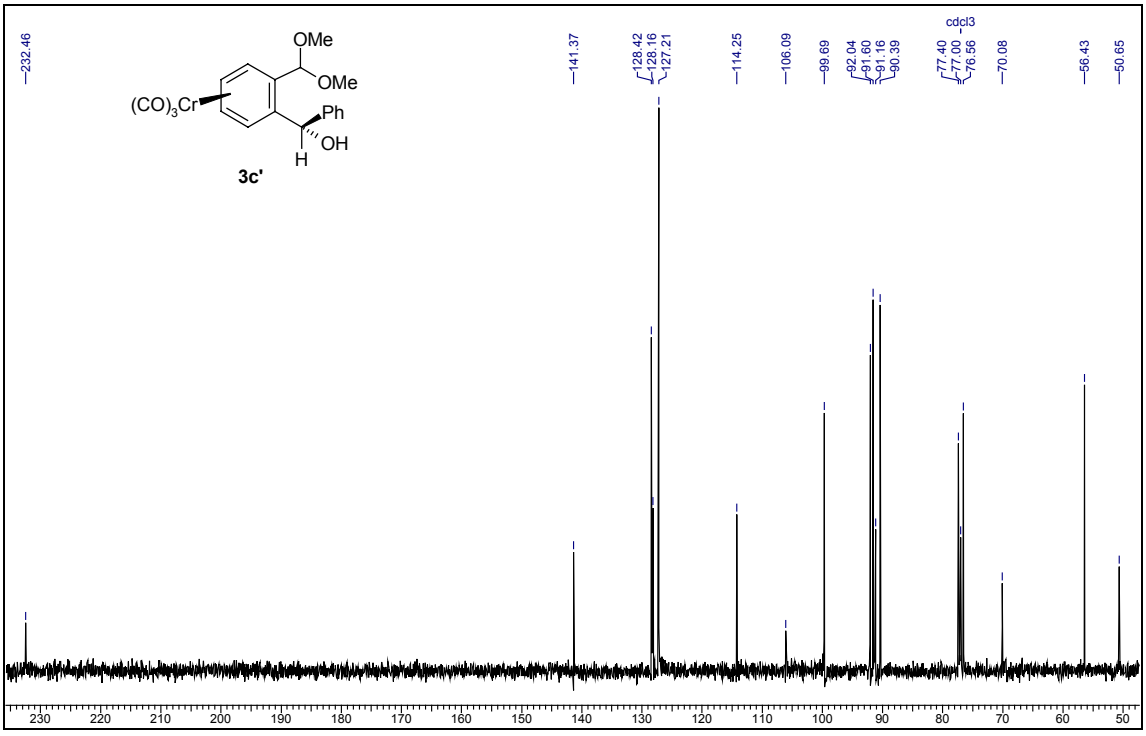
7.39
7.38
7.36
7.34
7.33
7.27
5.81
5.80
5.77
5.75
5.74
5.73
5.72
5.71
5.71
5.44
5.42
5.41
5.39
3.55
2.90
2.43
2.42
OMe
OMe
Ph
OH
H
(CO)3Cr
3c'
5.26
1.02
2.53
3.01
3.17
1.13
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5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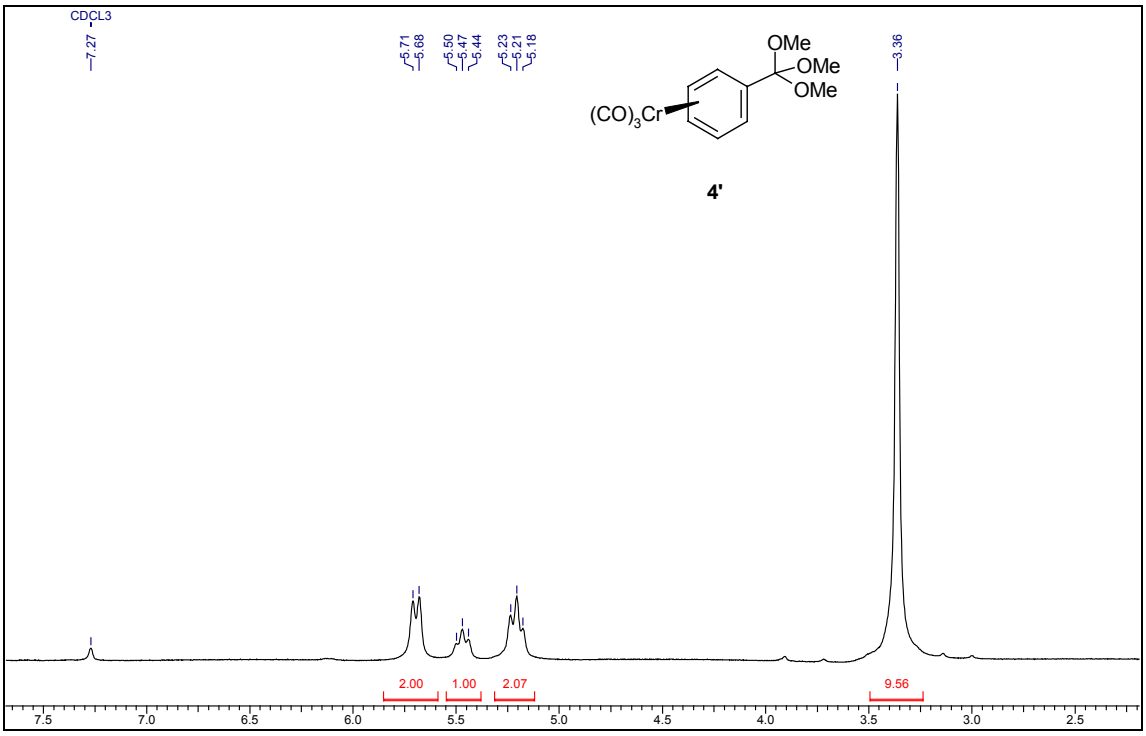
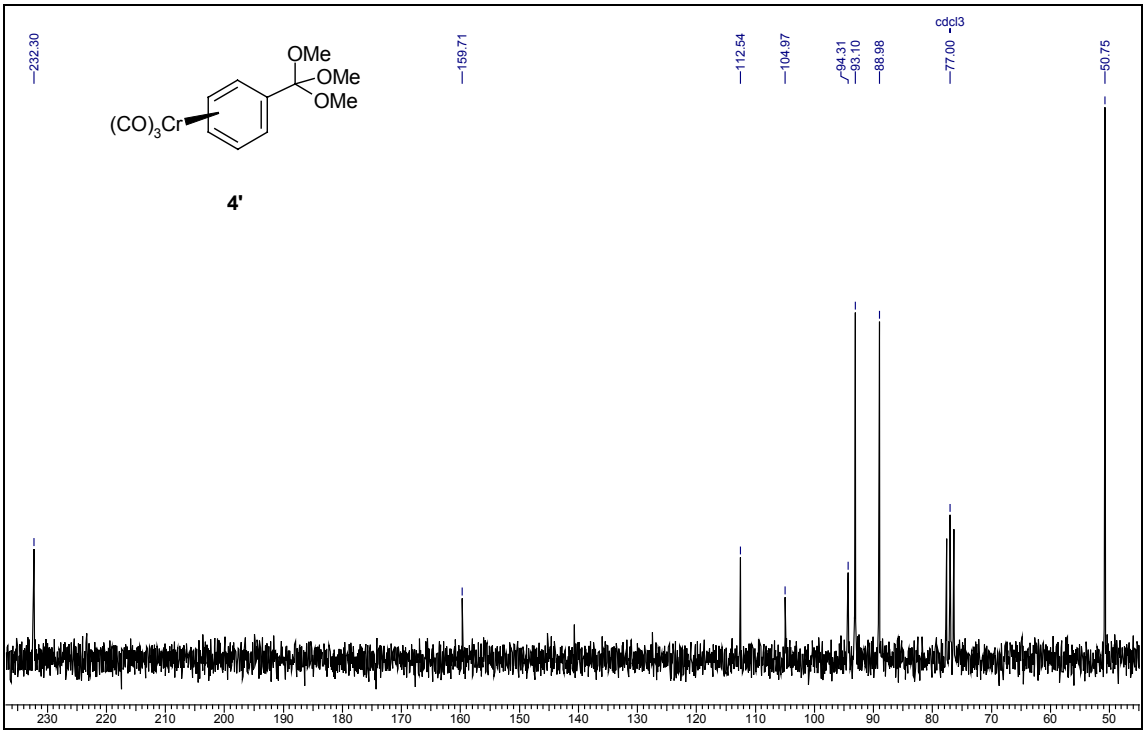
128.16
127.21
114.25
106.09
99.69
92.04
91.60
91.16
90.39
cdcl3
77.40
77.00
76.56
70.08
56.43
50.65
OMe
OMe
Ph
OH
H
(CO)3Cr
3c'
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50


CDCL3
7.27
5.71
5.68
5.50
5.47
5.44
5.23
5.21
5.18
3.36
OMe
OMe
OMe
(CO)3Cr
4'
2.00
1.00
2.07
9.56
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5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93.10
88.98
cdcl3
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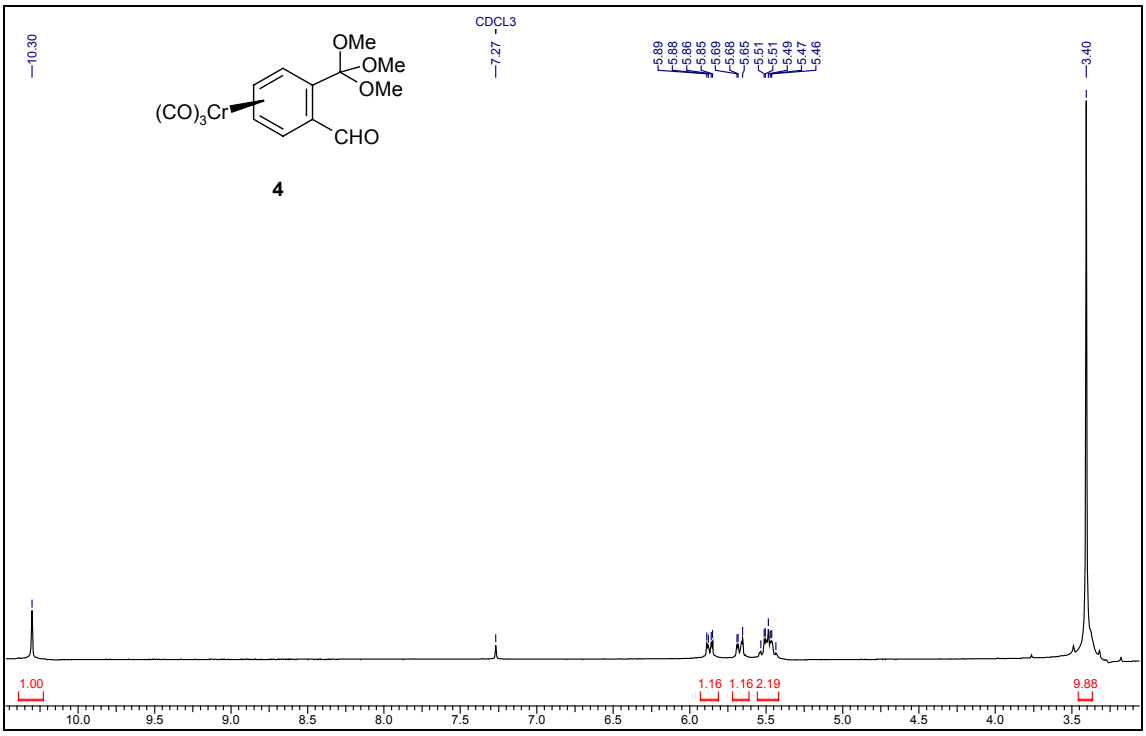
50.75
OMe
OMe
OMe
(CO)3Cr
4'
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50


CDCL3
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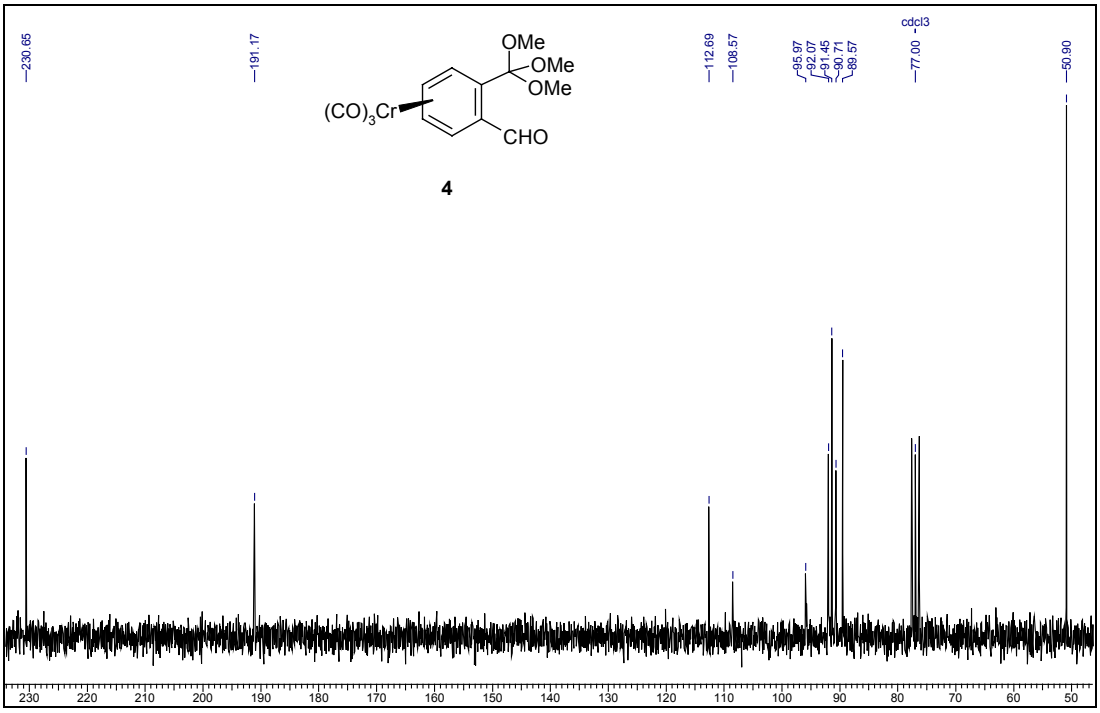
5.86
5.85
5.69
5.68
5.65
5.51
5.51
5.49
5.47
5.46
3.40
OMe
OMe
OMe
(CO)3Cr
CHO
4
1.00
1.16
1.16
2.19
9.88


230.65
191.17
112.69
108.57
95.97
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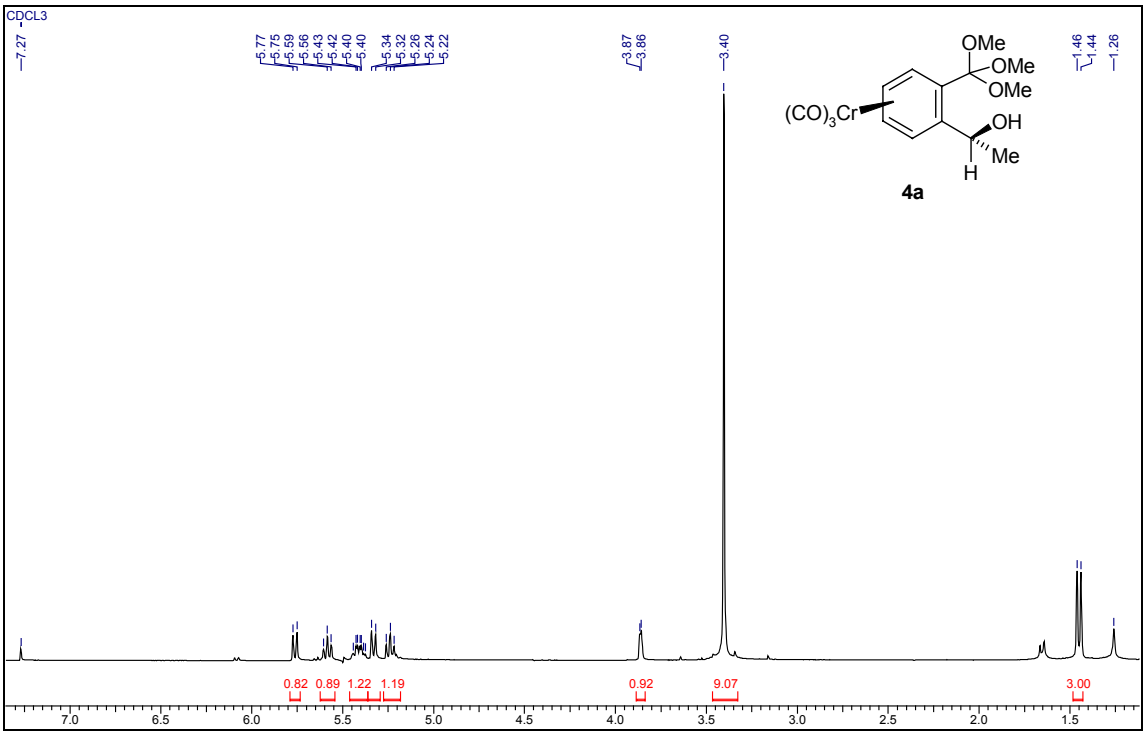
88.57
cdcl3
77.00
50.90
OMe
OMe
OMe
(CO)3Cr
CHO
4


CDCL3
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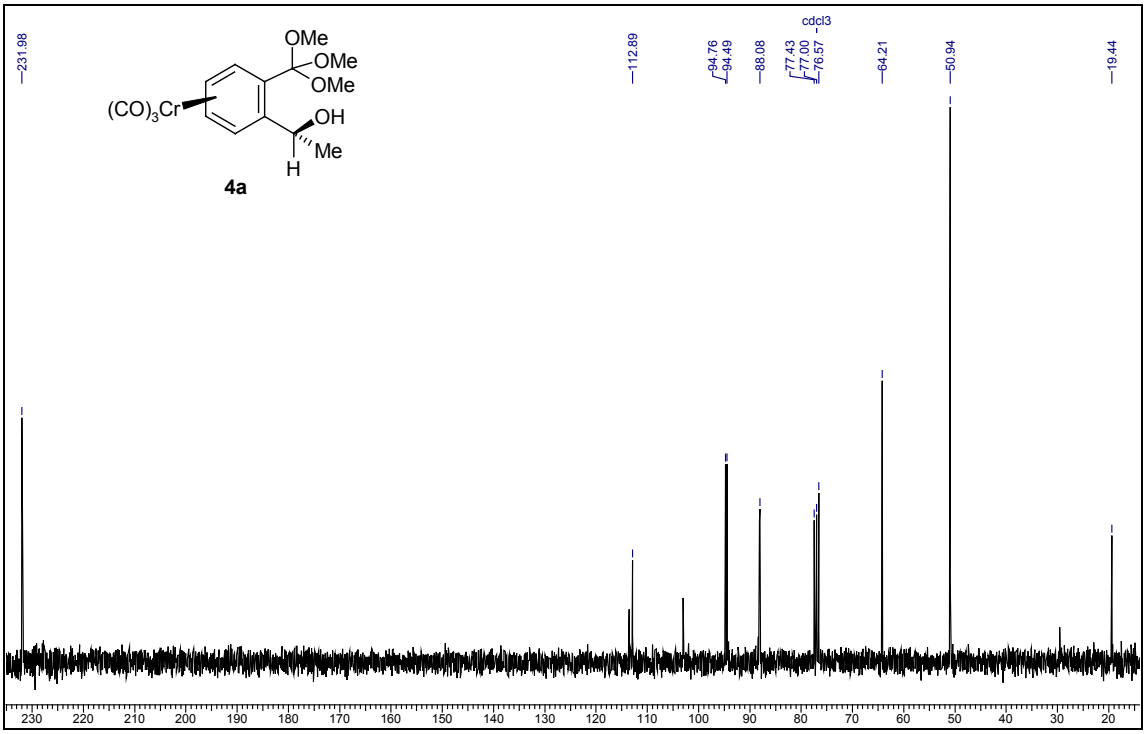
5.75
5.59
5.56
5.43
5.42
5.40
5.40
5.34
5.32
5.26
5.24
5.22
3.87
3.86
3.40
1.46
1.44
1.26
OMe
OMe
OMe
(CO)3Cr
OH
Me
H
4a
0.82
0.89
1.22
1.19
0.92
9.07
3.00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OMe
OMe
(CO)3Cr
OH
Me
H
4a
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94.49
88.08
cdcl3
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77.00
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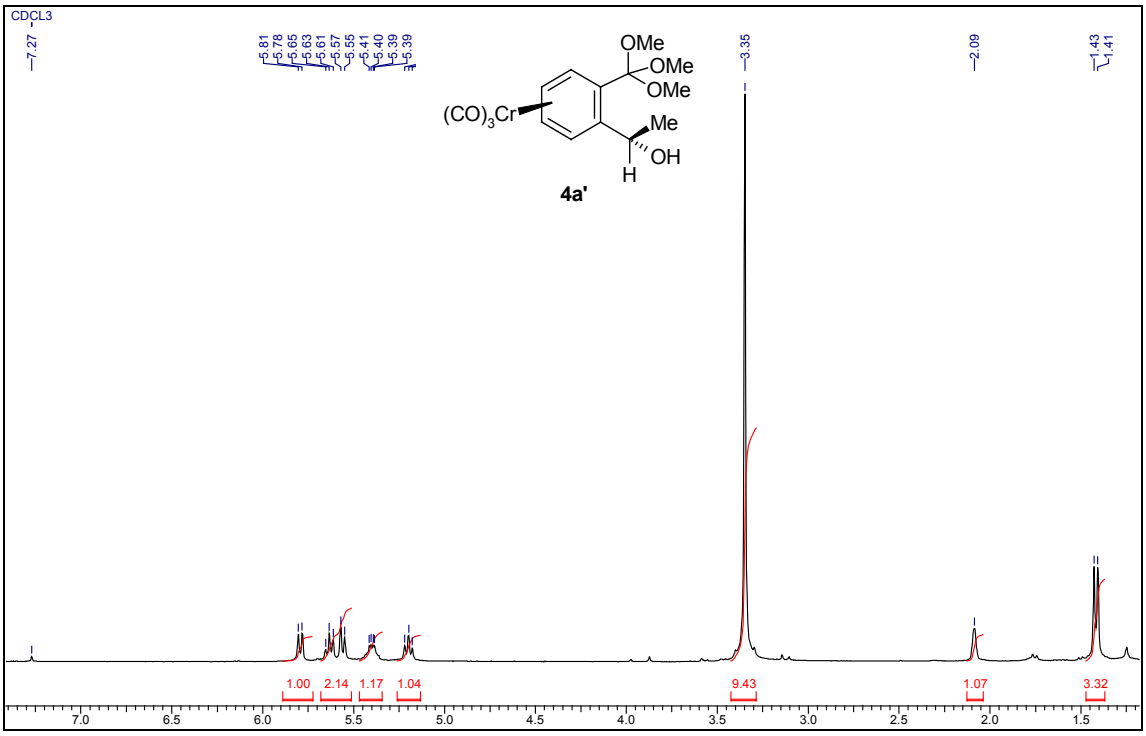
64.21
50.94
19.44


CDCL3
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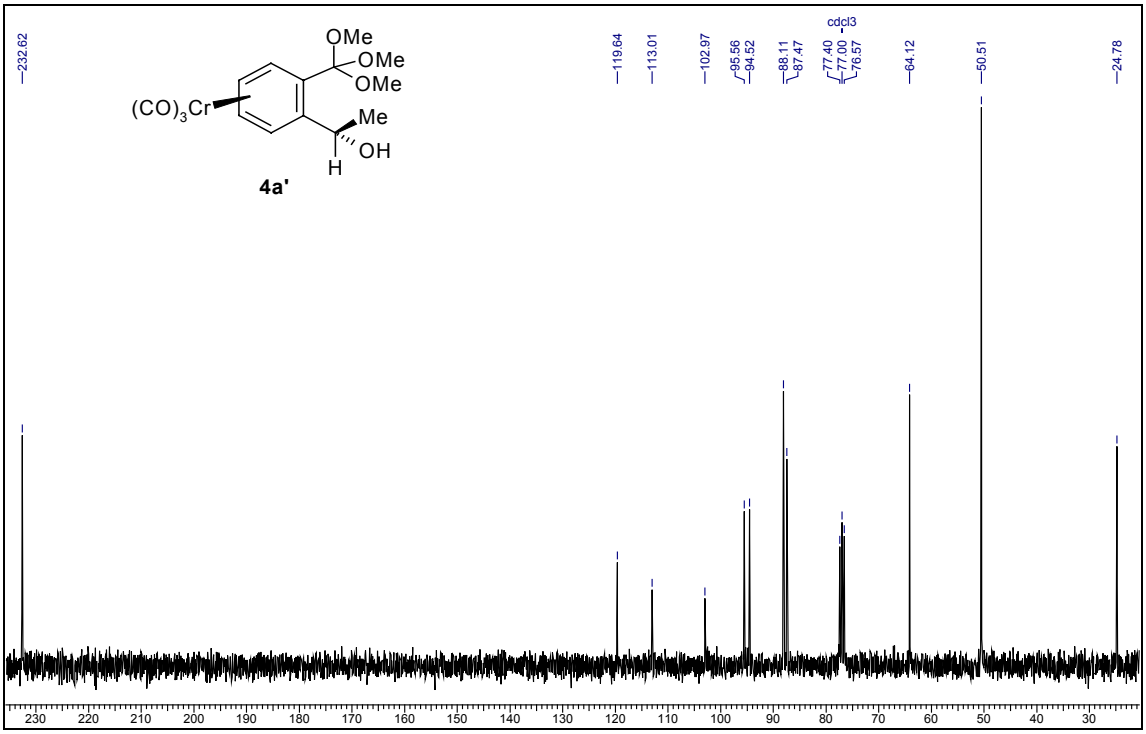
5.57
5.55
5.41
5.40
5.39
5.39
3.35
2.09
1.43
1.41
OMe
OMe
OMe
(CO)3Cr
Me
OH
H
4a'
1.00
2.14
1.17
1.04
9.43
1.07
3.32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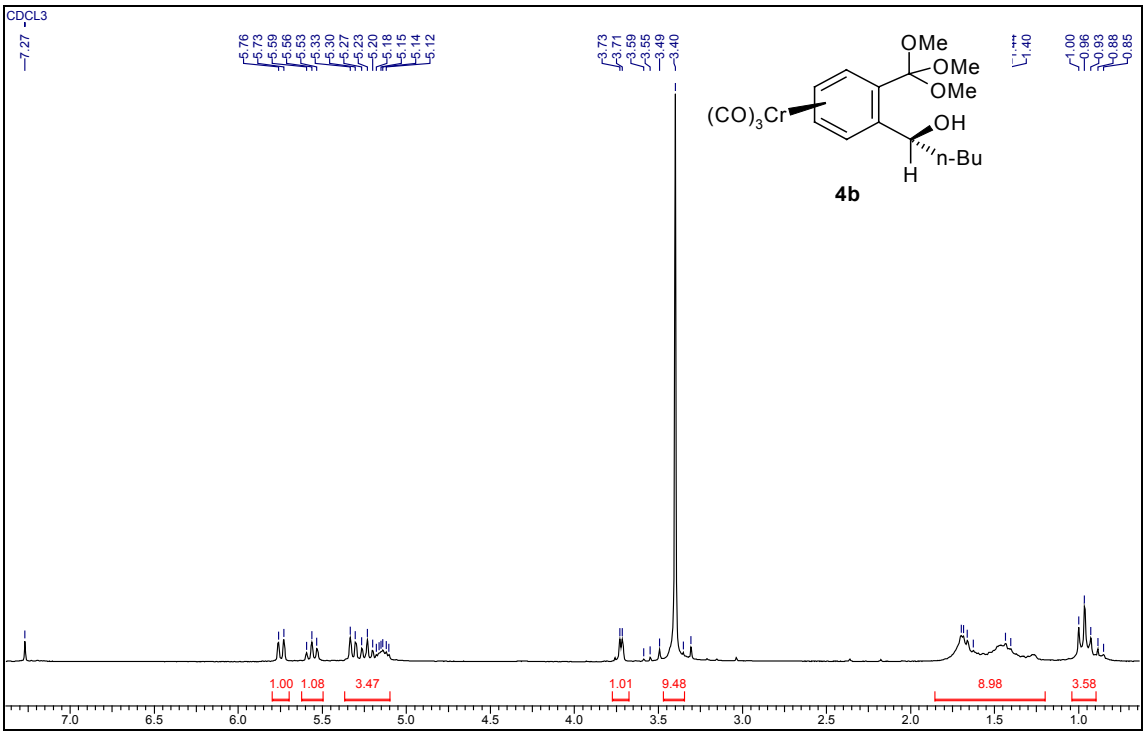
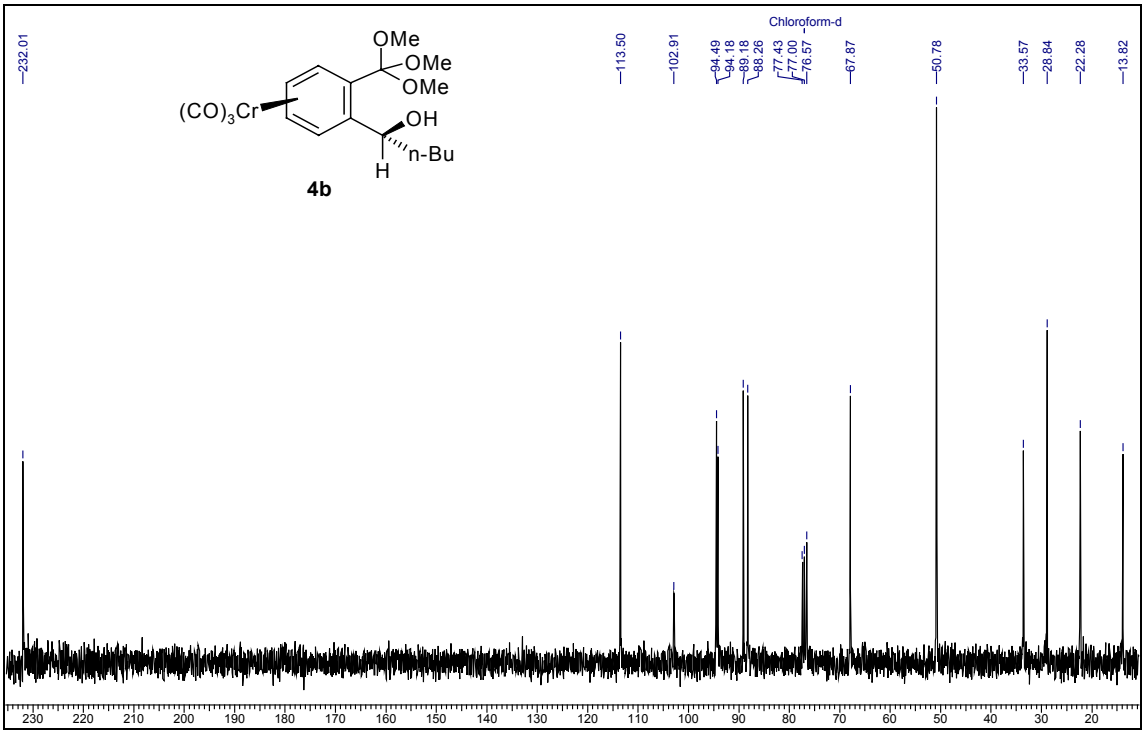
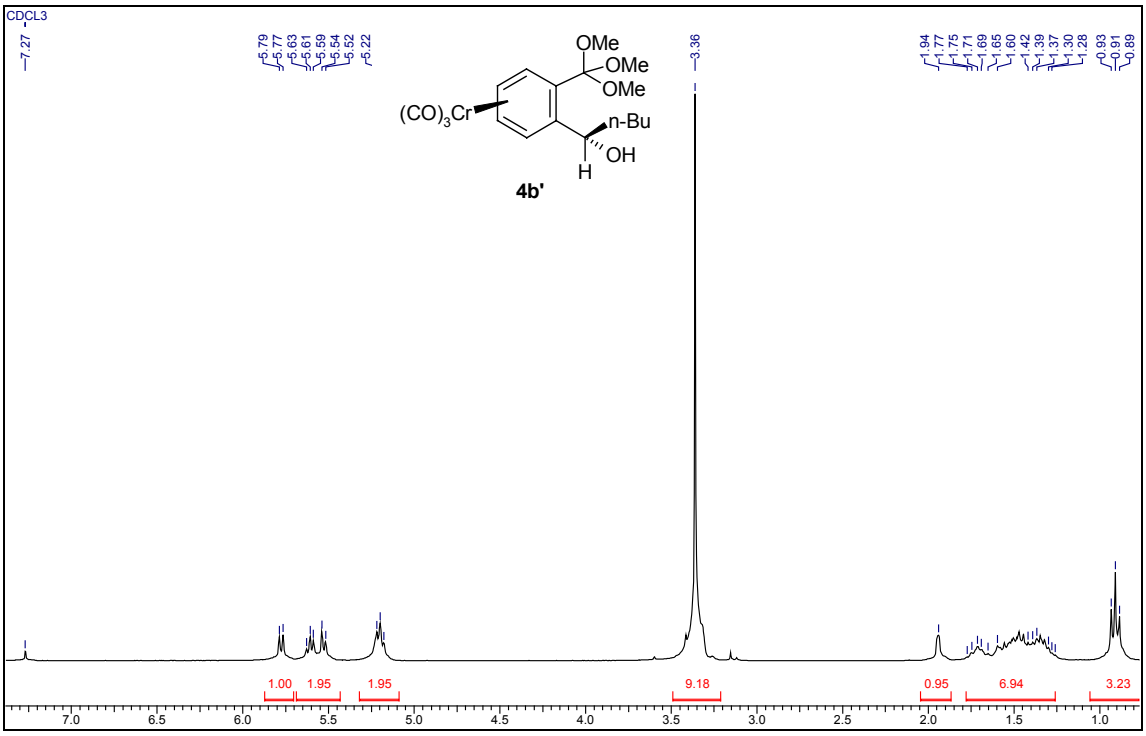
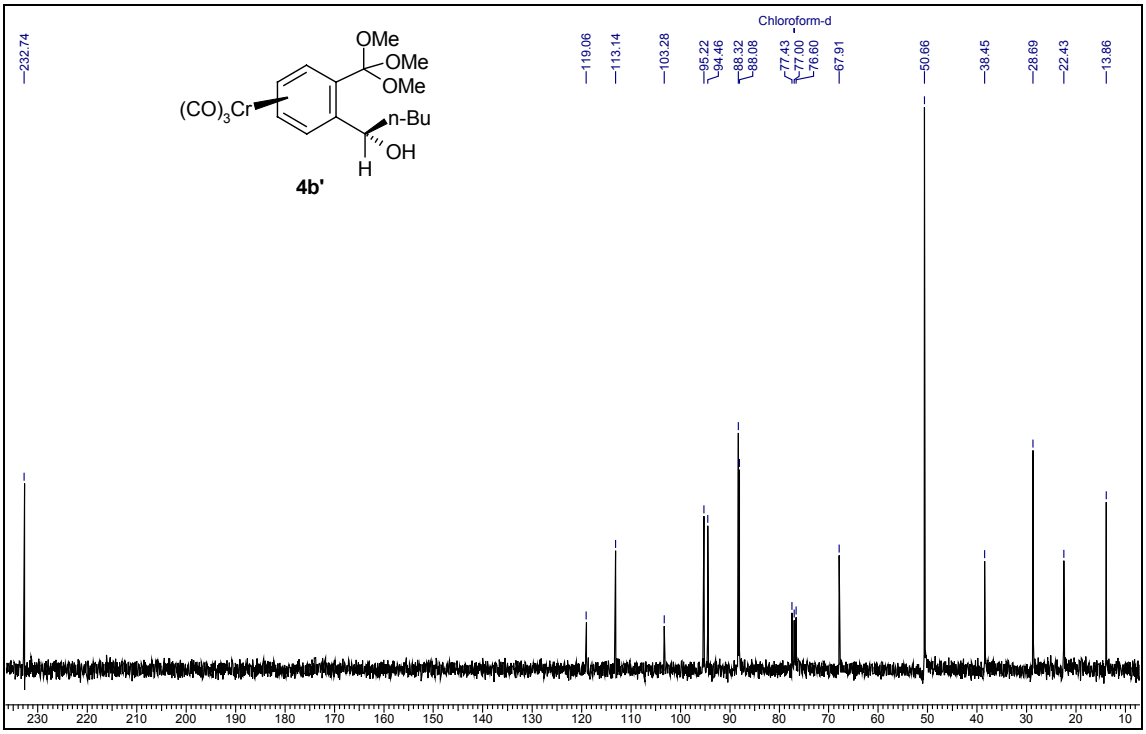
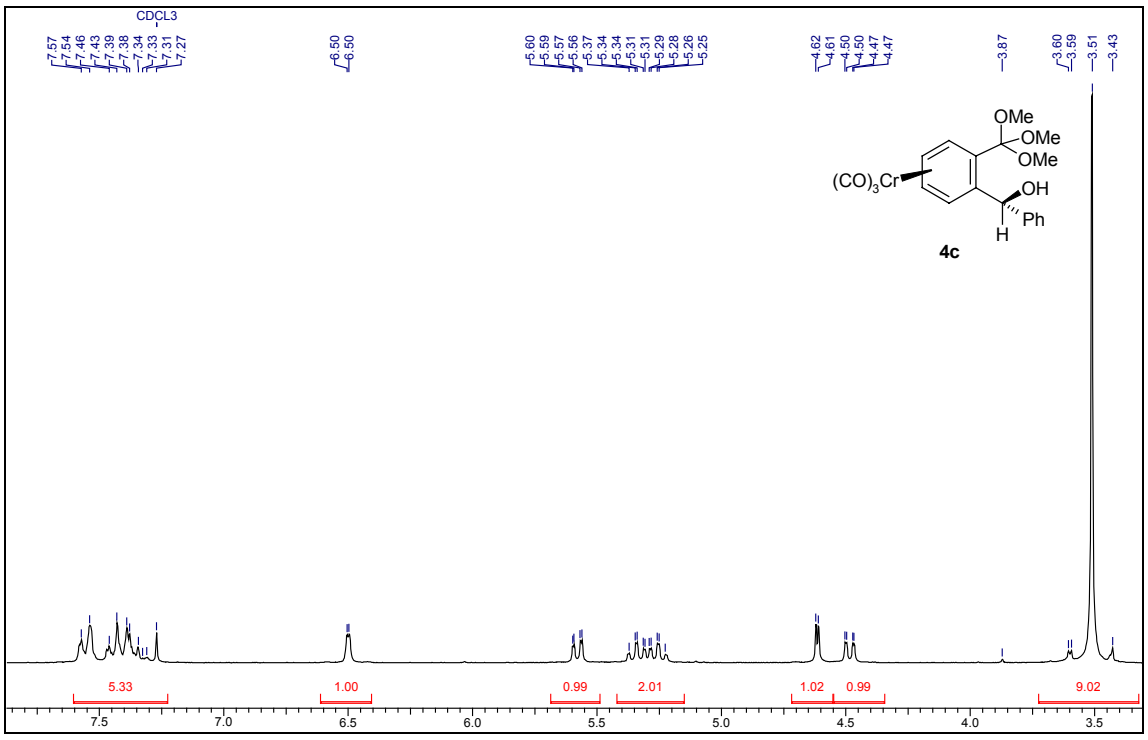
88.11
87.47
cdcl3
77.40
77.00
76.57
64.12
50.51
24.78
OMe
OMe
OMe
(CO)3Cr
Me
OH
H
4a'


