REDUCTION CHEMISTRY OF DIBENZOTHIOPHENE MANGANESE TRICARBONYL CATION AND REACTIONS OF PHOSPHOLES WITH GROUP SIX METAL CARBONYLS

by

GRETCHEN LEE METZ

Submitted in Partial Fulfillment of the Requirements

for the Degree of

Master of Science

in the

Chemistry

Program

YOUNGSTOWN STATE UNIVERSITY

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ABSTRACT

The content of the research presented in this thesis is based on the synthesis, purification, and characterization of phospholes with group six metal carbonyls, and reduction chemistry of dibenzothiophene manganese tricarbonyl cation. The cyclic voltammetry of η^6-DBTMn(CO)$_3$BF$_4$ was performed at various scan rates with different working electrodes. Dibenzothiophenes may be useful in producing polymers while phospholes are important due to their unique bonding and C--P chemistry.

ABSTRACT

The content of the research presented in this thesis is based on the synthesis, purification, and characterization of phospholes with group six metal carbonyls, and reduction chemistry of dibenzothiophene manganese tricarbonyl cation. The cyclic voltammetry of η^6-DBTMn(CO)$_3$BF$_4$ was performed at various scan rates with different working electrodes. Dibenzothiophenes may be useful in producing polymers while phospholes are important due to their unique bonding and C--P chemistry.

ACKNOWLEDGEMENTS

I would like to thank my research advisor Dr. Sherri Lovelace for all the patience, help, encouragement, direction, and friendship that she has given me over the past two years while completing both my research and my thesis. I would also like to thank the members of my thesis committee Dr. Larry Curtin and Dr. Daryl Mincey, as well as the chemistry department faculty, and secretaries for all their help and words of encouragement.

I would also like to thank Dr. N. John Cooper, University of Pittsburgh, for the use of his equipment.

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LIST OF COMPOUNDS

Compound I:	η^4-dibenzothiophene manganese tricarbonyl η^4-$(SC_{12}H_8)Mn(CO)_3$
Compound II:	η^5-benzothiophene, benzylcyclohexadienyl manganese tricarbonyl complex n^5-$(SC_{19}H_{15})Mn(CO)_3$
Compound III:	η^5-benzothiophene, tin tri-n-butylcyclohexadienyl manganese tricarbonyl complex $\eta5$-$(SC_{24}H_{35})Mn(CO)_3$
Compound IV:	η^4-dibenzothiophene manganese tricarbonyl bis(triphenylphosphoranylidene)ammonium salt $[\eta^4$-$(SC_{12}H_8)Mn(CO)_3][(C_6H_5)_6N]$
Compound VIII:	η^4-pentaphenylphosphole tungsten tricarbonyl η^4-$[(C_6H_5)_5C_4P]W(CO)_3$

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Compound VIII:	η^4-pentaphenylphosphole tungsten tricarbonyl η^4-$[(C_6H_5)_5C_4P]W(CO)_3$

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LIST OF ABBREVIATIONS

Abbreviation	**Description**
br	broad
c	complex multiplet
°C	degrees Celcius
^{13}C	carbon 13
$[(\eta^6-C_{12}H_8S)Mn(CO)_3]BF_4$	(η^6-dibenzothiophene)manganese tricarbonyl tetrafluoroborate
C_5Me_5	pentamethylcyclopentadienyl
(C_6H_5R)	R substituted benzene
ca.	about
$CDCl_3$	deuterochloroform
cm	centimeter
CO	carbonyl
Cp	cyclopentadienyl
$CpFe(MeCN)_2$	cyclopenteneiron(III)diacetonitrile
CV	cyclic voltammetry
δ	parts per million
d	deuterated
(d)	doublet
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene [1, 5-5]

LIST OF ABBREVIATIONS

Abbreviation	**Description**
br	broad
c	complex multiplet
°C	degrees Celcius
^{13}C	carbon 13
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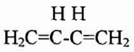
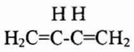
C_5Me_5	pentamethylcyclopentadienyl
(C_6H_5R)	R substituted benzene
ca.	about
$CDCl_3$	deuterochloroform
cm	centimeter
CO	carbonyl
Cp	cyclopentadienyl
$CpFe(MeCN)_2$	cyclopenteneiron(III)diacetonitrile
CV	cyclic voltammetry
δ	parts per million
d	deuterated
(d)	doublet
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene [1, 5-5]
DME	ethylene glycol dimethyl ether
(d of d)	doublet of doublets
E_p	peak potential
eq.	equivalent
FTIR	fourier transform infrared spectroscopy
g	gram
GC	glassy carbon
^1H	hydrogen 1
 $H_2C{=}\overset{H}{C}{-}\overset{H}{C}{=}CH_2$	1,3-butadiene
h	hour
HBF_4	fluoroboric acid
HDS	hydrodesulfurization
HOMO	Highest Occupied Molecular Orbital
H_3PO_4	phosphoric acid
Hz	Hertz
I_{pc}	cathodic peak current
J	coupling constant in Hertz
kcal/mol	kilocalories/mole
KNAP	potassium naphthalide
LUMO	Lowest Unoccupied Molecular Orbital
(M)	molarity
M	metal

DME	ethylene glycol dimethyl ether
(d of d)	doublet of doublets
E_p	peak potential
eq.	equivalent
FTIR	fourier transform infrared spectroscopy
g	gram
GC	glassy carbon
^1H	hydrogen 1
 $H_2C{=}\overset{H}{C}{-}\overset{H}{C}{=}CH_2$	1,3-butadiene
h	hour
HBF_4	fluoroboric acid
HDS	hydrodesulfurization
HOMO	Highest Occupied Molecular Orbital
H_3PO_4	phosphoric acid
Hz	Hertz
I_{pc}	cathodic peak current
J	coupling constant in Hertz
kcal/mol	kilocalories/mole
KNAP	potassium naphthalide
LUMO	Lowest Unoccupied Molecular Orbital
(M)	molarity
M	metal

