To

My Parents

And

Brothers

Selectivity in C-C Bond Forming Reactions on Arene-Tricarbonylchromium Template

A THESIS

SUBMITTED TO THE

UNIVERSITY OF POONA

FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN CHEMISTRY

BY

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DIVISION OF ORGANIC CHEMISTRY (SYNTHESIS)

NATIONAL CHEMICAL LABORATORY

PUNE 411 008

CERTIFICATE

This is to certify that the work incorporated in the thesis entitled **"Selectivity in C-C Bond Forming Reactions on Arene-Tricarbonylchromium Template"** *submitted by Sunil Kumar Mandal 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 : 16 Feb, '99

National Chemical Laboratory

Pune 411 008

(Dr. Amitabha Sarkar)

Research Guide

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No words are enough to express my feelings for my wife, without her constant encouragement, care, moral support and help, I would not have been able to finish this work.

I thank CSIR for providing financial assistance. Finally I am thankful to Dr. K. N. Ganesh, Head, Division of Organic Chemistry (Synthesis) and the Director, NCL, for providing the necessary infrastructure and for permitting me to submit this work in the form of a thesis.

Sunil Kumar Mandal

Sunil Kumar Mandal

CONTENTS

SYNOPSIS OF THE THESIS

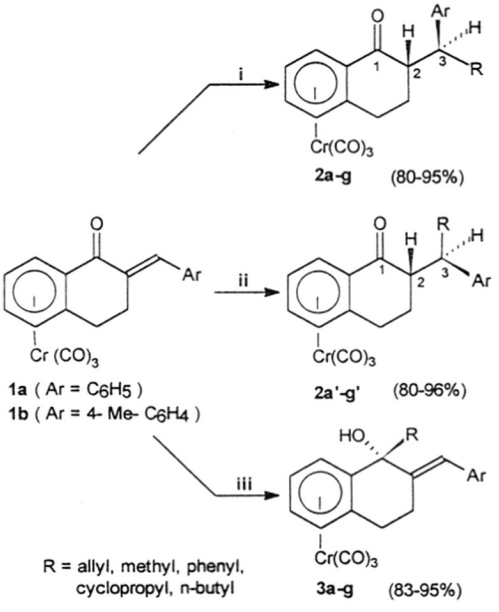
Compound numbers in the synopsis are not identical to the numbers in the thesis

PART - A. Nucleophilic Addition to Enones Anchored on Arene Tricarbonylchromium : Effect of Lewis acid on the Regio and Stereochemistry of Addition.

Two conformationally rigid 2-arylidene-1-tetralone $Cr(CO)_3$ complexes (**1a-b**) were treated with organolithium or organomagnesium reagent in presence of $TiCl_4$ (Scheme-1, reaction condition: **i**). The products obtained were diastereomerically pure (**2a-g**) resulting from attack of the nucleophile from the same side of the metal carbonyl moiety (*endo*-attack).

On the other hand, a different set of diastereomerically pure, *exo*-selective conjugate addition products (**2a'-g'**) were obtained from reaction of organocuprates (reaction condition: **ii**) with the same substrates.

Scheme-1



i : $TiCl_4$ <M->90°C 15 min ; RLi or RMgX <M->90°C 15 min

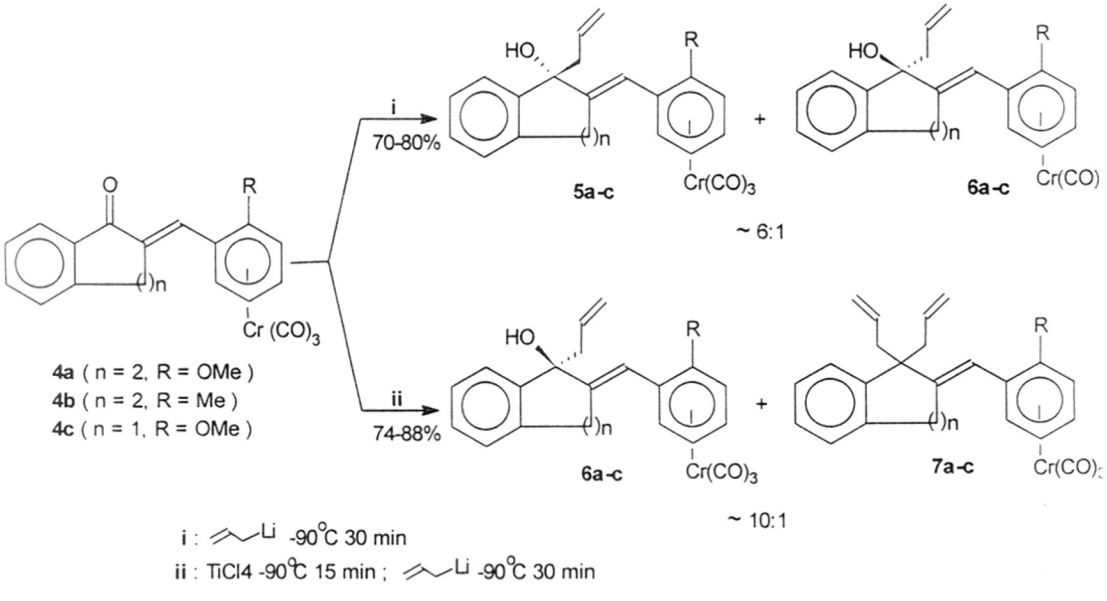
ii : $R_2Cu(CN)Li_2$ <M->78°C ~1 h

iii : RLi <M->90°C 30 min

The formation of products obtained under condition **i** attests to the fact that the Lewis acid coordinates to the ketone carbonyl in an out-of-plane manner and encourages endo-selective addition. These two reaction conditions, therefore, provide convenient protocols for stereodivergent nucleophilic addition to these substrates. In addition, it has been shown that same organolithium reagents afford *exo*-1,2-adducts (**3a-g**) exclusively if Lewis acid is omitted from the reagents (condition **iii**).

A different set of enones were chosen to collect the additional evidences for the out-of-plane coordination of $TiCl_4$ onto ketone. The difference between the present set of substrates, **4a-c**, and those used in previous studies, lies in the positioning of enone function with respect to the arene ring complexed with tricarbonylchromium (Scheme-2). These new complexes were prepared readily by condensation of 1-tetralone or 1-indanone and aromatic aldehydes with pendant $Cr(CO)_3$ group.

Scheme-2



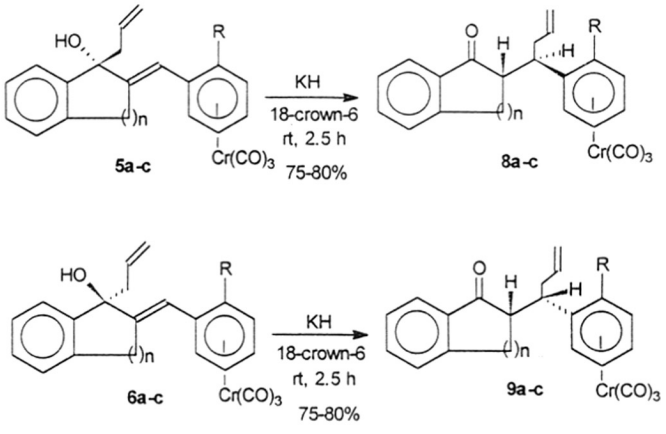
Reaction of **4a-c** with allyllithium afforded only 1,2-addition products – but the *exo*/*endo* selectivity was moderate (condition **i**). Diastereoselectivity did not improve when allylmagnesium bromide was used. The reversal of stereoface preference in nucleophilic addition was indeed more dramatic when the substrate was premixed with a strong Lewis acid like $TiCl_4$ in dichloromethane (condition **ii**). No *exo*-1,2-adduct was obseved – the addition was entirely *endo*-selective.

Strong Lewis acidity of $TiCl_4$, however, promoted a side-reaction – about 10% *gem*-diallylated product was always obtained. This undesired product became the only isolable product if excess of allylmagnesium bromide was present.

Nucleophilic addition by methyllithium displayed comparable selectivity. This set of observations clearly emphasized the importance of Lewis acid complexation with carbonyl function in bringing about stereodivergence in nucleophilic addition.

A highlight of this study is the planned execution of *endo*-allylation at the benzylic site (Scheme-3). This is significant, because benzylic sites are effectively shielded against *endo*-approach of reagents by the bulk of neighboring $Cr(CO)_3$ group. The *endo*-allylated carbinols (**6a-c**) on treatment with potassium hydride underwent smooth anion-assisted oxy-Cope rearrangement to furnish the ketones, **9a-c**. These are, formally, products of conjugate addition of allylmetal to enones **4a-c**, where the addition seemed to have occurred from the *endo*-face. The *exo*-allylated ketones **8a-c**, on the other hand, could be easily and stereospecifically obtained from rearrangement of the *exo*-carbinols **5a-c** (Scheme-3).

Scheme-3

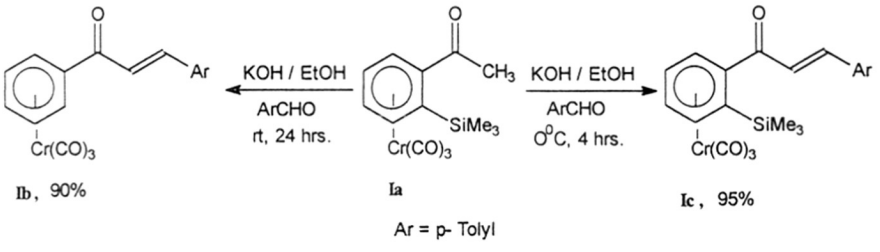


Although Hosomi-Sakurai reaction was the key reaction that provided the important example of exclusive *endo*-selectivity in a typical Lewis-acid mediated reaction, it failed with the substrates, **4a-c**. This observation is, however, not inconsistent with the emerging picture. It is conceivable that *exo*-complexation by $TiCl_4$ prevents *exo*-addition of allyltrimethylsilane. At the same time, $Cr(CO)_3$ precludes *endo*-approach of allyltrimethylsilane to benzylic carbon on steric ground. The reaction failed, but it is difficult to overlook an interesting implication. It is possible that out-of-plane complexation of $TiCl_4$ is a crucial factor for the success of Hosomi-Sakurai reaction in general, and a fresh scrutiny of the steric requirements of this reaction is warranted.

PART - B. Activation of Ar-Si Bonds through Complexation with $Cr(CO)_3$: Alkali metal Hydride or Hydroxide induced Cleavage and Functional Modification of $(CO)_3Cr$-Ar-$SiMe_3$ Bonds.

The study originated from the following two observations of facile cleavage of Ar-$SiMe_3$ bond, while attempting standard organic transformations like aldol-dehydration (Scheme-1) and anion assisted Cope rearrangement (Scheme-2). In both instances, desilylation could be suppressed only at low temperatures.

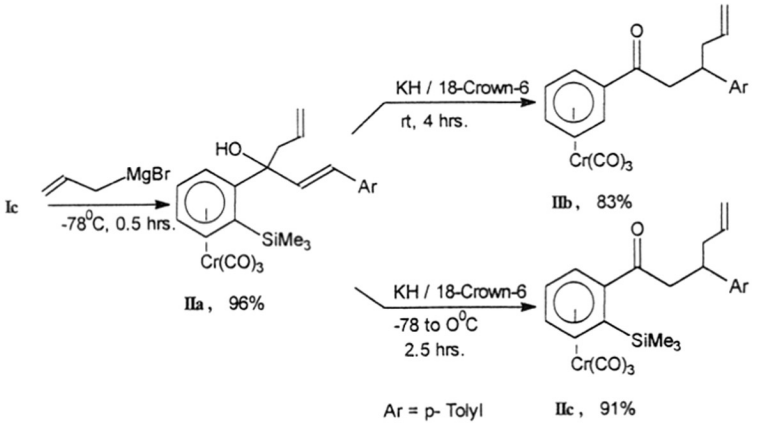
Scheme-1



Ib, 90% Ia Ic, 95%

Ar = p- Tolyl

Scheme-2



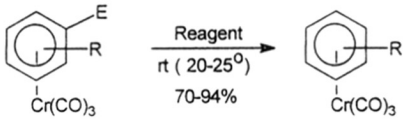
IIb, 83%

IIa, 96%

Ar = p- Tolyl IIc, 91%

We found that several common bases used in organic reactions readily effected desilylation of a chromium-complexed aromatic ring (Scheme-3). However, desilylation does not readily occur for uncomplexed arylsilanes except with fluoride ion catalysis, or when strong electron-withdrawing substituents (*eg.* NO_2) are present on the aromatic ring.

Scheme-3



E = $SiMe_3$, $SnMe_3$
R= H, 2-OMe, 4-OMe, 4-Me, 2-$COCH_3$ *etc.*

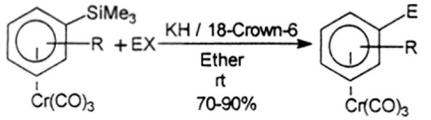
Reagents: A = *KH / 18-Crown-6 / ether*; B = *50% aq NaOH / TBAB / CH_2Cl_2*; C = *K_2CO_3 / 18-Crown-6 / acetone*; D = *KOH / EtOH*; E = *NaOMe / ether.*

We observed that potassium hydride in the presence of a catalytic quantity of 18-crown-6 (reagent-A) effected desilylation in ether in a short period of time. Sodium hydride can replace potassium hydride. Potassium or sodium hydride is believed to act as a *nucleophile* that reacts with the tetrasubstituted silicon to initiate desilylation. Destannylation was also similarly achieved for $Cr(CO)_3$-Ar-$SnMe_3$ complexes.

The aryl anion stabilized by co-ordination with a $Cr(CO)_3$ group was expected to be trapped regiospecifically by electrophiles. In absence of any other electrophile, solvent DMF itself reacts with the aryl anion to afford the corresponding aromatic aldehyde complex in good yield (67-90%), along with some protiodesilylated product (5-20%), as presented in Scheme-4. This

capability was readily adapted for introduction of other electron-withdrawing functional groups to the aromatic nucleus. When tricarbonylchromium complex of phenyltrimethylsilane was allowed to react with electrophiles like ketone, dialkyl or diaryl carbonate in presence of KH / 18-crown-6 in ether, carbinol and ester complexes were obtained in moderate to good yield.

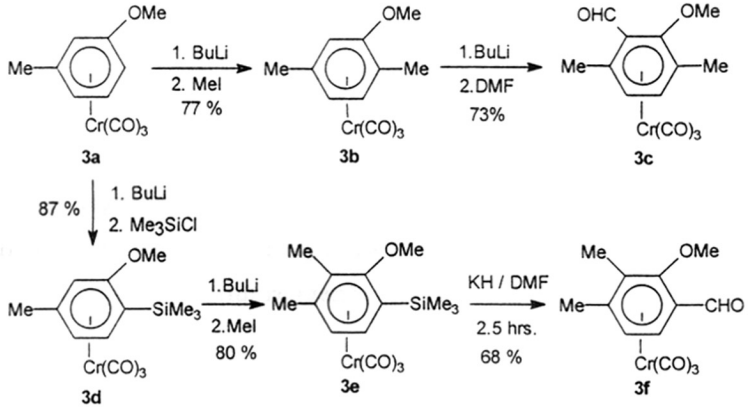
Scheme-4



EX	E
DMF	CHO
$(RO)_2CO$	CO_2R
R_2CO	$C(OH)R_2$

One important aspect of this method of functionalisation is its complete regioselectivity. Scheme-5 summarizes two routes to regioisomeric aromatic products (**3c** and **3f**). This sequence uses the trimethylsilyl unit as a site-protective group as well as a precursor of formyl function.

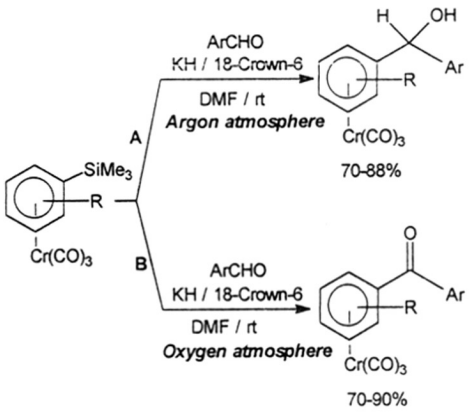
Scheme-5



This should prove to be a useful synthetic method for such complexes since these are not readily obtainable by direct complexation route.

When desilylation was carried out using 1.0-1.2 equiv. KH and 10 mol% of 18-crown-6 in the presence of an aromatic aldehyde under *an atmosphere of dry argon,* the major product was the expected carbinol (70-88%) contaminated with a small amount (5-15%) of protiodesilylated product (Scheme -6). However, when the same reaction was carried out with 2.0-2.2 equiv. potassium hydride under *an atmosphere of dry oxygen,* the major product was a biaryl ketone (70-90%) instead of a carbinol.

Scheme-6



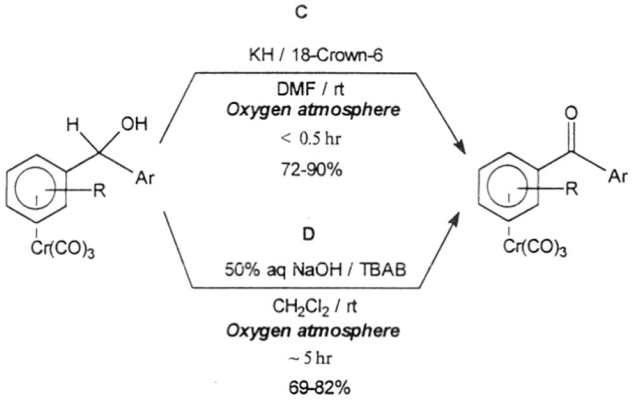
R = H, 2-OMe, 4-OMe, 2-Me, 4-Me, 2-Cl

Ar = C_6H_5, 4-Me-C_6H_4, 2-Thienyl, 2-Pyridyl, 4-$OMeC_6H_4$, 2-Furyl, 4-Cl-C_6H_4, Ferrocenyl, 4-NMe_2-C_6H_4, 4-NO_2-C_6H_4

The most significant advantage of this method is that the desilylated species can tolerate sensitive groups such as NO_2, which are not compatible with Grignard or organolithium reagents.

Expectedly, the complexed carbinols afforded the corresponding ketone complexes when treated with 1.0-1.2 equiv. potassium hydride under *oxygen atmosphere* (Scheme-7). Biphasic autoxidation of carbinols could also be effected with 50% aqueous sodium hydroxide in presence of tetrabutylammonium bromide (TBAB) as phase transfer catalyst, albeit with a lesser efficiency.

Scheme -7



Oxidative processes involving reactions of molecular oxygen with organic substrates is well known. But, autoxidations are not often used for preparative purposes since they frequently result in a complex mixture of products. However, the autoxidation described above is a preparatively useful reaction. Mild condition and short reaction time permit tricarbonylchromium group to survive even in the presence of oxygen.

GENERAL REMARKS

1. All melting points (recorded on a Thermonik Campbell melting point apparatus) are uncorrected and are recorded on the Celsius scale.
2. IR spectra were recorded as nujol mull or chloroform, on a Perkin-Elmer Infrared Spectrometer Model 599-B, Model 1600 FT-IR and ATI Mattson, UK, Model-RS-1 FT-IR, using sodium chloride optics. IR bands are expressed in frequency (cm^{-1}).
3. Proton NMR spectra were recorded using tetramethylsilane as internal reference on Bruker MSL-300, Bruker AC-200, Chemical shifts were recorded in parts per million (δ). Abbreviations, *viz.*, s = singlet, d = doublet, t = triplet, dd = doublet of doublet, ddd = doublet of doublet of doublet, brs = broad singlet, br = broar peak and m = multiplet have been used. $CDCl_3$ was used as the solvent unless otherwise mentioned.
4. ^{13}C NMR spectra were recorded on Bruker AC-500, Inova-AC-400, Bruker MSL-300 and Bruker AC-200 instrument operating at 125.7 MHz, 100.6 MHz, 75.2 MHz and 50.3 MHz respectively.
5. Mass spectra were recorded on a Finnigan-Mat 1020C mass spectrophotometer at 70 eV.
6. Elemental analyses (C, H, N) were obtained on a Carlo-Erba 1100 automatic analyzer by Dr. S. Y. Kulkarni and his group at NCL.
7. The progress of the reaction was monitored by analytical thin layer chromatography with TLC 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.

PART - A

Nucleophilic Addition to Enones Anchored on Arene Tricarbonylchromium : Effect of Lewis Acid on the Regio and Stereochemistry of Addition.

Part of this work has been accepted for publication : *Journal of Organic Chemistry* **1999** (in press)

Introduction

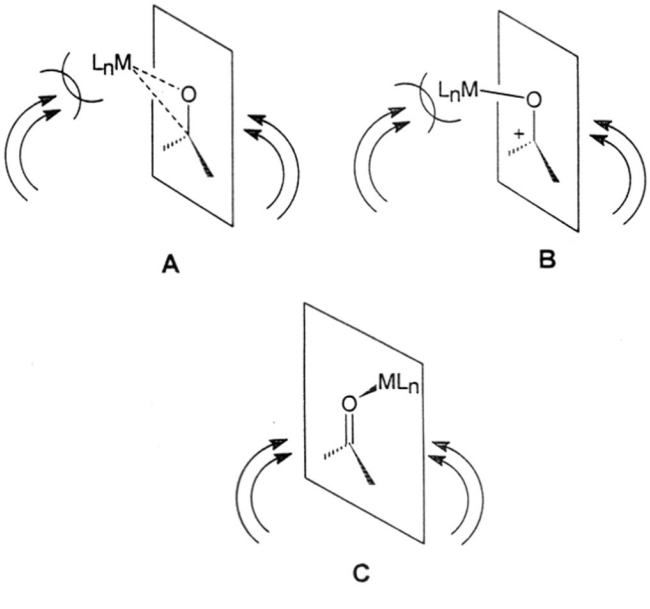
Lewis acids play a prominent role in organic synthesis by virtue of their ability to activate carbonyl groups.[1] They are used as catalysts for nucleophilic addition to carbonyl compounds as well as in many other important carbon-carbon bond forming reactions.[2] Recent reports show that the attachment of chiral ligands to Lewis acidic metals can bring about significant asymmetric induction.[3] However, the true origins of 'Lewis acid effect' is not clearly understood yet.

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 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.[5]

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 (Figure-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,[6] 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. On the other hand, an *in-plane* bound Lewis acid does not impose a π-facial discrimination,[7] as seen in **C**.

Figure-1

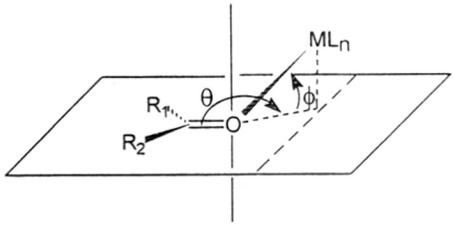


In Lewis acid mediated reactions, therefore, the steric and electronic requirements of the carbonyl ligand and its immediate neighbourhood determine the mode of coordination, and consequently, the steric course of the reaction.

Because the stereoelectronic variables contributing to Lewis acid mediated reactions are many, it has been difficult to propose a structural model which applies to all such reactions. Yet, a large number of studies pertaining to the structure of Lewis acid-carbonyl complexes by crystallography and NMR methods have been carried out.[8] Theoretical studies of Lewis acid carbonyl interactions indicate that cationic Lewis acids prefer a linear geometry though distortions upto 15° are noted.[9] Neutral Lewis acids, on the other hand, prefer a bent, planar geometry in the direction of one of the sp^2 hybridized lone pairs.[10] In case of α,β-unsaturated carbonyl complexes the *transoid* geometry seems to be preferred since it minimizes adverse steric interactions.[11] It is observed that when a Lewis acid forms complexes with aldehydes, the Lewis acid prefers *anti* complexation with simple aldehydes and *syn* complexation with α-heterosubstituted aldehydes.[12] Between the two limiting modes of complexation, the σ complexation is more common for most main group metals, early transition metals and lanthanides, whereas the π complexation is found only for electron rich transition metal complexes.[6] In the σ mode, the Lewis acid can be located in many different positions

(Figure-2)[8] defined by three variables, the Lewis acid-oxygen distance, r, and the two angles, θ and ϕ.

Figure-2

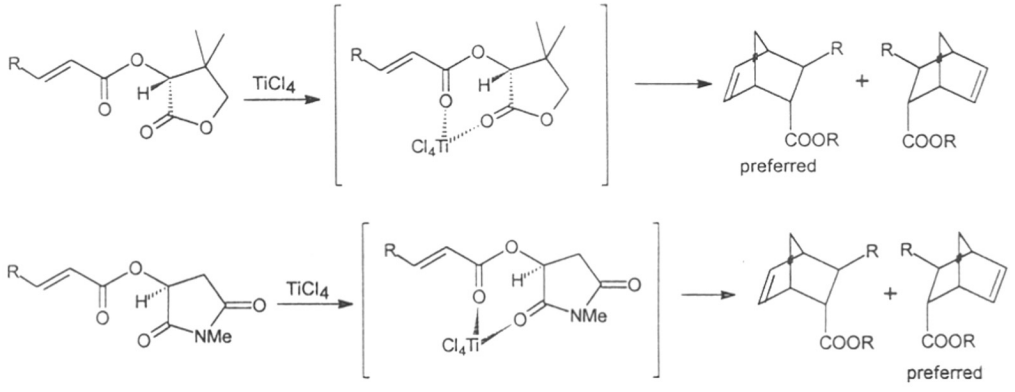


Crystal structures indicate[13] that complexes of Lewis acids with aldehydes are planar (ϕ = 0) and bent (θ = 120°±15°). However, in case of ketones and esters there are a few cases where the Lewis acid is complexed *out-of-plane* (ϕ > 0) with the carbonyl group.[14] The determining factor in such cases appear to be unfavorable steric crowding around the carbonyl group.

Attempts have been made to correlate the structure with reactivity patterns and models have been proposed to predict the outcome of individual types of reactions. The most popular among all these reactions is the Lewis acid mediated Diels-Alder reaction.[15]

Helmchen and co-workers have reported *out-of-plane* complexation of enolates with $TiCl_4$ and their effect in Diels-Alder reaction with cyclopentadiene (Scheme-1). It was postulated that the diastereofacial selectivity encountered in these reactions (>97% in favour of the major isomer) was due to a selective shielding of one face of the enoate by the $TiCl_4$.

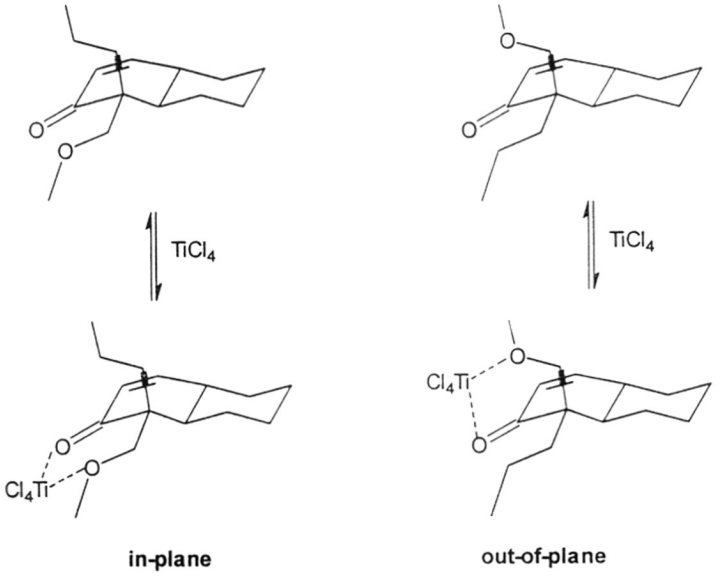
Scheme-1



In Diels-Alder reaction of fumarates with cyclopentadiene, the Lewis acid free route and the $TiCl_4$ mediated reaction afforded opposite diastereomers.[16] The explanation stated that $TiCl_4$ was bound to the ester unit in an *out-of-plane* mode and consequently directed the diene to approach from the opposite face.

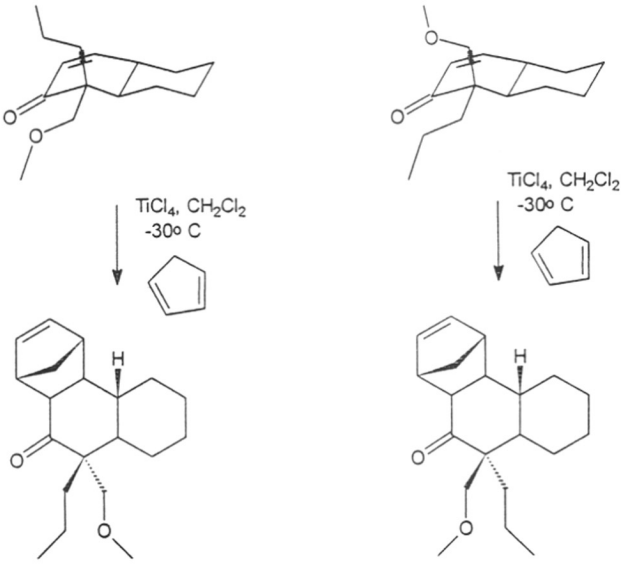
Recently, Corcoran and co-workers have illustrated that such stereocontrol can also be engineered using suitably designed enones.[17] The enones have properly positioned methoxymethyl groups to direct *in-plane* and *out-of-plane* coordination of $TiCl_4$ with the carbonyl function (Scheme-2).

Scheme-2



The two complexes formed on addition of $TiCl_4$, were isolated and characterized. X-ray structure analyses confirmed the predicted geometry of the Lewis acid-carbonyl complexes. These $TiCl_4$-complexed enones were separately treated with cyclopentadiene to form Diels-Alder adducts (Scheme-3).

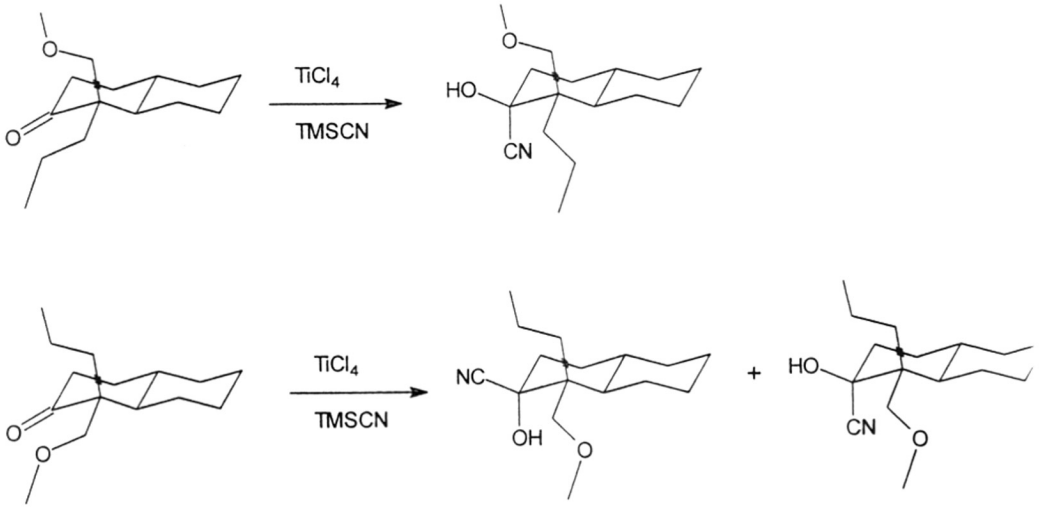
Scheme-3



The *out-of-plane* complexed adduct reacted 15 times faster than the *in-plane* complex.[18] The study shows that the *out-of-plane* coordinated complex is less stable than the *in-plane* complex by at least 6 kcal mol^{-1} which is consistent with the rate difference.

TMSCN added directly to the carbonyl group of similar substrates in presence of $TiCl_4$ (Scheme-4). The stereochemistry of the products depended on the stereochemistry of the alkoxy appendage.[17c]

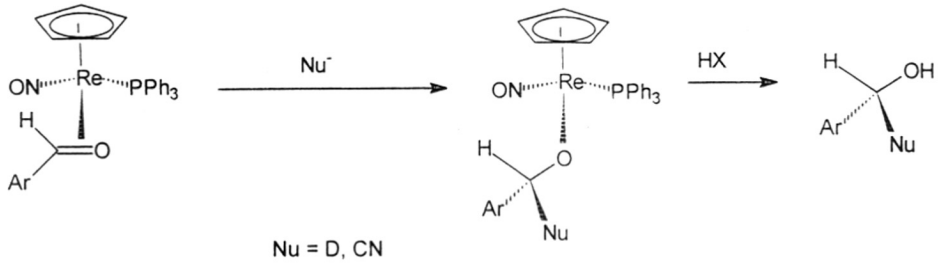
Scheme-4



In all these examples, however, the molecule has a handle to direct $TiCl_4$ complexation with carbonyl- in plane or out-of-plane. In substrates without such a handle, it is much more difficult to precisely define orientation of $TiCl_4$ with respect to carbonyl group.

Although an *out-of-plane* coordination of the Lewis acid is expected to direct the trajectory of the incoming group,[19] reports describing such an effect are rare.[5a,b,20] Gladysz and co-workers reported η^2 coordinated complexes of aldehydes with $CpRe(NO)PPh_3$ cation.[5a,b] In enatiomerically pure form, they undergo nucleophilic additions with high enantioselectivities (Scheme-5).

Scheme-5

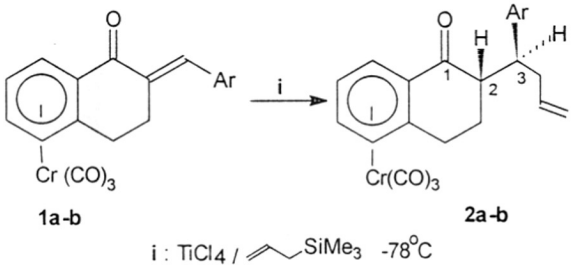


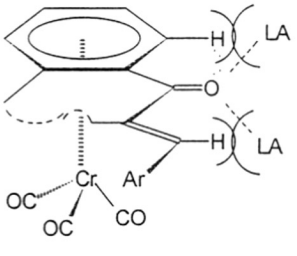
Nu = D, CN

The present work originated from a chance discovery[21] of *endo*-selective Hosomi-Sakurai reaction on 2-arylidene-1-tetralone tricarbonylchromium complexes (Scheme-6). In this case, the chromium-complexed aromatic ring and the enone functionality are coplanar and the array of sp^2 carbons form part of a rigid bicyclic system. The oxygen atom is also sp^2 -hybridized, and hence the two nonbonded electron pairs on oxygen are coplanar with these carbons. In this situation, the *peri* proton of the aromatic ring as well as the olefinic proton can shield the oxygen electron pairs from approach of the Lewis acid from either end (Scheme-6). Probably this factor is responsible for the failure of the allylsilane addition to the substrates in presence of $BF_3.OEt_2$ as Lewis acid. Titanium being a transition metal, is capable of *out-of-plane* coordination with the C=O π-bond, and the reaction proceeded in presence of $TiCl_4$ as described above.

Out-of-plane coordination of titanium with the CO π-bond has been structurally characterized. Although such coordination has sometimes been described as η^2, in reality, the Ti-O distance is evidently shorter than Ti-C bond. One should more appropriately consider a bond between Ti and a sp^3 oxygen, which in turn implies that the carbonyl center is rendered cationic, and thus the enone function is activated for reaction with allyltrimethylsilane. It is then likely that $TiCl_4$ would occupy the *exo* face (opposite to the tricarbonylchromium) and force the allyltrimethylsilane to approach from the *endo* face of the molecule at C-3.

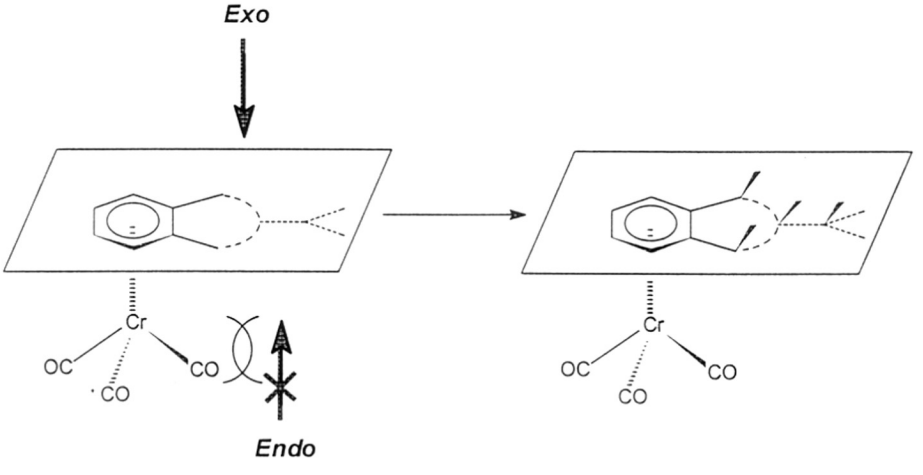
Scheme-6





Although in arene tricarbonylchromium complexes,[22] *exo*-selective functionalization[22a,22c,23] is a normal trend (Figure-3), the above example of the complete reversal of stereoface selection due to out-of-plane coordination of Lewis acid, suggested a possible way of engineering *endo*-selectivity on such substrates.

Figure-3



Present work

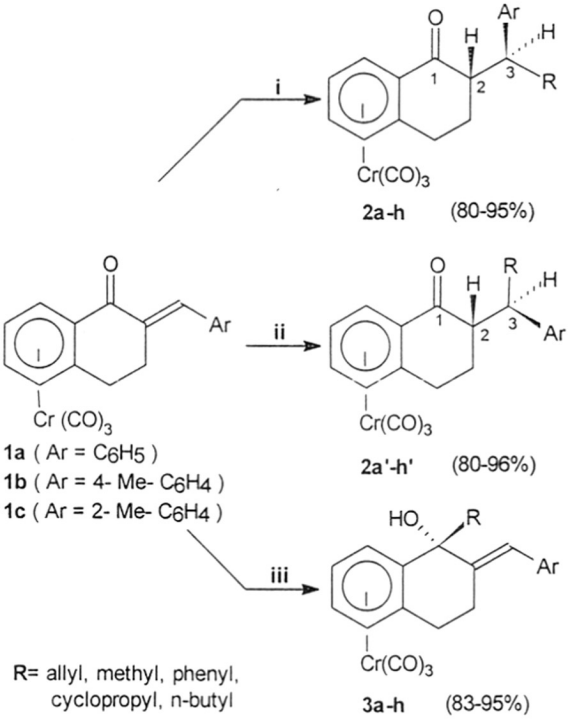
The stereochemically rigid enone structure of substrates **1a-c** (Scheme-7) offers two well- defined faces (*endo*- and *exo*, i.e *syn* and *anti* with respect to metal carbonyl respectively). We argued earlier that $TiCl_4$ coordinates with the carbonyl in an out-of-plane manner from the *exo* face and sterically prevents allylsilane approach from the same face. It was therefore of interest to investigate whether approach of nucleophilic reagents (RLi or RMgX) would be guided by similar considerations, provided the nucleophilic addition proceeds faster than metal-exchange reaction. Moreover, if the strategy succeeds, we would have method to direct endo-functionalization of these molecules, adding to the flexibility of future synthetic design.

In order to maximize the Lewis acid complexation with the carbonyl function, dichloromethane was used as main solvent since it has been widely used in $TiCl_4$ mediated reactions. The organometallic reagent was added as ether or THF solution as appropriate, and constituted only about 10% of the total solvent used. However, the fact that this solvent is not commonly used with RLi or RMgX reagents,[24] was an obvious concern. The reaction temperature was sought to be maintained as low as possible (-90°C) to minimize anticipated side reaction that might consume organometallic reagents.

It was gratifying to note that the reactions proceeded with high yield of isolated products.

When representative organolithium and organomagnesium reagents (1.5 equiv) in ether or THF were added to the conformationally rigid racemic enone substrates[21] **1a-c** *pretreated with excess of* $TiCl_4$ (2 equiv) in dichloromethane at -90°C (reaction condition: **i**), only conjugate addition products **2a-h** were obtained as a single diastereomer in very good to excellent isolated yield (Scheme-7, Table-1). In a typical procedure, a solution of enone in dichloromethane was stirred with $TiCl_4$ at –90° C for 15 minutes. The organolithium or organomagnesium reagent in ether was added dropwise with stirring at same temperature. Reaction was complete within 15 minutes (TLC). Excess $TiCl_4$ was destroyed by careful addition of methanol and evacuation of the system to remove HCl at low temperature . This process was necessary to avoid decomposition of product complexes. The crystal structure of complex **2b** was determined earlier in our laboratory.[21] Thus the relative stereochemistry of all the compounds were fixed by analogy.

Scheme – 7



i : $TiCl_4$ -90°C 15 min ; RLi or RMgX -90°C 15 min

ii : $R_2Cu(CN)Li_2$ -78°C ~1 h

iii : RLi -90°C 30 min

Table-1

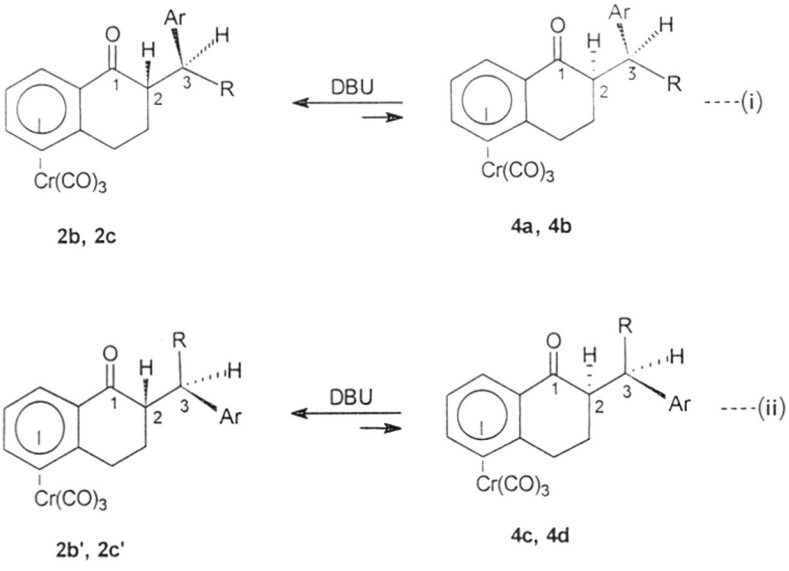
Substrate	**R**	**Product** (isolated yield %)			
		Condition: i		**Condition: ii**	**Condition: iii**
		$TiCl_4$/ RLi	**$TiCl_4$/ RMgX**		
1a	CH_2=CH-CH_2-	**2a** (81)	**2a** (90)	**2a'** (86)	**3a** (92)
1b	CH_2=CH-CH_2-	**2b** (80)	**2b** (88)	**2b'** (91)	**3b** (89)
1a	Me	**2c** (90)	**2c** (91)	**2c'** (90)	**3c** (87)
1b	Me	**2d** (90)	**2d** (87)	**2d'** (95)	**3d** (83)
1b	Ph	**2e** (90)	**2e** (85)	**2e'** (80)	**3e** (88)
1b	Cyclopropyl	**2f** (90)	**2f** (90)	**2f'** (94)	**3f** (91)
1b	n-Butyl	**2g** (92)	**2g** (95)	**2g'** (96)	**3g** (95)
1c	CH_2=CH-CH_2-	**2h** (80)	**2h** (87)	**2h'** (85)	**3h** (83)

On the other hand, a different set of diastereomerically pure, conjugate addition products were obtained from reaction of organocuprates (reaction condition: **ii**) with the same substrates (Scheme-7, Table-1, products- **2a'-h'**). In a typical procedure, the cuprate was prepared *in situ* by addition of 2 equivalent of organolithium reagent (in ether or hexane) to a slurry of CuCN (1 equivalent) in diethyl ether at –78°C. Temperature was slowly raised to –20°C to complete the formation of cuprate. A solution of the enone in toluene was added dropwise to the freshly prepared cuprate solution at –78°C. The starting material was consumed after an hour. The

reaction was worked up and the product was isolated by flash column chromatography. The relative stereochemistry of all the complexes were ascribed by comparison with that of **2b′** whose crystal was structure already determined in our laboratory.[21]

Equilibration of ketone **2b** and **2c** with DBU/CH_2Cl_2 yielded minor isomers **4a** and **4b** respectively which were shown to be epimeric at C-2 (carbon adjacent to ketone). Similar equilibration of **2b′** and **2c′** yielded their C-2 epimers **4c** and **4d** respectively (Scheme-8). So it was established that the isomeric pairs (**2b, 2b′**), (**2c, 2c′**) are epimeric at C-3 only. This holds good for the remaining pairs as well.

Scheme-8

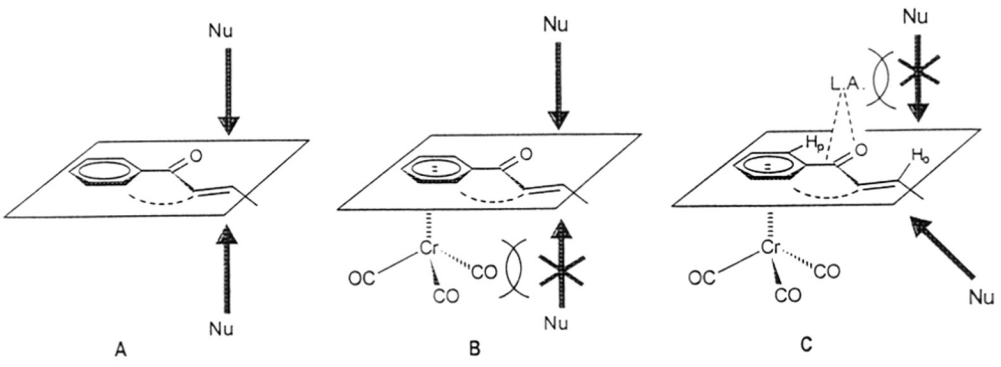


Thus, the Lewis acid mediated procedure provided a remarkable, completely *endo*-selective 1,4-addition on enones anchored on a $Cr(CO)_3$ template, while cuprates yielded normal *exo*-adducts. Significantly, the organolithium or the organomagnesium reagents were found to be compatible with dichloromethane as solvent (CH_2Cl_2 : ether ≈ 10 : 1) at low temperatures. In other words, the conjugate addition occurred with considerably higher rate than decomposition of reagent (the reaction was complete within 15 minutes). It was also established that the nucleophile was not an organotitanium species (e.g. $RTiCl_3$),[25] since : (i) no reaction took place and starting material was quantitatively recovered, if the organolithium or organomagnesium reagent was allowed to react with $TiCl_4$ first, and the substrate was added subsequently; (ii) use of BuLi posed no problem of β-hydride elimination,[26] which would be expected of a butyltitanium intermediate; and, (iii) no noticeable side reaction occurred with cyclopropyllithium reagent.

Reagent approach in π-systems with conflicting stereochemical bias can be visualized with the help of Figure-4. While both the faces of the enone are equally accessible to a reagent or reaction partner in structure **A**, one of the faces of **B** is blocked by metal coordination. In structure **C**, the Lewis acid is forced to coordinate from the *exo*-face in an out-of-plane manner,[8,27] since access from *endo*-face is prevented by $Cr(CO)_3$ group and in-plane coordination is discouraged by two flanking hydrogens (the *peri* proton H_p of the aromatic ring of

tetralone, and the β- olefinic proton H_o) on both sides of the ketone function.

Figure-4



As represented in structure **C**, the Lewis acid bound to the *exo*-face of the ketone sterically hinders *exo*-approach of the nucleophile for both 1,2 and 1,4-addition. Also, the bulky $Cr(CO)_3$ group does not permit *endo*-selective 1,2-addition. Therefore, the addition can occur only in a conjugate manner from the *endo* face of the substrate. In absence of Lewis acid coordination, *exo*-selective 1,2-additions of different nucleophiles are observed as expected (reaction condition: **iii,** Scheme-7)[28]

If the arene ring of tetralone is *not complexed* with tricarbonylchromium, the propensity of organolithium reagents for preferential 1,2-addition is not altered by Lewis acid. $TiCl_4$ might still

coordinate with the ketone carbonyl in an out-of-plane manner owing to the presence of *peri* hydrogens. Yet, the opposite face of the π-system remains accessible to nucleophiles. Indeed, we observed that 1,2-adducts were almost exclusively produced[29] when uncomplexed substrates were used, even in presence of excess (5 equiv) $TiCl_4$ (Scheme-9, Table-2).

Scheme – 9

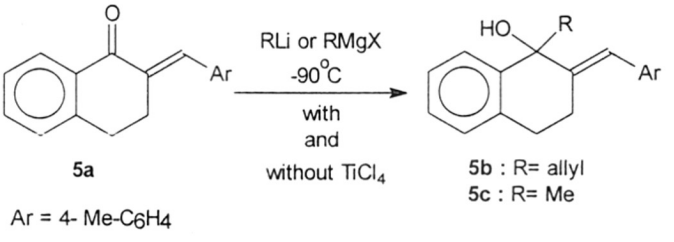


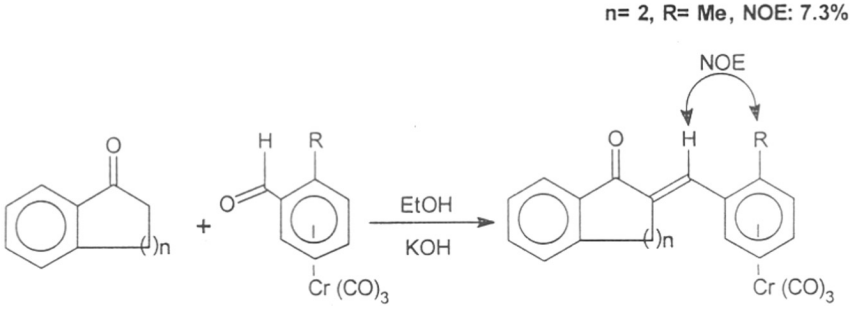
Table-2

Reagent	product	Yield (%)
Allyllithium/THF	**5b**	89
Methyllithium/THF	**5c**	94
$TiCl_4$/allyllithium/CH_2Cl_2	**5b**	81
$TiCl_4$/methyllithium/ CH_2Cl_2	**5c**	79
Allylmagnesium bromide/THF	**5b**	80
Methylmagnesium iodide/THF	**5c**	83

Encouraged by the completely *endo*-selective nucleophilic addition induced by out-of-plane coordinated Lewis acid on conformationally rigid enones anchored on $Cr(CO)_3$, we proceeded to check the validity of our postulate of Lewis acid-carbonyl coordination and its stereochemical outcome for a different set of substrates.

The difference between the present set of substrates, **6a-c** (Scheme-10), and those used in previous studies (Scheme-7, complex enones: **1a-c**), lies in the positioning of enone function with respect to the arene ring complexed with tricarbonylchromium. These new complexes were prepared readily by condensation of 1-tetralone or 1-indanone and aromatic aldehydes with pendant $Cr(CO)_3$ group[30] (Scheme-10). In a typical procedure ethanolic KOH was added dropwise to a solution of tetralone or indanone and the complexed aldehyde in ethanol at room temperature. The reaction took 2.5-3.0 hours for completion (TLC).

Scheme-10



6a (n = 2, R = OMe)
6b (n = 2, R = Me)
6c (n = 1, R = OMe)

The chemical shift 7.50-7.80 ppm of the olefinic proton is indicative of a *trans* olefin geometry.[31] The orientation of the *ortho*-substituent *syn* to the olefinic proton (as depicted in Scheme-10) was deduced with the help of NOE difference spectra. Thus, these complexes constitute a set of conformationally rigid substrates with well-defined π-planes, which, in principle, make an unambiguous determination of steric course of nucleophilic addition possible. Preliminary experiments were conducted with allyllithium.

Reaction of **6a-c** with allyllithium afforded only 1,2-addition products – but the *exo*/*endo* selectivity was moderate (Scheme-11, Table-3). Diastereoselectivity did not improve when allylmagnesium bromide was used. In a typical procedure allyllithium in THF was added dropwise to a solution of enone in THF at –90°C. Reaction was complete within 30 minutes (TLC). The isomeric products were separated by flash chromatography, purified by crystallization and individually characterized by spectral data. The stereochemical assignment was confirmed by crystal structure determination of a representative complex, **7a** (see Fig. 5), a major isomer. As anticipated the allyl group added from the *exo*-face. Therefore, complexes **8a-c** must have resulted from *endo*-addition of the allyl group.

Scheme-11

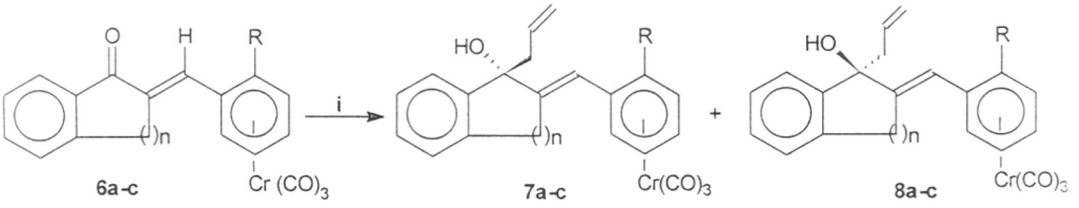
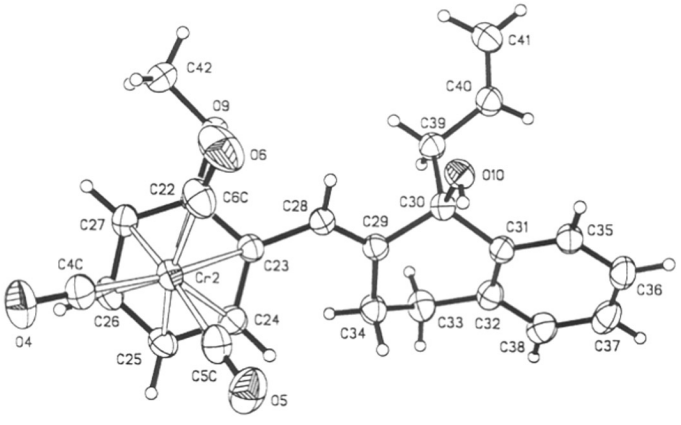


Table-3

Enone	Reaction Condition	Products	Isolated yield(%)	Ratio of products (isolated)
6a	**i**	**7a + 8a**	76	5.5 : 1
6b	**i**	**7b + 8b**	81	6.2 : 1
6c	**i**	**7c + 8c**	73	5.8 : 1

This was somewhat unexpected, since stabilized nucleophile like nitromethane or diethyl malonate or ethyl acetoacetate anion has been shown to add in a conjugated manner to the third carbon (from complexed aromatic ring) with complete exo-selectivity;[23e] the stereorandom addition may be attrributed to the higher reactivity of lithium reagents.

Figure-5



(X-Ray crystal structure of complex **7a**. Structure was solved by Prof. Karl S. Hagen of Emory University, USA)

When the substrate was premixed with a strong Lewis acid like $TiCl_4$ (2.2 equivalent with respect to substrate[32]) in dichloromethane (Scheme-12), a dramatic reversal of stereoface preference in nucleophilic addition was observed. No *exo* 1,2- allylated adduct was isolated-the addition was entirely *endo*-selective. Strong Lewis acidity of $TiCl_4$, however, promoted a side-reaction – about 10% gem-diallylated product was always obtained (Scheme-12, products: **9a-c**). This undesired product became the only isolable product if excess allylmagnesium bromide was used.[33]

Scheme- 12

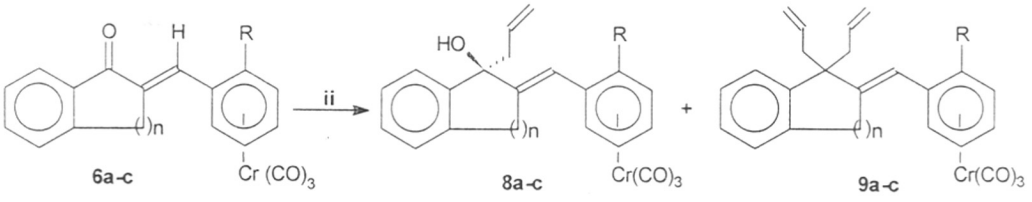
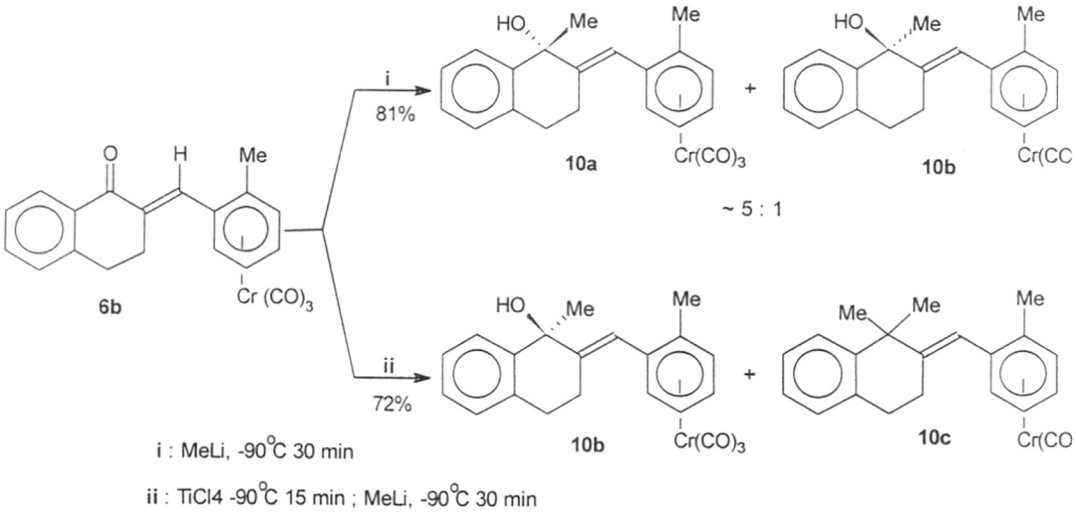


Table-4

Enone	Reaction Condition	Products	Isolated yield(%)	Ratio of products (isolated)
6a	**ii**	**8a + 9a**	71	10 : 1
6b	**ii**	**8b + 9b**	68	9.7 : 1
6c	**ii**	**8c + 9c**	70	11.2 : 1

Similar stereodivergence methyllithium addition was also observed depending on absence and presence of Lewis acid (Scheme-13).

Scheme-13

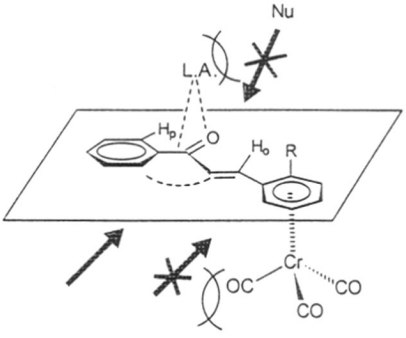


Thus this phenomenon is not an exceptional situation for allyl addition. In a typical procedure a solution of enone in dichloromethane was stirred with $TiCl_4$ for 15 minutes at –90°C and then organolithium reagent in THF was added dropwise with stirring at that temperature. Reaction was complete within 30 min.

In a predominantly noncoordinating solvent medium (CH_2Cl_2 : ether = 10 : 1), $TiCl_4$ probably forms chloro-bridged aggregates which crowd the more accessible *exo*-face of the carbonyl group (access from the *endo* face is prevented by $Cr(CO)_3$ moiety and in plane coordination is discouraged by two flanking hydrogens, the peri proton, H_p of the aromatic ring of tetralone/indanone and the β-

olefinic proton, H_o on both sides of the ketone function) as shown in Figure-6.

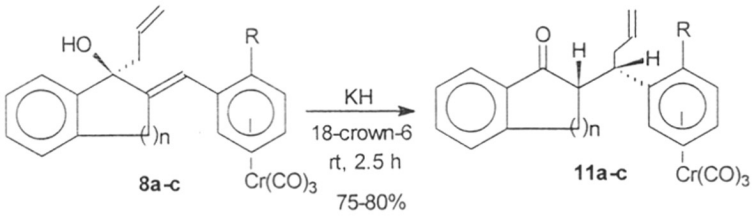
Figure-6



The Lewis acid bound to the *exo*-face of the ketone sterically hinders *exo*-approach of the nucleophile for both 1,2 and 1,4-addition. Also, the bulky $Cr(CO)_3$ group does not permit *endo*-selective 1,4-addition in its vicinity. Therefore, the addition can occur only in a 1,2-manner from the *endo*- face of the substrate.

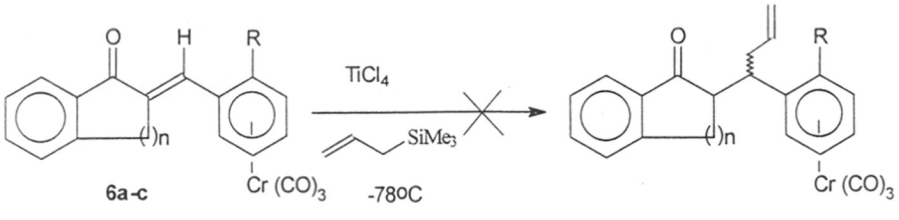
The *endo*-allylated carbinols (**8a-c**) on treatment with potassium hydride underwent smooth anion-assisted oxy-Cope rearrangement[34] to furnish the ketones, **11a-c**. These are, formally, products of conjugate addition of allylmetal to enones **6a-c**, where the addition seemed to have occurred from the *endo*-face (Scheme-14).

Scheme-14



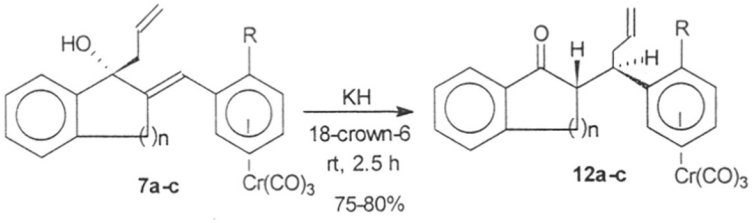
This is a notable achievement, since *endo*-allylation is effected efficiently at a benzylic position. The steric bulk of the neighboring $Cr(CO)_3$ moiety clearly discourages reagent approach to the benzylic site from the *endo* face, and *endo*-allylated products are not readily accessible. It should be mentioned here, that Hosomi-Sakurai reaction failed for these substrates, presumably for the same reason (*exo*-addition is also precluded by Lewis acid complexation – see Figure: 6, Scheme-15).

Scheme-15



The *exo*-allylated ketones **12a-c**, on the other hand, could be easily and stereospecifically obtained from rearrangement of the *exo*-allylated carbinols **7a-c** (Scheme-16).

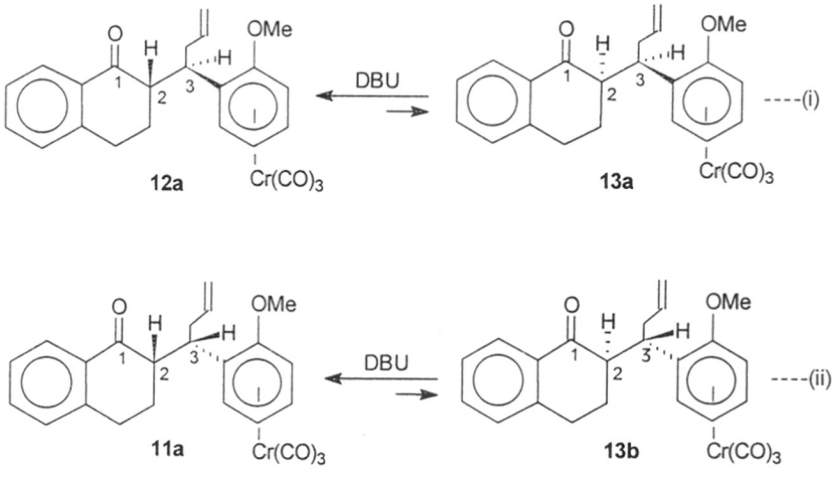
Scheme-16



In a typical procedure a suspension of KH in ether was added dropwise to a solution of alcohol and 18-crown-6 (0.1 equiv.) in ether at 0°C and stirred at room temperature for 2.5 h.

Stereochemical relationship among all the isomers was established by preparing all four possible diastereomers. Base catalyzed equilibration of ketone **12a** yielded a minor isomer **13a** which is epimeric at C-2 (adjacent to carbonyl carbon). Similar equilibration of **11a** yielded its C-2 epimer **13b** (Scheme-17). So it is established that ketone **12a** is epimeric with **11a** at C-3 . Similar relationship should hold good for **12b** and **11b** and for **12c** and **11c** as well.

Scheme-17



Summary

To sum up, we have efficiently exploited the out-of-plane binding mode of Lewis acid to carbonyl group to achieve completely ***endo***-selective 1,2- as well as 1,4- addition of a variety of strong nucleophiles to enones anchored on arene-$Cr(CO)_3$ template, depending on the position of $Cr(CO)_3$ group. In absence of Lewis acid, corresponding ***exo***-adducts were obtained predominantly (in some cases exclusively). Together, they present an eminently useful example of stereodivergent functionalization of these substrates. Applying a two step procedure (1,2-allylation and oxy-Cope rearrangement) it was possible to achieve an efficient *endo*-allylation at the benzylic center of a $Cr(CO)_3$ complexed aromatic ring. Direct *endo* addition of a group at the benzylic center of a complexed ring is difficult to achieve due to steric bias imposed by $Cr(CO)_3$.

It may be pertinent to point out that this strategy of stereoreversal of addition reaction is not limited, in principle, to arene-chromium substrates alone. The concept appears to be general and adaptable to any stereochemically biased system, and promises to be an area of active research.

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.[35]

General procedure for the preparation of enones (1a-c) : Following a reported procedure[36] all three enones were prepared from tetralone $Cr(CO)_3$ complex (0.5g, 1.77 mmol), aromatic aldehydes (1.78 mmol) and KOH (0.12g, 2.14 mmol) using Claisen-Schmidt condensation. In a typical procedure ethanolic KOH was added dropwise to a solution of tetralone complex and aromatic aldehyde in ethanol 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. Enones **1a** and **1b** have been reported earlier.[36]

Complex 1c:	yield 91%
Color :	red
MP:	135°C
IR ($CHCl_3$):	1980, 1920, 1660 cm^{-1}
^1H NMR ($CDCl_3$) : (200 MHz)	2.35 (s, 3H), 2.60-2.78 (m, 1H), 2.85-3.20 (m, 3H), 5.15 (d, 1H, J=6.6Hz), 5.35 (t, 1H, J=6.6Hz), 5.65 (t, 1H, J=6.6Hz), 6.29 (d, 1H, J=6.6Hz), 7.05-7.40 (m, 4H), 7.90 (s, 1H)
^{13}C NMR ($CDCl_3$): (50.3 MHz)	20.10, 25.83, 27.74, 29.82, 89.95, 90.24, 91.74, 94.51, 115.12, 125.78, 129.11, 130.52, 133.23, 134.53, 137.44, 137.96, 165.35, 186.21, 231.20
Analysis: ($C_{21}H_{16}O_4Cr$)	Calcd.: C: 65.79, H: 4.17 Found : C: 65.69, H: 4.21

General procedure for the preparation of 2a-h from 1a-c :

To a solution of the complexed enone (n mmol) in dichloromethane ($20n$ mL), titanium tetrachloride ($2n$ mmol) was added dropwise with stirring at -90°C. After stirring for 15 minutes, organolithium or organomagnesium reagent ($1.5n$ mmol) in diethyl ether was added dropwise with stirring at the same temperature. After completion of the reaction (TLC, 15 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 product obtained after evaporation of solvent was purified by flash column chromatography.

Reactions were performed in 0.5-2.0 mmol scale and isolated yields are indicated in Table-1.

Complex 2a:

Color :	Orange
MP:	118-119°C
IR ($CHCl_3$):	1980, 1910, 1670 cm^{-1}
^1H NMR ($CDCl_3$) : (200 MHz)	1.85-2.20 (m, 2H), 2.30-2.90 (m, 5H), 3.80-3.95 (m, 1H), 4.85-5.10 (m, 3H), 5.30 (t, 1H, J=7Hz), 5.55-5.80 (m, 2H), 6.20 (d, 1H, J=7Hz), 7.15-7.35 (m, 5H)
^{13}C NMR ($CDCl_3$): (50.3 MHz)	21.9, 28.2, 32.7, 43.1, 53.8, 89.0, 89.3, 91.3, 94.4, 116.2, 126.3, 128.3, 128.5, 136.5, 142.1, 196.0, 230.5
Analysis: ($C_{23}H_{20}O_4Cr$)	Calcd. C: 67.15, H: 4.86 Found : C: 67.00, H: 5.05.

Complex 2b:

Color :	Orange
MP:	160-162°C
IR ($CHCl_3$):	1980, 1910, 1670 cm^{-1}
^1H 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=6.8Hz), 5.55-5.80 (m, 2H), 6.20 (d, 1H, J=6Hz), 7.15 (s, 4H).
^{13}C NMR ($CDCl_3$): (50.3 MHz)	20.8, 21.7, 28.2, 32.6, 42.4, 54.0, 89.0, 89.4, 91.3, 93.0, 94.4, 114.9, 116.2, 128.0, 129.0,

	135.9, 136.6, 138.9, 196.2, 230.6
Analysis:	Calcd. C: 67.76, H: 5.17
($C_{24}H_{22}O_4Cr$)	Found : C: 67.66, H: 5.10.

Complex 2c:

Color :	orange
MP:	125°C
IR ($CHCl_3$):	1985, 1915, 1680 cm^{-1}
^1H NMR ($CDCl_3$) : (200 MHz)	1.25 (d, 3H, J=7.2 Hz), 1.72-1.90 (m, 1H), 2.05 (ddd, 1H, J=21.2, 17.3, 4.15 Hz), 2.45-2.75 (m, 2H), 2.76-2.95 (m, 1H), 3.90 (ddd, 1H, J=21.2, 17.3, 4.15 Hz), 5.10 (d, 1H, J=6.5Hz), 5.35 (t, 1H, J=6.5Hz), 5.60 (t, 1H, J=6.5Hz), 6.21 (d, 1H, J=6.5Hz), 7.15-7.45 (m, 5H).
^{13}C NMR ($CDCl_3$): (50.3 MHz)	13.24, 21.24, 28.30, 29.86, 36.95, 89.80, 90.30, 91.37, 93.50, 94.70, 115.34, 126.50, 127.95, 128.57, 129.84, 196.83, 231.04
Analysis:	Calcd. C: 65.25, H: 4.66
($C_{21}H_{18}O_4Cr$)	Found : C: 64.96, H: 4.73.

Complex 2d:

Color :	red
MP:	151°C
IR ($CHCl_3$):	1980, 1910, 1667 cm^{-1}

^{1}H NMR ($CDCl_3$) : (200 MHz)	1.28 (d, 3H, J=7.5 Hz), 1.78-1.91 (m, 1H), 1.92-2.18 (ddd, 1H, J=21.0, 17.1, 4.2 Hz), 2.35 (s, 3H), 2.45-2.60 (m, 1H), 2.60-2.95 (m, 2H), 3.98 (ddd, 1H, J=21.0, 17.1, 4.2 Hz), 5.10 (d, 1H, J=6.4Hz), 5.34 (t, 1H, J=6.4Hz), 5.60 (t, 1H, J=6.4Hz), 6.20 (d, 1H, J=6.4Hz), 7.19 (s, 4H)
^{13}C NMR ($CDCl_3$): (50.3 MHz)	13.33, 21.12, 21.18, 28.24, 36.50, 54.23, 89.84, 90.35, 91.35, 93.55, 94.74, 115.42, 127.77, 129.24, 135.94, 141.50, 196.87, 231.10
Analysis: ($C_{22}H_{20}O_4Cr$)	Calcd. C: 66.00, H: 5.00 Found C: 65.87, H: 4.99.

Complex 2e:

Color :	orange
MP:	150°C
IR ($CHCl_3$):	1982, 1910, 1675 cm^{-1}
^{1}H NMR ($CDCl_3$) : (200 MHz)	1.77-2.10 (m, 2H), 2.34 (s, 3H), 2.63-2.85 (m, 1H), 2.90-3.10 (m, 1H), 3.17-3.37 (m, 1H), 4.84 (d, 1H, J=7.2 Hz), 5.08 (d, 1H, J=6.5Hz), 5.25 (t, 1H, J=6.5Hz), 5.65 (t, 1H, J=6.5Hz), 6.18 (d, 1H, J=6.5Hz), 7.08-7.40 (m, 9H).
^{13}C NMR ($CDCl_3$): (50.3 MHz)	21.14, 25.68, 28.42, 49.38, 51.51, 88.70, 89.13, 92.38, 93.26, 95.28, 115.13, 126.58, 128.00, 128.61, 128.95, 129.32, 135.90, 140.40, 142.33, 196.53, 230.7
Analysis: ($C_{27}H_{22}O_4Cr$)	Calcd. C: 70.13, H: 4.76 Found C: 70.00, H: 4.86.

Complex 2f:

Color :	red
MP:	158°C
IR ($CHCl_3$):	1980, 1910, 1670 cm^{-1}
^1H NMR ($CDCl_3$) : (200 MHz)	0.02-0.19 (m, 1H), 0.45-0.60 (m, 2H), 0.6-0.79 (m, 1H), 1.05-1.32 (m, 1H), 2.05-2.20 (m, 1H), 2.25-2.45 (m, 1H), 2.35 (s, 3H), 2.47-2.70 (m, 1H), 2.70-2.80 (m, 1H), 2.80-2.97 (m, 1H), 3.05 (m, 1H), 5.07 (d, 1H, J=6.4 Hz), 5.30 (t, 1H, J=6.4Hz), 5.65 (t, 1H, J=6.4Hz), 6.25 (d, 1H, J=6.4Hz), 7.10-7.32 (m, 4H).
^{13}C NMR ($CDCl_3$): (50.3 MHz)	4.53, 6.30, 11.01, 21.14, 22.72, 28.63, 47.10, 54.51, 83.88, 89.00, 89.51, 91.87, 93.45, 95.07, 115.80, 128.05, 129.13, 135.80, 141.75, 165.60, 196.35, 230.93
Analysis: ($C_{24}H_{22}O_4Cr$)	Calcd. C: 67.60, H: 5.16 Found : C: 67.32, H: 5.00.

Complex 2g:

Color :	red
MP:	140°C
IR ($CHCl_3$):	1974, 1901, 1678cm^{-1}
^1H NMR ($CDCl_3$) : (200 MHz)	0.85 (t, 3H, J=7.3 Hz), 1.08-1.37(m, 3H), 1.38-1.57 (m, 2H), 1.70-1.90 (m, 2H), 1.90-2.20 (m, 2H), 2.35 (s, 3H), 2.55-3.90 (m, 2H), 3.75 (m, 1H), 5.10 (d, 1H, J=6.5 Hz), 5.30 (t, 1H, J=6.5Hz), 5.60 (t, 1H, J=6.5Hz), 6.20 (d, 1H, J=6.5Hz), 7.15 (s, 4H).

^{13}C NMR ($CDCl_3$): (50.3 MHz)	13.98, 21.12, 22.06, 22.82, 28.21, 28.55, 30.50, 43.10, 54.80, 89.48, 89.92, 91.54, 94.70, 115.42, 128.64, 129.36, 136.00, 196.70, 230.98
Analysis: ($C_{25}H_{26}O_4Cr$)	Calcd. C: 67.87, H: 5.88 Found : C: 68.01, H: 5.92

Complex 2h:

Color :	red
MP:	140°C
IR ($CHCl_3$):	1980, 1915, 1680 cm^{-1}
^{1}H NMR ($CDCl_3$) : (200 MHz)	1.90-2.20 (m, 2H), 2.25-2.45 (m, 1H), 2.26 (s, 3H), 2.55-2.90 (m, 4H), 4.15-4.30 (m, 1H), 4.90-5.15 (m, 3H), 5.35 (t, 1H, J=6.4 Hz), 5.55-5.75 (m, 2H), 6.21 (d, 1H, J=6.4Hz), 7.05-7.25 (m, 4H).
^{13}C NMR ($CDCl_3$): (50.3 MHz)	19.56, 21.95, 28.70, 32.94, 38.10, 52.20, 89.45, 89.87, 91.72, 93.51, 94.88, 115.31, 116.60, 125.97, 126.50, 127.52, 131.16, 136.62, 136.90, 140.56, 196.45, 231.02
Analysis: ($C_{24}H_{22}O_4Cr$)	Calcd. C: 67.76, H: 5.17 Found : 67.68, H: 4.98.

General procedure for the preparation of 2a'-h' from 1a-c : To a slurry of CuCN (n mmol) in diethyl ether (n mL), organolithium reagent ($2n$ 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.

Reactions were performed in 0.5-2.0 mmol scale and isolated yields are indicated in Table-1.

Complex 2a':

Color :	red
MP:	123°C
IR ($CHCl_3$):	1980, 1910, 1680 cm^{-1}
^1H NMR ($CDCl_3$) : (200 MHz)	1.56-1.74 (m, 1H), 1.93-2.06 (m, 1H), 2.50-2.98 (m, 5H), 3.81 (m, 1H), 4.98-5.25 (m, 4H), 5.57-5.81 (m, 2H), 6.19 (d, 1H, J=6.8 Hz), 7.23-7.35 (m, 5H).
^{13}C NMR ($CDCl_3$): (50.3 MHz)	23.63, 27.62, 37.14, 43.02, 51.26, 88.85, 89.32, 91.89, 93.00, 95.14, 115.88, 116.92, 126.74, 128.40, 128.80, 136.81, 141.08, 196.90, 230.67
Analysis: ($C_{23}H_{20}O_4Cr$)	Calcd. 67.15, H: 4.86 Found : 66.44, H: 4.73

Complex 2b′:

Color :	red
MP:	131°C
IR ($CHCl_3$):	1985, 1915, 1680 cm^{-1}
^1H NMR ($CDCl_3$) : (200 MHz)	1.66-1.72 (m, 1H), 1.90- 2.04 (m, 1H), 2.30 (s, 3H), 2.59-2.94 (m, 5H), 3.78 (m, 1H), 4.95-5.10 (m, 3H), 5.20 (t, 1H, J= 6.7Hz), 5.62-5.80 (m, 2H), 6.20 (d, 1H, J= 6.7Hz), 7.10 (s, 4H)
^{13}C NMR ($CDCl_3$): (50.3 MHz)	21.25, 23.77, 27.55, 37.29, 42.87, 51.37, 88.86, 89.36, 91.88, 93.12, 95.14, 115.94, 116.79, 128.62, 129.09, 136.16, 136.44, 138.00, 197.08, 230.72
Analysis: ($C_{24}H_{22}O_4Cr$)	Calcd. C: 67.76, H: 5.17 Found : C: 67.62, H: 5.16.

Complex 2c′:

Color :	red
MP:	110°C
IR ($CHCl_3$):	1975, 1915, 1680 cm^{-1}
^1H NMR ($CDCl_3$) : (200 MHz)	1.42 (d, 3H, J=7.25 Hz), 1.51-1.70 (m, 1H), 1.90-2.10 (m, 1H), 2.45-2.65 (m, 1H), 2.66-3.00 (m, 2H), 3.65-3.84 (m, 1H), 5.03 (d, 1H, J=6.5 Hz), 5.72 (t, 1H, J=6.5 Hz), 5.60 (t, 1H, J=6.5Hz), 6.21 (d, 1H, J=6.5 Hz), 7.10-7.40 (m, 5H).
^{13}C NMR ($CDCl_3$): (50.3 MHz)	19.75, 24.54, 27.62, 38.50, 53.75, 89.22, 89.73, 92.12, 93.33, 95.40, 116.05, 126.74, 128.16, 128.65, 143.68, 197.20, 231.02

Analysis:	Calcd. C: 65.25, H: 4.66
($C_{21}H_{18}O_4Cr$)	Found : C: 65.21, H: 4.66.

Complex 2d′:

Color :	red
MP:	142°C
IR ($CHCl_3$):	1980, 1910, 1670 cm^{-1}
^1H NMR ($CDCl_3$) : (200 MHz)	1.44 (d, 3H, J=7.2 Hz), 1.50-1.77 (m, 1H), 1.85-2.05 (m, 1H), 2.31 (s, 3H), 2.40-2.60 (m, 1H), 2.65-2.95 (m, 2H), 3.55-3.75 (m, 1H), 5.05 (d, 1H, J=6.6 Hz), 5.24 (t, 1H, J=6.6 Hz), 5.61 (t, 1H, J=6.6 Hz), 6.20 (d, 1H, J=6.6 Hz), 7.13 (s, 4H).
^{13}C NMR ($CDCl_3$): (50.3 MHz)	19.90, 21.21, 24.68, 27.50, 38.36, 53.75, 88.99, 89.46, 91.96, 93.25, 95.10, 115.83, 127.88, 129.30, 136.20, 140.64, 197.35, 230.87
Analysis:	Calcd. C: 66.00, H: 5.00
($C_{22}H_{20}O_4Cr$)	Found : C: 65.80, H: 4.98.

Complex 2e′:

Color :	red
MP:	165°C
IR ($CHCl_3$):	1990, 1920, 1680 cm^{-1}

^{1}H NMR ($CDCl_3$) : (200 MHz)	1.75-2.15 (m, 2H), 2.30 (s, 3H), 2.65-2.82 (m, 1H), 2.90-3.11 (m, 1H), 3.20-3.38 (m, 1H), 4.82 (d, 1H, J=7.5 Hz), 5.08 (d, 1H, J=6.8 Hz), 5.22 (t, 1H, J=6.8 Hz), 5.63 (t, 1H, J=6.8 Hz), 6.18 (d, 1H, J=6.8 Hz), 7.10 (s, 4H), 7.15-7.40 (m, 5H).
^{13}C NMR ($CDCl_3$): (50.3 MHz)	21.16, 25.76, 28.49, 49.59, 51.57, 88.80, 89.22, 92.47, 93.39, 95.38, 115.23, 126.45, 128.22, 128.65, 128.90, 129.40, 136.26, 139.15, 143.77, 196.54, 230.83
Analysis: ($C_{27}H_{22}O_4Cr$)	Calcd. C: 70.13, H: 4.76 Found : C: 69.99, H: 4.70.

Complex 2f':

Color :	orange
MP:	122°C
IR ($CHCl_3$):	1980, 1910, 1675 cm^{-1}
^{1}H NMR ($CDCl_3$) : (200 MHz)	0.15-0.45 (m, 2H), 0.55-0.75 (m, 1H), 1.20-1.45 (m, 1H), 1.55-1.90 (m, 2H), 2.02-2.20 (m, 1H), 2.35 (s, 3H), 2.50-2.85 (m, 2H), 2.85-3.10 (m, 2H), 5.00 (d, 1H, J=6.5 Hz), 5.17 (t, 1H, J=6.5 Hz), 5.50 (t, 1H, J=6.5 Hz), 6.17 (d, 1H, J=6.5 Hz), 6.85-7.25 (m, 4H).
^{13}C NMR ($CDCl_3$): (50.3 MHz)	5.85, 5.96, 13.99, 21.11, 23.67, 28.24, 47.68, 53.52, 88.63, 89.10, 91.85, 95.11, 116.09, 128.54, 128.84, 135.89, 138.21, 196.58, 230.58
Analysis: ($C_{24}H_{22}O_4Cr$)	Calcd. C: 67.60, H: 5.16 Found C: 67.30, H: 5.00

Complex 2g′:

Color :	red
MP:	110°C
IR ($CHCl_3$):	1980, 1915, 1675 cm^{-1}
^1H NMR ($CDCl_3$) : (200 MHz)	0.85 (t, 3H, J=7.5 Hz), 1.05-1.45 (m, 5H), 1.70-1.80 (m, 2H), 1.80-2.05 (m, 1H), 2.32 (s, 3H), 2.42-2.65 (m, 1H), 2.70-2.85 (m, 2H), 3.35-3.51 (m, 1H), 5.05 (d, 1H, J=6.5 Hz), 5.20 (t, 1H, J=6.5 Hz), 5.60 (t, 1H, J=6.5 Hz), 6.20 (d, 1H, J=6.5 Hz), 7.10 (s, 4H)
^{13}C NMR ($CDCl_3$): (50.3 MHz)	14.21, 23.36, 24.10, 30.03, 31.89, 44.55, 53.81, 74.23, 82.88, 84.00, 85.01, 87.71, 88.10, 90.36, 116.32, 128.10, 129.51, 131.26, 136.65, 139.44, 197.13, 231.04
Analysis: ($C_{25}H_{26}O_4Cr$)	Calcd. C: 67.87, H: 5.88 Found C: 67.77, H: 6.02

Complex 2h′:

Color :	red
MP:	108°C
IR ($CHCl_3$):	1975, 1910, 1675 cm^{-1}
^1H NMR ($CDCl_3$) : (200 MHz)	1.65-1.95 (m, 2H), 2.42 (s, 3H), 2.45-2.70 (m, 2H), 2.70-3.00 (m, 3H), 3.55-3.70 (m, 1H), 4.80-5.05 (m, 2H), 5.15 (d, 1H, J=6.5 Hz), 5.25 (t, 1H, J=6.5 Hz) 5.50-5.75 (m, 2H), 6.18 (d, 1H, J=6.5Hz), 7.05-7.30 (m, 4H).

^{13}C NMR ($CDCl_3$): (50.3 MHz)	20.51, 26.26, 28.46, 39.46, 40.56, 52.21, 89.30, 89.70, 91.98, 94.55, 94.90, 114.98, 116.57, 126.27, 126.41, 127.44, 130.85, 136.64, 137.30, 140.65, 197.90, 230.97
Analysis: ($C_{24}H_{22}O_4Cr$)	Calcd. C: 67.76, H: 5.17 Found : C: 67.60, H: 5.16.

General procedure for the preparation of 3a-h from 1a-c: To a solution of the complexed enone (**1a-c**), (n mmol) in THF ($20n$ mL), organolithium reagent ($1.5n$ mmol) in diethyl ether 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 product obtained after evaporation of solvent was purified by flash column chromatography.

Reactions were performed in 0.5-2.0 mmol scale. For isolated yield see Table-1.

Complex 3a:

Color :	yellow
MP:	110-112°C
IR ($CHCl_3$):	1980, 1910, cm^{-1}

^{1}H NMR ($CDCl_3$) : (200 MHz)	2.13 (s, 1H), 2.52-2.80 (m, 5H), 2.94-3.05 (m, 1H), 5.00-5.17 (m, 4H), 5.43 (t, 1H, J=6.7 Hz), 5.75-5.90 (m, 2H), 6.94 (s, 1H), 7.25-7.45 (m, 5H).
^{13}C NMR ($CDCl_3$): (50.3 MHz)	21.40, 24.68, 27.21, 48.27, 74.15, 90.72, 90.94, 92.05, 93.32, 110.78, 116.50, 119.20, 125.53, 129.06, 129.20, 132.89, 134.53, 136.72, 139.93, 233.44
Analysis: ($C_{23}H_{20}O_4Cr$)	Calcd. C: 67.15, H: 4.86 Found C: 66.87, H: 5.05.

Complex 3b:

Color :	yellow
MP:	91°C
IR ($CHCl_3$):	3400-3600(br) 1980, 1910 cm^{-1}
^{1}H NMR ($CDCl_3$) : (200 MHz)	2.10 (s, 1H), 2.37 (s, 3H), 2.62-2.77 (m, 5H), 2.91-3.01 (m, 1H), 4.98-5.14 (m, 2H), 5.22-5.39 (m, 2H), 5.41 (t, 1H, J= 6Hz), 5.76-5.90 (m, 2H), 6.89 (s, 1H), 7.22 (s, 4H)
^{13}C NMR ($CDCl_3$): (50.3 MHz)	21.37, 24.60, 27.14, 48.15, 74.11, 90.74, 90.99, 92.08, 93.41, 110.85, 116.52, 119.19, 125.38, 129.02, 129.16, 132.84, 134.50, 136.65, 139.90, 233.47
Analysis: ($C_{24}H_{22}O_4Cr$)	Calcd. C: 67.76, H: 5.17 Found : C: 67.49, H: 5.39.

Complex 3c:

Color :	yellow
MP:	112°C
IR ($CHCl_3$):	1990, 1915 cm^{-1}
^1H NMR ($CDCl_3$) : (200 MHz)	1.65 (s, 3H), 2.01 (s, 1H), 2.59-2.75 (m, 3H), 2.85-3.15 (m, 1H), 5.20-5.45 (m, 3H), 5.90 (d, 1H, J=6.7 Hz), 7.01 (s, 1H) 7.18-7.50 (m, 5H).
^{13}C NMR ($CDCl_3$): (50.3 MHz)	18.24, 25.02, 27.40, 32.58, 42.80, 60.07, 72.28, 90.17, 91.34, 92.31, 93.01, 102.85, 110.68, 117.96, 124.14, 126.88, 128.39, 128.98, 137.45, 142.92, 233.36
Analysis: ($C_{21}H_{18}O_4Cr$)	Calcd. C: 65.25, H: 4.66 Found : C: 65.09, H: 4.70.

Complex 3d:

Color :	yellow
MP:	110°C
IR ($CHCl_3$):	1980, 1910 cm^{-1}
^1H NMR ($CDCl_3$) : (200 MHz)	1.63 (s, 3H), 2.05 (s, 1H), 2.38 (s, 3H), 2.70 (m, 3H), 2.88-3.05 (m, 1H), 5.21-5.48 (m, 3H), 5.90 (d, 1H, J=6.6Hz), 6.98 (s, 1H), 7.19 (s, 4H).
^{13}C NMR ($CDCl_3$): (50.3 MHz)	21.14, 25.02, 27.21, 32.50, 72.13, 89.96, 91.27, 92.27, 92.78, 110.57, 117.81, 123.94, 128.76, 128.93, 134.24, 136.45, 142.04, 233.26

Analysis:	Calcd. C: 66.00, H: 5.00
($C_{22}H_{20}O_4Cr$)	Found C: 66.01, H: 4.92

Complex 3e:

Color :	yellow
MP:	140°C
IR ($CHCl_3$):	1990, 1910 cm^{-1}
^1H NMR ($CDCl_3$) : (200 MHz)	2.39 (s, 3H), 2.49 (s, 1H), 2.48-2.60 (m, 1H), 2.60-2.78 (m, 2H), 2.85-3.10 (m, 1H), 5.13-5.32 (m, 2H), 5.50 (t, 1H, J=6.7 Hz), 5.98 (d, 1H, J=6.7 Hz), 7.09 (s, 1H), 7.10-7.40 (m, 9H)
^{13}C NMR ($CDCl_3$): (50.3 MHz)	21.30, 24.45, 27.32, 76.62, 89.92, 91.03, 92.38, 94.06, 112.13, 116.35, 124.57, 127.02, 128.09, 128.49, 129.02, 129.13, 134.34, 136.65, 140.81, 144.40, 233.22
Analysis:	Calcd. C: 70.13, H: 4.76
($C_{27}H_{22}O_4Cr$)	Found : C: 70.20, H: 4.89.

Complex 3f:

Color :	yellow
MP:	126°C
IR ($CHCl_3$):	1995, 1895 cm^{-1}
^1H NMR ($CDCl_3$) : (200 MHz)	0.40-0.60 (m, 2H), 0.62-0.75 (m, 2H), 1.10-1.40 (m, 1H), 1.80 (s, 1H), 2.35 (s, 3H), 2.55-3.07 (m, 4H), 5.20-5.45 (m, 3H), 5.85 (d, 1H, J=6.7Hz), 6.83 (s, 1H), 7.05-7.30 (m, 4H).

^{13}C NMR ($CDCl_3$): (50.3 MHz)	2.34, 2.66, 21.40, 23.87, 25.27, 27.27, 72.24, 90.51, 91.34, 92.56, 93.07, 111.09, 117.18, 124.36, 129.14, 134.61, 136.66, 141.37, 233.58
Analysis: ($C_{24}H_{22}O_4Cr$)	Calcd. C: 67.60, H: 5.16 Found C: 67.77, H: 5.21.

Complex 3g:

Color :	yellow
MP:	133°C
IR ($CHCl_3$):	1990, 1910 cm^{-1}
^1H NMR ($CDCl_3$) : (200 MHz)	0.80-1.05 (m, 3H), 1.15-1.50 (m, 5H), 1.65-2.85 (m, 1H), 2.00 (s, 1H), 2.38 (s, 3H), 2.50-2.65 (m, 1H), 2.70-2.90 (m, 2H), 2.85-3.10 (m, 1H), 5.15-5.35 (m, 2H), 5.45 (t, 1H, J=6.5Hz), 5.90 (d, 1H, J=6.5Hz), 6.90 (s, 1H), 7.10-7.30 (m, 4H).
^{13}C NMR ($CDCl_3$): (50.3 MHz)	14.41, 21.20, 23.33, 25.11, 27.12, 28.00, 31.45, 44.44, 75.10, 91.36, 91.82, 94.33, 96.01, 111.01, 118.24, 125.60, 127.81, 128.03, 128.64, 135.32, 137.64, 140.83, 233.54
Analysis: ($C_{25}H_{26}O_4Cr$)	Calcd. C: 67.87, H: 5.88 Found C: 68.02, H: 5.99.

Complex 3h:

Color :	yellow
MP:	100°C
IR ($CHCl_3$):	1980, 1910 cm^{-1}
^1H NMR ($CDCl_3$) : (200 MHz)	2.15 (s, 1H), 2.29 (s, 3H), 2.35-2.45 (m, 1H), 2.53-2.90 (m, 5H), 5.00-5.35 (m, 4H), 5.45 (t, 1H, J=6.5 Hz), 5.75-6.15 (m, 2H), 6.85 (s, 1H), 7.05-7.25 (m, 4H).
^{13}C NMR ($CDCl_3$): (50.3 MHz)	20.17, 24.10, 27.45, 48.37, 74.28, 90.43, 91.17, 91.70, 93.76, 111.01, 116.92, 119.00, 124.84, 125.80, 127.32, 129.13, 130.10, 133.03, 136.80, 140.24, 165.15, 233.43
Analysis: ($C_{24}H_{22}O_4Cr$)	Calcd. C: 67.76, H: 5.17 Found C: 67.79, H: 5.20.

Preparation of enone 5a :

Following the same procedure as described for complexed enone, it was prepared from tetralone (0.5g, 3.42 mmol), *p*-tolualdehyde (0.42g, 3.42 mmol) and KOH (0.2g, 3.57 mmol) using Claisen-Schmidt condensation. The enone has been reported earlier[36].

General procedure for the preparation of alcohol 5b, 5c from enone 5a :

Procedure for the reaction of organolithium and Grignard reagents was same as mentioned in case of complexed enones.

Alcohol 5b:

Color :	Colorless
MP:	oil
IR ($CHCl_3$):	3300-3600 (br), 1600 cm^{-1}
^1H NMR ($CDCl_3$) : (200 MHz)	2.25 (s, 1H), 2.41 (s, 3H), 2.50-2.68 (m, 1H), 2.68-2.85 (m, 2H), 2.90-3.10 (m, 2H), 3.10-3.22 (m, 1H), 5.00-5.28 (m, 2H), 5.80-6.05 (m, 1H), 6.85 (s, 1H), 7.05-7.40 (m, 7H), 7.78 (d, 1H, J=8.2 Hz).
^{13}C NMR ($CDCl_3$): (50.3 MHz)	21.31, 25.26, 30.34, 48.31, 75.48, 118.44, 123,62, 126.32, 126.66, 127.28, 128.14, 128.99, 133.87, 135.19, 136.12, 136.37, 142.71, 143.46
Analysis: ($C_{21}H_{22}O$)	Calcd. C: 86.89, H: 7.58: Found C :86.88, H: 7.60.

Alcohol 5c:

Color :	Colorless
MP:	oil
IR ($CHCl_3$):	3500-3600 (br), 1600 cm^{-1}
^1H NMR ($CDCl_3$) : (200 MHz)	1.79 (s, 3H), 2.47 (brs, 1H), 2.50 (s, 3H), 2.55-2.75 (m, 1H), 2.85-3.05 (m, 2H), 3.10-3.25 (m, 1H), 7.05 (s, 1H), 7.13-7.40 (m, 7H), 7.80 (d, 1H, J=8.2 Hz).

