SYNTHESIS, REACTIVITY AND CONFORMATIONAL STUDIES OF NEW FISCHER CARBENE COMPLEXES OF TUNGSTEN

A THESIS
SUBMITTED TO THE
UNIVERSITY OF POONA
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
IN CHEMISTRY

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CERTIFICATE

This is to certify that the work incorporated in the thesis entitled " ***Synthesis, Reactivity and Conformational Studies of New Fischer Carbene Complexes of Tungsten*** *" submitted by Mr. Malay Nandi 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.*

(Dr. A. Sarkar)
Research Guide

Date : 7 Feb. '94
National Chemical Laboratory
Pune - 411 008

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Malay Nandi

Malay Nandi

TO MY PARENTS AND MY BROTHER

CONTENTS

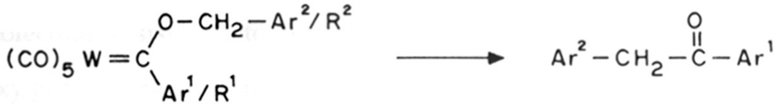
Synopsis of the Thesis

Chapter - 1 *Reactivity of Fischer Carbene Complexes of Tungsten --- A Review*

Thermal reactions of Fischer carbene complexes of tungsten has been reviewed as a background for the present work.

Chapter - 2 *Synthesis and Novel Thermal Rearrangement of Aryl Arylmethyloxy Fischer Carbene Complexes of Tungsten*

In order to explore the chelating ability of furan as a ligand, phenyl furfuryloxy tungsten carbene complex was prepared. Thermolysis of this compound in benzene furnished phenyl 2-furylmethyl ketone as the only product, as a result of an unprecedented rearrangement reaction. A series of aryl arylmethyloxy tungsten carbene complexes were prepared and thermolyzed in benzene or toluene. All the carbene complexes **(1a-g)** were prepared for the first time and fully characterized by spectroscopy and elemental analyses. The aryl arylmethyl ketones were isolated in all cases in good to very good yield. The methyl furfuryloxy tungsten carbene complex did not afford the desired ketone though the starting material underwent decomposition on heating. No reaction took place on heating the phenyl ethoxy tungsten carbene complex in toluene.



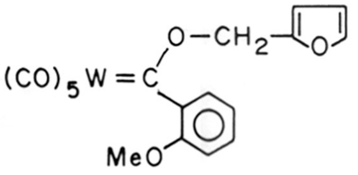
$$(CO)_5W=C(O-CH_2-Ar^2/R^2)(Ar^1/R^1) \longrightarrow Ar^2-CH_2-\overset{O}{\overset{\|}{C}}-Ar^1$$

1 **2**

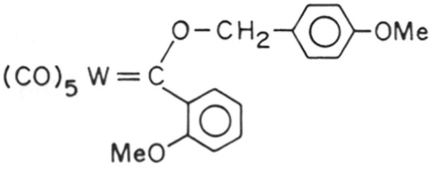
	Ar^1/R^1	Ar^2/R^2
a	Ph	Ph
b	Ph	4-Me-C_6H_4
c	Ph	2-Furyl
d	4-Me-C_6H_4	2-Furyl
e	4-OMe-C_6H_4	2-Furyl
f	Me	2-Furyl
g	Ph	Me

Chapter - 3 *Study of the Scope and Mechanism of the Rearrangement*

A tentative mechanism for the rearrangement was formulated. Photolysis of the phenyl furfuryloxy tungsten carbene complex afforded the product ketone at room temperature, suggesting that the initial CO loss could be the rate-determining step in the overall transformation. To further confirm the presumption that CO loss was indeed the slowest step in the rearrangement, intramolecular chelation to facilitate decarbonylation was probed with suitable substrates (**3a-e**). These carbene complexes were new and characterized fully by spectral and analytical methods. Only the complex **3c** could not be isolated at room temperature since it readily underwent intramolecular cyclopropanation. The cyclopropane was fully characterised by spectral and analytical means. The complex **3e** remained unchanged after refluxing in toluene, suggesting that no intramolecular assistance to decarbonylation was provided by the pendant methoxy group. The aryl propargyloxy carbenes **3d** were prepared to probe the extent of carbonium ion stabilization by the acetylenic bond. A systematic solvent study revealed that benzene and toluene were most suitable for this reaction.



3a



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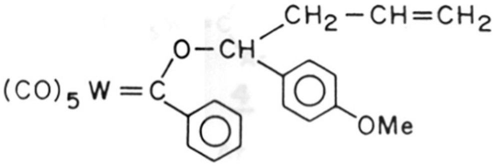

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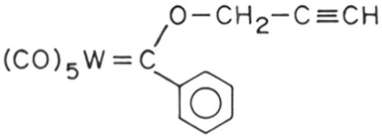
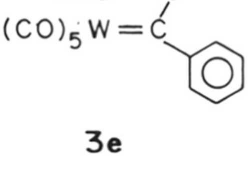


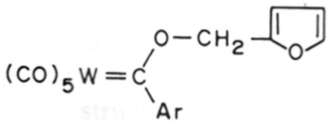
3d



3e

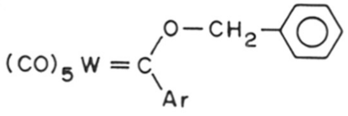
Chapter - 4 *Conformational Studies on the Aryl Arylmethyloxy Fischer Carbene Complexes of Tungsten - Substituent Effects*

Stereoelectronic effects of various substituents on the conformational equilibria of aryl arylmethyloxy Fischer carbenes of tungsten were investigated by variable temperature NMR experiments. Restricted rotation about $C_{carbene}$ - C_{aryl} and $C_{carbene}$ - OR bonds were studied. The orientation of the aryl ring with respect to the metal-carbon π-plane was determined definitively in the solution phase. The effect of the substituents on the conformer population as well as the free energy of activation (rotation barrier) was studied. All the compounds were prepared for the first time.



4

	Ar
a	2-OMe−C_6H_4
b	2-Me−C_6H_4
c	3-OMe−C_6H_4
d	3-Me−C_6H_4
e	1-naphthyl

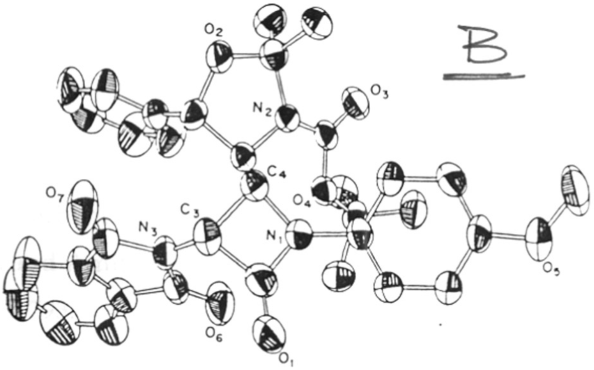


5

	Ar
a	2-OMe−C_6H_4
b	2-Me−C_6H_4
c	3-OMe−C_6H_4
d	3-Me−C_6H_4
e	1-naphthyl
f	2-Me-4-OMe−C_6H_3
g	2,4 di-OMe−C_6H_3

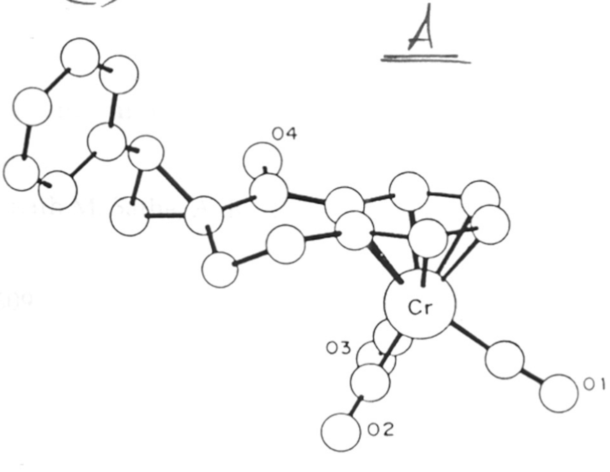
Appendix - 1 *Crystal Structure Solution of Trans-2 (phenyl cyclopropyl)-1-Tetralone Chromium Tricarbonyl Complex* (A)

The structure of the compound was solved [Cell dimensions: a = 7.616(2) b = 10.100(2) c = 22.916 A°, β = 95.92(1)°, V = 1753.4 A^{o3}, monoclinic, Space group $P2_1/n$, Rf = 0.038] by direct methods (MULTAN-80) using NRCVAX package and the refinement also was done using same package.



Appendix - 2 *Crystal Structure Solution of (3R,4S,4'S,5'S) N-(p-anisyl)-3-phthalimido-4-(N-t-butoxycarbonyl-2',2'-dimethyl-5'-phenyl-1',3'-oxazolidin-4'-yl)-azetidin-2-one* (B)

Crystal structure of the compound was solved [Cell dimensions: a = 9.735(2), b = 15.402(1), c = 11.233(6) A°, β = 112.39(3)°, V = 1557.1(9) A^{o3}, monoclinic, Space group $P2_1$, Rf = 0.052] using SHELX-86 (PC version) and the refinement was done using NRCVAX (PC version) package to obtain the final structure.



Note : The compound numbers incorporated in the synopsis are different from those in the thesis.

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1. Unusual Rearrangement of Fischer Carbene Complexes to Ketones
   Malay Nandi, Kashinath M. Sathe, and Amitabha Sarkar
   J. Chem. Soc. Chem. Commun., 1992, 793.

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   Inorg. Chem., 1993, **32**, 1301.

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4. Complete Reversal of Streochemistry in Cyclopropanation of 2-Arylidene-1-tetrolone Tricarbonylchromium Complexes
   Sambasivam Ganesh, Kashinath M. Sathe, **Malay Nandi**, Pinak Chakrabarty, and Amitabha Sarkar.
   J. Chem. Soc. Chem. Commun., 1993, 224.

PAPERS TO BE SUBMITTED

1. Severe Distortion of π-Allyl Orientation in a Molybdenum Complex Containing a sterically Demanding Ligand : X-ray Structure of Hydridotris (3,5 dimethylpyrazolyl) borato - (π-cinnamyl) - Dicarbonylmolybdenum
   Vijaya S. Joshi, Kashinath M. Sathe, **Malay Nandi**, Pinak Chakrabarty, and Amitabha Sarkar.

2. Fischer Carbene Complexes to Ketones : Mechanistic and Stereochemical Study of a Novel Rearrangement
   Kashinath M. Sathe, **Malay Nandi**, and Amitabha Sarkar.

CHAPTER 1

REACTIVITY OF FISCHER CARBENE COMPLEXES OF TUNGSTEN - A REVIEW

> *"There are four steps to accomplishment :*
>
> *Plan Purposefully.*
>
> *Prepare Prayerfully.*
>
> *Proceed Positively.*
>
> *Pursue Persistently."*

INTRODUCTION

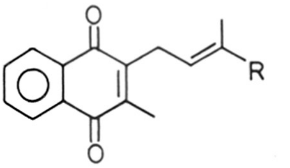
The chemistry of transition metal carbene complexes was pioneered thirty years ago by E. O. Fischer who discovered the first stable complex.[1] Since then, the chemistry of Fischer carbene complexes of group VI transition metals continues to be an area of intense research.[2] In addition to the well-established and synthetically useful reactions,[3] current emphasis is on the modulation of reactivity of these compounds by structural variations[4] with a view to discovering new reactions. While the chromium carbenes have been extensively studied, the analogous tungsten carbenes have received less attention.

A variety of useful reactions of Fischer carbene complexes are known e.g. Diels-Alder reaction,[5] cyclopropanation reaction,[6] alkylation at the α-carbon[7], benzannulation reaction,[3a-f,3h,3k-m,8] etc. A variety of complex target compounds have been synthesized using benzannulation as the key steps[2h] (**Chart 1**).

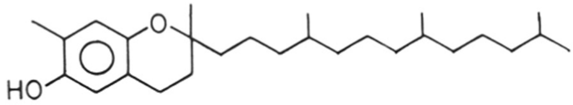
In many cases the reactivity patterns of chromium and tungsten carbene complexes are similar. But there are instances where the reaction of analogous chromium and tungsten carbene complexes take different courses.

In this review, emphasis has been given to such reactivity difference between chromium and tungsten carbene complexes with respect to thermal reactions, as a pertinent background for the present work. The coverage is illustrative rather than comprehensive.

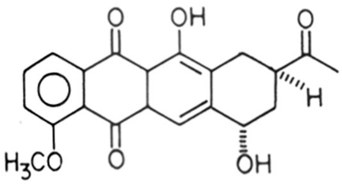
Chart 1



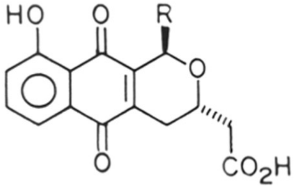
Vit K series



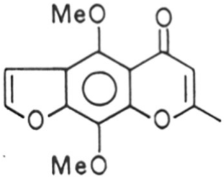
Vit E



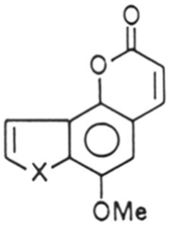
Daunomycinone



Deoxyfrendicin R = n-Pr
Nanaomycin R = Me



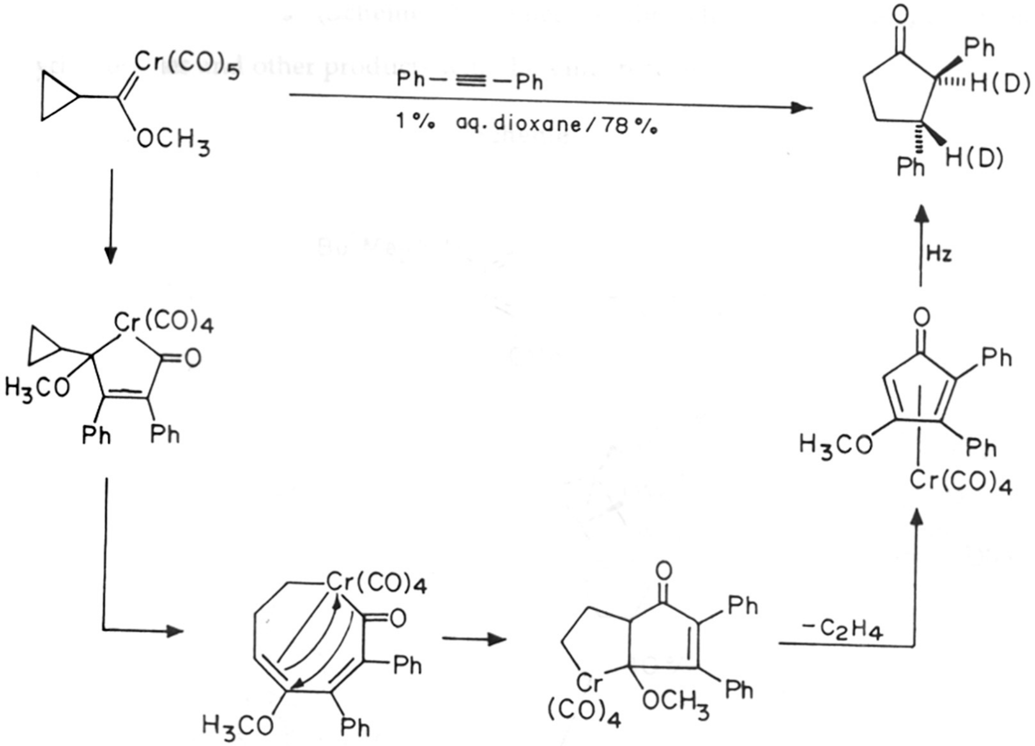
Khellin



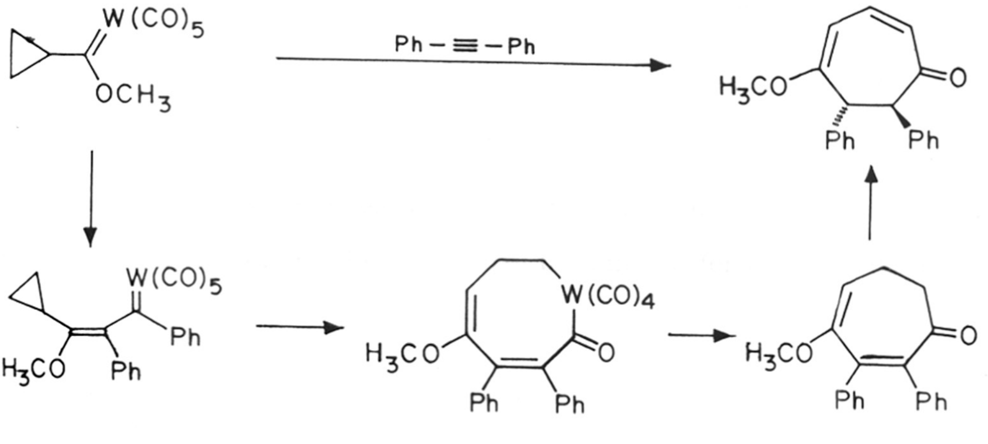
Sphondin X = O
Thiosphondin X = S

Cyclopropyl methoxycarbene complex of chromium[4i] reacts with alkynes to afford cyclopentenones (**Scheme 1a**). But corresponding tungsten[4j] complex reacts with alkynes *via* a different pathway to provide cycloheptadienones[4i-k] (**Scheme 1b**).

Scheme 1a

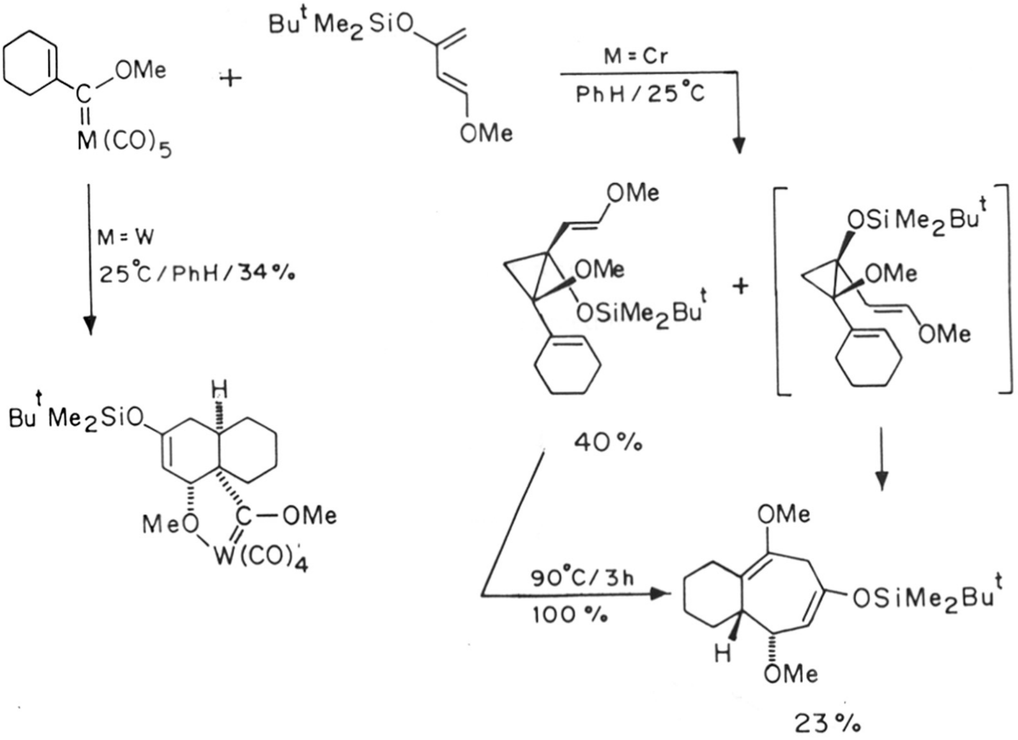


Scheme 1b



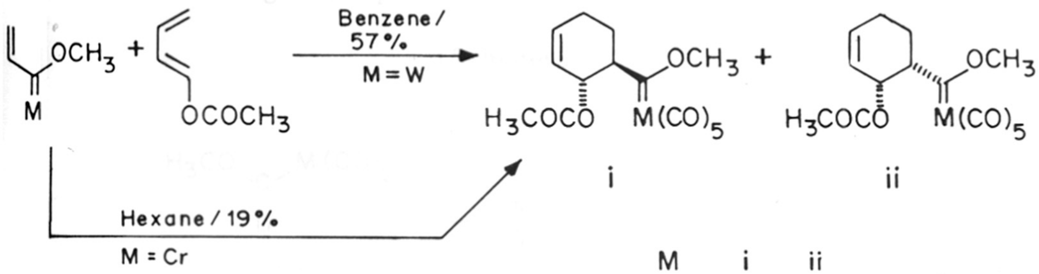
The α,β-unsaturated alkoxy carbene complexes of tungsten form Diels-Alder adducts with dienes (**Scheme** 2), whereas the chromium analogue yields cyclopropanes and other products with the same reactants.[9]

Scheme 2



Where the Diels-Alder reaction proceeds with both chromium and tungsten carbene complexes, the product ratio may be different for different metal used[5b] (**Scheme** 3).

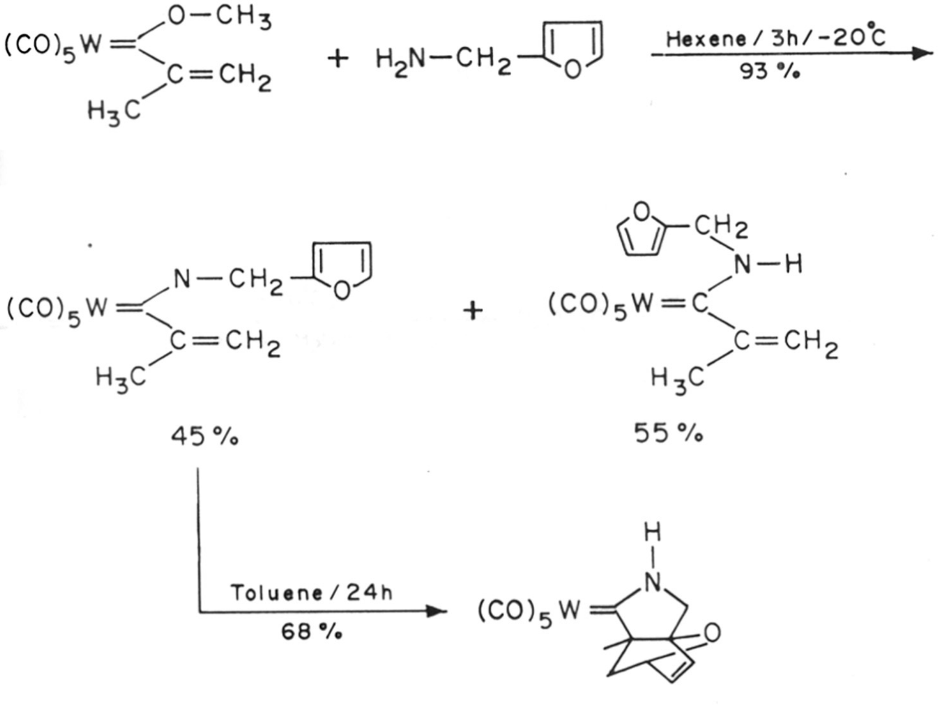
Scheme 3



M	i	ii
Cr	1	1·1
W	1	2·8

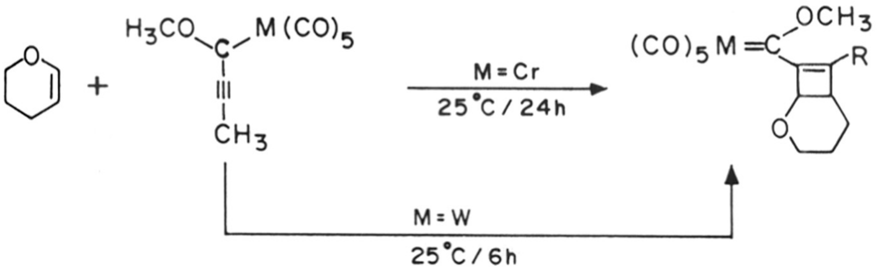
The first Diels-Alder reaction of a tungsten amino carbene complex was reported by Doetz[10] (**Scheme 4**). This reaction is not observed for the chromium amino carbene complexes.

Scheme 4



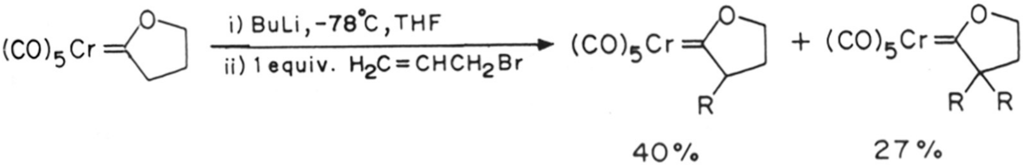
The rate of reaction may be faster in case of tungsten carbene complexes compared to its chromium analogs[11] as depicted in **Scheme 5**.

Scheme 5

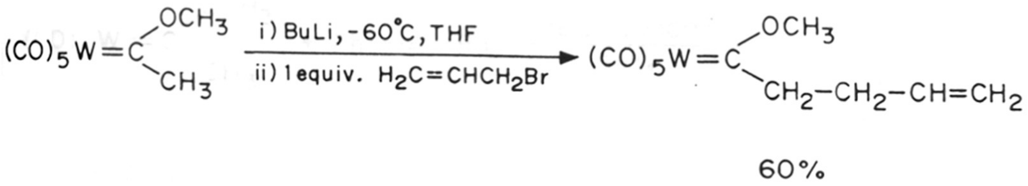


The cyclic chromium carbene complex can be alkylated in good yield with allyl bromide and significant dialkylation was reported[12a] (**Scheme 6a**). With the tungsten carbene complex, on the other hand, no dialkylation product was observed[12b] (**Scheme 6b**).

(**Scheme 6a**)

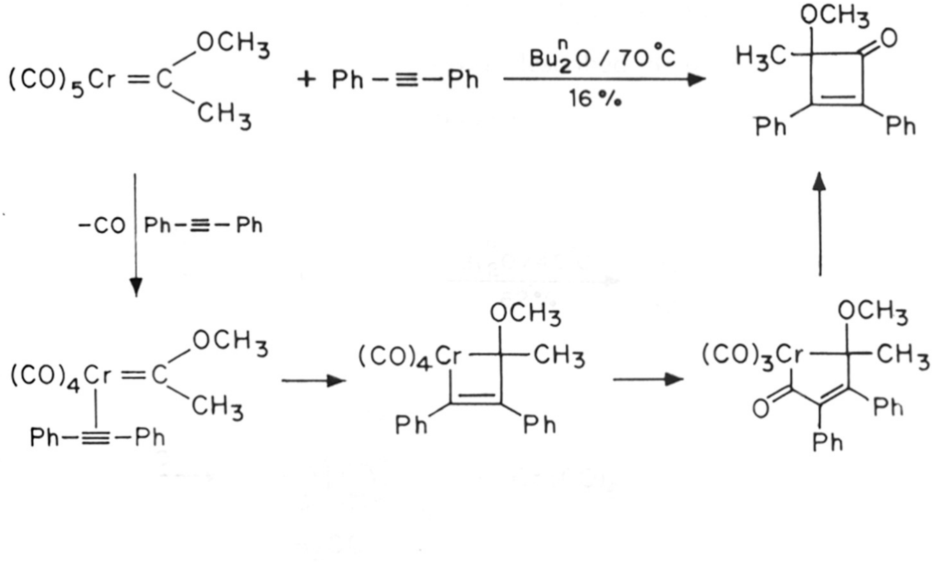


Scheme 6b

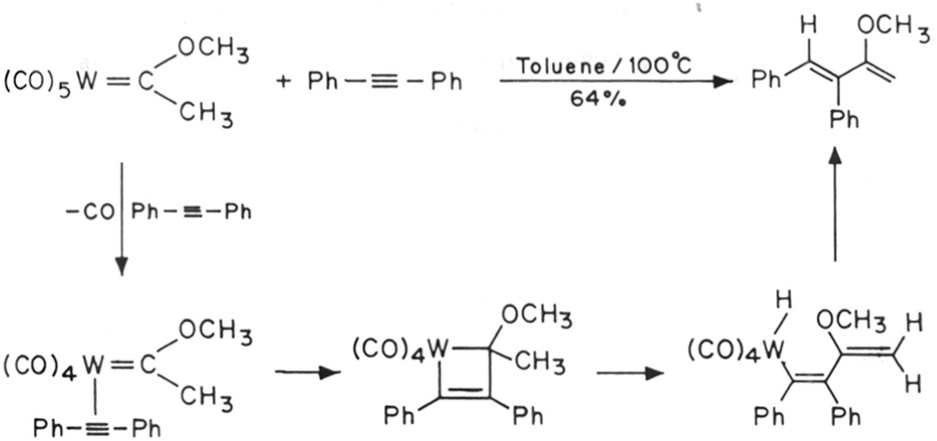


The most thoroughly examined reaction of Fischer carbene complexes is that with alkynes. The methyl alkoxy carbene complex of chromium on heating with diphenylacetylene furnished a cyclobutenone[13a] (**Scheme 7a**) whereas the carbene complex of tungsten yielded a different product.[13b-c] Facile CO-insertion in the case of the chromium complex would account for the difference in product formation (**Scheme 7b**).

Scheme 7a

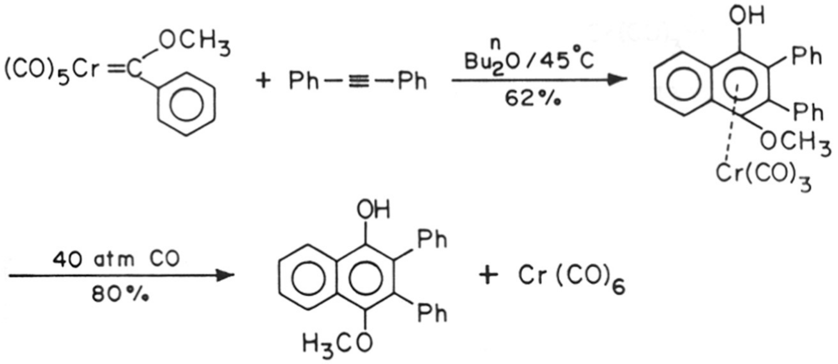


Scheme 7b



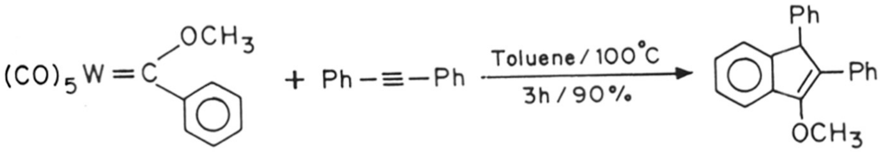
Benzannulation, in which a new benzene ring is generated in the coordination sphere of the metal under neutral conditions at near ambient temperatures, is the most extensively used reaction of carbene complexes in organic synthesis. The first report of this reaction was published in 1975 by Doetz[8a] in which the reaction of phenyl methoxychromium carbene complex with diphenylacetylene to afford a naphthyl-chromium tricarbonyl complex, was described (**Scheme** 8).

Scheme 8



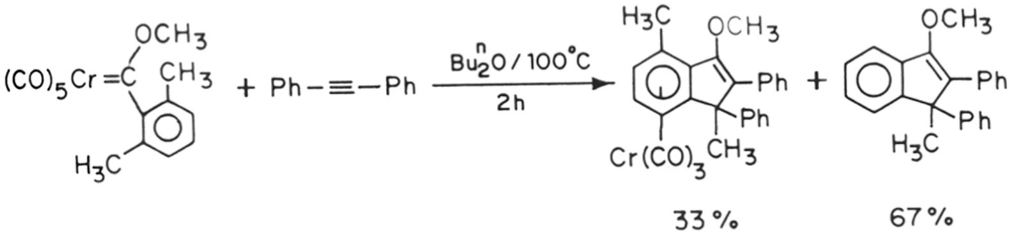
While unsubstituted aryl complexes of chromium react with alkynes to give benzannulation products, the tungsten carbene complex was reported[14] to react with diphenylacetylene to give an indene derivative in 90% yield (**Scheme 9**).

Scheme 9



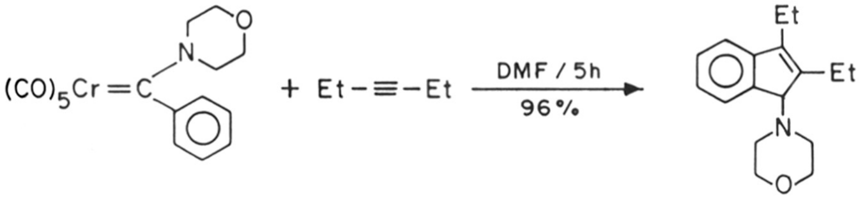
Formation of five member cyclic products were observed even from chromium carbene complexes, if the pathway leading to a six member ring is blocked[15] (**Scheme 10**).

Scheme 10



The amino carbene complexes of chromium also give indene with alkynes[16] (**Scheme 11**).

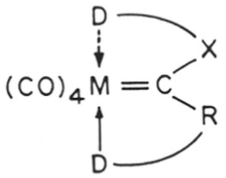
Scheme 11



One major factor which contributes to the difference in reactivity of chromium and tungsten carbene complexes, is the difference in bond energies of M-CO bond. The W-CO bond (178 kj/mol) is stronger than the Cr-CO bond (108 kj/mol).[14] This is manifested both in the requirement of energy to effect the first decarbonylation of the complex as well as insertion of CO at any subsequent step of reaction. Owing to lesser bond energy of Cr-CO bond, both decarbonylation and CO insertion is facile with chromium carbene complexes.

The reluctance of tungsten carbene complexes towards CO insertion leads to the formation of indene rather than naphthalene in the reactions with alkynes. If a W-CO bond is to be broken with greater ease, the bond dissociation energy must be compensated by an attending bond formation, as in intramolecular chelates.[17] Chelation can be effected by two ways as depicted below :

Scheme 12



A donor group is preferred on the heteroatom substituent since in most instances, it can be later dispensed with.

In the present work, the utility of furan as an intramolecular donor for tungsten carbene complex was sought to be investigated, as detailed in the following chapters.

"When you follow two separate chains of thought,

you will find some point of intersection which

should approximate the truth."

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CHAPTER 2

SYNTHESIS AND NOVEL THERMAL REARRANGEMENT OF ARYL ARYLMETHYLOXY FISCHER CARBENE COMPLEXES OF TUNGSTEN

" All glory comes from
daring to begin. "

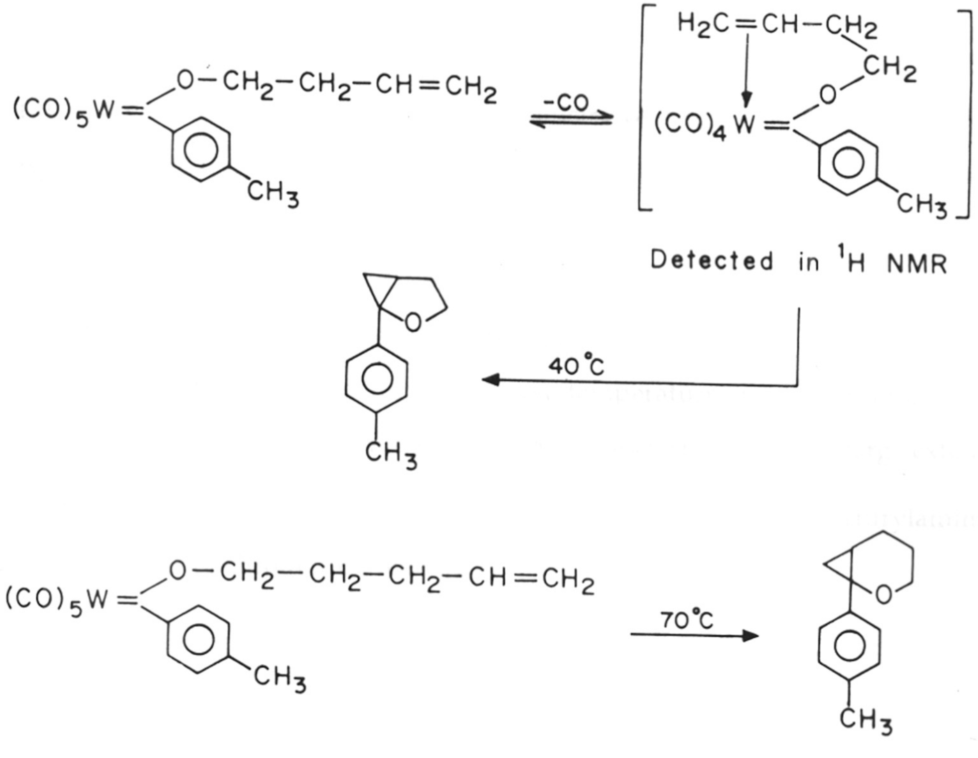
Part of this work has been published in J. Chem. Soc. Chem. Commun., 1992, 793

INTRODUCTION

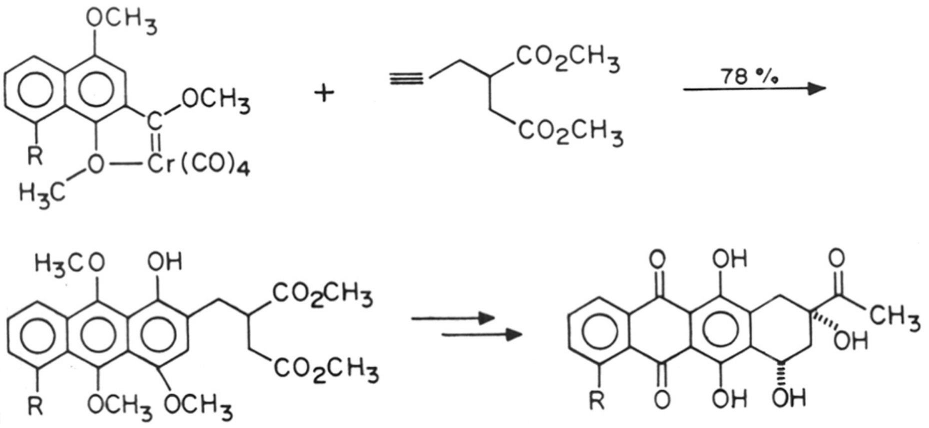
The first step of the benzannulation or the cyclopropanation reaction is the dissociation of a CO ligand which generates a coordinatively unsaturated 16e species. In most instances, this first step is also the rate-determining step. So, in principle, the scope of benzannulation reaction can be improved, if the initial decarbonylation process can be made facile.

It has been demonstrated that such facility may be derived from intramolecular chelation by suitable donor groups which stabilize the intermediate. A double bond can form a chelate by π-participation,[1] while a methoxy group can coordinate through the lone pair of electrons of oxygen[2] as shown in **Scheme 1a** and **1b** respectively.

Scheme 1a



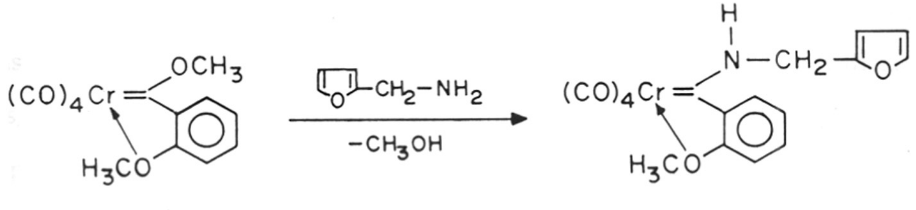
Scheme 1b



The tungsten carbene complexes are usually less air-sensitive and more thermally stable than the chromium analogs. But the chemistry of tungsten complexes are far less exploited. Initial CO dissociation is not facile for tungsten carbene complexes (W-CO bond dissociation energy is higher than that of a Cr-CO bond). As a result, thermal reactions of tungsten carbene complexes require elevated temperatures, limiting their synthetic utility. If the initial dissociation of a CO ligand from a tungsten carbene complex can be carried out at a lower temperature using intramolecular chelation, the impediment to its synthetic application can be removed to a large extent.

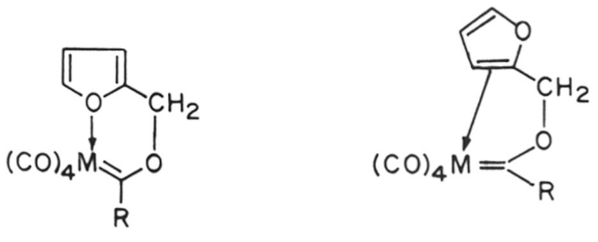
Doetz has reported[2] the formation of a chelated *ortho*-methoxyaryl furfurylamino carbene complexes of chromium (**Scheme 2**).

Scheme 2



The methoxy group of this carbene complex is preferentially chelated to the metal center. Ideally, the donor group which assists decarbonylation by intramolecular chelation should be a weak ligand. It should be possible to displace this donor group (or atom) readily by the reactants. In this regard, furan appeared to offer a unique, ambident donor property. Furan could coordinate *via* the oxygen lone pair or one of its double bonds, and in any case, the coordination to the metal would be weak (**Scheme 3**).

Scheme 3

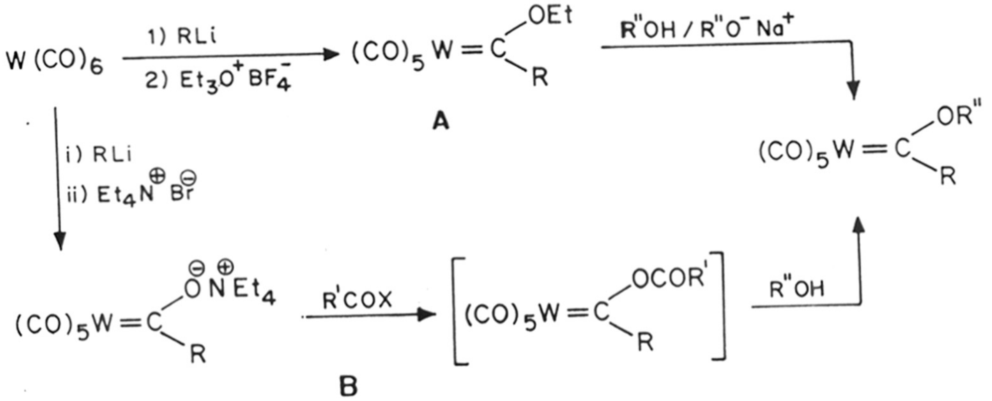


Two points must be noted in this experiment. First, the preferential coordination by the methoxy group does not permit assessment of coordinative ability of the furan moiety. Secondly, the furan should attain *syn* orientation with respect to the metal for effective coordination. Since, the rotation about the C_{carb}-N bond is restricted, such orientation might not have been achieved in the observed temperature range. To explore coordination by furan, one needs to ensure absence of a competing donor as well as restricted bond rotation that precludes desired conformation. On these two counts, the furfuryloxy phenyl tungsten carbene complex appeared to be a more appropriate molecule to investigate.

RESULTS :

It is possible to prepare alkoxy Fischer carbene complexes by two different methods (**Scheme 4**).[3]

Scheme 4



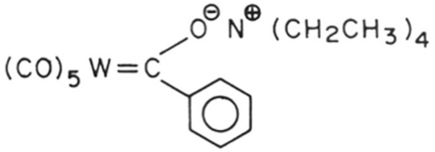
Path A requires excess alcohol and the alcohol exchange[3c] is catalyzed by sodium alkoxide. On the other hand, path B requires[3b,5] a little more than equivalent amount of alcohol. Since the tetralkylammonium metal acylate is relatively air stable and can be stored in the refrigerator for several weeks without appreciable decomposition, the path B was considered the standard method of choice for the present experiments.

While this study was nearing completion, an alternative method of preparation of carbene complexes was reported.[4]

In general, acylating agents like acetyl chloride,[5] acetyl bromide,[6] pivaloyl chloride,[7] etc can be used to acylate the carbene salt. The reactivity order of these reagents is : pivaloyl chloride > acetyl bromide > acetyl chloride. Acetyl chloride was used for its ready availability and convenience.

The carbene complexes were characterized by their IR, ^{1}H, and ^{13}C NMR spectra as well as elemental analyses.

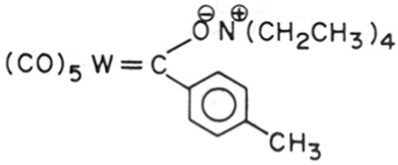
Preparation of pentacarbonyl [(phenyl) {(tetraethylammonio)oxy}carbene] tungsten(0) (2.1a)



2·1a

The tungsten carbene salt was prepared following a reported procedure.[3b] Freshly prepared phenyllithium was added dropwise to the ethereal suspension of $W(CO)_6$. The solution became homogeneous after the addition of required amount of phenyllithium and the color of the solution turned orange. Solid lithio complex was obtained after removal of ether under reduced pressure. The lithio salt was dissolved in water and lithium cation was exchanged using tetraethylammonium bromide. The yellow salt (yield 94%) can be stored in refrigerator under argon for several weeks without noticeable decomposition.

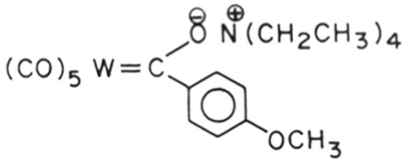
Preparation of pentacarbonyl {(*p*-methylphenyl) [(tetraethylammonio)oxy]carbene}tungsten(0) (2.1b)



2·1b

The carbene salt **2.1b** (yield 90%) was prepared similarly. The red carbene salt could be preserved in the refrigerator for several weeks.

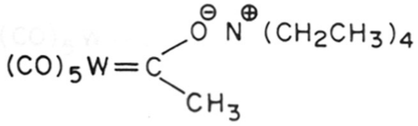
Preparation of pentacarbonyl {(*p*-methoxyphenyl) [(tetraethylammonio)oxy] carbene}tungsten(0) (2.1c)



2·1c

The carbene salt **2.1c** (yield 78%) was obtained as a red solid. It was less stable than those described above.

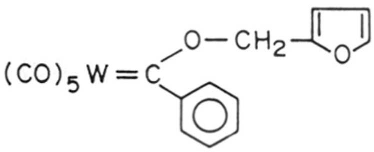
Preparation of pentacarbonyl {(methyl) [(tetraethylammonio)oxy]carbene} tungsten(0) (2.1g)



2·1g

Methyllithium was added to a stirred suspension of W(CO)$_6$ in ether at room temperature to yield the lithium salt of carbene, which was isolated as the tetraethylammonium salt **2.1g** (yield 83%), a yellow solid following a similar procedure.

Preparation and characterization of carbene complex 2.2a



2·2a

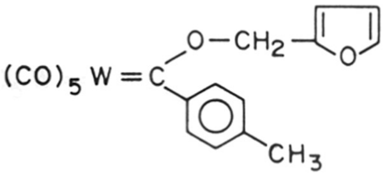
The salt **2.1a** was dissolved in methylene chloride and treated with acetyl chloride at -40°C to generate the unstable acetoxy carbene, which was allowed to react with furfuryl alcohol to furnish the desired product **2.2a** (yield 45%) as a dark red solid.

The carbene complex **2.2a** was fully characterized by spectroscopic methods. The IR spectrum showed bands at 2040 cm^{-1}, 1990 cm^{-1} and 1940 cm^{-1} which were characteristic of carbene complexes. In the ^1H NMR spectrum the sharp signal at 5.88 ppm was assigned to the two methylene protons (O-CH_2). Two furan protons appeared at 6.42 and 6.6 ppm as multiplets. Five aromatic protons appeared at 7.42 ppm as multiplet together with the furan 5-H.

The ^{13}C NMR spectrum was consistent with the expected structure. The peak at 77.29 ppm was assigned to the methylene carbon (O-CH_2). The phenyl ring carbons appeared at 126.51, 128.35, 131.90 and 155.72 ppm. Four furan carbons appeared as two sets of peaks at 111.18 and 112.39 ppm and 144.59 and 148.04 ppm. The peak at 202.62 ppm and 197.44 ppm were assigned to the *trans* CO and four *cis* CO's respectively. The peak at 320.48 ppm was assigned to the carbene carbon.

Finally, elemental analysis (Calculated C : 40.07 H : 1.96 Found C : 40.85 H : 2.23) was also in agreement with the structure of the carbene complex.

Preparation and characterization of carbene complex 2.2b



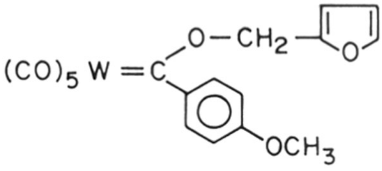
2·2b

Following a similar procedure the carbene complex **2.2b** (yield 42%) was prepared as a red solid. The crystals were hard and could be stored in the refrigerator for months.

The characteristic IR absorptions confirmed the formation of the carbene complex. In the ^{1}H NMR spectrum the methyl group appeared at 2.33 ppm as a sharp singlet. The aromatic protons showed the pattern corresponding to 1,4 substitution pattern.

The methyl group appeared at 21.76 ppm in the ^{13}C NMR spectrum.

Preparation and characterization of carbene complex 2.2c

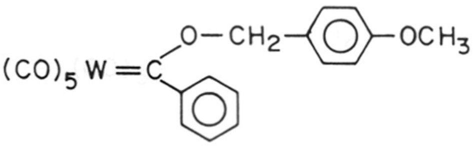


2·2c

The carbene complex **2.2c** (yield 41%) was prepared similarly. The air-stable, hard, red crystals could be kept in the refrigerator for months without decomposition.

In the IR spectrum typical CO absorptions were observed. The singlet at 3.82 ppm was assigned to the methoxy group. In the ^{13}C NMR spectrum corresponding signal appeared at 77.23 ppm.

Preparation and characterization of carbene complex 2.2d

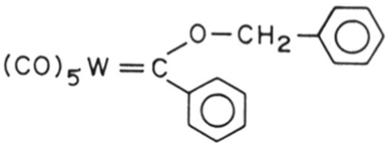


2·2d

Following the same experimental procedure, the carbene complex **2.2d** (yield 67%) was obtained as a air-stable, red solid.

The IR spectrum showed the characteristic absorptions, while the ^{1}H NMR spectrum displayed expected signals. The sharp singlet at 3.82 ppm was assigned to the methoxy group. In the ^{13}C NMR spectrum the methoxy group appeared at 55.54 ppm.

Preparation and characterization of carbene complex 2.2e

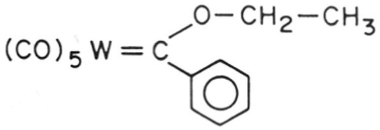


2·2e

The carbene complex **2.2e** (yield 63%) was obtained as a air stable, red solid following the same experimental procedure.

The structural assignment of the complex was supported by characteristic IR absorptions. The ^{1}H and ^{13}C NMR spectra showed the features consistent with the structure.

Preparation and characterization of carbene complex 2.2f



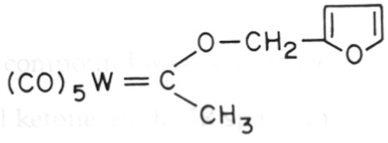
2·2f

Freshly prepared phenyllithium was added to $W(CO)_6$ in ether. The lithio salt was dissolved in distilled and degassed water and petroleum ether was added into it. Meerwein salt was added to the stirred reaction mixture to generate and extract the carbene complex 2.2f (yield 62%) in petroleum ether solution. Air-stable, red crystals were obtained after crystallization from petroleum ether solution at -5°C. The complex could be stored in the refrigerator for months.

The IR spectrum showed typical absorptions of the carbene complex. In the ^1H NMR spectrum the methyl proton appeared as a triplet at 1.71 ppm (t, J = 7Hz, 3H) and the methylene proton appeared as a quartet at 5.02 ppm (q, J = 7Hz, 2H).

In the ^{13}C NMR spectrum the peaks at 15.12 ppm and 80.37 was assigned to the methyl and methylene groups respectively.

Preparation and characterization of carbene complex 2.2g

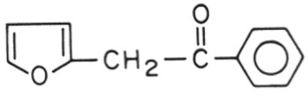


2·2g

Red crystals of the carbene complex **2.2g** (yield 32%) were obtained following a similar experimental procedure. The carbene complex was extremely air-sensitive and the yield was poor compared to other furfuryloxy carbene complexes.

The structural assignment of the complex was supported by characteristic IR absorptions. In the ^{1}H NMR spectrum, the peak at 2.88 ppm was assigned to the methyl group. The ^{13}C NMR spectrum could not obtained as the compound decomposed in solution in a few minutes.

Thermolysis of the carbene complex 2.2a : formation of the product 2.3a



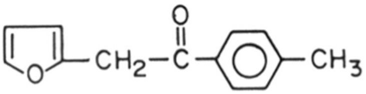
2·3a

A solution of the carbene complex **2.2a** in dry degassed benzene was refluxed for two hours. The initial red color of the solution turned pale yellow. TLC indicated total consumption of **2.2a** and formation of a new product which took intense color in iodine chamber. Solvent was removed under reduced pressure followed by filtration (neutral alumina) of the crude material. The compound **2.3a** (yield 90%) was isolated as a pale yellow liquid after column chromatography (silica gel, 10% ethyl acetate/petroleum ether).

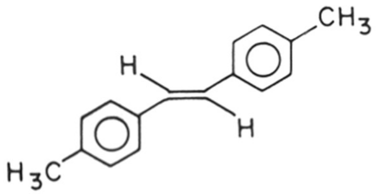
The structure of the compound was established by usual spectroscopic methods as (2-furyl)methyl phenyl ketone. In the IR spectrum, the peak at 1680 cm^{-1} indicated the presence of ketone. In the ^{1}H NMR spectrum a sharp singlet at 4.26 ppm was assigned to the methylene protons. The other proton signals were assigned as follows, 6.22 (m, 2H, Fu), 7.35 (m, 4H, 3Ph+1Fu) and 7.93 (m, 2H, Ph) ppm.