CDCL3
7.27
5.76
5.73
5.59
5.56
5.53
5.33
5.30
5.27
5.23
5.20
5.18
5.15
5.14
5.12
3.73
3.71
3.59
3.55
3.49
3.40
1.40
1.00
0.96
0.93
0.88
0.85
OMe
OMe
OMe
(CO)3Cr
OH
n-Bu
H
4b
1.00
1.08
3.47
1.01
9.48
8.98
3.58


232.01
OMe
OMe
OMe
(CO)3Cr
OH
n-Bu
H
4b
Chloroform-d
113.50
102.91
94.49
94.18
89.18
88.26
77.43
77.00
76.57
67.87
50.78
33.57
28.84
22.28
13.82


CDCL3
7.27
5.79
5.77
5.63
5.61
5.59
5.54
5.52
5.22
3.36
1.94
1.77
1.75
1.71
1.69
1.65
1.60
1.42
1.39
1.37
1.30
1.28
0.93
0.91
0.89
OMe
OMe
OMe
(CO)3Cr
n-Bu
OH
H
4b'
1.00
1.95
1.95
9.18
0.95
6.94
3.23


232.74
119.06
113.14
103.28
95.22
94.46
88.32
88.08
77.43
77.00
76.60
67.91
50.66
38.45
28.69
22.43
13.86
Chloroform-d
OMe
OMe
OMe
(CO)3Cr
n-Bu
OH
H
4b'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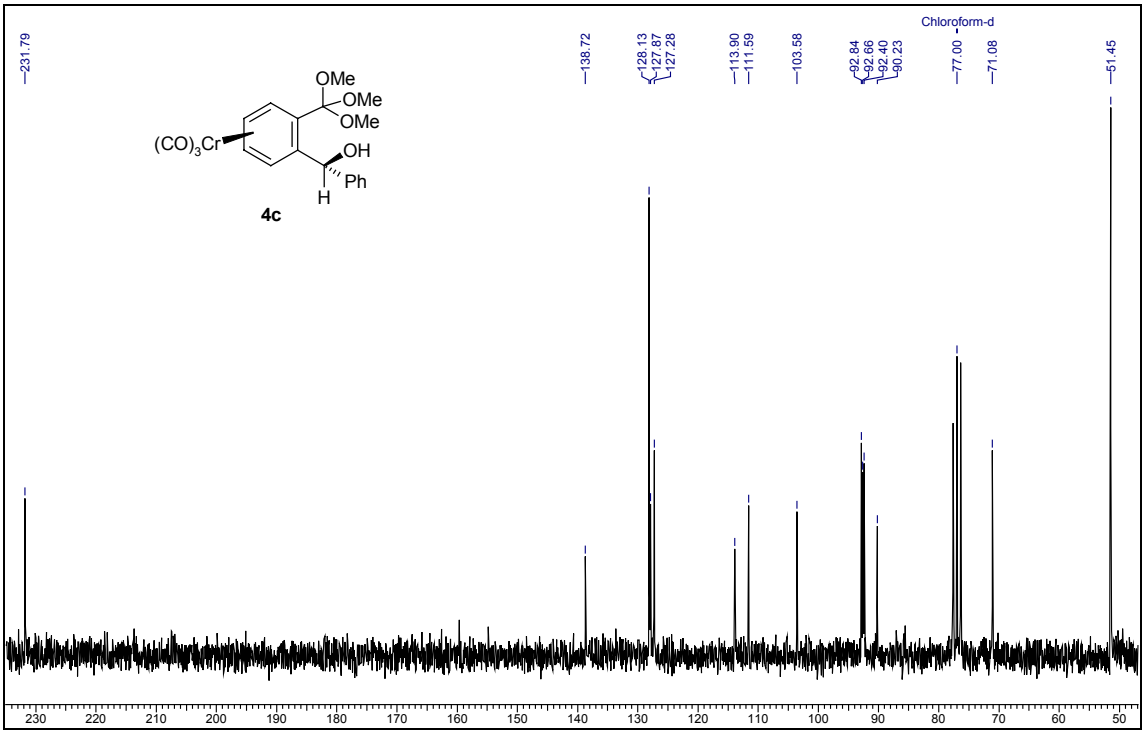
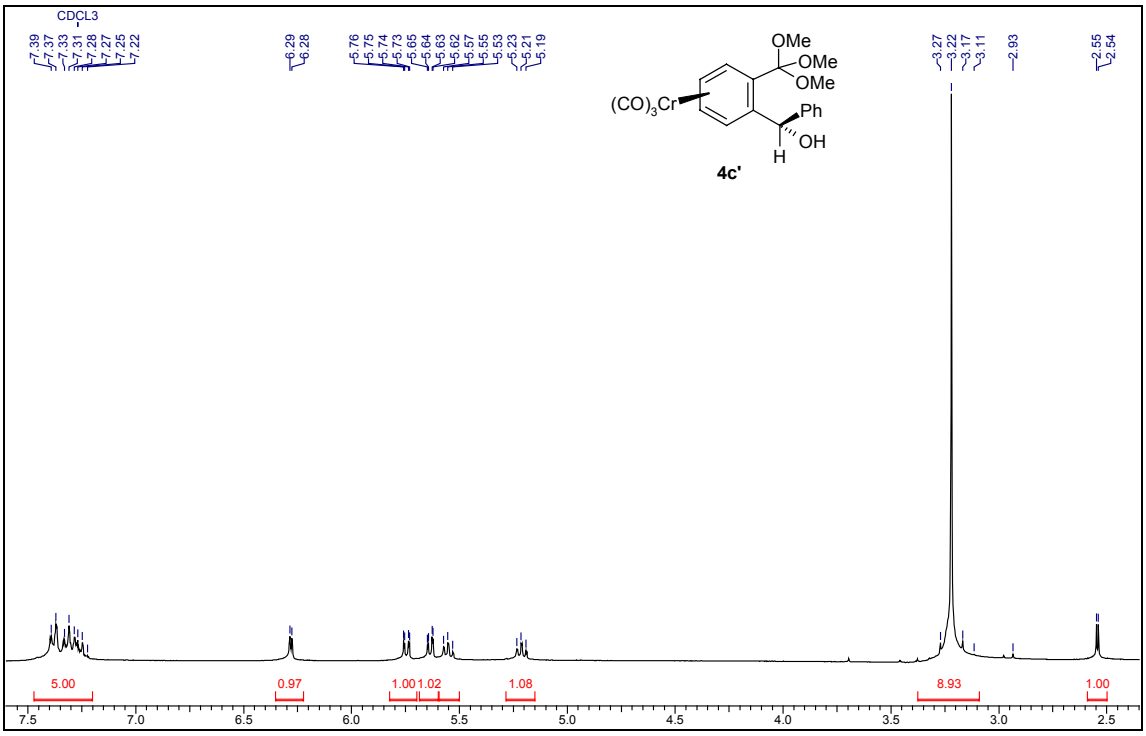
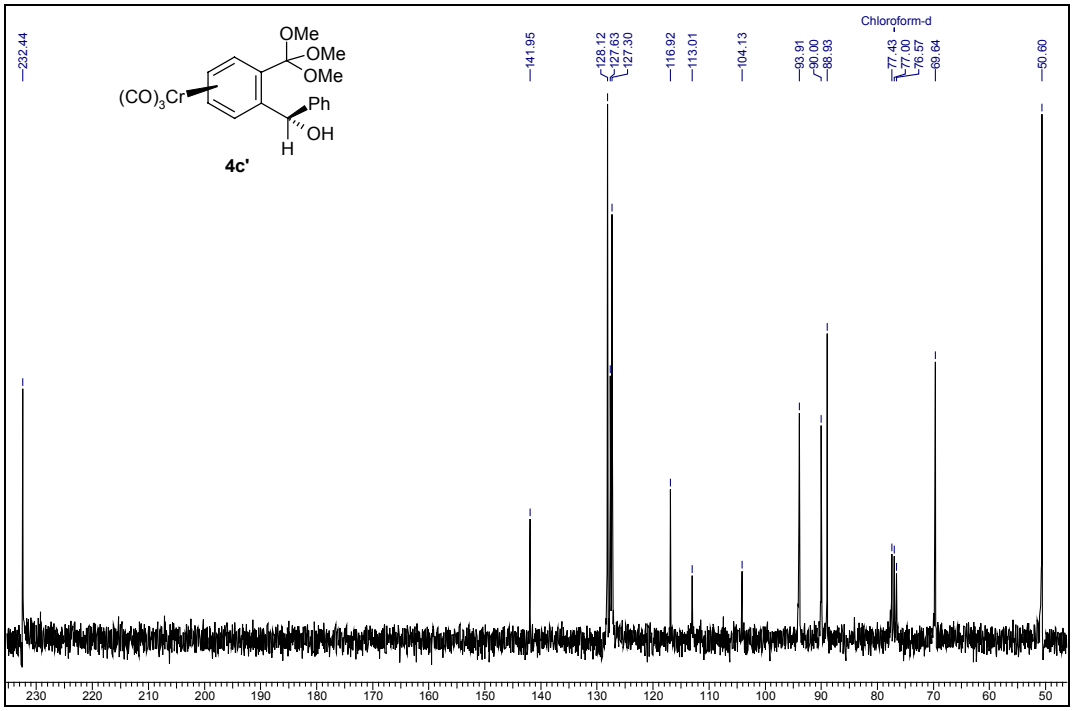
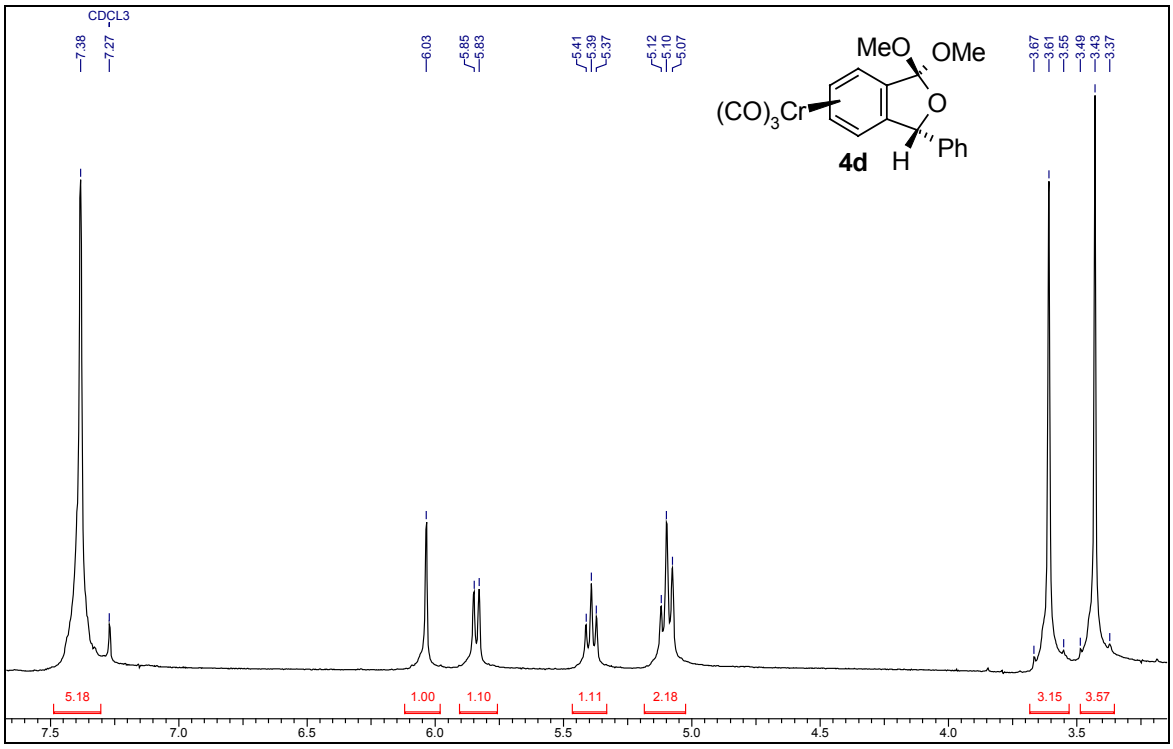
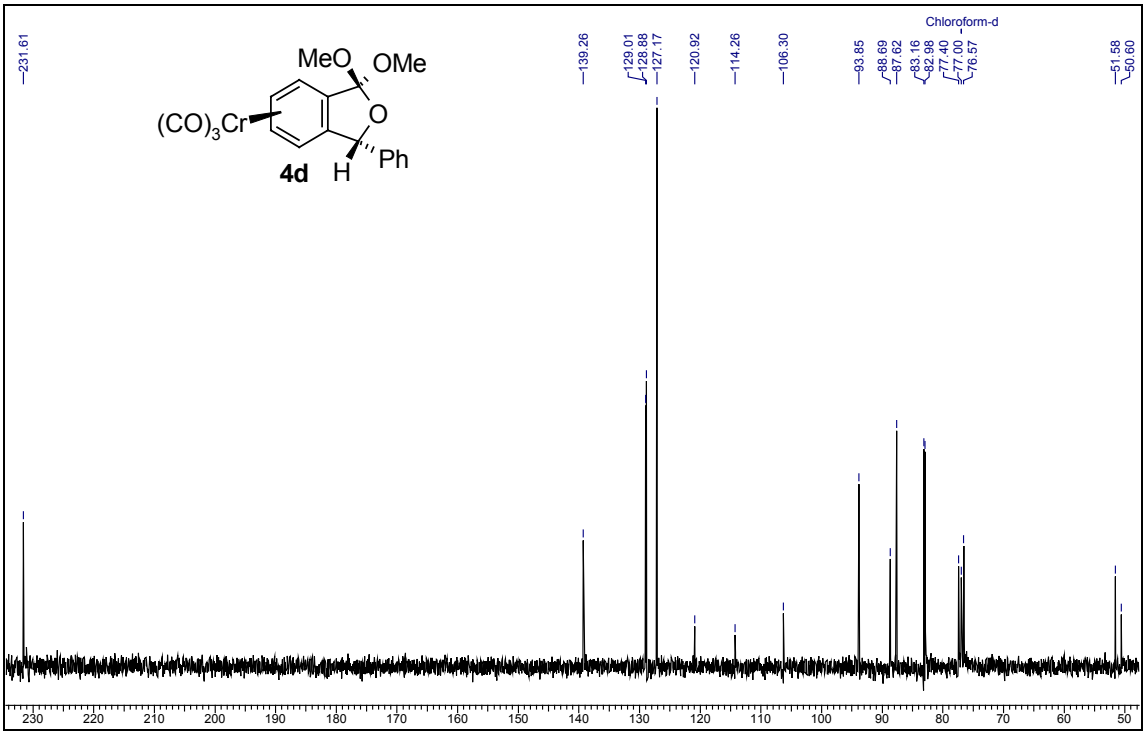
7.54
7.46
7.43
7.39
7.38
7.34
7.33
7.31
7.27
6.50
6.50
5.60
5.59
5.57
5.56
5.37
5.34
5.34
5.31
5.31
5.29
5.28
5.26
5.25
4.62
4.61
4.50
4.50
4.47
4.47
3.87
3.60
3.59
3.51
3.43
OMe
OMe
OMe
(CO)3Cr
OH
Ph
H
4c
5.33
1.00
0.99
2.01
1.02
0.99
9.02
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5

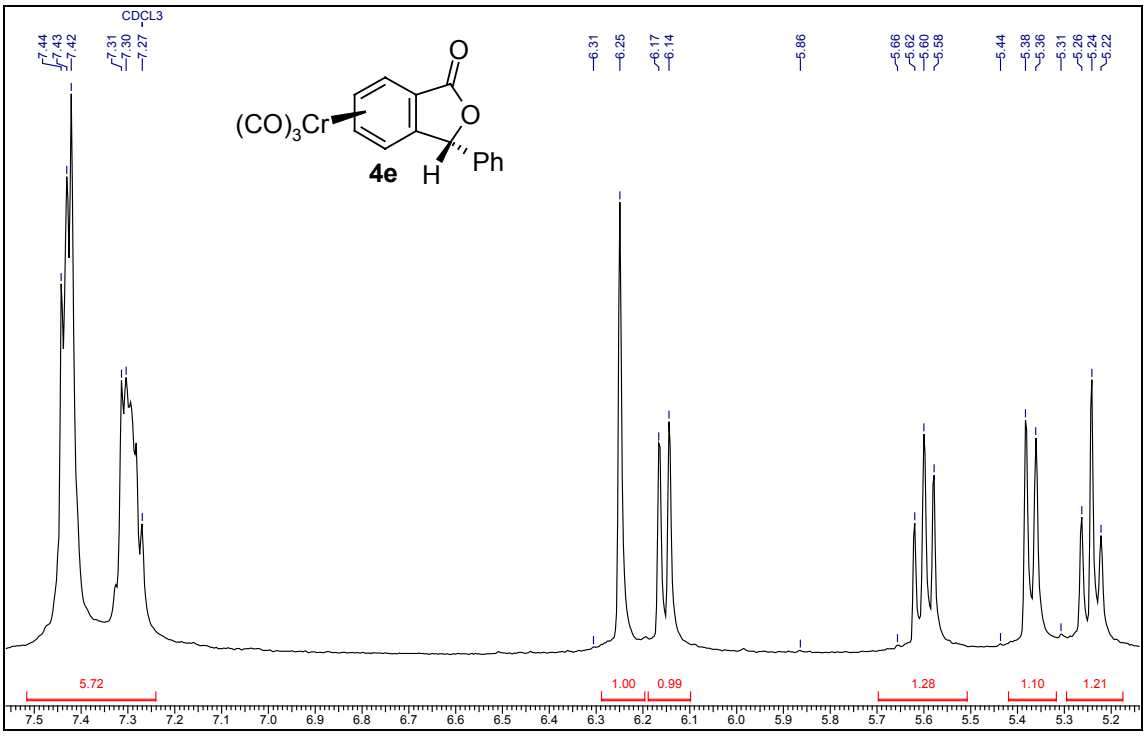

231.79
138.72
128.13
127.87
127.28
113.90
111.59
103.58
92.84
92.66
92.40
90.23
Chloroform-d
77.00
71.08
51.45
OMe
OMe
OMe
(CO)3Cr
OH
Ph
H
4c
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50

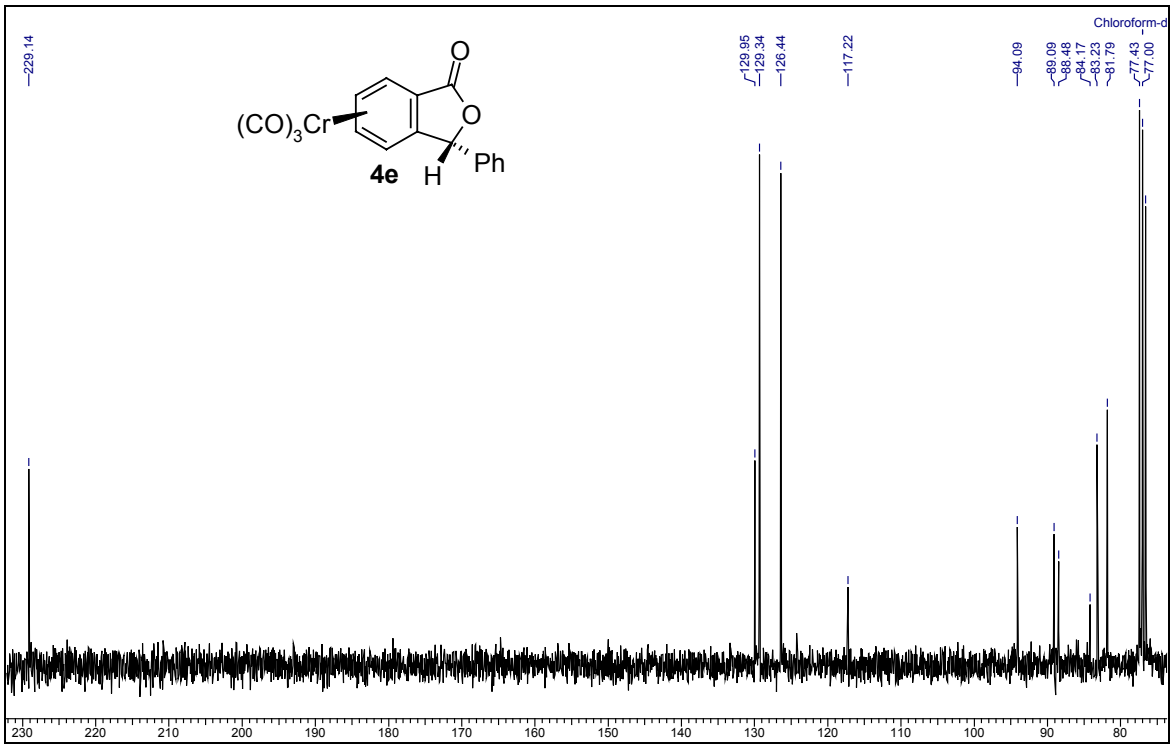

CDCL3
7.39
7.37
7.33
7.31
7.28
7.27
7.25
7.22
6.29
6.28
5.76
5.75
5.74
5.73
5.65
5.64
5.63
5.62
5.57
5.55
5.53
5.23
5.21
5.19
3.27
3.22
3.17
3.11
2.93
2.55
2.54
OMe
OMe
OMe
(CO)3Cr
Ph
OH
H
4c'
5.00
0.97
1.00
1.02
1.08
8.93
1.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5

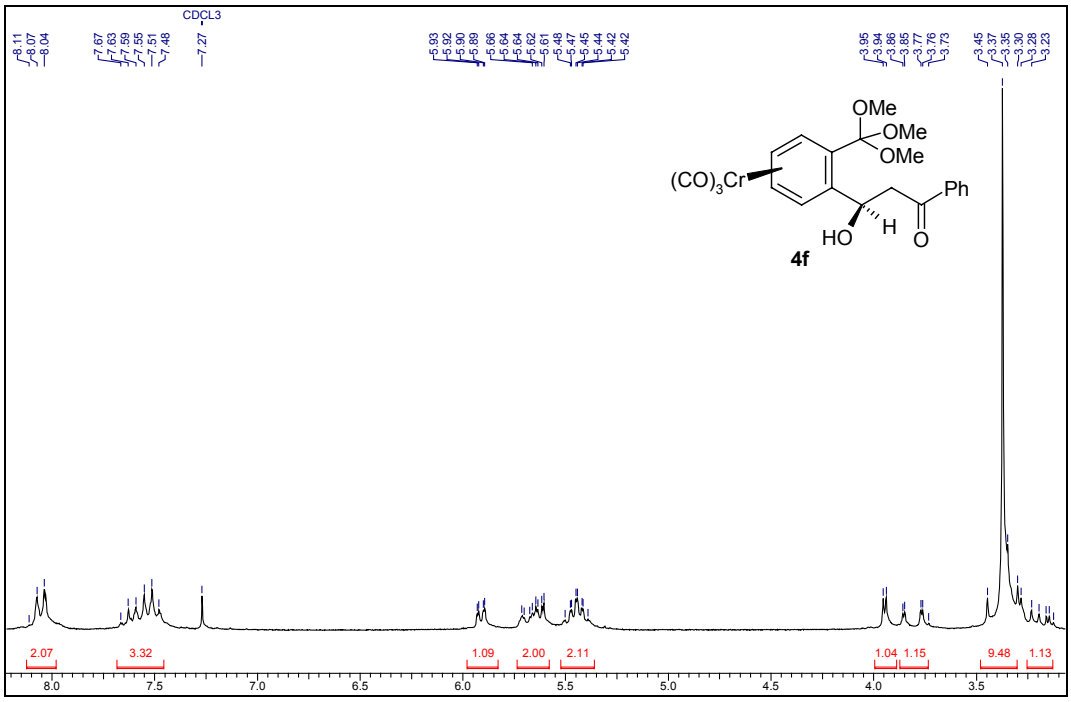

232.44
OMe
OMe
OMe
(CO)3Cr
Ph
OH
H
4c'
141.95
128.12
127.63
127.30
116.92
113.01
104.13
93.91
90.00
88.93
Chloroform-d
77.43
77.00
76.57
69.64
50.60
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50

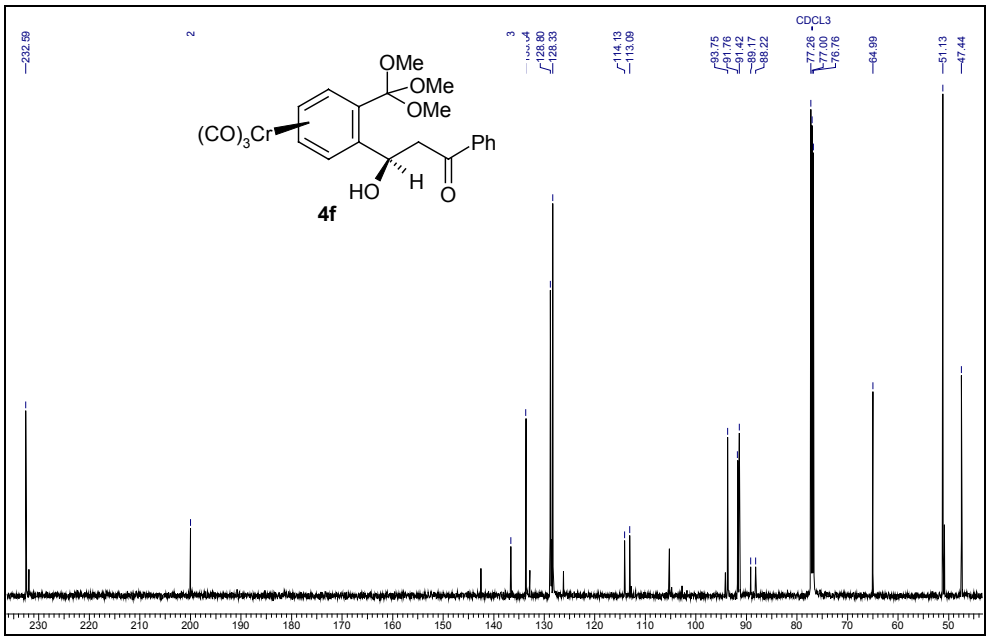

CDCL3
7.38
7.27
6.03
5.85
5.83
5.41
5.39
5.37
5.12
5.10
5.07
3.67
3.61
3.55
3.49
3.43
3.37
MeO
OMe
(CO)3Cr
O
Ph
4d
H
5.18
1.00
1.10
1.11
2.18
3.15
3.57
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5