^{13}C NMR ($CDCl_3$): (50.3 MHz)	21.16, 25.36, 29.75, 30.52, 32.68, 73.96, 121.78, 126.27, 126.67, 126.93, 127.84, 128.80, 128.87, 135.16, 135.78, 136.06, 144.34, 145.48
Analysis: ($C_{19}H_{20}O$)	Calcd. C: 86.36, H: 7.57 Found : C: 86.52, H: 7.55.

General procedure for equilibration of 2b, 2b′, 2c and 2c′ : The complex (0.5mmol) was dissolved in 5 mL of dichloromethane and treated with 10 mol% DBU in dichloromethane at 0°C. The reaction was monitored by TLC. In all cases equilibrium was reached in about 2 hours. Working up involved removal of solvent, washing with water and extracting with dichloromethane. The solvent was removed and residue was chromatographed to yield a pair of diastereomers. Ratio of diastereomers : **2b : 4a** = 89 : 11, **2b′ : 4c** = 85 : 15, **2c : 4b** = 80 : 20, **2c′ : 4d** = 78 : 22. **4a** and **4c** have been reported earlier.[21]

Complex 4b:

Color :	red
MP:	136°C
IR ($CHCl_3$):	1980, 1910, 1675 cm^{-1}
^{1}H NMR ($CDCl_3$) : (200 MHz)	1.25 (d, 3H, J=7.2 Hz), 1.80-2.20 (m, 2H), 2.50-2.62 (m, 1H), 2.65-2.81 (m, 2H), 3.82-4.15 (m, 1H), 5.15 (d, 1H, J=6.5 Hz), 5.32 (t, 1H, J=6.5 Hz) 5.65 (t, 1H, J=6.5 Hz), 6.25 (d, 1H, J=6.5 Hz), 7.20-7.40 (m, 5H).

^{13}C NMR ($CDCl_3$): (50.3 MHz)	13.39, 17.38, 22.87, 23.98, 29.65, 38.88, 56.17, 62.65, 82.30, 87,10, 91.43, 94.70, 102.10, 113.56, 120.10, 127.98, 128.62, 197.27, 231.20
Analysis: ($C_{22}H_{20}O_4Cr$)	Calcd. C: 65.28, H: 4.66 Found : C: 65.30, H: 4.86.

Complex 4d:

Color :	red
MP:	123°C
IR ($CHCl_3$):	1980, 1910, 1675 cm^{-1}
^{1}H NMR ($CDCl_3$) : (200 MHz)	1.30 (d, 3H, J=7.3 Hz), 2.00-2.15 (m, 2H), 2.65-3.05 (m, 3H), 3.50-3.70 (m, 1H), 5.11 (d, 1H, J=6.5 Hz), 5.20 (t, 1H, J=6.5 Hz), 5.60 (d, 1H, J=6.5 Hz), 6.20 (d, 1H, J=6.5 Hz), 7.05-7.40 (m, 5H).
^{13}C NMR ($CDCl_3$): (50.3 MHz)	14.20, 16.33, 23.09, 23.74, 26.44 32.03, 52.25, 81.92, 86.86, 89.51, 92,59, 95.45, 115.64, 127.83, 127.99, 128.55, 144.32, 196.50, 231.09
Analysis: ($C_{22}H_{20}O_4Cr$)	Calcd. C: 65.28, H: 4.66 Found C: 65.33, H: 4.73.

General procedure for the preparation of enones (6a-c): Following a reported[36] procedure all three enones were prepared from 1-tetralone or 1-

indanone (2.0 mmol) and $Cr(CO)_3$ complexed aromatic aldehydes[30] (2.0 mmol) and KOH (2.20 mmol) using Claisen-Schmidt condensation.

Complex 6a:	yield 82%
Color :	red
MP:	145°C
IR ($CHCl_3$):	1950, 1860(br), 1660 cm^{-1}
^1H NMR ($CDCl_3$) : (200 MHz)	2.90-3.20 (m, 4H), 3.80 (s, 3H), 4.98 (t, 1H, J=6.6Hz), 5.15 (d, 1H, J=6.6Hz), 5.62 (t, 1H, J=6.6Hz), 5.71 (d, 1H, J=6.6Hz), 7.25 (m, 1H), 7.40 (t, 1H, J=8.2Hz), 7.55 (t, 1H, J=8.2Hz), 7.70 (brs, 1H); 8.15 (d, 1H, J=8.2Hz)
^{13}C NMR ($CDCl_3$): (50.3 MHz)	12.72, 19.34, 27.87, 28.95, 63.36, 90.57, 92.38, 96.72, 102.34, 107.96, 127.40, 128.51, 129.50, 133.14, 133.66, 138.46, 143.30, 186.63, 232.97
Analysis: ($C_{21}H_{16}O_5Cr$)	Calcd. C: 63.00, H: 4.00 Found C: 62.86, H: 4.03

Complex 6b:	yield 79%
Color :	red
MP:	135°C
IR ($CHCl_3$):	1935, 1850, 1655 cm^{-1}
^1H NMR ($CDCl_3$) : (200 MHz)	2.20 (s, 3H), 2.85-3.25 (m, 4H), 5.25 (m, 2H), 5.45 (m, 2H), 7.25 (m, 1H), 7.40 (t, 1H, J=8.1Hz), 7.50 (m, 1H), 7.56 (s, 1H), 8.15 (d, 1H, J=8.1Hz)

^{13}C NMR ($CDCl_3$): (50.3 MHz)	19.51, 27.52, 29.00, 89.33, 93.14, 93.64, 95.15, 103.02, 109.44, 127.12, 127.45, 128.57, 131.23, 133.01, 133.80, 138.90, 143.29, 186.62, 232.62
Analysis: ($C_{21}H_{16}O_4Cr$)	Calcd. C: 65.79, H: 4.17 Found C: 65.73, H: 4.30

Complex 6c:	yield 87%
Color :	red
MP:	170°C (dec)
IR ($CHCl_3$):	1960, 1865, 1660 cm^{-1}
^{1}H NMR ($CDCl_3$) : (200 MHz)	3.86 (s, 3H), 4.01 (brd, 2H, J=8.6Hz), 5.00 (t, 1H, J=6.3Hz), 5.15 (d, 1H, J=6.3Hz), 5.75 (t, 1H, J=6.3Hz), 6.15 (d, 1H, J=6.3Hz), 7.45 (t, 1H, J=7.6Hz), 7.55-7.70 (m, 2H), 7.80 (m, 1H), 7.95 (d, 1H, J=8Hz)
^{13}C NMR (CD_2Cl_2): (50.3 MHz)	34.02, 58.24, 76.18, 87.02, 93.05, 96.40, 97.50, 126.25, 127.79, 128.38, 129.88, 136.83, 138.01, 140.06, 145.14, 151.52, 185.59, 234.64
Analysis: ($C_{20}H_{14}O_5Cr$)	Calcd. C: 62.17, H: 3.62 Found C: 62.01, H: 3.71

General procedure for the addition of allyllithium to enones (6a-c): To a solution of the complexed enone (**6a-c**), (n mmol) in THF ($20n$ mL), allyllithium ($1.2\text{-}1.4n$ mmol) in THF 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.

Reactions were performed in 0.5-2.0 mmol scale. For isolated yield and product ratio see Table –2.

Complex 7a:

Color :	yellow
MP:	122°C
IR ($CHCl_3$):	3400-3600(br), 1940, 1850(br) cm^{-1}
^1H NMR ($CDCl_3$) : (200 MHz)	2.25 (s, 1H), 2.40-2.60 (m, 1H), 2.60-2.75 (m, 2H), 2.90-3.15 (m, 3H), 3.80 (s, 3H), 5.00 (t, 1H, J=6.2 Hz), 5.05-5.23 (m, 3H), 5.50 (t, 1H, J=6.2 Hz) 5.60 (d, 1H, J=6.2 Hz), 5.70-5.95 (m, 1H), 6.58 (s, 1H), 7.05-7.40 (m, 3H), 7.67 (d, 1H, J=8.2 Hz)
^{13}C NMR ($CDCl_3$): (50.3 MHz)	25.86, 30.41, 48.66, 56.17, 74.93, 75.84, 85.92, 93.44, 96.79, 98.29, 116.70, 118.64, 126.59, 126.98, 127.58, 128.25, 133.65, 136.10, 141.26, 143.08, 147.28, 233.55
Analysis: ($C_{24}H_{22}O_5Cr$)	Calcd. C: 65.15, H: 4.97 Found C: 64.83, H: 4.94.

Complex 7b:

Color :	yellow
MP:	140°C
IR ($CHCl_3$):	3400-3600(br) 1920, 1825(br) cm^{-1}
^1H NMR ($CDCl_3$) : (200 MHz)	2.20 (s, 3H), 2.25 (s, 1H), 2.29-2.50 (m, 1H), 2.50-2.75 (m, 2H), 2.77-3.17 (m, 3H), 5.00-5.25 (m, 2H), 5.27-5.48 (m, 4H), 5.70-5.97 (m, 1H), 6.55 (s, 1H), 7.10 (d, 1H, J= 8.1Hz), 7.20-7.48 (m, 2H), 7.70 (d, 1H, J= 8.1Hz)
^{13}C NMR ($CDCl_3$): (50.3 MHz)	19.64, 25.33, 30.48, 48.35, 75.79, 90.77, 93.24, 94.22, 95.16, 108.17, 108.69, 118.34, 119.23, 126.41, 126.90, 127.52, 128.20, 133.58, 135.60, 143.01, 147.71, 233.66
Analysis: ($C_{24}H_{22}O_4Cr$)	Calcd. C: 67.60, H: 5.16 Found C: 67.82, H: 5.08.

Complex 7c:

Color :	Yellow
MP:	122°C
IR ($CHCl_3$):	3400-3600(br), 1930, 1836 cm^{-1}
^1H NMR ($CDCl_3$) : (200 MHz)	2.38 (s, 1H), 2.55-2.75 (m, 2H), 3.50-3.75 (m, 1H), 3.80 (s, 3H), 3.95-4.15 (m, 1H), 4.90-5.10 (m, 3H), 5.20 (d, 1H, J=6.5 Hz), 5.45-5.71 (m, 2H), 5.80 (d, 1H, J=6.5 Hz), 6.80 (brs, 1H) 7.15-7.40 (m, 3H), 7.45 (d, 1H, J=8.2 Hz)

^{13}C NMR ($CDCl_3$): (50.3 MHz)	27.09, 35.40, 47.55, 56.14, 75.05, 83.93, 85.89, 93.02, 95.79, 116.31, 118.73, 123.93, 124.74, 127.42, 128.86, 132.93, 139.51, 140.90, 145.83, 152.02, 233.45
Analysis: ($C_{23}H_{20}O_5Cr$)	Calcd. C: 64.48, H: 4.67 Found C: 64.72, H: 4.58.

Complex 8a:

Color :	yellow
MP:	128°C
IR ($CHCl_3$):	3400-3600(br), 1940, 1850(br) cm^{-1}
^{1}H NMR ($CDCl_3$) : (200 MHz)	2.23 (s, 1H), 2.48-2.74 (m, 3H), 2.82-3.15 (m, 3H), 3.71 (s, 3H), 4.91 (t, 1H, J=6.5 Hz), 5.05-5.29 (m, 3H), 5.50 (t, 1H, J=6.5 Hz) 5.62 (d, 1H, J=6.5 Hz), 5.70-6.01 (m, 1H), 6.58 (s, 1H), 7.05 (d, 1H, J=8.0 Hz); 7.15-7.37 (m, 2H), 7.70 (d, 1H, J=8.0 Hz)
^{13}C NMR ($CDCl_3$): (50.3 MHz)	25.48, 29.71, 30.63, 48.53, 55.69, 75.25, 85.65, 93.56, 97.18, 97.60, 116.25, 118.26, 126.12, 126.56, 127.16, 127.80, 133.35, 135.60, 141.29, 142.75, 146.36, 233.39
Analysis: ($C_{24}H_{22}O_5Cr$)	Calcd. C: 65.15, H: 4.97 Found C: 64.98, H: 4.99

Complex 8b:

Color :	yellow
MP:	110°C
IR ($CHCl_3$):	3500-3600(br) 1935, 1850(br) cm^{-1}
^1H NMR ($CDCl_3$) : (200 MHz)	2.15 (s, 3H), 2.22 (s, 1H), 2.50-2.71 (m, 3H), 2.72-2.88 (m, 1H), 2.89-3.11 (m, 2H), 5.05-5.80 (m, 4H), 5.81-5.50 (m, 2H), 5.70-6.00 (m, 1H), 6.51 (s, 1H), 7.00-7.15 (m, 1H), 7.15-7.37 (m, 2H), 7.68 (d, 1H, J= 8.2Hz)
^{13}C NMR ($CDCl_3$): (50.3 MHz)	19.41, 25.45, 30.16, 48.75, 75.29, 90.51, 93.26, 94.11, 96.11, 107.55, 108.99, 118.93, 119.06, 126.29, 126.88, 127.50, 128.10, 133.28, 135.64, 142.65, 147.18, 233.62
Analysis: ($C_{24}H_{22}O_4Cr$)	Calcd. C: 67.60, H: 5.16 Found C: 67.67, H: 4.99

Complex 8c:

Color :	yellow
MP:	134°C
IR ($CHCl_3$):	3400-3600(br), 1940, 1835 cm^{-1}
^1H NMR ($CDCl_3$) : (200 MHz)	2.28 (s, 1H), 2.65 (d, 2H, J=8.5 Hz), 3.70-3.85 (m, 2H), 3.80 (s, 3H), 4.95-5.20 (m, 4H), 5.45-5.80 (m, 2H), 5.87 (d, 1H, J=6.5 Hz), 6.80 (m, 1H), 7.17-

	7.40 (m, 3H) 7.49 (d, 1H, J=8.1 Hz)
^{13}C NMR ($CDCl_3$): (50.3 MHz)	29.90, 35.71, 47.88, 56.11, 74.45, 85.51, 89.38, 93.41, 116.76, 119.67, 123.88, 124.71, 127.63, 128.86, 132.45, 139.38, 141.34, 146.07, 150.74, 233.42
Analysis: ($C_{23}H_{20}O_5Cr$)	Calcd. C: 64.48, H: 4.67 Found C: 64.40, H: 4.55

General procedure for the $TiCl_4$ mediated allyllithium addition to enones (6a-c) : To a solution of the complexed enone (n mmol) in dichloromethane ($20n$ mL), titanium tetrachloride ($2n$ mmol) was added dropwise with stirring at -90°C. After stirring for 15 minutes allyllithium ($1.1n$ mmol) in THF 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 -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. All reactions were performed in 0.5-2.0 mmol scale. For details about the isolated yield and ratio of products see table-2.

Complex 9a:

Color :	yellow
MP:	70°C
IR ($CHCl_3$):	1950, 1860(br) cm^{-1}
^1H NMR ($CDCl_3$) : (200 MHz)	2.33-2.51 (m, 2H), 2.51-2.69 (m, 1H), 2.70-3.10 (m, 2H), 3.25-3.72 (m, 2H), 3.85 (s, 3H), 4.12-4.29 (m, 1H), 4.80 (t, 1H, J=6.5Hz), 4.87-5.21 (m, 7H), 5.57 (t, 1H, J=6.5Hz), 5.62-5.80 (m, 1H), 5.91-6.15 (m, 1H), 7.08-7.23 (m, 3H), 7.35 (d, 1H, J=8.2Hz)
^{13}C NMR ($CDCl_3$): (50.3 MHz)	25.30, 28.83, 33.10, 38.07, 40.83, 55.90, 73.28, 83.96, 94.78, 96.96, 104.36, 115.84, 116.52, 124.50, 126.59, 127.13, 132.19, 135.70, 136.39, 136.88, 137.24, 142.01, 166.37, 233.43
Analysis: ($C_{27}H_{26}O_4Cr$)	Calcd. C: 69.52, H: 5.58 Found C: 69.77, H: 5.50.

Complex 9b:

Color :	yellow
MP:	138°C
IR ($CHCl_3$):	1935, 1850(br) cm^{-1}
^1H NMR ($CDCl_3$) : (200 MHz)	2.37 (s, 3H), 2.39-2.65 (m, 3H), 2.66-3.19 (m, 2H), 3.30-3.68 (m, 2H), 3.86-4.01 (m, 1H), 4.86-5.22 (m, 7H), 5.51-5.79 (m, 3H), 5.95-6.18 (m, 1H), 6.99-7.42 (m, 4H)

^{13}C NMR ($CDCl_3$): (50.3 MHz)	14.23, 19.72, 22.84, 26.00, 28.75, 33.39, 39.35, 42.61, 87.56, 91.51, 95.06, 96.09, 109.43, 113.37, 115.95, 116.95, 124.43, 126.69, 127.07, 133.31, 134.45, 136.14, 136.33, 136.63, 233.34
Analysis: ($C_{27}H_{26}O_3Cr$)	Calcd. C: 72.00, H: 5.77 Found C: 72.01, H: 5.86

Complex 9c:

Color :	yellow
MP:	95°C
IR ($CHCl_3$):	1945, 1860(br) cm^{-1}
^{1}H NMR ($CDCl_3$) : (200 MHz)	2.61-2.80 (m, 2H), 3.30-3.65 (m, 3H), 3.85 (s, 3H), 4.10-4.28 (m, 1H), 4.75 (t, 1H, J=6.4Hz), 4.90-5.25 (m, 6H), 5.40-5.60 (m, 2H), 5.60-5.80 (m, 1H), 5.85-6.10 (m, 1H), 7.10-7.51 (m, 4H)
^{13}C NMR ($CDCl_3$): (50.3 MHz)	30.03, 41.35, 52.81, 56.66, 65.28, 74.44, 85.31, 87.71, 95.50, 98.33, 107.29, 117.22, 118.36, 119.48, 122.26, 125.53, 126.61, 128.90, 138.80, 140.01, 144.39, 145.11, 145.50, 234.11
Analysis: ($C_{26}H_{24}O_4Cr$)	Calcd. C: 69.02, H: 5.31 Found C: 68.98, H: 5.40.

Addition of methyllithium to enone 6b in absence and presence of $TiCl_4$:

Procedure was same as mentioned earlier for allyllithium. Addition of

methyllithium in absence of Lewis acid resulted in the formation of two diastereomeric 1,2-adducts (total yield 81%, *exo* : *endo* = 5 : 1). In presence of $TiCl_4$ (yield 72%) trace of *gem* dimethylated product was also formed in addition to 1,2-*endo* adduct.

Exo-1,2-adduct (10a):

Color :	Light yellow
MP:	145°C
IR ($CHCl_3$):	3500-3600(br), 1935, 1825 cm^{-1}
^1H NMR ($CDCl_3$) : (200 MHz)	1.68 (s, 3H), 1.97 (s, 1H), 2.20 (s, 3H), 2.35-2.60 (m, 1H), 2.80-3.04 (m, 3H), 5.16-5.43 (m, 4H), 6.70 (s, 1H), 7.10 (d, 1H, J=8.1 Hz), 7.18-7.40 (m, 2H), 7.75 (d, 1H, J=8.1 Hz)
^{13}C NMR ($CDCl_3$): (50.3 MHz)	15.15, 19.93, 26.26, 30.48, 33.53, 72.17, 92.39, 95.61, 96.09, 97.12, 108.64, 109.21, 118.39, 126.11, 127.23, 128.33, 129.61, 135.42, 233.57
Analysis: ($C_{22}H_{20}O_4Cr$)	Calcd. C: 66.00, H: 5.00 Found C: 66.21, H: 4.98.

***Endo*-1,2-adduct (10b):**

Color :	Light yellow
MP:	mp 162°C
IR ($CHCl_3$):	3500-3600(br), 1920, 1825 cm^{-1}
^1H NMR ($CDCl_3$) : (200 MHz)	1.70 (s, 3H), 1.94 (s, 1H), 2.19 (s, 3H), 2.48-2.80 (m, 1H), 2.80-3.19 (m, 3H), 5.18-5.50 (m, 4H), 6.70 (s, 1H), 7.09 (d, 1H, J=8.1 Hz), 7.16-7.39 (m, 2H), 7.73 (d, 1H, J=8.1 Hz)
^{13}C NMR ($CDCl_3$): (50.3 MHz)	15.53, 21.64, 25.55, 31.12, 33.64, 54.59, 91.12, 94.53, 95.08, 96.81, 109.31, 109.76, 120.21, 124.53, 127.81, 128.10, 129.12, 135.64, 233.32
Analysis: ($C_{22}H_{20}O_4Cr$)	Calcd. C: 66.00, H: 5.00 Found C: 65.92, H: 5.16.

General procedure for the oxy-Cope rearrangement of 1,2-allyl adducts to 1,4-allyl adducts : To a solution of 1,2-allyl adduct (**7a-c** and **8a-c**) (*n* mmol) and 18-crown-6 (0.1n mmol) in diethyl ether (20*n* mL), suspension of potassium hydride (1.1 *n* mmol) in ether was added dropwise with stirring at 0°C. It was then stirred at room temperature. After completion of the reaction (TLC, 2.0-2.5 h) the reaction mixture was quenched with degassed methanol at 0°C and finally extracted with ether. The residue obtained after evaporation of solvent was purified by flash column chromatography. Reactions were performed in 0.5-2.0 mmol scale. Product was purified by column

chromatography (10-20% ethylacetate/petroleum ether) followed by recrystallization from dichloromethane/petroleum ether.

Complex 11a: yield 77%

Color :	yellow
MP:	65°C
IR ($CHCl_3$):	1964, 1867, 1670 cm^{-1}
^1H NMR ($CDCl_3$) : (200 MHz)	1.90-2.15 (m, 2H), 2.35-2.65 (m, 2H), 2.66-2.87 (m, 1H), 2.88-3.15 (m, 2H), 3.68 (s, 3H), 4.00-4.20 (m, 1H), 4.85-5.15 (m, 4H), 5.48 (t, 1H, J=6.3 Hz), 5.69 (d, 1H, J=6.3 Hz), 5.75-6.05 (m, 1H). 7.10-7.38 (m, 2H). 7.45 (t, 1H, J=8.1 Hz), 8.03 (d, 1H, J=8.1 Hz)
^{13}C NMR ($CDCl_3$): (50.3 MHz)	24.57, 29.45, 34.97, 35.83, 52.25, 55.99, 73.68, 82.51, 85.24, 93.58, 95.27, 105.60, 116.97, 126.91, 127.83, 128.79, 133.44, 137.02, 141.40, 143.72, 197.64, 233.41
Analysis:	Calcd. C: 67.16, H: 4.97
($C_{24}H_{22}O_5Cr$)	Found C: 65.19, H: 4.86

Complex 11b: yield 78.7%

Color :	yellow
MP:	97°C
IR ($CHCl_3$):	1962, 1860, 1667 cm^{-1}
^1H NMR ($CDCl_3$) : (200 MHz)	1.90-2.15 (m, 2H), 2.25 (s, 3H), 2.30-2.50 (m, 3H), 2.72-3.10 (m, 2H), 4.05-4.15 (m, 1H), 4.80-5.10 (m, 2H), 5.10-5.31 (m, 2H), 5.40 (t, 2H, J=6.5 Hz), 5.65-

	5.90 (m, 1H), 7.15-7.40 (m, 2H), 7.49 (t, 1H, J=8.2 Hz), 8.05 (d, 1H, J=8.2 Hz)
^{13}C NMR ($CDCl_3$): (50.3 MHz)	18.98, 22.56, 29.50, 29.85, 34.22, 37.23, 53.08, 90.01, 92.60, 93.79, 108.56, 114.95, 117.05, 127.04, 127.97, 128.80, 132.75, 133.69, 136.62, 143.58, 196.83, 233.51
Analysis: ($C_{24}H_{22}O_4Cr$)	Calcd. C: 67.60, H: 5.16 Found C: 67.66, H: 5.25.

Complex 11c:	yield 78%
Color :	yellow
MP:	121°C
IR ($CHCl_3$):	1965, 1860, 1660 cm^{-1}
^{1}H NMR ($CDCl_3$) : (200 MHz)	2.05-2.15 (m, 1H), 2.35-2.60 (m, 2H), 2.60-2.80 (m, 1H), 3.05-3.39 (m, 2H), 3.80 (s, 3H), 4.85-5.20 (m, 4H), 5.40-5.60 (m, 1H), 5.60-6.00 (m, 2H), 7.40 (t, 1H, J=8.1 Hz) 7.50-7.70 (m, 2H), 7.80 (d, 1H, J=8.1Hz)
^{13}C NMR ($CDCl_3$): (50.3 MHz)	29.48, 30.92, 39.46, 53.86, 56.30, 75.41, 88.19, 92.53, 96.66, 101.32, 117.32, 117.97, 128.56, 120.67, 121.24, 135.14, 138.13, 140.00, 156.80, 205.58, 233.32
Analysis: ($C_{23}H_{20}O_5Cr$)	Calcd. C: 64.48, H: 4.67 Found C: 64.51, H: 4.71.

Complex 12a:	yield 80%
Color :	Yellow
MP:	110°C
IR ($CHCl_3$):	1960, 1865, 1672 cm^{-1}
^1H NMR ($CDCl_3$) : (200 MHz)	1.95-2.25 (m, 1H), 2.27-2.49 (m, 2H), 2.55-2.75 (m, 1H), 2.77-3.40 (m, 3H), 3.75 (s, 3H), 4.20-4.39 (m, 1H), 4.75-5.15 (m, 4H), 5.55-5.90 (m, 3H). 7.17-7.40 (m, 2H). 7.42-7.60 (m, 1H). 8.12 (d, 1H, J=8.3 Hz)
^{13}C NMR ($CDCl_3$): (50.3 MHz)	24.39, 29.33, 33.03, 34.54, 55.48, 55.98, 72.91, 83.54, 95.54, 99.44, 106.47, 117.02, 126.68, 127.78, 128.99, 131.93, 132.66, 136.56, 142.62, 144.27, 197.79, 233.70
Analysis: ($C_{24}H_{22}O_5Cr$)	Calcd. : C: 67.16, H: 4.97 Found : C: 66.94, H: 5.01.

Complex 12b:	yield 75%
Color :	yellow
MP:	110°C
IR ($CHCl_3$):	1965, 1860, 1660 cm^{-1}
^1H NMR ($CDCl_3$) : (200 MHz)	2.25 (s, 3H), 2.30-2.68 (m, 4H), 2.80-3.18 (m, 4H), 4.70-4.95 (m, 2H), 5.05 (d, 1H, J=6.4 Hz) 5.15 (t, 1H, J=6.4 Hz) 5.30-5.48 (m, 1H), 5.50-5.75 (m, 1H), 6.15 (d, 1H, J=6.4 Hz), 7.05-7.55 (m, 3H), 8.05 (d, 1H, J=8.4 Hz)
^{13}C NMR ($CDCl_3$): (50.3 MHz)	20.17, 29.39, 29.92, 30.70, 38.98, 43.24, 53.53, 90.43, 92.77, 94.84, 96.41, 110.10, 117.28,

	118.12, 127.03, 127.80, 128.77, 133.69, 135.97, 143.85, 199.13, 233.77
Analysis:	Calcd. C: 67.60, H: 5.16
($C_{24}H_{22}O_4Cr$)	Found. C: 67.56, H: 5.12.

Complex 12c:	yield 78%
Color :	yellow
MP:	113°C
IR ($CHCl_3$):	1960, 1860, 1665 cm^{-1}
^1H NMR ($CDCl_3$) : (200 MHz)	2.25-2.55 (m, 3H), 2.65-2.90 (m, 1H), 3.15-3.45 (m, 2H), 3.75 (s, 3H), 4.75-5.20 (m, 4H), 5.35-5.70 (m, 3H), 7.40 (t, 1H, J=7.9 Hz) 7.50-7.70 (m, 2H), 7.75 (d, 1H, J=7.9 Hz)
^{13}C NMR ($CDCl_3$): (50.3 MHz)	31.04, 39.02, 43.37, 52.82, 53.56, 55.99, 74.81, 86.19, 93.51, 97.24, 99.32, 118.16, 123.98, 125.72, 128.04, 135.10, 136.37, 141.91, 156.30, 206.18, 233.35
Analysis:	Calcd. C: 64.48, H: 4.67
($C_{23}H_{20}O_5Cr$)	Found C: 64.40, H: 4.65

General procedure for the base catalysed equilibration of 12a and 11a : The complex (0.5mmol) was dissolved in 5 mL of dichloromethane and treated with 10 mol% DBU in dichloromethane at 0°C. The reaction was monitored by TLC. In all cases equilibrium was reached in about 2 hours. Working up involved removal of solvent, washing with water and extracting with

dichloromethane. Dichloromethane was removed and residue was chromatographed to yield a pair of diastereomers. Ratio of diastereomers : **12a** : **13a** = 80 : 20, **11a** : **13b** = 85 : 15.

Complex 13a:

Color :	yellow
MP:	96°C
IR ($CHCl_3$):	1958, 1860, 1665 cm^{-1}
^1H NMR ($CDCl_3$) : (200 MHz)	1.92-2.20 (m, 1H), 2.22-2.45 (m, 1H), 2.55-2.75 (m, 2H), 2.85-3.10 (m, 3H), 3.30-3.50 (m, 1H), 3.78 (s, 3H), 4.80-5.05 (m, 4H), 5.55 (t, 1H, J=6.3 Hz) 5.60-5.90 (m, 1H), 6.20 (d, 1H, J=6.3 Hz), 7.15-7.40 (m, 2H), 7.45-7.60 (m, 1H). 8.05 (d, 1H, J=8.0Hz)
^{13}C NMR ($CDCl_3$): (50.3 MHz)	28.49, 29.42, 29.87, 38.29, 40.63, 52.63, 55.77, 73.71, 85.36, 94.64, 99.29, 106.20, 117.29, 126.85, 127.67, 128.79, 133.55, 137.06, 142.66, 144.02, 199.29, 233.70
Analysis: ($C_{24}H_{22}O_5Cr$)	Calcd. C: 65.16, H: 4.97 Found C: 65.40, H: 4.99.

Complex 13b:

Color :	yellow
MP:	82°C
IR ($CHCl_3$):	1960, 1865, 1660 cm^{-1}
^1H NMR ($CDCl_3$) : (200 MHz)	1.90-2.20 (m, 2H), 2.45-2.75 (m, 2H), 2.76-2.80 (m, 1H), 2.80-3.05 (m, 2H), 3.45-3.60 (m, 1H),

	3.68 (s, 3H), 4.85-5.25 (m, 4H), 5.45 (t, 1H, J=6.4 Hz), 5.81-6.05 (m, 2H), 7.10-7.35 (m, 2H), 7.45 (t, 1H, J=8.2Hz), 7.95 (d, 1H, J=8.2 Hz)
^{13}C NMR ($CDCl_3$): (50.3 MHz)	28.36, 29.88, 35.53, 38.08, 51.52, 55.96, 73.59, 85.35, 86.68, 93.53, 96.02, 105.31, 117.31, 126.89, 127.48, 128.73, 133.47, 137.15, 141.93, 146.88, 199.20, 233.58
Analysis: ($C_{24}H_{22}O_5Cr$)	Calcd. C: 65.16, H: 4.97 Found C: 65.29, H: 4.88.

Attempted Hosomi-Sakurai reaction of enones 6a-c:

To a solution of enone (1 mmol) in dichloromethane (10 mL) at –78°C, $TiCl_4$ (2 mmol) was added dropwise with stirring. After 30 minutes allylsilane (1.5 mmol) was added dropwise at that temperature. Reaction was monitored by TLC. There was no reaction after stirring for 12 hours at –78°C followed by stirring at –20°C for 8 hours. After usual workup, starting material was recovered (80-90%).

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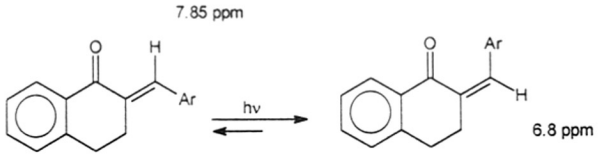
28. Stereochemistry of the complex **3b** was known from earlier studies,[21] therefore, relative stereochemistry of remaining products was fixed by analogy, supported by a large number of preceedents.[22,23]

29. Only a trace amount, (<5%) of conjugate addition product could be isolated with organomagnesium reagents and in $TiCl_4$ mediated reactions.

30. For preparation of complexed aldehydes see: a) *J. Org. Chem.* **1979**, *44*, 4189. b) Ph. D. dissertation of Dr. S. Sur, **1997**, University of Poona, India. c) Mandal, S. K.; Sarkar, A. *J. Org. Chem.* **1998**, *63*, 1901.

31. The stereochemistry of the double bond was further confirmed by photolysis of 2-(*p*-tolylidene)-1-tetralone at 350 nm for five hours in chloroform-*d*. It afforded a mixture of *Z* and *E* stereoisomers; the olefinic proton in each appeared at 6.8 and 7.85 ppm respectively (Scheme-18). [21]

Scheme-18



In rigid and stereochemically defined structures such as isomeric □-benzylidenecamphors, the chemical shift of the *syn* (with respect to the carbonyl group) olefinic proton is 7.4 ppm while that of the *anti* olefinic proton is 6.45 ppm. The deshielding of *syn* olefinic proton is ascribed to the deshielding effect of the coplanar carbonyl group anisotropy. See also Kossanyi, J.; Furth, B.; Morizur, J. P. *Tetrahedron* **1970**, *26*, 395

32. It has been shown by Prof. Denmark that a 1:1 carbonyl-$TiCl_4$ complex is formed when excess $TiCl_4$ is used, lesser amount of TiCl4 led predominantly to complexes of composition $TiCl_4$-carbonyl 1:2. For our purpose, it was desirable that at least 1:1 complexes are formed for best stereoselectivity, and we did not reduce the amount of $TiCl_4$ any lower than two equivalents. See ref. 27.

33. For Lewis acid mediated substitution of hydroxyl group with alkyl group See Ref. 23b and references cited therein.

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36. a) Ph. D. dissertation of Dr. S. Ganesh, 1993, University of Poona, India. b) Sur, S.; Ganesh, S.; Puranik, V. G.; Sarkar, A. *J. Chem. Soc. Perkin Trans. 1*. **1998**, 977-982.

PART – B

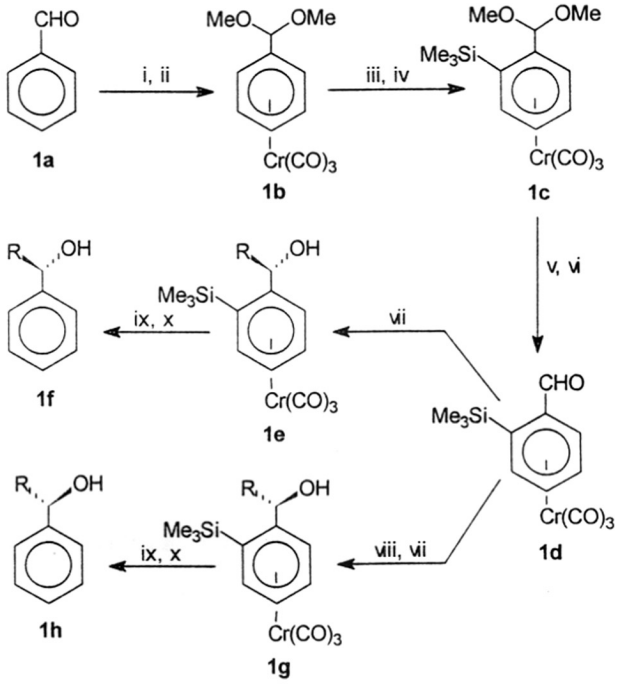
Activation of Ar-Si Bonds through Complexation with $Cr(CO)_3$: Alkali metal Hydride or Hydroxide induced Cleavage and Functional Modification of $(CO)_3Cr$-Ar-$SiMe_3$ Bonds.

Part of this work has been published in **J. Org. Chem. 1998**, *63*, 1901-1905 and **J. Org. Chem. 1998**, *63*, 5672-5674.

Introduction

In arene-tricarbonylchromium chemistry,[1] an *ortho*-trimethylsilyl group has often been used as a means to effect high diastereoselectivity at benzylic centres.[1,2] If one begins with an enantiopure substrate, high diastereoselectivity translates into high enantioselectivity as well, and desilylation eventually affords an optically pure benzyl derivative (Scheme–1).[3]

Scheme-1

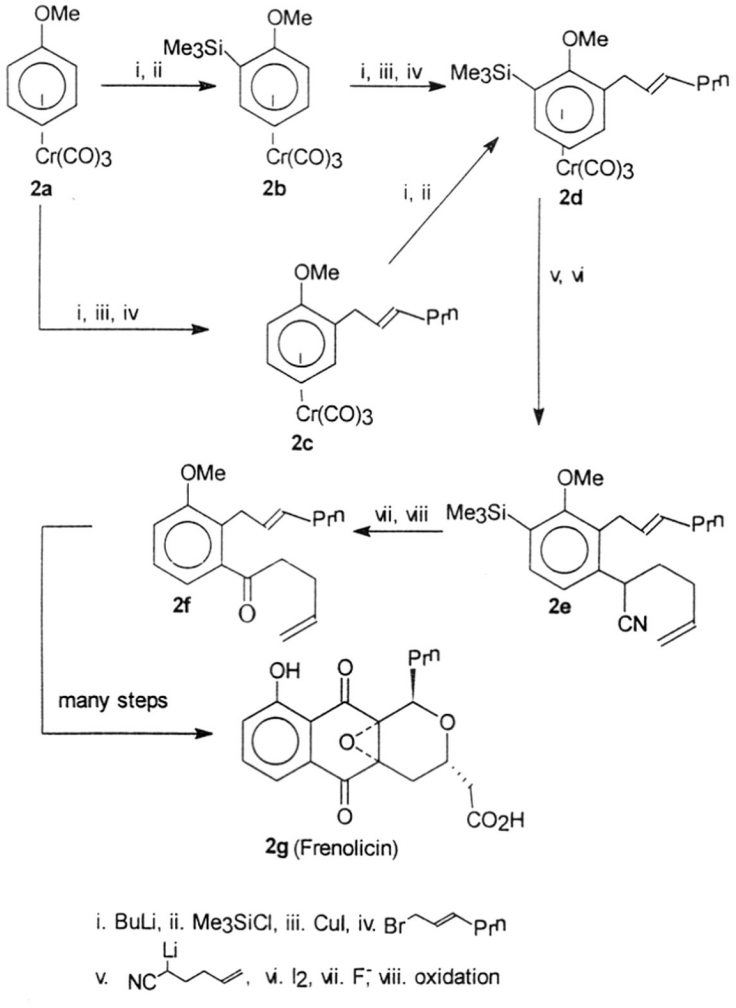


i. $HC(OMe)_3$, H^+; ii. $Cr(CO)_6$; iii. BuLi; iv. Me_3SiCl;
v. H^+; vi. resolution; vii. RLi; viii.$MgBr_2$, ix. F^-; x. removal of metal

As depicted in Scheme-1, the bulky trimethylsilyl group and aldehyde carbonyl of complex **1d** are placed *syn* to each other, as expected on the ground of a stabilizing Si--O interection.[3a] Hence the product **1e** results from an *exo* attack by the nucleophile (e.g., RLi) on the *syn* conformer. However, prior coordination of a Lewis acid (e.g., $MgBr_2$, $TiCl_4$, BF_3) to the carbonyl oxygen favors the *anti* conformation for steric reasons, and in their presence the complementary diastereomer **1g** is formed. If the substrate **1d** is optically pure, subsequent protiodesilylation with fluoride ion and removal of tricarbonylchromium results in the formation of two enantiomeric benzyl derivatives (**1f** and **1h** from **1e** and **1g** respectively).

It is also possible to use $SiMe_3$ as a site-protecting group on the aromatic ring so that a functionalization can be directed to alternative sites.[4] A convincing illustration of such utility of $SiMe_3$ group is the synthesis of frenolicin (Scheme-2).[4c-e] The intermediate **2d** may be obtained from the precursor **2a** *via* sequential *ortho*-lithiation and quenching with electrophile (the order of the electrophile selected is not critical). Nucleophilic addition of a carbonyl anion equivalent was done regioselectively to obtain a tetrasubstituted arene **2e** after iodine oxidation. Addition is regioselective for the less hindered *meta* position with respect to the methoxy group. Synthesis of frenolicin (**2g**) was completed following several other steps from intermediate **2f**.

Scheme-2

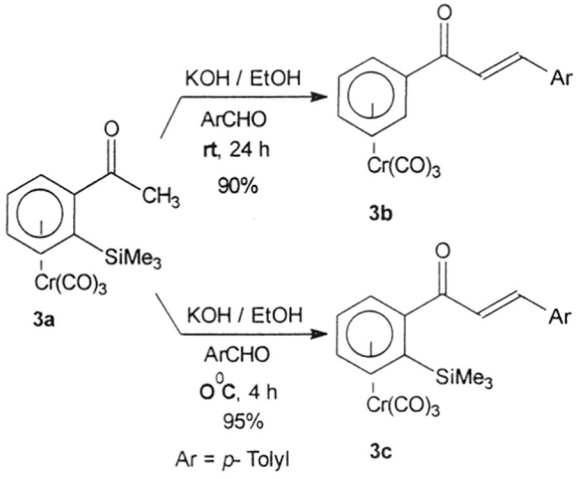


Cleavage of the Ar-Si bond at an appropriate stage by protiolysis or conversion of $SiMe_3$ group to a useful functionality has direct impact on the efficiency of a synthetic plan. This aspect has been addressed in the work described herein.

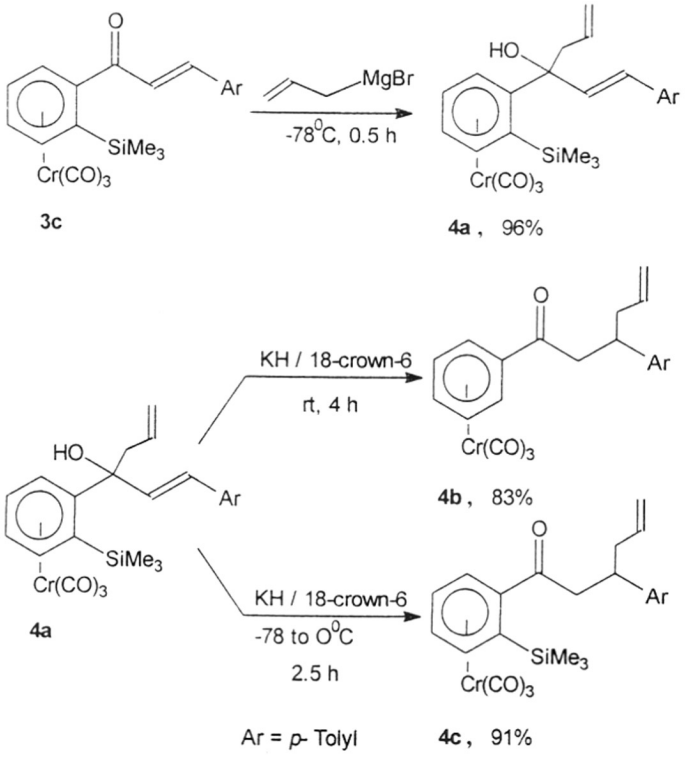
Present Work

The study originated from the following two observations[5] of facile cleavage of Ar-$SiMe_3$ bond, while attempting standard organic transformations like aldol-dehydration (Scheme-3) and anion assisted Cope rearrangement (Scheme-4). In both instances, desilylation could be suppressed only at low temperatures.

Scheme-3



Scheme-4

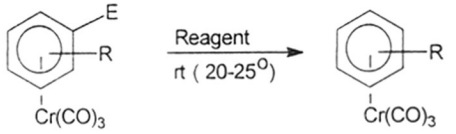


While the facility of Ar-Si bond cleavage can be attributed to stabilization of an anionic aryl group complexed with tricarbonylchromium, this observation sounds a note of caution for the use of nucleophilic bases in reactions with such substrates.

We found that several common bases used in organic reactions readily effected desilylation of a chromium-complexed aromatic ring (Scheme-5). However, desilylation does not readily occur for uncomplexed arylsilanes except with fluoride ion catalysis,[6] or when

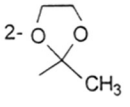
strong electron-withdrawing substituents are present on the aromatic ring.[7]

Scheme-5



5a-i **5a'-g'**

Table-1: Desilylation of complexed aromatic ring

Substrate	R	Reagent	Time(h)	Product	Yield(%
5a	H	A	1.25	**5a'**	77
E = $SiMe_3$		B	4.00		89
		C	5.50		70
		D	60.00		66
		E	48.00		72
5b	2-$COCH_3$	A	2.00	**5b'**	98
E = $SiMe_3$		B	2.25		92
		C	2.50		91
		D	24.00		89
		E	32.00		84
5c		A	2.00	**5c'**	91
E = $SiMe_3$		B	6.00		76
5d	2- OMe	A	1.25	**5d'**	87

E = $SiMe_3$		B	4.00		92.5
5e	4- OMe	A	1.50	**5d'**	78
E = $SiMe_3$		B	4.50		81
5f	4- Me	A	1.00	**5e'**	78
E = $SiMe_3$		B	3.50		75
5g	2,6- $(OMe)_2$	A	0.75	**5f'**	92
E = $SiMe_3$		B	3.50		92
5h	4-O-(4-$C_6H_4SiMe_3$)	A	3.00	**5g'**	91
E = $SiMe_3$		B	5.00		89
5i	H	A	1.00	**5a'**	91
E = $SnMe_3$		B	2.50		86
		D	9.00		88

Reagents: **A** = *KH / 18-Crown-6 / ether*; **B** = *50% aq NaOH /Tetrabutylammonium bromide (TBAB), 10 mol% / CH_2Cl_2*; **C** = *K_2CO_3 / 18-Crown-6 / acetone*; **D** = *KOH / EtOH*; **E** = *NaOMe / ether.*

We observed that potassium hydride in the presence of a catalytic quantity of 18-crown-6 (reagent-A) effected desilylation in ether in a short period of time. The PTC was always used to ensure maximum efficiency of the reaction. In a typical run, a suspension of potassium hydride in ether was added dropwise to a stirred solution of the complexed arylsilane and 18-crown-6 (10 mol%) in ether. Complete conversion of the substrate was observed (TLC) in all cases. The reaction course remained virtually unchanged when an ether solution of the complex was added to a suspension of potassium hydride in ether containing 10 mol% 18-crown-6. After completion of

the reaction it was quenched with degassed water at ice-cold condition and then extracted with ether. Crude product obtained after removal of ether was purified by column chromatography. Sodium hydride can replace potassium hydride. Potassium or sodium hydride is believed to act as a nucleophile[8] which reacts with the tetrasubstituted silicon to initiate desilylation. In Complex **5h**, $SiMe_3$ on uncomplexed ring remained unaffected during desilylation of the complexed ring. Under biphasic condition (reagent-B), desilylation was found to reach completion within three to six hours. Other mild bases like K_2CO_3, KOH, NaOMe can also be used for desilylation (Table-1; reaction of compounds- **5a** and **5b**). Tertiary amines like triethylamine, DBU or DABCO were not effective. Destannylation was observed when an $SnMe_3$ group was present on the complexed aromatic ring instead of $SiMe_3$ group (Table - 1; complex **5i**).

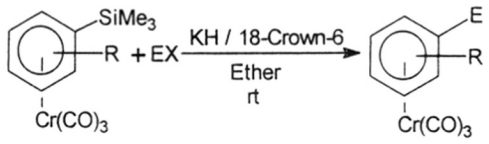
The aryl anion stabilized by co-ordination with a $Cr(CO)_3$ group was expected to be trapped regiospecifically by electrophiles. In absence of any other electrophile, solvent DMF itself reacts with the aryl anion to afford the corresponding aromatic aldehyde complex in good yield (70-90%), along with some protiodesilylated product (5-15%), as presented in the Scheme-6 and Table-2.

Direct complexation of aromatic aldehydes with $Cr(CO)_6$ using conventional thermal method[9] is difficult due to thermal instability of the organic ligands and electron withdrawing nature of formyl group.[10] The present method of formylation is, therefore, a clearly acceptable solution to this problem. Tricarbonylchromium complexes of a wide

range of substituted aromatic aldehydes can now be conveniently prepared.[4(a),11]

This approach was readily adapted for introduction of electron-withdrawing functional groups (other than formyl) to the aromatic nucleus. When tricarbonylchromium complex of phenyltrimethylsilane (**5a**) was allowed to react with electrophiles like ketone, dialkyl or diaryl carbonate in presence of KH / 18-crown-6 in ether, desired product complexes were obtained in moderate to good yields (see Table-2). However, protiodesilylation could not be completely suppressed in these reactions. When DMF was used as solvent[12] this reaction proceeded much faster but formylation (20-50%) was always a competing reaction in DMF.

Scheme-6



5a, 5d-g **6a-k**

Table-2 : Desilylation-Functionalization of complexed arylsilanes

Substrate	R	EX	Time(h)	Product	E	Yield(%)
5a	H	DMF*	1.0	**6a**	CHO	70 (15)
5d	2 - OMe	DMF*	1.5	**6b**	CHO	70 (10)
5e	4 - OMe	DMF*	1.5	**6c**	CHO	84 (6)
5f	4 - Me	DMF*	1.0	**6d**	CHO	90 (<5)
5a	H	$(MeO)_2CO$	8.0	**6e**	CO_2Me	81 (13)
5a	H	$(EtO)_2CO$	10.0	**6f**	CO_2Et	73 (9)
5a	H	$(PhO)_2CO$	7.0	**6g**	CO_2Ph	75 (10)
5a	H	Ethylene Carbonate	10.0	**6h**	$CO_2(CH_2)_2OH$	78 (10)
5a	H	Ph_2CO	12.0	**6i**	$C(OH)Ph_2$	85 (<5)
5a	H	$PhCOCF_3$	4.0	**6j**	$C(OH)PhCF_3$	80 (10)
5g	2,6-$(OMe)_2$	DMF*	2.5	**6k**	CHO	74 (15)

b: *Numbers in parentheses indicate percentage yields of protiodesilylated products.* * DMF *was used as solvent.*

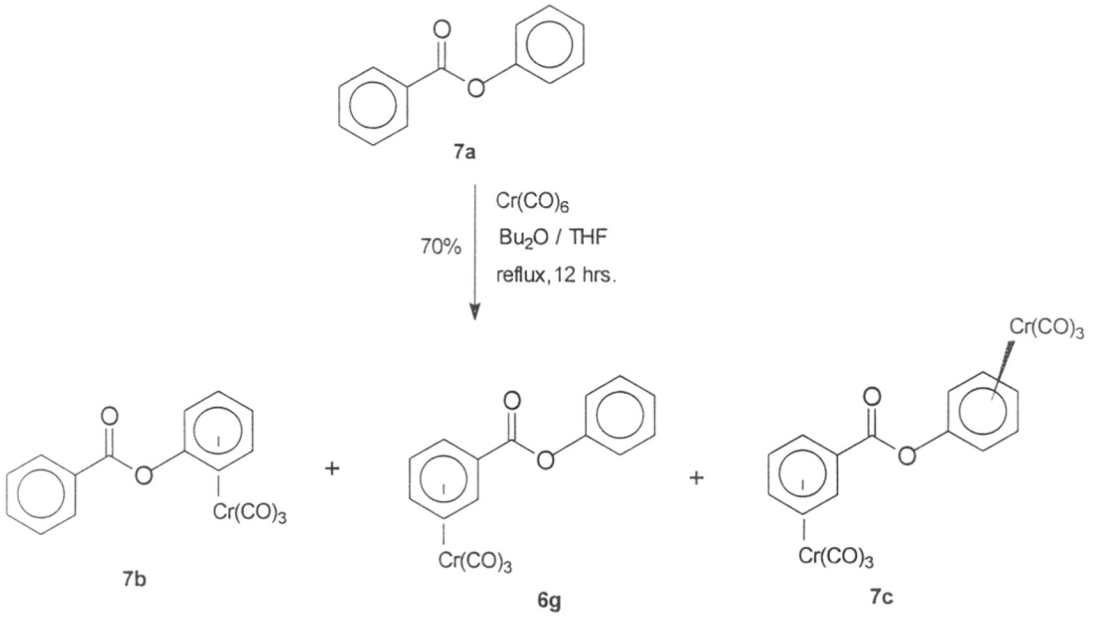
In a typical procedure, a suspension of potassium hydride (1.2-1.3 equiv) in ether was added dropwise to a solution of complexed arylsilane, electrophile, and 18-crown-6 (0.1 equiv) in ether at room temperature. In case of formylation DMF itself used as solvent. In all the cases complete consumption of the substrate was observed (TLC). Work up involved quenching of excess potassium hydride with water at 0°C followed by extraction with diethyl ether. Crude product

obtained after removal of diethyl ether was purified by column chromatography followed by recrystalization.

Another advantage of the method can be highlighted. It is known that direct thermal complexation of a substrate containing more than one aromatic ring with $Cr(CO)_6$ always gives a mixture of products.[13] For instance, Thermal complexation of phenyl benzoate (Scheme-7) resulted in a mixture of three products (**7b**: **6g**: **7c** = 15 : 10 : 1). In the first major product **7b**, $Cr(CO)_3$ is anchored on electron rich phenoxy ring; in second major product **6g** the metal is attached to a different ring. In minor product **7c**, both rings are complexed to $Cr(CO)_3$.

Using the present method, pure complex **6g** could be readily obtained when desilylation was carried out in presence of diphenyl carbonate (Scheme-6). Similarly, by proper choice of substrate and electrophile, it is possible to prepare a compound in which only the desired aromatic ring is complexed to tricarbonylchromium (see Table-2, complex: **6i**, **6j**).

Scheme-7

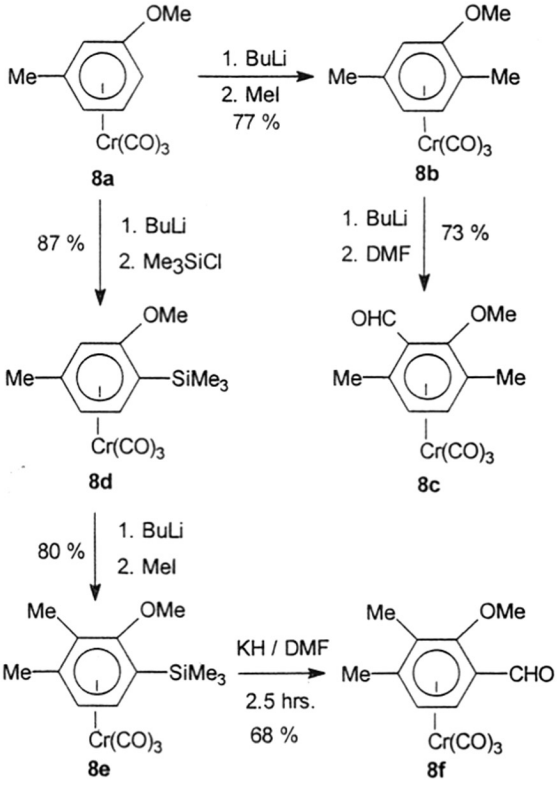


7b : 6g : 7c = 15 : 10 : 1

One important aspect of this method of functionalization is its complete regioselectivity. Scheme-8 summarizes two routes to regioisomeric aromatic products. Normal *ortho*-lithiation of complex **8a** occurred at the sterically less congested site, and addition of methyl iodide led to the corresponding methyl substituted derivative **8b**. Subsequent treatment with BuLi generated aryl anion at the alternative site (adjacent to OMe group), where formylation could be readily effected to produce aldehyde **8c**. To obtain a regioisomer of this aldehyde, the first *ortho*-lithiated derivative from **8a** was treated with Me_3SiCl so that a silylated product **8d** was obtained. A second

lithiation-alkylation led to the derivative **8e**. Now, the trimethylsilyl group was transformed to a formyl group by the procedure described earlier, so that the complex **8f**, isomer of complex **8c**, was obtained. This sequence uses the trimethylsilyl unit as a site-protective group as well as a precursor of formyl function.

Scheme-8



As an usual precaution, the reactions were all performed under an inert atmosphere of argon. Inadventitious exposure to oxygen led to the following interesting and useful observation.

When desilylation was carried out using 1.0-1.2 equiv. KH and 10 mol% of 18-crown-6 in the presence of an aromatic aldehyde under *an atmosphere of dry argon,* the major product was the expected carbinol (70-88%) contaminated with a small amount (5-15%) of protiodesilylated product (Scheme -9; Table-3). In these reactions, DMF was used as solvent.[14] Interestingly, there was no perceptible reaction with DMF. The desilylated species reacted much faster with the aromatic aldehyde than with DMF. Reactions of aromatic aldehydes with *ortho* substituted arylsilanes (substrate-**5d**, **9e**, **9f**) were moderately diastereoselective[15] (diastereomeric ratios in **10j**, **10k**, **10l** are 5:1, 4:1, 4.5:1 respectively). In all the cases diastereoisomers were separable by column chromatography.

Scheme-9

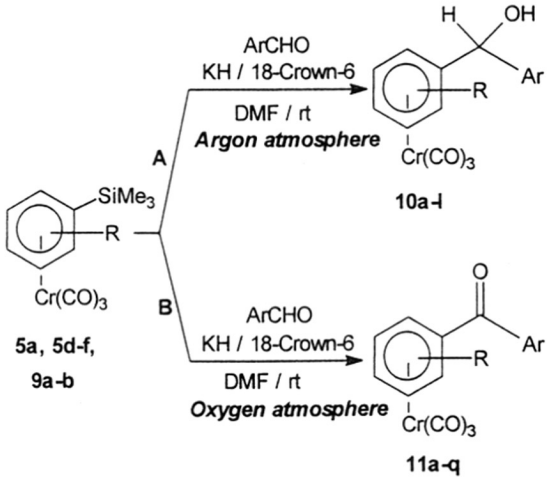


Table-3 : Desilylation and Reaction with aromatic aldehyde under an atmosphere of Argon and Oxygen

Entry	Substrate	R	Ar	Condition	Time (hr)	Product	Yield (%)[a]
1	**5a**	H	C_6H_5	**A**	0.5	**10a**	78 (10)
				B	0.5	**11a**	81 (14)
2	**5a**	H	4-Me C_6H_4	**A**	0.5	**10b**	70 (10)
				B	0.75	**11b**	90 (6)
3	**5a**	H	2-Thienyl	**A**	0.5	**10c**	80 (6)
				B	0.5	**11c**	78 (9)
4	**5a**	H	$Cr(CO)_3C_6H_5$	**A**	0.25	**10d**	80 (10)
				B	0.25	**11d**	89 (9)
5	**5a**	H	2-Pyridyl	**A**	0.5	**10e**	80 (<5)
				B	0.5	**11e**	77 (13)
6	**5e**	4-OMe	4-OMe C_6H_4	**A**	0.5	**10f**	70 (10)
				B	0.5	**11f**	70 (10)
7	**5a**	H	2-Furyl	**A**	0.5	**10g**	76 (12)
				B	0.5	**11g**	90 (<5)
8	**5f**	4-Me	4-Me C_6H_4	**A**	0.5	**10h**	82 (<5)
				B	0.5	**11h**	75 (10)
9	**5a**	H	4-Cl C_6H_4	**A**	0.5	**10i**	77 (<5)
				B	0.5	**11i**	78 (10)

10	**5d**	2-OMe	C_6H_5	**A**	0.5	**10j**[b]	80 (10)
				B	0.75	**11j**	80 (<5)
11	**9a**	2-Me	C_6H_5	**A**	1.0	**10k**[b]	88 (6)
12	**9b**	2-Cl	C_6H_5	**A**	0.5	**10l**[b]	87 (<5)
13	**5a**	H	4-OMe C_6H_4	**B**	0.5	**11k**	79 (6)
14	**5a**	H	Ferrocenyl	**B**	0.5	**11l**	77 (10)
15	**5a**	H	2-Cl C_6H_4	**B**	0.5	**11m**	74 (10)
16	**5a**	H	4-NMe_2 C_6H_4	**B**	0.75	**11n**	81 (13)
17	**5e**	4-OMe	C_6H_5	**B**	0.5	**11o**	72 (10)
18	**5a**	H	2-OMe	**B**	0.5	**11p**	77 (<5)
19	**5a**	H	4-NO_2 C_6H_4	**B**	0.25	**11q**	90 (<5)
20	**5a**	H	2-Furyl	**B**[c]	2.5	**10g**[d]	74 (10)
21	**5b**	4-OMe	4-OMe C_6H_4	**B**[c]	3.0	**10f**[d]	70 (10)
22	**5a**	H	C_6H_5[e]	**A**	0.5	**10a**	75 (10)
23	**5d**	2-OMe	C_6H_5[e]	**A**	0.5	**10j**	78 (10)

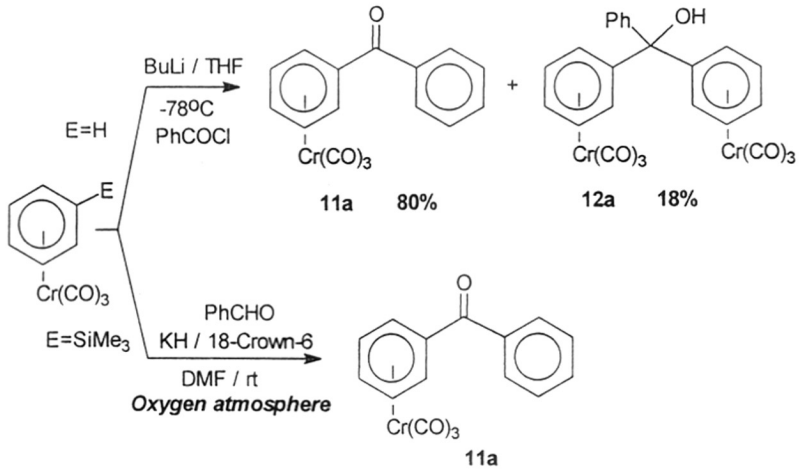
a: *Numbers in the parenthesis indicate percent yield of protiodesilylated products. b: Mixture of two diastereoisomers, which were separated by chromatography; Yields mentioned for two diastereoisomers together. c: Cesium fluoride was used instead of potassium hydride. d: Even after stirring for ten hours corresponding ketone was obtained in less than 5% yield. e: In addition to benzaldehyde, equivalent amount of ethyl benzoate and 2,2,2-trifluoroacetophenone were added.*

However, when the same reaction was carried out with 2.0-2.2 equiv. potassium hydride under *an atmosphere of dry oxygen*, the major product was a biaryl ketone, **11a-q,** (70-90%) instead of a carbinol (Scheme-9, Table-3). In a typical procedure, potassium hydride was added dropwise as suspension in ether to a solution of the substrate, the aldehyde and a catalytic amount of 18-crown-6 in DMF at room temperature. In most of the reactions (Table-3, entry- 1, 2, 3, 5, 6, 7, 8, 9, 10, 11, 12, 13, 15, 16, 17, 18, 19), a deep blue-green color developed instantly on addition of the potassium hydride suspension, which persisted for a few minutes before changing to the deep red color of the ketone complex. In some cases the color change (from blue-green to red) was almost instantaneous. When Ar is ferrocene or $(CO)_3CrC_6H_4$ (entry-4, 14) the blue-green color was probably masked by the intense color of the aldehydes. Rate of this reaction was comparatively slow in ether or THF in which appreciable amount of decomplexation of both the starting material and the product was observed. The reactions in DMF, on the other hand, were complete in less than an hour with minimal oxidative decomplexation.

This method has certain advantages over the existing ones reported in the literature. For instance, direct thermal complexation of biaryl methanols and biaryl ketones following Pauson-Mahaffy method[16] always produce mixture of all possible mono- as well as *bis*-tricarbonyl chromium complexes.[17] Using our method, it is possible to control and direct metal complexation to a desired aromatic ring .

Secondly, we observed that lithiation of benzene tricarbonylchromium followed by quenching with benzoyl chloride resulted in a mixture of two products (Scheme-10). The major product was **11a** (80%) and minor product was identified as the carbinol **12a** (18%) (generated from an additional equivalent of lithiated species and complex **11a**). Formation of such side product can be avoided following our method of tandem desilylation-nucleophilic addition-oxidation.

Scheme-10



The third and significant advantage of this method is that the desilylated species can tolerate sensitive groups such as NO_2 (Table-3, entry-19). Grignard or organolithium reagents are not compatible.[18] In

an earlier attempt,[17] Top and Jaouen failed to prepare complex **11q** from 4-nitrobenzophenone applying direct thermal complexation. The mild conditions of the present reaction affords **11q** readily in 90% yield.

Desilylated species can also react chemoselectively with the aldehyde function in presence of ketone or ester functionality. To illustrate this, when substrate **5a** and **5d** were separately subjected to the reaction condition **A** in the presence of equivalent amounts of benzaldehyde, ethyl benzoate and 2,2,2-trifluoroacetophenone, only **10a** and **10j** were obtained in 75% and 78% yield respectively (Table-3, entry- 22, 23).

The likely mechanism appears to involve potassium hydride as a *nucleophile* in the desilylation step,[8,19] and as a *base* in the autoxidation reaction.[20] Sodium hydride worked equally well. While aqueous alkali metal hydroxides were able to effect desilylation, the desilylated aryl species underwent proton quench in aqueous medium before reacting with an electrophile. Attempted autoxidation using fluoride produce a very small amount (<5%) of ketone after ten hours (Table-3, entry- 20, 21).

Expectedly, the complexed carbinols **10a-e** afforded the corresponding ketone complexes when treated with 1.0-1.2 equiv. potassium hydride under *oxygen atmosphere* (Scheme-11). The deep blue-green color developed instantly on addition of potassium hydride suspension and ultimately turned to red. Biphasic autoxidation of carbinols could also be effected with 50% aqueous sodium hydroxide

in presence of tetrabutylammonium bromide (TBAB) as phase transfer catalyst, albeit with a lesser efficiency (Scheme-11).

Scheme -11

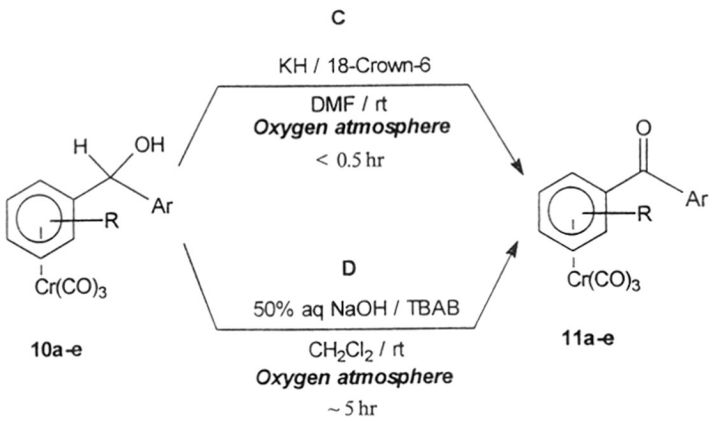


Table-4 : Autoxidation of Benzyhydrols to Benzophenones

Substrate	Ar	Condition	Time(hr)	Product	Yield(%)
10a	C_6H_5	**C**	0.25	**11a**	80
10a	C_6H_5	**D**	5.0	**11a**	71
10b	4-Me C_6H_4	**C**	0.25	**11b**	72
10b	4-Me C_6H_4	**D**	4.5	**11b**	69
10c	2-Thienyl	**C**	0.25	**11c**	83
10c	2-Thienyl	**D**	5.5	**11c**	78

10d	$(CO)_3C_6H_5$	**C**	0.25	**11d**	82
10d	$(CO)_3C_6H_5$	**D**	4.5	**11d**	73
10e	2-Pyridyl	**C**	0.25	**11e**	90
10e	2-Pyridyl	**D**	6.0	**11e**	82

Oxidative processes involving reactions of molecular oxygen with organic substrates is well known. But, autoxidations are not often used for preparative purposes since they frequently result in a complex mixture of products.[21] However, the autoxidation described above is a preparatively useful reaction. Mild condition and short reaction time permit tricarbonylchromium group to stay even in the presence of oxygen. Though base catalysed autoxidation of benzohydrol to benzophenone was studied[20] with a catalytic quantity of anthraquinone and stoichiometric amount of aluminium-*t*-butoxide, little is known about the autoxidation of biaryl methanols and their synthetic utility in general.

Benzhydrol or benzophenone complexes when exposed to light and oxygen it decomplexed to benzhydrols and benzophenones in almost quantitative yields. Thus from the various combination of complexed arylsilanes and aromatic aldehydes it is possible to synthesize a large number of polyfunctional biaryl methanols and biaryl ketones. Importance of biaryl ketones as speciality chemicals has been highlighted in a recent review.[22] For instance, benzophenone, the most familiar member of biaryl ketone family, is a

useful triplet-sensitizer in organic photochemistry, as well as a fixative for heavy perfumes, such as geranium or newmown hay, especially when used in soaps. It is also a useful precursor for the manufacture of antihistamines, hypnotics, insecticides *etc.*[22,23] Symmetrical biaryl ketones and some of their immediate derivatives are frequently used for absorption of ultraviolet light in paints and plastics. The biaryl, aryl-heteroaryl ketone moieties occur in many natural (papaveraldine, cotain, *etc.*) and biologically active, synthetic molecules (ketoprofen, suprofen, isoxepac, ketorolac, amfenac, zomepirac, *etc.*). Mexeone, oxybenzone, octabenzone, salisobenzone, *etc.* are used in ultra-violet screens. Anthraquinone and Michler's ketone are important starting materials for the manufacture of dyes.

Summary

In summary, we have disclosed a facile cleavage of an Ar-$SiMe_3$ bond where the aromatic ring is complexed with tricarbonylchromium, by nucleophilic bases. Potassium or sodium hydride effects a clean reaction in aprotic medium. It is possible to trap the intermediate anionic species by different electrophiles to prepare metal-complexed arenes with electron-withdrawing functional groups. A second development, the tandem desilylation-nucleophilic addition-oxidation method, should prove to be a useful synthetic method for biaryl ketones since chromium survives this oxidative condition. The high-point of this desilylation - functionalization protocol is its mild condition and high functional group tolerance – a feature that complements normal aryl-metal reactions to attain sensitive targets. Unlike fluoride, these nucleophilic bases are selective for the desilylation of complexed aromatic ring in presence of an uncomplexed silylated one.

Experimental

All reactions except autoxidatios were performed under an inert atmosphere of argon, using freshly distilled, degassed solvents. Autoxidations were performed under a dry atmosphere of oxygen. DMF was purified by distillation over calcium hydride under reduced pressure. Diethyl ether, dibutyl ether and THF were freshly distilled over sodium benzophenone ketyl. Chromium hexacarbonyl and 18-crown-6 were purchased from Aldrich and used as received. Potassium hydride and sodium hydride were also purchased from Aldrich and both were washed with portions of hexane and anhydrous diethyl ether immediately before use. Chlorotrimethylsilane was distilled over zinc powder under argon, prior to use. Dimethyl and diethyl carbonate were distilled under reduced pressure. A solution of n-BuLi in hexane (*ca.* 1.5 M) was prepared using standard procedure and titrated prior to use.[26]

Preparation of 3b and 3c:

The o-trimethylsilylacetophenone complex **3a**[3] (328 mg, 1mmol) and *p*-tolualdehyde (240 mg, 2mmol) were dissolved in distilled and degassed EtOH (20 mL). It was cooled to <0°C in an ice-salt bath. Ethanolic KOH (112 mg KOH in 8 mL EtOH) was then added to this cooled solution dropwise. The color of the solution started darkening. Reaction was complete within four hours (TLC). Ethanol was removed under reduced pressure and the mixture extracted with

dichloromethane. The organic fractions were dried over Na_2SO_4 and solvent evaporated to afford complex **3c** (408.5 mg, 95%). When the same reaction was performed at room temperature (~ 25°C) for 24 hours, complex **3b** was obtained (322.2 mg, 90%).

Complex 3b:

Color :	red
MP:	m.p. 140-142°C
IR ($CHCl_3$):	1980, 1925 (br), 1680, 1600 cm^{-1}
^1H NMR ($CDCl_3$) : (200 MHz)	2.45 (s, 3H), 5.35 (t, 2H, *J*=6.5 Hz), 5.66 (t, 1H, *J*=6.5 Hz), 6.2 (d, 2H, *J*=6.5 Hz), 7.06-7.40 (m, 3H), 7.55 (d, 2H, *J*=7.1Hz), 7.90 (d, 1H, *J*=16 Hz).
^{13}C NMR ($CDCl_3$): (50.3 MHz)	21.78, 89.73, 94.54, 95.14, 98.01, 118.00, 128.94, 130.02, 131.96, 141.88, 145.86, 186.88, 231.05
Analysis:	For $C_{19}H_{14}O_4Cr$: Calcd : C: 63.68, H: 3.91 Found : C: 63.55, H: 3.90

Complex 3c:

Color :	red
MP:	m.p. 148°C
IR ($CHCl_3$):	1980, 1920, 1660, 1620 cm^{-1}
^1H NMR ($CDCl_3$) : (200 MHz)	0.40 (s, 9H), 2.40 (s, 3H), 5.45 (m, 1H), 5.60 (m, 2H), 5.75 (d, 1H, *J*=6.2Hz), 7.10-7.25 (m, 3H), 7.55 (d, 2H, *J*=9 Hz), 7.85 (d, 1H, *J*=16.2 Hz),
^{13}C NMR ($CDCl_3$): (50.3 MHz)	0.71, 21.80, 92.91, 93.40, 99.00, 101.36, 108.34, 120.25, 128.9, 130.0, 131.80, 142.01, 146.11, 191.45, 232.10.

Analysis: For $C_{22}H_{27}O_4SiCr$:
Calcd: C: 61.38, H: 5.15
Found : C: 61.10, H: 5.15

Preparation of 4a :

Allyl magnesium bromide was freshly prepared by dropwise addition of allyl bromide (0.4 mL, 5 mmol) to magnesium turnings (300 mg, 12.5 mmol) activated by iodine in diethyl ether (5 mL). The reagent (ca 1.2 mL, ~1.2mmol) was added dropwise to a solution of the enone **3c** (430 mg, 1 mmol) in dry THF (10 mL) at -78°C. Reaction was completed after 30 minutes (TLC). It was quenched with degassed water at 0°C and extracted with dichloromethane. Removal of solvent under reduced pressure followed by flash column chromatography (15% ethylacetate-petroleum ether) afforded pure alcohol **4a** (453.2 mg, 96%).

Complex 4a:

Color : yellow

MP: m.p. 164°C

IR ($CHCl_3$): 1960, 1880 cm^{-1}

^1H NMR ($CDCl_3$) : (200 MHz) 0.45 (s, 9H), 2.40 (s, 3H), 2.45 (s, 1H), 2.75 (m, 2H), 5.10 (m, 2H), 5.25 (m, 2H), 5.60 (t, 1H, *J*=6.2Hz), 5.70-5.95 (m, 2H), 6.40 (d, 1H, *J*=16Hz), 6.75 (d, 1H, *J*=16 Hz), 7.20 (d, 2H, *J*=9 Hz), 7.40 (

d, 2H, *J*=9 Hz).

^{13}C NMR ($CDCl_3$): (50.3 MHz) 3.7, 21.4, 49.2, 76.3, 89.8, 90.0, 102.1, 121.0, 126.1, 126.9, 129.4, 129.6, 131.3, 132.7, 133.6, 138.2, 233.4

Analysis: For $C_{25}H_{28}O_4SiCr$:
Calcd: C: 63.54, H: 5.97
Found : C: 63.21, H: 5.90

Preparation of 4b and 4c:

To a cooled (-78°C) suspension of potassium hydride (35% dispersion in meneral oil, 57 mg, 0.5 mmol) in anhydrous ether (5 mL) solution of alcohol **4a** (236 mg, 0.5 mmol) in ether (10 mL) was added dropwise with stirring. A catalytic amount of 18-crown-6 (13 mg, 0.05 mmol) was then added. Reaction was slowly warmed upto 0°C. During which period (about 2.5 h) reaction was completed (TLC). It was quenched with degassed methanol at 0°C and finally extracted with ether. Purification by flash column chromatography afforded the ketone **4c** (215 mg, 91%). When the same reaction was performed at room temperature (~ 25°C) for four hours, desilylated ketone **4b** was formed (196 mg, 83%).

Complex 4b:

Color :	red
MP:	m.p. 162°C
IR ($CHCl_3$):	1990, 1935, 1680 cm^{-1}
^1H NMR ($CDCl_3$) : (200 MHz)	2.35 (s, 3H), 2.41 (t, 2H, *J*=7.2 Hz), 3.05 (m, 2H), 3.42 (m, 1H), 4.92-5.10 (m, 2H), 5.12-5.37 (m, 2H), 5.60-5.82 (m, 2H), 5.95 (d, 1H, *J*=6.2 Hz), 6.07 (d, 1H, *J*=6.2 Hz). 7.15 (s, 4H).
^{13}C NMR ($CDCl_3$): (50.3 MHz)	21.23, 40.89, 43.55, 88.64, 94.32, 95.16, 117.87, 126.76, 127.11, 127.98, 129.89, 147.12, 141.34, 197.32, 231.34
Analysis:	For $C_{22}H_{20}O_4Cr$: Calcd : C: 66.00, H: 5.00 Found : C: 65.88, H: 5.12

Complex 4c:

Color :	red
MP:	gummy oil
IR ($CHCl_3$):	1980, 1920, 1700 cm^{-1}
^1H NMR ($CDCl_3$) : (200 MHz)	0.45 (s, 9H), 2.30 (s, 3H), 2.45 (t, 2H, *J*=8 Hz), 3.05 (m, 2H), 3.40 (m, 1H), 4.90-5.15 (m, 2H), 5.40-5.50 (m, 3H), 5.60-5.80 (m, 2H), 7.20 (bs, 4H),
^{13}C NMR ($CDCl_3$): (50.3 MHz)	0.47, 20.9, 29.7, 40.3, 40.7, 43.9, 91.7, 93.2, 93.3, 98.2, 116.9, 127.4, 129.2, 136.0, 136.3, 199.6, 231.4
Analysis:	For $C_{25}H_{28}O_4SiCr$: Calcd: C: 63.54, H: 5.97 Found : C: 63.57, H: 5.83

General procedure for preparation of Tricarbonyl(η^6-arylsilane or arylstannane)-chromium(0) complexes:

Parent arenes of all five complexes[7,25a-b] (**5a**, **5d-f** and **5i**) were prepared by literature methods from appropriate bromo compounds *via* Grignard reaction followed by quenching with chlorotrimethylsilane (in case of **5a, 5d, 5e, 5f**) or chlorotrimethyltin (in case of **5i**). The arene and chromium hexacarbonyl were thermolysed in a mixture of dibutyl ether-THF (10:1) (bath temperature: 150°C) for 12 to 24 hours to prepare the complexes, as described in standard procedure.[9] The complexes **5b** and **5c** were prepared following reported procedures[3a].

Preparation of Tricarbonyl[η6-2-trimethylsilyl resorcinol dimethylether] chromium(0) (5g):

A hexane solution of n-BuLi (1.56 M, 1.3 mL, 2.0 mmol) was added dropwise to a cooled (-78°C) solution of tricarbonyl[η6-resorcinol dimethylether]chromium(0)[25c] (548 mg, 2.0 mmol) in THF (15 mL) and the mixture was stirred at -78°C for 2h. Chlorotrimethylsilane (218 mg, 0.3 mL, 2 mmol) was added and stirring was continued (-78°C, 2h) to ensure complete reaction. Degassed methanol (5 mL) was slowly added to quench the reaction and the mixture was allowed to reach room temperature. Solvent was evaporated to afford the crude complex, which was purified by column chromatography. Recrystallisation from dichloromethane-hexane gave the title compound as yellow crystals (554 mg, 80%).

Complex 5g:

Color :	Yellow
MP:	145°C
IR ($CHCl_3$):	1960, 1860 cm^{-1}
^1H NMR ($CDCl_3$) : (200 MHz)	0.35 (s, 9H), 3.70 (s, 6H), 4.72 (d, 2H, *J*=6.5Hz), 5.73 (t, 1H, *J*=6.5Hz)
^{13}C NMR ($CDCl_3$): (50.3 MHz)	1.8, 55.6, 70.0, 81.1, 93.6, 148.7, 234.5 ;;
Analysis:	For $C_{14}H_{18}O_5SiCr$: Calcd: C: 48.55, H: 5.24 ; Found : C: 48.51 , H: 5.32 .

Preparation of Tricarbonyl [η6-4-trimethylsilylphenylether] chromium(0) (5h):

Grignard reaction of 4-bromophenyl ether (10g, 0.03 mol) and magnesium (0.063 mol) in ether (25 mL) followed by quenching with trimethylsilyl chloride (7g, 0.065 mol) gave 4-trimethylsilylphenyl ether as colorless oil (7g, 73%)

4-trimethylsilylphenyl ether

Color :	colorless
BP:	150°C (Kugelrohr bath temp.) / 1.0 mm
IR ($CHCl_3$):	3020, 1580, 1480 cm^{-1}

^{1}H NMR ($CDCl_3$) :	0.45 (s, 18H), 7.17 (d, 4H, *J*=8.6Hz),
(200 MHz)	7.66 (d, 4H, *J*=8.6Hz)
^{13}C NMR ($CDCl_3$):	^{13}C NMR ($CDCl_3$): -0.68, 129.90, 134.60,
(50.3 MHz)	135.10, 158.13
Mass:	M^+ = 314

4-Trimethylsilylphenyl ether was (3g, 9.55 mmol) subjected to complexation under standard condition using chromium hexacarbonyl (3g, 13.6mmol), dibutyl ether (100mL) and THF (10mL) to yield the title compound **5h** as yellow crystals (1.85g, 43%).

Complex 5h:

Color :	Yellow
MP:	m.p. 93-95°C
IR ($CHCl_3$):	1960, 1880 (br), 1590, cm^{-1}
^{1}H NMR ($CDCl_3$) :	0.29 (s, 9H), 0.31 (s, 9H), 5.10 (d, 2H, *J*=6.4Hz), 5.54
(200 MHz)	(d, 2H, *J*=6.4Hz), 7.19 (d, 2H, *J*=8.1Hz), 7.50 (d, 2H, *J*=8.1Hz)
^{13}C NMR ($CDCl_3$):	-0.83, -0.32, 80.0, 94.14, 99.70, 120.85, 135.56,
(50.3 MHz)	138.47, 143.77, 153.90, 233.60
Analysis:	For $C_{21}H_{26}O_4Si_2Cr$:
	Calcd: C: 55.98, H: 5.82
	Found : C: 56.06, H: 5.90

General procedure for desilylation:

Using reagent A (KH /18-Crown-6 /ether): To a solution of the complex (n mmol) and 18-Crown-6 (10 mol%) in ether (5n mL), a suspension of KH (1.2-1.3n mmol) in ether (3n mL) was added dropwise with stirring at room temperature. After complete consumption of starting material (TLC), the reaction was quenched with degassed water at 0-5 °C and the product was extracted with ether.

Using reagent B (50% aq NaOH / TBAB / CH_2Cl_2): To a solution of the complex (n mmol) and tetrabutylammonium bromide (TBAB, 10 mol%) in CH_2Cl_2 (3n mL), 50% aq NaOH (n mL) was added dropwise with stirring at room temperature. After completion of reaction (TLC) it was diluted with water and extracted with dichloromethane.

Using reagent C (K_2CO_3 / 18-Crown-6 / acetone): A solution of the complex (n mmol) in acetone (5n mL) was added dropwise to a stirred suspension of K_2CO_3 (1.5n mmol) and 18-Crown-6 (10 mol%) in acetone (3n mL) at room temperature. After completion of the reaction (TLC), inorganic salts were removed by filtration. Crude complex obtained after evaporation of acetone was purified by chromatography followed by crystallization.

Using reagent D (KOH / EtOH): To a solution of the complex (n mmol) in EtOH (5n mL), 1.5n mmol KOH in ethanol (1 mL) was added dropwise with stirring at room temperature. After completion of reaction (TLC), the reaction mixture was diluted with water and the product was extracted with dichloromethane.

Using reagent E (NaOMe /ether): A solution of the complex (n mmol) in ether (5n mL) was added dropwise to the stirred suspension of NaOMe (1.5n mmol) in ether (3n mL) at room temperature. After completion of reaction it was quenched with degassed water under ice-cold condition and extracted with ether.

In all the cases reactions were performed in 0.5-2.0 mmol scale. Purification of products were done by column chromatography (10-20% ethyl acetate in Petroleum ether) followed by crystallization (dichloromethane/petroleum ether). Yields of isolated pure products were indicated in Table-1.

Several of the desilylated products have been reported earlier : **Complex 5a′, 5b′, 5d′, 5e′ :** ref. 25(d), **Complex 5c′:** ref. 3a, **Complex 5f′:** ref. 25(c).

Complex 5g':

Color :	Yellow
MP:	140^{0}C
IR ($CHCl_3$):	1985, 1915 (br) cm^{-1}
^{1}H NMR ($CDCl_3$) : (200 MHz)	0.3 (s, 9H), 4.89 (t, 1H, *J*=6.3Hz); 5.15 (d, 2H, *J*=6.3Hz), 5.55 (t, 2H, *J*=6.3Hz), 7.17 (d, 2H, *J*=8.5Hz), 7.51 (d, 2H, *J*=8.5Hz)
^{13}C NMR ($CDCl_3$): (50.3 MHz)	-1.20, 76.93, 85.62, 94.26, 120.31, 135.20, 136.13, 142.04, 153.48, 232.85
Analysis:	For $C_{18}H_{18}O_4SiCr$: Calcd: C: 57.13 , H: 4.79 Found : C: 57.10 , H: 4.85.

General procedure for the functionalization of $Cr(CO)_3$ complexed arylsilanes:

To a solution of the complexed arylsilane (n mmol), electrophile (1.5n mmol) and 18-crown-6 (10 mol%) in ether (5n mL), a suspension of KH (1.2-1.3n mmol) in ether (3n mL) was added dropwise with stirring at room temperature. When the electrophile was DMF, it was used as the solvent as well. After completion of the reaction (time mentioned in Table-2), the reaction mixture was quenched with degassed water at ice- cold temperature and extracted with ether. The crude product obtained after evaporation of solvent was purified by column chromatography. In all the cases reactions were performed in 0.5-2.0 mmol scale. Purification of products were done by column chromatography (10-15% ethyl acetate in Petroleum ether) followed by

crystallization (dichloromethane/petroleum ether). Yields of isolated pure products were indicated in Table-2.

Some products have been reported earlier. viz. **Complex 6a:** ref. 25(b), **Complex 6b:** ref. 25(e). **Complex 6e:** ref. 25(d). **Complex 6f:** ref. 25(f). **Complex 6i:** ref. 25(b).

Complex 6c:

Color :	Red
MP:	108-110^{0}C
IR ($CHCl_3$):	1985, 1915 (br), 1690 cm^{-1}
^{1}H NMR ($CDCl_3$) : (200 MHz)	3.80 (s, 3H), 5.22 (d, 2H, *J*=6.7Hz); 6.08 (d, 2H, *J*=6.7Hz), 9.40 (s, 1H)
^{13}C NMR ($CDCl_3$): (50.3 MHz)	55.9, 76.8, 90.6, 94.6, 144.8, 186.6, 230.0
Analysis:	For $C_{11}H_8O_5Cr$ Calcd: C : 48.54 , H : 2.96 Found : C : 48.63 , H : 2.97

Complex 6d:

Color :	Red
MP:	90^{0}C
IR ($CHCl_3$):	1985, 1915 (br), 1690 cm^{-1}
^{1}H NMR ($CDCl_3$) : (200 MHz)	2.35 (s, 3H), 5.17 (d, 2H, *J*=6.4Hz); 6.00 (d, 2H, *J*=6.4Hz), 9.46 (s, 1H)
^{13}C NMR ($CDCl_3$): (50.3 MHz)	20.6, 90.4, 93.0, 95.1, 112.1, 187.3, 230.2

Analysis: For $C_{11}H_8O_4Cr$
Calcd: C : 51.56 , H : 3.15
Found : C : 51.49 , H : 3.14

Complex 6g:

Color : Orange
MP: 100°C
IR ($CHCl_3$): 1980, 1910 (br), 1730 cm^{-1}
^1H NMR ($CDCl_3$) : (200 MHz) 5.35 (t, 2H, *J*=6.6Hz); 5.65 (t, 1H, *J*=6.6Hz), 6.27 (d, 2H, *J*=6.6Hz), 7.21 (d, 2H, *J*=8.4Hz), 7.29 (t, 1H, *J*=8.4Hz), 7.45 (t, 2H, *J*=8.4Hz)
^{13}C NMR ($CDCl_3$): (50.3 MHz) 88.4, 89.9, 95.0, 121.7, 126.5, 129.8, 150.6, 164.5, 230.8
Analysis: For $C_{16}H_{10}O_5Cr$
Calcd: C : 57.49 , H : 3.03
Found : C : 57.51 , H : 3.13

Complex 6h:

Color : Red
MP: Gummy oil
IR ($CHCl_3$): : 3600-3300 (br), 1980, 1910 (br), 1720 cm^{-1}
^1H NMR ($CDCl_3$) : (200 MHz) 2.09 (brs, 1H), 3.94 (m, 2H), 4.48 (m, 2H), 5.32 (t, 2H, *J*=6.4Hz), 5.58 (t, 1H, *J*=6.4Hz), 6.15 (d, 2H, *J*=6.4Hz)
^{13}C NMR ($CDCl_3$): (50.3 MHz) 60.9, 67.3, 89.2, 89.6, 94.6, 94.7, 165.9, 230.8
Analysis: Not satisfactory

Complex 6j:

Color :	Yellow
MP:	130^{0}C
IR ($CHCl_3$):	1975, 1895(br) cm^{-1}
^{1}H NMR ($CDCl_3$) : (200 MHz)	2.98 (s, 1H), 5.00 (t, 1H, *J*=6.7Hz); 5.18 (m, 2H), 5.55 (t, 1H, *J*=6.7Hz), 6.16 (d, 1H, *J*=6.7Hz), 7.45 (m, 3H), 7.65 (m, 2H)
^{13}C NMR ($CDCl_3$): (50.3 MHz)	87.3, 88.2, 94.9, 96.0, 96.1, 109.4, 127.1, 128.7, 129.7, 137.0, 231.8
Analysis:	For $C_{17}H_{11}O_4F_3Cr$ Calcd: C : 52.59 , H : 2.86 Found : C : 52.68 , H : 2.93

Complex 6k:

Color :	Red
MP:	mp 130^{0}C (dec)
IR ($CHCl_3$):	1975, 1895(br), 1680 cm^{-1}
^{1}H NMR ($CDCl_3$) : (200 MHz)	3.81 (s, 6H), 4.82 (d, 2H, *J*=6.3Hz), 5.82 (t, 1H, *J*=6.3Hz), 10.1 (s, 1H)
^{13}C NMR ($CDCl_3$): (50.3 MHz)	56.3, 68.7, 91.9, 103.9, 145.1, 185.2, 231.2
Analysis:	For $C_{12}H_{10}O_6Cr$ Calcd: C : 47.68 , H : 3.34 Found : C : 47.58 , H : 3.36

Thermal complexation of phenyl benzoate 7a:

Phenyl benzoate (2g, 0.01 mol) and chromium hexacarbonyl (2.2g, 0.01 mol) were thermolysed in a mixture of dibutyl ether (100 mL)-

THF (10 mL) (bath temperature: 150°C) for 12 hours as described in standard procedure.[9] Removal of solvents followed by column chromatographic separation yielded three products : **7b** (1.2g, 36%), **6g** (0.8g, 24%), **7c** (0.08 mg, 2.4%).

Complex 7b:

Color :	yellow
MP:	110°C
IR ($CHCl_3$):	1980, 1910 (br), 1725 cm^{-1}
^1H NMR ($CDCl_3$) : (200 MHz)	5.05 (t, 1H, *J*=6.4Hz); 5.45 (d, 2H, *J*=6.4Hz), 6.60 (t, 2H, *J*=6.4Hz), 7.50 (t, 2H, *J*=8.0Hz), 7.65 (t, 1H, *J*=8.0Hz), 8.17 (d, 2H, *J*=8.1Hz)
^{13}C NMR ($CDCl_3$): (50.3 MHz)	86.01, 88.00, 92.89, 128.12, 128.56, 130.34, 130.98, 132.56, 162.59, 231.33
Analysis:	For $C_{16}H_{10}O_5Cr$
	Calcd: C : 57.49 , H : 3.03
	Found : C : 57.42 , H : 2.97

Complex 7c:

Color :	Orange
MP:	130^{0}C
IR ($CHCl_3$):	1985, 1910 (br), 1732 cm^{-1}
^1H NMR ($CDCl_3$) : (200 MHz)	5.05 (t, 1H, *J*=6.4Hz); 5.25-5.45 (m, 4H), 5.95 (t, 2H, *J*=6.4Hz), 5.65 (t, 1H, *J*=6.4Hz), 6.20 (d, 2H, *J*=6.4Hz)
Analysis:	For $C_{19}H_{10}O_8Cr_2$ Calcd: C : 48.51 , H : 2.12 Found : C : 48.70 , H : 2.21

Preparation of Tricarbonyl[η6-3-methylanisole]chromium(0) (8a):

3-Methylanisole (3g, 25 mmol) was subjected to complexation under standard condition using chromium hexacarbonyl (3g, 13.6mmol), dibutyl ether (100mL) and THF (10mL) to yield the title compound (**8a**) as yellow crystal (2.2g, 63%)

Complex 8a:

Color :	Yellow
MP:	80°C ;
IR ($CHCl_3$):	1960, 1880 (br), cm^{-1}
^1H NMR ($CDCl_3$) : (200 MHz)	2.25 (s, 3H), 3.69 (s, 3H), 4.75 (d, 1H, *J*=6.0Hz), 5.03 (d, 1H, *J*=6.0Hz), 5.08 (s, 1H), 5.56 (t, 1H, *J*=6.0Hz)
^{13}C NMR ($CDCl_3$): (50.3 MHz)	20.96, 55.63, 76.30, 80.76, 87.12, 95.40, 111.23, 144.00, 233.90
Analysis:	For $C_{11}H_{10}O_4Cr$ Calcd: C: 51.17, H: 3.90 Found : C: 51.32, H: 4.02

Preparation of Tricarbonyl[η6-2,5-dimethylanisole]chromium(0) (8b) [26(g)]**:**

Following the same procedure as used for **5g,** it was prepared from **8a** (516 mg, 2.0 m mol), using n-BuLi (1.56 M, 1.3 mL, 2.0 mmol) and methyl iodide (300 mg, 0.15 mL, 2.1 mmol). Recrystallization from dichloromethane-hexane gave the title compound as yellow crystals (419 mg, 77%).