The structure of the compound was further established by mass spectrum.

Thermolysis of the carbene complex 2.2b : formation of the product 2.3b & 2.3b′



2·3b

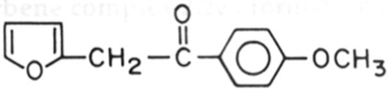


2·3b'

Thermolysis of the carbene complex **2.2b** was carried out similarly. The compounds **2.3b** (yield 65%) and **2.3b′** (yield 15%) were isolated after column chromatography (silica gel, 10% ethyl acetate/petroleum ether) as a pale yellow liquid and a white solid respectively. The IR spectrum of the compound **2.3b** showed the presence a of ketone. In the ^{1}H NMR spectrum, the singlet at 2.34 ppm was assigned to the methyl group.

In case of compound **2.3b′** in the ^{1}H NMR spectrum peaks appeared at 2.34 (s, 6H, Me) and 7.31(m, 10H, Ph+CH).

Thermolysis of the carbene complex 2.2c : formation of the product 2.3c

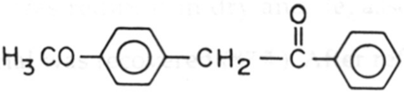


2·3c

Two different solvents (benzene and toluene) were used for the thermolysis of the complex **2.2c**. The compound **2.3c** was isolated in usual manner. In toluene the yield of **2.3c** (50%) was more than in benzene (36%).

The IR spectrum of this compound showed ketone absorption. In the ^{1}H NMR spectrum, the methoxy group appeared at 3.84 ppm as a singlet.

Thermolysis of the carbene complex 2.2d : formation of the product 2.3d

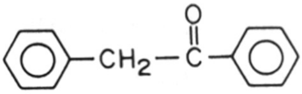


2·3d

Thermolysis of the complex **2.2d** was complete in 16 h in benzene following the same procedure. The compound **2.3d** (yield 56%) was isolated as a white solid.

The characteristic ketone absorption was observed in the IR spectrum. In the ^1H NMR spectrum, the methoxy protons appeared at 3.71 ppm as singlet.

Thermolysis of the carbene complex 2.2e : formation of the product 2.3e



2·3e

The compound 2.3**e** (yield 56%) was isolated as a pale yellow liquid on thermolysis of 2.2e.

The structural assignment of the compound was supported by characteristic IR absorption. The ^1H NMR spectrum showed features consistent with the structure.

Thermolysis of the carbene complex 2.2f

The carbene complex **2.2f** was refluxed in dry and degassed benzene for 5 h hours. Unchanged starting material was recovered (87%). After refluxing in toluene for 12 h, the starting material was recovered (83%).

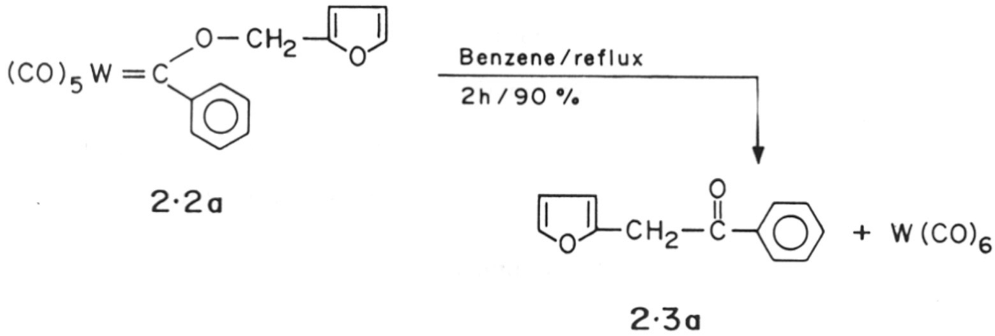
Thermolysis of the carbene complex 2.2g

The complex **2.2g** was thermolyzed in benzene for 2 h. Starting material was completely decomposed. TLC showed the presence of a number of spots and crude IR of this complex mixture did not show the ketone absorption. No attempt was made to isolate compounds from this mixture of products.

DISCUSSION

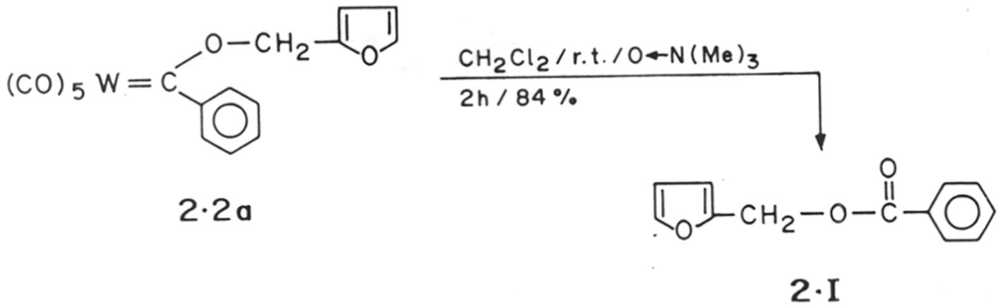
In order to explore whether furan would facilitate the decarbonylation of tungsten carbenes by intramolecular chelation, the 2-furfuryloxy phenyltungsten carbene complex **2.2a** was heated in benzene under reflux. Within 2 h the carbene complex was consumed, and the ketone **2.3a** was isolated as the only organic product in 90% yield. Some amount of $W(CO)_6$ was also obtained (**Scheme 5**).

Scheme 5



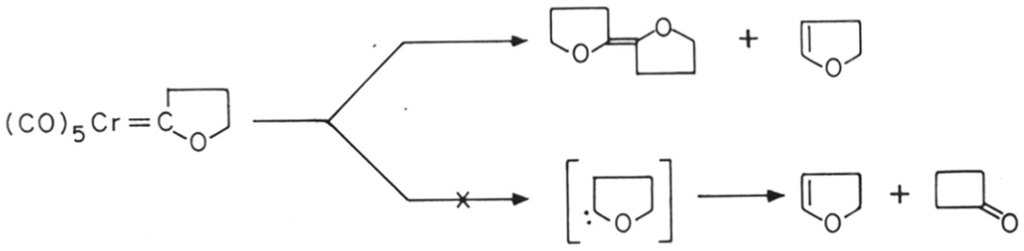
It was ascertained that an ester was not obtained from the oxidation of the carbene complex. When the carbene complex **2.2a** was oxidized with trimethylamine N-oxide, furfuryl benzoate was obtained. For this ester, the methylene protons appeared at 5.2 ppm whereas the methylene protons of the ketone **2.3a** appeared at 4.2 ppm (**Scheme 6**).

Scheme 6



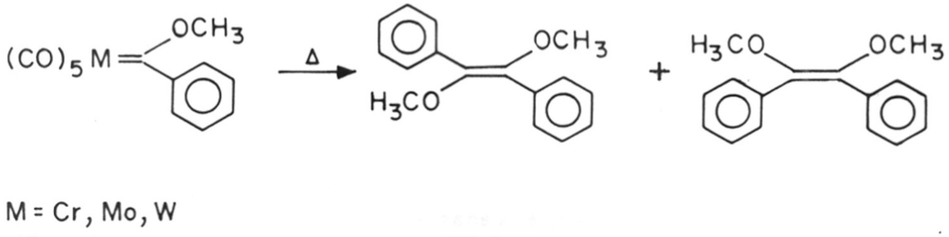
Thus the ketone **2.3a** was formed by an unprecedented rearrangement of the carbene complex **2.2a**. At a first glance, it would appear that the ketone is a rearrangement product of the free carbene derived from the metal complex. But, the formation of a free carbene from Fischer carbene complexes have never been observed so far. The thermolysis of cyclic carbene complex (**Scheme** 7) did not give cyclobutanone which is known to be a characteristic stable rearrangement product of metal free 2-tetrahydrofurylidene.[8]

Scheme 7



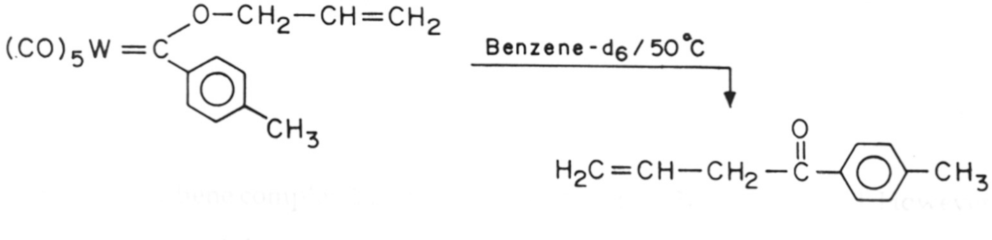
Thermal decomposition of carbene complexes leading to decomposition of the carbene ligand, and, cyclopropanation of activated double bonds are known to proceed without the intermediacy of free carbenes (**Scheme** 8).[9]

Scheme 8



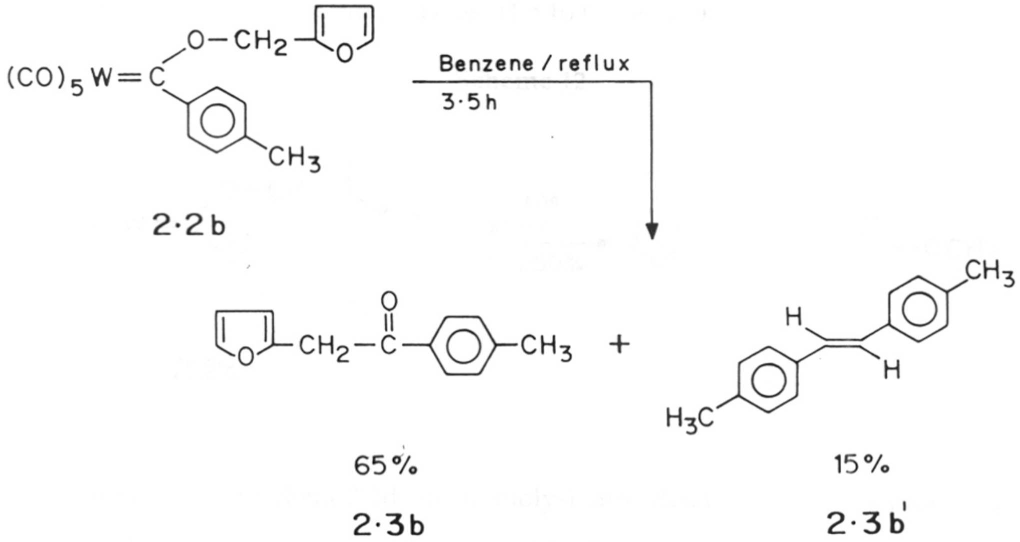
An observation reported by Casey pertaining to the formation of a ketone on thermolysis of a Fischer carbene complex is, as far as the product formation is concerned, related to the present rearrangement (**Scheme** 9).[3c]

Scheme 9



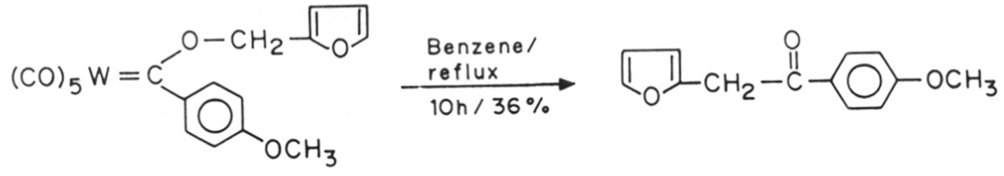
To study the generality of this unusual rearrangement, thermolysis of variously substituted analogs of **2.2a** were carried out. When the complex **2.2b** was thermolyzed, *trans*-stilbene **2.3b′** was obtained as a minor product along with the keto compound **2.3b** (**Scheme** 10).

Scheme 10



From the carbene complex **2.2c**, the expected ketone **2.3c** was obtained. However, the yield was less and the reaction period was longer (10 h) (**Scheme 11**).

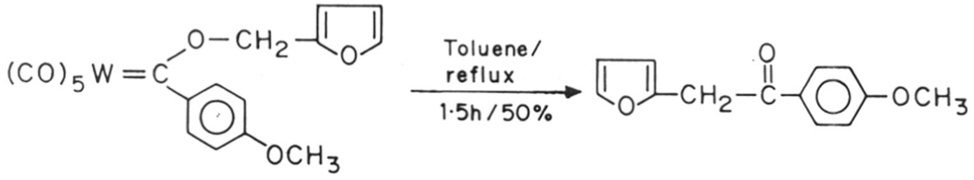
Scheme 11



2·2c 2·3c

When the thermolysis was carried out in refluxing toluene, the yield was slightly improved but the reaction time was less (1.5 h) (**Scheme 12**).

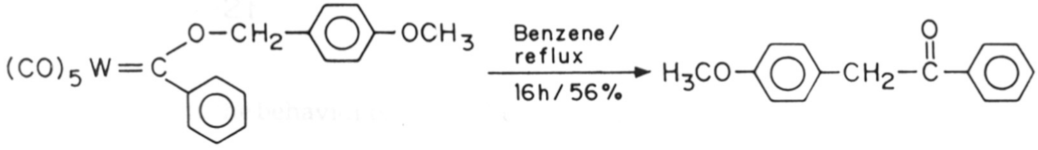
Scheme 12



2·2c 2·3c

The benzyloxy carbene **2.2d**, on thermolysis afforded the rearranged product **2.3d** although the rate was considerably slow (16 h) (**Scheme 13**).

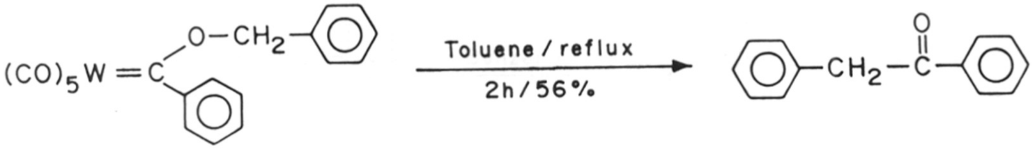
Scheme 13



2·2d 2·3d

The benzyloxy carbene **2.2e** required higher temperature (toluene reflux) for the rearrangement to occur. No perceptible reaction was observed in refluxing benzene for several hours (>15 h) (**Scheme 14**).

Scheme 14

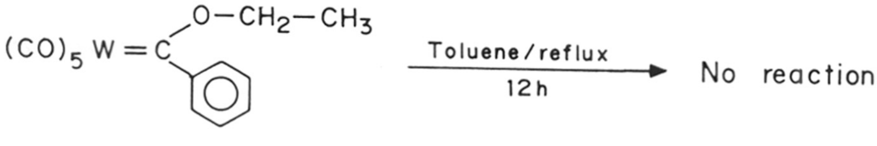


2·2e

2·3e

The carbene complex **2.2f** did not undergo the thermal rearrangement even under prolonged reflux in benzene or toluene. The starting material was recovered in near quantitative yield (**Scheme 15**).

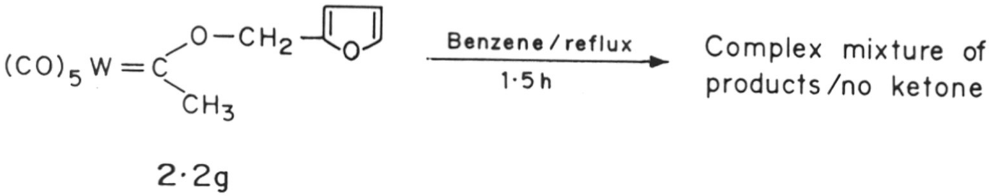
Scheme 15



2·2f

In contrast to the behavior of aryl carbene complexes, the methyl carbene complex 2.2g did not undergo the same rearrangement. Though the carbene complex slowly decomposed on heating in benzene yielding a complex mixture of products, no carbonyl absorption around 1700 cm^{-1} was observed in the IR spectrum of the crude mixture (**Scheme 16**).

Scheme 16



These experiments indicate that this rearrangement is feasible for aryl arylmethoxy carbene complexes of tungsten. Similar results were also obtained for structurally related chromium carbene complexes.[10] The furfuryloxy carbene complexes reacted in refluxing benzene while benzyloxy carbene complexes had to be heated in refluxing toluene. Methyl carbenes did not undergo such rearrangement. This could perhaps be attributed to the inherent reactivity difference between alkyl and aryl Fischer carbene complexes.

SUMMARY

A new thermal rearrangement of the Fischer carbene complexes of tungsten was observed and certain structural parameters related to such unusual reactivity were identified.

"We cannot direct the
wind...But we can adjust
the sails."

GENERAL REMARKS

1. All melting points (recorded on Thermonik Campbell melting point apparatus) are uncorrected and are recorded on Celsius scale.

2. IR spectra were recorded as films of nujol or chloroform solution, on a Perkin-Elmer Infracord Spectrophotometer Model 599-B using sodium chloride optics. IR bands are expressed in frequency (cm^{-1}). Abbreviations, *viz.* s = strong, m = medium and sh = shoulder have been used.

3. ^1H NMR spectra were recorded using tetramethylsilane as internal reference on FT-80 A (Varian 80 MHz FT NMR Spectrometer), WH-90 (Bruker 90 MHz FT NMR Spectrometer) or AC-200 (Bruker 200 MHz FT NMR Spectrometer), ^{13}C NMR spectra were recorded on AC-200 (Bruker 200 MHz FT NMR Spectrometer) at 50 MHz frequency and the chemical shifts are recorded in parts per million (δ). Abbreviations, *viz.* s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, b = broad and m = multiplet have been used.

4. EI Mass spectra were recorded on a Finnigan Mat-1020 Spectrometer with a direct inlet system.

5. Elementary analyses (C, H) were obtained on a Carlo-Erba 1100 automatic analyser by Dr. S. Y. Kulkarni and his group at NCL.

6. References pertaining to each chapter are given at the end of that particular chapter.

GENERAL EXPERIMENTAL

a> Solvents were purified as follows : Benzene, toluene and THF were distilled over potassium-benzophenone under argon freshly before use; methylene chloride was distilled over phosphorous pentoxide under argon; diethyl ether was distilled successively over phosphorous pentoxide lithium aluminium hydride over argon; petroleum ether and water were distilled and degassed.

b> All the apparatus were assembled hot and cooled under argon.

c> All the reagents were distilled under argon atmosphere prior to the reaction.

d> Solvents were transferred to the reaction flask through cannula under vacuum.

f> All the reactions were carried out under argon atmosphere.

g> 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 (230-400 mesh, 9385 grade).

h> Wherever possible, the source of materials purchased has been identified in the experimental procedure where these materials have been used.

EXPERIMENTAL

Tungsten hexacarbonyl, *p*-bromoanisole, *p*-iodotoluene, trifluoroboron etherate, epichlorohydrine, *o*-hydroxybenzaldehyde and *p*-methoxybenzaldehyde were purchased from ALDRICH. Tetraethylammonium bromide was purchased from SISCO chemicals. Lithium aluminium hydride and sodium borohydride were purchased from LOBA chemicals. Bromobenzene, benzophenone, benzyl alcohol, dimethyl sulfate and furfural were purchased from SD chemicals.

PREPARATION OF ARYL LITHIUM

Freshly distilled aryl halide was taken into a RB flask and ether (100 mg/1 ml) was transferred to the flask. The flask was flushed with argon two to three times. n-Butyllithium was added dropwise to the etheral solution of aryl halide by syringe at 25°C and the reaction mixture was stirred for 15 minutes. This solution was directly used for the preparation of aryl carbene salt. In the case of aryl iodide, the experiment was performed at 5°C.

PREPARATION OF CARBENE SALT

Aryl lithium was added dropwise by syringe to the ethereal solution of tungsten hexacarbonyl (100 mg/1 ml) at 25°C with stirring. During the addition of aryl lithium the color of the solution changes to yellow and finally it became red and all the tungsten hexacarbonyl dissolved. The reaction mixture was stirred for 30 minutes at room temperature and solvent was evaporated under reduced pressure and dried in high vacuum (5 torr) until it was free flowing. The solid lithio complex was dissolved in cold (O°C-5°C) water. This solution was directly filtered into a cold (O°-5°C) aqueous solution of $N(Et)_4Br$(100 mg/5 ml) and kept in the refrigerator (10°C) to precipitate out the solid carbene salt. The salt was filtered and dried in high vacuum and used for next reaction.

PREPARATION OF CARBENE COMPLEX

The solution of the carbene salt (100 mg/2 ml) in methylene chloride was cooled to -40°C (acetonitrile-dry ice bath). Freshly distilled acetyl chloride (one equiv) was added to this solution and stirred for 45 minutes at -30°C. The color of the solution changes from orange-red to dark red. The reaction mixture was again cooled to -40°C, alcohol was added and it was warmed to O°C over a period of two hours and stirred for four hours at that temperature. The formation of the carbene complex was monitored by TLC using petroleum ether or 5% ethyl acetate/petroleum ether as eluent. Red spot moved in the solvent chamber. This spot was UV active and took intense color in iodine chamber. After addition of alcohol the color of the reaction mixture gradually changes from dark red to red. The solvent was then evaporated under reduced pressure at room temperature and dried in high vacuum. Degassed petroleum ether was added to the crude material of the reaction flask and extracted. Petroleum ether extract was concentrated under reduced pressure at room temperature and kept for crystallization at -5°C.

In case of benzyloxy carbene complexes the initial purification was done by flash column chromatography followed by crystallization. Furfuryloxy carbene complexes decomposed gradually during crystallization. The rate of decomposition during crystallization was reduced considerably by stirring a petroleum ether solution of crude carbene complexes with basic alumina at room temperature for 30 minutes. This decomposition could also be checked, if initial purification was done by flash column chromatography, followed by crystallization.

THERMOLYSIS REACTION

The compound was heated in dry and degassed benzene / toluene (100 mg / 10 ml) and the progress of the reaction was monitored by TLC. The solvent was removed under reduced pressure and the crude material was filtered through a small column of neutral alumina using methylene chloride as eluent. Finally the desired compound was isolated by column chromatography.

Preparation of pentacarbonyl {(phenyl) [(tetraethylammonio)oxy]carbene} tungsten(0) (2.1a)

From $W(CO)_6$ (3.034 gm, 8.64 mmol), phenyllithium [freshly prepared from n-butyllithium (10 ml, 13 mmol & bromobenzene (1.36 ml, 13 mmol)] and tetraethylammonium bromide (1.816 gm, 8.65 mmol), the carbene salt **2.1a** was obtained as a yellow solid (4.506 gm, 94%).

Preparation of pentacarbonyl {(*p*-methylphenyl) [(tetraethylammonio)oxy]carbene} tungsten(0) (2.1b)

From $W(CO)_6$ (1.408 gm, 4.01 mmol), *p*-methylphenyllithium [freshly prepared from n-butyllithium (6 ml, 6 mmol) & 4-iodotoluene (1.308 gm, 6 mmol)] and tetraethylammonium bromide (845 mg, 4.02 mmol), the carbene salt **2.1b** was obtained as a red solid (1.9 gm, 90%).

^{13}C NMR (Acetone-d_6) 7.46; 52.89; 126.86; 128.37; 138.17; 154.82; 204.65; 208.52; 276.05

Preparation of pentacarbonyl {(*p*-methoxyphenyl) [(tetraethylammonio)oxy] carbene}tungsten(0) (2.1c)

From $W(CO)_6$ (1.5 gm, 4.27 mmol), *p*-methoxyphenyllithium [freshly prepared from n-butyllithium (6.4ml, 6.4 mmol) & 4-bromoanisole (0.8 ml, 6.4 mmol)] and tetraethylammonium bromide (900 mg, 4.27 mmol), the carbene salt **2.1c** was obtained as a red solid (1.95 gm, 78%).

^{13}C NMR (Acetone-d_6)	7.36; 52.72; 55.22; 112.66; 128.92; 149.95; 160.88; 204.60; 208.33; 273.59

Preparation of pentacarbonyl {(methyl) [(tetraethylammonio)oxy]carbene} tungsten(0) (2.1g)

From $W(CO)_6$ (1.3 gm, 3.7 mmol), methyllithium (5 ml, 5 mmol) and tetraethylammonium bromide (780 mg, 3.7 mmol), the carbene salt **2.1g** obtained as a yellow solid (1.52 gm, 83%).

Preparation of pentacarbonyl[(furfuryloxy)(phenyl)carbene]tungsten(0) (2.2a)

From the carbene salt **2.1a** (1.104 gm, 1.97 mmol), acetyl chloride (0.14 ml, 1.97 mmol), and furfuryl alcohol (0.17 ml, 1.97 mmol), the carbene complex **2.2a** was obtained as a dark red solid (375 mg, 37%). The carbene complex was purified by crystallization from petroleum ether at -5°C.

IR ($CHCl_3$)	2040(m); 1990(sh); 1940(s)
^{1}H NMR ($CDCl_3$)	5.88 (s, 2H); 6.42 (m, 1H); 6.6 (m, 1H); 7.42 (m, 6H)
^{13}C NMR ($CDCl_3$)	77.29; 111.18; 112.39; 126.51; 128.35; 131.90; 144.59; 148.04; 155.72; 197.44; 202.62; 320.48

Analysis Calculated : C 40.07 H 1.96

Found : C 40.85 H 2.23

Preparation of pentacarbonyl [(furfuryloxy)(*p*-methylphenyl)carbene] tungsten(0) (2.2b)

From the carbene salt **2.1b** (1.08 gm, 1.88 mmol), acetyl chloride (0.13 ml, 1.88 mmol), and furfuryl alcohol (0.16 ml, 1.88 mmol), the carbene complex **2.2b** was obtained as a dark red solid (420 mg, 42%). The carbene complex was purified by crystallization from petroleum ether at -5°C.

IR ($CHCl_3$) 2040(m); 1985(sh); 1940(s)

^{1}H NMR ($CDCl_3$) 2.33 (s, 3H); 5.91 (s, 2H); 6.42 (m, 2H); 6.82 (m, 1H); 7.13 (m, 1H); 7.15 (d, J = 8Hz, 2H); 7.51 (m, 3H)

^{13}C NMR ($CDCl_3$) 21.76; 77.35; 111.12; 112.32; 128.29; 129.03; 143.82; 144.50; 148.04; 152.46; 197.62; 2203.49; 317.26

Analysis Calculated : C 41.30 H 2.29

Found : C 41.12 H 2.01

Preparation of pentacarbonyl [(furfuryloxy)(*p*-methoxyphenyl)carbene] tungsten(0) (2.2c)

From the tetraethyl ammonium carbene salt **2.1c** (3.873 gm, 6.58 mmol), acetyl chloride (0.46 ml, 6.58 mmol), and furfuryl alcohol (0.57 ml, 6.58 mmol), the carbene complex **2.2c** was obtained as a dark red solid (1.48 gm, 41%). The carbene complex was purified by crystallization from petroleum ether at -5°C.

IR ($CHCl_3$) 2040(m); 1980(sh); 1935(s)

^{1}H NMR (CDCl$_3$)	3.82 (s, 3H); 5.88 (s, 2H); 6.40 (m, 1H); 6.55 (m, 1H); 6.82 (d, J = 9Hz, 2H); 7.46 (m, 1H); 7.8 (d, J = 9Hz, 2H)
^{13}C NMR (CDCl$_3$)	55.74; 77.23; 111.06; 112.11; 113.57; 124.68; 132.58; 144.41; 148.19; 164.32; 197.80; 203.08; 312.93
Analysis	Calculated : C 40.07 H 2.22 Found : C 39.18 H 2.77

Preparation of pentacarbonyl [(*p*-methoxybenzyloxy)(phenyl)carbene] tungsten(0) (2.2d)

From the carbene salt **2.1a** (1.117 gm, 2.0 mmol), acetyl chloride (0.14 ml, 2.0 mmol), and *p*-methoxybenzyl alcohol (0.17 ml, 2.0 mmol), the carbene complex **2.2d** was obtained as a dark red solid (736 mg, 67%). The carbene complex was purified by crystallization from petroleum ether at -5°C.

IR (CHCl$_3$)	2030(m); 1970(sh); 1930(s)
^{1}H NMR (CDCl$_3$)	3.82 (s, 3H); 5.88 (s, 2H); 6.95 (d, J = 9Hz, 2H); 7.42 (m, 7H)
^{13}C NMR (CDCl$_3$)	55.54; 86.20; 114.71; 126.45; 126.69; 128.30; 130.58; 131.89; 15.48; 160.79; 197.65; 203.81; 319.77
Analysis	Calculated : C 43.71 H 2.55 Found : C 44.17 H 2.98

Preparation of pentacarbonyl[(benzyloxy)(phenyl)carbene]tungsten(0) (2.2e)

From the carbene salt **2.1e** (800 mg, 1.43 mmol), acetyl chloride (0.10 ml, 1.43 mmol), and benzyl alcohol (0.12 ml, 1.43 mmol), the carbene complex **2.2e** was obtained as a dark red solid (472 mg, 63%). The carbene complex was purified by crystallization from petroleum ether at -5°C.

IR ($CHCl_3$)	2035(m); 1980(sh); 1930(s)
^1H NMR ($CDCl_3$)	5.97 (s, 2H); 7.48 (m, 10H)
^{13}C NMR ($CDCl_3$)	86.09; 126.94; 128.45; 128.84; 129.32; 129.54; 132.13; 134.51; 155.47; 197.64; 203.85; 320.18
Analysis	Calculated : C 43.93 H 2.31
	Found : C 44.12 H 2.60

Preparation of pentacarbonyl[(ethoxy)(phenyl)carbene]tungsten(0) (2.2f)

From $W(CO)^6$, (1.0 gm, 2.8 mmol), Meerwein salt (453 mg, 2.8 mol) and phenyllithium [freshly prepared from n-butyllithium (3.3 ml, 3.3 mmol) & bromobenzene (0.34 ml, 3.3 mmol)] the carbene complex **2.2f** was obtained as a dark red solid (980 mg, 76%). The carbene complex was purified by crystallization from petroleum ether at -5°C.

IR ($CHCl_3$)	2030(m); 1980(sh); 1935(s)
^1H NMR ($CDCl_3$)	1.71 (t, J = 7Hz, 3H); 5.02 (q, J = 7Hz, 2H); 7.4 (m, 5H)
^{13}C NMR ($CDCl_3$)	15.12; 80.37; 128.26; 126.36; 131.76; 155.62; 197.54; 203.85; 320.19
Analysis	Calculated : C 36.48 H 2.19
	Found : C 36.98 H 2.52

Preparation of pentacarbonyl[(furfuryloxy)(methyl)carbene]tungsten(0) (2.2g)

From the carbene salt **2.1g** (1.08 gm, 2.17 mmol), acetyl chloride (0.15 ml, 2.17 mmol), and furfuryl alcohol (0.18 ml, 2.17 mmol), the carbene complex **2.2g** was obtained as a red solid (330 mg, 32%). The carbene complex was purified by crystallization from petroleum ether at -5°C.

IR ($CHCl_3$)	2040(m); 2010(sh); 1950(s)

^{1}H NMR ($CDCl_3$)	2.88 (s, 3H); 5.73 (s, 2H); 6.51 (m, 2H); 7.48 (m, 1H)
Analysis	Calculated : C 32.21 H 1.78 Found : C 32.31 H 1.49

Preparation of furfuryl benzoate 2.I

From the carbene complex **2.2a** (200 mg, 0.39 mmol) in methylene chloride (30 ml), with stirring for 2 h with trimethylamine N-oxide (35 mg, 0.46 mmol), the compound **2.I**, (66 mg, 84%) was obtained as a pale yellow liquid.

Thermolysis of carbene complex 2.2a

The carbene complex **2.2a**, (0.9 gm, 1.76 mmol), on refluxing in benzene for 2 h yielded the compound **2.3a** (0.295 gm, 90%) as a pale yellow liquid.

IR ($CHCl_3$)	1680 (m)
^{1}H NMR ($CDCl_3$)	4.26 (s, 2H); 6.22 (m, 2H); 7.35 (m, 4H); 7.93 (m, 2H)
MS	186(M^+); 105; 81; 77

Thermolysis of carbene complex 2.2b

The carbene complex **2.2b**, (271 mg, 0.51 mmol), when refluxed in benzene for 3.5 h furnished the compound **2.3b** (67 mg, 65%) as pale yellow liquid along with compound **2.3b′** (16 mg, 15%) as a white solid.

Compound 2.3b

IR ($CHCl_3$)	1680 (m)
^{1}H NMR ($CDCl_3$)	2.34 (s, 3H); 4.24 (s, 2H); 6.23 (m, 2H); 7.26 (m, 3H); 7.86 (d, J = 8Hz, 2H)
MS	200(M^+); 119; 91, 81

Compound 2.3b′

^{1}H NMR (CDCl$_3$)	2.34 (s, 6H); 7.31 (m, 10H)
M.P.	98°C
MS	208(M$^+$); 193; 178; 115; 91; 77

Thermolysis of carbene complex 2.2c

The carbene complex **2.2c**, (612 mg, 1.13 mmol), by heating (80°C) for 10 h in benzene yielded the compound **2.3c** (90 mg, 36%) as a pale yellow liquid.

Similarly, the carbene complex **2.2c**, (760 mg, 1.41 mmol), on refluxing in toluene for 1.5 h furnished the compound **2.3c** (153 mg, 50%) as a pale yellow liquid.

IR (CHCl$_3$)	1670 (m)
^{1}H NMR (CDCl$_3$)	3.84 (s, 3H); 4.23 (s, 2H); 6.26 (m, 2H); 6.92 (d, J = 9 Hz, 2H); 7.34 (m, 1H); 7.97 (d, J = 9 Hz, 2H)
MS	216(M$^+$); 135; 107; 92; 81; 77

Thermolysis of carbene complex 2.2d

The carbene complex **2.2d** (300 mg, 0.54 mmol), on refluxing in benzene for 16 h yielded the compound **2.3d** (69 mg, 56%) as a white solid.

IR (CHCl$_3$)	1690 (m)
^{1}H NMR (CDCl$_3$)	3.71 (s, 3H); 4.04 (s, 2H); 6.78 (d, J = 8 Hz, 2H); 7.14 (d, J = 8 Hz, 2H); 7.4 (m, 3H); 7.92 (d, J = 8 Hz, 2H)
M.P.	110°C
MS	226(M$^+$); 121; 105; 91; 77

Thermolysis of carbene complex 2.2e

The carbene complex **2.2e** (200 mg, 0.38 mmol), on refluxing in toluene for 2 h yielded the compound **2.3e** (40 mg, 56%) as a pale yellow liquid.

IR ($CHCl_3$)	1680 (m)
^1H NMR ($CDCl_3$)	4.26 (s, 2H); 7.24 (m, 8H); 7.97 (dd, J = 8 Hz, and 2 Hz, 2H)
MS	196(M^+); 105; 91; 77

Thermolysis of carbene complex 2.2f

The carbene complex **2.2f** (218 mg, 0.47 mmol) on refluxing in benzene for 5 h the starting material (compound **2.2f**) was recovered (190 mg, 87%).

The carbene complex **2.2f** (94 mg, 0.2 mmol) on refluxing in toluene for 12 h the starting material (compound **2.2f**) was recovered (70 mg, 83%).

Thermolysis of carbene complex 2.2g

The carbene complex **2.2g** (300 mg, 0.67 mmol) was refluxed in benzene for 1.5 h. It decomposed completely, IR spectrum of the reaction mixture did not show any peak corresponding to ketone.

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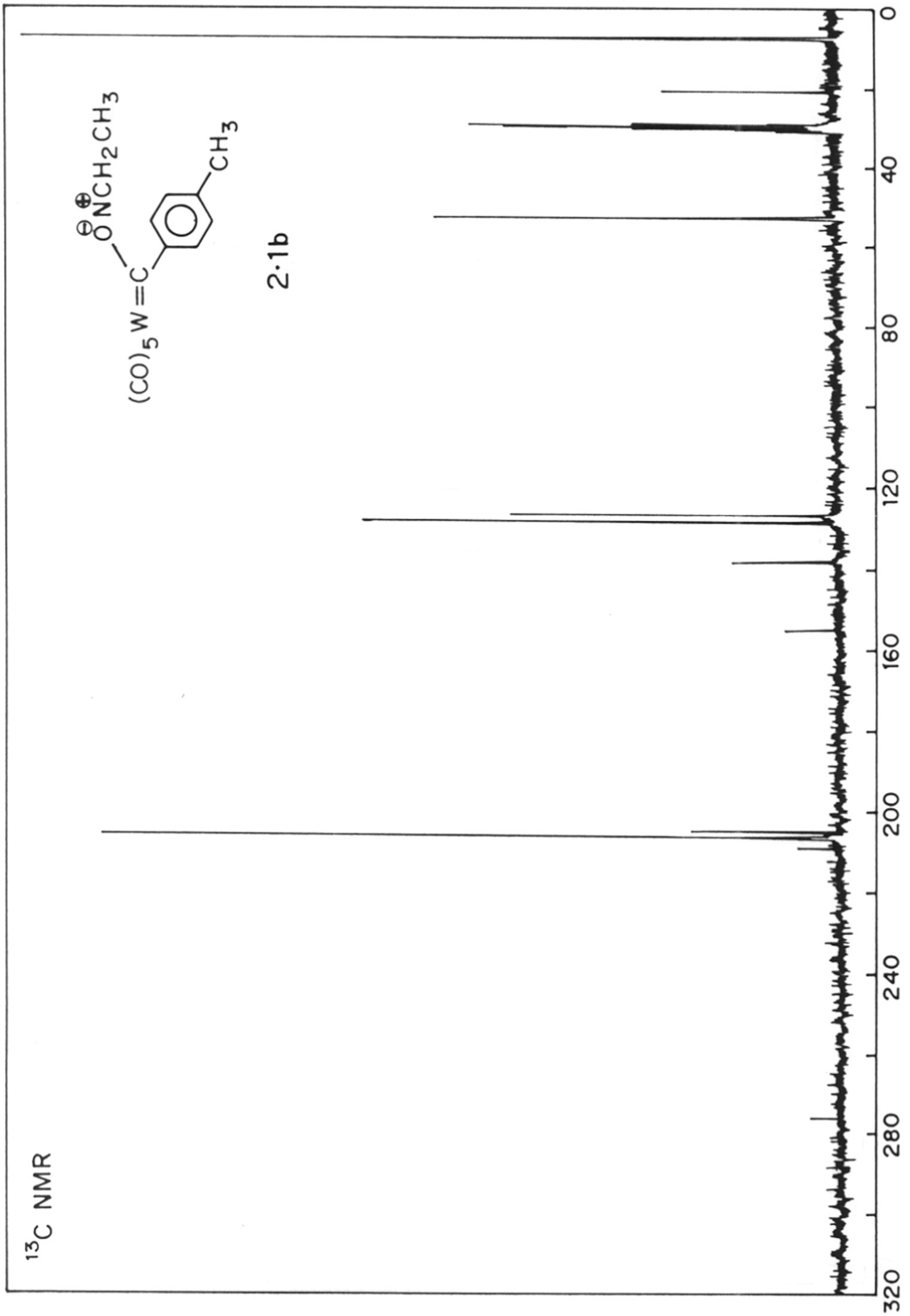

^{13}C NMR
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$\overset{\ominus}{O}\overset{\oplus}{N}CH_2CH_3$
CH_3
2·1b
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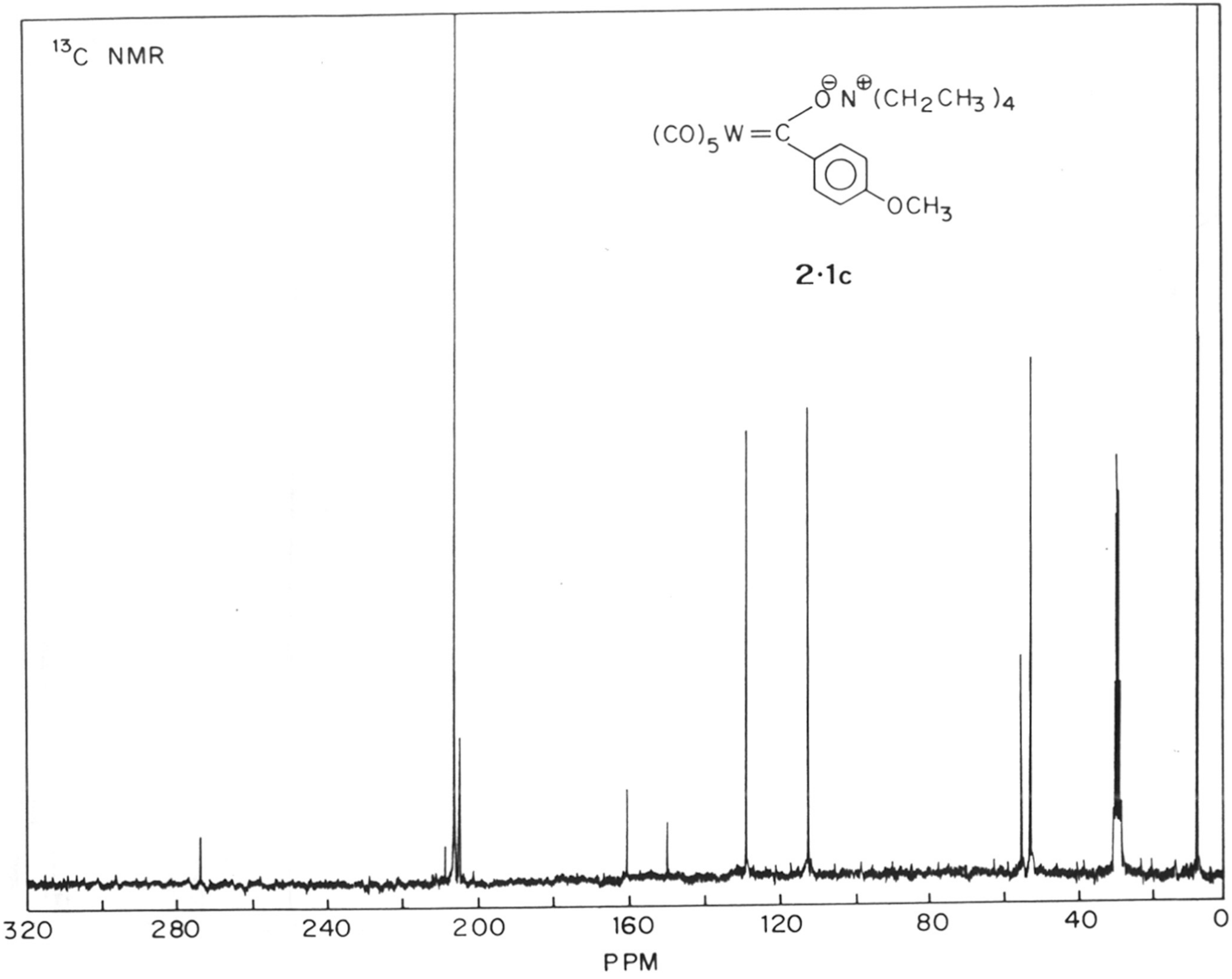
40
80
120
160
200
240
280
320
PPM



^{13}C NMR
(CO)$_5$W=C
O$^{\ominus}$ N$^{\oplus}$(CH$_2$CH$_3$)$_4$
OCH$_3$
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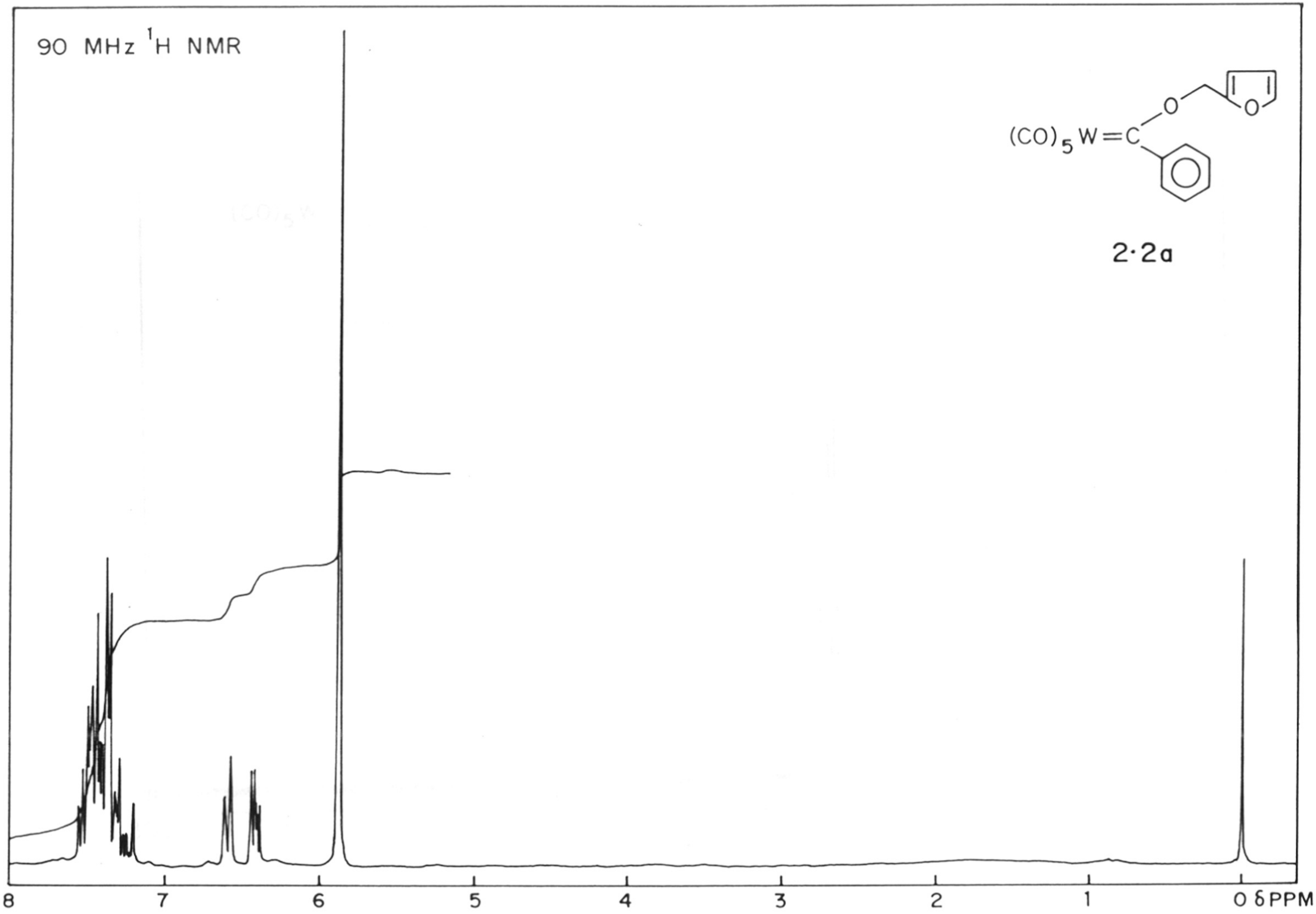
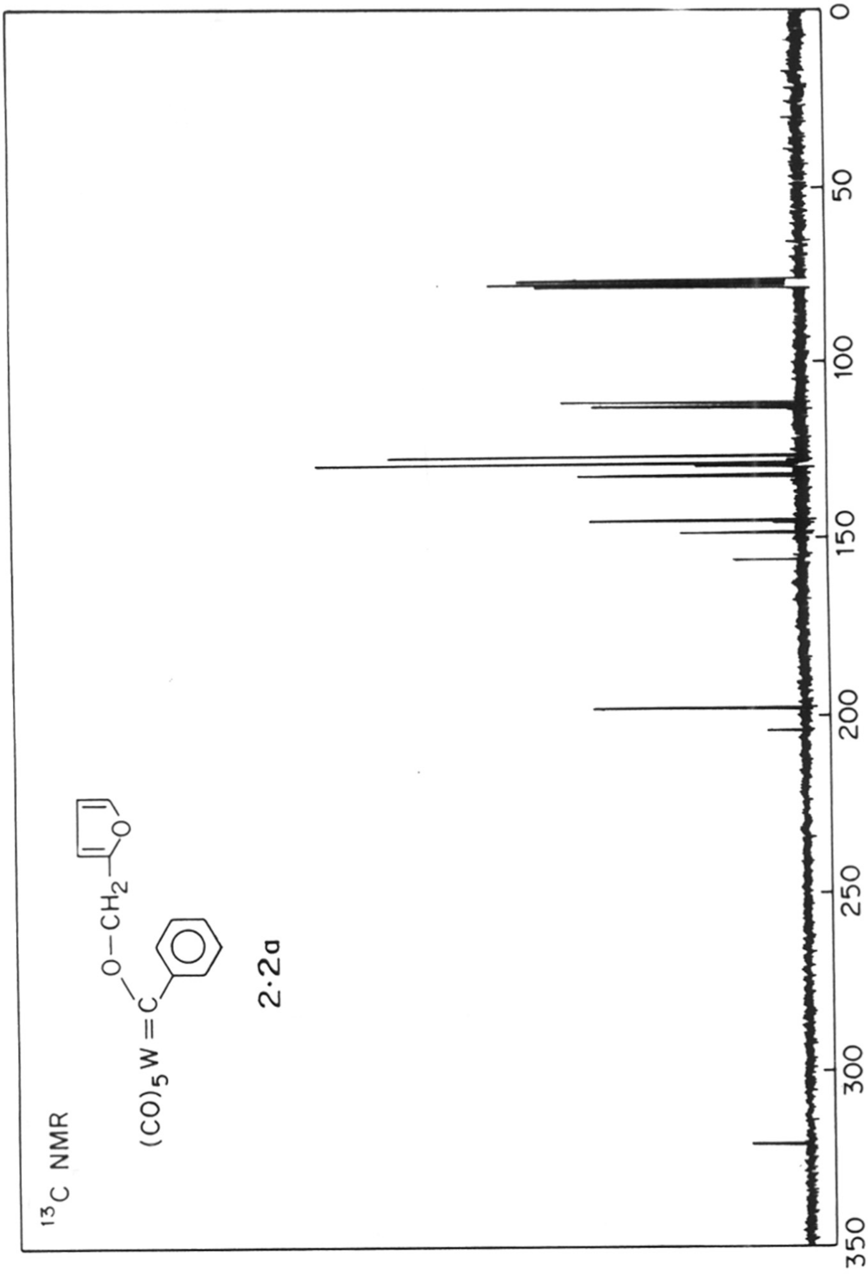
280
240
200
160
120
80
40
0
PPM

