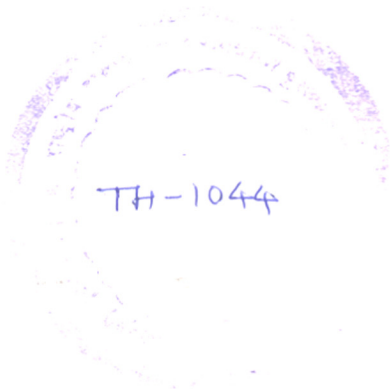


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**SYNTHESIS, STRUCTURE AND NEW REACTIVITY  
OF FISCHER CARBENE COMPLEXES**

A THESIS

SUBMITTED TO THE

**UNIVERSITY OF POONA**

FOR THE DEGREE OF

**DOCTOR OF PHILOSOPHY**

IN CHEMISTRY

**SK. RASIDUL AMIN**

DIVISION OF ORGANIC CHEMISTRY (SYNTHESIS)

NATIONAL CHEMICAL LABORATORY

PUNE 411 008



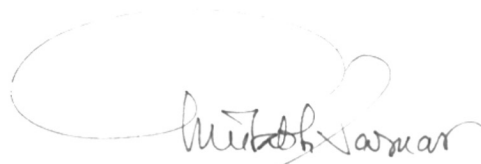
## CERTIFICATE

*This is to certify that the work incorporated in the thesis entitled "**Synthesis, Structure and New Reactivity of Fischer Carbene Complexes**" submitted by Sk. Rasidul Amin was carried out by him under my supervision at the National Chemical Laboratory. Such material as has been obtained from other sources has been duly acknowledged in the thesis.*

Date :

National Chemical Laboratory

Pune 411 008



( Dr. A. Sarkar )

Research Guide

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Sk. Rasidul Amin

DEDICATED TO PEOPLE WHO SUFFER FROM  
AND STAND AGAINST RELIGION

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## GENERAL REMARKS

1. All melting points (recorded on Thermo-nik Campbell melting point apparatus) are recorded on Celsius scale and are uncorrected.
2. IR spectra were recorded in chloroform, on a Perkin-Elmer Infrared Spectrometer Model 599-B using sodium chloride optics. IR bands are expressed in frequency ( $\text{cm}^{-1}$ ). Abbreviations, viz., s = strong, m = medium and sh = shoulder have been used.
3.  $^1\text{H}$  NMR spectra were recorded using trimethylsilane as internal reference on C-200 (Bruker 200 MHz FT NMR spectrometer) and  $^{13}\text{C}$  NMR spectra were recorded on C-200 at 50 MHz frequency and the chemical shifts were recorded in parts per million ( $\delta$ ). Abbreviations, viz., s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, dt = doublet of triplet, ddd = doublet of doublet of doublet, bs = broad singlet and m = multiplet have been used.  $\text{CDCl}_3$  was used as the solvent unless otherwise mentioned.
4. Known compounds were characterized by their IR,  $^1\text{H}$  NMR, and mass spectra.
5. Elemental analyses (C, H, N, S) were obtained on a Carlo-Erba 1100 automatic analyzer by Dr. S. Y. Kulkarni and his group at NCL.

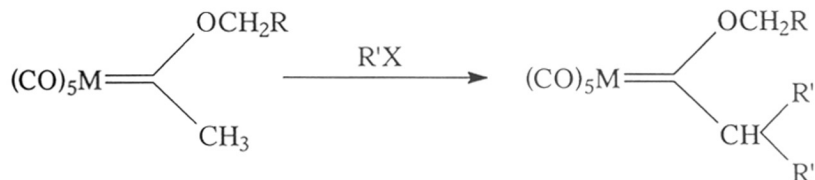
**ABBREVIATIONS**

BF <sub>3</sub> .Et <sub>2</sub> O	Borontrifluoridediethyletherate
BuLi	n-Butyl lithium
DMF	Dimethylformamide
Et <sub>2</sub> O	Diethyl ether
<i>m</i>	Meta
<i>o</i>	Ortho
<i>p</i>	Para
TB B	Tetrabutylammonium bromide
Tf	Trifluoromethylsulfonyl
THF	Tetrahydrofuran
TMS	Trimethylsilyl
Ts	<i>p</i> -Toluenesulfonyl

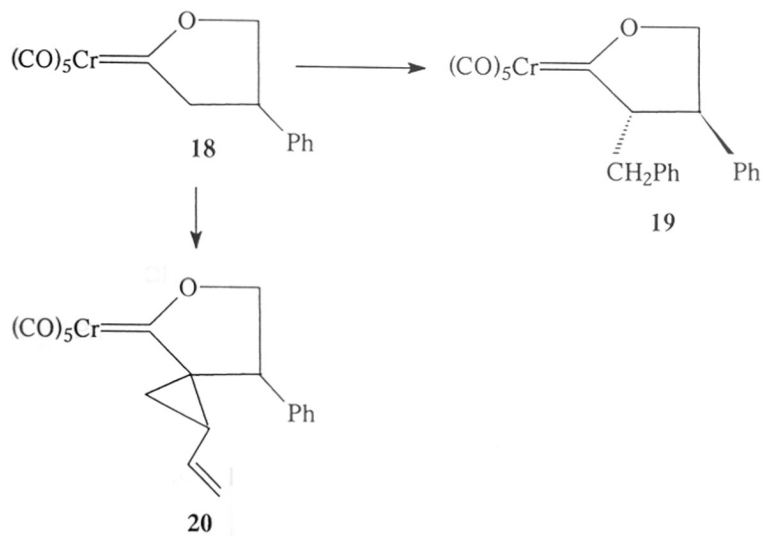
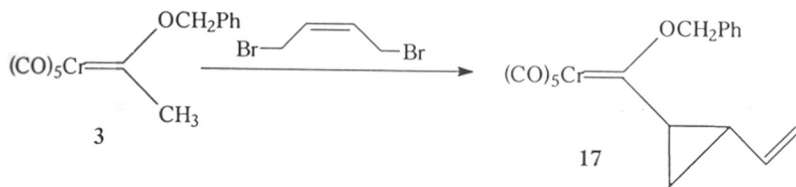
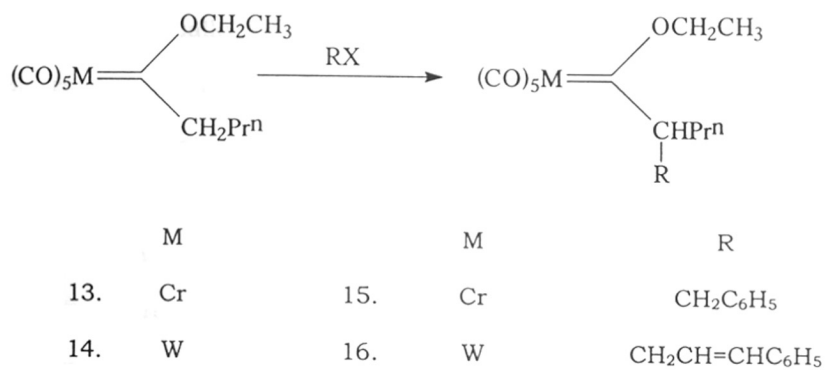
## SYNOPSIS OF THE THESIS

### Chapter-I. Phase-Transfer Catalysed Alkylation of Fischer Carbene Complexes

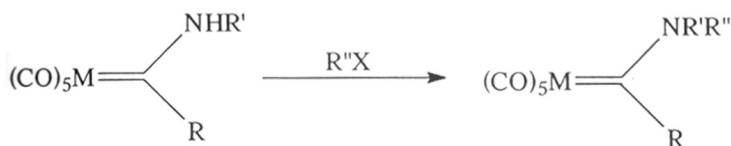
Taking cue from the pKa of Fischer carbene complexes measured in aqueous solvent, a new and practical synthetic procedure was developed to C-alkylate alkyl alkoxy carbene complexes of chromium and tungsten. Several structural types can be generated using this convenient protocol. Methyl carbene complexes underwent dialkylation with ease, and n-butyl carbene complex could be alkylated at the secondary position without difficulty. Diastereoselectivity of alkylation was probed using a bifunctional electrophile or cyclic, substituted carbene complexes. 11 new compounds were purified by chromatography and crystallisation. Structural assignments were based on spectral and microanalytical data. Stereochemical assignments were corroborated by X-ray crystallography.



	M	R		M	R	R'
1.	Cr	H	7a.	Cr	H	CH <sub>2</sub> CH=C(CH <sub>3</sub> ) <sub>2</sub>
2.	Cr	CH <sub>3</sub>	8a.	Cr	CH <sub>3</sub>	CH <sub>3</sub>
3.	Cr	C <sub>6</sub> H <sub>5</sub>	8b.	Cr	CH <sub>3</sub>	CH <sub>2</sub> CH=CH <sub>2</sub>
4.	W	H	8c.	Cr	CH <sub>3</sub>	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>
5.	W	CH <sub>3</sub>	9a.	Cr	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>
6.	W	C <sub>6</sub> H <sub>5</sub>	9b.	Cr	C <sub>6</sub> H <sub>5</sub>	CH <sub>2</sub> CH=CH <sub>2</sub>
			10a.	W	H	CH <sub>3</sub>
			10b.	W	H	CH <sub>2</sub> CH=C(CH <sub>3</sub> ) <sub>2</sub>
			11a.	W	CH <sub>3</sub>	CH <sub>2</sub> CH=CH <sub>2</sub>
			11b.	W	CH <sub>3</sub>	CH <sub>2</sub> CH=CHC <sub>6</sub> H <sub>5</sub>
			11c.	W	CH <sub>3</sub>	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>
			12a.	W	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>
			12b.	W	C <sub>6</sub> H <sub>5</sub>	CH <sub>2</sub> CH=CH <sub>2</sub>



The PTC procedure could be conveniently used for N-alkylation of amino carbene complexes. Typically, monoalkylamino complexes were converted to dialkylamino carbene complexes in excellent yield. Stereochemistry of the amino substituents with respect to the  $M(CO)_5$  fragment before and after alkylation was compared. When allyl halides were used as electrophile in N-alkylation of chromium carbene complexes, intramolecular chelation by the double bond of the allyl group was observed. Structural assignments relied mostly on the  $^1H$  NMR spectra of the complexes. 11 new complexes gave satisfactory spectral and analytical results.

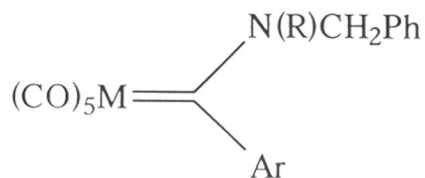
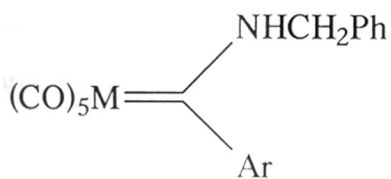


	M	R	R'		M	R	R'	R''
21a.	W	CH <sub>3</sub>	CH <sub>3</sub>	23a.	W	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>2</sub> CH=CH <sub>2</sub>
21b.	W	CH <sub>3</sub>	CH <sub>2</sub> Ph	23b.	W	CH <sub>3</sub>	CH <sub>2</sub> Ph	CH <sub>2</sub> CH=CH <sub>2</sub>
21c.	W	CH <sub>3</sub>	CH <sub>2</sub> Ph	23c.	W	CH <sub>3</sub>	CH <sub>2</sub> Ph	CH <sub>2</sub> Ph
21d.	W	Ph	CH <sub>2</sub> Ph	23d.	W	Ph	CH <sub>2</sub> Ph	CH <sub>2</sub> CH=CH <sub>2</sub>
22a.	Cr	CH <sub>3</sub>	CH <sub>3</sub>	24a.	Cr	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>2</sub> CH=CH <sub>2</sub>
22b.	Cr	CH <sub>3</sub>	CH <sub>3</sub>	24b.	Cr	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>2</sub> Ph
22c.	Cr	CH <sub>3</sub>	CH <sub>2</sub> Ph	24c.	Cr	CH <sub>3</sub>	CH <sub>2</sub> Ph	CH <sub>2</sub> CH=CH <sub>2</sub>
22d.	Cr	Ph	CH <sub>3</sub>	24d.	Cr	Ph	CH <sub>3</sub>	CH <sub>2</sub> Ph

Part of the work has been published : *Organometallics* **1995**, *14*, 547.

**Chapter-II.** *Conformational Study of Amino Carbene Complexes in Solution :  
Diastereotopicity as an Internal Stereochemical Probe*

A series of structurally related amino carbene complexes of chromium and tungsten were prepared and completely characterised. Many of the complexes featured N-CH<sub>2</sub>-Ph group(s) where the two methylene protons were found to be diastereotopic. This property was utilised in deducing relative orientation of the aromatic ring attached to the carbene carbon with respect to the metal-carbene  $\pi$ -plane. Using unsymmetrically substituted aromatic rings, it was possible to demonstrate with the help of <sup>1</sup>H NMR spectra at room temperature, that the aromatic ring prefers to remain in an orthogonal orientation with respect to the metal-carbene plane in solution, an aspect earlier known only in the solid state.



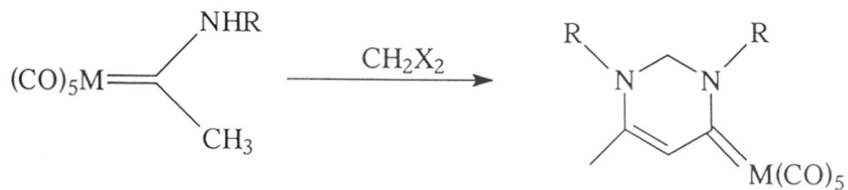
	M	Ar		M	Ar	R
1.	Cr	2-MeC <sub>6</sub> H <sub>4</sub>	10.	Cr	2-MeC <sub>6</sub> H <sub>4</sub>	Me
2.	Cr	2-OMeC <sub>6</sub> H <sub>4</sub>	11.	Cr	2-MeC <sub>6</sub> H <sub>4</sub>	CH <sub>2</sub> Ph
3.	Cr	3-MeC <sub>6</sub> H <sub>4</sub>	12.	Cr	2-OMeC <sub>6</sub> H <sub>4</sub>	CH <sub>2</sub> Ph
4.	Cr	3-OMeC <sub>6</sub> H <sub>4</sub>	13.	Cr	2-OMeC <sub>6</sub> H <sub>4</sub>	Me
5.	Cr	4-OMe-3-MeC <sub>6</sub> H <sub>3</sub>	14.	Cr	3-MeC <sub>6</sub> H <sub>4</sub>	CH <sub>2</sub> Ph
6.	Cr	4-MeC <sub>6</sub> H <sub>4</sub>	15.	Cr	3-OMeC <sub>6</sub> H <sub>4</sub>	CH <sub>2</sub> Ph
7.	Cr	1-Naphthyl	16.	Cr	4-OMe-3-MeC <sub>6</sub> H <sub>3</sub>	CH <sub>2</sub> Ph
8.	W	2-OMeC <sub>6</sub> H <sub>4</sub>	17.	Cr	4-MeC <sub>6</sub> H <sub>4</sub>	CH <sub>2</sub> Ph
9.	W	3-MeC <sub>6</sub> H <sub>4</sub>	18.	Cr	C <sub>6</sub> H <sub>5</sub>	CH <sub>2</sub> Ph
			19.	Cr	1-Naphthyl	CH <sub>2</sub> Ph
			20.	W	2-OMeC <sub>6</sub> H <sub>4</sub>	CH <sub>2</sub> Ph
			21.	W	3-MeC <sub>6</sub> H <sub>4</sub>	CH <sub>2</sub> Ph

Occasionally, accidental degeneracy of non-equivalent protons was observed. The degeneracy was lifted in certain cases by change of solvent. Where such solvent effect was not observed, the substitution pattern of the aromatic ring was altered to observe the non-equivalent methylene protons distinctly.

Part of the work has been submitted for publication in *Organometallics*.

### Chapter-III. A Novel Alkylation-Annulation Sequence of Amino Carbene Complexes.

When the solution of a monoalkylamino carbene complex in dichloromethane was stirred with 50% aq NaOH solution in the presence of a catalytic amount of tetrabutylammonium bromide at room temperature for 4 h, a new product was obtained. The structure of this new class of compounds was determined from the spectral data and the crystal structure solution of a representative compound. The formation of the product from two molecules of the starting complex has a close parallel with classical aldol condensation followed by cyclodehydration observed for 1,5-diketones (last steps of a Robinson annulation). The  $^{13}\text{C}$  chemical shifts of the carbene carbons in these new complexes are the lowest (most shielded carbene carbons) among the complexes reported so far.



	M	R		M	R
1a.	W	CH <sub>2</sub> Ph	2a.	W	CH <sub>2</sub> Ph
1b.	W	CH <sub>2</sub> CH=CH <sub>2</sub>	2b.	W	CH <sub>2</sub> CH=CH <sub>2</sub>
1c.	W	CH <sub>3</sub>	2c.	W	CH <sub>3</sub>
1d.	Cr	CH <sub>2</sub> Ph	2d.	Cr	CH <sub>2</sub> Ph
1e.	Cr	CH <sub>3</sub>	2e.	Cr	CH <sub>3</sub>

Part of the work has been published : *Organometallics* **1995**, 14, 3617.



## Chapter - I

# Phase-Transfer Catalyzed Alkylation of Fischer Carbene Complexes

## I.1 INTRODUCTION

Fischer carbene complexes<sup>1</sup> have emerged as versatile organometallic intermediates for a diverse array of target structures relevant to organic chemists. Among others, C-C bond formation *via* carbanions generated next to the carbene carbon, features prominently as a parallel to well-established enolate chemistry<sup>2</sup> in organic syntheses. Since the subject matter of this chapter pertains to such alkylation reactions, pertinent literature is being reviewed in the following pages as a background to the present work.

## I.2 BACKGROUND

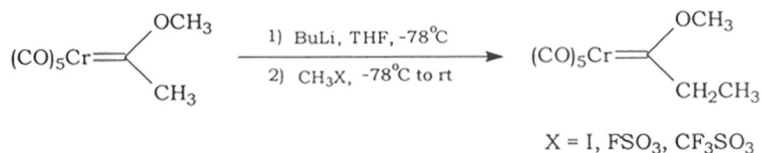
It is well known that the Fischer carbene complex is a relatively strong carbon acid. Kreiter<sup>3</sup> have shown that in a dilute solution of NaOCH<sub>3</sub> in CH<sub>3</sub>OD,  $\alpha$ -CH<sub>3</sub> of a Fischer carbene complex can be converted rapidly into  $\alpha$ -CD<sub>3</sub>. The basicity of Fischer carbene complex was first estimated by Casey<sup>4</sup> from a study of proton quench of the carbanion derived from methoxymethylchromiumcarbene complex, by different Bronsted acids. It was concluded that the  $pK_a$  of the relevant proton was 8.0, comparable to that of *p*-cyanophenol.

### Reactions of Carbene Anions

**Alkylation of Methyl Carbene Complexes.** Deprotonation of the methyl group is generally effected in tetrahydrofuran using *n*-butyl lithium as the base at -78°C. Casey and Anderson<sup>5</sup> have shown that alkylation of methoxymethylchromiumcarbene complex with methyl iodide produced the monoalkylated product in 22% yield (based on 9% recovery of the starting material). Methylation with methyl fluorosulfonate<sup>4</sup>

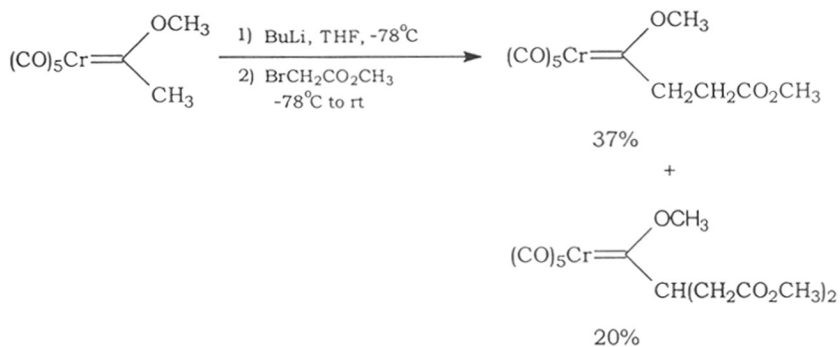
increased the yield of the product methoxyethylchromiumcarbene complex to 50%. Use of highly reactive methylating agent, e.g., methyl trifluoromethylsulfonate resulted in 83% yield of the product<sup>6</sup> (Scheme I.1).

### Scheme I.1



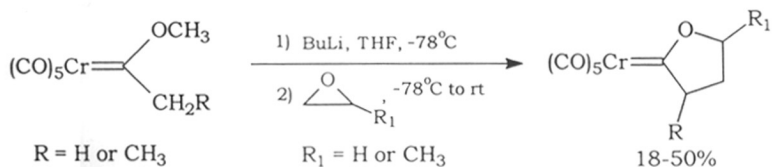
Reaction with methyl bromoacetate<sup>7</sup> afforded the monoalkylated product in 37% yield and the dialkylated product in 20% yield (Scheme I.2).

### Scheme I.2



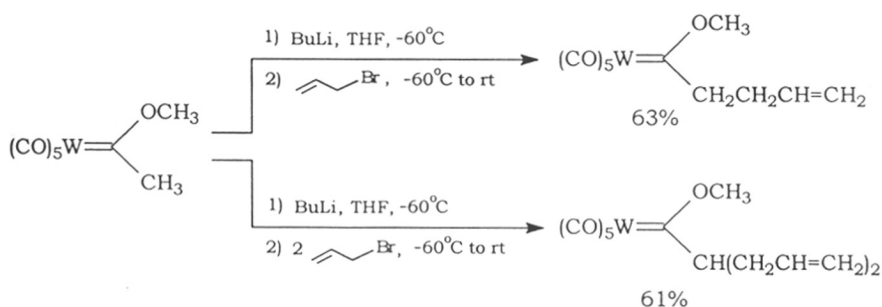
Anion of methoxymethylchromiumcarbene complex reacts with a variety of epoxides (Scheme I.3) to generate 2-oxacyclopentylidene carbene complexes.<sup>6</sup>

### Scheme I.3



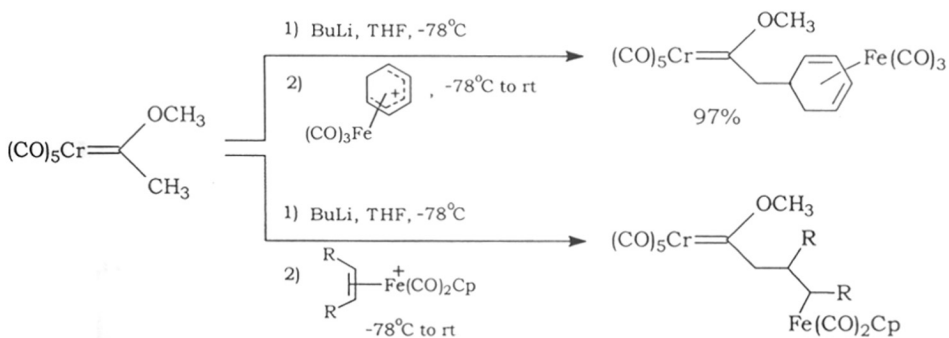
Maiorana<sup>8</sup> have shown that the yield and scope of the reaction can be increased in the presence of boron trifluoride etherate as the Lewis acid. With unsymmetrical epoxides, it was possible to get complete regioselectivity where the carbene anion attacks the less hindered position. In case of styrene oxide, the reverse regioisomeric product was obtained. Rudler<sup>9</sup> have shown that methoxymethyltungstencarbene complex can be mono- or diallylated (Scheme I.4) using *n*-butyllithium/allyl bromide at  $-60^{\circ}\text{C}$  in good yield.

**Scheme I.4**



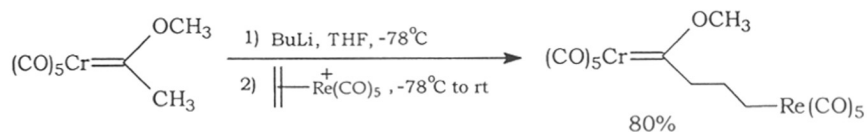
Kelley<sup>10</sup> observed that the anion of methoxymethylchromiumcarbene complex can undergo alkylation with  $\eta^5$ -cyclohexadienyl iron cations as well as cationic iron alkene complexes (Scheme I.5).

**Scheme I.5**



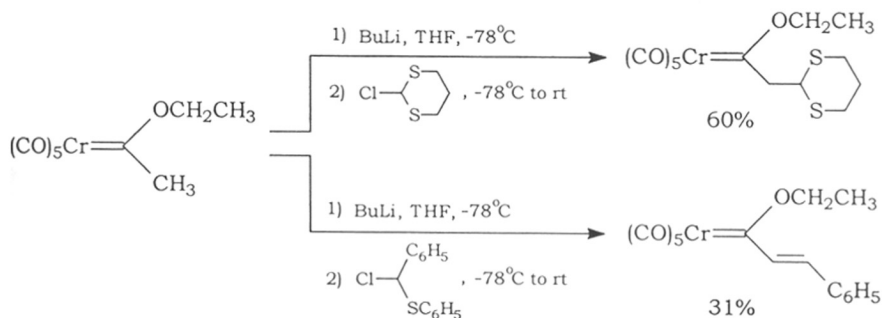
Similar nucleophilic addition can take place on cationic rhenium alkene complex<sup>11</sup> (Scheme I.6).

### Scheme I.6



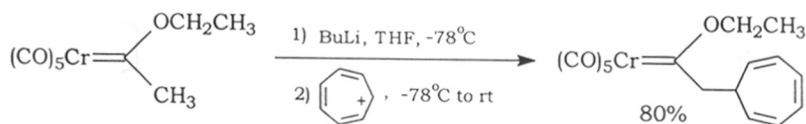
Raubenheimer<sup>12</sup> reported that 2-chloro-1,3-dithianes and  $\alpha$ -chloro sulfides can also be alkylated with carbene anion to produce 2-substituted dithiane and  $\alpha,\beta$ -unsaturated carbene complexes respectively (Scheme I.7).

### Scheme I.7



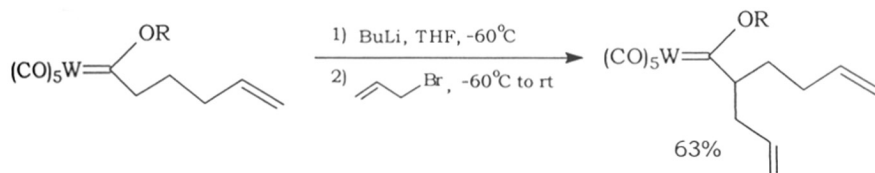
One can also alkylate tropylium cation (Scheme I.8) as shown by Aumann<sup>13</sup> and Breimair.<sup>14</sup>

### Scheme I.8



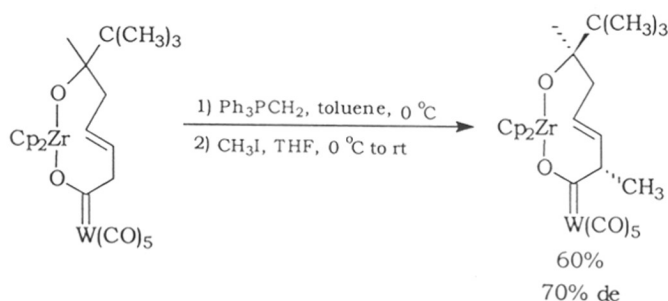
**Alkylation at secondary center.** Relatively few examples are known for alkylation at secondary center. Rudler<sup>8</sup> observed that secondary center of tungsten carbene complex can be allylated with allylbromide in the presence of n-butyllithium in tetrahydrofuran (Scheme I.9).

**Scheme I.9**



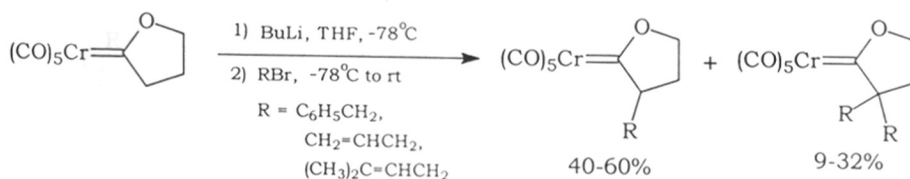
Erker<sup>17</sup> established that with a suitable cyclic tungsten carbene complex, a remote 1,5-asymmetric induction can be achieved (Scheme I.10).

**Scheme I.10**



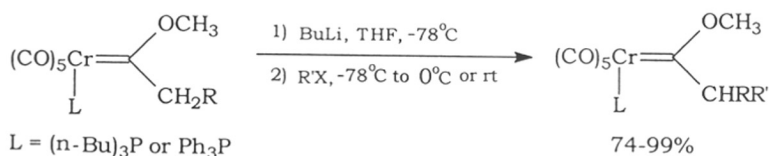
Casey<sup>18</sup> found that alkylation of pentacarbonyl(2-oxacyclopentylidene)chromium-carbene complex with reactive electrophiles (Scheme I.11) was fraught with problem of dialkylation.

**Scheme I.11**



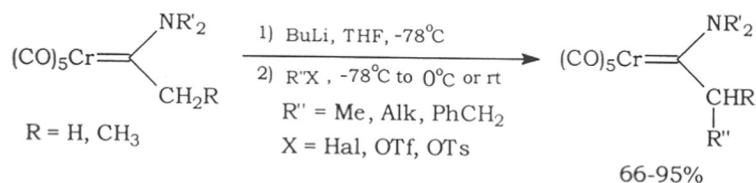
**Alkylation of Modified Carbene Complex.** Wulff<sup>5</sup> established that the reactivity of carbene anions towards various electrophiles can be increased by replacing one of the carbonyl group with tri-n-butylphosphine which is more electron donating in nature than that of a carbonyl group and makes the  $pK_a$  of  $\alpha$ -proton higher ( $\sim 19$ ). Thus, a wide range of electrophiles reacts with carbene complexes (Scheme I.12) in excellent yield (74-99%) to generate synthetically more useful intermediates.

**Scheme I.12**



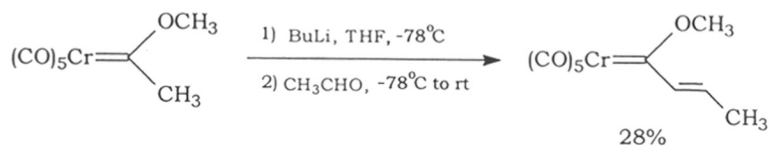
**Alkylation of Aminocarbene Complexes.** Since  $pK_a$  of amino carbene complexes (20.5) are higher than that of alkoxy analogue,<sup>15</sup> anion of amino carbene complexes are expected to be more reactive, which was indeed observed. Unlike alkoxy carbene complexes, amino analogues can be alkylated with simple aliphatic halides,<sup>16</sup> e.g., iodides, bromides and even tosylates (Scheme I.13) in good to excellent yield (66-95%).

**Scheme I.13**



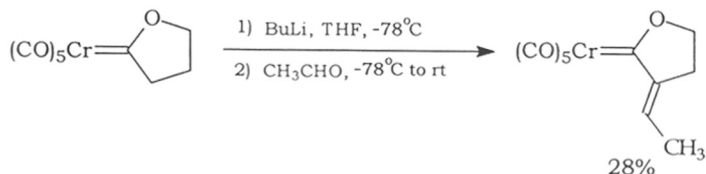
**Aldol reaction.** Casey<sup>19</sup> reported the first aldol reaction of carbene complexes but observed that<sup>19b</sup> only nonenolisable aldehydes can provide the condensation product with methylmethoxychromiumcarbene complex (Scheme I.14) in poor to moderate yield.

**Scheme I.14**



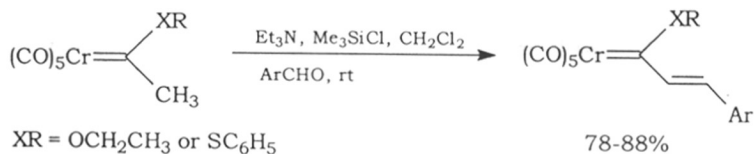
With the 2-oxacyclopentylidene complex, enolisable aldehydes can also produce the condensation product (Scheme I.15) albeit in low yield.<sup>19a</sup>

**Scheme I.15**



Aumann<sup>20</sup> developed a convenient procedure so that aromatic aldehydes can be condensed with Fischer carbene complexes (Scheme I.16) in very good yields (78-88%).

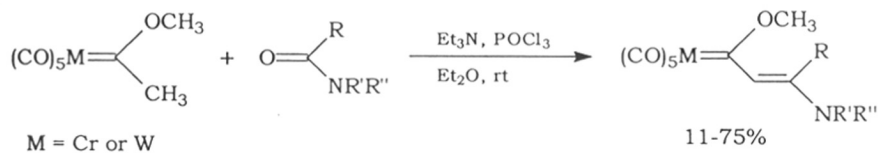
**Scheme I.16**





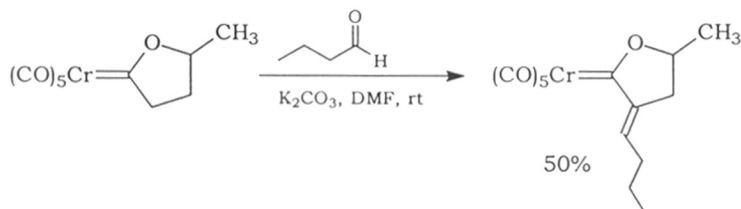
In a similar type of reaction,<sup>21</sup> using phosphorous oxychloride instead of trimethylsilyl chloride as an activating agent for the aldehyde, N,N-dialkylamides has been used and it was observed that formic acid and benzoic acid amides gave the best results (Scheme I.17).

**Scheme I.17**



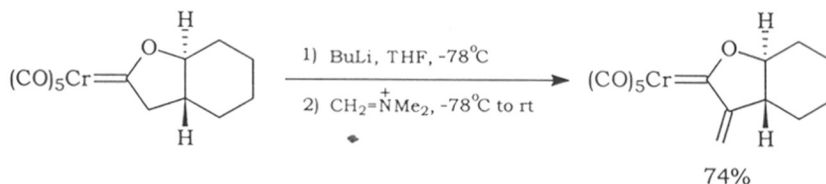
Another example of aldol reaction has been reported by Maiorana<sup>22</sup> where 2-oxacyclopentylidencarbene complex condensed with n-butanal in the presence of potassium carbonate in N,N-dimethylformamide (Scheme I.18).

**Scheme I.18**



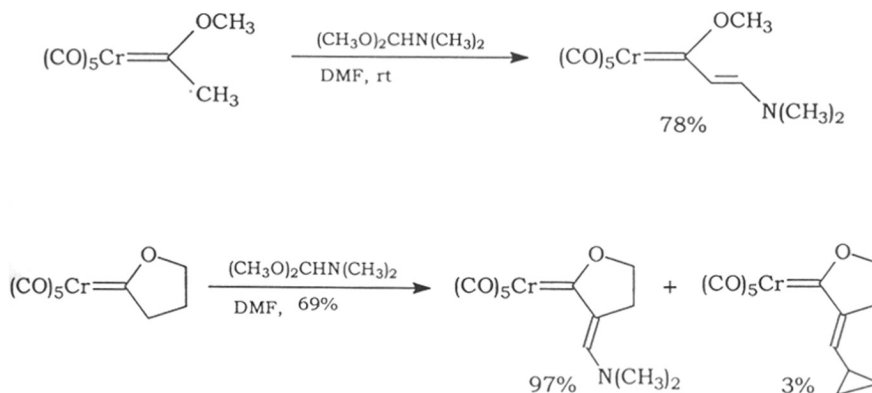
In a related aldol reaction,<sup>23</sup> Eschenmoser's salt was used (Scheme I.19).

**Scheme I.19**



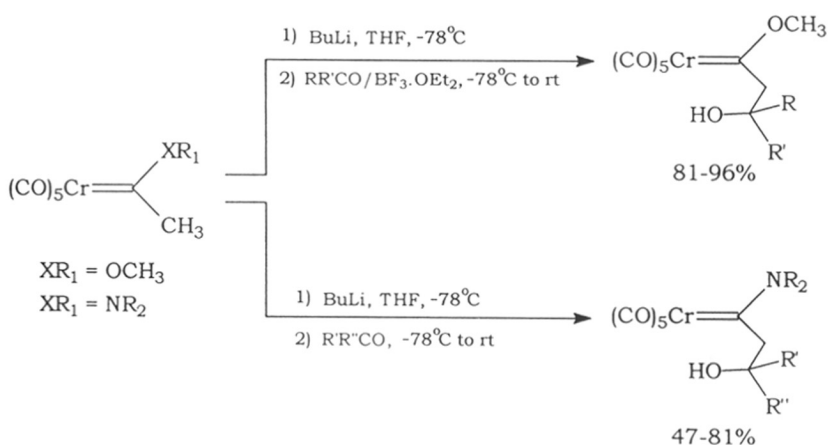
Dimethylformamide dimethyl acetal can also be used for the aldol reaction with carbene complexes (Scheme I.20) as shown by Maiorana.<sup>24</sup> In case of 2-oxacyclopentylidene complex, an unexpected product was obtained in minor amount (3%).

**Scheme I.20**



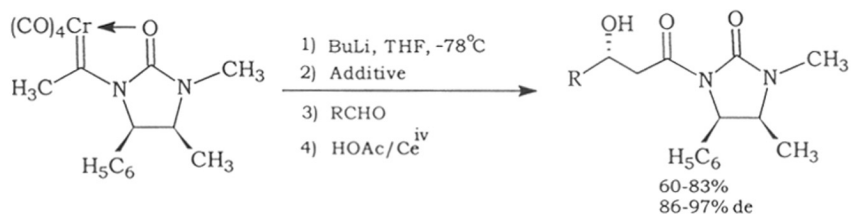
In 1985, Wulff<sup>25</sup> established that aldol reactions can be generalized for all types of carbonyl compounds provided they are preactivated by a Lewis acid. In case of amino carbene complexes, aldol reaction can take place without the presence of a Lewis acid (Scheme I.21) which reflects greater reactivity of the aminocarbene anion.<sup>26</sup>

**Scheme I.21**



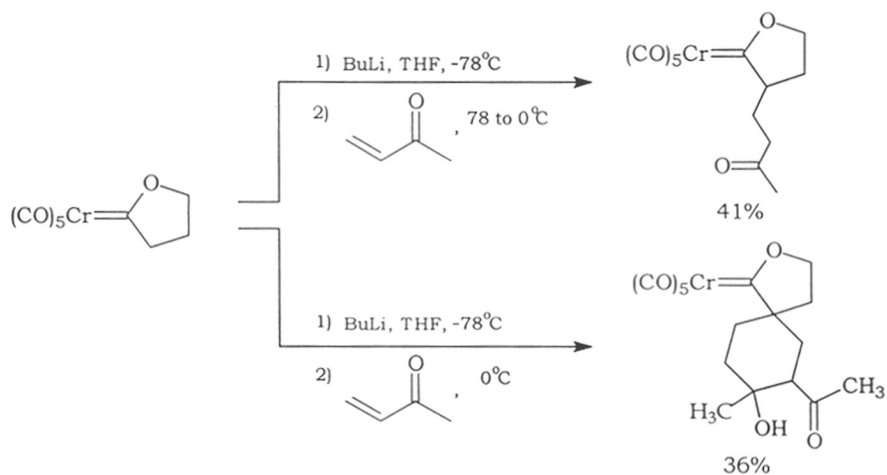
Wulff<sup>27</sup> achieved very good diastereoselectivity in asymmetric aldol reactions starting from chiral aminocarbene complex and aldehydes in good yields (Scheme I.22).

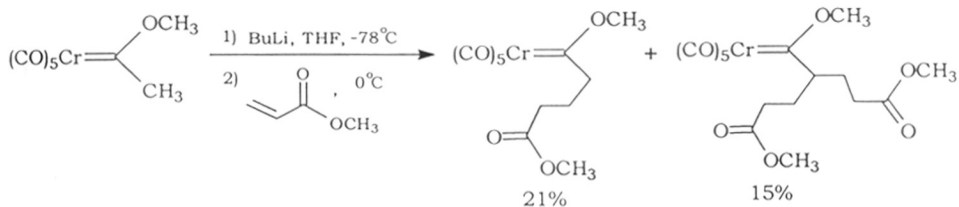
**Scheme I.22**



**Michael Addition Reactions.** In 1977, Casey<sup>28</sup> reported the first Michael addition reaction of alkoxy-carbene anion to  $\alpha,\beta$ -unsaturated carbonyl compounds. For 2-oxacyclopentylidene-carbene complex, either mono- or di-substituted product was obtained by using stoichiometric or catalytic amount of base respectively. An acyclic carbene complex provided a mixture of mono- and di-substituted products (Scheme I.23).

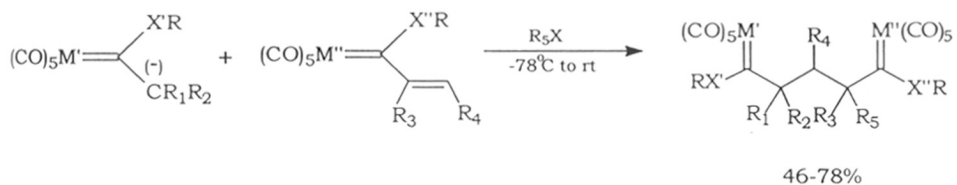
**Scheme I.23**





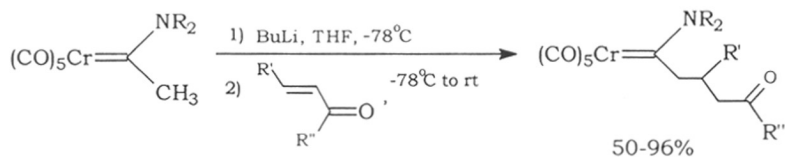
Macomber<sup>29</sup> established a general route for the preparation of  $[\mu\text{-bis(carbene)}]\text{dimetal}$  complexes starting from carbene complexes both as a Michael donor and an acceptor (Scheme I.24).

**Scheme I.24**



Exploiting the higher reactivity of aminocarbene anions, Wulff<sup>30</sup> developed a general method of Michael addition reaction between an aminocarbene anion and  $\alpha,\beta$ -unsaturated carbonyl compounds (Scheme I.25).

**Scheme I.25**



Using optically pure aminocarbene complexes derived from optically pure L(-)-prolinol, it is possible to obtain<sup>30</sup> moderate to good diastereoselectivity (60-95% *de*).

*Michael addition of nucleophiles with  $\alpha,\beta$ -unsaturated carbene complex<sup>31</sup> have been studied extensively but not discussed here.*

A few general trends, therefore, emerge from the discussion of  $\alpha$ -carbanion chemistry of Fischer carbene complexes. Although the *pK<sub>a</sub>* of methyl proton in the prototype complex  $(\text{CO})_5\text{Cr}=\text{C}(\text{OCH}_3)\text{CH}_3$  was estimated as 8.0 and widely cited,<sup>4</sup> in most instances a strong base such as *n*-butyllithium has been used to generate the carbanion. To effect a C-C bond formation, the electrophiles used were either highly reactive (e.g. triflates) or activated by the presence of an excess of Lewis acid. Often, dialkylation has been a disturbing side-reaction rather than a preparatively useful conversion.<sup>32</sup> Alkylation of a secondary carbanion was not efficient. However, since the Fischer carbene complexes are considered ester or amide equivalents, carbanion chemistry of these complexes were revisited to explore alternative, effective procedures.

### 1.3 PRESENT WORK

In 1989, Gandler and Bernasconi<sup>33</sup> determined the *pK<sub>a</sub>* of  $(\text{CO})_5\text{Cr}=\text{C}(\text{OCH}_3)\text{CH}_3$  in aqueous piperidine as 12.3, which was different from the previous estimate.<sup>4</sup> The value of 12.3 was in the same domain of *pK<sub>a</sub>* of 1,3-dicarbonyl compounds like dimethyl malonate (*pK<sub>a</sub>* 13.0)<sup>33</sup> or ethyl acetoacetate (*pK<sub>a</sub>* 11).<sup>34</sup> This suggested that a strong base was certainly not essential to deprotonate the methyl group adjacent to carbene carbon in Fischer carbene complexes. It was also tempting to retain water in the reaction medium so that the magnitude of *pK<sub>a</sub>* determined in aqueous medium

remains relevant. While considering a parallel between alkylation of 1,3-dicarbonyl compounds and alkylation of alkyl carbene complexes, it occurred to us that a biphasic condition using a phase-transfer catalyst may be explored.

Phase-transfer catalysis has been a versatile experimental tool for a wide variety of organic<sup>35</sup> and organometallic<sup>36</sup> reactions. As a common practice, the non-polar substrates are dissolved in a suitable organic solvent which is immiscible with water. The polar reagent is dissolved in the aqueous phase. A tetraalkylammonium or phosphonium salt is employed catalytically to transport the reagent from the aqueous to the organic phase (or the phase-boundary) where the reaction takes place to yield the product. Immiscibility of the two layers assist in conveniently separating the product from the reagent. While this is an example of liquid-liquid phase-transfer catalysis, solid-liquid phase-transfer is also quite common.

Hoye<sup>37</sup> reported the first use of quaternary ammonium salts in an improved alkylation of acylmetallates *en route* to preparation of Fischer carbene complexes. These results established the compatibility of carbene complexes with phase-transfer conditions.

In the context of alkylation of Fischer carbene complexes, two advantages were envisaged. First, given the pKa range, the unsolvated OH anion in organic phase was considered adequate to effect deprotonation of alkyl carbene complexes. Second, non-coordinating cation like tetraalkylammonium or tetraalkylphosphonium, would not form a tight ion-pair so as to diminish the nucleophilicity of the carbene carbanion, and yield of alkylated product would be enhanced.

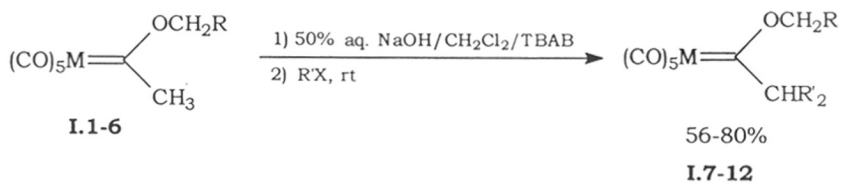
### **Dialkylation of Methylcarbene Complex**

In the first set of experiments, 50% aq NaOH was taken as the base, dichloromethane as the organic solvent and tetrabutylammonium bromide as PTC.

Experiments were conducted in 1-2 mmol scale under argon using degassed solvents at room temperature. The substrate complexes **I.1-I.6** were prepared following literature procedures (see experimental).

The alkylation proceeded smoothly at room temperature with reactive halides like methyl iodide, allyl chlorides or bromides and benzyl bromide. The products were always the dialkylated carbene complexes **I.7 - I.12b** (Scheme-I.26).

**Scheme-I.26**

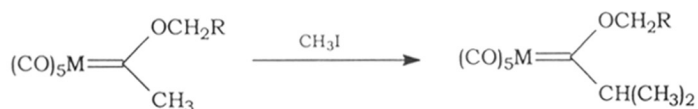


Substrate	M	R	Product	M	R	R'	Time	Yield (%)
<b>I.1</b>	Cr	H	<b>I.7</b>	Cr	H	CH <sub>2</sub> CH=C(CH <sub>3</sub> ) <sub>2</sub>	4 h	73
<b>I.2</b>	Cr	CH <sub>3</sub>	<b>I.8a</b>	Cr	CH <sub>3</sub>	CH <sub>3</sub>	15 h	64
<b>I.3</b>	Cr	C <sub>6</sub> H <sub>5</sub>	<b>I.8b</b>	Cr	CH <sub>3</sub>	CH <sub>2</sub> CH=CH <sub>2</sub>	3.5 h	70
<b>I.4</b>	W	H	<b>I.8c</b>	Cr	CH <sub>3</sub>	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	3 h	56
<b>I.5</b>	W	CH <sub>3</sub>	<b>I.9a</b>	Cr	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	15 h	64
<b>I.6</b>	W	C <sub>6</sub> H <sub>5</sub>	<b>I.9b</b>	Cr	C <sub>6</sub> H <sub>5</sub>	CH <sub>2</sub> CH=CH <sub>2</sub>	3 h	80
			<b>I.10a</b>	W	H	CH <sub>3</sub>	15 h	58
			<b>I.10b</b>	W	H	CH <sub>2</sub> CH=C(CH <sub>3</sub> ) <sub>2</sub>	4 h	70
			<b>I.11a</b>	W	CH <sub>3</sub>	CH <sub>2</sub> CH=CH <sub>2</sub>	3 h	63
			<b>I.11b</b>	W	CH <sub>3</sub>	CH <sub>2</sub> CH=CHC <sub>6</sub> H <sub>5</sub>	1.5 h	56
			<b>I.11c</b>	W	CH <sub>3</sub>	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	3 h	62
			<b>I.12a</b>	W	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	15 h	61
			<b>I.12b</b>	W	C <sub>6</sub> H <sub>5</sub>	CH <sub>2</sub> CH=CH <sub>2</sub>	3.5 h	78

The products were readily identified by their proton NMR spectra which showed additional peaks due to two units of the electrophile. After purification by flash column chromatography, all solids were recrystallized to yield analytically pure samples. The liquid complexes, in most instances, did not provide satisfactory elemental analysis.<sup>38</sup> The <sup>13</sup>C NMR spectra of the complexes revealed the presence of deshielded carbene carbon around 338-345 (for tungsten complexes) and 364-370 (for chromium complexes), while other peaks were consistent with the relevant structures.

**Reaction with Methyl Iodide.** After methylation (Scheme I.27), a doublet around 1.00 for the two methyl groups and a heptet for the methine proton around 4.20 appear in <sup>1</sup>H NMR spectra for the isopropyl group of the product, instead of the methyl peak around 3.00 of the starting material is absent. The <sup>13</sup>C NMR spectra shows peaks at around 18.0 and 60.0-62.0 for the methyl and methine carbon respectively of the isopropyl group.

**Scheme I.27**

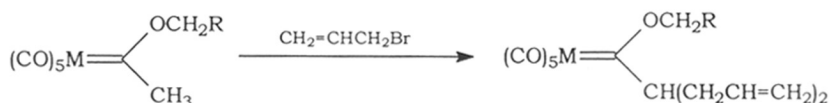


Substrate	M	R	Product	Yield (%)
I.2	Cr	CH <sub>3</sub>	I.8a	64
I.3	Cr	C <sub>6</sub> H <sub>5</sub>	I.9a	64
I.4	W	H	I.10a	58
I.6	W	C <sub>6</sub> H <sub>5</sub>	I.12a	61



**Reaction with Allyl Bromide.** The characteristic peaks in  $^1\text{H}$  NMR spectra for the allylated products (Scheme I.28) are two multiplets in the range of 1.90-2.45 for the two sets of methylene protons and a pentet for the methine proton at around 4.25. Also, olefinic protons of the two allyl groups appear at 4.90-5.20 for the four methylene protons and at 5.60-5.90 for the two methine protons. The characteristic peaks in  $^{13}\text{C}$  NMR spectra are due to two methylene carbons around 36.0 and two olefinic carbons around 117.0 (methylene carbons) and 135.0 (methine carbons).

**Scheme I.28**

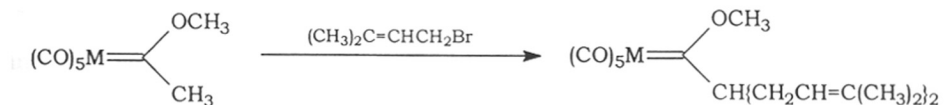


Substrate	M	R	Product	Yield (%)
<b>I.2</b>	Cr	CH <sub>3</sub>	<b>I.8b</b>	70
<b>I.3</b>	Cr	C <sub>6</sub> H <sub>5</sub>	<b>I.9b</b>	80
<b>I.5</b>	W	CH <sub>3</sub>	<b>I.11a</b>	63
<b>I.6</b>	W	C <sub>6</sub> H <sub>5</sub>	<b>I.12b</b>	78

**Reaction with Prenyl Bromide.** After reaction with prenyl bromide (Scheme I.29), in the  $^1\text{H}$  NMR spectra of the products, methyl peak of the starting material around 3.00 disappears. Instead, two singlets appear at around 1.55 and 1.65 for the four methyl groups. Other characteristic peaks are two multiplets around 1.80-2.30 for two methylene groups; one pentet around 4.13 for the methine proton and a multiplet around 5.15 for the two olefinic CH protons. In  $^{13}\text{C}$  NMR spectra, characteristic peaks around 17.0 and 25.0-28.0 appear for the four methyl carbons. The signal around

31.0 is due to two methylene carbons and four olefinic carbons appear around 121.0 (two methylene carbons) and 133.0 (two methine carbons).

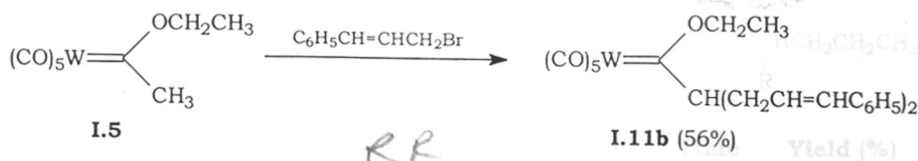
**Scheme I.29**



Substrate	M	Product	Yield (%)
I.1	Cr	I.7	73
I.4	W	I.10b	70

**Reaction with Cinnamyl Chloride.** New characteristic peaks in  $^1\text{H}$  NMR spectrum for the product **I.11b** which has been obtained by the reaction of **I.5** with cinnamyl chloride (Scheme I.30) are the two multiplets for the two methylene groups in the range of 2.20-2.65; one pentet at 4.35 for the methine proton; a multiplet at 6.10-6.50 for the olefinic protons and multiplet due to the phenyl protons at 7.20-7.45. In  $^{13}\text{C}$  NMR spectrum, new signals appear at 35.53 due to two methylene carbons, 72.38 due to the methine carbon and 126.85-137.38 for the olefinic and aromatic carbons.

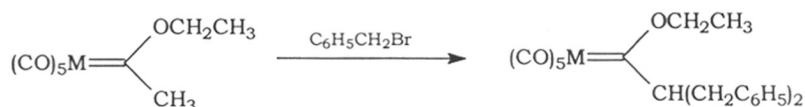
**Scheme I.30**



RR  
547.313(043)  
AMI

**Reaction with Benzyl Bromide.** In  $^1\text{H}$  NMR spectra, new peaks due to the products **I.8c** and **I.11c** (Scheme I.31) appear around 2.50 and 3.00 as AB quartet for two sets of methylene protons; a pentet around 4.60 for the methine proton and a multiplet at 7.00-7.50 for the phenyl protons. The characteristic peaks in  $^{13}\text{C}$  NMR spectra are the two methylene carbons signal which appear at around 37.0, one methine carbon around 75.0 and aromatic signals around 126.0 to 139.0.

**Scheme I.31**

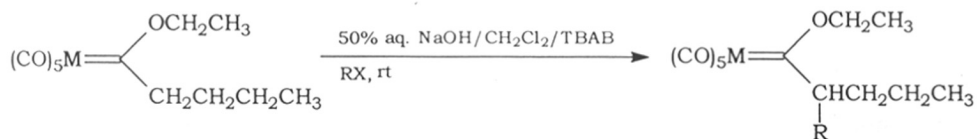


Substrate	M	Product	Yield (%)
<b>I.2</b>	Cr	<b>I.8c</b>	56
<b>I.5</b>	W	<b>I.11c</b>	62

### Monoalkylation of Methylenecarbene Complex

Dissimilar substitution at the carbon atom adjacent to the carbene carbon can be achieved if one begins with a R-CH<sub>2</sub>- group in the carbene, as in the case of complex **I.13** or **I.14** shown below (Scheme-I.32).

**Scheme I.32**



Substrate	M	Product	M	R	Time	Yield (%)
<b>I.13</b>	Cr	<b>I.15</b>	Cr	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	4.5 h	67
<b>I.14</b>	W	<b>I.16</b>	W	CH <sub>2</sub> CH=CHC <sub>6</sub> H <sub>5</sub>	2 h	69

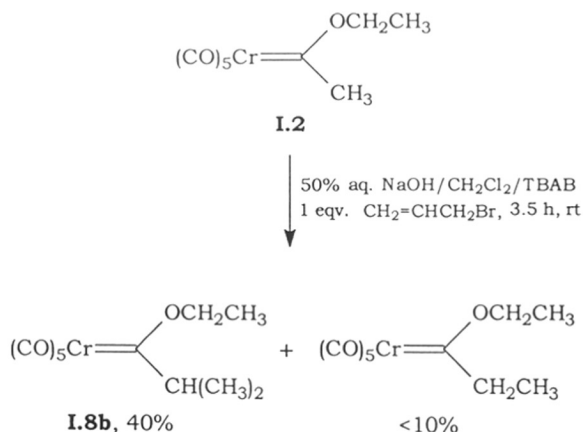
Different group can be introduced by alkylation of the  $\alpha$ -carbon. Under PTC condition, with excess benzyl bromide or cinnamyl chloride, yields of 67 and 69% were obtained for the corresponding monoalkylated products. Benzylation of the complex **I.13** causes disappearance of the triplet at 3.55 for the methylene protons adjacent to the carbene carbon and new peaks has been observed at 2.45 and 2.47 as two AB quartets due to two benzylic protons. Also, methine proton signal at 4.15-4.30 as a multiplet and aromatic protons at 7.06-7.32 are the characteristic signals of the product. In  $^{13}\text{C}$  NMR spectrum of **I.15**, benzylic carbon appears at 38.17 and aromatic carbon signals have been observed in the region of 126-140.

Formation of the product **I.16** was established from the observation of characteristic peaks in  $^1\text{H}$  NMR spectrum, *viz.*, two multiplets at 2.10-2.55 due to two methylene protons of the cinnamyl group; a pentet at 4.20 due to methine proton attached to carbene carbon as well as olefinic and aromatic proton signals in the expected positions. In  $^{13}\text{C}$  NMR spectrum, the significant signals are observed at 35.84 due to the methylene carbon of cinnamyl group, while olefinic and aromatic carbon peaks appear in the range of 126.0-137.0.

While such flexibility in functionalization of carbene complexes is useful, the PTC protocol adds to it the convenience of operational ease.

**Attempted Monoalkylation of Methylcarbene complex.** Several attempts to stop the reaction at the monoalkylated stage did not succeed. When ethoxymethylchromiumcarbene complex **I.2** and an equivalent amount of allyl bromide was used, the reaction product consisted of a mixture containing the dialkylated product **I.8b** (40%), starting material (30%) and a little monoalkylated product (<10%) after stirring 3.5 h (Scheme I.33).

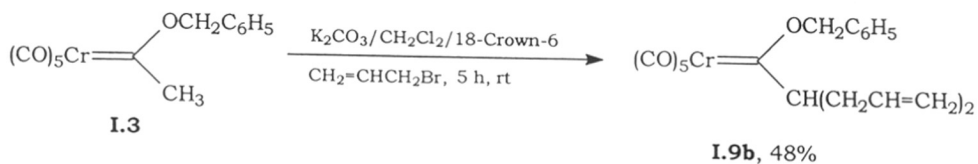
## Scheme I.33



Monoalkylated and dialkylated products could not be separated. Earlier, it was known from the work of Casey<sup>18a</sup> that the anion of methyl carbene complex is 2-5 times more reactive than that of the corresponding methylene depending on the nature of electrophiles. The above experiment also confirmed that secondary anion is kinetically more reactive than the primary anion.

**Alternative PTC conditions.** Alkylation reaction has been tried in the presence of other phase-transfer catalysts. Benzyloxymethylchromiumcarbene complex **I.3** was treated with allyl bromide in the presence of potassium carbonate as the base and 18-Crown-6 as the catalyst (Scheme I.34). The reaction required longer time (5 h) for completion than necessary for usual catalyst (TBAB, 3 h) and yield of the product **I.9b** suffered (48% as compared to 80%).

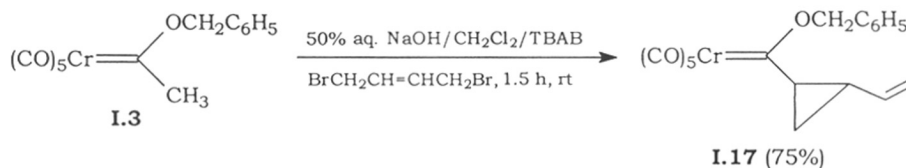
## Scheme I.34



**Limitations of electrophiles.** Only reactive electrophiles, *viz.*, methyl iodide, allyl bromide or chloride and benzyl bromide do alkylate under PTC conditions which shows that the reaction is rather limited and can not be used for a wide range of electrophiles.<sup>39</sup>

**Reaction of I.3 with 1,4-Dibromo-2-butene.** Since the methyl alkoxy carbene complexes were found to undergo convenient and exclusive dialkylation with reactive alkylating agents, cyclization was attempted with a bifunctional electrophile such as 1,4-dibromo-2-butene. As precedented<sup>40</sup> and as would be anticipated from the relative facility of 3- over 5-membered ring-closure, dialkylation resulted in the formation of a vinylcyclopropane derivative (Scheme I.35) as a single diastereomer in 75% yield.