Preparation of Tricarbonyl [η6-2-methoxy-3,6-dimethylbenzaldehyde] chromium(0) (8c):

As described above, it was prepared from **8b** (272 mg, 1.0 mmol) using n-BuLi (1.56 M, 0.7 mL, 1.0 mmol) and DMF (109 mg, 0.1 mL, 1.5 mmol). Chromatographic purification gave the title compound as a red viscous oil (219 mg, 73%)

Complex 8c:

Color :	Red
MP:	viscous oil
IR ($CHCl_3$):	1975, 1900(br), 1680 cm^{-1}
^1H NMR ($CDCl_3$) : (200 MHz)	2.20 (s, 3H), 2.45 (s, 3H), 3.79 (s, 3H), 4.79 (d, 1H, *J*=6.3Hz), 5.74 (d, 1H, *J*=6.3Hz), 10.06 (s, 1H)
^{13}C NMR ($CDCl_3$): (50.3 MHz)	22.96, 30.00, 31.80, 64.30, 84.45, 89.07, 91.1, 131.48, 146.67, 188.90, 230.74
Analysis:	For $C_{13}H_{12}O_5Cr$ Calcd: C : 52.00 , H : 4.03 Found : C : 52.03 , H : 4.06

Preparation of Tricarbonyl[η6-2-trimethylsilyl-5-methylanisole]chromium(0) (8d):

It was prepared from **8a** (258 mg, 1.0 mmol) following the same procedure as above using n-BuLi (1.56 M, 0.7 mL, 1.0 mmol) and trimethylsilyl chloride (110 mg, 0.15 mL, 1.0 mmol). Recrystallisation

from dichloromethane-hexane gave the title compound as yellow crystals (287 mg, 87%)

Complex 8d:

Color :	Yellow
MP:	125°C
IR ($CHCl_3$):	1955, 1895, 1870, cm^{-1}
^1H NMR ($CDCl_3$) : (200 MHz)	0.28 (s, 9H), 2.28 (s, 3H), 3.73 (s, 3H), 4.68 (d, 1H, *J*=6.4Hz), 4.89 (s, 1H), 5.33 (d, 1H, *J*=6.4Hz)
^{13}C NMR ($CDCl_3$): (50.3 MHz)	-0.45, 21.20, 55.40, 76.60, 87.21, 87.42, 101.70, 111.51, 147.96, 234.25
Analysis:	For $C_{14}H_{18}O_4SiCr$ Calcd : C : 50.90, H : 5.49 Found : C : 50.88 , H : 5.48

Preparation of Tricarbonyl[η6-2,3-dimethyl-6-trimethylsilylanisole]chromium(0) (8e):

It was prepared from **8d** (330 mg, 1.0 mmol) following the same procedure as above , using n-BuLi (1.56 M, 0.7 mL, 1.0 mmol) and methyl iodide (300 mg, 0.15 mL, 2.1 mmol). Recrystallisation from dichloromethane-hexane gave the title compound as yellow crystals (275 mg, 80%)

Complex 8e:

Color :	Yellow
MP:	110°C
IR ($CHCl_3$):	1940, 1860 (br) cm^{-1}
^1H NMR ($CDCl_3$) : (200 MHz)	0.38 (s, 9H), 2.20 (s, 3H), 2.31 (s, 3H), 3.76 (s, 3H), 4.86 (d, 1H, *J*=6.7Hz), 5.38 (d, 1H, *J*=6.7Hz)
^{13}C NMR ($CDCl_3$): (50.3 MHz)	0.00, 13.33, 19.33, 62.33, 90.67, 91.67, 98.67, 101.00, 112.00, 147.67, 234.33
Analysis:	For $C_{15}H_{20}O_4SiCr$ Calcd: C : 52.31, H : 5.85 Found : C : 52.30 , H : 5.91

Preparation of Tricarbonyl[η6-2-methoxy-3,4-dimethyl benzaldehyde] chromium(0) (8f):

Following the general procedure of functionalisation it was prepared from **8e** (172 mg, 0.5 mmol) using DMF (5 mL), 18-Crown-6 (13 mg, 10 mol%) and KH (26 mg, 0.65 mmol) . Recrystallisation from dichloromethane-hexane gave the title compound as red crystals (102 mg, 68%)

Complex 8f:

Color :	Red
MP:	135°C
IR ($CHCl_3$):	1945, 1870 (br), 1660 cm^{-1}
^1H NMR ($CDCl_3$) : (200 MHz)	2.21 (s, 3H), 2.40 (s, 3H), 3.85 (s, 3H), 5.00 (d, 1H, *J*=6.5Hz), 5.99 (d, 1H, *J*=6.5Hz), 9.90 (s, 1H)

^{13}C NMR ($CDCl_3$): 12.18, 19.62, 64.72, 89.12, 89.14, 90.66, 99.90, 111.10, 144.36, 185.80, 231.00
(50.3 MHz)

Analysis: For $C_{13}H_{12}O_5Cr$
Calcd: C : 52.00, H : 4.03
Found : C : 52.03 , H : 4.00

General procedure for the preparation of carbinols (10a-l) from arylsilanes (5a, 5d-f, 9a-b) : To a solution of the complexed arylsilane (n mmol), aromatic aldehyde (n mmol) and 18-crown-6 (10 mol%) in DMF (5n mL), a suspension of KH (1.0-1.2n mmol) in ether (3n mL) was added dropwise with stirring at room temperature. After completion of the reaction (TLC), the reaction mixture was quenched with degassed methanol at ice cold temperature and extracted with ether. Crude complex obtained after evaporation of solvent was purified by chromatography.

All reactions were performed in 0.5-2.0 mmol scale and yields are indicated in Table-3. Analytically pure samples were prepared by crystallization from dichloromethane/petroleum ether.

Some products have been reported earlier. viz. **Complex 10a, 10d, 10f, 10h :** ref. 24, **Complex 10b, 10I, 10k :** ref. 14, **Complex 10j, 10l :** ref. 15.

Complex 10c:

Color :	Yellow
MP:	98-100^{0}C (dec)
IR ($CHCl_3$):	3400-3600 (br), 1970, 1890 (br) cm^{-1}
^{1}H NMR ($CDCl_3$) : (200 MHz)	2.59 (brs, 1H), 5.29 (m, 3H), 5.40 (m, 1H), 5.69 (m, 2H), 6.97 (m, 2H), 7.26 (d, 1H, J=5.2Hz)
^{13}C NMR ($CDCl_3$): (50.3 MHz)	70.60, 89.90, 91.7, 92.4, 92.7, 125.7, 126.4, 127.1, 145.7, 232.9
Analysis:	For $C_{14}H_{10}O_4SCr$ Calcd: C: 51.54, H: 3.09, S: 9.83 Found : C: 51.56, H: 3.16, S: 9.93

Complex 10e:

Color :	Yellow
MP:	112-114^{0}C (dec)
IR ($CHCl_3$):	3400-3600 (br), 1970, 1890 (br) cm^{-1}
^{1}H NMR ($CDCl_3$) : (200 MHz)	^{1}H NMR ($CDCl_3$) : 4.70 (brs, 1H), 5.23 (d, 1H, J=6.4Hz), 5.32 (t, 3H, J=6.4Hz), 5.43 (brs, 1H), 5.62 (d, 1H, J=6.4Hz), 7.29 (t, 1H, J=7.4Hz), 7.47 (d, 1H, J=7.4Hz), 7.75 (t, 1H, J=7.4Hz), 8.56 (d, 1H, J=5.6)
^{13}C NMR ($CDCl_3$): (50.3 MHz)	73.40, 91.75, 92.16, 92.54, 93.11, 121.55, 123.64, 137.45, 148.66, 158.97, 232.82
Analysis:	For $C_{15}H_{11}O_4NCr$: Calcd: C: 56.08, H: 3.45, N: 4.36 Found : C: 56.11, H: 3.65, N: 4.34

Complex 10g:

Color :	Yellow
MP:	60°C
IR ($CHCl_3$):	3400-3600 (br), 1975, 1885 (br) cm^{-1}
^1H NMR ($CDCl_3$) : (200 MHz)	2.65 (d, 1H, J=5.8 Hz), 5.35 (m, 4H), 5.55 (d, 1H, J=5.8 Hz), 5.70 (d, 1H, J=6.5 Hz), 6.35 (m, 2H), 7.45 (s, 1H)
^{13}C NMR ($CDCl_3$): (50.3 MHz)	68.09, 90.80, 91.95, 92.14, 92.31, 92.60, 108.07, 110.52, 111.93, 143.11, 153.76, 232.79
Analysis:	For $C_{14}H_{10}O_5Cr$ Calcd: C: 54.20, H: 3.25 Found : C: 54.21, H: 3.22

General procedure for the preparation of complexed ketones (11a-q) from arylsilanes (5a, 5d-f, 5e): Procedure was same as in the preparation of carbinols, except for the cover of a blanket of dry oxygen, and use of potassium hydride in excess (2.0-2.2 equivalent of arylsilane).

All reactions were performed in 0.5-2.0 mmol scale and yields indicated in Table-3.

Several of the biaryl ketone complexes have been reported earlier : viz. **Complex 11a, 11d, 11f, 11h, 11l :** ref. 24; **Complex 11b, 11i, 11k, 11n :** ref. 17.

Complex 11c:

Color :	Red
MP:	100-102^{0}C
IR ($CHCl_3$):	1990, 1920, 1640 cm^{-1}
^{1}H NMR ($CDCl_3$) : (400 MHz)	5.36 (t, 2H, J=6.8 Hz), 5.62 (t, 1H, J=6.8 Hz), 6.13(d, 2H, J=6.8 Hz), 7.23 (dd, 1H, J=5.2, 3.6 Hz), 7.76 (d, 1H, J=3.7 Hz), 7.90 (d, 1H, J=5.2Hz)
^{13}C NMR ($CDCl_3$): (100.6 MHz)	90.03, 94.65, 95.20, 98.6, 128.36, 133.8, 134.53, 140.97, 184.34, 230.96
Analysis:	For $C_{14}H_8O_4SCr$ Calcd: C: 51.86, H: 2.49, S: 9.89 Found : C: 51.79, H: 2.47, S: 9.80

Complex 11e:

Color :	Red
MP:	60^{0}C
IR ($CHCl_3$):	1990, 1920, 1670 cm^{-1}
^{1}H NMR ($CDCl_3$) : (400 MHz)	5.32 (t, 2H, J=6.8Hz), 5.70 (t, 1H, J=6.8Hz), 6.78 (d, 2H, J=6.8Hz), 7.51 (m, 1H), 7.92 (dd, 1H, J=7.5, 5.5Hz), 8.06 (d, 1H, 7.6Hz), 8.70 (d, 1H, J=5.4Hz)
^{13}C NMR ($CDCl_3$): (100.6 MHz)	89.03, 94.58, 95.32, 97.68, 124.28, 126.65, 137.28, 148.04, 154.45, 189.63, 230.77
Analysis:	For $C_{15}H_9O_4NCr$ Calcd: C: 54.56, H: 2.62 N: 4.39 Found : C: 54.59 , H: 2.69, N: 4.40

Complex 11g:

Color :	Red
MP:	93°C
IR ($CHCl_3$):	1990, 1920, 1650 cm^{-1}
^1H NMR ($CDCl_3$) : (400 MHz)	5.34 (t, 2H, J=6.7Hz), 5.69 (t, 1H, J=6.7Hz), 6.45 (d, 2H, J=6.7Hz), 6.65 (m, 1H), 7.46 (d, 1H, J=3.7Hz), 7.70 (s, 1H)
^{13}C NMR ($CDCl_3$): (100.6 MHz)	89.07, 95.62, 95.82, 112.6, 119.95, 146.64, 151.70, 177.94, 230.67
Analysis:	For $C_{14}H_8O_5Cr$ Calcd: C: 54.56, H: 2.62 Found : C :54.55, H: 2.69

Complex 11j:

Color :	Orange
MP:	115°C
IR ($CHCl_3$):	1995, 1925, 1670 cm^{-1}
^1H NMR ($CDCl_3$) : (400 MHz)	3.65 (s, 3H), 4.95 (t, 1H, J=6.4 Hz), 5.10 (d, 1H, J=6.5 Hz), 5.70 (t, 1H, J=6.5 Hz), 5.90 (d, 1H, J=6.5 Hz), 7.45 (t, 2H, J=7.8 Hz), 7.55 (t, 1H, J=7.8 Hz), 7.90 (d, 2H, J=7.8 Hz)
^{13}C NMR ($CDCl_3$): (100.6 MHz)	56.00, 72.22, 83.13, 94.63, 96.62, 128.36, 129.48, 133.25, 137.31, 141.70, 191.54, 231.61
Analysis:	For $C_{17}H_{12}O_5Cr$ Calcd: C: 58.63, H: 3.47 Found : C: 58.68, H: 3.45

Complex 11m:

Color :	Red
MP:	110-112^{0}C
IR ($CHCl_3$):	1990, 1920, 1660 cm^{-1}
^{1}H NMR ($CDCl_3$) : (400 MHz)	5.27 (t, 2H, J=6.6 Hz), 5.73 (t, 1H, J=6.6 Hz), 5.97 (d, 2H, J=6.6 Hz), 7.43 (m, 4H)
^{13}C NMR ($CDCl_3$): (100.6 MHz)	89.06, 93.81, 95.78, 96.03, 127.34, 129.20, 130.06, 130.67, 131.72, 136.72, 192.61, 230.31
Analysis:	For $C_{16}H_9O_4ClCr$ Calcd: C: 54.49, H: 2.57 Found : C: 54.44, H: 2.55.

Complex 11o:

Color :	Red
MP:	85^{0}C
IR ($CHCl_3$):	1995, 1925, 1670 cm^{-1}
^{1}H NMR ($CDCl_3$) : (400 MHz)	3.80 (s, 3H), 5.20 (d, 2H, J=6.7 Hz), 6.20 (d, 2H, J=6.7 Hz), 7.45-7.65 (m, 3H), 7.55 (d, 2H, J=7.8 Hz)
^{13}C NMR ($CDCl_3$): (100.6 MHz)	55.60, 89.72, 94.50, 95.84, 98.07, 113.78, 128.88, 131.40, 163.43, 191.94, 230.90
Analysis:	For $C_{17}H_{12}O_5Cr$ Calcd: C: 58.63, H: 3.47 Found : C: 58.66, H: 3.49

Complex 11p:

Color :	Red
MP:	135^{0}C
IR ($CHCl_3$):	1995, 1925, 1670 cm^{-1}
^{1}H NMR ($CDCl_3$) : (400 MHz)	3.80 (s, 3H), 5.23 (t, 2H, J=6.5 Hz), 5.63 (t, 1H, J=6.5 Hz), 6.00 (d, 2H, J=6.5 Hz), 6.98 (d, 1H, J=7.8 Hz), 7.05 (t, 1H, J=7.8 Hz), 7.27 (d, 1H, J=7.8 Hz), 7.42 (t, 1H, J=7.8 Hz)
^{13}C NMR ($CDCl_3$): (100.6 MHz)	55.60, 88.97, 95.32, 95.54, 95.97, 111.20, 120.97, 126.92, 128.89, 132.07, 156.37, 193.70, 230.60
Analysis:	For $C_{17}H_{12}O_5Cr$ Calcd: C: 58.63, H: 3.47 Found : C: 58.70, H: 3.44.

Complex 11q:

Color :	Red
MP:	115^{0}C
IR ($CHCl_3$):	1970, 1900, 1650, 1520 cm^{-1}
^{1}H NMR ($CDCl_3$) : (400 MHz)	5.35 (t, 2H, J=6.5 Hz), 5.70 (t, 1H, J=6.5 Hz), 6.00 (d, 2H, J=6.5 Hz), 7.90 (d, 2H, J=8.4 Hz), 8.40 (d, 2H, J=8.4 Hz)
^{13}C NMR ($CDCl_3$): (100.6 MHz)	89.80, 94.10, 95.34, 95.64, 124.01, 129.47, 142.22, 149.87, 192.42, 230.24
Analysis:	For $C_{16}H_9O_6NCr$ Calcd: C: 52.91, H:2.50, N: 3.86 Found : C: 52.88, H: 2.50, N: 3.79

Reaction in presence CsF instead of KH or NaH : Reactions were performed following the reported procedure[14] under an dry atmosphere of oxygen. To a solution of aryl silane (**5a-b**) (n mmol) and cesium fluoride (2n mmol) in DMF (5n mL), aromatic aldehyde was added dropwise with stirring at room temperature. In addition to carbinol (major product) only a trace of ketone was isolated even after 10 hours (Table-3, entry- 20, 21).

General procedure for the conversion of complexed carbinols (10a-e) to complexed ketones (11a-e) :

Using KH / 18-Crown-6 : To a solution of the complexed carbinol (n mmol), and 18-crown-6 (10 mol%) in DMF (5n mL), a suspension of KH (1.0-1.2n mmol) in ether (3n mL) was added dropwise with stirring at room temperature. After completion of the reaction (TLC), the reaction mixture was quenched with degassed methanol at ice cold temperature and extracted with ether.

Using 50% aq NaOH / TBAB : To a solution of the complexed carbinol (n mmol) and tetrabutylammonium bromide (TBAB) (10 mol%) in CH_2Cl_2 (5n mL), 50% aq NaOH (1.5-2n mmol) was added with stirring at room temperature. After completion of the reaction (TLC), the reaction mixture was diluted with degassed water and extracted with dichloromethane.

All reactions were performed in 0.5-2.00 mmol scale. Products were purified by column chromatography followed by crystallization. Yields are indicated in Table-4.

Reaction of Tricarbonyl[η6-benzene]chromium(0), BuLi and benzoyl chloride: Butyllithium in hexane (1.56 M, 0.7 mL, 1.0 m mol) was added dropwise to a cooled (-78°C) THF solution of benzene tricarbonylchromium (214 mg, 1.0 mmol) and the mixture stirred at -78°C for 2h. Benzoyl chloride (168 mg, 1.2 mmol) was added and stirring was continued (-78°C, 2h). Degassed methanol (5 mL) was slowly added to quench the reaction and the mixture was allowed to attain room temperature. Solvent was evaporated to afford crude mixture of products, which were separated by column chromatography to yield **11a** (242 mg, 80%); **12a**[17] (48mg, 18%).

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(5) Purpose of the preparation of enone **3c** was to study the effect of Lewis acid on the regio and stereochemistry of nucleophilic addition on such conformationally flexible enone. Ref. (a) Sur, S.; Mandal, S. K.; and Sarkar, A. *unpublished results.* (b) Mandal, S. K. *unpublished results.*

(6) For fluoride induced desilylation from uncomplexed aromatic ring: (a) Hayes, M. A. One or More =CH Bond(s) Formed by Substitution or Addition. In *Comprehensive Organic Functional Group Transformations.* Katritzky, A. R.; Meth-Cohn, O.; Rees, C. W.; Eds.: Pergamon: Oxford, **1995**; Vol-1, p 447-448 and refs. Cited therein.

(7) For desilylation of electron defficient aromatic ring using Potassium *tert.*

Butoxide: (a) Effenberger, F.; Spiegler, W. *Chem. Ber.*, **1985**, *118*, 3900. (b) Effenberger, F.; Schollkopf, K. *Angew. Chem., Int. Ed. Engl.*, **1981**, *20*. 226. (c) Streitweiser, A.; Boerth, D. W. *J. Am. Chem. Soc.*, **1978**, *100*, 755.

(8) Potassium Hydride as nucleophile: Pinnick, H. W. *Org. Prepn. And Proc. Int.*, **1983**, *15(3)*, 199.

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(11) Synthetic uses of some substituted aromatic aldehyde complexes: (a) Sur, S.; Mandal, S. K.; and Sarkar, A. *Unpublished result.* (b) Ref. 1(c) p1044-1048 and refs. cited therein. (c) Taniguchi, N.; Kaneta, N.; Uemura, M. *J. Org. Chem.* **1996**, *61*, 6088. (d) Mukai, C.; Hirai, S.; Kim, I. J.; Hanaoka, M. *Tet. Lett.* **1996**, *37*, 5389.

(12) When DMF was used as the solvent, reaction was complete within two hours. In ether it took more than five hours for completion.

(13) Ref. (10), p 1010

(14) Precedence for the use of DMF as solvent. Ref. Effenberger, F.; Schollkopf, K. *Angew. Chem., Int. Ed. Engl.*, **1981**, *20*. 226.

(15) Direct *ortho*- lithiation of anisole and chlorobenzene complexes and

subsequent reaction of the aryl anions with benzaldehyde was reported to provide approximately 60:40 mixture of diastereoisomers. In comparison, the present diastereoselectivities appear respectable, which may be a consequence of counterion effect. : Ref. : Semmelhack. M. F.; Bisaha, J. J; Czarny, M. *J. Am. Chem. Soc.*, **1979**, *101*, 768.

(16) Mahaffy, C. A. L.; Pauson, P. L. *Inorg. Synth.*, **1979**, *19*, 154.

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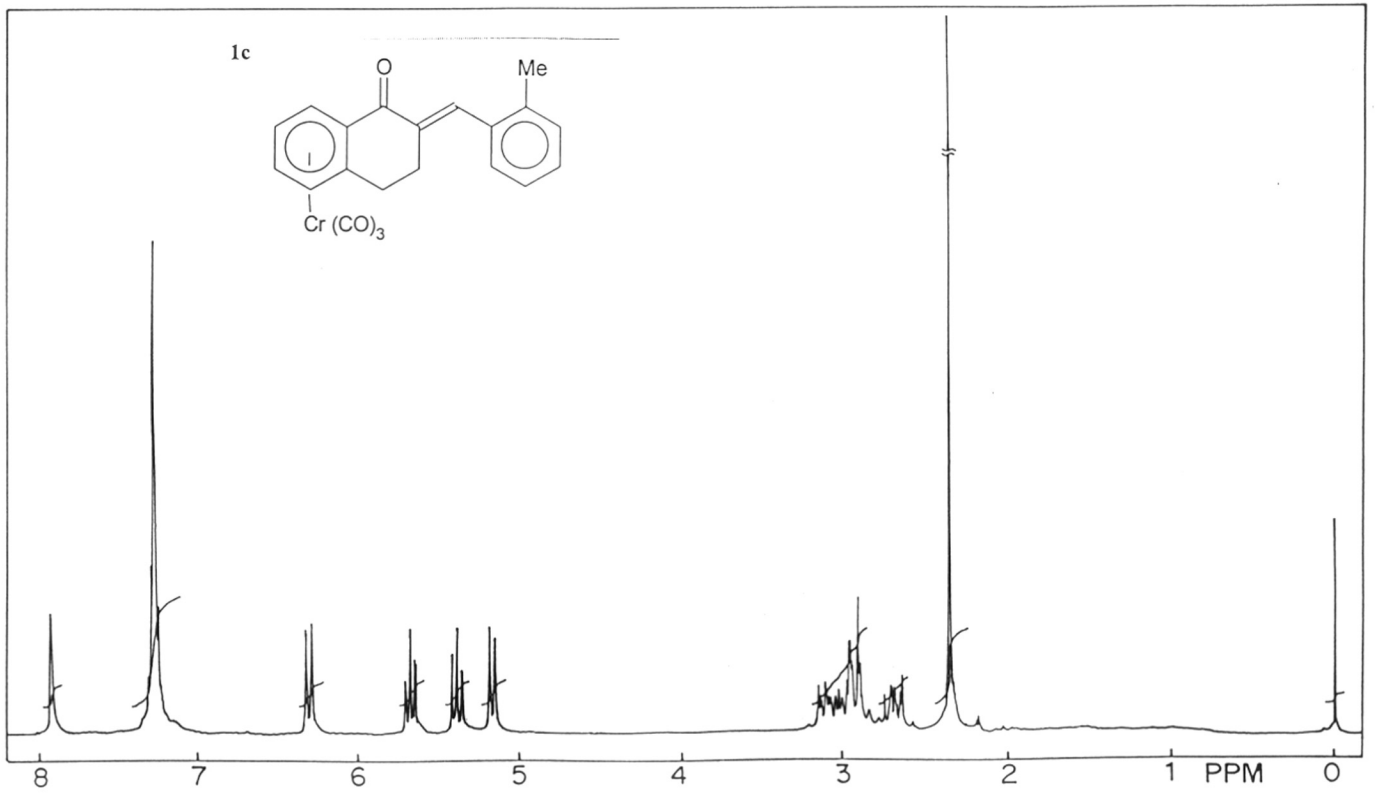
Appendix-**I**