2·1c



2·2a



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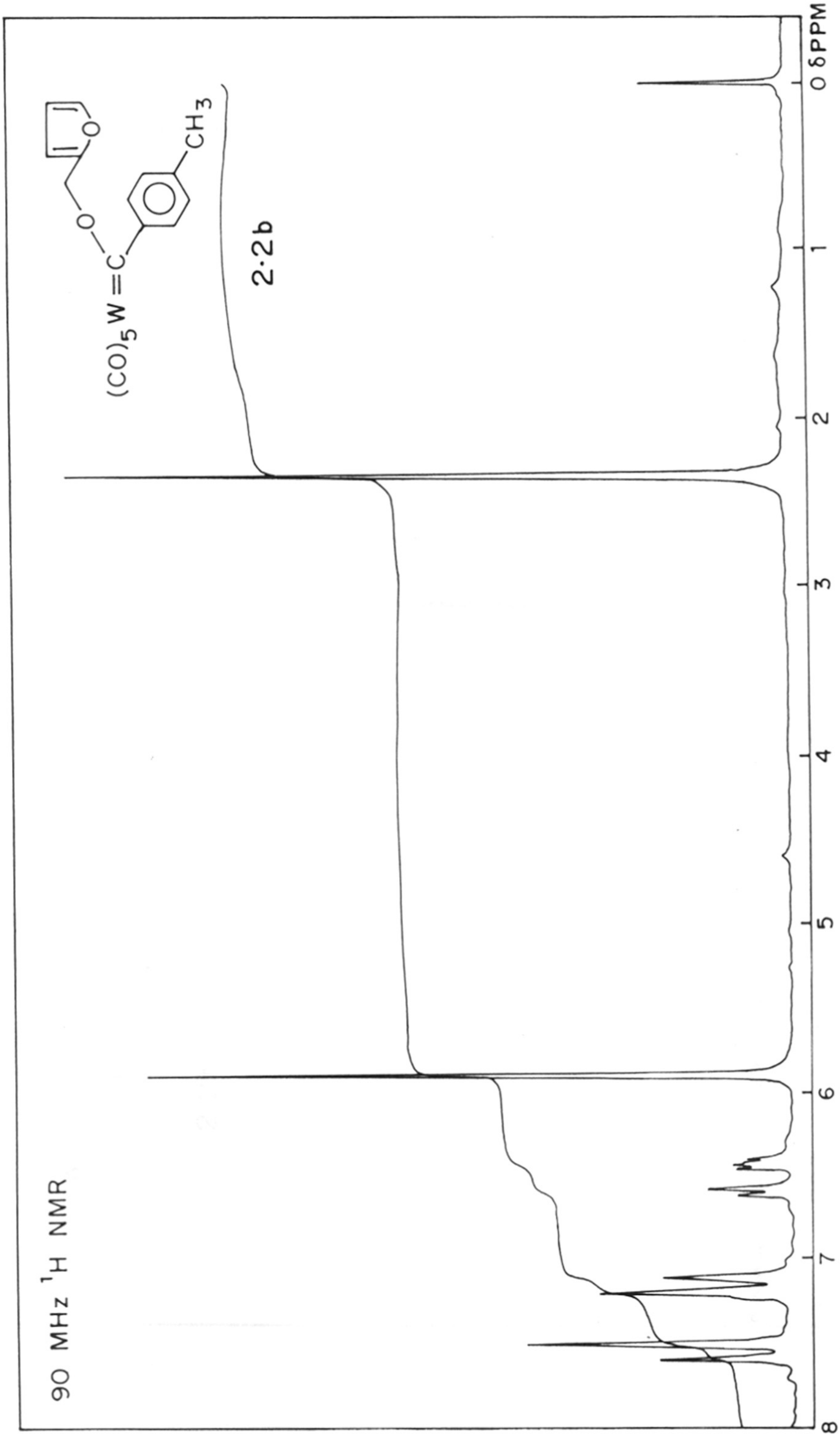
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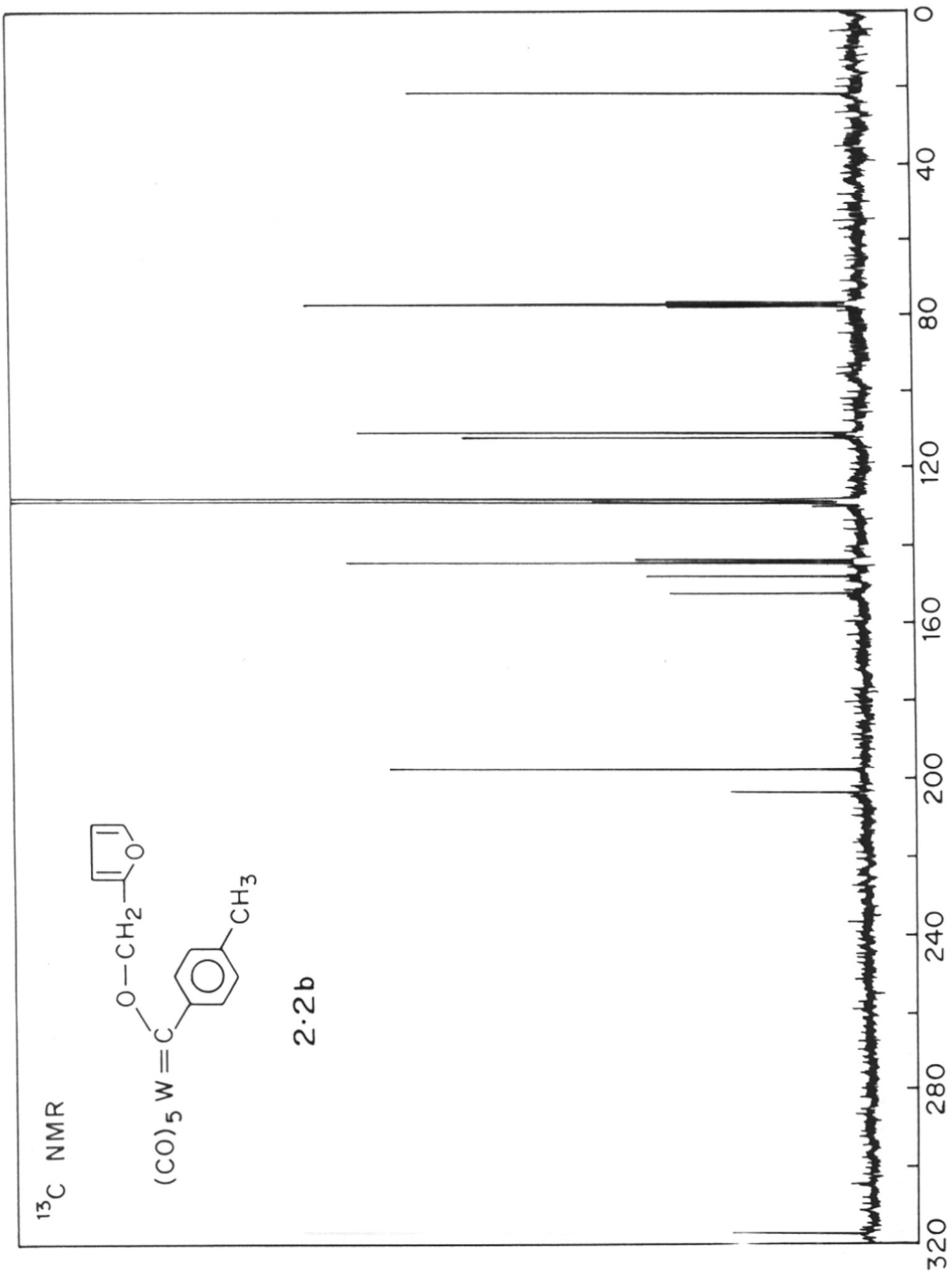
6
7
8



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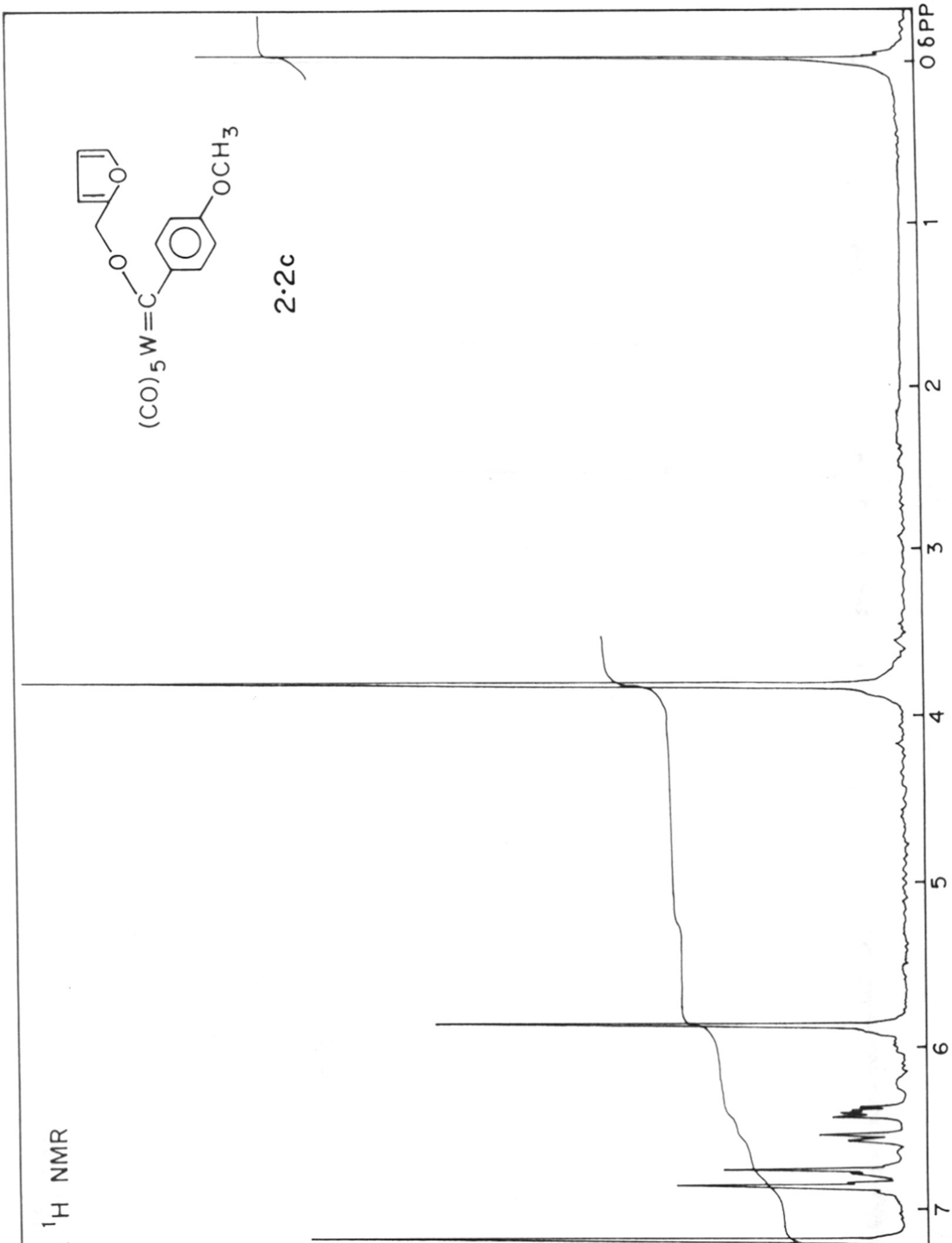
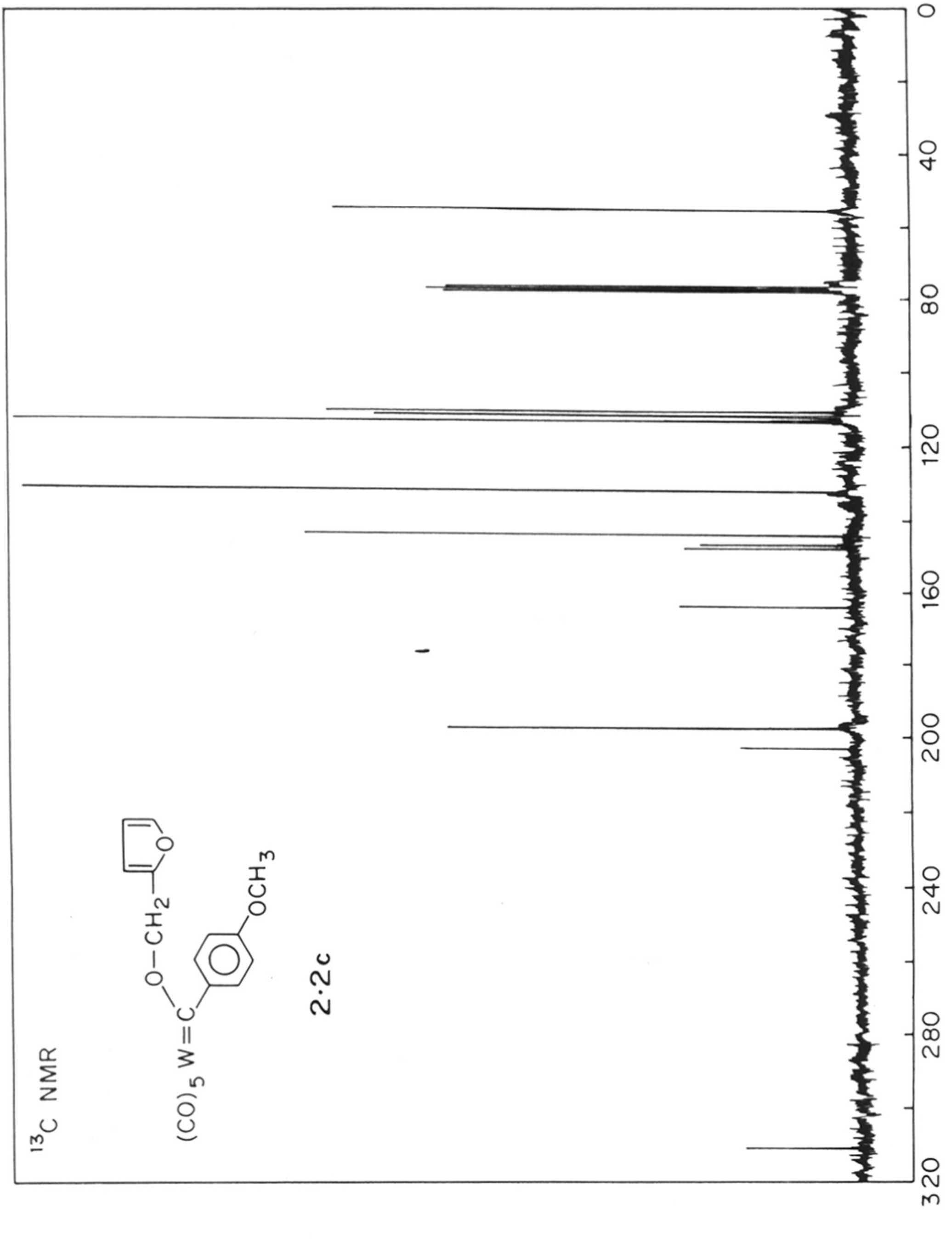
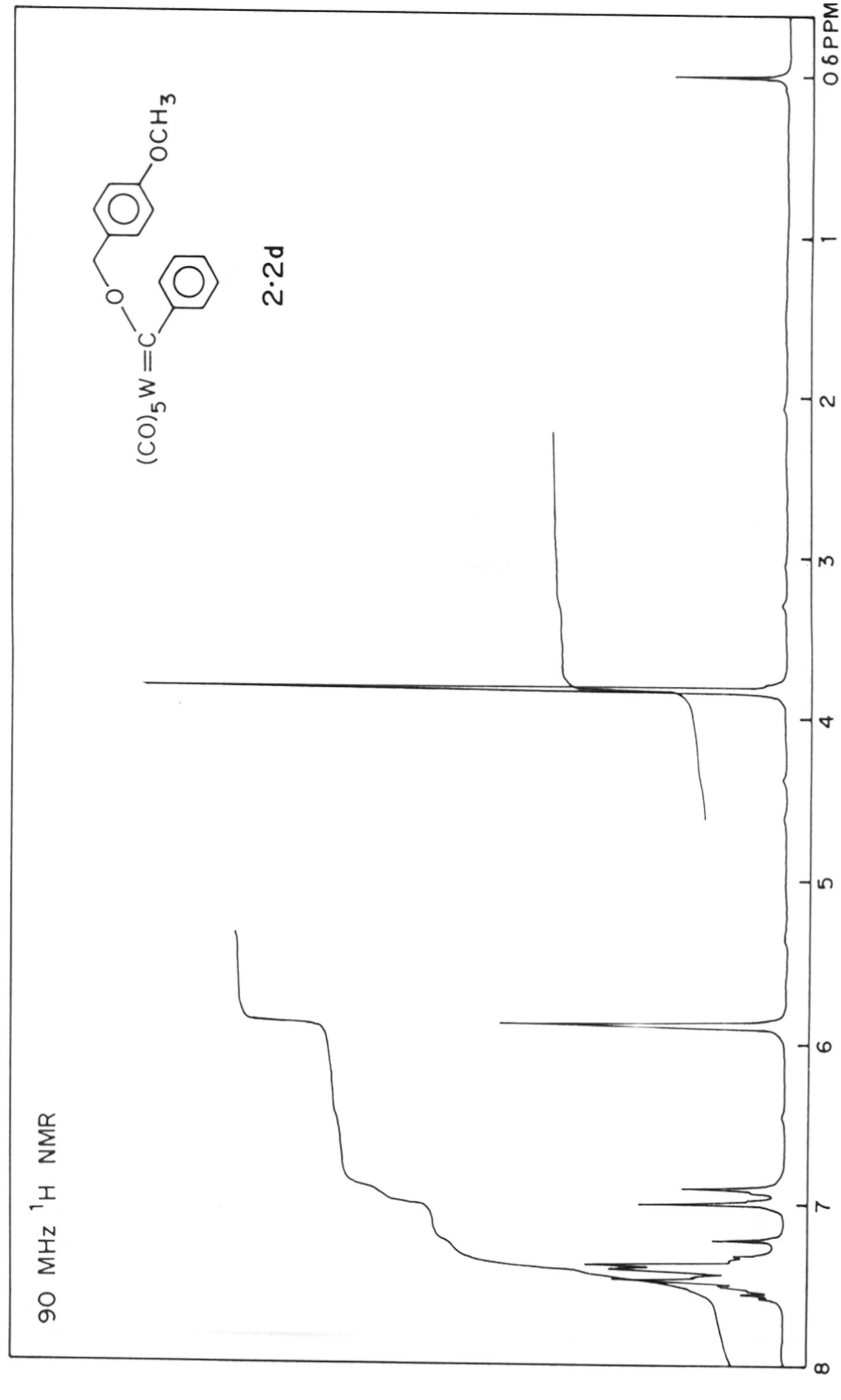


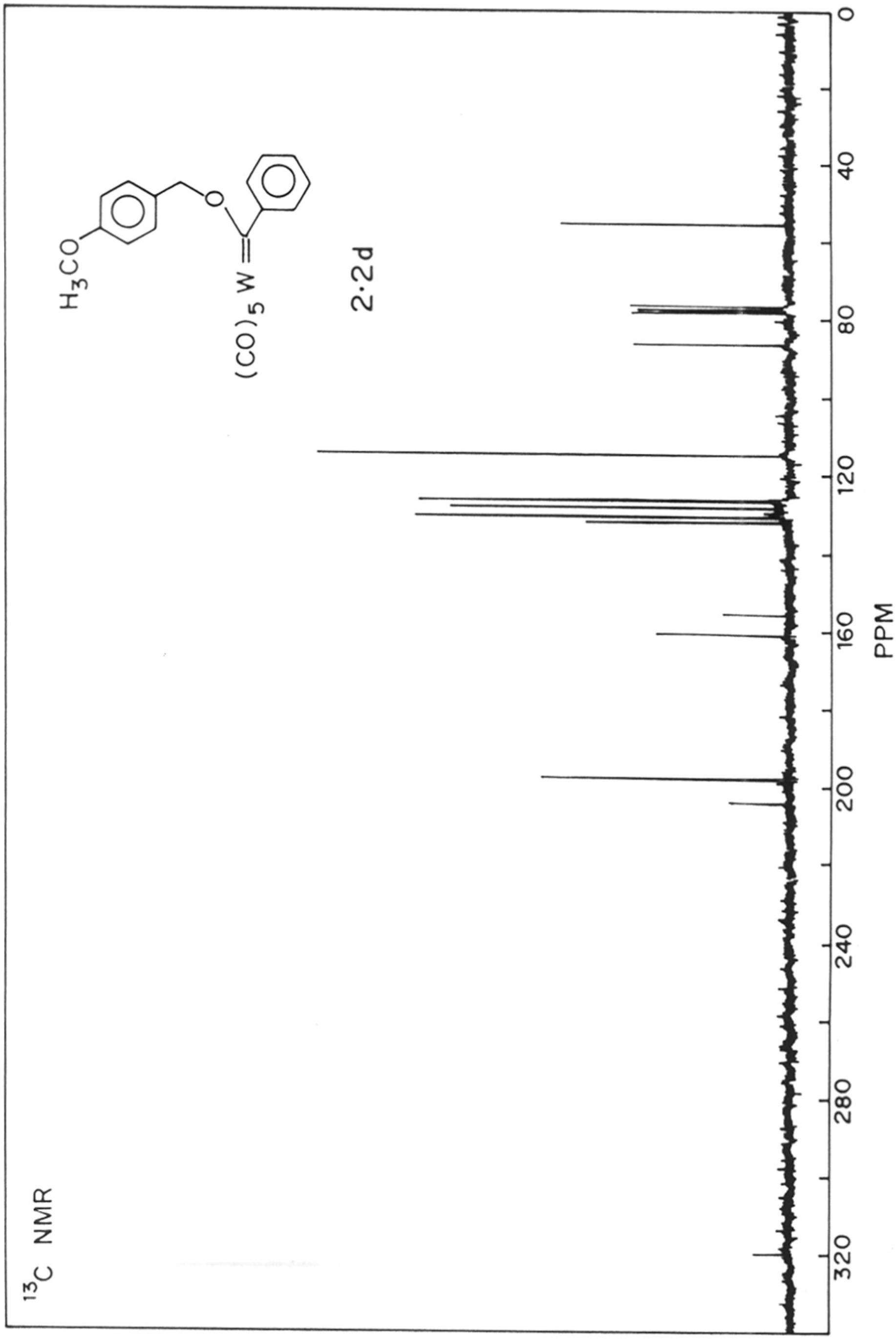
2·2c



2·2c



2·2d



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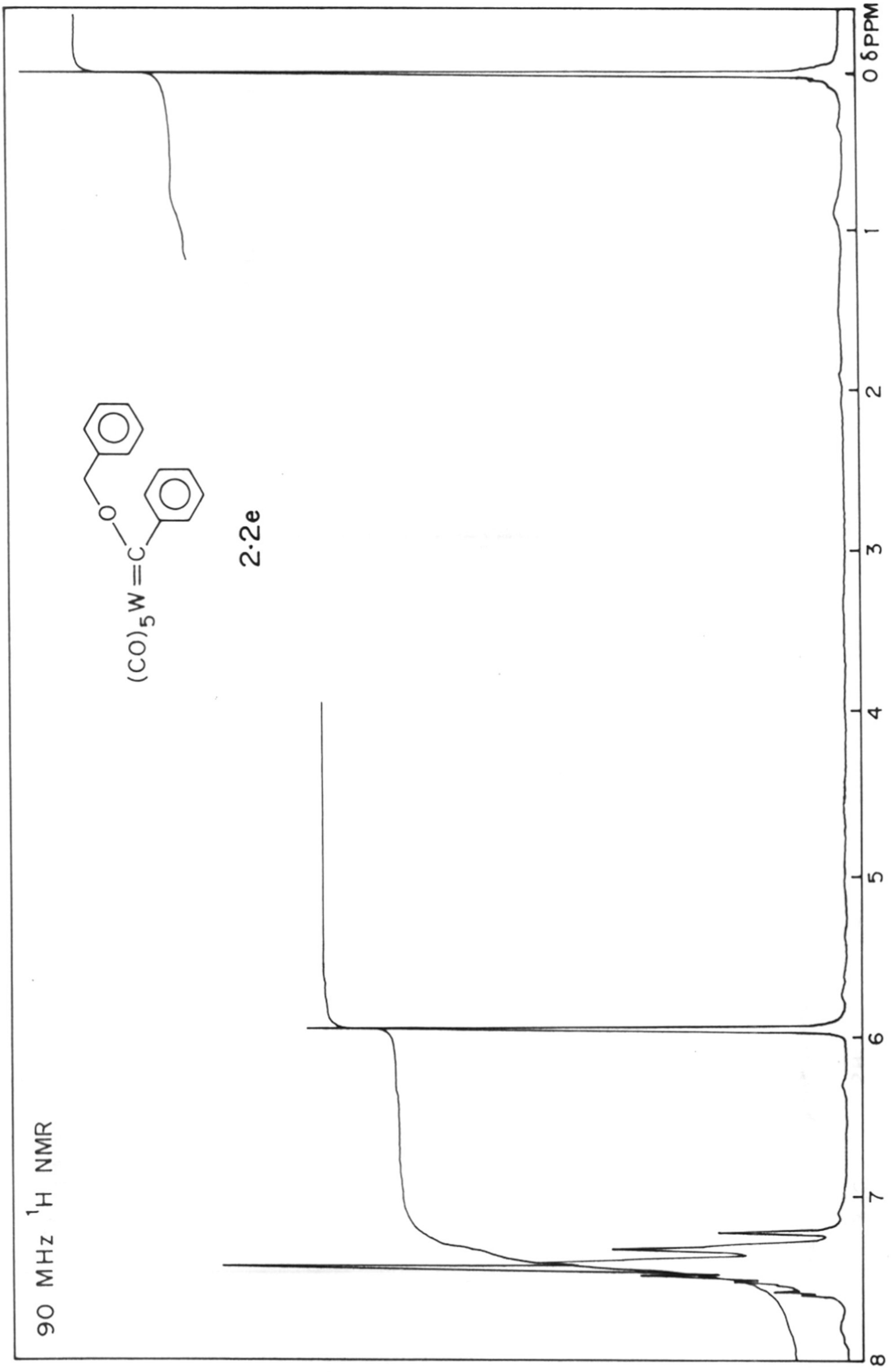
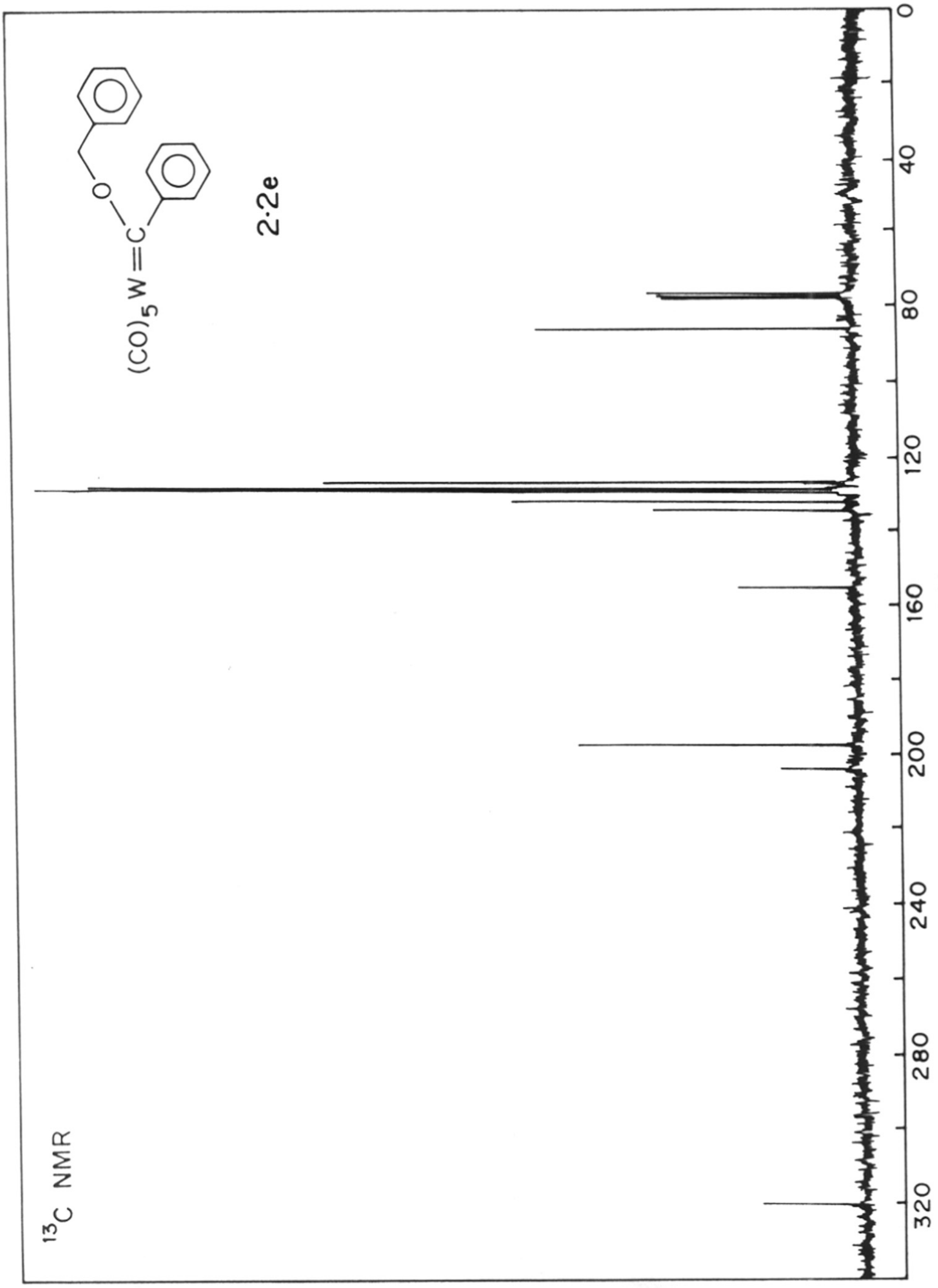
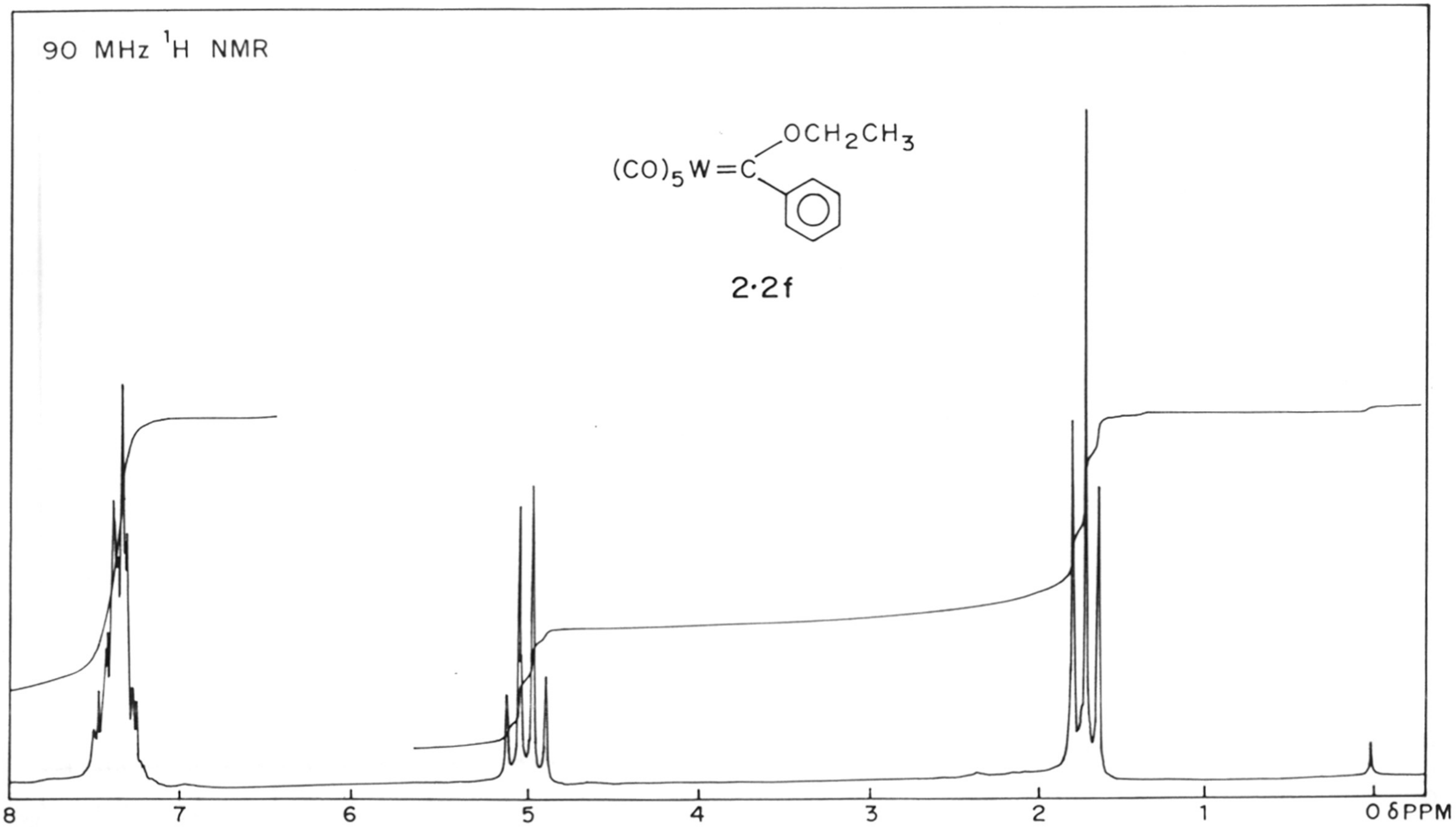


2·2e



2·2e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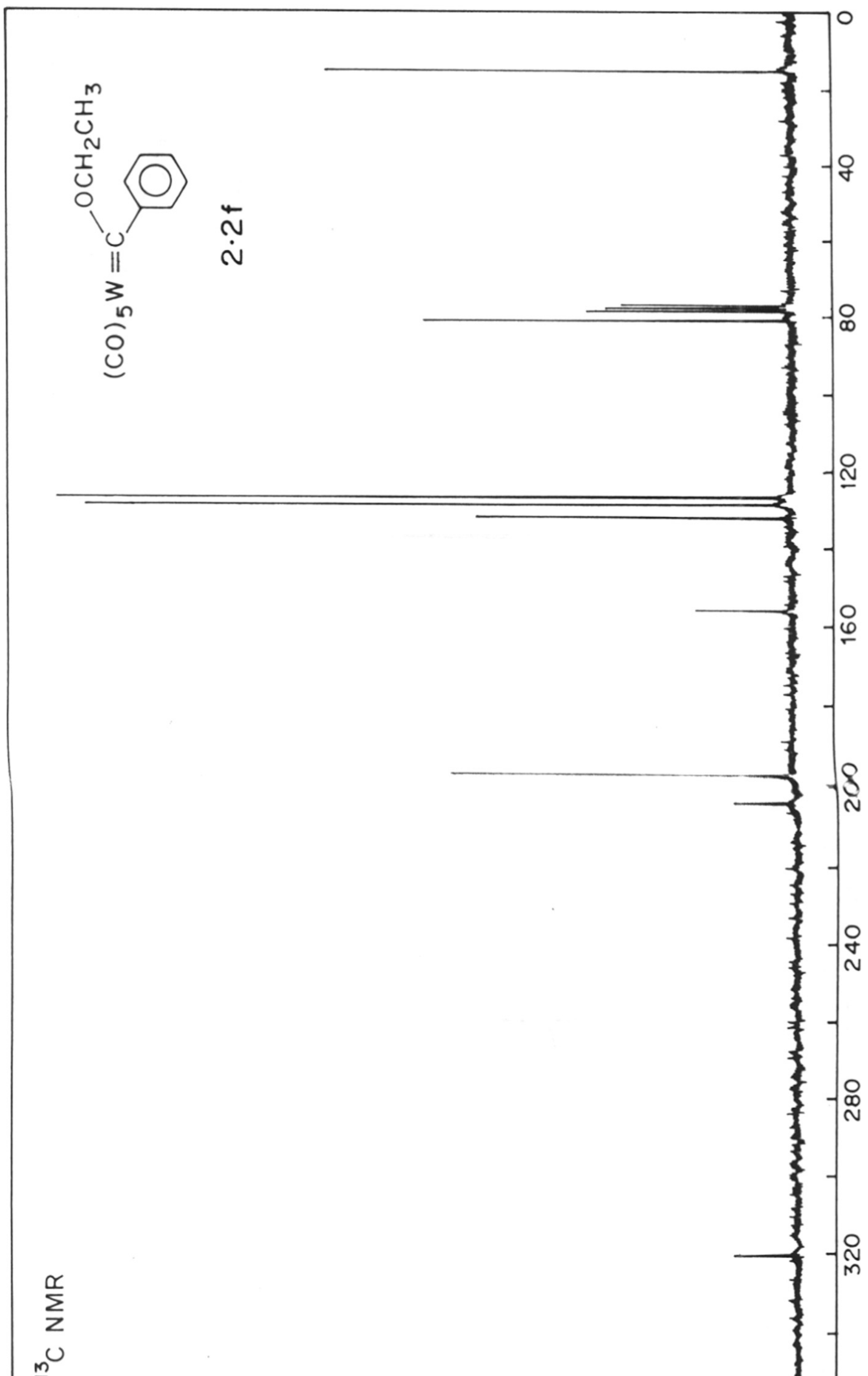
0 δPPM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2·2f
PPM
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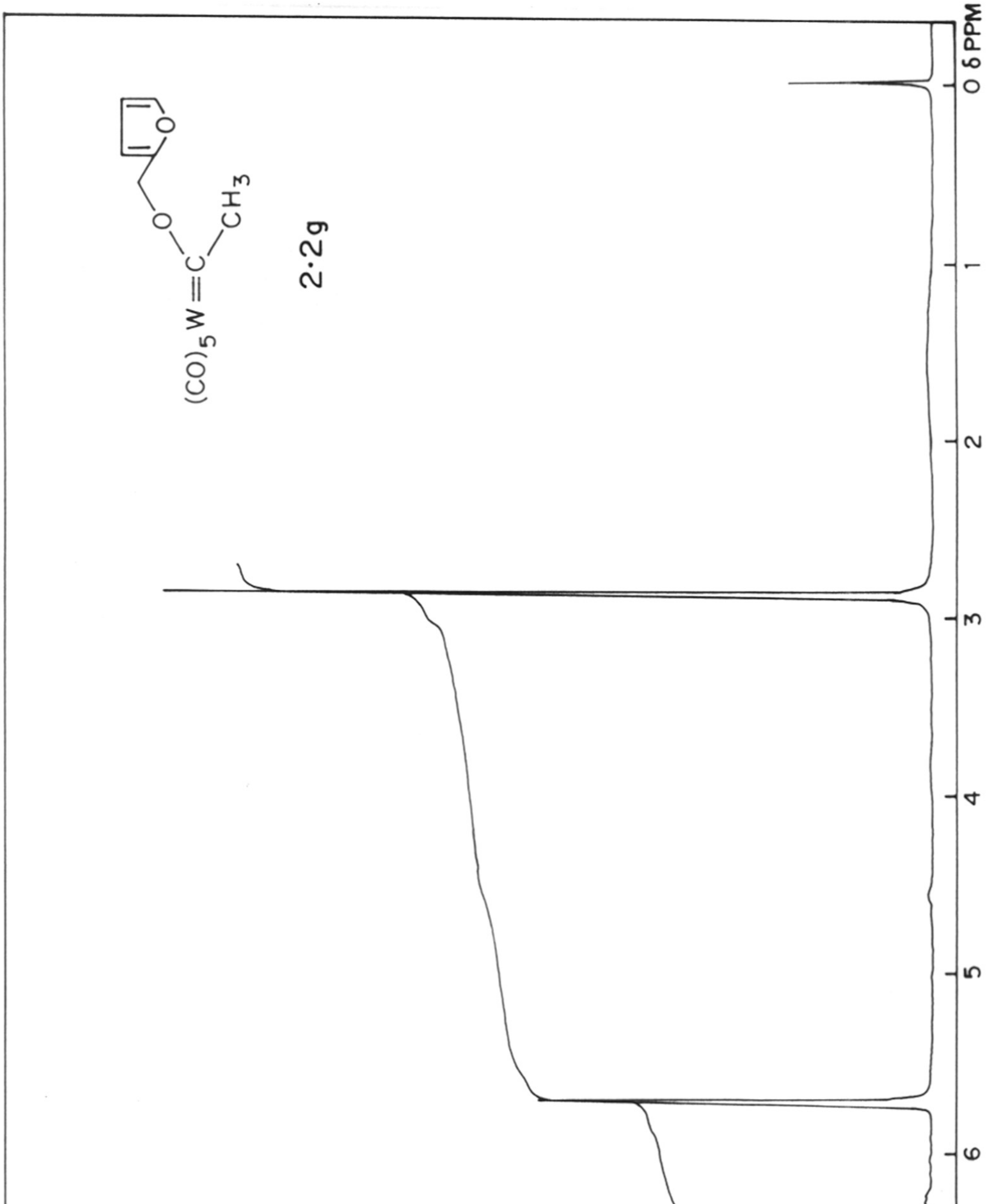
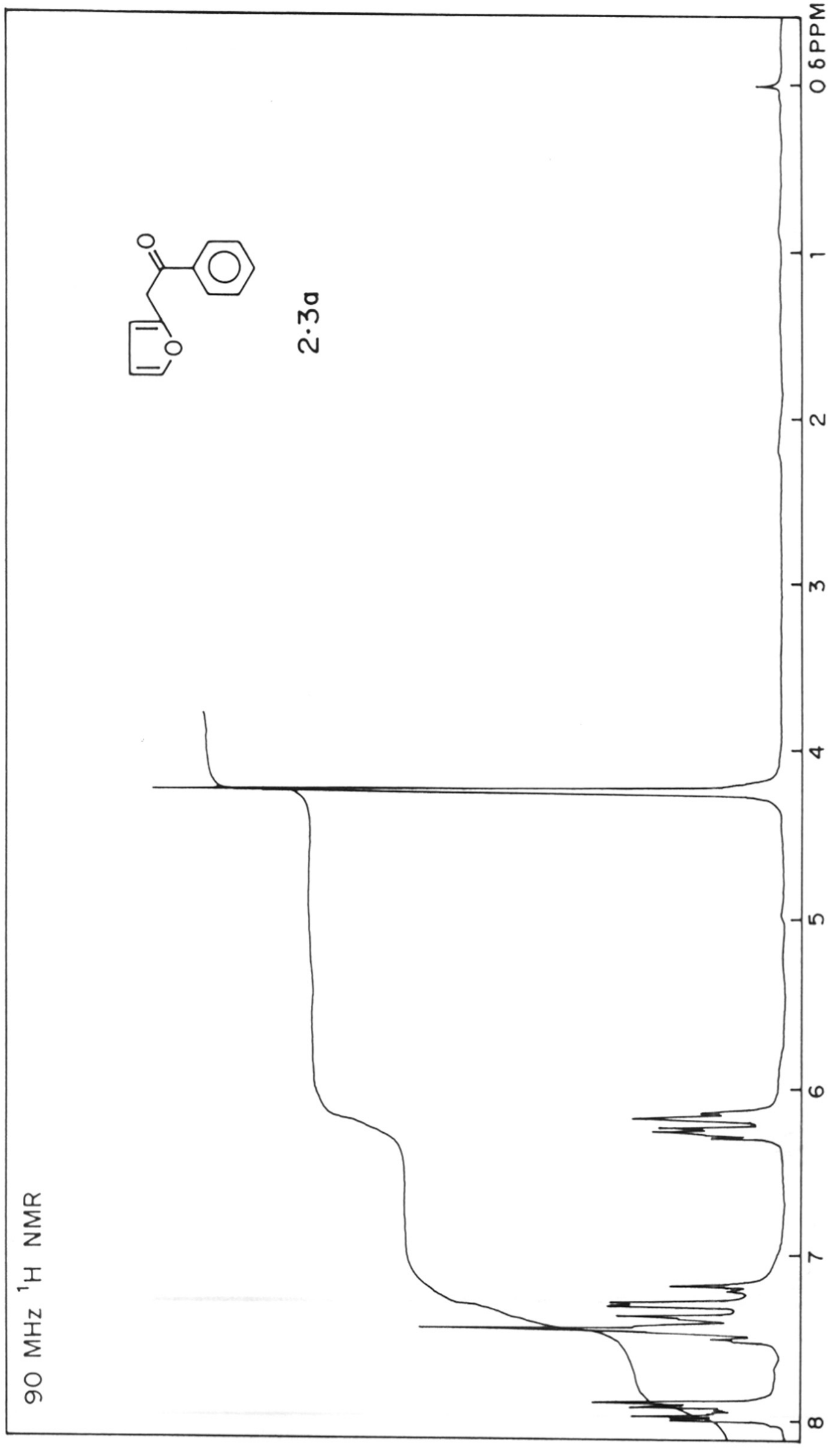


2·2g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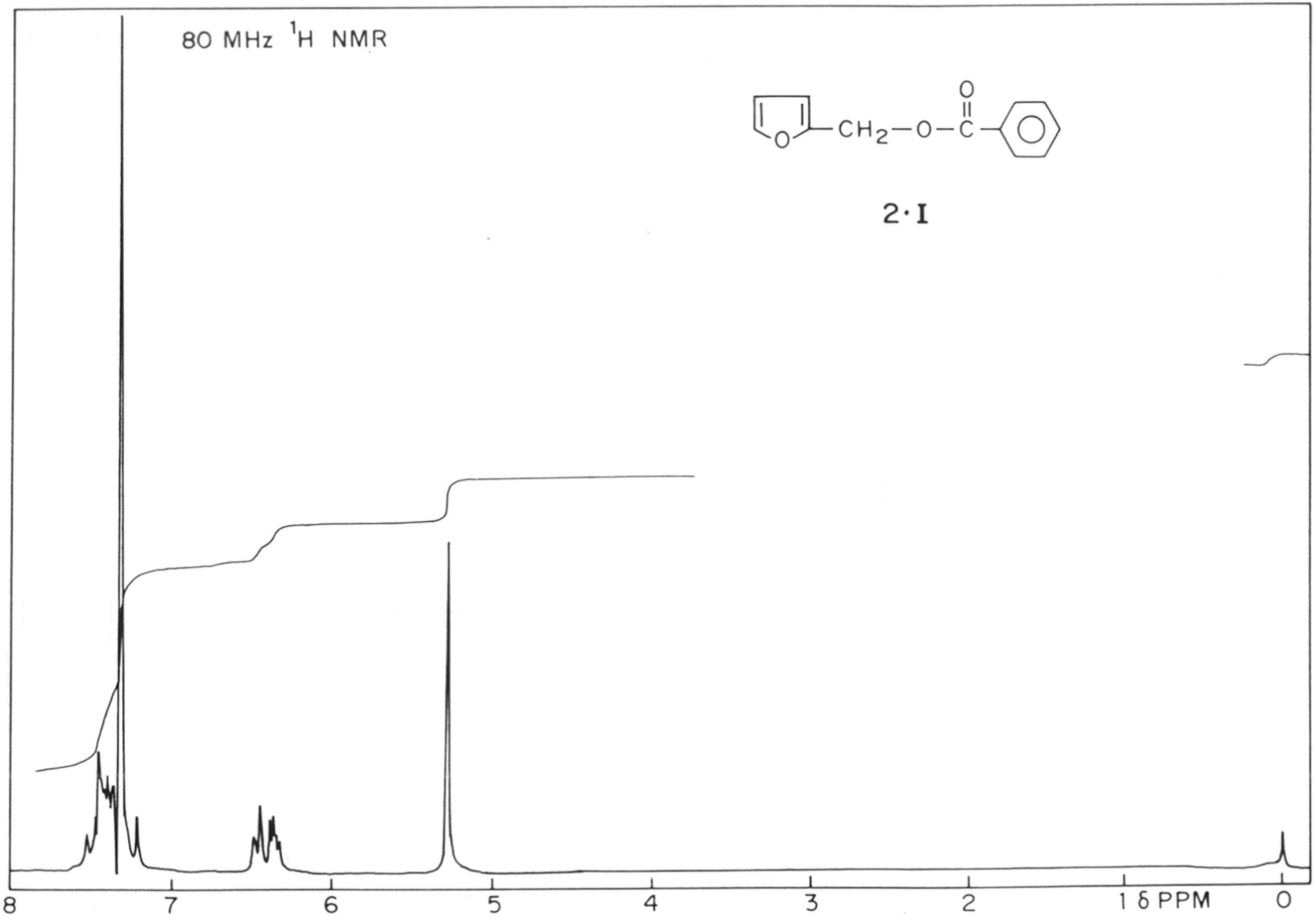
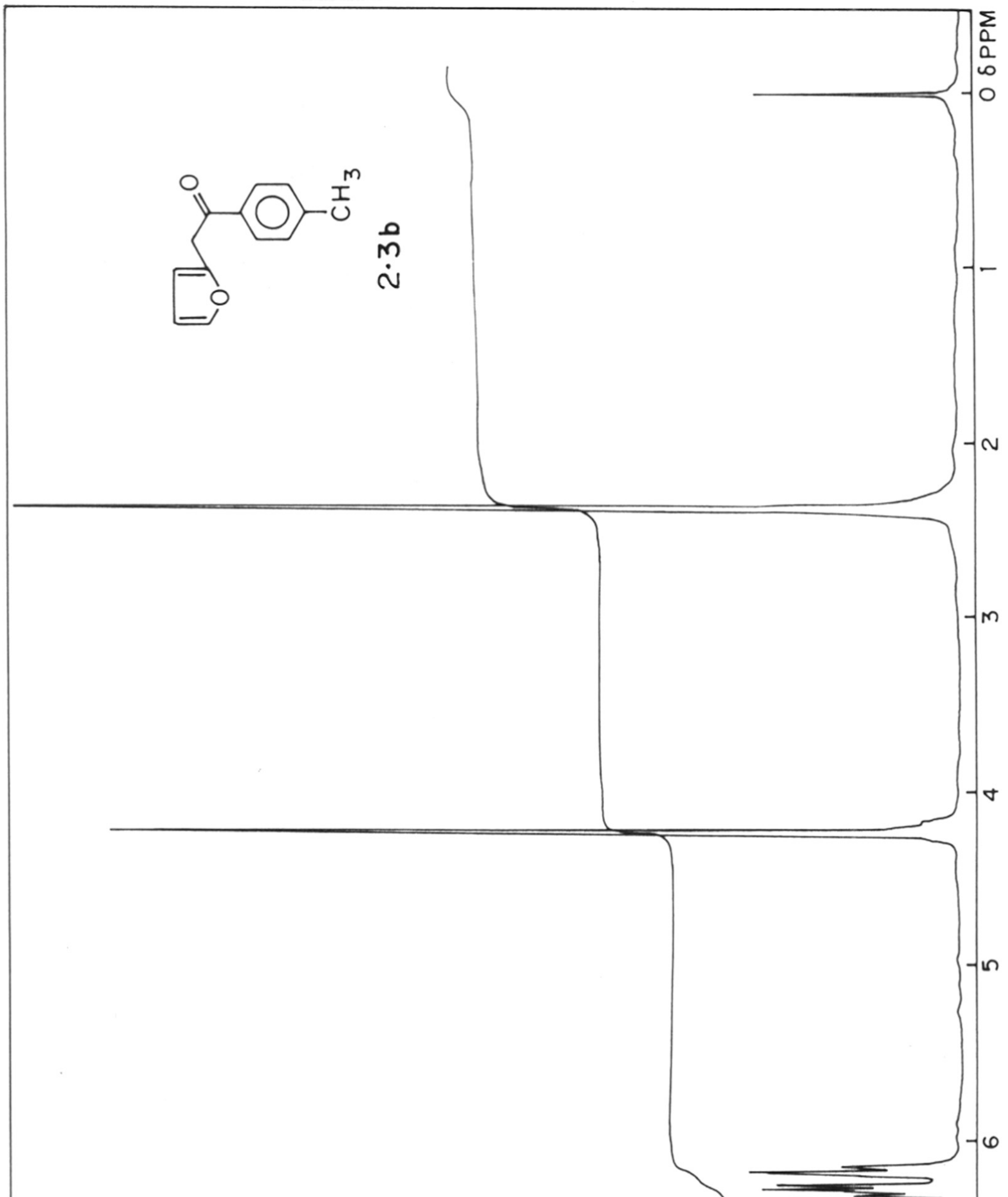
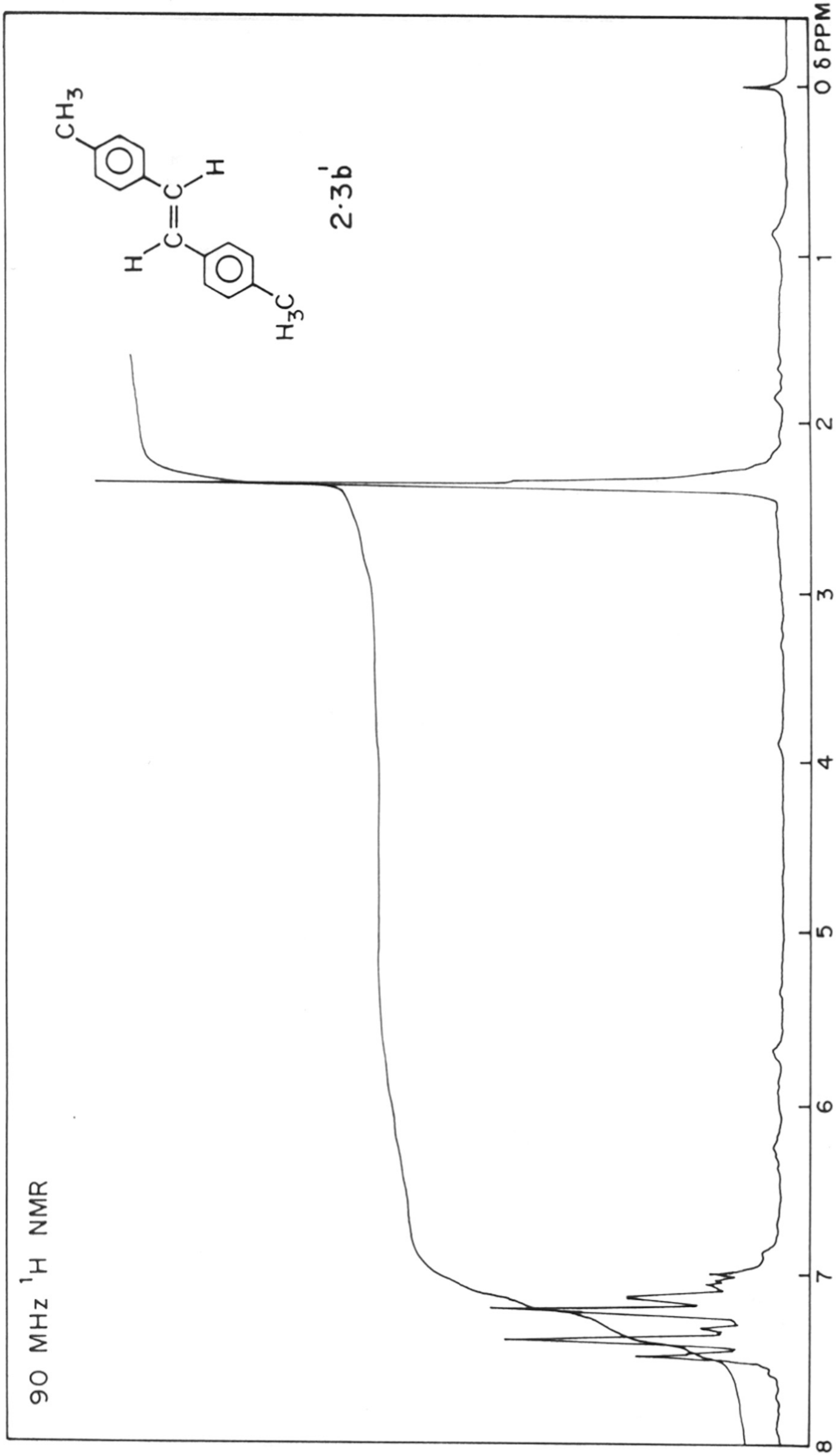
2·3a
O
O
8
7
6
5
4
3
2
1
0 δPPM