**Scheme I.35**

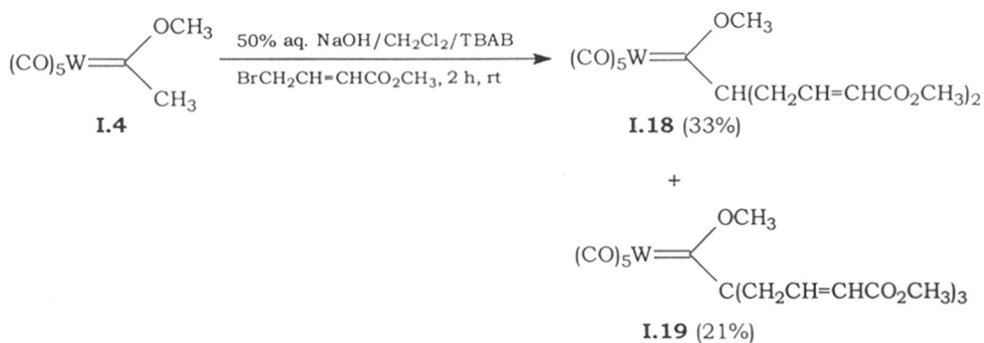


In <sup>1</sup>H NMR spectrum, the methyl signal due of the starting material **I.3** disappears and new peaks observed are consistent with the formation of a vinyl cyclopropane moiety. Four cyclopropane proton signals appear at four different positions and were assigned by decoupling experiments. Multiplets at 1.22-1.38 and 1.78-1.90 are due to the methylene protons of the cyclopropane ring; a doublet of doublet of doublet at 2.25 is due to methine proton attached to the vinyl group and a multiplet at 3.42-3.55 is due to the methine proton attached to the carbene carbon. Vinyl methylene

and methine protons appear as two multiplets at 4.98-5.23 and 5.40-5.60 respectively. The coupling constant of 3.6 Hz between two methine protons on the cyclopropane indicated their *trans* relationship.<sup>41</sup> Characteristic <sup>13</sup>C NMR signals appear at 24.4, 36.1 and 50.9 due to three carbons of cyclopropane ring besides two olefinic carbon signals at 115.9 and 137.7.

**Reaction of I.4 with 4-Bromocrotonate.** Methyl bromocrotonate was tested as another bifunctional electrophile which offers the possibility of alkylation followed by Michael addition to the conjugated double bond to provide a three-membered ring. However, only alkylation products (Scheme I.36) were observed. Interestingly in this instance up to three molecules of crotonate were found to have been appended to the carbene.

**Scheme I.36**

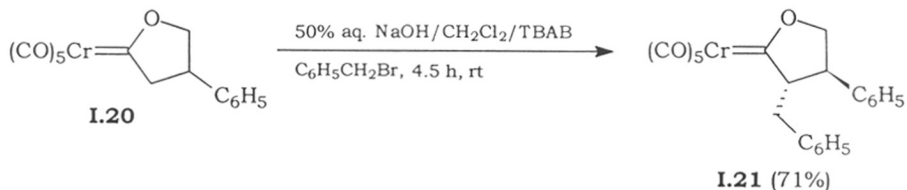


From <sup>1</sup>H NMR spectroscopy, one can easily distinguish the dialkylated product **I.18** from the trialkylated one (**I.19**). For instance, the methine proton attached to carbene carbon at 4.22 as a pentet is present in **I.18** whereas in **I.19** it is absent due to quaternary nature of the carbon. Another distinctive signal is due to methylene

protons of the crotonate group. In case of the dialkylated product **I.18**, it shows two multiplets at 2.05-2.50 whereas in the corresponding trialkylated product **I.19**, a doublet of doublet at 2.75 is observed due to coupling with the adjacent allylic proton and a further small allylic coupling.

**Reaction of I.20 with Benzyl Bromide.** Diastereoselectivity of alkylation was probed with the cyclic substrate **I.20**, prepared from the methyl methoxy chromium carbene complex **I.1** and styrene oxide following a reported procedure.<sup>8d</sup> Such cyclic structures are relevant for synthesis of butenolides and other natural products with a  $\gamma$ -butyrolactone skeleton.<sup>42</sup> Alkylation of **I.20** with one equivalent of benzyl bromide (Scheme I.37) yielded a diastereomerically pure product **I.21** in 71% isolated yield.

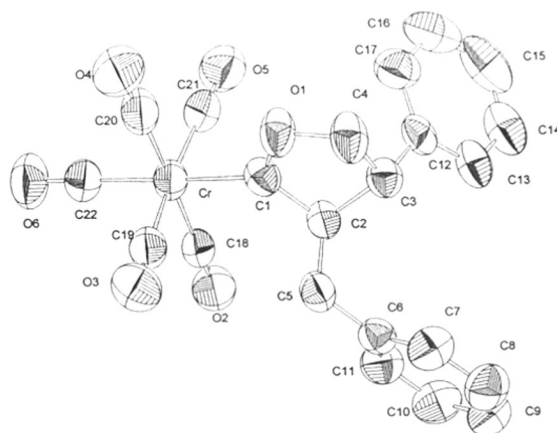
**Scheme I.37**



The product was characterized by its spectral data. Characteristic new peaks appear at 2.40 and 3.72 which are doublet of doublets and represent two benzylic protons. Also, assignment of the signals have been confirmed by decoupling experiments. A multiplet at 3.12-3.25 and a doublet of doublet of doublet at 4.31 are due to methine protons attached to the phenyl ring and the carbene carbon respectively. Coupling constant between these two protons (1.5 Hz, established by irradiating OCH<sub>2</sub> protons) indicates that the phenyl and benzyl group are *trans* to each other. The structure of the complex has been established unambiguously by single crystal X-ray diffraction which indeed shows two groups in *trans* stereochemical relationship (Fig. I.1).

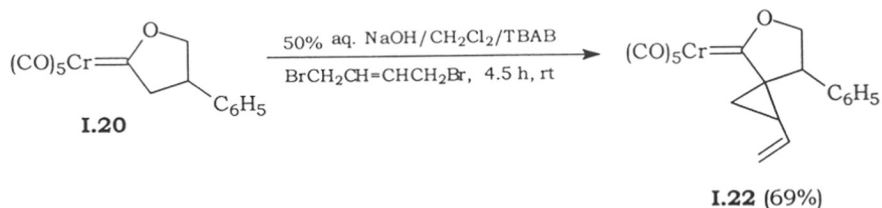


Fig. I.1



The metal-carbene bond is in the usual range (1.993 Å), so is the carbene-oxygen distance (1.313 Å). The metal-CO<sub>trans</sub> distance is longer (1.898 Å) than other M-CO bonds. The cyclopentane ring is slightly puckered (dihedral angles : C1-O1-C4-C3 16.7°, C1-C2-C3-C4 27.2° ) but aligned parallel (eclipsed) to the Cr-C20-O4 plane (dihedral angle : O1-C1-Cr-C20 -4.1° ), though in many structures the staggered orientation is observed.<sup>43</sup> The *trans* relationship of the two vicinal substituents is evident from the structure (dihedral angle : C5-C2-C3-C12 147.5°).

**Reaction of I.20 with 1,4-Dibromo-2-butene.** With a bifunctional electrophile, a spirocyclic molecule can also be prepared. Reaction of the complex **I.20** with 1,4-dibromo-2-butene resulted in the formation of a single diastereomer of the spirobicyclic product **I.22** as shown in Scheme-I.38. The stereochemistry of the product was not decisively determined. However, the scope of diverse functionalization on these substrates appears to be unlimited. Recently there has been an interest in these cyclic carbene structures in terms of synthetic modifications, in other groups.<sup>8</sup>

**Scheme I.38**

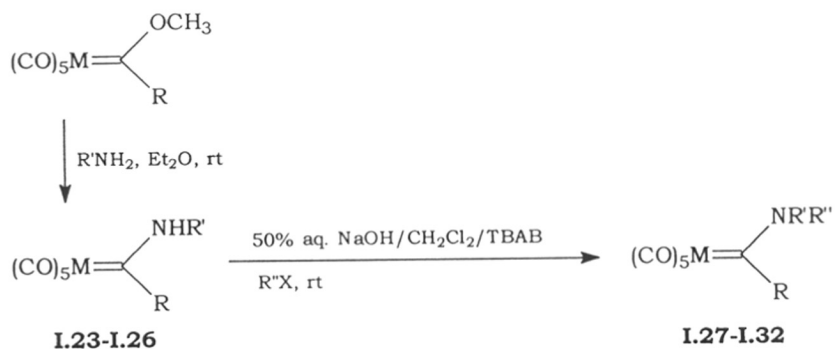
In <sup>1</sup>H NMR spectrum, the characteristic peaks for the product are three cyclopropyl protons at 1.30, 2.50 and 3.15-3.35 as a triplet, a doublet of doublet and a multiplet respectively. Two multiplets at 5.25-5.50 and 5.50-5.80 account for the methylene and methine protons of the olefin moiety respectively. In <sup>13</sup>C NMR spectrum, olefinic carbons appear at 120.66 and 141.56.

The observed diastereoselectivity in these reactions is extremely attractive since further elaboration of the skeleton promises to afford structures of higher complexity with substantial stereocontrol.

**N-Alkylation of Fischer Carbene Complexes**

In addition to C-alkylation, the PTC protocol seemed eminently adaptable to N-alkylation of monoalkylamino carbene complexes. As with C-alkylation, reactive halides produced dialkylamino complexes in high yield (Scheme-I.39). Normally, the alkyl substituent of the substrates adopt predominantly *E*-configuration. After alkylation, the ratio is altered. In comparison with the existing methods for N-alkylation,<sup>44</sup> the present procedure offers considerable advantage of convenience and yield.

Scheme-I.39



Substrate	M	R	R'	E/Z
<b>I.23</b>	Cr	C <sub>6</sub> H <sub>5</sub>	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	62:38
<b>I.24</b>	W	CH <sub>3</sub>	CH <sub>2</sub> CH=CH <sub>2</sub>	66:33
<b>I.25</b>	W	CH <sub>3</sub>	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	100:0
<b>I.26</b>	W	C <sub>6</sub> H <sub>5</sub>	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	44:56

Product	M	R	R'	R''	Yield (%)	E/Z
<b>I.27</b>	Cr	C <sub>6</sub> H <sub>5</sub>	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	84	56:44
<b>I.28</b>	W	CH <sub>3</sub>	CH <sub>2</sub> CH=CH <sub>2</sub>	CH <sub>3</sub>	91	15:85
<b>I.29</b>	W	CH <sub>3</sub>	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	86	18:82
<b>I.30</b>	W	CH <sub>3</sub>	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	CH <sub>2</sub> CH=CH <sub>2</sub>	83	45:55
<b>I.31</b>	W	CH <sub>3</sub>	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	85	-
<b>I.32</b>	W	C <sub>6</sub> H <sub>5</sub>	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	89	48:52

It is well known from the work of Fischer<sup>45b,c</sup> and Casey,<sup>45a</sup> that a group *syn* to metal is more deshielded. The chemical shift difference between *syn* and *anti* N-CH<sub>3</sub> and/or N-CH<sub>2</sub> groups ranges from 0.48 to 0.67 ppm when a methyl group is attached to the carbene carbon and 0.92 to 0.99 ppm when a phenyl group is attached. The clear separation of signals also provide a direct means to estimate isomer population in these complexes.

#### I.4 SUMMARY

A convenient, phase-transfer catalysed alkylation procedure for Fischer carbene complexes has been developed. Both C-alkylation and N-alkylation proceeded with reactive halides in high yield. A high degree of diastereoselectivity in C-alkylation was also achieved in a stereochemically defined set of substrates.

## GENERAL EXPERIMENTAL

1. Wherever possible the source of materials purchased has been identified in the experimental procedure where these materials have been used.
2. Silica gel (LOBA/SD chemicals, 60-120 mesh) was used for normal column chromatography. Flash column chromatography was carried out with silica gel obtained from Merck (230 to 400 mesh, 9385 grade).
3. Solvents were purified as follows : Benzene, tetrahydrofuran and diethyl ether were distilled over sodium-benzophenone ketyl under argon freshly before use; methylene chloride was distilled over phosphorous pentoxide under argon.
4. Usual workup procedure involves extraction with an appropriate organic solvent, washing with water, brine and then drying over anhydrous sodium sulfate unless otherwise mentioned. The solutions were concentrated on a Büchi rotavapor connected to a water aspirator.
5. **Preparation of Carbene Salts:** Chromium or tungsten hexacarbonyl ( $n$  mmol) in diethyl ether ( $5n$  ml) was treated with RLi (R = alkyl or aryl,  $n$  mmol) at  $15\text{ }^{\circ}\text{C}$  under argon and stirred for 30 min. Solvent was evaporated under reduced pressure and the dried lithium salt was dissolved in ice-cold water followed by direct filtration into an ice-cold solution of tetraethylammonium bromide ( $1.2n$  mmol). The precipitated carbene salt was filtered and dried under vacuo.
6. **Preparation of Alkoxycarbene Complexes:** All alkoxycarbene complexes were prepared following reported procedure.<sup>37</sup> Carbene salt ( $n$  mmol) was treated with methyl/ethyl iodide or benzyl bromide ( $2$ - $10$  mmol) in dichloromethane ( $5n$  ml) in the presence of tetrabutylammonium bromide ( $0.1n$  mmol) under argon and stirred overnight. Solvent was evaporated under reduced pressure and the residue was extracted with petroleum ether. Extracts were collected and concentrated under reduced pressure. Pure product was obtained by flash chromatography using petroleum ether as the eluant.

## I.5 EXPERIMENTAL SECTION

Allyl bromide, allyl chloride, benzyl bromide, cinnamyl chloride, 1,4-dibromo-2-butene, Prenyl bromide, allylamine benzylamine, methyllithium and n-butyllithium were purchased from Aldrich Chemicals, USA. Methyl iodide, ethyl iodide, tetraethylammonium bromide, tetrabutylammonium bromide, methylamine and bromobenzene were obtained from SD Fine Chemicals, India. Methyl 4-bromocrotonate was prepared from crotonic acid by esterification followed by bromination using N-bromosuccinimide. Methyllithium was prepared from methyl iodide and lithium in diethyl ether by standard procedure. n-Butyllithium was prepared in petroleum ether from n-butyl chloride and lithium.

Complex **I.1**,<sup>46</sup> **I.2**,<sup>47</sup> **I.3**,<sup>48</sup> **I.4**,<sup>47</sup> **I.5**,<sup>46</sup> **I.6**,<sup>47</sup> **I.13**,<sup>47</sup> **I.14**,<sup>47</sup> were prepared following a standard procedure.<sup>37</sup> Complex **I.20** was prepared according to a literature procedure.<sup>8d</sup> The crystal structure solution of complex **I.21** was carried out by Dr.(Mrs.) V.G. Puranik at NCL. Relevant tables are appended at the end of this section.

### General Procedure for the C-Alkylation of Carbene Complexes

**Method A:** The carbene complex (n mmol) and tetrabutylammonium bromide (TBAB) (0.1n mmol) in dichloromethane (15n ml) was treated with 50% aq NaOH and the halide (3-10n mmol). The mixture was stirred at room temperature under argon until starting material was consumed (TLC). The reaction mixture was diluted with water, extracted with dichloromethane, dried and concentrated under reduced pressure. The pure product was isolated by flash chromatography.

**Method B:** The carbene complex (n mmol), potassium carbonate, and 18-Crown-6 (0.05n mmol) was treated with the halide (3-10n mmol). The pure product was isolated as described in method A.

**Reaction of I.1 with prenyl bromide:** Complex **I.1** (250 mg, 1 mmol), TBAB (32 mg, 0.1 mmol), 50% aq. NaOH and prenyl bromide (0.35 ml, 3 mmol) in dichloromethane (15 ml) were stirred for 4 h yielded the product **I.7** (282 mg, 73%) as an orange oil.

IR : 2050 (m), 1975 (sh), 1930 (s)

<sup>1</sup>H NMR : 1.58 (s, 6H), 1.70 (s, 6H), 1.85-2.05 (m, 2H), 2.10-2.30 (m, 2H), 4.12 (p, J= 6.6 Hz, 1H), 4.82 (s, 3H), 5.02-5.18 (m, 2H)

<sup>13</sup>C NMR : 17.75, 25.85, 30.90, 67.82, 71.93, 121.74, 133.45, 216.52, 223.55, 370.53

**Reaction of I.2 with methyl iodide:** Complex **I.2** (264 mg, 1 mmol), TBAB (32 mg, 0.1 mmol), 50% aq. NaOH and methyl iodide (0.62 ml, 10 mmol) in dichloromethane (15 ml) were stirred for overnight yielded the product **I.8a** (187 mg, 64%) as a yellow solid.

m.p. : 39 °C

IR : 2060 (m), 1990 (sh), 1945 (s)

<sup>1</sup>H NMR : 1.00 (d, J= 6.5 Hz, 6H), 1.62 (t, J= 7 Hz, 3H), 4.15 (h, J= 6.5 Hz, 1H), 5.10 (q, J= 7 Hz, 2H)

$^{13}\text{C}$  NMR : 14.74, 18.27, 60.01, 78.08, 216.61, 223.40, 364.39

Analysis : Calcd : C = 45.20, H = 4.10

Found : C = 45.70, H = 4.40

**Reaction of I.2 with allyl bromide:** Complex **I.2** (264 mg, 1 mmol), TBAB (32 mg, 0.1 mmol), 50% aq. NaOH and allyl bromide (0.43 ml, 5 mmol) in dichloromethane (15 ml) were stirred for 3.5 h yielded the product **I.8b** (241 mg, 70%) as an orange oil.

**Reaction of I.2 with allyl chloride:** Complex **I.2** (264 mg, 1 mmol), TBAB (32 mg, 0.1 mmol), 50% aq. NaOH and allyl chloride (0.4 ml, 5 mmol) in dichloromethane (15 ml) were stirred for 3.5 h yielded the product **I.8b** (175 mg, 51%) as an orange oil.

IR : 2055 (m), 1985 (sh), 1945 (s)

$^1\text{H}$  NMR : 1.65 (t,  $J$  = 7 Hz, 3H), 1.92-2.10 (m, 2H), 2.18-2.38 (m, 2H), 4.14 (p,  $J$  = 6.8 Hz, 1H), 4.94-5.07 (m, 4H), 5.13 (q,  $J$  = 7 Hz, 2H), 5.64-5.87 (m, 2H)

$^{13}\text{C}$  NMR : 15.23, 36.29, 69.90, 78.20, 117.44, 135.59, 216.56, 223.35, 364.47

**Reaction of I.2 with benzyl bromide:** Complex **I.2** (264 mg, 1 mmol), TBAB (32 mg, 0.1 mmol), 50% aq. NaOH and benzyl bromide (0.36 ml, 3 mmol) in dichloromethane (15 ml) were stirred for 3 h yielded the product **I.8c** (249 mg, 56%) as an orange oil.



IR : 2050 (m), 1990 (sh), 1945 (s)

$^1\text{H}$  NMR : 1.70 (t,  $J$ = 7 Hz, 3H), 2.45 (dd,  $J$ = 14.2, 7.1 Hz, 2H), 2.98 (dd,  $J$ = 14.2, 7.1 Hz, 2H), 4.55 (p,  $J$ = 7.1 Hz, 1H), 5.17 (q,  $J$ = 7 Hz, 2H), 7.05-7.40 (m, 10H)

$^{13}\text{C}$  NMR : 15.08, 38.03, 74.50, 78.00, 126.66, 128.70, 129.46, 139.12, 216.12, 223.28, 365.72

**Reaction of I.3 with methyl iodide:** Complex **I.3** (326 mg, 1 mmol), TBAB (32 mg, 0.1 mmol), 50% aq. NaOH and methyl iodide (0.62 ml, 10 mmol) in dichloromethane (15 ml) were stirred for overnight yielded the product **I.9a** (226 mg, 64%) as a yellow solid.

m.p. : 52 °C

IR : 2080 (m), 2000 (sh), 1960 (s)

$^1\text{H}$  NMR : 1.00 (d,  $J$ = 6.5 Hz, 6H), 4.20 (h,  $J$ = 6.5 Hz, 1H), 6.00 (s, 2H), 7.45 (s, 5H)

$^{13}\text{C}$  NMR : 18.57, 60.58, 83.90, 128.40, 129.22, 129.42, 134.42, 216.66, 223.40, 365.74

Analysis : Calcd : C = 54.24, H = 3.90  
Found : C = 54.84, H = 4.49

**Reaction of I.3 with allyl bromide in 50% Aq. NaOH:** Complex **I.3** (326 mg, 1 mmol), TBAB (32 mg, 0.1 mmol), 50% aq. NaOH and allyl bromide (0.43 ml, 5 mmol) in dichloromethane (15 ml) were stirred for 3.5 h yielded the product **I.9b** (325 mg, 80%) as an orange oil.

**Reaction of I.3 with allyl bromide in Anh. Potassium Carbonate:** Complex **I.3** (326 mg, 1 mmol), 18-crown-6 (13 mg, 0.05 mmol), anh. potassium carbonate and allyl bromide (0.43 ml, 5 mmol) in dichloromethane (15 ml) were stirred for 5 h yielded the product **I.9b** (195 mg, 48%) as an orange oil.

IR : 2060 (m), 1990 (sh), 1950 (s)

<sup>1</sup>H NMR : 1.93-2.12 (m, 2H), 2.20-2.38 (m, 2H), 4.20 (p, J= 6.5 Hz, 1H), 4.90-5.10 (m, 4H), 5.64-5.88 (m, 2H), 6.03 (s, 2H), 7.50 (s, 5H)

<sup>13</sup>C NMR : 36.42, 70.36, 84.06, 117.49, 128.85, 129.24, 129.58, 134.24, 135.54, 216.52, 223.21, 365.60

**Reaction of I.4 with methyl iodide:** Complex **I.4** (382 mg, 1 mmol), TBAB (32 mg, 0.1 mmol), 50% aq. NaOH and methyl iodide (0.62 ml, 10 mmol) in dichloromethane (15 ml) were stirred for overnight yielded the product **I.10a** (238 mg, 58%) as a yellow solid.

m.p. : 66°C

IR : 2060 (m), 1980 (sh), 1930 (s)

<sup>1</sup>H NMR : 1.02 (d, J= 6.5 Hz, 6H), 4.15 (h, J= 6.5 Hz, 1H), 4.62 (s, 3H)

$^{13}\text{C}$  NMR : 18.02, 61.84, 70.67, 197.28, 203.25, 342.45

Analysis : Calcd : C = 29.27, H = 2.44

Found : C = 29.62, H = 2.47

**Reaction of I.4 with prenyl bromide:** Complex **I.4** (382 mg, 1 mmol), TBAB (32 mg, 0.1 mmol), 50% aq. NaOH and prenyl bromide (0.35 ml, 3 mmol) in dichloromethane (15 ml) were stirred for 4 h yielded the product **I.10b** (362 mg, 70%) as an orange oil.

IR : 2060 (m), 1980 (sh), 1920 (s)

$^1\text{H}$  NMR : 1.58 (s, 6H), 1.70 (s, 6H), 1.92-2.08 (m, 2H), 2.13-2.30 (m, 2H), 4.10 (p,  $J = 6.6$  Hz, 1H), 4.62 (s, 3H), 5.05-5.22 (m, 2H)

$^{13}\text{C}$  NMR : 17.80, 28.89, 30.94, 70.58, 73.29, 121.68, 133.49, 197.58, 203.80, 345.25

**Reaction of I.5 with allyl bromide:** Complex **I.5** (396 mg, 1 mmol), TBAB (32 mg, 0.1 mmol), 50% aq. NaOH and allyl bromide (0.43 ml, 5 mmol) in dichloromethane (15 ml) were stirred for 3 h yielded the product **I.11a** (300 mg, 63%) as an orange oil.

IR : 2080 (m), 1995 (sh), 1955 (s)

$^1\text{H}$  NMR : 1.63 (t,  $J = 7.0$  Hz, 3H), 1.98-2.15, (m, 2H), 2.24-2.43 (m, 2H), 4.15 (p,  $J = 6.8$  Hz, 1H), 4.95 (q,  $J = 7$  Hz, 2H), 5.00-5.15 (m, 4H), 5.65-5.90 (m, 2H)

$^{13}\text{C}$  NMR : 14.98, 36.23, 71.50, 80.86, 117.44, 135.49, 197.54, 203.52, 339.06

**Reaction of I.5 with cinnamyl chloride:** Complex **I.5** (396 mg, 1 mmol), TBAB (32 mg, 0.1 mmol), 50% aq. NaOH and cinnamyl chloride (0.42 ml, 3 mmol) in dichloromethane (15 ml) were stirred for 1.5 h yielded the product **I.11b** (351 mg, 56%) as an orange oil.

IR : 2080 (m), 1995 (sh), 1950 (s)

$^1\text{H}$  NMR : 1.65 (t,  $J$ = 7 Hz, 3H), 2.21-2.40 (m, 2H), 2.45-2.63 (m, 2H), 4.35 (p,  $J$ = 7 Hz, 1H), 4.98 (q,  $J$ = 7 Hz, 2H), 6.10-6.50 (m, 4H), 7.15-7.45 (m, 10H)

$^{13}\text{C}$  NMR : 15.08, 35.53, 72.38, 80.86, 126.85, 127.53, 128.24, 128.79, 132.86, 137.38, 197.49, 203.50, 338.77

**Reaction of I.5 with benzyl bromide:** Complex **I.5** (396 mg, 1 mmol), TBAB (32 mg, 0.1 mmol), 50% aq. NaOH and benzyl bromide (0.36 ml, 3 mmol) in dichloromethane (15 ml) were stirred for 3 h yielded the product **I.11c** (357 mg, 62%) as an orange oil.

IR : 2085 (m), 2000 (sh), 1950 (s)

$^1\text{H}$  NMR : 1.64 (t,  $J$ = 7 Hz, 3H), 2.45 (dd,  $J$ = 13.1, 7.3 Hz, 2H), 2.92 (dd,  $J$ = 13.1, 7.3 Hz, 2H), 4.50 (p,  $J$ = 7.3 Hz, 1H), 4.90 (q,  $J$ = 7 Hz, 2H), 6.96-7.40 (m, 10H)

$^{13}\text{C}$  NMR : 14.56, 37.61, 75.64, 80.33, 126.38, 128.41, 129.15, 138.75,  
196.92, 203.09, 339.47

**Reaction of I.6 with methyl iodide:** Complex **I.6** (458 mg, 1 mmol), TBAB (32 mg, 0.1 mmol), 50% aq. NaOH and methyl iodide (0.62 ml, 10 mmol) in dichloromethane (15 ml) were stirred for overnight yielded the product **I.12a** (296 mg, 61%) as a yellow solid.

m.p. : 60 °C

IR : 2090 (m), 2000 (sh), 1950 (s)

$^1\text{H}$  NMR : . 1.02 (d,  $J= 6.4$  Hz, 6H), 4.20 (h,  $J= 6.4$  Hz, 1H), 5.82 (s, 2H), 7.45 (s, 5H)

$^{13}\text{C}$  NMR : 118.38, 62.31, 86.54, 128.31, 129.17, 129.33, 134.26, 197.49,  
203.41, 339.98

Analysis : Calcd : C = 39.50, H = 2.88  
Found : C = 39.73, H = 2.87

**Reaction of I.6 with allyl bromide:** Complex **I.6** (458 mg, 1 mmol), TBAB (32 mg, 0.1 mmol), 50% aq. NaOH and allyl bromide (0.43 ml, 5 mmol) in dichloromethane (15 ml) were stirred for 3.5 h yielded the product **I.12b** (420 mg, 78%) as an red oil.

IR : 2080 (m), 2000 (sh), 1955 (s)

$^1\text{H}$  NMR : 1.95-2.15 (m, 2H), 2.23-2.42 (m, 2H), 4.20 (p,  $J= 6.6$  Hz, 1H),  
4.92-5.10 (m, 4H), 5.65-5.90 (m, 2H), 5.82 (s, 2H), 7.42 (s, 5H)

$^{13}\text{C}$  NMR : 36.37, 71.97, 86.73, 117.53, 128.80, 129.23, 129.56, 134.10,  
135.48, 197.54, 203.41, 339.88

**Reaction of I.13 with benzyl bromide:** Complex **I.13** (306 mg, 1 mmol), TBAB (32 mg, 0.1 mmol), 50% aq. NaOH and benzyl bromide (0.36 ml, 3 mmol) in dichloromethane (15 ml) were stirred for 4.5 h yielded the product **I.15** (265 mg, 67%) as an orange oil.

IR : 2080 (m), 1995 (sh), 1950 (s)

$^1\text{H}$  NMR : 0.85 (t,  $J= 6.9$  Hz, 3H), 1.10-1.58 (m, 4H), 1.63 (t,  $J= 7$  Hz, 3H),  
2.36 (dd,  $J= 12.3$  7.3 Hz, 1H), 2.90 (dd,  $J= 12.3$ , 5.3 Hz, 1H),  
4.15-4.30 (m, 1H), 5.12 (q,  $J= 7$  Hz, 2H), 7.06-7.32 (m, 5H)

$^{13}\text{C}$  NMR : 14.83, 15.03, 21.09, 34.49, 38.17, 72.99, 78.10, 126.56, 128.64,  
129.47, 139.48, 216.51, 223.30, 365.60

**Reaction of I.14 with cinnamyl chloride:** Complex **I.14** (438 mg, 1 mmol), TBAB (32 mg, 0.1 mmol), 50% aq. NaOH and cinnamyl chloride (0.28 ml, 2 mmol) in dichloromethane (15 ml) were stirred for 2 h yielded the product **I.16** (382 mg, 69%) as an orange oil.

IR : 2075 (m), 1985 (sh), 1940 (s)

$^1\text{H}$  NMR : 0.86-1.00 (m, 3H), 1.23-1.62 (m, 4H), 1.64 (t,  $J$ = 7 Hz, 3H), 2.12-2.30 (m, 1H), 2.38-2.55 (m, 1H), 4.10-4.25 (m, 1H), 4.95 (q,  $J$ = 7 Hz, 2H), 6.08-6.44 (m, 2H), 7.15-7.40 (m, 5H)

$^{13}\text{C}$  NMR : 14.96, 21.19, 34.47, 35.84, 72.61, 80.86, 126.29, 127.39, 127.48, 128.79, 132.53, 137.48, 197.64, 203.48, 339.88

**Reaction of I.3 with 1,4-dibromo-2-butene:** Complex **I.3** (326 mg, 1 mmol), TBAB (32 mg, 0.1 mmol), 50% aq. NaOH and 1,4-dibromo-2-butene (321 mg, 1.5 mmol) in dichloromethane (15 ml) were stirred for 2 h yielded the product **I.17** (283 mg, 75%) as a yellow solid.

m.p. : 65 °C

IR : 2060 (m), 1995 (sh), 1945 (s)

$^1\text{H}$  NMR : 1.22-1.38 (m, 1H), 1.78-1.90 (m, 1H), 2.25 (ddd,  $J$ = 15.3, 8.2, 3.6 Hz, 1H), 3.42-3.55 (m, 1H), 4.98-5.23 (m, 2H), 5.40-5.60 (m, 1H), 5.90 (s, 2H), 7.33-7.55 (m, 5H)

$^{13}\text{C}$  NMR : 24.37, 36.13, 50.94, 82.56, 115.95, 128.46, 129.19, 129.41, 134.47, 137.72, 216.85, 223.59, 347.79

Analysis : Calcd : C = 57.14, H = 3.70

Found : C = 56.93, H = 3.94

**Reaction of I.4 with Methyl 4-bromocrotonate:** Complex **I.4** (352 mg, 1 mmol), TBAB (32 mg, 0.1 mmol), 50% aq. NaOH and methyl 4-bromocrotonate (0.35 ml, 3 mmol) in dichloromethane (15 ml) were stirred for 2 h yielded the product **I.18** (190 mg, 33%) and **I.19** (142 mg, 21%) as red oil.

**Complex I.18:**

IR : 2070 (m), 1980 (sh), 1920 (s), 1723 (s), 1657 (m)

<sup>1</sup>H NMR : 2.05-2.25 (m, 2H), 2.30-2.50 (m, 2H), 3.67 (s, 6H), 4.22 (p, J= 6.85 Hz, 1H), 4.60 (s, 3H), 5.75 (d, J= 15.5 Hz, 2H), 6.80 (td, J= 15.5, 7.7 Hz, 2H)

<sup>13</sup>C NMR : 34.18, 51.66, 70.18, 70.65, 123.94, 144.64, 166.34, 196.91, 202.88, 338.28

**Complex I.19:**

IR : 2069 (m), 1985 (sh), 1939 (s), 1731 (s), 1651 (m)

<sup>1</sup>H NMR : 2.75 (dd, J= 7.8, 1.0 Hz, 6H), 3.75 (s, 9H), 4.80 (s, 3H), 5.87 (d, J= 15.6 Hz, 3H), 6.74 (td, J= 15.6, 7.8 Hz, 3H)

<sup>13</sup>C NMR : 40.42, 51.85, 67.23, 71.17, 125.26, 142.76, 166.25, 197.00, 201.32, 347.51

**Reaction of I.20 with benzyl bromide:** Complex **I.20** (338 mg, 1 mmol), TBAB (32 mg, 0.1 mmol), 50% aq. NaOH and benzyl bromide (0.36 ml, 3 mmol) in



dichloromethane (15 ml) were stirred for 4.5 h yielded the product **I.21** (287 mg, 71%) as a yellow solid.

m.p. : 58°C

IR : 2060 (m), 1985 (sh), 1940 (s)

<sup>1</sup>H NMR : 2.40 (dd, J= 14, 12 Hz, 1H), 3.12-3.25 (m, 1H), 3.72 (dd, J= 14, 4 Hz, 1H), 4.31 (ddd, J= 12, 4, 1.5 Hz, 1H), 5.05-5.20 (m, 2H), 6.65-6.80 (m, 2H), 7.10-7.50 (m, 8H)

<sup>13</sup>C NMR : 37.20, 44.57, 81.59, 90.19, 126.12, 127.40, 127.47, 129.16, 129.32, 137.86, 142.15, 216.50, 223.20, 346.33

Analysis : Calcd : C = 61.68, H = 3.74  
Found : C = 61.27, H = 4.16

**Reaction of I.20 with 1,4-dibromo-2-butene:** Complex **I.20** (338 mg, 1 mmol), TBAB (32 mg, 0.1 mmol), 50% aq. NaOH and 1,4-dibromo-2-butene (321 mg, 1.5 mmol) in dichloromethane (15 ml) were stirred for 2 h yielded the product **I.22** (269 mg, 69%) as a red oil.

IR : 2065 (m), 1985 (sh), 1940 (s)

<sup>1</sup>H NMR : 1.30 (t, J= 7.3 Hz, 1H), 2.50 (dd, J= 8.0, 7.3 Hz, 1H), 2.92 (dd, J= 8.0, 7.3 Hz, 1H), 3.15-3.35 (m, 1H), 4.95-5.20 (m, 2H), 5.25-5.50 (m, 2H), 5.50-5.80 (m, 1H), 6.90-7.55 (m, 5H)

$^{13}\text{C}$  N R : 23.09, 37.08, 42.89, 65.88, 89.74, 120.66, 127.39, 127.77,  
129.43, 133.51, 141.56, 216.81, 222.44, 334.80

### General Procedure for the N-Alkylation of Carbene Complexes

The carbene complex (n mmol) and tetrabutylammonium bromide (TBAB) (0.1n mmol) in dichloromethane (10n ml) was treated with 50% aq NaOH and the halide (2-5n mmol). The mixture was stirred at room temperature under argon until starting material was consumed (TLC). The reaction mixture was diluted with water, extracted with dichloromethane, dried and concentrated under reduced pressure. The pure product was isolated by flash chromatography.

**Reaction of I.23 with Methyl Iodide:** Complex **I.23** (0.77 g, 2 mmol), TBAB (64 mg, 0.2 mmol), 50% aq. NaOH and methyl iodide (0.62 ml, 10 mmol) in dichloromethane (20 ml) were stirred for 3 h yielded the product **I.27** (0.67 g, 84%) as a yellow oil.

IR : 2050 (m), 1970 (sh), 1920 (s)

$^1\text{H}$  N R : *E:Z* = 65:35. **E-I.27.** 3.88 (s, 3H); 4.65 (s, 2H). **Z-I.27.** 2.89 (s, 3H); 5.63 (s, 2H). **Combined peaks.** 6.60-7.78 (m, 10H and 10H)

$^{13}\text{C}$  N R : **E-I.27.** 49.12; 61.98; 119.55; 134.33; 152.94; 217.72; 224.46; 278.17. **Z-I.27.** 43.67; 67.83; 119.07; 134.56; 153.45; 216.98; 223.68; 277.41. **Combined peaks.** 126.26; 127.52; 127.98; 129.33; 129.54; 129.78; 130.44

**Reaction of I.24 with Methyl Iodide:** Complex **I.24** (0.81 g, 2 mmol), TBAB (64 mg, 0.2 mmol), 50% aq. NaOH and methyl iodide (0.62 ml, 10 mmol) in dichloromethane (20 ml) were stirred for 3 h yielded the product **I.28** (0.80 g, 91%) as a yellow oil.

IR : 2080 (m), 1990 (sh), 1950 (s)

<sup>1</sup>H N R : *E:Z* = 14:86. **E-I.28**. 2.82 (s, 3H); 3.78 (s, 3H); 4.25-4.33 (m, 2H); 5.06-5.20 (m, 2H). **Z-I.28**. 2.82 (s, 3H); 3.20 (s, 3H); 4.70-5.88 (m, 2H); 5.30-5.53 (m, 2H). **Combined peaks**. 5.70-6.03 (m, 1H and 1H)

<sup>13</sup>C N R : **E-I.28**. 41.57; 53.89; 56.51; 118.61; 129.28; 199.17; 203.99; 256.34. **Z-I.28**. 38.83; 42.52; 70.77; 120.74; 131.71; 198.85; 203.75; 255.75

**Reaction of I.25 with Methyl Iodide:** Complex **I.25** ( 0.91 g, 2 mmol), TBAB (64 mg, 0.2 mmol), 50% aq. NaOH and methyl iodide (0.62 ml, 10 mmol) in dichloromethane (20 ml) were stirred for 3 h yielded the product **I.29** (0.81 g, 86%) as a yellow oil.

IR : 2075 (m), 1970 (sh), 1930 (s)

<sup>1</sup>H N R : *E:Z* = 16:84. **E-I.29**. 2.91 (s, 3H); 3.80 (s, 3H); 4.93 (s, 2H); 7.03-7.16 (m, 2H). **Z-I.29**. 2.91 (s, 3H); 3.13 (s, 3H); 5.41 (s, 2H); 7.20-7.33 (m, 2H). **Combined peaks**. 7.34-7.55 (m, 3H and 3H)

<sup>13</sup>C N R : **E-I.29.** 38.97; 53.93; 57.98; 133.10; 199.08; 205.34; 256.45.  
**Z-I.29.** 38.97; 42.28; 71.55; 134.32; 198.71; 203.70; 255.97.  
**Combined peaks.** 126.34; 127.56; 128.36; 128.58; 129.21;  
 129.47

**Reaction of I.25 with Allyl Bromide:** Complex **I.25** (0.91 g, 2 mmol), TBAB (64 mg, 0.2 mmol), 50% aq. NaOH and allyl bromide (0.34 ml, 4 mmol) in dichloromethane (20 ml) were stirred for 2 h yielded the product **I.30** (0.82 g, 83%) as a yellow oil.

IR : 2075 (m), 1980 (sh), 1925 (s)

<sup>1</sup>H N R : *E:Z* = 41:51. **E-I.30.** 2.91 (s, 3H); 4.79-4.90 (m, 2H); 4.92 (s, 2H); 5.84-6.10 (m, 1H); 7.02-7.17 (m, 2H). **Z-I.30.** 2.98 (s, 3H); 4.09-4.31 (m, 2H); 5.42 (s, 2H); 5.60-5.83 (m, 1H); 7.22-7.33 (m, 2H). **Combined peaks.** 5.01-5.57 (m, 2H and 2H); 7.33-7.62 (m, 3H and 3H)

<sup>13</sup>C N R : **E-I.30.** 42.54; 53.68; 68.38; 198.82; 203.70; 258.16. **Z-I.30.** 41.92; 53.02; 69.07; 198.74; 203.56; 258.32. **Combined peaks.** 118.21; 120.73; 126.08; 127.62; 128.24; 128.44; 128.64; 129.24; 129.51; 130.31; 133.29; 133.53; 134.45

**Reaction of I.25 with Benzyl Bromide:** Complex **I.25** (0.91 g, 2 mmol), TBAB (64 mg, 0.2 mmol), 50% aq. NaOH and benzyl bromide (0.36 ml, 3 mmol) in dichloromethane (20 ml) were stirred for 2 h yielded the product **I.31** (0.93 g, 85%) as a yellow oil.

IR : 2070 (m), 1975 (sh), 1925 (s)

<sup>1</sup>H N R : 3.03 (s, 3H); 4.81 (s, 2H); 5.46 (s, 2H); 6.97-7.21 (m, 2H); 7.22-7.33 (m, 2H); 7.33-7.61 (m, 6H)

<sup>13</sup>C N R : 42.63; 53.81; 69.15; 126.18; 126.86; 127.65; 128.37; 128.76; 128.93; 129.34; 129.61; 133.25; 134.38; 198.78; 203.56; 259.60

**Reaction of I.26 with Methyl Iodide:** Complex **I.26** (1.04 g, 2 mmol), TBAB (64 mg, 0.2 mmol), 50% aq. NaOH and methyl iodide (0.64 ml, 10 mmol) in dichloromethane (20 ml) were stirred for 3 h yielded the product **I.32** (0.95 g, 89%) as a yellow oil.

IR : 2065 (m), 1970 (sh), 1920 (s)

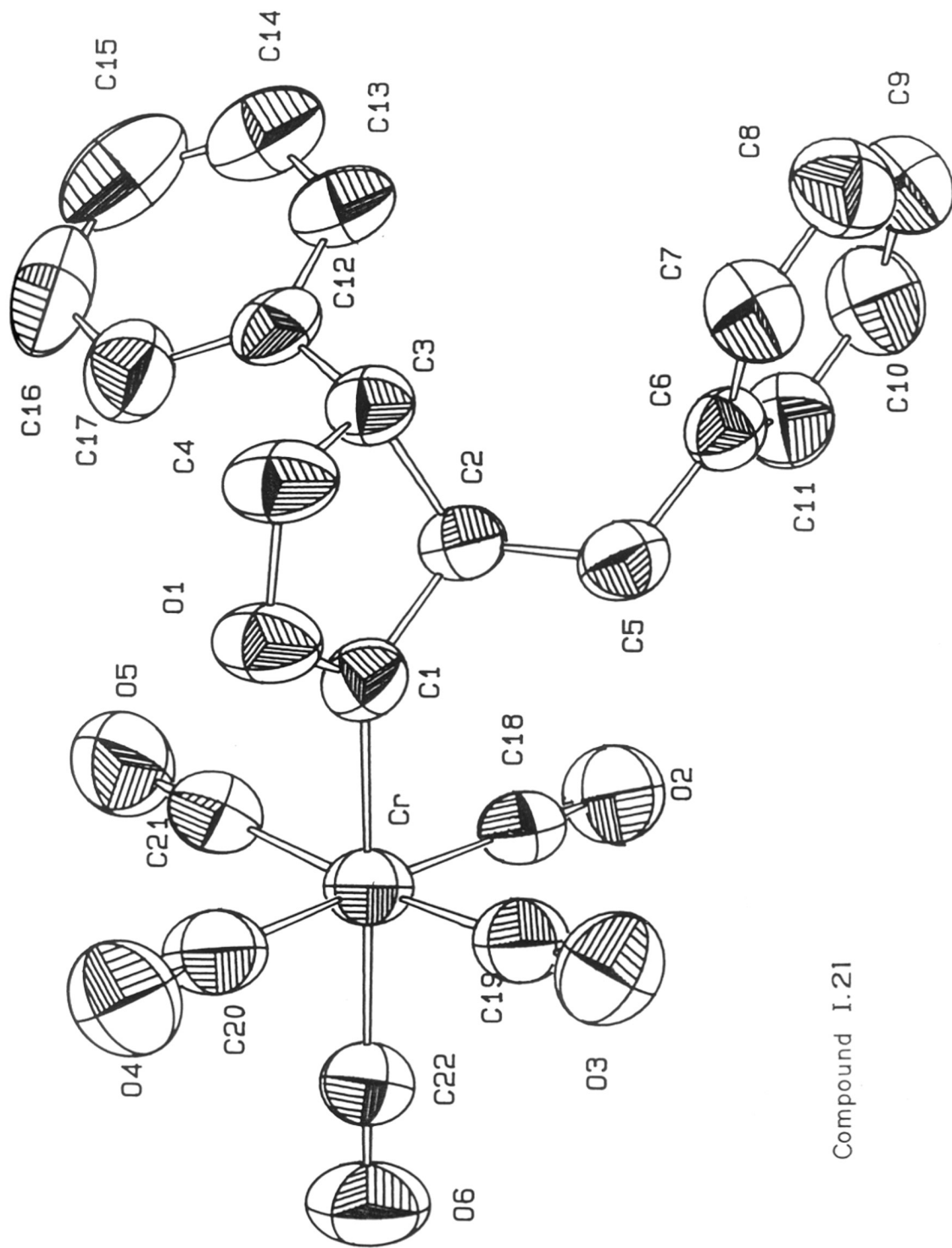
<sup>1</sup>H N R : *E:Z* = 48:52. **E-I.32.** 3.82 (s, 3H); 4.61 (s, 2H). **Z-I.32.** 2.90 (s, 3H); 5.57 (s, 2H). **Combined peaks.** 6.80-7.00 (m, 2H and 2H); 7.09-7.31 (m, 2H and 2H); 7.33-7.62 (m, 6H and 6H)

<sup>13</sup>C N R : **E-I.32.** 51.28; 60.58; 119.73; 134.19; 153.77; 198.41; 204.45; 260.41. **Z-I.32.** 41.88; 69.65; 133.97; 153.16; 198.73; 203.93; 260.20. **Combined peaks.** 126.57; 127.52; 127.73; 128.65; 128.85; 128.98; 129.52; 129.59

## STRUCTURE SOLUTION BY X-RAY DIFFRACTION

**Crystallographic Data for C<sub>25</sub>H<sub>16</sub>O<sub>6</sub>Cr (I.21).**

formula	C <sub>25</sub> H <sub>16</sub> O <sub>6</sub> Cr
fw	464.38
cryst system	triclinic
space group	<i>P</i> -1
a (Å)	9.994 (3)
b (Å)	10.546 (3)
c (Å)	11.853 (3)
α (deg)	104.64(2)
β (deg)	81.00(2)
γ (deg)	110.94(2)
V (Å <sup>3</sup> )	1125.9 (5)
Z	2
Dcal (g/cm <sup>3</sup> )	1.370
μ(mm <sup>-1</sup> )	0.546
F(000)	476
radiation	oKα (λ = 0.7093 Å)
cryst size (mm <sup>3</sup> )	.25 x .33 x 1.2
temp(°K)	298
scan type	ω/2θ
scan width(°)	0.80 + 0.35t, θ
2θ range (°)	3-47
reflections collected	3460
reflections observed (I ≥ 2.5σ(I))	2589
parameters varied	289
GOF	1.054
R	0.0576
Rw	0.0919



Compound I.21

**Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $\text{C}_{25}\text{H}_{16}\text{O}_6\text{Cr}$  (I.21).  $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.**

Atom	x	y	z	$U(\text{eq})$
Cr	1381(1)	3359(1)	461(1)	62(1)
O(1)	3981(3)	3737(4)	1501(3)	76(1)
O(2)	-757(4)	4477(4)	2137(3)	84(1)
O(3)	2901(4)	6136(5)	-231(4)	95(1)
O(4)	3411(5)	2195(5)	-1330(4)	114(2)
O(5)	227(5)	708(4)	1366(3)	100(1)
O(6)	-715(4)	2322(5)	-1432(3)	99(1)
C(1)	2769(5)	4005(5)	1692(4)	59(1)
C(2)	2687(4)	4829(4)	2930(3)	54(1)
C(3)	3787(5)	4568(5)	3563(4)	58(1)
C(4)	4837(5)	4277(6)	2542(4)	78(2)
C(5)	3027(5)	6379(5)	2943(4)	63(1)
C(6)	2838(5)	7187(4)	4171(4)	57(1)
C(7)	4006(5)	8002(5)	4812(5)	77(1)
C(8)	3823(6)	8701(6)	5957(5)	88(2)
C(9)	2447(7)	8591(6)	6455(5)	84(2)
C(10)	1292(6)	7785(6)	5827(5)	81(2)
C(11)	1478(5)	7089(5)	4702(4)	71(1)
C(12)	3091(4)	3435(5)	4231(4)	59(1)
C(13)	2619(5)	3802(6)	5405(4)	69(1)
C(14)	1948(6)	2830(8)	6045(5)	91(2)
C(15)	1728(7)	1484(9)	5576(8)	106(2)
C(16)	2148(7)	1041(6)	4425(8)	104(2)
C(17)	2835(6)	2045(6)	3732(5)	81(2)
C(18)	65(5)	4071(5)	1516(4)	62(1)
C(19)	2312(6)	5102(6)	15(4)	69(1)
C(20)	2678(6)	2637(6)	-638(4)	78(1)
C(21)	635(6)	1694(6)	1017(4)	70(1)
C(22)	56(6)	2701(5)	-713(4)	71(1)
C(23)	6422(12)	50(12)	9646(19)	168(4)
C(24)	5707(19)	171(11)	8828(8)	155(4)
C(25)	5882(24)	682(10)	10833(15)	212(6)



**Bond lengths [Å] for C<sub>25</sub>H<sub>16</sub>O<sub>6</sub>Cr (I.21).**

Cr-C(21)	1.889(6)	C(6)-C(11)	1.386(6)
Cr-C(18)	1.892(5)	C(7)-C(8)	1.390(8)
Cr-C(22)	1.898(5)	C(8)-C(9)	1.385(8)
Cr-C(20)	1.906(6)	C(9)-C(10)	1.363(8)
Cr-C(19)	1.907(6)	C(10)-C(11)	1.370(7)
Cr-C(1)	1.993(4)	C(12)-C(17)	1.380(7)
O(1)-C(1)	1.313(5)	C(12)-C(13)	1.401(6)
O(1)-C(4)	1.485(5)	C(13)-C(14)	1.349(7)
O(2)-C(18)	1.141(5)	C(14)-C(15)	1.337(10)
O(3)-C(19)	1.127(6)	C(15)-C(16)	1.377(10)
O(4)-C(20)	1.136(6)	C(16)-C(17)	1.418(9)
O(5)-C(21)	1.132(6)	C(23)-C(24)	1.35(2)
O(6)-C(22)	1.137(5)	C(23)-C(25)	1.50(2)
C(1)-C(2)	1.512(6)	C(24)-C(25)	1.57(2)
C(2)-C(5)	1.543(6)	C(25)-C(24)	1.57(2)
C(2)-C(3)	1.558(6)	C(6)-C(7)	1.381(7)
C(3)-C(12)	1.501(6)	C(5)-C(6)	1.511(6)
		C(3)-C(4)	1.518(6)

**Bond angles [deg] for C<sub>25</sub>H<sub>16</sub>O<sub>6</sub>Cr (I.21).**

C(21)-Cr-C(18)	89.8(2)
C(21)-Cr-C(22)	93.2(2)
C(18)-Cr-C(22)	89.7(2)
C(21)-Cr-C(20)	90.7(2)
C(18)-Cr-C(20)	178.4(2)
C(22)-Cr-C(20)	88.8(2)
C(21)-Cr-C(19)	173.3(2)
C(18)-Cr-C(19)	91.3(2)
C(22)-Cr-C(19)	93.4(2)
C(20)-Cr-C(19)	88.4(2)
C(21)-Cr-C(1)	85.6(2)
C(18)-Cr-C(1)	90.9(2)
C(22)-Cr-C(1)	178.7(2)
C(20)-Cr-C(1)	90.6(2)
C(19)-Cr-C(1)	87.8(2)
C(1)-O(1)-C(4)	112.9(3)
O(1)-C(1)-C(2)	108.4(4)
O(1)-C(1)-Cr	121.6(3)
C(2)-C(1)-Cr	130.0(3)
C(1)-C(2)-C(5)	110.7(3)
C(1)-C(2)-C(3)	104.8(4)
C(5)-C(2)-C(3)	113.0(3)
C(12)-C(3)-C(4)	115.8(4)
C(12)-C(3)-C(2)	112.5(3)
C(4)-C(3)-C(2)	100.8(3)
O(1)-C(4)-C(3)	104.9(3)
C(6)-C(5)-C(2)	110.8(3)
C(7)-C(6)-C(11)	118.0(4)
C(7)-C(6)-C(5)	121.3(4)
C(11)-C(6)-C(5)	120.6(4)
C(6)-C(7)-C(8)	121.0(5)
C(9)-C(8)-C(7)	119.3(5)
C(10)-C(9)-C(8)	119.9(5)
C(9)-C(10)-C(11)	120.6(5)
C(10)-C(11)-C(6)	121.2(5)
C(17)-C(12)-C(13)	118.4(5)
C(17)-C(12)-C(3)	123.2(4)
C(13)-C(12)-C(3)	118.3(4)
C(14)-C(13)-C(12)	121.2(5)
C(15)-C(14)-C(13)	120.7(6)
C(14)-C(15)-C(16)	121.5(6)
C(15)-C(16)-C(17)	118.7(6)
C(12)-C(17)-C(16)	119.5(6)
O(2)-C(18)-Cr	178.3(4)
O(3)-C(19)-Cr	177.7(5)
O(4)-C(20)-Cr	177.0(5)
O(5)-C(21)-Cr	177.8(5)
O(6)-C(22)-Cr	178.5(4)
C(24)-C(23)-C(25)	108.9(10)
C(23)-C(24)-C(25)	101.9(9)
C(23)-C(25)-C(24)	112.4(9)

**Torsion angles (deg) for C<sub>25</sub>H<sub>16</sub>O<sub>6</sub>Cr (I.21).**

C18	CR	C1	O1	176.3( 0)	C18	CR	C1	C2	-3.7( 0)
C19	CR	C1	O1	-92.5( 0)	C19	CR	C1	C2	87.6( 0)
C20	CR	C1	O1	-4.1( 0)	C20	CR	C1	C2	175.9( 0)
C21	CR	C1	O1	86.5( 0)	C21	CR	C1	C2	-93.4( 0)
C22	CR	C1	O1	59.4( 0)	C22	CR	C1	C2	-120.6( 0)
C1	CR	C18	O2	-154.2( 0)	C19	CR	C18	O2	118.0( 0)
C20	CR	C18	O2	40.5( 0)	C21	CR	C18	O2	-68.6( 0)
C22	CR	C18	O2	24.7( 0)	C1	CR	C19	O3	21.2( 0)
C18	CR	C19	O3	112.0( 0)	C20	CR	C19	O3	-69.5( 0)
C21	CR	C19	O3	12.6( 0)	C22	CR	C19	O3	-158.2( 0)
C1	CR	C20	O4	-173.0( 0)	C18	CR	C20	O4	-7.7( 0)
C19	CR	C20	O4	-85.2( 0)	C21	CR	C20	O4	101.4( 0)
C22	CR	C20	O4	8.2( 0)	C1	CR	C21	O5	-19.1( 0)
C18	CR	C21	O5	-110.0( 0)	C19	CR	C21	O5	-10.5( 0)
C20	CR	C21	O5	71.5( 0)	C22	CR	C21	O5	160.3( 0)
C1	CR	C22	O6	-116.9( 0)	C18	CR	C22	O6	126.2( 0)
C19	CR	C22	O6	35.0( 0)	C20	CR	C22	O6	-53.3( 0)
C21	CR	C22	O6	-143.9( 0)	C4	O1	C1	CR	-178.4( 0)
C4	O1	C1	C2	1.6( 0)	C1	O1	C4	C3	16.7( 0)
CR	C1	C2	C3	161.2( 0)	CR	C1	C2	C5	-76.6( 0)
O1	C1	C2	C3	-18.8( 0)	O1	C1	C2	C5	103.4( 0)
C1	C2	C3	C4	27.2( 0)	C1	C2	C3	C12	-96.8( 0)
C5	C2	C3	C4	-93.5( 0)	C5	C2	C3	C12	142.5( 0)
C1	C2	C5	C6	175.8( 0)	C3	C2	C5	C6	-66.9( 0)
C2	C3	C4	O1	-26.1( 0)	C12	C3	C4	O1	95.6( 0)
C2	C3	C12	C13	-91.0( 0)	C2	C3	C12	C17	86.0( 0)
C4	C3	C12	C13	153.8( 0)	C4	C3	C12	C17	-29.2( 0)
C2	C5	C6	C7	102.2( 0)	C2	C5	C6	C11	-75.5( 0)
C5	C6	C7	C8	-177.6( 0)	C11	C6	C7	C8	.2( 0)
C5	C6	C11	C10	178.1( 0)	C7	C6	C11	C10	.3( 0)
C6	C7	C8	C9	-.9( 0)	C7	C8	C9	C10	1.1( 0)
C8	C9	C10	C11	-.6( 0)	C9	C10	C11	C6	-.1( 0)
C3	C12	C13	C14	178.1( 0)	C17	C12	C13	C14	.9( 0)
C3	C12	C17	C16	-178.9( 0)	C13	C12	C17	C16	-1.8( 0)
C12	C13	C14	C15	.7( 0)	C13	C14	C15	C16	-1.4( 0)
C14	C15	C16	C17	.4( 0)	C15	C16	C17	C12	1.2( 0)