Spectra of **all new** compounds of PART-A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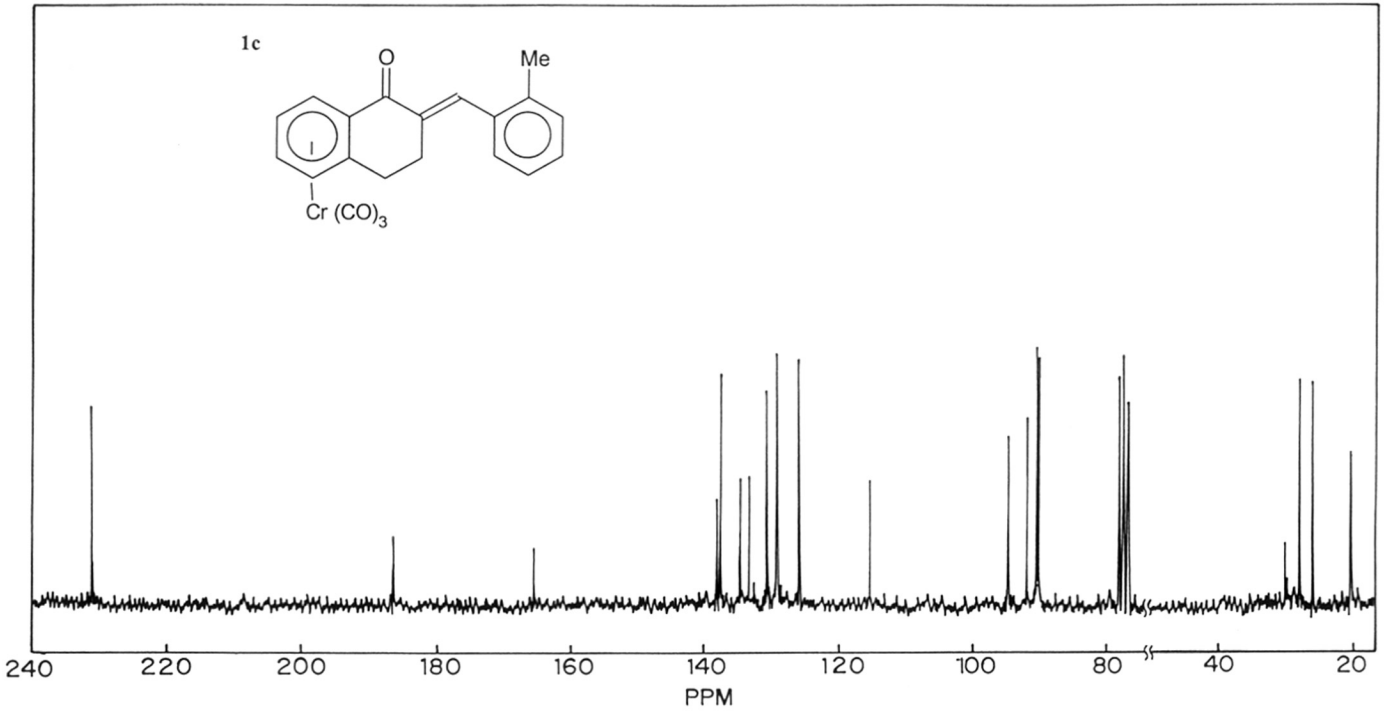
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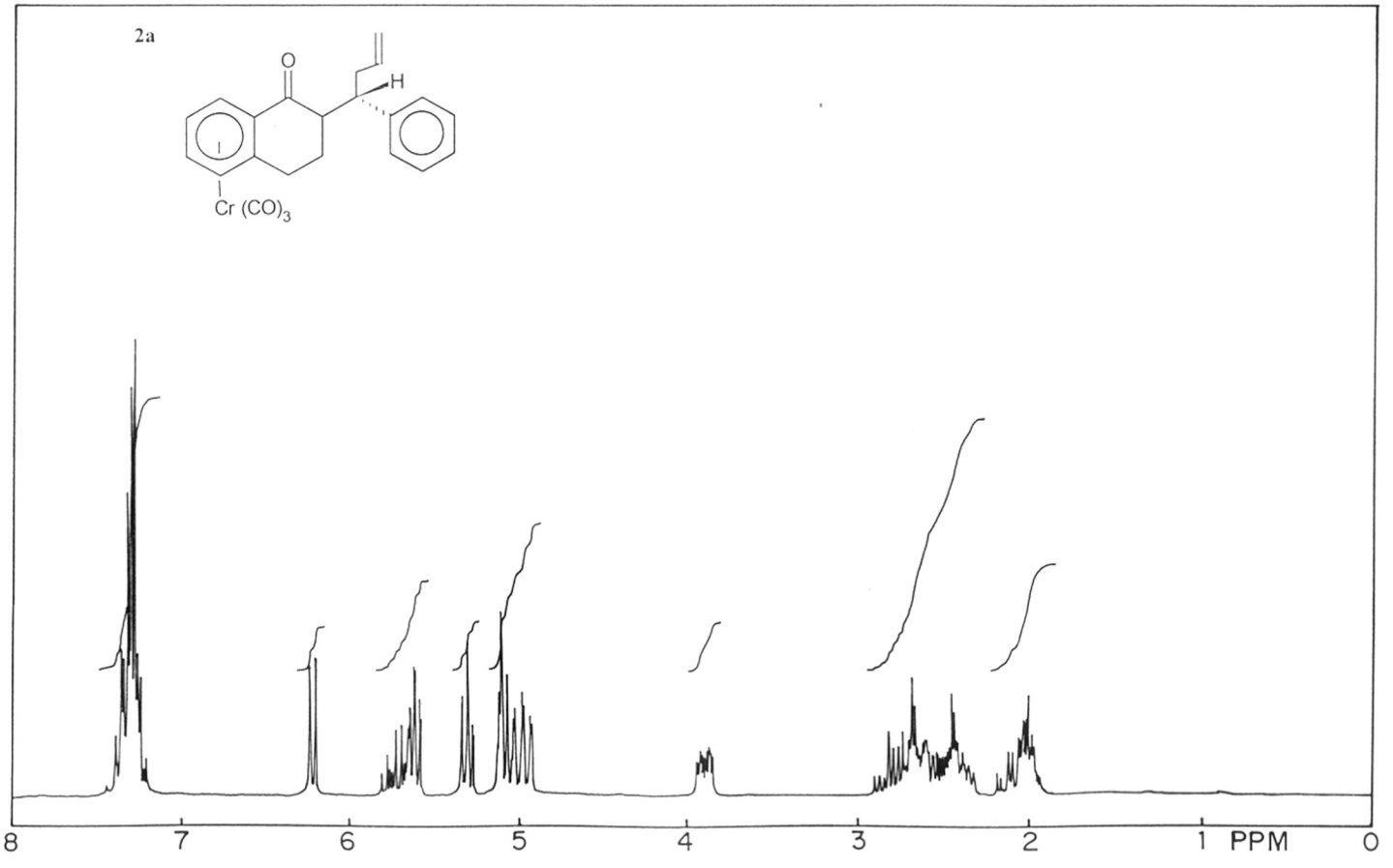
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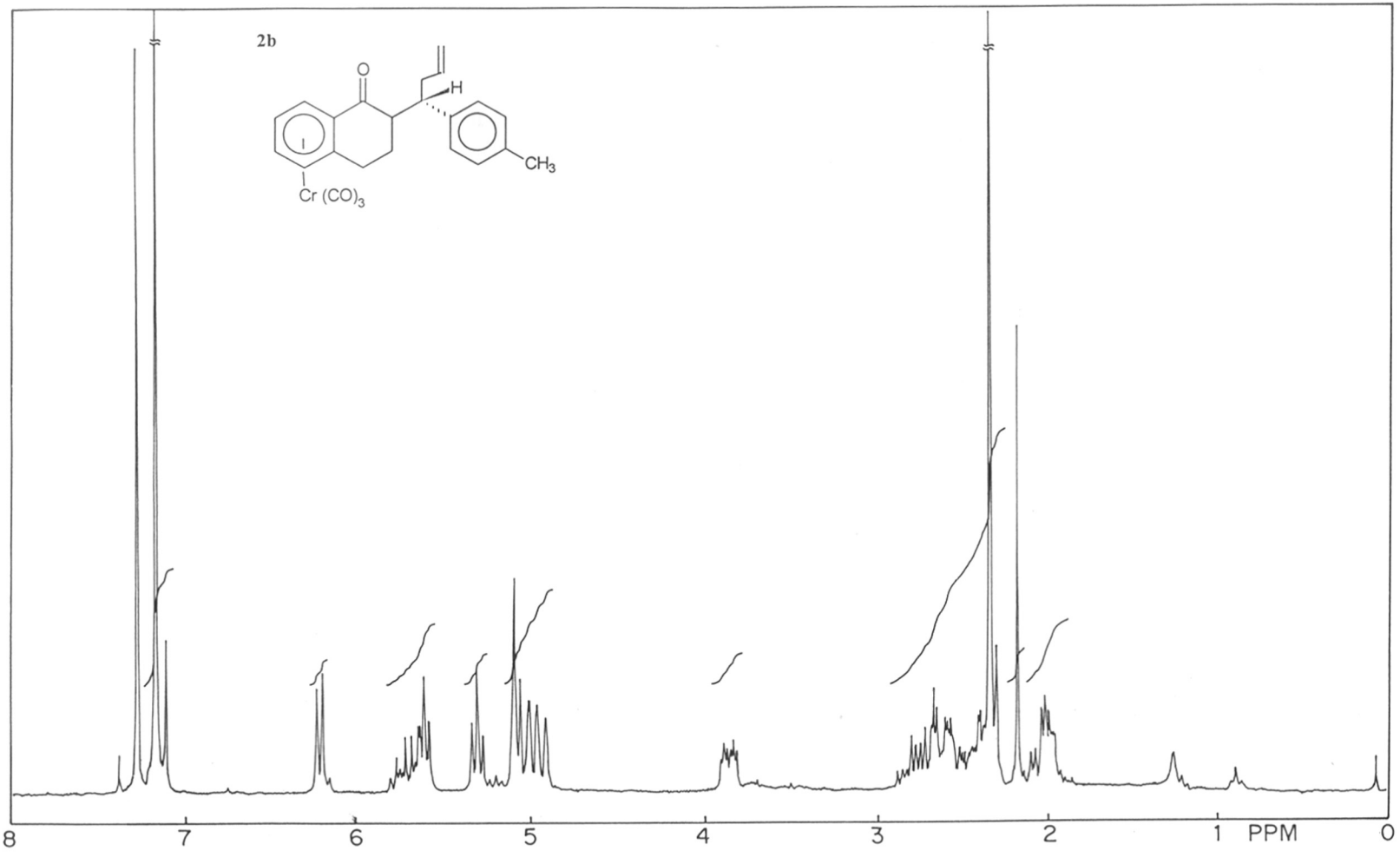
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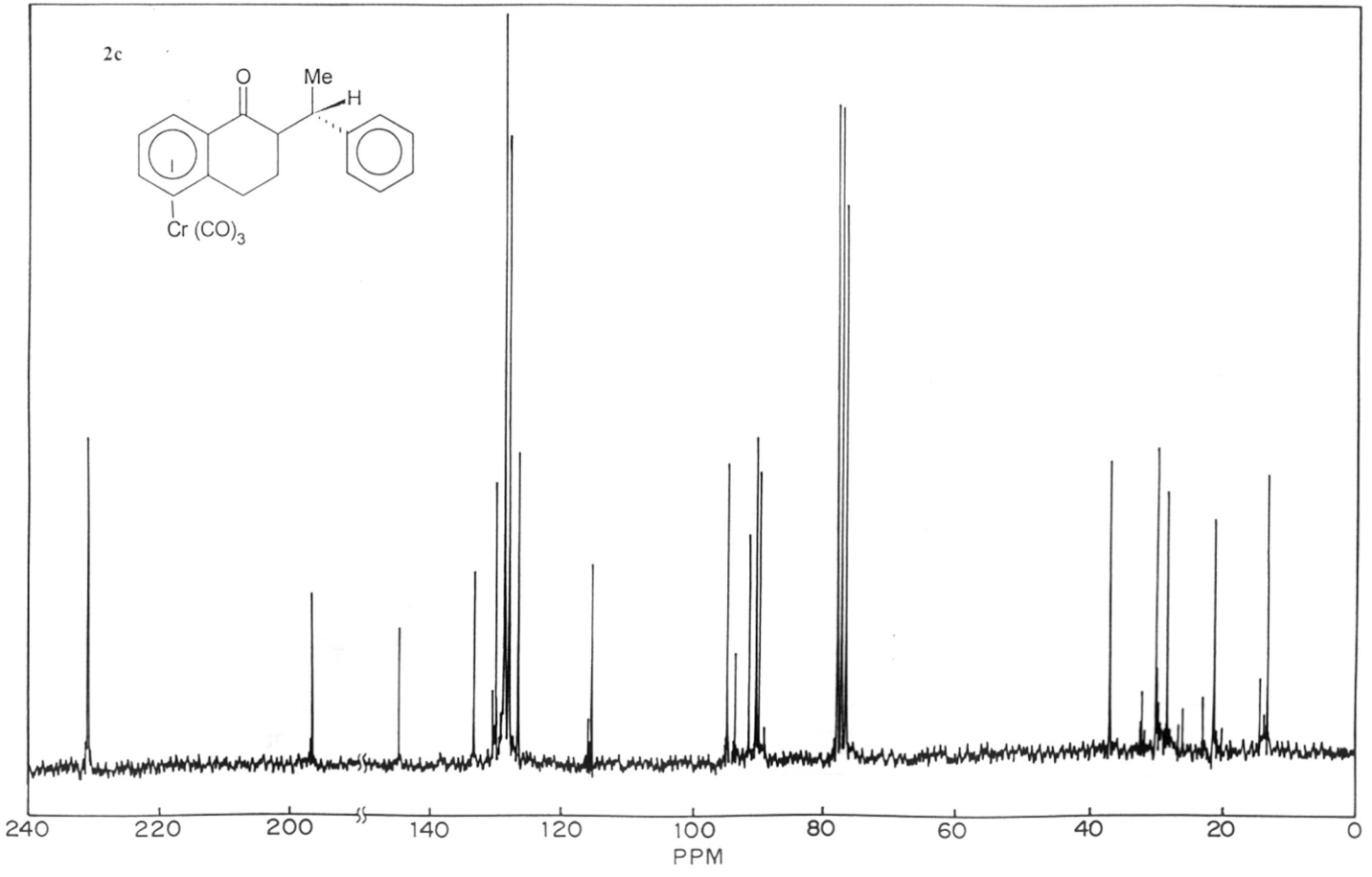
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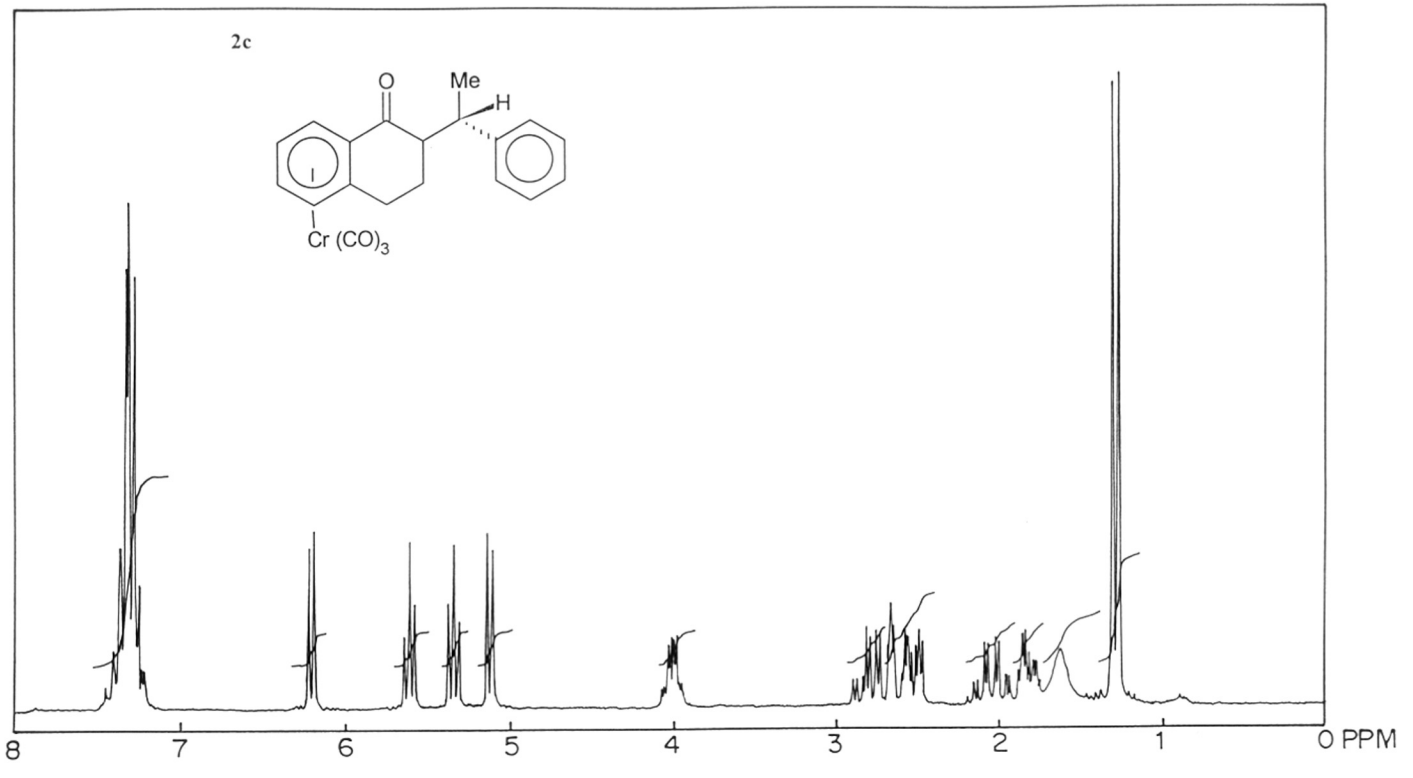
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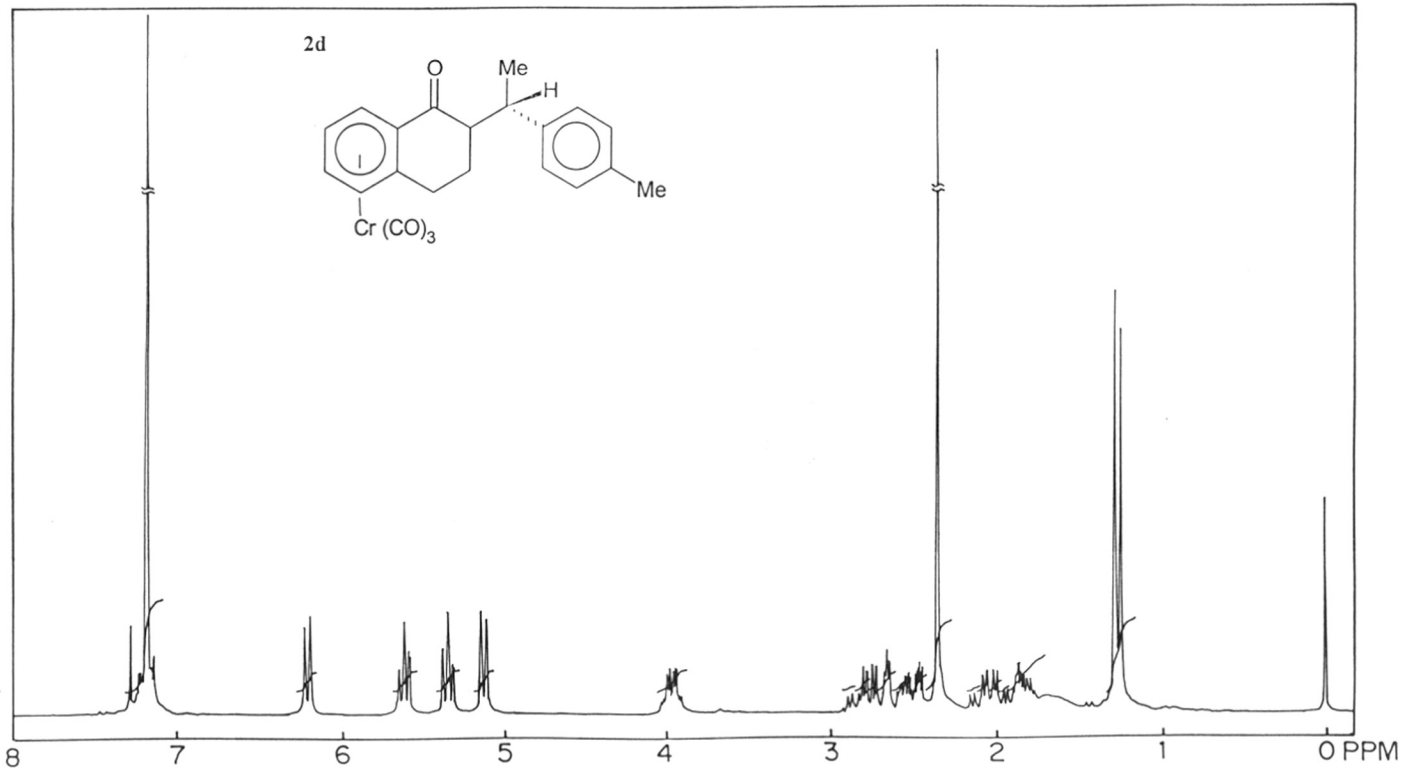
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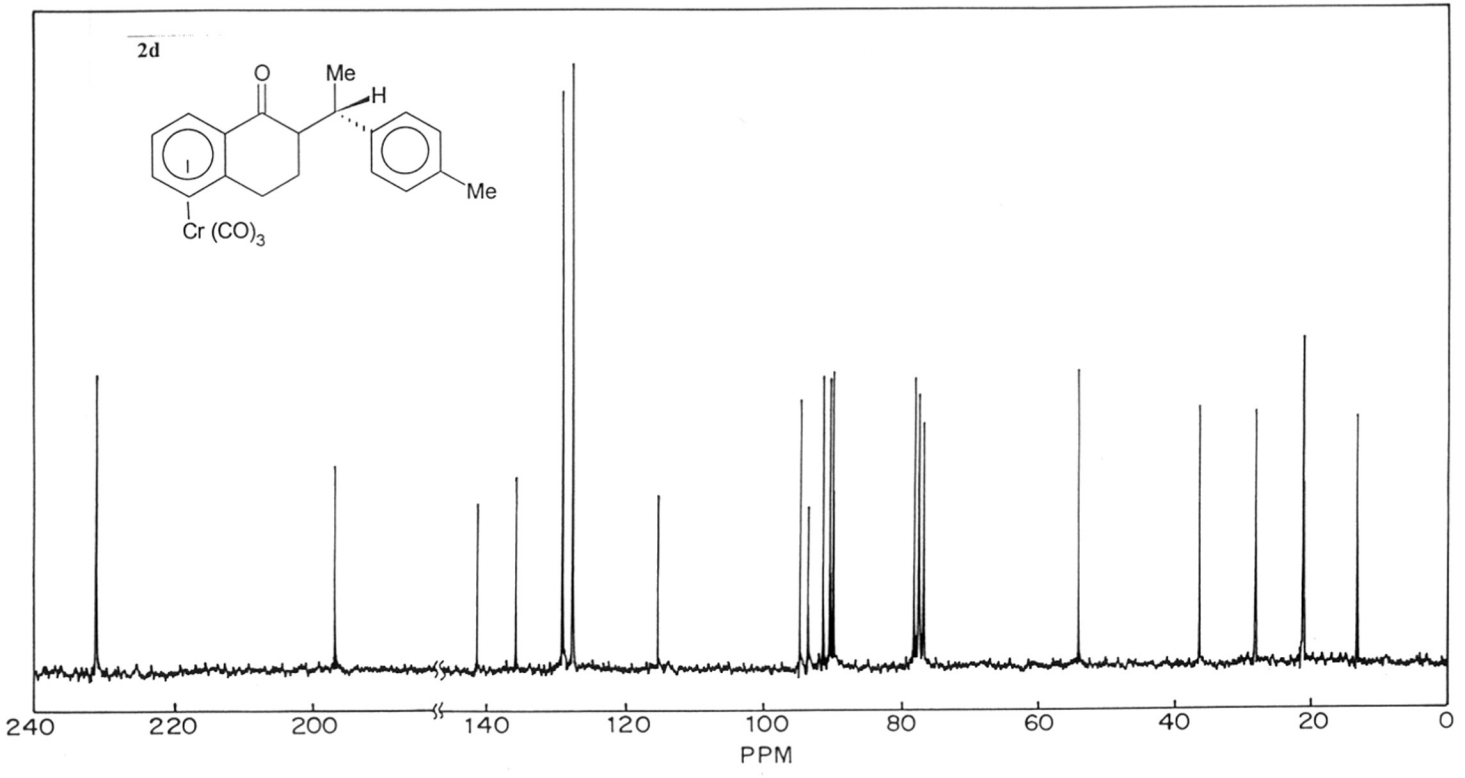
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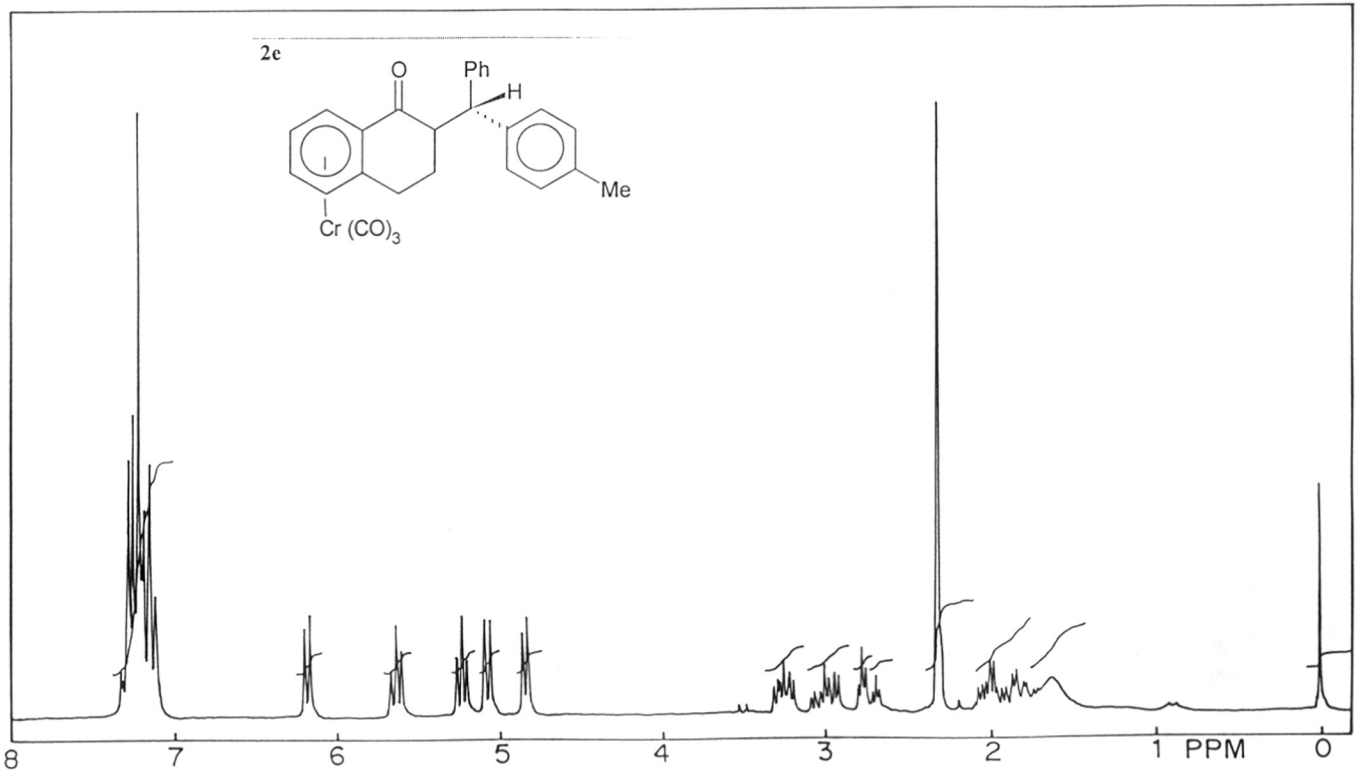
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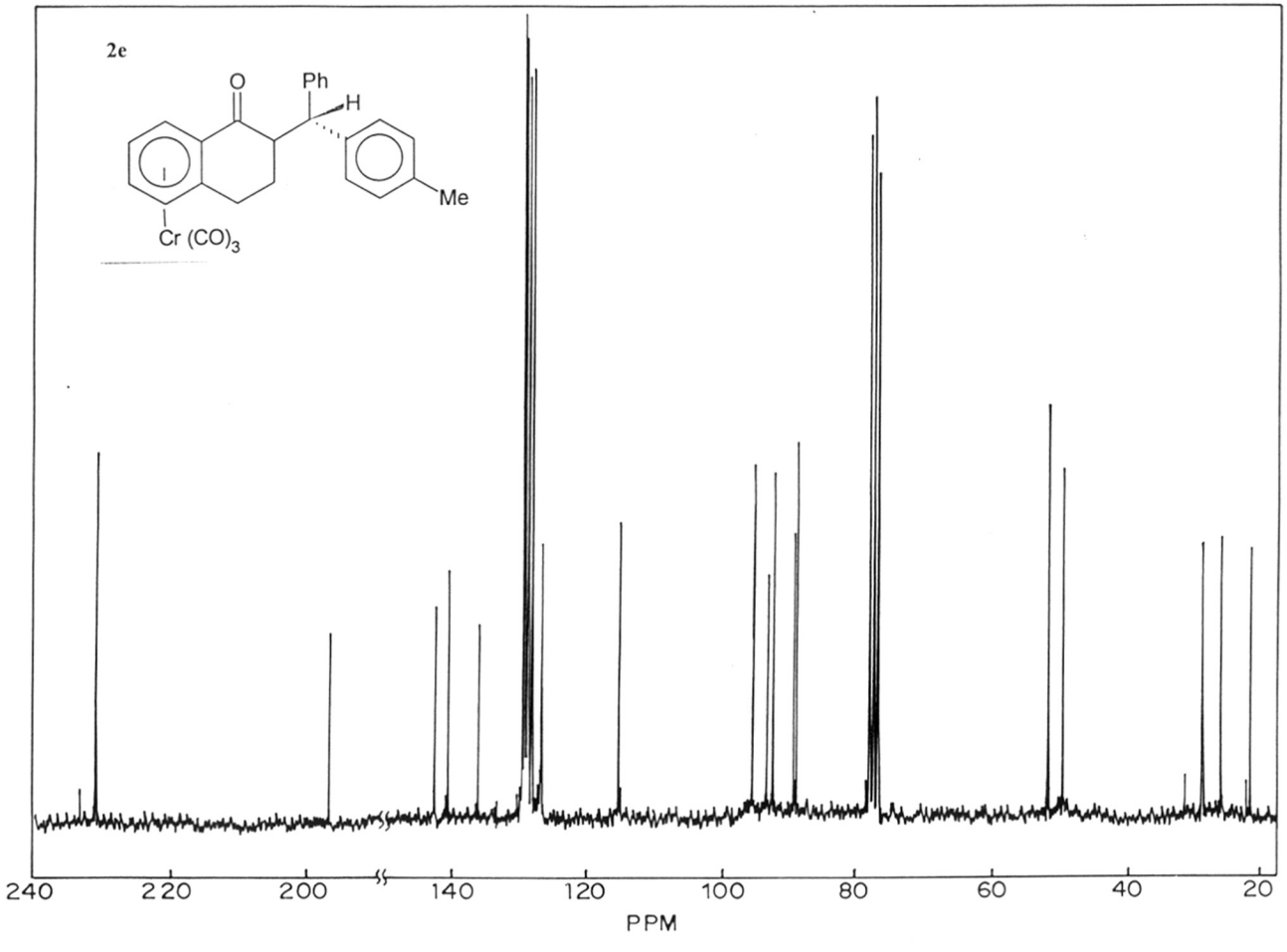
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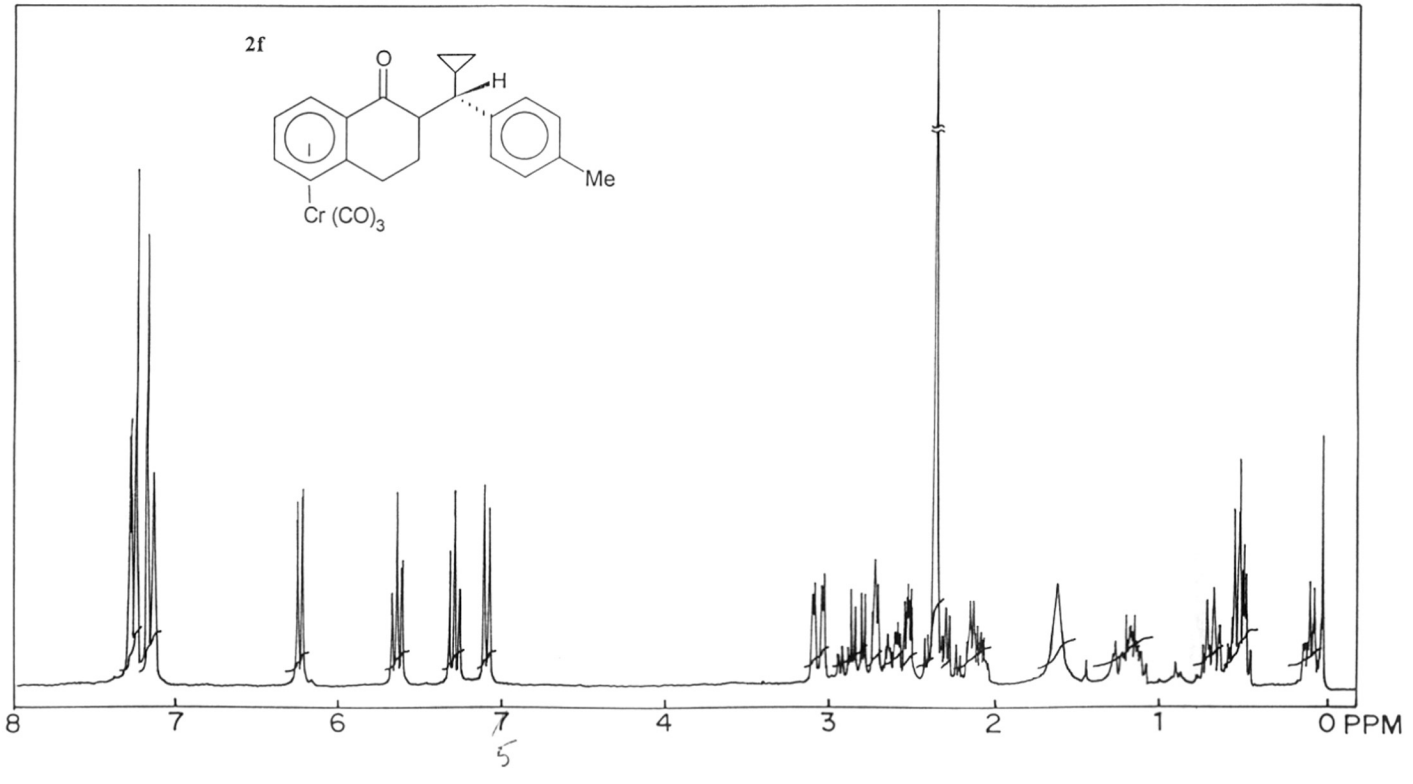
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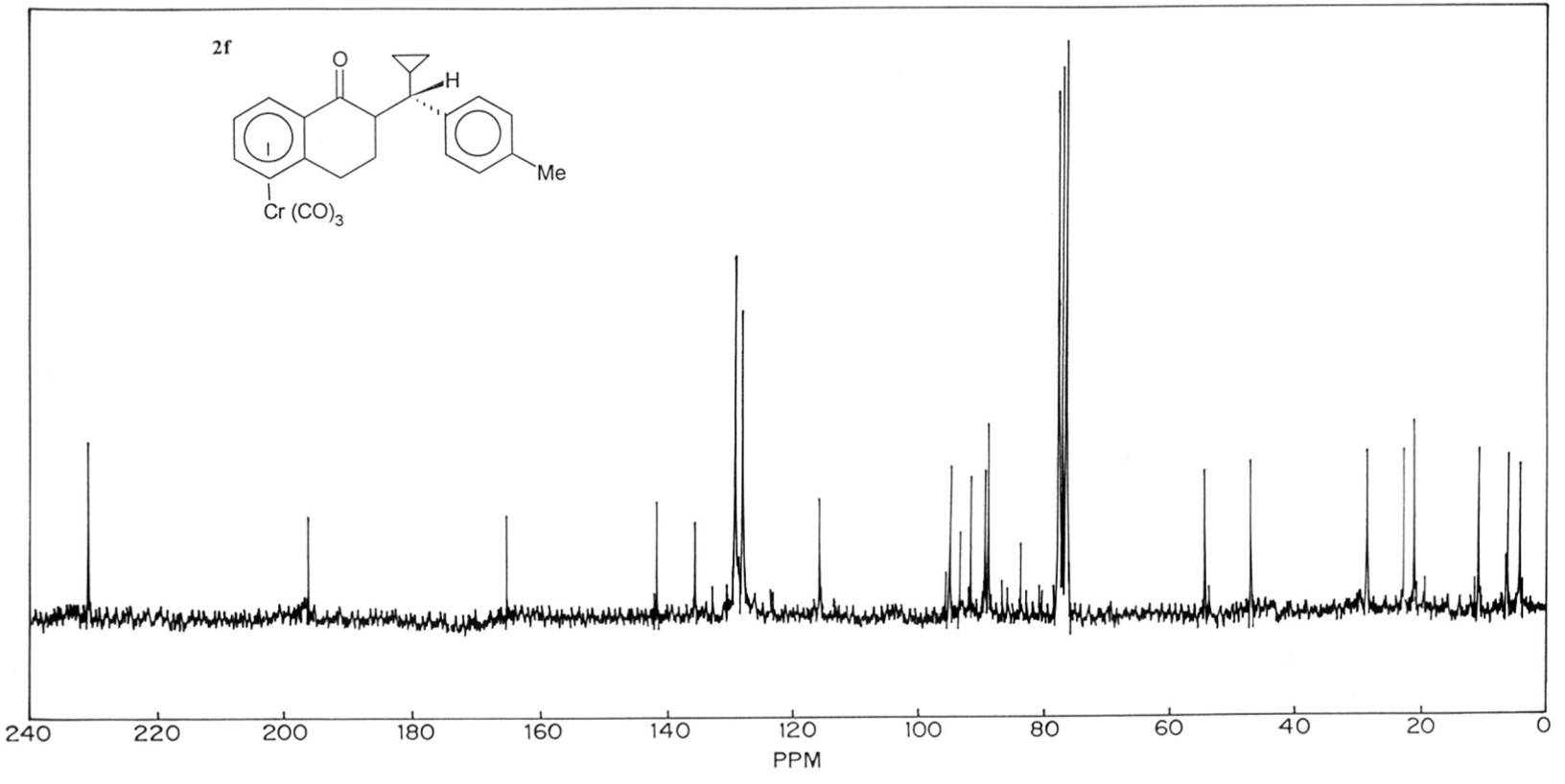
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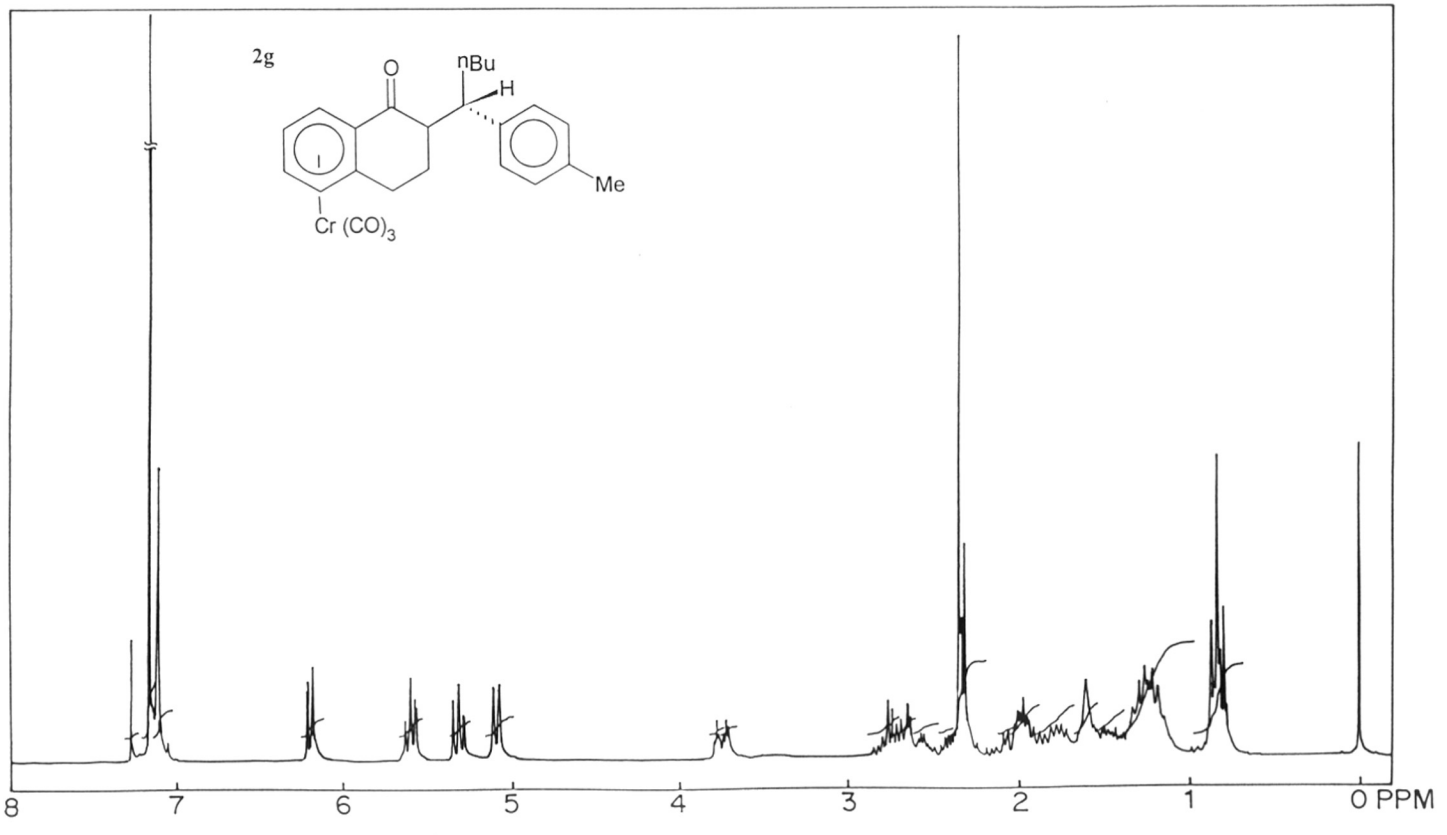
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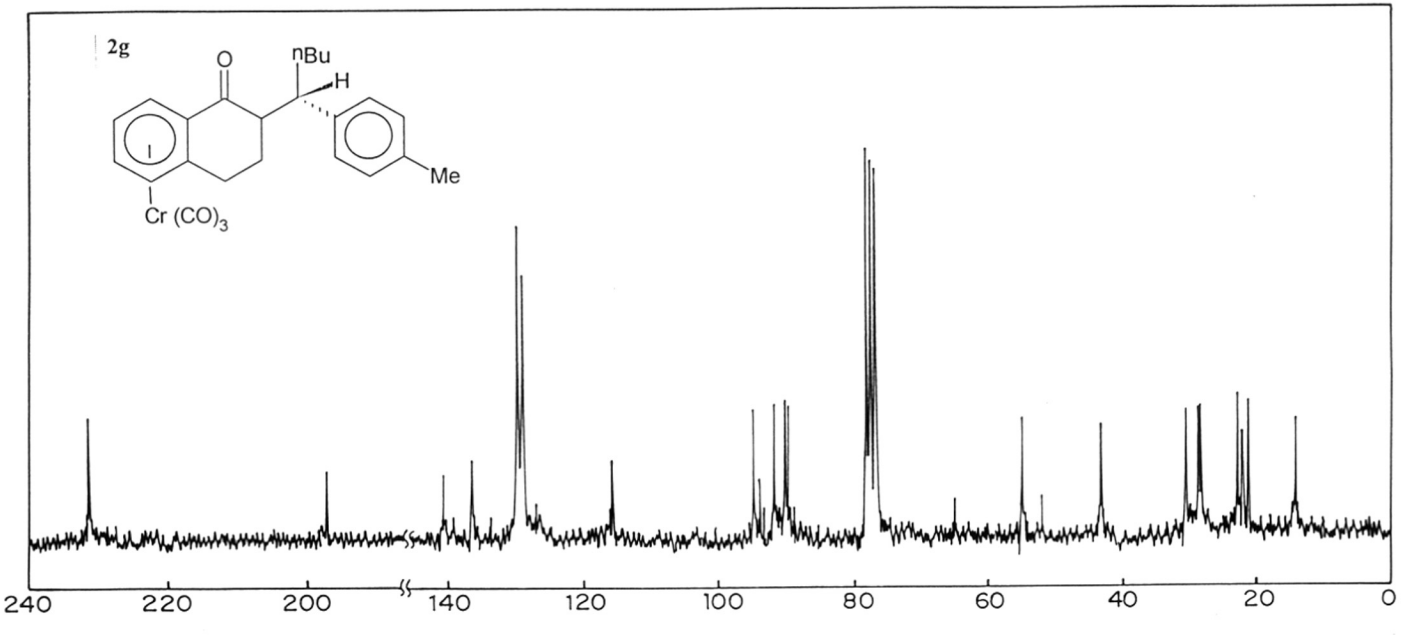
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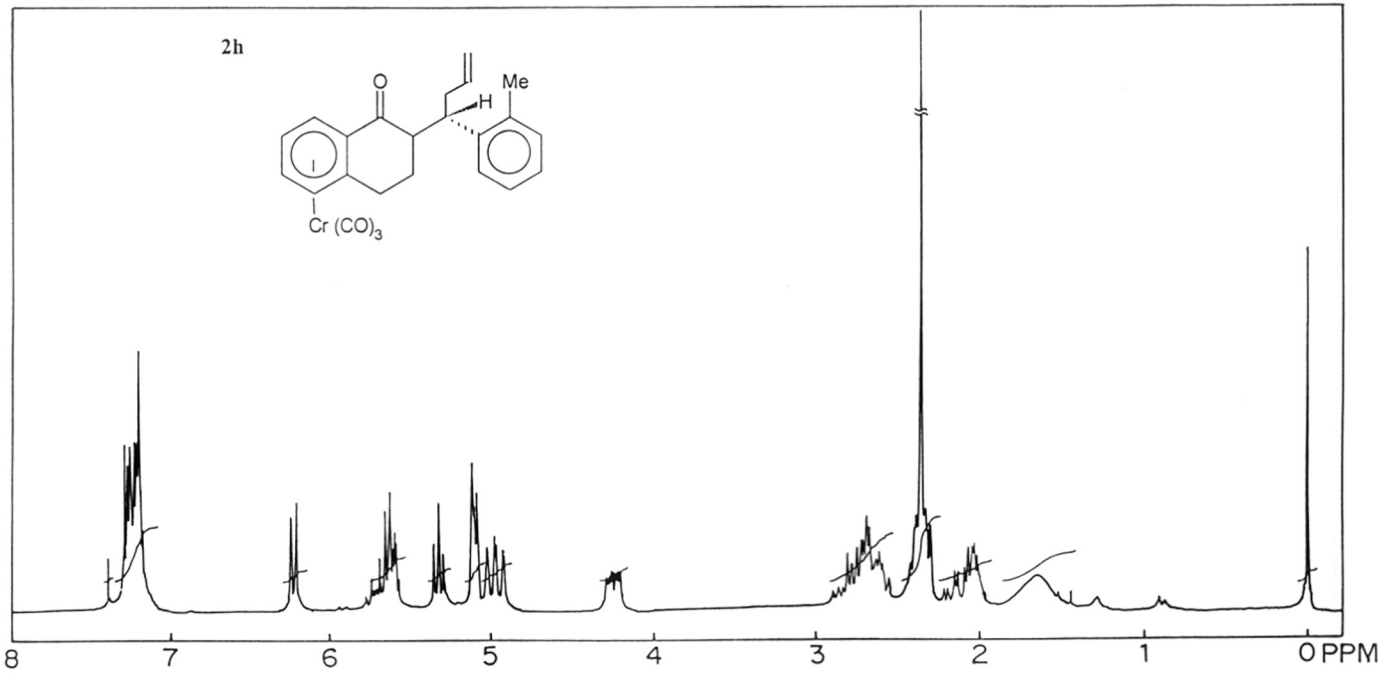
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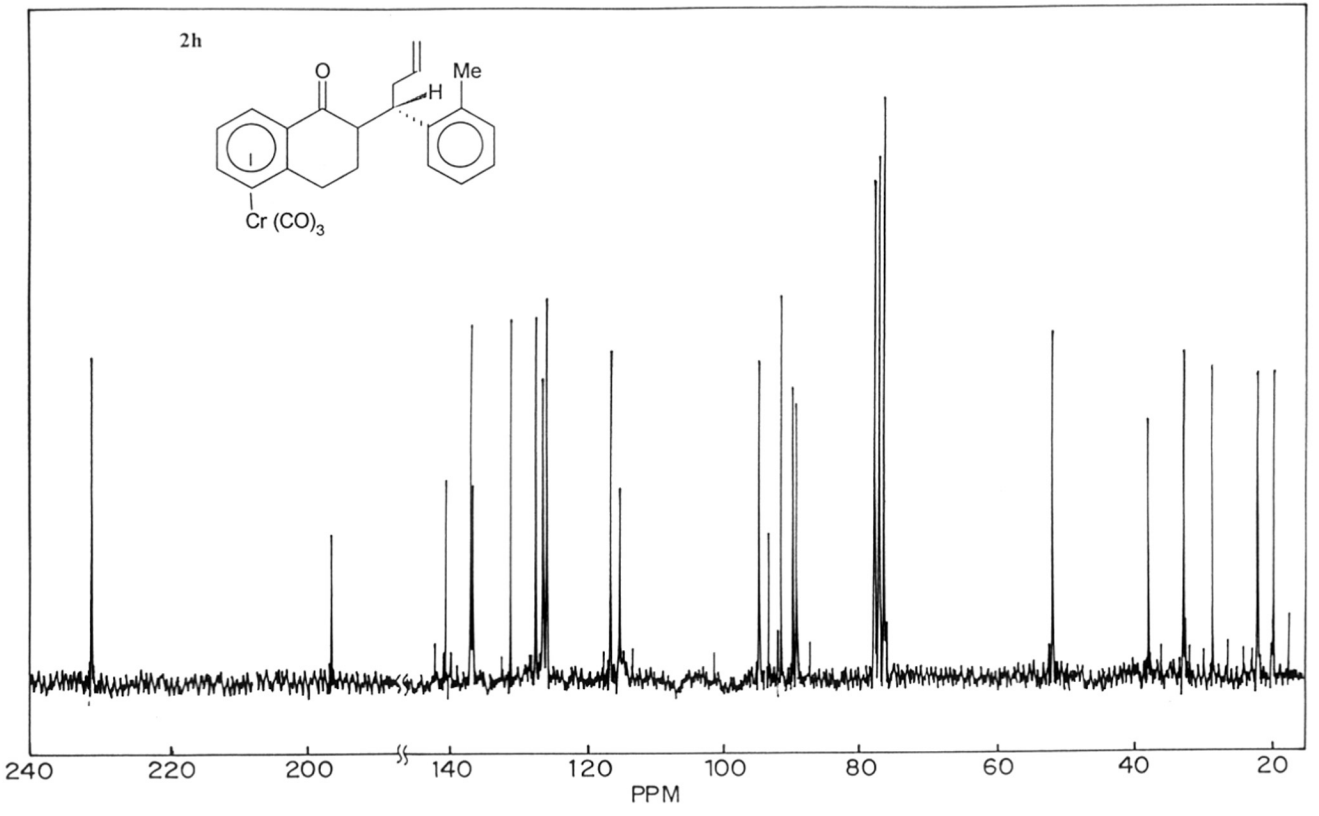
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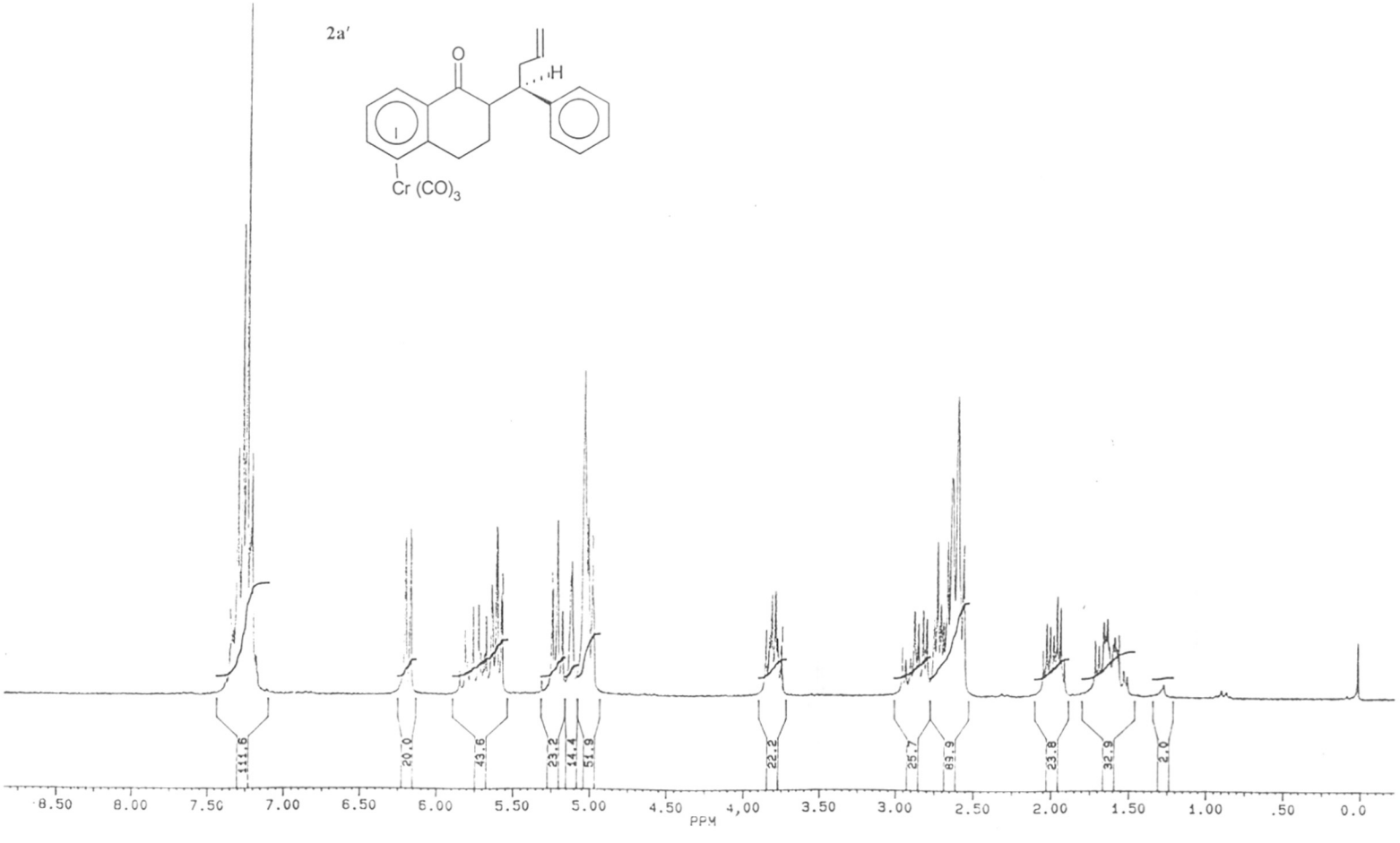
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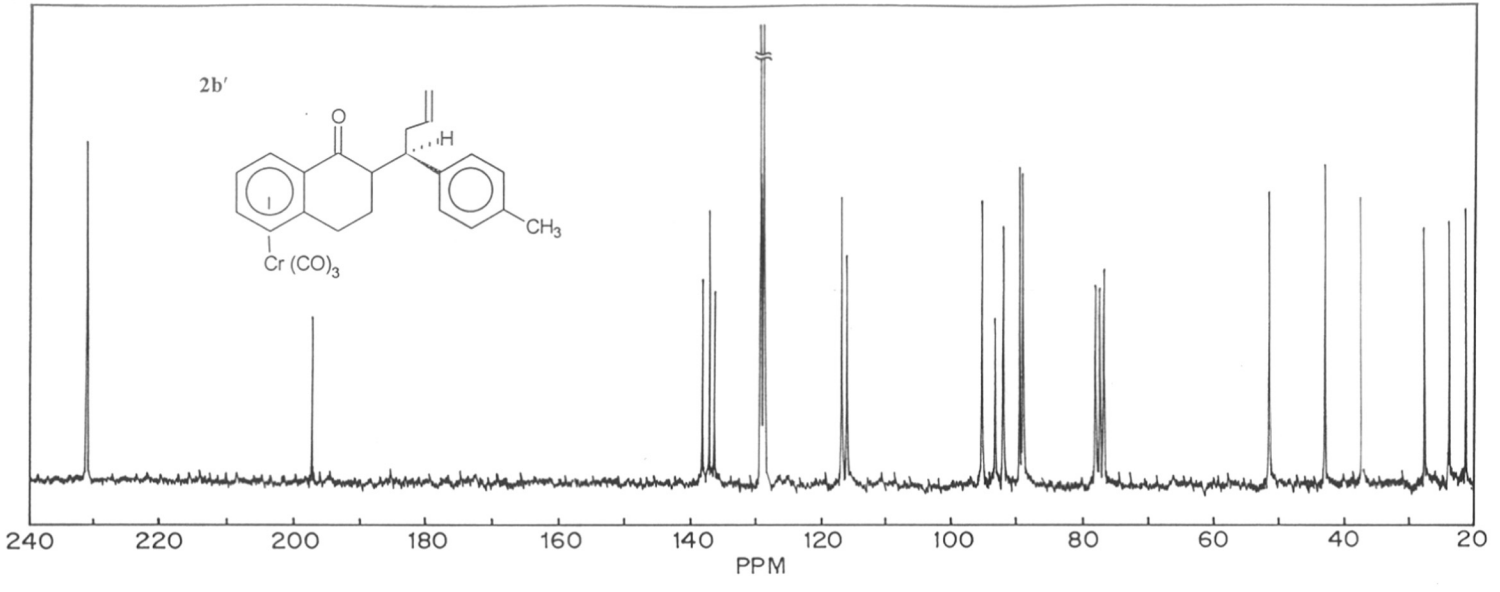
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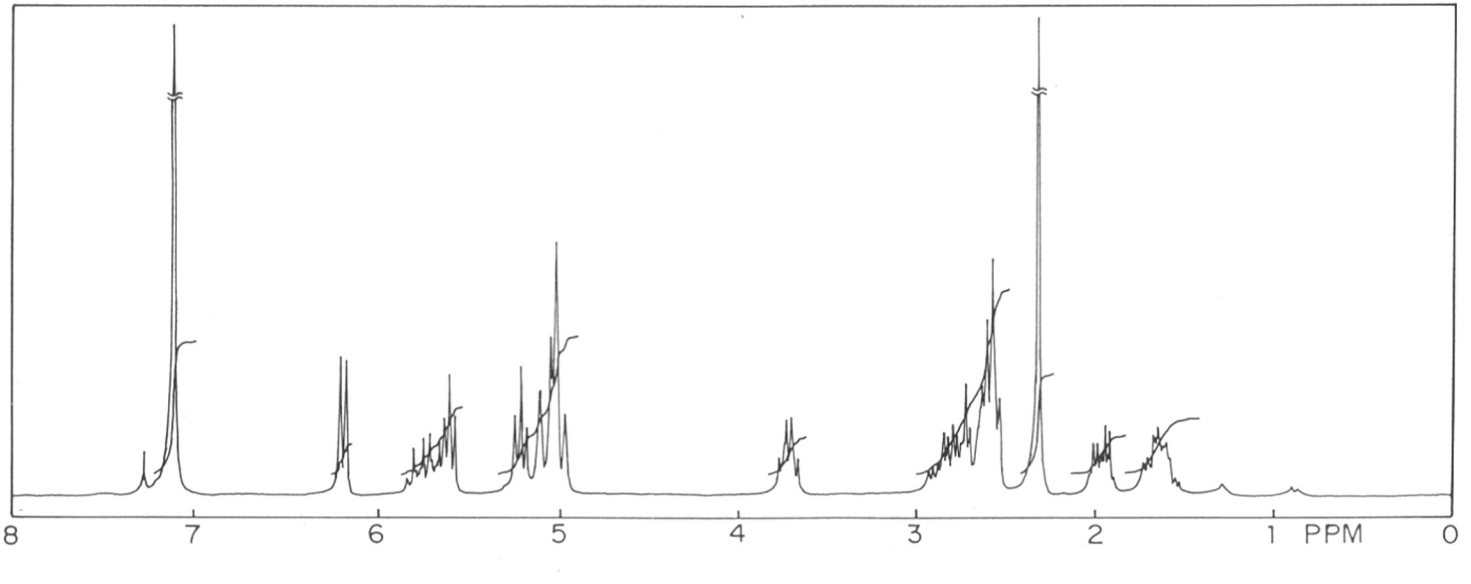
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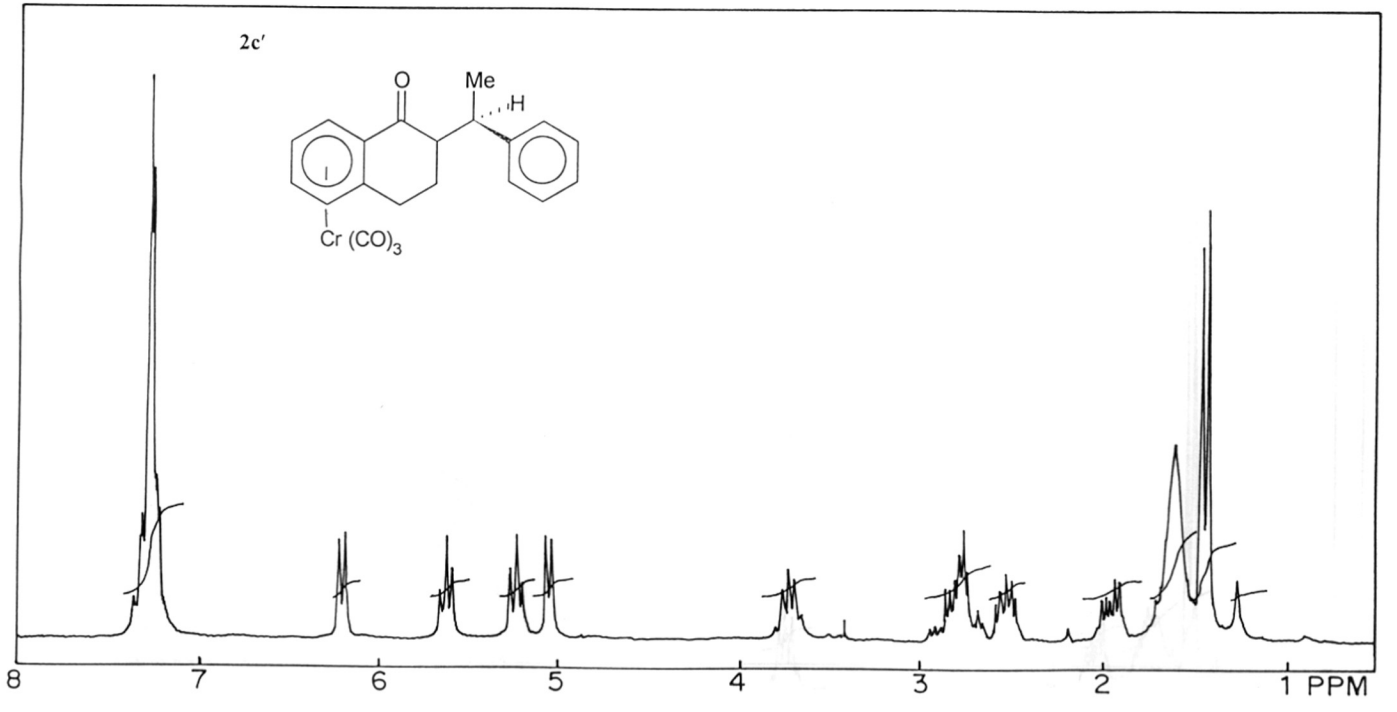
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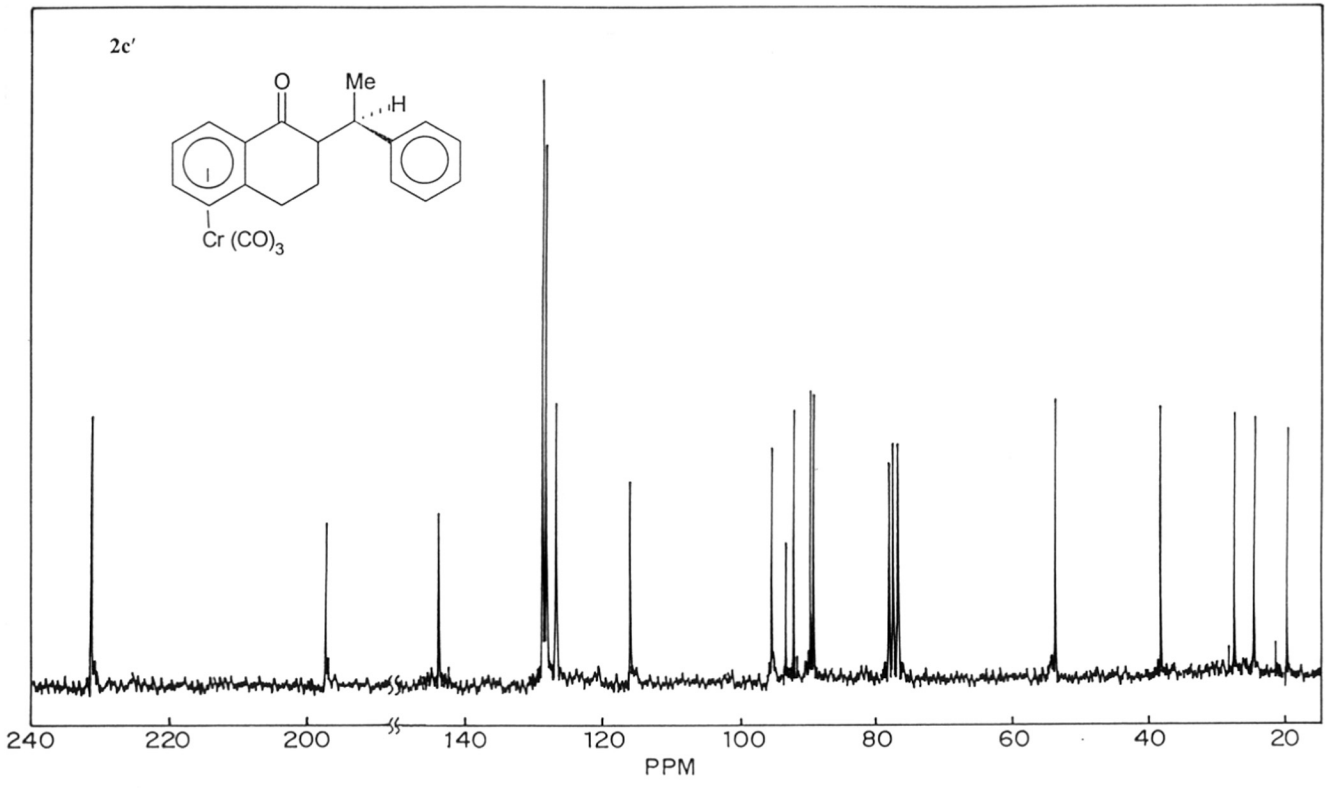
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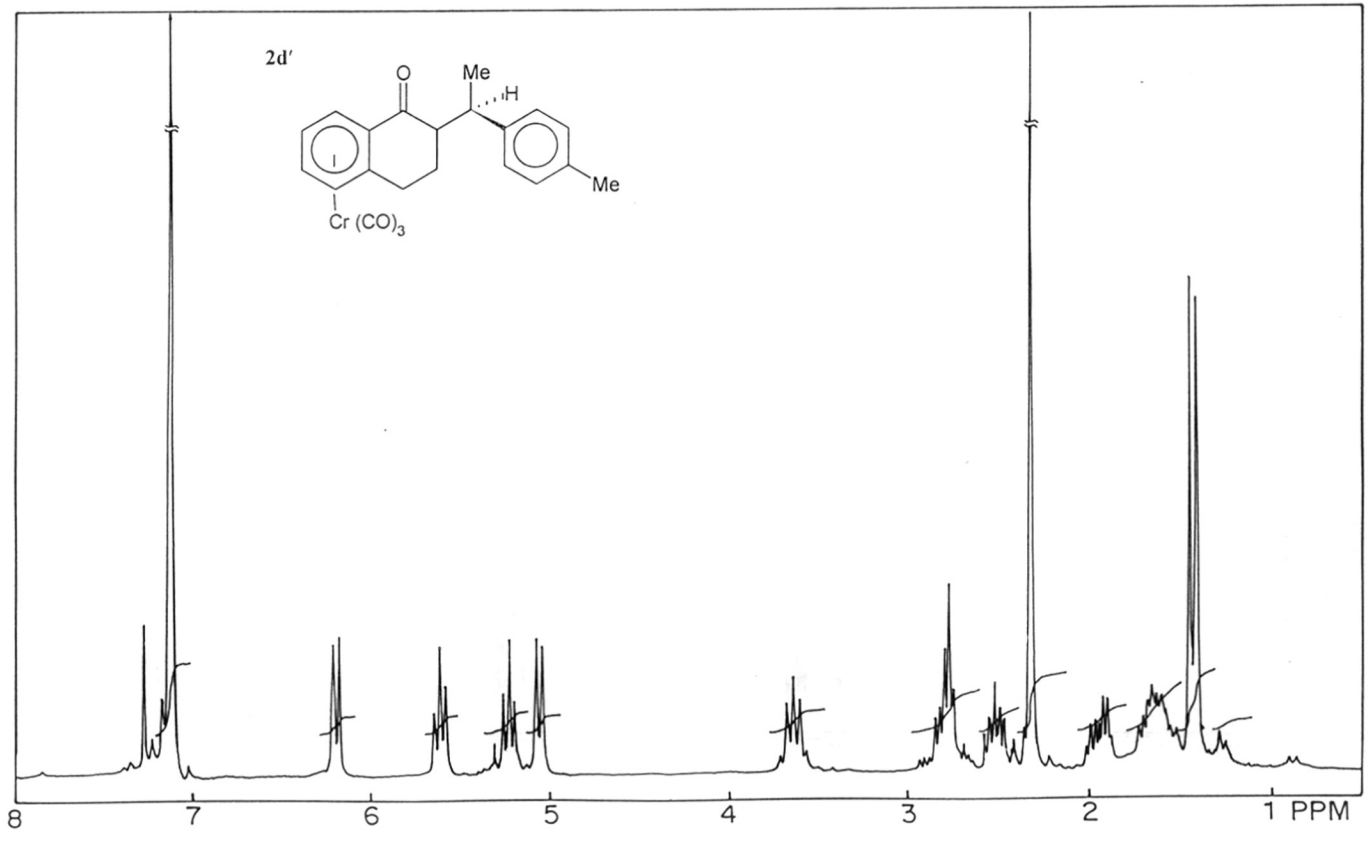
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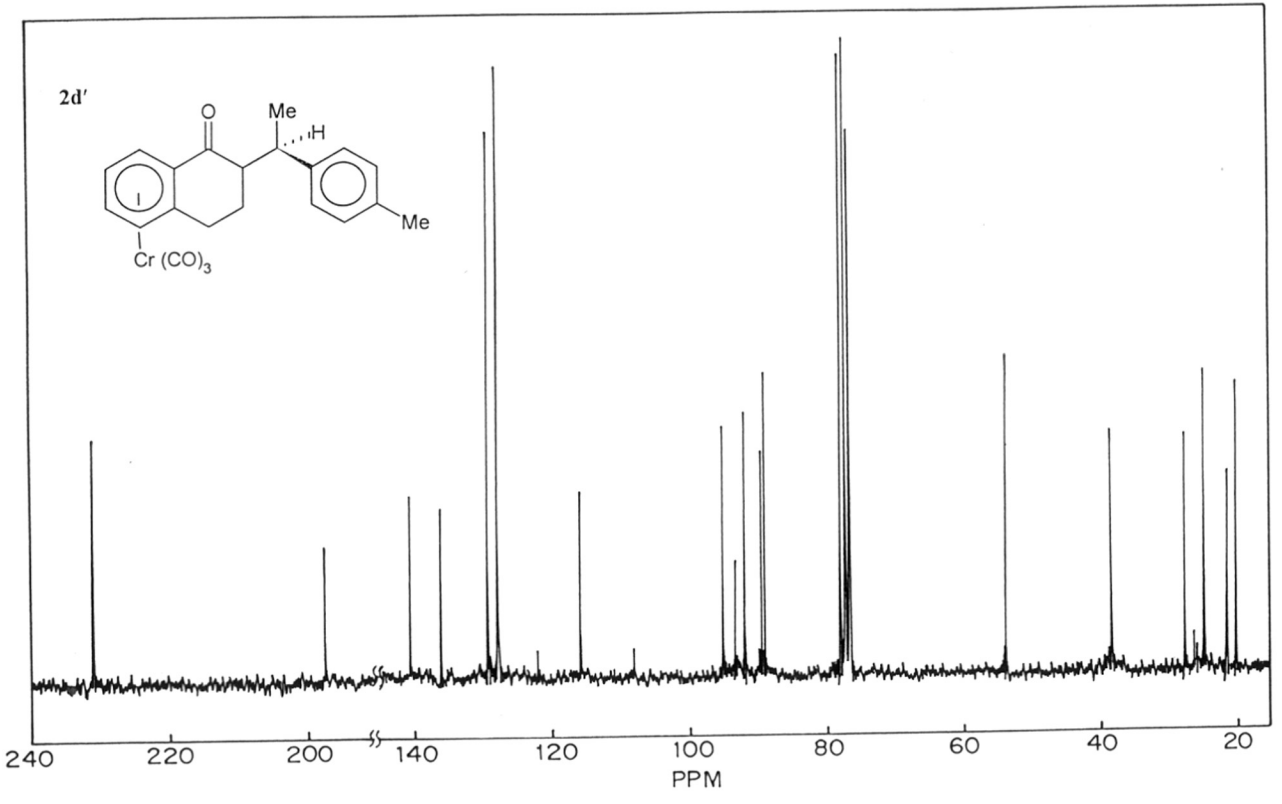
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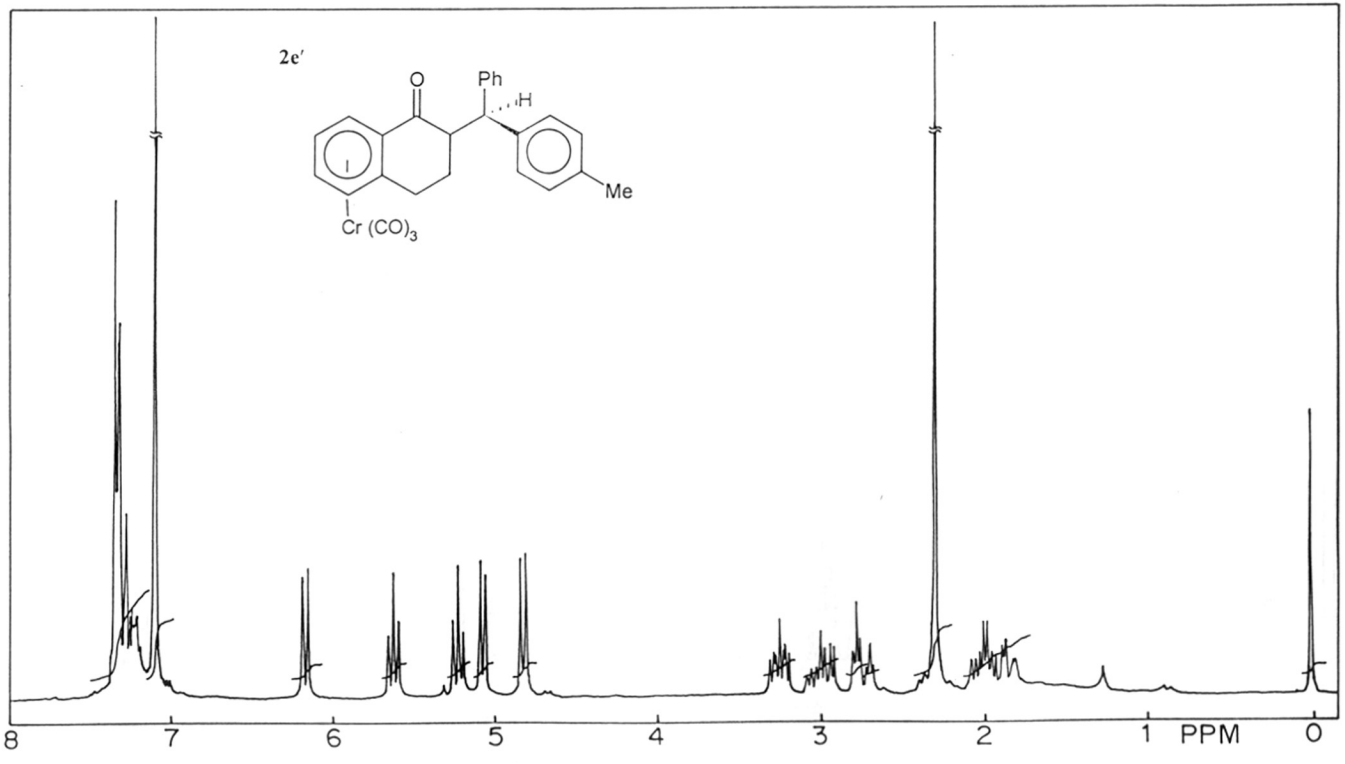
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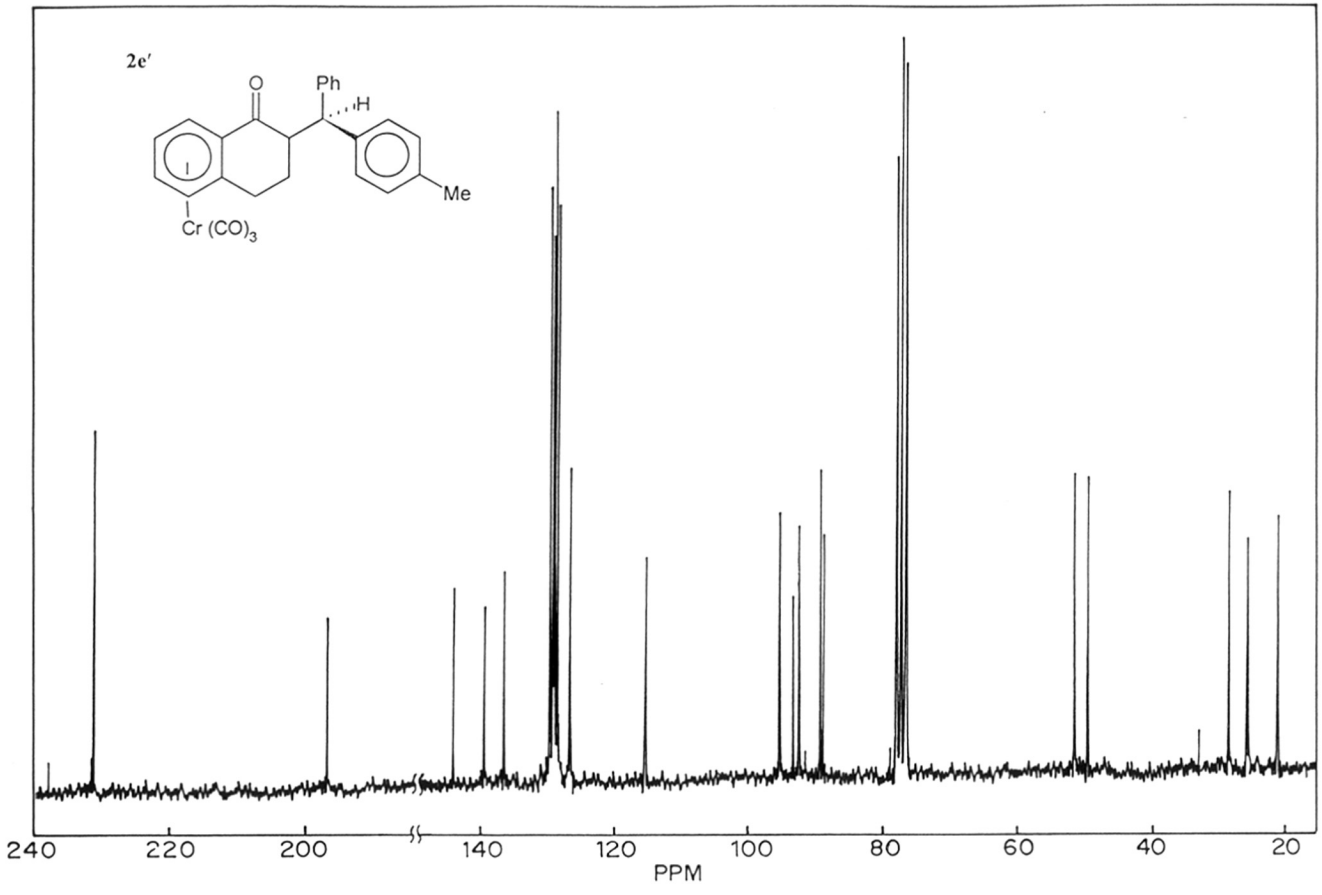
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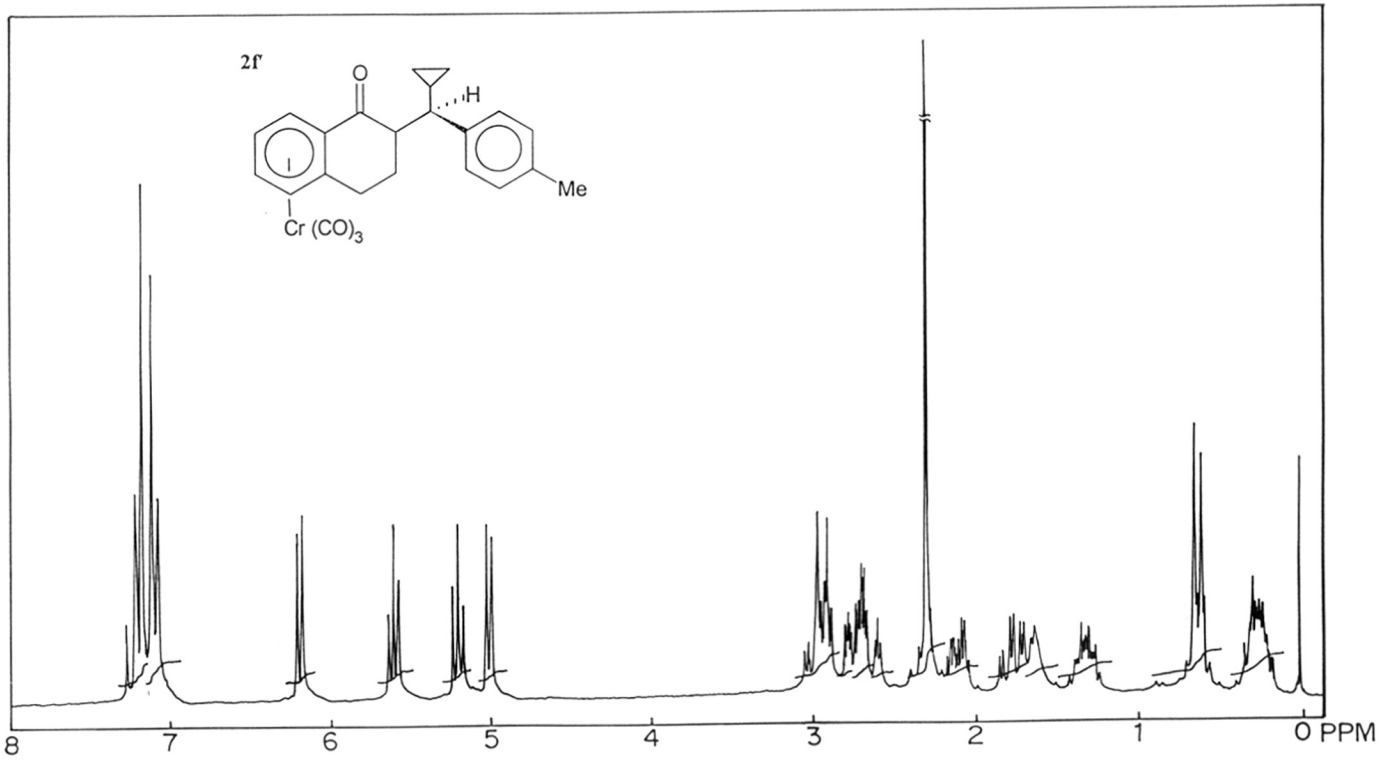
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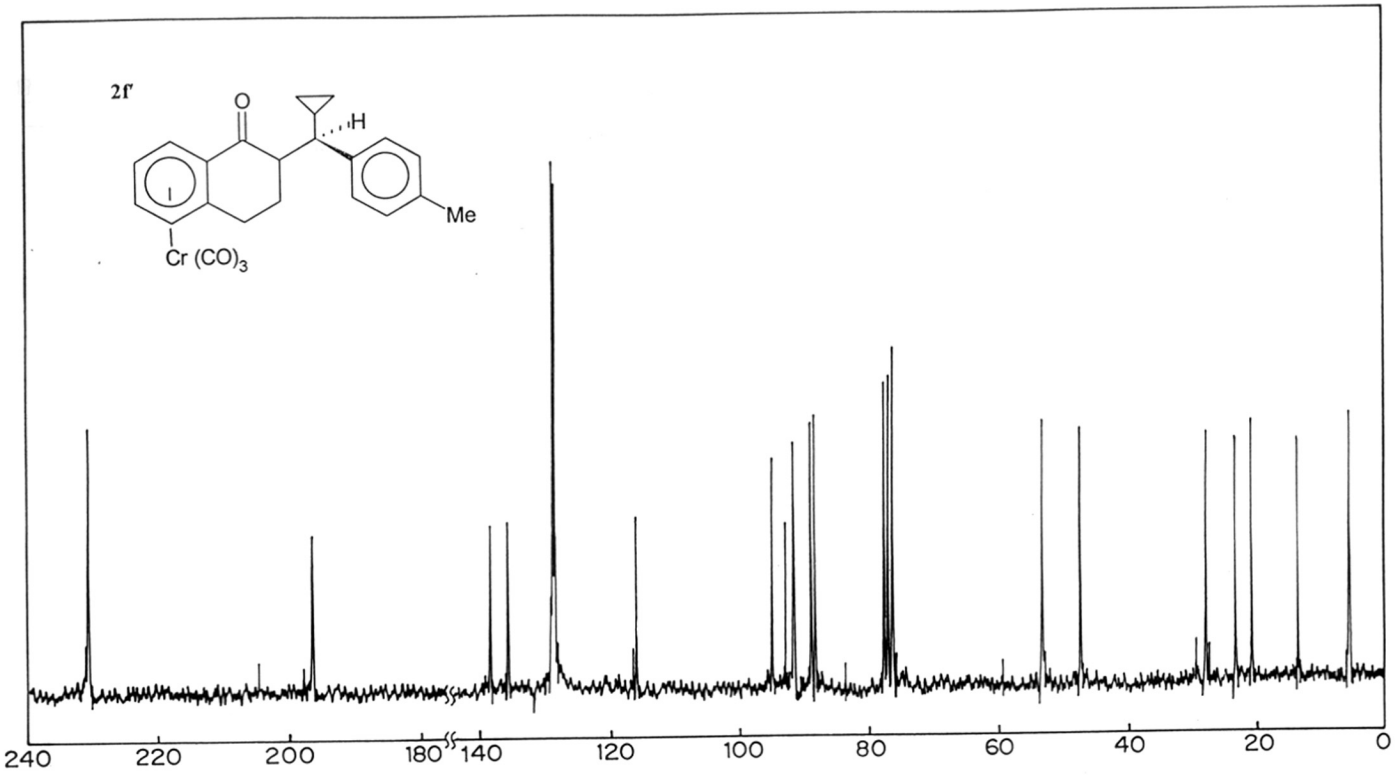
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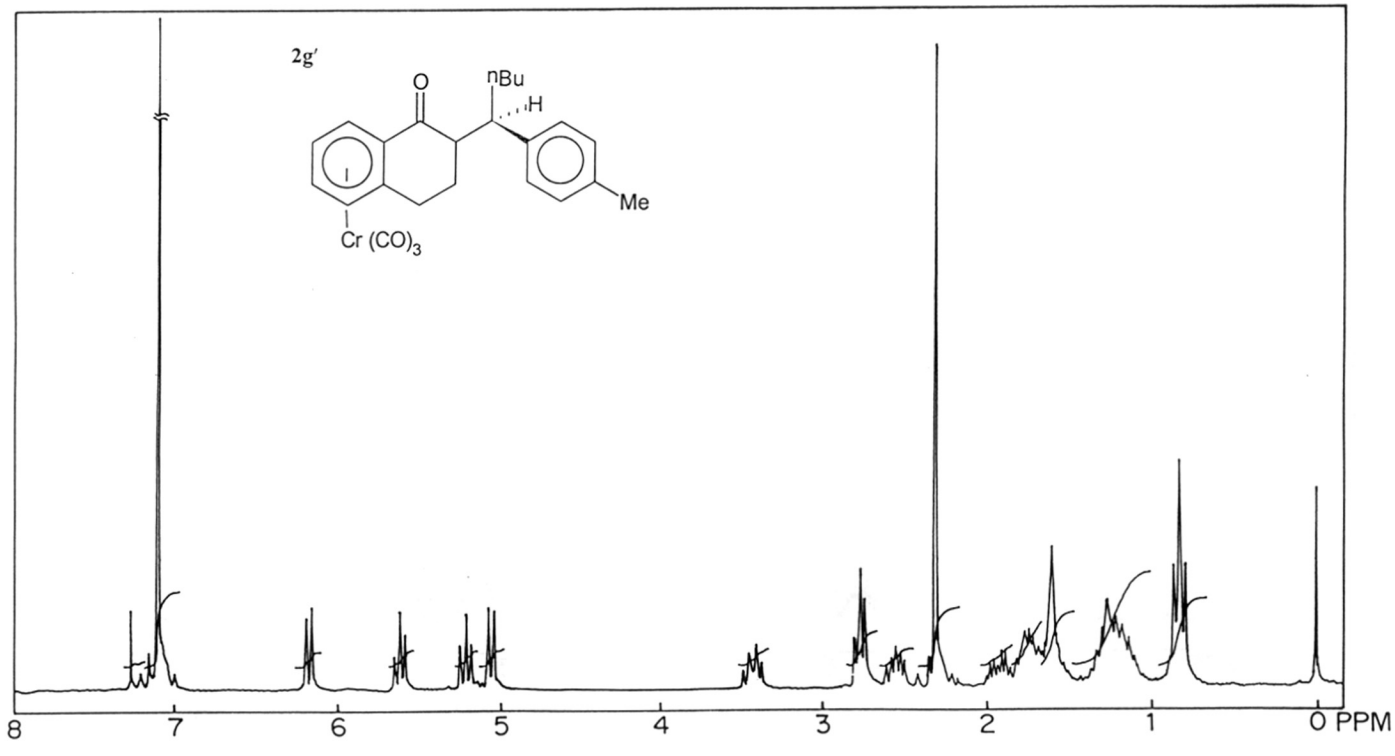
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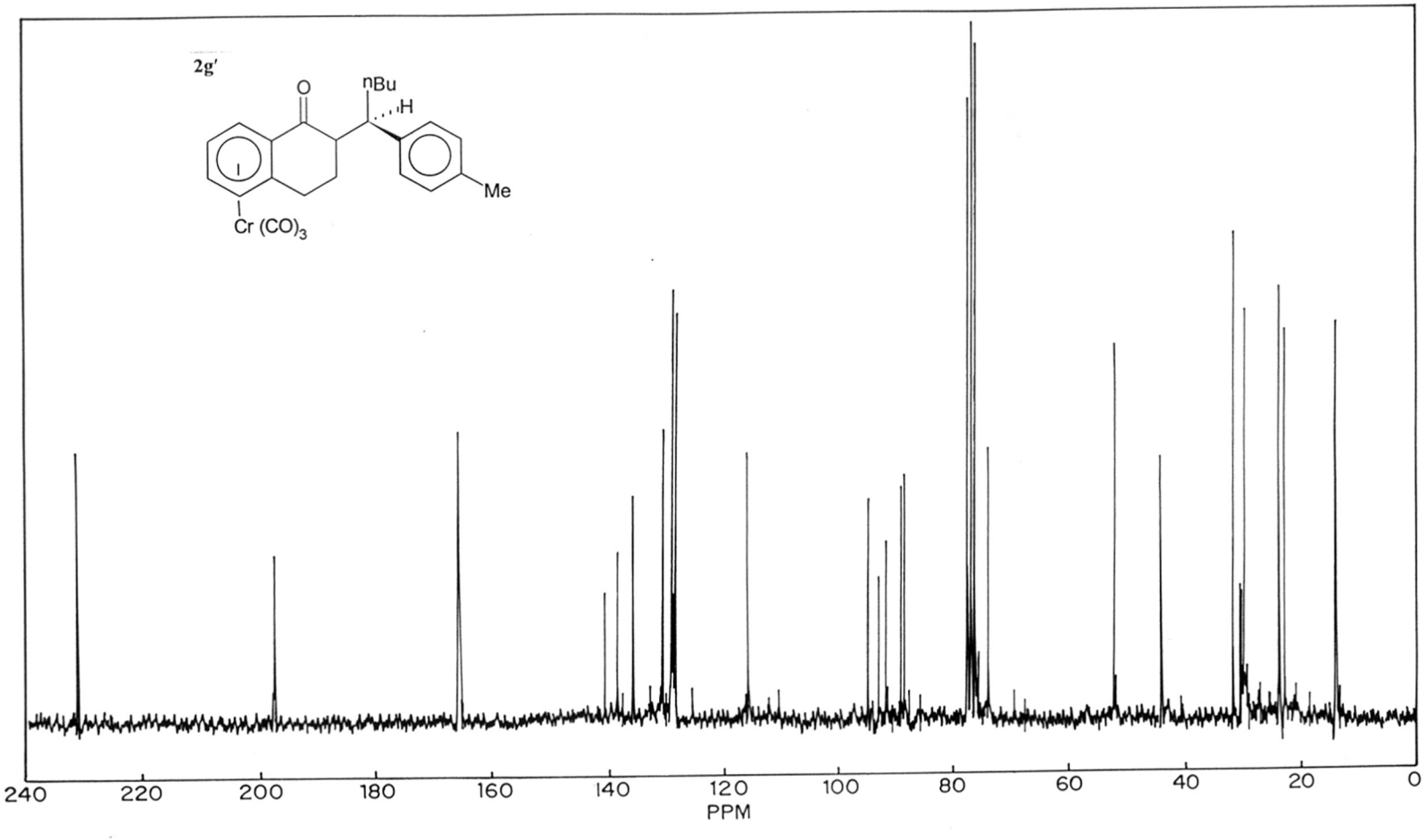
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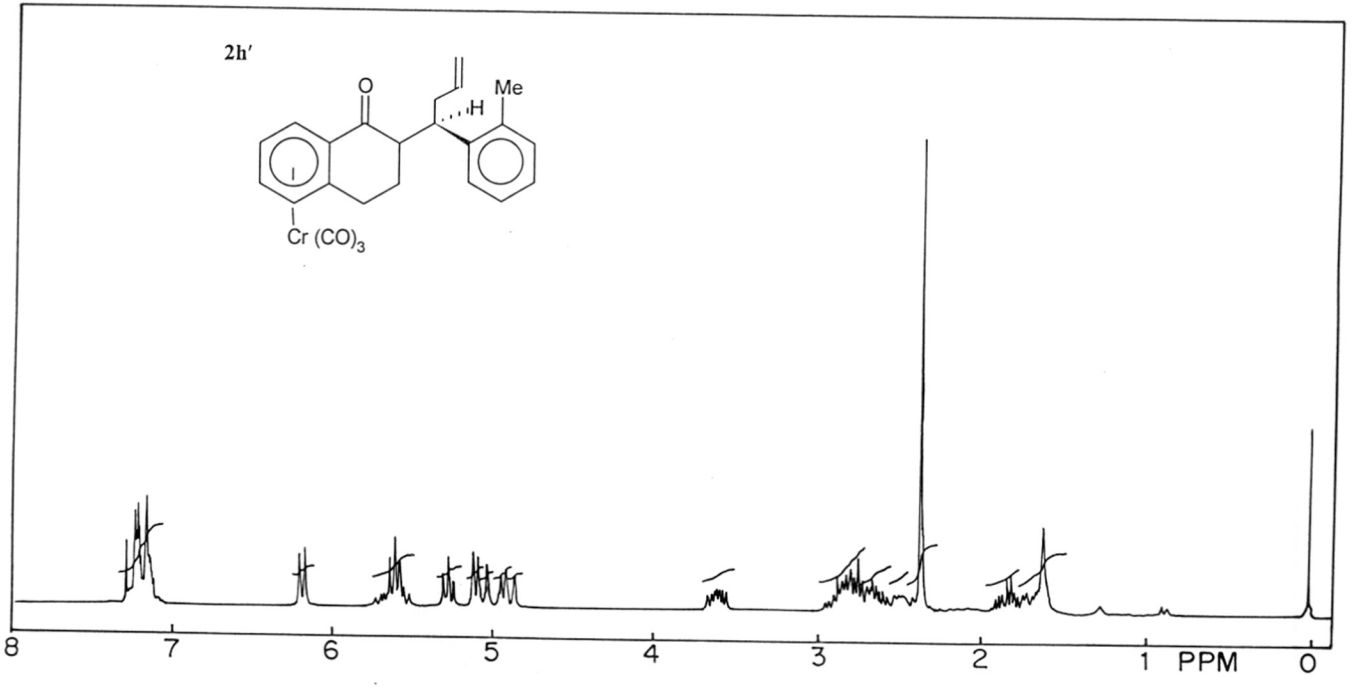
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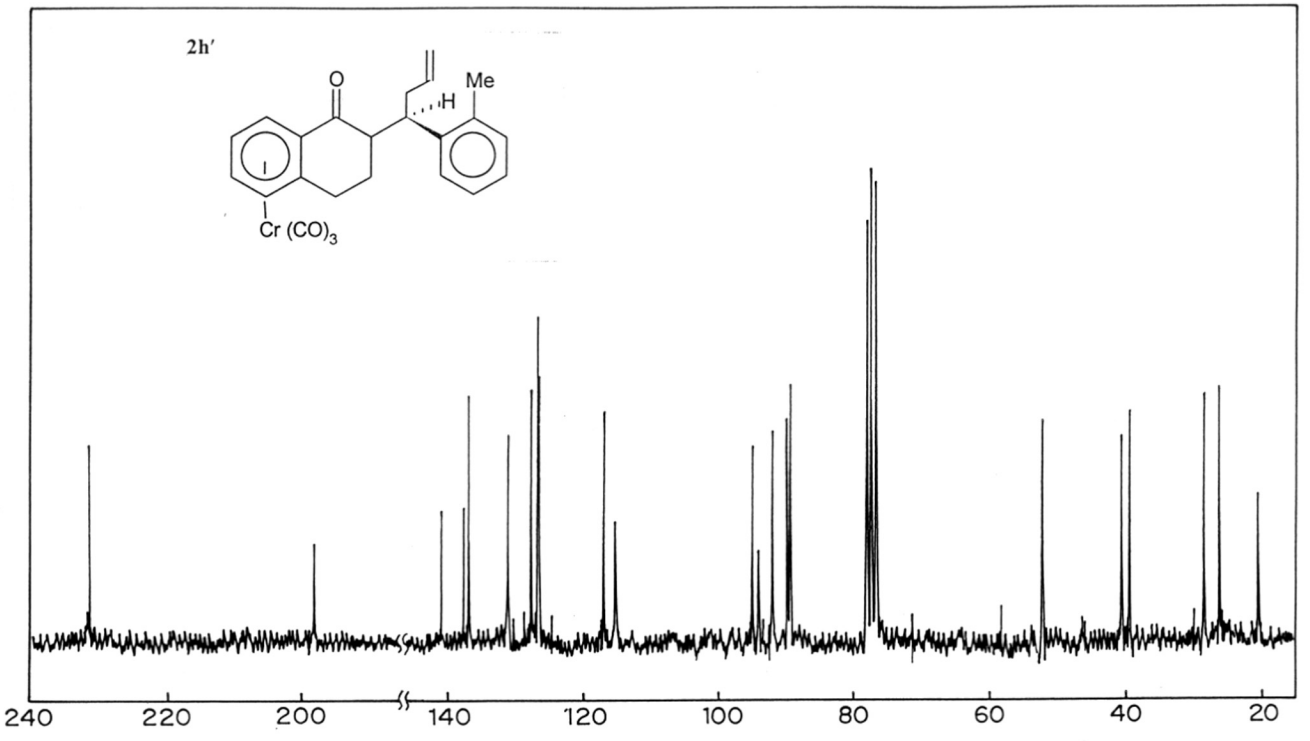
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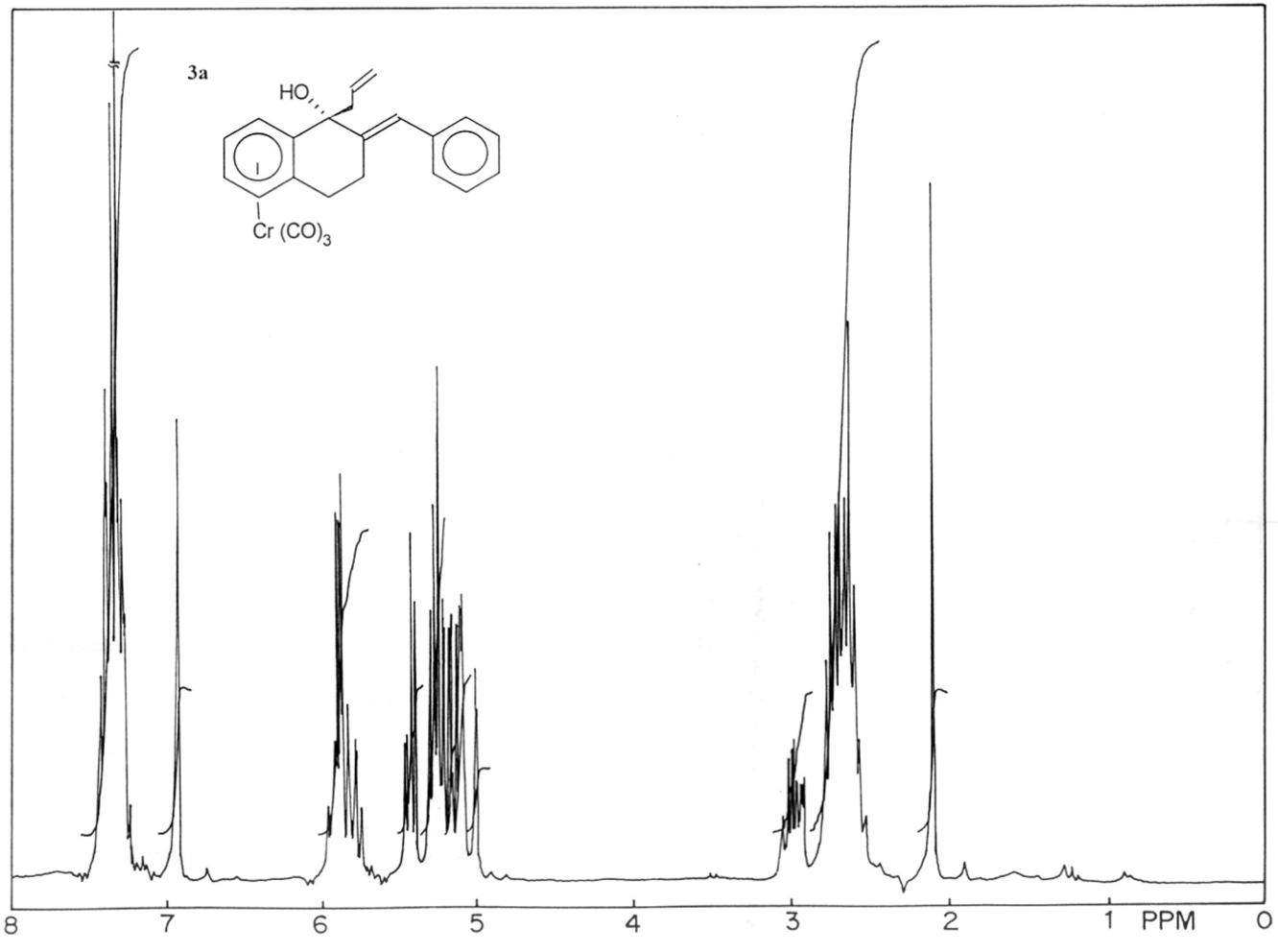
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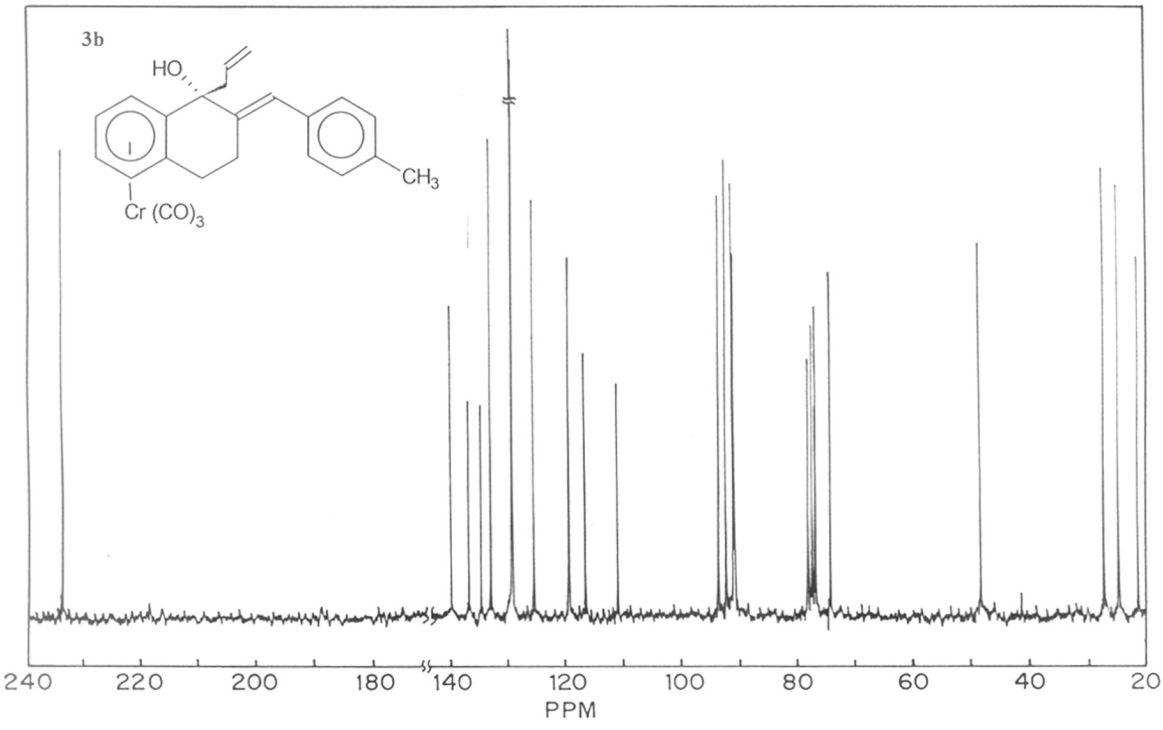
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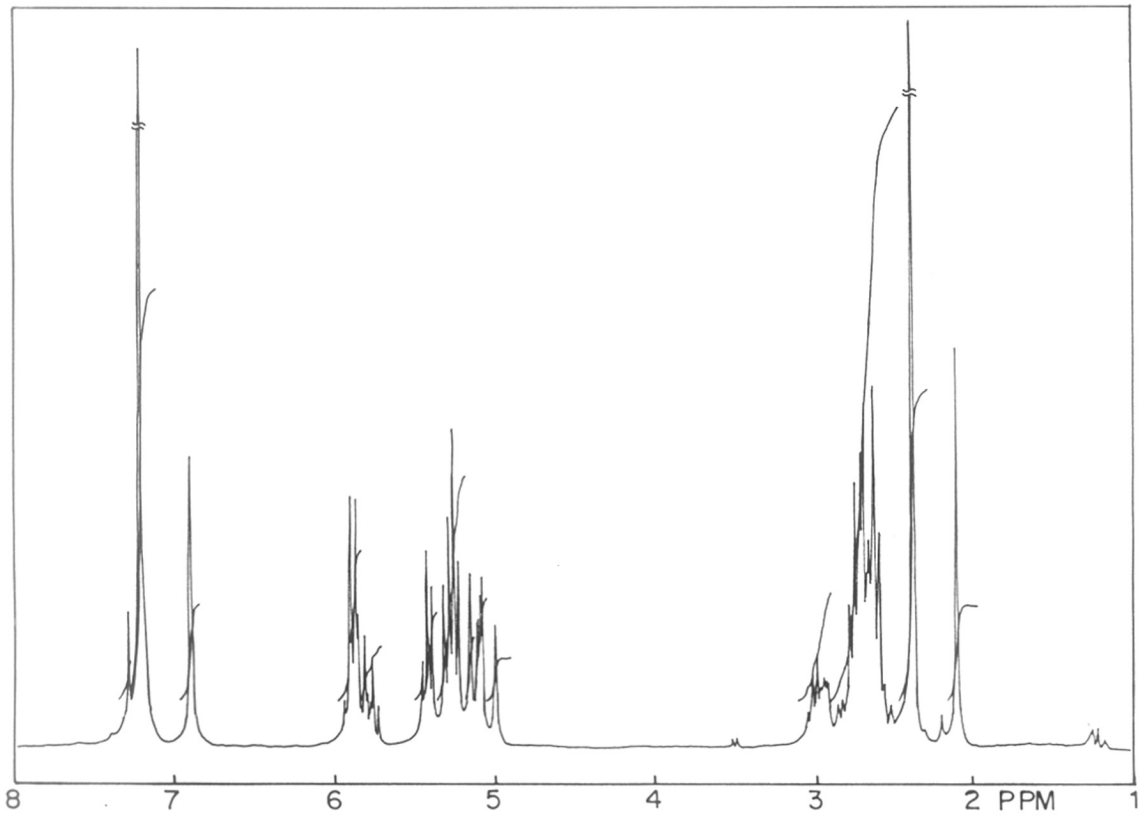
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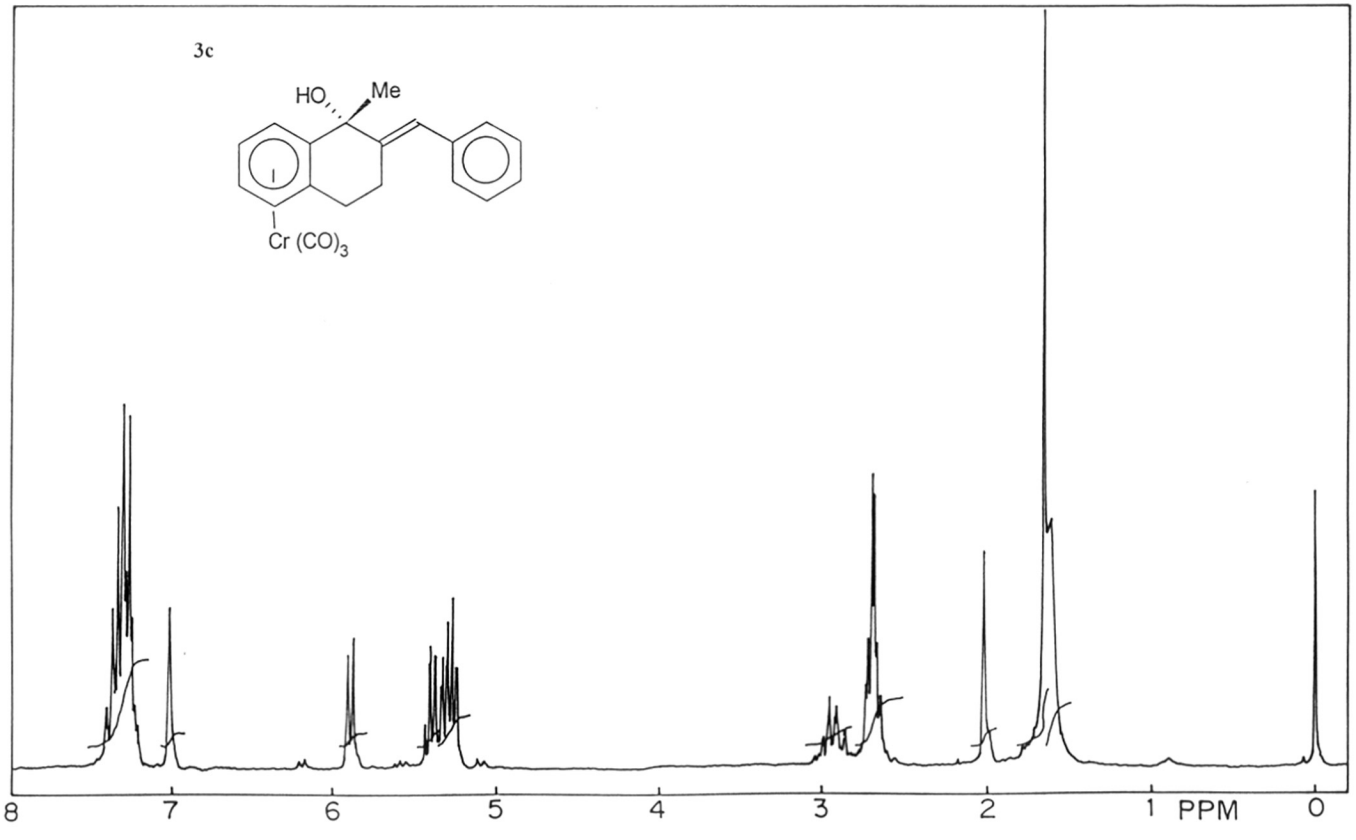
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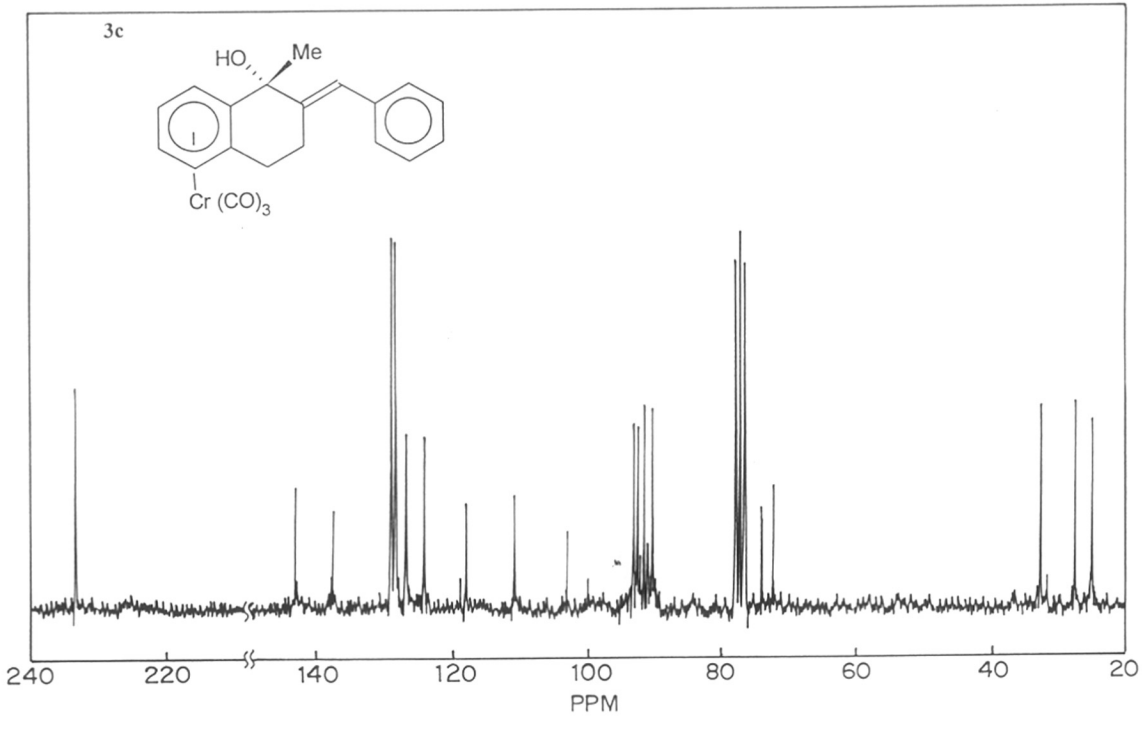
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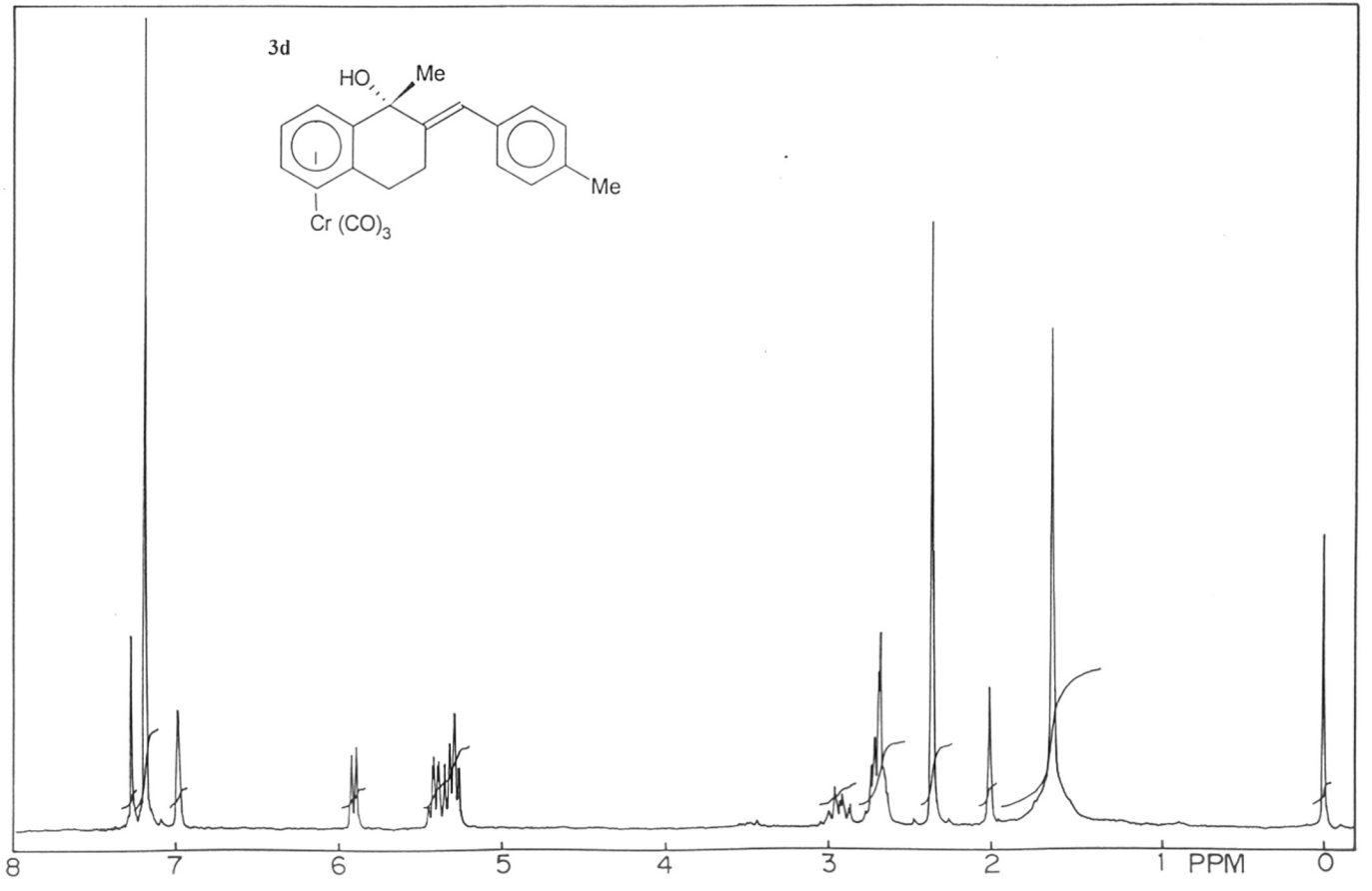
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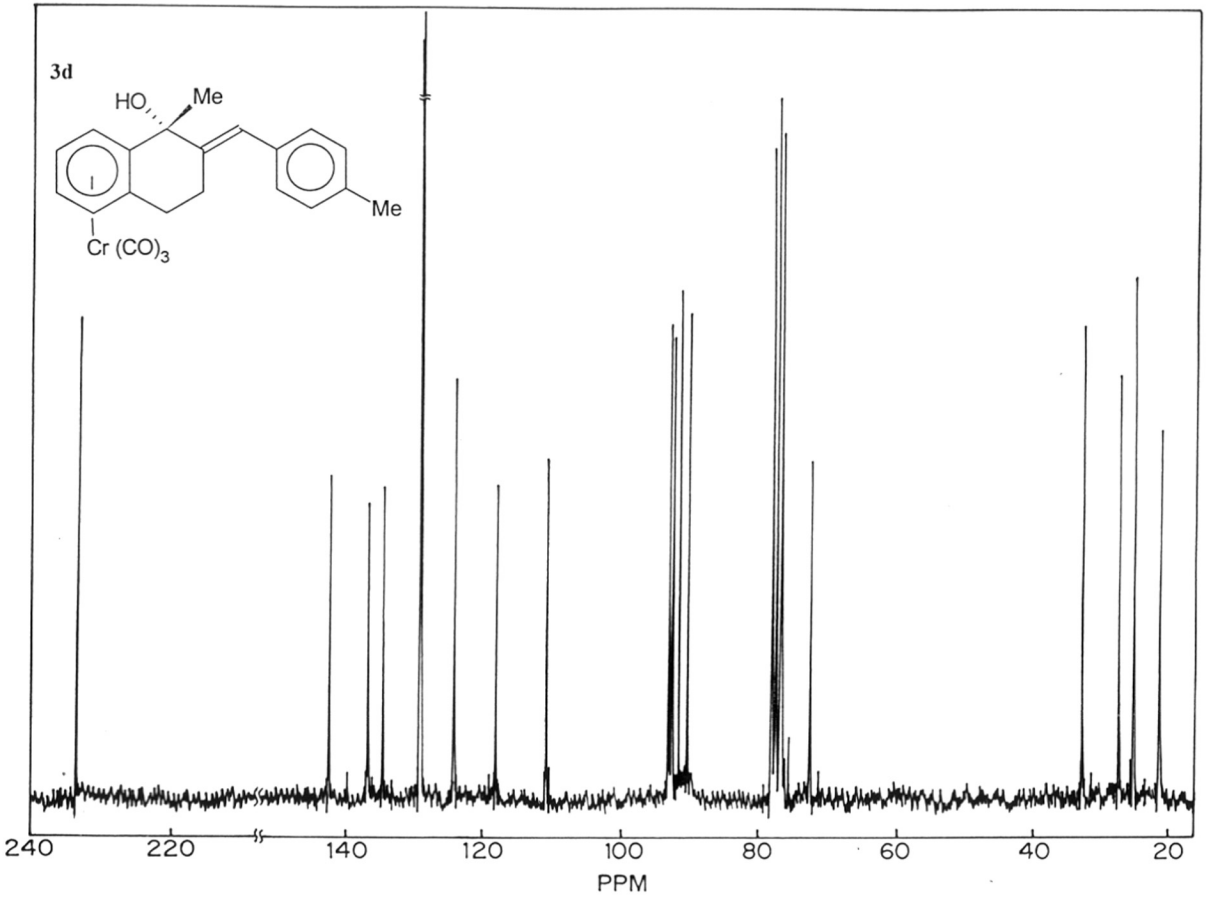
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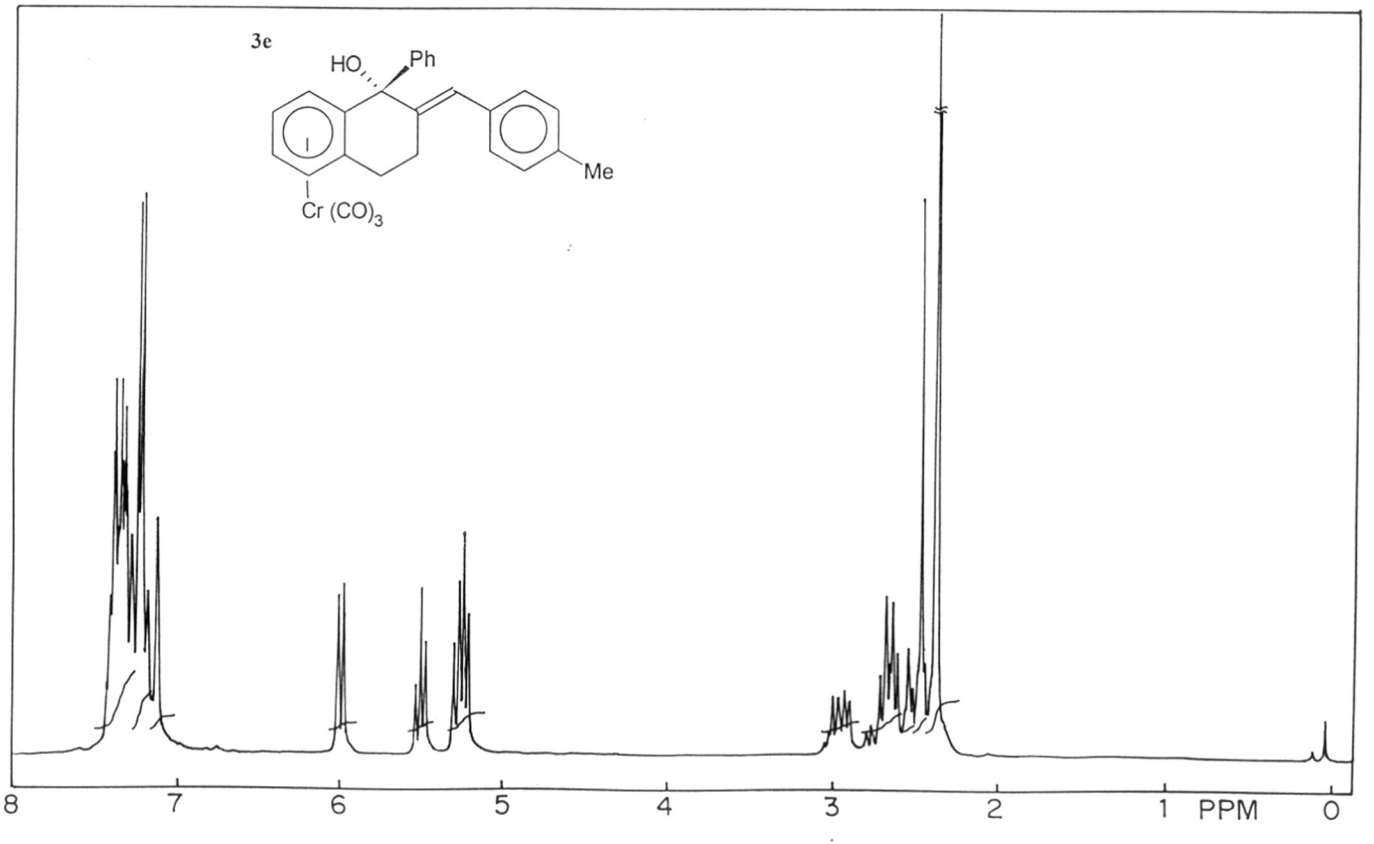
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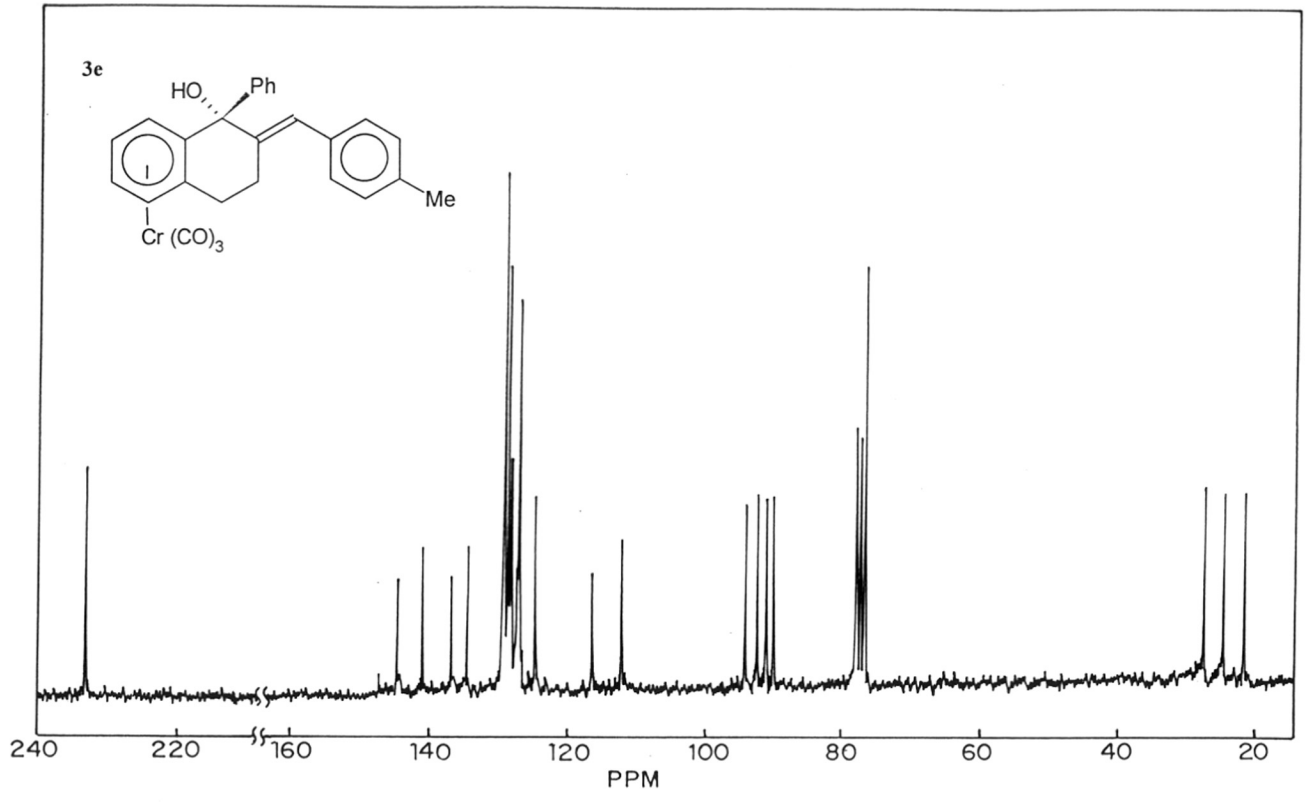
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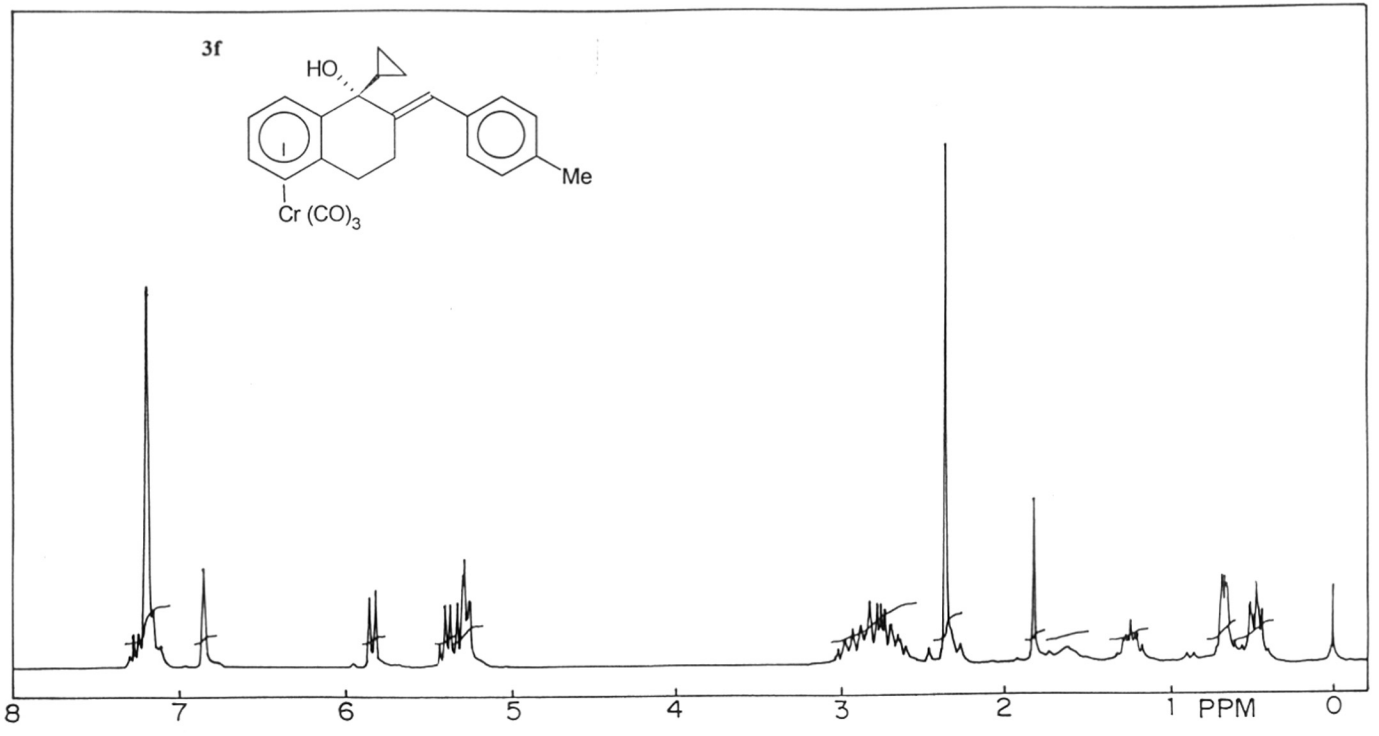
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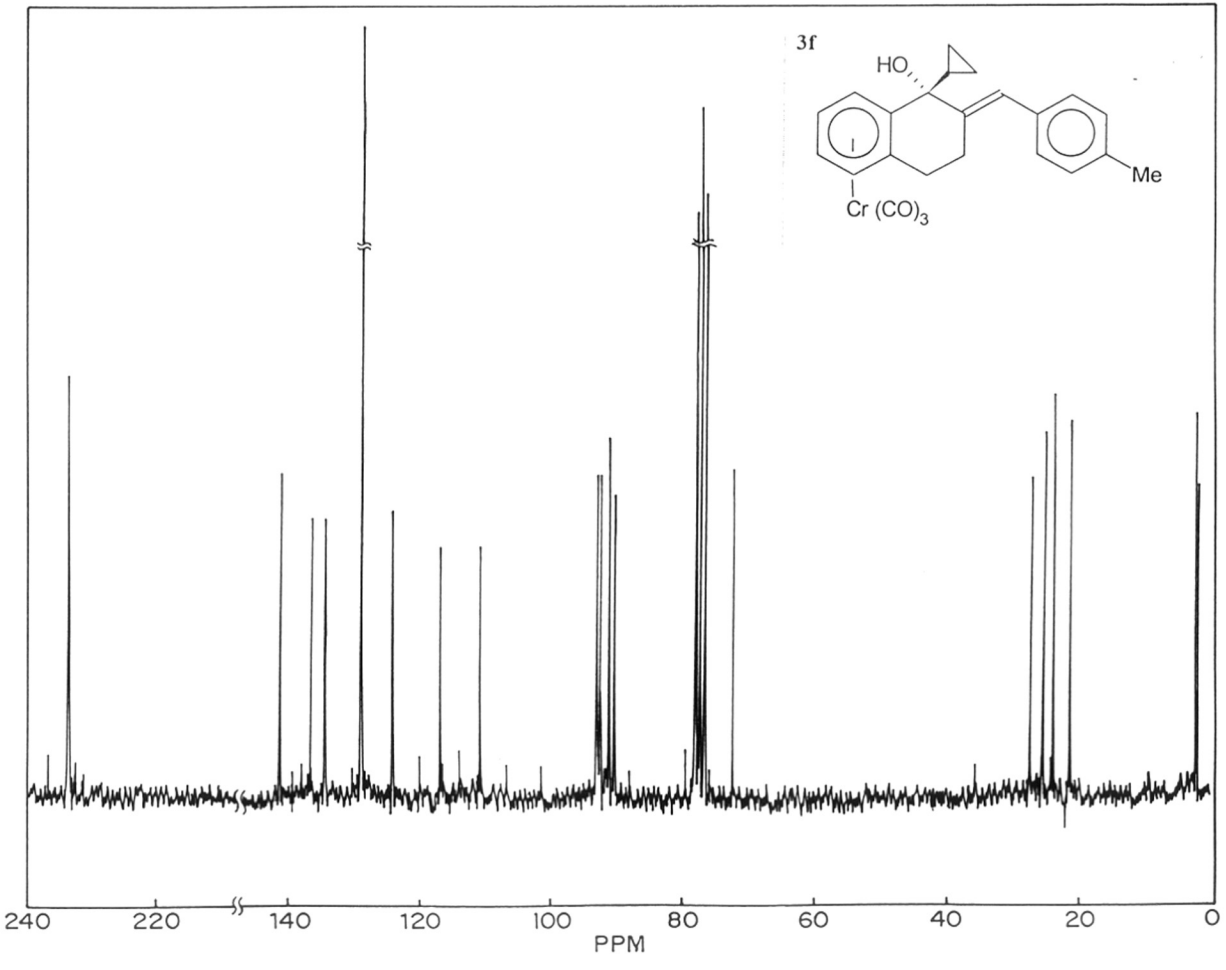
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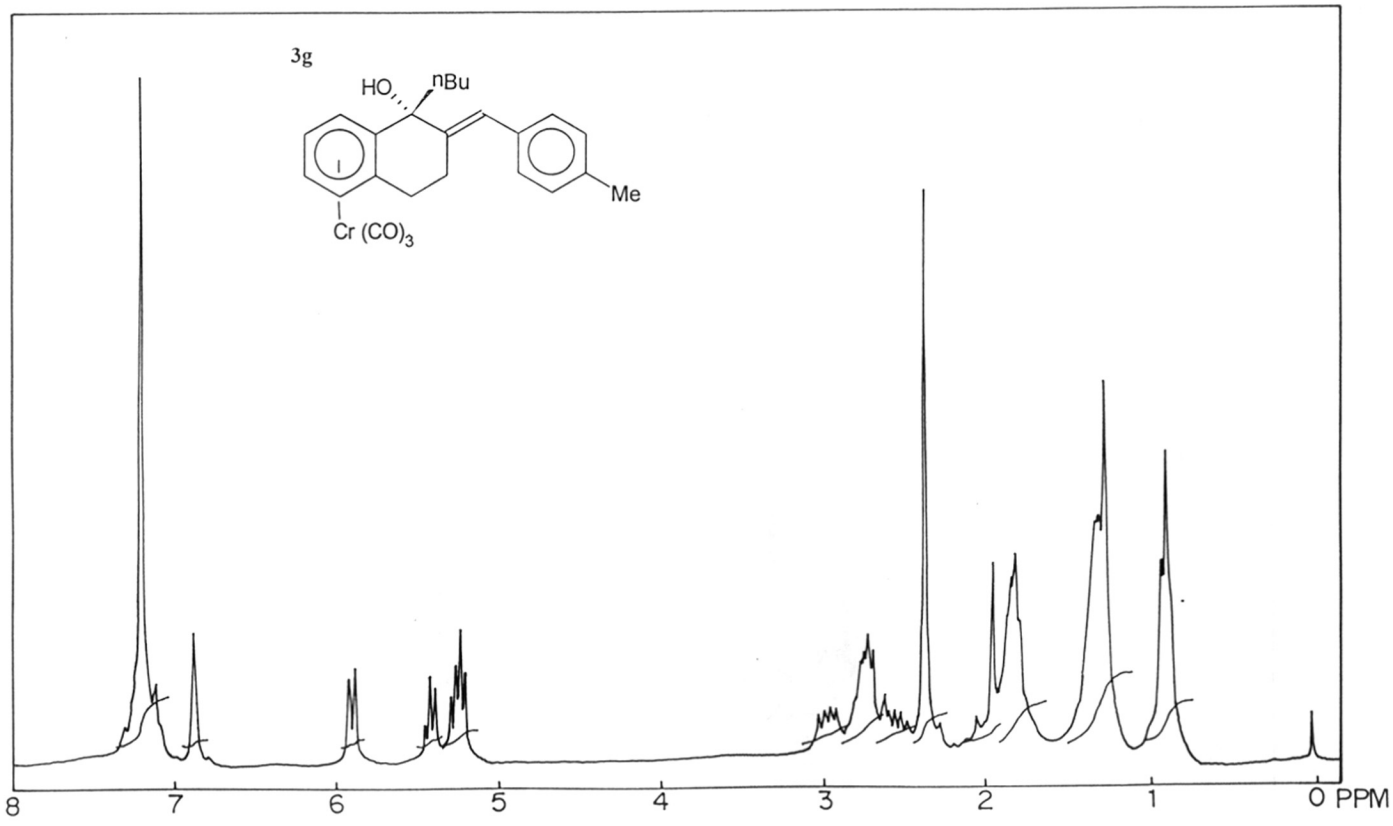
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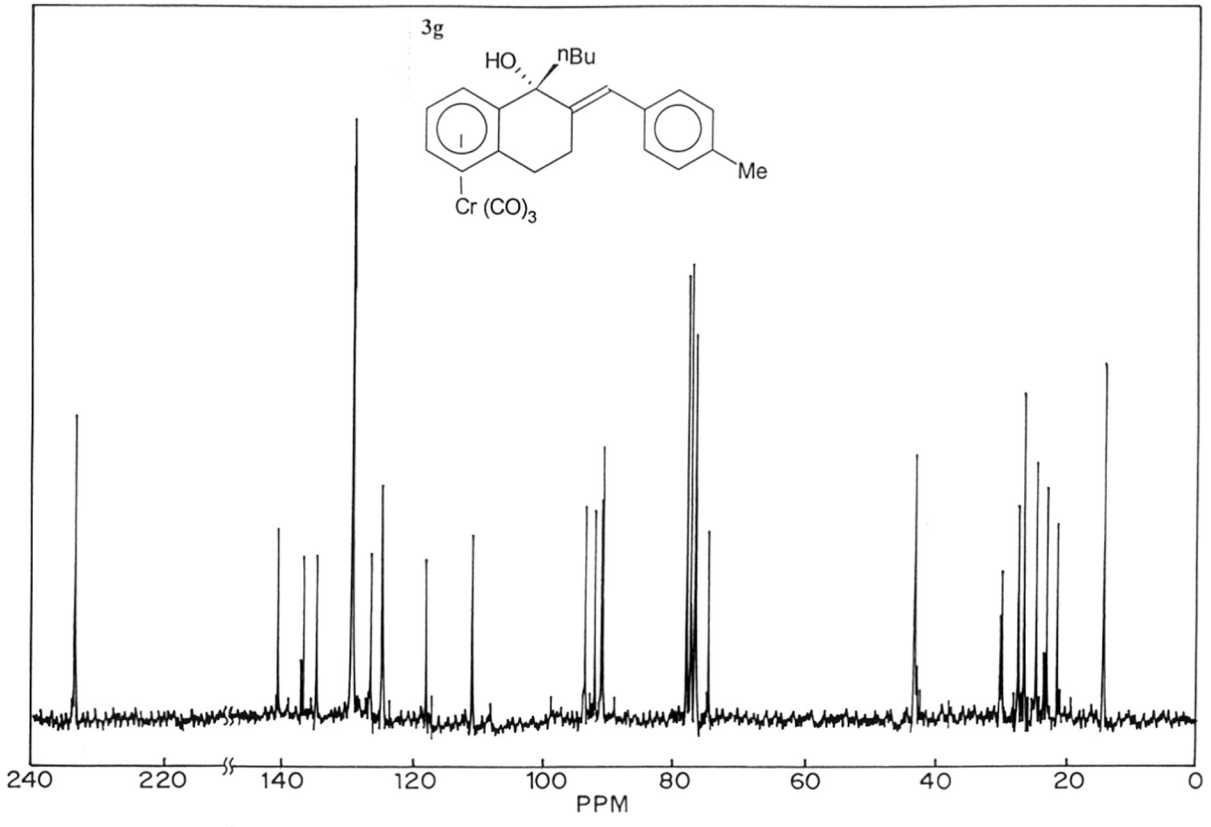
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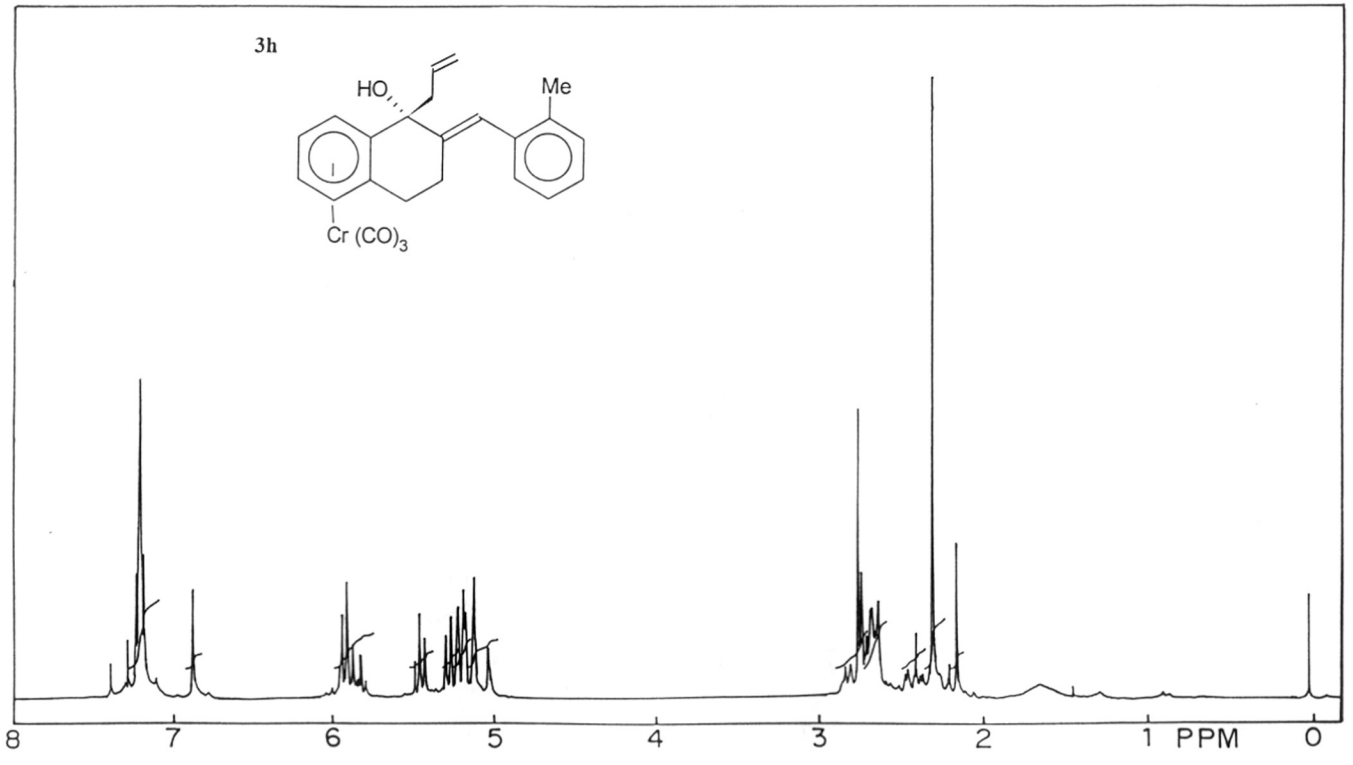
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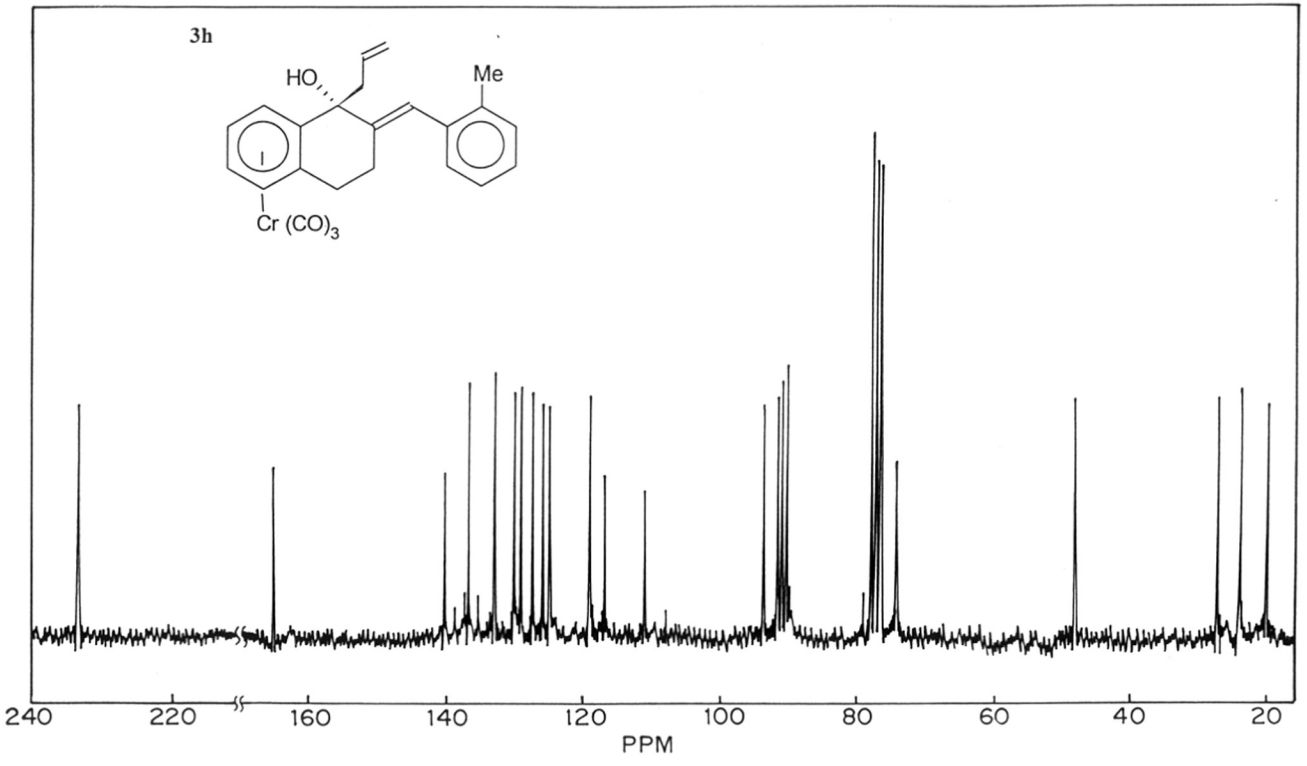
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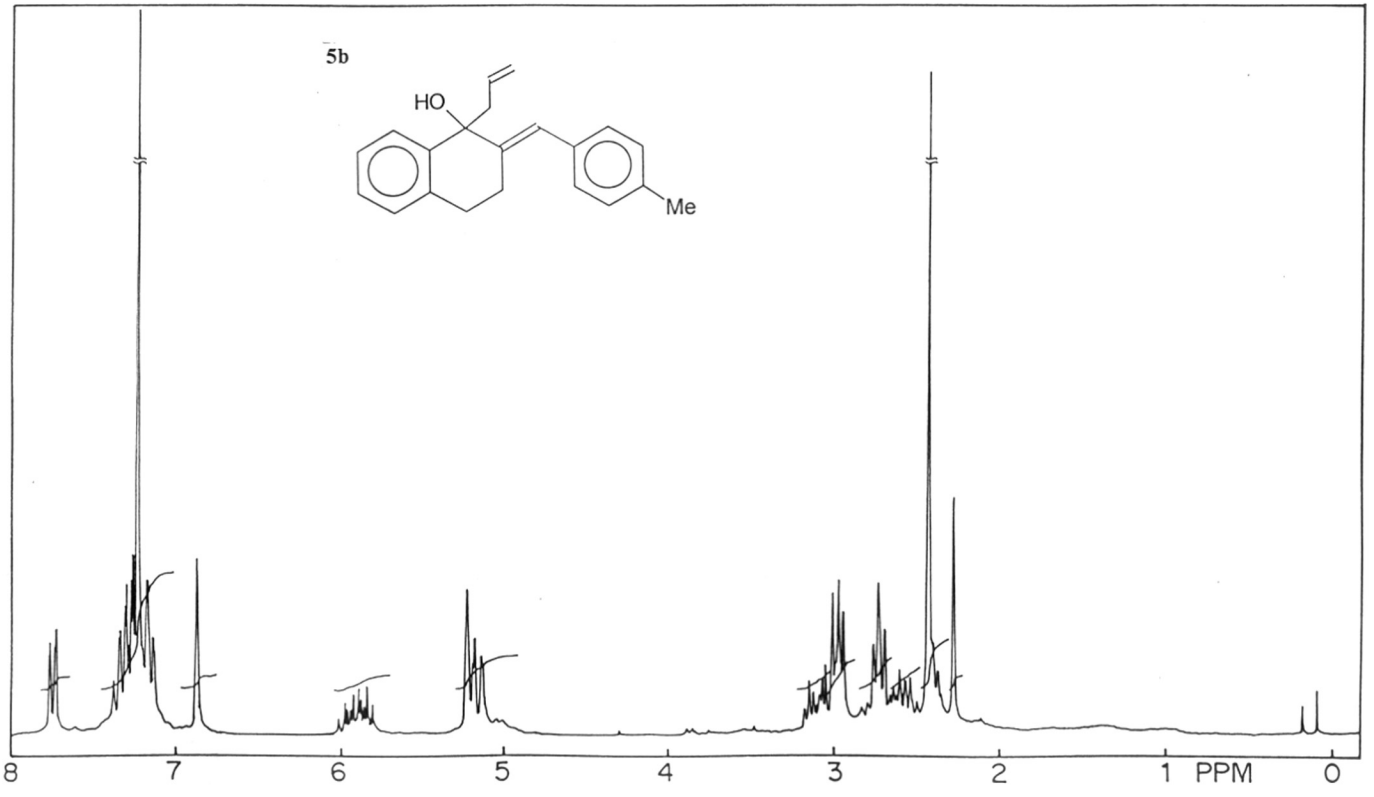
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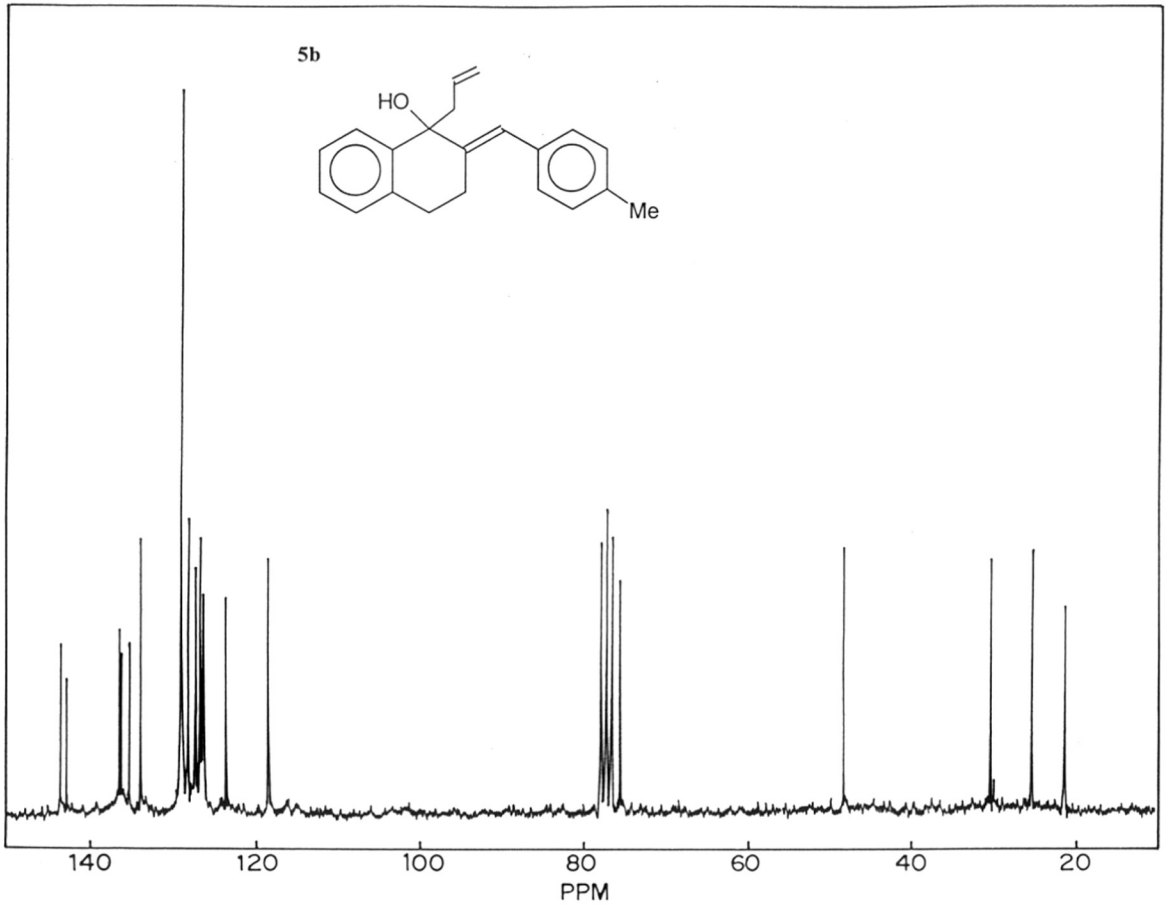
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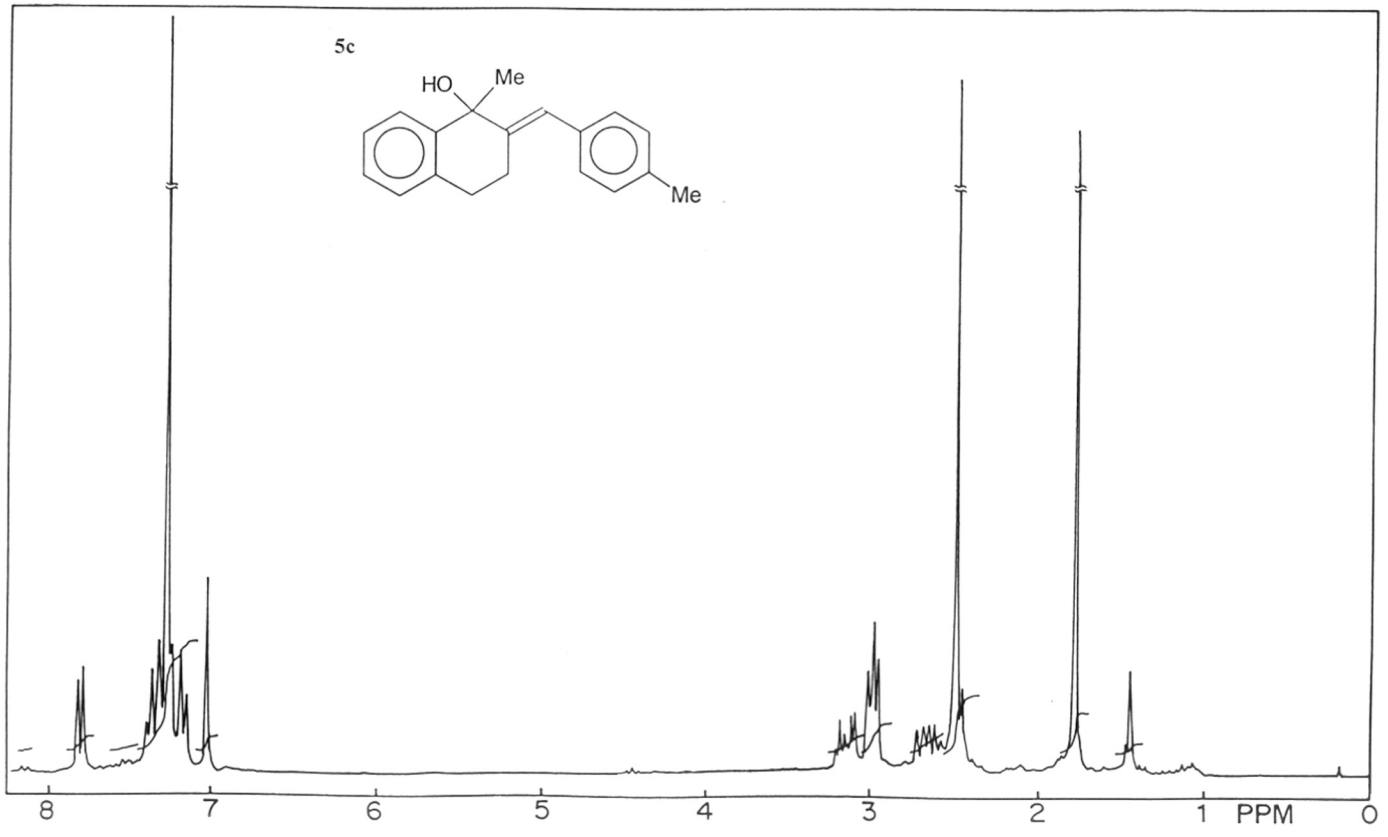
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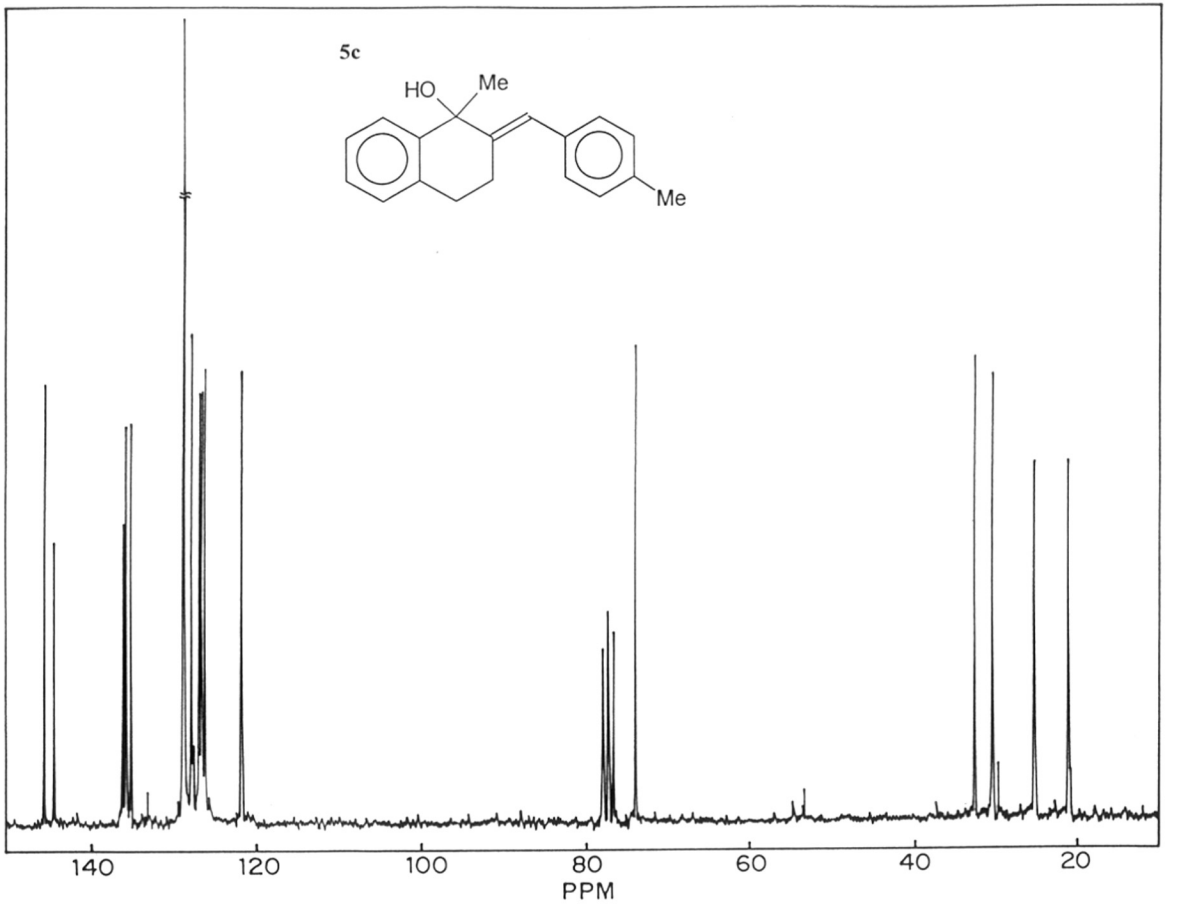
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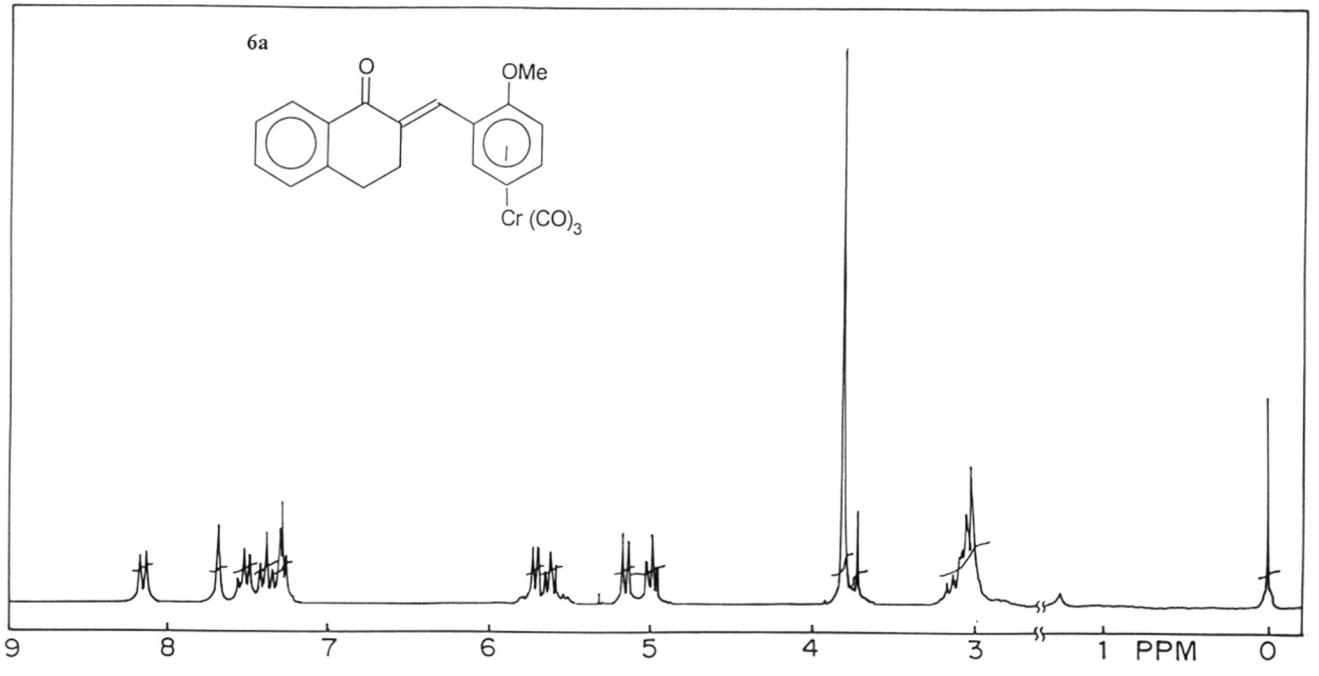
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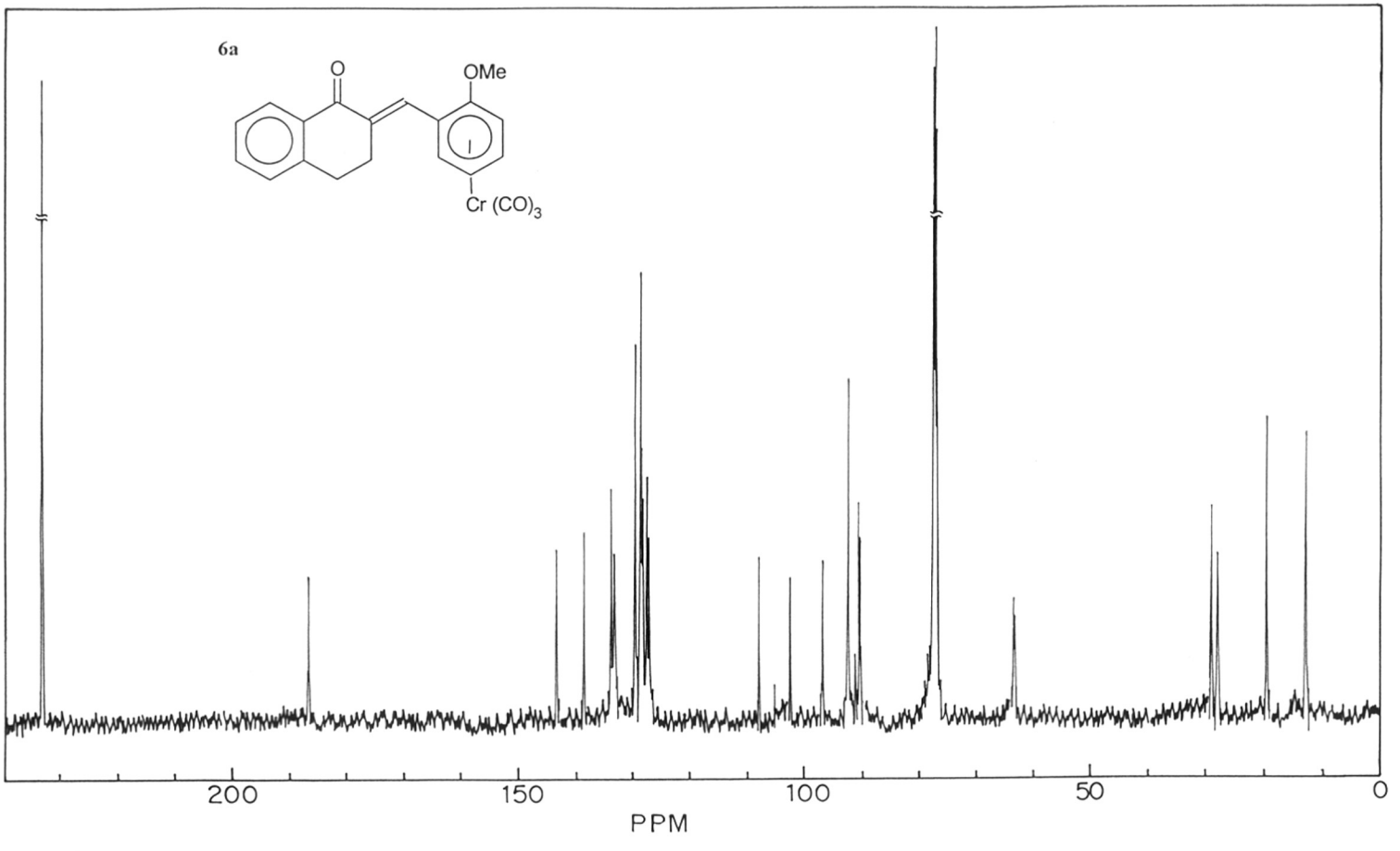
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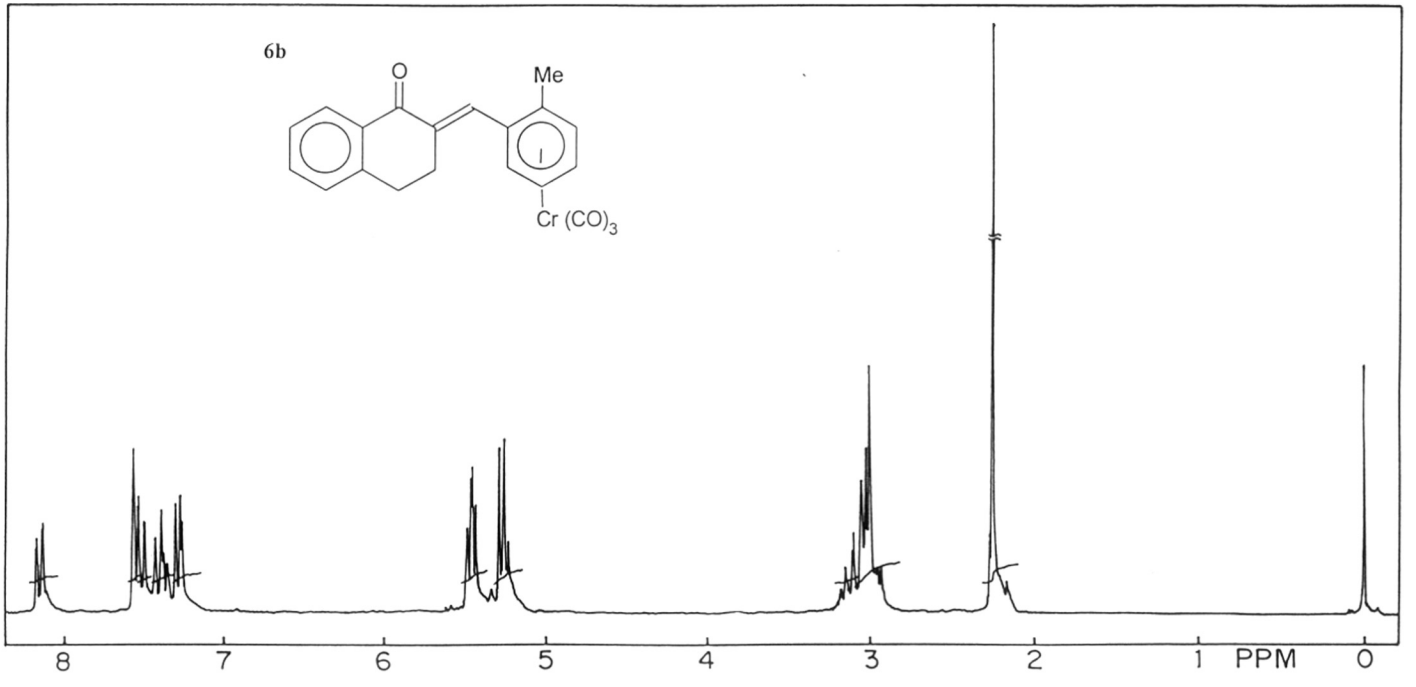
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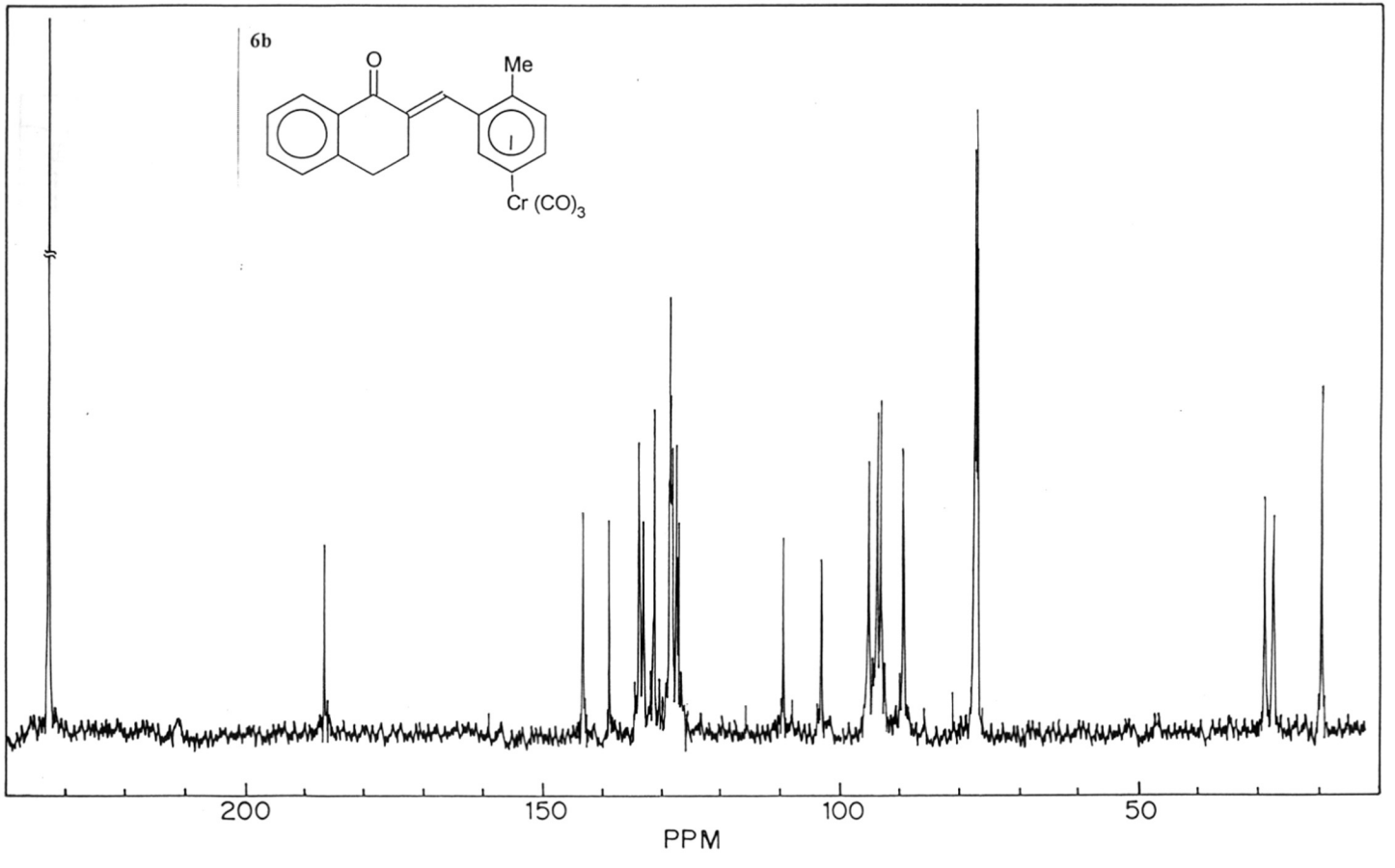
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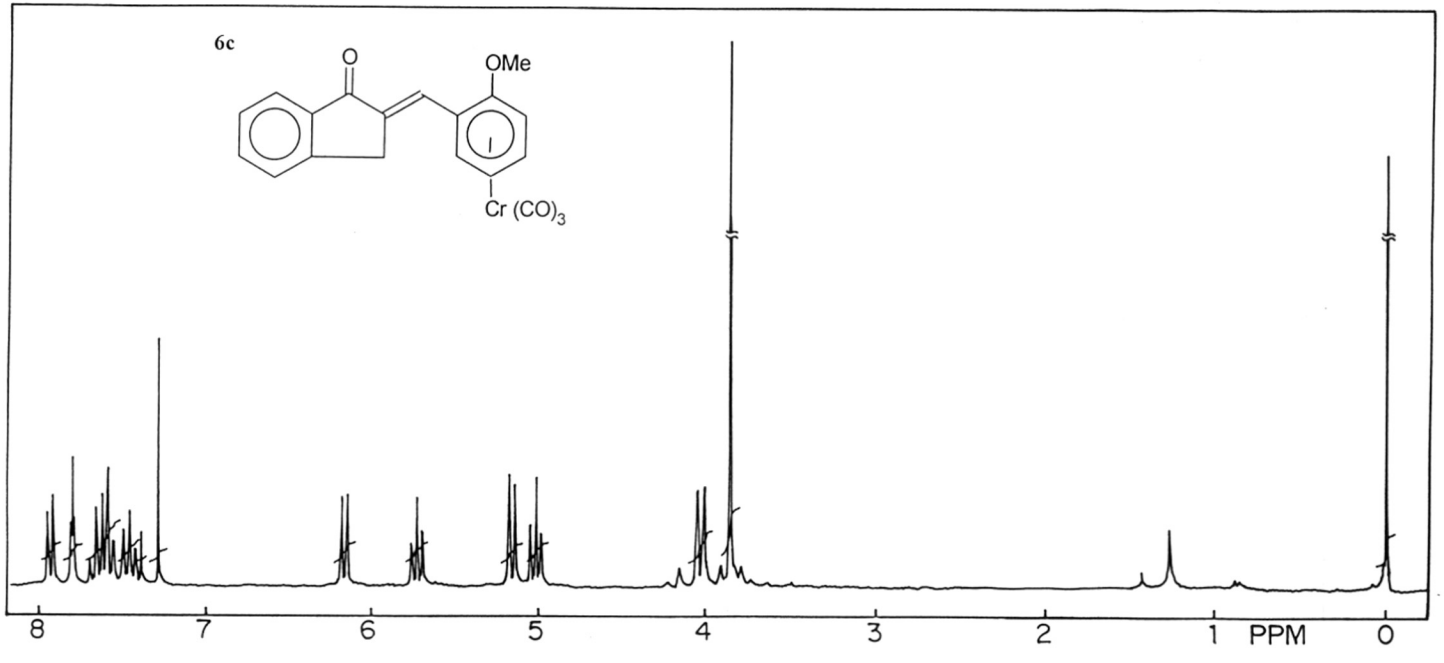
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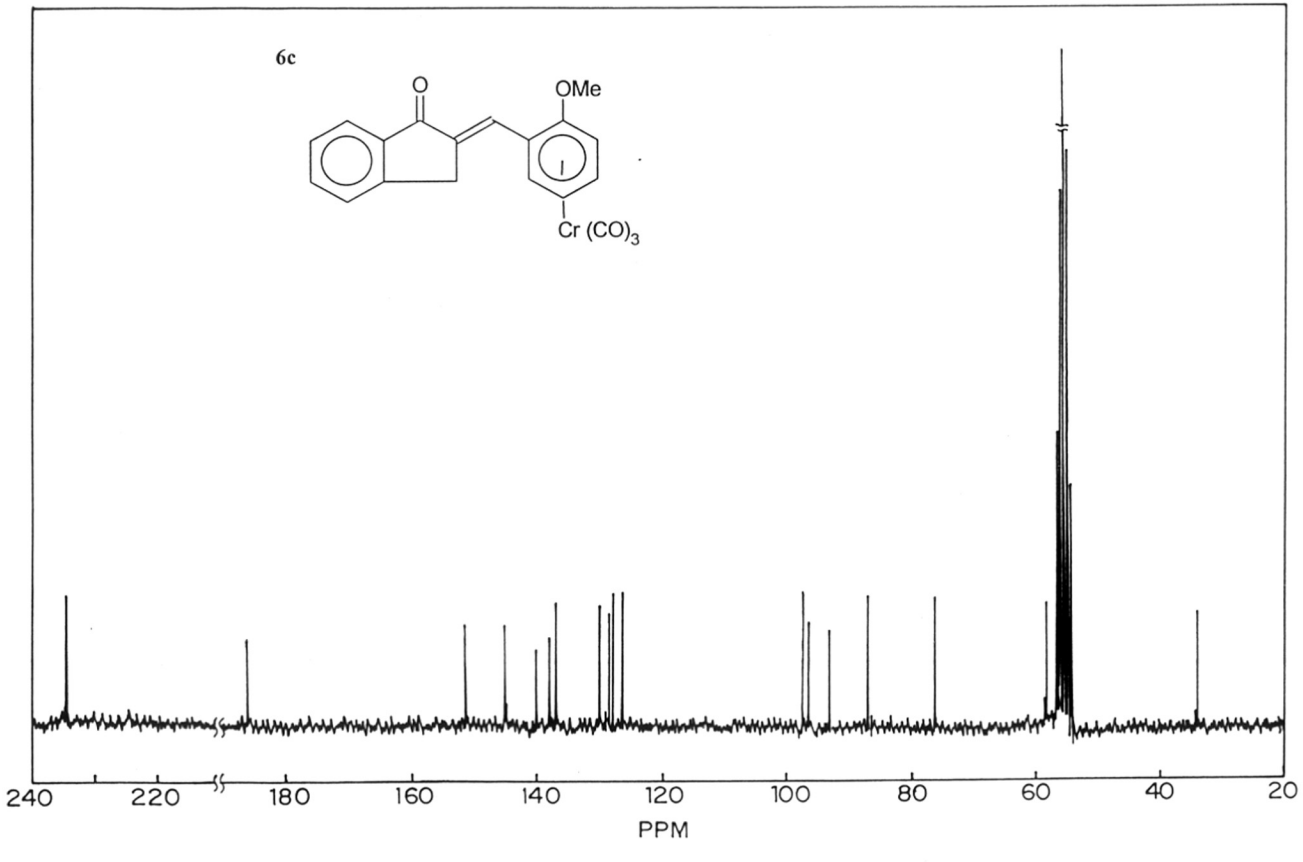
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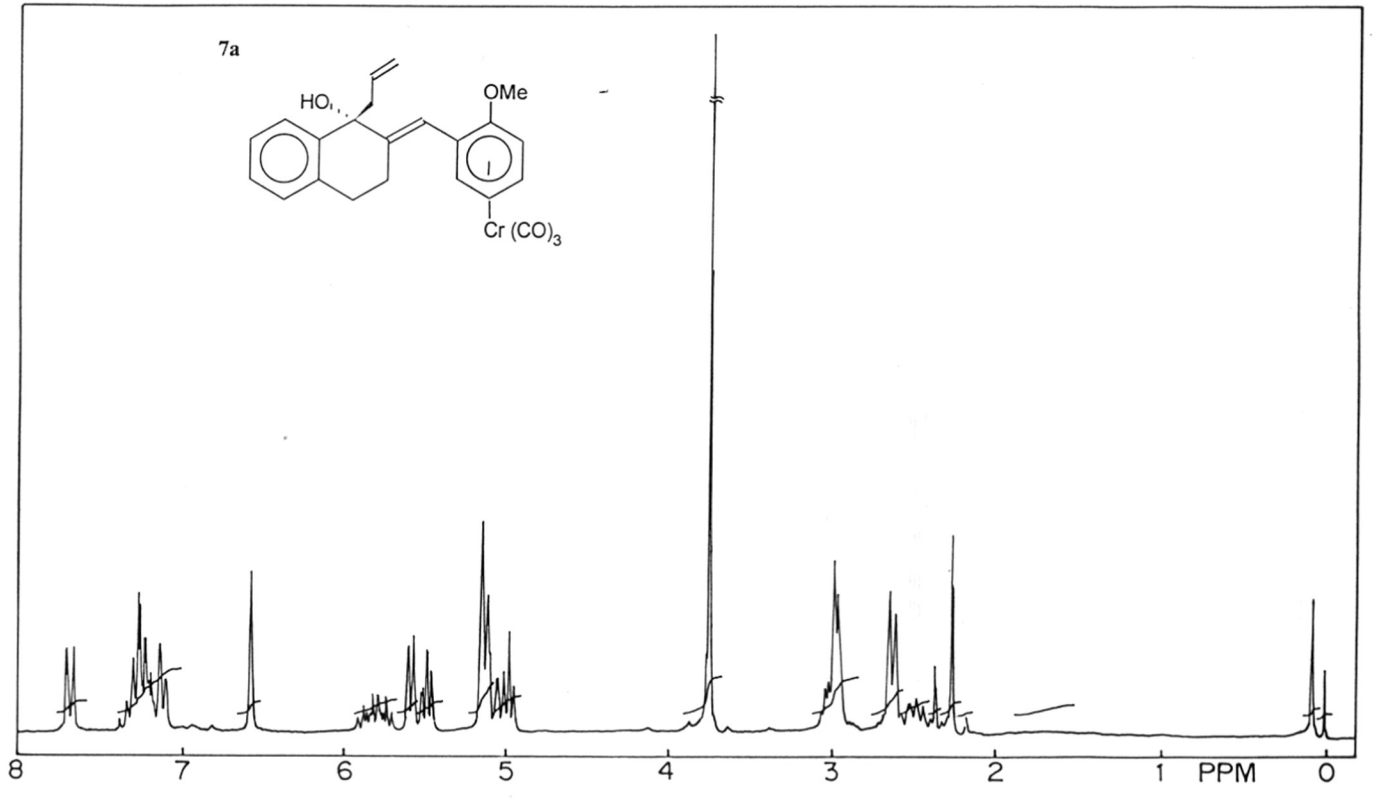
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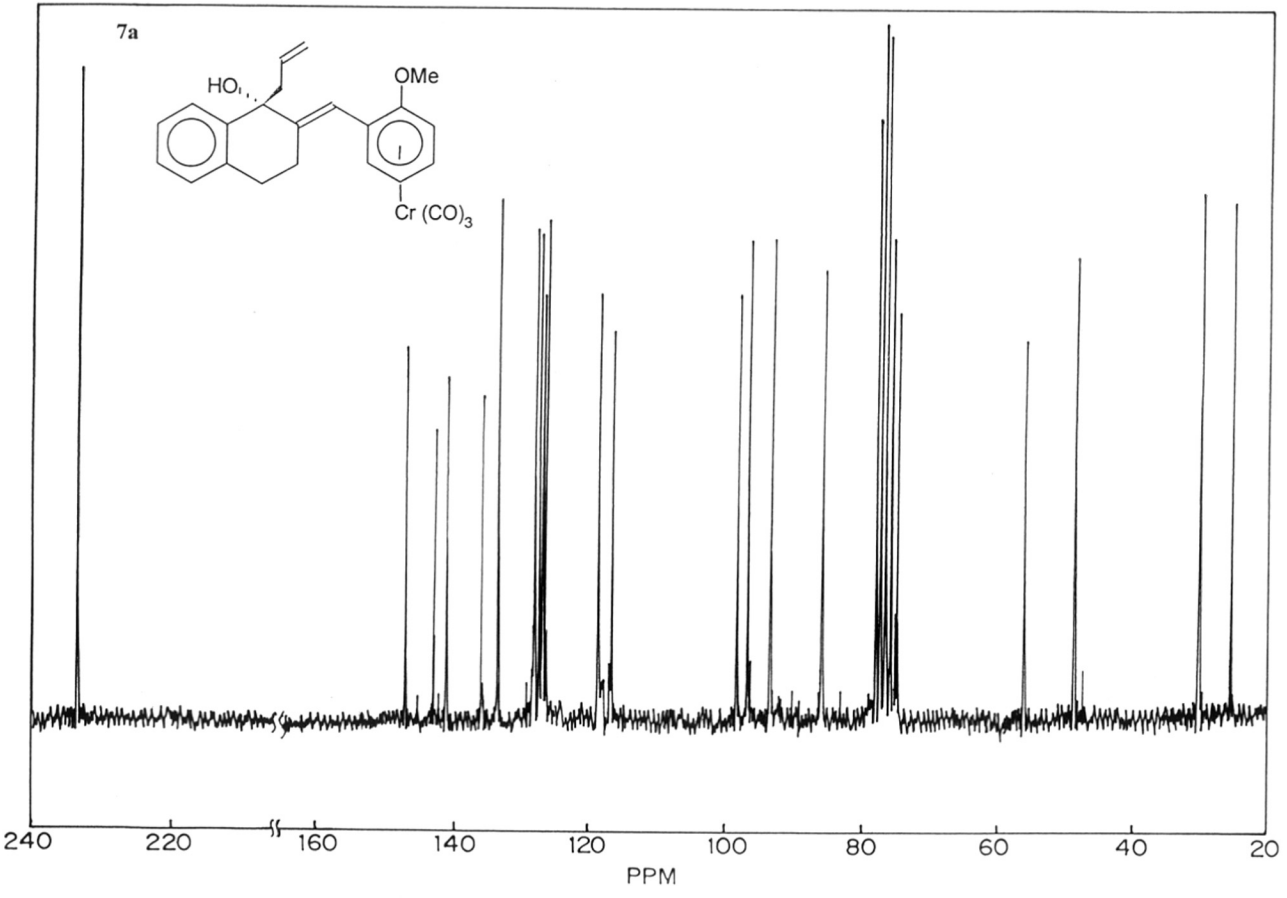
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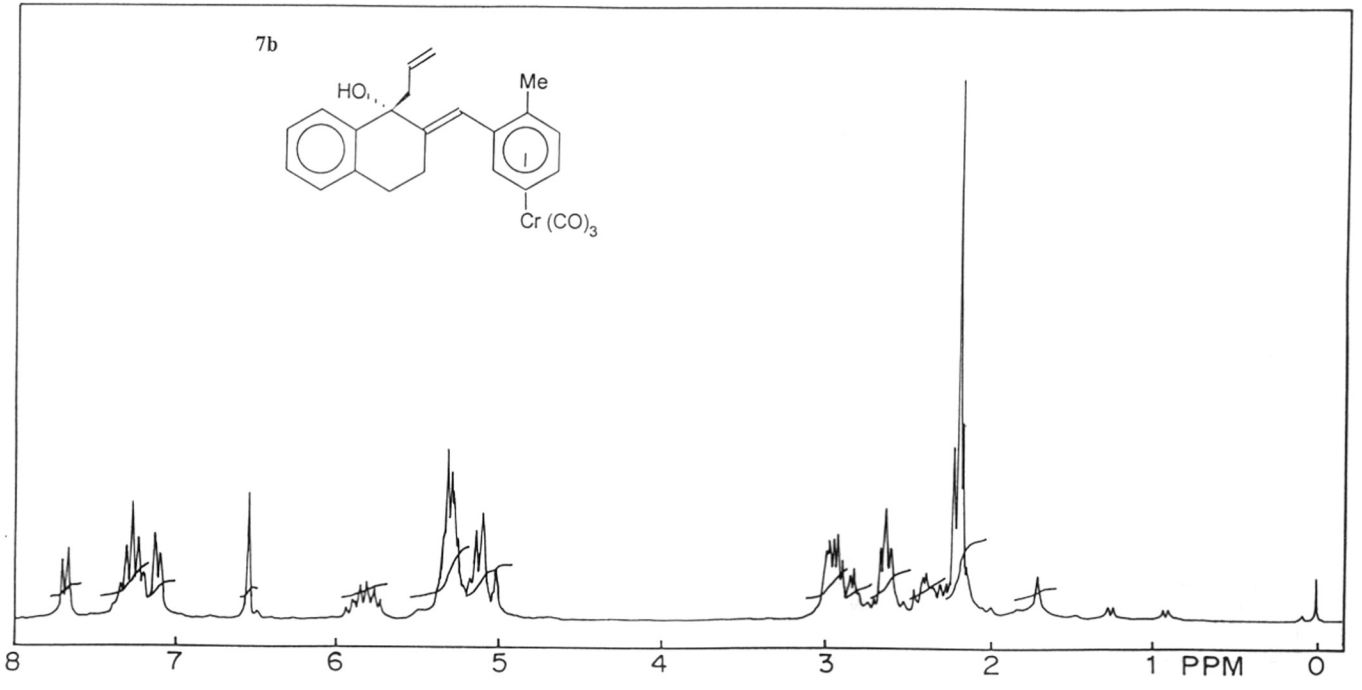
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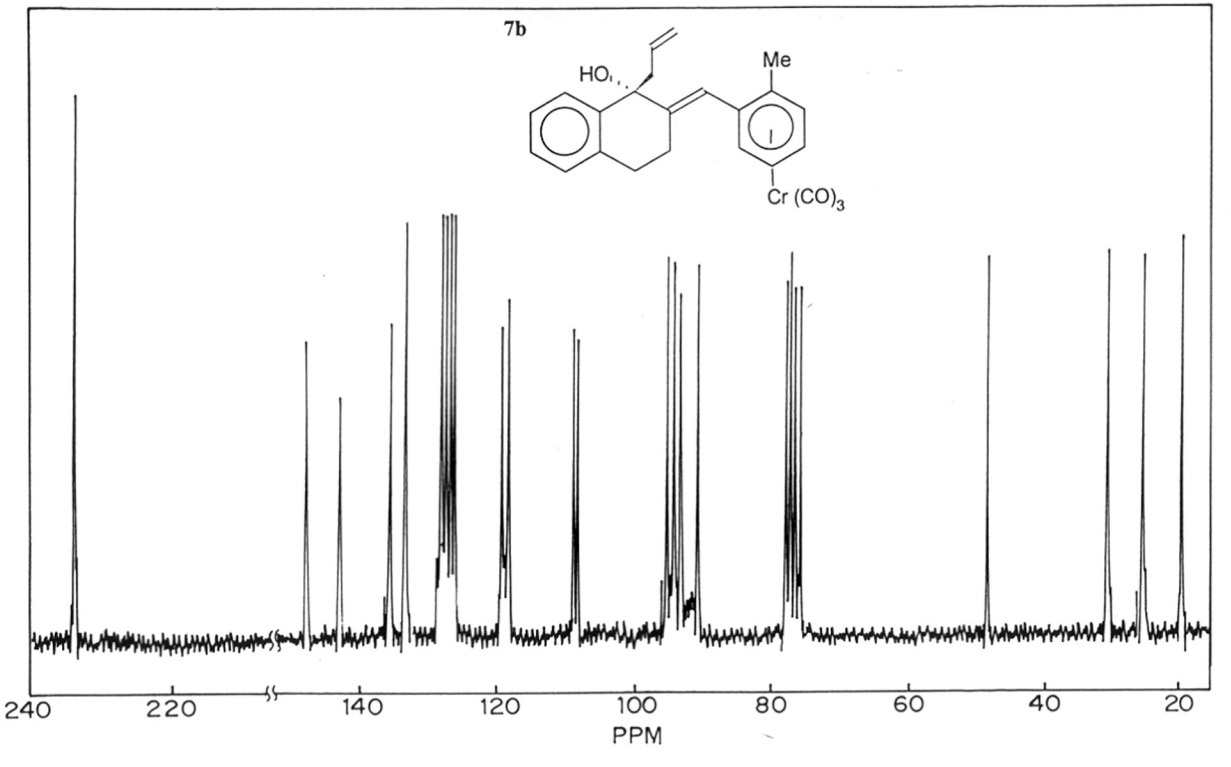
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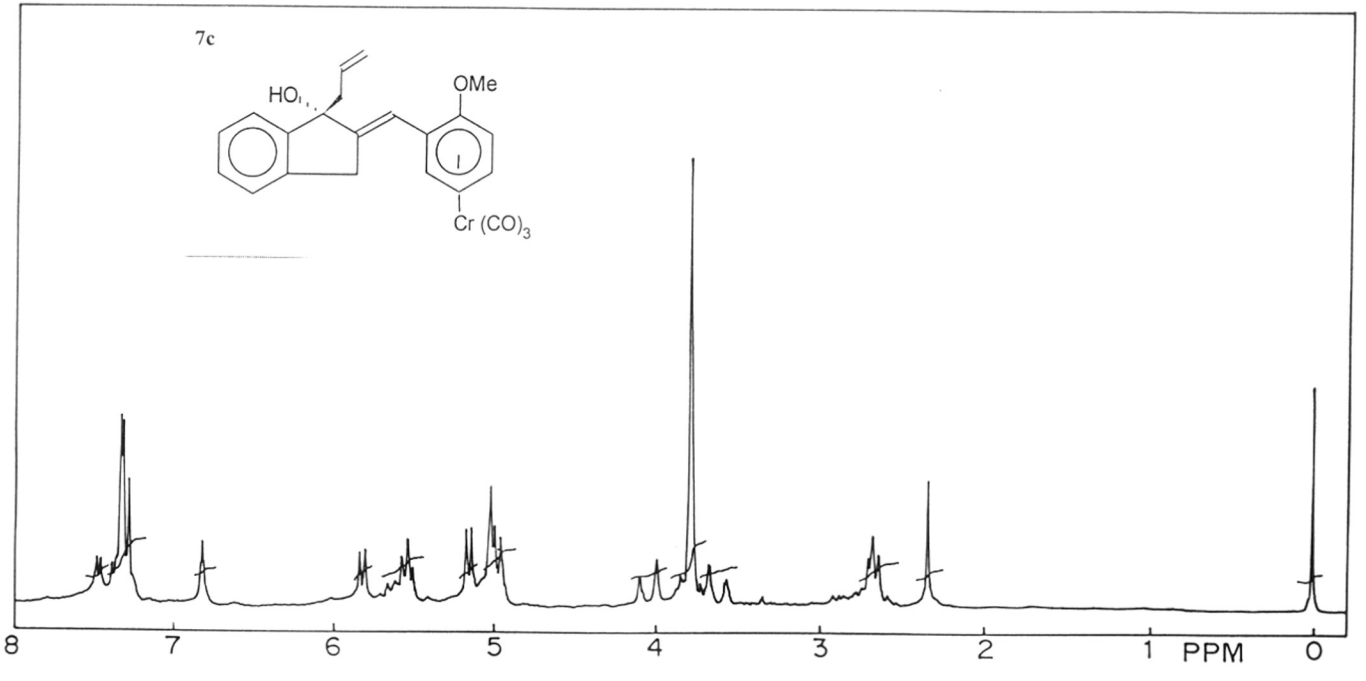
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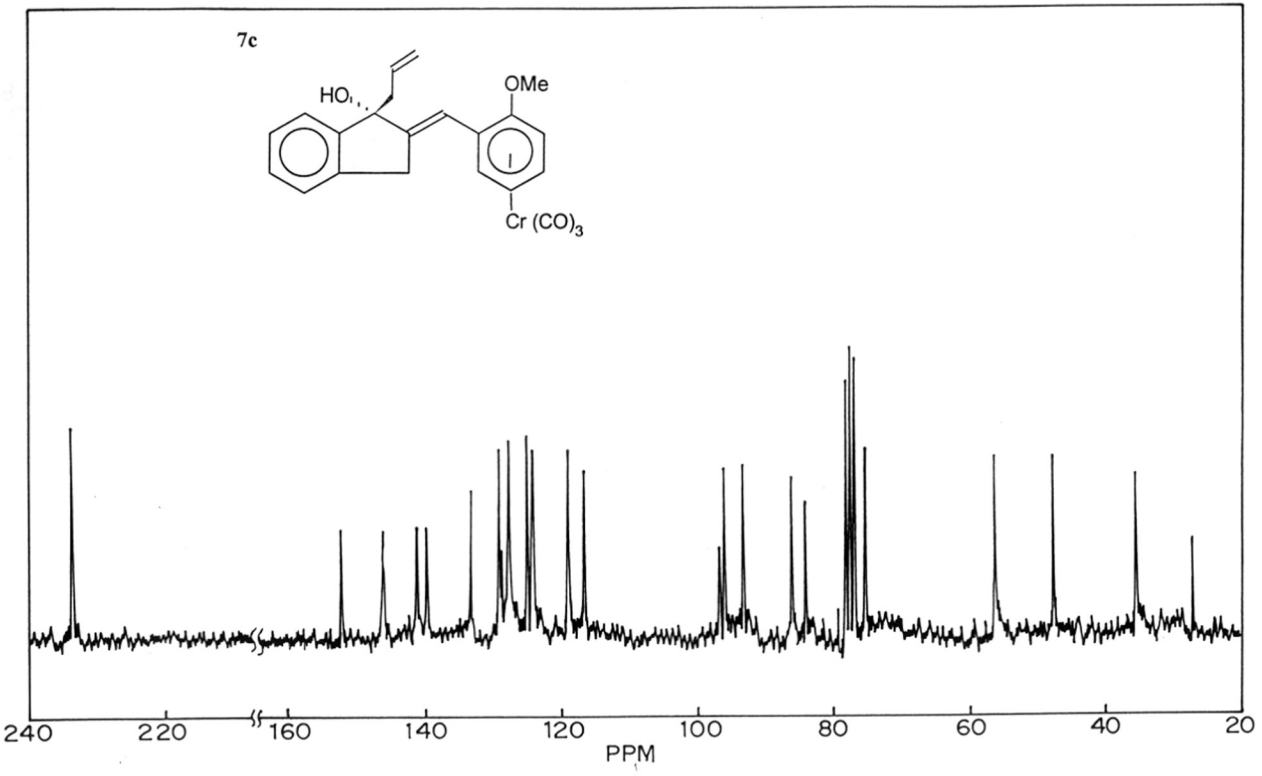
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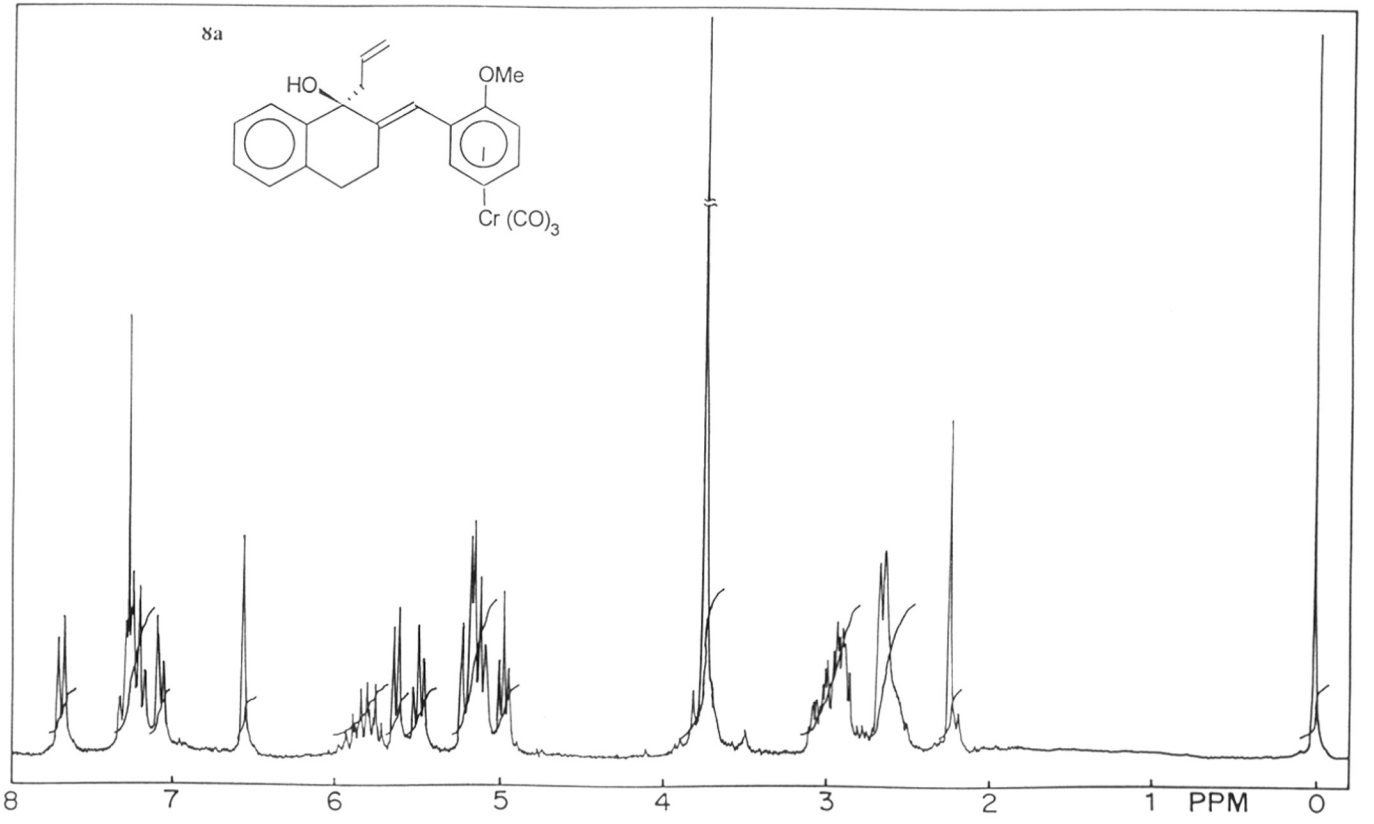
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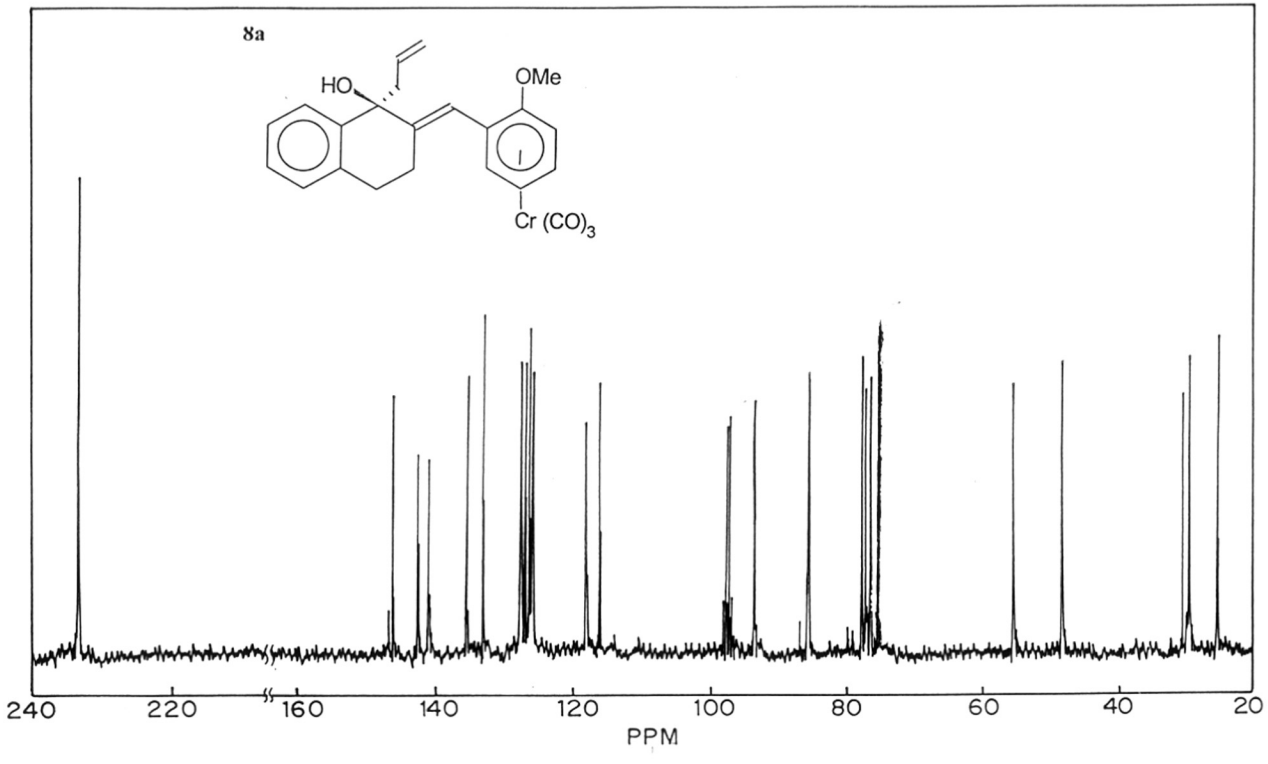
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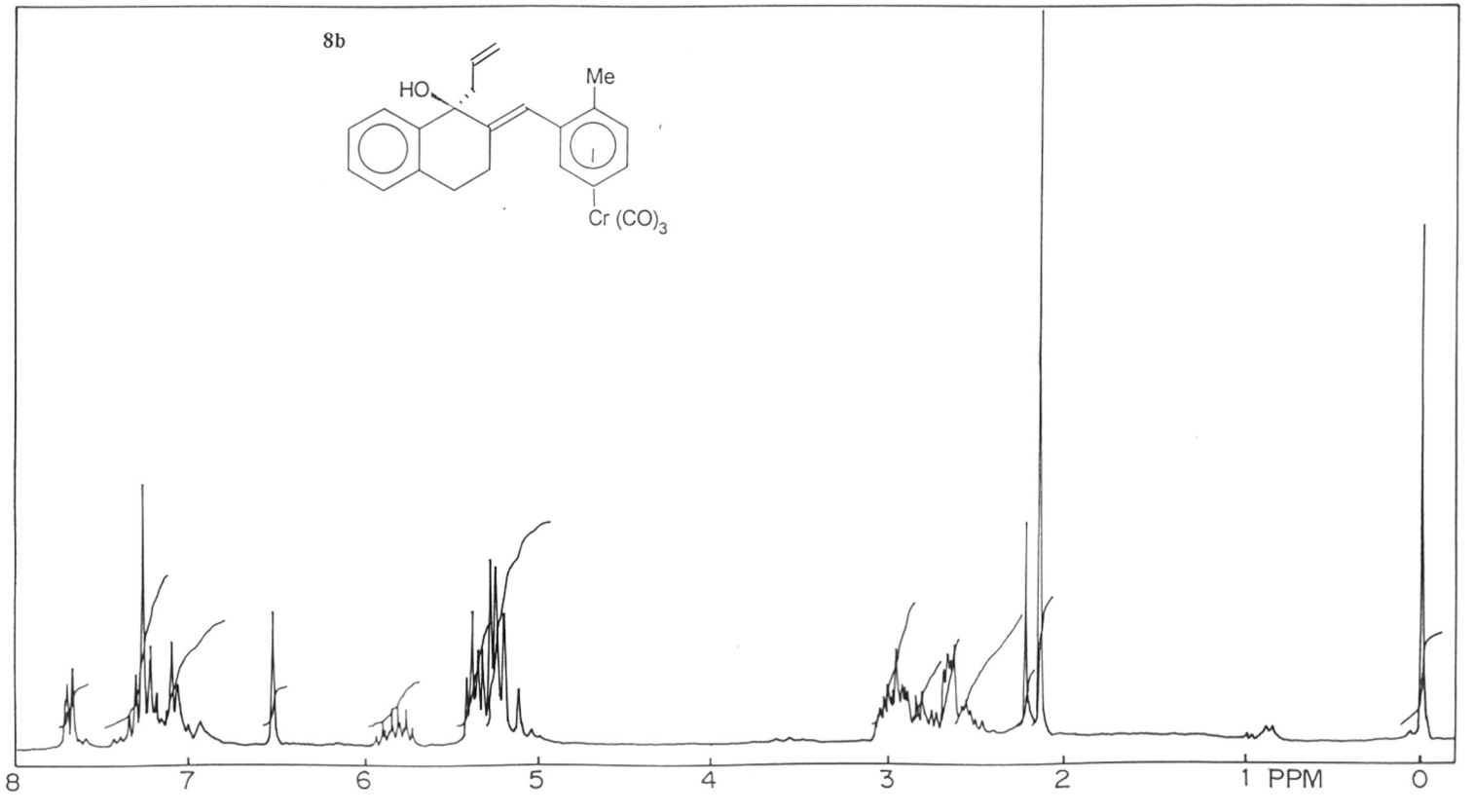
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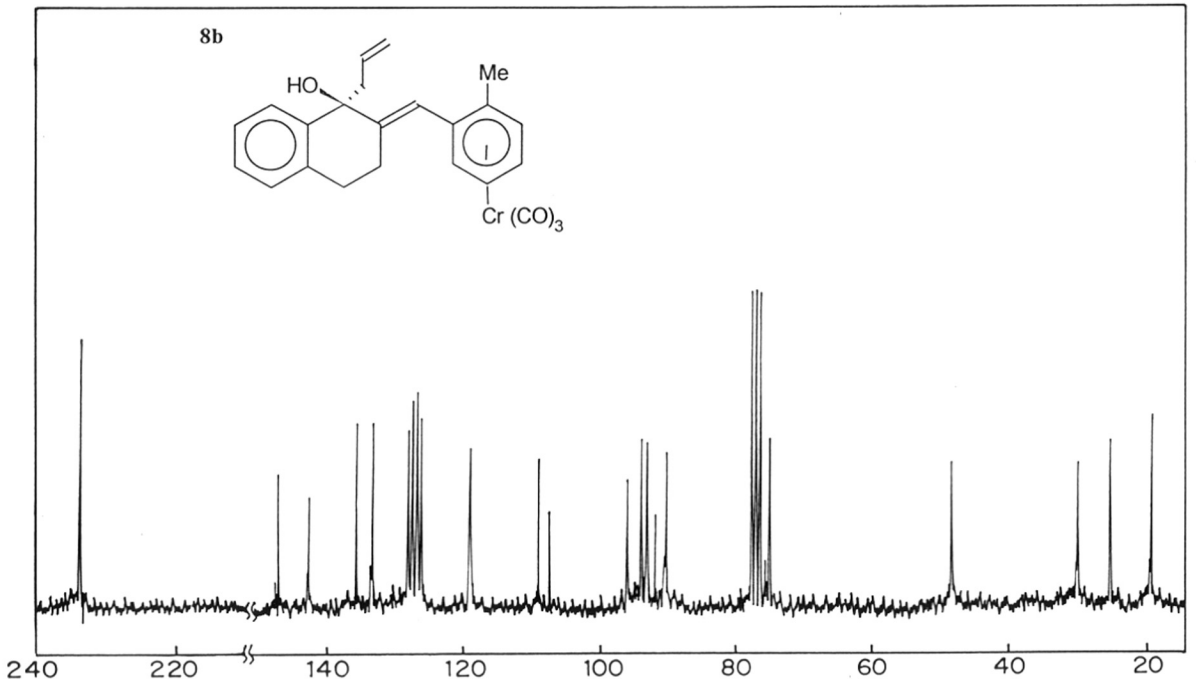
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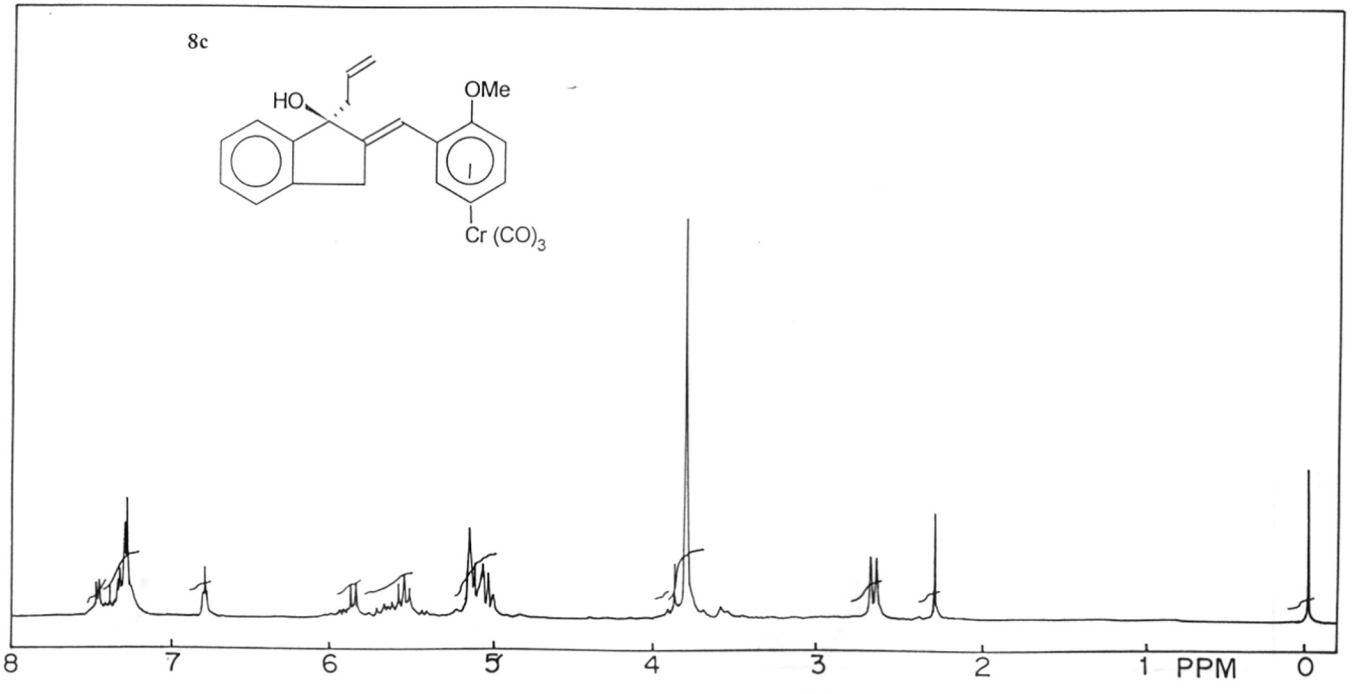
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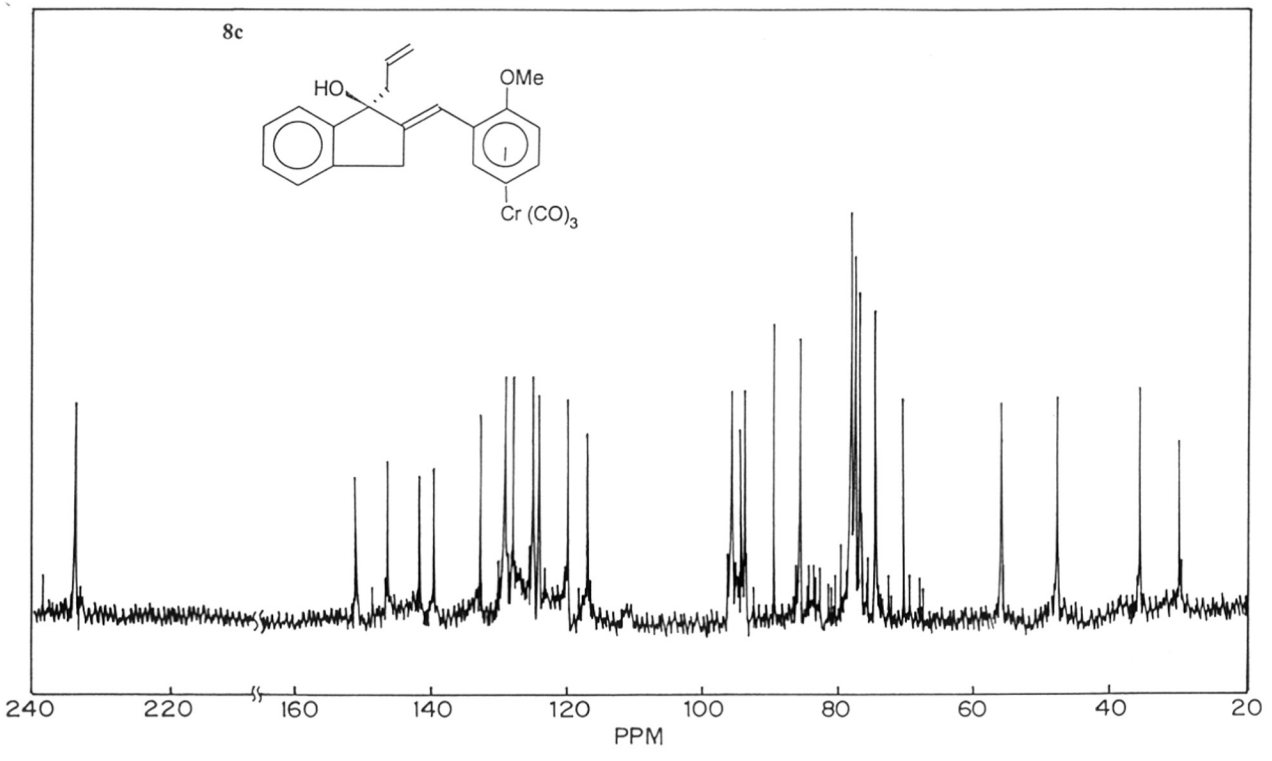
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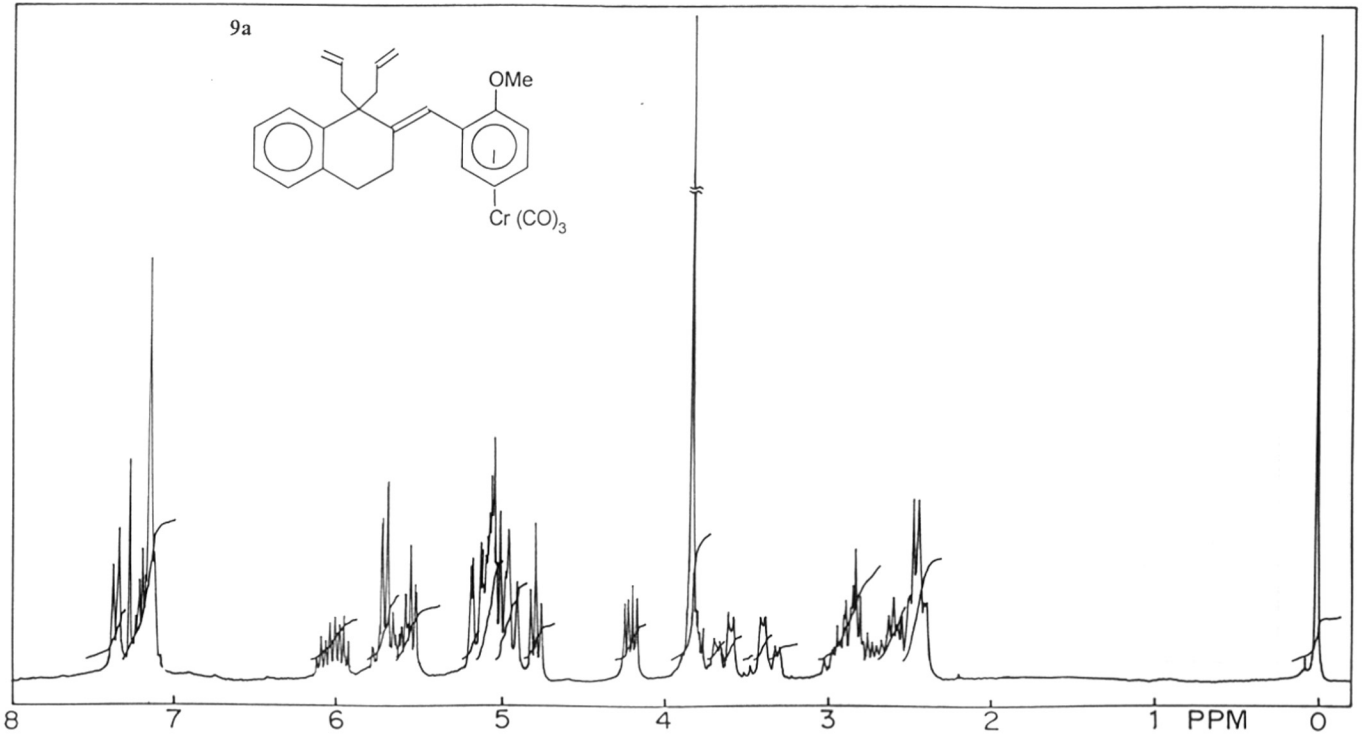
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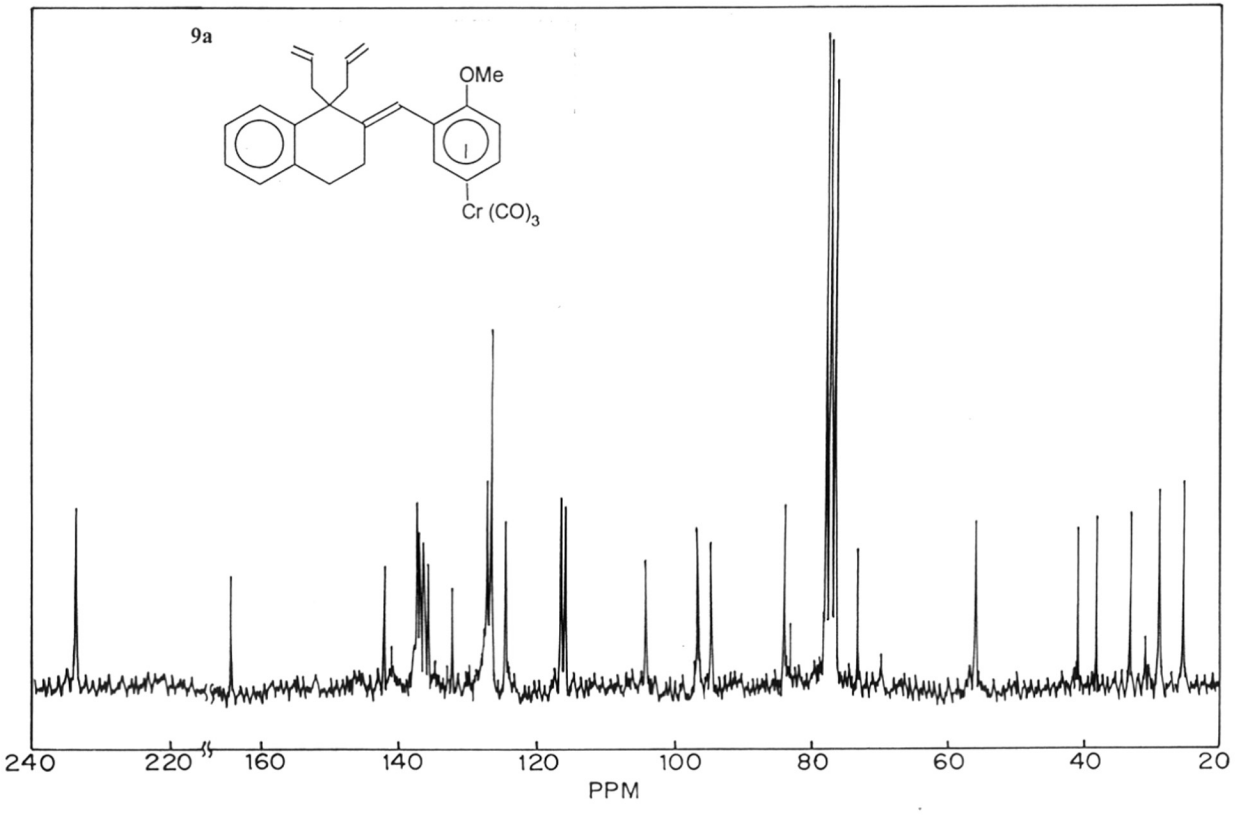
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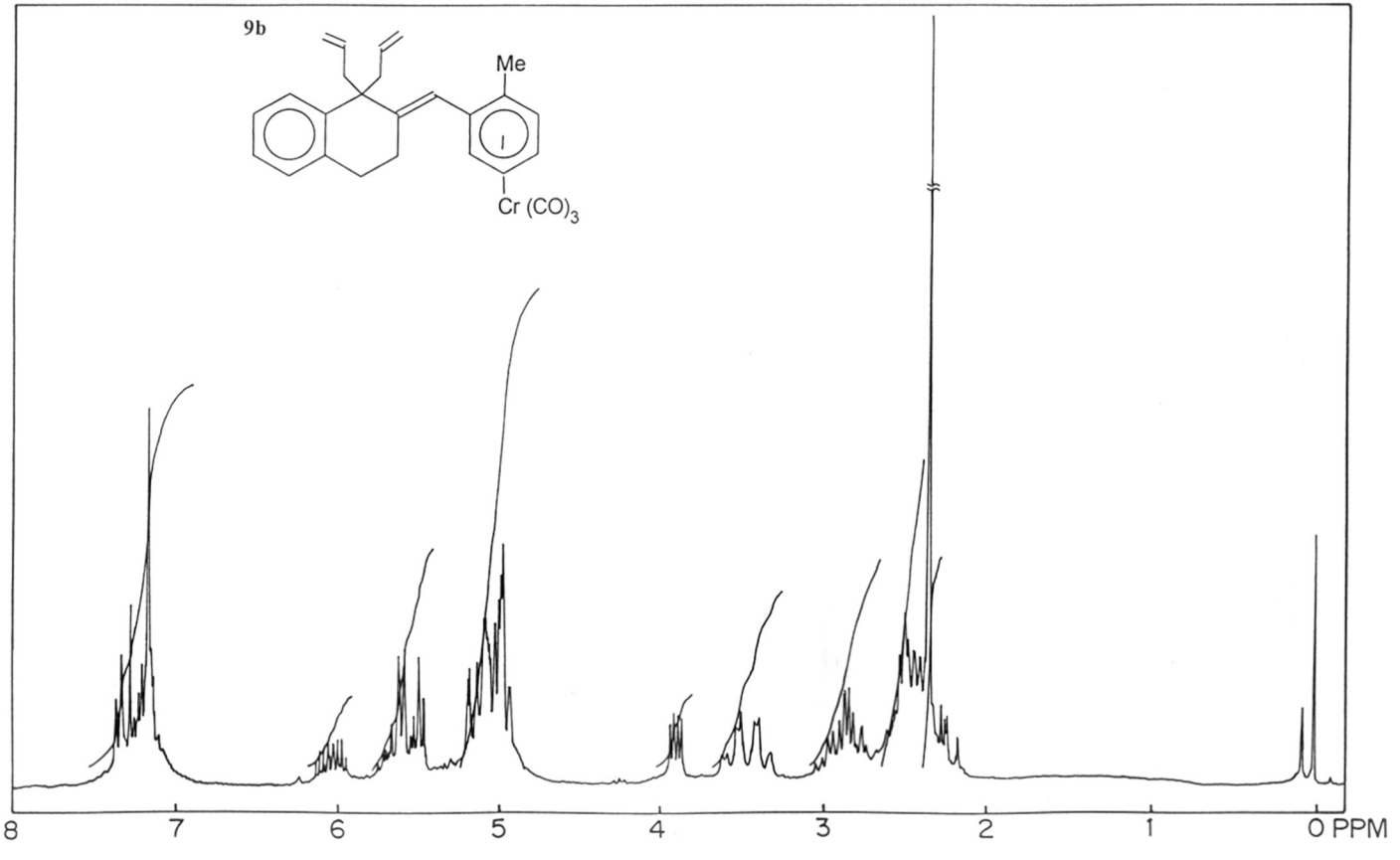
OMe
Cr (CO)3
240
220
160
140
120
100
80
60
40
20
PPM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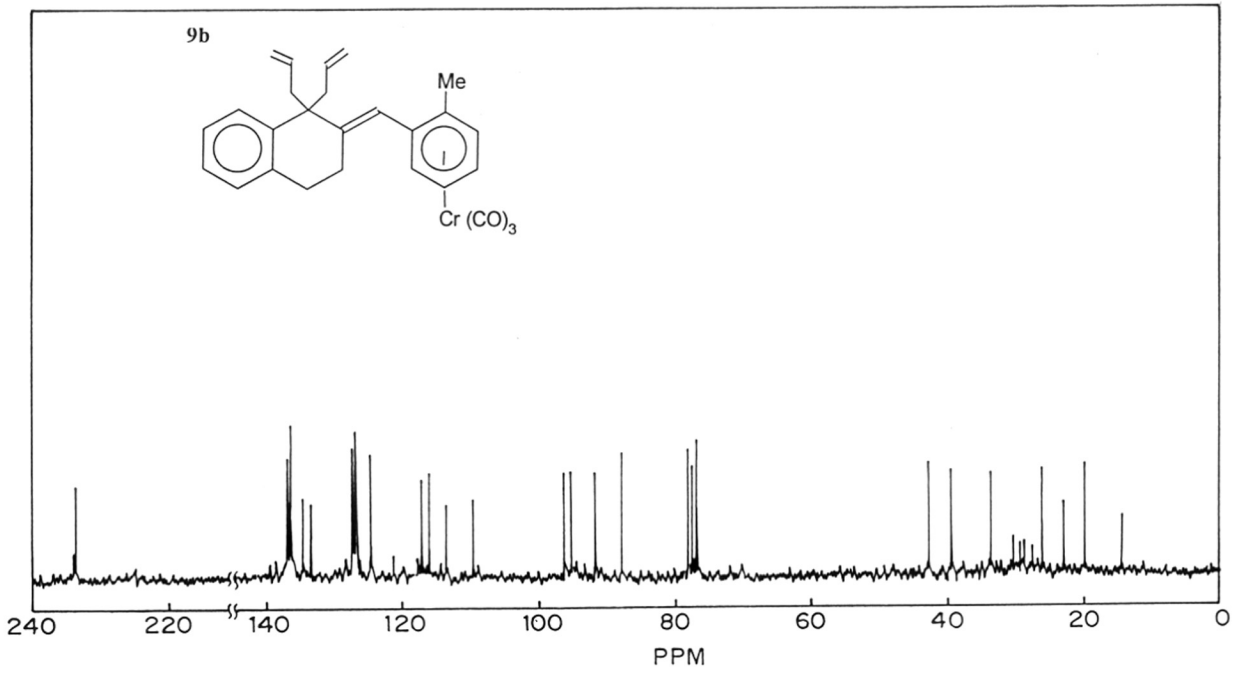
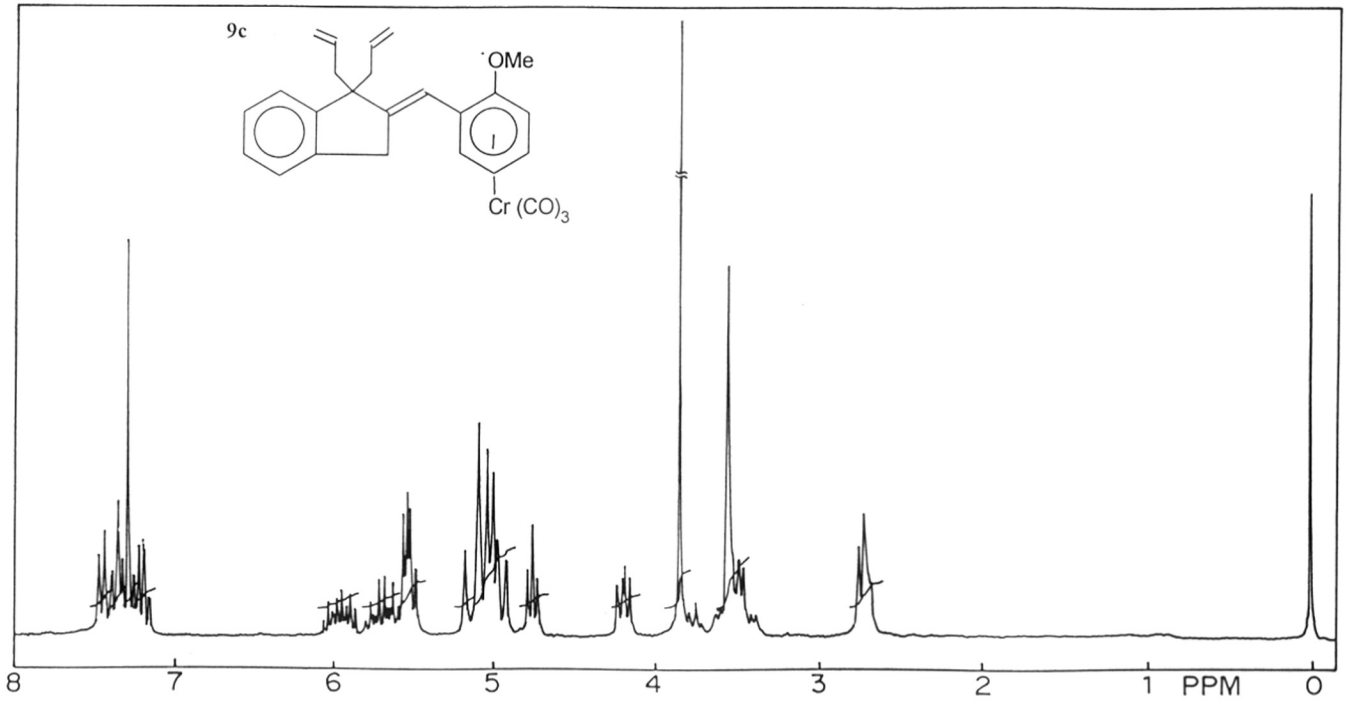
Me
Cr (CO)3
8
7
6
5
4
3
2
1
0 PPM


