Synthesis, Structure and Conformation of New Molybdenum π-Allyl Complexes

A THESIS

SUBMITTED TO THE

UNIVERSITY OF POONA

FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN CHEMISTRY

BY

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NATIONAL CHEMICAL LABORATORY

PUNE 411 008

CERTIFICATE

*This is to certify that the work incorporated in the thesis entitled "**Synthesis, Structure and Conformation of New Molybdenum π-Allyl Complexes**" submitted by Sanjoy Kumar Chowdhury was carried out by him under my supervision at the National Chemical Laboratory. Such material as has been obtained from other sources has been duly acknowledged in the thesis.*

Date : 17 Jan. '97

National Chemical Laboratory

Pune 411 008

(Dr. A. Sarkar)

Research Guide

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Whatever I am and whatever I intend to be in future is because of the goodwill and unstinted support that I have received from my parents, brothers and family. There kind cooperation helped me in pursuing the Ph. D. study and no words are enough to acknowledge them.

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Sanjoy Kumar Chowdhury

(Sanjoy K. Chowdhury)

To

My Parents

And

Brothers

I have yet to see any problem, however complicated, which, when you looked at in the right way, did not become still more complicated.

-Paul Anderson.

CONTENTS

GENERAL REMARKS

1. All melting points (recorded on a Thermonik Campbell melting point apparatus) are uncorrected and are recorded on the Celsius scale.
2. IR spectra were recorded as nujol mull or chloroform, on a Perkin-Elmer Infrared Spectrometer Model 599-B, Model 1600 FT-IR and ATI Mattson, UK, Model-RS-1 FT-IR, using sodium chloride optics. IR bands are expressed in frequency (cm^{-1}).
3. Proton NMR spectra were recorded using tetramethylsilane as internal reference on Bruker AC-400, Bruker MSL-300, Bruker AC-200, Bruker WH-90, Bruker FT-80A. Chemical shifts were recorded in parts per million (δ). Abbreviations, *viz.*, s = singlet, d = doublet, t = triplet, dd = doublet of doublet, bt = doublet of a triplet, brs = broad singlet, br = broar peak and m = multiplet have been used. $CDCl_3$ was used as the solvent unless otherwise mentioned.
4. ^{13}C NMR spectra were recorded on Bruker AC-400, Bruker MSL-300 and Bruker AC-200 instrument operating at 100.6 MHz, 75.2 MHz and 50.3 MHz respectively.
5. Mass spectra were recorded on a Finnigan-Mat 1020C mass spectrophotometer at 70 eV.
6. X-ray crystal diffraction data were obtained from Enraf-Nonius CAD-4 diffractometer.
6. Elemental analyses (C, H, N) were obtained on a Carlo-Erba 1100 automatic analyzer by Dr. S. Y. Kulkarni and his group at NCL.
7. The progress of the reaction was monitored by analytical thin layer chromatography with TLC plates precoated with silica gel 60 F_{254}(Merck). Column chromatography of molybdenum complexes were carried out with silica gel obtained from Merck (230-400 mesh, 9385 grade) under argon or nitrogen pressure.
8. Known compounds were characterised by IR and proton NMR.
9. All optical rotations were measured on a JASCO-181 digital polarimeter using Na light (4893 Å). Concentrations are expressed in g/100 ml.
10. Pet-ether refers to the fraction boiling between 60-80 °C.

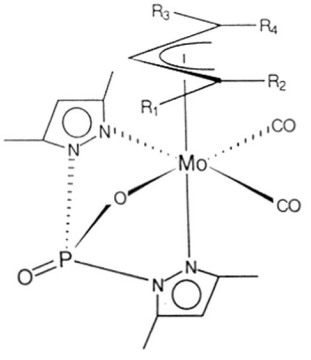
ABBREVIATIONS

NH_4Cl	Ammonium chloride
$AlCl_3$	Aluminium chloride
CCl_4	Carbon tetrachloride
$CHCl_3$	Chloroform
CH_2Cl_2	Dichloromethane
Et_2O	Diethyl ether
EtOAc	Ethyl acetate
MeOH	Methanol
$NaHCO_3$	Sodium bicarbonate
Na_2CO_3	Sodium carbonate
Na_2SO_4	Sodium sulfate
$Na_2S_2O_3$	Sodium thiosulfate
TBAB	Tetrabutylammonium bromide
PBr_3	Tribromophosphine
PCl_3	Trichlorophosphine
THF	Tetrahydrofuran

SYNOPSIS OF THE THESIS

Chapter- I. *Conformation of Molybdenum π-Allyl Complexes with Unsymmetrical Tridentate Ligand O=P(pz')$_2$ O$^-$: Role of CH/π Interaction.*

The non-bonding interaction between the methyl group of pyrazole in the ligand and terminal allyl substituent determines conformational preferences in a series of new, isostructural π-allyl complexes of molybdenum ligated to a tridentate, uninegative chelating ligand. A close examination of the trend reveals that CH/π interaction often plays a crucial role in determining conformational preferences of these complexes in solution. The stereochemical details are derived from the analysis of their DNMR data.



1a. $R_1 = R_2 = CH_3$, $R_3 = R_4 = H$

1b. $R_1 = R_3/R_4 = CH_3$, $R_2 = R_4/R_3 = H$

1c. $R_1 = CH_3$, $R_2 = H$, $R_3 = C_6H_5$, $R_4 = H$

1d. $R_1 = R_3 = C_6H_5$, $R_2 = R_4 = H$

1e. R_1/R_3 = 4-NO_2-C_6H_4, $R_3/R_1 = R_2 = R_4 = H$

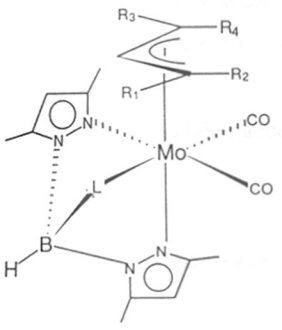
1f. R_1/R_3 = 3,4,5-OMe-C_6H_2, $R_3/R_1 = R_2 = R_4 = H$

Part of this work has been published in *Organometallics*, 1994, *13*, 4092.

Chapter- II. *Terminally Substituted π-Allyl Complexes of Molybdenum with Dihydro-bis(3,5-dimethyl-1- pyrazolyl)borate Ligand.*

A series of new π-allyl complexes of molybdenum were synthesised and structurally characterised, where the dicarbonylmolybdenum(II) was ligated to dihydro*bis*-(3,5-dimethyl-1-pyrazolyl)borate ligand. A number of these complexes have terminally substituted allyl group. In some, a double bond in conjugation with

the allyl group is incorporated. Both in acyclic (**2a-2g**) and cyclic (**2h**) π-allyl systems, there was no evidence of η^5-coordination.



2a. $R_1 = C_6H_5$, $R_2 = R_3 = R_4 = H$, L = H

2b. $R_1 = CH_3$, $R_2 = R_3 = R_4 = H$, L = H

2c. $R_1 = R_2 = CH_3$, $R_3 = R_4 = H$, L = H

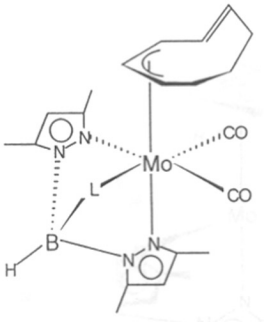
2d. $R_1 = C_6H_5\text{-}C{=}O$, $R_2 = R_3 = R_4 = H$, L = H

2e. $R_1 = CH_3$, $R_3 = C_6H_5$, $R_2 = R_4 = H$, L = H

2f. $R_1 = CH{=}CH\text{-}CH_3$, $R_2 = R_3 = R_4 = H$, L = H

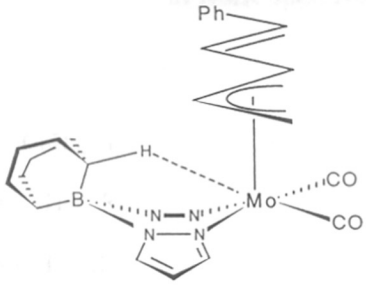
2g. $R_1 = CH{=}CH\text{-}C_6H_5$, $R_2 = R_3 = R_4 = H$, L = H

2j. $R_1 = CH{=}CH\text{-}CH_3$, $R_2 = R_3 = R_4 = H$, L = $O\text{-}CH_2\text{-}C_6H_5$



2h. L = H

2i. L = $O\text{-}CH_2\text{-}C_6H_5$



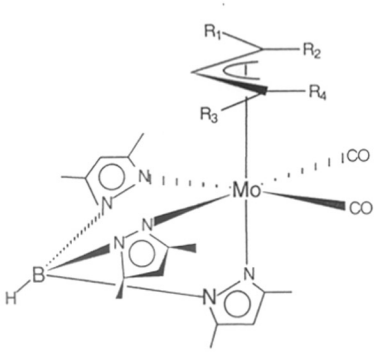
2 k

On reaction with benzaldehyde, the complex (**2h** and **2f**) did not show any change of coordination of the allyl group though the ligand structure was modified as in **2i** and **2j** respectively. For comparison, a complex **2k** featuring *bis*pyrazolylborate ligand derived from 9-BBN was also synthesised and characterised. Proton NMR spectrum provided a clear evidence of a C-H-Mo agostic interaction.

Part of this work has been accepted for publication in *Organometallics*, 1997 (in press).

Chapter- III. *Intramolecular Steric Strain in Tp'(CO)$_2$ Mo(π-Allyl) Complexes.*

The 3-methyl groups in *tris*-(3,5-dimethyl-1-pyrazolyl)borate ligand lie in close proximity of the terminal substituent on the allyl moiety. This results in a deviation from the normal orientation of the allyl group. A phenyl ring attached to a terminus of the allyl moiety tends to move into the space between two pyrazolyl groups, a sterically congested environment. In order to assess the factors responsible for such unusual preference of orientation, a series of structurally related complexes were synthesised and their solution conformation probed by proton NMR spectroscopy.



3a. $R_1/R_2 = C_6H_5$, $R_2/R_1=H$, $R_3=R_4=H$.

3b. $R_1=R_4= C_6H_5$, $R_2=R_3=H$.

3c. $R_1=R_4= CH_3$, $R_2=R_3=H$.

3d. $R_1/R_2=CH_3$, $R_2/R_1=H$, $R_3=C_6H_5$, $R_4=H$.

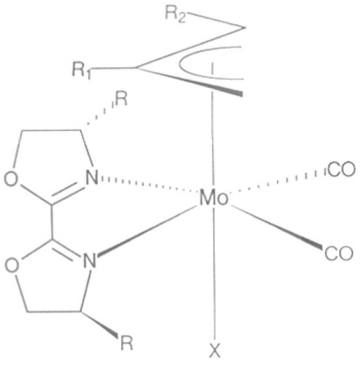
3e. $R_1/R_2 = CH=CH-C_6H_5$, $R_2/R_1=H$, $R_3=R_4=H$.

3f. $R_1/R_2 = CH=CH-CH_3$, $R_2/R_1=H$, $R_3=R_4=H$.

Part of this work has been accepted for publication in *Organometallics*, 1997 (in press).

Chapter- IV. *Molybdenum π-Allyl Complexes with C_2- Symmetric Homochiral Bis-oxazoline Ligands.*

Since homochiral *bis*-oxazoline ligands are important in asymmetric catalysis, preparation and structural characterisation of representative molybdenum π-allyl complexes seemed worthwhile. The ligands were prepared from R-(-)-phenylglycine and S-(+)-valine according to literature methods. The complexes were characterized by their NMR spectra and crystal structure determination.



4a. R_1 = H, R_2 = H, X = Cl, R = C_3H_7

4b. R_1 = C_6H_5, R_2 = H, X = Br, R = C_3H_7

4c. R_1 = CH_3, R_2 = H, X = Cl, R = C_3H_7

4d. R_1 = H, R_2 = CH_3, X = Br, R = C_3H_7

4e. R_1 = H, R_2 = C_6H_5, X = Cl, R = C_3H_7

4f. R_1 = C_6H_5, R_2 = H, X = Br, R = C_6H_5

4g. R_1 = CH_3, R_2 = H, X = Cl, R = C_6H_5

Chapter-I

Conformation of Molybdenum π-Allyl Complexes with Unsymmetrical Tridentate Ligand $O{=}P(pz')_2O^-$: Role of CH/π Interaction.

Part of this work has been published in *Organometallics*, 1994, *13*, 4092.

I. 1 Background

Molybdenum π-allyl complexes are useful intermediates in new C-C bond forming reactions. If the metal is rendered cationic, nucleophilic addition occurs at the allyl terminus from the face opposite to the metal (*Fig.-1*).

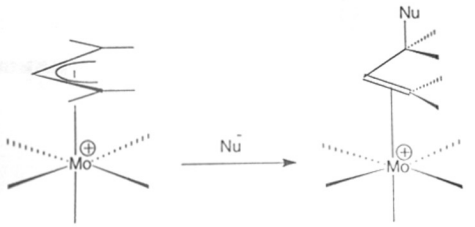


Fig.-1.

If the allyl terminus is substituted by dissimilar groups, addition a of nucleophile will create a chiral center. There is an inherent challenge to control the chirality of a newly formed center, and attempts to realize this goal are reported. Faller[1] used a chiral substituent on cyclopentadienyl ligand to induce chiral discrimination (*Fig.-2*).

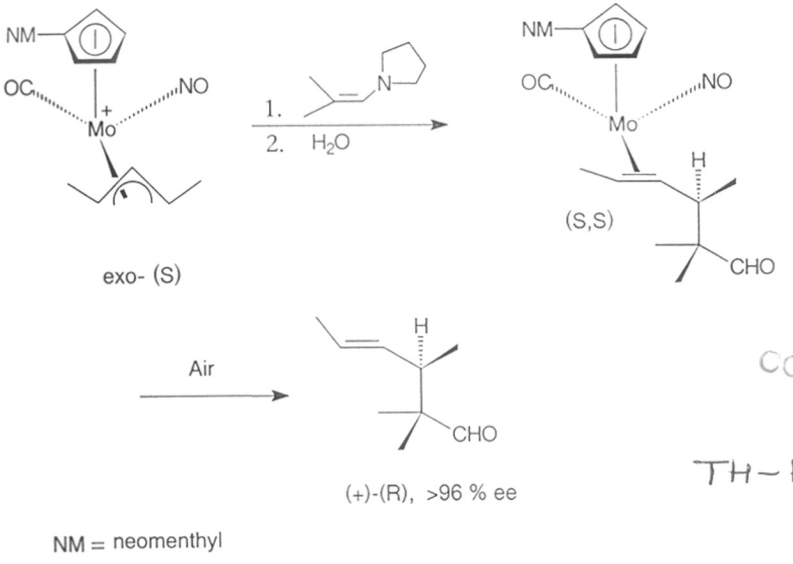


Fig.-2.

This is one way of addressing the problem. In principle, the bidentate ligands used by Trost and Lautens[2] are amenable to homochiral versions which should also effect chiral induction as above. The other way is to use a chiral metal center such that the two allyl termini are placed in non-equivalent environment in the complex and this could prompt stereo-differentiation in the new C-C bond formation step. Again, Faller[3] developed a stereoelectronic principle that guides selection of allyl terminus to be attacked by a nucleophile in a chiral complex (*Fig.-3*).

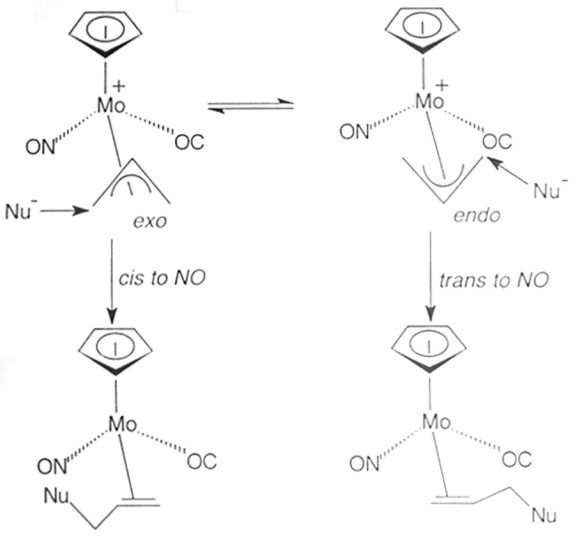


Fig.-3.

An unambiguous synthetic protocol was devised by Faller[4] to create complexes where the orientation of an unsymmetrical allyl group was controlled by the synthetic sequence adopted, so that the formation of product can be dictated by design (*Fig.-4*).

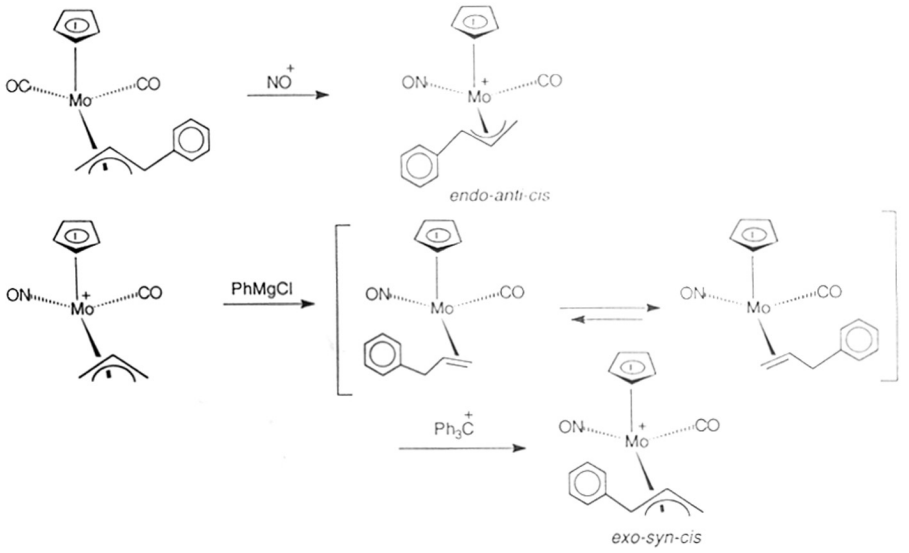
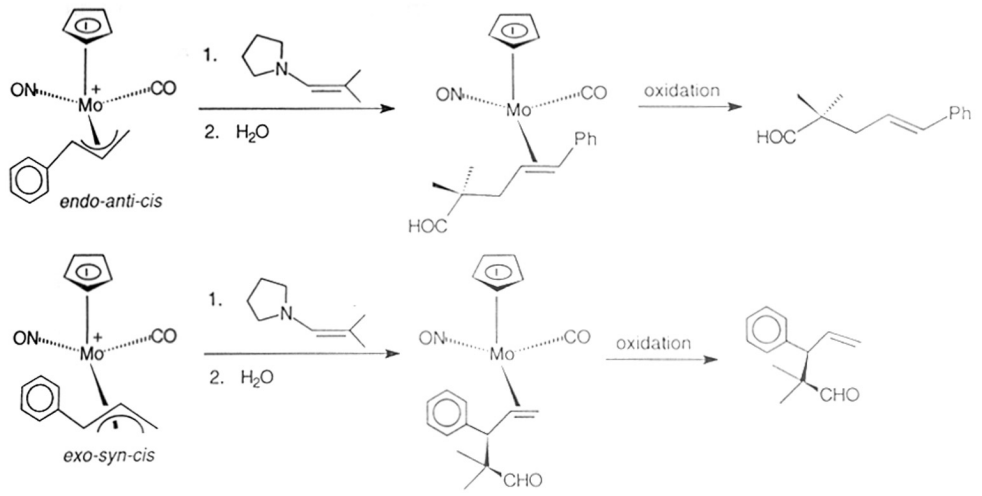


Fig.-4.

Stereoelectronic effect controlled nucleophilic addition to the cationic allyl complex to provide complementarity in product regiochemistry (*Scheme-1*).

Scheme-1



Sequential functionalization steps can also be performed with complete stereocontrol, *viz.* attack exclusively from the *exo* face (*Fig.-5*).

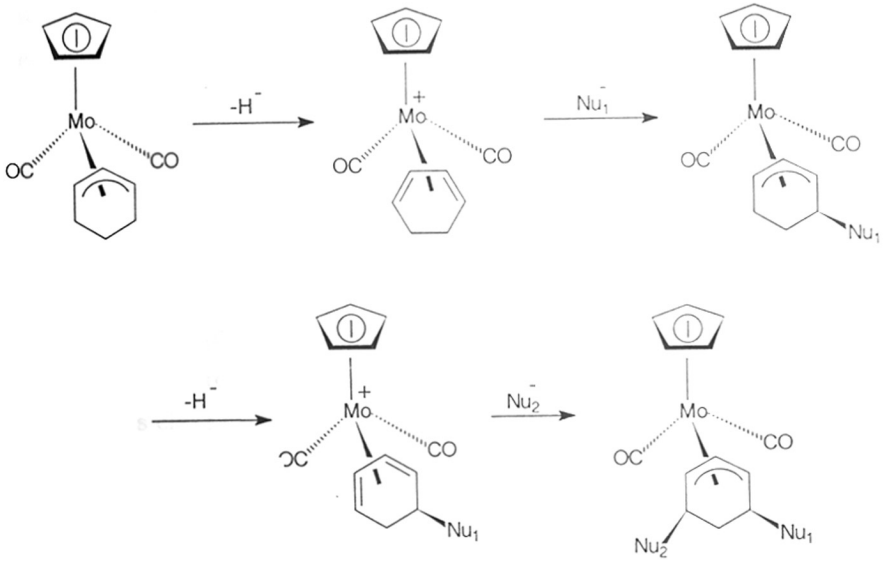
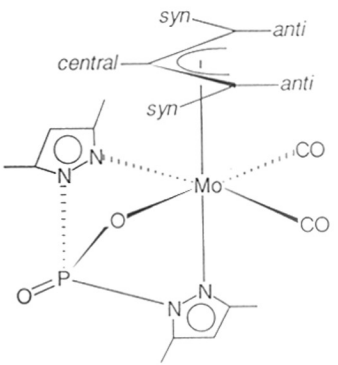


Fig.-5.

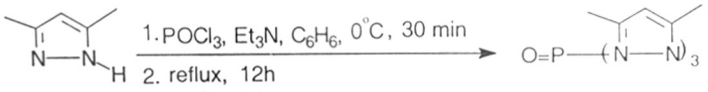
Pearson[5] followed this protocol to design various types of natural products. While Cp derivatives have been widely studied, notably from the laboratory of Liebeskind[6], similar investigations on a pyrazole-derived chelate are relatively rare[7], and prompted our efforts towards this direction.

During one of our earlier attempts[8] to prepare molybdenum π-allyl complexes with pyrazolyl chelates containing elements other than boron[9] as the "capping" atom, we prepared complexes of the following general structure :

Sructure and Scheme



The precursor for the ligand was a neutral *tris*-amide of phosphoric acid, prepared as follows:



In the complexes, the plane of symmetry bisecting the allyl group and the $Mo(CO)_2$ fragment is absent, rendering the two allyl termini *a* and *b* non-equivalent. Therefore, in this class of ligands, two possible arrangements are to be considered in terminally substituted allyl complexes (*Fig.-6*).

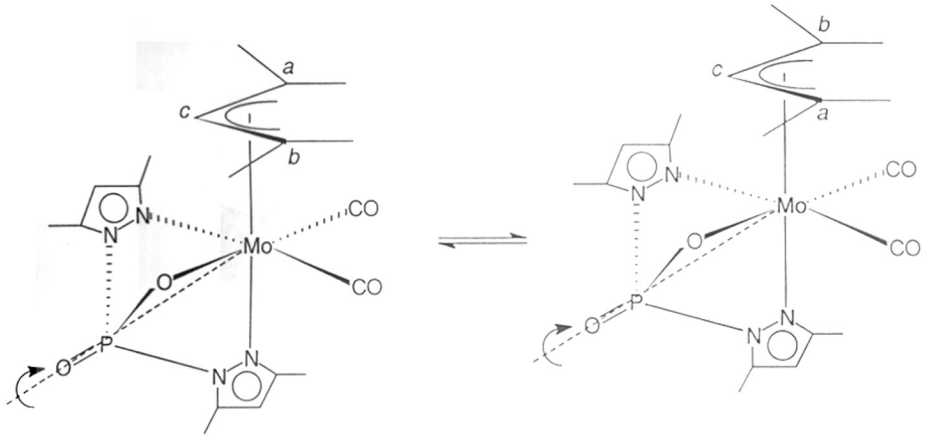


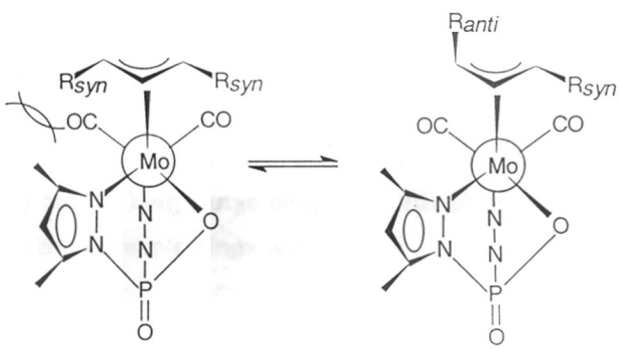
Fig.-6. Trigonal twist mechanism

We observed that the complexes were stereochemically non-rigid, and the two allyl termini interchanged by a mechanism termed "trigonal twist".[10] The three donor groups of the tridentate ligand rotate about the Mo-P axis to effect the conformational change. Use of the word "conformation" in this context is frequent in literature, since the motion described can be viewed as a torsional motion of one entire ligand with respect to the rest of the molecular fragment. This becomes a little inaccurate for the ligand that has discrete three point ligation (unlike Cp or π-aryl ligands where a symmetrical π-cloud is the donor), and may involve more than one dissociation-recombination steps.

I. 2 Present Work

While the preceding work[11] dealt with monosubstituted allyl groups, it was decided to examine steric effects in 1,3-disubstituted allyl complexes. In these complexes, one of the substituents would reside on the same side as the oxygen atom of the ligand while the other would be placed in proximity of the 3-methyl group of a pyrazole. For the former, the steric environment is relaxed; for the latter, an unfavorable interaction is not unlikely (*Chart-1*). This interaction may lead to an isomerization involving the allyl group as shown.

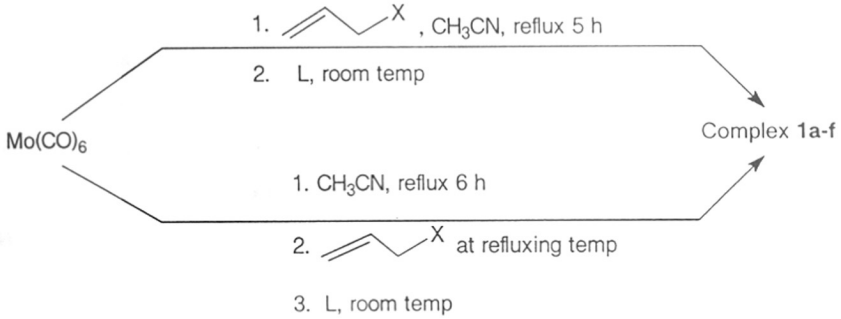
Chart-1



The chemical shifts of *syn*- and *anti*- substituents differ presumably owing to the anisotropy of the metal-ligand fragment. In order to obtain representative chemical shift values for *syn*- and *anti*-methyl groups, the prenyl complex **1a** was first prepared.

Synthetic procedures for all the complexes being discussed in this chapter are unexceptional.[12] Depending on the stability of the halides, either the *bis*(acetonitrile)-π-allyl complex was prepared first and then ligand exchange was carried out, or, allyl halide was added to preformed $(CH_3CN)_3Mo(CO)_3$ and ligand exchange was effected at room temperature (*Scheme-2*). Column chromatography followed by recrystallization yielded analytically pure complexes.

Scheme-2



The prenyl complex **1a** was isolated in 18 % yield as orange crystals. The IR spectrum displayed two sharp peaks of equal intensity appearing at 1931 cm^{-1} and 1834 cm^{-1} corresponding to the CO ligands. Two peaks of medium intensity at 1555 cm^{-1} and 1165 cm^{-1} were due to the double bonds between carbon-nitrogen in the pyrazole ring of the ligand and phosphorous-oxygen respectively. These peaks were present in all other complexes as well. The proton NMR spectrum displayed typical pyrazolyl 4-H signals at 5.87 and 5.92 ppm as doublets (J = 3 Hz) due to long range coupling with phosphorus. The four methyl groups attached to the pyrazole rings appeared at 2.40, 2.45, 2.47 and 2.80 ppm as singlets. The *anti* and *syn* methyl groups of the π-prenyl moiety appeared at 1.05 and 2.05 ppm respectively as singlets. The shielding of the *anti*-methyl group is typical of these complexes. In subsequent discussion, the chemical shift of methyl groups attached to the termini of π-allyl fragment has been assigned with reference to this model compound.

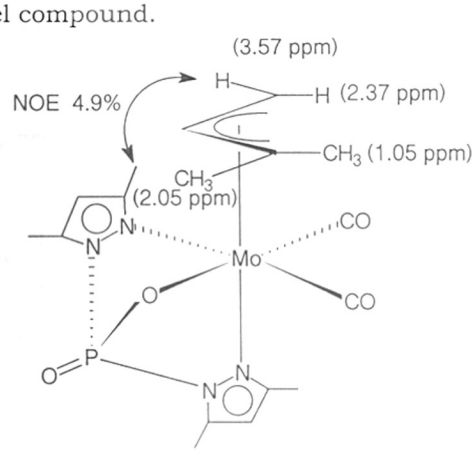


Fig.-7. Structure of **1a**

The protons of the allyl group, likewise, appeared at two distinctly different regions typifying their *syn* or *anti* orientation. The signal due to the *syn*-proton was observed as a doublet of a doublet (J = 7.5, 1.1 Hz) at 3.57 ppm, whereas the signal due to the *anti* proton appeared at 2.37 ppm (dd, J = 11.3, 1.1 Hz). The NOE difference spectrum indicated a 4.9 % NOE between the *syn* proton of the allyl group and a 3-Me signal of the pyrazole, suggesting that the dimethyl-substituted terminus of the allyl group was placed towards the oxygen of the ligand, as shown in *Fig.-7*. Both the CO ligands were clearly observed in the ^{13}C NMR spectrum of this complex at 229.1 and 232.3 ppm. Six peaks appeared at 11.4, 11.7, 14.2, 14.4, 22.3 and 25.4 ppm for four pyrazole methyls and two allyl methyls; three allyl carbons appeared at 61.3, 84.0 and 86.8 ppm; the C-4 of two pyrazole units appeared at 109.3 and 109.9 ppm; the C-3, C-5 ring carbons of pyrazole which are coupled with phosphorus appeared at 146.1, 147.2, 147.4, 155.5, 155.6, 157.4 and 157.5 ppm.

With reference to the spectral data of complex **1a**, the structure of complex **1b** could be readily assigned. At ambient temperature, the proton NMR spectrum displayed line broadening for two methyl signals, characteristic of a stereochemically non-rigid structure. The interconverting structures are depicted below (*Fig.-8*). Two isomeric species could be identified to exist in unequal proportions *ca.* (3:1).

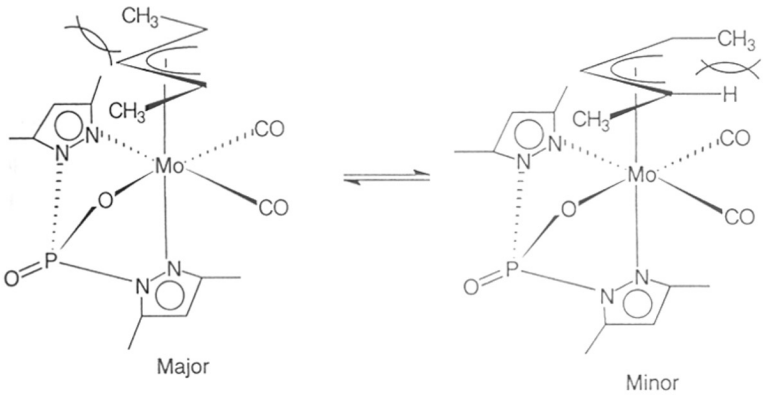


Fig.-8. Isomeric structures of **1b**

Assignments of proton NMR was done at -50 °C by a careful analysis of the COSY spectrum. It was observed that the major isomer had two *syn* methyl groups on the allyl fragment which resonated at 1.82 ppm and 2.04 ppm as two doublets, coupled with two *anti* allyl protons with coupling constants 6.3 Hz. Two *anti* allyl protons appeared at 1.68 ppm and 2.40 ppm as multiplets; and the four pyrazole methyl signals appeared as singlets at 2.33, 2.42, 2.44 and 2.73 ppm. The central allyl proton appeared at 3.81 ppm as a triplet (J = 9.7 Hz). The minor isomer had one *syn* methyl and one *anti* methyl group on the allyl fragment. They appeared at 1.19 ppm and 2.08 ppm as two doublets, coupled with *anti* and *syn* allyl protons with same coupling constant 6.3 Hz. The *anti* and *syn* protons appeared at 2.45 ppm and 4.17 ppm as two multiplets. The downfield chemical shift (4.17 ppm) proves the *syn* relationship of the allyl proton with respect to the central proton. The central proton appeared at 3.74 ppm as a triplet with coupling constant 9.6 Hz.

On heating under reflux in benzene for 5 h, this ratio changed to 1 : 1, indicating there is appreciable steric interaction between the *syn*-Me and the proximal 3-Me group of pyrazole. The competing steric interaction in this molecule is an unfavorable allylic 1,3 strain.

The complex **1c** has two different substituents at the termini of the allyl group, but the proton NMR spectrum clearly revealed the presence of only one species. One of the pyrazolyl methyl groups was found to be unusually shielded at 1.25 ppm. This shielding is reminiscent of the cinnamyl complex prepared in this laboratory earlier.[11] The crystal structure of that complex established that the phenyl ring on the allyl and the methyl group on a neighboring pyrazole were juxtaposed such that the anisotropy of the aromatic ring shielded the proximal methyl signal. This precedence immediately suggested that the phenyl ring on the allyl group in complex **1c** was similarly placed in proximity of a pyrazole (*Fig.-9*).

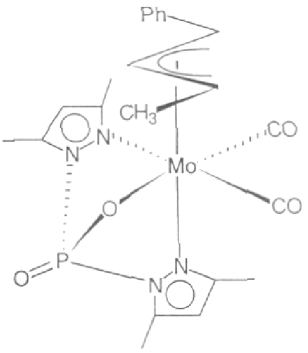


Fig.-9. Structure of complex **1c**

Similar upfield shift of pyrazole methyl signal (1.10 ppm) was also observed for the 1,3-diphenylallyl complex **1d**. This complex was prepared from the acetate, rather than from an unstable halide, by heating with $Mo(CO)_6$ under reflux in acetonitrile for 16 h followed by ligand exchange. At low temperature (-60 °C), the NMR spectral features indicated the presence of one molecular species with two *syn* phenyl groups on the π-allyl moiety (*Fig.-10*). A set of two doublets was observed for the *anti* protons at 2.64 ppm and 3.24 ppm where their coupling constants with the central proton were 9.6 Hz and 10.8 Hz respectively. The central proton appeared at 5.21ppm (t, J = 10.3 Hz). Both the CO ligands were clearly observed at 232.0 and 234.0 ppm in the ^{13}C NMR spectrum at -70 °C of this complex.

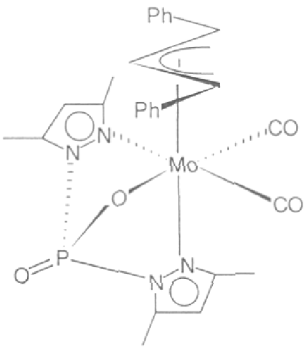


Fig.-10. Structure of complex **1d**

These structures raised an interesting question. It appeared that a phenyl ring was better accommodated in the vicinity of a pyrazole methyl compared to a methyl group. In the instance of complex **1b** it was observed that a definite steric destabilization due to Me/Me interaction forced the allyl methyl group into adopting an *anti*-orientation. In complex **1c**, this unfavorable steric interaction is avoided since the allyl methyl group is placed near the oxygen of the ligand. Absence of any other conformer in solution suggested that a Ph/Me interaction in this molecule could actually be stabilizing.

If appropriately oriented, a C-H bond can interact with a neighboring π-bond in a stabilizing manner as in donor-acceptor interaction between an acidic CH group and a basic π-system. Currently termed as CH/π interaction, such stabilization has now been identified in numerous molecular assemblies. The magnitude of the interaction is low, and weaker than a normal hydrogen bond in most instances.

The concept of CH/π interaction can be expected to be widely used in the interpretation of the behavior of molecular recognition, in determining specificities for organic reactions and stabilities of inclusion complexes, as well as in controlling specific functions of biopolymers. In one sense, a CH/π interaction is an extreme case of hydrogen bonding, which occurs between a soft acid and a soft base. It includes the dispersion force as well as contribution from charge transfer. Contribution from the coulombic force, on the other hand, is unimportant. The CH/π interaction, therefore, can manifest itself both in polar and nonpolar media, unlike normal hydrogen bonding. Current literature[13] contains two extensive reviews[14] compiling data on CH/π interaction drawn from various areas of chemistry and allied sciences.

In the case of isostructural cinnamyl complex (**A**), two conformers were identified at low temperature in a ratio of 3:4, while the crystal structure revealed only the structure of the minor conformer (shielded pyrazole methyl). For a similar complex **B**, the ratio was 1 : 1. For complex **1c** at room temperature, clearly the latter was the only conformer present (*Fig.-11*).

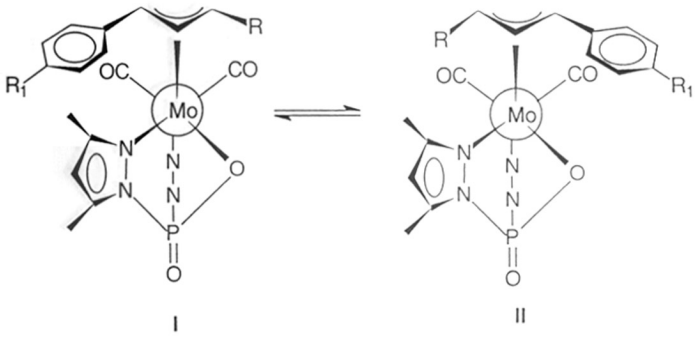


Fig.-11.

Complex No	**R**	**R_1**	**I/II**
A	H	H	3 : 4
B	H	*p*-OMe	1 : 1
1.c	CH_3	H	Only **I**

Since the CH/π interaction compares well with a donor-acceptor interaction where the aromatic ring is the donor, electronic perturbation of the aromatic ring was thought to be of significance in controlling the extent of stabilization. A systematic correlation would, in turn, vindicate operation of a CH/π interaction in these molecules. A *p*-OMe group was found to marginally improve the population of the minor conformer of the cinnamyl complex (**B**). We observed that even if three OMe groups are attached to the phenyl ring as in complex **1f** (*Fig.-12*), the donor character of the aromatic ring did not improve appreciably, rather steric factors destabilized the desired conformer.

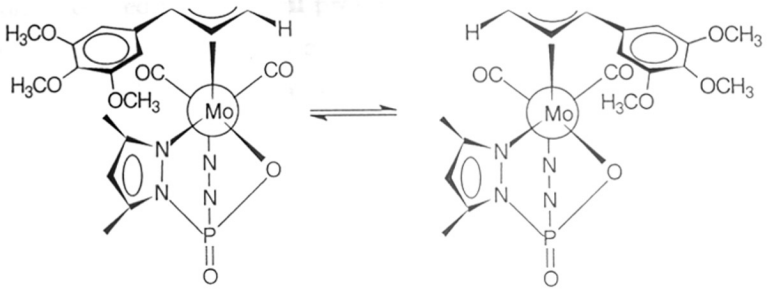


Fig.-12. Conformers of complex **1f**.

If the aromatic ring was sufficiently depleted of electron density, we reasoned, the balance of conformer population would be considerably affected. It should now be dictated by sterics alone.

Towards that end, *p*-NO_2-cinnamyl bromide was prepared from the corresponding alcohol using PBr_3. The proton NMR spectrum of the complex **1e** at low temperature (-35 °C) disclosed the presence of two conformers in the ratio 1 : 5, the balance tilted appreciably against the conformer that harbored proximal aromatic ring and pyrazolyl methyl group (*Fig.-13*)

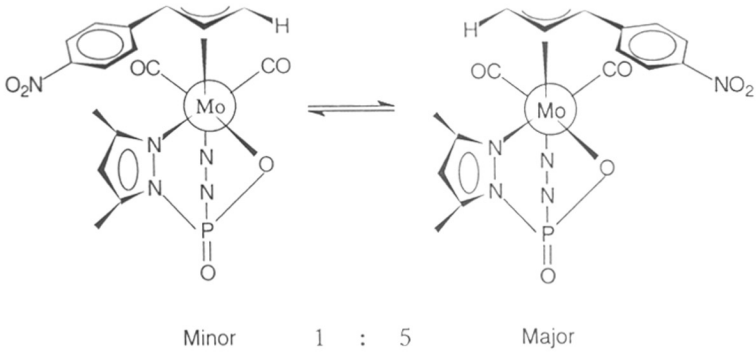


Fig.-13. Conformers of complex **1e**.

The *p*-NO_2-cinnamyl complex **1e** was isolated in 37 % yield as red crystals. The major conformer having two *anti* allyl protons appeared at 2.05 and 2.47 ppm

as a doublet, coupled with central proton, with coupling constants 10.3, 11.7 Hz respectively. The *syn* allyl proton appeared at 3.95 ppm as doublet (J = 6.9 Hz). Four pyrazole methyls appeared as singlets at 2.30, 2.45, 2.50 and 2.80 ppm. The central proton appeared at 4.65 ppm as a multiplet. The minor conformer had two *anti* allyl protons appeared at 1.62 and 2.97 ppm as a doublets (J = 8.8 and 11.3 Hz respectively). The *syn* allyl proton appeared at 3.55 ppm (J = 5.9 Hz). One pyrazole methyl signal appeared at 1.25 ppm as a singlet while the other three methyl singlets appeared at 2.25, 2.40 and 2.75 ppm. The central proton appeared at 4.65 ppm as a multiplet.

Thus, the complexes **A**, **B**, **1c**, **1d** and **1e** can be viewed as a set of molecules that exemplify the role of CH/π interaction determining conformational preferences in solution. In the cinnamyl complex **A** and the *p*-OMe-cinnamyl complex **B**, the conformer with aryl ring placed near the oxygen atom is clearly preferred on steric grounds alone. The prenyl complex **1a** exists in this conformation only. But, for both the complexes **A** and **B**, the other conformer, where the aryl group is located near the pyrazole donor, is almost equally populated. That is, there must be a factor which is stabilizing these conformers in **A** and **B** compared to the prenyl complex **1a**. This stabilization is attributed to an attractive CH/π interaction between the methyl group and the proximal aromatic ring. This premise is further supported by the only observable conformation of complex **1c**. Even for complex **1d**, one phenyl ring of the allyl group resides in the vicinity of the pyrazole methyl instead of isomerizing to the *anti*-orientation (as observed for methyl group in complex **1b**). The donor character of the aromatic ring is adversely affected by a *p*-nitro substituent and the CH/π stabilization is weakened. This is evidenced by the ratio of conformers observed in the low temperature NMR spectrum of the complex **1e**. The susceptibility of CH/π interaction to such electronic tuning provided compelling evidence for the existence of such weak interactions operative intramolecularly in these molecules.

I. 3 Summary

In a series of isostructural complexes, weak interactions like CH/π appeared to determine conformational preference in solution. Modulating the electron density on the donor aromatic π-system, the interplay of CH/π interaction could be inferred with reasonable confidence.

I. 4 EXPERIMENTAL

Acetophenone, *p*-nitrotoluene, magnesium turnings, pyridine, acetic anhydride, malonic acid, 3,4,5-trimethoxy benzaldehyde, 85% aq HBr solution, zinc wool, anhydrous aluminium chloride and acetonitrile were purchased from SD Fine Chemicals. Sodium borohydride and methyl iodide were purchased from Loba Chemie. Crotonaldehyde, cerium chloride heptahydrate, dimethylamino pyridine, prenyl alcohol, PBr_3, ethyl bromoacetate, phosphorus oxychloride, PCl_3 and *p*-nitro benzaldehyde were purchased from Aldrich Chemicals.

1. Preparation of *tris*(3,5-dimethyl-1-pyrazolyl) phosphine oxide.

The compound has been prepared from potassium-3,5-dimethyl pyrazolide and phosphorus oxychloride in 65% yield. A modified procedure was used in the present case.[15]

To a solution of 3,5-dimethyl pyrazole (12.66 g, 0.13 mol) and triethylamine (18.5 g, 0.18 mol) in benzene (125 ml) maintained at 0 to 5 °C, phosphorus oxychloride (8.2 g, 53.5 mmol) in benzene (25 ml) was added dropwise over a period of 30 minutes with stirring. The reaction mixture was stirred for 1h at room temperature and then heated under reflux for 10h (monitored by TLC). Then the mixture was cooled to room temperature, filtered and washed with dry benzene. Benzene was removed under reduced pressure and the colorless sticky residue so obtained was dissolved in CCL_4 (9 ml) followed by dilution with pet.ether (50 ml). The slightly turbid solution was kept in a refrigerator for 15 days to furnish colorless crystals of compound **1** (8.5 g, 59%).

Color	:	Colorless
MP	:	105°C (lit 105 to 108 °C)
IR	:	1560 (s), 1180 (s) cm^{-1}.
^{1}H NMR (200 MHz), 25 °C	:	2.15 (s, 9H), 2.25 (s, 9H), 5.95 (d, 3H, J = 4Hz).
^{13}C NMR (50.3 MHz), 25 °C	:	11.96, 13.61, 110.65, 110.82, 147.67, 147.91, 154.33, 154.64.
MS	:	332(M^+), 95(100%).

1.a.1. Preparation of 4-bromo-2-methyl-2-butene.

48% aqueous HBr (16.9 mL) was cooled in an ice bath, H_2SO_4 was added dropwise into it with constant stirring. Prenyl alcohol (10 mL, 98.45 mmol) was added dropwise to the above stirring mixture under cooled conditions. The reaction mixture was slowly warmed to room temperature and H_2SO_4 (4 mL) was added dropwise. The temperature of the reaction mixture was maintained at 70-80 °C for 0.5 h. The reaction mixture was distilled, and the distillate washed with 5% $NaHCO_3$ (2 X 20 mL) and water (3 X 10 mL), dried over anhydrous Na_2SO_4 and distilled (55-58 °C/59 mmHg) to obtain a colorless oily product (9.39 g, 64%).

1.b.1. Preparation of pent-3-ene-2-ol.

Methyl iodide (5 mL, 80.31 mmol) was added dropwise into a stirred suspension of activated magnesium turnings (2.15 g, 88.34 mmol) in anhydrous Et_2O (60 mL). The reaction started spontaneously. The reaction mixture was maintained at 40 °C for 1 h to sustain a gentle reflux. To the stirred solution, crotonaldehyde (6.2 mL, 75 mmol) in 30 mL anhydrous Et_2O was added dropwise and the reaction mixture was stirred for another 1 h. The reaction mixture was then cooled and saturated NH_4Cl solution (50 mL) was added, when a dense white precipitate settled at the bottom of the flask. It was allowed to stand for 1 h and the clear ethereal solution was decanted. The white precipitate was washed twice with Et_2O (2 X 30 mL). The combined organic fraction was dried over anhydrous Na_2SO_4 and Et_2O was removed, the oily product obtained, distilled at 119-121°C to afford pure 3- penten-2-ol (5.15 g, 80%) (lit. 120 °C/740 mmHg).[16]

1.b.2 Preparation of 4-Chloro-pent-2-ene.

The compound was prepared by slow addition of a mixture of pent-3-ene-2-ol (5 g, 58.14 mmol) and pyridine (1 g, 12.64 mmol) to PCl_3 (3 g, 21.84 mmol) cooled in dry ice-acetone. The mixture was allowed to stand at room temperature for 1.5 h. The upper layer was then decanted and distilled. (3.77 g, 62%) b.p.-65 °C /270mmHg, (lit. 68 °C /270 mmHg).[17]

1.c.1. Preparation of 4-Phenyl-but-3-ene-2-one (benzalacetone).

The compound was prepared by the reported method.[18] 10% solution of sodium hydroxide (5 mL) was added to a stirred solution of benzaldehyde (21 g, 40 mL) in 40 mL acetone. The temperature of the reaction mixture was maintained at 25-30 °C for 3 h. The reaction mixture was acidified with dil. HCl and stirred at room temperature for 2 h. The organic layer was removed and the aqueous layer was extracted with 20 mL benzene. After drying over anhydrous Na_2SO_4, the solvent was removed under reduced pressure. Fractional distillation afforded pure benzalacetone (20 g, 69%) 132-137 °C/16 mm.Hg (lit. 137-142 °C/16 mm.Hg).

1.c.2. Preparation of 4-phenyl-but-3-ene-2-ol.

This compound was prepared by a modified reported method.[19] Benzalacetone (1.46 g, 10 mmol) was mixed with cerium chloride heptahydrate (3.72 g, 10 mmoL) and dissolved in 25 mL MeOH. Sodium borohydride (0.38 g, 10 mmoL) was added pinchwise to the reaction mixture. A vigorous evolution of gases occurred, along with an elevation in temperature and a milky white solution was obtained. Stirring was continued for 0.5 h. MeOH was then removed under reduced pressure, 30 mL water was added followed by glacial acetic acid till a pH of 5 was reached. The solution was then extracted with EtOAc (3 X 30 mL). The organic layer was washed with water (3 X 20 mL), followed by $NaHCO_3$ (3 X 20 mL), to reach the pH of 8 and finally washed with brine. After drying over Na_2SO_4 the solvent was removed under reduced pressure to afford a colorless oily product (1.3g, 88%). The compound was used for the next reaction without further purification.

^{1}H NMR (90 MHz) : 1.3 (d, 3H, J = 1.5 Hz), 3.05 (brs, 1H), 4.5 (m, 1H), 6.1-6.6 (m, 2H) 7.1-7.4 (m, 5H).

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1.c.3. Preparation of 3-chloro-1-phenyl-butene.

The compound was prepared by a modified reported method.[20] 4-Phenyl-but-3-ene-2-ol (1.48 g, 10 mmoL) was dissolved in CCl_4 (15 mL, freshly distilled

RR
546-77; 54-07 (043)
CHO

over phosphorus pentoxide), triphenyl phosphine (3.41 g, 13 mmoL) was added into this solution and the mixture refluxed for 5 h in inert atmosphere. The reaction mixture was cooled to 25 °C and concentrated to 5 mL. 20 mL pet. ether was added and the solid was filtered. The filtrate was concentrated and distilled to afford the title compound as a colorless oil (0.93 g, 56%). The compound was used for complexation without further purification.

1.d.1. Preparation of 1,3-diphenyl-prop-2-ene-1-one.

The compound was prepared by the reported method.[21] Acetophenone (26 g, 216.7 mmol) was added into a solution of sodium hydroxide (11 g in 100 mL water and 62 mL rectified spirit). Benzaldehyde (23 g, 217 mmol) was added dropwise into the above stirred solution at a temperature below 25 °C. The crude yellow solid was crystallized from rectified spirit (35 g, 78%). m.p. 56 °C (lit. 56 - 57 °C).

1.d.2. Preparation of 1,3-diphenyl-prop-2-ene-1-ol.

The compound **1.d.2** was prepared following the same procedure and in the same scale as compound **1.c.2.** A colorless solid (1.93 g, 92%) was obtained by crystallization (CH_2Cl_2-pet.ether) of the colorless oil.

^{1}H NMR : 3.2 (brs, 1H), 5.1 (d, 1H, J = 5 Hz), 6.3 (m, 2H), 6.9-7.3 (m, 10H). (60 MHz)

1.d.3. Preparation of 3-acetoxy-1,3-diphenyl-prop-2-ene.

To a mixture of this 1,3-diphenyl-prop-2-ene-1-ol (1.035 g, 4.92 mmol) and N,N-dimethyl amino pyridine (0.722 g, 5.91 mmol) in Et_2O (10 mL), acetic anhydride (0.56 mL, 5.91 mmol) was added dropwise and it was stirred at room temperature overnight. The reaction mixture was washed with water (3 X 10 mL), 10% HCl (3 X 10 mL) and saturated $NaHCO_3$ (3 X 10 mL). Removal of Et_2O resulted in a colorless oil (0.757 g, 61%). This acetate was used for complexation without further purification.

^{1}H NMR : 2.1 (s, 3H), 5.15 (m, 1H), 6.15-6.6 (m, 2H), 7.1-7.5 (brs, 10H). (90 MHz)

1.e.1. Preparation of *p*-nitro cinnamic acid.

Anhydrous pyridine (30 mL) was added to *p*-nitrobenzaldehyde (10 g, 66.17 mmol) and malonic acid (15 g, 144.15 mmol), the mixture was then stirred till a homogeneous solution was obtained. Piperidine (1 mL) was added and the resultant mixture was then warmed to 80-90 °C when evolution of a gas began. After 0.5 h the mixture started solidifying. Pyridine (5 mL) was added to dissolve it and the temperature was increased to 120 °C and maintained till all gas evolution ceased (~1 h). The reaction mixture was then cooled to room temperature and was poured into an ice-cold solution of 5N HCl (250 mL) and stirred vigorously when a white solid precipitated. This was filtered, washed with cold water and dried thoroughly under vacuum to yield the desired product (9.86 g, 78%). m.p. 284-285 °C dec.

1.e.2. Preparation of *p*-nitro cinnamyl alcohol.

A solution of *p*-nitrocinnamic acid (3.86 g, 20 mmol in 40 mL THF) was slowly added to a suspension of sodium borohydride (0.912 g, 24 mmol) in 40 mL THF at room temperature (addition time ~15 min). The reaction mixture was stirred till gas evolution ceased. Iodine (2.54 g, 10 mmol in 40 mL THF) was added slowly (~ 15 min) to this mixture at 10 °C. Additional gas evolution was observed. It was further stirred for 1 h at 0 °C. 3N HCl (10 mL) was added carefully and the mixture was extracted with Et_2O. The Et_2O extract was washed with 3N sodium hydroxide (3 X 20 mL), followed by brine (3 X 20 mL), dried over anhydrous Na_2SO_4 and evaporated to yield the title compound which was recrystallized from benzene (0.966 g, 27%). m.p.- 125-127 °C.

1.e.3. Preparation of *p*-nitro cinnamyl bromide.

p-Nitrocinnamyl bromide was prepared by a reported method. The compound **1.e.2** (2 g, 11.16 mmol) was dissolved in freshly distilled CCl_4 (15 mL). The mixture was chilled to -10 °C, PBr_3 (0.36 mL, 3.82 mmol) added, the mixture

was stirred at 1 h at 10 °C, 1 h at room temperature and finally refluxed for 1 h. The mixture was then cooled to room temperature and poured onto crushed ice. The organic layer was washed with water, dried over anhydrous Na_2SO_4 and the solvent evaporated under reduced pressure. Recrystallization from MeOH gave the compound (1.57 g, 58%). m.p.- 57-59 °C (lit. 58-60 °C).[22]

1.f.1. Preparation of 3,4,5 trimethoxy ethyl cinnamate.

A 3 mL portion of a mixture of 3, 4, 5-trimethoxybenzaldehyde (5 gm, 25.48 mmol) and ethyl bromoacetate (2.5 mL, 23 mmol) in benzene (4 mL) and Et_2O (1 mL) was added dropwise to zinc wool (1.65 g, 25.3 mmol) with constant stirring. The reaction mixture was warmed to mild reflux and then the rest of the mixture was added. It was refluxed for a further 1 h after completion of addition. The reaction mixture was then cooled on an ice bath and 10% H_2SO_4 (9.4 mL) was added dropwise. The aqueous layer was then removed and the organic layer was washed with 5% H_2SO_4 (3 X 5 mL), saturated anhydrous Na_2CO_3 solution (3 X 5 mL) and finally with water (3 X 5 mL). The organic layer was dried over Na_2SO_4 and solvent was removed under reduced pressure to afford a red liquid (5.10 g), which upon refluxing with *para*-toluene sulfonic acid (0.25 g) in benzene (25 mL) for 6 h using Dean-Stark apparatus gave the dehydrated product. The pure title compound was obtained after crystallization from ethanol (3.35 g, 48%), m.p.- 65-66 °C (lit. 68-70 °C). [23]

1.f.2. Preparation of 3,4,5-trimethoxycinnamyl alcohol.

$AlCl_3$ (2.9 g, 20 mmol) was dissolved in Et_2O (15 mL). Lithium alumiunium hydride (2.035 g, 54.42 mmol) was suspended in Et_2O (110 mL) separately and chilled to 0 °C. The $AlCl_3$ solution was then added dropwise to this chilled solution. The solution was slowly warmed to room temperature and stirred for 2 h. This mixture was allowed to stand for 1 h. Ethyl 3,4,5-trimethoxycinnamate (2.414 g, 9.07 mmol) was then dissolved in Et_2O (50 mL) and cooled in an ice-salt bath. The supernatant liquid of the ethereal solution of aluminium hydride was then transferred using canula to the ester solution. The reaction mixture was then raised to room temperature and stirred for 2 h. After 2 h the reaction mixture was again cooled on an ice-bath followed by careful addition of water (4 mL),

15% sodium hydroxide solution (4 mL) and again water (12 mL). The slurry thus formed was stirred for 1 h and the organic layer was decanted out and dried over anhydrous Na_2SO_4 and the solvent evaporated to yield a colorless solid (1.65 g, 82%). This compound was used for the next step without further purification.[23]

^{1}H NMR (80 MHz) : 1.75 (s, 3H), 3.8 (s, 9H), 4.3 (d, 2H, J = 7.5 Hz), 6.1-6.6 (m, 4H).

1.f.3. Preparation of 3,4,5 trimethoxycinnamyl chloride.

A mixture of the 3,4,5-trimethoxycinnamyl alcohol (1.9 g, 9 mmol) and pyridine (0.15 mL) was added to PCl_3 (0.27mL, 3.09 mmol) in Et_2O (3 mL) and cooled to -78 °C. The mixture solidified. Et_2O (5 mL) was then added and the mixture was brought to room temperature, stirred for a further 1.5 h and diluted with Et_2O (20 mL). The Et_2O layer was then separated and washed thoroughly with saturated copper sulfate solution (3 X 10 mL) and then with brine (3 X 10 mL). Removal of solvent led to the colorless oily title compound (0.603 g, 29%). The compound was used for complexation without further purification.

General method of complexation

Method A:

In an oven dried two-necked flask cooled under argon, $Mo(CO)_6$ (2 mmol) in freshly distilled acetonitrile (30 mL) was refluxed for 6 h. The golden yellow solution of the resultant *tris*-acetonitrile $Mo(CO)_3$ complex was then treated with freshly distilled allyl halide (2.1 mmol) and the solution was refluxed for another 15 min for allyl chlorides; in case of the allyl bromides the solution was cooled immediately after addition. The volume of the reaction mixture was concentrated to approximately 5 mL by removal of acetonitrile under reduced pressure. A solution of the ligand (2.1 mmol) in CH_2Cl_2 (10 mL) was then added to the reaction mixture with vigorous stirring and stirring was continued at room temperature for a further 1.5 h. The reaction mixture was then concentrated and subjected to column chromatography to yield the colored complex. Further purification was done by crystallization.

Method B:

In an oven-dried two-necked flask cooled under argon, a suspension of freshly distilled acetonitrile (30 mL), $Mo(CO)_6$ (2 mmol) and freshly distilled allyl halide (2.1 mmol) was refluxed for 5 h. The resultant *bis*-acetonitrile $Mo(CO)_2$ complex was then cooled to room temperature. A solution of the ligand (2.1 mmol) in acetonitrile (10 mL) was then added to the reaction mixture with vigorous stirring and stirring was continued at room temperature for a further 1.5 h. The reaction mixture was then concentrated and subjected to column chromatography to yield the colored complex. Further purification was done by crystallization.

Preparation of complex 1.a.

The complex was prepared using **method B** from $Mo(CO)_6$ (0.528 g, 2 mmol) in acetonitrile (30 mL), allyl halide **1.a.1** (4-bromo-2-methyl-2-butene) (0.315 g, 2.1 mmol) and the ligand (0.83 g, 2.5 mmol). A yellow colored reaction mixture was obtained. Chromatography (25% EtOAc-pet.ether) and recrystallization from CH_2Cl_2-pet.ether (by diffusion method at 5 °C) afforded orange crystals (0.168 g, 18%).

Color	:	Orange
MP	:	234 °C (dec)
IR	:	1931 (s), 1834 (s), 1555 (m), 1165 (m) cm^{-1}.
^{1}H NMR (200 MHz), 25 °C	:	1.05 (s, 3H), 2.05 (s, 3H), 2.37 (dd, 1H, J = 11.3, 1.1Hz), 2.40 (s, 3H), 2.45 (s, 3H), 2.47 (s, 3H), 2.80 (s, 3H), 3.57 (dd, 1H, J = 7.5, 1.1Hz), 3.97 (dd, 1H, J = 11.2, 7.5 Hz), 5.87 (d, 1H, J = 3.0 Hz), 5.92 (d, 1H, J = 3.0 Hz).
^{13}C NMR (50.3 MHz), 25 °C	:	11.4, 11.7, 14.2, 14.4, 22.3, 25.4, 61.3, 84.0, 86.8, 109.3, 109.9, 146.1, 147.2, 147.4, 155.5, 155.6, 157.4, 157.5, 229.1, 232.3.
Analysis	:	Calcd. : C: 43.02; H: 4.85; N: 11.81. Found : C: 42.85; H: 4.76; N: 11.51.

Preparation of complex 1.b.

The complex was prepared from $Mo(CO)_6$ (0.528 g, 2 mmol) in acetonitrile (30 mL), allyl halide **1.b.2** (4-chloro-pent-2-ene) (0.418 g, 4.0 mmol) and the ligand (0.996 g, 3 mmol) using **method B**. A yellow colored reaction mixture was obtained. Chromatography (15% EtOAc-pet.ether) and recrystallization from CH_2Cl_2-pet.ether (by diffusion method at 5 °C) afforded orange crystals (0.252 g, 27%).

Color	:	Orange
MP	:	212 °C (dec)
IR	:	1927 (s), 1827 (s), 1556 (m), 1166 (m) cm^{-1}.
^{1}H NMR (500 MHz), -50 °C	:	Major isomer: 1.68 (m, 1H), 1.82 (d, 3H, J = 6.3 Hz), 2.04 (d, 3H, J = 6.3 Hz), 2.33 (s, 3H), 2.40 (m, 1H), 2.42 (s, 3H), 2.44 (s, 3H), 2.73 (s, 3H), 3.81 (t, 1H, J = 9.7 Hz), 5.92 (brs, 2H). Minor isomer: 1.19 (d, 3H, J = 6.3 Hz), 2.08 (d, 3H, J = 6.3 Hz), 2.35 (s, 3H), 2.39 (s, 3H), 2.40 (s, 3H), 2.45 (m, 1H), 2.81 (s, 3H), 3.74 (t, 1H, J = 9.6 Hz), 4.17 (m, 1H), 5.96 (brs, 2H).
^{13}C NMR (50.3 MHz), 25 °C	:	11.7, 12.0, 14.4, 14.8, 14.9, 15.6, 16.3, 17.2, 70.1, 75.6, 81.9, 86.9, 109.5, 109.6, 110.3, 110.4, 146.3, 147.5, 147.7, 156.1, 157.7, 157.9, 229.8, 230.5.
Analysis	:	Calcd. : C: 43.02; H: 4.85; N: 11.81. Found : C: 42.59; H: 4.90; N: 11.56.

Equilibration of complex 1.b.

The complex **1.b** (0.10 g, 0.21 mmol) was dissolved in benzene (8 mL) and the resulting solution was refluxed for 5 h. The solution was then cooled to room temperature and the solvent removed under reduced pressure. Chromatography (15% EtOAc-pet.ether) yielded a yellow colored solid (0.08 g, 85%). Proton NMR of the solid was similar to that of **1.b,** only the ratio of the isomers was found to be different (1 : 1). Refluxing the solution for more than 5 h resulted in extensive decomposition of the starting complex.

Preparation of complex 1.c.

The complex was prepared using **method B** from $Mo(CO)_6$ (0.396 g, 1.5 mmol) in acetonitrile (25 ml), allyl halide **1.c.3** (3-chloro-1-phenyl-butene) (0.254 g, 2.0 mmol) and the ligand (0.747 g, 2.2 mmol). A red colored reaction mixture was obtained. Chromatography (20% EtOAc-pet.ether) and recrystallization from CH_2Cl_2-pet.ether (by diffusion method at 5 °C) afforded red colored crystals (0.150 g, 14%).

Color	:	Red
MP	:	227 °C (dec)
IR	:	1933 (s), 1827 (s), 1561 (m), 1167 (m) cm^{-1}.
^{1}H NMR (200 MHz), 25 °C	:	1.25 (s, 3H), 2.00 (m, 1H), 2.20 (d, 3H, J = 9 Hz), 2.35 (s, 3H), 2.45 (s, 3H), 2.70 (s, 3H), 3.05 (d, 1H, J = 11.2 Hz), 4.50 (dd, 1H, J = 9.0, 11.2 Hz), 5.55 (d, 1H, J = 2.6 Hz), 5.90 (d, 1H, J = 2.9 Hz), 7.00 (brs, 5H).
^{13}C NMR (50.3 MHz), 25 °C	:	11.4, 11.9, 12.5, 14.3, 16.2, 66.4, 83.6, 85.0, 109.1, 109.2, 110.1, 110.2, 126.7, 127.9, 138.7, 145.9, 146.1, 147.8, 148.0, 156.6, 156.7, 158.4, 158.6, 231.6, 233.1.
Analysis	:	Calcd. : C: 49.25; H: 4.66; N: 10.44. Found : C: 49.99; H: 4.30; N: 9.70.

Preparation of complex 1.d.

$Mo(CO)_6$ (0.693 g, 2.62 mmol) was refluxed in acetonitrile (40 mL) was refluxed for 6 h. The golden solution of the resultant *tris*-acetonitrile $Mo(CO)_3$ complex was then treated with freshly prepared allyl acetate **1.d.3** (3-acetoxy-1,3-diphenyl-prop-2-ene) (0.730 g, 2.9 mmol) and the solution was refluxed for another 16 h. A deep red colored solution was formed. The reaction mixture was then cooled to room temperature and the volume was concentrated to 5 mL. It was diluted with 20 mL CH_2Cl_2 and the ligand (0.962 g, 2.9 mmol) was added. The red colored reaction mixture thus obtained was concentrated and chromatographed (40% EtOAc-pet.ether). Recrystallization from CH_2Cl_2-pet.ether (by diffusion method at 5 °C) afforded red colored crystals (0.358 g, 23 %).

Color	:	Red
MP	:	211 °C (dec)
IR	:	1925 (s), 1838 (s), 1560 (m), 1160 (m) cm^{-1}.
^{1}H NMR (400 MHz), -60 °C CD_2Cl_2	:	1.10 (s, 3H), 2.17 (s, 3H), 2.36 (s, 3H), 2.59 (s, 3H), 2.64 (d, 1H, J = 9.6 Hz), 3.24 (d, 1H, J = 10.8 Hz), 5.21 (t, 1H, J = 10.3 Hz), 5.59 (s, 1H), 5.80 (s, 1H), 6.68 (d, 1H, J = 9.7 Hz), 6.97 (t, 1H, J = 7.4 Hz), 7.26 (m, 5H), 7.50 (d, 1H, J = 7.3 Hz), 7.65 (d, 2H, J = 7.6 Hz).
^{13}C NMR (100.6 MHz), -70 °C CD_2Cl_2	:	11.8, 12.5, 14.6, 67.0, 78.9, 85.2, 109.1, 110.3, 125.9, 127.4, 127.6, 128.1, 128.4, 130.9, 137.9, 138.3, 146.1, 146.2, 148.3, 148.4, 156.7, 156.8, 158.9, 159.0, 232.0, 234.0.
Analysis	:	Calcd. : C: 54.10; H: 4.50; N: 9.30. Found : C: 53.70; H: 4.53; N: 9.14.

Preparation of complex 1.e.

The complex was prepared using **method A** from $Mo(CO)_6$ (0.264 g, 1 mmol) in acetonitrile (15 mL), allyl halide **1.e.3** (*p*-nitrocinnamyl bromide) (0.266 g, 1.1 mmol) and the ligand (0.498 g, 1.5 mmol). A deep red colored reaction mixture was obtained. Chromatography (2.5% MeOH-EtOAc) and recrystallization from CH_2Cl_2-pet.ether (by diffusion method at 5 °C) afforded crimson red colored crystals (0.210 g, 37 %).

Color	:	Crimson red
MP	:	195 °C (dec)
IR	:	1944 (s), 1852 (s), 1553 (m), 1167 (m) cm^{-1}.
^{1}H NMR (200 MHz), -35 °C	:	Major Conformer: 2.05 (d, 1H, J = 10.3 Hz), 2.30 (s, 3H), 2.45 (s, 3H), 2.47 (d, 1H, J = 11.7 Hz), 2.50 (s, 3H), 2.80 (s, 3H), 3.95 (d, 1H, J = 6.9 Hz), 4.65 (m, 1H), 5.92 (d, 1H, J = 3.1 Hz), 5.97 (d, 1H, J = 2.9 Hz), 7.67 (d, 2H, J = 8.8 Hz), 8.17 (d, 2H, J = 8.8 Hz). Minor Conformer: 1.25, (s, 3H), 1.62 (d, 1H, J = 8.8 Hz), 2.25 (s, 3H), 2.40 (s, 3H), 2.75 (s, 3H), 2.97 (d, 1H, J = 11.3 Hz), 3.55 (d, 1H, J = 5.9 Hz), 4.65 (m, 1H), 5.70 (d, 1H, J = 2.3 Hz), 5.95 (d, 1H, J = 2.3 Hz), 7.67 (d, 2H, J =

8.8 Hz), 8.17 (d, 2H, J = 8.8 Hz)

^{13}C NMR (50.3 MHz), 25 °C : 11.7, 11.9, 14.6, 63.2, 70.9, 79.5, 109.9, 110.6, 123.2, 128.7, 146.3, 146.6, 147.9, 156.6, 157.8, 228.7, 230.6.

Analysis : Calcd. : C: 44.44; H: 3.88; N: 12.34.
Found : C: 44.02; H: 3.71; N: 11.95.

Preparation of complex 1.f.

The complex was prepared using **method A** from $Mo(CO)_6$ (0.264 g, 1 mmol) in acetonitrile (15 mL), allyl halide **1.f.3** (3,4,5-trimethoxycinnamyl chloride) (0.267 g, 1.1 mmol) and the ligand (0.498 g, 1.5 mmol). A deep red colored reaction mixture was obtained. Chromatography (5 % EtOAc-CH_2Cl_2) and recrystallization from CH_2Cl_2-pet.ether (by diffusion method at 5 °C) afforded red colored crystals (0.209 g, 34 %).

Color : Red

MP : 204 °C (dec)

IR : 1940 (s), 1825 (s), 1563 (m), 1170 (m) cm^{-1}.

^{1}H NMR (400 MHz), -60 °C CD_2Cl_2 : Major Conformer: 1.84 (d, 1H, J = 10.2 Hz), 2.24 (s, 1H), 2.35 (s, 1H), 2.40 (s, 3H), 2.69 (s, 3H), 2.47 (d, 1H, J = 10.2 Hz), 3.65 (m, 1H), 3.67-3.78 (bunch of singlets, 9H), 4.49 (m, 1H), 5.88 (s, 1H), 5.91 (s, 1H), 6.72 (s, 2H).
Minor Conformer: 1.17 (s, 3H), 1.42 (d, 1H, J = 7.2 Hz), 2.25 (s, 3H), 2.66 (s, 3H), 3.00 (d, 1H, J = 11.4 Hz), 3.23 (s, 3H), 3.28 (d, 1H, J = 5.2 Hz), 3.67-3.78 (bunch of singlets, 9H), 4.35 (m, 1H), 5.69 (s, 1H), 5.73 (s, 1H), 6.62 (s, 1H), 6.72 (s, 1H).

^{13}C NMR (100.6 MHz), -70 °C CD_2Cl_2 : 11.3, 11.4, 11.7, 11.9, 14.1, 14.2, 14.3, 48.6, 54.8, 55.4, 55.5, 59.5, 60.2, 62.0, 74.6, 77.0, 77.2, 89.5, 100.4, 104.1, 105.8, 108.7, 109.7, 109.9, 132.3, 132.9, 135.7, 136.0, 145.7, 145.8, 145.9, 146.0, 147.0, 147.1, 147.9, 148.0, 151.8, 152.1, 152.3, 155.5, 155.6, 156.4, 156.5, 157.0, 157.1, 158.6, 158.7, 228.8, 230.4, 231.3.

Analysis : Calcd. : C: 47.05; H: 4.73; N: 9.15.
Found : C: 46.57; H: 4.70; N: 8.98.