**I.6 REFERENCES AND NOTES**

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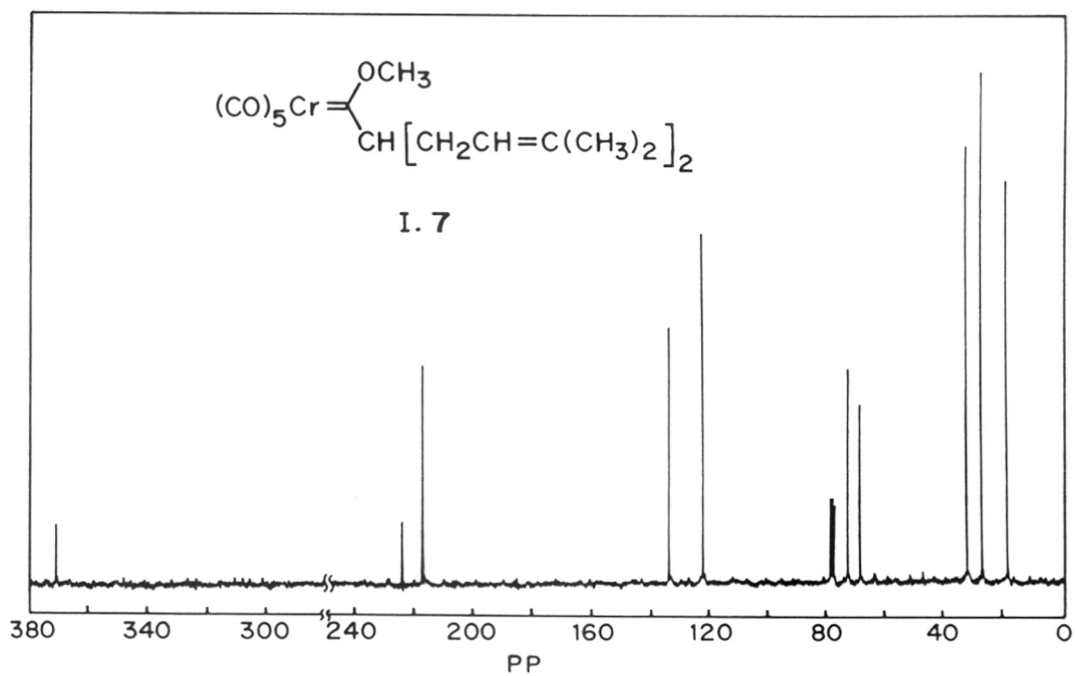
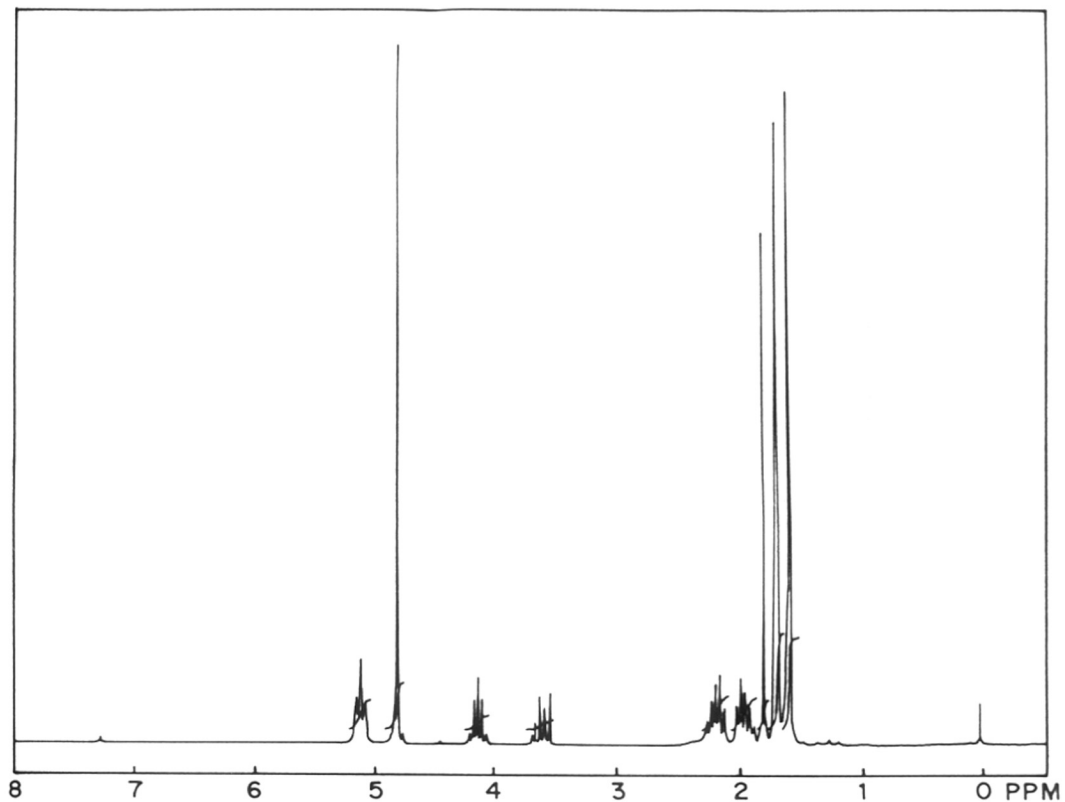
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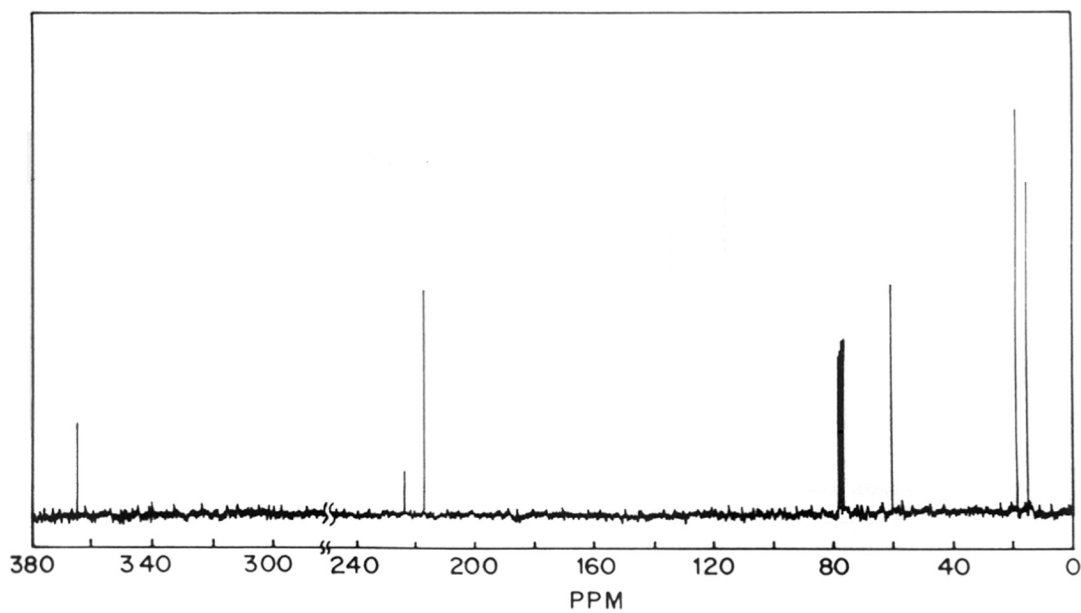
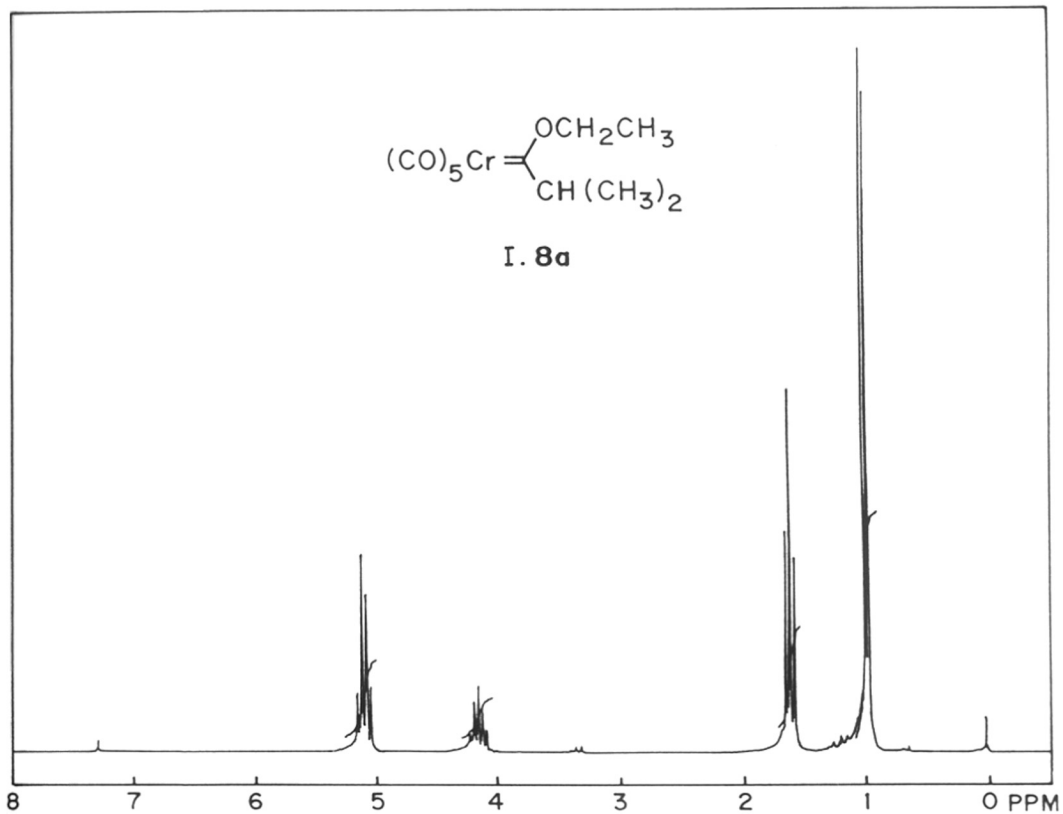
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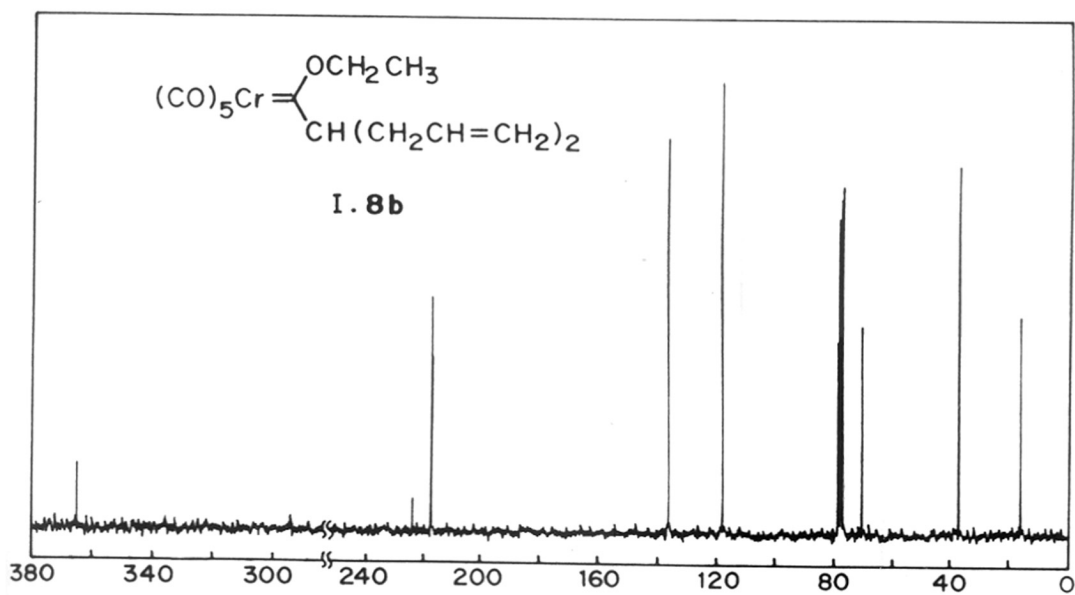
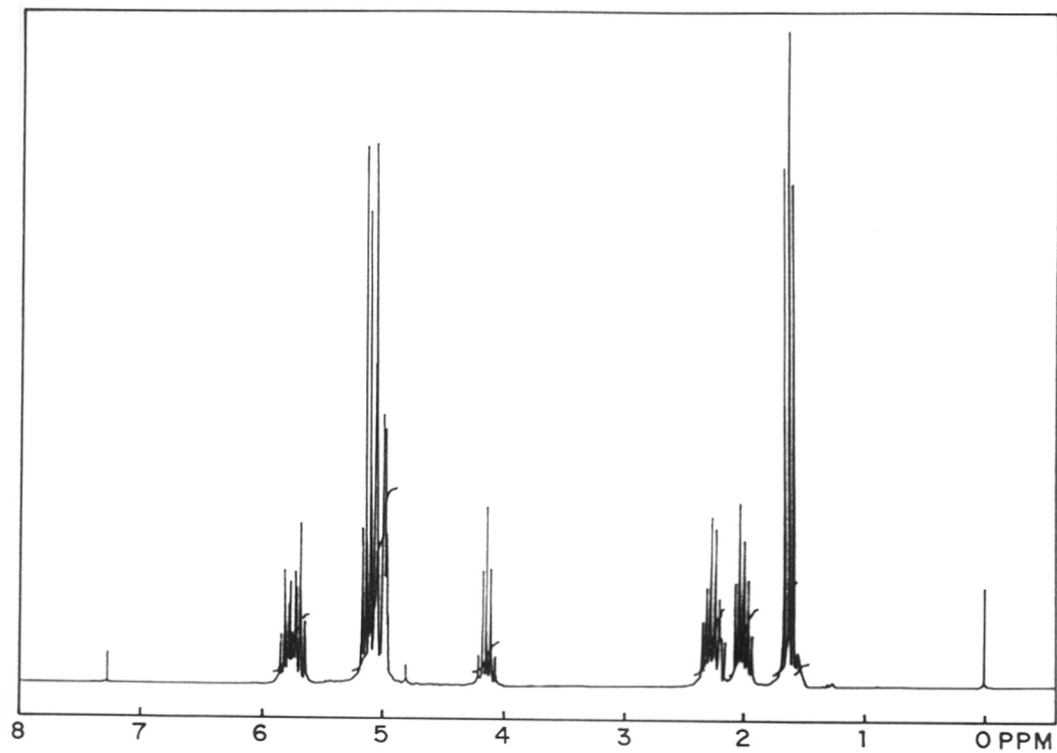
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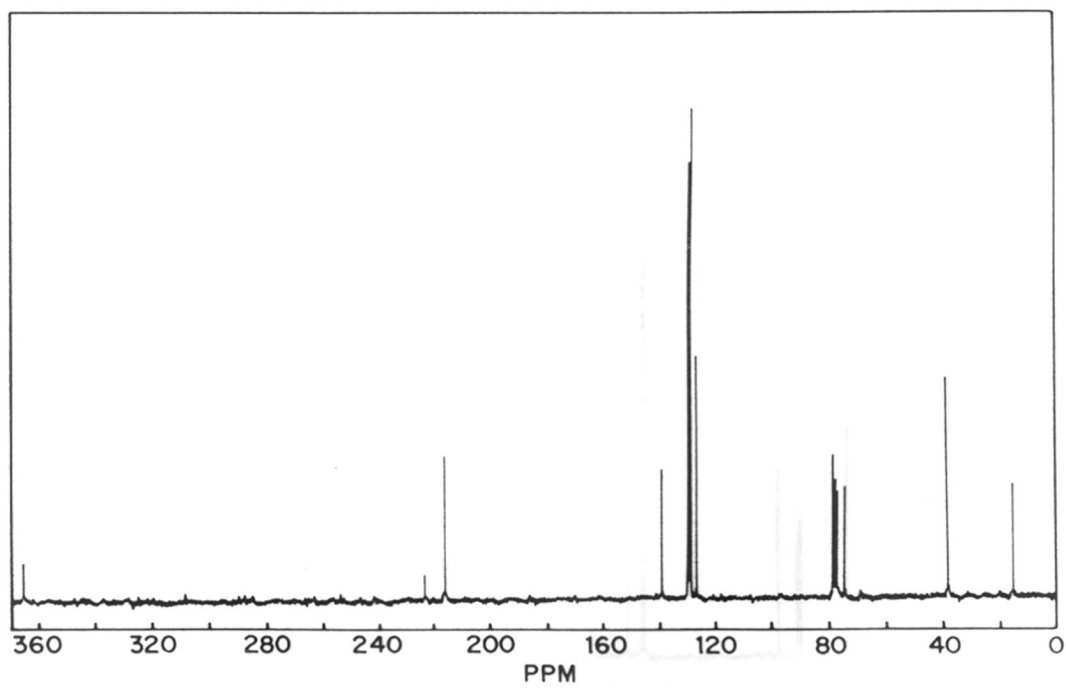
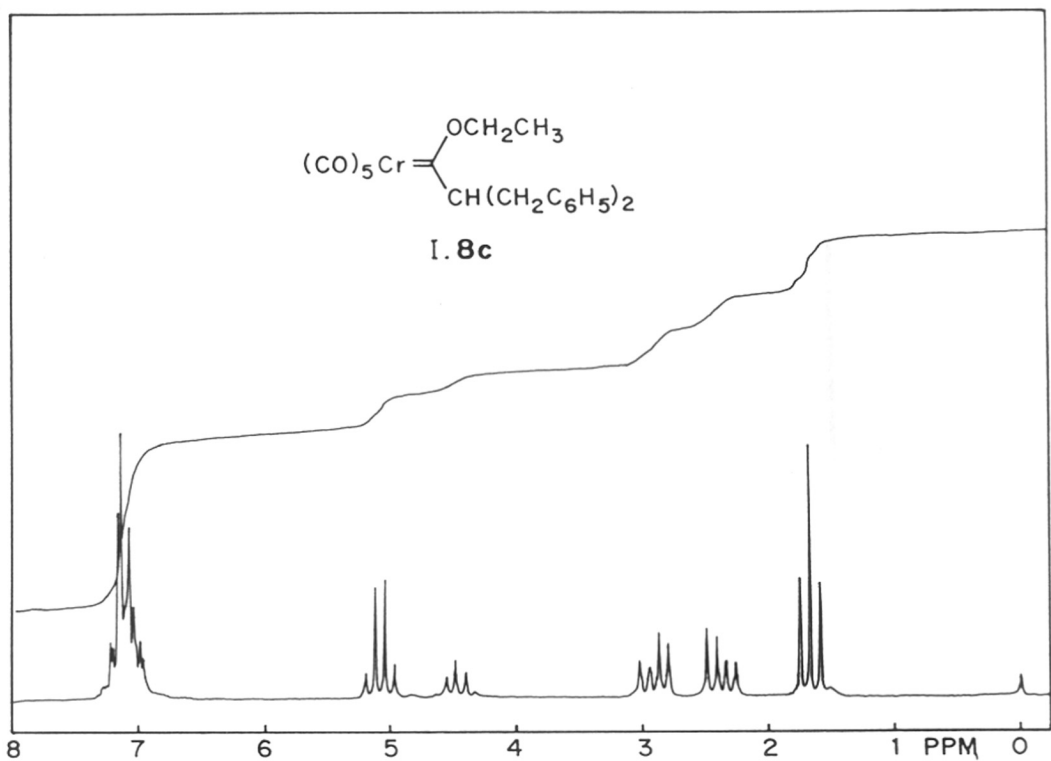
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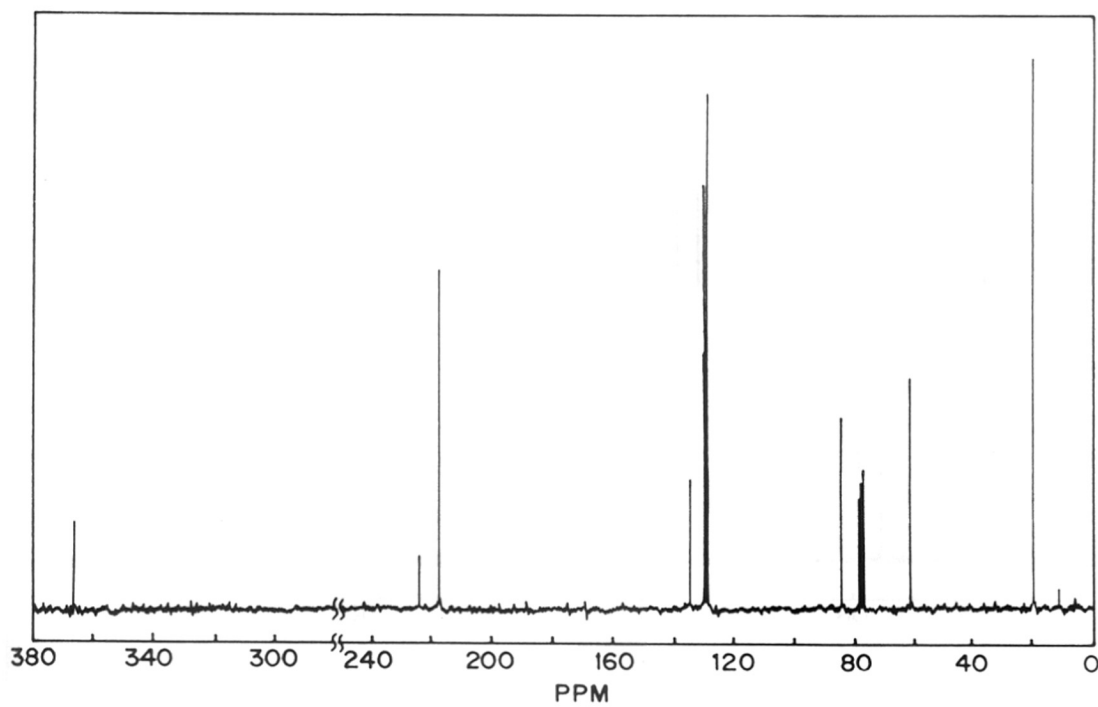
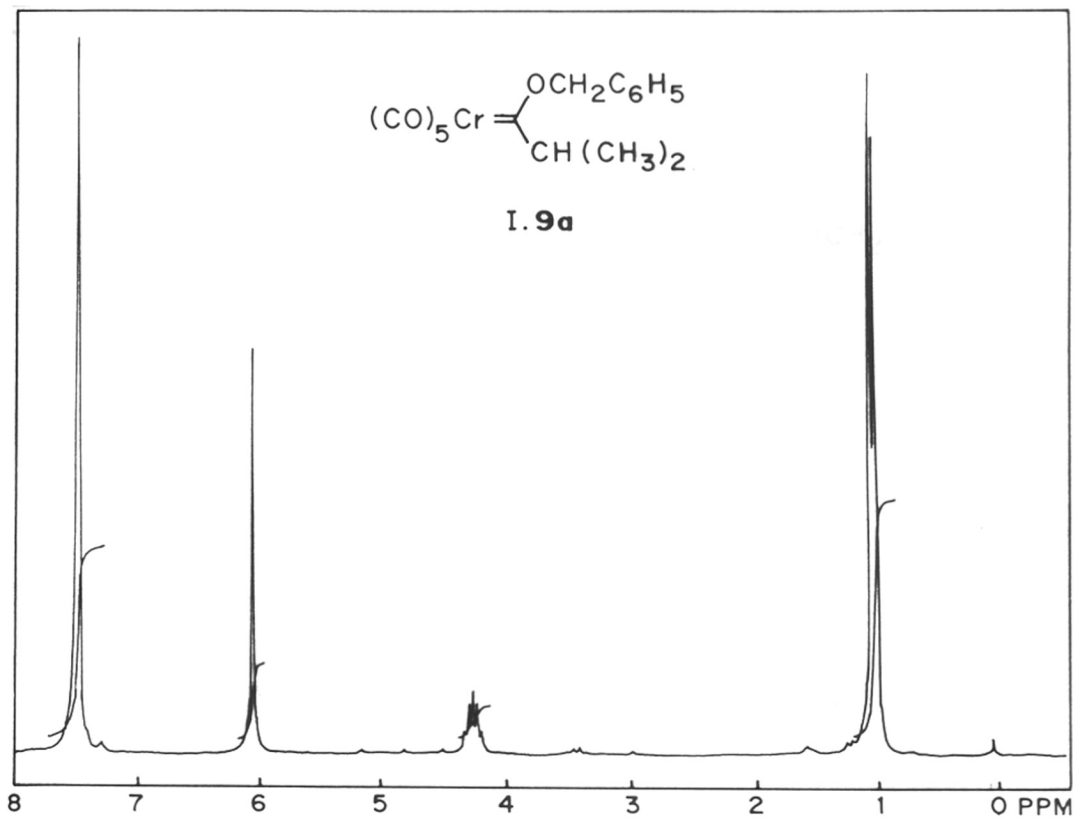


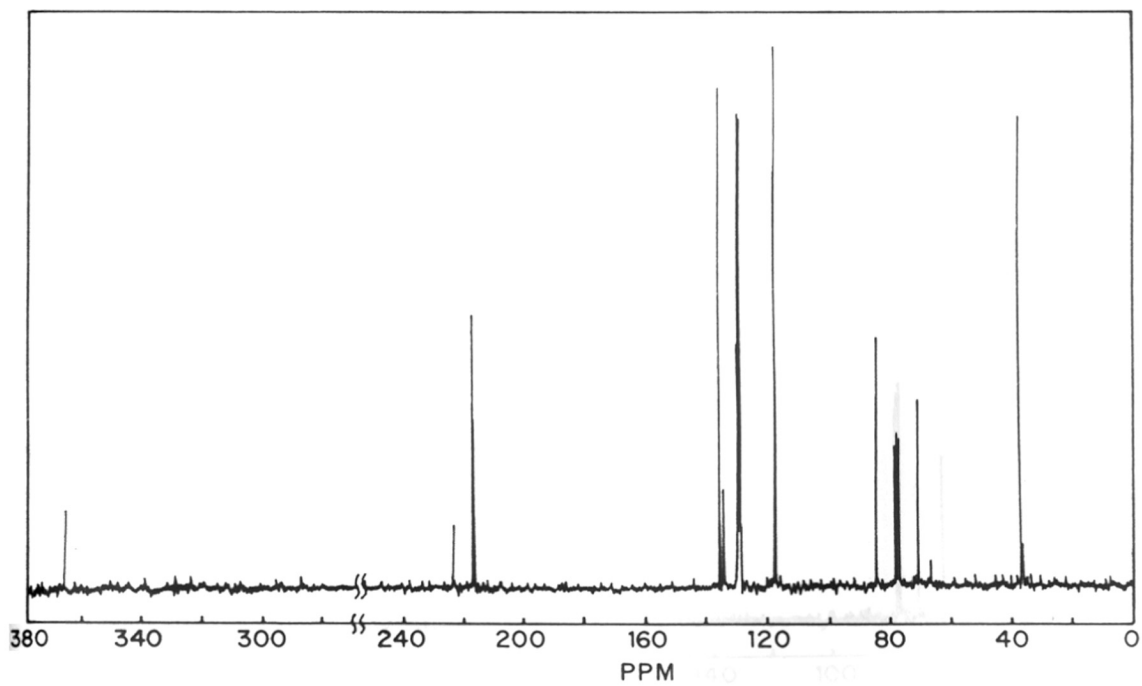
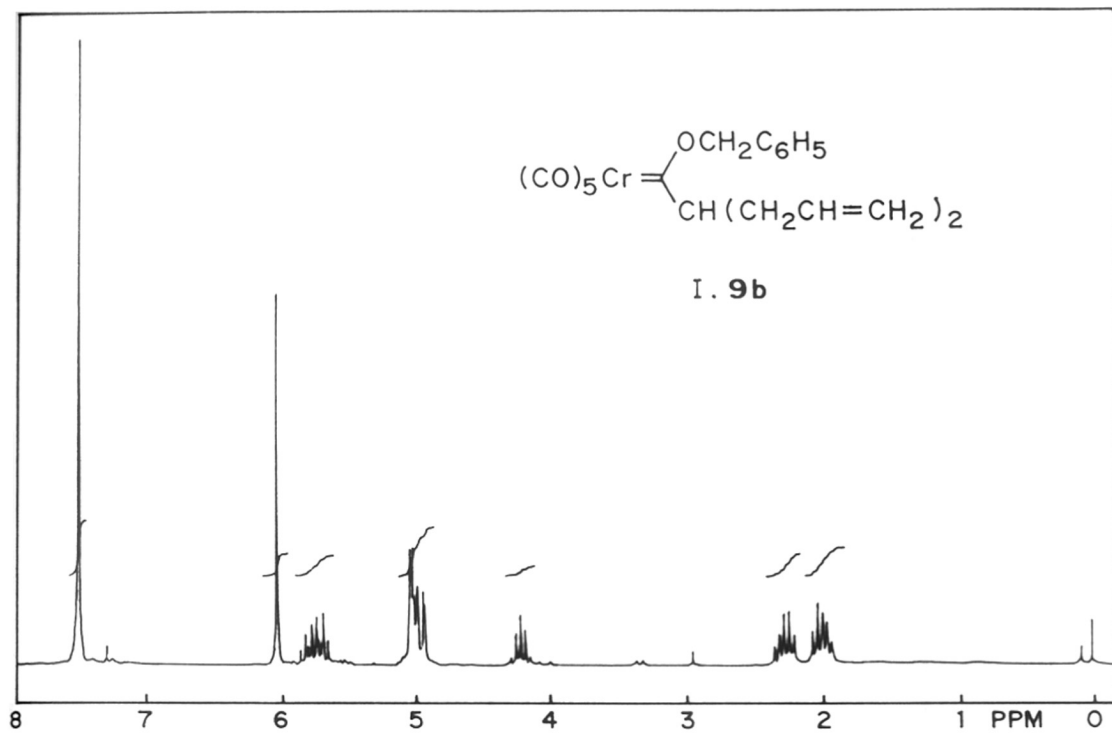


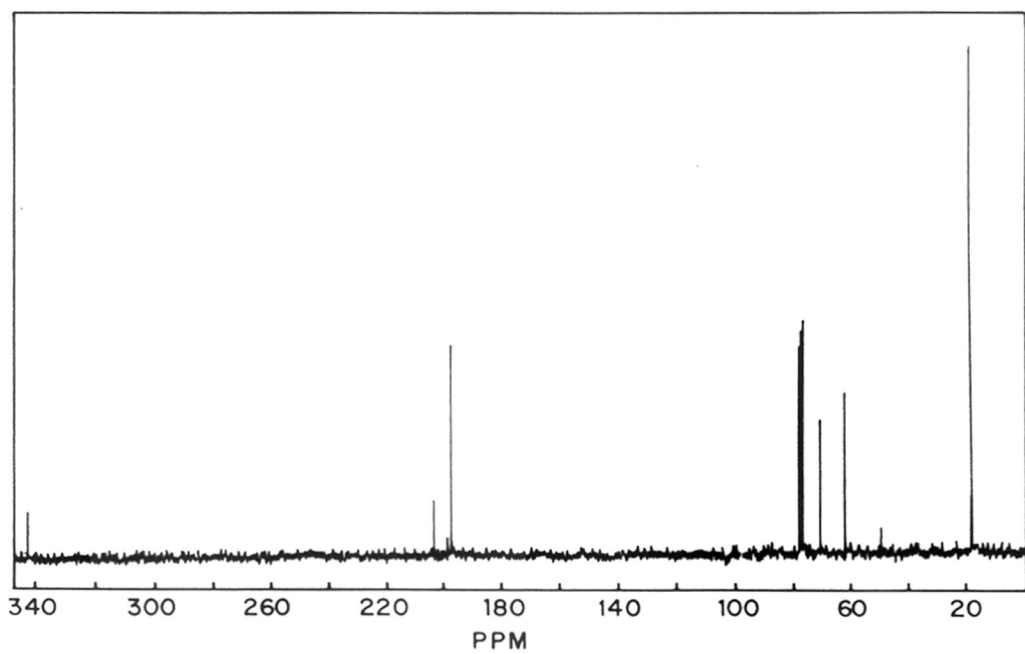
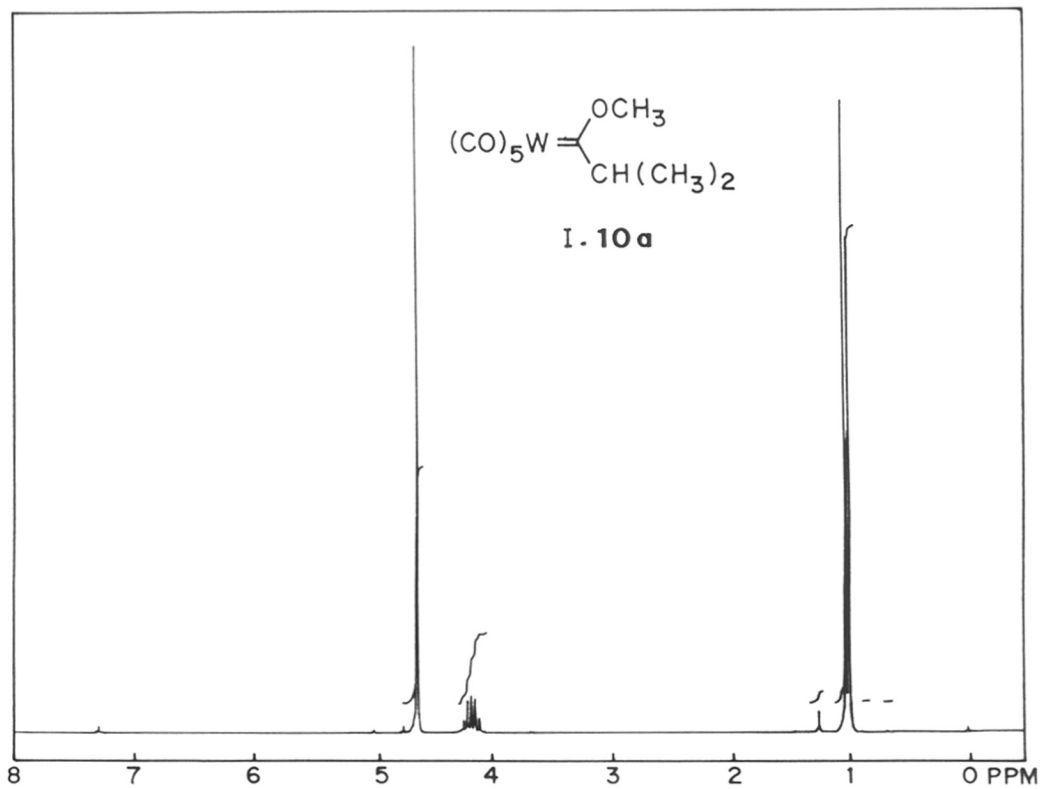


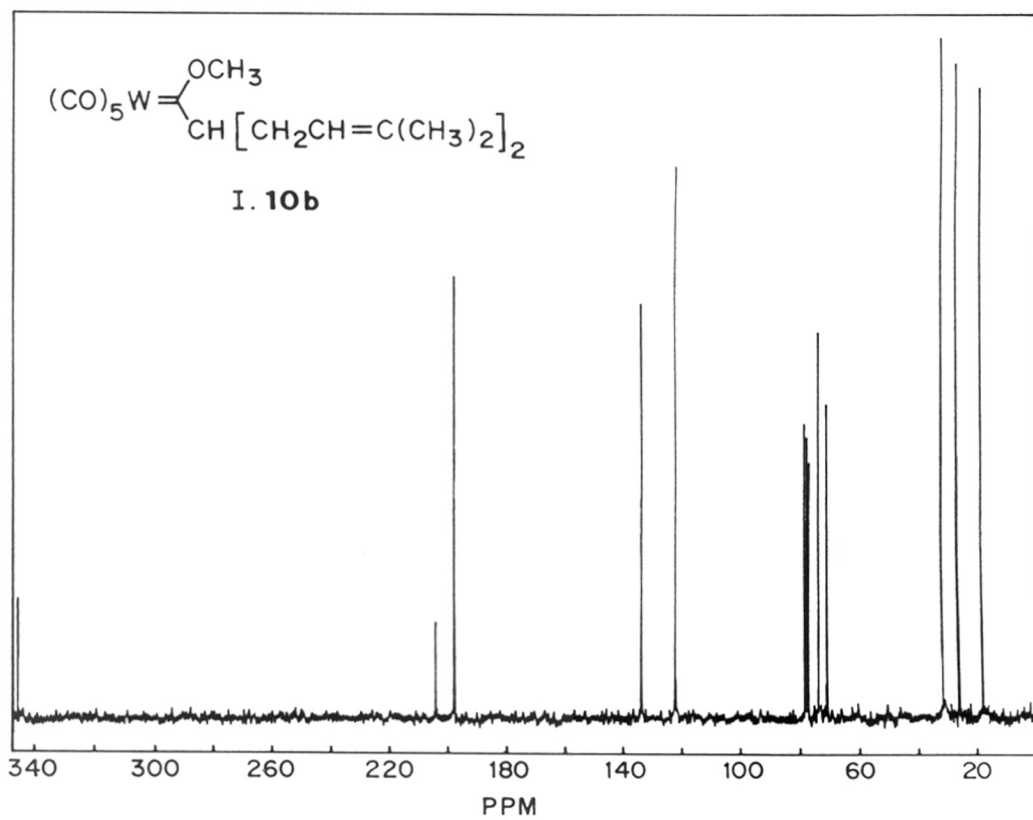
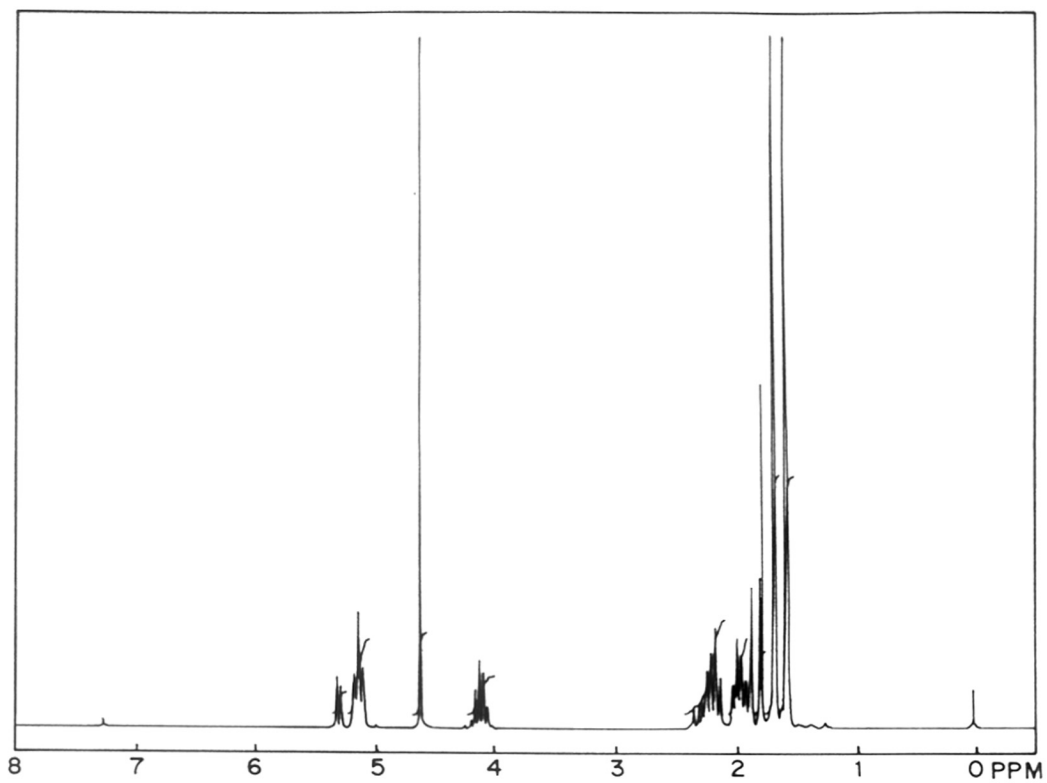




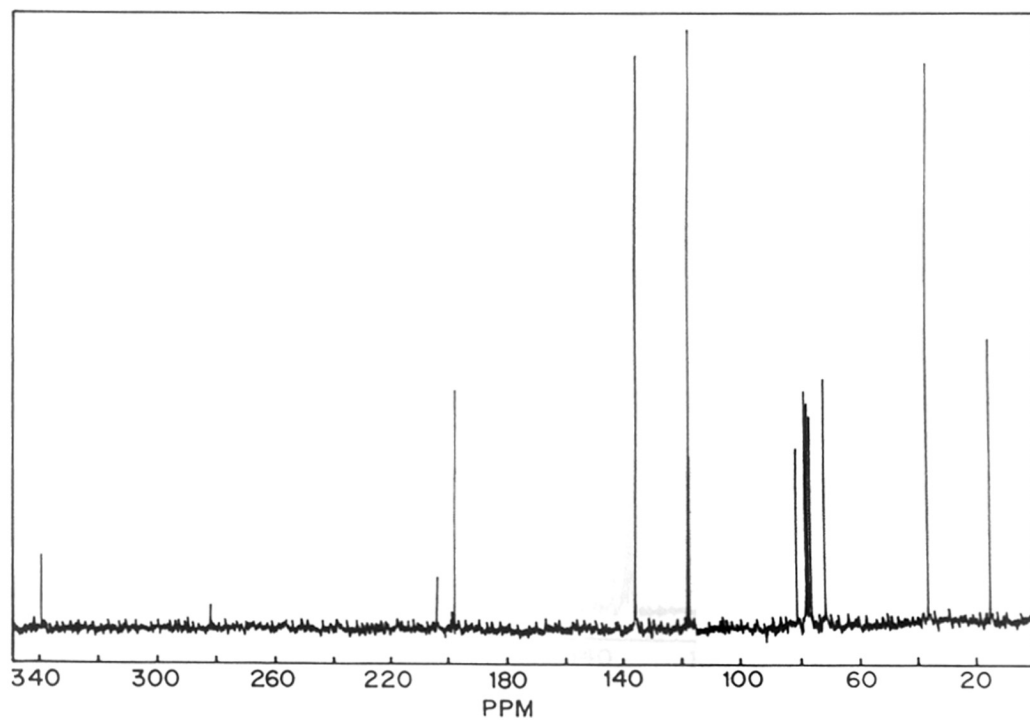
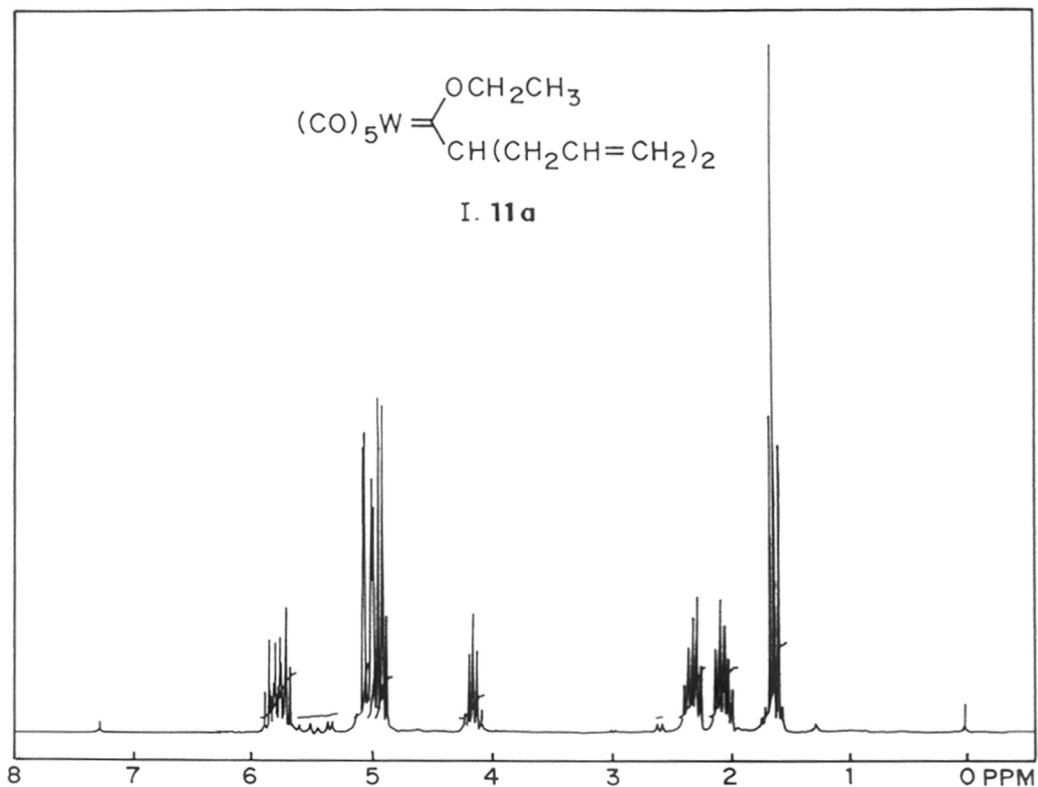


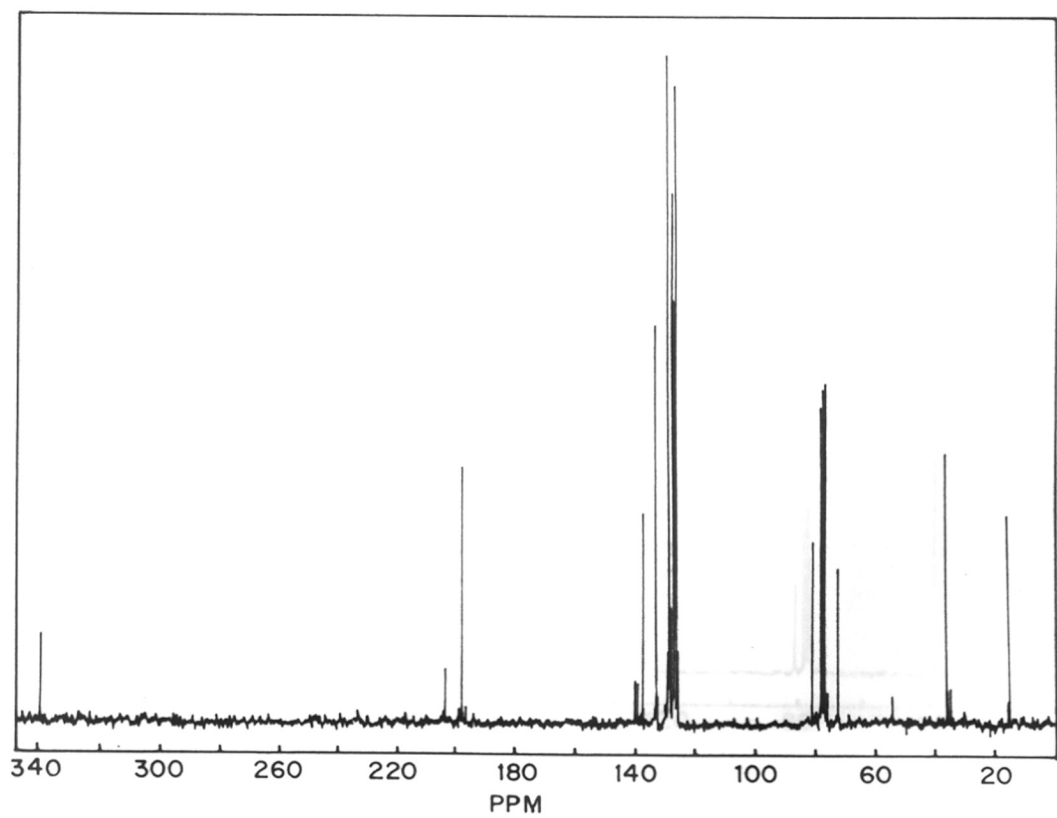
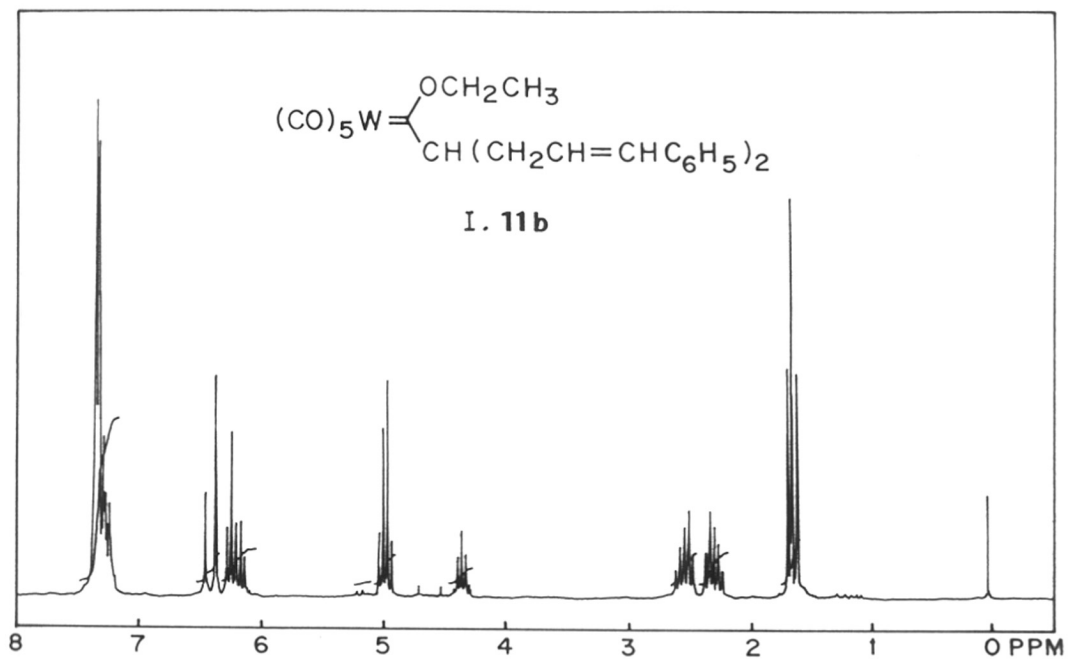


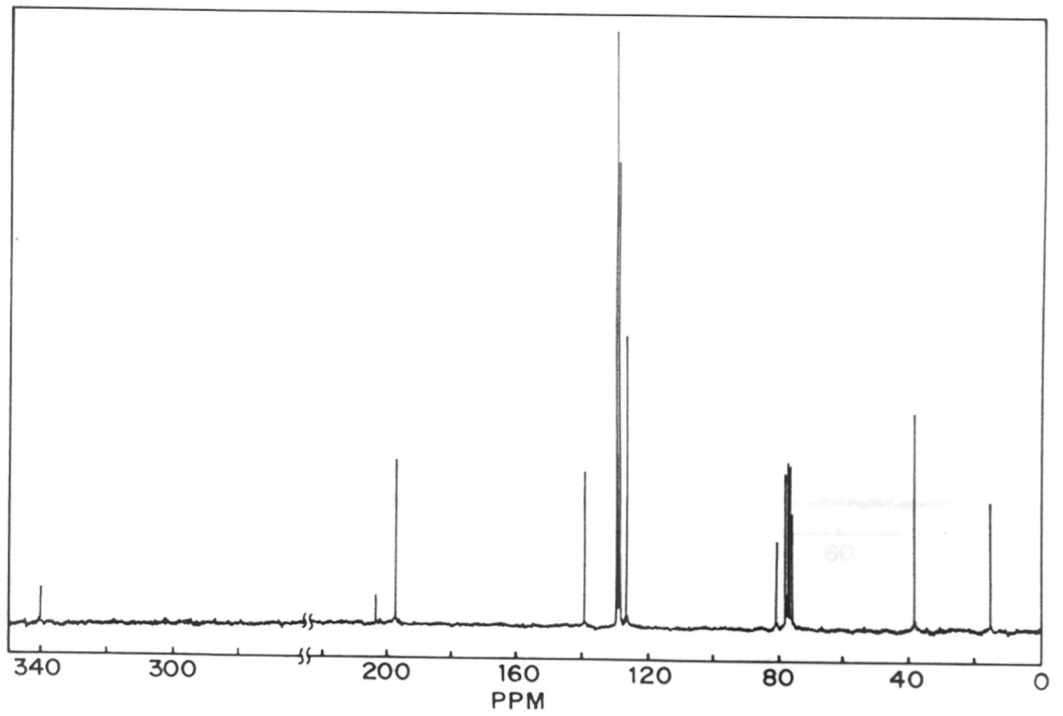
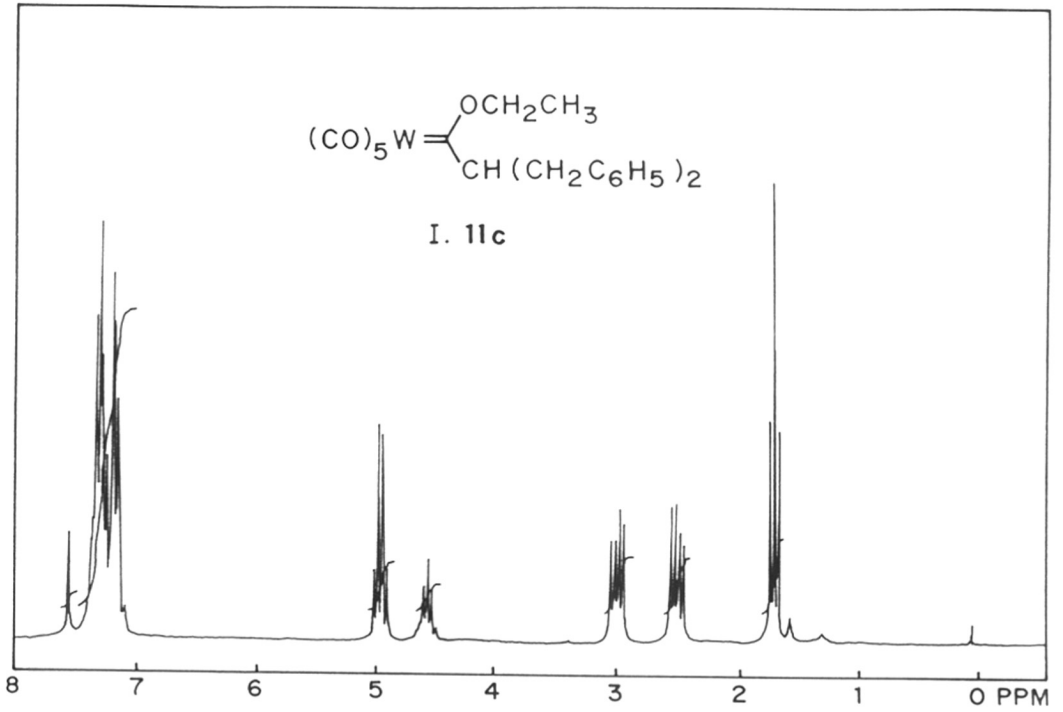


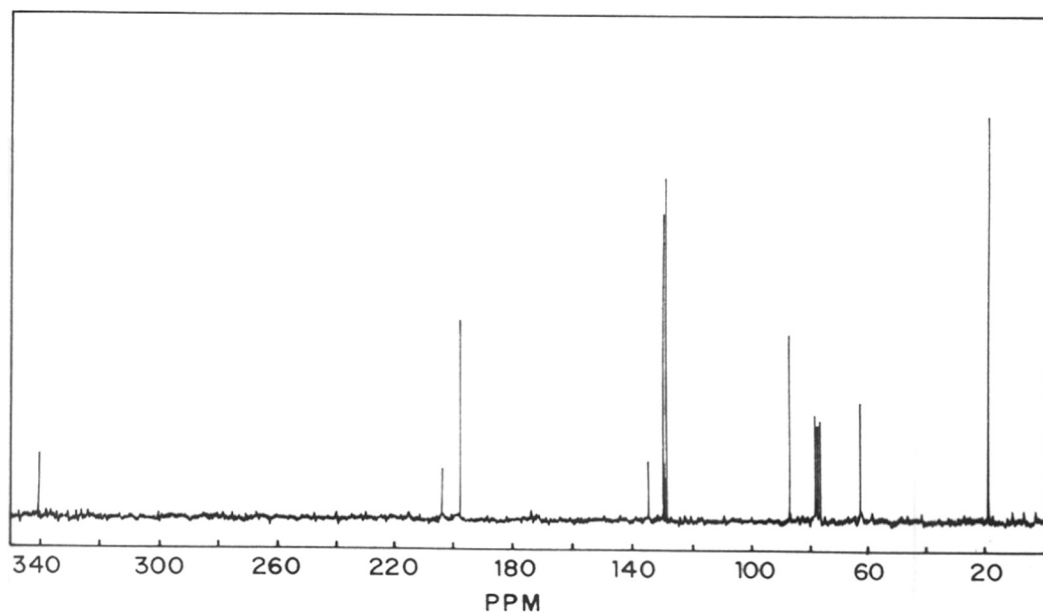
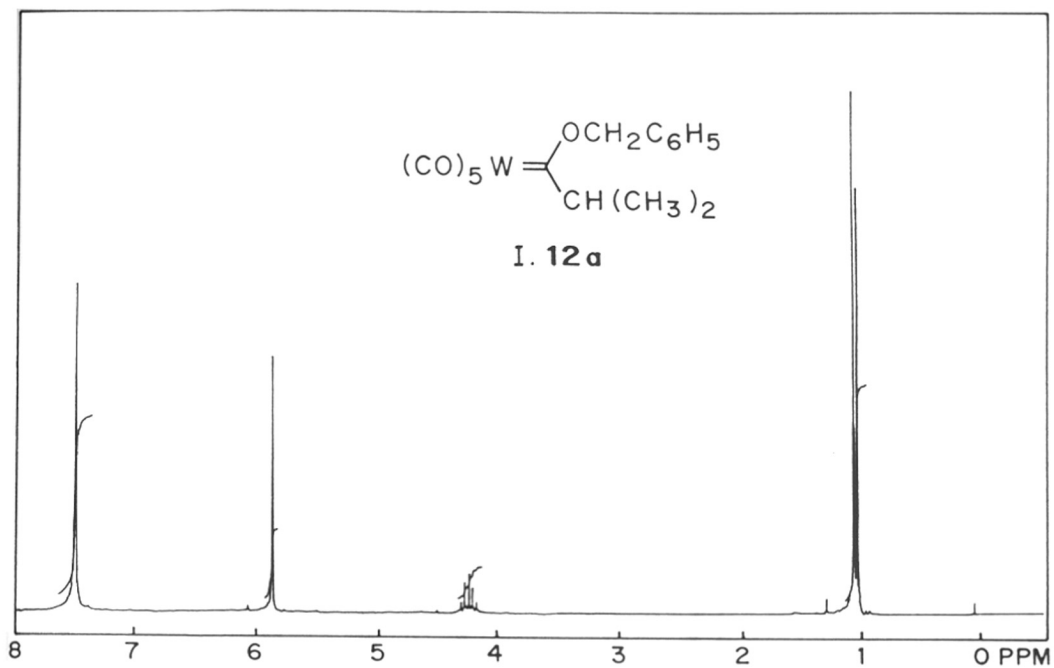


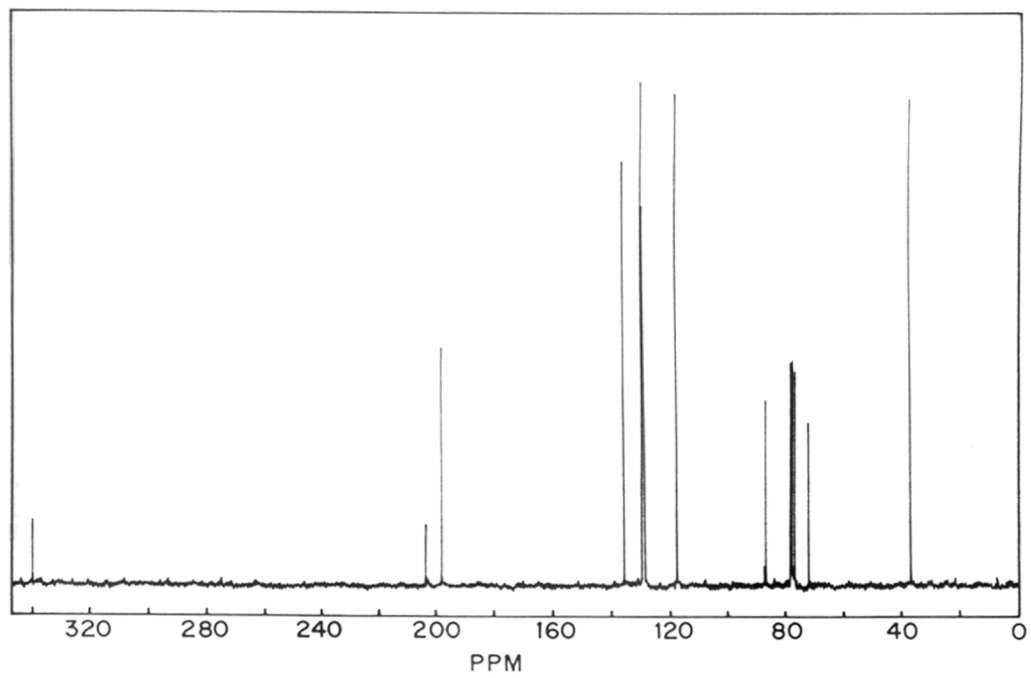
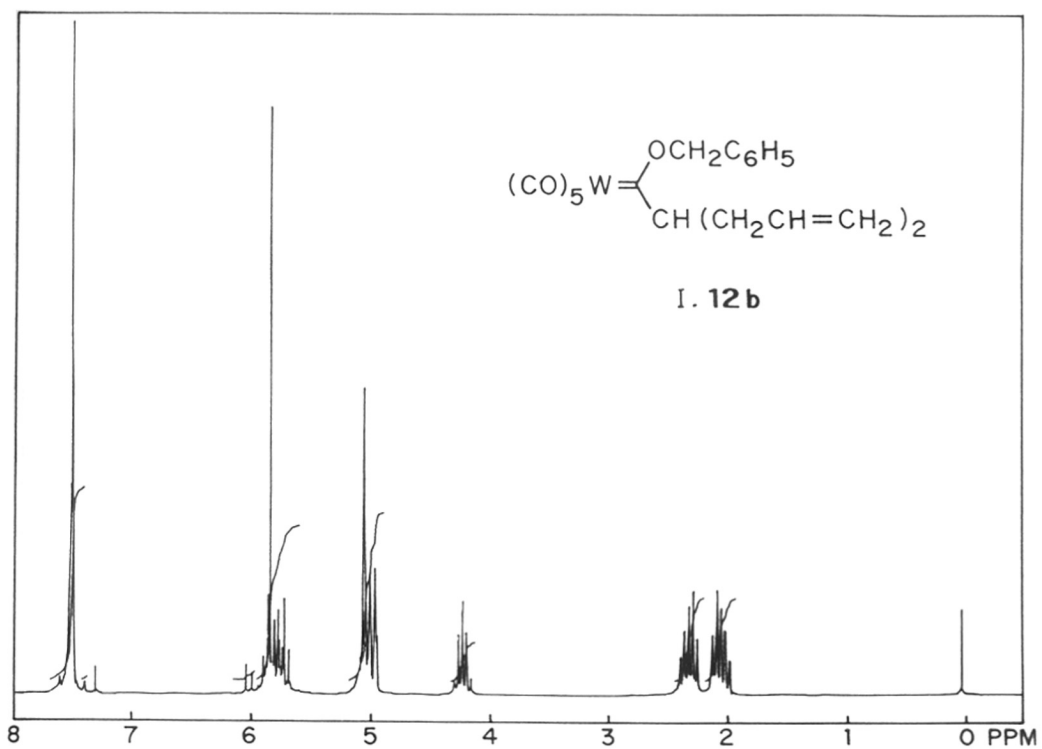


