TRANSITION METAL TEMPLATES FOR STEREOSELECTIVE SYNTHESIS

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TRANSITION METAL TEMPLATES FOR STEREOSELECTIVE SYNTHESIS

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PUNE - 411 008

CERTIFICATE

*This is to certify that the work incorporated in the thesis entitled “**Transition Metal Templates for Stereoselective synthesis**” submitted by Bikash C. Maity was carried out by him under my supervision at the National Chemical Laboratory. Such material as has been obtained from other sources has been duly acknowledged in the thesis.*

Date :

National Chemical Laboratory (Dr. Amitabha Sarkar)

Pune 411 008 Research Guide

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(Bikash C. Maity)

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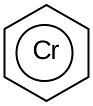
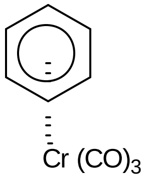
GENERAL REMARKS

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 AC-200. Chemical shifts were recorded in parts per million (δ). Abbreviations, *viz.*, s = singlet, d = doublet, t = triplet, dd = doublet of doublet, bs = broad singlet, bs = 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 Bruker AC-500 and Bruker AC-200 instrument operating at 125.76 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. Optical rotations were measured on JASCO DIP-118
7. The progress of the reaction was monitored by analytical thin layer chromatography plates precoated 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.
9. Pet-ether refers to the fraction boiling between 60-80 °C.

10 All the reactions were performed under argon atmosphere.

ABBREVIATIONS

BuLi or butyllithium	*n*- Butyl Lithium in hexane
DMF	Dimethylformamide
Et_2O or ether	Diethyl ether
o	*Ortho*
m	*Meta*
p	*Para*
THF	Tetrahydrofuran
r.t	Room temperature
LDA	Lithium diisopropyl amide
ee	Enantiomeric excess
de	Diastereomeric excess
RCM	Ring closing Metathesis
TLC	Thin layer chromatography
^{t}BuOK	Potassium *tert*-butoxide
	Represent trcarbonylchromium -complexed arene 
BOC-	*Tert*-butoxycarbonyl

Synopsis of the thesis

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

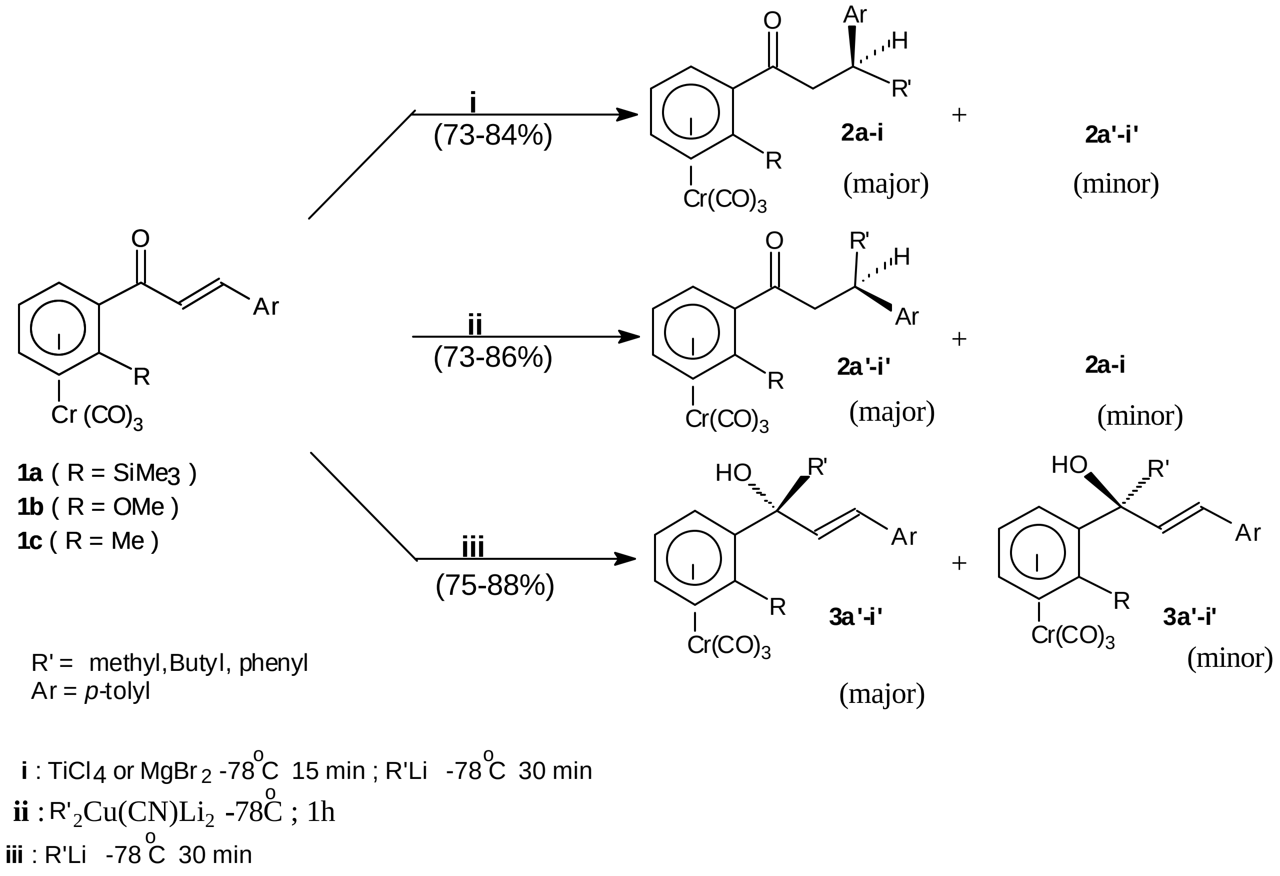
Chapter 1

Regio and Stereochemistry of Nucleophilic Addition to Conformationally Flexible Acyclic Enones Anchored on Arene Tricarbonyl Chromium : Effect of Lewis Acid

Because of its built-in flexibility, acyclic aryl alkenyl ketones complexed with $Cr(CO)_3$ can adopt several conformations of comparable energy in solution. As a result, the ? -faces become randomized and poor stereoselectivity in nucleophilic addition reaction is often observed. However, an *ortho*-substitution on the aromatic ring provides a definite barrier to rotation around the Ar-CO bond restricting the interconversion of accessible ? -faces of these enones. Once thus restricted, nucleophilic additions can be highly - and predictably – diastereoselective, as borne out by the following results.

A set of three substrates (**1a-c**) were allowed to react with organolithium reagents in presence or absence of a Lewis acid like $TiCl_4$ or $MgBr_2$ (Scheme-1) and compared with cuprate additions. In presence of Lewis acid, *endo*-selective conjugate addition of RLi or RMgX was observed as the predominant reaction, in contrast with *exo*-selective cuprate addition. Organolithium reagents afforded 1,2-addition products in absence of Lewis acid.

Scheme-1



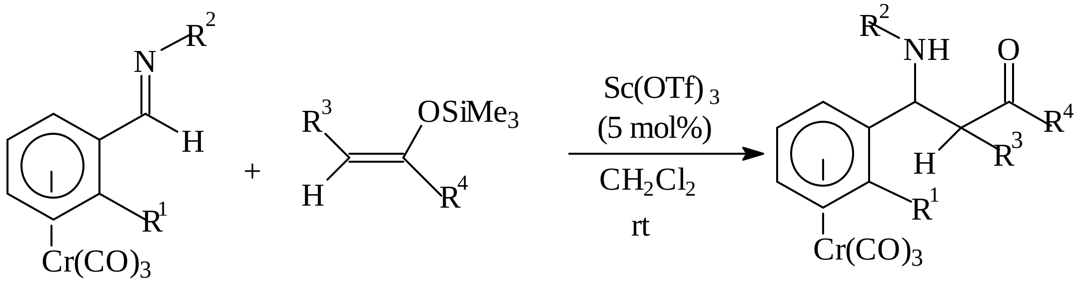
Formations of different products from different reactions have been explained in terms of preferred conformation of acyclic enones and mode of coordination of Lewis acid to the carbonyl function.

Chapter 2

ScandiumTriflate Catalyzed Diasteroselective Addition of Silyl Enol Ethers and Silyl Ketene Acetals to Imines Anchored on Arene Tricarbonylchromium

In presence of Sc(OTf)$_3$ (5mol%), silyl enol ethers (**5a-d**) added to chiral aldehyde complexes (**4a-d**) to yield β-amino ketones with high diastereselectivity (>98%) at ambient temperature (Scheme-2). Isolated yields ranged from 83 to 90%.

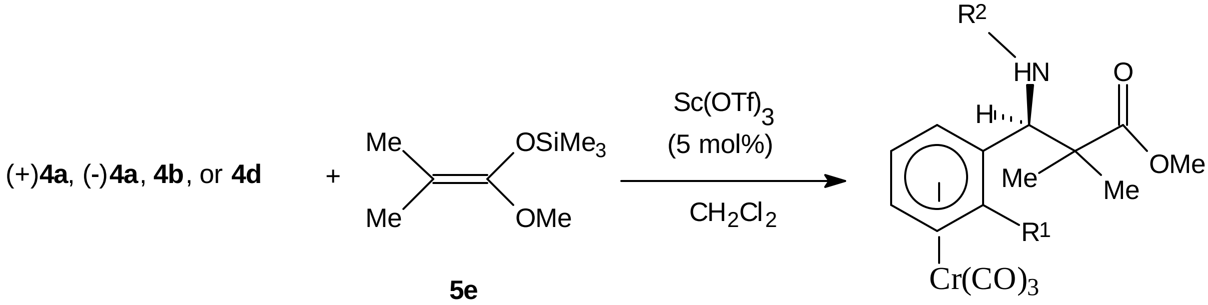
Scheme-2



	R^1	**R^2**		**R^3**	**R^4**		**R^1**	**R^2**	**R^3**	**R^4**
4a :	Me	*p*-MeO-C_6H_4-	**5a :**	H	Me	**6a :**	Me	*p*-MeO-C_6H_4	H	Me
4b :	F	,,	**5b :**	H	Ph	**6b :**	Me	"	H	Ph
4c :	OMe	,,	**5c :**	Me	Ph	**6c :**	Me	"	-$(CH_2)_4$-	
4d :	Me	-H_2C-CH=CH_2	**2d :**	-$(CH_2)_4$-		**6d :**	Me	"	Me	Ph
						6e :	F	"	H	Me
						6f :	F	"	H	Ph
						6g :	OMe	"	H	Me
						3h :	OMe	"	H	Ph

Silyl ketene acetal derived from methyl isobutyrate rapidly added to chiral imine complexes at room temperature producing diastereomerically pure β amino esters (Scheme-3) with very high isolated yields (90-95%).

Scheme-3

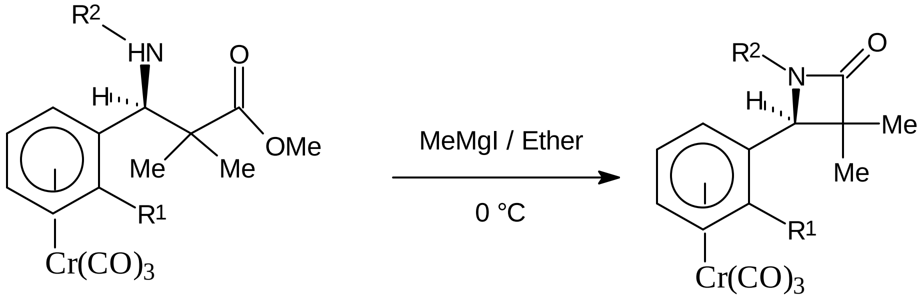


5e

(-)**7a**, (+)**7a**, **7b**, or **7c**

Stereochemistry of the product was confirmed by x-ray crystal structure determination of a representative molecule. β-Amino esters were efficiently cyclized to β-lactams on treatment with MeMgI in ether at 0 °C (Scheme-4). Optically pure products were obtained when the imines were derived from optically pure aldehyde complexes.

Scheme-4



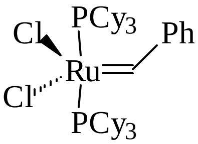
(-)**7a**, (+)**7a**, **7b**, or **7c**

(-)**8a**, (+)**8a**, **8b**, or **8c**

Chapter 3

Assembling Monocyclic, Spirocyclic and Fused Carbocycles by Ring Closing Metathesis on Arene Chromium Template

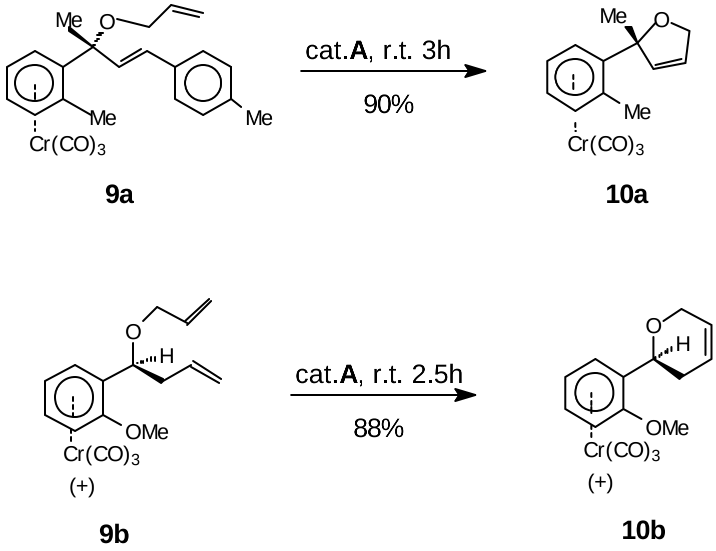
Over the past few years, Grubbs' ruthenium catalyst (**A**) has been widely used for synthesis of cyclo-olefines from dienes *via* 'ring closing metathesis' (RCM). The present work extends the use of RCM to synthesize a variety of diastereomerically pure carbocyclic and heterocyclic products at ambient temperature in good yield from differently substituted diene precursors assembled on arene tricarbonyl template.



(**A**)

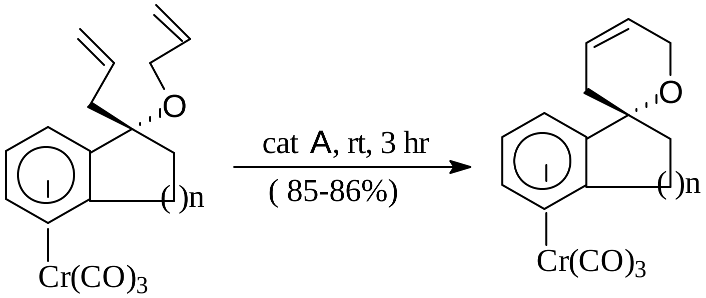
Monocyclic compounds (**10a-b**) from chiral dienes **(9a-b**) have been synthesized using 10 mol% of Grubbs' catalyst in dichloromethane at ambient temperature with respectable isolated yields (Scheme-5).

Scheme-5



Spirocycles **11b** and **12b** were obtained in high yield from corresponding substrates, **11a** and **12a** respectively (Scheme-6).

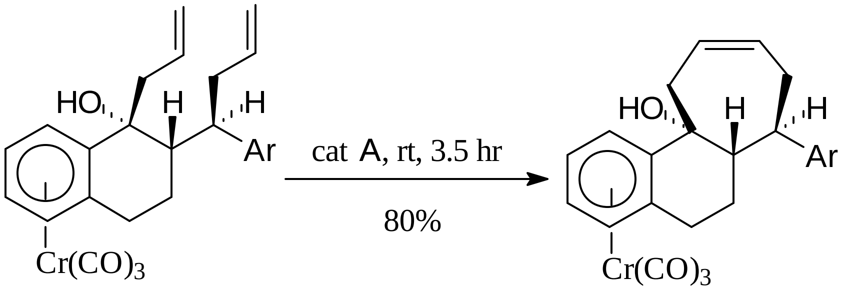
Scheme-6



11a (n = 1) 11b

12a (n = 2) 12b

Similarly, RCM afforded the fused tricyclic framework of **14**, where stereochemical features are defined by appropriate selection of synthetic sequences leading to the precursor **13** (Scheme-7).



13 14

All new compounds were characterized by spectral and analytical data, and details of synthesis and characterization have been discussed.

Chapter - I

Regio and Stereochemistry of Nucleophilic Addition to Conformationally Flexible Acyclic Enones Anchored on Arene Tricarbonyl Chromium : Effect of Lewis Acid

Introduction

Complexation of an arene ring to a tricarbonylchromium or $Cr(CO)_3$ group modifies the chemical properties[1] of an arene ring in a number of ways (Figure-1).

i) aromatic ring is more susceptible to nucleophilic additions,

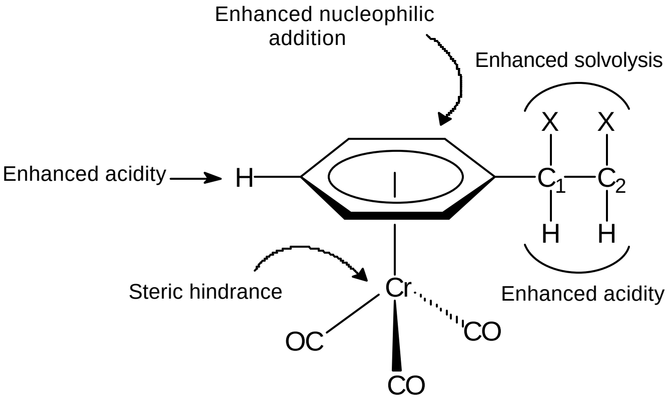
ii) kinetic acidity of the aromatic hydrogens is increased,

iii) $Cr(CO)_3$ group sterically hinders reagent approach from same face of the ring,

iv) carbanions at benzylic position are stabilized, and,

v) carbocations at benzylic positions are stabilized.

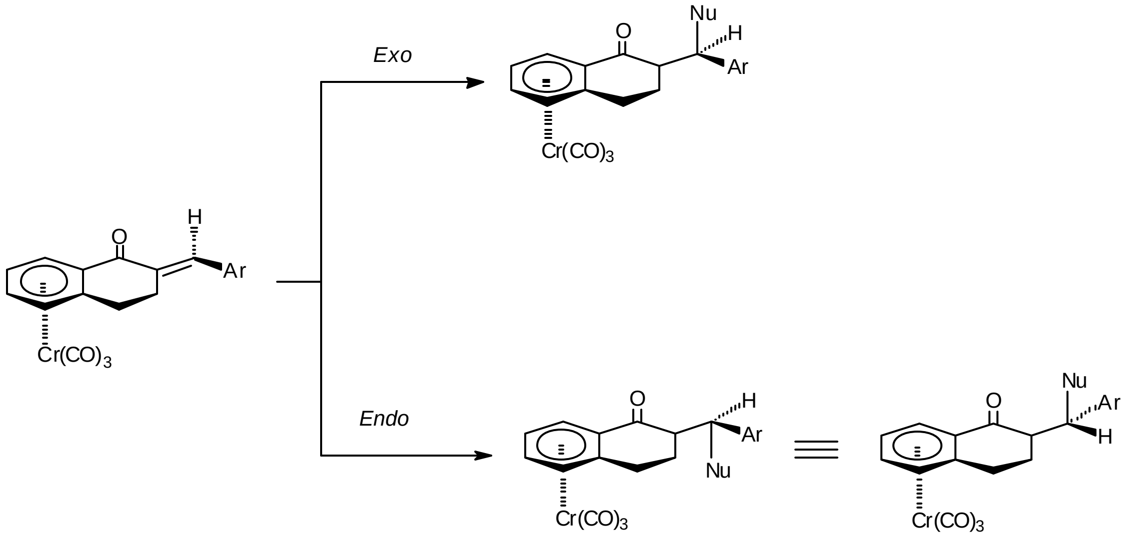
Figure -1



Of these, the stereodirecting effect of the metal-carbonyl group has been, by far, the most extensively studied aspect of the chemistry of η^6-arene tricarbonylchromium complexes. It is possible to carry out exclusive *anti* addition of reagents with respect to the $Cr(CO)_3$ group and accomplish diastereoselective synthesis of a large number of molecules. Efficient stereocontrol is routinely achieved at C-1 as well as C-2 centers.[2]

In the preliminary studies conducted in our laboratory, 2-arylidene-tetralone tricarbonylchromium complexes were chosen as the first set of substrates. This system offered many advantages. These could be prepared in high yield in two steps from 1-tetralone.[3] More over, a stereochemically rigid enone with fixed *cisoid* geometry would ensure a reliable correlation of product stereochemistry with mode of attack (*exo* or *endo*) by nucleophile (Scheme-1).

Scheme -1

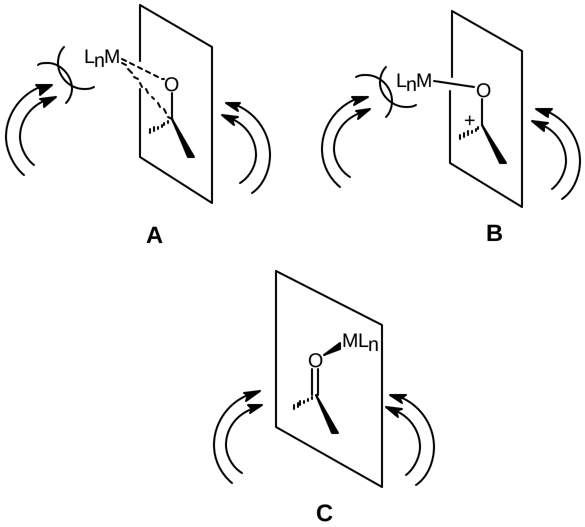


The propensity for *exo* attack by nucleophilic reagents to such substrates is well established.[2] If a Lewis acid is involved in a reaction, however, this straightforward situation changes.

A Lewis acid catalyzed reaction (*e.g.* nucleophilic addition or Diels-Alder reaction) is characterized by a dramatically enhanced rate compared to the original, uncatalyzed reaction.[4] This rate enhancement is rationalized in terms of an increase in the polar character of the carbonyl group. This indicates the structure of the Lewis acid carbonyl complex[5] probably has longer C-O bonds, an increased dipole moment, and a higher sp^3 character of the carbonyl oxygen. These features also influence the stereochemical outcome of the reaction.

In principle, the carbonyl group can coordinate to the Lewis acid either through its lone pair to form a σ bond or through the π system to form a η^2 metallo-oxirane (Chart-1). However, the η^2 mode of Lewis acid binding, **A**, is rather uncommon and is expected to occur only when the metal is sufficiently electron-rich to allow back-bonding, but a third possibility exists. A Lewis acid can bind to the carbonyl oxygen through initial *in-plane* coordination with a lone pair, and consequent to such binding, the oxygen may be rehybridized to an sp^3 atom. A torsion around the C-O bond can place the Lewis acid effectively *out-of-plane* with respect to the carbonyl plane, while the carbonyl carbon develops a positive charge and is now an activated electrophile, as shown in **B**. In terms of stereochemical consequence, these two situations are almost identical if C-O bond rotation in **B** is restricted in this position. Nucleophilic attack is sterically hindered from the face occupied by the Lewis acid in the case of both **A** and **B**. On the other hand, an *in-plane* bound Lewis acid does not impose a π-facial discrimination,[6] as seen in **C**.

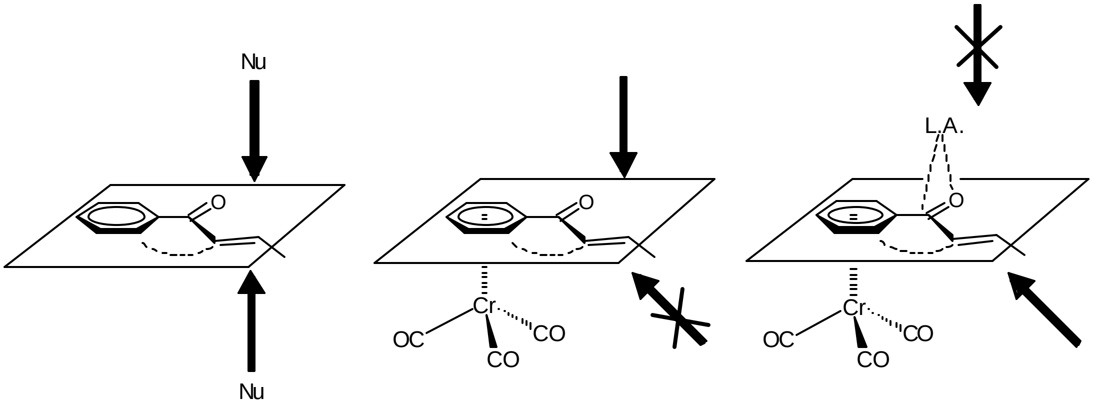
Chart-1



In Lewis acid mediated reactions, therefore, the steric and electronic requirements of the carbonyl ligand and the immediate groups surrounding it in the molecule of which it is a part, determine the mode of coordination and consequently the steric course of the reaction.

In the present context of arene-chromium complexes and an out-of-plane coordination mode of Lewis acid, it is likely that the Lewis acid would occupy the more accessible *exo* face. Then, an *endo* attack by the nucleophile would attest to the stereodirecting effect of Lewis acid coordination. Such a switch of stereochemical preference in presence of a Lewis acid is depicted in Chart-2.

Chart-2

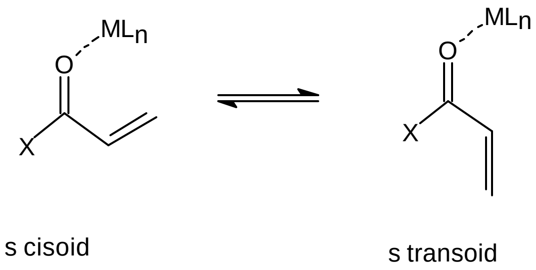


We have illustrated Lewis acid induced stereodivergent mode of nucleophilic attack to these substrates in our earlier studies.[7] Both $TiCl_4$ and $MgBr_2$ as Lewis acid gave consistent results. Given the well-defined, rigid structure of the tetralone complexes, correlation of product stereochemistry with direction of reagent approach was simple.

Present work

Encouraged by these results, we proceeded to investigate flexible acyclic substrates. In case of conformationally flexible, acyclic, α,β-unsaturated carbonyl compounds, the stereochemical outcome of a conjugate addition would depend on whether the reactive intermediate adopts a *cisoid* or *transoid* conformation (Scheme-2). Based on previous experiments, a *transoid* geometry of these enones was ruled out.

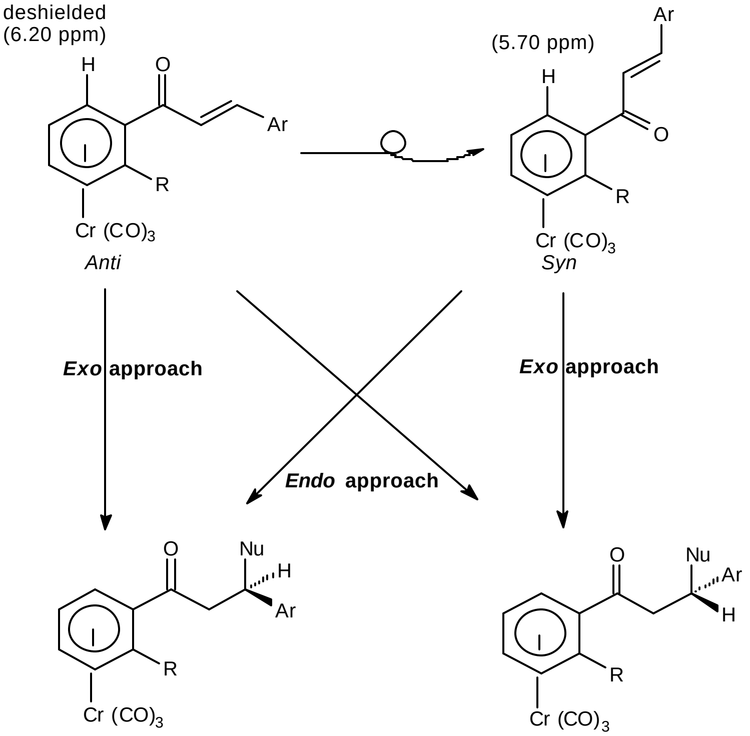
Scheme-2



A *cisoid* geometry of the enone was augmented further by the ^1H NMR signal of the β olefinic proton of the enone substrates at ~7.80 ppm. Such desheilding by the carbonyl group anisotropy is established for rigid molecules like benzylidene camphor,[8] the deshielded proton appears at 7.40 ppm, while the 'normal' absorption (of the geometric isomer) occurs at 6.45 ppm. For 2-benzylidene-1-tetralone, similar data were obtained. When isomeric products were generated by photolysis, signals of the two olefinic protons were obtained at 6.80 ppm and 7.85 ppm for *syn* and *anti* orientations respectively.

In order to ascertain the second structural factor, the *syn-anti* relationship of the enone carbonyl with the *ortho* substituent of complexed aromatic ring, the chemical shift of the *ortho* proton of the complexed aromatic ring was considered diagnostic. This proton is considerably deshielded (*ca.* 0.5 ppm) by the conformation of the enone as it lies in the deshielding zone of the carbonyl group anisotropy when the orientation of the keto group is *anti* with respect to the *ortho* substituent, R. The correlation between substrate conformation (*syn* or *anti*), stereoface-selectivity (*exo* or *endo* attack) and product stereochemistry is depicted in Chart-3.

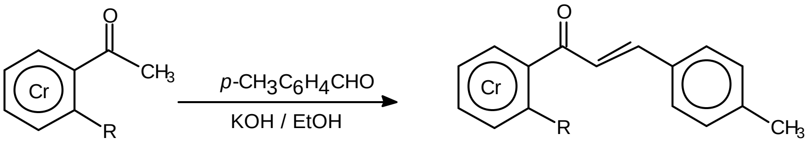
Chart-3



Results and Discussion

A set of four isostructural, acyclic enone $Cr(CO)_3$ complexes **1-3** were prepared from the corresponding substituted acetophenone complexes by conventional Claisen-Schmidt condensation with *p*-tolualdehyde (Scheme-3). The dark-red crystals were readily characterized by their typical IR bands (1980, 1910, 1680 and 1610 cm^{-1}) and ^{1}H NMR spectral features described earlier.[9]

Scheme -3

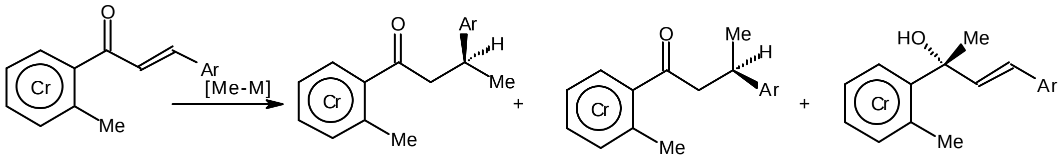


R	Complex
CH_3	**1**
OCH_3	**2**
$Si(CH_3)_3$	**3**

The nucleophiles were all organolithium reagents, *viz.* MeLi, BuLi and PhLi, that were used with or without additives like Lewis acids or copper(I) salt. The reagents were prepared in the laboratory by reported procedures and titrated prior to use. Titanium tetrachloride and magnesium bromide were the two Lewis acids used, while cuprous cyanide was used to generate cuprates. Reactions with Lewis acids were performed in dichloromethane in which the organolithium reagents were added as ether or hexane solution, keeping the amount of such solution <10% in dichloromethane. This was done to maximize Lewis acid binding to carbonyl function, and the reactions worked very well at the low temperature employed. Cuprate reagents were prepared in ether to which a toluene solution of the substrate was added, keeping the ratio ether:toluene about 5:1. Addition of organolithium to the complexed substrates was carried out in THF. In all cases, the reaction temperature was around –78 °C

NMR signal for the proton adjacent to the carbonyl group of complexed aromatic ring in **1** appears at 5.93 ppm, suggesting a possibility of randomization of π-face selectivity in addition to the carbonyl group. Indeed the observed stereoselectivity was moderate. Interestingly, addition of MeLi in THF yielded equal amounts of 1,2- and 1,4-addition products (Scheme-4). In presence of Lewis acids, formation of the 1,2-adducts was completely suppressed and two isomers of conjugate addition products were isolated. Although the stereoselectivity was moderate, the ratio of stereoisomers reversed for cuprate addition.

Scheme -4



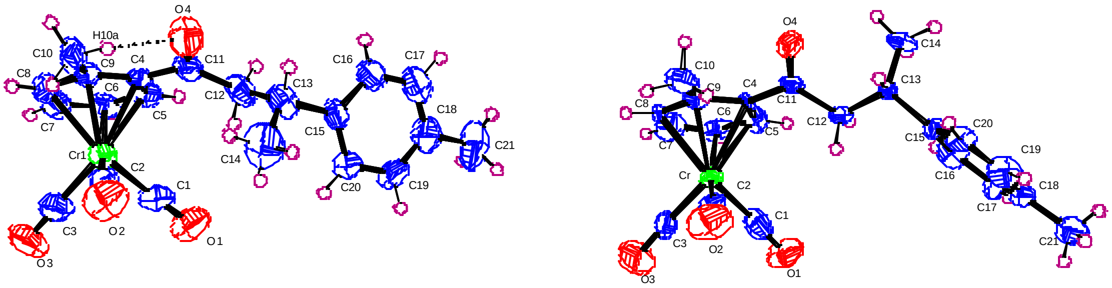
1 **4a** **4b** **4c**

Table -1

Nucleophile	Products (% yield)			Isomer distribution (%)		
	4a	**4b**	**4c**	**4a**	**4b**	**4c**
MeLi	8	18	61	9	20	70
MeLi/$TiCl_4$	61	23	0	72	27	0
MeLi/$MgBr_2$	58	22	0	72	27	0
MeLi/CuCN	26	56	0	31	68	0

The two 1,4-adducts, **4a** and **4b**, can be readily identified from the absence of olefinic protons, and methyl doublet between 1.3 and 1.4 ppm. There is a significant difference in the pattern of aromatic protons of the complexed ring. For **4a**, these protons appear as two clusters of peaks around 5.05 and 5.65 ppm while for **4b** these protons appear as four distinct, well-spaced signals from 4.98 to 5.88 ppm. The methylene protons adjacent to the carbonyl group are diastereotopic. The chemical shift difference between these two non-equivalent proton signals is larger in case of **4b** than for **4a**, such that for **4b** we can derive the two coupling constants (J_{AB} = 16.6 Hz, J_{AM} = 7 Hz) by first-order analysis. In order to understand the steric course of addition, it is vital that the structural assignments (relative stereochemistry) for these isomeric products are unequivocal. The stereochemistry depicted in the structures shown in Scheme-4 above, are based on crystal structure determination for both **4a** and **4b** (only one enantiomer is represented throughout). The ORTEP diagrams are displayed in Figure-2.

Figure -2



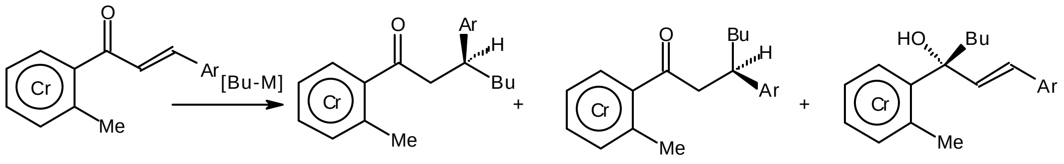
(a) ORTEP diagram for complex **4a**

(b) ORTEP diagram for complex **4b**

These structures support the initial hypothesis of this work – Lewis acid binding with the carbonyl group favors *anti* orientation on steric ground while out-of-plane coordination hinders nucleophilic approach from the *exo*-face of the substrate complex, as observed in previous examples with cyclic structures. In absence of Lewis acid, thus, cuprate addition results in formation of **4b** (*exo*-addition on *anti* conformer), while **4a** predominates in presence of Lewis acid. Interestingly, addition of MeLi in THF results in the formation of some 1,4-adduct although the expected allyl carbinol **4c** is indeed the major product. The assignment of stereochemistry for **4c** has been done based on a closely related precedent.[10]

In case of BuLi and related reagents, the situation is similar. Without additive, BuLi addition in THF provides almost 1:1 ratio of 1,2- and 1,4-addition products (Scheme-5).

Scheme -5



1

5a

5b

5c

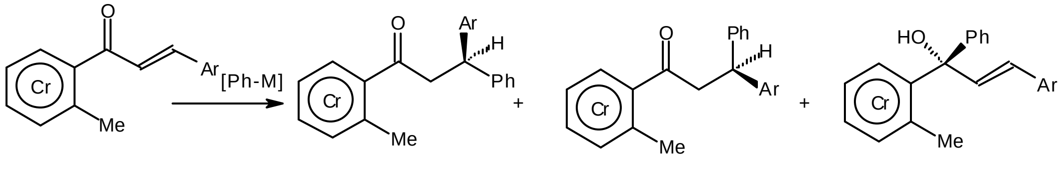
Table -2

Nucleophile	Products (% yield)			Isomer distribution (%)		
	5a	**5b**	**5c**	**5a**	**5b**	**5c**
BuLi	13	31	45	15	35	50
BuLi/$TiCl_4$	61	16	0	79	21	0
BuLi/$MgBr_2$	69	18	0	79	21	0
BuLi/CuCN	19	62	0	23	77	0

The NMR pattern of **5a** and **5b** shows similar differences in the region of complexed arene hydrogens – the former has only two two-proton clusters of multiplets, while the four proton signals are clearly separated in the other. Accidental degeneracy reduced the AB quartet of the diastereotopic methylene protons adjacent to the carbonyl group to a broad doublet. The low-field region of the spectrum for **5c** very closely resembled the pattern obtained for **4c** except that the most downfield signal of a complexed aromatic proton was actually a little shielded compared to the corresponding signal for complex **4c**.

Addition of phenyllithium reagents led to the formation of similar products, but there were perceptible differences with respect to product NMR patterns as well as isomer distribution under different conditions (Scheme-6). Formation of 1,4-prducts was very much suppressed when PhLi was the sole reagent used. Similarly, no 1,2-product was isolated from reactions wherein Lewis acid or CuCN was used. Despite moderate diastereoselectivity, the ratio of the two isomeric 1,4-adducts was clearly reversed when Lewis acid was used, compared to the ratio obtained in cuprate reaction.

Scheme -6



1 6a 6b 6c

Table -3

Nucleophile	Products (% yield)			Isomer distribution (%)		
	6a	**6b**	**6c**	**6a**	**6b**	**6c**
PhLi	1	4	85	1	4	85
PhLi/$TiCl_4$	67	17	0	80	20	0
PhLi/$MgBr_2$	70	18	0	80	20	0
PhLi/CuCN	17	65	0	21	79	0

The two isomeric conjugate addition products, **6a** and **6b**, could not be separated by chromatography. Ratio of the isomers in the mixture was determined using the integration of methyl signals of complex aromatic ring. The singlets were not very well-separated, however, hence the values are not extremely accurate, but they are reliable to the extent of following the trend of selectivity reversal (cuprate *vis-à-vis* Lewis acid). The 1,2-adduct was obtained as a single isomer as evident from both its proton and carbon NMR spectra. The new stereogenic center has been tentatively assigned a configuration assuming *exo*-selective addition on the *anti*-conformer of the substrate, based on precedents.

In case of substrate **2**, the repulsive interaction between the non-bonding electron pair on oxygen in methoxy and the carbonyl group considerably destabilizes the syn conformation, and the *anti*-conformation is evidenced by low-field signal of the *peri* proton (6.2 ppm) on the complexed aromatic ring. The π-face of this substrate is thus more or less invariant, and a greater degree of diastereoselectivity was anticipated for this substrate. Addition of MeLi alone to substrate **2** resulted in the formation of a single diastereomer of the 1,2-adduct, no conjugate addition product was isolated in this case (Scheme-7, Table-4). While there was expected reversal of selectivity in going from cuprate to Lewis acid mediated addition, the ratio of diastereomer still remained within the range of 3:1.

Scheme -7

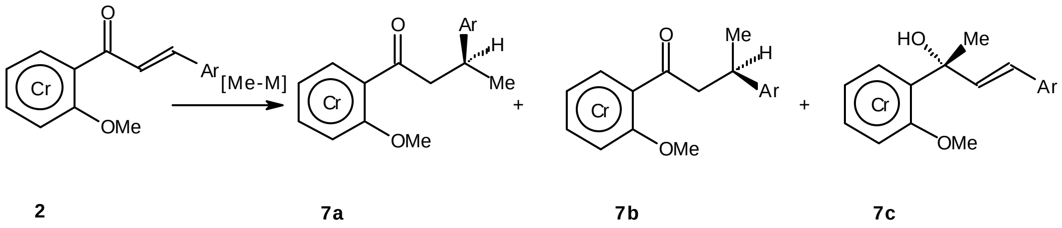


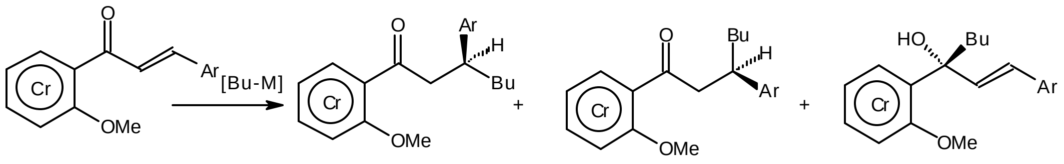
Table -4

Nucleophile	Products (% yield)			Isomer distribution (%)		
	7a	**7b**	**7c**	**7a**	**7b**	**7c**
MeLi	0	0	90	0	0	100
MeLi/$TiCl_4$	65	20	0	76	24	0
MeLi/$MgBr_2$	63	21	0	75	25	0
MeLi/CuCN	22	64	0	25	75	0

In the proton NMR spectrum of the 1,2-adduct, **7c**, the olefinic protons are less separated though the mid-point is still around 6.5 ppm as observed for analogues described above. The four aromatic protons of the complexed aromatic ring appear as well-separated signals in the spectral range of 4.5 to 6 ppm. For the isomeric 1,4-adducts, the doublet due to the *peri* proton of the complexed aromatic ring appears beyond 6.2 ppm, revealing the carbonyl group anisotropy effect in the *anti* conformation.

Reaction of **2** and BuLi as nucleophile yielded several unexpected results. Isomeric products were not separable under conditions of column chromatography, and isomer ratios were deduced from integration of peaks in the proton NMR spectra. In this case, the 1,2-adduct resulting from BuLi addition to complex **2** was obtained as a mixture of two isomers in the ratio of about 7:1. The major isomer is believed to have resulted from *exo*-addition to the *anti*-conformer of substrate **2**. Even more surprisingly, the selectivity of addition as well as yield suffered when BuLi was used as precursor for cuprate or in presence of Lewis acid, although the trend of stereoselectivity reversal was evident.

Scheme -8



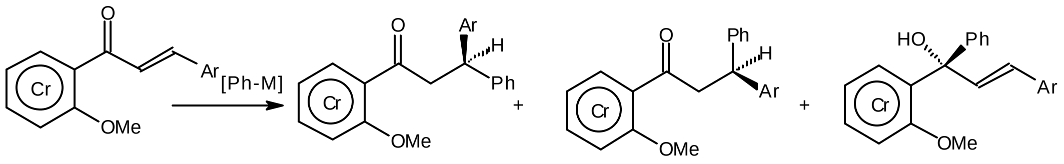
2 **8a** **8b** **8c**

Table -5

Nucleophile	Products (% yield)			Isomer distribution (%)		
	8a	**8b**	**8c**	**8a**	**8b**	**8c**
BuLi	0	0	87	0	0	100
BuLi/TiCl$_4$	51	26	0	66	34	0
BuLi/MgBr$_2$	49	24	0	67	33	0
BuLi/CuCN	17	62	0	21	79	0

Though addition of PhLi alone to substrate **2** afforded the 1,2-addition product with high stereoselectivity, no reaction occurred under standard condition with Lewis acids present in the reaction medium. As observed for BuLi, the cuprate addition provided a moderate stereoselectivity (Scheme-9).

Scheme -9



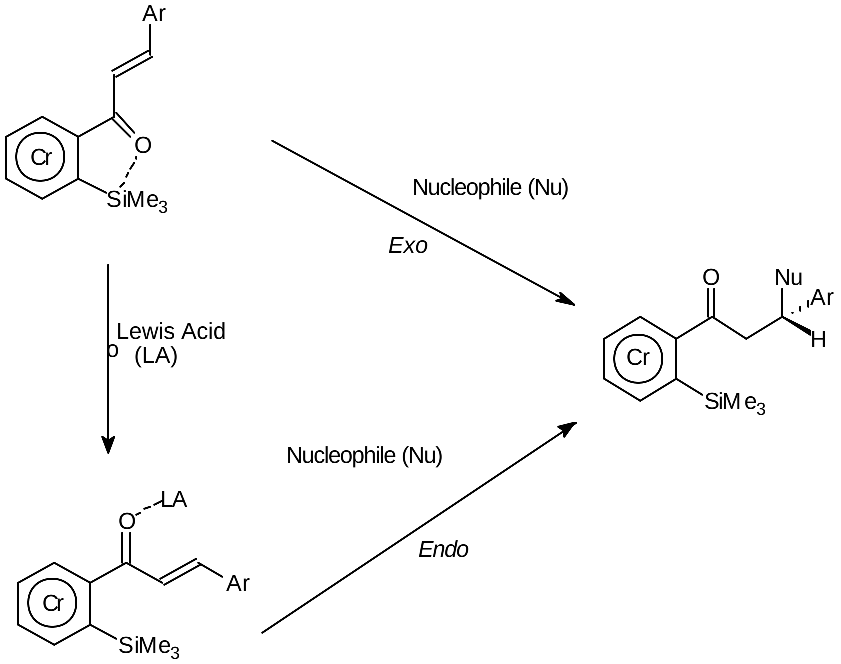
2 **9a** **9b** **9c**

Table -6

Nucleophile	Products (% yield)			Isomer distribution (%)		
	9a	**9b**	**9c**	**9a**	**9b**	**9c**
PhLi	0	0	84	0	0	100
PhLi/$TiCl_4$	-	-	-	-	-	-
PhLi/$MgBr_2$	-	-	-	-	-	-
PhLi/CuCN	16	62	0	20	80	0

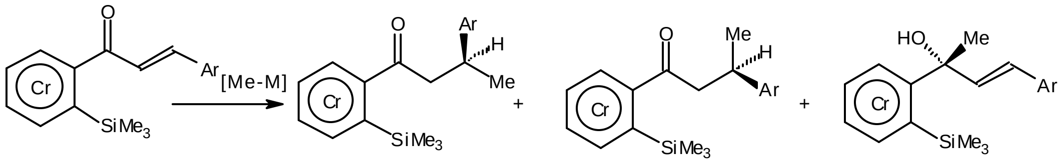
The substrate **3** has a trimethylsilyl substituent in *ortho*-position with respect to the ketone function. Owing to favourable Si-O interaction, *syn* conformer is the preferred[11] ground-state structure in this substrate. The *anti* conformer becomes dominant when Lewis acid complexes with the carbonyl group (Chart-4). For this substrate, however, the situation is somewhat exceptional. It needs to be appreciated that in absence of additives, *syn* conformer is likely to undergo *exo*-selective addition. In presence of Lewis acid, the *anti*-coformer is preferred, but the addition is likely to be *endo*-selective, thereby providing the same stereoisomer as before.

Chart-4



The yields of nucleophilic addition under different conditions are vastly improved in this case, and regioselectivity is excellent. For instance, in MeLi additions, no regioisomeric product mixture was obtained, though stereoselectivity was only moderate (Scheme-10, Table-7). The isomeric 1,4-adducts were separated by column chromatography.

Scheme –10



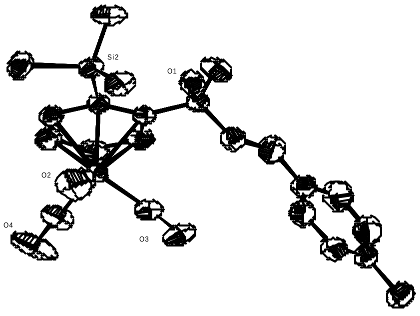
3 **10a** **10b** **10c**

Table-7

Nucleophile	Products (% yield)			Isomer distribution (%)		
	10a	**10b**	**10c**	**10a**	**10b**	**10c**
MeLi	0	0	86	0	0	100
MeLi/$TiCl_4$	61	25	0	71	29	0
MeLi/$MgBr_2$	58	25	0	70	30	0
MeLi/CuCN	22	67	0	24	76	0

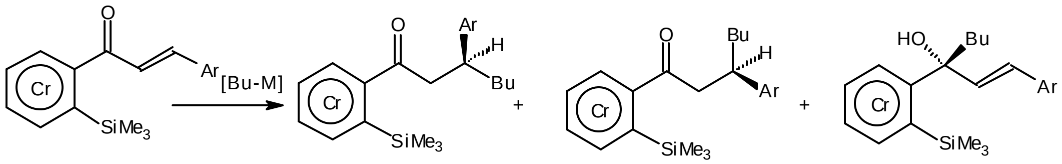
The reversal of stereoselectivity for cuprate *vis-à-vis* Lewis acid mediated addition is rather unexpected in this case for reasons explained above. Only perceptible difference in the proton NMR spectra of the isomeric 1,4-adducts concerns complexed aromatic ring protons. In the spectrum of **10a**, the ring proton peaks are almost overlapping around 5.5 ppm, while the peri proton doublet is relatively deshielded compared to others in the spectrum of **10b**. The 1,2-addition product, **10c**, has similar spectral feature as does **7c** or **4c**, and its relative stereochemistry was established by single-crystal structure determination, as depicted in Fig.-3.

Figure -3



The yields of BuLi reaction products are also quite good, though stereoselectivity is marginally improved than the MeLi addition described above. In this case also the reversal of stereoselectivity from cuprate to Lewis acid mediation is not anticipated. The regioselectivity is excellent, however (Scheme-11, Table-8).

Scheme -11



3 **11a** **11b** **11c**

Table -8

Nucleophile	Products (% yield)			Isomer distribution (%)		
	11a	**11b**	**11c**	**11a**	**11b**	**11c**
BuLi	0	0	88	0	0	100
BuLi/$TiCl_4$	61	18	0	77	23	0
BuLi/$MgBr_2$	64	19	0	77	23	0
BuLi/CuCN	18	68	0	21	79	0

The isomeric 1,4-adducts are not separable by chromatography, but their ratio could be determined from the integration of trimethylsilyl singlets at 0.21 and 0.31 ppm in the proton NMR spectra. The 1,2-adduct, **11c**, was obtained as a single diastereomer, and its stereochemistry is tentatively assigned identical to complex **10c** based on near identity of their proton NMR spectral pattern.

The 1,2-adduct obtained from PhLi addition to substrate **3** was a single diastereomer, whose relative stereochemistry is tentatively assigned by comparison with **10c** and **11c**. Only one and the same isomer of the 1,4-adduct was obtained for reaction mediated by Lewis acid or copper (I) in this case, as was originally anticipated.

Scheme -12

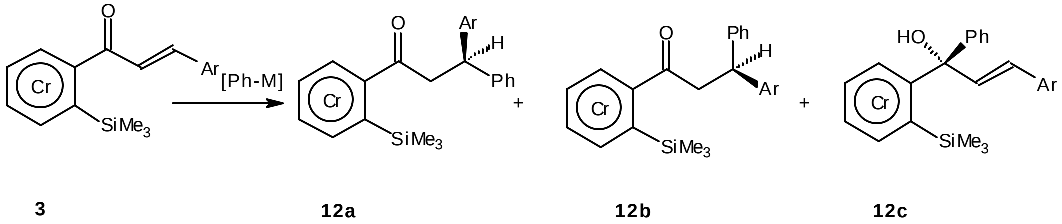


Table -9

Nucleophile	Products (% yield)			Isomer distribution (%)		
	12a	**12b**	**12c**	**12a**	**12b**	**12c**
PhLi	0	0	90	0	0	100
PhLi/$TiCl_4$	84	0	0	100	0	0
PhLi/$MgBr_2$	90	18	0	100	0	0
PhLi/CuCN	0	88	0	0	100	0

Crystal structure of the 1,4-adduct, **12a**, could not be determined since it was isolated as a liquid.

Summary

A series of chiral acyclic enone substrates were used to examine the stereoselectivity in addition of organolithium reagents in presence or absence of lewis acid. Except a few instances, diastereoselectivity was moderate. Interestingly, contrast to expectation, conjugate addition was observed with some organolithium reagents, the reason for which are not still understood.

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 freshly distilled over P_2O_5. Aromatic aldehydes were purchased from Aldrich, USA, and used as received. Organolithium and organomagnesium reagents were prepared following reported procedure.[12]

General procedure for the preparation of enones (1-3) : Following a reported procedure[10] all three enones were prepared from *ortho*-substituted acetophenone $Cr(CO)_3$ complex and *p*-tolualdehyde using Claisen-Schmidt condensation. In a typical procedure ethanolic KOH (10 mmol, 0.56 g in 20 mL ethanol) was added dropwise to a solution of *ortho*-substituted acetophenone-$Cr(CO)_3$ complex (10 mmol) and *p*-tolualdehyde (11 mmol) in ethanol (50 mL) at room temperature. Reaction was complete within 2.5 h (TLC). It was diluted with water, extracted with dichloromethane and dried over Na_2SO_4. Removal of solvent afforded red crystalline solid in all the cases pure product was obtained by crystallization from dichloromethane-pet ether. Enones **1, 2** and **3** have been reported earlier.[9]

Complex 1

Color :	Orange
MP :	129 °C
IR	1980, 1920, 1660 cm^{-1}
^{1}H NMR ($CDCl_3$) : (200 MHz)	2.40 (s, 3H), 2.41 (s, 3H), 5.10 (d, 1H, J = 6Hz), 5.20 (t, 1H, J = 7Hz), 5.65 (t, 1H, J = 6Hz), 5.935 (d, 1H, J = 6Hz), 7.16-7.27 (m, 3H), 7.55 (d, 2H, J = 8Hz), 7.80 (d, 1H, J = 16Hz).

Complex 2

Color :	Red
MP :	127 °C
IR	1980, 1920, 1660 cm^{-1}
^{1}H NMR ($CDCl_3$) : (200 MHz)	2.40 (s, 3H), 3.89 (s, 3H), 4.99 (t, 1H, J= 6 Hz), 5.07 (d, 1H, J = 8Hz), 5.82 (t, 1H, J= 6 Hz), 6.23 (d, 1H, J= 8Hz), 7.20 (d,

2H, J= 9Hz), 7.45 (d, 2H, J = 16 Hz), 7.21-7.28 (m, 3H), 7.49-7.55 (m, 2H), 7.79 (d, 1H, J= 16 Hz)

Complex 3

Color : Red

MP : 165 °C

IR 1989, 1925, 1663 cm^{-1}

^{1}H NMR ($CDCl_3$) : (200 MHz) 0.37 (s, 9H), 2.41 (s, 3H), 5.45 (t, 1H, J = 6 Hz), 5.55-5.62 (m, 2H), 5.765 (d, 1H, J = 6 Hz), 7.16 (d, 1H, J = 16 Hz), 7.25 (d, 2H, J = 8 Hz), 7.55 (d, 2H, J = 8 Hz), 7.87 (d, 1H, J = 16 Hz).

General procedure for the addition of organolithium reagents to enones (1-3): To a solution of the complexed enone **1-3** (*n* mmol) in THF (20*n* mL), organolithium (1.2*n* mmol) in diethyl ether or hexane was added dropwise with stirring at –90 °C. After completion of the reaction (TLC, 30 minutes), the reaction mixture was quenched with degassed methanol at –90 °C, followed by addition of water at room temperature, and finally extracted with dichloromethane. The crude mixture of products obtained after evaporation of solvent was separated by flash column chromatography (pet ether / EtOAc, 9:1).

Reactions were performed in 0.5-2.0 mmol scale. Isolated yield and product ratio are provided in the tables in the text.

Complex 4c

Color : Yellow

MP : 92 °C

IR ($CHCl_3$) : 3400-3600, 1967, 1892 cm^{-1}

^{1}H NMR ($CDCl_3$) : (200 MHz) 1.82 (s, 3H), 1.95 (s, 1H), 2.37 (s, 3H), 2.48 (s, 3H), 5-5.08 (m, 2H), 5.54 (t, 1H, J = 6.4 Hz), 5.83 (d, 1H, J = 6.4 Hz), 6.45 (d, 1H, J = 16 Hz), 6.69 (d, 1H, J = 16Hz,) 7.18 (d, 2H, J = 8 Hz), 7.37 (d, 2H, J = 8 Hz)

^{13}C NMR ($CDCl_3$) (50.3 MHz) 20.96, 21.36, 29.26, 74.33. 87.89, 93.74, 96.05, 110.43, 116.49, 126.89, 129.61, 129.94, 133.55, 138.32, 233.60

Analysis Calcd. C: 64.94, H: 5.15
($C_{21}H_{20}O_4Cr$) Found. C: 64.75, H: 5.23

Complex 5c

Color : Yellow
MP : Oil
IR (CHCl$_3$) : 3400-3600(br), 1963, 1880 cm$^{-1,}$
^{1}H NMR (CDCl$_3$) : 0.84 (t, 3H, J = 6.4 Hz), 1.30-1.51 (m, 4H), 1.95-2.08 (m, 3H), 2.38 (s, 3H) 2.55 (s, 3H), 4.98-5.06 (m, 2H), 5.52 (t, 1H, J = 8 Hz), 5.66 (d, 1H, J = 8 Hz), 6.45 (d, 1H, J= 16 Hz), 6.77 (d, 1H, J = 16 Hz), 7.20 (d, 2H, J = 8 Hz), 7.41 (d, 2H, J = 8Hz)
(200 MHz)
^{13}CNMR (CDCl$_3$) : 14.19, 21.43, 23.24, 26.91, 40.88, 76.83, 87.75, 93.70, 96.05, 96.86, 110.72, 116.82, 126.89, 129.65, 130.68, 132.26, 133.77,
138.18, 233.45
(50.3 MH$_Z$)
Analysis Calcd. C: 66.97, H: 6.04
($C_{24}H_{26}O_4Cr$) Found. C: 66.78, H: 5.99

Complex 6c

Color : Yellow
MP : 105 °C
IR (CHCl$_3$) : 3400-3600,1969, 1898 cm^{-1}
^{1}H NMR (CDCl$_3$) : 2.07 (s, 3H), 2.37 (s, 4H), 4.97 (d, 1H, J = 6 Hz), 5.09 (t, 1H, J = 6 Hz),5.61 (t, 1H, J = 6 Hz), 5.97 (d, 1H, J = 8Hz), 6.41(d, 1H,
J = 16 Hz), 6.63 (d, 1H, J = 16Hz), 7.18 (d, 2H, J = 8 Hz),
7.29-7.42 (m, 7H)
(200 MHz)

^{13}C NMR (CDCl$_3$) : (50.3 MH$_Z$)	20.30, 21.40, 78.30, 86.83, 93.48, 96.49, 98.52, 112.37, 117.89, 126.64, 127.00127.55, 128.44, 128.61, 131.30, 133.36, 138.40, 143.07, 232.02
Analysis (C$_{26}$H$_{22}$O$_4$Cr)	Calcd. C: 69.33, H: 4.88 Found. C: 69.45, H: 4.79

Complex 7c

Color :	Yellow
MP :	Oil
IR (CHCl$_3$) :	3400-3600, 1967, 1890cm^{-1}
^{1}H NMR (CDCl$_3$) : (200 MHz)	1.17 (s, 3H), 2.37 (s, 3H), 3.35 (s, 1H), 4.75 (m, 1H), 5.03 (d, 1H, J = 6Hz) 5.01 (m, 1H), 6.02 (d, 1H, J = 6Hz), 6.53 (d, 1H, J = 6 Hz), 6.63 (d, 1H, J = 6Hz), 7.17 (d, 2H, J = 6.5Hz), 7.34 (d, 2H, J = 6.5Hz)

^{13}C NMR (CDCl$_3$) : (50.3 MH$_Z$	20.95, 27.90, 55.76, 73.04, 73.30, 83.44, 94.85, 95.54, 106.60, 126.34, 127.33, 129.10, 133.62, 134.61, 137.33, 141.26, 233.01
Analysis (C$_{21}$H$_{20}$O$_5$Cr)	Calcd. C: 62.37, H: 4.72 Found. C: 62.43, H: 4.95

Complex 8c

Color :	Yellow
MP :	Oil
IR (CHCl$_3$) :	3400-3600(br), 1967, 1892 cm^{-1}
^{1}H NMR (CDCl$_3$) : (200 MHz	0.91 (t, 3H, J = 6.Hz), 1.16-1.48 (m, 4H), 1.83-2.20 (m, 2H), 2.36 (s, 3H), 2.63 (s, 1H), .3.80 (s, 3H), 4.82 (t, 1H, J = 6 Hz), 5.00 (d, 1H, J = 8Hz), 5.62 (t, 1H, J = 6Hz),

	6.17 (d, 1H, J =6Hz), 6.66 (bs, 2H, actually merging of two close doublet), 7.15 (d, 2H, J = 10Hz), 7.36 (d, 2H, J =1 0Hz) for minor isomer 2.32 (s, 3H), 3.85 (s, 3H)
^{13}C NMR (CDCl$_3$)(50.3 MH$_Z$	14.12, 21.21, 23.02, 25.92, 29.71, 40.00, 55.88, 73.63, 75.25, 83.67, 95.43 96.16, 106.93, 127.63, 129.32, 134.21, 135.09, 137.30, 141.41, 233.56 for minor isomer 22.72, 84.18, 129.10, 231.36
Analysis	Calcd. C: 64.57, H: 5.82
(C$_{24}$H$_{26}$O$_5$Cr)	Found. C: 64.45, H: 5.91

Complex 9c

Color :	Yellow
MP :	155 °C
IR (CHCl$_3$) :	1965, 1896 cm^{-1}
^{1}H NMR (CDCl$_3$) : (200 MHz)	2.37 (s, 3H), 3.77 (s, 3H), 3.97 (s, 1H), 4.86 (t, 1H, J = 6Hz), 4.99 (d, 1H, J = 8Hz), 5.30 (d, 1H, J = 6Hz), 5.61 (t, 1H, J = 6.5Hz) 6.468 (d, 1H, J = 16Hz), 6.85 (d, 1H, J = 16Hz), 7.17 (d, 2H, J = 8 Hz), 7.26-7.62 (m, 5H), 7.66 (d, 2H, J = 8Hz)
^{13}C NMR (CDCl$_3$) : (50.3 MH$_Z$)	21.43, 56.39, 73.15, 83.56, 94.95, 97.30, 107.45, 126.93, 127.74, 128.33, 129.58, 133.95, 138.03, 141.38, 142.96, 234.94
Analysis	Calcd. C: 66.95, H: 4.72
(C$_{26}$H$_{22}$O$_5$Cr)	Found. C: 67.08, H: 4.59

Complex 10c

Color :	Yellow
MP :	134 °C
IR (CHCl$_3$) :	3400-3600(br), 1965, 1892 cm^{-1}
^{1}H NMR (CDCl$_3$) : (200 MHz)	0.46 (s, 9H), 1.75 (s, 3H), 2.13 (s, 1H), 2.40 (s, 3H), 5 .03 (d, 1H, J = 8 Hz), 5.16 (t, 1H, J = 6 Hz), 5.57 (t, 1H, J = 6Hz), 5.76 (d, 1H, J = 8 Hz), 6.60 (d, 1H, J = 16Hz), 6.76 (d, 1H, J = 16 Hz), 7.21(d, 2H, J = 6 Hz), 7.41(d, 2H, J = 6Hz).
^{13}CNMR (CDCl$_3$)	3.53, 21.47, 31.32, 75.32, 89.84, 96.20, 96.71, 102.71,

(50.3 MH$_Z$)	127.00, 127.26, 129.76, 131.08, 133.11, 133.36, 138.58, 233.78
Analysis	Calcd. C: 61.88, H: 5.82
($C_{23}H_{26}O_4SiCr$)	Found. C: 61.91, H: 6.01

Complex 11c

Color :	Yellow
MP :	Oil
IR ($CHCl_3$) :	3415-3554(br), 1965, 1892 cm^{-1}
^{1}H NMR ($CDCl_3$) : (200 MHz)	0.42 (s, 9H), 0.91 (t, 3H, J = 6.8 Hz), 1.20-1.45 (m, 4H), 1.72-2.02 (m, 2H), 2.18 (s, 1H), 2.37 (s, 3H), 5.05 (d, 1H, J = 6Hz), 5.14 (t, 1H, J = 6.4 Hz), 5.58 (t, 1H, J = 6.4 Hz), 5.71 (d, 1H, J = 6.4 Hz), 6.38 (d, 1H J = 16 Hz), 6.67 (d, 1H, J = 16 Hz), 7.19 (d, 2H, J = 7.8 Hz), 7.38 (d, 2H, J = 7.8 Hz)
^{13}CNMR ($CDCl_3$) (50.3 MH$_Z$)	3.64, 14.12,20.95, 21.25, 21.40, 23.05, 26.65, 44.41, 89.95, 95.61, 97.05, 102.34, 127.26 129.72, 131.08,131.89, 133.80, 138.36, 233.56
Analysis	Calcd. C: 63.93, H: 6.55
($C_{26}H_{32}O_4SiCr$)	Found. C: 63.85, H: 6.59

Complex 12c

Color :	Yellow
MP :	145 °C
IR ($CHCl_3$) :	3400-3600, 1967, 1894 cm^{-1}
^{1}H NMR ($CDCl_3$) : (200 MHz)	-0.05 (s, 9H), 2.18 (s, 3H), 2.64 (s, 1H), 5.10-5.16 (m, 2H), 5.48 (t, 1H, J = 6.5 Hz) 5.61 (d, 1H, J = 6.4 Hz), 5.82 (d, 1H, J = 16 Hz), 6.5 (d, 1H, J = 16 Hz), 6.95-7.22 (m, 9H)
^{13}C NMR ($CDCl_3$) (50.3 MH$_Z$)	2.76, 21.47, 80.47, 90.58, 92.71, 95.32, 99.36, 102.82, 125.02, 127.08, 128.14, 129.69, 133.14, 133.91, 138.66, 144.13, 233.78
Analysis	Calcd. C: 66.14, H: 5.51
($C_{28}H_{28}O_4SiCr$)	Found. C: 65.98, H: 5.59

General procedure for the $TiCl_4$ mediated organolithium addition to enones (1-3) : To a solution of the complexed enone (*n* mmol) in dichloromethane (20*n* mL), titanium tetrachloride (2*n* mmol) was added dropwise with stirring at –78 °C. After stirring for 15 minutes, organolithium reagent (1.2*n* mmol) in THF or hexane was added dropwise with stirring at the same temperature. After completion of the reaction (TLC, 30 minutes), the reaction mixture was quenched with degassed methanol at –78 °C, followed by addition of water at room temperature, and finally extracted with dichloromethane. The crude mixture of products obtained after evaporation of solvent was separated by flash column chromatography (pet ether / EtOAc, 9:1).

All reactions were performed in 0.5-2.0 mmol scale. Isolated yield and ratio of products are provided in the tables.

General procedure for $MgBr_2$ mediated addition of organolithium to enone (1-3):

Dichloromethane (10*n* mL) was slowly introduced to a mixture of enone (*n* mmol) and $MgBr_2$ (3*n* mmol) with stirring at –78 °C. Color of the solution became durk purple. It was stirred for 15 min and then organolithium in ether or hexane (1.2*n* mmol) was added. After starting material was consumed completely (TLC, 15 minutes), the reaction mixture was quenched with degassed methanol (2 mL), and allowed to attain room temperature. Usual work up followed by removal of solvent afforded the crude product which was purified by flash column chromatography (pet ether / EtOAc, 9:1).

Reactions were performed in 0.5-2.0 mmol scale and isolated yields are indicated in Tables.

Complex 4a

Color :	Orange
MP :	68 °C
IR ($CHCl_3$) :	1975, 1903, 1687 cm^{-1}
^{1}H NMR ($CDCl_3$) : (200 MHz)	1.35 (d, 3H, J = 6.9H z), 2.34 (s, 3H), 2.37 (s, 3H), 3.42-3.53 (m, 1H), 32.96-3.05 (m, 2H), 5.01-5.11 (m, 2H), 5.56-5.70 (m, 2H), 7.10-7.18 (m, 4H)

^{13}C NMR (CDCl$_3$) : (50.3 MH$_Z$)	21.25, 21.84, 35.70, 48.75, 87.60, 92.08, 96.02, 96.20, 100.28, 110.57, 126.97, 129.54, 136.19,143.21,199.71, 231.58
Analysis	Calcd. C: 64.94, H: 5.15
(C$_{21}$H$_{20}$O$_4$Cr)	Found. C: 64.73, H: 4.97

Complex 5a (mixture)

Color :	Orange
MP :	Oil
IR (CHCl$_3$) :	1971, 1901 1639 cm^{-1}
^{1}H NMR (CDCl$_3$) : (200 MHz)	0.85 (t, 3H, J = 6Hz), 1.11-1.37 (m, 4H), 1.65-1.76 (m, 2H), 2.35 (bs, 6H), 3.03-3.10 (m, 2H), 3.18-3.35 (m, 1H), 4.95-5.12 (m, 2H), 7.14 (bs, 4H) signals separated for minor somer 2.21 (s, 3H), 5.855 (d, 1H, J = 6Hz)), 7.11 (bs, 4H).
^{13}C NMR (CDCl$_3$) : (50.3 MH$_Z$)	14.12, 21.18, 22.76, 29.85, 35.95, 41.47, 47.90, 87.49, 91.97, 95.98, 100.72, 110.39, 125.68, 127.63, 129.25, 129.47, 131.05, 131.93, 135.83, 136.12, 141.85, 199.97, 231.62. signals separated for minor isomer 14.30, 20.96, 36.47, 67.49, 91.61, 101.02, 110.61, 19.71, 231.40.
Analysis	Calcd. C: 66.97, H: 6.04
(C$_{24}$H$_{26}$O$_4$Cr)	Found. C: 66.95, H: 5.94

Complex 5a (pure)

Color :	Orange
MP :	Oil
IR (CHCl$_3$) :	1970, 1895 cm^{-1}

^{1}H NMR (CDCl$_3$) : (200 MHz)	0.85 (t, 3H, J= 6Hz), 1.11-1.37 (m, 4H), 1.62-1.80 (m, 2H), 2.32 (bs, 6H), 3.20-3.34 (m, 1H), 4.99-5.08 (m, 2H), 5.5-5.62 (m, 2H), 7.13 (bs, 4H).

Complex 6a

Color :	Orange
MP :	72-76 °C
IR (CHCl$_3$) :	1979, 1909, 1682 (1732for minor isomer) cm^{-1}
^{1}H NMR (CDCl$_3$) : (200 MHz)	2.23 (s, 3H), 2.31 (s, 3H), 3.48-3.51 (m, 2H), 4.73 (t, 1H, J= 6.5Hz), 4.98-5.20 (m, 2H), 5.63 (t, 1H, J= 6.5Hz), 4.9-5.15 (m, 2H), 5.63 (t, 1H, J= 6.5Hz), 5.79 (d, 1H, J= 6.5Hz), 7.14-7.32 (m, 9H)
^{1}H NMR (C$_6$D$_6$) :	2.01 (s, 3H), 2.13 (s, 3H), 3.15 (dd, 1H, J = 16 Hz, 9 Hz), 3.55 (dd, 1H, J = 16 Hz, 9 Hz), 4.01 (d, 1H, J = 6 Hz), 4.11 (t, 1H, J = 6 Hz), 4.67 (t, 1H, J = 6Hz), 4.87 (t, 1H, J = 6 Hz), 5.02 (d, 1H, J = 8 Hz) 6.98-7.42 (m, 9H) for minor isomer 2.02 (s,3H)
^{13}C NMR (CDCl$_3$) : (50.3 MH$_Z$)	21.03, 45.88, 46.36, 87.08, 91.72, 96.16, 96.27, 100.35, 110.79, 126.67, 127.85, 127.96, 128.84, 129.58, 136.63, 140.27, 141.23, 143.54, 144.46, 198.57, 231.47
Analysis (C$_{26}$H$_{22}$O$_4$Cr)	Calcd. C: 69.33, H: 4.88 Found. C: 69.49, H: 4.99

Complex 7a

Color :	Orange
MP :	108 °C
IR (CHCl$_3$) :	1978, 1907, 1672 cm^{-1}
^{1}H NMR (CDCl$_3$) : (200 MHz)	1.30 (d, 3H, J=6Hz), 2.34 (s, 3H), 3.14-3.20 (m, 2H), 3.43-3.54 (m, 1H) 3.82 (s, 3H), 4.94 (t, 1H, J=6Hz), 5.01 (d, 1H,

J=8Hz), 5.80 (t, 1H, J=6Hz) 6.25 (d, 1H, J=6.5Hz) 7.13 (d, 2H J=8Hz), 7.19 (d, 2H, J=8Hz)

^{13}C NMR (CDCl$_3$) (50.3 MH$_Z$) 21.18, 22.50, 35.48, 51.24, 56.13, 72.42, 84.22, 90.72, 95.50, 96.02, 126.93, 129.39, 135.86, 143.51, 144.28, 196.85, 231.33

Analysis Calcd. C: 62.37, H: 4.95
(C$_{21}$H$_{20}$O$_4$Cr) Found. C: 62.30, H: 4.81

Compex 8a

Color : Yellow

MP : 53 °C

IR (CHCl$_3$) : 1979, 1909, 1670 cm^{-1}

^{1}H NMR (CDCl$_3$) : (200 MHz) 0.73-1.00 (m, 3H), 1.06-1.44 (m, 4H), 1.53-1.80 (m, 2H), 2.32 (s, 3H) 3.05-3.37 (m, 3H), 3.86 (s, 3H), 4.83-5.95 (m, 1H), 5.00 (d, 1H, J = 8 Hz), 5.74 -5.86 (m, 1H), 6.10 (d, 1H, J = 6.4 Hz), 7.13 (bs, 4H),

for minor isomers

2.34 (s, 3H), 3.81 (s, 3H), 6.22(d, 1H, J=6.4Hz)

^{13}C NMR (CDCl$_3$) (50.3 MH$_Z$) 14.16, 21.18, 22.83, 29.85, 35.92, 36.43, 41.14, 50.18, 56.06,72.42 84.14, 90.80, 95.54, 96.02, 127.55, 129.21, 135.71, 141.78, 144.24, 196.73, 231.32

for minor isomer 23.13, 29.52, 40.81, 50.40, 72.56, 84.33, 95.76, 127.74, 142.40, 144.54, 196.38.231.00

Analysis Calcd. C: 64.57, H: 5.82
(C$_{24}$H$_{26}$O$_5$Cr) Found. C: 64.65, H: 5.81

Complex10a

Color : Orange

MP : Oil

IR (CHCl$_3$) : 1975, 1901, 1673 cm^{-1}

^{1}H NMR (CDCl$_3$) : (200 MHz) 0.34 (s, 9H), 1.36 (d, 3H, J = 6.9 Hz) 2.34 (s, 3H), 2.94-3.03 (m, 2H), 3.39-3.53 (m, 1H), 5.32-5.57 (m, 4H), 7.16 (bs, 4H)

^{13}CNMR **(CDCl$_3$)**(50.3 MH$_Z$)	0.85, 21.18, 21.73, 35.22, 47.09, 92.78, 93.19, 99.43, 101.38, 104.76, 126.97, 129.54, 136.23, 143.40, 200.37, 232.02
Analysis	Calcd. C: 61.88, H: 5.82
($C_{23}H_{26}O_4SiCr$)	Found. C: 61.70, H: 6.01

Complex11a

Color :	Orange
MP :	Oil
IR (CHCl$_3$) :	1975, 1901, 1673, 1675 cm^{-1}
^{1}H NMR (CDCl$_3$) : (200 MHz)	0.21 (s, 9H), 0.84 (t, 3H, J = 6.3Hz), 1.07-1.36 (m, 4H), 1.48-1.78 (m, 2H), 2.31 (s, 3H), 2.97-3.04 (m, 2H), 3.15-3.34 (m, 1H), 5.37-5.52 and 5.72-5.75 (m, 4H), 7.12 (bs, 4H) signal separated for minor isomer 0.31 (s, 9H)
^{13}CNMR (CDCl$_3$) : (50.3 MH$_Z$)	0.78, 14.12, 21.21, 22.83, 29.83, 36.32, 41.28, 45.70, 92.12, 92.93, 93.08 93.52, 98.66, 104.84, 127.74, 129.47, 136.16, 141.19, 200.15, 231.69 signals separated for minor isomer 35.81, 46.32, 99.18, 105.43, 141.82, 200.67, 232.06
Analysis	Calcd. C: 63.93, H: 6.55
($C_{26}H_{32}O_4SiCr$)	Found. C: 63.91, H: 6.51

Complex12a

Color :	Orange
MP :	Oil
IR (CHCl3) :	1976, 1909, 1689 cm^{-1}
^{1}H NMR (CDCl$_3$) :	0.22 (s, 9H), 2.33 (s, 3H), 3.52 (d, 2H, J = 8Hz), 4.76 (t, 1H, J=7.3Hz), 5.43-5.63 (m, 3H), 5.64 (d, 1H, J = 6Hz) 7.13-7.35 (m, 9H)
^{1}H NMR (C$_6$D$_6$):	0.30 (s, 9H), 2.15 (s, 3H), 3.05 (dd, 1H, J = 17.6Hz, 8.3Hz,), 3.44 (dd, 1H, J = 17.6Hz, 8.3Hz,), 4.51-4.63 (m, 2H), 4.77-4.84 (m, 2H), 5.03 (d, 1H, J = 6.4Hz), 6.97-7.37 (m, 9H)

^{13}CNMR ($CDCl_3$) : (50.3 MH$_Z$)	0.63, 21.18, 44.78, 45.95, 91.97, 93.59, 93.70, 98.37, 102.41, 104.99, 126.75, 127.92, 128.07, 128.91, 129.58, 136.38, 140.35, 144.46, 199.34, 231.80
Analysis	Calcd. C: 66.14, H: 5.51
($C_{28}H_{28}O_4SiCr$)	Found. C: 66.28, H: 5.69

General procedure for the addition of organocuprate to enone (1-3)*:* To a slurry of CuCN (*n* mmol) in diethyl ether (*n* mL), organolithium reagent (2*n* mmol) in hexane or ether was added dropwise with stirring at –78 °C. It was slowly warmed to –20 °C, during which time all of CuCN was dissolved. The solution was again cooled to –78 °C, followed by addition of complexed enone (0.75*n* mmol) in toluene (10*n* mL). After completion of the reaction (TLC, 0.75-1.0 h) the reaction mixture was allowed to attain room temperature, quenched with 10% ammonia in saturated aqueous ammonium chloride solution, followed by stirring for 0.5 h, and finally extracted with ether. The residue obtained after evaporation of solvent was purified by flash column chromatography (pet ether / EtOAc, 9:1).