(m)	medium
m	multiplicity
$[(\eta^6\text{-arene})Mn(CO)_3]^+$	$(\eta^6$arene)manganese tricarbonyl ion
m-xylene	meta-xylene
Me	methyl
MeCN	acetonitrile
MHz	megahertz
ml	milliliter
mol	mole
Mp	melting point
mV	millivolts
η	coordination mode
$[(\eta^6\text{-o-}C_6H_4(OMe)_2)Mn(CO)_3]^+$	η^6-ortho-dimethoxybenzene manganese tricarbonyl ion
No.	number
NMR	nuclear magnetic resonance spectroscopy
OEt_2	diethyl ether
π	pi
P_4	tetraphosphorus
P_5	cyclopentaphosphorus
^{31}P	phosphorus 31 nuclear magnetic resonance spectroscopy

(m)	medium
m	multiplicity
$[(\eta^6\text{-arene})Mn(CO)_3]^+$	$(\eta^6$-arene)manganese tricarbonyl ion
m-xylene	meta-xylene
Me	methyl
MeCN	acetonitrile
MHz	megahertz
ml	milliliter
mol	mole
Mp	melting point
mV	millivolts
η	coordination mode
$[(\eta^6\text{-o-}C_6H_4(OMe)_2)Mn(CO)_3]^+$	η^6-ortho-dimethoxybenzene manganese tricarbonyl ion
No.	number
NMR	nuclear magnetic resonance spectroscopy
OEt_2	diethyl ether
π	pi
P_4	tetraphosphorus
P_5	cyclopentaphosphorus
^{31}P	phosphorus 31 nuclear magnetic resonance spectroscopy

Ph	phenyl
pK_a	autoprotolysis constant
P_2O_5	phosphorus pentoxide
ppm	parts per million
PPNCl	bis(triphenylphosphoranylidene) ammonium chloride
PX_2	dichloro or dibromophosphine
q	quartet
R	substituent group
$Ru(NH_3)_5^{3+}$	ruthenium(III)pentaammine
(SC_4H_3R)	R substituted thiophene
s	singlet
(s)	strong
t	triplet
$(t\text{-Bu})_3$	tri-tertiarybutyl
TBA	tetrabutylammonium
TFA	trifluoroacetic anhydride
THF	tetrahydrofuran
V	Volts
V/cm	Volts/centimeter
V/s	Volts/sec
(vs)	very strong
(w)	weak

Ph	phenyl
pK_a	autoprotolysis constant
P_2O_5	phosphorus pentoxide
ppm	parts per million
PPNCl	bis(triphenylphosphoranylidene) ammonium chloride
PX_2	dichloro or dibromophosphine
q	quartet
R	substituent group
$Ru(NH_3)_5^{3+}$	ruthenium(III)pentaammine
(SC_4H_3R)	R substituted thiophene
s	singlet
(s)	strong
t	triplet
$(t\text{-}Bu)_3$	tri-tertiarybutyl
TBA	tetrabutylammonium
TFA	trifluoroacetic anhydride
THF	tetrahydrofuran
V	Volts
V/cm	Volts/centimeter
V/s	Volts/sec
(vs)	very strong
(w)	weak

w	working electrode
x	x-axis
X	chlorine or bromine

w	working electrode
x	x-axis
X	chlorine or bromine

1.0 Introduction

1.1 Dibenzothiophenes

Research interests in industry have developed due to (HDS) Hydrodesulfurization reactions of heavy crude oils and coal-derived liquids in the petroleum industry. Catalytic (HDS) is the process whereby hydrogen is added to thiophene and this process produces both 1-butene and 2-butene along with H_2S. Dibenzothiophenes are sulphur containing ring complexes[1-2a,b] (see Figure 1A).

In 1958, Fischer[2c] synthesized the first η^5-thiophene transition metal complex which was $Cr(CO)_3(\eta^5$-thiophene.) It was later structurally characterized by the Dahl group to involve the thiophene ring π-bonded to the metal moiety.[1] Several types of thiophenic organometallic complexes have been reported in literature.[2a] They fall into three categories which vary according to how the metal is bound to the thiophene (see Figure 1B).

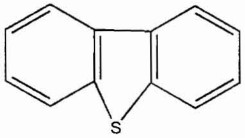


FIGURE 1A: STRUCTURE OF DIBENZOTHIOPHENE

1.0 Introduction

1.1 Dibenzothiophenes

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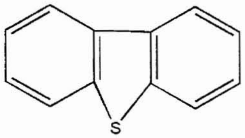


FIGURE 1A: STRUCTURE OF DIBENZOTHIOPHENE

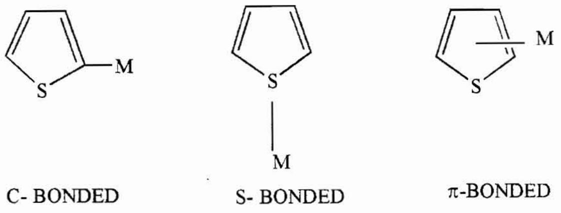


FIGURE 1B: METAL COMPLEXES OF THIOPHENE

Angelici describes the different structural aspects of thiophene binding complexes. These binding complexes are shown below (see figure 2A).[2b]

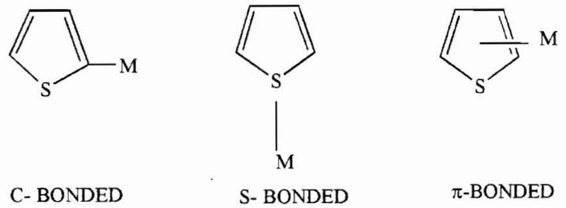


FIGURE 1B: METAL COMPLEXES OF THIOPHENE

Angelici describes the different structural aspects of thiophene binding complexes. These binding complexes are shown below (see figure 2A).[2b]