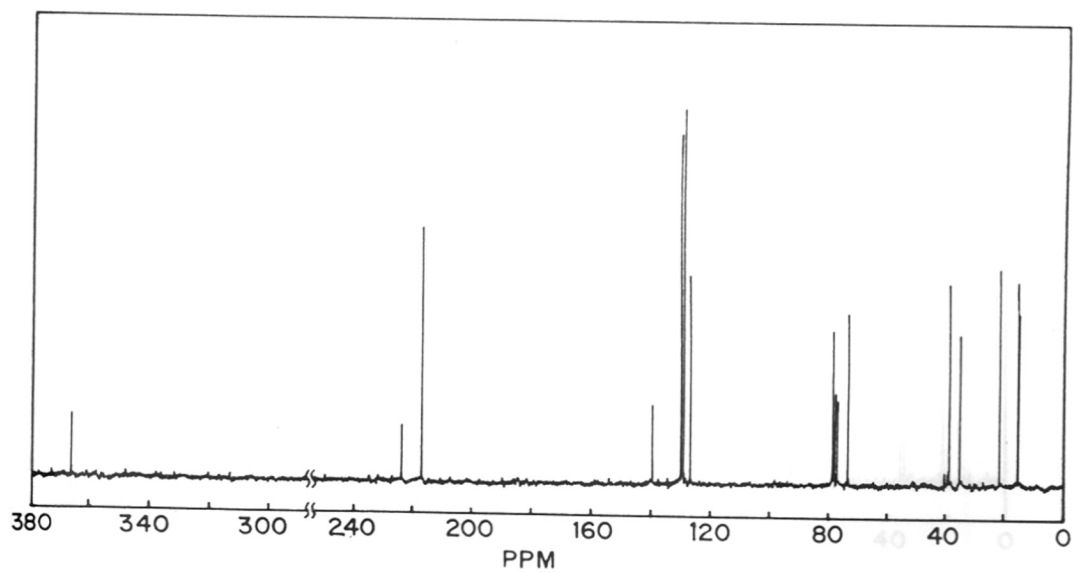
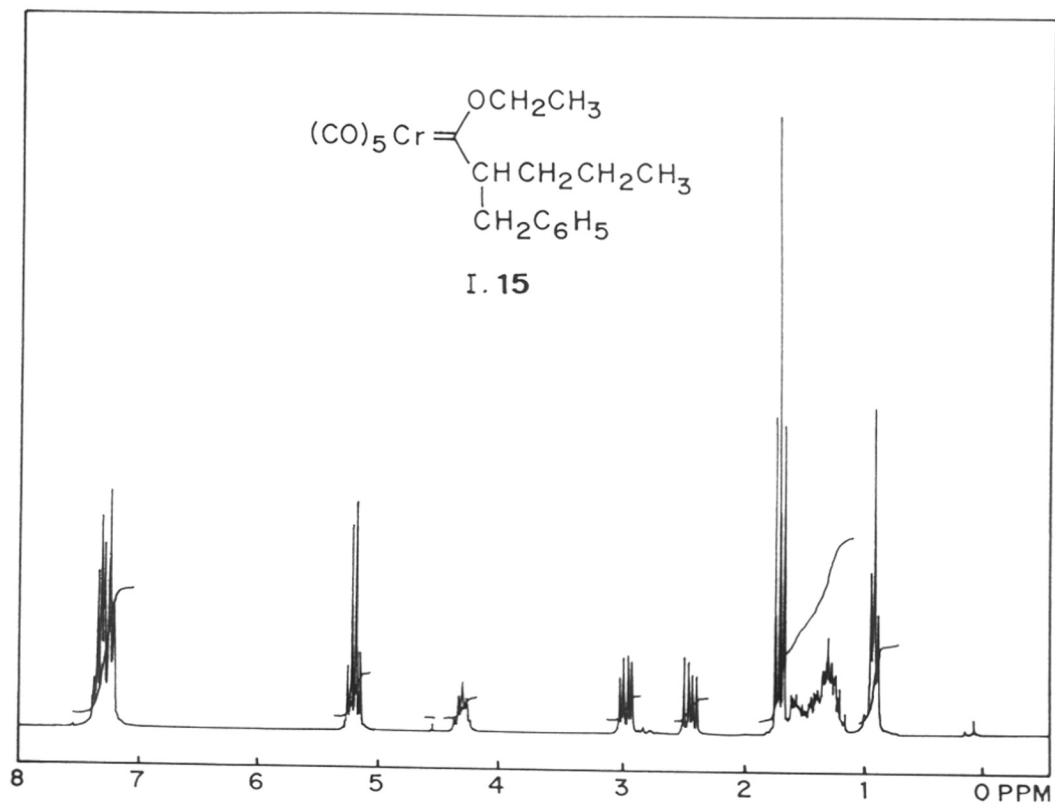


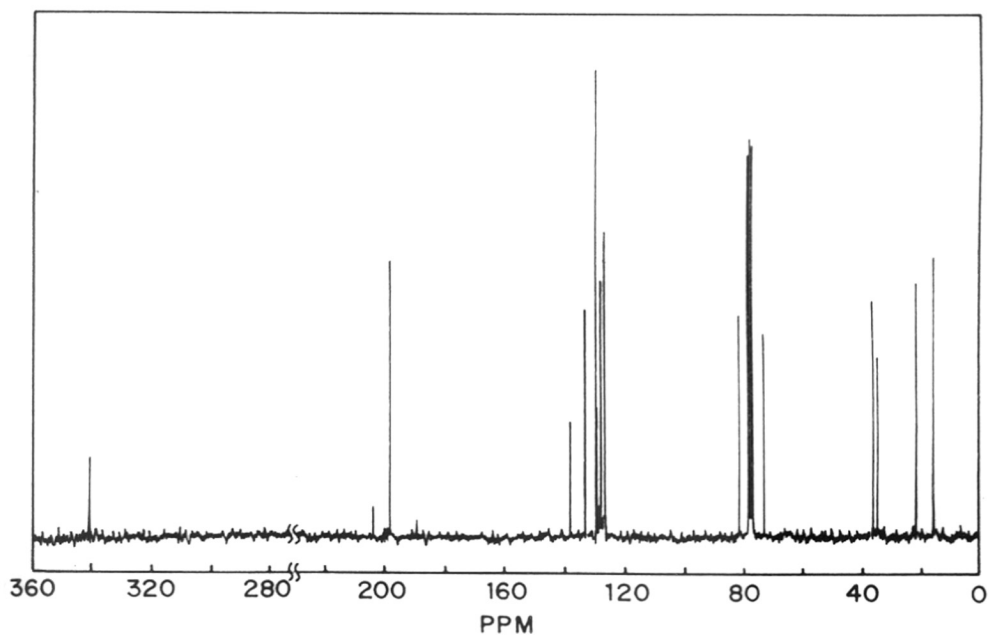
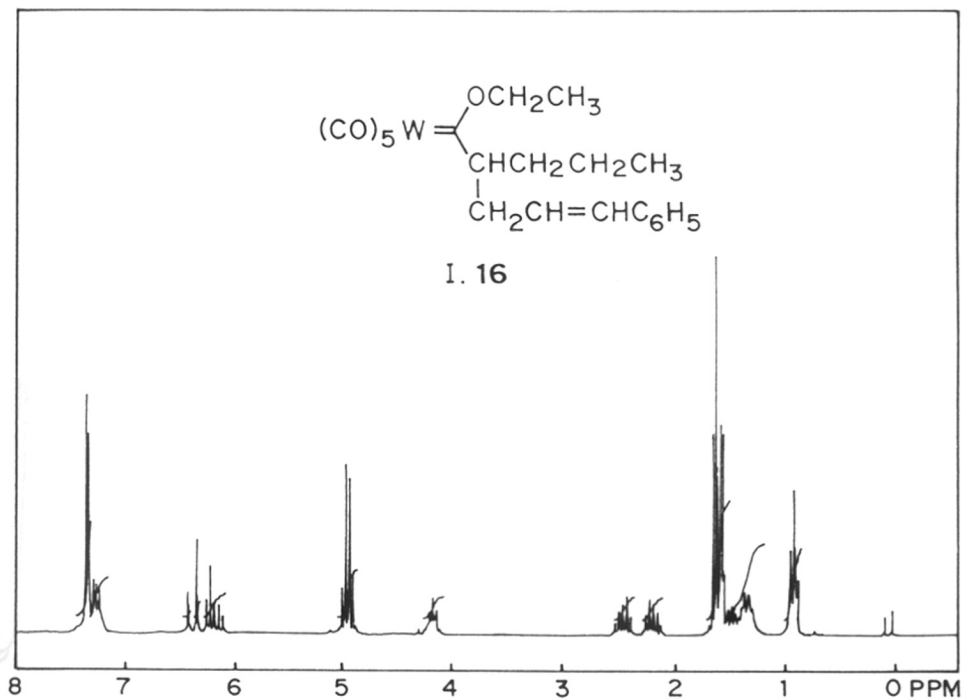


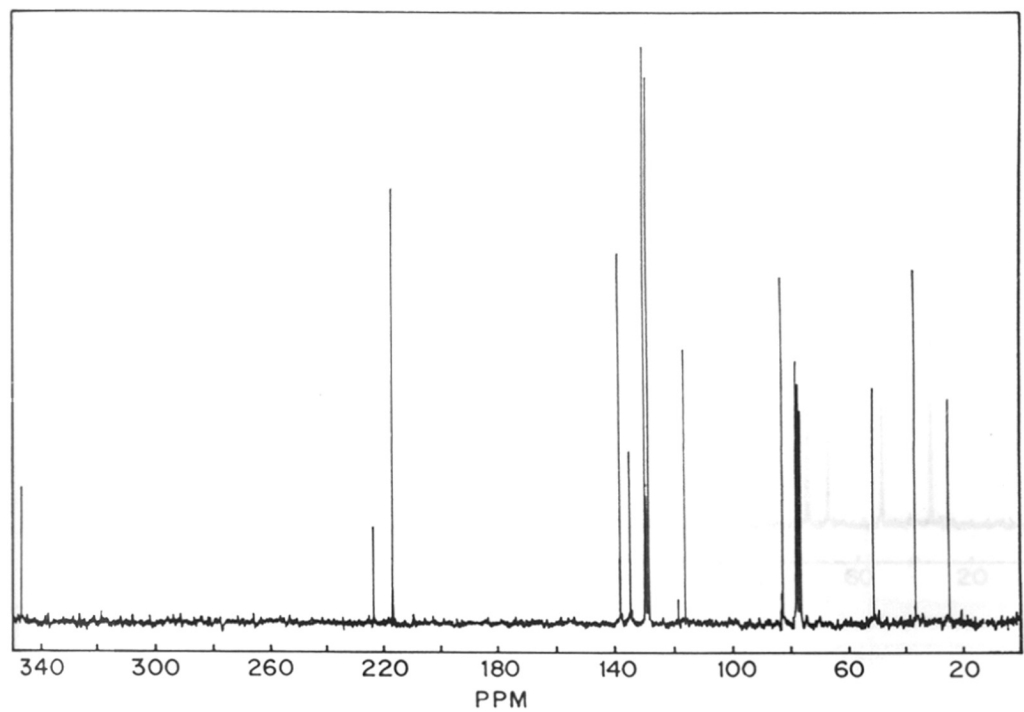
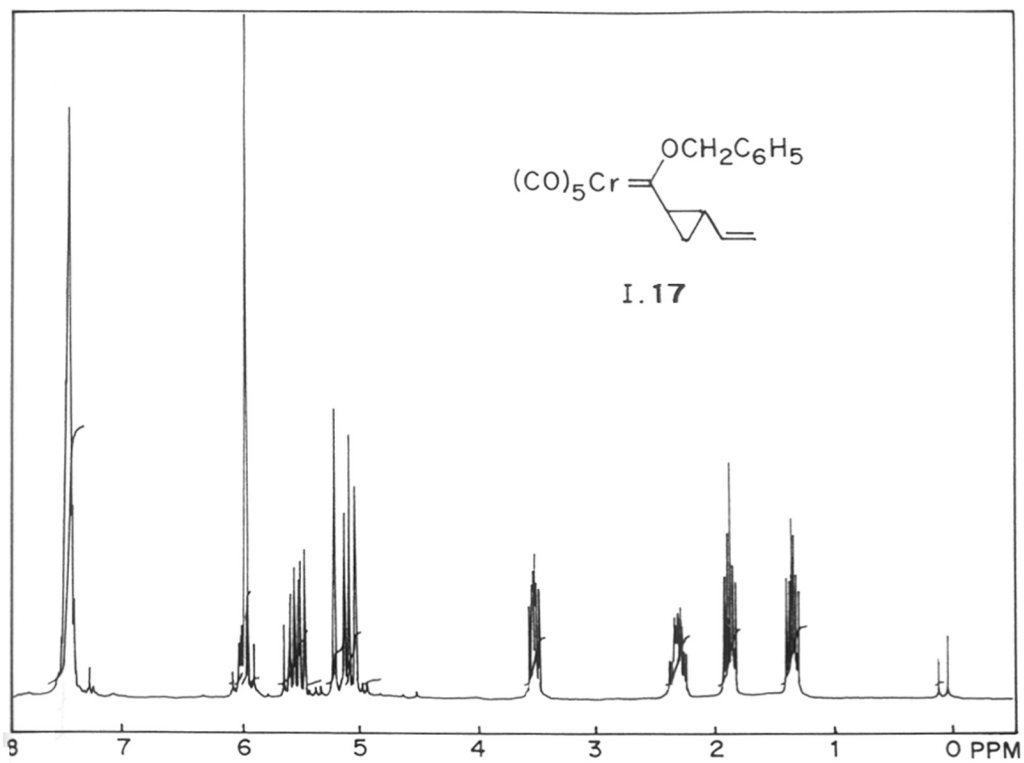




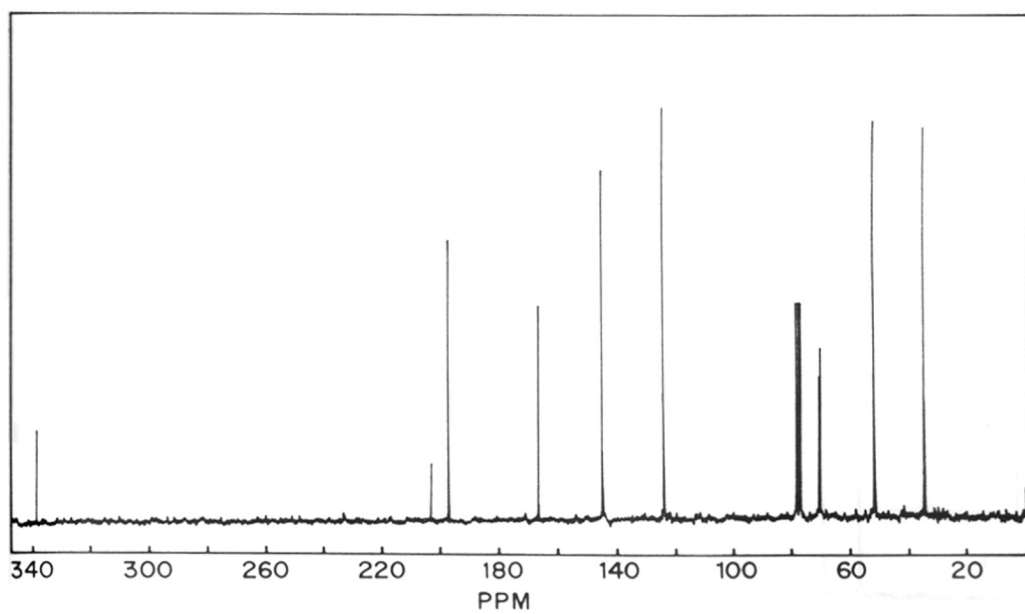
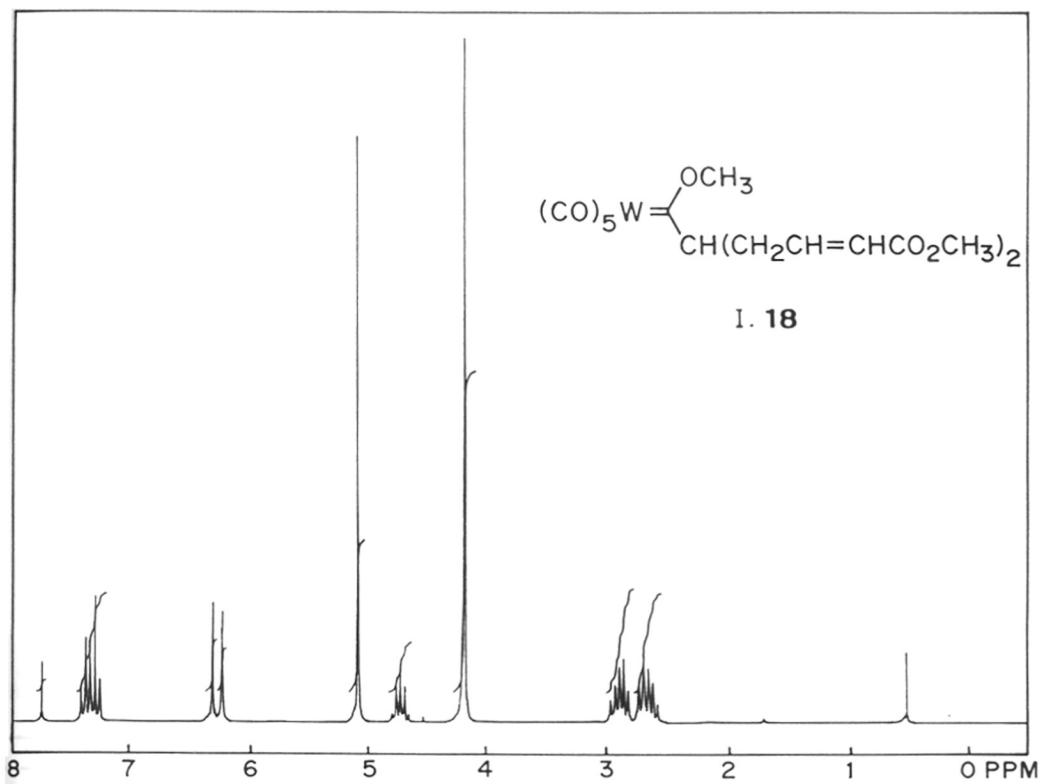


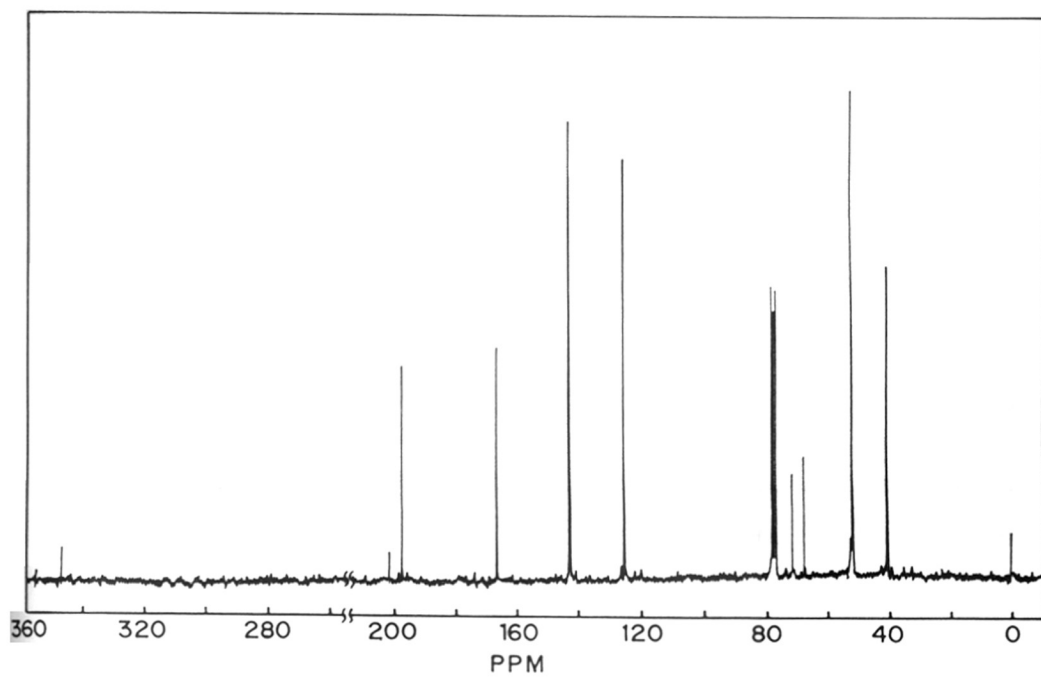
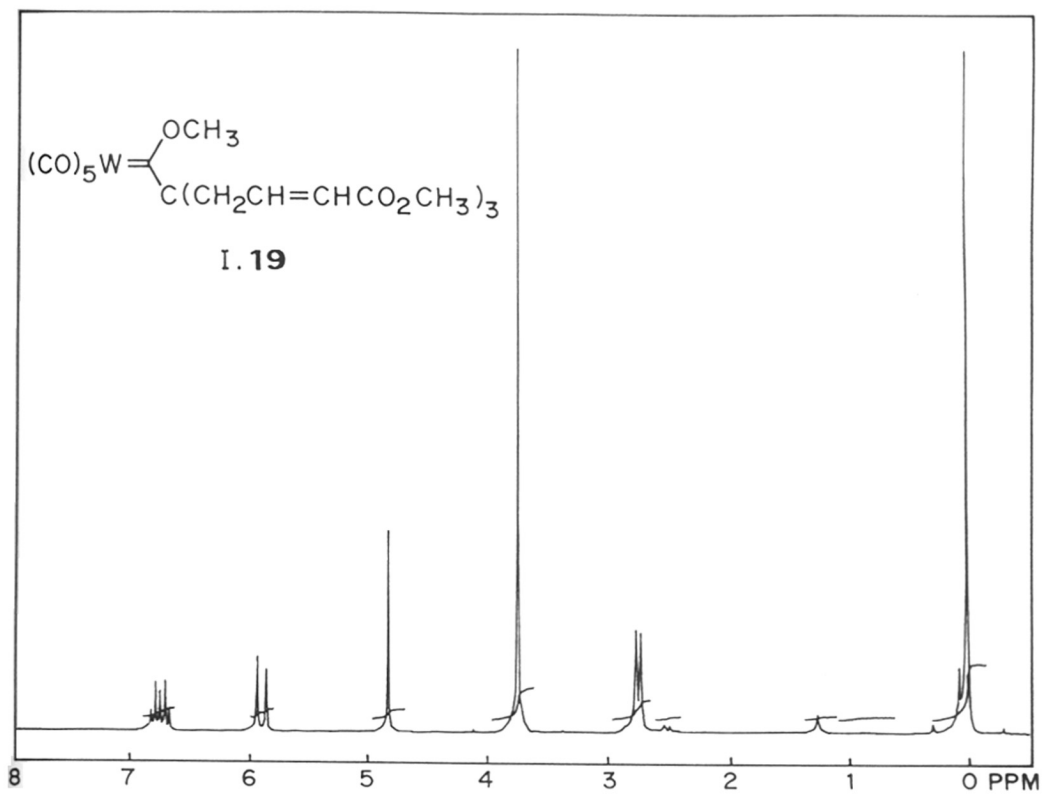


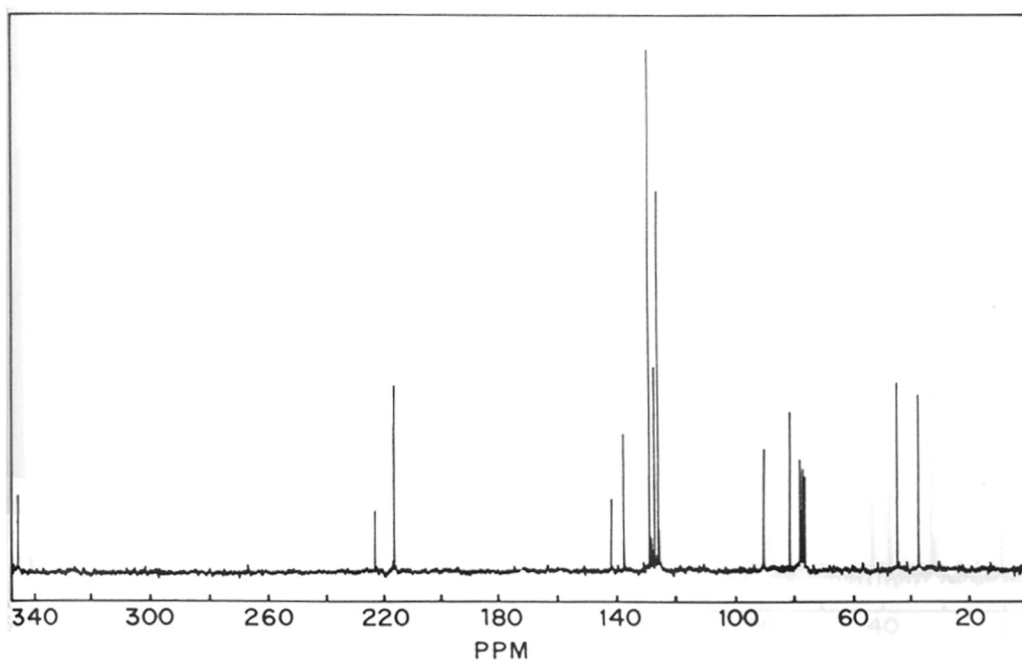
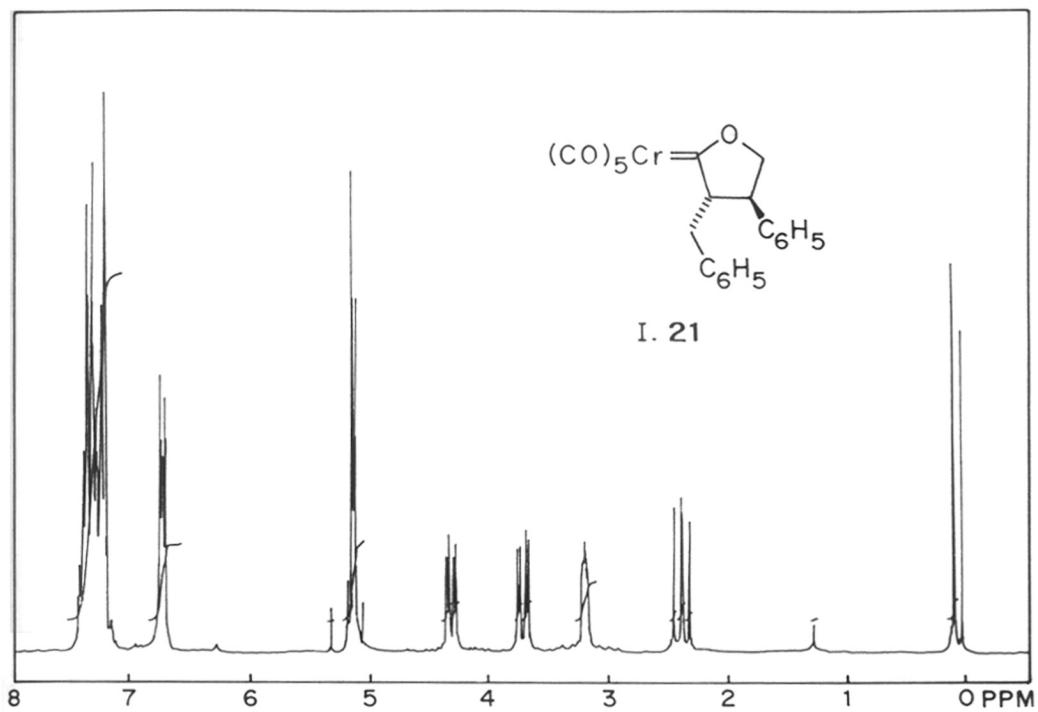


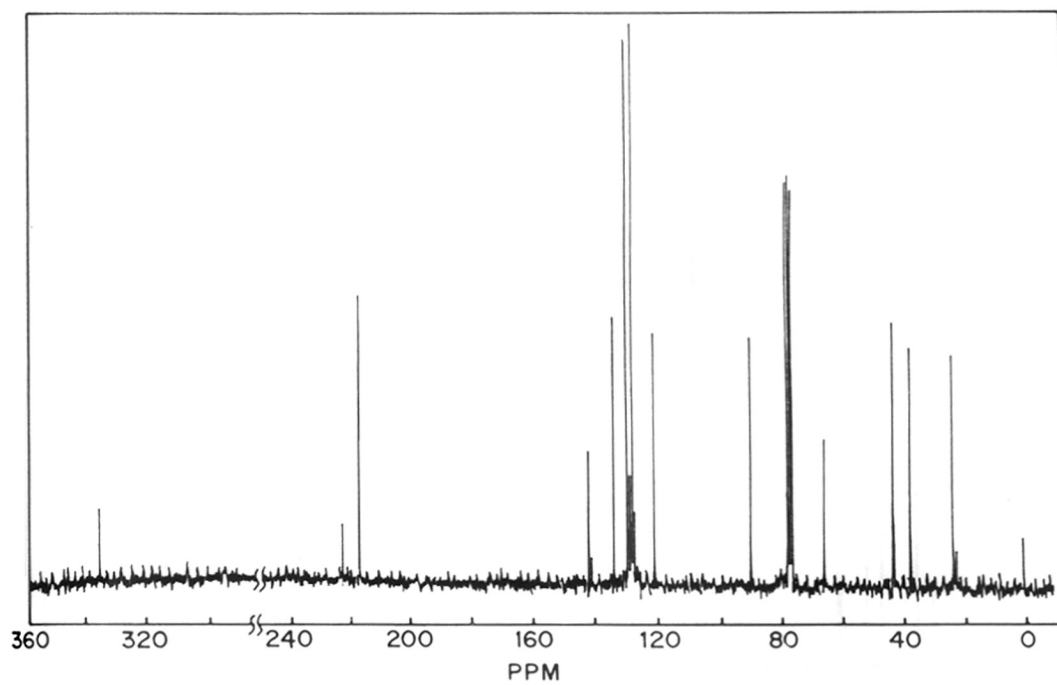
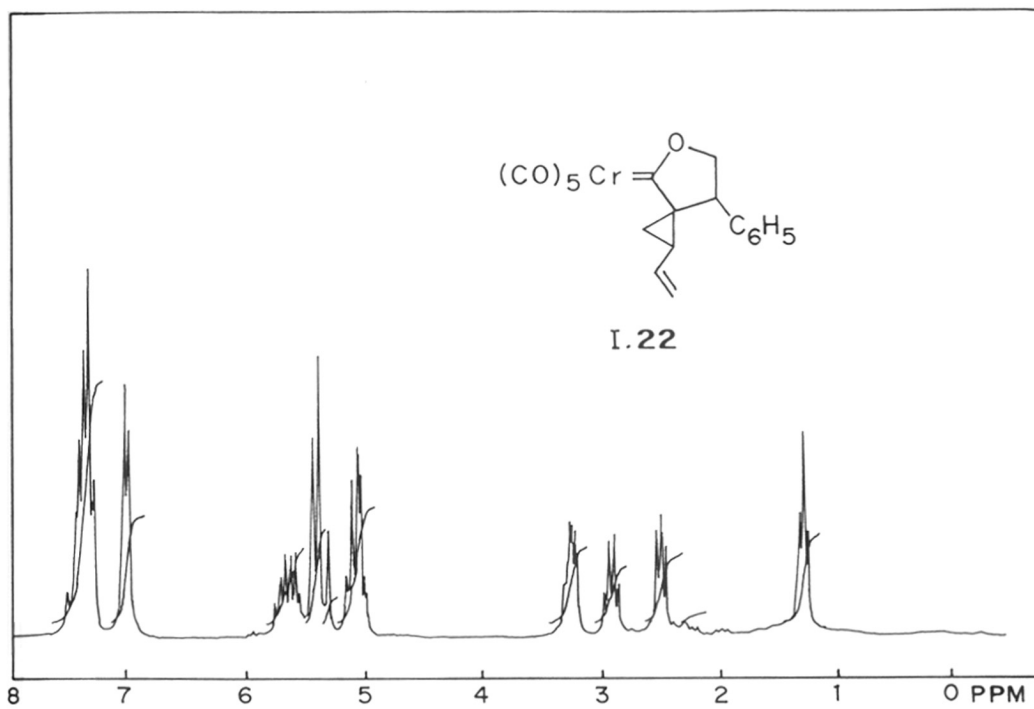


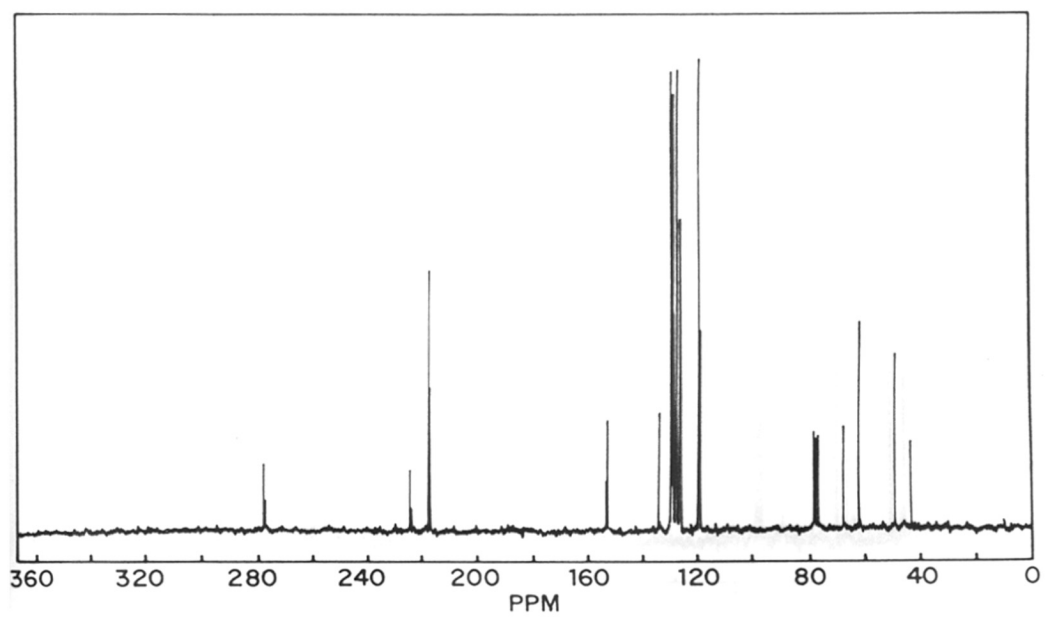
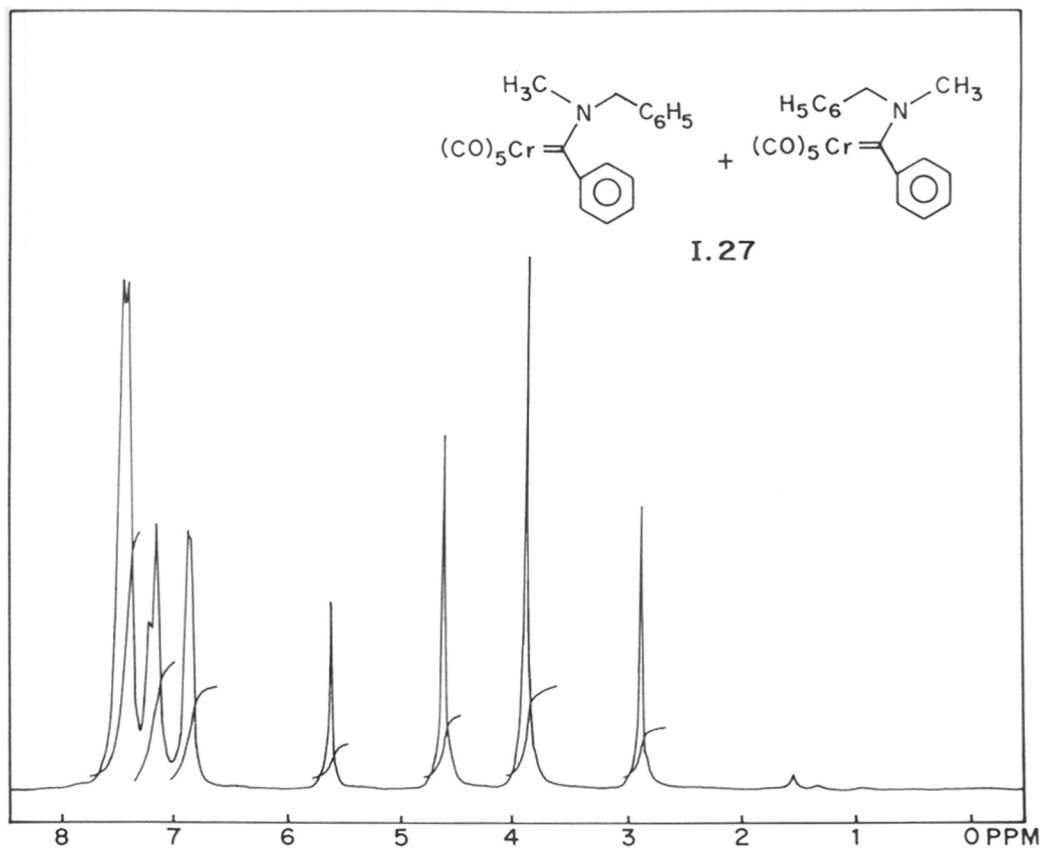


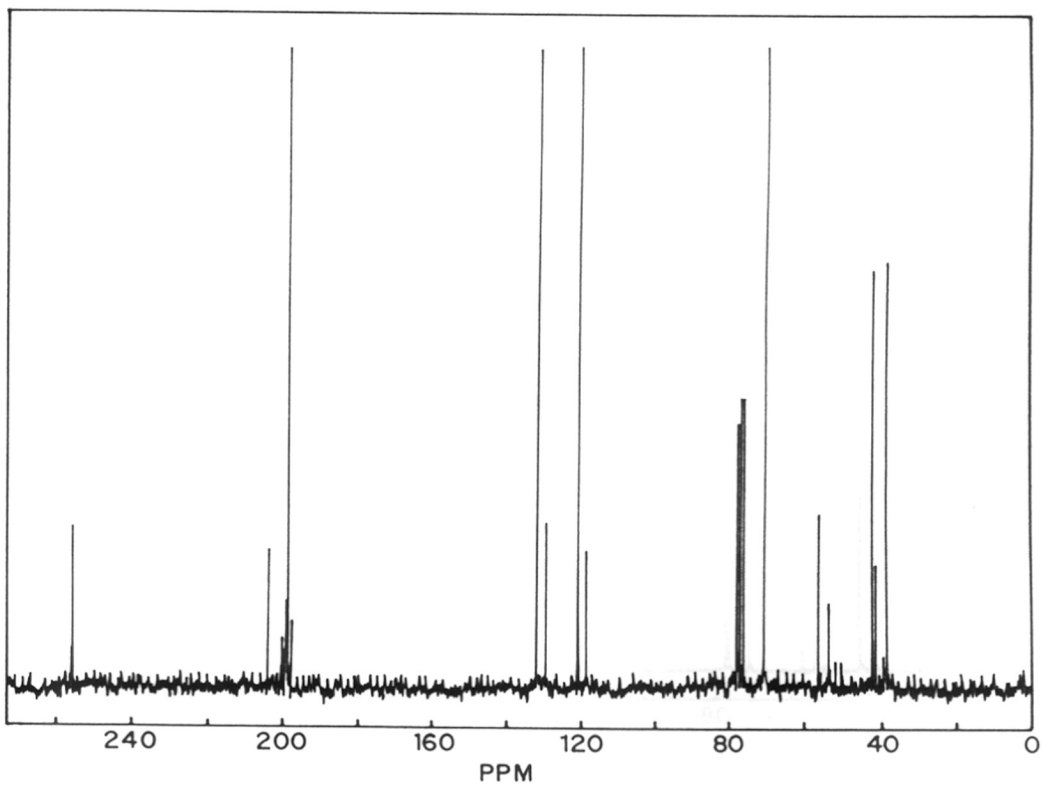
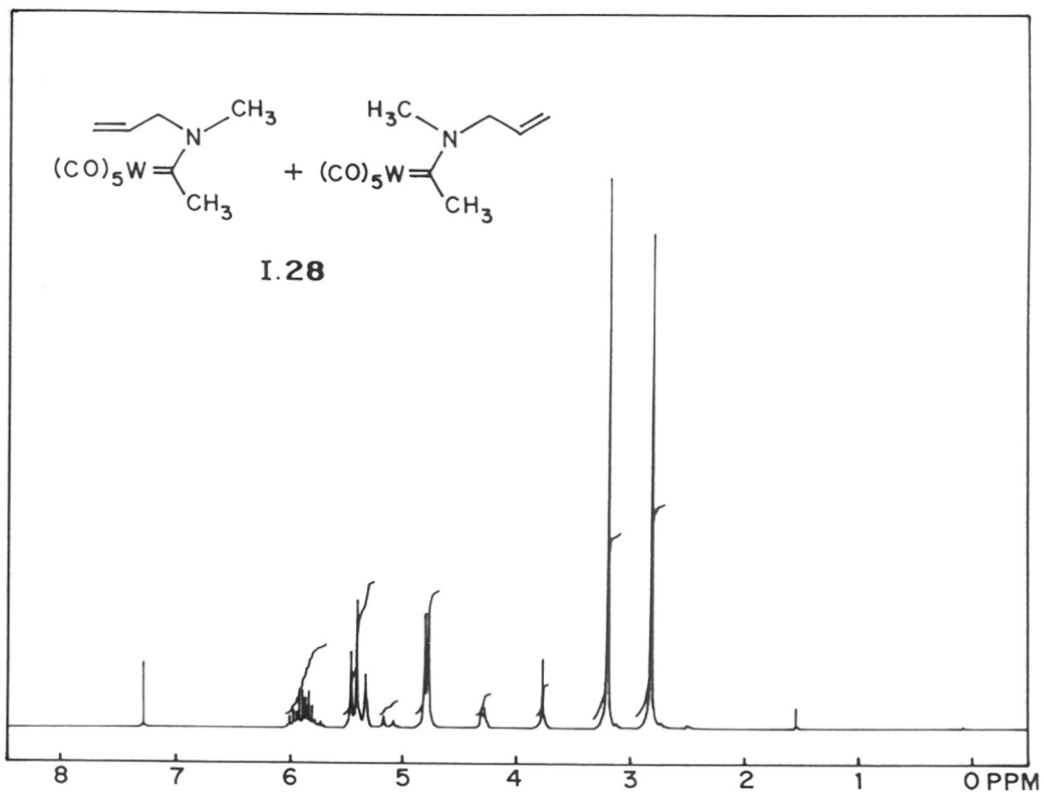


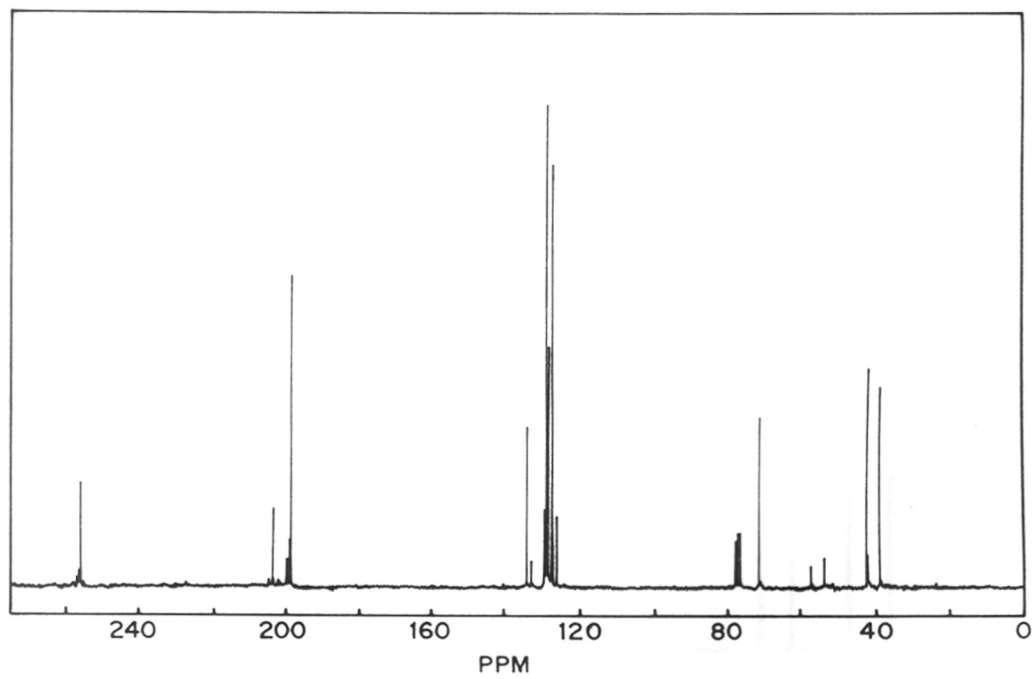
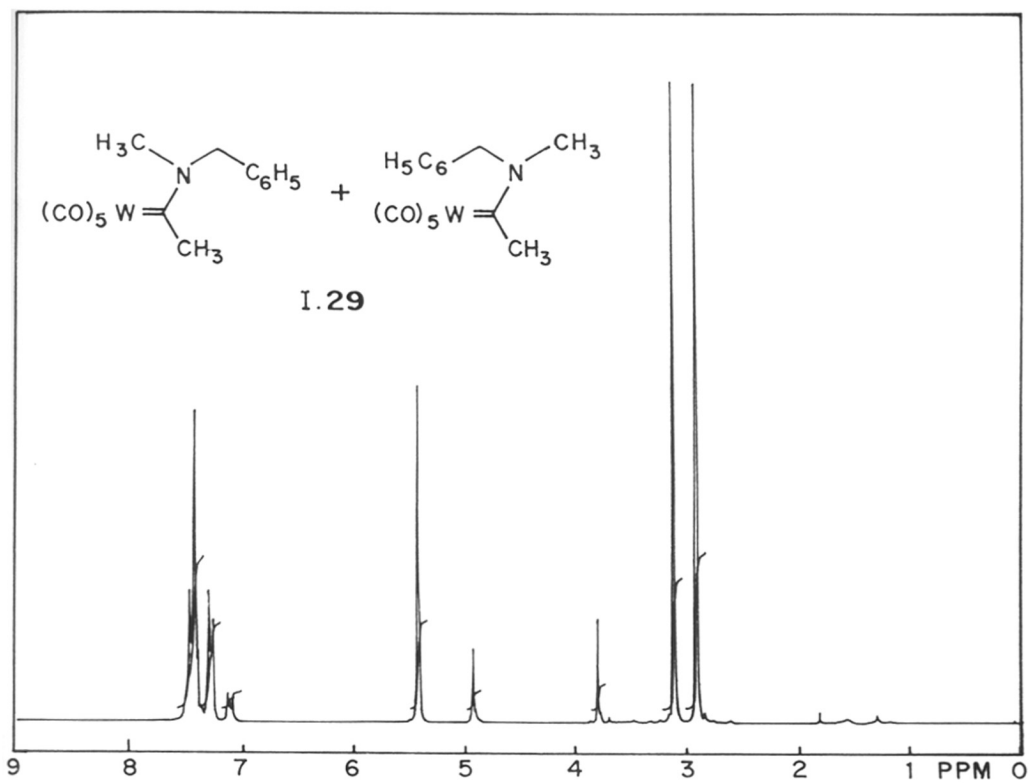


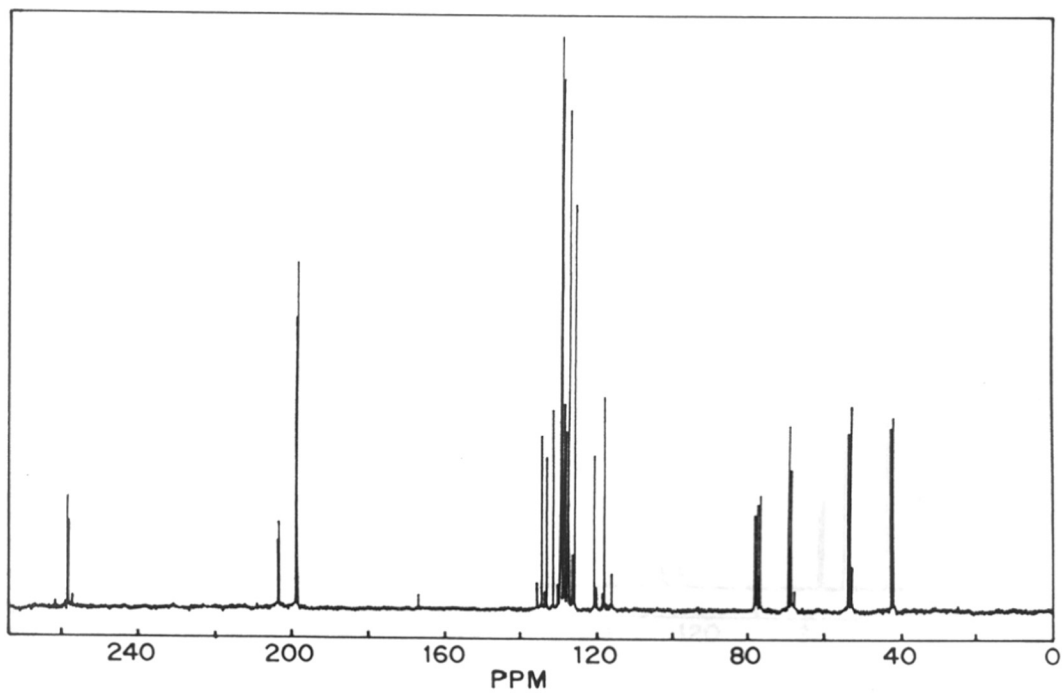
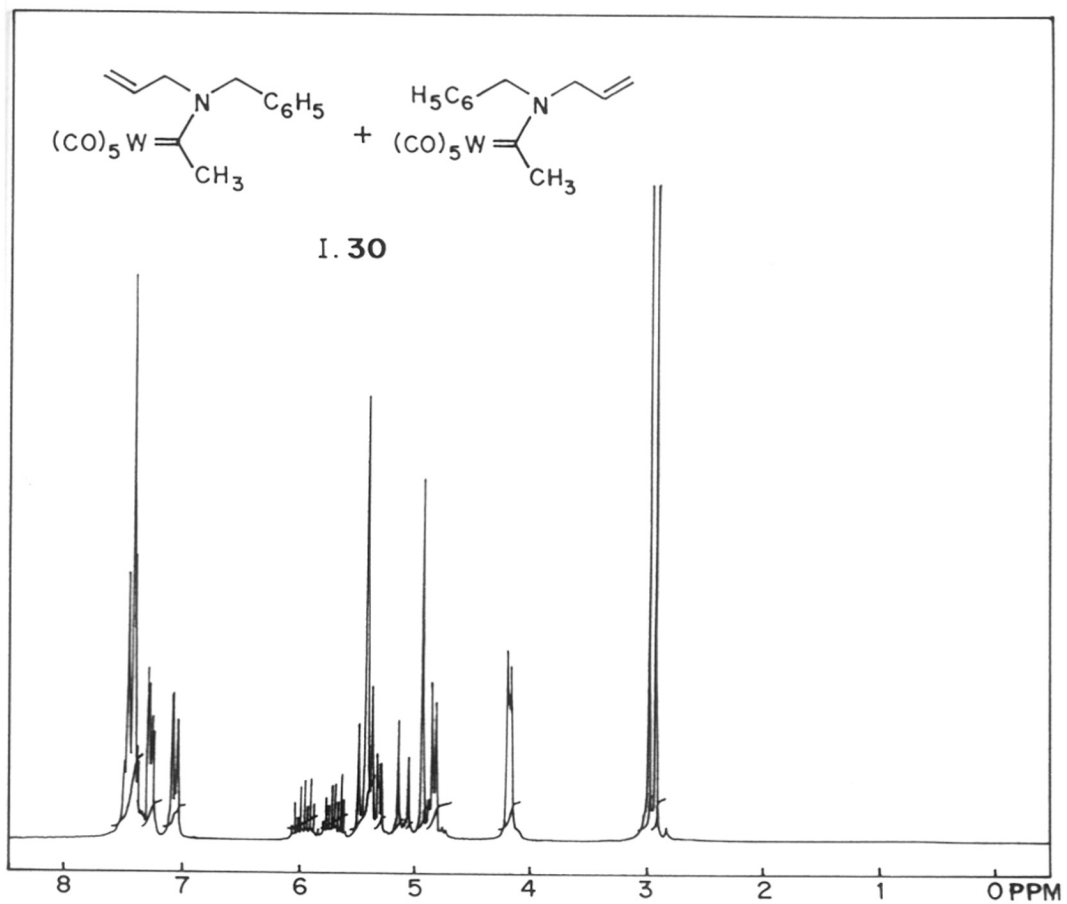




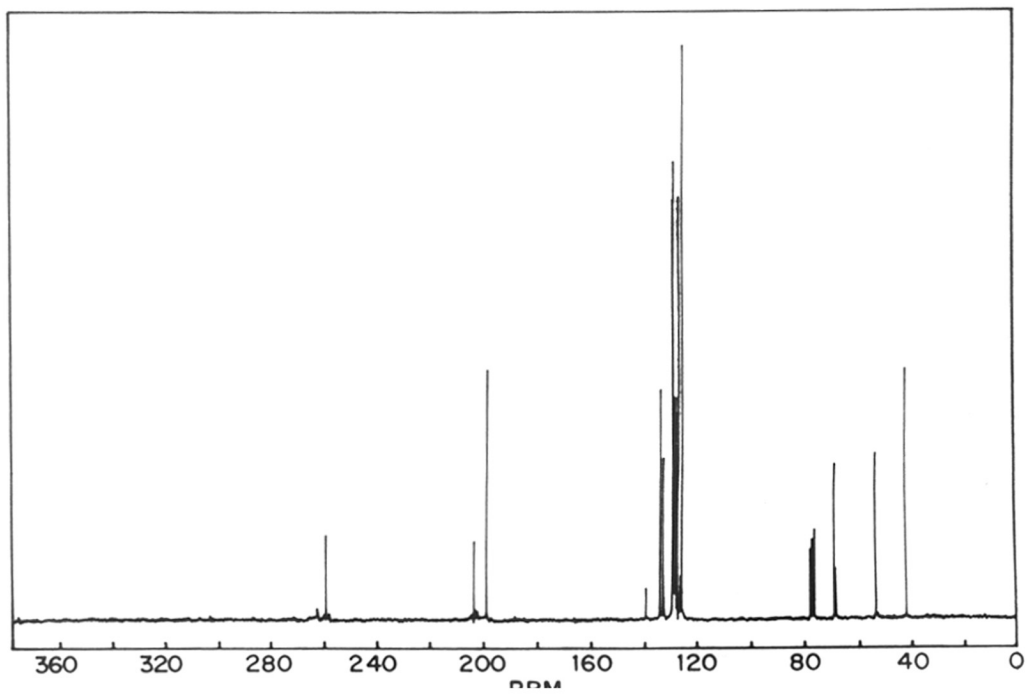
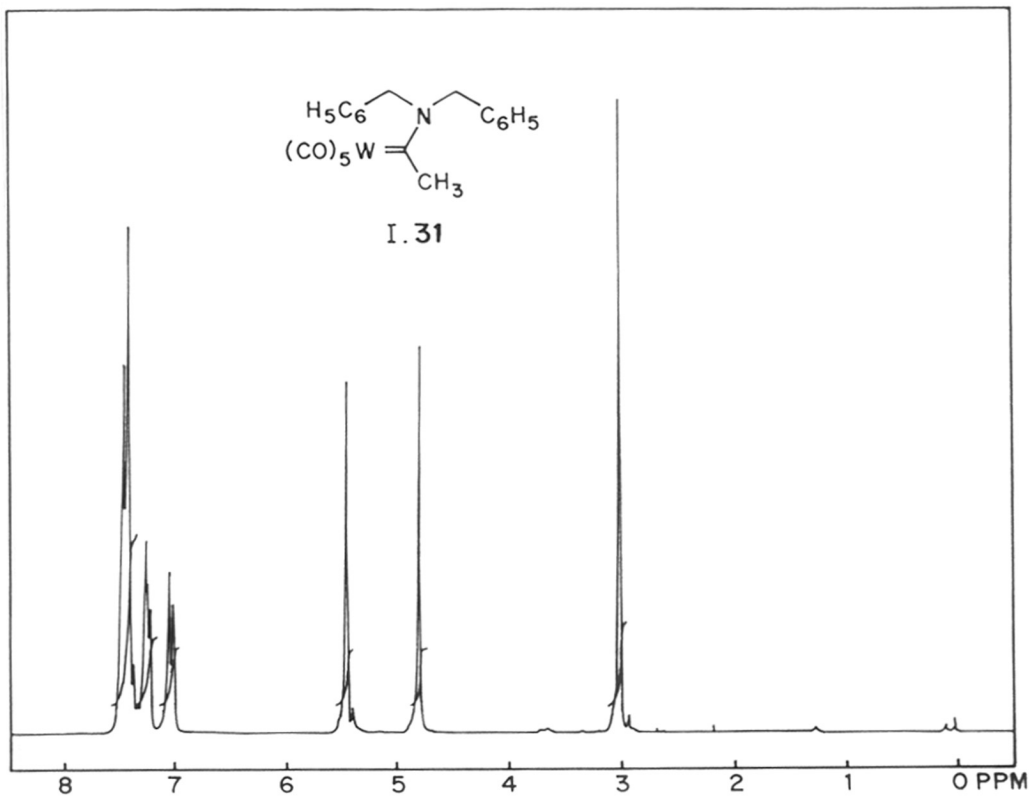


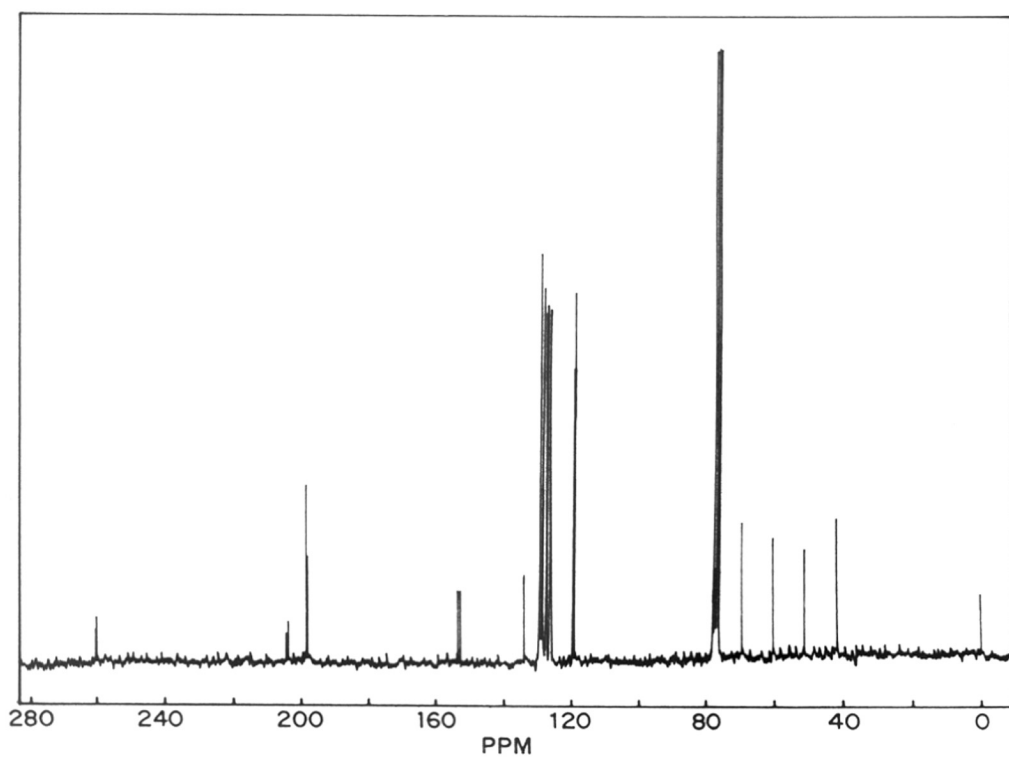
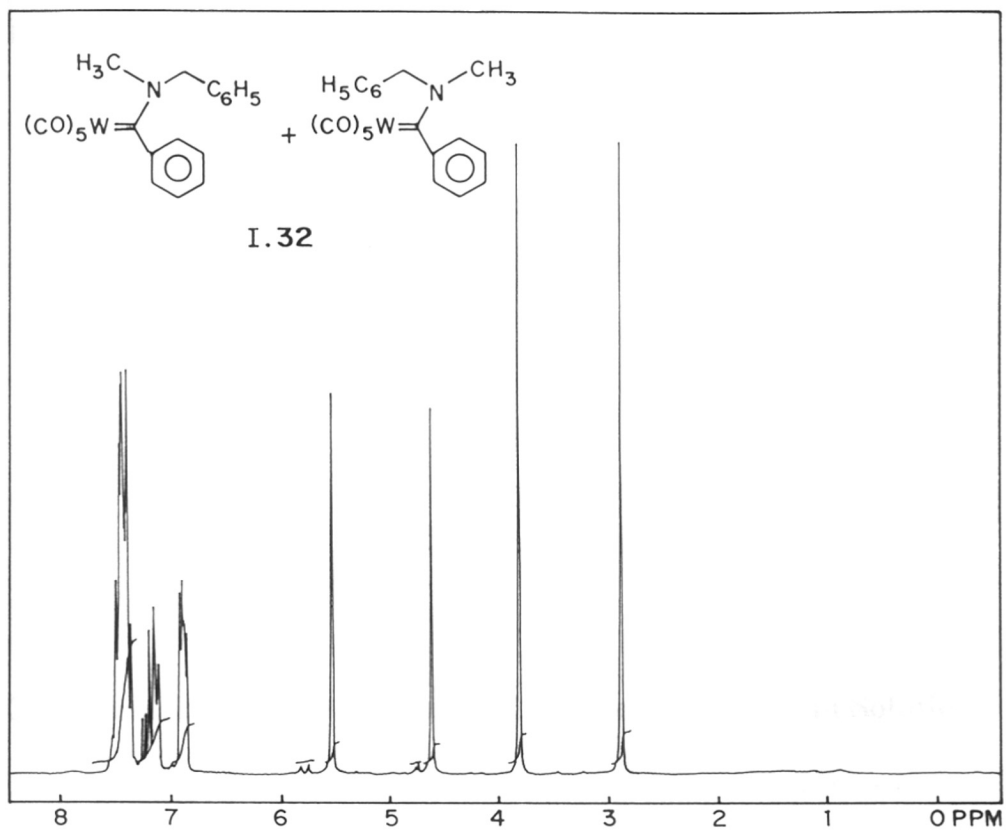












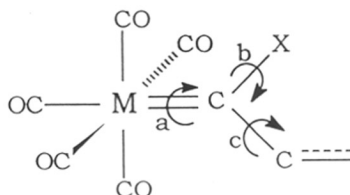
## **Chapter - II**

### **Conformational Study of Amino Carbene Complexes in Solution : Diastereotopicity as an Internal Stereochemical Probe**

## II.1 INTRODUCTION

In a discussion of conformation of Fischer carbene complexes, one needs to consider three different torsional modes (Chart-II.1). One concerns rotation about the metal-carbon double bond (rotation a). Another concerns the rotation about the bond between carbene carbon and the hetero atom (rotation b). A third mode is to be considered for molecules in which a C-C  $\pi$ -bond is attached to the carbene carbon (rotation c), where the relative orientation of the metal-carbene  $\pi$ -plane with the C-C  $\pi$ -plane is a conformational variable.