Reactions were performed in 0.5-2.0 mmol scale and isolated yields are indicated in Tables

Complex 4b

Color :	Yellow
MP :	118 °C
IR ($CHCl_3$) :	1979, 1907,1681 cm^{-1}
^{1}H NMR ($CDCl_3$) : (200 MHz)	1.33 (d, 3H, J= 6.9Hz), 2.25 (s, 3H), 2.32 (s, 3H), 2.98 (dd, 1H, J = 16.6 Hz, 7.3 Hz), 3.11 (dd, 1H, J = 16.6 Hz, 7.3 Hz), 3.41-3.51 (m, 1H), 4.99 (d, 1H, J = 6.3Hz), 5.07 (t, 1H, J = 6.3 Hz), 5.61 (t, 1H, J = 6.3Hz), 5.86 (d, 1H, J= 6Hz), 7.15 (bs, 4H).
^{13}C NMR ($CDCl_3$) (50.3 MH$_Z$)	21.03, 22.04, 35.66, 48.78, 87.16, 91.90, 95.91, 101.13, 110.57, 126.97, 129.54,136.19,142.88, 199.64, 231.43
Analysis	Calcd. C: 64.94, H: 5.15
($C_{21}H_{20}O_4Cr$)	Found. C: 64.99, H: 5.05

Complex 5b

Color : Orange

MP : Oil

IR (CHCl$_3$) : 1969, 1903, 1645 cm^{-1}

^{1}H NMR (CDCl$_3$) : 0.85 (t, 3H, J = 6Hz), 1.05-1.37 (m, 4H), 1.55-1.74 (m, 2H), 2.19 (s, 3H), 2.32 (s, 3H), 2.95-3.07 (m, 2H), 2.19 (s, 3H), 2.32 (s, 3H), 3.17-3.30 (m, 1H), 4.94-5.12 (m, 2H), 5.54-5.61 (m, 1H), 5.83 (d, 1H, J= 6Hz), 7.13 (bs, 4H).
(200 MHz)

signals separated for minor isomer 7.14 (bs, 4H).

^{13}C NMR (CDCl$_3$) : 14.12, 21.18, 22.79, 29.85, 36.25, 41.25, 47.53, 87.01, 91.64, 96.02, 100.76, 101.09, 110.65, 127.59, 129.36, 141.08, 199.71, 231.40
(50.3 MH$_Z$)

signal separated for minor isomer

35.95, 41.47, 47.90, 87.53, 92.01, 110.43, 141.67, 199.97, 231.66

Analysis Calcd. C: 66.97, H: 6.04
($C_{24}H_{26}O_4Cr$) Found. C: 66.93, H: 5.92

Complex 5b
(pure)

Color : Orange

MP : Oil

IR (CHCl$_3$) : 1968, 1898 cm^{-1}

^{1}H NMR (CDCl$_3$) : 0.85 (t, 3H, J = 6 Hz), 1.08-1.42 (m, 4H), 1.57-1.75 (m, 2H), 2.19 (s, 3H), 2.32 (9s, 3H), 2.95-3.15 (m, 2H), 3.16-3.34 (m, 1H), 4.95 (d, 1H, J = 6 Hz), 5.05 (t, 1H, J= 6 Hz), 5.55 (t, 1H, J = 6 Hz), 5.80 (d, 1H, J = 6 Hz), 7.14 (bs, 4H).
(200 MHz)

Complex 6b

Color : Yellow

MP : 138-140 °C

IR ($CHCl_3$) : 1979, 1905, 1732 (1682 for minor isomer) cm^{-1}

^{1}H NMR ($CDCl_3$) : (200 MHz) 2.24 (s, 3H), 2.31 (s, 3H) 3.35-3.15 (m, 2H), 4.73 (t, 1H, J = 6 Hz), 4.95-5.15 (m, 2H), 5.62 (t, 1H, J = 6 Hz), 5.78 (d, 1H, J = 6Hz), 7.05-7.45 (m, 9H)

^{1}H NMR (C_6D_6) : 2.02 (s, 3H), 2.14 (s, 3H), 3.09 (dd, 1H, J = 16 Hz, 6 Hz), 3.55 (dd, 1H, J = 16 Hz, 8 Hz), 4.01 (d, 1H, J=6 Hz) 4.11 (t, 1H, J=6Hz), 4.67 (t, 1H, J=6Hz), 4.88 (t ,1H, J=6Hz), 5.00 (d, 1H, J=8Hz), 6.95-7.43 (m, 9H)

for minor isomer 2.01 (s, 3H)

^{13}C NMR ($CDCl_3$) : (50.3 MHz) 21.03, 46.95, 46.43, 87.05, 91.72, 96.09, 100.46, 110.76, 126.71, 128.00, 129.54, 136.30, 140.27, 144.24, 146.01, 198.64, 231.47

Analysis ($C_{26}H_{22}O_4Cr$) Calcd. C: 69.33, H: 4.88

Found. C: 69.51, H: 4. 92

Complex 7b

Color : Yellow

MP : 105 °C

IR ($CHCl_3$) : 1978, 1907, 1674 cm^{-1}

^{1}H NMR ($CDCl_3$) : (200 MHz) 1.31(d, 3H, J = 6 Hz), 2.32 (s, 3H), 3.08 (dd, 1H, J = 16.6 Hz, 6.8 Hz), 3.30 (dd, 1H, J = 16.6 Hz, 6.8 Hz), 3.38-3.51 (m, 1H), 3.86 (s, 3H), 4.89 (t, 1H, J = 6 Hz) 5.00 (d, 1H, J = 6 Hz), 5.78

(t, 1H J = 6Hz), 6.14 (d, 1H, J = 6 Hz), 7.15 (bs, 4H)

^{13}C NMR ($CDCl_3$) (50.3 MHz) 21.21, 21.80, 35.15, 51.43, 56.13, 72.53, 84.40, 90.91, 95.69, 127.11, 129.43, 135.86, 144.13, 144.68, 196.81, 231.51

Analysis ($C_{21}H_{20}O_4Cr$) Calcd. C: 62.37, H: 4.95

Found. C: 62.41, H: 4.83

Compound 8b

Color : Yellow

MP :	112 °C
IR (CHCl$_3$) :	1977, 1905, 1674 cm^{-1}
^{1}H NMR (CDCl$_3$): (200 MHz)	0.84 (t, 3H, J= 6.3Hz), 1.09-1.40 (m, 4H), 1.54-1.74 (m, 2H), 2.34 (s, 3H), 3.05-3.38 (m, 3H), 3.81 (s, 3H), 4.83-5.02 (m, 2H), 5.79 (t, 1H, J = 6Hz), 6.22 (d, 1H, J = 6.4HZ), 7.14(bs, 4H) for minor isomers 2.32 (s,3H), 3.86 (s, 3H), 6.10 (d, 1H, J = 6.3Hz)
^{13}CNMR (CDCl$_3$)(50.3 MH$_Z$	14.16, 21.25, 22.83, 29.89, 35.95, 40.84, 50.51, 56.06, 72.49, 84.29, 91.02, 95.65, 96.02, 127.81, 129.25, 135.71, 142.48, 144.54, 196.99,231.54 for minor isomer 36.43, 41.21, 50.29, 127.63, 213.29
Analysis (C$_{24}$H$_{26}$O$_5$Cr)	Calcd. C: 64.57, H: 5.82 Found. C: 64.75, H: 5.61

Compound 9b

Color :	Orange
MP :	136-140 °C
IR (CHCl$_3$):	1977, 1902, 1674 cm^{-1}
^{1}H NMR (CDCl$_3$): (200 MHz)	2.32 (s, 3H), 3.58 (dd, 1H J = 18 Hz, 6 Hz), 3.82 (dd, 1H, J = 18 Hz, 6Hz), 3.82 (s, 3H), 4.77 (t, 1H, J = 6Hz, 4.89 (t, 1H, J = 6Hz), 5.01 (t, 1H, J = 6Hz), 5.80 (t, 1H, J = 6.5Hz), 6.17 (d, 1H, J = 6Hz), 7.09-7.32 (m, 9H)
^{1}H NMR (C$_6$D$_6$) :	2.31 (s, 3H), 2.97 (s, 3H), 3.76 (dd, 1H, J = 18 Hz, 6 Hz), 3.97-4.09 (m, 2H), 4.45 (dd, 1H, J = 18 Hz, 8Hz), 4.96 (t, 1H, J= 6.5Hz), 5.20-5.27 (m, 1H), 6.14 (d, 1H, J= 6.Hz), 7.17-7.72 (m, 9H) for minor isomer 2.35 (s, 3H), 2.96 (s, 3H)
^{13}C NMR (CDCl$_3$) : (50.3 MH$_Z$)	21.18, 45.70, 49.15, 56.17, 72.38, 84.22, 90.21, 95.72, 96.02, 126.45, 127.96, 128.66, 129.43, 135.97, 141.82, 144.10, 144.50, 195.63, 231.32
Analysis (C$_{26}$H$_{22}$O$_5$Cr)	Calcd. C: 66.95, H: 4.72 Found. C: 66.73, H: 4.89

Complex 10b

Color : Orange

MP : Oil

IR ($CHCl_3$) : 1977, 1902, 1681 cm^{-1}

^{1}H NMR ($CDCl_3$) : (200 MHz) 0.26 (s, 9H), 1.34(d, 3H, J= 6.8Hz), 2.33 (s, 3H), 2.95-3.03 (m, 2H), 3.40-3.51(m, 1H), 5.40-5.54 (m, 3H), 5.62 (bd, 1H), 7.15 (bs, 4H)

^{13}CNMR ($CDCl_3$) (50.3 MH$_Z$) 0.78, 21.18, 22.17, 35.44, 46.61, 92.60, 93.26, 99.07, 101.93, 104.73, 126.97, 129.50, 136.16, 142.88, 200.23, 231.80

Analysis ($C_{23}H_{26}O_4SiCr$)
Calcd. C: 61.88, H: 5.82
Found. C: 61. 76, H: 5.97

Complex 11b

Color : Orange

MP : Oil

IR ($CHCl_3$) : 1967, 1892 , 1673, 1675 cm^{-1}

^{1}H NMR ($CDCl_3$) : (200 MHz) 0.31 (s, 9H), 0.84 (t, 3H, J = 6Hz), 1.04-1.39 (m, 4H), 1.51-1.79, (m, 2H), 2.32 (s, 3H), 3.02 (t, 2H, J = 6Hz), 3.21-3.31 (m, 1H), 5.37-5.52 (m, 4H), 7.12 (bs, 4H)

signals separated for minor isomer 0.21 (s, 9H
), 2.31 (s, 3H), 5.75 (d, 1H, J = 6Hz).

^{13}CNMR ($CDCl_3$) (50.3 MH$_Z$) 0.78, 14.08, 21.21, 22.79, 29.85, 35.81, 41.21, 26.28, 92.12, 92.89, 93.08, 93.33, 93.84, 99.18, 101.81, 105.43, 127.70, 129.50, 136.16, 141.82, 200.67, 232.02

signals separated for minor isomer
36.29, 45.70, 98.63, 102.23, 104.84, 141.19, 200.15, 231.69.

Analysis ($C_{26}H_{32}O_4SiCr$)
Calcd. C: 63.93, H: 6.55
Found. C: 64.15, H: 5.6.49

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Chapter - II

ScandiumTriflate Catalyzed Diasteroselective Addition of Silyl Enol Ethers and Silyl Ketene Acetals to Imines Anchored on Arene Tricarbonylchromium

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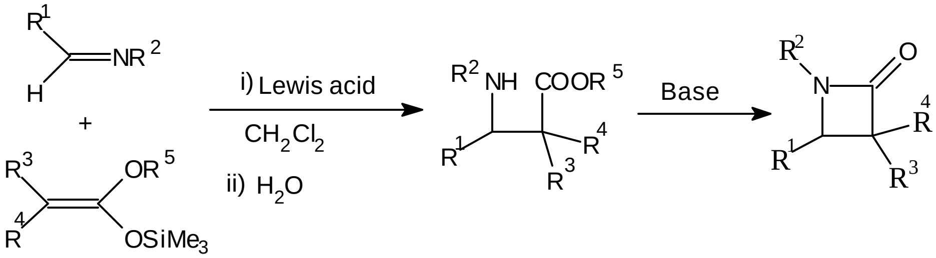
Introduction

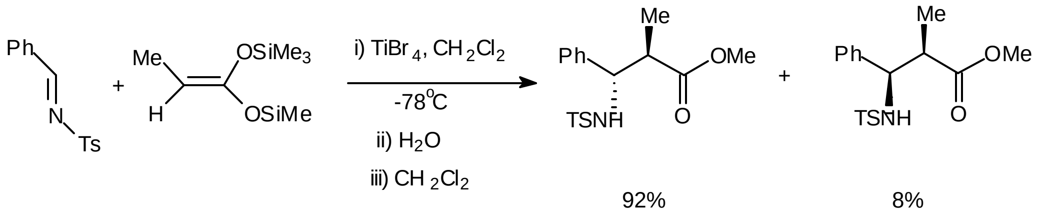
Imines are important intermediates for the synthesis of nitrogen containing compounds,[1a] such as alkaloids, amino acids, β-lactams, amino sugars and terpenes. They are easily prepared from carbonyl compounds like aldehydes or ketones by treatment with primary amine. A dehydrating agent is used to eliminate a water molecule to produce the C=N double bond.[1f] Imines have lower reactivity than corresponding carbonyl compounds; therefore Lewis acid activation usually facilitates addition of nucleophiles. Addition of enolates of carbonyl compounds or carboxylic esters to imines afford a valuable synthon like a β-amino carbonyl compound.[2] Although ester enolates do add to imines, a more convenient and common practice is to use Lewis acid mediated addtion of silyl ketene acetal to imines[3,4] (Scheme-1).

Scheme -1



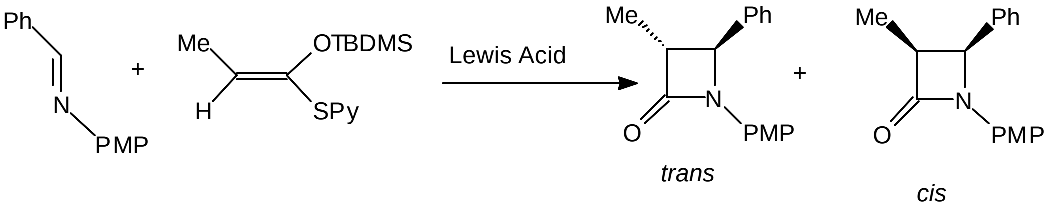
Largely stimulated by research on β-lactam antibiotics, several investigations focus on stereochemical issues pertaining to imine condensation, especially those concerning diastereoselectivity induced by a chiral auxiliary. It is believed that Lewis acid mediated addition proceeds through an organized transition state, where the Lewis acidic metal center is bound to both the reacting partners through oxygen and nitrogen atoms. The sterics of the substituents and configuration of stereogenic centers present in one or both of these molecules determine the energy of the transition state. Therefore, often a pronounced *threo* or *erythro* selectivity is manifested in the product composition. For example, Shimada reported[5] that N-tosylaldimines react with a silyl ketene acetal in presence of $TiBr_4$ to produce the *trans*-β-amino esters exclusively (Scheme-2).

Scheme -2



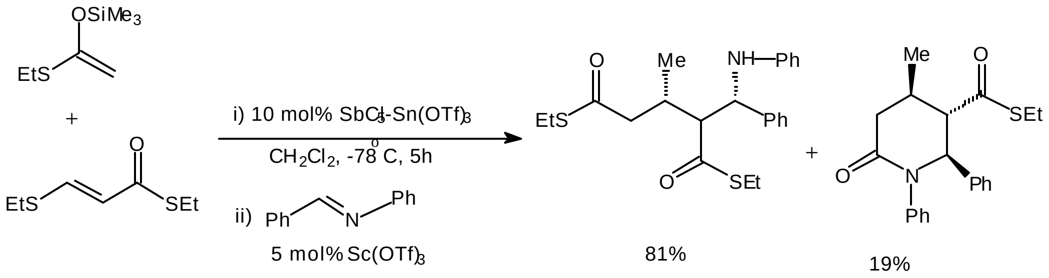
Annunziata and co-workers[6] synthesized β-lactams in one–pot procedure by the reaction of 2-pyridyl thioketene acetals with aldimines in presence of Lewis acid like $TiCl_4$, $BF_3.OEt_2$, TBDMSOTf, $EtAlCl_2$, or $Yb(OTf)_3$ (Scheme-3). They achieved high *trans*-selectivity (*trans: cis* 98:2 to 78:12 , depending on Lewis acid).

Scheme -3



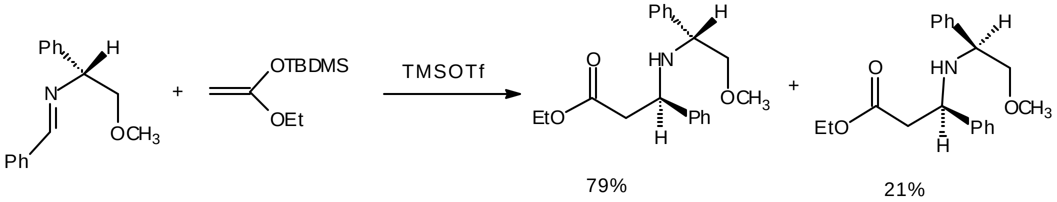
Kobayashi has shown[7] that three-component (or four- component) coupling reactions of silyl thioketene acetal, α, β-unsaturated thioesters and imines (or amines and aldehydes) proceed smoothly in presence of Lewis acid catalyst to produce δ-amino ester and δ-lactam with complete diastereoselectivity (Scheme-4).

Scheme -4



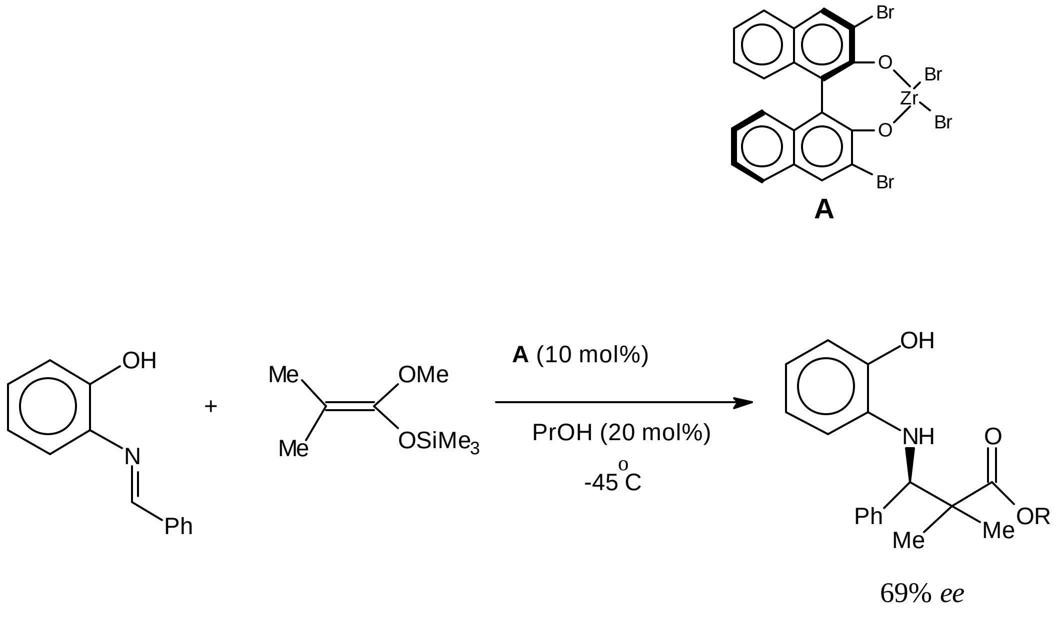
Presence of a stereogenic center in one partner, such as imine in the following example, can influence the dominant configuration of the new stereogenic center, as shown by Higashiyama and co-workers[8] during diastereoselective addition of silylketene acetals in presence Lewis acid like $TiCl_4$, BF_3.OEt, TMSOTf, or $SnCl_4$ (Scheme-5).

Scheme -5



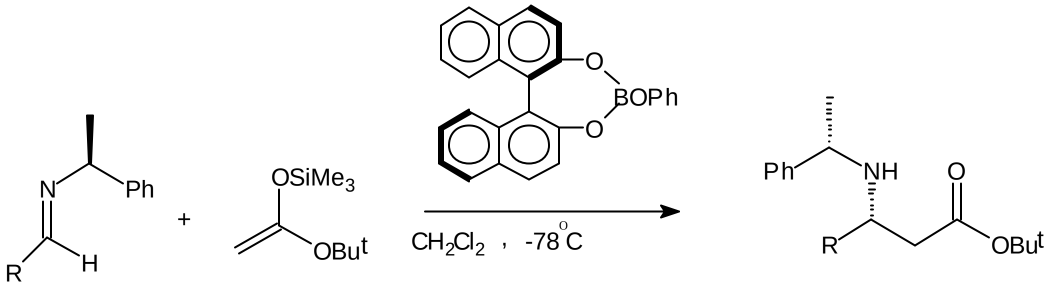
In the following two examples, optically active, Lewis acid catalysts have been used to effect steeoselectivity in the addition reaction. Kobayashi recently reported[9] the use of a chiral zirconium catalyst for enantioselective addition of silyl ketene acetal to imine where none of the reactants was chiral (Scheme-6).

Scheme -6



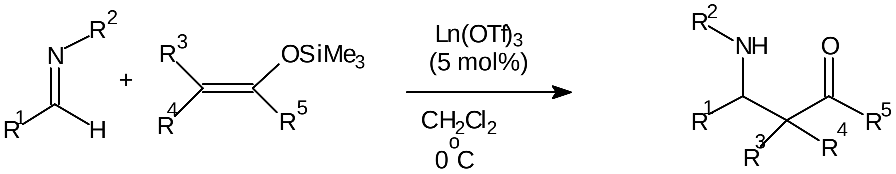
Based on the fact that BF_3.OEt_2 is also an effective Lewis acid for such addition, Yamamoto and others[10] developed BINOP-based chiral boron reagents for asymmetric aldol type addition to chiral imine (Scheme-7). The high selectivity could be a result of double stereodiferentiation in this instance.

Scheme -7



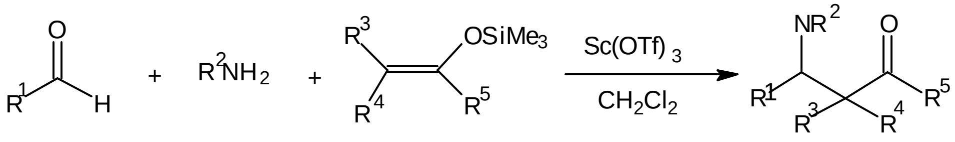
In 1993, Kobayashi introduced[11] scandium trifluoromethanesulfonate (or triflate) [Sc(OTf)$_3$] as a promising Lewis acid catalyst for various types of carbon-carbon bond formation reaction under mild condition. The range of reactions includes aldol type addition of silyl ketene acetals or silylenol ethers to imine (Scheme-8).[11]

Scheme-8



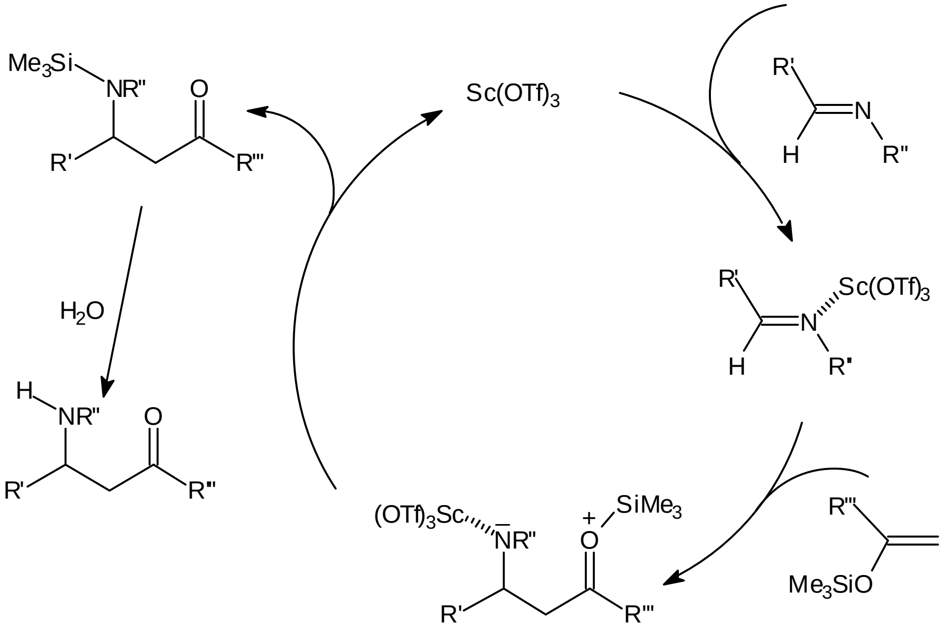
Aldol type reactions with imine were initially carried out in presence of stoichiometric amount of classical Lewis acid such as $TiCl_4$[3], $BF_3.OEt_2$[12] etc. In order to accommodate acid sensitive functional groups in the substrates milder catalysts were developed later. Among such catalysts are TMSOTf, $Sn(OTf)_2$, Me_3SiI, and $SnCl_4$.[12] Although these are milder, yet the difficulties associated with such Lewis acids, *viz.* moisture-sensitivity, hazardous nature and disposal problems continue to be a cause of concern. Kobayashi's triflate catalysts are free of many of these discouraging attributes. Kobayashi[13] used either ytterbium triflate or scandium triflate to catalyze a three-component reaction comprising of an aldehyde, an imine and a silyl ketene acetal to afford of β-amino ester in good yield (Scheme-9).

Scheme - 9



Scandium triflate catalyzed addition of silyl ketene acetal and silyl enol ether is believed to proceed through the same catalytic cycle (Figure-1) as suggested in Mukaiyama aldol reaction.

Figure -1

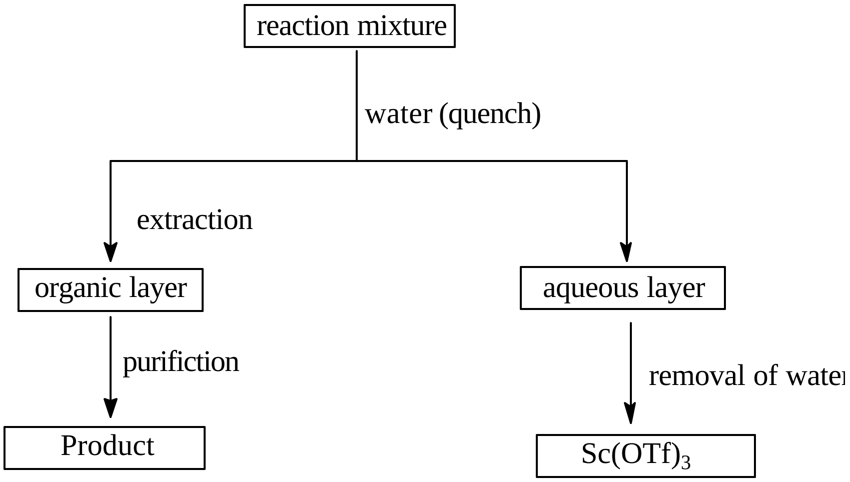


Of all rare earth triflates, $Sc(OTf)_3$ has drawn special attention because of its reactivity is in between aluminium and lanthanum. It can be prepared very easily from Sc_2O_3 and an aqueous solution of triflic acid (eq-1).

Equation 1 $Sc_2O_3 + 6TfOH \rightarrow 2Sc(OTf)_3 + 3H_2O$

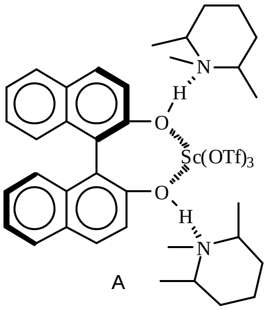
A significant advantage of using scandium triflate is that it is not only water-tolerant, but also more soluble in water than in organic solvent such as dichloromethane. This property permits this catalyst to be recovered from the aqueous layer after the rection is completed (Scheme-10).

Scheme -10



Chiral scandium triflate has also been used for asymmetric reaction. A recent example is the BINOL based scandium triflate **A** (Figure-2).[14]

Figure -2

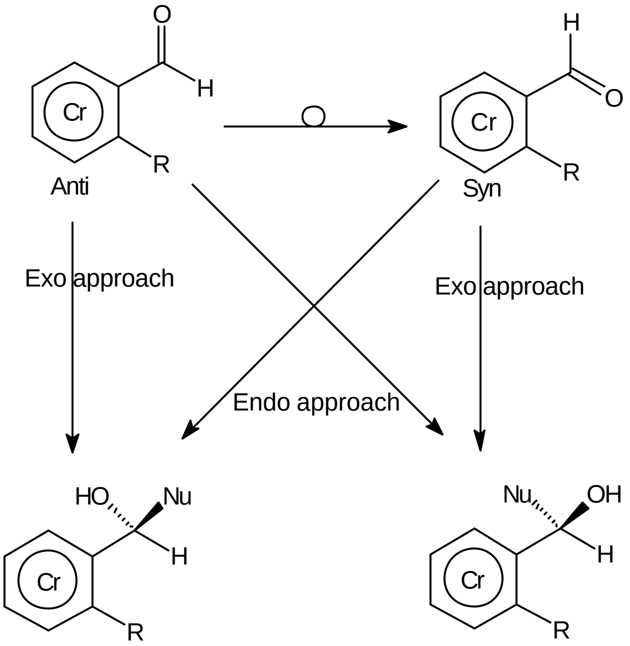


A

Present Work

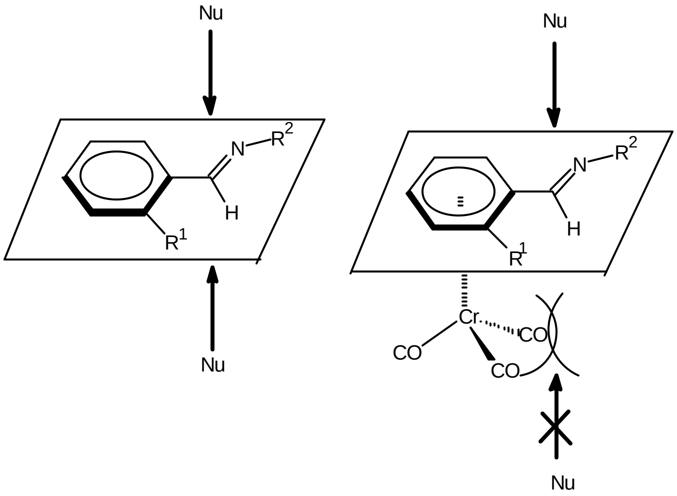
In nucleophilic addition to chiral arene-chromium complexes such as *o*-substituted aryl aldehydes complexed with tricarbonylchromium shown in Chart-1, it is evident that configuration of the new stereogenic center would depend on the preferred *syn* or *anti* orientation of the carbonyl group if diastereoface selectivity remains the same. These substrates have been widely used for the stereoselective synthesis of a number of interesting products.[15]

Chart-1



The *anti* conformer[16] is the predominant one when the *ortho* substituent is an alkyl group, an alkoxy group or a halide. Nucleophiles, as a general rule, add to the bezylic site preferentially from the face opposite to bulky tricarbonylchromium (*exo* addition). It is also well-established[17] that nucleophilic addition to correpondin g imine complexes follows a similar pattern (Figure-3).

Figure -3



Buttero[18] has shown that enolate addition to imine derived from a chiral tricrbonylchromium complex is highly diastereoselective (Scheme-11).

Scheme -11

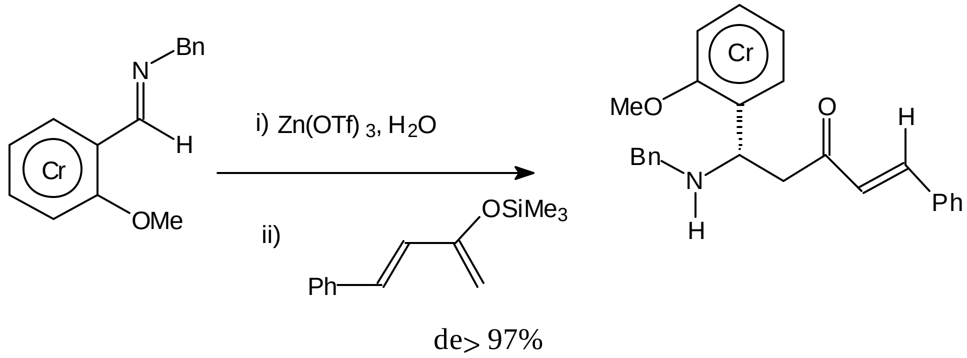
R' = Me, OMe

R" = H, OMe

R''' = Me, PhCONH

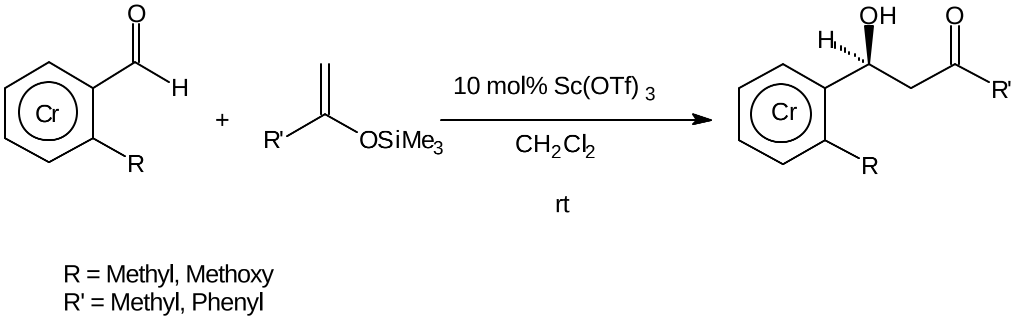
Recently, Ishimaru and co-workers[19] have reported $Zn(OTf)_2$ catalyzed diastereoselective Mannich-type reaction on benzaldimine –tricarbonylchromium derivatives (Scheme-12)

Scheme -12



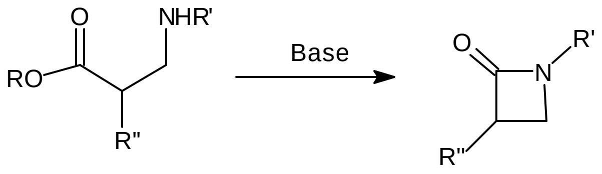
We have earlier reported from this laboratory that triflate-catalyzed addition of silyl enol ethers and silyl ketene acetals to chiral, chromium-complexed aryl aldehydes at ambient temperature is highly diastereoselective (Scheme-13).[20]

Scheme - 13



It was of interest, therefore, to examine the utility of imine derived from *o*–substituted benzaldehyde chromium complexes as starting material for diastereoselective synthesis of β-amino carbonyl compounds. Use of rare earth triflate as the Lewis acid catalyst was also of interest in view of practical advantages. If we could indeed obtain diastereomerically pure β-amino carbonyl compounds, synthesis of optically pure β-amino esters and β-lactams by the reported procedure[21] would be an obvious next step (Scheme-14).

Scheme -14

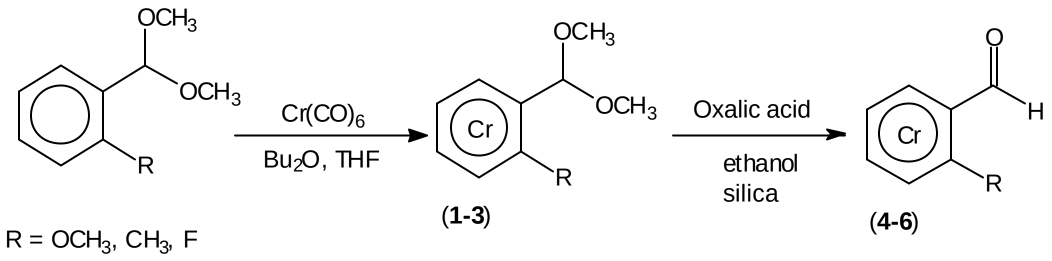


Kobayashi have performed[11] addition of silyl enol ether or silyl ketene acetals on imines in presence of 5 mol% of $Sc(OTf)_3$ at 0 °C in dichloromethane. This precedence was an encouraging starting point.

Results and Discussion

The dimethyl acetal complexes (**1-3**) were prepared[22] by thermolysis of $Cr(CO)_6$ in presence of corresponding aromatic acetals (Scheme-15) in a mixture of dibutyl ether and tetrahyrofuran (10:1) at 130 °C for 16-18 h. The aldehydes (**4-6**) were obtained by deprotection of the corresponding dimethyl acetal complexes under acidic condition.

Scheme -15

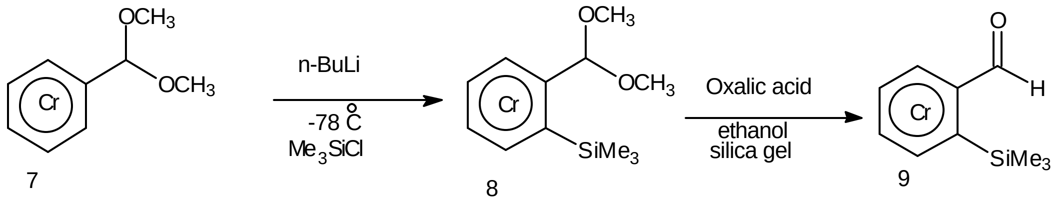


R = OCH_3	**1**	**4**
CH_3	**2**	**5**
F	**3**	**6**

For the preparation of *ortho*-trimethylsilyl aldehyde[23] complex, **7**, the trimethylsilyl group was introduced by lithiation of benzaldehyde dimethyl acetal complex at –78 °C in THF followed by quenching with chlorotrimethylsilane.

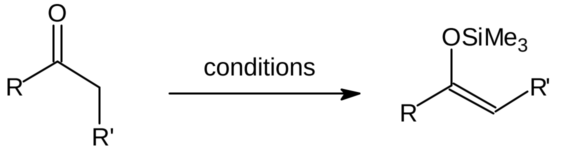
Acidic hydrolysis of the *ortho* trimethylsilyl acetal complex gave the desired aldehyde complex, **9** (Scheme-16).

Scheme -16



Silyl enol ether of acetophenone (**10b**) or cyclohexanone (**10c**) was prepared[24] by refluxing acetophenone or cyclohexanone with chlorotrimethylsilane and triethylamine in DMF (Scheme-17). Silyl enol ether of acetone (**10a**) was synthesized[25] by treating acetone with chlorotrimethylsilane in the presence of sodium iodide and triethylamine in acetonitrile. Propiophenone silyl enol ether was prepared[26] by treatment of propiophenone with LDA in THF at –78 °C and quenching the enolate with chlorotrimethylsilane at-78 °C. This afforded only the Z-isomer as indicated by the proton NMR spectrum and comparison with reported[25] data. Silyl ketene acetal of methyl phenylacetate was prepared by the same method[27] as for propiophenone. It afforded a mixture of silyl ketene acetals in the ratio of *E: Z* = 76:24 (determined by relative peak are for signals due to $OSiMe_3$, OMe).

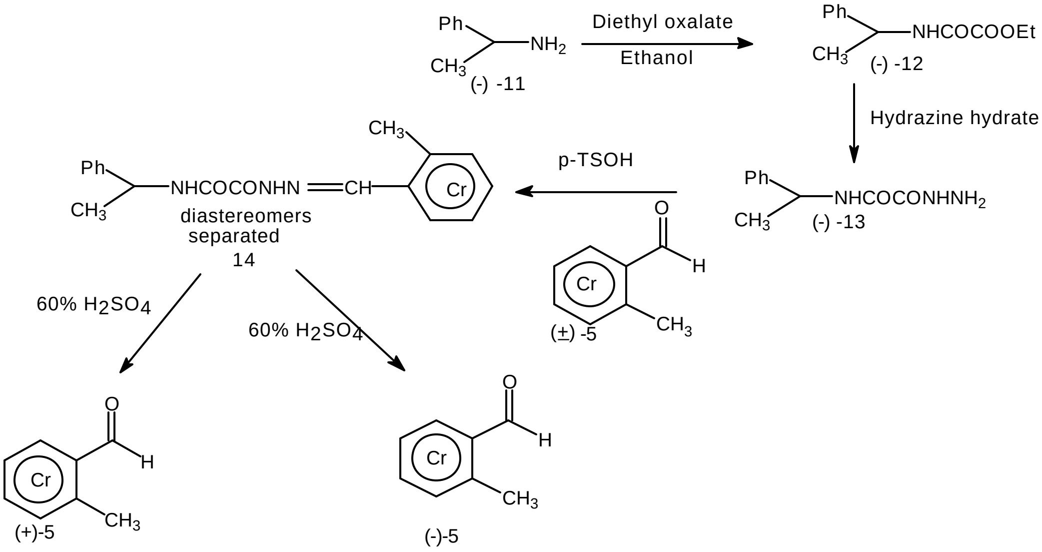
Scheme -17



Enolsilane	R	R’	Conditions
10a	CH_3	H	TMSCl, NaI, Et_3N, acetone, reflux
10b	Ph	H	TMSCl, Et_3N, DMF, reflux
10c	$-(-CH_2-)_4-$	$-(-CH_2-)_4-$	TMSCl, Et_3N, DMF, reflux
10d	Ph	CH_3	LDA/ THF, TMSCl, -78 °C

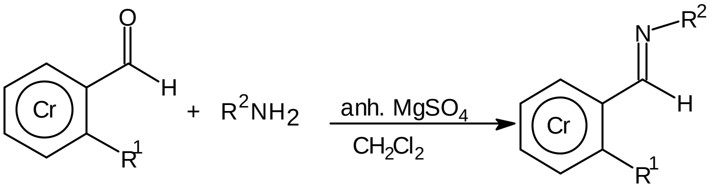
Racemic *ortho*-methoxy benzaldehyde complex (+)-**5** was resolved to enantiopure aldehydes by Solladie′-Cavallo's method [28] (Scheme-18) using (S)-(-)-5-(α-phenylethyl) semioxazamide. The reagent (S)-(-)-5-(α-phenylethyl)semioxazamide was synthesized in two steps from (S)-(-)- α-phenylethyamine. First step is the preparation of (S)-(-)- α-phenylethyloxamide from diethyl oxalate and (S)-(-)- α-phenylethyamine. Second step is the reacton of (S)-(-)- α-phenylethyloxamide with 85% hydrazine hydrate to produce (S)-(-)-5-(α-phenylethyl)semioxazamide. Then (S)-(-)-5-(α-phenylethyl)semioxazamide on refluxing with racemic aldehyde (±)-**5** in benzene in presence of catalytic amount of *p*-toluenesulfonic acid produced diastereomeric pair of semioxazone **14**, which were separated by column chromatography. These semioxazones were separately hydrolyzed with 60% H_2SO_4 in benzene to produce both the enantiomers of chromium tricarbonyl complex of *ortho*-methoxy-benzaldehyde, (+)-**5** and (-)-**5**.

Scheme -18



Complexed imines (**16a-d**) were prepared according to standard procedure[18] by overnight stirring of a mixture of complex aldehyde (**4-6**), amine and anhydrous magnesium sulphate in dichloromethane (Scheme-19). All new imine complexes were isolated and characterized by their spectral and analytic al data.

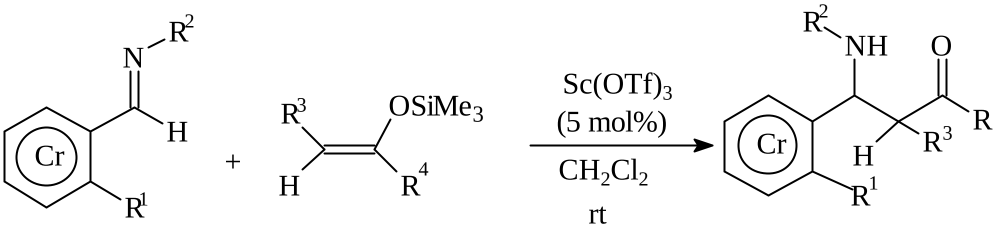
Scheme -19



Imine	R^1	R^2
16a	Me	*p*-MeO-C_6H_4-
16b	F	*p*-MeO-C_6H_4-
16c	OMe	*p*-MeO-C_6H_4-
16d	Me	-$(CH_2)_4$-

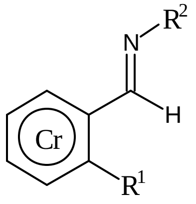
The reaction of tricarbonylchromium complex aldimines, **16a-d**, with silyle enol ether was performed in dichloromethane using 5 mol% $Sc(OTf)_3$ as catalyst following a literature procedure[11] (Scheme-20).

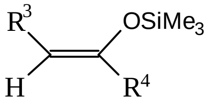
Scheme -20



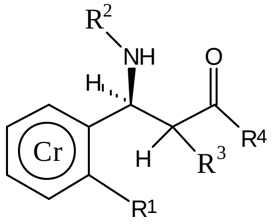
A set of representative starting materials (metal-complexed aryl aldimines, **16a-d**, and enolsilanes **10a-d** and the product **17a-h** obtained are displayed in Chart-2. β-Amino carbonyl compounds were obtained in excellent yield with very high diastereoselectivity even at room temperature. In almost all cases, only a single diastereomer was isolated after purification by chromatography.

Chart-2





10a-d



17a-h

16a-d

	R^1	R^2		R^3	R^4
16a :	Me	*p*-MeO-C_6H_4-	**10a :**	H	Me
16b :	F	,,	**10b :**	H	Ph
16c :	OMe	,,	**10c :**	Me	Ph
16d :	Me	-H_2C-CH=CH_2	**10d :**	-$(CH_2)_4$-	

	R^1	R^2	R^3	R^4
17a :	Me	*p*-MeO-C_6H_4	H	Me
17b :	Me	"	H	Ph
17c :	Me	"	-$(CH_2)_4$-	
17d :	Me	"	Me	Ph
17e :	F	"	H	Me
17f :	F	"	H	Ph
17g :	OMe	"	H	Me
17h :	OMe	"	H	Ph

An interesting substrate was the unsymmetrically substituted - but stereoisomerically pure - silyl enol ether, **10c**, which would result in a product with more than one stereogenic center. We found that at room temperature, the reaction produced a diastereomeric mixture of ketone **17d** (80:20). But when the reaction was performed at –78 °C, a single diastereomer of **17d** was obtained. Based on the *Z*-configuration of the silyl enol ether **2c**, *exo*-selective addition to the *anti*-conformer of the imine and vicinal coupling constant (6 Hz) of the benzylic proton with adjacent methine proton in **3c**, the *erythro* stereochemistry of **3c** has been tentatively proposed. The reaction condition and yields are summarized in Table-1.

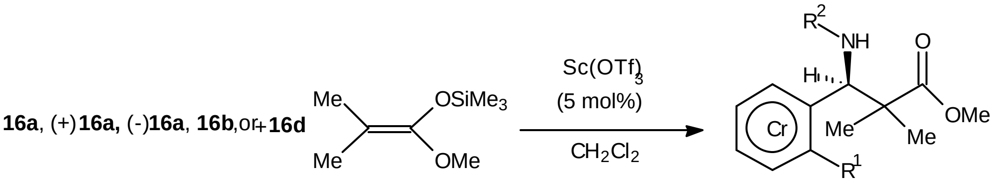
Table-1

Product	Imine	Enol silane	Temp. °C	Time (min)	Yield(%)
17a	**16a**	**10a**	rt	15	90
17b	**16a**	**10b**	rt	15	90
17c	**16a**	**10d**	rt	15	91
17d	**16a**	**10c**	-78	40	87
17e	**16b**	**10a**	rt	15	86

17f	**16b**	**10b**	rt	15	83
17g	**16c**	**10a**	rt	15	86
17h	**16c**	**10b**	rt	15	84

Silyl ketene acetals (**10e**) derived from methyl *iso*-butyrate by the treatment of LDA and chlorotrimethylsilane, rapidly added to the some of the imine complexes, *viz.* (+)-**16a**, (-)-**16a**, **16b**, and **16d**, at room temperature to produce corresponding β-amino esters with excellent yield and diastereoselectivity (Scheme-21).

Scheme -21



10e

18a, (-)**18a**, (+)**18a**, **18b**, or **18c**

(+)**16a** : $[\alpha]_D^{25} = +\,323$, (c 0.40, $CHCl_3$)

(-)**16a** : $[\alpha]_D^{25} = -\,320$, (c 0.40, $CHCl_3$)

(-)**18a** : $[\alpha]_D^{25} = -\,88.00$ (c 0.40, $CHCl_3$)

(+)**18a** : $[\alpha]_D^{25} = +\,90.00$ (c 0.40, $CHCl_3$)

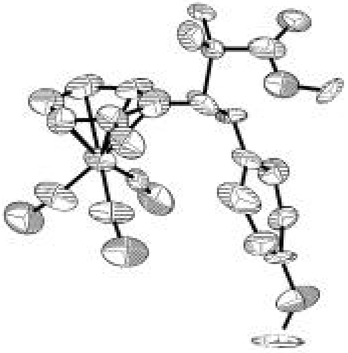
Table -2

Imine	Product	Temp. °C	Time (min)	Yield(%)
16	**18a**	rt	10	93
(+) **16a**	(-) **18a**	rt	10	95
(-) **16a**	(+) **18a**	rt	10	90
16b	**18b**	rt	10	92
16d	**18c**	rt	10	90

We believe the addition of enol silane or silyl ketene acetal to metal-complexed imines to be *exo*-selective (takes place from the face opposite to the metal) on the *anti*-conformer (*ortho*-substituent and N facing away from each other).

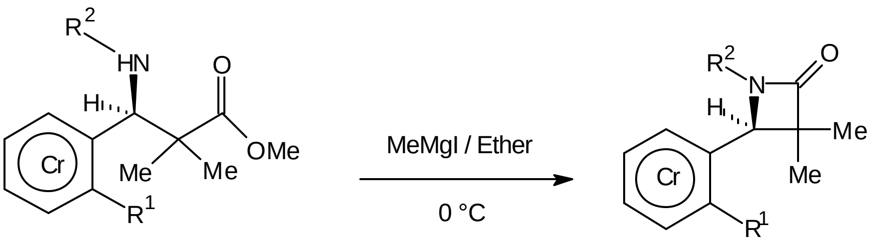
This is consistent with the literature precedent[18] and also confirmed by the crystal structure of β-amino ester **18a** as depicted in Figure-4.

Figure-4. X-ray crystal structure of compound **18a**



The next objective was to transform suitable, diastereomerically or enantiomerically pure β-amino esters to biologically significant β-lacatams. Among several available methods for converting β-amino ester to β-lactam by treatment with base like MeMgI, *t*-BuOK, LDA,[3b] we selected MeMgI as our reagent. Treatment of freshly prepared MeMgI in ether to β-amino esters **18b** and **18d** at 0 °C readily resulted in cyclization to afford corresponding β-lactams, **19b** and **19d** respectively, in excellent isolated yield (Scheme-22). From optically pure β-amino ester, (+)-**18a** and (-)-**18a**, optically pure β-lactam products, (+)-**19a** and (-)-**19a** were prepared by the same method. The yellow crystalline products were characterized by the typical IR absorption of to β-lactam moiety at 1753cm^{-1} and NMR spectral pattern was consistent with their structures.

Scheme -22



18a, (-) **18a**, (+) **18a**, **18b**, or **18c**

19a, (-)**19a**, (+)**19a**, **19b**or **19c**

(-)**19a** : $[\alpha]_D^{25}$ = -100.36 (*c* 0.20, $CHCl_3$)

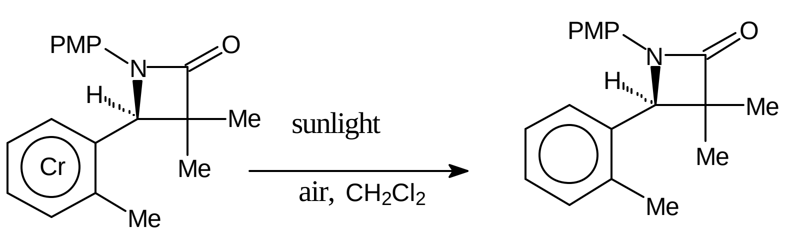
(+)**19a**: $[\alpha]_D^{25}$ = + 100.76 (*c* 0.20, $CHCl_3$)

Table -3

b -aminoester	b-lactam	Temp. °C	Time (min)	Yield(%)
18	**19a**	0	10	90
(+) **18a**	(-) **19a**	0	10	92
(-) **18a**	(+) **19a**	0	10	90
18b	**19b**	0	10	85
18d	**19c**	0	10	88

Finally, uncomplexed **20a** was obtained almost quantitatively by exposure of **19a** to air and sunlight in dichloromethane solution (Scheme-23).

Scheme -23

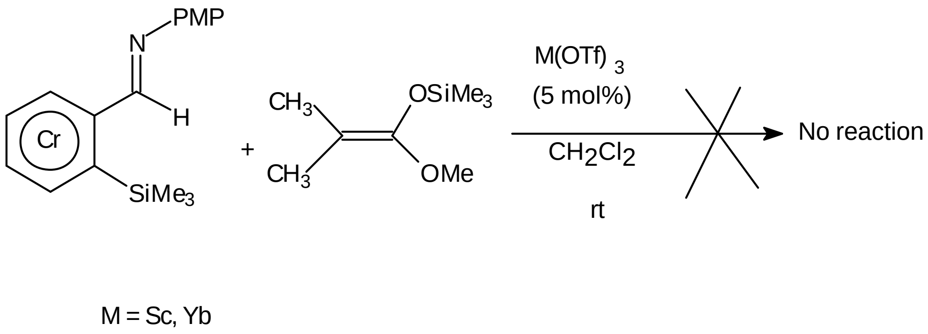


19a

20a

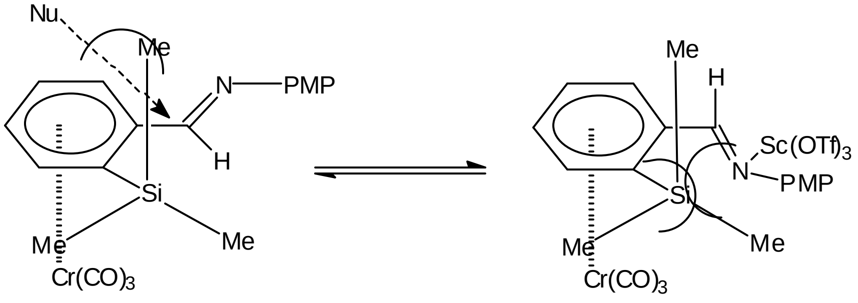
It was found that ytterbium triflate was also as effective as scandium triflate. Two reactions were carried out on imine **16a** - with acetone enol silane and with methyl trimethylsilyl ketene acetal - using ytterbium triflate as the catalyst in dichloromethane. Under the same set of reaction conditions, comparable yield of products were obtained. In our hands, reaction of *ortho*-trimethylsilyl-substituted imine complex with methyl trimethylsilyl dimethyl ketene acetal, **10e**, under the same set of conditions did not give the desired product (Scheme-24). Increasing the amount of catalyst up to 30%, changing to acetonitrile as the reaction medium, or switching from scandium triflate to ytterbium triflate as catalyst failed to improve the situation.

Scheme -24



In the light of a reported reaction, [23] a probable explanation of this failure can be offered. The imine function can adopt two possible conformations with respect to the *ortho*-substituent (Chart-3). While for conformer **B**, nucleophilic approach is unhindered, the conformer **B** is highly destabilized as the Lewis acid co-ordinates with the nitrogen atom of imine. If conformer **A** is considered, the bulky trimethylsilyl group obstructs the trajectory of the nucleophile along the preferred angle of attack (*ca.* 109°) and the required transition state is not attained.

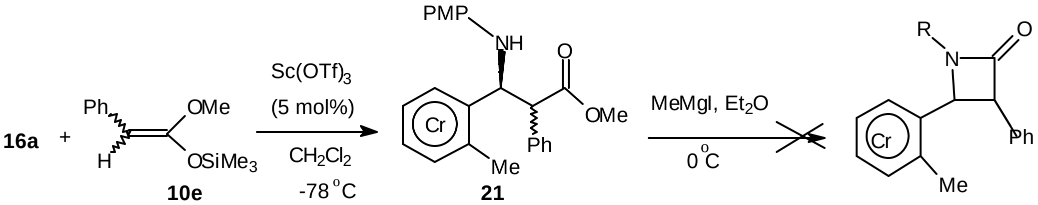
Chart-3



(**A**) (**B**)

With a view to introducing one additional stereogenic center in the β-amino ester and eventually in the target β-lactam, silyl ketene acetal **10f** was prepared from methyl ester of phenylacetic acid using LDA and chlorotrimethylsilane at –78 °C. The product **10f** was obtained as a mixture of stereoisomers (*E:Z* = 76:24). Upon treatment of 1.5 equivalents of silyl ketene acetal **10f** with imine **16a** at –78 °C in dichloromethane (Scheme-25), the β-amino ester was obtained in 82% yield as a diastereomeric mixture (*dr* 80:20). However, when the imine **16a** was treated with a large excess (5 equivalents) of silyl ketene acetal **10f**, single diastereomer of the product **21** was obtained. Unfortunately this product did not undergo cyclization on subsequent treatment with MeMgI, LDA or ^{t}BuOK to furnish the desired β-lactam.

Scheme-25



Summary

We have demonstrated that $Sc(OTf)_3$ or $Yb(OTf)_3$ is an efficient yet mild catalyst for diastereoselective addition of silyl enol ethers or silyl ketene acetals to chromium tricarbonyl complex imines. Reaction is very faster than observed for uncomplexed aldimine. The practical advantages of catalyst stability and ambient temperature add to the merit of this reaction.

Experimental

All the reactions were performed under an inert atmosphere of argon. Scandium oxide and Ytterbium oxides were purchased from Strem Chemicals, USA. Scandium and ytterbium triflates were prepared according to the reported procedure. Chlorotrimethylsilane and triflic acid were purchased from Aldrich Chemical Company, and used as received. Dichloromethane and acetonitrile were dried over anhydrous P_2O_5. DMF was freshly distilled over calcium hydride.

Silyl enol ether and silylketene acetals were prepared according to the reported[24-27] procedure. *Ortho*-substituted benzaldehyde tricarbonylchromium complex and their corresponding imines were prepared by standard literature procedure.[22-23]

General Procedure for the preparation of imines (16a, 16b, 16c, 16d): of complex aldehyde (1mmol) and amine (1.1 mmol) were stirred overnight in 10 mL of dichloromethane in presence of 1 equivalent of anhydrous $MgSO_4$ under inert atmosphere of argon. It was then filtered through celite -pad and crystallized from dichloromethane/pet ether. Yields from reactions performed in 4 mmol scale were in the range of 95-98%. **16a** and **16c** are reported earlier.[18]

Complex 16a

Yield	95%
Color :	Orange
MP :	97 °C, lit. 97 °C
^{1}H NMR ($CDCl_3$) : (200 MHz)	2.46 (s, 3H), 3.85 (s, 3H), 5.15 (d, 1H, J = 6 Hz), 5.32 (t, 1H, J = 4 Hz), 5.58 (t, 1H, J = 6.5 Hz,), 6.44 (d, 1H, J = 6 Hz), 6.95 (d, 2H, J = 8 Hz), 7.25 (d, 2H, J = 8 Hz), 8.35 (s, 1H).

Complex 16b

Yield	92%
Color :	Orange
MP :	76 °C

IR ($CHCl_3$) : 1616, 1896, 1969 cm^{-1}

^{1}H NMR ($CDCl_3$) : (200 MHz) 2.37 (s, 3H), 4.23 (d, 2H, J = 2 Hz), 5.09-5.35 (m, 4H), 5.53 (t, 1H, J = 6 Hz), 5.92-6.12 (m, 1H), 6.25 (d, 1H, J = 8Hz), 8.17 (s, 1H)

^{13}C NMR ($CDCl_3$) : (50.3 MH_Z) 18.57, 63.34, 89.55, 92.89, 93.11, 94.80, 98.99, 109.87, 116.53, 135.53, 156.63, 232.54.

Analysis Calcd. C: 56.95, H: 4.43, H: 4.74

($C_{14}H_{13}O_3NCr$) Found. C: 56.83, H: 4.51, H: 4.72

Complex 16c

Yield 98%

Color : Orange

MP : *138 °C, lit. 138 °C*

^{1}H NMR ($CDCl_3$) : (200 MHz) 3.84 (s, 3H), 3.85 (s, 3H), 5.01-5.07 (m, 2H), 5.72 (t, 2H, J = 6 Hz), 6.645 (d, 1H, J = 6 Hz), 6.93 (d, 2H, J = 8 Hz), 7.23 (d, 2H, J = 8 Hz)

Complex 16d

Yield 95%

Color : Yellow

MP : *110 °C*

IR ($CHCl_3$) : 1637, 1899, 1971 cm^{-1}

^{1}H NMR ($CDCl_3$) : (200 MHz) 3.84 (s, 3H), 4.99-5.08 (m, 1H), 5.42 (t, 1H, J=6Hz), 5.58-5.70 (m, 1H), 6.53-6.58 (m, 1H), 6.95 (d, 2H, J= 10Hz), 7.26 (d, 2H, J=10Hz), 8.40 (s, 1H)

^{13}C NMR ($CDCl_3$) :(50.3 MH_Z) 55.69, 78.37, 78.78, 86.50, 89.66, 90.72, 92.97, 114.76, 122.78, 143.69, 147.55, 230.88

Analysis	Calcd. C: 55.89, H: 3.31, H: 3.83
($C_{17}H_{12}O_4NCrF$)	Found. C: 55.95, H: 3.51, H: 4.10

Preparatiom of silyl enol ether of propiophenone (10c): To a solution of 1.5 mL (11 mmol) of diisopropylamine in 20 mL THF, at 0 °C was added dropwise a solution of n-BuLi (7 mL, 1.56M, 11 mmol) in hexane. After 15 min, the solution was cooled to -78°C and 1.34 mL (9.98 mmol) propiophenone in 5mL THF was added dropwise over 5min. After stirring at -78°C for 1 h chlorotrimethylsilane (1.52 mL, 11 mmol) was added and the solution was allowed to warm to room temperature during1 hr. Then reaction mixture was quenched with saturated ammonium chloride solution at 0 °C (2 mL). THF and excess diisopropylamine were removed under vacuum, diluted successively with pentane, washed with 1.5 N HCl, saturated $NaHCO_3$ solution and finally with brine solution.The pentane extract was dried over anh. Na_2SO_4, concentrated under reduced pressure and finally kugelrohr distillation afforded propiophenone silylenol ether (**10c**) with 90% yield. This compound has been reported earlier.[26]

^{1}H NMR ($CDCl_3$) :	0.15 (s, 9H), 1.75 (t, 3H, J = 6 Hz), 5.78 (q, 1H, J = 8Hz),
(200 MHz)	7.15-7.55 (m, 5H)

Preparation of silylketene acetal from methyl phenyl acetate (10f) : To a solution of diisopropylamine (1.0 mL 7.3 mmol) in 10 mL of anhydrous THF at 0 °C was added dropwise a solution of BuLi (4.7 mL, 1.56 M, 7.3 mmol) and the solution was stirred for another 30 min . Then it was cooled to –78 °C and stirred for another15 min. A solution of methyl phenyl acetate (1 g 6.6, mmol) in 5 mL THF was added dropwise. The solution was stirred for another 30 min at –78 °C and chlorotrimethylsilane 1.0 mL (8 mmol) was added dropwise. After stirring for 1 hr at –78 ° C, reaction mixtures was allowed to come to room temperature for 2 h. Solvent was rapidly evaporated under reduced pressure. The crude residue was distilled under vacuum to afford silyl ketene acetal (**10f**). ^{1}HNMR of the product showed the mixure of E & Z isomer in the ratio 76: 24. **10f** is reported earlier.[27]

10f

^{1}H NMR (CDCl$_3$) :	0.4 (s, 9H), 3.8 (s, 3 H), 4.80 (s, 1H), 7.10 (t, 1H, J = 6 Hz), 7.35 (t, 2H, J = 6 Hz), 7.40-7.55 (m, 2H).
(200 MHz)	signals separated for minor isomer 0.35 (s, 9H), 3.70 (s, 3H), 4.70 (s, 3H).

Resolution of racemic chiral complex aldehyde (±)-5 to optically pure aldehydes: i) Synthesis of oxamide (-)-**12**: To a 5.0 g (0.04 mol) of distilled (S)- (-)- α-phenyl ethylamine in 50 mL of absolute ethanol at room temperature was added slowly with stirring to distilled diethyl oxalate (12.6 mL, 8.3 mol).The reaction mixture was allowed to stir for 24 hours, and a small amount of diamide was removed by filtration. Ethanol and unreacted diethyl oxalate was removed by vacuum distillation. The residue, which solidified, was recrystallized from absolute ethanol to give 6.8 g (80%) of colorless needles, m.p. 55 °C; lit.[29] 54 °C.

ii) Synthesis of semioxazamide (-)-**13**: To a solution of 5 g (0.025 mol) of oxazamide (-)-**12** in 50 mL of absolute ethanol was added with stirring 1.5 g (0.025 mol) of 85% hydrazine hydrate. A precipitate formed immediately and the entire contents of the reaction flask became a semi-solid mass. The crude product was dissolved in 95% of ethanol and the solution was filtered to remove traces of dihydrazide of oxalic acid. The very fine needles, which separated from the filtrate, were recrystallized from ethanol to give 4.90 g (90%) of semioxazamide (-)-**13**, m.p. 155 °C, and lit.[29] 157 °C.

iii) Preparation of semioxazones **14**: A mixture of semioxazamide (0.770 g, 0.004 mol), tricarbonylchromium-complexed aldehyde (1.00 g, 0.004 mol) and *p*-toluenesulfonic acid (0.076 g, 0.0004mol) was refluxed in benzene until no more starting aldehyde could be detected by TLC (approximately 3 hours). After being cooled, washed (NaHCO$_3$) and dried (Na$_2$SO$_4$), the solvent was removed under vacuum to give orange-red crystal of diastereomeric semioxazones with 80% yield. The pure diastereomers were separated by flash column chromatography (ether/ pet ether 90:10).

iv)The pure diastereomers were independently hydrolyzed by refluxing with 60% H_2SO_4 in benzene until no starting material could be detected by TLC (approximate 3 hours). Reaction mixture was cooled, washed with saturated solution of $NaHCO_3$ and water, dried over Na_2SO_4 and concentrated. Flash column chromatography (ether/pet ether 8:2) afforded pure enantiomer of complex **5**, optical rotation was recorded and compared with reported[28] value.

(+)-**5** Recorded : $[\alpha]_D^{25}$ = + 660 ° (*c* 0.22, $CHCl_3$) Lit.[28].$[\alpha]_D^{25}$ = + 665° (*c* 0.22, $CHCl_3$)
(-)-**5** Recorded : $[\alpha]_D^{25}$ = - 662° (*c* 0.22, $CHCl_3$) Lit.[28].$[\alpha]_D^{25}$ = - 664° (*c* 0.22, $CHCl_3$)

Typical procedure of the addition of sily enol ethers (10a-10d) to complex imine (16a-16d): To a suspension of $Sc(OTf)_3$ (0.02 mmol) in CH_2Cl_2 (2 mL), a mixture of silyl enol ether or silyl ketene acetals and imine (1 mmol) in CH_2Cl_2 (3 mL) was added dropwise under an argon atmosphere at room temperature. After stirring for 10-15 min, water was added and the product was extracted with CH_2Cl_2. The crude products were purified by flash chromatography (15% acetone-pet ether). Reactions were performed in 0.5-0-2.0 mmol scale and isolated yields are indicated in table-1.