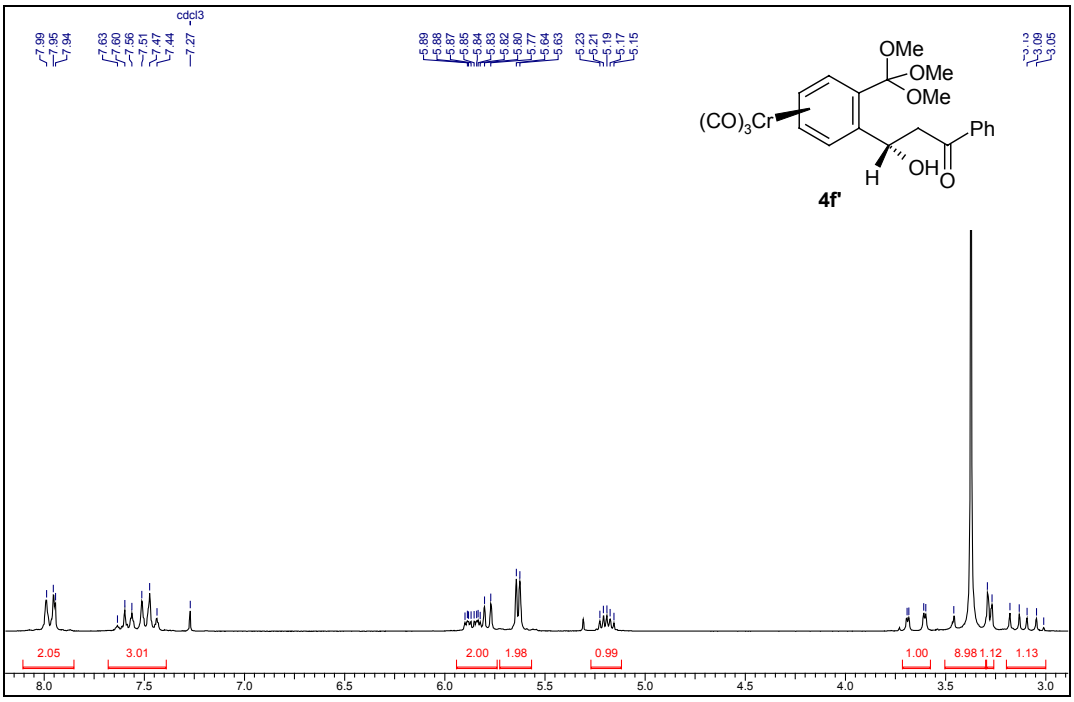

231.61
MeO
OMe
(CO)3Cr
O
Ph
4d
H
139.26
129.01
128.88
127.17
120.92
114.26
106.30
93.85
88.69
87.62
83.16
82.98
77.40
77.00
76.57
Chloroform-d
51.58
50.60
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50

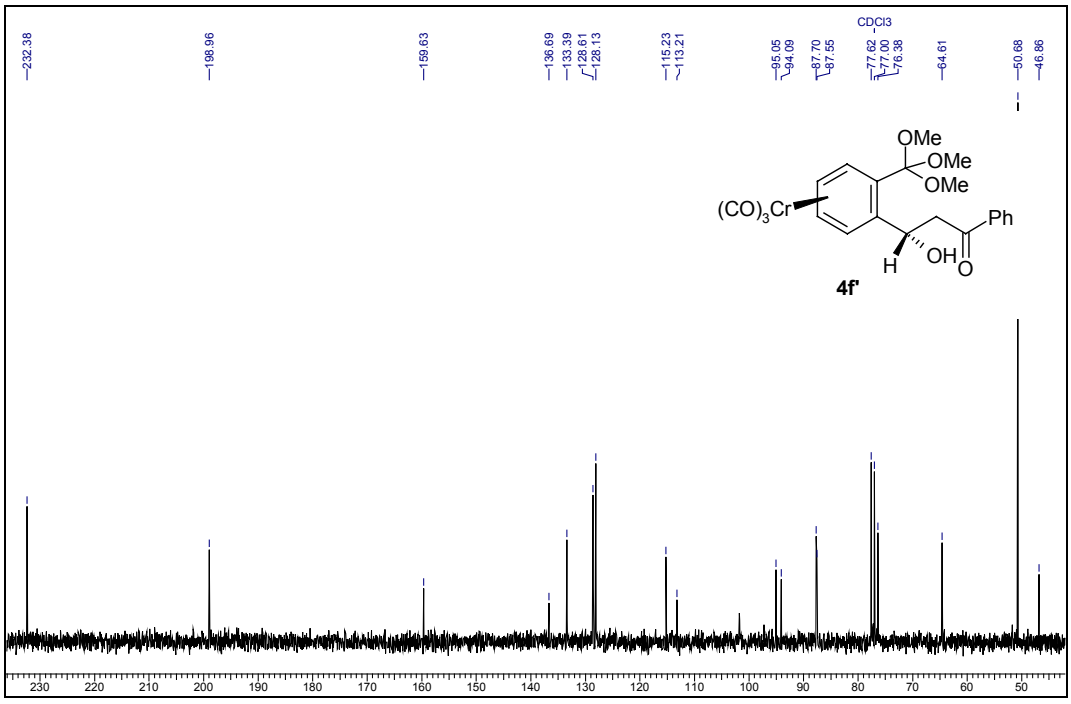

CDCL3
7.44
7.43
7.42
7.31
7.30
7.27
6.31
6.25
6.17
6.14
5.86
5.66
5.62
5.60
5.58
5.44
5.38
5.36
5.31
5.26
5.24
5.22
O
O
(CO)3Cr
Ph
H
4e
5.72
1.00
0.99
1.28
1.10
1.21
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
6.3
6.2
6.1
6.0
5.9
5.8
5.7
5.6
5.5
5.4
5.3
5.2

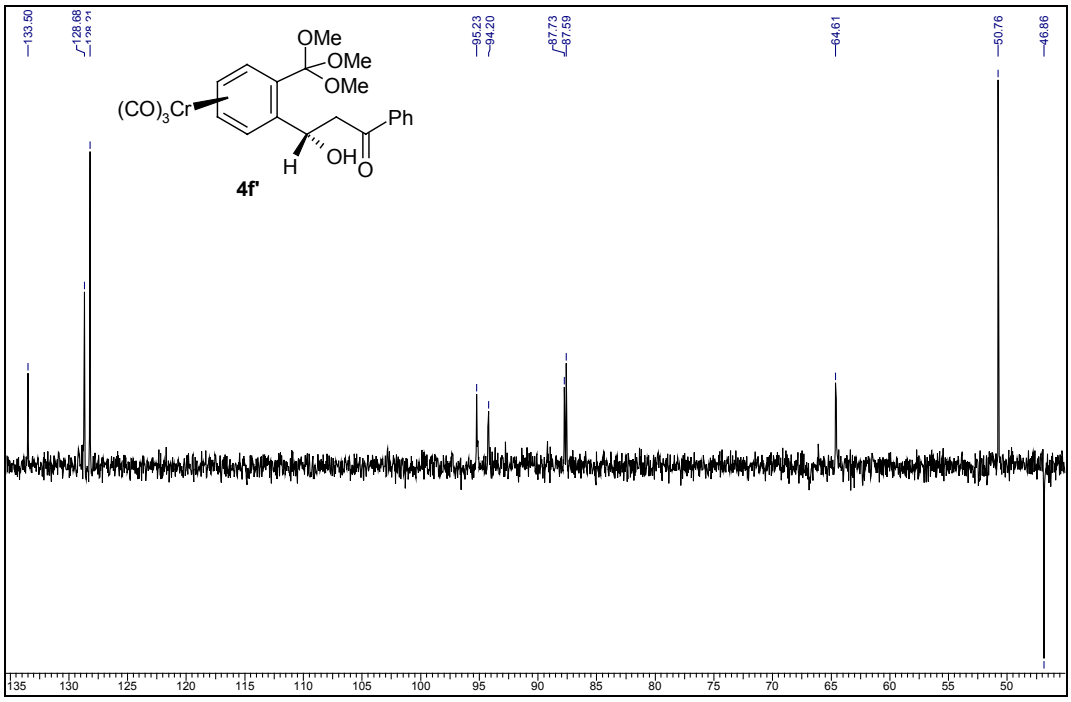

Chloroform-d
229.14
129.95
129.34
126.44
117.22
94.09
89.09
88.48
84.17
83.23
81.79
77.43
77.00
O
O
(CO)3Cr
Ph
H
4e
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80

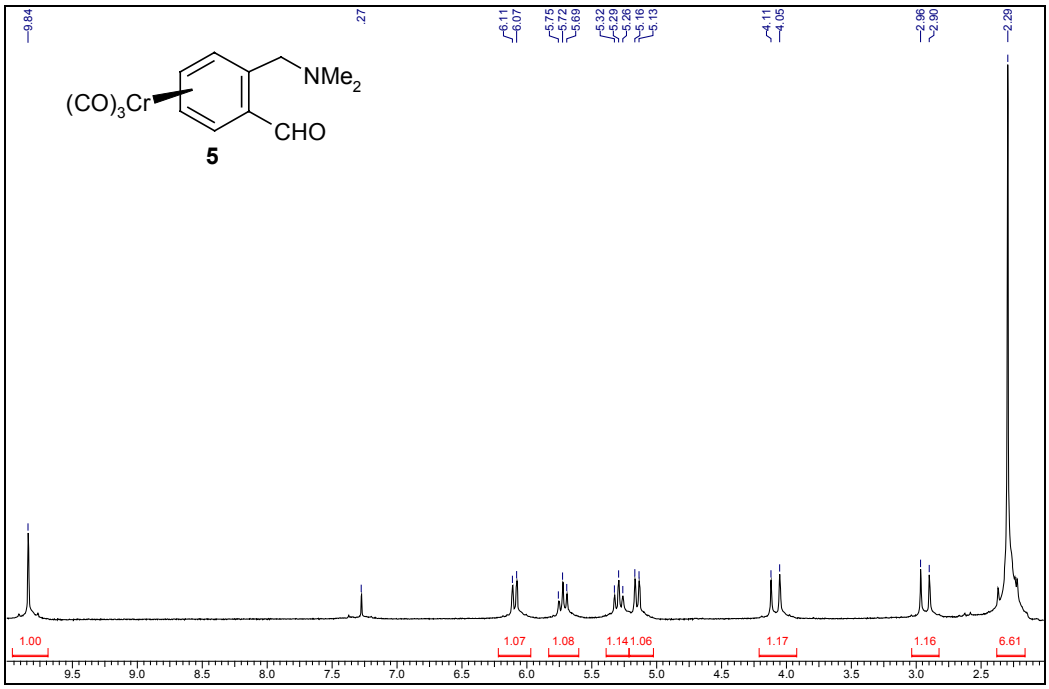

CDCL3
8.11
8.07
8.04
7.67
7.63
7.59
7.55
7.51
7.48
7.27
5.93
5.92
5.90
5.89
5.66
5.64
5.64
5.62
5.61
5.48
5.47
5.45
5.44
5.42
5.42
3.95
3.94
3.86
3.85
3.77
3.76
3.73
3.45
3.37
3.35
3.30
3.28
3.23
OMe
OMe
OMe
(CO)3Cr
Ph
HO
H
O
4f
2.07
3.32
1.09
2.00
2.11
1.04
1.15
9.48
1.13
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5

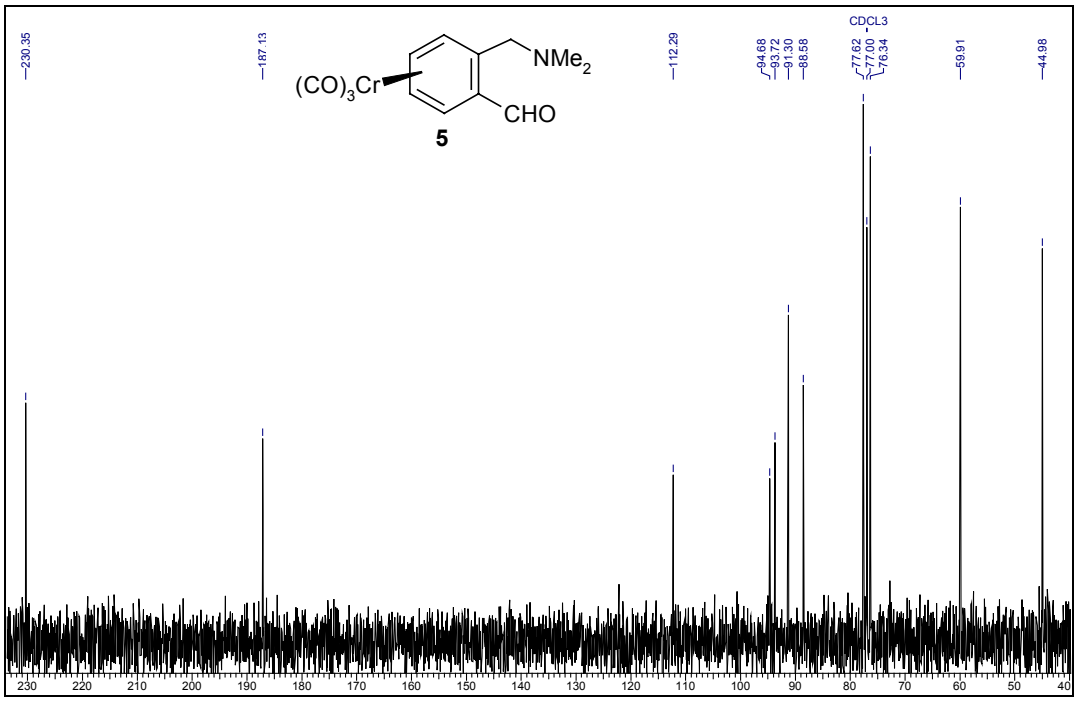

232.59
2
3
128.80
128.33
114.13
113.09
93.75
91.76
91.42
89.17
88.22
CDCL3
77.26
77.00
76.76
64.99
51.13
47.44
OMe
OMe
OMe
(CO)3Cr
Ph
HO
H
O
4f
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50

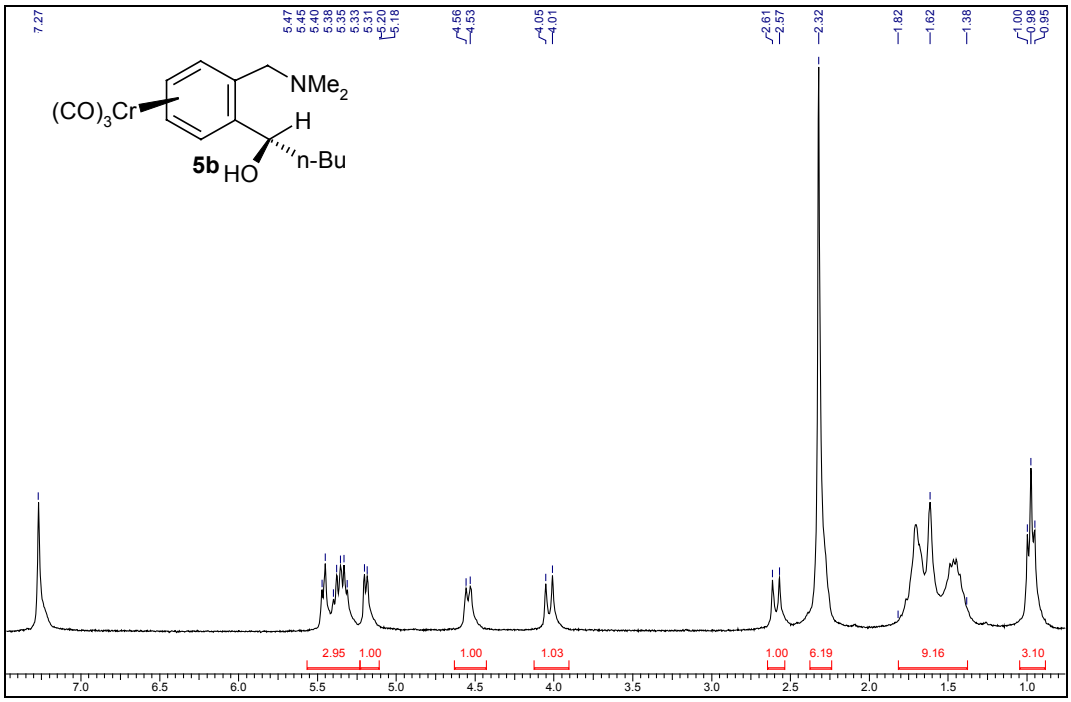

cdcl3
7.99
7.95
7.94
7.63
7.60
7.56
7.51
7.47
7.44
7.27
5.89
5.88
5.87
5.85
5.84
5.83
5.82
5.80
5.77
5.64
5.63
5.23
5.21
5.19
5.17
5.15
3.13
3.09
3.05
OMe
OMe
OMe
(CO)3Cr
Ph
H
OH
O
4f'
2.05
3.01
2.00
1.98
0.99
1.00
8.98
1.12
1.13
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0


232.38
198.96
159.63
136.69
133.39
128.61
128.13
115.23
113.21
95.05
94.09
87.70
87.55
CDCl3
77.62
77.00
76.38
64.61
50.68
46.86
OMe
OMe
OMe
(CO)3Cr
Ph
H
OH
O
4f'
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50


133.50
128.68
95.23
94.20
87.73
87.59
64.61
50.76
46.86
OMe
OMe
OMe
(CO)3Cr
Ph
H
OH
O
4f'


9.84
6.11
6.07
5.75
5.72
5.69
5.32
5.29
5.26
5.16
5.13
4.11
4.05
2.96
2.90
2.29
NMe2
(CO)3Cr
CHO
5
1.00
1.07
1.08
1.14
1.06
1.17
1.16
6.61


230.35
187.13
112.29
94.68
93.72
91.30
88.58
CDCL3
77.62
77.00
76.34
59.91
44.98
(CO)3Cr
NMe2
CHO
5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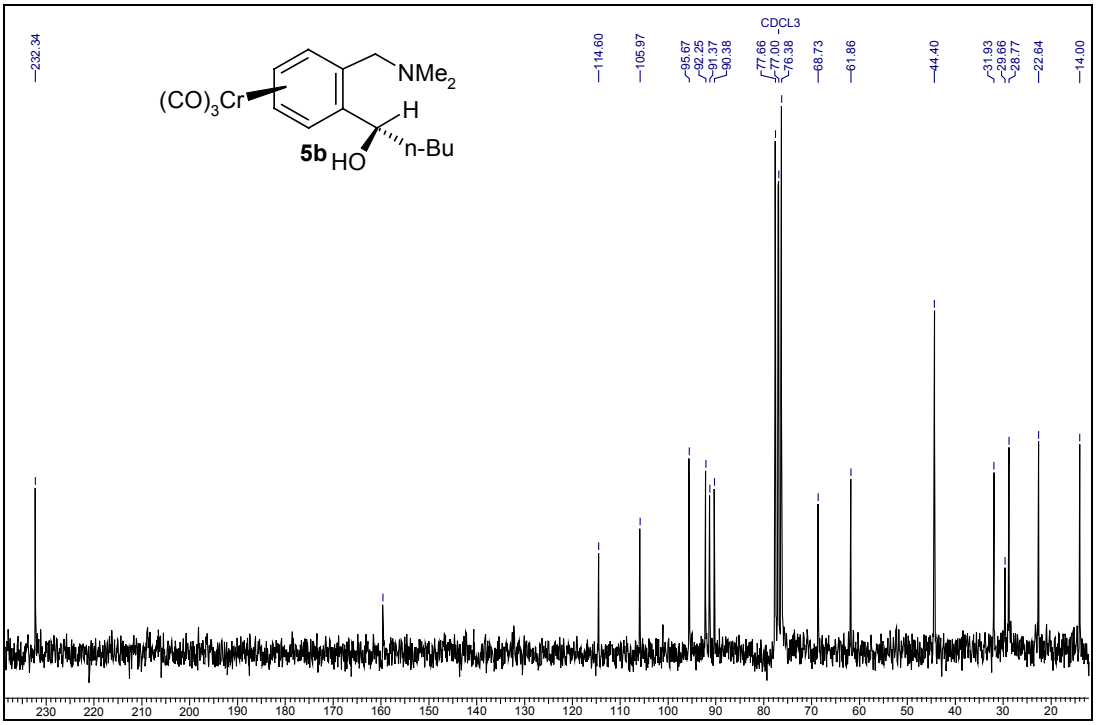
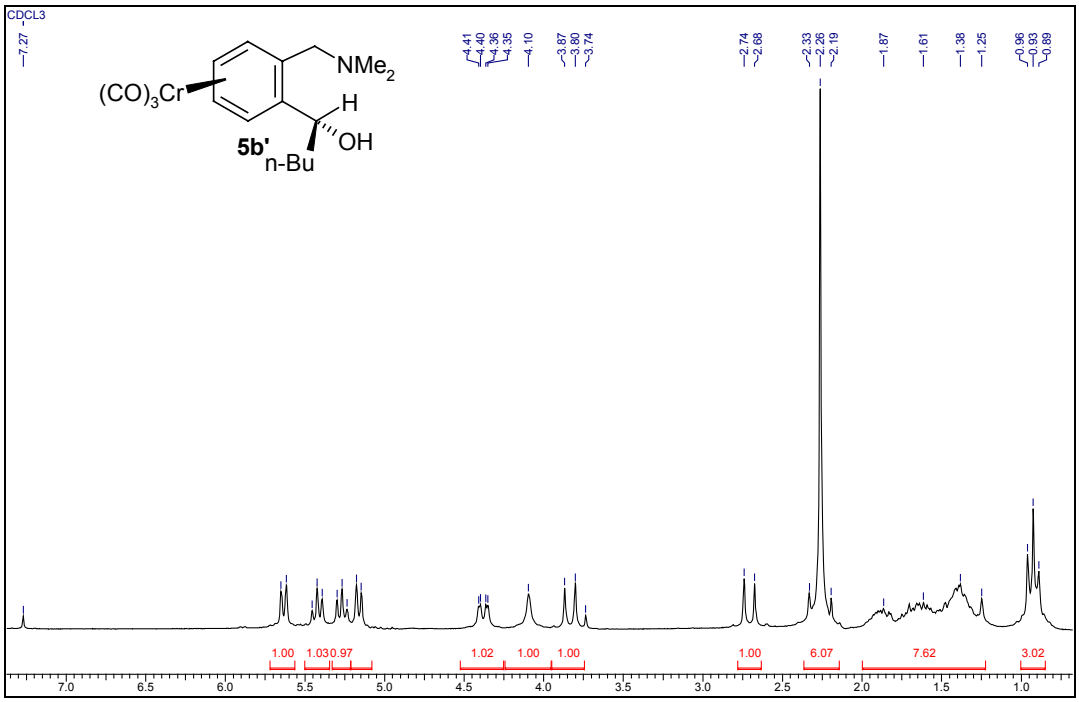
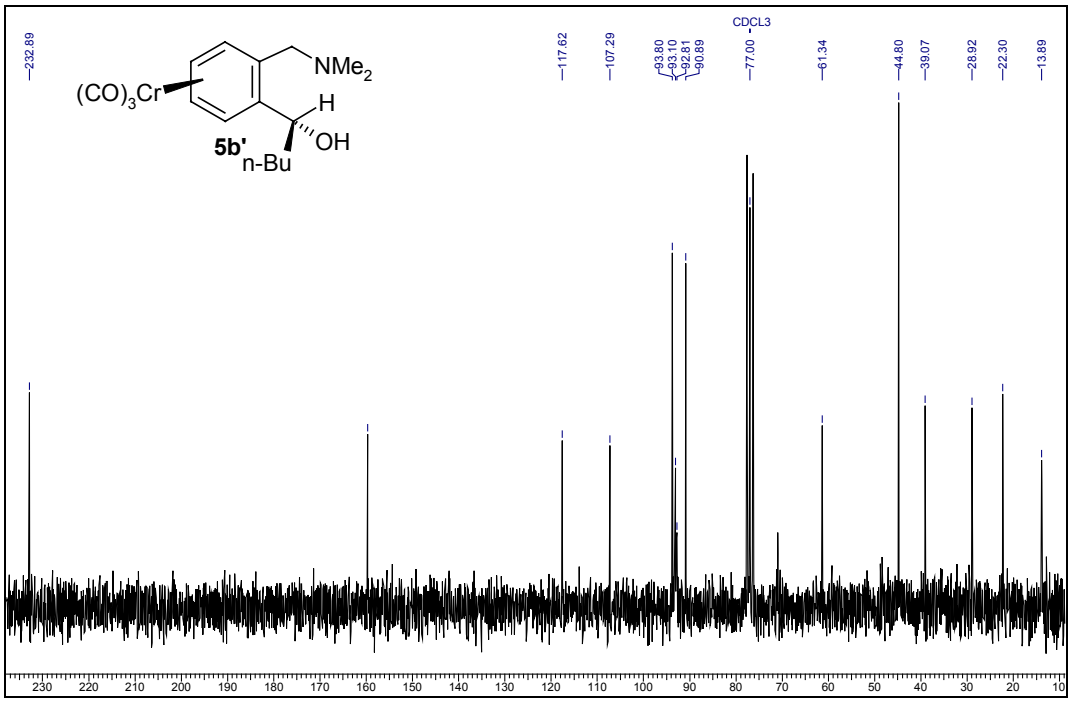
5.47
5.45
5.40
5.38
5.35
5.33
5.31
5.20
5.18
4.56
4.53
4.05
4.01
2.61
2.57
2.32
1.82
1.62
1.38
1.00
0.98
0.95
(CO)3Cr
NMe2
H
n-Bu
HO
5b
2.95
1.00
1.00
1.03
1.00
6.19
9.16
3.10

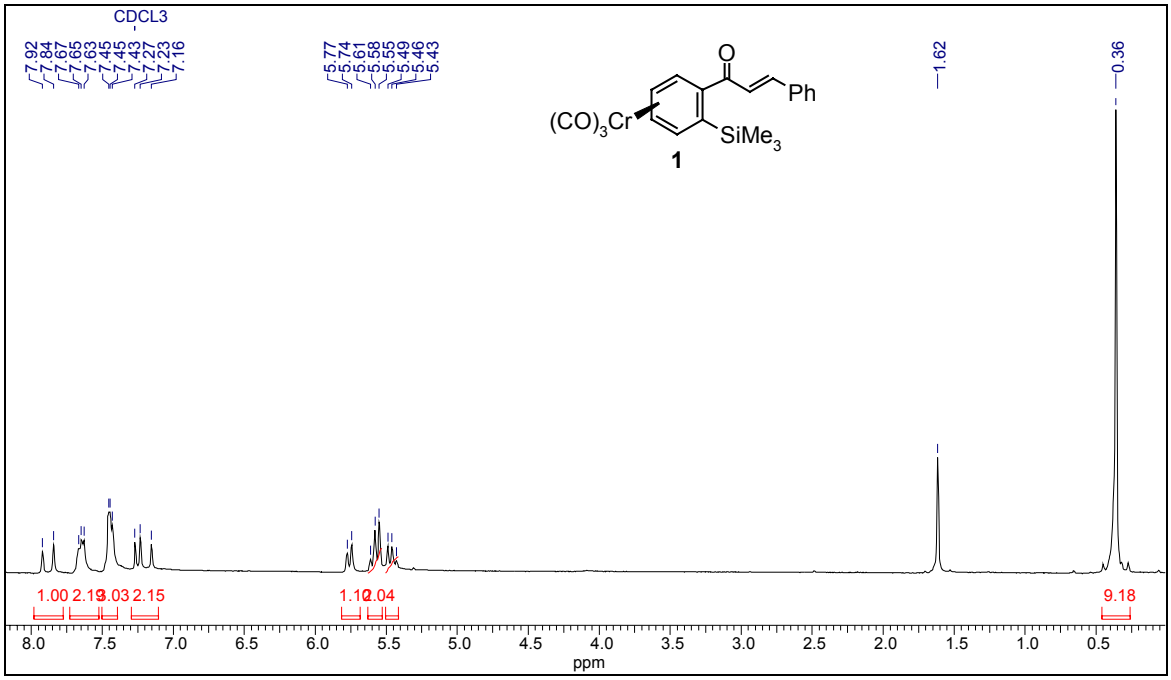

CDCL3
232.34
114.60
105.97
95.67
92.25
91.37
90.38
77.66
77.00
76.38
68.73
61.86
44.40
31.93
29.66
28.77
22.64
14.00
NMe2
(CO)3Cr
H
n-Bu
5b
HO

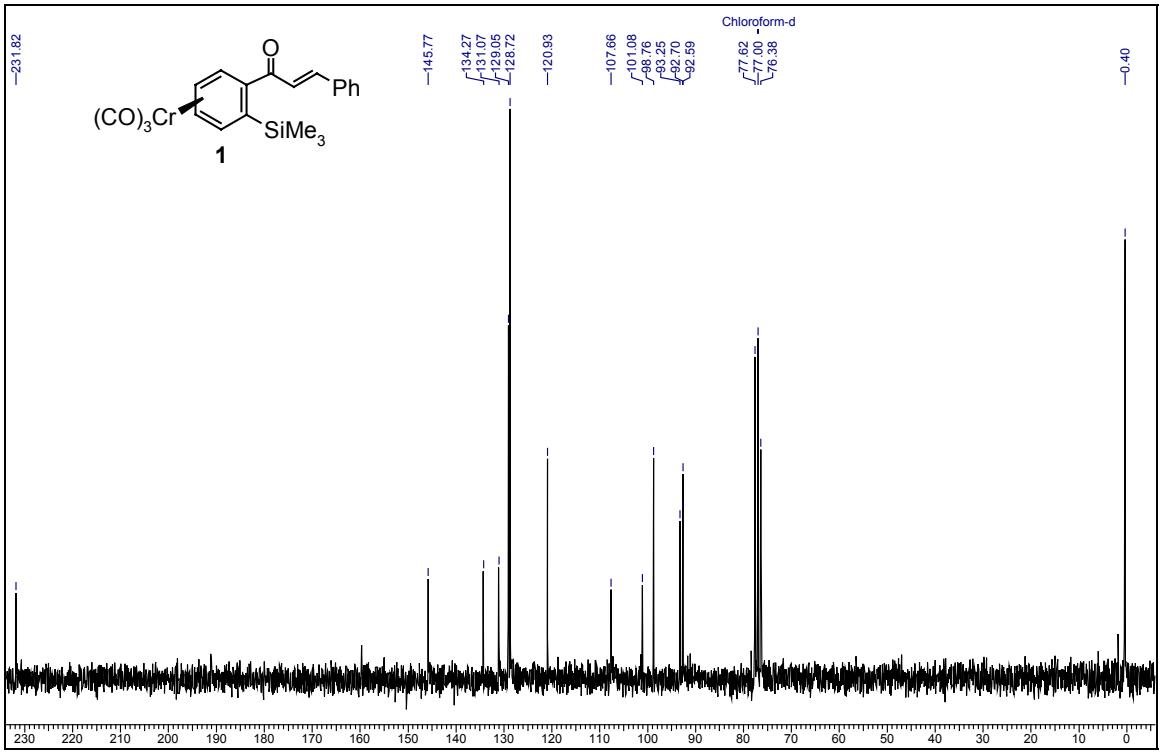

CDCL3
7.27
4.41
4.40
4.36
4.35
4.10
3.87
3.80
3.74
2.74
2.68
2.33
2.26
2.19
1.87
1.61
1.38
1.25
0.96
0.93
0.89
NMe2
(CO)3Cr
H
OH
5b'
n-Bu
1.00
1.03
0.97
1.02
1.00
1.00
1.00
6.07
7.62
3.02

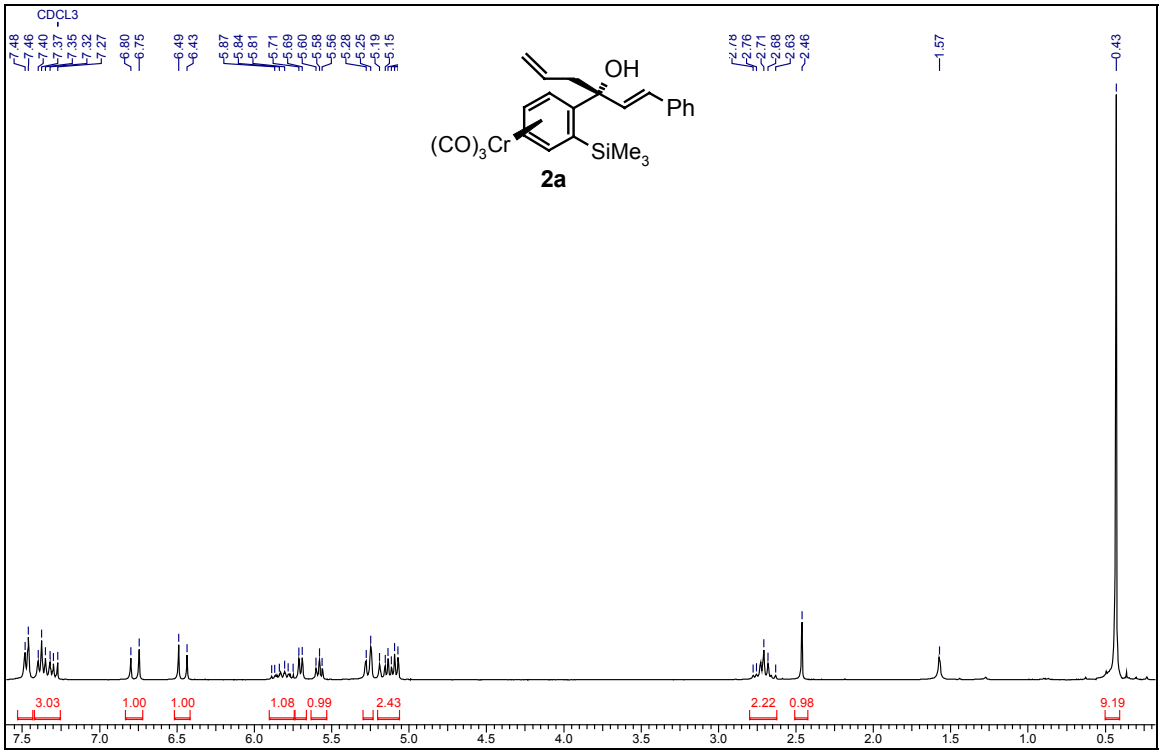

232.89
117.62
107.29
93.80
93.10
92.81
90.89
CDCL3
77.00
61.34
44.80
39.07
28.92
22.30
13.89
NMe2
(CO)3Cr
H
OH
5b'
n-Bu
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