**Chart-II.1**



Theoretical calculations<sup>1</sup> revealed that the barrier to rotation of metal-carbene double bond is less than 1 kcal/mol, *i.e.* the rotation is free for all practical purposes in the normal range of temperature of experiments. This is in accordance with the intuitive chemical logic that the lone pair on the hetero atom is delocalized to the C-M bond thereby reducing its bond order. Calculations also suggest that the stable conformation is the one in which the carbene fragment adopts a staggered conformation with respect to the  $M(CO)_4$  plane.<sup>2</sup>

The rotation barrier of the carbene-hetero atom bond has been extensively studied by Fischer and documented in a series of papers.<sup>3</sup> The barrier of rotation

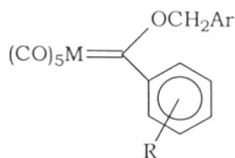
about a C-O bond<sup>3a</sup> was found to be lower than the barrier for a C-N bond,<sup>3d</sup> as in the case of esters and amides. That is, the conformers due to an alkoxy carbene complex can be observed only at a lower temperature (rotation barrier ~14 kcal/mol)<sup>3a</sup> while the conformers of the corresponding amino carbene complexes are observed at ambient temperature (rotation barrier ~25 kcal/mol).<sup>3d</sup> For aryl carbene complexes, the barrier was found to be greater when an *ortho*-substituent was present on the aromatic ring than when there was none.<sup>3a</sup>

Solid state structures revealed<sup>4</sup> that the Fischer carbene complexes containing an aromatic ring attached to the carbene carbon atom, shared a common conformational feature - the aromatic rings were oriented orthogonal to the metal-carbene  $\pi$ -plane. Fischer observed<sup>3a</sup> that the barrier of rotation about the carbene-hetero atom bond is lowered if an electron-releasing *para*-substituent is present on the aromatic ring. This was explained by assuming coplanarity of the ring with the metal-carbene  $\pi$ -plane in solution. In this context, solution conformation of Fischer carbene complexes was examined closely, and some of the results are discussed in this chapter.

## II.2 BACKGROUND

In the course of our studies with rearrangement of aryl benzyloxy carbene complexes,<sup>5</sup> it was observed that the methylene proton signals in complexes like **A-D** (Chart II.2) were broad at room temperature and it decoalesced at lower temperature into two separate signals of different multiplicity.

Chart II.2



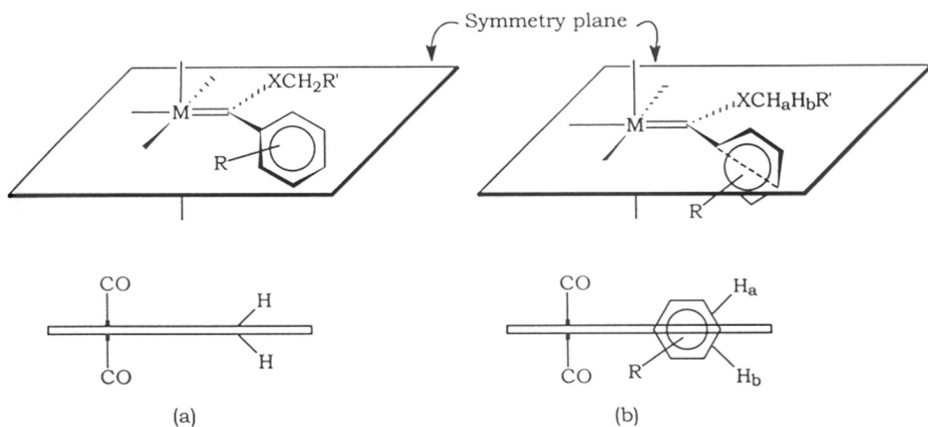
	<b>M</b>	<b>R</b>	<b>Ar</b>
<b>A</b>	W	2-OCH <sub>3</sub>	4-OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>
<b>B</b>	W	2-OCH <sub>3</sub>	2-furyl
<b>C</b>	Cr	2-OCH <sub>3</sub>	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>
<b>D</b>	Cr	2-CH <sub>3</sub>	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>

This observation appeared to indicate that the aromatic ring attached to the carbene carbon was oriented orthogonal to the carbene plane, the basis of which is described below.

### II.3 PRESENT WORK

To apply diastereotopy in the context of carbene complexes, it is convenient to define a molecular symmetry plane as shown in Chart-II.3. If the aromatic ring remains coplanar with the carbene fragment, substituents of the aromatic ring would not alter the symmetry of the molecule. The benzylic protons of a benzyloxy carbene complex would remain enantiotopic (Chart-II.3a) and hence indistinguishable by NMR spectroscopy. But, if the aromatic ring attached to the carbene carbon is oriented orthogonal to the metal-carbene plane, an unsymmetrical substitution pattern on the aromatic ring would destroy the plane of symmetry. As a result, the two benzylic protons ( $H_a$  and  $H_b$ ) would be diastereotopic (Chart II.3b) and may provide two distinct signals.

## Chart-II.3

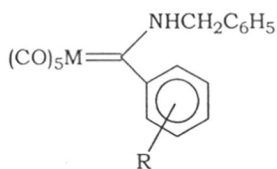


Initial experiments by Nandi<sup>6</sup> and Sathe<sup>7</sup> using benzyloxy carbene complexes revealed diastereotopic benzylic signals in spectra recorded at low temperatures. Since the situation should not change for amino carbene complexes, we reasoned, the diastereotopic signals should be observed in the case of benzylamino or related complexes at room temperature itself, adding to the convenience of experimentation. A series of amino carbene complexes were therefore synthesized and structurally characterized using aminolysis reaction of parent alkoxy carbene complexes.

### Preparation and characterization of amino carbene complexes

The monoalkylamino carbene complexes (**II.2a-j**, Chart-II.4) were prepared by stirring alkoxy carbene complexes with benzylamine in ether at room temperature until the starting material was consumed (TLC). The reactions were usually complete within minutes.

Chart-II.4



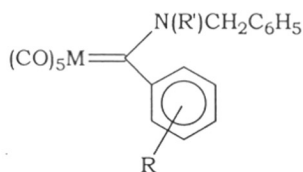
II.2a-j

Complex	M	R	Yield (%)
II.2a	Cr	2-CH <sub>3</sub>	92
II.2b	Cr	2-OCH <sub>3</sub>	96
II.2c	Cr	2,3-fused benzene	95
II.2d	Cr	3-CH <sub>3</sub>	98
II.2e	Cr	3-OCH <sub>3</sub>	89
II.2f	Cr	4-OCH <sub>3</sub> , 3-CH <sub>3</sub>	89
II.2g	Cr	4-CH <sub>3</sub>	93
II.2h	Cr	H	97
II.2i	W	2-OCH <sub>3</sub>	89
II.2j	W	3-CH <sub>3</sub>	97

Dialkylamino complexes (**II.3a-1**, Chart-II.5) were synthesized by alkylation of these complexes (**II.2**) with benzyl bromide or methyl iodide following a PTC-procedure described in Chapter-1. All new, solid compounds purified by flash column chromatography provided satisfactory elemental analyses.



Chart-II.5

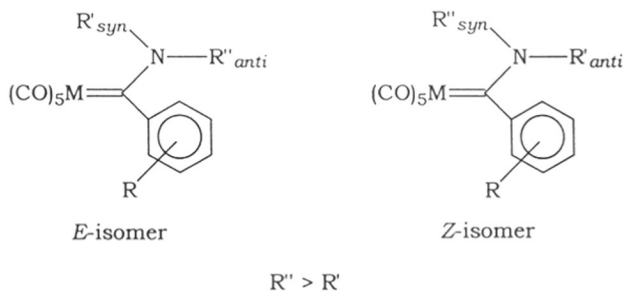


II.3a-1

Complex	M	R	R'	Yield (%)
II.3a	Cr	2-CH <sub>3</sub>	CH <sub>3</sub>	87
II.3b	Cr	2-CH <sub>3</sub>	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	93
II.3c	Cr	2-OCH <sub>3</sub>	CH <sub>3</sub>	93
II.3d	Cr	2-OCH <sub>3</sub>	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	89
II.3e	Cr	2,3-fused benzene	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	84
II.3f	Cr	3-CH <sub>3</sub>	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	91
II.3g	Cr	3-OCH <sub>3</sub>	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	97
II.3h	Cr	4-OCH <sub>3</sub> , 3-CH <sub>3</sub>	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	88
II.3i	Cr	4-CH <sub>3</sub>	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	91
II.3j	Cr	H	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	87
II.3k	W	2-OCH <sub>3</sub>	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	93
II.3l	W	3-CH <sub>3</sub>	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	97

For the present discussion, the conformers of amino carbene complexes have been described using *E* and *Z* nomenclature assuming partial double bond character of the carbene-nitrogen bond (Chart II.6). A substituent is designated as **syn** if it lies closer to the metal fragment or as **anti** if it is oriented away.

Chart-II.6

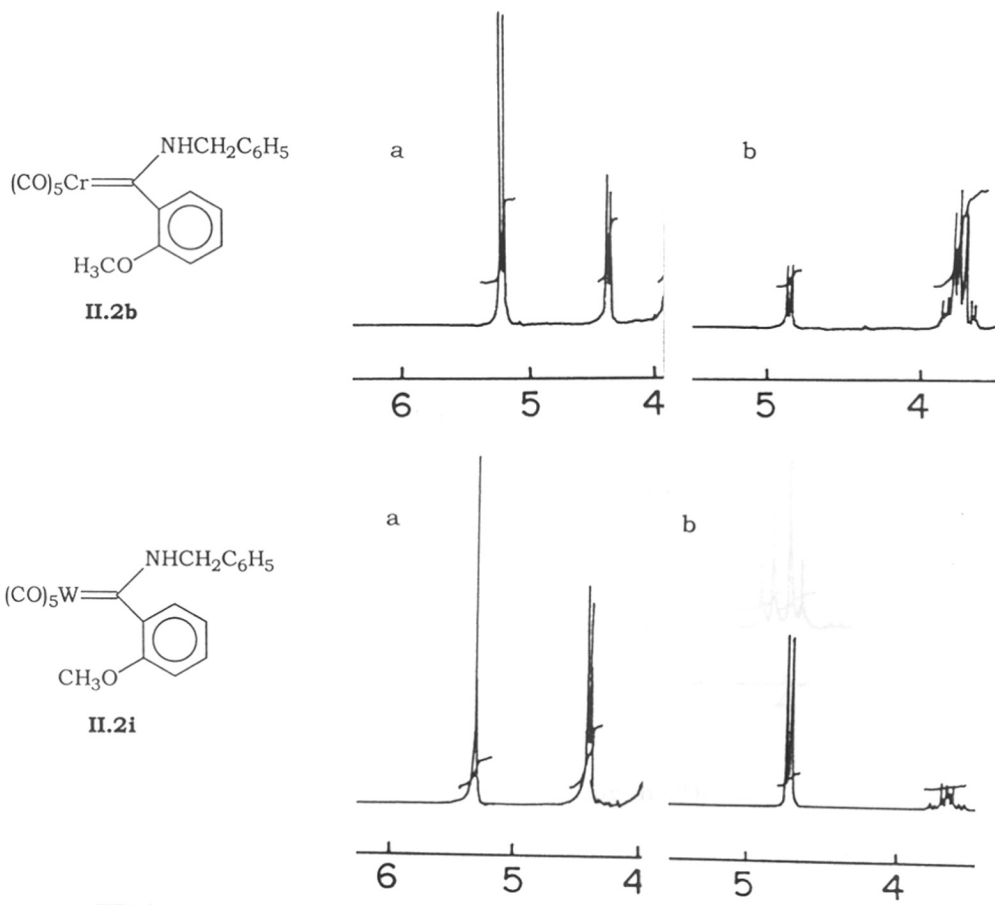


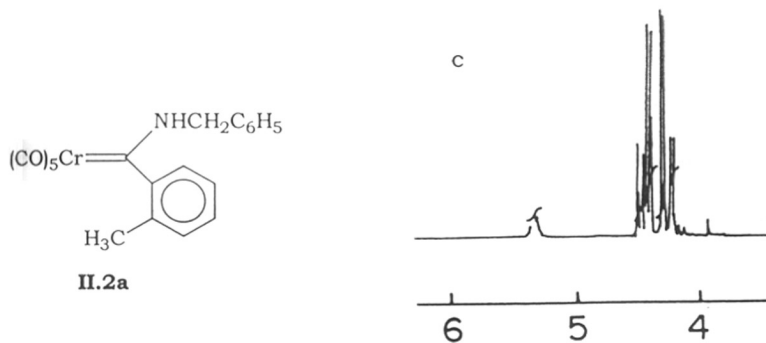
In the monoalkylamino series, the *E*-conformer generally predominates for *ortho*-substituted aryl ring (complexes **II.2a-c**). In the *E*-conformer of the complex **II.2a**, the benzylic protons in  $^1\text{H}$  NMR spectrum appear at 4.27 and 4.42 as two doublet of doublets in  $\text{CDCl}_3$ . The signal is shielded by about 0.3 ppm with respect to the benzylic proton signal of the corresponding benzylaminomethyl complex **I.25** which appears at 4.63. As observed for the benzyloxy complexes, the *Z*-benzylic signals of **II.2a** appear as a doublet at 5.32, the multiplicity due to geminal non-equivalence of benzylic methylene protons is not seen. For complexes with *meta*- or *para*-substituted aryl ring (**II.2d-f**, **II.2j**), populations of *E*- and *Z*-conformers are comparable in some cases. Significantly, benzylic protons of both the conformers appeared as doublets in  $\text{CDCl}_3$  or  $\text{C}_6\text{D}_6$ .

It should be mentioned here that the *E/Z* ratio of conformers reflects the composition of mixture as obtained during the preparation of the complexes. No attempt was made to determine the equilibrium composition, since only the chemical shifts and peak multiplicities of the benzylic protons were of primary interest in the present study.

Shielding of the benzylic signal of the *E*-conformer and chemical shift non-equivalence of geminal benzyl protons corroborate the findings with benzyloxyaryl carbene complexes. This is consistent with the orthogonal orientation of the aromatic ring attached to the carbene carbon with respect to the metal-carbene  $\pi$ -plane. An orthogonal aromatic ring faces the *E*-benzyl group and thus the ring-current anisotropy causes shielding of these protons. On the other hand, with reference to Chart-II.3, the unsymmetrical substitution on the aromatic ring orthogonally oriented, renders the benzyl protons non-equivalent.

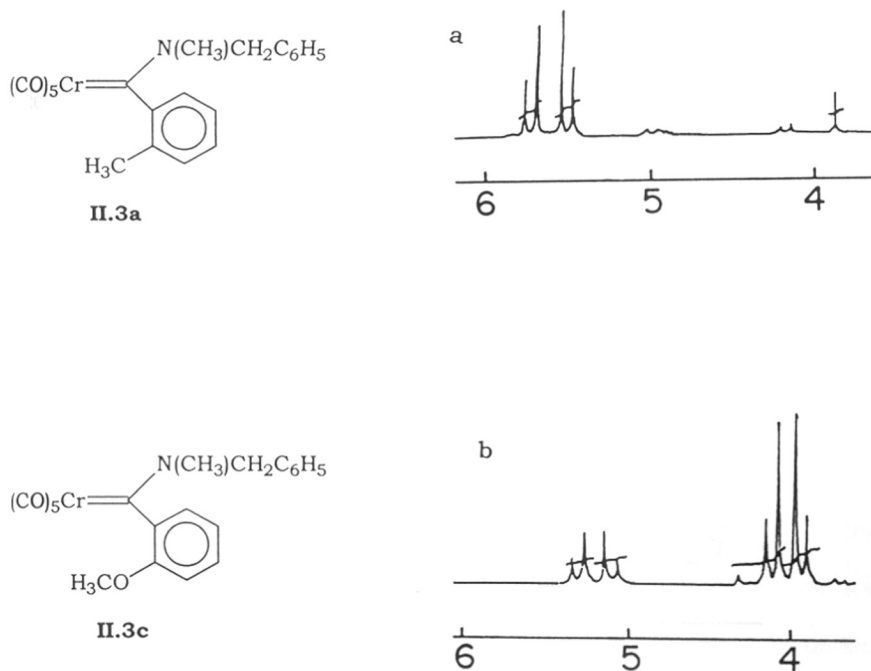
Accidental degeneracy of geminally non-equivalent benzyl protons has been observed, as in case of complexes **II.2b** or **II.2i**. The *E*-benzyl protons appear as a doublet in  $\text{CDCl}_3$  (Fig. II.1a). The degeneracy can be lifted by using  $\text{C}_6\text{D}_6$  as the solvent (Fig. II.1b). No such degeneracy is observed for complex **II.2a** (Fig. II.1c).





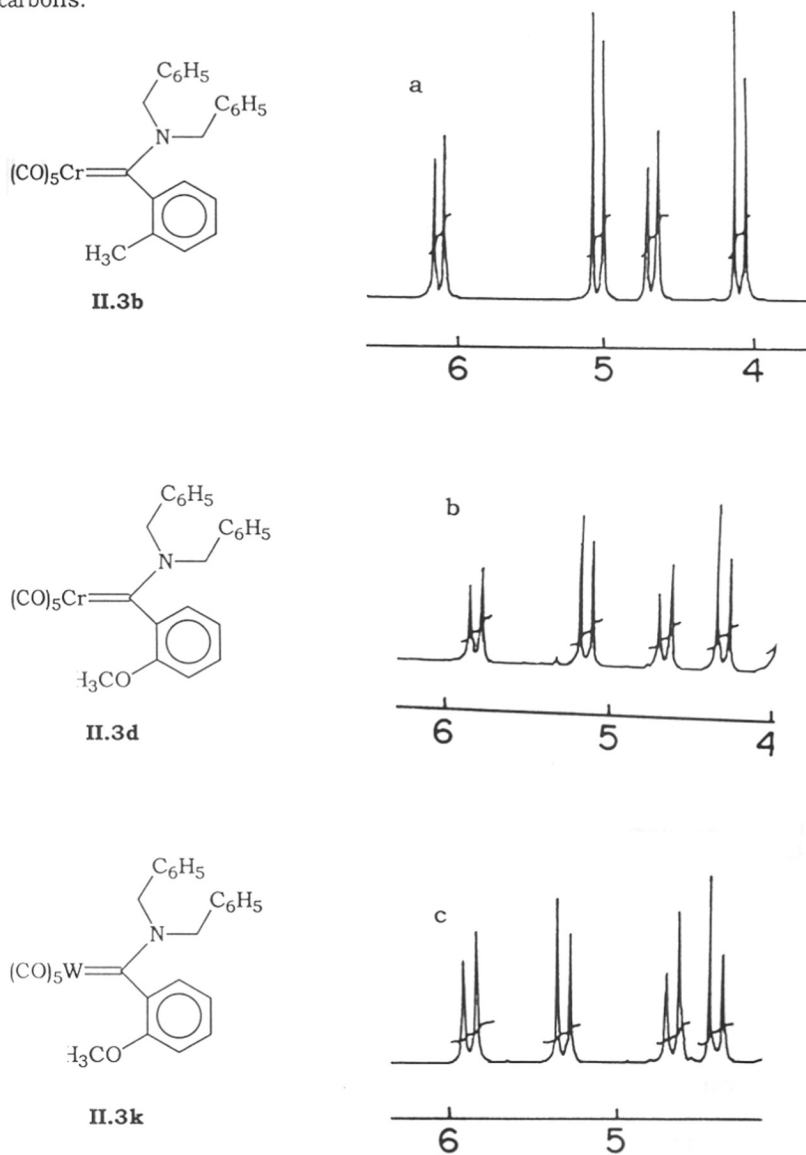
**Figure II.1:** a) <sup>1</sup>H NMR spectra of **II.2b** and **II.2i** in CDCl<sub>3</sub>. b) <sup>1</sup>H NMR spectra of **II.2b** and **II.2i** in C<sub>6</sub>D<sub>6</sub> and c) <sup>1</sup>H NMR spectrum of **II.2a** in CDCl<sub>3</sub>.

The change of solvent has no effect on the pattern of the benzyl protons in *Z*-conformer. However, in benzylmethylamino complexes such as **II.3a** and **II.3c**, the *Z*-benzyl signals display geminal non-equivalence (Fig. II.2a and II.2b) in CDCl<sub>3</sub>.



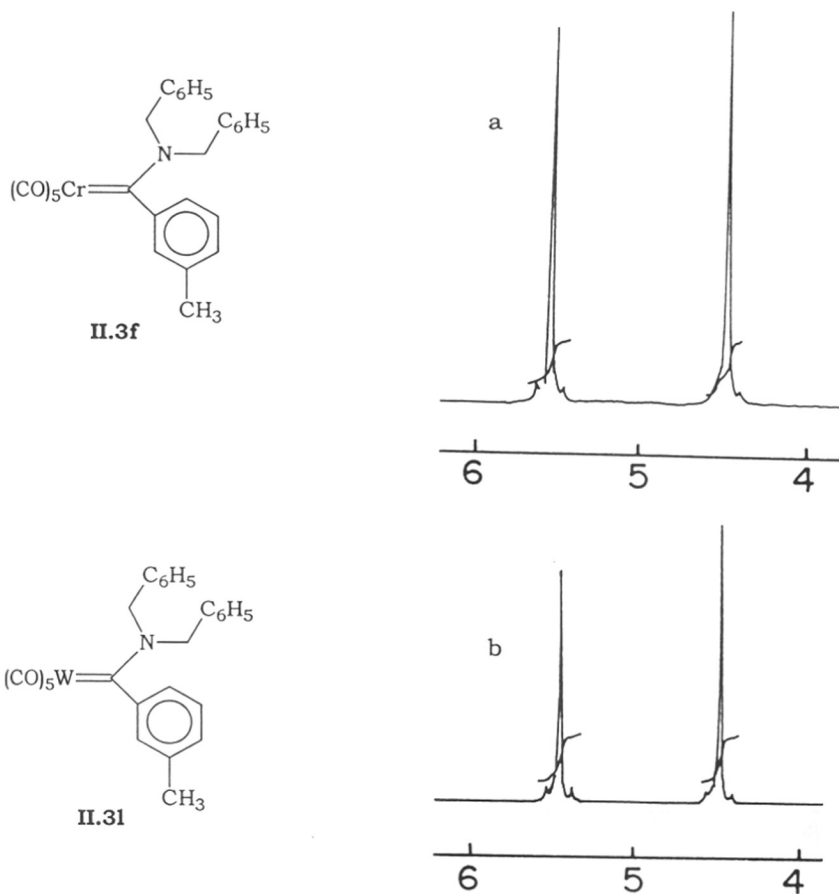
**Figure II.2:** <sup>1</sup>H NMR spectrum of a) **II.3a** and b) **II.3c** in CDCl<sub>3</sub>.

The non-equivalence of geminal protons of the benzyl group is most pronounced in the dibenzylamino carbene complexes (**II.3b**, **II.3d** and **II.3k**). Four distinct doublets are observed in the  $^1\text{H}$  NMR spectral region of 4.10 to 6.12 (Fig. II.3a, II.3b and II.3c). All these complexes have *ortho*-substituted aryl rings attached to the carbene carbons.



**Fig. II.3:**  $^1\text{H}$  NMR spectrum of a) **II.3b**, b) **II.3d** and c) **II.3k** in  $\text{CDCl}_3$ .

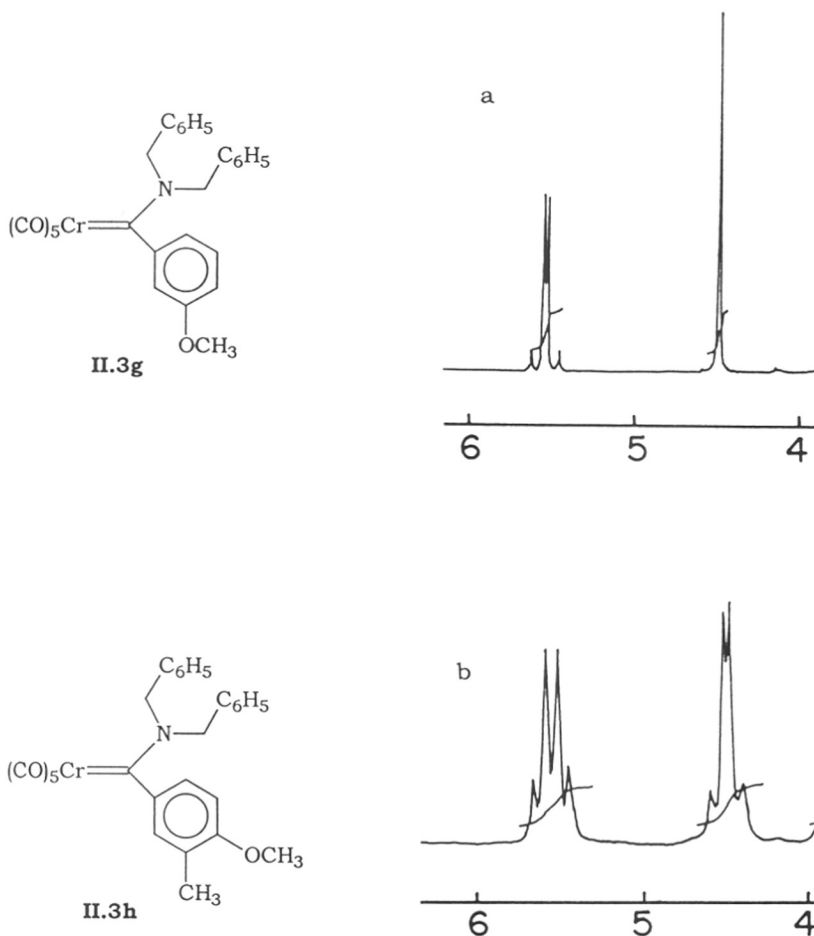
The naphthyl complex **II.3e** also has similar spectral features. For complexes with *meta*-substituted aromatic rings **II.3f** and **II.31**, the chemical shift difference of the geminal benzyl protons is less and consequently the corresponding peak patterns are simplified, showing singlets in both  $\text{CDCl}_3$  and  $\text{C}_6\text{D}_6$  (Fig.II.4).



**Fig.II.4:** a)  $^1\text{H}$  NMR spectrum of a) **II.3f** and b) **II.31** in  $\text{CDCl}_3$ .

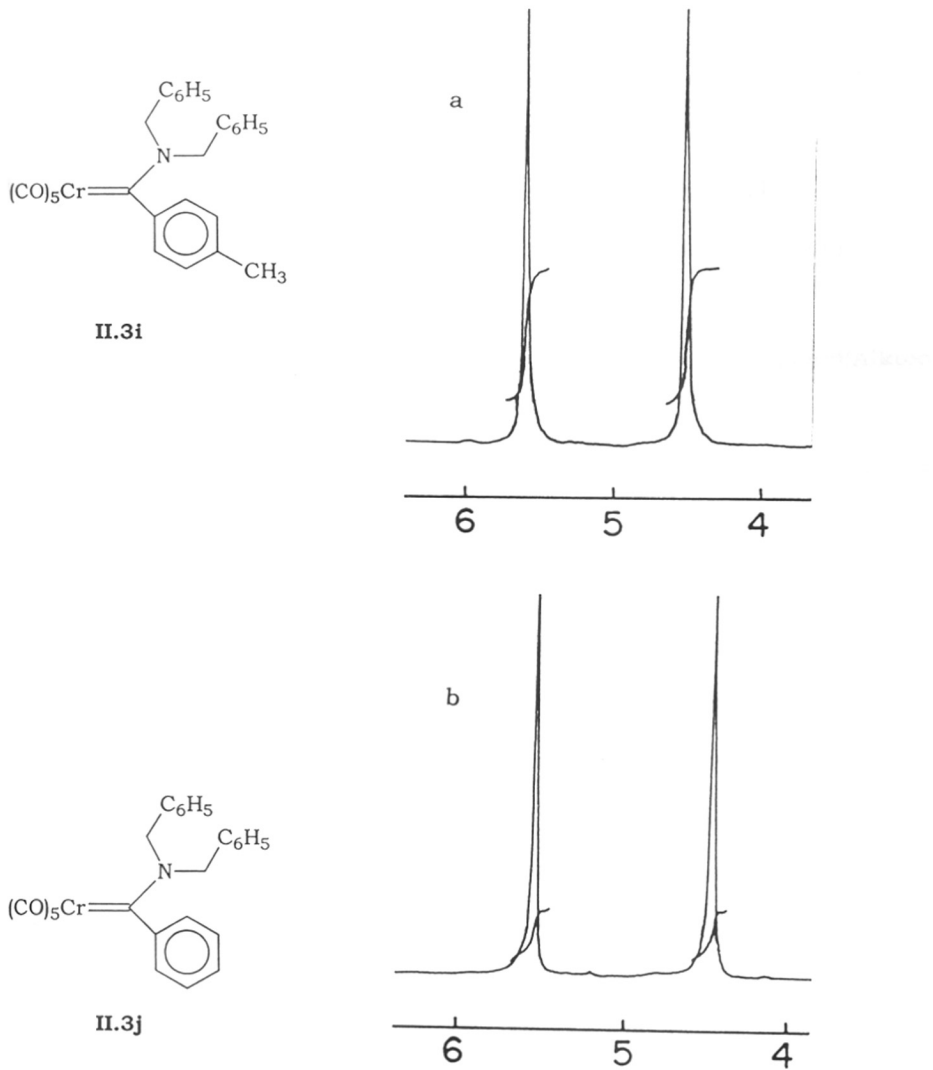
However, for two other *meta*-substituted complexes (**II.3g** and **II.3h**), the situation is different. For complex **II.3g**, the benzyl proton signals actually present a diametrically opposite trend with respect to benzyloxycarbene complexes; the *syn*-benzyl protons appear as a four-line AB quartet while the *anti*-benzyl protons are degenerate (Fig.II.5a). When a *p*- $\text{OCH}_3$  group is present in addition to the *m*- $\text{CH}_3$  group on the

aromatic ring as in the complex **II.3h**, degeneracy of benzyl protons is lifted (Fig.II.5b).



**Fig.II.5:**  $^1\text{H}$  NMR spectrum of a) **II.3g** and b) **II.3h** in  $\text{CDCl}_3$ .

As depicted in Chart-II.3, for carbene complexes with symmetrically substituted (or unsubstituted) aromatic rings attached to the carbene carbon, the benzyl protons are enantiotopic and therefore no chemical shift non-equivalence is observed, as shown in the spectra of complexes **II.i** and **II.j** (Fig. II.6a and II.6b).



**Fig.II.6:**  $^1\text{H}$  NMR spectrum of a) **II.3i** and b) **II.3j** in  $\text{CDCl}_3$ .

#### II.4 SUMMARY

The diastereotopicity of benzyl protons provided a useful internal probe to ascertain conformation of Fischer carbene complexes as they exist *in solution*. The results, in essence, supplement the observations made for their solid state structures.



## II.5 EXPERIMENTAL SECTION

2-Iodotoluene, 2-bromoanisole, 3-iodotoluene, 3-iodoanisole, 4-iodoanisole, 4-methoxy-3-methyl iodobenzene were prepared from the corresponding anilines by standard procedure and distilled before use.

### **General Procedure for the Preparation of Pentacarbonyl(Alkoxyaryl)-chromium/tungsten(0) Complexes**

All alkoxy carbene complexes were prepared according to the procedure of Hoye.<sup>8</sup> Tetraethylammonium (oxyarylmethylidene)chromate(0) or tungstate(0) salt (*n* mmol) and tetrabutylammonium bromide(TBAB) (0.1*n* mmol) in dichloromethane (*n* ml) was treated with alkyl iodide (10*n* mmol) for overnight under an argon atmosphere. Solvent was evaporated and the residue was extracted with petroleum ether. Pure product was obtained after filtration through a small plug of flash silica.

**Preparation of Complex 1a:** Reaction of tetraethylammonium pentacarbonyl{oxy-(2-methylphenyl)methylidene}chromate(0) (2.20 g, 5 mmol), TBAB (161 mg, 0.5 mmol) in dichloromethane (20 ml) with methyl iodide (3.12 ml, 50 mmol) yielded the product (1.09 g, 67%) as a red liquid.

IR : 2085 (m); 2000 (sh); 1955 (s)

<sup>1</sup>H NMR : 2.20 (s, 3H); 4.30 (s, 3H); 6.80-7.00 (m, 1H); 7.07-7.45 (m, 3H)

<sup>13</sup>C NMR : 18.72; 65.64; 120.63; 126.05; 126.37; 128.41; 130.84; 152.66;  
216.21; 224.70; 359.84

**Preparation of Complex 1b:** Reaction of tetraethylammonium pentacarbonyl{oxy- (3-methylphenyl)methylidene}chromate(0) (2.28 g, 5 mmol), TBAB (161 mg, 0.5 mmol) in dichloromethane (20 ml) with methyl iodide (3.12 ml, 50 mmol) yielded the product (1.21 g, 71%) as a red liquid.

IR : 2055 (m); 1985 (sh); 1935 (s)

<sup>1</sup>H NMR : 2.43 (s, 3H); 4.70 (s, 3H); 7.01-7.45 (m, 4H)

<sup>13</sup>C NMR : 21.66; 67.20; 120.66; 123.22; 128.32; 131.22; 138.21; 154.12;  
216.49; 224.47; 351.85

**Preparation of Complex 1c:** Reaction of tetraethylammonium pentacarbonyl{oxy- (4-methoxy-3-methylphenyl)methylidene}chromate(0) (2.35 g, 5 mmol), TBAB (161 mg, 0.5 mmol) in dichloromethane (20 ml) with ethyl iodide (4.0 ml, 50 mmol) yielded the product (1.15 g, 62%) as a red solid.

m.p. : 87°C

IR : 2055 (m); 1985 (sh); 1935 (s)

<sup>1</sup>H NMR : 1.74 (t, J = 7 Hz, 3H); 2.27 (s, 3H); 3.92 (s, 3H); 5.15 (q, J = 7 Hz, 2H); 6.87 (d, J = 8 Hz, 1H); 7.45 (s, 1H); 7.72 (dd, J = 1 and 8 Hz, 1H)

<sup>13</sup>C NMR : 15.34; 16.48; 55.59; 77.09; 108.97; 126.23; 128.64; 128.84;  
146.03; 161.66; 217.25; 224.18; 339.14

Analysis : Calcd : C = 51.90, H = 3.81  
 Found : C = 52.01, H = 3.62

**Preparation of Complex 1d:** Reaction of tetraethylammonium pentacarbonyl(oxy- (3-methylphenyl)methylidene)tungstate(0) (2.86 g, 5 mmol), TBAB (161 mg, 0.5 mmol) in dichloromethane (20 ml) with methyl iodide (3.12 ml, 50 mmol) yielded the product (1.58 g, 69%) as a red solid.

m.p. : 64 °C

IR : 2055 (m); 1985 (sh); 1935 (s)

<sup>1</sup>H NMR : 2.42 (s, 3H); 4.78 (s, 3H); 7.26-7.50 (m, 4H)

<sup>13</sup>C NMR : 21.60; 70.28; 124.33; 126.56; 128.21; 132.73; 138.05; 155.62;  
 197.59; 203.86; 322.76

Analysis : Calcd : C = 36.71, H = 2.20  
 Found : C = 36.51, H = 2.10

**General Procedure for the Preparation of Amino Carbene Complexes 2a-j** All amino carbene complexes were prepared according to the literature procedure.<sup>9</sup> Pentacarbonyl(alkoxyarylmethylidene)chromium/tungsten(0) (n mmol) in diethyl ether (3n ml) was treated with benzylamine (1.2n mmol) at room temperature under argon until the color changes from red to yellow. Solvent was evaporated in vacuo

and the pure product was isolated by flash chromatography using dichloromethane (10-20%) in petroleum ether as the eluant.

**Preparation of complex 2a:** Reaction of the complex **1a** (0.98 g, 3 mmol) in diethyl ether (9 ml) and benzylamine (0.39 ml, 3.6 mmol) afforded the product (1.10 g, 92%) as a Yellow liquid.

IR : 2050 (m), 1985 (sh), 1930 (s)

<sup>1</sup>H NMR : *E:Z* = 93:7. **E-2a**. 2.27 (s, 3H); 4.27 (dd, *J* = 5.2 and 15.2 Hz, 1H); 4.42 (dd, *J* = 6.3 and 15.2 Hz 1H); 6.88 (d, *J* = 7.6 Hz, 1H); 9.38 (bs, 1H). **Z-2a**. 2.22 (s, 3H); 5.32 (d, *J* = 5.2 Hz, 2H); 6.96 (d, *J* = 7.6 Hz, 1H); 8.68 (bs, 1H). **Combined peaks**. 7.13-7.95 (m, 8H and 8H)

<sup>13</sup>C NMR : **E-2a**. 19.08; 54.89; 119.91; 126.38; 127.25; 127.92; 128.91; 129.52; 130.89; 134.38; 134.75; 148.79; 217.28; 223.33; 284.34

**Preparation of Complex 2b:** Reaction of pentacarbonyl(methoxy2-methoxyphenylmethylidene)chromium(0) (1.03 g, 3 mmol) in diethyl ether (9 ml) and benzylamine (0.39 ml, 3.6 mmol) afforded the product (1.20 g, 96%) as a Yellow liquid.

IR : 2055 (m), 1975 (sh), 1930 (s)

<sup>1</sup>H NMR : *E:Z* = 80:20. **E-2b**. 3.90 (s, 3H); 4.40 (d, *J* = 5.8 Hz, 2H); 9.31 (bs, 1H). **Z-2b**. 3.85 (s, 3H); 5.33 (s, 2H); 8.85 (bs, 1H).

**Combined peaks.** 6.85-7.19 (m, 3H and 3H); 7.20-7.73 (m, 6H and 6H)

$^1\text{H}$  NMR :  $E:Z = 87:13$ . **E-2b.** 3.37 (s, 3H); 3.69 (dd,  $J = 5.8$  and  $14.8$  Hz, 1H); 3.82 (dd,  $J = 5.8$  and  $14.8$  Hz, 1H); 6.52 (d,  $J = 7.8$  Hz, 1H); 8.96 (bs, 1H). **Z-2b.** 3.44 (s, 3H); 4.88 (d,  $J = 5.8$  Hz, 2H); 7.76 (bs, 1H). **Combined peaks.** 6.70-7.40 (m, 9H)

$^{13}\text{C}$  NMR : **E-2b.** 55.11; 55.29; 111.06; 120.84; 127.98; 128.48; 128.54; 128.87; 129.33; 134.79; 138.03; 149.05; 217.51; 223.79; 280.26. **Z-2b.** 55.11; 57.79; 64.84; 111.38; 120.42; 121.91; 127.62; 128.18; 128.69; 132.26; 143.13; 150.15; 217.51; 223.89; 278.52

**Preparation of complex 2c:** Reaction of the complex pentacarbonyl(methoxyl-naphthyl)chromium(0) (1.08 g, 3 mmol) in diethyl ether (9 ml) and benzylamine (0.39 ml, 3.6 mmol) afforded the product (1.24 g, 95%) as a Yellow liquid.

IR : 2055 (m), 1980 (sh), 1920 (s)

$^1\text{H}$  NMR :  $E:Z = 73:27$ . **E-2g.** 4.20 (dd,  $J = 4.8$  and  $15$  Hz, 1H); 4.35 (dd,  $J = 5.8$  and  $15$  Hz, 1H); 9.55 (bs, 1H). **Z-2g.** 5.45 (d,  $J = 4.8$  Hz, 2H); 8.90 (bs, 1H). **Combined peaks.** 6.95-8.25 (m, 12H and 12H)

$^{13}\text{C}$  NMR : **E-2g.** 55.46; 117.15; 146.54; 217.25; 223.51; 283.84. **Z-2g.** 58.27; 117.95; 151.14; 217.25; 223.76; 282.32. **Combined**

**peaks.** 124.31; 124.47; 125.04; 125.45; 125.99; 126.47;  
126.77; 127.00; 127.43; 127.58; 127.91; 128.59; 128.88;  
129.07; 129.44; 129.89; 133.63; 133.81; 134.32

**Preparation of complex 2d:** Reaction of the complex **II.1b** (0.98 g, 3 mmol) in diethyl ether (9 ml) and benzylamine (0.39 ml, 3.6 mmol) afforded the product (1.17 g, 98%) as a Yellow liquid.

IR : 2080 (m), 1995 (sh), 1950 (s)

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) : *E:Z* = 58:42. **E-2c.** 2.07 (s, 3H); 3.68 (d, *J* = 5.8 Hz, 2H); 8.94 (bs, 1H). **Z-2c.** 2.12 (s, 3H); 4.87 (d, *J* = 5.8 Hz, 2H); 7.91 (bs, 1H). **Combined peaks.** 6.43-8.11 (m, 9H and 9H)

<sup>13</sup>C NMR : **E-2c.** 21.60; 54.76; 116.43; 119.88; 135.06; 138.59; 149.71; 217.44; 223.69; 282.27. **Z-2c.** 21.49; 57.97; 118.42; 121.76; 134.72; 138.34; 155.18; 217.51; 223.96; 278.68. **Combined peaks.** 127.59; 127.71; 128.48; 128.95; 129.40; 129.81

**Preparation of Complex 2e:** Reaction of the complex pentacarbonyl(methoxy3-methoxyphenyl)chromium(0) (1.02 g, 3 mmol) in diethyl ether (9 ml) and benzylamine (0.39 ml, 3.6 mmol) afforded the product (1.11 g, 89%) as a Yellow solid.

m.p. : 87°C

IR : 2080 (m), 1970 (sh), 1910 (s)

$^1\text{H}$  NMR :  $E:Z = 74:26$ . **E-2d**. 3.30 (s, 3H); 3.70 (d,  $J = 6.2$  Hz, 2H); 8.95 (C<sub>6</sub>D<sub>6</sub>) (bs, 1H). **Z-2d**. 3.40 (s, 3H); 4.85 (d,  $J = 6.2$  Hz, 2H); ); 7.95 (bs, 1H). **Combined peaks**. 6.15-7.40 (m, 9H and 9H)

$^{13}\text{C}$  NMR : **E-2d**. 55.00; 55.44; 105.27; 111.60; 112.55; 134.82; 150.83; 159.92; 217.37; 223.56; 282.44. **Z-2d**. 55.44; 58.10; 107.40; 113.37; 113.54; 134.55; 156.35; 159.57; 217.37; 223.88; 278.68. **Combined peaks**. 127.68; 128.66; 128.83; 129.23; 129.52; 130.00; 130.29

Analysis : Calcd : C = 57.56, H = 3.62, N = 3.36  
 Found : C = 57.29, H = 3.48, N = 3.29

**Preparation of Complex 2f:** Reaction of the complex **1c** (1.11 g, 3 mmol) in diethyl ether (9 ml) and benzylamine (0.39 ml, 3.6 mmol) afforded the product (1.15 g, 89%) as a Yellow liquid.

IR : 2050 (m), 1980 (sh), 1928 (s)

$^1\text{H}$  NMR :  $E:Z = 61:39$ . **E-2e**. 2.23 (s, 3H); 3.30 (s, 3H); 3.76 (d,  $J = 4.9$  Hz, 2H); 8.96 (bs, 1H). **Z-2e**. 2.23 (s, 3H); 3.34 (s, 3H); 4.91 (d,  $J = 4.9$  Hz, 2H); 7.95 (bs, 1H). **Combined peaks**. 6.28-7.70 (m, 8H and 8H)

$^{13}\text{C}$  NMR : **E-2e**. 16.36; 54.68; 55.36; 109.78; 118.50; 122.40; 134.91; 142.02; 156.86; 217.39; 223.50; 283.54. **Z-2e**. 16.36; 55.36; 57.93; 109.57; 120.96; 124.59; 134.70; 147.96; 157.95;

217.57; 223.79; 277.60. **Combined peaks.** 126.88; 127.09;  
127.48; 128.54; 128.97; 129.35

**Preparation of Complex 2g:** Reaction of pentacarbonyl(methoxy 4-methylphenyl)chromium(0) (0.98 g, 3 mmol) in diethyl ether (9 ml) and benzylamine (0.39 ml, 3.6 mmol) afforded the product (1.11 g, 93%) as a Yellow liquid.

IR : 2050 (m), 1970 (sh), 1920 (s)

<sup>1</sup>H NMR : *E:Z* = 59:41. **E-2f.** 2.39 (s, 3H); 4.43 (d, *J* = 5.8 Hz, 2H); 6.83 (d, *J* = 8.4 Hz, 2H); 9.31 (bs, 1H). **Z-2f.** 2.35 (s, 3H); 5.30 (d, *J* = 5.8 Hz, 2H); 6.98 (d, *J* = 8.4 Hz, 2H); 8.73 (bs, 1H). **Combined peaks.** 7.07-7.60 (m, 7H and 7H)

<sup>13</sup>C NMR : **E-2f.** 21.16; 54.78; 119.53; 134.87; 136.95; 146.99; 217.45; 223.74; 283.02. **Z-2f.** 21.16; 58.03; 121.53; 134.67; 138.14; 152.71; 217.57; 224.03; 278.67. **Combined peaks.** 127.62; 128.56; 128.70; 129.24; 129.42

**Preparation of Complex 2h:** Reaction of pentacarbonyl(methoxy 2-methoxyphenyl)tungsten(0) (1.42 g, 3 mmol) in diethyl ether (9 ml) and benzylamine (0.39 ml, 3.6 mmol) afforded the product (1.46 g, 89%) as a yellow solid.

m.p. : 97°C

IR : 2070 (m), 1985 (sh), 1930 (s)



<sup>1</sup>H NMR (CDCl<sub>3</sub>) *E:Z* = 43:57. **E-2i**. 3.87 (s, 3H); 4.35 (d, *J* = 5.8 Hz, 2H); 9.17 (bs, 1H). **Z-2i**. 3.84 (s, 3H); 5.19 (d, *J* = 5.8 Hz, 2H); 8.68 (bs, 1H). **Combined peaks**. 6.82-7.16 (m, 3H and 3H); 7.18-7.35 (m, 2H and 2H); 7.38-7.62 (m, 4H and 4H)

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) : *E:Z* = 30:70. **E-2i**. 3.32 (s, 3H); 3.62 (dd, *J* = 5.9 and 14.5 Hz, 1H); 3.74 (dd, *J* = 5.9 and 14.5 Hz, 1H); 8.77 (bs, 1H). **Z-2i**. 3.35 (s, 3H); 4.71 (d, *J* = 5.9 Hz, 2H); 7.52 (bs, 1H). **Combined peaks**. 6.30-6.51 (m, 1H and 1H); 6.65-7.17 (m, 8H and 8H)

<sup>13</sup>C NMR : **E-2i**. 54.92; 55.35; 111.09; 120.84; 121.53; 134.56; 138.45; 149.51; 198.71; 204.47; 258.43. **Z-2i**. 55.35; 59.82; 111.23; 120.35; 122.78; 134.56; 143.26; 150.78; 198.27; 204.39; 257.66. **Combined peaks**. 128.03; 128.41; 128.74; 128.90; 128.98; 129.34

Analysis : Calcd : C = 43.74, H = 2.75, N = 2.55  
 Found : C = 43.51, H = 2.70, N = 2.50

**Preparation of Complex 2i:** Reaction of the complex **1d** (1.37 g, 3 mmol) in diethyl ether (9 ml) and benzylamine (0.39 ml, 3.6 mmol) afforded the product (1.55 g, 97%) as a yellow liquid.

IR : 2070 (m), 1985 (sh), 1935 (s)

<sup>1</sup>H NMR : *E:Z* = 33:67. **E-2j**. 2.40 (s, 3H); 4.38 (d, *J* = 5.4 Hz, 2H); 9.17 (bs, 1H). **Z-2j**. 2.37 (s, 3H); 5.15 (d, *J* = 5.4 Hz, 2H); 8.60 (bs,

1H). **Combined peaks.**  $\delta$  6.70-7.92 (m, 9H)

$^{13}\text{C}$  NMR : **E-2j.**  $\delta$  21.59; 54.51; 116.91; 120.40; 134.71; 138.40; 150.10; 198.61; 204.33; 260.90. **Z-2i.**  $\delta$  21.48; 60.05; 119.24; 122.59; 134.44; 138.27; 155.23; 198.27; 204.03; 258.43. **Combined peaks.**  $\delta$  127.62; 127.98; 128.17; 128.41; 128.94; 129.13; 129.28; 129.38

**General Procedure for the Alkylation of Amino Carbene Complexes 2a-i:** The carbene complex (n mmol) and tetrabutylammonium bromide (0.1n mmol) in dichloromethane (10n ml) was treated with 50% aqueous NaOH and benzyl bromide (1.5n mmol) or methyl iodide (5 mmol). The mixture was stirred at room temperature under argon until the starting material was consumed (TLC, 1.5-3 h). The reaction mixture was diluted with water, extracted with dichloromethane, dried, and concentrated under reduced pressure. The pure product was isolated by flash chromatography.

**Preparation of Complex 3a:** Complex **2a** (0.80 g, 2 mmol), TBAB (64 mg, 0.2 mmol), 50% aq. NaOH and methyl iodide (0.62 ml, 10 mmol) in dichloromethane (20 ml) were stirred for 3 h yielded the product **3a** (0.72 g, 87%) as yellow solid.

m.p. : 98°C

IR : 2050 (m), 1975 (sh), 1930 (s)

$^1\text{H}$  NMR : *E:Z* = 6:94. **E-3a.**  $\delta$  2.16 (s, 3H); 3.88 (s, 3H); 4.19 (d, *J* = 14.6 Hz, 1H); 4.98 (d, *J* = 14.6 Hz, 1H); 6.90 (d, *J* = 7.8 Hz, 1H). **Z-**

**3a.**  $\delta$  2.18 (s, 3H); 3.86 (s, 3H); 5.49 (d,  $J = 14.6$  Hz, 1H); 5.72 (d,  $J = 14.6$  Hz, 1H); 6.81 (d,  $J = 7.8$  Hz, 1H). **Combined peaks.**  $\delta$  7.07-7.34 (m, 3H); 7.41-7.56 (m, 5H)

$^{13}\text{C}$  NMR : **Z-3a.**  $\delta$  19.23; 42.49; 67.52; 119.76; 125.70; 126.53; 126.60; 127.93; 128.99; 129.56; 131.16; 134.32; 152.25; 217.14; 223.64; 279.01

Analysis : Calcd : C = 60.73, H = 4.13, N = 3.37  
 Found : C = 60.60, H = 4.17, N = 3.45

**Preparation of Complex 3b:** Complex **2a** (0.80 g, 2 mmol), TBAB (64 mg, 0.2 mmol), 50% aq. NaOH and benzyl bromide (0.35 ml, 3 mmol) in dichloromethane (20 ml) were stirred for 1.5 h yielded the product **3b** (0.91 g, 93%) as a yellow solid.

m.p. : 93°C

IR : 2050 (m), 1980 (sh), 1925 (s)

$^1\text{H}$  NMR : 2.31 (s, 3H); 4.10 (d,  $J = 14.8$  Hz, 1H); 4.69 (d,  $J = 14.8$  Hz, 1H); 5.05 (d,  $J = 14.8$  Hz, 1H); 6.12 (d,  $J = 14.8$  Hz, 1H); 6.88-7.60 (m, 14H)

$^{13}\text{C}$  NMR : 19.93; 56.82; 64.22; 120.59; 125.89; 126.23; 126.71; 127.75; 128.60; 128.70; 129.09; 129.38; 129.46; 131.06; 133.66; 134.15; 151.80; 217.14; 223.64; 281.71

Analysis : Calcd : C = 65.99, H = 4.31, N = 2.85

Found : C = 66.20, H = 4.50, N = 3.20

**Preparation of Complex 3c:** Complex **2b** (0.83 g, 2 mmol), TBAB (64 mg, 0.2 mmol), 50% aq. NaOH and methyl iodide (0.62 ml, 10 mmol) in dichloromethane (20 ml) were stirred for 3 h yielded the product **3c** (0.80 g, 93%) as a yellow solid.

m.p. : 90°C

IR : 2070 (m), 1975 (sh), 1925 (s)

<sup>1</sup>H NMR : *E:Z* = 76:24. **E-3d**. 3.32 (s, 3H); 3.36 (s, 3H); 3.95 (d, *J* = 14.5 Hz, 1H); 4.12 (d, *J* = 14.5 Hz, 1H). **Z-3d**. 2.26 (s, 3H); 3.38 (s, 3H); 5.10 (d, *J* = 14.5 Hz, 1H); 5.30 (d, *J* = 14.5 Hz, 1H). **Combined peaks**. 6.50 (t, *J* = 7.8 Hz, 1H and 1H); 6.63-7.35 (m, 8H and 8H)

<sup>13</sup>C NMR : **E-3d**. 48.30; 55.11; 61.82; 111.05; 120.83; 127.75; 129.24; 134.26; 141.15; 148.56; 217.69; 224.43; 275.04. **Z-3d**. 42.77; 55.28; 67.33; 111.05; 121.04; 127.58; 128.46; 134.53; 141.61; 148.12; 217.29; 224.81; 274.61

Analysis : Calcd : C = 58.47, H = 3.97, N = 3.25  
 Found : C = 58.68, H = 4.18, N = 3.05

**Preparation of Complex 3d:** Complex **2b** (0.83 g, 2 mmol), TBAB (64 mg, 0.2 mmol), 50% aq. NaOH and benzyl bromide (0.35 ml, 3 mmol) in dichloromethane (20 ml) were stirred for 1.5 h yielded the product **3d** (0.96 g, 89%) as a yellow solid.

m.p.	:	108°C
IR	:	2040 (m), 1975 (sh), 1920 (s)
<sup>1</sup> H NMR	:	3.96 (s, 3H); 4.39 (d, J = 14.6 Hz, 1H); 4.65 (d, J = 14.6 Hz, 1H); 5.30 (d, J = 14.6 Hz, 1H); 5.86 (d, J = 14.6 Hz, 1H); 6.89-7.18 (m, 5H); 7.18-7.32 (m, 1H); 7.32-7.64 (m, 8H)
<sup>13</sup> C NMR	:	55.14; 57.74; 63.36; 111.00; 120.87; 121.28; 127.73; 127.87; 128.42; 128.55; 129.19; 134.28; 134.47; 141.28; 148.24; 217.34; 224.08; 277.84
Analysis	:	Calcd : C = 63.91, H = 4.17, N = 2.76 Found : C = 64.10, H = 4.40, N = 2.90

**Preparation of Complex 3e:** Complex **2c** (0.87 g, 2 mmol), TBAB (64 mg, 0.2 mmol), 50% aq. NaOH and benzyl bromide (0.35 ml, 3 mmol) in dichloromethane (20 ml) were stirred for 1.5 h yielded the product **3e** (0.88 g, 84%) as a yellow solid.

m.p.	:	115°C
IR	:	2035 (m), 1970 (sh), 1915 (s)
<sup>1</sup> H NMR	:	4.20 (d, J = 14.6 Hz, 1H); 4.52 (d, J = 14.6 Hz, 1H); 5.33 (d, J = 14.6 Hz, 1H); 6.10 (d, J = 14.6 Hz, 1H); 6.80-7.02 (m, 2H); 7.08 (d, J = 7.3 Hz, 1H); 7.20-7.64 (m, 11H); 7.70 (d, J = 7.3

Hz, 2H); 7.88 (dd,  $J = 0.9$  and  $7.3$  Hz, 1H)

$^{13}\text{C}$  NMR : 58.01; 63.98; 116.87; 124.69; 125.11; 125.31; 126.66; 126.79;  
127.78; 128.48; 129.05; 129.22; 129.47; 133.77; 134.13;  
149.14; 217.06; 223.89; 281.34

Analysis : Calcd : C = 68.18, H = 3.97, N = 2.84  
Found : C = 67.96, H = 3.91, N = 2.75

**Preparation of Complex 3f:** Complex **2d** (0.80 g, 2 mmol), TBAB (64 mg, 0.2 mmol), 50% aq. NaOH and benzyl bromide (0.35 ml, 3 mmol) in dichloromethane (20 ml) were stirred for 1.5 h yielded the product **3f** (0.89 g, 91%) as a yellow solid.

m.p. : 150°C

IR : 2060 (m), 1985 (sh), 1935 (s)

$^1\text{H}$  NMR : 2.37 (s, 3H); 4.48 (s, 2H); 5.55 (s, 2H); 6.60-6.82 (m, 2H); 6.90-7.15 (m, 3H); 7.18-7.65 (m, 9H)

$^{13}\text{C}$  NMR : 21.87; 57.73; 63.43; 116.35; 119.90; 126.94; 127.33; 127.68;  
128.49; 128.69; 128.85; 129.39; 129.49; 134.37; 138.62;  
152.84; 217.29; 224.06; 280.85

Analysis : Calcd : C = 62.30, H = 4.04, N = 2.69  
Found : C = 62.49, H = 4.10, N = 2.68

**Preparation of Complex 3g:** Complex **2e** (0.83 g, 2 mmol), TBAB (64 mg, 0.2 mmol), 50% aq. NaOH and benzyl bromide (0.35 ml, 3 mmol) in dichloromethane (20 ml) were stirred for 1.5 h yielded the product **3g** (0.98 g, 97%) as a yellow liquid.