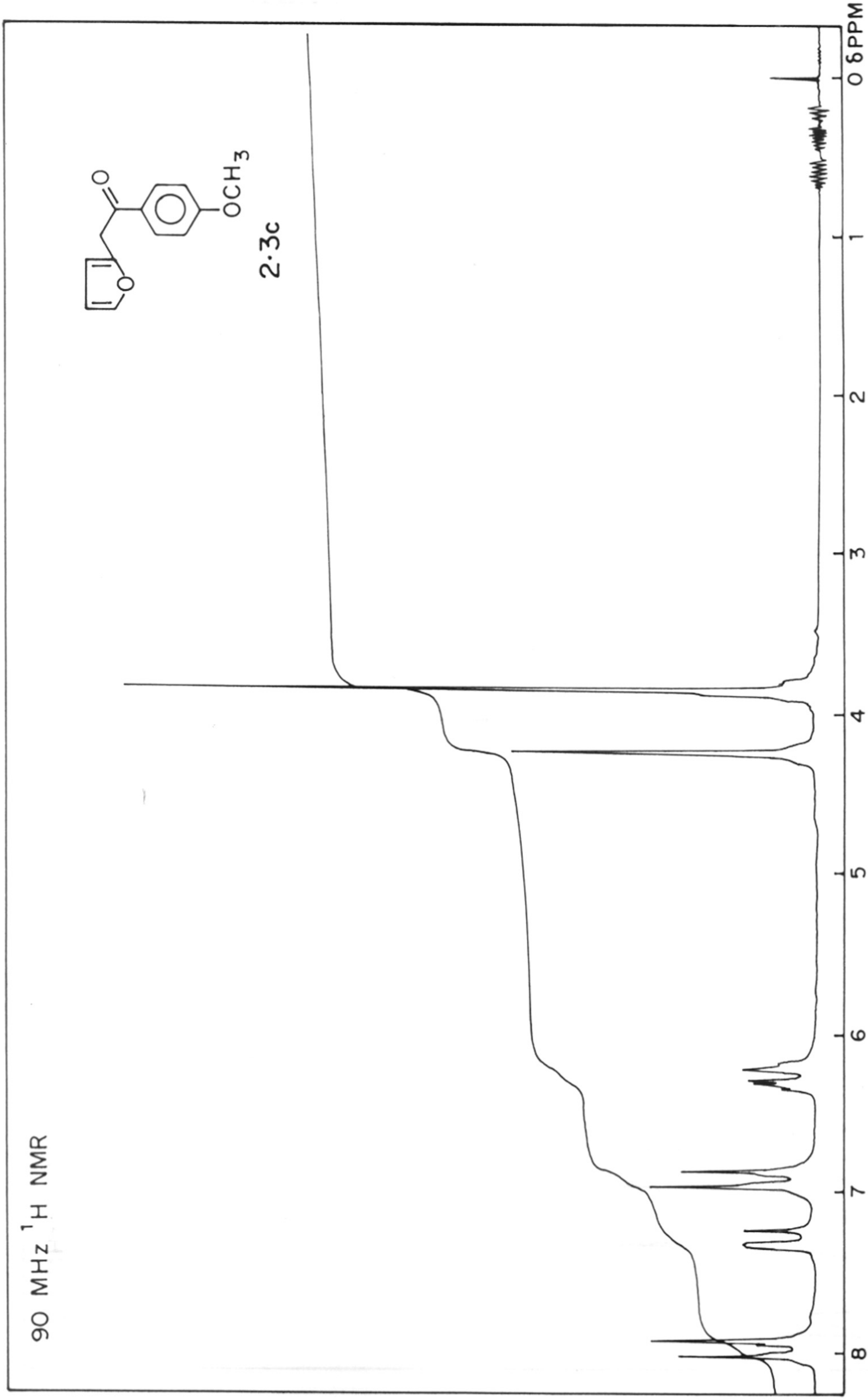
2·I



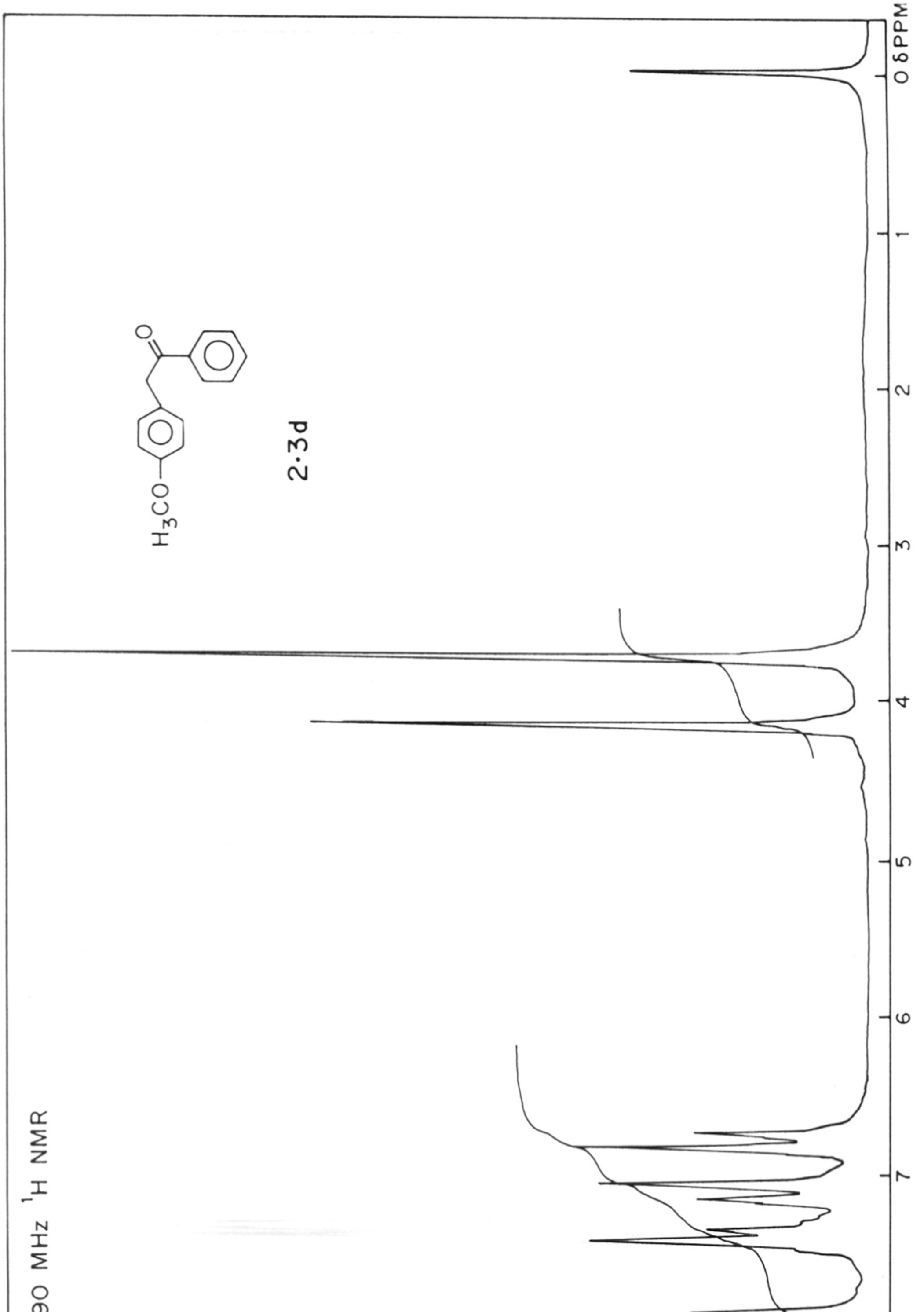
2·3b



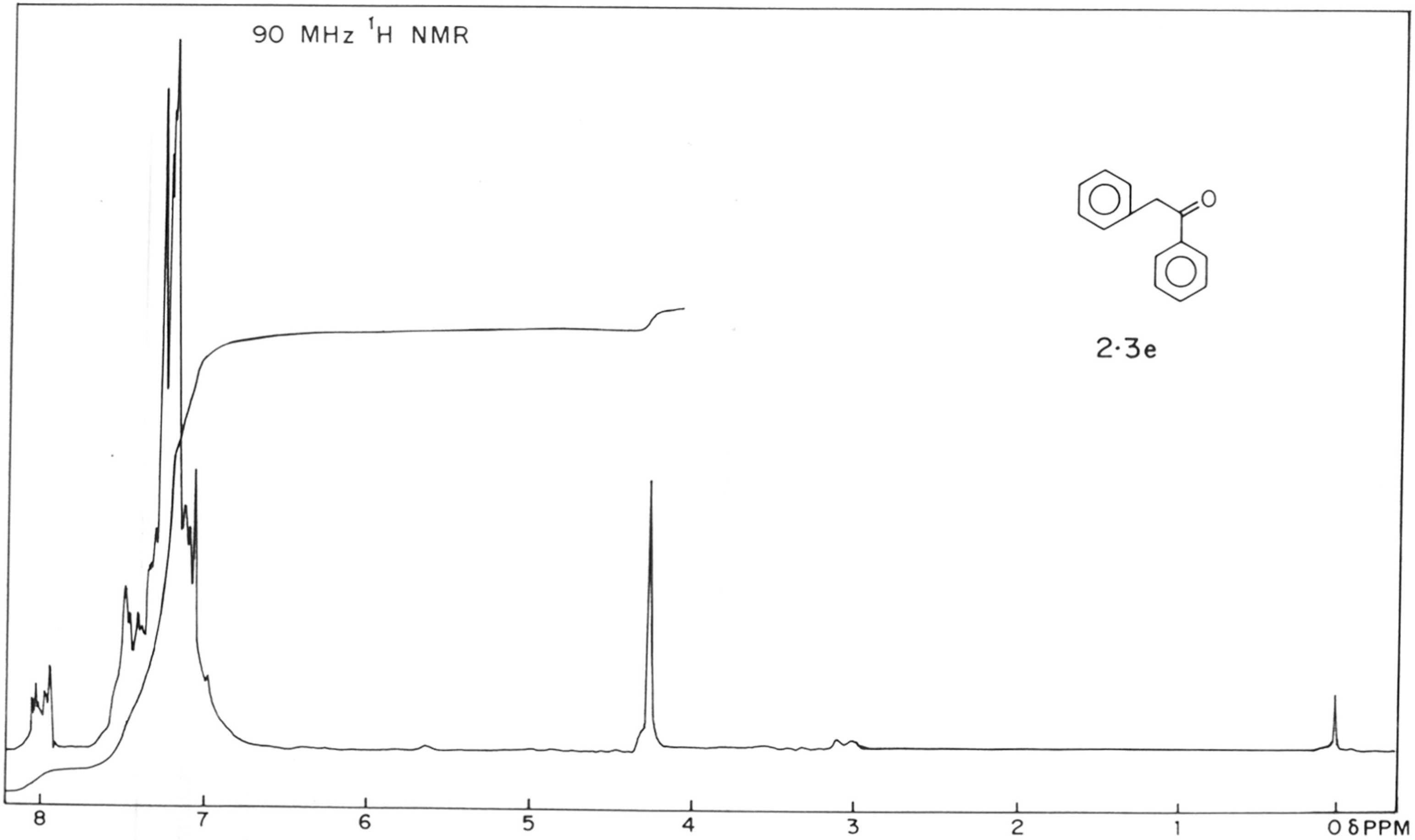
2·3b'



2·3c



2·3d



2·3e

CHAPTER 3

STUDY OF THE SCOPE AND MECHANISM OF THE REARRANGEMENT

> *"Choice, not chance,*
> *determines destiny."*

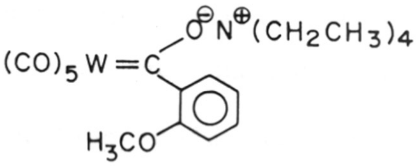
INTRODUCTION

Since the thermal rearrangement of Fischer carbene complexes of tungsten described in the previous chapter was without precedence, it was of interest to probe the mechanism of this unusual transformation. Experiments carried out in that direction are described herein.

RESULTS

In general, the carbene complexes were prepared following the same procedure as described in **Chapter-2**, and were characterized by their IR, ^1H and ^{13}C NMR spectra as well as elemental analyses.

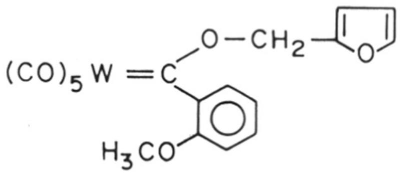
Preparation of pentacarbonyl [(*o*-methoxyphenyl) {(tetraethylammonio)oxy} carbene]tungsten(0) (3.1a)



3·1a

The yellow solid carbene salt **3.1a** (yield 83%) was prepared following the usual procedure.

Preparation of carbene complex 3.2a



3·2a

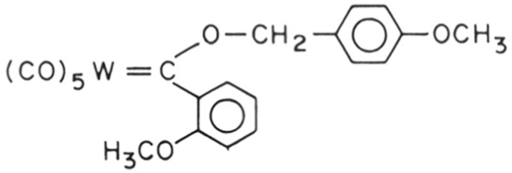
The dark red solid crystals of the carbene complex **3.2a** (yield 37%) was obtained from the carbene salt **3.1a**. These crystals were air-stable and could be preserved in the refrigerator for several months.

In the IR spectrum, the typical peaks at 2040, 2000 and 1950 cm^{-1} indicated the formation of a carbene complex. In the ^1H NMR spectrum, the singlet at 3.87 ppm was assigned to the methoxy group. The benzylic protons (OCH_2) appeared as a broad peak at 5.50 ppm. Three furan protons appeared at 6.45, 6.55, and 7.52 ppm as multiplets. The multiplets at 6.97 and 7.3 ppm were assigned to aromatic protons.

The benzylic carbon (OCH_2) appeared as broad peak at 74.71 ppm in the ^{13}C NMR spectrum. The peak at 150.20 ppm was assigned to the *ipso* carbon (carbon attached to carbene carbon). The two carbonyl carbon peaks appeared at 197.34 ppm (*cis*) and 205.78 ppm (*trans*). The carbene peak was observed at 325.21 ppm. Other aromatic carbon peaks appeared at 111.08, 111.37, 112.19, 120.45, 122.39, 130.19, 144.27, and 148.00 ppm. The aromatic carbon connected to the methoxy group was not observed. The peak at 55.63 ppm was assigned to the methoxy group.

The elemental analysis (Calculated : C 40.07, H 2.22 Found : C 40.10, H 2.43) further corroborated the structural assignment.

Preparation of carbene complex 3.2b



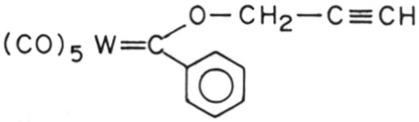
3·2b

The red crystals of the complex **3.2b** (yield 55%) were obtained from the carbene salt **3.1a**. The crystals were stable at room temperature in air. It remained unchanged in the refrigerator for several months.

The structural assignment of the complex was supported by characteristic IR absorptions. The ^{1}H NMR spectrum showed features consistent with the structure. The two benzylic protons appeared as a broad peak at 5.5 ppm. The peak at 3.8 ppm was assigned to the two methoxy groups.

In ^{13}C spectrum two methoxy groups appeared at 55.51 ppm

Preparation of carbene complex 3.2c



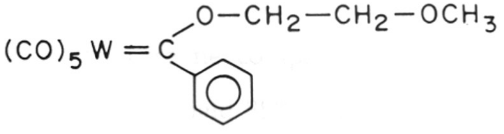
3·2c

Following a similar experimental procedure, the red, air-stable crystals of the complex 3.2c (yield 62 %) were obtained from the carbene salt **2.1a**.

The typical carbonyl absorptions was observed in the IR spectrum. The methylene proton appeared as doublet at 5.62 ppm, whereas the acetylenic proton appeared as triplet at 2.8 ppm, in the ^{1}H NMR spectrum.

In the ^{13}C NMR spectrum, the methylene group appeared at 78.28 ppm. Two acetylenic carbons appeared at 70.76 and 76.44 ppm.

Preparation of carbene complex 3.2d



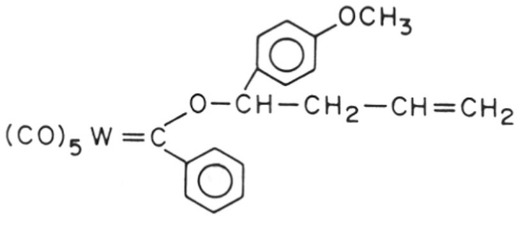
3·2d

The red, air-stable crystals of the complex **3.2d** (yield 80%) were obtained from the carbene salt **2.1a**. These crystals were reasonably stable at room temperature and could be stored in refrigerator for several months.

The IR spectrum showed the characteristic absorptions, while the ^{1}H NMR spectrum displayed expected signals. The singlet at 3.22 ppm was assigned to the methoxy group. Two methylene groups appeared at 3.75 and 4.84 ppm as multiplets.

In the ^{13}C NMR spectrum, the peak at 59.50 ppm was assigned to the methoxy group. The peaks at 70.67 and 82.89 ppm were assigned to two methylene groups.

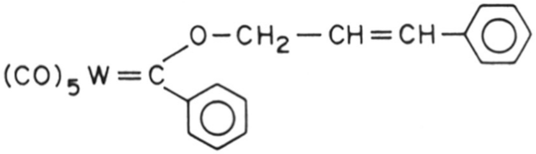
Attempted Preparation of carbene complex 3.2e



3·2e

Attempts were made to isolate the carbene complex **3.2e** by the usual method. However, the cyclopropanation product (yield 85%) was obtained directly from the reaction mixture during work-up. The structure and stereochemistry of the compound **3.3e** was assigned by comparison with reported data for a similar compound[1].

Preparation of carbene complex 3.2f



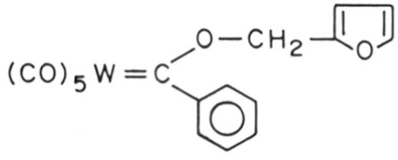
3·2f

The complex **3.2f** was obtained as a red liquid (yield 56%) from the carbene salt **2.1a**. This complex was thermally labile and air-sensitive.

The IR spectrum showed characteristic CO absorptions of the carbene complex. The benzylic protons appeared as a doublet (J = 4Hz) at 5.65 ppm. Two olefin protons appeared as multiplets at 6.65 and 6.95 ppm.

In the ^{13}C spectrum, expected peaks were observed and they could be easily assigned. However, satisfactory elemental analysis could not be obtained.

Photolysis of the carbene complex 2.2a



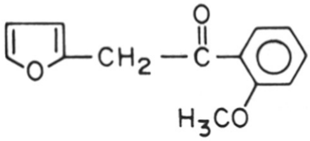
2·2a

Photolysis of the carbene complex **2.2a** was carried out at room temperature at 350 nm. The complex was dissolved in dry and degassed benzene prior to irradiation. During the course of reaction, initial red color of the solution gradually faded and it became almost colorless over a period of 10 hours, and the product **2.3a** (yield 57%) was isolated by silica gel column chromatography using 10% ethyl acetate/petroleum ether.

Thermal rearrangement of the complex 2.2a in benzene-d_6 in NMR probe

A solution of the complex **2.2a** in benzene-d_6 (10 mg/0.5 ml) was heated in a NMR tube inside the probe. The initial temperature was kept at 43°C and the temperature was raised to 65°C over a period of 2 hours and spectra were recorded at regular interval. No peak other than those belonged to starting material and the rearranged product, was observed.

Thermolysis of the carbene complex 3.2a : formation of the product 3.3a

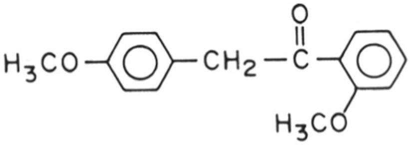


3·3a

Thermolysis was carried out following the same experimental procedure as described in **Chapter-2**. The product **3.3a** (yield 57% in benzene and 63% in toluene) was isolated as a pale yellow liquid. The rate of the reaction was better in toluene (2 h) than in benzene (10 h).

The IR spectrum showed usual absorption for ketone. In the ^{1}H NMR spectrum, the singlet at 3.95 ppm was assigned to the methoxy group.

Thermolysis of the carbene complex 3.2b : formation of the product 3.3b



3·3b

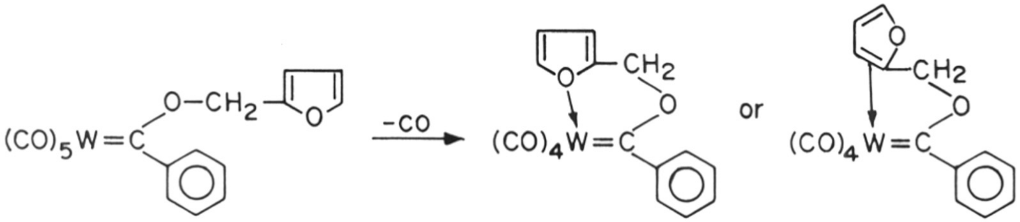
The product **3.3b** was obtained (yield 53% in benzene, 14 h, 57% in toluene, 3 h) as a white solid from the thermolysis of the carbene complex **3.2b**.

Identity of the product was established from the IR absorption in the carbonyl region. Two methoxy groups appeared at 3.68 ppm as a singlet in ^{1}H NMR spectrum.

DISCUSSION

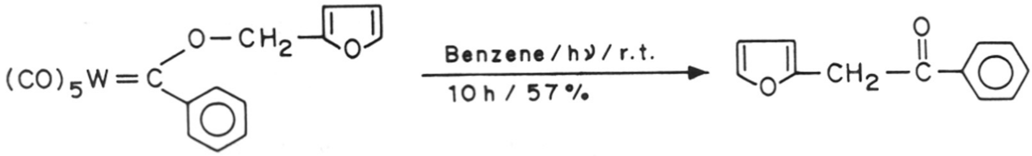
In general, furfuryloxy carbene complexes (**2.2a-c**) required less time and lower temperature for the rearrangement than the benzyloxy carbene complex **2.2e**. Although the complex **2.2d** was rearranged to the ketone (**2.3d**) at lower temperature (benzene reflux), the reaction was considerably slow. It was also observed that the corresponding benzyloxy carbene complexes of chromium required less temperature for this unusual rearrangement[2]. Since a W-CO bond is stronger than a Cr-CO bond, higher temperature is usually necessary to remove a CO ligand from the tungsten complex than from chromium. It is possible that intramolecular participation of the furan moiety in the displacement of a CO ligand, reduces the reaction temperature for the furfuryloxy carbene complexes of tungsten as shown below (**Scheme 1**).

Scheme 1



Taken together, these facts indicate that the initial CO dissociation could be the rate determining step in the overall transformation. In such a case, if a CO ligand is selectively removed by photolysis, the reaction should proceed at room temperature. Indeed, photolysis of the complex **2.2a** in benzene at room temperature resulted in the formation of the keto compound **2.3a** (**Scheme 2**).

Scheme 2

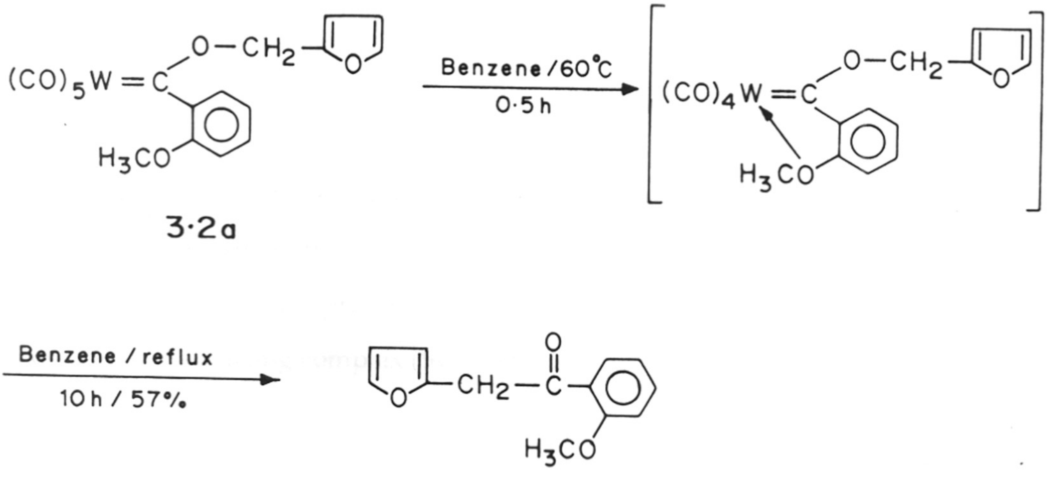


2·2a 2·3a

The initial loss of CO ligand leads to a coordinatively unsaturated intermediate. If a donor group present in the molecule can form a chelate and thus generate a stable 18e intermediate, it might be even isolated and characterized[3]. Such a chelated complex could then undergo the rearrangement on further heating in benzene or toluene.

Thus, the complex **3.2a** was heated in benzene at 60°C. Formation of a new complex was observed (TLC) within half an hour. Heating was continued for 10 h during which period the product ketone **3.3a** was formed in moderate yield (**Scheme 3**).

Scheme 3

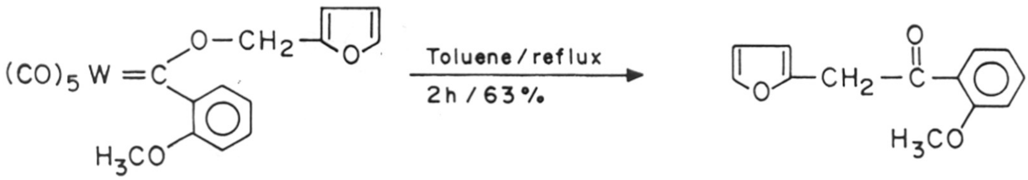


3·3a

During the initial stages of the reaction (2 h), TLC showed spots corresponding to the starting material and the presumed chelated complex resulting from initial CO dissociation. All attempts to isolate this intermediate by chromatography failed. Eventually the spot corresponding to this labile intermediate diminished in intensity as the spot corresponding to the product ketone developed.

When the reaction was carried out in toluene, the complex **3.2a** underwent rearrangement within two hours to furnish the keto compound **3.3a** in comparable yield (**Scheme 4**).

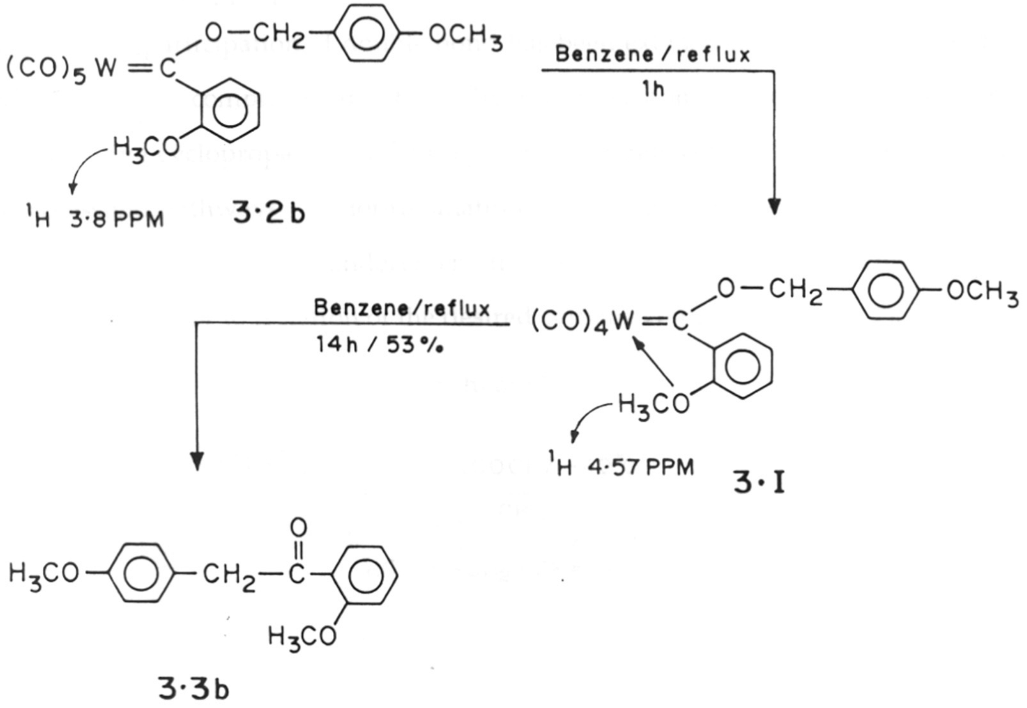
Scheme 4



3·2a   3·3a

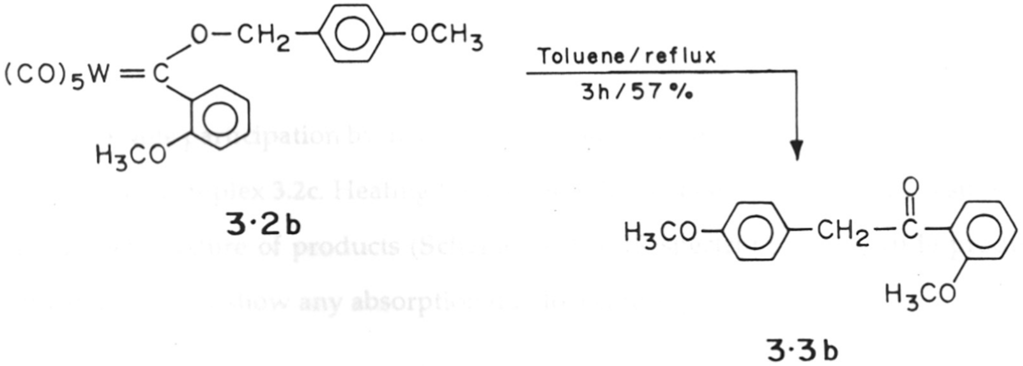
The reaction of the complex **3.2b** was similar to that of the complex **3.2a**. In this case, a small amount of the chelated intermediate (I) could be isolated. In the ^{1}H NMR spectrum, the methoxy proton resonance was shifted downfield compared to its position in the starting complex (**Scheme 5**).

Scheme 5



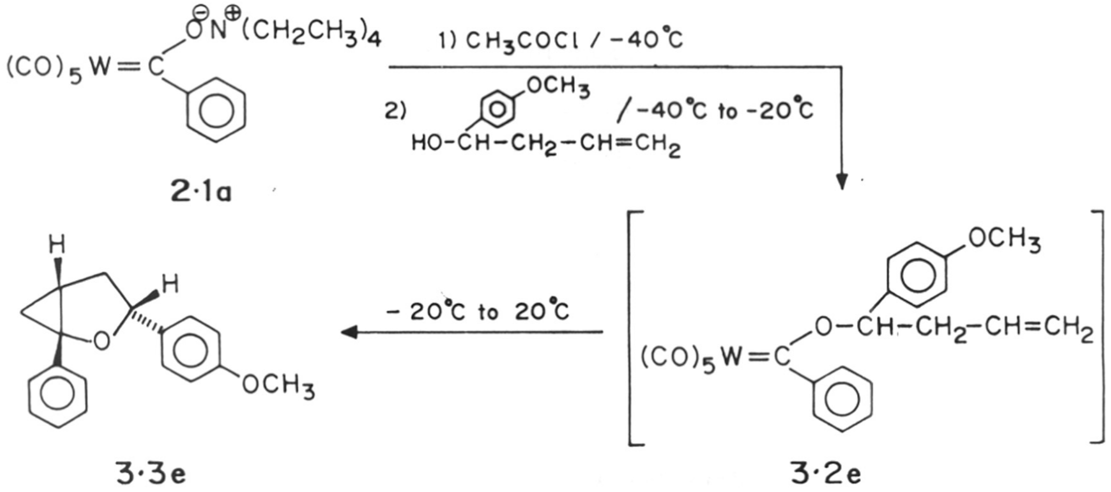
The rate of rearrangement of the complex **3.2b** in toluene was much faster than the rate observed in benzene (**Scheme** 6).

Scheme 6



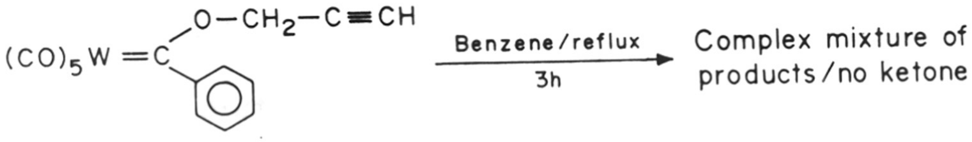
On a similar line, one could envisage that assistance to CO dissociation might also be effected by appropriate donor substituents on the alkoxy group of the carbene complex. The participation of double bond has been extensively studied[4]. While the allyloxy carbene complexes are thermally unstable, homoallyloxy complexes are known to give cyclopropanes[5] on heating. To investigate competitive rates for these two accessible pathways - cyclopropanation *vs* rearrangement - the preparation of carbene complex **3.2e** was undertaken. It was found that cyclopropanation had occurred even prior to isolation of the desired carbene complex (**Scheme** 7).

Scheme 7



Possible participation by an acetylenic group was investigated by thermolysis of the carbene complex **3.2c**. Heating the complex **3.2c** in benzene or toluene resulted in a complex mixture of products (**Scheme** 8). The IR spectrum of the crude product, however did not show any absorption due to a carbonyl function.

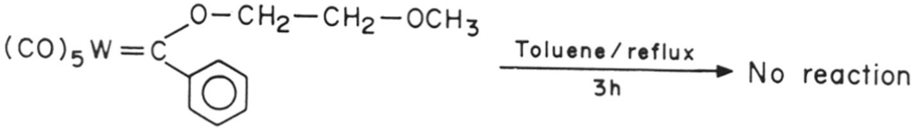
Scheme 8



3·2c

No change was observed when the carbene complex **3.2d** was heated in refluxing benzene or toluene for long periods of time (12 h), indicating that the aliphatic methoxy group could not complex with the metal as readily as was observed for the complex **3.2a** or **3.2b** (**Scheme** 9).

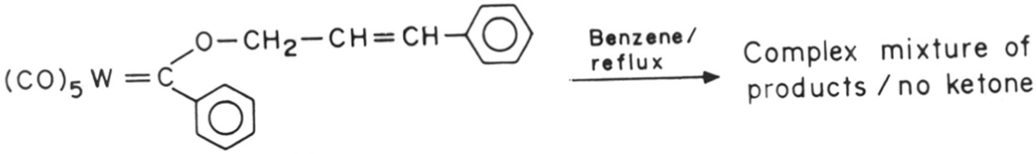
Scheme 9



3·2d

The fate of the complex **3.2f** was similar to that of complex **3.2c**. No ketone could be identified in a complex product mixture (**Scheme** 10).

Scheme 10

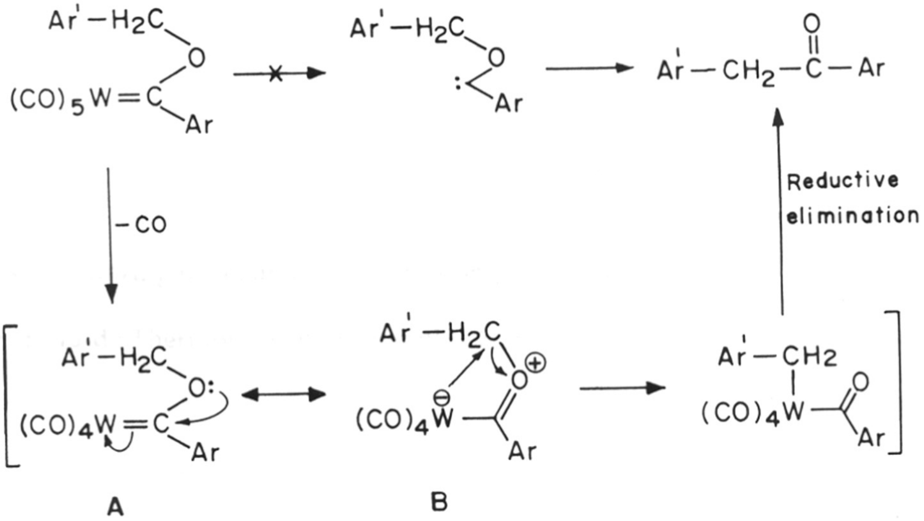


3·2f

Failure of the complex **3.2d** as well as **2.2f** to undergo rearrangement further indicated that a benzylic center was necessary adjacent to the oxygen atom for the reaction to proceed. Since initial CO loss is the rate determining step, this would also imply some sort of participation by an aromatic ring in facilitating decarbonylation (probably *via* η^2-coordination).

Tentatively, the following mechanistic scheme was considered (**Scheme 11**):

Scheme 11



Loss of a CO ligand in the first step of the reaction leads to the unsaturated intermediate **A**. The possible electronic polarization of **A** can be represented by the zwitterionic intermediate **B**, which furnishes the product ketone *via* an acylmetal intermediate which readily undergoes reductive elimination to furnish the rearranged product. If the reaction indeed involves a zwitterionic intermediate **B**, in principle, the reaction would be sensitive to substitution in either Ar or Ar′. The aromatic group may assume on important role in stabilizing the developing positive charge at the benzylic center in **B**.

On the other hand, an electron-donating substituent at the *para* position of Ar would compete with the resonance depicted in **A**, and thereby render the zwitterionic structure **B** less significant, which, in turn, would render the rearrangement less efficient. Such a situation is presented by the carbene complexes **2.2c**, and the rearrangement was indeed less efficient for this complex.

Several attempts were made to identify possible intermediates of this rearrangement by different spectroscopic methods. The reaction was carried out in NMR probe in benzene-d_6 solvent. Initial temperature of the probe was kept at 40°C which was raised to 60°C over a period of 2.5 hours and spectra were recorded in regular interval (15 minutes). The formation of the ketone was monitored by the appearance of a peak at 4.2 ppm. No other peak (except the peak of the compound **2.3a**) was seen during the course of the reaction (**Figure 1a-d**).

Figure 1a-d : Thermolysis of the complex **2.2a** in NMR probe in benzene-d^6

Figure 1a

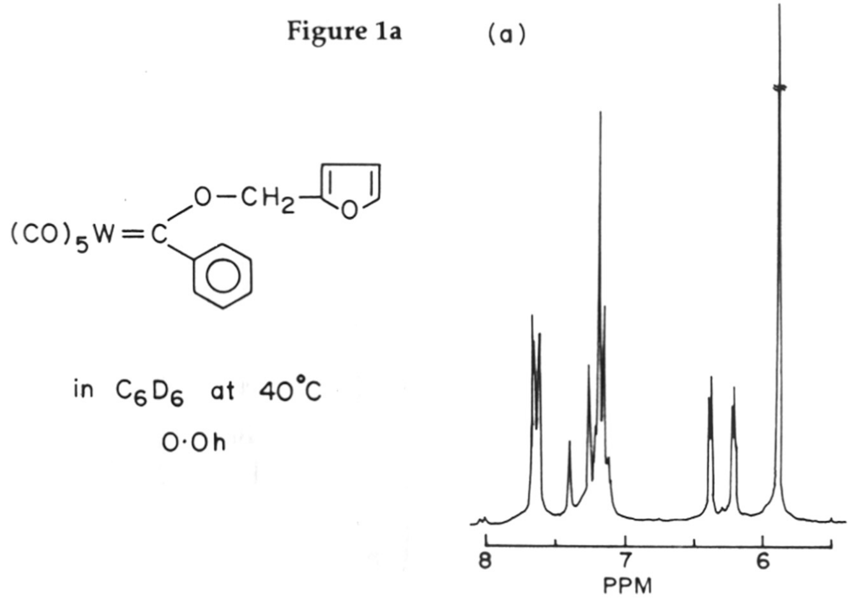


Figure 1b

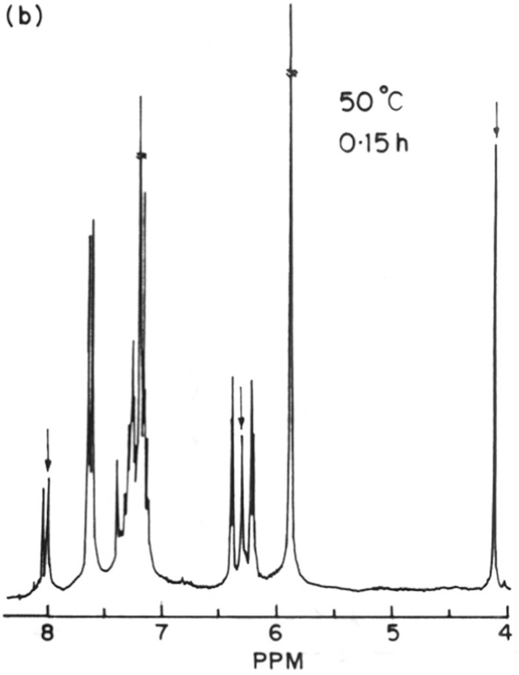


Figure 1c

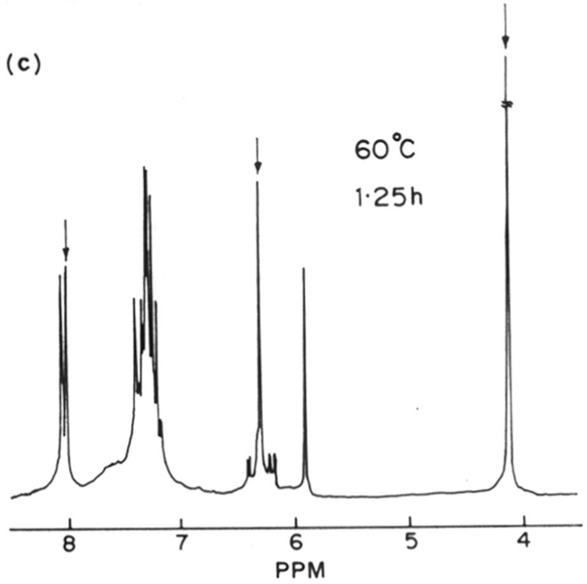
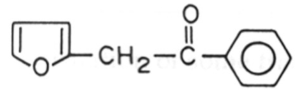
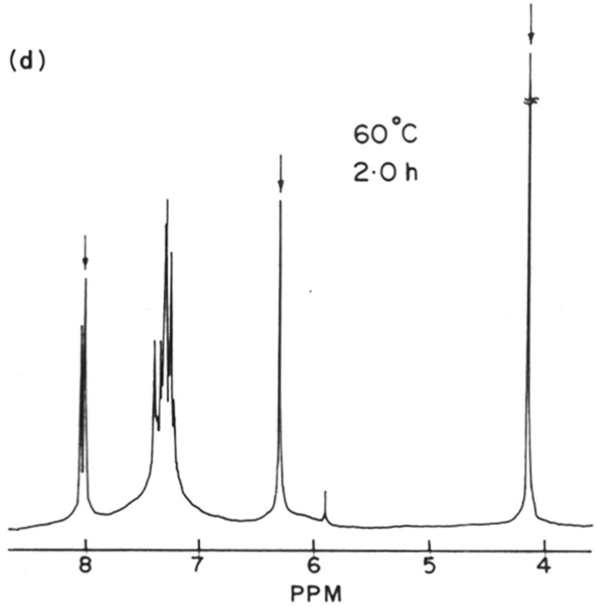


Figure 1d



2·3a



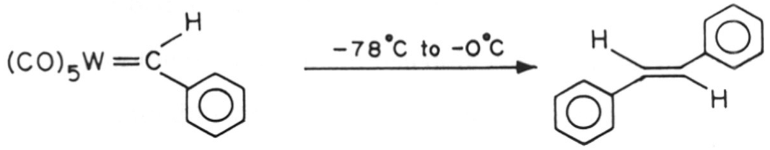
A systematic solvent study of the carbene complex **2.2a** was carried out and the results are presented in Table-1. It was found that benzene gave the best result. While coordinating solvents like acetonitrile and tetrahydrofuran gave poor yield, reasonable yield was obtained in dimethoxyethane. No clear trend emerged from these experiments.

Table 1 : Effect of Solvent on rearrangement reaction

Solvent	Time (in hour)	Yield (%)
Benzene	2	90
Toluene	0.5	56
Dimethoxy ethane	1.5	69
Tetrahydrofuran	2	33
Acetonitrile	3	31
1,4-dioxan	1	26
Ethylene dichloride	1	59
Methylene chloride	> 72	trace amount
cyclohexane	2	67
isoöctane	0.5	56

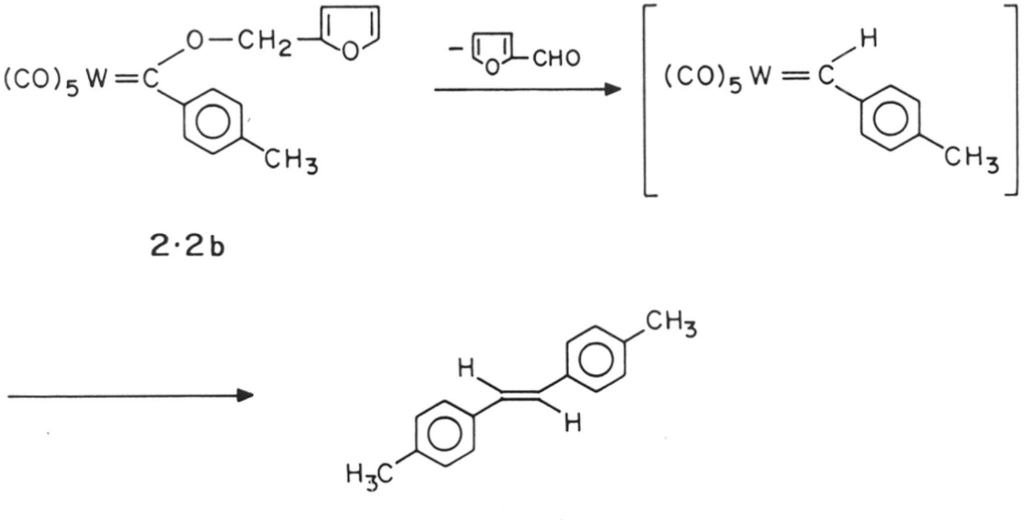
Formation of some *trans*-stilbene was observed on heating the carbene complex **2.2b** (**Chapter-2**), as a result of a parallel reaction. It was reported earlier[6] that *trans*-stilbene could be the product of dimerization of the organic ligand of a carbene complex (**Scheme 12**).

Scheme 12



The following pathway scheme can be considered (**Scheme 13**) for the generation of *trans*-stilbene from a Fischer carbene precursor.

Scheme 13



2·2b

2·3b'

Although, no aldehyde was isolated from the product mixture, an aldehyde proton was often observed in the ^{1}H NMR spectra of crude reaction mixture.

SUMMARY

Experiments described in this **Chapter** indicated that initial CO loss is the rate determining step of the rearrangement reaction. However, no intermediate could be intercepted or identified to strengthen the proposed mechanism, which is consistent with the results obtained so far.

"No experiment is ever a failure ---- it can

always serve as a negative example."

EXPERIMENTAL

o-Bromoanisole, allyl bromide and cinnamyl alcohol were purchased from Aldrich. Propargyl alcohol and *p*-anisaldehyde were purchased from Fluka and SD chemicals respectively.

All the complexes were prepared following the similar procedure as described in **Chapter 2.**

Preparation of Pentacarbonyl{(*o*-methoxyphenyl) [tetraethylammonio)oxy]carbene} tungsten (0) (3.1a)

From tungsten hexacarbonyl (787 mg, 2.24 mmol), a solution of o-methoxyphenyllithium [freshly prepared from *o*-bromoanisole (0.41 ml, 3.36 mmol) and n-butyllithium (2.8 ml, 3.36 mmol)] and tetraethylammonium bromide (470 mg, 2.24 mmol), the desired salt **3.1a** was obtained as a yellow solid (1.094 gm, 83%).

^{13}C NMR (Acetone-d_6) 7.79; 53.19; 55.37; 111.69; 120.67; 121.70; 126.68; 153.63; 154.58; 204.59; 209.50; 280.50

Preparation of Pentacarbonyl[(furfuryloxy)(*o*-methoxy phenyl)carbene]tungsten(0) (3.2a)

From the tetraethylammonium carbene salt **3.1a** (1.104 gm, 1.87 mmol), acetyl chloride (0.13 ml, 1.87 mmol), and furfuryl alcohol (0.16 ml, 1.87 mmol), the carbene complex **3.2a** was obtained as a dark red solid (375 mg, 37%). The carbene complex was purified by crystallization from petroleum ether at -5°C.

IR ($CHCl_3$) 2040(m); 2000(sh); 1950(s)

^{1}H NMR ($CDCl_3$) 3.87 (s, 3H); 5.5 (b, 2H); 6.45 (m, 1H); 6.55 (m, 1H,); 6.97 (m, 3H,); 7.3 (m, 1H,) 7.52 (m, 1H,)

^{13}C NMR ($CDCl_3$)	55.63; 74.71; 111.08; 111.37; 112.19; 120.45; 122.39; 130.19; 144.27; 148.00; 150.20; 197.34; 205.78; 325.21
Analysis	Calculated : C 40.07 H 2.22 Found : C 40.10 H 2.43

Preparation of Pentacarbonyl[(*p*-methoxybenzyloxy)(*o*-methoxy phenyl)carbene] tungsten(0) (3.2b)

From the tetraethylammonium carbene salt **3.1a** (1.5 gm, 2.55 mmol), acetyl chloride (0.18 ml, 2.55 mmol), and *p*-methoxybenzyl alcohol (0.35 ml, 2.81 mmol), the carbene complex **3.2b** was obtained as a red solid (817 mg, 55%). The carbene complex was purified by crystallization from petroleum ether extract at -5°C.

IR ($CHCl_3$)	2030; 1990; 1940
^{1}H NMR ($CDCl_3$)	3.8 (s, 6H); 5.5 (b, 2H); 6.88 (m, 5H); 7.25 (m, 3H)
^{13}C NMR ($CDCl_3$)	55.51; 83.48; 111.28; 114.38; 120.39; 122.15; 126.56; 130.00; 130.20; 150.11; 160.43; 197.49; 205.88; 325.17
Analysis	Calculated : C 46.06 H 2.92 Found : C 46.37 H 3.21

Preparation of Pentacarbonyl [(propargyloxy)(*o*-methoxyphenyl)carbene] tungsten(0) (3.2c)

From the tetraethylammonium carbene salt **2.1a** (558 mg, 1 mmol), acetyl chloride (0.07 ml, 1 mmol), and propargyl alcohol (0.06 ml, 1 mmol), the carbene complex **3.2c** was obtained as a red solid (290 mg, 62%). Carbene complex was purified by crystallization from petroleum ether at -5°C.

IR ($CHCl_3$)	2040 (s); 2000 (sh); 1950 (m)

^{1}H NMR (CDCl$_3$) 2.8 (t, J = 2.5 Hz, 1H); 5.62 (d, J = 2.5 Hz, 2H); 7.53 (m, 5H)

^{13}C NMR (CDCl$_3$) 70.76; 76.44; 78.28; 126.46; 128.30; 132.04; 156.32; 203.50; 321.28

Analysis Calculated : C 38.54 H 1.71

Found : C 38.67 H 1.91

Preparation of Pentacarbonyl[(1-methoxy ethyloxy)(phenyl)carbene]tungsten(0) (3.2d)

From the tetraethylammonium carbene salt **2.1a** (1 gm, 1.79 mmol), acetyl chloride (0.12 ml, 1.79 mmol), and 1-methoxyethanol (0.14 ml, 1.79 mmol), the carbene complex **3.2d** was obtained as a red solid (662 mg, 80%). The carbene complex was purified by crystallization from petroleum ether at -5°C.

IR (CHCl$_3$) 2030 (s); 1985 (sh); 1940 (m)

^{1}H NMR (CDCl$_3$) 3.2 (s, 3H); 3.75 (m, 2H); 4.84 (m, 2H); 7.24 (m, 5H)

^{13}C NMR (CDCl$_3$) 59.50; 70.67; 82.89; 126.76; 128.36; 132.04; 155.62; 197.53; 203.83; 321.04

Analysis Calculated : C 36.96 H 2.46

Found : C 37.16 H 2.53

Attempted preparation of carbene complex (3.2e)

From the tetraethyl ammonium carbene salt **2.1a** (2.17 gm, mmol), acetyl chloride (0.27 ml, mmol), and α-allyl *p*-methoxybenzyl alcohol (700 mg 3.95 mmol), the compound **3.3e** was obtained as a colorless liquid (900 mg, 85%) during the work up of the reaction.

^{1}H NMR (CDCl$_3$) 1.35 (m, 2H); 1.86 (m, 2H); 2.66 (m, 1H); 3.68 (s, 3H); 5.46 (t, J = 7Hz, 1H); 6.77 (d, J = 7Hz, 2H); 7.17 (m, 5H)

MS	266; 161; 147; 134; 121; 105; 91; 77

Preparation of Pentacarbonyl[(cinnamyloxy)(phenyl)carbene]tungsten(0) (3.2f)

From the tetraethylammonium carbene salt **2.1a** (1.519 gm, 2.7 mmol), acetyl chloride (0.18 ml, 2.7 mmol), and cinnamyl alcohol (0.34 ml, 2.7 mmol), the carbene complex **3.2f** was obtained as a red liquid (830 mg, 56%). Carbene complex was purified by flash column chromatography using 5% ethyl acetate/petroleum ether as eluent.