Complex 17a

Color:	Yellow
MP:	138 °C
IR (CHCl$_3$):	1712, 1905, 1978 cm^{-1}
^{1}H NMR (CDCl$_3$): (200 MHz)	2.13 (s, 3H), 2.33 (s, 3H), 2.83-3.06 (m, 2H two close dd merges), 3.75 (s, 4H, actually, N-H merges here with OCH$_3$), 4.69 (t, 1H, J = 6 Hz) 5.01-5.11 (m, 2H), 5.48 (t, 1H, J = 6 Hz), 5.74 (d, 1H, J = 8 Hz), 6.70 (d, 2H, J=10 Hz), 6.81(d, 2H, J = 10 Hz)
^{13}C NMR (CDCl$_3$): (50.3 MH$_Z$)	19.08, 30.77, 49.70, 50.88, 55.88, 87.86, 91.79, 94.22, 95.94 109.36,112.36, 115.17, 116.12, 140.20, 153.20, 206.40, 233.05
Analysis ($C_{21}H_{21}O_5NCr$)	Calcd. C: 60.13, H: 5.05, N: 3.34 Found. C: 59. 96, H: 5.02, N: 3.50

Complex 17b

Color:	Yellow
MP:	150 °C
IR (CHCl$_3$):	1710, 1899, 1973 cm^{-1}
^{1}H NMR (CDCl$_3$): (200 MHz)	2.38 (s, 3H), 3.50 (dd, 1H, J = 18 Hz, 10 Hz), 3.62 (dd, 1H, J = 18 Hz, 10 Hz) 3.75 (s, 3H), 3.87 (bs, 1H), 4.88 (t, 1H, J = 6 Hz), 5.02-5.08 (m, 2H), 5.48 (t, 1H, J = 6 Hz), 5.78 (d, 1H, J = 8 Hz), 6.73 (d, 2H, J = 8 Hz), 6.82 (d, 2H, J = 8 Hz), 7.43-7.64 (m, 2H), 7.90 (d, 2H, J = 8 Hz)
^{13}C NMR (CDCl$_3$): (50.3 MH$_Z$)	19.41, 44.59, 51.14, 56.06, 87.64, 91.75, 94.06, 95.98, 110.21, 113.40, 115.42, 116.23, 128.29, 129.06, 133.88, 136.93, 140.42, 198.09, 233.09

Analysis Calcd. C: 64.85, H: 4.78, N: 2.91
Found. C: 64. 76, H: 5.02, N: 2.70
($C_{26}H_{23}O_5NCr$)

Complex 17c

Color: Yellow
MP: 101 °C
IR ($CHCl_3$): 1712, 1903, 1975 cm^{-1}
^{1}H NMR ($CDCl_3$): (200 MHz) 1.53-1.82 (m, 2H), 1.95-2.52 (m, 9H, include aromatic methyl), 2.56-2.81 (m, 1H), 3.52 (bs, 1H), 3.74 (s, 3H), 4.80 (bs, 1H), 4.95-4.06 (m, 2H), 5.47 (t, 1H, J = 6 Hz), 5.66 (d, 1H, J = 6 Hz),
6.71-6.81(m, 4H)
^{13}C NMR ($CDCl_3$) : (50.3 MHz) 19.67, 25.22, 27.39, 29.52, 42.46, 52.05, 55.91, 57.09, 86.97, 91.09, 94.18, 96.24, 110.24, 114.25, 115.02, 115.46, 141.08, 152.84, 210.59, 233.09.
Analysis Calcd. C: 62.74, H: 5.48, N: 3.08
($C_{24}H_{25}O_5NCr$) Found. C: 62.56, H: 5.52, N: 2.94

17d

Color: Yellow
MP: 125 °C
IR ($CHCl_3$): 1715, 1908, 1981 cm^{-1}
^{1}H NMR ($CDCl_3$): (200 MHz) 1.35 (d, 3H, J = 8 Hz), 2.42 (s, 3H), 3.75 (s, 3H), 3.91-4.04 (m, 1H), 4.55-4.65 (m, 1H), 4.84-4.91(m, 3H), 5.35 (t, 1H, J = 6 Hz), 5.71(d, 1H, J = 6Hz) 6.75-6.85 (m, 4H), 7.37-7.59 (m, 3H), 7.73 (d, 2H, J = 6 Hz)
^{13}CNMR ($CDCl_3$) (50.3 MHz) 16.83, 19.35, 29.92, 45.81, 56.01, 58.22, 87.03, 90.54,94.39, 96.12, 107.96, 110.43, 115.15,115.41,128.33,
128.98, 133.84, 137.14, 141.72, 152.81, 203.69, 232.98
Analysis Calcd. C: 65.45, H: 5.08, N: 2.82
($C_{27}H_{25}O_5NCr$) Found. C: 65.37, H: 5.15, N: 2.98

Complex 17e

Color: Yellow

MP: 101 °C

IR (CHCl$_3$): 1710, 1905, 1976 cm^{-1}

^{1}H NMR (CDCl$_3$): (200 MHz) 2.17 (s, 3H), 3.06 (d, 2H, J = 6 Hz), 3.73 (s, 3H), 4.09 (d, 1H, J = 9 Hz), 4.65-4.95 (m, 2H), 5.24 (t, 1H, J = 6.4 Hz), 5.45 (t, 1H, J = 6 Hz), 5.75 (t, 1H, J = 6 Hz), 6.70-6.82 (m, 4H)

^{13}C NMR (CDCl$_3$): (50.3 MH$_Z$) 29.89, 49.15, 49.96, 55.14, 75.98, 77.05, 84.29, 93.48, 93.70, 99.96, 100.04, 114.47, 115.68, 139.17, 152.70, 205.74, 231.03

Analysis ($C_{20}H_{18}O_5NCrF$)
Calcd. C: 56.74, H: 4.28, N: 3.30
Found. C: 56.68, H: 4.15, N: 3.25

Complex 17f

Color: Yellow

MP: 141 °C

IR (CHCl$_3$): 1708, 1897, 1972 cm^{-1}

^{1}H NMR (CDCl$_3$): (200 MHz) 3.61-3.67 (m, 2H), 3.75 (s, 3H), 4.22-4.35 (bs, 1H), 4.80 (t, 1H, J = 6 Hz), 4.97-5.12 (bs, 1H), 5.22-5.31 (m, 2H), 5.46 (t, 1H, J = 6 Hz), 5.92 (t, 1H, J = 6 Hz), 6.79 (bs, 4H), 7.44-7.65 (m, 3H), 7.39 (d, 2H, J = 6Hz), 7.44 –7.65 (m, 3H), 7.92 (d, 2H, J = 6 Hz)

^{13}C NMR (CDCl$_3$): (50.3 MH$_Z$) 44.78, 51.17, 55.91, 77.56, 84.84, 93.96, 94.44, 100.61, 100.98, 115.20, 116.56, 128.29, 128.99, 133.9, 136.67, 140.02, 143.07, 153.51, 197.84, 231.69,

Analysis ($C_{25}H_{20}O_5NCrF$)
Calcd. C: 61.85, H: 4.15, N: 2.88
Found. C: 61.73, H: 4.18, N: 2.79

Complex 17g

Color: Yellow

MP: 130 °C

IR ($CHCl_3$):	1712, 1906, 1979 cm^{-1}
^{1}H NMR ($CDCl_3$) :(200 MHz)	2.16 (s, 3H), 2.98-3.11 (m, 2H), 3.73 (s, 3H), 3.83 (s, 3H), 4.03-4.19 (bs, 1H), 4.75-4.91 (m, 2H), 4.96 (d, 1H, J = 6 Hz), 5.50 (t, 1H, J = 6 Hz), 5.84 (d, 1H, J = 6 Hz), 6.70 (d, 2H, J = 8 Hz), 6.78 (d, 2H, J = 8 Hz), 6.68- 6.80 (m, 4H)
^{13}C NMR ($CDCl_3$) :(50.3 MH$_Z$)	30.65, 49.95, 51.80, 56.10, 73.00, 83.75, 95.01, 96.81, 101.72, 115.13, 116.39, 140.35, 141.41, 153.29, 207.06, 233.01.
Analysis ($C_{21}H_{21}NCrO_6$)	Calcd. C: 57.93, H: 4.86, N: 3.21 Found. C: 57.67,H: 5.02, N: 3.30

Complex 17h

Color :	Yellow
MP :	154-155 °C
IR ($CHCl_3$) :	1718, 1907, 1981 cm^{-1}
^{1}H NMR ($CDCl_3$) : (200 MHz)	1.23 (s, 3H), 3.50-3.59 (m, 2H), 3.69 (s, 3H), 3.81(s, 3H), 4.77 (t, 1H, J = 6 Hz), 4.92-5.03 (m, 2H), 5.47 (t, 1H, J = 6 Hz), 5.93 (d, 1H, J = 6 Hz), 6.72 (bs, 4H), 7.30-7.60 (m, 3H), 7.90 (d, 2H, J = 8 Hz)
^{13}CNMR ($CDCl_3$) :(50.3 MH$_Z$)	44.88, 52.03, 55.99, 72.96, 83.82, 94.92, 96.76, 102.12, 115.13, 116.47, 128.38, 128.93, 133.67, 137.01, 140.55, 141.43, 153.25, 198.45, 233.05
Analysis ($C_{26}H_{23}NCrO_6$)	Calcd. C: 62.77, H: 4.66, N: 2.81 Found. C: 62.71, H: 4.59, N: 2.88

General procedure for the addition of the addition of methyl trimethylsilyldimethyl ketene acetal (10e) on the complex imine 16a, 16b, 16d*:*

To a suspension of $Sc(OTf)_3$ (0.02 mmol) in CH_2Cl_2 (2 mL), a mixture of silyl enol ether or silyl ketene acetals and imine (1 mmol) in CH_2Cl_2 (3 mL) was added dropwise under an argon atmosphere at room temperature. After stirring for 10-15 min, water was added and the product was extracted with CH_2Cl_2. The crude product was purified by flash chromatography (15% acetone-pet ether). Reactions were performed in 0.5-0-2.0 mmol scale and isolated yields are indicated in Table-2

Complex 18a

Color :	Yellow
MP :	114 °C
IR ($CHCl_3$) :	1728, 1890, 1969 cm^{-1}
^{1}H NMR ($CDCl_3$) : (200 MHz)	1.21 (s, 3H), 1.27 (s, 3H), 2.41 (s, 3H), 3.59 (s, 3H), 3.75 (s, 3H), 4.34 (d, 1H, J = 8 Hz), 4.41(d, 1H, J = 8 Hz), 4.90 (d, 1H, J = 8 Hz), 5.02 (t, 1H, J = 6 Hz), 5.50 (t, 1H, J = 6Hz), 5.57 (d, 1H, J = 6 Hz), 6.66 (d, 2H, J = 8 Hz), 6.80 (d, 2H, J = 8 Hz)
^{13}C NMR ($CDCl_3$) : (50.3 MHz)	20.59, 21.21, 24.74, 49.92, 52.24, 55.95, 59.96, 86.24, 89.77, 94.33, 96.53, 110.24, 110.43, 115.20, 141.45, 152.84, 176.33, 232.76
Analysis ($C_{23}H_{25}O_6NCr$)	Calcd. C: 59.60, H: 5.43, N: 3.02 Found. C: 59.58, H: 5.41, N: 3.01

Complex 18b

Color :	Yellow
MP :	160 °C
IR ($CHCl_3$) :	1732, 1891, 19671 cm^{-1}
^{1}H NMR ($CDCl_3$) : (200 MHz)	1.21 (s, 3H), 1.30 (s, 3H), 3.60 (s, 3H), 3.75 (s, 3H), 4.46 (d, 1H, J = 6 Hz), 4.60 (d, 1H, J = 6 Hz), 4.76 (d, 1H, J = 6 Hz), 5.20 (t, 1H, J = 6Hz), 5.5 (t, 1H, J = 6 Hz), 5.66 (t, 1H, J = 6.3 Hz), 6.68-6.83 (m, 4H)
^{13}C NMR ($CDCl_3$) :(50.3 MHz)	21.25, 24.93, 49.33, 52.38, 55.99, 57.75, 83.63, 92.89, 94.14, 94.29, 114.87, 115.09, 140.86, 152.81, 176.33, 231.43
Analysis ($C_{22}H_{22}O_6NCrF$)	Calcd. C: 56.53, H: 4.74, N: 2.99 Found. C: 56.48, H: 4.62, N: 2.89

Complex 18c

Color :	Yellow
MP :	60 °C
IR ($CHCl_3$) :	1738, 1899, 19978 cm^{-1}
^{1}H NMR ($CDCl_3$) :	1.11 (s, 3H), 1.14 (s, 3H), 2.27 (s, 3H), 3.31(dd, 1H,

(200 MHz) J = 14 Hz, 6 Hz,), 3.56 (dd, 1H, J = 14 Hz, 6 Hz,), 3.70 (s, 3H), 3.80 (bs, 3H), 4.95 (d, 1H, J = 6 Hz), 5.04-5.28 (m, 3H), 5.57 (t, 1H, J=6Hz), 5.75-5.97 (m, 2H)

^{13}CNMR (CDCl$_3$) : 19.96, 20.59, 23.97, 49.44, 51.58, 52.16, 60.32,
(50.3 MH$_Z$) 86.64, 90.50, 95.35, 97.45, 109.87, 111.23, 116.71, 136.93, 176.77, 233.42

Analysis Calcd. C: 57.42, H: 5.83, N: 3.52
(C$_{19}$H$_{23}$O$_5$NCr) Found. C: 57.47, H: 5.69, N: 3.50

General procedure for the cyclization of b- amino esters to b-lactams*:* To a solution of freshly prepared methyl magnesium iodide (1.1 mmol) in 10 mL of dry ether was added dropwise a solution of the *b*- amino ester (1 mmol) in 10 mL of dry THF under ice cooling. After addition was over, the reaction was stirred for another 15 min. Then reaction mixture was quenched with saturated ammonium chloride solution under ice cooling. Solvent was removed under reduced pressure. Reaction mixture was extracted with chloroform, dried over anhydrous sodium sulphate, concentrated under reduced pressure and purified by flash column chromatography (15% acetone/ pet ether). Yields were in the range (90-95%).

Complex 19a

Color : Yellow

MP : 183-184 °C

IR (CHCl$_3$) : 1753, 1899, 1971 cm^{-1}

^{1}H NMR (CDCl$_3$) : 1.00 (s, 3H), 1.59 (s, 3H), 2.25 (s, 3H), 3.79 (s, 3H), 4.94 (s,
(200 MHz) 1H), 5.13-5.18 (m, 2H), 5.295 (d, 1H, J = 6 Hz), 5.44 (t, 1H, J = 6 Hz), 6.95 (d, 2H, J = 8 Hz), 7.53 (d, 2H, J = 8 Hz)

^{13}C NMR (CDCl$_3$): 17.94, 19.23, 21.19, 55.77, 56.47,63.15, 89.51, 91.90, 92.49,
(50.3 MH$_Z$) 94.47, 105.68, 114.87, 120.31, 130.02, (157.11), 170.27, 232.68

Analysis Calcd. C: 61.25, H: 4.90, N: 3.24
(C$_{22}$H$_{21}$O$_5$NCr) Found. C: 61.19, H: 4.97, N: 3.21

Complex 19b

Color :	Yellow
MP :	160 °C
IR ($CHCl_3$):	1755, 1902, 1972 cm^{-1}
^{1}H NMR ($CDCl_3$) : (200 MHz)	1.06 (s, 3H), 1.55 (s, 3H), 3.80 (s, 3H), 4.86 (t, 1H, J = 6 Hz), 5.03 (bs, 1H), 5.31-5.54 (m, 3H), 6.96 (d, 2H, J = 8 Hz), 7.53 (d, 2H, J = 8 Hz)
^{13}C NMR ($CDCl_3$) : (50.3 MH$_Z$	18.24, 22.39, 55.88, 57.05, 60.80, 86.02, 90.69, 92.56, 95.54, 95.83, 115.20, 120.17, 130.24, 157.37, 170.67, 230.99
Analysis ($C_{21}H_{18}O_5NCrF$)	Calcd. C: 57.93, H: 4.16, N: 3.21 Found. C: 57.73, H: 4.15, N: 3.24

Complex 19c

Color :	Yellow
MP :	134 °C
IR ($CHCl_3$) :	1759, 1905, 1981 cm^{-1}
1H NMR ($CDCl_3$) : (200 MHz)	0.93 (s, 3H), 1.48 (s, 3H), 2.16 (s, 3H), 3.52-3.72 (m, 1H), 4.20-4.36 (m, 1H), 4.42 (s, 1H), 5.12-5.44 (m, 6H), 5.75-6.00 (m, 1H)
^{13}C NMR ($CDCl_3$): (50.3 MH$_Z$)	17.12, 18.79, 22.46, 43.60, 56.65, 62.16, 89.91, 90.94, 93.74, 94.03, 104.99, 106.93, 119.9, 131.05, (159.86), 173.72, 232.94
Analysis ($C_{18}H_{19}O_4NCr$)	Calcd. C: 59.17, H: 5.20, N: 3.83 Found. C: 58.94, H: 4.97, N: 3.60

Decompexation of b-lactam (19a) to uncomplexed b-lactam (20a): A solution of **(19a)** in (100 mg, 0.21 mmol) in 10 mL of CH_2Cl_2 was exposed to air and sunlight for about 2 h (the reaction was monitored by TLC). The solution was filtered over a pad of celite to remove the chromium salt and celite pad was washed 3 times with 10 mL portion of CH_2Cl_2. The filtrate was evaporated and the residue was crystallized from petroleum ether. The uncomplexed β-lactam (**20a**) was obtained as white crystalline solid **20a** (68 mg, 97%). This compound reported in literaure.[18]

Compound 20a

Color :	White
MP :	154 °C lit. 155 °C
^{1}H NMR (CDCl$_3$) : (200 MHz)	0.8 (s, 3H), 1.6 (s, 3H), 2.4 (s, 3H), 3.8 (s, 3H), 6.8-7.3 (m, 8H)

Trimethylsilyl methyl phenyl ketene acetal (10f) addition to imime (16a): To a suspension of Sc(OTf)$_3$ (0.034g, 5 mol%) in 10 mL CH_2Cl_2 at -78°C, a mixture of **16a** (0.5g, 1.38 mmol) and **10f** (0.92g, 5.14 mmol) was added dropwise . After stirring for 30 min, color of the solution changes from deep violet to pale yellow. The rection mixture was quenched with water, extracted with dichloromethane and chromtographed to furnish β-amino ester **21** in 80% yield (0.56 g)

Complex 21

Color :	Yellow
MP :	137-138 °C
IR (CHCl$_3$) :	1736, 1896, 1972 cm^{-1}
^{1}H NMR (CDCl$_3$) : (200 MHz)	2.29 (s, 3H), 3.61 (s, 3H), 3.73 (s, 3H), 3.98 (d, 1H, J = 6 Hz), 4.93-5.01 (m, 3H), 5.38-5.50 (m, 2H), 6.62 (d, 2H, J = 8 Hz), 6.75 (d, 2H, J = 8 Hz), 7.18-7.39 (m, 5H)
^{13}C NMR (CDCl$_3$): (50.3 MHz)	19.38, 52.46, 55.88, 56.69, 58.27, 86.94, 90.69, 94.29, 95.98 109.51, 110.01, 114.91, 116.16, 128.24, 129.91, 133.91, 140.53, 153.21, 171.81, 232.87.
Analysis	Calcd. C: 63.40, H: 4.92, N: 2.73
($C_{27}H_{25}O_6NCr$)	Found. C: 63.36, H: 4.90, N: 2.53

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Chapter - III

Assembling Monocyclic, Spirocyclic and Fused Carbocycles by Ring Closing Metathesis on Arene Chromium Template

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Part of this work has been published in *Tetrahedron Letters* **2001**

Introduction

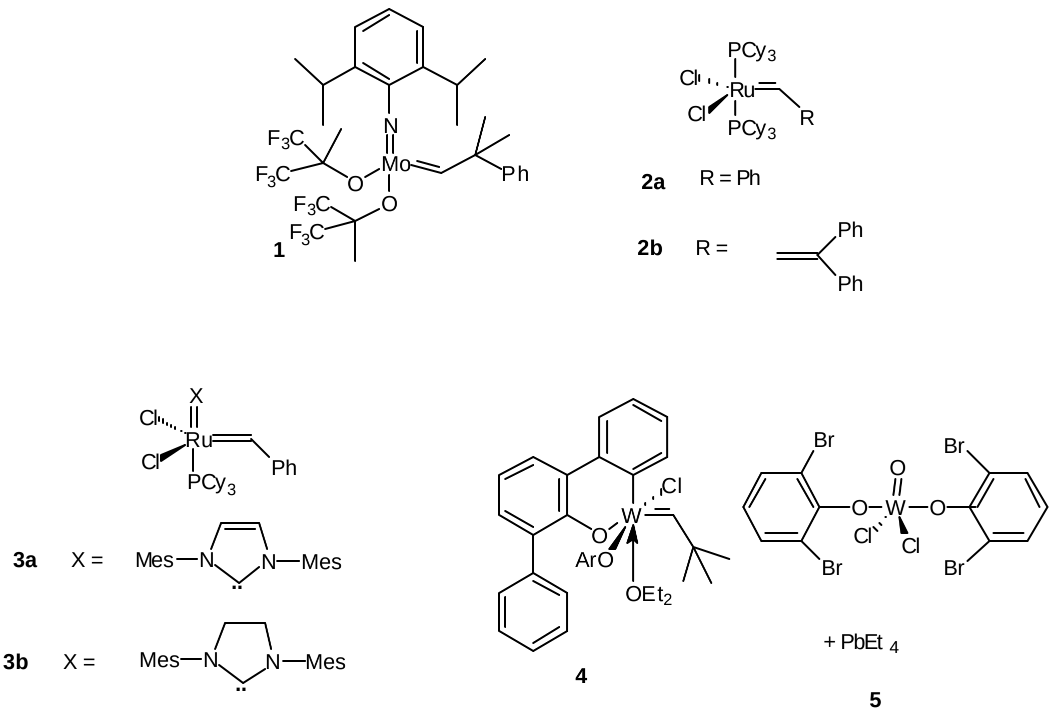
A primary activity of organic synthesis concerns efficient and selective carbon-carbon bond formation reactions. Alkene metathesis brought about a renaissance in synthetic organic chemistry during the last couple of years. Although double bond scrambling reactions were initially reported[1] in 1950s, the formal scission of a pair of double bonds followed by the interchange of their carbon atoms, *i.e.* alkene metathesis (Chart-1, is known since 1967 from the report of Calderon and coworkers[2]. The scope of such reaction was limited at that time by harsh reaction conditions and unacceptable catalytic efficiency.

Chart-1

From 1950 to early 1980, alkene metathesis was catalyzed by transition metal salts[3] along with a promoter or support, *e.g.* WCl_6/ Bu_4Sn, $WOCl_4/EtAlCl_2$, MoO_3/ SiO_2 or Re_2O_7/Al_2O_3 but application in organic synthesis was limited due to sensitivity of functionalized organic molecules to strong Lewis acid at elevated temperature.

Recently, basic research in organometallic chemistry has successfully met the long-standing challenge to deliver efficient, structurally well-defined, functional group tolerant catalysts. The discovery that metal alkylidene complexes provide the key intermediates in alkene metathesis, combined with the insight into the reaction mechanism of double bond redistribution, resulted in the synthesis of a few very useful catalyst precursors (Chart-2). Tungsten and molybdenum alkylidene complexes (**1**) developed by Schrock and co-workers[4] are among the first ones synthesized and used in metathesis under mild conditions with complex substrates containing diverse, sensitive functional groups. In spite of their wide adaptability in terms of functional group tolerance, their use in routine organic synthesis has been somewhat restricted by their high sensitivity to oxygen and moisture. Ruthenium complexes (**2a-b**) were later developed by Grubbs[5] as a new, versatile set of catalysts that performed even in presence of air and moisture. They are relatively easy to prepare and they are now commercially available. A second-generation catalyst (**3a-b**) evolved a few years later[6] as a more reactive variation; its design was inspired by the findings of Herrmann[7] that imidazolylidene ligands enhance catalytic reactivity and efficiency. Compared to these, other catalysts like **4**[8] or **5**[9] found rather limited application in organic synthesis.

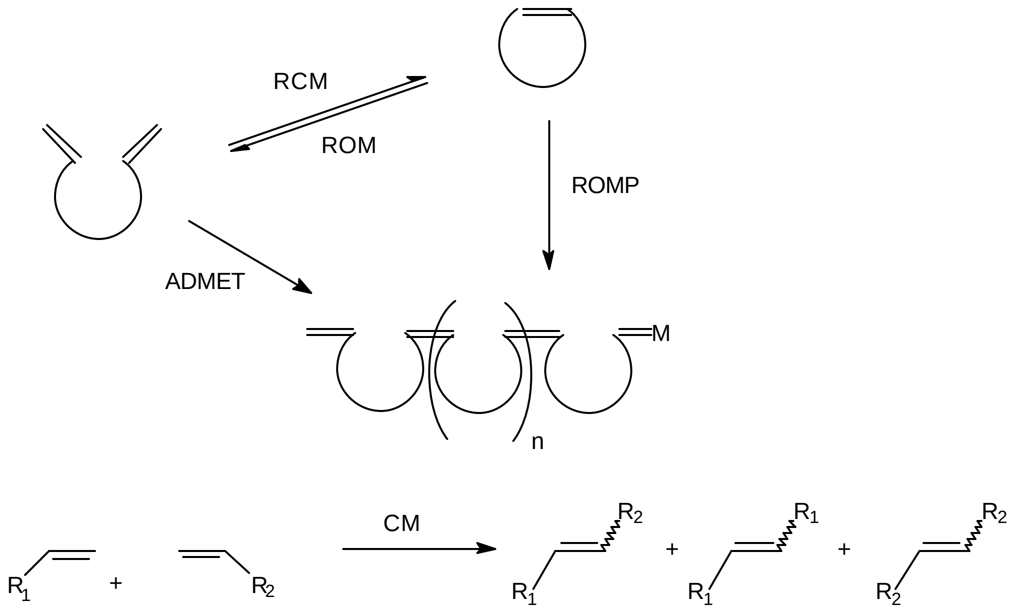
Chart-2. Some typical metathesis catalysts.



While diverse metal centers are known to provide cataytically active complexes, chemoselectivity varies across the periodic table. Results show that tungsten catalysts are more strongly disposed to olefinate ketones and esters. Molybdenum catalysts are more reactive toward olefins, although they also react with aldehyde and the other polar and protic groups. Ruthenium complexes react preferentially with alkenes in presence of polar functional groups like alcohols, amides, aldehydes and carboxylic acids.

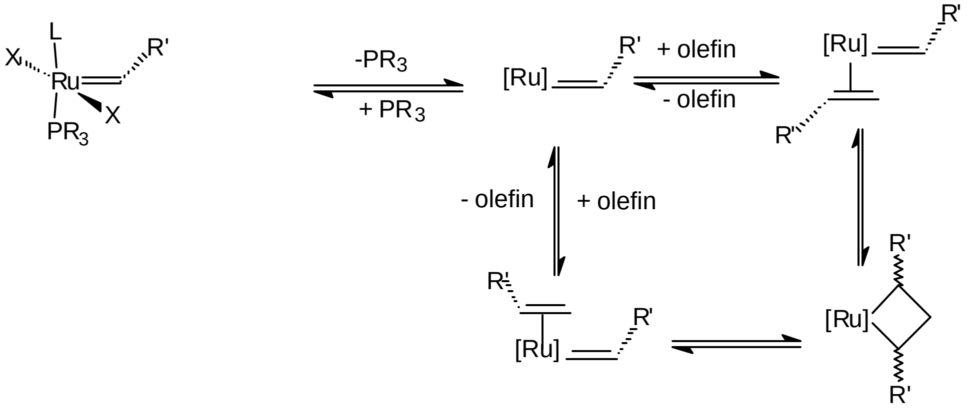
From the perspective of synthetic chemists, a diene substrate is interesting because it offers different possibilities : one is cyclization, where ethylene is a gaseous product and its expulsion favours the equilibrium to the cyclized product (RCM: ring-closing metathesis[10a]); the other is an intermolecular reaction that can lead to oligomerization (ADMET: acyclic diene metathesis) - this reaction is a competing reaction of RCM and can be suppressed only by high dilution. The intermolecular version, for simple alkenes, is referred to as cross-metathesis, where the proportion of the desired cross-product depends on the preference of alkene partners towards itself. Since the metathesis reaction is equilibrium controlled, it is conceivable that strained cycloalkenes could undergo an energy-releasing ring-opening process to yield polymeric products (ROMP: ring-opening polymerization[10b] - the opposite reaction of RCM). Indeed this process has become a major "living" polymerization reaction preferred for its mild condition and excellent functional group compatibility. The reactions are illustrated in Chart-3.

Chart-3



The current understanding about the mechanism of alkene metathesis[11] is summarized in the Scheme-1.

Scheme -1

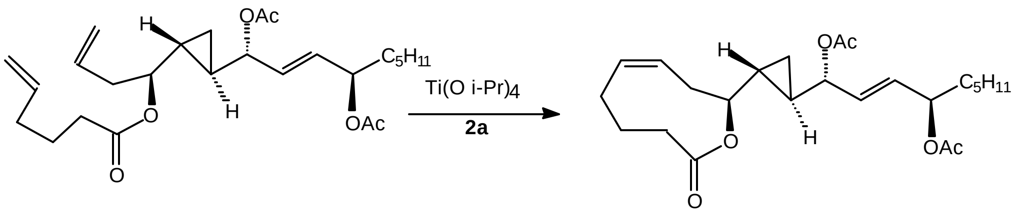


[Ru] = X_2LRu

Kinetic evidence as well as dependence of initiation rate on sterics of halogen, alkylidene or ancillary ligand suggests that dissociation of one tricyclohexylphosphine is a critical and often the rate-determining step.

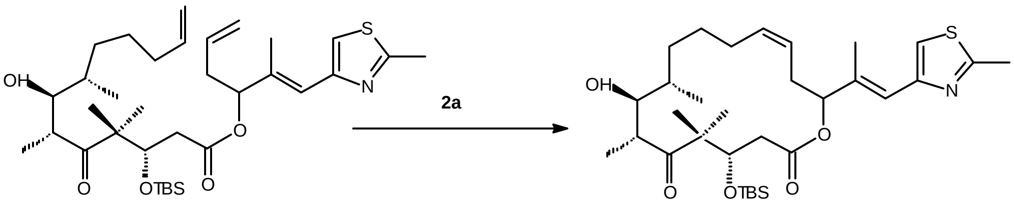
Since alkene metathesis concerns formation of double bonds, and barring geometrical isomerism which is occasionally of some concern, this reaction does not directly address stereoselectivity that relates to tetrahedral stereogenic centers. However, stereochemically complex, cyclic scaffolds can result from ring-closing metathesis of pre-assembled chiral dienes. Recently, Takemoto and co-workers have synthesized (Scheme-2) Helicholactone using RCM as key step from chiral diene precursors[12] and catalyst **2a.**

Scheme -2



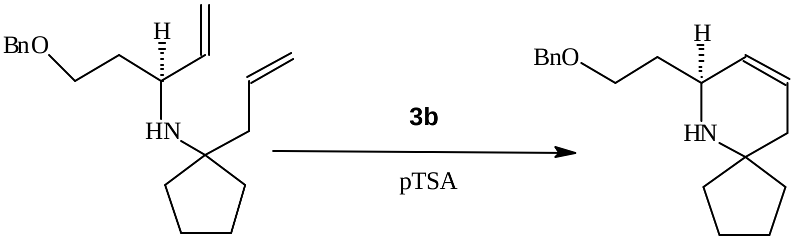
RCM, which perhaps represents the present “state of the art” of natural product synthesis, has been used as the key step, to synthesize a large mumbers of natural products like epothilone A[13] (Scheme-3), peptide[14] and catenates.[15]

Scheme -3



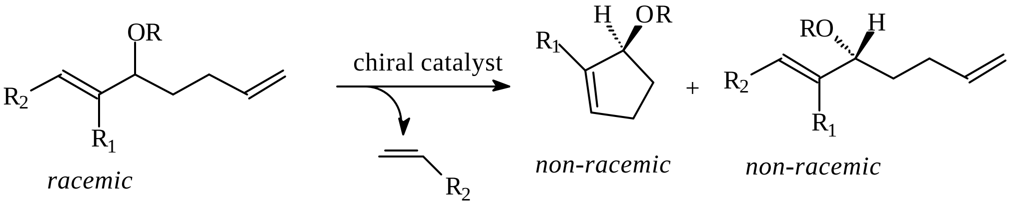
Earlier it was known that free amines are typically incompatible with metathesis reaction catalyzed by **2a-b** owing to catalyst inhibition by basic nitrogen. Recently Wright and co-workers[16] have shown that Grubb's second-generation catalysts bearing an imidazolidine ligand can cyclize dienes containing free amine group (Scheme 4).

Scheme -4



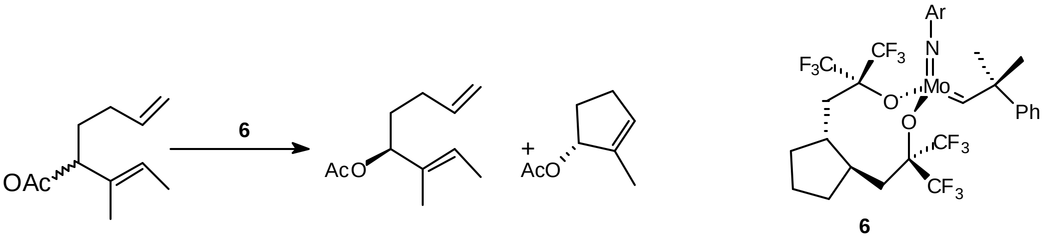
All the examples cited above and numerous related applications pertain to ring-closure of pre-assembled chiral centers. However, optically active products can result from an alkene metathesis in two ways. One concerns kinetic resolution. If the substrate features a stereogenic center and it is in the racemic form, use of a chiral catalyst – chirality imparted by an optically pure chiral ligand – results in a diastereomeric transition state of unequal energies of activation. As a result, one of the enantiomer of the substrate molecule reacts at a higher rate than the other effecting a kinetic resolution (Chart- 4).

Chart-4



Such a strategy was first utilized by Grubbs[17a] with an optically active molybdenum catalyst designed after Schrock's original version (Scheme-5).

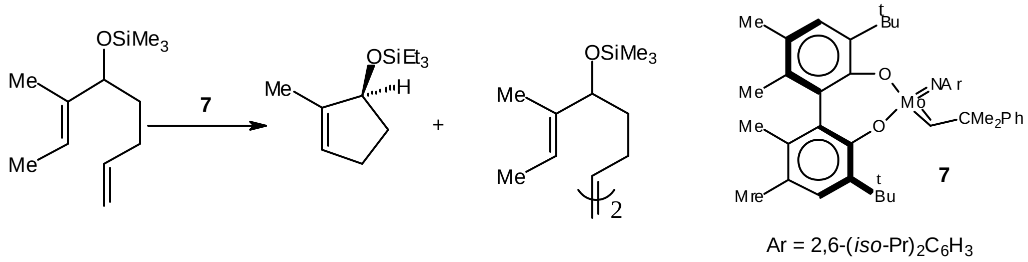
Scheme-5



10% (ee 87%) 90% (ee>99%)

Schrock and coworkers[17b] provided a similar illustration with a different optically active version of their molybdenum-based catalyst (Scheme-6).

Scheme-6

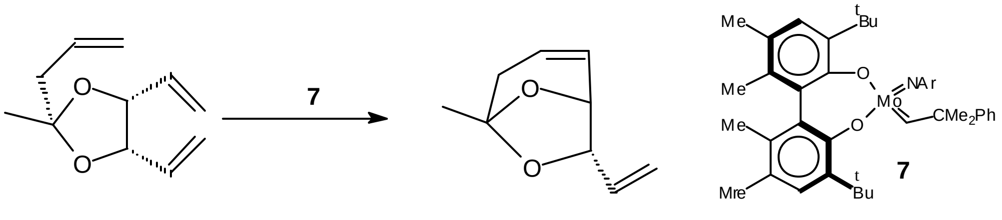


Ar = 2,6-(*iso*-Pr)$_2$C$_6$H$_3$

Reaction time: 10 min, conversion: 81%, product: 43%, dimer: 38%,
unreacted substrate: *ee*> 99%, cyclized product: *ee* 93%

The second option for producing chiral products enantioselectively involves desymmetrization of a symmetrical diene substrate where the product of metathesis is a cycloalkene that is chiral. Burke[18] developed a new strategy to synthesis natural products based on enantioselective desymmetrization of a *meso*-triene *via* ring-closing metathesis catalyzed by an optically active, chiral molybdenum-based catalyst (Scheme-7).

Scheme -7

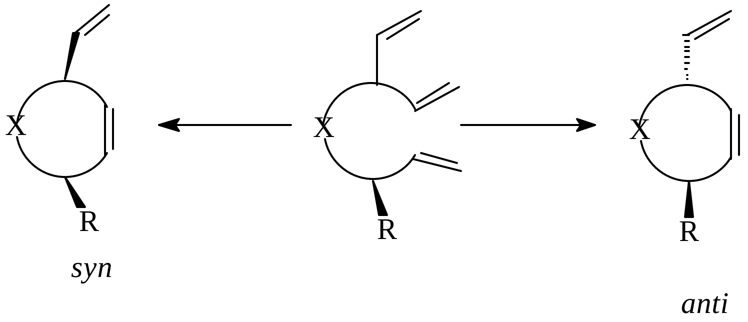


Ar = 2,6-(*iso*-Pr)$_2$C$_6$H$_3$

55-59% ee

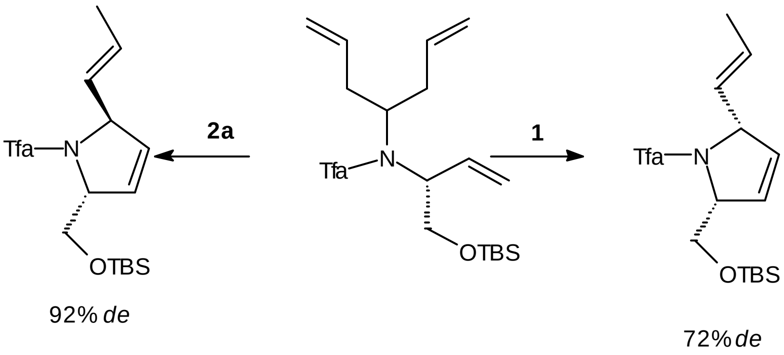
A stereogenic center in the substrate triene can induce stereoselectivity during the ring-formation step in RCM, as shown below (Chart-5). This is clearly a diastereoselective process.

Chart-5



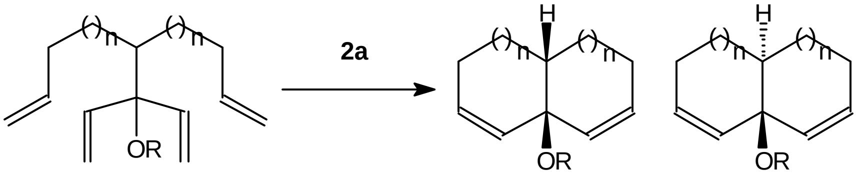
The first illustration of this concept was provided by Blechert[19] who used a chiral triene (Scheme-8).

Scheme -8



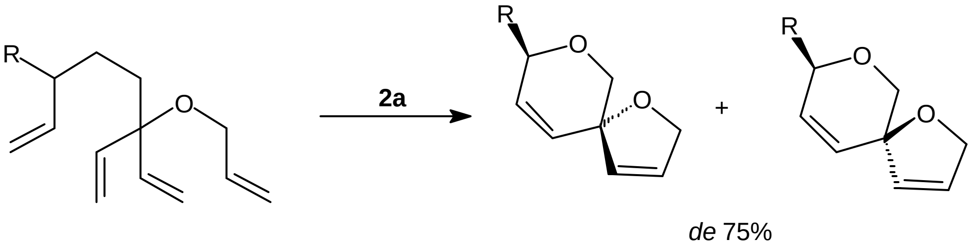
Lautens[20] developed a diastereoselective RCM approach (Scheme-9) to synthesize a novel class of bicyclic diallylic alcohol and ether, synthons for the tetrahydronaphthalene skeleton present in the HMG CoA reductase inhibitor, (+)-mevinolin.

Scheme -9



Schmidt[21] and others[22] have reported diastereoselective ring closing metathesis (Scheme-10) using Grubbs' catalys (**2a**).

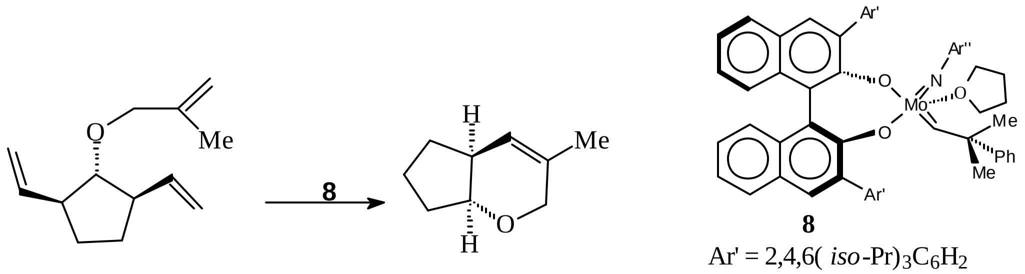
Scheme -10



R = 4-methoxyphenyl

Schrock[23] has recently reported desymmetrization in ring closing metathesis (Scheme-11) using a chiral molybdenum catalyst while Grubbs[24] has described the first example of enantioselective catalysis of alkene metathesis by a chiral derivative of new generation ruthenium complex (Scheme-12).

Scheme –11

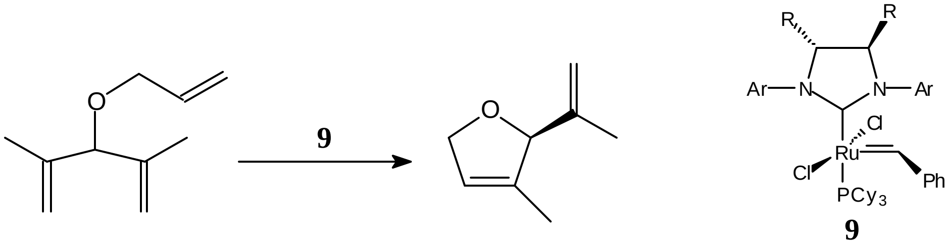


8

Ar' = 2,4,6(*iso*-Pr)$_3$C$_6$H$_2$
Ar'' = 2,6(*iso*-Pr)$_3$C$_6$H$_3$

84% (99% *ee*)

Scheme -12



9

ee 23%

Ar = o-methylphenyl
R = Phenyl

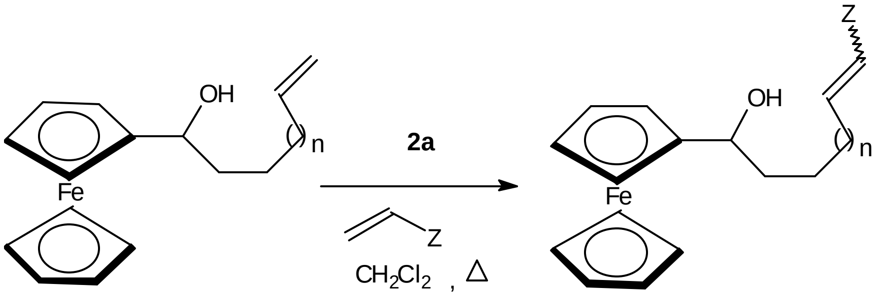
Present Work

The objective of the present work was to develop a widely adaptable approach to assemble chiral dienes of moderately complex structure with very high diastereoselectivity (as single enantiomer in some cases), which can be cyclized by RCM to chemically interesting scaffolds of different dimensions. Similar to some of the examples quoted above, it was not intended that RCM would introduce additional chiral element, hence a chiral catalyst was not necessary for these targets.

Organometallic π-complexes have often been used as stereochemical templates that provide steric protection to one face of the molecule so that reagents preferentially approach the reacting site from the *exo* (opposite-to-the-metal) face, and a stereoselective functionalization is achieved.

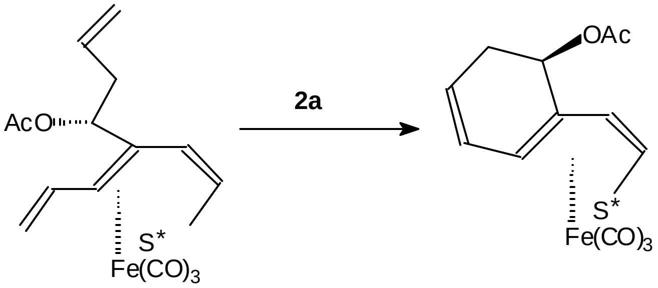
Although there was no evidence of RCM on dienes tethered on organometallic groups till early 1999, Lovely[25] recently reported the first example of organometallic derivatives participating in alkene metathesis (Scheme-13).

Scheme -13



Subsequently, Paley and co-workers[26] reported that they have used enantiopure η^4-(1-sulfinyldiene)-tricarbonyl-iron(0) complexes as template for constructing a carbocycle via RCM. A six-membered carbocycle (with one chiral center) and seven-, eight-, and nine-membered carbocycles (with two chiral centers) were obtained from respective pre-assembled chiral dienes using Grubbs' catalyst (Scheme-14)

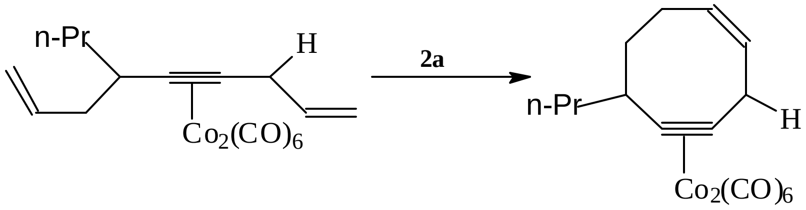
Scheme –14



S* = (R)-*p*-tolyl sulfoxide

Two groups independently described[27a-b] RCM in presence of haxacarbonyldicobalt-alkyne complex (Scheme-15).

Scheme -15

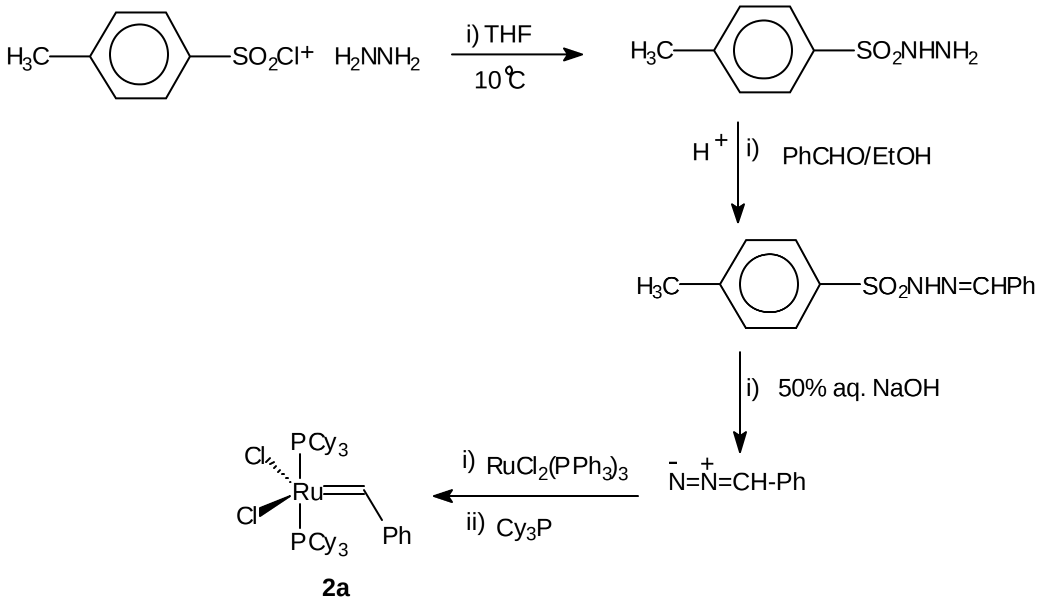


Arene-tricarbonylchromium has been used over last several years as a stereodirecting template for diastereoselective synthesis of diverse targets. In our laboratory, we have earlier synthesized a variety of functional structures with excellent diastereocontrol. It was therefore considered worthwhile to assemble several dienes stereoselectively on arene-chromium template as substrates for subsequent RCM reaction using Grubbs' ruthenium catalyst, **2a**.

Results and Discussion

We synthesized Grubbs' ruthenium catalyst (**2a**) in two steps starting from ruthenium trichloride following the reported procedure.[28] In the first step ruthenium trichloride was converted to $RuCl_2(PPh_3)_3$ and the complex was converted by a one-pot operation to the catalyst **2a** by sequential reaction with phenyldiazomethane and tricyclohexylphosphine, as shown in Scheme-16. The preparation was usually carried out in batches of 1-3 g and purity of the catalyst was established with the help of its proton NMR spectrum. The diagnostic signal at 20.02 ppm corresponds to the proton attached to the carbene carbon. The purple complex **2a** was stored in capped vials in a desiccator and usually used within a month.

Scheme -16



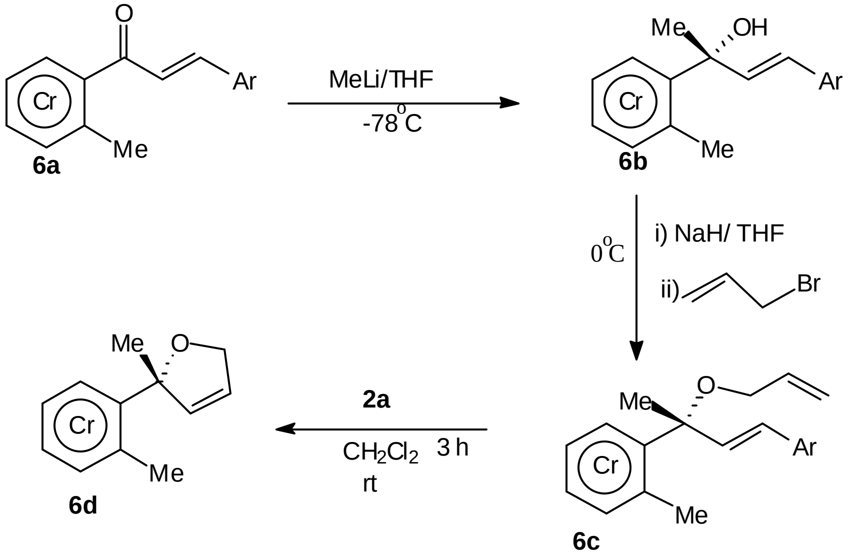
Tricarbonylchromium complexes were prepared by usual thermolysis reaction[29], purified by flash column chromatography and characterized by upfield proton resonances of the complexed aromatic ring protons. The ketone complexes are usually red in colour, while the others are yellow.

Most of the substrate dienes were prepared essentially following the procedures developed earlier in this laboratory and elsewhere. For some of them, specific preparative methods were developed. Advantage was taken of highly stereoselective nucleophilic addition to carbonyl functions adjacent to the Cr-complexed aromatic ring.

In all instances the relative stereochemistry of the stereogenic centers involved are either established earlier or closely precedented. Since RCM does not affect these centers, the stereochemistry depicted in the following schemes are acceptable. Terms like ‘complete diastereoselectivity’ and ‘single diastereomer’in the following passages imply that signals due to only one diastereomer of the purified product was observed and identified by proton NMR spectra recorded at 200 MHz.

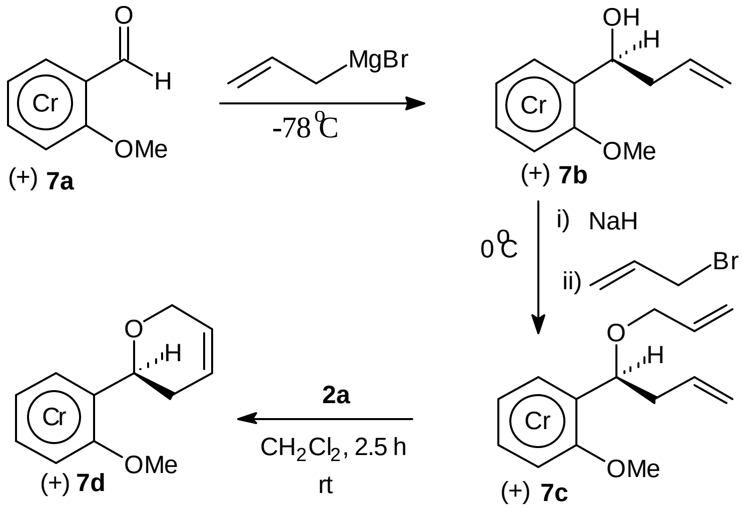
Reaction of methyllithium with enone complex **6a** at low temperature yielded the carbinol **6b** as a pure diastereomer. Unfavorable steric interaction between the *ortho*-Me substituent and carbonyl oxygen keeps them facing away from each other so that only one face of the carbonyl group is always exposed for nucleophilic attack.[30] This explains the high degree of diastereoselectivity observed in methyllithium addition. The low-field resonance of the β-olefinic proton (δ 7.49ppm) in **6a** is absent in the proton NMR spectrum of the product **6b** which features two olefinic protons at 6.69 ppm and 7.18 ppm respectively. The methyl singlet appears at 1.82 ppm confirming the addition. The carbinol **6b** was then converted to its allyl ether **6c** by treatment with sodium hydride and allyl bromide in THF. Room temperature stirring of a solution of **6c** in dichloromethane in presence of 10 mol% of the catalyst **2a** resulted in clean RCM within 3 h (Scheme-17). The product **6d** was isolated as a yellow solid in 90% yield, characterized by its typical proton signals in the NMR spectrum. A significant change is the disappearance of AB quartet at 3.97 ppm due to diastereotopic -O-CH_2- group present in the spectrum of **6c**, along with several typical multiplets due to terminal olefins, and the appearance of a different set of signals due to -O-CH_2- group at 4.78 ppm as well as the olefinic two-proton signal at 6.06 ppm for the five-membered ring.

Scheme - 17



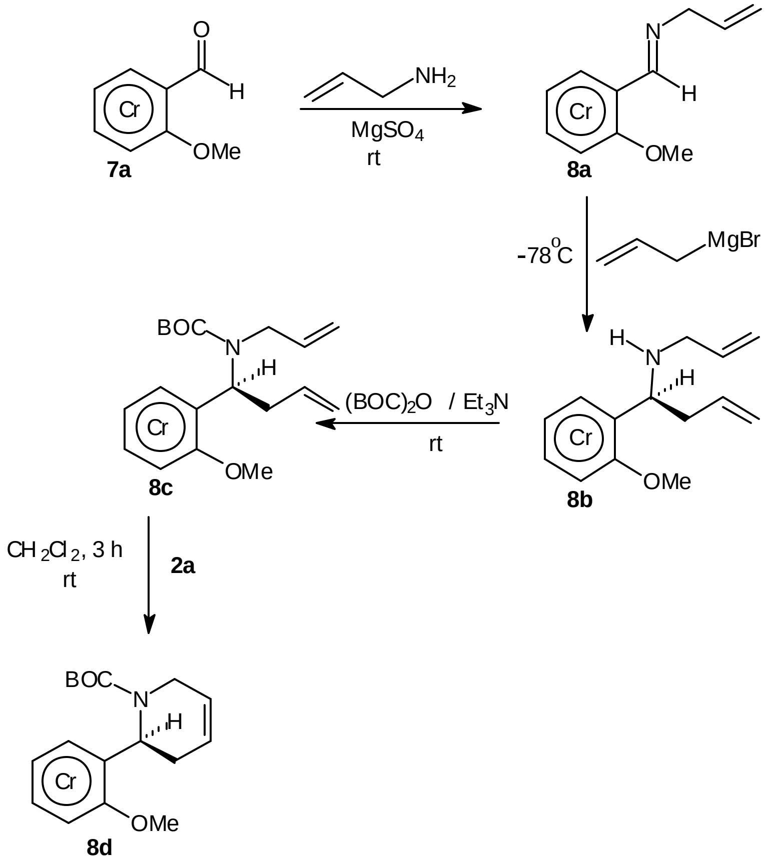
Optically pure, six-membered oxa-heterocycle **7d** was synthesized from optically pure *o*-anisaldehyde-Cr(CO)$_3$ complex, **7a** [the resolution of the racemic complex was carried out as described for complex **4c** in Chapter-II]. Addition of allylmagnesium bromide to (+)-**7a** at low temperature resulted in completely diastereoselective formation of the carbinol (+)-**7b** (*exo* addition to the *anti* conformer as above). This alcohol was converted to corresponding allyl ether, (+)-**7c**, on treatment with NaH/THF and allyl bromide. Optically active heterocycle (+)-**7d** was obtained on treatment with Grubbs' catalyst **2a** in dichloromethane at ambient temperature in excellent yield within 2.5 h (Scheme-18).

Scheme -18



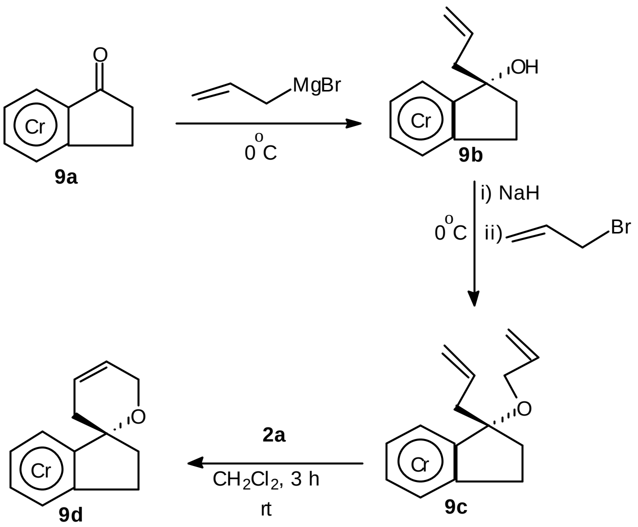
The chiral imine, **8a**, was prepared from *o*-anisaldehyde-Cr(CO) $_3$ complex, **7a**, and allylamine in presence of anhydrous $MgSO_4$ in dichloromethane by reported[31] procedure. The *exo*-selective addition of allylmagnesium bromide to imine **8a** resulted in the formation of diastereomerically pure amine, **8b** (predominant anti conformation). The free amine was protected[32] as *tert*-butyl carbamate **8c** by overnight stirring with di-*tert*-butyl carbonate in dichloromethane at room temperature in presence of triethylamine. The diene **8c** underwent RCM with Grubbs' ruthenium catalyst **2a** at ambient temperature in dichloromethane for 3 h to afford the corresponding azaheterocycle in good chemical yield (Scheme-19).

Scheme-19



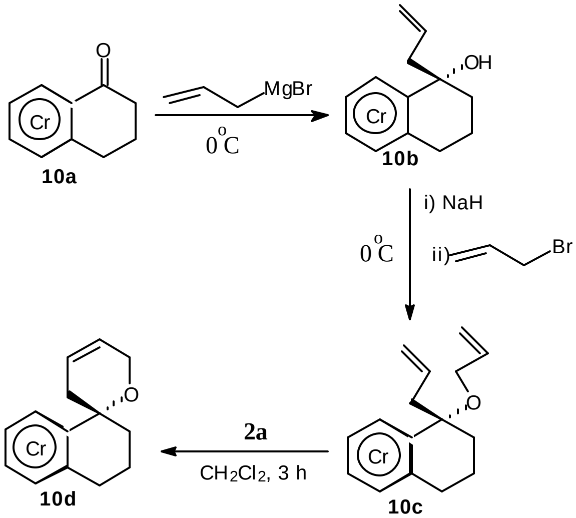
It is well established[33] that nucleophile adds to the carbonyl function of indanone-$Cr(CO)_3$ complex[34] **9a** exclusively from the *exo* face with complete diastereoselectivity. Thus, they are useful starting materials for the synthesis of chiral spirocycles. Addition of allylmagnesium bromide in THF at low temperature on complex **9a** produced diastereomerically pure allylic alcohol, **9b**. The corresponding allyl ether **9c** furnished the spirocycle, **9d**, by RCM as described above (Scheme-20).

Scheme -20



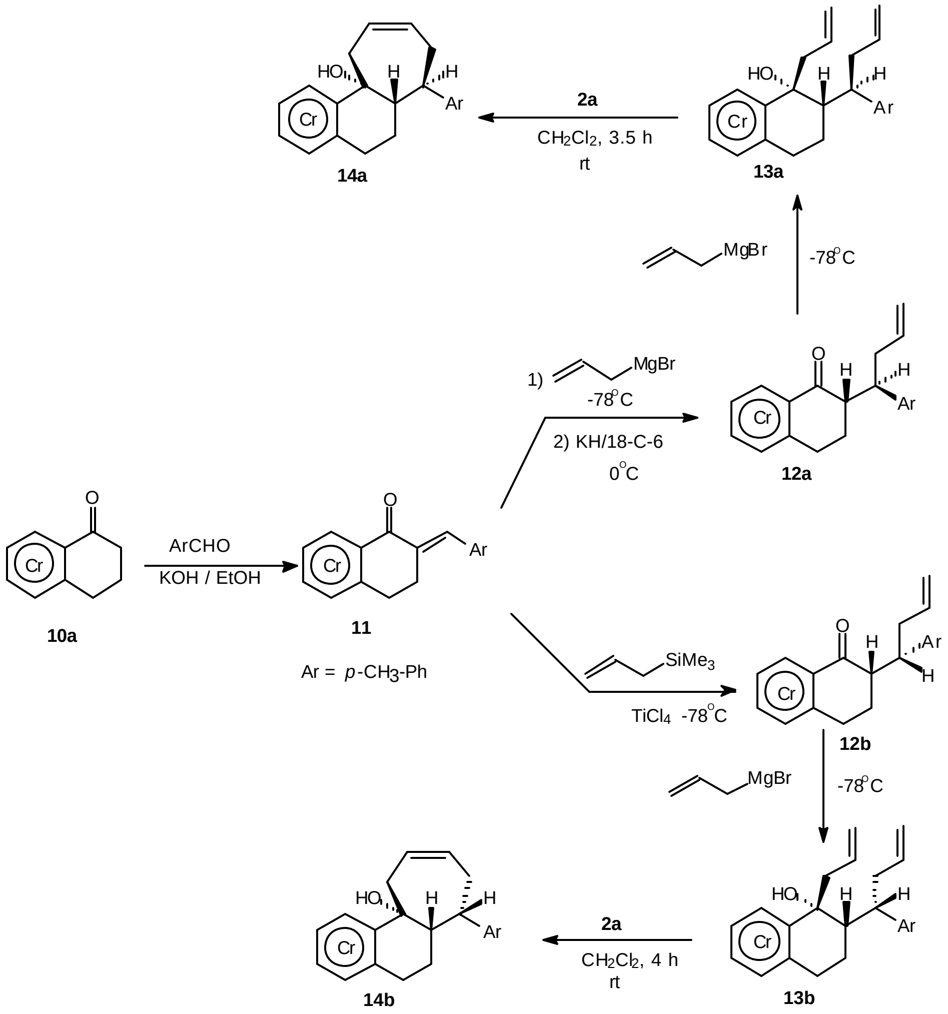
The higher homologue of **9d** was synthesized following essentially the same reaction sequence from 1-tetralone-$Cr(CO)_3$ complex[34], **10a** (Scheme-21). The allyl carbinol[33] **10b** was protected as an allyl ether, **10c**, which was subsequently subjected to RCM under usual condition.

Scheme -21



We proceeded further to create structures of higher complexity, and decided to use previous work[35] done in this laboratory towards that goal. For instance, it was possible to add an allyl group on chromium-anchored enone **11** in a stereodivergent manner - allylmagnesium bromide addition and followed by anionic oxy-Cope rearrangement by KH/Et_2O afforded exclusively *exo*-selective, formal 1,4-addition product **12a**, while allylithium or allylmagnesium bromide underwent exclusively *endo*-selective addition in presence of Lewis acid like $TiCl_4$ producing ketone **12b** (Scheme-22). These products were further elaborated to introduce a second allyl group with high *exo*-selectivity by treatment with allylmagnesium bromide. RCM at ambient temperature in dichloromethane afforded fused tricyclic systems whose stereochemical features were well-defined. Remarkably, the RCM proceeded without loss of efficiency in spite of the presence of an adjacent alcohol function.

Scheme -22



Summary

These reactions established the feasibility of a flexible synthetic design based on stereoselective functionalization attainable *via* arene-$Cr(CO)_3$ complexes. Ease of operation, reasonable reaction times, ambient temperature and low catalyst requirement are indeed convenient and useful features for this strategy, as exemplified by seven substrates leading to monocyclic products, spirocycles and fused polycyclic rings. These are the first examples of ring closing metathesis on tricarbonylchromium arene complexes.

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 dried over anhydrous P_2O_5. *O*-substituted aromatic aldehydes, tricyclohexylphosphine, $RuCl_3$, were purchased from Aldrich, USA and used as received. Allyl amine and allyl bromide were distilled before used. Grubbs' catalyst (**2a**) was prepared according to reported procedure[28] described bellow.

Typical procedure for the preparation of allylmagnesium bromide:

A two-necked flask, equipped with a double-surfaced condenser and a septum-capped dropping funnel fitted with a pressure equalizer, was cooled under argon. Allyl bromide (0.8 mL, 10 mmol) in 10 mL ether was added dropwise from the dropping funnel to the magnesium turning (300 mg, 12.5 mmol) activated by iodine in diethyl ether (5 mL). Approximately one third of the allyl bromide solution was added and the contents were allowed to stir until the ether began to reflux slowly. The remaining allyl bromide was added at such a rate that reflux is maintained without external heating. After the addition was complete, the reaction mixture was stirred at room temperature for 1-2 hrs.

General procedure for the preparation of carbinol complex [(+) 7b, 9b, 10b, 12a, 12b] from carbonyl complex [(+)7a, 9a, 10a, 13a, 13b] *:* To a solution of the complexed aldehyde (*n* mmol) in dry THF (20*n* mL), freshly prepared allylmagnesium bromide (1.5*n* mmol) in diethyl ether was added dropwise with stirring at –78 °C , after completion of the reaction (TLC, 30 min), the reaction mixture was quenched with degassed methanol at –78 °C followed by addition of water at room temperature, and finally extracted with dichloromethane. The crude product obtained was isolated by flash column chromatography. Reactions were performed in 1 mmol scale.

7b has been reported earlier.[36]

Complex (+)7b

Yield	90%
IR ($CHCl_3$):	3600 (br) 1961, 1870 cm^{-1}

^{1}H NMR (CDCl$_3$): (200 MHz)	1.95(s, 1H), 2.30-2.40(m, 1H), 2.50-2.60(m, 1H), 3.75 (s, 3H), 4.90-5.15 (m, 5H), 5.55 (t, 1H, J = 6Hz), 5.80-5.97 (m, 2H)
$[\alpha]_D^{25}$	(+) 100 (C = 0.065 CHCl$_3$)

Complex 9b

Yield	85%
Color:	Yellow
MP:	116 °C
IR (CHCl3):	3600 (br) 1961, 1870 cm^{-1}
^{1}H NMR (CDCl$_3$): (200 MHz)	1.86-2.10 (m, 2H), 2.15-2.49 (m, 3H), 2.62-2.78 (m, 2H), 4.95-5.30 (m, 4H), 5.47 (t, 1H, J = 6 Hz), 5.65 (d, 1H, J = 6 Hz), 5.76-5.97(m, 1H)
^{13}C NMR (CDCl$_3$): (50.3 MH$_Z$)	28.49, 39.19, 44.96, 81.28, 87.49, 88.92, 90.61, 95.35, 115.06, 119.39, 119.73, 132.66, 233.20
Analysis ($C_{15}H_{14}O_4Cr$)	Calcd. C: 58.06, H: 4.54 Found. C: 58.18, H: 4.40

10b

Yield	93%
Color:	Yellow
MP:	111 °C
IR (CHCl$_3$):	1956, 1886 cm^{-1}
^{1}H NMR (CDCl$_3$): (200 MHz)	1.60-1.95 (m, 5H), 2.49-2.95 (m, 4H), 5.00-5.25 (m, 4H), 5.50 (t, 1H, J = 6 Hz), 5.75-6.01 (m, 2H)
^{13}C NMR (CDCl$_3$): (50.3 MH$_Z$)	18.68, 27.35, 35.48, 46.72, 70.69, 89.18, 90.54, 92.41, 95.39, 112.26, 118.14, 119.28, 133.14, 233.56
Analysis ($C_{16}H_{16}O_4Cr$)	Calcd. C: 59.26, H: 4.97 Found. C: 59.23, H: 5.13

13a

Yield	89%

Color:	yellow
MP:	110 °C
IR (CHCl3):	1964, 1886 cm^{-1}
^{1}H NMR (CDCl$_3$): (200 MHz)	1.25-1.50 (m, 1H), 1,75-1.95(m, 2H including -OH), 2.00-2.10 (m, 1H), 2.34 (s, 3H), 2.36-2.75 (m, 2H), 2.80-2.95 (m, 1H), 3.15-3.25 (m, 1H), 4.85-5.25 (m, 6H), 5.30-5.70 (m, 3H), 5.75 (d, 1H, J = 6 Hz), 7.10-7.25(m, 4H)
^{13}C NMR (CDCl$_3$): (50.3 MH$_Z$)	21.21, 22.65, 30.04, 40.01, 44.96, 45.40, 47.75, 73.48, 89.58, 90.72, 92.05, 94.77, 113.59, 116.53, 118.14, 120.09, 129.28, 132.99, 136.12, 137.44, 139.44, 233.09
Analysis ($C_{27}H_{28}O_5Cr$)	Calcd. C: 66.93, H: 5.82 Found. C: 66.83, H: 5.96

13b

Yield	88%
Color:	Yellow
MP:	56 °C
IR (CHCl3):	1966, 1880 cm^{-1}
^{1}H NMR (CDCl$_3$): (200 MHz)	1.75-2.10 (m, 4H including –OH), 2.34 (s, 3H), 2.39-2.85 (m, 6H), 3.23-3.36 (m, 1H), 4.75-5.10 (m, 5H), 5.15-5.45 (m, 2H), 5.50-5.75 (m, 2H), 5.81 (d, 1H, J = 7 Hz), 7.16 (m, 4H)
^{13}C NMR (CDCl$_3$): (50.3 MH$_Z$)	20.63, 21.21, 29.34, 36.21, 43.23, 46.72, 47.39, 73.37, 88.57 89.99, 92.86, 95.76, 114.21, 116.27, 117.26, 119.95, 128.18, 129.43, 132.88, 135.97, 137.41, 142.37, 233.09.
Analysis ($C_{27}H_{28}O_5Cr$)	Calcd. C: 66.93, H: 5.82 Found. C: 66. 76 H: 5.91

General procedure for the preparation of allyl ether (6c, 7c, 9c, 10c) from carbinol (6b, 7b, 9b, 10b)*:* NaH (48 mg, 60% dispersion in mineral oil, 1.2 mmol,) was washed with dry benzene and then dry ether, dried by removing ether under vacuum. To the stirring suspension of NaH in 5 mL THF at 0 °C, alcohol (1 mmol) in 5mL THF was added slowly. The reaction mixture was allowed to stir at room temperature for one hour. Allyl bromide 0.1 mL (1.2 mmol) was added and stirred for one more hour. Reaction mixture was quenched with saturated ammonium chloride solution. THF was removed under vacuum. Reaction mixture was extracted with ether. Ether layer was washed with water for several times. Ether layer was dried over sodium sulphate and concentrated in vacuo. The crude product was then flash chromatographed using petroleum ether/ acetone as eluent to yield pure allyl ether in good yield.

Complex 6c

Yield	85%
Color :	Yellow
MP :	78 °C
IR (CHCl$_3$) :	1966, 1888 cm^{-1}
^{1}H NMR (CDCl$_3$) : (200 MHz)	1.75 (s, 3H), 2.36 (s, 3H), 2.42 (s, 3H), 4.95-5.05 (m, 2H), 5.17 (d, 1H, J = 10 Hz), 5.37 (d, 1H, J = 16 Hz), 5.53 (t, 1H, J = 6 Hz), 5.80(d, 1H, J = 6 Hz), 6.33 (d, 1H, J = 18 Hz), 6.70 (d, 1H, J = 18 Hz)
^{13}C NMR (CDCl$_3$) :(50.3 MH$_Z$)	20.21, 20.84, 22.18, 64.00, 78.59, 87.30, 93.22, 95.94, 96.01, 111.31, 114.65, 115.90, 126.82, 129.65, 131.38,132.59,133.66, 135.35,138.14, 233.60
Analysis	Calcd. C: 67.8; H: 5.56;
($C_{24}H_{24}O_4Cr$)	Found C: 67.53, H 5.43.

Complex (+) 7c

Yield	84%
Color:	Yellow
MP:	66 °C
IR (CHCl$_3$):	1964, 1886 cm^{-1}
^{1}H NMR (CDCl$_3$): (200 MHz)	2.25-2.38 (m, 1H), 2.45-2.65 (m, 1H), 3.74 (s, 1H), 4.14 (dd, 1H, J = 6 Hz, 12 Hz), 4.40 (dd, 1H, J = 6 Hz, 12 Hz), 4.52-4.58 (m, 1H), 4.89-5.08 (m, 4H), 5.23 (d, 1H, J = 10 Hz), 5.39 (d, 1H J = 16 Hz), 5.53 (t, 1H, J = 6 Hz), 5.79-6.09 (m,

	3H)
^{13}CNMR (CDCl$_3$): (50.3 MH$_Z$)	41.65, 55.92, 71.90, 73.70, 74.26, 85.06, 93.41, 94.36, 102.08, 117.48, 17.74, 134.21, 134.94, 140.57, 233.49
Analysis ($C_{17}H_{18}O_5Cr$)	Calcd. C: 57.62, H: 5.12 Found. C: 57.42, H: 5.29
$[\alpha]_D^{25}$	+ 82.2 (C, 0.35 CHCl$_3$)

Complex 9c

Yield	89%
Color:	Yellow
MP:	72 °C
IR (CHCl$_3$):	1952, 1867 cm^{-1}
^{1}H NMR (CDCl$_3$): (200 MHz)	2.00-2.45 (m, 3H), 2.55-2.85 (m, 3H), 4.13 (d, 2H, J = 6 Hz), 4.85-5.20 (m, 5H), 5.35-5.45 (m, 2H), 5.59 (d, 1H, J = 6.3 Hz), 5.76-6.10 (m, 2H)
^{13}CNMR (CDCl$_3$): (50.3 MH$_Z$)	29.01, 34.92, 42.42, 64.70, 85.50, 87.01, 88.22, 91.38, 94.77, 113.62, 116.01,116.90, 119.21, 132.44, 135.31, 233.38
Analysis ($C_{18}H_{18}O_4Cr$)	Calcd. C: 61.71, H: 5.18 Found. C: 61.59, H: 5.27

Complex 10c

Yield	94%
Color:	Yellow
MP:	55 °C
IR (CHCl$_3$):	1958, 1866 cm^{-1}
^{1}H NMR (CDCl$_3$): (200 MHz)	1.72-2.10 (m, 4H), 2.35-2.86 (m, 4H), 4.08 (dd, 1H, J = 12 Hz 6 Hz,), 4.33 (dd, 1H, J = 12 Hz, 6 Hz,), 4.94-5.15 (m, 5H), 5.20-5.50(m, 2H), 5.69-6.11 (m, 3H)
^{13}C NMR (CDCl$_3$): (50.3 MH$_Z$)	18.90, 27.02, 30.26, 45.95, 63.34, 75.13, 88.22, 90.21, 92.71, 95.24, 11.31, 114.43, 115.83, 118.84, 133.18, 135.64, 233.78
Analysis	Calcd. C: 62.63, H: 5.53

($C_{19}H_{20}O_4Cr$)	Found. C: 62.72, H: 5.42

Typical procedure for the preparation of cyclic compound (6d-10d, 14a, 14b) from diene (6c-10c, 13a, 13b) : To a solution of diene (*n* mmol) in CH_2Cl_2 (15*n* mL) was added $RuCl_2(Pcy_3)_2CHC_6H_5$ (10 mol%) with stirring under an inert atmosphere of argon at room temperature for 2.5-4.0 hour. The reaction mixture was concentrated in vacuo, and the crude product was purified by flash column chromatography (pet ether/ EtOAc 10:1) to obtained the desired product as yellow solid (78-90%). All reactions were carried out in 1mmol scale.