IR : 2065 (m), 1975 (sh), 1920 (s)

<sup>1</sup>H NMR : 3.80 (s, 3H); 4.50 (s, 2H); 5.48 (d, J = 14.3 Hz, 1H); 5.56 (d, J = 14.3 Hz, 1H); 6.40-6.56 (m, 2H); 6.65-6.75 (m, 1H); 6.97-7.12 (m, 2H); 7.23-7.57 (m, 9H)

<sup>13</sup>C NMR : 55.35; 57.78; 63.42; 105.36; 111.62; 127.19; 127.59; 128.46; 128.85; 129.42; 130.14; 134.27; 153.88; 159.73; 217.25; 223.97; 279.87

**Preparation of Complex 3h:** Complex **2f** (0.86 g, 2 mmol), TBAB (64 mg, 0.2 mmol), 50% aq. NaOH and benzyl bromide (0.35 ml, 3 mmol) in dichloromethane (20 ml) were stirred for 1.5 h yielded the product **3h** (0.91 g, 88%) as a yellow solid.

m.p. : 116°C

IR : 2050 (m), 1980 (sh), 1935 (s)

<sup>1</sup>H NMR : 2.25 (s, 3H); 3.84 (s, 3H); 4.41 (d, J = 14.8 Hz, 1H); 4.60 (d, J = 14.8 Hz, 1H); 5.46 (d, J = 14.8 Hz, 1H); 5.62 (d, J = 14.8 Hz, 1H); 6.55-6.89 (m, 3H); 6.94-7.14 (m, 2H); 7.21-7.72 (m, 8H)

<sup>13</sup>C NMR : 16.52; 55.61; 57.89; 63.68; 110.18; 117.88; 122.19; 127.35; 127.76; 128.46; 128.84; 129.39; 129.47; 134.62; 146.31;

156.23; 217.48; 224.21; 282.44

Analysis : Calcd : C = 64.49, H = 4.45, N = 2.69  
 Found : C = 64.32, H = 4.63, N = 2.76

**Preparation of Complex 3i:** Complex **2g** (0.80 g, 2 mmol), TBAB (64 mg, 0.2 mmol), 50% aq. NaOH and benzyl bromide (0.35 ml, 3 mmol) in dichloromethane (20 ml) were stirred for 1.5 h yielded the product **3i** (0.89 g, 91%) as a yellow solid.

m.p. : 98°C

IR : 2060 (m), 1955 (sh), 1915 (s)

<sup>1</sup>H NMR : 2.39 (s, 3H), 4.48 (s, 2H); 5.58 (s, 2H); 6.90 (d, J = 7.5 Hz, 2H);  
 7.01-7.18 (m, 2H); 7.22 (d, 7.5 Hz, 2H); 7.34-7.72 (m, 8H)

<sup>13</sup>C NMR : 21.15; 57.5 ; 63.36; 119.22; 127.22; 127.58; 128.44; 128.80;  
 129.32; 132.41; 134.20; 134.32; 135.85; 150.37; 217.27;  
 224.10; 281.06

Analysis : Calcd : C = 65.99, H = 4.30, N = 2.85  
 Found : C = 65.56, H = 4.30, N = 2.64

**Preparation of Complex 3j:** Penacarbonyl(benzylaminophenyl)chromium(0) (0.77 g, 2 mmol), TBAB (64 mg, 0.2 mmol), 50% aq. NaOH and benzyl bromide (0.35 ml, 3 mmol) in dichloromethane (20 ml) were stirred for 1.5 h yielded the product **3j** (0.83 g, 87%) as a yellow solid.



m.p.	:	100°C
IR	:	2040 (m), 1980 (sh), 1920 (s)
<sup>1</sup> H NMR	:	4.48 (s, 2H); 5.55 (s, 2H); 6.90 (d, J = 7.8 Hz, 2H); 7.00-7.65 (m, 13H)
<sup>13</sup> C NMR	:	57.41; 63.08; 118.89; 125.90; 126.88; 127.27; 128.15; 128.44; 129.03; 129.12; 133.80; 133.90; 152.45; 216.86; 223.68; 280.15
Analysis	:	Calcd : C = 65.41, H = 4.01, N = 2.93 Found : C = 65.10, H = 4.10, N = 3.09

**Preparation of Complex 3k:** Complex **2h** (1.09 g, 2 mmol), TBAB (64 mg, 0.2 mmol), 50% aq. NaOH and benzyl bromide (0.35 ml, 3 mmol) in dichloromethane (20 ml) were stirred for 1.5 h yielded the product **3k** (1.18 g, 93%) as a yellow solid.

m.p.	:	111°C
IR	:	2070 (m), 1975 (sh), 1915 (s)
<sup>1</sup> H NMR	:	3.95 (s, 3H); 4.82 (d, J = 14.6 Hz, 1H); 4.70 (d, J = 14.6 Hz, 1H); 5.13 (d, J = 14.6 Hz, 1H); 5.82 (d, J = 14.6 Hz, 1H); 6.89-7.13 (m, 5H); 7.14-7.27 (m, 1H); 7.32-7.63 (m, 8H)

$^{13}\text{C}$  NMR : 55.17; 56.31; 65.27; 110.94; 120.70; 121.86; 127.74; 127.82;  
128.14; 128.54; 129.19; 134.03; 134.18; 141.56; 148.74;  
198.47; 204.14; 258.97

Analysis : Calcd : C = 63.91, H = 4.17, N = 2.76  
Found : C = 64.07, H = 4.31, N = 2.47

**Preparation of Complex 31:** Complex **2i** (1.06 g, 2 mmol), TBAB (64 mg, 0.2 mmol), 50% aq. NaOH and benzyl bromide (0.35 ml, 3 mmol) in dichloromethane (20 ml) were stirred for 1.5 h yielded the product **31** (1.20 g, 97%) as a yellow solid.

m.p. : 146°C

IR : 2050 (m), 1975 (sh), 1920 (s)

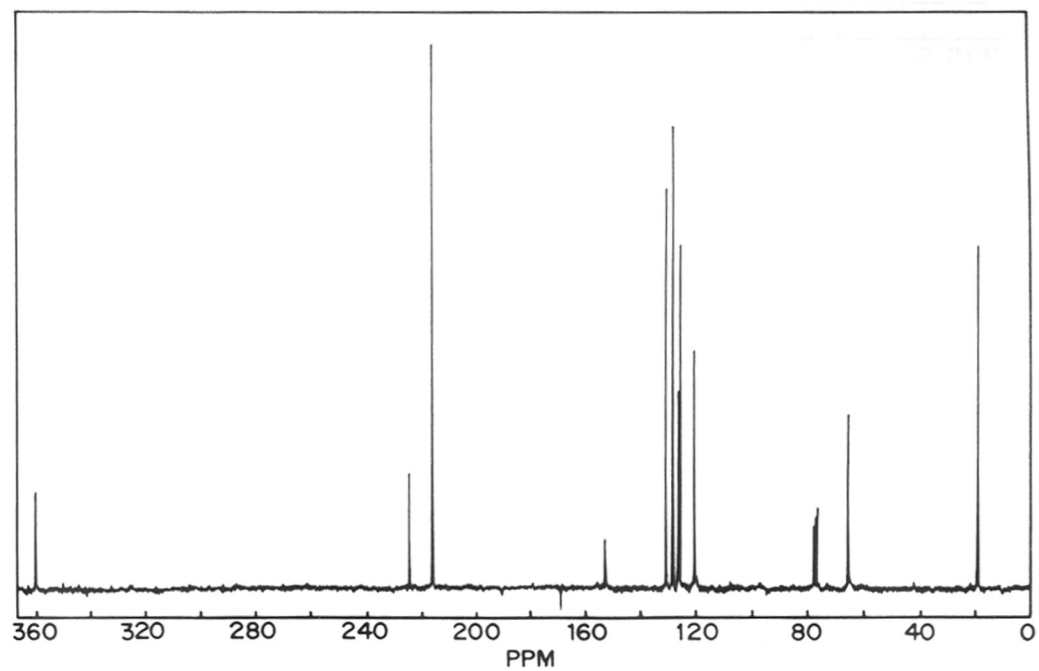
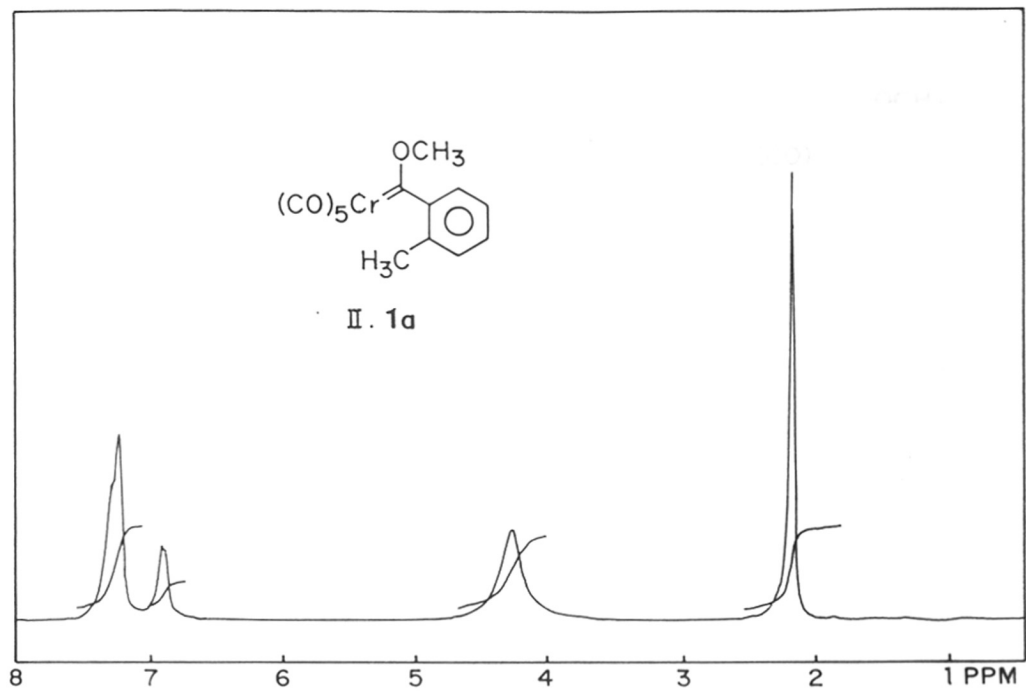
$^1\text{H}$  NMR : 2.35 (s, 3H); 4.49 (s, 2H); 5.48 (s, 2H); 6.72-6.80 (m, 2H); 6.93-  
7.08 (m, 3H); 7.22-7.58 (m, 9H)

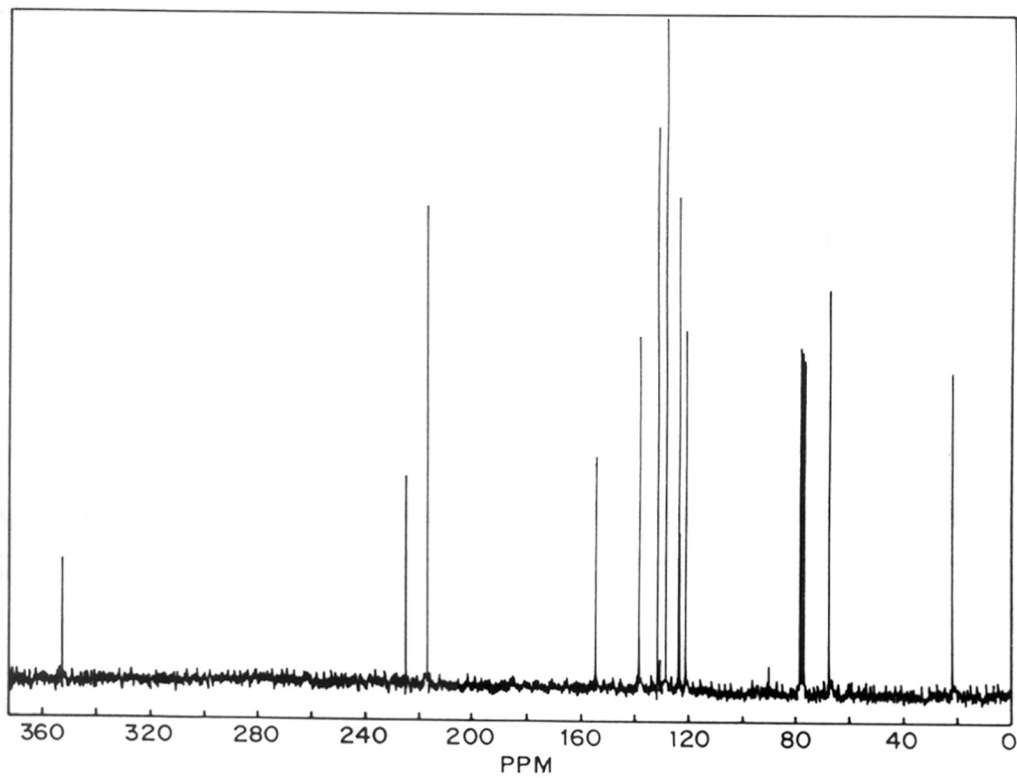
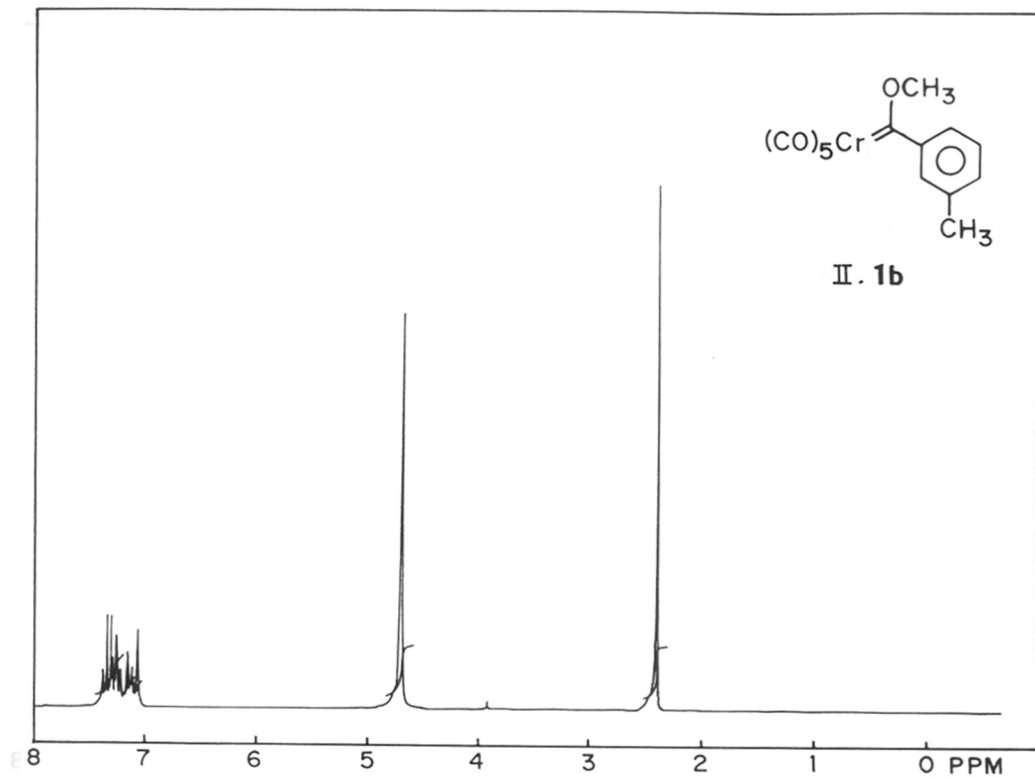
$^{13}\text{C}$  NMR : 21.91; 56.36; 65.41; 116.78; 124.38; 127.34; 127.48; 127.81;  
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204.22; 262.66

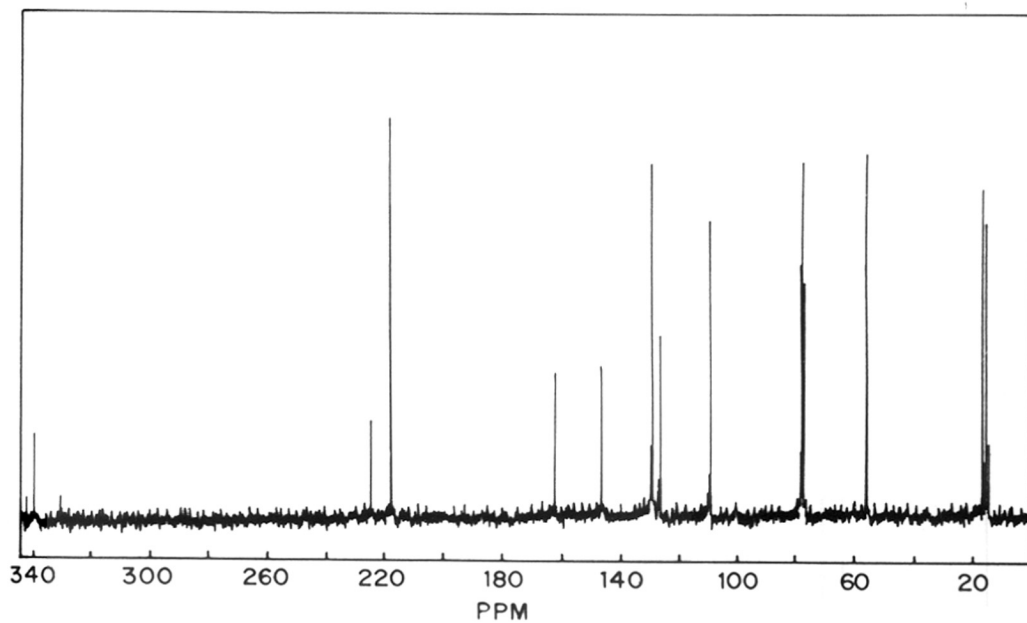
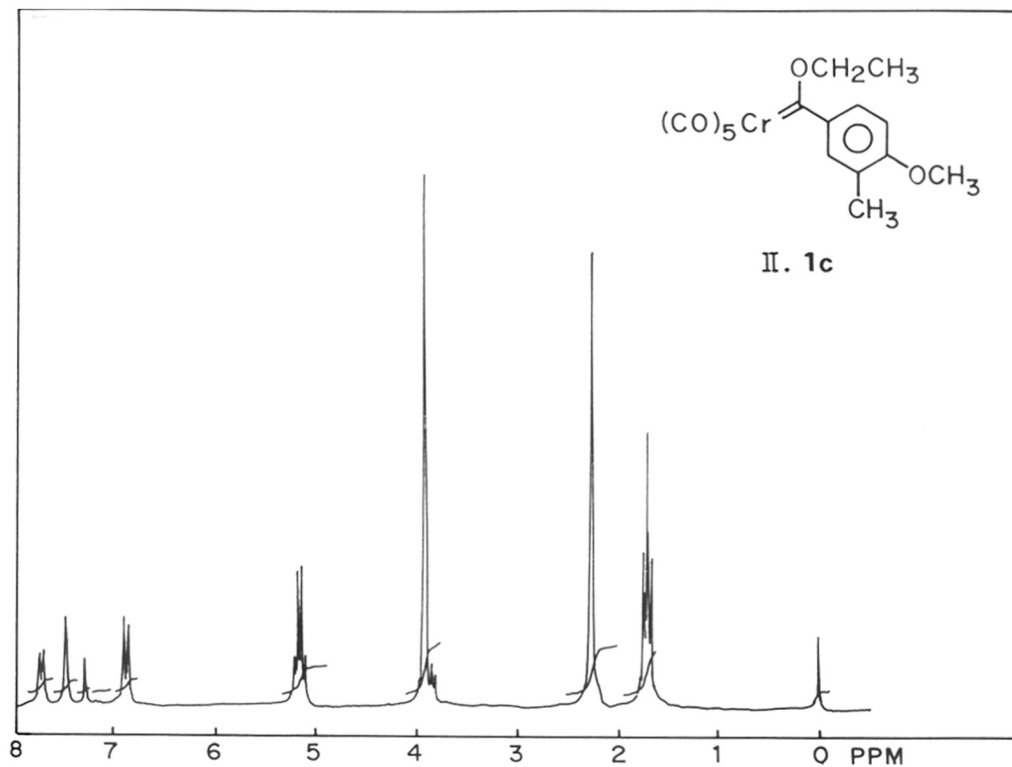
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Found : C = 52.39, H = 3.27, N = 2.17

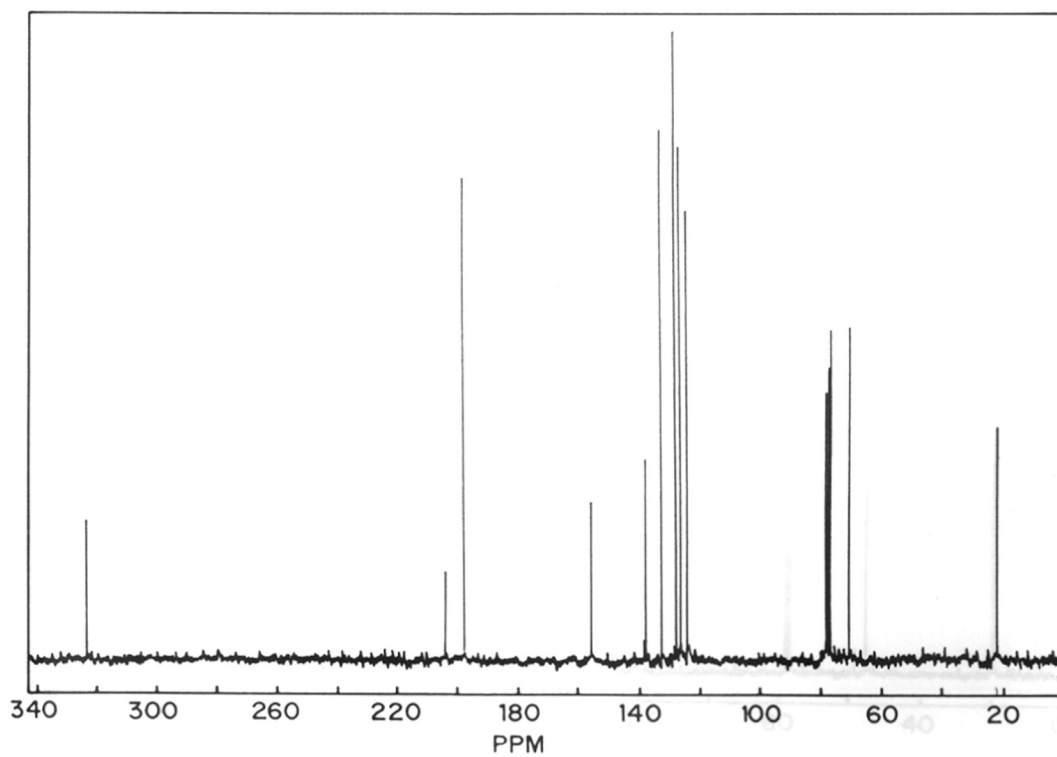
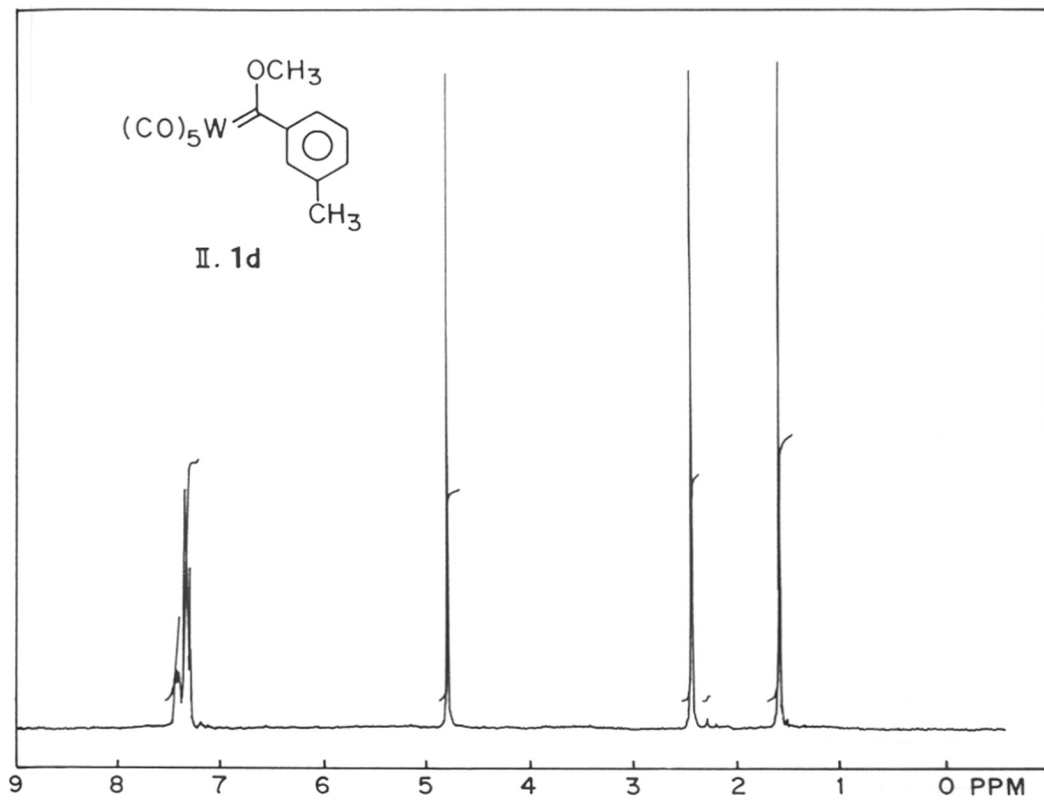
**II.6 REFERENCES AND NOTES**

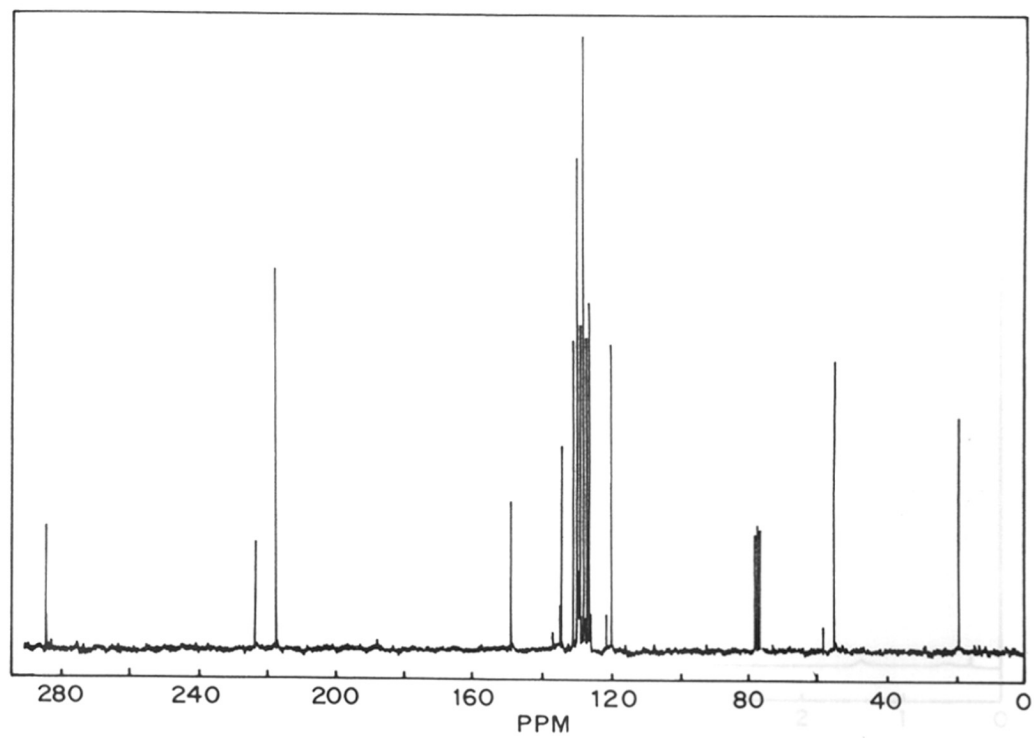
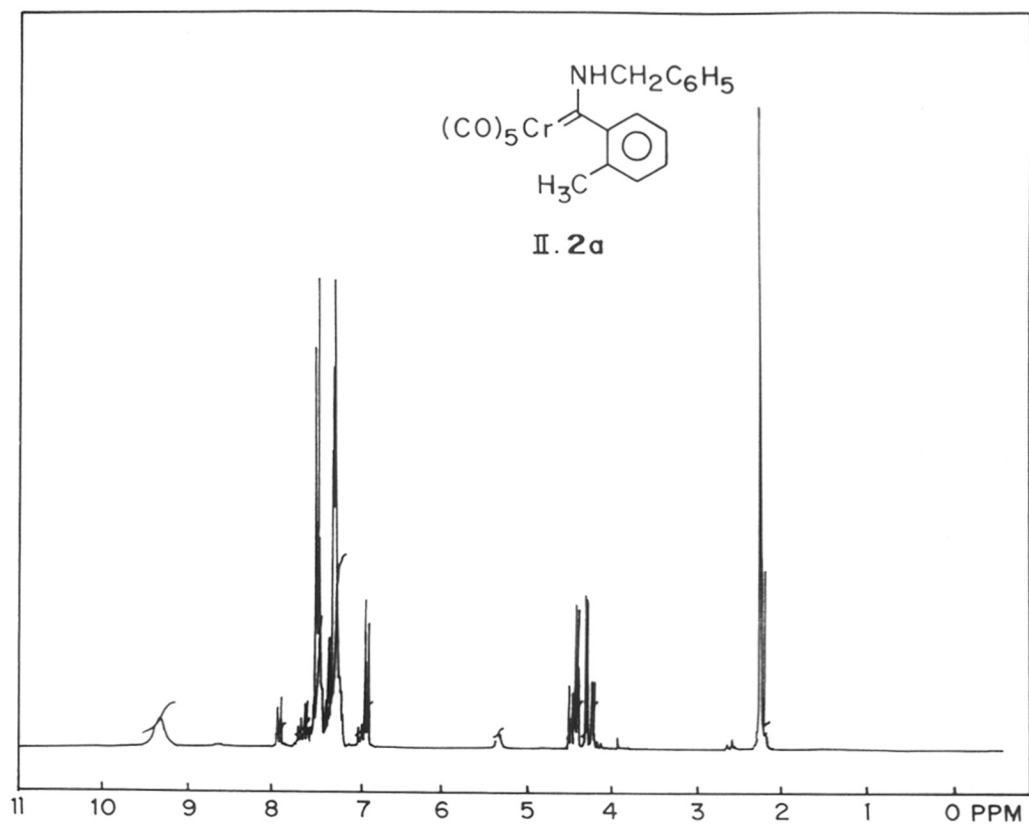
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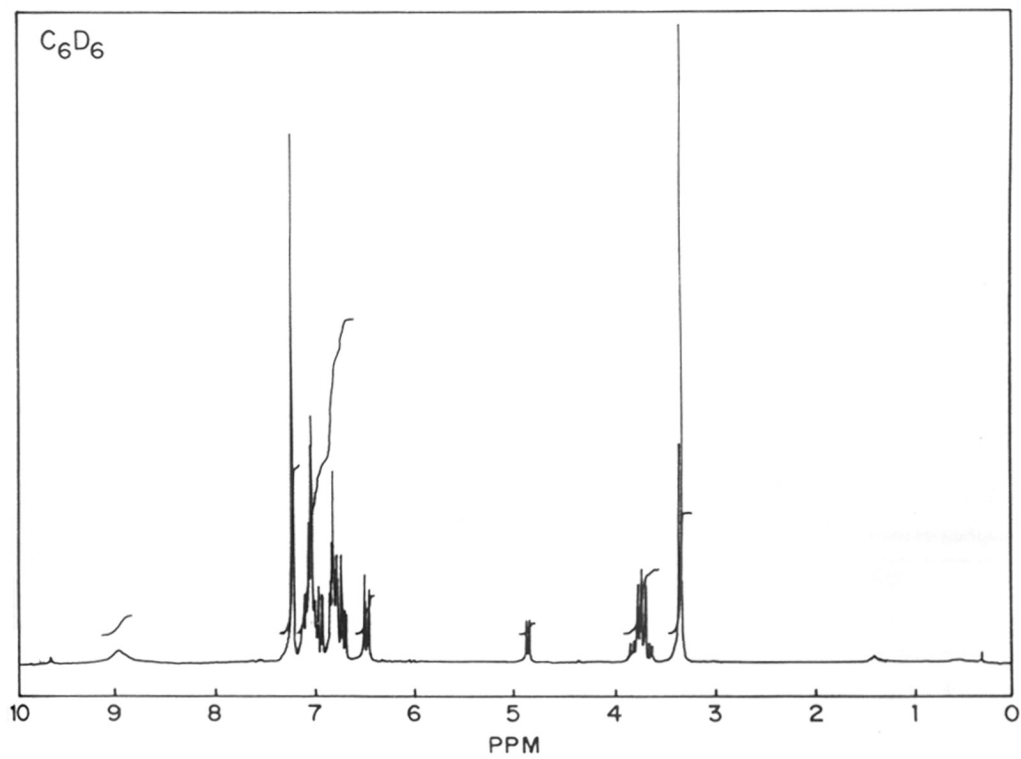
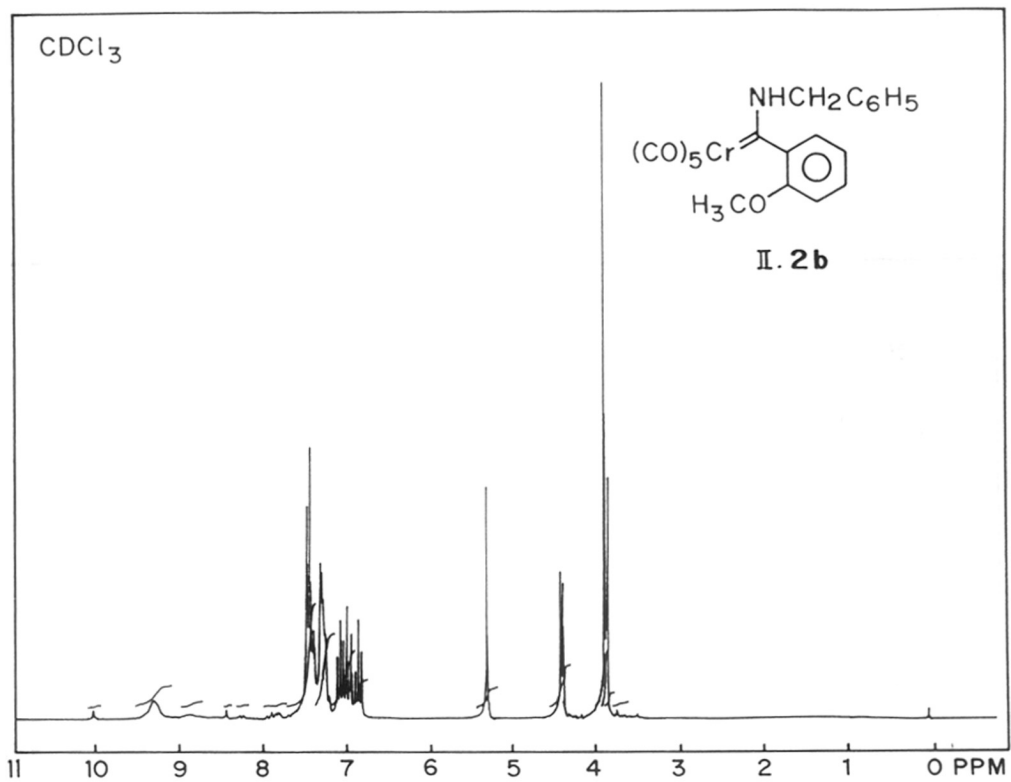


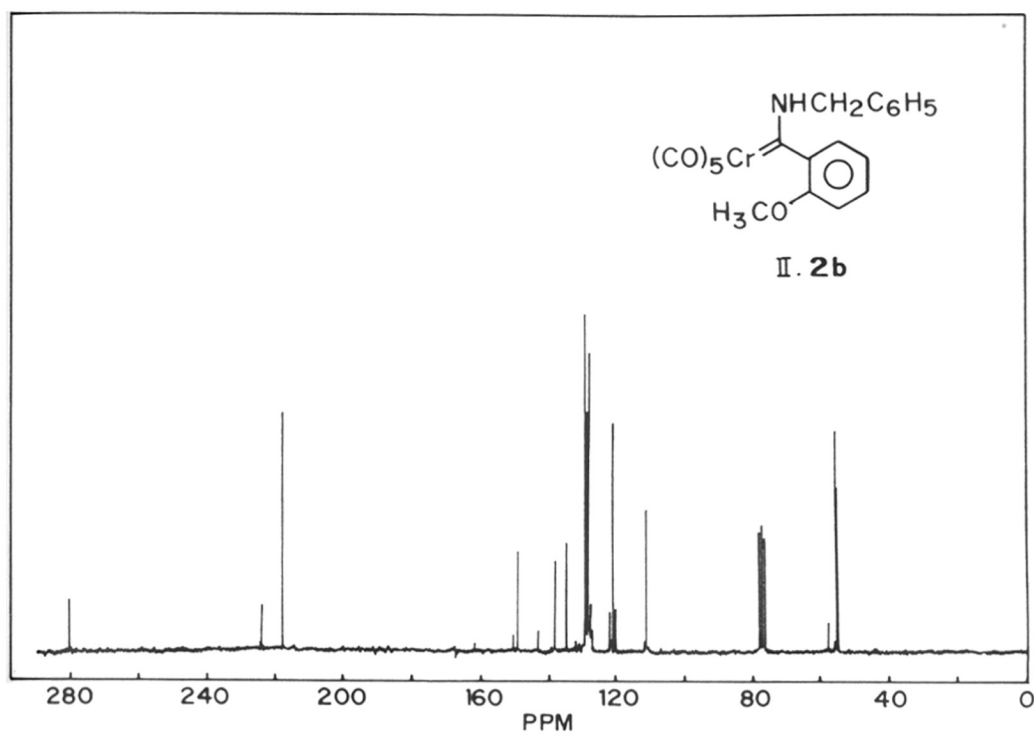


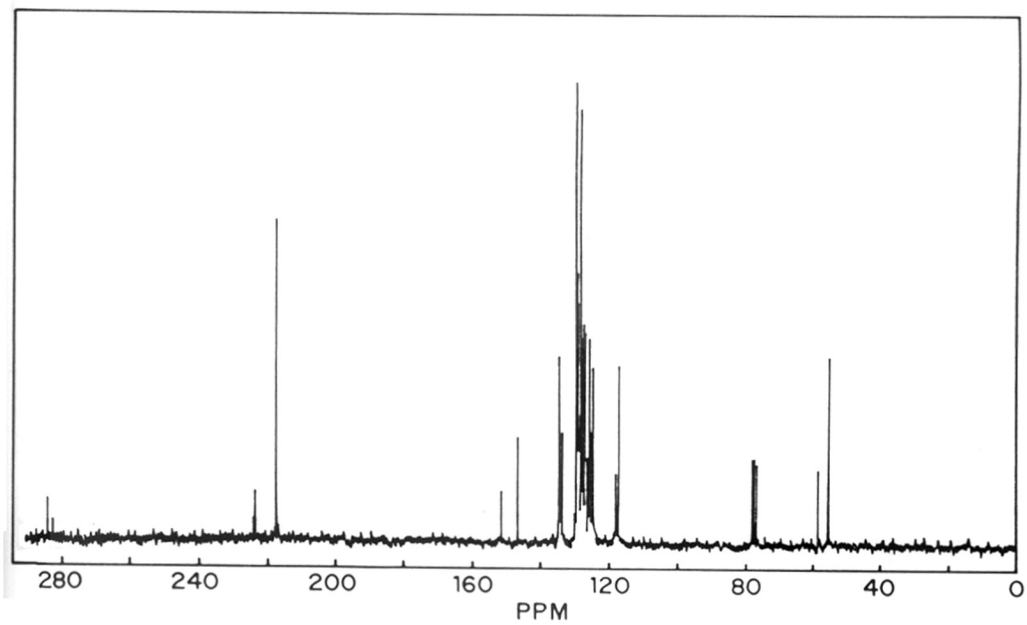
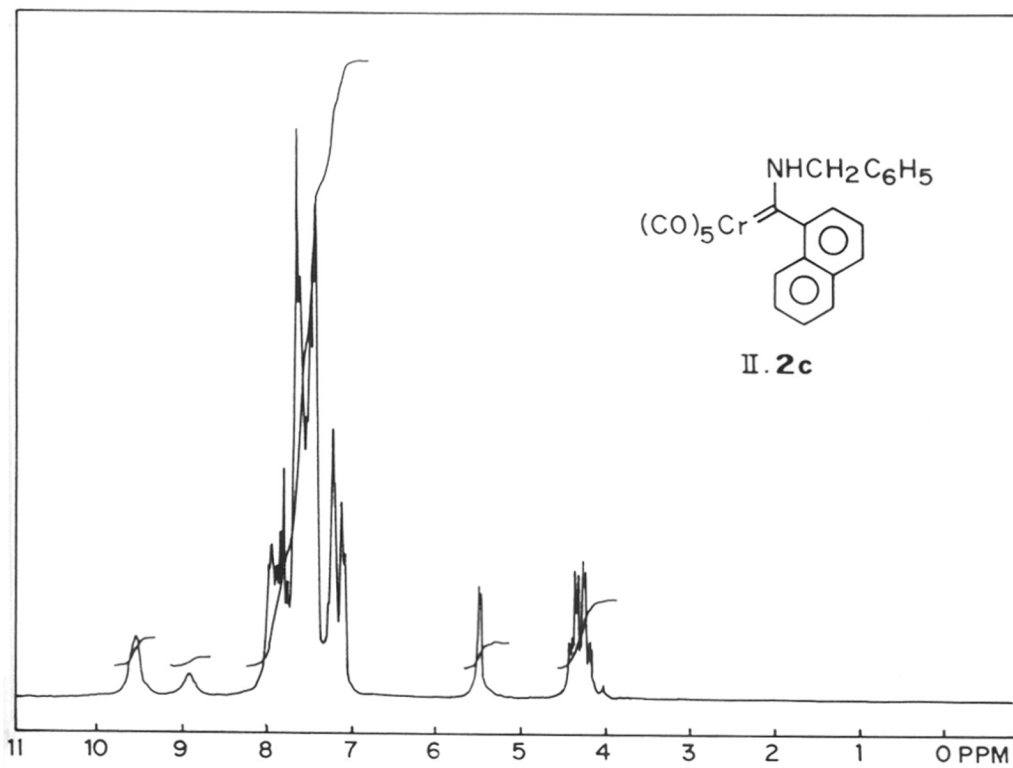


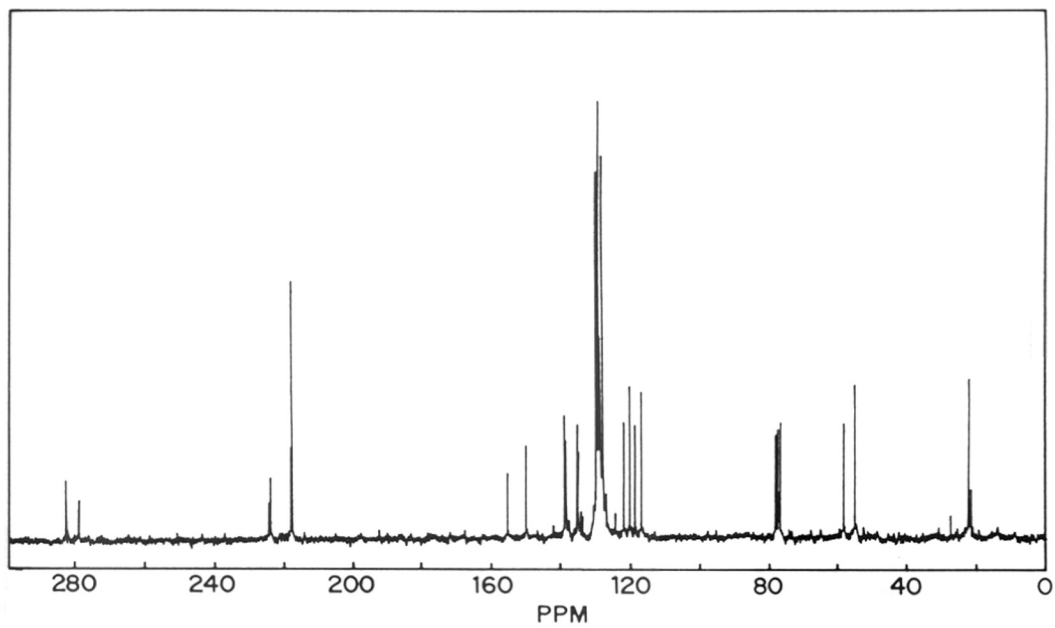
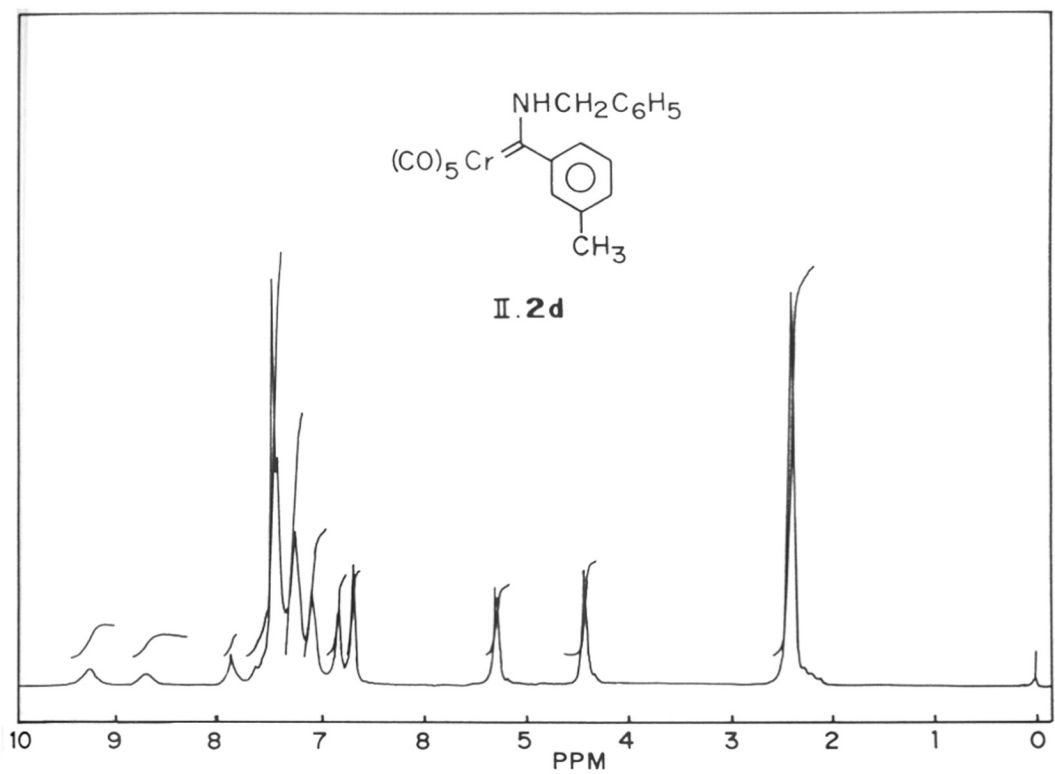


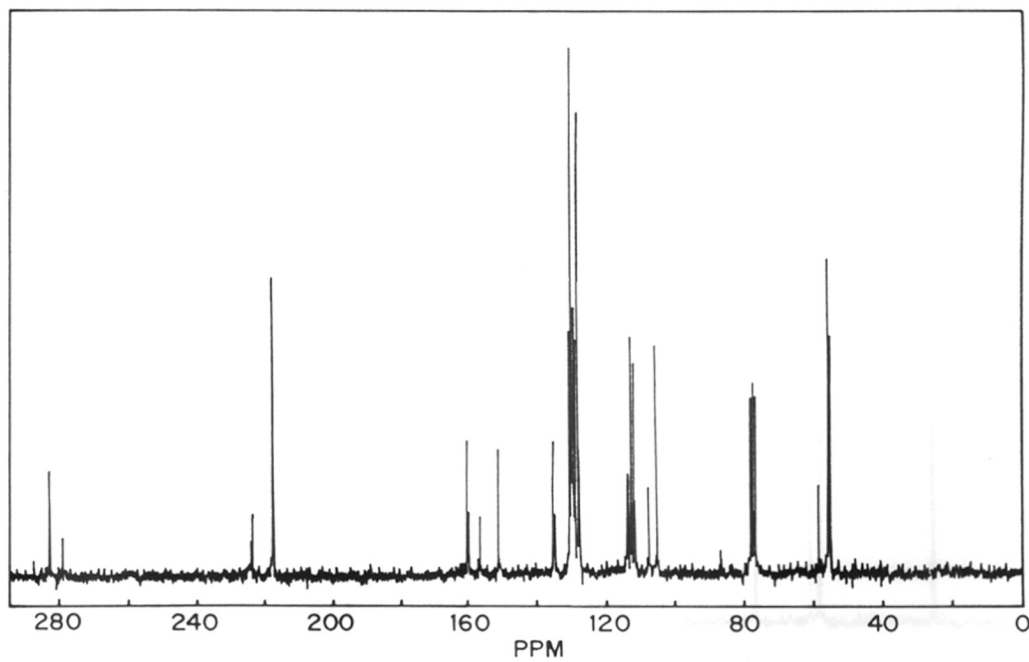
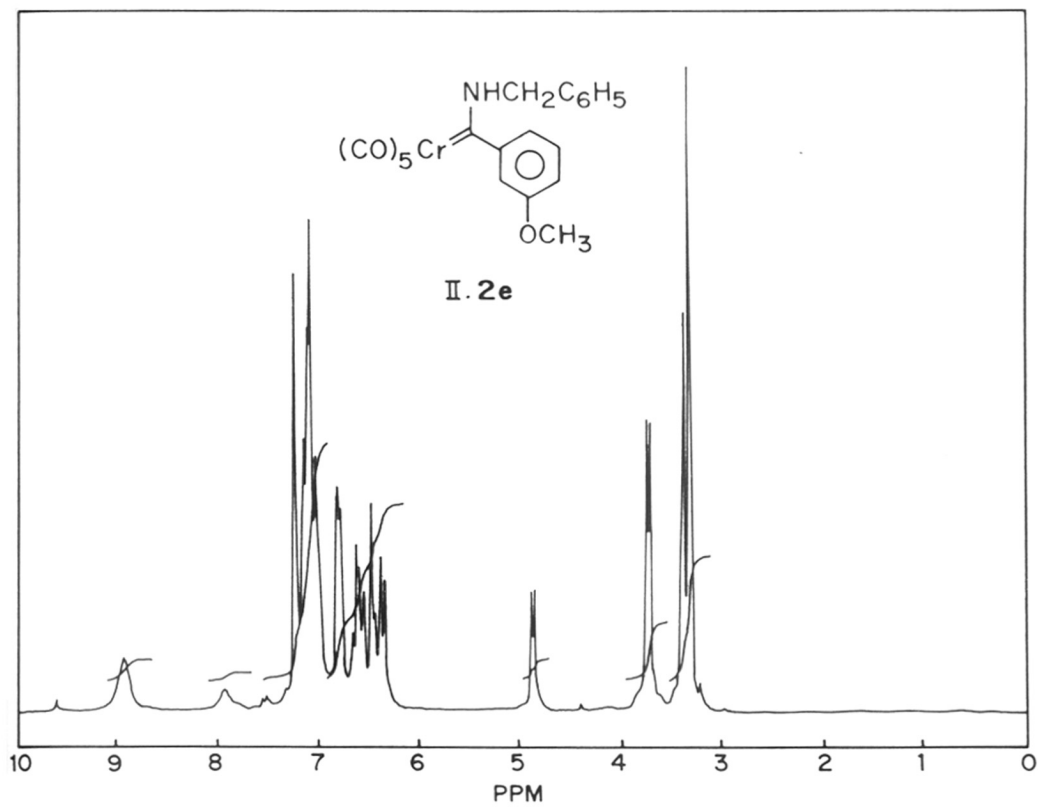


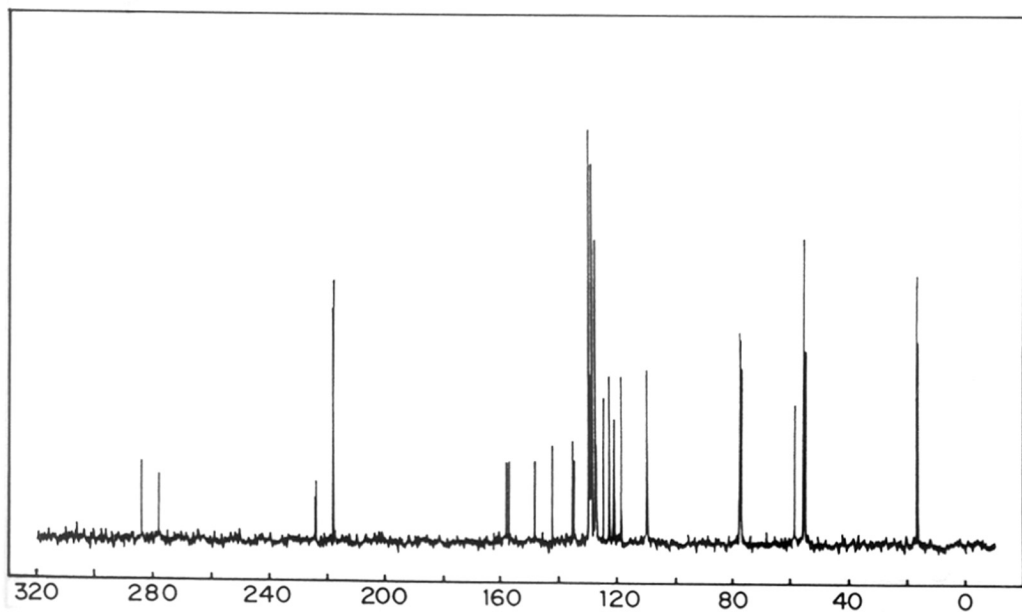
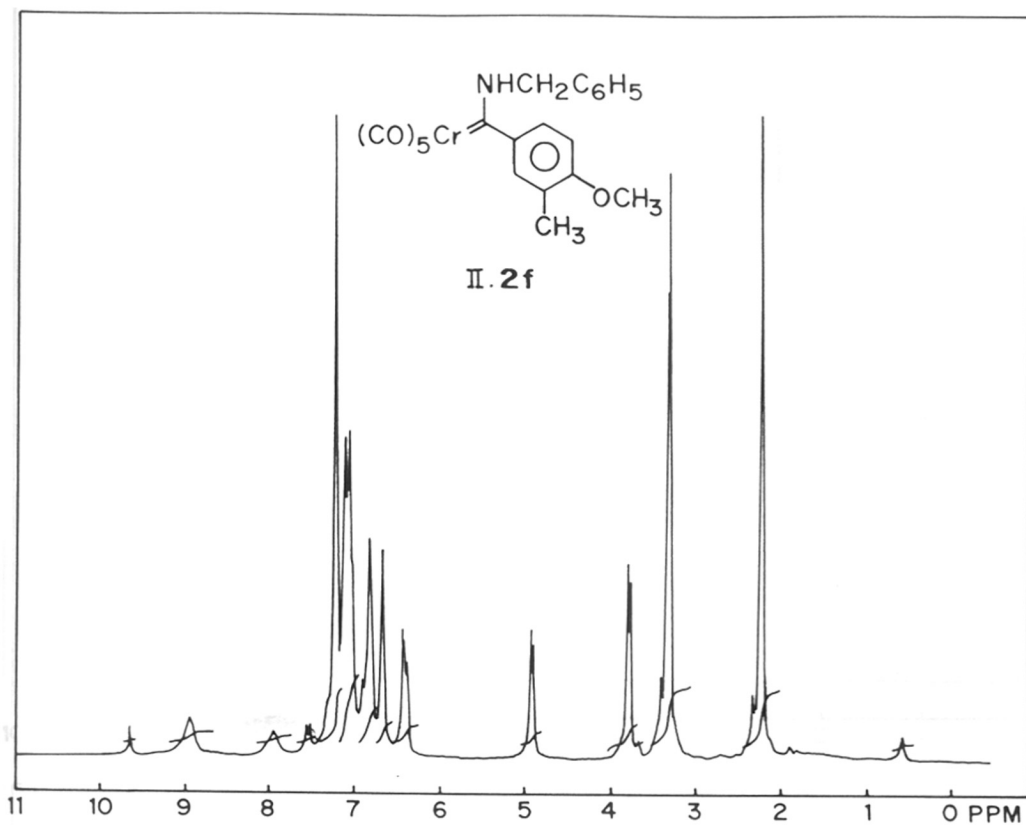


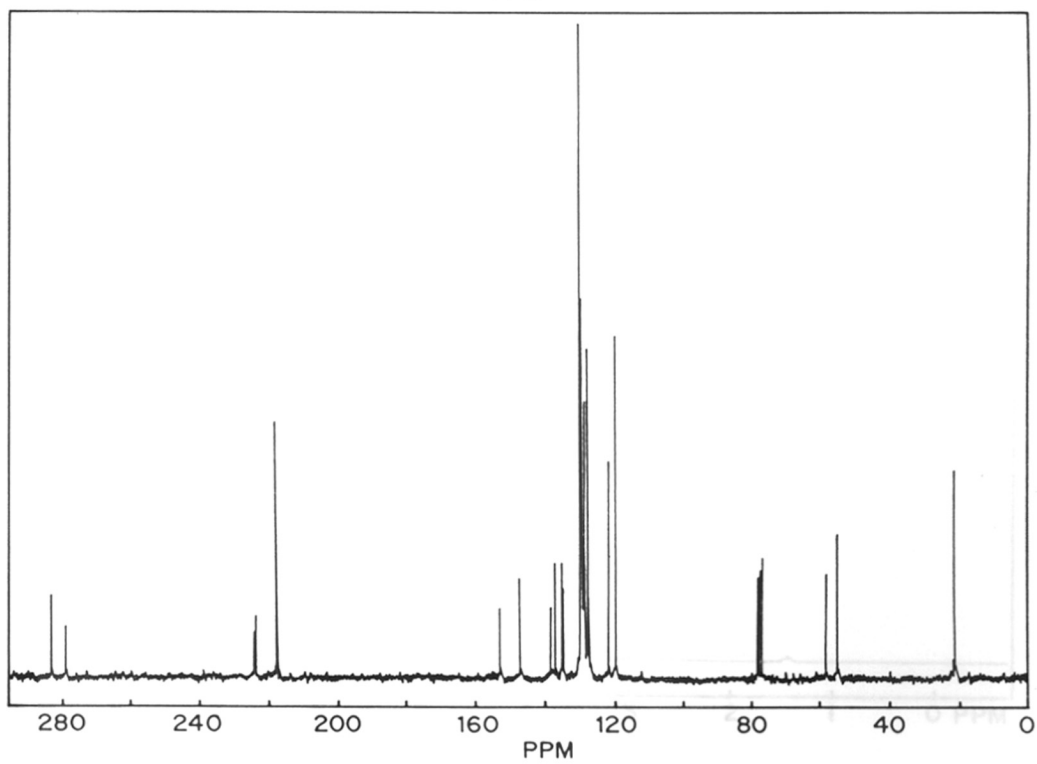
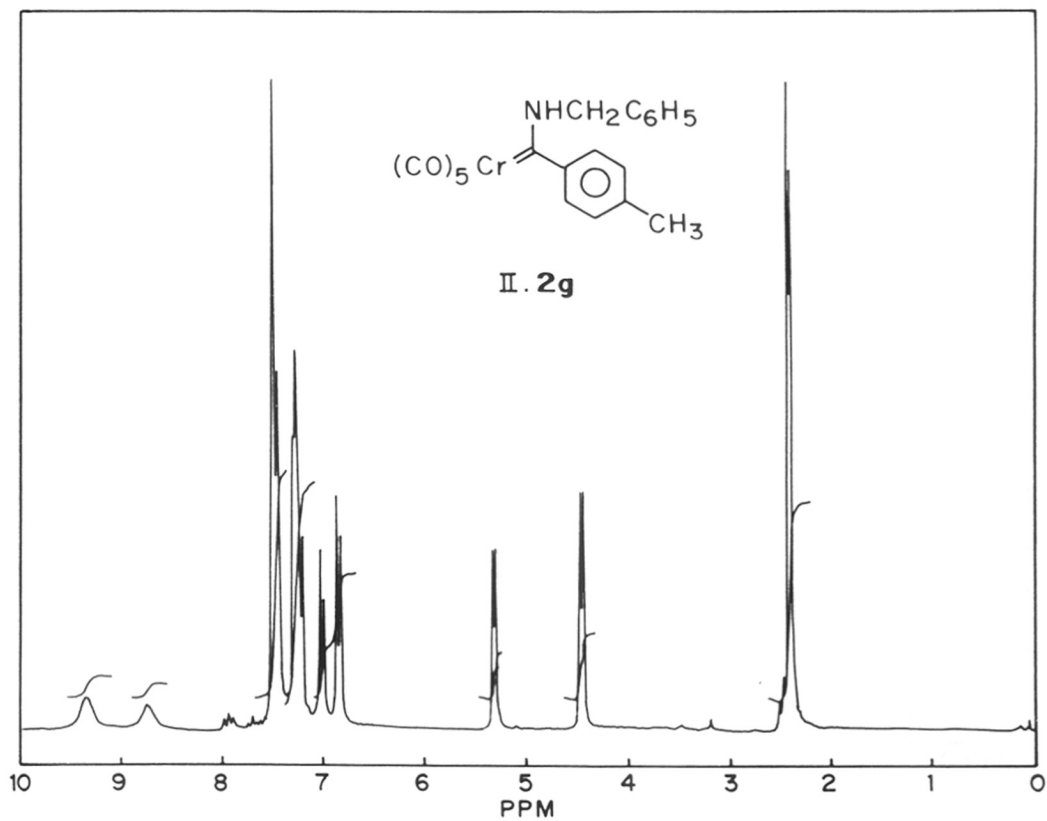