IR (CHCl$_3$)	2030; 1985; 1945
^{1}H NMR (CDCl$_3$)	5.65 (d, J = 4Hz, 2H); 6.65 (m, 1H); 6.95 (m, 1H,); 7.45 (m, 10H)
^{13}C NMR (CDCl$_3$)	84.66; 121.65; 126.45; 127.11; 128.32; 128.97; 131.85; 136.761; 135.93; 155.61; 197.51; 203.78; 320.38
Analysis	Satisfactory elemental analysis could not be obtained

Thermolysis of carbene complex 3.2a

The carbene complex **3.2a**, (305 mg, 0.56 mmol) on heating for 2 h in toluene, yielded the compound **3.3a** (77 mg, 63%) as pale yellow liquid.

The carbene complex **3.2a** (210 mg, 0.39 mmol) on heating for 10 h in benzene, yielded the compound **3.3a** (48 mg, 57%) as pale yellow liquid.

IR (CHCl$_3$)	1684 (m)
^{1}H NMR (CDCl$_3$)	3.95 (s, 3H); 4.4 (s, 2H); 6.2 (m, 1H); 6.35 (m, 1H); 7.02 (m, 2H); 7.35 (m, 1H); 7.5 (m, 1H); 7.75 (m, 1H)
MS	216; 135; 107; 81; 77

Thermolysis of carbene complex 3.2b

The carbene complex **3.2b**, (200 mg, 0.34 mmol) on heating for 3 h in toluene, yielded the compound **3.3b** (51 mg, 57%) as white solid.

The carbene complex **3.2b**, (150 mg, 0.26 mmol) on heating for 14 h in benzene, yielded the compound **3.3b** (35 mg, 53%) as white solid.

IR ($CHCl_3$)	1680
^1H NMR ($CDCl_3$)	3.68 (s, 6H); 3.84 (s, 2H) 6.82 (m, 8H)
M.P.	89^{0}C
MS	256(M^+); 135; 121; 107

Thermolysis of carbene complex 3.2c

The carbene complex (**3.2c**) when heated in benzene (3 h, 80°C) or in toluene (4 h, 70°C), resulted in the complex mixture of products. The IR spectrum of the crude reaction mixture did not show the presence of ketone.

Thermolysis of carbene complex 3.2d

When the carbene complex **3.2d** was heated in benzene (6 h, 80°C) and in toluene (3 h, 110°C), the starting material was recovered in 93% and 86% yield respectively. The recovered starting material was characterized by IR and ^1H NMR spectra.

Thermolysis of carbene complex 3.2f

Thermolysis of the carbene complex (**3.2f**) in benzene (3 h, 80°C) as well as in toluene (4 h, 70°C) resulted in complex mixture of products. IR spectrum of the crude reaction mixture did not show the presence of ketone.

Photolysis of carbene complex 2.2a

The carbene complex **2.2a** (100 mg, 0.17 mmol) was photolysed (350 nm) in benzene at room temperature for 10 hours. Initial red color of the solution gradually disappeared. The compound **2.3a** (21 mg) was isolated as the only product in 57% yield after purification by column chromatography.

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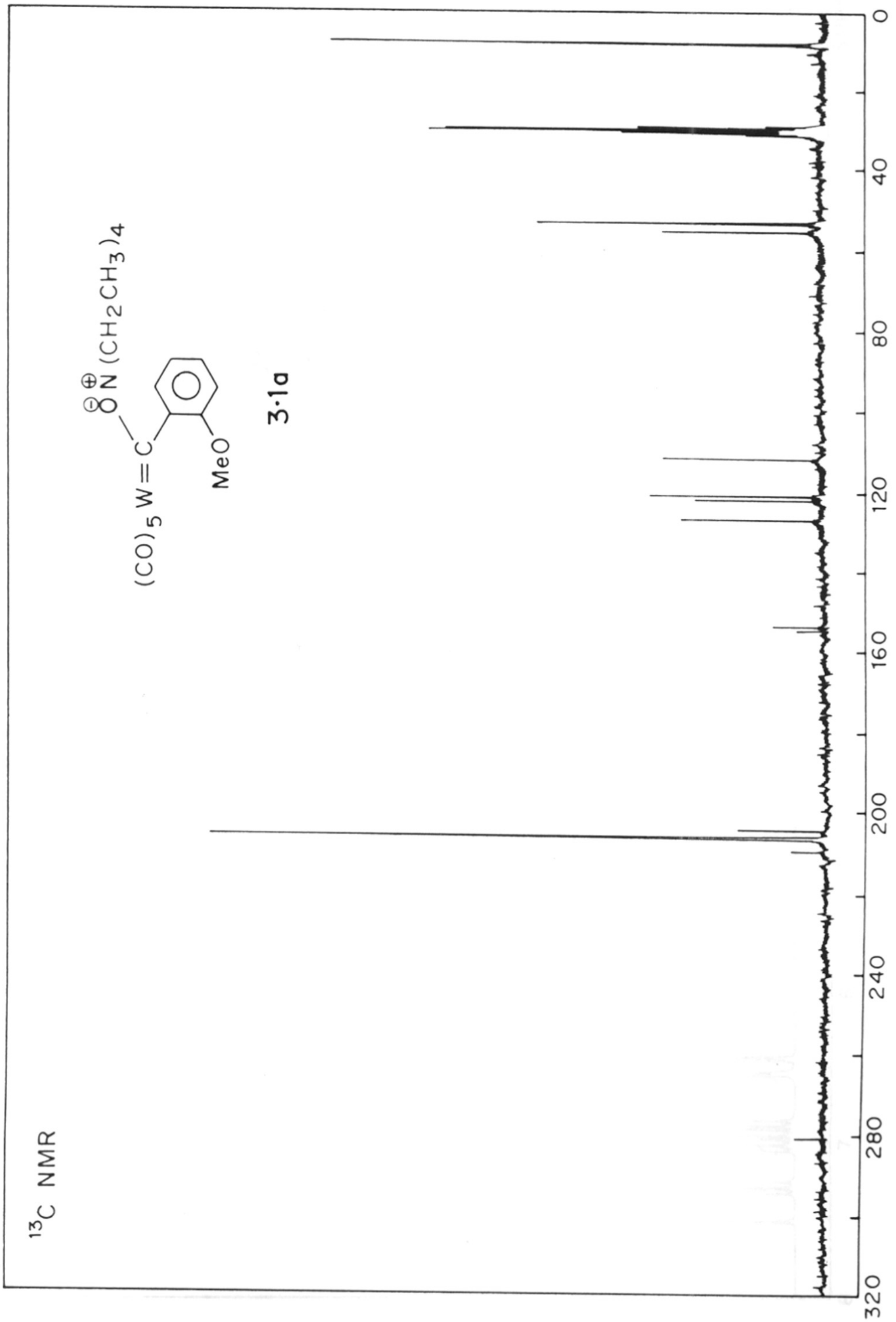
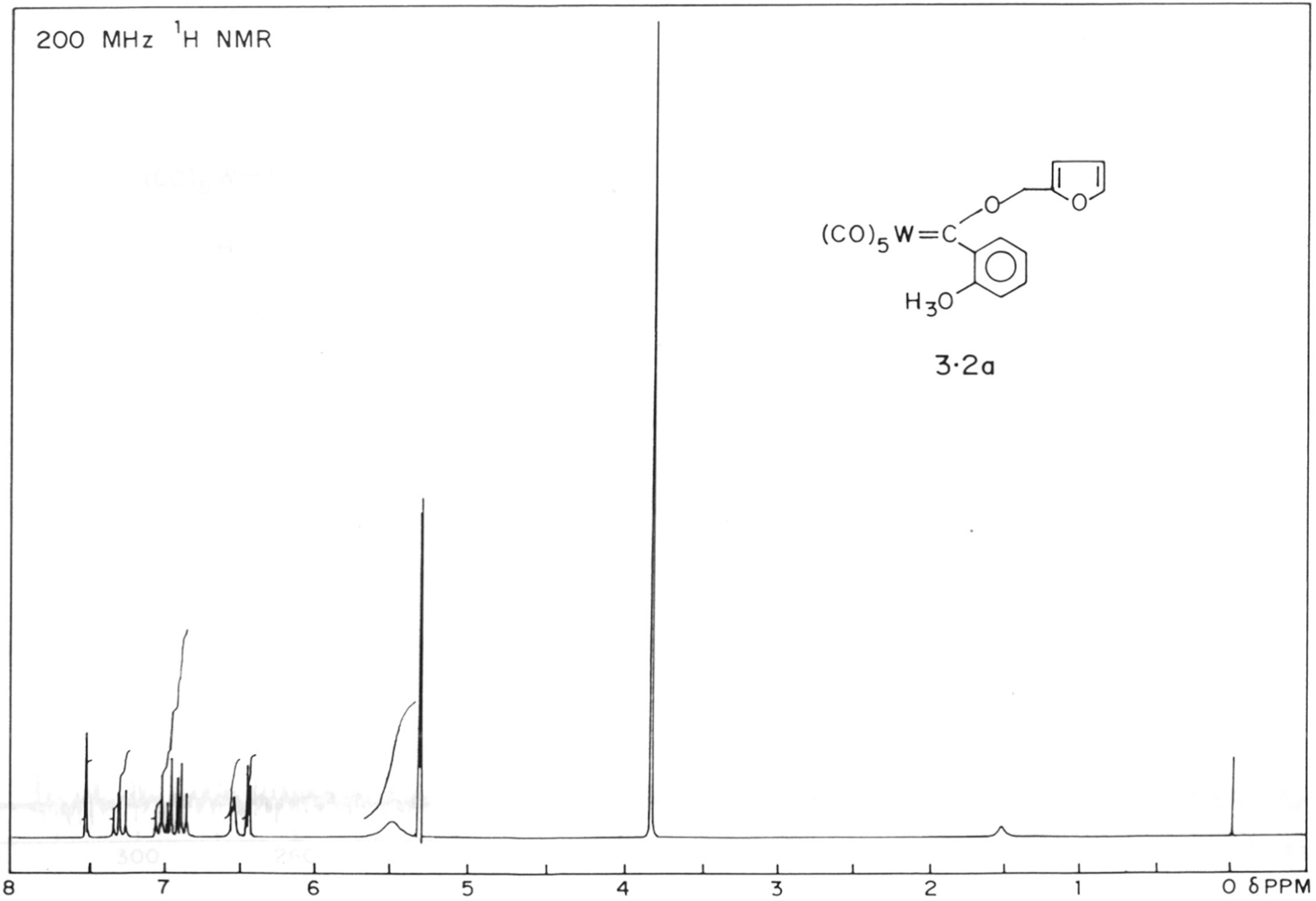


3·1a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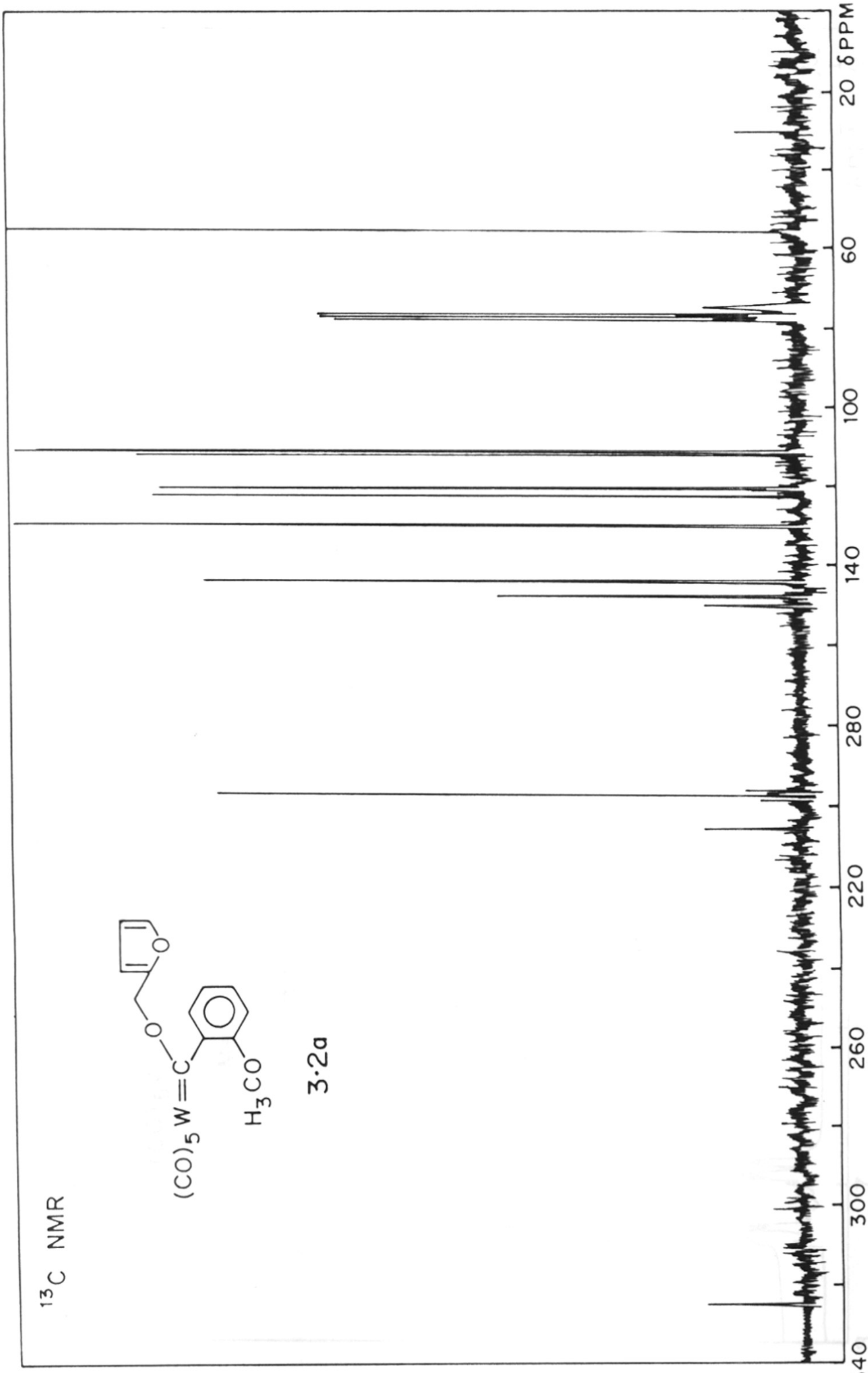
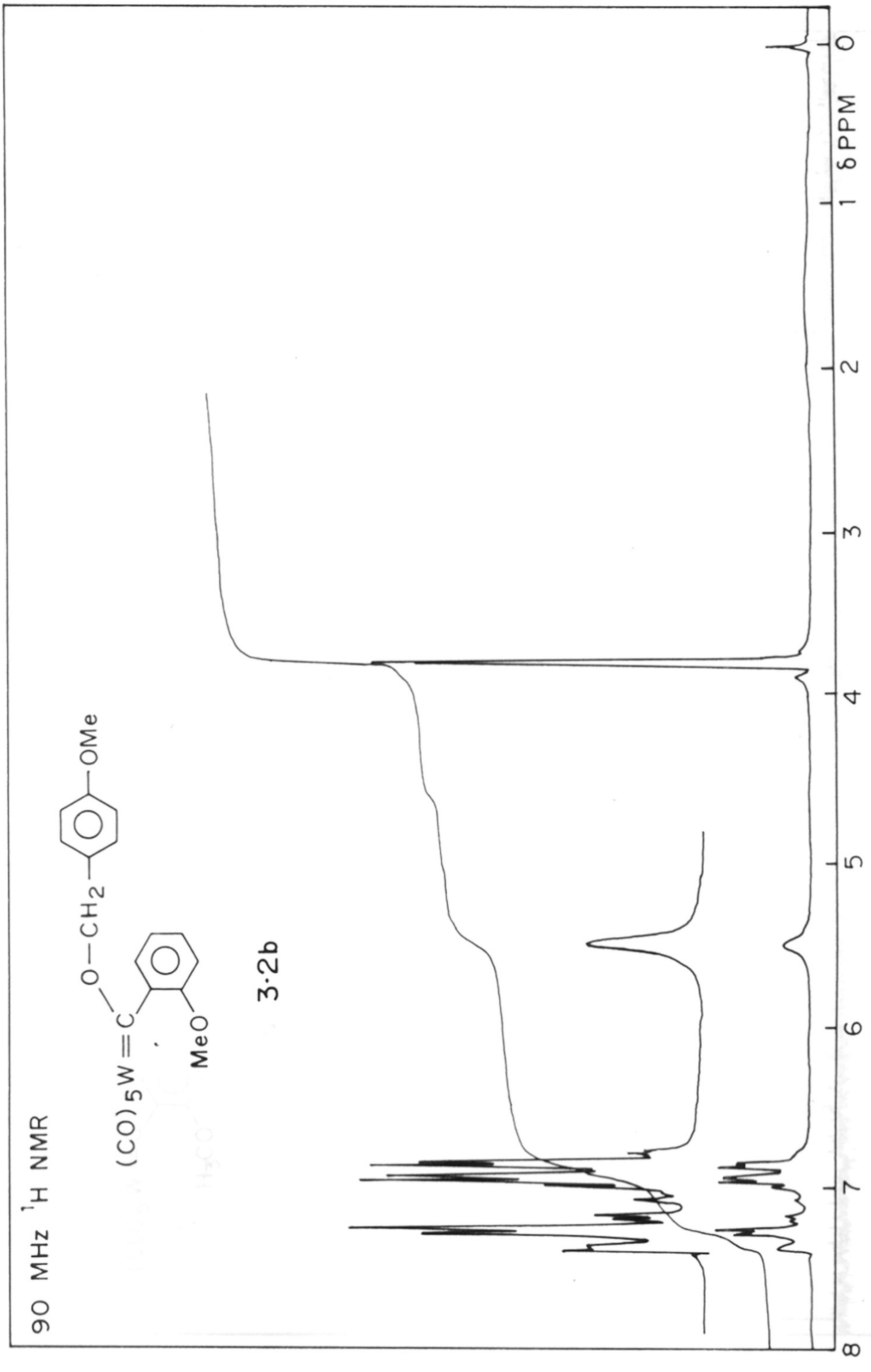
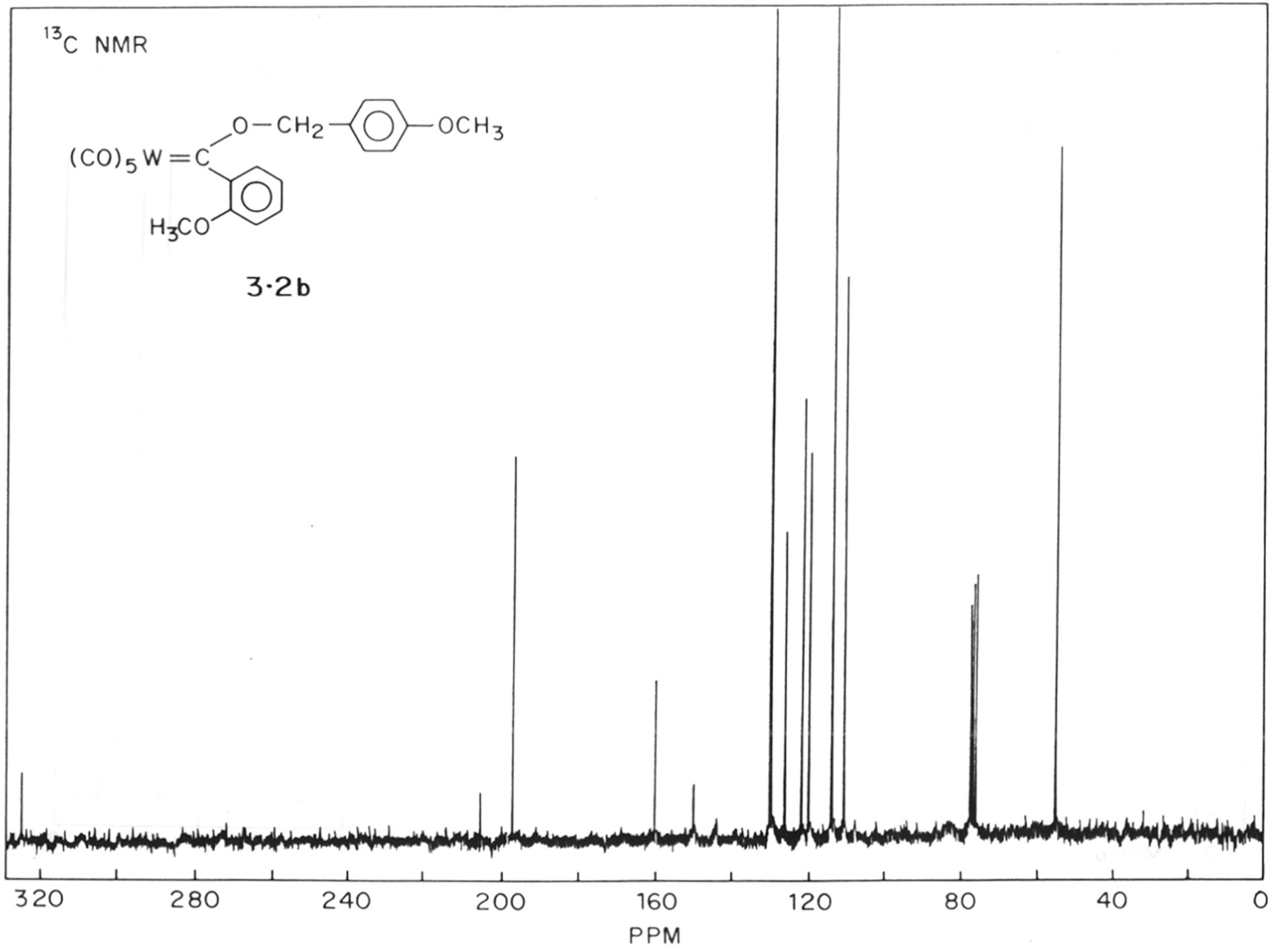
O
O
H_3O
3·2a
8
7
6
5
4
3
2
1
0 δPPM



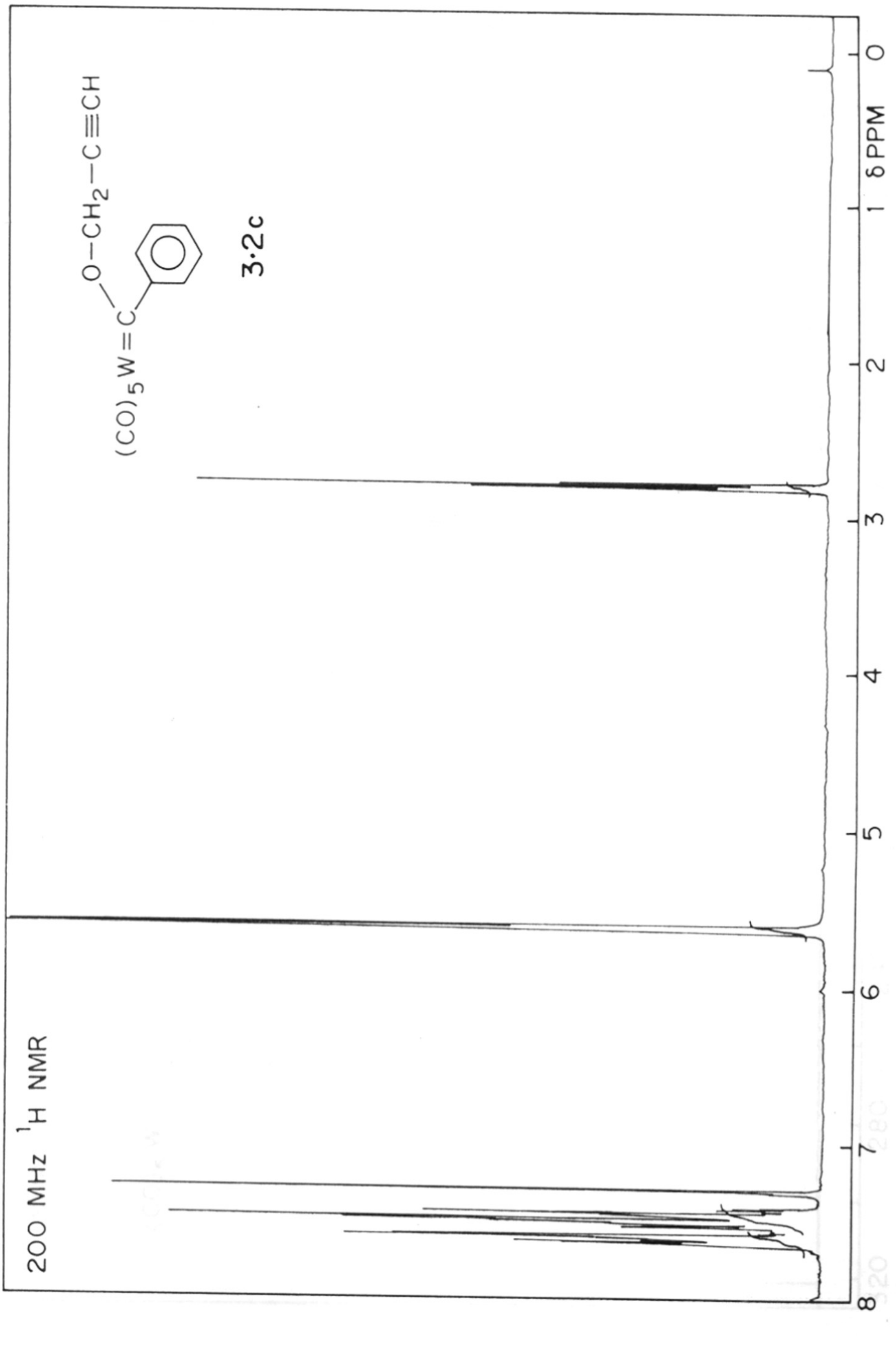
3·2a



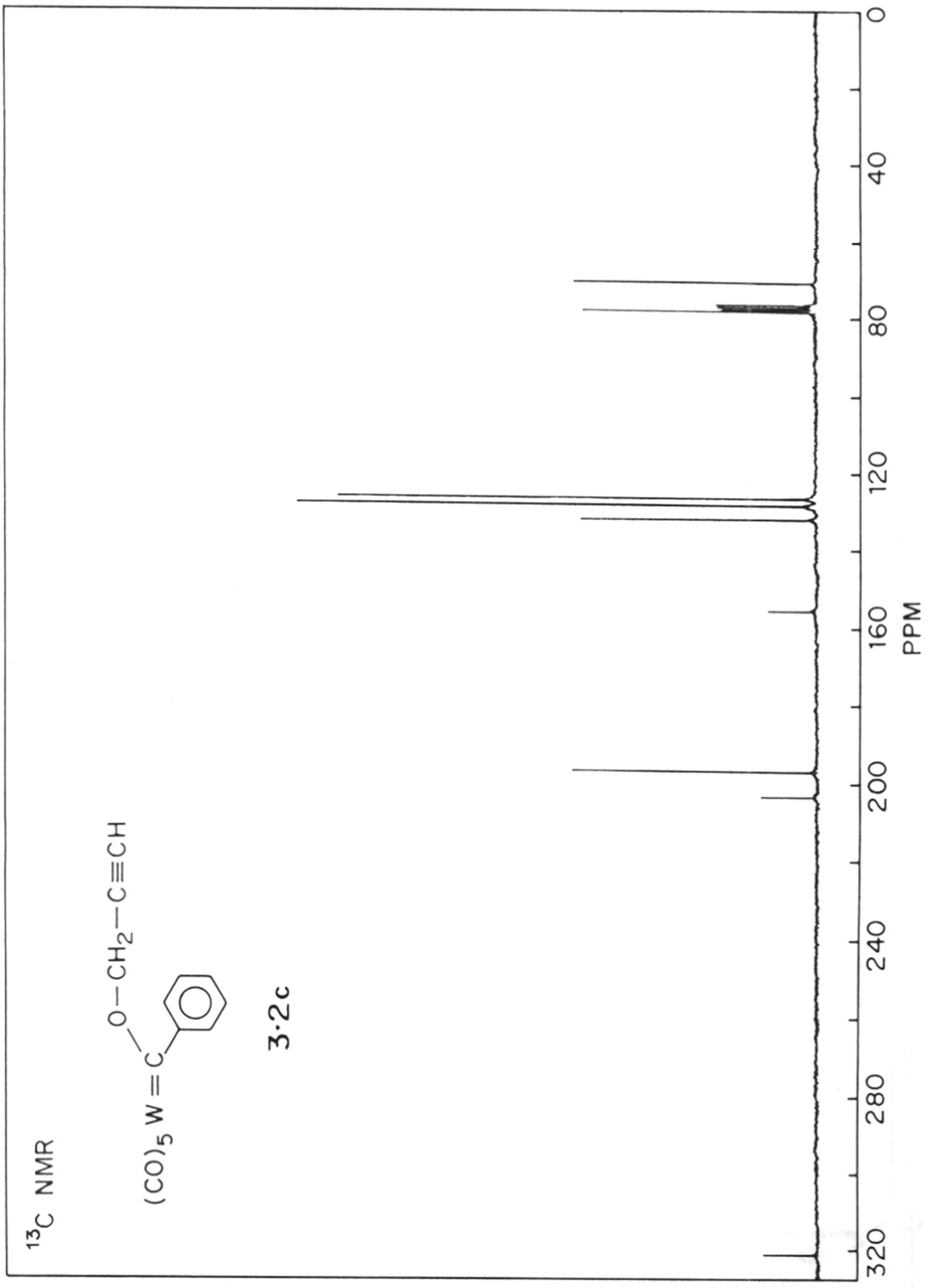
3·2b



3·2b

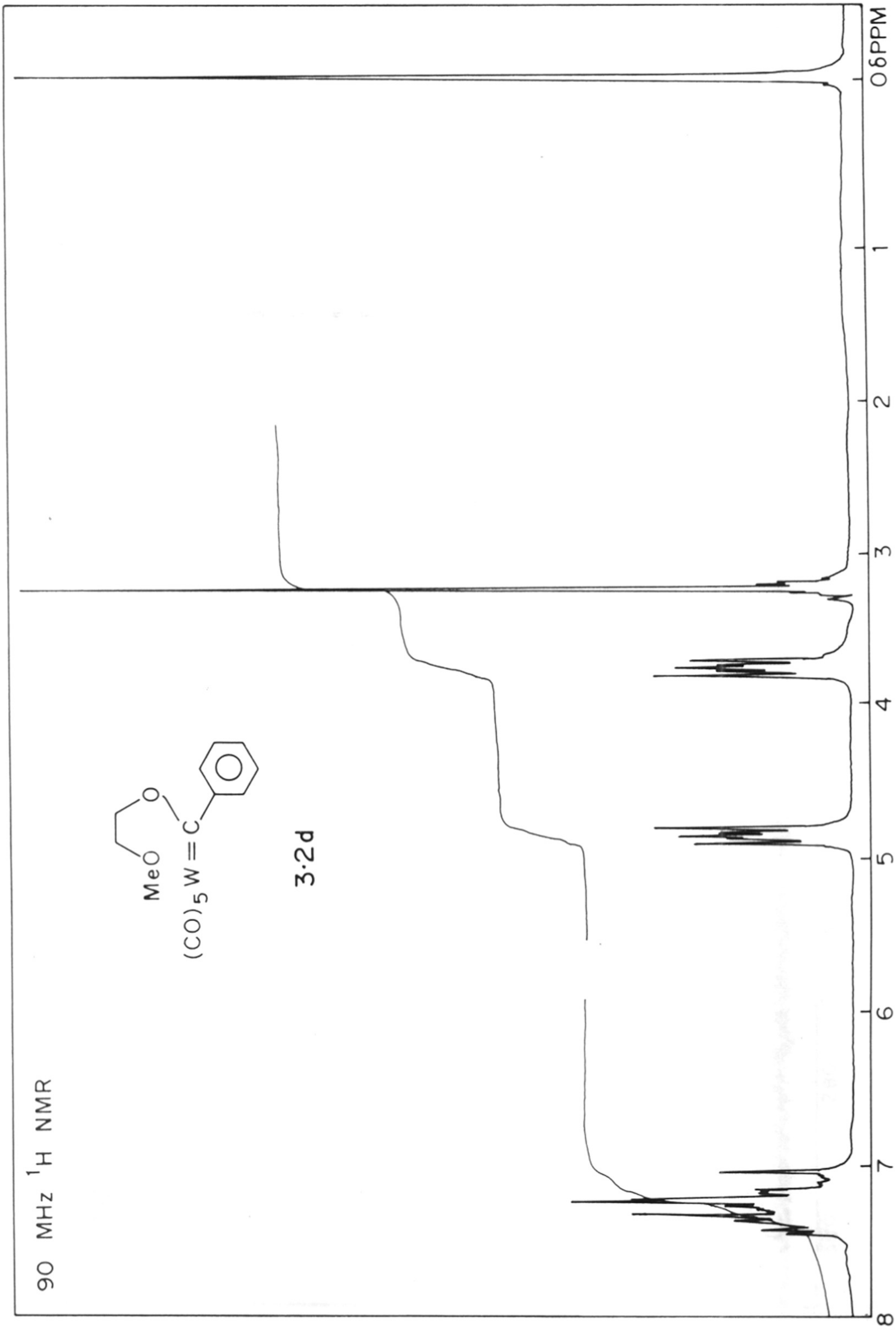


3·2c

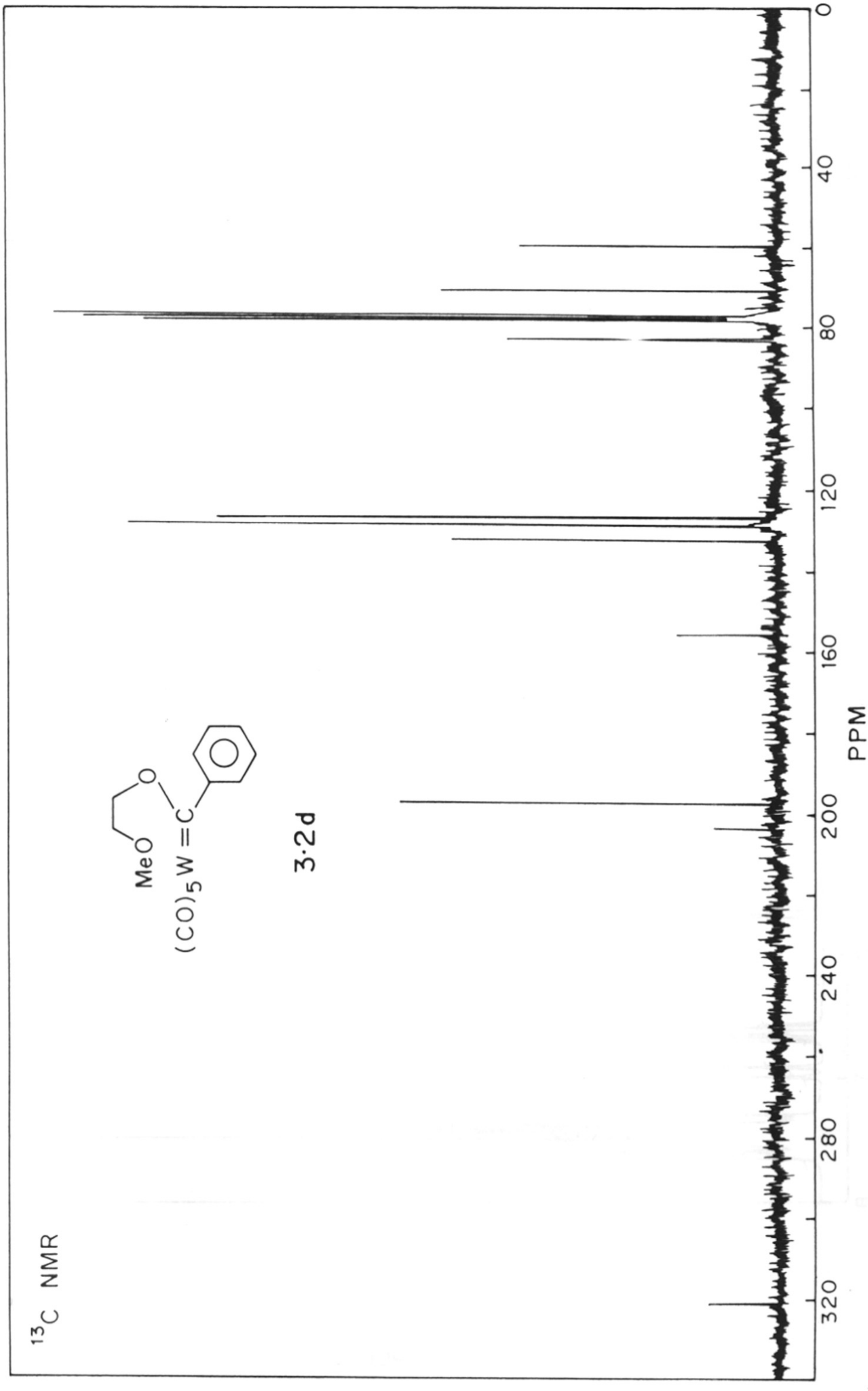


^{13}C NMR
$(CO)_5W=C(Ph)-O-CH_2-C\equiv CH$
PPM
0
40
80
120
160
200
240
280
320

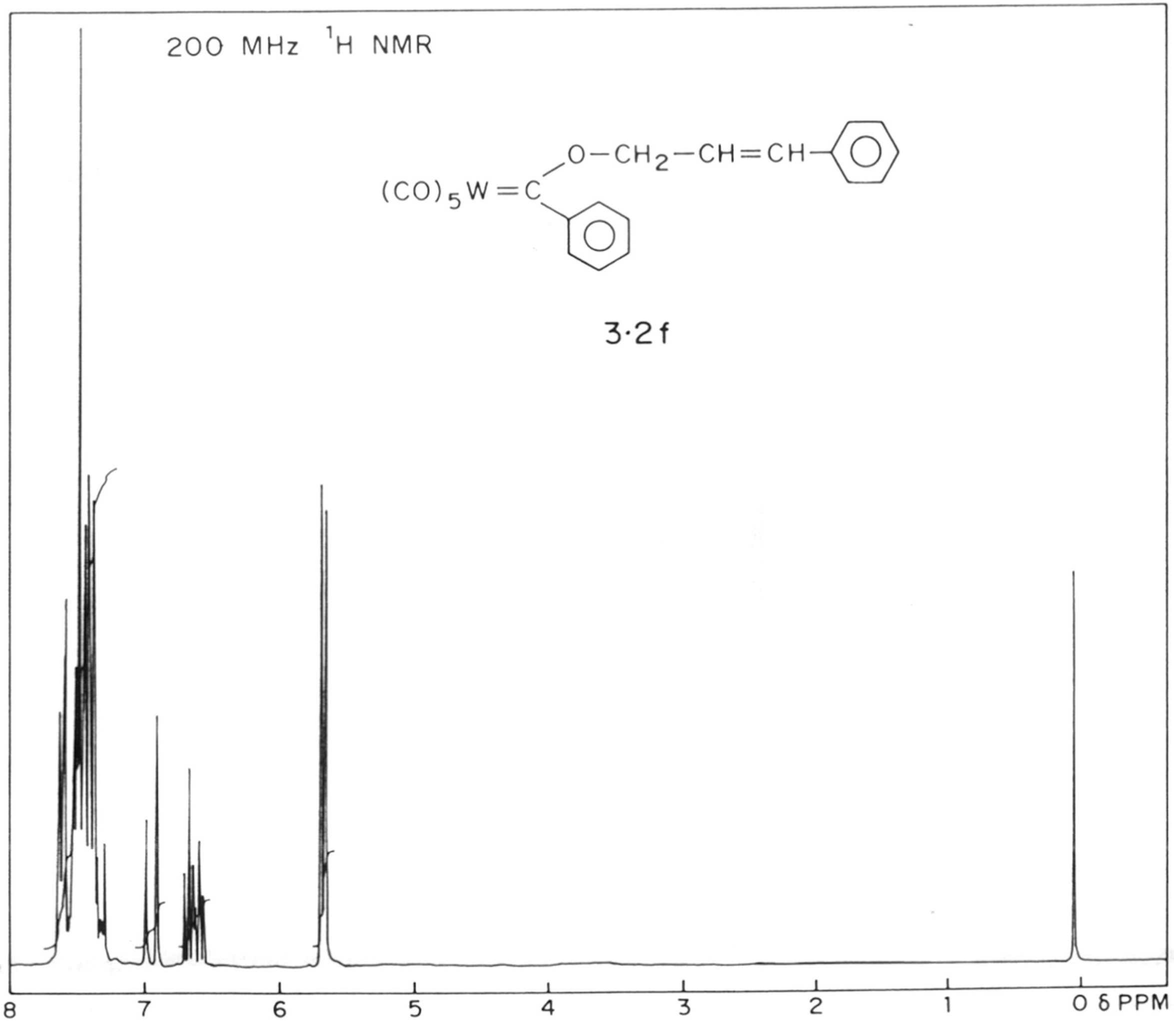
3·2c



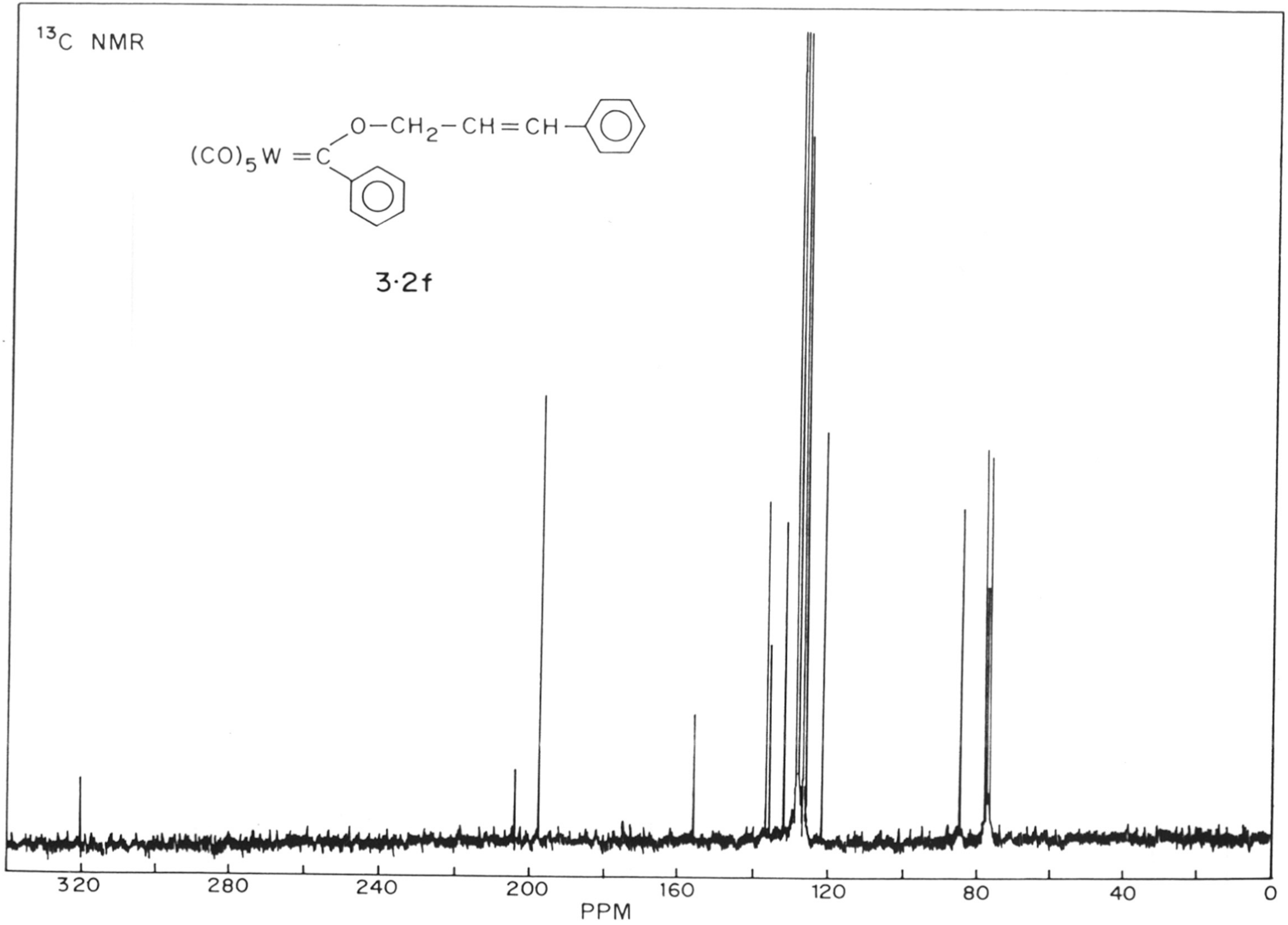
3·2d



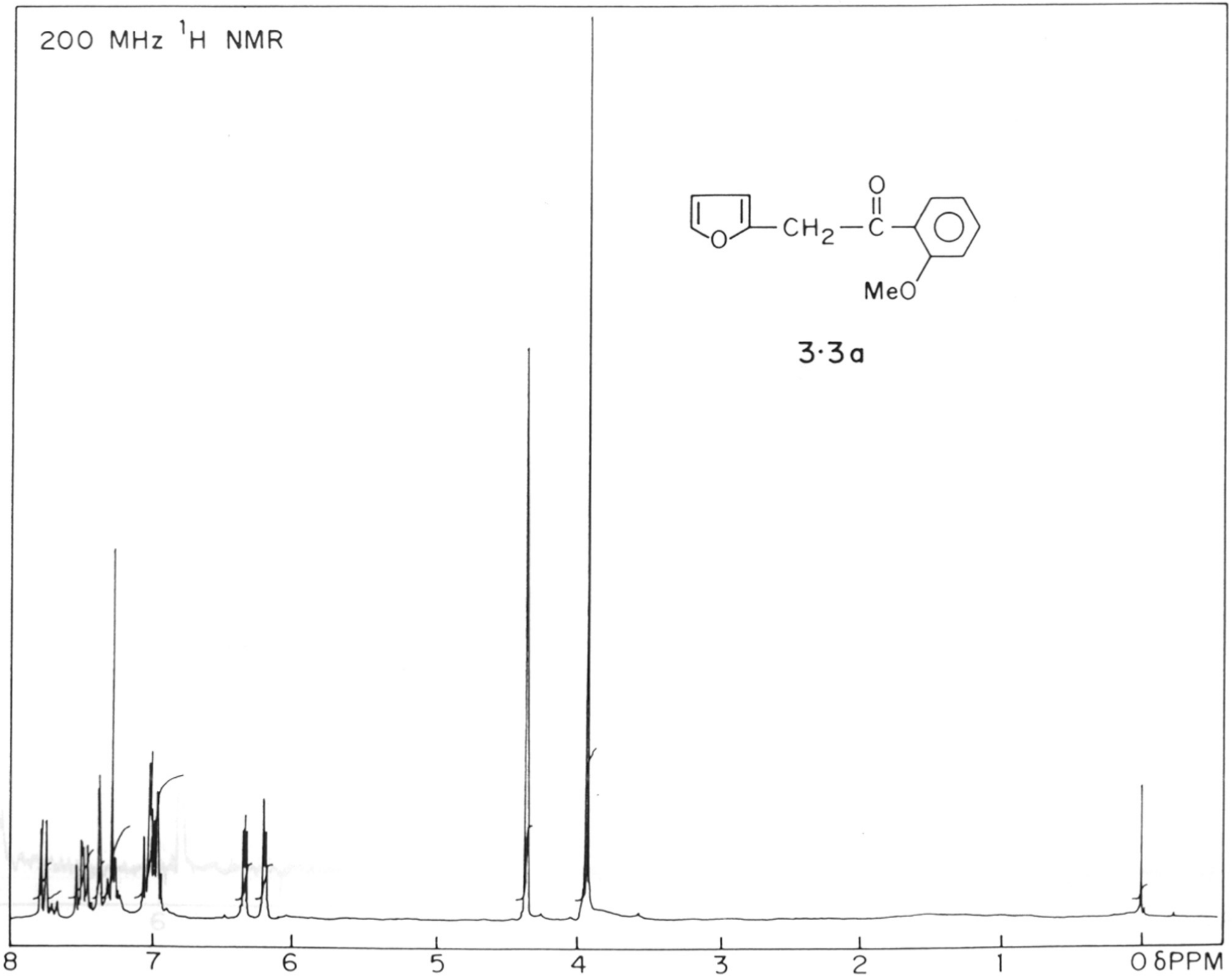
3·2d



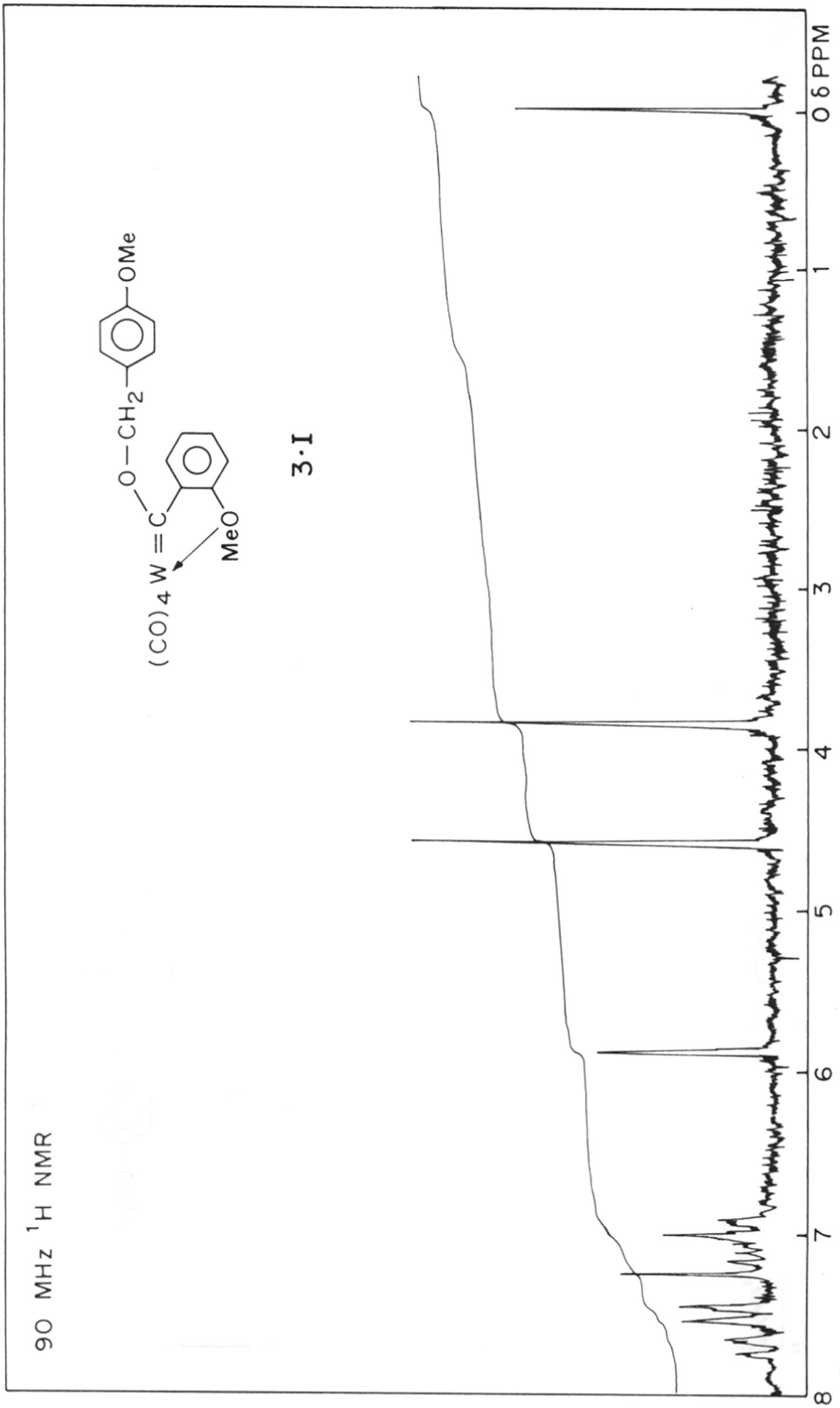
3·2f



3·2f



3·3a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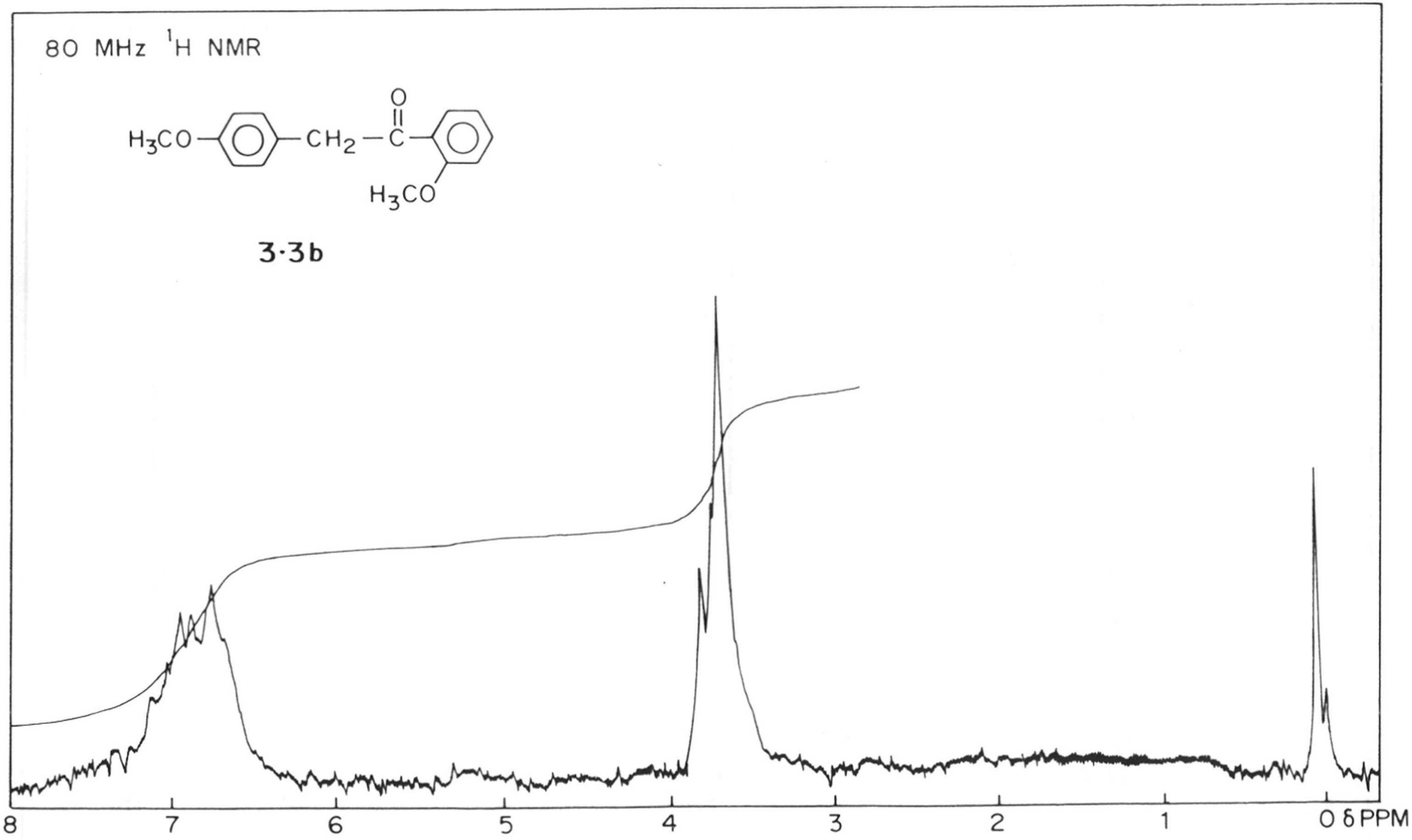
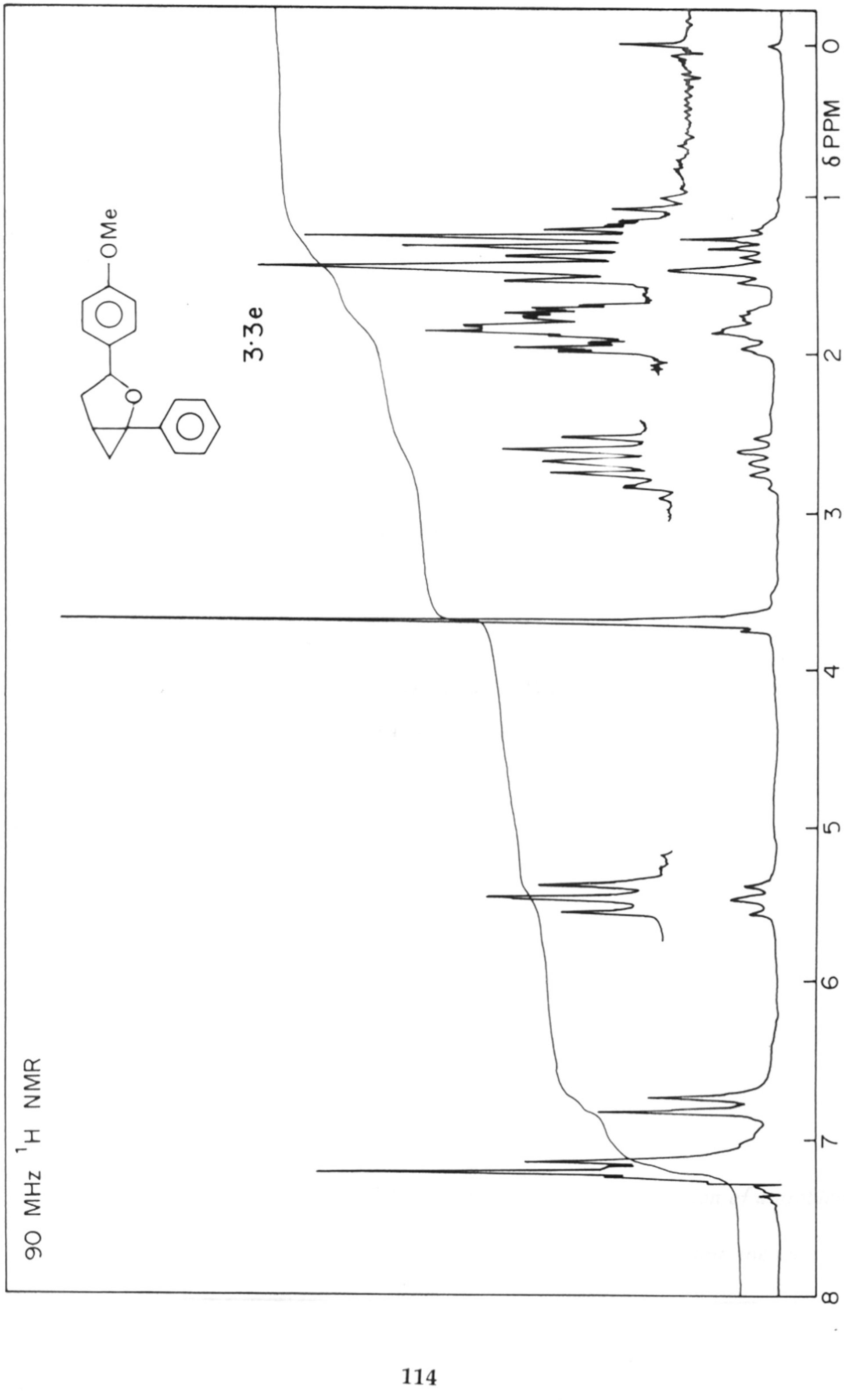
OMe
MeO
3·I
8
7
6
5
4
3
2
1
0 δ PPM



3·3b


90 MHz ¹H NMR
3·3e
OMe
O
8
7
6
5
4
3
2
1
δ PPM
0

CHAPTER 4

CONFORMATIONAL STUDIES ON THE ARYL ARYLMETHYLOXY FISCHER CARBENE COMPLEXES OF TUNGSTEN - SUBSTITUENT EFFECTS

> *"When working toward the solution of a problem,*
> *it always helps if you know the answer."*

INTRODUCTION

The bonding between the metal and carbene fragment essentially consists of two components : the lone pair of the carbene fragment is donated to an empty, acceptor orbital of the metal, and back donation from a filled metal *d*-orbital to the empty *p*-orbital of the carbene ligand further augments the bonding, as evident from the shortening of metal-carbon distance (**Scheme 1**).