Complex 6d

Yield	90%
Color:	Yellow
MP:	118 °C
IR ($CHCl_3$):	1964, 1866 cm^{-1}
^{1}H NMR ($CDCl_3$): (200 MHz)	1.64 (s, 3H), 2.44 (s, 3H), 4.69-4.84 (m, 2H), 5.49 (t, 1H, J = 6 Hz), 5.60 (d, 1H, J = 6 Hz), 5.91-6.05 (m, 2H)
^{13}C NMR ($CDCl_3$): (50.3 MHz)	20.48, 29.52, 75.06, 87.23, 90.06, 92.89,95.10, 110.10, 95.98, 115.24, 128.40, 131.63, 233.53
Analysis	Calcd. C: 58.06, H: 4.54
($C_{15}H_{14}O_4Cr$)	Found. C: 58.17, H: 4.32

Complex (+)7d

Yield	88%
Color:	Yellow
MP:	78 °C
IR ($CHCl_3$):	1956, 1866 cm^{-1}
^{1}H NMR ($CDCl_3$): (200 MHz)	1.95-2.11 (m, 1H), 2.30-2.50 (m, 1H), 3.76 (s, 3H), 4.31-4.44 (m, 2H), 5.09 (d, 1H, J = 6 Hz) 4.56 (dd, 1H, J = 2 Hz, 10 Hz), 4.96 (t, 1H, J = 6 Hz), 5.44(t, 1H, J = 6 Hz), 5.81-5.88(m, 3H)

^{13}C NMR (CDCl$_3$): (50.3 MH$_Z$)	32.65, 50.06, 66.87, 69.77, 74.66, 86.20, 92.45, 92.93, 103.66, 124.10, 126.60, 140.35, 233.60
Analysis	Calcd. C: 55.22, H: 4.32
($C_{15}H_{14}O_5Cr$)	Found. C: 55.20, H: 4.25
$[\alpha]_D^{25}$	+ 67.2 (C, 0.35 in CHCl$_3$)

Complex 8d

Yield	78%
Color:	Yellow
MP:	135 °C
IR (CHCl$_3$):	1962, 1874, 1692 cm^{-1}
^{1}H NMR (CDCl$_3$): (200 MHz)	1.46 (s, 9H), 2.38-2.48 (m, 1H), 2.61-2.79 (m, 1H), 3.42 (d, 1H, J = 8 Hz), 3.75 (s, 3H), 4.30 (d, 1H, J = 8 Hz), 4.80 (t, 1H, J = 6.4 Hz), 5.00 (d, 1H, J = 6.4 Hz), 5.51-5.60 (m, 2H), 5.75-5.85 (m, 2H), 5.95-6.05 (m, 1H)
^{13}C NMR (CDCl$_3$): (50.3 MH$_Z$)	28.43, 40.51, 46.14, 55.91, 73.48, 80.03, 83.96, 94.84, 95.32, 101.20, 124.58, 124.83, 142.70, 154.58, 233.16
Analysis	Calcd. C: 56.46, H: 5.45, N: 3.29
($C_{20}H_{23}O_6NCr$)	Found. C: 56.31, H: 5.41, N: 3.03

Complex 9d

Yield	86%
Color:	Yellow
MP:	152 °C
IR (CHCl$_3$):	1968, 1896 cm^{-1}
^{1}H NMR (CDCl$_3$): (200 MHz)	1.92-2.31 (m, 4H), 2.72-2.78 (m, 2H), 4.34 (bs, 2H), 5.10-5.37 (m, 3H), 5.45 (d, 1H, J = 6 Hz), 5.83 (bs, 2H)
^{13}C NMR (CDCl$_3$):	28.57, 34.34. 34.78, 63.15, 80.50, 87.67, 89.62, 93.74, 113.55,

(50.3 MH$_{Z}$)	118.66, 122.67, 126.82, 233.38
Analysis	Calcd. C: 59.63, H: 4.37
($C_{16}H_{14}O_{4}Cr$)	Found. C: 59.71, H: 4.31

Complex 10d

Yield	85%
Color:	Yellow
MP:	142 °C
IR ($CHCl_3$):	1966, 1890 cm^{-1}
^{1}H NMR ($CDCl_3$): (200 MHz)	1.66-1.72 (m, 2H), 1.94-2.00 (m, 1H), 2.10-2.45 (m, 3H), 2.53-2.90 (m, 2H), 4.37 (bs, 2H), 5.07-5.17 (qt, 2H, J = 6 Hz), 5.38 (t, 1H, J = 6.4 Hz), 5.75-5.95 (m, 3H)
^{13}C NMR ($CDCl_3$): (50.3 MH$_{Z}$)	18.90, 27.43, 28.49, 36.51, 61.91, 70.03, 89.62, 90.58, 92.16, 93.59, 111.05, 117.15, 122.70, 126.27, 233.78
Analysis	Calcd. C: 60.71, H: 4.79
($C_{17}H_{16}O_{4}Cr$)	Found. C: 60.68, H: 4.91

Complex 14a

Yield	80%
Color:	Yellow
MP:	170 °C
IR ($CHCl_3$):	1968, 1892 cm^{-1}
^{1}H NMR ($CDCl_3$): (200 MHz)	1.28-1.65 (m, 3H), 1.92-2.09(td, 1H, J = 3Hz, 12Hz) 2.21 (s, 1H), 2.36 (s, 3H), 2.38-2.61(m, 3H), 2.69-3.04 (m, 3H), 5,02 (d, 1H, J = 6 Hz), 5.21 (t, 1H, J = 6 Hz), 5.49 (t, 1H, J = 6 Hz), 5.72-5.87 (m, 1H), 5.95 (d, 1H, J = 6 Hz), 6.03-6.16 (m, 1H), 7.12 (bs, 4H)
^{13}C NMR ($CDCl_3$): (50.3 MH$_{Z}$)	21.21, 24.38, 31.29, 35.88, 45.14, 45.40, 52.61, 69.51, 88.19, 89.40, 93.70, 96.24, 114.29, 120.31, 126.86, 127.52, 129.54, 132.26, 136.01, 143.95, 233.01
Analysis	Calcd. C: 65.78, H: 5.30
($C_{25}H_{24}O_{5}Cr$)	Found. C: 65.71, H: 5.19

Complex 14b

Yield	80%
Color:	Yellow
MP:	90 °C
IR (CHCl$_3$):	1970, 1886 cm^{-1}
^{1}HNMR (CDCl$_3$): (200 MHz)	0.81-1.04 (m, 1H), 1.29-1.57 (m, 2H), 2.09 (s, 1H), 2.15-2.30 (m, 1H), 2.34 (s, 3H), 2.36-2.72(m, 3H), 2.74-2.90 (m, 3H), 3.30-3.41 (m, 1H), 5.15-5.21 (m, 2H), 5.41-5.49 (m, 2H), 5.63-5.72 (m, 1H), 5.79 (d, 1H, J = 8 Hz), 5.94-6.12 (m, 1H), 7.11(d, 2H, J = 8 Hz), 7.27 (d, 2H, J = 8 Hz)
^{13}CNMR (CDCl$_3$): (50.3 MH$_Z$)	21.14, 23.57, 29.96, 31.76, 44.15, 47.50, 48.01, 72.09, 88.52, 90.65, 92.01, 95.13, 112.63, 121.49, 126.42, 126.82, 127.48, 129.06,129.50, 131.01, 136.08, 140.27, 233.05
Analysis	Calcd. C: 65.78, H: 5.30
($C_{25}H_{24}O_5Cr$)	Found. C: 65.71, H: 5.19

Synthesis of chiral diene 8c: This compound was synthesized in three steps starting from *o*-anisaldehyde complex from **7a.**

Preparation of allylimine complex 8a: The mixture of **7a** (1.08g, 4.00 mmol)**,** allyl amine (0.36mL, 4.8 mmol) and anhydrous MgSO$_4$ (0.48g, 4mmol) was stirred in CH$_2$Cl$_2$ for overnight. The mixture was filtered through celite and recrystallization from CH$_2$Cl$_2$ / pet ether afforded crystalline imine **8a** (1.2g, 97%).

Complex 8a

Yield	97%
Color:	Yellow
MP:	71 °C
IR (CHCl$_3$):	1616, 1896, 1969 cm^{-1}

^{1}H NMR (CDCl$_3$): (200 MHz)	3.84 (s, 3H), 4.22 (d, 2H, J = 4 Hz), 4.96-5.28 (m, 4H), 5.69 (t, 1H, J = 6 Hz),5.93-6.12 (m, 1H), 6.47 (d, 1H, J = 8 Hz), 8.34 (s, 1H)
^{13}C NMR (CDCl$_3$): (50.3 MH$_Z$)	56.06, 63.19, 73.48, 85.28, 90.32, 93.26, 94.73, 116.34, 135.75, 143.29, 154.98, 234.54
Analysis	Calcd. C: 54.02, H: 4.21, N: 4.50
($C_{14}H_{13}NCrO_4$)	Found C: 54.19, H: 4.11, N: 4.40

Preparation of complexed amine 8b: Freshly prepared allylmagnesium bromide (4.6 mmol) in ether was added to the solution of imine **8a** (1.2g, 3.8 mmol) in THF at –78 °C. After completion of the reaction (TLC, 15 minutes), the reaction mixture was quenched with degassed methanol at –78 °C followed by addition of water at room temperature and finally was extracted with dichloromethane and washed several times with water. It was then dried dried over anhydrous Na_2SO_4, concentrated in vacuum, and crude product was flash chromatographed (pet ether/acetone, 9:1) to obtained isolated amine **8b** (1.25g, 92%).

Complex 8b

Yield	92%
Color:	Yellow
MP:	65 °C
IR (CHCl$_3$):	1968, 1859 cm^{-1}
^{1}H NMR (CDCl$_3$): (200 MHz)	1.5 (bs, 1H), 2.23-2.39(m, 1H), 2.57-2.68 (m, 1H), 3.01-3.21(m, 2H), 3.78 (s, 3H), 3.81-3.88 (m, 1H), 4.85 (t, 1H, J = 6 Hz), 4.88-5.25 (m, 5H), 5.59 (t, 1H, J = 6 Hz), 5.73-6.02 (m, 3H)
^{13}CNMR (CDCl$_3$): (50.3 MH$_Z$)	41.28, 50.69, 53.38 55.77, 73.93, 85.28, 94.40, 104.84, 115.94, 118.37, 134.50, 136.96, 141.38, 233.64
Analysis	Calcd. C: 57.78, H: 5.42, N: 3.96
($C_{17}H_{19}O_4NCr$)	Found. C: 57.61, H: 5.49, N: 3.85

Protection of amine 8b as *tert*-butyl carbamate 8c: A solution of di-*tert*-butyl carbonate (0.253g, 2.4 mmol) in CH_2Cl_2 (5 mL) was added to the stirred solution of complex of amine **8b** (0.706g, 2.4 mmol) and triethylamine (0.33 mL, 2.4 mmol) in CH_2Cl_2 (10 mL) at ambient temperature. After 3 hours stirring, solvent was evaporated under vacuum, and the residue was dissolved in EtOAc (20 mL). The solution was washed with water and brine. The organic layer was dried over anhydrous Na_2SO_4, concentrated and crude product was flash chromatographed (pet ether/acetone, 10:1) to furnish 85% (0.770 g) yield of BOC-protected amine complex **8c.**

Complex 8c	
Yield	85%
Color:	Yellow
MP:	Oil
IR ($CHCl_3$):	1969, 1864, 1689 cm^{-1}
^1H NMR ($CDCl_3$): (200 MHz	1.42 (s, 3H), 1.48 (s, 6H), 2.42-2.87 (m, 2H), 3.57-3.66 (m, 1H), 3.73 (s, 3H), 3.79-3.88 (m, 1H), 4.91-5.18 (m, 7H), 5.49-5.95 (m, 4H),
^{13}C NMR	Was not taken as the complex is very unstable in solution.
Analysis	Calcd. C: 58.27, H: 6.00, N: 3.08
($C_{22}H_{27}O_6NCr$)	Found. C: 58.10, H: 5.85, N: 3.13

Preparation of 2-benzylidene-1-tetralone complex 11: A solution of *p*-tolualdehyde (0.65 mL, 5.5 mmol) and 1- tetralone tricarbonyl complex **10a** (1.41g, 5.0 mmol in ethanol (30 mL) was cooled in an ice-salt bath. An ethanolic solution of KOH (0.366g, 6.0 mmol) in 10 mL ethanol was added dropwise via syringes. The reaction was monitored by TLC. After complete disappearance of starting material (3 hours), the reaction mixture was worked up as usual to provide deep orange solid product.The crude products were washed with petroleum ether (3 x 20 mL) and recrystallized from CH_2Cl_2-petether to afford analytical pure crystalline complex **11** (1.82g, 95%). **11** is reported in ref. 36.

Preparation of 12a from complex 11: Freshly prepared allylmagnesium bromide (4.8 mmol) in ether was added to the complex tetralone benzilidine **11** (1.53 g, 4mmol) in THF at –78 °C. After 30 minute stirring, reaction mixture was quenched with saturated ammonium chloride solution at room temperature. After usual workup the crude product (1.56 g, 90%) was obtained. Then to the ethereal suspension of thoroughly washed KH (17 mg, 3.60 mmol), a solution of crude product (1.56g, 3.59 mmol) in ether was added slowly at 0 °C. Finally, 18-C-6 (0.47 mg, 5mol%) was added. Reaction mixture was allowed to stir at 0 °C. The reaction was monitored by TLC and upon consumption of starting material (2.5 h) it was quenched with saturated ammonium chloride solution and extracted with ether. Purification of crude product by flash column chromatography afforded ketone **12a** (1.06g, 83%). The complex **12a** has been reported reported earlier.[36]

Complex 12a	
Yield	83%
Color:	Yellow
MP:	131 °C
IR ($CHCl_3$):	1980, 1910, 1680 cm^{-1}
^{1}HNMR ($CDCl_3$): (200 MHz)	166-1.72 (m, 1H), 1.90-2.04 (m, 1H), 2.30 (s, 3H), 2.59 –2.94 (m, 5H), 3.73 (m, 1H), 4.95-5.10 (m, 3H), 5.20 (t, 1H, J = 6 Hz), 5.62-5.80 (m, 2H), 6.20 (d, 1H, J = 6.8 Hz), 7.07 (bs, 4H).

1,4 Allyl addition on complex 11 to produce ketone 12b*:* To a solution of complexed enone **11** (1.53g, 4.0 mmol) in dichloromethane (30mL), titanium tetrachloride (0.90mL, 8.0mmol) was added with stirring at -78°C. After stirring for 15 minutes allylmagnesium bromide (4.8 mmol) in dichloromethane was added dropwise with stirring at the same temperature. After completion of the reaction (TLC, 30 minutes), the reaction mixtures was quenched with degassed methanol at -78°C, followed by addition of water at room temperature, and finally extracted with dichloromethane. The crude mixtures of products obtained by evaporation of solvent, was separated by flash column chromatography. Yield of **12b** (1.36g, 79%). **12b** is also reported earlier.[36]

12b

Color: Orange

MP: 160-162 °C

IR ($CHCl_3$): 1980, 1910, 1670 cm^{-1}

^{1}H NMR ($CDCl_3$): (200 MHz) 1.90-2.10(m, 2H), 2.40 (s, 3H), 2.45-2.90 (m, 5H), 3.80-3.90 (m, 1H), 4.85-5.15 (m, 3H), 5.30 (t, 1H, J = 7 Hz), 5.55-5.80 (m, 2H), 6.20 (d, 1H, J = 6 Hz), 7.10-7.20 (bs, 4H)

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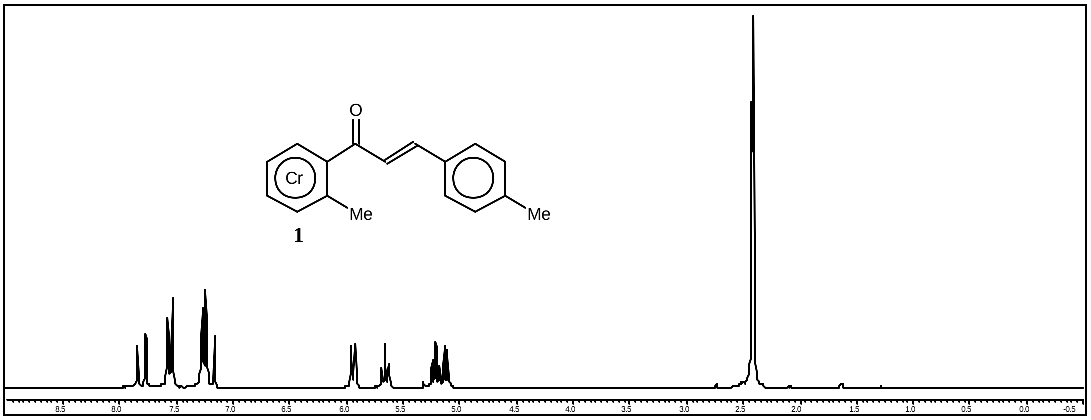
36. Ph. D. dissertation of Dr. S. Sur, **1997**, University of Poona, India.

Appendix-I

Spectra of Compounds – Chapter I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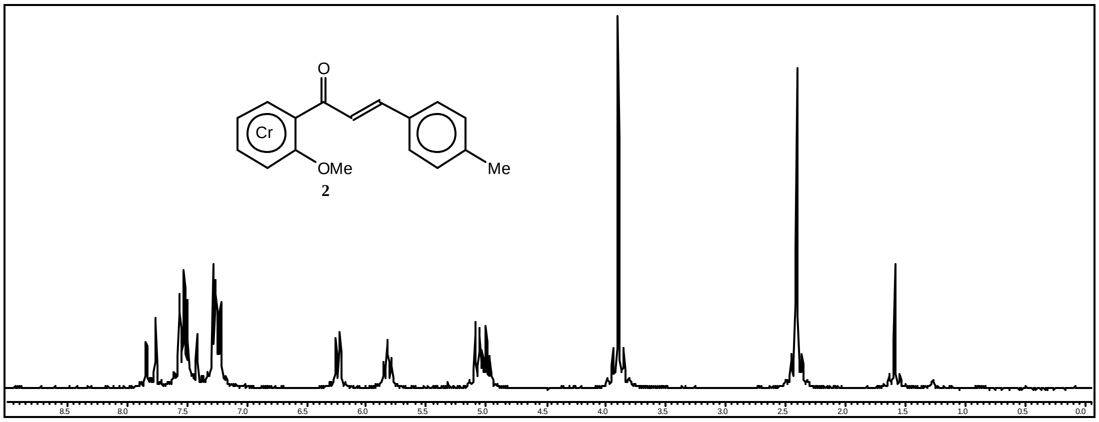
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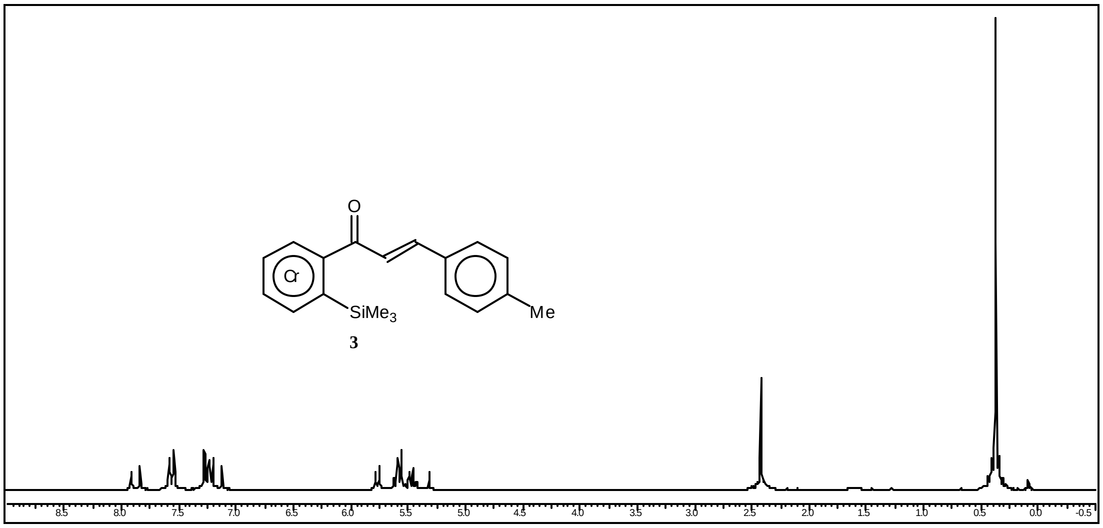
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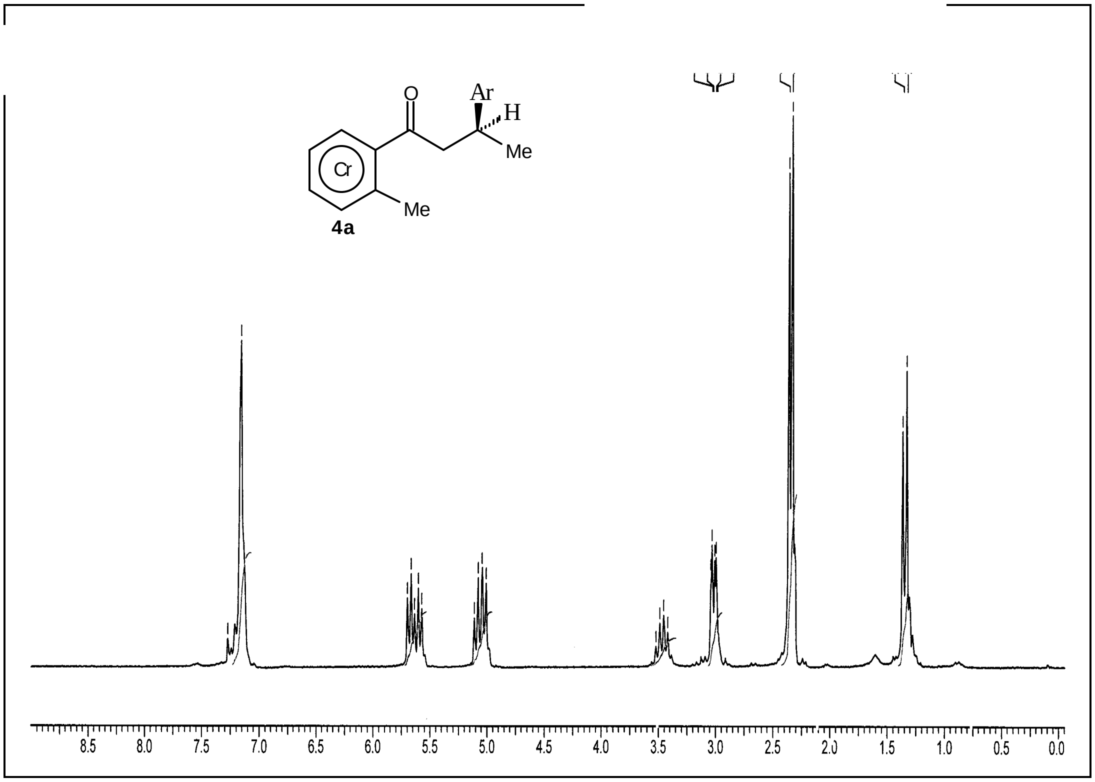
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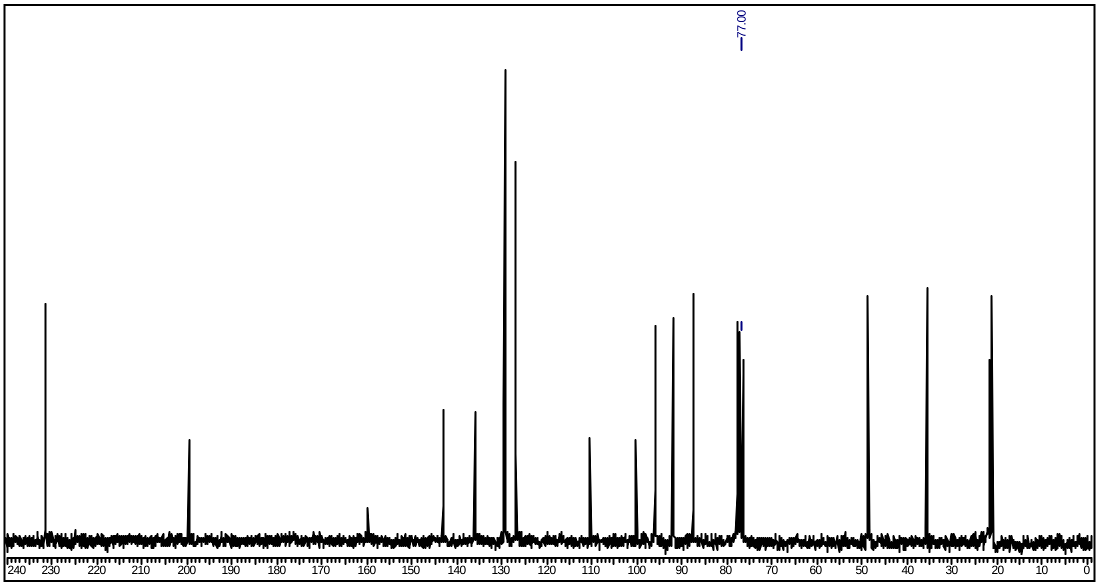
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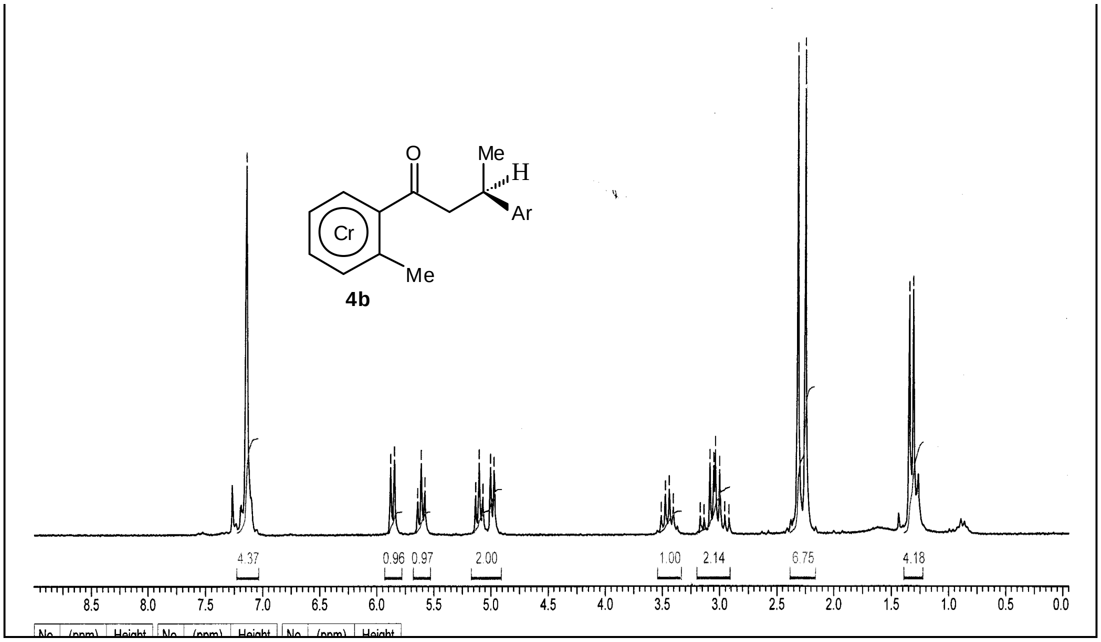
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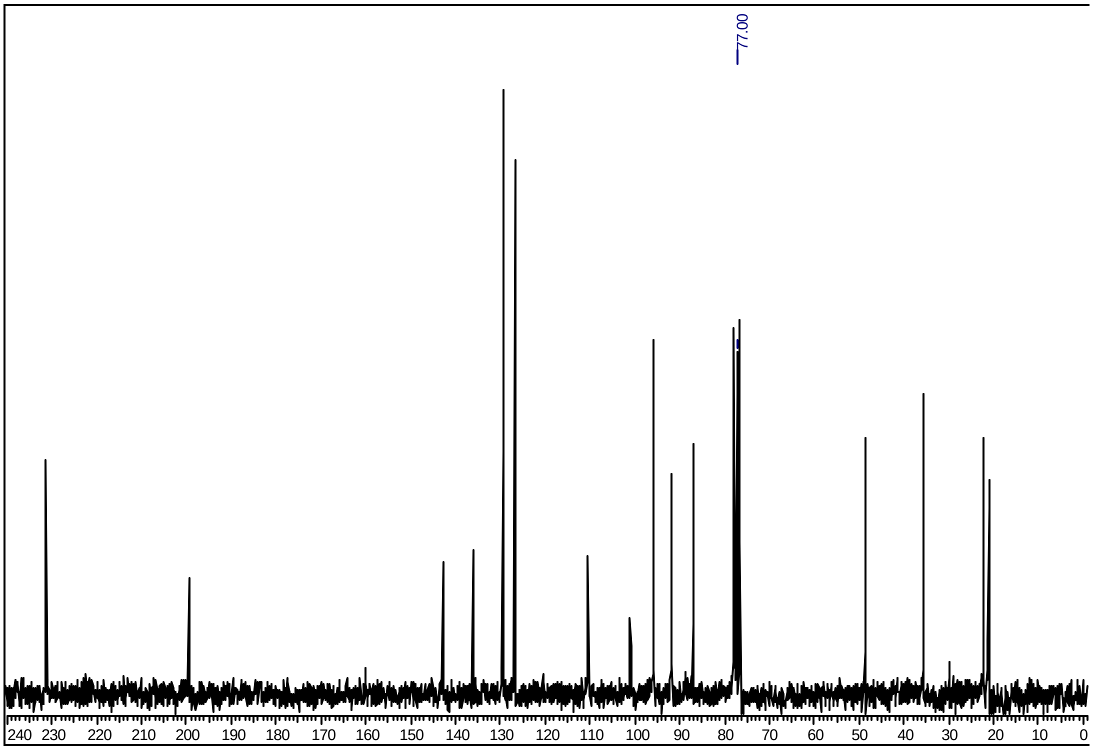
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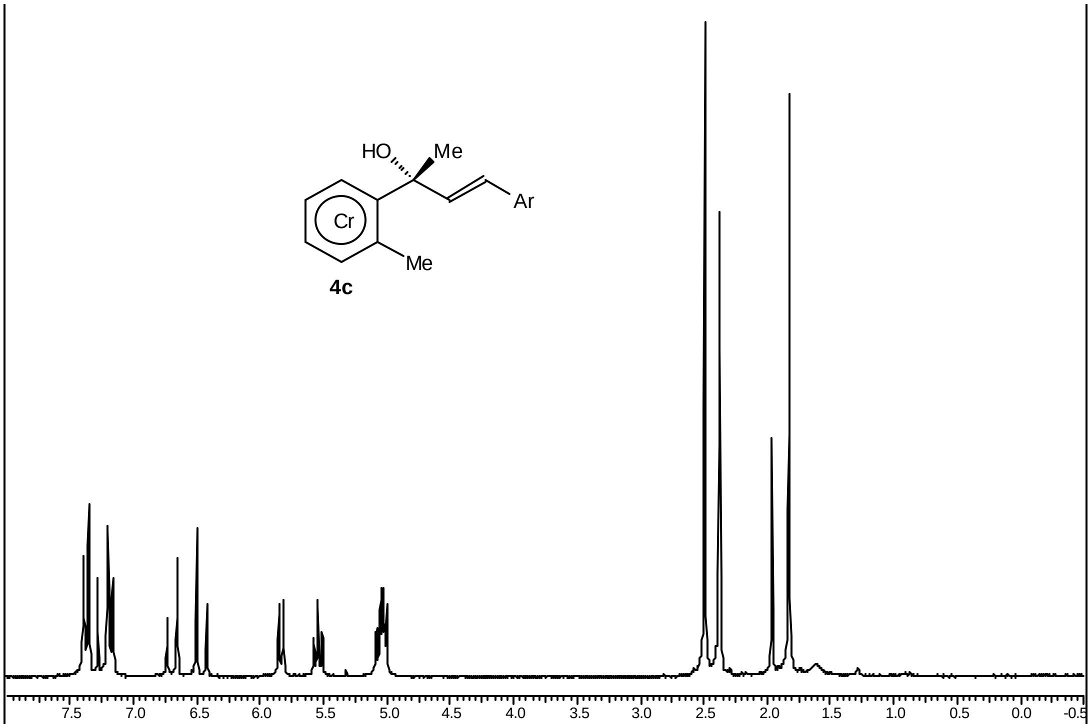
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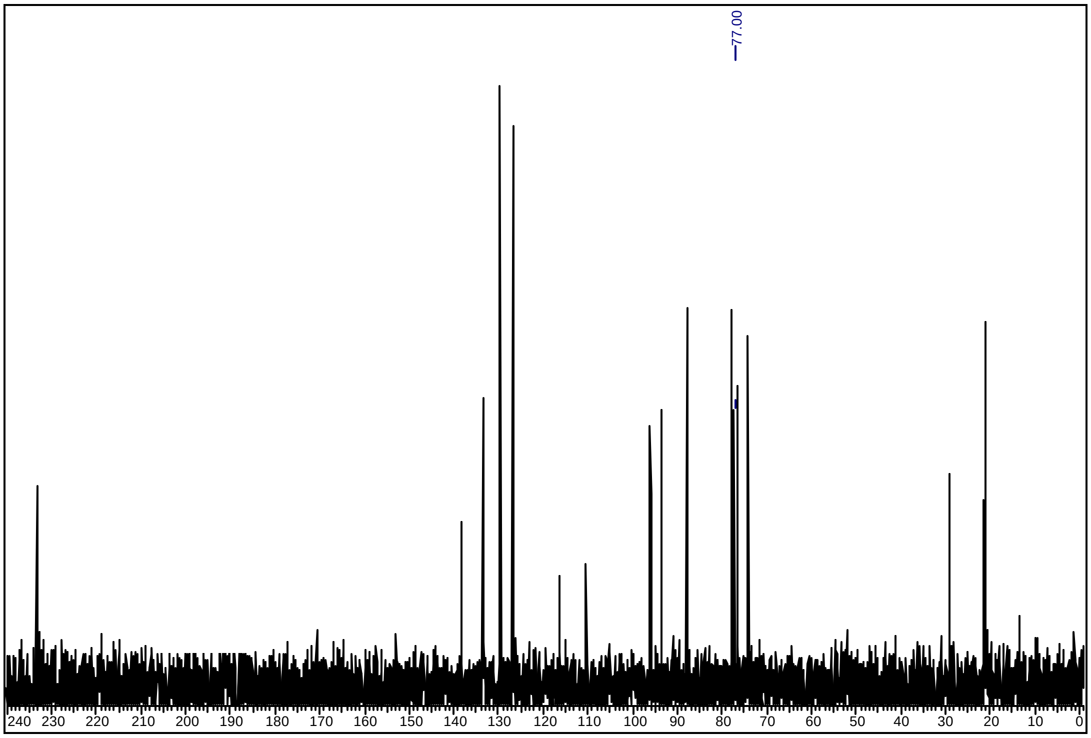
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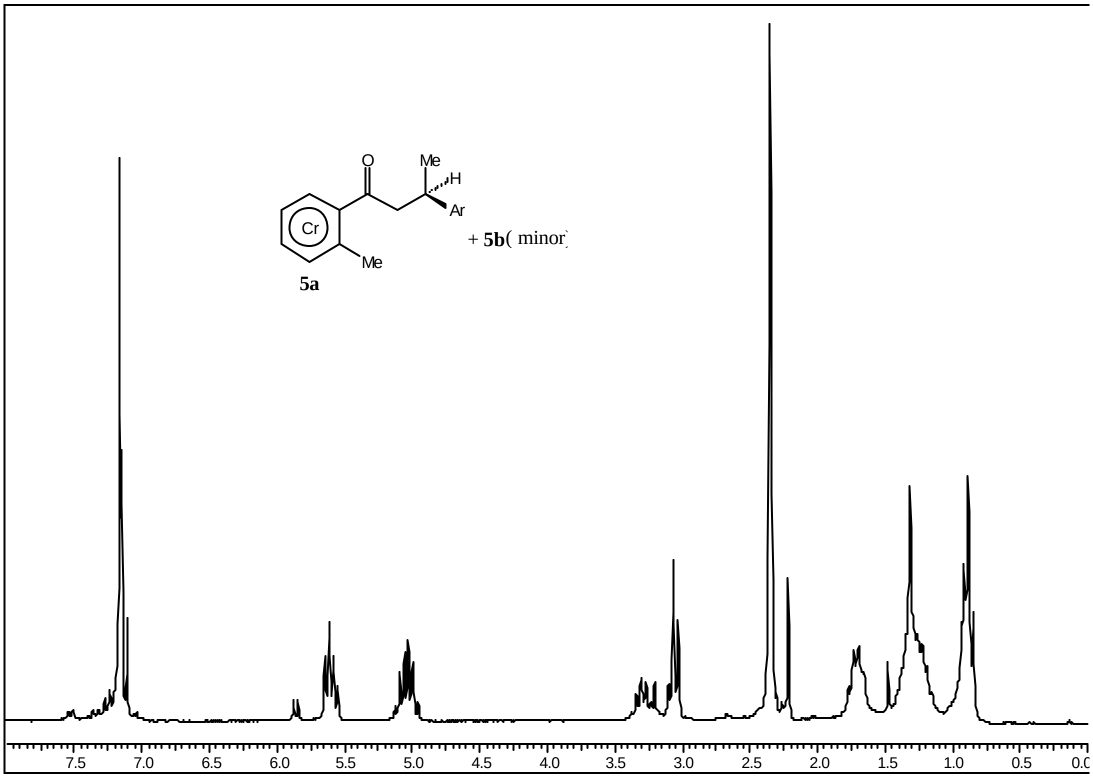
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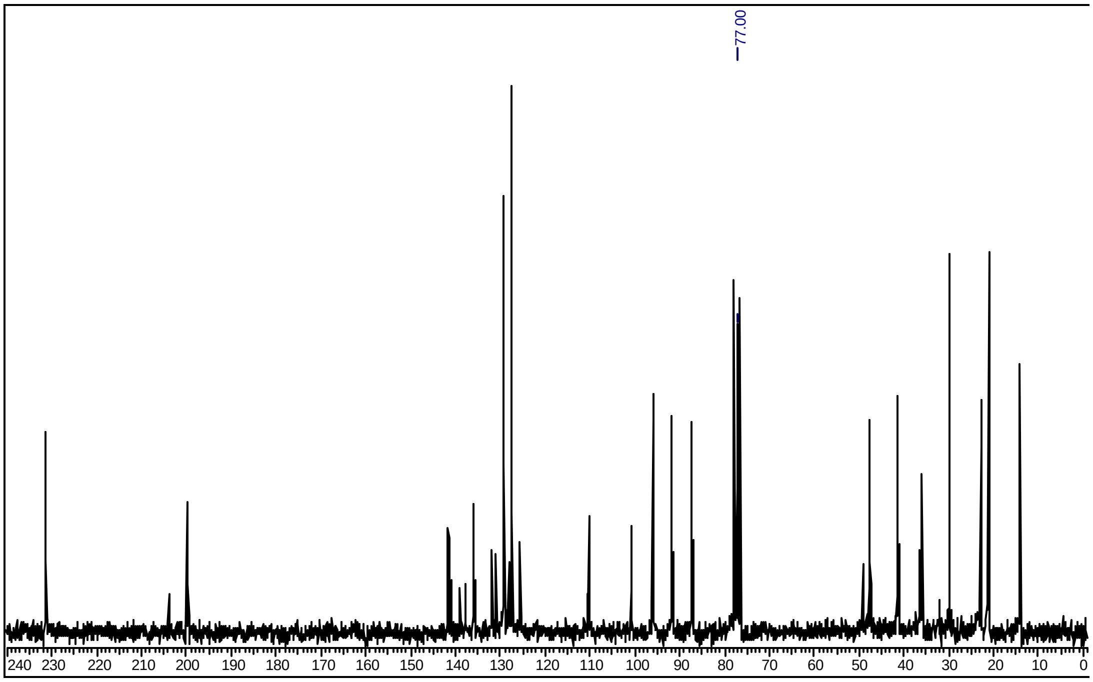
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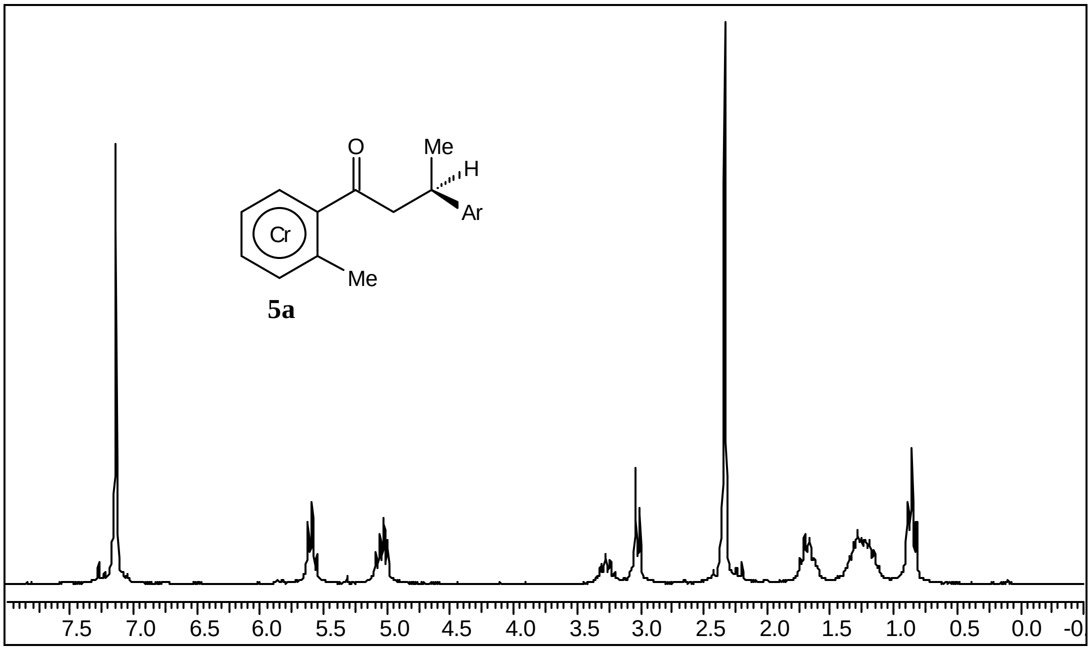
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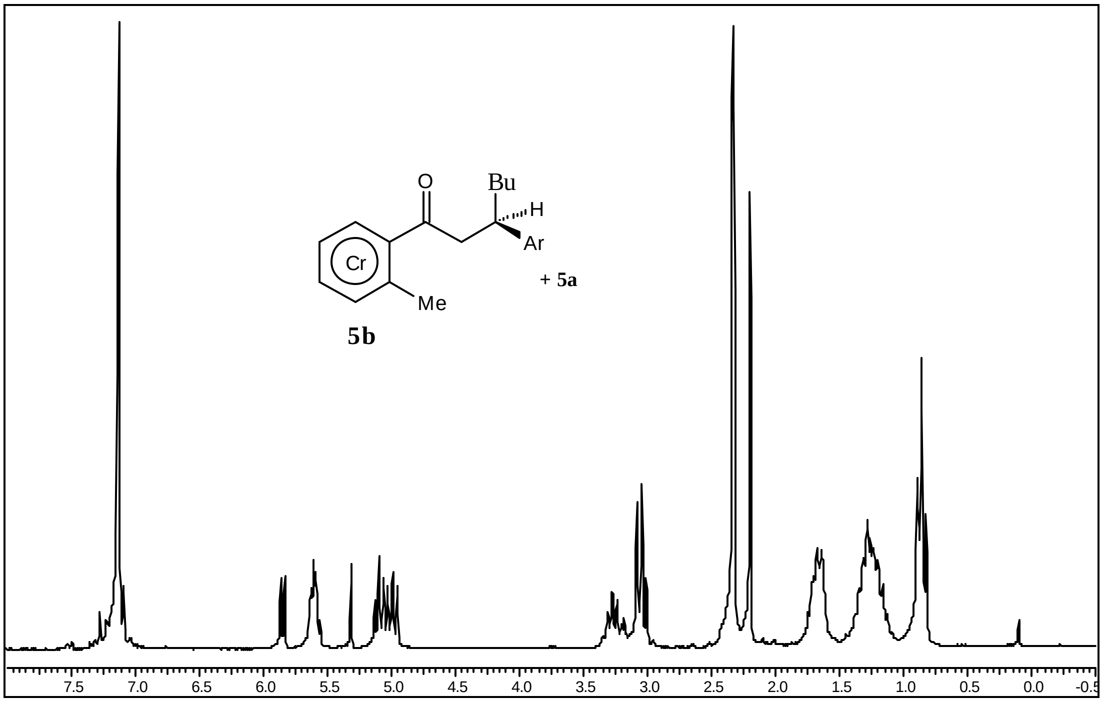
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Bu
H
Ar
Cr
Me
+ 5a
5b
7.5
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6.5
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5.5
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3.0
2.5
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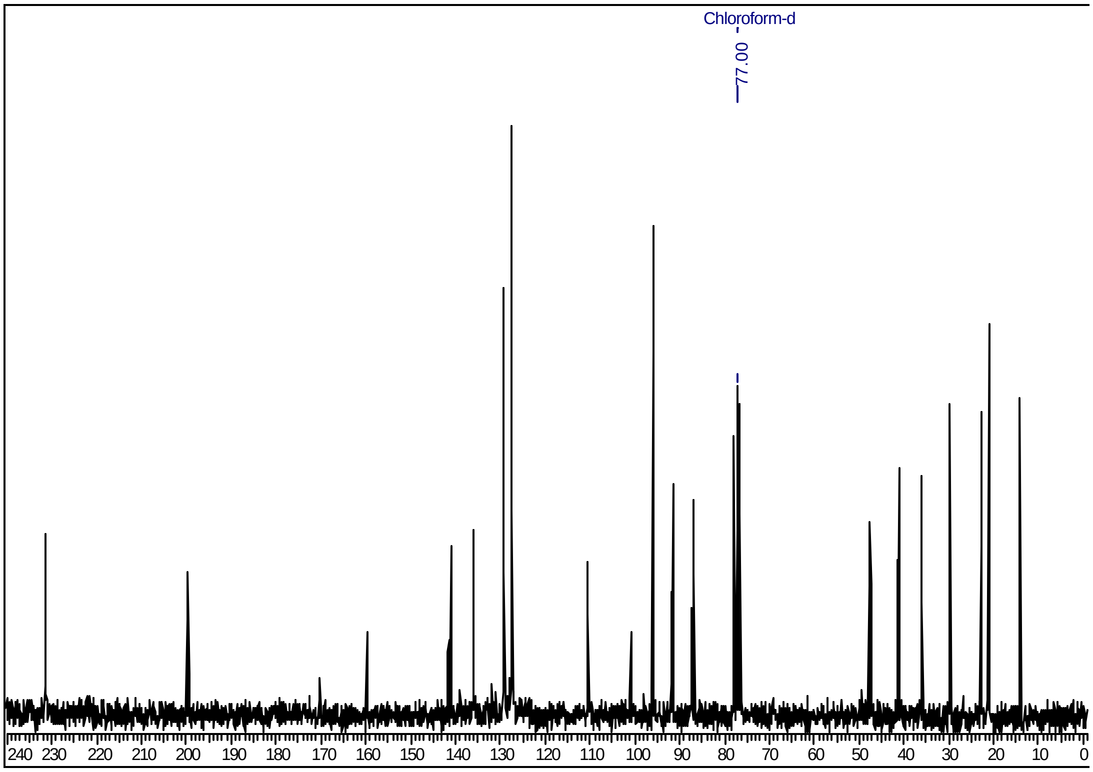
-0.5


Chloroform-d
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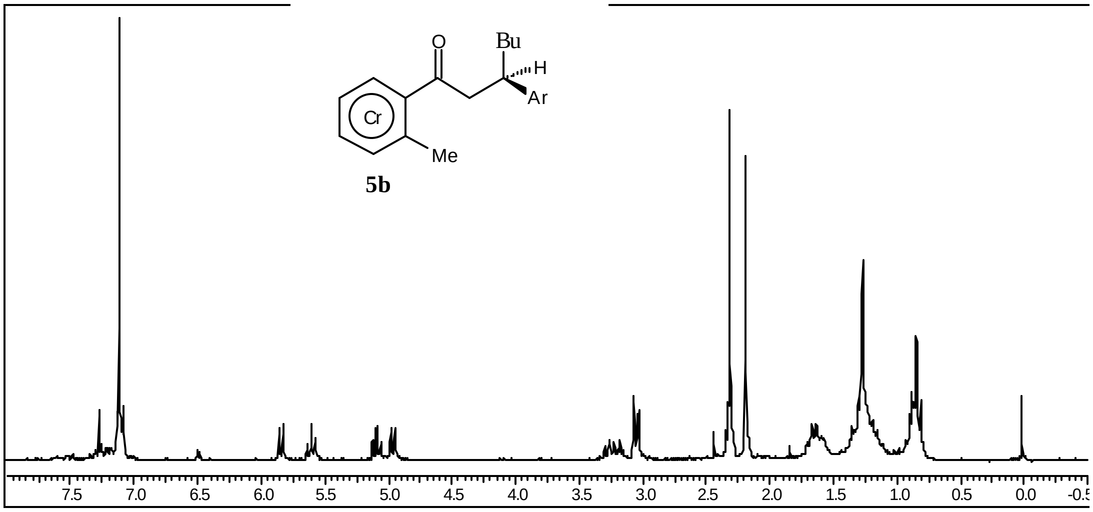
O
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H
Ar
Cr
Me
5b
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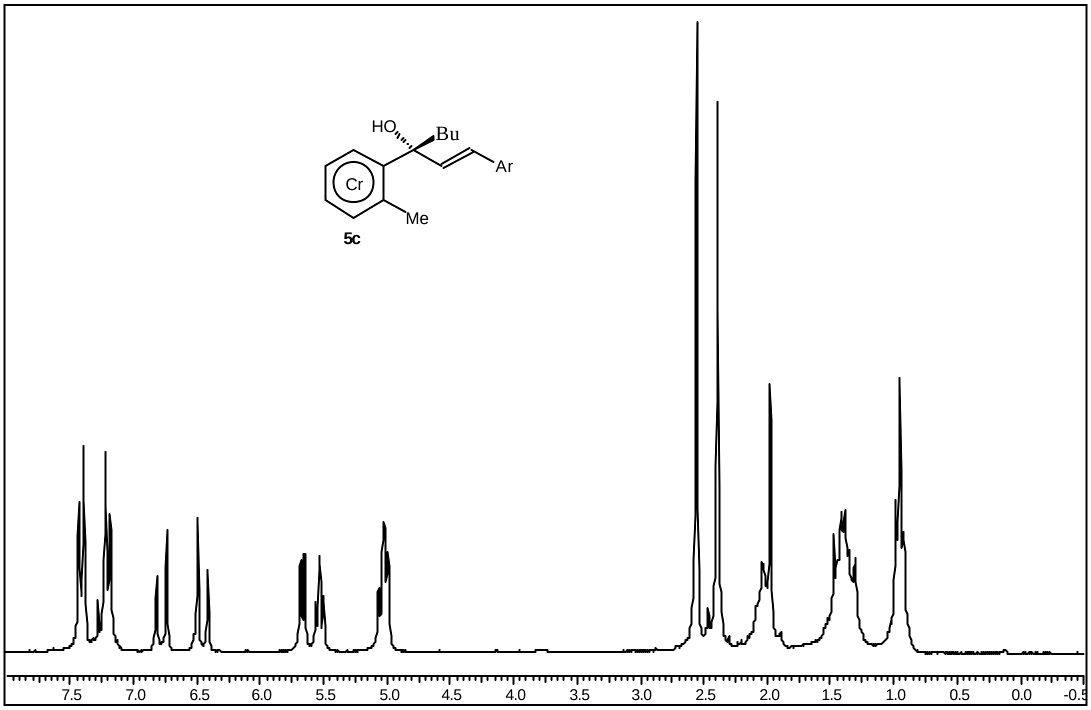
-0.5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Cr
Me
5c
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1.5
1.0
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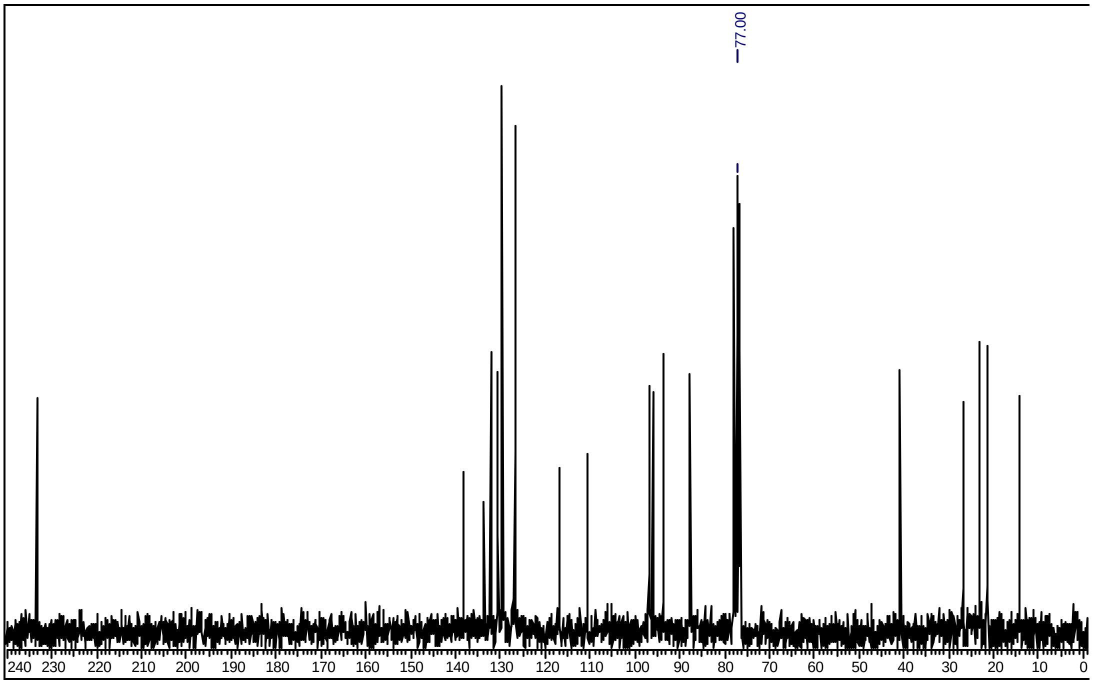
-0.5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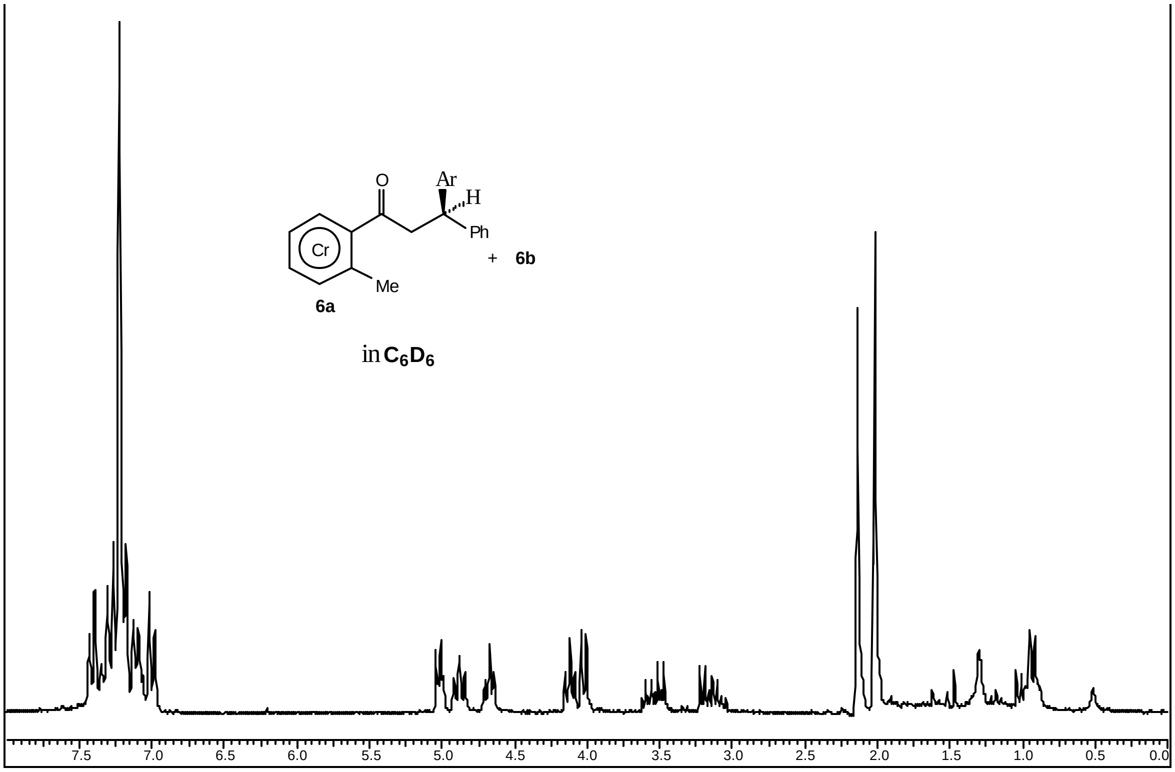
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Ar
H
Ph
Cr
Me
+ 6b
6a
in C_6D_6
7.5
7.0
6.5
6.0
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4.0
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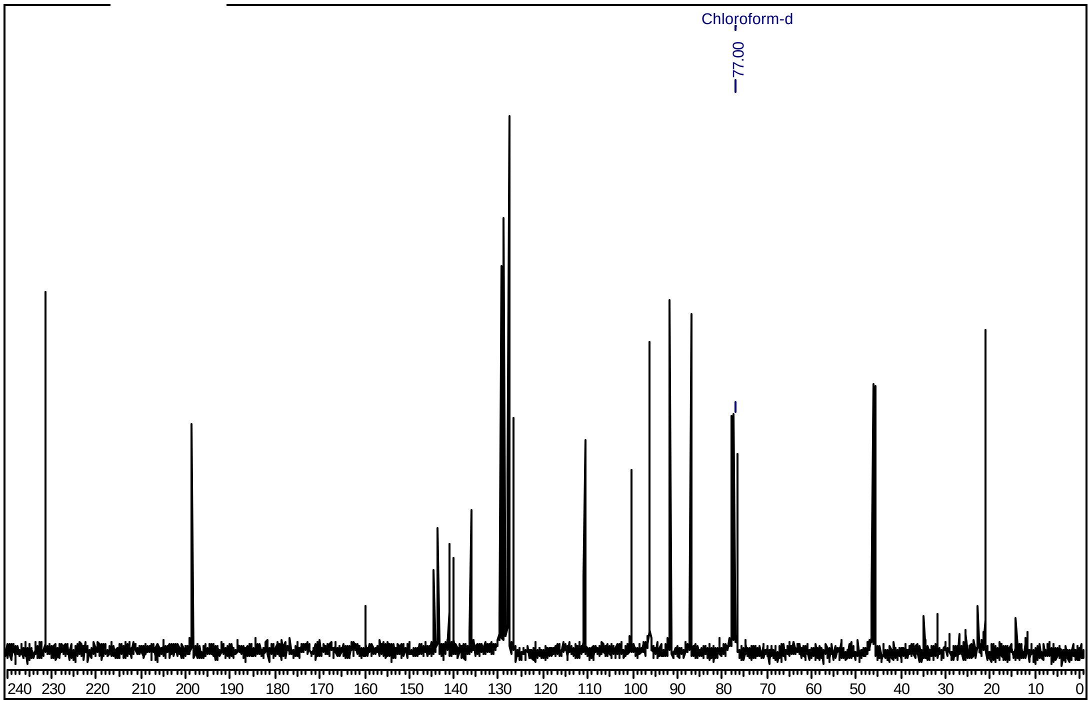
Chloroform-d
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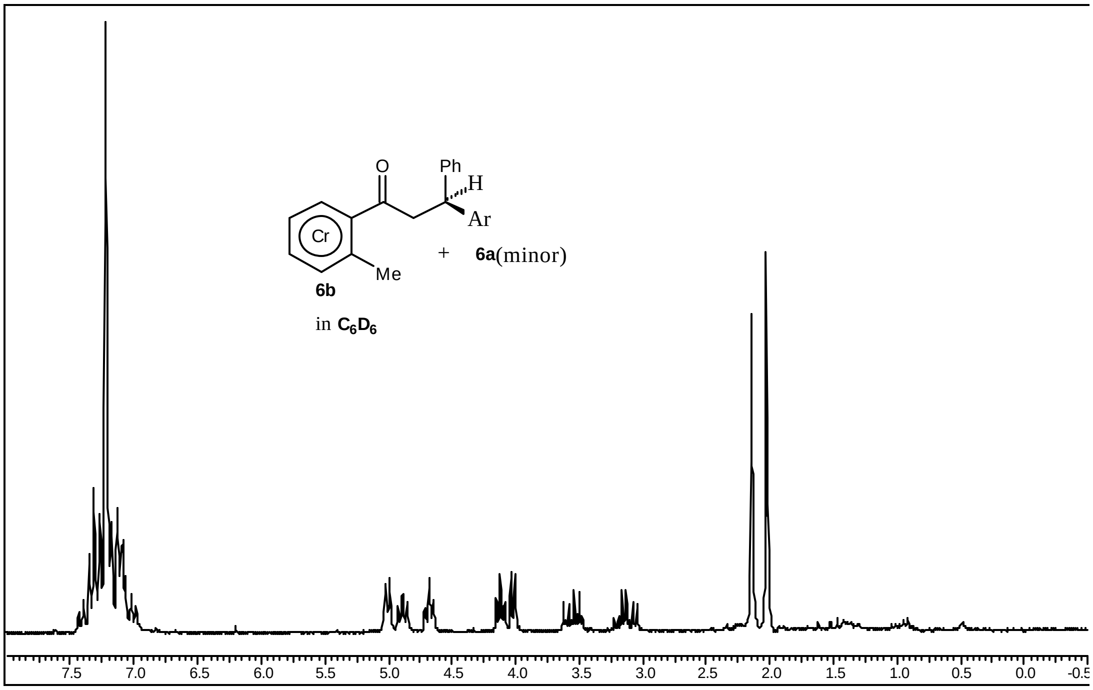
O
Ph
H
Ar
Cr
Me
+
6a(minor)
6b
in C_6D_6
7.5
7.0
6.5
6.0
5.5
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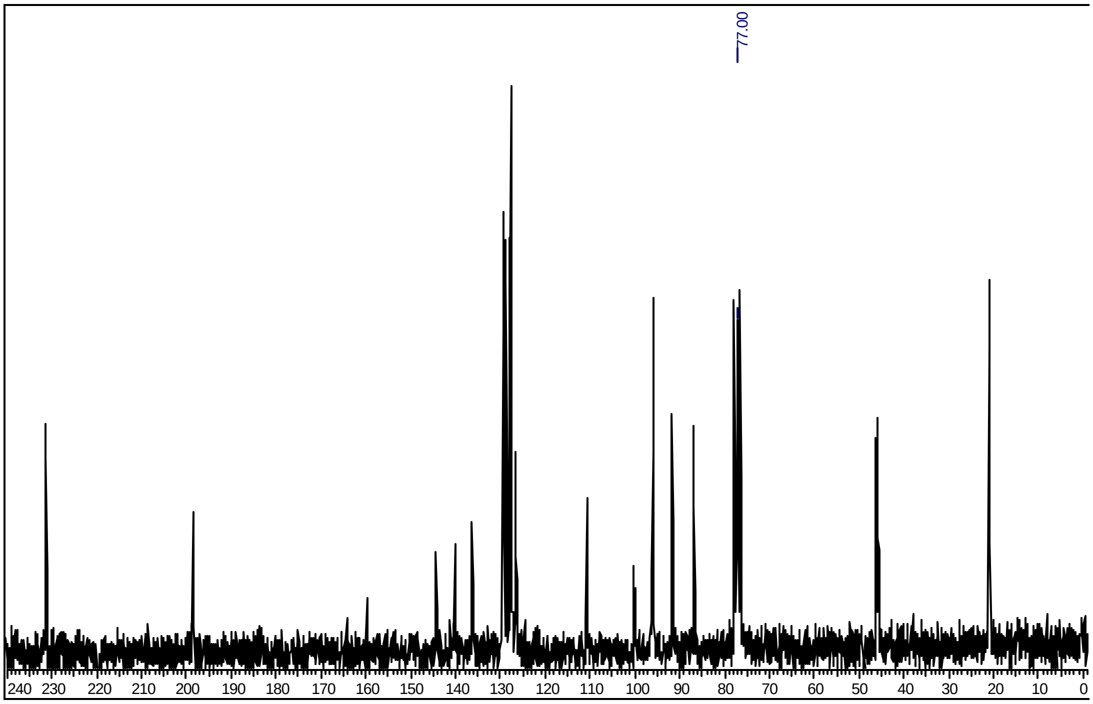
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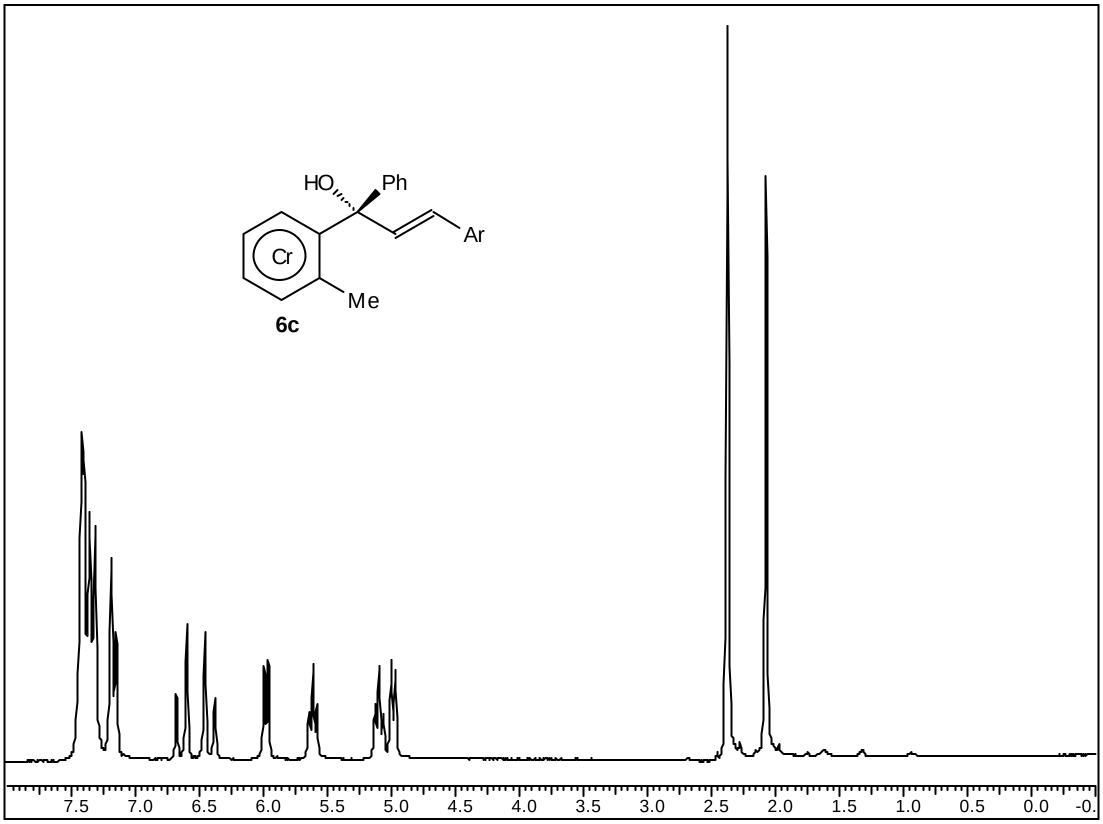
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Ph
Ar
Cr
Me
6c
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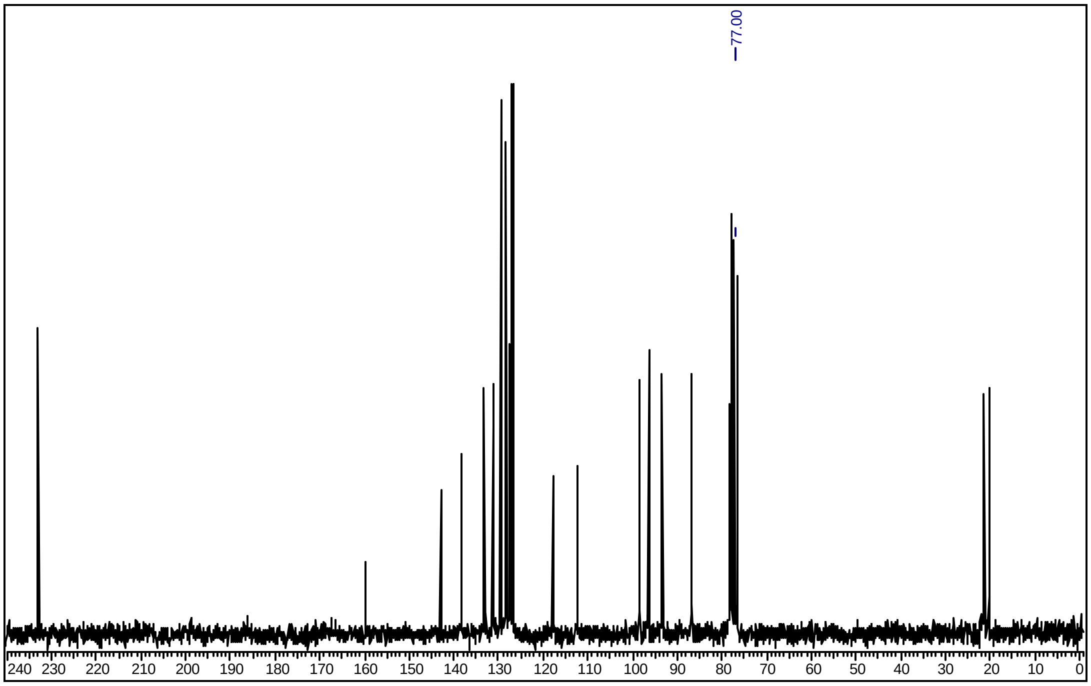
-0.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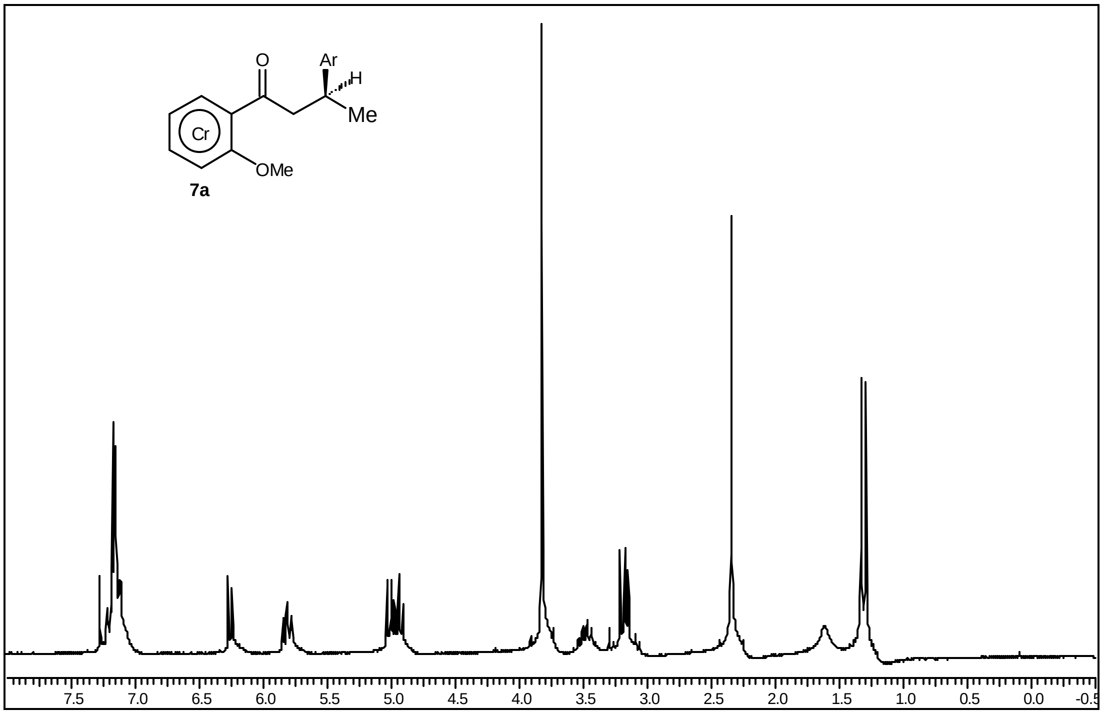
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Ar
H
Me
Cr
OMe
7a
7.5
7.0
6.5
6.0
5.5
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1.5
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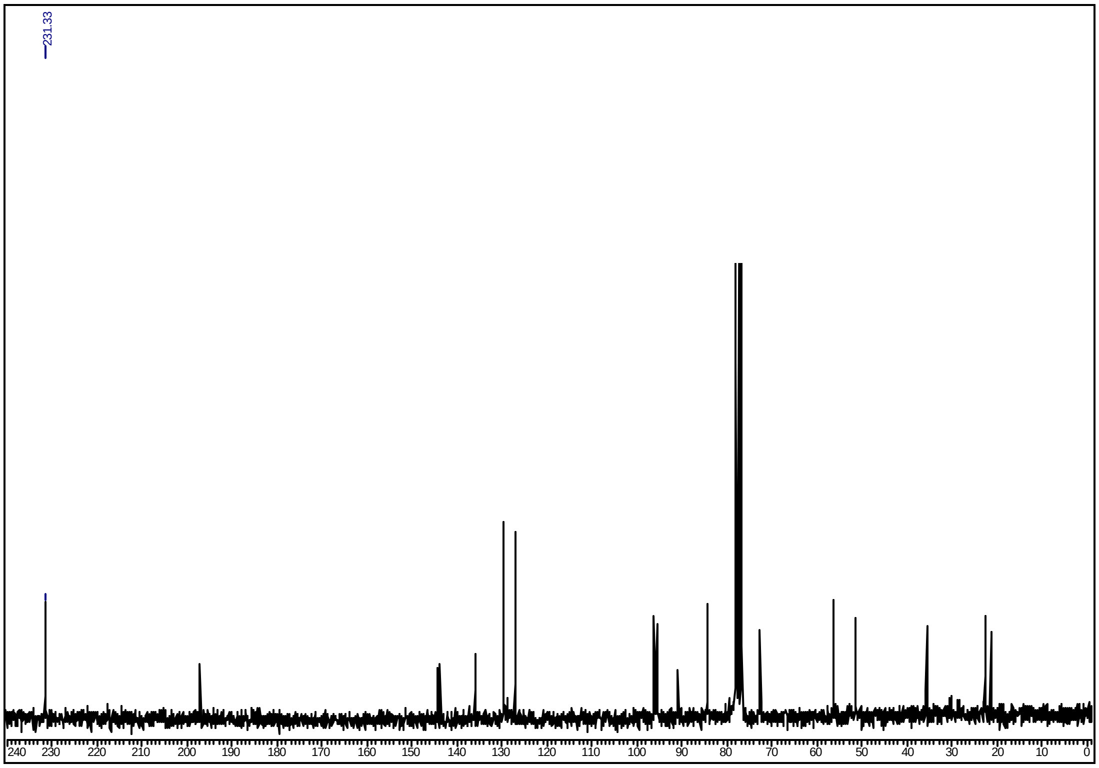
231.33
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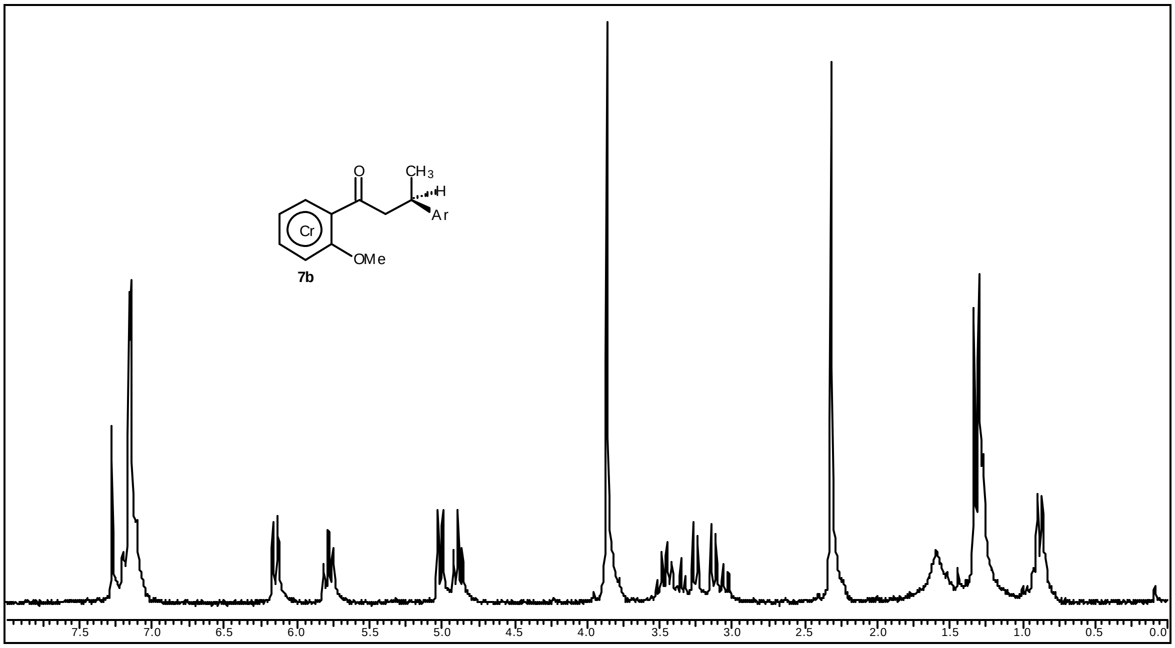
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CH3
H
Ar
Cr
OMe
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6.0
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1.5
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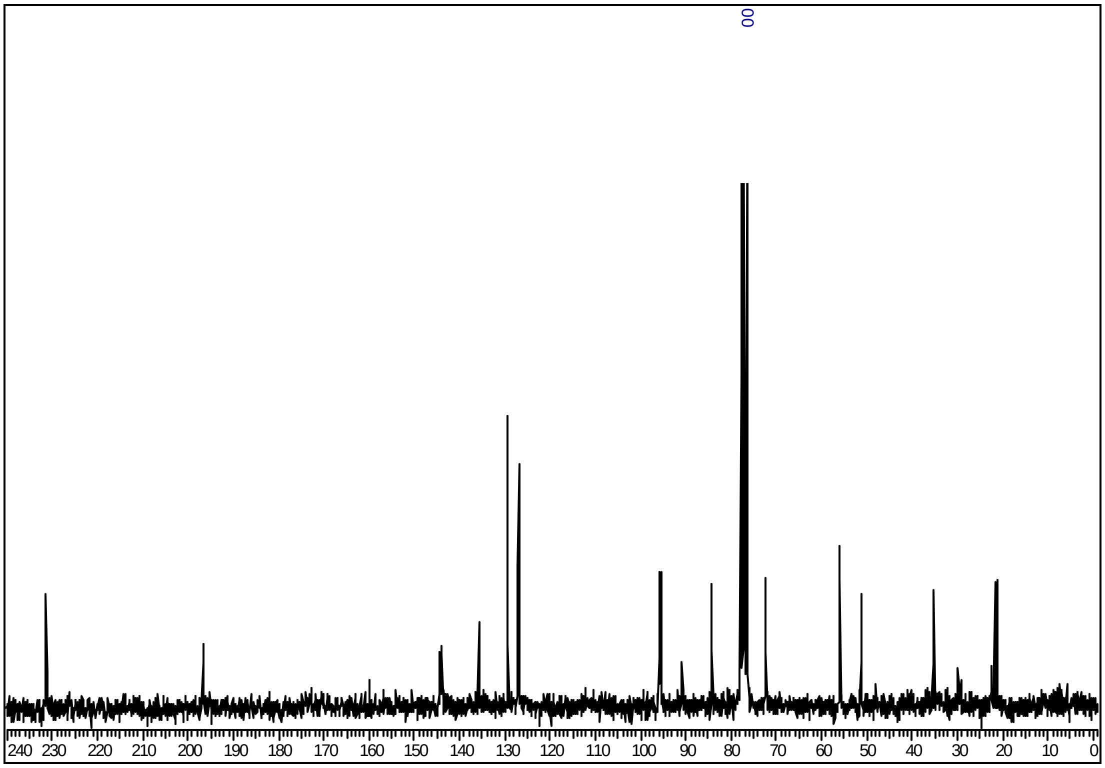
7b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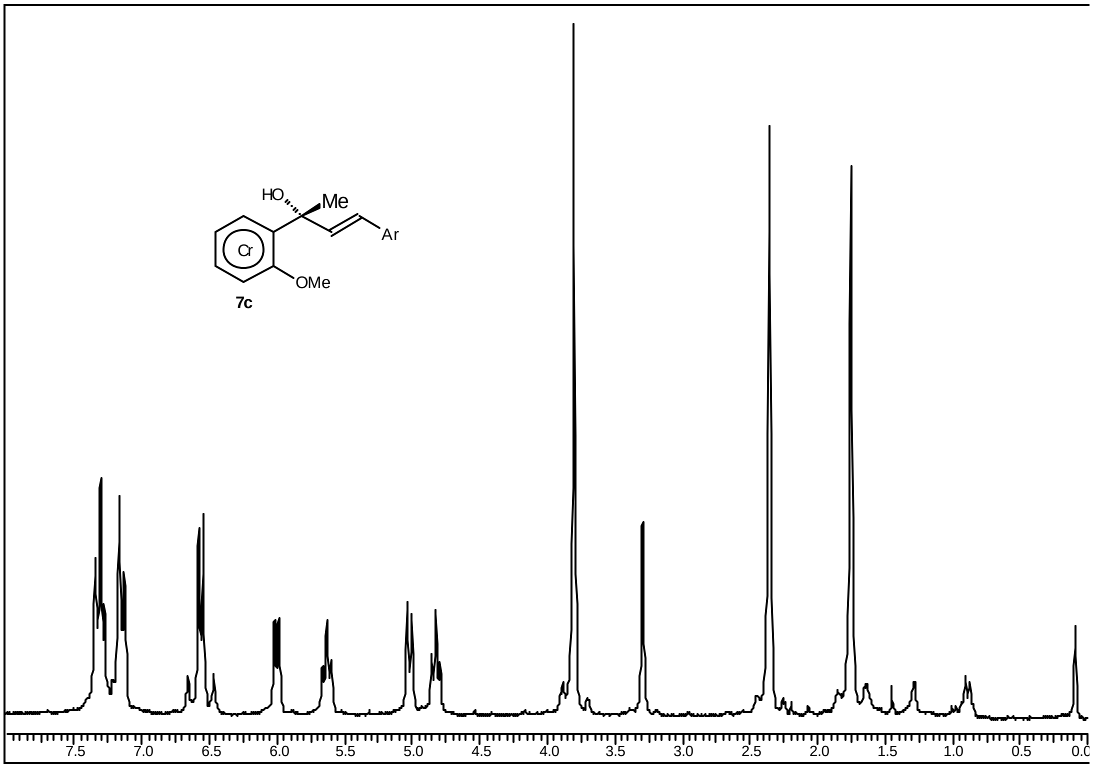
7c