Appendix-II

Spectra of compounds - Part B


CDCL3
7.92
7.84
7.67
7.65
7.63
7.45
7.45
7.43
7.27
7.23
7.16
5.77
5.74
5.61
5.58
5.55
5.49
5.46
5.43
1.62
0.36
O
Ph
(CO)3Cr
SiMe3
1
1.00
2.19
3.03
2.15
1.10
2.04
9.18
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


231.82
145.77
134.27
131.07
129.05
128.72
120.93
107.66
101.08
98.76
93.25
92.70
92.59
Chloroform-d
77.62
77.00
76.38
0.40
O
Ph
(CO)3Cr
SiMe3
1
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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5.81
5.71
5.69
5.60
5.58
5.56
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5.15
2.78
2.76
2.71
2.68
2.63
2.46
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OH
Ph
(CO)3Cr
SiMe3
2a
3.03
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1.00
1.08
0.99
2.43
2.22
0.98
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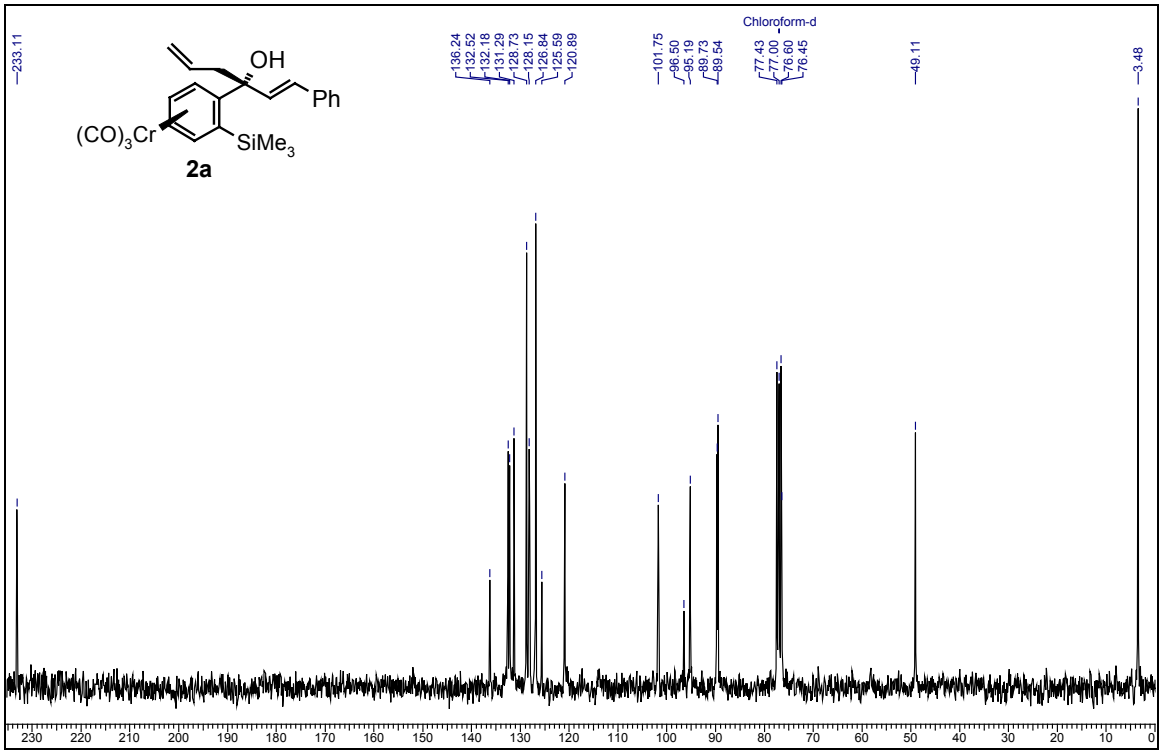
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2a
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128.15
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120.89
101.75
96.50
95.19
89.73
89.54
Chloroform-d
77.43
77.00
76.60
76.45
49.11
3.48
230
220
210
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150
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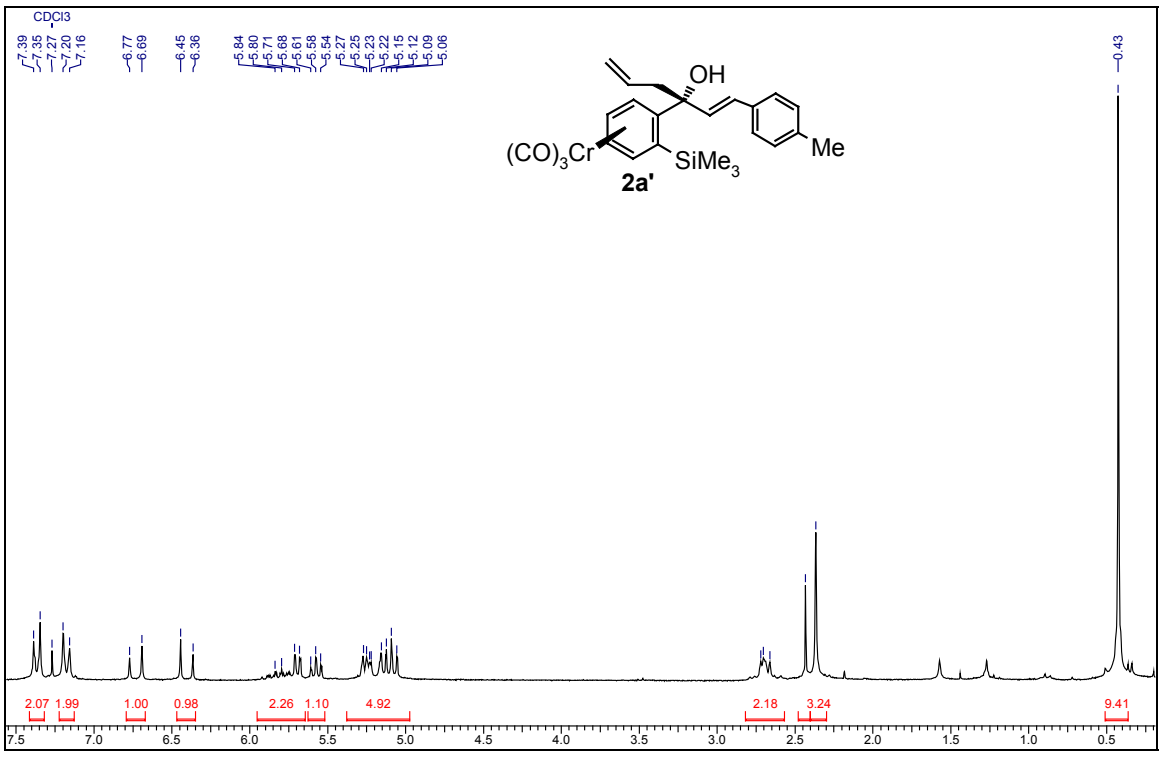
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5.58
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5.25
5.23
5.22
5.15
5.12
5.09
5.06
0.43
OH
(CO)3Cr
SiMe3
Me
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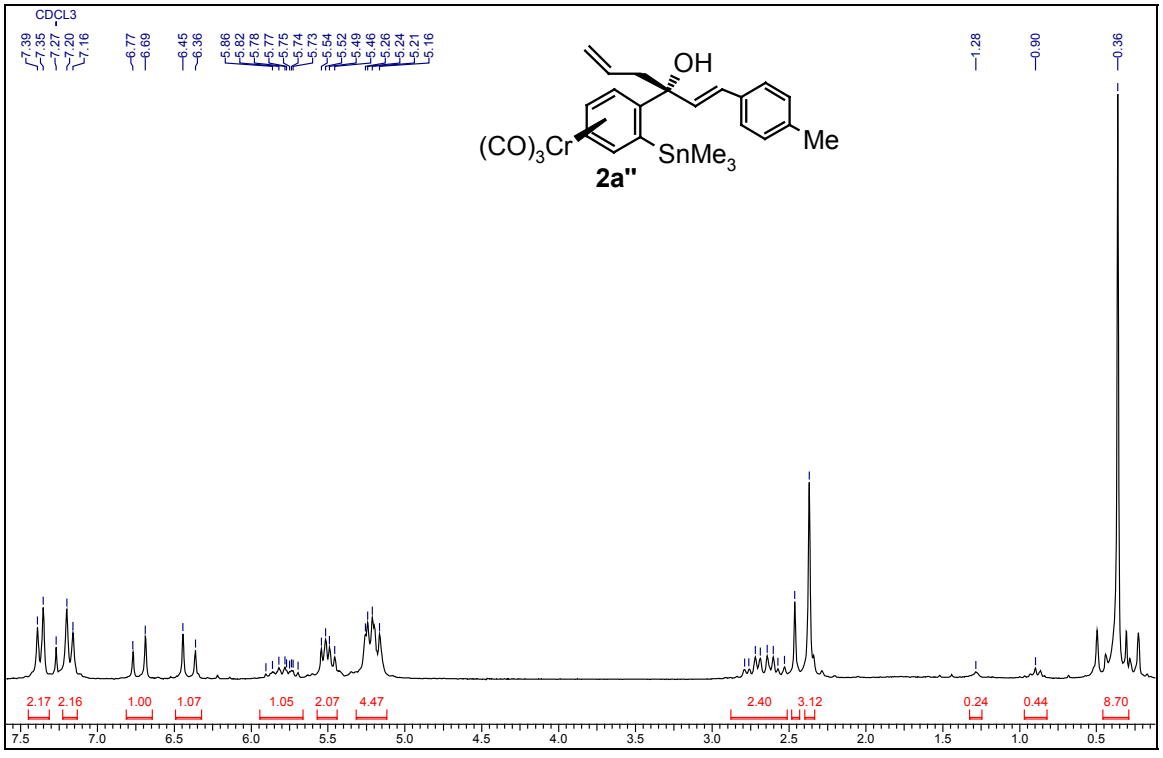
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6.36
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5.78
5.77
5.75
5.74
5.73
5.54
5.52
5.49
5.46
5.26
5.24
5.21
5.16
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0.36
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SnMe3
Me
2a''
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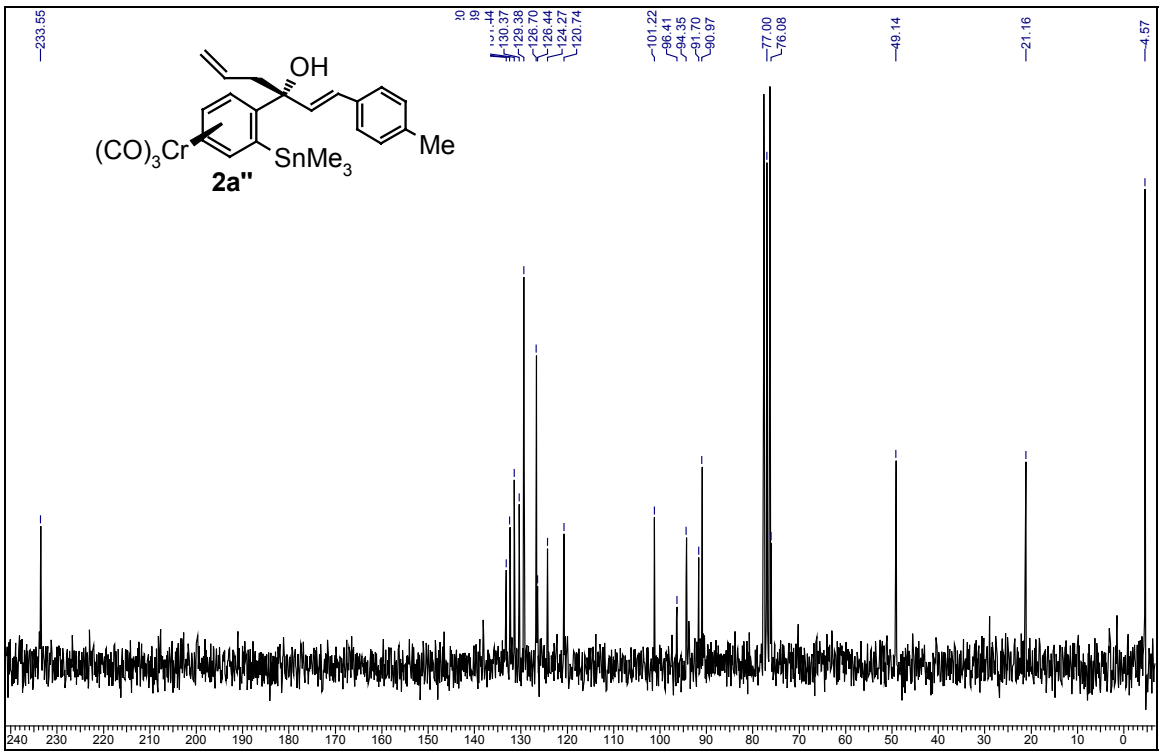
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OH
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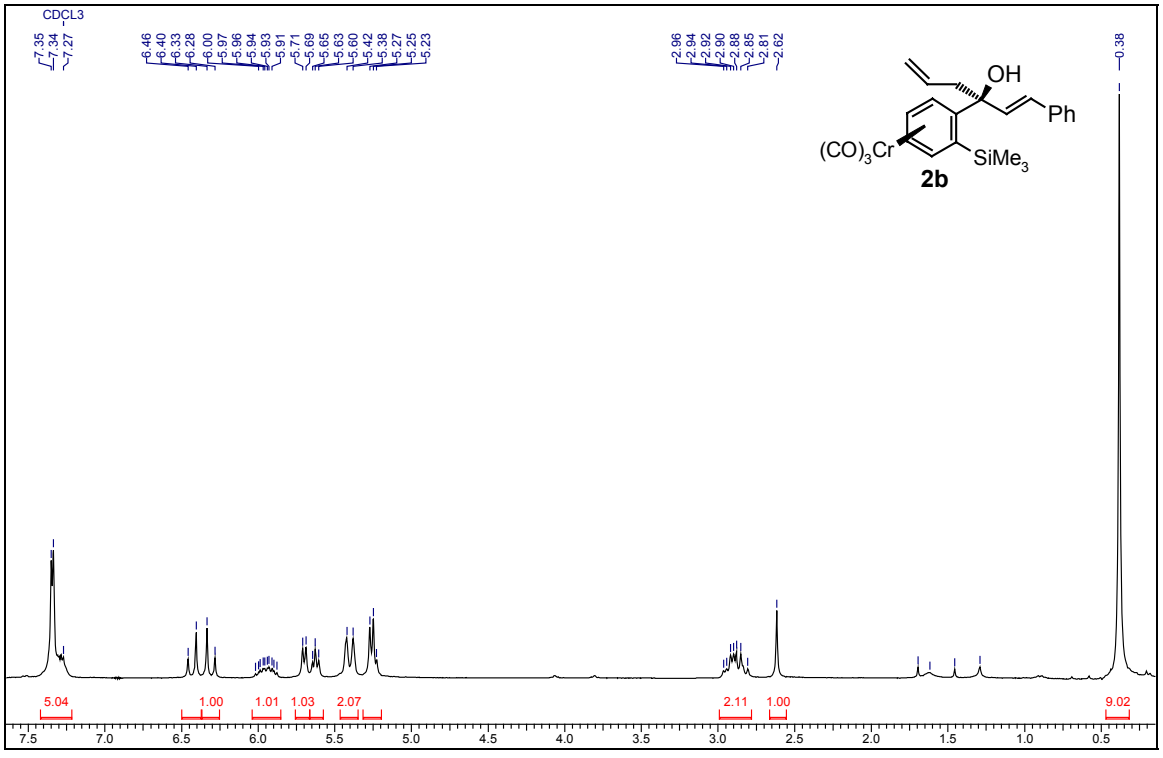
SnMe3
Me
2a"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5.38
5.27
5.25
5.23
2.96
2.94
2.92
2.90
2.88
2.85
2.81
2.62
0.38
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Ph
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SiMe3
2b
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1.03
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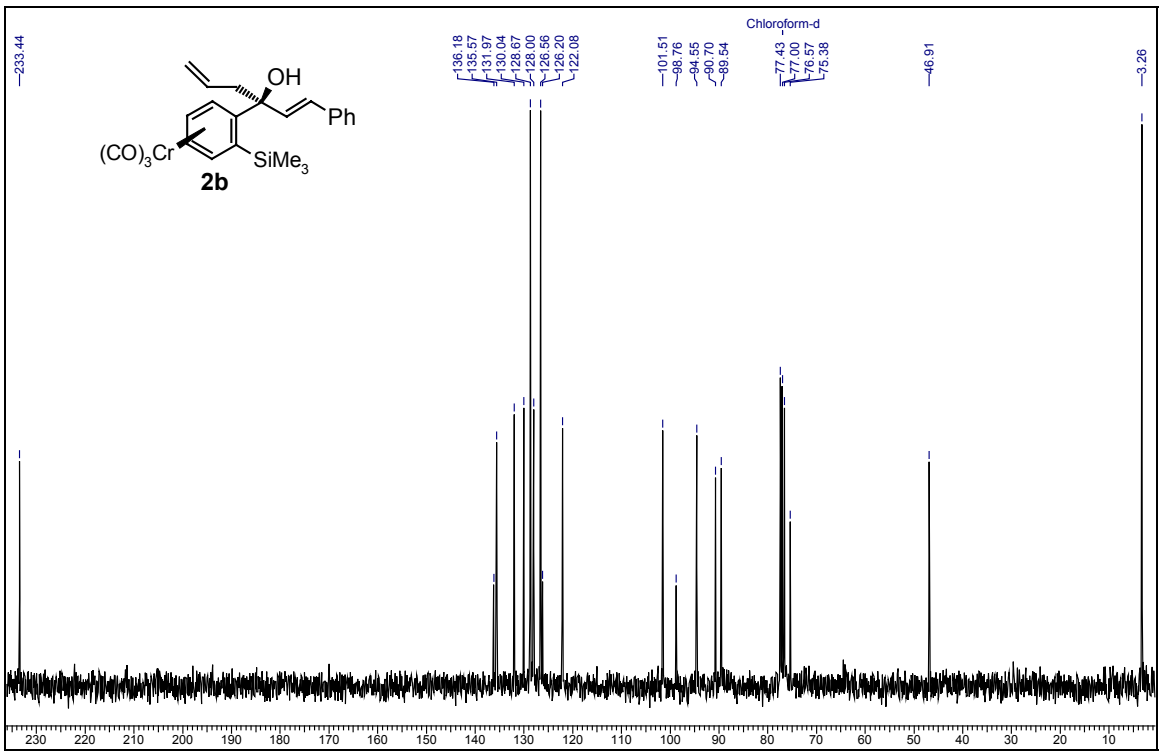
1.00
9.02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128.00
126.56
126.20
122.08
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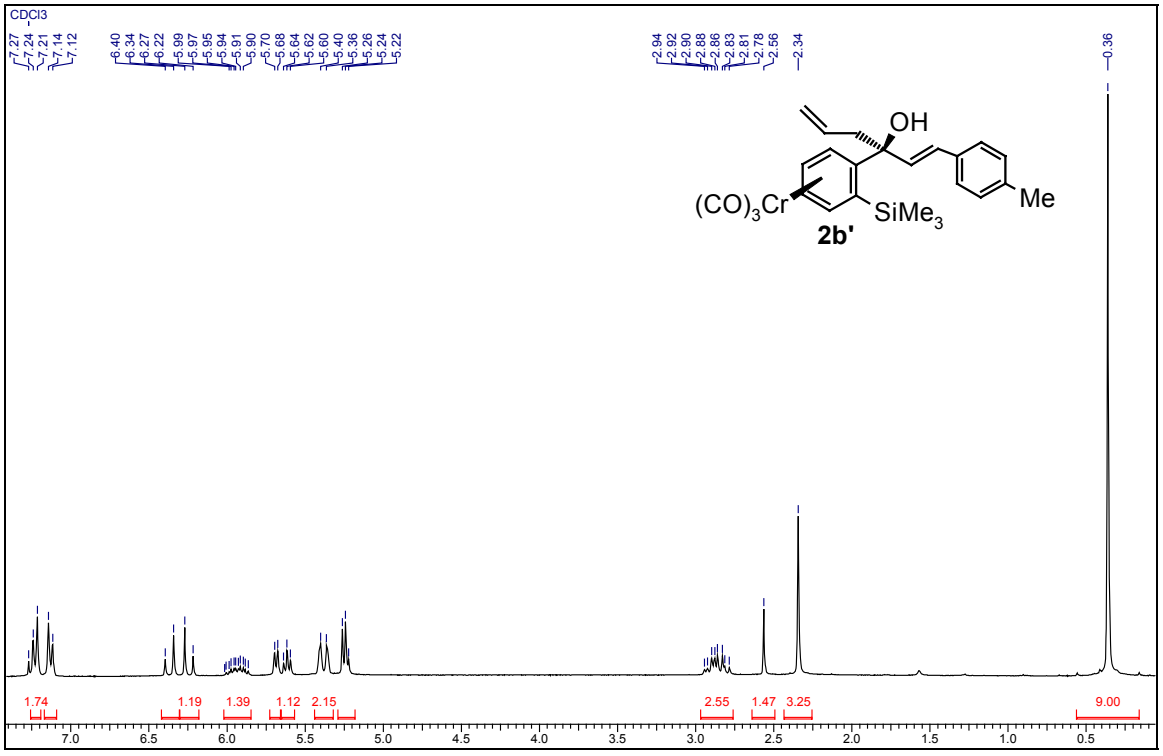
98.76
94.55
90.70
89.54
77.43
77.00
76.57
75.38
46.91
3.26
OH
Ph
(CO)3Cr
SiMe3
2b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6.34
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5.97
5.95
5.94
5.91
5.90
5.70
5.68
5.64
5.62
5.60
5.40
5.36
5.26
5.24
5.22
2.94
2.92
2.90
2.88
2.86
2.83
2.81
2.78
2.56
2.34
0.36
OH
(CO)3Cr
SiMe3
Me
2b'
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1.39
1.12
2.15
2.55
1.47
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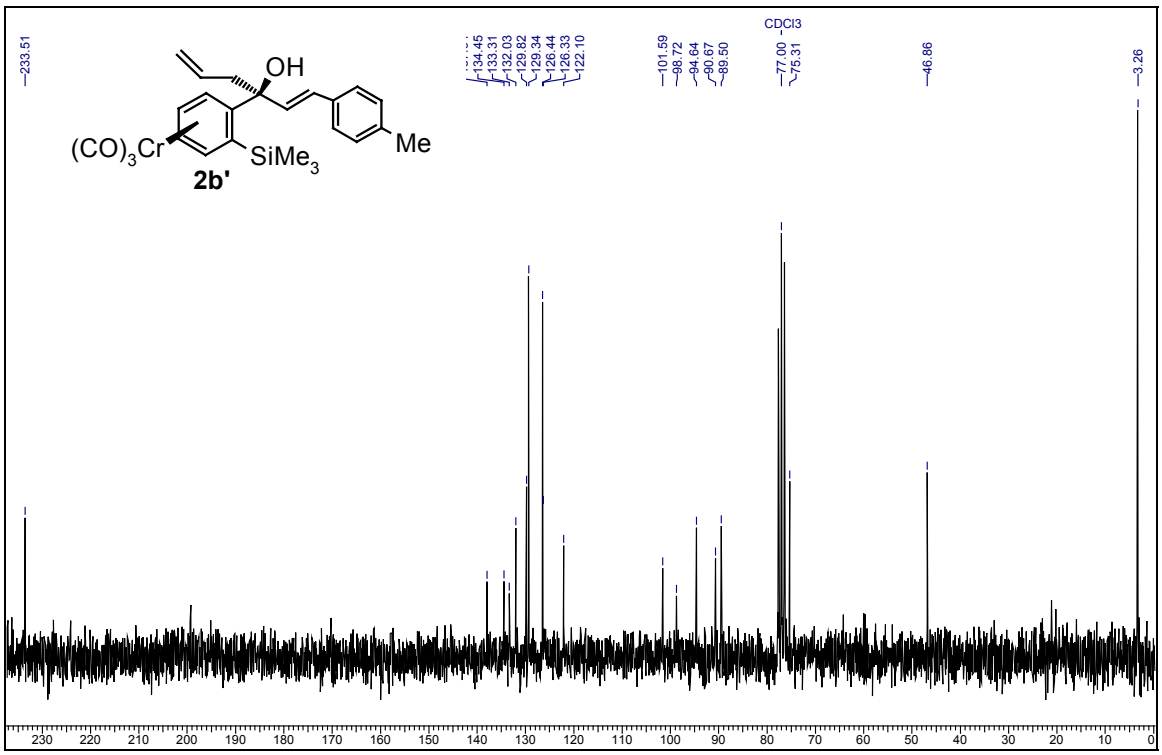
9.00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126.44
126.33
122.10
101.59
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77.00
75.31
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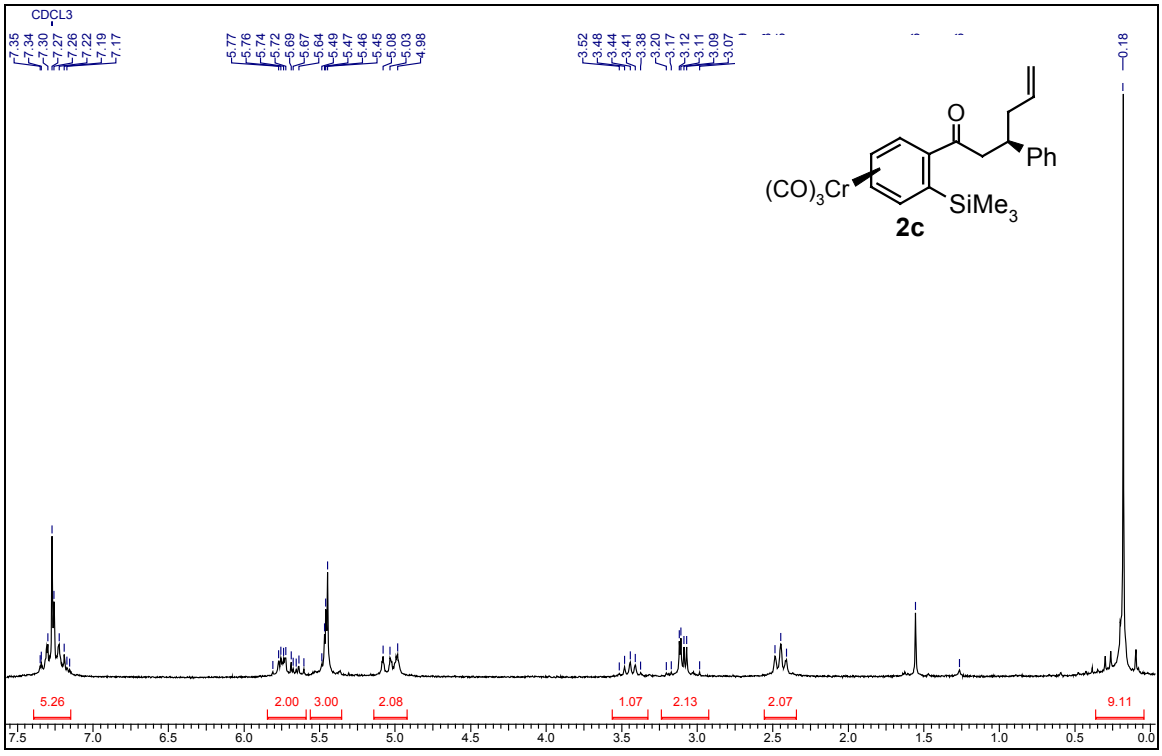
OH
(CO)3Cr
SiMe3
Me
2b'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7.22
7.19
7.17
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5.76
5.74
5.72
5.69
5.67
5.64
5.49
5.47
5.46
5.45
5.08
5.03
4.98
3.52
3.48
3.44
3.41
3.38
3.20
3.17
3.12
3.11
3.09
3.07
0.18
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Ph
(CO)3Cr
SiMe3
2c
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3.00
2.08
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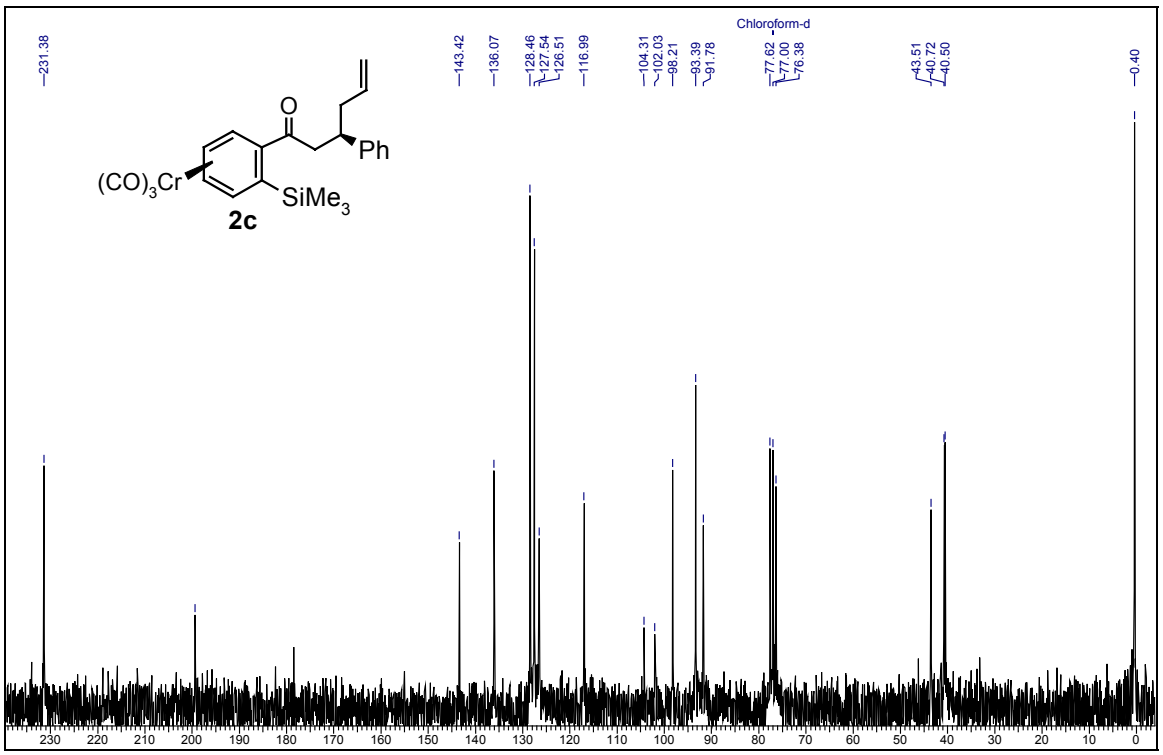
2.13
2.07
9.11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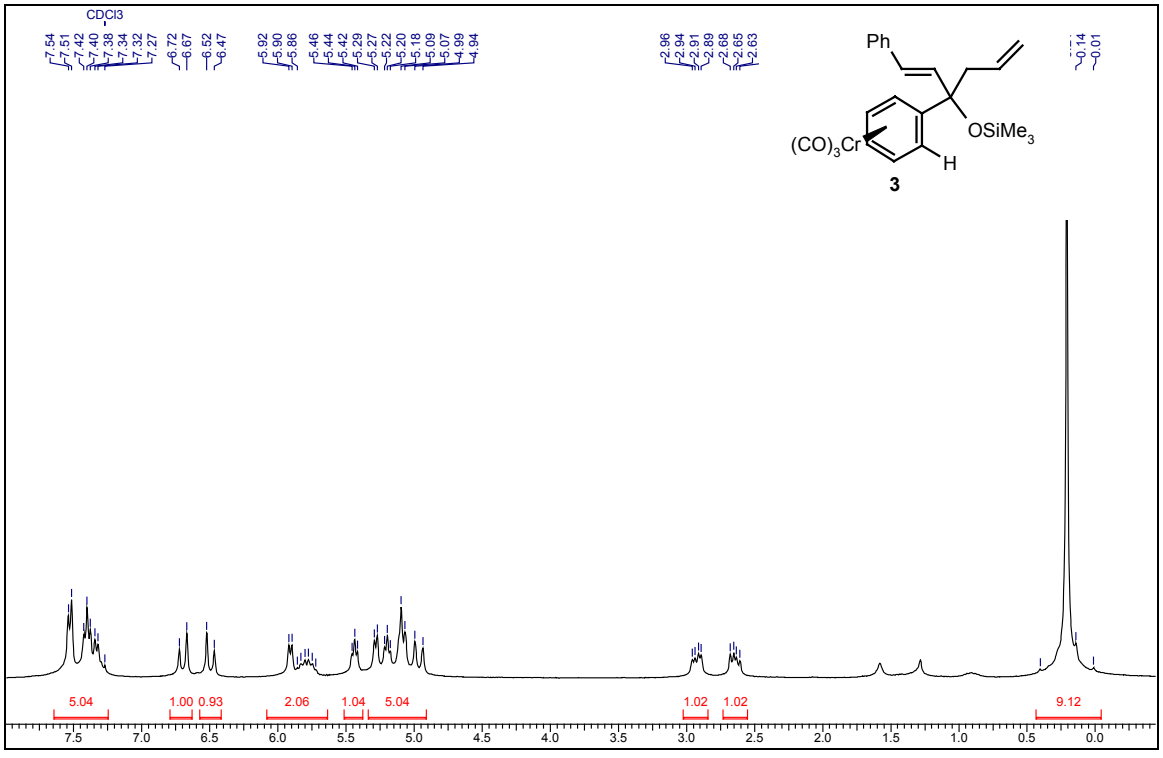
Ph
(CO)3Cr
SiMe3
2c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7.32
7.27
6.72
6.67
6.52
6.47
5.92
5.90
5.86
5.46
5.44
5.42
5.29
5.27
5.22
5.20
5.18
5.09
5.07
4.99
4.94
2.96
2.94
2.91
2.89
2.68
2.65
2.63
0.14
0.01
Ph
OSiMe3
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H
3
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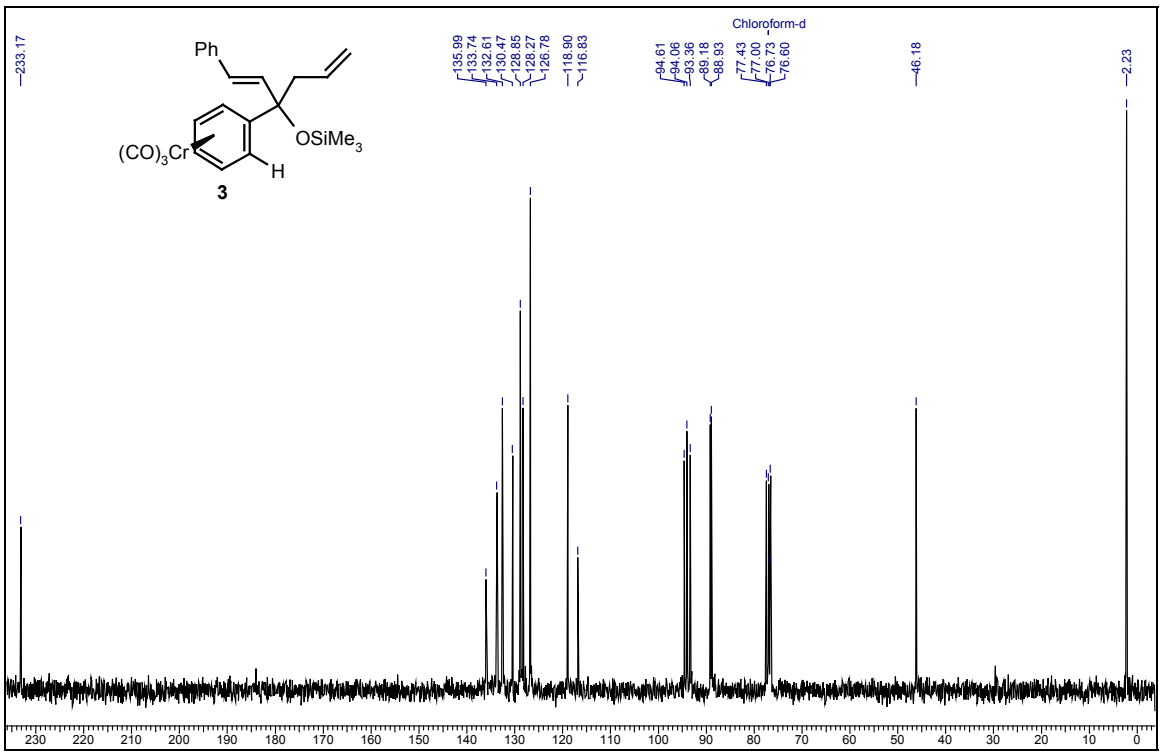
9.12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(CO)3Cr
H
3
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126.78
118.90
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77.43
77.00
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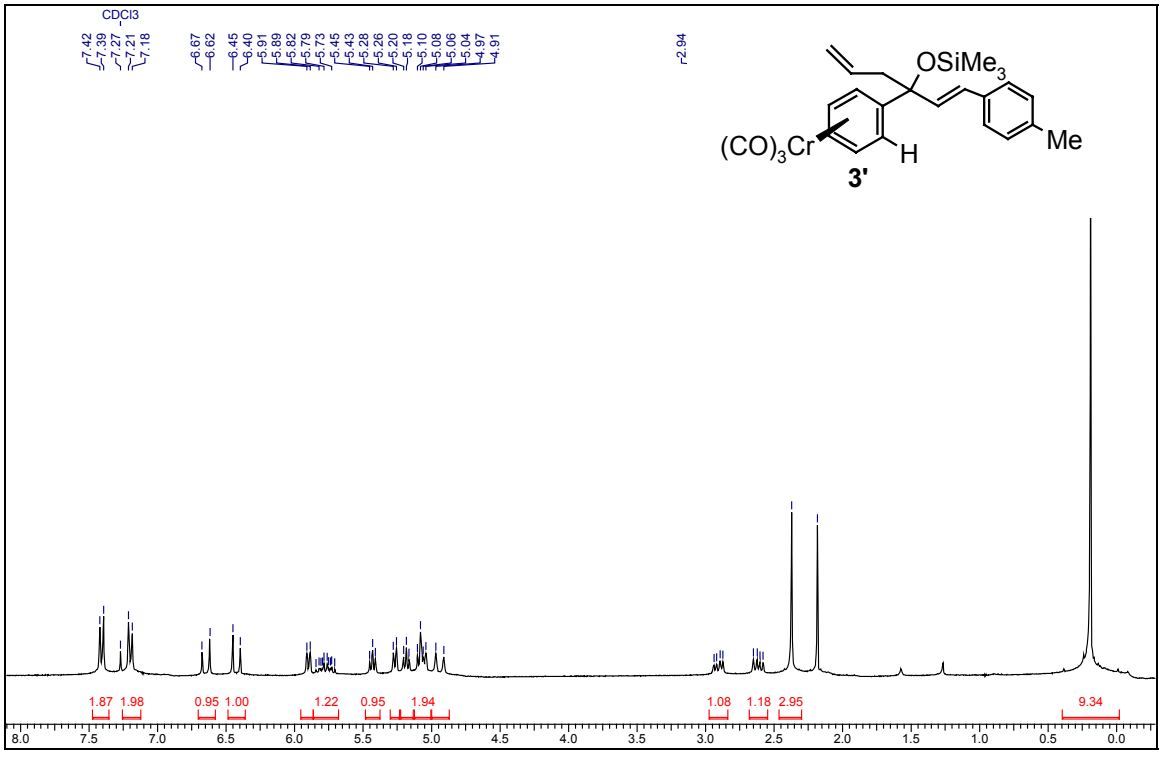
2.23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6.45
6.40
5.91
5.89
5.82
5.79
5.73
5.45
5.43
5.28
5.26
5.20
5.18
5.10
5.08
5.06
5.04
4.97
4.91
2.94
OSiMe3
(CO)3Cr
H
Me
3'
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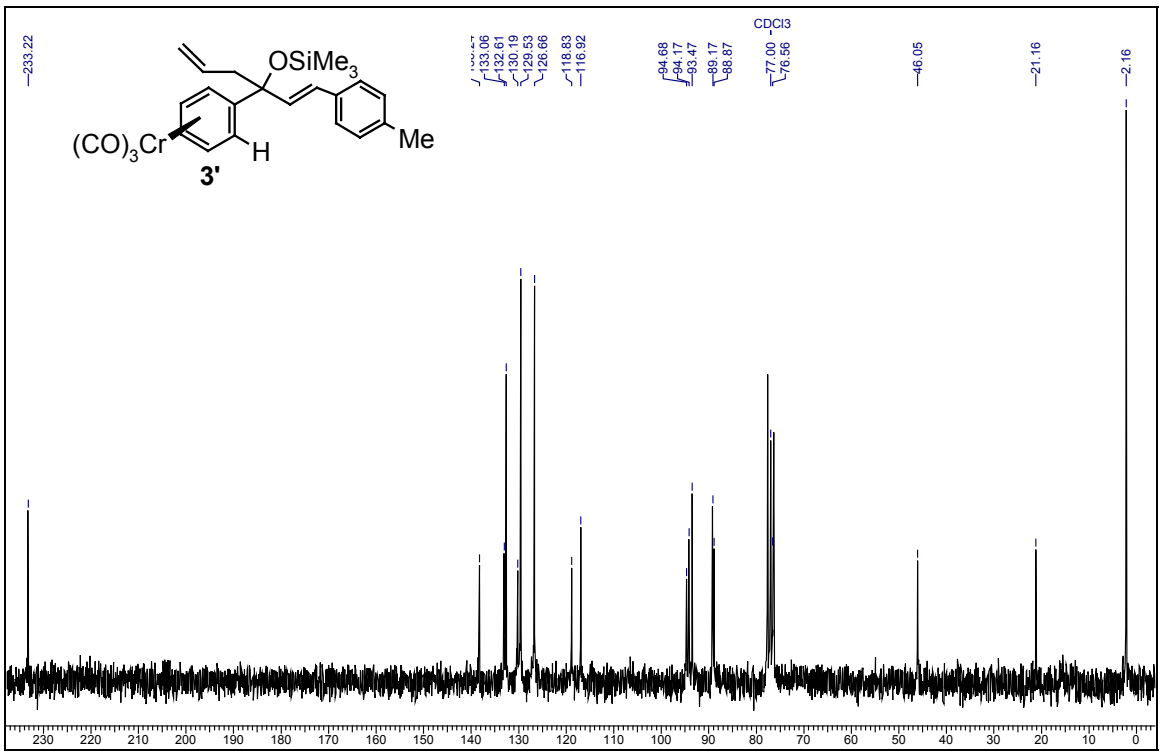
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94.17
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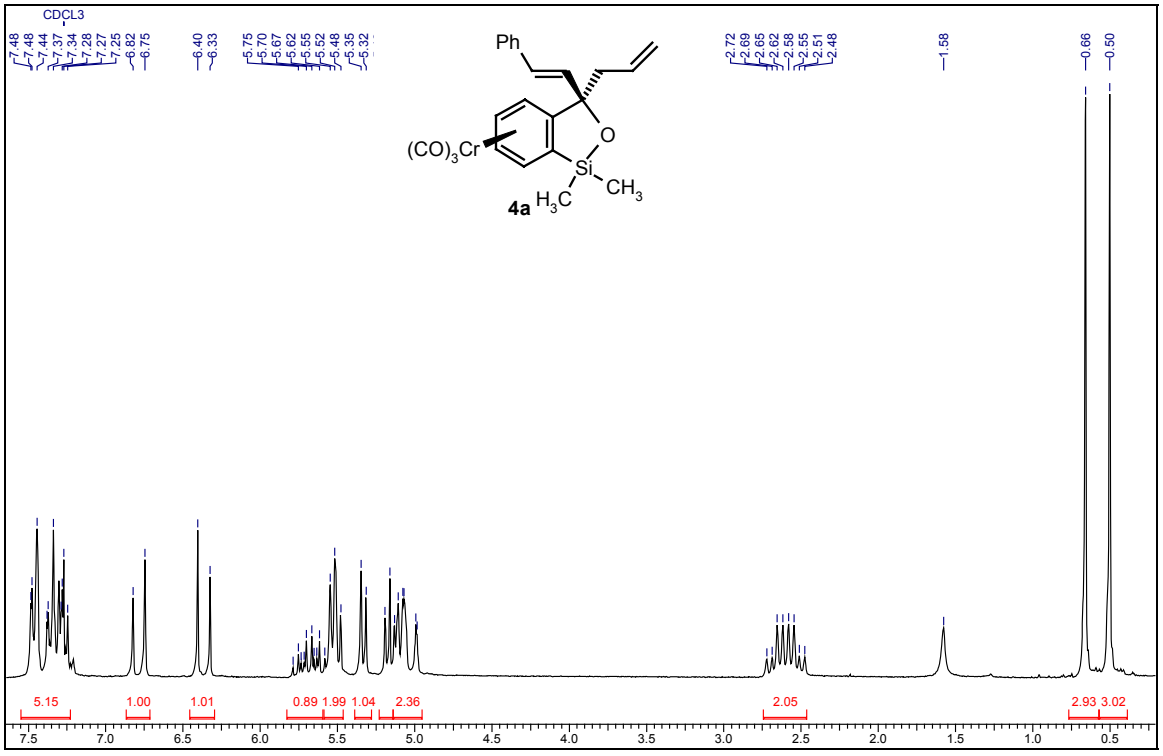
OSiMe3
(CO)3Cr
H
Me
3'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5.70
5.67
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5.55
5.52
5.48
5.35
5.32
2.72
2.69
2.65
2.62
2.58
2.55
2.51
2.48
1.58
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0.50
Ph
O
(CO)3Cr
Si
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1.04
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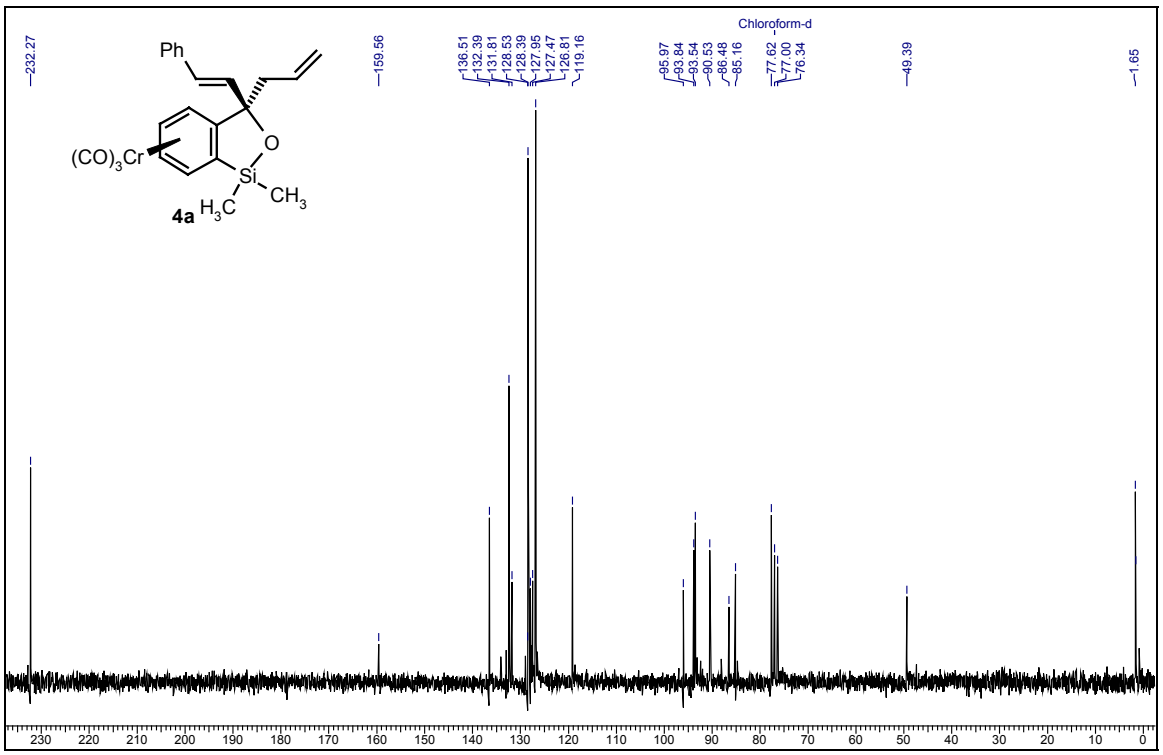
2.93
3.02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127.47
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90.53
86.48
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77.00
76.34
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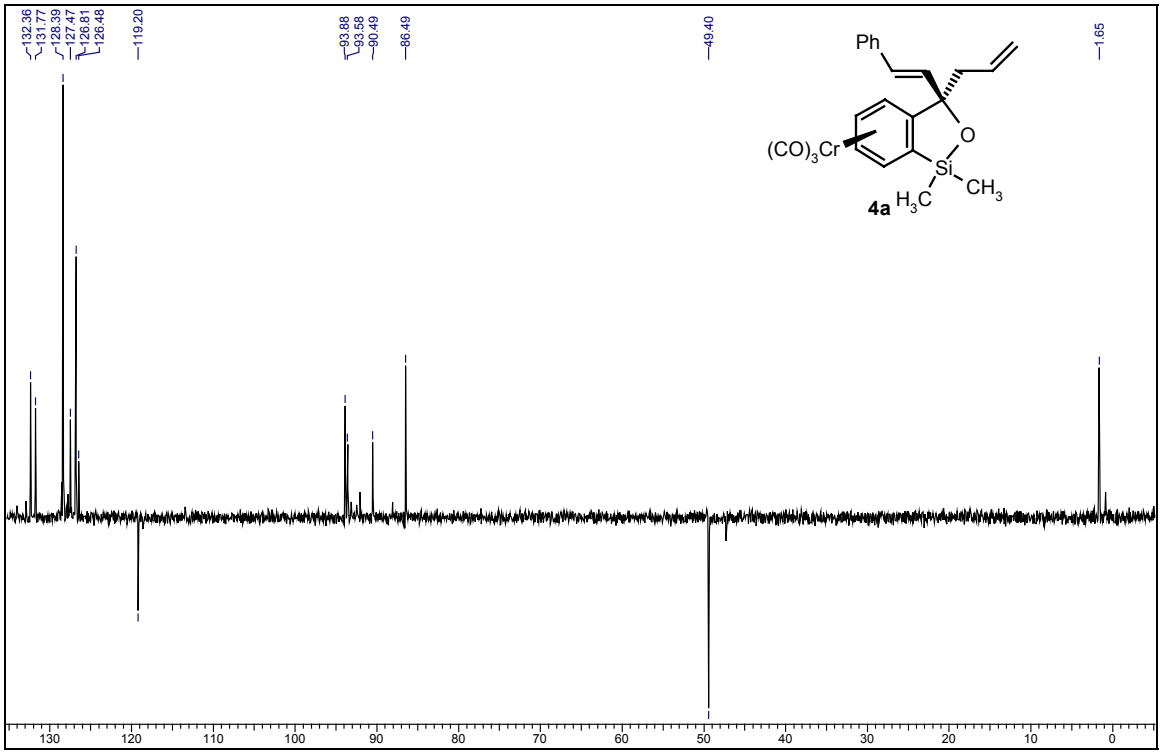
O
Si
CH3
H3C
(CO)3Cr
4a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O
Si
CH3
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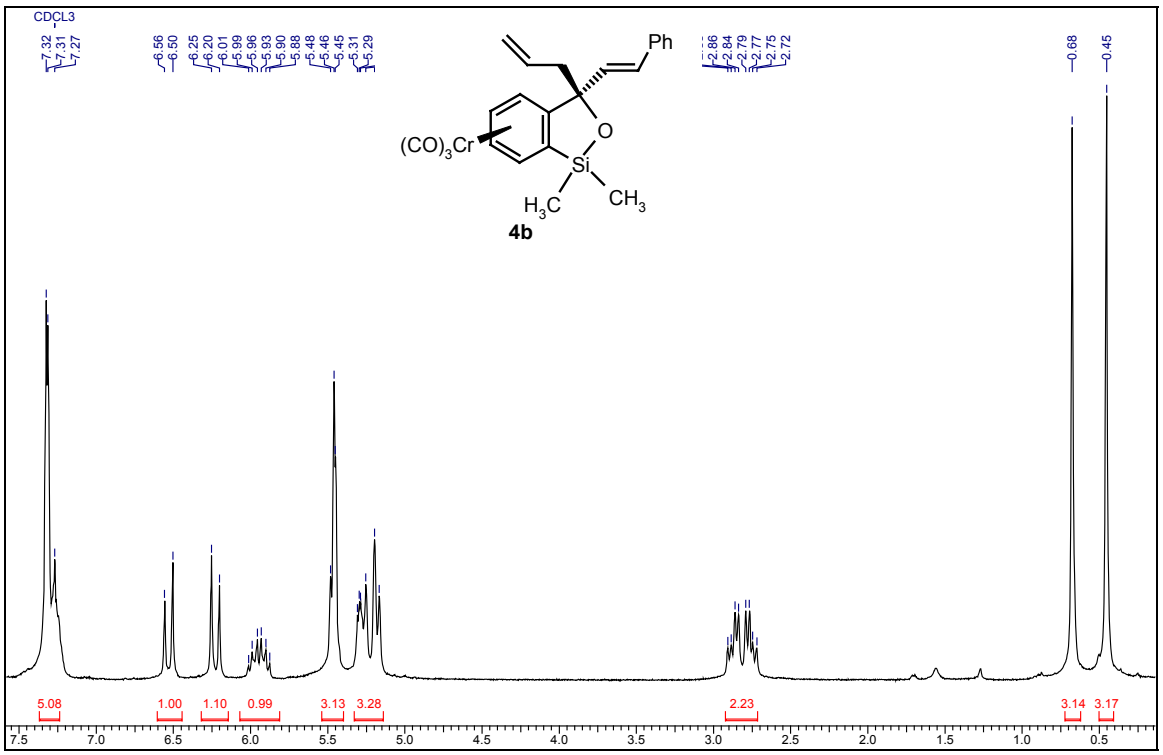
(CO)3Cr
4a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5.88
5.48
5.46
5.45
5.31
5.29
2.86
2.84
2.79
2.77
2.75
2.72
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0.45
Ph
O
Si
(CO)3Cr
H3C
CH3
4b
5.08
1.00
1.10
0.99
3.13
3.28
2.23
3.14
3.17
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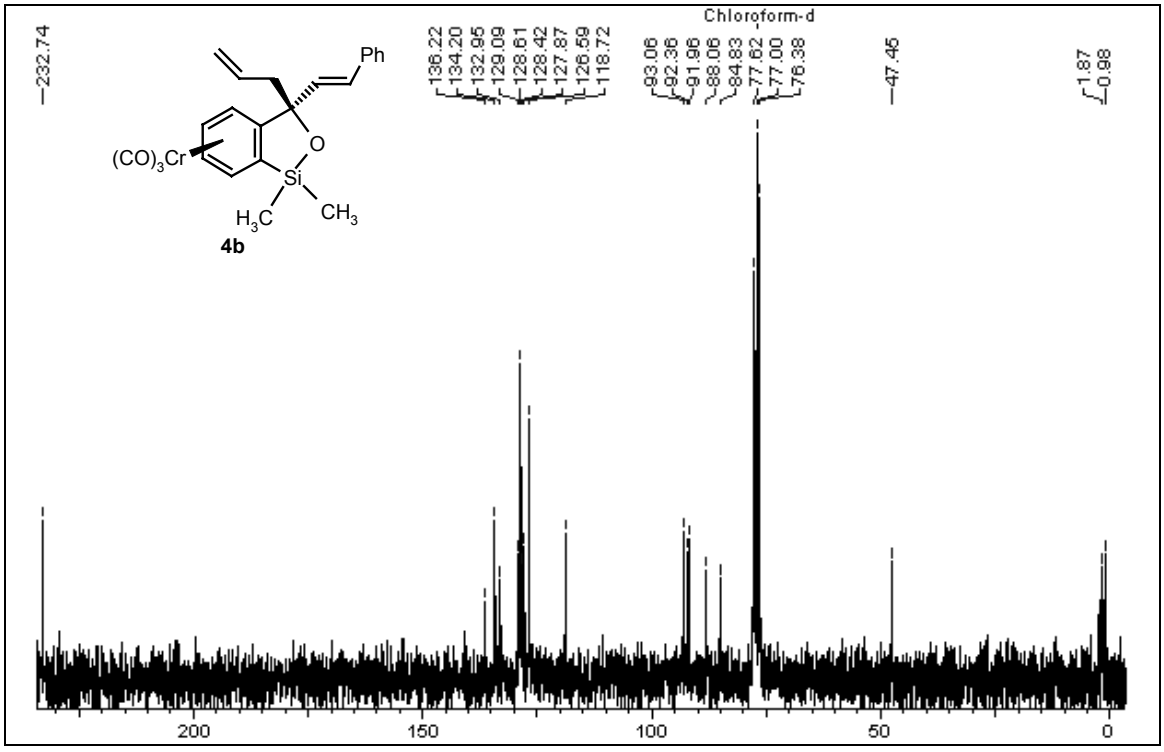
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88.06
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77.62
77.00
76.38
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Ph
O
Si
(CO)3Cr
H3C
CH3
4b
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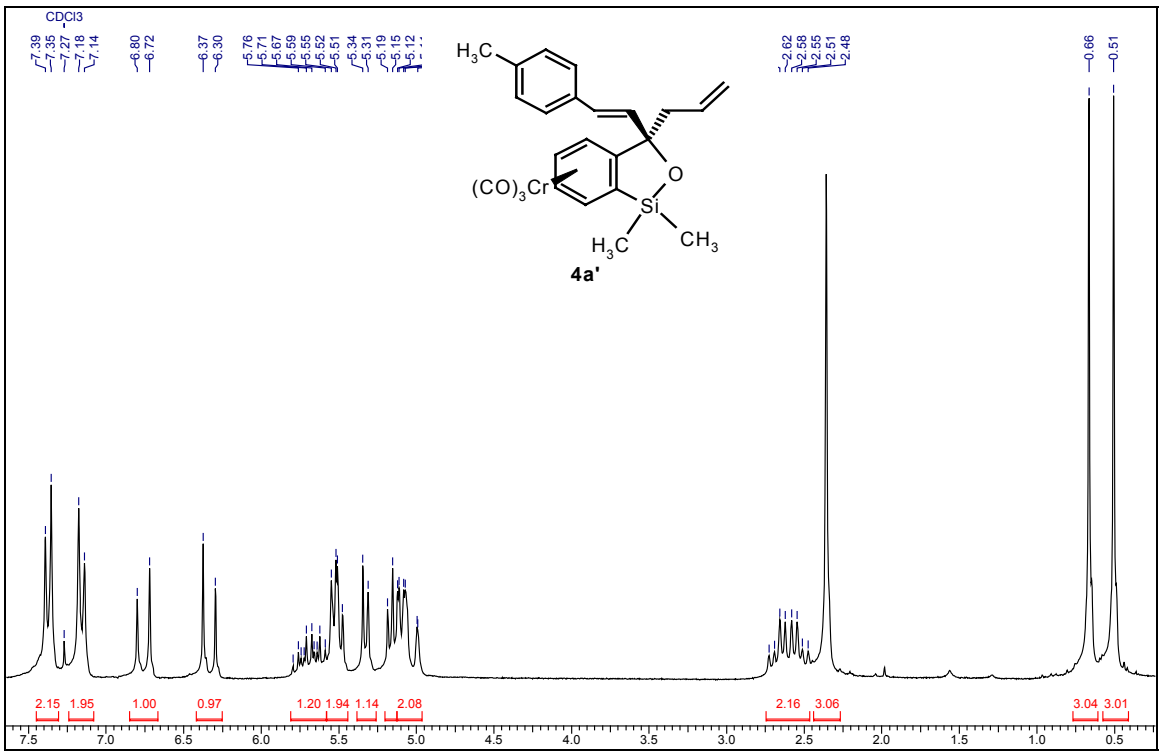
0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5.59
5.55
5.52
5.51
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5.19
5.15
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2.55
2.51
2.48
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0.51
2.15
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1.20
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1.14
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2.16
3.06
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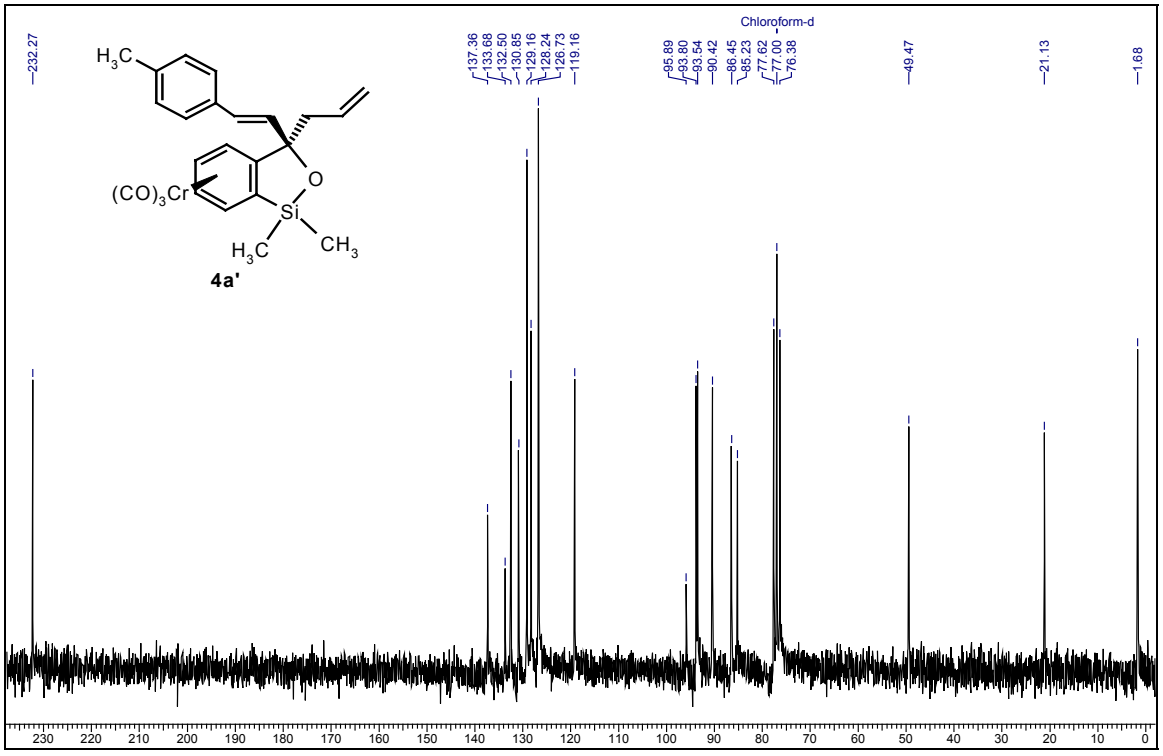
4a'