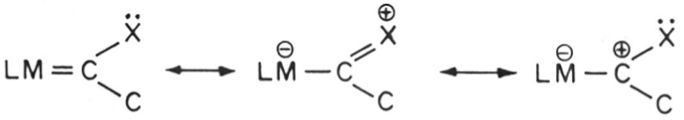
Scheme 1

σ bond π bond

The methylidene complex $Cp_2MeTa{=}CH_2$ provided the first example[1a] in which, as revealed by the spectral data and X-ray crystallography, a full double bond exists between the metal and the carbene ligand. The metal carbene rotational barrier is greater than 21 kcal/mole.

In Fischer carbene complexes, delocalisation of the lone pair of electrons on the heteroatom gives rise to the following resonance structures (**Scheme 2**).

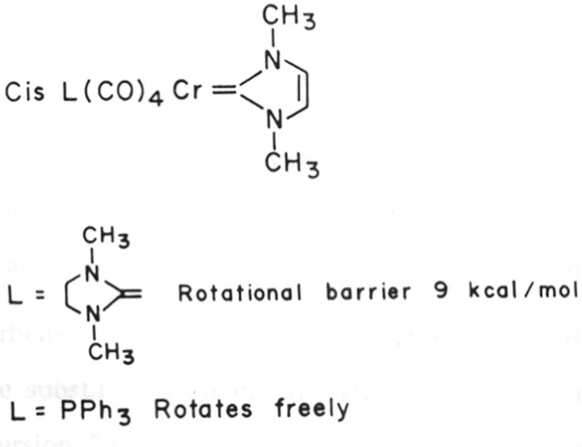
Scheme 2



This results in the lowering of barrier to rotation of the carbene fragment about the Metal-C_{carb} axis, while there is a restricted rotation about the C-X bond. This is consistent with the theoretical calculation.[1b]

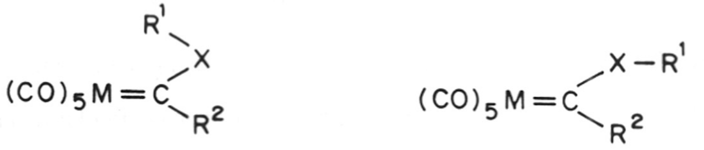
The NMR spectroscopic studies indicate that a barrier to rotation about the C_{carb}-Metal bond is not present unless there is severe steric crowding among the ligands (**Scheme 3**).[2]

Scheme 3



Restricted rotation about C_{carb}-heteroatom bond is manifested in the following conformers (**Scheme 4**).

Scheme 4



anti

syn

The rotation barrier of C-O bond (P)[3a] is less than the C-N bond[3b] (Q) reminiscent of the trend in esters compared to amides (**Scheme** 5).

Scheme 5

P

25 kcal/mol

Q

12 kcal/mol

Thus, the conformers of amino carbene complexes are clearly observed in the NMR spectra at ambient temperature,[4] but alkoxy carbenes require lower temperature to arrest conformational interchange. Dynamic NMR spectroscopy is a useful tool to monitor such phenomena and determine relevant thermodynamic parameters.

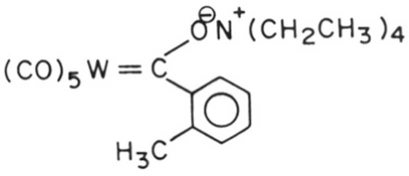
For aryl methoxy carbene complexes of general structure [$(CO)_5CrC(OMe)Ar$], Fischer showed[3a] that the substituents on the aromatic ring affect the barrier to conformational interconversion. Since such effects could be a direct consequence of electron delocalisation from the aromatic ring towards the carbene carbon, the relative orientation of the aromatic π-plane and the Metal-C_{carb} π-plane could contribute to an additional stereochemical feature to be considered in such analyses.

In the crystal structures the aryl ring is oriented orthogonal to the metal carbene π-plane[5]. However, it has not been ascertained if the aryl ring is oriented perpendicular even in solution. In the course of our study, we obtained the first direct evidence of a non-planar orientation of the aryl group in solution, as detailed below.

RESULTS

In general, the carbene complexes were prepared following the same procedure as described in **Chapter-2**, and were characterized by their IR, ^{1}H, ^{13}C NMR spectra as well as elemental analyses.

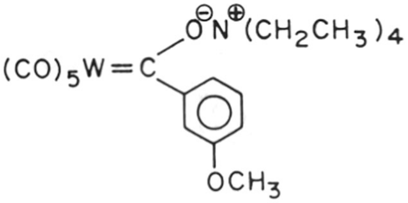
Preparation of pentacarbonyl {(*o*-methylphenyl) [(tetraethylammonio)oxy] carbene}tungsten(0) (4.1c)



4·1c

To a stirred solution of $W(CO)_6$ in ether, freshly prepared *o*-methylphenyl lithium was added at room temperature. The tetramethylammonium salt **4.1c** (yield 89%) was isolated as a yellow solid. The salt was stored in the refrigerator for next reaction.

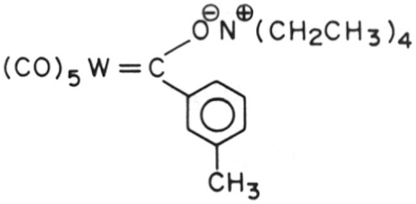
Preparation of pentacarbonyl {(*m*-methoxyphenyl) [(tetraethylammonio)oxy] carbene}tungsten(0) (4.1e)



4·1e

The carbene salt **4.1e** (yield 91%) was obtained as a red solid and stored in the refrigerator for next reaction.

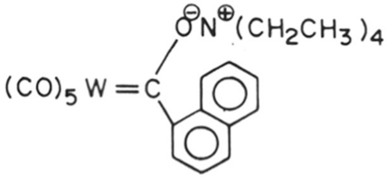
Preparation of pentacarbonyl {(*m*-methylphenyl)[(tetraethylammonio)oxy] carbene}tungsten(0) (4.1g)



4·1g

The carbene salt **4.1g** (yield 83%) was prepared following a similar procedure. The solid red carbene salt was preserved in the refrigerator.

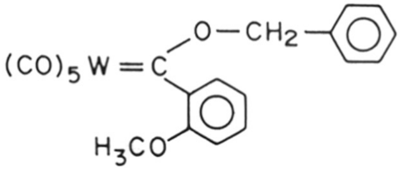
Preparation of pentacarbonyl {(α-naphthyl)[(tetraethylammonio)oxy] carbene}tungsten(0) (4.1i)



4·1i

Freshly prepared α-naphthyl lithium was added to the ethereal solution of $W(CO)_6$ at room temperature. The lithio salt was exchanged by tetraethyl ammonium cation using tetraethyl ammonium bromide. The carbene salt **4.1i** (yield 89%) was obtained as yellow solid and stored in the refrigerator for next reaction.

Preparation and characterization of carbene complex 4.2b

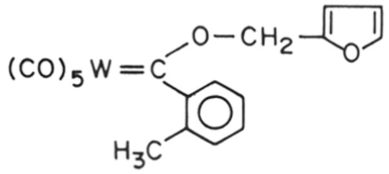


4·2b

The carbene complex **4.2b** (yield 58%) was obtained as air-stable, red solid. The complex could be stored in refrigerator for several months.

The IR spectrum showed typical carbonyl absorptions. The peak at 3.85 ppm in the ^{1}H NMR spectrum was assigned to methoxy group, whereas in ^{13}C NMR spectrum it appeared at 55.25 ppm.

Preparation and characterization of carbene complex 4.2c

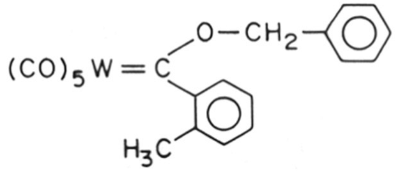


4·2c

The carbene complex **4.2c** (yield 43%) was obtained from the carbene salt **4.1c** as a dark red solid.

The typical carbonyl absorptions in the IR spectrum indicated the formation of carbene complex. The methyl group appeared at 2.18 ppm in the ^{1}H NMR spectrum while in the ^{13}C NMR spectrum it appeared at 19.14 ppm.

Preparation and characterization of carbene complex 4.2d

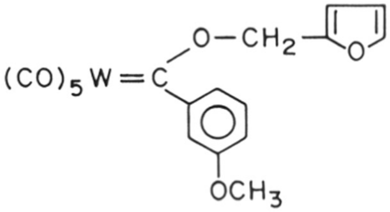


4·2d

The carbene complex **4.2d** was prepared in a similar manner. The solid red crystals (yield 56%) were air-stable and could be stored in refrigerator for months.

IR spectrum displayed characteristic bands. In the ^{1}H NMR spectrum the peak at 2.2 ppm was assigned to the methyl group. In the ^{13}C NMR spectrum the peak at 19.34 ppm was assigned to the methyl carbon.

Preparation and characterization of carbene complex 4.2e

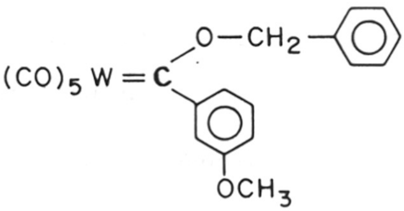


4·2e

The carbene complex **4.2e** (yield 38%) was obtained as air-stable red crystals following similar experimental procedure.

The IR spectrum showed typical carbonyl absorptions. In the ^{1}H NMR spectrum the two methylene protons appeared as sharp singlet at 5.95 ppm. The sharp singlet at 3.87 ppm was assigned to the methoxy group. In the ^{13}C NMR spectrum, the peak at 55.25 ppm was assigned to the methoxy group. The sharp peak at 77.09 ppm was assigned to the OCH_2 group.

Preparation and characterization of carbene complex 4.2f

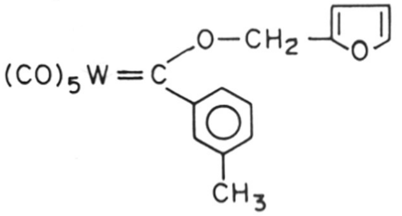


4·2f

The carbene complex **4.2f** (yield 59%) was obtained as a air-stable red sold.

The characteristic IR peaks confirmed the formation of the carbene complex. In the ^1H NMR spectrum, the methoxy protons appeared at 3.9 ppm. The methylene protons appeared as a sharp singlet at 6.02 ppm. In the ^{13}C NMR spectrum the peaks at 55.67 and 85.94 ppm were assigned to the methoxy and methylene group respectively.

Preparation and characterization of carbene complex 4.2g

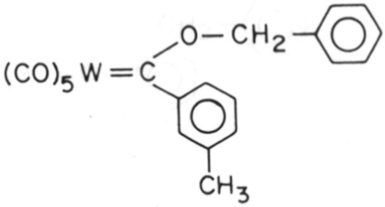


4·2g

The complex **4.2g** (yield 36%) was obtained as red, air-stable crystals following the same experimental procedure. The IR spectrum supported the formation of this complex. In the ^1H NMR spectrum the peaks at 2.38 and 5.95 ppm were assigned to the methyl and methylene group respectively.

The methyl and methylene carbons were appeared at 21.57 and 77.47 ppm respectively in the ^{13}C NMR spectrum.

Preparation and characterization of carbene complex 4.2h

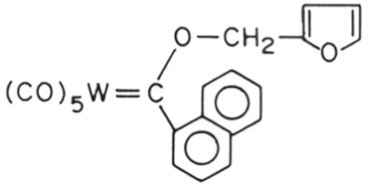


4·2h

The complex **4.2h** (yield 62%) was obtained as air-stable red crystals.

The IR spectrum indicated the formation of this carbene complex, while the ^1H and ^{13}C NMR spectra showed the features consistent with the structure.

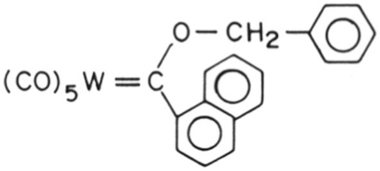
Preparation and characterization of carbene complex 4.2i



4·2i

The carbene **4.2i** (yield 39%) was obtained as air-stable, dark red crystals which could be stored in the refrigerator for several months. The characteristic carbonyl absorptions in the IR spectrum indicated the formation of the carbene complex. Similar to the *o*-substituted complexes, the methylene protons appeared as a broad peak at 5.68 ppm in the ^1H NMR spectrum. In the ^{13}C NMR spectrum the methylene carbon peak was not observed.

Preparation and characterization of carbene complex 4.2j



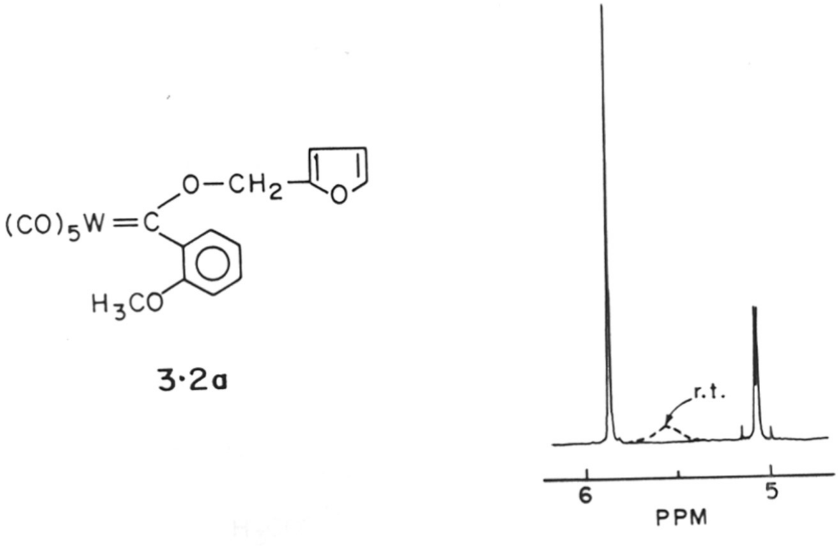
4·2j

The red, air-stable crystals of the complex **4.2j** (yield 50%) were obtained following the same experimental procedure. The IR and ^{1}H and NMR spectra showed the features consistent with the structure. In the ^{13}C NMR spectrum the methylene group appeared as a broad peak at 83.32 ppm.

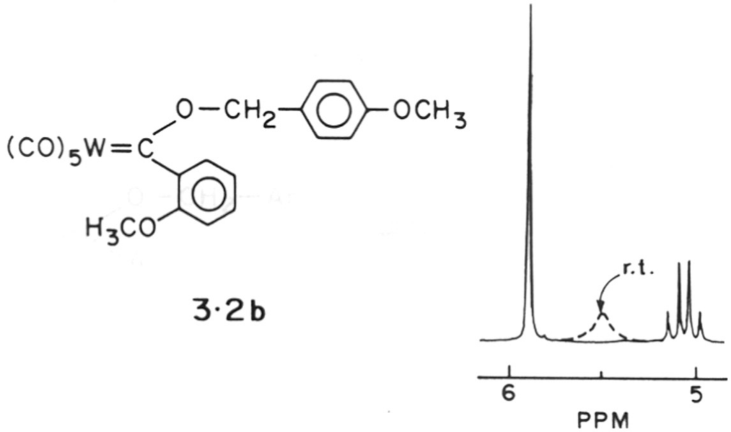
DISCUSSION

It was observed in **Chapter-3** that the two methylene protons of the carbene complex **3.2a** and **3.2b** showed broad peak in the room temperature ^{1}H NMR spectrum. The broad peak was eventually resolved into two peaks at lower temperature (**Scheme 6a** and **6b**).

Scheme 6a



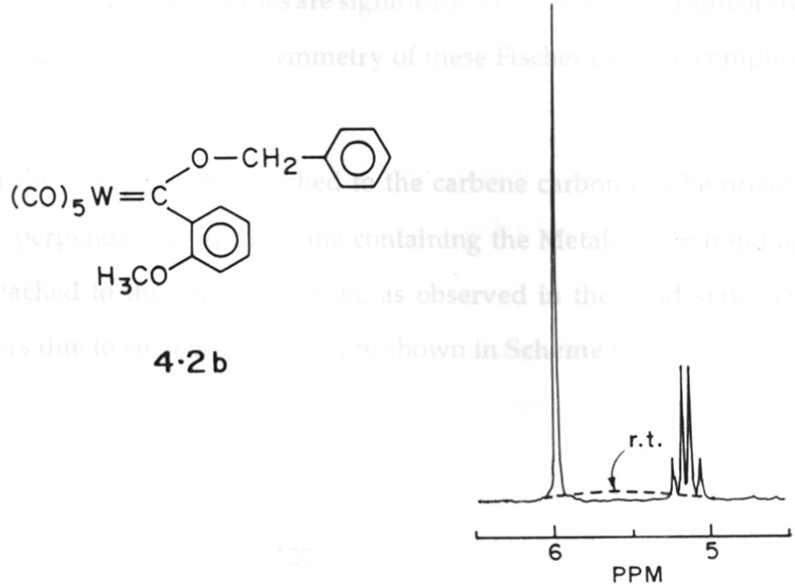
Scheme 6b



3·2b

One was a broad singlet [5.87 ppm (**3.2a**), 5.90 ppm (**3.2b**)] whereas the other was a doublet of doublet [5.07 ppm (**3.2a**), 5.05 ppm (**3.2b**)]. A similar phenomenon was observed for the carbene complex **4.2b**. The downfield peak at 5.97 ppm was a singlet and the upfield peak at 5.14 ppm was a doublet of doublet (Scheme 7).

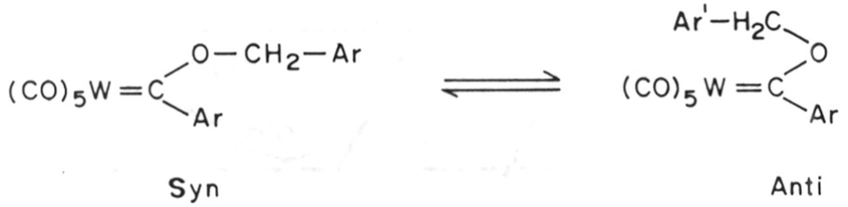
Scheme 7



4·2b

Decoalescence of a broad signal to two sets of peaks at lower temperature is consistent with the equilibrium between two conformers, *syn* and *anti* (**Scheme 8**).

Scheme 8

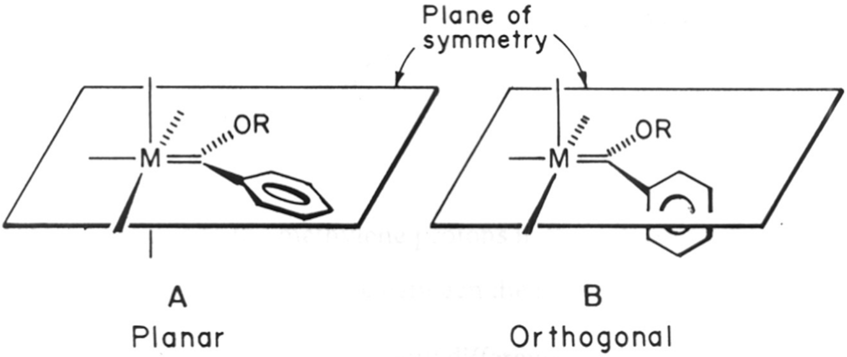


The *syn* and *anti* nomenclature relates to orientation of the alkoxy group with respect to the aryl group attached to carbene carbon, as used originally by Fischer.[4,6] The upfield signal of methylene protons was assigned to the *syn* conformer and the downfield signal to the *anti* conformer, according to precedence.[6]

Apart from the chemical shift differences between the two sets of signals due to the methylene protons, their multiplicities are significant. To address the origin of such difference in line shape, the molecular symmetry of these Fischer carbene complexes is considered in some detail.

The plane of the aromatic ring attached to the carbene carbon can be oriented either coplanar or perpendicular to the plane containing the Metal-C_{carb} π-bond and the two atoms attached to the carbene carbon, as observed in the solid state. Two possible conformers due to such orientations are shown in **Scheme 9**.

Scheme 9

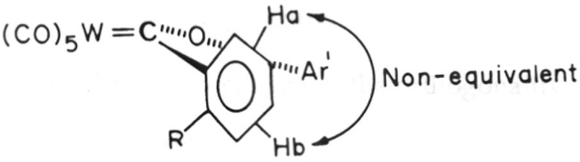


The carbon attached to the oxygen can be also considered to be coplanar with the other four atoms, since the lone pair delocalisation implies that oxygen is *sp2-hybridised.*

In the conformer A, the aromatic ring is contained in the symmetry plane of the molecule. As such, the substituent on the aromatic ring would not contribute to any molecular dissymmetry. On the other hand, in the orthogonal conformation of the aromatic ring as shown in B, only the *ipso* carbon and C-4 lie on the symmetry plane. Thus, unsymmetrical substitution at *ortho* or *meta* position would destroy this molecular plane of symmetry. This, in turn, would render the methylene protons magnetically non-equivalent.[7]

The proximal aromatic ring-current anisotropy for the methylene protons of the *syn* conformer accentuate such non-equivalence and four lines corresponding to two doublets are observed (**Scheme 10**).

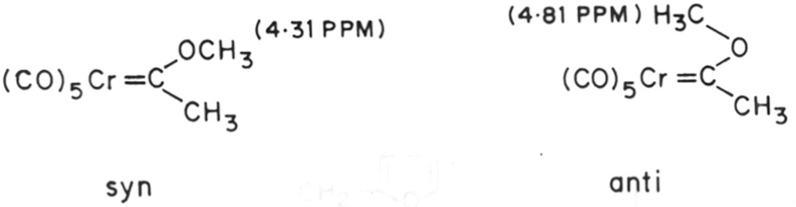
Scheme 10



The signal due to the methylene protons in the *anti* conformer is a broad singlet where the chemical shift difference between the nonequivalent proton nuclei is small.

Fischer had noted the chemical shift difference between *syn* and *anti* OCH_3 signals also in methyl methoxy carbene complexes of chromium (**Scheme 11**).[6]

Scheme 11



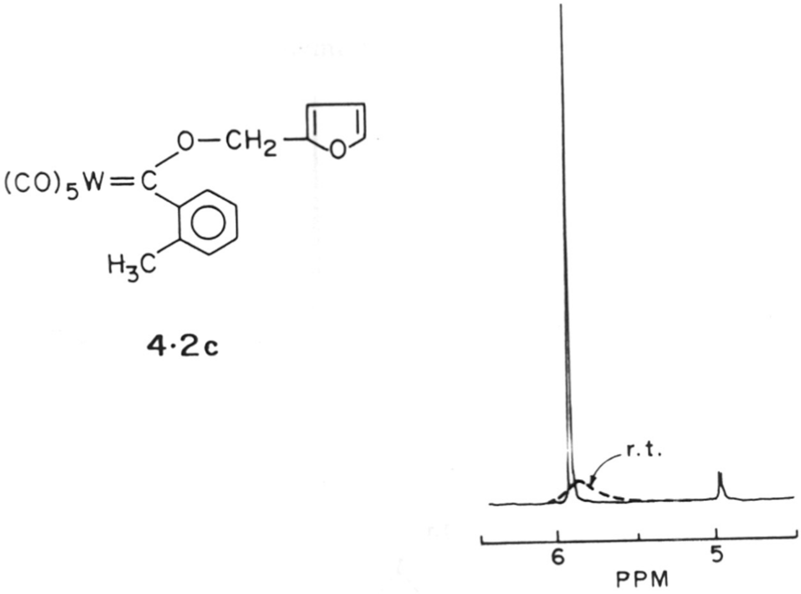
This difference (Δv ≅ 0.5 ppm) is smaller than those observed for aryl methoxycarbene complexes of chromium (Δv ≅ 0.90 ppm).[5] The greater upfield shift of the OCH_3 group in the *syn* conformer could be a consequence of aromatic ring (orthogonal) anisotropy as well. In the present set of examples, the observation of multiplicity of signals due to non-equivalent methylene protons of the *syn* conformer further substantiates this possibility. The fact that the chemical shift of the exchange-averaged signal at ambient temperature is the weighted average based on conformer population at the two sites, indicate that the orthogonality of the aromatic ring is retained in solution at that temperature.

Thus, this is the first direct observation of the orthogonality of aromatic ring in Fischer carbene complexes *in solution*.

The variable-temperature ^{1}H NMR spectra of the related complexes can be explained in these terms. The anisotropic effect of the substituted aromatic ring was further corroborated by the variation in multiplicity patterns of the *syn* methylene protons depending on the aryl ring attached to the carbene carbon.

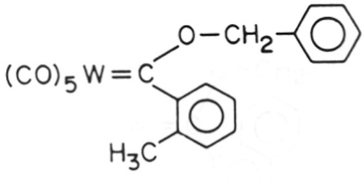
For instance, *ortho*-tolyl group reduced the chemical shift difference compared to the *ortho*-methoxyphenyl groups as seen from the spectra of complexes **4.2c** and **4.2d** (**Scheme 12a** and **12b**).

Scheme 12a

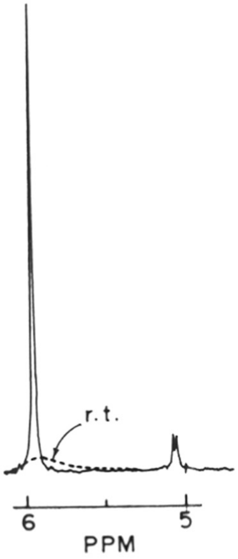


4·2c

Scheme 12b

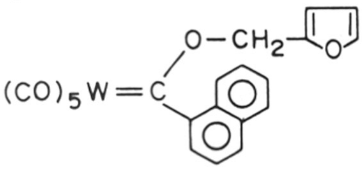


4·2d

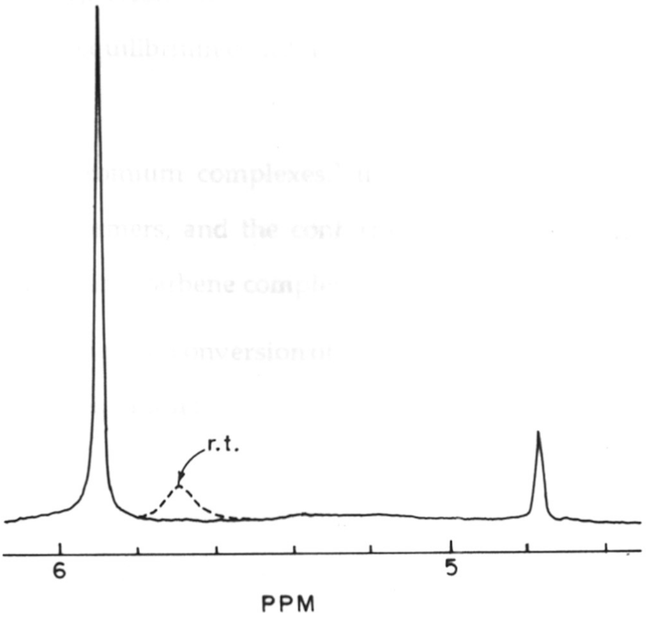


In the naphthyl complexes **4.2i** and **4.2j**, the difference of chemical shift of the non-equivalent methylene protons was further reduced, though the *syn* methylene protons were more shielded (**Scheme 13a and 13b**).

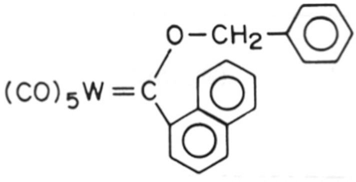
Scheme 13a



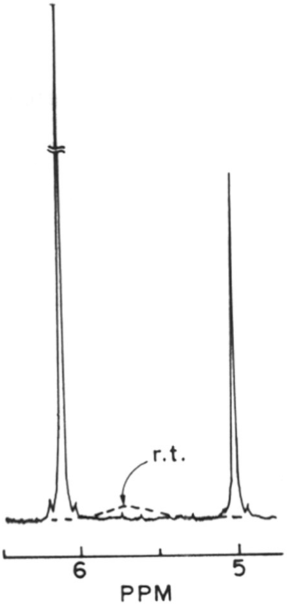
4·2i



Scheme 13b



4·2j



In all the instances where *syn* and *anti* conformers could be frozen, the population of *anti* conformer was greater (**Table 1**). While *meta*-substitution also destroyed the plane of symmetry, the conformational equilibrium could not be arrested for complex **4.2e-h** even at -80°C.

For a corresponding series of chromium complexes,[9] the population of *syn* conformers was greater than *anti* conformers, and the conformational equilibrium could be arrested for a *meta*-substituted aryl carbene complex at -50°C.

The rotational barrier[8] (**Table 1**) of the interconversion of these carbene complexes were calculated and using the Eyring's equation :

$\Delta G^{\dagger} = 4.57T_C\,[9.97 + \log(T_C + \Delta\nu)$ cal where T_C is the coalescence temperature and $\Delta\nu$ is the difference of the two peaks at T_C in Hz, it was found that the energy barrier was around 12 to 13 kcal/mol.

Table 1 : Data for Tc, $\Delta\nu$, $\Delta G^{\dagger}$ and population density

Complex	Syn (%)	Anti (%)	$\Delta\nu$ (δ)	$T_C{}^{a}$ (K)	Rotational barrier $\Delta G^{\dagger b}$ (kcal/mol) at T_C
3.2a	63	37	0.80	276	13.00
3.2b	63	37	0.82	284	13.36
4.2b	58	42	0.83	278	12.89
4.2c	88	12	0.97	280	13.02
4.2d	86	14	0.89	281	13.09
4.2i	83	17	1.11	279	12.79
4.2j	64	36	1.10	278	12.93

a. The accuracy of the temperature is in the range of ±0.1°C. b. Although this equation is essentially applicable to equal population of conformers, it was used to approximately estimate the $\Delta G^{\dagger}$ for the present set of data where conformers populations are not widely varied. For more accurate estimate, the formulation described by H. Shanan-Atidi and K. H. Bar-Eli could be applied : J. Phy. Chem., ***74****, 961, 1970.*

That a *para*-methoxy group in the aromatic ring lowered the rotational barrier of the C_{carb}-O bond was inferred from the sharp singlet at 3.82 ppm for the methylene protons (**Chapter 2**, complex **2.2c**). This trend is also consistent with Fischer's observations.[3a]

This barrier is directly related to the efficiency of delocalisation of the oxygen lone pair along the metal-C_{carb} bond, i.e., the extent of double bond character of the C_{carb}-O bond. Competetive mesomeric electron donation by the aromatic group would reduce the extent of electron-donation from the oxygen and thus the C_{carb}-O bond order. This, in turn, would decrease the barrier of restricted rotation.

Interestingly, the present observations revealed that an *ortho*-methoxyphenyl group does not effect electron delocalisation towards the metal-C_{carb} fragment to the extent the *para*-methoxyphenyl group does. In other words, the position in the aromatic ring which promote electron-delocalisation by resonance participation with the metal-C_{carb} bond, can be arranged in the order : *ortho* < *meta* < *para*.

It may be recalled that an ortho-methoxy substituent on the phenyl ring did not impair the rearrangement reaction (**Chapter 3**) to the extent a *para-methoxy* substituent did (**Chapter 2**). This could also be taken as an evidence to support a greater degree of mesomeric electron delocalisation by the *para-methoxyphenyl* group.

SUMMARY

Low temperature ^{1}H NMR spectra of a set of Fischer carbene complexes revealed that the aromatic ring attached to the carbene carbon can remain orthogonal to Metal-C_{carb} π-plane in solution, and, therefore, this orientation was not a solid-state effect.

"The solution to a problem

changes the nature of the problem."

EXPERIMENTAL

o-iodotoluene, *m*-iodotoluene and *m*-iodoanisole were prepared according to established procedures.

All the complexes were prepared following a similar procedure as described in **Chapter 2**.

Preparation of pentacarbonyl{(*o*-methyl phenyl)[(tetraethylammonio)oxy]carbene} tungsten(0) (4.1c)

From $W(CO)_6$ (1.20 gm, 3.41 mmol); *o*-methylphenyllithium [freshly prepared from n-butyllithium (5 ml, 5 mmol) & *o*-iodotoluene (0.63 ml, 5 mmol)]; and tetraethylammonium bromide (716 mg, 3.41 mmol); the carbene salt **4.1c** was obtained as a yellow solid (1.742 gm, 89%)

^{13}C NMR (Acetone-d_6) 7.82; 19.04; 53.18; 123.27; 125.29; 125.56; 128.02; 130.89; 164.31; 204.60; 209.37; 285.58

Preparation of pentacarbonyl{(*m*-methoxy phenyl)[(tetraethylammonio)oxy] carbene} tungsten(0) (4.1e)

From $W(CO)_6$ (1.50 gm, 4.27 mmol); *m*-methoxyphenyllithium [freshly prepared from n-butyllithium (6 ml, 6 mmol) & *m*-iodoanisole (0.71 ml, 6 mmol)]; and tetraethylammonium bromide (900 mg, 4.27 mmol); the carbene salt **4.1e** was obtained as a red solid (2.286 gm, 91%)

^{13}C NMR (Acetone-d_6) 7.57; 52.99; 55.31; 111.57; 114.61; 118.81; 128.87; 159.09; 160.09; 204.44; 208.75; 277.60

Preparation of pentacarbonyl{(*m*-methylphenyl)[(tetraethylammonio)oxy]carbene} tungsten(0) (4.1g)

From $W(CO)_6$ (1.10 gm, 3.13 mmol); *m*-methylphenyllithium [freshly prepared from n-butyllithium (5 ml, 5 mmol) & *m*-iodotoluene (0.64 ml, 5 mmol)]; and tetraethylammonium bromide (660 mg, 3.13 mmol); the carbene salt **4.1g** was obtained as a red solid (1.490 gm, 83%)

^{13}C NMR (Acetone-d_6) 7.78; 21.74; 53.18; 124.17; 126.88; 128.07; 129.37; 137.29; 158.04; 204.86; 208.85; 278.24

Preparation of pentacarbonyl {(α-naphthyl)[(tetraethylammonio)oxy] carbene}tungsten(0) (4.1i)

From $W(CO)_6$ (406 mg, 1.15 mmol); α-naphthyllithium [freshly prepared from n-butyllithium (1.73 ml, 1.73 mmol) & α-bromonaphthalene (0.24 ml, 1.72 mmol)]; and tetraethylammonium bromide (245 mg, 1.15 mmol); the carbene salt **4.1i** was obtained as a yellow solid (624 mg, 89%)

^{13}C NMR (Acetone-d_6) 7.60; 52.99; 119.54; 125.63; 126.694 127.55; 128.56; 134.99; 159.25; 223.58; 228.93; 297.49

Preparation of pentacarbonyl[(benzyloxy)(o-methoxy phenyl)carbene]tungsten(0) (4.2b)

From the tetraethylammonium carbene salt **4.1a** (600 mg, 1.02 mmol), acetyl chloride (0.07 ml, 1.02 mmol), and benzyl alcohol (0.12 ml, 1.15 mmol), the carbene complex **4.2b** was obtained as a dark red solid (322 mg, 58%). Carbene complex was purified by flash column chromatography followed by crystallization from petroleum ether at -5°C.

IR ($CHCl_3$)	2040(m); 1995(sh); 1945(s)
^1H NMR ($CDCl_3$)	3.85 (s, 3H); 5.6 (b, 2H); 6.97 (m, 4H); 7.37 (m,5H)
^{13}C NMR ($CDCl_3$)	55.25; 86.62; 111.00; 120.13; 121.97; 127.94; 128.67; 129.77; 134.34; 144.21; 149.83; 197.15; 205.51; 325.34
Analysis	Calculated : C 43.71 H 2.55 Found : C 43.61 H 2.60

Preparation of pentacarbonyl[(furfuryloxy)(*o*-methylphenyl)carbene]tungsten(0) (4.2c)

From the tetraethylammonium carbene salt **4.1c** (1.32 gm, 2.3 mmol), acetyl chloride (0.16 ml, 2.3 mmol), and furfuryl alcohol (0.2 ml, 2.3 mmol), the carbene complex **4.2c** was obtained as a red solid (520 mg, 43%). Carbene complex was purified by flash column chromatography followed by crystallization from petroleum ether at -5°C.

IR ($CHCl_3$)	2025(m); 1985(sh); 1930(s)
^1H NMR ($CDCl_3$)	2.18 (s, 3H); 5.88 (b, 2H); 6.42 (m, 1H); 6.6 (m, 1H); 7.2 (m, 4H); 7.5 (m, 1H)
^{13}C NMR ($CDCl_3$)	19.14; 76.32; 111.15; 112.66; 122.57; 125.48; 127.39; 128.73; 130.85; 144.55; 147.64; 197.04; 204.59; 330.25
Analysis	Calculated : C 43.71 H 2.55 Found : C 40.89 H 2.52

Preparation of pentacarbonyl[(benzyloxy)(*o*-methylphenyl)carbene]tungsten(0) (4.2d)

From the tetraethylammonium carbene salt **4.1c** (986 mg, 1.72 mmol), acetyl chloride (0.12 ml, 1.72 mmol), and benzyl alcohol (0.18 ml, 1.8 mmol), the carbene complex **4.2d** was obtained as a red solid (505 mg, 56%). The carbene complex was purified by flash column chromatography followed by crystallization from petroleum ether at -5°C.

IR ($CHCl_3$)	2030(m); 1990(sh); 1940(s)
^1H NMR ($CDCl_3$)	2.2 (s, 3H); 5.8 (b, 2H); 7.23 (m, 4H); 7.5 (m, 5H);
^{13}C NMR ($CDCl_3$)	19.34; 84.60; 122.33; 125.58; 127.24; 128.76; 129.22; 129.51; 130.90; 134.20; 155.86; 197.29; 204.79; 330.61
Analysis	Calculated : C 45.02 H 2.62 Found : C 45.72 H 2.94

Preparation of pentacarbonyl[(furfuryloxy)(*m*-methoxyphenyl)carbene]tungsten(0) (4.2e)

From the tetraethylammonium carbene salt **4.1e** (1.00 gm, 1.7 mmol), acetyl chloride (0.12 ml, 1.7 mmol), and furfuryl alcohol (0.15 ml, 1.73 mmol), the carbene complex **4.2e** was obtained as a dark red solid (337 mg, 38%). The carbene complex was purified by crystallization from petroleum ether at -5°C.

IR ($CHCl_3$)	2030(m); 2000(sh); 1950(s)
^1H NMR ($CDCl_3$)	3.87 (s, 3H); 5.95 (s, 2H); 6.52 (m, 1H); 6.68 (m, 1H); 7.1 (m, 3H); 7.32 (m, 1H); 7.57 (m, 1H)
^{13}C NMR ($CDCl_3$)	55.25; 77.09; 110.77; 111.34; 112.05; 117.44; 118.36; 128.99; 144.18; 147.53; 156.46; 159.03; 197.02; 203.28; 319.79

Analysis Calculated : C 40.07 H 2.22

Found : C 40.00 H 2.39

Preparation of pentacarbonyl[(benzyloxy)(*m*-methoxyphenyl)carbene]tungsten(0) (4.2f)

From the tetraethylammonium carbene salt **4.1e** (800 mg, 1.36 mmol), acetyl chloride (0.1 0ml, 1.4 mmol), and benzyl alcohol (0.15 ml, 1.44 mmol), the carbene complex **4.2f** was obtained as a red solid (438 mg, 59%). The carbene complex was purified by flash column chromatography followed by crystallization from petroleum ether at -5°C.

IR ($CHCl_3$) 2030(m); 1990(sh); 1940(s)

^1H NMR ($CDCl_3$) 3.9 (s, 3H); 6.02 (s, 2H); 7.1 (m, 3H); 7.38 (m, 1H); 7.52 (m, 5H)

^{13}C NMR ($CDCl_3$) 55.67; 85.94; 111.92; 117.87; 118.86; 128.05; 128.69; 129.27; 129.44; 134.47; 156.77; 159.44; 197.58; 203.78; 320.21

Analysis Calculated : C 43.71 H 2.55

Found : C 43.70 H 2.56

Preparation of pentacarbonyl[(furfuryloxy)(*m*-methylphenyl)carbene]tungsten(0) (4.2g)

From the tetraethylammonium carbene salt **4.1g** (900 mg, 1.57 mmol), acetyl chloride (0.11 ml, 1.57 mmol), and furfuryl alcohol (0.13 ml, 1.57 mmol), the carbene complex **4.2g** was obtained as a dark red solid (301 mg, 36%). The carbene complex was purified by crystallization from petroleum ether at -5°C.

IR ($CHCl_3$) 2025(m); 1980(sh); 1930(s)

^1H NMR ($CDCl_3$) 2.38 (s, 3H); 5.95 (s, 2H); 6.48 (m, 1H); 6.67 (m, 1H); 7.32 (m, 4H); 7.55 (m, 1H)

^{13}C NMR ($CDCl_3$)	21.57; 77.47; 111.13; 112.44; 124.18; 126.79; 128.17; 132.72; 138.01; 144.52; 147.90; 155.62; 197.47; 203.75; 320.48
Analysis	Calculated : C 41.30 H 2.29
	Found : C 40.97 H 2.46

Preparation of pentacarbonyl[(benzyloxy)(*m*-methyl phenyl)carbene]tungsten(0) (4.2h)

From the tetraethylammonium carbene salt **4.1g** (714 mg, 1.24 mmol), acetyl chloride (0.09 ml, 1.26 mmol), and benzyl alcohol (0.13 ml, 1.25 mmol), the carbene complex **4.2h** was obtained as a red solid (410 mg, 62%). The carbene complex was purified by flash column chromatography followed by crystallization from petroleum ether at -5°C.

IR ($CHCl_3$)	2030(m); 1980(sh); 1940(s)
^{1}H NMR ($CDCl_3$)	2.45 (s, 3H); 6.02 (s, 2H); 7.43 (m, 9H)
^{13}C NMR ($CDCl_3$)	21.24; 85.54; 123.75; 126.66; 127.84; 128.31; 128.82; 129.01; 132.32; 134.09; 137.68; 155.18; 197.25; 203.46; 320.26
Analysis	Calculated : C 45.02 H 2.62
	Found : C 45.11 H 2.80

Preparation of pentacarbonyl[(furfuryloxy)(α-naphthyl)carbene] tungsten(0) (4.2i)

From the tetraethylammonium carbene salt **4.1i** (775 mg, 1.27 mmol), acetyl chloride (0.09 ml, 1.27 mmol), and furfuryl alcohol (0.11 ml, 1.27 mmol), the carbene complex **4.2i** was obtained as a dark red solid (276 mg, 39%). The carbene complex was purified by crystallization from petroleum ether at -5°C.

IR ($CHCl_3$)	2025(m); 1995(sh); 1950(s)
^{1}H NMR ($CDCl_3$)	5.68 (b, 2H); 6.42 (m, 1H); 6.53 (m, 1H); 7.18 (m, 1H); 7.53 (m, 5H); 7.82 (m, 2H)
^{13}C NMR ($CDCl_3$)	110.75; 112.12; 119.31; 124.35; 124.53; 126.28; 126.77; 128.37; 128.61; 133.13; 144.13; 147.34; 153.21; 196.77; 204.81; 328.82
Analysis	Calculated : C 45.08 H 2.14 Found : C 45.06 H 2.38

Preparation of pentacarbonyl[(benzyloxy)(α-naphthyl)carbene] tungsten(0) (4.2j)

From the tetraethylammonium carbene salt **4.1i** (700 mg, 1.15 mmol), acetyl chloride (0.08 ml, 1.15 mmol), and benzyl alcohol (0.12 ml, 1.15 mmol), the carbene complex **4.2j** was obtained as a red solid (325 mg, 50%). The carbene complex was purified by crystallization from petroleum ether at -5°C.

IR ($CHCl_3$)	2035(m); 1985(sh); 1945(s)q
^{1}H NMR ($CDCl_3$)	5.7 (b, 2H); 7.2 (m, 1H); 7.42 (m, 4H); 7.55 (m, 5H); 7.87 (m, 2H)
^{13}C NMR ($CDCl_3$)	83.32; 119.03; 124.35; 124.47; 124.62; 126.29; 126.72; 127.97; 128.45; 128.52; 128.72; 128.91; 133.15; 133.99; 152.42; 196.92; 204.85; 329.12

Analysis Calculated : C 47.17 H 2.39

Found : C 48.68 H 2.55

Low temperature ^{1}H NMR of 3.2a, 3.2b, and 4.2b-j

The sample [in $CDCl_3$ or CD_2Cl_2 (**3.2a, 3.2b, 4.2i** and **4.2e-h**)] was deareated. The room temperature (27°C) spectrum was taken first. The temperature was lowered at 10°C steps till the broad signal due to methylene protons gave rise to two sets of peaks. The experiment was stopped when there was no change in the signals on further cooling.