HO
Me
Ar
Cr
OMe
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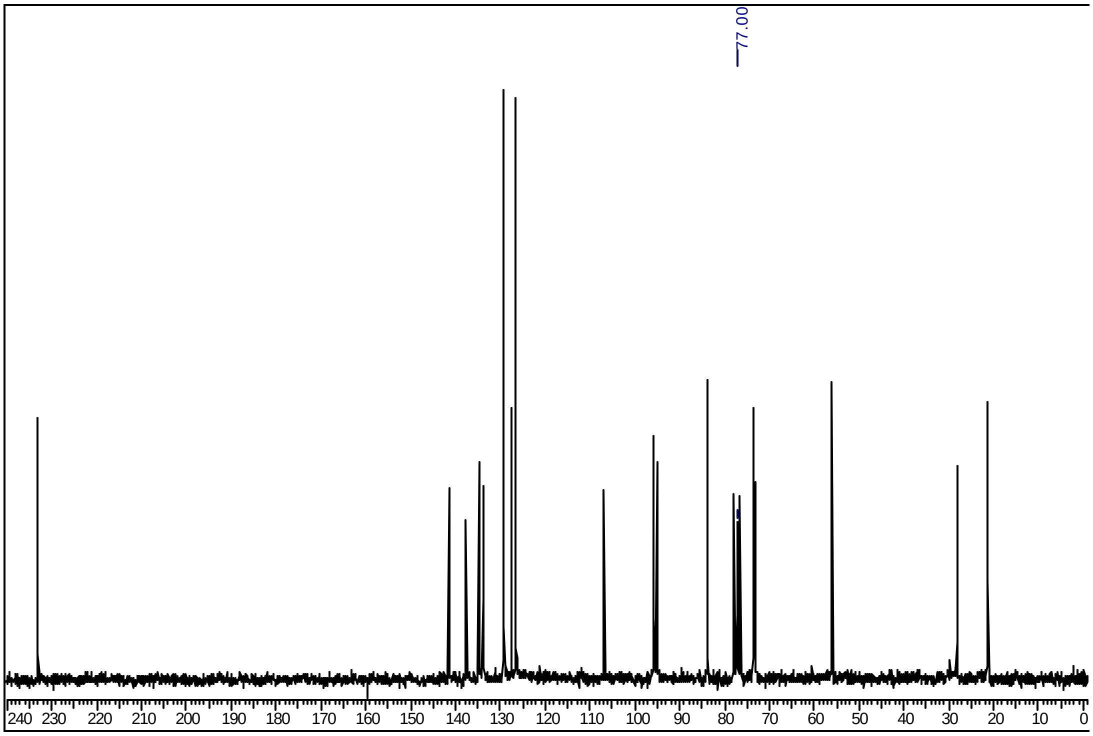
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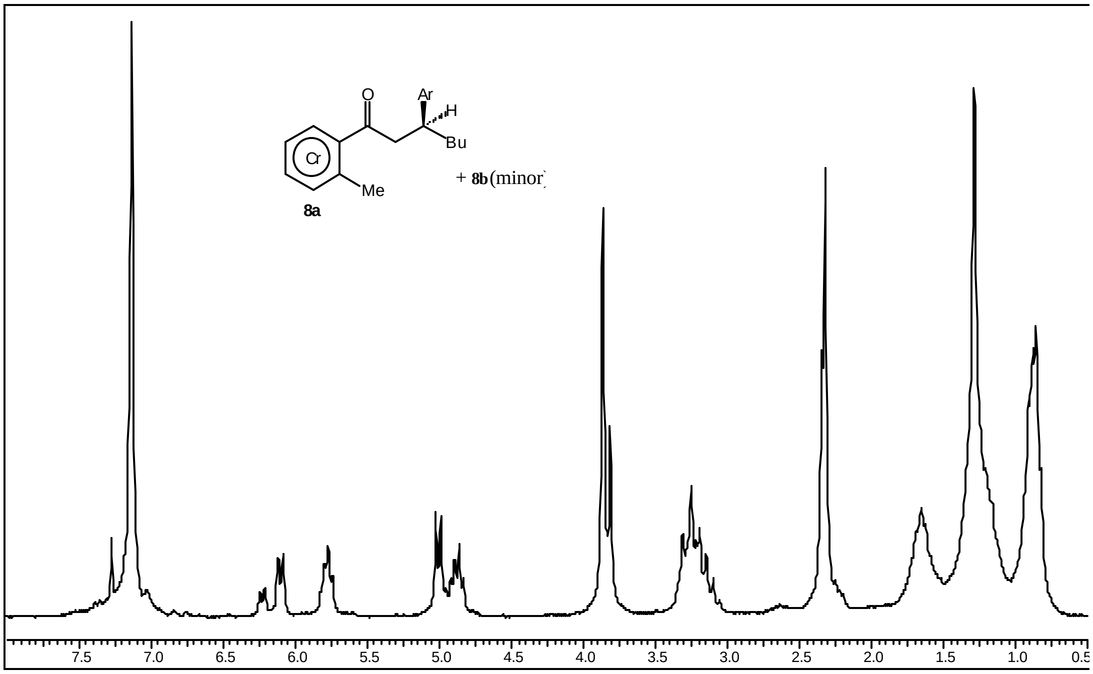
O
Ar
H
Bu
Cr
Me
8a
+ 8b(minor)
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7.0
6.5
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4.5
4.0
3.5
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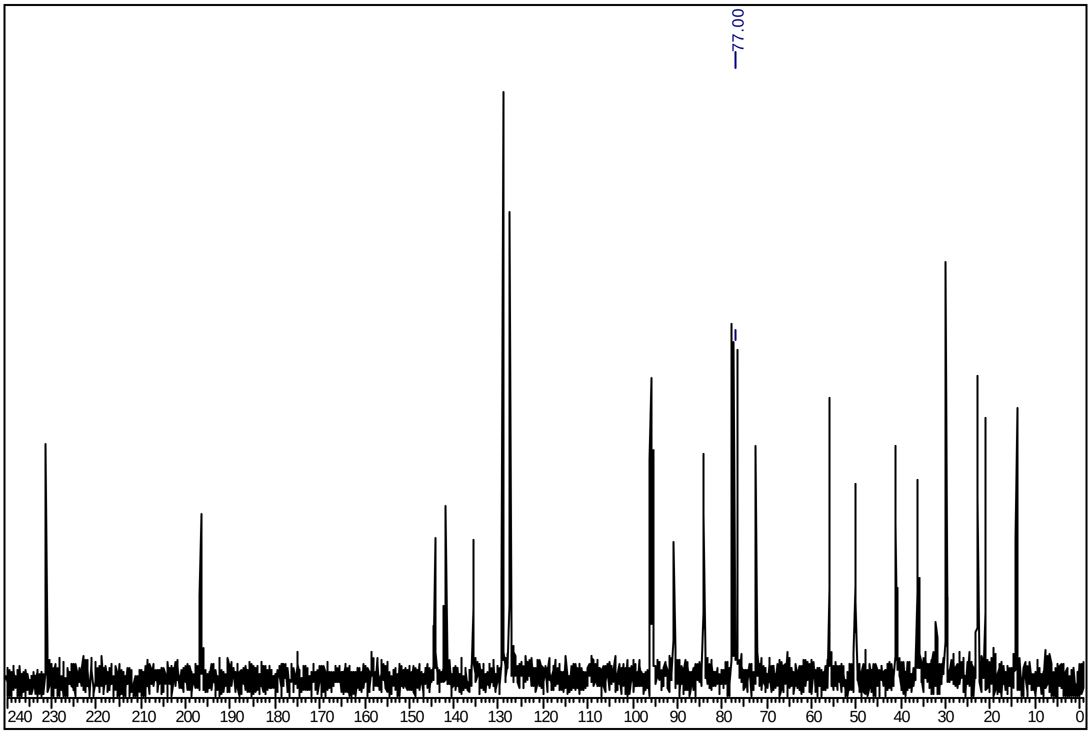
2.5
2.0
1.5
1.0
0.5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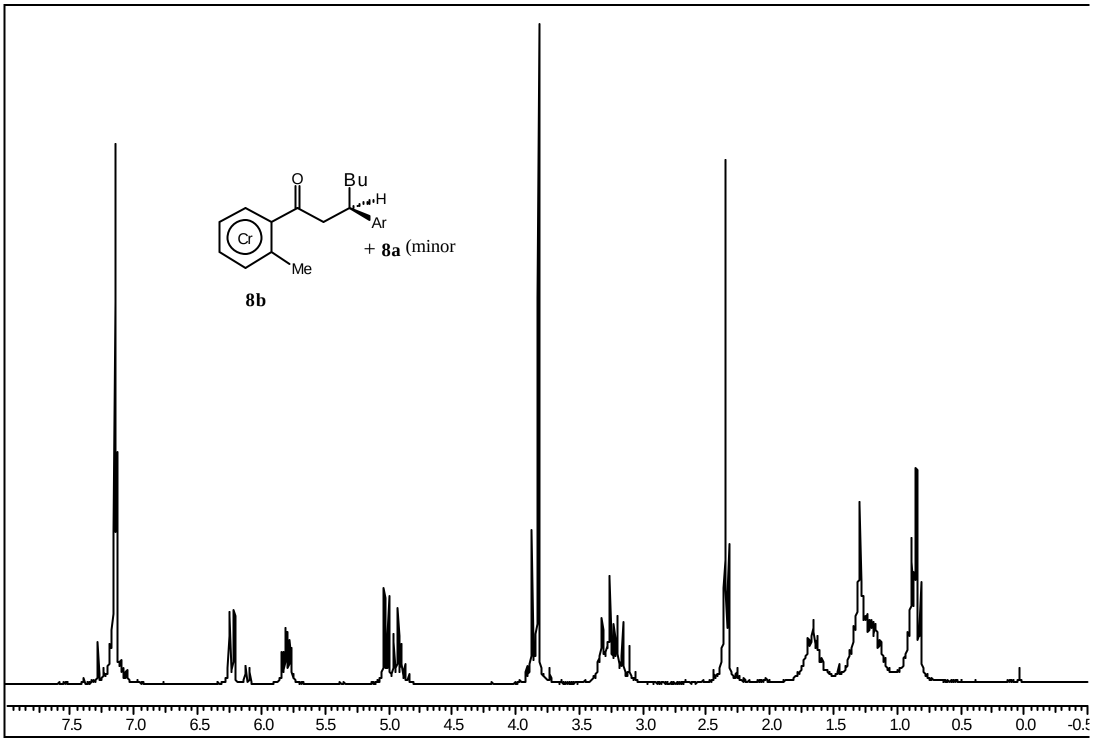
O
Bu
H
Ar
Cr
Me
+ 8a (minor
8b
7.5
7.0
6.5
6.0
5.5
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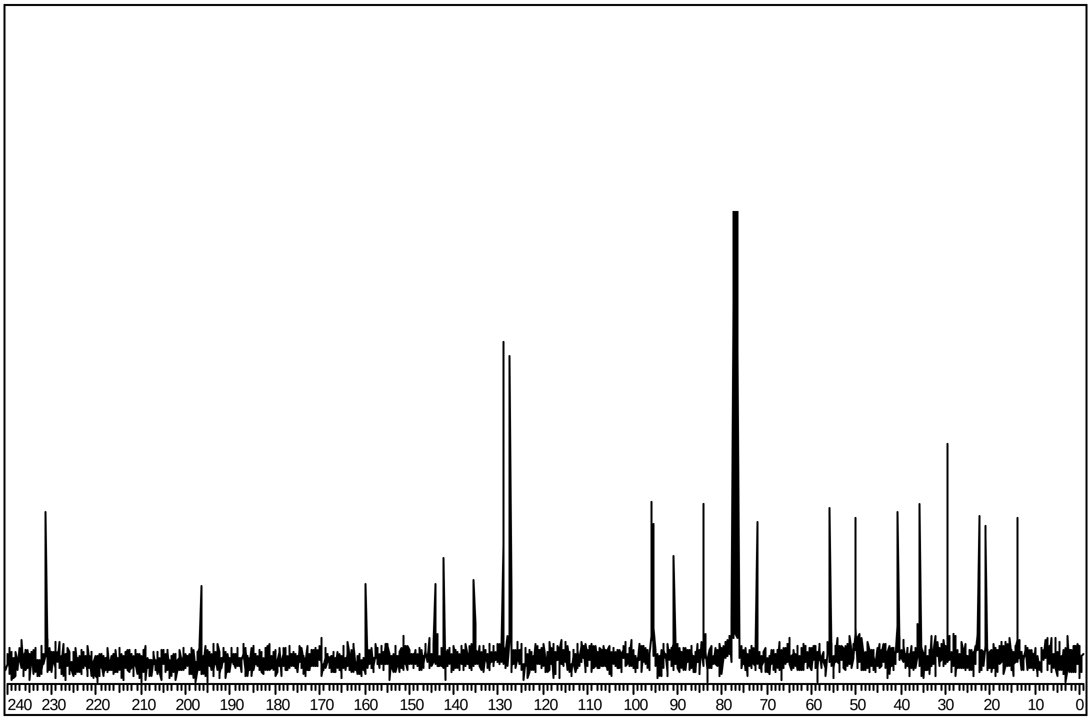
-0.5


240
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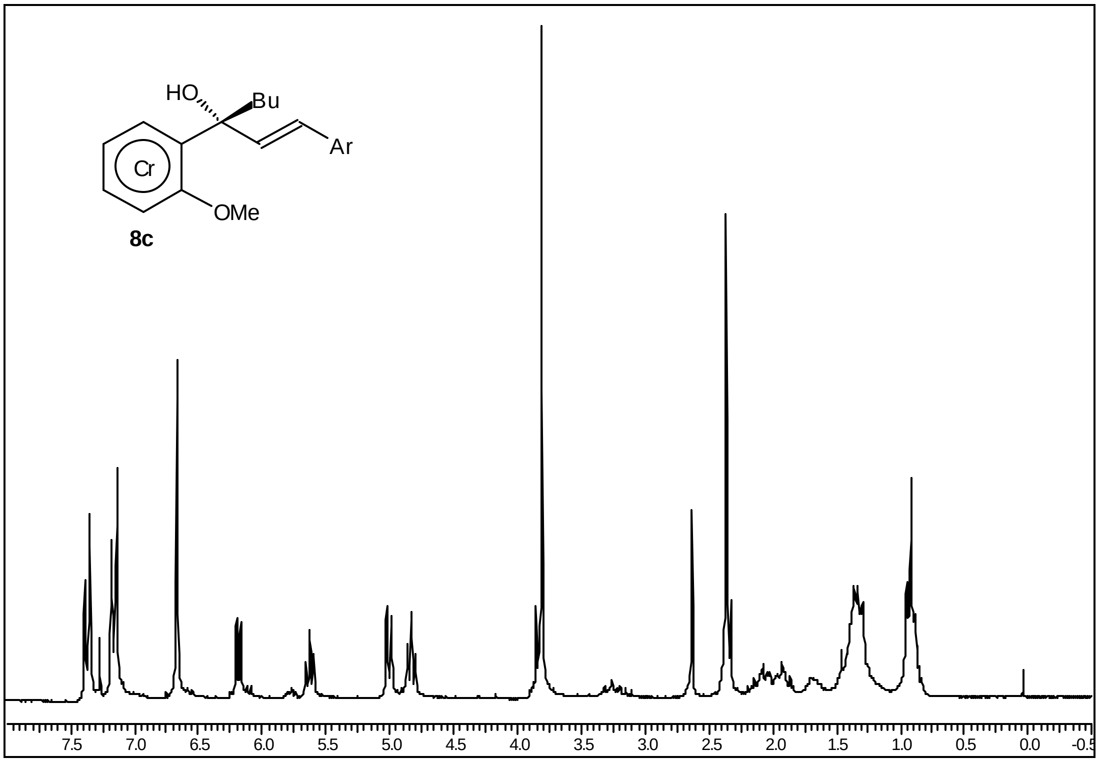
HO
Bu
Ar
Cr
OMe
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
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2.0
1.5
1.0
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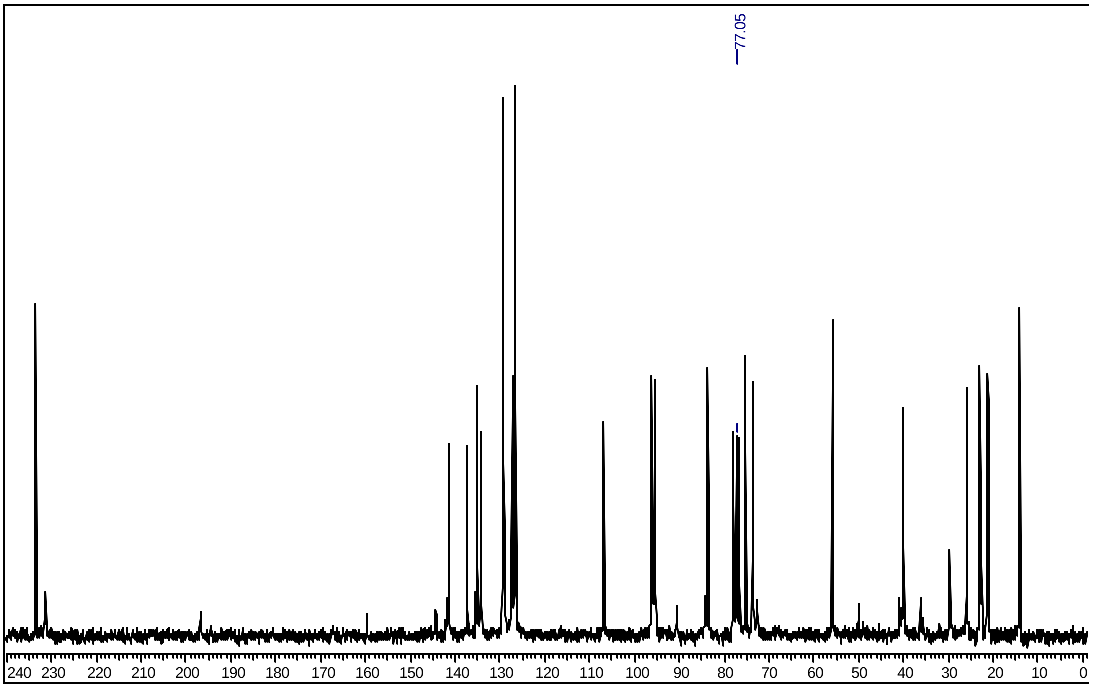
-0.5

8c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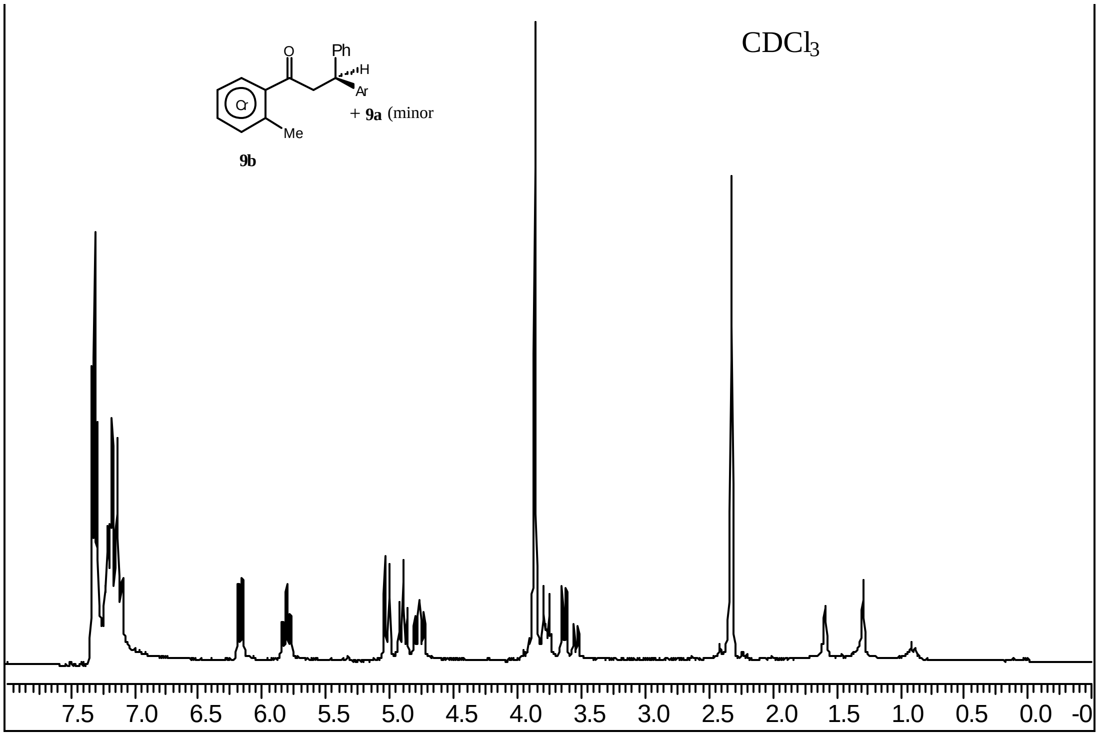
O
Ph
H
Ar
Cr
Me
+ **9a** (minor
9b
CDCl$_3$
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1.5
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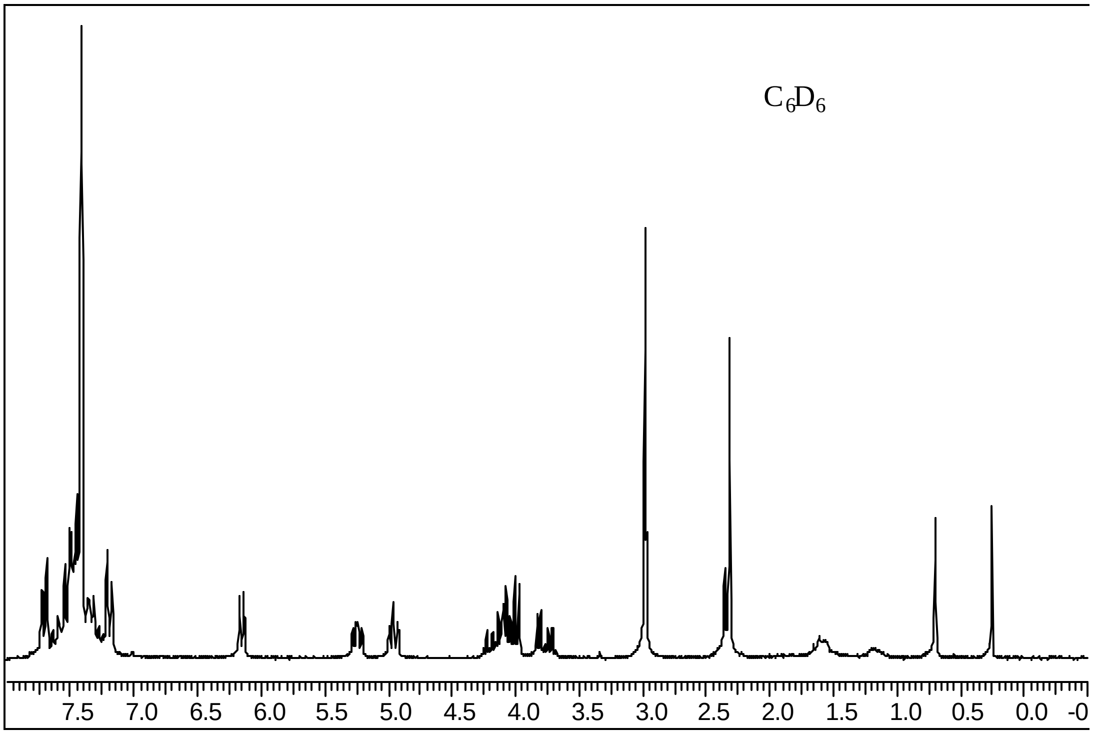
C$_6$D$_6$
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6.0
5.5
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1.5
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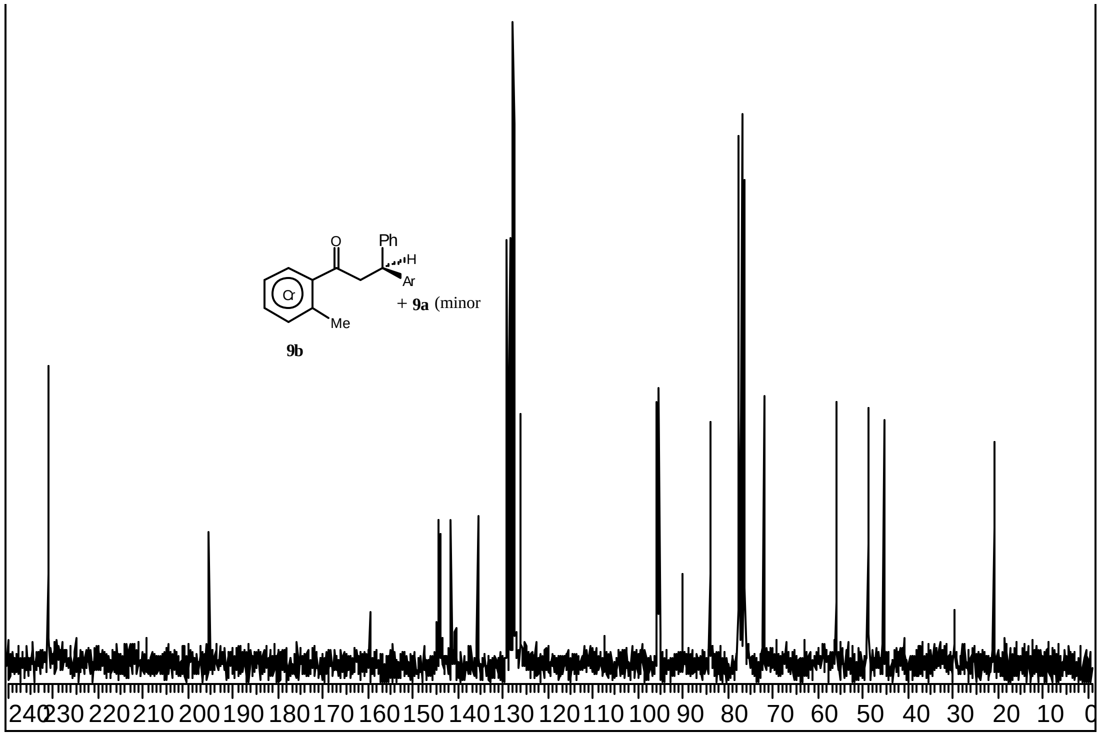
O
Ph
H
Ar
Cr
Me
+ **9a** (minor
240
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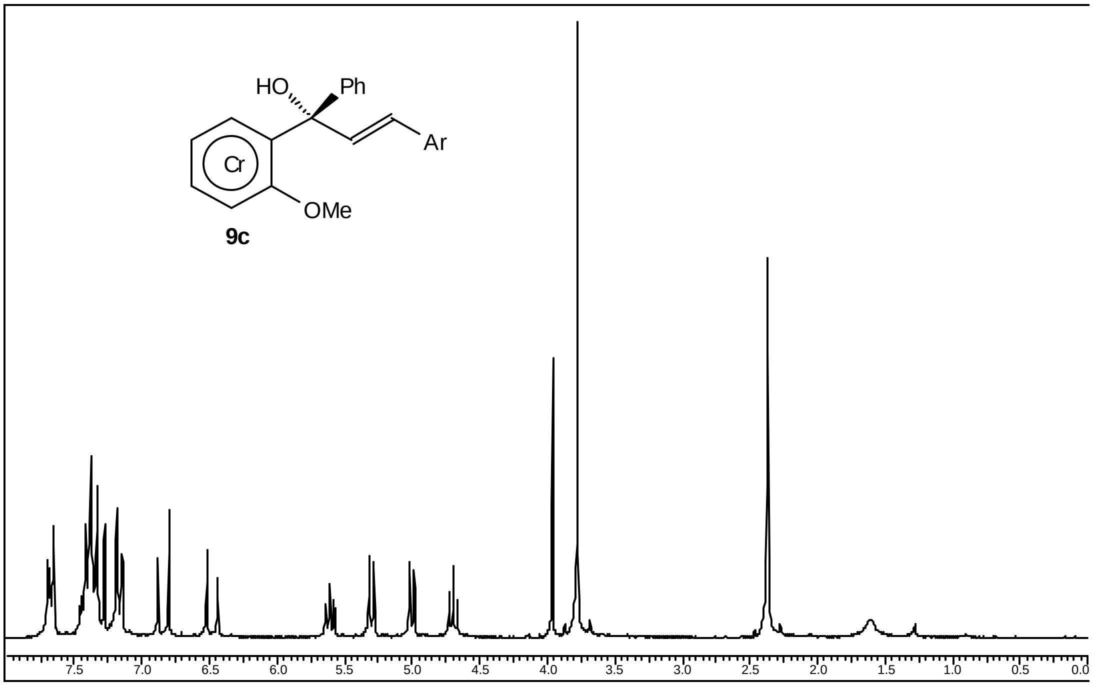
9b


HO
Ph
Cr
Ar
OMe
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6.5
6.0
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2.0
1.5
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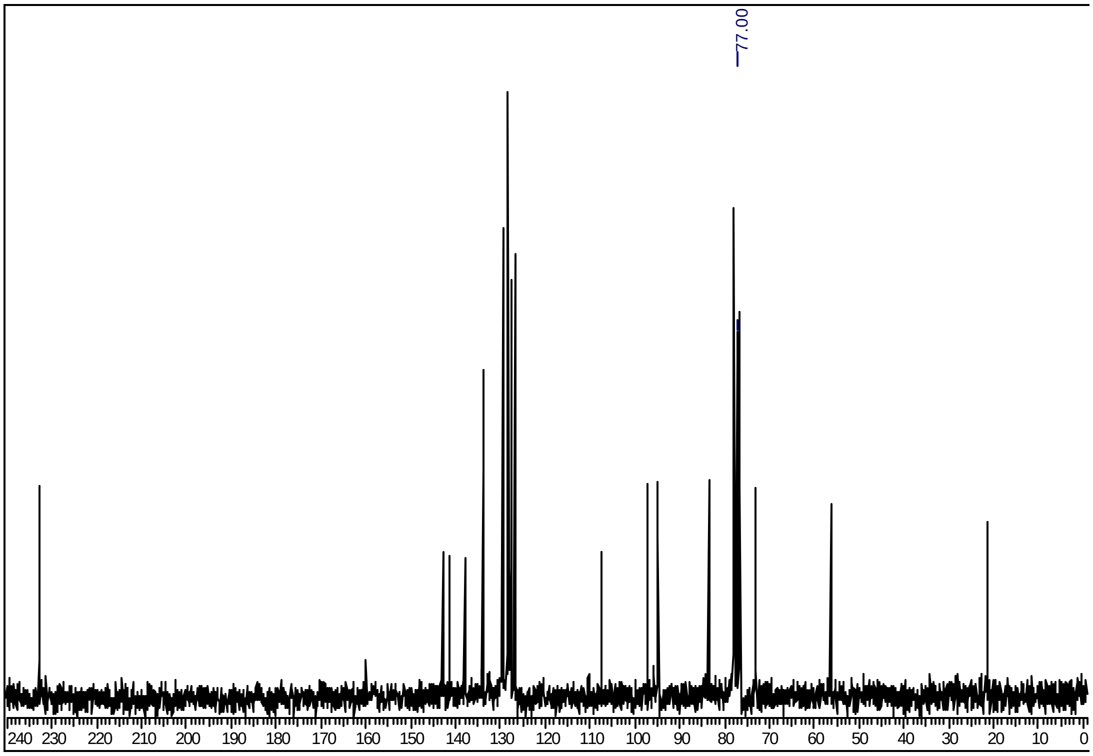
9c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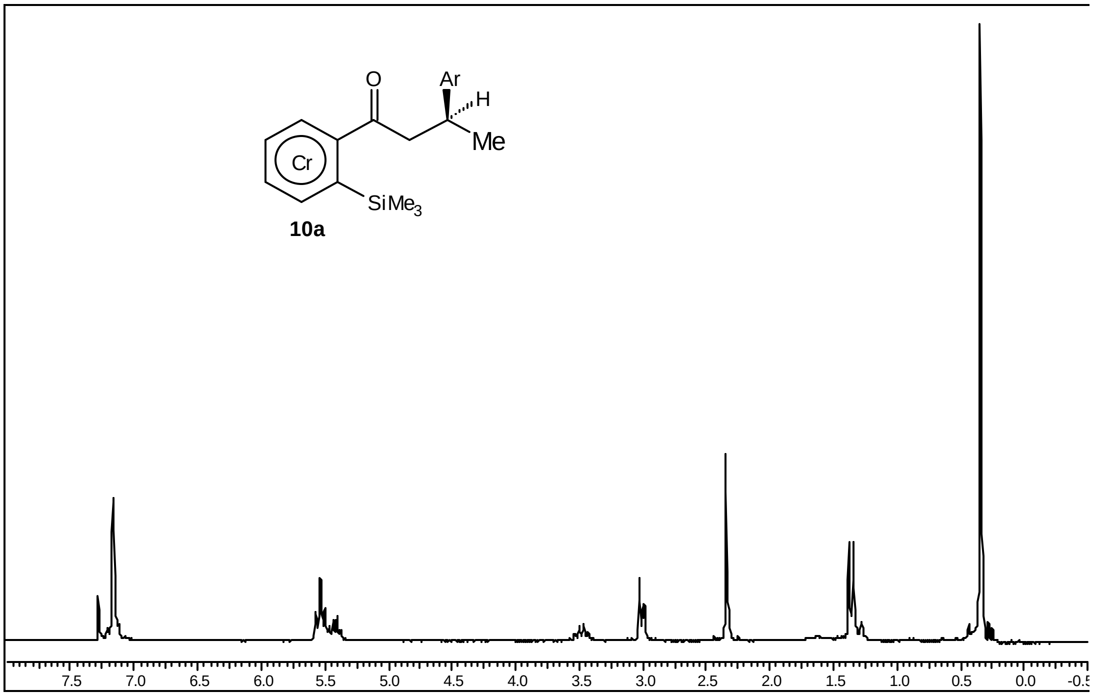
O
Ar
H
Me
Cr
SiMe$_3$
10a
7.5
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6.5
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3.0
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2.0
1.5
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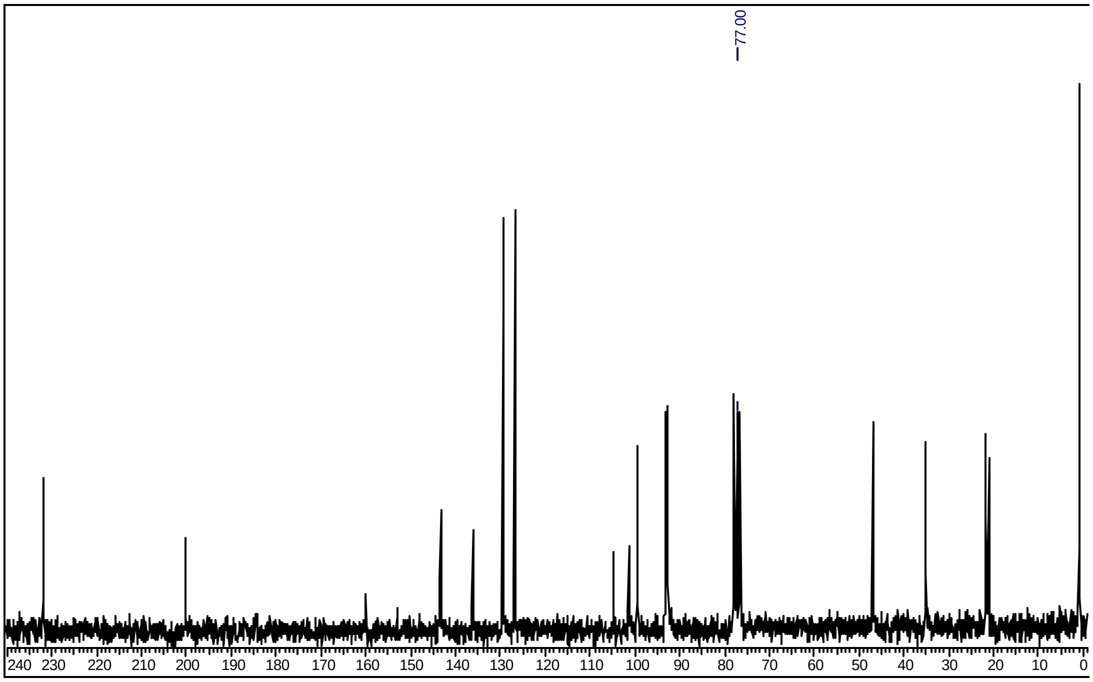
77.00
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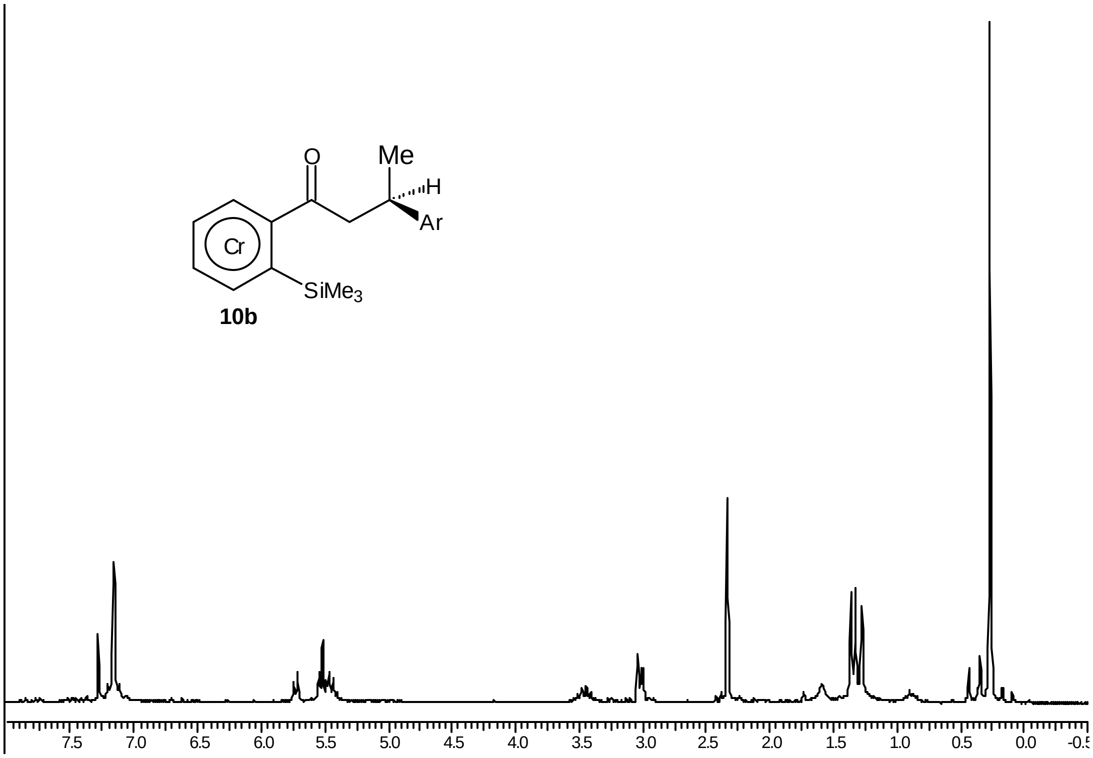
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H
Ar
Cr
SiMe3
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5.0
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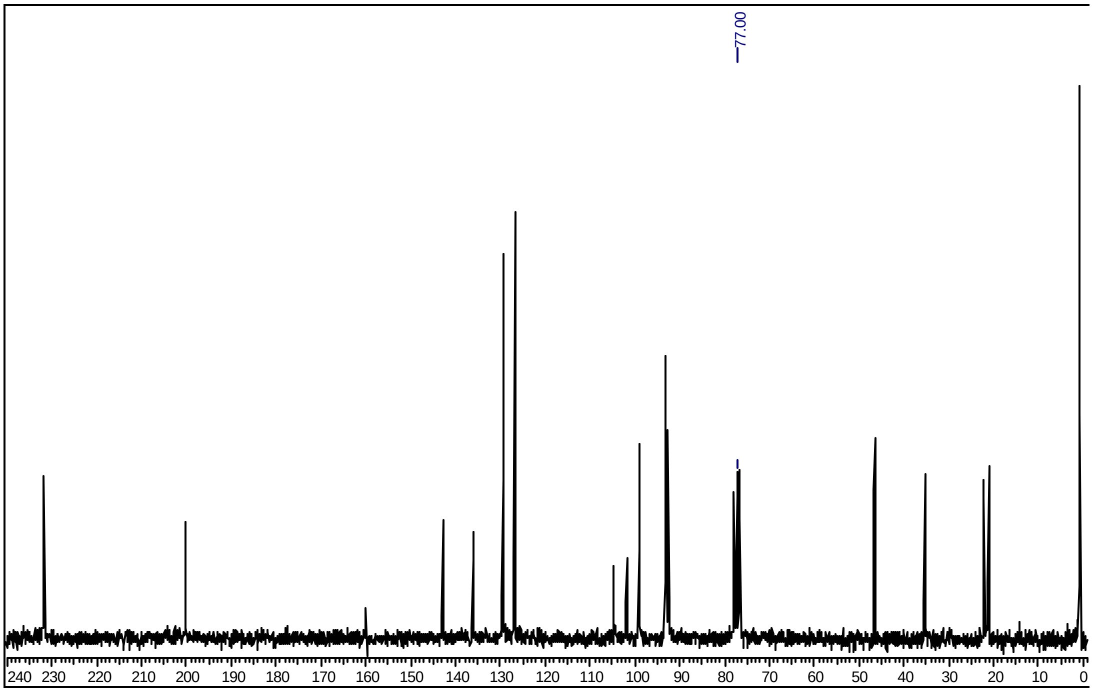
0.5
0.0
-0.5

10b


77.00
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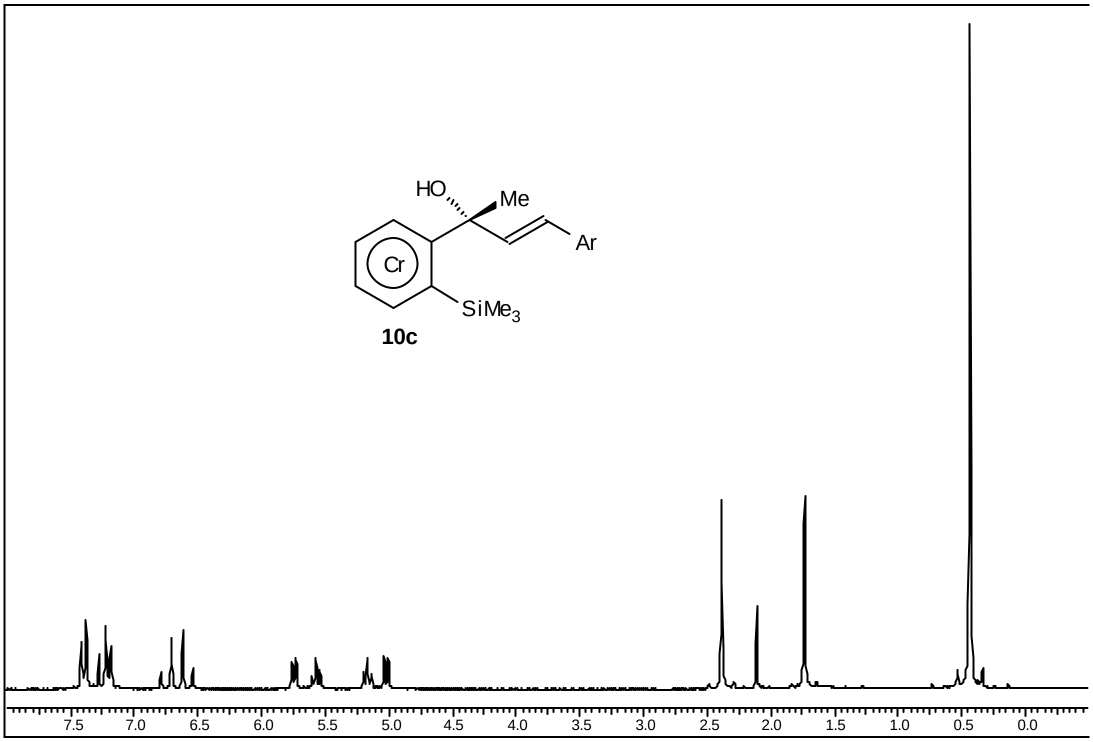

10c

HO
Me
Ar
Cr
SiMe3
7.5
7.0
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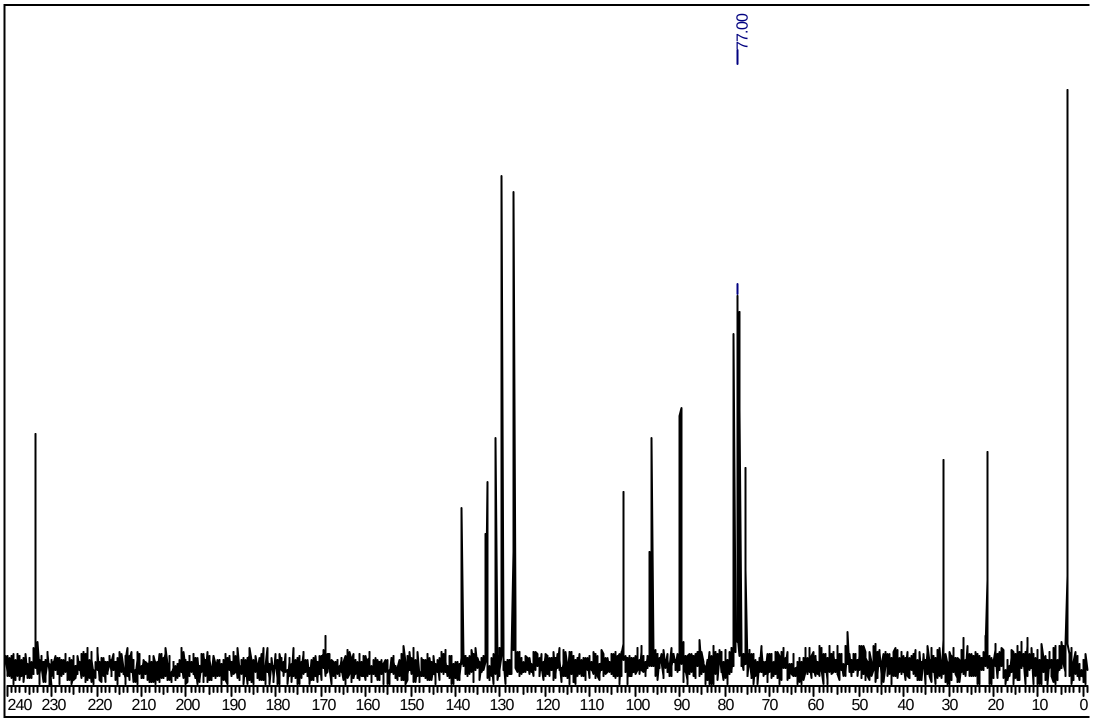

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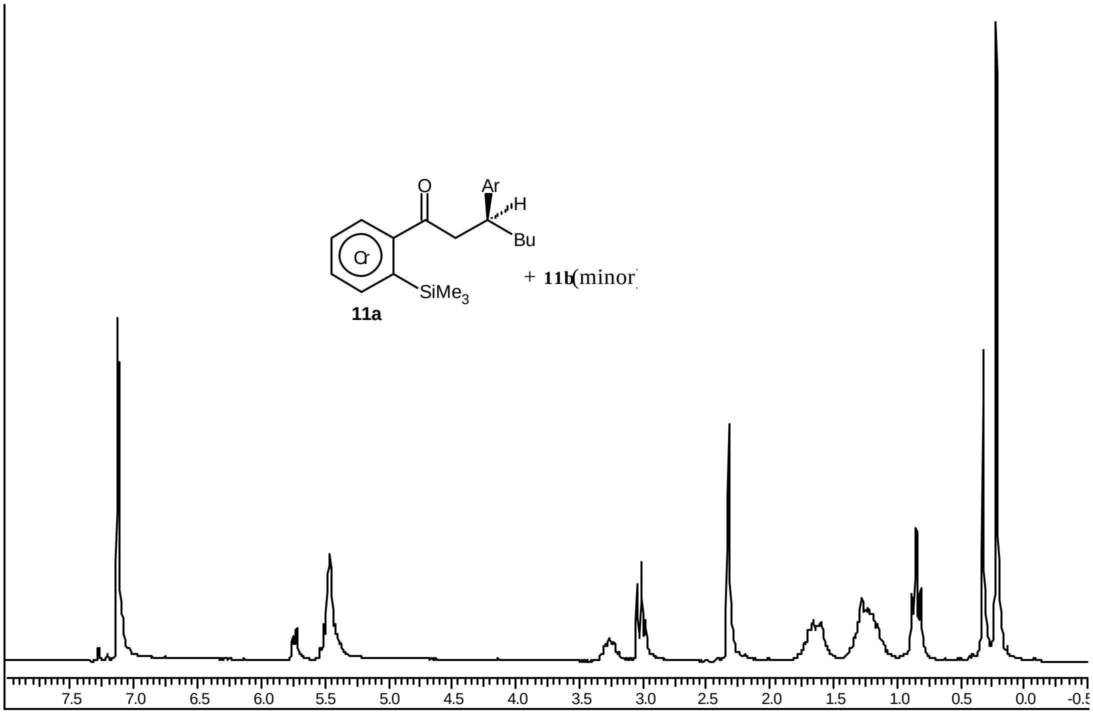
O
Ar
H
Bu
Cr
SiMe$_3$
11a
+ 11b (minor)
7.5
7.0
6.5
6.0
5.5
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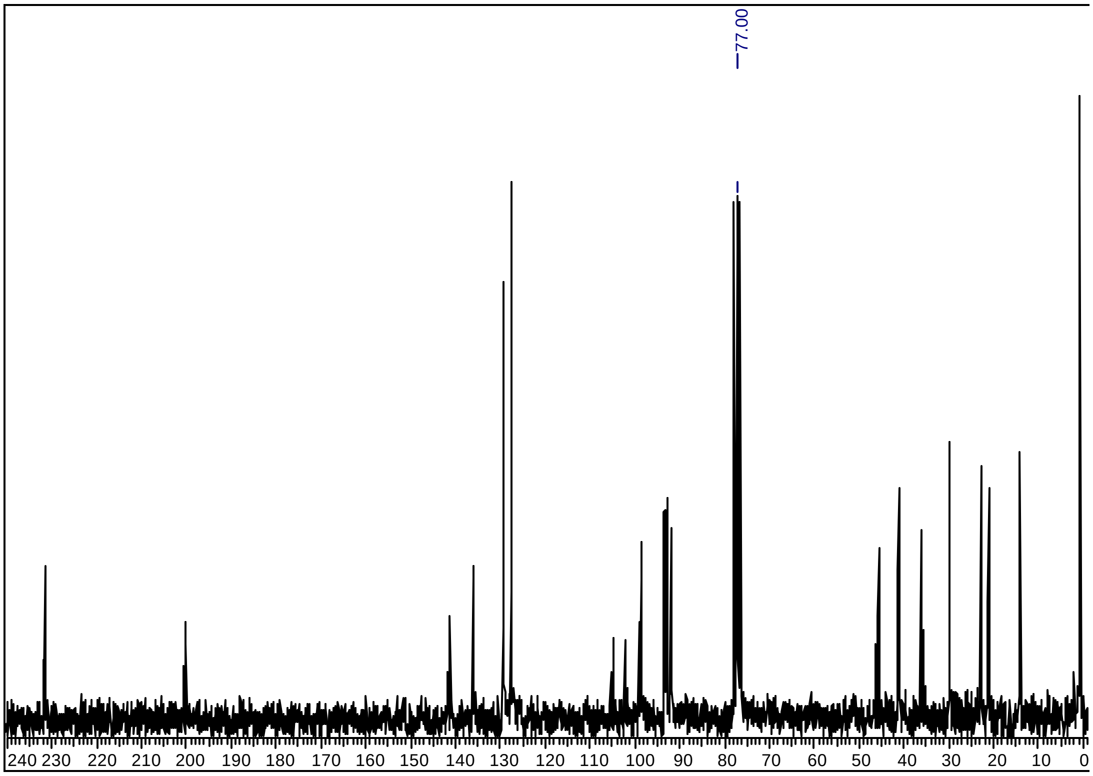
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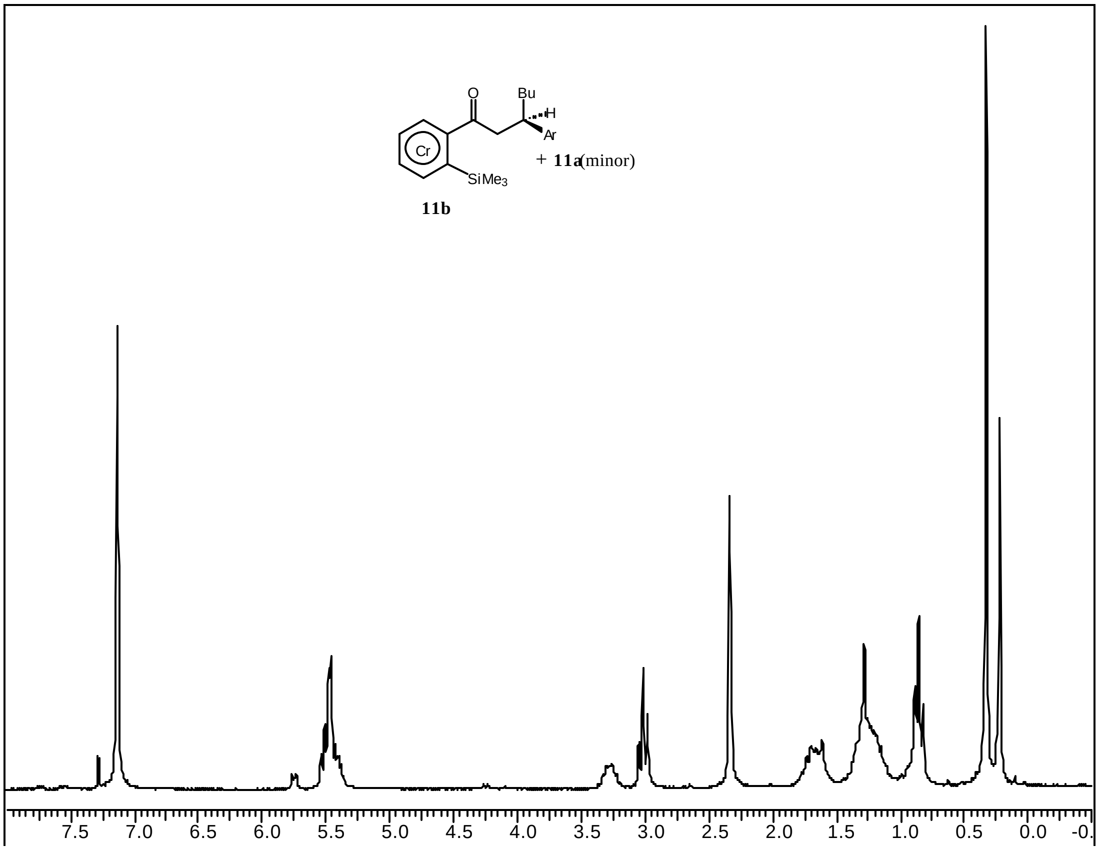
O
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Cr
SiMe3
+ 11a(minor)
11b
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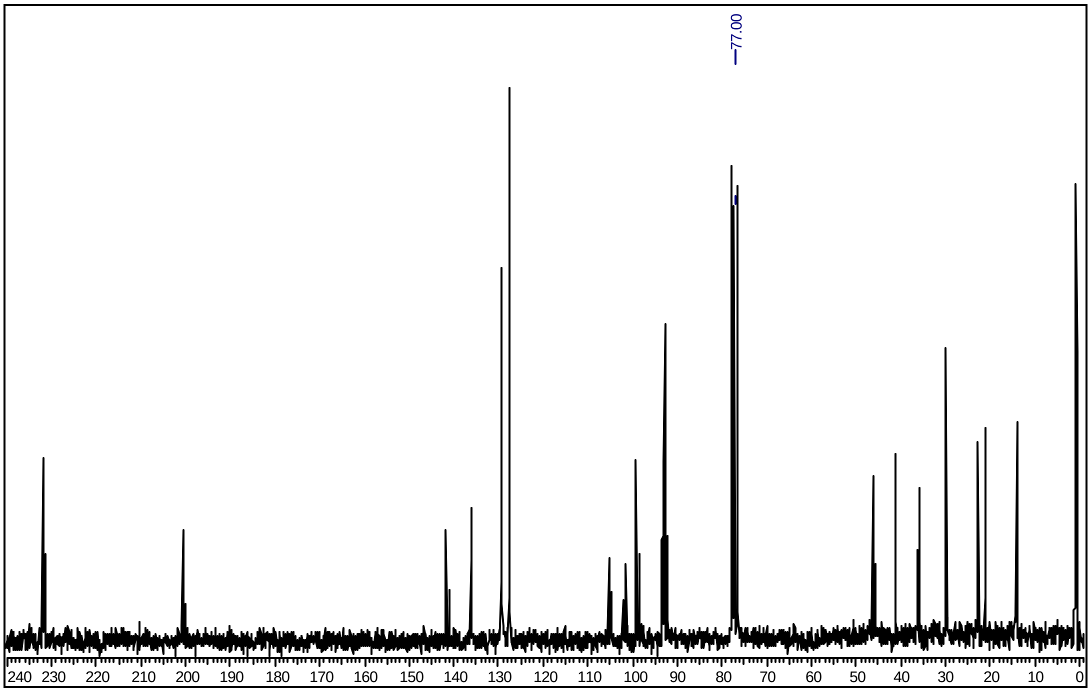
77.00
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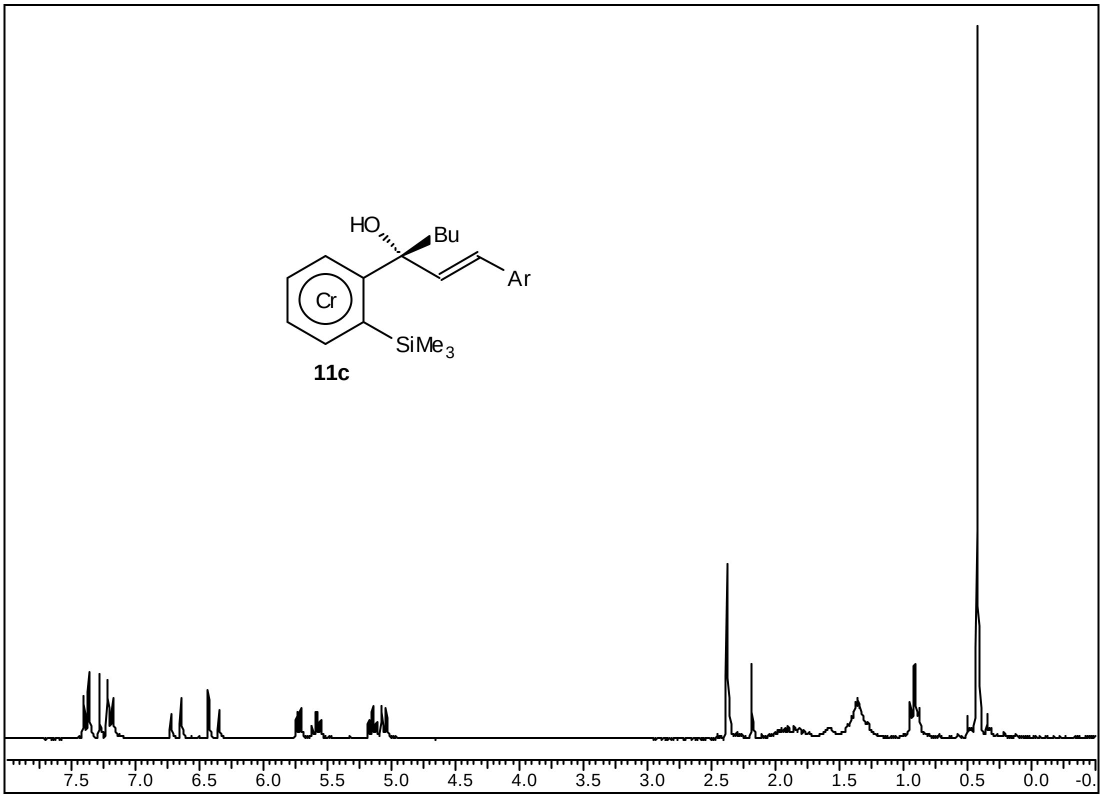
HO
Bu
Ar
Cr
SiMe$_3$
11c
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6.0
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1.5
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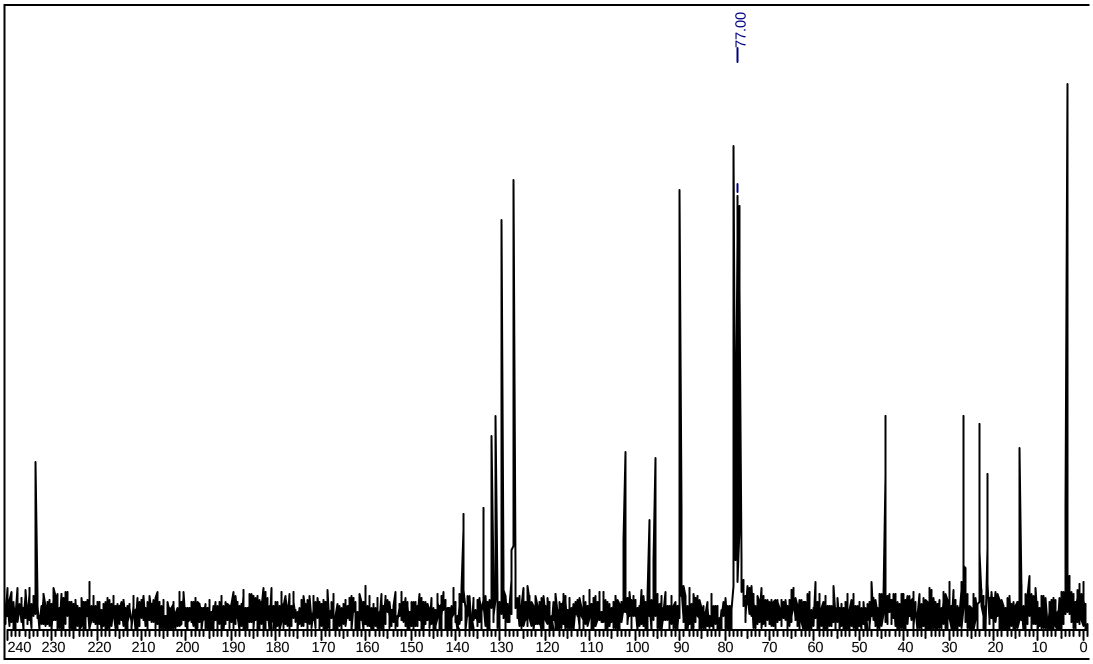
77.00
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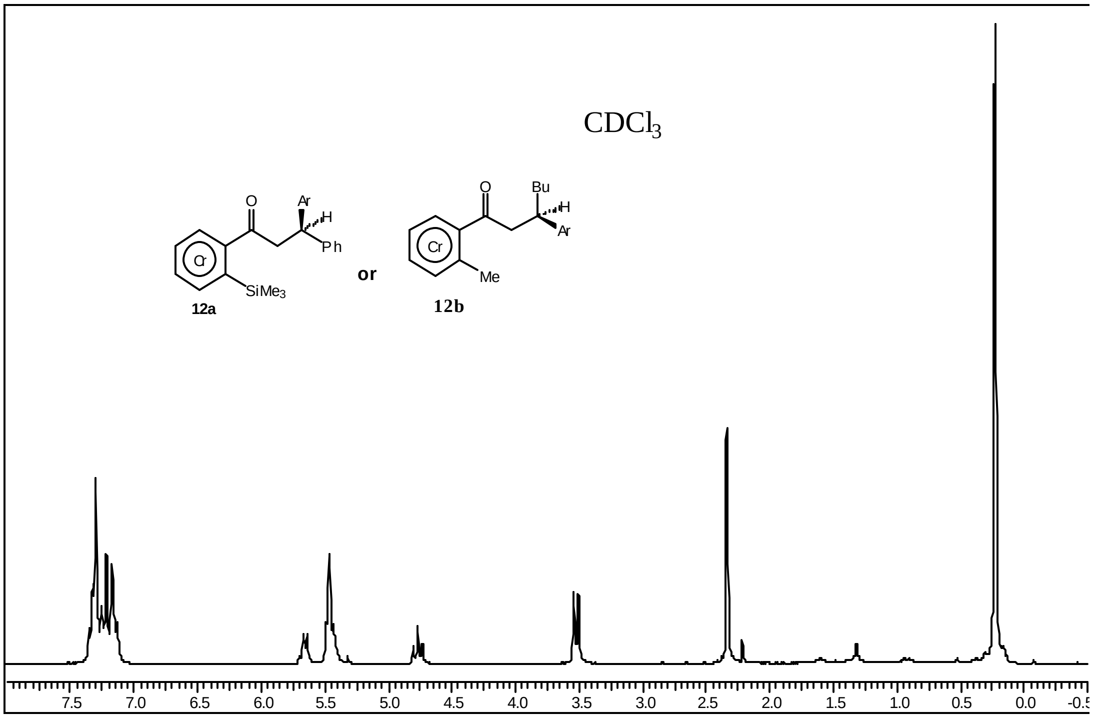
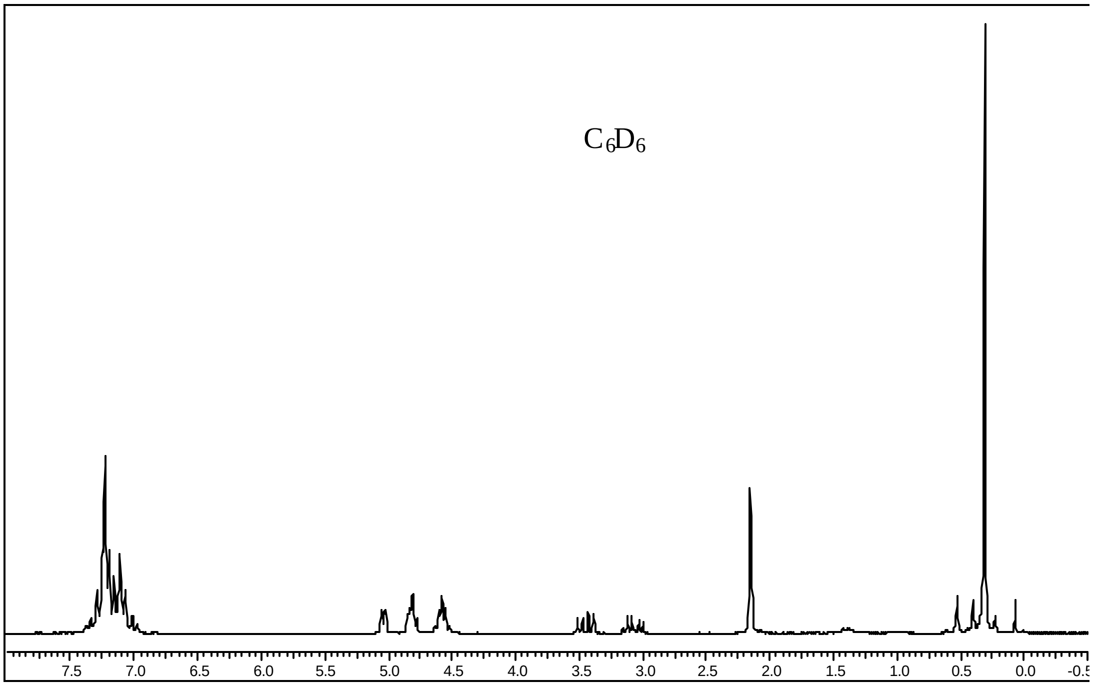
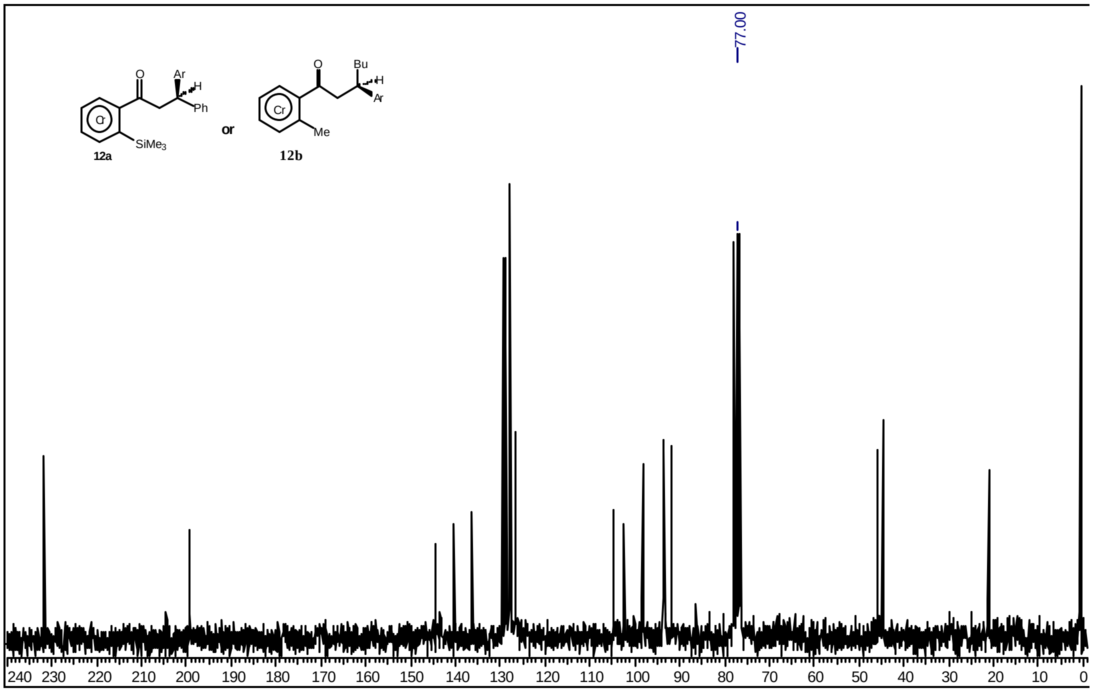
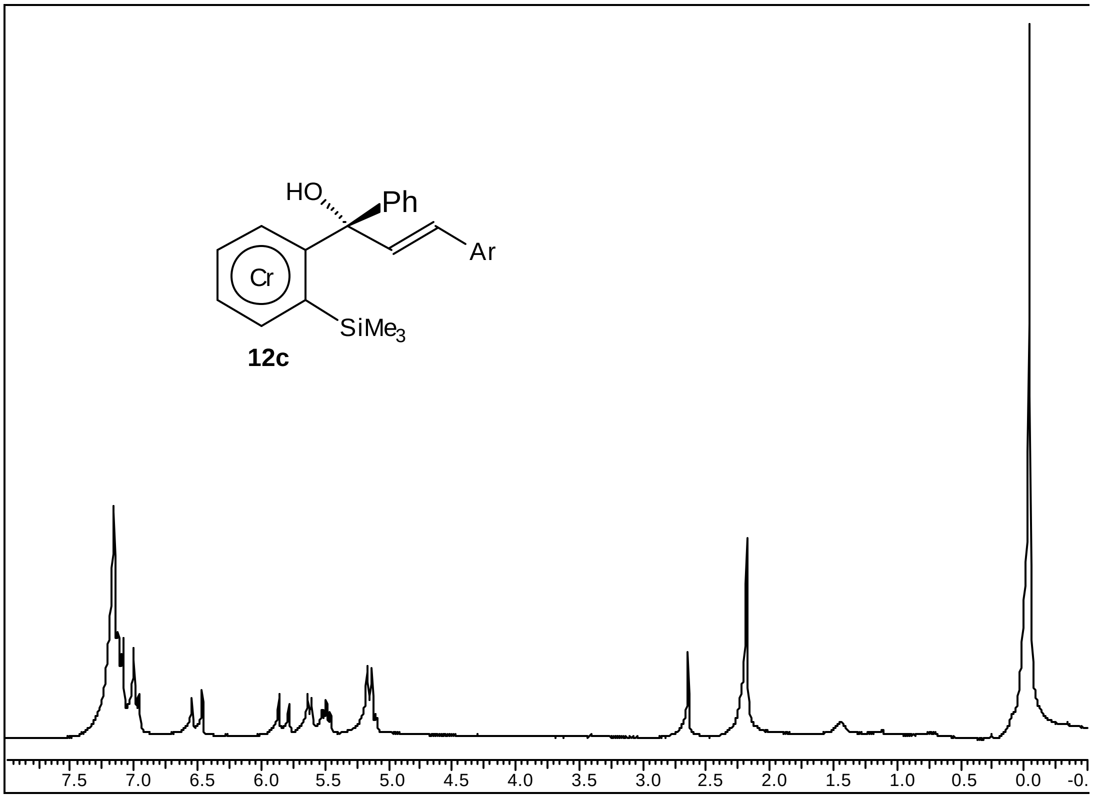
10
0

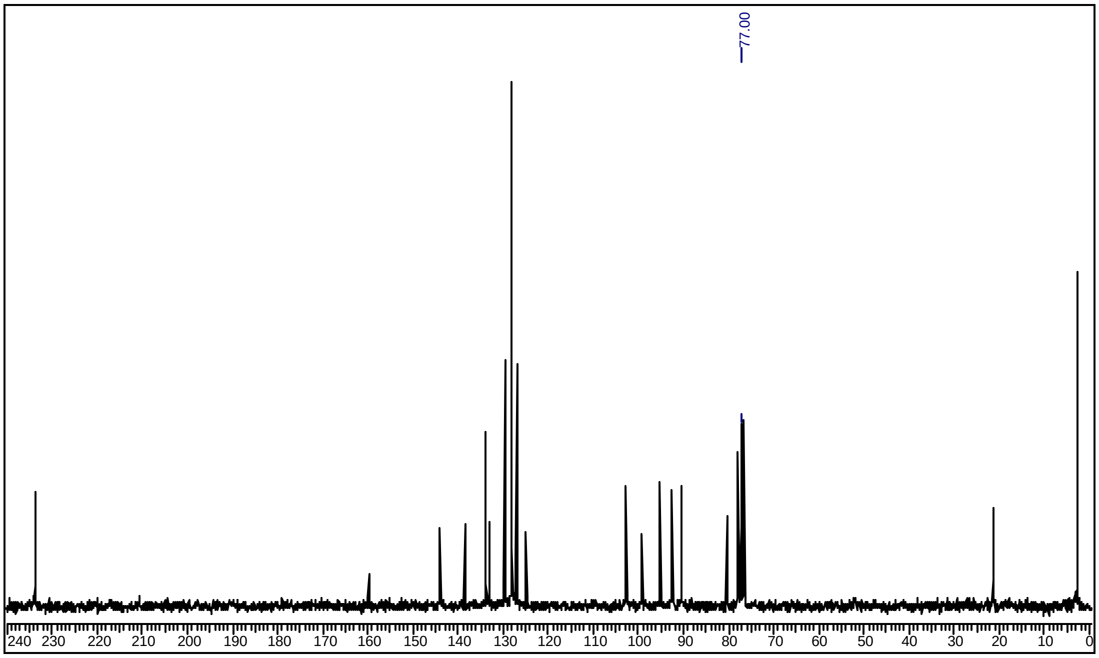

CDCl$_3$
O
Ar
H
Ph
Cr
SiMe$_3$
12a
or
O
Bu
H
Ar
Cr
Me
12b
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5


C$_6$D$_6$
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5



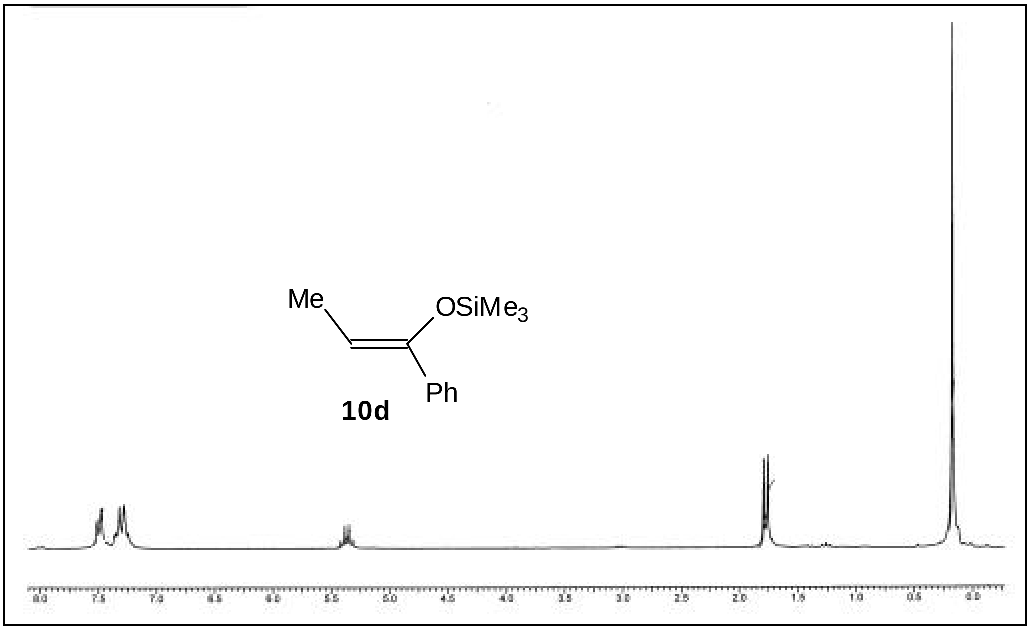
O
Ar
H
Ph
Cr
SiMe$_3$
12a
or
O
Bu
H
Ar
Cr
Me
12b
77.00
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


HO
Ph
Ar
Cr
SiMe3
12c
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.