Chloroform-d
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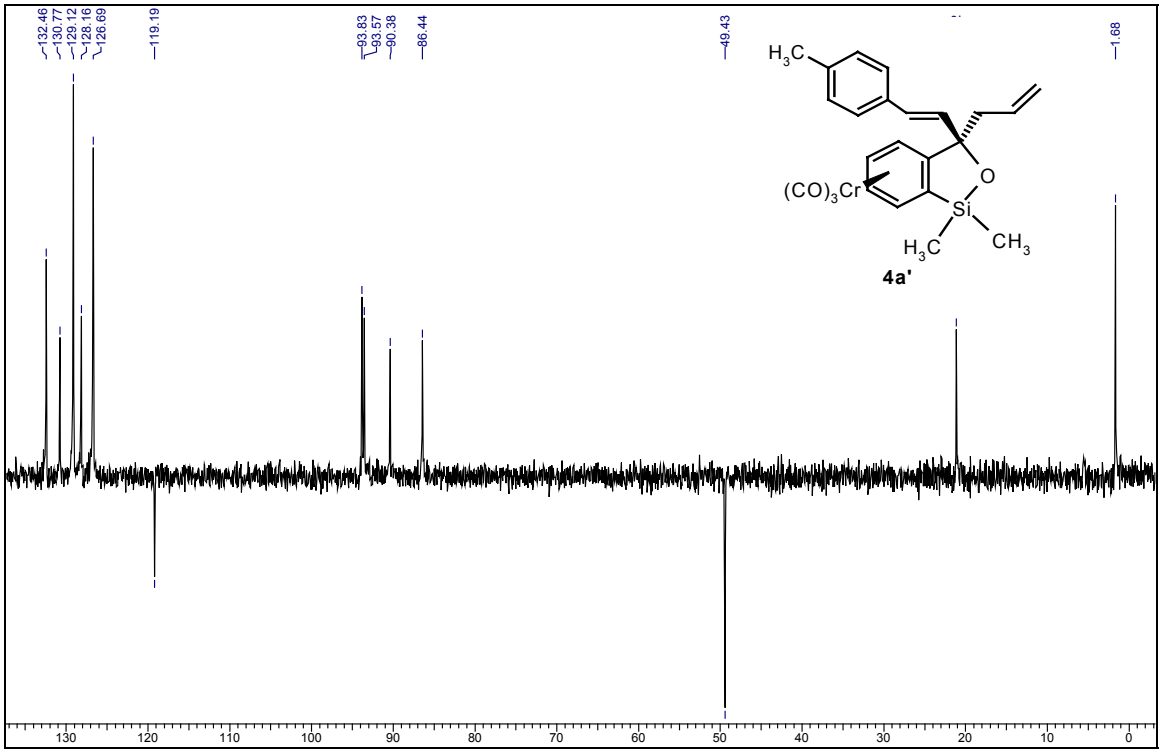
4a'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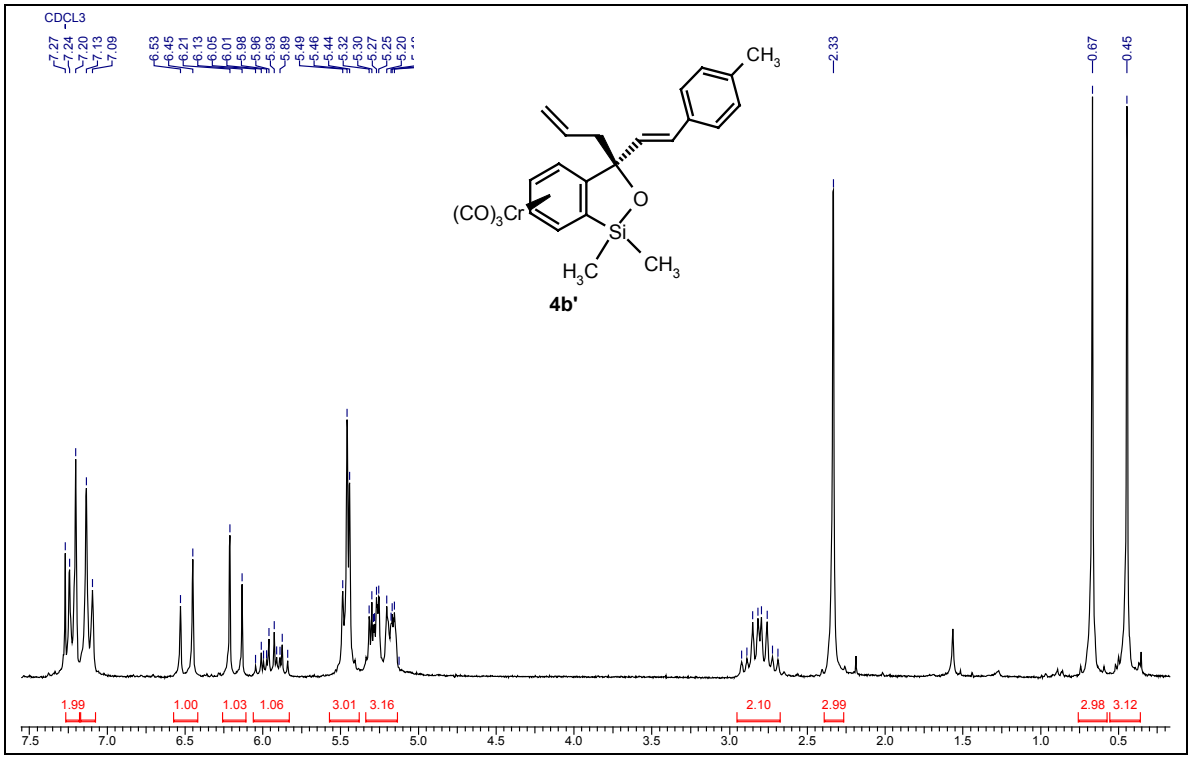
O
Si
H3C
CH3
4a'