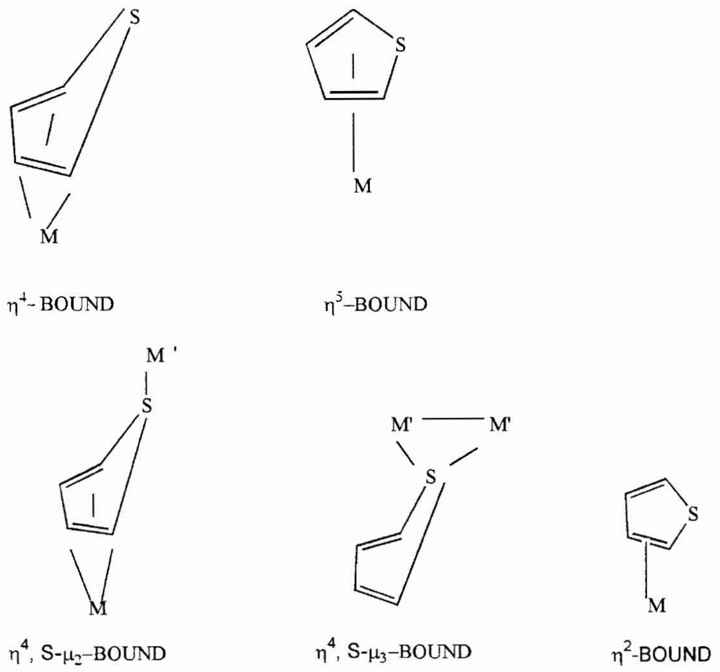
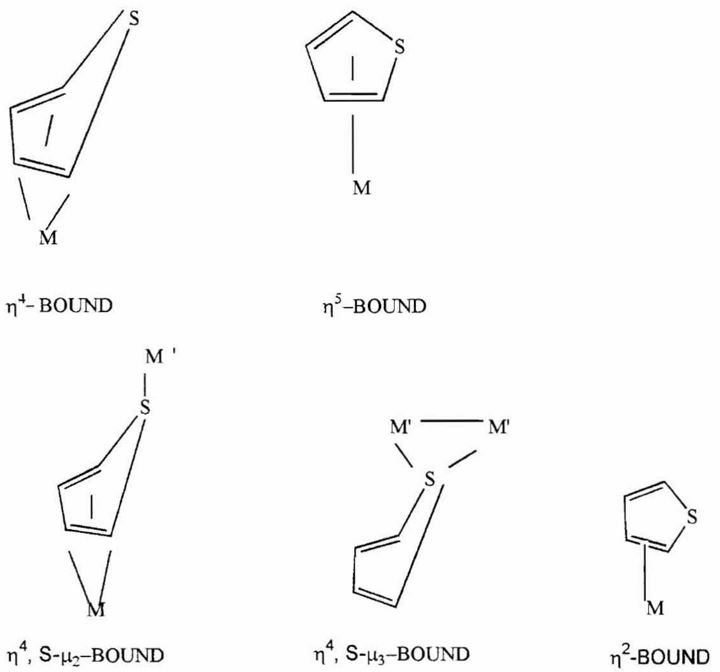


FIGURE 2A: BONDING MODES OF TRANSITION METAL COMPLEXES OF THIOPHENES

The most common form is the C bonded thiophene; however, it has not been suggested as a structure in the catalytic HDS of thiophene. The S-bonded thiophene has been suggested as an intermediate in the catalytic HDS process, but the S atom is very weakly coordinating. The two S-bonded complexes which have been reported to date are Ru(NH$_3$)$_5$(thiophene) and CpFe(MeCN)$_2$(2,5-dimethylthiophene).[2a-e] Both were shown to be very unstable, resulting in partial characterization of compounds.[2d,e] Two examples of π-bonded thiophenes to discrete metal centers are Mn(CO)$_3$(η^5-thiophene) and



η^4- BOUND

η^5–BOUND

η^4, S-μ_2–BOUND

η^4, S-μ_3–BOUND

η^2-BOUND

FIGURE 2A: BONDING MODES OF TRANSITION METAL COMPLEXES OF THIOPHENES

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π–Arene complexes of transition metals or "polyphenyl chromium compounds" were first prepared by Hein prior to 1920.[3a] In 1956, Fischer and Hafner prepared cationic π-aromatic compounds by using strong Lewis acids and reductive conditions. A compound synthesized from this method was $[(\eta^6\text{-arene})FeCp]^{+}$,[3ab].

In 1981, Pauson suggested that (arene) manganese cations could be prepared using both the $[Mn(CO)_5]^+$ silver(I) ion method and the halide abstraction method.[3c] A variety of arene Mn cations have been prepared using this method.[3d] An example of this is the $[(\eta^6\text{-o-}C_6H_4(OMe)_2)Mn(CO)_3]^+$ which Pearson synthesized. Other types of compounds synthesized from the silver(I) ion preparation are indoles and aromatic steroids.[3a] A third pathway, developed by soviet scientists, also exists for synthesizing $[(\eta^6\text{-arene})Mn(CO)_3]^+$ using the trifluoroacetic anhydride (TFA) method. In 1994, Jackson et al. synthesized (η^6-dibenzothiophene)$Mn(CO)_3BF_4$ complex by the TFA anhydride method in high yield.[3a]

Solvents such as MeCN tend to cause or promote a nucleophilic attack of arene and (thiophene)$Cr(CO)_3$ monocations.[4] The oxidation of the $(C_6H_5R)Cr(CO)_3$ and $(SC_4H_3R)Cr(CO)_3$ complexes was reported to be irreversible while the oxidation of Mo and W $(C_6H_5R)M(CO)_3$ complexes were reversible. Crayston's experiments led to an understanding that M arene bond energies increase Cr < Mo < W: 191, 280, 362 $kJmol^{-1}$.[4-6]

Chemical reduction of (η^6–benzophenone)$Cr(CO)_3$ and (η^6-benzophenone)$(Cr(CO)_3)_2$ in the presence of alkyl chlorides, which are used as alkylating agents, have been carried

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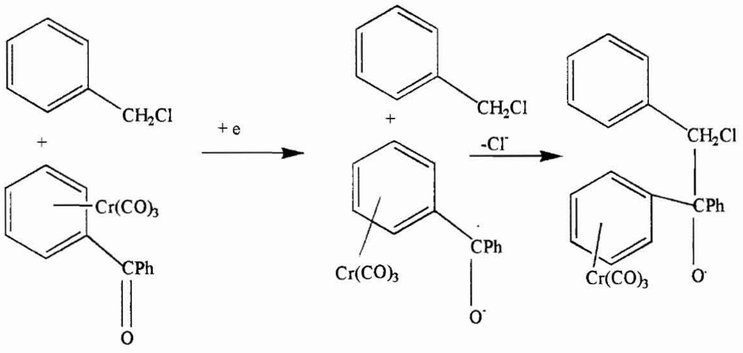