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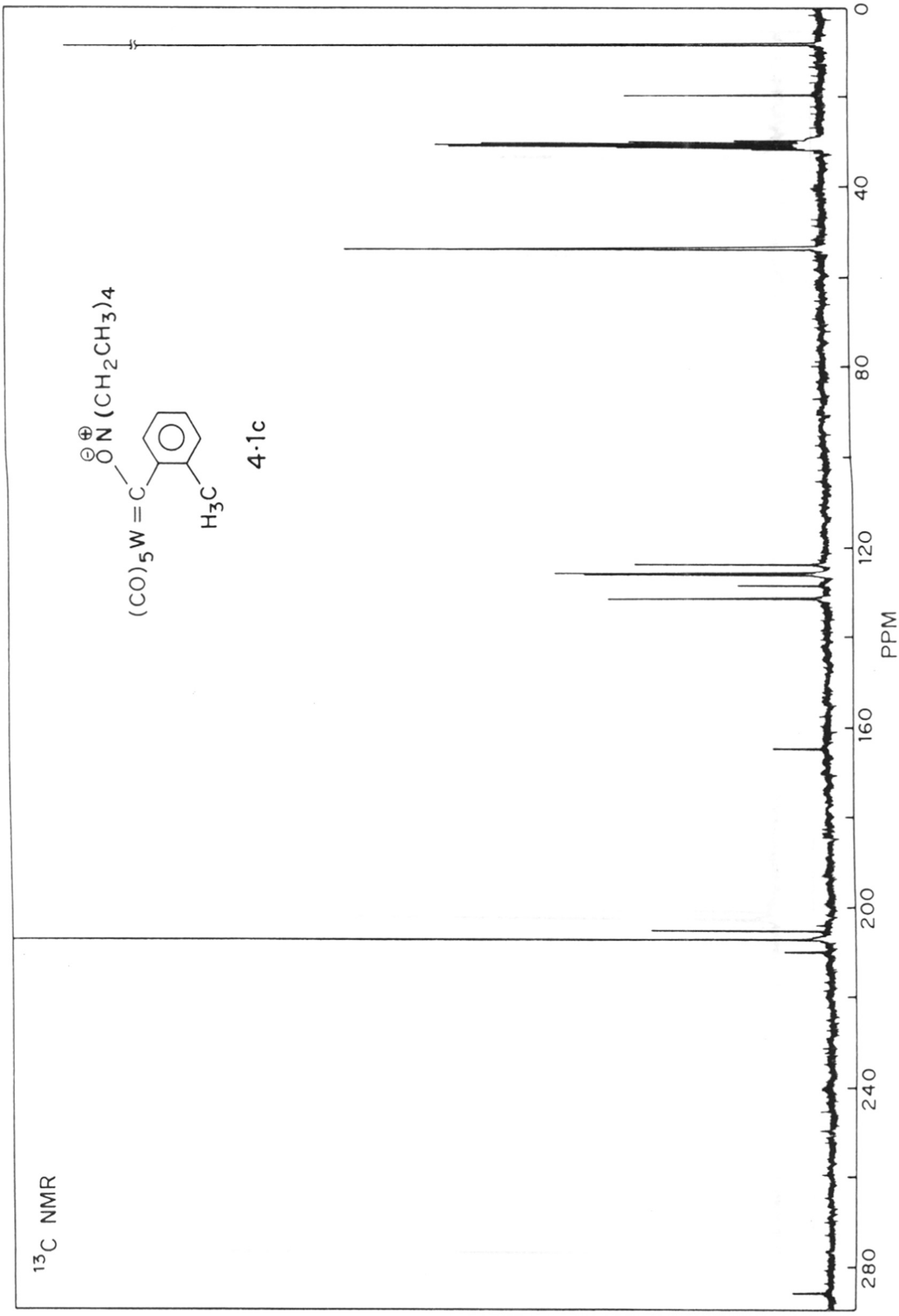
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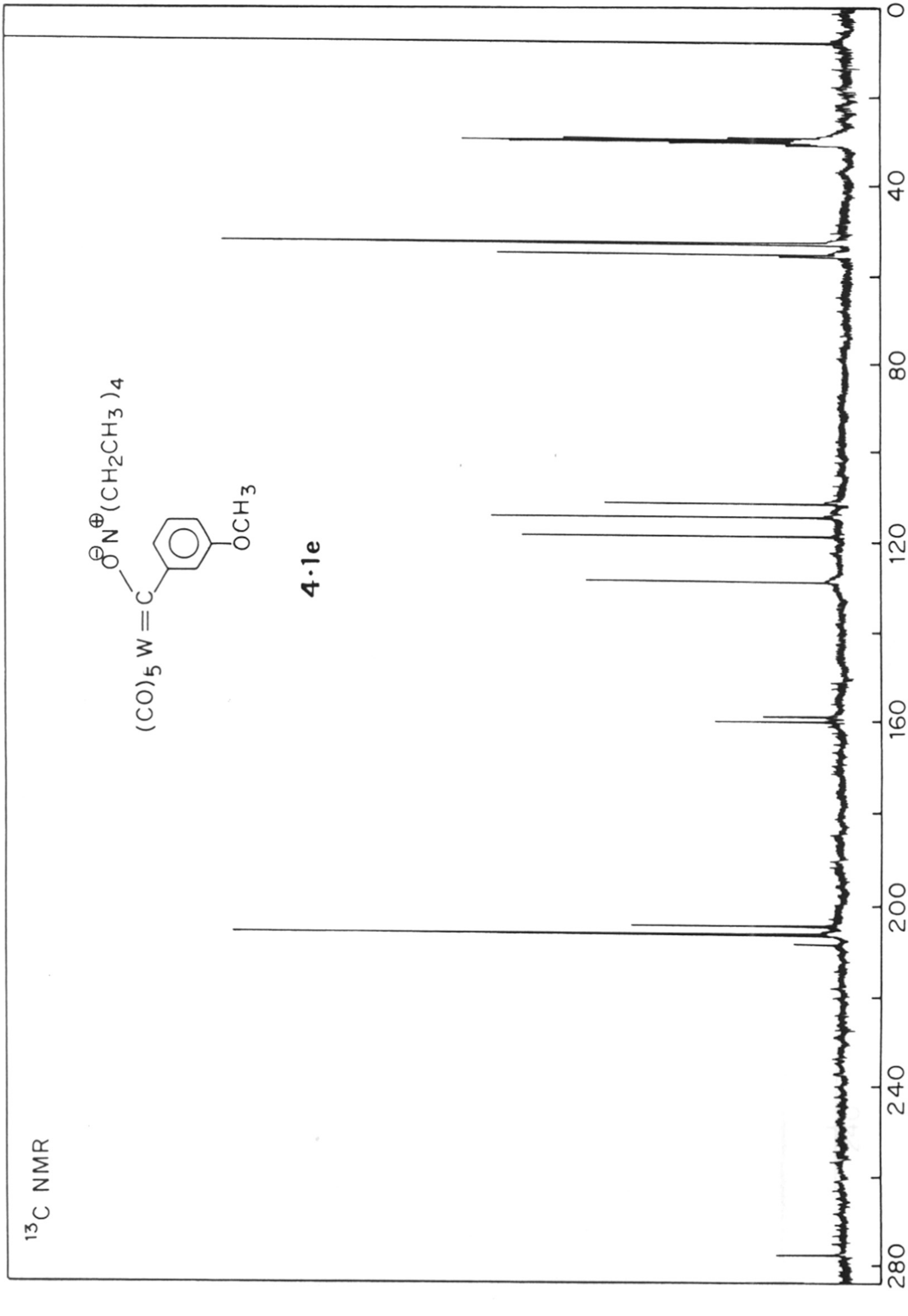
200
240
280
PPM



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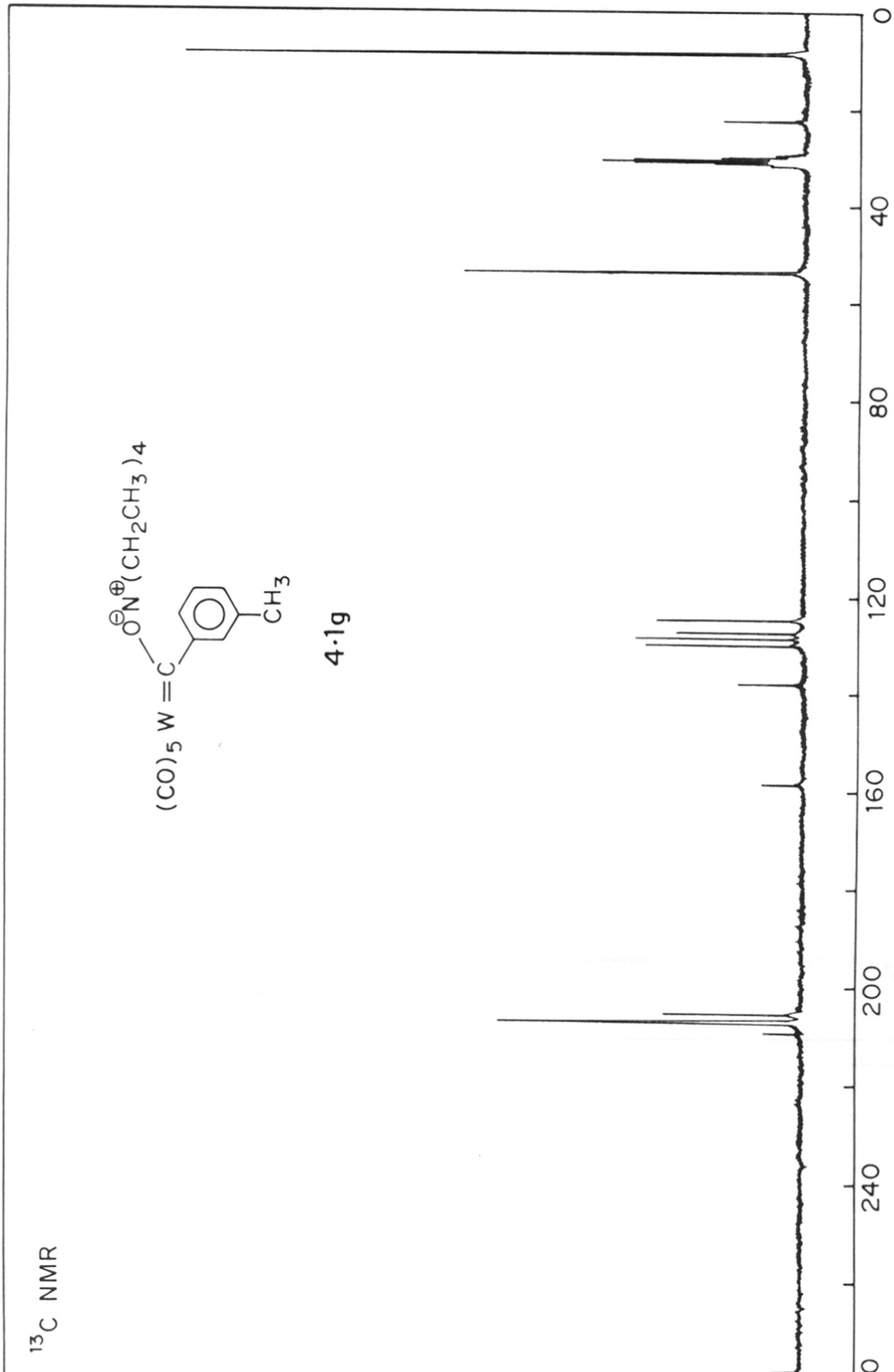

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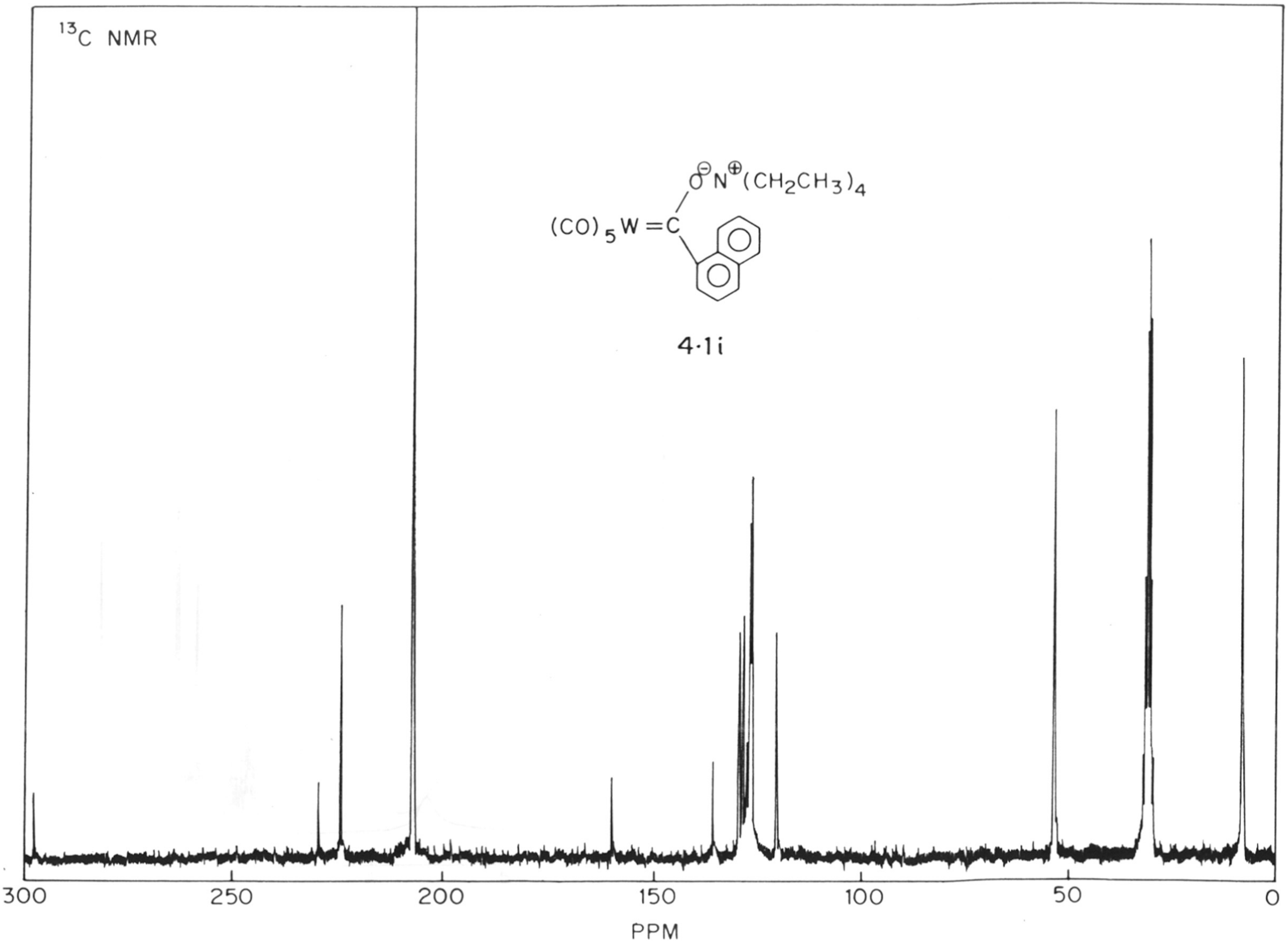
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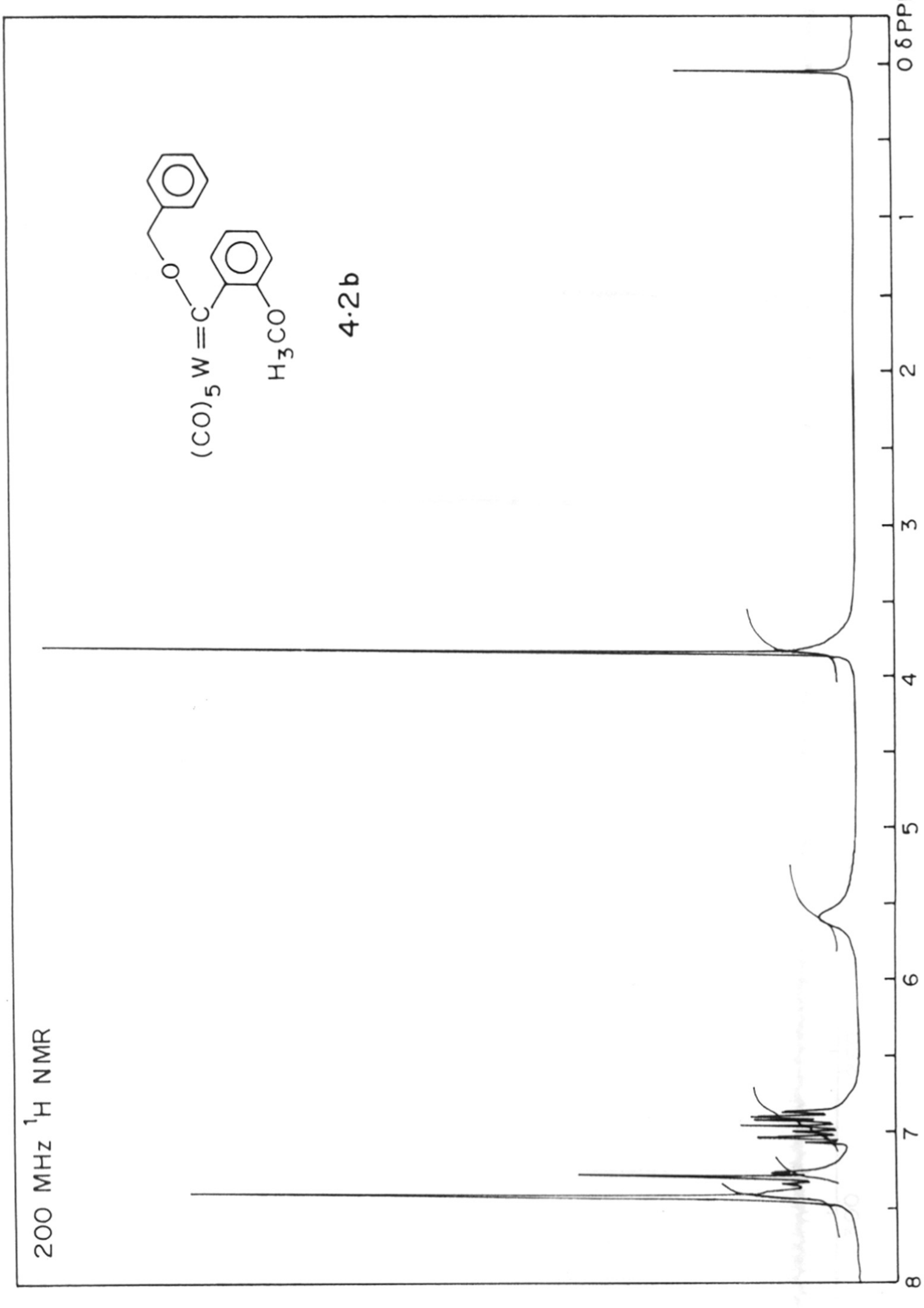
50
0
PPM

4·1i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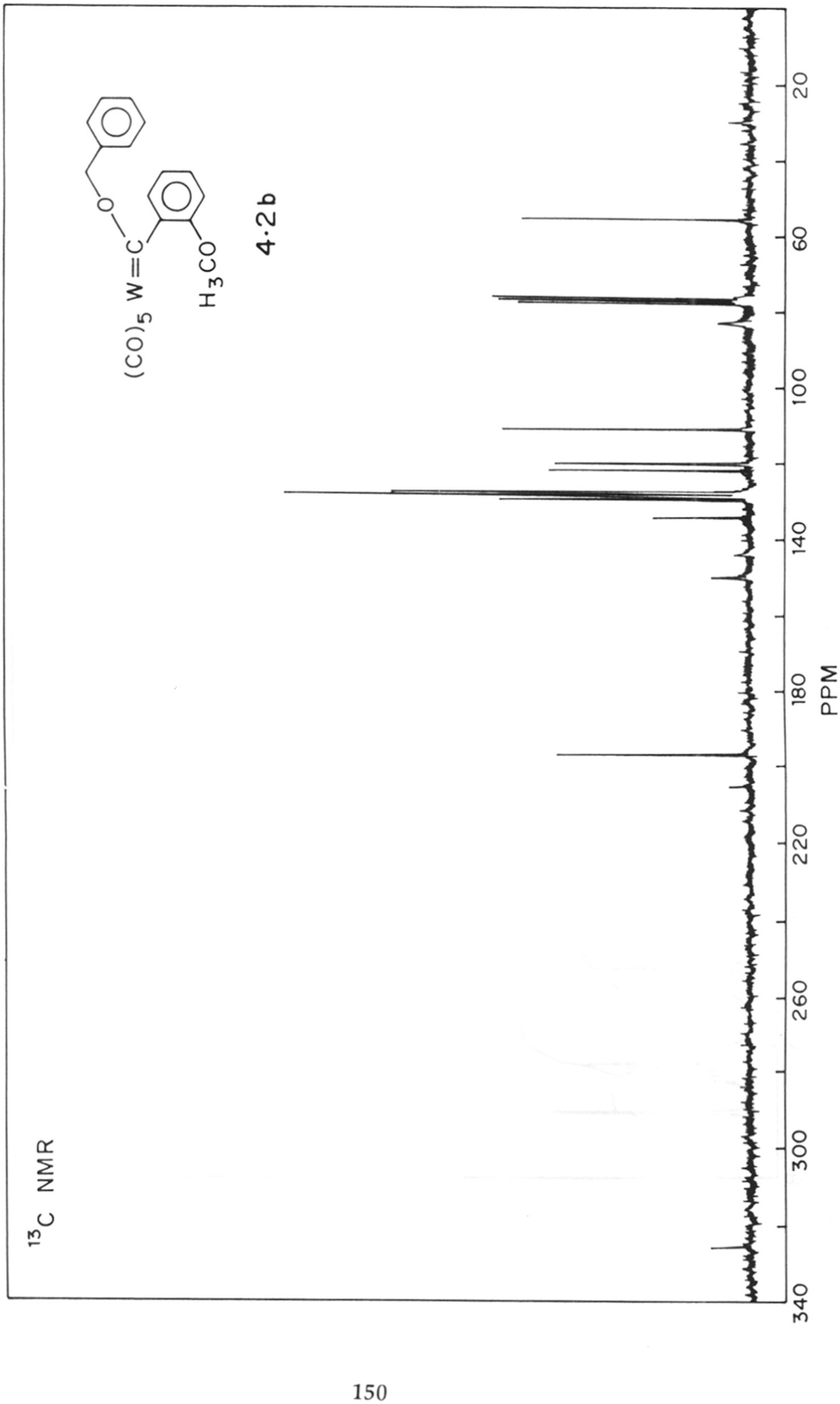
6
5
4
3
2
1
0 δ PPM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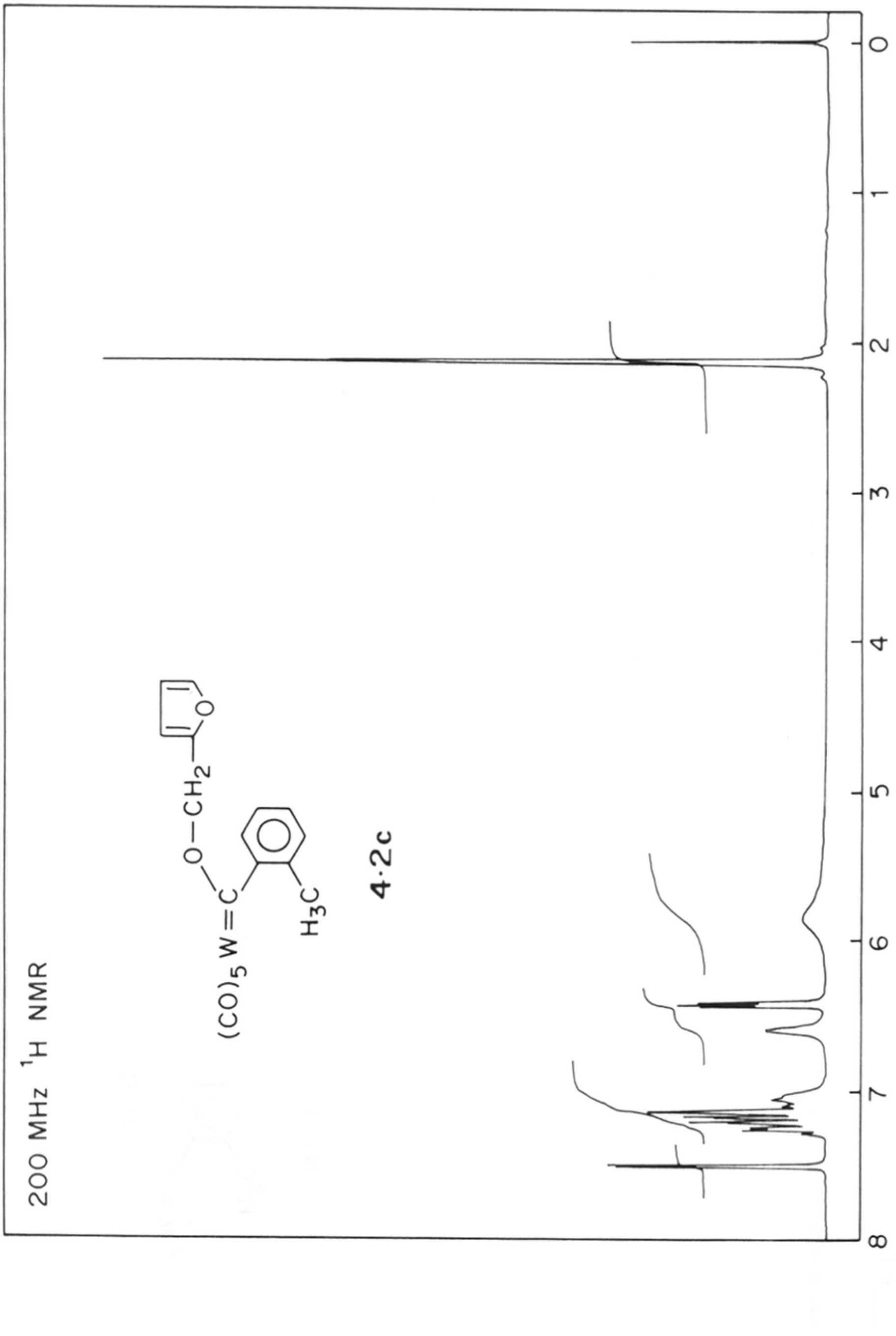
140
100
60
20
PPM



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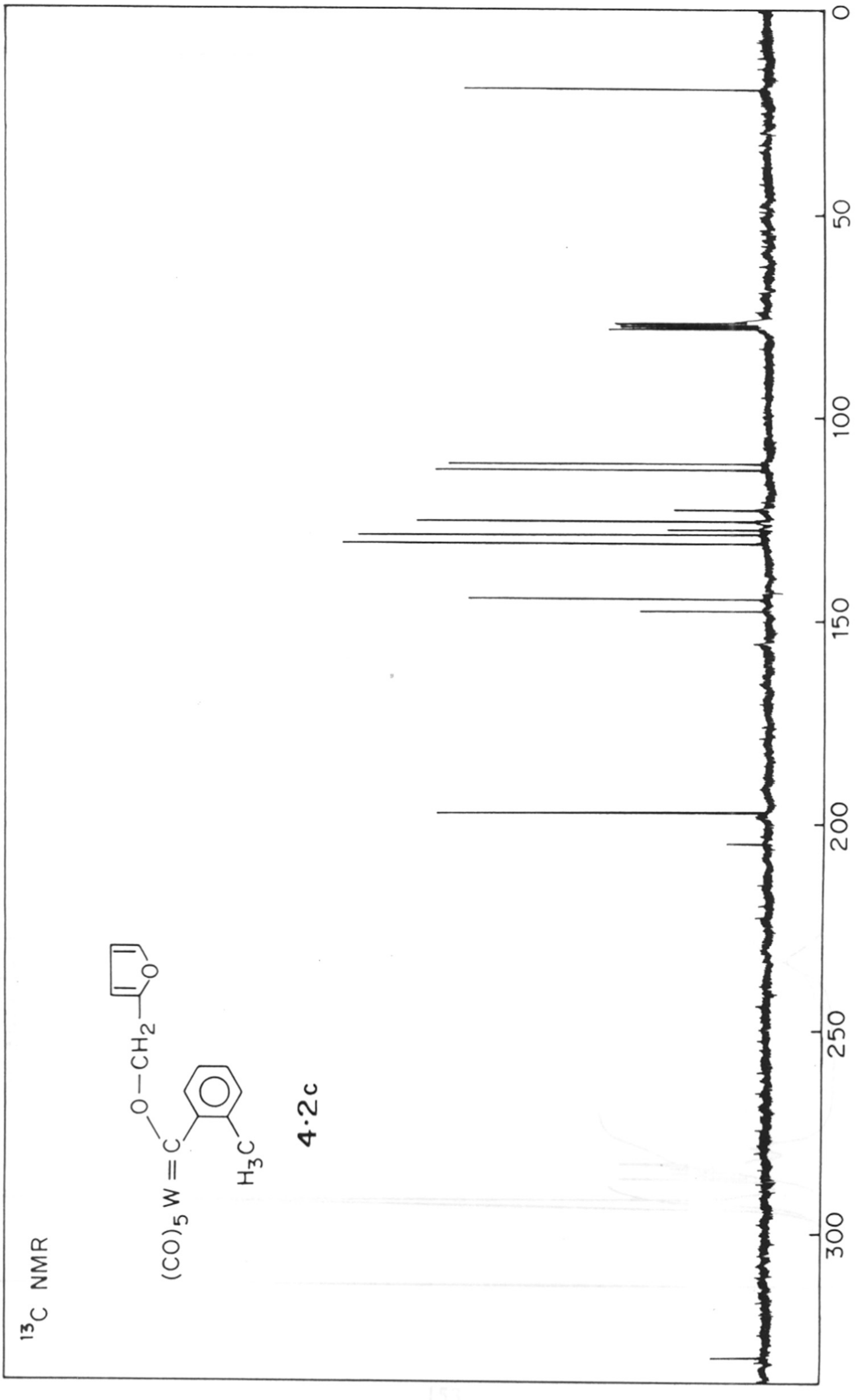

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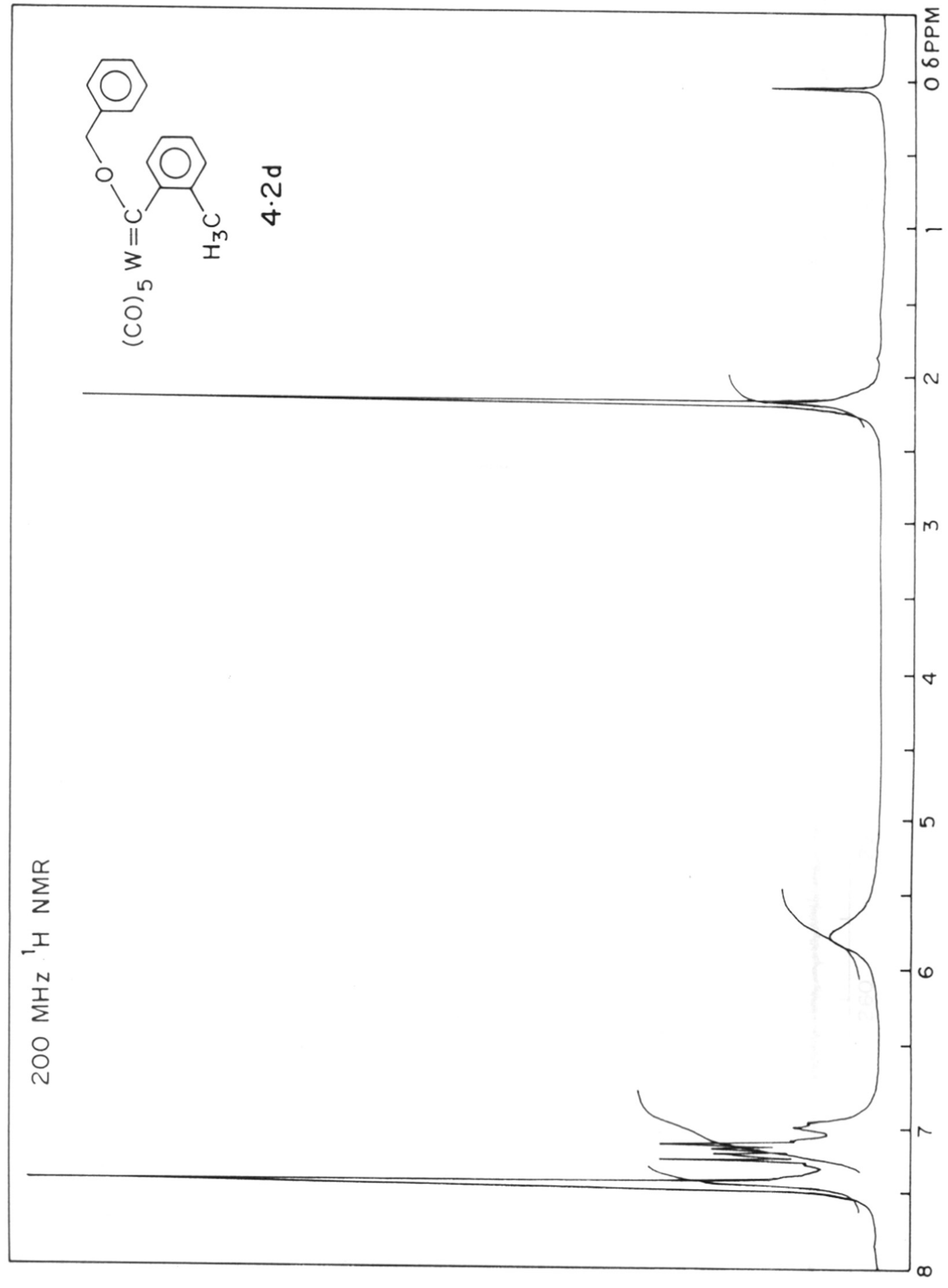
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1
2
3
4
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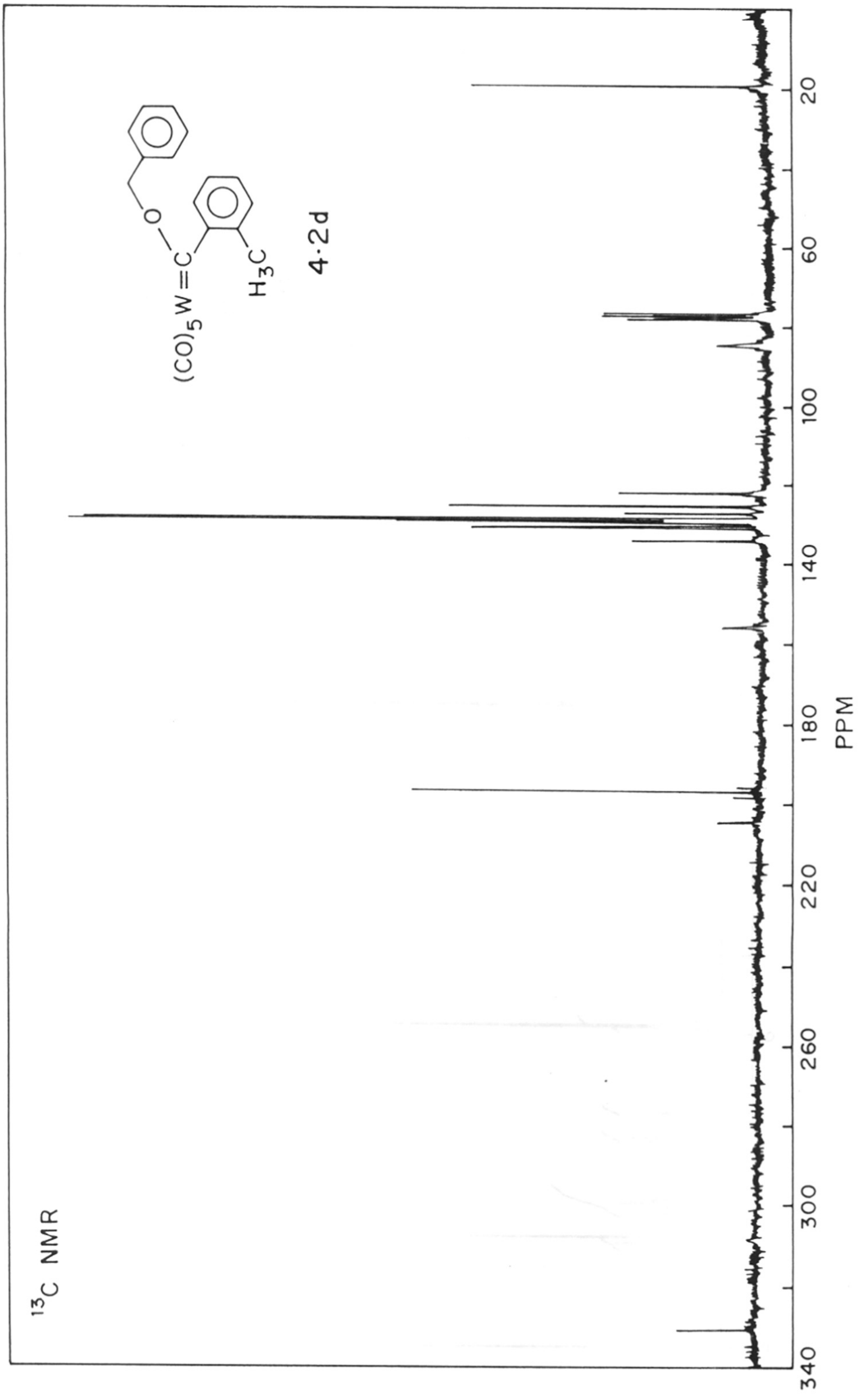
6
7
8



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O
H_3C
4·2d
20
60
100
140
180
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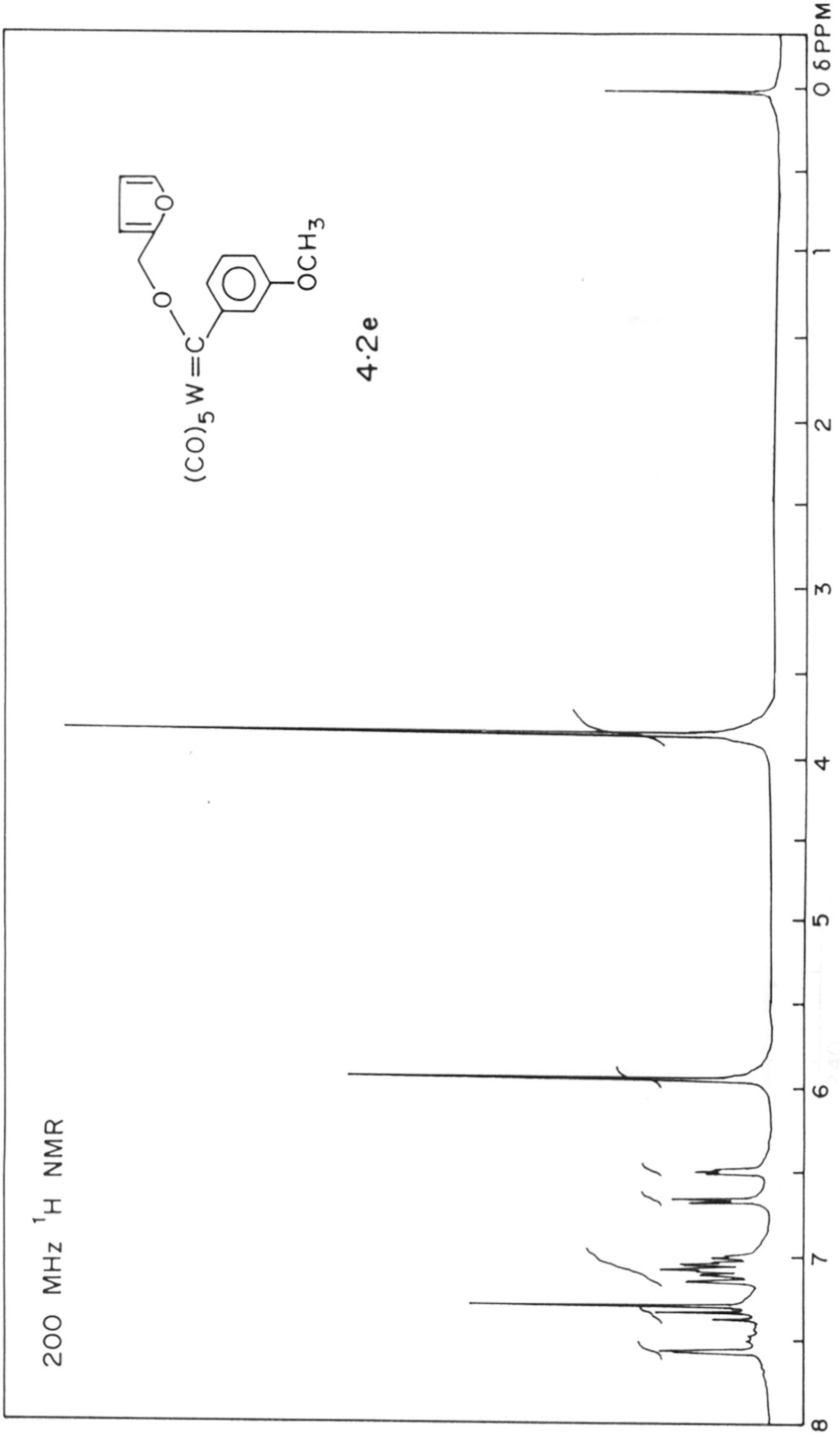
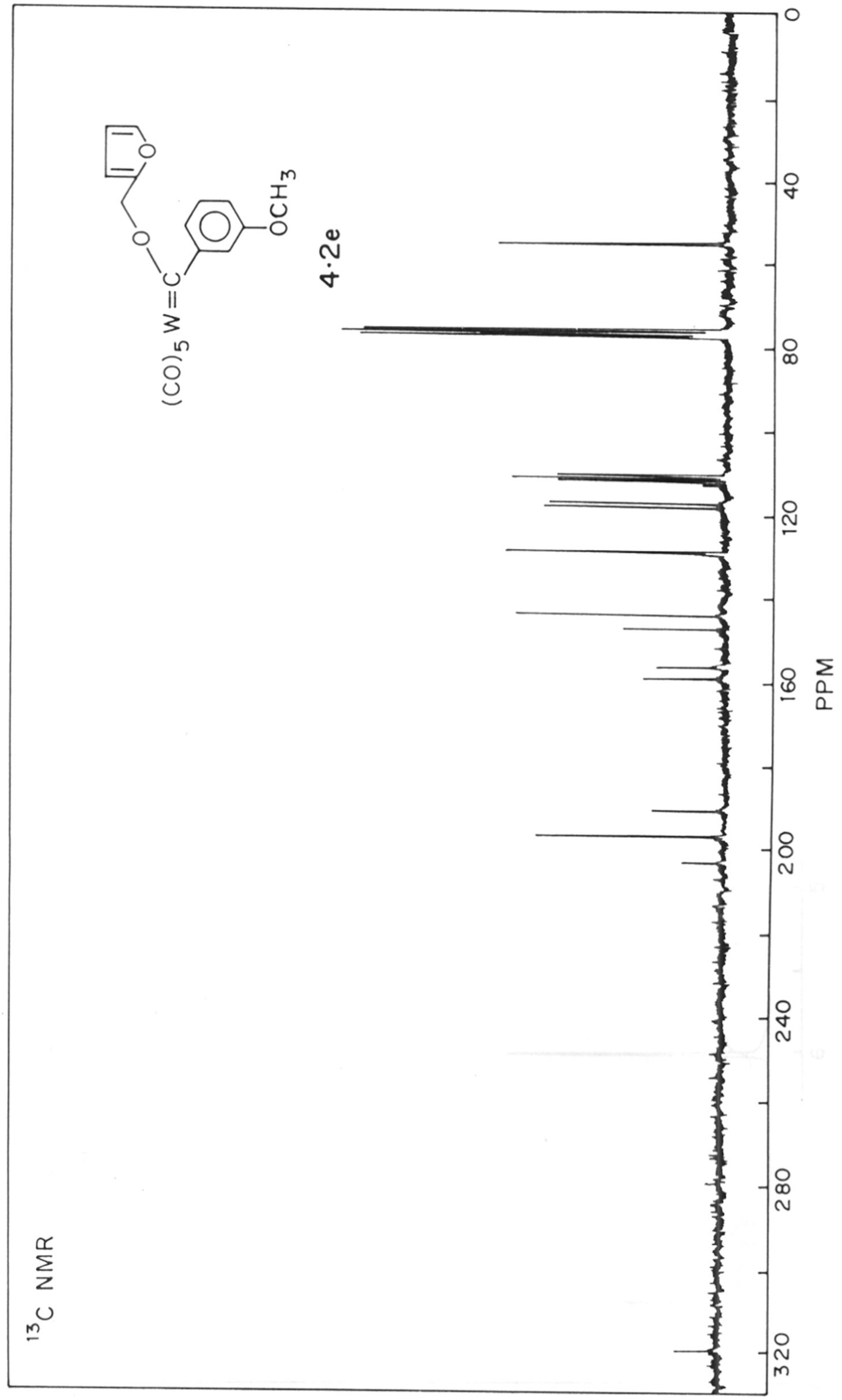
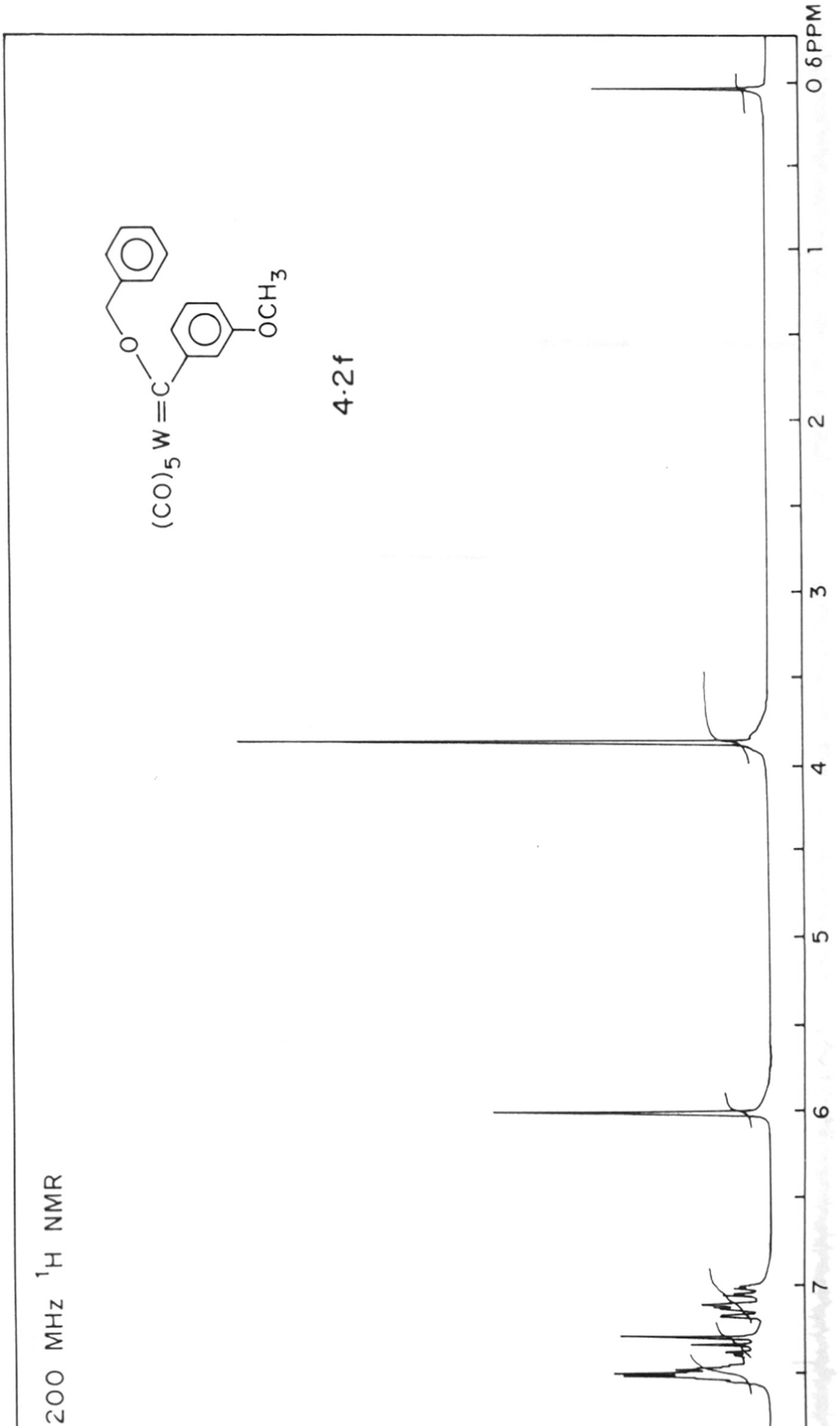
260
300
340
PPM



4·2e


4·2e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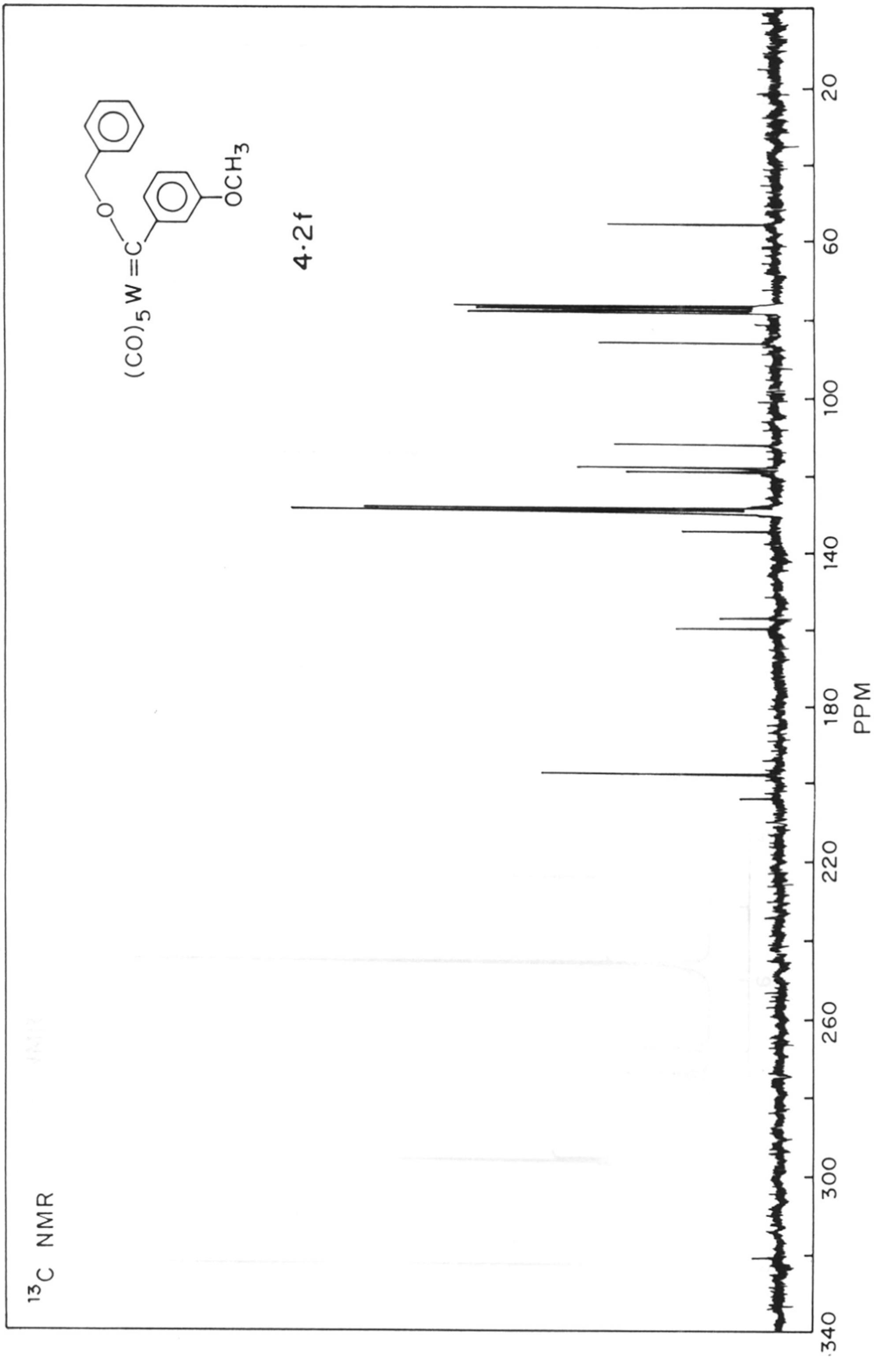
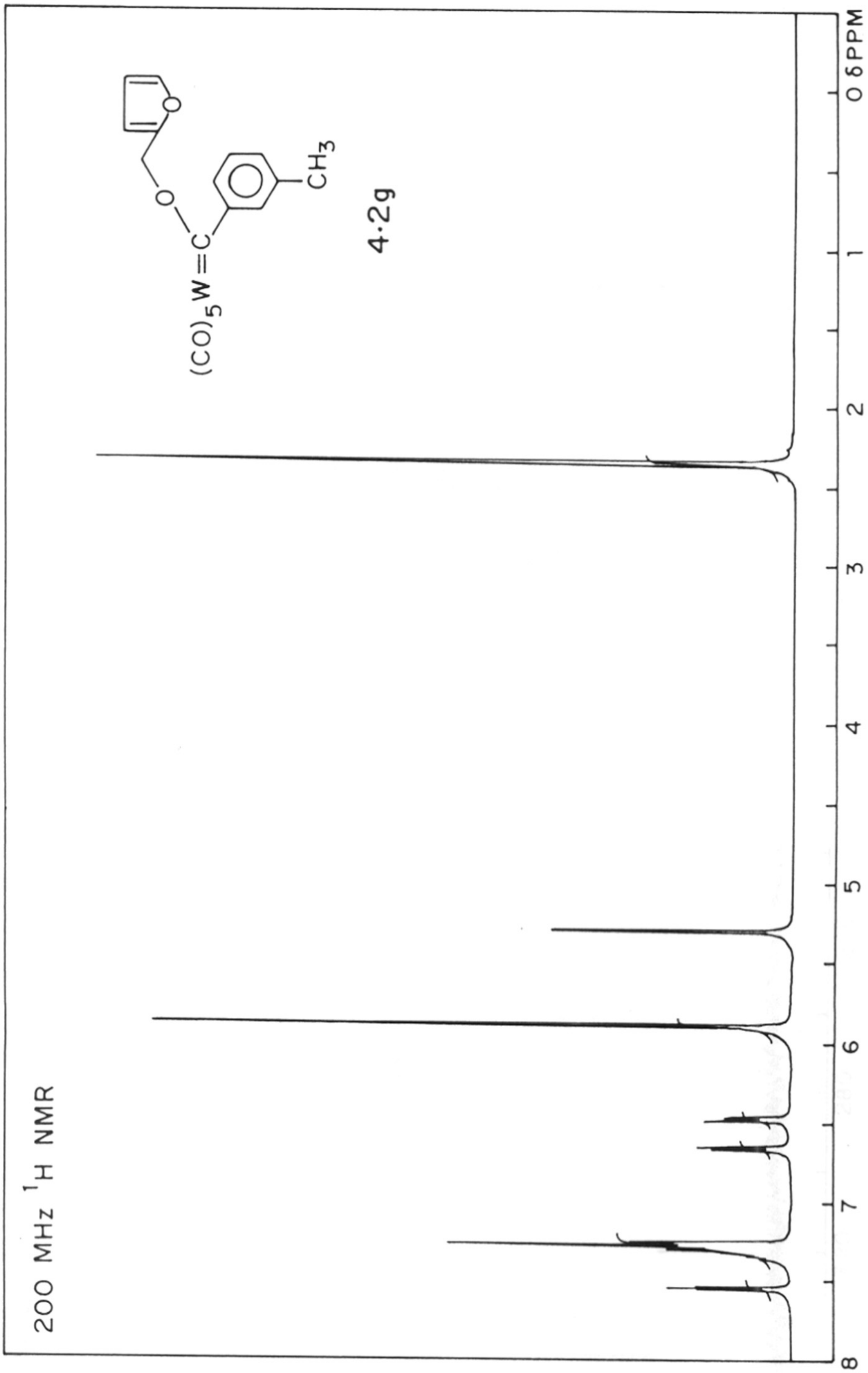
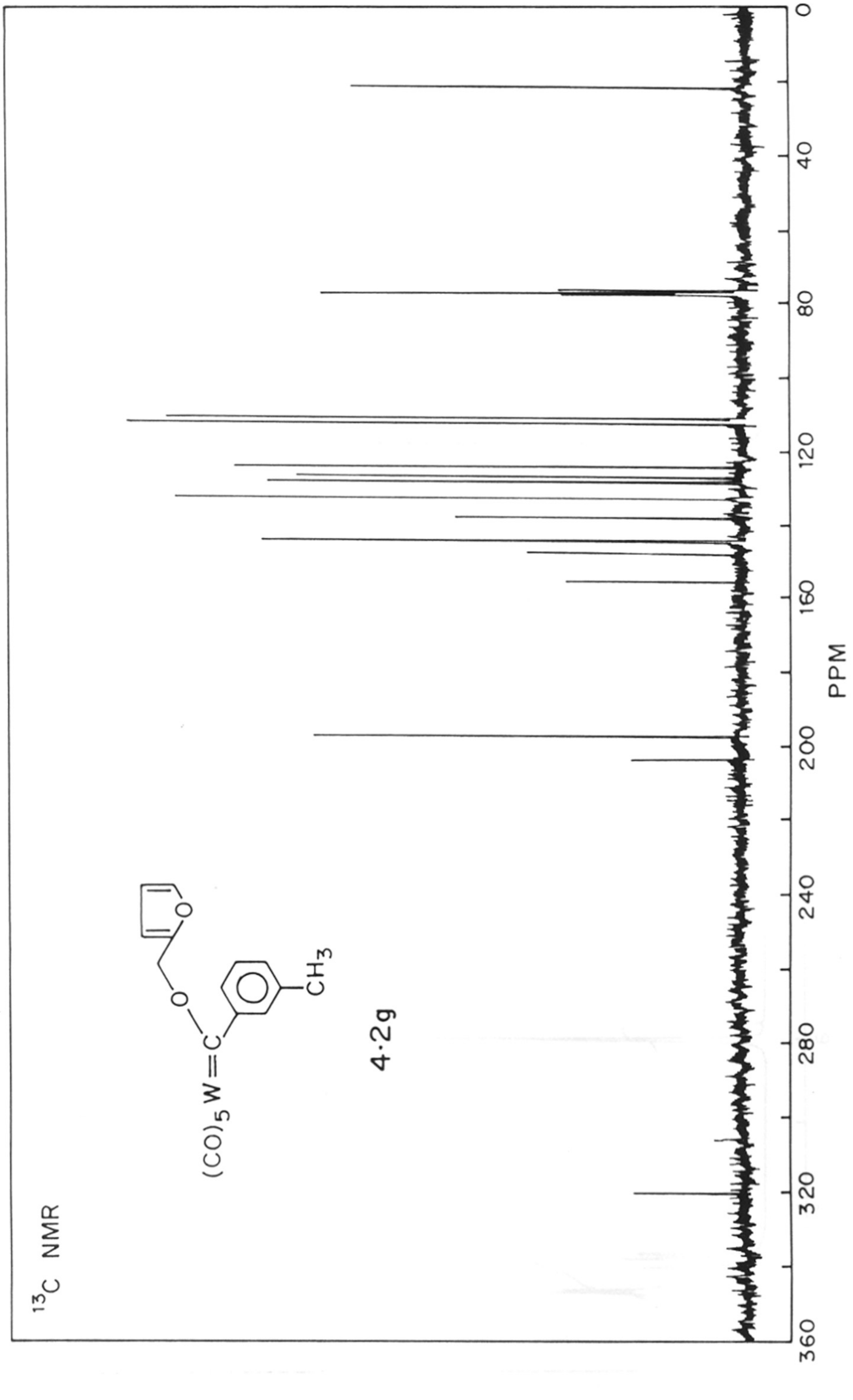
4·2f