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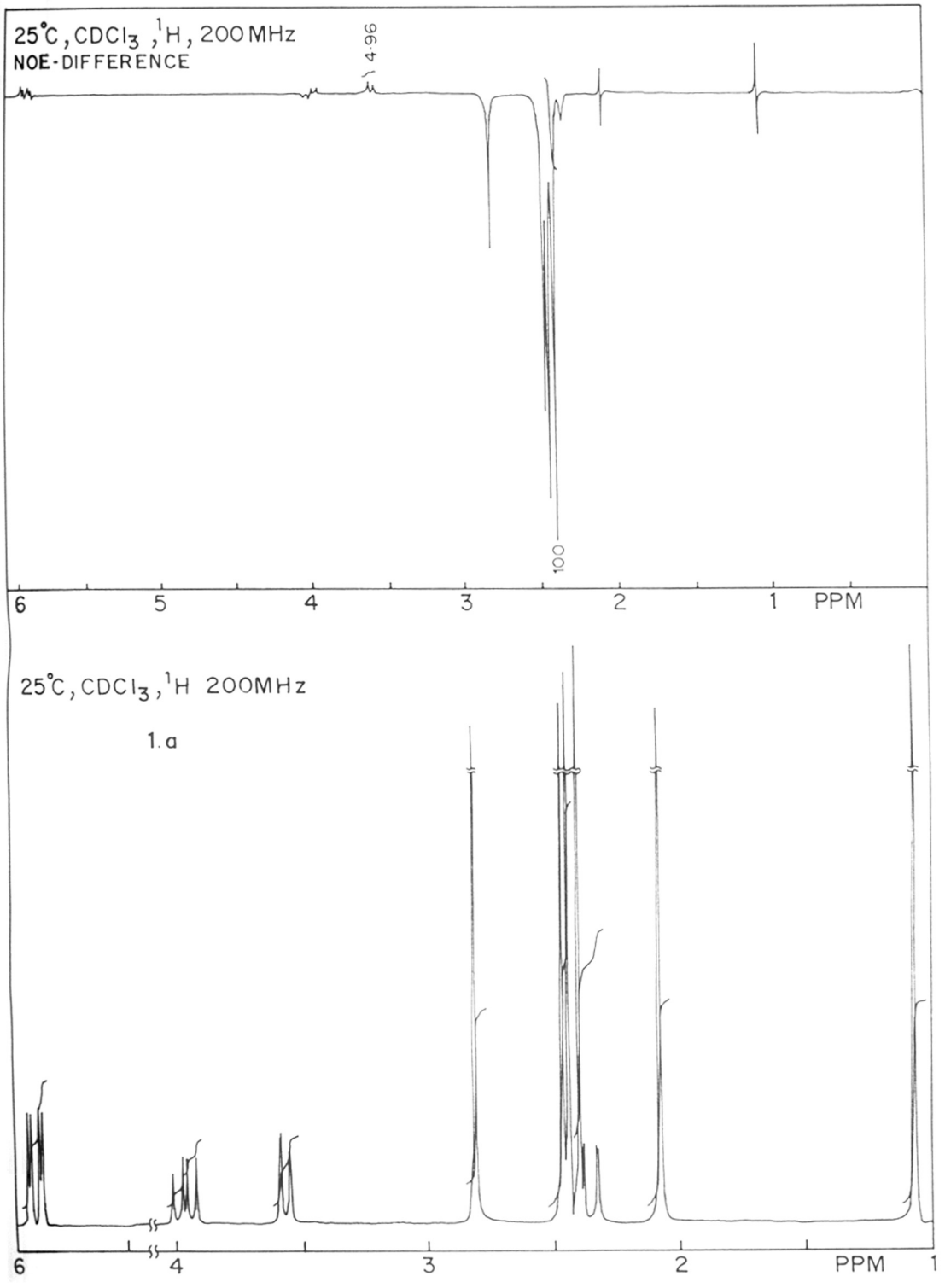
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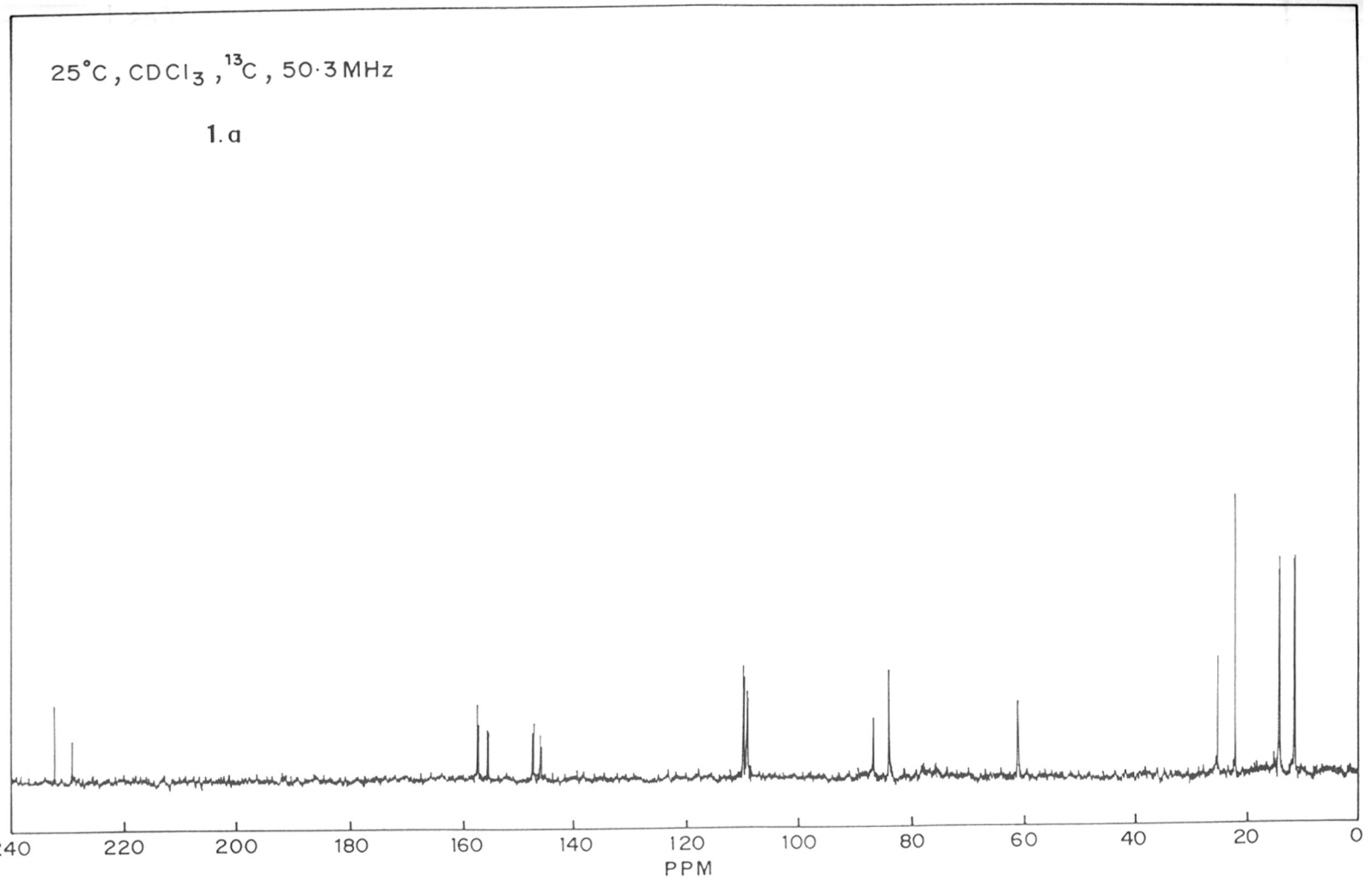
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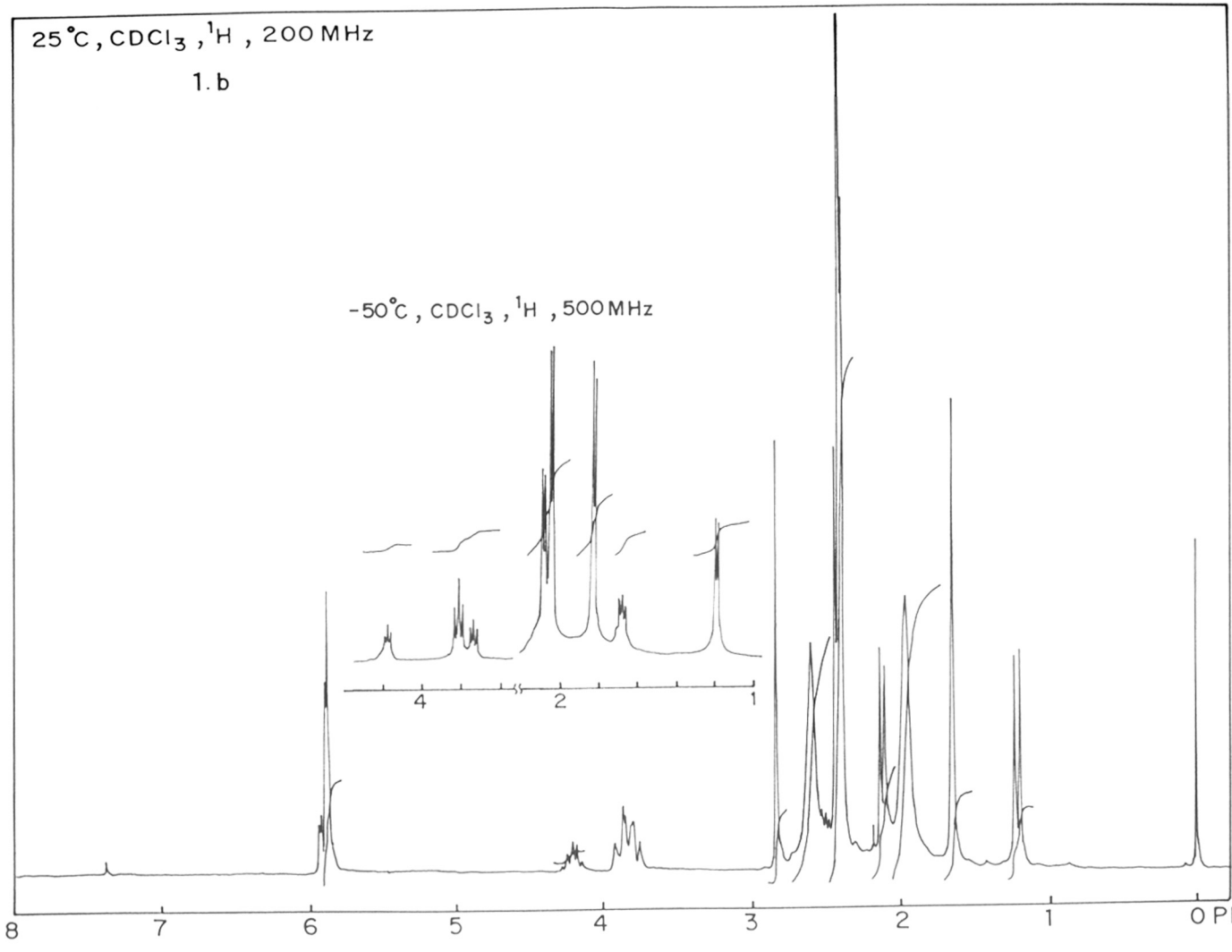
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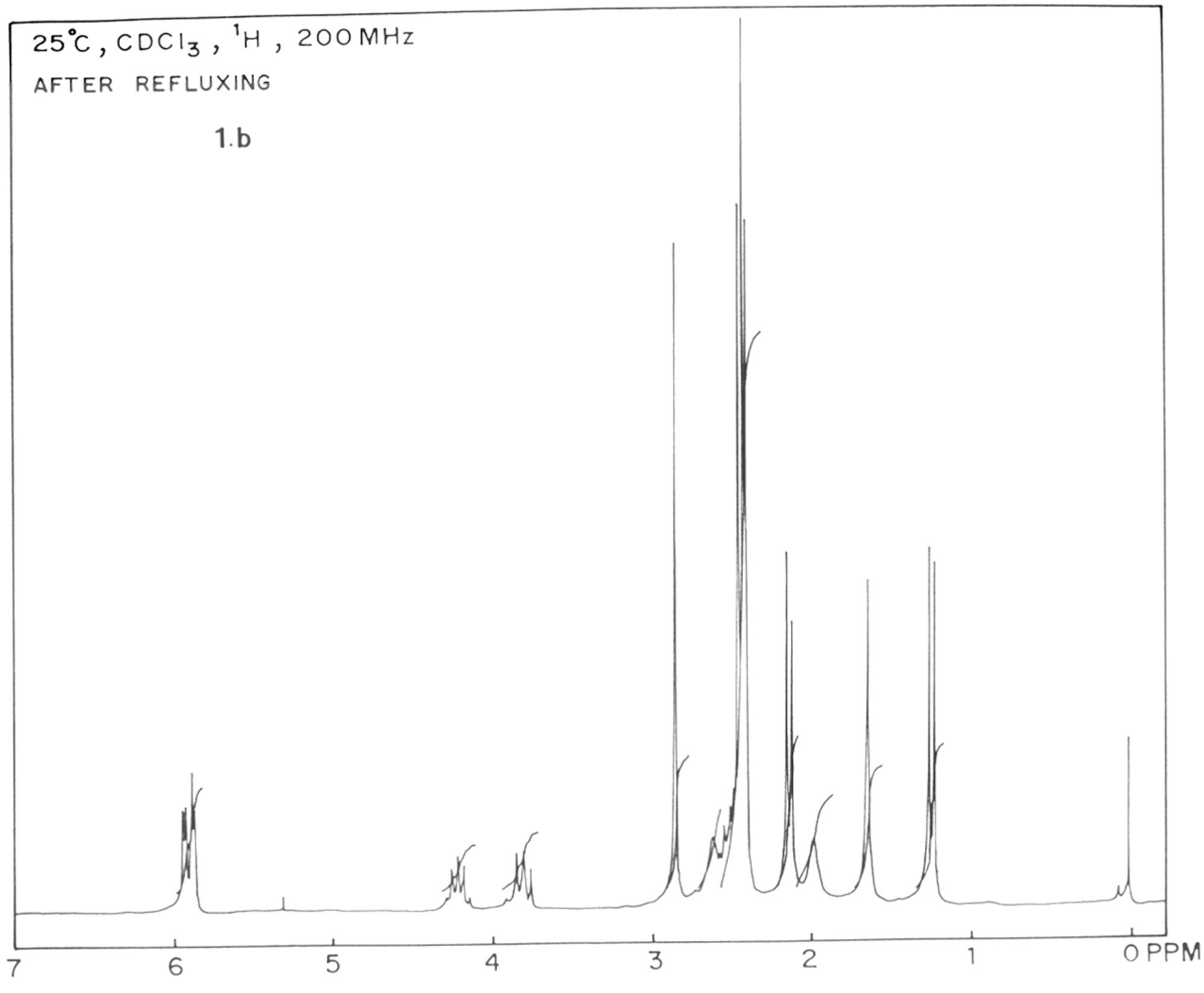
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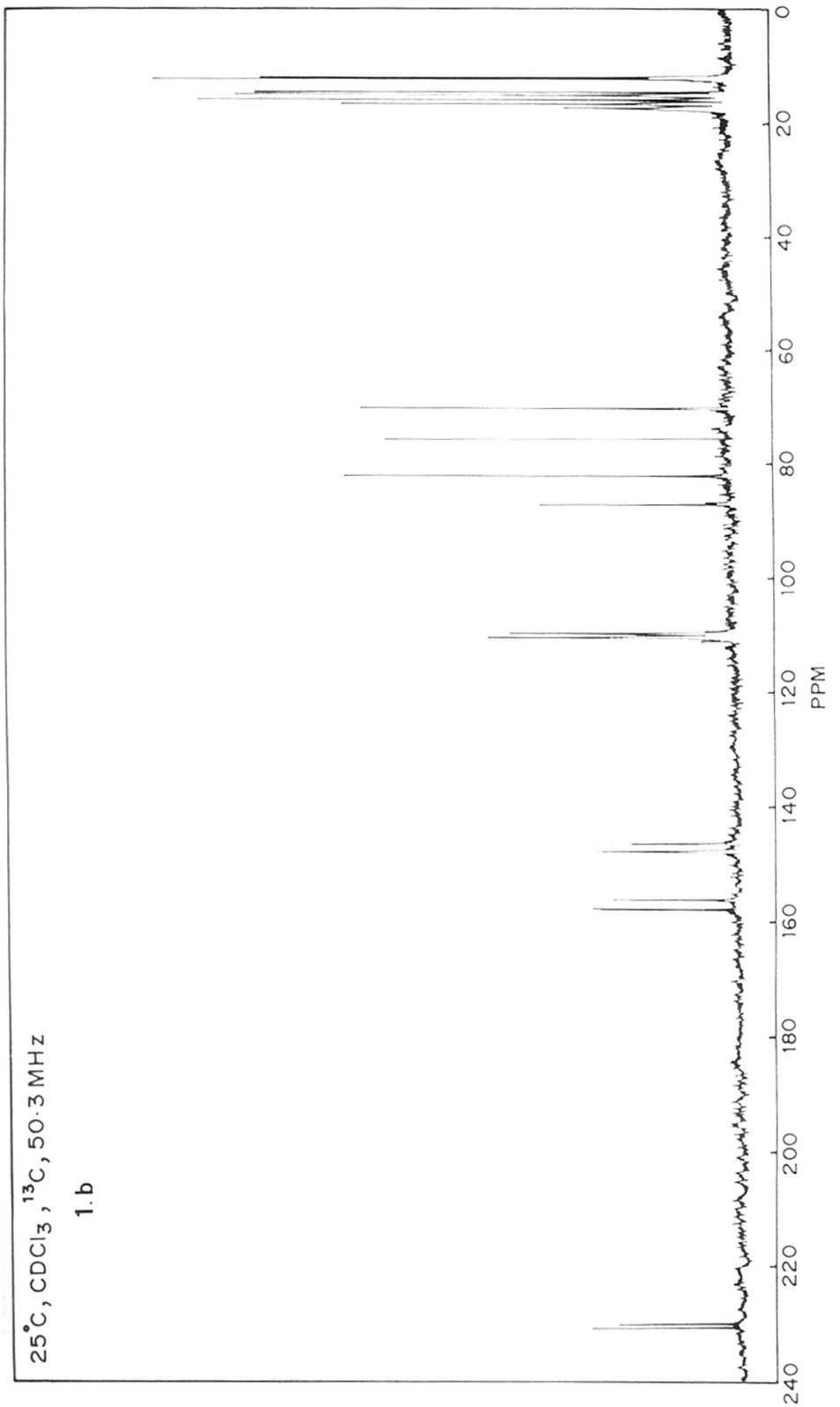
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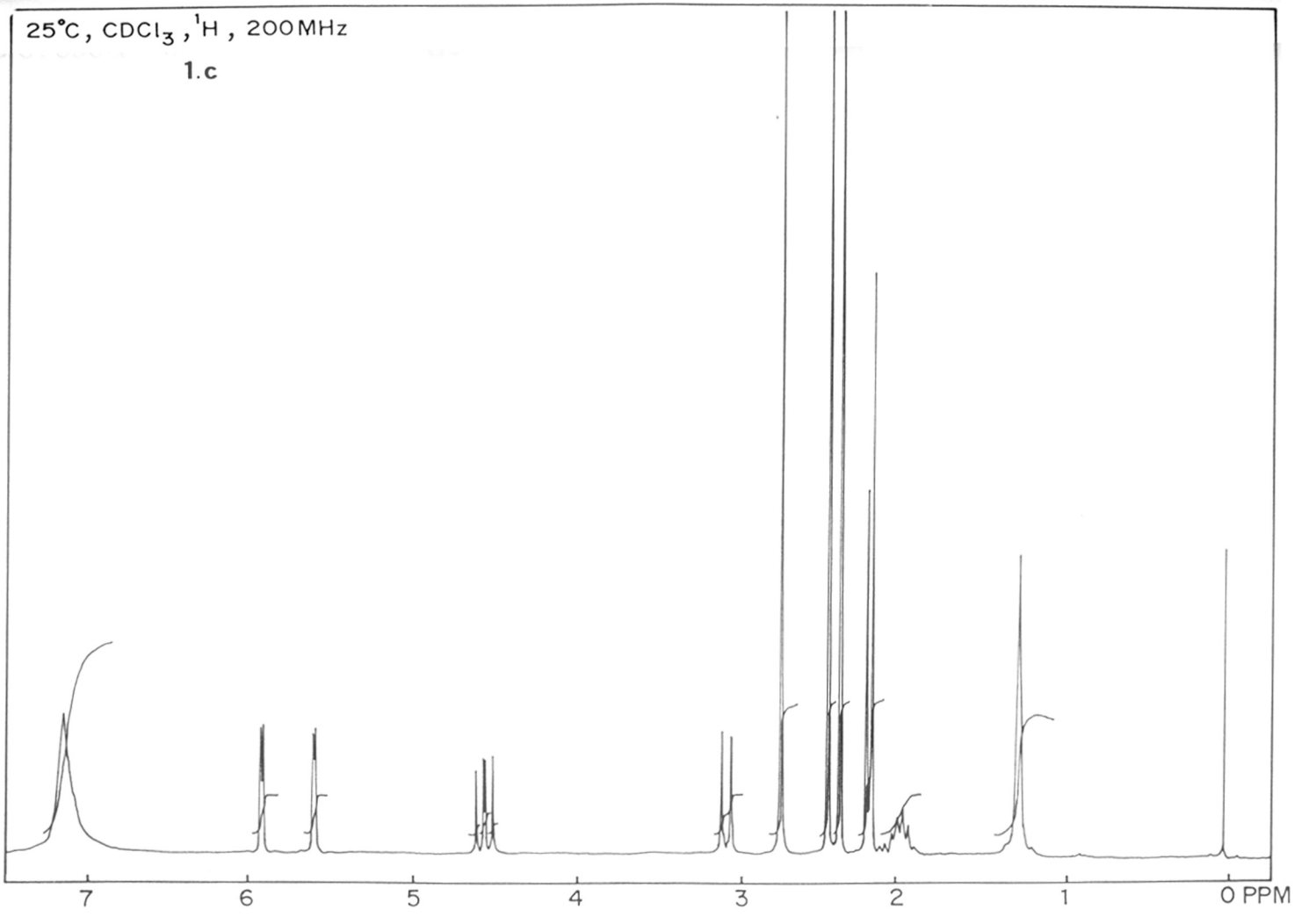
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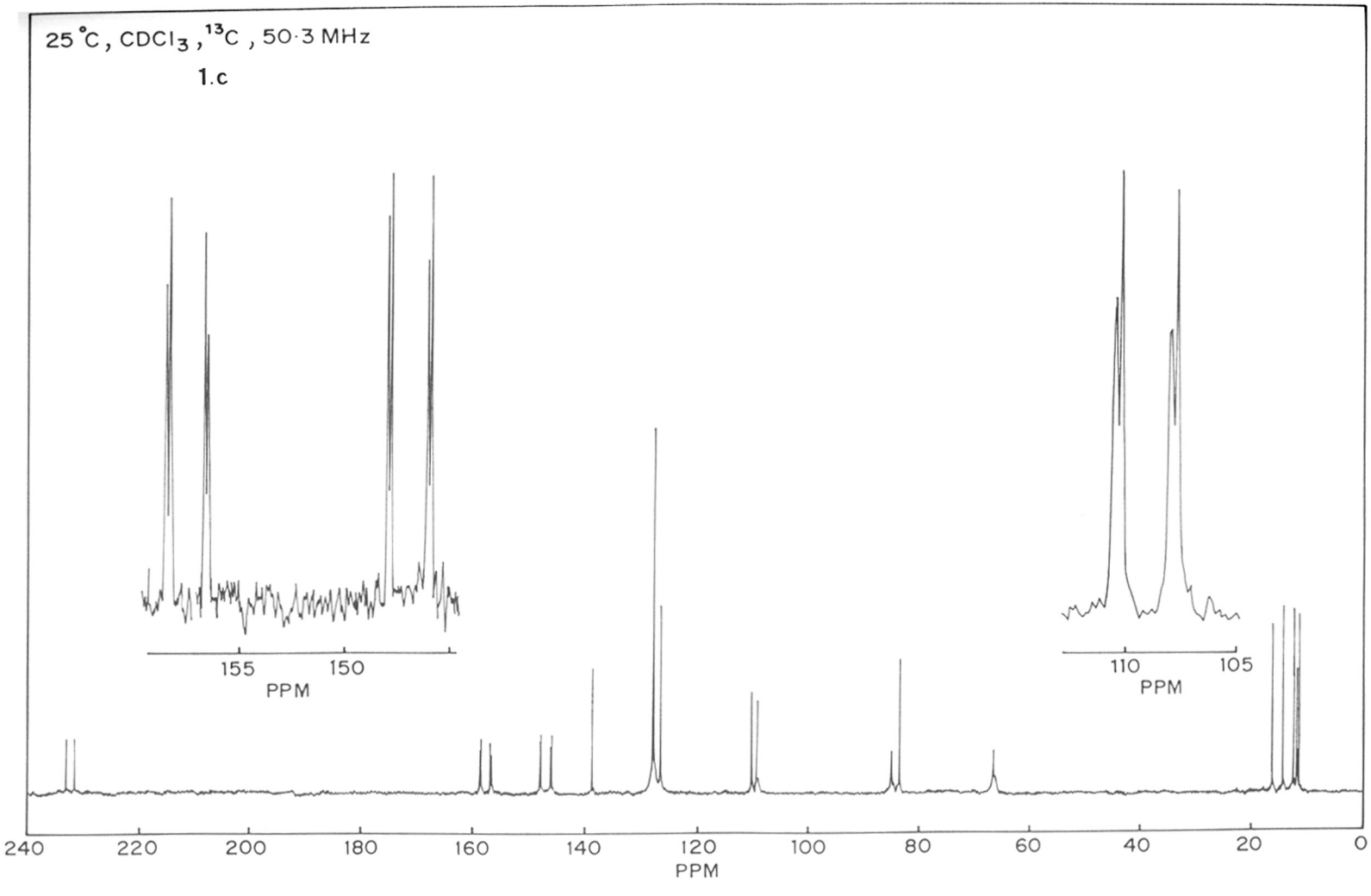
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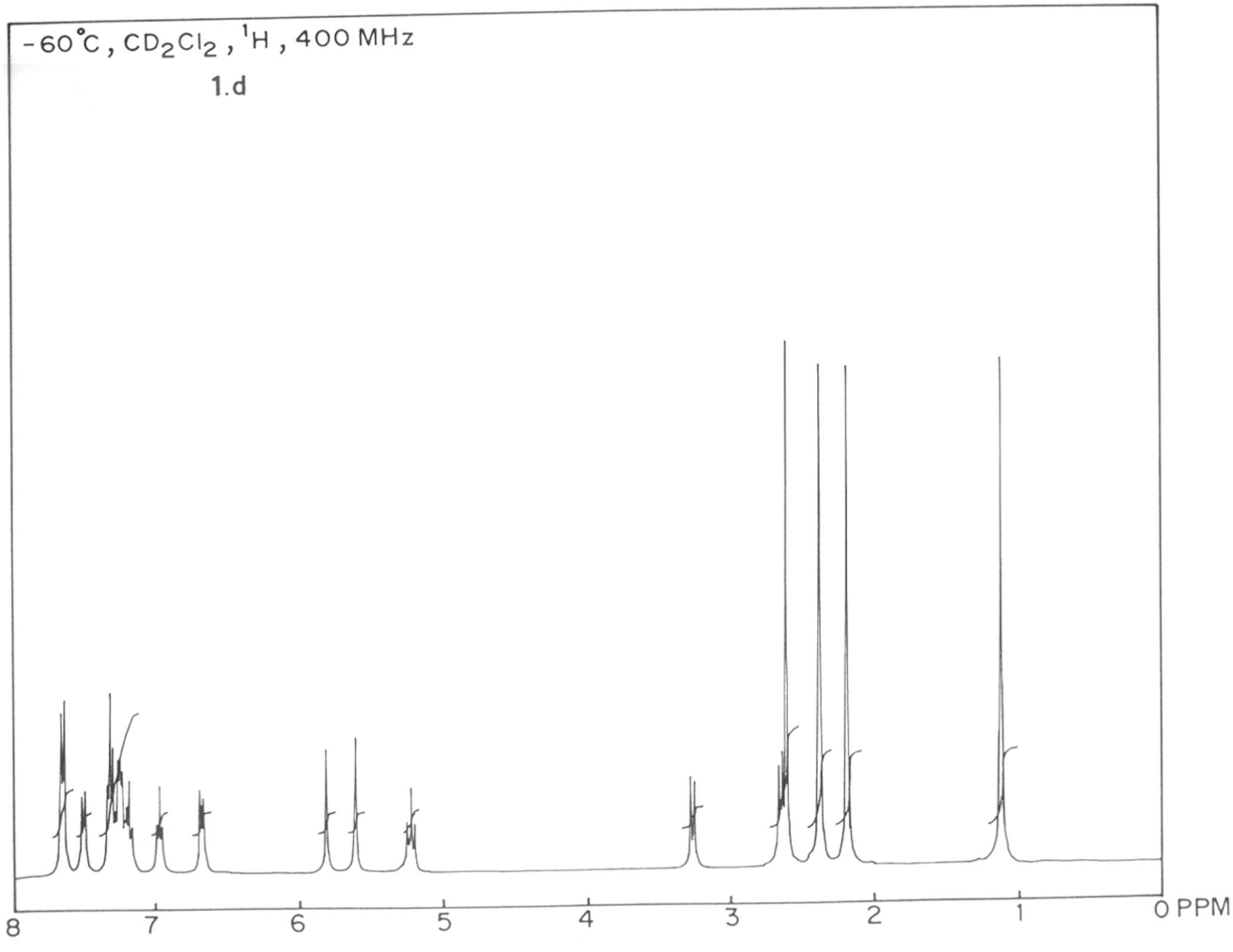
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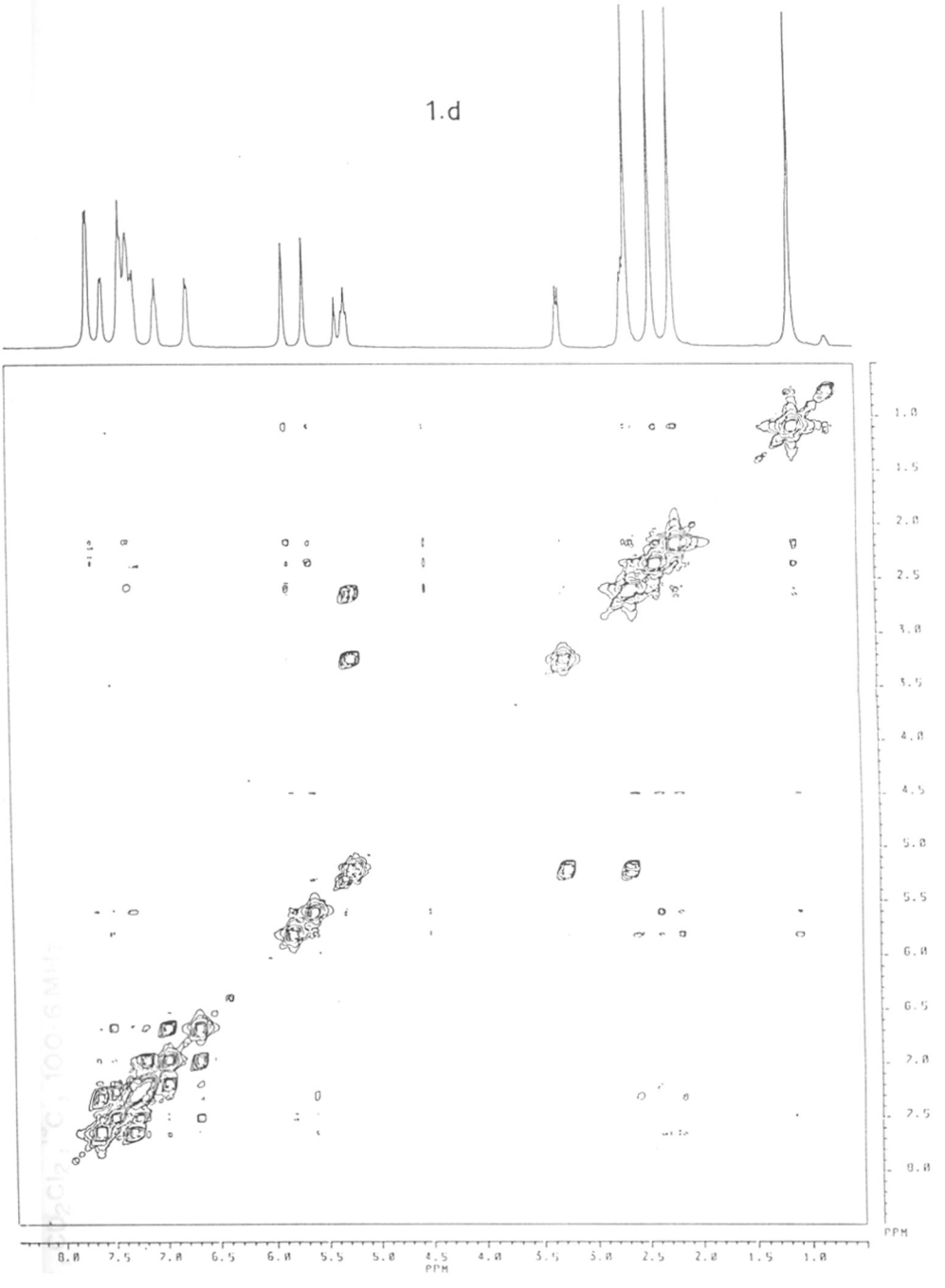
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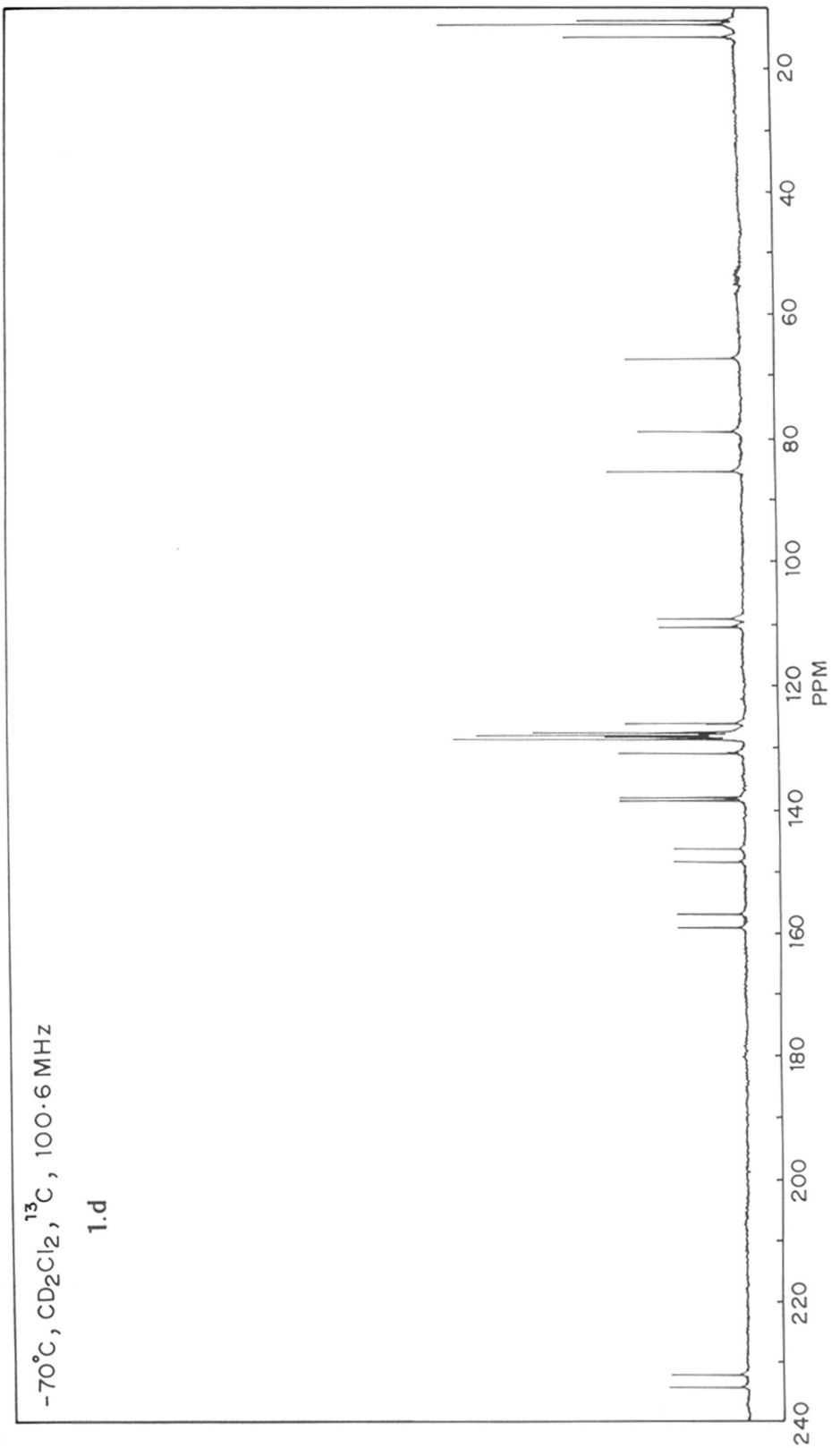
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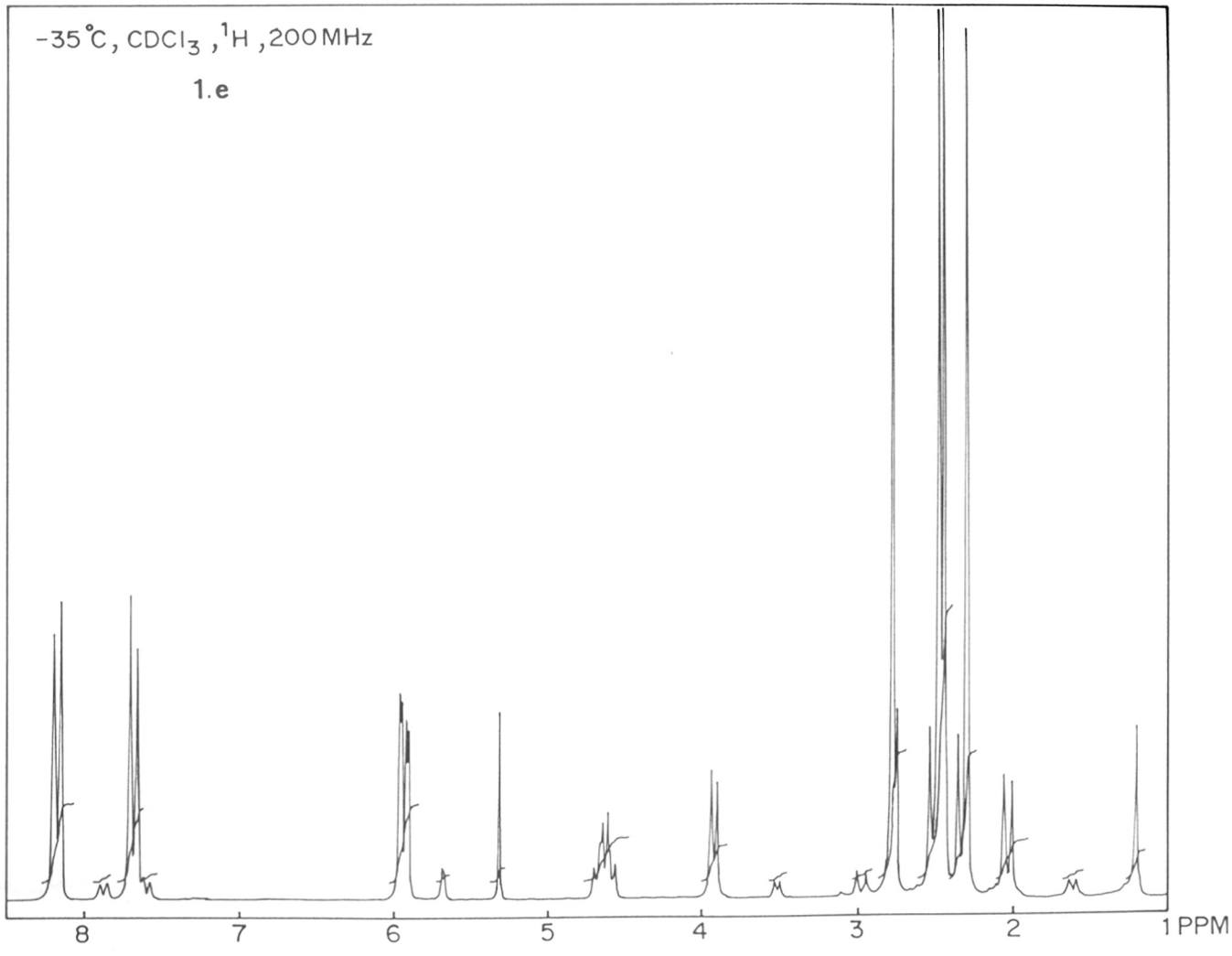
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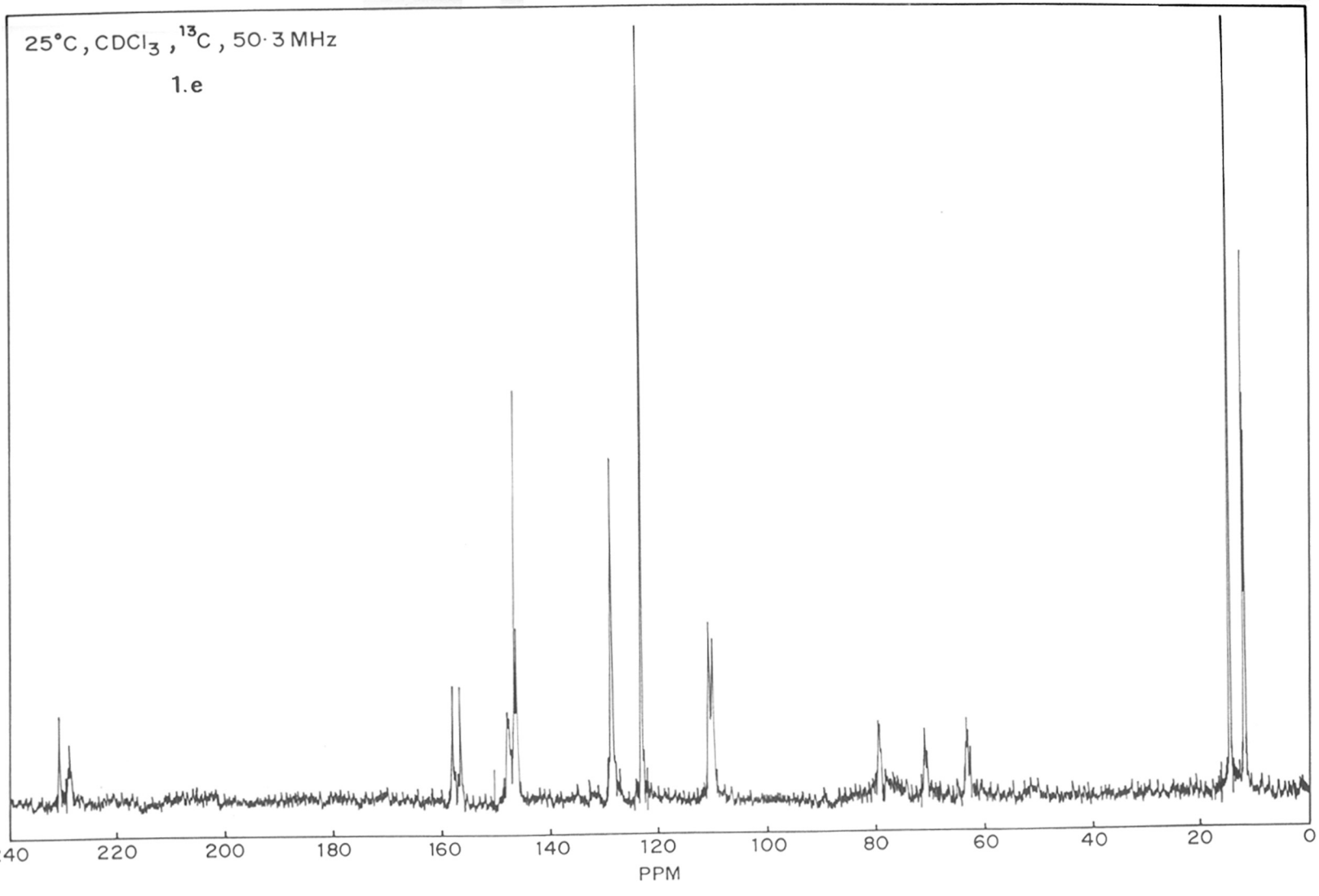
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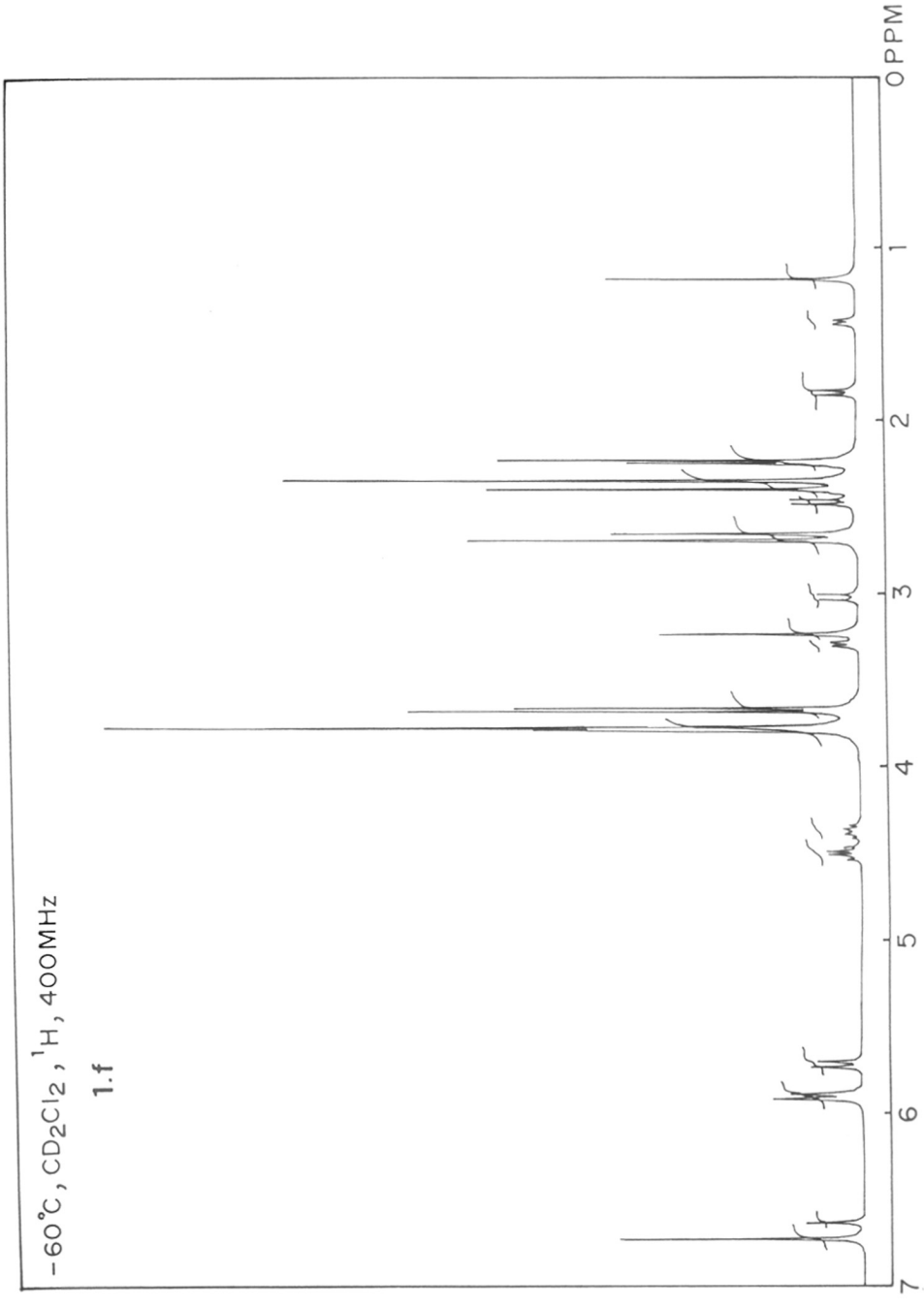
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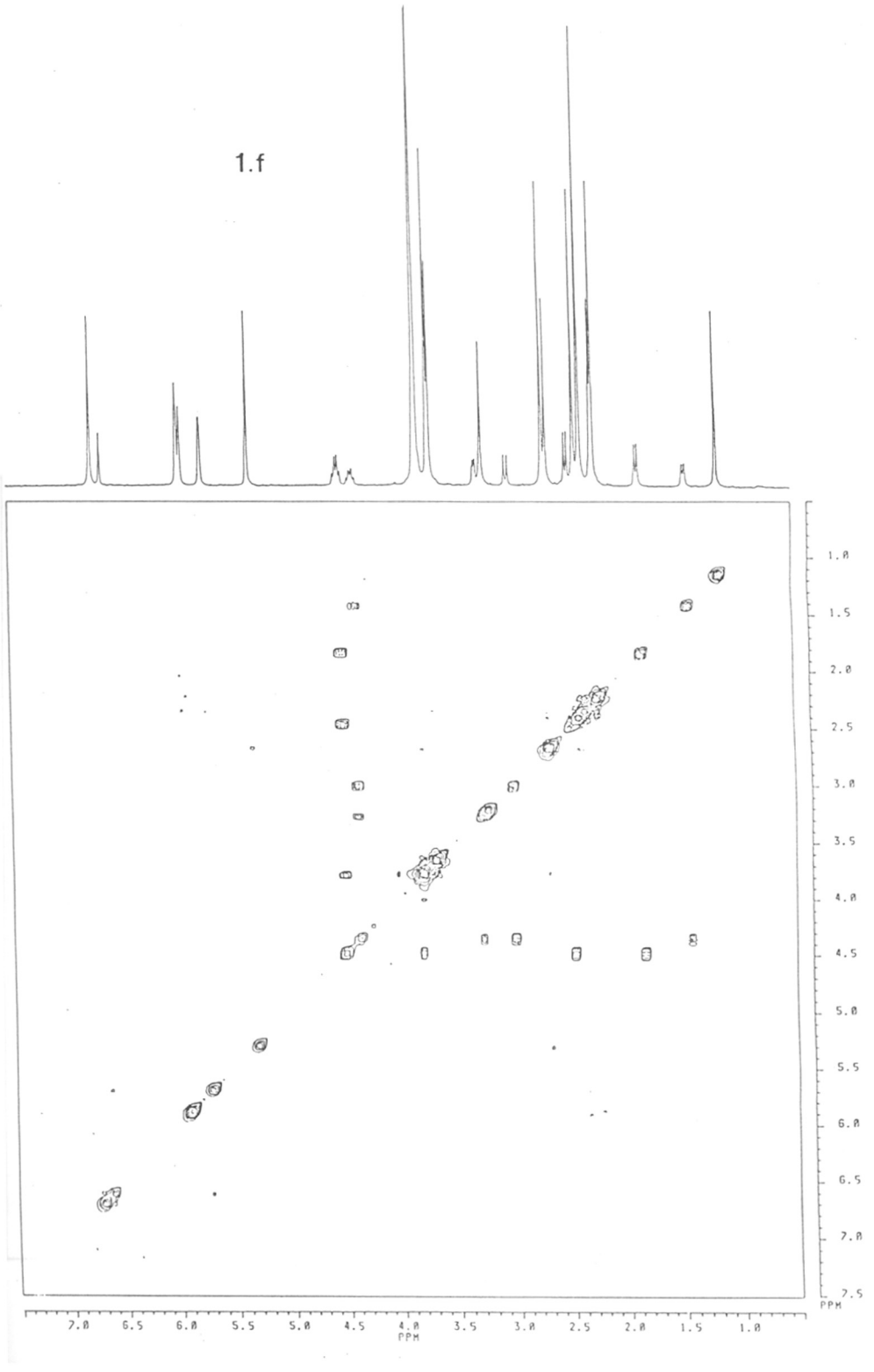
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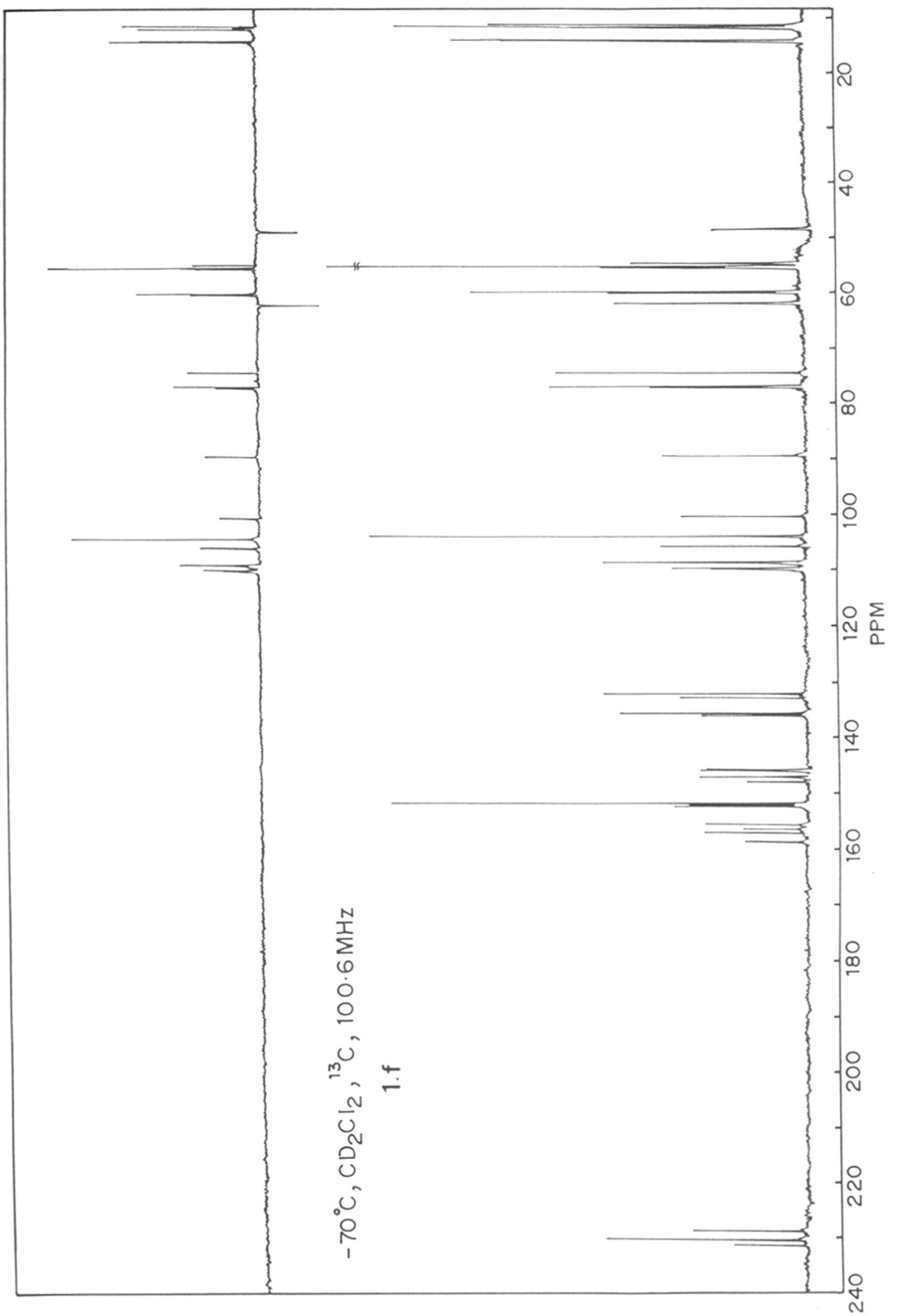
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Chapter-II

Terminally Substituted π-Allyl Complexes of Molybdenum with Dihydro-*bis*(3,5-dimethyl-1-pyrazolyl)borate Ligand.

Part of this work has been accepted for publication in *Organometallics*, **1997** (in press).

II. 1 BACKGROUND

The $(pz')_2PO_2$- ligand described in the previous chapter is a uninegative six-electron donor ligand. In octahedral molybdenum π-allyl complexes, the preferred orientation of the ligand is the placement of a pyrazole and an oxygen atom *trans* to the CO ligands while the second pyrazole is placed *trans* to the π-allyl group.[1] This renders the environment of the two allyl termini non-equivalent. In a sense, the dihydro-*bis*pyrazolylborate ligand compares well with this ligand system.[2] This is also a uninegative ligand where one pyrazole is *trans* to a CO group and the other is placed *trans* to the π-allyl moiety. In place of an oxygen as in the preceding ligand, a three-center-two-electron B-H-Mo bridge completes the tridentate description for this ligand. While crystal structures of a few representative complexes were solved earlier[3], no systematic study was available with terminally substituted allyl groups. In addition, it was of interest to explore whether a double bond attached to a terminus of the allyl group (and in conjugation with it) would slip from a η^3 to η^5 mode at the expense of the weak B-H-Mo bond. The complexes described in this chapter were prepared and scrutinized structurally from this point of view.

II. 2 PRESENT WORK

The complexes were prepared essentially following the two types of procedures described in the previous chapter (for details, see experimental section).

The complexes **2a-d** featuring terminally substituted allyl groups (*Fig.-1*) displayed sharp lines in the NMR spectra and indicated the presence of one conformer in each case.

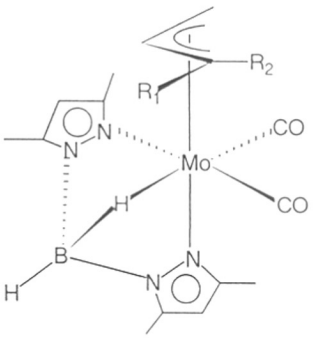


Fig.-1. Structure of complex **2a-d**

Complex No.	R_1	R_2	yield (%)
2a	C_6H_5	H	53
2b	CH_3	H	37
2c	CH_3	CH_3	30
2d	C_6H_5-CO	H	24

The *syn* allyl substituent was placed on the sterically less congested site near the B-H-Mo bridge. This assignment gains credibility from the NOE difference spectrum of complex **2b**, which shows a 0.5% NOE between a pyrazole methyl group and the *syn* proton of the allyl group. The proton NMR spectra for all the complexes were readily interpreted in terms of the assigned structures. Typically, the B-H proton appears at -0.8 to -2.3 ppm in all these complexes. Infrared stretch for the terminal B-H group was observed around 2465-2483 cm^{-1} and B-H of B-H-Mo was observed arround 2011-2029 cm^{-1} while the C=N absorption was observed at 1530-1545 cm^{-1}. The ^{13}C NMR spectra also displayed peaks for one set of conformers for all complexes.

The complex **2e** bearing two different substituents (phenyl and methyl) at the termini of the allyl group (*Fig.-2*), displayed broad signals in the proton NMR spectrum at ambient temperature. The spectrum became well-resolved as the temperature was lowered to -70 °C to reveal the presence of only one conformer. The reason for the line broadening may be due to a "*trigonal twist*" involving the unsymmetrical ligand system (same observation was true for complex **2h**).

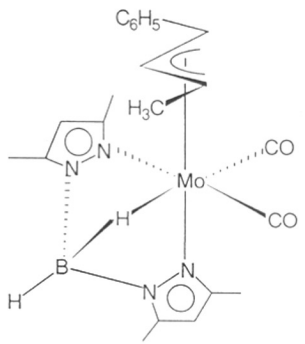


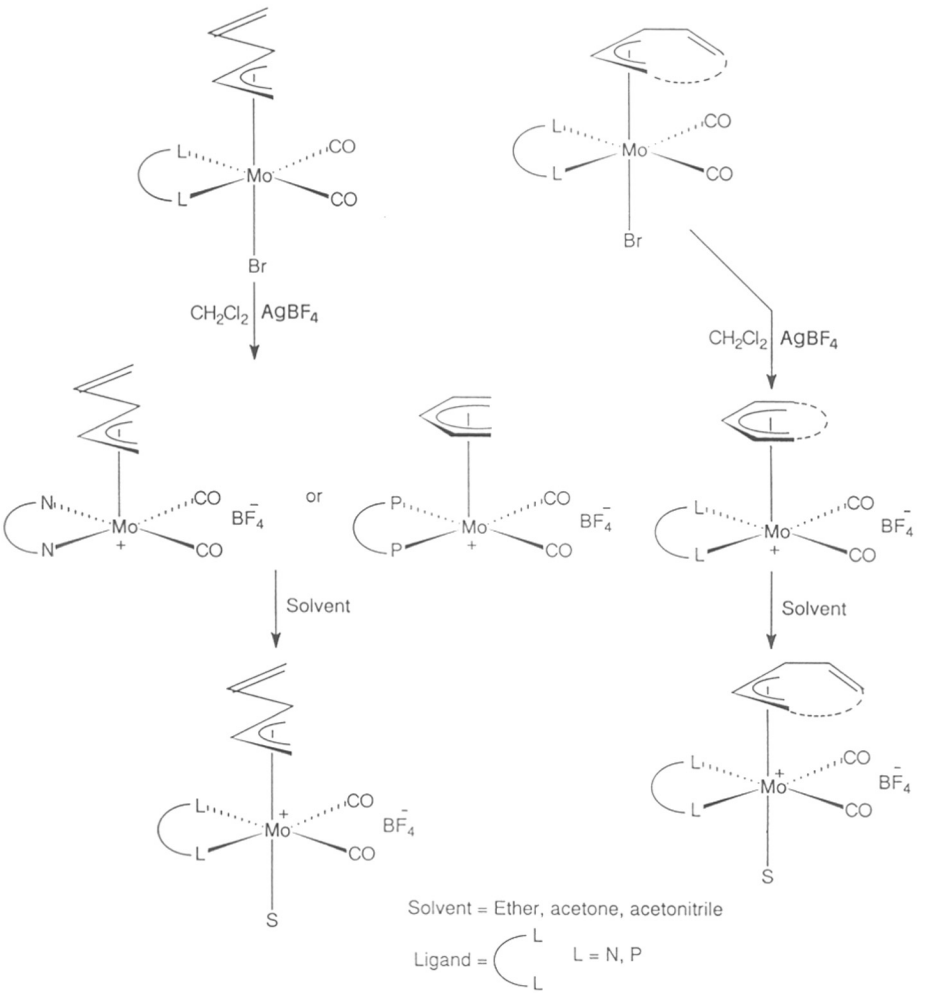
Fig.-2. Structure of complex **2e**

The proton NMR spectrum was consistent with the structure. Two *anti* allyl protons appeared at 1.85 ppm (m) and 2.91 ppm (d, $J_{benzylic\ anti/central}$ = 10.9 Hz). The central allyl proton appeared at 4.61 ppm (dd, J = 8.9, 10.5 Hz). The upfield shift of one pyrazole 3-methyl at 0.88 ppm, indicated that the phenyl ring was in close proximity of one pyrazole unit and thus established the conformation of the complex **2e**.

Two types of pentadienyl complexes were investigated for attempted slippage from η^3 to η^5 coordination : one cyclic - cyclooctadienyl, and another acyclic - derived from 1-chloro-5-phenyl-2,4-pentadiene or 1-bromo-2,4-hexadiene.

Numerous examples are known[4] for the slippage of a pentadienyl ligand from η^1 to η^3 to η^5 coordination mode. In molybdenum(II) complexes, a pattern already exists.[5] In the absence of a donor ligand, a cationic, *16e*, η^3-pentadienyl complex slips readily to η^5-pentadienyl structure; a donor solvent can reverse this slippage back to the η^3-mode[6], indicating a delicate energy balance in such a process (*Scheme-1*).

Scheme-1



In a neutral, formally *16e* complex like dihydro*bis*(3,5-dimethylpyrazolyl)borato-η^3-cycloheptatrienyl-dicarbonyl-molybdenum(II), slippage to η^5-coordination appeared to be precluded by a B-H-Mo bonding interaction.[3,7] The complexes we examined did not differ in this essential observation.

Reaction of 1-bromo-2,4-hexadiene with $(CH_3CN)_3Mo(CO)_3$ in acetonitrile followed by ligand exchange in dichloromethane afforded the complex **2f** in 45 % yield.[8] The proton NMR spectrum at room temperature displayed sharp signals indicating the presence of one conformer or stereoisomer. The structure of this complex (*Fig.-4*) was deduced by comparison with preceding examples.

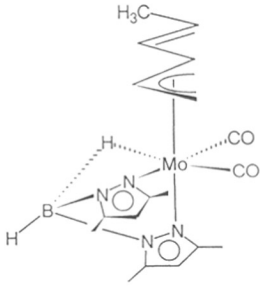
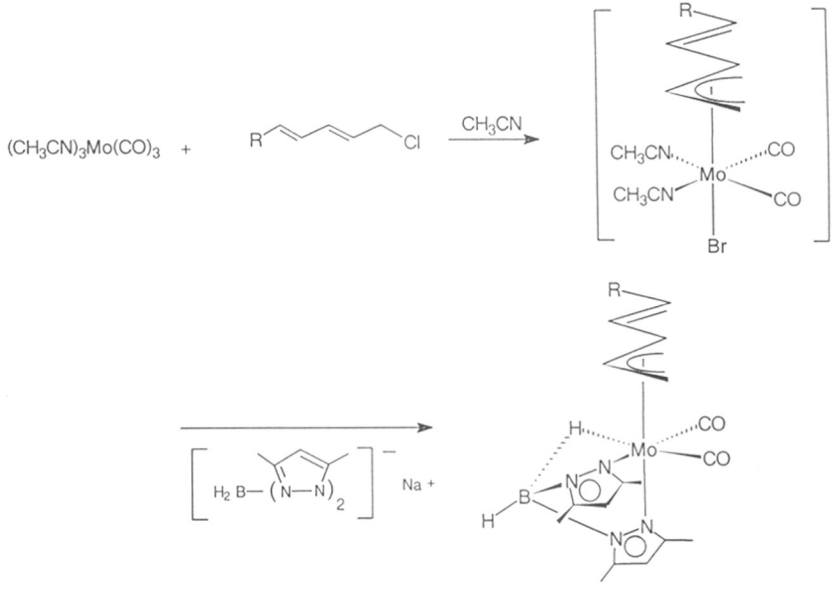


Fig.-4. Structure of complex **2f**

The observation of olefinic protons at 5.87 ppm as a multiplet and π-allyl protons at usual positions (two *anti* allyl protons at 1.64 and 2.39 ppm as doublets, J = 10.2 and 9.7 Hz respectively; the *syn* proton at 3.65 ppm as a doublet, J = 6.9 Hz; the central proton at 4.09 as a multiplet) confirmed the η^3-coordination mode of the pentadienyl ligand.

A closely related complex **2g** was prepared from the appropriate halide following a similar procedure (*Scheme-2*).

Scheme-2



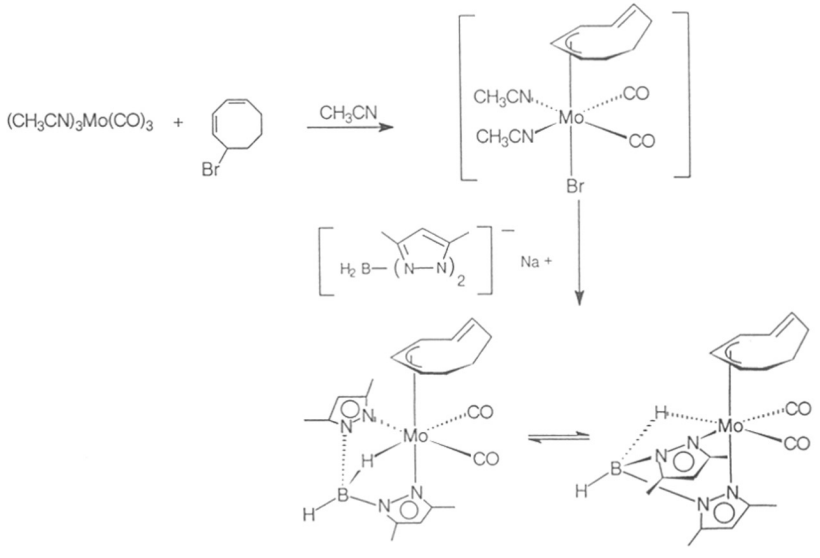
Complex No	**R**
2f	CH_3
2g	C_6H_5

In the structure of the product, the cinnamyl side-chain has been placed on the less sterically congested site since only one conformer was observed. The complex was characterized by NMR spectroscopy (^{1}H, ^{13}C and COSY). The η^3-dienyl ligand was identified from the styryl proton signals (6.55 and 6.77 ppm, J = 15.5 Hz) and the allyl proton positions (two *anti* allyl protons at 1.81 and 2.58 ppm as doublet and triplet, J = 11.2 and 9.8 Hz respectively; the *syn* proton at 3.77 ppm as a doublet, J = 7.3 Hz; the central proton at 4.32 as a multiplet) as in the case of complex **2f**.

Initially it was thought that the η^3-dienyl coordination resulted from kinetic control, i.e. it was formed during the formation of these complexes and slippage to η^5-dienyl product could have a high barrier of conversion. But no change was observed even after heating a toluene solution of either of these complexes under reflux for 4 h. The complexes slowly undergo decomposition under reflux for longer period.

Complex **2h** was synthesized from 1-bromo-cycloocta-2,4-diene[9], $Mo(CO)_6$ and sodium dihydro*bis*(3,5-dimethyl-1-pyrazolyl)borate (*Scheme-3*), and purified by column chromatography. It was obtained as an air-stable, red, crystalline solid (66%) with good solubility in common organic solvents.

Scheme-3



The proton NMR spectral lines that were broad at room temperature, became well-resolved as the temperature was lowered (-30 °C) to reveal the presence of two conformers equally populated. Assignment of the pentadienyl protons in each conformer was made by the use of 2D spectrum. It was clear that an η^3-allyl, rather than η^5-pentadienyl coordination, was present. Coupling correlations allowed us to assign, for instance, the multiplets at 4.10 and 4.20 ppm to be associated with the central π-allyl proton of the two conformers. In one conformer, the two *syn* protons appeared at 4.45 and 4.57 ppm as a multiplet and a broad doublet respectively. These protons in the other conformer appeared at 4.10 and 4.75 ppm with similar multiplicity. The olefinic protons appeared together at 5.30 ppm (both conformers) as a multiplet and at 6.35 and 6.55 ppm as two peaks (doublet of doublet, J = 10.2, 2.4 Hz, same for each case). The proton that bridges boron and molybdenum appeared as a broad signal at -1.65 ppm. Two sets of CO signals were observed (227.2, 229.4, 233.9 and 235.9 ppm) in the ^{13}C NMR spectrum of this complex, consistent with the presence of two conformers. No change in the spectra was observed after the complex was heated under reflux in toluene or methanol for 3 h. Although precedence suggests that acyclic pentadienyl system is more prone to slippage to η^5-coordination, the B-H-Mo bridge did not allow such slippage to take place even in the molecule. This outcome, however, is not totally unexpected.[3b,c]

Two possible intramolecular processes can account for the dynamic behavior of these complexes. A *trigonal twist*[10], well-established for this ligand system[11], can probably explain the dynamic NMR spectra for both these complexes. Alternatively, in the complex **2h** (also for the complex **2e**), a boat-boat interconversion involving the 6-membered ring containing molybdenum and two pyrazoles may be significant.[12,7]

The X-ray crystal structure of the complex **2h** confirmed the η^3-dienyl assignment (*Fig.-5*). Only one conformer was observed in the crystalline state. The structure is best described as a distorted octahedron.

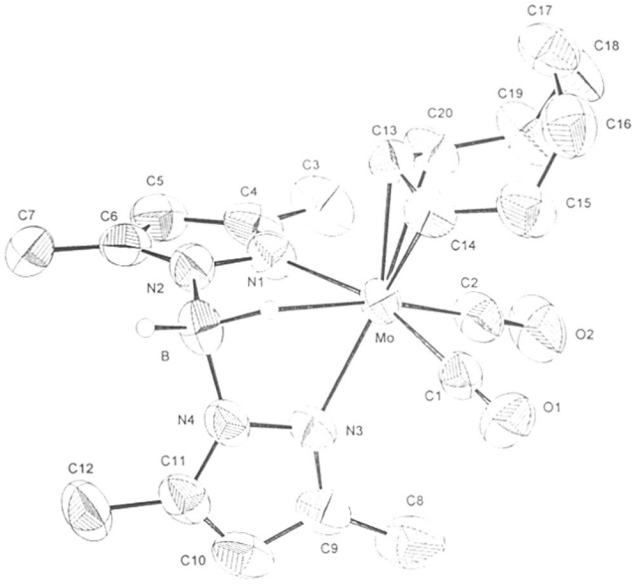


Fig.-5. ORTEP view of the molecular structure of **2h**

The bond between molybdenum and the pyrazole nitrogen *trans* to the allyl moiety is shorter (2.17 Å) than the other Mo-N bond (2.22 Å). Location of the hydrogen involved in the B-H-Mo bond was ascertained by difference Fourier method. The B-H distance of the bridging hydrogen is longer (1.15 Å) than the non-bridging B-H bond (1.11 Å). The Mo-H bond length was 1.95 Å, typical of a bridging hydride rather than a metal hydride.[13] The central carbon of the allyl system is nearest to molybdenum (2.22 Å, as compared to *Mo-C14* 2.35 Å and *Mo-C20* 2.42 Å). While the sp^2 character of the allyl carbons is reflected in the bond angle (*C14-C13-C20* 122.5°), deviation from planarity of the π-allyl group was evident from the relevant dihedral angles (*C15-C14-C13-C20* 44.8°; *C14-C13-C20-C19* -43.4°). The *C18-C19* bond was assigned to be the olefinic bond (1.39 Å); considerable puckering was evident around this bond too (*C17-C18-C19-C20* 36.6°). Such deviations probably are intrinsic to the cyclooctane ring.

Treatment of the complex **2h** with an excess of benzaldehyde (toluene, 90 °C, 3 h) produced a new complex **2i**. The proton NMR spectrum revealed that only one benzyl group was present, and the molecule existed in two distinct conformations in solution (^{13}C NMR peaks for CO at 228.5, 231.0, 231.7 and

232.8 ppm are consistent with this). The proton NMR peaks due to the conformers present in unequal amounts (1.6 : 1) could be assigned with the help of the COSY spectrum. The B-H proton signal was absent in the usual region of -0.9 to -2.6 ppm, which suggested possible absence of a B-H-Mo bond.[14] The pentadienyl proton signals were similar in overall pattern to that described above (except minor variations), so as to conclude that there was no slippage to the η^5 coordination mode. This was clear from the crystal structure (*Fig.-6*). The complex **2i** did not react with benzaldehyde any further.

The ORTEP diagram shows one out of a pair of enantiomeric molecules present in one asymmetric unit. The molybdenum center is coordinated to two pyrazole donors and the oxygen atom of the new benzyloxy group (*Mo-O3* 2.29 Å and 2.30 Å). In molybdenum chemistry, this is a new structural type with a B-O-Mo bridge.[15] This mode of ligation did not appreciably change the conformation of the six-membered pyrazole-chelate. Even the conformation of the eight-membered ring was not significantly different. The free double bond of the η^3-dienyl group was on the same side as the pyrazole, as in the structure of complex **2h**.