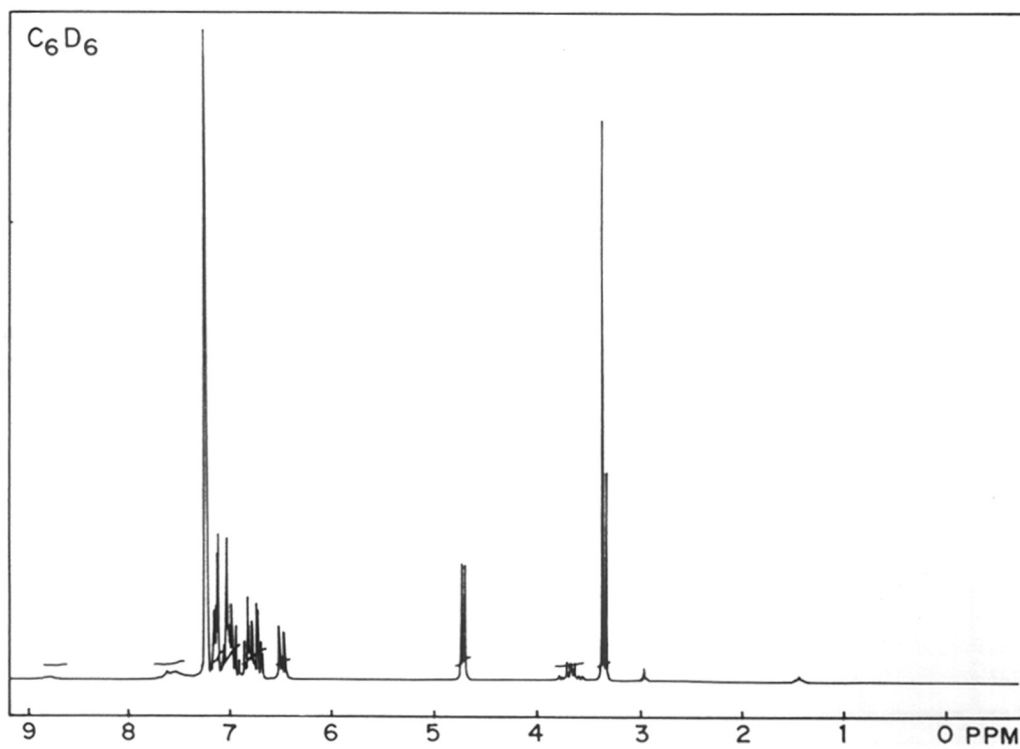
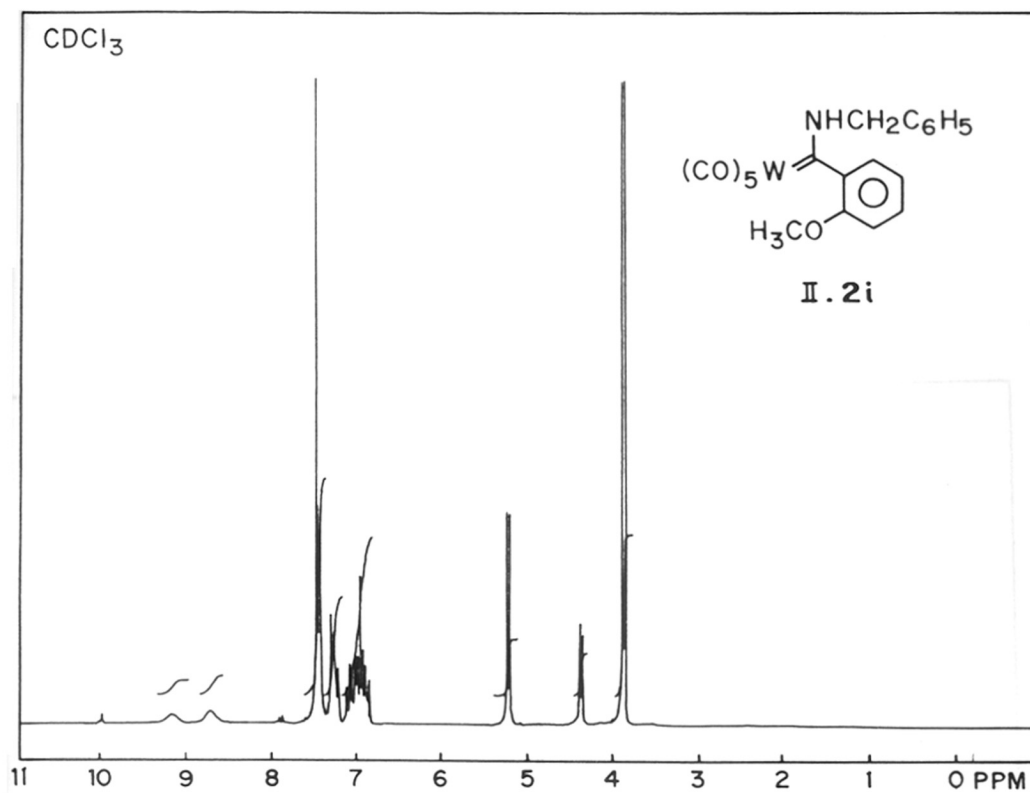




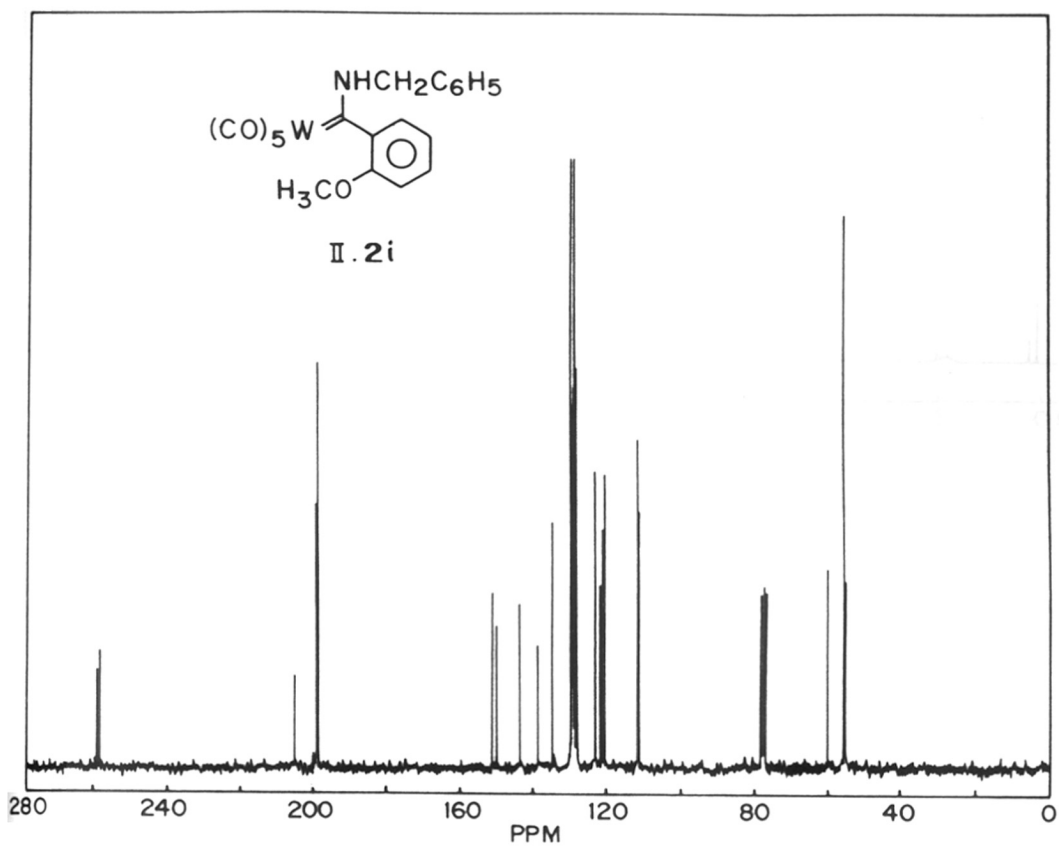


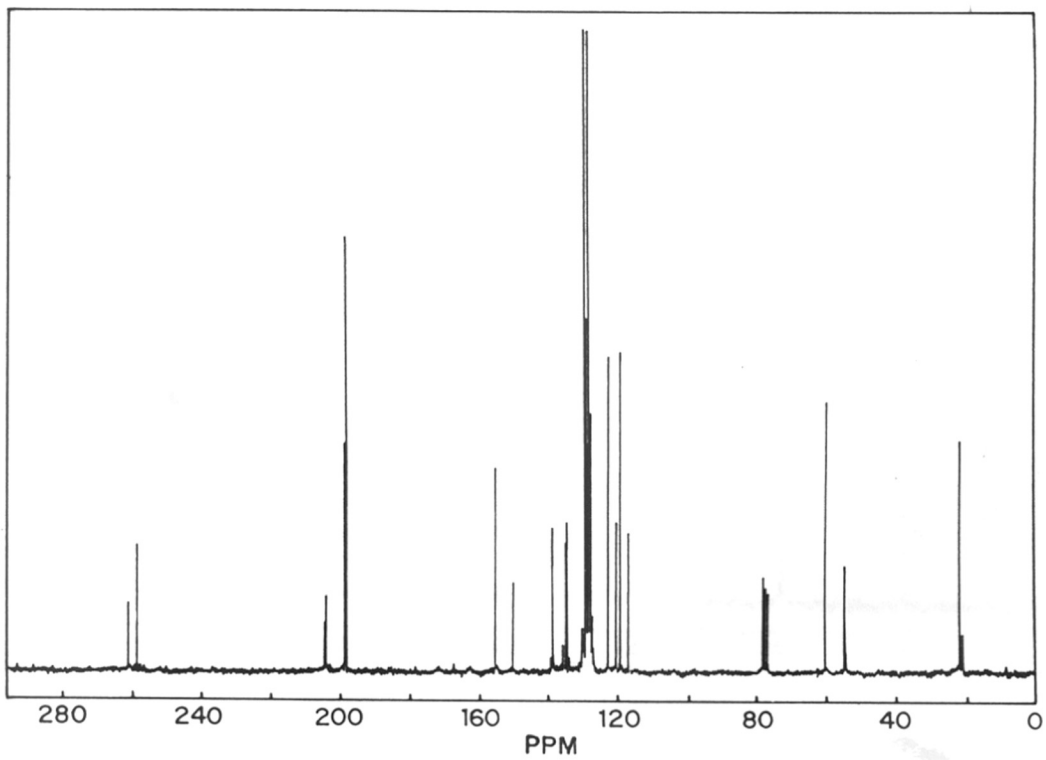
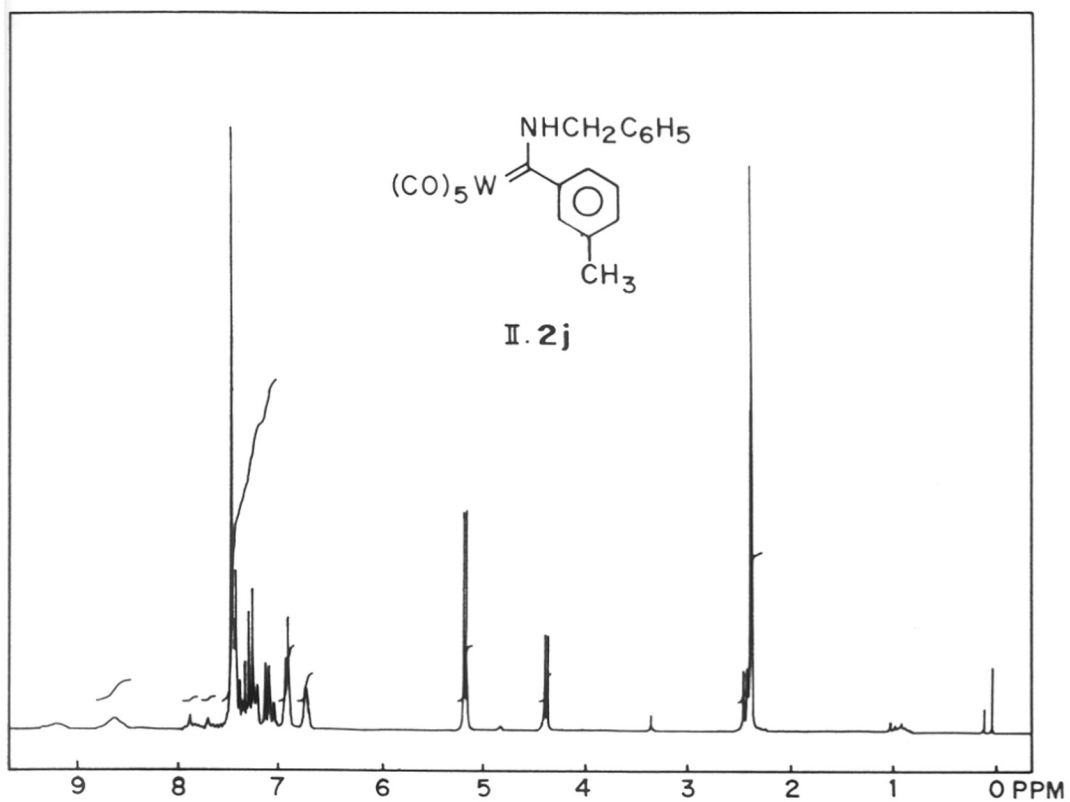


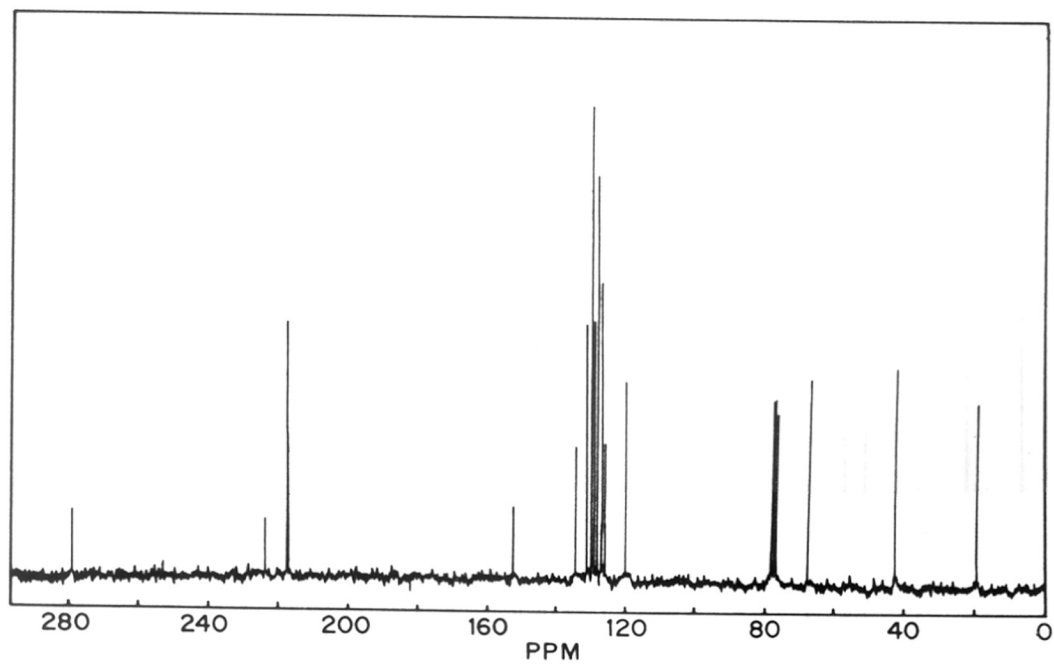
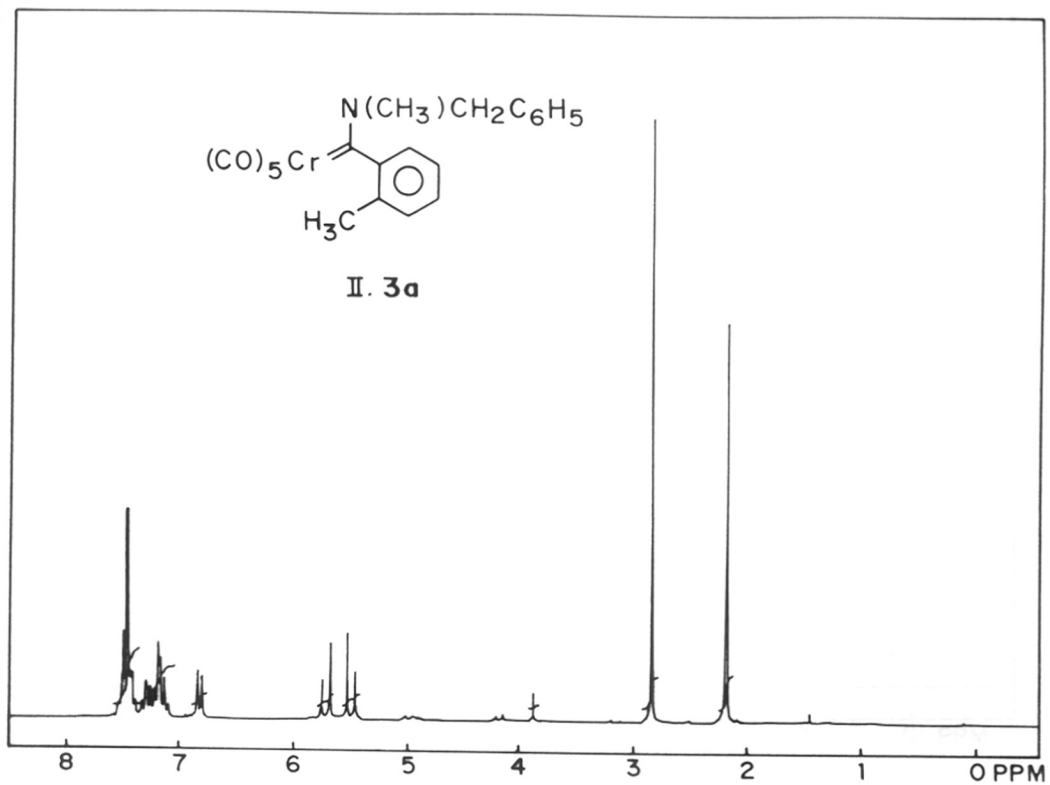


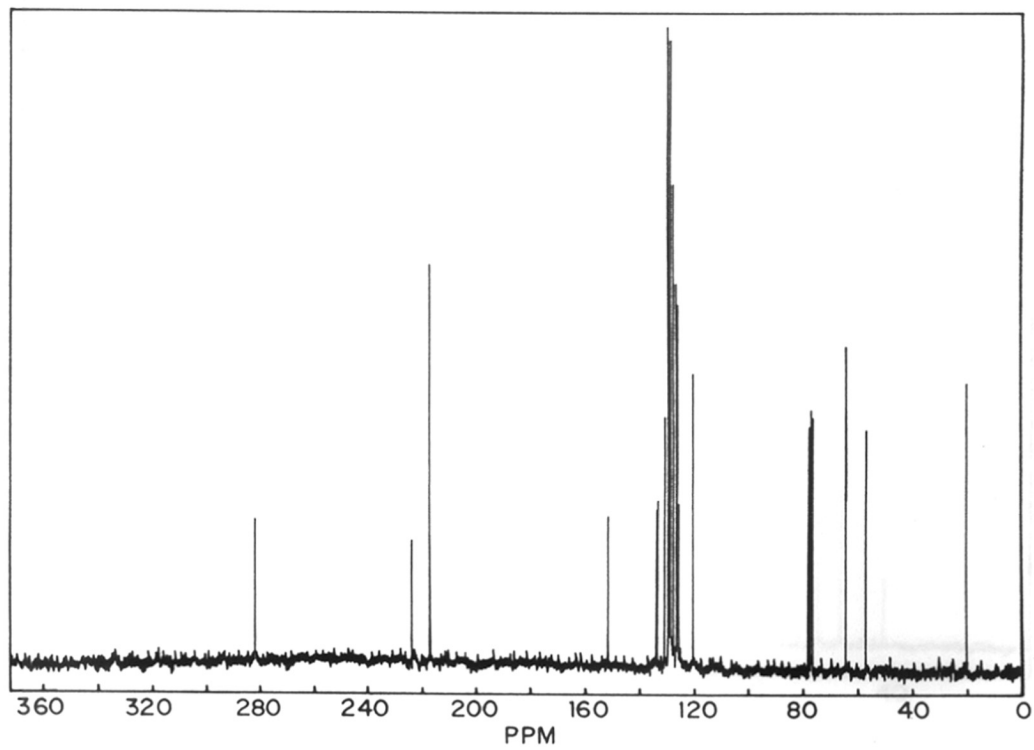
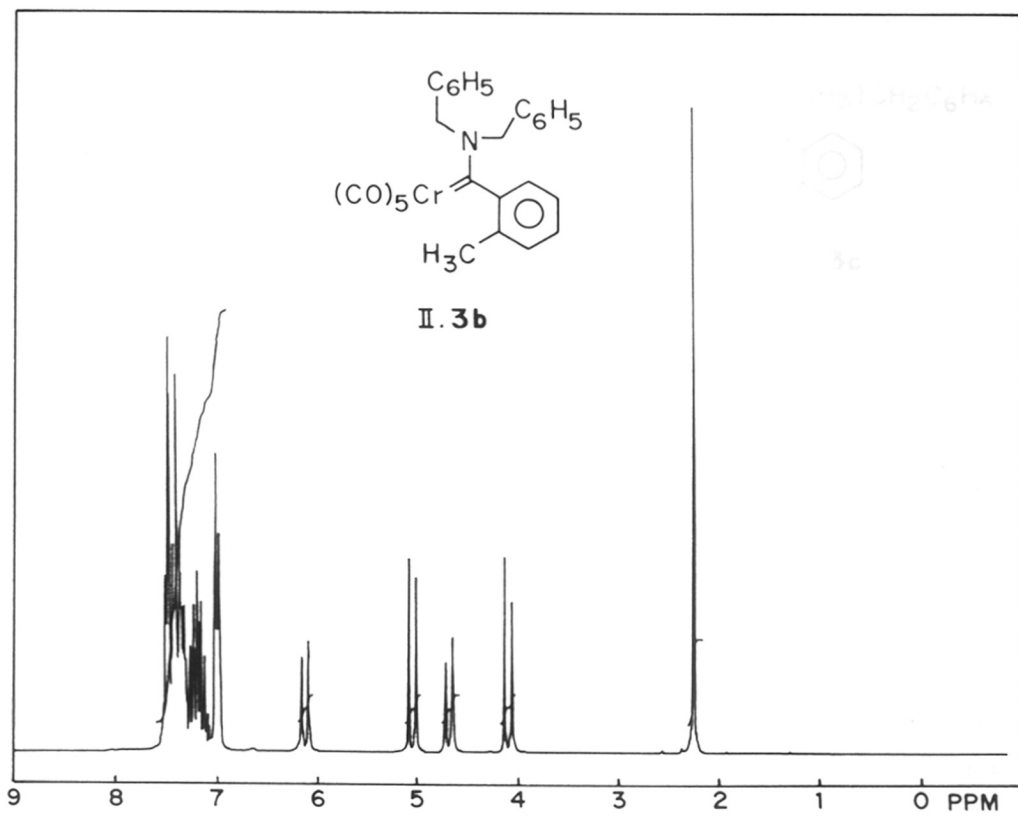


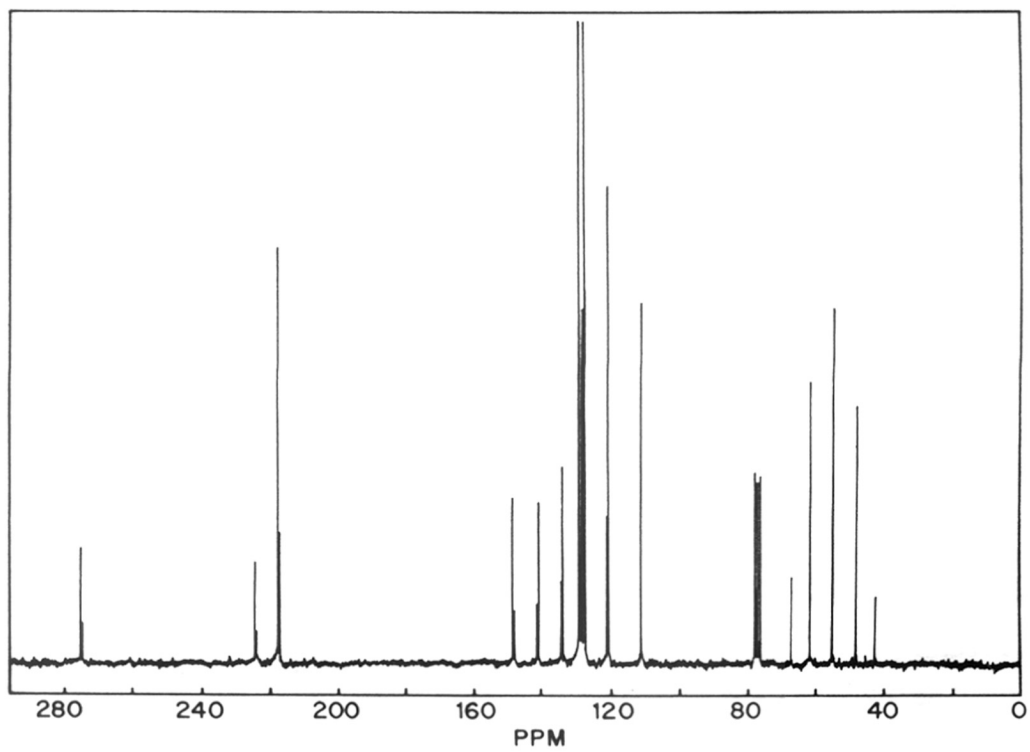
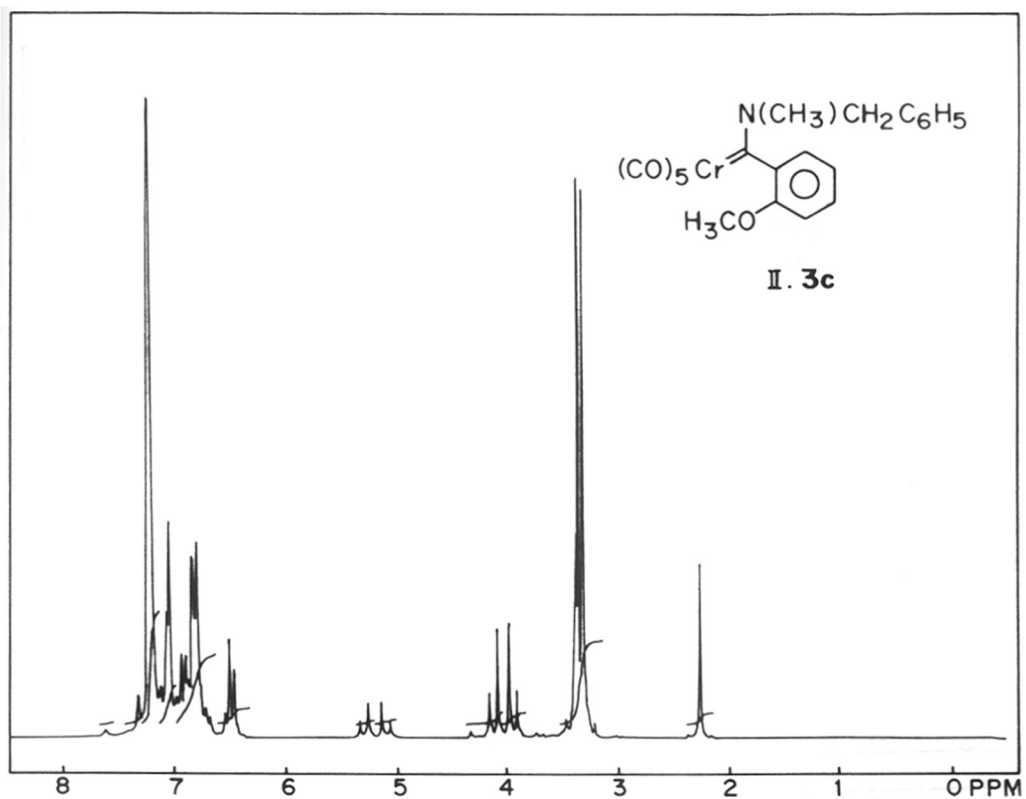


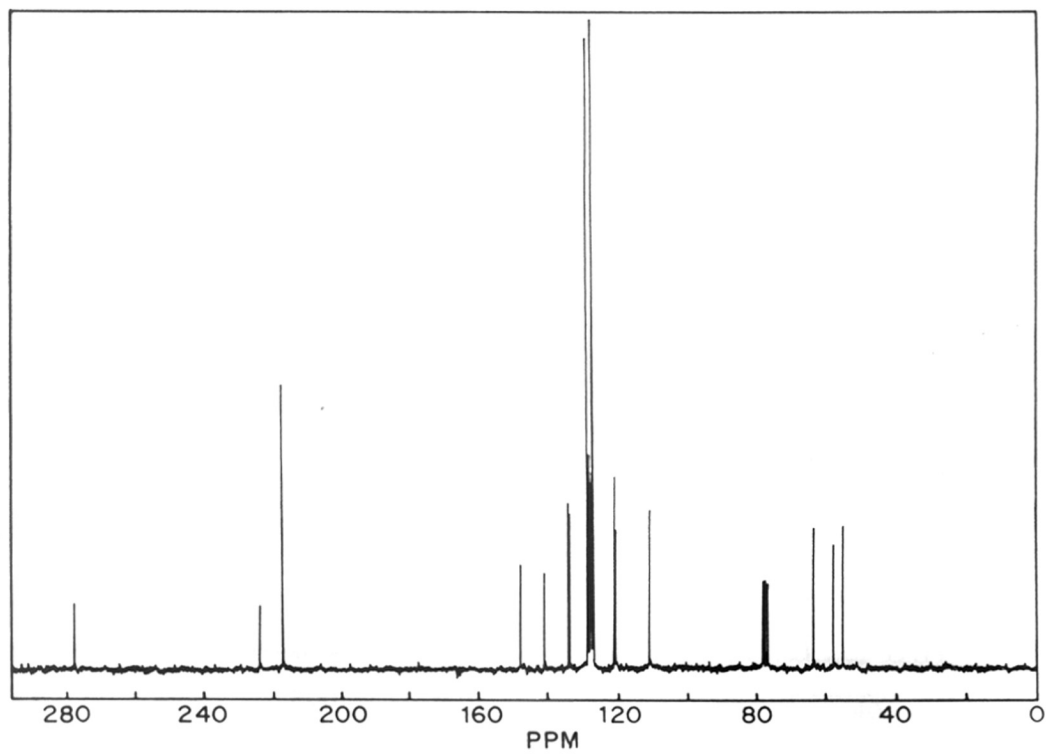
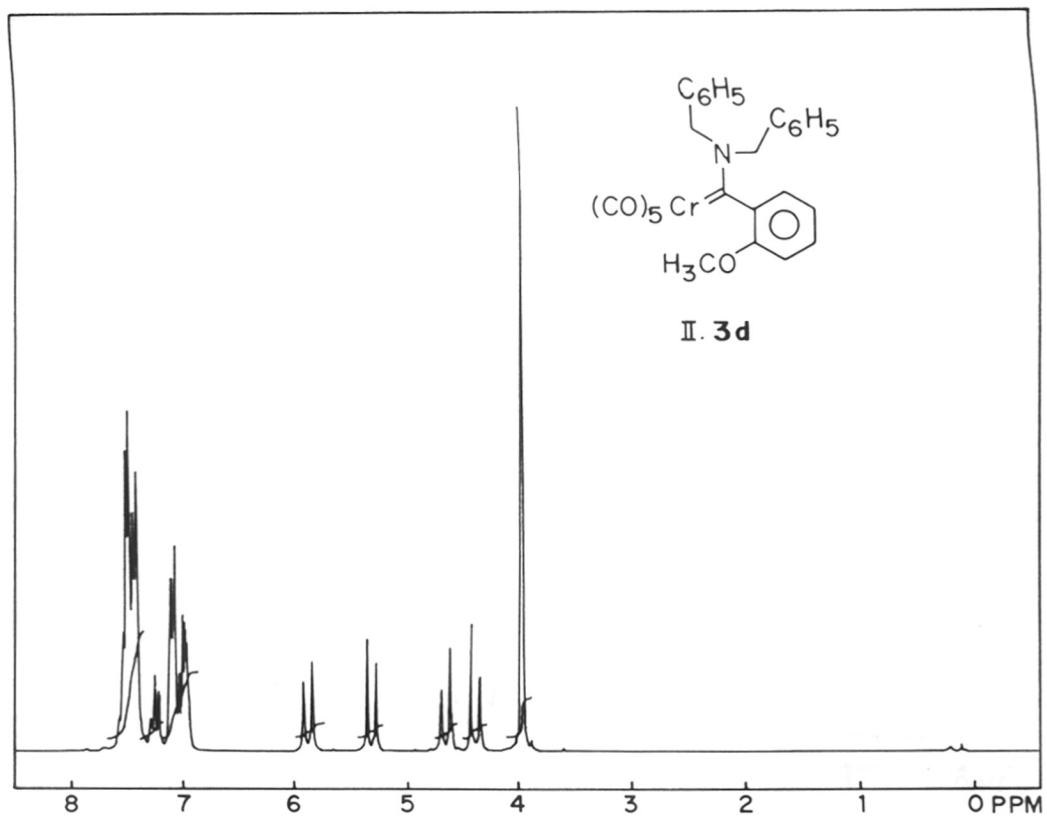


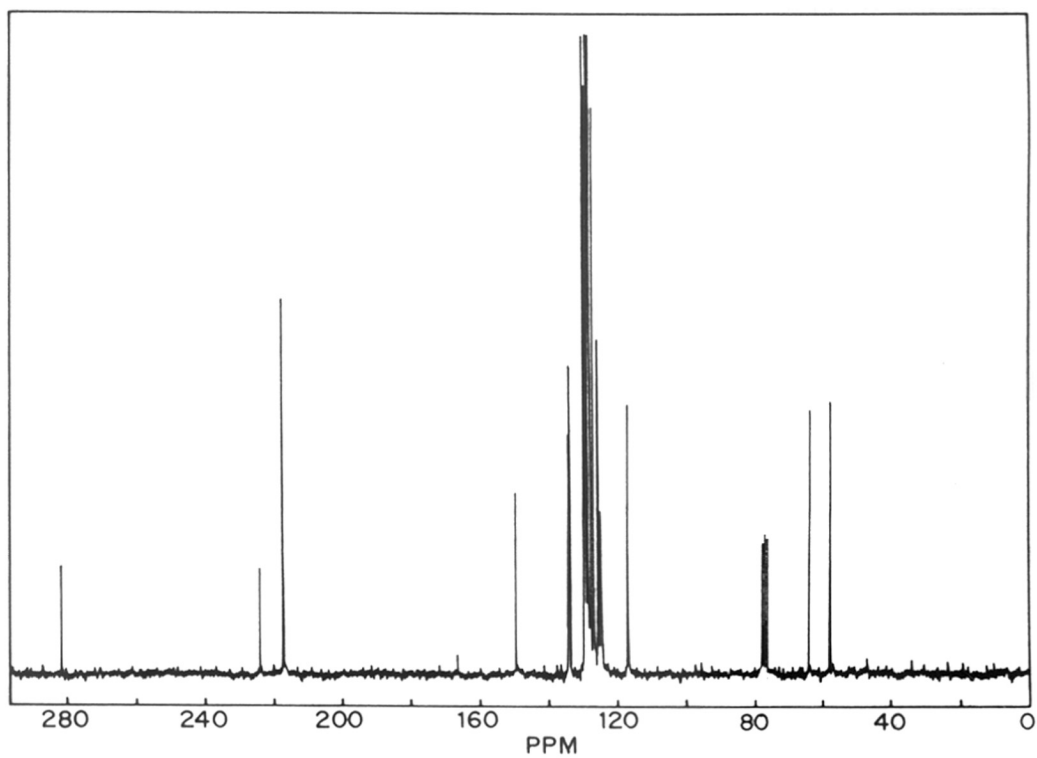
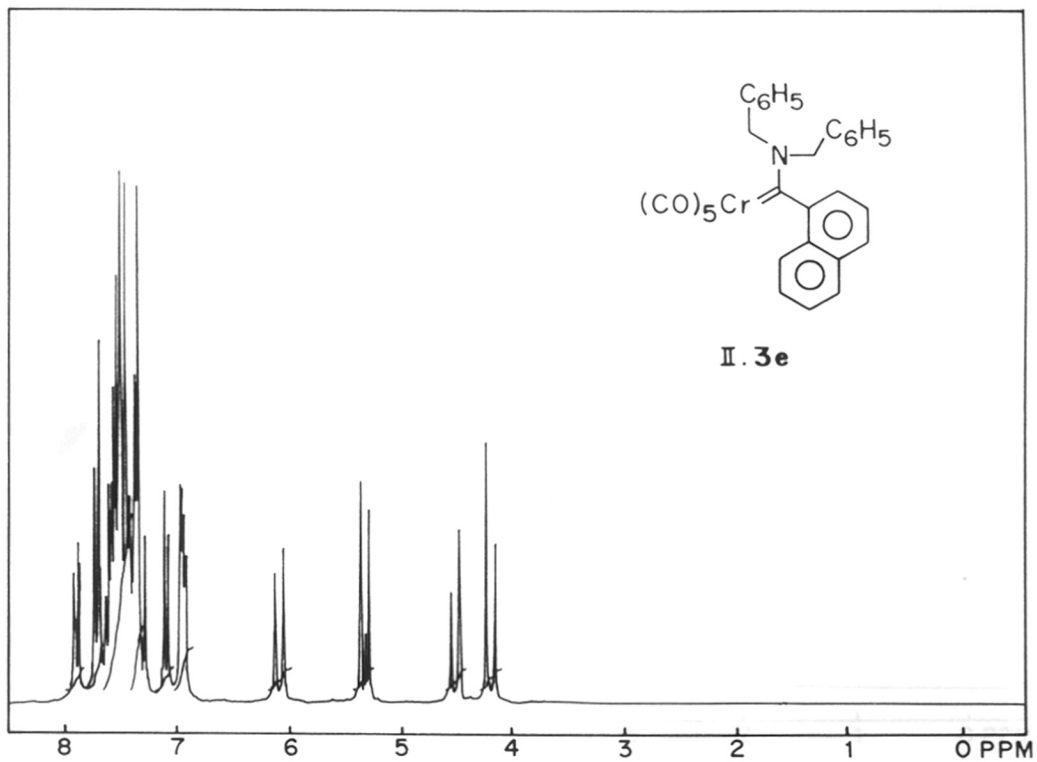


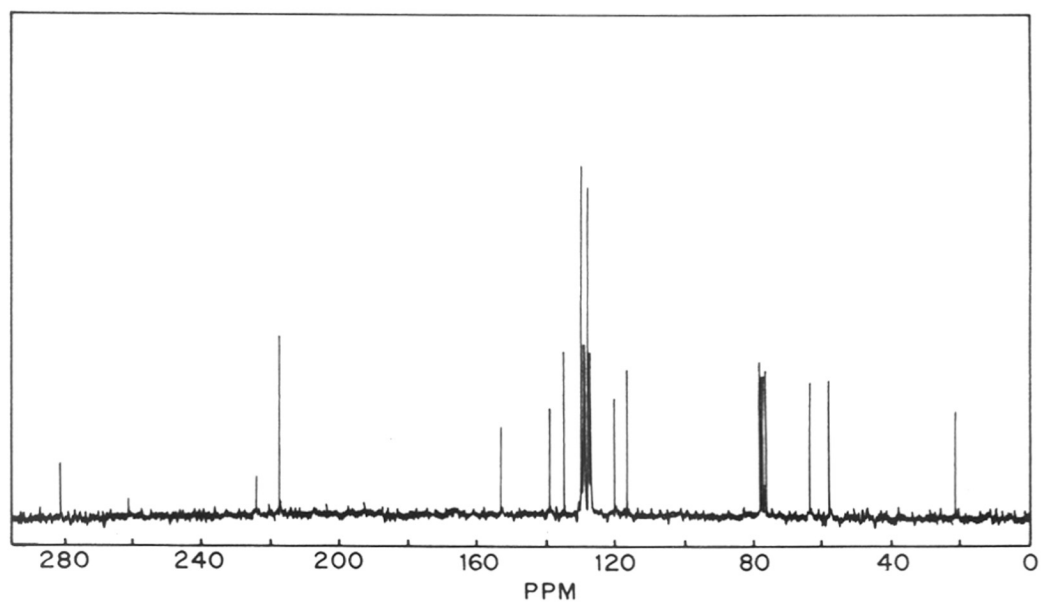
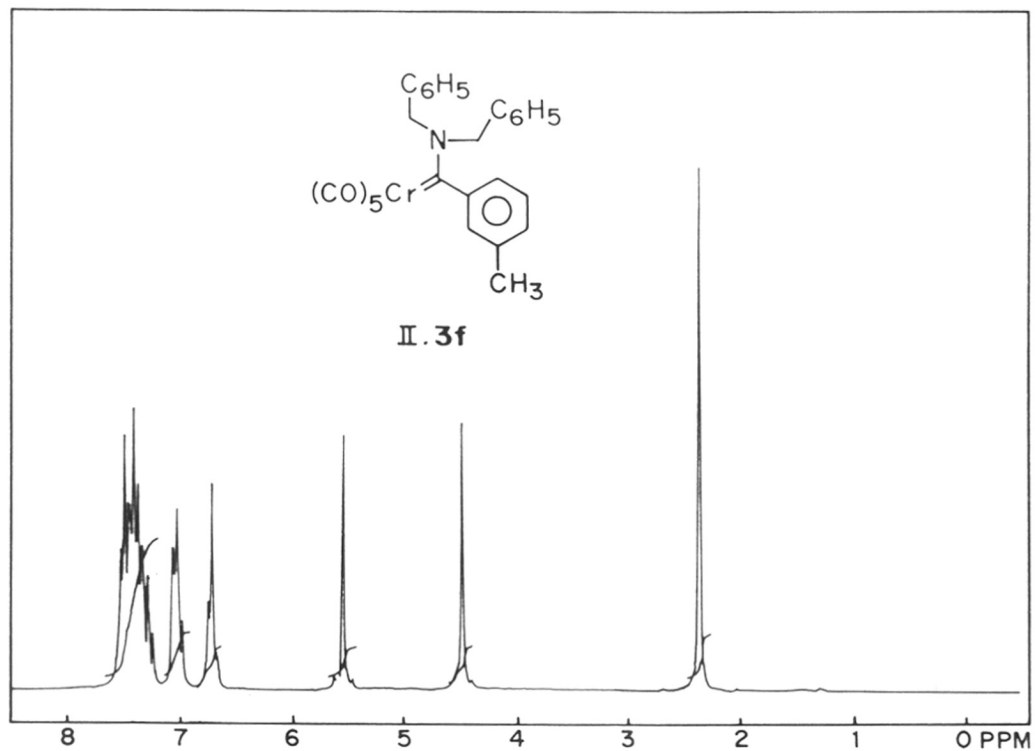




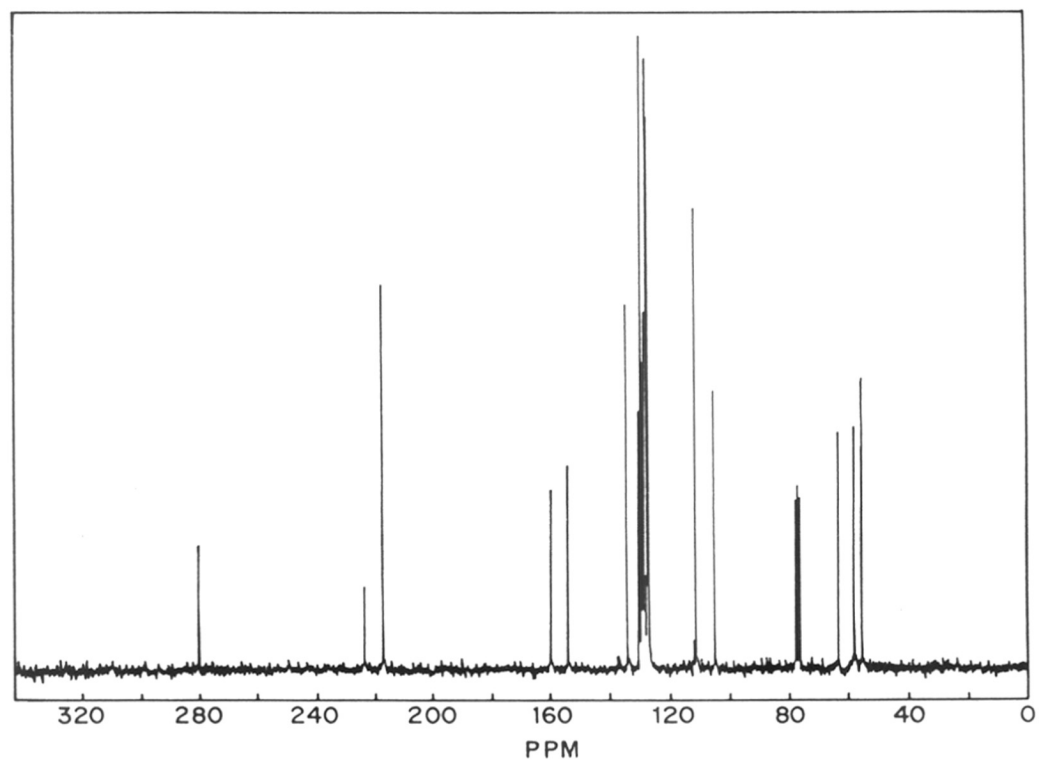
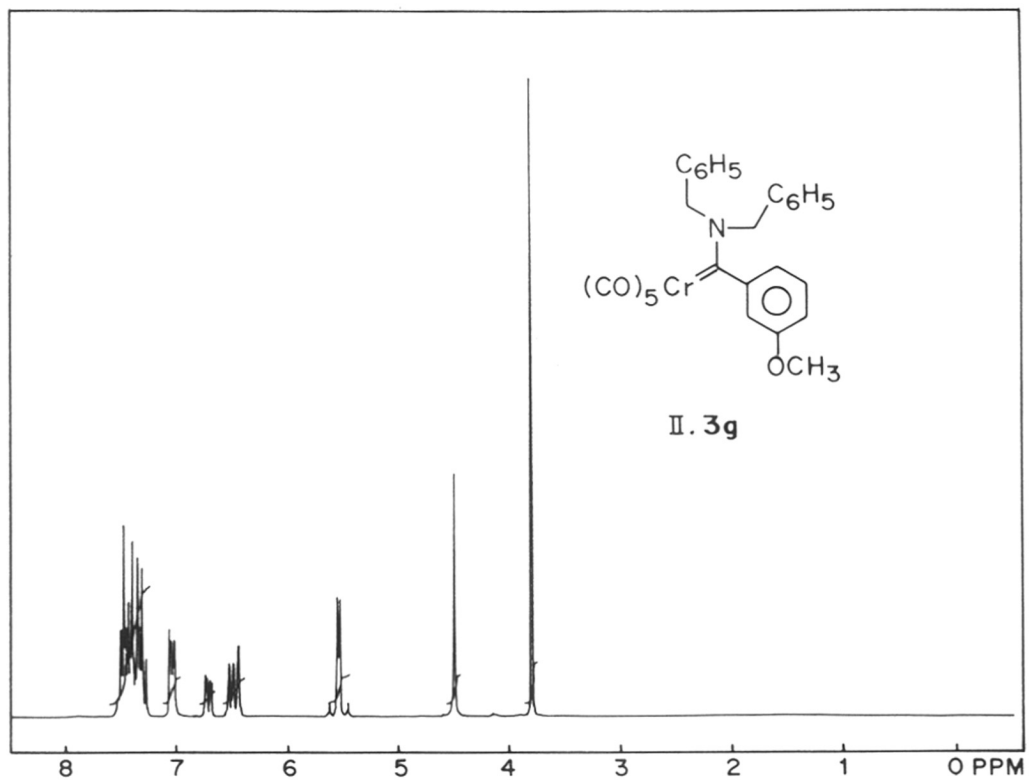


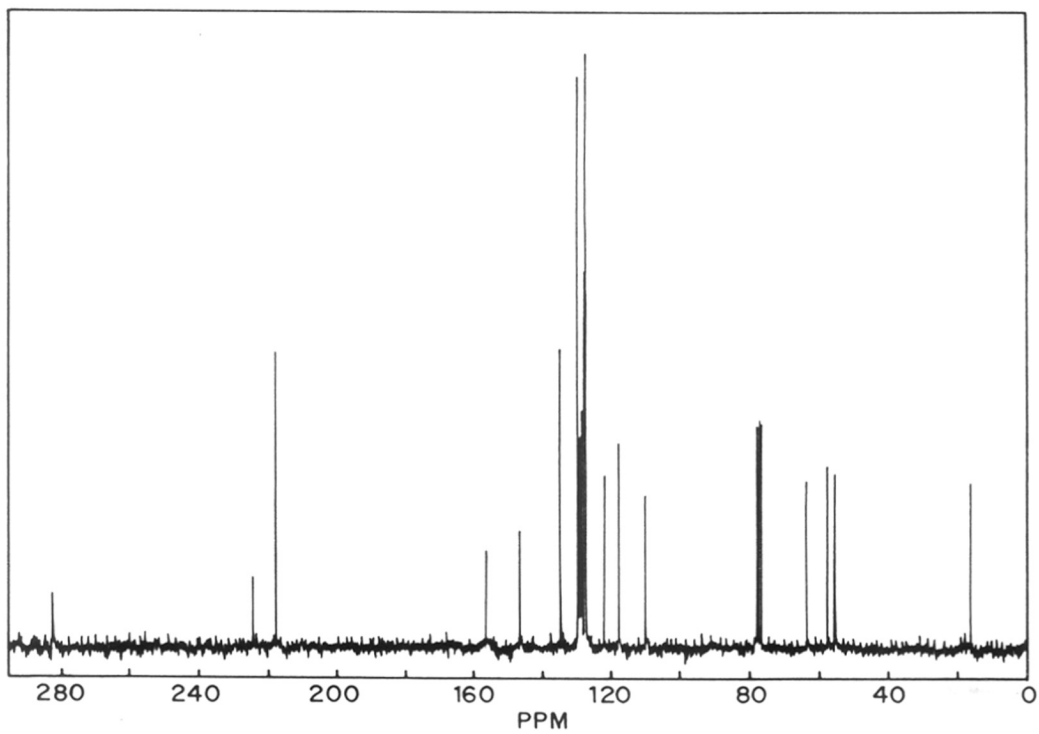
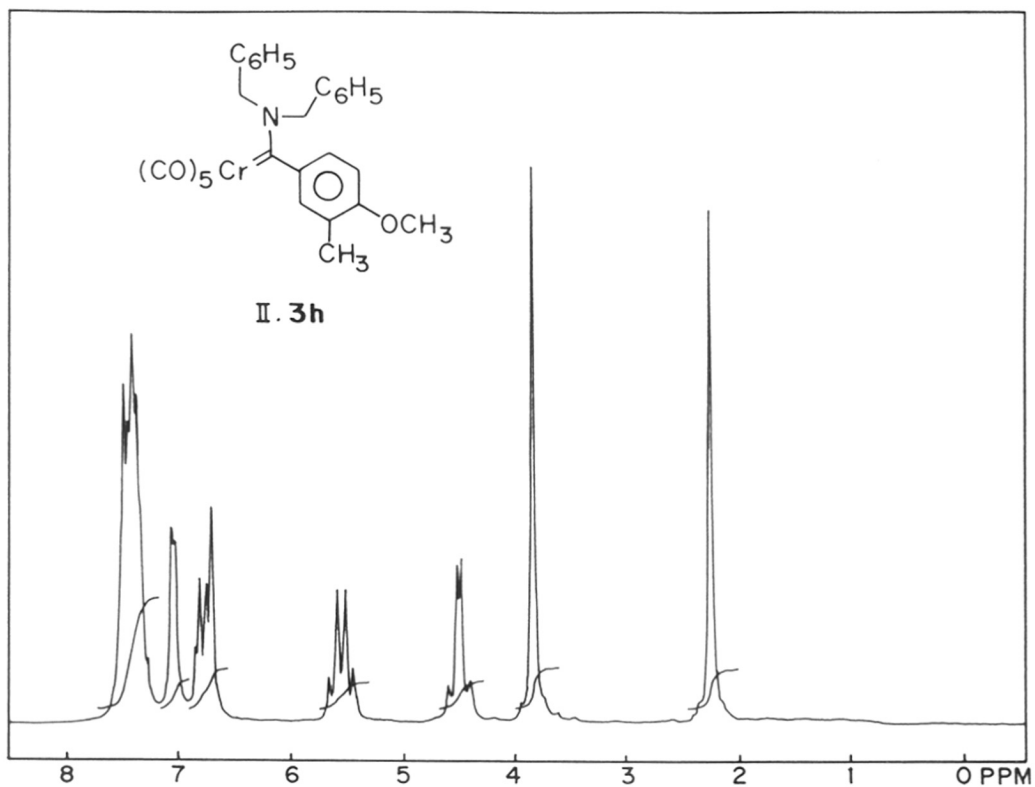


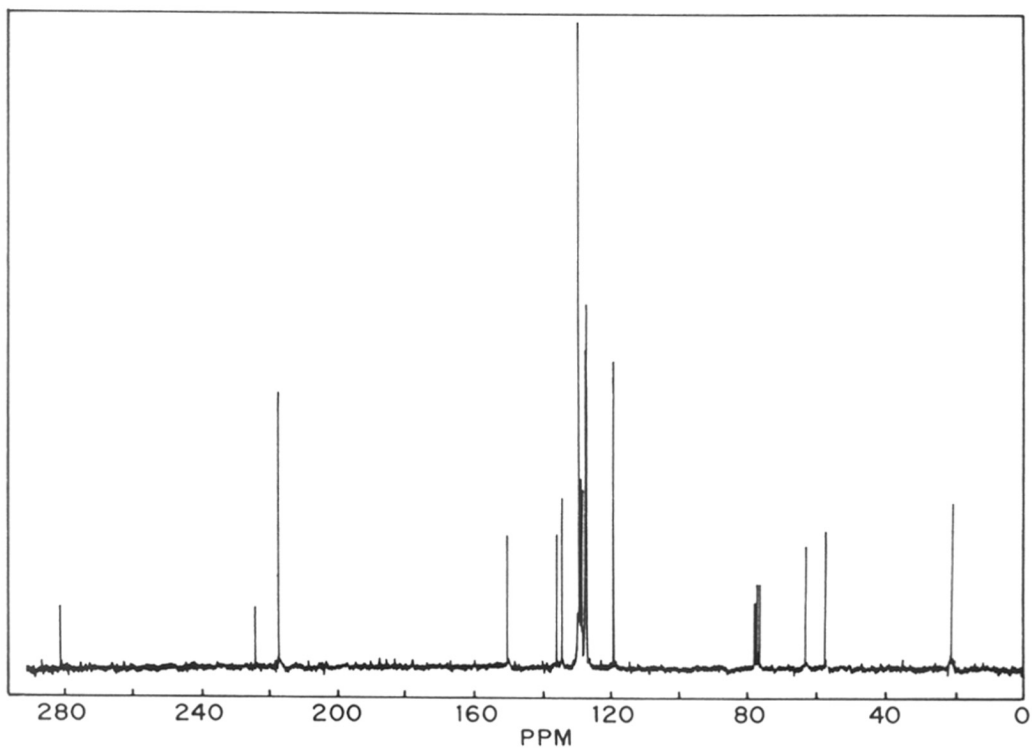
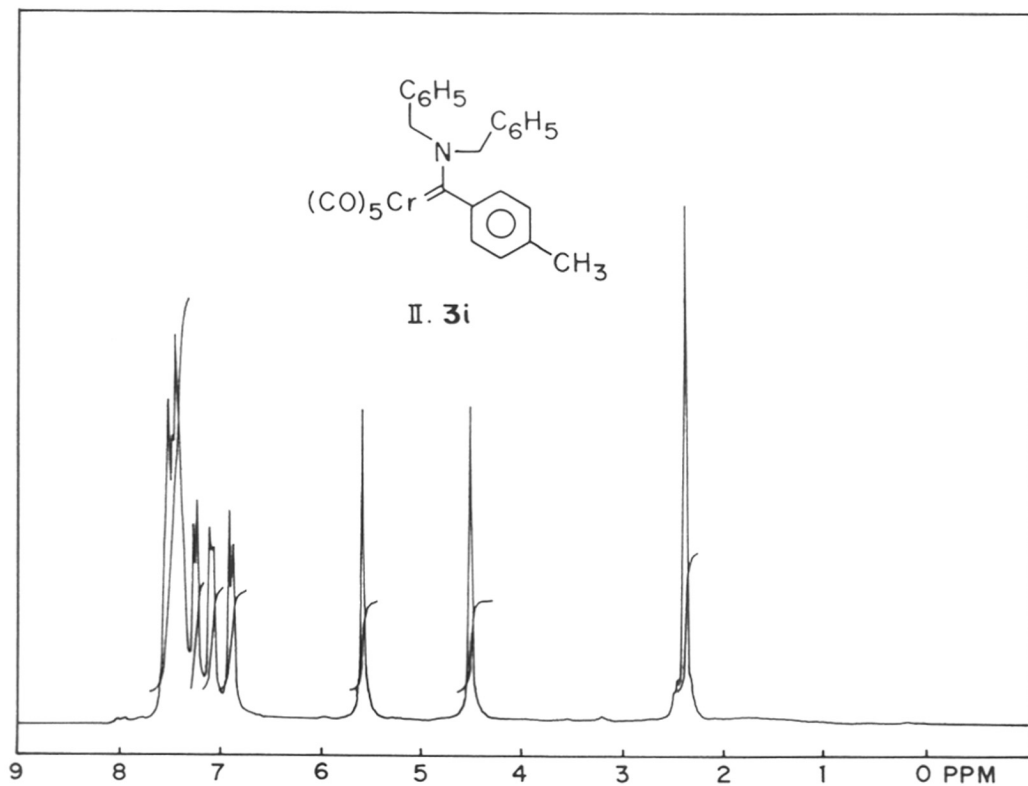