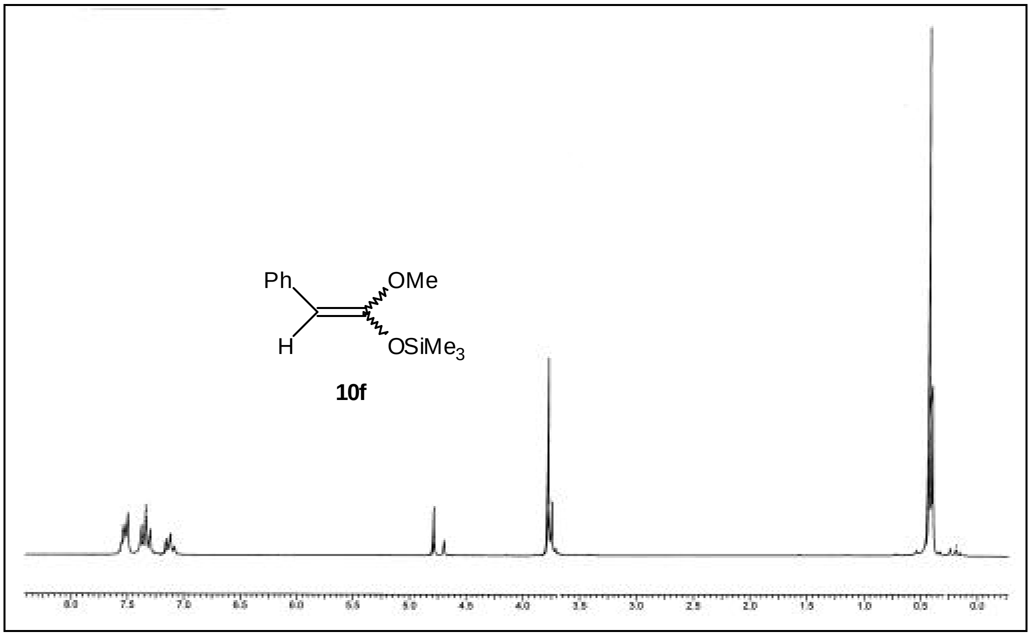

77.00
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

Appendix-II

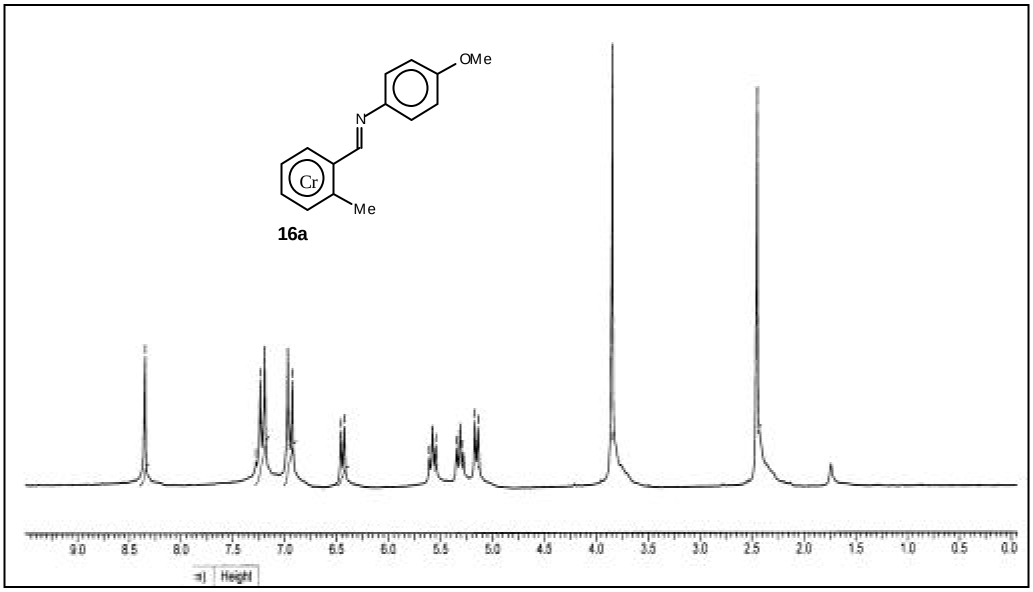
Spectra of Compounds – Chapter II

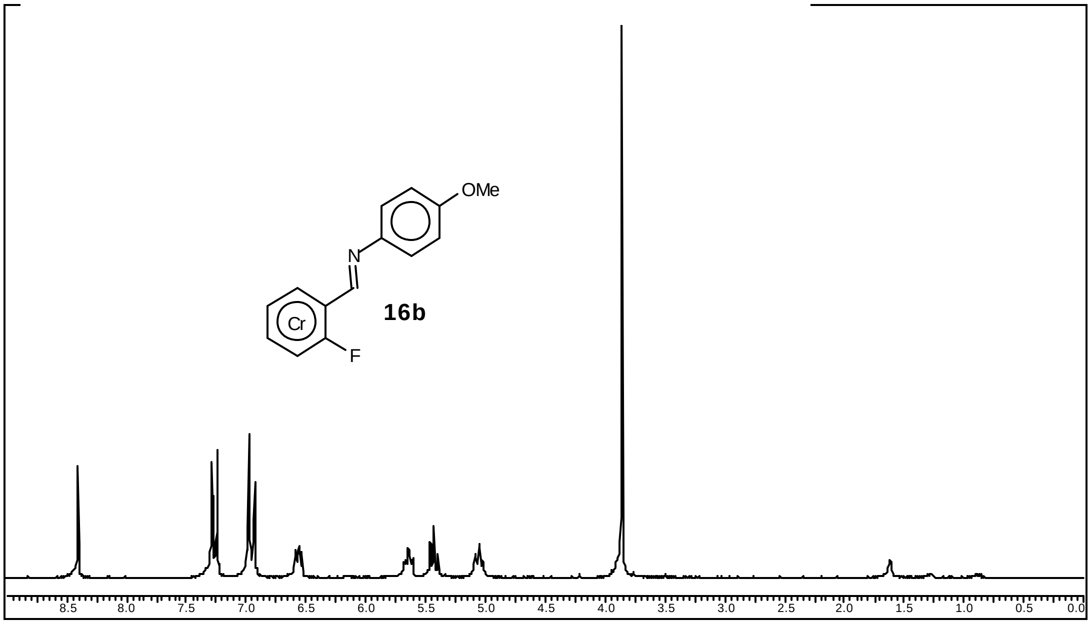

Me
OSiMe3
Ph
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

10d

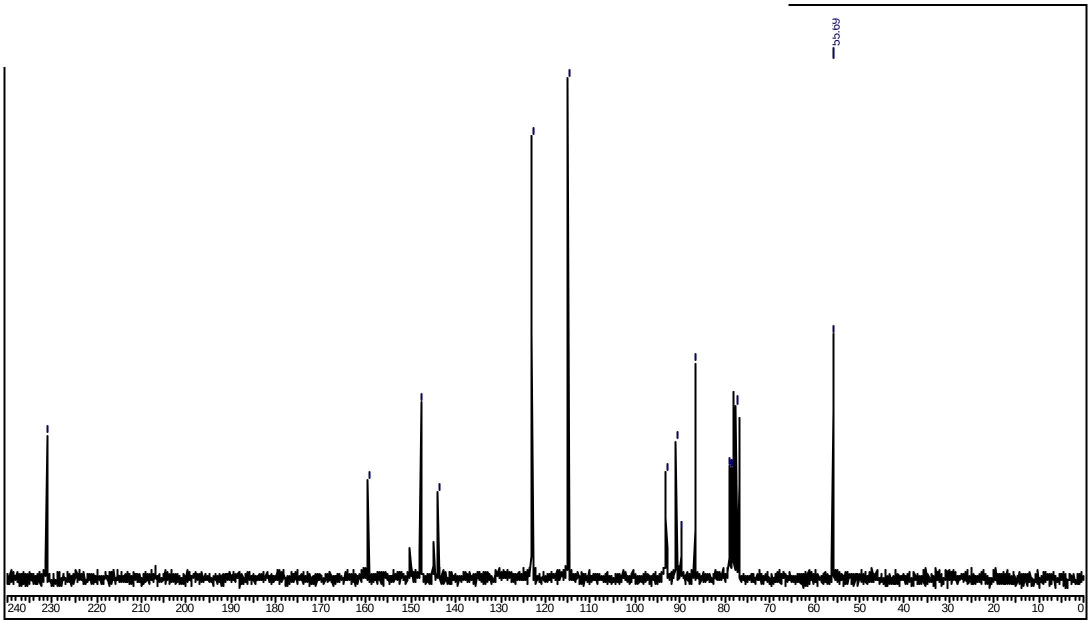

Ph
OMe
H
OSiMe3
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

10f


OMe
N
Cr
Me
16a
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Height


OMe
N
Cr
F
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

16b


55.69
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
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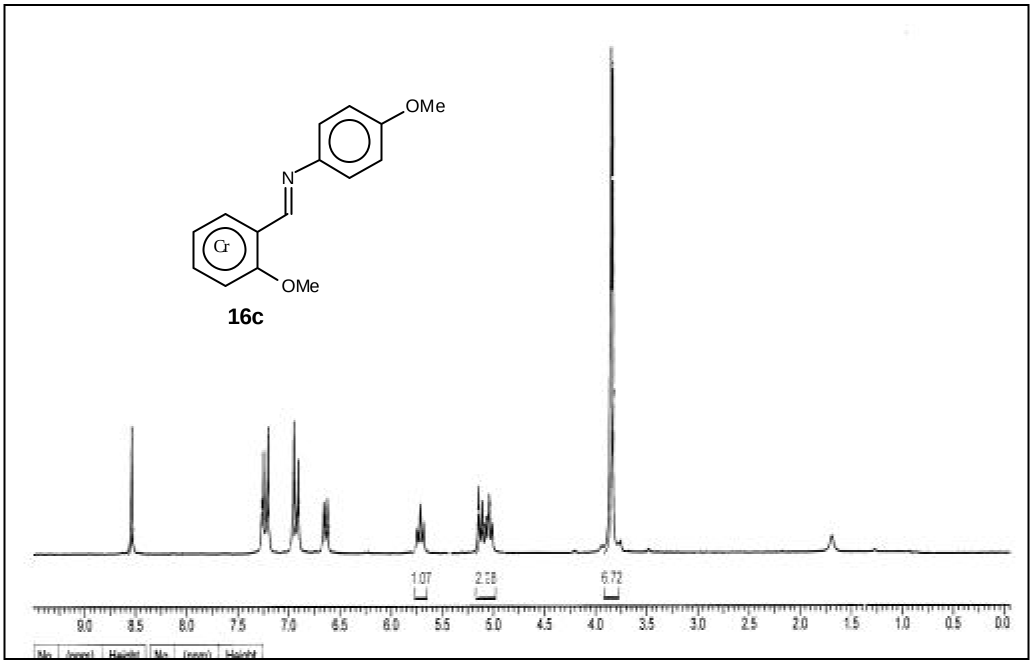
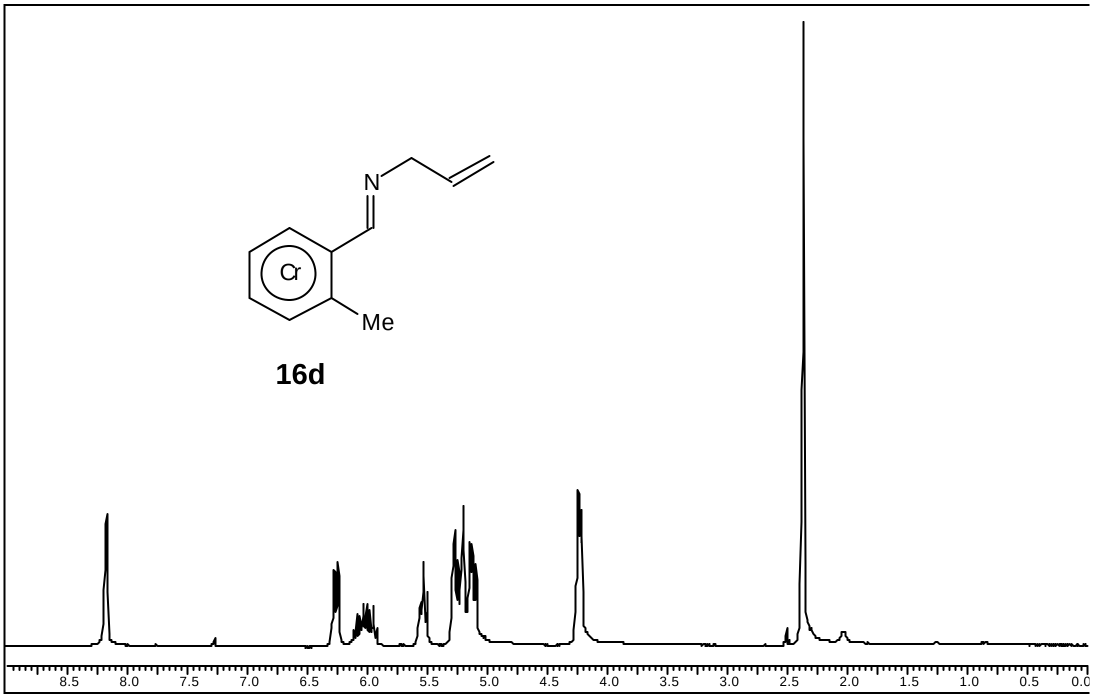
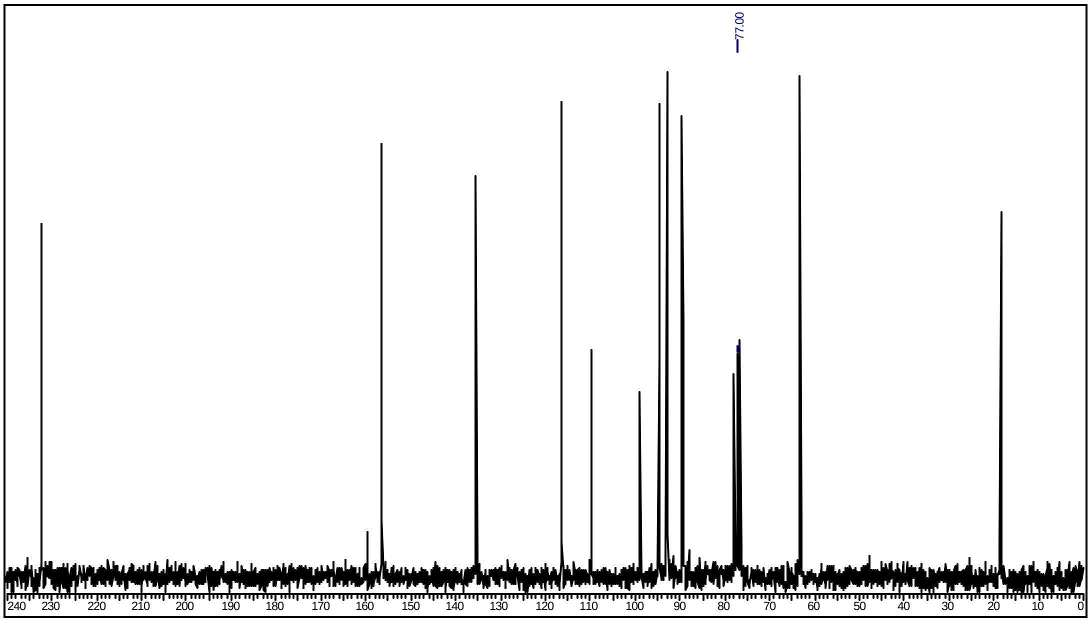
50
40
30
20
10
0


OMe
N
Cr
OMe
16c
1.07
2.28
6.72
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
No. (ppm) Height No. (ppm) Height


N
Cr
Me
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

16d


77.00
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
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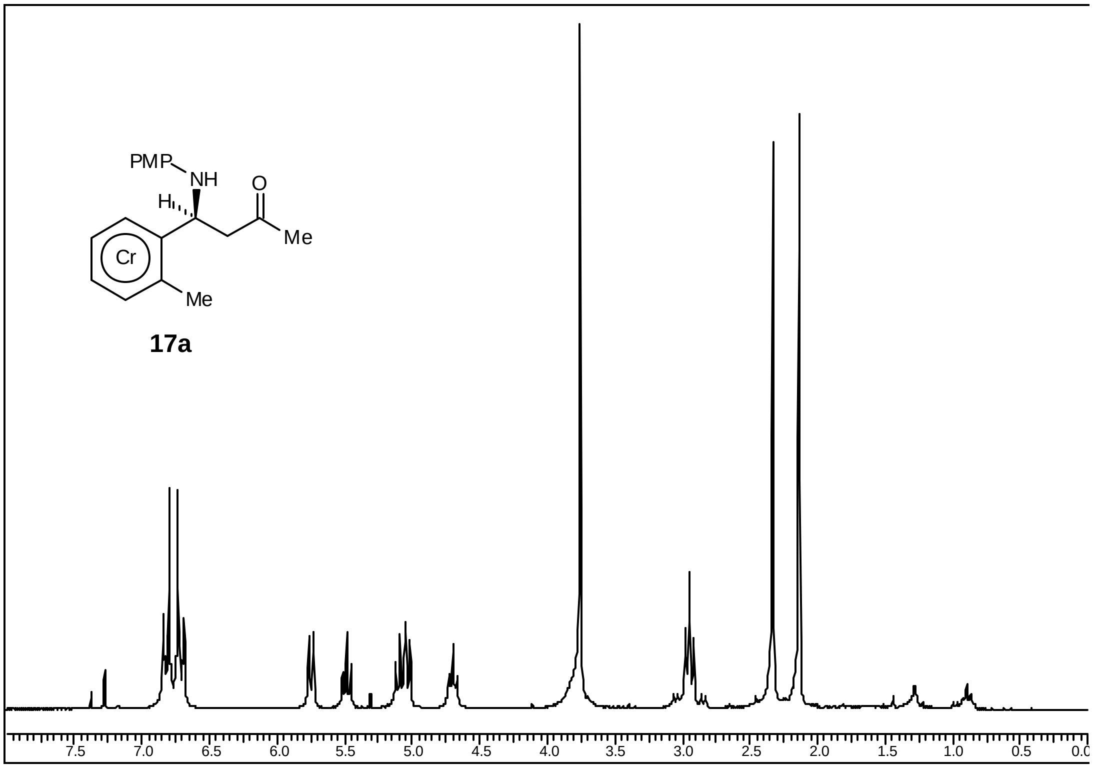
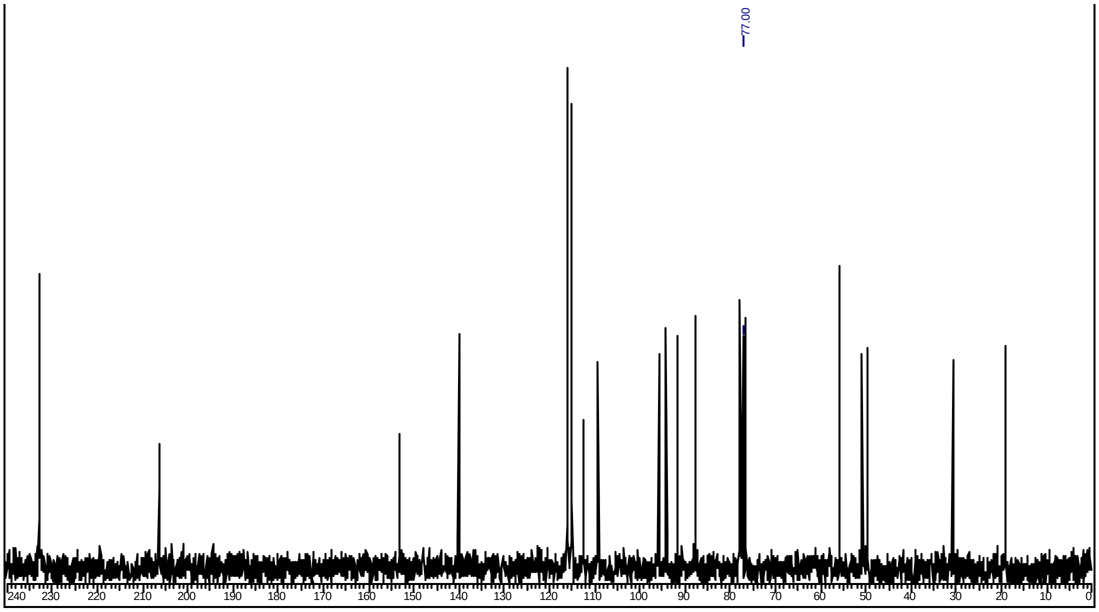
50
40
30
20
10
0


PMP
NH
O
H
Cr
Me
Me
17a
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


77.00
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
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50
40
30
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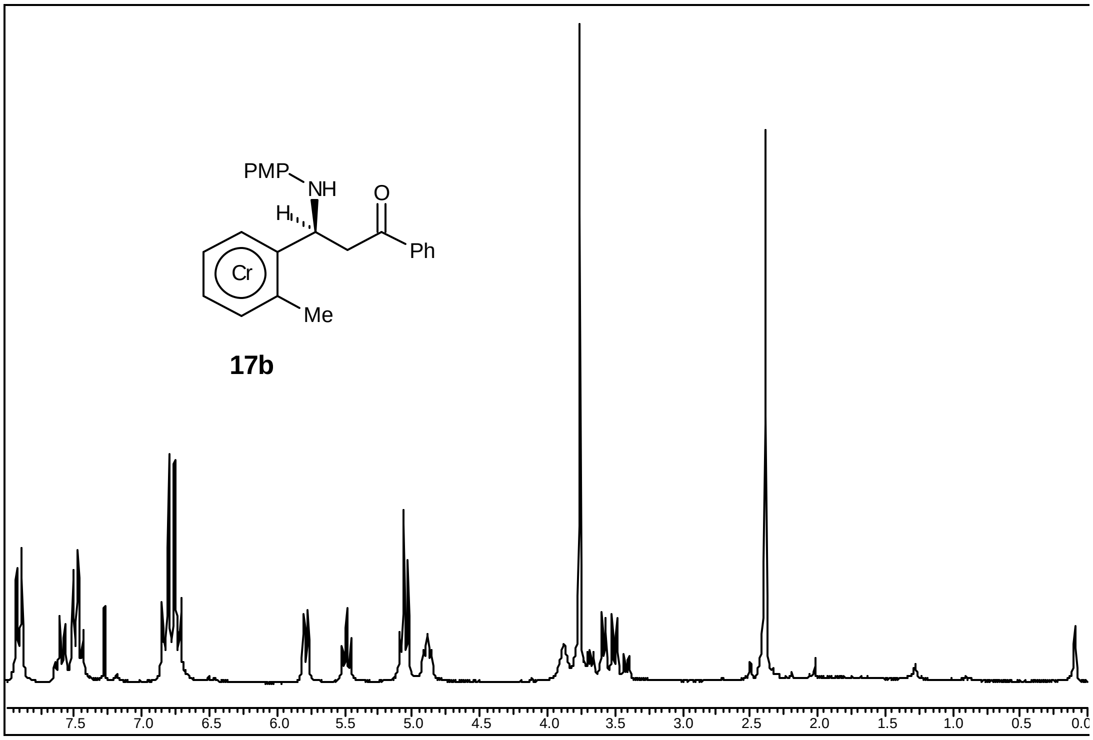
10
0


PMP
NH
O
H
Ph
Cr
Me
7.5
7.0
6.5
6.0
5.5
5.0
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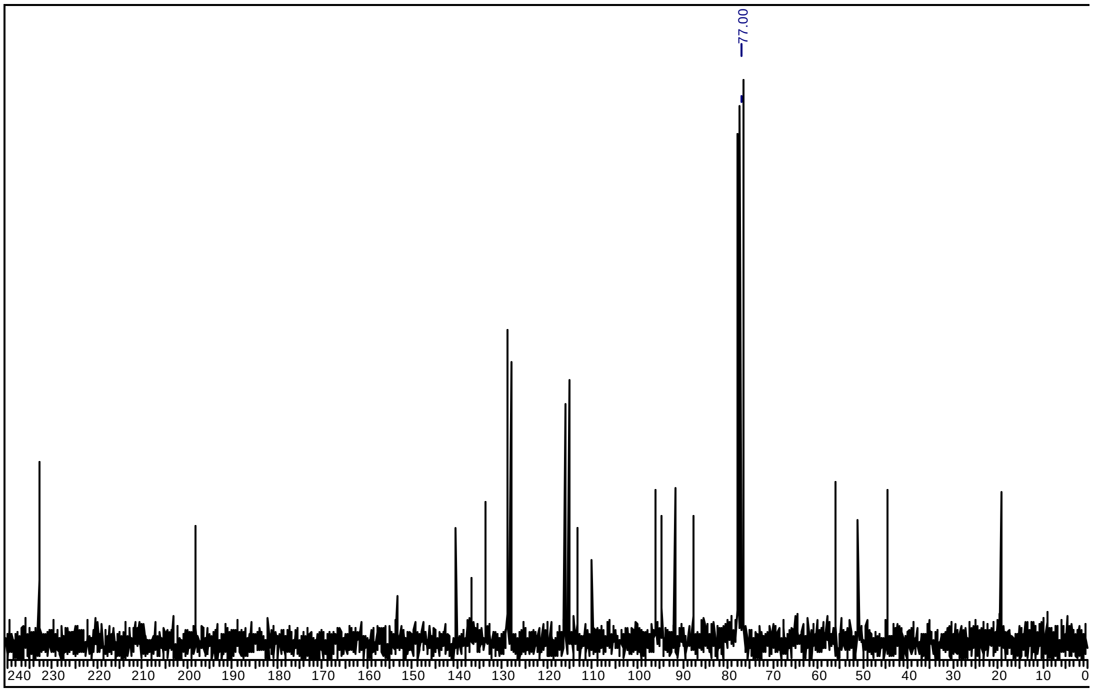
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

17b


77.00
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
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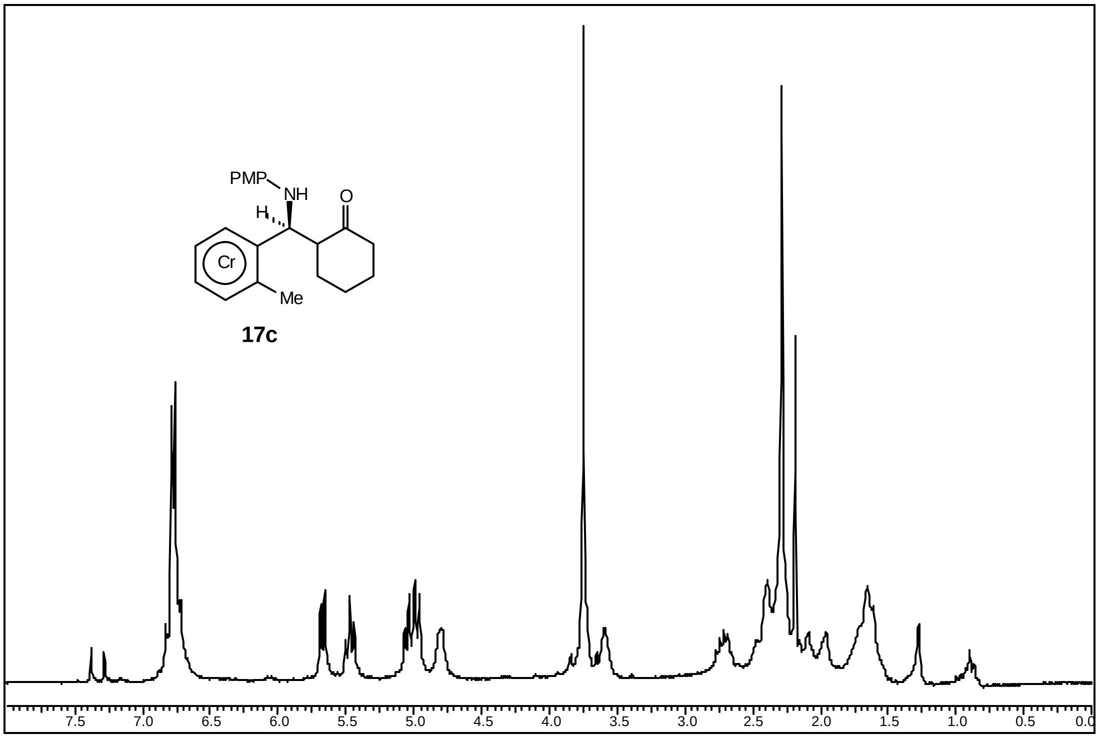
50
40
30
20
10
0



17c

PMP
NH
H
O
Cr
Me
7.5
7.0
6.5
6.0
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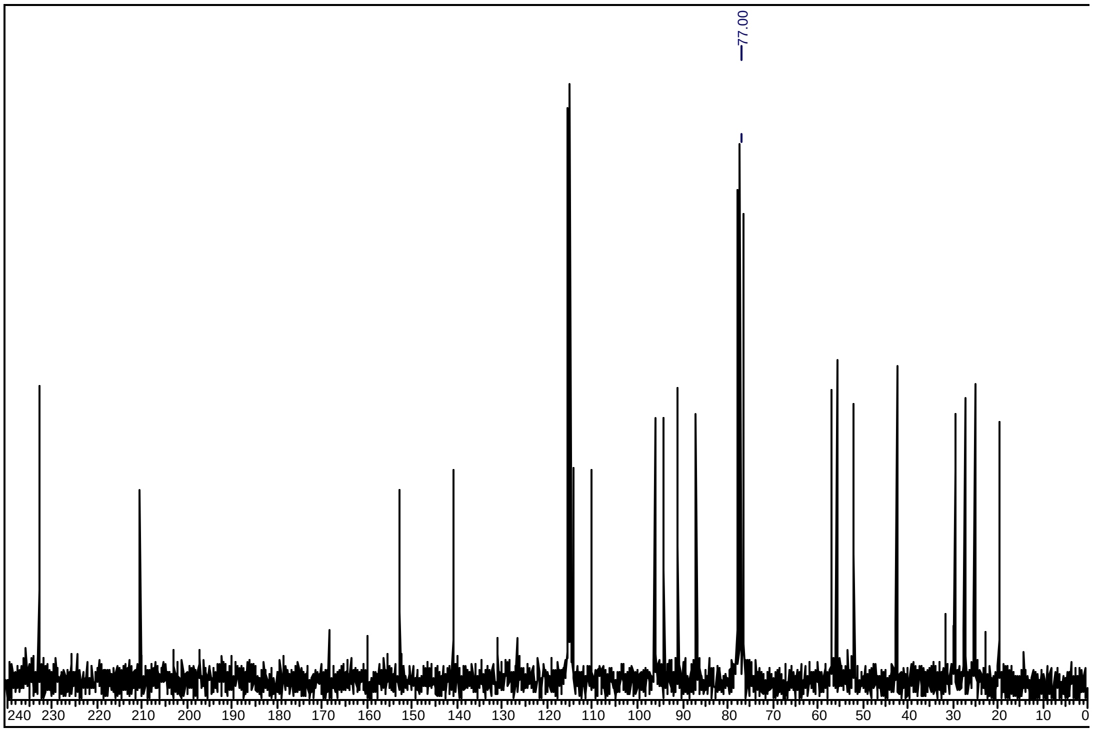
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0



77.00
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
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50
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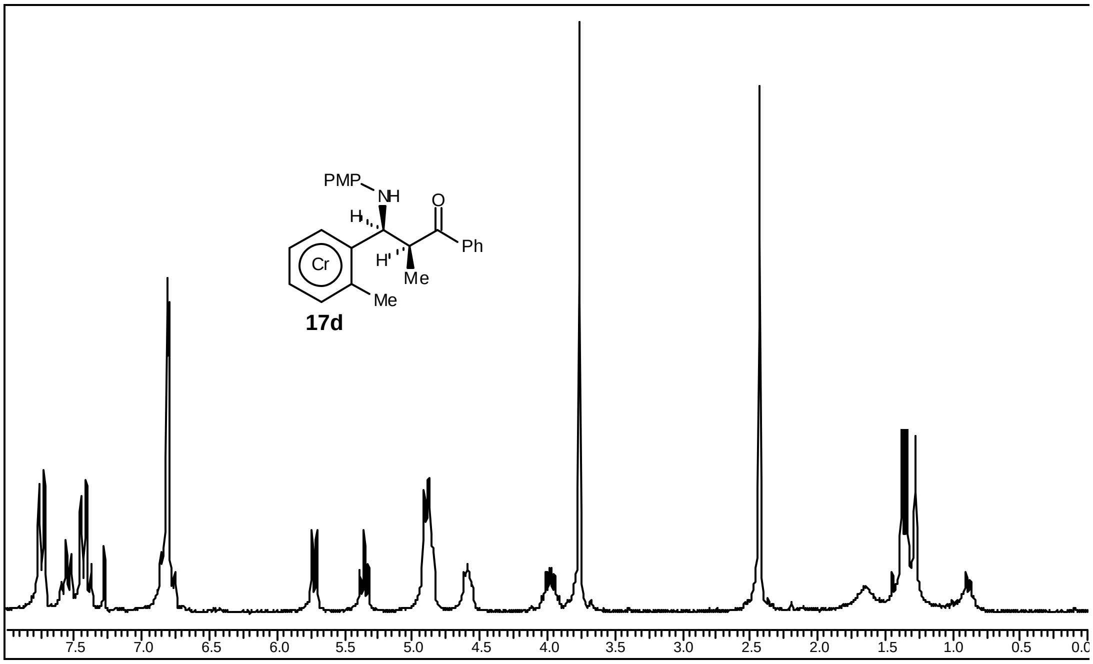
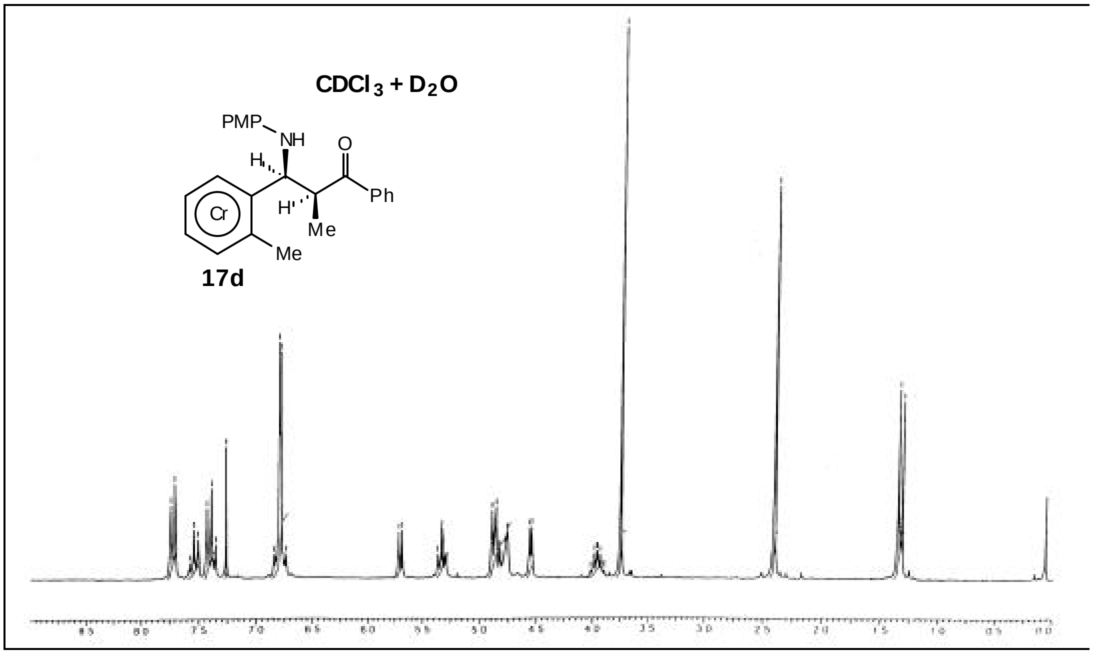
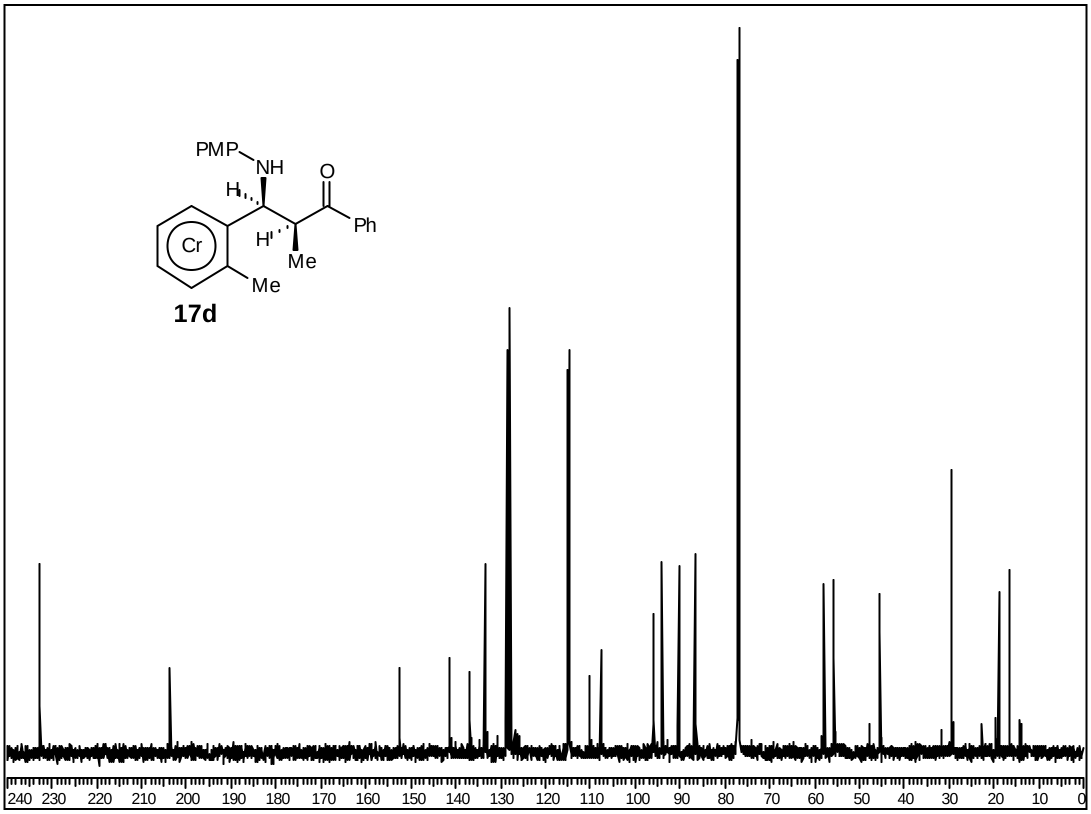
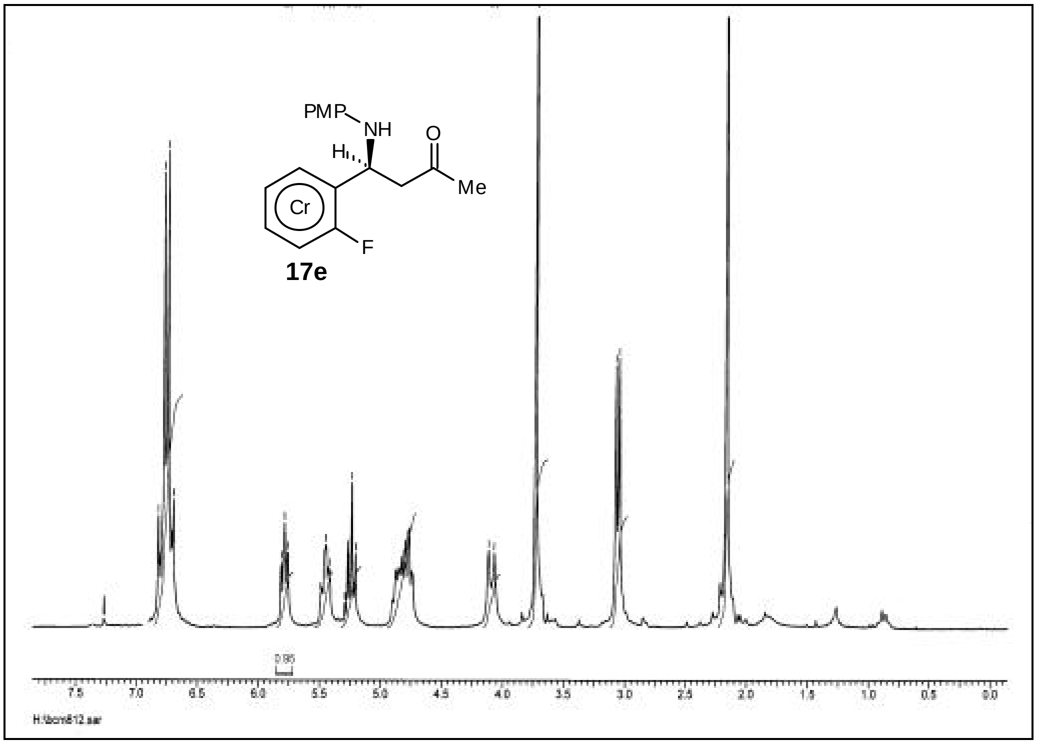
30
20
10
0

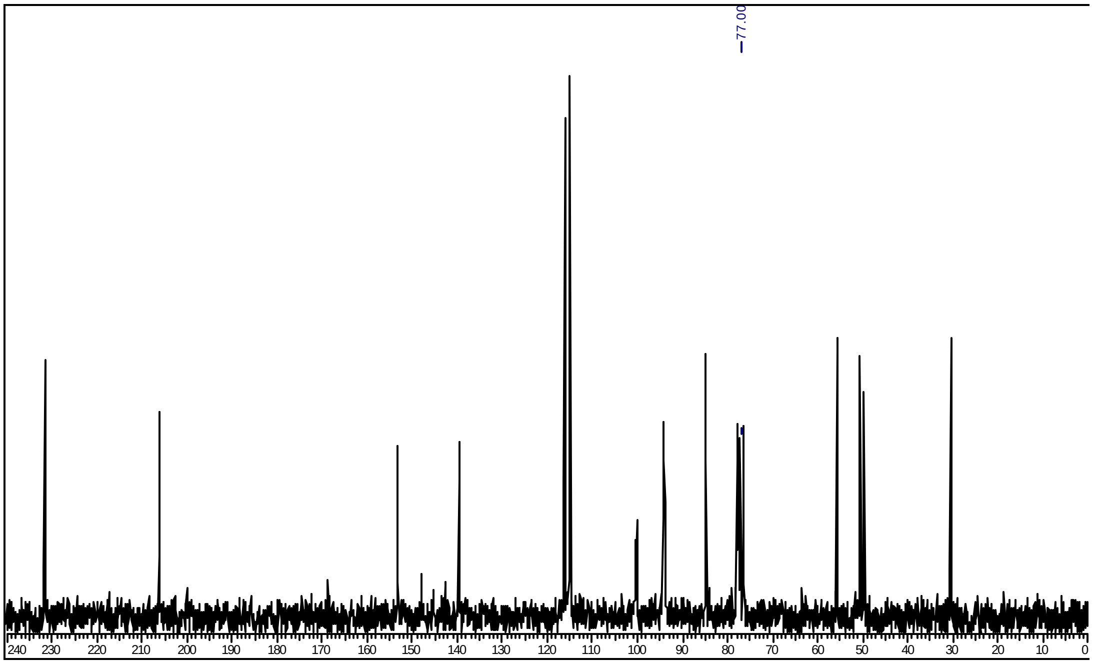

PMP
NH
H
O
Ph
Cr
H'
Me
Me
17d
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


CDCl3 + D2O
PMP
NH
H
O
Ph
Cr
H'
Me
Me
17d


PMP
NH
H
O
Ph
Cr
H
Me
Me
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

17d


PMP
NH
H
O
Me
Cr
F
17e
0.95
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
H:\bcm812.sar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230
220
210
200
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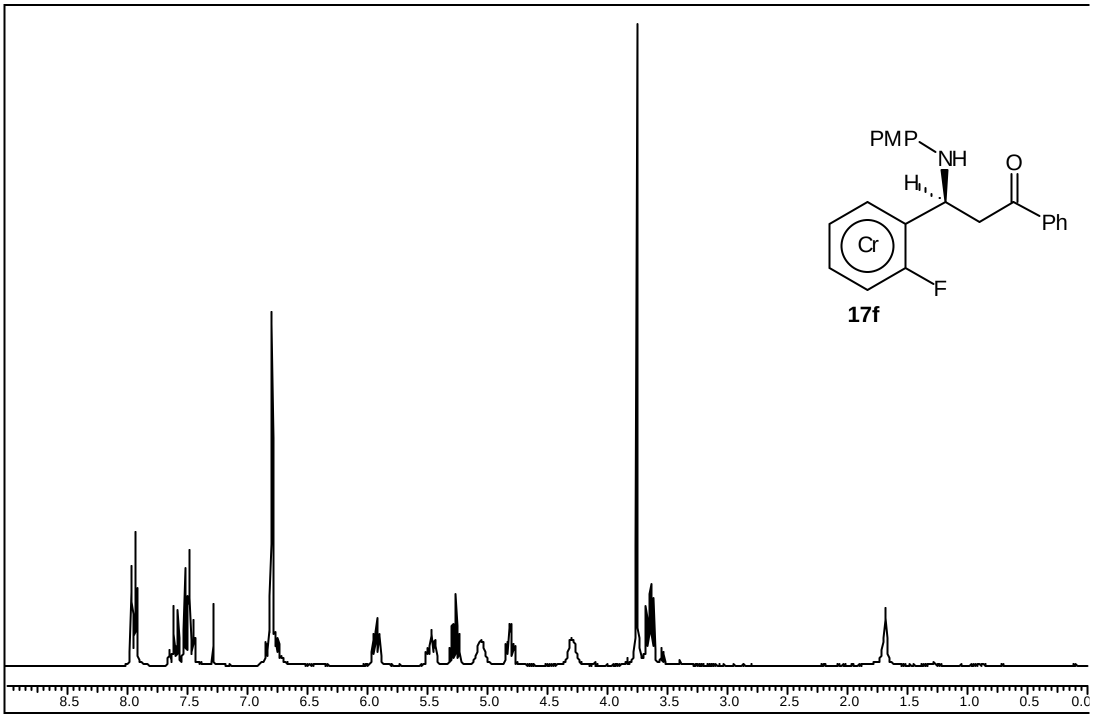
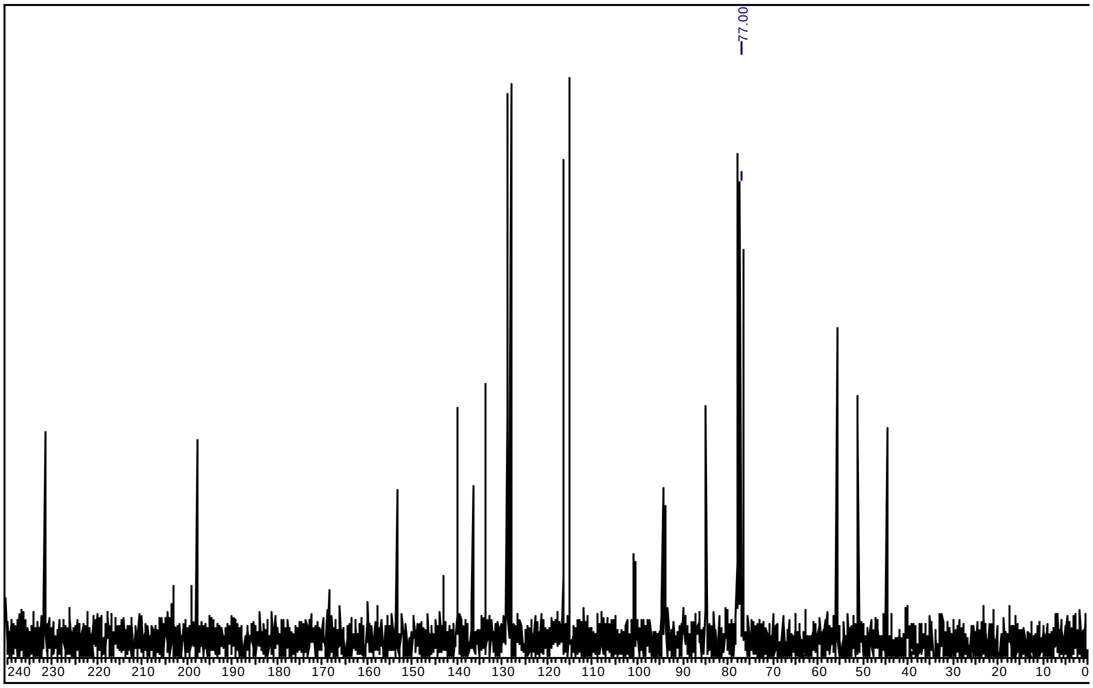
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


PMP
NH
H
O
Ph
Cr
F
17f
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


77.00
240
230
220
210
200
190
180
170
160
150
140
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120
110
100
90
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70
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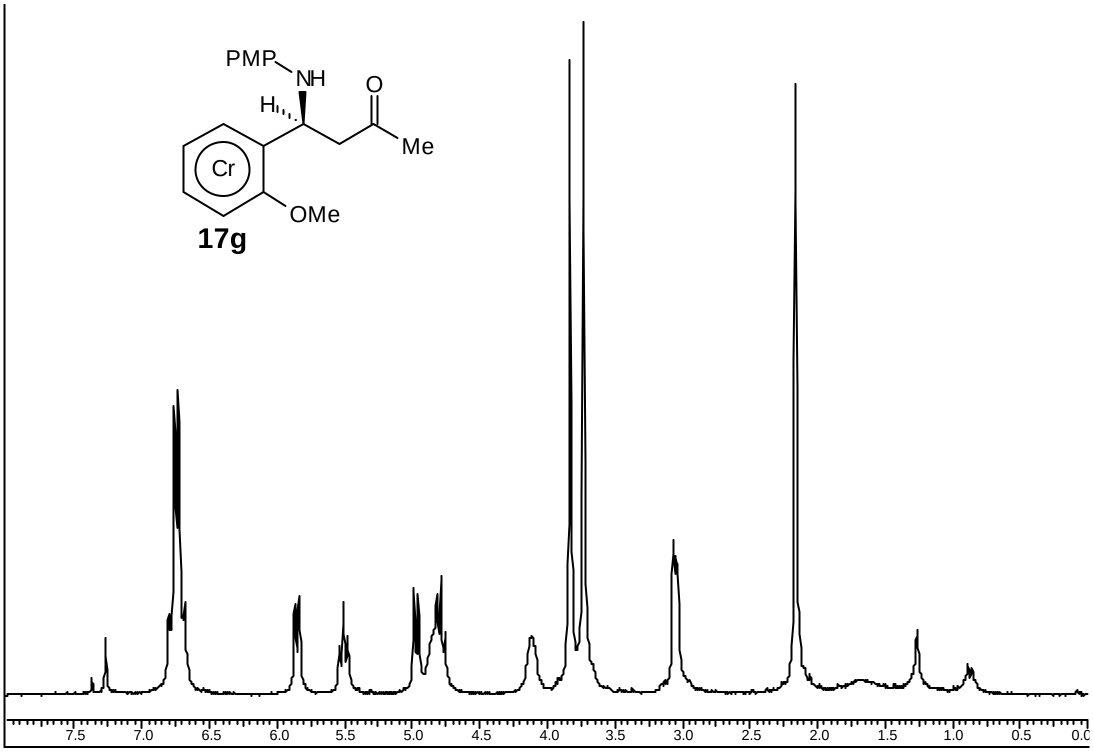
50
40
30
20
10
0


PMP
NH
H
O
Me
Cr
OMe
7.5
7.0
6.5
6.0
5.5
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3.5
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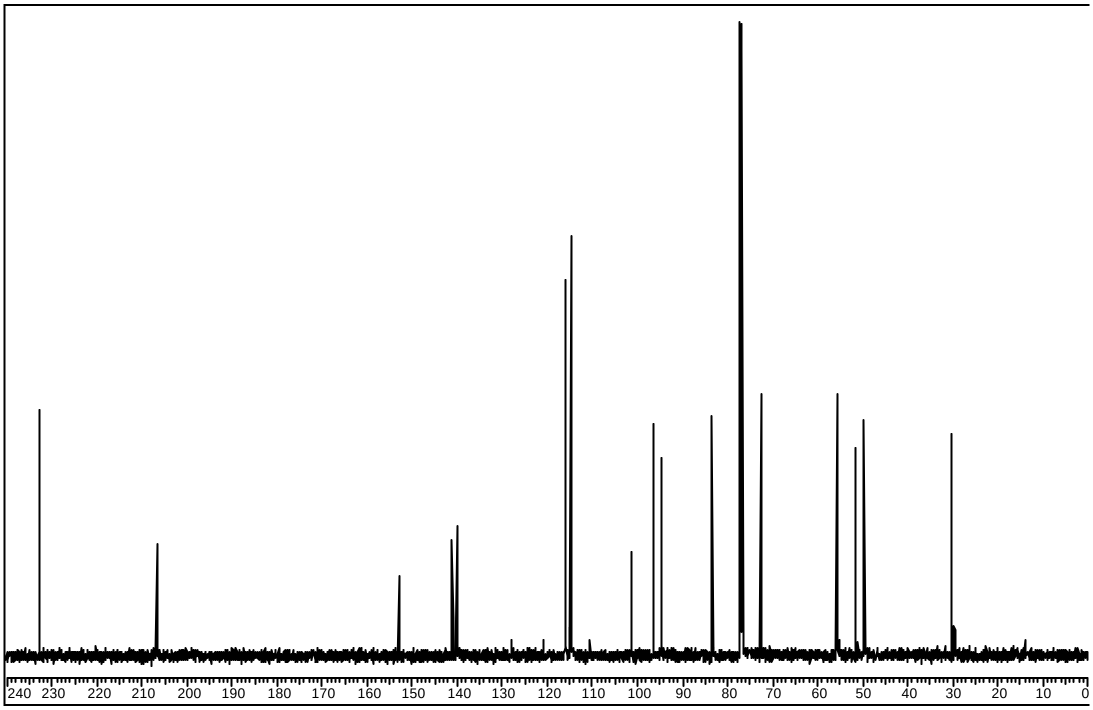
1.5
1.0
0.5
0.0

17g


240
230
220
210
200
190
180
170
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150
140
130
120
110
100
90
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70
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50
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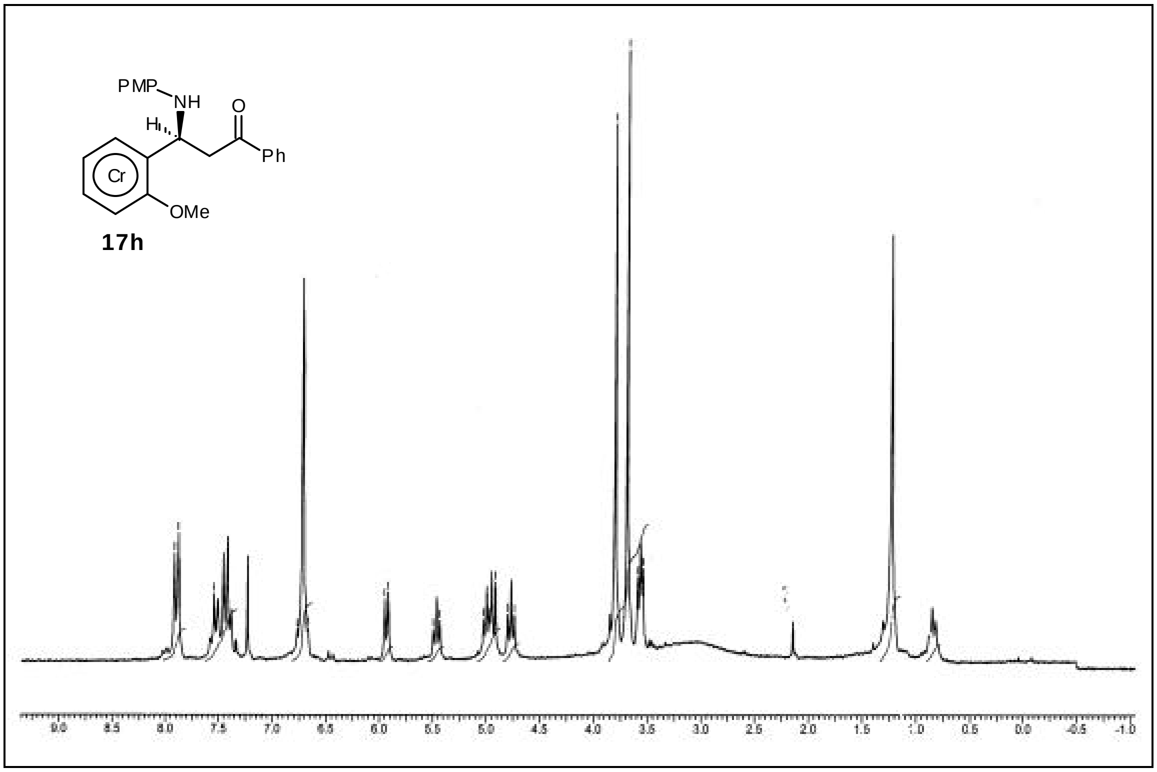
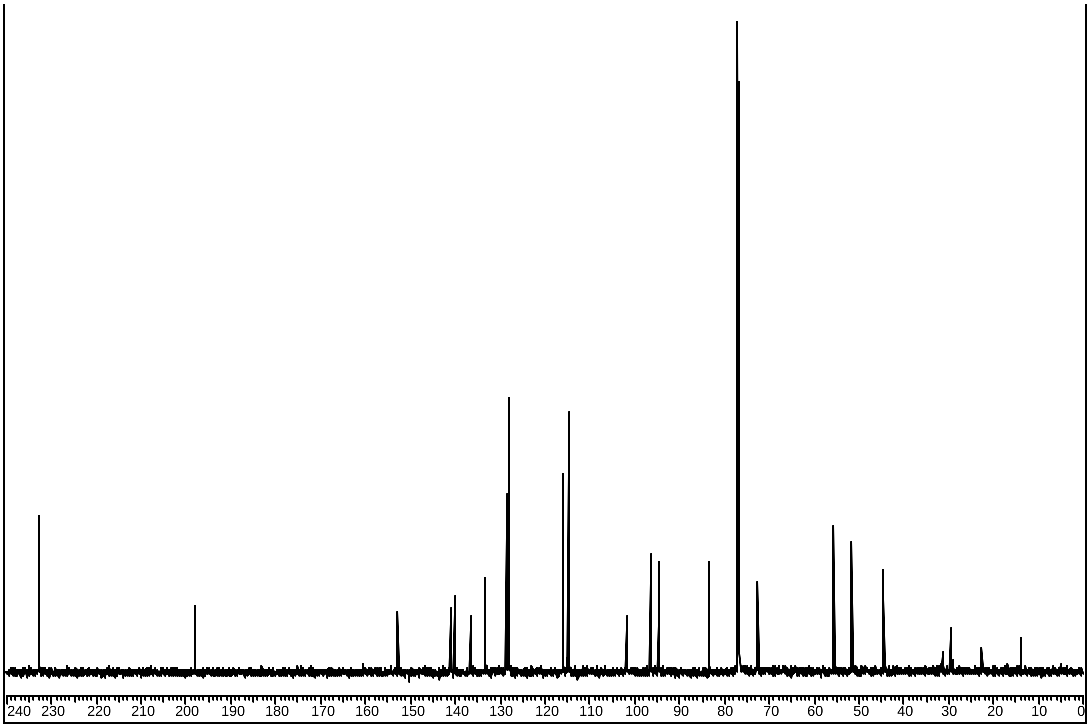
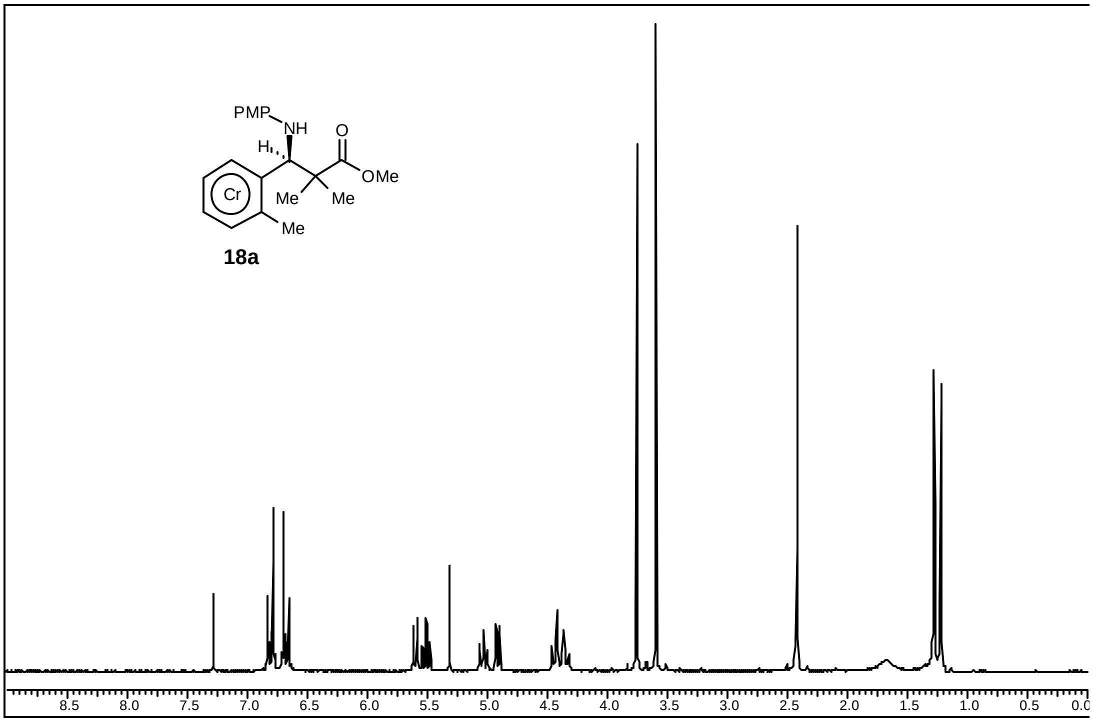
30
20
10
0

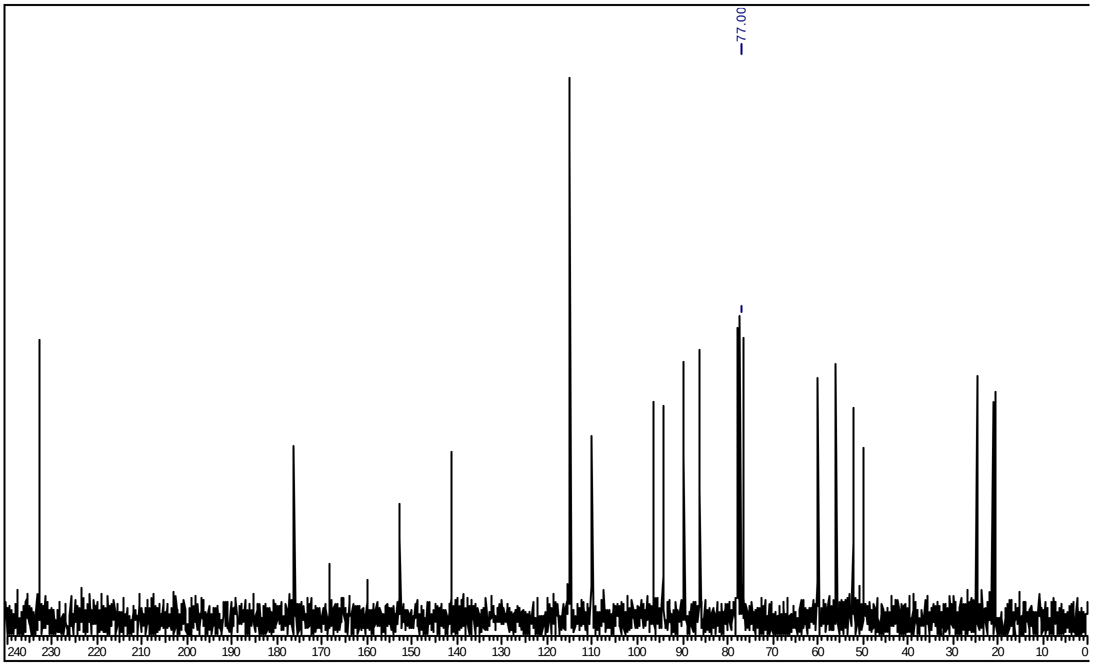

PMP
NH
H
O
Ph
Cr
OMe
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0

17h


240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


PMP
NH
H
O
OMe
Cr
Me
Me
Me
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

18a


77.00
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
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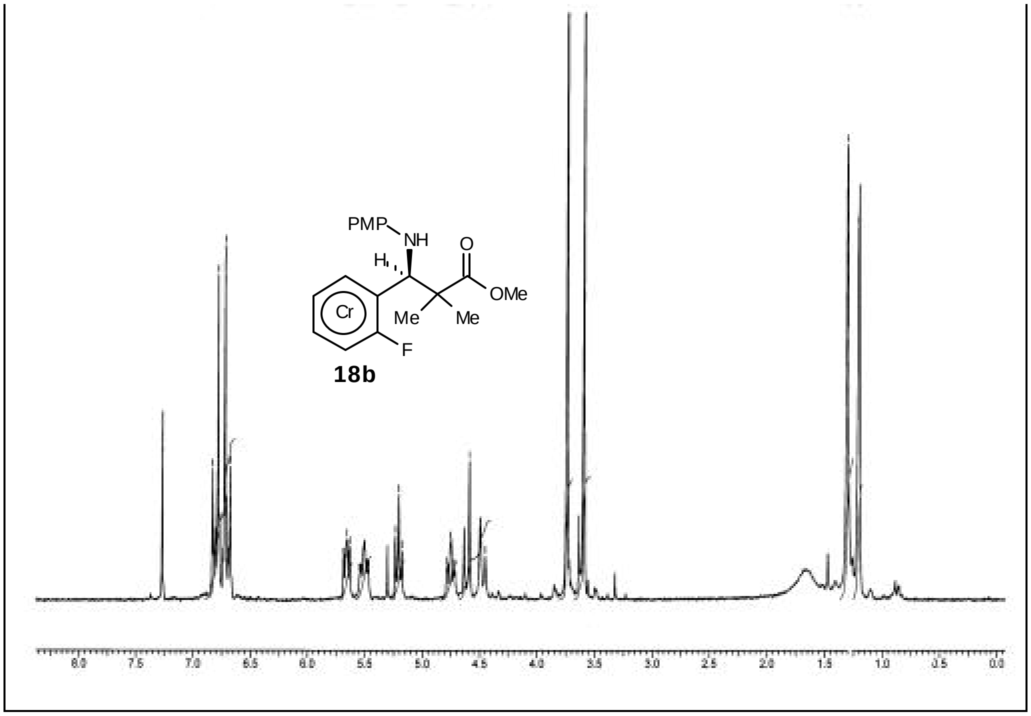
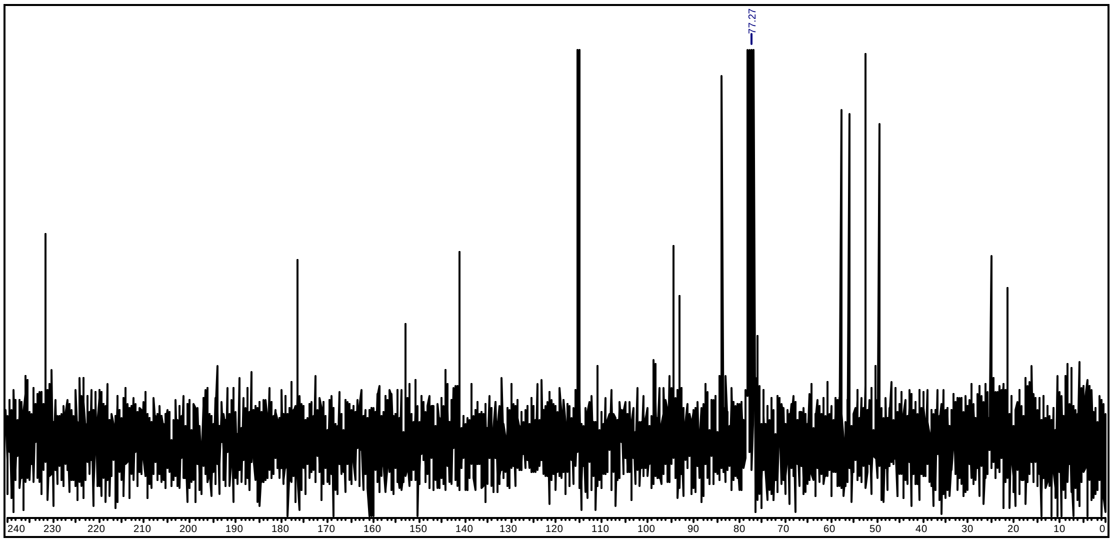
50
40
30
20
10
0