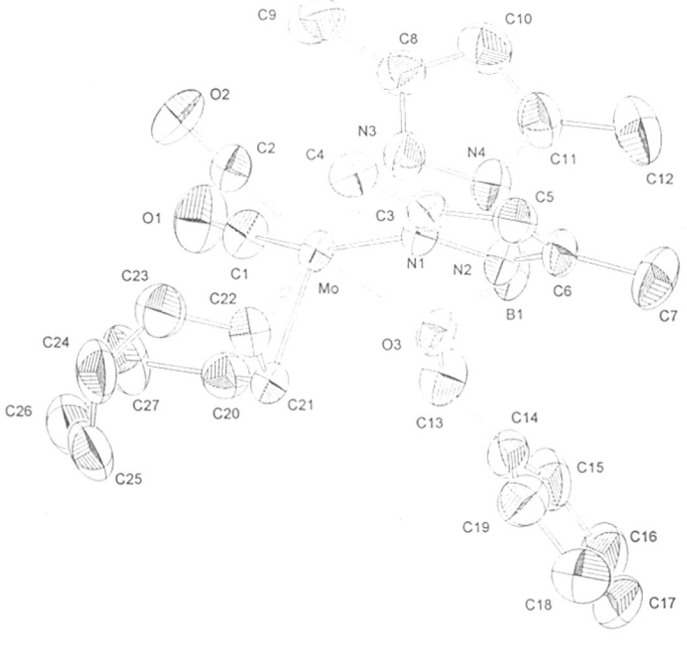
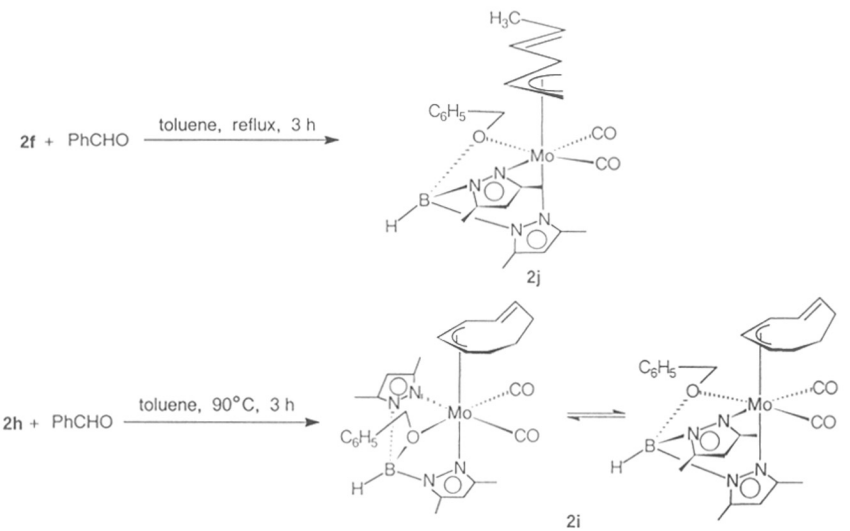


Fig.-6. ORTEP view of the molecular structure of **2i**

Similarity of NMR spectral pattern of the minor conformer prompted the assigned structure (*Scheme-4*).

Scheme-4

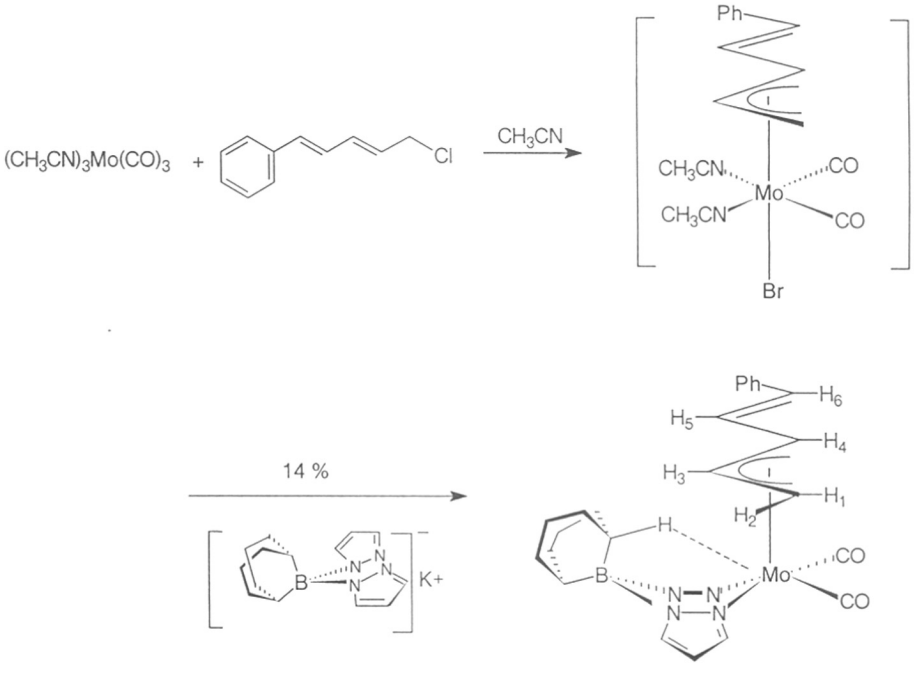


Heating complex **2f** with excess benzaldehyde resulted in a similar reaction yielding a structurally similar complex **2j** in 58 % yield as an analytically pure solid. However, the proton NMR spectrum revealed the presence of two different species in a ratio of 3.5:1. While the signals due to the major component was consistent with the structure proposed, the structure of the minor component could not be categorically assigned. The most likely structure, of course, would be the one in which the vinylic substituent occupies *anti* position with respect to the central allyl proton. Appearance of a complex multiplet for the corresponding *syn* proton precluded the determination of coupling constant for the coupling with the central proton. However, the positions of vinyl proton signals were comparable with those of a similar complex described in *Chapter - III* (complex **3e**). The major isomer[16] showed two doublets at 1.65 ($J_{anti/central}$ = 10.0 Hz) ppm and 2.42 ($J_{anti/central}$ = 12.5 Hz) ppm for two *anti* allyl protons. The *syn* allyl proton appeared at 3.79 ppm (d, $J_{syn/central}$ = 6.8 Hz) and the central allyl proton appeared as a multiplet at 4.02 ppm. Two olefinic protons appeared as a multiplet at 5.90 ppm and the methyl group attached to the olefin appeared at 1.32 ppm (d, J = 5.1 Hz).

Two benzylic protons appeared as a AB quartet at 4.23 and 4.76 ppm with identical coupling constants 15.2 Hz.

The interesting ligand derived from 9-BBN and developed by Trofimenko[17] was used to find whether a C-H-Mo interaction is strong enough to compete with a η^5-dienyl coordination mode in these complexes. The complex **2k** was prepared by the usual method (*Scheme-5*).

Scheme.-5



In the proton NMR spectrum, no significant change was observed in the temperature range of -50 °C to +50 °C, except that minimal line broadening was observed at low temperature and the peaks were slightly sharper at +50 °C. Therefore, coupling constants were determined from decoupling experiments at +50 °C, while connectivity relationship was deduced from the 2D spectrum recorded at 25 °C. A doublet of a triplet at 4.30 ppm (J = 10.0, 6.9 Hz) was assigned to the central π-allyl proton (H_3). The coupling of H_3 with H_4 was 10.1

Hz which established their *anti* relationship. The *syn* methylene proton (H_2) at 3.81 ppm appeared as a doublet (J = 6.8 Hz), coupled with H_3. The *anti* protons H_1 and H_4 appeared at 1.80 (merged with methylene protons), 2.74 as a triplet (J = 10.1 Hz, due to the same coupling with H_3 and H_5) respectively. The protons of the *trans* double bond appeared at 6.55 (H_5) as a doublet of doublet (J = 10.5, 15.6 Hz) and at 6.87 (H_6) as a doublet (J = 15.6 Hz). While typical signals indicated an η^3-dienyl coordination rather than an η^5 mode, a C-H-Mo agostic interaction was clearly evident from the one proton signal at -5.10 ppm.

Carbon-hydrogen bonds, especially those of saturated sp^3 carbon centers, are normally considered to be chemically inert. There is enough evidence which shows that C-H bonds can act as ligands to transition metal centers by formation of 3-center-2-electron bonds (3c-2e) and that the extent of the interaction is such as to have a marked effect on the molecular and electronic structure and hence the reactivity of the molecule. The term 'agostic' was first used by Brookhart and Green[18], to describe the covalent interactions between C-H group and transition metal centers in organometallic compounds, in which the hydrogen atom is covalently bonded simultaneously to both carbon atom (or with B, N, Si, Cl and F) and to a transition metal.[19]

The ^{13}C NMR spectrum recorded at 100.6 MHz (24 °C), however, showed considerable line broadening for certain carbons as a result of stereochemical non-rigidity. For instance, signals due to two allyl carbons were not observed at all, and two methylene signals at 20.4 and 35.7 ppm were barely visible above the base line.

II. 3 Summary

The results seem to indicate that weak interaction like B-H-Mo or C-H-Mo can effectively prevent η^3 to η^5 slippage in neutral Mo(II)-π-allyl complexes. This, in turn, might suggest that a η^5- dienyl coordination on Mo(II) metal-center does not have a significant stability advantage over the η^3-mode.

II. 4 EXPERIMENTAL

N-bromosuccinimide, acetylacetone, triphenylphosphine, magnesium turning, bromobenzene, potassium permanganate, N,N-dimethyl acetamide, aluminium chloride, PCl_3 and 48% aqueous HBr were purchased from SD Fine Chemicals. Sodium borohydride and iodine were purchased from Loba Chemie. Crotonaldehyde, cerium chloride heptahydrate, cinnamaldehyde, cinnamyl chloride, crotyl bromide, prenyl alcohol, PBr_3, ethyl bromoacetate, 1,3-cyclooctadiene, pyrazole, lithium aluminium hydride and 9-borabicyclo-(3.3.1) nonane were purchased from Aldrich.

2. Preparation of sodium dihydro *bis*(3, 5-dimethyl pyrazolyl)borate.

The compound was prepared from 3, 5-dimethyl pyrazole (prepared from acetylacetone and hydrazine hydrate) and sodium borohydride in 80% yield. A modified procedure was used in the present case.[2]

A mixture of sodium borohydride (1.9 g, 50 mmol) and 3, 5-dimethylpyrazole (10.56 g, 110 mmol) was refluxed in N,N-dimethyl acetamide (50 mL) for 12 h (until hydrogen evolution stopped). The mixture was concentrated under reduced pressure to a thick slurry. This slurry was mixed with Et_2O (25 mL) and filtered. The resulting solid was further purified by washing twice with Et_2O (12.5 mL) and recrystallized from toluene to afford the analytically pure title compound (12.79 g. 80%). Melting point and spectral data were comparable with the reported values.

2 (I). Preparation of potassium cyclooctane-1,5-diyl*bis*(pyrazol-1-yl)borate.

The compound has been prepared from pyrazole, potassium hydroxide and 9-borabicyclo-(3.3.1) nonane in 93% yield. A modified procedure was used in the present case.[17]

A mixture of pyrazole (0.816 g, 12 mmol), 12.5 mL of dry toluene and powdered potassium hydroxide (0.28 g, 5 mmol) was stirred and refluxed for 18 h at a bath temperature of 140 °C in a Dean-Stark trap to remove all water. The suspension containing a white precipitate was allowed to cool to 60 °C, and a distillation assembly was mounted in place of Dean-Stark trap. The 9-borabicyclo-

(3.3.1) nonane (10 mL of a 0.5 M solution in dry and degassed THF) was then added dropwise through a syringe at such a rate that THF distilled out while the H_2 gas evolution continued. The reaction mixture was maintained at this condition for 1.5 h. Then slowly the temperature was increased to 140 °C to remove toluene (8 mL). The reaction mixture was cooled and diluted with 20 mL hexane. The resulting precipitate was removed by filtration, the residue washed three times with hot hexane and then dried *in vacuo*. Recrystallization from THF-hexane afforded a pure solid (1.17 g, 75%). m.p. >240 °C (lit. m.p. >240 °C).

2. a. 1. Preparation of 4-bromo-2-methyl-2-butene.

The title compound was prepared by a procedure identical to that reported earlier as in section **1.a.1**.

2. b. 1. Preparation of 1-phenyl-2-butene-1-ol.

Magnesium (0.583 g, 24 mmol) was taken in 25 ml Et_2O with a pinch of iodine. Bromobenzene (2.1 mL, 20 mmol) was added dropwise into this stirred mixture and the mixture warmed to 40 °C. The reaction was initiated with the disappearance of the color of iodine. The mixture was refluxed for a further 2h. A solution of crotonaldehyde (1.65 mL, 20 mmol) in Et_2O (5 mL) was then added to this reaction mixture dropwise and the latter stirred at room temperature for a further 1h. The reaction was quenched using saturated NH_4Cl (10 mL) and extracted with Et_2O (3 X 10 mL). After drying over anhydrous Na_2SO_4 the solvent was removed under reduced pressure and fraction distillation afforded the pure title compound (2.1 g, 71%) 130 °C/20 mmHg (lit. 125-126 °C/15 mmHg).[20]

2. b. 2. Preparation of 1-Phenyl-2-butene-1-one.

1-Phenyl-2-butene-1-ol (2.1 g, 14.18 mmol) was taken in CH_2Cl_2 (40 mL). Freshly prepared manganese dioxide (12.34 g, 141.89 mmol) was added into this and the mixture was stirred for 6h. The mixture was filtered through a Celite pad and washed with CH_2Cl_2. Removal of solvent and purification by column

chromatography (10% EtOAc-pet.ether) resulted in a colorless liquid (1.24 g, 60%).[21]

^{1}H NMR : 1.97 (d, 3H, J = 5.5 Hz), 6.9-7.3 (m, 2H), 7.3-8.0 (m, 3H).
(90 MHz)

2. b. 3. Preparation of 4-bromo-1-Phenyl-2-butene-1-one.

1-Phenyl-2-butene-1-one (0.690 g, 4.72 mmol) was taken in CCl_4 (10 mL, freshly distilled over phosphorus pentoxide). N-bromosuccinimide (0.13 g, 5.13 mmol) and a pinch of benzoyl peroxide (freshly crystallized from $CHCl_3$-pet.ether) were added to the reaction mixture and it was refluxed for 2 h. On cooling to room temperature, the free succinimide was filtered off and the filtrate washed with portions of $Na_2S_2O_3$, brine and dried over anhydrous Na_2SO_4. The CCl_4 solution was concentrated under reduced pressure. The viscous liquid thus obtained was diluted with pet.ether and refrigerated overnight to crystallize out the remaining succinimide. After filtering off the succinimide, the filtrate was concentrated to afford the title compound as a colorless liquid (0.47 g, 45%). This bromide was used for complexation without further purification.

2. c. 1. Preparation of 3-chloro-1-phenylbutene.

The title compound was prepared by a procedure identical to that reported earlier as in section **1.c.3**.

2. d. 1. Preparation of ethyl pent-1,3-diene-1-carboxylate.

Crotonaldehyde (3 mL, 36.23 mmol) was taken in benzene (90 mL), to which (carbethoxymethylene) triphenyl phosphorane (15.13 g, 43.47 mmol) was added and the mixture was refluxed for 12 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. The triphenyl phosphinoxide formed was filtered after dilution with pet.ether (50 mL). The mother liquor was subjected to column chromatography (1% EtOAc-pet.ether). A white solid (3.54 g, 70%) was obtained as the product.

^{1}H NMR (90 MHz) : 1.3 (t, 3H, J = 7.1 Hz), 1.85 (d, 3H, J = 4.5 Hz), 4.2 (q, 2H, J = 7 Hz), 5.8 (d, 1H, J = 16 Hz), 6.0-6.6 (m, 2H), 7.25 (m, 1H).

2. d. 2. Preparation of hex-2,4-diene-1-ol.

$AlCl_3$ (1.98 g, 14.85 mmol) was dissolved in Et_2O (10 mL). Lithium aluminium hydride (1.69 g, 44.55 mmol) was suspended in Et_2O (100 mL) separately and chilled to 0 °C. The $AlCl_3$ solution was then added dropwise to this chilled solution. The solution was slowly warmed to room temperature and stirred for 2 h. This mixture was allowed to stand for 1h. The ethyl hex-2,4-diene-1-carboxylate (3 g, 14.85 mmol) was then dissolved in Et_2O (50 mL) and cooled in an ice-salt bath. The supernatant liquid of the ethereal solution of aluminium hydride was then transferred using a canula to the ester solution. The reaction mixture was then brought to room temperature and stirred for 2h, cooled again on an ice-bath, followed by careful addition of water (3 mL), 15% aqueous sodium hydroxide (3 mL) and again water (9 mL). The slurry thus formed was stirred for 1 h and the organic layer was decanted out and dried over anhydrous Na_2SO_4 and the solvent evaporated to yield a colorless solid (1.32 g, 63%). This compound was used for the next step without further purification.[22]

^{1}H NMR (90 MHz) : 1.7 (d, 3H, J = 4.4 Hz), 2.4 (s, 1H), 4.1 (brs, 2H), 5.6 (m, 2H), 6.0-6.2 (m, 2H).

2. d. 3. Preparation of 1-bromo-hex-2,4-diene.

PBr_3 (0.5 mL, 5.26 mmol) was cooled under ice-salt and hex-2,4-diene-1-ol (0.450 g, 4.59 mmol) was added dropwise with vigorous stirring. The color of the reaction mixture turned black. It was stirred at the same temperature for 1h. The reaction mixture was slowly raised to room temperature and stirred for 3 h till the color of the solution became yellow. The mixture was then diluted with Et_2O (10 mL) and the yellow solution was poured into ice and extracted with EtOAc. The EtOAc extract was washed with ice cold water and dried over Na_2SO_4 and concentrated to yield a pale yellow liquid (0.5 g, 67%). This compound was used for complexation in the next step without further purification.[22]

2. e. 1. Preparation of 4- phenyl-ethyl-but-1,3-diene-1-carboxylate.

The title compound was prepared by a procedure identical to that reported earlier as in section **2.d.1**. Cinnamaldehyde (2.86 mL, 21.66 mmol) was taken in benzene (60 mL), (carbethoxymethylene) triphenyl phosphorane (8.29 g, 23.83 mmol) was added into it and the mixture was refluxed for 10 h. The mother liquor was subjected to column chromatography (5% EtOAc-pet.ether) obtaining a colorless solid (3.28 g, 75%) as the product.

^{1}H NMR (90 MHz) : 1.3 (t, 3H, J = 7 Hz), 4.2 (q, 2H, J = 7 Hz), 5.9 (d, 1H, J = 15 Hz), 6.8 (m, 2H), 7.2-7.5 (m, 6H).

2. e. 2. Preparation of 5-Phenyl-Pent-2,4-diene-1-ol.

The title compound was prepared by a procedure identical to that reported earlier as in section **2.d.2**. $AlCl_3$ (1.34 g, 10.05 mmol) was dissolved in Et_2O (10 mL). Lithium aluminium hydride (1.14 g, 30 mmol) was suspended in Et_2O (80 mL) separately and chilled to 0 °C. The $AlCl_3$ solution was then added dropwise to the lithium aluminium hydride suspension to afford an ethereal solution of aluminium hydride. The 4-phenyl-ethyl-but-1,3-diene-1-carboxylate (1.5 g, 7.42 mmol) was then dissolved in Et_2O (50 mL) and reduced using aluminium hydride. This was worked up carefully by quenching with water (2 mL), 15% aqueous sodium hydroxide (2 mL) and again water (6 mL) was added carefully. The Et_2O layer was collected and dried over anhydrous Na_2SO_4. Evaporation of the ether afforded an oily product, which was purified by column chromatography (20% EtOAc-pet.ether). A colorless solid (0.84 g, 71%) was obtained as the product.

^{1}H NMR (90 MHz) : 1.65 (brs, 1H), 4.35 (d, 2H, J = 6.5 Hz), 6.0 (m, 1H), 6.4-6.65 (m, 2H), 6.85 (m, 1H), 7.35 (m, 5H).

2. e. 3. Preparation of 1-chloro-5-phenyl-pent-2,4-diene.

Anhydrous Et_2O (37 mL) was cooled on an ice-salt bath and dry HCl gas was passed through it for 1 h. 5-Phenyl-pent-2,4-diene-1-ol (2.48 g, 15.5 mmol) was dissolved in Et_2O (30 mL) and added dropwise into the ethereal solution of

HCl at the same temperature. The reaction mixture was stirred and slowly brought to room temperature, and stirred for a further 1 h. The reaction mixture was washed with ice cold water, saturated $NaHCO_3$ and finally with brine to a neutral pH. The organic layer was collected and dried over anhydrous Na_2SO_4 and the solvent removed to yield the title compound as a viscous oil. It was crystallized from Et_2O to yield the pure compound (2.24 g, 81%) as a colorless solid.

2. f. 1. Preparation of 1-bromocycloocta-2,4-diene.

Freshly distilled 1,3-cyclooctadiene (5 mL, 40.76 mmol) was taken in CCl_4 (50 mL, freshly distilled over phosphorus pentoxide) to which N-bromosuccinimide (7.98 g, 44.84 mmol) and a pinch of benzoyl peroxide (freshly crystallized from $CHCl_3$-pet.ether) were added and the reaction mixture refluxed for 2.5-3 h. The mixture was cooled to room temperature. The free succinimide was filtered off and the filtrate washed with portions of $Na_2S_2O_3$, brine and dried over anhydrous Na_2SO_4. The CCl_4 solution was concentrated under reduced pressure. The pale yellow colored viscous liquid thus obtained was diluted with pet.ether and refrigerated overnight to crystallize out the remaining succinimide. After filtering off the succinimide, the filtrate was concentrated and it was distilled bulb to bulb to afford the title compound as a colorless liquid (5.3 g, 69%). This bromide decomposed on standing (it became yellowish in color) and thus was freshly distilled before complexation.[9]

General method of complexation

Method A:

In an oven dried two-necked flask cooled under argon, freshly distilled acetonitrile (30 mL) and $Mo(CO)_6$ (2 mmol) were refluxed for 6 h. The golden solution of the resultant *tris*-acetonitrile $Mo(CO)_3$ complex was then treated with freshly distilled allyl halide (2.1 mmol) and the solution was refluxed for another 15 min for allyl chlorides, in case of the allyl bromides the solution was cooled immediately after addition. The volume of the reaction mixture was concentrated to approximately 5 mL by removal of acetonitrile under reduced pressure. A solution of the ligand (2.1 mmol) in CH_2Cl_2 (10 mL) was then added to the

reaction mixture with vigorous stirring and stirring was continued at room temperature for another 1.5 h. The reaction mixture was then concentrated and subjected to column chromatography to yield the colored complex. Further purification was done by crystallization.

Method B:

In an oven dried two-necked flask cooled under argon, a suspension of freshly distilled acetonitrile (30 mL), $Mo(CO)_6$ (2 mmol) and freshly distilled allyl halide (2.1 mmol) was refluxed for 5 h. The resultant *bis*-acetonitrile $Mo(CO)_2$ complex was then cooled to room temperature. The volume of the reaction mixture was concentrated to approximately 5 mL by removal of acetonitrile under reduced pressure. A solution of the ligand (2.1 mmol) in CH_2Cl_2 (10 mL) was then added to the reaction mixture with vigorous stirring and stirring was continued at room temperature for a further 1.5 h. The reaction mixture was then concentrated and subjected to column chromatography to yield the colored complex. Further purification was done by crystallization.

Preparation of complex 2.a.

The complex was prepared using **method B** from $Mo(CO)_6$ (0.792 g, 3 mmol) in acetonitrile (40 mL), cinnamyl chloride (0.534 g, 3.5 mmol) and the ligand **2** (0.791 g, 3.5 mmol). A red colored reaction mixture was obtained. Chromatography (20% CH_2Cl_2 -pet.ether) and recrystallization from CH_2Cl_2-pet.ether (by diffusion method at 5 °C) afforded red colored crystals (0.752 g, 53%).

Color	:	Red
MP	:	192 °C (dec)
IR	:	2478(m), 2015(m), 1941(s), 1860(s), 1536(m) cm^{-1}.
^{1}H NMR (200 MHz), 25 °C	:	-2.10 (brs, 1H), 1.92 (d, 1H, J = 10.4 Hz), 2.04 (s, 3H), 2.17 (s, 3H), 2.38 (s, 3H), 2.57 (d, 1H, J = 9.6 Hz), 2.68 (s, 3H), 3.90 (d, 1H, J = 6.6 Hz), 4.66 (m, 1H), 5.70 (s, 2H), 7.30 (m, 3H), 7.55 (m, 2H).

^{13}C NMR (50.3 MHz), 25 °C	:	10.5, 10.8, 13.7, 13.9, 61.4, 69.2, 75.4, 105.6, 105.9, 127.0, 127.3, 128.5, 140.0, 142.8, 144.5, 150.0, 152.5, 228.9, 233.1.
Analysis	:	Calcd. : C: 53.38; H: 5.29; N: 11.86. Found : C: 53.72; H: 5.37; N: 11.95.

Preparation of complex 2.b.

The complex was prepared using **method B** from $Mo(CO)_6$ (0.528 g, 2 mmol) in acetonitrile (30 mL), crotyl bromide (0.405 g, 3.0 mmol) and the ligand **2** (0.565 g, 2.5 mmol). A yellow colored reaction mixture was obtained. Chromatography (6% CH_2Cl_2 -pet.ether) and recrystallization from CH_2Cl_2-pet.ether (by diffusion method at 5 °C) afforded orange colored crystals (0.300 g, 37%).

Color	:	Orange
MP	:	183 °C (dec)
IR	:	2469(m), 2014(m), 1935(s), 1848(s), 1536(m) cm^{-1} .
^{1}H NMR (200 MHz), 25 °C	:	-2.20 (brs, 1H), 1.57 (d, 1H, J = 10.2 Hz), 1.82 (m, 1H), 2.04 (d, 3H, J = 6.4 Hz), 2.12 (s, 3H), 2,15 (s, 3H), 2,32 (s, 3H), 2.70 (s, 3H), 3.58 (d, 1H, J = 6.8 Hz), 3.95 (m, 1H), 5.64 (s, 1H), 5.76 (s, 1H).
^{13}C NMR (50.3 MHz), 25 °C	:	10.6, 10.8, 13.8, 13.9, 20.6, 61.9, 67.4, 79.5, 105.6, 105.8, 142.9, 144.3, 149.9, 152.5, 228.6, 233.0.
Analysis	:	Calcd. : C: 46.82; H: 5.60; N: 13.65. Found : C: 46.90; H: 5.24; N: 13.33.

Preparation of complex 2.c.

The complex was prepared using **method B** from $Mo(CO)_6$ (0.528 g, 2 mmol) in acetonitrile (30 mL), allyl halide **2.a.1** (4-bromo-2-methyl-2-butene) (0.45 g, 3.0 mmol) and the ligand **2** (0.565 g, 2.5 mmol). A yellow colored reaction mixture was obtained. Chromatography (25% CH_2Cl_2 -pet.ether) and recrystallization from CH_2Cl_2-pet.ether (by diffusion method at 5 °C) afforded orange colored crystals (0.257 g, 30%).

Color	:	Orange
MP	:	155 °C (dec)
IR	:	2478(m), 2027(m), 1937(s), 1839(s), 1536(m) cm^{-1}.
^{1}H NMR (200 MHz), 25 °C	:	-2.00 (brs, 1H), 1.10 (s, 3H), 2.05 (s, 3H), 2.15 (s, 3H), 2.18 (s, 3H), 2.27 (d, 1H, J = 12.6 Hz), 2.35 (s, 3H), 2.70 (s, 3H), 3.62 (d, 1H, J = 7.9 Hz), 4.15 (dd, 1H, J = 6.7, 13.2 Hz), 5.67 (s, 1H), 5.77 (s, 1H).
^{13}C NMR (50.3 MHz), 25 °C	:	10.6, 10.8, 13.8, 13.9, 22.1, 30.1, 60.9, 79.7, 81.3, 105.6, 105.8, 142.8, 144.2, 149.9, 152.5, 230.2, 233.1.
Analysis	:	Calcd. : C: 48.11; H: 5.89; N: 13.20. Found : C: 48.63; H: 6.55; N: 13.05.

Preparation of complex 2.d.

The complex was prepared using **method A** from $Mo(CO)_6$ (0.528 g, 2 mmol) in acetonitrile (30 mL), allyl halide **2.b.3** (4-bromo-1-phenyl-2-butene-1-one) (0. g, 2.5 mmol) and the ligand **2** (0.565 g, 2.5 mmol). A dark red colored reaction mixture was obtained. Chromatography (55% CH_2Cl_2 -pet.ether) and recrystallization from CH_2Cl_2-pet.ether (at -10 °C) afforded red colored crystals (0.236 g, 24%).

Color	:	Red
MP	:	181 °C (dec)
IR	:	2475 (m), 2015(w), 1937 (s), 1845 (s), 1778 (s), 1542 (m) cm^{-1}.
^{1}H NMR (200 MHz), 25 °C	:	-1.90 (brs, 1H), 2.06 (s, 3H), 2.14 (s, 3H), 2.22 (d, 1H, J = 11.2 Hz), 2.38 (s, 3H), 2.60 (brs, 3H), 2.81 (d, 1H, J = 9.0 Hz), 4.07 (d, 1H, J = 6.6 Hz), 5.28 (m, 1H), 5.67 (s, 1H), 5.69 (s, 1H), 7.52 (m, 3H), 8.07 (m, 2H).
^{13}C NMR (50.3 MHz), 25 °C	:	10.4, 10.7, 13.7, 13.9, 57.5, 64.2, 82.4, 105.8, 105.9, 128.4, 128.5, 132.8, 137.8, 143.4, 144.9, 149.9, 152.2, 196.4, 229.4, 232.2.
Analysis	:	Calcd. : C: 52.83; H: 5.04; N: 11.20. Found : C: 52.97; H: 4.93; N: 10.95.

Preparation of complex 2.e.

The complex was prepared using **method A** from $Mo(CO)_6$ (0.792 g, 3 mmol) in acetonitrile (40 mL), allyl halide **2.c.1** (3-chloro-1-phenylbutene) (0.45 g, 3.0 mmol) and the ligand **2** (0.565 g, 2.5 mmol). A red colored reaction mixture was obtained. Chromatography (15% CH_2Cl_2 -pet.ether) and recrystallization from CH_2Cl_2-pet.ether (at -10 °C) afforded orange colored crystals (0.580 g, 40%).

Color	:	Orange
MP	:	174 °C (dec)
IR	:	2468(m), 2029(m), 1939(s), 1841(s), 1536(m) cm^{-1}.
^{1}H NMR (400 MHz), -70 °C CD_2Cl_2	:	0.88 (s, 3H), 1.85 (m, 1H), 2.02 (brs, 6H), 2.10 (s, 3H), 2.52 (s, 3H), 2.91 (d, 1H, J = 10.9 Hz), 4.61 (dd, 1H, J = 8.9, 10.5 Hz), 5.41 (s, 1H), 5.72 (s, 1H), 6.38 (d, 1H, J = 7.9 Hz), 6.96 (t, 1H, J = 7.5 Hz), 7.21 (m, 2H), 7.38 (d, 1H, J = 7.4 Hz).
^{13}CNMR (100.6 MHz), -70 °C CD_2Cl_2	:	10.1, 10.5, 11.0, 13.1, 20.8, 60.4, 78.0, 83.6, 104.6, 105.0, 125.2, 126.7, 127.7, 127.8, 129.8, 137.8, 142.9, 145.4, 151.4, 151.9, 230.6, 235.3.
Analysis	:	Calcd. : C: 54.32; H: 5.55; N: 11.52. Found : C: 54.43; H: 5.98; N: 11.20.

Preparation of complex 2.f.

The complex was prepared using **method A** from $Mo(CO)_6$ (0.528 g, 2 mmol) in acetonitrile (30 mL), allyl halide **2.d.3** (1-bromo-hex-2,4-diene) (0.618 g, 3.8 mmol) and the ligand **2** (0.565 g, 2.5 mmol). The halide in this case was added at reaction temp: 60 °C. A dark colored reaction mixture was obtained. Chromatography (22% EtOAc -pet.ether) and recrystallization from CH_2Cl_2-pet.ether (at -10 °C) afforded orange colored crystals (0.394 g, 45%).

Color	:	Orange
MP	:	142 °C (dec)
IR	:	2483 (m), 2011(w), 1938 (s), 1842(s), 1531 (m) cm^{-1}.

^{1}H NMR (200 MHz), 25 °C	:	-2.00 (brs, 1H), 1.64 (d, 1H, J = 10.2 Hz), 1.79 (d, 1H, J = 5.1 Hz), 2.10 (s, 3H), 2.13 (s, 3H), 2.30 (brs, 3H), 2.39 (d, 1H, J = 9.7 Hz), 2.69 (s, 3H), 3.65 (d, 1H, J = 6.9 Hz), 4.09 (m, 1H), 5.64 (s, 1H), 5.73 (s, 1H), 5.87 (m, 2H).
^{13}C NMR (50.3 MHz), 25 °C	:	10.6, 10.8, 13.9, 18.7, 61.5, 72.7, 77.5, 105.6, 105.8, 126.8, 133.0, 142.6, 144.4, 149.9, 152.6, 228.2, 233.7.
Analysis	:	Calcd. : C: 49.54; H: 5.73; N: 12.84. Found : C: 49.45; H: 5.82; N: 12.49.

Preparation of complex 2.g.

The complex was prepared using **method A** from $Mo(CO)_6$ (0.528 g, 2 mmol) in acetonitrile (30 mL), allyl halide **2.e.3** (1-chloro-5-phenyl-pent-2,4-diene) (0.535 g, 3.0 mmol) and the ligand **2** (0.565 g, 2.5 mmol). A red colored reaction mixture was obtained. Chromatography (20% CH_2Cl_2 -pet.ether) and recrystallization from CH_2Cl_2-pet.ether (by diffusion method at 5 °C) afforded red colored crystals (0.424 g, 42%).

Color	:	Red
MP	:	199 °C (dec)
IR	:	2476 (m), 2013(m), 1946 (s), 1856 (s), 1537 (m) cm^{-1}.
^{1}H NMR (200 MHz), 25 °C	:	-1.95 (broad hump, 1H), 1.81 (d, 1H, J = 11.2 Hz), 2.12 (s, 3H), 2.18 (s, 3H), 2.35 (s, 3H), 2.58 (t, 1H, J = 9.8 Hz), 2.70 (s, 3H), 3.77 (d, 1H, J = 7.3 Hz), 4.32 (m, 1H), 5.69 (s, 1H), 5.72 (s, 1H), 6.55 (m, 1H), 6.77 (d, 1H, J = 15.5 Hz), 7.34 (m, 5H).
^{13}C NMR (50.3 MHz), 25 °C	:	10.6, 10.8, 13.8, 13.9, 61.9, 71.9, 79.1, 105.7, 105.9, 126.6, 127.4, 128.8, 129.1, 131.7, 137.7, 143.0, 144.5, 149.9, 152.6, 227.8, 233.7.
Analysis	:	Calcd. : C: 55.45, H: 5.46, N: 11.24. Found : C: 55.38, H: 5.68, N: 11.32.

Preparation of complex 2.h.

The complex was prepared from $Mo(CO)_6$ (0.528 g, 2 mmol) in acetonitrile (30 mL), allyl halide **2.f.1** (1-bromocycloocta-2,4-diene) (0.467 g, 2.5 mmol) and the ligand **2** (0.565 g, 2.5 mmol) using **method A**. A red colored reaction mixture was obtained. Chromatography (10% CH_2Cl_2 -pet.ether) and recrystallization from CH_2Cl_2-pet.ether (by diffusion method at 5 °C) afforded hexagonal red crystals (0.613 g, 66%).

Color	:	Red
MP	:	189 °C (dec)
IR	:	2475 (m), 2017(m), 1933 (s), 1842 (s), 1537 (m) cm^{-1}.
^{1}H NMR (200 MHz), -30 °C	:	Conformer A: 4.10 (m, 1H), 4.45 (m, 1H), 4.57 (brd, 1H), 5.30 (m, 1H), 6.35 (dd, 1H, J = 10.2, 2.4 Hz). Conformer B: 4.10 (m, 1H), 4.20 (m, 1H), 4.75 (brd, 1H), 5.30 (m, 1H), 6.55 (dd, 1H, J = 10.2, 2.4 Hz). Bridging H for two conformers of B-H-Mo appeared as broad hump at -1.65 ppm. Methyl protons appeared at 2.10 (s, 6H), 2.15 (s, 6H), 2.35 (s, 3H), 2.40 (s, 3H), 2.70 (s, 3H), 2.75 (s, 3H). Twelve methylene protons appeared as broad humps at 0.70, 1.25, 1.65, 2.10, 2.35, 2.85. Four pyrazole protons appeared at 5.65 (s, 1H), 5.70 (s, 1H) 5.80 (s, 2H).
^{13}C NMR (50.3 MHz), 25 °C	:	10.7, 10.8, 14.0, 24.9, 25.1, 28.4, 31.5, 32.1, 63.6, 66.0, 77.6, 78.4, 80.4, 82.4, 105.7, 126.7, 127.0, 134.8, 135.0, 142.8, 144.5, 149.9, 152.7, 152.9, 227.2, 229.4, 233.9, 235.9.
Analysis	:	Calcd. : C: 51.97, H: 5.89, N: 12.12. Found : C: 51.29, H: 6.00, N: 11.80.

Preparation of complex 2.i.

Complex **2.h** (0.25 g, 0.54 mmol) was dissolved in toluene (7 mL) at room temperature to which benzaldehyde (0.06 mL, 0.95 mmol) was added dropwise. The temperature was slowly raised to 90-95 °C with constant stirring and maintained for 3 h. The reaction mixture was then cooled to room temperature

and toluene was removed under reduced pressure. A pure yellow complex **2.i** was obtained by column chromatography (8% EtOAc-pet.ether), recrystallized from CH_2Cl_2/pentane (at -10 °C) to obtain orange colored crystals (0.26 g, 85%).

Color	:	Orange
MP	:	149 °C (dec)
IR	:	2468 (m), 1927 (s), 1834 (s), 1541 (m) cm^{-1}.
^{1}H NMR (200 MHz), 25 °C	:	Conformer A: 2.15 (s, 6H), 2.47 (s, 3H), 2.85 (s, 3H), 3.65 (m, 1H), 3.95 (m, 1H), 4.80 (m, 1H), 5.30 (m, 1H), 6.60 (dd, 1H J = 11.2, 2.6 Hz), Conformer B: 2.17 (s, 6H), 2.42 (s, 3H), 2.90 (s, 3H), 3.80 (m, 1H), 4.20 (brd, 1H), 4.40 (m, 1H), 5.30 (m, 1H), 6.30 (dd, 1H, J = 11.2, 2.6 Hz). Twelve methylene protons appeared as complex multiplets at 0.80, 1.25, 1.50, 2.05, 2.25, 2.35, 2.75, four pyrazole protons at 5.67, 5.75, 5.82, four benzylic protons at 4.40-4.80 and ten phenyl protons at 7.35.
^{13}C NMR (75.2 MHz), 25 °C	:	11.7, 11.9, 14.8, 24.5, 24.7, 27.8, 28.3, 31.0, 31.2, 67.9, 69.1, 72.8, 73.0, 77.4, 78.9, 80.0, 80.8, 81.3, 105.8, 106.3, 126.0, 126.3, 126.5, 127.2, 128.0, 128.3, 128.5, 134.6, 134.7, 139.4, 142.3, 143.4, 143.5, 150.7, 153.1, 153.3, 228.5, 231.0, 231.7, 232.8.
Analysis	:	Calcd. : C: 57.06; H: 5.85; N: 9.86. Found : C: 56.78; H: 5.15; N: 9.76.

Preparation of complex 2.j.

To the complex **2.f** (0.263 g, 0.6 mmol) in toluene (10 mL) at room temperature, benzaldehyde (0.10 mL, 1.00 mmol) was added dropwise and the resultant mixture refluxed for 3 h with constant stirring. The reaction mixture was then cooled to room temperature and toluene was removed under reduced pressure. Pure yellow complex **2.j** was obtained by column chromatography (4% EtOAc-pet.ether) (at -10 °C), recrystallized from pentane to obtain orange colored crystals (0.19 g, 58%).

Color	:	Orange
MP	:	124 °C (dec)
IR	:	2482 (m), 1929 (s), 1833 (s), 1536 (m) cm^{-1}.
^{1}H NMR (200 MHz), 25 °C	:	Major Isomer: 1.32 (d, 3H, J = 5.1 Hz), 1.65 (d, 1H, J = 10.0 Hz), 2.08 (s, 3H), 2.18 (s, 3H), 2.39 (s, 3H), 2.42 (d, 1H, J = 12.5 Hz), 2.87 (s, 3H), 3.79 (d, 1H, J = 6.8 Hz), 4.02 (m, 1H), 4.23 (d, 1H, J = 15.2 Hz), 4.76 (d, 1H, J = 15.2 Hz), 5.71 (s, 1H), 5.78 (s, 1H), 5.90 (m, 2H), 7.30 (m, 5H). Minor Isomer: 1.15 (dd, 1H, J = 2.4, 10.2 Hz), 1.75 (d, 3H, J = 5.3 Hz), 2.10 (s, 3H), 2.12 (m, 1H), 2.20 (s, 3H), 2.25 (s, 3H), 2.77 (s, 3H), 2.93 (m, 1H), 3.10 (t, 1H, J = 10.2 Hz), 4.02 (m, 1H), 4.44 (d, 1H, J = 14.1 Hz), 4.57 (d, 1H, J = 14.5 Hz), 5.66 (s, 1H), 5.73 (s, 1H), 5.87 (m, 1H), 7.30 (m, 5H).
^{13}C NMR (75.2 MHz), 25 °C	:	11.6, 11.8, 14.8, 15.0, 17.8, 18.4, 47.4, 48.9, 60.5, 72.4, 73.5, 78.7, 79.3, 80.3, 88.1, 92.9, 105.3, 105.6, 105.7, 106.2, 106.5, 125.1, 126.2, 126.5, 127.2, 128.1, 128.6, 128.8, 131.3, 132.6, 138.7, 139.5, 139.7, 142.2, 142.7, 143.5, 143.8, 150.8, 151.0, 152.1, 153.1, 229.4, 230.7, 231.3, 233.3.
Analysis	:	Calcd. : C: 55.37; H: 5.76; N: 10.33. Found : C: 55.20; H: 5.51; N:10.26.

Preparation of complex 2.k.

The title complex was prepared using the same allyl halide **2.e.3** (1-chloro-5-phenyl-pent-2,4-diene) following the same procedure as for **2.g** from molybdenum hexacarbonyl (0.195 g, 0.73 mmol), acetonitrile (15 mL), 1-chloro-5-phenyl-2,4-pentadiene (0.196 g, 1.1 mmol), and the ligand **2.(I)** (0.294 g, 1 mmol). The pure, red complex **2.k** (0.055 g, 14%) was obtained by column chromatography (30% CH_2Cl_2-pet.ether) and was recrystallized from CH_2Cl_2-pet.ether (at -10 °C).

Color	:	Red
MP	:	175 °C (dec)
IR	:	1939 (s), 1852 (s) cm^{-1}.
^{1}H NMR (200 MHz), 50 °C	:	-5.10 (s, 1H), 0.85-2.10 (br, 13H), 1.90 (m, 1H), 2.74 (t, 1H, J = 10.1 Hz), 3.81 (d, 1H, J = 6.8 Hz), 4.30 (dt, 1H, J = 10.0, 6.9 Hz), 6.17 (t, 1H, J = 2.2 Hz), 6.21 (t, 1H, J = 2.1 Hz), 6.55 (dd, 1H, J = 10.5, 15.6 Hz), 6.87 (d, 1H, J = 15.6 Hz), 7.20-7.50 (m, 7H), 7.86 (d, 1H, J = 2.0 Hz), 8.25 (d, 1H, J = 1.9).
^{13}C NMR (100.6 MHz), 21 °C	:	20.4, 24.3, 24.7, 30.8, 30.9, 32.2, 32.5, 35.7, 79.4, 105.2, 105.5, 126.4, 127.6, 128.7, 129.0, 131.4, 133.0, 133.4, 137.1, 142.8, 145.8, 229.9, 230.2.
Analysis	:	Calcd. : C: 58.93; H: 5.68; N: 10.18. Found : C: 58.26; H: 6.05; N: 9.88.

II. 5 References And Notes

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13 Representative B-H distances : (a) B-H-Mo 1.33 Å , $B\text{-}H_{(t)}$ 0.94 Å and 1.02 Å in $CpMo(CO)_2\{P(Ph)\{N[Si(CH3)_3]\}(\mu\text{-}H\text{-}BH_2)$; McNamara, W. F.; Duesler, E. N.; Paine, R. T.; Ortiz, J. V.; Kölle, P.; Nöth, H. *Organometallics* **1986,** *5*, 380. (b) $B\text{-}H_{(t)}$ 1.196 Å, $B\text{-}H_{(br)}$ 1.339 Å in B_2H_6; Bartell, L. S.; Carroll, B. L.; *J. Chem. Phys.***1965**, *42*, 1135. Representative Mo-H distances in Mo(II) hydride : (a) 1.436 Å; in $Tp'Mo(CO)_3H$; Protasiewicz, J. D.; Theopold, K. H.; *J. Am. Chem. Soc.* **1993**, *115*, 5559. (b) 1.63 Å; in $C_5Me_5(CO)_2(CN^tBu)MoH$; Alt, H. G.; Engelhardt, H. E.; Frister, T.; Rogers, R. D.; *J.Organomet.Chem* **1989**, *366*, 297. Representative bridged Mo(II) hydride : $Mo_1\text{-}H$ 1.76 Å; $Mo_2\text{-}H$ 1.93Å; in $[(Ph_3P)_2N]^+$ $[Mo_2(CO)_{10}(\mu\text{-}H)]$; Petersen, J. L.; Masino, A.; *J. Organomet.Chem* **1981**, *208*, 55.

14 Curiously, the literature is silent about ^1H chemical shift of B-H in pyrazolylborate complexes. We find that the B-H proton is observable only if it is bridged between boron and molybdenum.

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16 Note: The structure of the minor isomer/conformer could not be assigned due to low intensity and overlapping signals.