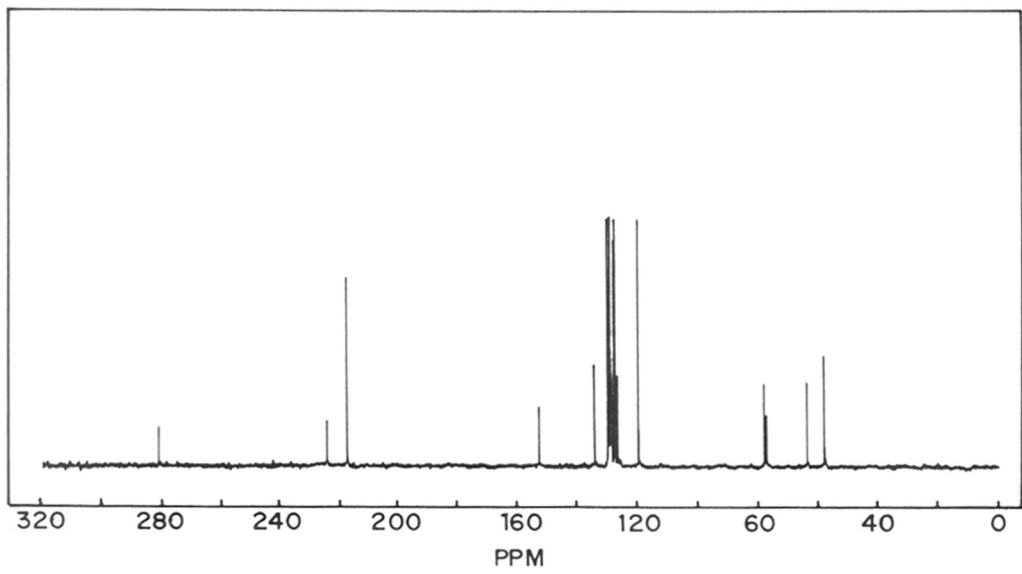
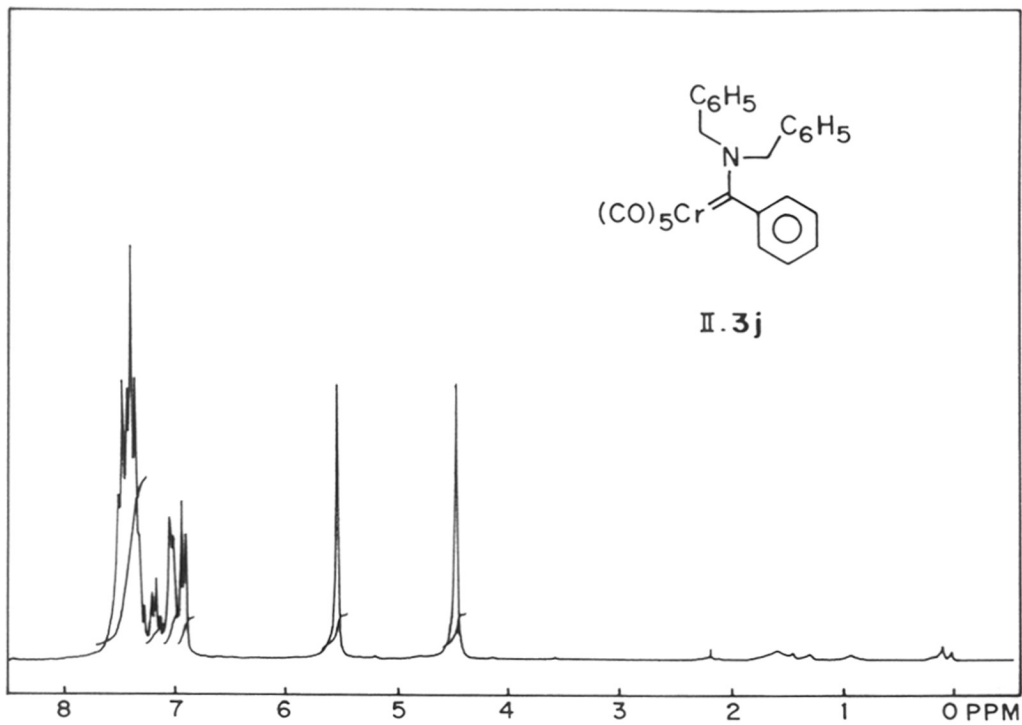


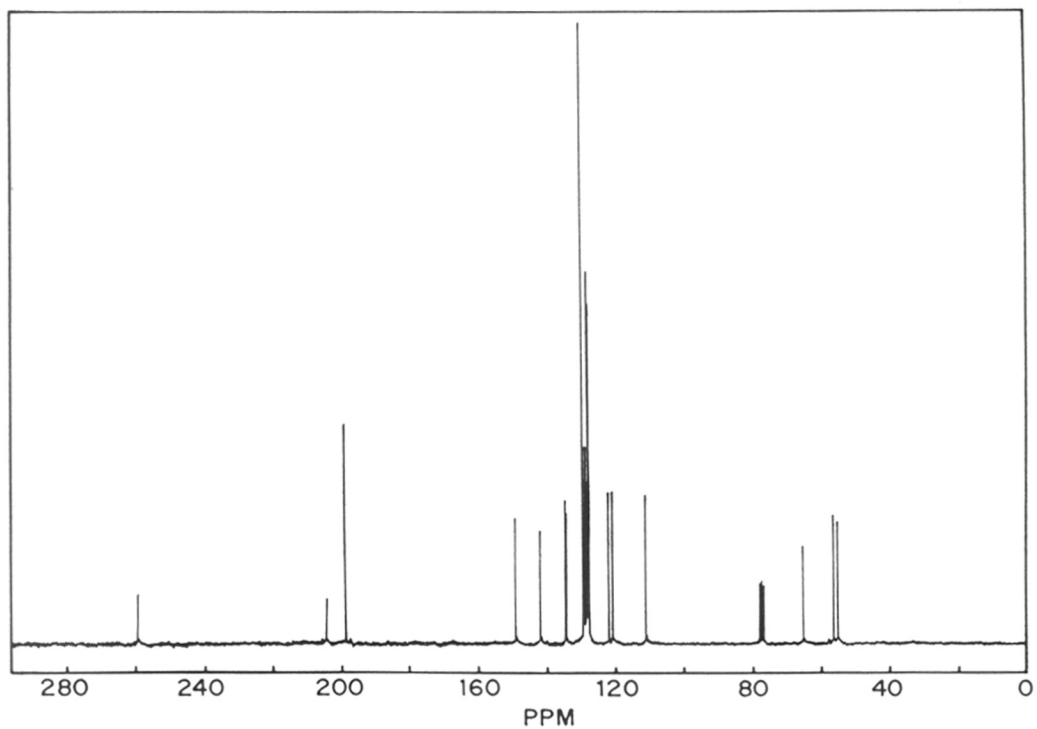
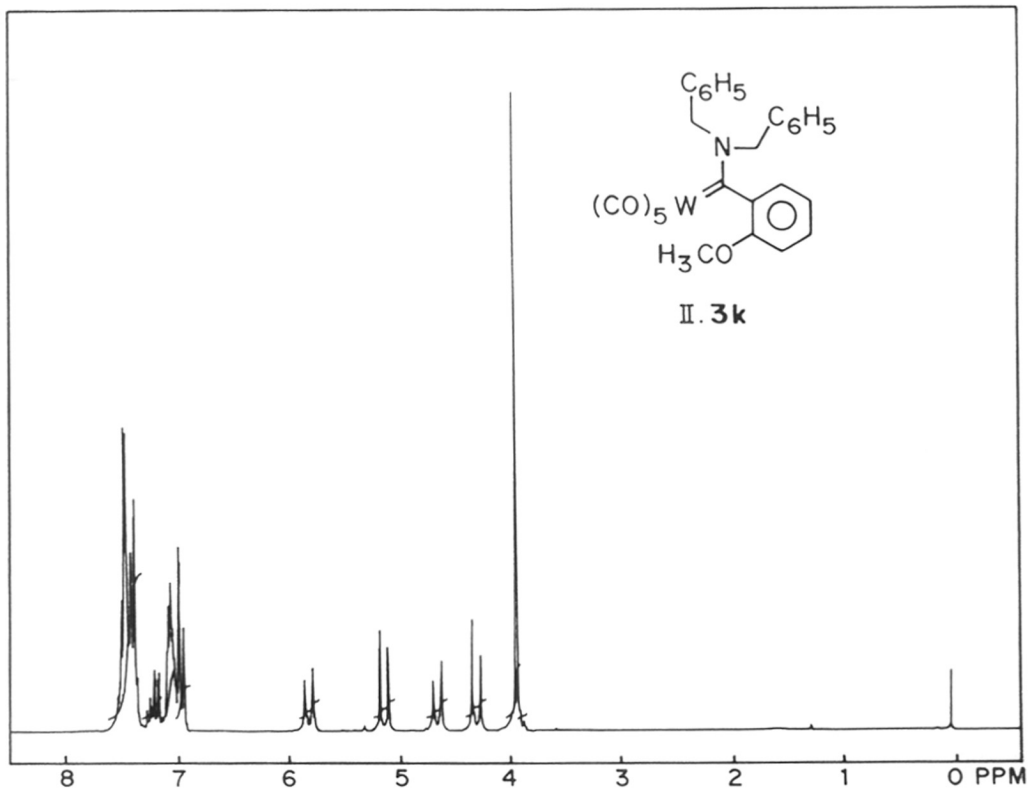


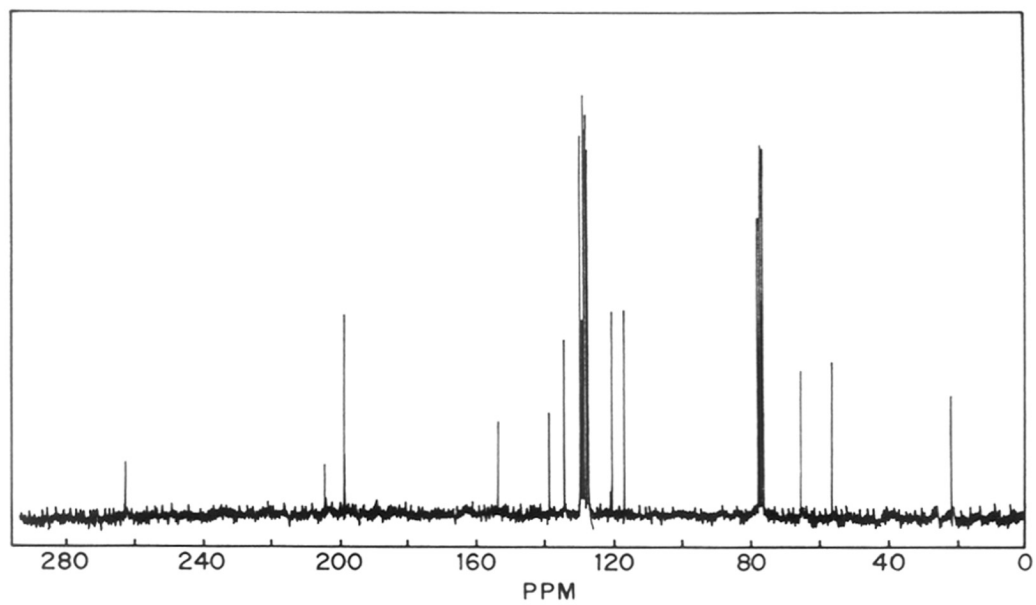
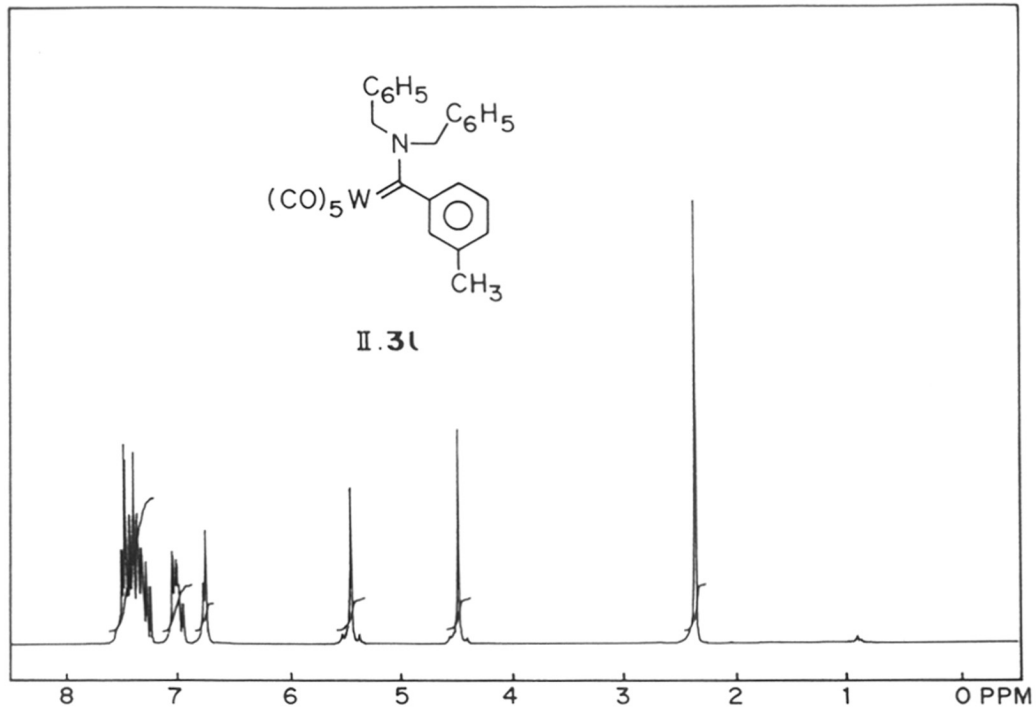












## Chapter - III

### A Novel Alkylation-Annulation Sequence of Amino Carbene Complexes

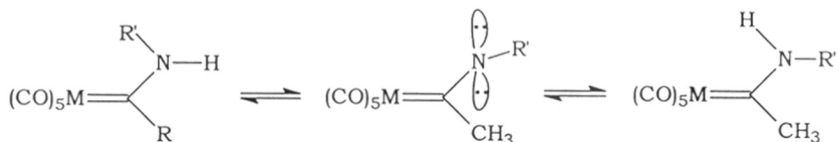
### III.1 INTRODUCTION

In spite of extensive studies on Fischer carbene complexes carried out for several decades, new reaction modes or pathways continue to be discovered, apparently as consequence of minor structural or experimental variations. In this chapter, one such unprecedented reaction is described.

### III.2 BACKGROUND

During alkylation of monoalkylamino carbene complexes as described in the Chapter-I, it was observed that the *E/Z* ratio of conformers were different before and after alkylation. In  $(\text{CO})_5\text{M}=\text{C}(\text{R})(\text{NHR}^1)$ , Fischer showed<sup>1</sup> that *E/Z* interconversion could be readily effected by addition of a base (Scheme-III.1).

**Scheme III.1**



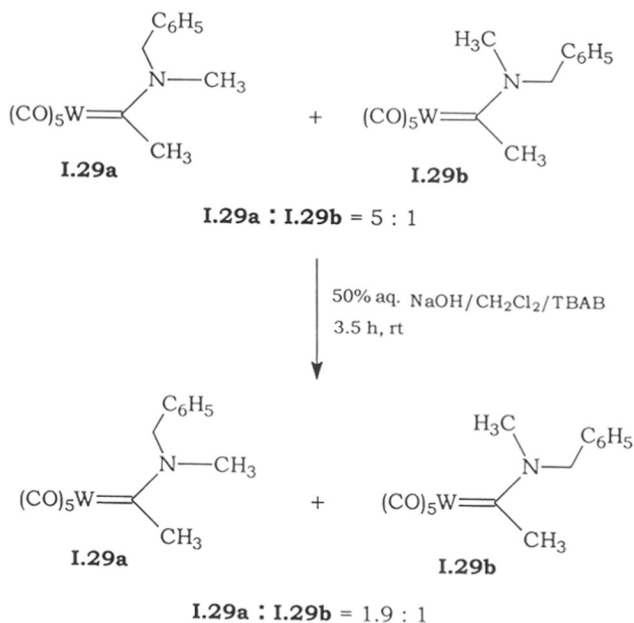
Understandably, on deprotonation by base, there would be two lone pair of electrons on nitrogen and conformer equilibration is possible. Fischer showed<sup>1</sup> that the position of equilibrium depended on the base used. It was of interest, therefore, to study the base-induced interconversion for monoalkylamino carbene complexes, and monitor the effect of electrophile (used for alkylation of monoalkylamino complexes) on this equilibria.



### III.3 PRESENT WORK

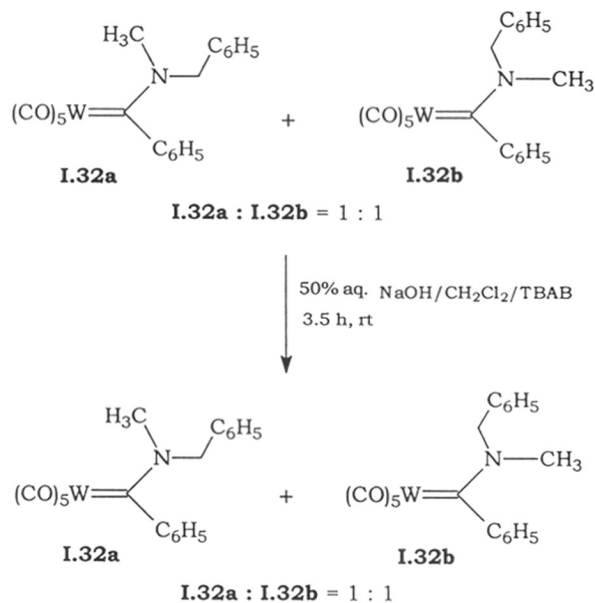
The rotation barrier of carbene-hetero atom bond in dialkylamino carbene complexes is due to the delocalization of the lone pair of electrons from nitrogen to the metal. Such delocalization is also facilitated by strong  $\pi$ -acceptor ligands like CO surrounding the metal. A competing electron delocalization towards the metal is possible by generation of a carbanion adjacent to the carbene carbon. This should impede delocalization of lone pair from nitrogen and thus reduce the partial double bond character of the carbene-hetero atom bond. This, in effect, would reduce the rotation barrier around the said bond allowing facile conformational interconversion. Initial experiment with the carbene complex **I.29** corroborated this expectation (Scheme-III.2).

**Scheme III.2**



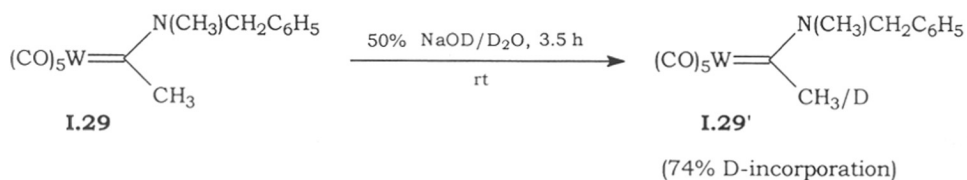
This was further established by the fact that if phenyl instead of methyl is attached to carbene carbon (**I.32**), ratio of two conformers did not change (Scheme III.3).

### Scheme III.3



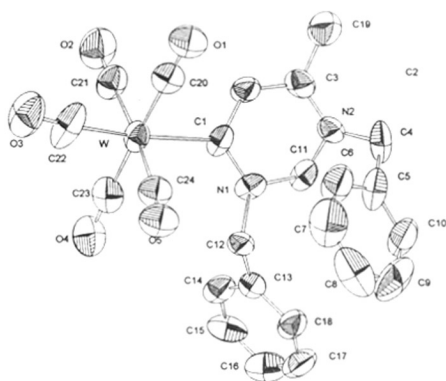
Deuterium exchange experiment (Scheme III.4) established the formation of carbanion which allowed the conformer ratio to be altered. However, this carbanion could not be alkylated because of an unfavorable pK<sub>a</sub> of about 20.<sup>2</sup>

### Scheme III.4



Alkylation studies used dichloromethane as solvent, 50% aq. sodium hydroxide as the base and tetrabutylammonium bromide as the phase-transfer catalyst. When benzylaminomethyltungstencarbene complex **III.1** was stirred in this reaction mixture in the absence of an electrophile, after 4 h a new complex was isolated from the reaction mixture along with the starting material. Though the IR spectrum of the new complex suggested the presence of a  $M(CO)_5$  fragment, a corresponding carbene carbon signal was not present in the  $^{13}C$  NMR spectrum - the most deshielded signal appears at 215.9 only. Normally, amino carbene complexes exhibit a signal due to the carbene carbon at 255-265 (for tungsten carbene complex) and 275-285 (for chromium carbene complex). The olefinic proton signal at 6.60 was not expected, and the simplified spectral pattern did not permit a straightforward assignment of structure. Since the complex could be readily crystallized from dichloromethane-pentane solvent mixture, determination of crystal structure was undertaken. The ORTEP diagram is displayed in Fig. III.1.

**Fig. III.1**

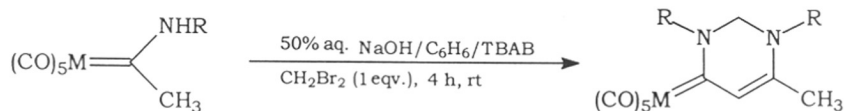


The complex was thus found to be a cyclic compound with two benzylamino groups being appended to a six-membered ring bearing a  $C=W(CO)_5$  linkage. The metal-

carbene bond length is 2.30 Å. The W-CO distances reveal that the *trans* effect is not prominent in this complex (W-CO<sub>trans</sub> 1.96 Å, W-CO<sub>cis</sub> 1.88-2.04 Å). The N-C bond order is higher than single bond (1.34 and 1.35 Å; N-C single bond length in methylamine is 1.47 Å whereas in formamide it is 1.36 Å). The C2-C3 double bond retains its olefinic bond length as seen from the bond length of 1.38 Å (marginally longer than double bond in ethylene, 1.34 Å) in spite of its enamine character, presumably because of lack of planarity (dihedral angle : C1-C2-C3-N2 29.0° ). The ring is staggered with respect to the W(CO)<sub>4</sub> groups (dihedral angles : C20-W-C1-C2 -42.5° , C21-W-C1-C2 50.7° ) and it is considerably puckered. The edge-to-face orientation of the two benzene rings might suggest a CH/π type stabilisation.<sup>3</sup>

It was found that a better yield could be obtained if the reaction was performed in benzene using dibromomethane (1 equivalent) as the electrophile. This reaction was found to be a general one for the convenient preparation of analogous products **III.7-III.10** as shown in Scheme-III.5.

### Scheme-III.5

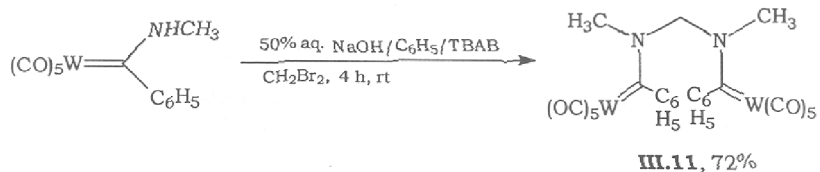


Substrate	M	R	Product	Yield (%)	<sup>13</sup> C (C <sub>car</sub> ), δ (ppm)
<b>III.1</b>	W	CH <sub>2</sub> Ph	<b>III.6</b>	73	215.9
<b>III.2</b>	W	CH <sub>2</sub> CH=CH <sub>2</sub>	<b>III.7</b>	71	215.6
<b>III.3</b>	W	CH <sub>3</sub>	<b>III.8</b>	80	217.3
<b>III.4</b>	Cr	CH <sub>2</sub> Ph	<b>III.9</b>	76	232.3
<b>III.5</b>	Cr	CH <sub>3</sub>	<b>III.10</b>	87	233

Characteristic peaks of complexes **III.6-III.10** in  $^1\text{H}$  NMR spectra were: i) a singlet at 6.18-6.41 due to olefinic proton of the ring; ii) a singlet at 2.00-2.17 for the  $\gamma$ -methyl group, and, iii) a singlet at 4.04-4.30 for the methylene protons flanked between two nitrogen atoms. In  $^{13}\text{C}$  NMR spectra, the carbene carbon appears at 215.6-217.4 for the tungsten complex and at 232.3-233.0 for the chromium complex. The signals at 118.4-122.5 and 141.5-145.4 appear due to the olefinic methylene and methine carbon of the ring respectively, N-CH<sub>2</sub>-N carbon peak appears at 63.7-66.5 and the signal due to  $\gamma$ -methyl carbon appears at 17.2-17.7.

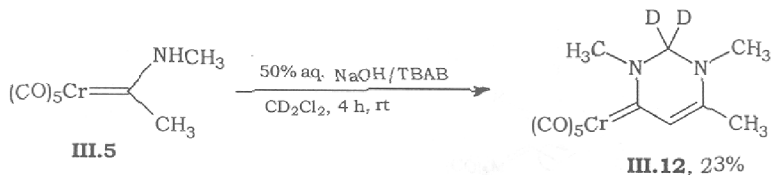
The product resulted from the union of two carbene fragments *via* the methylene group of dichloromethane or dibromomethane. This was supported by two experiments: (a) a *bis*-carbene complex **III.11** was prepared from methylaminophenyltungstencarbene complex, isolated and fully characterized (Scheme-III.11):

#### Scheme-III.11



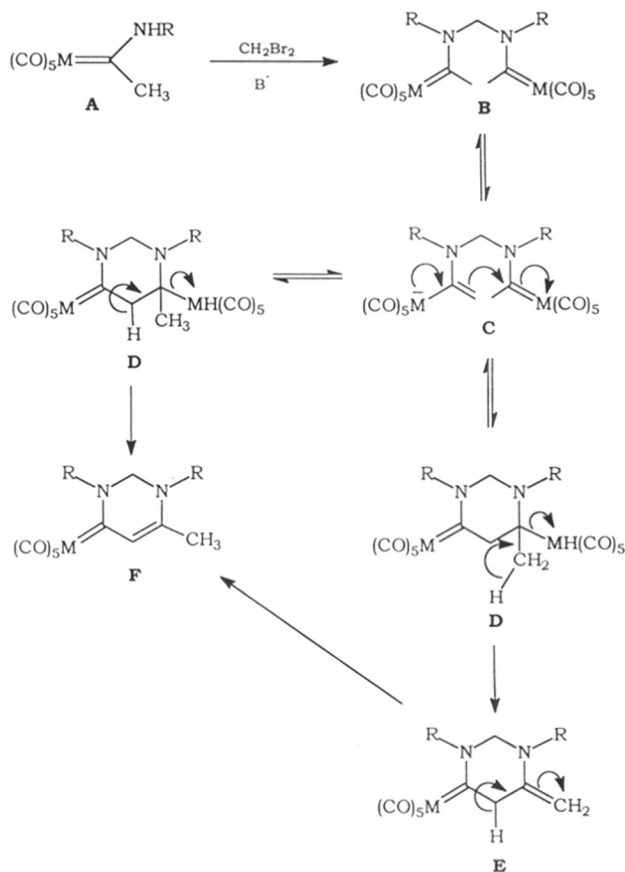
(b) no methylene signal was observed when CD<sub>2</sub>Cl<sub>2</sub> was used instead of normal dichloromethane (Scheme-III.12).

#### Scheme-III.12



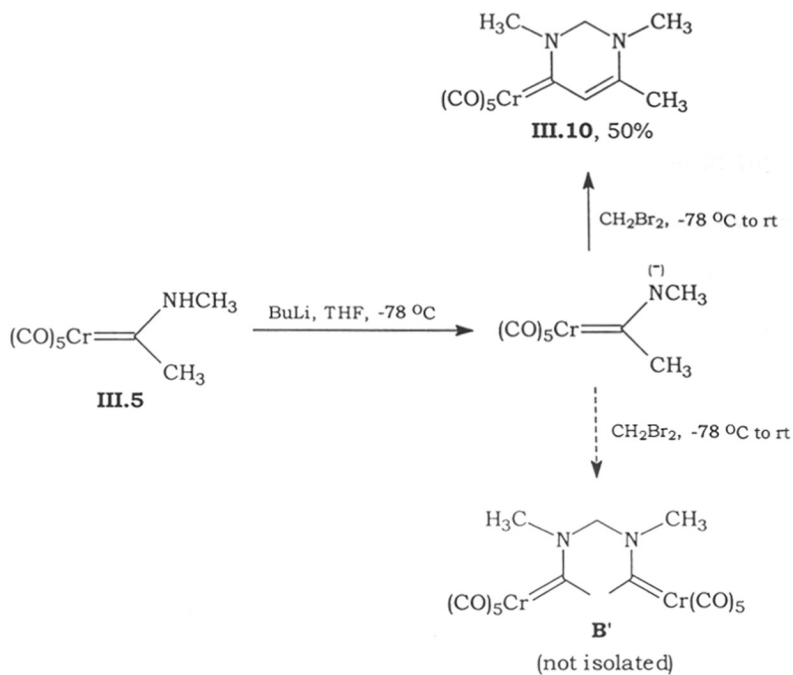
A possible mechanism for the transformation is outlined in Scheme-III.13. First, N-alkylation of monoaminocarbene complex **A** with dichloromethane or dibromomethane provides a *bis*-carbene intermediate **B**. This symmetrical intermediate, on deprotonation, provides a carbanion which intramolecularly reacts with the other metal-carbene bond to close the six-membered ring as in **D**. It is intriguing how this metal fragment is expelled to form the product. Normally, one would expect a ring-opening by cleavage of carbene-nitrogen bond as in amides. Casey's preparation of *gem*-diphenyltungstencarbene complex is a pertinent example.<sup>3</sup> For the present, two pathways based on  $\beta$ -elimination have been envisaged for conversion of intermediate **D** to the final product **F**.

**Scheme-III.13**



To isolate the *bis*-carbene intermediate **B**, methylaminomethylchromiumcarbene complex (**III.5**) was treated with 1 equivalent *n*-butyl lithium at -78 °C in tetrahydrofuran followed by 0.5 equivalent of dibromomethane (Scheme III. 14). Instead of the expected product **B'**, the cyclic compound **III.10** was obtained in 50% isolated yield (based on recovered starting material, 43%).

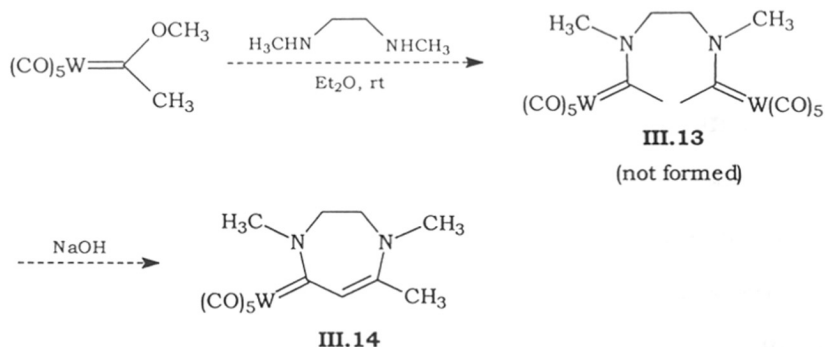
**Scheme III. 14**



Potassium carbonate with 18-Crown-6 was also used as a base to obtain **B'**, but the starting material was recovered almost quantitatively after 4 h.

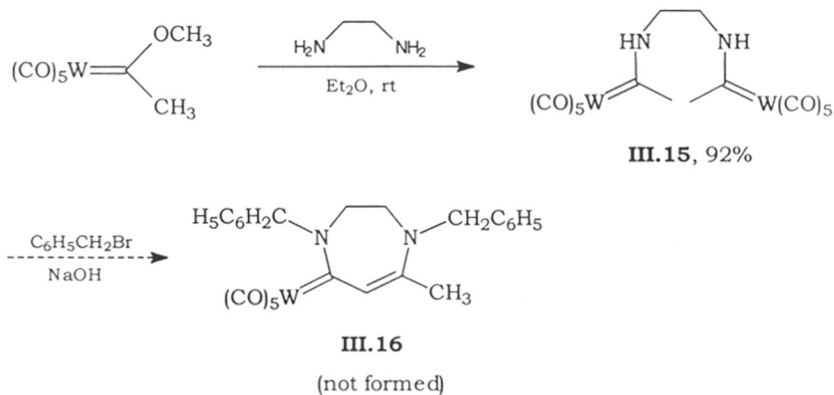
To generate a higher homologue of the cyclic product, efforts were made to produce the *bis*-carbene complex **III.13** (Scheme III.15) which could later be cyclized to the corresponding cyclic product **III.14**. To achieve this, methoxymethyltungstencarbene complex was treated with *N,N'*-dimethylethylenediamine in ether but the expected product **III.13** did not form.

## Scheme III.15



Next we strived to make the *bis*-carbene complex **III.15** (Scheme III.16) which can also be cyclized after N-alkylation. Complex **III.15** was prepared by treating two equivalent of methoxymethyltungstencarbene complex with one equivalent of ethylenediamine in ether at room temperature and characterized. However, attempted cyclization in the presence of benzyl bromide gave a complex mixture of products in which the expected product **III.16** could not be traced. Also, attempted N-alkylation of **III.15** in presence of n-butyl lithium and electrophile (2 eq. base and 2 equiv. electrophile, or, sequential addition of 1 eq. base, 1 eq. electrophile, 1 eq. base, 1 eq. electrophile) led to the formation of a complex, uncharacterized mixture of products.

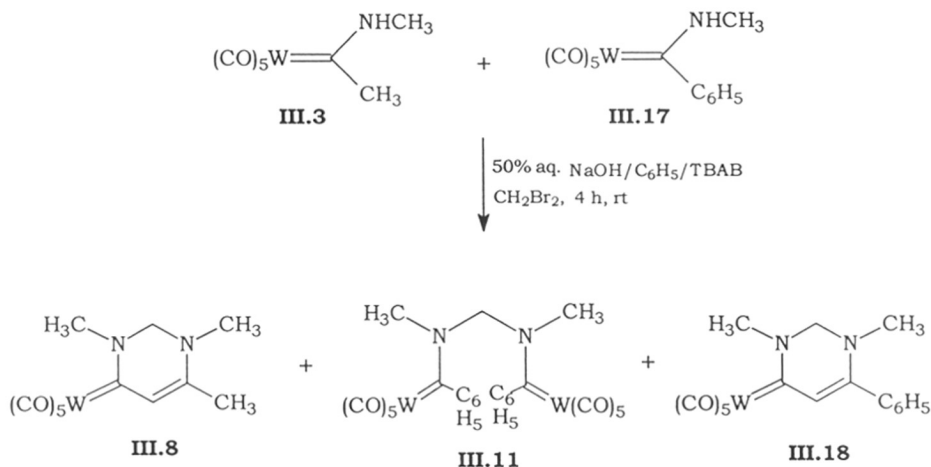
## Scheme III.16





It was of interest to examine whether a *bis*-carbene generated from a alkyl- and an arylaminocarbene complex would cyclise to provide a  $\beta$ -phenyl derivative. To verify this possibility, a mixture of 1 equivalent each of methylaminomethyltungstencarbene complex **III.3** and methylaminophenyltungstencarbene complex **III.17** was treated with dibromomethane in presence of a base (Scheme III.17). The product mixture was found to contain three compounds which were identified by their proton NMR spectral data. Two were identified as compounds **III.8** and **III.11** (described previously) and the third one had the spectral features expected of cyclic compound **III.18** derived from the mixed *bis*-carbene. Two N-methyl groups appear as two singlets at 2.91 and 3.73 whereas the methylene protons between two nitrogen atoms appear at 4.54 as a singlet. The olefinic proton comes as a singlet at 6.85. This last product could not be separated from **III.8** and **III.11** despite repeated efforts.

**Scheme III.17**



Though the desired product was not isolated in pure form, the experiment established that cyclization did not depend on the kind of group attached to the carbene carbon, alkyl or aryl.

### III.4 SUMMARY

While studying base-induced E/Z interconversion in amino carbene complexes, an unusual cyclisation reaction of Fischer carbene complexes was discovered. The carbanion generated at the carbon adjacent to the carbene fragment underwent a formal aldol-type cyclization on a second metal-carbene bond. Intermolecular version of this reaction has not been successful.

### III.5 EXPERIMENTAL SECTION

Dibromomethane, ethylenediamine, N,N'-dimethylethylenediamine were purchased from Aldrich Chemicals, USA. The X-ray structure of the complex **III.6** was solved by Dr.(Mrs.) V. G. Puranik at NCL, Pune. Relevant tables are appended at the end of this section.

#### General Procedure for the Cyclization Reaction

The carbene complex (n mmol) and tetrabutylammonium bromide (TBAB) (0.1n mmol) in benzene (10n ml) was treated with dibromomethane (n mmol) and 50% aq. NaOH. The reaction mixture was stirred for 4 h at room temperature under an inert atmosphere of argon. The mixture was diluted with water, extracted with dichloromethane, dried, and concentrated under reduced pressure. The pure product was isolated by flash chromatography using dichloromethane (5-50%) in petroleum ether as an eluant.

**Preparation of complex III.6:** The reaction of the complex **III.1** (685 mg, 1.5 mmol), TBAB (48 mg, 0.15 mmol), 50% aq. NaOH, dibromomethane (0.1 ml, 1.5 mmol) in benzene (15 ml) yielded the product **III.6** (328 mg, 73%) as a yellow solid.

m.p. : 120 °C

IR : 2050 (m), 1960 (sh), 1910 (s)

<sup>1</sup>H PMR : 2.07 (s, 3H), 4.04 (s, 4H), 4.92 (s, 2H), 6.41 (s, 1H), 6.80-6.94 (m, 2H), 7.06-7.22 (m, 2H), 7.22-7.45 (m, 6H)

$^{13}\text{C}$  NMR : 17.71, 52.99, 62.20, 64.37, 122.46, 127.13, 128.21, 128.51,  
129.21, 129.31, 135.64, 135.86, 144.33, 199.66, 203.78, 215.92

Analysis : Calcd. : C = 48.00, H = 3.33, N = 4.66  
Found : C = 48.62, H = 3.58, N = 4.71

**Preparation of complex III.7:** The reaction of the complex **III.2** (610 mg, 1.5 mmol), TBAB (48 mg, 0.15 mmol), 50% aq. NaOH, dibromomethane (0.1 ml, 1.5 mmol) in benzene (15 ml) yielded the product **III.7** (266 mg, 71%) as a yellow solid.

m.p. : 51 °C

IR : 2005 (sh), 1975 (s)

$^1\text{H}$  PMR : 2.08 (s, 3H), 3.83-3.92 (m, 2H), 4.24 (s, 2H), 4.52-4.4.65 (m, 2H),  
5.03-5.45 (m, 4H), 5.67-5.99 (m, 2H), 6.41 (s, 1H)

$^{13}\text{C}$  NMR : 17.18, 52.06, 62.15, 63.67, 118.32, 119.61, 121.45, 132.25,  
132.89, 145.01, 199.63, 203.96, 215.65

Analysis : Calcd. : C = 38.40, H = 3.20, N = 5.60  
Found : C = 38.21, H = 2.78, N = 5.66

**Preparation of complex III.8:** The reaction of the complex **III.3** (571 mg, 1.5 mmol), TBAB (48 mg, 0.15 mmol), 50% aq. NaOH, dibromomethane (0.1 ml, 1.5 mmol) in benzene (15 ml) yielded the product **III.8** (269 mg, 80%) as a yellow solid.

m.p. : 177 °C

IR : 2055 (m), 1965 (sh), 1915 (s)

$^1\text{H}$  PMR : 2.00 (s, 3H), 3.06 (s, 3H), 3.62 (s, 3H), 4.30 (s, 2H), 6.29 (s, 1H)

$^{13}\text{C}$  NMR : 17.58, 36.81, 49.20, 66.54, 120.69, 145.38, 199.96, 203.96, 217.46

Analysis : Calcd. : C = 32.14, H = 2.67, N = 6.25  
Found : C = 32.64, H = 2.92, N = 6.24

**Preparation of complex III.9:** The reaction of the complex **III.4** (487 mg, 1.5 mmol), TBAB (48 mg, 0.15 mmol), 50% aq. NaOH, dibromomethane (0.1 ml, 1.5 mmol) in benzene (15 ml) yielded the product **III.9** (267 mg, 76%) as a yellow solid.

m.p. : 130 °C

IR : 2050 (m), 1970 (sh), 1910 (s)

$^1\text{H}$  PMR : 2.17 (s, 3H), 4.10 (s, 4H), 4.96 (s, 2H), 6.46 (s, 1H), 6.84-7.05 (m, 2H), 7.12-7.26 (m, 2H), 7.26-7.55 (m, 6H)

$^{13}\text{C}$  NMR : 17.62, 52.80, 62.39, 63.00, 120.44, 127.11, 128.18, 128.49, 129.20, 129.29, 135.82, 136.00, 141.52, 219.07, 224.04, 232.29

Analysis : Calcd. : C = 61.50, H = 4.27, N = 5.98  
Found : C = 60.84, H = 4.32, N = 5.96

**Preparation of complex III.10:** The reaction of the complex **III.5** (373 mg, 1.5 mmol), TBAB (48 mg, 0.15 mmol), 50% aq. NaOH, dibromomethane (0.1 ml, 1.5 mmol) in benzene (15 ml) yielded the product **III.10** (206 mg, 87%) as a yellow solid.

m.p. : 180 °C

IR : 2050 (m), 1965 (sh), 1915 (s)

<sup>1</sup>H PMR : 2.00 (s, 3H), 3.06 (s, 3H), 3.67 (s, 3H), 4.30 (s, 2H), 6.18 (s, 1H)

<sup>13</sup>C NMR : 17.33, 36.50, 46.84, 67.23, 118.40, 142.87, 219.18, 224.06, 232.96

Analysis : Calcd. : C = 45.57, H = 3.79, N = 8.86

Found : C = 45.51, H = 3.86, N = 8.85

**Preparation of complex III.11:**

Pentacarbonyl(methylaminophenylmethylidene)tungsten(0) complex (886 mg, 2 mmol), dibromomethane (0.13 ml, 2 mmol) and TBAB (64 mg, 0.2 mmol) were stirred in benzene (20 ml) for 4 h at room temperature under argon. After usual work-up as described in cyclization procedure, the pure product was obtained as a yellow crystalline solid (646 mg, 72%) by flash chromatography using dichloromethane in petroleum ether as an eluant.

m.p. : 210°C

IR	:	2050 (m), 1975 (sh), 1930 (s)
<sup>1</sup> H PMR	:	<i>E:Z</i> = 57:43. <b>E-2c.</b> 3.77 (s, 6H); 6.83 (s, 2H). <b>Z-2c.</b> 3.06 (s, 6H); 4.83 (s, 2H). <b>Combined peaks.</b> 6.67-6.78, 6.86-6.97, 7.18-7.38 and 7.40-7.60 (m, total 20H)
<sup>13</sup> C NMR	:	48.31; 49.00; 69.07; 88.89; 118.14; 118.57; 118.92; 119.44; 119.87; 127.37; 128.98; 129.32; 151.85; 153.20; 197.75; 197.93; 203.15; 204.04; 271.54; 271.96
Analysis	:	Calcd. : C = 36.08, H = 2.00, N = 3.12 Found : C = 36.03, H = 1.95, N = 3.04

**Preparation of complex III.12:** The carbene complex **III.5** (249 mg, 1 mmol) and TBAB (32 mg, 0.1 mmol), was treated with dichloromethane-d (3 ml) and 50% aq. NaOH. The reaction mixture was stirred for 5 h at room temperature under an inert atmosphere of argon. The mixture was diluted with water, extracted with dichloromethane, dried, and concentrated under reduced pressure. The pure product was isolated by flash chromatography using dichloromethane (5-50%) in petroleum ether as an eluant which yielded a yellow solid (68 mg, 43%) after solvent evaporation.

m.p. : 190 °C

IR : 2045 (m), 1965 (sh), 1915 (s)

$^1\text{H}$  PMR : 2.02 (s, 3H), 3.06 (s, 3H), 3.66 (s, 3H), 6.16 (s, 1H)

$^{13}\text{C}$  NMR : 17.35, 31.14, 36.54, 46.91, 118.32, 145.86, 220.49, 225.14,  
228.88

Analysis : Calcd. : C = 45.28, H = 4.40, N = 8.80

Found : C = 45.36, H = 4.39, N = 8.43

**Preparation of complex III.15:** Pentacarbonyl(methoxyethylidene)tungsten(0) (764 mg, 2 mmol) was treated with ethylenediamine (0.07 ml, 1 mmol) in ether at room temperature under argon. solvent was evaporated and the residue was flash chromatographed using dichloromethane in petroleum ether to get the pure product as a yellow solid (699 mg, 92%).

m.p. : 164°C

IR : 2050 (m), 1970 (sh), 1920 (s)

$^1\text{H}$  PMR : *E:Z* = 52:48. **E-2c**. 2.94 (s, 6H); 3.87 (dt, *J* = 5.9 and 12.8 Hz, 4H);  
8.95 (bs, 1H). **Z-2c**. 2.81 (s, 6H); 4.30 (dt, *J* = 5.9 and 12.8 Hz, 2H)

$^{13}\text{C}$  NMR : 38.11; 46.29; 46.83; 55.50; 199.43; 199.91; 207.80; 207.90;  
256.11; 259.15

Analysis : Calcd. : C = 25.26, H = 1.58, N = 3.68

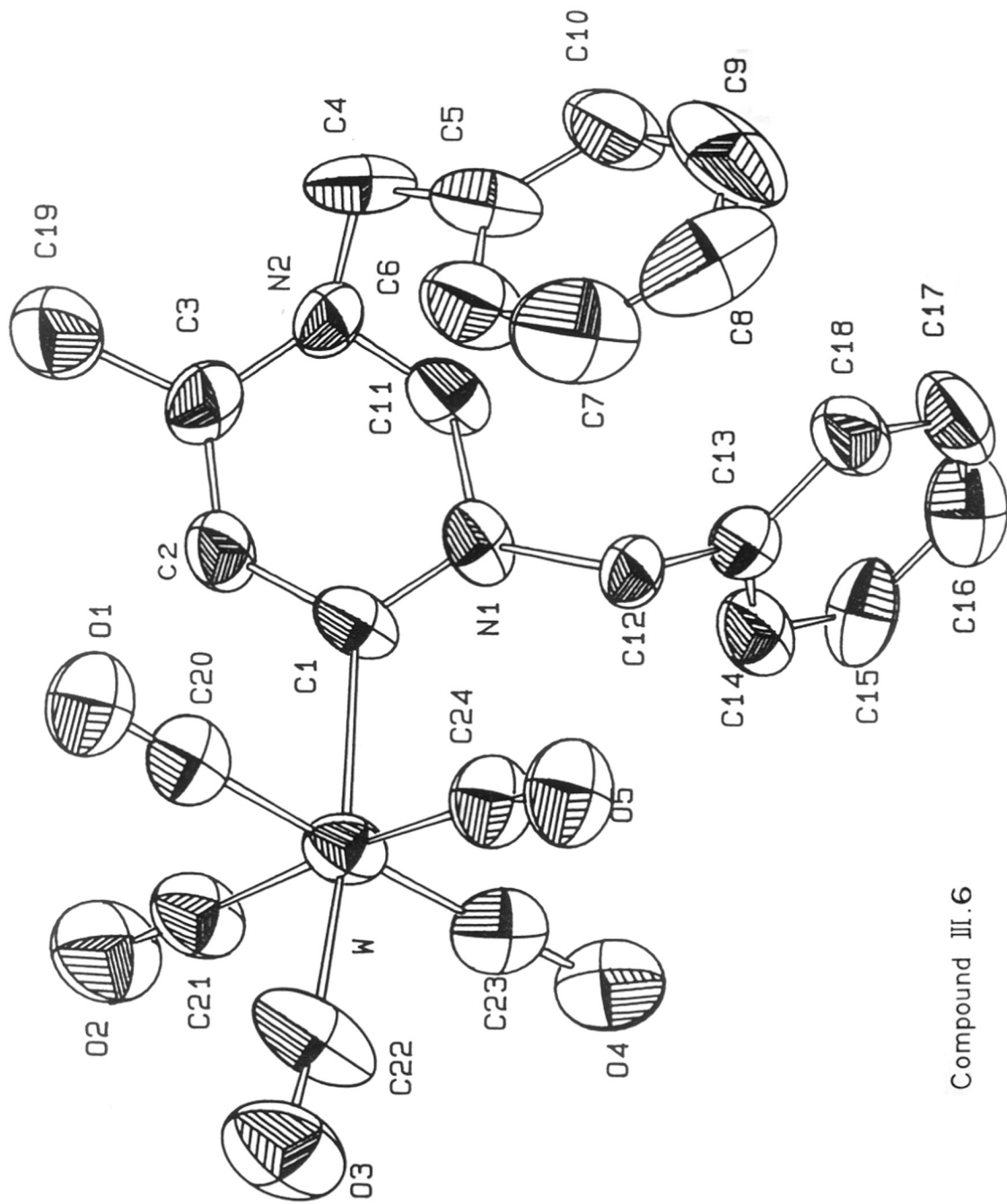
Found : C = 25.45, H = 1.67, N = 3.67



## STRUCTURE SOLUTION BY X-RAY DIFFRACTION

**Crystallographic Data for C<sub>24</sub>H<sub>20</sub>O<sub>5</sub>N<sub>2</sub>W (III.6).**

formula	C <sub>24</sub> H <sub>20</sub> O <sub>5</sub> N <sub>2</sub> W
fw	600.28
cryst system	monoclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>
a (Å)	12.1190 (20)
b (Å)	17.461 (6)
c (Å)	12.099 (20)
β (deg)	113.800 (20)
V (Å <sup>3</sup> )	2342.5 (10)
Z	4
D <sub>cal</sub> (g/cm <sup>3</sup> )	1.702
μ (mm <sup>-1</sup> )	5.07
F(000)	1167.67
radiation	MoKα (λ = 0.7093 Å)
cryst size (mm <sup>3</sup> )	0.08 x 0.35 x 1.20
temp (°K)	298
scan type	ω/2θ
scan width (°)	0.80 + 0.35t, θ
2θ range (°)	3-47
reflections collected	3640
reflections observed (1 ≥ 2.5σ(I))	3459
parameters varied	289
GOF	1.098
R	0.071
R <sub>w</sub>	0.086



Compound III.6

Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters  
( $\text{\AA}^2 \times 10^3$ ) for  $\text{C}_{24}\text{H}_{20}\text{O}_5\text{N}_2\text{W}$  (III.6).

Atom	x	y	z
W	.11216( 8)	.31993( 5)	.11492( 7)
O 1	.088( 1)	.499( 1)	.133( 1)
O 2	.270( 1)	.309( 1)	.398( 1)
O 3	.356( 1)	.346( 1)	.089( 1)
O 4	.126( 1)	.143( 1)	.083( 1)
O 5	-.007( 1)	.335( 1)	-.168( 1)
N 1	-.161( 1)	.276( 1)	.088( 1)
N 2	-.278( 1)	.370( 1)	.141( 1)
C 1	-.060( 2)	.316( 1)	.150( 1)
C 2	-.068( 2)	.365( 1)	.238( 2)
C 3	-.174( 2)	.404( 1)	.216( 2)
C 4	-.390( 2)	.407( 1)	.064( 2)
C 5	-.419( 2)	.395( 1)	-.068( 2)
C 6	-.339( 2)	.421( 1)	-.115( 2)
C 7	-.355( 3)	.413( 2)	-.229( 2)
C 8	-.451( 3)	.368( 2)	-.297( 2)
C 9	-.537( 2)	.340( 2)	-.254( 2)
C10	-.517( 2)	.353( 2)	-.136( 2)
C11	-.260( 2)	.288( 1)	.129( 2)
C12	-.191( 2)	.235( 1)	-.029( 2)
C13	-.250( 2)	.161( 1)	-.030( 1)
C14	-.185( 2)	.101( 1)	.046( 2)
C15	-.235( 2)	.029( 1)	.046( 2)
C16	-.347( 2)	.013( 1)	-.031( 2)
C17	-.413( 2)	.071( 1)	-.104( 2)
C18	-.365( 2)	.144( 1)	-.109( 2)
C19	-.176( 2)	.485( 1)	.263( 2)
C20	.098( 2)	.431( 1)	.124( 1)
C21	.212( 2)	.309( 1)	.296( 2)
C22	.262( 2)	.334( 2)	.093( 2)
C23	.122( 2)	.213( 1)	.101( 2)
C24	.026( 2)	.329( 1)	-.067( 2)

**Bond Distances (Å) for C<sub>24</sub>H<sub>20</sub>O<sub>5</sub>N<sub>2</sub>W (III.6).**

W-C(1)	2.30(2)	C(1)-C(2)	1.40(3)
W-C(20)	1.95(2)	C(2)-C(3)	1.38(3)
W-C(21)	2.04(2)	C(3)-C(19)	1.53(3)
W-C(22)	1.96(2)	C(4)-C(5)	1.51(3)
W-C(23)	1.88(2)	C(5)-C(6)	1.39(3)
W-C(24)	2.02(2)	C(5)-C(10)	1.35(3)
O(1)-C(20)	1.20(2)	C(6)-C(7)	1.32(3)
O(2)-C(21)	1.15(2)	C(7)-C(8)	1.38(4)
O(3)-C(22)	1.18(3)	C(8)-C(9)	1.43(4)
O(4)-C(23)	1.25(3)	C(9)-C(10)	1.37(4)
O(5)-C(24)	1.13(2)	C(12)-C(13)	1.47(3)
N(1)-C(1)	1.34(2)	C(13)-C(14)	1.41(3)
N(1)-C(11)	1.48(2)	C(13)-C(18)	1.37(3)
N(1)-C(12)	1.49(2)	C(14)-C(15)	1.38(3)
N(2)-C(3)	1.35(3)	C(15)-C(16)	1.33(3)
N(2)-C(4)	1.45(3)	C(16)-C(17)	1.37(4)
N(2)-C(11)	1.47(3)	C(17)-C(18)	1.41(3)

**Bond Angles (deg) for C<sub>24</sub>H<sub>20</sub>O<sub>5</sub>N<sub>2</sub>W (III.6).**

C(1)-W-C(20)	85.0(8)	N(2)-C(3)-C(19)	120.0(18)
C(1)-W-C(21)	89.5(7)	C(2)-C(3)-C(19)	122.7(18)
C(1)-W-C(22)	174.1(9)	N(2)-C(4)-C(5)	112.3(16)
C(1)-W-C(23)	94.6(8)	C(4)-C(5)-C(6)	119.1(19)
C(1)-W-C(24)	95.4(7)	C(4)-C(5)-C(10)	119.1(19)
C(20)-W-C(21)	93.2(8)	C(6)-C(5)-C(10)	121.6(20)
C(20)-W-C(22)	89.6(10)	C(5)-C(6)-C(7)	124.2(23)
C(20)-W-C(23)	178.3(8)	C(6)-C(7)-C(8)	114.7(24)
C(20)-W-C(24)	88.1(7)	C(7)-C(8)-C(9)	122.7(21)
C(21)-W-C(22)	88.6(8)	C(8)-C(9)-C(10)	118.9(22)
C(21)-W-C(23)	88.5(8)	C(5)-C(10)-C(9)	117.4(21)
C(21)-W-C(24)	175.0(9)	N(1)-C(11)-N(2)	110.2(14)
C(22)-W-C(23)	90.9(10)	N(1)-C(12)-C(13)	111.0(14)
C(22)-W-C(24)	86.6(8)	C(12)-C(13)-C(14)	120.9(17)
C(23)-W-C(24)	90.3(8)	C(12)-C(13)-C(18)	123.4(18)
C(1)-N(1)-C(11)	114.3(14)	C(14)-C(13)-C(18)	115.6(18)
C(1)-N(1)-C(12)	126.7(14)	C(13)-C(14)-C(15)	123.1(18)
C(11)-N(1)-C(12)	117.8(14)	C(14)-C(15)-C(16)	121.1(20)
C(3)-N(2)-C(4)	128.0(17)	C(15)-C(16)-C(17)	117.1(20)
C(3)-N(2)-C(11)	111.2(16)	C(16)-C(17)-C(18)	123.6(20)
C(4)-N(2)-C(11)	120.0(15)	C(13)-C(18)-C(17)	119.3(20)
W-C(1)-N(1)	127.2(12)	W-C(20)-O(1)	177.7(15)
W-C(1)-C(2)	117.3(13)	W-C(21)-O(2)	174.8(19)
N(1)-C(1)-C(2)	115.2(16)	W-C(22)-O(3)	174.3(19)
C(1)-C(2)-C(3)	119.8(17)	W-C(23)-O(4)	175.3(15)
N(2)-C(3)-C(2)	117.1(17)	W-C(24)-O(5)	171.3(19)

Torsion angles for C<sub>24</sub>H<sub>20</sub>O<sub>5</sub>N<sub>2</sub>W (III.6).

C20 W C 1 N 1	130.9( 13)	C20 W C 1 C 2	-42.5( 10)
C21 W C 1 N 1	-135.9( 13)	C21 W C 1 C 2	50.7( 10)
C22 W C 1 N 1	153.0( 14)	C22 W C 1 C 2	-20.4( 10)
C23 W C 1 N 1	-47.5( 9)	C23 W C 1 C 2	139.2( 14)
C24 W C 1 N 1	43.2( 9)	C24 W C 1 C 2	-130.1( 14)
C 1 W C20 O 1	42.5( 9)	C21 W C20 O 1	-46.7( 10)
C22 W C20 O 1	-135.3( 15)	C23 W C20 O 1	119.4( 14)
C24 W C20 O 1	138.1( 14)	C 1 W C21 O 2	-102.9( 14)
C20 W C21 O 2	-17.9( 10)	C22 W C21 O 2	71.5( 13)
C23 W C21 O 2	162.5( 17)	C24 W C21 O 2	86.8( 13)
C 1 W C22 O 3	37.0( 11)	C20 W C22 O 3	59.0( 12)
C21 W C22 O 3	-34.1( 11)	C23 W C22 O 3	-122.6( 17)
C24 W C22 O 3	147.2( 18)	C 1 W C23 O 4	103.4( 13)
C20 W C23 O 4	26.6( 9)	C21 W C23 O 4	-167.2( 15)
C22 W C23 O 4	-78.7( 12)	C24 W C23 O 4	7.9( 9)
C 1 W C24 O 5	177.0( 16)	C20 W C24 O 5	92.2( 13)
C21 W C24 O 5	-12.8( 9)	C22 W C24 O 5	2.5( 10)
C23 W C24 O 5	-88.4( 13)	C11 N 1 C 1 W	-177.2( 15)
C11 N 1 C 1 C 2	-3.7( 10)	C12 N 1 C 1 W	-10.4( 7)
C12 N 1 C 1 C 2	163.1( 19)	C 1 N 1 C11 N 2	48.1( 11)
C12 N 1 C11 N 2	-119.9( 17)	C 1 N 1 C12 C13	140.1( 19)
C11 N 1 C12 C13	-53.5( 12)	C 4 N 2 C 3 C 2	-151.8( 21)
C 4 N 2 C 3 C19	22.9( 12)	C11 N 2 C 3 C 2	18.0( 10)
C11 N 2 C 3 C19	-167.3( 20)	C 3 N 2 C 4 C 5	113.3( 19)
C11 N 2 C 4 C 5	-55.6( 13)	C 3 N 2 C11 N 1	-55.3( 12)
C 4 N 2 C11 N 1	115.4( 17)	W C 1 C 2 C 3	137.3( 17)
N 1 C 1 C 2 C 3	-36.9( 11)	C 1 C 2 C 3 N 2	29.0( 10)
C 1 C 2 C 3 C19	-145.5( 21)	N 2 C 4 C 5 C 6	-59.2( 15)
N 2 C 4 C 5 C10	114.7( 21)	C 4 C 5 C 6 C 7	179.6( 26)
C10 C 5 C 6 C 7	5.9( 14)	C 4 C 5 C10 C 9	-176.7( 25)
C 6 C 5 C10 C 9	-2.9( 13)	C 5 C 6 C 7 C 8	-8.1( 12)
C 6 C 7 C 8 C 9	8.2( 13)	C 7 C 8 C 9 C10	-5.9( 13)
C 8 C 9 C10 C 5	3.0( 12)	N 1 C12 C13 C14	-67.6( 13)
N 1 C12 C13 C18	116.7( 18)	C12 C13 C14 C15	-178.0( 22)
C18 C13 C14 C15	-2.0( 11)	C12 C13 C18 C17	178.9( 22)
C14 C13 C18 C17	3.0( 11)	C13 C14 C15 C16	2.5( 11)
C14 C15 C16 C17	-3.8( 11)	C15 C16 C17 C18	5.0( 11)
C16 C17 C18 C13	-4.8( 11)		

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