FIGURE 2B: INTERMEDIATE FORMATION OF A CHARGE TRANSFER COMPLEX

One of the complexes previously synthesized was $[(\eta^6\text{-}C_{12}H_8S)Mn(CO)_3]BF_4$.[3a] This compound was synthesized by refluxing the reaction mixture at 74°C for five hours. This bright yellow powder appears to be air stable. In solution, it decomposes within an hour under an argon atmosphere. In analyzing the substance by IR, two peaks appeared at 2077(s) and 2025 cm^{-1}(m, br) which represent the CO stretches (see Figure 3).[3a]

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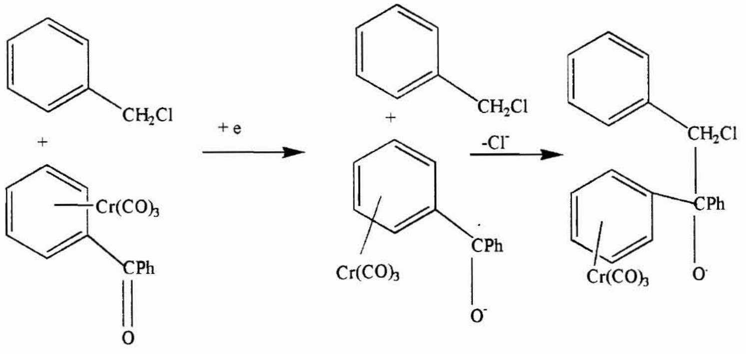

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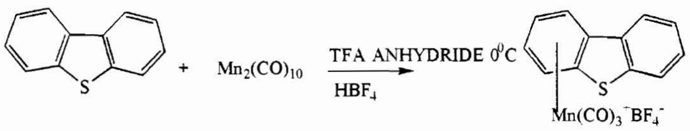


FIGURE 3: PREPARATION OF [(η^6-DIBENZOTHIOPHENE)Mn(CO)$_3$]BF$_4$ BY THE TFA ANHYDRIDE METHOD.

Much progress has been made in the electrochemical analysis of Cr(CO)$_3$, Mo(CO)$_3$, and W(CO)$_3$ thiophene compounds. The electrogenerated radicals containing seventeen electrons and nineteen electrons were of most interest to the Crayston et al. group because of their lability and their catalytic activity.[4-6] Crayston et al. demonstrated that (C$_6$H$_5$R)Cr(CO)$_3$ and (SC$_4$H$_3$R)Cr(CO)$_3$ undergo a one electron oxidation through the (MeCN)$_3$Cr(CO)$_3$ intermediate. The one electron oxidation leaves the Cr(CO)$_3$ moiety intact and results in the loss of the arene ligand (see Figure 4).

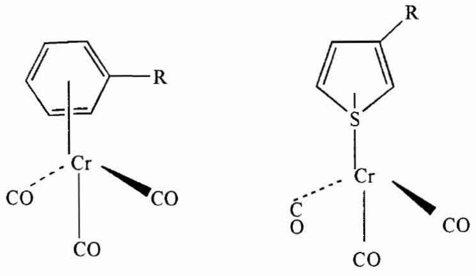
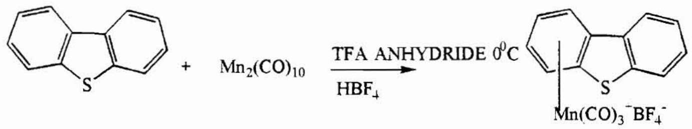


FIGURE 4: PRODUCTS OXIDIZED BY THE CRAYSTON ET AL GROUP



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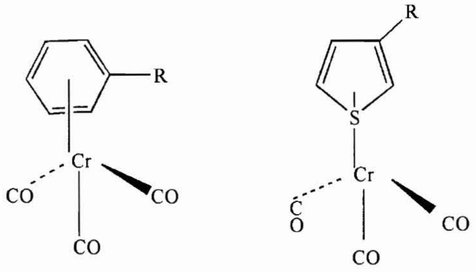

FIGURE 4: PRODUCTS OXIDIZED BY THE CRAYSTON ET AL GROUP

The oxidized $(MeCN)_3Cr(CO)_3^+$ suffered no loss of CO groups and Mo and W arene tricarbonyl cations did not suffer any arene ligand displacement.[4]

1.2 Phospholes

Another area of interest in organometallic chemistry is the delocalized π-bonding systems of hydrocarbons and phosphorus heterocycles. They are important because of their unique bonding and their synthetic potential. Similiar to these are the P and C - pπ bonding systems which have also become a major interest to researchers because of their bonding possibilities, electronic properties, magnetic properties, and catalytic properties of the transition metal moieties attached to them.[7b] For example, five member P, C-heterocycles are capable of bonding in an η^5 and η^3 coordination mode to the metal fragment. Some examples of these complexes are 2,3-diphenyl-phosphindolyl where the lithium metal is found in both an η^5 and an η^3 coordination mode (see Figure 5).[8]

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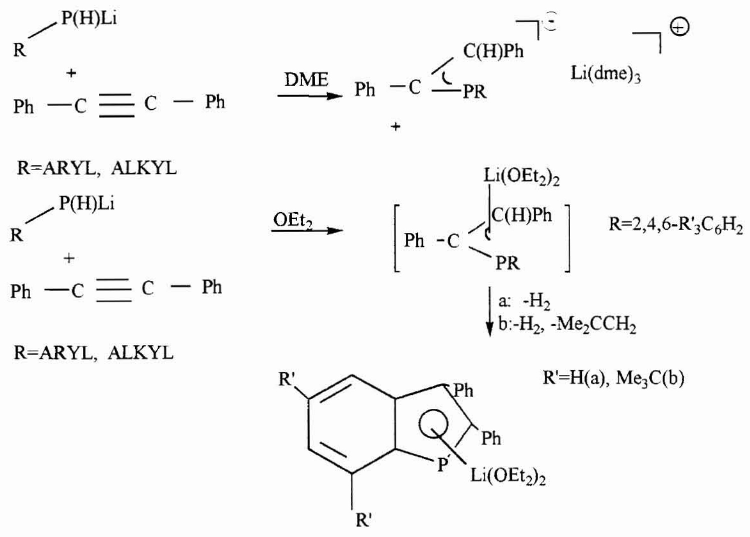
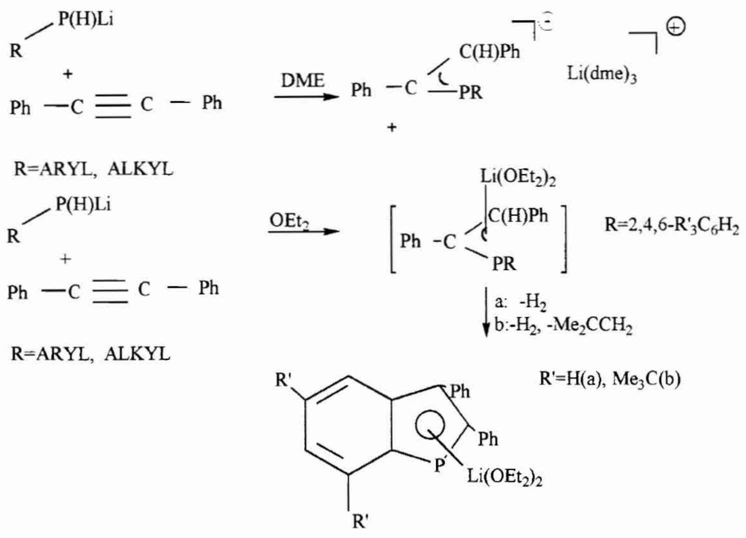