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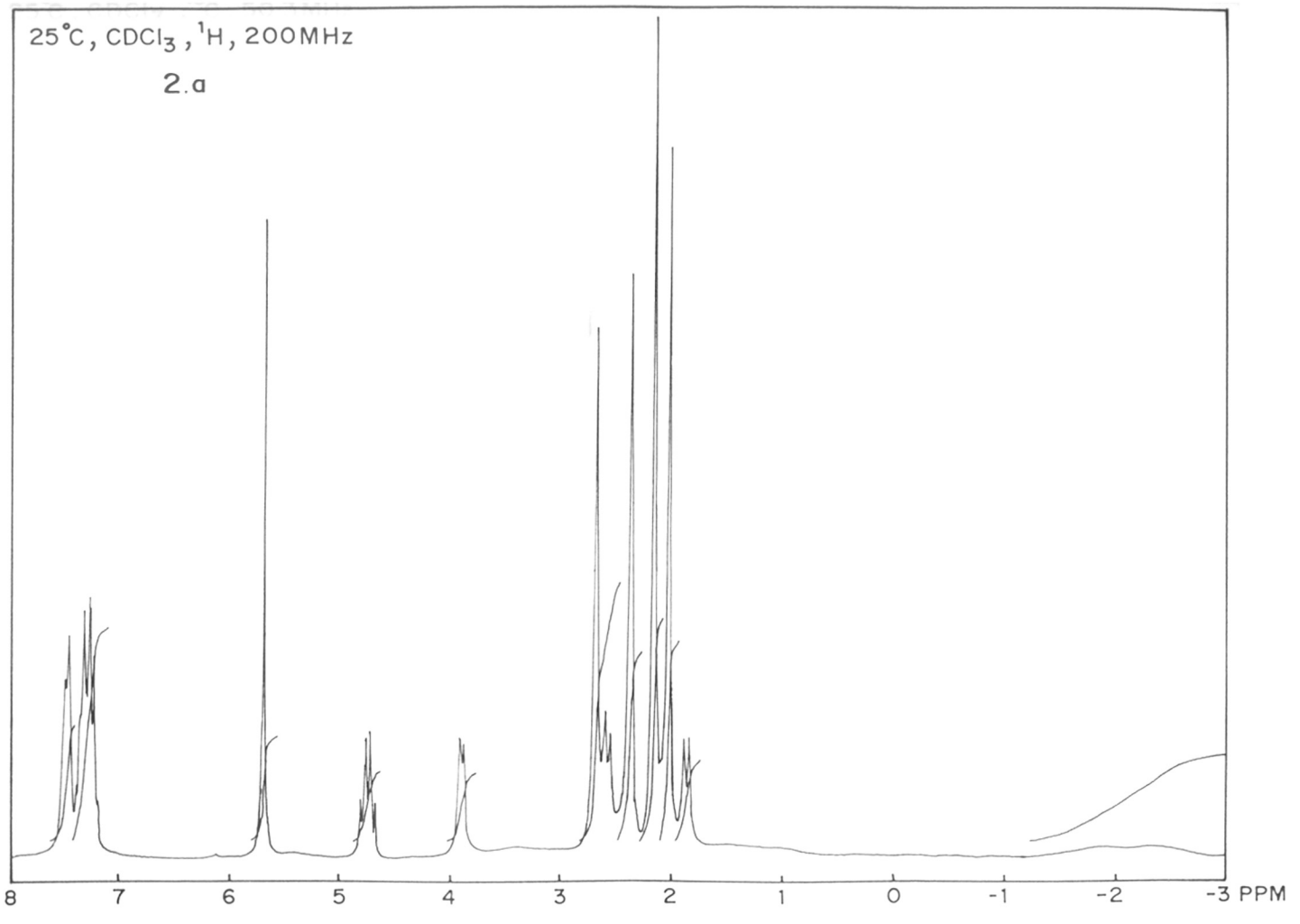
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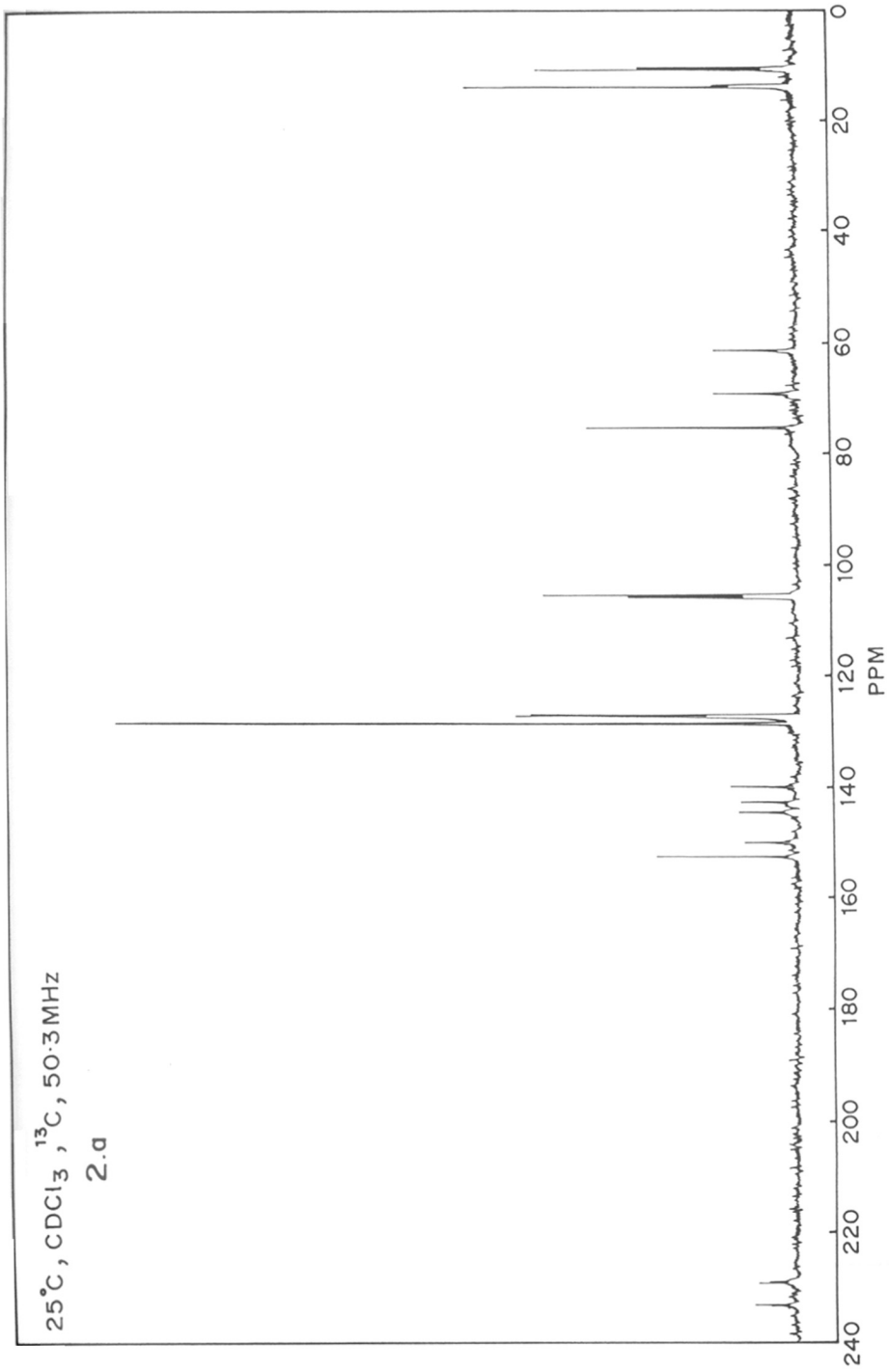
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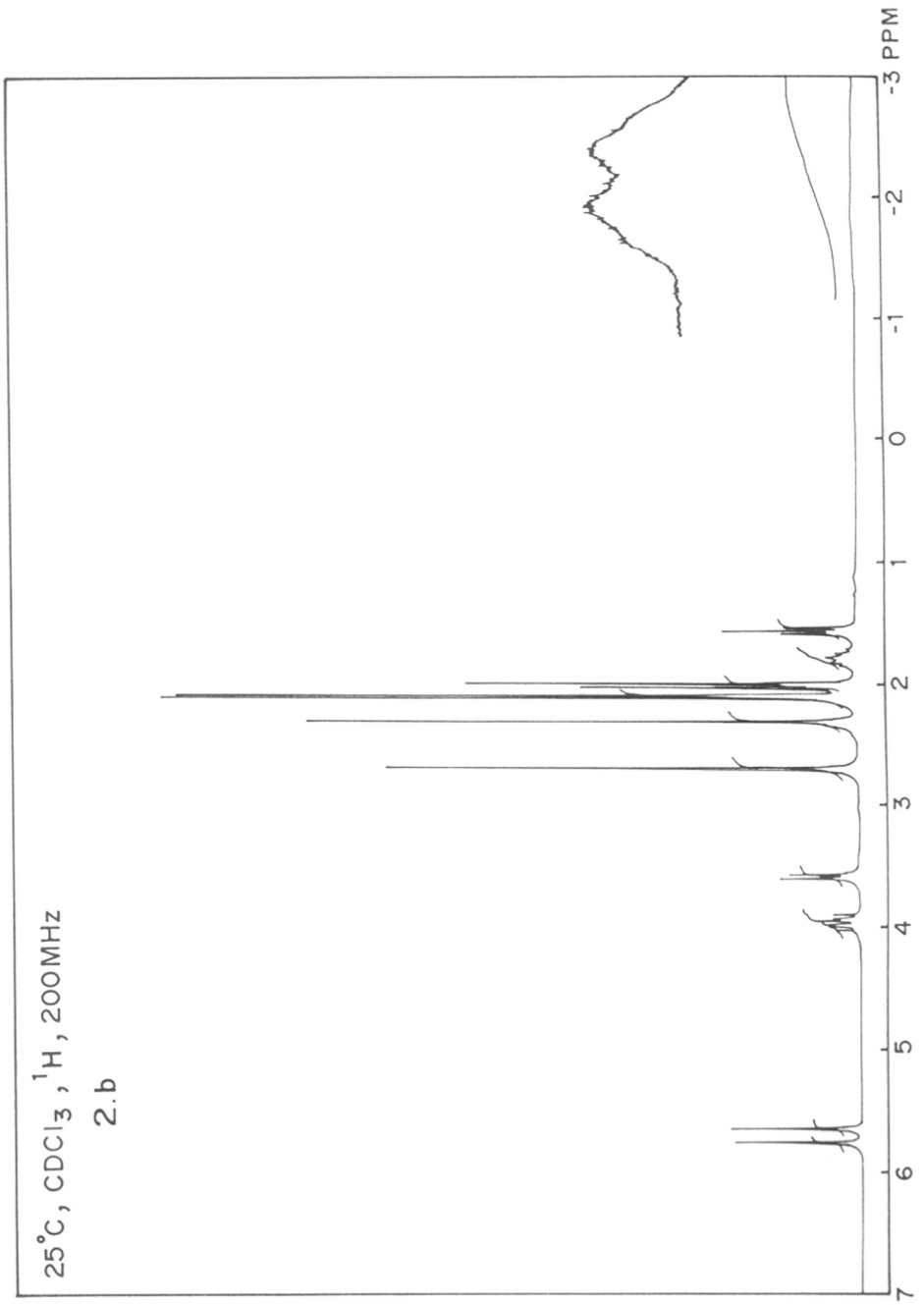
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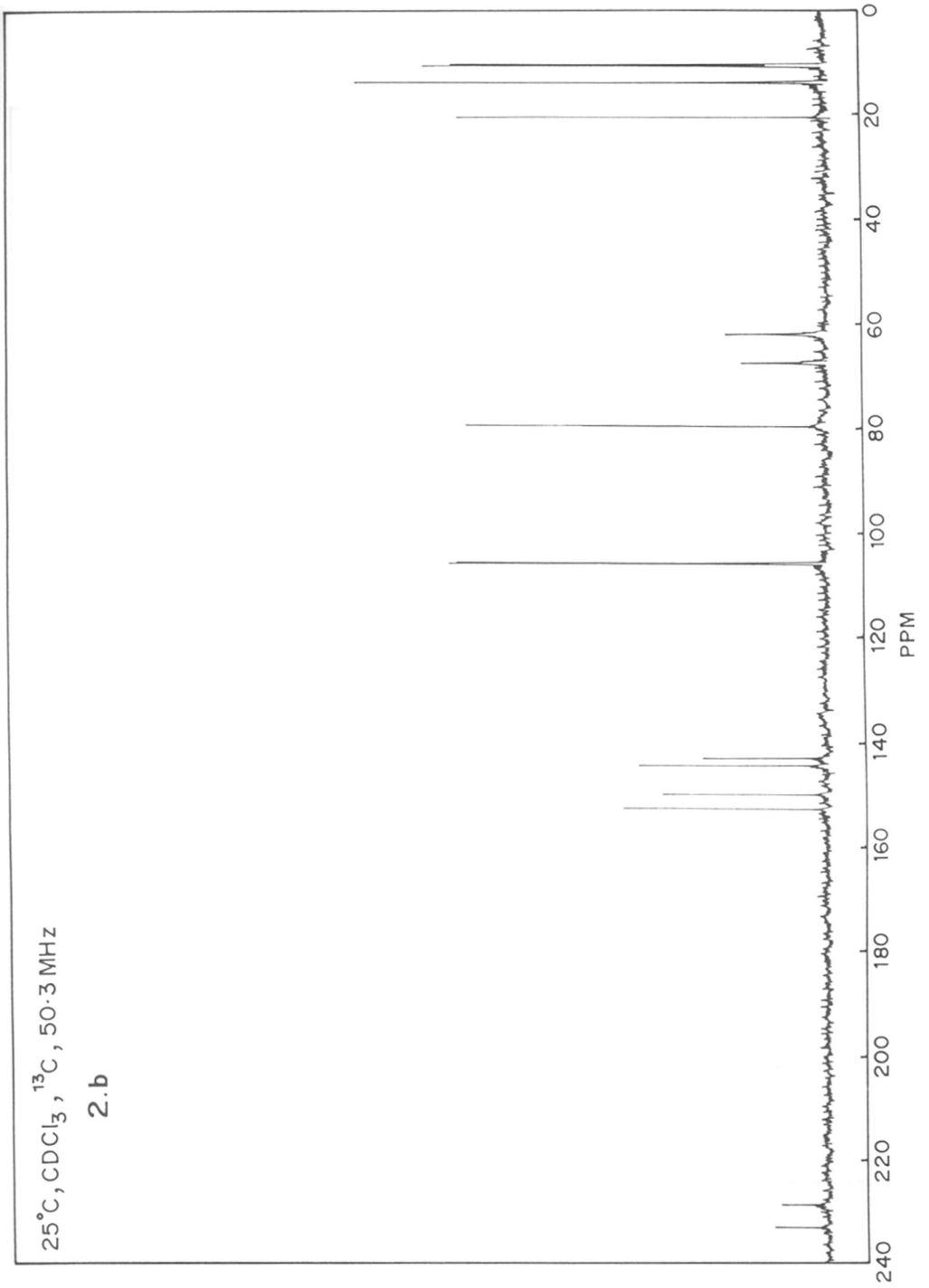
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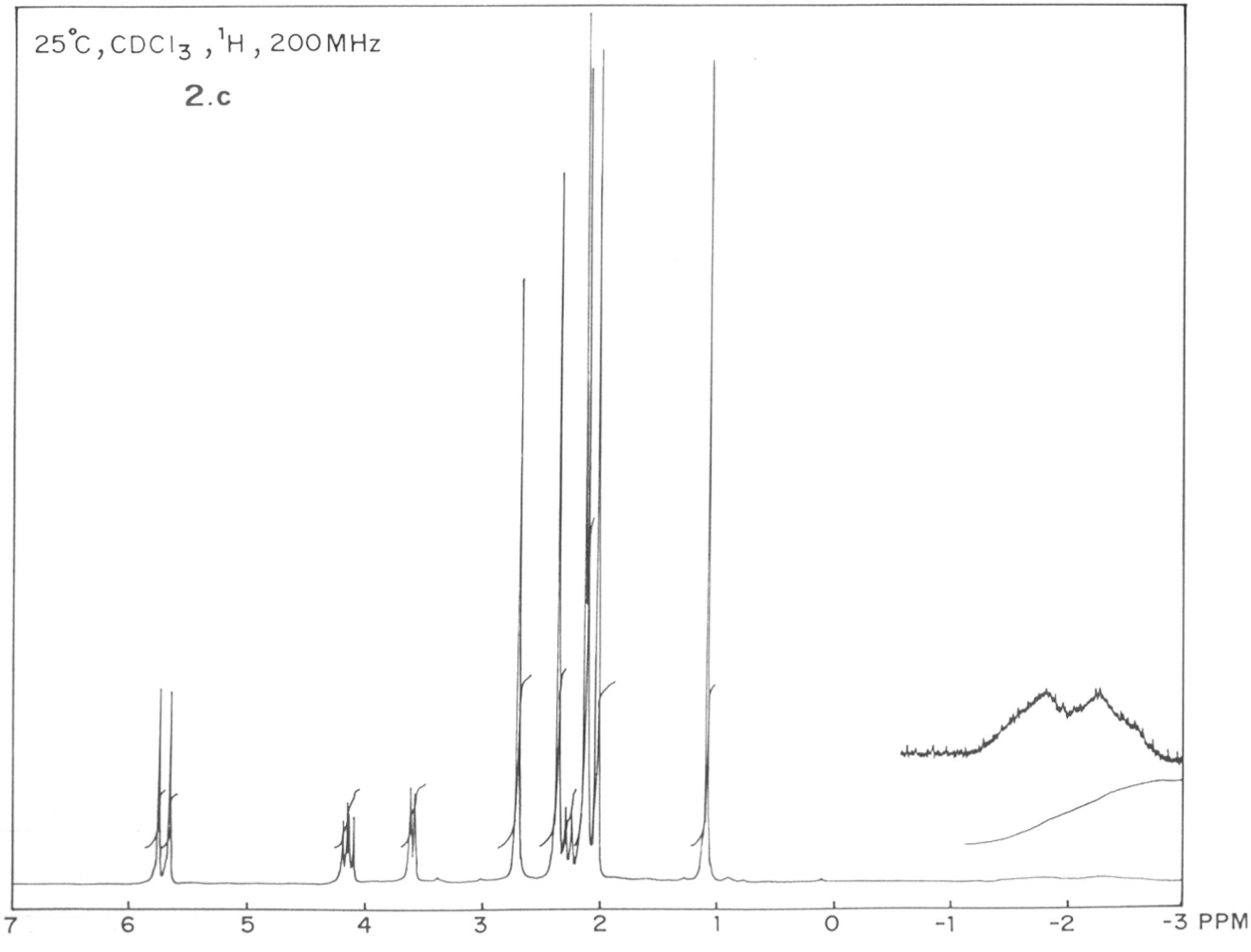
PPM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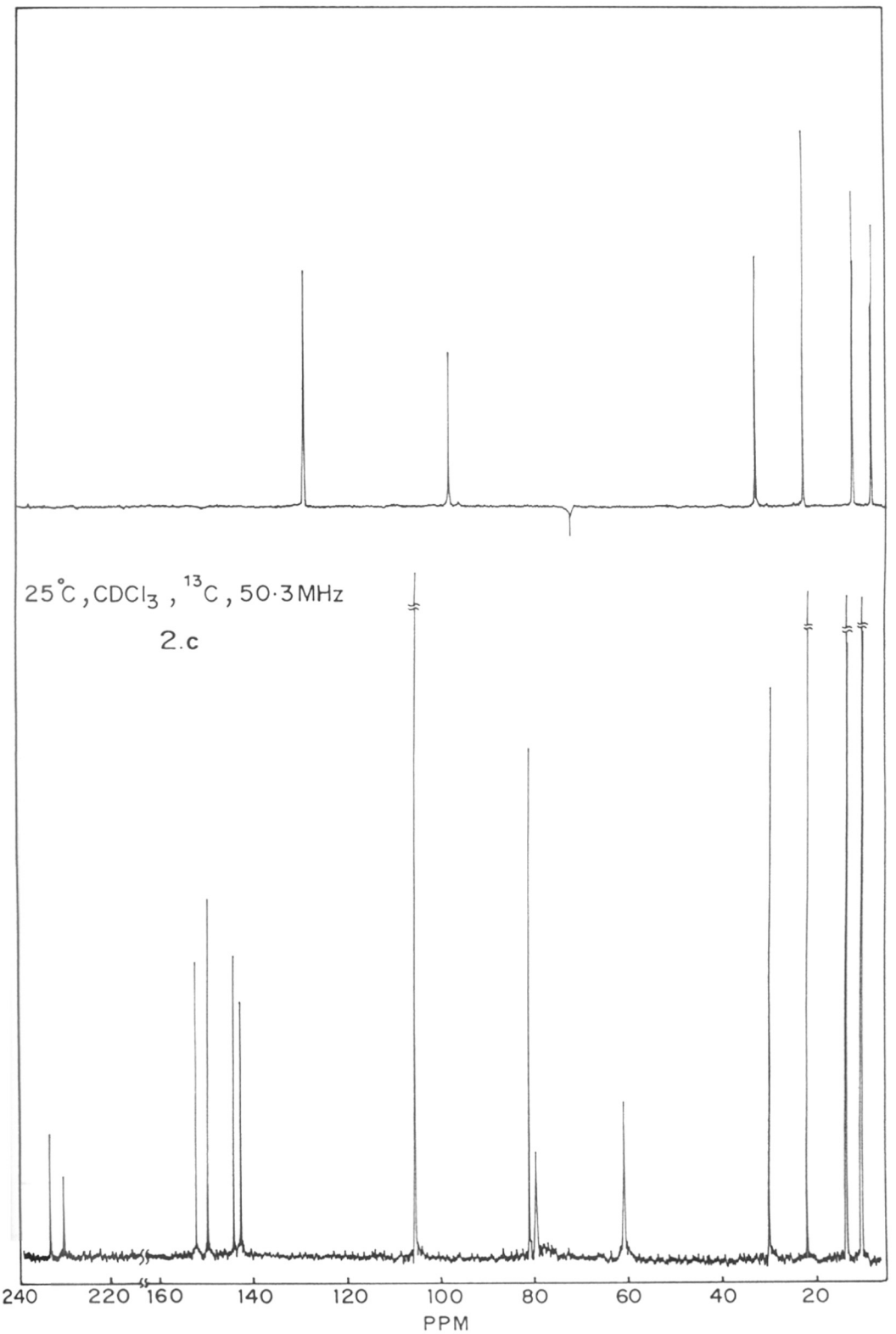
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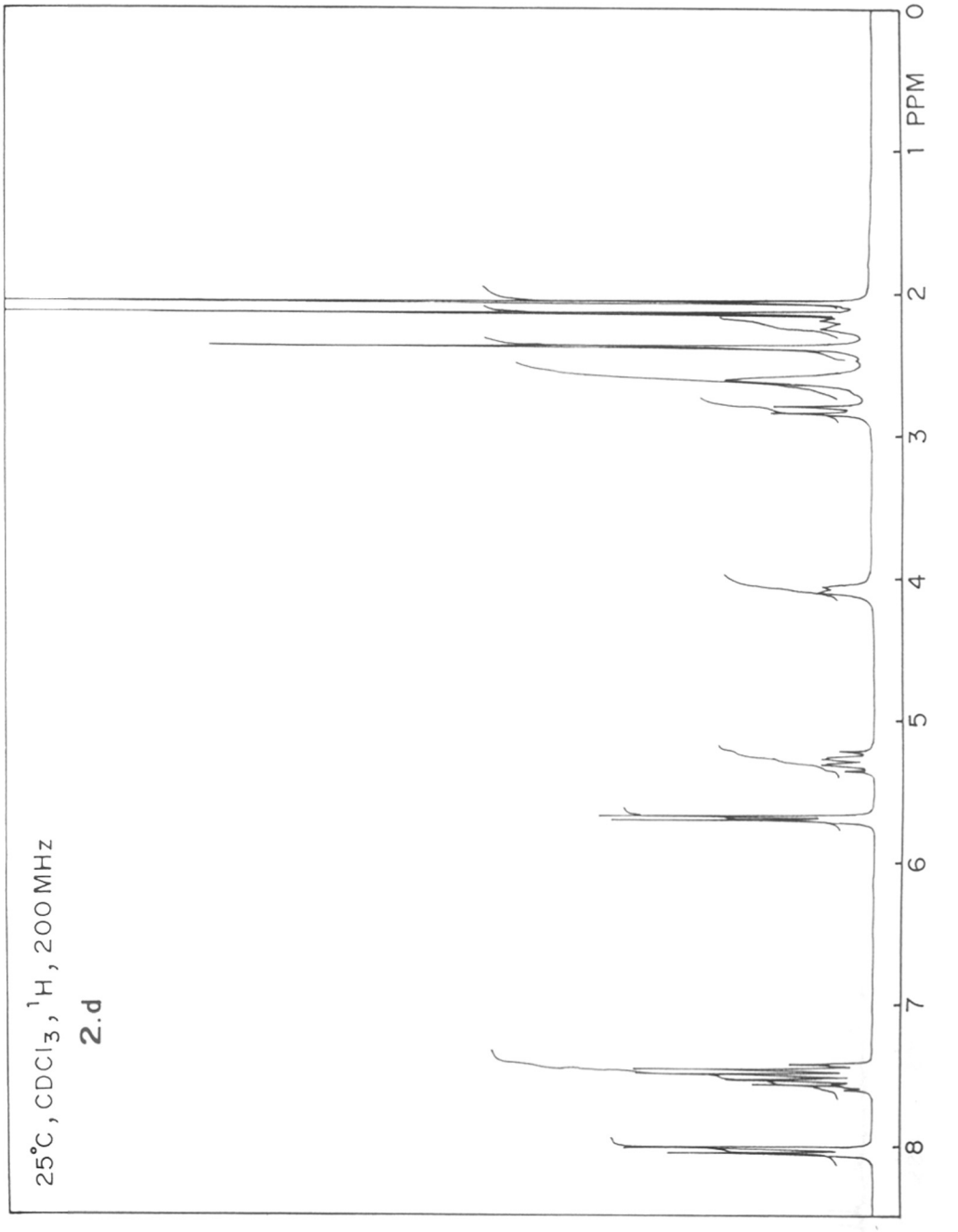
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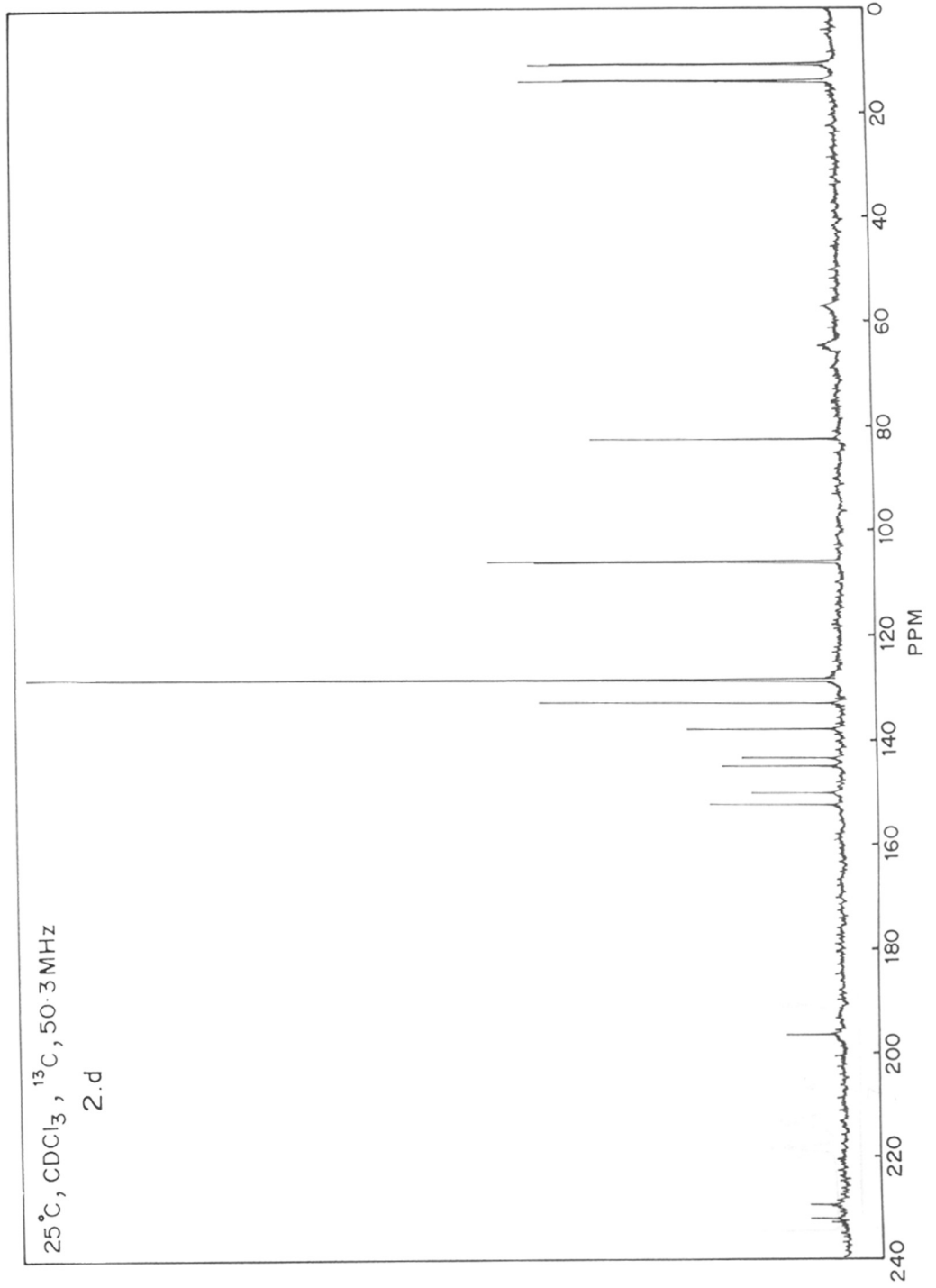
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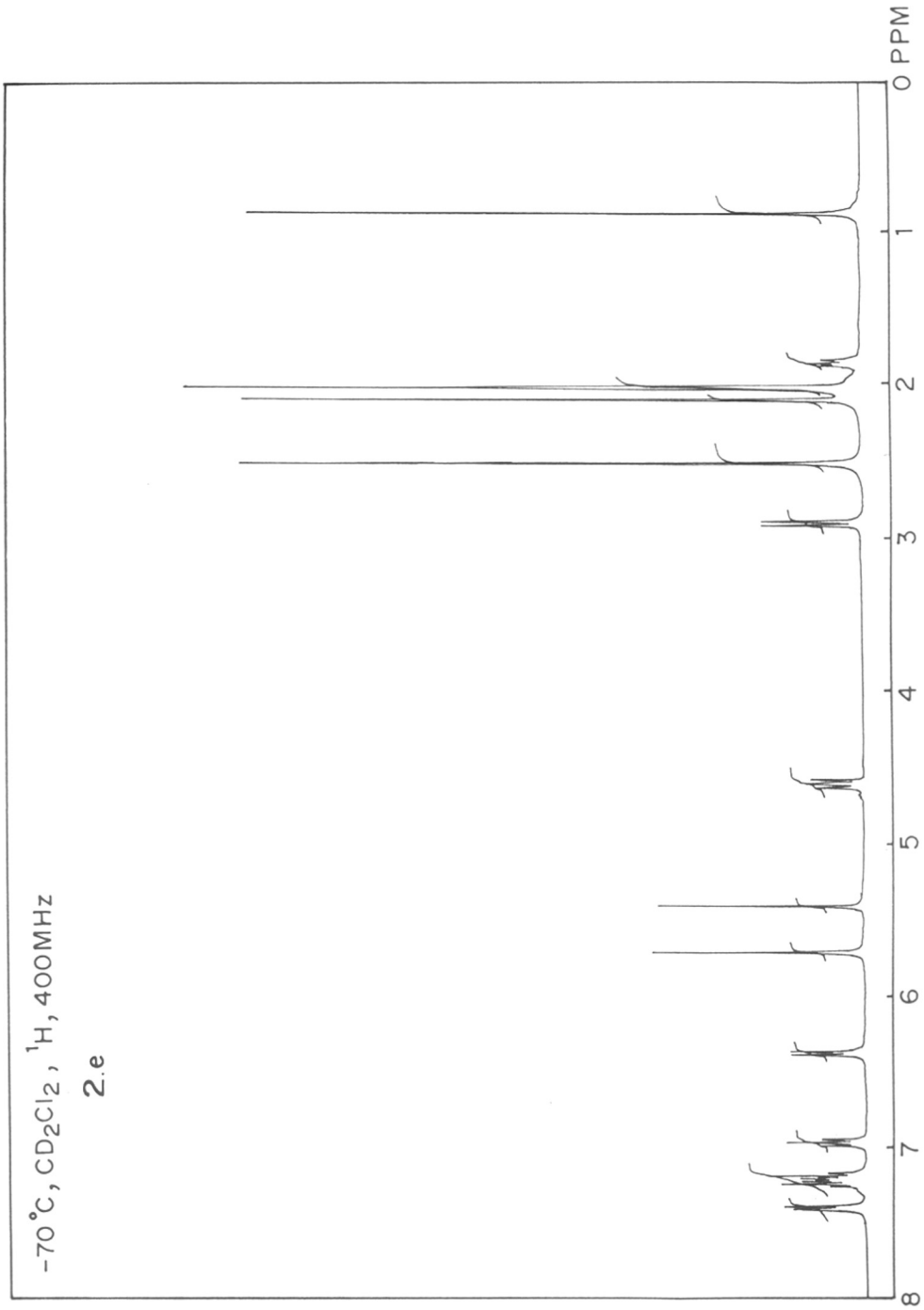
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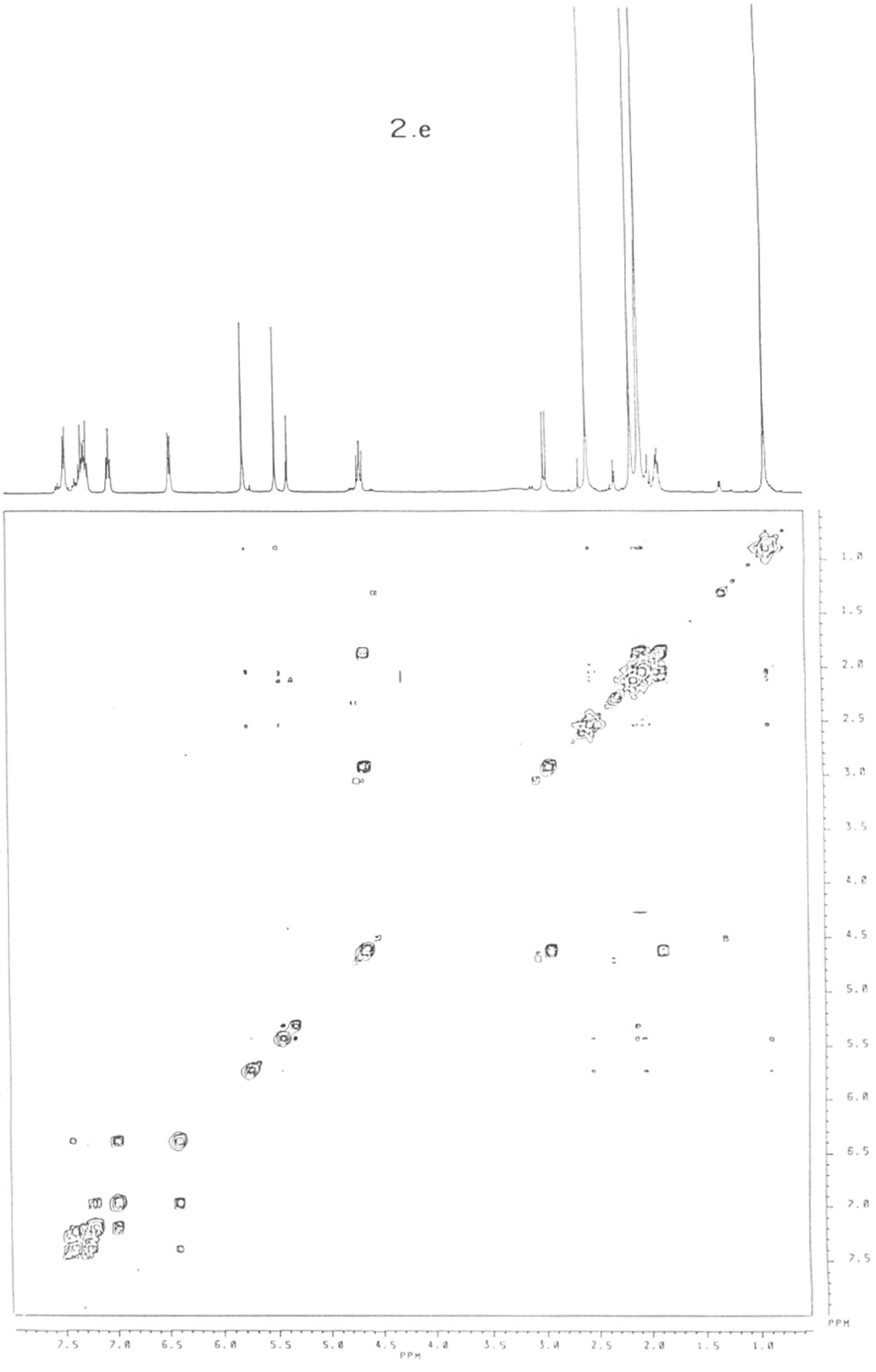
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5.0
5.5
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6.5
7.0
7.5
PPM
7.5
7.0
6.5
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4.5
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3.0
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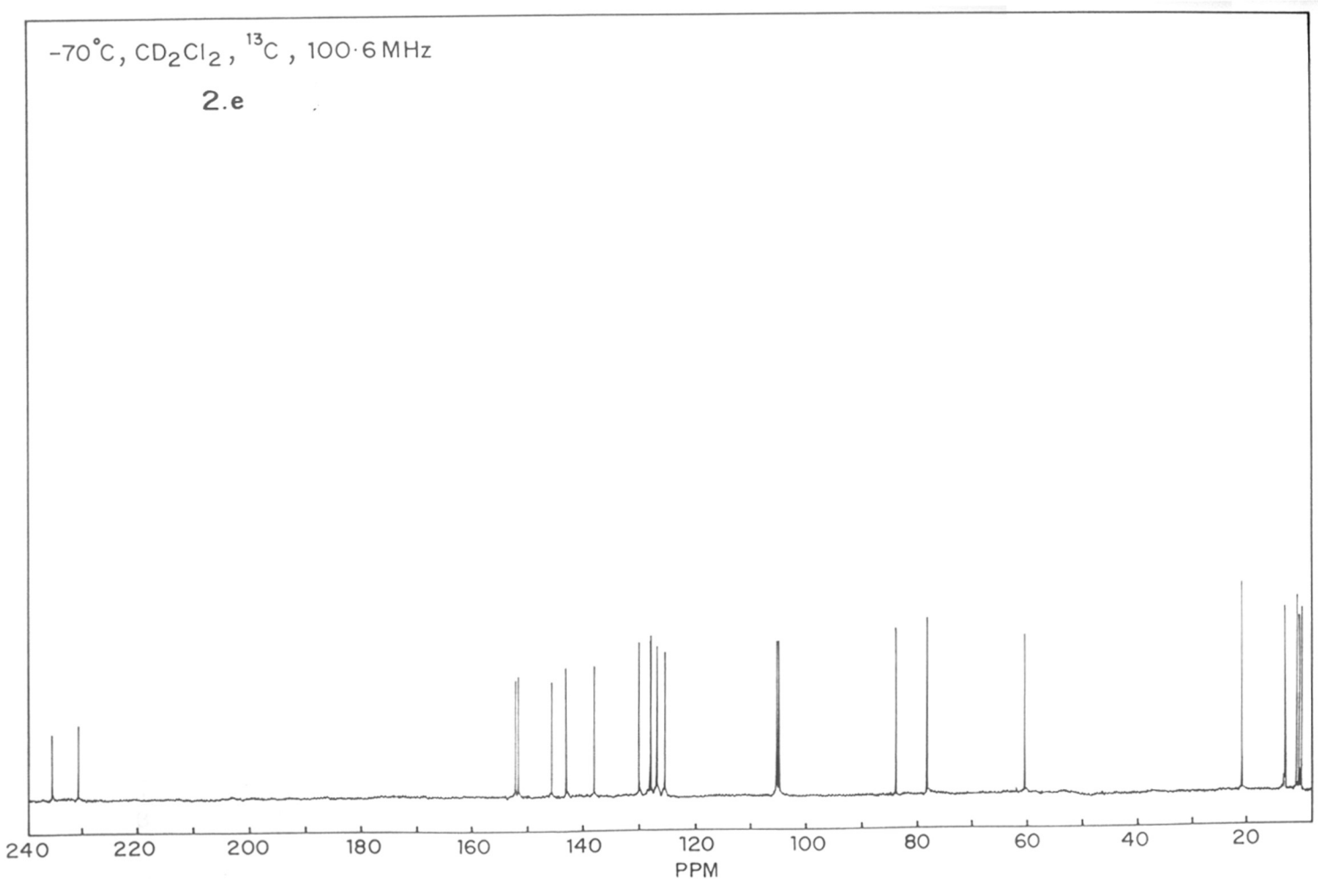
1.5
1.0
PPM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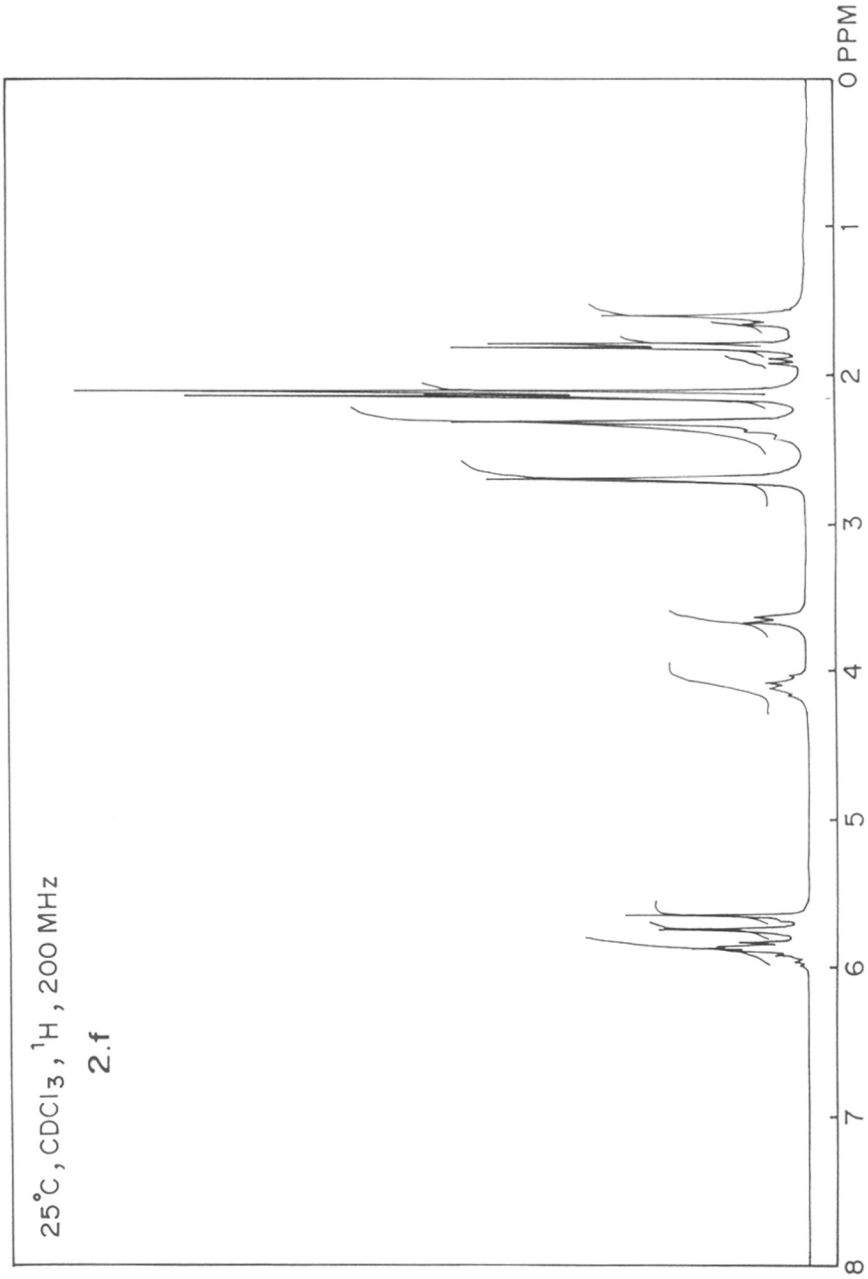
20
PPM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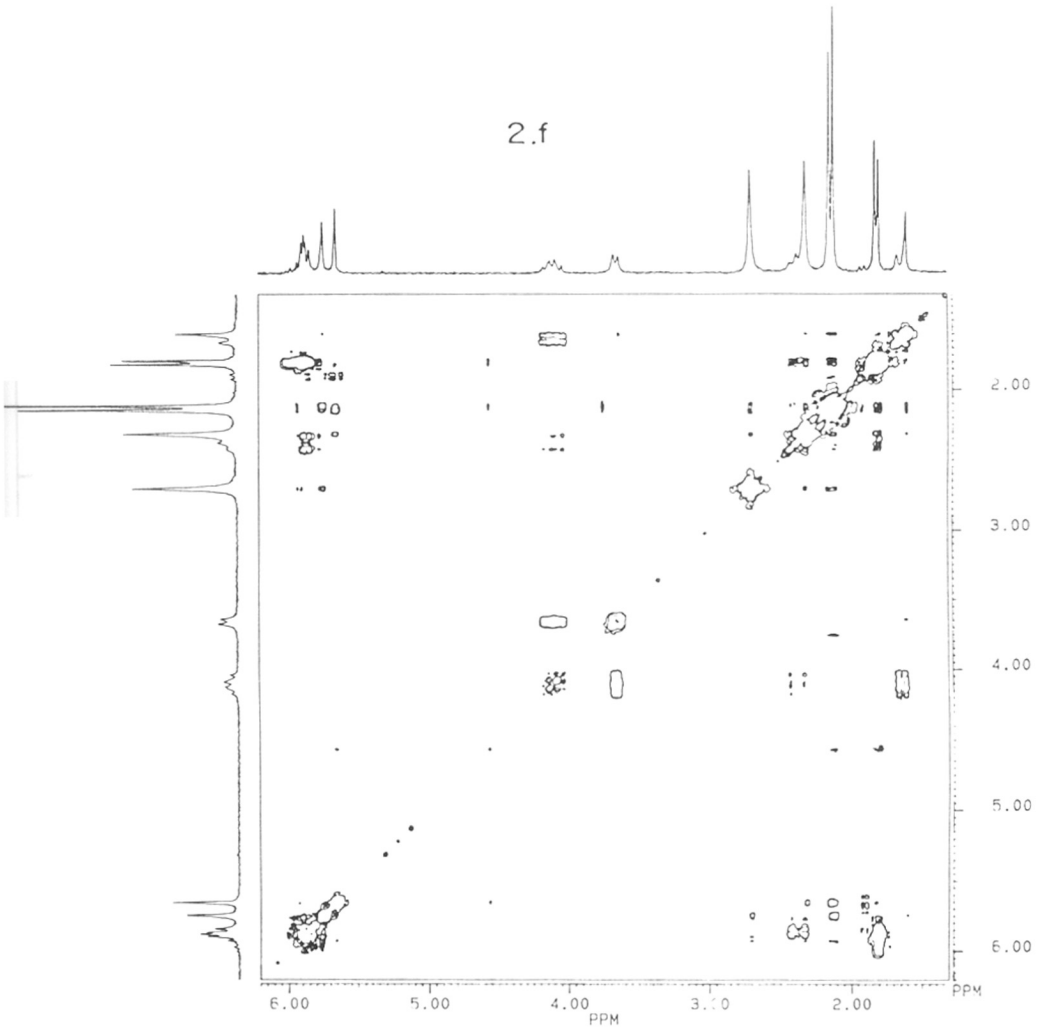
0 PPM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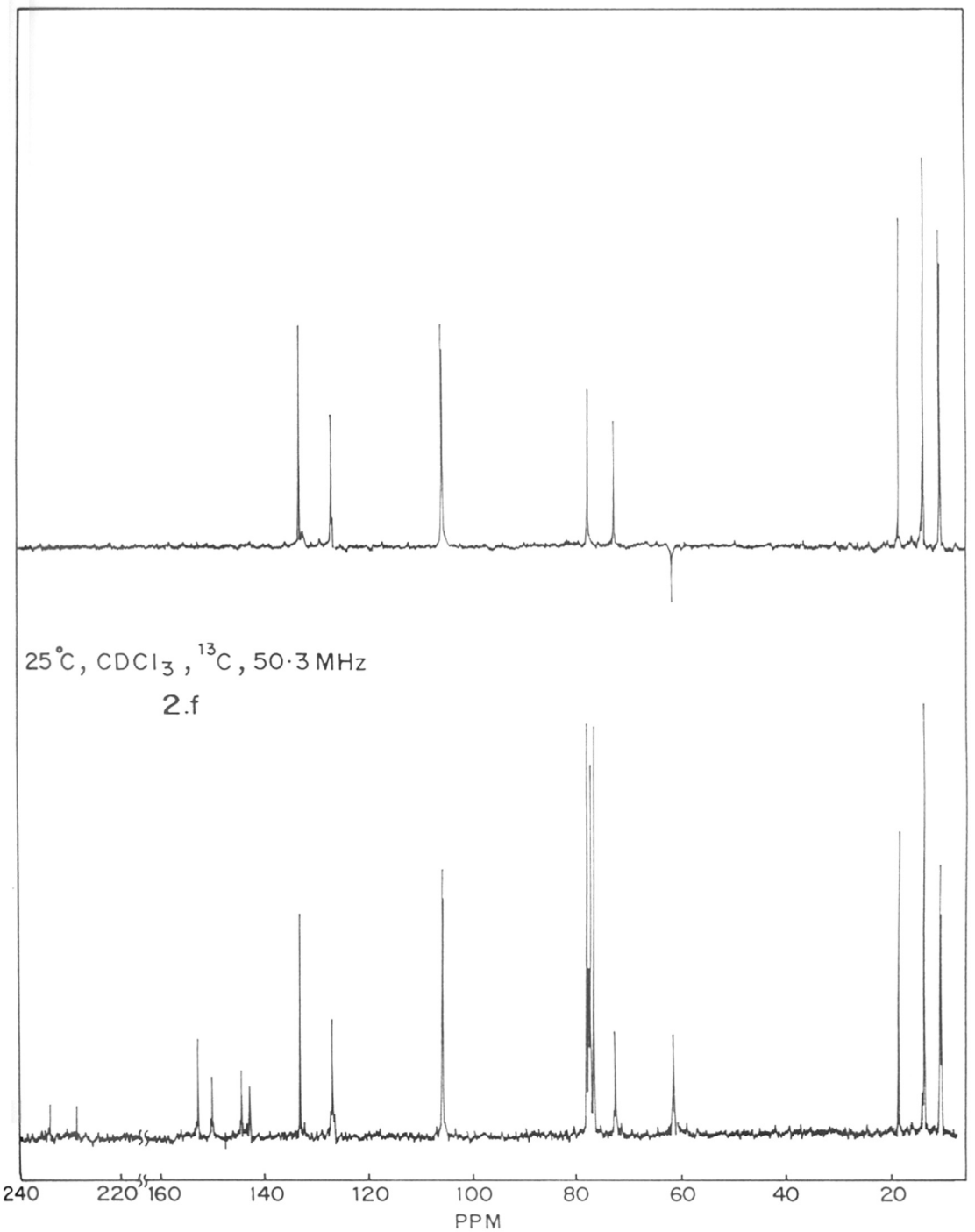
PPM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140
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60
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20
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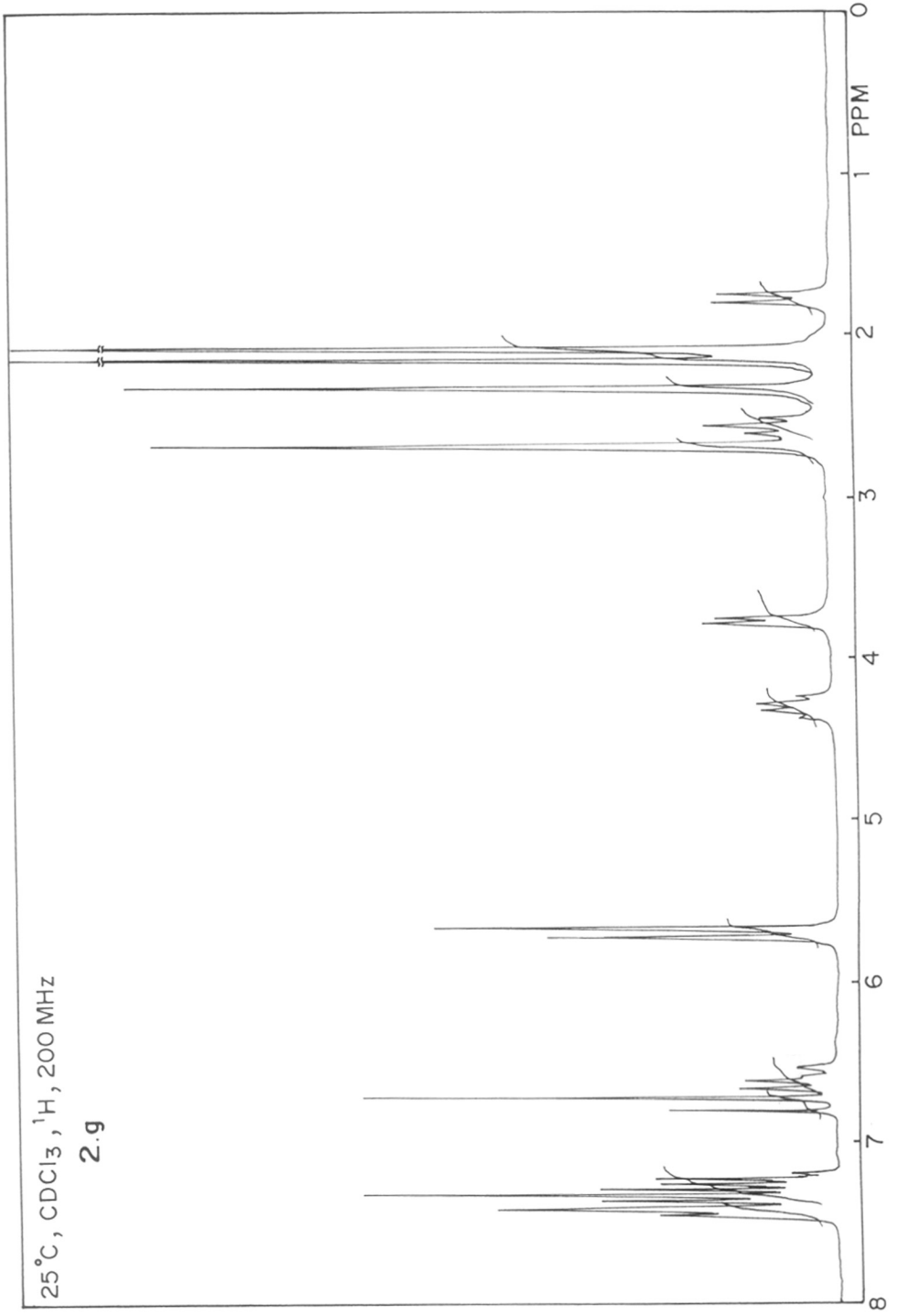
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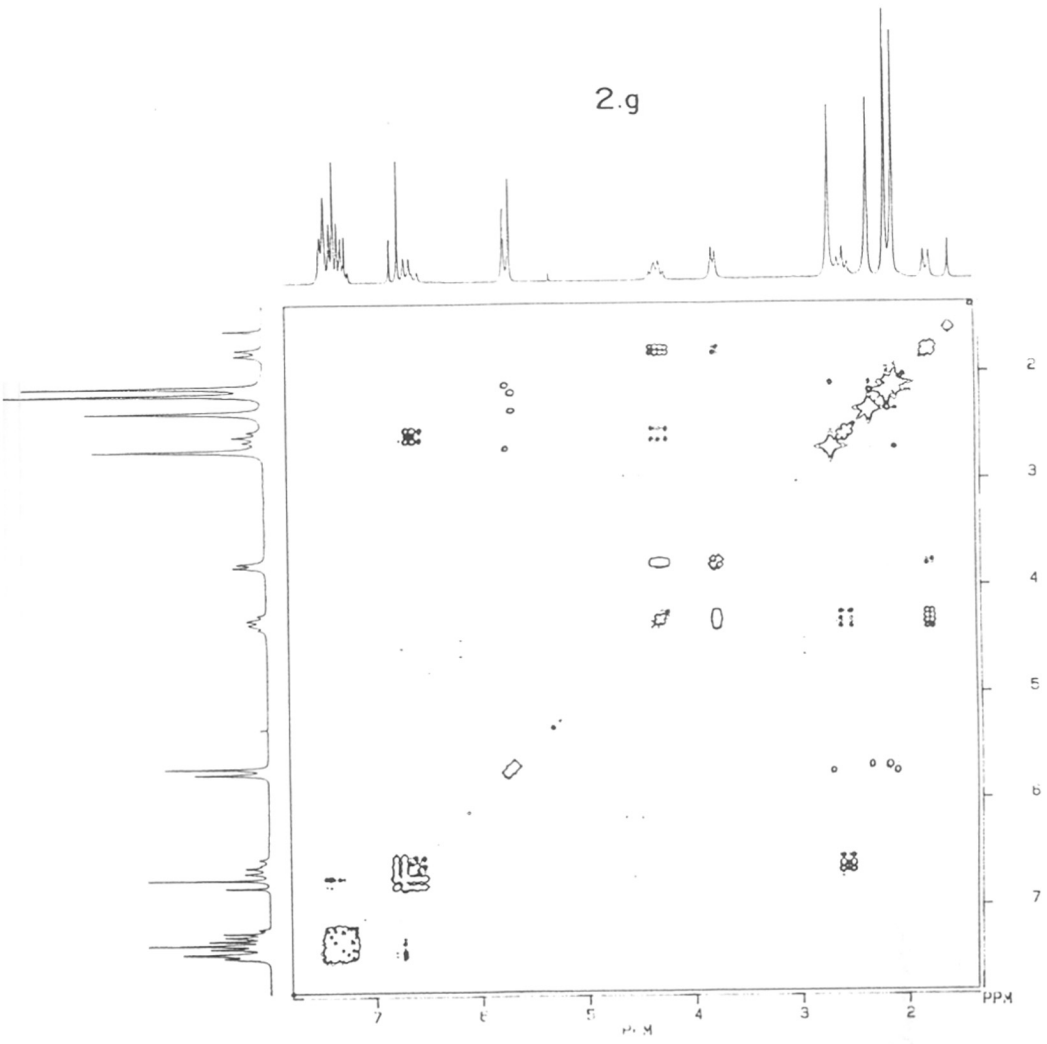
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3
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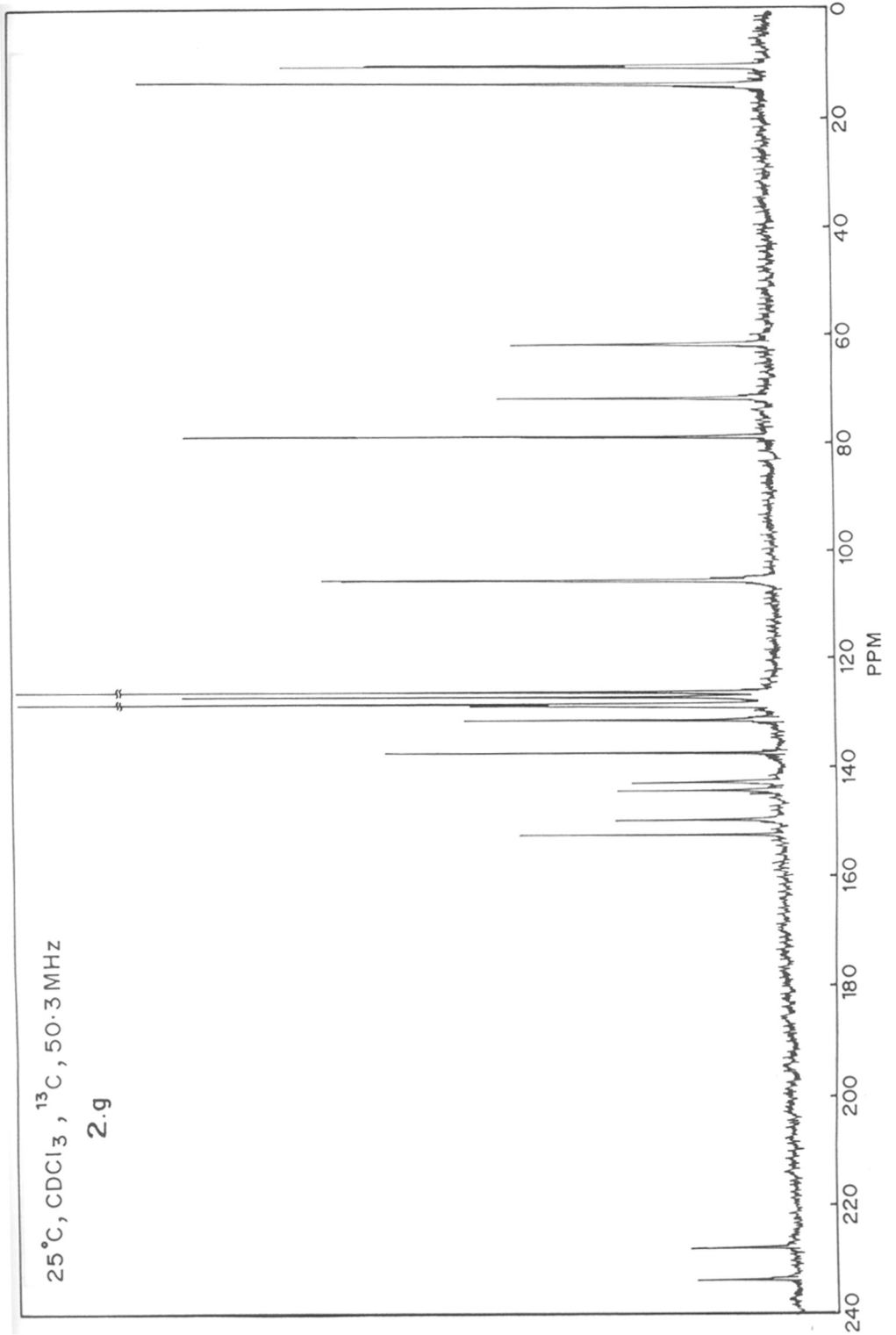
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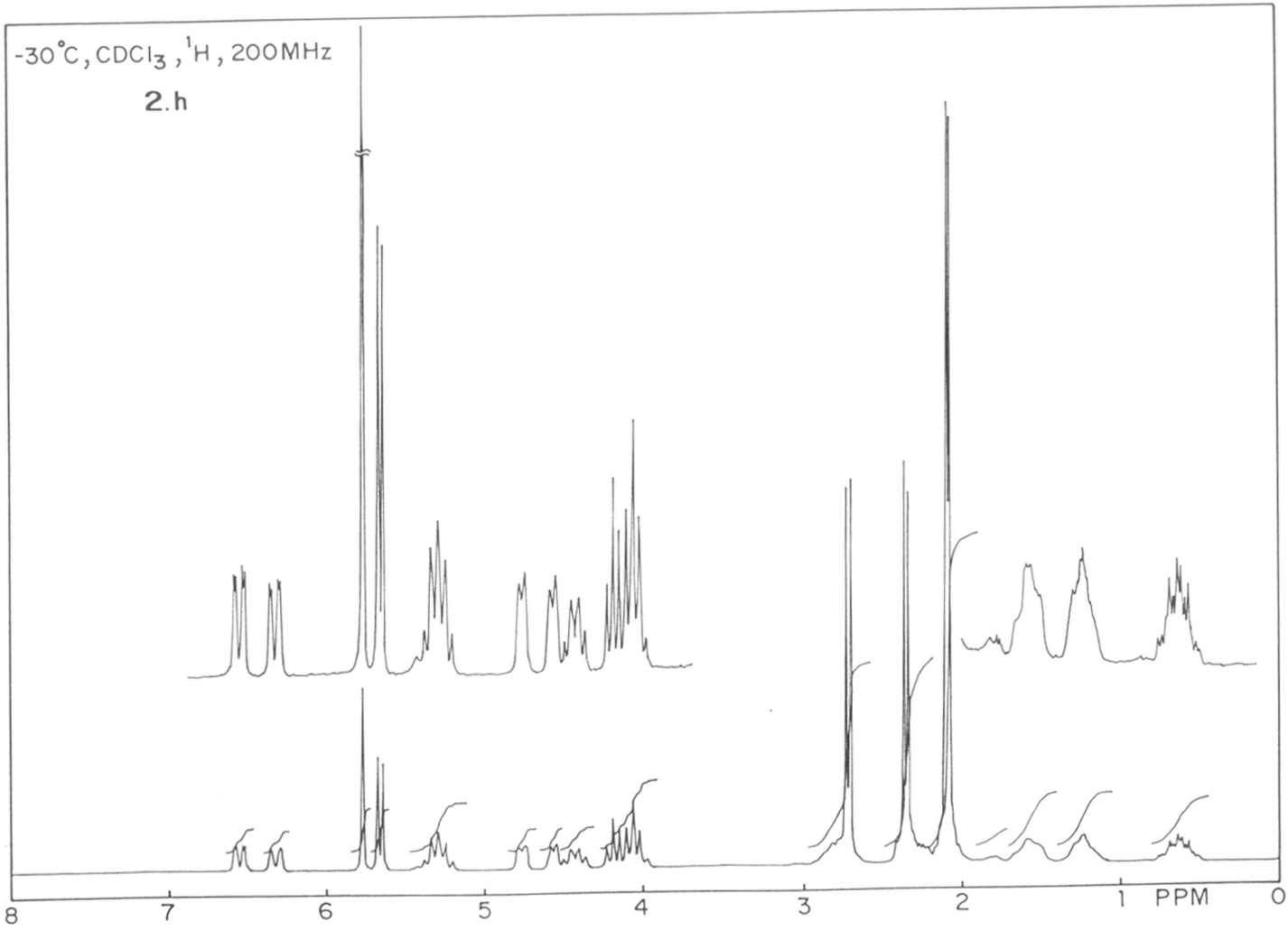
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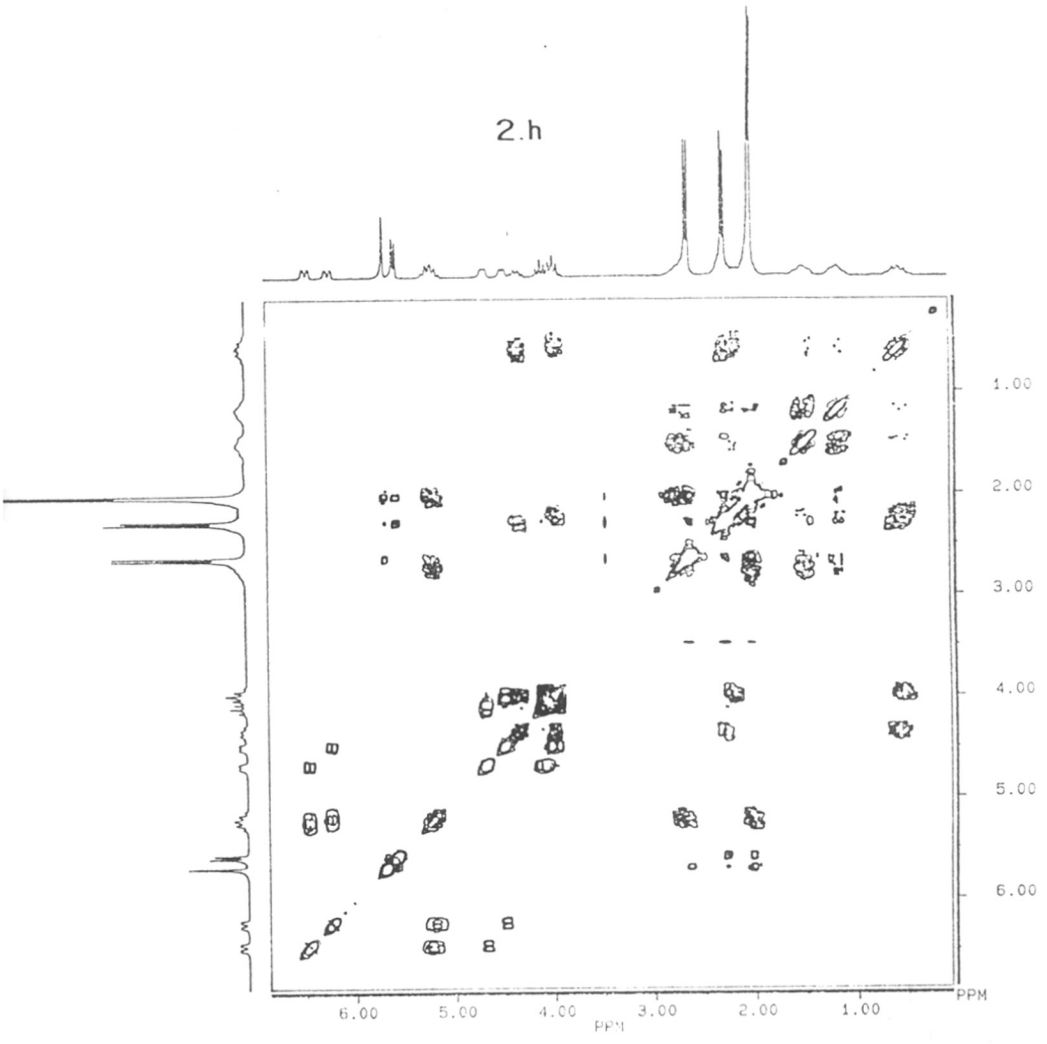
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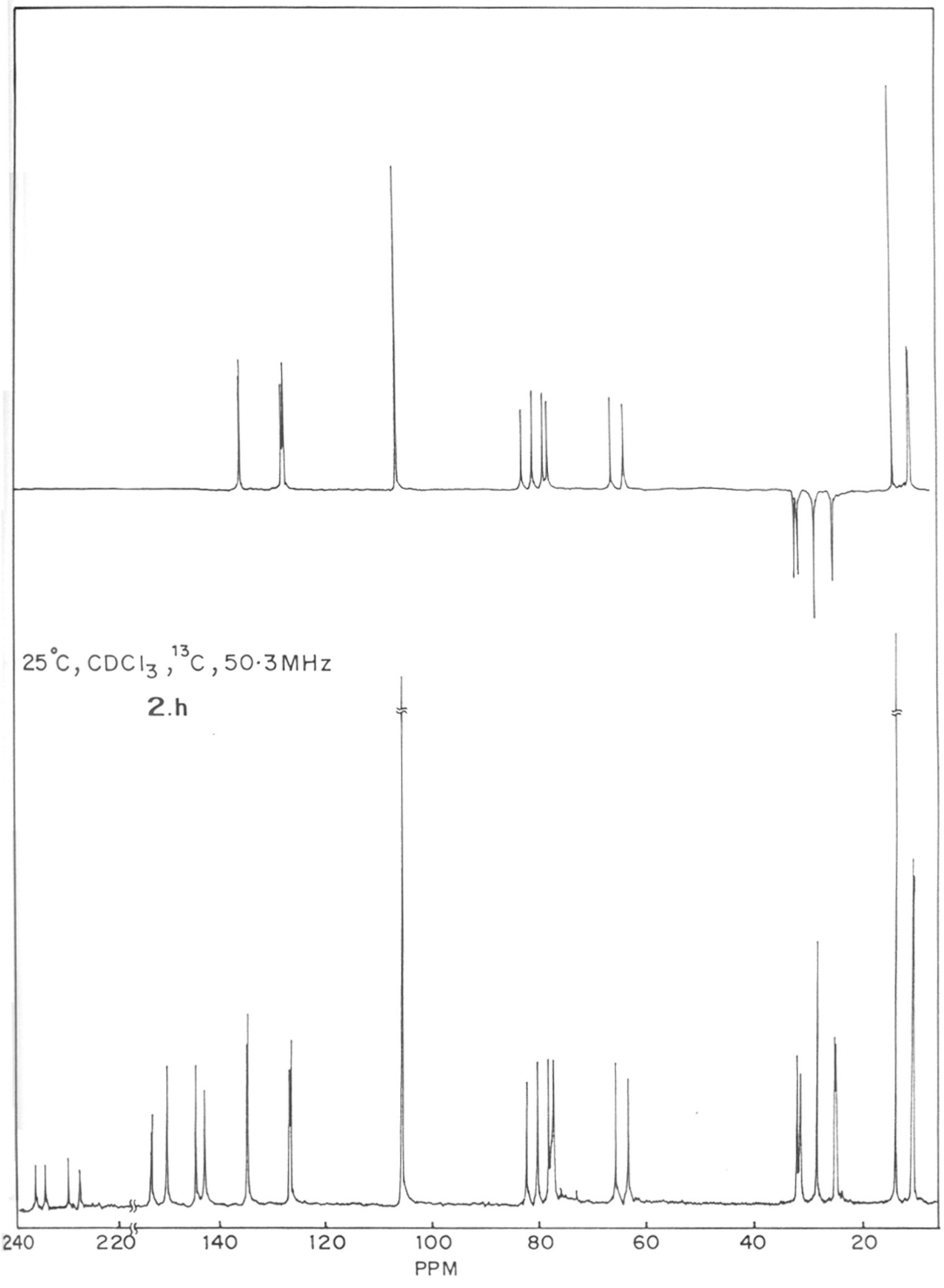
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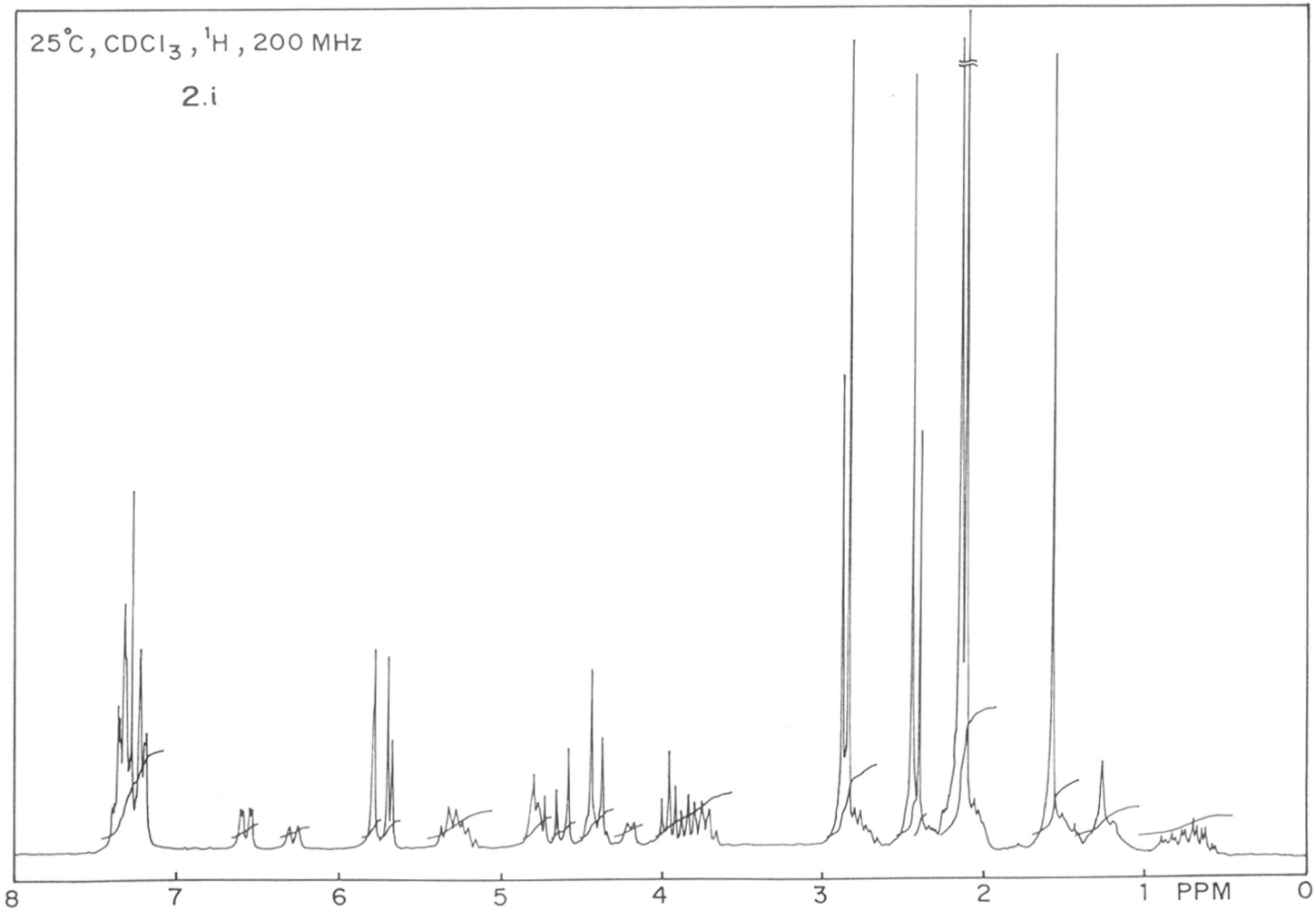
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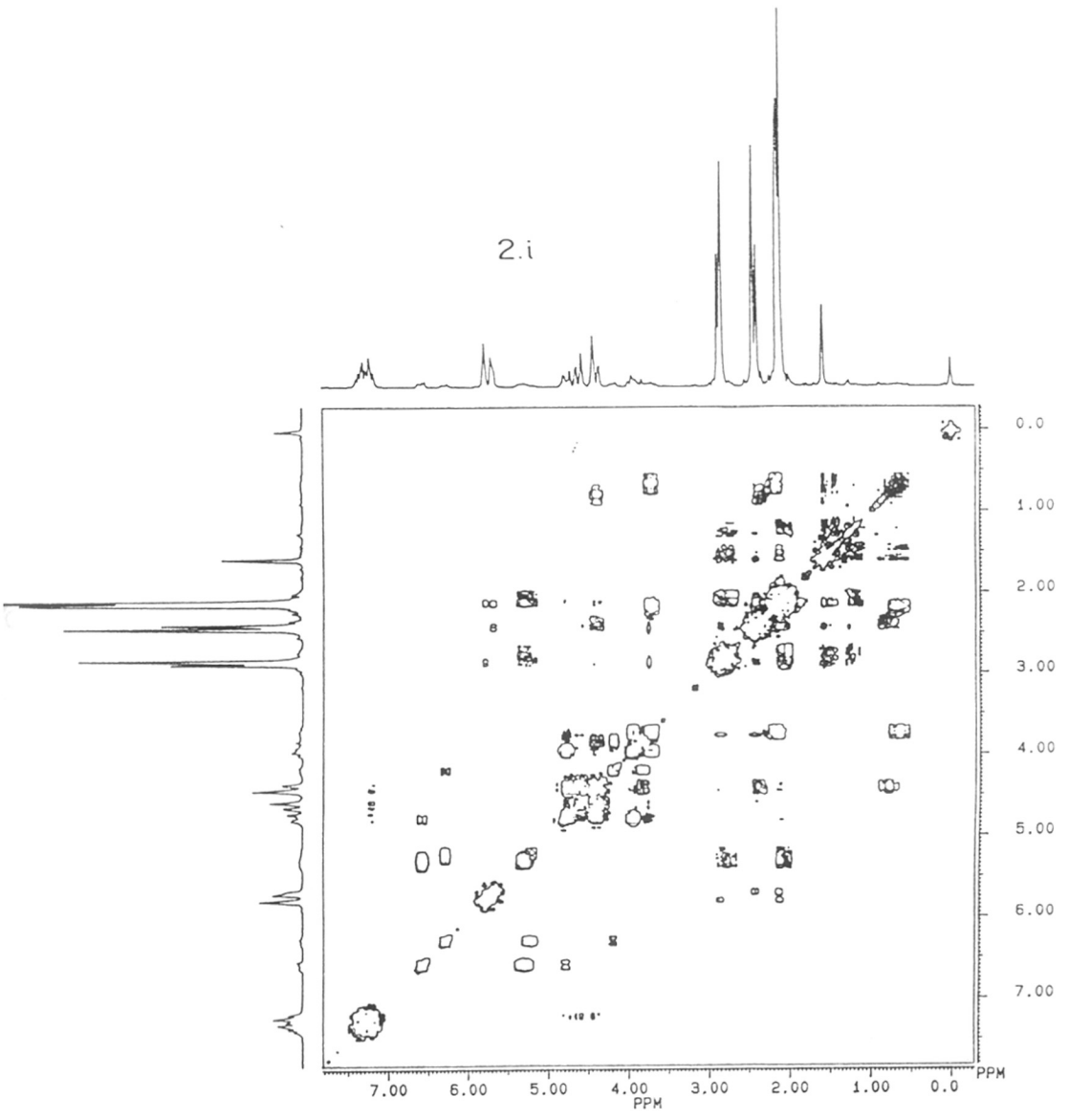
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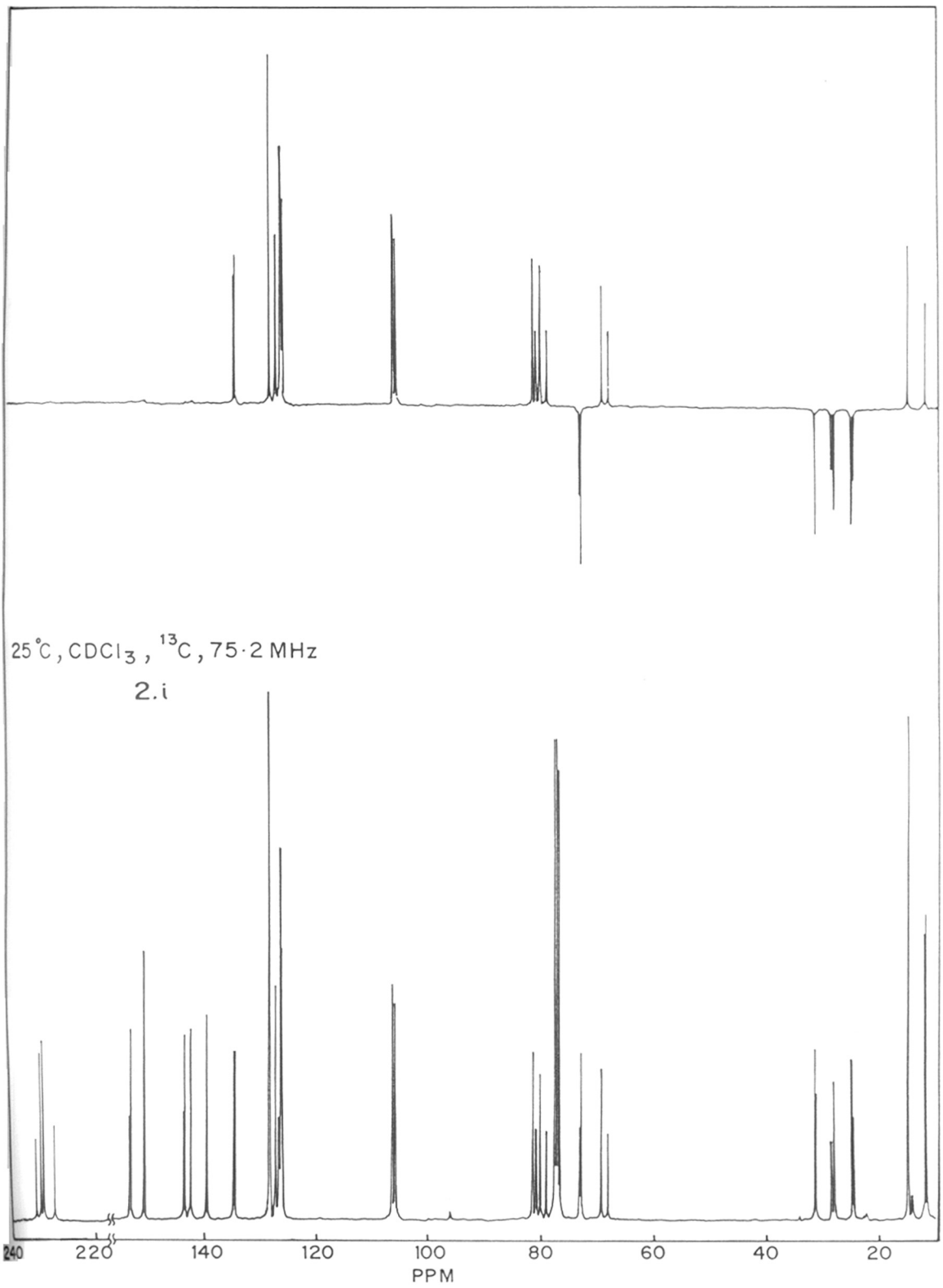
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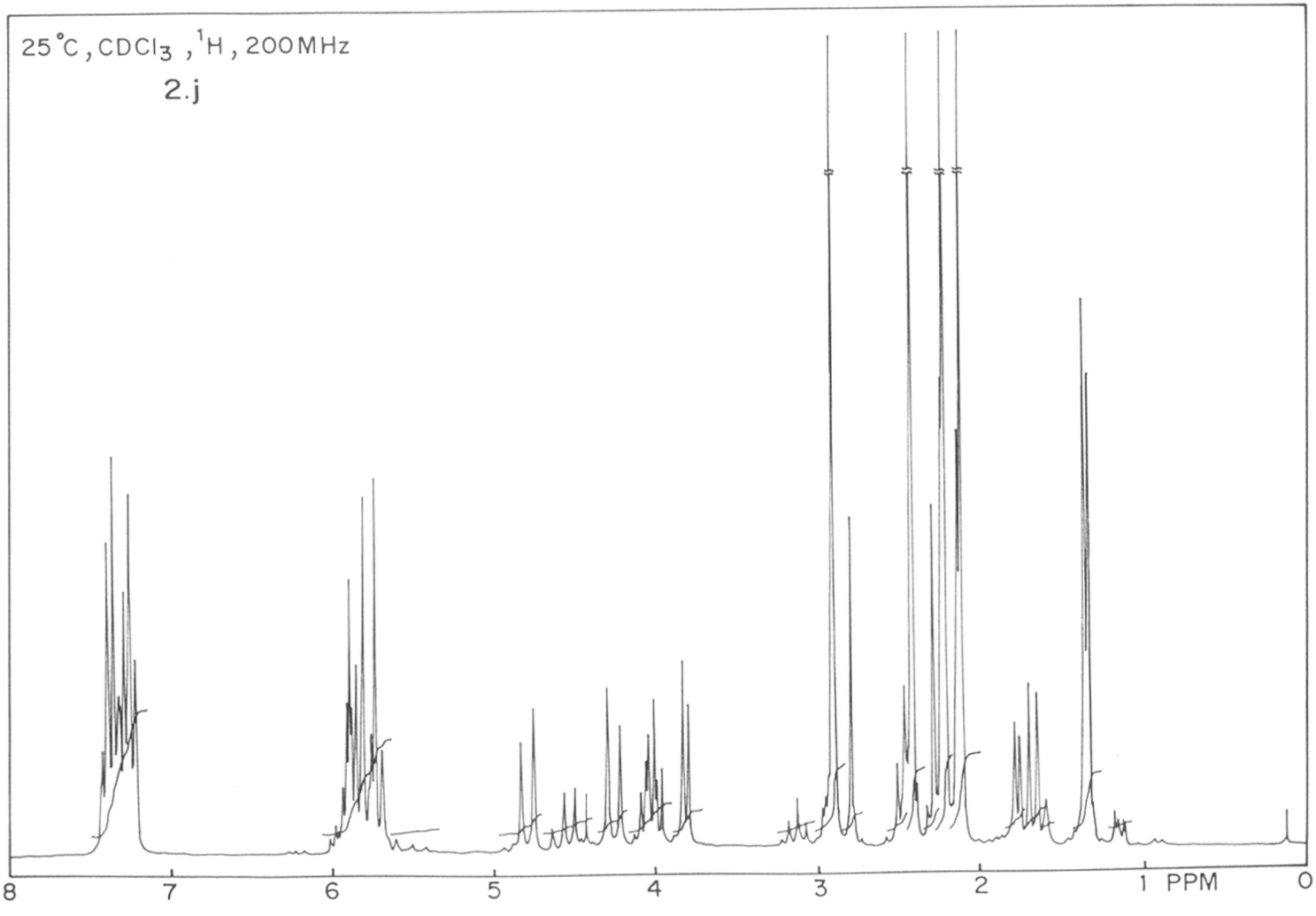
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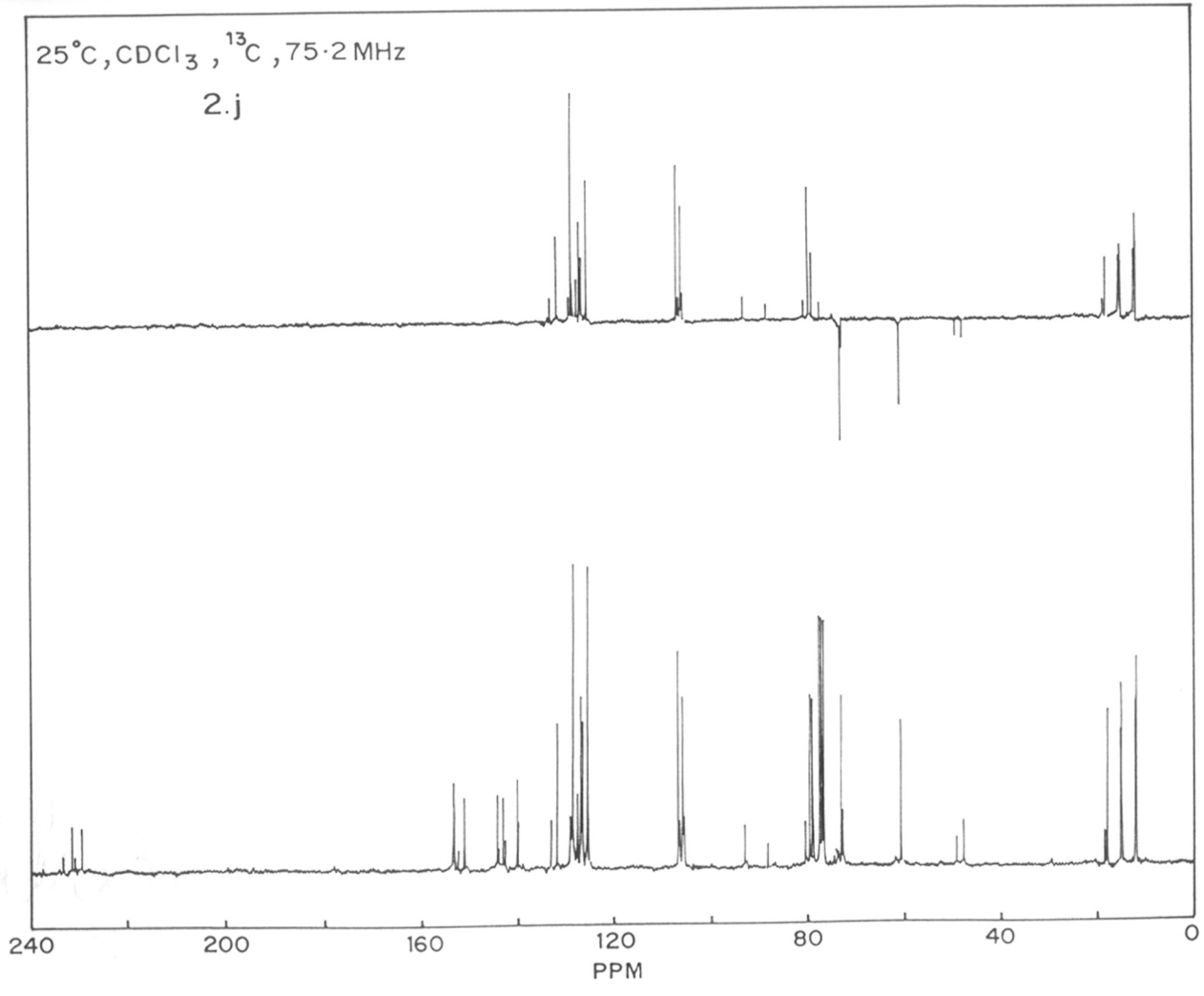
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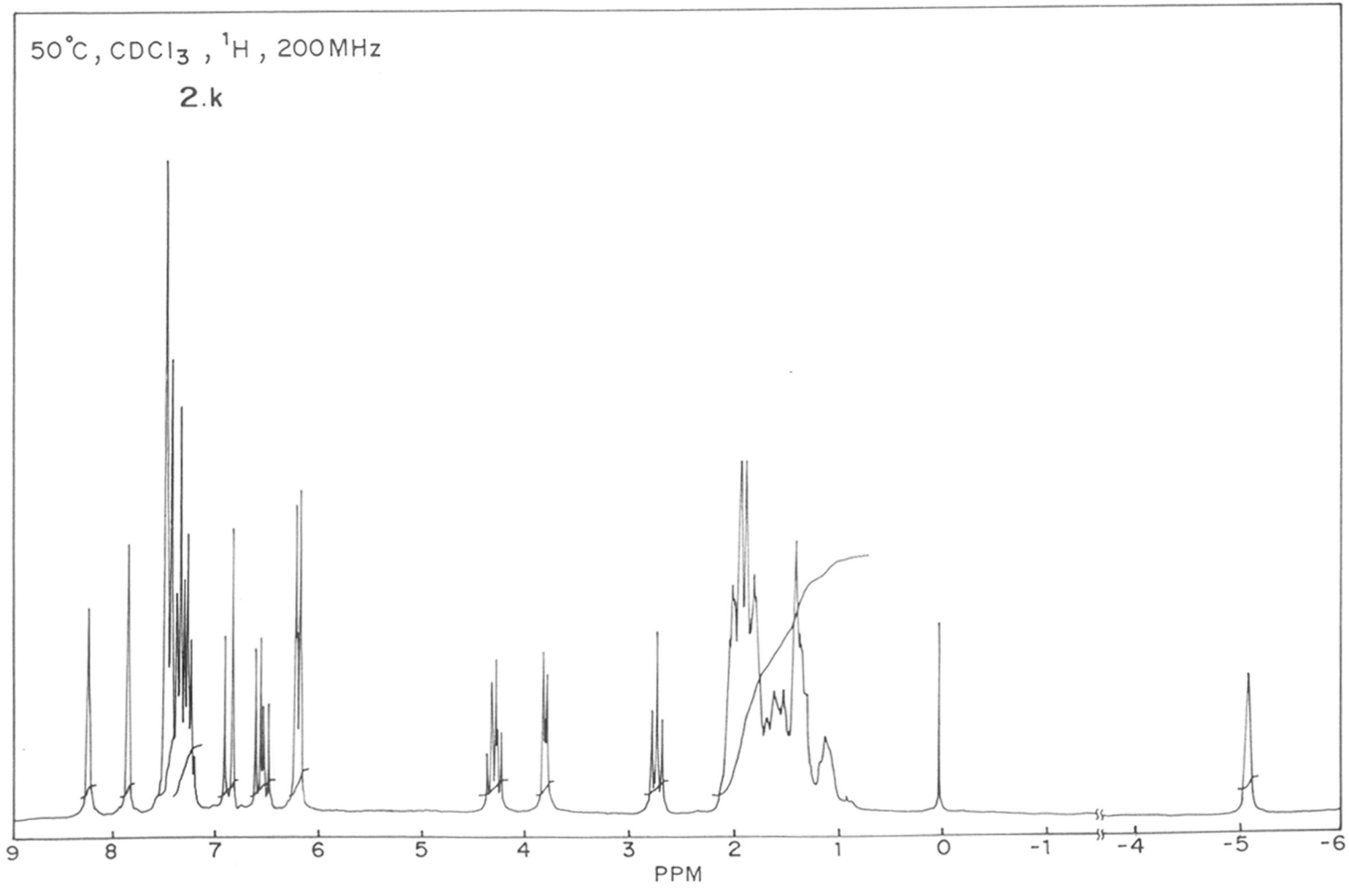
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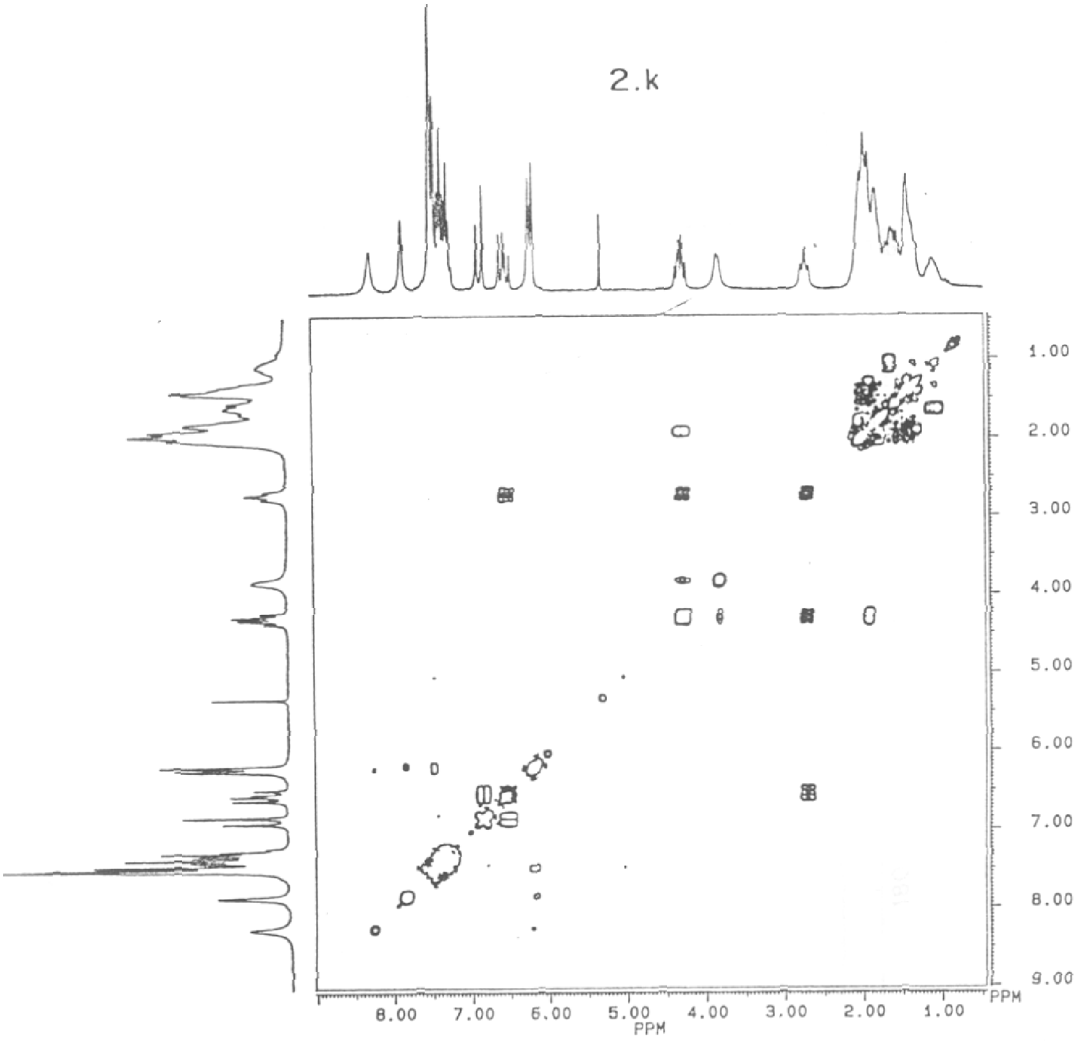
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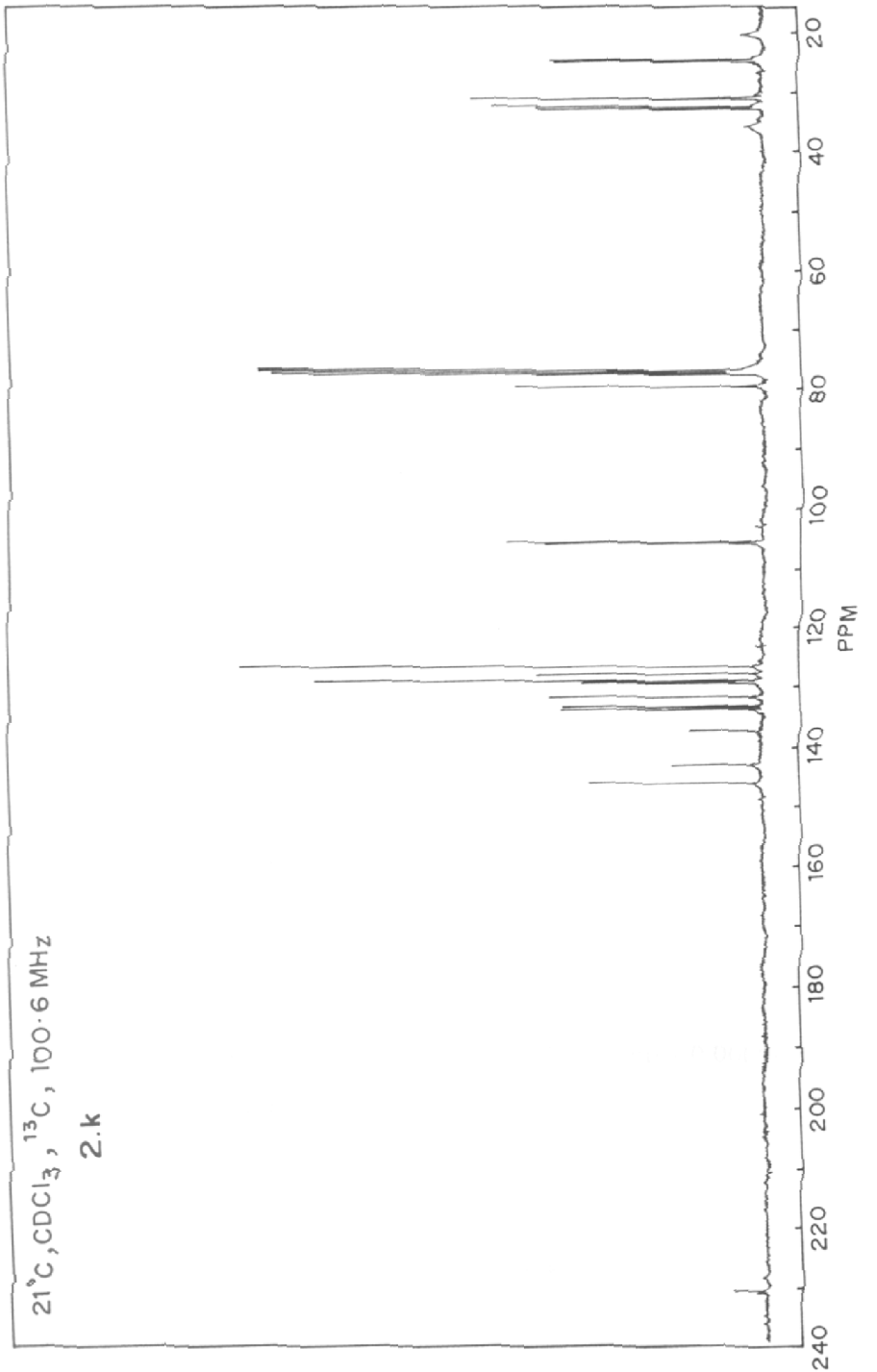
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2.k
240
220
200
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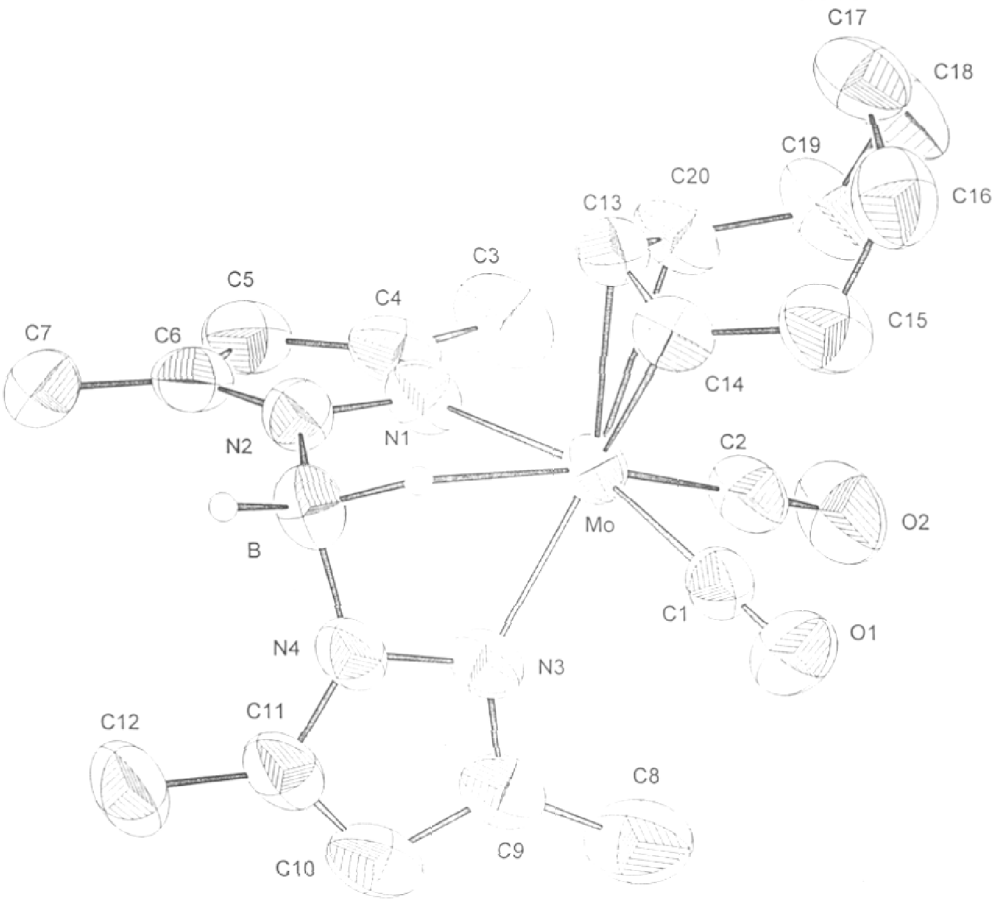
160
140
120
100
80
60
40
20
PPM

Table 1. X-ray Crystallographic Data and Structure Refinement of Complex C20H27BMoN4O2 (**2h**).

formula	$C_{20}H_{27}BMoN_4O_2$
fw	462.21
crys syst	Orthorhombic
space group	P c 2_1 n
a(Å)	8.486(2)
b(Å)	12.296(3)
c(Å)	20.476(3)
V(A^3)	2136.5(8)
Z	4
D_{calcd} (mg m^{-3})	1.437
μ (mm^{-1})	0.636
F (000)	952
cryst size (mm)	0.06 x 0.22 x 1.2
radiation	MoKα (λ = 0.70930 Å)
temp(K)	293(2)
scan type	ω/2θ
scan width (deg)	0.8 + 0.35 tanθ
2θ range (deg)	1.99-23.45
no. of rflns collected	1668
no. of rflns obsd	1668 [R (int) = 0.0000]
no. of params varied	260
GOF	1.084
R [I > 2 sigma (I)]	0.0258
R_w [I > 2 *sigma (I)*]	0.0691



ORTEP view of the molecular structure of **2h**

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for C20H27BMoN4O2 (2h). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Mo	1664(1)	0	691(1)	43(1)
O(1)	4734(5)	191(5)	1511(2)	81(1)
O(2)	630(7)	1670(4)	1726(2)	88(1)
N(1)	-160(5)	199(4)	-80(2)	52(1)
N(2)	404(5)	-239(4)	-653(2)	51(2)
N(3)	2865(5)	1095(4)	25(2)	49(1)
N(4)	3020(6)	631(5)	-575(2)	53(1)
B	2201(10)	-479(6)	-629(3)	52(2)
B(HA)	2735(5)	-1019(4)	-1006(2)	36(1)
B(HB)	2432(8)	-733(5)	-95(3)	74(2)
C(1)	3600(6)	106(7)	1208(2)	52(1)
C(2)	996(7)	1039(5)	1341(3)	60(1)
C(3)	-2523(8)	1196(6)	282(3)	77(2)
C(4)	-1560(6)	636(5)	-213(3)	59(2)
C(5)	-1891(7)	459(6)	-889(3)	66(2)
C(6)	-627(5)	-83(6)	-1133(2)	55(1)
C(7)	-332(8)	-472(6)	-1818(3)	72(2)
C(8)	3479(8)	2860(7)	551(4)	86(2)
C(9)	3417(5)	2117(5)	-19(3)	56(1)
C(10)	3887(8)	2288(6)	-657(3)	67(2)
C(11)	3625(6)	1349(6)	-991(3)	62(2)
C(12)	3924(8)	1042(8)	-1701(3)	85(2)
C(13)	554(6)	-1568(4)	977(3)	51(1)
C(14)	2103(6)	-1666(4)	1221(3)	53(1)
C(15)	2495(8)	-1730(6)	1931(3)	78(2)
C(16)	1660(9)	-2446(7)	2356(3)	83(2)
C(17)	-56(9)	-2575(5)	2280(3)	76(2)
C(18)	-988(10)	-1548(6)	2370(3)	96(2)
C(19)	-803(9)	-675(5)	1945(3)	80(2)
C(20)	-530(6)	-857(5)	1241(3)	59(1)

Table 3. Bond Lengths (A) and Bond Angles (deg) for C20H27BMoN4O2 (2h).