CDCL3
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6.13
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5.93
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5.46
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5.25
5.20
2.33
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0.45
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(CO)3Cr
O
Si
H3C
CH3
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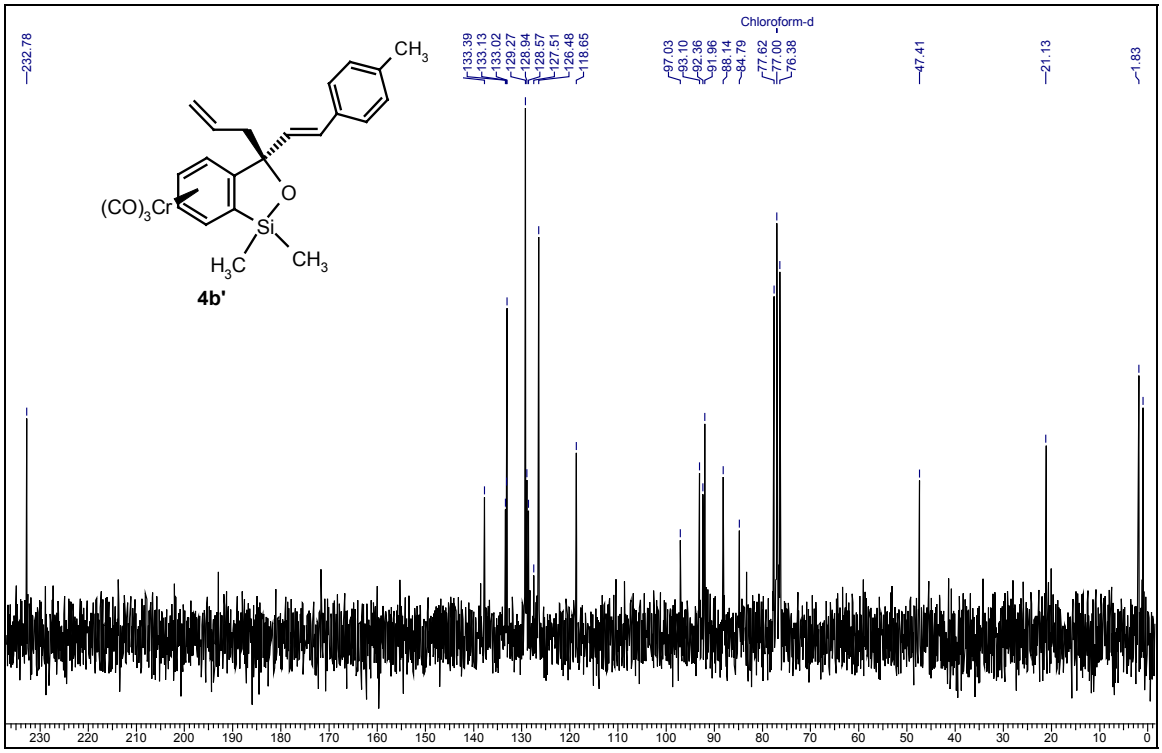
3.12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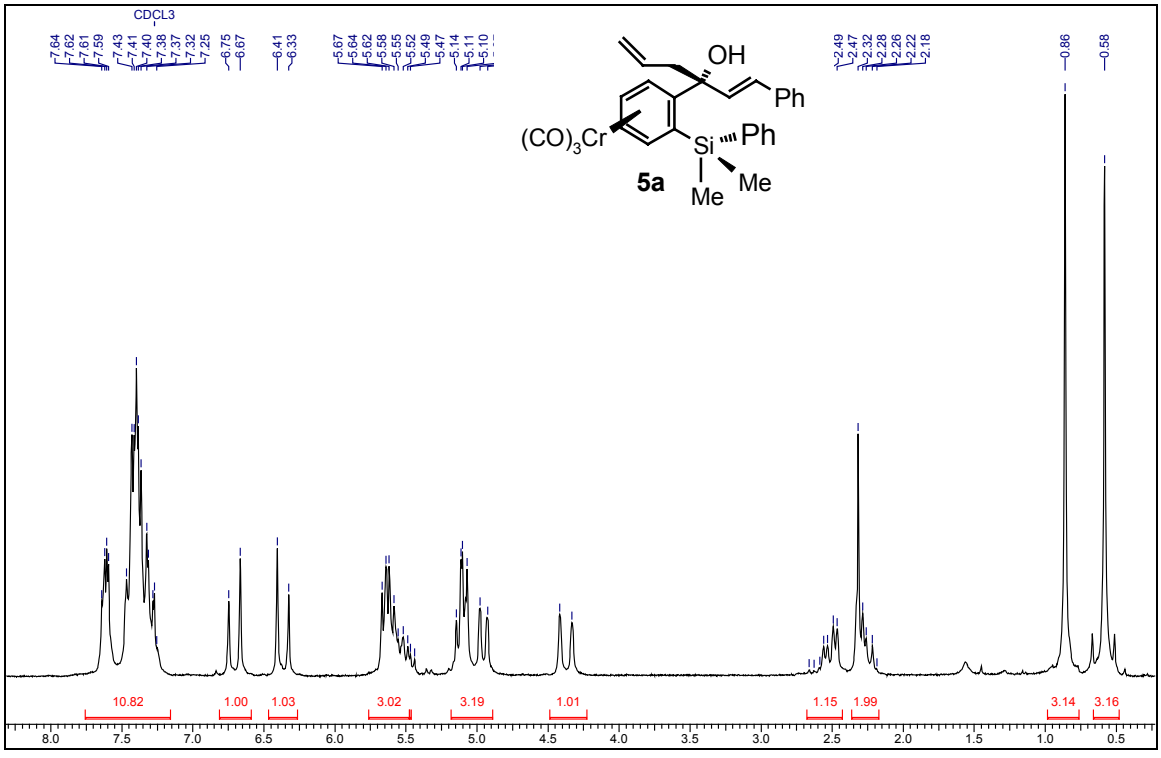
O
Si
H3C
CH3
4b'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2.22
2.18
0.86
0.58
OH
Ph
(CO)3Cr
Si
Ph
Me
Me
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3.02
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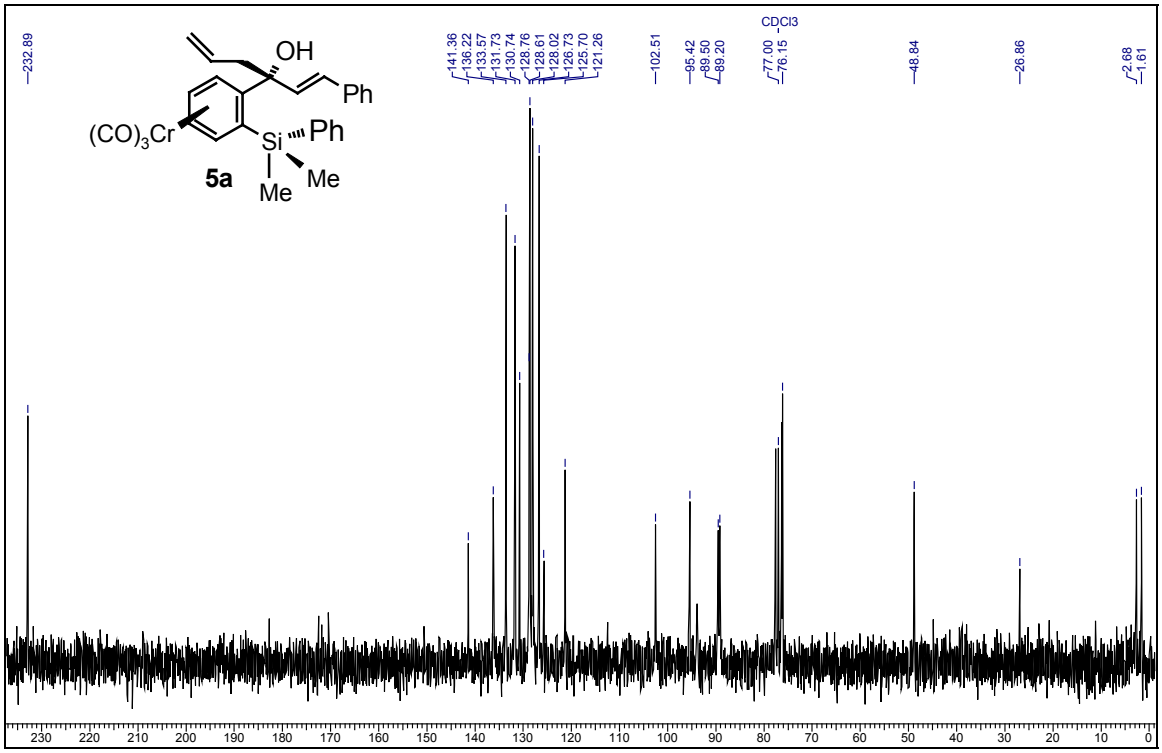
1.01
1.15
1.99
3.14
3.16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Ph
(CO)3Cr
Si
Ph
Me
Me
5a
CDCl3
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133.57
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130.74
128.76
128.61
128.02
126.73
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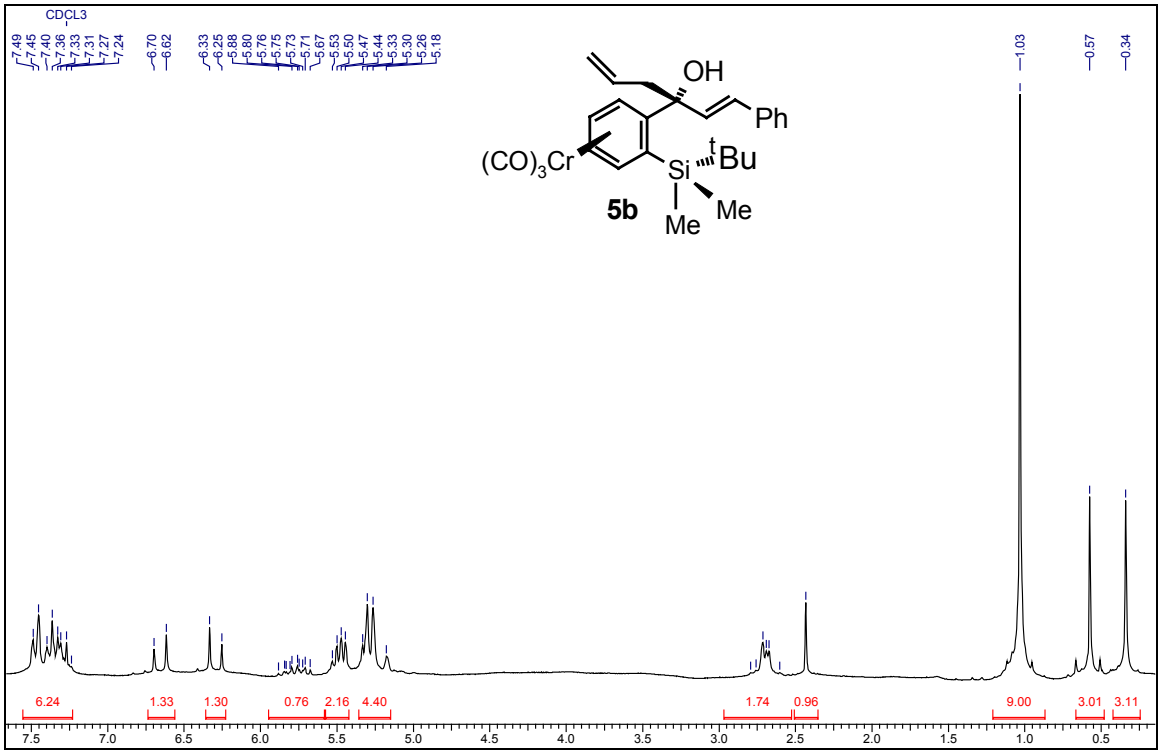
1.61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6.62
6.33
6.25
5.88
5.80
5.76
5.75
5.73
5.71
5.67
5.53
5.50
5.47
5.44
5.33
5.30
5.26
5.18
OH
Ph
(CO)3Cr
Si
tBu
Me
Me
5b
1.03
0.57
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1.30
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1.74
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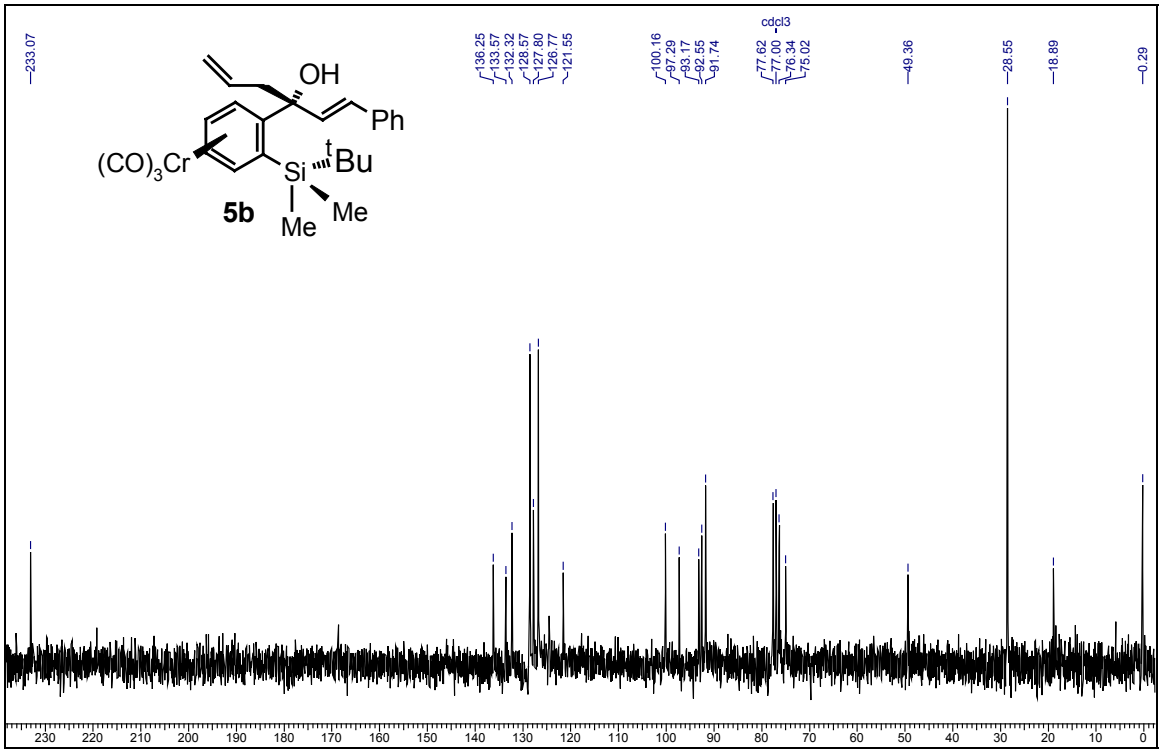
9.00
3.01
3.11


OH
Ph
(CO)3Cr
Si
tBu
Me
Me
5b
cdcl3
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132.32
128.57
127.80
126.77
121.55
100.16
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91.74
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77.00
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75.02
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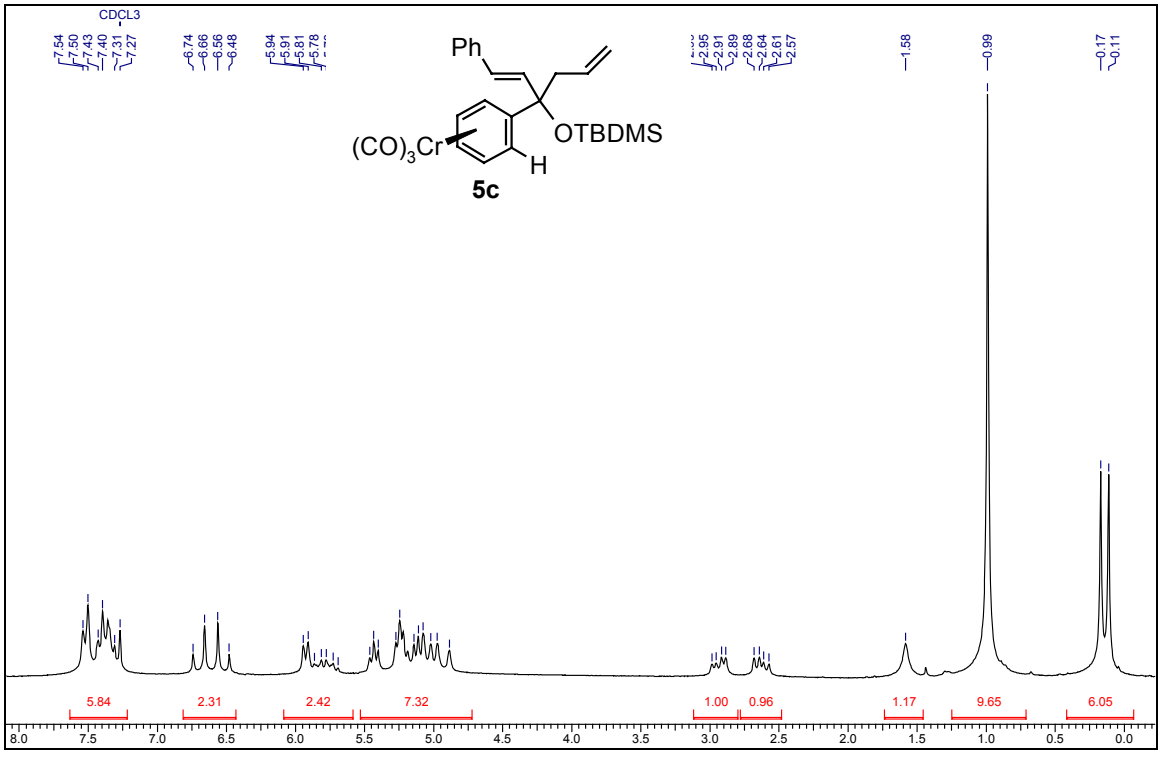
CDCL3
Ph
OTBDMS
(CO)3Cr
H
5c
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7.43
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7.31
7.27
6.74
6.66
6.56
6.48
5.94
5.91
5.81
5.78
2.95
2.91
2.89
2.68
2.64
2.61
2.57
1.58
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2.42
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1.00
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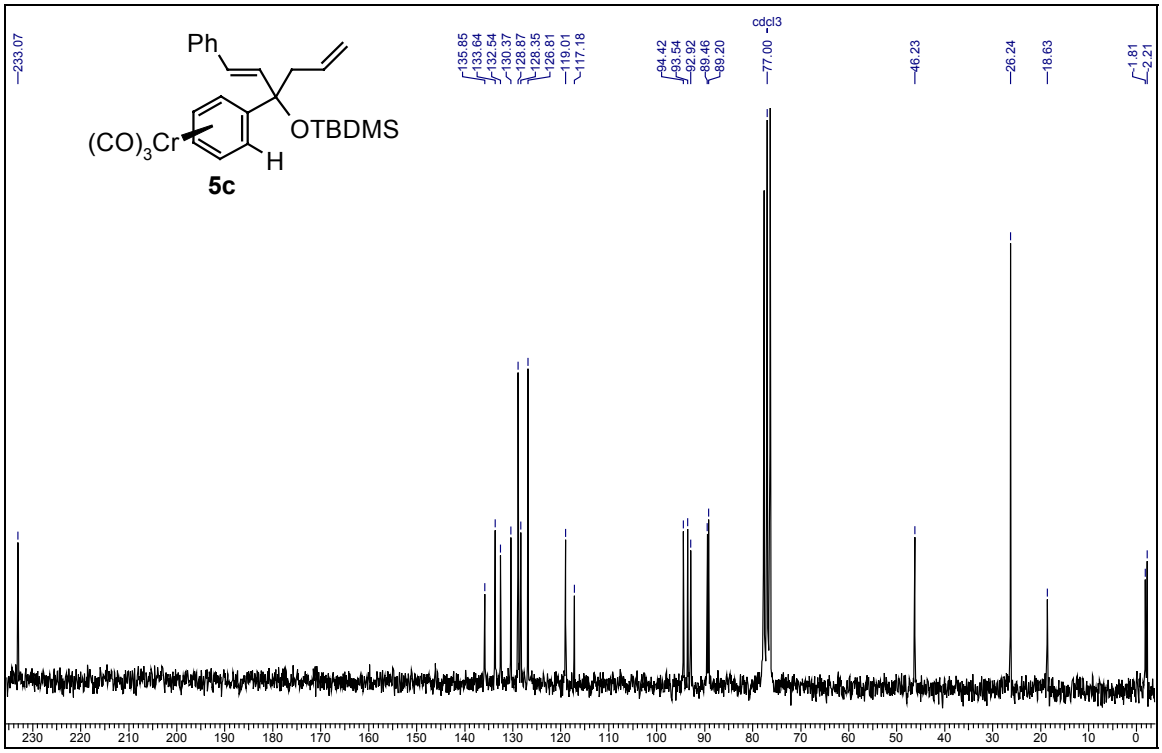
1.17
9.65
6.05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5c
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126.81
119.01
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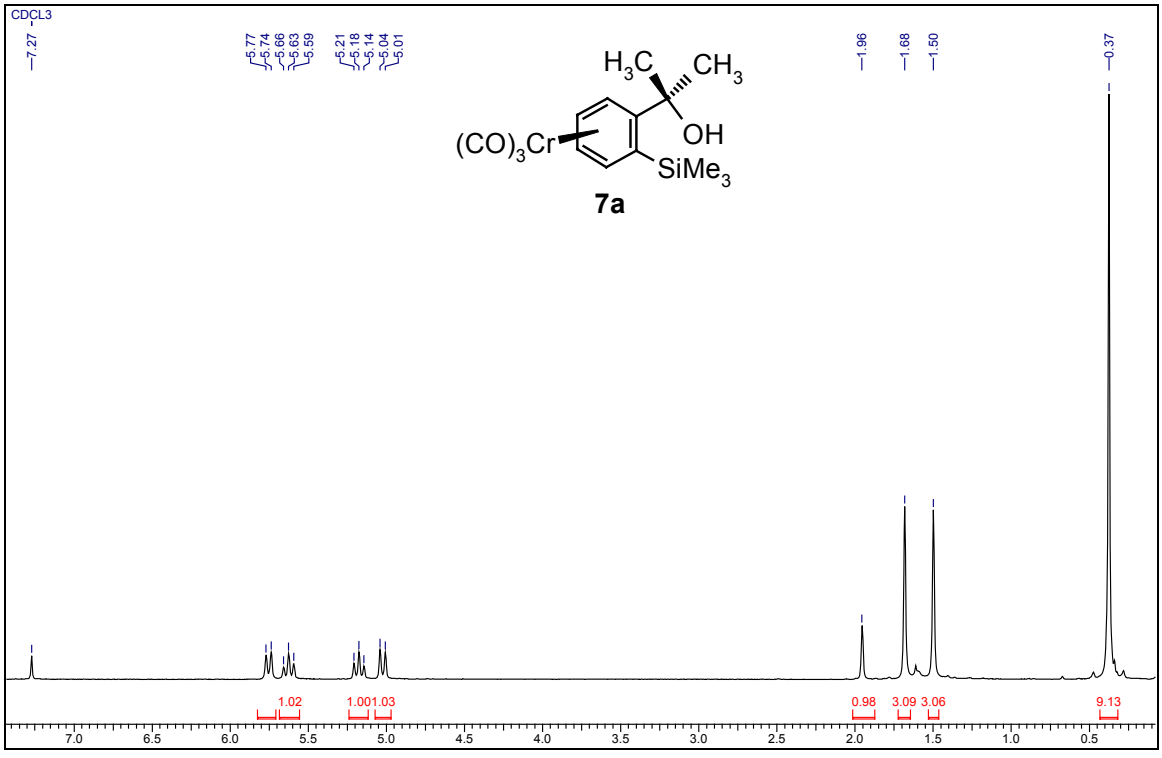
46.23
26.24
18.63
1.81
2.21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5.21
5.18
5.14
5.04
5.01
H3C
CH3
OH
(CO)3Cr
SiMe3
7a
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1.68
1.50
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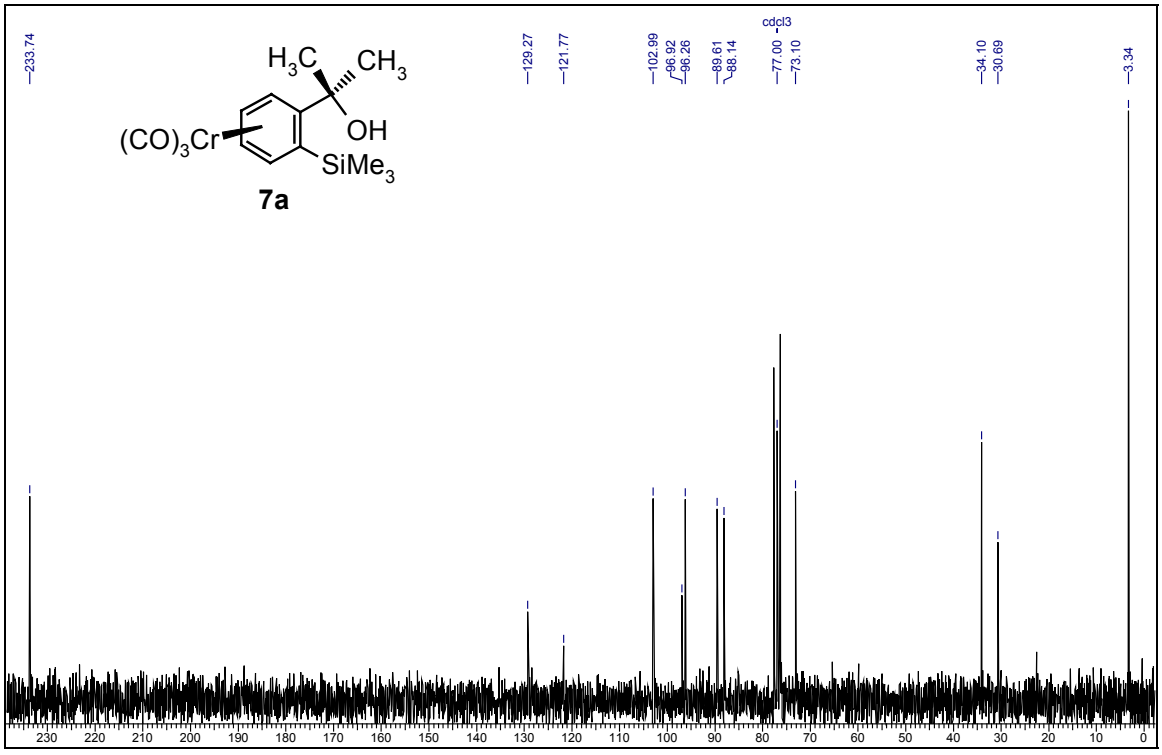
1.02
1.00
1.03
0.98
3.09
3.06
9.13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96.26
89.61
88.14
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73.10
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30.69
3.34
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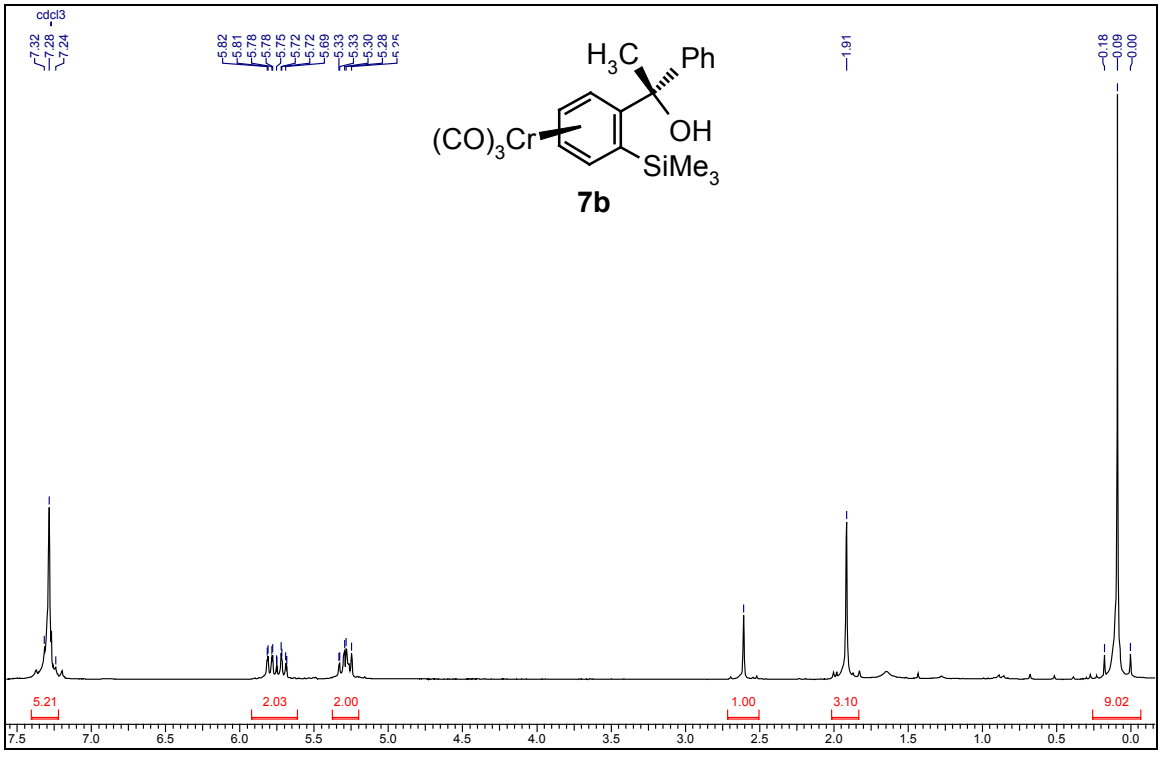
CH3
OH
(CO)3Cr
SiMe3
7a