FIGURE 5: η^5 and η^3 COORDINATION OF A METAL FRAGMENT

Figure five represents the actual synthetic pathway taken to produce the η^5 and η^3 phosphoallyllithium complexes. Product a is η^5–coordinated due to it's loss of the two hydrogens while product b is η^3-coordinated due to its loss of two hydrogens and the Me_2CCH_2.

Another type of C-P-heterocycle is the phosphole. Phospholes are synthesized by the following reaction : (see figure 6A).[9]



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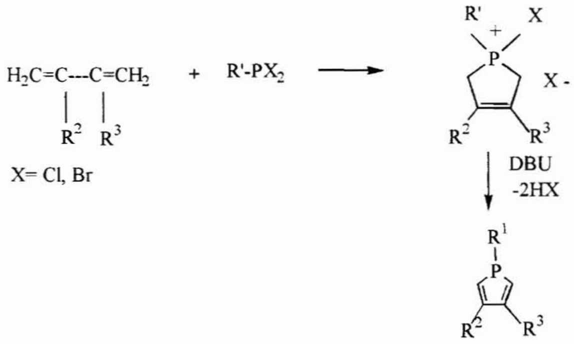
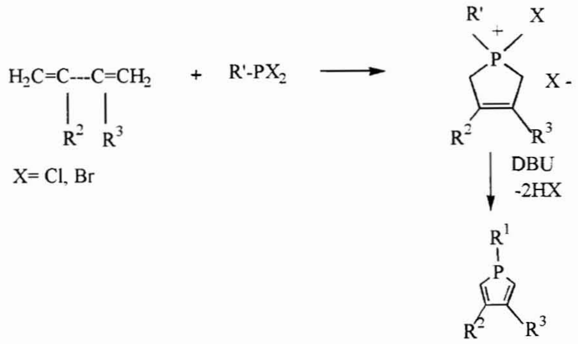


	R^1	R^2	R^3
a	C_6H_5	CH_3	CH_3
b	C_6H_5	H	CH_3
c	C_6H_5	H	H
d	$CH_2C_6H_5$	CH_3	CH_3
e	CH_3	CH_3	CH_3

FIGURE 6A: SYNTHESIS OF A PHOSPHOLE

1,8-Diazabicyclo[5.4.0] undec-7-ene[1,5-5] (DBU) is used in this reaction because of its high basicity and low nucleophilicity.[9] Attempts have been made by Mathey et al . to replace DBU since it is rather costly , difficult to purify, and to keep dry. Some compounds used in place of DBU are 2-methylpyridine and 1-methylpyrrolidine. Both substances gave increased yields of the phosphole products. Some of the different types of phospholes synthesized were 3,4-dimethyl-1-phenyl-phosphole, 3-methyl-1-



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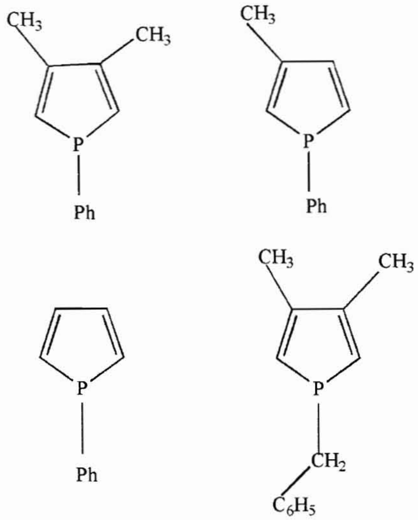
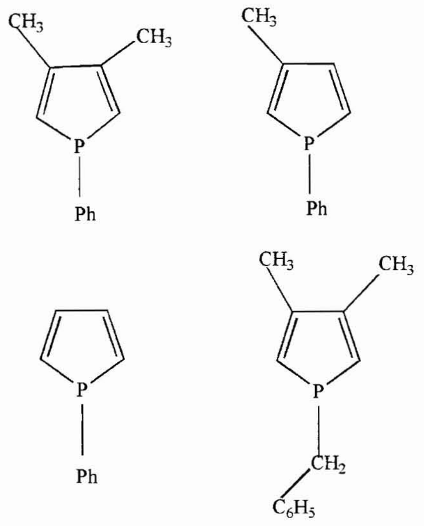


FIGURE 6B: STRUCTURES OF PHOSPHOLES

In 1970, Coggon et al. analyzed 1-benzylphosphole using X-ray crystallography techniques.[10a-10b] They found that the phosphorus atom adopted a pyramidal structure with long internal P-C bonds of 1.783 Angstroms. These two features suggested that phospholes were only weakly aromatic and were highly basic: pK_a ca. 0.5 for 1-methylphosphole. Photoelectron spectroscopic UV-visible studies indicated that the energy of the phosphorus lone pair orbital remained almost unchanged upon saturation of the phosphole diene system.[10b] Mislow[10b,c], in favor of phosphole aromaticity, indicated that the phosphole pyrmidal inversion barrier was 20 kcal/mol lower than for the saturated phenylphosphole, 1-phenylphosphole, and 1-benzyl-3,4-dimethylphosphole[9] (see Figure 6B).