Mo-C(2)	1.930(6)
Mo-C(1)	1.959(5)
Mo-N(3)	2.170(4)
Mo-N(1)	2.224(4)
Mo-C(13)	2.225(5)
Mo-C(14)	2.348(5)
Mo-C(20)	2.417(5)
Mo-B(HB)	1.955(2)
O(1)-C(1)	1.150(6)
O(2)-C(2)	1.148(7)
N(1)-C(4)	1.333(6)
N(1)-N(2)	1.376(6)
N(2)-C(6)	1.330(6)
N(2)-B	1.554(9)
N(3)-C(9)	1.345(7)
N(3)-N(4)	1.360(7)
N(4)-C(11)	1.329(9)
N(4)-B	1.535(9)
B-B(HA)	1.115(1)
B-B(HB)	1.155(1)
C(3)-C(4)	1.474(9)
C(4)-C(5)	1.428(9)
C(5)-C(6)	1.359(9)
C(6)-C(7)	1.503(9)
C(8)-C(9)	1.482(10)
C(9)-C(10)	1.382(8)
C(10)-C(11)	1.360(10)
C(11)-C(12)	1.524(8)
C(13)-C(20)	1.379(8)
C(13)-C(14)	1.411(8)
C(14)-C(15)	1.492(8)
C(15)-C(16)	1.427(10)
C(16)-C(17)	1.473(10)
C(17)-C(18)	1.503(10)
C(18)-C(19)	1.390(9)
C(19)-C(20)	1.477(9)
C(2)-Mo-C(1)	80.2(3)
C(2)-Mo-N(3)	99.3(2)
C(1)-Mo-N(3)	84.5(2)
C(2)-Mo-N(1)	102.3(2)
C(1)-Mo-N(1)	163.7(2)
N(3)-Mo-N(1)	79.2(2)
C(2)-Mo-C(13)	105.5(2)
C(1)-Mo-C(13)	105.6(3)
N(3)-Mo-C(13)	154.4(2)
N(1)-Mo-C(13)	89.3(2)
C(2)-Mo-C(14)	107.7(2)
C(1)-Mo-C(14)	71.0(3)
N(3)-Mo-C(14)	139.2(2)

C(13)-Mo-C(14)	35.8(2)
C(2)-Mo-C(20)	75.0(2)
C(1)-Mo-C(20)	115.0(2)
N(3)-Mo-C(20)	157.6(2)
N(1)-Mo-C(20)	81.0(2)
C(13)-Mo-C(20)	34.2(2)
C(14)-Mo-C(20)	61.7(2)
C(4)-N(1)-N(2)	107.1(4)
C(4)-N(1)-Mo	144.1(4)
N(2)-N(1)-Mo	108.7(3)
C(6)-N(2)-N(1)	110.2(4)
C(6)-N(2)-B	134.1(4)
N(1)-N(2)-B	112.9(4)
C(9)-N(3)-N(4)	107.4(5)
C(9)-N(3)-Mo	141.7(4)
N(4)-N(3)-Mo	110.7(4)
C(11)-N(4)-N(3)	109.7(6)
C(11)-N(4)-B	136.0(6)
N(3)-N(4)-B	113.2(4)
N(4)-B-N(2)	106.1(4)
Mo-B(HB)-B	126.7(1)
B(HA)-B-B(HB)	115.2(1)
O(1)-C(1)-Mo	178.6(7)
O(2)-C(2)-Mo	178.5(5)
N(1)-C(4)-C(5)	108.2(5)
N(1)-C(4)-C(3)	122.9(6)
C(5)-C(4)-C(3)	129.0(5)
C(6)-C(5)-C(4)	106.0(5)
N(2)-C(6)-C(5)	108.5(5)
N(2)-C(6)-C(7)	122.3(5)
C(5)-C(6)-C(7)	129.2(5)
N(3)-C(9)-C(10)	107.7(6)
N(3)-C(9)-C(8)	122.5(5)
C(10)-C(9)-C(8)	129.8(6)
C(11)-C(10)-C(9)	107.4(6)
N(4)-C(11)-C(10)	107.8(5)
N(4)-C(11)-C(12)	120.7(7)
C(10)-C(11)-C(12)	131.6(6)
C(20)-C(13)-C(14)	122.5(5)
C(20)-C(13)-Mo	80.6(3)
C(14)-C(13)-Mo	76.9(3)
C(13)-C(14)-C(15)	123.8(5)
C(13)-C(14)-Mo	67.3(3)
C(15)-C(14)-Mo	122.2(4)
C(16)-C(15)-C(14)	121.1(6)
C(15)-C(16)-C(17)	119.5(6)
C(16)-C(17)-C(18)	114.6(7)
C(19)-C(18)-C(17)	120.8(5)
C(18)-C(19)-C(20)	120.8(6)
C(13)-C(20)-C(19)	125.6(5)
C(13)-C(20)-Mo	65.2(3)
C(19)-C(20)-Mo	120.7(5)

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for C20H27BMoN4O2 (2h).
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Mo	44(1)	45(1)	42(1)	0(1)	5(1)	7(1)
O(1)	71(2)	94(4)	76(2)	2(3)	-20(2)	-18(3)
O(2)	128(4)	60(3)	77(3)	-18(2)	37(3)	13(3)
N(1)	42(2)	62(4)	53(2)	9(2)	3(2)	6(2)
N(2)	47(2)	59(4)	48(2)	3(2)	-3(2)	0(2)
N(3)	47(2)	49(3)	52(3)	3(2)	11(2)	1(2)
N(4)	41(2)	72(3)	47(2)	6(2)	6(2)	-3(2)
B	45(3)	65(4)	47(3)	1(3)	5(3)	17(3)
C(1)	59(3)	52(3)	45(2)	-3(3)	7(2)	-2(3)
C(2)	68(4)	54(3)	57(3)	7(3)	11(3)	1(3)
C(3)	64(4)	81(4)	87(4)	20(4)	17(3)	23(3)
C(4)	46(3)	53(3)	78(4)	26(3)	3(2)	4(2)
C(5)	57(4)	66(4)	74(4)	25(3)	-14(3)	-7(3)
C(6)	50(2)	54(3)	62(3)	14(4)	-8(2)	-10(3)
C(7)	82(4)	75(4)	59(3)	-1(3)	-12(3)	-23(3)
C(8)	85(5)	58(4)	117(6)	-11(4)	28(4)	-5(3)
C(9)	41(3)	58(3)	69(4)	10(3)	9(2)	6(2)
C(10)	43(3)	72(4)	84(4)	24(3)	6(3)	-2(3)
C(11)	33(2)	94(5)	57(3)	16(3)	4(2)	-1(3)
C(12)	60(3)	142(7)	54(3)	10(4)	9(3)	-10(4)
C(13)	55(3)	47(3)	51(3)	-1(2)	2(2)	-6(2)
C(14)	50(3)	47(3)	63(3)	6(3)	7(2)	9(2)
C(15)	74(4)	85(4)	77(4)	27(4)	-7(3)	3(4)
C(16)	99(5)	79(5)	72(4)	-5(4)	4(3)	11(4)
C(17)	87(4)	60(3)	83(4)	19(3)	15(3)	-1(3)
C(18)	122(6)	81(5)	84(4)	27(4)	55(5)	26(5)
C(19)	110(5)	53(4)	76(4)	13(3)	42(4)	29(4)
C(20)	53(3)	62(3)	62(3)	23(3)	10(2)	9(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for C20H27BMoN4O2 (2h).

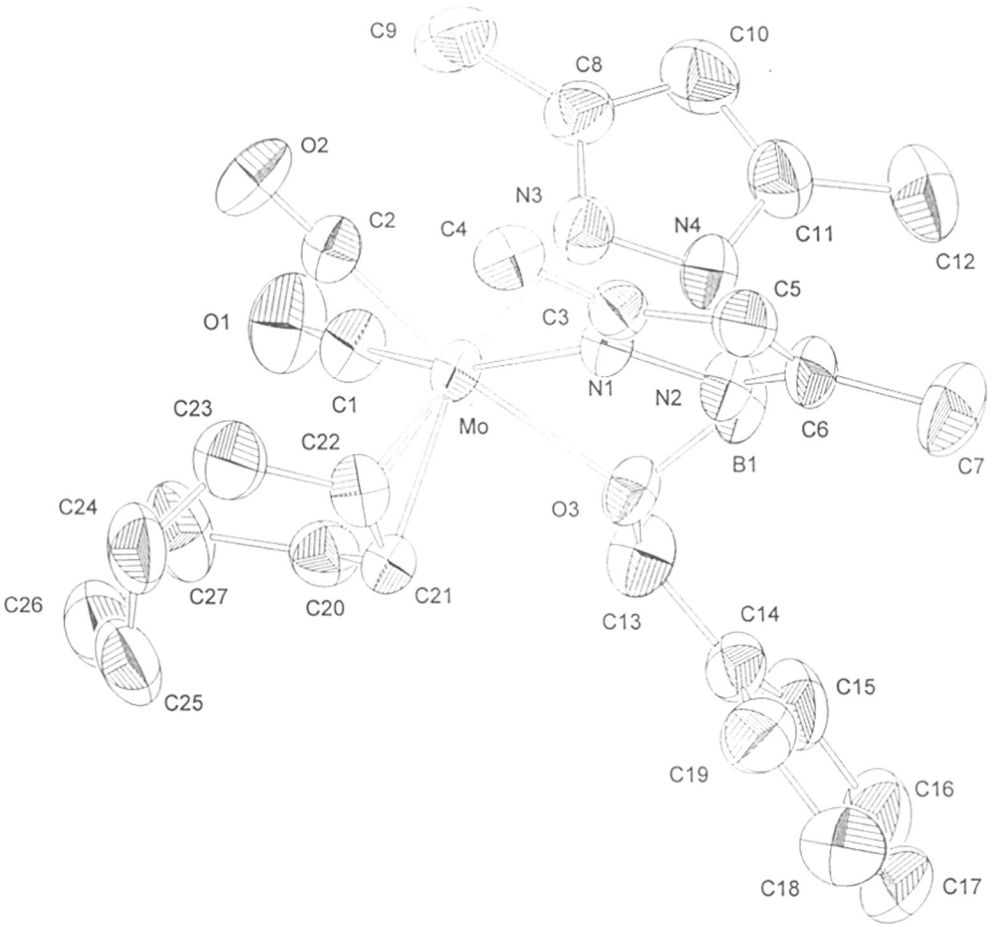
	x	y	z	U(eq)
BHA	2735(55)	-1019(38)	-1006(22)	36(11)
BHB	2432(81)	-733(53)	-95(32)	74(19)
H(3C)	-3527	1497	118	79
H(3A)	-2753	700	669	79
H(3B)	-1885	1842	479	79
H(5)	-2893	690	-1108	66
H(7C)	-1200	-310	-2119	70
H(7A)	686	-138	-1999	70
H(7B)	-136	-1306	-1830	70
H(8C)	3922	3563	428	87
H(8A)	2391	2944	737	87
H(8B)	4164	2507	902	87
H(10)	4331	2979	-844	69
H(12C)	4373	1726	-1949	84
H(12A)	4641	449	-1760	84
H(12B)	2876	892	-1934	84
H(13)	270	-1973	562	56
H(14)	3014	-1748	895	60
H(17A)	-509	-3172	2584	78
H(17B)	-317	-2870	1811	78
H(18)	-1664	-1490	2769	84
H(19)	-834	81	2132	76
H(20)	-1245	-464	929	65
H(15A)	2341	-990	2119	84
H(15B)	3635	-1945	1978	84
H(16A)	2165	-3183	2320	85
H(16B)	1827	-2173	2819	85

Torsion angles C20H27BMoN4O2(2h)

N3	MO	N1	N2	63.9(4)	N3	MO	N1	C4	-107.3(5)
C1	MO	N1	N2	61.2(5)	C1	MO	N1	C4	-110.0(6)
C2	MO	N1	N2	161.1(6)	C2	MO	N1	C4	-10.2(4)
C13	MO	N1	N2	-93.2(5)	C13	MO	N1	C4	95.5(5)
N1	MO	N3	N4	-59.0(4)	N1	MO	N3	C9	114.2(5)
C1	MO	N3	N4	120.3(5)	C1	MO	N3	C9	-66.5(5)
C2	MO	N3	N4	-160.2(6)	C2	MO	N3	C9	13.0(4)
C13	MO	N3	N4	5.3(3)	C13	MO	N3	C9	178.5(6)
N1	MO	C1	O1	50.9(5)	N3	MO	C1	O1	48.3(5)
C2	MO	C1	O1	-51.9(6)	C13	MO	C1	O1	-155.6(8)
N1	MO	C2	O2	-127.6(7)	N3	MO	C2	O2	-46.2(5)
C1	MO	C2	O2	36.9(5)	C13	MO	C2	O2	140.3(7)
N1	MO	C13	C14	158.7(6)	N1	MO	C13	C20	-75.7(5)
N3	MO	C13	C14	96.1(5)	N3	MO	C13	C20	-138.2(6)
C1	MO	C13	C14	-14.5(4)	C1	MO	C13	C20	111.2(6)
C2	MO	C13	C14	-98.7(6)	C2	MO	C13	C20	26.9(5)
MO	N1	N2	B	-11.2(4)	MO	N1	N2	C6	-176.8(7)
C4	N1	N2	B	163.5(9)	C4	N1	N2	C6	-2.1(5)
MO	N1	C4	C3	-6.9(4)	MO	N1	C4	C5	173.1(8)
N2	N1	C4	C3	-178.3(10)	N2	N1	C4	C5	1.8(4)
N1	N2	B	N4	-67.3(6)	C6	N2	B	N4	94.2(8)
N1	N2	C6	C5	1.6(5)	N1	N2	C6	C7	-179.4(10)
B	N2	C6	C5	-160.2(10)	B	N2	C6	C7	18.8(5)
MO	N3	N4	B	3.8(4)	MO	N3	N4	C11	174.7(7)
C9	N3	N4	B	-171.9(8)	C9	N3	N4	C11	-.9(5)
MO	N3	C9	C8	7.9(4)	MO	N3	C9	C10	-172.4(8)
N4	N3	C9	C8	-178.8(9)	N4	N3	C9	C10	.9(5)
N3	N4	B	N2	73.5(6)	C11	N4	B	N2	-94.0(8)
N3	N4	C11	C10	.6(5)	N3	N4	C11	C12	-179.7(9)
B	N4	C11	C10	168.4(10)	B	N4	C11	C12	-11.9(5)
N1	C4	C5	C6	-.9(5)	C3	C4	C5	C6	179.2(11)
C4	C5	C6	N2	-.4(4)	C4	C5	C6	C7	-179.4(11)
N3	C9	C10	C11	-.6(4)	C8	C9	C10	C11	179.1(11)
C9	C10	C11	N4	.0(4)	C9	C10	C11	C12	-179.6(11)
MO	C13	C14	C15	114.1(7)	C20	C13	C14	C15	43.5(6)
MO	C13	C20	C19	-111.4(7)	C14	C13	C20	C19	-42.5(6)
C13	C14	C15	C16	47.7(7)	C14	C15	C16	C17	-39.5(6)
C15	C16	C17	C18	-60.3(8)	C16	C17	C18	C19	64.0(8)
C17	C18	C19	C20	36.0(6)	C18	C19	C20	C13	-47.8(7)

Table 1. X-ray Crystallographic Data and Structure Refinement of Complex $C_{27}H_{33}BMoN_4O_3$ (**2I**).

formula	$C_{27}H_{33}BMoN_4O_3$
fw	568.32
crys syst	Monoclinic
space group	$P2_1/n$
a(Å)	22.194(5)
b(Å)	10.493(2)
c(Å)	23.562(4)
β (deg)	96.058(10)
V(A^3)	5456(2)
Z	8
D_{calcd} (mg m^{-3})	1.384
μ (mm^{-1})	0.515
F (000)	2352
cryst size (mm)	0.25 x 0.40 x 1.15
radiation	MoKα (λ = 0.70930 Å)
temp(K)	293(2)
scan type	ω/2θ
scan width (deg)	0.8 + 0.35 tanθ
2θ range (deg)	1.20-23.46
no. of rflns collected	8030
no. of rflns obsd	8030 [R(int) = 0.0000]
no. of params varied	657
GOF	1.223
R [I > 2 sigma (I)]	0.0524
R_w [I > 2 sigma (I)]	0.1432



ORTEP view of the molecular structure of **2i**

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for C27H33BMoN4O3(2i). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
MoA	7698(1)	782(1)	5776(1)	36(1)
O(1A)	7398(3)	-1740(5)	5113(2)	77(2)
O(2A)	7804(3)	-1231(5)	6733(2)	70(2)
O(3A)	7483(2)	2413(4)	5139(2)	46(1)
N(1A)	7594(2)	2546(4)	6295(2)	38(1)
N(2A)	7329(2)	3536(5)	5979(2)	43(1)
N(3A)	6709(2)	1015(5)	5701(2)	48(1)
N(4A)	6514(2)	2189(5)	5492(2)	50(1)
C(1A)	7515(3)	-771(6)	5339(3)	50(2)
C(2A)	7763(3)	-458(6)	6372(3)	47(2)
C(3A)	7746(3)	2998(6)	6824(3)	40(1)
C(4A)	8030(3)	2197(7)	7299(3)	50(2)
C(5A)	7563(3)	4256(6)	6851(3)	49(2)
C(6A)	7304(3)	4571(6)	6309(3)	50(2)
C(7A)	7036(5)	5805(7)	6077(4)	74(2)
C(8A)	6214(3)	362(7)	5804(3)	52(2)
C(9A)	6251(4)	-989(8)	6018(4)	69(2)
C(10A)	5704(3)	1101(8)	5675(4)	69(2)
C(11A)	5906(3)	2245(7)	5478(3)	60(2)
C(12A)	5552(4)	3408(9)	5278(4)	85(3)
C(13A)	7382(4)	2267(7)	4535(3)	58(2)
C(14A)	7516(3)	3468(7)	4226(3)	53(2)
C(15A)	7940(4)	4319(8)	4449(4)	71(2)
C(16A)	8082(5)	5411(10)	4127(5)	92(3)
C(17A)	7797(6)	5547(10)	3585(5)	95(3)
C(18A)	7367(5)	4713(11)	3364(4)	94(3)
C(19A)	7227(4)	3664(9)	3694(3)	74(2)
C(20A)	8497(3)	118(7)	5243(3)	54(2)
C(21A)	8644(3)	1149(6)	5602(3)	44(1)
C(22A)	8731(3)	1056(6)	6191(3)	48(2)
C(23A)	9077(3)	51(9)	6529(3)	70(2)
C(24A)	9605(4)	-408(8)	6390(4)	77(2)
C(25A)	9791(4)	-407(8)	5800(4)	75(2)
C(26A)	9417(4)	-1329(9)	5405(4)	76(2)
C(27A)	8771(4)	-1206(8)	5361(4)	80(3)
B(1A)	7014(4)	3154(7)	5392(3)	52(2)
MoB	4700(1)	10746(1)	7512(1)	38(1)
O(1B)	3894(3)	8324(6)	7478(3)	81(2)
O(2B)	5586(2)	8591(5)	7292(2)	72(2)
O(3B)	4061(2)	12470(4)	7531(2)	50(1)
N(1B)	5208(2)	12418(5)	7204(2)	40(1)
N(2B)	4839(2)	13450(5)	7069(2)	47(1)
N(3B)	4266(2)	10973(5)	6642(2)	47(1)
N(4B)	4047(2)	12179(5)	6514(2)	48(1)

C(1B)	4178(3)	9247(7)	7514(3)	54(2)
C(2B)	5254(3)	9428(6)	7372(3)	50(2)
C(3B)	5770(3)	12751(7)	7120(3)	51(2)
C(4B)	6292(3)	11898(8)	7207(3)	61(2)
C(5B)	5761(4)	14019(7)	6927(3)	62(2)
C(6B)	5180(4)	14432(6)	6899(3)	58(2)
C(7B)	4903(5)	15667(7)	6714(5)	92(3)
C(8B)	4178(3)	10294(7)	6154(3)	51(2)
C(9B)	4360(4)	8929(7)	6123(3)	60(2)
C(10B)	3919(3)	11062(8)	5726(3)	60(2)
C(11B)	3850(3)	12241(7)	5951(3)	56(2)
C(12B)	3597(4)	13455(8)	5688(3)	67(2)
C(13B)	3450(3)	12436(6)	7665(3)	58(2)
C(14B)	3258(3)	13585(6)	7965(3)	49(2)
C(15B)	3663(4)	14425(8)	8237(4)	71(2)
C(16B)	3461(5)	15453(9)	8536(5)	95(3)
C(17B)	2851(6)	15649(9)	8569(5)	92(3)
C(18B)	2444(4)	14824(10)	8286(4)	82(3)
C(19B)	2643(3)	13825(7)	7985(3)	59(2)
C(20B)	4475(3)	10138(7)	8441(3)	57(2)
C(21B)	4882(3)	11165(6)	8444(3)	45(2)
C(22B)	5474(3)	11032(7)	8309(3)	51(2)
C(23B)	5906(3)	10015(9)	8511(3)	70(2)
C(24B)	5975(4)	9582(9)	9044(4)	85(3)
C(25B)	5470(5)	9576(8)	9416(4)	77(3)
C(26B)	4968(5)	8691(9)	9229(4)	90(3)
C(27B)	4664(4)	8810(8)	8644(4)	78(3)
B(2B)	4166(4)	13174(7)	7010(3)	50(2)

Table 3. Bond lengths [A] and angles [deg] for C27H33BMoN4O3(2i).

MoA-C(2A)	1.908(7)
MoA-C(1A)	1.948(7)
MoA-N(3A)	2.196(5)
MoA-C(21A)	2.216(6)
MoA-N(1A)	2.244(5)
MoA-O(3A)	2.293(4)
MoA-C(20A)	2.383(7)
MoA-C(22A)	2.413(7)
O(1A)-C(1A)	1.164(8)
O(2A)-C(2A)	1.172(8)
O(3A)-C(13A)	1.427(8)
O(3A)-B(1A)	1.474(9)
N(1A)-C(3A)	1.342(8)
N(1A)-N(2A)	1.374(7)
N(2A)-C(6A)	1.340(8)
N(2A)-B(1A)	1.535(9)
N(3A)-C(8A)	1.339(8)
N(3A)-N(4A)	1.379(7)
N(4A)-C(11A)	1.348(9)
N(4A)-B(1A)	1.539(10)
C(3A)-C(5A)	1.384(9)
C(3A)-C(4A)	1.486(9)
C(5A)-C(6A)	1.384(10)
C(6A)-C(7A)	1.503(10)
C(8A)-C(10A)	1.379(10)
C(8A)-C(9A)	1.504(10)
C(10A)-C(11A)	1.380(11)
C(11A)-C(12A)	1.500(11)
C(13A)-C(14A)	1.500(10)
C(14A)-C(19A)	1.363(10)
C(14A)-C(15A)	1.363(11)
C(15A)-C(16A)	1.427(13)
C(16A)-C(17A)	1.37(2)
C(17A)-C(18A)	1.36(2)
C(18A)-C(19A)	1.401(14)
C(20A)-C(21A)	1.391(9)
C(20A)-C(27A)	1.530(11)
C(21A)-C(22A)	1.382(9)
C(22A)-C(23A)	1.487(10)
C(23A)-C(24A)	1.340(11)
C(24A)-C(25A)	1.491(12)
C(25A)-C(26A)	1.526(13)
C(26A)-C(27A)	1.432(12)
MoB-C(2B)	1.903(7)
MoB-C(1B)	1.953(7)
MoB-N(3B)	2.184(5)
MoB-C(21B)	2.235(6)
MoB-N(1B)	2.247(5)
MoB-O(3B)	2.302(4)
MoB-C(20B)	2.383(7)

MoB-C(22B)	2.425(6)
O(1B)-C(1B)	1.154(8)
O(2B)-C(2B)	1.173(8)
O(3B)-C(13B)	1.424(8)
O(3B)-B(2B)	1.471(9)
N(1B)-C(3B)	1.331(8)
N(1B)-N(2B)	1.374(7)
N(2B)-C(6B)	1.363(9)
N(2B)-B(2B)	1.513(10)
N(3B)-C(8B)	1.349(8)
N(3B)-N(4B)	1.377(7)
N(4B)-C(11B)	1.354(8)
N(4B)-B(2B)	1.569(9)
C(3B)-C(5B)	1.405(10)
C(3B)-C(4B)	1.460(10)
C(5B)-C(6B)	1.356(11)
C(6B)-C(7B)	1.480(11)
C(8B)-C(10B)	1.369(10)
C(8B)-C(9B)	1.491(10)
C(10B)-C(11B)	1.360(10)
C(11B)-C(12B)	1.500(10)
C(13B)-C(14B)	1.483(9)
C(14B)-C(15B)	1.368(11)
C(14B)-C(19B)	1.393(9)
C(15B)-C(16B)	1.389(12)
C(16B)-C(17B)	1.38(2)
C(17B)-C(18B)	1.372(14)
C(18B)-C(19B)	1.364(12)
C(20B)-C(21B)	1.406(10)
C(20B)-C(27B)	1.518(11)
C(21B)-C(22B)	1.390(9)
C(22B)-C(23B)	1.479(10)
C(23B)-C(24B)	1.329(11)
C(24B)-C(25B)	1.494(13)
C(25B)-C(26B)	1.482(14)
C(26B)-C(27B)	1.473(13)

C(2A)-MoA-C(1A)	79.3(3)
C(2A)-MoA-N(3A)	97.6(2)
C(1A)-MoA-N(3A)	84.3(2)
C(2A)-MoA-C(21A)	104.8(3)
C(1A)-MoA-C(21A)	101.3(3)
N(3A)-MoA-C(21A)	157.5(2)
C(2A)-MoA-N(1A)	99.5(2)
C(1A)-MoA-N(1A)	162.0(2)
N(3A)-MoA-N(1A)	78.0(2)
C(21A)-MoA-N(1A)	96.4(2)
C(2A)-MoA-O(3A)	170.0(2)
C(1A)-MoA-O(3A)	105.1(2)
N(3A)-MoA-O(3A)	74.2(2)
C(21A)-MoA-O(3A)	83.4(2)
N(1A)-MoA-O(3A)	73.4(2)
C(2A)-MoA-C(20A)	100.7(3)
C(1A)-MoA-C(20A)	66.6(3)
N(3A)-MoA-C(20A)	141.6(2)

C(21A)-MoA-C(20A)	35.0(2)
N(1A)-MoA-C(20A)	130.8(2)
O(3A)-MoA-C(20A)	89.3(2)
C(2A)-MoA-C(22A)	77.8(3)
C(1A)-MoA-C(22A)	116.8(3)
N(3A)-MoA-C(22A)	156.6(2)
C(21A)-MoA-C(22A)	34.4(2)
N(1A)-MoA-C(22A)	80.1(2)
O(3A)-MoA-C(22A)	107.4(2)
C(20A)-MoA-C(22A)	61.3(2)
C(13A)-O(3A)-B(1A)	114.6(5)
C(13A)-O(3A)-MoA	124.9(4)
B(1A)-O(3A)-MoA	103.7(4)
C(3A)-N(1A)-N(2A)	106.7(5)
C(3A)-N(1A)-MoA	140.1(4)
N(2A)-N(1A)-MoA	113.0(3)
C(6A)-N(2A)-N(1A)	109.8(5)
C(6A)-N(2A)-B(1A)	133.8(5)
N(1A)-N(2A)-B(1A)	114.8(5)
C(8A)-N(3A)-N(4A)	106.8(5)
C(8A)-N(3A)-MoA	139.5(5)
N(4A)-N(3A)-MoA	113.7(4)
C(11A)-N(4A)-N(3A)	108.9(6)
C(11A)-N(4A)-B(1A)	134.7(6)
N(3A)-N(4A)-B(1A)	116.0(5)
O(1A)-C(1A)-MoA	175.2(6)
O(2A)-C(2A)-MoA	179.2(6)
N(1A)-C(3A)-C(5A)	109.5(6)
N(1A)-C(3A)-C(4A)	123.0(5)
C(5A)-C(3A)-C(4A)	127.4(6)
C(6A)-C(5A)-C(3A)	106.3(6)
N(2A)-C(6A)-C(5A)	107.7(5)
N(2A)-C(6A)-C(7A)	121.7(6)
C(5A)-C(6A)-C(7A)	130.6(6)
N(3A)-C(8A)-C(10A)	110.1(6)
N(3A)-C(8A)-C(9A)	121.7(6)
C(10A)-C(8A)-C(9A)	128.2(7)
C(11A)-C(10A)-C(8A)	106.0(7)
N(4A)-C(11A)-C(10A)	108.2(6)
N(4A)-C(11A)-C(12A)	122.3(7)
C(10A)-C(11A)-C(12A)	129.5(7)
O(3A)-C(13A)-C(14A)	112.0(6)
C(19A)-C(14A)-C(15A)	119.7(7)
C(19A)-C(14A)-C(13A)	118.4(8)
C(15A)-C(14A)-C(13A)	121.9(6)
C(14A)-C(15A)-C(16A)	120.2(9)
C(17A)-C(16A)-C(15A)	118.2(10)
C(18A)-C(17A)-C(16A)	121.8(9)
C(17A)-C(18A)-C(19A)	118.8(9)
C(14A)-C(19A)-C(18A)	121.3(10)
C(21A)-C(20A)-C(27A)	122.3(6)
C(21A)-C(20A)-MoA	65.9(4)
C(27A)-C(20A)-MoA	118.3(5)
C(20A)-C(21A)-C(22A)	123.6(6)
C(20A)-C(21A)-MoA	79.1(4)

C(22A)-C(21A)-MoA	80.6(4)
C(21A)-C(22A)-C(23A)	126.7(6)
C(21A)-C(22A)-MoA	64.9(4)
C(23A)-C(22A)-MoA	123.2(5)
C(24A)-C(23A)-C(22A)	122.6(7)
C(23A)-C(24A)-C(25A)	124.3(7)
C(24A)-C(25A)-C(26A)	112.4(8)
C(27A)-C(26A)-C(25A)	117.7(7)
C(26A)-C(27A)-C(20A)	118.1(8)
O(3A)-B(1A)-N(2A)	103.2(5)
O(3A)-B(1A)-N(4A)	105.4(5)
N(2A)-B(1A)-N(4A)	107.5(6)
C(2B)-MoB-C(1B)	79.0(3)
C(2B)-MoB-N(3B)	98.4(3)
C(1B)-MoB-N(3B)	83.5(3)
C(2B)-MoB-C(21B)	105.1(3)
C(1B)-MoB-C(21B)	101.6(3)
N(3B)-MoB-C(21B)	156.5(2)
C(2B)-MoB-N(1B)	99.0(2)
C(1B)-MoB-N(1B)	161.3(3)
N(3B)-MoB-N(1B)	78.3(2)
C(21B)-MoB-N(1B)	96.9(2)
C(2B)-MoB-O(3B)	170.2(2)
C(1B)-MoB-O(3B)	105.4(2)
N(3B)-MoB-O(3B)	73.8(2)
C(21B)-MoB-O(3B)	82.8(2)
N(1B)-MoB-O(3B)	74.0(2)
C(2B)-MoB-C(20B)	99.6(3)
C(1B)-MoB-C(20B)	66.4(3)
N(3B)-MoB-C(20B)	141.0(2)
C(21B)-MoB-C(20B)	35.3(2)
N(1B)-MoB-C(20B)	131.8(2)
O(3B)-MoB-C(20B)	90.2(2)
C(2B)-MoB-C(22B)	78.9(3)
C(1B)-MoB-C(22B)	118.0(3)
N(3B)-MoB-C(22B)	156.8(2)
C(21B)-MoB-C(22B)	34.4(2)
N(1B)-MoB-C(22B)	79.4(2)
O(3B)-MoB-C(22B)	106.0(2)
C(20B)-MoB-C(22B)	61.4(2)
C(13B)-O(3B)-B(2B)	115.9(5)
C(13B)-O(3B)-MoB	126.0(4)
B(2B)-O(3B)-MoB	103.1(4)
C(3B)-N(1B)-N(2B)	107.8(5)
C(3B)-N(1B)-MoB	139.7(4)
N(2B)-N(1B)-MoB	112.5(3)
C(6B)-N(2B)-N(1B)	109.1(5)
C(6B)-N(2B)-B(2B)	133.7(6)
N(1B)-N(2B)-B(2B)	115.4(5)
C(8B)-N(3B)-N(4B)	106.5(5)
C(8B)-N(3B)-MoB	138.7(4)
N(4B)-N(3B)-MoB	114.6(4)
C(11B)-N(4B)-N(3B)	109.2(5)
C(11B)-N(4B)-B(2B)	135.2(6)
N(3B)-N(4B)-B(2B)	114.9(5)

O(1B)-C(1B)-MoB	174.3(7)
O(2B)-C(2B)-MoB	178.1(6)
N(1B)-C(3B)-C(5B)	108.3(6)
N(1B)-C(3B)-C(4B)	124.1(6)
C(5B)-C(3B)-C(4B)	127.6(7)
C(6B)-C(5B)-C(3B)	107.5(6)
C(5B)-C(6B)-N(2B)	107.4(6)
C(5B)-C(6B)-C(7B)	131.1(7)
N(2B)-C(6B)-C(7B)	121.5(8)
N(3B)-C(8B)-C(10B)	109.1(6)
N(3B)-C(8B)-C(9B)	122.2(6)
C(10B)-C(8B)-C(9B)	128.6(7)
C(11B)-C(10B)-C(8B)	107.7(6)
N(4B)-C(11B)-C(10B)	107.5(6)
N(4B)-C(11B)-C(12B)	120.9(6)
C(10B)-C(11B)-C(12B)	131.6(7)
O(3B)-C(13B)-C(14B)	114.4(5)
C(15B)-C(14B)-C(19B)	117.7(7)
C(15B)-C(14B)-C(13B)	122.6(6)
C(19B)-C(14B)-C(13B)	119.6(6)
C(14B)-C(15B)-C(16B)	120.5(8)
C(17B)-C(16B)-C(15B)	121.0(9)
C(18B)-C(17B)-C(16B)	118.6(8)
C(19B)-C(18B)-C(17B)	120.3(8)
C(18B)-C(19B)-C(14B)	121.9(8)
C(21B)-C(20B)-C(27B)	123.1(7)
C(21B)-C(20B)-MoB	66.6(4)
C(27B)-C(20B)-MoB	117.3(5)
C(22B)-C(21B)-C(20B)	122.9(6)
C(22B)-C(21B)-MoB	80.3(4)
C(20B)-C(21B)-MoB	78.1(4)
C(21B)-C(22B)-C(23B)	126.4(7)
C(21B)-C(22B)-MoB	65.3(4)
C(23B)-C(22B)-MoB	122.9(5)
C(24B)-C(23B)-C(22B)	123.9(8)
C(23B)-C(24B)-C(25B)	122.4(8)
C(24B)-C(25B)-C(26B)	114.5(8)
C(27B)-C(26B)-C(25B)	118.8(8)
C(26B)-C(27B)-C(20B)	117.2(8)
O(3B)-B(2B)-N(2B)	105.2(5)
O(3B)-B(2B)-N(4B)	104.9(5)
N(2B)-B(2B)-N(4B)	106.4(6)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for C27H33BMoN4O3(2i). The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
MoA	44(1)	27(1)	36(1)	3(1)	0(1)	0(1)
O(1A)	92(4)	46(3)	87(4)	-22(3)	-14(3)	-10(3)
O(2A)	94(4)	54(3)	59(3)	26(3)	-1(3)	-7(3)
O(3A)	59(3)	38(2)	38(2)	7(2)	0(2)	4(2)
N(1A)	43(3)	31(3)	40(3)	1(2)	1(2)	2(2)
N(2A)	54(3)	32(3)	42(3)	4(2)	-2(2)	5(2)
N(3A)	41(3)	42(3)	57(3)	1(3)	-3(2)	0(2)
N(4A)	56(3)	43(3)	47(3)	4(2)	-5(2)	8(3)
C(1A)	55(4)	45(4)	47(4)	0(3)	-4(3)	-4(3)
C(2A)	51(4)	39(4)	49(4)	1(3)	0(3)	0(3)
C(3A)	38(3)	35(3)	49(4)	-4(3)	7(3)	-5(3)
C(4A)	56(4)	50(4)	43(4)	-3(3)	4(3)	-8(3)
C(5A)	54(4)	41(4)	55(4)	-7(3)	11(3)	-3(3)
C(6A)	55(4)	27(3)	70(4)	-1(3)	11(3)	5(3)
C(7A)	113(7)	35(4)	75(5)	0(4)	7(5)	3(4)
C(8A)	47(4)	56(4)	51(4)	4(3)	2(3)	-4(3)
C(9A)	65(5)	64(5)	77(5)	11(4)	12(4)	-18(4)
C(10A)	45(4)	75(5)	85(5)	-1(4)	3(4)	-5(4)
C(11A)	49(4)	59(5)	71(5)	0(4)	-2(3)	9(4)
C(12A)	74(6)	90(7)	89(6)	-1(5)	-1(5)	34(5)
C(13A)	75(5)	53(4)	43(4)	-2(3)	-9(3)	3(4)
C(14A)	68(4)	54(4)	37(4)	12(3)	11(3)	17(4)
C(15A)	65(5)	69(5)	79(6)	16(4)	8(4)	1(4)
C(16A)	88(7)	85(7)	109(9)	8(6)	35(6)	1(6)
C(17A)	119(8)	82(7)	92(7)	47(6)	50(6)	34(6)
C(18A)	115(8)	97(8)	73(6)	37(6)	25(6)	51(7)
C(19A)	84(6)	85(6)	52(4)	11(4)	5(4)	40(5)
C(20A)	56(4)	57(4)	50(4)	0(3)	9(3)	-1(3)
C(21A)	45(3)	35(3)	52(4)	7(3)	9(3)	2(3)
C(22A)	47(4)	46(4)	50(4)	-4(3)	-1(3)	5(3)
C(23A)	59(5)	90(6)	61(5)	26(4)	-1(4)	16(4)
C(24A)	78(6)	74(6)	78(6)	15(5)	1(4)	38(5)
C(25A)	48(4)	72(5)	104(7)	-4(5)	8(4)	19(4)
C(26A)	81(6)	72(6)	77(6)	0(5)	13(5)	23(5)
C(27A)	63(5)	56(5)	119(8)	-38(5)	-6(5)	8(4)
B(1A)	66(5)	34(4)	54(5)	9(4)	1(4)	11(4)
MoB	33(1)	31(1)	48(1)	2(1)	-2(1)	0(1)
O(1B)	84(4)	63(4)	94(5)	3(3)	-7(3)	-36(3)
O(2B)	63(3)	57(3)	93(4)	-13(3)	-7(3)	20(3)
O(3B)	48(2)	39(2)	62(3)	3(2)	6(2)	10(2)
N(1B)	39(3)	34(3)	46(3)	0(2)	1(2)	-5(2)
N(2B)	51(3)	35(3)	53(3)	6(2)	-9(2)	-4(3)
N(3B)	45(3)	40(3)	51(3)	1(3)	-10(2)	0(2)
N(4B)	39(3)	41(3)	60(3)	6(3)	-13(2)	5(2)
C(1B)	52(4)	50(4)	60(4)	1(3)	-1(3)	-5(3)

C(2B)	48(4)	41(4)	58(4)	-6(3)	-7(3)	2(3)
C(3B)	60(4)	50(4)	44(4)	-3(3)	4(3)	-15(3)
C(4B)	43(4)	74(5)	65(5)	-9(4)	8(3)	-11(4)
C(5B)	75(5)	55(4)	56(4)	1(4)	7(4)	-26(4)
C(6B)	81(6)	36(4)	56(4)	3(3)	-4(4)	-15(4)
C(7B)	114(8)	36(4)	123(8)	22(5)	5(6)	-13(4)
C(8B)	34(3)	52(4)	63(4)	-8(3)	-7(3)	-2(3)
C(9B)	80(5)	48(4)	48(4)	-16(3)	-6(4)	2(4)
C(10B)	68(5)	63(5)	46(4)	-6(4)	-11(4)	1(4)
C(11B)	55(4)	58(4)	51(4)	6(4)	-14(3)	1(3)
C(12B)	87(6)	67(5)	43(4)	6(4)	-18(4)	13(4)
C(13B)	41(4)	42(4)	90(5)	-4(4)	4(3)	-3(3)
C(14B)	53(4)	41(4)	53(4)	10(3)	1(3)	10(3)
C(15B)	61(5)	68(5)	81(5)	-15(4)	-3(4)	11(4)
C(16B)	109(9)	71(6)	102(7)	-26(5)	2(6)	-2(6)
C(17B)	126(9)	66(6)	89(7)	2(5)	34(6)	35(6)
C(18B)	87(6)	75(6)	89(6)	32(5)	37(5)	41(5)
C(19B)	50(4)	61(5)	67(4)	18(4)	11(3)	13(3)
C(20B)	55(4)	59(4)	57(4)	12(4)	14(3)	1(4)
C(21B)	50(4)	35(3)	49(4)	3(3)	-4(3)	8(3)
C(22B)	49(4)	58(4)	43(4)	0(3)	-4(3)	-1(3)
C(23B)	59(5)	88(6)	61(5)	8(5)	-3(4)	21(4)
C(24B)	84(7)	71(6)	97(6)	25(5)	5(5)	29(5)
C(25B)	103(7)	60(5)	65(5)	11(4)	-12(5)	21(5)
C(26B)	121(8)	64(6)	85(6)	22(5)	14(6)	12(6)
C(27B)	93(6)	58(5)	83(6)	25(4)	4(5)	-17(5)
B(2B)	61(5)	35(4)	54(4)	8(3)	-4(4)	9(4)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for C27H33BMoN4O3(2i).

	x	y	z	U(eq)
HBA	6873(24)	3973(52)	5135(23)	31(14)
H(4AA)	7765	2176	7597	40
H(4AB)	8011	1378	7177	40
H(4AC)	8440	2178	7264	40
H(5A)	7601	4980	7160	40
H(7AA)	7124	6388	6300	40
H(7AB)	6620	5592	5905	40
H(7AC)	7178	5999	5690	40
H(9AA)	5868	-1411	6152	40
H(9AB)	6433	-1013	6336	40
H(9AC)	6528	-1400	5668	40
H(10A)	5260	800	5670	40
H(12A)	5616	4000	5543	40
H(12A)	5172	3400	5422	40
H(12A)	5645	3600	4935	40
H(13A)	7764	1600	4435	40
H(13A)	6972	2000	4347	40
H(15A)	8114	4400	4839	40
H(16A)	8409	6200	4334	40
H(17A)	7908	6415	3380	40
H(18A)	7209	4618	2850	40
H(19A)	6864	3217	3458	40
H(20A)	8423	400	4815	40
H(21A)	8581	2000	5427	40
H(22A)	8749	1988	6394	40
H(23A)	8972	-219	6943	40
H(24A)	9805	-1018	6680	40
H(25A)	9738	600	5645	40
H(25A)	10169	-804	5776	40
H(26A)	9493	-1200	4979	40
H(26A)	9563	-2400	5553	40
H(27A)	8577	-1800	4986	40
H(27A)	8461	-1800	5334	40
HBB	3874(34)	14080(68)	6967(31)	64(22)
H(4BA)	6210	10976	7373	40
H(4BB)	6532	11976	7485	40
H(4BC)	6564	11781	6917	40
H(5B)	6182	14382	6816	40
H(7BA)	5046	16186	6460	40
H(7BB)	4976	16381	6904	40
H(7BC)	4551	15781	6982	40
H(9BA)	4429	8596	5751	40
H(9BB)	4027	8187	6348	40
H(9BC)	4379	8584	6547	40
H(10B)	3788	10800	5306	40
H(12B)	3808	14197	5819	40

H(12B)	3668	13400	5344	40
H(12B)	3222	13594	5881	40
H(13B)	3132	11977	7375	40
H(13B)	3400	11580	7921	40
H(15B)	4117	14182	8157	40
H(16B)	3702	15990	8823	40
H(17B)	2767	16390	8826	40
H(18B)	1970	14985	8436	40
H(19B)	2329	13177	7736	40
H(20B)	4042	10386	8496	40
H(21B)	4667	11984	8421	40
H(22B)	5719	11782	8171	40
H(23B)	6311	9783	8304	40
H(24B)	6324	8794	9064	40
H(25B)	5640	9200	9745	40
H(25B)	5258	10400	9496	40
H(26B)	4590	8800	9448	40
H(26B)	5039	7597	9249	40
H(27B)	5040	8385	8383	40
H(27B)	4306	8188	8641	40

Torsion angles C27H33BMoN4O3(2i).

N3A	MOA	N1A	N2A	-62.6(	0)	N3A	MOA	N1A	C3A	123.4(	0)
C1A	MOA	N1A	N2A	-73.7(	0)	C1A	MOA	N1A	C3A	112.4(	0)
C2A	MOA	N1A	N2A	-158.5(	0)	C2A	MOA	N1A	C3A	27.6(	0)
C21A	MOA	N1A	N2A	95.3(	0)	C21A	MOA	N1A	C3A	-78.6(	0)
N1A	MOA	N3A	N4A	55.7(	0)	N1A	MOA	N3A	C8A	-123.3(	0)
C1A	MOA	N3A	N4A	-127.8(	0)	C1A	MOA	N3A	C8A	53.3(	0)
C2A	MOA	N3A	N4A	153.9(	0)	C2A	MOA	N3A	C8A	-25.1(	0)
C21A	MOA	N3A	N4A	-21.8(	0)	C21A	MOA	N3A	C8A	159.2(	0)
N1A	MOA	C1A	O1A	-70.7(	0)	N3A	MOA	C1A	O1A	-81.6(	0)
C2A	MOA	C1A	O1A	17.3(	0)	C21A	MOA	C1A	O1A	120.4(	0)
N1A	MOA	C2A	O2A	178.0(	0)	N3A	MOA	C2A	O2A	98.9(	0)
C1A	MOA	C2A	O2A	16.3(	0)	C21A	MOA	C2A	O2A	-82.8(	0)
N1A	MOA	C21A	C20A	-170.8(	0)	N1A	MOA	C21A	C22A	62.1(	0)
N3A	MOA	C21A	C20A	-96.8(	0)	N3A	MOA	C21A	C22A	136.1(	0)
C1A	MOA	C21A	C20A	5.8(	0)	C1A	MOA	C21A	C22A	-121.3(	0)
C2A	MOA	C21A	C20A	87.6(	0)	C2A	MOA	C21A	C22A	-39.5(	0)
B1A	O3A	C13A	C14A	74.9(	0)	C13A	O3A	B1A	N2A	-161.9(	0)
C13A	O3A	B1A	N4A	85.5(	0)	MOA	N1A	N2A	C6A	-177.4(	0)
MOA	N1A	N2A	B1A	15.1(	0)	C3A	N1A	N2A	C6A	-1.5(	0)
C3A	N1A	N2A	B1A	-169.0(	0)	MOA	N1A	C3A	C4A	-7.7(	0)
MOA	N1A	C3A	C5A	176.0(	0)	N2A	N1A	C3A	C4A	178.1(	0)
N2A	N1A	C3A	C5A	1.9(	0)	N1A	N2A	C6A	C5A	.5(	0)
N1A	N2A	C6A	C7A	180.0(	0)	B1A	N2A	C6A	C5A	164.8(	0)
B1A	N2A	C6A	C7A	-15.8(	0)	N1A	N2A	B1A	O3A	-51.1(	0)
N1A	N2A	B1A	N4A	60.0(	0)	C6A	N2A	B1A	O3A	145.3(	0)
C6A	N2A	B1A	N4A	-103.6(	0)	MOA	N3A	N4A	C11A	-178.3(	0)
MOA	N3A	N4A	B1A	-4.4(	0)	C8A	N3A	N4A	C11A	.9(	0)
C8A	N3A	N4A	B1A	174.8(	0)	MOA	N3A	C8A	C9A	-3.2(	0)
MOA	N3A	C8A	C10A	177.8(	0)	N4A	N3A	C8A	C9A	177.8(	0)
N4A	N3A	C8A	C10A	-1.2(	0)	N3A	N4A	C11A	C10A	-.3(	0)
N3A	N4A	C11A	C12A	179.2(	0)	B1A	N4A	C11A	C10A	-172.6(	0)
B1A	N4A	C11A	C12A	6.9(	0)	N3A	N4A	B1A	O3A	41.2(	0)
N3A	N4A	B1A	N2A	-68.3(	0)	C11A	N4A	B1A	O3A	-146.9(	0)
C11A	N4A	B1A	N2A	103.5(	0)	N1A	C3A	C5A	C6A	-1.6(	0)
C4A	C3A	C5A	C6A	-177.6(	0)	C3A	C5A	C6A	N2A	.6(	0)
C3A	C5A	C6A	C7A	-178.8(	0)	N3A	C8A	C10A	C11A	1.0(	0)
C9A	C8A	C10A	C11A	-177.9(	0)	C8A	C10A	C11A	N4A	-.4(	0)
C8A	C10A	C11A	C12A	-179.8(	0)	O3A	C13A	C14A	C15A	29.8(	0)
O3A	C13A	C14A	C19A	-154.1(	0)	C13A	C14A	C15A	C16A	176.1(	0)
C19A	C14A	C15A	C16A	.1(	0)	C13A	C14A	C19A	C18A	-174.8(	0)
C15A	C14A	C19A	C18A	1.4(	0)	C14A	C15A	C16A	C17A	-2.4(	0)
C15A	C16A	C17A	C18A	3.4(	0)	C16A	C17A	C18A	C19A	-2.1(	0)
C17A	C18A	C19A	C14A	-.4(	0)	C27A	C20A	C21A	MOA	-109.4(	0)
C27A	C20A	C21A	C22A	-38.4(	0)	C21A	C20A	C27A	C26A	-58.1(	0)
MOA	C21A	C22A	C23A	113.9(	0)	C20A	C21A	C22A	C23A	43.7(	0)
C21A	C22A	C23A	C24A	41.0(	0)	C22A	C23A	C24A	C25A	-25.8(	0)
C23A	C24A	C25A	C26A	-69.2(	0)	C24A	C25A	C26A	C27A	54.0(	0)
C25A	C26A	C27A	C20A	49.8(	0)	N3B	MOB	N1B	N2B	62.5(	0)
N3B	MOB	N1B	C3B	-119.8(	0)	C1B	MOB	N1B	N2B	77.0(	0)
C1B	MOB	N1B	C3B	-105.3(	0)	C2B	MOB	N1B	N2B	159.2(	0)
C2B	MOB	N1B	C3B	-23.0(	0)	C21B	MOB	N1B	N2B	-94.2(	0)
C21B	MOB	N1B	C3B	83.5(	0)	N1B	MOB	N3B	N4B	-53.7(	0)

N1B	MOB	N3B	C8B	119.8(	0)
C1B	MOB	N3B	C8B	-55.6(	0)
C2B	MOB	N3B	C8B	22.3(	0)
C21B	MOB	N3B	C8B	-160.0(	0)
N3B	MOB	C1B	O1B	60.0(	0)
C21B	MOB	C1B	O1B	-143.3(	0)
N3B	MOB	C2B	O2B	-104.8(	0)
C21B	MOB	C2B	O2B	76.2(	0)
N1B	MOB	C21B	C22B	-59.7(	0)
N3B	MOB	C21B	C22B	-136.2(	0)
C1B	MOB	C21B	C22B	123.2(	0)
C2B	MOB	C21B	C22B	41.5(	0)
C13B	O3B	B2B	N2B	161.4(	0)
MOB	N1B	N2B	C6B	178.6(	0)
C3B	N1B	N2B	C6B	.1(	0)
MOB	N1B	C3B	C4B	3.3(	0)
N2B	N1B	C3B	C4B	-178.9(	0)
N1B	N2B	C6B	C5B	.0(	0)
B2B	N2B	C6B	C5B	-163.5(	0)
N1B	N2B	B2B	O3B	50.3(	0)
C6B	N2B	B2B	O3B	-147.0(	0)
MOB	N3B	N4B	C11B	173.4(	0)
C8B	N3B	N4B	C11B	-2.2(	0)
MOB	N3B	C8B	C9B	6.1(	0)
N4B	N3B	C8B	C9B	180.0(	0)
N3B	N4B	C11B	C10B	2.5(	0)
B2B	N4B	C11B	C10B	171.8(	0)
N3B	N4B	B2B	O3B	-40.3(	0)
C11B	N4B	B2B	O3B	150.9(	0)
N1B	C3B	C5B	C6B	.1(	0)
C3B	C5B	C6B	N2B	.0(	0)
N3B	C8B	C10B	C11B	.6(	0)
C8B	C10B	C11B	N4B	-1.9(	0)
O3B	C13B	C14B	C15B	-18.2(	0)
C13B	C14B	C15B	C16B	-176.8(	0)
C13B	C14B	C19B	C18B	175.8(	0)
C14B	C15B	C16B	C17B	.3(	0)
C16B	C17B	C18B	C19B	.8(	0)
C27B	C20B	C21B	MOB	108.3(	0)
C21B	C20B	C27B	C26B	55.7(	0)
C20B	C21B	C22B	C23B	-44.8(	0)
C22B	C23B	C24B	C25B	29.8(	0)
C24B	C25B	C26B	C27B	-55.7(	0)

C1B	MOB	N3B	N4B	130.9(	0)
C2B	MOB	N3B	N4B	-151.2(	0)
C21B	MOB	N3B	N4B	26.6(	0)
N1B	MOB	C1B	O1B	45.7(	0)
C2B	MOB	C1B	O1B	-39.9(	0)
N1B	MOB	C2B	O2B	175.8(	0)
C1B	MOB	C2B	O2B	-23.1(	0)
N1B	MOB	C21B	C20B	173.5(	0)
N3B	MOB	C21B	C20B	97.0(	0)
C1B	MOB	C21B	C20B	-3.7(	0)
C2B	MOB	C21B	C20B	-85.3(	0)
B2B	O3B	C13B	C14B	-82.1(	0)
C13B	O3B	B2B	N4B	-86.5(	0)
MOB	N1B	N2B	B2B	-14.6(	0)
C3B	N1B	N2B	B2B	166.9(	0)
MOB	N1B	C3B	C5B	-177.9(	0)
N2B	N1B	C3B	C5B	-.1(	0)
N1B	N2B	C6B	C7B	178.6(	0)
B2B	N2B	C6B	C7B	15.1(	0)
N1B	N2B	B2B	N4B	-60.7(	0)
C6B	N2B	B2B	N4B	102.0(	0)
MOB	N3B	N4B	B2B	1.6(	0)
C8B	N3B	N4B	B2B	-173.9(	0)
MOB	N3B	C8B	C10B	-172.9(	0)
N4B	N3B	C8B	C10B	1.0(	0)
N3B	N4B	C11B	C12B	-178.9(	0)
B2B	N4B	C11B	C12B	-9.6(	0)
N3B	N4B	B2B	N2B	70.9(	0)
C11B	N4B	B2B	N2B	-98.0(	0)
C4B	C3B	C5B	C6B	178.8(	0)
C3B	C5B	C6B	C7B	-178.5(	0)
C9B	C8B	C10B	C11B	-178.4(	0)
C8B	C10B	C11B	C12B	179.7(	0)
O3B	C13B	C14B	C19B	163.0(	0)
C19B	C14B	C15B	C16B	2.1(	0)
C15B	C14B	C19B	C18B	-3.0(	0)
C15B	C16B	C17B	C18B	-1.7(	0)
C17B	C18B	C19B	C14B	1.6(	0)
C27B	C20B	C21B	C22B	38.2(	0)
MOB	C21B	C22B	C23B	-113.7(	0)
C21B	C22B	C23B	C24B	-42.0(	0)
C23B	C24B	C25B	C26B	67.2(	0)
C25B	C26B	C27B	C20B	-47.4(	0)

Chapter-III

Intramolecular Steric Strain in $Tp'(CO)_2$ Mo(π-Allyl) Complexes.

Part of this work has been accepted for publication in *Organometallics*, **1997** (in press).

III. 1 BACKGROUND

Trofimenko stated[1] that a 3-substituent on pyrazole in *tris*pyrazolylborate ligand enhances thermal stability of metal complexes as well as its stability towards oxidation. Though 3-methyl substituent has been the most common, several bulkier groups[2] like isopropyl[3], phenyl[4] or tert-butyl[5] have been used lately, and these served to widen the scope of chemistry of the metal derivatives.[6]

In $Tp'Mo(CO)_2$-π-allyl complexes[7], the 3-methyl group lies in close proximity of the π-allyl group so much so that terminal allyl substituents can have considerable steric interaction with proximal 3-methyl substituents. A consequence of such interaction is a noticeable distortion from the ideal π-allyl orientation[8], as shown in the X-ray structure of a typical complex, $Tp'Mo(CO)_2$-π-cinnamyl, and it could be identified from an unusually deshielded central proton of the allyl group in the NMR spectrum. The unfavorable steric interaction between the terminal allyl substituent and the 3-methyl group of pyrazole also lowered the barrier of π–σ–π interconversion which leads to isomerization of the allyl substituents. In the isomerization process, when a *syn*-substituent is converted to an *anti*-substituent a σ-allyl intermediate is mandatory[9], but never observed in Tp or Tp′ series (*Fig.-1*).

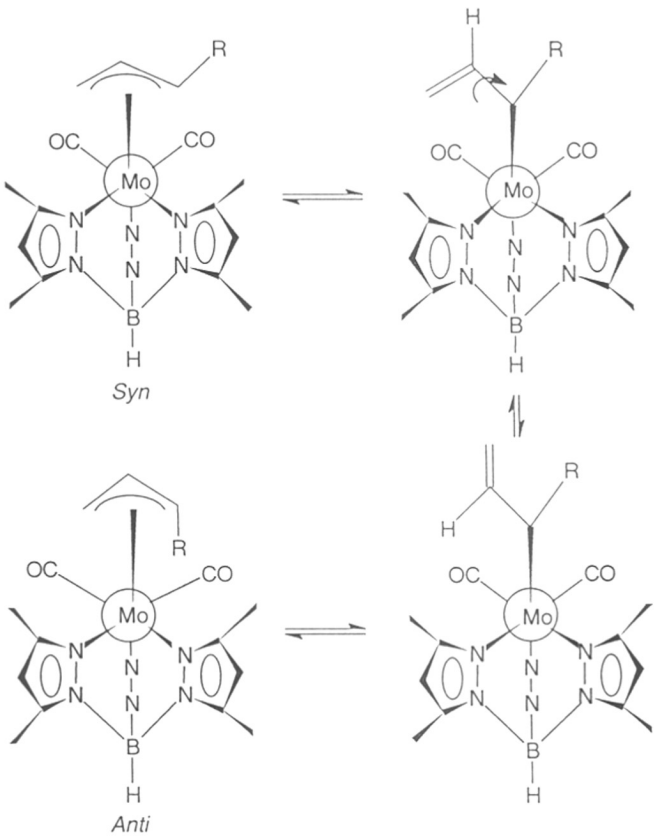


Fig.-1. π–σ–π Interconversion

Liebeskind showed[10] in a recent, definitive paper that it is possible to prepare and isolate different stereoisomers of Tp complexes where isomerism occurs due to different configuration of the π-allyl group. Stereoisomer interconversion takes place at elevated temperatures. In the case of Tp′ complexes described in this chapter, interconversion of stereoisomers had to be arrested at subambient temperatures so that NMR spectra attesting their presence could be recorded, but isomers could not be separately isolated.

III. 2 PRESENT WORK

All complexes were prepared by reaction of the intermediate $(CH_3CN)_3Mo(CO)_3$ with appropriate allyl halide or acetate (details are provided with experimental section).

The synthesis and structure of complex **3a** has been reported earlier.[8] The proton NMR spectrum (400 MHz) of this complex at 20 °C consisted of only one set of signals (*Fig.-2*).

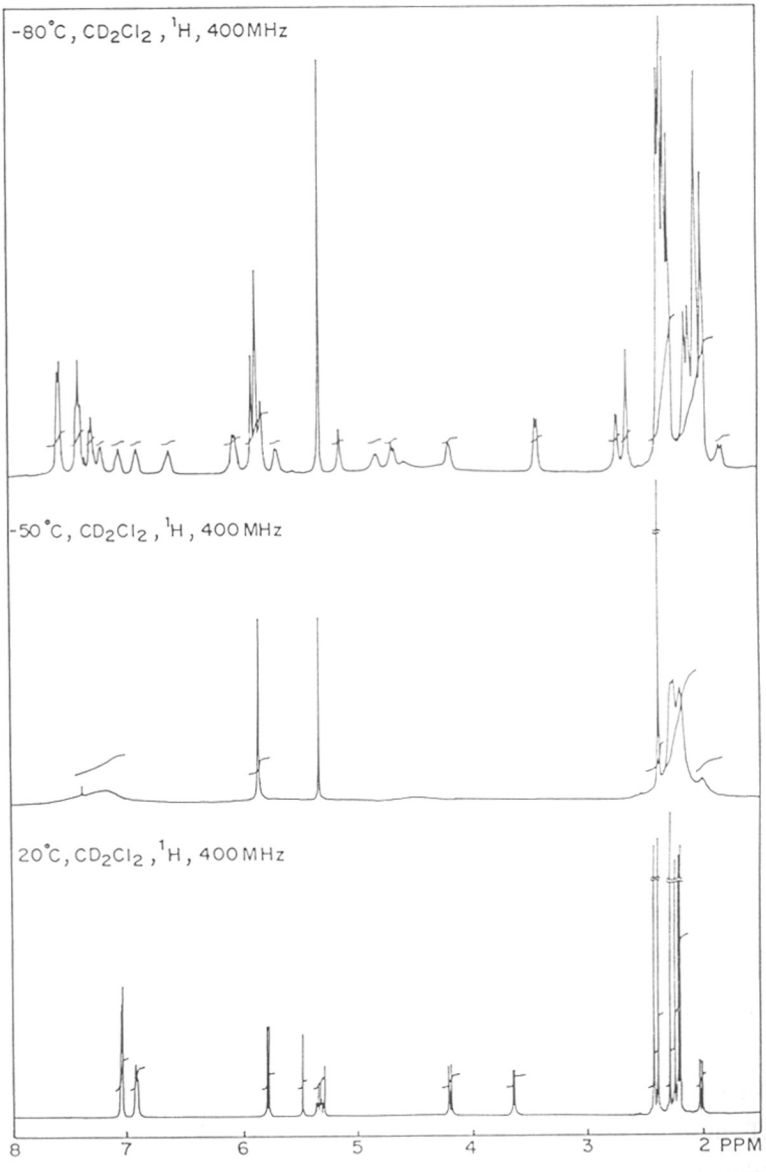


Fig.-2. NMR spectra of complex **3a** at variable temperature

This was interpreted in terms of the structure obtained from X-ray diffraction studies. The structure revealed a significant distortion of the allyl orientation from its commonly observed position[11] in similar molybdenum π-allyl complexes. Such deviation was correlated to the relatively deshielded central proton signal observed in the proton NMR spectrum as a diagnostic feature.

As the temperature was lowered, extensive broadening of signals was observed until the peaks completely decoalesced and a well-resolved spectrum was obtained at -80 °C. The signals now represented two sets of isostructural but isomeric species present in a ratio of 2.2 : 1 (*Fig.-3*).

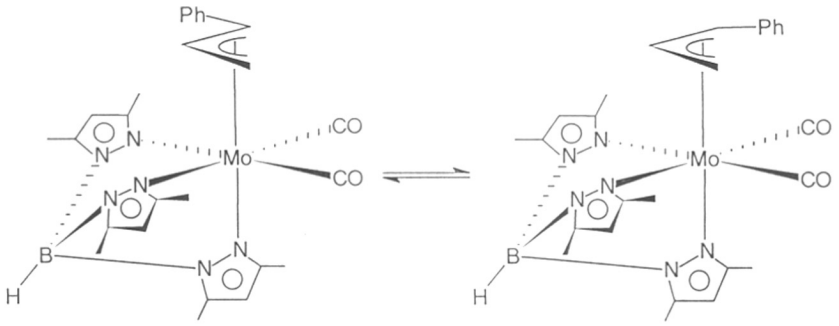


Fig.-3. Isomeric structures of **3a**

The peaks due to each species were identified by careful analysis of the COSY spectrum recorded at low temperature. The most dramatic difference was observed for the two phenyl ring proton sets. While the signals due to the phenyl ring of the major isomer (identified as the *anti* phenyl ring) exhibited three sets of multiplets at 7.54, 7.38 and 7.27 ppm (2 : 2 : 1), the *syn* phenyl proton signals showed five distinct signals at 7.19, 7.07, 6.87, 6.59 and 5.66 ppm. The high-field signal at 5.66 ppm was assigned to an *ortho* proton (coupled only with the proton at 6.59 ppm) which was placed close to a pyrazole ring (a tilted aromatic ring flanked by two pyrazole rings is observed in the crystal structure) and was

thereby affected by the anisotropic effect of a shielding ring current. The assignment of *syn/anti* phenyl groups was made based on the identification of relevant allyl proton signals. For instance, the major isomer with *anti*-phenyl group displayed signals due to the *syn*-benzylic proton at 3.40 ($J_{syn/central}$ = 7.1 Hz), the central proton at 6.03 (*m*), a *syn*-proton at 2.70 ($J_{syn/central}$ = 5.0 Hz) and another *anti*-proton at 2.10 ppm ($J_{anti/central}$ = 12.8 Hz); the minor isomer with *syn*-phenyl group displayed signals due to the *anti*-benzylic proton at 4.65 ($J_{anti/central}$ = 10.0 Hz), the central proton at 4.79 (m), a *syn*-proton at 4.17 (m) and another *anti*-proton at 1.82 ppm ($J_{anti/central}$ = 9.7 Hz). We found that the pattern of signals for aromatic protons in *syn* or *anti* orientation remains consistent throughout the series (*vide infra*).

It was now clear that the proton NMR spectrum recorded at 20 °C actually represented an exchange-averaged spectrum. The central proton of the allyl group appeared at 6.03 (major isomer) and 4.79 ppm (minor isomer) indicating that the distortion of the allyl orientation persists in both the isomers (more in the major isomer). Surprisingly the crystal structure revealed the structure of the minor isomer alone. The dynamic NMR spectral pattern is consistent with a π–σ–π interconversion that leads to the isomerization involving the allylic substituent.[12] We found that this trend was present in a set of isostructural 1,3-disubstituted π-allyl complexes **3b-3d**. Throughout the series, however, the central proton of the terminally substituted allyl groups was distinctly deshielded in comparison with Tp-analogs[10]; more deshielding probably reflects greater steric strain resulting from picket-fence interaction with 3-methyl groups leading to greater deviation from usual orientation of the allyl group.

The allyl acetate was added to the $(CH_3CN)_3Mo(CO)_3$ complex followed by addition of ligand to afford the complex **3b** as shining black crystals. The IR spectrum displayed two sharp peaks of equal intensity appearing at 1940 cm^{-1} and 1839 cm^{-1} corresponding to the CO ligands. Two peaks of medium and weak intensity at 1543 cm^{-1} and 2510 cm^{-1} were due to the double bonds between carbon-nitrogen in the pyrazole ring of the ligand and B-H stretching respectively. These peaks were present in all the other complexes as well.

At 20 °C, an averaged spectrum was observed for complex **3b** (*Fig.-4*).

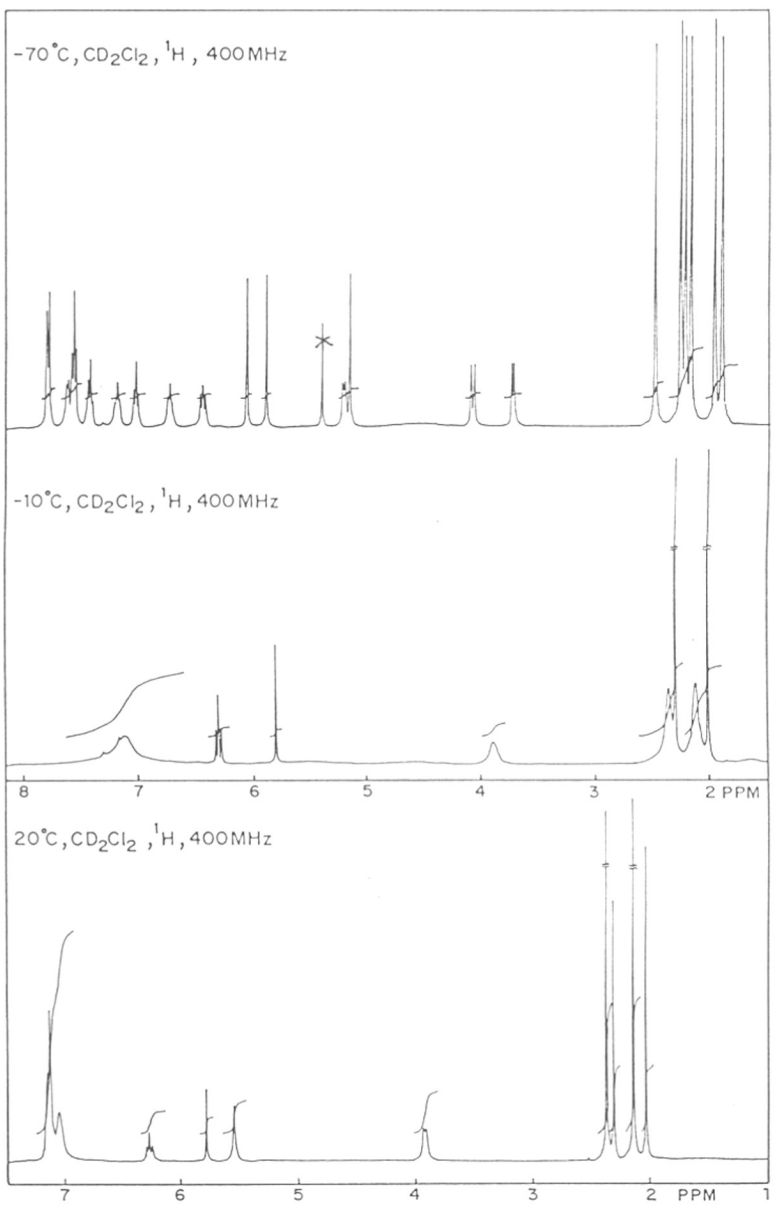


Fig.-4. NMR spectra of complex **3b** at variable temperature

The aromatic protons appeared as broad multiplets at 7.04-7.14 ppm, the pyrazole 4-H at 5.77 and 5.54 ppm (1 : 2), central allyl proton at 6.27 ppm, two benzylic allyl protons at 3.91 (broad doublet, J = 8.2 Hz) and the four methyl signals appeared at 2.36, 2.30, 2.14 and 2.03 ppm (2 : 1 : 2 : 1). The symmetrical, averaged structure was also evident from the only one ^{13}C NMR signal for the CO at 234.5 ppm.