PMP
NH
H
O
OMe
Cr
Me
Me
F
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

18b


77.27
240
230
220
210
200
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180
170
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150
140
130
120
110
100
90
80
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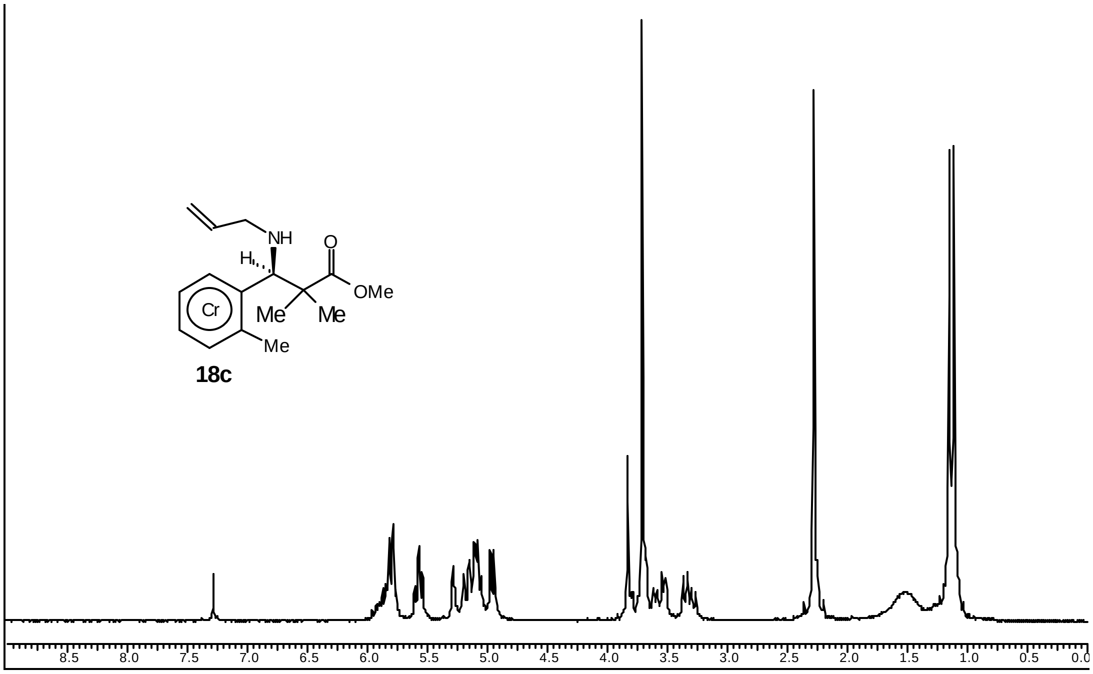
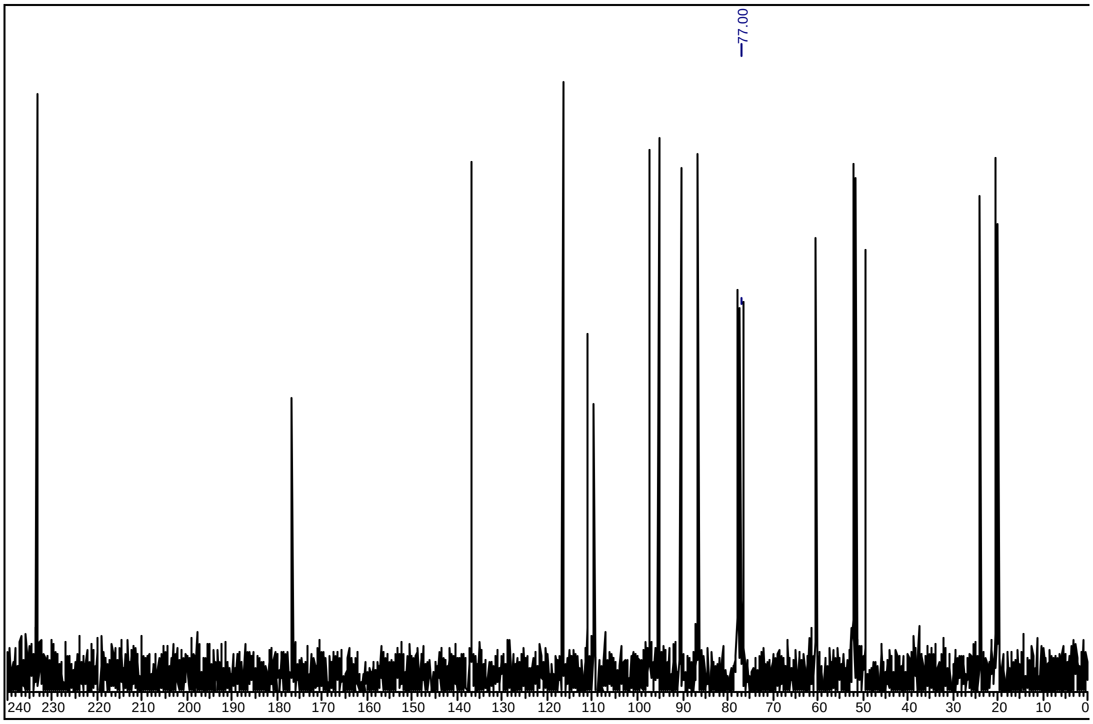
50
40
30
20
10
0


18c

NH
H
O
OMe
Cr
Me
Me
Me
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


77.00
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
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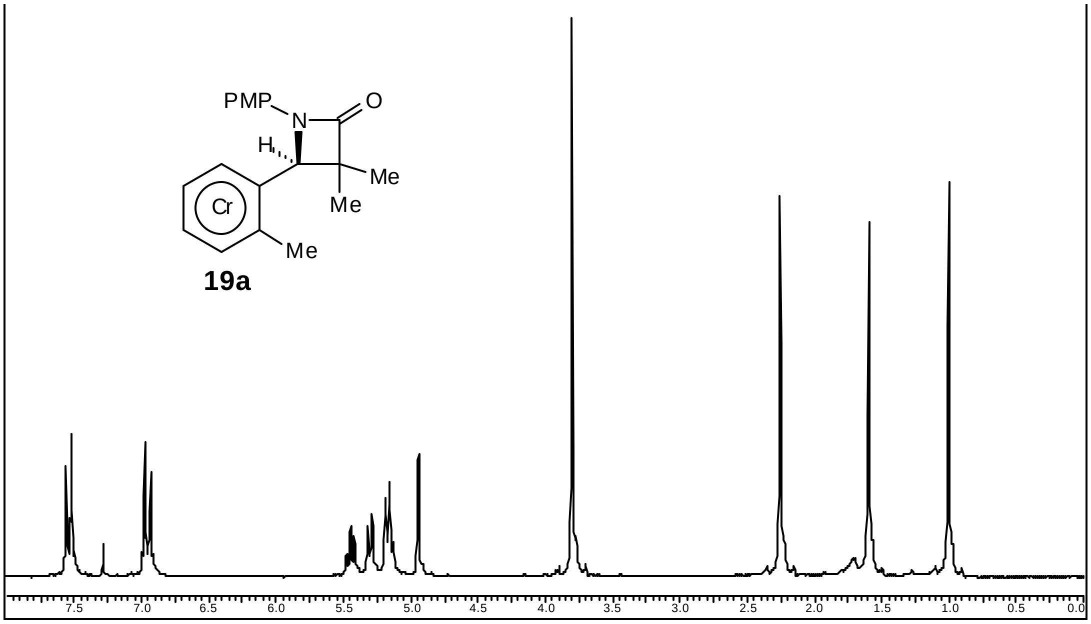
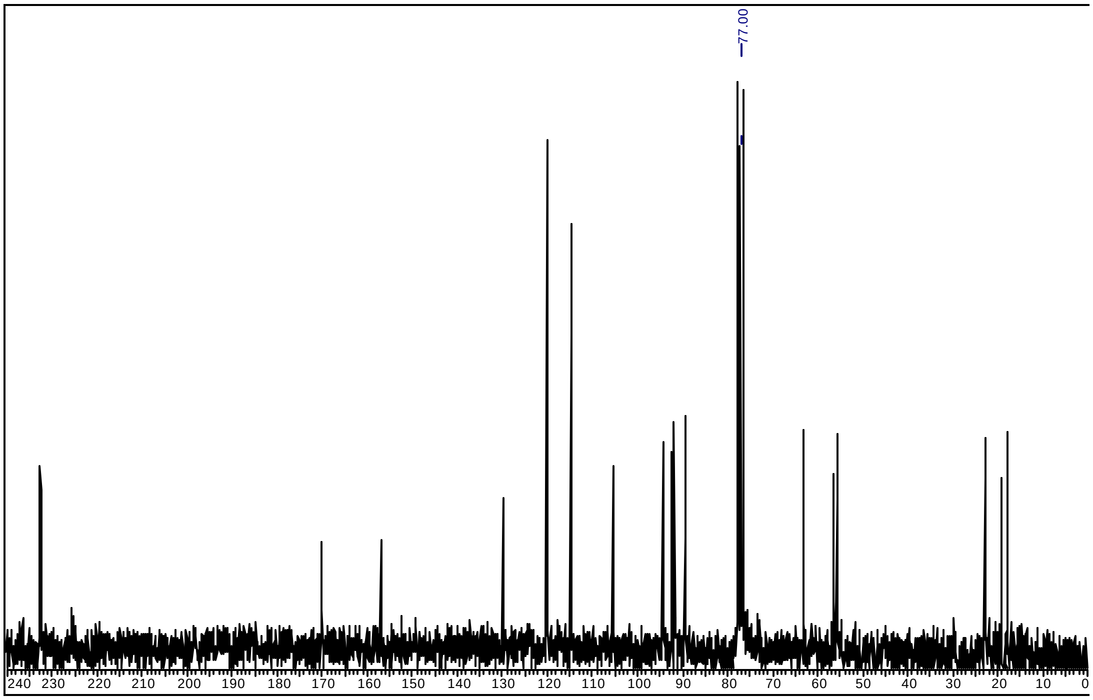
50
40
30
20
10
0


PMP
N
O
H
Me
Me
Cr
Me
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

19a


77.00
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
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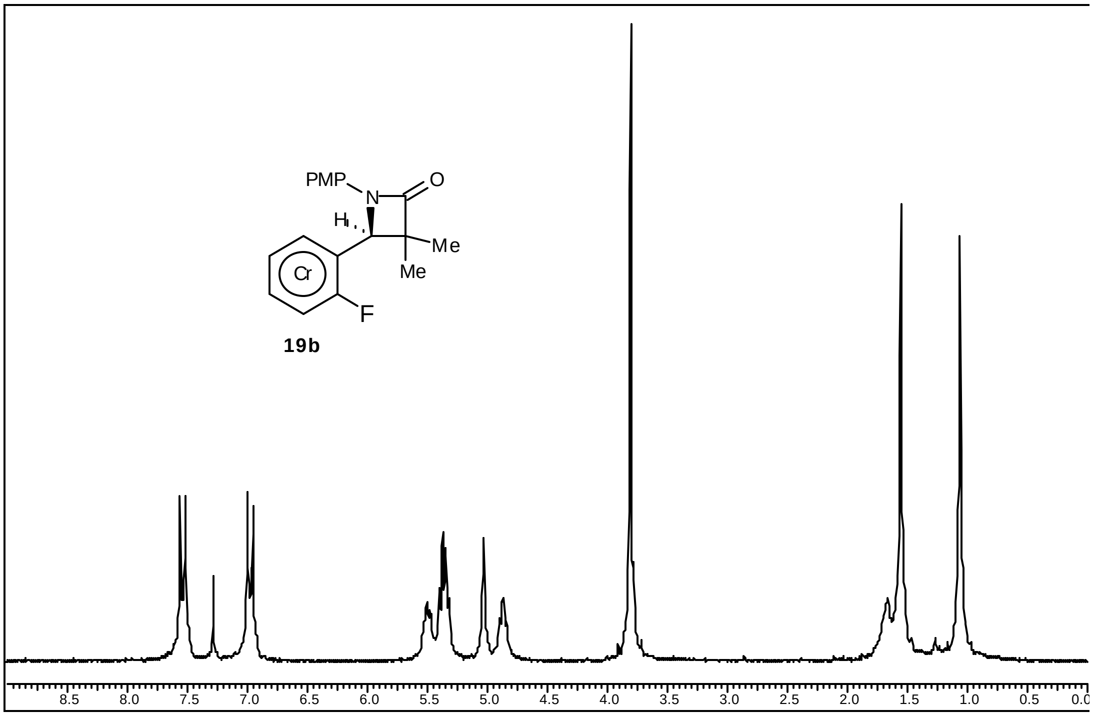
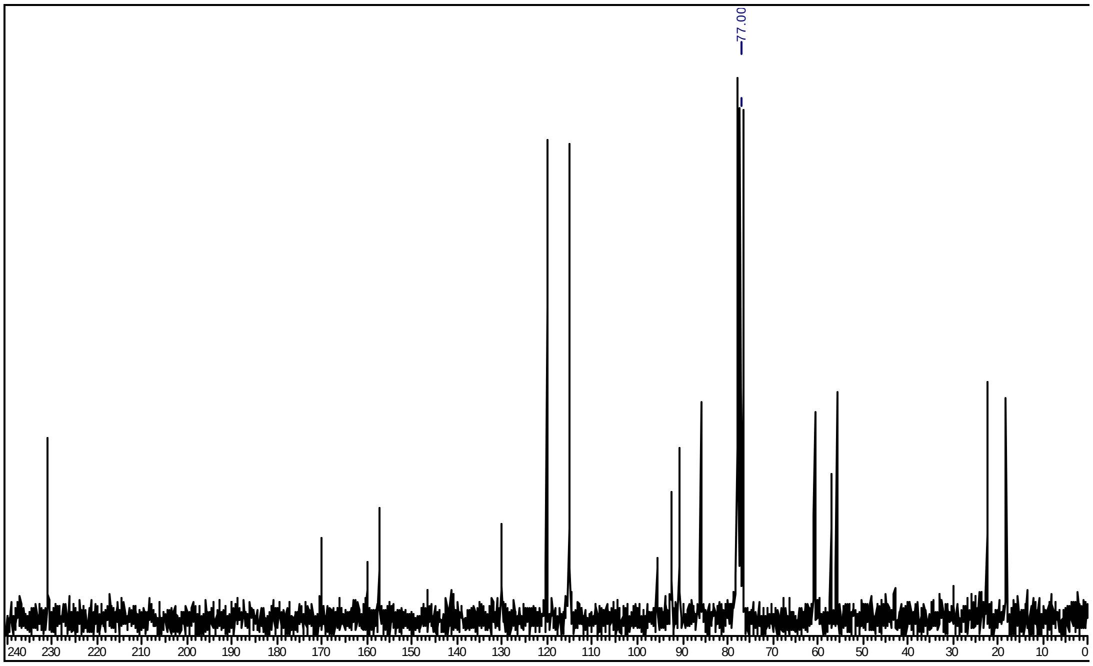
50
40
30
20
10
0


PMP
N
O
H
Me
Me
Cr
F
19b
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


77.00
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
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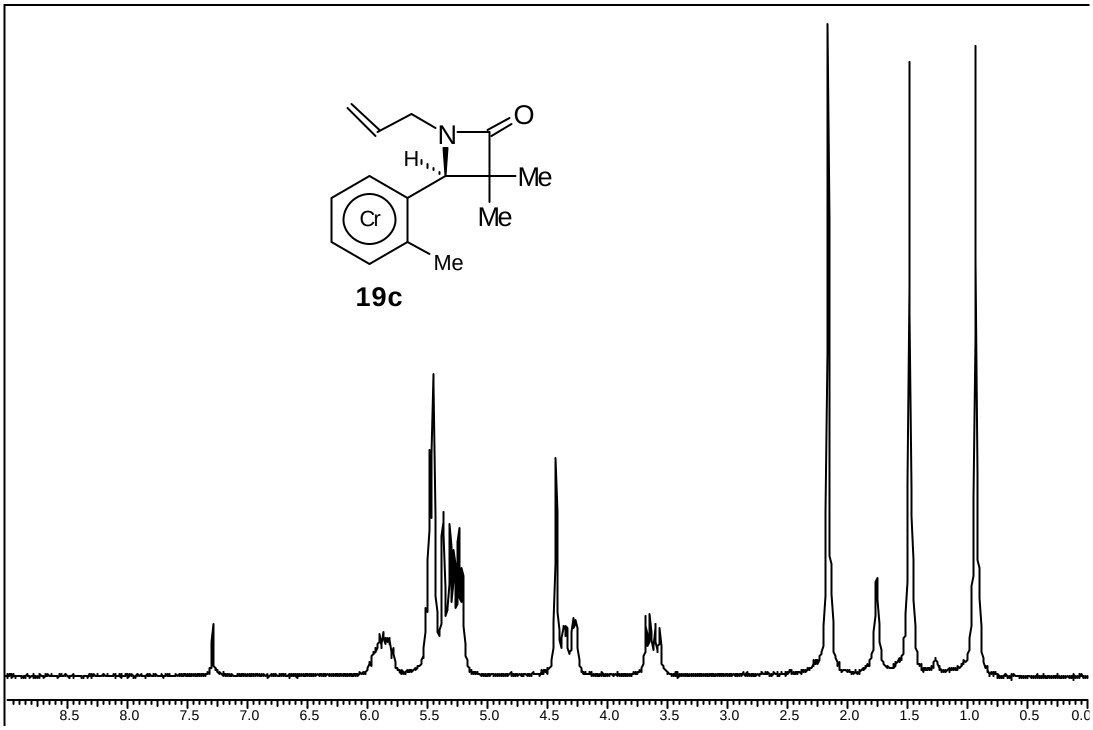
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O
N
H
Me
Me
Cr
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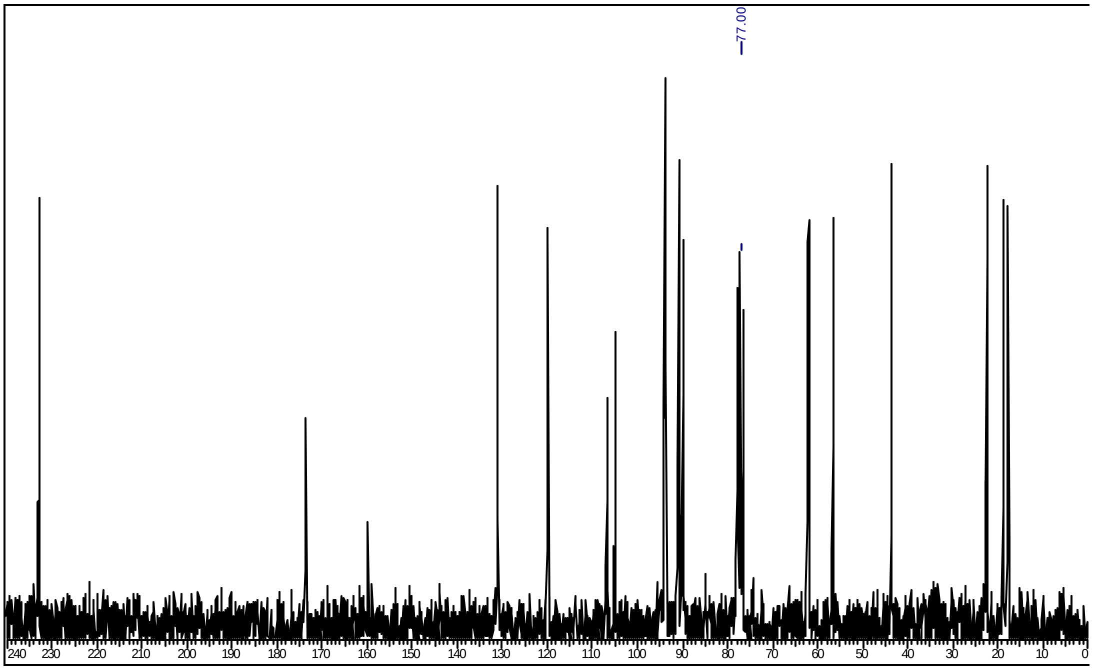
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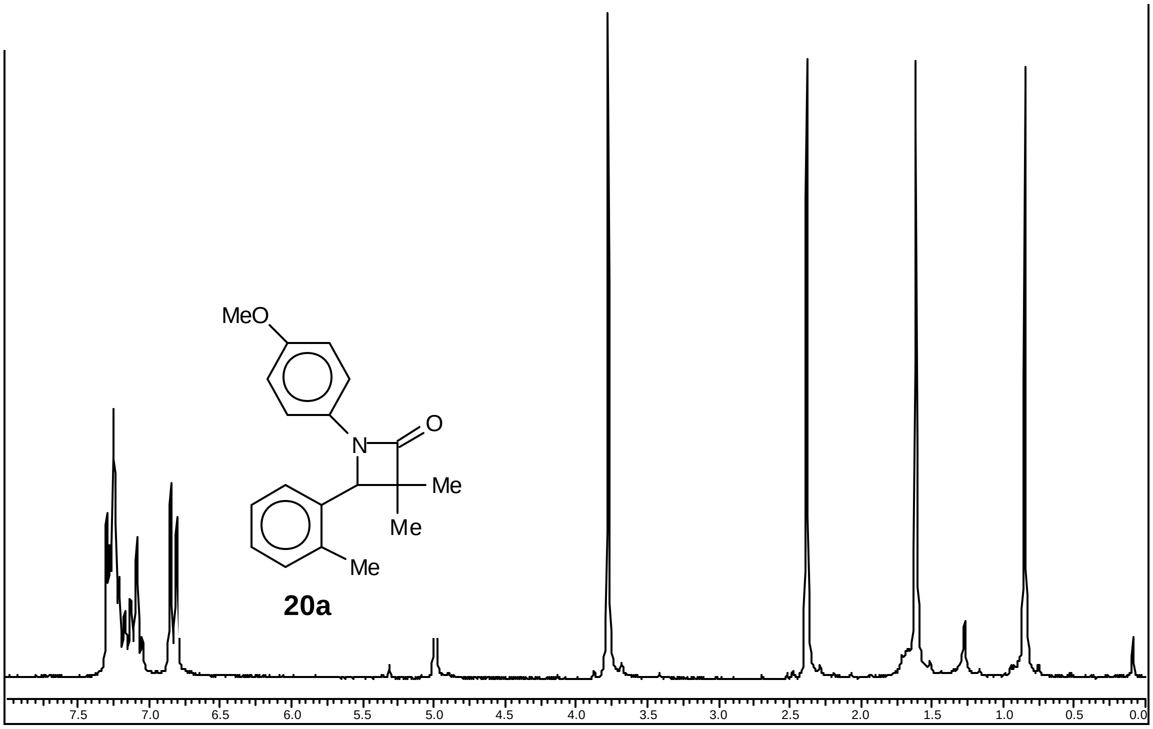
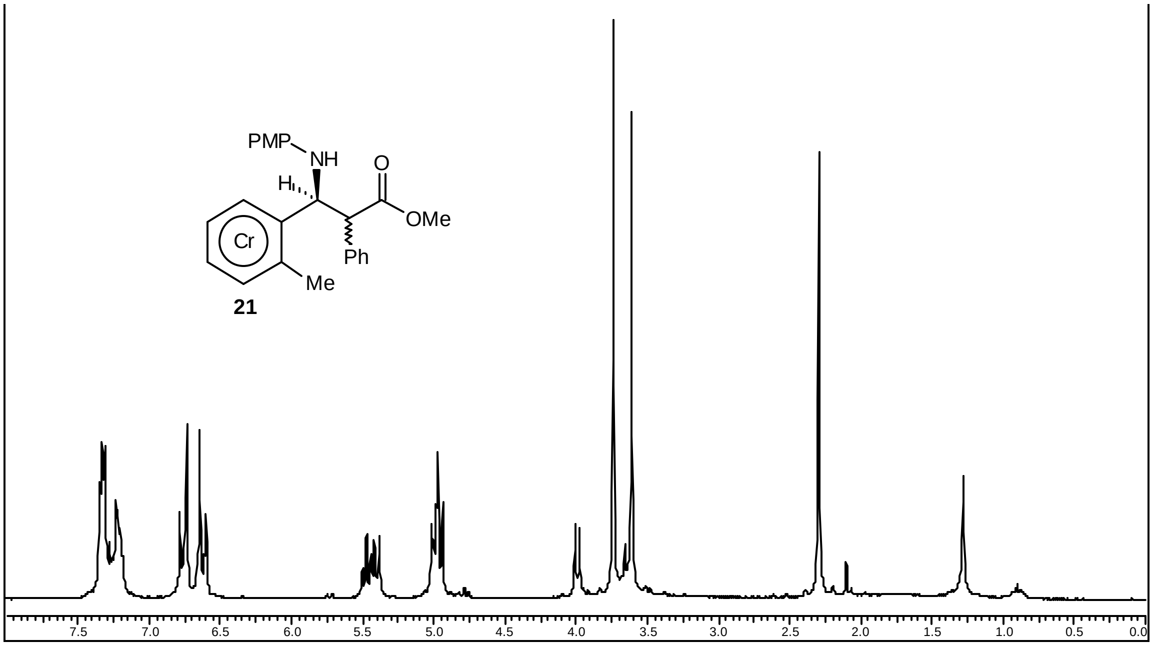


20a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OMe
Cr
Ph
Me
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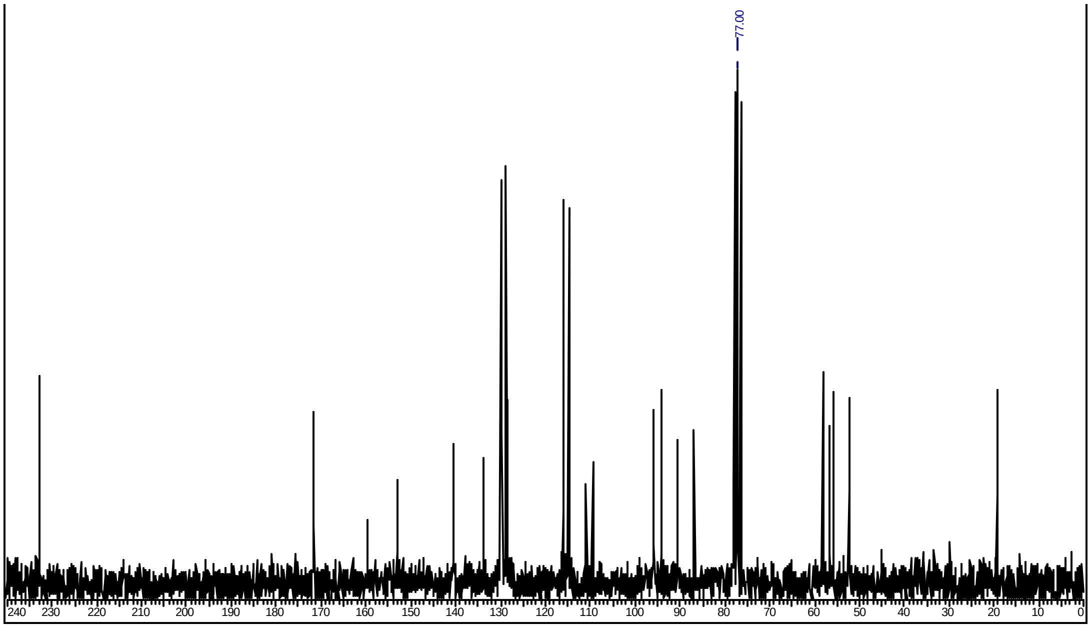
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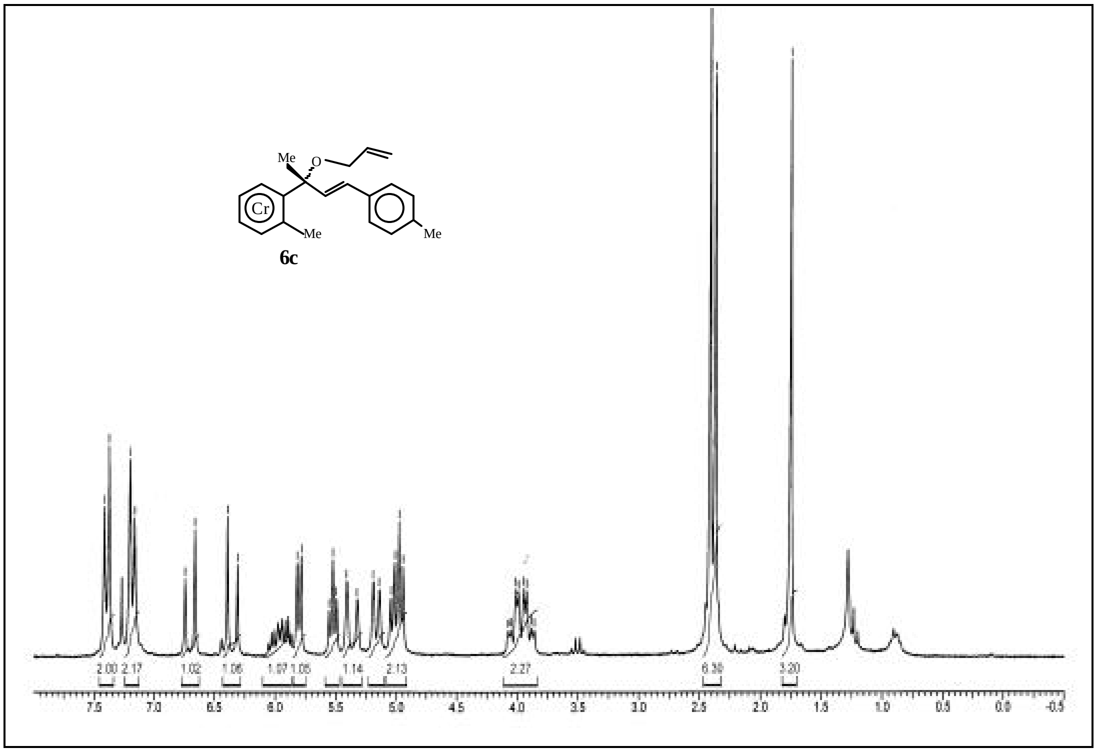
Appendix-III

Spectra of Compounds – Chapter III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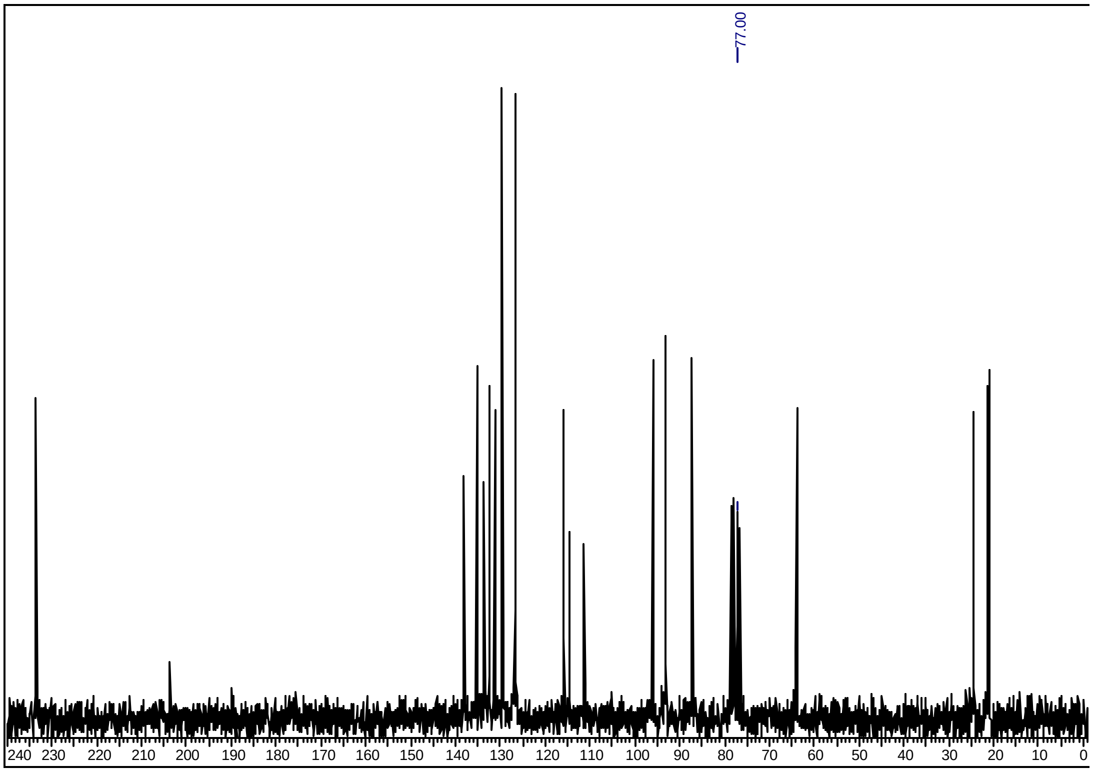
Cr
Me
Me
2.00 2.17 1.02 1.06 1.07 1.05 1.14 2.13 2.27 6.30 3.20
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

6c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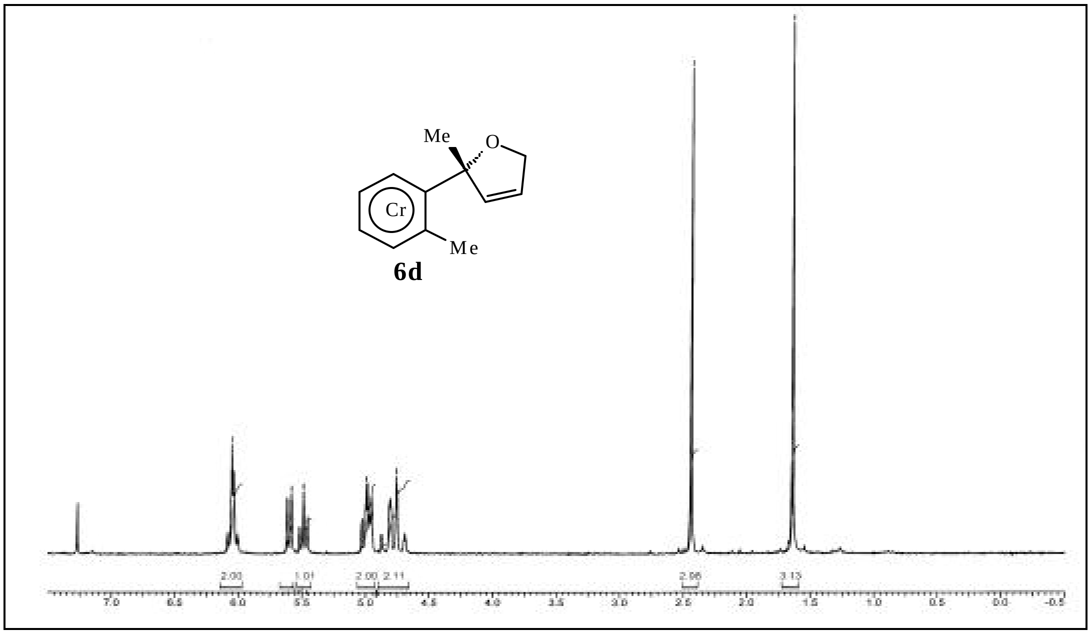
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1.0
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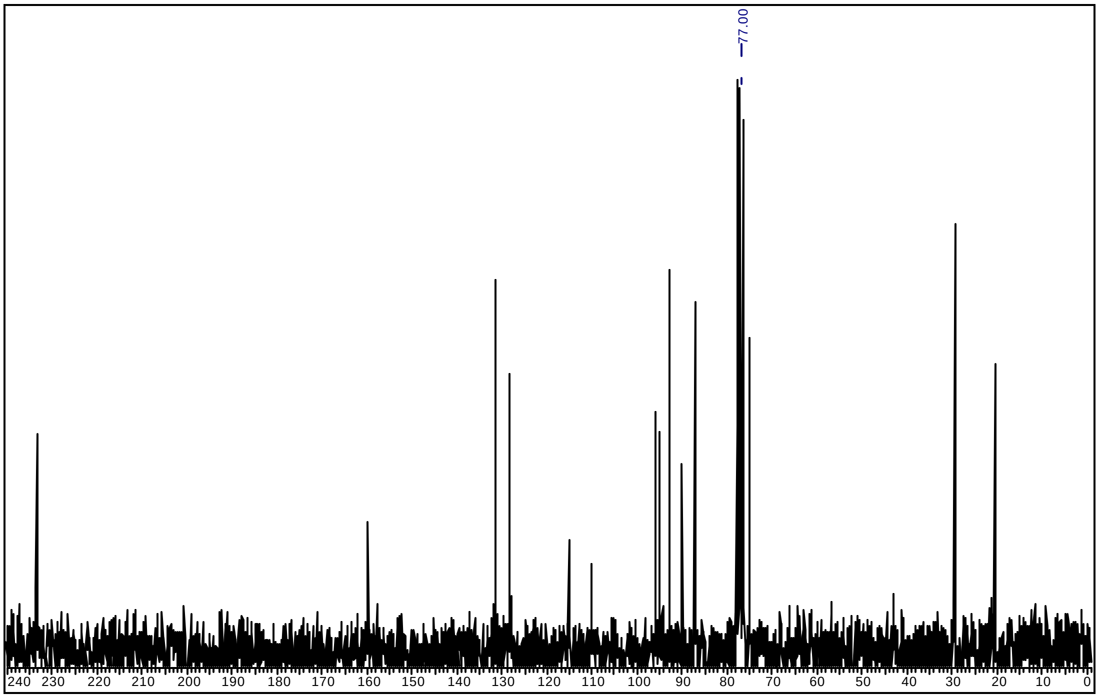
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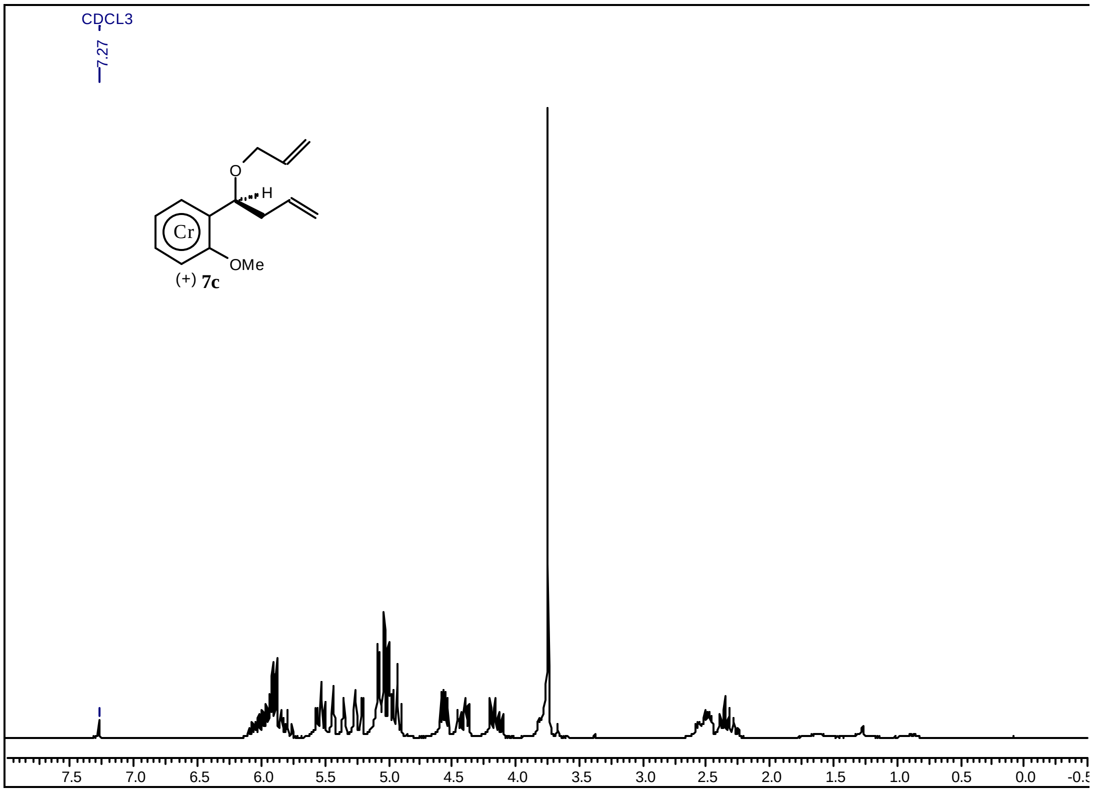
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O
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Cr
OMe
(+) 7c
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5.5
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0.0
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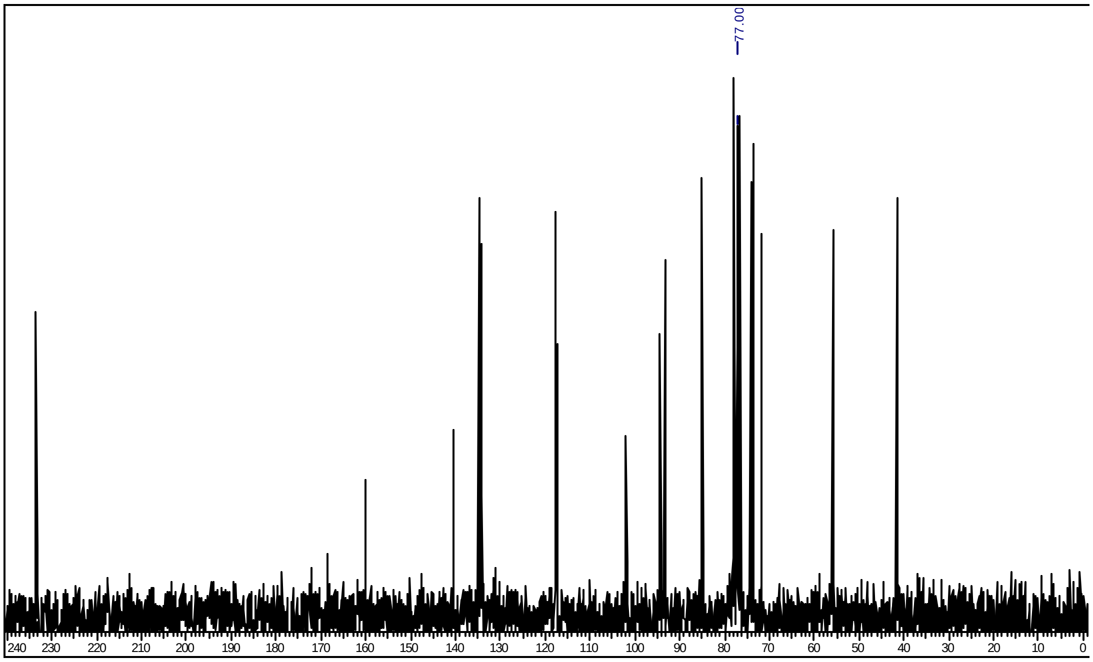
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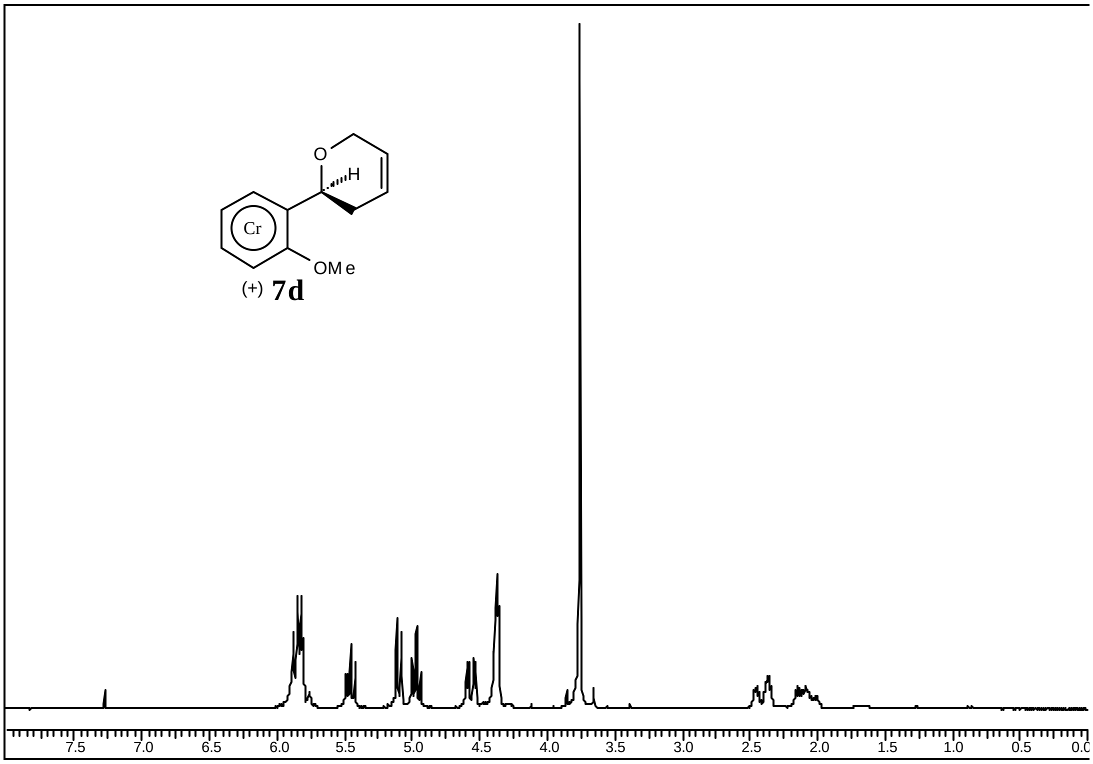
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2.5
2.0
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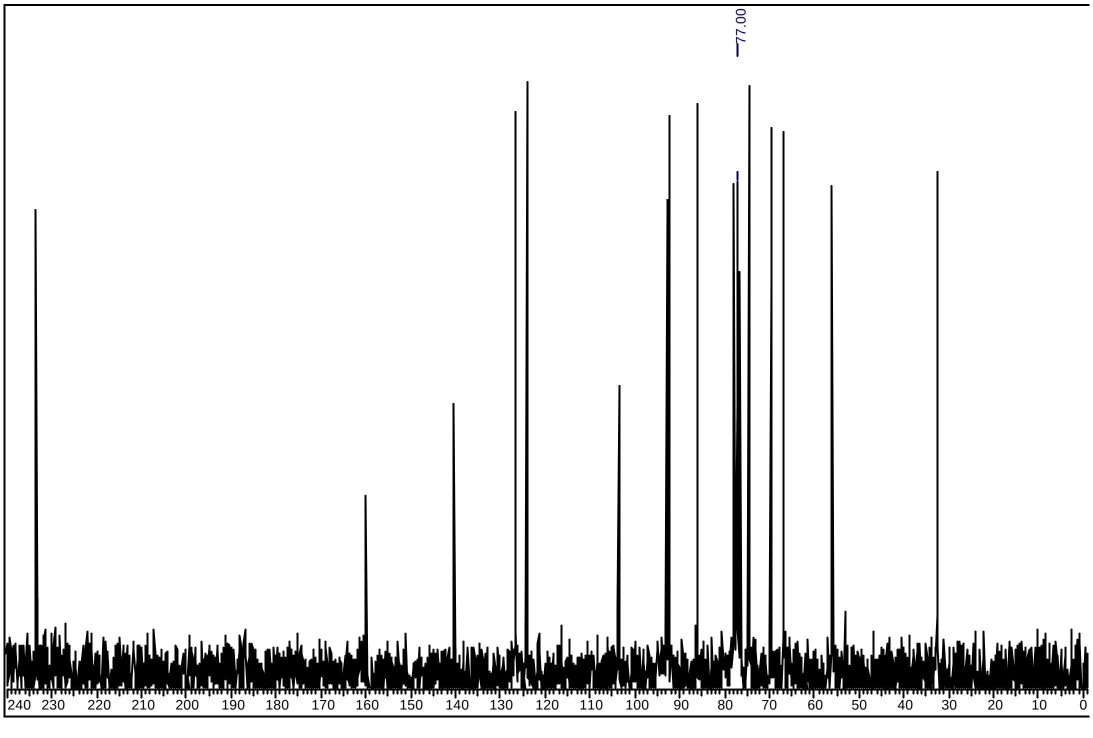
0.0

(+) **7d**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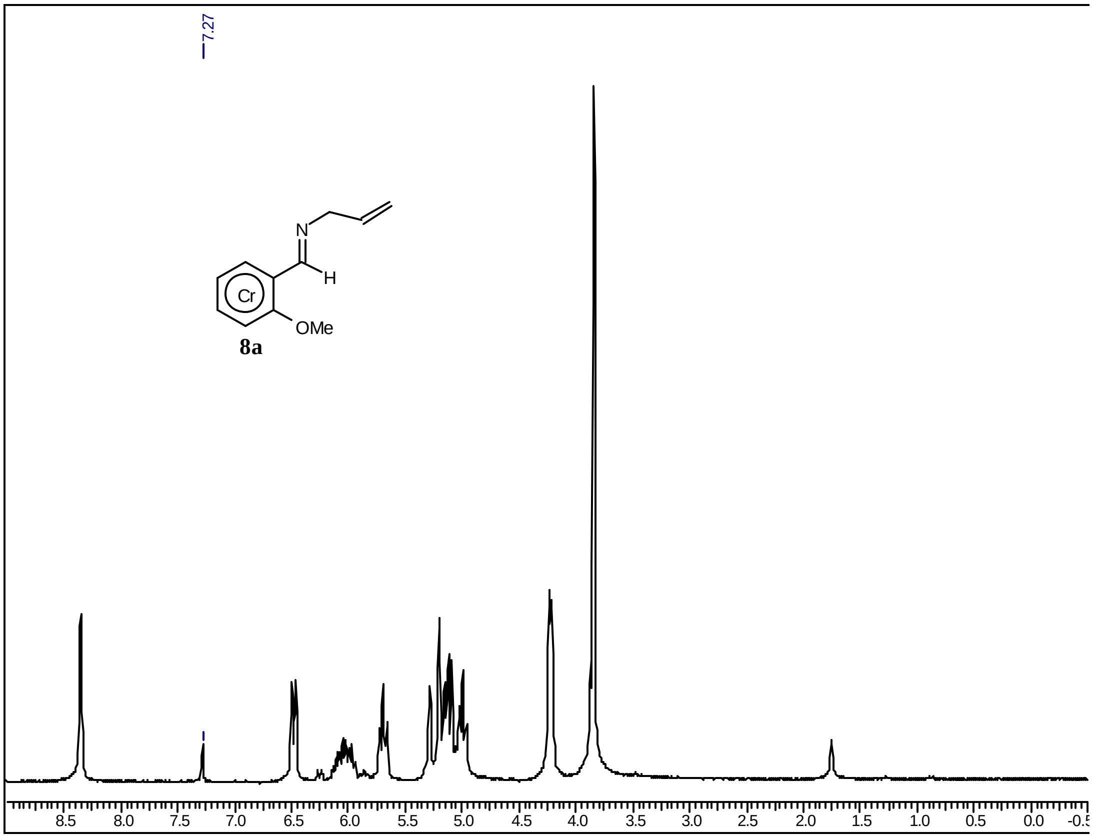
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H
Cr
OMe
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7.0
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6.0
5.5
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4.5
4.0
3.5
3.0
2.5
2.0
1.5
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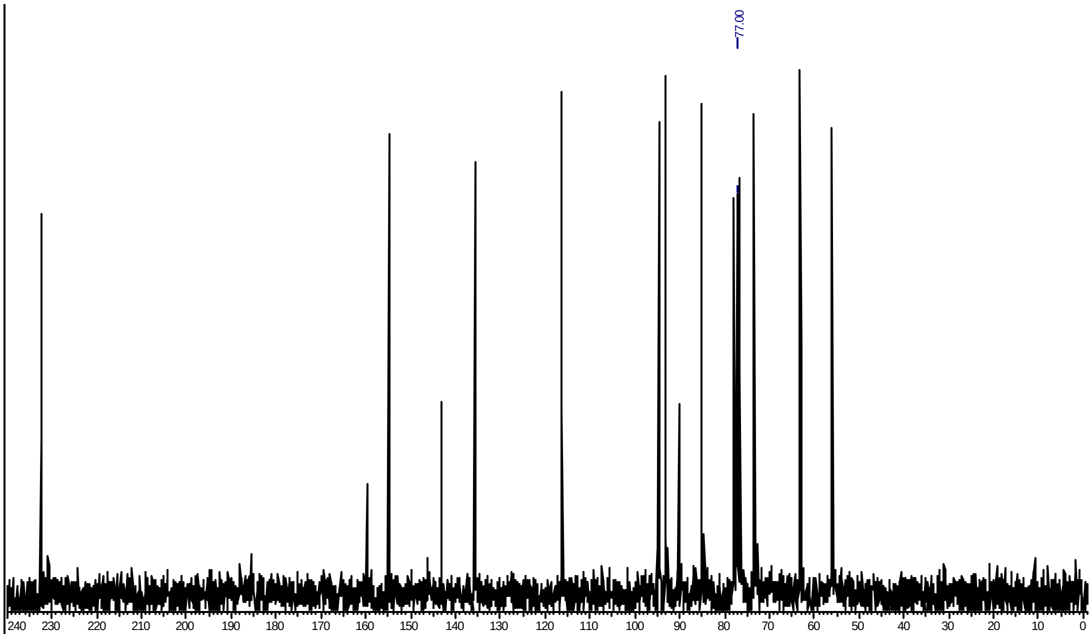
0.5
0.0
-0.5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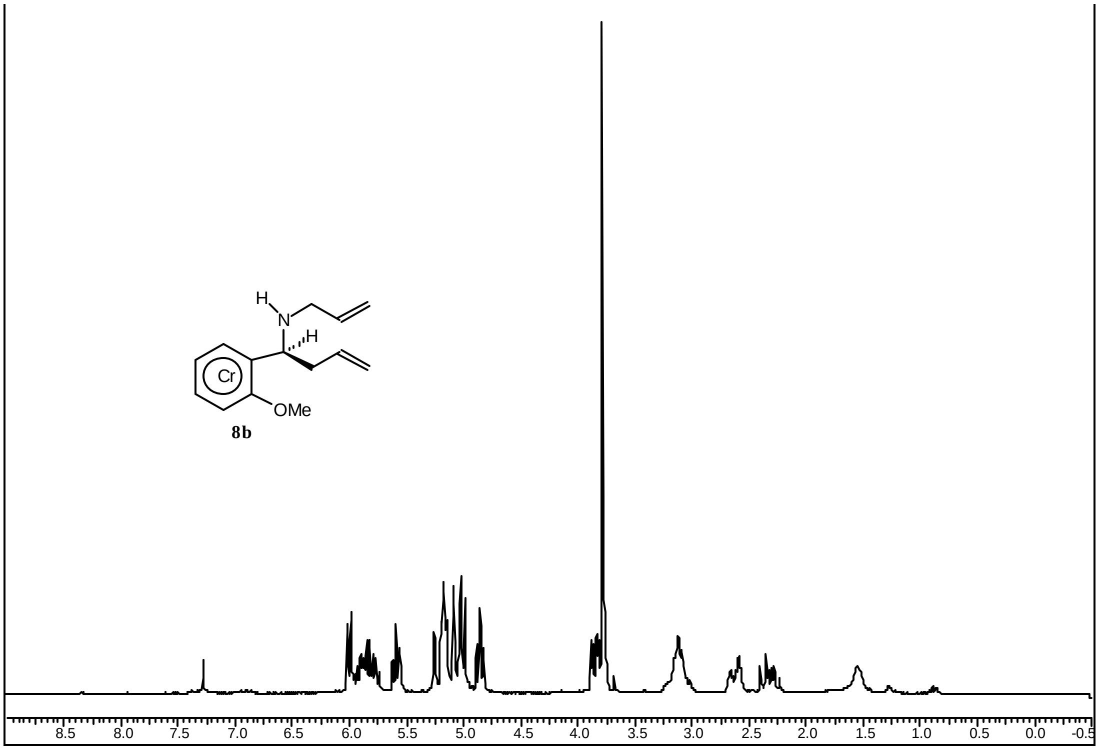
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Cr
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3.5
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1.5
1.0
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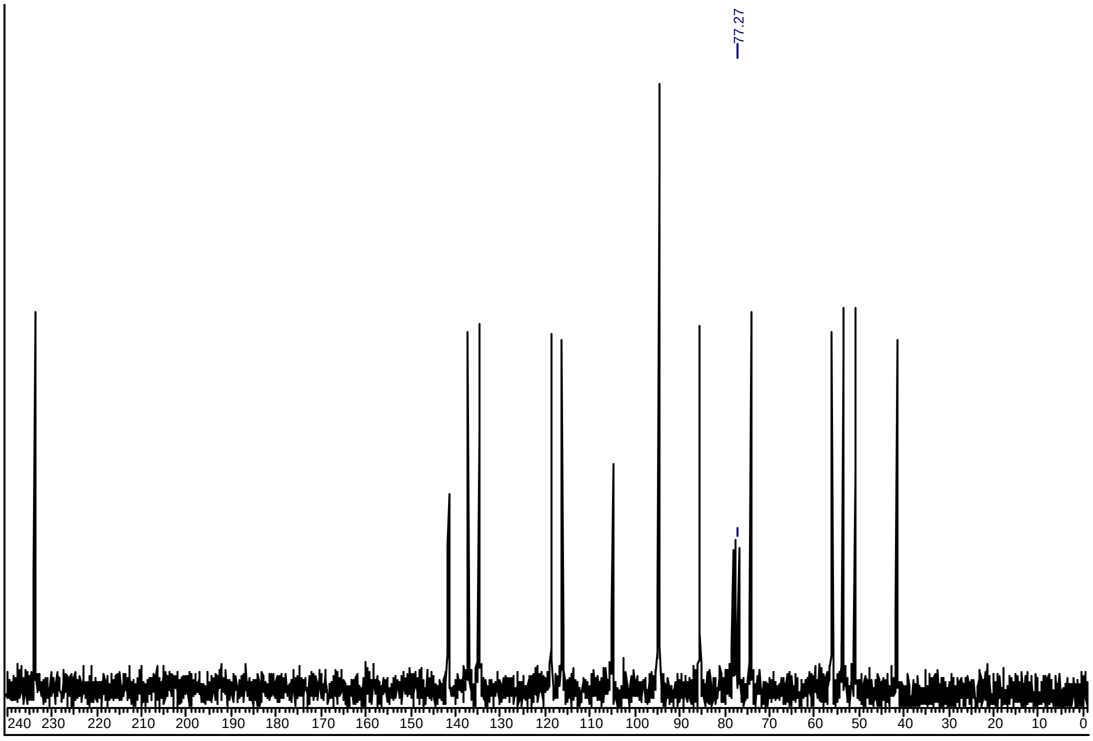
0.0
-0.5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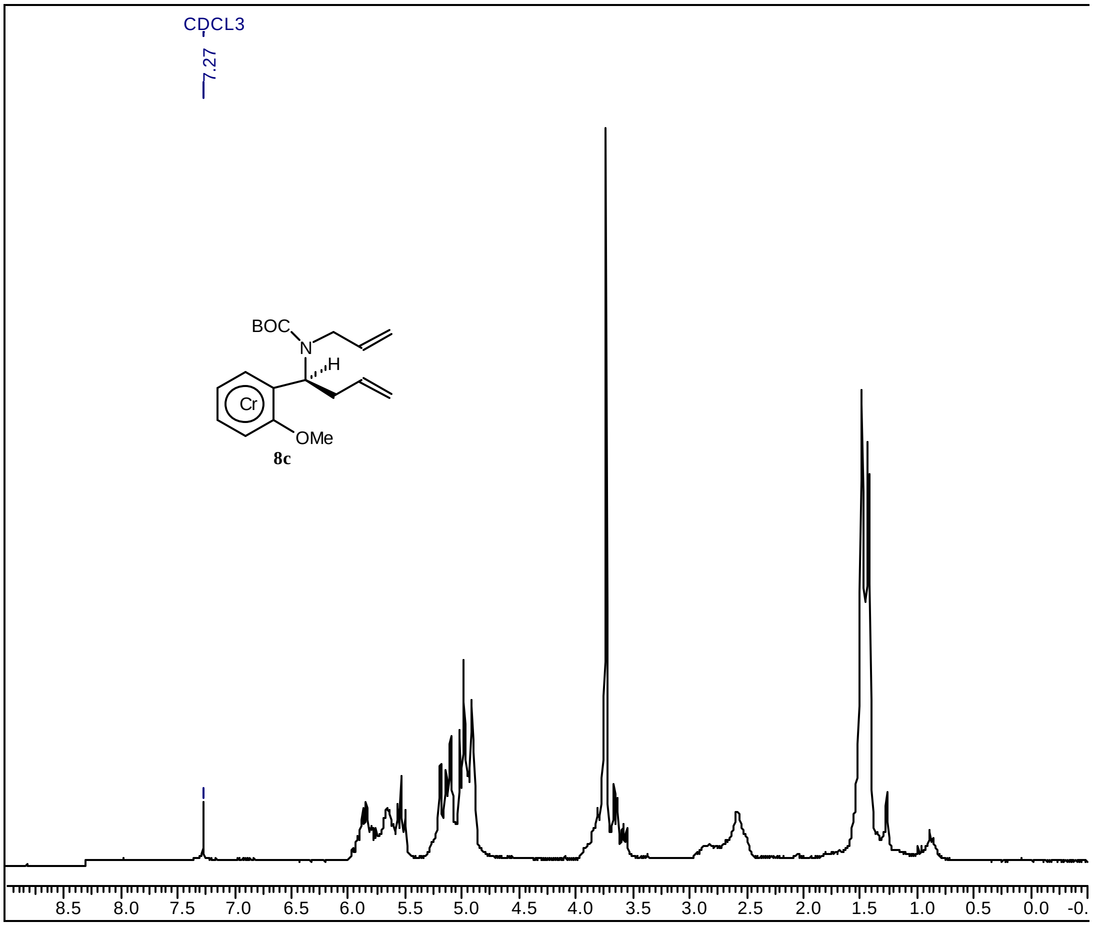
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OMe
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5.0
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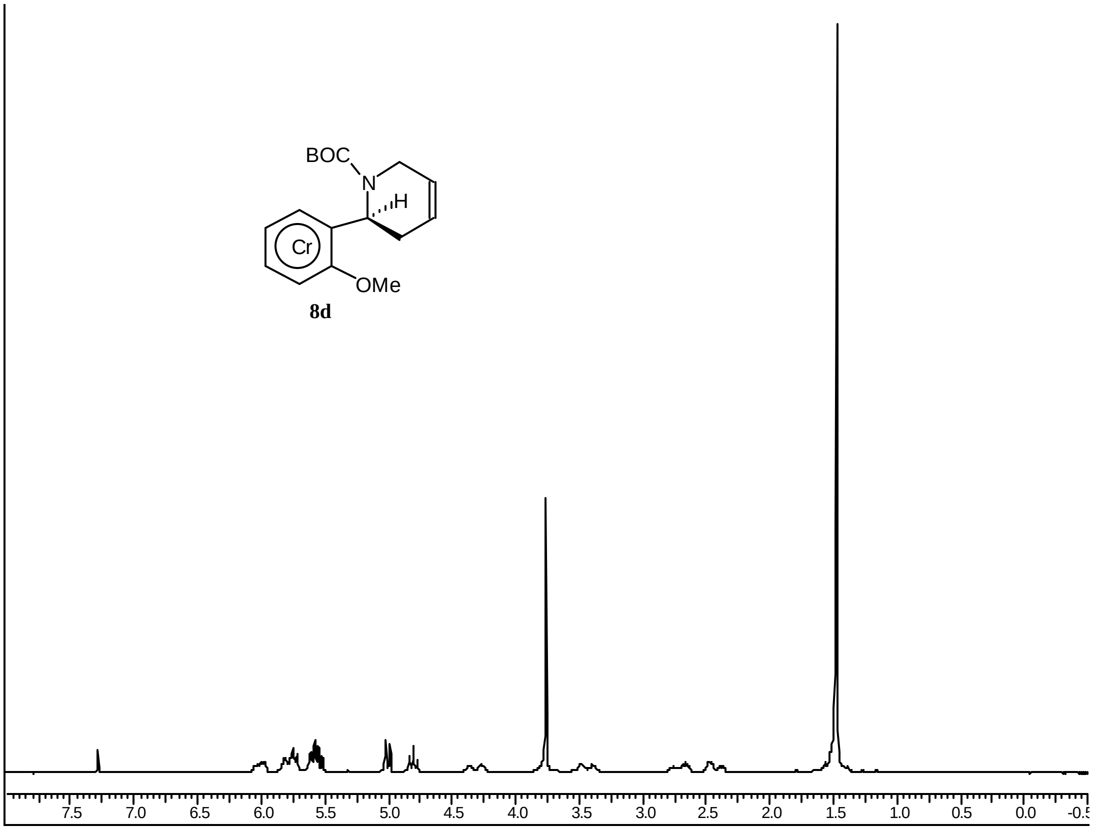
8c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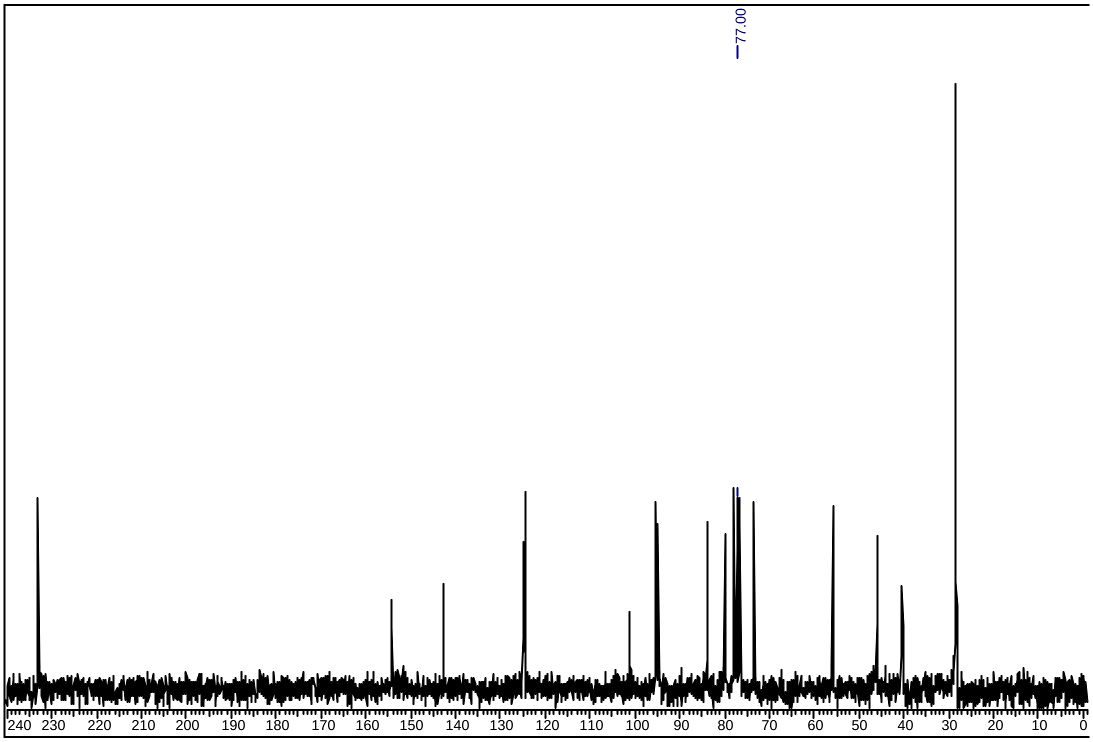
8d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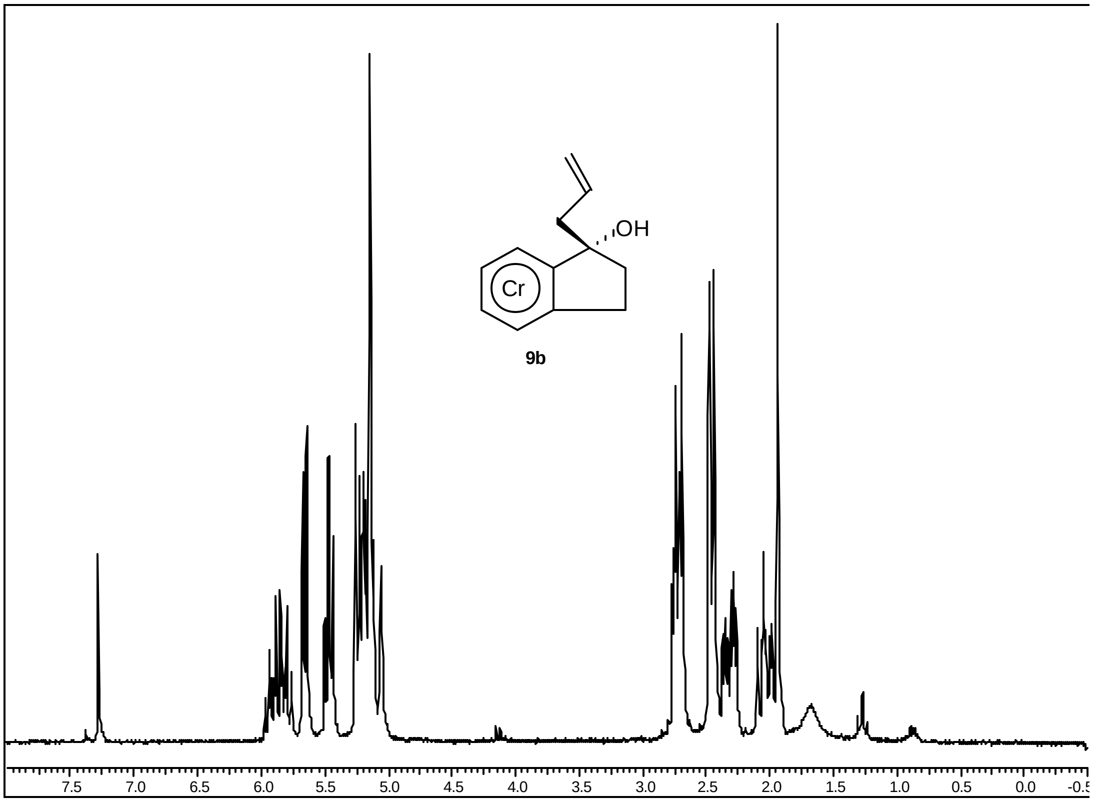
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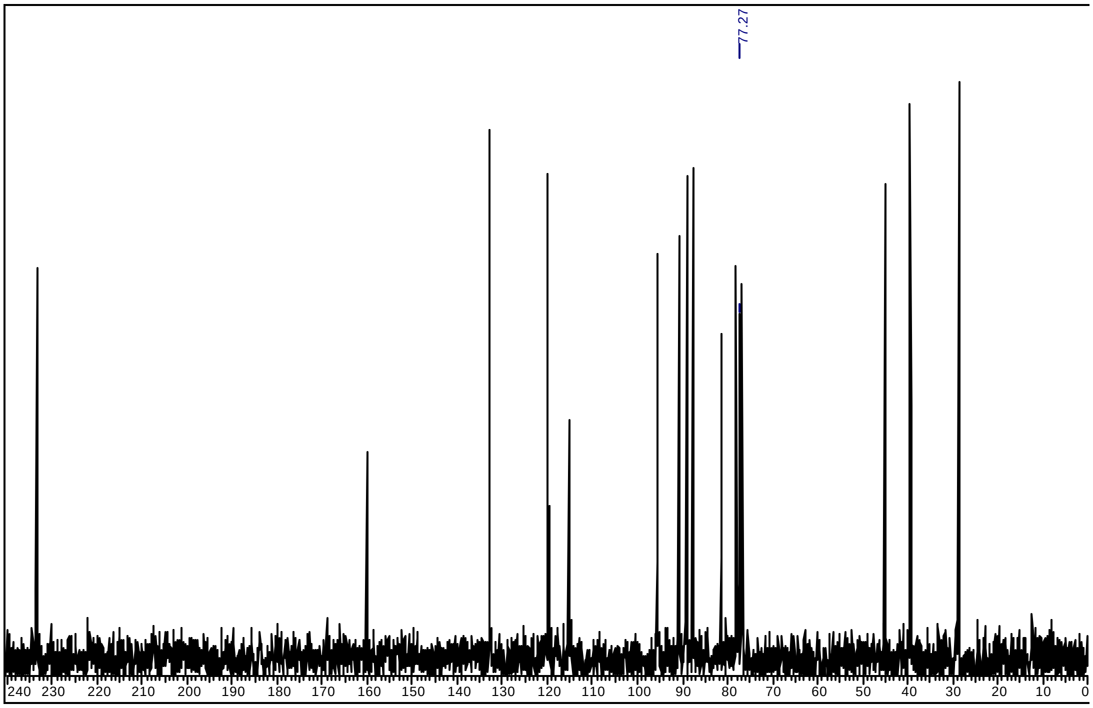
-0.5