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In 1976, Becker discovered the first stable phosphaalkenes. Since then much research has been done in the area of P=Cπ–bond chemistry. This led to the possibility that phosphaorganic chemistry in which sp^2 hybridized phosphorus could possibly mimic sp^2 hybridized carbon chemistry.[11] A theoretical study characterized the P=Cπ bond characteristics of phosphaethylene as two closely spaced highest occupied orbitals, the HOMO corresponding to the π-bond and the next orbital, corresponding to the lone pair is the HOMO-1. By substitution at either the phosphorus or the carbon, inversion of these levels can occur, e.g., $Me_3CP=C(SiMe_3)_2$. The π-bond appears to be almost apolar whereas the σ bond displays significant P^+--C^-polarity. The π(HOMO)-π^*(LUMO) separation is significantly lower than in ethylene. The P=C π-bond is much weaker than the C=C π-bond, ca. 45 versus 65 kcal/mol. The above data suggests that the P=C double bond will be more reactive than C=C double bond.[11]

Mathey, in discussing (1,5) sigmatropic shifts, found a significant overlap exists between the σ-orbital corresponding to the P-R exocyclic bond and the π-system. (1,5) sigmatropic shifts of the P-R substituents lead to 2H- and 3H-phospholes (see Figure 7).[11]

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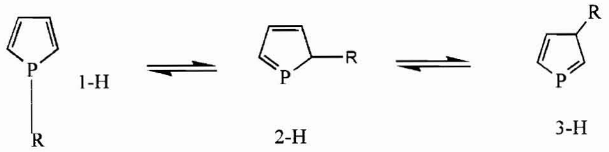


1-H

2-H

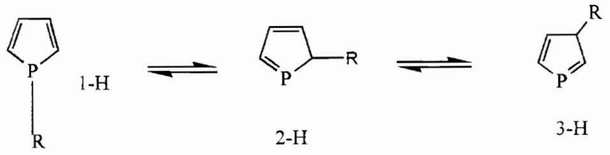
3-H

FIGURE 7: (1,5) SIGMATROPIC SHIFTS OF THE R SUBSTITUENTS

Mathey et al. found the following order of migrating ability for the R substituents: H > $SiMe_3$ > PR_2 > sp carbon > sp^2 carbon > sp^3 carbon.[11]

Substitution of a CH fragment by a P atom in phosphinine, C_5H_5P, constitutes a severe perturbation of the electronic structure which is caused by the changes in effective electronegativity (C versus P) and bond length (C-C versus C-P). The substitution yields a loss of π-orbital degeneracies and increased electron affinity of phosphinine, compared to benzene, as well as the presence of a dipole moment for the heteroarene.[12]

Heteroarenes are capable of forming sandwich complexes with transition metals, analogous to Cp_2Fe. Elschenbroich et al. have synthesized two of these such as *bis*(2,4,6-tri-tert-butyl-η^6-phosphinine) metal(M=Cr and V). The metals were converted to the gas phase by means of metal-atom ligand-vapor cocondensation (see Figure 8).[12]



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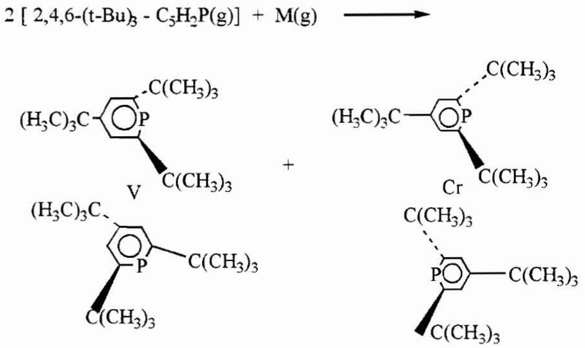
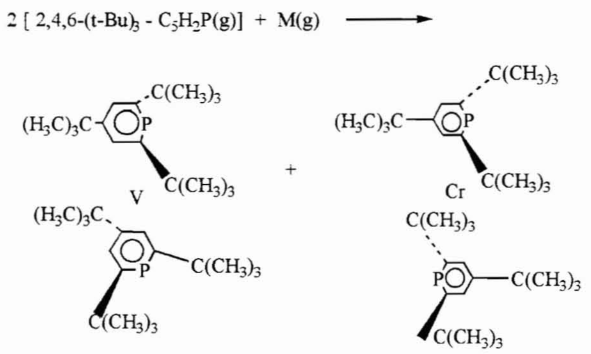


FIGURE 8: *bis*(2, 4, 6-TRI-TERT-BUTYL-η^6-PHOSPHININE) VANADIUM AND CHROMIUM

Scherer et al. demonstrated that cyclo-P_5 could be stabilized as a bridging ligand in the mixed-valent triple decker complex ((η^5-C_5Me_5)Cr(μ, η^5-P_5)Cr(η^5-C_5Me_5)). The cyclo-P_5^+ is a 6π electron donor. Scherer succeeded in synthesizing Pentamethylcyclopentadienylpentaphosphaferrocene by the following reaction: (see Figure 9).[13a]



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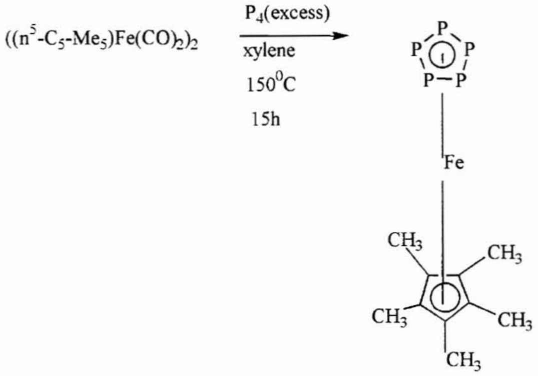