Extensive decoalescence of proton NMR signals was observed as the sample was cooled in the NMR probe. At -70 °C, sharp signals were obtained, which permitted assignment of individual peaks by the use of a COSY spectrum recorded also at that temperature. The spectrum revealed the presence of only one type of molecule. The two aromatic proton sets appeared as described above for complex **3a**. One set consisted of three peaks at 7.63, 7.42 and 7.28 ppm (2 : 2 : 1). The other set had five clear signals at 7.47, 7.04, 6.88, 6.59 and 5.11 ppm. The former indicated an *anti* phenyl group and the latter a *syn* phenyl group. The central allyl proton appears at 6.32 ppm, indicating no change from the spectrum recorded at ambient temperature. The structure of complex **3b** (*Fig.-5*) was thus assigned to be as shown, with one phenyl ring in the *syn* (*anti* benzylic proton at 4.00 ppm, $J_{anti/central}$ = 11. Hz) and the other in the *anti* (*syn* benzylic proton at 3.66 ppm, $J_{syn/central}$ = 7.3 Hz) configuration. ^{13}C NMR signals (-70 °C) for the CO ligand appeared at 232.9 and 233.9 ppm.

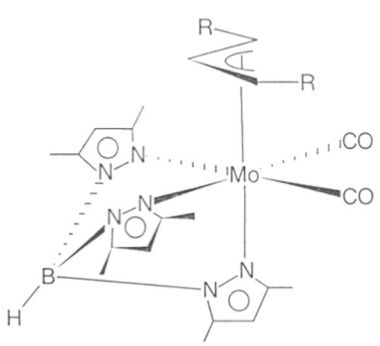


Fig.-5. Structure of complex **3b-c**

Complex No.	R	Isolated yield(%)
3b	C_6H_5	13
3c	CH_3	51

The proton NMR spectrum of the 1,3-dimethylallyl complex **3c** recorded at -40 °C revealed the presence of predominantly one isomer (*Fig.-5*). As described in the case of complex **3b**, it has one methyl group in the *syn* (2.23 ppm, J = 5.8 Hz) and the other in *anti* (0.85 ppm, J = 6.2 Hz) orientation. Two allyl protons appeared at 2.54 ppm and 2.87 ppm as multiplets corresponding to *anti* and *syn* allyl protons respectively; the central proton of the allyl group is less deshielded in this case and appears at 5.01 ppm (dd, $J_{anti/central}$ = 10.5 Hz; $J_{syn/central}$ = 6.8 Hz). The spectrum at room temperature showed broad features indicating averaging of signals. Taken together, the spectral data of both complexes **3b** and **3c** indicate the dynamic process involved in site-exchange of allyl substituents between *syn* and *anti* orientation, though the overall structures remain the same because of the symmetry of the ligand.

In the complex **3d** (15 %, shining black crystals), one terminus of the allyl group contains a phenyl ring and the other terminus contains a methyl substituent (*Fig.-6*).

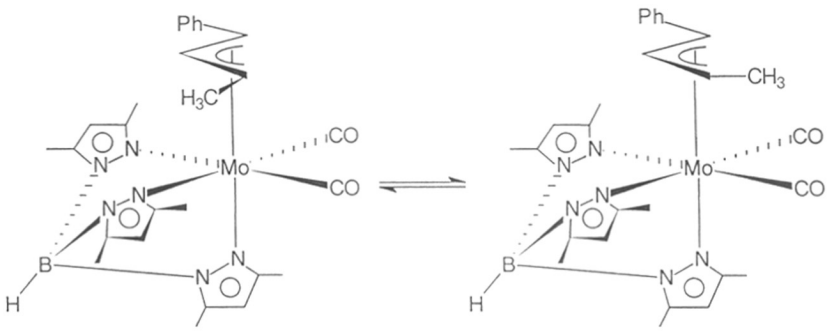


Fig.-6. Isomeric structures of **3d**

From the proton NMR spectrum at room temperature, presence of two isomers in unequal amounts (2 : 1) can be ascertained. In this series this is the only complex that displayed sharp signals except in the aromatic region such that two isomers could be observed at ambient temperature. Two clusters of multiplets due to the aromatic protons of the two isomers decoalesced to five signals each, on cooling to

-70 °C. It was clearly evident from the signal pattern of aromatic protons that in both the isomers, the rings were *syn* oriented. The aromatic ring protons appeared as multiplets for the major isomer at 5.10, 6.50, 6.60, 7.05 and 7.35 ppm and for the minor isomer at 5.60, 6.50, 6.60, 7.05 and 7.25 ppm. The methyl group was placed *syn* (2.34 ppm, d, J = 6.6 Hz) in one isomer (major) and *anti* (1.43 ppm, d, J = 6.0 Hz) in the other (minor). The corresponding methine protons appeared at 2.81 (m) and 5.10 (m) ppm respectively. The *anti* benzylic methine protons appeared at 3.78 ppm (d, $J_{anti/central}$ = 11.0 Hz) for the major isomer and 5.13 ppm (d, $J_{anti/central}$ = 11.2 Hz) for the minor isomer. The central proton of the allyl group appeared as multiplets at 5.60 (major isomer) and 4.90 ppm (minor isomer). Four carbonyl carbon signals corresponding to the two isomers appeared in the ^{13}C NMR spectrum at 233.65 and 232.06 (major) and 236.10 and 228.25 ppm (minor) respectively.

An additional support for the assignment of five separate signals to a *syn* phenyl group was provided by the complex **3e** which has a double bond intervening the allyl and the phenyl group.[13] The proton NMR spectrum of this complex at room temperature displayed two sets of isomers in the ratio 2 : 1 (*Fig.-7*), in which the *syn*-substituted isomer was the major one. The phenyl proton signals appeared as a complex multiplet between 7.13 - 7.32 ppm, and in both isomers the phenyl ring was placed away from the pyrazole groups. The central proton of the allyl group appeared at 5.30-5.37 ppm in the major isomer and at 4.42 ppm in the minor isomer, indicating less distortion of the allyl group. In the major isomer, the signals of styryl protons were observed at 6.45 ppm (d, J = 15.6 Hz) and 6.63 ppm (dd, J = 10.2, 15.5 Hz), and in the minor isomer they appeared at 5.28-5.34 ppm (m) and 6.68 ppm (d, J = 14.6 Hz) . The π-allyl protons for the major isomer appeared at the usual positions as mentioned for other cases, *viz.* two *anti* allyl protons at 2.09 and 3.57 ppm as multiplet and triplet (J = 9.4 Hz) respectively; the *syn* proton at 3.10 ppm as a doublet (J = 6.3 Hz). In the minor isomer, π-allyl protons appeared at expected positions as follows: two *syn* allyl protons at 3.62 ppm (d, J = 7.4 Hz) and 5.35 ppm as a multiplet respectively; the *anti* proton at 3.22 ppm as a doublet (J = 11.0 Hz). Four carbonyl carbon signals corresponding to the two isomers appeared in the ^{13}C NMR spectrum at 232.8 and 233.9 (major) and 228.5 and 232.1 ppm (minor) respectively.

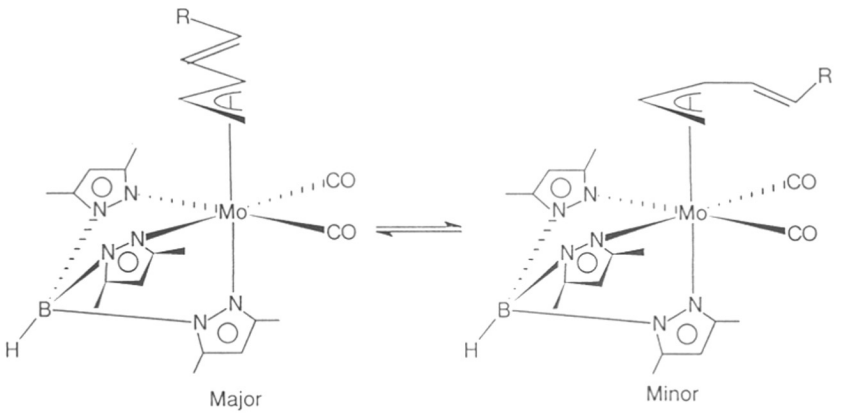


Fig.-7. Isomeric structures of **3e-f**

Complex No	R	Isolated yield(%)	Ratio
3e	C_6H_5	18	2:1
3f	CH_3	47	4:1

In comparison, the complex **3f** (*Fig.-7*), where a methyl group is present at the end of the double bond in place of the phenyl, the ratio of *syn : anti* was found to be 4:1. The assignment was made by comparison with the spectra of the preceding complex **3e**. The peaks due to the major isomer could be readily identified. The low-intensity peaks due to the minor isomer proved more difficult to identify and assign. The central proton of the allyl group appeared at 5.29 ppm in the major isomer and at 4.40 ppm in the minor isomer, indicating less distortion of the allyl group. The olefinic protons were observed at 5.70-5.90, 6.06 ppm (for major) and 5.70-5.90, 4.55 ppm (for minor) as multiplets. The π-allyl protons were assigned as before. Four carbonyl carbon signals corresponding to the two isomers appeared in the ^{13}C NMR spectrum at 233.7 and 233.8 (major) and 232.5 and 227.8 ppm (minor) respectively.

III. 3 Summary

Variable temperature proton NMR spectra of a set of Tp/Mo(CO)$_2$-π-allyl complexes provided clear evidence that the fluxionality of these molecules originated from a π–σ–π interconversion of the π-allyl group as reflected in the *syn/anti* interconversion of terminal allyl substituents, but the barrier heights were generally low compared to isostructural Tp complexes described by Liebeskind.[10]

III. 4 EXPERIMENTAL

Triphenylphosphine, magnesium turnings, PCl_3, pyridine, $AlCl_3$, acetic anhydride and ethyl bromide were purchased from SD Fine Chemicals. Sodium borohydride and iodine were purchased from Loba Chemie. 2-Bromomesitylene, triethyl orthoformate, crotonaldehyde, cerium chloride heptahydrate, cinnamaldehyde, PBr_3, ethyl bromoacetate and lithium aluminium hydride were purchased from Aldrich.

3. Preparation of sodium hydro*tris*(3,5-dimethyl-1-pyrazolyl)borate.

The compound has been prepared from 3,5-dimethyl pyrazole (prepared from acetylacetone and hydrazine hydrate) and sodium borohydride in 65% yield. A modified procedure was used in the present case.[14]

A mixture of sodium borohydride (1.9 g, 50 mmol) and 3, 5-dimethylpyrazole (16.8 g, 175 mmol) were ground together into a fine powder and slowly heated in an oil bath. Gas evolution ceased around 230 °C to 240 °C indicating completion of reaction. The melt was cooled to 160 °C and toluene was added with stirring. The reaction mixture was cooled to room temperature, chilled on ice water and filtered to get an amorphous solid. The pure, ligand was obtained by further crystallization from toluene (10.4 g, 65 %). Melting point and spectral data were comparable with the reported values.

3.a.1. Preparation of 3-acetoxy-1,3-diphenyl-prop-2-ene.

The title compound was prepared by a procedure identical to that reported earlier as in section **1.d.3.**

3.b.1. Preparation of 4-chloro-pent-2-ene.

The title compound was prepared by a procedure identical to that reported earlier as in section **1.b.2.**

3. c. 1. Preparation of 3-chloro-1-phenylbutene.

The title compound was prepared by a procedure identical to that reported earlier as in section **1.c.3.**

3.d.1. Preparation of 1-chloro-5-phenyl-pent-2,4-diene.

The title compound was prepared by a procedure identical to that reported earlier as in section **2.e.3.**

3.e.1. Preparation of 1-bromo-hex-2,4-diene.

The title compound was prepared by a procedure identical to that reported earlier as in section **2.d.3.**

General method of complexation

In an oven dried two-necked flask cooled under argon, a suspension of $Mo(CO)_6$ (2 mmol) in freshly distilled acetonitrile (30 mL) was refluxed for 6 h. The golden solution of the resultant *tris*-acetonitrile $Mo(CO)_3$ complex was then treated with freshly distilled allyl halide (2.1 mmol) and the solution was refluxed for another 15 min for allyl chlorides. In case of the allyl bromides the solution was cooled immediately after addition. The reaction mixture was cooled to room temperature and the volume of the solution was reduced to approximately 5 mL under reduced pressure. A solution of the ligand (2.1 mmol) in CH_2Cl_2 (10 mL) was then added to the reaction mixture with vigorous stirring which was continued for 1.5 h. The reaction mixture was then concentrated and subjected to column chromatography to isolate the desired complex. Crystallization afforded analytically pure sample.

Low Temperature ^{1}H NMR of Complex 3.a.

Two isomers were present in a ratio 2.2 : 1.

^{1}H NMR (400 MHz), -80 °C CD_2Cl_2	:	Major isomer: 1.90-2.30 (6s, 18H), 2.10 (d, 1H, J = 12.8 Hz), 2.70 (d, 1H, J = 5.0 Hz), 3.40 (d, 1H, J = 7.1 Hz), 5.79-5.88 (m, 3H), 6.03 (m, 1H), 7.27 (m, 1H), 7.38 (m, 2H), 7.54 (m, 2H). Minor isomer: 1.90-2.30 (5s, 15H), 1.82 (d, 1H, J = 9.7 Hz), 2.62 (s, 3H), 4.17 (m, 1H), 4.65 (d, 1H, J = 10.0 Hz), 4.79 (m, 1H), 5.66 (m, 1H), 5.79-5.88 (m, 3H), 6.59 (m, 1H), 6.87 (m, 1H), 7.07 (m, 1H), 7.19 (m, 1H).

Preparation of complex 3.b.

Complexation was carried out using the same procedure as for **1.d**. $Mo(CO)_6$ (0.792 g, 3 mmol) was refluxed in acetonitrile (40mL) for 6 h to afford golden solution of *tris*-acetonitrile $Mo(CO)_3$ complex. Freshly prepared allyl acetate **3.a.1** (3-acetoxy-1,3-diphenyl-prop-2-ene) (0.882 g, 3.5 mmol) was added to the refluxing solution and it was further refluxed for 16 h. The reaction mixture was then cooled to room temperature and the volume was concentrated to 5 mL. It was diluted with 20 mL CH_2Cl_2 and the ligand (**3**) (1.12 g, 3.5 mmol) was then added and stirred for 1 h. The red colored reaction mixture thus obtained was concentrated and chromatographed (20% EtOAc-pet.ether). Recrystallization from CH_2Cl_2-MeOH (at -10 °C) afforded shining black crystals (0.25 g, 13%).

Color	:	Black
MP	:	185 °C (dec)
IR	:	2510 (w), 1940 (s), 1839 (s), 1543 (m) cm^{-1}.
^{1}H NMR (400 MHz), 20 °C CD_2Cl_2		2.03 (s, 3H), 2.14 (s, 6H), 2.30 (s, 3H), 2.36 (s, 6H), 3.91 (brd, 2H, J = 8.2 Hz), 5.54 (s, 2H), 5.77 (s, 1H), 6.27 (t, 1H, J = 9.2 Hz), 7.04-7.14 (m, 10H).
^{1}H NMR (400 MHz), -70 °C CD_2Cl_2	:	1.89 (s, 3H), 1.95 (s, 3H), 2.20 (s, 3H), 2.23 (s, 3H), 2.29 (s, 3H), 2.45 (s, 3H), 3.66 (d, 1H, J = 7.3 Hz), 4.00 (d, 1H, J = 11.0 Hz), 5.06 (s, 1H), 5.11 (d, 1H, J = 7.1 Hz), 5.78 (s, 1H), 5.94 (s, 1H), 6.32 (dd, 1H, J = 7.9, 10.5 Hz), 6.59 (t, 1H, J = 8.0 Hz), 6.88 (t, 1H, J = 7.2 Hz), 7.04 (m, 1H), 7.28 (m, 1H), 7.42 (t, 2H, J = 7.5 Hz), 7.47 (d, 1H, J

		= 7.1 Hz), 7.63 (d, 2H, J = 7.6 Hz).
^{13}C NMR (100.6 MHz), 20 °C CD_2Cl_2		13.2, 13.7, 15.7, 16.2, 83.2, 107.2, 107.8, 127.3, 128.0, 128.1, 139.9, 145.7, 147.1, 151.1, 152.8, 234.5.
^{13}C NMR (100.6 MHz), -70 °C CD_2Cl_2	:	12.7, 13.2, 13.5, 15.2, 15.3, 16.5, 68.3, 83.0, 88.2, 106.4, 106.6, 107.8, 126.7, 126.9, 127.2, 128.1, 137.7, 140.4, 145.1, 145.4, 146.7, 150.4, 151.4, 152.7, 232.9, 233.9.
Analysis	:	Calcd. : C: 59.81; H : 5.45; N : 13.08. Found : C: 59.85; H: 5.69; N: 12.84.

Preparation of complex 3.c.

The complex was prepared using the general method from $Mo(CO)_6$ (0.528 g, 2 mmol), acetonitrile (30 mL), allyl halide **3.b.1** (4-chloro-pent-2-ene) (0.418 g, 4 mmol) and the ligand (**3**) (0.740 g, 2.3 mmol). The pure complex **3.c** was obtained by column chromatography (25% EtOAc-pet.ether) and was recrystallized from CH_2Cl_2-pet.ether (by diffusion method at 5 °C) to obtain red crystals (0.530 g, 51%).

Color	:	Red
MP	:	161 °C (dec)
IR	:	2530 (w), 1916 (s), 1820 (s), 1543 (m) cm^{-1}.
^{1}H NMR (400 MHz), -40 °C CD_2Cl_2	:	0.85 (d, 3H, J = 6.2 Hz), 1.90 (s, 3H), 2.21 (s, 3H), 2.23 (d, 3H, J = 5.8), 2.26 (s, 3H), 2.29 (s, 3H), 2.31 (s, 3H), 2.34 (s, 3H), 2.54 (m, 1H), 2.87 (m, 1H), 5.01(dd, 1H, J = 6.8, 10.5 Hz), 5.81 (s, 1H), 5.83 (s, 1H), 5.85 (s, 1H).
^{13}C NMR (100.6 MHz), -60 °C CD_2Cl_2	:	12.1, 12.3, 12.4, 13.7, 14.2, 14.8, 15.1, 19.8, 64.3, 87.6, 91.5, 105.6, 106.0, 106.6, 143.8, 145.0, 145.4, 149.5, 150.7, 151.3, 231.4, 232.9.
Analysis	:	Calcd. : C: 50.96; H : 5.98; N : 16.21. Found : C: 50.42; H: 5.81; N: 15.81.

Preparation of complex 3.d.

The complex **3.d** was prepared using the general method from $Mo(CO)_6$ (0.528 g, 2 mmol), acetonitrile (30 mL), allyl halide **3.c.1** (3-chloro-1-phenyl-butene) (0.366 g, 2.2 mmol) and the ligand (**3**) (0.704 g, 2.2 mmol). The pure complex **3.d** was obtained by column chromatography (30% CH_2Cl_2-pet.ether). Recrystallization from CH_2Cl_2-MeOH (at -10 °C) yielded shining black crystals (0.175 g, 15%).

Color	:	Black
MP	:	189 °C (dec)
IR	:	2520 (w), 1909 (s), 1811 (s), 1544 (m) cm^{-1}.
^{1}H NMR (400 MHz), -70 °C CD_2Cl_2	:	Major isomer: 1.76 (s, 3H), 2.01-2.45 (5s, 15H), 2.34 (d, 3H, J = 6.6 Hz), 2.81 (m, 1H), 3.78 (d, 1H, J = 11.0 Hz), 5.06 (brs, 1H) 5.10 (m, 1H), 5.60 (m, 1H), 5.87 (s, 1H), 5.90 (s, 1H), 6.50 (m, 1H), 6.60 (m, 1H), 7.05 (m, 1H), 7.35 (m, 1H). Minor isomer: 1.43 (d, 3H, J = 6.0 Hz), 2.05-2.65 (6s, 18H), 4.90 (m, 1H), 5.10 (m, 1H), 5.13 (d, 1H, J = 11.2 Hz), 5.31 (s, 1H), 5.60 (m, 1H), 5.83 (s, 1H), 5.85 (s, 1H), 6.50 (m, 1H), 6.60 (m, 1H), 7.05 (m, 1H), 7.25 (m, 1H).
^{13}C NMR (100.6 MHz), -70 °C CD_2Cl_2	:	Major isomer: 12.23, 12.69, 12.79, 13.00, 14.37, 15.08, 20.52, 65.46, 86.28, 86.92, 105.61, 106.02, 107.05, 125.82, 126.29, 126.37, 126.71, 127.01, 137.42, 144.44, 144.69, 146.26, 149.82, 150.82, 152.15, 232.06, 233.65. Minor isomer: 12.11, 12.55, 14.37, 14.67, 15.72, 16.26, 17.24, 66.32, 84.12, 96.07, 105.90, 106.17, 107.53, 125.06, 125.82, 125.94, 126.86, 128.58, 138.36, 144.44, 144.90, 151.55, 151.83, 153.16, 228.25, 236.10.
Analysis	:	Calcd. : C: 55.86; H: 5.73; N: 14.48. Found : C: 55.20: H: 5.53; N: 13.96.

Preparation of complex 3.e.

The complex was prepared using the general method from $Mo(CO)_6$ (0.528 g, 2 mmol) in acetonitrile (30 mL), allyl halide **3.d.1** (1-chloro-5-phenyl-pent-2,4-diene) (0.535 g, 3.0 mmol) and the ligand (**3**) (0.8 g, 2.5 mmol). A red colored reaction mixture was obtained. Chromatography (10% CH_2Cl_2-pet.ether) and recrystallization from CH_2Cl_2-MeOH (at -10 °C) afforded shining black colored crystals (0.177 g, 18%).

Color	:	Black
MP	:	184 °C (dec)
IR	:	2545 (w), 1932 (s), 1821 (s), 1546 (m) cm^{-1}.
^{1}H NMR (400 MHz), 20 °C	:	Major isomer: 2.09 (m, 1H), 2.26 (s, 3H), 2.31 (s, 3H), 2.32 (s, 3H), 2.33 (s, 3H), 2.34 (s, 3H), 2.35 (s, 3H), 3.10 (d, 1H, J = 6.3 Hz), 3.57 (t, 1H, J = 9.4 Hz), 5.30-5.37 (m, 1H), 5.73 (s, 1H), 5.75 (s, 1H), 5.78 (s, 1H), 6.45 (d, 1H, J = 15.6 Hz), 6.63 (dd, 1H, J = 10.2, 15.5 Hz), 7.13-7.32 (m, 5H). Minor isomer: 1.97 (s, 3H), 2.12 (s, 3H), 2.13 (s, 3H), 2.46 (s, 3H), 2.57 (s, 3H), 2.81 (s, 3H), 3.22 (d, 1H, J = 11.0 Hz), 3.62 (d, 1H, J = 7.4 Hz), 4.42 (m, 1H), 5.28-5.34 (m, 1H), 5.35 (m, 1H), 5.72 (s, 1H), 5.76 (s, 1H), 5.79 (s, 1H), 6.68 (d, 1H, J = 14.6 Hz), 7.13-7.32 (m, 5H).
^{13}C NMR (100.6 MHz), 21 °C	:	12.6, 12.9, 14.7, 14.9, 15.4, 15.5, 16.2, 60.7, 61.9, 79.7, 82.1, 83.1, 87.4, 106.6, 106.7, 107.2, 107.4, 107.9, 108.0, 126.2, 126.3, 126.8, 127.0, 127.2, 128.4, 129.8, 130.0, 130.5, 137.6, 137.8, 143.9, 144.4, 144.5, 145.0, 145.2, 151.0, 151.8, 152.0, 153.2, 154.1, 228.5, 232.1, 232.8, 233.9.
Analysis	:	Calcd. : C: 56.75; H: 5.57; N: 14.18. Found : C : 56.85; H: 5.74; N: 13.81.

Preparation of complex 3.f.

The complex was prepared using the general method from $Mo(CO)_6$ (0.528 g, 2 mmol) in acetonitrile (30 mL), allyl halide **3.e.1** (1-bromo-hex-2,4-diene) (0.618 g, 3.8 mmol) and the ligand (**3**) (0.800 g, 2.5 mmol). The halide in this case was added at the reaction temperature of 60 °C. A dark colored reaction mixture was obtained. Chromatography (10% EtOAc-pet.ether) and recrystallization from CH_2Cl_2-pet.ether (by diffusion method at 5 °C) afforded red colored crystals (0.5 g, 47%).

Color	:	Red
MP	:	182 °C (dec)
IR	:	2548 (w), 1923 (s), 1832 (s), 1543 (m) cm^{-1}.
^{1}H NMR (400 MHz), -50 °C	:	Major isomer: 1.85 (d, 3H, J = 6.7 Hz), 1.99 (m, 1H), 2.04-2.38 (s, 18H), 2.72 (d, 1H, J = 6.4 Hz), 3.21 (t, 1H, J = 8.8 Hz), 5.29 (m, 1H), 5.7-5.9 (m, 4H), 6.06 (m, 1H). Minor isomer: 1.77 (d, 3H, J = 6.4 Hz), 2.16 (s, 3H), 2.22 (s, 3H), 2.54 (s, 3H), 2.83 (s, 3H), 2.33-2.38 (s, 6H), 3.33 (d, 1H, J = 11.0 Hz), 3.49 (d, 1H, J = 7.5 Hz), 4.40 (m, 1H), 4.55 (m, 1H), 5.35 (m, 1H), 5.7-5.9 (m, 4H).
^{13}C NMR (100.6 MHz), -50 °C	:	13.0, 13.2, 13.6, 14.3, 14.9, 15.5, 15.7, 16.0, 16.1, 18.4, 18.6, 63.3, 73.9, 80.7, 81.3, 85.6, 87.1, 106.5, 106.7, 107.1, 107.4, 107.8, 126.3, 126.8, 127.7, 130.7, 131.6, 143.0, 144.1, 144.2, 144.7, 145.0, 150.2, 150.9, 151.7, 151.8, 151.9, 152.2, 153.6, 227.8, 232.5, 233.7, 233.8.
Analysis	:	Calcd. : C : 52.09; H : 5.89; N : 15.85. Found : C : 51.64; H : 5.97; N : 15.39.

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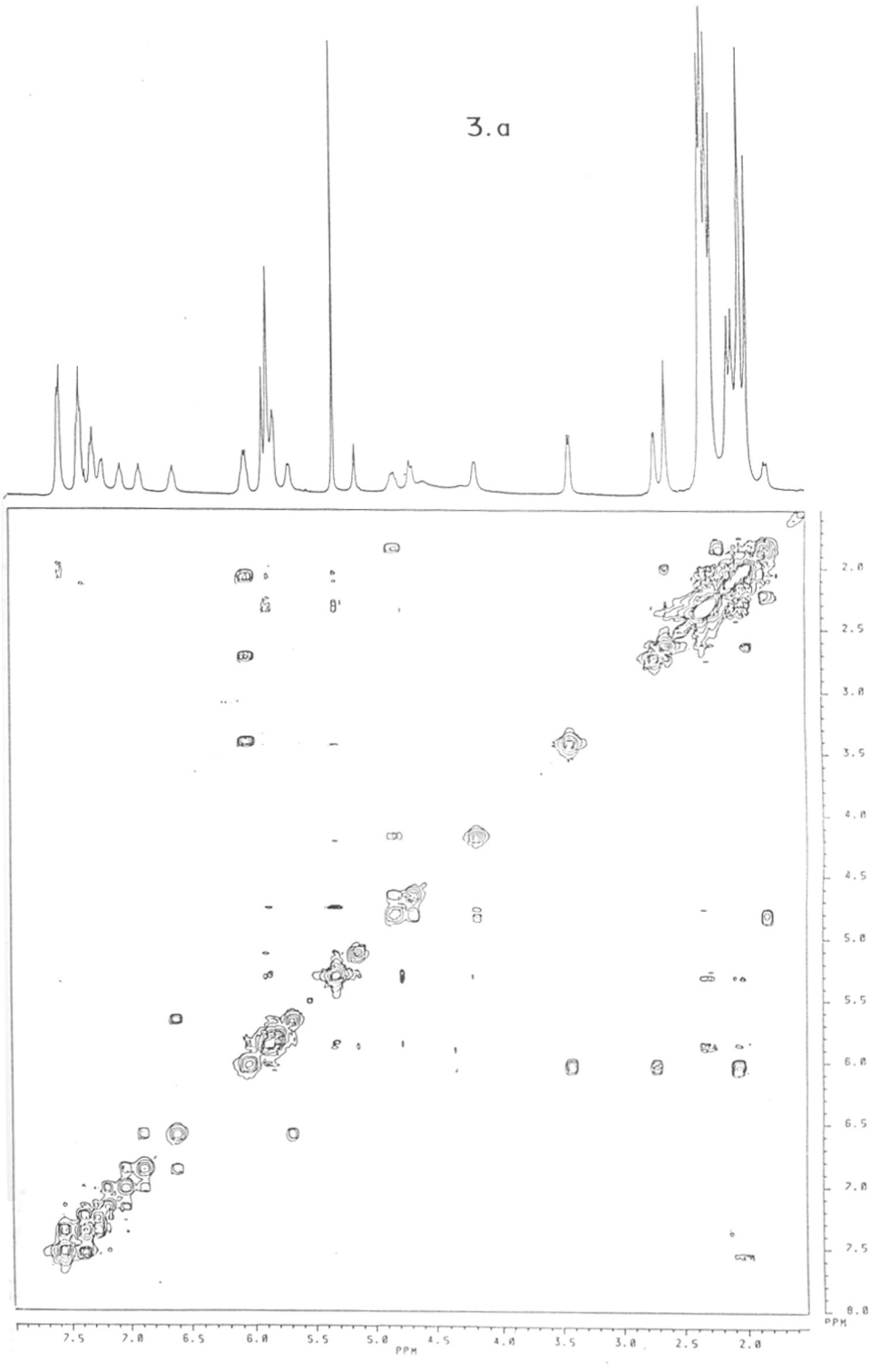
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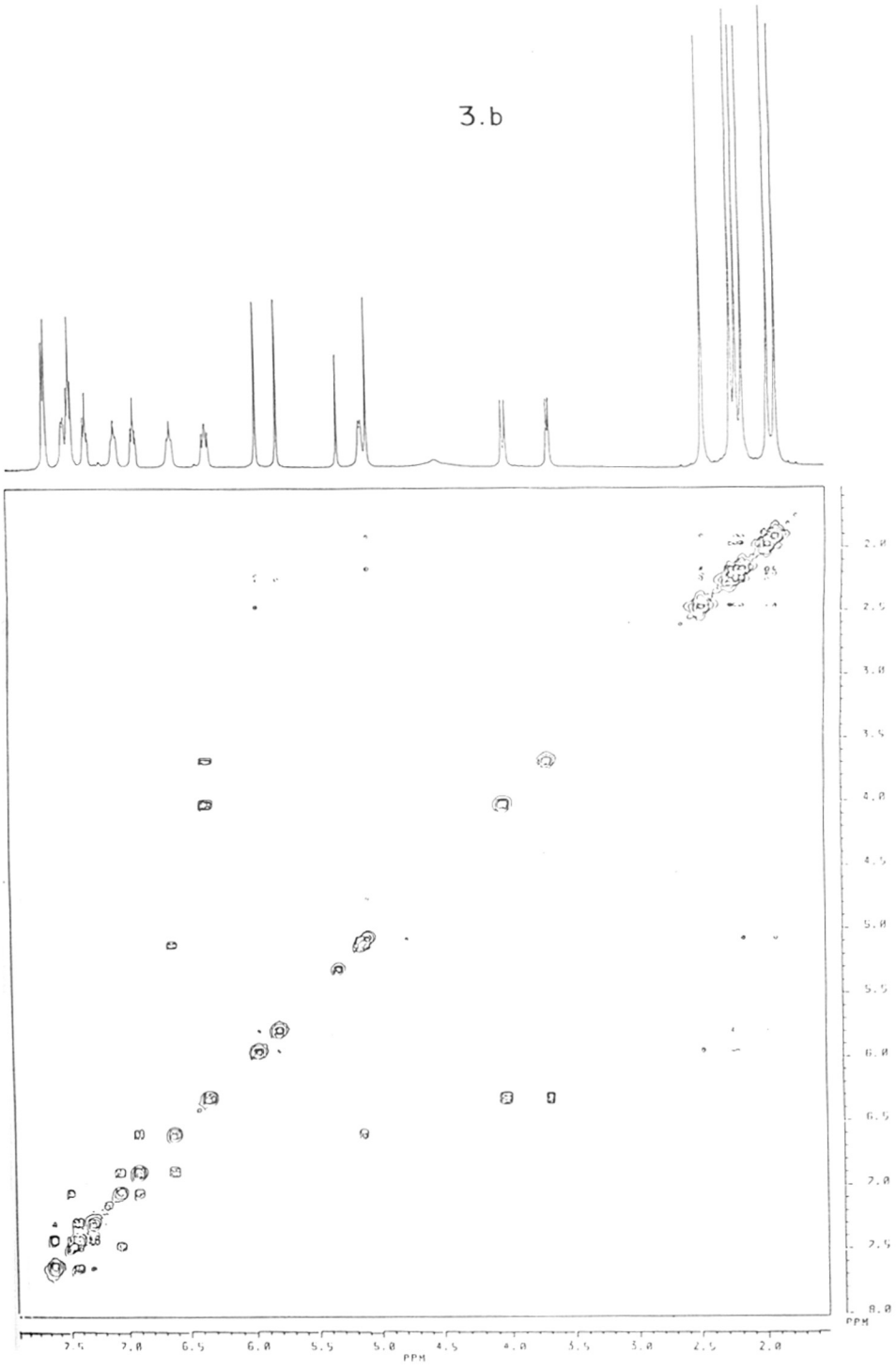
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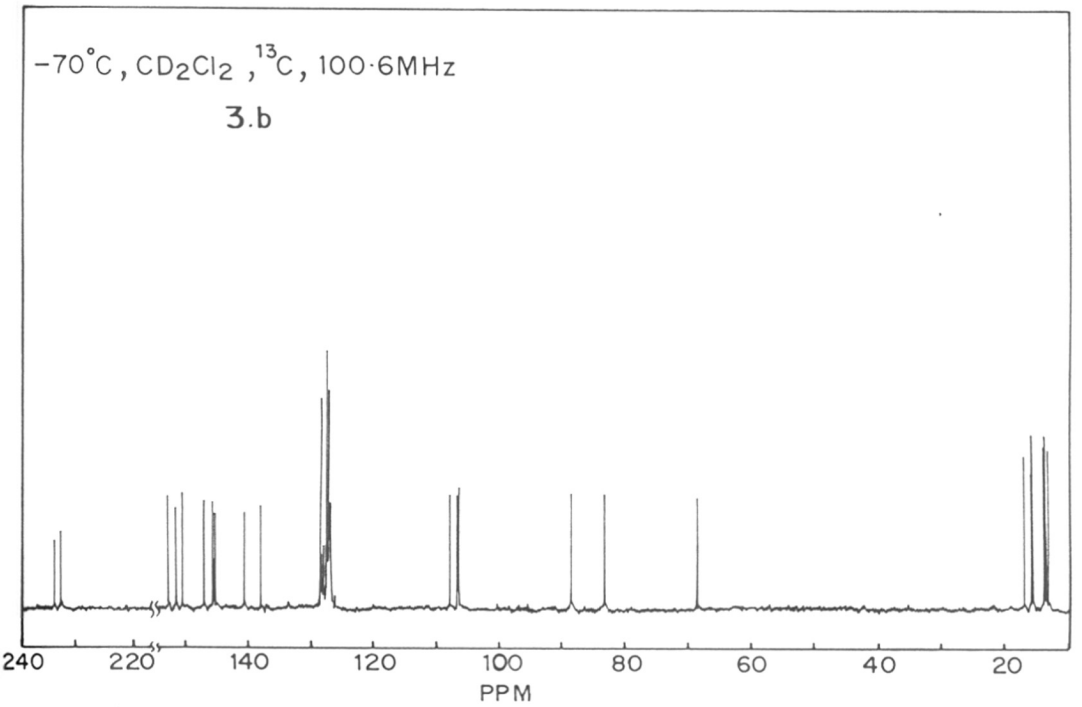
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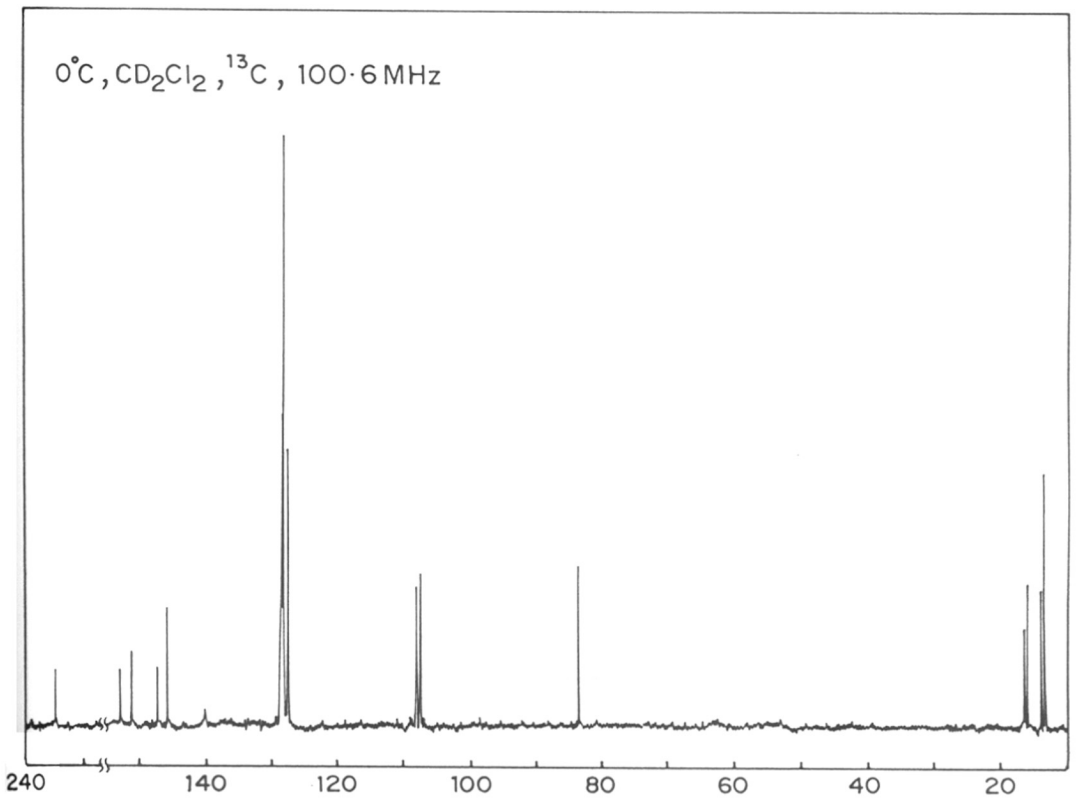
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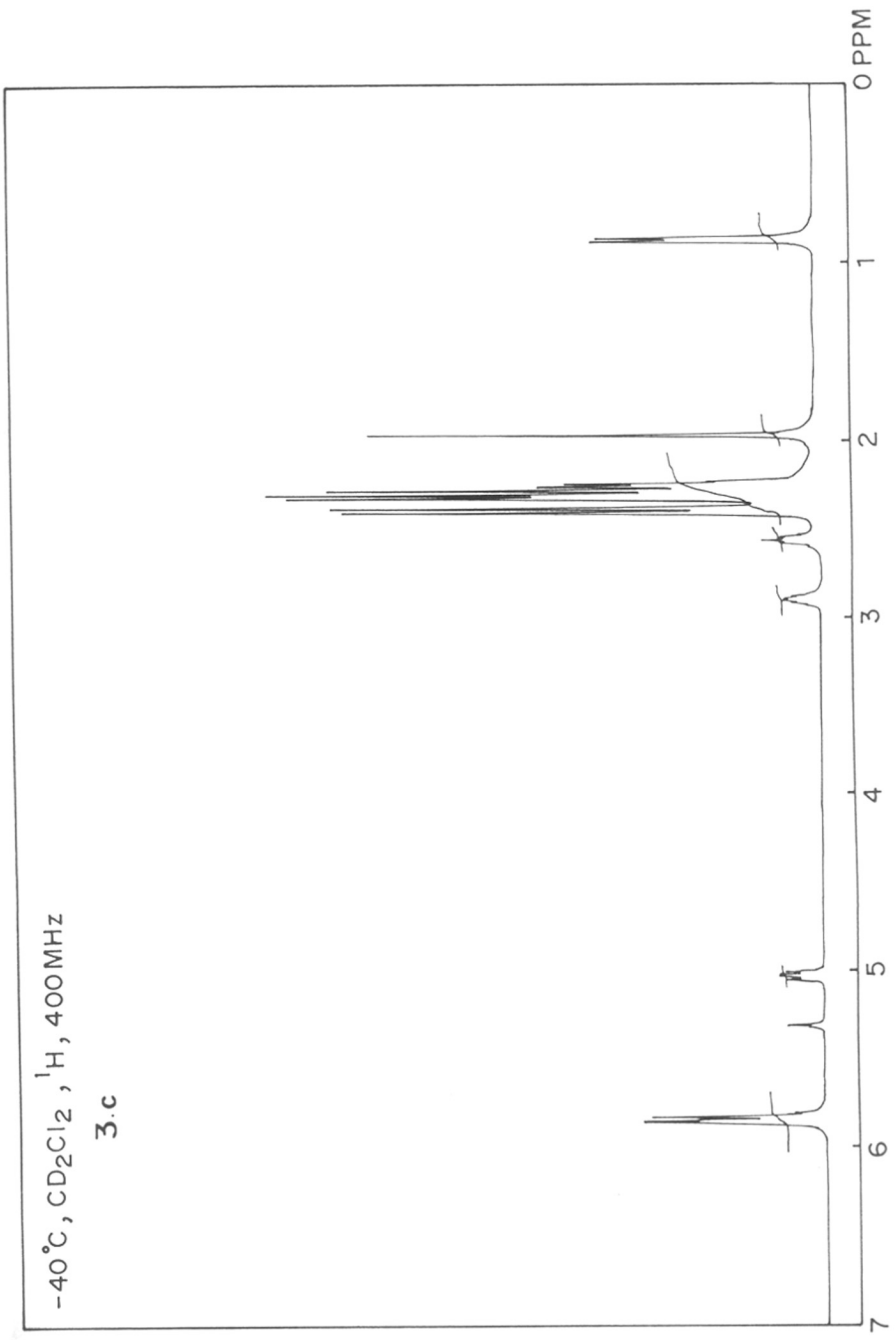
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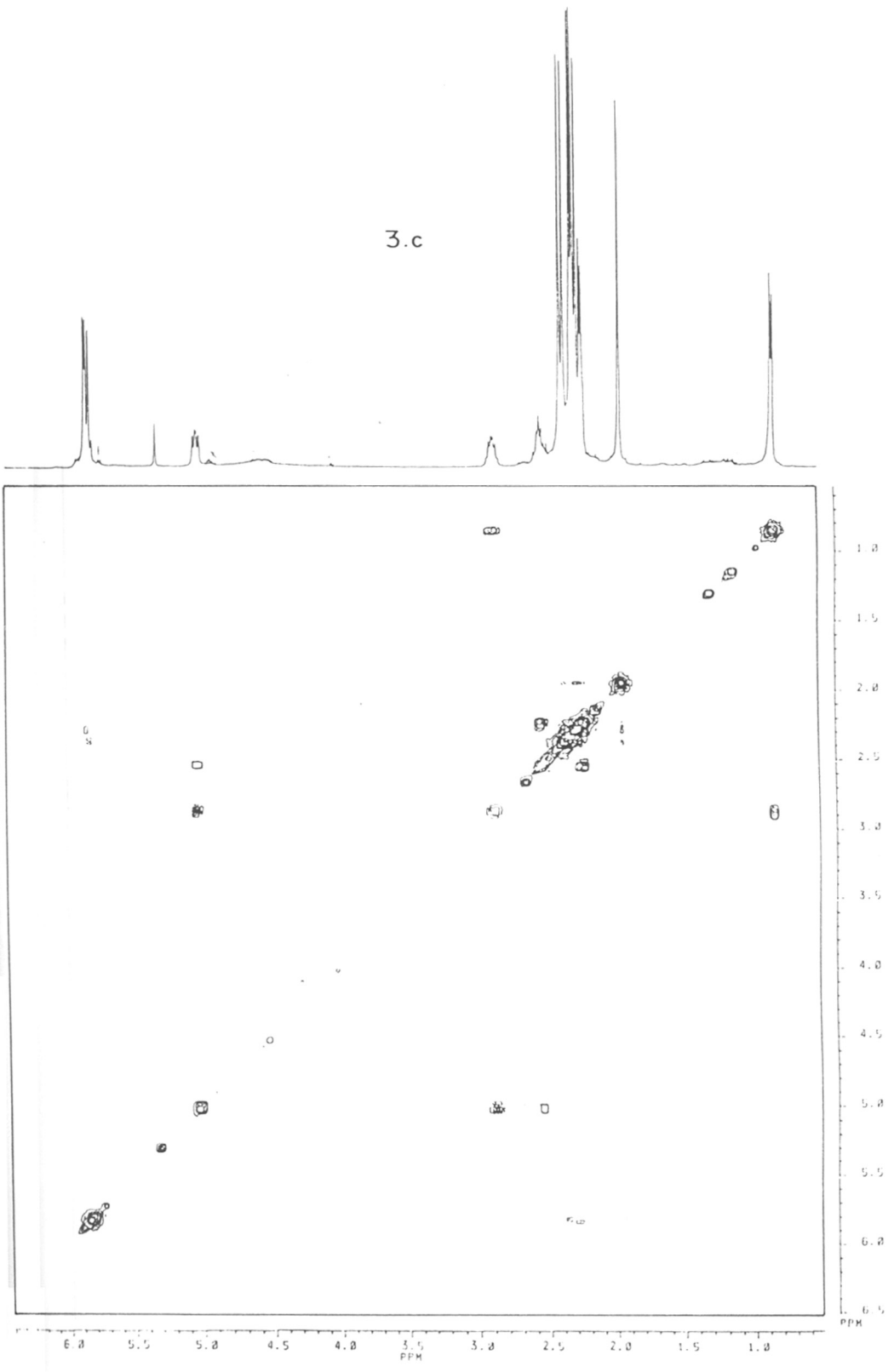
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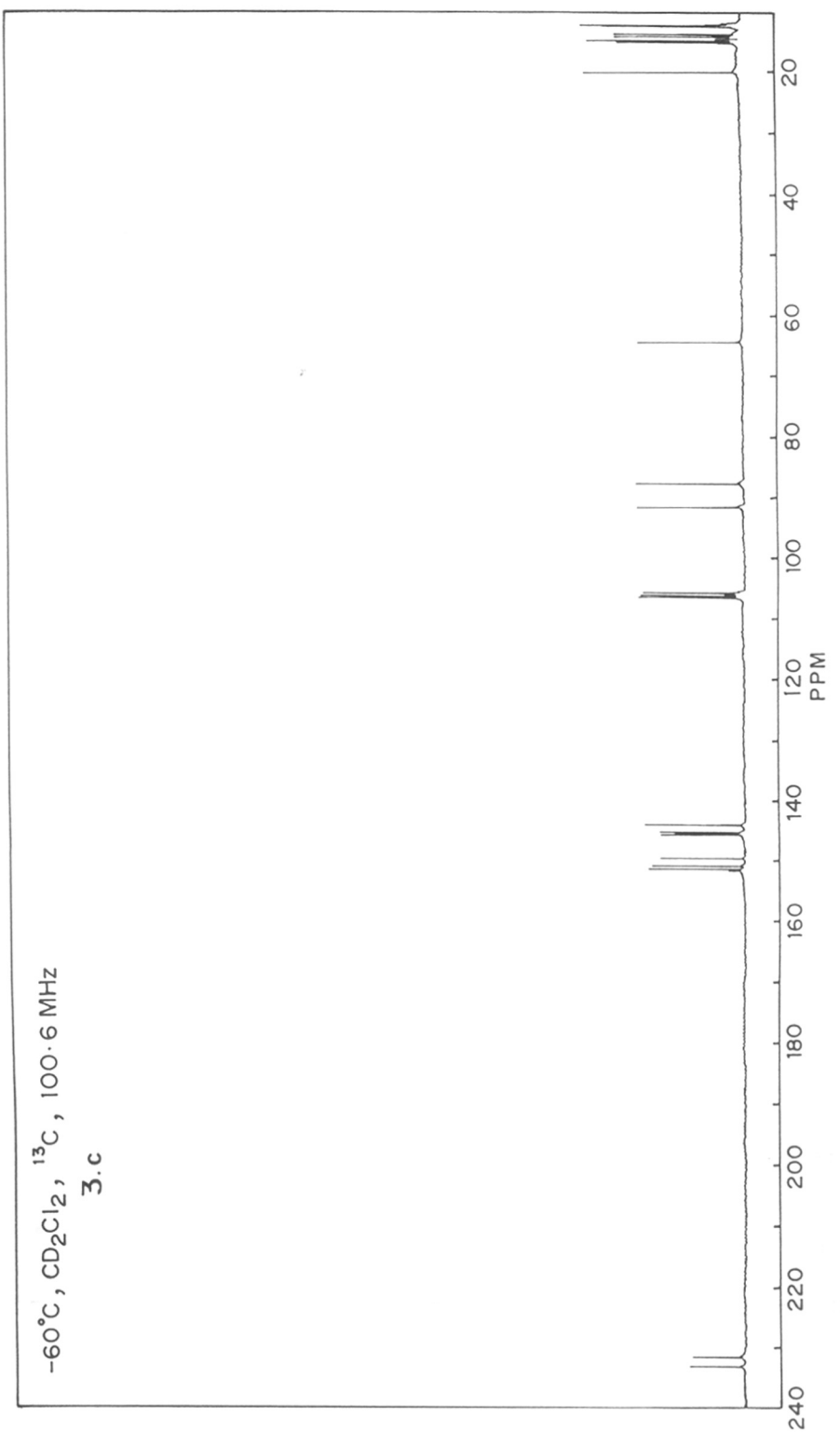
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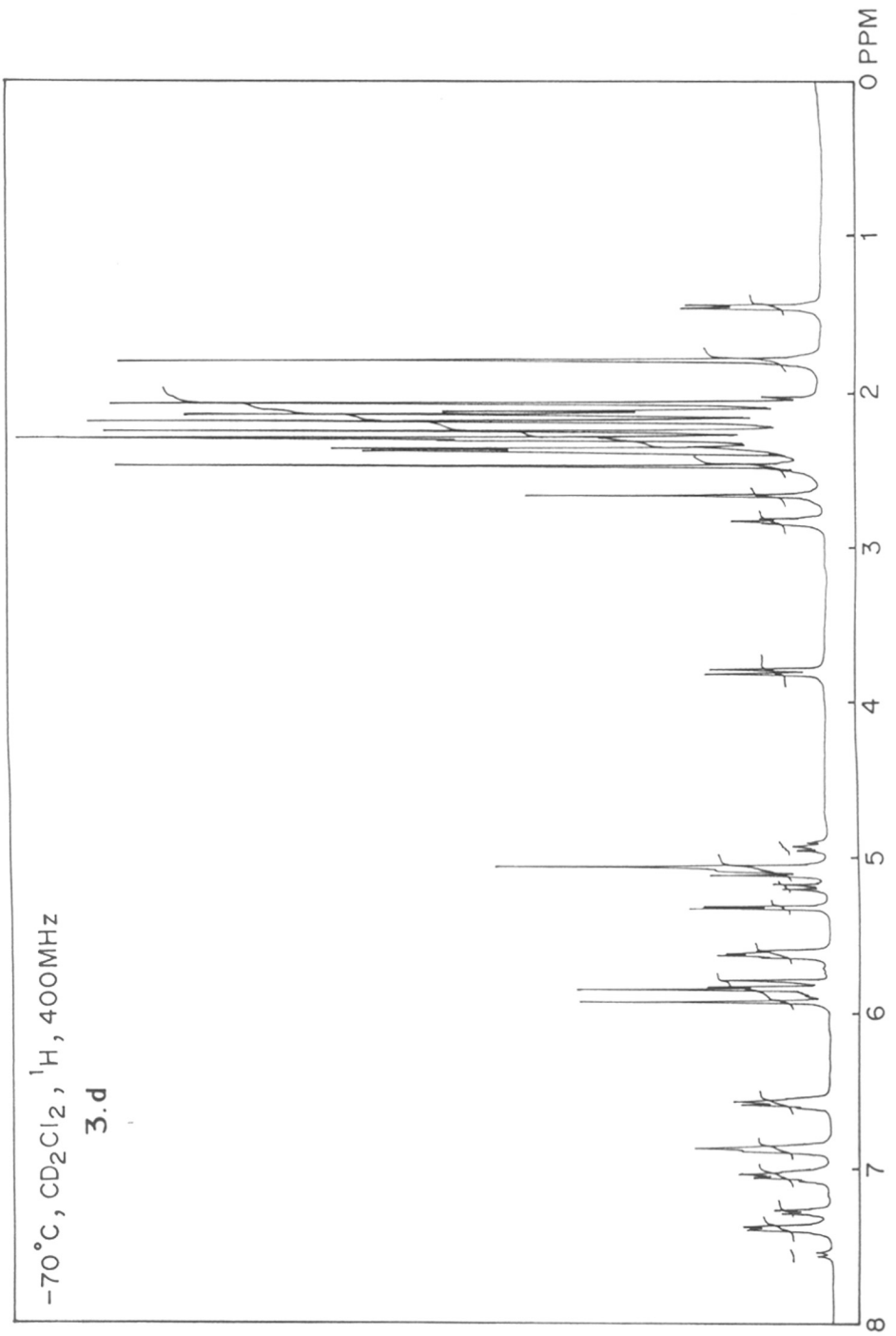
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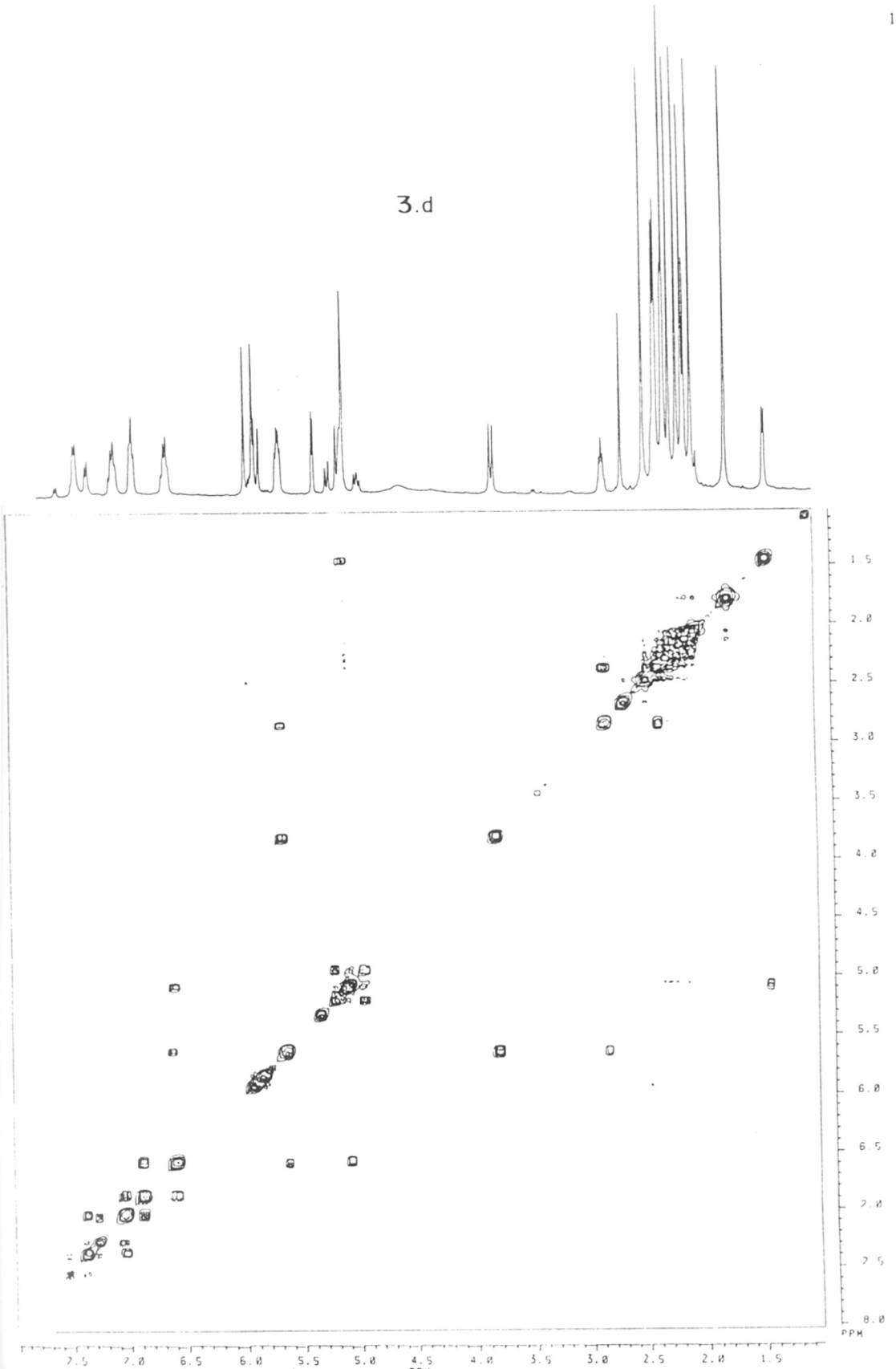
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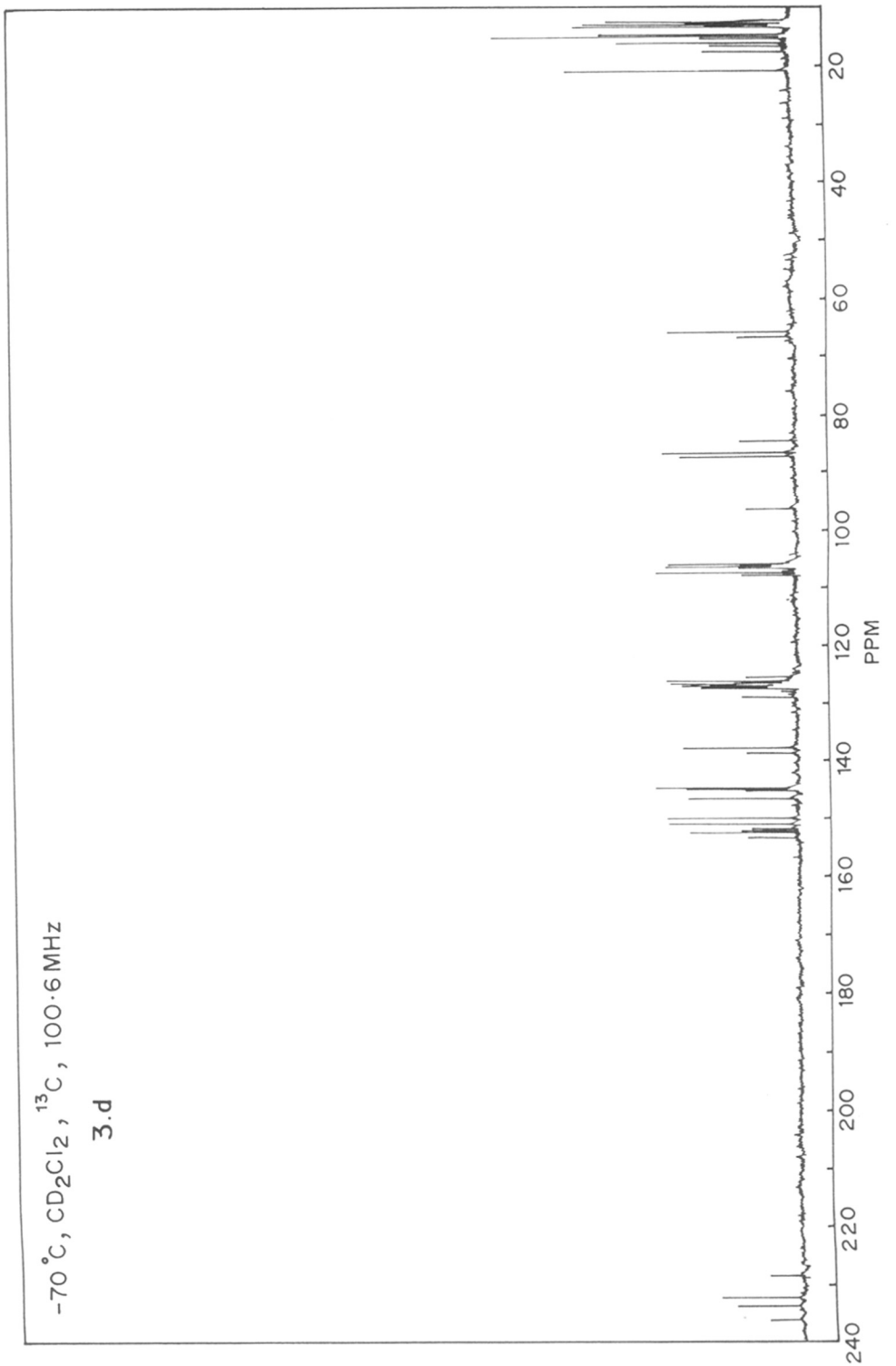
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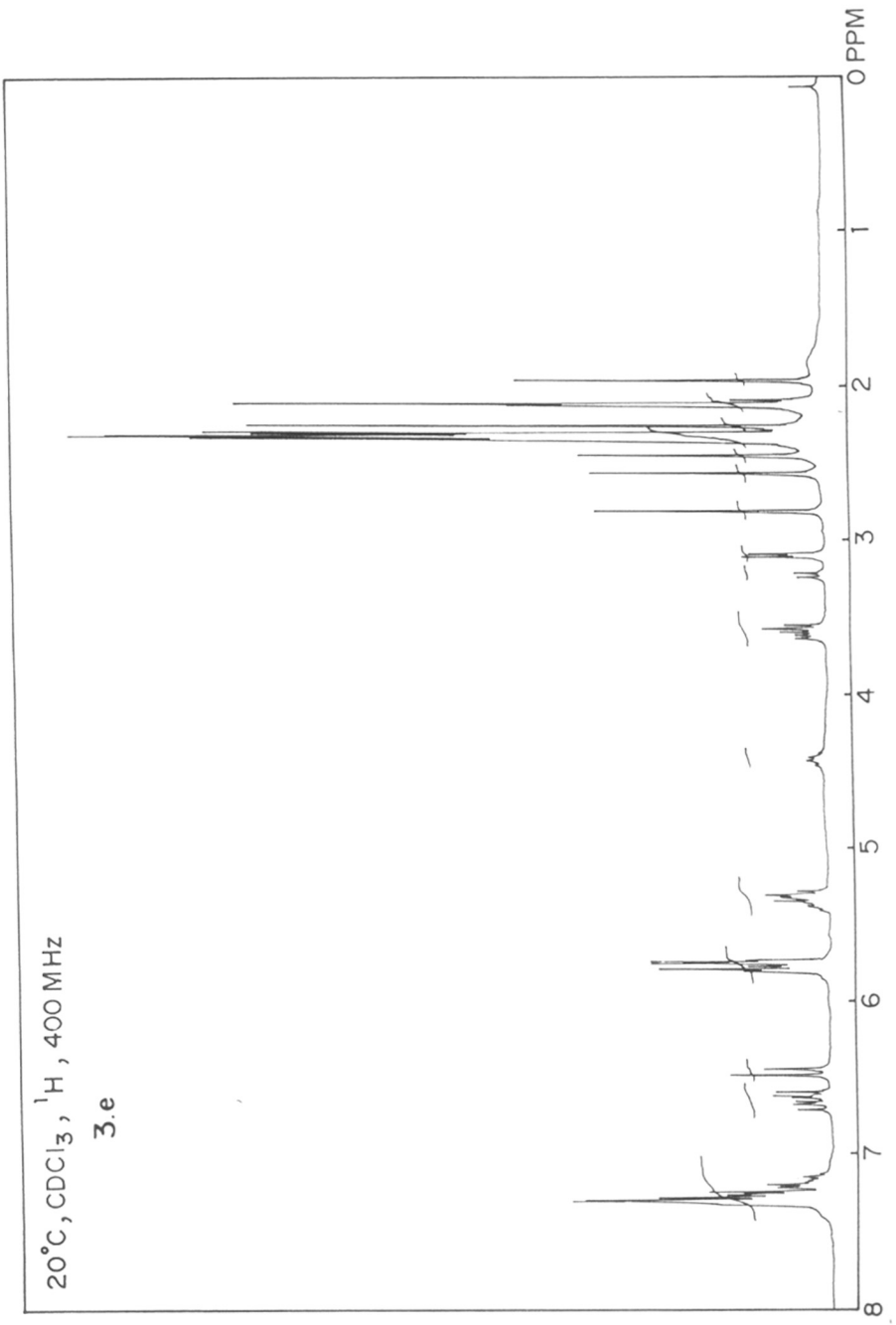
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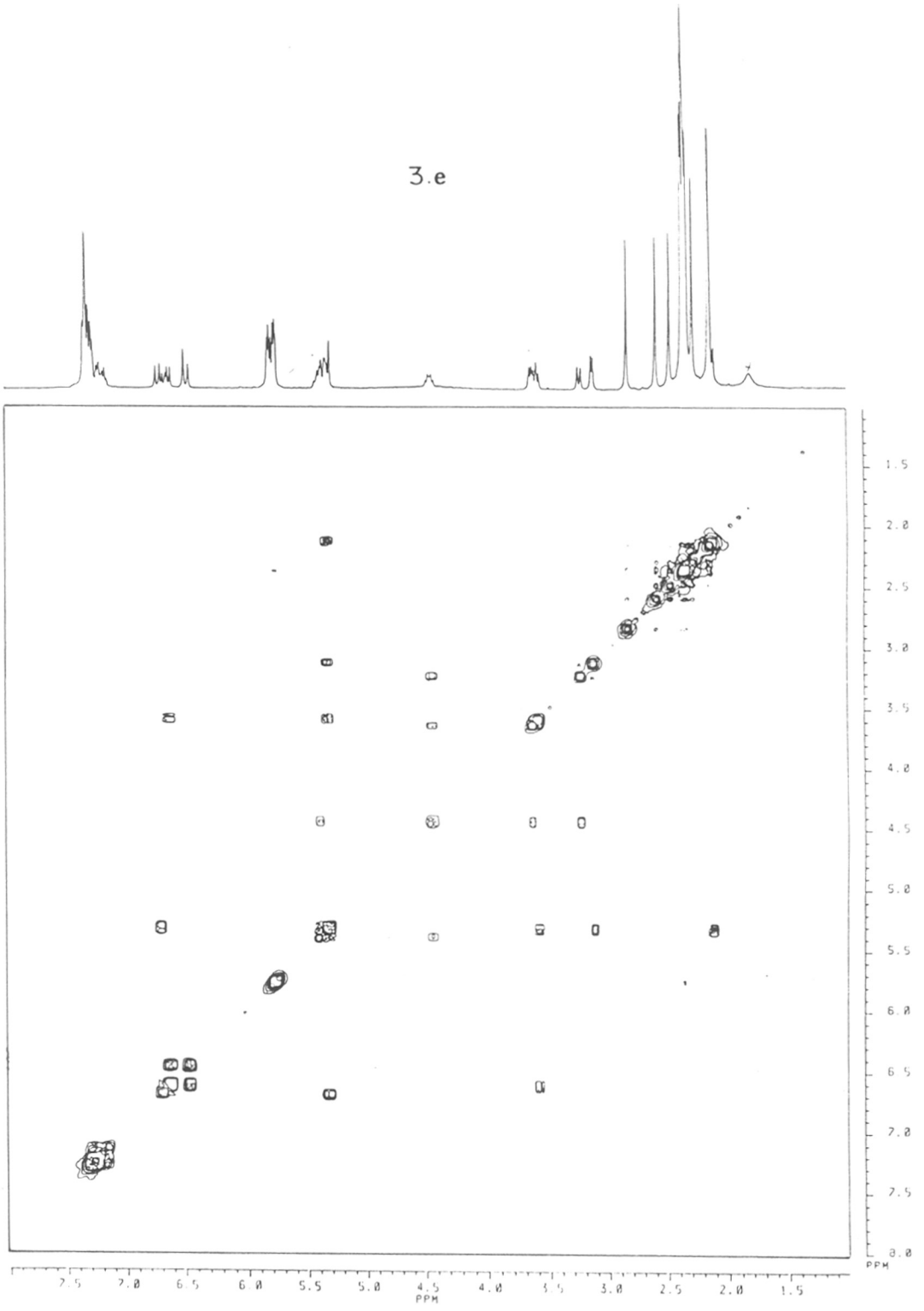
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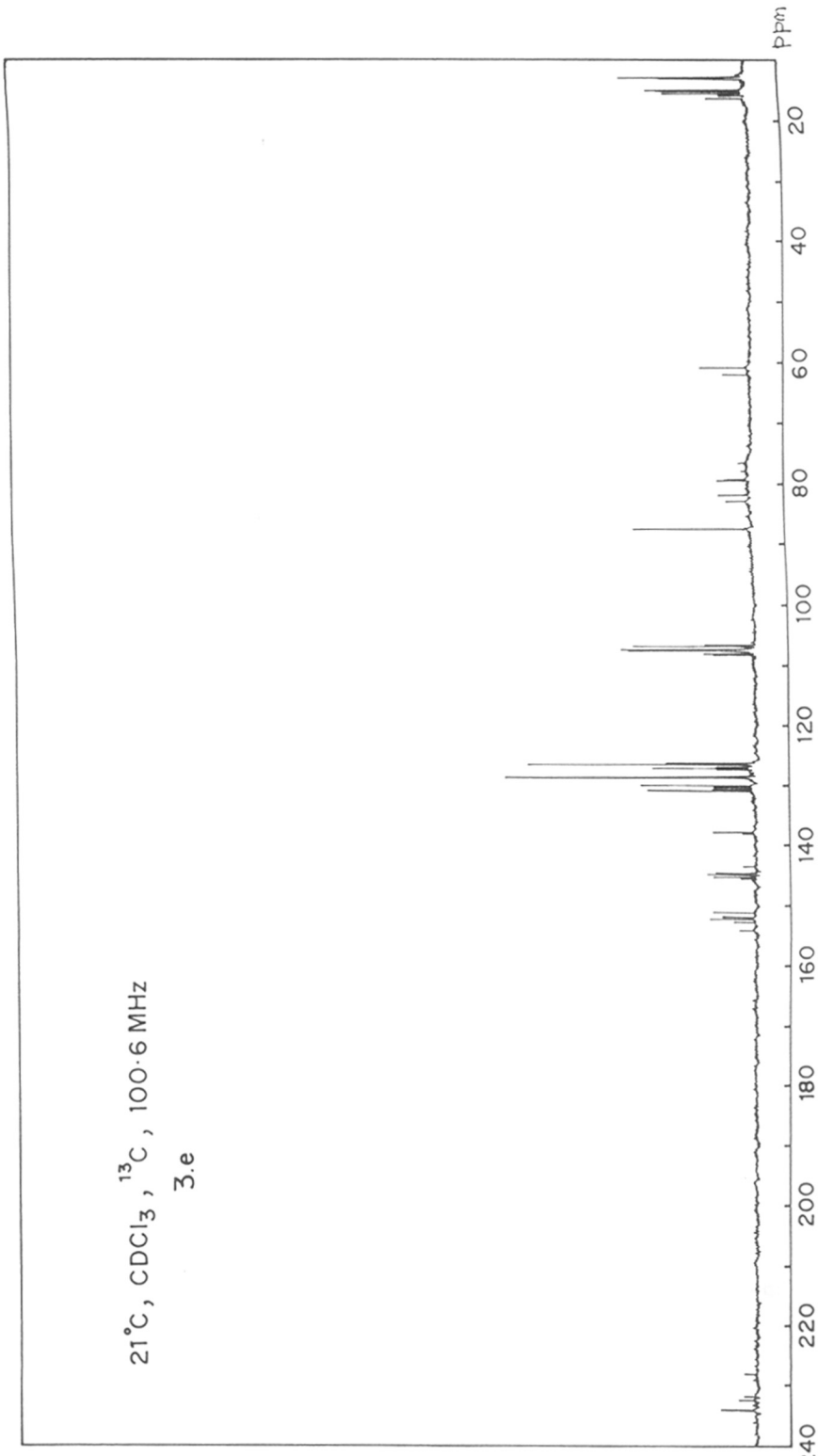
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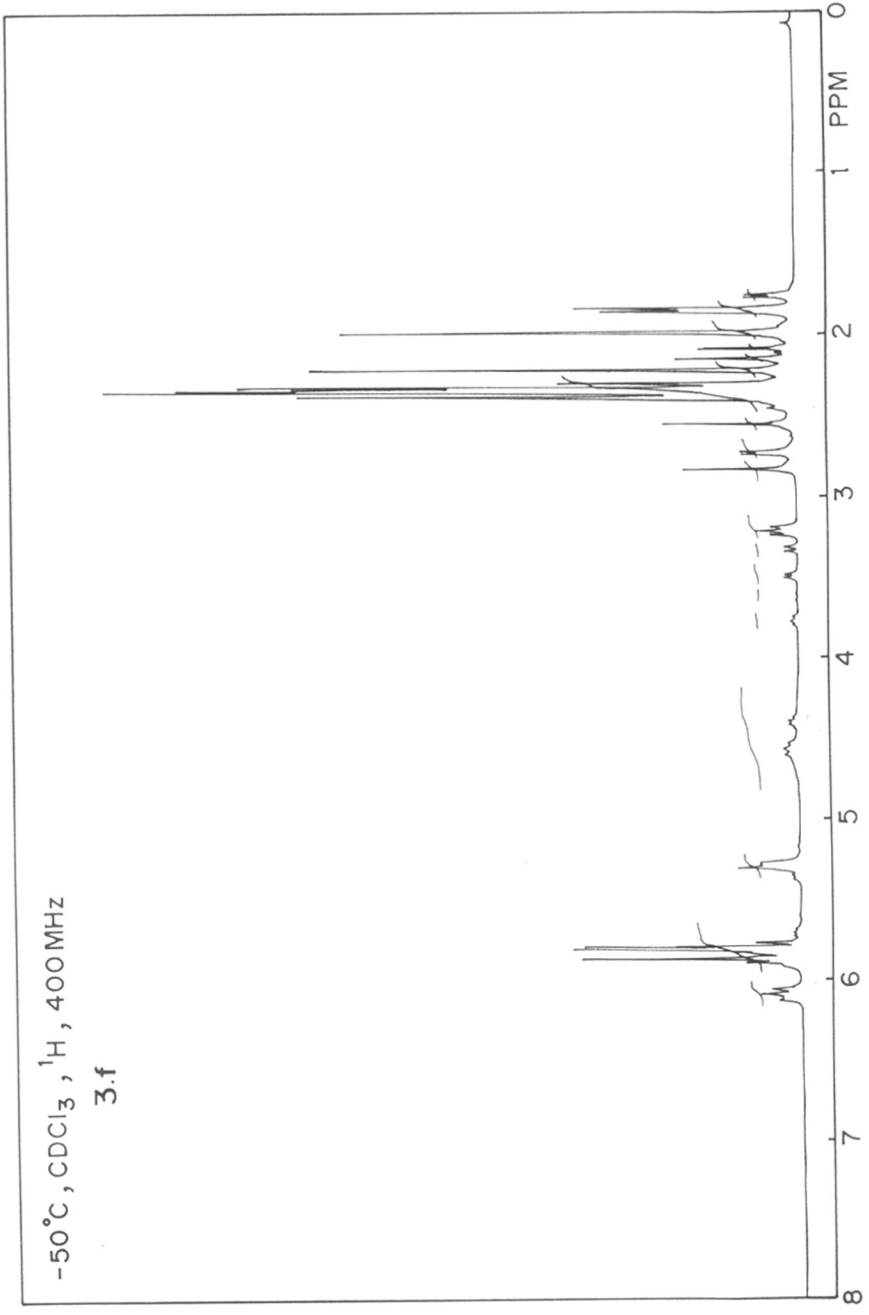
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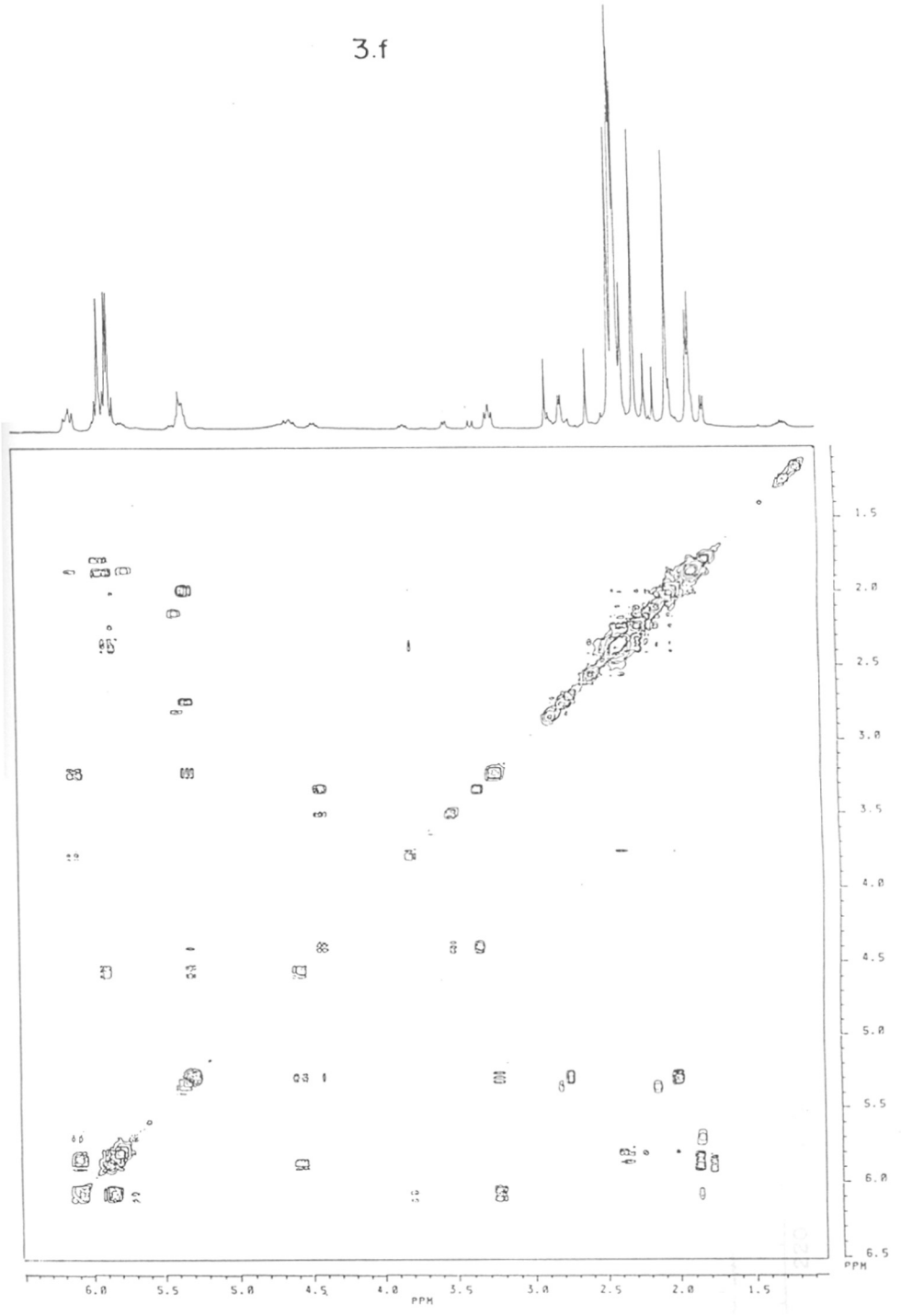
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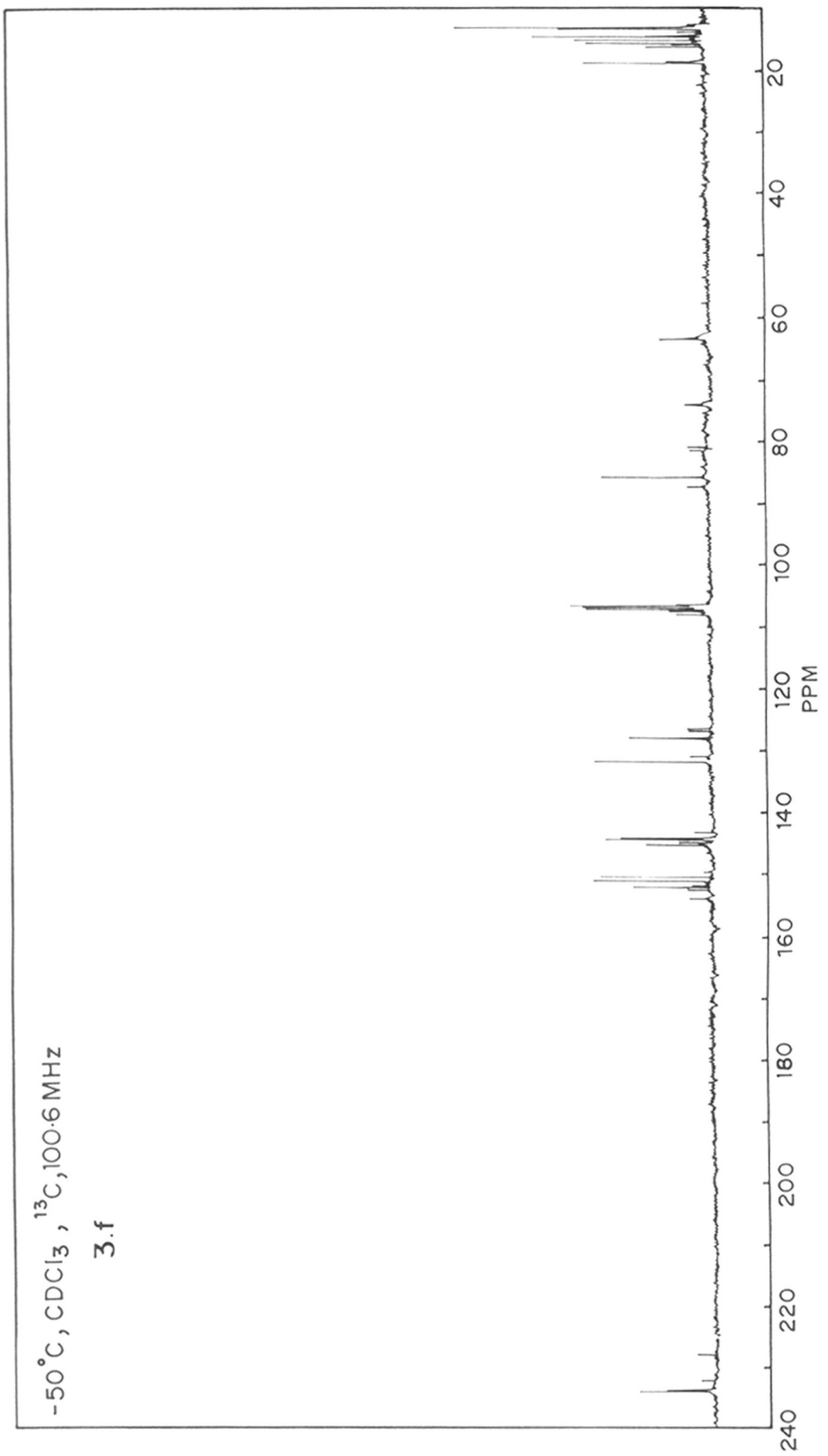
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Chapter-IV

Molybdenum π-Allyl Complexes with C_2- Symmetric Homochiral *Bis*-oxazoline Ligands.