cdcl3
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5.81
5.78
5.78
5.75
5.72
5.72
5.69
5.33
5.33
5.30
5.28
1.91
0.18
0.09
0.00
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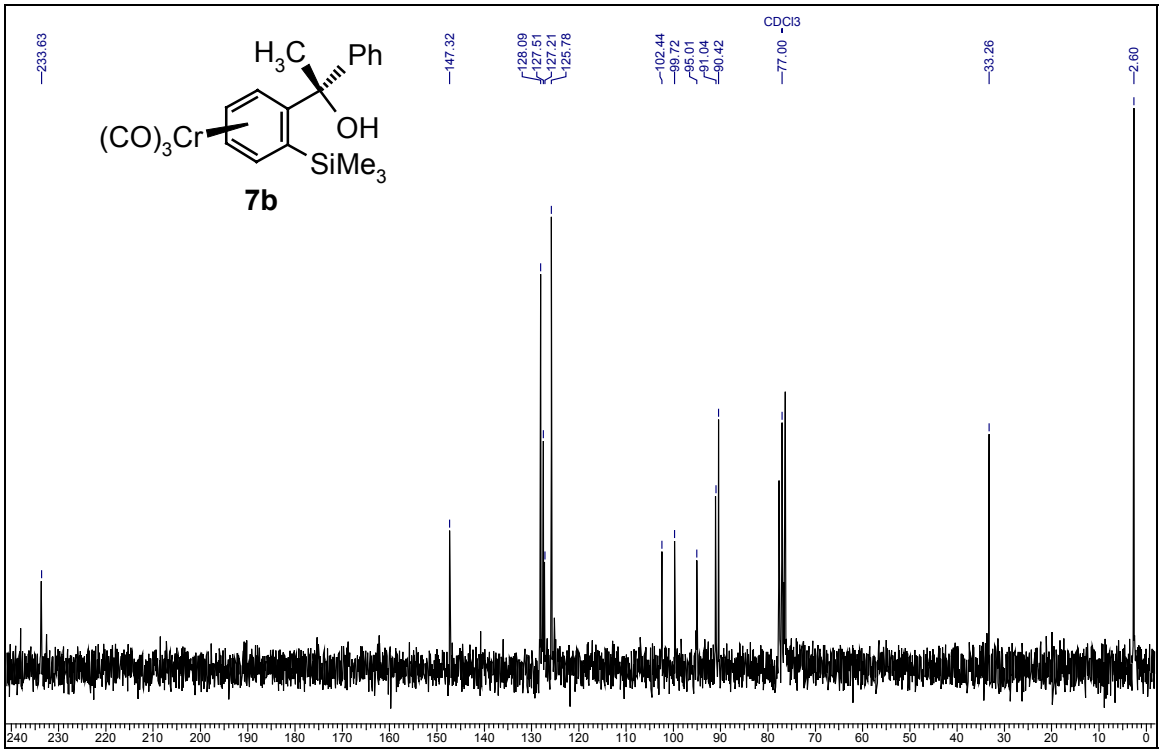
Ph
OH
(CO)3Cr
SiMe3
7b
5.21
2.03
2.00
1.00
3.10
9.02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127.21
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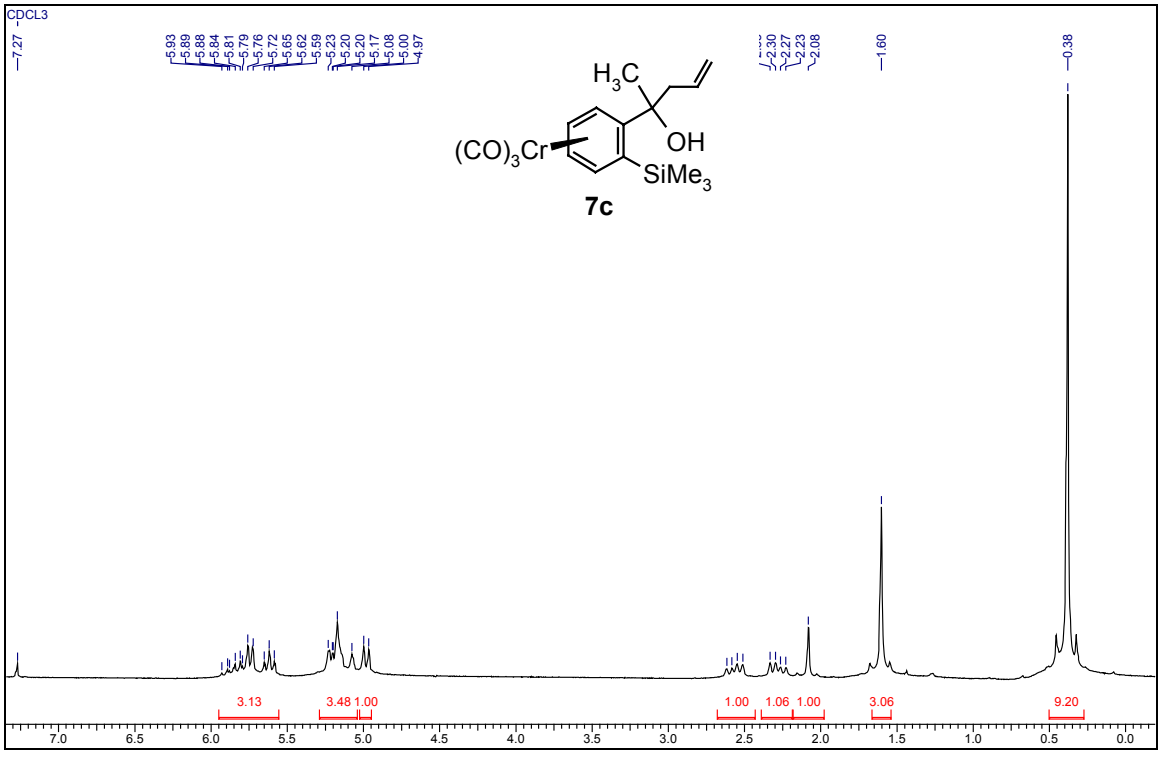
90.42
77.00
33.26
2.60
H3C
Ph
OH
(CO)3Cr
SiMe3
7b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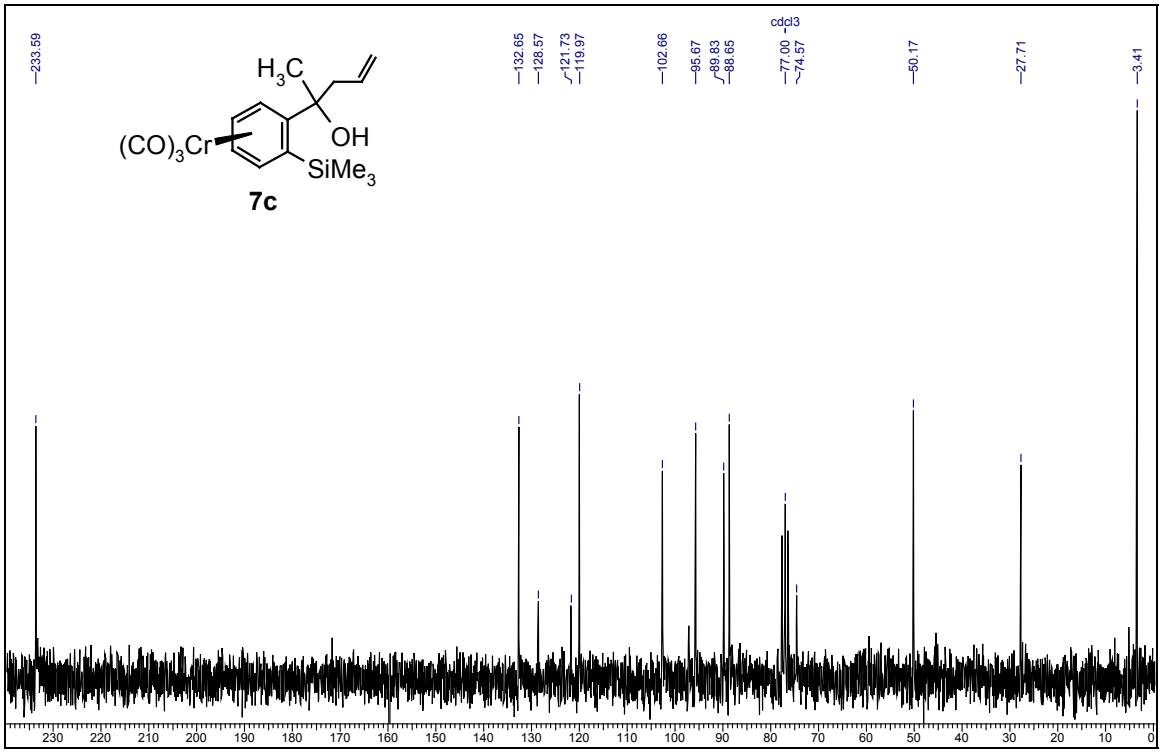
5.79
5.76
5.72
5.65
5.62
5.59
5.23
5.20
5.20
5.17
5.08
5.00
4.97
2.30
2.27
2.23
2.08
1.60
0.38
H3C
OH
(CO)3Cr
SiMe3
7c
3.13
3.48
1.00
1.00
1.06
1.00
3.06
9.20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77.00
74.57
50.17
27.71
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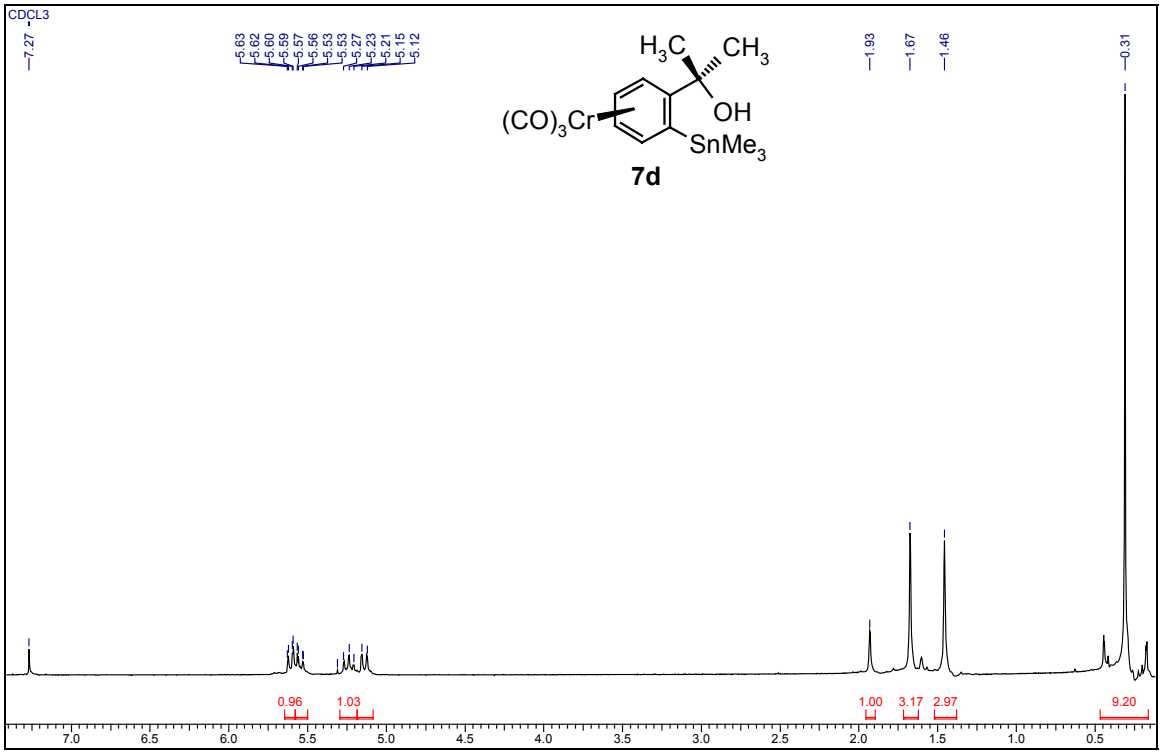
H3C
OH
(CO)3Cr
SiMe3
7c


CDCL3
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5.63
5.62
5.60
5.59
5.57
5.56
5.53
5.53
5.27
5.23
5.21
5.15
5.12
1.93
1.67
1.46
0.31
H3C
CH3
OH
(CO)3Cr
SnMe3
7d
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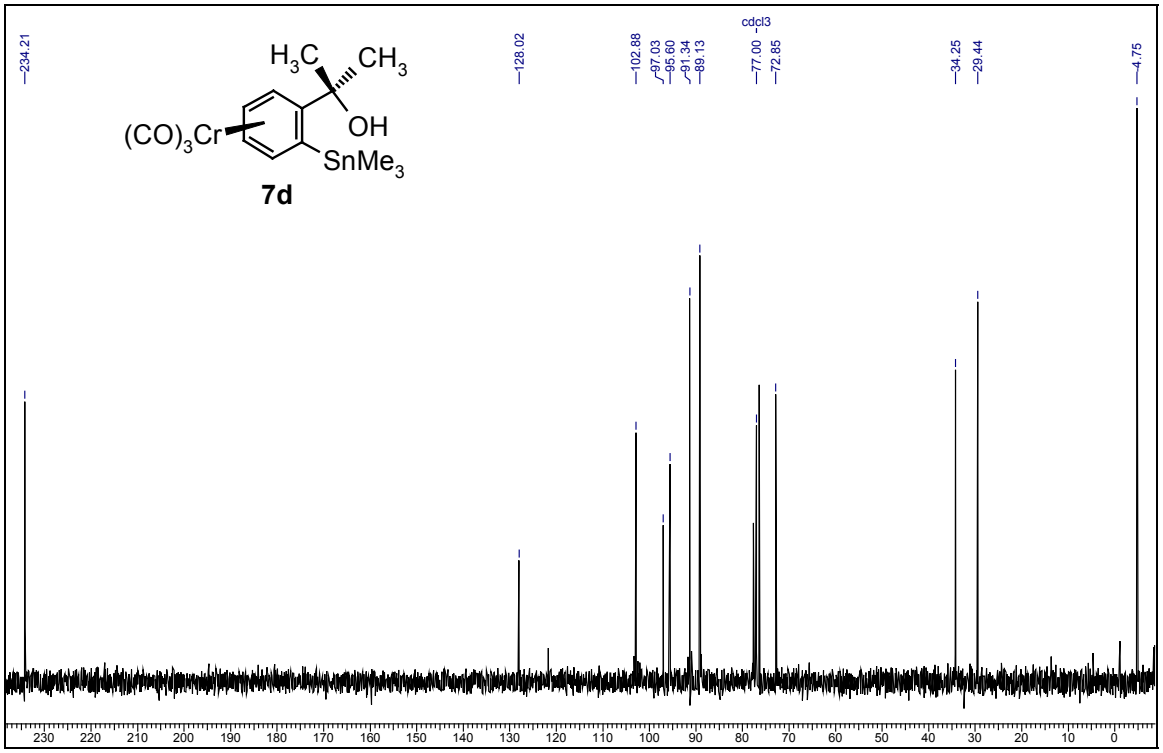
1.03
1.00
3.17
2.97
9.20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102.88
97.03
95.60
91.34
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34.25
29.44
4.75
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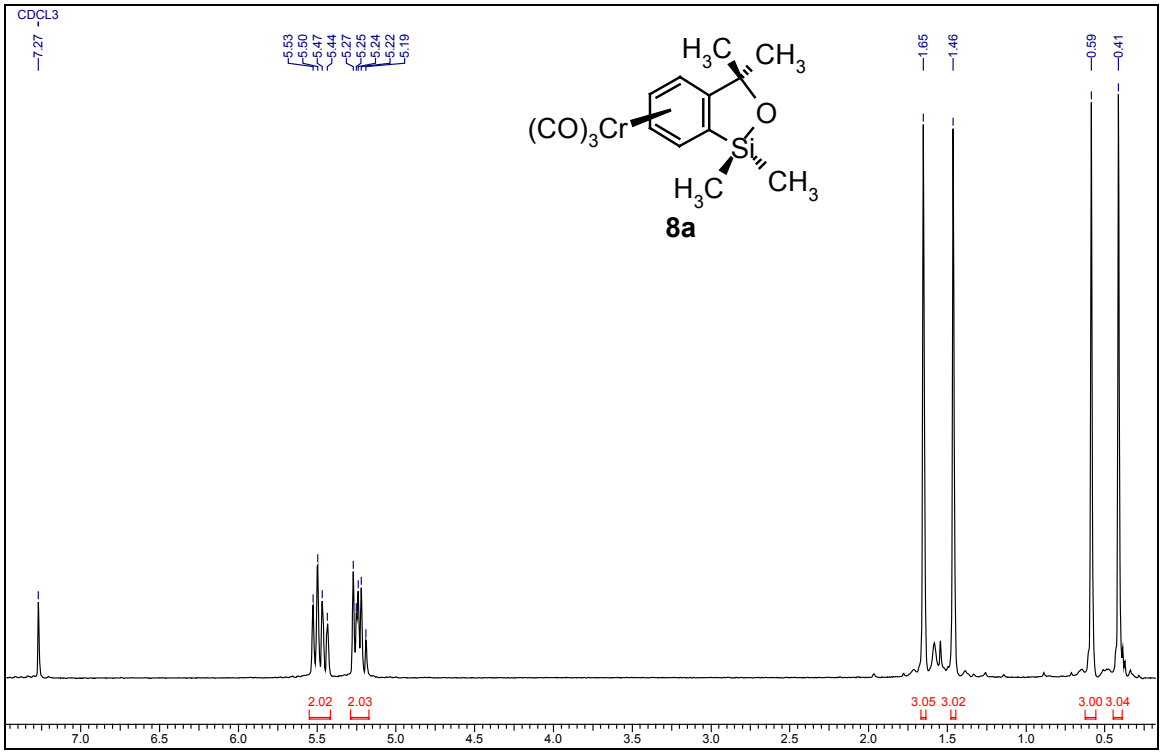
CH3
(CO)3Cr
OH
SnMe3
7d


CDCL3
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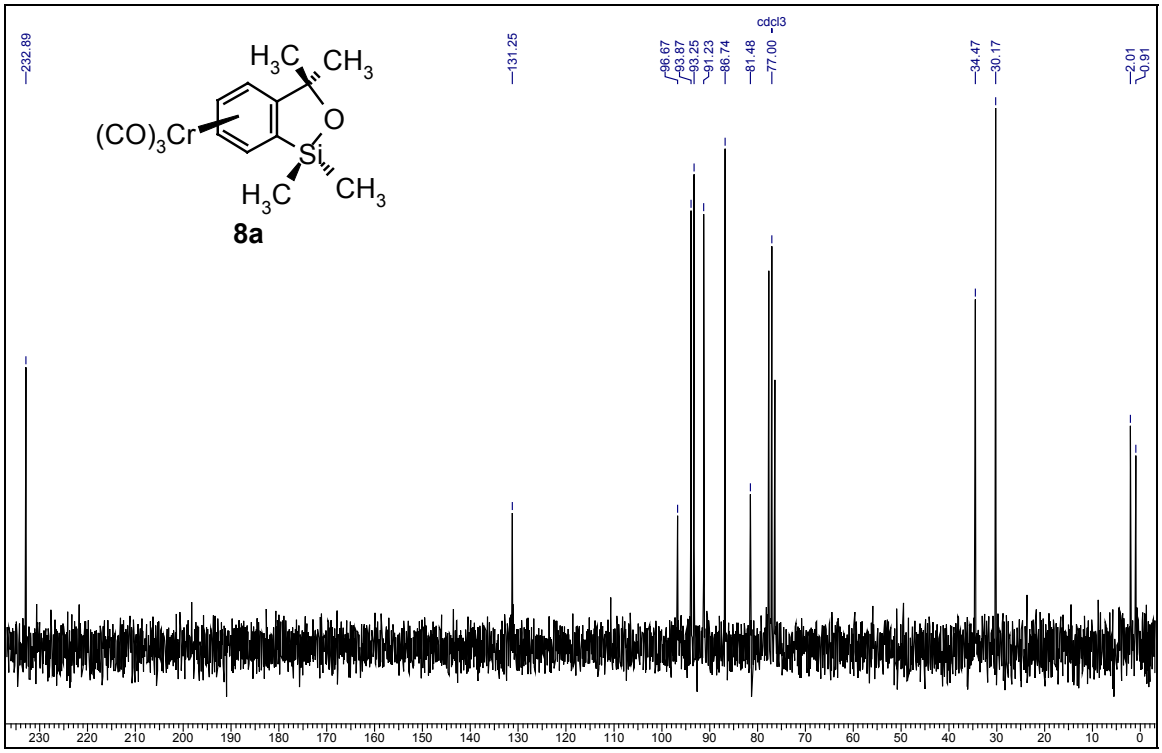
5.53
5.50
5.47
5.44
5.27
5.25
5.24
5.22
5.19
1.65
1.46
0.59
0.41
H3C
CH3
(CO)3Cr
O
Si
H3C
CH3
8a
2.02
2.03
3.05
3.02
3.00
3.04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131.25
96.67
93.87
93.25
91.23
86.74
81.48
77.00
cdcl3
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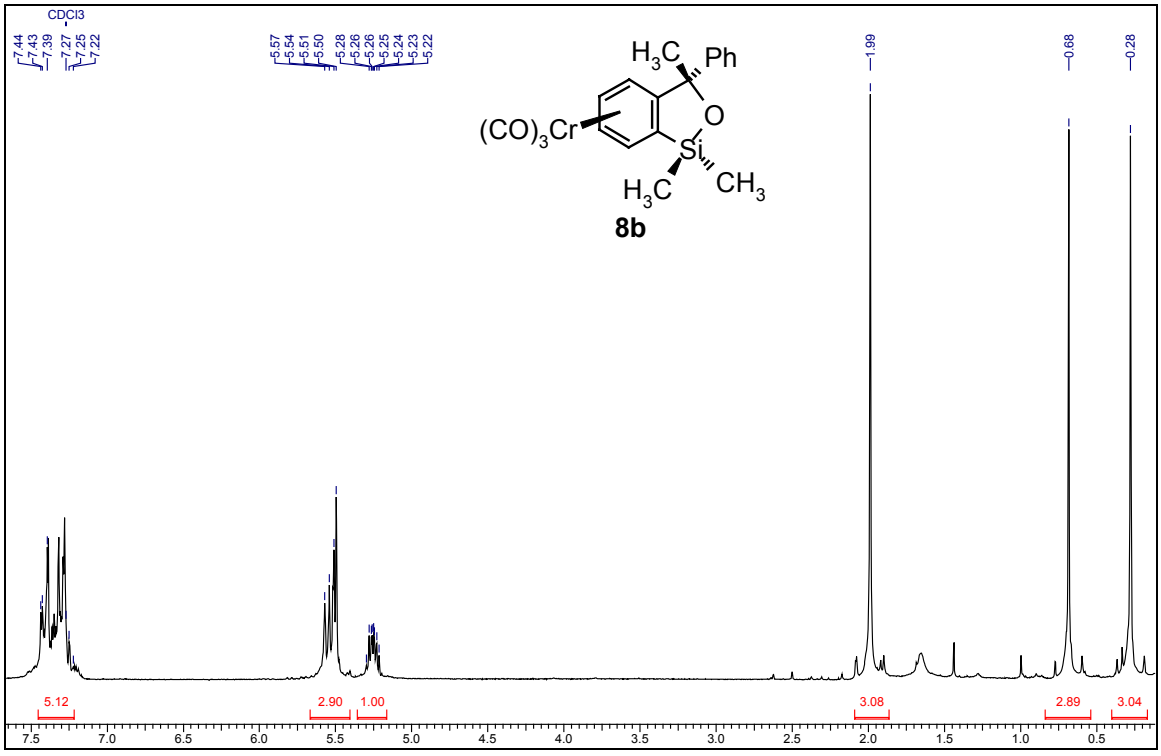
30.17
2.01
0.91
H_3C
CH_3
$(CO)_3Cr$
O
Si
H_3C
CH_3
8a


CDCl3
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7.39
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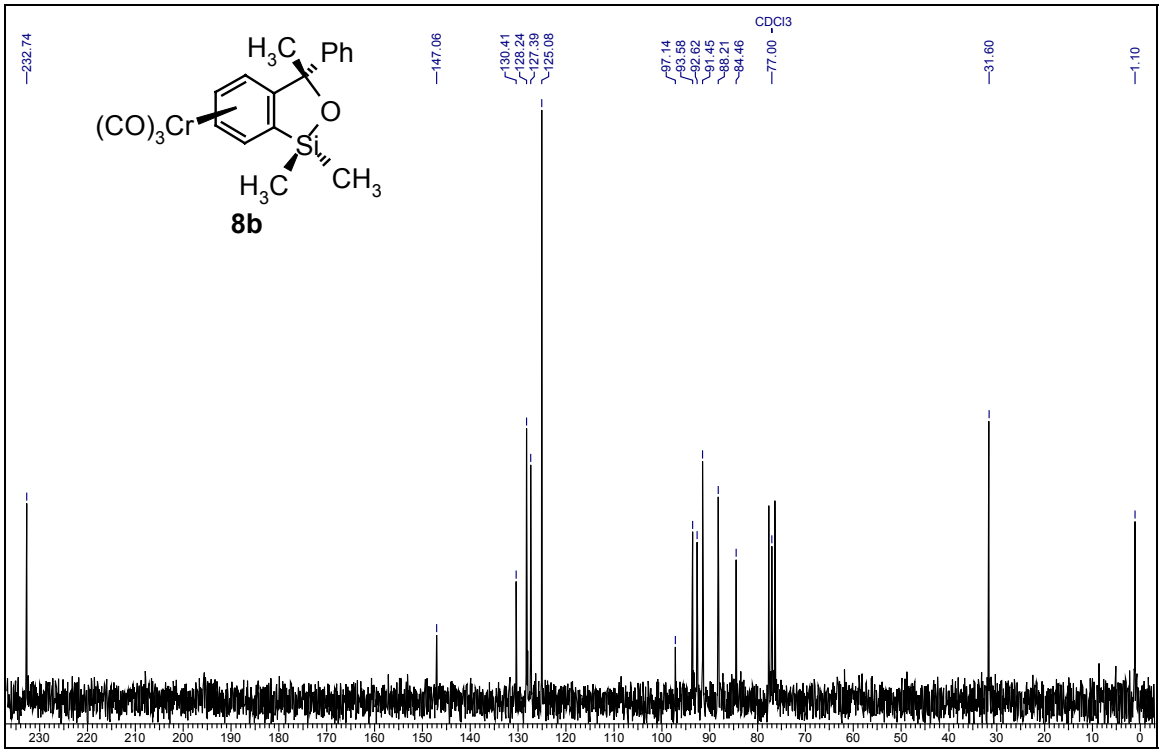
7.25
7.22
5.57
5.54
5.51
5.50
5.28
5.26
5.26
5.25
5.24
5.23
5.22
1.99
0.68
0.28
H_3C
Ph
$(CO)_3Cr$
O
Si
H_3C
CH_3
8b
5.12
2.90
1.00
3.08
2.89
3.04


CDCl3
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127.39
125.08
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91.45
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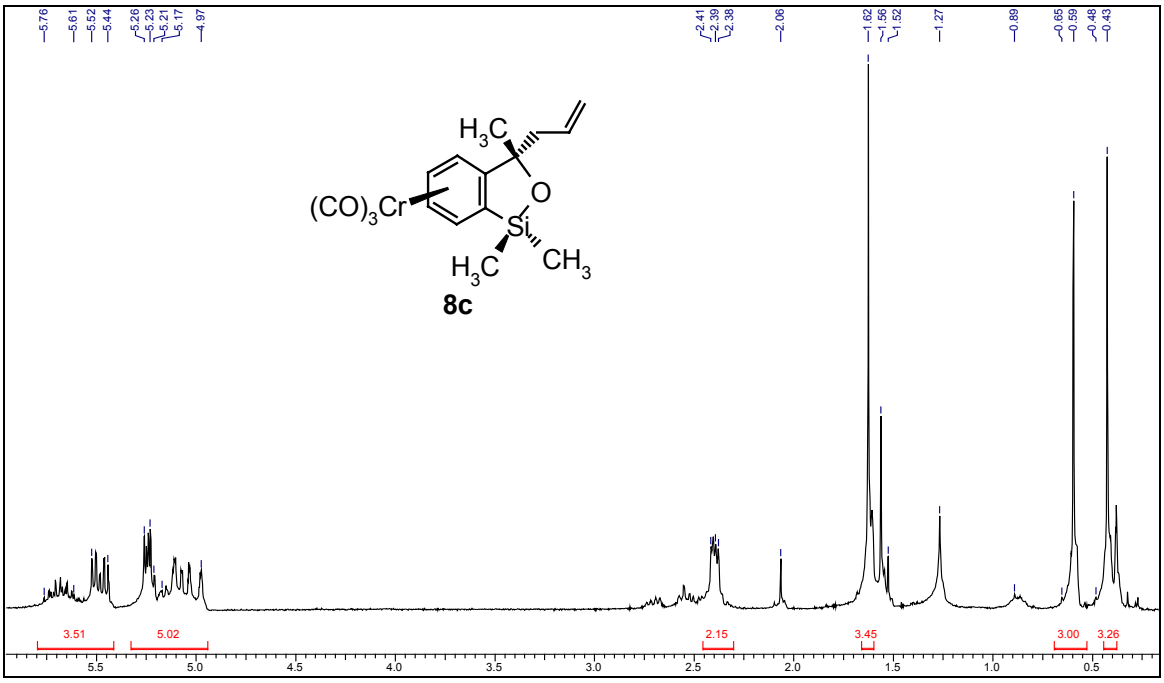
77.00
31.60
1.10
Ph
O
Si
CH3

8b


5.76
5.61
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5.26
5.23
5.21
5.17
4.97
2.41
2.39
2.38
2.06
1.62
1.56
1.52
1.27
0.89
0.65
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0.43
3.51
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2.15
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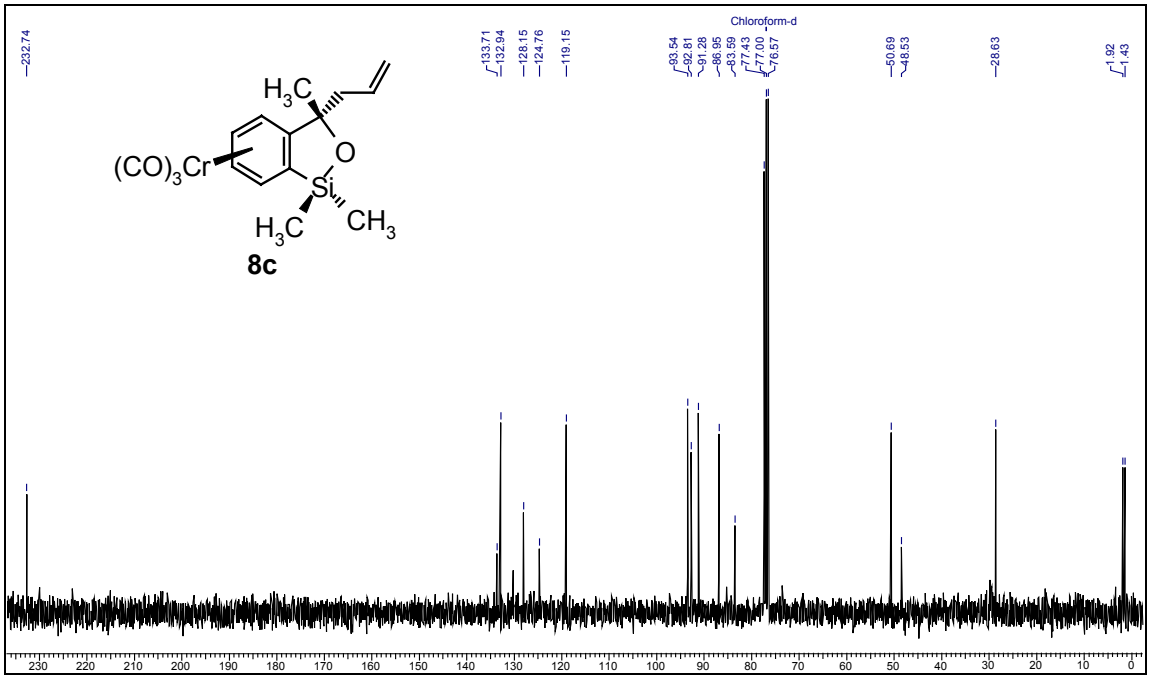
3.00
3.26
O
Si
CH3

8c


Chloroform-d
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91.28
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77.00
76.57
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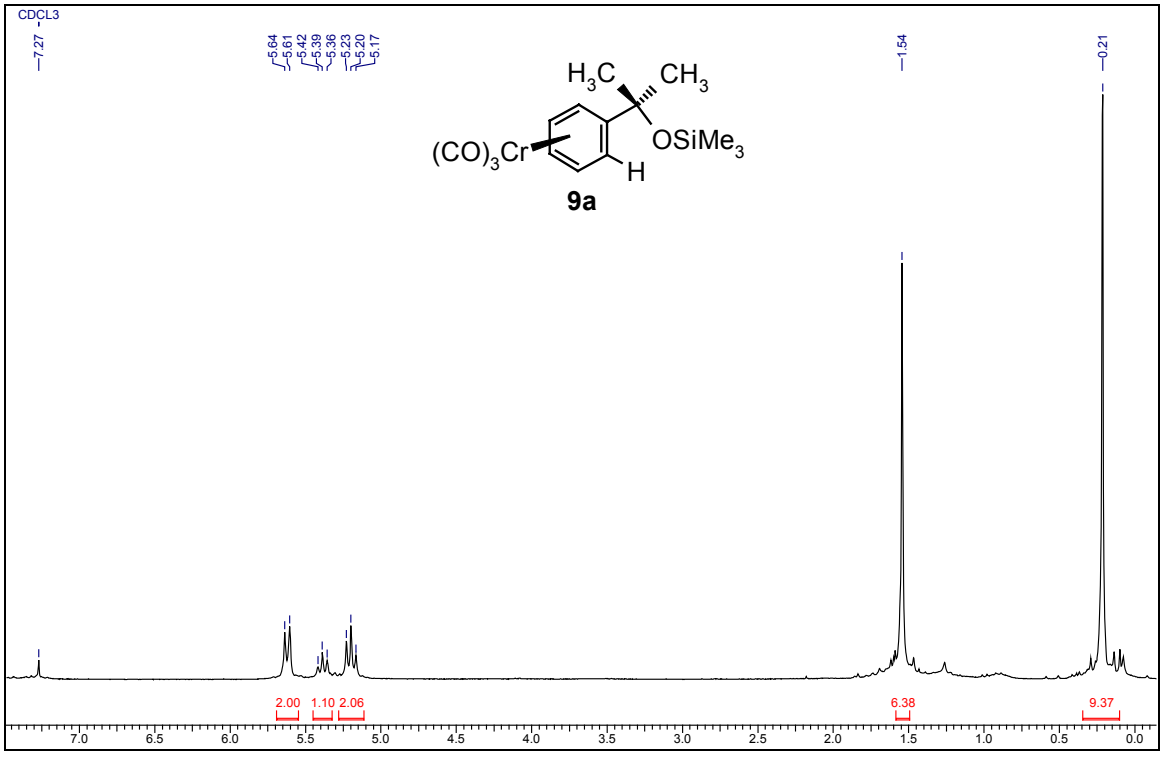
48.53
28.63
1.92
1.43
H3C
(CO)3Cr
O
Si
H3C
CH3
8c