4·2f



4·2g



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O
CH$_3$
4·2g
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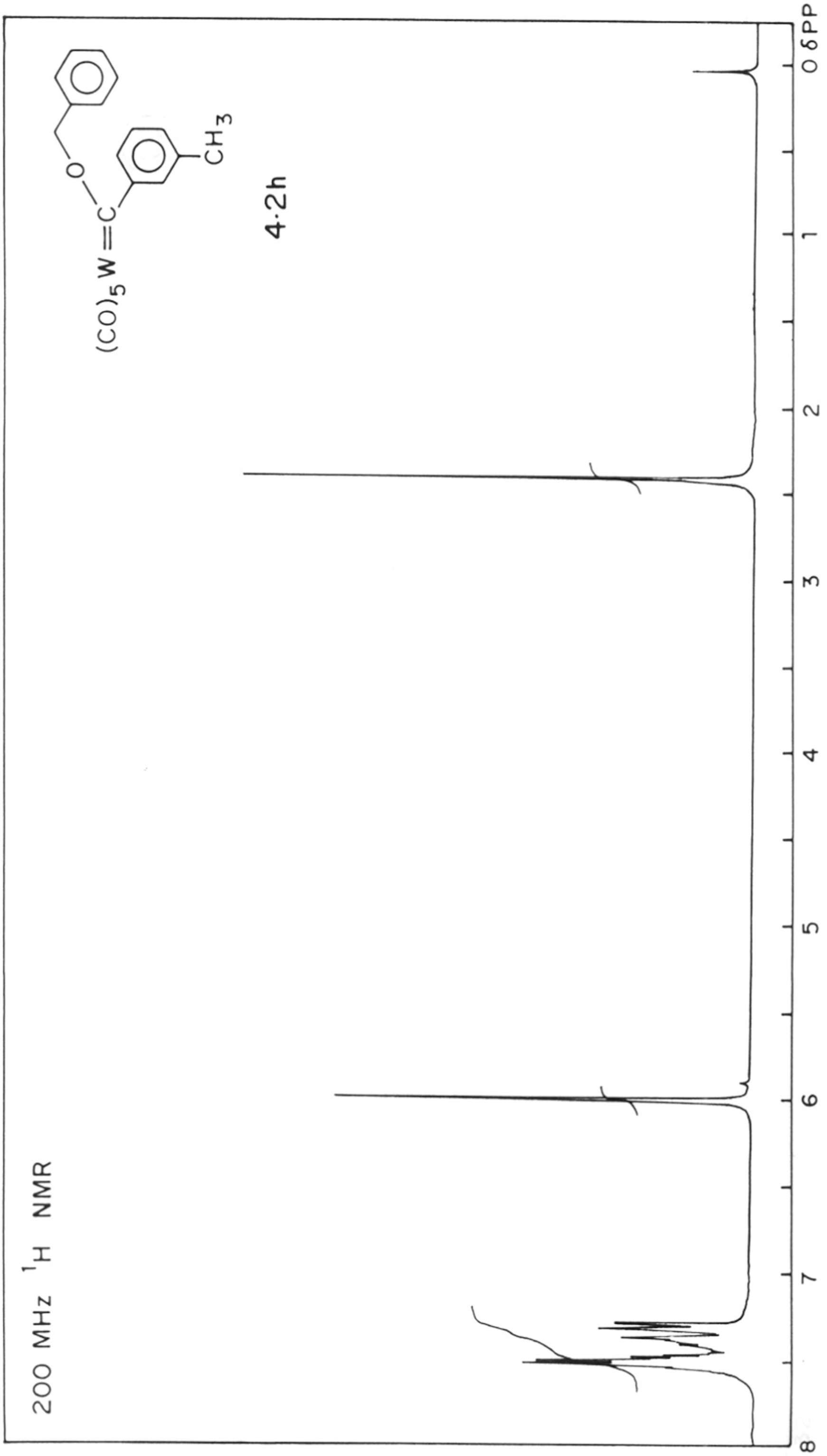
40
80
120
160
200
240
280
320
360
PPM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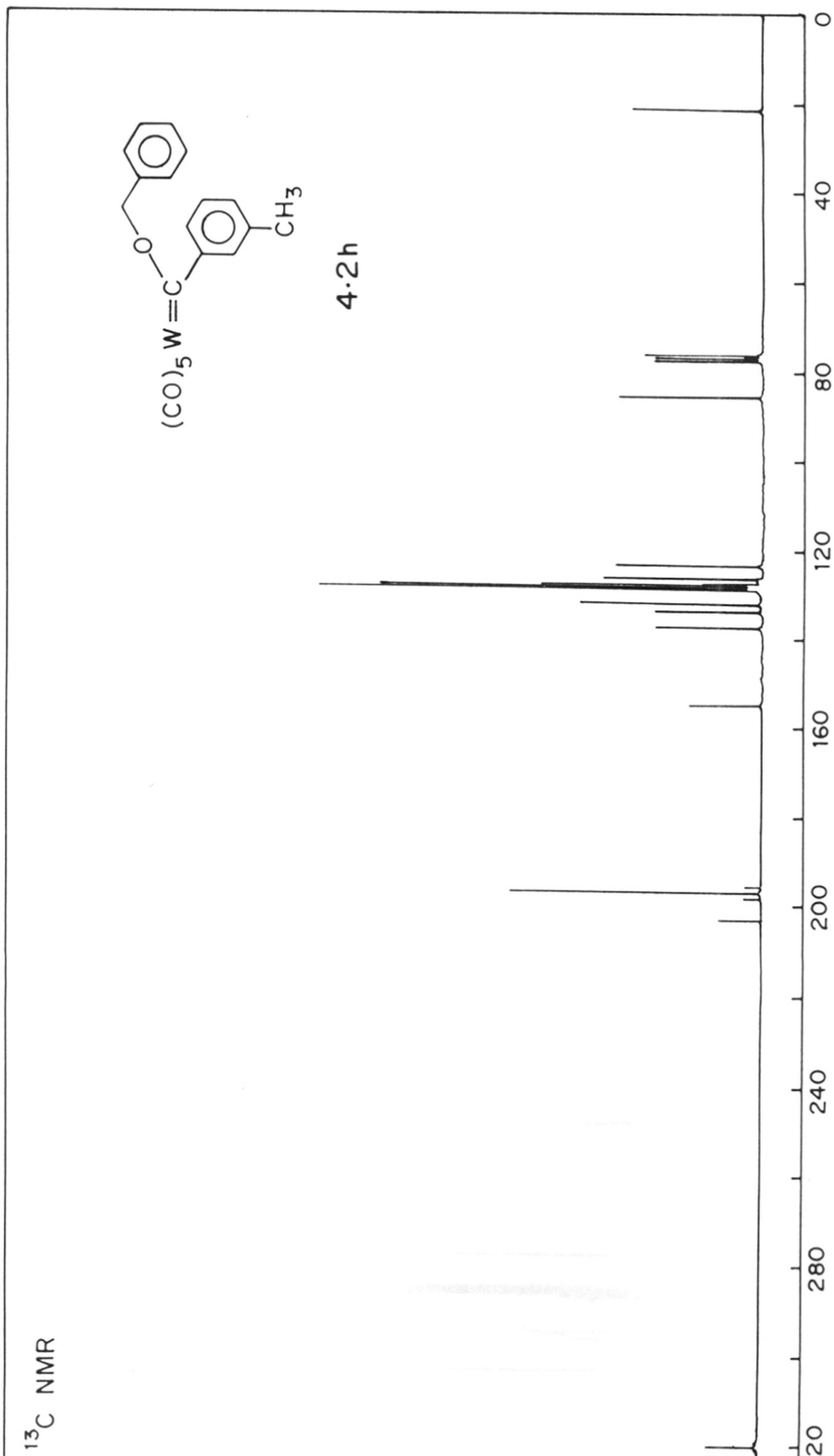
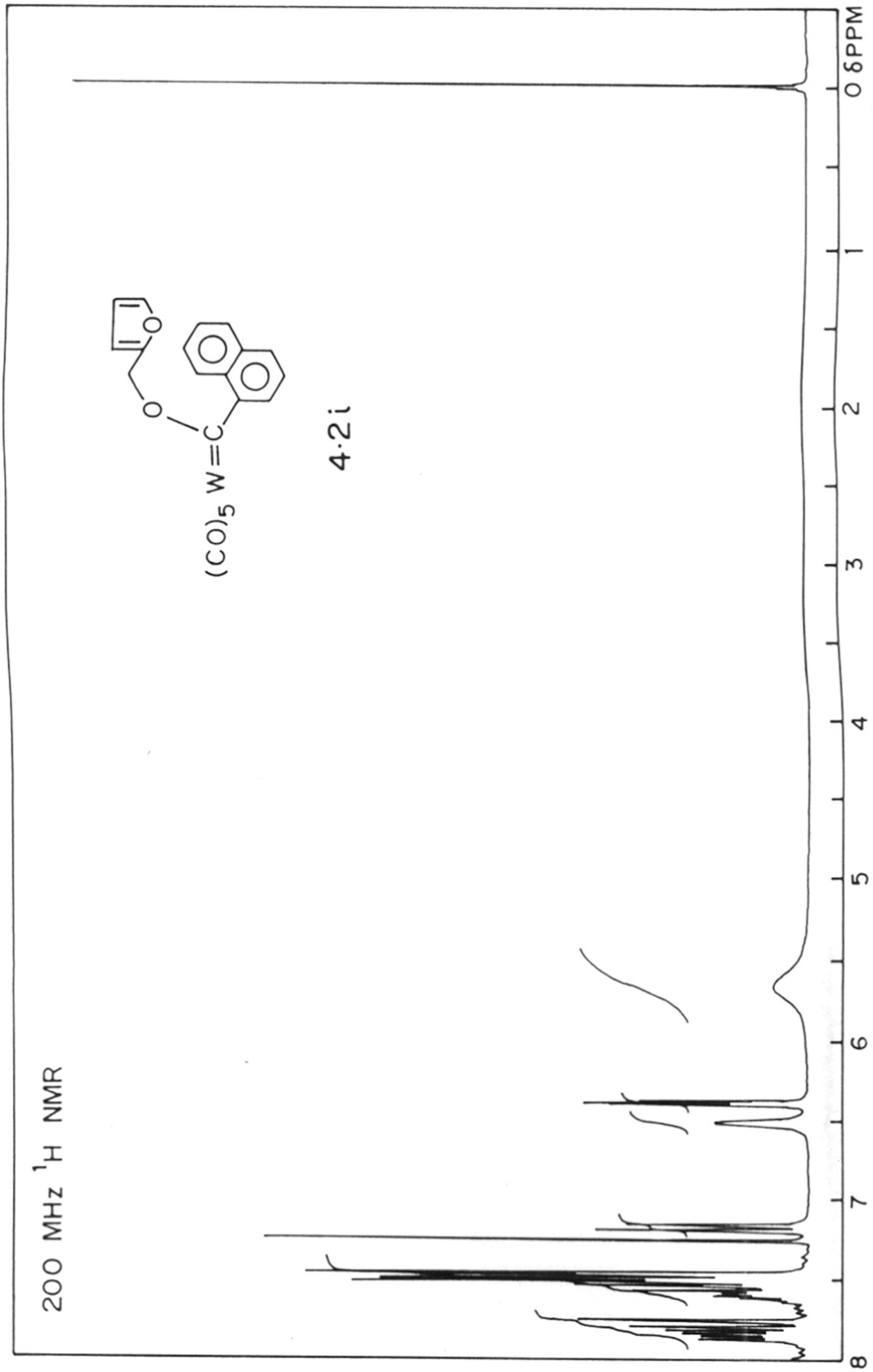
O
CH_3
4·2h
0 δPPM
1
2
3
4
5
6
7
8



4·2h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O
O
4·2i
8
7
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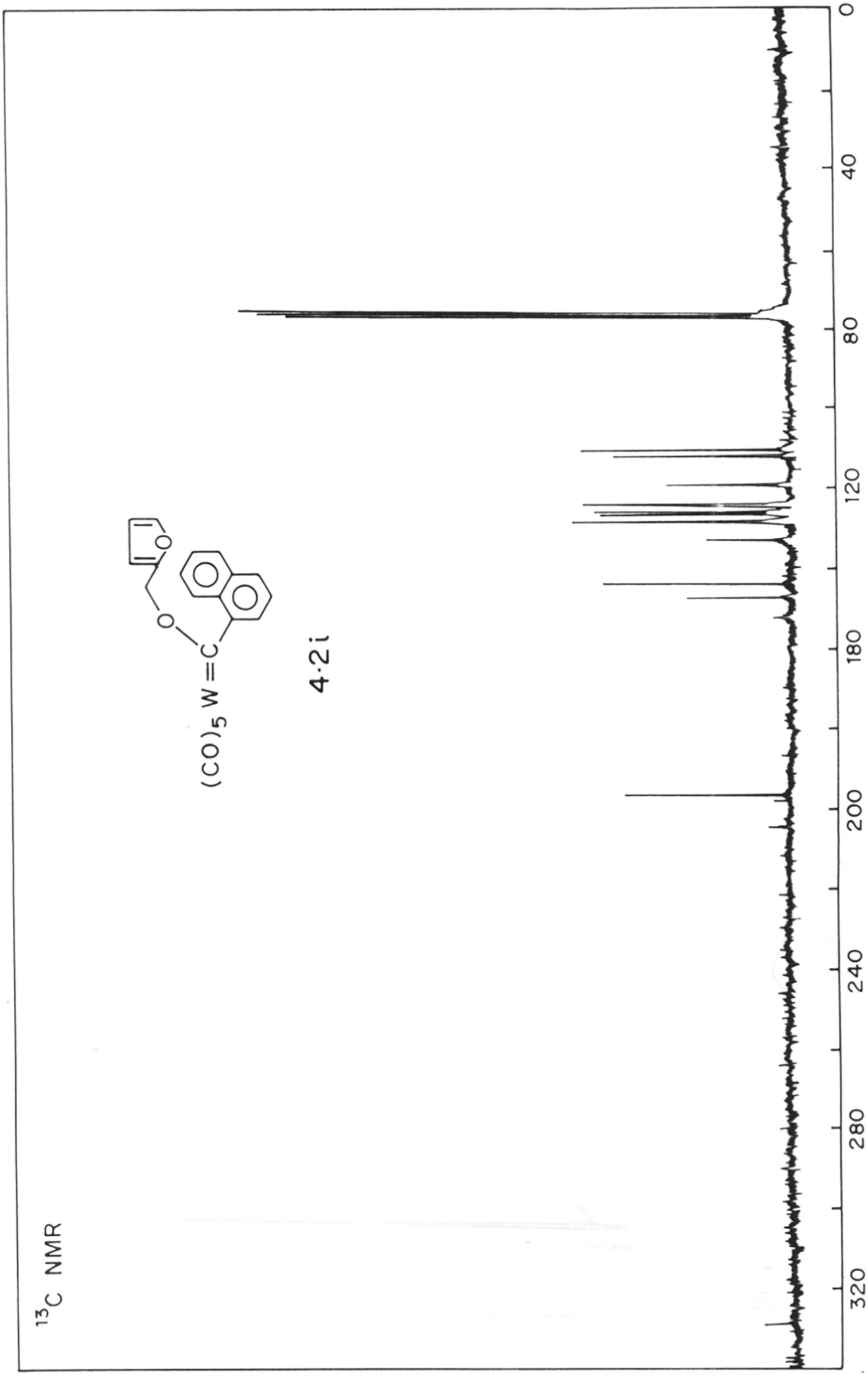
5
4
3
2
1
0 δPPM



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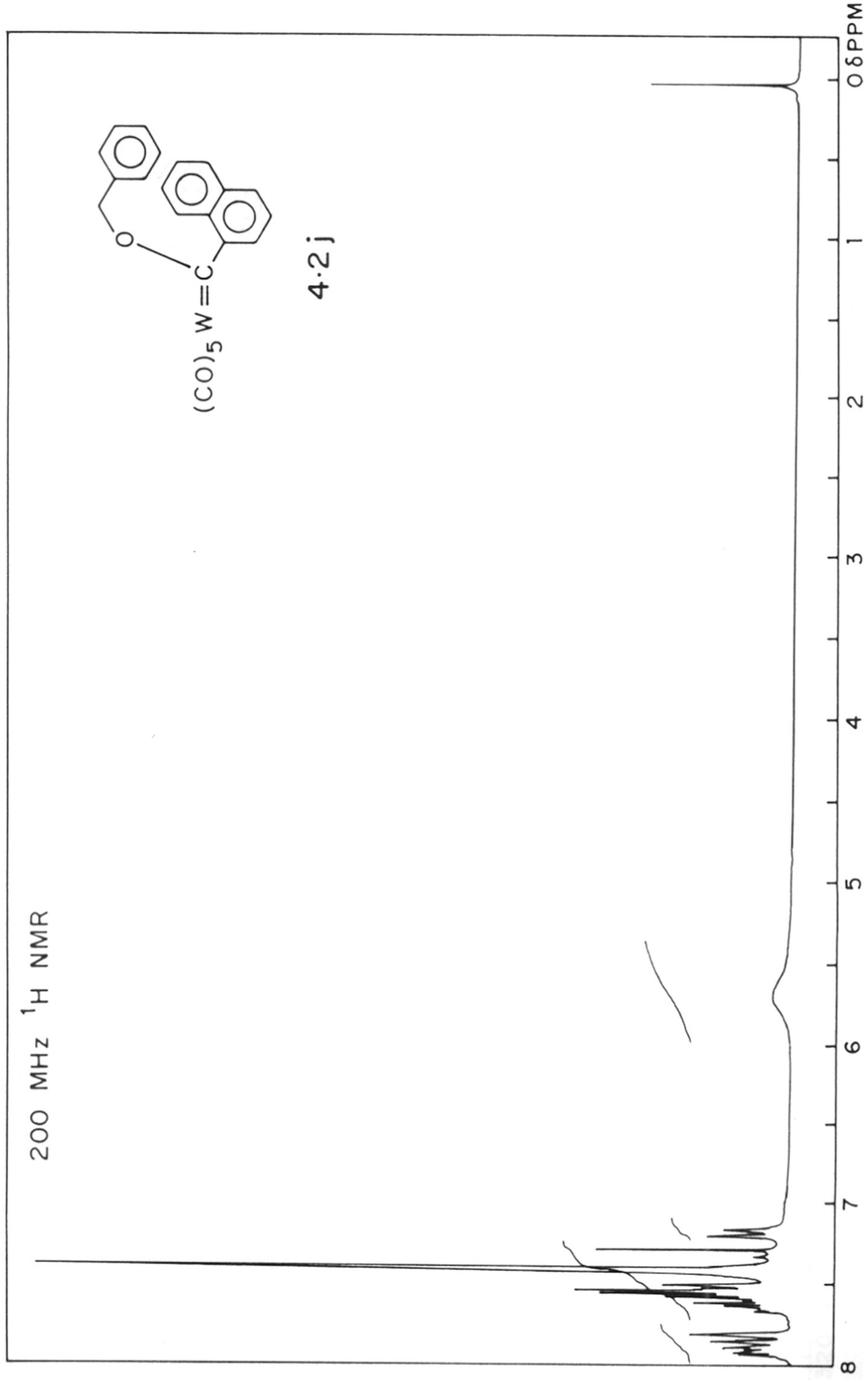
4·2i
PPM
0
40
80
120
180
200
240
280
320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O
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7
6
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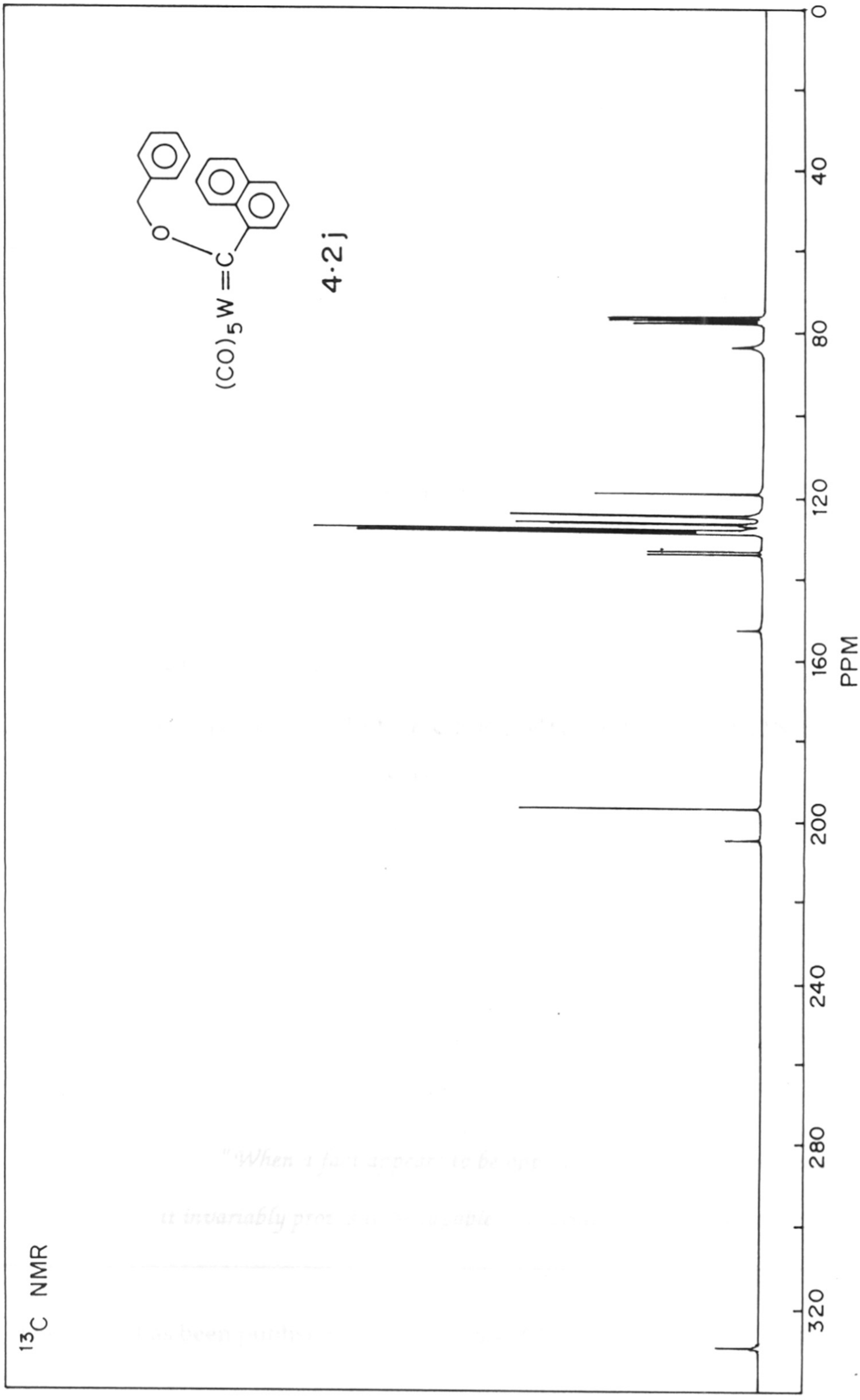
2
1
0 δPPM



13C NMR
(CO)5W=C
O
4·2j
PPM
0
40
80
120
160
200
240
280
320

APPENDIX 1

CRYSTAL STRUCTURE SOLUTION OF TRANS-2 (PHENYL CYCLOPROPYL)-1-TETRALONE CHROMIUM TRICARBONYL COMPLEX

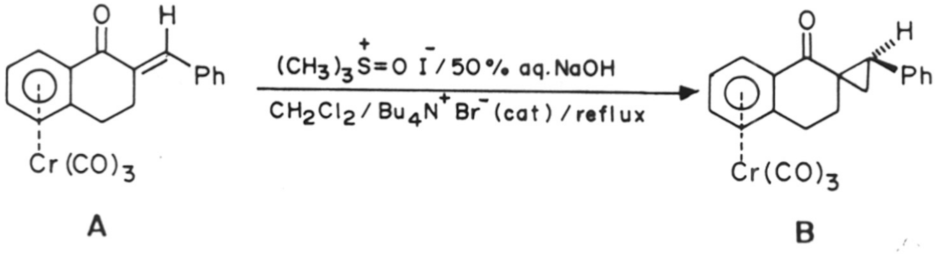
> *"When a fact appears to be opposed to a long chain of deduction*
> *it invariably proves to be capable of bearing some other interpretation."*

This work has been published in *J. Chem. Soc. Chem. Commun.*, 1993, 224

INTRODUCTION

Arene-tricarbonylchromium complexes have found considerable utility in organic synthesis.[1a-c] The tricarbonylchromium unit has often been used as a stereoface-directing group whereby a reagent preferentially approaches the substrate from the face away from the metal. The steric bulk of tricarbonylchromium can be realized even two or three carbon atoms away from the metal-complexed aromatic ring[1d]. In this laboratory, the cyclopropanated complex (**B**) was obtained from 2-benzylidene-1-tetralone tricarbonylchromium complex (**A**) and sulfoxonium ylide under phase-transfer catalysis in refluxing methylene chloride (**Scheme 1**).

Scheme 1



The structure of the complex **B** was tentatively deduced from its IR, ^{1}H and ^{13}C NMR data. A single diastereomer of the product was formed (200 MHz NMR and HPLC). In order to establish the spatial relationship between phenyl, carbonyl and methylene groups unambiguously, a single crystal X-ray structure determination was undertaken.

RESULTS

The orange crystals were obtained from ethyl acetate / hexane solvent system. These crystals were checked under microscope and a single crystal with good shape and sharp edges was chosen for X-ray analysis. The crystal was attached to a capillary and mounted on a Goniometer. The initial 25 reflections were collected after centering the crystal. The cell dimensions were obtained and the crystal was found to be monoclinic.

The intensity data were collected using the $\theta/2\theta$ scan mode. Total number of reflections measured were 2809 with maximum $2\theta = 47^{\circ}$, in the hkl range, -8 to 8, 0 to 11 and 0 to 25, out of which the number of unique reflections were 2568. A total of 1723 reflections with $I > 2.5\sigma(I)$ were processed further. The rest of the reflections were not considered for structure solution due to their weak intensity. The standard reflections were measured every hour.

The NRCVAX PC version structure determination package[2] was used to solve and refine the structure. The phase set with maximum combined figure of merit and minimum residuals was chosen for electron density map calculation. The highest electron density peak in the E map was assigned to the chromium atom. All the atoms were located using Unimol, Pltmol and the difference Fourier routine of the package. Refinement was carried out first by the least-squares block-matrix and then by full matrix. All the nonhydrogen atoms were refined anisotropically. Hydrogen atoms were located by difference Fourier and refined isotropically. The final R factor was found to be 3.8%.

The PLUTO and ORTEP diagrams of the complex (**B**) are displayed in Figures 1 and 2 respectively.

Figure 1

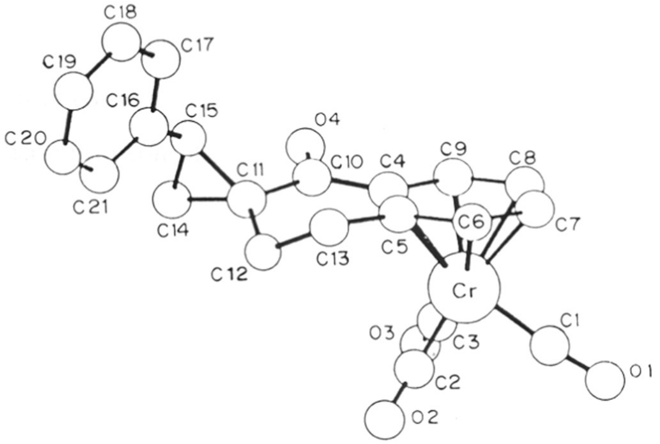
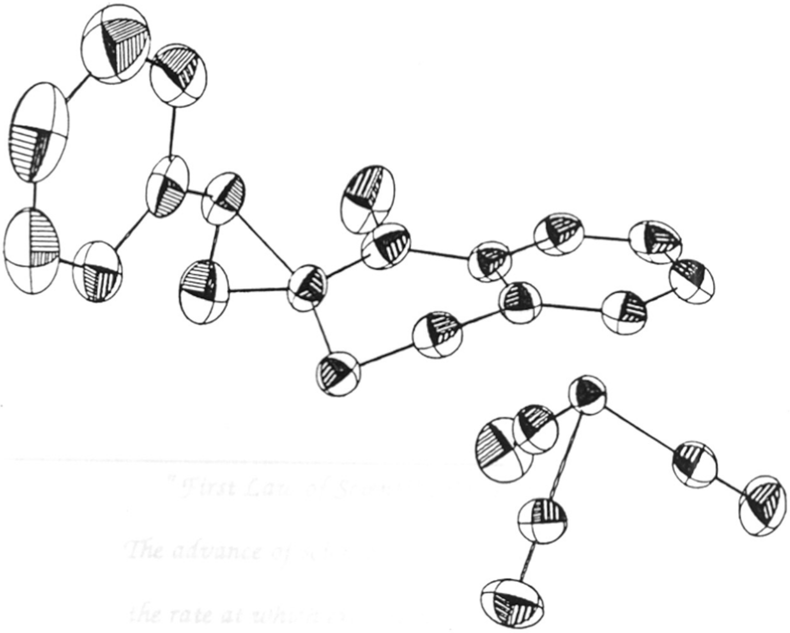


Figure 2



SUMMARY

The X-ray diffraction analysis revealed that the cyclopropane was appended from the same face of the molecule as occupied by the tricarbonylchromium group. To the best of our knowledge, this constituted the first example of *endo*-selective nucleophilic addition to arene-chromium complexes.

> *"First Law of Scientific Progress :*
> *The advance of science can be measured by*
> *the rate at which exceptions to previously*
> *held laws accumulate."*

EXPERIMENTAL

A summary of the crystal data, intensity date collection and structure solution

Crystal Data

Empirical Formula	$Cr\,C_{21}\,H_{16}\,O_4$
Color	Red
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 7.616(23), b = 10.1005(17), c = 22.916(22) Å, $\alpha = \gamma$ = 90° and β = 95.924(11)°
Volume Å^3	1753.41
Z	4
Formula weight	384.35
F (000)	791.89

Data Collection

Diffractometer used	Enraf Nonius CAD-4
Radiation	Mo Kα (λ = 0.7093 Å)
Temperature	300 K
Monochromator	Graphite crystal
2θ range	0° to 47°
Standard reflections	Three per hour
Index ranges	h = - 8 to 8, k = 0 to 11 and l = 0 to 25

Reflections collected	2809
Unique reflections	2586
Reflections processed	1723
Absorption correction	Not applied
Solution and Refinement	
System used	NRCVAX Structure Determination Package
Solution	Direct methods (MULTAN-80)
Refinement method	Least squares full matrix
Hydrogen atoms	Located by difference fourier and refined isotropically
Weighting scheme	Counting statistics
No. Of parameters refined	235
Final R indicies[a]	R = 3.8% Rw[b] = 3.3%
Goodness of fit[c]	3.07

a : $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$,

b : $R_W = \left[\Sigma \sqrt{w} (|F_o| - |F_c|)\right] / \Sigma \sqrt{w} |F_o|$,

c : $GOF = \left[\Sigma w (F_o^2 - F_c^2)^2 / (n - p)\right]^{1/2}$,

Where p is the number of refined parameters, n is the number of refluctions and W is the weighting factor.

Table 1 : Atomic coordinates

Name	X	Y	Z
Cr	0.69525(10)	0.1816(7)	0.06859(3)
O(1)	0.3131(4)	0.2049(4)	0.0244(14)
O(2)	0.7669(5)	0.1182(3)	- 0.0545(13)
O(3)	0.7289(6)	0.4713(4)	0.0432(16)
O(4)	0.7922(5)	0.3794(4)	0.2271(13)
C(1)	0.4596(6)	0.1959(5)	0.0418(18)
C(2)	0.7402(6)	0.1456(4)	- 0.0075(20)
C(3)	0.7181(7)	0.3605(5)	0.0530(20)
C(4)	0.7342(5)	0.1947(5)	0.1658(16)
C(5)	0.6235(6)	0.0853(4)	0.1503(17)
C(6)	0.6794(6)	- 0.0133(4)	0.1134(17)
C(7)	0.8457(6)	- 0.0012(5)	0.0911(19)
C(8)	0.9558(6)	0.1058(5)	0.1064(20)
C(9)	0.8998(6)	0.2052(5)	0.1431(18)
C(10)	0.6831(6)	0.2981(5)	0.2073(18)
C(11)	0.5012(6)	0.2916(4)	0.2252(16)
C(12)	0.3698(6)	0.2081(5)	0.1874(17)
C(13)	0.4489(5)	0.0733(4)	0.1757(17)

C(14)	0.4379(7)	0.4129(5)	0.2573(20)
C(15)	0.4962(6)	0.2925(5)	0.2936(17)
C(16)	0.3703(7)	0.2094(5)	0.3229(18)
C(17)	0.4436(7)	0.1156(5)	0.3633(21)
C(18)	0.3364(9)	0.0395(6)	0.3956(23)
C(19)	0.1592(9)	0.0567(6)	0.3885(25)
C(20)	0.0843(7)	0.1467(6)	0.3485(24)
C(21)	0.1898(7)	0.2238(5)	0.3162(20)

Table 2 : Bond lengths and bond angles

Bond lengths (A)

Cr-C(1)	1.841(5)	C(5)-C(13)	1.510(6)
Cr-C(2)	1.846(5)	C(6)-C(7)	1.419(7)
Cr-C(3)	1.1.853(5)	C(7)-C(8)	1.391(7)
Cr-C(4)	2.221(4)	C(8)-C(9)	1.403(7)
Cr-C(5)	2.228(4)	C(10)-C(11)	1.487(6)
Cr-C(6)	2.229(4)	C(11)-C(12)	1.512(6)
Cr-C(7)	2.206(5)	C(11)-C(14)	1.532(7)
Cr-C(8)	2.218(4)	C(11)-C(15)	1.571(5)

Cr-C(9)	2.202(4)	C(12)-C(13)	1.525(6)
O(1)-C(1)	1.150(6)	C(14)-C(15)	1.514(7)
O(2)-C(2)	1.151(6)	C(15)-C(16)	1.486(7)
O(3)-C(3)	1.147(6)	C(16)-C(17)	1.399(7)
O(4)-C(10)	1.225(6)	C(16)-C(21)	1.375(7)
C(4)-C(5)	1.413(6)	C(17)-C(18)	1.390(8)
C(4)-C(9)	1.417(6)	C(18)-C(19)	1.353(10)
C(4)-C(10)	1.490(6)	C(19)-C(20)	1.373(9)
C(5)-C(6)	1.402(6)	C(20)-C(21)	1.386(8)

Important bond angles (degree)

Cr-C(1)-O(1)	179.2(4)	C(11)-C(12)-C(13)	110.4(3)
C(11)-C(14)-C(15)	62.1(3)	C(11)-C(15)-C(14)	59.5(4)
C(15)-C(16)-C(17)	116.7(4)	C(15)-C(16)-C(21)	125.0(4)

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APPENDIX 2

CRYSTAL STRUCTURE SOLUTION OF (3R,4S,4′S,5′S) N-(*p*-ANISYL)-3-PHTHALIMIDO-4- (N-*t*-BUTOXYCARBONYL-2′,2′-DIMETHYL-5′-PHENYL-1′,3′-OXAZOLIDIN-4′-YL) -AZETIDIN-2-ONE

> *"In any collection of data, the figure most obviously the correct, beyond all need of checking, is the mistake."*

This work has been published in *Tetrahedron Asymmetry*, 1993, **4**, 609.

INTRODUCTION

Optically pure β-lactams with known absolute configuration can serve as important starting materials for various biologically active compounds besides β-lactam antibiotics. For optically pure β-lactams derived from optically pure starting materials, the method of choice to determine relative configuration of the molecule is X-ray crystal structure solution. Since the absolute configuration of the chiral precursor is known, the absolute configuration of the β-lactam can be deduced from relative stereochemistry of chiral centers. In order to establish such steric relationship of an optically pure β-lactam synthesized from readily available (1S,2S)-2-amino-1-phenylpropane-1,3-diol, X-ray crystal structure analysis of the molecule was undertaken.

RESULTS

White crystals of compound **A** were obtained from methylene chloride / petroleum ether solvent system. These crystals were checked under microscope and a single crystal having good shape and sharp edges was selected for X-ray analysis. The crystal was attached to a capillary and mounted on a Goniometer. The centering was done and initial 24 reflections were collected to obtain the cell dimensions. It was found to be a monoclinic crystal.

The intensity data were collected using the $\theta/2\theta$ scan mode. The total number of reflections measured were 2552, with maximum $2\theta = 46.9°$, in the hkl range, - 10 to 9, 0 to 16 and 0 to 12. The total number of unique reflections were 2396. A total of 2093 reflections with $I > 2.5\ \sigma(I)$ were processed further. The rest of the unique reflections were not considered for structure solution due to their weak intensity. During data collection the standard reflections were measured every hour. Absorption correction was not applied.

The NRCVAX PC version package[2] failed to give the structure. The SHELXS-86[3] was then used to obtain the structure. The structure was refined by the method of least-square block matrix using the NRCVAX package. The nonhydrogen atoms were treated anisotropically , and towards the end, a few cycles of full matrix least-squares refinement were carried out. Hydrogen atoms were located by difference Fourier and were not refined. The final R factor was found to be 5.2%.

The PLUTO and ORTEP diagrams of the compound (**A**) are displayed in **Figures** 1 and 2 respectively.

Figure 1

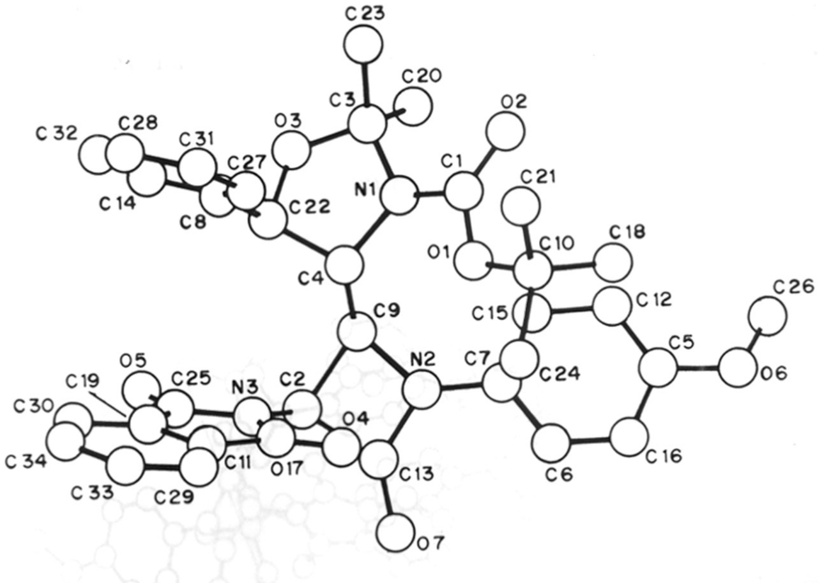
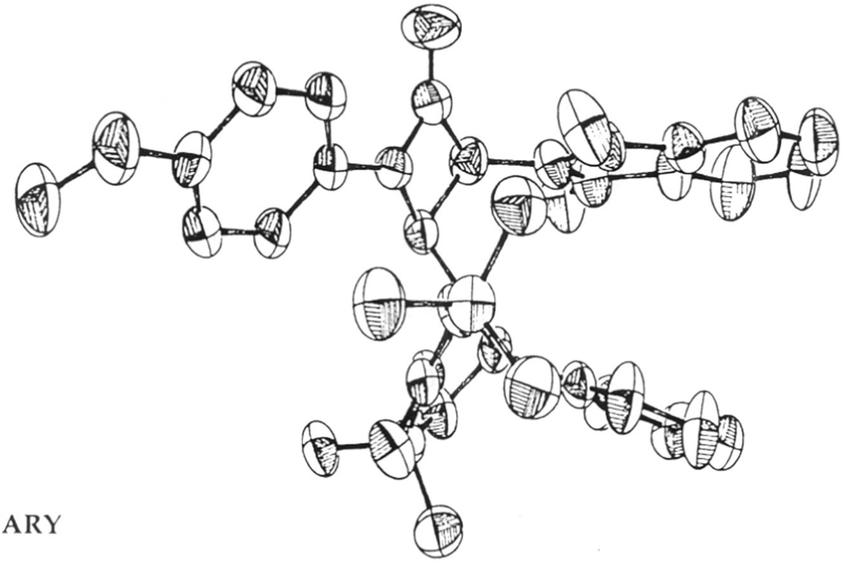


Figure 2



SUMMARY

The compound was found to be a *cis* β-lactam. The two molecules in one unit cell were packed in such a way that the two phenyl rings stacked[4] against each other [(**Figure** 3) (**Table 1**)].

Figure 3

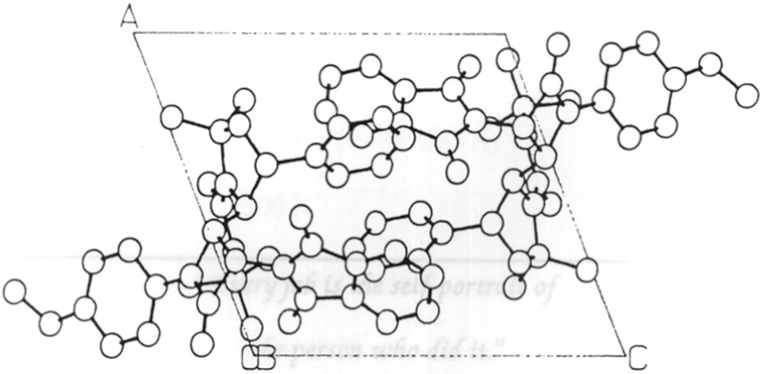


Table 1 : Intermolecular Distances

Molecule 1	Molecule 2	Distance (A)
C6	C28	3.61
C12	C31	3.79
C16	C28	3.80
C16	C32	3.78
C30	C31	3.73

"Every job is the self-portrait of

the person who did it."

EXPERIMENTAL

A summary of the crystal data, intensity data collection and structure solution

Crystal Data

Empirical Formula	$C_{34} H_{35} N_3 O_7$
Colour	White
Crystal system	Monoclinic
Space group	$P2_1$
Unit cell dimensions	a = 9.735(2), b = 15.402(1), c = 11.233(6) Å,α = γ = 90° and β = 112.39(3)°
Volume Å^3	1557.1(9)
Z	2
Formula weight	597.66
F (000)	631.90

Data Collection

Diffractometer used	Enraf Nonius CAD-4
Radiation	Mo Kα (λ = 0.7093 Å)
Temperature	300 K
Monochromator	Graphite crystal
2θ range	0° to 46.9°
Standard reflections	Three per hour
Index ranges	h = - 10 to 9, k = 0 to 16 and l = 0 to 12

Reflections collected	2552
Unique reflections	2396
Reflections processed	2093
Absorption correction	Not applied

Solution and Refinement

System used	SHELX-86 Structure Determination Package and refinement was done using NRCVAX Package
Solution	SHELX-86
Refinement method	Least squares full matrix
Hydrogen atoms	Located by difference Fourier
Weighting scheme	Counting statistics
No. Of parameters refined	396
Final R indicies	R = 5.2% Rw = 5.0%
Goodness of fit	7.59

Table 2 : Atomic coordinates

Name	X	Y	Z
O(1)	0.3231(4)	0.50830	0.0478(3)
N(1)	0.5288(4)	0.5848(3)	0.0928(4)
O(2)	0.5294(4)	0.4414(3)	0.0469(3)

N(2)	0.2436(5)	0.6975(3)	- 0.0918(4)
O(3)	0.7120(4)	0.6830(3)	0.1895(3)
N(3)	0.2723(5)	0.7956(3)	0.1672(4)
O(4)	0.1039(5)	0.6838(3)	0.1289(4)
C(1)	0.4649(6)	0.5057(4)	0.0606(4)
C(2)	0.2915(6)	0.7979(4)	0.0434(5)
C(3)	0.6913(6)	0.5994(4)	0.1323(5)
C(4)	0.4576(6)	0.6597(3)	0.1243(4)
C(5)	0.1422(6)	0.5317(4)	- 0.4089(5)
C(6)	0.0648(6)	0.6169(4)	- 0.2654(5)
O(5)	0.4293(6)	0.9094(3)	0.2650(4)
C(7)	0.2101(6)	0.6399(4)	- 0.1975(5)
C(8)	0.6181(6)	0.6878(4)	0.3674(5)
C(9)	0.3834(6)	0.7227(4)	0.0133(5)
C(10)	0.3234(6)	0.6084(5)	- 0.2315(5)
O(6)	0.0954(5)	0.4780(3)	- 0.5174(4)
C(11)	0.1816((7)	0.7696(4)	0.3257(6)
C(12)	0.2866(6)	0.5517(5)	- 0.3392(5)
C(13)	0.1595(7)	0.7630(4)	- 0.0739(5)
C(14)	0.7070(7)	0.7441(5)	0.4563(5)

O(7)	0.0336(5)	0.7848(4)	- 0.1317(4)
C(15)	0.2312(6)	0.4295(4)	0.0246(5)
C(16)	0.0290(6)	0.5629(4)	- 0.3739(5)
C(17)	0.1747(6)	0.7420(4)	0.1954(5)
C(18)	0.2141(7)	0.3885(4)	- 0.1056(6)
C(19)	0.2834(7)	0.8348(4)	0.3684(5)
C(20)	0.7351(6)	0.6038(4)	0.0148(5)
C(21)	0.2988(7)	0.3663(4)	0.1361(6)
C(22)	0.5894(6)	0.7069(4)	0.2233(5)
C(23)	0.7887(6)	0.5326(4)	0.2275(5)
C(24)	0.0826(6)	0.4661(4)	0.0196(6)
C(25)	0.3417(7)	0.8563(4)	0.2655(5)
C(26)	0.1938(8)	0.4669(5)	- 0.5807(6)
C(27)	0.5578(8)	0.6173(5)	0.4048(5)
C(28)	0.6725(8)	0.6640(5)	0.6245(6)
C(29)	0.1032(8)	0.73849(4)	0.3960(6)
C(30)	0.3199(10)	0.8727(5)	0.4894(6)
C(31)	0.5887(8)	0.6051(6)	0.5372(6)
C(32)	0.7351(8)	0.7328(5)	0.5872(5)
C(33)	0.1377(9)	0.7763(5)	0.5162(7)

C(34)	0.2451(10)	0.8384(6)	0.5628(6)

Table 3 : Bond lengths and bond angles

Bond lengths (A)

O(1)-C(1)	1.334(6)	C(6)-C(16)	1.405(8)
O(1)-C(15)	1.471(6)	O(5)-C(25)	1.183(8)
N(1)-C(1)	1.353(7)	C(7)-C(10)	1.386(8)
N(1)-C(3)	1.488(7)	C(8)-C(14)	1.355(8)
N(1)-C(4)	1.457(6)	C(8)-C(22)	1.562(7)
O(2)-C(1)	1.213(7)	C(8)-C(27)	1.374(9)
N(2)-C(7)	1.417(7)	C(10)-C(12)	1.422(8)
N(2)-C(9)	1.474(7)	O(6)-C26)	1.405(8)
N(2)-C(13)	1.362(8)	C(11)-C(17)	1.500(8)
O(3)-C(3)	1.418(7)	C(11)-C(19)	1.363(9)
O(3)-C(22)	1.432(6)	C(11)-C(29)	1.377(9)
N(3)-C(2)	1.473(7)	C(13)-O(7)	1.196(7)
N(3)-C(17)	1.384(7)	C(14)-C(32)	1.399(8)
N(3)-C(25)	1.408(7)	C(15)-C(18)	1.543(8)
O(4)-C(17)	1.202(7)	C(15)-C(21)	1.522(8)
C(2)-C(9)	1.576(8)	C(15)-C(24)	1.534(8)

C(2)-C(13)	1.544(8)	C(19)-C(25)	1.505(8)
C(3)-C(20)	1.536(7)	C(19)-C(30)	1.397(8)
C(3)-C(23)	1.526(8)	C(27)-C(31)	1.413(8)
C(4)-C(9)	1.527(7)	C(28)-C(31)	1.357(10)
C(4)-C(22)	1.525(7)	C(28)-C(32)	1.366(12)
C(5)-O(6)	1.397(7)	C(29)-C(33)	1.390(10)
C(5)-C(12)	1.358(8)	C(30)-C(34)	1.396(10)
C(5)-C(16)	1.389(8)	C(33)-C34)	1.365(12)
C(6)-C(7)	1.373(8)		

Important bond angles (degree)

C(7)-N(2)-C(13)	128.9(4)	N(3)-C(2)-C(9)	118.1(5)
C(9)-C(2)-C(13)	85.2(4)	C(2)-C(9)-C(4)	115.0(4)

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