9b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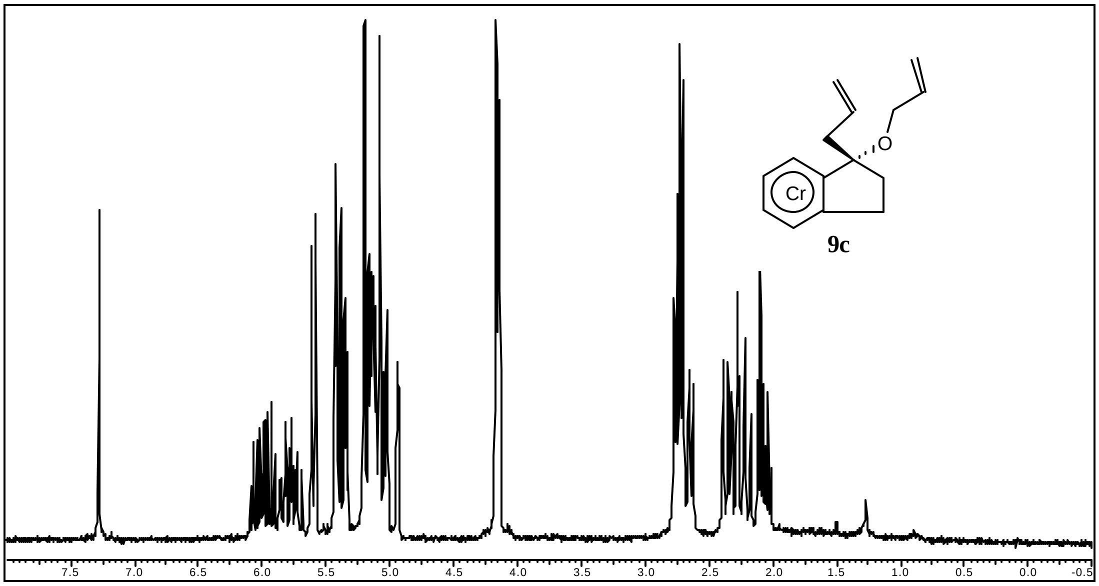

9c

Cr
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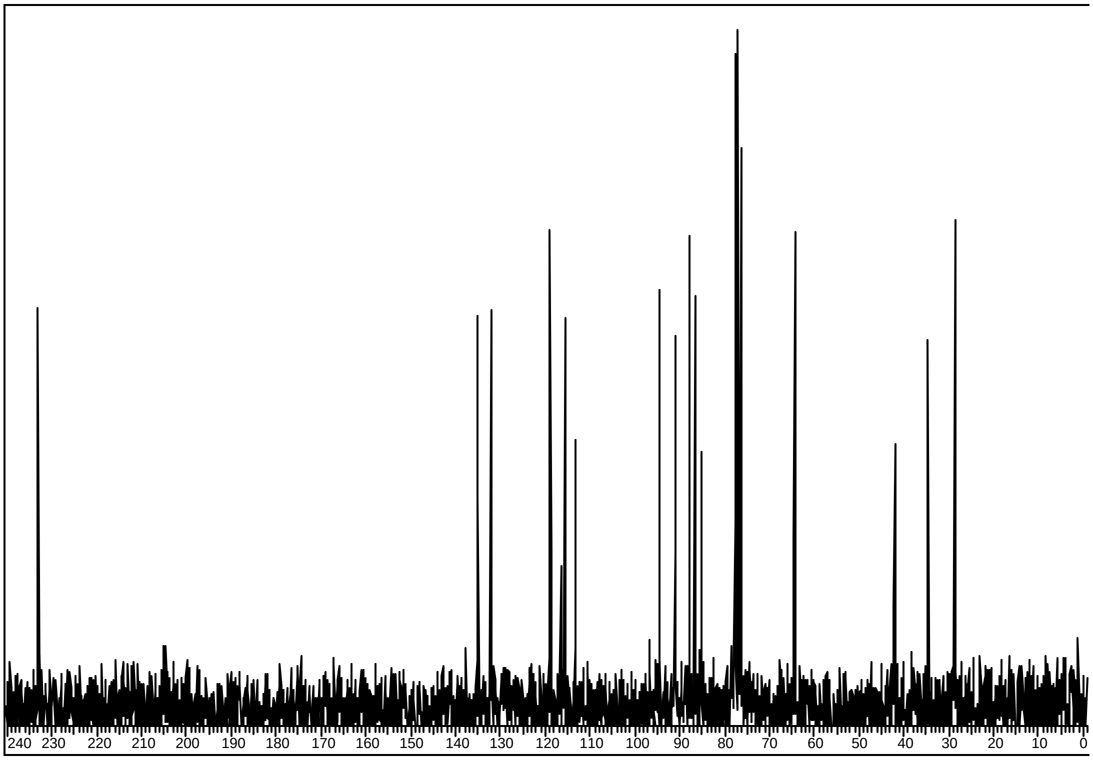

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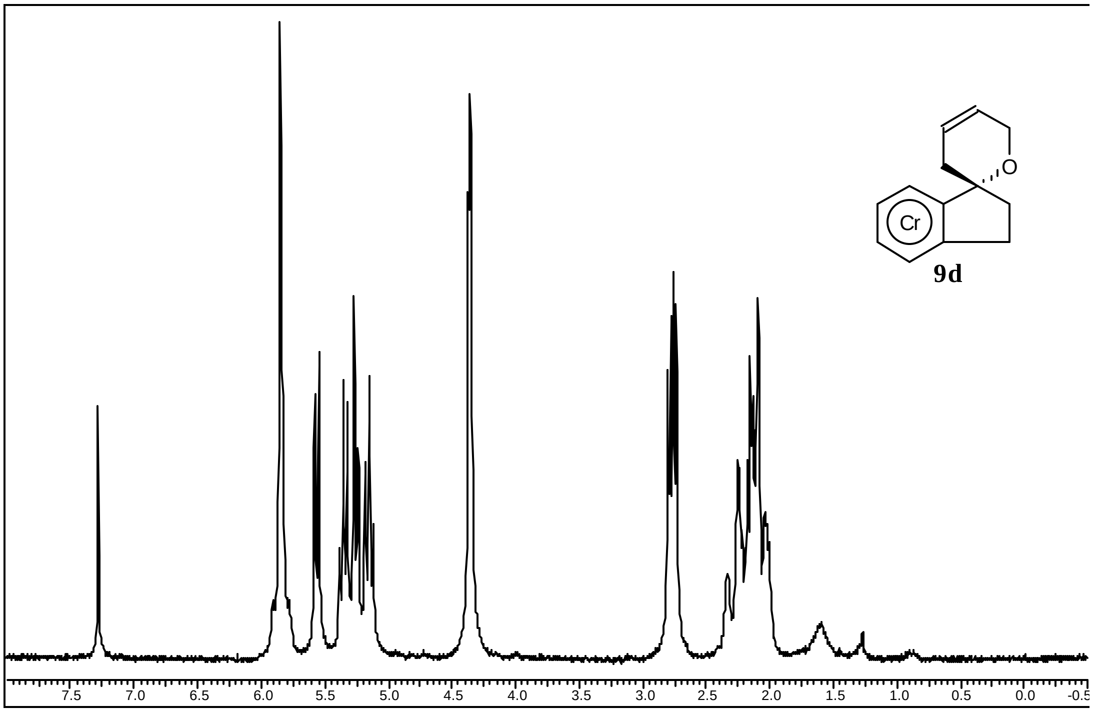
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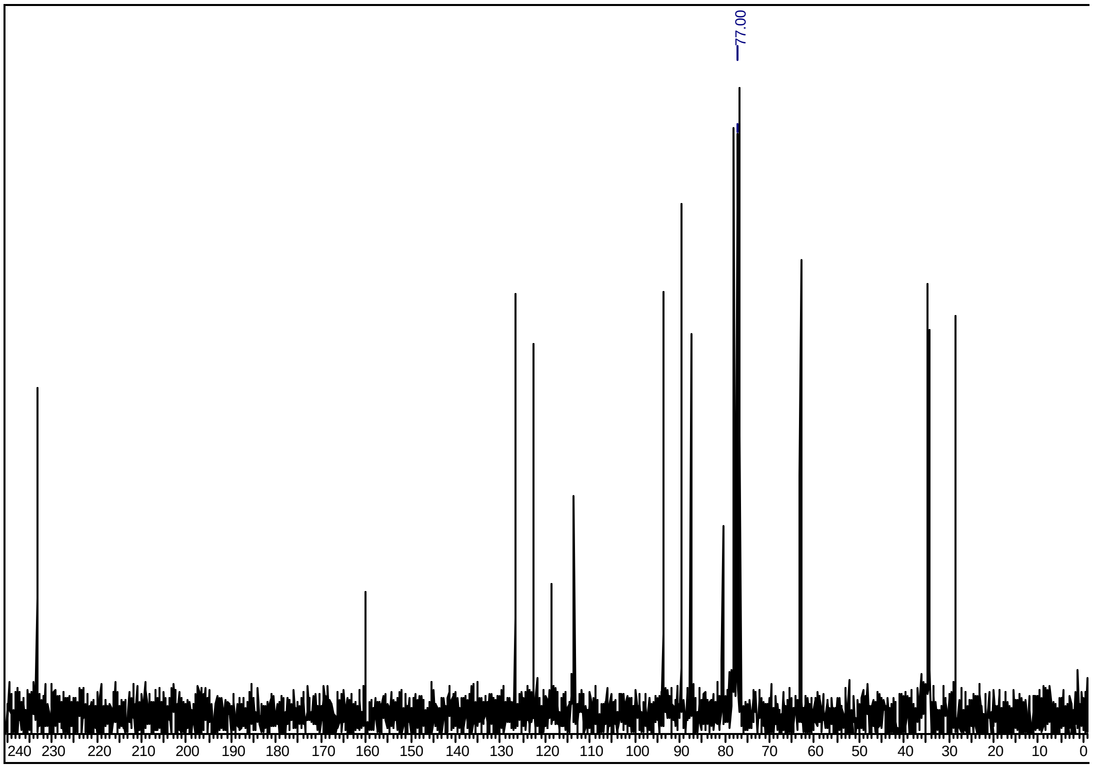
9d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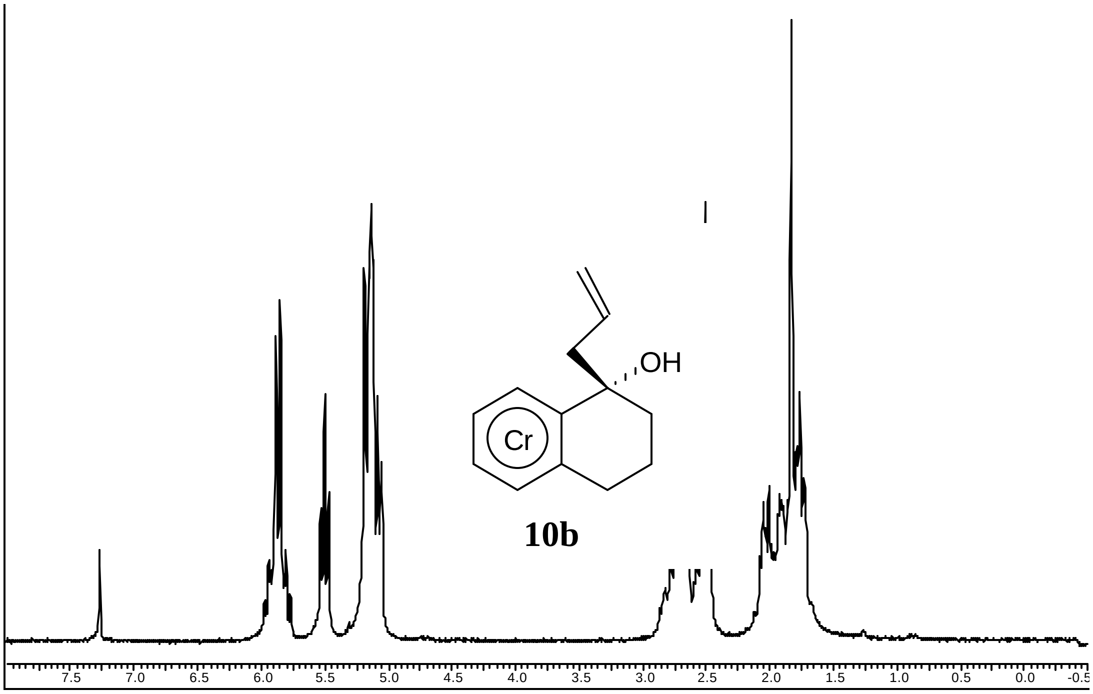

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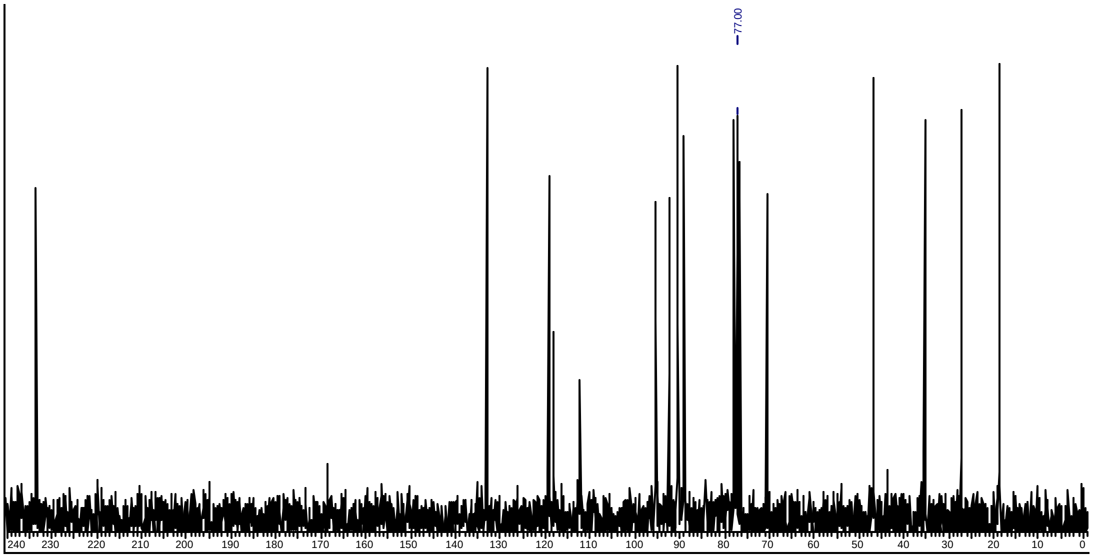
10b



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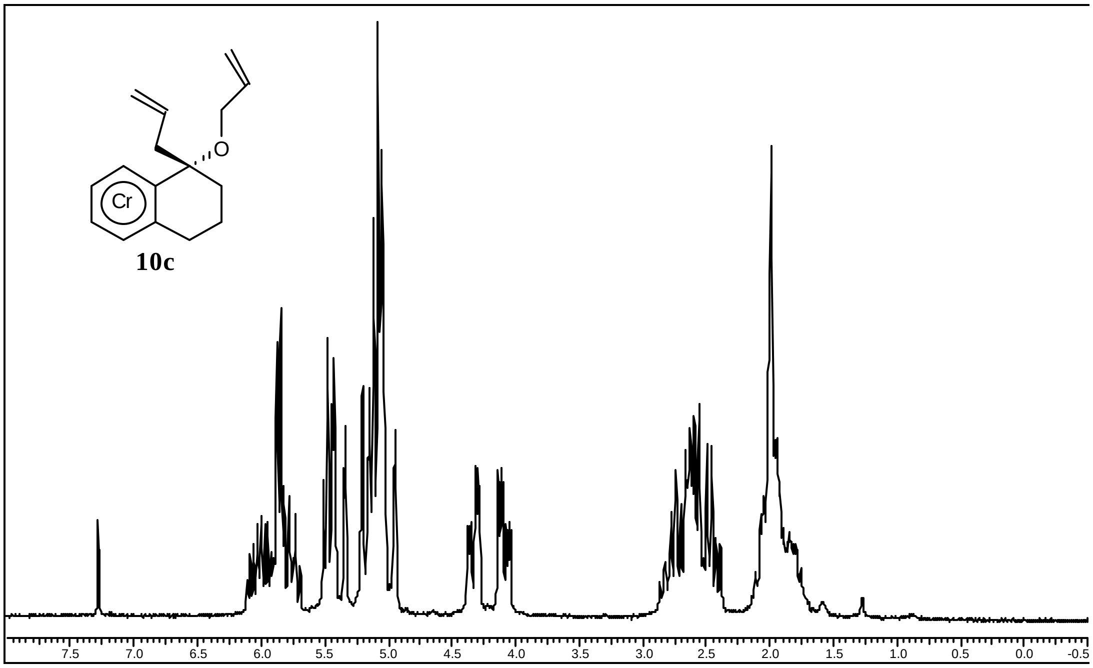
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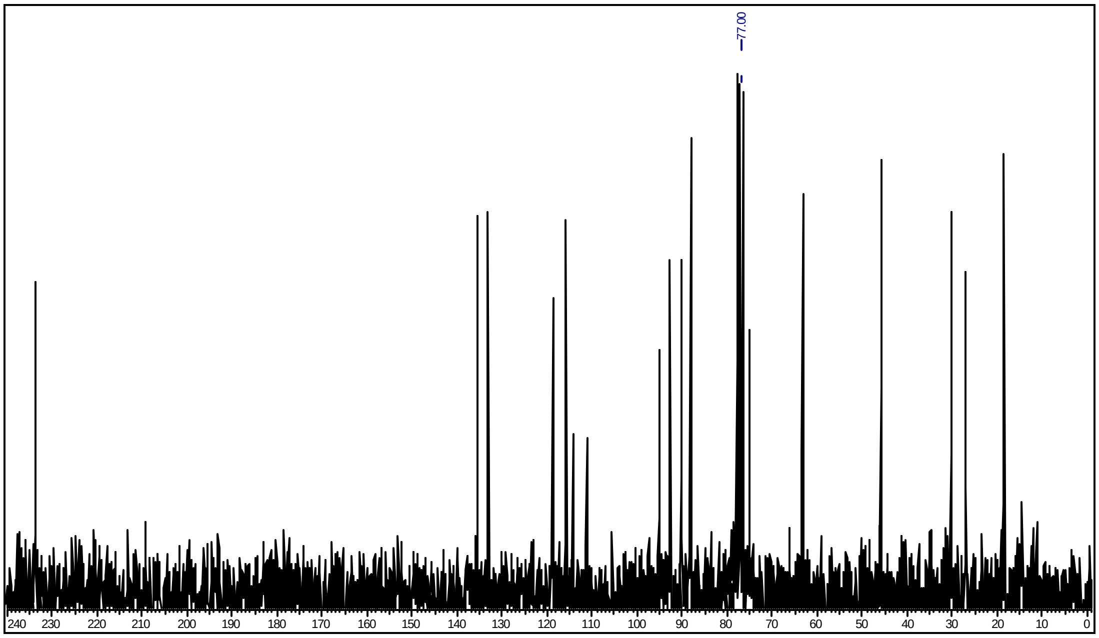
10c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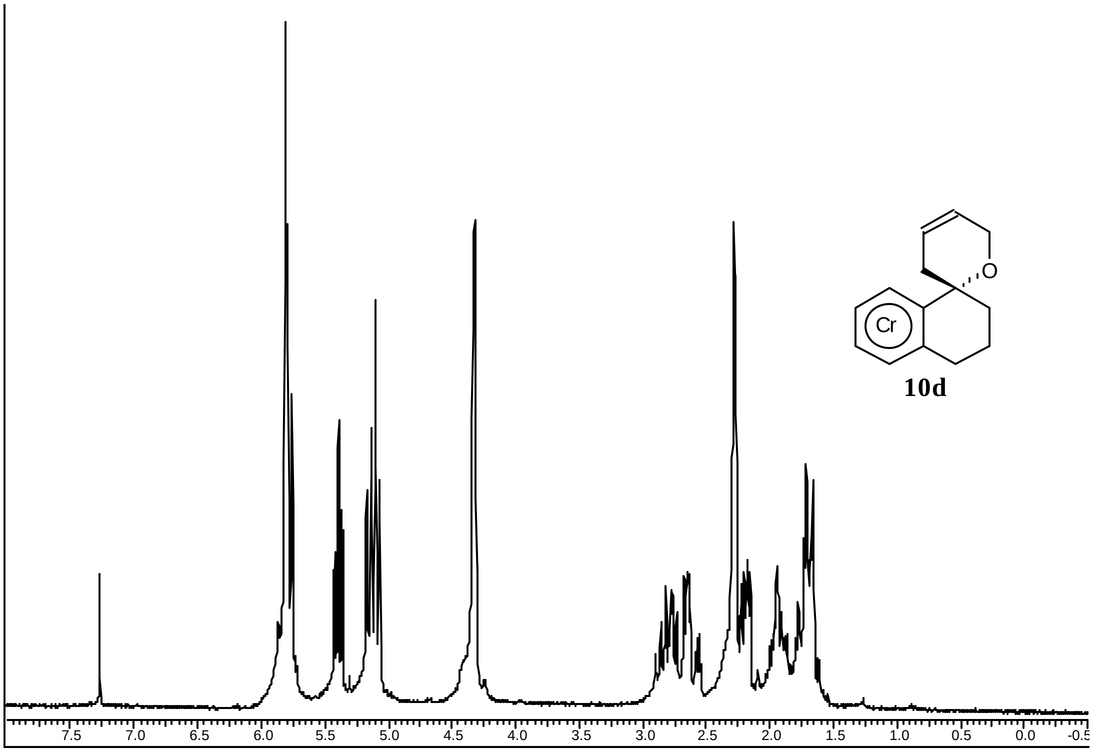
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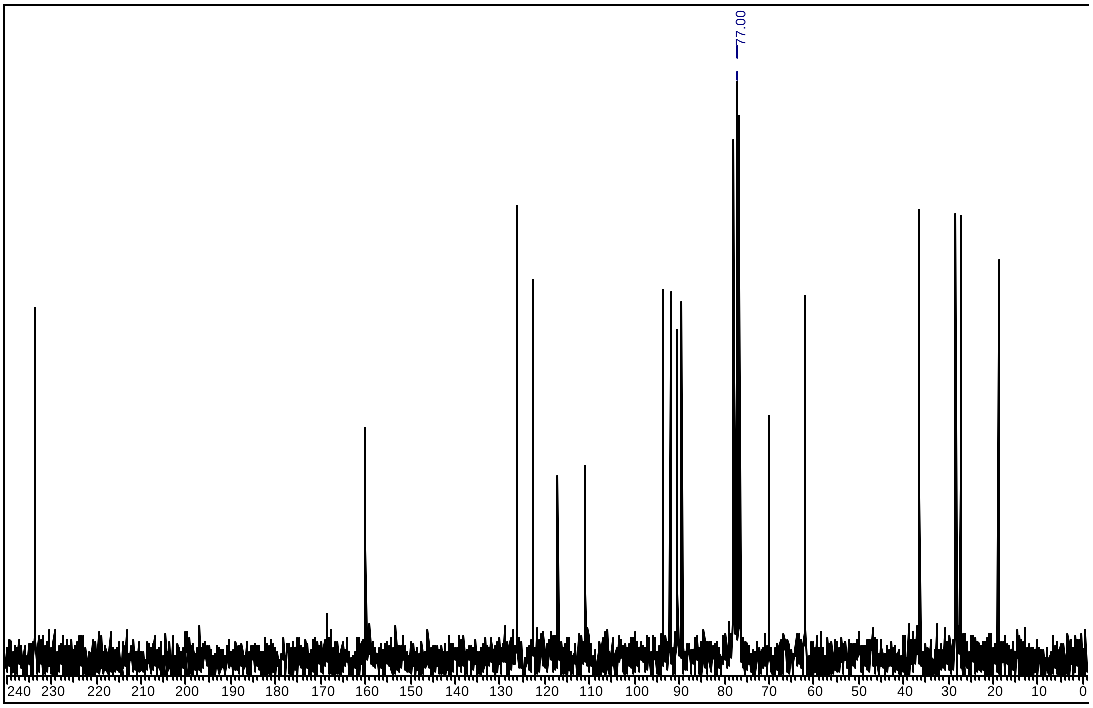
10d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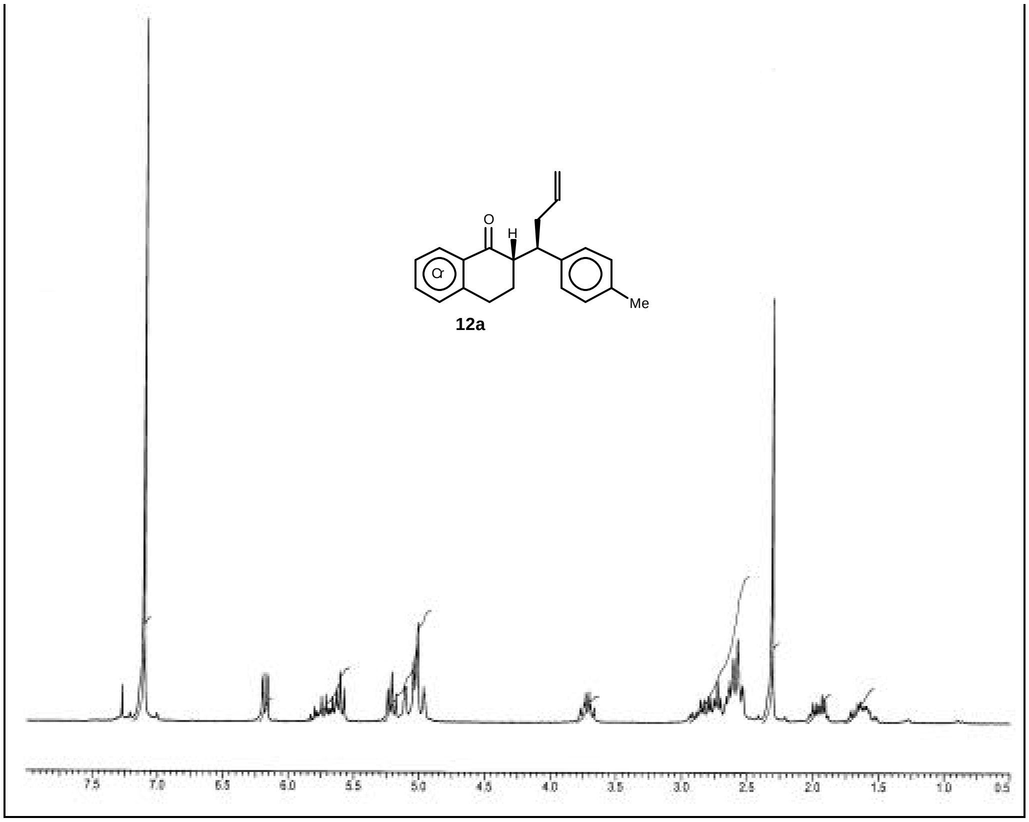
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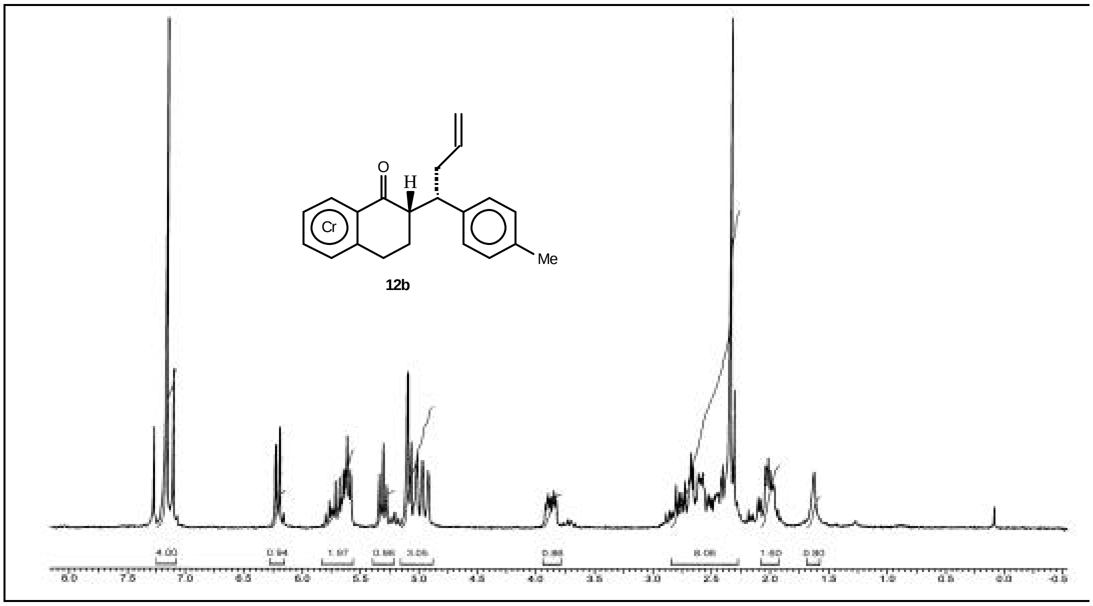
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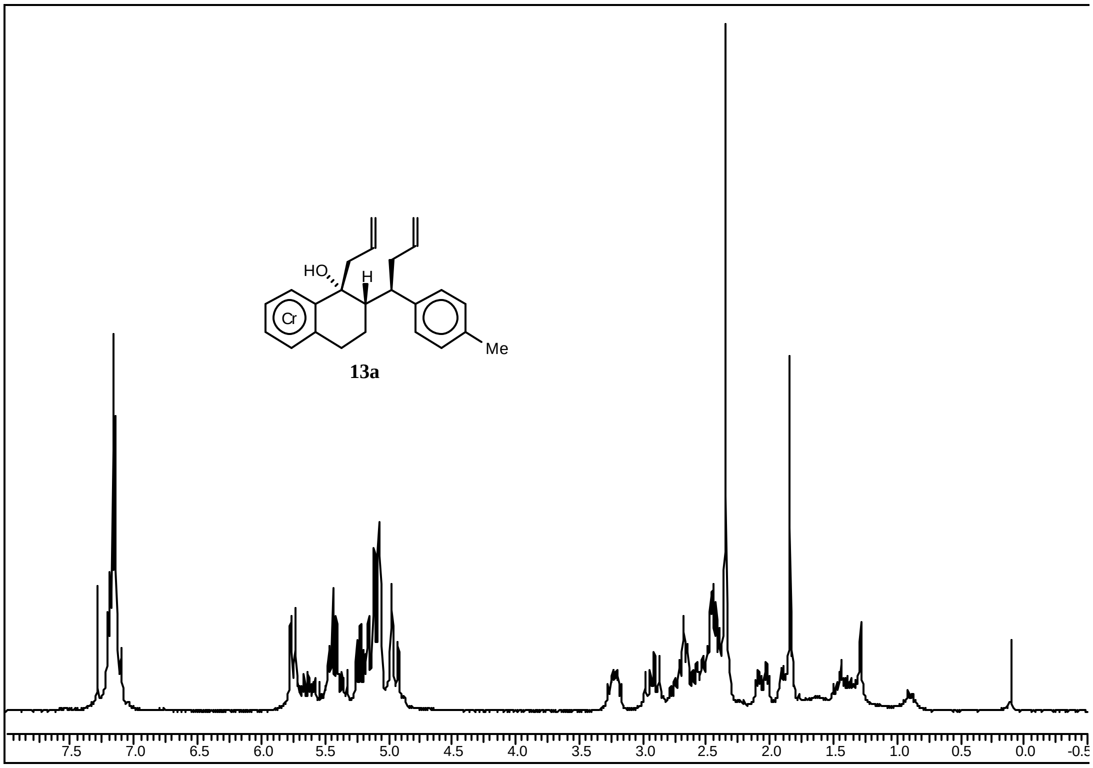
12b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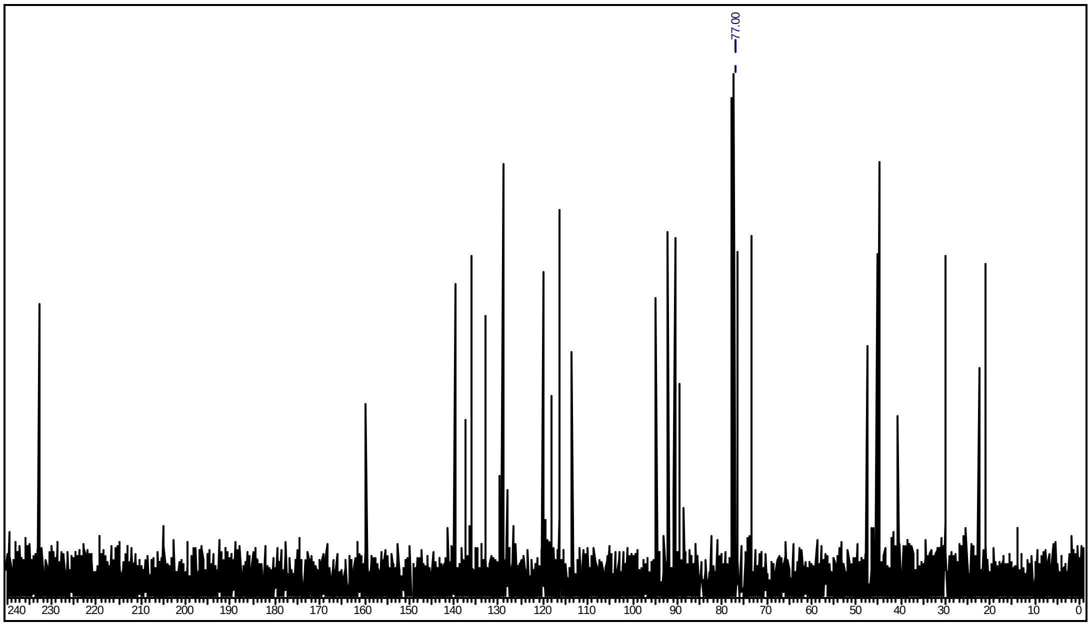
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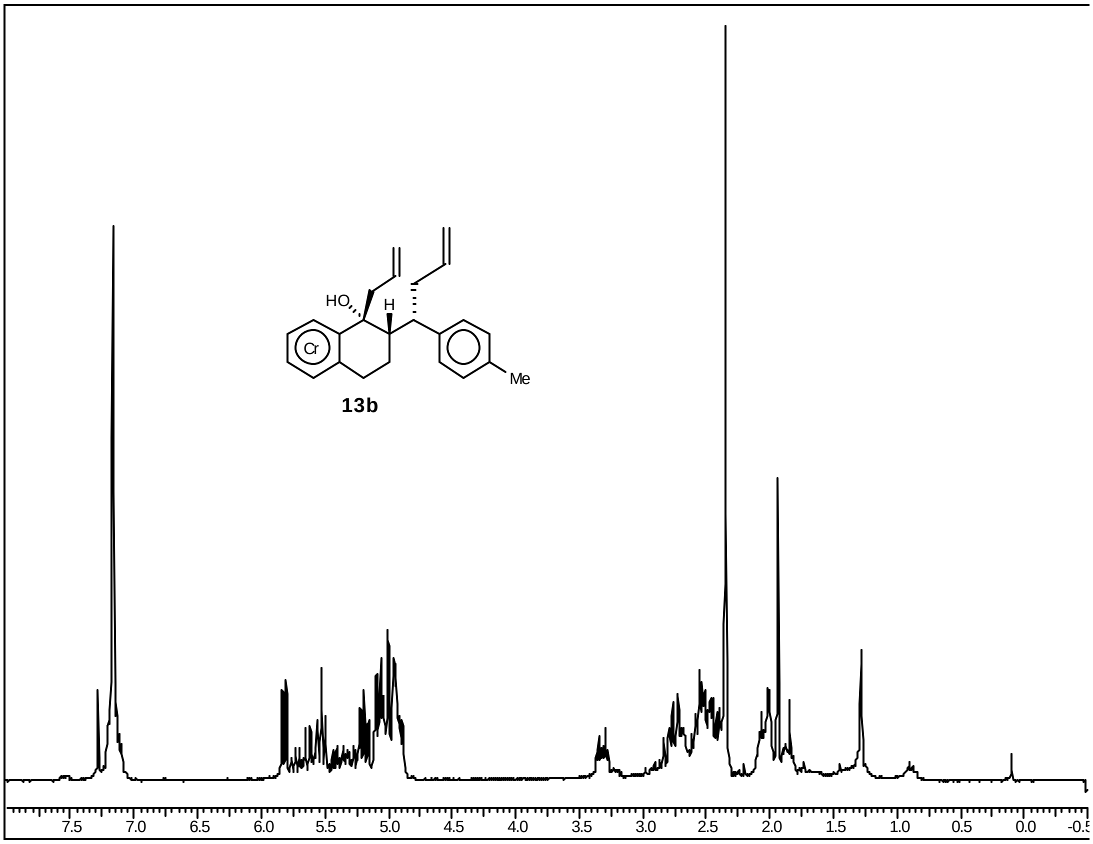
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Cr
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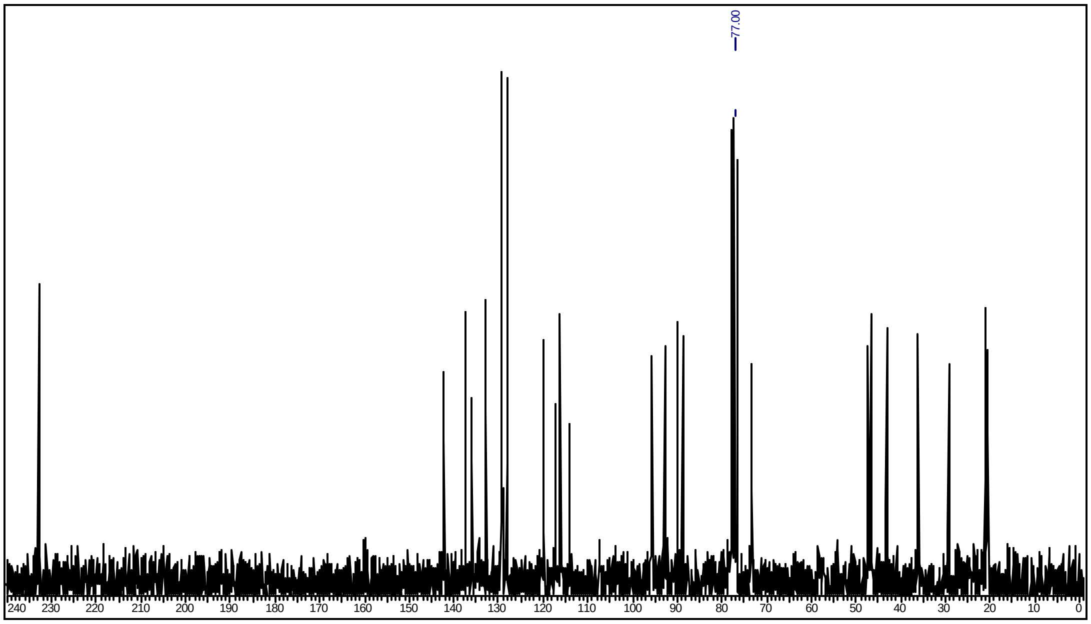
13b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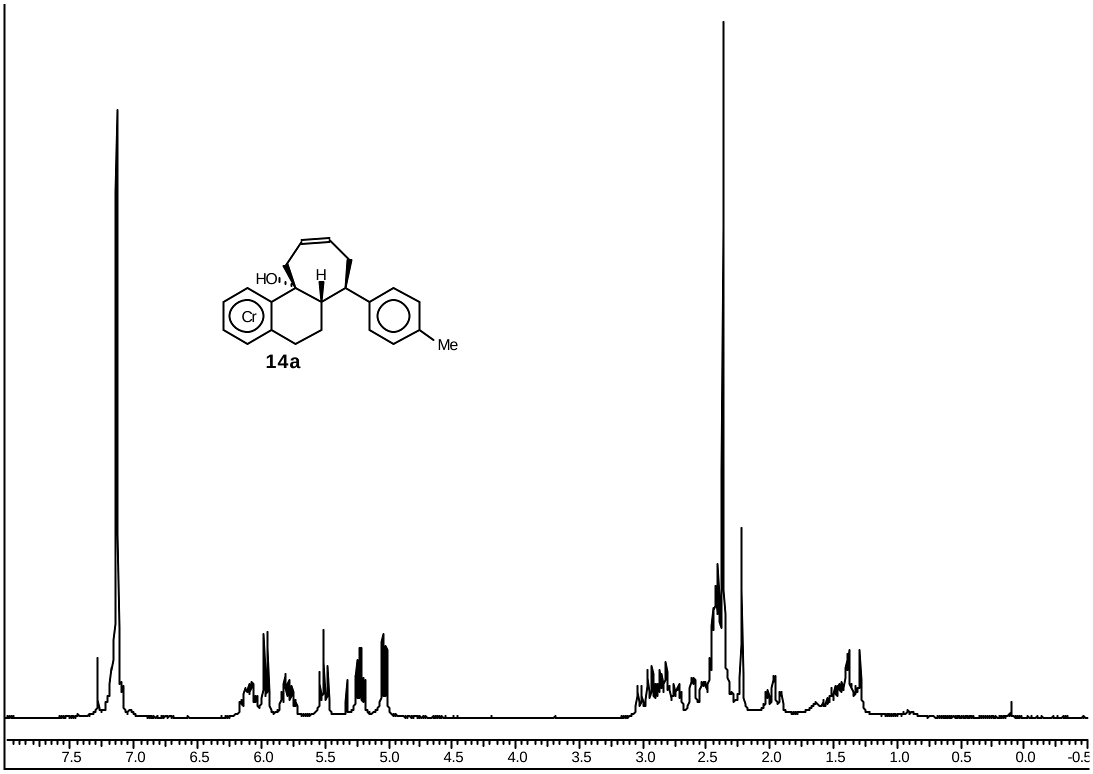
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Cr
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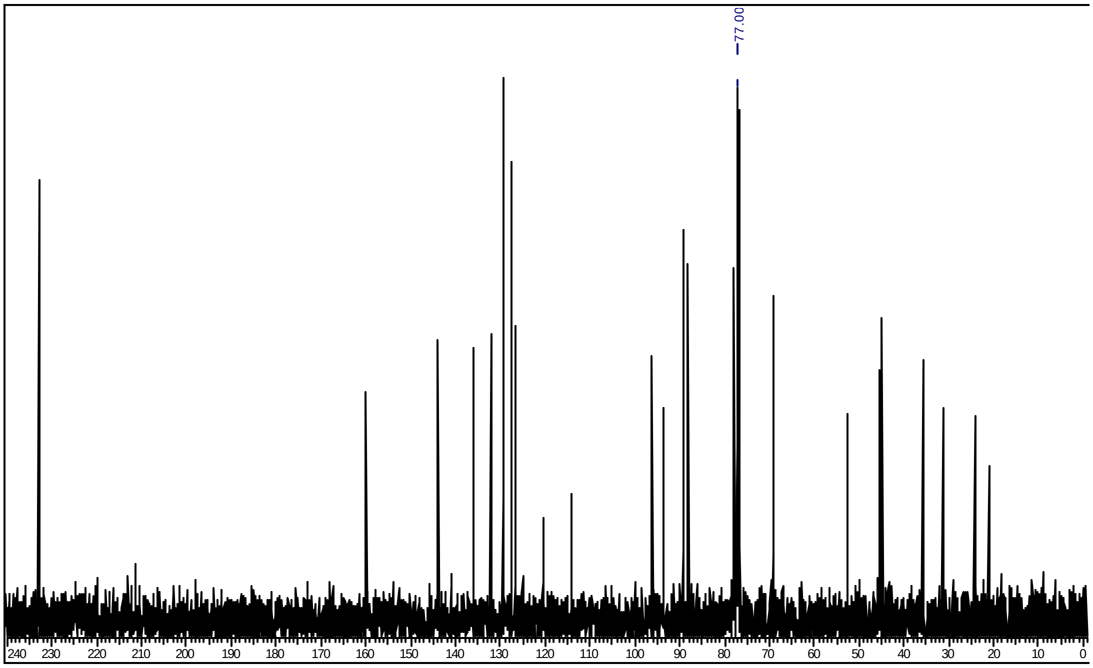
14a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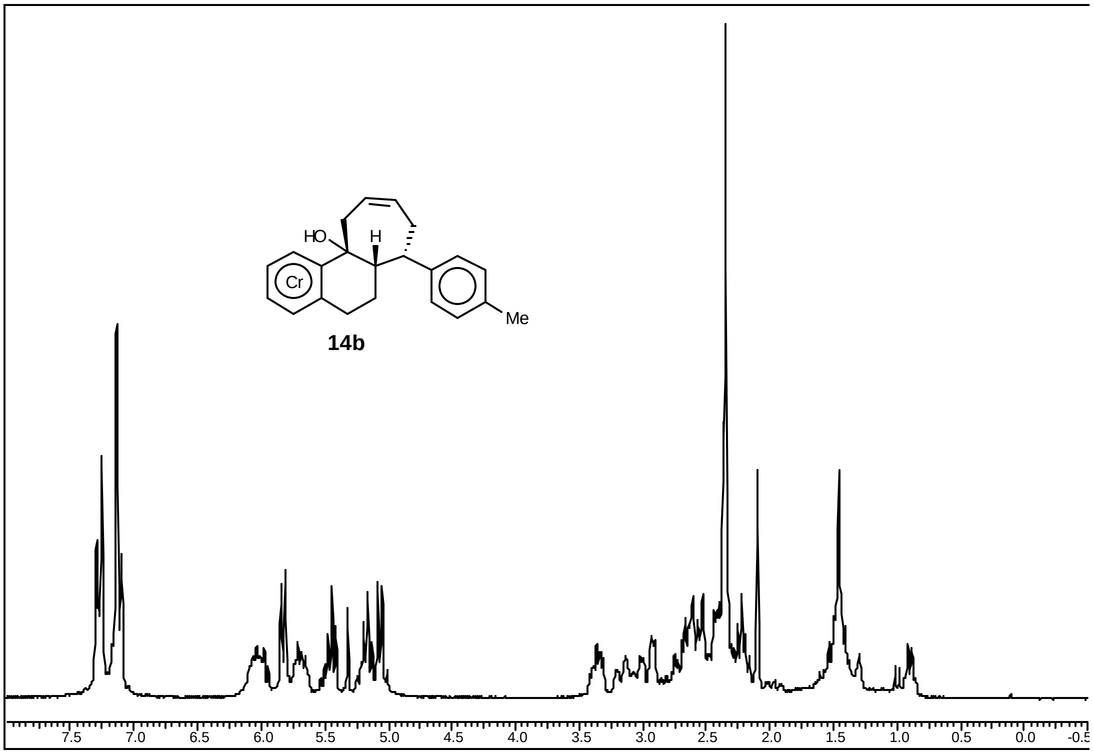
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Cr
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3.0
2.5
2.0
1.5
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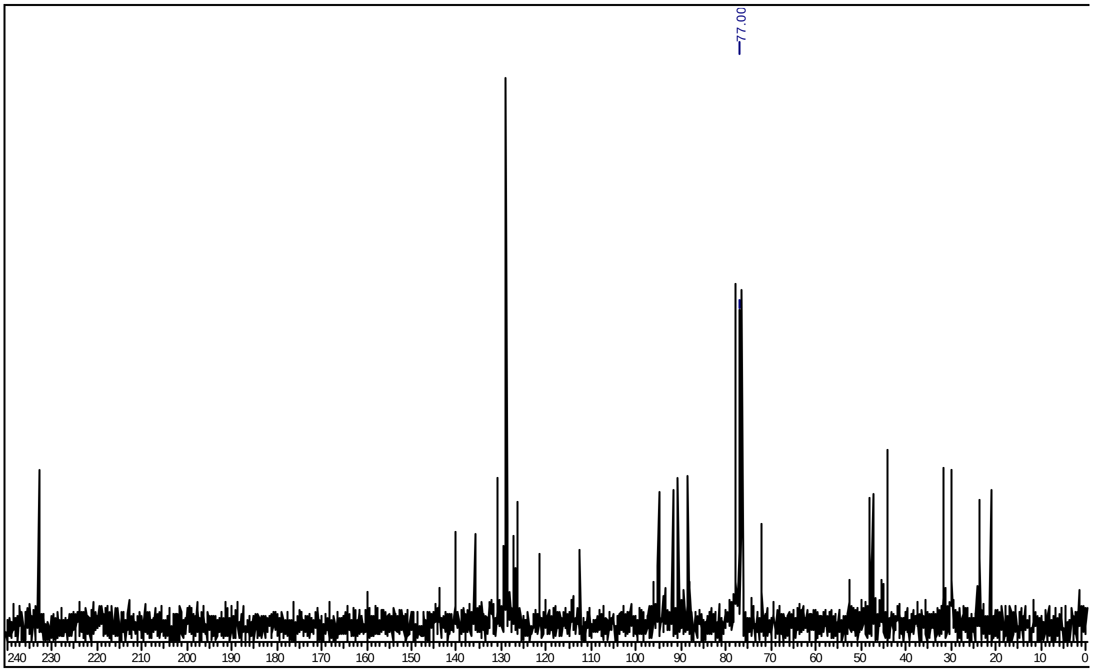
0.5
0.0
-0.5

14b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Appendix-IV

X-ray crystallographic data and structure refinement

Table 1. Crystal data and structure refinement for **4a**.

Empirical formula	$C_{21} H_{20} Cr O_4$
Formula weight	388.37 Å
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P_{21}/n
Unit cell dimensions	a = 12.1675(4) Å
	b = 24.7186(5) Å
beta = 96.507(2) deg.	
	c = 12.7642(4) Å
Volume	3814.28(19) $Å^3$
Z, Calculated density	8, 1.353 Mg/m^3
Absorption coefficient	0.622 mm^{-1}
F(000)	1616
Theta range for data collection	1.88 to 23.22 deg.
Index ranges	-3<=h<=6, -26<=k<=19, -14<=l<=12
Reflections collected / unique	4365 / 2389 [R(int) = 0.0494]
Completeness to 2theta = 23.22	42.6%
Refinement method	Full-matrix-block least-squares on F^2
Data / restraints / parameters	2389 / 0 / 469
Goodness-of-fit on F^2	1.128
Final R indices [I>2sigma(I)]	R1 = 0.0547, wR2 = 0.1146
R indices (all data)	R1 = 0.0851, wR2 = 0.1376

Largest diff. peak and hole 0.319 and -0.207 e. Å^{-3}

Table 2. Selected atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **4a**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Cr(1)	2316(1)	2527(1)	4717(1)	51(1)
O(1)	3788(7)	1894(3)	6311(6)	89(3)
O(2)	3840(7)	2221(3)	3113(6)	92(3)
O(3)	3704(8)	3518(3)	5218(6)	98(3)
O(4)	813(6)	1228(3)	2969(5)	86(3)
C(1)	3228(9)	2144(5)	5699(7)	63(4)
C(2)	3267(10)	2351(4)	3718(8)	57(4)
C(3)	3164(11)	3138(5)	5028(8)	69(4)
C(4)	980(7)	1953(4)	4188(6)	42(3)
C(5)	939(7)	2086(4)	5275(6)	48(3)
C(6)	851(8)	2619(5)	5613(8)	59(3)
C(7)	843(8)	3036(4)	4878(8)	60(3)
C(8)	855(7)	2915(4)	3795(7)	55(3)
C(9)	908(8)	2389(4)	3440(7)	44(3)
C(10)	933(8)	2295(4)	2268(6)	63(3)
C(11)	1109(8)	1374(4)	3870(7)	55(3)
C(12)	1576(8)	966(4)	4683(6)	60(3)
C(13)	2191(9)	490(4)	4254(7)	59(3)
C(14)	3219(10)	681(5)	3778(9)	101(5)
C(15)	2431(11)	64(4)	5107(8)	54(3)
C(16)	1704(9)	-347(5)	5202(8)	61(3)
C(17)	1864(11)	-731(4)	6013(10)	71(4)
C(18)	2784(13)	-699(5)	6753(9)	70(4)
C(19)	3521(10)	-294(6)	6649(9)	76(4)
C(20)	3345(10)	89(5)	5855(9)	70(4)
C(21)	2979(10)	-1110(4)	7632(8)	103(4)
Cr(1')	2376(1)	5542(1)	5234(1)	54(1)
O(1')	923(8)	6206(4)	3699(6)	123(4)
O(2')	1000(7)	5939(3)	6890(6)	90(3)
O(3')	892(9)	4574(4)	4808(8)	122(4)
O(4')	4217(6)	6703(3)	7078(5)	78(2)
C(1')	1506(11)	5943(5)	4279(8)	82(4)
C(2')	1523(10)	5778(4)	6253(7)	64(4)
C(3')	1447(11)	4949(6)	4964(9)	77(5)
C(4')	3868(7)	6029(4)	5763(6)	43(3)

C(5')	3812(7)	5931(4)	4666(6)	51(3)
C(6')	3731(7)	5401(4)	4239(7)	54(3)
C(7')	3677(8)	4963(4)	4921(8)	60(4)
C(8')	3746(7)	5049(4)	6008(8)	58(3)
C(9')	3844(7)	5564(4)	6449(6)	47(3)
C(10')	3920(8)	5621(4)	7640(6)	76(4)
C(11')	3906(8)	6601(4)	6165(7)	49(3)
C(12')	3574(8)	7050(4)	5378(6)	54(3)
C(13')	3172(8)	7570(4)	5876(6)	47(3)
C(14')	2118(9)	7450(4)	6396(8)	78(4)
C(15')	3008(10)	7999(4)	5023(7)	42(3)
C(16')	3797(9)	8382(4)	4928(7)	55(3)
C(17')	3693(11)	8763(4)	4119(9)	70(4)
C(18')	2800(14)	8774(5)	3383(10)	73(4)
C(19')	1980(10)	8385(6)	3460(8)	74(4)
C(20')	2088(8)	8002(4)	4287(8)	59(3)
C(21')	2649(10)	9174(4)	2467(8)	115(5)

Table 3. Selected bond lengths [Å] and angles [deg] for **4a**.

O(1)-C(1)	1.156(10)
O(2)-C(2)	1.143(10)
O(3)-C(3)	1.156(11)
O(4)-C(11)	1.219(9)
C(4)-C(9)	1.436(11)
C(4)-C(5)	1.433(10)
C(4)-C(11)	1.501(12)
C(5)-C(6)	1.394(12)
C(6)-C(7)	1.394(12)
C(7)-C(8)	1.415(11)
C(8)-C(9)	1.381(11)
C(9)-C(10)	1.517(10)
C(11)-C(12)	1.511(12)
C(12)-C(13)	1.530(11)
C(13)-C(15)	1.519(13)
C(13)-C(14)	1.525(12)
C(15)-C(16)	1.362(12)
C(15)-C(20)	1.382(12)
C(16)-C(17)	1.401(13)
C(17)-C(18)	1.382(14)
C(18)-C(19)	1.361(14)
C(18)-C(21)	1.512(14)
C(19)-C(20)	1.386(14)
Cr(1')-C(9')	2.229(9)
O(1')-C(1')	1.164(11)
O(2')-C(2')	1.159(10)

O(3')-C(3')	1.151(11)
O(4')-C(11')	1.210(9)
C(4')-C(5')	1.416(10)
C(4')-C(9')	1.448(11)
C(4')-C(11')	1.502(12)
C(5')-C(6')	1.418(11)
C(6')-C(7')	1.395(12)
C(7')-C(8')	1.396(11)
C(8')-C(9')	1.390(12)
C(9')-C(10')	1.519(10)
C(11')-C(12')	1.522(11)
C(12')-C(13')	1.538(11)
C(13')-C(15')	1.516(12)
C(13')-C(14')	1.539(11)
C(15')-C(16')	1.363(11)
C(15')-C(20')	1.378(11)
C(16')-C(17')	1.392(13)
C(17')-C(18')	1.353(14)
C(18')-C(19')	1.397(14)
C(18')-C(21')	1.527(15)
C(19')-C(20')	1.413(14)
C(5')-C(4')-C(9')	117.3(9)
C(5')-C(4')-C(11')	119.7(8)
C(9')-C(4')-C(11')	122.9(7)
C(7')-C(8')-Cr(1')	71.4(6)
C(8')-C(9')-C(4')	119.3(8)
C(8')-C(9')-C(10')	118.9(8)
C(4')-C(9')-C(10')	121.8(9)
C(8')-C(9')-Cr(1')	70.8(5)
C(4')-C(9')-Cr(1')	70.6(5)
C(10')-C(9')-Cr(1')	130.6(7)
O(4')-C(11')-C(4')	121.3(8)
O(4')-C(11')-C(12')	120.9(9)
C(4')-C(11')-C(12')	117.8(7)
C(11')-C(12')-C(13')	114.2(7)
C(15')-C(13')-C(12')	108.0(7)
C(15')-C(13')-C(14')	113.3(8)
C(12')-C(13')-C(14')	109.7(8)
C(16')-C(15')-C(20')	117.5(10)
C(16')-C(15')-C(13')	120.8(10)
C(20')-C(15')-C(13')	121.7(10)
C(15')-C(16')-C(17')	122.0(11)
C(18')-C(17')-C(16')	121.8(12)
C(17')-C(18')-C(19')	117.4(13)
C(17')-C(18')-C(21')	124.2(13)
C(19')-C(18')-C(21')	118.3(14)
C(18')-C(19')-C(20')	120.5(11)
C(15')-C(20')-C(19')	120.8(10)

Table 1. Crystal data and structure refinement for **4b**

Identification code	bcn
Empirical formula	$C_{21} H_{20} Cr O_4$
Formula weight	388.37
Temperature	293(2) K
Wavelength	0.71073 c
Crystal system, space group	Orthorhombic, P212121
Unit cell dimensions	a = 7.7446(18) b = 10.094(2) Å c = 24.204(5) Å
Volume	1892.0(7) ^{A3}
Z, Calculated density	4, 1.363 Mg/m^3
Absorption coefficient	0.627 mm^{-1}
F(000)	808
Theta range for data collection	1.68 to 20.81 deg.
Index ranges	-7<=h<=7, -10<=k<=9, -23<=l<=24
Reflections collected / unique	5518 / 1984 [R(int) = 0.0892]
Completeness to 2theta = 20.81	99.7%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1984 / 0 / 238
Goodness-of-fit on F^2	1.332
Final R indices [I>2sigma(I)]	R1 = 0.1041, wR2 = 0.2079
R indices (all data)	R1 = 0.1217, wR2 = 0.2154

Absolute structure parameter	0.58(10)
Largest diff. peak and hole	0.476 and -0.618 e.A^{-3}

Table 2. Selected atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 4b.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(4)	6577(13)	6150(10)	7533(4)	49(3)
O(3)	12080(2)	2388(14)	9397(6)	120(6)
O(1)	9579(16)	750(12)	8092(6)	89(4)
O(2)	12365(19)	4295(14)	7962(6)	99(5)
C(9)	8358(18)	5509(14)	8588(6)	48(4)
C(8)	8593(19)	5127(16)	9134(6)	45(4)
C(7)	7790(2)	4020(2)	9349(7)	64(5)
C(6)	6770(2)	3166(16)	9040(7)	60(5)
C(5)	6609(17)	3505(16)	8471(5)	45(4)
C(4)	7312(16)	4671(13)	8232(4)	23(3)
C(10)	9180(2)	6743(15)	8374(6)	64(4)
C(11)	6913(16)	5026(16)	7663(5)	33(3)
C(12)	6909(18)	3972(13)	7209(5)	37(4)
C(13)	6260(17)	4409(13)	6655(4)	32(4)
C(14)	4310(2)	4715(18)	6686(7)	86(6)
C(15)	6628(15)	3367(16)	6193(4)	31(3)
C(16)	6019(19)	2073(15)	6233(6)	52(4)
C(17)	6298(19)	1203(14)	5794(6)	48(4)
C(18)	7230(2)	1607(19)	5326(5)	55(4)
C(19)	7790(2)	2872(19)	5312(6)	58(5)
C(20)	7523(19)	3748(13)	5729(6)	44(4)
C(21)	7490(2)	632(19)	4852(6)	84(6)
C(3)	10990(3)	2812(16)	9096(6)	65(5)
C(1)	9490(2)	1795(17)	8286(7)	63(4)
C(2)	11180(2)	3958(14)	8207(6)	49(4)

Table 3. Selected bond lengths [Å] and angles [deg] for **4b**.

O(4)-C(11)	1.205(15)

O(3)-C(3)	1.194(18)
O(1)-C(1)	1.156(17)
O(2)-C(2)	1.146(19)
C(9)-C(8)	1.390(19)
C(9)-C(4)	1.453(18)
C(9)-C(10)	1.49(2)
C(8)-C(7)	1.38(2)
C(7)-C(6)	1.39(2)
C(6)-C(5)	1.425(19)
C(5)-C(4)	1.419(18)
C(4)-C(11)	1.457(16)
C(11)-C(12)	1.530(17)
C(12)-C(13)	1.498(16)
C(13)-C(14)	1.54(2)
C(13)-C(15)	1.561(17)
C(15)-C(20)	1.376(18)
C(15)-C(16)	1.392(18)
C(16)-C(17)	1.396(18)
C(17)-C(18)	1.405(19)
C(18)-C(19)	1.35(2)
C(18)-C(21)	1.52(2)
C(19)-C(20)	1.36(2)
C(7)-C(8)-C(9)	121.7(14)
C(7)-C(6)-C(5)	114.8(15)
O(4)-C(11)-C(4)	121.6(12)
O(4)-C(11)-C(12)	117.9(12)
C(4)-C(11)-C(12)	120.6(13)
C(13)-C(12)-C(11)	116.0(11)
C(12)-C(13)-C(14)	110.2(11)
C(12)-C(13)-C(15)	112.4(10)
C(14)-C(13)-C(15)	110.4(11)
C(20)-C(15)-C(16)	119.3(12)
C(20)-C(15)-C(13)	119.3(13)
C(16)-C(15)-C(13)	121.4(11)
C(15)-C(16)-C(17)	119.1(12)
C(16)-C(17)-C(18)	120.7(13)
C(19)-C(18)-C(17)	117.4(14)
C(19)-C(18)-C(21)	123.4(16)
C(17)-C(18)-C(21)	119.1(17)
C(18)-C(19)-C(20)	123.3(14)
C(19)-C(20)-C(15)	120.2(13)

Table 1. Crystal data and structure refinement for **10a**.

Empirical formula	$C_{23}\ H_{26}\ Cr\ O_4\ Si$
Formula weight	446.53
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, Pbca
Unit cell dimensions	a = 12.328(2) Å
	b = 18.110(3) Å
	c = 20.079(3) Å
Volume	4482.7(13) $Å^3$
Z, Calculated density	8, 1.323 Mg/m^3
Absorption coefficient	0.589 mm^{-1}
F(000)	1872
Crystal size	0.104 x 0.344 x 0.578 mm
Theta range for data collection	2.03 to 28.22 deg.
Index ranges	-14<=h<=16, -24<=k<=23, -26<=l<=17
Reflections collected / unique	25330 / 5271 [R(int) = 0.0302]
Completeness to 2theta = 28.22	86.5%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5271 / 0 / 269
Goodness-of-fit on F^2	1.042
Final R indices [I>2sigma(I)]	R1 = 0.0487, wR2 = 0.1357
R indices (all data)	R1 = 0.0576, wR2 = 0.1444
Extinction coefficient	0.0000(3)

Table 2. Selected atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **10a**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Cr	8452(1)	1614(1)	3560(1)	38(1)
Si	8906(1)	1946(1)	5457(1)	39(1)
O(1)	7362(2)	855(1)	5343(1)	56(1)
O(2)	7417(2)	3032(1)	3986(1)	80(1)
O(3)	6314(2)	1238(2)	2942(1)	94(1)
O(4)	8896(3)	2290(2)	2232(1)	116(1)
C(1)	5148(2)	-371(2)	3783(1)	66(1)
C(2)	4962(3)	-1052(2)	3494(2)	80(1)
C(3)	4088(3)	-1165(2)	3085(2)	83(1)
C(4)	3361(2)	-628(2)	2947(1)	68(1)
C(5)	3507(2)	52(2)	3233(2)	67(1)
C(6)	4391(3)	190(2)	3650(1)	67(1)
C(7)	2409(3)	-782(3)	2490(2)	111(2)
C(8)	6155(2)	-313(2)	4184(2)	67(1)
C(9)	6584(2)	272(2)	4411(1)	65(1)
C(10)	7634(2)	374(1)	4812(1)	45(1)
C(11)	8501(2)	782(1)	4400(1)	37(1)
C(12)	8806(2)	449(1)	3785(1)	45(1)
C(13)	9656(2)	717(1)	3394(1)	49(1)
C(14)	10204(2)	1350(2)	3605(1)	50(1)
C(15)	9906(2)	1697(1)	4201(1)	43(1)
C(16)	9045(2)	1432(1)	4619(1)	36(1)
C(17)	7576(2)	2386(2)	5662(1)	56(1)
C(18)	9856(2)	2758(2)	5420(1)	62(1)
C(19)	9456(2)	1325(2)	6115(1)	59(1)
C(20)	7130(2)	1366(2)	3198(1)	58(1)
C(21)	8730(3)	2035(2)	2746(1)	66(1)
C(22)	7817(2)	2487(1)	3828(1)	52(1)
C(23)	8137(3)	-332(2)	5085(2)	65(1)

Table 3. Selected bond lengths [A] and angles [deg] for **10a**.

Si-C(19)	1.863(3)
Si-C(17)	1.869(2)
Si-C(18)	1.881(3)
Si-C(16)	1.931(2)
O(1)-C(10)	1.416(3)
C(3)-C(4)	1.351(5)
C(3)-H(3)	0.9300
C(4)-C(5)	1.370(5)
C(4)-C(7)	1.515(4)
C(5)-C(6)	1.397(4)
C(10)-C(23)	1.524(3)
C(10)-C(11)	1.541(3)
C(11)-C(16)	1.424(3)
C(11)-C(12)	1.425(3)
C(12)-C(13)	1.396(3)
C(19)-H(19C)	0.9600
C(23)-H(23A)	0.9600
C(23)-H(23B)	0.9600
C(23)-H(23C)	0.9600

Table 1. Crystal data and structure refinement for **18a**.

Empirical formula	$2[C_{23}H_{25}NO_6Cr]$
Formula weight	926.88
Temperature	293(2) K
Wavelength	0.70930 A
Crystal system, space group	Monoclinic, P21
Unit cell dimensions	a = 8.310(1) Å
b = 17.938(3) Å	
beta = 96.43(1) deg.	
c = 15.736(2) Å	
Volume	2330.9(5) Å^3
Z, Calculated density	2, 1.321 Mg/m^3
Absorption coefficient	0.528 mm^{-1}
F(000)	968
Crystal size	0.3 x 0.28 x 0.4 mm
Theta range for data collection	1.30 to 24.91 deg.
Index ranges	0<=h<=9, 0<=k<=21, -18<=l<=18
Completeness to 2theta = 24.91	73.3%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3103 / 1 / 570
Goodness-of-fit on F^2	1.057
Final R indices [I>2sigma(I)]	R1 = 0.0607, wR2 = 0.1490
R indices (all data)	R1 = 0.0970, wR2 = 0.1831
Absolute structure parameter	0.03(8)
Extinction coefficient	0.0004(11)
Largest diff. peak and hole	0.390 and -0.576 e.A^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **18a**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
N(1)	665(16)	5918(7)	4071(8)	43(4)
C(1)	2200(3)	4424(13)	6132(9)	77(6)
C(2)	4210(3)	4993(10)	5200(12)	56(5)
C(3)	4470(3)	3691(18)	5754(15)	113(9)
C(4)	295(18)	3965(11)	4748(11)	55(5)
C(5)	1030(2)	3312(13)	4771(13)	69(6)
C(6)	2380(3)	3154(14)	4364(13)	96(9)
C(7)	2990(2)	3751(13)	3878(15)	88(8)
C(8)	2130(2)	4456(12)	3781(9)	53(5)
C(9)	700(2)	4587(11)	4225(11)	57(5)
C(10)	-1110(3)	4042(14)	5268(13)	82(7)
C(11)	-270(2)	5260(11)	4070(9)	54(5)
C(12)	-1480(3)	5154(10)	3193(10)	52(5)
C(13)	-2850(2)	4593(8)	3285(11)	57(5)
C(14)	-500(3)	5044(13)	2430(8)	75(7)
C(15)	-2280(3)	5911(14)	3065(14)	68(7)
C(16)	-3780(2)	6858(9)	3718(11)	60(5)
C(17)	1080(2)	6324(9)	4800(10)	49(4)
C(18)	2280(19)	6908(11)	4721(11)	49(4)
C(19)	2900(2)	7203(12)	5463(12)	61(6)
C(20)	2170(3)	7133(13)	6269(11)	74(6)
C(21)	1050(4)	6688(13)	6255(11)	97(8)
C(22)	630(4)	6256(14)	5589(13)	122(12)
C(23)	2810(5)	7400(2)	7687(13)	198(19)
N(2)	9460(2)	6809(10)	979(9)	78(5)
C(24)	5480(2)	9068(10)	-753(8)	55(5)
C(25)	5830(3)	7787(19)	-213(13)	85(8)
C(26)	7760(2)	8220(14)	-1238(14)	79(7)
C(27)	9830(2)	8789(13)	258(12)	66(6)
C(28)	9329(18)	8258(11)	797(9)	48(5)
C(29)	7960(3)	8341(14)	1180(13)	81(7)
C(30)	7070(3)	8986(15)	1183(10)	71(7)
C(31)	7520(2)	9538(13)	717(13)	70(7)
C(32)	8800(3)	9504(11)	257(14)	88(8)
C(33)	11250(2)	8759(12)	-267(11)	68(6)
C(34)	10320(2)	7537(9)	954(10)	48(5)
C(35)	11490(3)	7538(11)	1789(12)	58(6)

C(36)	12690(3)	8160(15)	1722(11)	99(9)
C(37)	10670(2)	7767(10)	2567(10)	65(5)
C(38)	12307(19)	6810(10)	1891(10)	48(4)
C(39)	13740(3)	5953(17)	1222(13)	120(11)
C(40)	8760(2)	6435(11)	202(9)	54(5)
C(41)	7570(3)	5952(12)	204(13)	57(5)
C(42)	7040(3)	5406(13)	-426(14)	68(6)
C(43)	7510(3)	5564(11)	-1131(13)	74(6)
C(44)	8730(5)	6137(15)	-1284(16)	122(12)
C(45)	9480(2)	6561(13)	-560(9)	84(8)
C(46)	7760(6)	5170(2)	-2689(18)	230(2)

Table 3. Bond lengths [Å] and angles [deg] for **18a**

N(1)-C(17)	1.37(2)
N(1)-C(11)	1.41(2)
C(4)-C(5)	1.32(3)
C(4)-C(9)	1.45(3)
C(4)-C(10)	1.50(2)
C(5)-C(6)	1.38(3)
C(6)-C(7)	1.44(3)
C(7)-C(8)	1.45(3)
C(8)-C(9)	1.46(2)
C(9)-C(11)	1.46(3)
C(11)-C(12)	1.62(2)
C(12)-C(15)	1.52(3)
C(12)-C(13)	1.54(3)
C(12)-C(14)	1.53(2)
C(17)-C(22)	1.34(3)
C(17)-C(18)	1.46(2)
C(18)-C(19)	1.33(2)
C(19)-C(20)	1.47(3)
C(20)-C(21)	1.23(3)
C(21)-C(22)	1.32(3)
N(2)-C(40)	1.46(2)
N(2)-C(34)	1.49(2)
C(27)-C(28)	1.37(2)
C(27)-C(33)	1.51(3)
C(27)-C(32)	1.54(3)
C(28)-C(29)	1.35(3)
C(28)-C(34)	1.54(3)
C(29)-C(30)	1.37(3)
C(30)-C(31)	1.31(3)
C(31)-C(32)	1.36(3)
C(34)-C(35)	1.55(3)
C(35)-C(38)	1.47(3)
C(35)-C(37)	1.52(3)
C(35)-C(36)	1.51(3)

C(40)-C(41)	1.31(3)
C(40)-C(45)	1.42(2)
C(41)-C(42)	1.43(3)
C(42)-C(43)	1.25(3)
C(43)-C(44)	1.49(3)
C(44)-C(45)	1.45(3)

C(5)-C(4)-C(9)	124.1(15)
C(5)-C(4)-C(10)	116.9(16)
C(9)-C(4)-C(10)	118.9(16)
C(7)-C(8)-C(9)	120.3(18)
C(4)-C(9)-C(11)	124.9(17)
C(4)-C(9)-C(8)	113.8(16)
C(11)-C(9)-C(8)	121.1(18)
N(1)-C(11)-C(9)	113.4(15)
N(1)-C(11)-C(12)	112.7(14)
C(9)-C(11)-C(12)	108.8(14)
C(15)-C(12)-C(13)	106.1(16)
C(15)-C(12)-C(14)	105.9(16)
C(13)-C(12)-C(14)	116.8(16)
C(15)-C(12)-C(11)	103.2(15)
C(13)-C(12)-C(11)	113.0(14)
C(14)-C(12)-C(11)	110.7(17)
C(22)-C(17)-N(1)	131.0(17)
C(22)-C(17)-C(18)	114.0(18)
N(1)-C(17)-C(18)	114.9(13)
C(19)-C(18)-C(17)	114.3(17)
C(18)-C(19)-C(20)	124.4(19)
C(21)-C(20)-O(6)	132(2)
C(21)-C(20)-C(19)	115.3(18)
O(6)-C(20)-C(19)	113(2)
C(20)-C(21)-C(22)	122(2)
C(17)-C(22)-C(21)	127(2)
C(29)-Cr(2)-C(30)	36.2(8)
C(31)-Cr(2)-C(30)	34.1(7)
C(38)-O(11)-C(39)	117.6(16)
C(43)-O(12)-C(46)	121(2)
C(40)-N(2)-C(34)	121.9(15)
C(30)-C(31)-C(32)	124(2)
N(2)-C(34)-C(35)	103.7(14)
N(2)-C(34)-C(28)	119.6(14)
C(35)-C(34)-C(28)	114.3(15)
C(38)-C(35)-C(37)	113.2(16)
C(38)-C(35)-C(36)	111.4(19)
C(37)-C(35)-C(36)	102.4(16)
C(38)-C(35)-C(34)	109.3(15)
C(37)-C(35)-C(34)	112.6(17)
C(36)-C(35)-C(34)	107.5(15)
O(10)-C(38)-O(11)	125.6(16)
O(10)-C(38)-C(35)	123.3(15)

O(11)-C(38)-C(35)	110.8(16)
C(41)-C(40)-C(45)	119.9(17)
C(41)-C(40)-N(2)	122.1(17)
C(45)-C(40)-N(2)	117.9(17)
(42)-C(43)-C(44)	126(2)
C(42)-C(43)-O(12)	119.7(19)
C(44)-C(43)-O(12)	114.1(18)
C(45)-C(44)-C(43)	118.5(19)
C(40)-C(45)-C(44)	113.2(19)