9b
Me
Cr (CO)3
240
220
140
120
100
80
60
40
20
0
PPM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OMe
Cr (CO)3
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PPM
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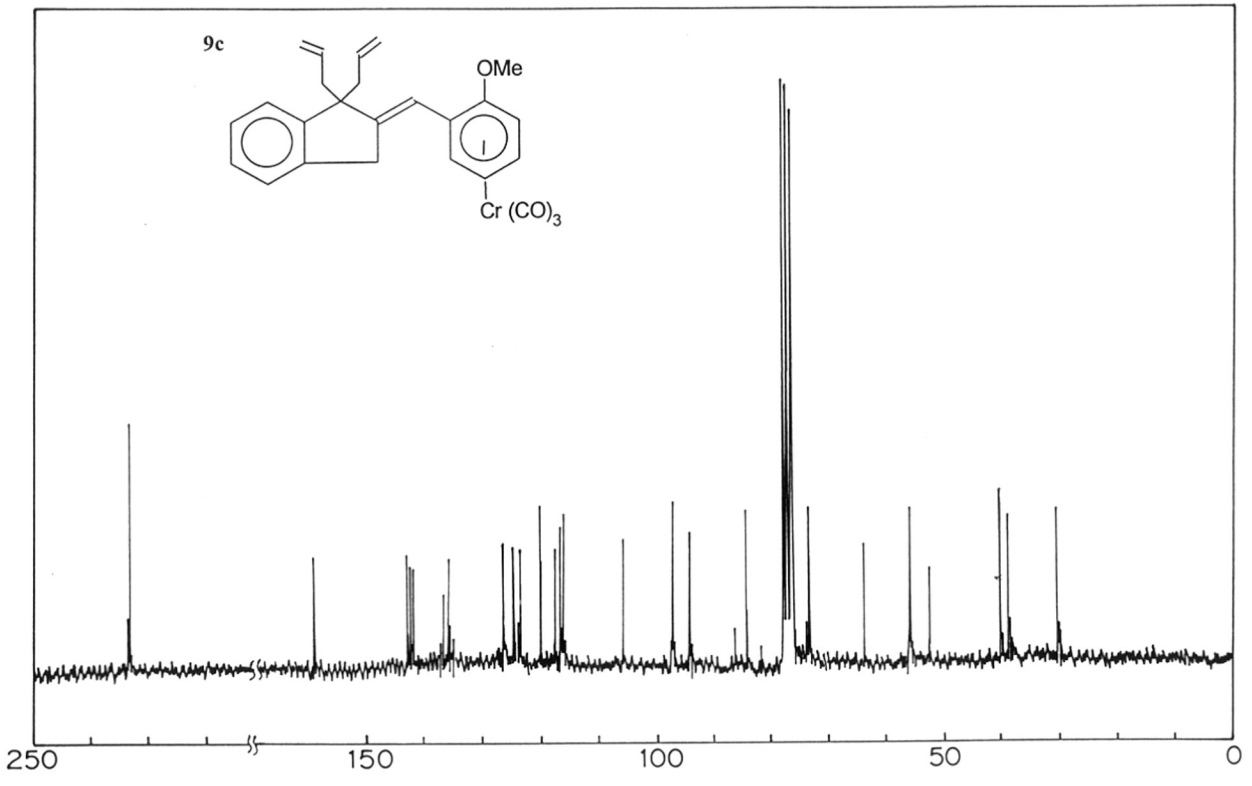
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Cr (CO)3
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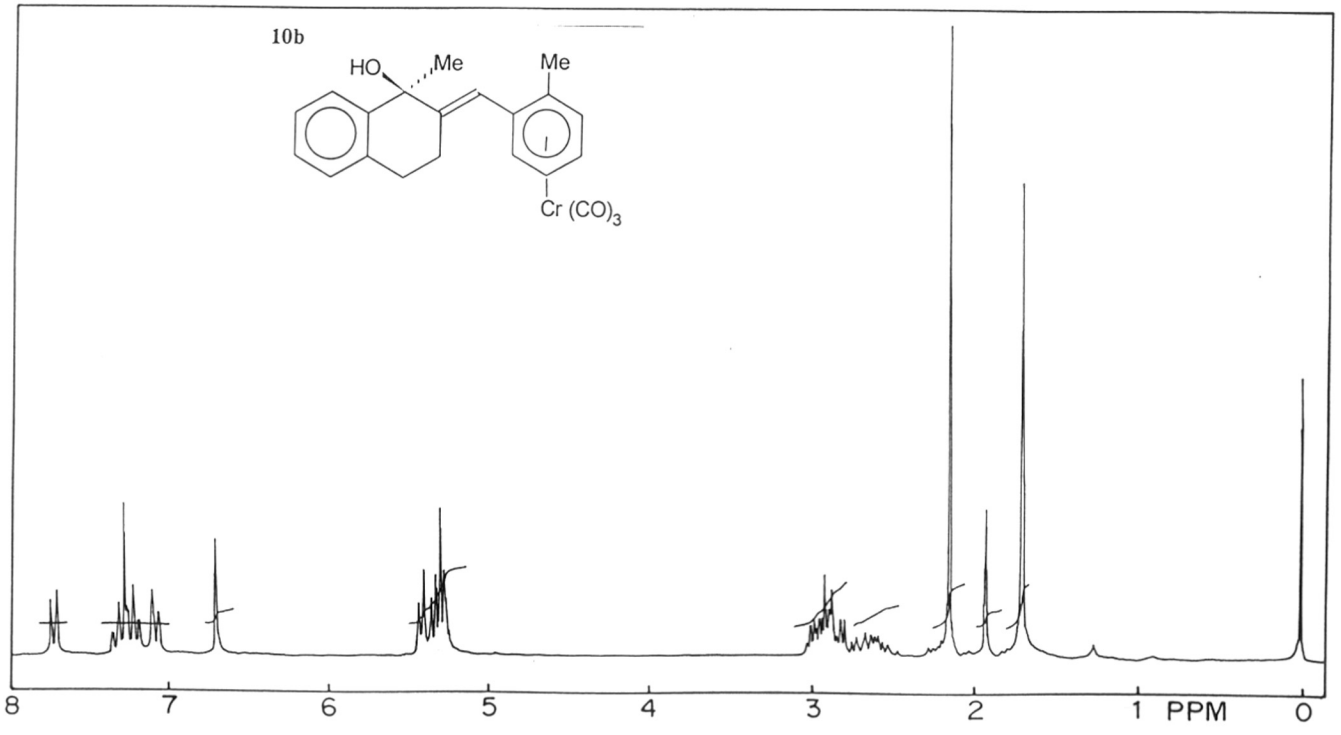
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Me
Cr (CO)3
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5
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PPM
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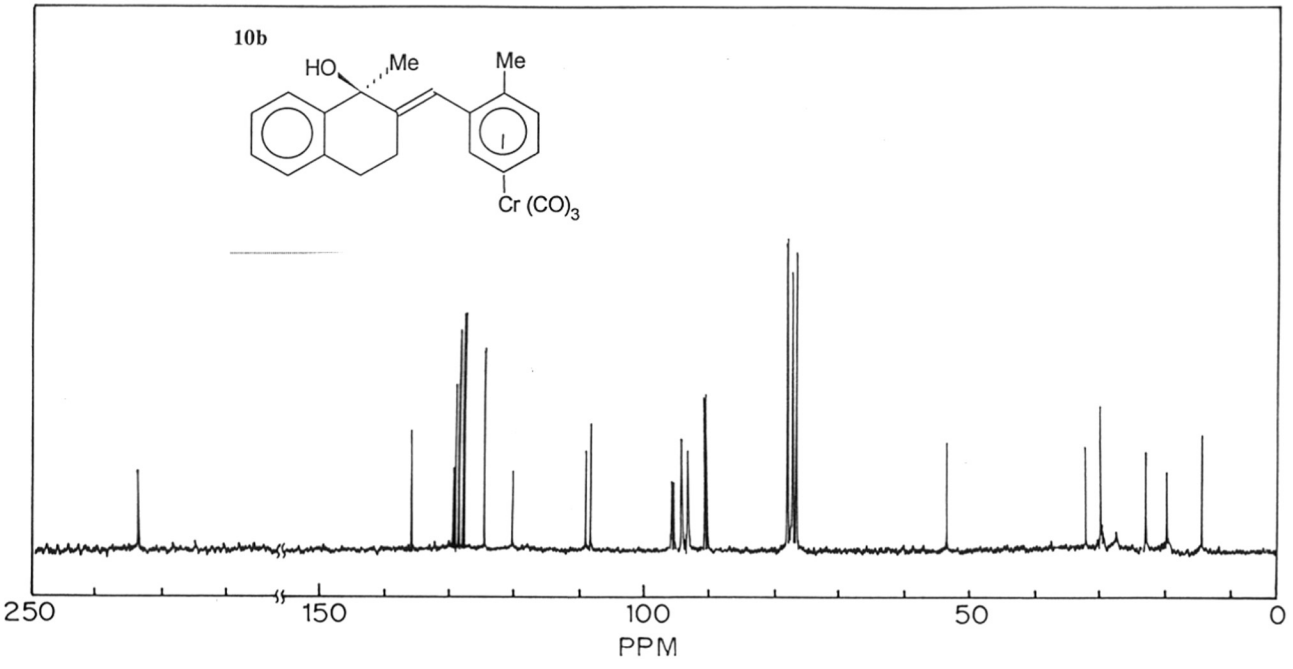
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Me
Me
Cr (CO)3
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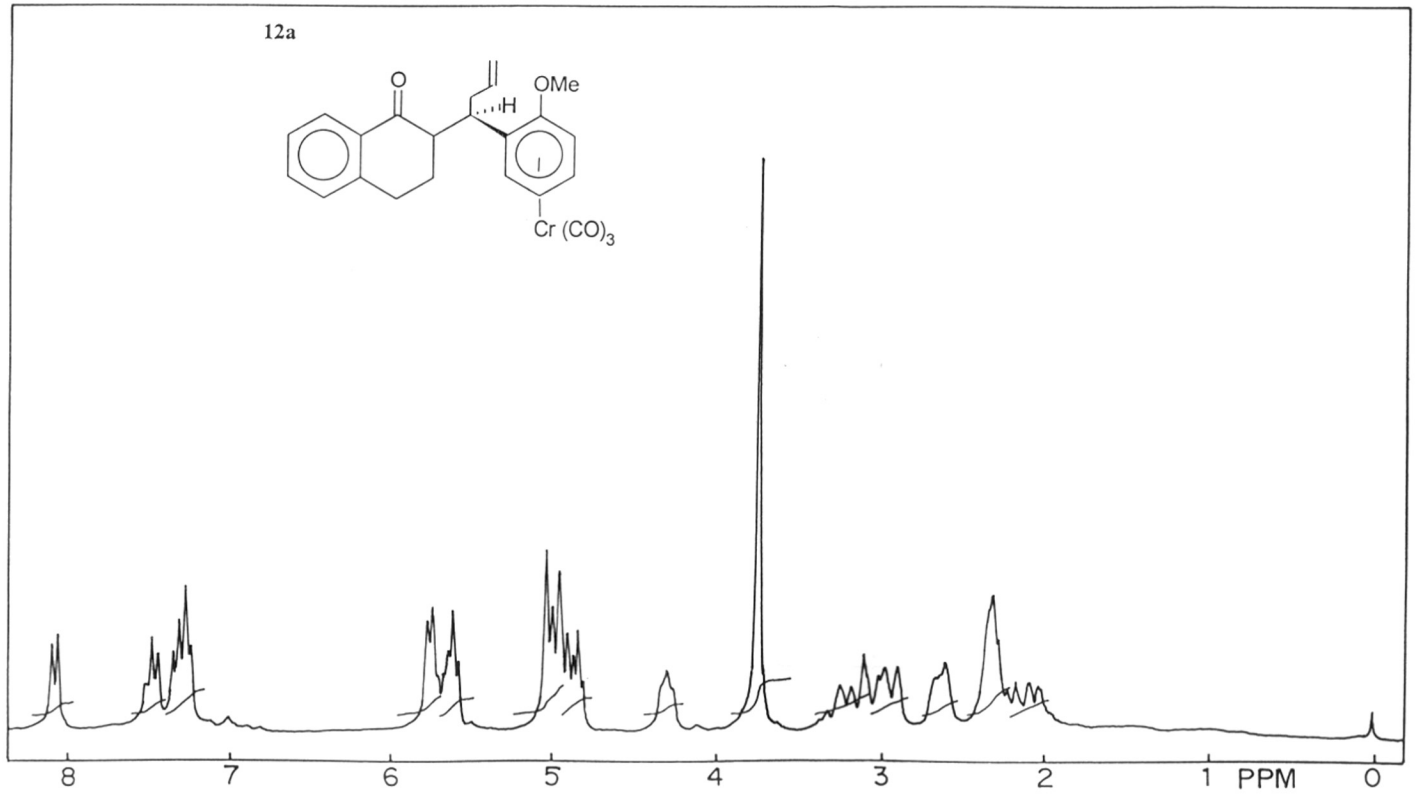
PPM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OMe
H
Cr (CO)3
8
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6
5
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PPM
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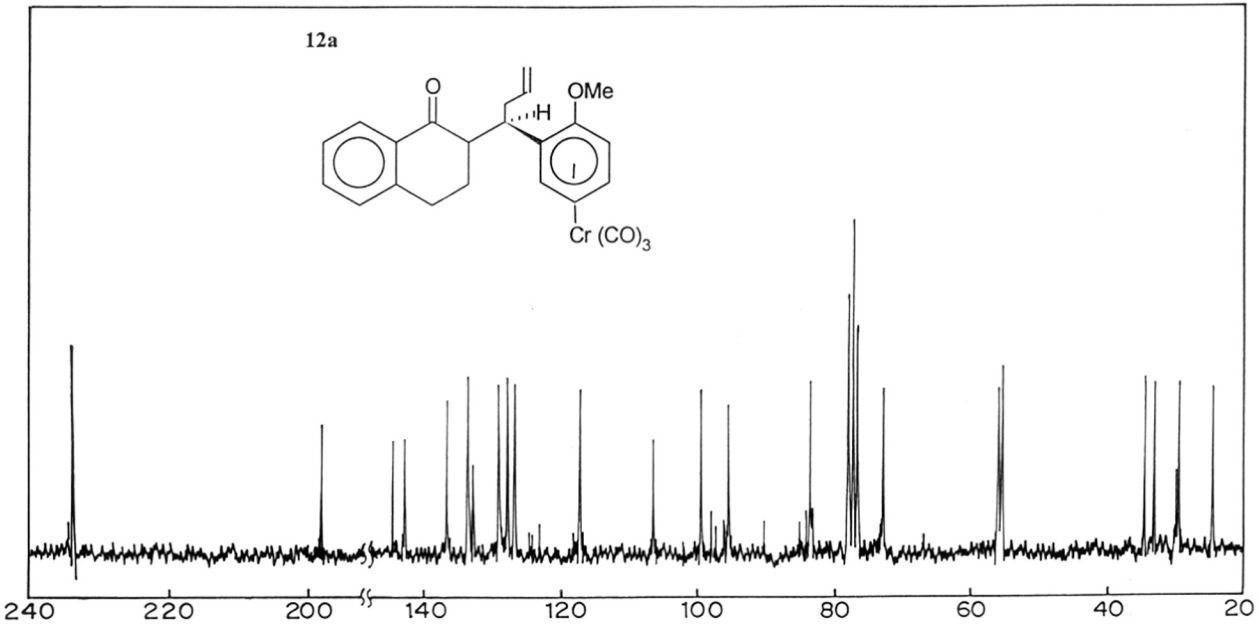
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OMe
Cr (CO)3
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220
200
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60
40
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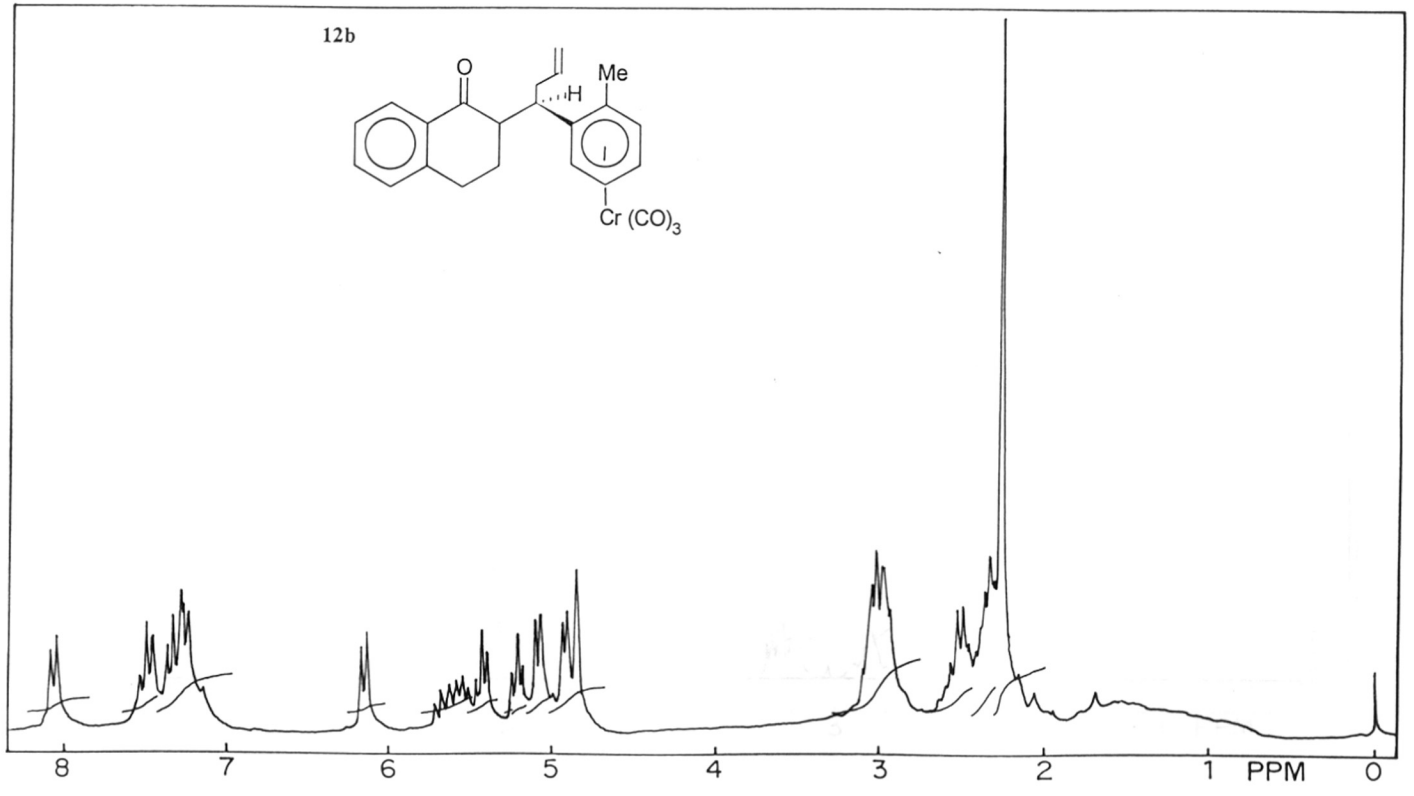
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O
H
Me
Cr (CO)3
8
7
6
5
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3
2
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PPM
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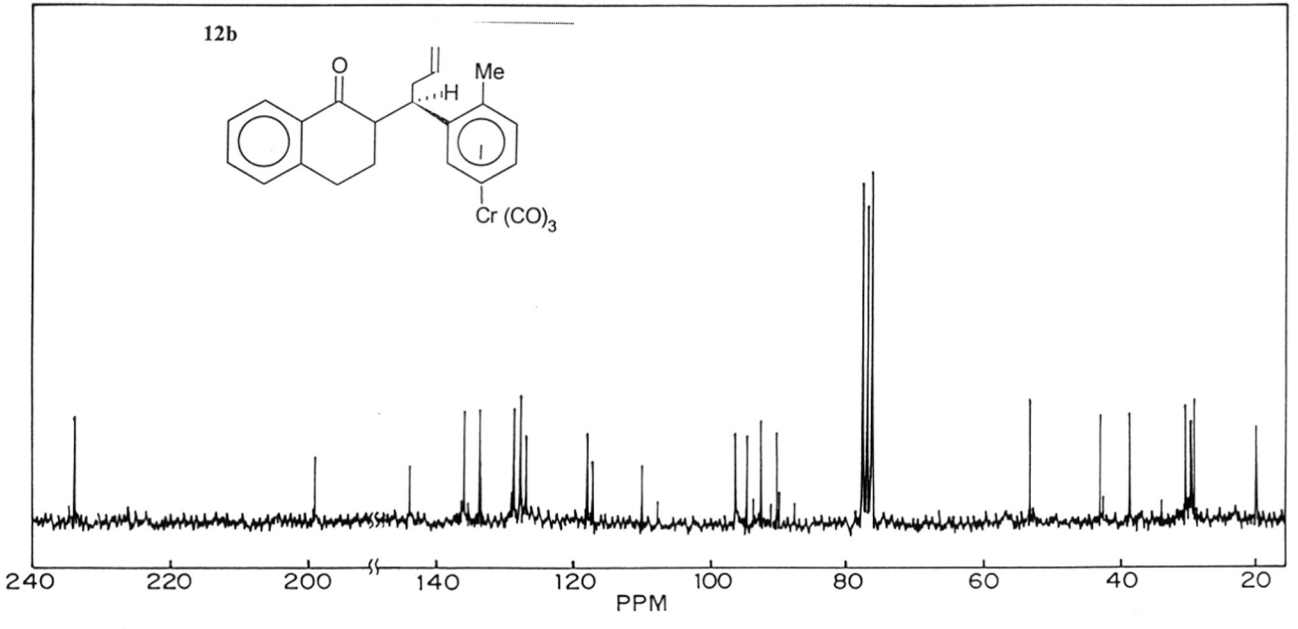
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O
H
Me
Cr (CO)3
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220
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140
120
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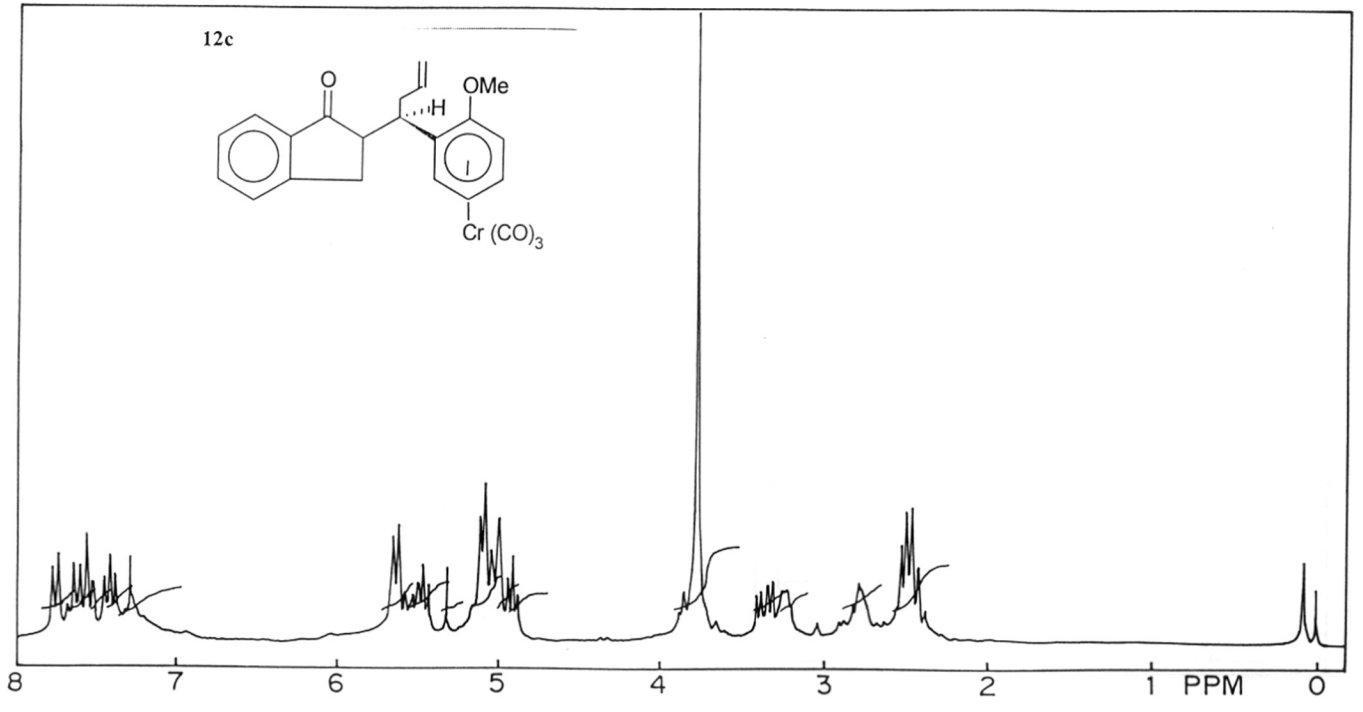
60
40
20
PPM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OMe
H
Cr (CO)3
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6
5
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2
1
PPM
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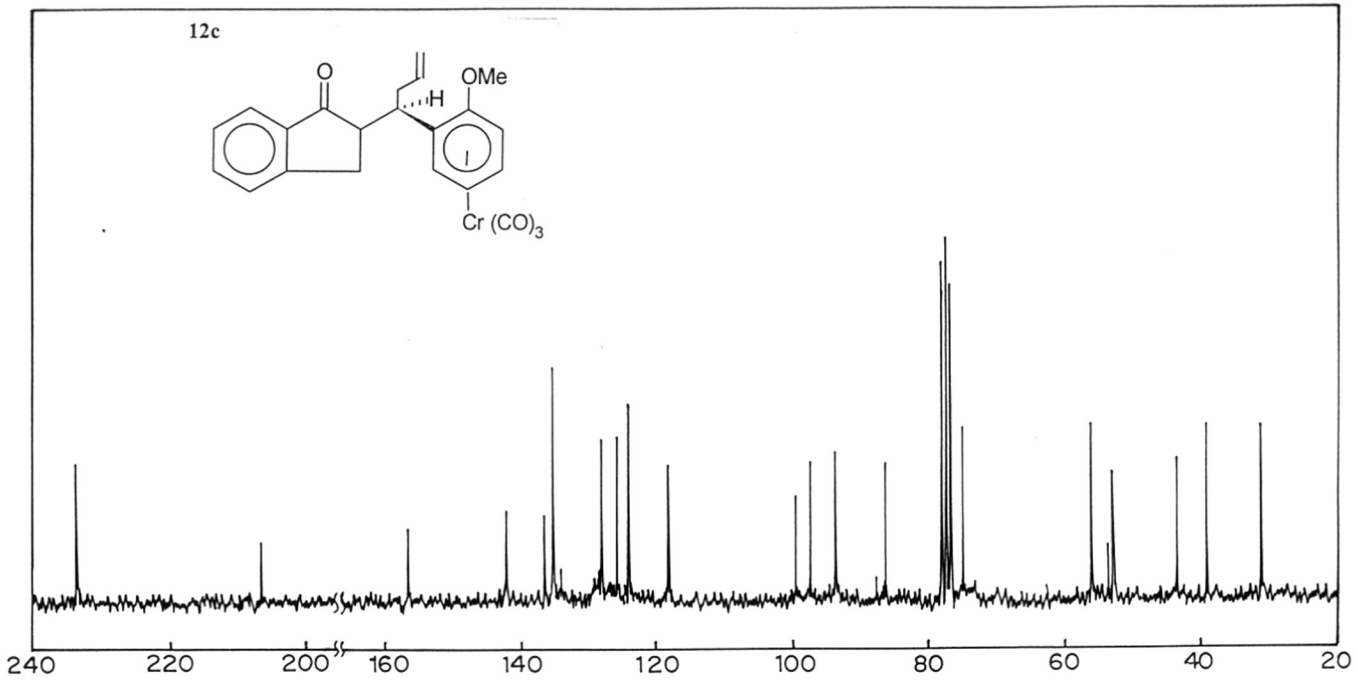
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OMe
H
Cr (CO)3
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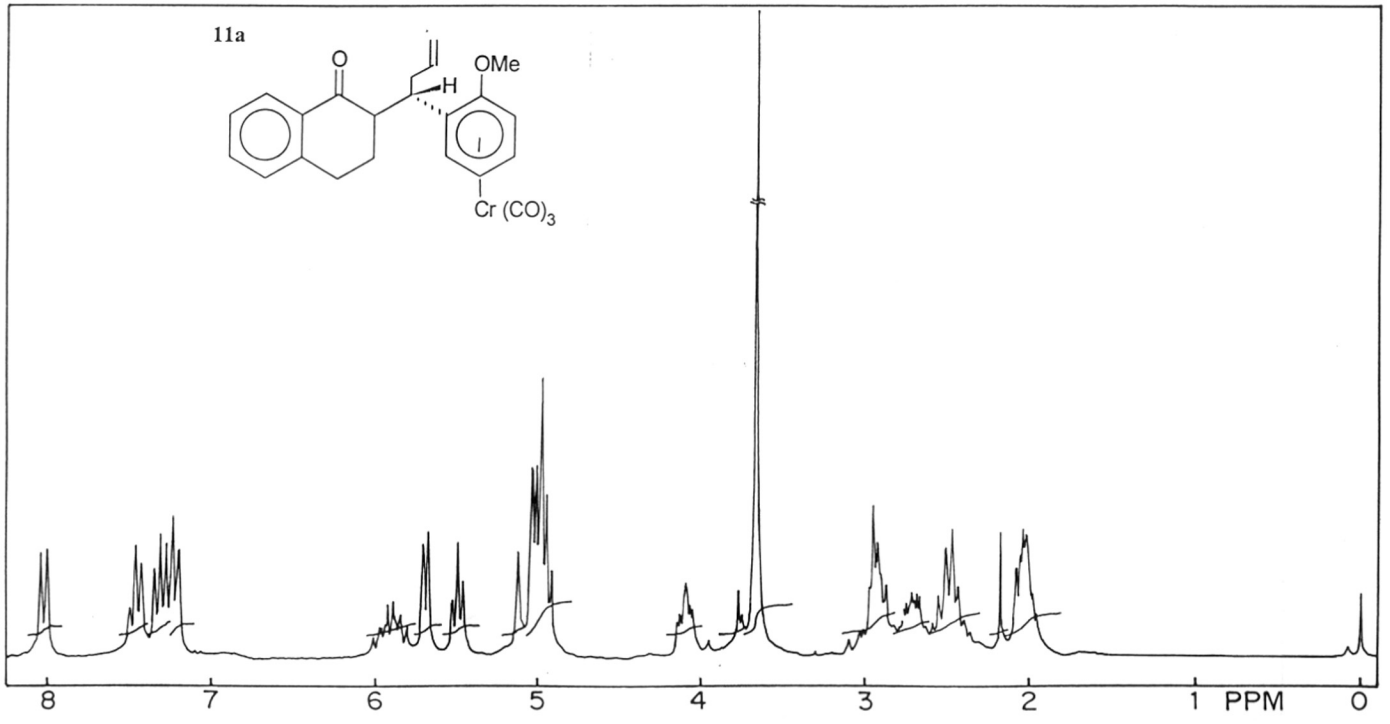
220
200
160
140
120
100
80
60
40
20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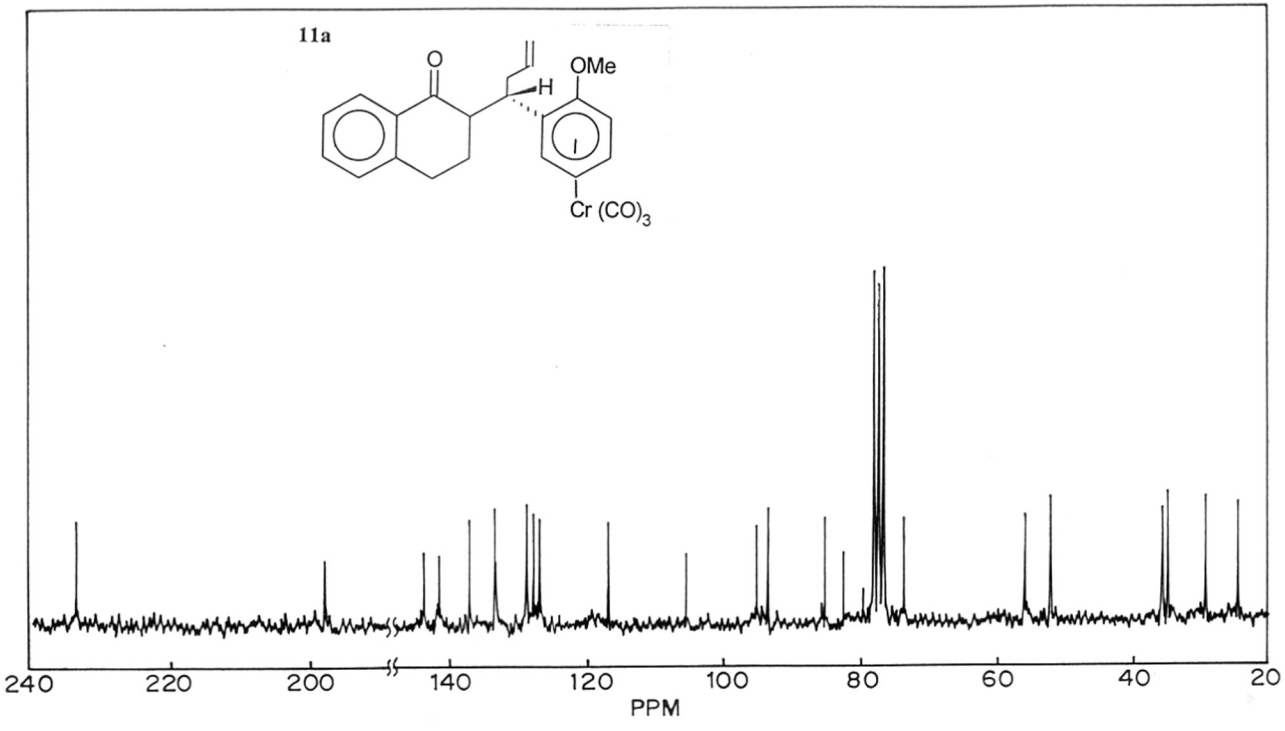
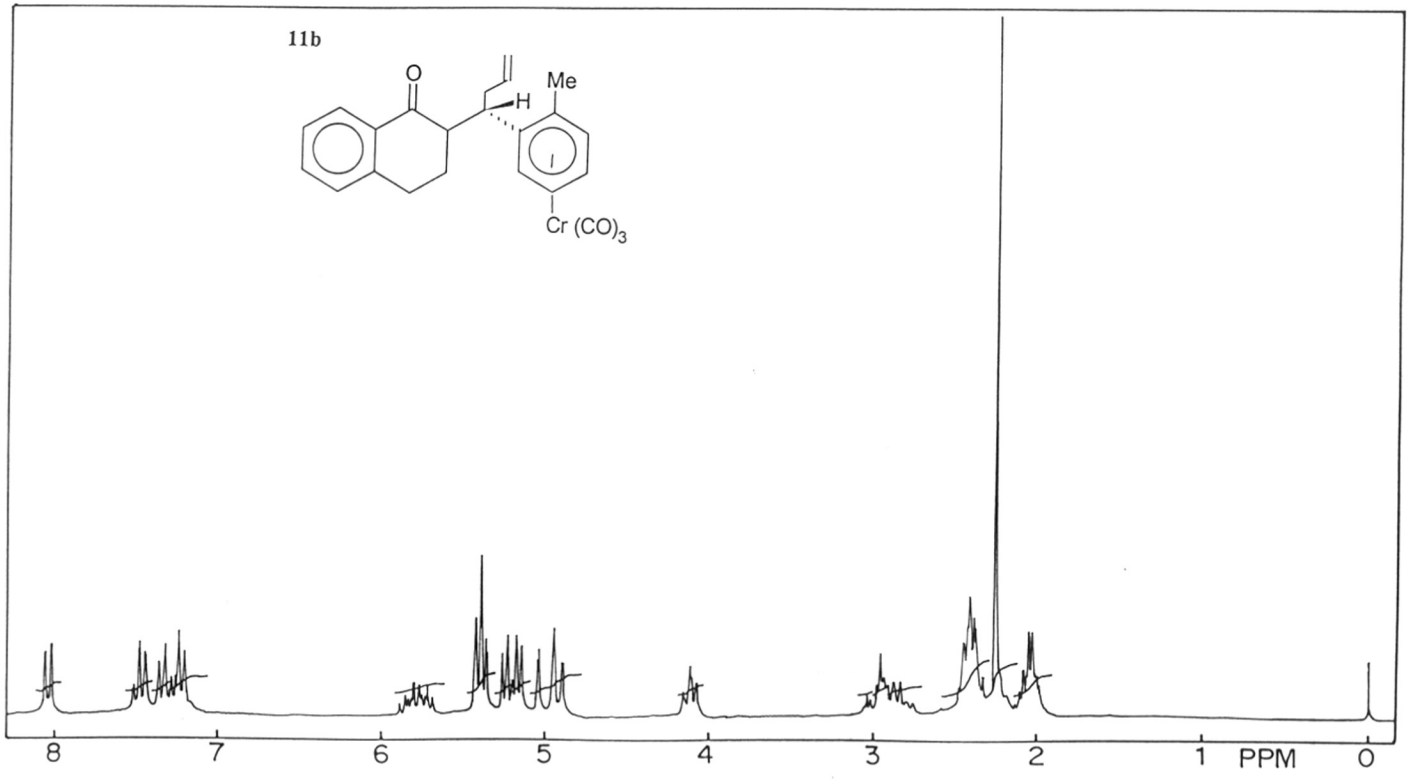
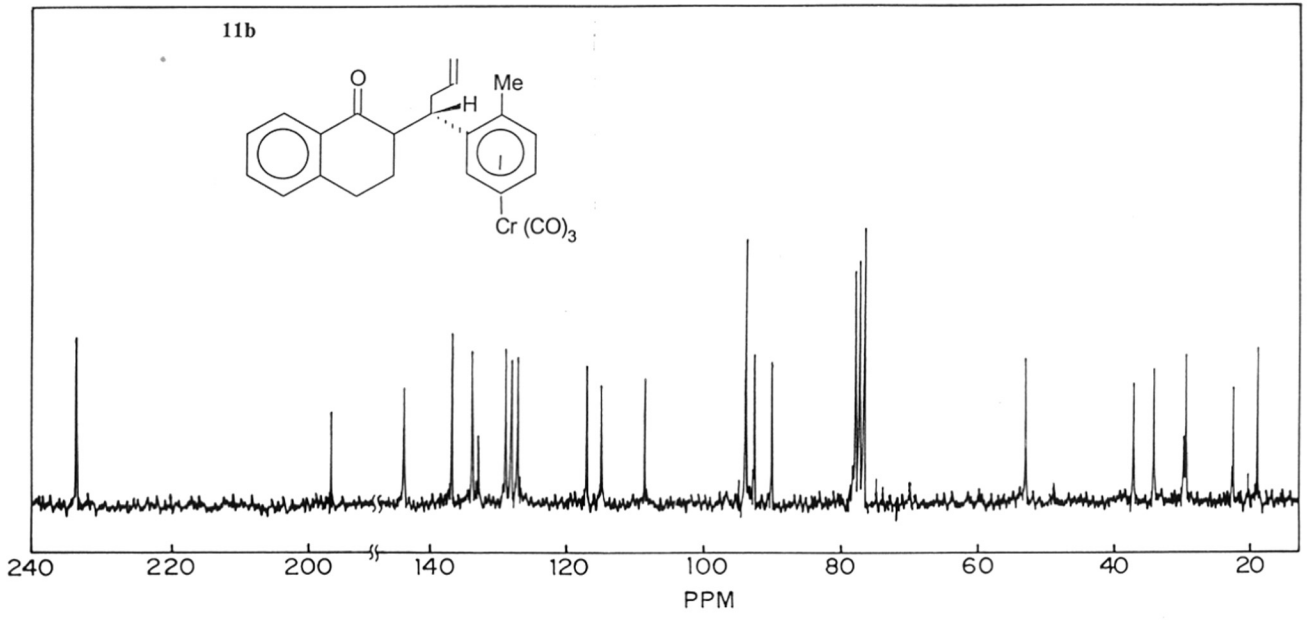
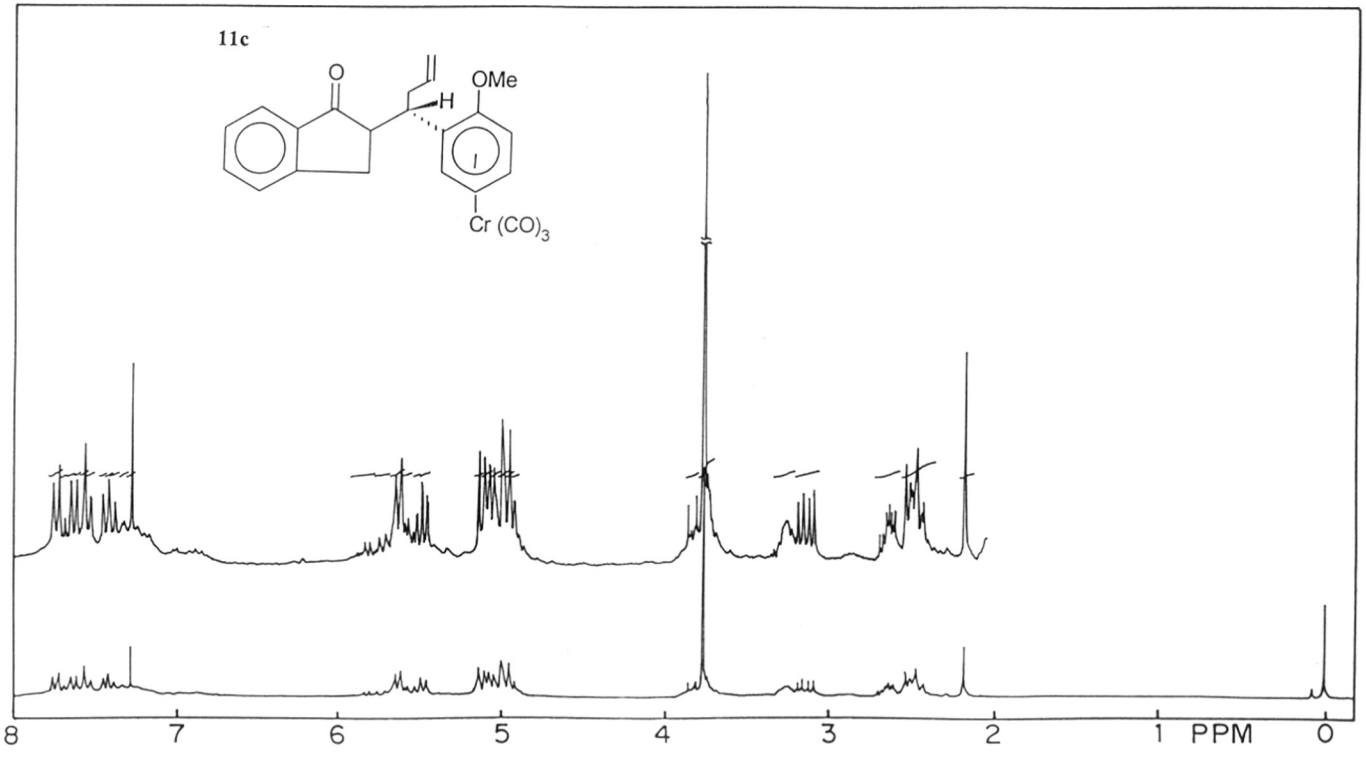
O
OMe
H
Cr (CO)3
8
7
6
5
4
3
2
1
PPM
0