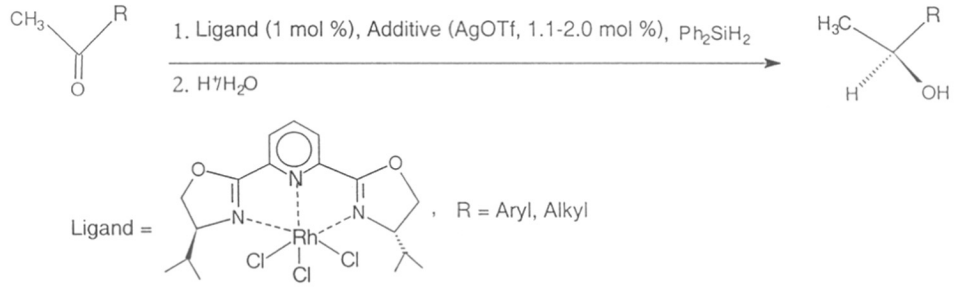
IV. 1 Background

Molybdenum carbonyl derivatives have been studied as catalysts for allylation reactions of different kinds[1], although results are not as impressive as with palladium catalysis of similar reactions.[2] Of direct interest to the theme of molybdenum allyl complexes with nitrogen donor ligands, are the instances where bidentate chelating ligands were successfully used to catalyze allylation.[3] In principle, use of homochiral ligands in these cases should result in catalytic, enantioselective allylation reactions.[4]

An immediate choice of N-donor ligands is C_2-symmetric, homochiral *bis*-oxazoline series. While the chiral oxazolines were popularized by Mayers[5] as efficient auxiliaries for alkylation or Michael addition reactions, homochiral *bis* oxazoline ligands were found to be highly effective in the catalytic asymmetric reactions like hydrosilylation of ketones[6], hydrogenation of aryl-alkyl ketones[7], cyclopropanation of olefins[8], Diels-Alder reaction[9], and nucleophilic allylic substitutions.[10]

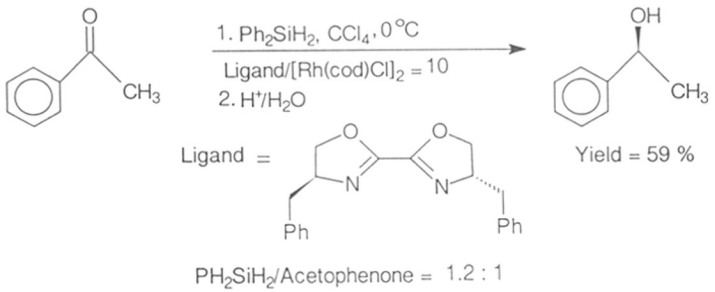
Brunner[6c] achieved excellent results in transition metal catalyzed enantioselective hydrosilylations of ketones and monophenylations of *meso*-diols using optically pure oxazoline ligands. Nishiyama[6b] carried out asymmetric hydrosilylation of aliphatic or aromatic ketones, catalyzed by *bis*(oxazolinylpyridine)-rhodium(III) complex to obtain secondary alcohols with *S* configuration (*Scheme-1*) in high optical purity (*ee*: 56-94%) and high chemical yield (61-96%).

Scheme-1



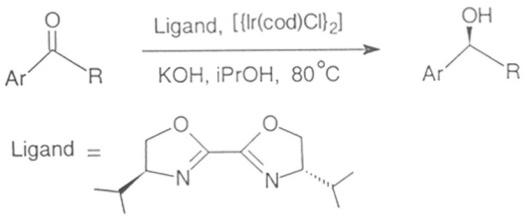
Helmchen[6a] achieved a maximum of 84% enantiomeric excess in a related reaction, where differently substituted homochiral *bis*-oxazolines and *bis*-thiazolines were used as ligands for Rh(I). However, chemical yields were not very attractive (*Scheme-2*)

Scheme-2



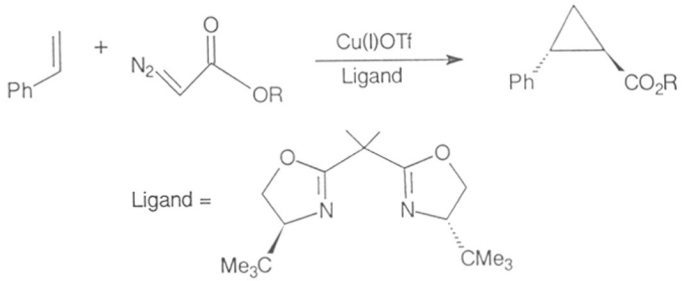
Catalytic asymmetric hydrogenation of aryl alkyl ketones (*Scheme-3*) was investigated by Pfaltz.[7] The reaction was catalyzed by an iridium complex (formed *in situ* from [{Ir(cod)Cl}$_2$] and an optically pure *bis*-oxazoline ligand to yield optically active alcohols with enantiomeric excesses between 47-91%.

Scheme-3



Evans[8e] showed that a Cu(I) complex derived from an optically pure *bis*-oxazoline and Cu(I) triflate is an attractive catalyst for asymmetric cyclopropanation of mono- and 1,1-disubstituted olefins by achiral diazo esters at ambient temperature (*Scheme-4*). Asymmetric induction in excess of 99% and 1000-fold catalytic turnover was observed.

Scheme- 4

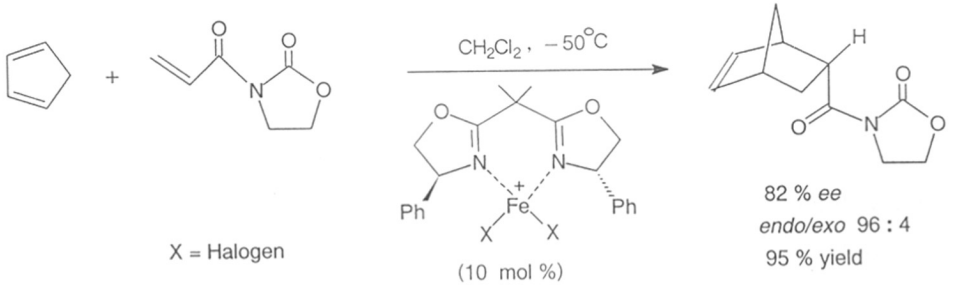


R	*trans/cis*	(R,R)
Ethyl	73 : 27	99 % *ee*
Tert-butyl	81 : 19	96 % *ee*
BHT	94 : 6	99 % *ee*

(2,6-di-*tert*-butyl-4-methyl phenol)

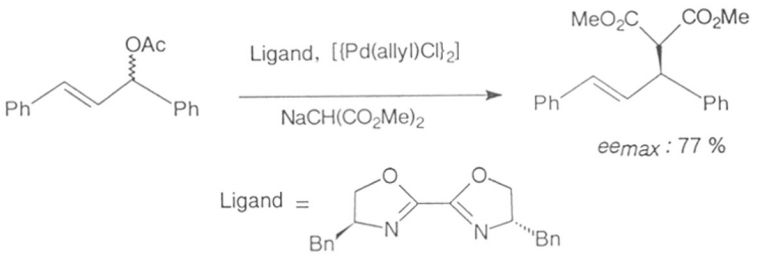
Corey[9d] used a *bis*-oxazoline-Fe(III) complex to catalyze enantioselective Diels-Alder reaction (*Scheme-5*).

Scheme-5



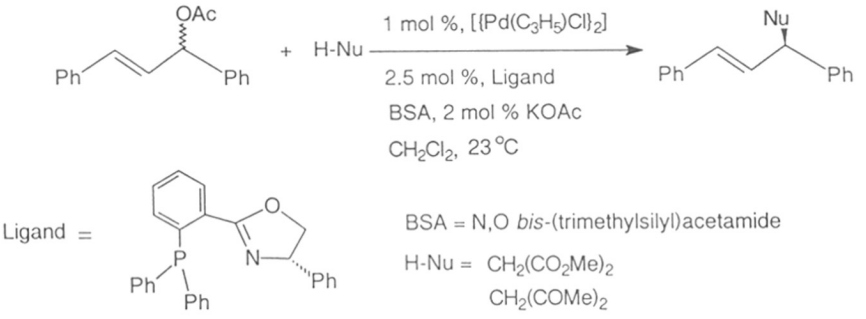
In a different set of study, Pfaltz[10b] established that nucleophilic allylic substitution of 1, 3-diphenylprop-2-enyl acetate with dimethyl sodiomalonate could be catalyzed by a *bis*-oxazoline complex of palladium (II) (*Scheme-6*).

Scheme-6



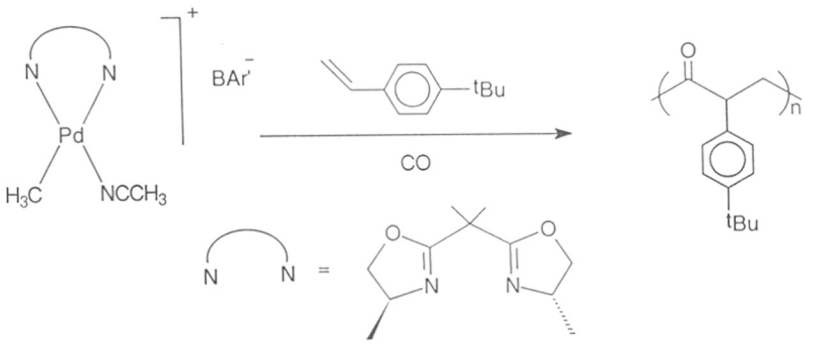
A structurally related monooxazoline ligand was found to be more effective in terms of chemical and optical yield[10a], for the same transformation (*Scheme-7*).

Scheme-7



Brookhart[11] developed a new strategy for synthesis of stereoblock polymers involving ancillary ligand exchange during a living transition-metal-catalyzed polymerization (*Scheme-8*). Highly stereoregular, optically active polyketones were obtained when the catalyst was derived from enantiomerically pure C_2-symmetric *bis*-oxazoline ligand.

Scheme-8



Ar' = 3,5-$(CF_3)_2C_6H_3$

The efficacy of *bis*-oxazoline ligands derived from optically pure precursors in inducing chiral bias for a variety of C-C bond-forming reactions inspired the study of molybdenum π-allyl complexes with homochiral 2,2'-*bis*-oxazoline ligands. The study reported in this chapter, therefore, concerns - a) synthesis of homochiral *bis*-oxazoline ligands from appropriate precursors; and, b) synthesis and structure elucidation of stable molybdenum π-allyl complexes derived from this ligand.

IV. 2 Present Work

As is known in literature[12], the *bis*-oxazoline ligands were synthesized from diethyl oxalate and suitably substituted 2-amino alcohols. The first step consisted of heating the two reactants together to produce the corresponding diamide. The hydroxyl groups were converted to chlorides using thionyl chloride, followed by cyclization in refluxing methanolic sodium hydroxide. However, during the course of our work, we found an improved procedure for cyclization, which furnished higher yield and comparable optical purity. It involved treatment of a dichloromethane solution of the dihalide with 50% aqueous sodium hydroxide in presence of a catalytic amount of TBAB at room temperature for 2-3 h.

Two homochiral amino alcohols used in this study were derived from R-(-)-phenylglycine and S-(+)-valine. Reduction of the amino acid to the alcohol with sodium borohydride and sulphuric acid in THF[13] was generally a high yield conversion, except for some runs which did not yield the product. Efficient stirring is a key requirement for the success of this reaction. The alcohols were characterized by their IR and proton NMR spectra which compared well with reported data. Final *bis*-oxazoline products were crystallized to constant rotation [**4(I)** : $[\alpha]_D$ + 111° (c 1, $CH\mathfrak{Cl}_3$), **4(II)** : $[\alpha]_D$ -147 ° (c 0.7, $CHCl_3$)], and the data were in agreement with reported values.[8c] Detailed steps are described in the experimental section.

Complexes were prepared by the usual procedure. Appropriate allyl halides were added to the $(CH_3CN)_3Mo(CO)_3$ complex followed by addition of ligand. These complexes were soluble in common organic solvents and fairly stable in solid state. Their solutions are fairly air-sensitive and difficulties were often encountered in their chromatographic purification over silica gel (for details, *vide* experimental section).

The complex **4a** was obtained as red crystals (81 %). The IR spectrum of **4a** showed two sharp peaks of equal intensity appearing at 1930 and 1851 cm^{-1} corresponding to the CO ligands. The peak of weak intensity at 1629 cm^{-1} was assigned to the carbon-nitrogen double bonds in the bis-oxazoline ligand. This observation was the same for all other complexes described in this chapter. The proton NMR spectrum at ambient temperature displayed broad lines. Chilling this solution to -70 °C did not result in significant improvement. However, the presence of two species in the ratio 2 : 1 could now be seen. Conclusive structural deductions regarding the identity of the two species could not be made from this spectrum. The ^{13}C NMR, however, revealed the presence of four carbonyl groups, at 221.6 and 225.1 ppm for the major species and at 223.3 and 225.3 ppm for the minor species. To establish the identity of the complex **4a** a single crystal X-ray structure analysis was undertaken. The crystal structure showed the presence of only one type of molecule (*Fig.-1*).

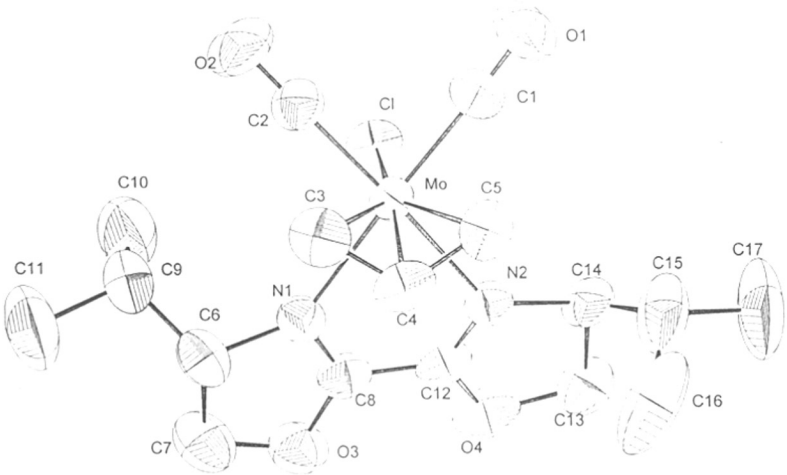


Fig.-1. ORTEP view of the molecular structure of **4a**

The microanalytical data was consistent with the structure determined by crystallography. Though the broadness of the proton NMR spectrum did not allow us to extract accurate coupling information, chemical shift values and perusal of a 2D COSY spectrum suggested that the determined structure was that of the major species. The major species had two *anti* allyl protons at 1.05 (merged with isopropyl methyl signals) and 1.24 ppm (d = $J_{anti/central}$ = 9.4 Hz). The *syn* allyl protons appeared as broad singlets at 3.21 and 3.81 ppm. The central proton appeared as a broad multiplet at 4.06 ppm. The signals due to the isopropyl methyl groups appeared as broad multiplets in the range 0.68-1.09 ppm. The isopropyl methine protons showed up as broad signals at 2.01 and 3.03 ppm. In the case of the minor species the isopropyl methyl and the two *anti* methyl signals appeared merged with those of the major species. The *syn* methyl signals appeared as a broad singlet at 3.03 ppm. The central proton appeared at 3.49 ppm. The isopropyl methine protons showed up as broad signals at 2.13 and 2.34 ppm.

The crystal structure (*Fig.-1*) clearly shows the expected, symmetrical structure of the complex **4a**. Two allyl termini are non-equivalent due to chirality of the bidentate ligand. The structure is also in conformity with the observed structures of related complexes.[14] There is no significant deviation from an octahedral geometry.

The presence of the minor species is in itself intriguing. Stereochemical non-rigidity in this type of complex most probably arises from π–σ–π interconversion, the allyl termini exchanging sites. In this instance, it makes no difference in the overall structure. At this point we believe the minor species could be a chlorine-bridged dimer where molybdenum is heptacoordinated.

The IR spectrum of **4b** indicated that the desired complex was formed, which showed two sharp peaks of equal intensity appearing at 1958 and 1880 cm^{-1} corresponding to the CO ligands. The peak of weak intensity at 1635 cm^{-1} was assigned to the carbon-nitrogen double bonds in the *bis*-oxazoline ligand.

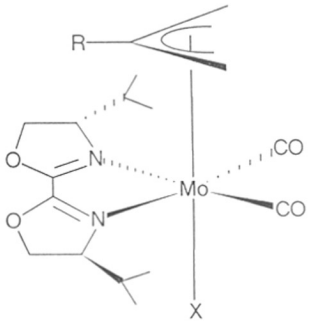


Fig.-2. Structure of complex **4b-c**

Complex No.	R	X	Yield (%)
4b	C_6H_5	Br	24
4c	CH_3	Cl	26

The complexes **4b-c** featuring centrally substituted allyl groups (*Fig.-2*) displayed sharp lines in the NMR spectra and indicated the presence of only one conformer in each case.

The complex **4b** showed two *anti* allyl proton signals at 1.23 ppm and 1.57 ppm respectively as doublets coupled with the *syn* protons with geminal coupling 2.7 Hz. The *syn* allyl protons appeared at 3.40 ppm and 3.48 ppm as multiplets. Four methyl groups appeared at 0.80, 0.90, 1.11 and 1.17 ppm as doublets (J = 5.9-6.5 Hz), and two isopropyl methine protons appeared at 2.05 and 2.55 ppm as multiplets. Fifteen aromatic protons resonated at 7.15-7.40 ppm.

The ^{13}C NMR spectrum at ambient temperature showed four peaks at 15.5, 16.9, 19.1 and 21.0 ppm for four isopropyl methyl carbons; the two isopropyl

methine carbons appeared at 28.5 and 29.7 ppm. Two methylene carbons of the *bis*-oxazoline ligand appeared at 43.6 and 49.4 ppm and carbons attached to isopropyl groups appeared at 69.2 and 72.6 ppm, two allyl methylene carbons at 71.8 and 72.6 ppm and the central allyl carbon at 83.4 ppm. The phenyl carbons appeared at 124.4, 126.7, 127.9 ppm and the *ipso* carbon at 138.7; two tertiary carbons of the ligand showed up at 157.4 and 159.0 ppm and the two carbonyl carbons appeared at 221.8 and 224.1 ppm.

The complex **4c** was obtained as deep red crystals. The proton NMR spectrum recorded at ambient temperature showed sharp signals corresponding to a single conformer (*Fig.-1*). The complex **4c** displayed proton signals at the usual positions (two *anti* allyl protons at 1.17 and 1.22 ppm as singlets; the *syn* protons at 2.77 ppm and 2.87 ppm as multiplets and the central methyl allyl protons at 1.88 ppm as singlet) confirming the η^3-coordination mode.

The complexes **4d-e** feature a terminally monosubstituted allyl group. The complex **4d** (*Fig.-3*) displayed sharp lines in the proton NMR spectra.

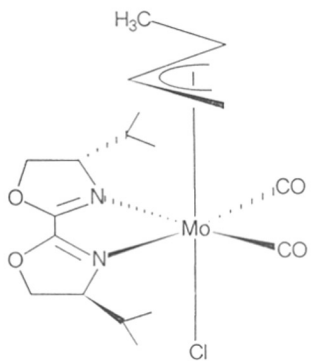


Fig.-3. Structure of complex **4d**

Signals were observed at usual positions for π-allyl protons. Two *anti* allyl protons appeared at 1.02 ppm (dd, 1H, $J_{syn/anti}$ = 2.6, $J_{anti/central}$ = 8.9 Hz) and 1.79 ppm (m), the *syn* allyl proton was observed at 3.01 ppm (dd, 1H, $J_{syn/anti}$ = 2.6 Hz, $J_{syn/central}$ = 6.7 Hz) and the central proton at 4.03 ppm (dt, 1H, J = 6.8, 9.3 Hz). The methyl allyl protons appeared at 2.25 ppm (d, 3H, J = 6.5 Hz).

The complex **4e** featuring a terminal phenyl substituent on the allyl group, displayed broad signals in the proton NMR spectrum at ambient temperature. The

spectrum became well-resolved as the temperature was lowered to -70 °C to reveal the presence of two species.

The crystal structure of complex **4e** revealed a symmetrical, octahedral arrangement around the metal (*Fig.-4*).

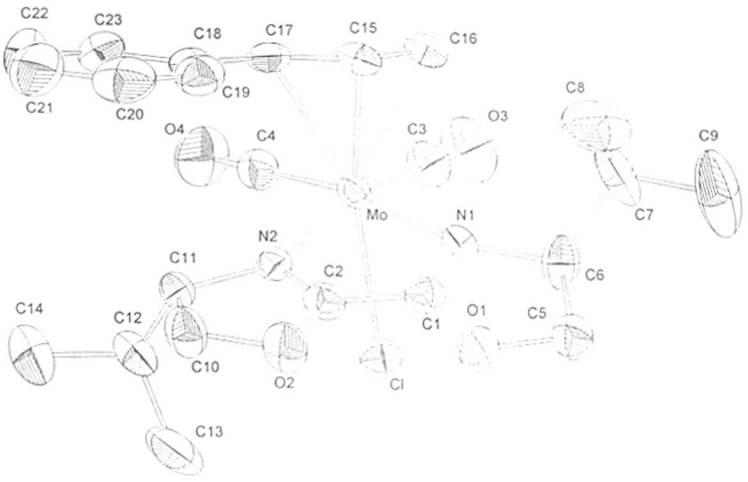


Fig.-4. ORTEP view of the molecular structure of **4e**

The carbonyl groups were placed *trans* to the donor atoms of the oxazoline ring. The phenyl ring attached to the allyl group was accommodated in the less congested side of the ligand. This places the methine hydrogen of an oxazoline ring sufficiently close to the phenyl ring so that shielding is observed in the proton NMR spectrum. Among the two sets of signals in the ratio 2 : 1, signals due to the major species could be now assigned to this structure. Two methine protons of the *bis*-oxazoline ligand appeared at 1.60 (m) and 3.94 ppm (t, J = 9.5 Hz). The unusual upfield shift of one of these protons is due to anisotropy of the phenyl ring. Two *anti* allyl proton signals appeared at 1.22 ppm (m) and 3.17 ppm (m, benzylic proton). The *syn* allyl protons appeared at 3.00 ppm as a doublet ($J_{syn/central}$ = 9.8 Hz) and the central allyl proton at 4.30-4.35 ppm (m). Four methyl groups of the two isopropyl units appeared at 0.41, 0.57 and 0.89 ppm as doublets (J = 6.4-7.0 Hz) containing 3H, 3H and 6H respectively, and the two isopropyl methine protons appeared at 1.60 and 2.43 ppm as multiplets.

Possible structure of the minor species could not be deduced due to extensive overlap of signals that defeated all attempts to obtain detailed coupling information. Similarity of peak positions suggest equivalent structures, such as four isopropyl methyl groups appearing at 0.84, 0.96, 0.99 and 1.09 ppm as doublets; two isopropyl protons at 2.22 and 3.06 ppm as multiplets. But steric considerations prevent us from suggesting the alternative placement of the phenyl ring, i.e. near the β-isopropyl group. The possibility of an *anti* phenyl group on the allyl can not, however, be ruled out. This would occur *via* a π–σ–π mechanism.

The presence of two species was also indicated in the ^{13}C NMR spectrum as it showed four peaks corresponding to the metal-carbonyl groups, 226.2 and 229.0 ppm for the major species and 224.2 and 228.2 ppm for the minor species.

The complex **4f-g** were prepared by the same procedure as for other complexes using (+)-2,2′- *bis*-[(4R)-phenyl]-1,3-oxazoline ligand. The complexes were soluble in a common organic solvent and were fairly stable in solid state, but decomposed rapidly on silica gel, hence analytically pure complexes (**4f-g**) were obtained only by repeated crystallization. These complexes featuring centrally substituted allyl groups (*Fig.-5*) displayed sharp lines in the proton NMR spectra at ambient temperature and indicated the presence of one molecular species in both the cases.

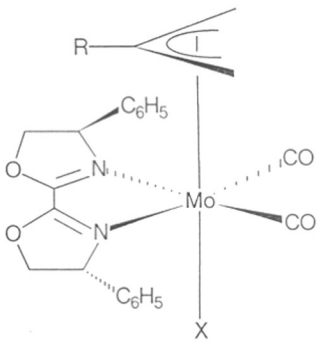


Fig.-5. Structure of complex **4f-g**

Complex No.	R	X	Yield (%)
4f	C_6H_5	Br	37
4g	CH_3	Cl	26

The complex **4f** showed signals at usual positions [two *anti* allyl protons at 0.87 ppm (d, $J_{syn/anti}$ = 2.2 Hz) and 0.95 ppm (d, $J_{syn/anti}$ = 2.0 Hz) respectively and the *syn* protons at 2.16 ppm and 3.19 ppm as multiplets]. Four diastereotopic methylene protons of the *bis*-oxazoline ligand appeared as four different triplets at 4.33 ppm (J = 9.6 Hz), 4.58 ppm (J = 9.6 Hz), 4.88 ppm (J = 10.3 Hz) and 5.52 ppm (J = 10.4 Hz) respectively, two methine protons appeared together at 5.01 ppm as doublet of a doublet (J = 4.9, 10.3 Hz). ^{13}C NMR showed the signals of two CO ligands coinciding at 222.2 ppm.

The complex **4g** showed two *anti* allyl protons at 0.61 and 0.76 ppm as singlets; the *syn* allyl protons at 1.45 and 2.50 ppm as broad singlets and the central methyl allyl protons at 1.75 ppm as singlet. ^{13}C NMR showed the signals of two CO ligands at 224.5 and 224.6 ppm.

IV. 3 Summary

A series of molybdenum π-allyl complexes have been prepared and structurally characterized. DNMR spectroscopy indicated more than one molecular species in solution, but only the major component, i.e. the expected structure, could be unambiguously determined at this point.

IV. 4 EXPERIMENTAL

Allyl chloride, diethyl oxalate and thionyl chloride, were purchased from SD Fine Chemicals. Sodium borohydride was purchased from Loba Chemie. R-(-)-phenyl glycine, S-(+)-valine, methylallyl chloride, crotyl bromide and cinnamyl chloride were purchased from Aldrich.

4(I) Preparation of 2,2′-*Bis*-[(4R)-phenyl]-1,3-oxazoline.

To a suspension of sodium borohydride (10 g, 263.1 mmol) in THF (100 mL), R-(-)-phenyl glycine (15.1 g, 100 mmol) was added and the reaction mixture was cooled in an ice bath. An ethereal solution of concentrated H_2SO_4 (6.6 mL in 13.5 mL Et_2O) was prepared separately. This solution was added dropwise to the above stirred solution such that the temperature of the reaction mixture never exceeded 20 °C. The reaction mixture was further stirred for 10 h at room temperature. MeOH (20 mL) was added dropwise to the cold stirred solution. The mixture was then concentrated to 50 mL, and 100 mL 5N sodium hydroxide was added. All solvent below 100 °C was distilled out and refluxed the resultant mixture for 3 h. The turbid aqueous solution was cooled and filtered through a Celite pad and washed with little water. The filtrate was extracted with CH_2Cl_2 (5 X 30 mL), dried over anhydrous Na_2SO_4, and solvent was removed. The semisolid mass was recrystallized from EtOAc-pet.ether to furnish R-phenyl glycinol as a colorless solid (10.97 g, 80%). m.p. 77-78 °C.

Diethyl oxalate (4.07 mL, 30 mmol) was added to R-phenyl glycinol (8.22 g, 60 mmol). The resultant solution was refluxed for 4 h. The reaction mixture solidified. The mixture was cooled, washed with pet.ether, powdered and dried under vacuum to yield the N,N′ *bis*-[2R-phenyl-1-hydroxyethyl]-1,2-ethanediamide (19.6 g, 92%).

The *bis*-amide (14.75 g, 45 mmol) prepared was added to freshly distilled thionyl chloride (30 mL, excess) and refluxed for 2 h. The reaction mixture was cooled and thionyl chloride was removed by distillation. The last traces were removed by azeotropic distillation using benzene. The resultant solid was recrystallized from EtOAc-pet.ether to afford N,N′ *bis*-[2R-phenyl-1-chloroethyl]-1,2-ethanediamide as an amorphous solid (11.3 g, 69%).

Sodium hydroxide (3 g, 75 mmol) was dissolved in a minimum volume of water. CH_2Cl_2 was then added to this followed by TBAB (1 g) and the mixture stirred vigorously. The *bis*-chloroamide (11.3 g, 30.9 mmol) was then added into this solution in small portions. After complete addition of the *bis*-chloroamide, the reaction mixture was then stirred for 3 h at room temperature. After completion of reaction the mixture was diluted with water (50 mL) and extracted with CH_2Cl_2 (5 X 20 mL). The extract was dried over anhydrous Na_2SO_4 and the solvent removed to furnish a solid. Recrystallization from CH_2Cl_2-pet.ether afforded the title compound (7.2 g, 80%).

^{1}H NMR (200 MHz), 25 °C : 4.42 (t, 2H, J = 8.69 Hz), 4.92 (dd, 2H, J = 8.69, 10.86 Hz), 5.50 (t, 2H, J = 8.69 Hz), 7.25-7.47 (m, 10H).

4(II) Preparation of 2,2′-*Bis*-[(4S)-(1 methyl ethyl)]-1,3-oxazoline.

S-Valinol (8.03 g, 78%) was prepared according to the same procedure for phenylglycinol from S-(+)-Valine (11.7 g) in THF (100 mL), sodium borohydride (10 g) and ethereal H_2SO_4 (6.6 mL in 13.4 mL ether).

N,N′ *bis*-[2S-(1-methylethyl)-1-hydroxyethyl]-1,2-ethanediamide (4.46 g, 46%) was prepared from S-Valinol (3.82 g, 37.04 mmol) and diethyl oxalate (2.51 mL, 18.5 mmol).

N,N′ *bis*-[2S-(1-methylethyl)-1-choroethyl]-1,2-ethanediamide (3.8 g, 75%) was prepared from the corresponding *bis*-hydroxyamide (4.46 g, 17.15 mmol) and thionyl chloride (10 mL, excess).

The title compound (2.18 g, 76%)[2] was prepared from the corresponding *bis*-chloroamide (3.8 g, 12.79 mmol), sodium hydroxide (1.3 g) and CH_2Cl_2 (50 mL) with TBAB (0.5 g) as catalyst.

General method of complexation

In an oven dried two-necked flask cooled under argon, freshly distilled acetonitrile (30 mL) and $Mo(CO)_6$ (2 mmol) were refluxed for 6 h. The golden solution of the resultant *tris*-acetonitrile $Mo(CO)_3$ complex was then treated with freshly distilled allyl halide (2.1 mmol) and the solution was refluxed for another

15 min for allyl chlorides; in case of the allyl bromides the solution was cooled immediately after addition. The volume of the reaction mixture was concentrated to approximately 5 mL by removal of acetonitrile under reduced pressure. A solution of the ligand (2.1 mmol) in CH_2Cl_2 (10 mL) was then added to the reaction mixture with vigorous stirring which was continued at room temperature for a further 1.5 h. The reaction mixture was then concentrated and subjected to column chromatography to yield the colored complex. Further purification was carried out by crystallization.

Preparation of complex 4.a.

The complex was prepared using a general method from $Mo(CO)_6$ (0.792 g, 3 mmol) in acetonitrile (40 mL), allyl chloride (0.237 g, 3.1 mmol) and the ligand **4(II)** (0.784 g, 3.5 mmol). A dark red colored reaction mixture was obtained. Chromatography (80 % CH_2Cl_2-pet.ether) and recrystallization from CH_2Cl_2-pet.ether (at -10 °C) afforded deep red crystals (1.10 g, 81%).

Color	:	Deep red
MP	:	146 °C (dec)
IR	:	1930 (s), 1851 (s), 1629 (w) cm^{-1}.
^{1}H NMR (400 MHz), -70 °C CD_2Cl_2	:	Major species: 0.68-1.09 (Bunch of multiplets, 12H), 1.05 (m, 1H), 1.24 (d, 1H, J = 9.4 Hz), 2.01 (br, 1H), 3.03 (br, 1H), 3.21 (br, 1H), 3.81 (br, 1H), 4.06 (m, 1H), 4.26-4.77 (m, 6H). Minor species: 0.68-1.09 (Bunch of multiplets, 14H), 2.13 (br, 1H), 2.34 (br, 1H), 3.03 (br, 2H), 3.49 (m, 1H), 4.26-4.77 (m, 6H).
^{13}C NMR (100.6 MHz), -70 °C CD_2Cl_2	:	13.7, 14.1, 14.2, 14.5, 18.7, 19.2, 27.5, 28.9, 29.3, 29.6, 51.2, 52.9, 61.7, 69.0, 69.6, 70.5, 70.8, 71.7, 71.8, 72.0, 72.5, 153.4, 155.3, 157.1, 157.4, 221.6, 223.3, 225.1, 225.3.
Analysis	:	Calcd. : C: 45.10; H: 5.57; N: 6.19. Found : C: 44.72; H: 5.45; N: 5.89.

Preparation of complex 4.b.

The complex was prepared using general method from $Mo(CO)_6$ (0.792 g, 3 mmol) in acetonitrile (40 mL), phenylallyl bromide (0.614 g, 3.1 mmol) and the ligand **4(II)** (0.784 g, 3.5 mmol). A dark red colored reaction mixture was obtained. Chromatography (60 % CH_2Cl_2-pet.ether) and recrystallization from CH_2Cl_2-pet.ether (at -10 °C) afforded deep brown crystals (0.420 g, 24%).

Color	:	Deep brown
MP	:	183 °C (dec)
IR	:	1958 (s), 1880 (s), 1635 (w) cm^{-1}.
^{1}H NMR (200 MHz), 25 °C	:	0.80 (d, 3H, J = 6.5 Hz), 0.90 (d, 3H, J = 6.2 Hz), 1.11 (d, 3H, J = 6.5 Hz), 1.17 (d, 3H, J = 5.9 Hz), 1.23 (d, 1H, J = 2.7 Hz), 1.57 (d, 1H, J = 2.7 Hz), 2.05 (m, 1H), 2.55 (m, 1H), 3.40 (m, 1H), 3.48 (m, 1H), 3.75 (m, 2H), 4.10-4.67 (m, 4H), 7.15-7.40 (m, 5H).
^{13}C NMR (50.3 MHz), 25 °C	:	15.5, 16.9, 19.1, 21.0, 28.5, 29.7, 43.6, 49.4, 69.2, 71.8, 72.6, 83.4, 124.4, 126.7, 127.9, 138.7, 157.4, 159.0, 221.8, 224.1.
Analysis	:	Calcd. : C: 48.18; H: 5.1; N: 4.89. Found : C: 47.7; H: 5.02; N: 4.55.

Preparation of complex 4.c.

The complex was prepared using general method from $Mo(CO)_6$ (0.792 g, 3 mmol) in acetonitrile (40 mL), methylallyl choride (0.543 g, 6 mmol) and the ligand **4(II)** (0.896 g, 4 mmol). A dark red colored reaction mixture was obtained. Chromatography (5% acetonitrile-CH_2Cl_2) and recrystallization from CH_2Cl_2-pet.ether (at -10 °C) afforded deep red colored crystals (0.365 g, 26%).

Color	:	Deep red
MP	:	169 °C (dec)
IR	:	1965 (s), 1880 (s), 1640 (w) cm^{-1}.

^{1}H NMR (200 MHz), 25 °C	:	0.93 (d, 6H, J = 5.8 Hz), 0.98 (d, 6H, J = 9.7 Hz), 1.17 (s, 1H), 1.22 (s, 1H), 1.88 (s, 3H), 2.38 (m, 1H), 2.55 (m, 1H), 2.77 (m, 1H), 2.87 (m, 1H), 4.20-4.68 (m, 6H).
^{13}C NMR (75.2 MHz), 25 °C	:	15.1, 15.4, 19.3, 19.5, 19.7, 27.8, 29.9, 51.5, 53.0, 70.0, 72.1, 82.1, 158.4, 158.8, 224.1, 226.2.
Analysis	:	Calcd. : C: 46.31; H: 5.83; N: 6.00. Found : C: 46.62; H: 5.82; N: 5.66.

Preparation of complex 4.d.

The complex was prepared using the general method from $Mo(CO)_6$ (0.528 g, 2 mmol) in acetonitrile (30 mL), crotyl bromide (0.544 g, 4 mmol) and the ligand **4(II)** (0.465 g, 2.08 mmol). A dark red colored reaction mixture was obtained. Chromatography (5% acetonitrile-CH_2Cl_2) and recrystallization from acetone-pet.ether (by diffusion method at 5 °C) afforded black crystals (0.135 g, 13%).

Color	:	Black
MP	:	153 °C (dec)
IR	:	1942 (s), 1845 (s), 1639 (w) cm^{-1}.
^{1}H NMR (400 MHz), 20 °C	:	0.88 (d, 3H, J = 4.8 Hz), 0.97 (d, 3H, J = 4.3 Hz), 1.02 (dd, 1H, J = 2.6, 8.9 Hz), 1.08 (d, 3H, J = 7.3 Hz), 1.12 (d, 3H, J = 6.8 Hz), 1.79 (m, 1H), 2.11 (m, 1H), 2.25 (d, 3H, J = 6.5 Hz), 3.01 (dd, 1H, J = 2.6, 6.7 Hz), 3.15 (m, 1H), 4.03 (dt, 1H, J = 6.8, 9.3 Hz), 4.29 (m, 1H), 4.56 (m, 2H), 4.68 (m, 3H).
^{13}C NMR (100.6 MHz), 21°C	:	14.6, 15.0, 19.1, 19.4, 19.6, 28.9, 30.0, 49.7, 70.7, 71.6, 71.8, 72.7, 82.5, 154.2, 156.0, 223.3, 227.7.
Analysis	:	Calcd. : C: 42.29; H: 5.32; N: 5.48. Found : C: 42.10; H: 5.87; N: 5.29.

Preparation of complex 4.e.

The complex was prepared using the general method from $Mo(CO)_6$ (0.792 g, 3 mmol) in acetonitrile (40 mL), cinnamyl chloride (0.61 g, 4 mmol) and the ligand **4(II)** (0.856 g, 3.80 mmol). A dark red colored reaction mixture was obtained. Chromatography (15% acetonitrile-$CHCl_3$) and recrystallization from CH_2Cl_2-pet.ether (at room temperature) afforded shining deep red crystals (0.662 g, 42 %).

Color	:	Red
MP	:	165 °C (dec)
IR	:	1945 (s), 1839 (s), 1628 (m) cm^{-1}.
^{1}H NMR (400 MHz), -40 °C CD_2Cl_2	:	Major species: 0.41 (d, 3H, J = 7.0 Hz), 0.57 (d, 3H, J = 6.5 Hz), 0.89 (t, 6H, J = 6.4 Hz), 1.22 (m, 1H), 1.60 (m, 2H), 2.43 (m, 1H), 3.00 (d, 1H, J = 9.8 Hz), 3.17 (m, 1H), 3.94 (t, 1H, J = 9.5 Hz), 4.16-4.71 (m, 4H), 4.30-4.35 (m, 1H), 7.21-7.54 (m, 5H). Minor species: 0.84 (d, 3H, J = 6.7 Hz), 0.96 (d, 3H, J = 7.0 Hz), 0.99 (d, 3H, J = 7.1 Hz), 1.09 (d, 3H, J = 6.7 Hz), 1.18 (m, 1H), 2.22 (m, 1H), 2.28 (d, 1H, J = 10.4 Hz), 3.06 (m, 1H), 3.17 (m, 1H), 4.37 (m, 1H), 4.56-4.58 (m, 1H), 4.16-4.66 (m, 2H), 4.51 (m, 1H), 4.66-4.71 (m, 2H), 7.21-7.54 (m, 5H).
^{13}C NMR (100.6 MHz), -40 °C	:	14.1, 14.2, 14.9, 19.1, 19.2, 28.2, 28.9, 29.0, 30.2, 47.8, 48.2, 67.8, 68.8, 69.8, 69.9, 71.1, 71.6, 71.8, 72.3, 72.6, 76.2, 84.3, 127.0, 127.5, 127.6, 128.4, 128.8, 136.6, 140.0, 154.2, 156.0, 157.9, 158.1, 224.2, 226.2, 228.2, 229.0.
Analysis	:	Calcd. : C: 52.23; H: 5.53; N: 5.30. Found : C: 51.91; H: 5.68; N: 5.14.

Preparation of complex 4.f.

The complex was prepared using the general method from $Mo(CO)_6$ (0.528 g, 2 mmol) in acetonitrile (30 mL), phenylallyl bromide (0.410 g, 2.08 mmol) and the ligand **4(I)** (0.607 g, 2.08 mmol). A dark red colored reaction mixture was obtained. The title complex was purified by filtration (50% acetonitrile-$CHCl_3$) and

repeated recrystallization from CH_2Cl_2-pet.ether (by layer separation at room temperature) afforded needle shaped black crystals (0.470 g, 37%).

Color	:	Black
MP	:	145 °C (dec)
IR	:	1946 (s), 1856 (s), 1637 (w) cm^{-1}.
^{1}H NMR (200 MHz), 25 °C	:	0.87 (d, 1H, J = 2.2 Hz), 0.95 (d, 1H, J = 2.0 Hz), 2.16 (m, 1H), 3.19 (m, 1H), 4.33 (t, 1H, J = 9.6 Hz), 4.58 (t, 1H, J = 9.6 Hz), 4.88 (t, 1H, J = 10.3 Hz), 5.01 (dd, 2H, J = 4.9, 10.3 Hz), 5.52 (t, 1H, J = 10.4 Hz), 7.10-7.65 (m, 15H).
^{13}C NMR (50.3 MHz), 25 °C	:	43.8, 48.5, 68.5, 70.4, 77.5, 78.6, 83.4, 124.2, 126.9, 127.7, 128.8, 129.3, 130.0, 134.5, 135.5, 138.3, 158.3, 158.6, 222.2.
Analysis	:	Calcd. : C: 48.08; H: 5.09; N: 4.88. Found : C: 47.82; H: 4.95; N: 4.81.

Preparation of complex 4.g.

The complex was prepared using the general method from $Mo(CO)_6$ (0.528 g, 2 mmol) in acetonitrile (30 mL), methylallyl chloride (0.362 g, 4 mmol) and the ligand **4(I)** (0.607 g, 2.08 mmol). A dark red colored reaction mixture was obtained. The title complex was purified by repeated recrystallization from CH_2Cl_2-pet.ether (at room temperature) affording shining black crystals (0.280 g, 26%).

Color	:	Shining black
MP	:	136 °C (dec)
IR	:	1939 (s), 1862 (s), 1654 (w) cm^{-1}.
^{1}H NMR (200 MHz), 25 °C	:	0.61 (s, 1H), 0.76 (s, 1H), 1.45 (brs, 1H), 1.75 (s, 3H), 2.50 (brs, 1H), 4.53 (dd, 1H, J = 5.6, 10.2 Hz), 4.77 (t, 1H, J = 9.7 Hz), 5.05-5.40 (m, 4H), 7.35-7.65 (m, 10H).
^{13}C NMR (50.3 MHz), 25 °C	:	19.6, 51.8, 52.7, 69.8, 70.8, 78.9, 79.8, 82.9, 128.8, 129.0, 129.2, 129.3, 129.5, 129.7, 136.0, 136.4, 159.1, 160.0, 224.5, 224.6.
Analysis	:	Calcd. : C: 46.31; H: 5.83; N: 6.00. Found : C: 45.91; H: 5.59; N: 5.77.