FIGURE 9: PENTAMETHYCYCLOPENTADIENYL-PENTAPHOSPHAFERROCENE

Cyclic voltammetry has been done to compare the potentials for the η^6-phosphinine complexes with those of their carbocyclic analogues. Reversible waves were observed for electron transfer to and from the $HOMO_{a1g}$ (mainly metal 3dz^2) only. For example, for one electron oxidation and reduction of the bis(arene)vanadium and oxidation of the bis(arene)chromium species, all other processes were irreversible. The incorporation of a P atom into the π-bonded arene results in anodic shifts of 260 mV for the chromium complex, which reflects the increased π-accepting nature of the phosphinine as compared to benzene. The central metal atom thus acquires a somewhat larger positive partial charge in the phosphinine complexes, and its oxidation potential increases.[12, 13b]

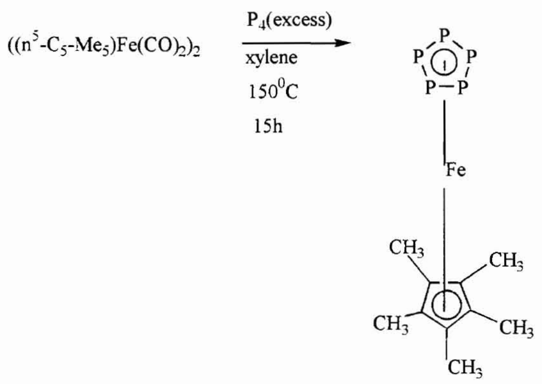

FIGURE 9: PENTAMETHYCYCLOPENTADIENYL-PENTAPHOSPHAFERROCENE

Cyclic voltammetry has been done to compare the potentials for the η^6-phosphinine complexes with those of their carbocyclic analogues. Reversible waves were observed for electron transfer to and from the HOMO$_{a_{1g}}$ (mainly metal 3dz^2) only. For example, for one electron oxidation and reduction of the bis(arene)vanadium and oxidation of the bis(arene)chromium species, all other processes were irreversible. The incorporation of a P atom into the π-bonded arene results in anodic shifts of 260 mV for the chromium complex, which reflects the increased π-accepting nature of the phosphinine as compared to benzene. The central metal atom thus acquires a somewhat larger positive partial charge in the phosphinine complexes, and its oxidation potential increases.[12, 13b]

CHAPTER II

2.0 EXPERIMENTAL

2.1 GENERAL

Melting points are uncorrected since the Mel Temp apparatus was not calibrated. All reactions were carried out under a positive pressure of argon or nitrogen using standard Schlenk tube techniques or a Vacuum Atmospheres Dri-lab glove box. All glassware was either flame dried under vacuum, or dried in an oven (12 hours, 118 °C), before each use. Filtrations were performed using positive pressure of argon to force solutions through a filtration cannula which was constructed by attaching teflon tubing to the Luer-Lok end of a glass observation tube. The other end of the observation tube was fitted with a piece of hardened filter paper (Whatman's No. 42) which was wired in place.[14] All reactions were carried out at room temperature unless otherwise noted. A magnetic stirbar was used to stir all reactions. Low temperature baths were maintained at -78 °C with dry ice and acetone. A J-KEM Scientific Model 210 Thermocouple was used to control the temperature in reactions which were heated.

2.2 SOLVENTS, REAGENTS, AND MATERIALS

Tetrahydrofuran (THF) and diethyl ether were distilled from sodium metal and benzophenone under argon. Acetone was predried over potassium permanganate and distilled under argon. Methylene chloride was distilled from P_2O_5. Acetonitrile was

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freshly distilled under nitrogen from calcium hydride. All solvents refluxed overnight prior to use. The following reagents were used as supplied: neutral alumina Brockman Activity I (Fisher, Certified), $Mn_2(CO)_{10}$ (Aldrich, 98%), tetrabutylammonium iodide (Aldrich, 99%), ammonium hexafluorophosphate (Aldrich, 95%), TFA anhydride (Aldrich, 99+%), HBF_4 (Fluka, 50% water solution), CH_2Cl_2 (Fisher, reagent grade), acetone (Fisher, reagent grade), diethyl ether (Fisher, reagent grade), THF (Fisher, reagent grade), potassium (Aldrich), Naphthalene (Fisher, laboratory formally purified grade), argon gas (Gas Technics, ultra high purity grade), nitrogen gas (Gas Technics, ultra high purity grade), petroleum ether (VWR, reagent grade), deuterated acetone (Aldrich, 99%+), deuterated benzene (Aldrich, 99%+), deuterated chloroform (Aldrich, 99%+), benzyl chloride (Baker, reagent grade), tributyltin hydride (Aldrich, 97%), bis(triphenylphosphoranylidene)ammonium chloride (Aldrich, 97%), pentane (Baker, reagent grade), benzene (Baker, reagent grade), $Mo(CO)_6$ (Pressure Chem. Co., technical grade), $Cr(CO)_6$ (Pressure Chem Co., technical grade), propionitrile (Aldrich, 99%), P_4 (Strem, yellow sticks), xylene (Fisher, reagent grade), $W(CO)_6$ (Aldrich, 99%), pyridine (Fisher, reagent grade), diphenylacetylene (Aldrich, 98%), lithium shot (Aldrich, 99%), phenyldichlorophosphine (Pfaltz and Bauer, 97%), m-xylene (Eastman, reagent grade), $Mn(CO)_5Br$ (Aldrich, 98%), $AlCl_3$ (Aldrich, 99.99%), heptane (Fisher, reagent grade), toluene (Fisher, reagent grade), HPF_6 (Aldrich, 60% wt. in solution with water).