11a
O
H
OMe
Cr (CO)3
240
220
200
140
120
100
80
60
40
20
PPM


11b
O
H
Me
Cr (CO)3
8
7
6
5
4
3
2
1
PPM
0


11b
O
H
Me
Cr (CO)3
240
220
200
140
120
100
80
60
40
20
PPM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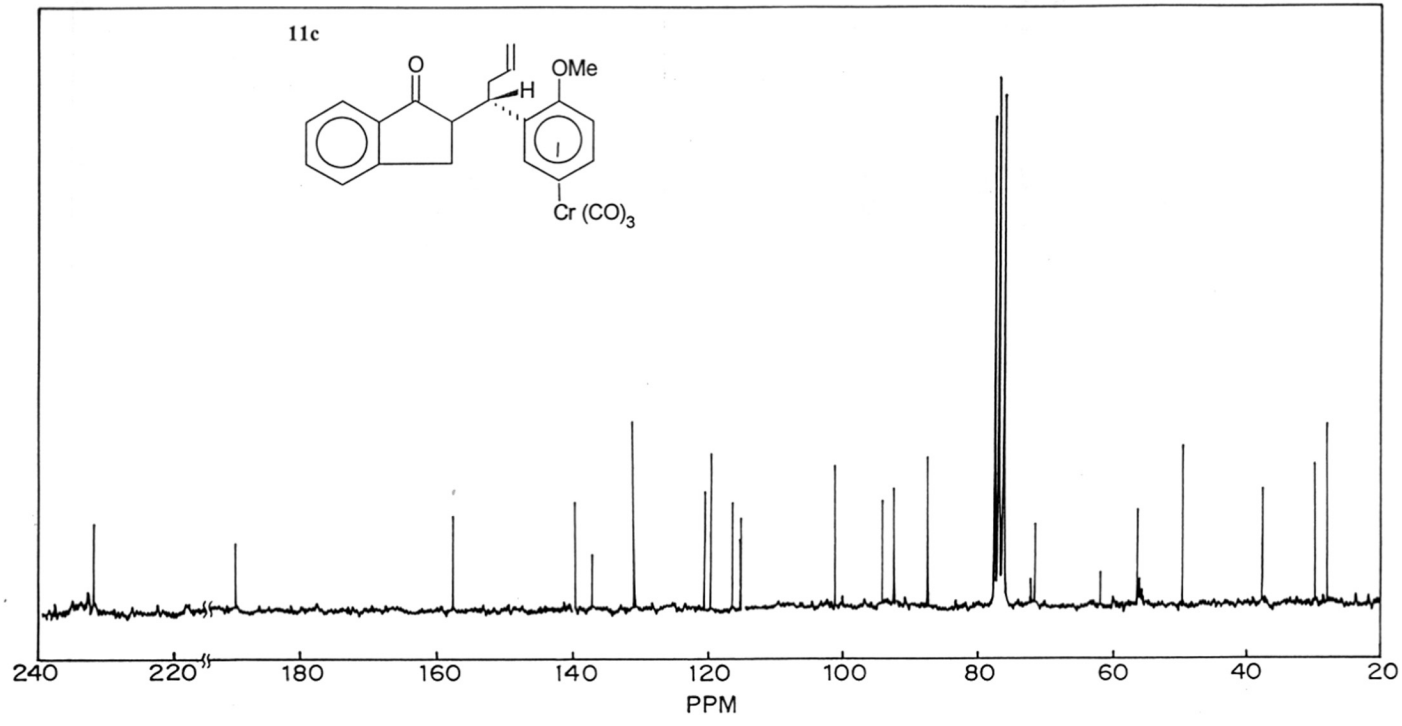
O
OMe
H
Cr (CO)3
8
7
6
5
4
3
2
1
PPM
0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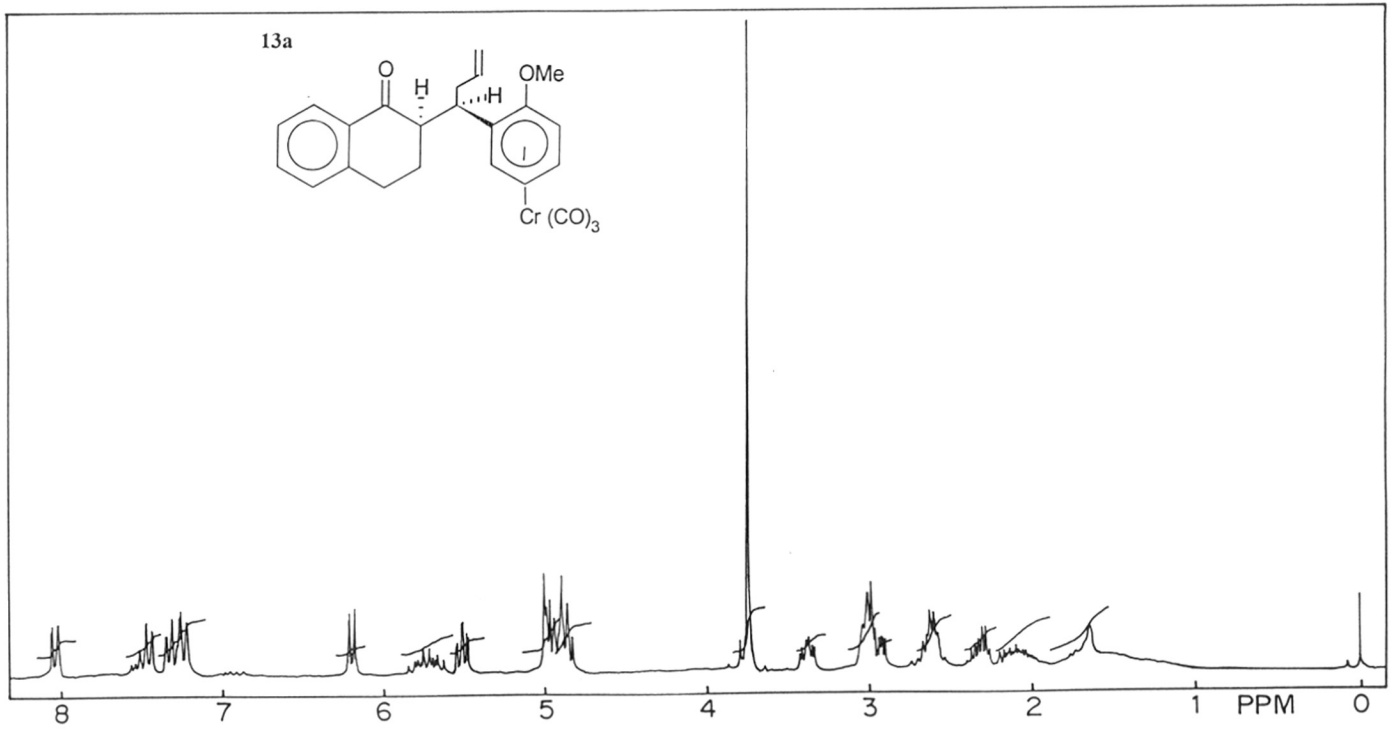
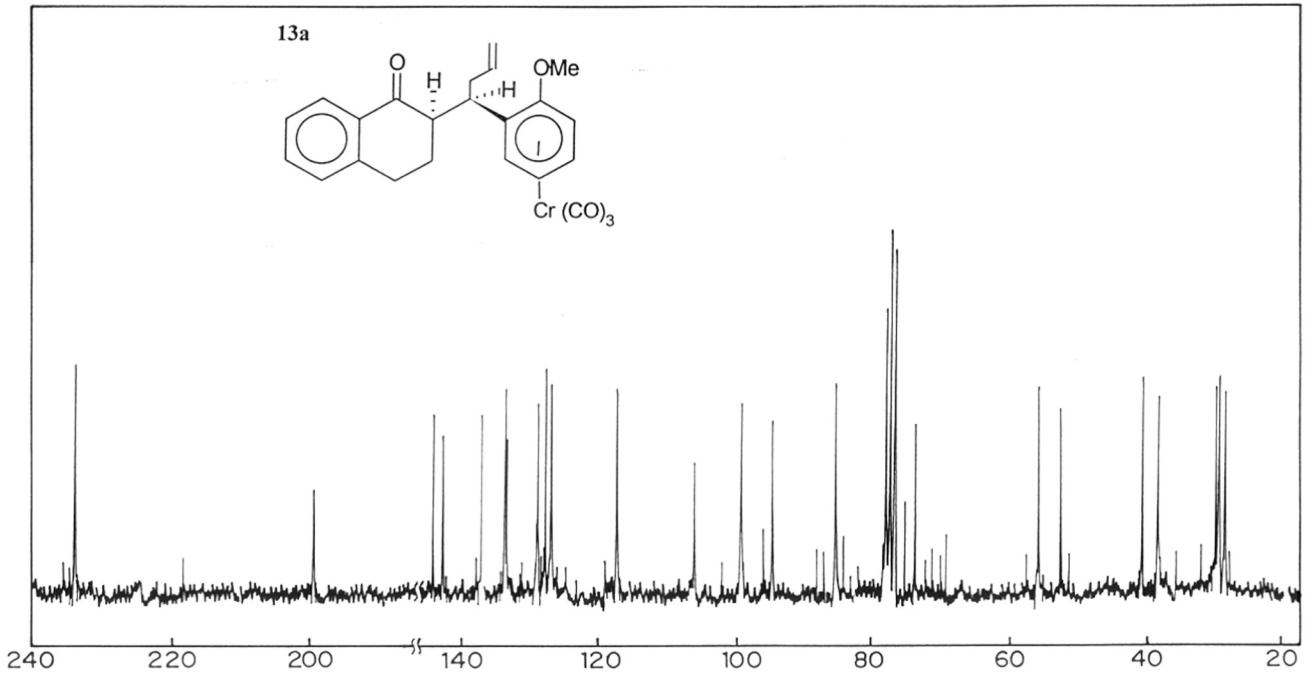
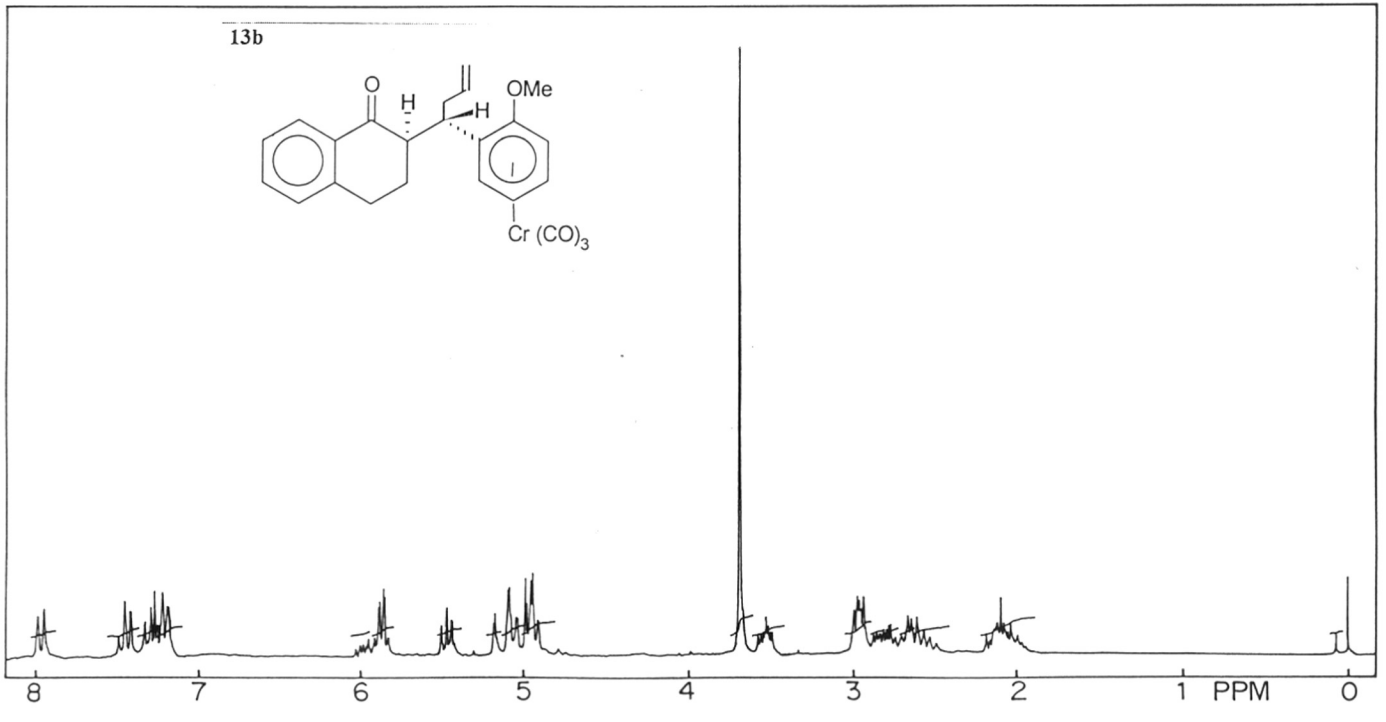
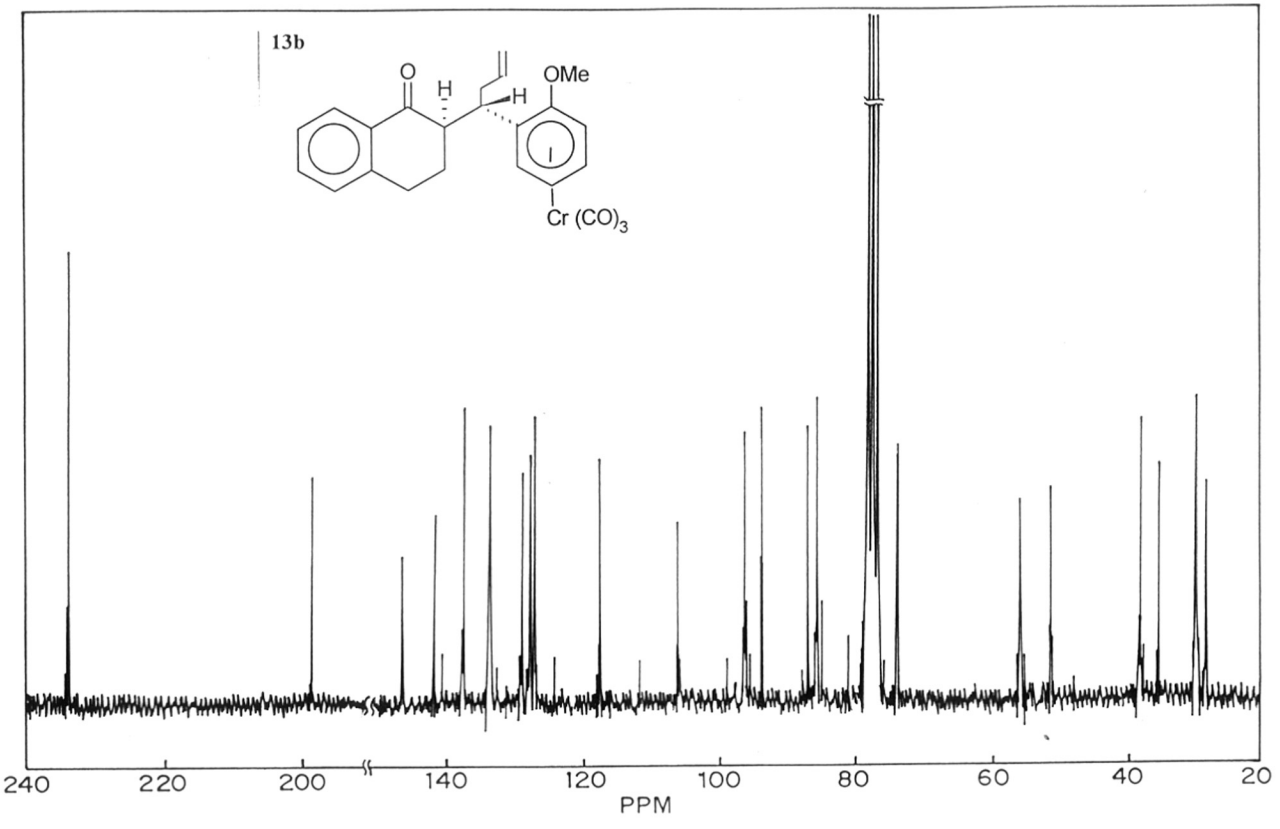
O
H
OMe
Cr (CO)3
240
220
180
160
140
120
100
80
60
40
20
PPM