CDCL3
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5.39
5.36
5.23
5.20
5.17
1.54
0.21
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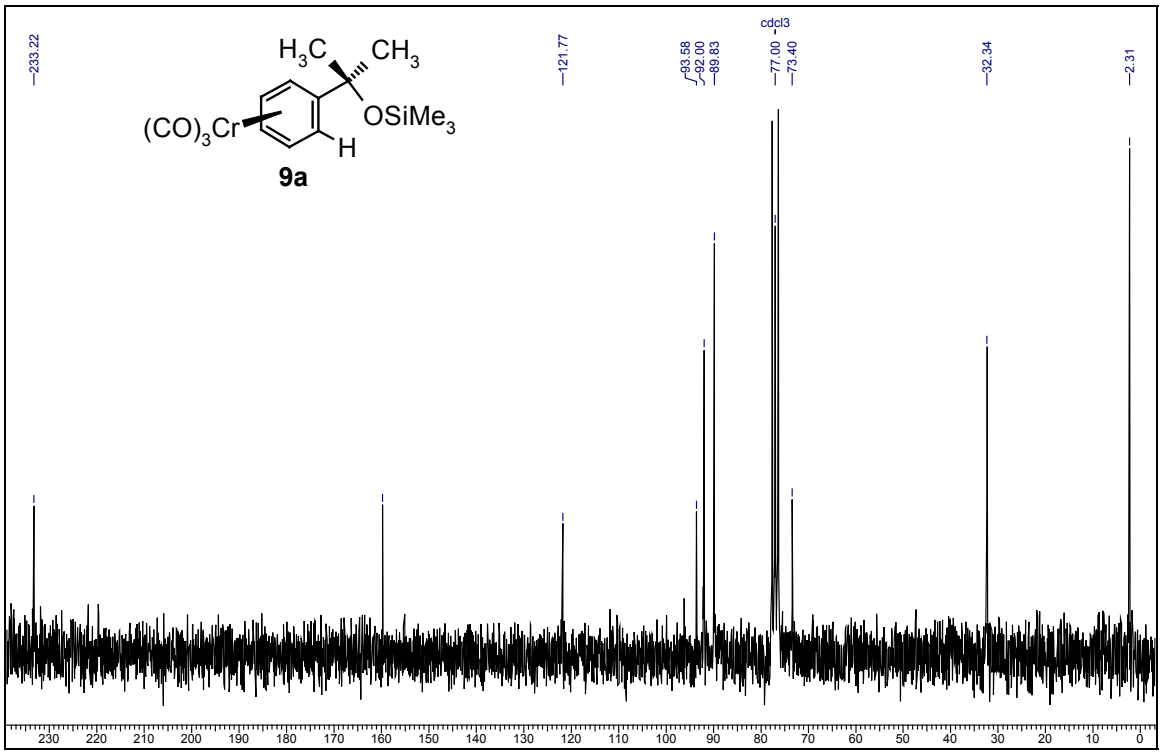
CH3
(CO)3Cr
OSiMe3
H
9a
2.00
1.10
2.06
6.38
9.37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73.40
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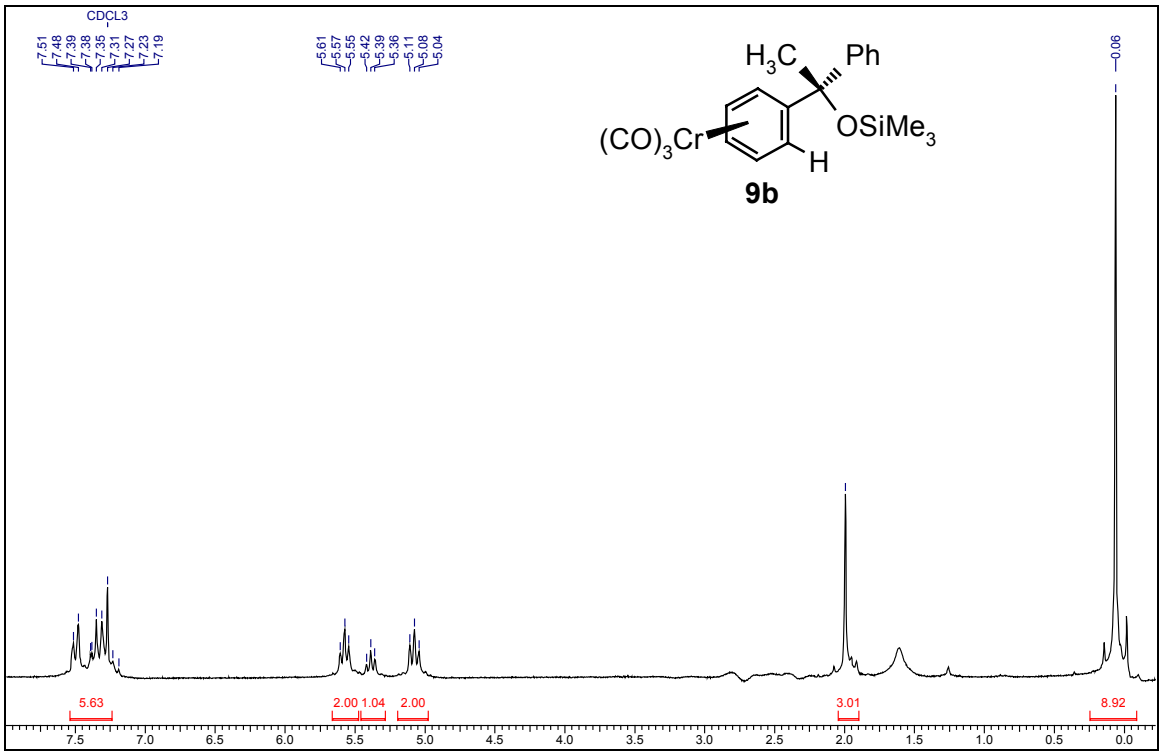
2.31
H3C
CH3
OSiMe3
(CO)3Cr
H
9a


CDCL3
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7.39
7.38
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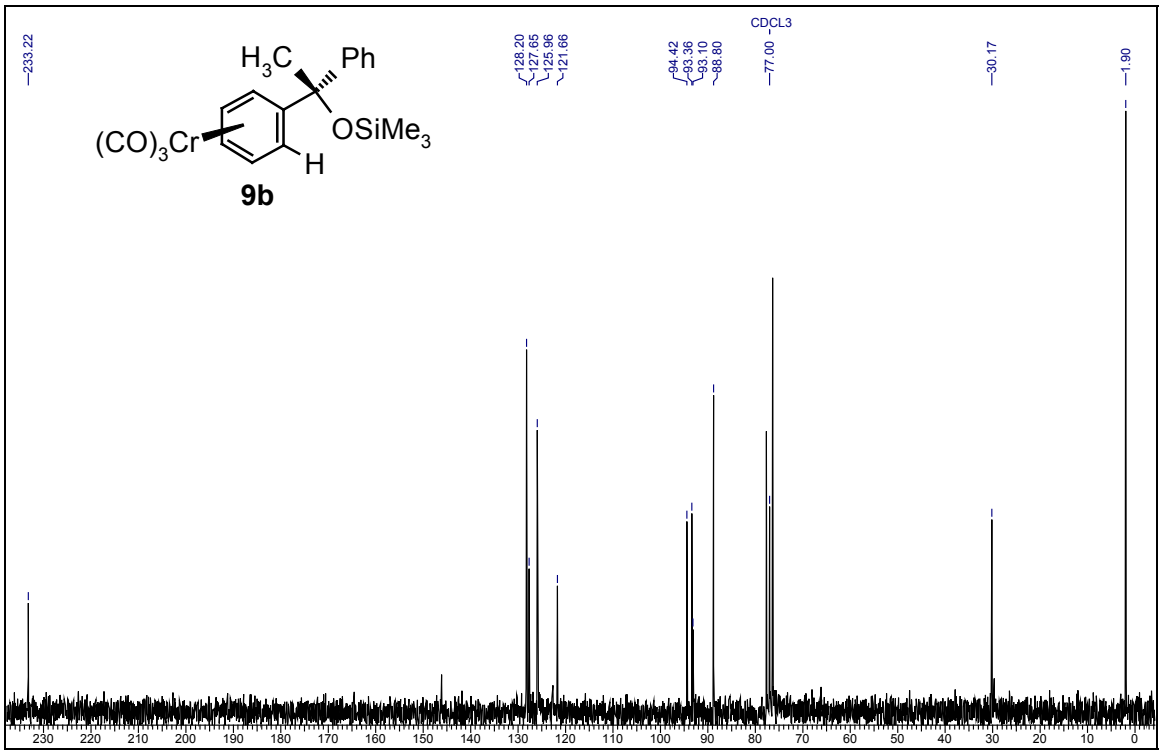
7.31
7.27
7.23
7.19
5.61
5.57
5.55
5.42
5.38
5.36
5.11
5.08
5.04
0.06
H3C
Ph
OSiMe3
(CO)3Cr
H
9b
5.63
2.00
1.04
2.00
3.01
8.92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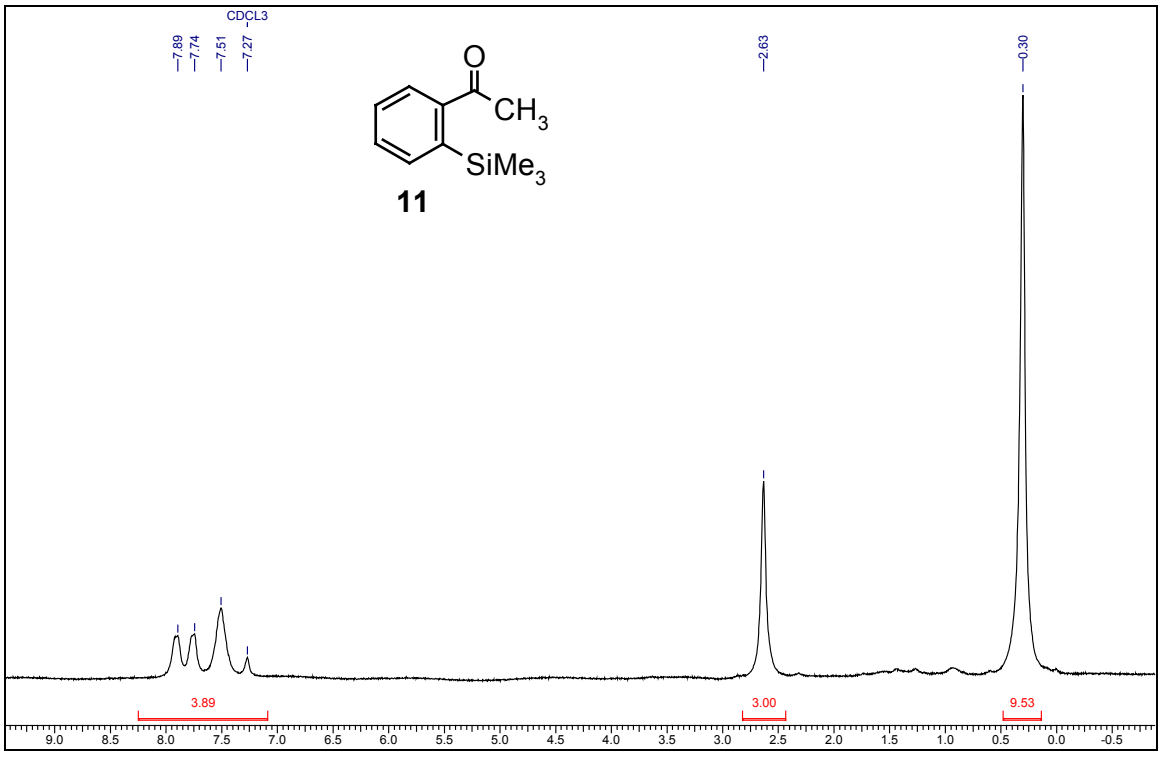
121.66
94.42
93.36
93.10
88.80
CDCL3
77.00
30.17
1.90
H3C
Ph
OSiMe3
(CO)3Cr
H
9b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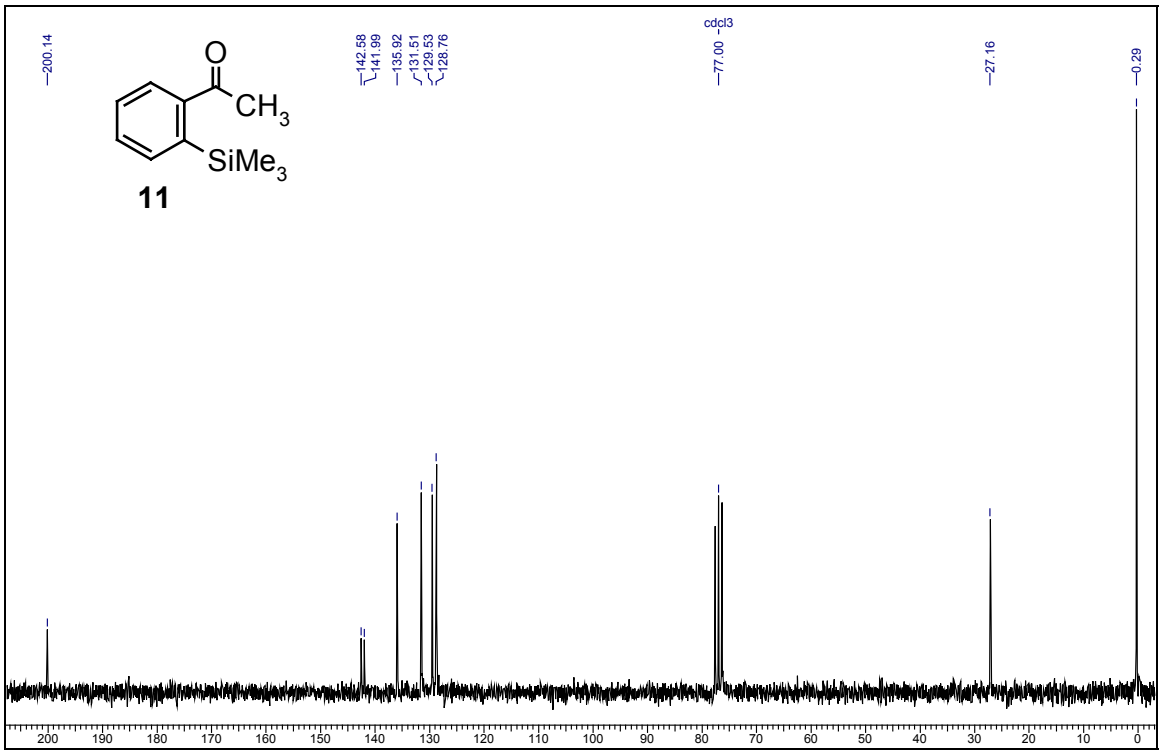
O
CH3
SiMe3
11
3.89
3.00
9.53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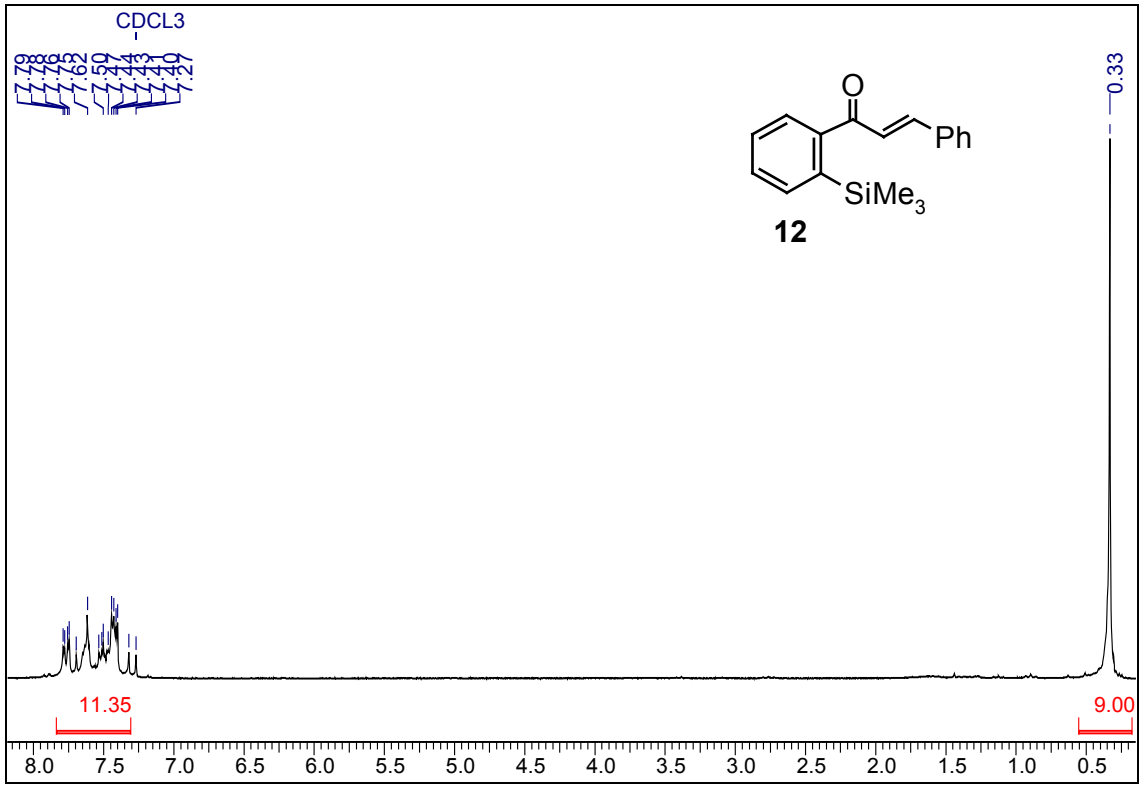
129.53
128.76
cdcl3
77.00
27.16
0.29
O
CH3
SiMe3
11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7.43
7.41
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O
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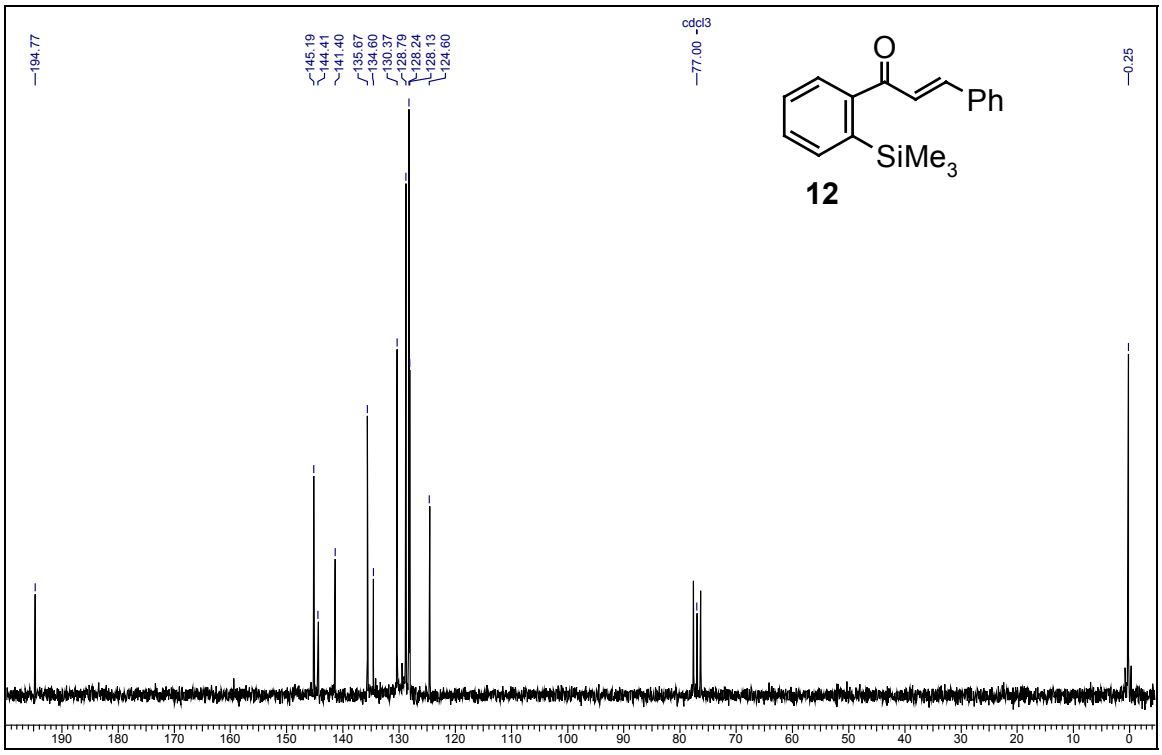
SiMe3
12
11.35
9.00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128.79
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128.13
124.60
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Ph
SiMe3
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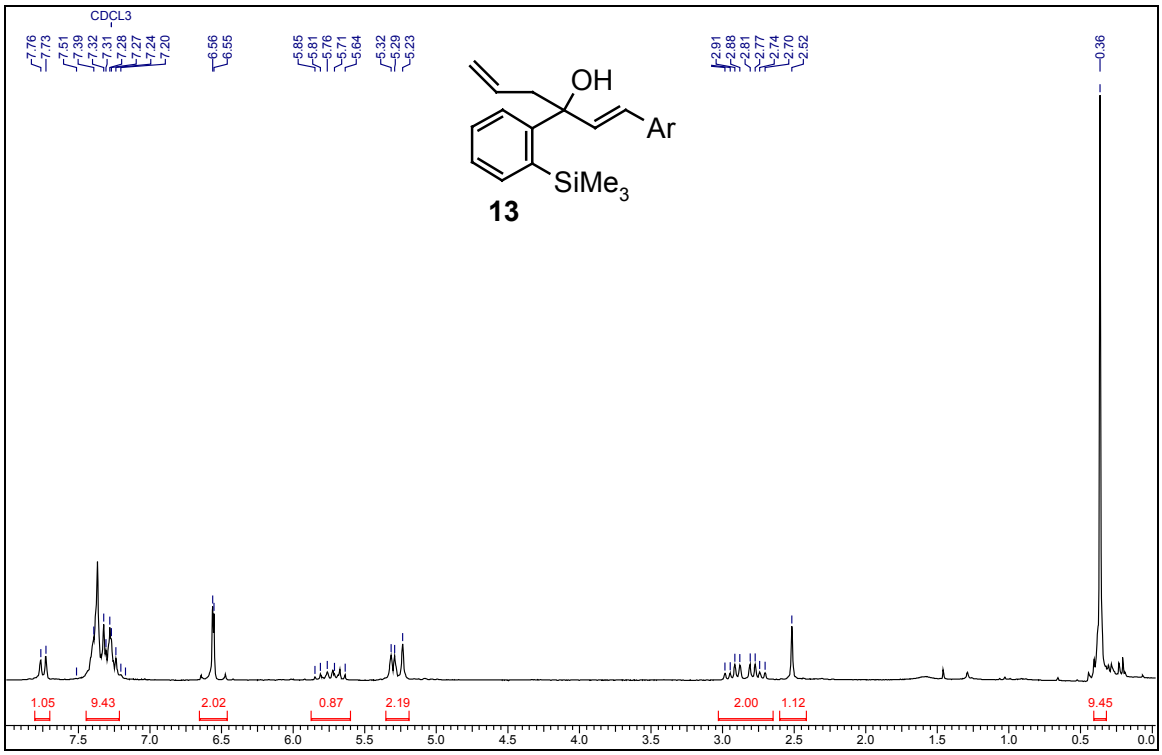
CDCL3
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7.32
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7.28
7.27
7.24
7.20
6.56
6.55
5.85
5.81
5.76
5.71
5.64
5.32
5.29
5.23
2.91
2.88
2.81
2.77
2.74
2.70
2.52
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SiMe3
13
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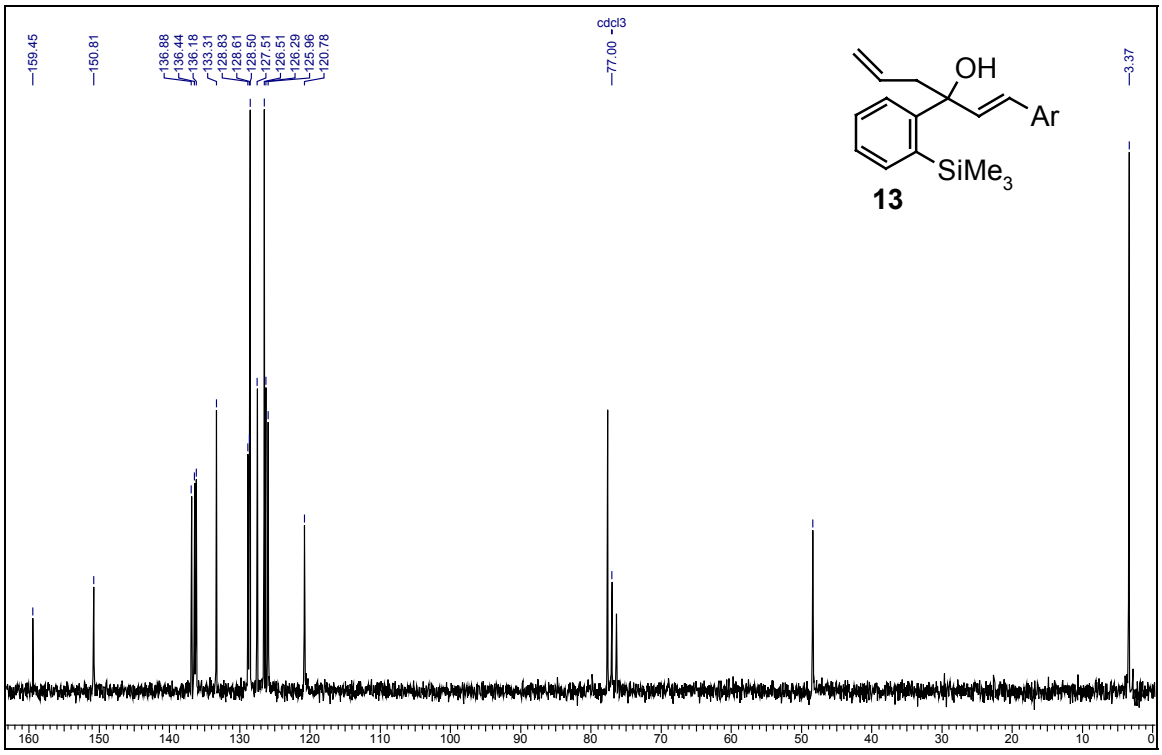
9.43
2.02
0.87
2.19
2.00
1.12
9.45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128.61
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126.51
126.29
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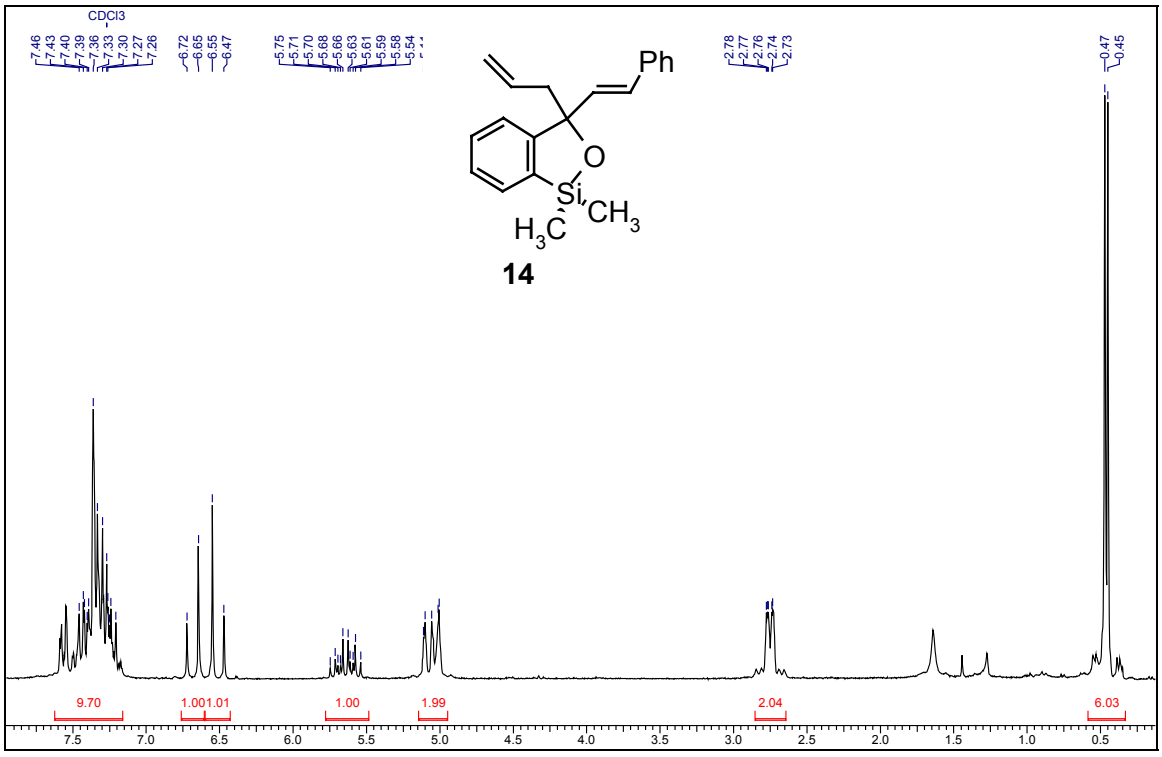
77.00
3.37
OH
Ar
SiMe3
13


CDCl3
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7.36
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7.26
6.72
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5.75
5.71
5.70
5.68
5.66
5.63
5.61
5.59
5.58
5.54
2.78
2.77
2.76
2.74
2.73
0.47
0.45
Ph
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Si
CH3
H3C
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1.01
1.00
1.99
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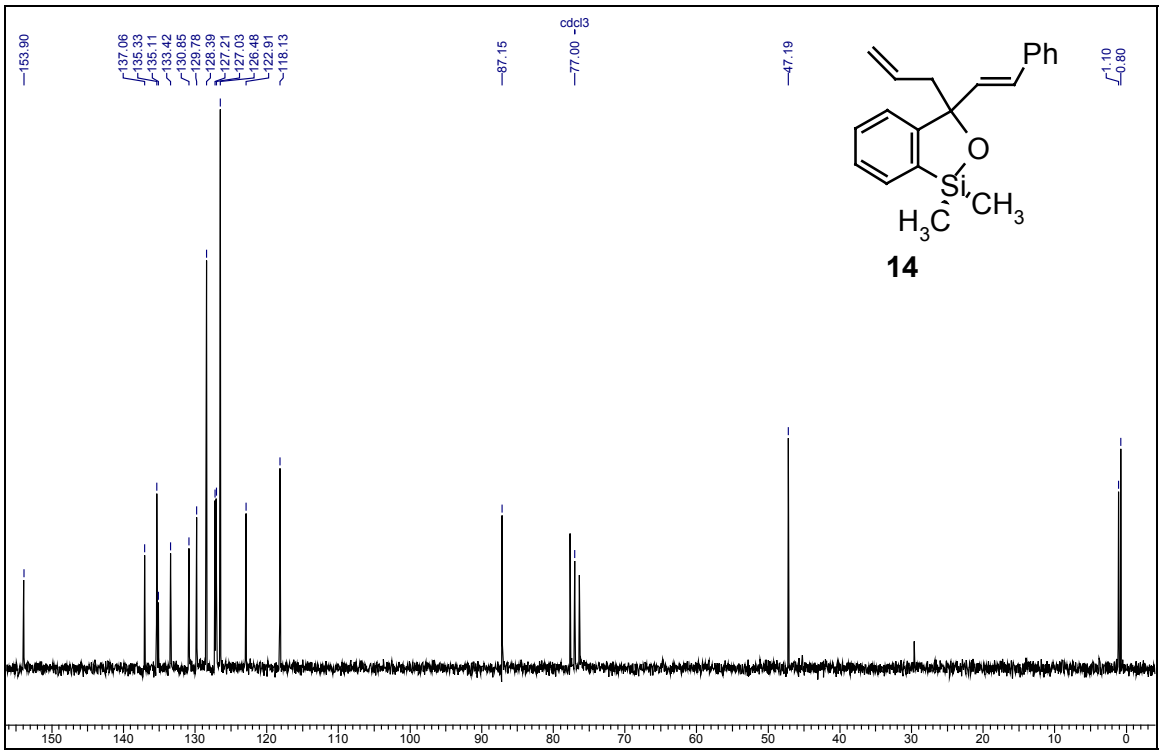
6.03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129.78
128.39
127.21
127.03
126.48
122.91
118.13
87.15
77.00
47.19
1.10
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Ph
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14
150
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130
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