IV. 5 References

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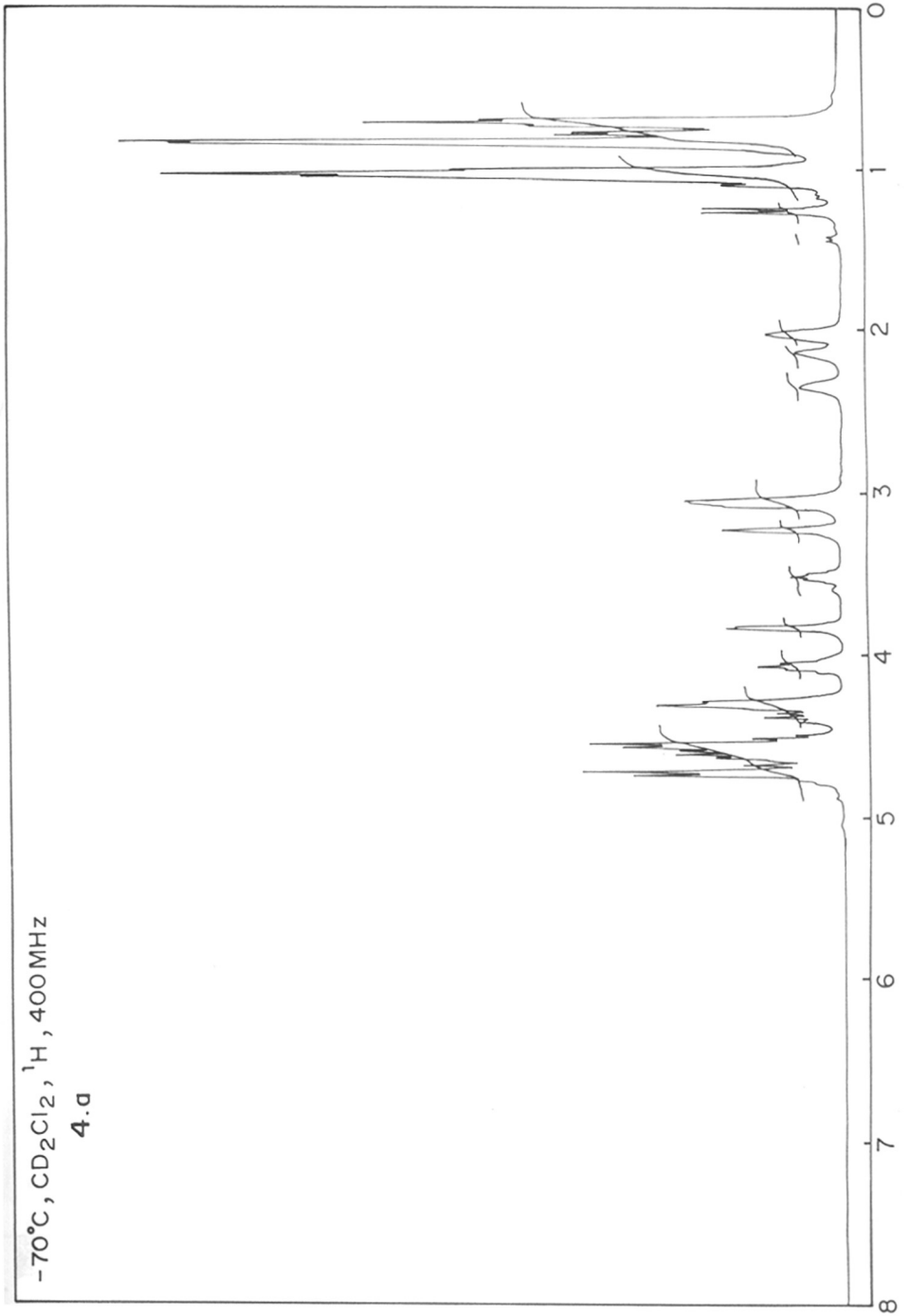
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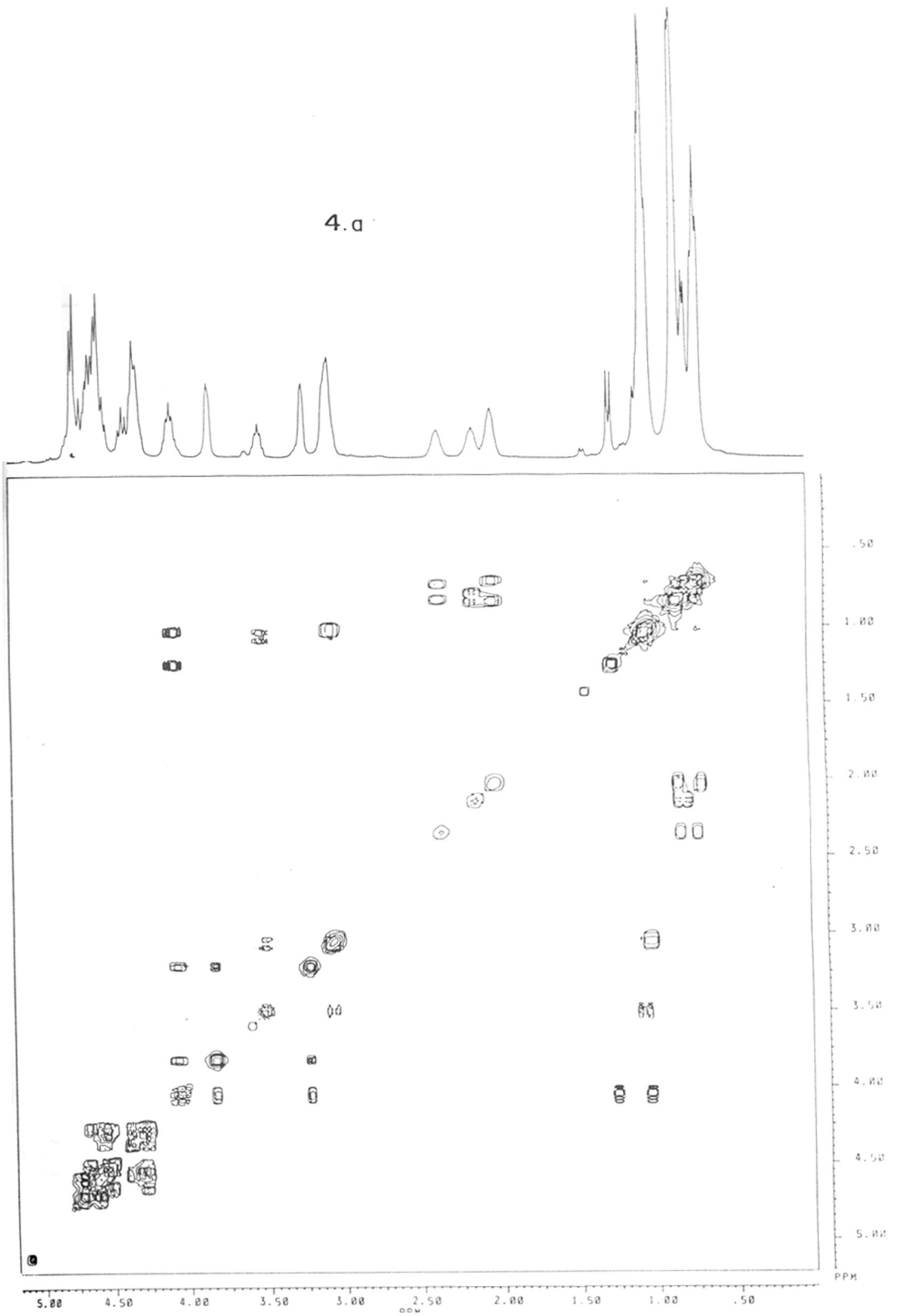
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1.00
1.50
2.00
2.50
3.00
3.50
4.00
4.50
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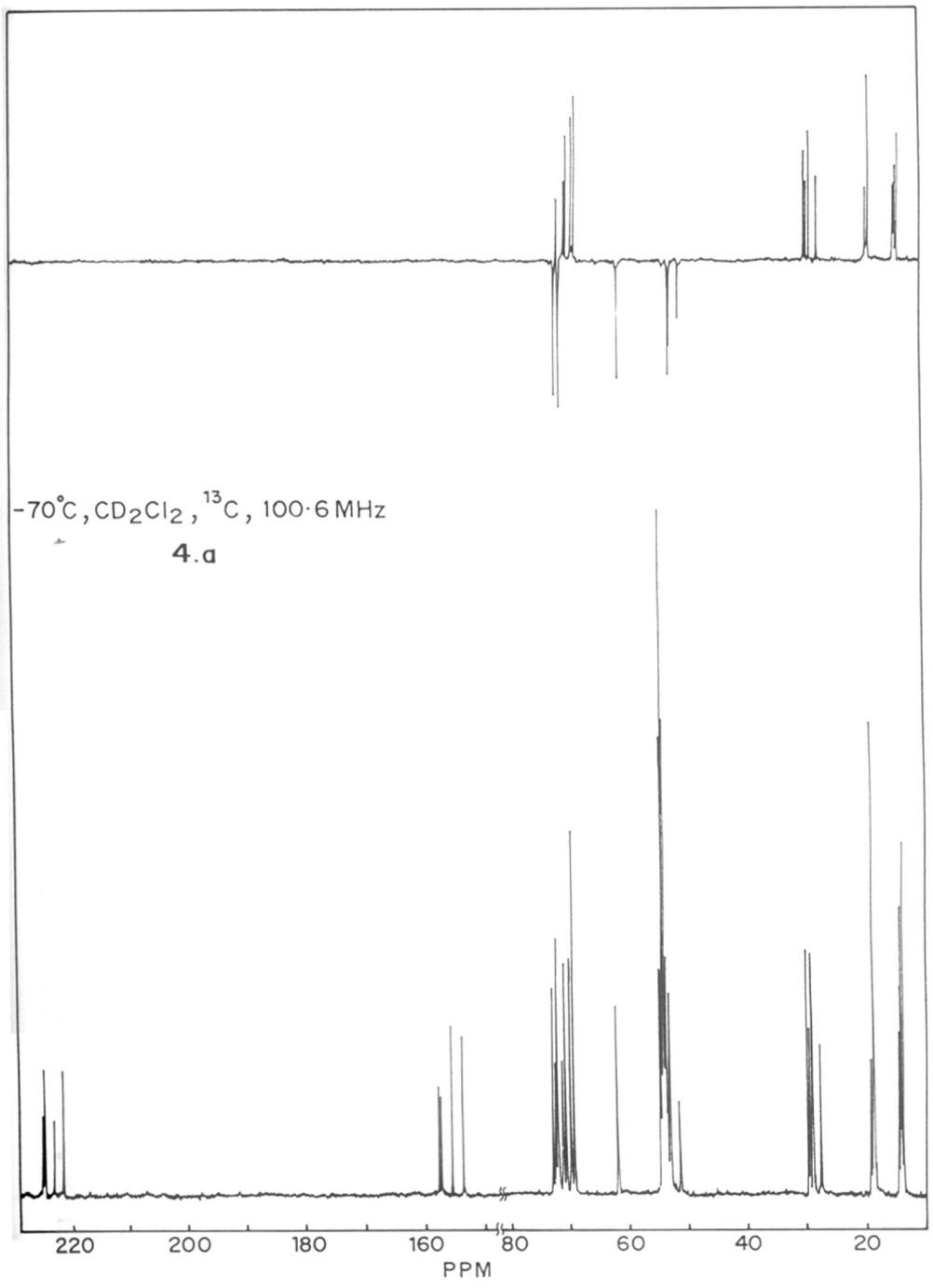
3.00
2.50
2.00
1.50
1.00
.50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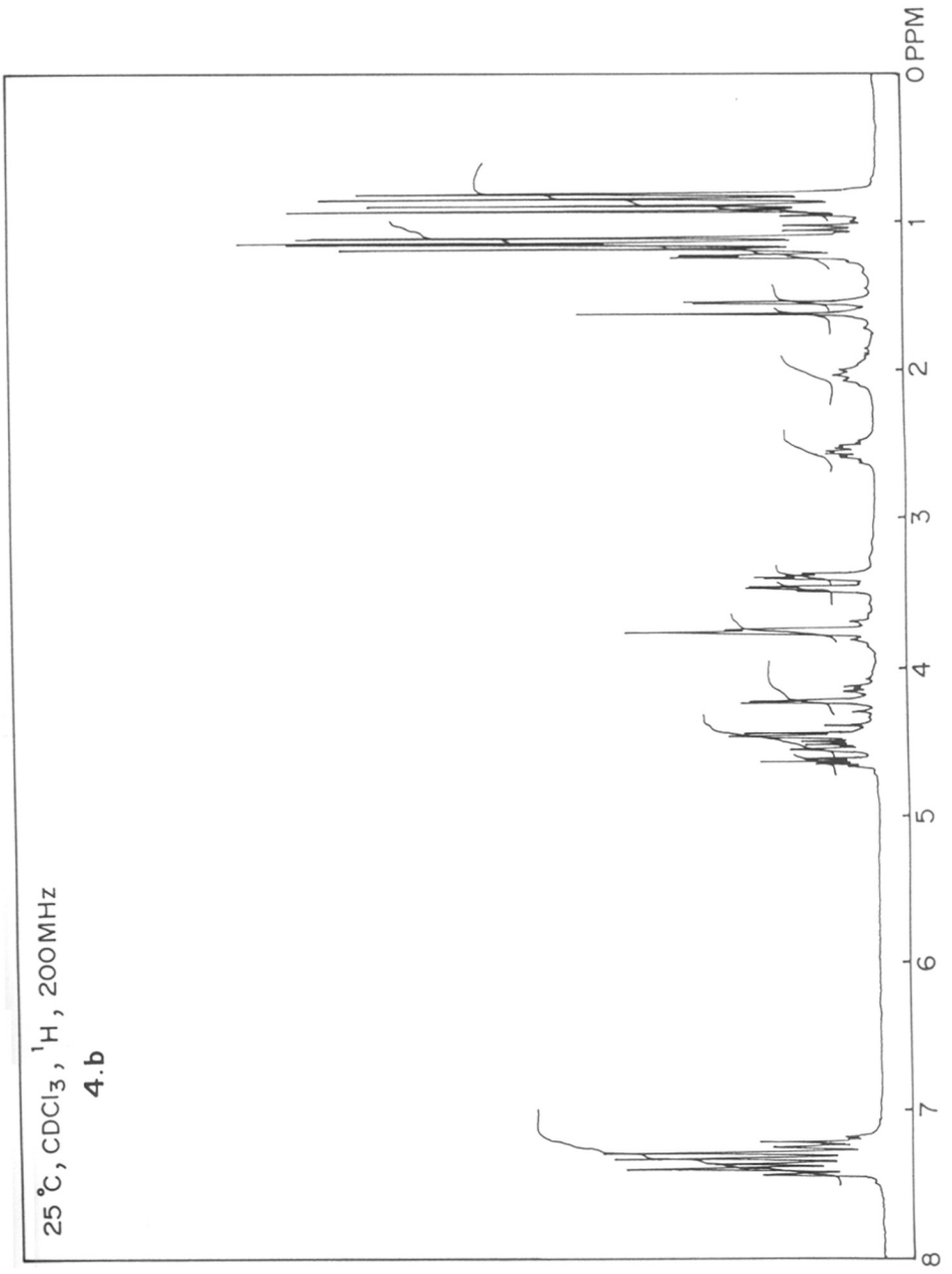
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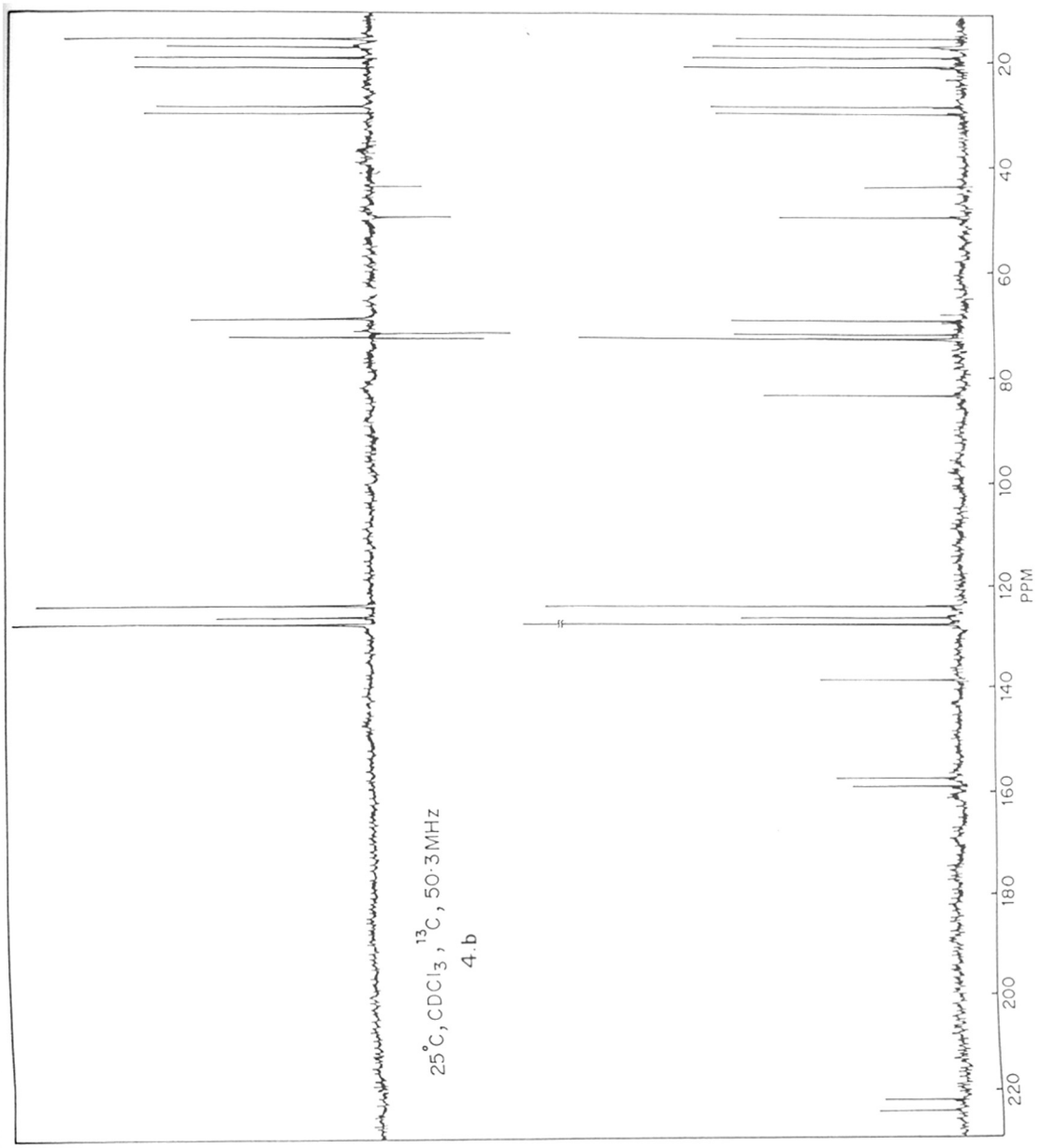
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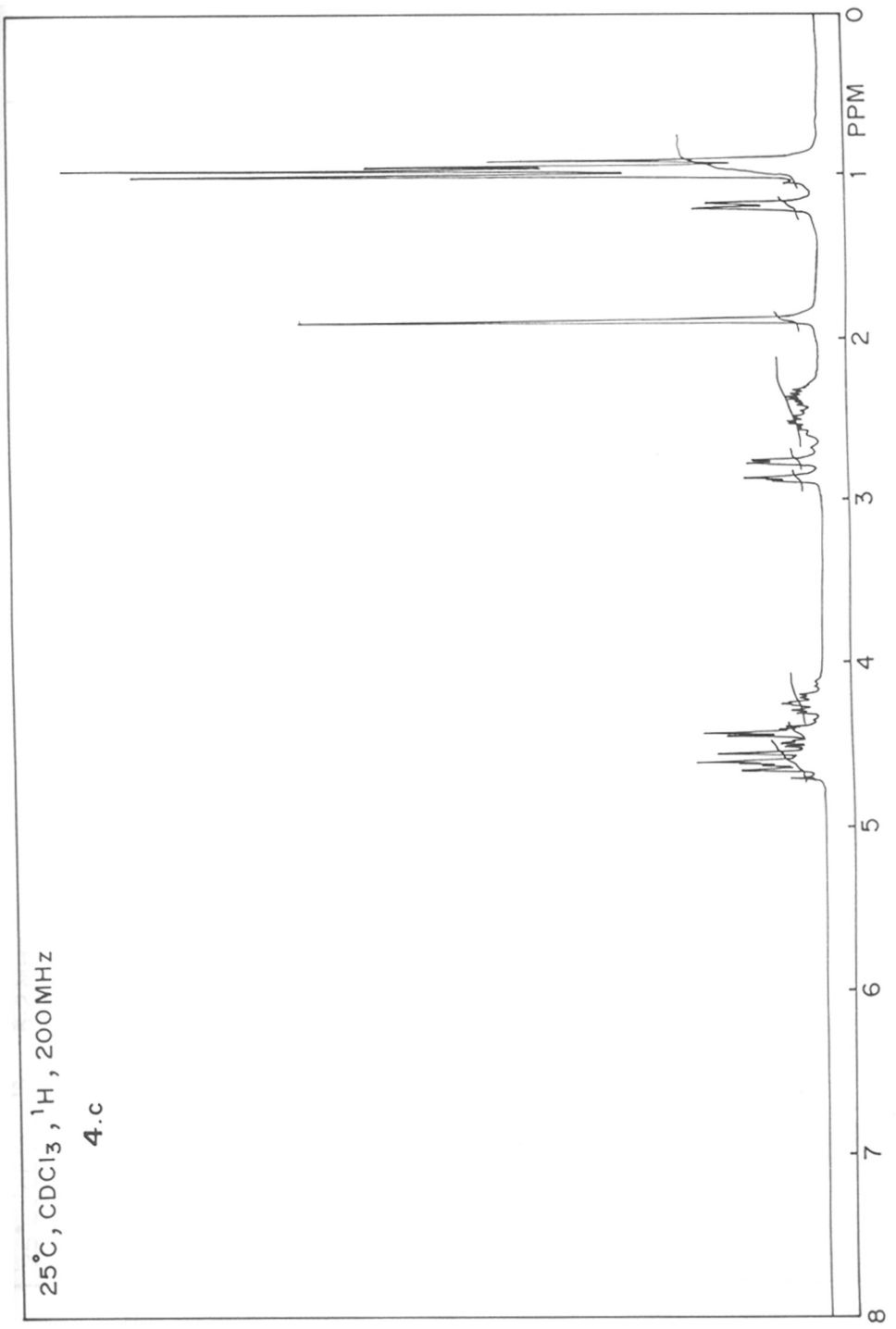
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PPM
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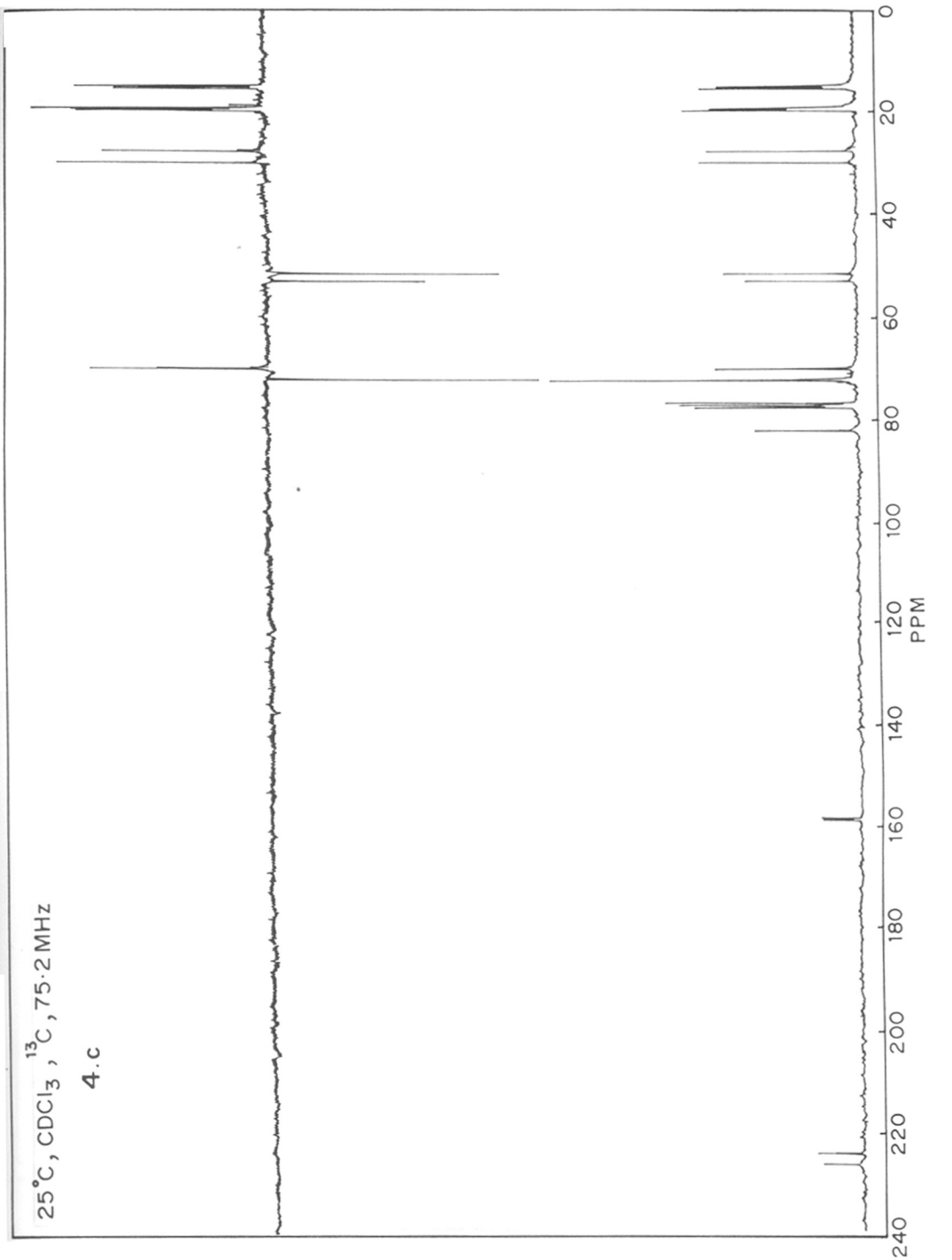
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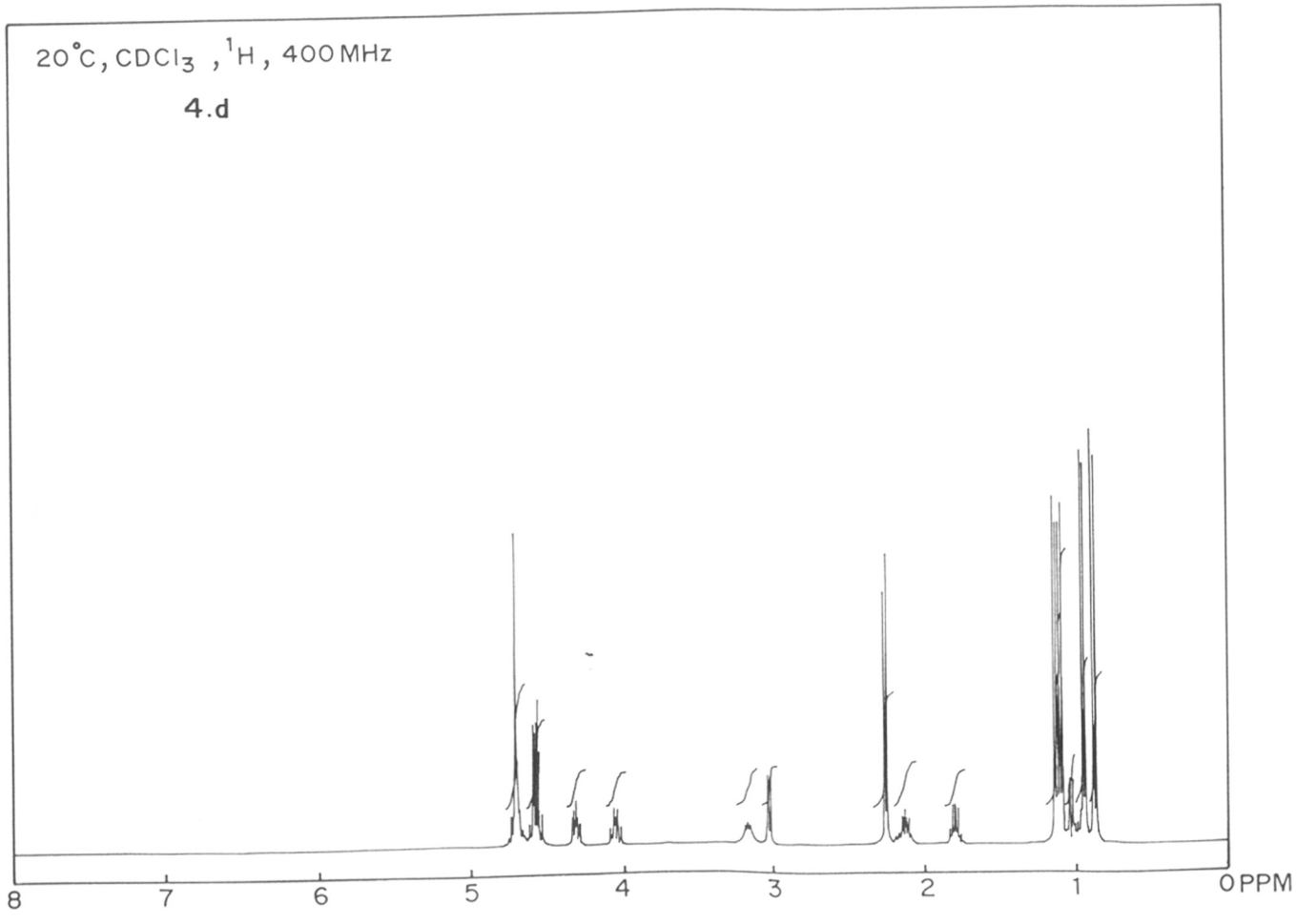
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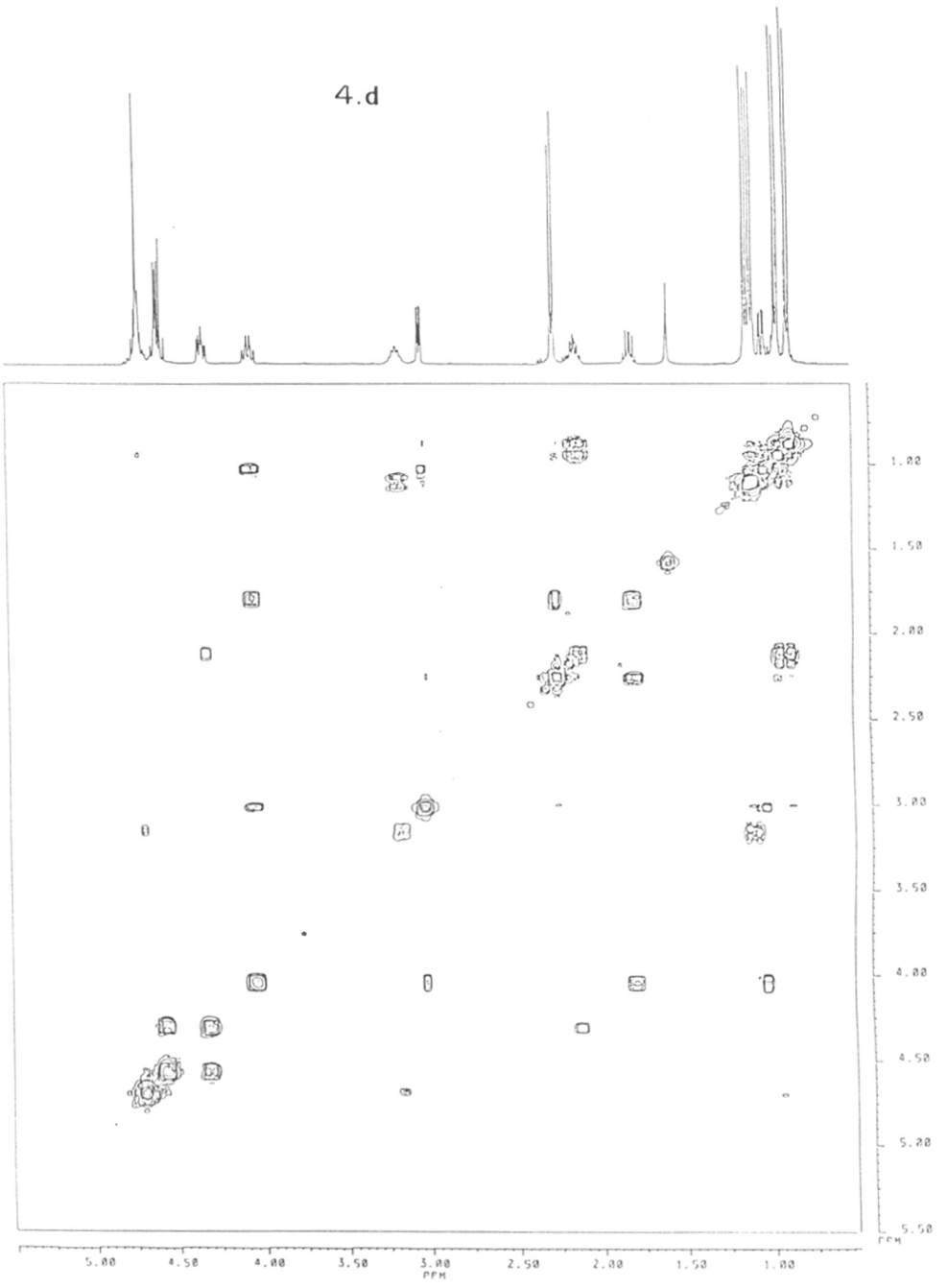
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3.00
3.50
4.00
4.50
5.00
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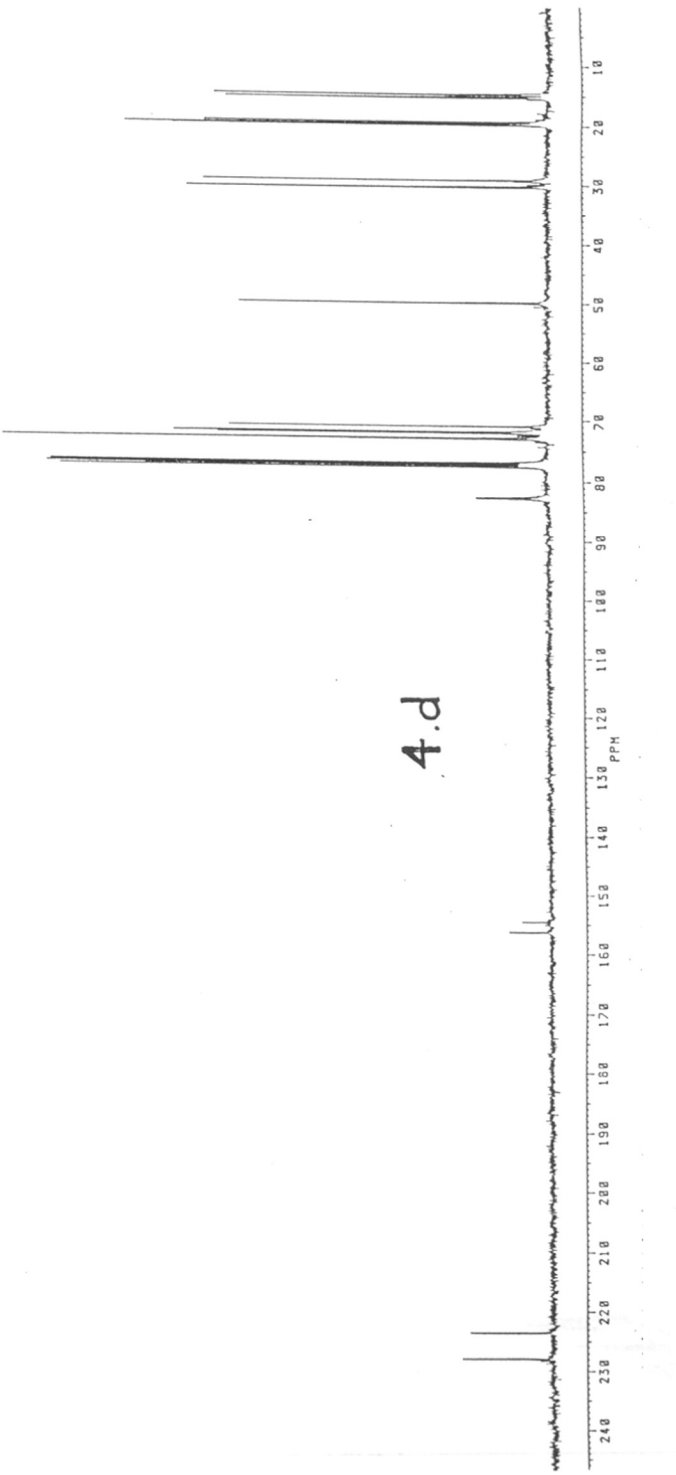
PPM
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
PPM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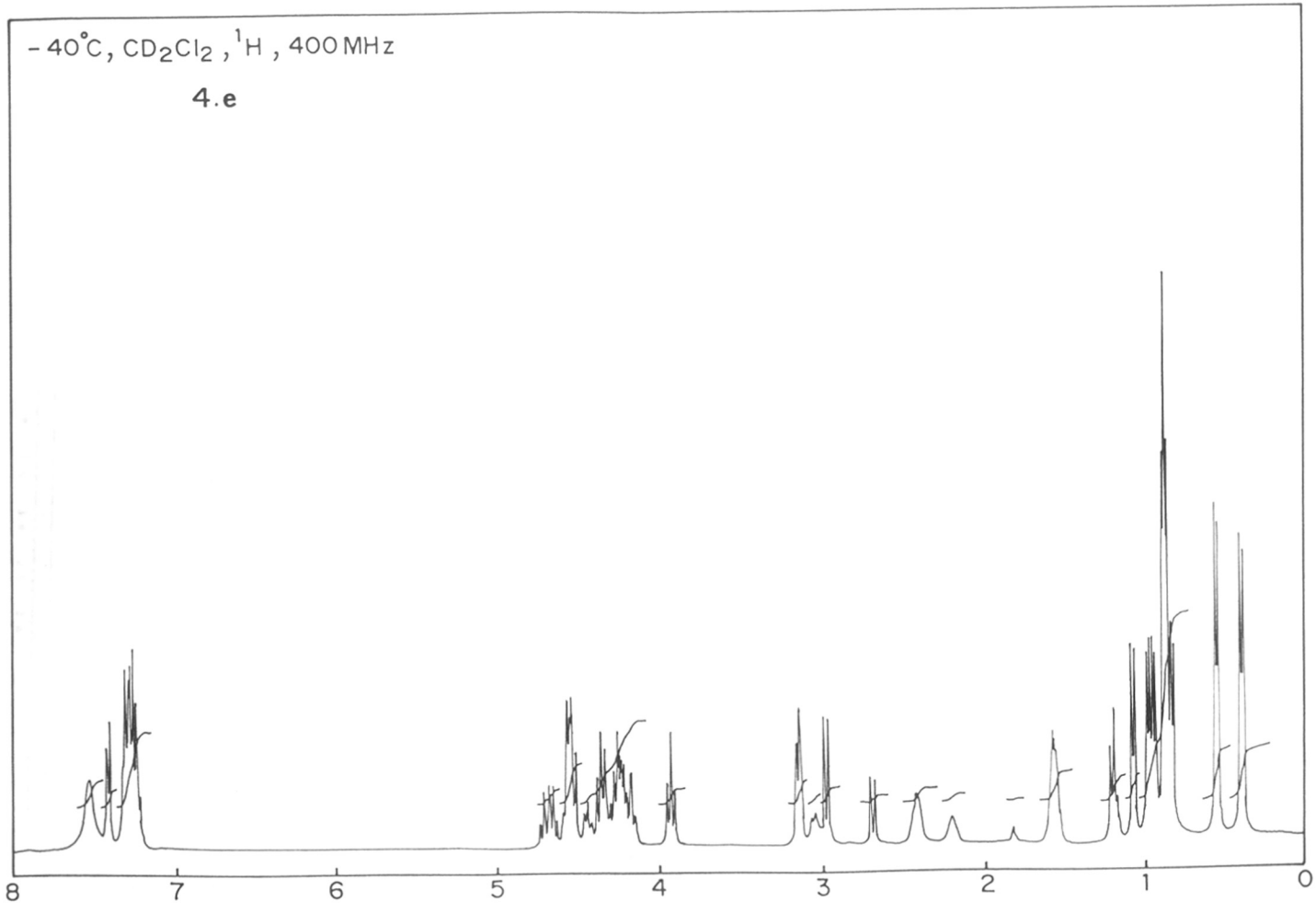
40
30
20
10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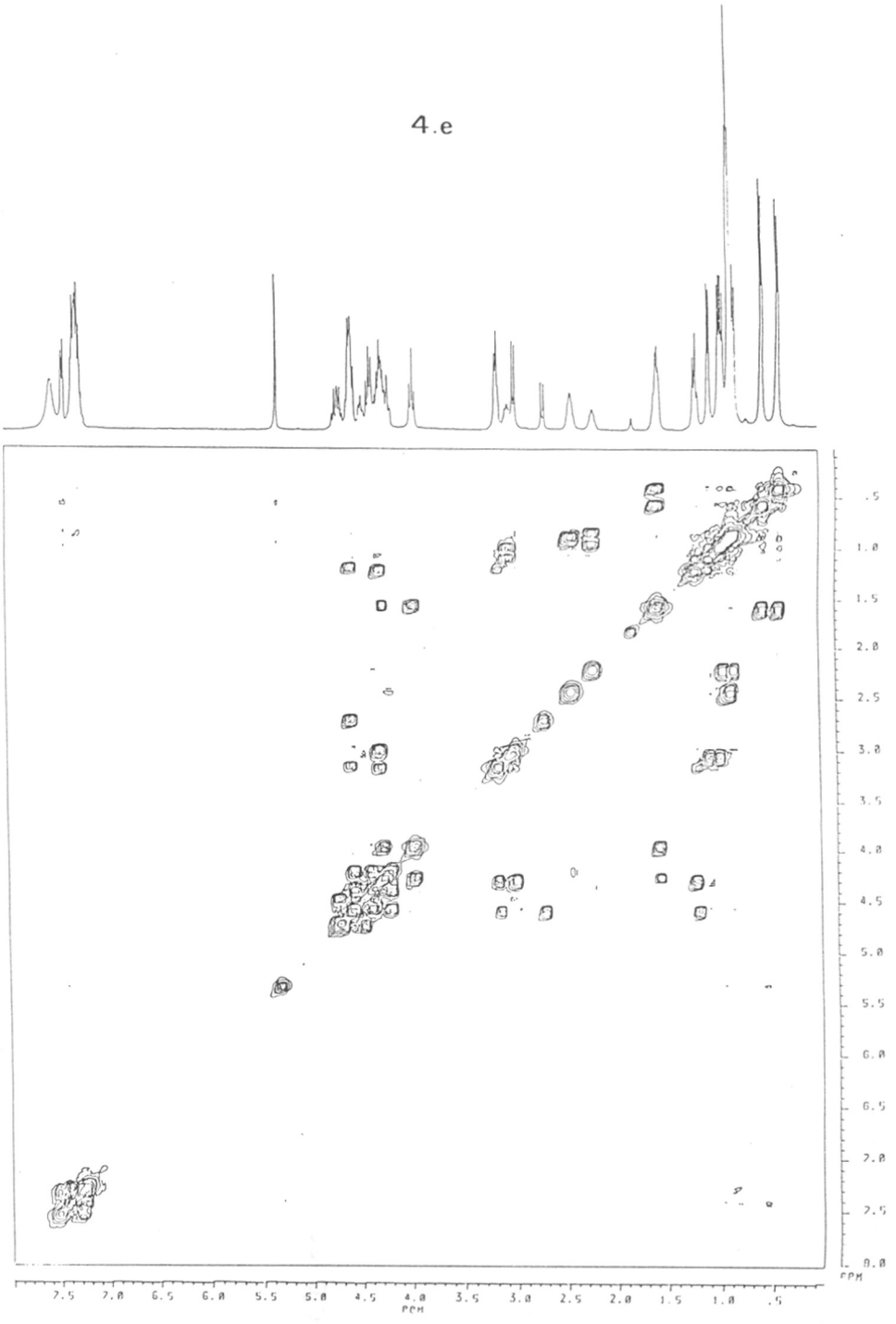
7
6
5
4
3
2
1
0 PPM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7.0
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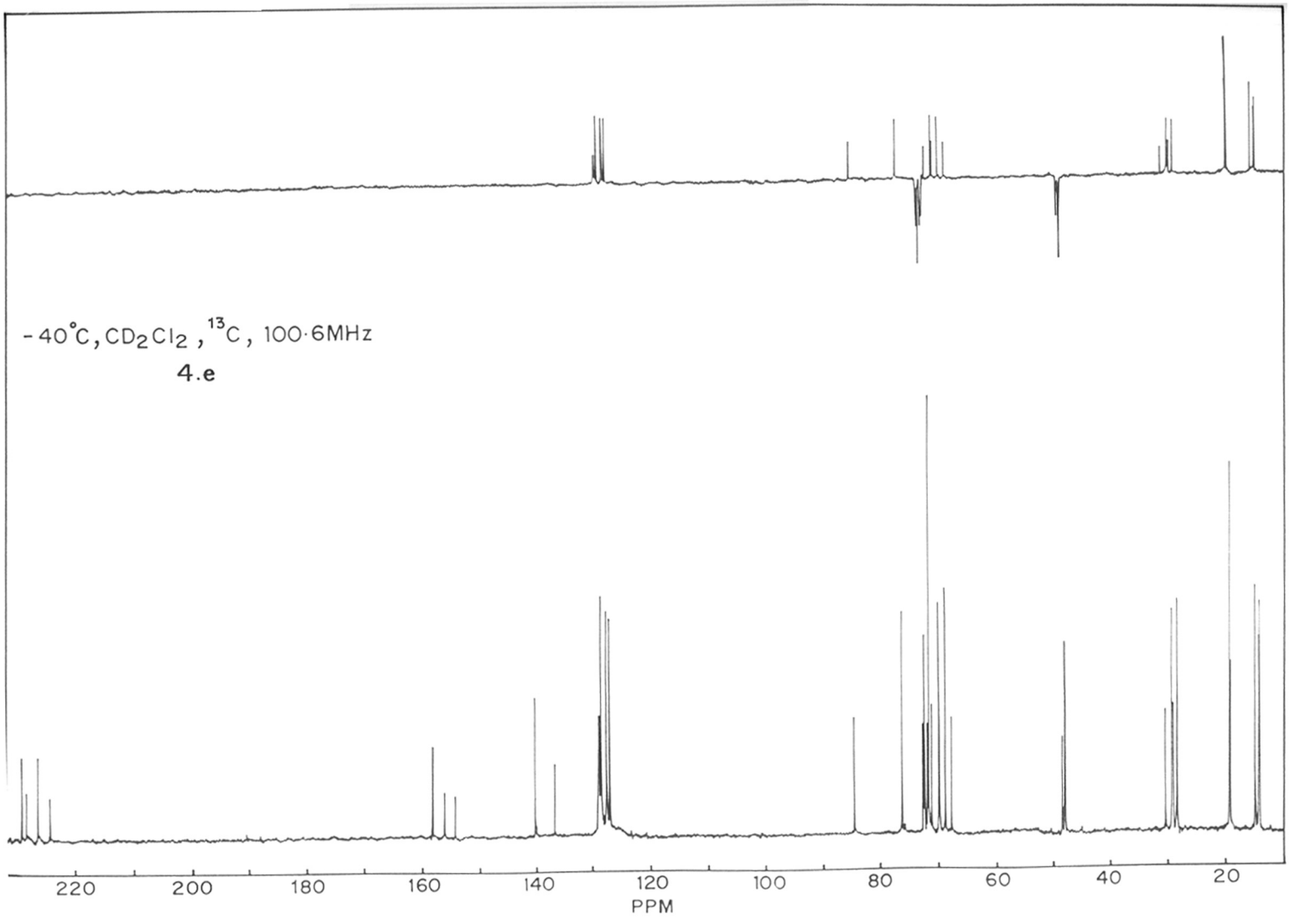
1.0
.5
PPM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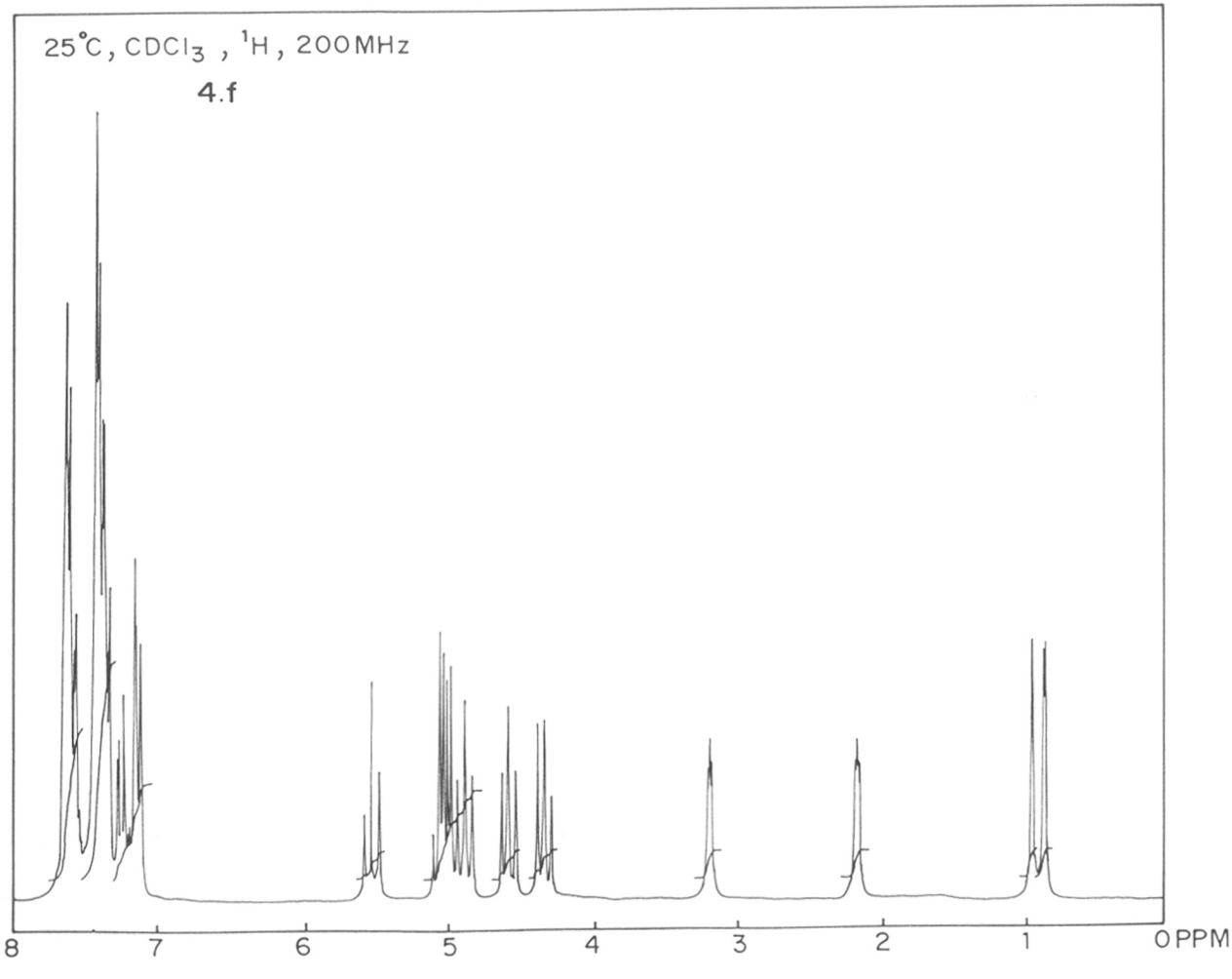
20
PPM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7
6
5
4
3
2
1
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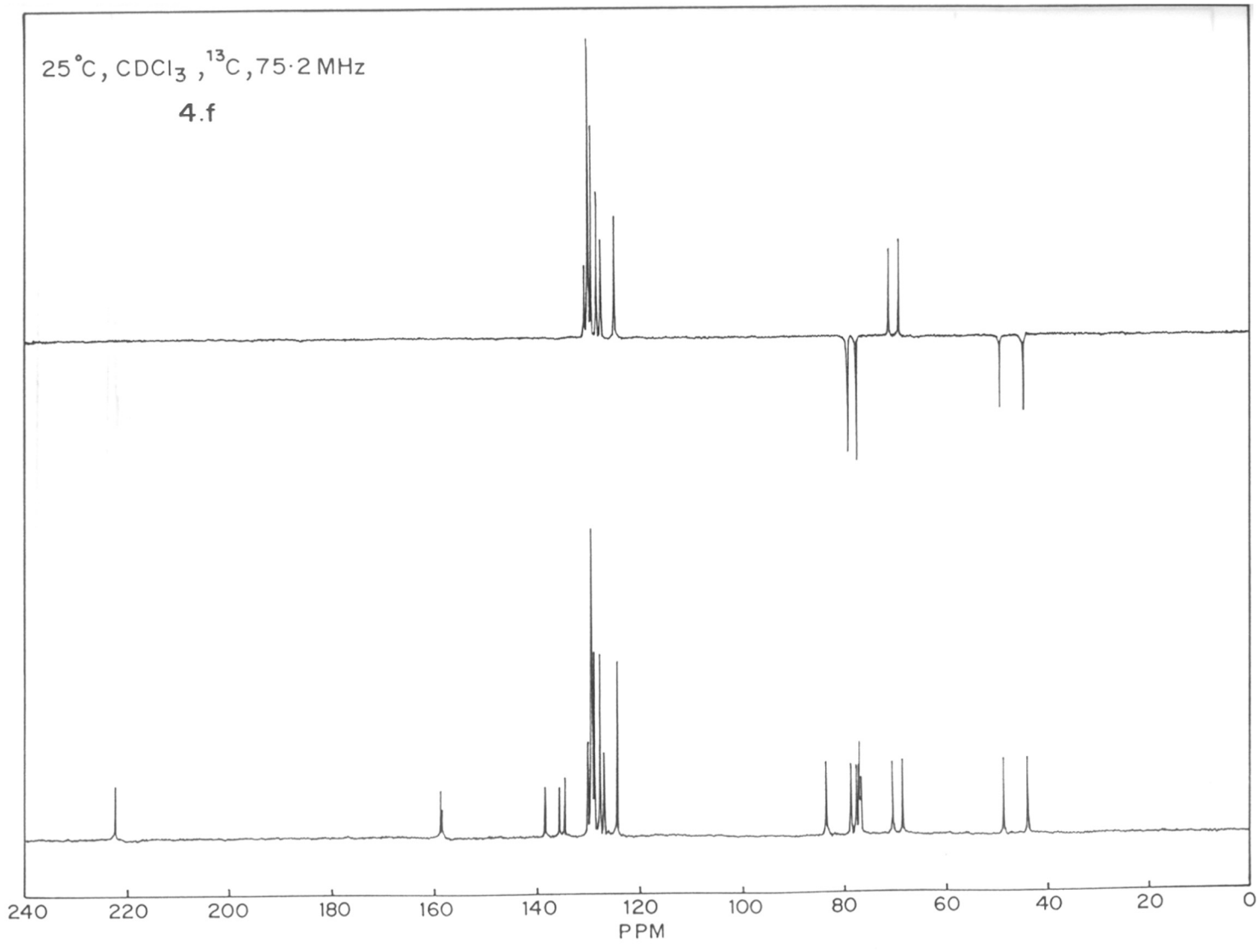
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4.f
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200
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100
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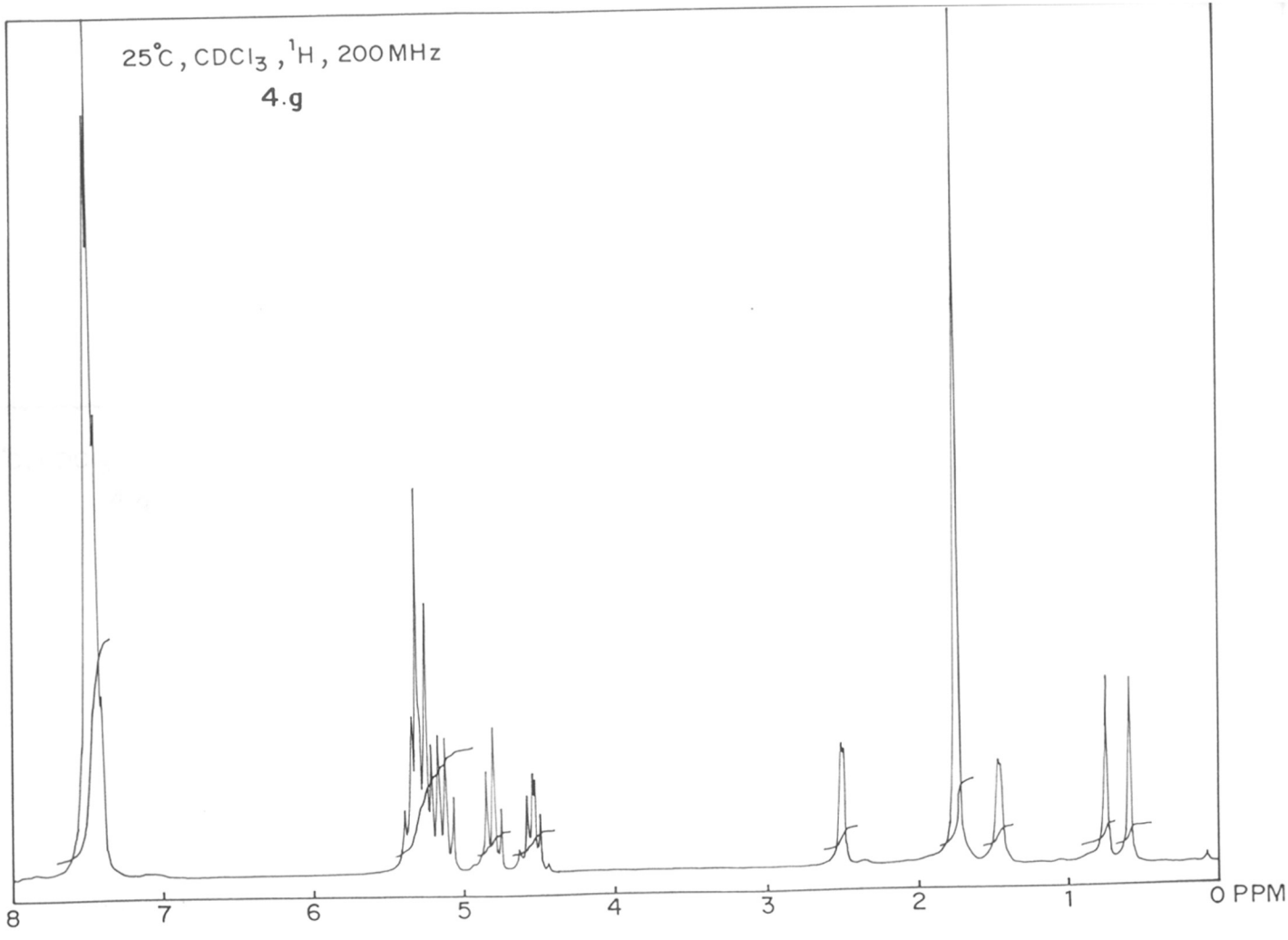
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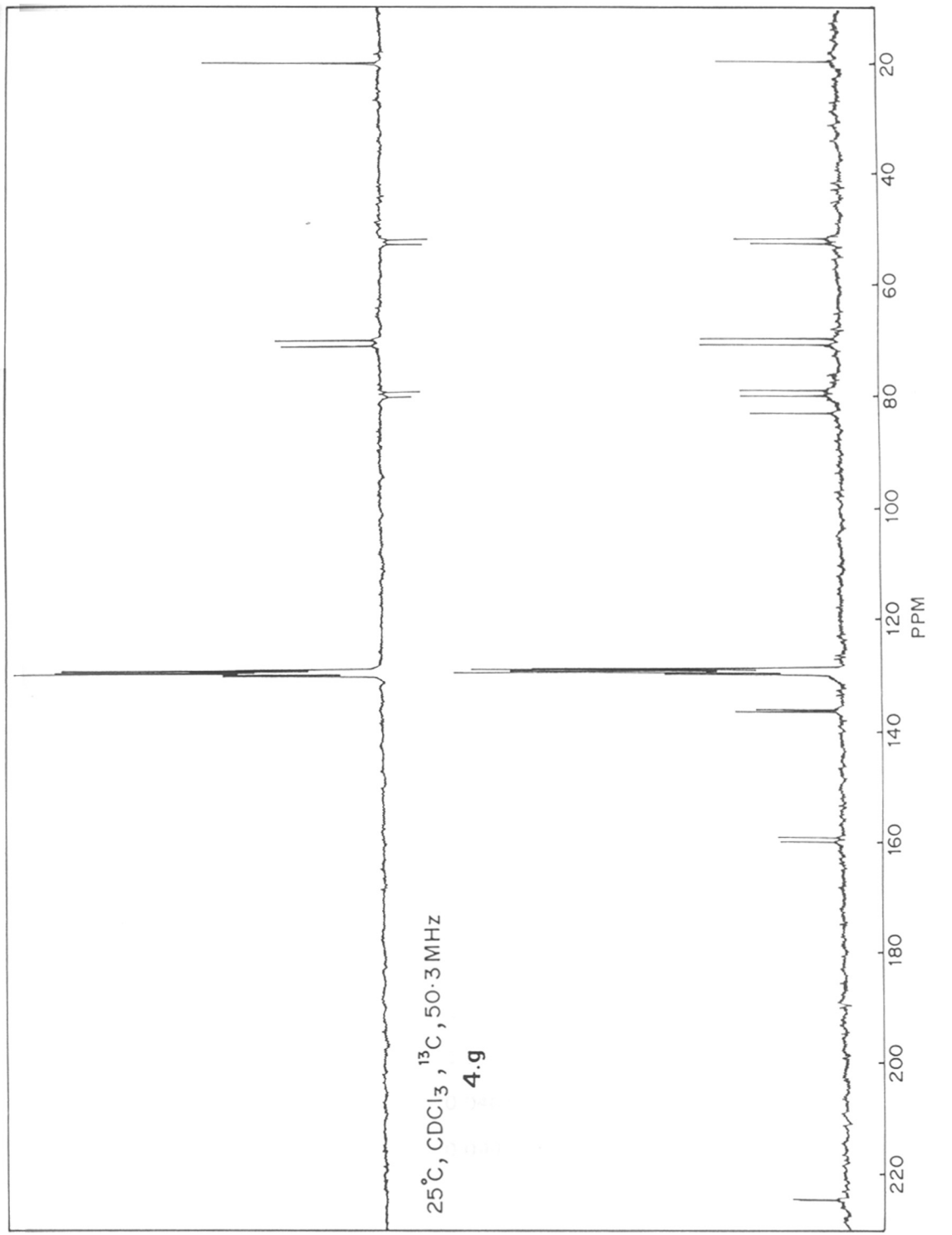
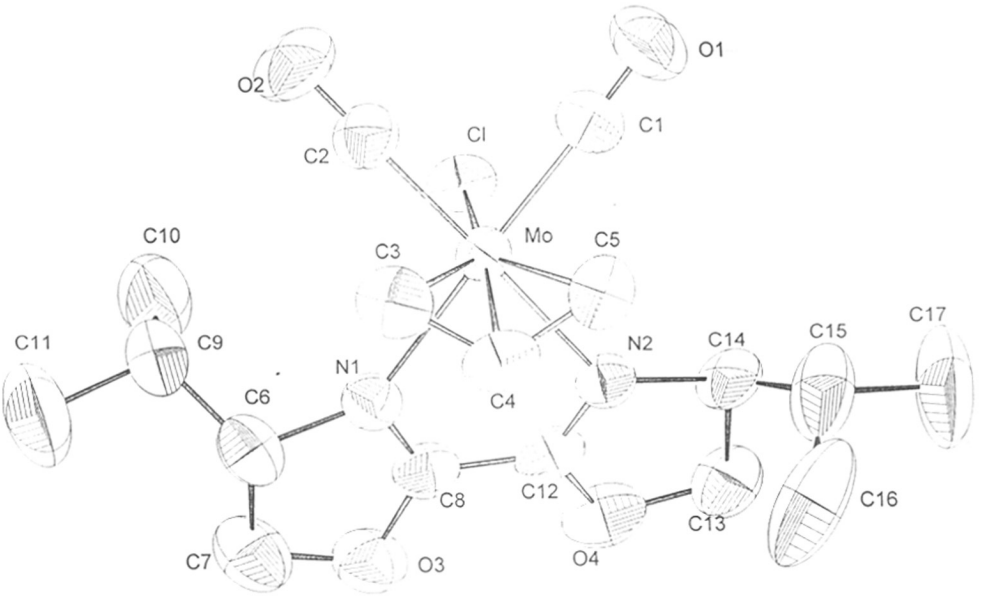

25°C, CDCl3 , 13C , 50·3 MHz
4.g
220
200
180
160
140
120
100
80
60
40
20
PPM

Table 1. X-ray Crystallographic Data and Structure Refinement of $C_{17}H_{25}ClMoN_2O_4$ (**4a**)

formula	$C_{17}H_{25}ClMoN_2O_4$
fw	452.78
crys syst	Orthorhombic
space group	$P2_12_12_1$
a(Å)	6.460(1)
b(Å)	15.826(3)
c(Å)	20.143(4)
V(A^3)	2059.3(6)
Z	4
D_{calcd} (mg m^{-3})	1.460
μ (mm^{-1})	0.788
F (000)	928
cryst size (mm)	0.325 x 0.475 x 0.6
radiation	MoKα (λ = 0.70930 Å)
temp(K)	293(2)
scan type	$\omega/2\theta$
scan width (deg)	0.8 + 0.35 tanθ
2θ range (deg)	1.63-23.39
no. of rflns collected	1766
no. of rflns obsd	1766 [R (int) = 0.0000]
no. of params varied	226
GOF	1.19
R [I > 2 sigma (I)]	0.0401
R_w [I > 2 sigma (I)]	0.099



ORTEP view of the molecular structure of **4a**

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for C17H25ClMoN2O4.U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Mo	2191(1)	5302(1)	720(1)	40(1)
Cl	5049(2)	4522(1)	136(1)	50(1)
O(1)	4833(10)	5290(5)	2000(3)	84(2)
O(2)	4814(12)	6905(4)	441(4)	96(2)
O(3)	-864(9)	4151(4)	-962(3)	69(2)
O(4)	39(9)	2905(3)	-20(3)	67(2)
N(1)	553(9)	5126(4)	-267(3)	49(1)
N(2)	892(8)	3948(3)	698(3)	45(1)
C(1)	3864(11)	5277(5)	1530(3)	54(2)
C(2)	3796(13)	6320(5)	559(4)	60(2)
C(3)	58(14)	6483(5)	770(5)	68(2)
C(4)	-842(11)	5777(5)	1066(4)	59(2)
C(5)	114(13)	5490(5)	1646(4)	60(2)
C(6)	-183(13)	5633(5)	-853(4)	65(2)
C(7)	-1037(18)	4945(7)	-1313(4)	85(3)
C(8)	17(11)	4355(4)	-385(3)	50(2)
C(9)	1469(16)	6220(6)	-1115(4)	83(3)
C(10)	3353(16)	5796(11)	-1351(6)	124(5)
C(11)	502(27)	6759(8)	-1676(6)	125(5)
C(12)	309(11)	3724(4)	123(3)	51(2)
C(13)	359(15)	2462(5)	604(4)	68(2)
C(14)	1205(13)	3143(4)	1087(4)	58(2)
C(15)	155(25)	3137(6)	1736(5)	94(4)
C(16)	-2143(26)	3292(8)	1690(7)	135(6)
C(17)	645(34)	2287(7)	2086(5)	149(7)

Table 3.Bond lengths [A] and angles [deg] for C17H25ClMoN2O4(4a).

Mo-C(2)	1.943(8)
Mo-C(1)	1.957(7)
Mo-C(4)	2.211(7)
Mo-N(1)	2.269(5)
Mo-N(2)	2.302(5)
Mo-C(5)	2.317(7)
Mo-C(3)	2.324(7)
Mo-Cl	2.513(2)
O(1)-C(1)	1.135(9)
O(2)-C(2)	1.160(10)
O(3)-C(8)	1.335(9)
O(3)-C(7)	1.447(12)
O(4)-C(12)	1.339(8)
O(4)-C(13)	1.454(10)
N(1)-C(8)	1.290(9)
N(1)-C(6)	1.505(9)
N(2)-C(12)	1.267(8)
N(2)-C(14)	1.509(9)
C(3)-C(4)	1.392(12)
C(4)-C(5)	1.399(12)
C(6)-C(9)	1.510(13)
C(6)-C(7)	1.533(12)
C(8)-C(12)	1.442(11)
C(9)-C(10)	1.47(2)
C(9)-C(11)	1.547(13)
C(13)-C(14)	1.551(11)
C(14)-C(15)	1.472(14)
C(15)-C(16)	1.51(2)
C(15)-C(17)	1.550(14)
C(2)-Mo-C(1)	82.0(3)
C(2)-Mo-C(4)	104.1(3)
C(1)-Mo-C(4)	103.5(3)
C(2)-Mo-N(1)	101.8(3)
C(1)-Mo-N(1)	170.1(3)
C(4)-Mo-N(1)	84.5(3)
C(2)-Mo-N(2)	164.4(3)
C(1)-Mo-N(2)	101.4(3)
C(4)-Mo-N(2)	90.0(2)
N(1)-Mo-N(2)	72.5(2)
C(2)-Mo-C(5)	109.7(3)
C(1)-Mo-C(5)	69.6(3)
C(4)-Mo-C(5)	35.9(3)
N(1)-Mo-C(5)	116.8(3)
N(2)-Mo-C(5)	85.6(2)
C(2)-Mo-C(3)	70.0(3)
C(1)-Mo-C(3)	107.9(3)
C(4)-Mo-C(3)	35.6(3)
N(1)-Mo-C(3)	82.0(3)

N(2)-Mo-C(3)	122.2(3)
C(5)-Mo-C(3)	61.2(3)
C(2)-Mo-Cl	86.4(2)
C(1)-Mo-Cl	88.6(2)
C(4)-Mo-Cl	164.9(2)
N(1)-Mo-Cl	82.6(2)
N(2)-Mo-Cl	78.54(14)
C(5)-Mo-Cl	149.9(2)
C(3)-Mo-Cl	148.3(2)
C(8)-O(3)-C(7)	104.4(6)
C(12)-O(4)-C(13)	105.2(6)
C(8)-N(1)-C(6)	106.0(6)
C(8)-N(1)-Mo	113.7(5)
C(6)-N(1)-Mo	140.3(5)
C(12)-N(2)-C(14)	106.2(5)
C(12)-N(2)-Mo	112.7(4)
C(14)-N(2)-Mo	136.6(4)
O(1)-C(1)-Mo	177.8(7)
O(2)-C(2)-Mo	176.6(8)
C(4)-C(3)-Mo	67.8(4)
C(3)-C(4)-C(5)	115.7(8)
C(3)-C(4)-Mo	76.6(4)
C(5)-C(4)-Mo	76.2(4)
C(4)-C(5)-Mo	67.9(4)
N(1)-C(6)-C(9)	112.2(7)
N(1)-C(6)-C(7)	102.1(7)
C(9)-C(6)-C(7)	118.7(8)
O(3)-C(7)-C(6)	107.1(6)
N(1)-C(8)-O(3)	120.2(7)
N(1)-C(8)-C(12)	119.3(6)
O(3)-C(8)-C(12)	120.4(6)
C(10)-C(9)-C(6)	114.7(9)
C(10)-C(9)-C(11)	110.5(10)
C(6)-C(9)-C(11)	108.0(9)
N(2)-C(12)-O(4)	120.4(7)
N(2)-C(12)-C(8)	119.6(6)
O(4)-C(12)-C(8)	120.0(6)
O(4)-C(13)-C(14)	104.9(6)
C(15)-C(14)-N(2)	113.9(7)
C(15)-C(14)-C(13)	113.0(7)
N(2)-C(14)-C(13)	102.3(6)
C(14)-C(15)-C(16)	113.5(10)
C(14)-C(15)-C(17)	108.4(10)
C(16)-C(15)-C(17)	111.7(12)

Table 4.Anisotropic displacement parameters (A^2 x 10^3) for C17H25ClMoN2O4(4a). The anisotropic displacement factor exponent takes the form:-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Mo	45(1)	30(1)	44(1)	-4(1)	0(1)	0(1)
Cl	41(1)	44(1)	64(1)	-12(1)	4(1)	2(1)
O(1)	80(4)	115(5)	57(3)	0(3)	-16(3)	-1(4)
O(2)	88(5)	52(3)	148(6)	17(4)	-14(5)	-26(4)
O(3)	68(3)	84(4)	54(3)	-13(3)	-7(3)	-12(3)
O(4)	66(4)	49(2)	87(4)	-28(3)	2(3)	-10(3)
N(1)	45(3)	53(3)	48(3)	-2(2)	1(3)	2(3)
N(2)	46(3)	38(3)	50(3)	-5(3)	-1(3)	-2(2)
C(1)	55(4)	56(4)	52(4)	-10(4)	-4(3)	7(4)
C(2)	59(4)	47(4)	74(5)	4(4)	-4(4)	0(4)
C(3)	71(5)	48(4)	83(6)	-14(4)	-3(5)	16(4)
C(4)	46(4)	51(4)	79(5)	-17(4)	12(4)	2(4)
C(5)	70(5)	52(4)	60(4)	-5(3)	16(4)	6(4)
C(6)	67(5)	68(5)	60(5)	4(4)	-9(4)	15(4)
C(7)	96(7)	107(7)	52(4)	-10(5)	-17(5)	-9(6)
C(8)	44(4)	53(4)	53(4)	-12(3)	4(3)	-5(3)
C(9)	88(6)	94(6)	67(5)	26(5)	-9(5)	-3(6)
C(10)	68(7)	196(14)	107(8)	70(9)	11(6)	7(8)
C(11)	167(13)	113(9)	95(8)	43(7)	-29(9)	10(10)
C(12)	44(4)	45(3)	62(4)	-16(3)	9(3)	-8(3)
C(13)	83(5)	39(4)	82(5)	-7(4)	1(5)	-9(4)
C(14)	62(4)	29(3)	84(5)	2(3)	-7(4)	-7(3)
C(15)	166(12)	48(5)	69(5)	3(4)	7(7)	-18(7)
C(16)	177(14)	85(7)	143(10)	3(7)	106(11)	-15(9)
C(17)	292(22)	70(6)	86(7)	37(5)	-32(11)	-31(10)

Table 5.Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for C17H25ClMoN2O4(4a).

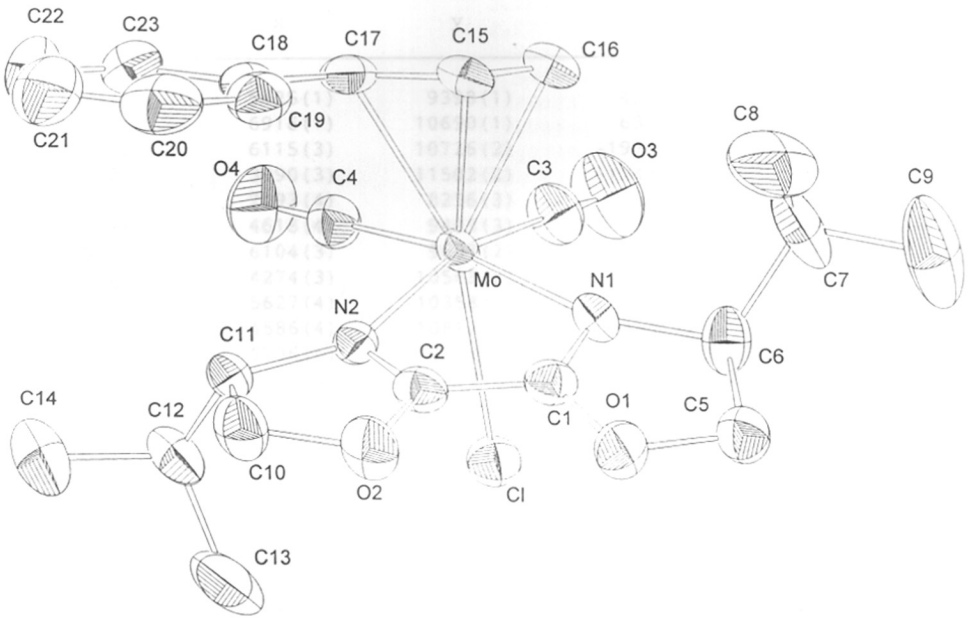
	x	y	z	U(eq)
H(3A)	-808	6628	369	76
H(3B)	1220	6831	943	76
H(4)	-2072	5431	920	68
H(5A)	-562	4987	1852	64
H(5B)	1347	5794	1869	64
H(6)	-1357	5974	-715	64
H(7A)	-167	4927	-1768	86
H(7B)	-2493	5079	-1475	86
H(9)	1861	6622	-767	87
H(10C)	4348	6196	-1539	108
H(10A)	3965	5450	-993	108
H(10B)	2938	5375	-1731	108
H(11C)	1525	7142	-1667	113
H(11A)	2	6349	-2063	113
H(11B)	-740	7068	-1532	113
H(13A)	-1015	2222	780	76
H(13B)	1351	1989	561	76
H(14)	2679	3025	1175	65
H(15)	708	3616	2022	101
H(16C)	-2803	3295	2154	122
H(16A)	-2462	3832	1470	122
H(16B)	-2617	2811	1438	122
H(17C)	83	2246	2551	139
H(17A)	274	1792	1826	139
H(17B)	2287	2256	2154	139

Torsion angles C17H25ClMoN2O4(4a)

CL	MO	N1	C6	-110.8(0)	CL	MO	N1	C8	70.6(0)
C1	MO	N1	C6	-138.0(0)	C1	MO	N1	C8	43.4(0)
C2	MO	N1	C6	-26.1(0)	C2	MO	N1	C8	155.3(0)
C4	MO	N1	C6	77.2(0)	C4	MO	N1	C8	-101.4(0)
CL	MO	C1	O1	121.7(0)	N1	MO	C1	O1	148.6(0)
C2	MO	C1	O1	35.1(0)	C4	MO	C1	O1	-67.5(0)
CL	MO	C2	O2	14.0(0)	N1	MO	C2	O2	-67.7(0)
C1	MO	C2	O2	103.0(0)	C4	MO	C2	O2	-154.9(0)
CL	MO	C4	C3	-115.8(0)	CL	MO	C4	C5	123.0(0)
N1	MO	C4	C3	-83.9(0)	N1	MO	C4	C5	154.9(0)
C1	MO	C4	C3	102.0(0)	C1	MO	C4	C5	-19.2(0)
C2	MO	C4	C3	16.9(0)	C2	MO	C4	C5	-104.2(0)
C8	O3	C7	C6	-1.3(0)	C7	O3	C8	N1	-2.0(0)
C7	O3	C8	C12	175.6(0)	C13	O4	C12	N2	5.1(0)
C13	O4	C12	C8	-177.4(0)	C12	O4	C13	C14	-9.2(0)
MO	N1	C6	C7	176.9(0)	MO	N1	C6	C9	48.7(0)
C8	N1	C6	C7	-4.5(0)	C8	N1	C6	C9	-132.7(0)
MO	N1	C8	O3	-176.5(0)	MO	N1	C8	C12	5.8(0)
C6	N1	C8	O3	4.4(0)	C6	N1	C8	C12	-173.2(0)
C14	N2	C12	O4	1.8(0)	C14	N2	C12	C8	-175.7(0)
C12	N2	C14	C13	-7.3(0)	C12	N2	C14	C15	-129.5(0)
N1	C6	C7	O3	3.5(0)	C9	C6	C7	O3	127.4(0)
N1	C6	C9	C10	60.8(0)	N1	C6	C9	C11	-175.5(0)
C7	C6	C9	C10	-57.9(0)	C7	C6	C9	C11	65.7(0)
O3	C8	C12	O4	11.8(0)	O3	C8	C12	N2	-170.7(0)
N1	C8	C12	O4	-170.5(0)	N1	C8	C12	N2	6.9(0)
O4	C13	C14	N2	9.9(0)	O4	C13	C14	C15	132.8(0)
N2	C14	C15	C16	56.5(0)	N2	C14	C15	C17	-178.8(0)
C13	C14	C15	C16	-59.6(0)	C13	C14	C15	C17	65.1(0)

Table 1. X-ray Crystallographic Data and Structure Refinement of $C_{23}H_{29}ClMoN_2O_4$ (**4e**)

formula	$C_{23}H_{29}ClMoN_2O_4$
fw	528.87
crys syst	Orthorhombic
space group	$P2_12_12_1$
a(Å)	10.954(3)
b(Å)	14.462(3)
c(Å)	15.686(3)
V(A^3)	2484.9(9)
Z	4
D_{calcd} (mg m^{-3})	1.414
μ (mm^{-1})	0.665
F (000)	1088
cryst size (mm)	0.85 x 0.65 x 0.60
radiation	MoKα (λ = 0.70930 Å)
temp(K)	293(2)
scan type	ω/2θ
scan width (deg)	0.8 + 0.35 tanθ
2θ range (deg)	1.91-23.37
no. of rflns collected	2086
no. of rflns obsd	2086 [R(int) = 0.0000]
no. of params varied	280
GOF	1.111
R [I > 2 sigma (I)]	0.0259
R_w [I > 2 sigma (I)]	0.0676



ORTEP view of the molecular structure of **4e**

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for C23H29ClMoN2O4 (4e). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Mo	5425(1)	9398(1)	435(1)	32(1)
Cl	6916(1)	10690(1)	632(1)	45(1)
O(1)	6115(3)	10726(2)	-1974(2)	54(1)
O(2)	3990(3)	11502(2)	-1243(2)	61(1)
O(3)	7493(4)	8256(3)	1289(3)	89(1)
O(4)	4618(4)	9403(3)	2327(2)	82(1)
N(1)	6104(3)	9657(2)	-933(2)	36(1)
N(2)	4274(3)	10563(2)	-119(2)	35(1)
C(1)	5627(4)	10358(3)	-1278(3)	40(1)
C(2)	4586(4)	10812(3)	-862(3)	41(1)
C(3)	6736(5)	8659(4)	949(3)	52(1)
C(4)	4904(4)	9407(3)	1614(3)	48(1)
C(5)	7240(5)	10192(4)	-2127(3)	58(1)
C(6)	7205(4)	9434(4)	-1437(3)	52(1)
C(7)	7208(8)	8448(4)	-1782(4)	86(3)
C(8)	6174(10)	8249(5)	-2336(4)	110(3)
C(9)	8354(9)	8229(6)	-2237(4)	129(4)
C(10)	2982(5)	11722(4)	-661(3)	59(1)
C(11)	3292(4)	11209(3)	168(3)	43(1)
C(12)	3692(5)	11798(3)	928(3)	60(1)
C(13)	4655(8)	12513(4)	750(5)	96(2)
C(14)	2585(8)	12226(5)	1346(6)	101(3)
C(15)	4244(5)	8304(3)	-159(3)	50(1)
C(16)	5319(6)	7848(3)	75(4)	65(2)
C(17)	3482(4)	8593(3)	490(3)	46(1)
C(18)	2307(4)	9065(3)	365(3)	49(1)
C(19)	1862(5)	9313(4)	-442(4)	60(1)
C(20)	756(6)	9749(4)	-536(5)	80(2)
C(21)	38(6)	9928(5)	160(6)	89(2)
C(22)	439(6)	9664(5)	962(5)	87(2)
C(23)	1576(5)	9235(4)	1071(4)	66(2)

Table 3. Bond lengths [A] and angles [deg] for C23H29ClMoN2O4(4e).

Mo-C(4)	1.935(5)
Mo-C(3)	1.963(5)
Mo-C(15)	2.246(5)
Mo-N(2)	2.277(3)
Mo-N(1)	2.303(3)
Mo-C(16)	2.315(4)
Mo-C(17)	2.428(4)
Mo-Cl	2.5001(12)
O(1)-C(1)	1.327(5)
O(1)-C(5)	1.474(6)
O(2)-C(2)	1.334(5)
O(2)-C(10)	1.468(6)
O(3)-C(3)	1.146(6)
O(4)-C(4)	1.162(6)
N(1)-C(1)	1.262(5)
N(1)-C(6)	1.477(6)
N(2)-C(2)	1.266(6)
N(2)-C(11)	1.494(5)
C(1)-C(2)	1.469(7)
C(5)-C(6)	1.542(7)
C(6)-C(7)	1.527(8)
C(7)-C(8)	1.456(12)
C(7)-C(9)	1.478(11)
C(10)-C(11)	1.536(7)
C(11)-C(12)	1.529(7)
C(12)-C(13)	1.503(9)
C(12)-C(14)	1.512(9)
C(15)-C(17)	1.381(7)
C(15)-C(16)	1.399(8)
C(17)-C(18)	1.470(6)
C(18)-C(23)	1.389(7)
C(18)-C(19)	1.402(8)
C(19)-C(20)	1.374(8)
C(20)-C(21)	1.370(10)
C(21)-C(22)	1.386(11)
C(22)-C(23)	1.402(9)
C(4)-Mo-C(3)	80.1(2)
C(4)-Mo-C(15)	103.4(2)
C(3)-Mo-C(15)	102.0(2)
C(4)-Mo-N(2)	101.3(2)
C(3)-Mo-N(2)	164.7(2)
C(15)-Mo-N(2)	92.5(2)
C(4)-Mo-N(1)	170.0(2)
C(3)-Mo-N(1)	103.6(2)
C(15)-Mo-N(1)	85.1(2)
N(2)-Mo-N(1)	72.68(12)
C(4)-Mo-C(16)	103.0(2)
C(3)-Mo-C(16)	67.0(2)
C(15)-Mo-C(16)	35.7(2)

N(2)-Mo-C(16)	126.6(2)
N(1)-Mo-C(16)	86.9(2)
C(4)-Mo-C(17)	73.2(2)
C(3)-Mo-C(17)	111.5(2)
C(15)-Mo-C(17)	34.1(2)
N(2)-Mo-C(17)	83.28(14)
N(1)-Mo-C(17)	113.2(2)
C(16)-Mo-C(17)	60.0(2)
C(4)-Mo-Cl	93.97(14)
C(3)-Mo-Cl	83.0(2)
C(15)-Mo-Cl	162.51(13)
N(2)-Mo-Cl	81.72(9)
N(1)-Mo-Cl	77.45(9)
C(16)-Mo-Cl	141.8(2)
C(17)-Mo-Cl	157.91(12)
C(1)-O(1)-C(5)	105.2(4)
C(2)-O(2)-C(10)	104.5(4)
C(1)-N(1)-C(6)	106.5(4)
C(1)-N(1)-Mo	113.4(3)
C(6)-N(1)-Mo	136.6(3)
C(2)-N(2)-C(11)	107.1(4)
C(2)-N(2)-Mo	114.3(3)
C(11)-N(2)-Mo	138.2(3)
N(1)-C(1)-O(1)	120.5(4)
N(1)-C(1)-C(2)	119.3(4)
O(1)-C(1)-C(2)	120.0(4)
N(2)-C(2)-O(2)	119.6(4)
N(2)-C(2)-C(1)	119.5(4)
O(2)-C(2)-C(1)	120.9(4)
O(3)-C(3)-Mo	176.2(5)
O(4)-C(4)-Mo	178.3(4)
O(1)-C(5)-C(6)	103.7(4)
N(1)-C(6)-C(7)	113.3(5)
N(1)-C(6)-C(5)	103.9(4)
C(7)-C(6)-C(5)	114.5(4)
C(8)-C(7)-C(9)	109.3(6)
C(8)-C(7)-C(6)	113.2(6)
C(9)-C(7)-C(6)	111.9(7)
O(2)-C(10)-C(11)	104.8(4)
N(2)-C(11)-C(12)	112.2(4)
N(2)-C(11)-C(10)	101.9(4)
C(12)-C(11)-C(10)	117.0(4)
C(13)-C(12)-C(14)	111.2(5)
C(13)-C(12)-C(11)	116.1(5)
C(14)-C(12)-C(11)	109.7(5)
C(17)-C(15)-C(16)	117.3(5)
C(17)-C(15)-Mo	80.2(3)
C(16)-C(15)-Mo	74.9(3)
C(15)-C(16)-Mo	69.4(2)
C(15)-C(17)-C(18)	124.8(5)
C(15)-C(17)-Mo	65.7(3)
C(18)-C(17)-Mo	122.7(3)
C(23)-C(18)-C(19)	118.3(5)
C(23)-C(18)-C(17)	118.7(5)
C(19)-C(18)-C(17)	122.9(5)

C(20)-C(19)-C(18)	121.4(6)
C(21)-C(20)-C(19)	120.5(7)
C(20)-C(21)-C(22)	119.3(6)
C(21)-C(22)-C(23)	121.0(6)
C(18)-C(23)-C(22)	119.5(6)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for C23H29ClMoN2O4(4e). The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Mo	36(1)	24(1)	35(1)	1(1)	1(1)	5(1)
Cl	42(1)	45(1)	48(1)	-8(1)	-5(1)	-5(1)
O(1)	68(2)	50(2)	45(2)	10(2)	17(2)	6(2)
O(2)	71(2)	47(2)	66(2)	23(2)	8(2)	24(2)
O(3)	90(3)	85(3)	90(3)	12(3)	-22(3)	43(3)
O(4)	104(3)	102(3)	39(2)	2(2)	15(2)	-5(4)
N(1)	44(2)	31(2)	34(2)	-5(2)	-2(2)	7(2)
N(2)	32(2)	29(2)	46(2)	5(2)	2(2)	2(2)
C(1)	47(2)	36(2)	36(2)	-2(2)	-2(2)	-5(2)
C(2)	43(2)	32(2)	49(2)	5(2)	-7(2)	2(2)
C(3)	58(3)	48(3)	49(3)	3(2)	-6(3)	13(3)
C(4)	51(2)	44(3)	48(3)	1(2)	2(2)	0(2)
C(5)	67(3)	49(3)	58(3)	2(2)	18(3)	4(3)
C(6)	49(2)	69(3)	37(2)	2(3)	3(2)	14(3)
C(7)	161(7)	51(3)	47(3)	12(3)	39(4)	55(4)
C(8)	187(8)	84(5)	59(4)	-35(4)	24(5)	-43(6)
C(9)	197(9)	123(6)	67(4)	45(4)	67(5)	99(7)
C(10)	57(3)	53(3)	67(3)	4(3)	0(3)	21(3)
C(11)	38(2)	28(2)	64(3)	2(2)	6(2)	9(2)
C(12)	70(3)	38(3)	73(3)	-10(3)	2(3)	14(3)
C(13)	103(5)	41(3)	144(6)	-29(4)	0(5)	10(4)
C(14)	104(6)	71(4)	128(6)	-18(4)	34(5)	25(4)
C(15)	61(3)	28(2)	62(3)	-8(2)	4(2)	-7(2)
C(16)	72(3)	24(2)	99(4)	-5(3)	23(3)	1(3)
C(17)	49(2)	30(2)	60(3)	4(2)	2(2)	-11(2)
C(18)	44(2)	31(2)	71(3)	1(2)	8(3)	-10(2)
C(19)	54(3)	54(3)	71(3)	-5(3)	-6(3)	-12(3)
C(20)	59(4)	70(4)	113(5)	10(4)	-33(4)	-11(3)
C(21)	50(3)	86(5)	131(6)	2(5)	-2(4)	-1(3)
C(22)	57(4)	82(4)	123(6)	-4(4)	32(4)	2(4)
C(23)	70(3)	54(3)	73(3)	2(3)	22(3)	-14(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for C23H29ClMoN2O4(4e).

	x	y	z	U(eq)
H(5A)	7149	9935	-2815	40
H(5B)	7998	10562	-2013	40
H(6)	7875	9417	-1140	40
H(7)	6925	8048	-1368	40
H(8A)	6013	8507	-2870	40
H(8B)	5494	7825	-2677	40
H(8C)	5429	8322	-2083	40
H(9A)	3710	6383	2536	40
H(9B)	4021	6583	1860	40
H(9C)	3700	7545	2315	40
H(10A)	2195	11395	-954	40
H(10B)	3130	12394	-492	40
H(11)	2511	10847	404	40
H(12)	4039	11350	1417	40
H(13A)	4318	12983	307	40
H(13B)	4375	12987	1186	40
H(13C)	4856	12349	445	40
H(14A)	1995	11643	1562	40
H(14B)	7875	7576	3151	40
H(14C)	2400	12594	1056	40
H(15)	4053	8497	-788	40
H(16A)	5875	7514	-315	40
H(16B)	5243	7407	548	40
H(17)	3484	8250	1135	40
H(19)	2625	9083	-978	40
H(20)	4625	9929	3858	40
H(21)	-824	10325	313	40
H(22)	65	9841	1687	40
H(23)	1894	8932	1776	40

Torsion angles C23H29O4N2CLMO(4e)

CL	MO	N2	C2	76.2(0)	CL	MO	N2	C11	-96.4(0)
C3	MO	N2	C2	74.9(0)	C3	MO	N2	C11	-97.7(0)
C4	MO	N2	C2	168.6(0)	C4	MO	N2	C11	-3.9(0)
C15	MO	N2	C2	-87.2(0)	C15	MO	N2	C11	100.2(0)
C16	MO	N2	C2	-75.6(0)	C16	MO	N2	C11	111.8(0)
CL	MO	C3	O3	64.5(0)	N2	MO	C3	O3	65.8(0)
C4	MO	C3	O3	-30.8(0)	C15	MO	C3	O3	-132.5(0)
C16	MO	C3	O3	-139.6(0)	CL	MO	C4	O4	-73.4(0)
N2	MO	C4	O4	-155.8(0)	C3	MO	C4	O4	8.7(0)
C15	MO	C4	O4	108.9(0)	C16	MO	C4	O4	72.2(0)
CL	MO	C15	C16	93.8(0)	CL	MO	C15	C17	-144.2(0)
N2	MO	C15	C16	164.0(0)	N2	MO	C15	C17	-74.1(0)
C3	MO	C15	C16	-11.3(0)	C3	MO	C15	C17	110.6(0)
C4	MO	C15	C16	-93.8(0)	C4	MO	C15	C17	28.2(0)
C16	MO	C15	C16	.0(0)	C16	MO	C15	C17	121.9(0)
CL	MO	C16	C15	-151.0(0)	N2	MO	C16	C15	-20.1(0)
C3	MO	C16	C15	168.0(0)	C4	MO	C16	C15	94.9(0)
C15	MO	C16	C15	.0(0)	C5	O1	C1	N1	-4.2(0)
C5	O1	C1	C2	170.6(0)	C1	O1	C5	C6	4.4(0)
C10	O2	C2	N2	-5.9(0)	C10	O2	C2	C1	176.3(0)
C2	O2	C10	C11	12.4(0)	C6	N1	C1	O1	1.8(0)
C6	N1	C1	C2	-173.1(0)	C1	N1	C6	C5	1.4(0)
C1	N1	C6	C7	-123.5(0)	MO	N2	C2	O2	-178.7(0)
MO	N2	C2	C1	-.9(0)	C11	N2	C2	O2	-3.9(0)
C11	N2	C2	C1	174.0(0)	MO	N2	C11	C10	-175.9(0)
MO	N2	C11	C12	58.1(0)	C2	N2	C11	C10	11.2(0)
C2	N2	C11	C12	-114.7(0)	O1	C1	C2	O2	11.1(0)
O1	C1	C2	N2	-166.7(0)	N1	C1	C2	O2	-174.0(0)
N1	C1	C2	N2	8.2(0)	O1	C5	C6	N1	-3.5(0)
O1	C5	C6	C7	120.7(0)	N1	C6	C7	C8	59.4(0)
N1	C6	C7	C9	-176.5(0)	C5	C6	C7	C8	-59.6(0)
C5	C6	C7	C9	64.5(0)	O2	C10	C11	N2	-14.1(0)
O2	C10	C11	C12	108.5(0)	N2	C11	C12	C13	69.1(0)
N2	C11	C12	C14	-163.8(0)	C10	C11	C12	C13	-48.1(0)
C10	C11	C12	C14	78.9(0)	MO	C15	C16	MO	.0(0)
C17	C15	C16	MO	-70.3(0)	MO	C15	C17	C18	114.1(0)
C16	C15	C17	C18	-178.7(0)	C15	C17	C18	C19	-3.2(0)
C15	C17	C18	C23	173.7(0)	C17	C18	C19	C20	179.6(0)
C23	C18	C19	C20	2.6(0)	C17	C18	C23	C22	-178.4(0)
C19	C18	C23	C22	-1.4(0)	C18	C19	C20	C21	-1.9(0)
C19	C20	C21	C22	-.1(0)	C20	C21	C22	C23	1.3(0)
C21	C22	C23	C18	-.6(0)					