13a
O
H
H
OMe
Cr (CO)3
8
7
6
5
4
3
2
1
PPM
0

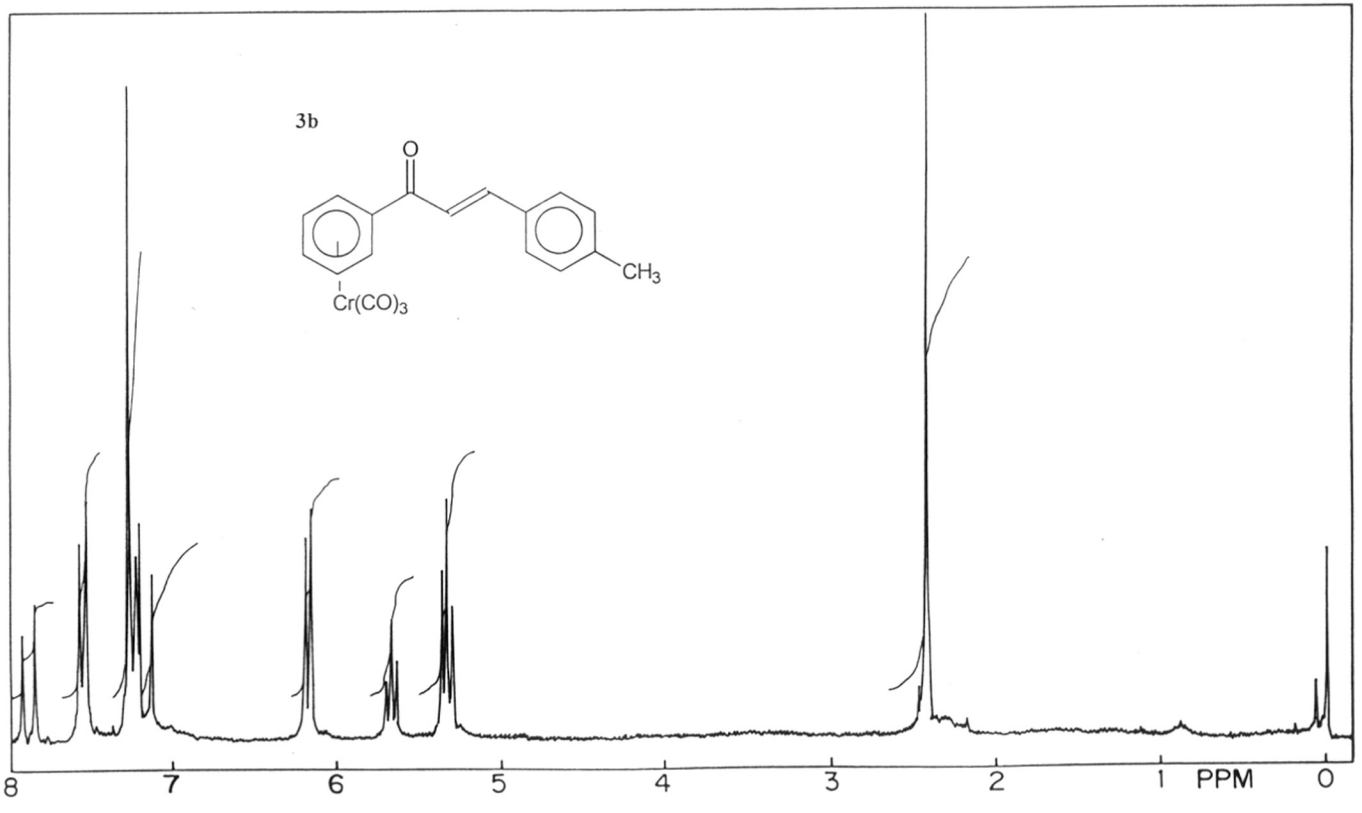

13a
O
H
H
OMe
Cr (CO)3
240
220
200
140
120
100
80
60
40
20

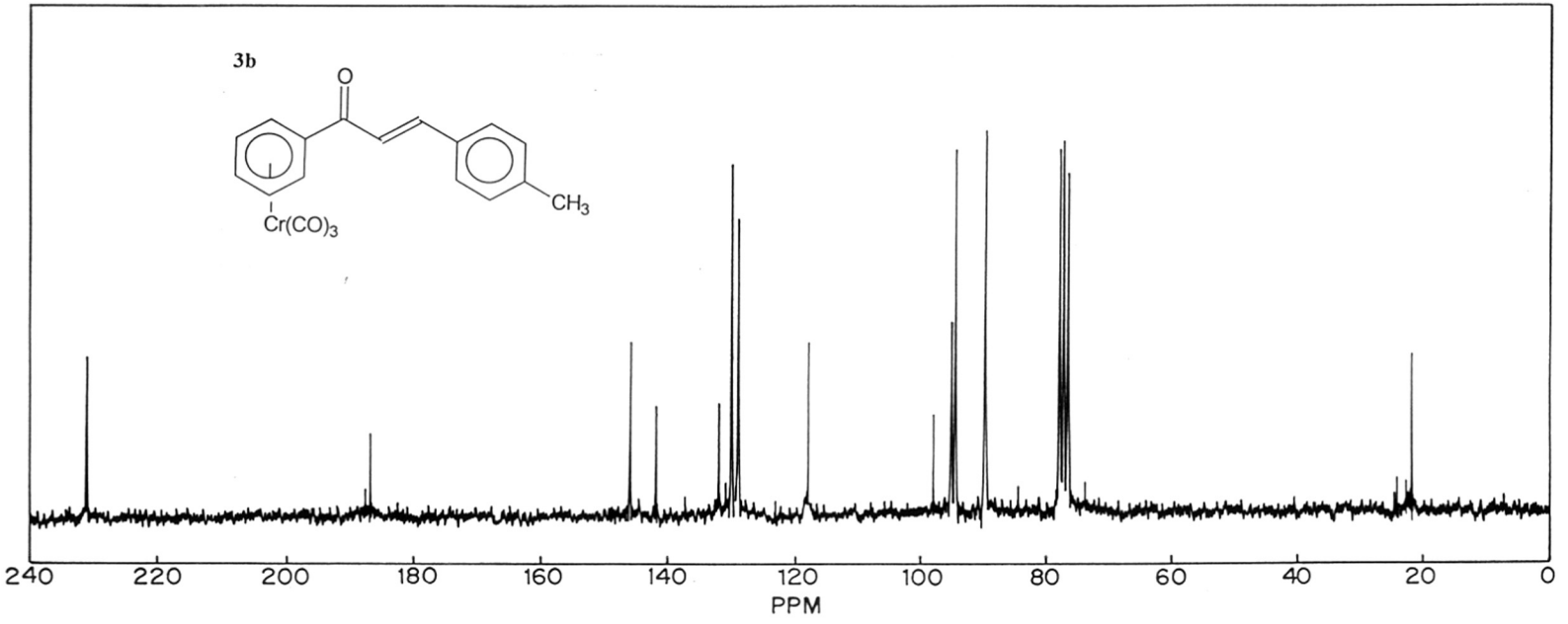

13b
O
H
H
OMe
Cr (CO)3
8
7
6
5
4
3
2
1
PPM
0

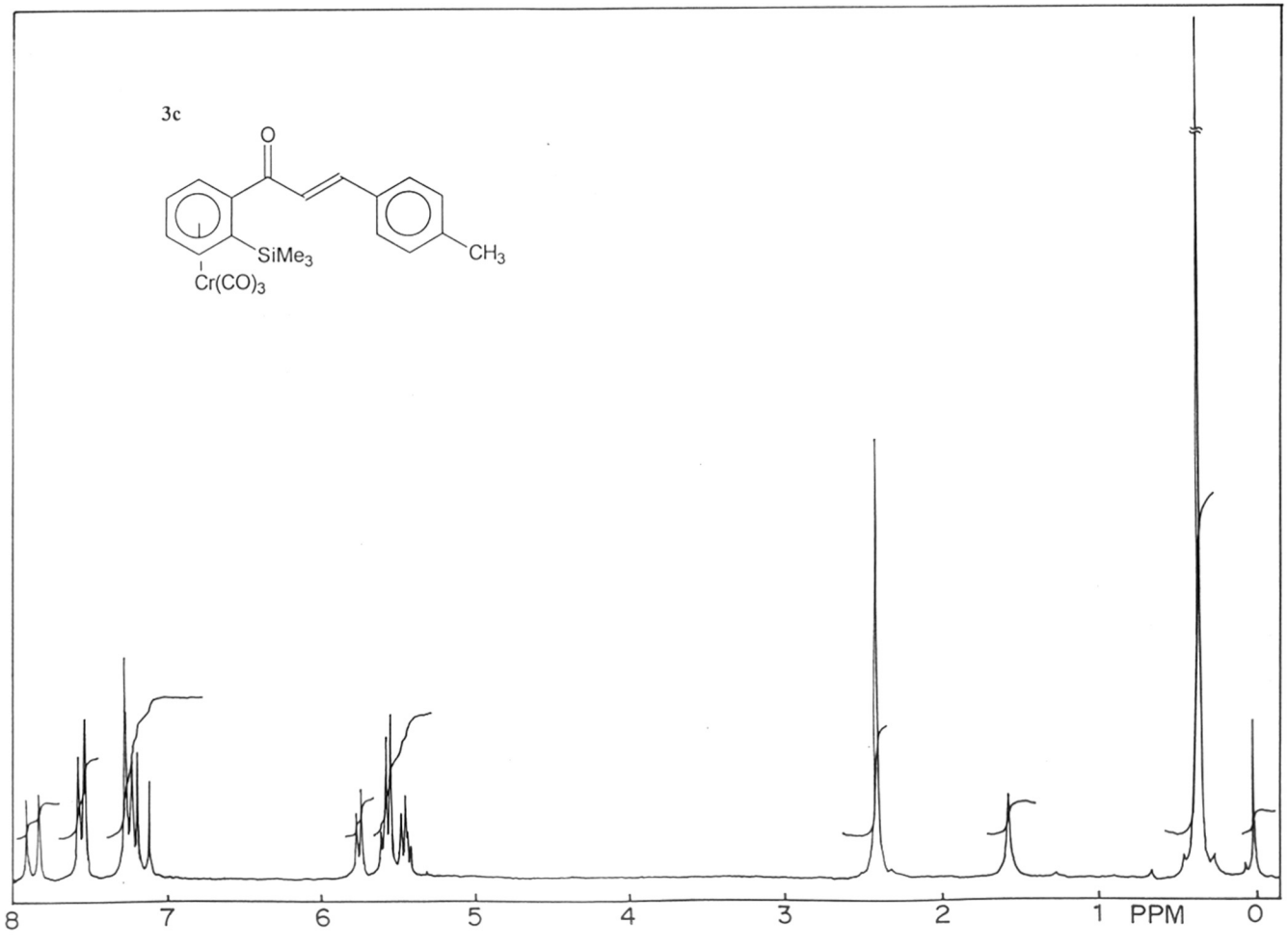

13b
O
H
H
OMe
Cr (CO)3
240
220
200
140
120
100
80
60
40
20
PPM

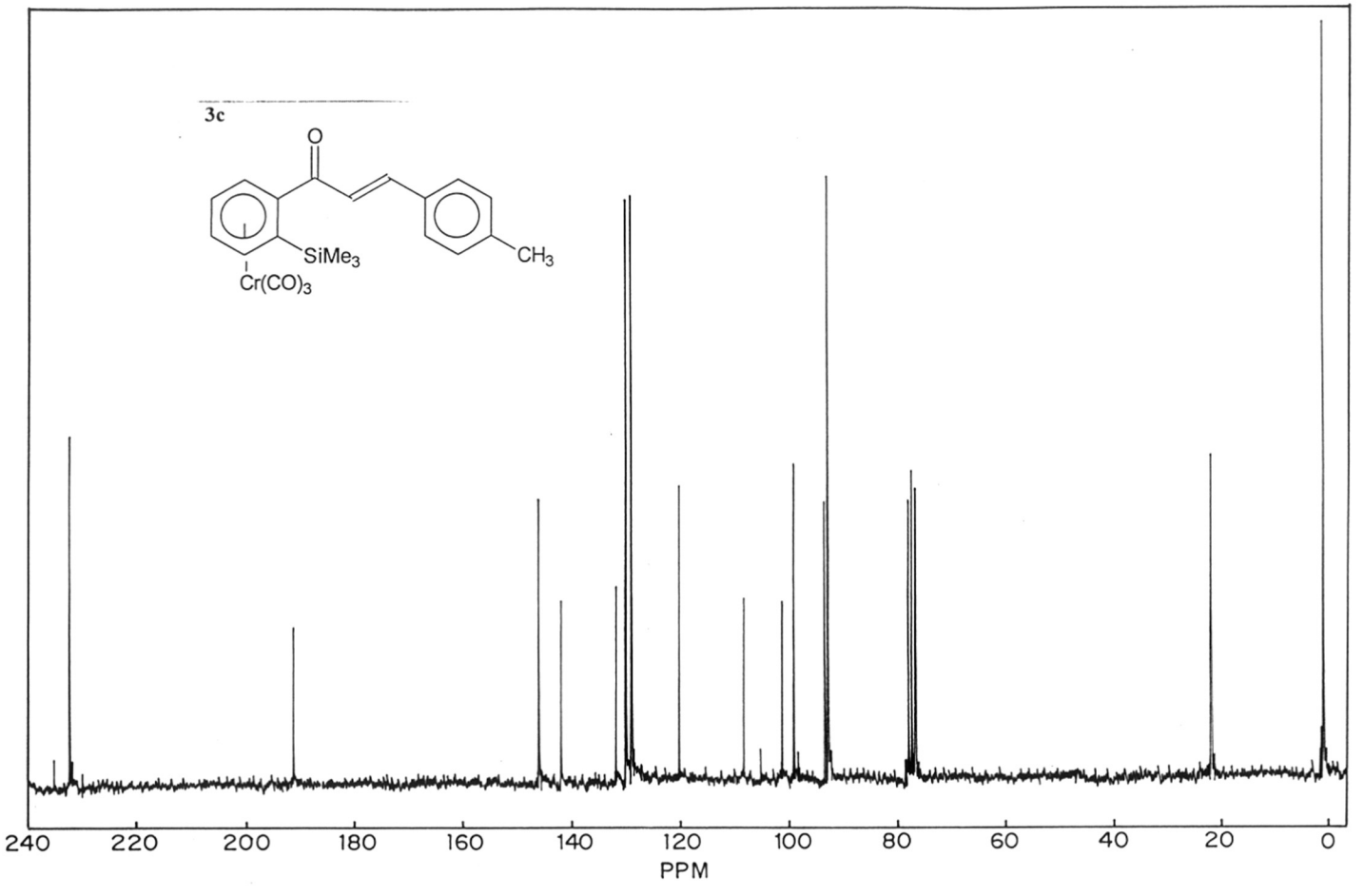
Appendix-**II**

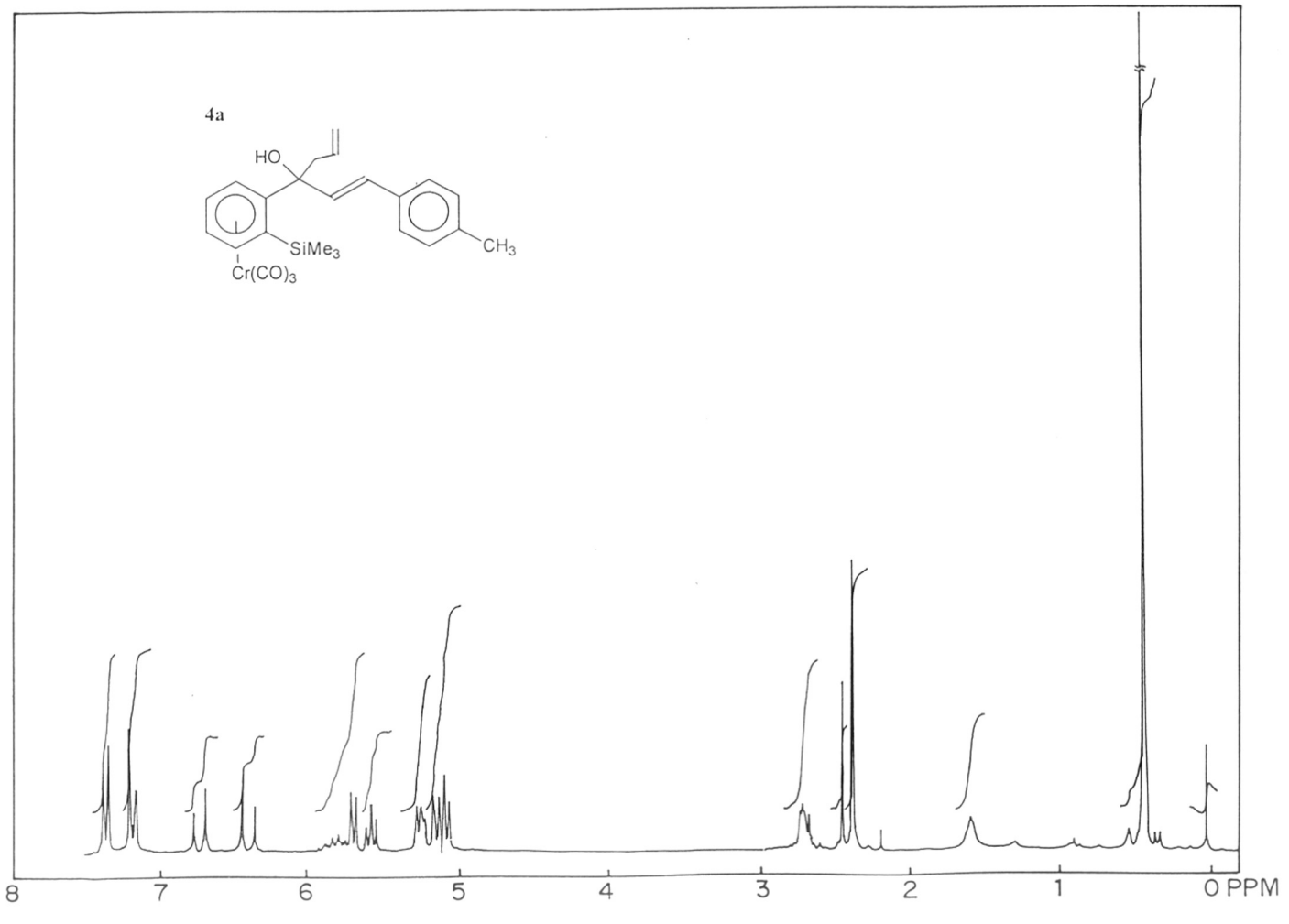
Spectra of all new compounds of PART-B

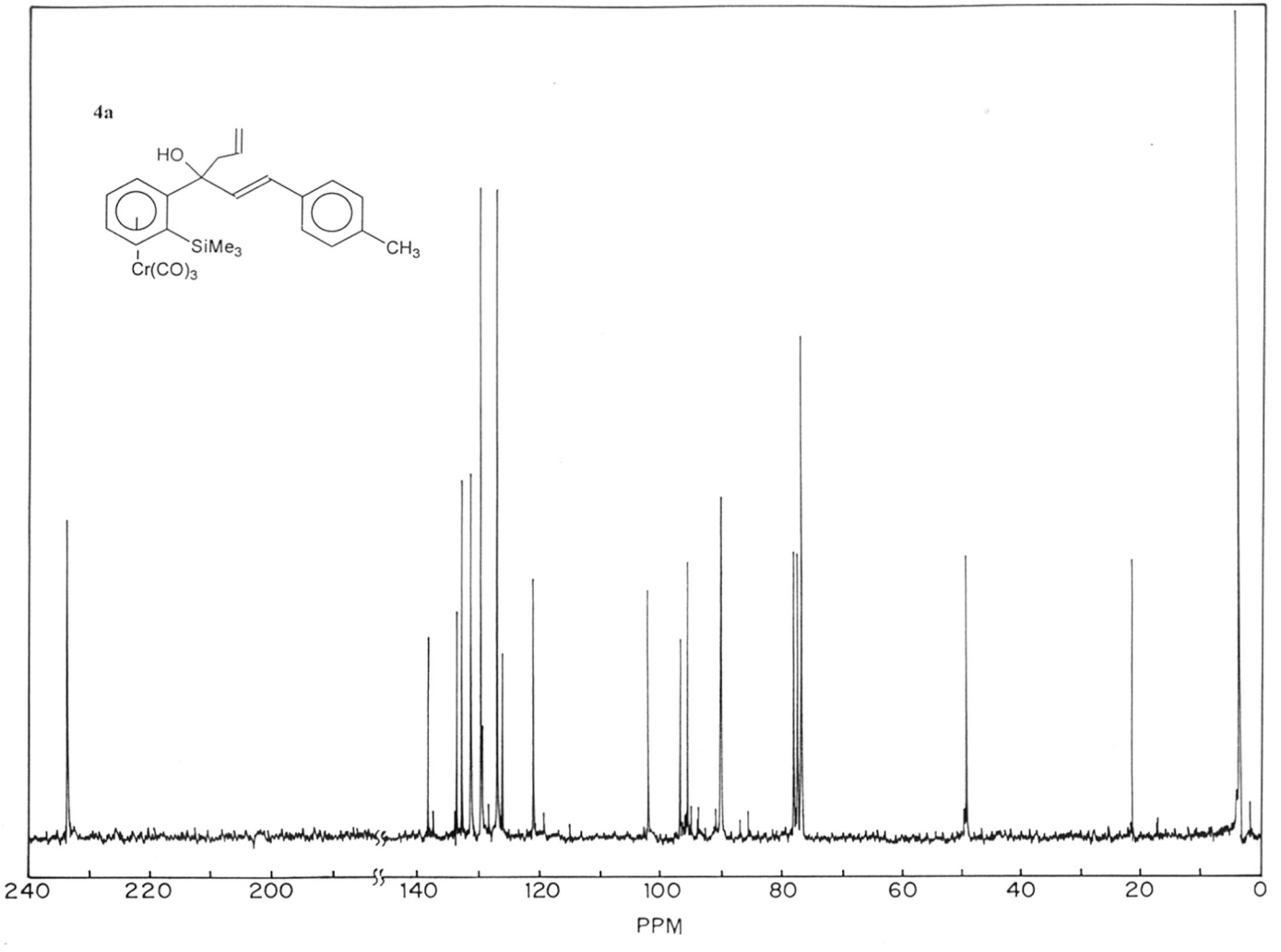

3b
O
CH3
Cr(CO)3
8
7
6
5
4
3
2
1
PPM
0

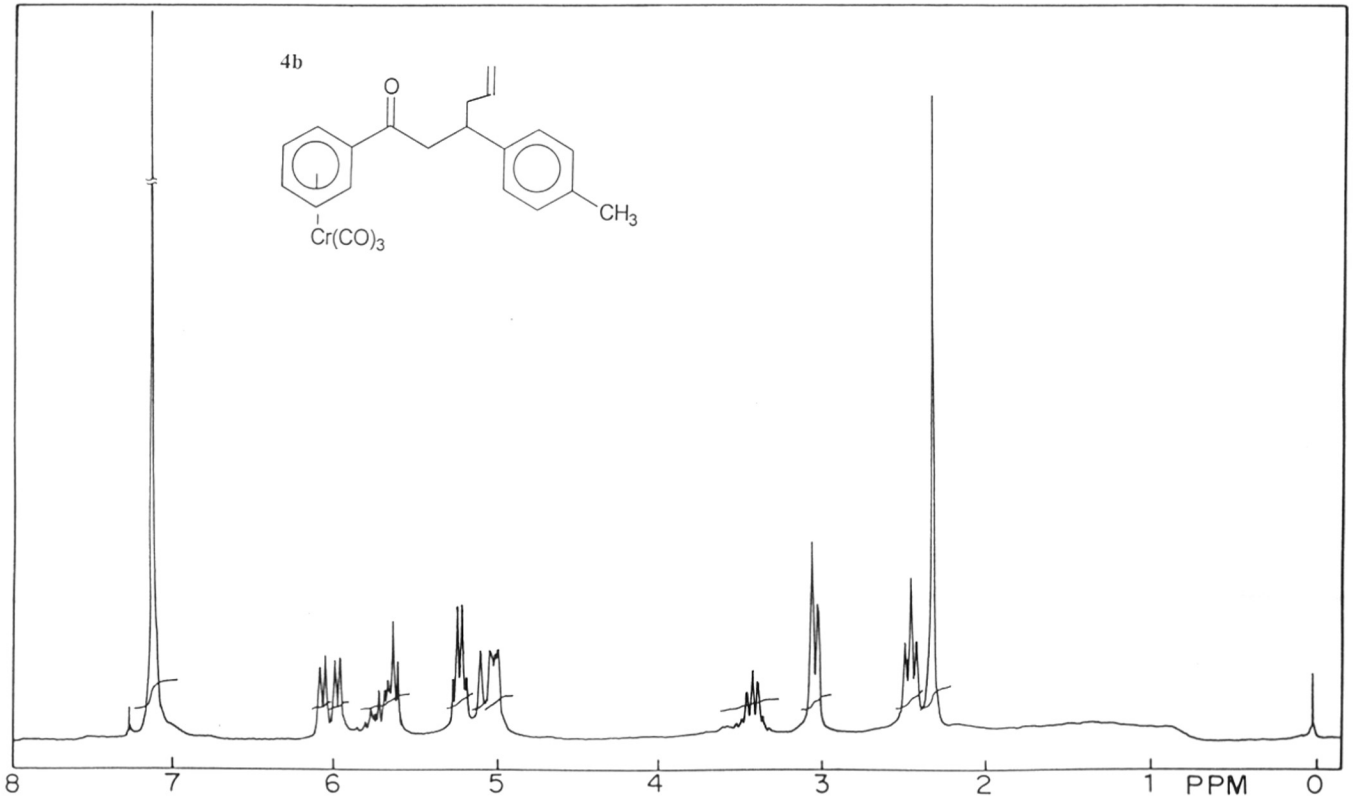

3b
O
CH3
Cr(CO)3
240
220
200
180
160
140
120
100
80
60
40
20
0
PPM

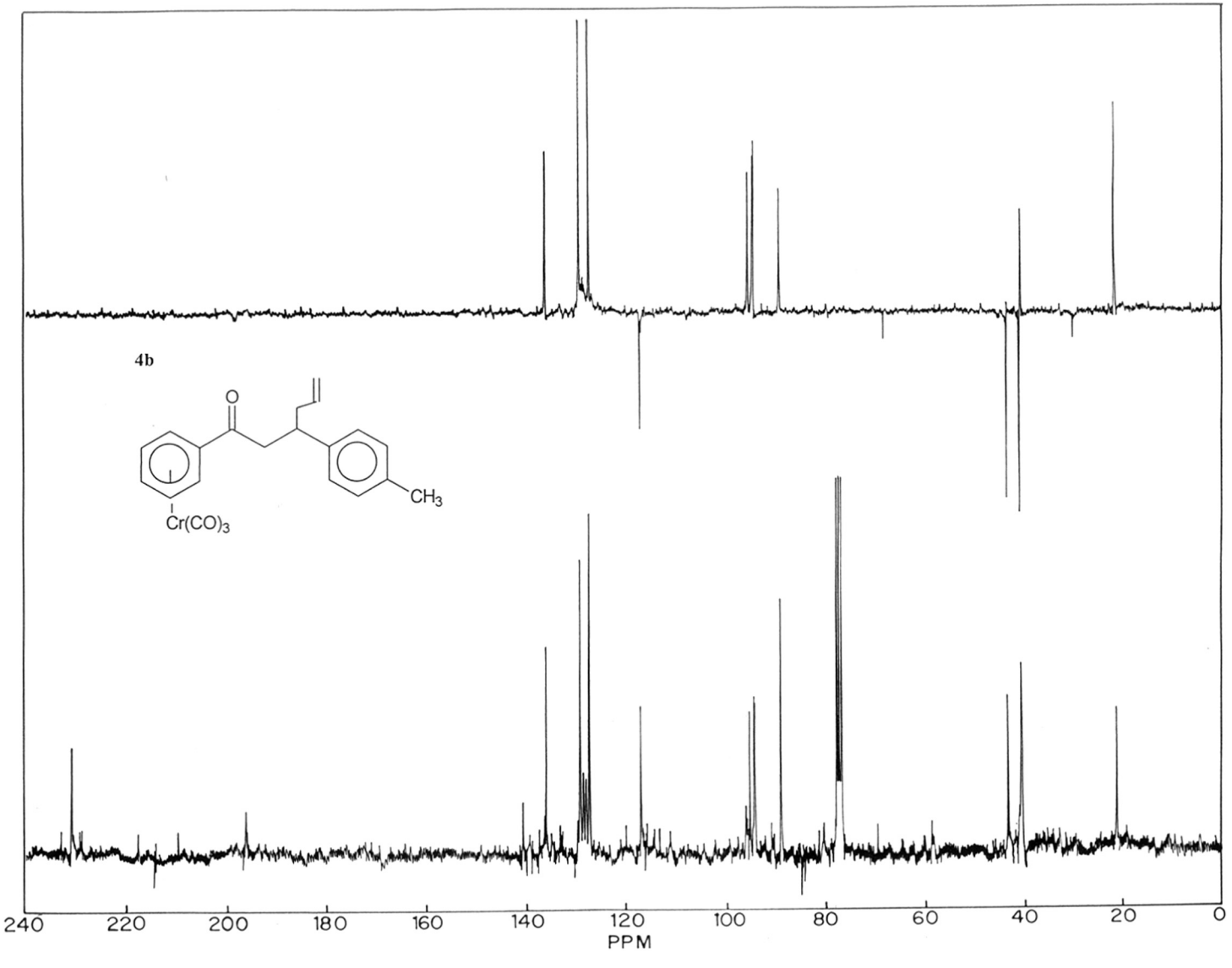

3c
O
SiMe3
Cr(CO)3
CH3
8
7
6
5
4
3
2
1
PPM
0

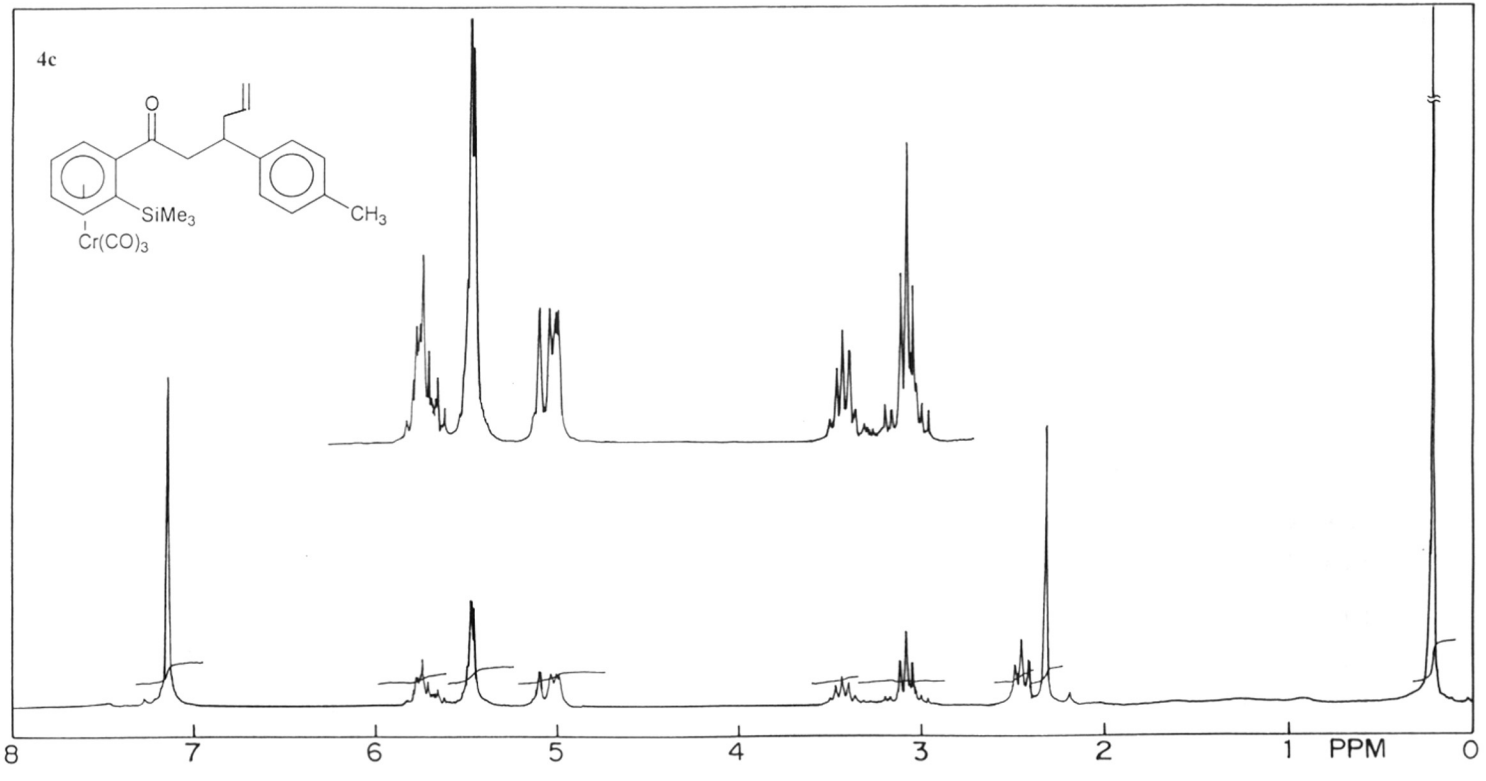

3c
O
SiMe3
Cr(CO)3
CH3
240
220
200
180
160
140
120
100
80
60
40
20
0
PPM

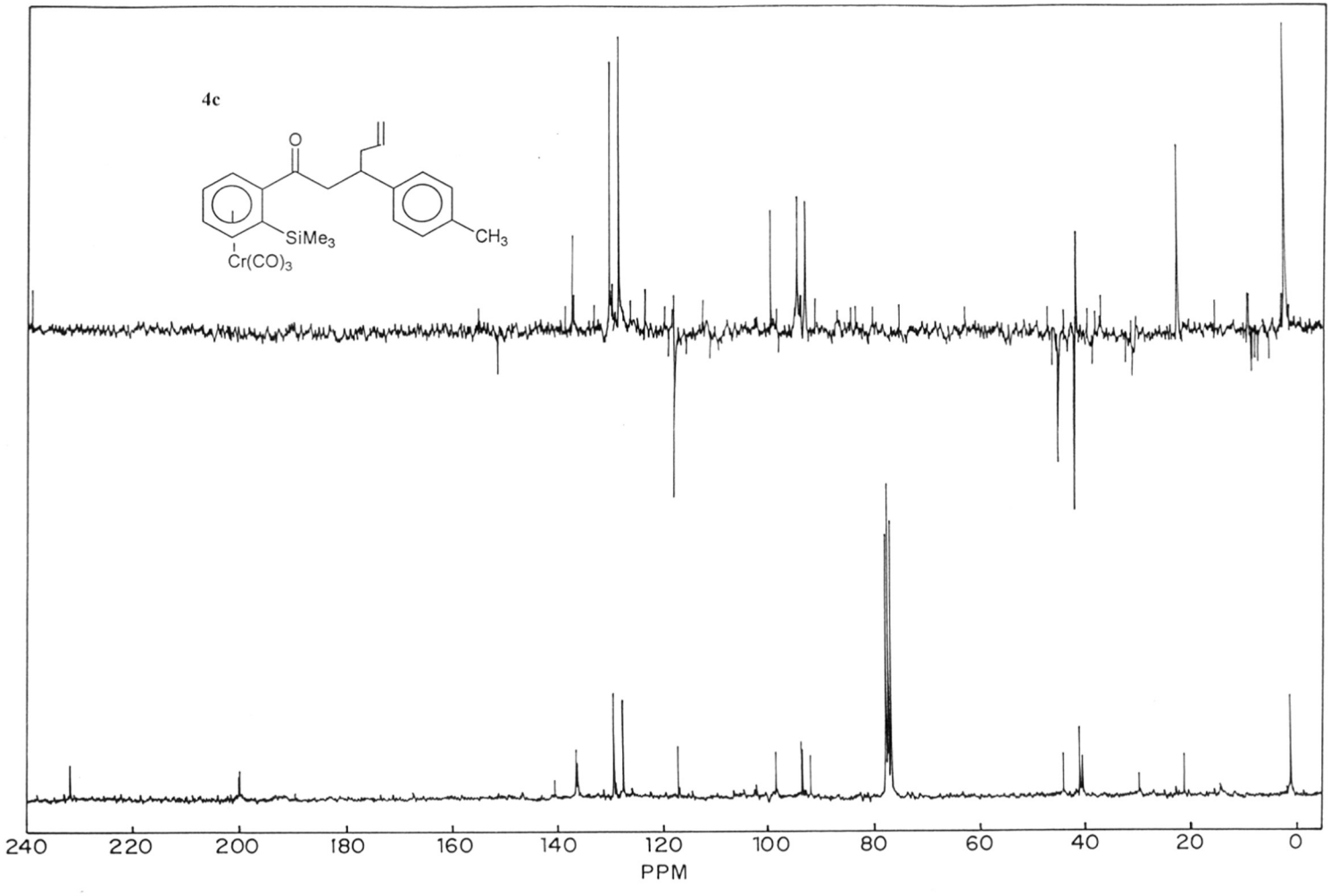

4a
HO
SiMe3
Cr(CO)3
CH3
8
7
6
5
4
3
2
1
0 PPM

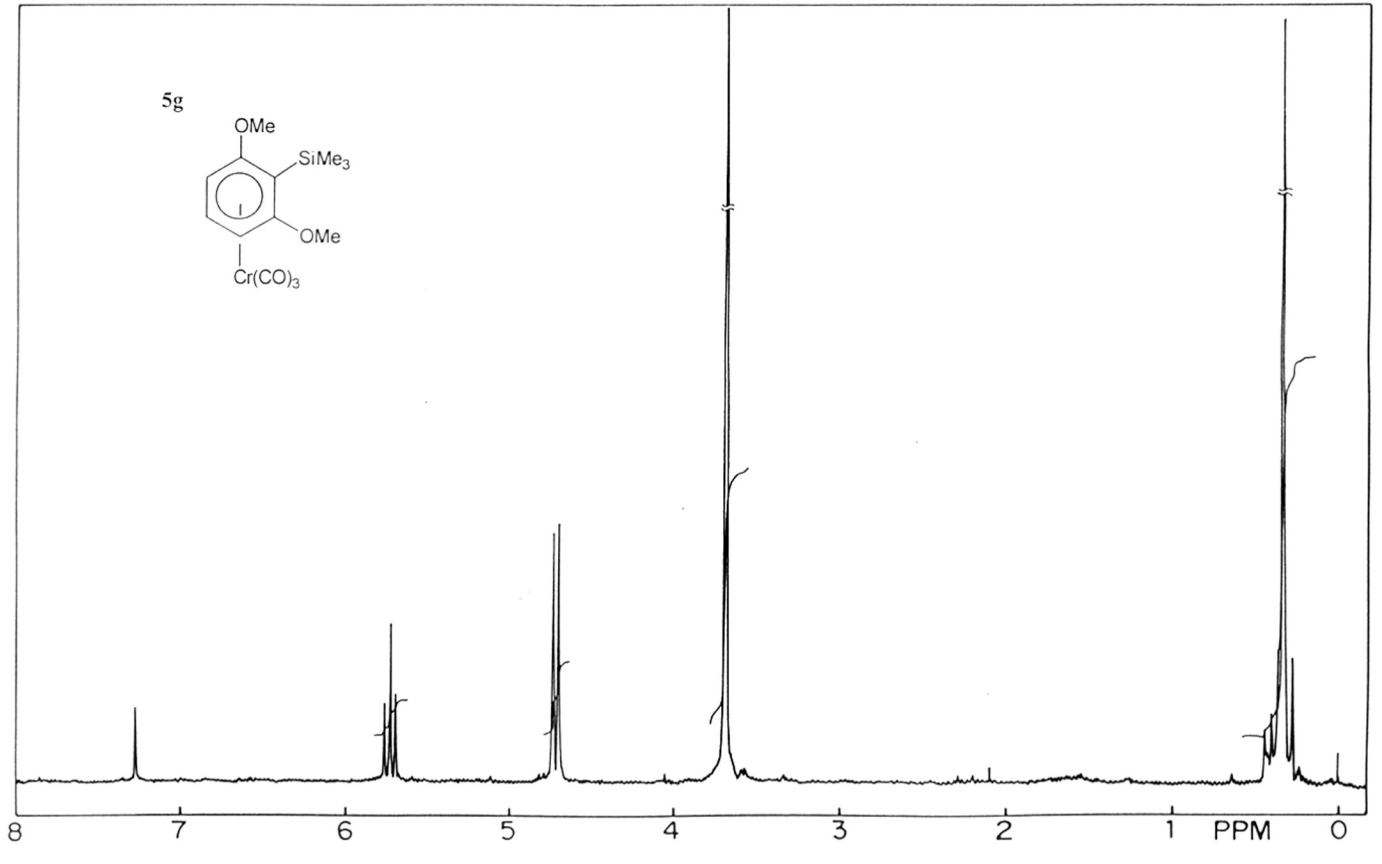

4a
HO
SiMe3
Cr(CO)3
CH3
240
220
200
140
120
100
80
60
40
20
0
PPM

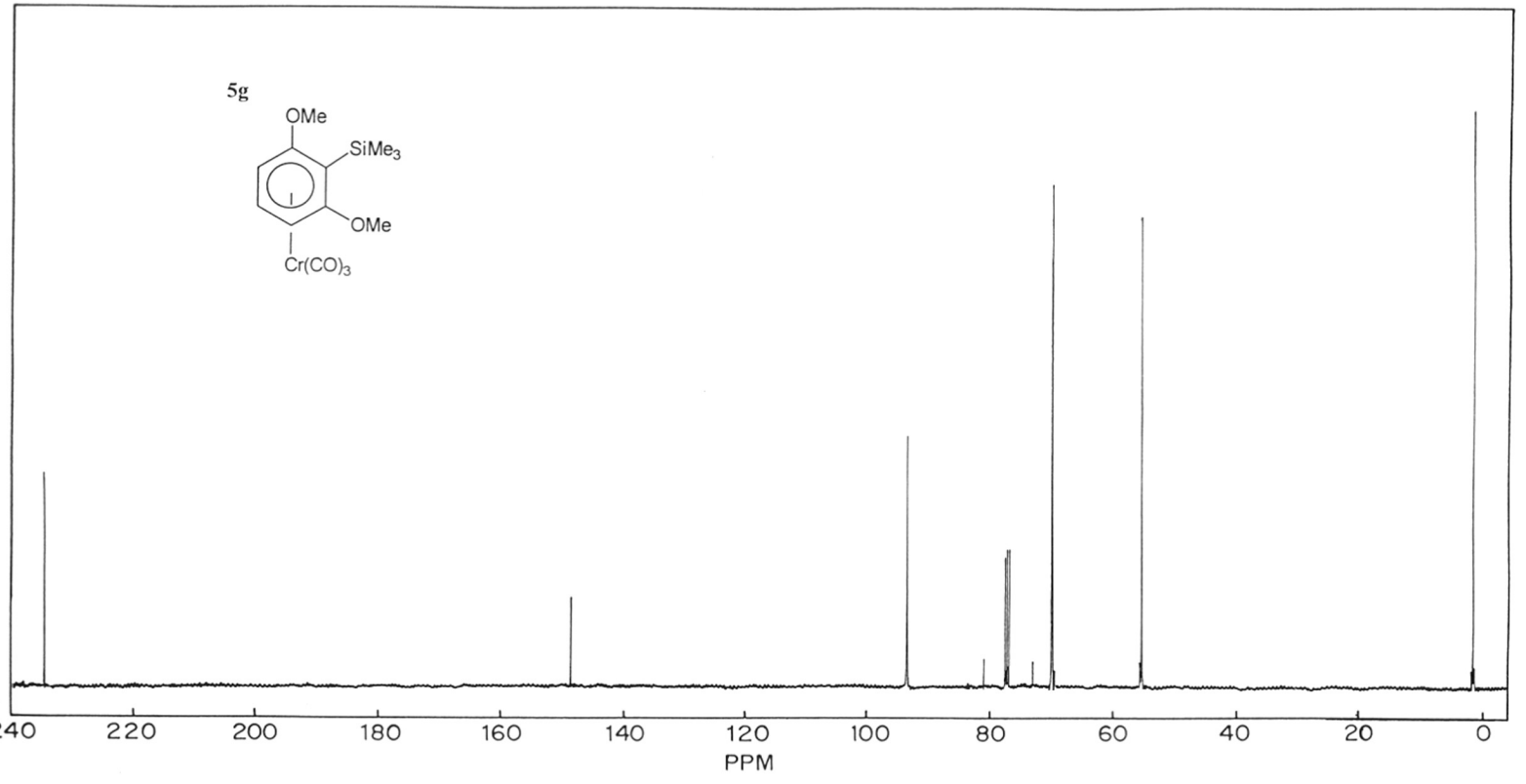

4b
O
CH3
Cr(CO)3
8
7
6
5
4
3
2
1
PPM
0

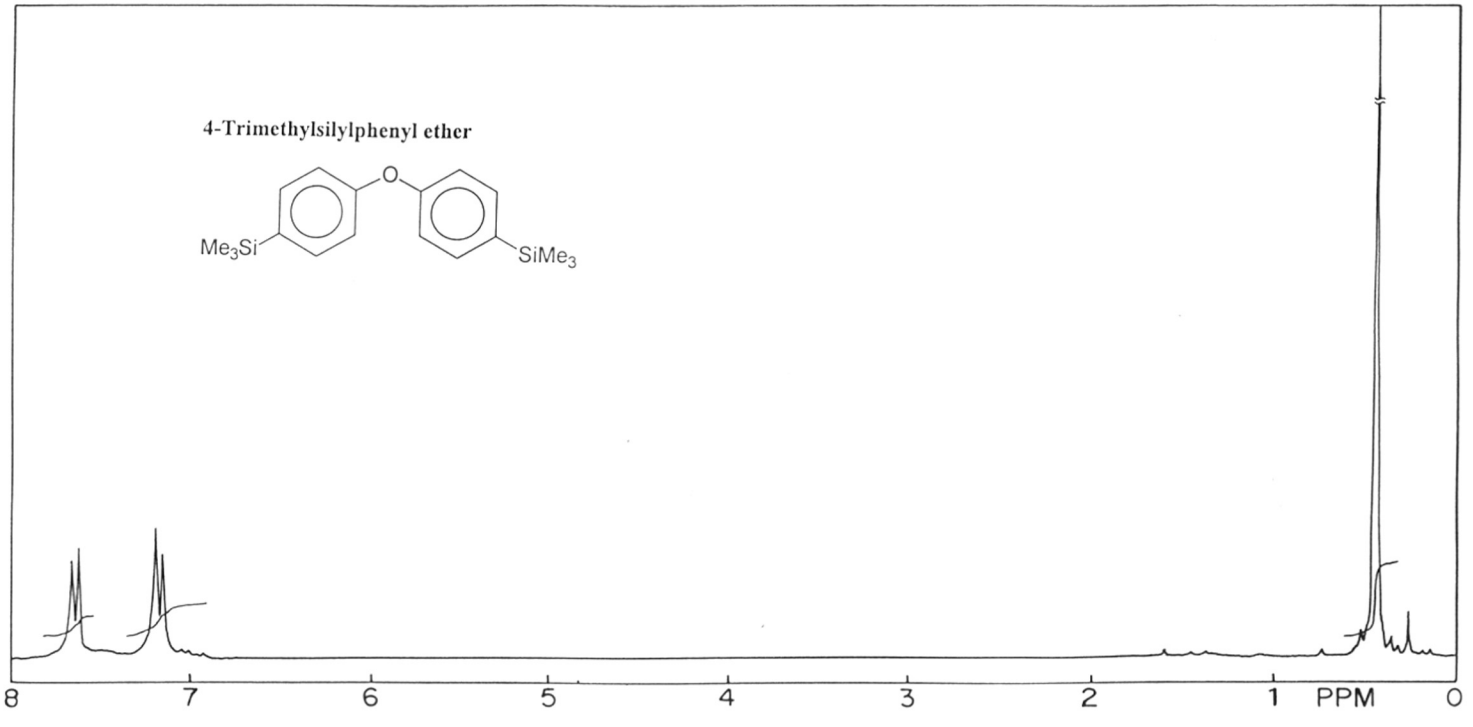

4b
O
CH3
Cr(CO)3
240
220
200
180
160
140
120
100
80
60
40
20
0
PPM

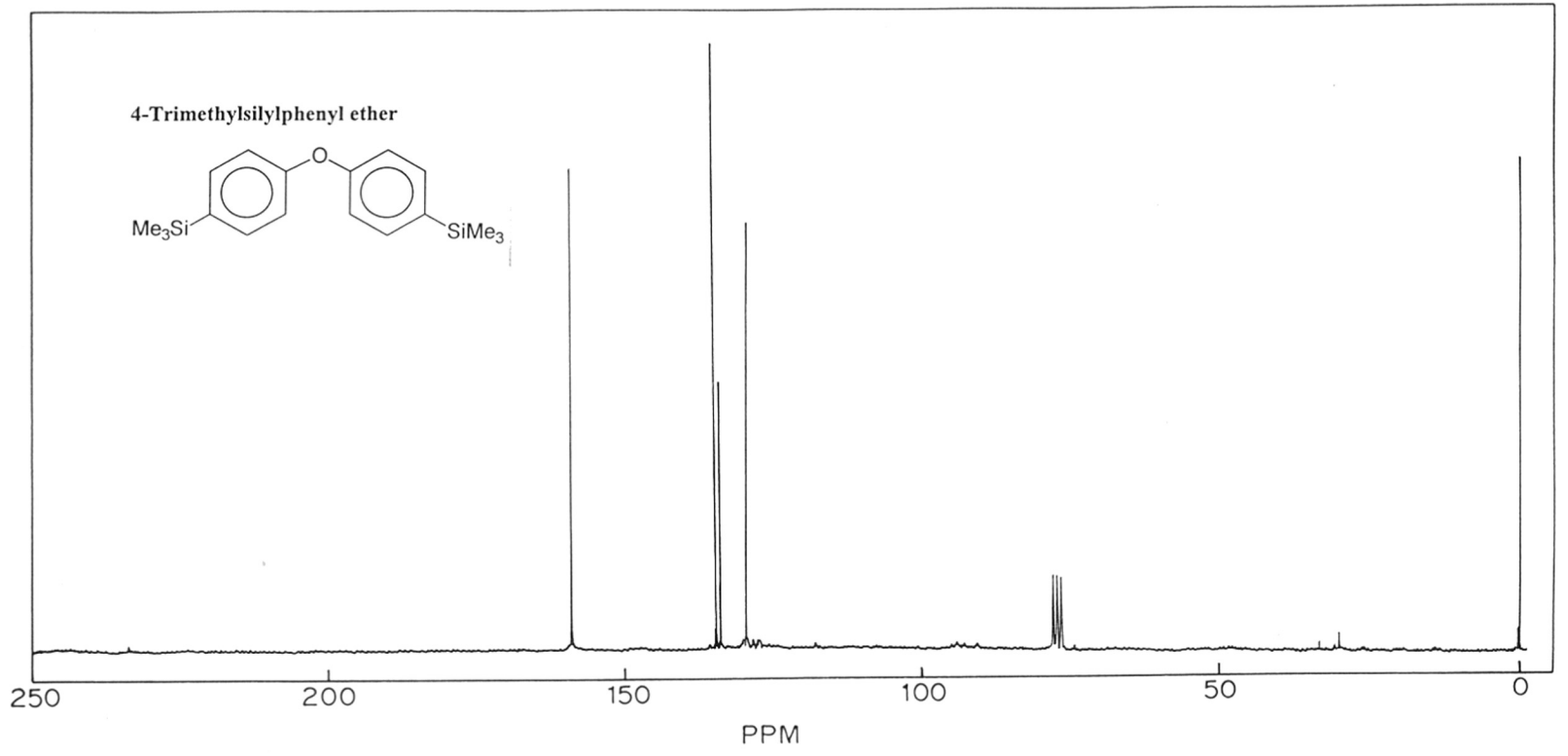

4c
O
SiMe3
Cr(CO)3
CH3
8
7
6
5
4
3
2
1
PPM
0

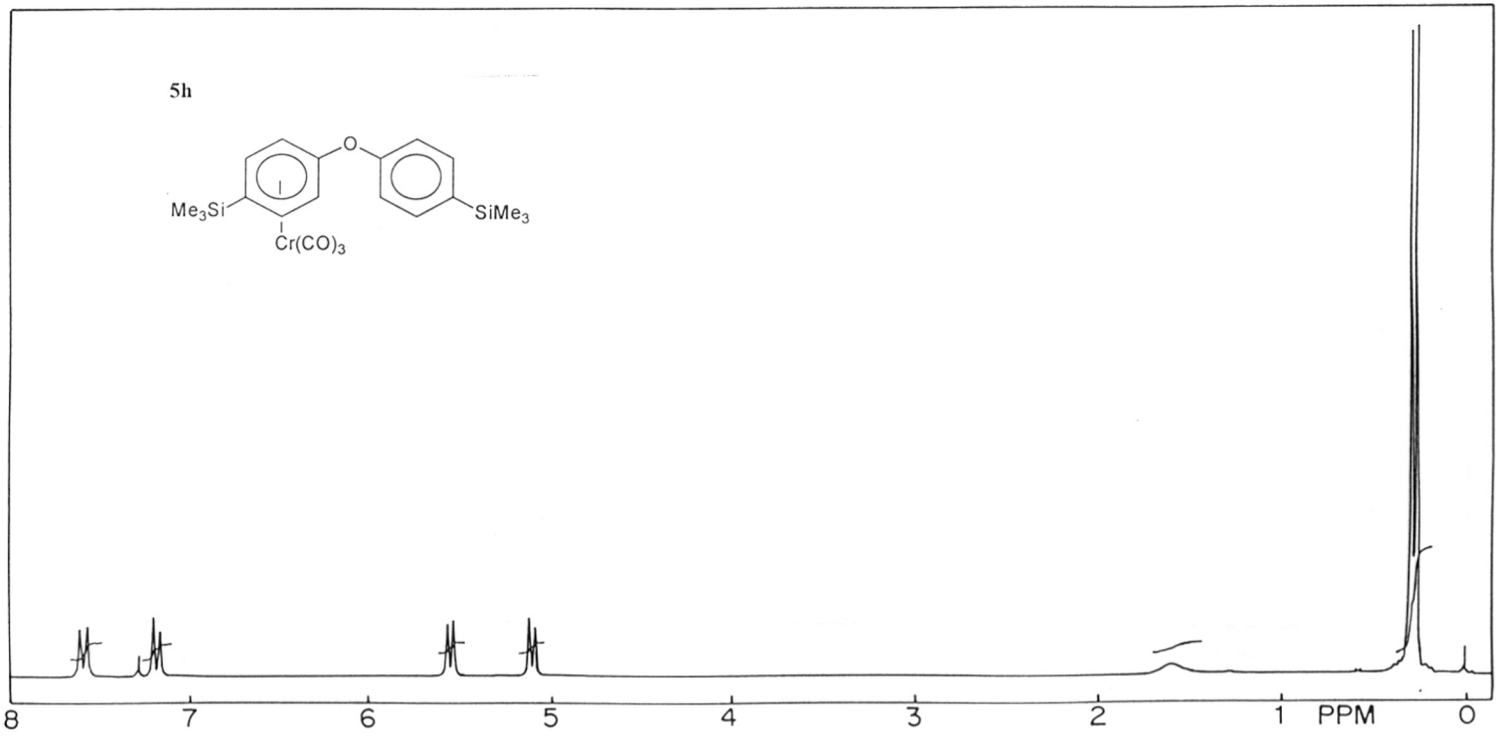

4c
O
SiMe3
Cr(CO)3
CH3
240
220
200
180
160
140
120
100
80
60
40
20
0
PPM

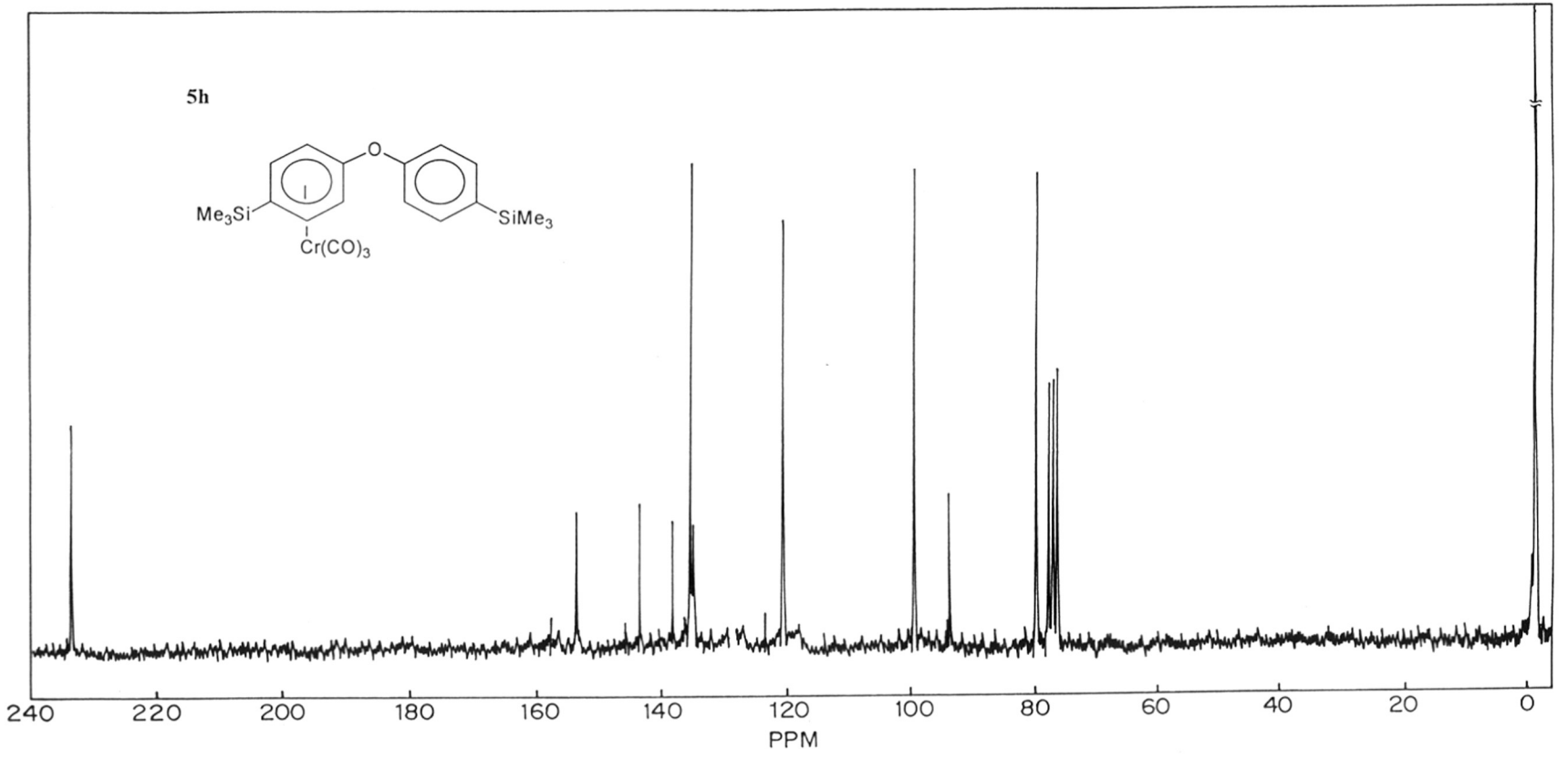

5g
OMe
SiMe3
OMe
Cr(CO)3
8
7
6
5
4
3
2
1
PPM
0

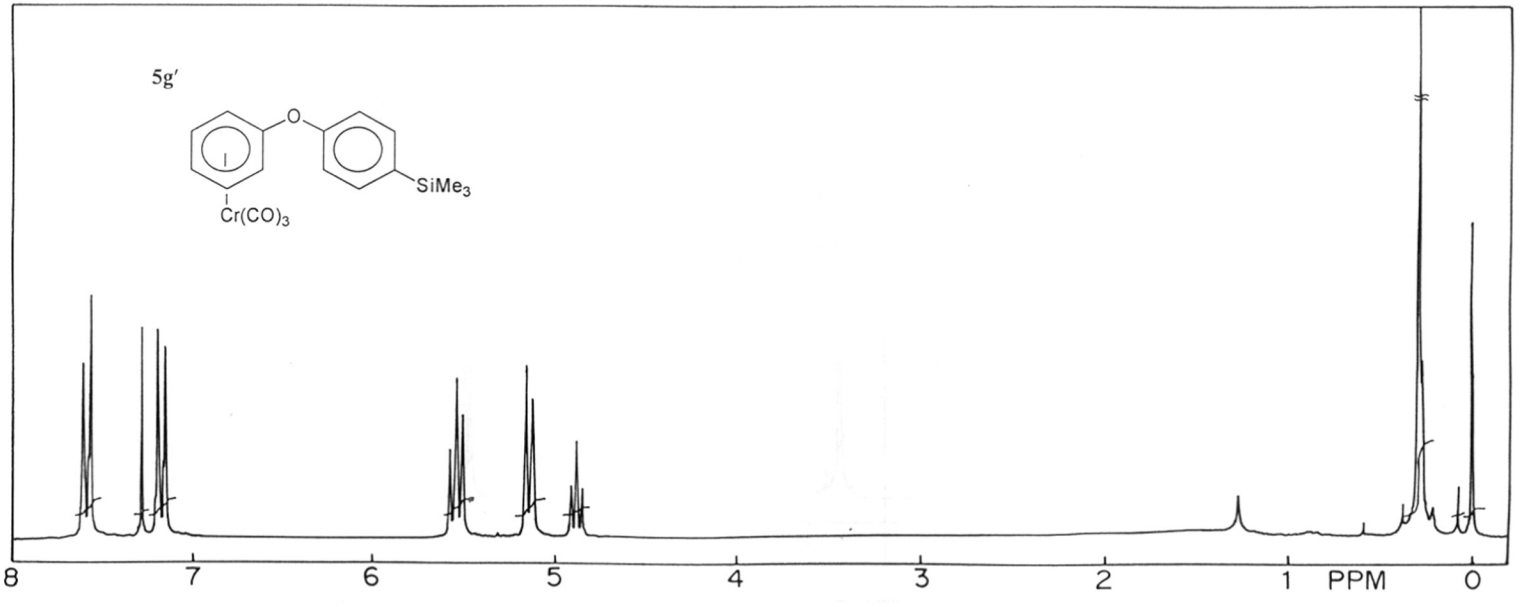

5g
OMe
SiMe3
OMe
Cr(CO)3
240
220
200
180
160
140
120
100
80
60
40
20
0
PPM


4-Trimethylsilylphenyl ether
O
Me3Si
SiMe3
8
7
6
5
4
3
2
1
PPM
0


4-Trimethylsilylphenyl ether
O
Me3Si
SiMe3
250
200
150
100
50
0
PPM


5h
O
Me3Si
SiMe3
Cr(CO)3
8
7
6
5
4
3
2
1
PPM
0


5h
Me3Si
SiMe3
Cr(CO)3
O
240
220
200
180
160
140
120
100
80
60
40
20
0
PPM


5g′
O
SiMe3
Cr(CO)3
8
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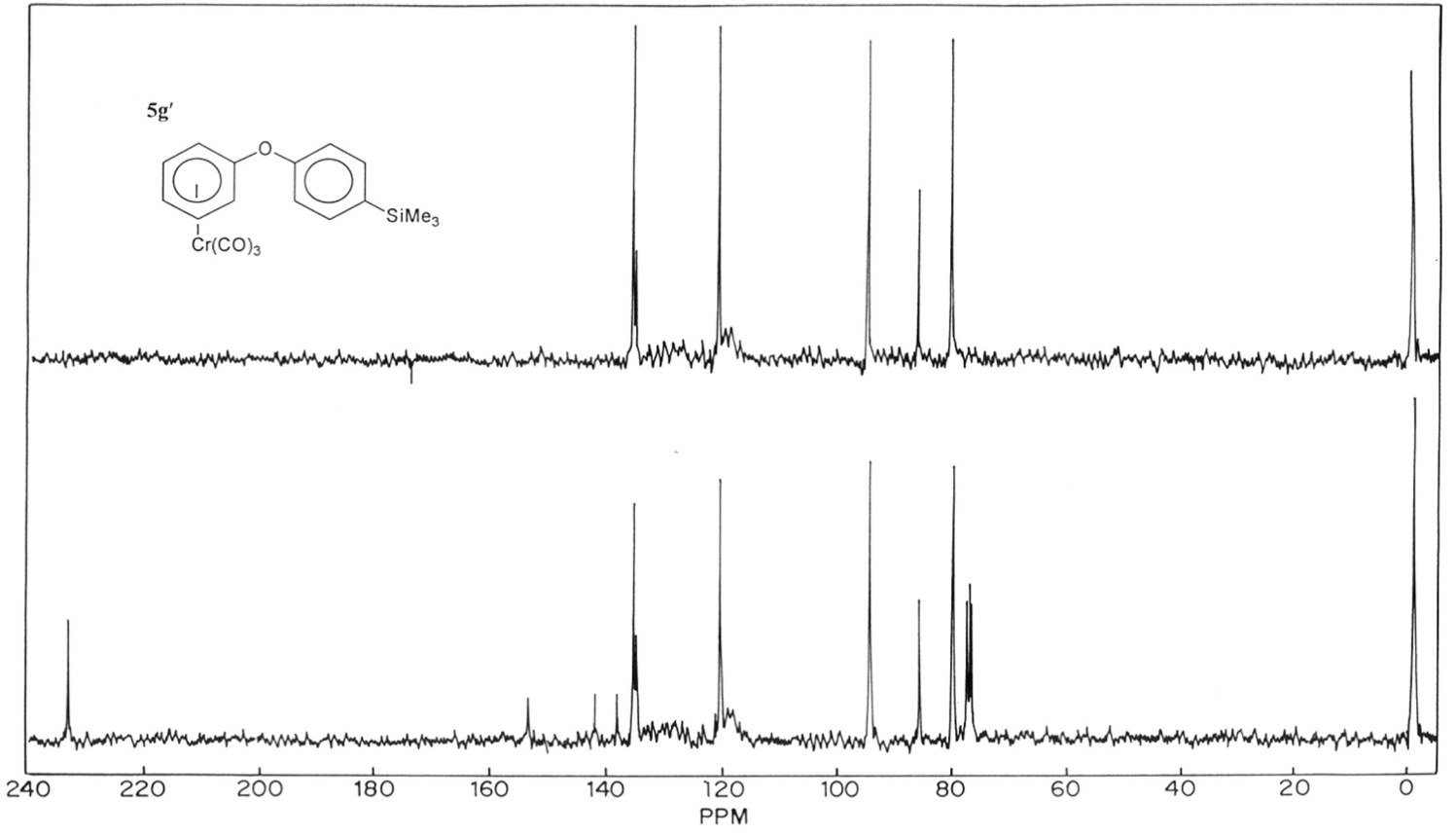
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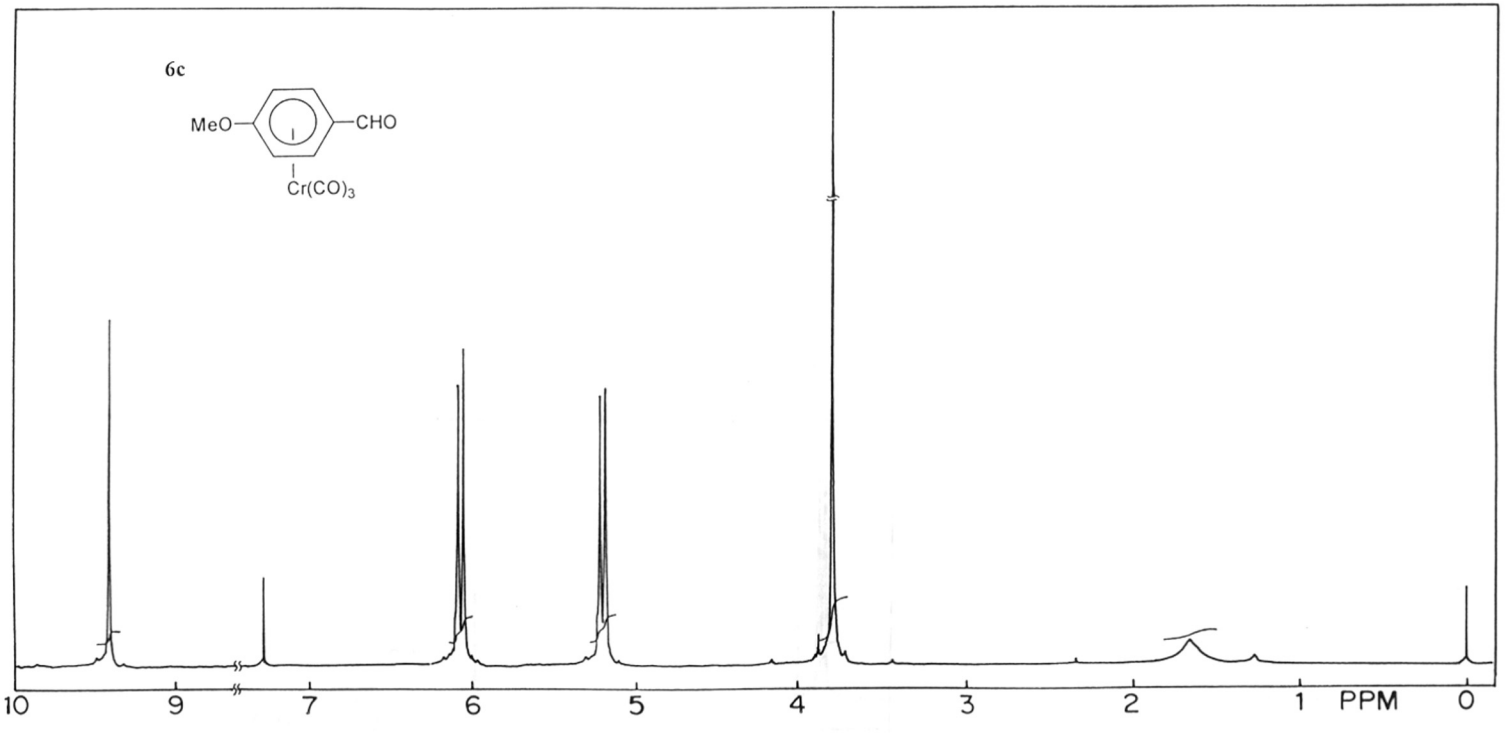
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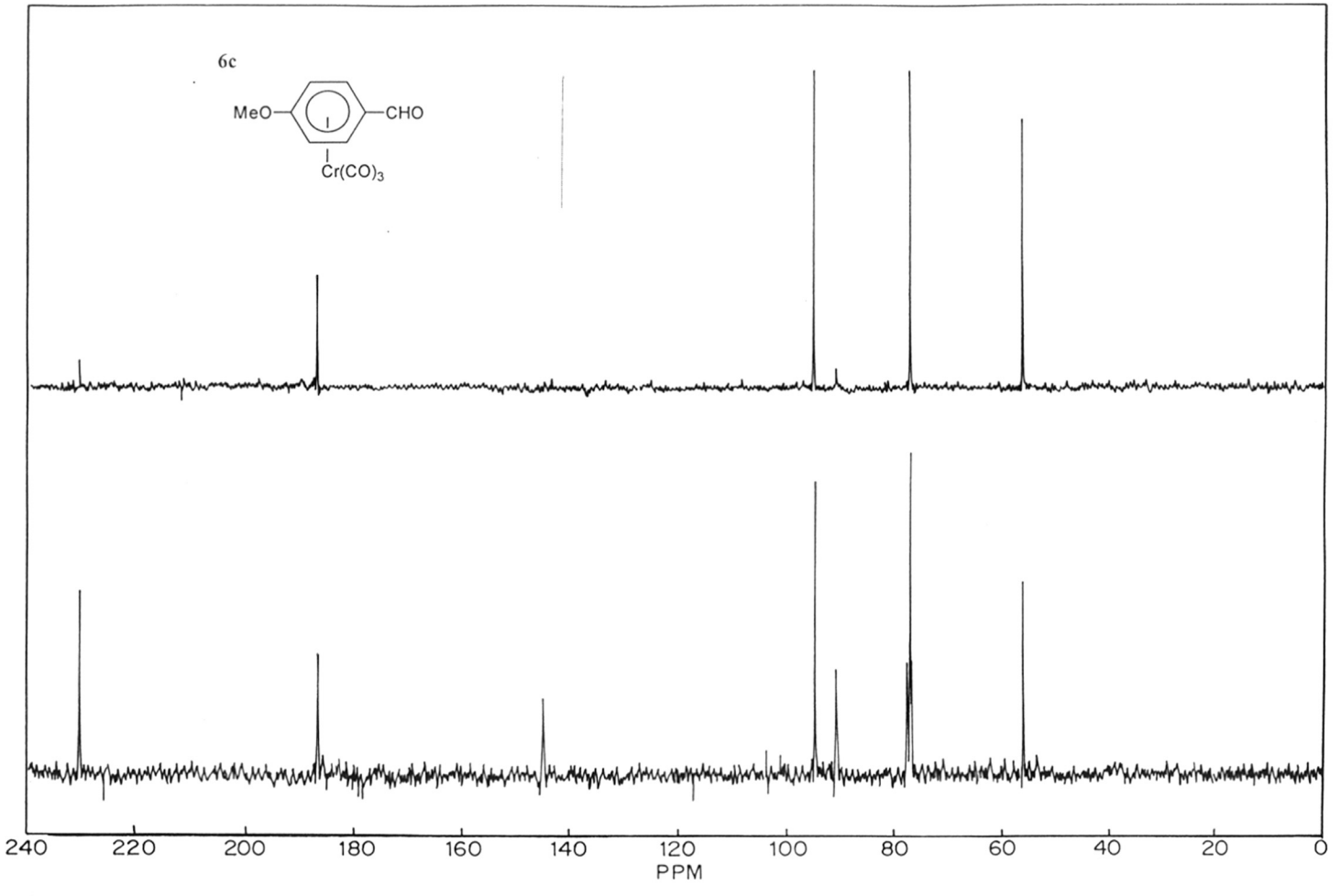
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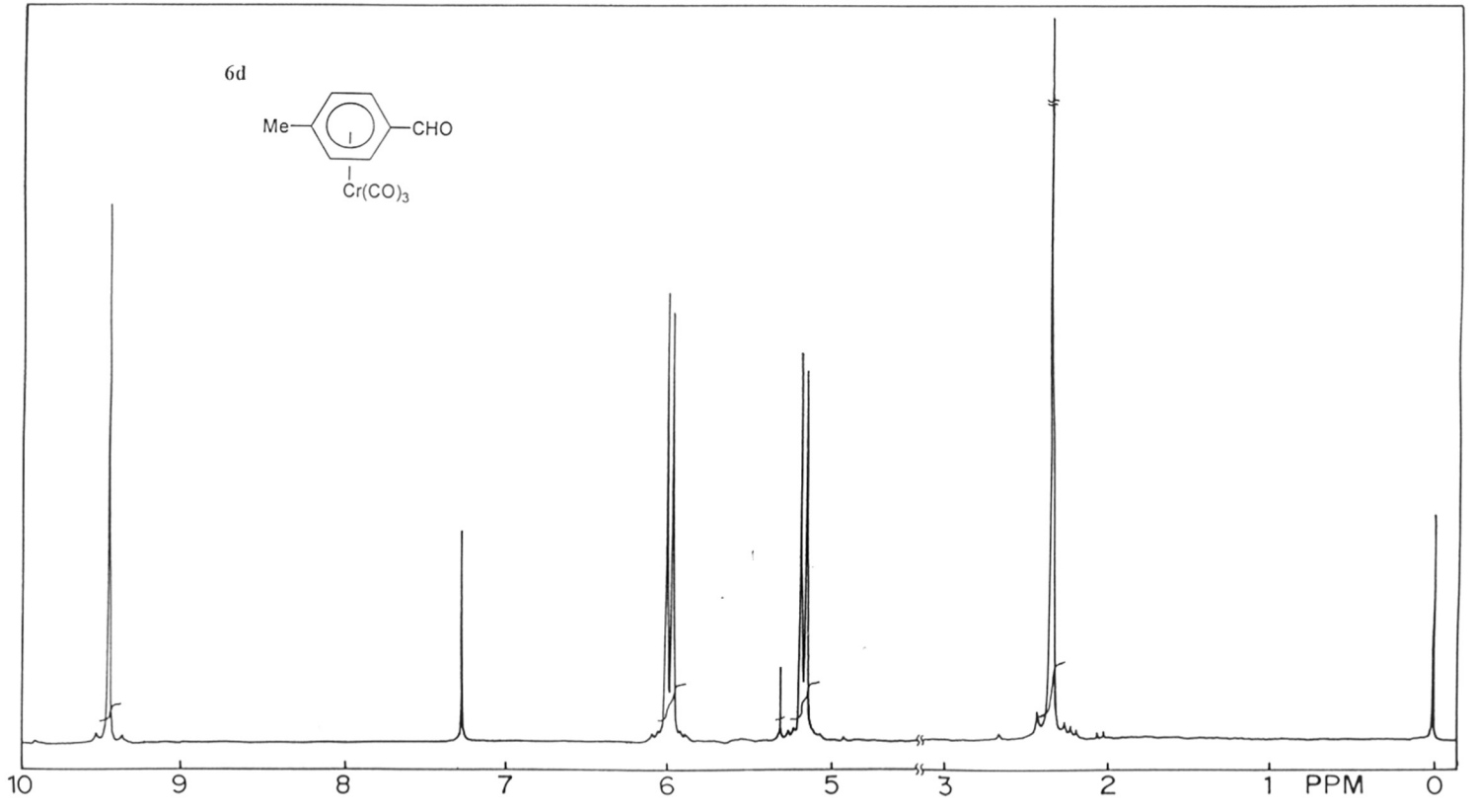
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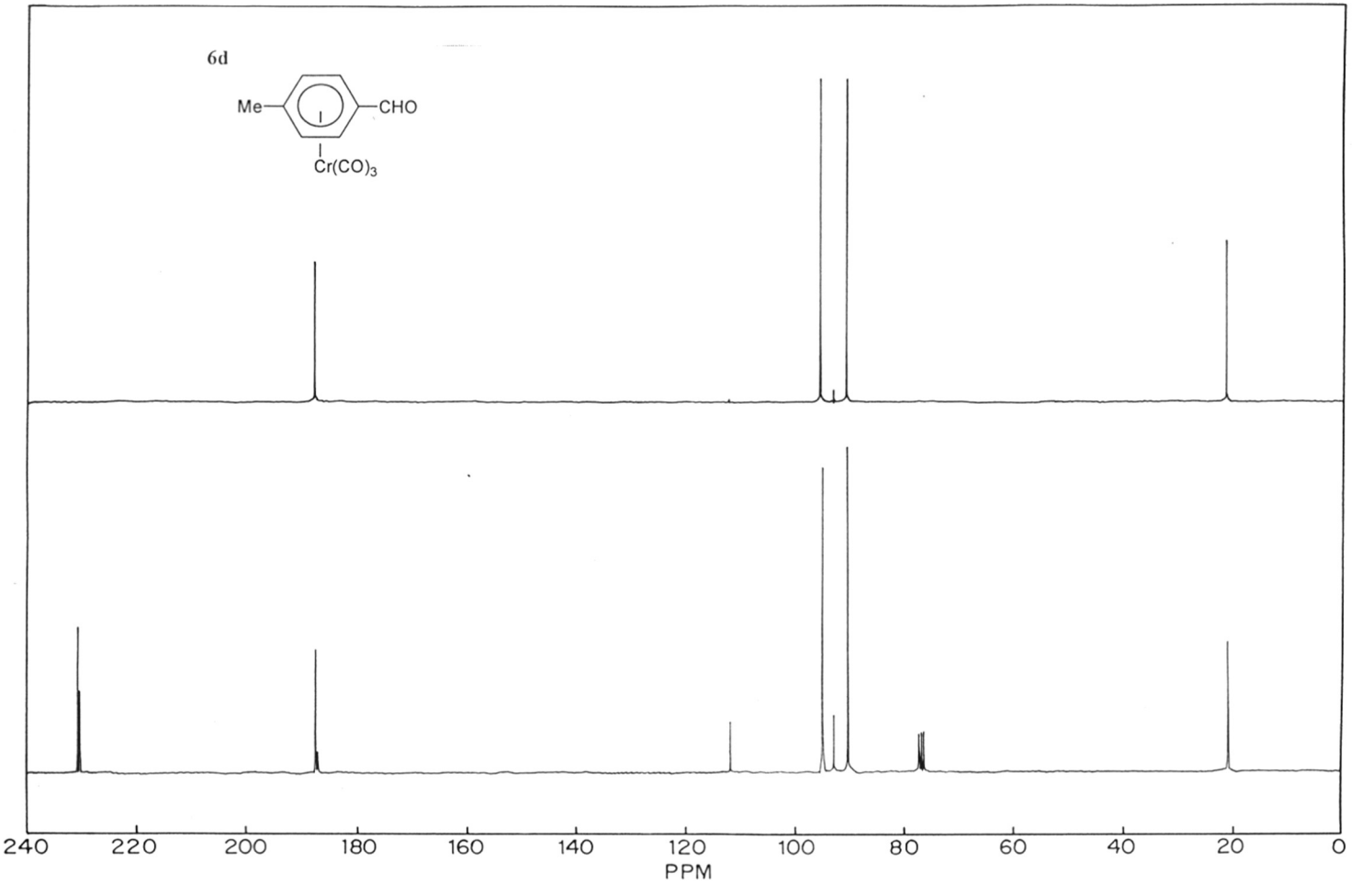
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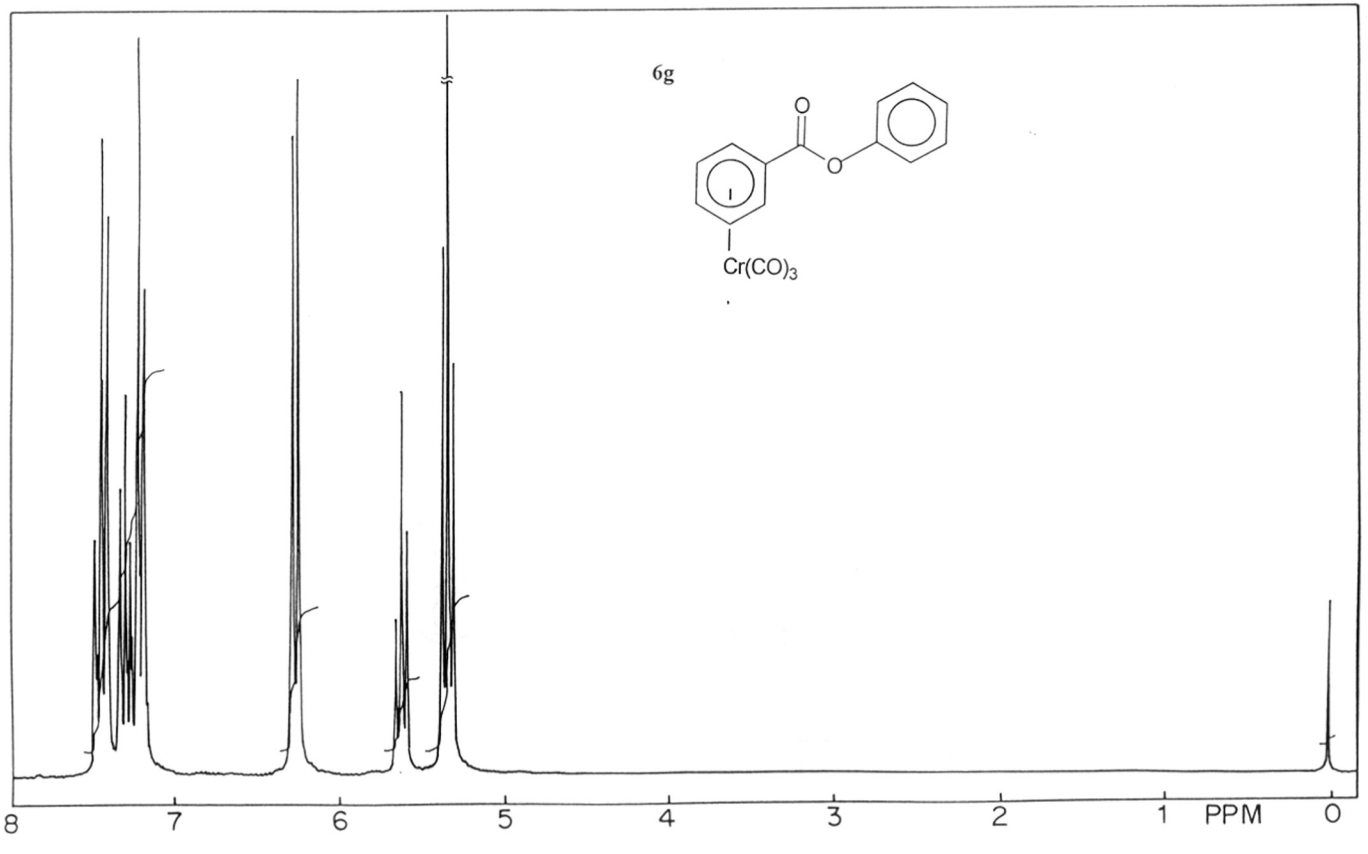
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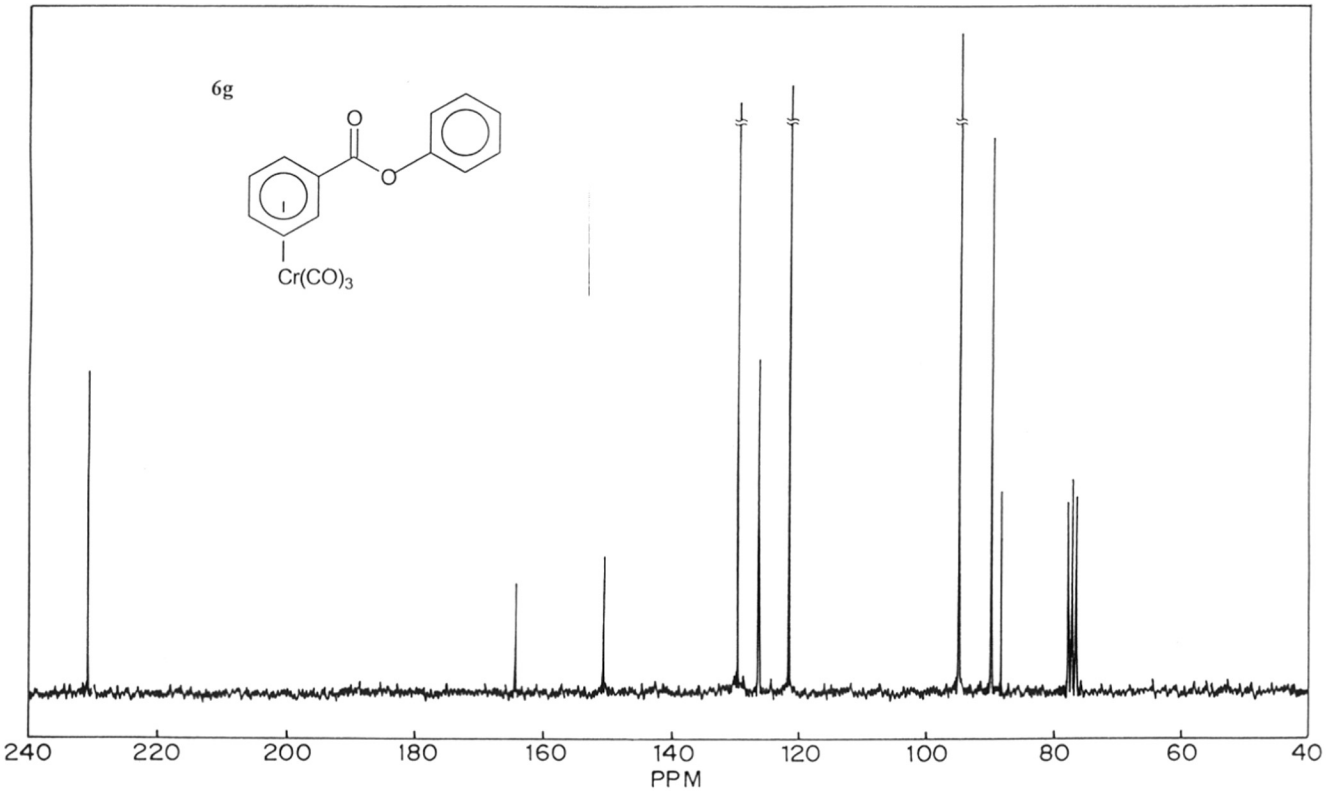
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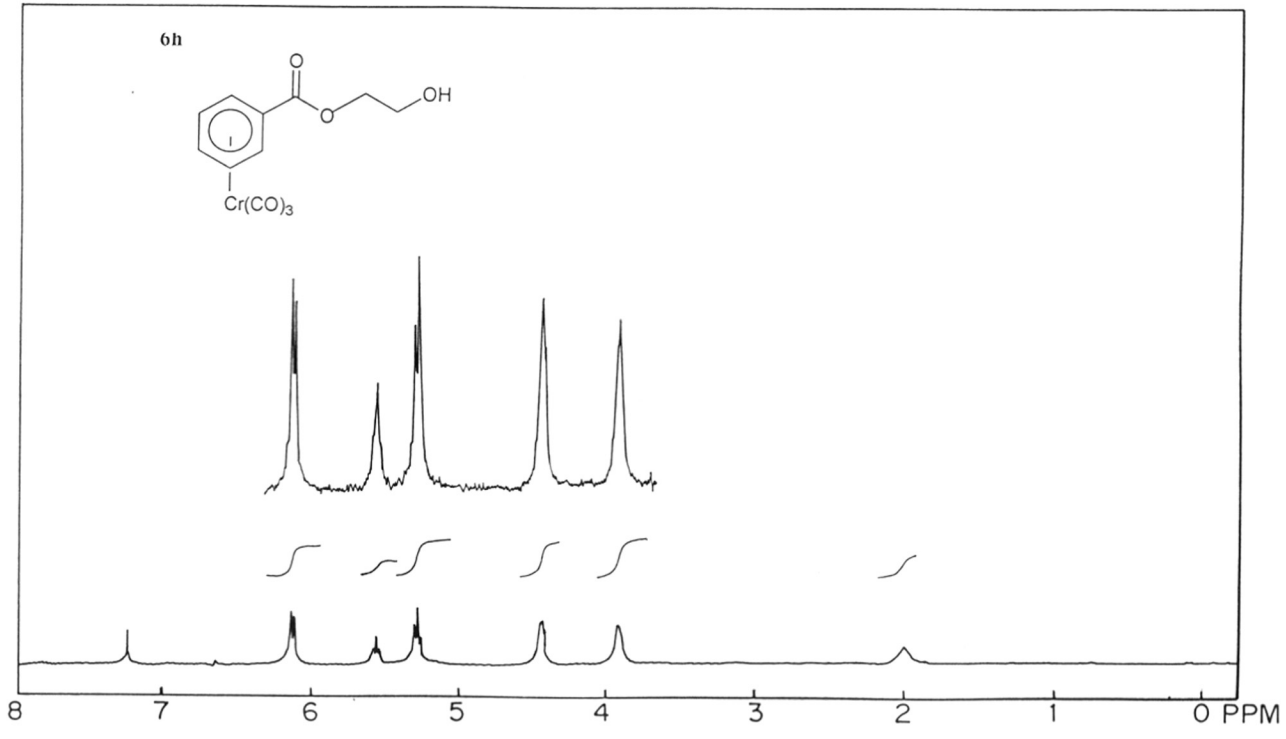
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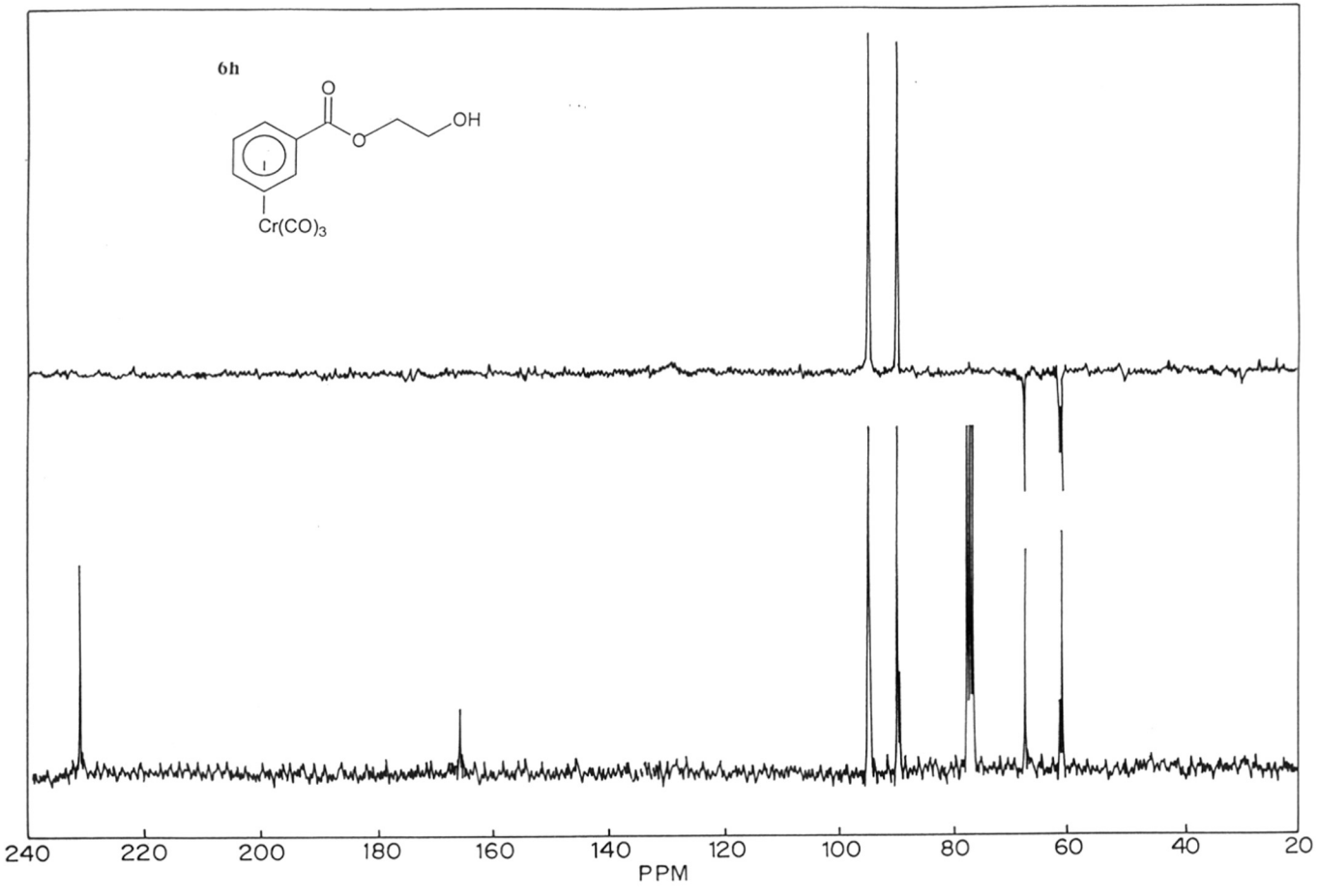
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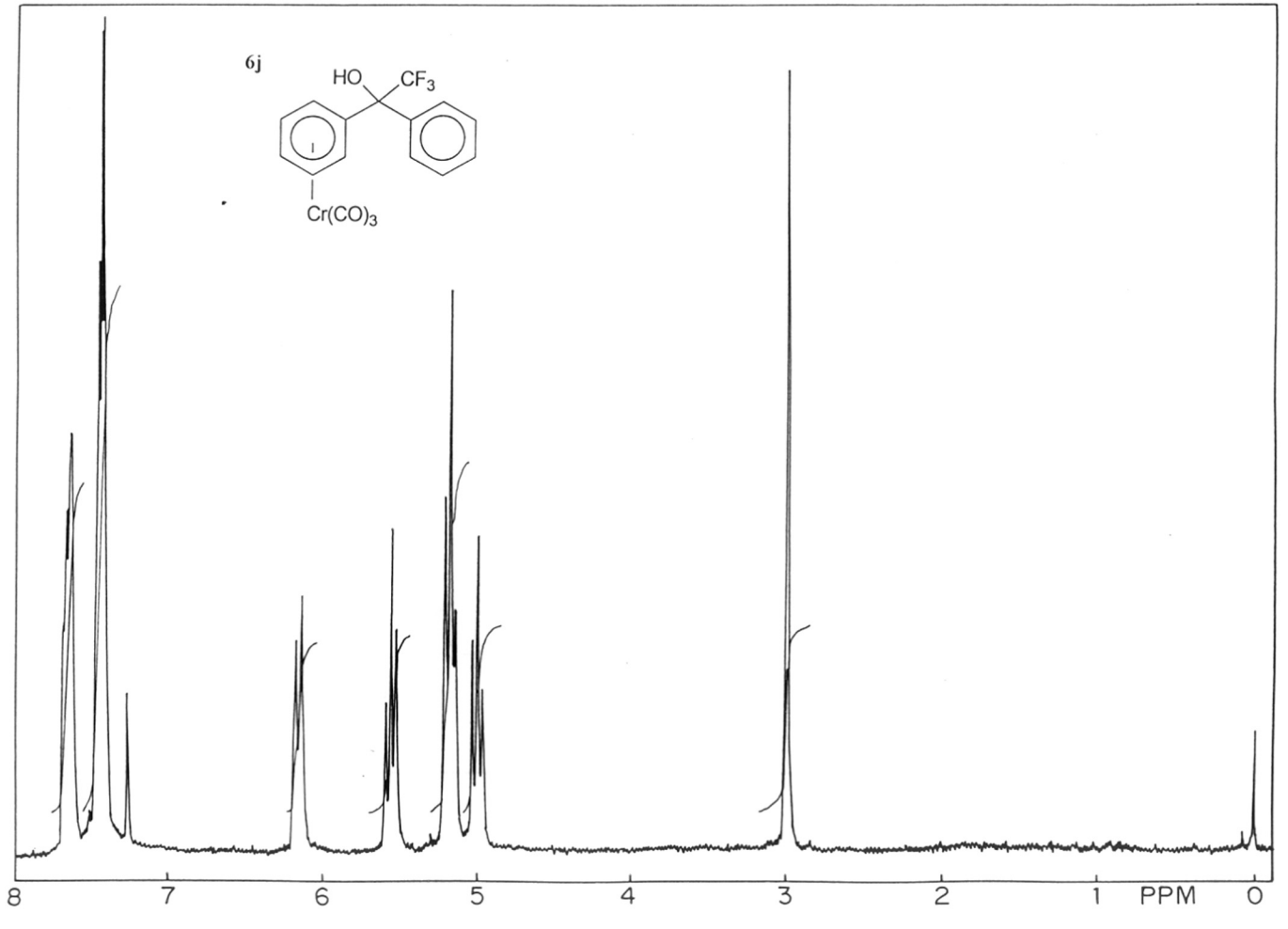
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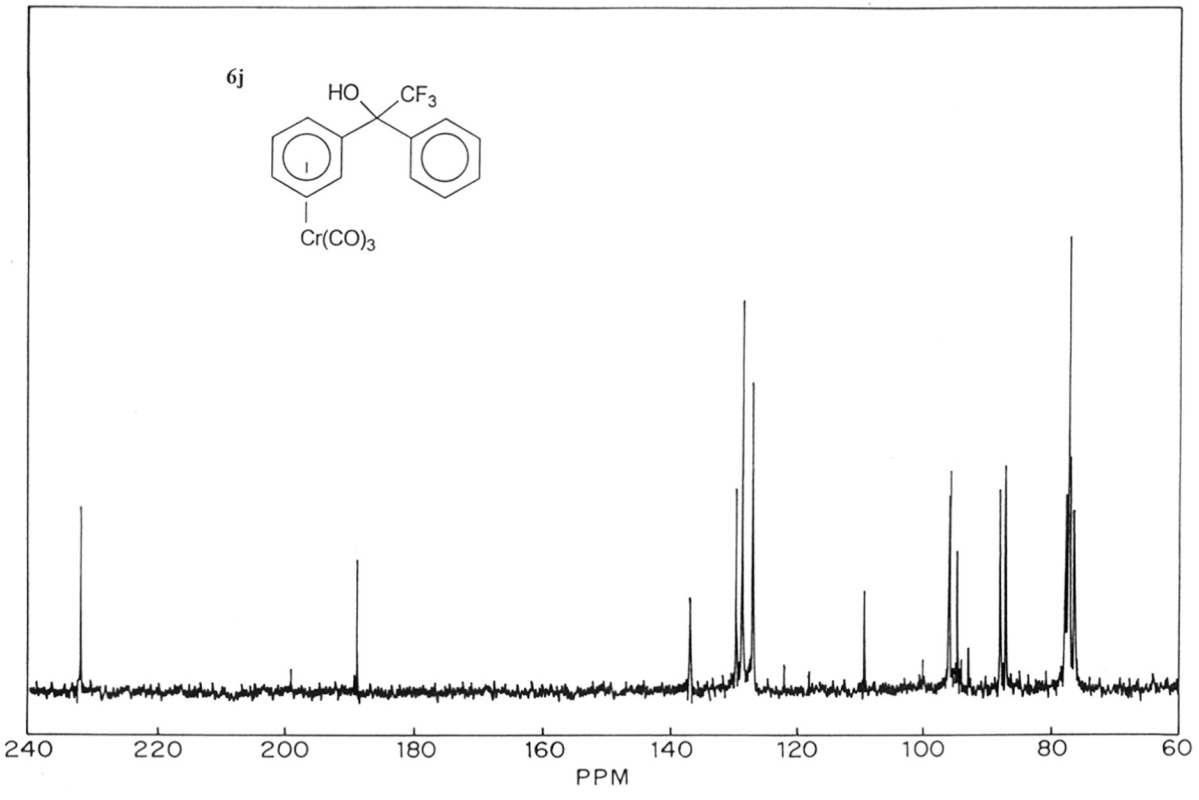
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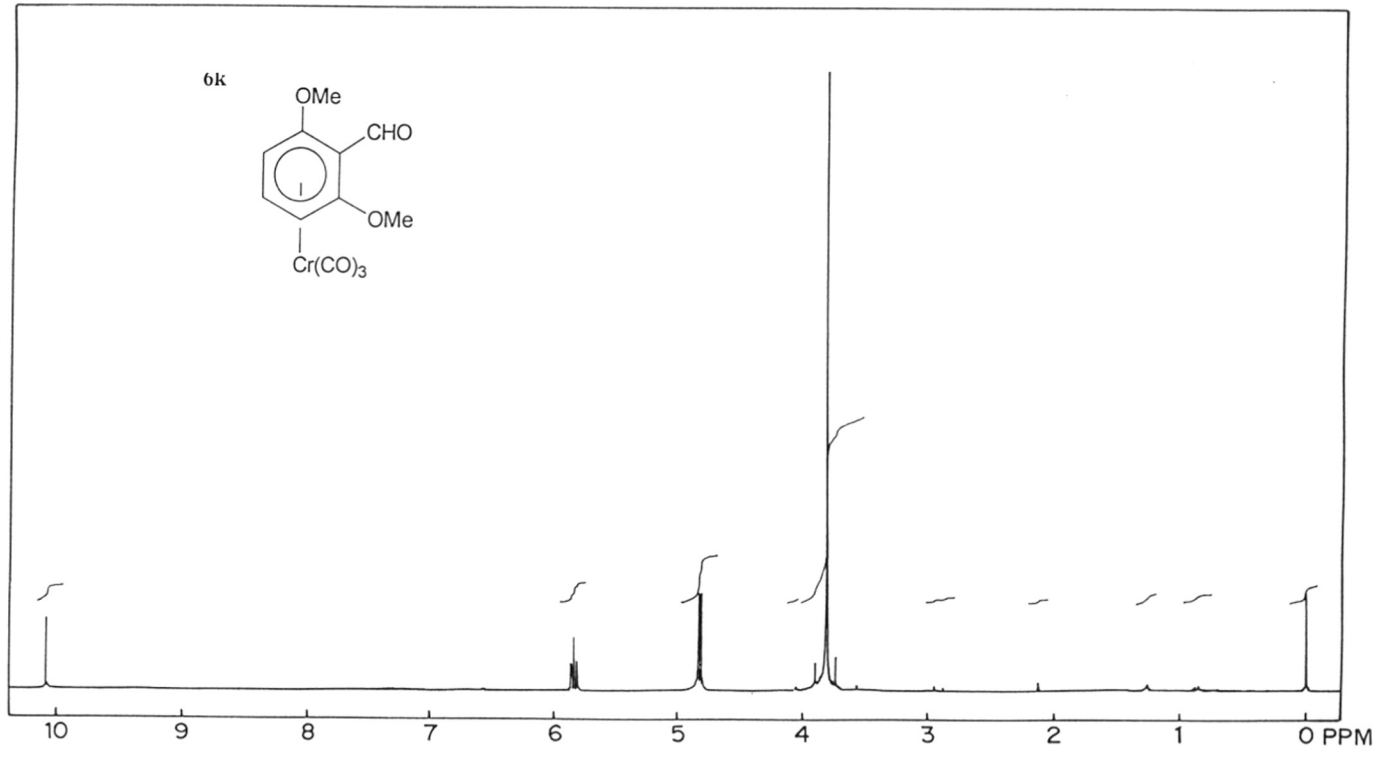
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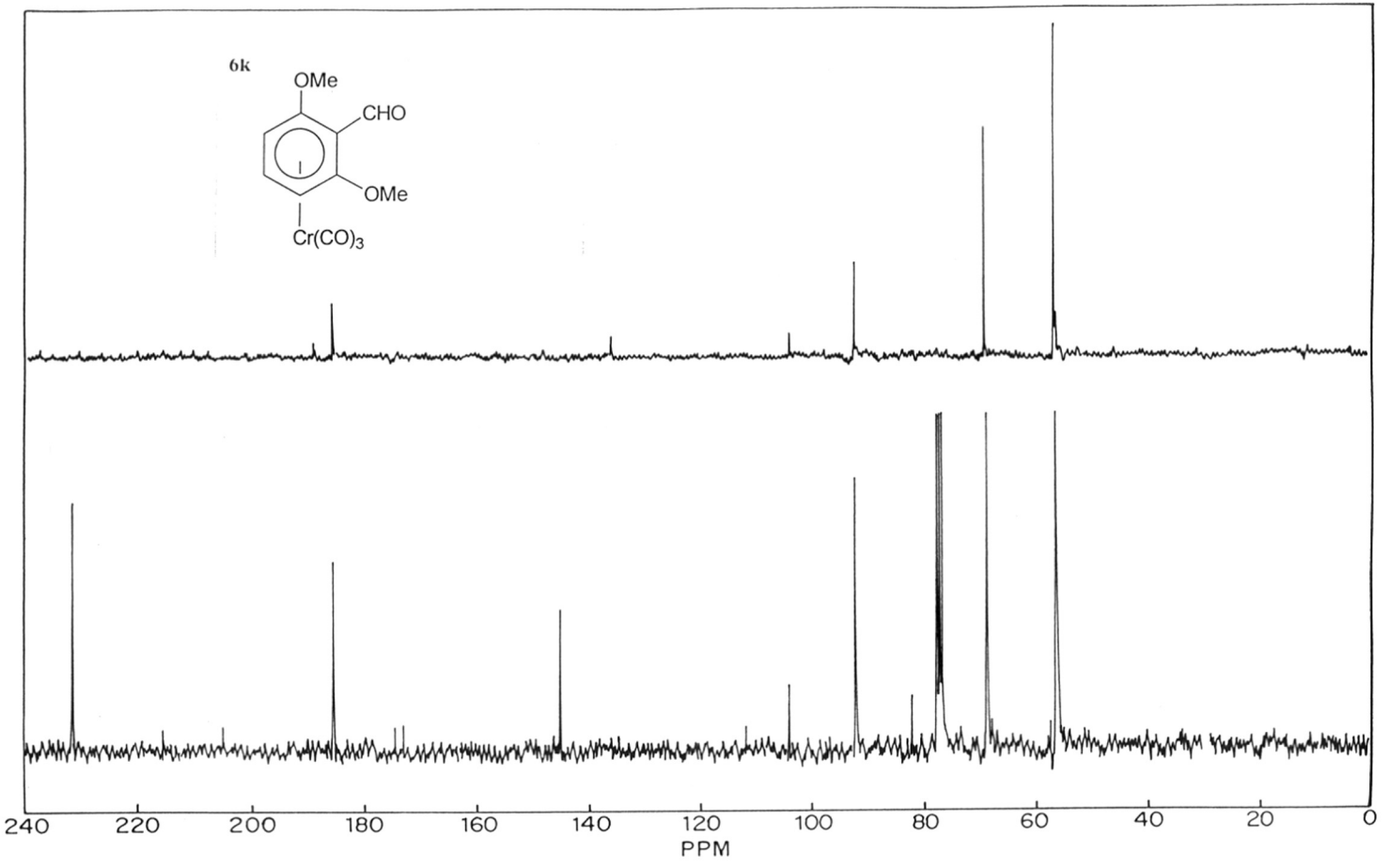
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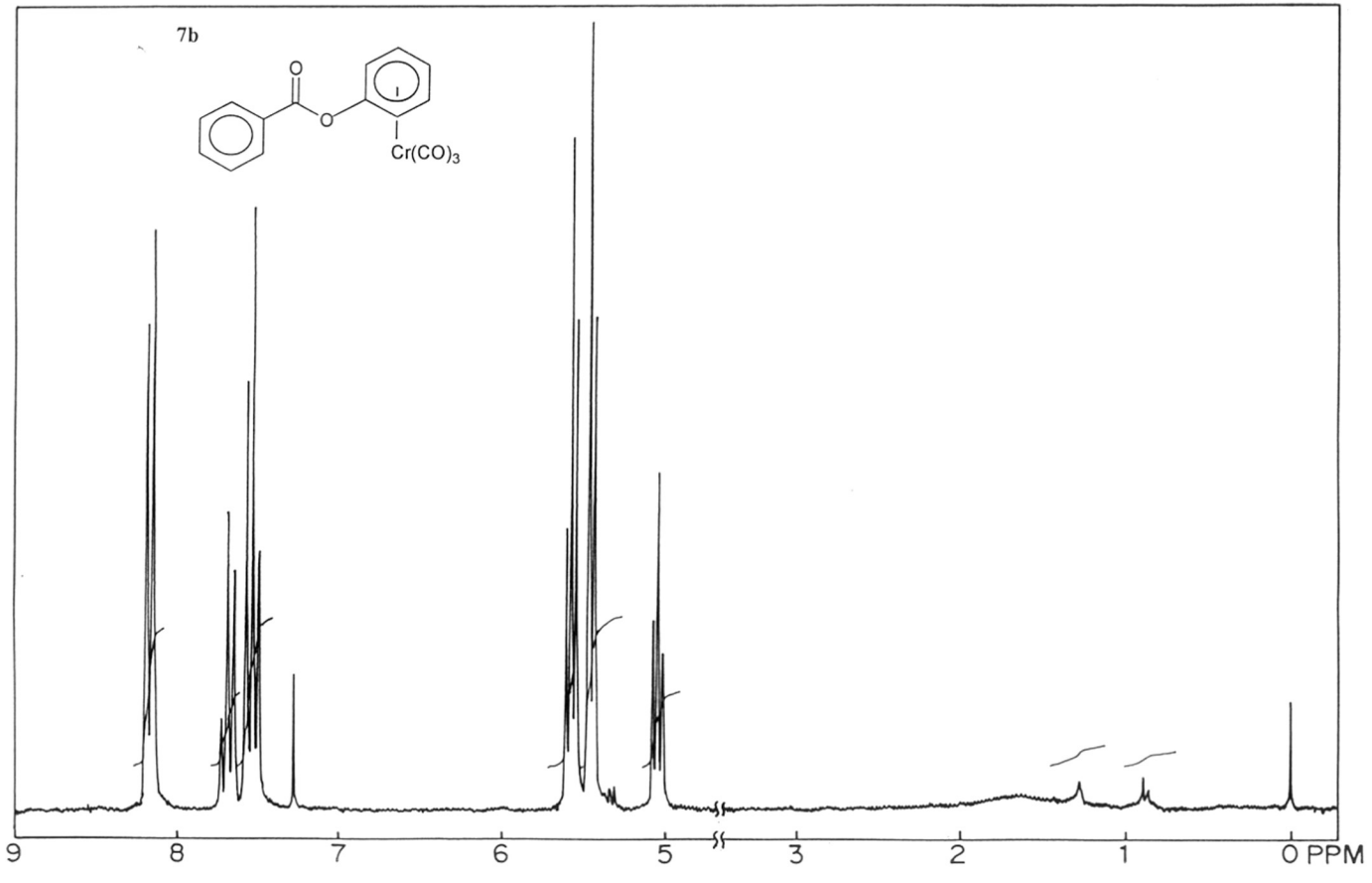
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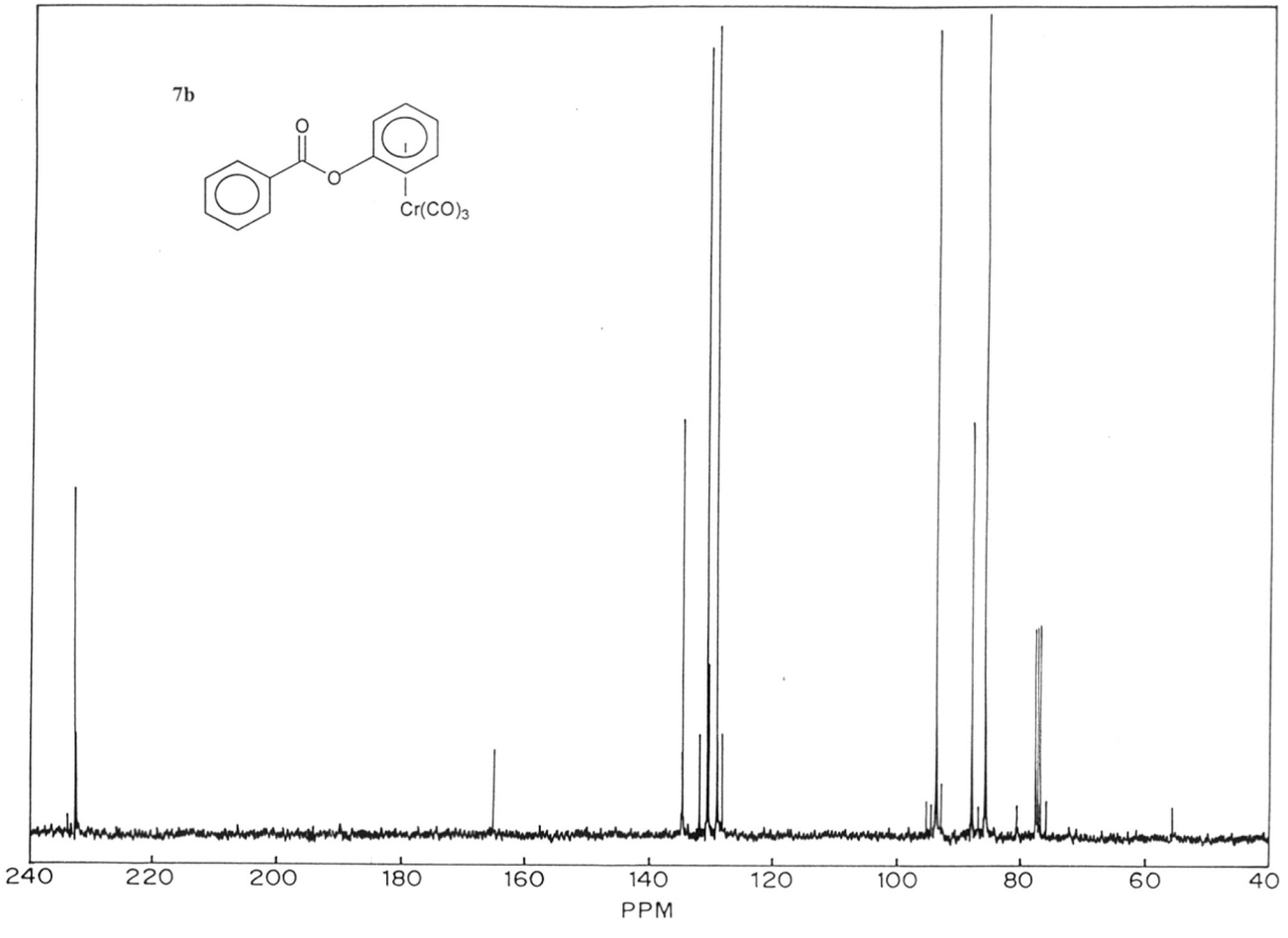
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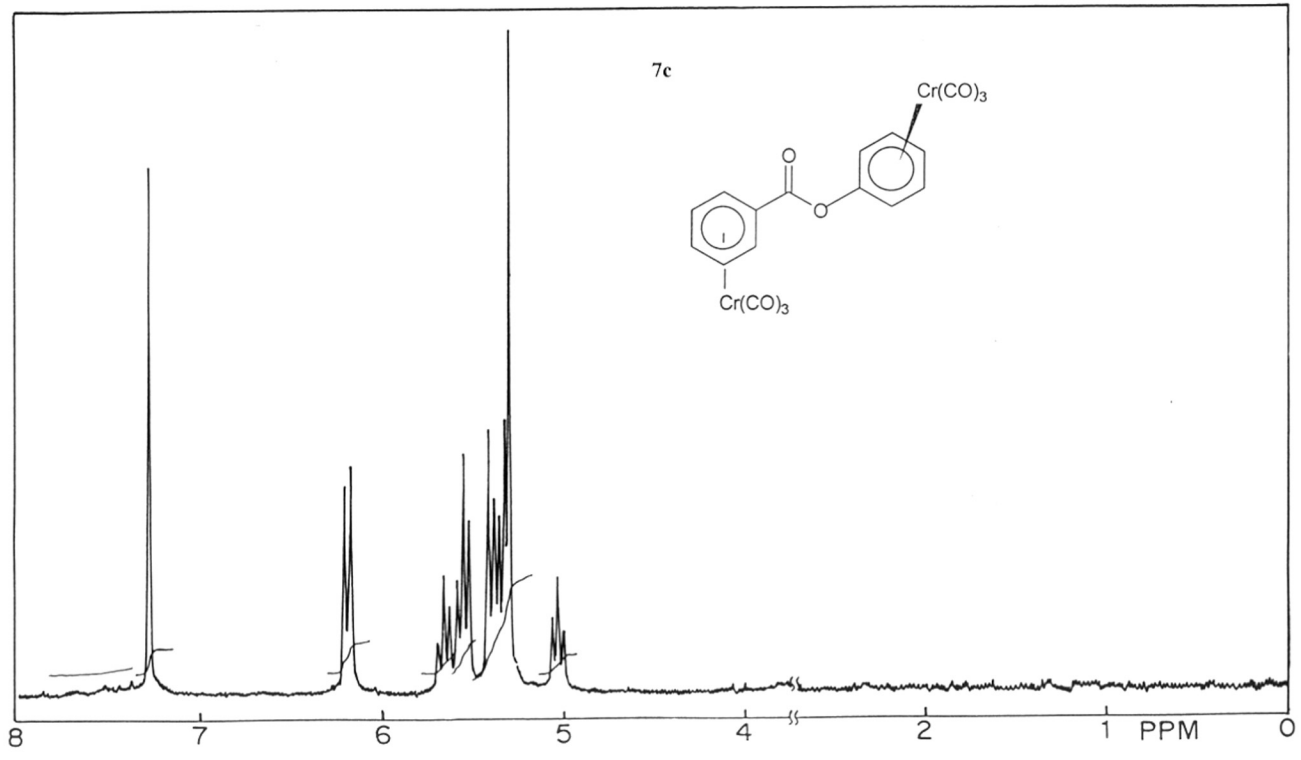
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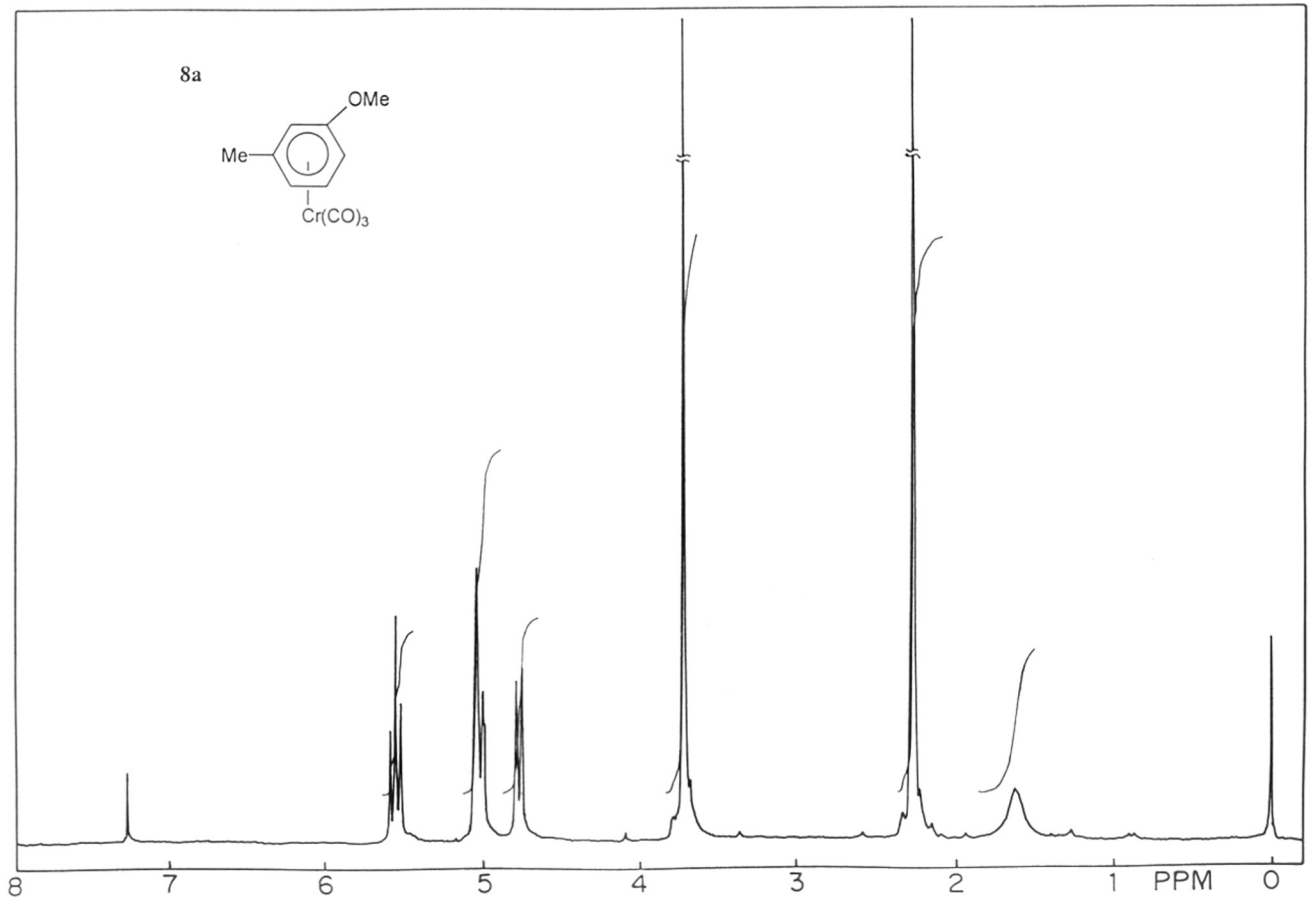
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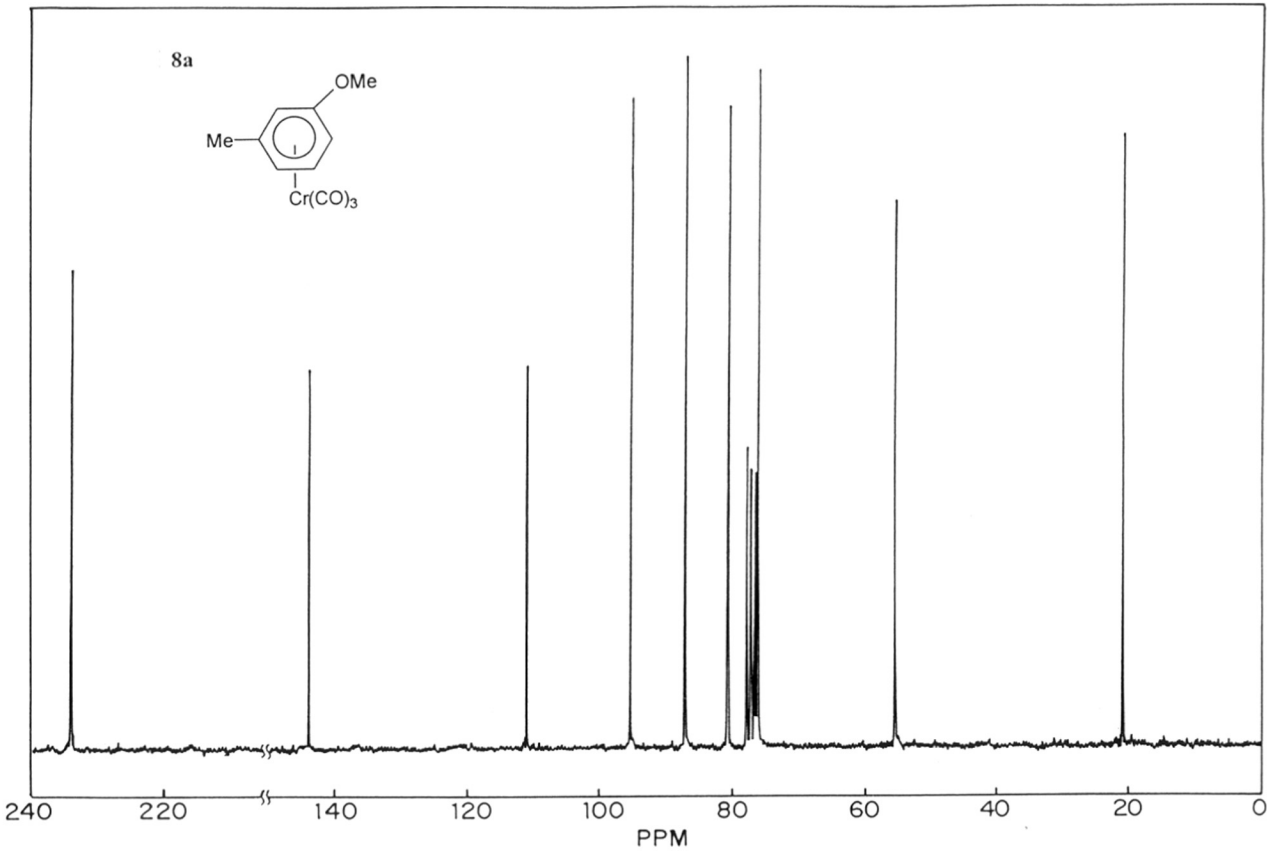
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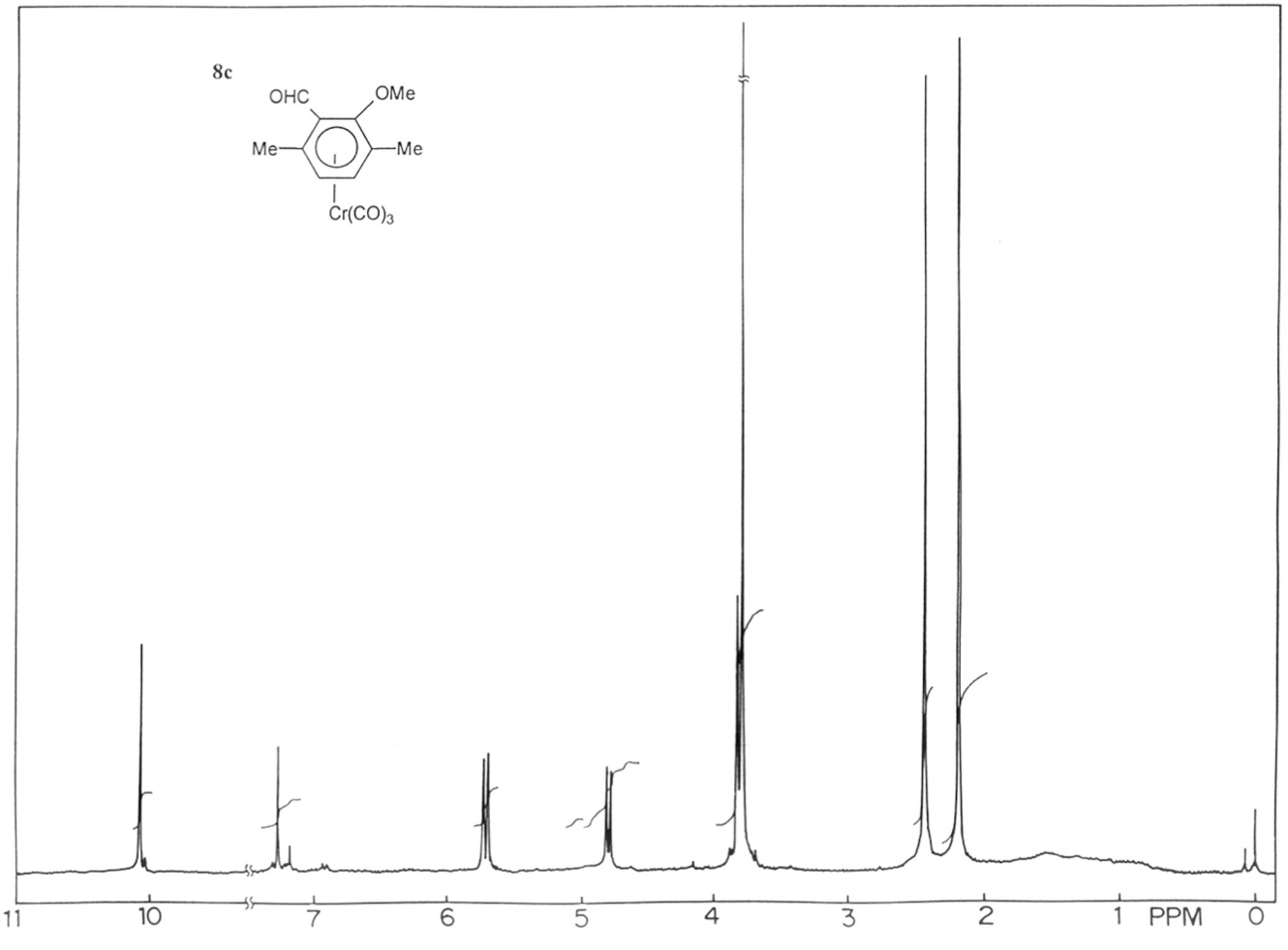
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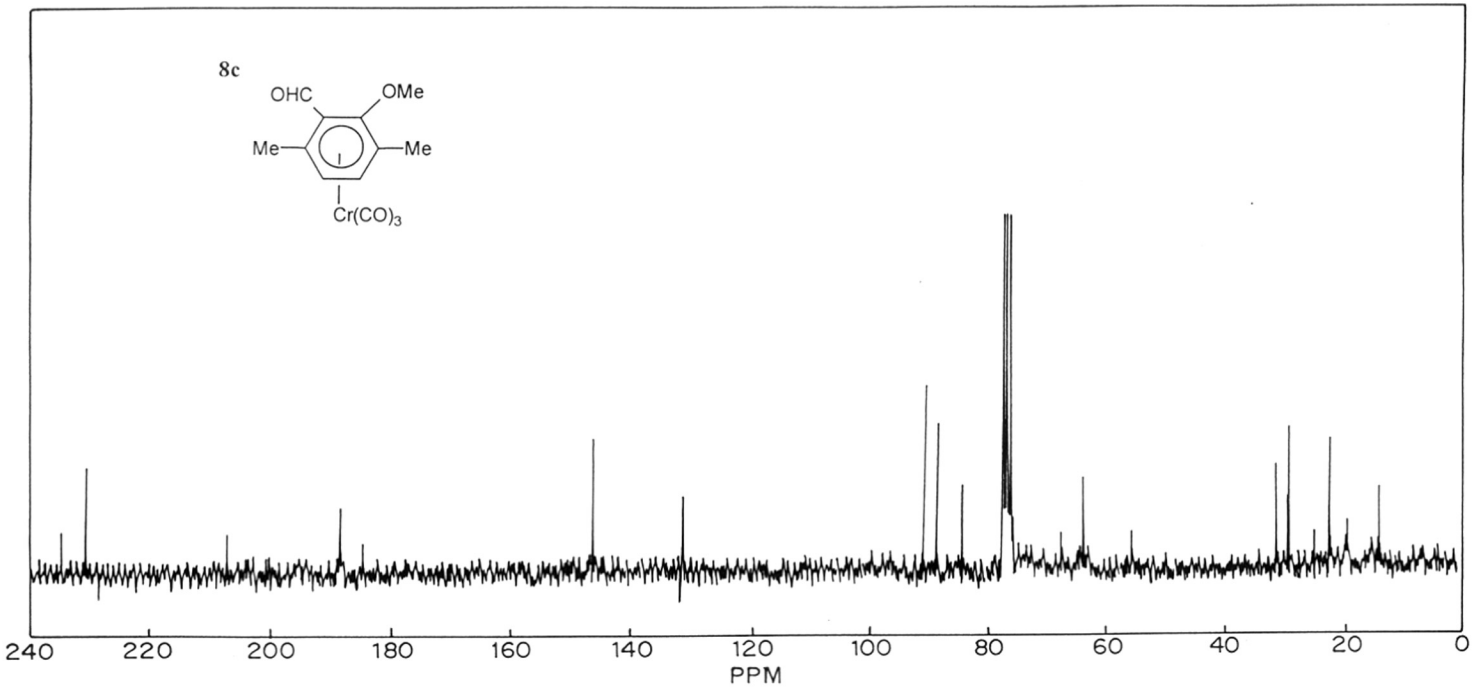
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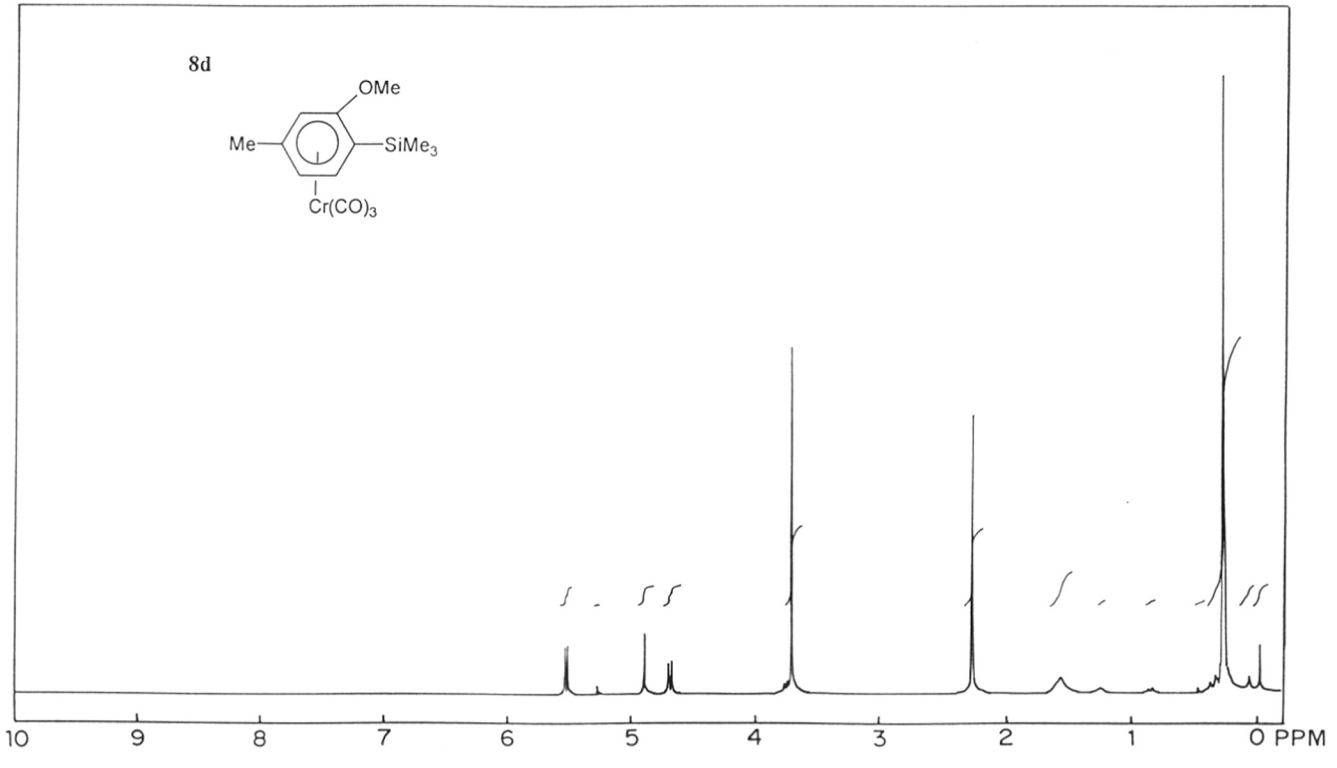
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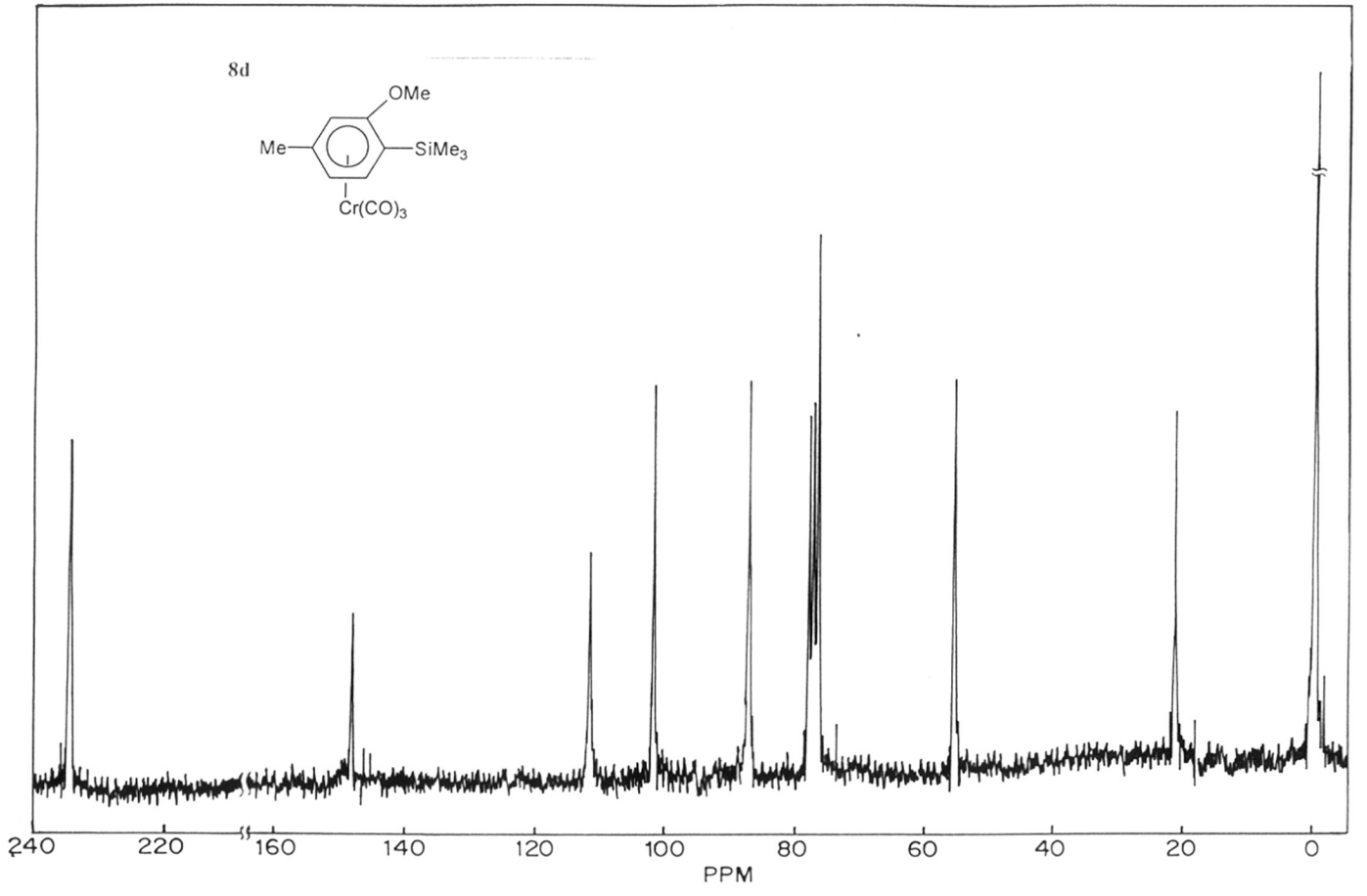
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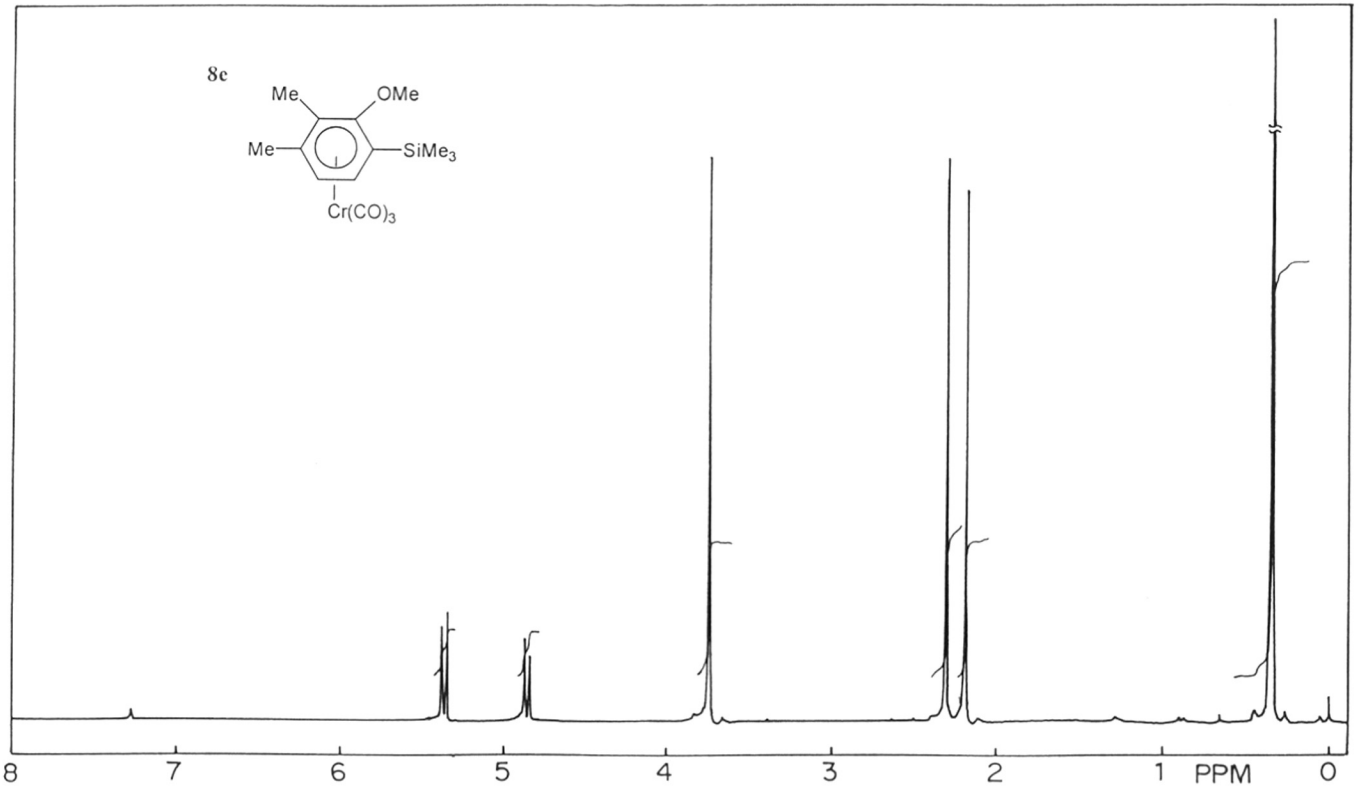
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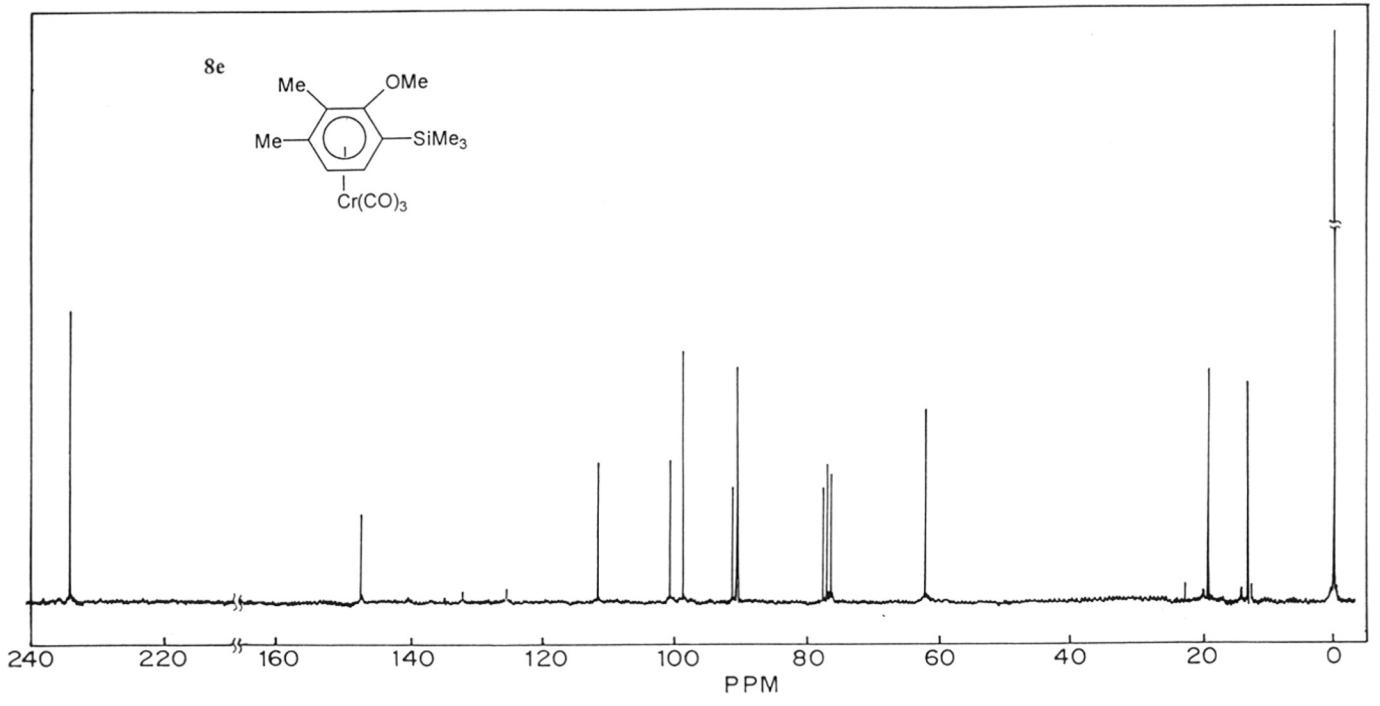
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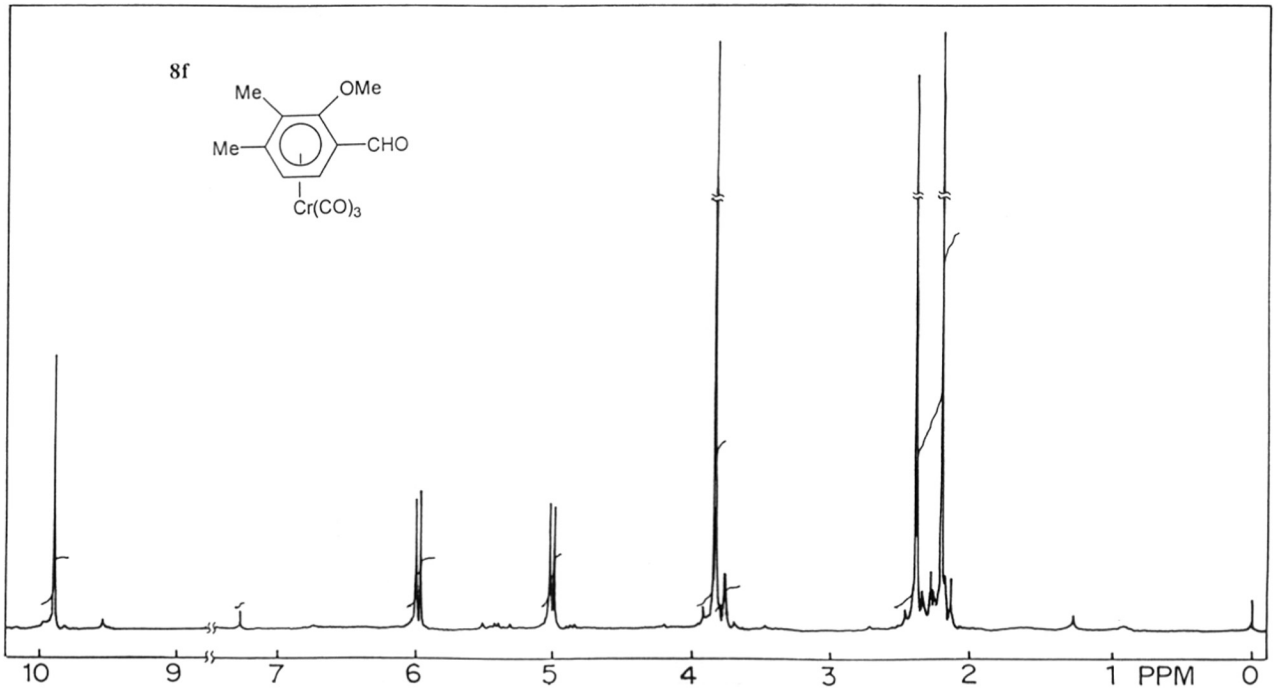
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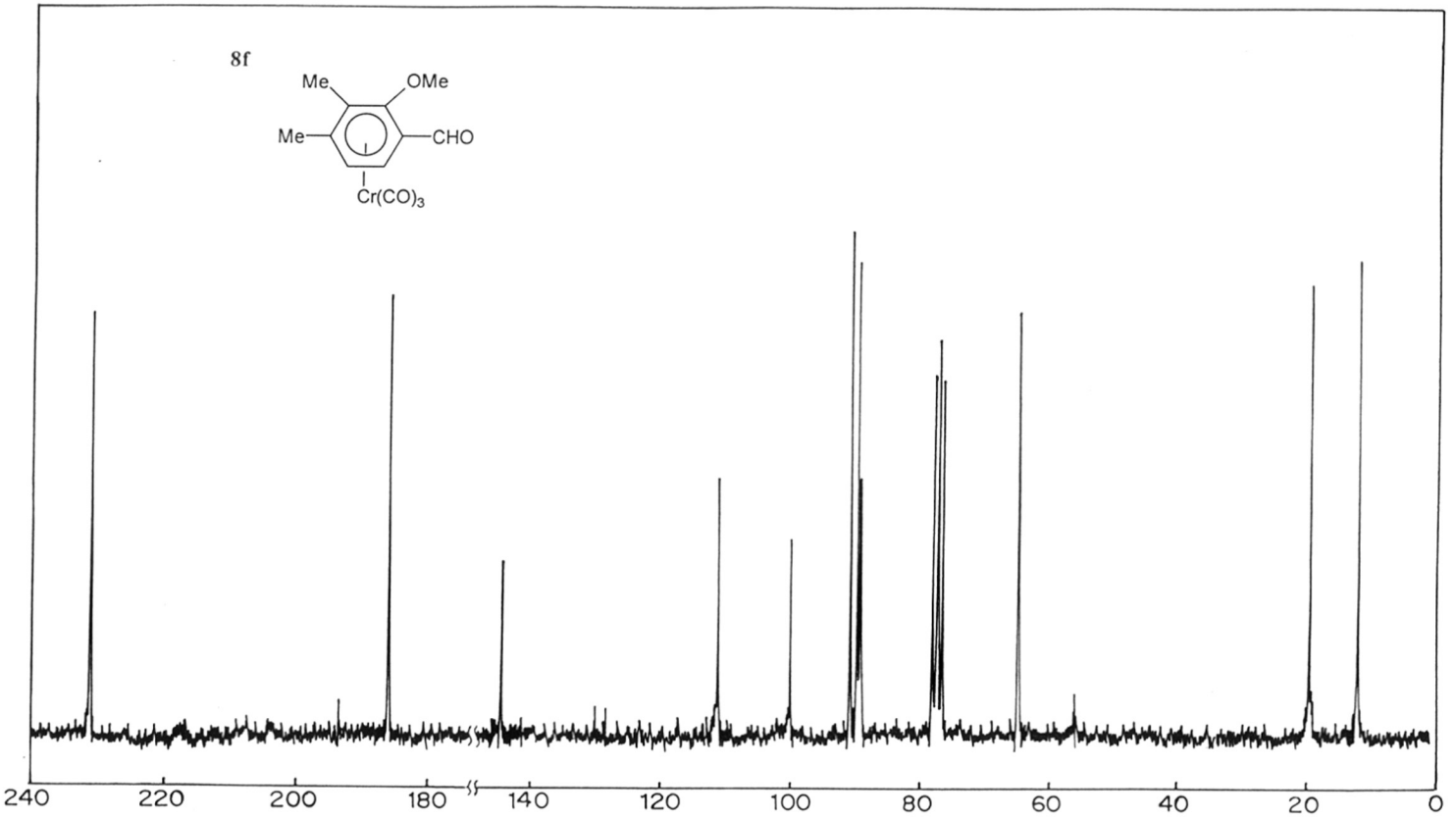
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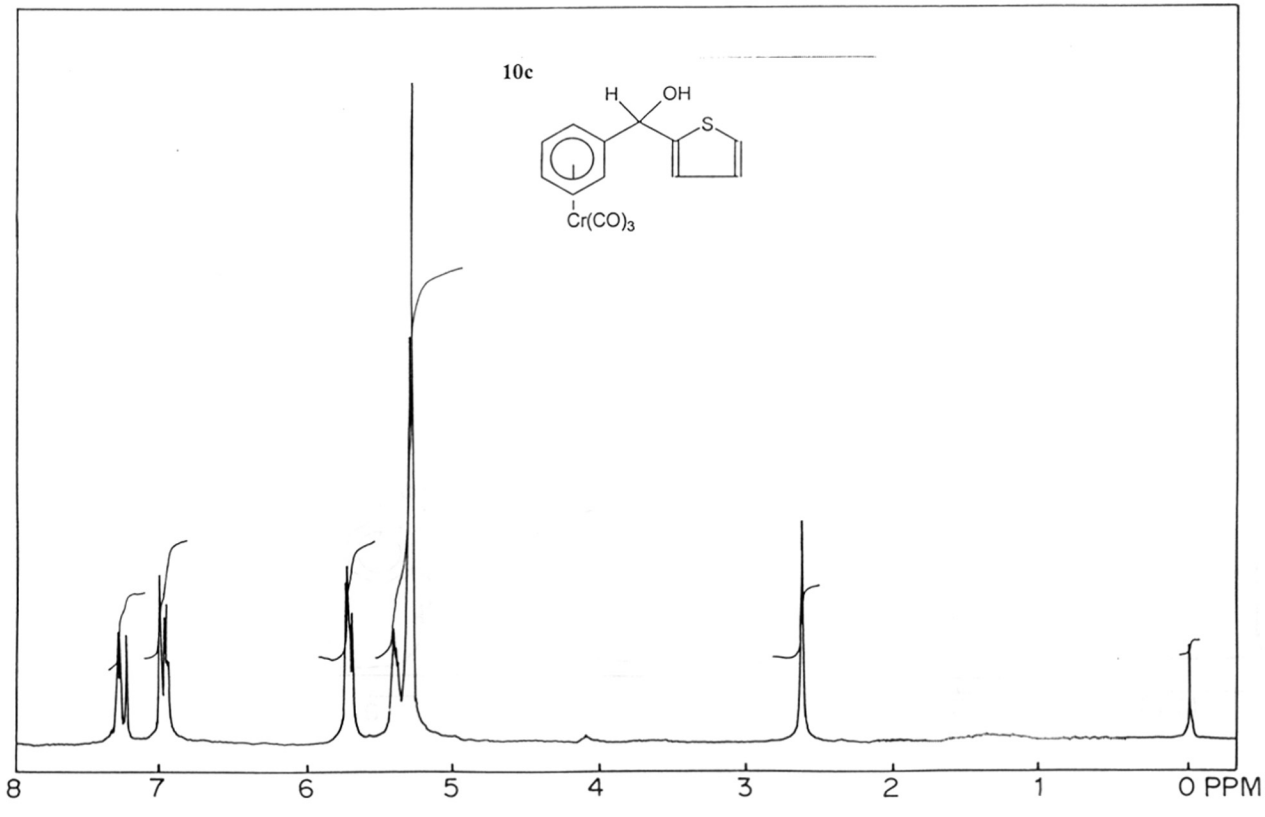
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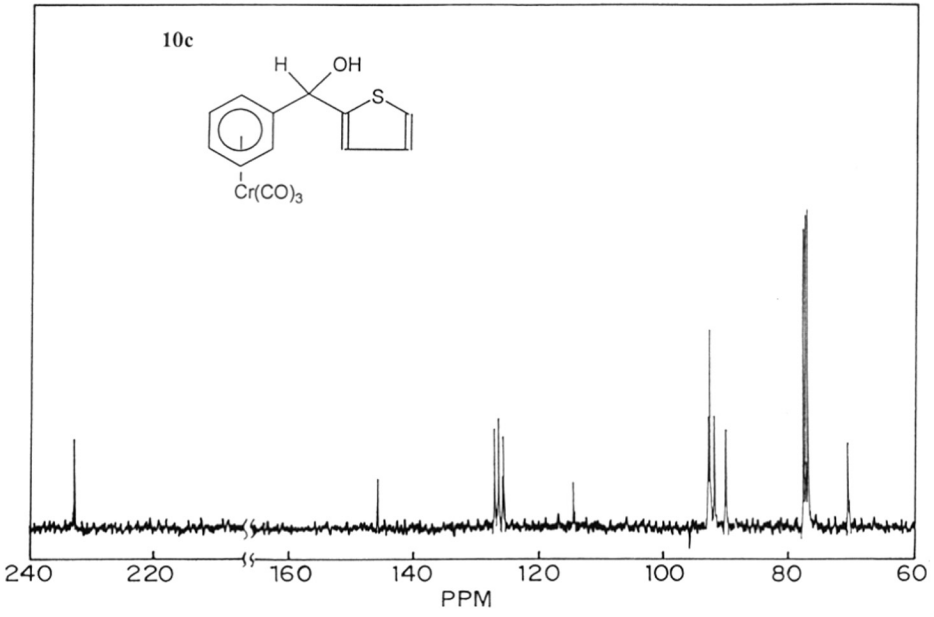
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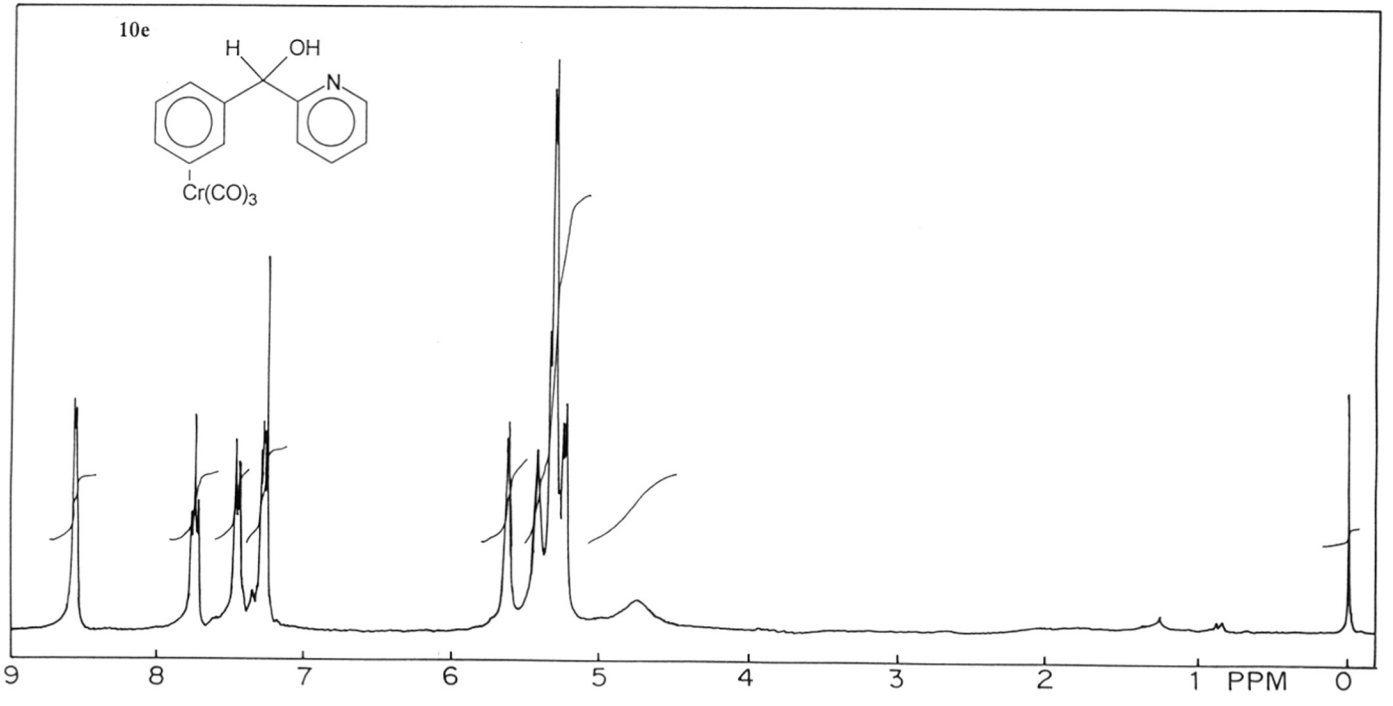
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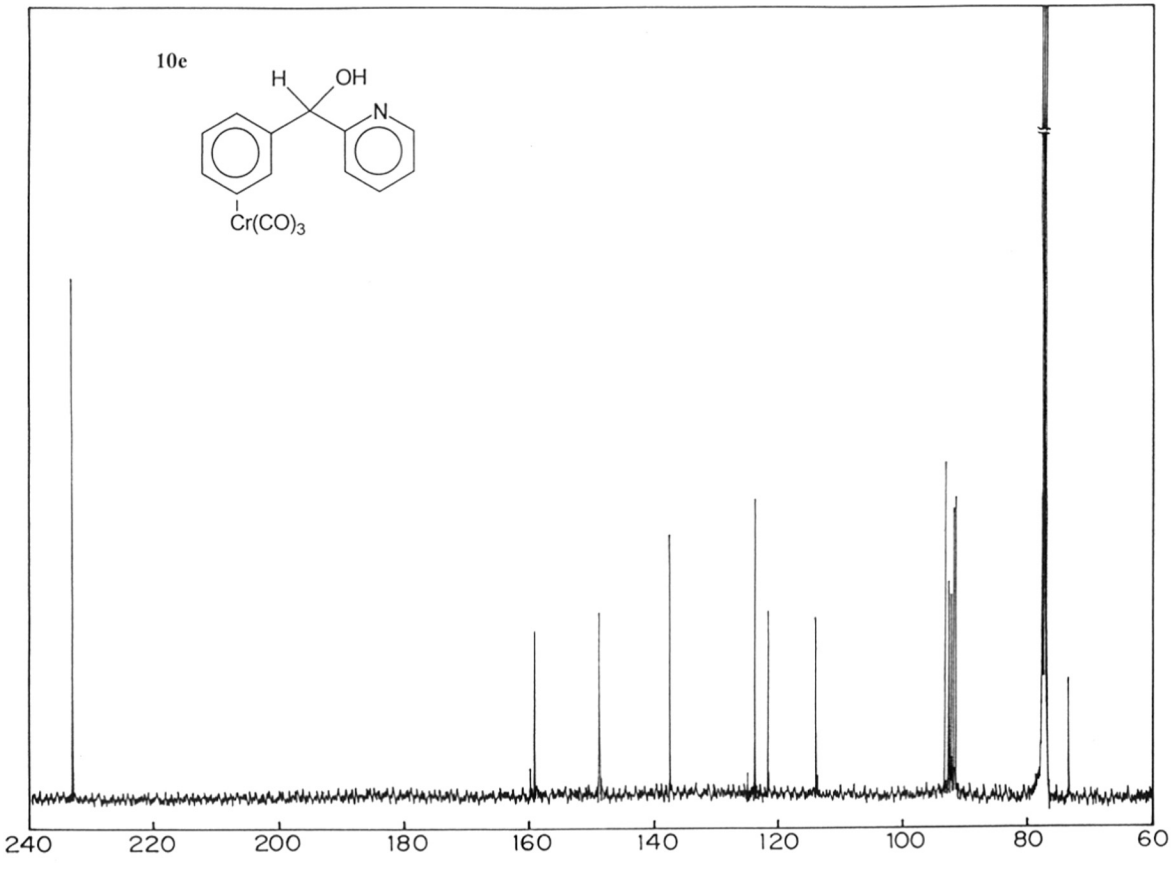
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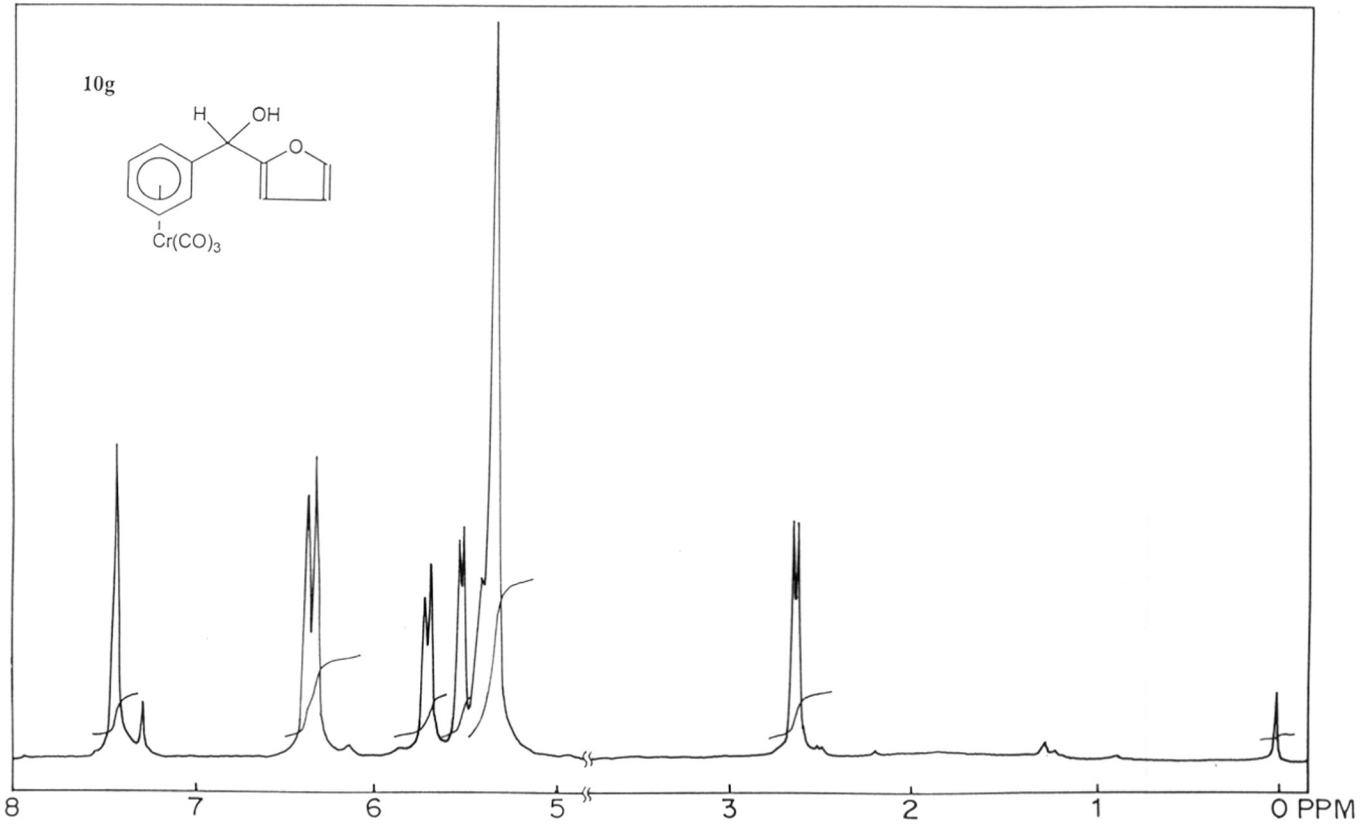
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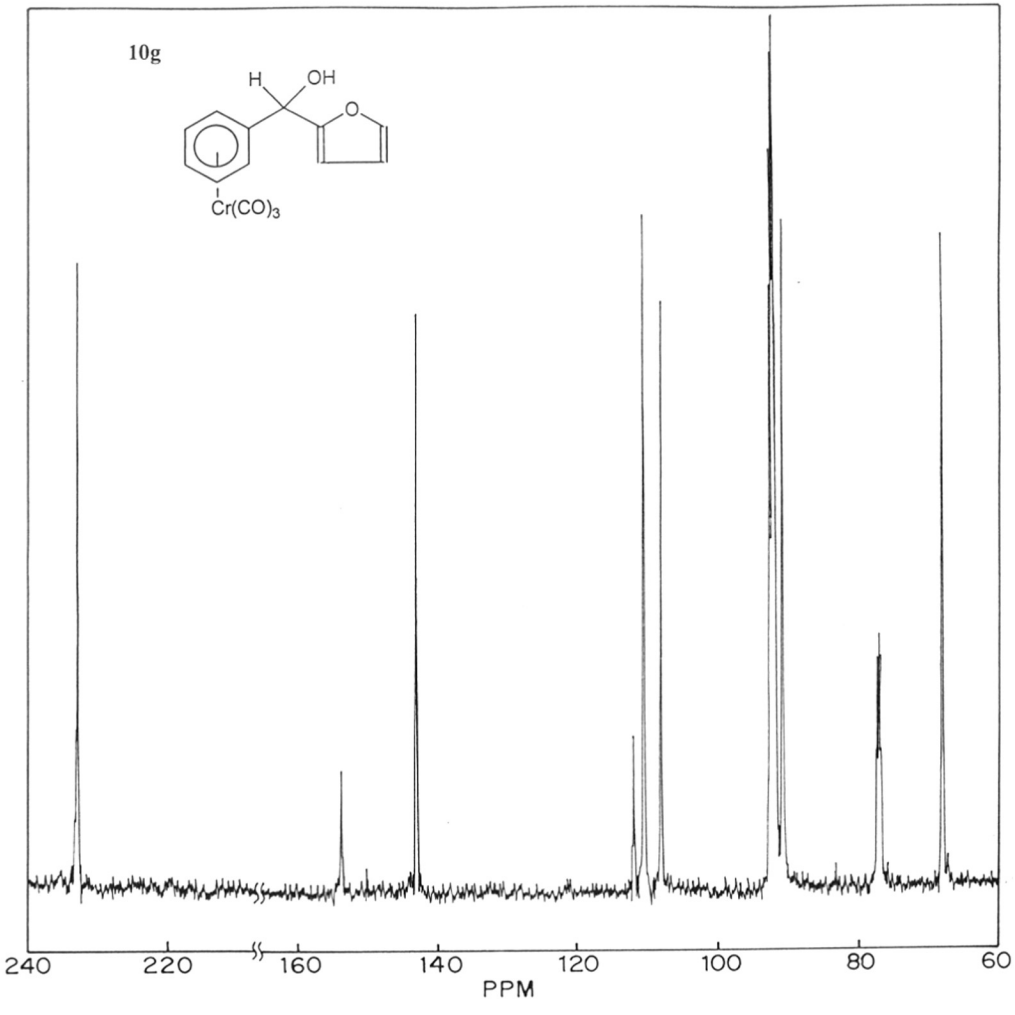
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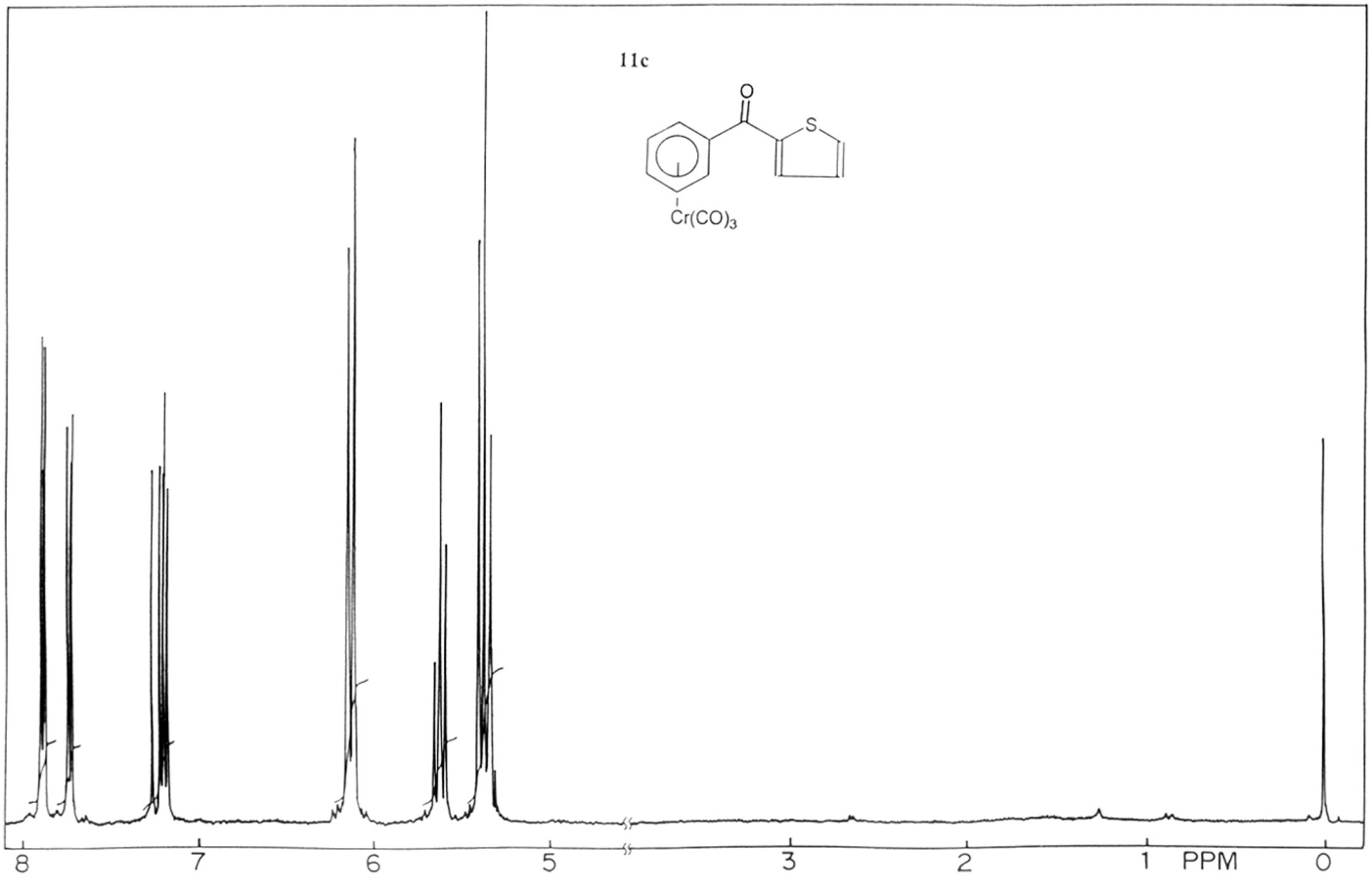
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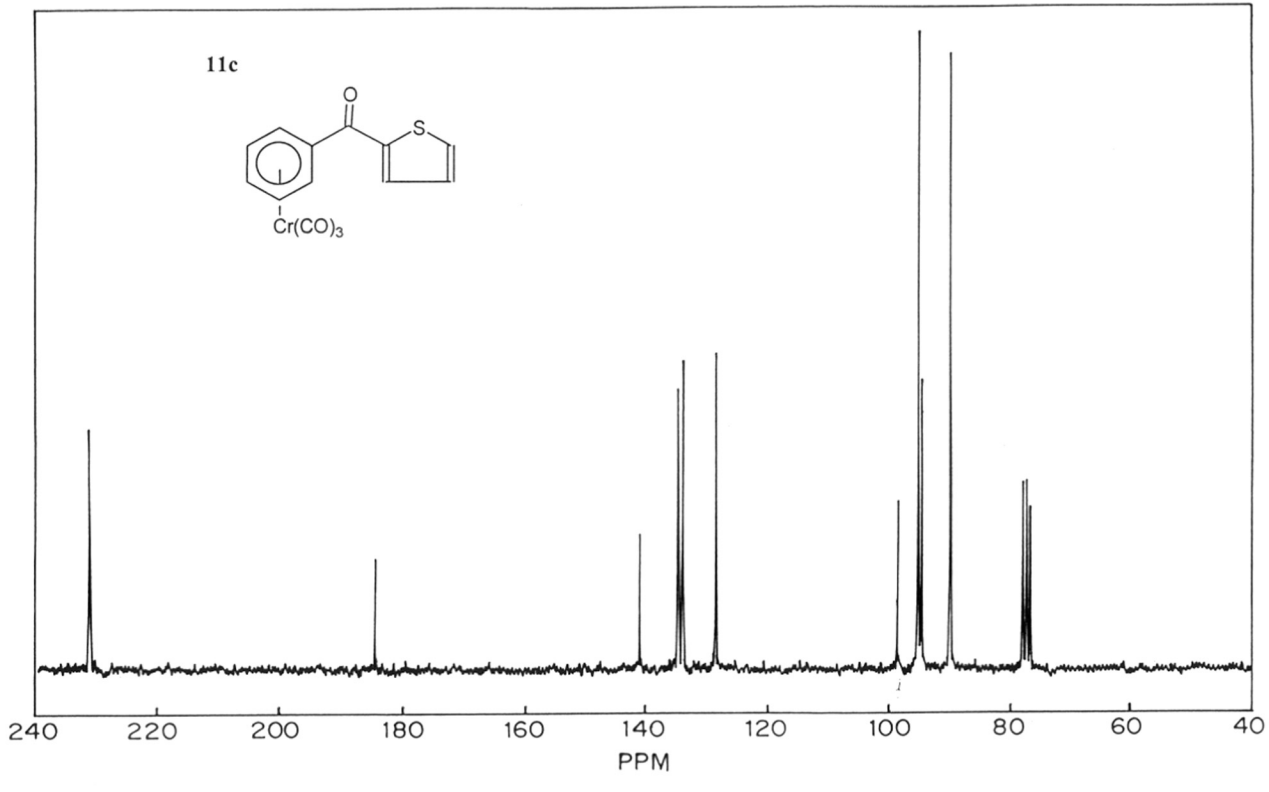
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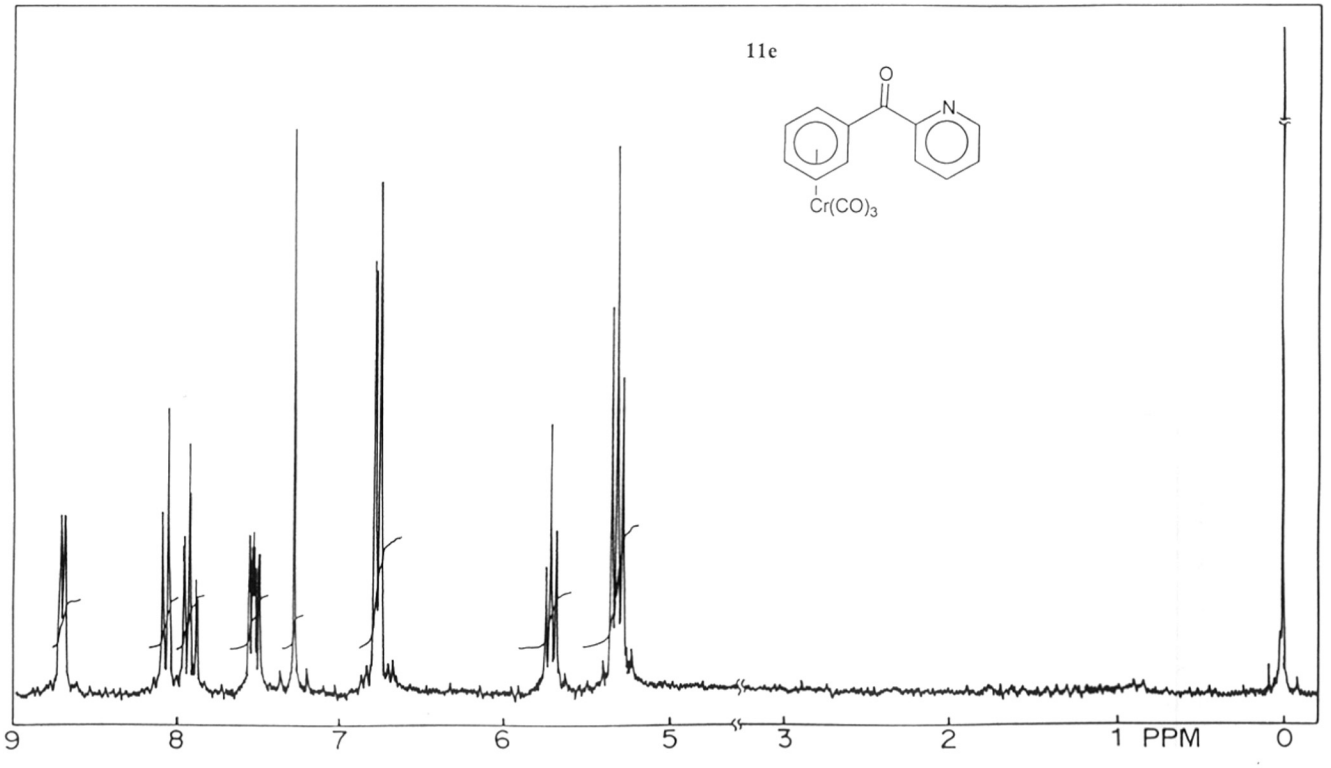
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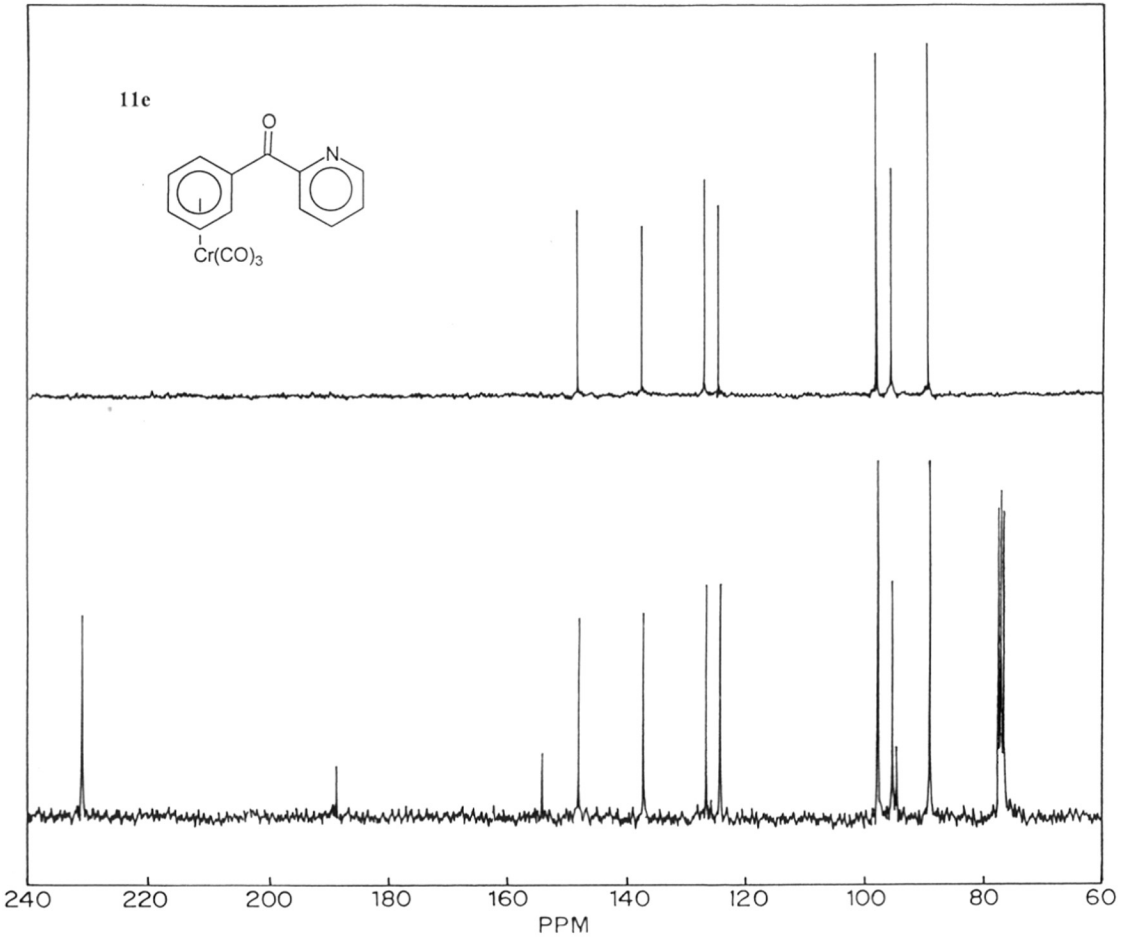
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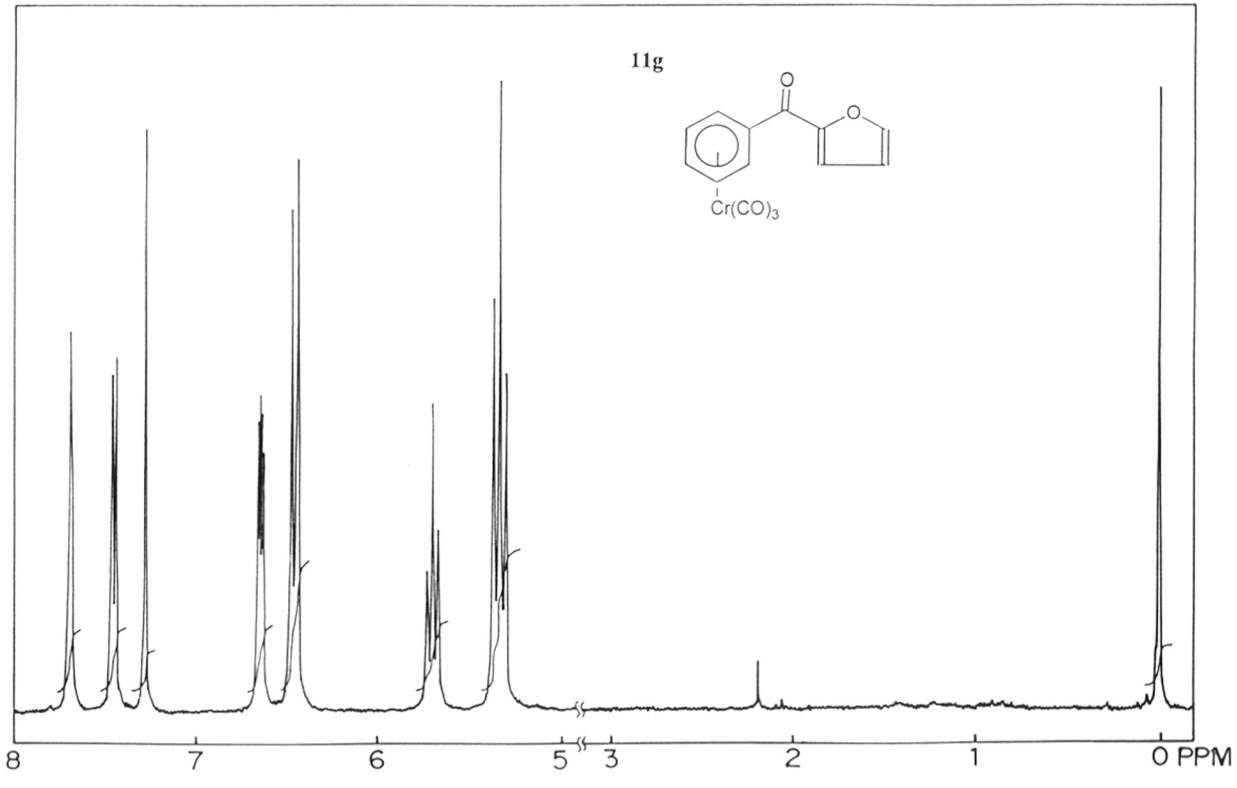
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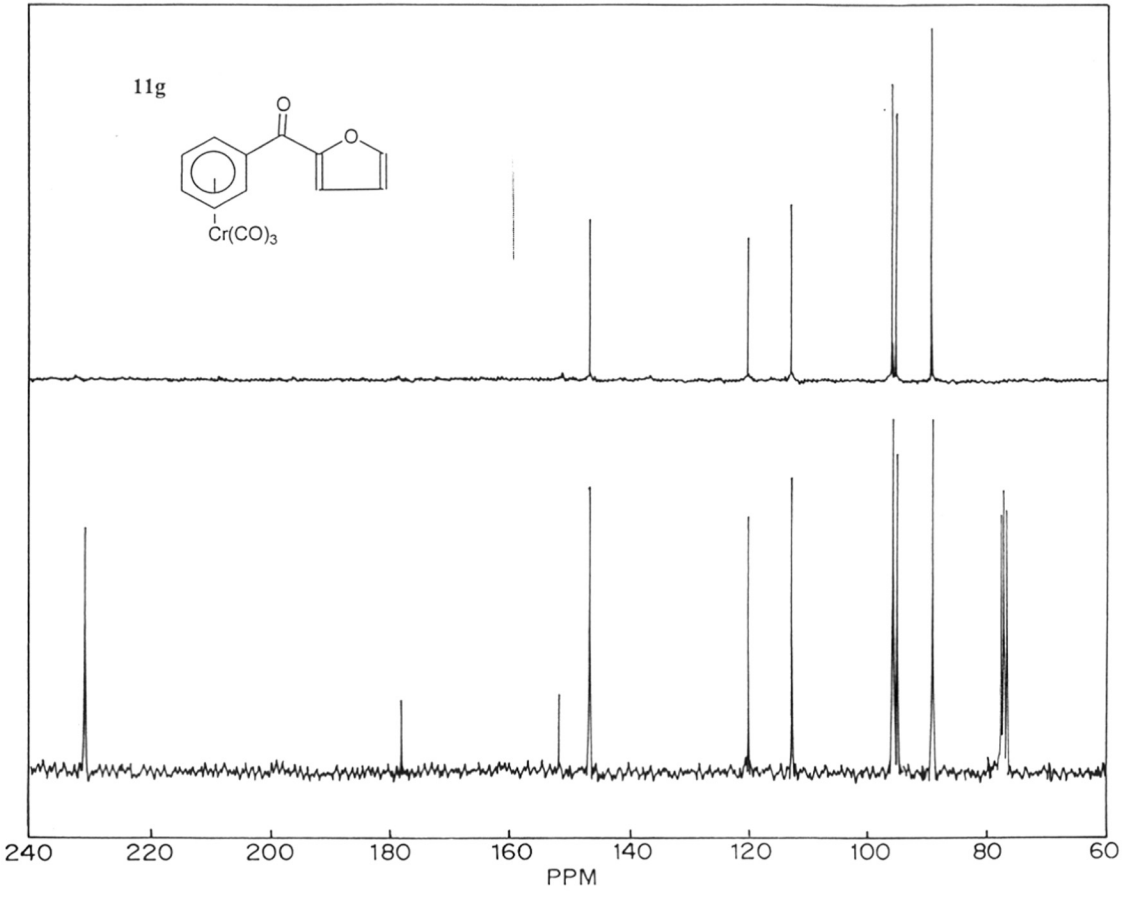
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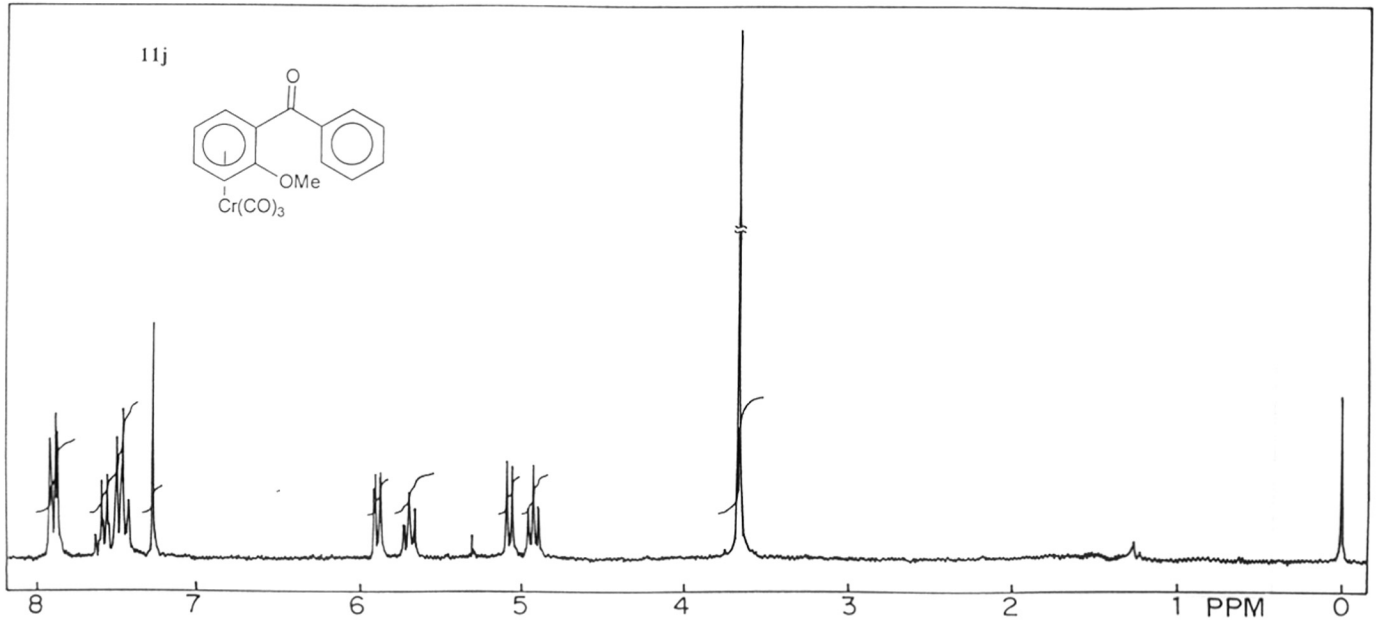
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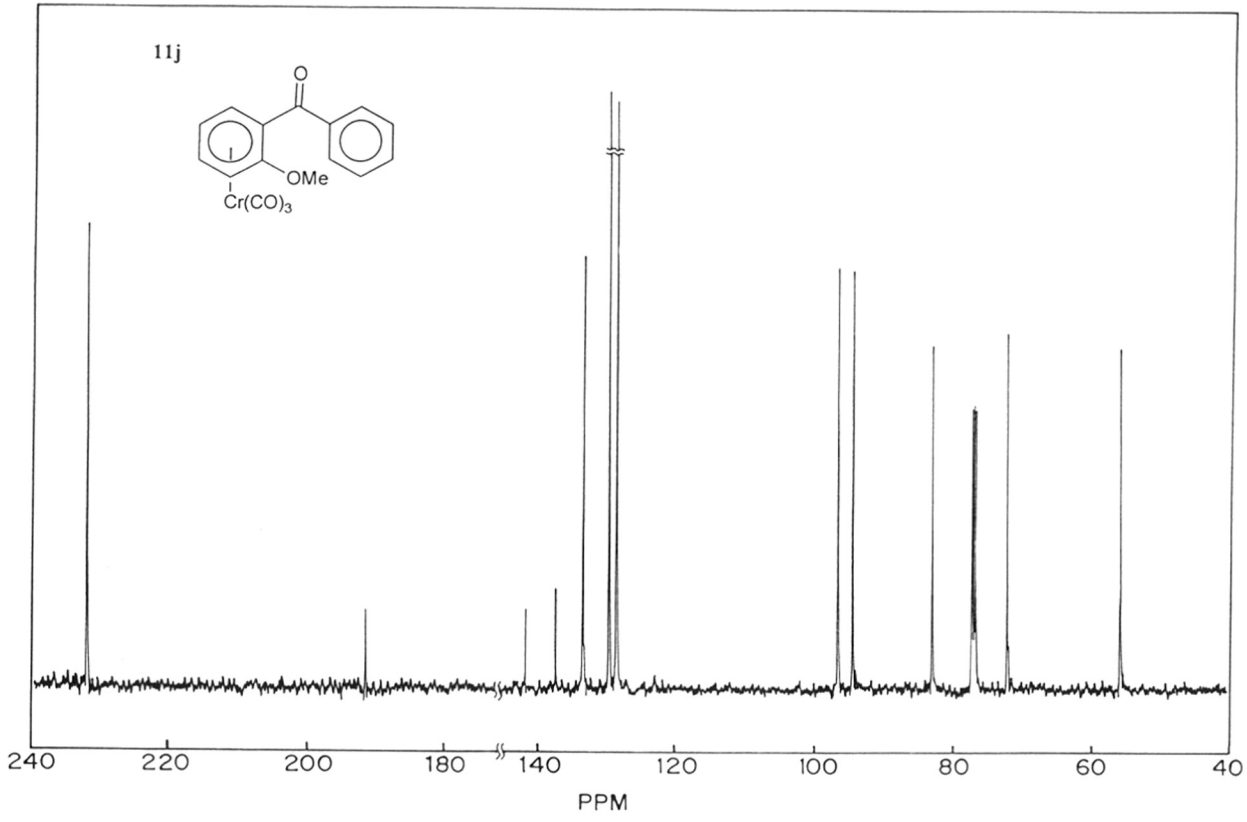
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80
60
40
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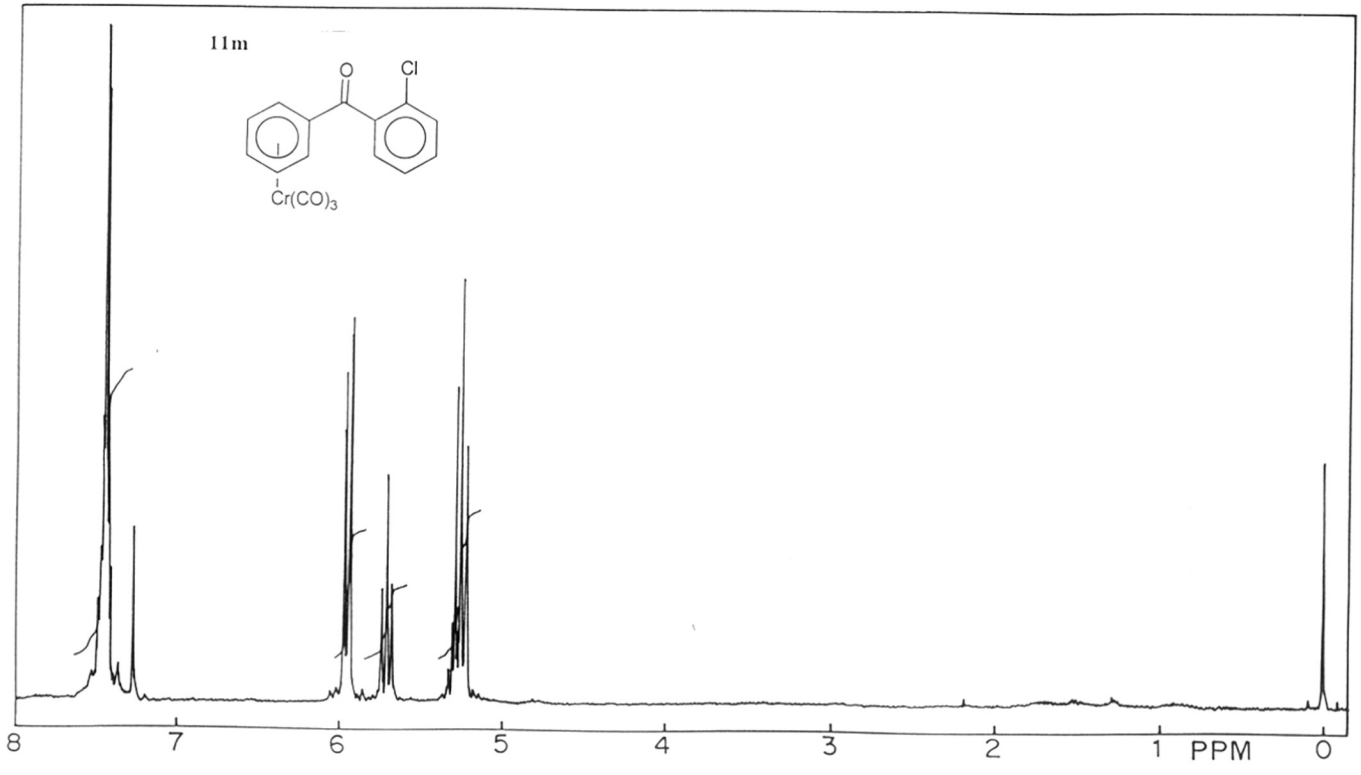
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Cr(CO)3
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6
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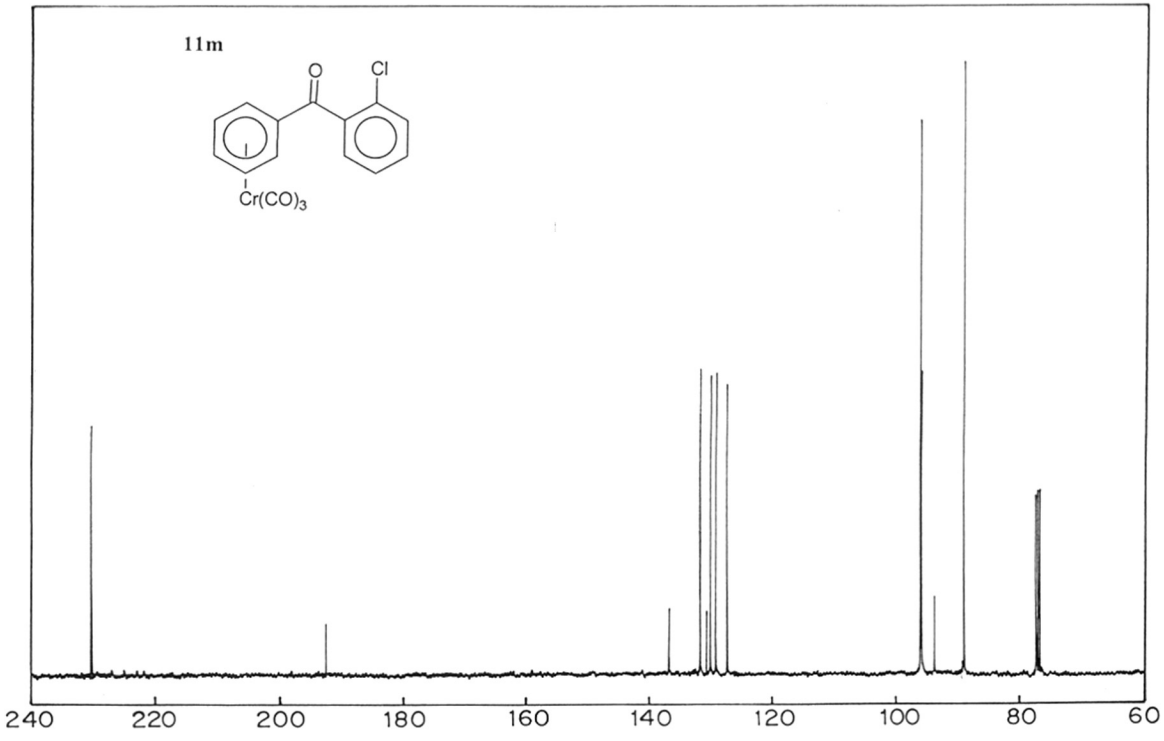
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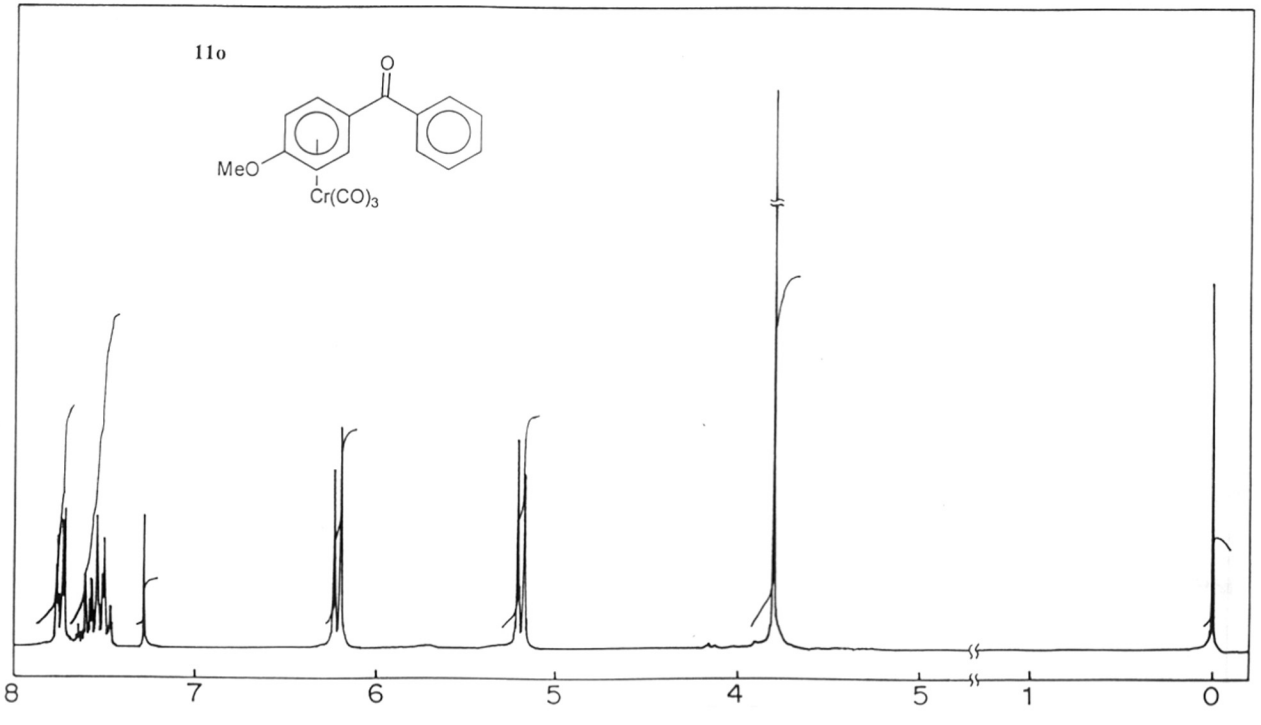
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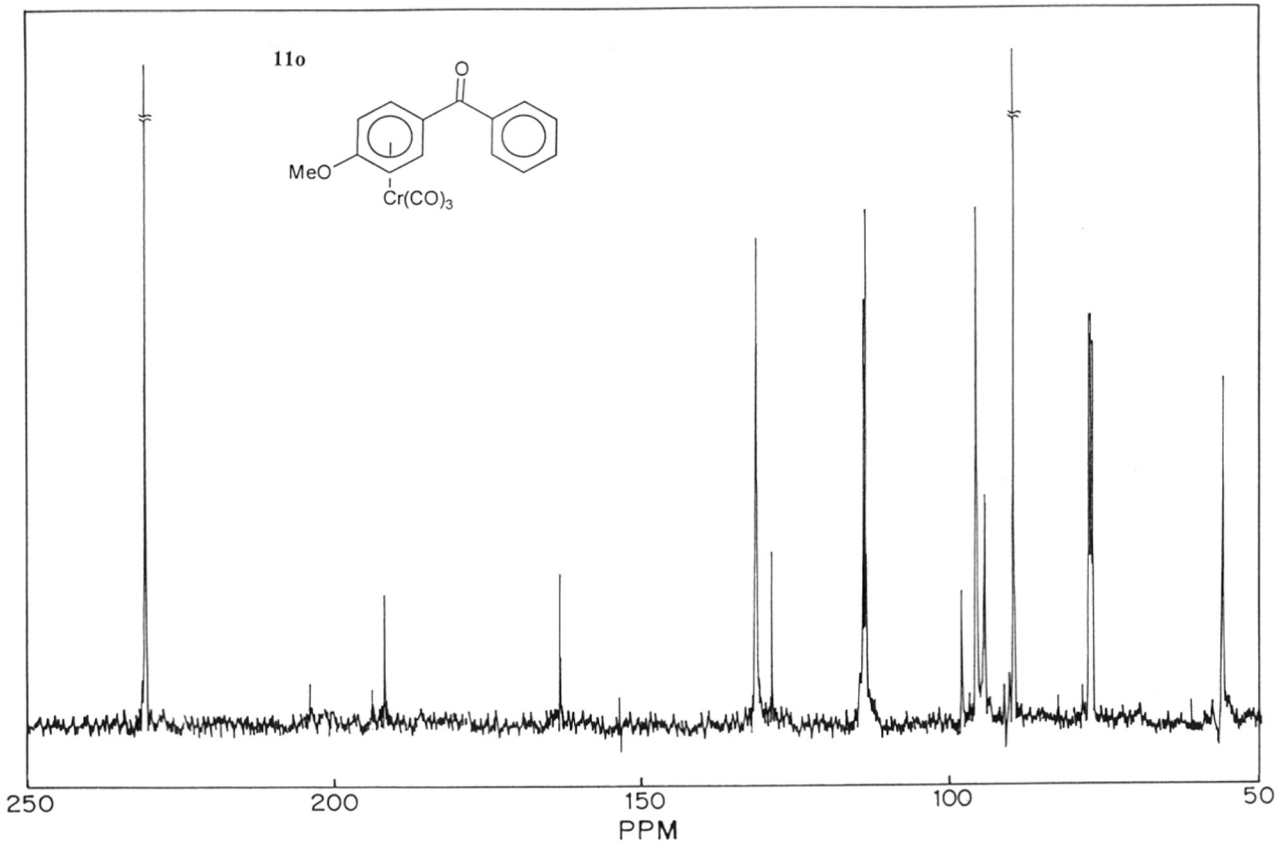
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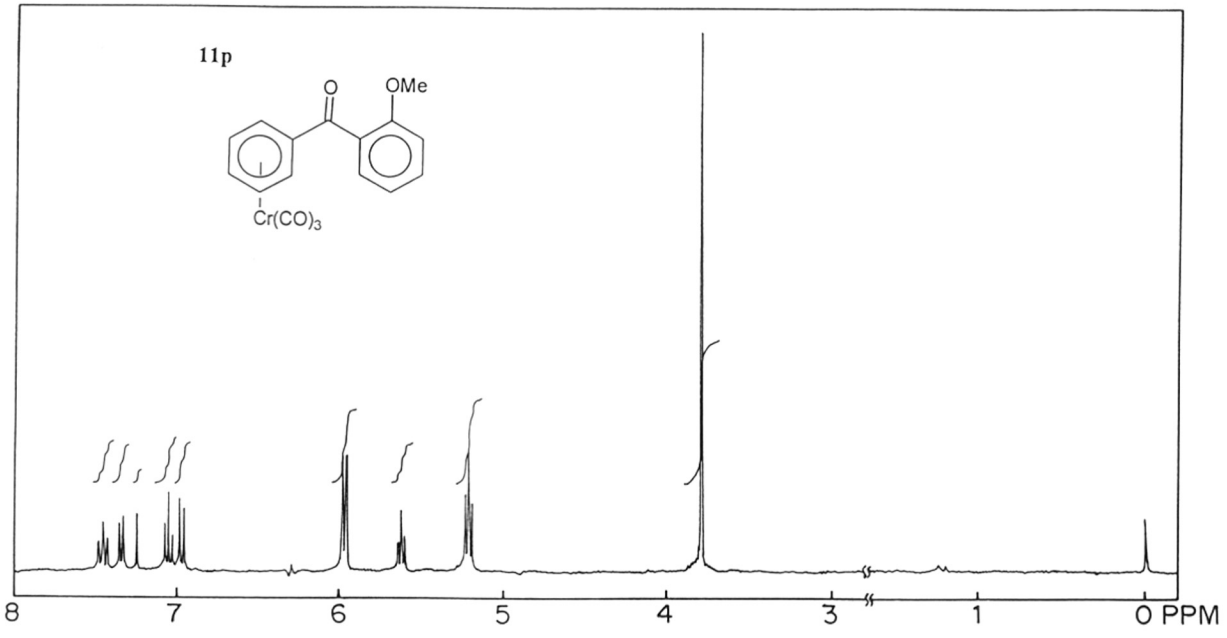
PPM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Cr(CO)3
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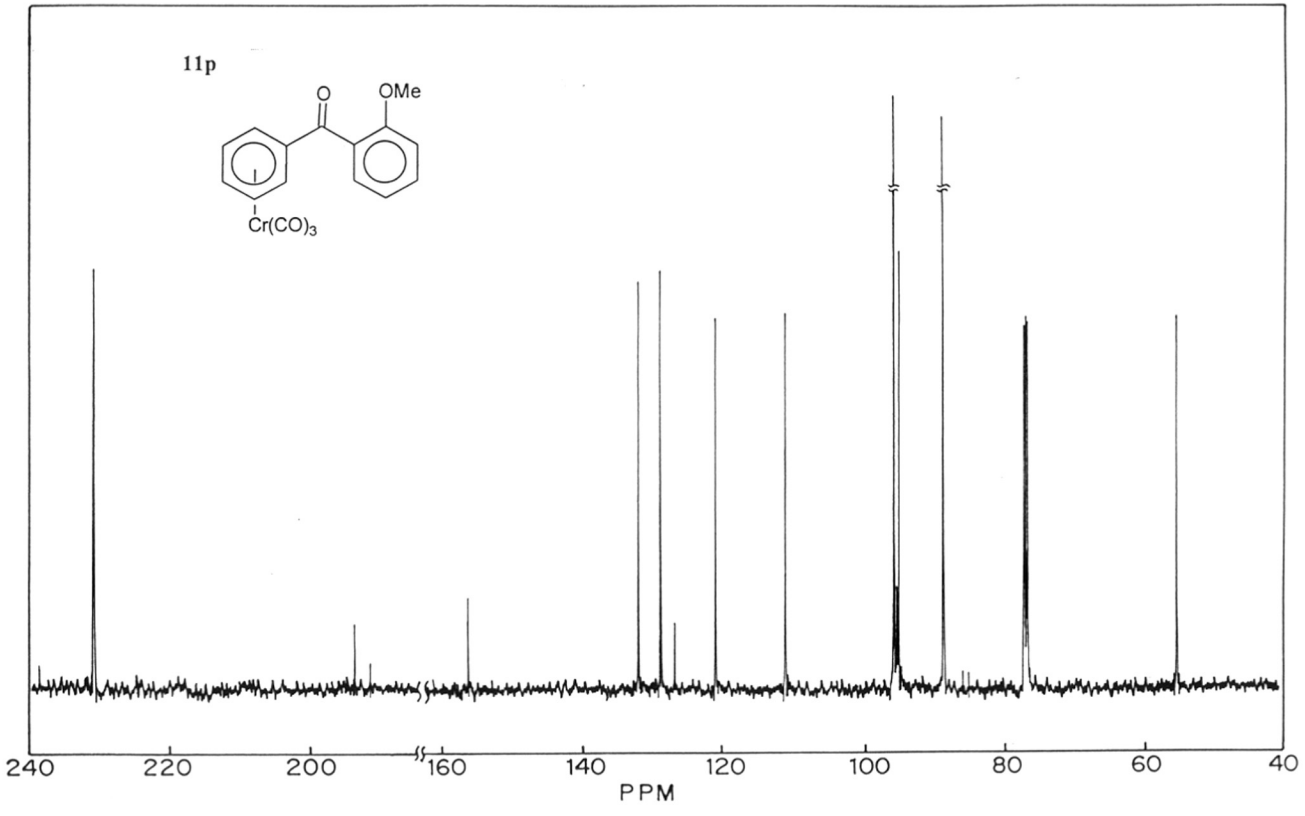
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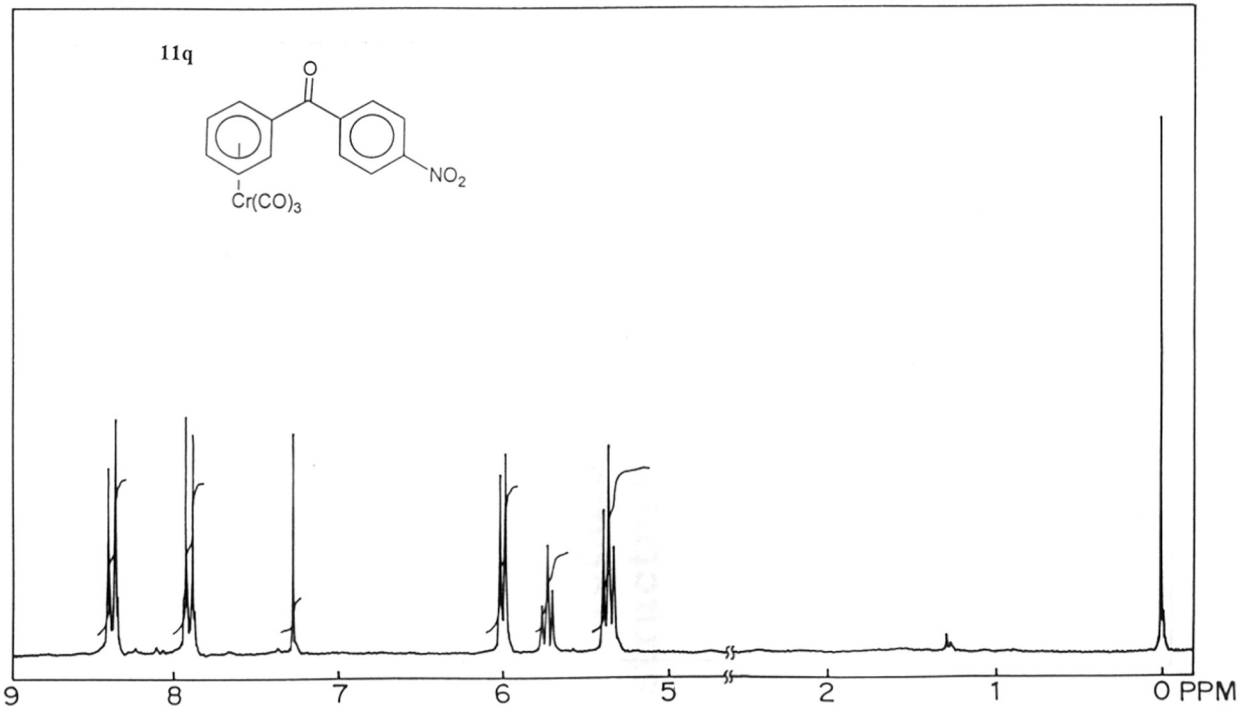
PPM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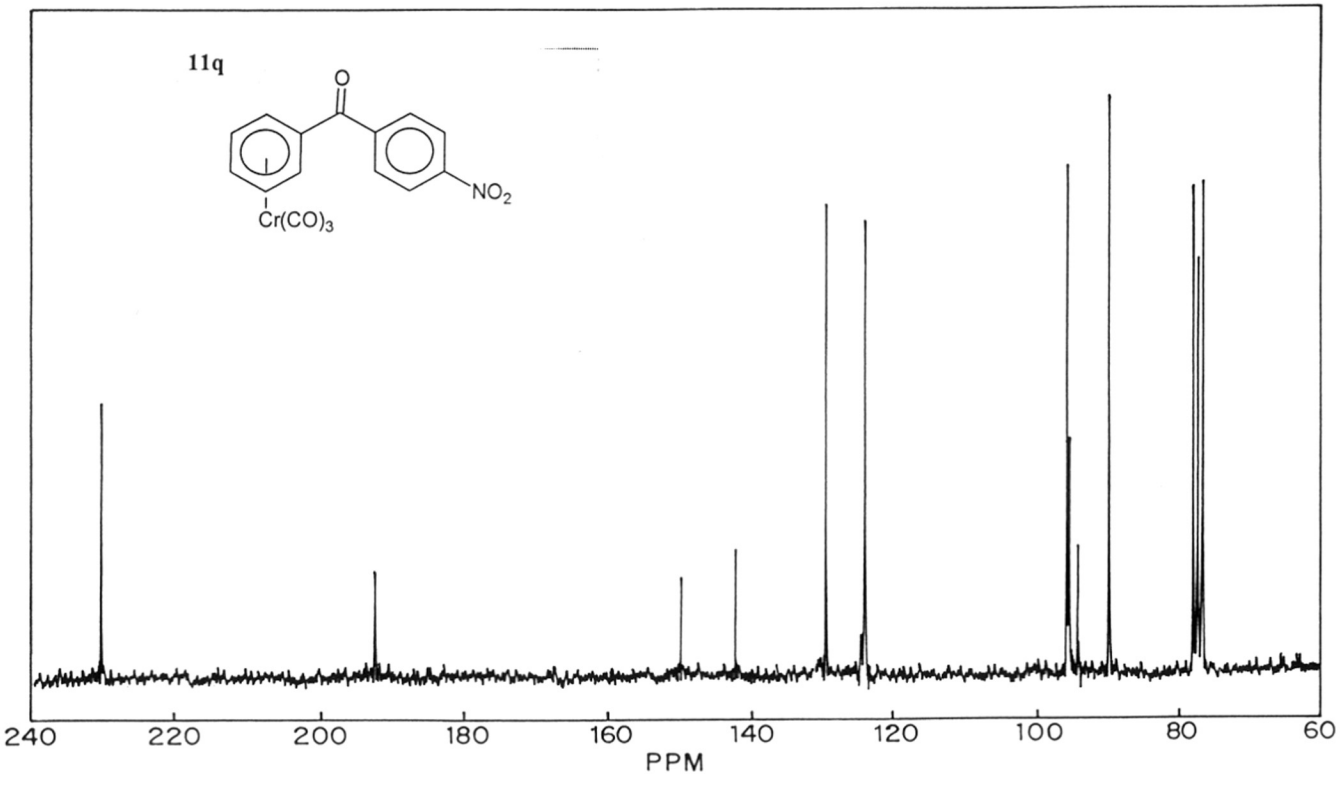
Cr(CO)3
9
8
7
6
5
2
1
0 PPM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NO2
Cr(CO)3
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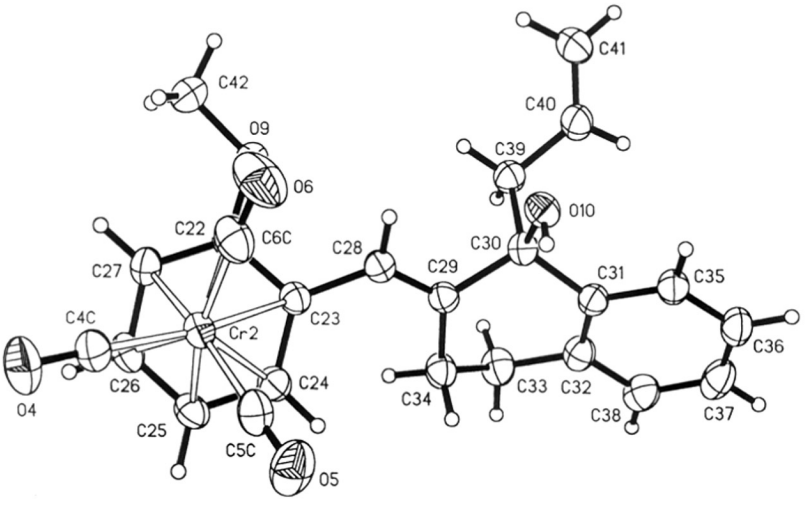
60
PPM

Appendix-**III**

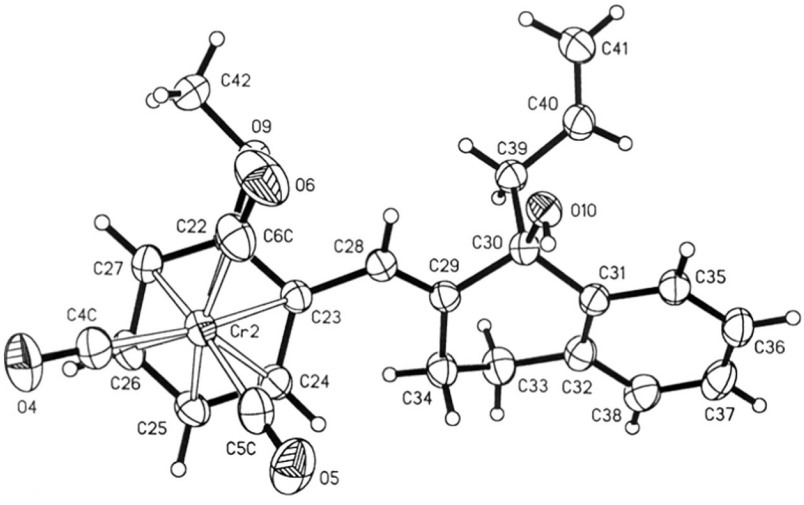
X-ray crystallographic data and structure refinement



(X-Ray crystal structure of complex **7a** of Part-A. Structure was solved by Prof. Karl S. Hagen of Emory University, USA)

Table 1. Crystal data and structure refinement for Complex- **7a** of Part-A

Empirical formula	C_{24} H_{22} Cr O
Formula weight	442.42
Temperature	301(2) K
Wavelength	1.54178 A
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 11.3514(6) A alpha = 85.271(4) deg
	b = 13.8365(6) A beta = 80.676(6) deg.
	c = 14.2539(5) A gamma = 70.564(4) deg.
Volume	2082.32(16) A^3
Z	4
Density (calculated)	1.411 Mg/m^3
Absorption coefficient	4.801 mm^-1
F(000)	920
Crystal size	0.42 x 0.38 x 0.34 mm
Theta range for data collection	3.14 to 56.74 deg
Index ranges	-1<=h<=12, -14<=k<=15, -15<=l<=15
Reflections collected	6531
Independent reflections	5517 [R(int) = 0.0257]
Absorption correction	Empirical
Max. and min. transmission	0.1240 and 0.0363
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5517 / 0 / 56
Goodness-of-fit on F^2	1.009
Final R indices [I>2sigma(I)]	R1 = 0.0350, wR2 = 0.0987
R indices (all data)	R1 = 0.0391, wR2 = 0.1023
Extinction coefficient	0.0054(3)
Largest diff. peak and hole	0.227 and -0.277 e.A^-3



(X-Ray crystal structure of complex **7a** of Part-A. Structure was solved by Prof. Karl S. Hagen of Emory University, USA)

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for Complex-**7a**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Cr(1)	254(1)	1857(1)	1042(1)	47(1)
C(1C)	-1125(3)	1413(2)	1215(2)	57(1)
O(1)	-2007(2)	1150(2)	1348(2)	78(1)
C(2C)	-863(3)	3164(2)	1093(2)	62(1)
O(2)	-1566(3)	3987(2)	1094(2)	100(1)
C(3C)	190(3)	1791(2)	2340(2)	59(1)
O(3)	182(2)	1736(2)	3153(2)	89(1)
C(1)	1617(2)	2481(2)	50(2)	53(1)
C(2)	983(2)	2061(2)	-514(2)	48(1)
C(3)	1016(3)	1045(2)	-307(2)	53(1)
C(4)	1660(3)	440(2)	412(2)	57(1)
C(5)	2248(3)	873(2)	968(2)	59(1)
C(6)	2223(3)	1896(2)	787(2)	59(1)
C(7)	332(2)	2696(2)	-1280(2)	49(1)
C(8)	454(2)	2411(2)	-2170(2)	46(1)
C(9)	-265(2)	3141(2)	-2905(2)	49(1)
C(10)	-735(2)	2555(2)	-3552(2)	50(1)
C(11)	-405(2)	1493(2)	-3536(2)	50(1)
C(12)	465(3)	831(2)	-2870(2)	57(1)
C(13)	1280(2)	1392(2)	-2566(2)	51(1)
C(14)	-1542(3)	3134(2)	-4191(2)	63(1)
C(15)	-1997(3)	2664(3)	-4798(2)	71(1)
C(16)	-1661(3)	1611(3)	-4785(2)	67(1)
C(17)	-885(3)	1038(2)	-4159(2)	61(1)
C(18)	593(3)	3685(2)	-3520(2)	62(1)
C(19)	865(3)	4471(3)	-3024(2)	71(1)

C(20)	767(4)	5396(3)	-3355(4)	91(1)
C(21)	1970(5)	3995(3)	438(3)	108(2)
O(7)	1576(2)	3456(2)	-201(1)	67(1)
O(8)	-1308(2)	3953(1)	-2469(1)	54(1)
Cr(2)	-5317(1)	2633(1)	-6681(1)	48(1)
C(4C)	-5173(3)	2522(2)	-7977(2)	60(1)
O(4)	-5084(2)	2470(2)	-8790(2)	88(1)
C(5C)	-3765(3)	2819(2)	-6890(2)	63(1)
O(5)	-2797(2)	2944(2)	-7020(2)	89(1)
C(6C)	-4481(3)	1252(2)	-6543(2)	68(1)
O(6)	-3944(3)	396(2)	-6431(2)	105(1)
O(9)	-6920(2)	1562(1)	-5013(1)	60(1)
O(10)	-3778(2)	1237(1)	-3011(1)	54(1)
C(22)	-6799(2)	2419(2)	-5493(2)	50(1)
C(23)	-6024(2)	2878(2)	-5111(2)	47(1)
C(24)	-5877(3)	3780(2)	-5578(2)	54(1)
C(25)	-6495(3)	4231(2)	-6368(2)	58(1)
C(26)	-7225(3)	3758(2)	-6724(2)	59(1)
C(27)	-7377(2)	2839(2)	-6291(2)	56(1)
C(28)	-5435(2)	2388(2)	-4270(2)	48(1)
C(29)	-5271(2)	2846(2)	-3538(2)	46(1)
C(30)	-4742(2)	2167(2)	-2695(2)	47(1)
C(31)	-4268(2)	2730(2)	-2038(2)	50(1
C(32)	-4900(3)	3758(2)	-1869(2)	56()
C(33)	-5977(3)	4319(2)	-2410(2)	64(1)
C(34)	-5653(3)	3991(2)	-3441(2)	56(1)
C(35)	-3248(3)	2211(2)	-1564(2)	59(1)
C(36)	-2895(3)	2700(3)	-900(2)	70(1)
C(37)	-3533(3)	3719(3)	-732(2)	76(1)
C(38)	-4515(3)	4253(3)	-1220(2)	69(1)
C(39)	-5810(2)	1800(2)	-2129(2)	54(1)
C(40)	-5458(3)	1087(2)	-1304(2)	61(1)
C(41)	-5518(3)	159(3)	-1226(3)	71(1)

C(42)	-7480(4)	950(3)	-5437(3)	87(1)

Table 3. Bond lengths [A] and angles [deg] for Complex-**7a**.

Cr(1)-C(2C)	1.830(3)
Cr(1)-C(3C)	1.836(3)
Cr(1)-C(1C)	1.837(3)
Cr(1)-C(3)	2.209(3)
Cr(1)-C(5)	2.210(3)
Cr(1)-C(4)	2.223(3)
Cr(1)-C(6)	2.224(3)
Cr(1)-C(1)	2.263(3)
Cr(1)-C(2)	2.267(2)
C(1C)-O(1)	1.158(3)
C(2C)-O(2)	1.153(3)
C(3C)-O(3)	1.154(3)
C(1)-O(7)	1.355(3)
C(1)-C(6)	1.399(4)
C(1)-C(2)	1.429(4)
C(2)-C(3)	1.402(4)
C(2)-C(7)	1.478(3)
C(3)-C(4)	1.406(4)
C(4)-C(5)	1.397(4)
C(5)-C(6)	1.409(4)
C(7)-C(8)	1.331(3)
C(8)-C(13)	1.505(3)
C(8)-C(9)	1.529(3)
C(9)-O(8)	1.429(3)
C(9)-C(10)	1.536(4)
C(9)-C(18)	1.545(4)

C(10)-C(11)	1.390(4)
C(10)-C(14)	1.404(4)
C(11)-C(17)	1.400(4)
C(11)-C(12)	1.508(4)
C(12)-C(13)	1.521(4)
C(14)-C(15)	1.377(4)
C(15)-C(16)	1.378(4)
C(16)-C(17)	1.369(4)
C(18)-C(19)	1.482(4)
C(19)-C(20)	1.302(5)
C(21)-O(7)	1.431(4)
Cr(2)-C(5C)	1.839(3)
Cr(2)-C(6C)	1.839(3)
Cr(2)-C(4C)	1.844(3)
Cr(2)-C(24)	2.193(3)
Cr(2)-C(25)	2.209(3)
Cr(2)-C(26)	2.214(3)
Cr(2)-C(27)	2.240(3)
Cr(2)-C(22)	2.260(3)
Cr(2)-C(23)	2.264(2)
C(4C)-O(4)	1.152(3)
C(5C)-O(5)	1.152(4)
C(6C)-O(6)	1.149(4)
O(9)-C(22)	1.355(3)
O(9)-C(42)	1.433(3)
O(10)-C(30)	1.433(3)
C(22)-C(27)	1.393(4)
C(22)-C(23)	1.433(4)
C(23)-C(24)	1.412(4)
C(23)-C(28)	1.473(3)
C(24)-C(25)	1.414(4)
C(25)-C(26)	1.387(4)
C(26)-C(27)	1.419(4)

C(28)-C(29)	1.332(3)
C(29)-C(34)	1.509(4)
C(29)-C(30)	1.536(3)
C(30)-C(31)	1.529(3)
C(30)-C(39)	1.551(3)
C(31)-C(32)	1.384(4)
C(31)-C(35)	1.390(4)
C(32)-C(38)	1.397(4)
C(32)-C(33)	1.506(4)
C(33)-C(34)	1.524(4)
C(35)-C(36)	1.386(4)
C(36)-C(37)	1.375(5)
C(37)-C(38)	1.375(5)
C(39)-C(40)	1.489(4)
C(40)-C(41)	1.303(4)
C(2C)-Cr(1)-C(3C)	90.87(12)
C(2C)-Cr(1)-C(1C)	87.05(13)
C(3C)-Cr(1)-C(1C)	87.97(12)
C(2C)-Cr(1)-C(3)	122.33(11)
C(3C)-Cr(1)-C(3)	146.76(11)
C(1C)-Cr(1)-C(3)	91.86(11)
C(2C)-Cr(1)-C(5)	146.67(13)
C(3C)-Cr(1)-C(5)	87.13(11)
C(1C)-Cr(1)-C(5)	126.07(12)
C(3)-Cr(1)-C(5)	66.34(10)
C(2C)-Cr(1)-C(4)	158.65(11)
C(3C)-Cr(1)-C(4)	110.11(11)
C(1C)-Cr(1)-C(4)	97.34(11)
C(3)-Cr(1)-C(4)	37.00(10)
C(5)-Cr(1)-C(4)	36.73(10)
C(2C)-Cr(1)-C(6)	110.04(12)
C(3C)-Cr(1)-C(6)	93.13(11)
C(1C)-Cr(1)-C(6)	162.85(12)

C(3)-Cr(1)-C(6)	77.90(10)
C(5)-Cr(1)-C(6)	37.06(11)
C(4)-Cr(1)-C(6)	66.21(11)
C(2C)-Cr(1)-C(1)	87.72(11)
C(3C)-Cr(1)-C(1)	122.85(11)
C(1C)-Cr(1)-C(1)	148.80(11)
C(3)-Cr(1)-C(1)	65.49(10)
C(5)-Cr(1)-C(1)	66.01(10)
C(4)-Cr(1)-C(1)	77.70(10)
C(6)-Cr(1)-C(1)	36.32(10)
C(2C)-Cr(1)-C(2)	92.56(11)
C(3C)-Cr(1)-C(2)	159.04(11)
C(1C)-Cr(1)-C(2)	112.85(11)
C(3)-Cr(1)-C(2)	36.47(9)
C(5)-Cr(1)-C(2)	78.71(10)
C(4)-Cr(1)-C(2)	66.44(9)
C(6)-Cr(1)-C(2)	66.30(10)
C(1)-Cr(1)-C(2)	36.78(9)
O(1)-C(1C)-Cr(1)	177.9(3)
O(2)-C(2C)-Cr(1)	177.8(3)
O(3)-C(3C)-Cr(1)	178.3(3)
O(7)-C(1)-C(6)	124.9(2)
O(7)-C(1)-C(2)	114.5(2)
C(6)-C(1)-C(2)	120.6(2)
O(7)-C(1)-Cr(1)	131.16(19)
C(6)-C(1)-Cr(1)	70.35(15)
C(2)-C(1)-Cr(1)	71.80(14)
C(3)-C(2)-C(1)	117.4(2)
C(3)-C(2)-C(7)	122.8(2)
C(1)-C(2)-C(7)	119.8(2)
C(3)-C(2)-Cr(1)	69.51(14)
C(1)-C(2)-Cr(1)	71.43(14)
C(7)-C(2)-Cr(1)	130.25(17)

C(2)-C(3)-C(4)	122.4(3)
C(2)-C(3)-Cr(1)	74.02(15)
C(4)-C(3)-Cr(1)	72.04(15)
C(5)-C(4)-C(3)	119.2(3)
C(5)-C(4)-Cr(1)	71.13(15)
C(3)-C(4)-Cr(1)	70.97(15)
C(4)-C(5)-C(6)	119.9(3)
C(4)-C(5)-Cr(1)	72.15(5)
C(6)-C(5)-Cr(1)	72.02(16)
C(1)-C(6)-C(5)	120.4(3)
C(1)-C(6)-Cr(1)	73.33(15)
C(5)-C(6)-Cr(1)	70.93(16)
C(8)-C(7)-C(2)	125.6(2)
C(7)-C(8)-C(13)	125.8(2)
C(7)-C(8)-C(9)	120.9(2)
C(13)-C(8)-C(9)	113.3(2)
O(8)-C(9)-C(8)	112.02(19)
O(8)-C(9)-C(10)	109.6(2)
C(8)-C(9)-C(10)	110.7(2)
O(8)-C(9)-C(18)	104.7(2)
C(8)-C(9)-C(18)	110.3(2)
C(10)-C(9)-C(18)	109.4(2)
C(11)-C(10)-C(14)	118.8(2)
C(11)-C(10)-C(9)	123.6(2)
C(14)-C(10)-C(9)	117.6(2)
C(10)-C(11)-C(17)	118.9(2)
C(10)-C(11)-C(12)	121.2(2)
C(17)-C(11)-C(12)	119.9(2)
C(11)-C(12)-C(13)	111.1(2)
C(8)-C(13)-C(12)	109.7(2)
C(15)-C(14)-C(10)	121.1(3)
C(14)-C(15)-C(16)	120.1(3)
C(17)-C(16)-C(15)	119.5(3)

C(16)-C(17)-C(11)	121.7(3)
C(19)-C(18)-C(9)	114.9(2)
C(20)-C(19)-C(18)	125.1(4)
C(1)-O(7)-C(21)	117.6(2)
C(5C)-Cr(2)-C(6C)	87.57(14)
C(5C)-Cr(2)-C(4C)	87.42(12)
C(6C)-Cr(2)-C(4C)	90.96(12)
C(5C)-Cr(2)-C(24)	87.57(12)
C(6C)-Cr(2)-C(24)	126.89(11)
C(4C)-Cr(2)-C(24)	141.51(11)
C(5C)-Cr(2)-C(25)	98.36(13)
C(6C)-Cr(2)-C(25)	162.16(12)
C(4C)-Cr(2)-C(25)	106.04(11)
C(24)-Cr(2)-C(25)	37.47(10)
C(5C)-Cr(2)-C(26)	130.09(12)
C(6C)-Cr(2)-C(26)	142.22(13)
C(4C)-Cr(2)-C(26)	88.23(11)
C(24)-Cr(2)-C(26)	66.63(10)
C(25)-Cr(2)-C(26)	36.55(10)
C(5C)-Cr(2)-C(27)	164.54(12)
C(6C)-Cr(2)-C(27)	106.20(13)
C(4C)-Cr(2)-C(27)	99.11(11)
C(24)-Cr(2)-C(27)	78.58(10)
C(25)-Cr(2)-C(27)	66.42(11)
C(26)-Cr(2)-C(27)	37.14(10)
C(5C)-Cr(2)-C(22)	141.54(11)
C(6C)-Cr(2)-C(22)	87.07(12)
C(4C)-Cr(2)-C(22)	130.71(11)
C(24)-Cr(2)-C(22)	65.99(10)
C(25)-Cr(2)-C(22)	77.81(10)
C(26)-Cr(2)-C(22)	65.69(10)
C(27)-Cr(2)-C(22)	36.07(9)
C(5C)-Cr(2)-C(23)	106.00(11)

C(6C)-Cr(2)-C(23)	95.25(11)
C(4C)-Cr(2)-C(23)	165.40(11)
C(24)-Cr(2)-C(23)	36.88(9)
C(25)-Cr(2)-C(23)	66.95(9)
C(26)-Cr(2)-C(23)	78.76(10)
C(27)-Cr(2)-C(23)	66.47(9)
C(22)-Cr(2)-C(23)	36.94(9)
O(4)-C(4C)-Cr(2)	178.8(3)
O(5)-C(5C)-Cr(2)	179.4(3)
O(6)-C(6C)-Cr(2)	177.7(3)
C(22)-O(9)-C(42)	118.4(2)
O(9)-C(22)-C(27)	123.7(2)
O(9)-C(22)-C(23)	114.6(2)
C(27)-C(22)-C(23)	121.7(2)
O(9)-C(22)-Cr(2)	131.01(18)
C(27)-C(22)-Cr(2)	71.18(15)
C(23)-C(22)-Cr(2)	71.68(14)
C(24)-C(23)-C(22)	117.0(2)
C(24)-C(23)-C(28)	124.2(2)
C(22)-C(23)-C(28)	118.8(2)
C(24)-C(23)-Cr(2)	68.82(14)
C(22)-C(23)-Cr(2)	71.38(14)
C(28)-C(23)-Cr(2)	130.56(17)
C(23)-C(24)-C(25)	121.7(3)
C(23)-C(24)-Cr(2)	74.29(15)
C(25)-C(24)-Cr(2)	71.86(15)
C(26)-C(25)-C(24)	119.6(3)
C(26)-C(25)-Cr(2)	71.92(16)
C(24)-C(25)-Cr(2)	70.67(15)
C(25)-C(26)-C(27)	120.6(2)
C(25)-C(26)-Cr(2)	71.53(16)
C(27)-C(26)-Cr(2)	72.44(15)
C(22)-C(27)-C(26)	119.3(2)

C(22)-C(27)-Cr(2)	72.75(15)
C(26)-C(27)-Cr(2)	70.42(16)
C(29)-C(28)-C(23)	127.7(2)
C(28)-C(29)-C(34)	124.8(2)
C(28)-C(29)-C(30)	118.0(2)
C(34)-C(29)-C(30)	117.1(2)
O(10)-C(30)-C(31)	111.0(2)
O(10)-C(30)-C(29)	111.34(19)
C(31)-C(30)-C(29)	112.6(2)
O(10)-C(30)-C(39)	104.1(2)
C(31)-C(30)-C(39)	109.7(2)
C(29)-C(30)-C(39)	107.73(19)
C(32)-C(31)-C(35)	119.2(2)
C(32)-C(31)-C(30)	119.8(2)
C(35)-C(31)-C(30)	120.8(2)
C(31)-C(32)-C(38)	119.7(3)
C(31)-C(32)-C(33)	118.6(2)
C(38)-C(32)-C(33)	121.7(3)
C(32)-C(33)-C(34)	110.2(2)
C(29)-C(34)-C(33)	113.2(2)
C(36)-C(35)-C(31)	120.7(3)
C(37)-C(36)-C(35)	119.7(3)
C(36)-C(37)-C(38)	120.3(3)
C(37)-C(38)-C(32)	120.3(3)
C(40)-C(39)-C(30)	115.7(2)
C(41)-C(40)-C(39)	123.9(3)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for Complex-**7a**
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Cr(1)	49(1)	47(1)	43(1)	1(1)	-10(1)	-11(1)
C(1C)	60(2)	55(2)	53(2)	-6(1)	-8(1)	-13(1)
O(1)	66(1)	77(1)	97(2)	-11(1)	-10(1)	-30(1)
C(2C)	72(2)	60(2)	49(2)	3(1)	-3(1)	-15(2)
O(2)	109(2)	61(1)	90(2)	5(1)	5(1)	13(1)
C(3C)	53(2)	66(2)	54(2)	1(1)	-11(1)	-16(1)
O(3)	89(2)	128(2)	47(1)	4(1)	-18(1)	-28(2)
C(1)	52(2)	58(2)	50(1)	4(1)	-9(1)	-20(1)
C(2)	49(1)	49(1)	42(1)	0(1)	-5(1)	-11(1)
C(3)	53(2)	52(2)	48(1)	-4(1)	-5(1)	-9(1)
C(4)	55(2)	50(1)	56(2)	1(1)	-7(1)	-5(1)
C(5)	48(2)	63(2)	58(2)	8(1)	-10(1)	-7(1)
C(6)	50(2)	71(2)	58(2)	2(1)	-15(1)	-20(1)
C(7)	49(1)	47(1)	47(1)	0(1)	-8(1)	-12(1)
C(8)	44(1)	48(1)	46(1)	0(1)	-6(1)	-14(1)
C(9)	51(1)	47(1)	44(1)	-2(1)	-5(1)	-11(1)
C(10)	49(1)	59(2)	42(1)	0(1)	-5(1)	-16(1)
C(11)	49(1)	55(2)	46(1)	-3(1)	-2(1)	-18(1)
C(12)	64(2)	51(2)	54(2)	-4(1)	-9(1)	-14(1)
C(13)	49(1)	51(1)	46(1)	-1(1)	-6(1)	-10(1)
C(14)	68(2)	64(2)	51(2)	1(1)	-15(1)	-11(1)
C(15)	68(2)	95(2)	50(2)	2(2)	-20(1)	-22(2)
C(16)	68(2)	88(2)	52(2)	-9(2)	-9(1)	-34(2)
C(17)	62(2)	68(2)	56(2)	-7(1)	-2(1)	-27(2)

C(18)	67(2)	63(2)	53(2)	4(1)	-3(1)	-24(1)
C(19)	70(2)	82(2)	69(2)	6(2)	-16(2)	-36(2)
C(20)	104(3)	76(3)	105(3)	3(2)	-13(2)	-46(2)
C(21)	173(4)	85(2)	106(3)	22(2)	-74(3)	-74(3)
O(7)	86(1)	65(1)	62(1)	11(1)	-24(1)	-39(1)
O(8)	56(1)	48(1)	50(1)	2(1)	-6(1)	-8(1)
Cr(2)	50(1)	49(1)	43(1)	2(1)	-11(1)	-12(1)
C(4C)	58(2)	65(2)	56(2)	2(1)	-16(1)	-17(1)
O(4)	93(2)	119(2)	48(1)	-3(1)	-16(1)	-28(2)
C(5C)	61(2)	76(2)	48(2)	-4(1)	-10(1)	-16(2)
O(5)	61(1)	132(2)	81(2)	-13(1)	-7(1)	-39(1)
C(6C)	75(2)	66(2)	50(2)	-2(1)	-7(1)	-7(2)
O(6)	129(2)	60(1)	93(2)	3(1)	-19(2)	13(2)
O(9)	76(1)	64(1)	54(1)	6(1)	-19(1)	-38(1)
O(10)	52(1)	52(1)	54(1)	1(1)	-6(1)	-12(1)
C(22)	50(1)	54(2)	47(1)	0(1)	-8(1)	-18(1)
C(23)	51(1)	46(1)	44(1)	-2(1)	-8(1)	-13(1)
C(24)	61(2)	50(1)	50(2)	-3(1)	-9(1)	-17(1)
C(25)	66(2)	45(1)	56(2)	4(1)	-12(1)	-10(1)
C(26)	56(2)	59(2)	55(2)	6(1)	-16(1)	-7(1)
C(27)	51(2)	66(2)	53(2)	-2(1)	-14(1)	-19(1)
C(28)	54(2)	46(1)	46(1)	0(1)	-11(1)	-17(1)
C(29)	44(1)	49(1)	45(1)	2(1)	-6(1)	-16(1)
C(30)	45(1)	49(1)	47(1)	-2(1)	-8(1)	-13(1)
C(31)	50(2)	60(2)	43(1)	2(1)	-7(1)	-23(1)
C(32)	56(2)	67(2)	47(1)	-8(1)	-5(1)	-22(1)
C(33)	70(2)	58(2)	58(2)	-13(1)	-11(1)	-11(1)
C(34)	64(2)	50(1)	53(2)	-4(1)	-17(1)	-11(1)
C(35)	57(2)	72(2)	55(2)	10(1)	-16(1)	-28(1)
C(36)	69(2)	98(2)	53(2)	10(2)	-21(1)	-39(2)
C(37)	81(2)	113(3)	52(2)	-10(2)	-12(2)	-54(2)
C(38)	80(2)	77(2)	55(2)	-13(1)	-5(2)	-34(2)
C(39)	51(2)	61(2)	53(2)	3(1)	-9(1)	-22(1)

C(40)	61(2)	77(2)	49(2)	7(1)	-10(1)	-32(2)
C(41)	77(2)	68(2)	67(2)	12(2)	-15(2)	-25(2)
C(42)	125(3)	88(2)	80(2)	13(2)	-39(2)	-69(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for Complex-**7a**

	x	y	z	U(eq)
H(3A)	462	785	-602	64
H(4A)	1558	-229	599	68
H(5A)	2560	504	1542	71
H(6A)	2509	2231	1242	71
H(7A)	-209	3351	-1128	58
H(12A)	1003	208	-3185	69
H(12B)	-31	638	-2312	69
H(13A)	1764	984	-2085	61
H(13B)	1867	1498	-3107	61
H(14A)	-1772	3845	-4206	76
H(15A)	-2532	3059	-5216	85
H(16A)	-1960	1291	-5199	81
H(17A)	-670	327	-4148	73
H(18A)	1387	3171	-3750	74
H(18B)	196	4009	-4070	74
H(19A)	1126	4289	-2430	85
H(20A)	500(40)	5530(30)	-3950(30)	93(13)
H(20B)	900(50)	5890(40)	-3030(40)	145(19)
H(21A)	1892	4674	183	162
H(21B)	2834	3636	513	162
H(21C)	1448	4036	1044	162
H(8)	-1780(30)	3740(20)	-2210(20)	53(10)

H(10)	-3290(30)	1380(20)	-3310(20)	62(11)
H(24A)	-5238	4041	-5409	65
H(25A)	-6282	4798	-6731	69
H(26A)	-7512	3993	-7341	71
H(27A)	-7763	2445	-6610	67
H(28A)	-5144	1675	-4247	58
H(33A)	-6144	5052	-2390	77
H(33B)	-6732	4170	-2116	77
H(34A)	-6380	4321	-3765	67
H(34B)	-4969	4227	-3753	67
H(35A)	-2798	1528	-1693	71
H(36A)	-2230	2340	-570	84
H(37A)	-3299	4049	-286	91
H(38A)	-4925	4948	-1117	82
H(39A)	-6505	2399	-1900	65
H(39B)	-6114	1463	-2562	65
H(40A)	-5179	1318	-814	73
H(41A)	-5820(30)	-110(30)	-1750(30)	93(11)
H(41B)	-5370(30)	-250(30)	-700(30)	84(11)
H(42A)	-7501	369	-5024	130
H(42B)	-6989	716	-6038	130
H(42C)	-8324	1353	-5531	130