Potassium naphthalide (KNAP) was prepared inside a glovebox by adding .1173g (0.0030 moles) freshly cut potassium metal added to a Schlenk tube containing 30 mL THF. Afterwards, .3845g (0.0030 moles) naphthalene was also added to the same freshly distilled under nitrogen from calcium hydride. All solvents refluxed overnight prior to use. The following reagents were used as supplied: neutral alumina Brockman Activity I (Fisher, Certified), $Mn_2(CO)_{10}$ (Aldrich, 98%), tetrabutylammonium iodide (Aldrich, 99%), ammonium hexafluorophosphate (Aldrich, 95%), TFA anhydride (Aldrich, 99+%), HBF_4 (Fluka, 50% water solution), CH_2Cl_2 (Fisher, reagent grade), acetone (Fisher, reagent grade), diethyl ether (Fisher, reagent grade), THF (Fisher, reagent grade), potassium (Aldrich), Naphthalene (Fisher, laboratory formally purified grade), argon gas (Gas Technics, ultra high purity grade), nitrogen gas (Gas Technics, ultra high purity grade), petroleum ether (VWR, reagent grade), deuterated acetone (Aldrich, 99%+), deuterated benzene (Aldrich, 99%+), deuterated chloroform (Aldrich, 99%+), benzyl chloride (Baker, reagent grade), tributyltin hydride (Aldrich, 97%), bis(triphenylphosphoranylidene)ammonium chloride (Aldrich, 97%), pentane (Baker, reagent grade), benzene (Baker, reagent grade), $Mo(CO)_6$ (Pressure Chem. Co., technical grade), $Cr(CO)_6$ (Pressure Chem Co., technical grade), propionitrile (Aldrich, 99%), P_4 (Strem, yellow sticks), xylene (Fisher, reagent grade), $W(CO)_6$ (Aldrich, 99%), pyridine (Fisher, reagent grade), diphenylacetylene (Aldrich, 98%), lithium shot (Aldrich, 99%), phenyldichlorophosphine (Pfaltz and Bauer, 97%), m-xylene (Eastman, reagent grade), $Mn(CO)_5Br$ (Aldrich, 98%), $AlCl_3$ (Aldrich, 99.99%), heptane (Fisher, reagent grade), toluene (Fisher, reagent grade), HPF_6 (Aldrich, 60% wt. in solution with water).

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Schlenk tube. A dark green color was observed immediately upon addition of the naphthalene to the potassium and THF mixture. The solution was stirred for 30 minutes and used immediately. (η^6-DBT)$Mn(CO)_3BF_4$, $Cr(CO)_3(C_2H_5CN)_3$, $Mo(CO)_3(C_2H_5CN)_3$, $W(CO)_3(C_5H_5N)_3$, $Mo(CO)_3(C_5H_5N)_3$, $[Mn(\eta^6\text{-}C_6H_4(CH_3)_2)(CO)_3]PF_6$, and pentaphenylphosphole were prepared by established literature methods.[3a, 15-18a] $TBAPF_6$ was prepared by metathesis from $(C_4H_9)_4NI$ with NH_4PF_6 in acetone.[18b]

2.3 PHYSICAL METHODS

NMR spectra (^1H, ^{13}C, and ^{31}P) were recorded with a Varian Gemini 2000, 400 MHz spectrometer, with d_6-acetone, d_6-benzene or $CDCl_3$ as the solvent. The ^1H and ^{13}C chemical shifts are reported in parts per million downfield from $(CH_3)_4Si$, while ^{31}P chemical shifts are reported in parts per million downfield from H_3PO_4 (-16.24 ppm), which was the external standard. NMR solvents were purchased from Aldrich and Cambridge Isotope Labs. The solvents were used without any further purification. Multiplicities are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; and c, complex multiplet. Fourier transform infrared spectra (FTIR) were recorded with a Perkin-Elmer 1600 FT-IR Spectrophotometer in solution with THF and *meta*-xylene as solvents using the designations: vs, very strong; s, strong; m, medium; w, weak. Cyclic voltammograms (CV's) were recorded and analyzed on a BAS 100 computer controlled electrochemical analyzer. Mass spectrometry was performed on a Finnigan GCQ GC-MS.

2.4 PREPARATION OF COMPOUNDS

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2.4 PREPARATION OF COMPOUNDS

COMPOUND I: η^4-dibenzothiophene manganese tricarbonyl

0.0051 g (0.0000124 mol) $(\eta^6\text{–DBT})Mn(CO)_3BF_4$, which had previously been dried, was added to a Schlenk tube equipped with a magnetic stirbar. The Schlenk tube was placed inside a -78 °C (acetone/dry ice bath) for an hour. The yellow powder was then placed under argon and 25 mL THF was added. The resulting solution was cooled for an hour at -78 °C. 2.75 mL (0.00055 mol) or 1.1 equivalent KNAP solution was added to this mixture. The solution changed color from light yellow to dark green immediately after the KNAP was added. After an hour stirring at -78 °C, the solution became a yellowish/brown color. The product was dried in vacuo at 0 °C for two hours, and then it was dried in vacuo overnight at room temperature. The yellowish-brown colored solid product was redissolved in 15 mL THF and filtered by cannulation. The filtrate was dried by cannulation of argon from an empty Schlenk tube. The crude product was washed with petroleum ether and pumped dry in vacuo overnight. A dark brown gel product remained. Purification attempts were made by using a column filled with neutral alumina and pentane as the eluent, under argon gas. The compound was dissolved into 5 mL THF before it was placed onto the column. Samples were collected in Schlenk tubes and dried in vacuo overnight. A white gelatinous substance was present. In attempting to dry the compound, the substance was dried in vacuo for two days. The substance still appeared gelatinous. Attempts were made to dry the compound by washing it with various solvents such as petroleum ether and methylene chloride. Afterwards, the compounds were dried in vacuo for 2 days. After two days, the material still had its white gelatinous appearance. Both the ^{13}C NMR and the ^1H NMR were of the crude products. ^1H NMR in d_6-acetone: δ

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COMPOUND II: η^5-benzothiophene, benzylcyclohexadienyl manganese tricarbonyl complex

0.0051 g (0.0000124 mol) (η^6–DBT)Mn(CO)$_3$BF$_4$, which had previously been dried, was added to a Schlenk tube equipped with a magnetic stirbar. The Schlenk tube was placed inside a -78 °C (acetone/dry ice bath) for an hour. The yellow powder was then placed under argon and 25 mL THF was added and the resulting solution was cooled at -78 °C for an hour. 5.50 mL (0.0011 mol) or 2.2 equivalent KNAP solution was added to this mixture. The solution changed color from light yellow to dark green immediately after the KNAP was added. After an hour stirring at -78 °C, the solution became a yellowish/brown color. 0.0575 mL (0.0005 mol) benzyl chloride was added by syringe. The solution immediately turned a brown color. The product was dried in vacuo at 0 °C for two hours, and then it was dried in vacuo overnight at room temperature. The brownish colored solid product was redissolved in 15 mL THF and filtered by cannulation. The filtrate was dried by cannulation of argon from an empty Schlenk tube. The crude product was washed with petroleum ether and pumped dry in vacuo overnight. A dark brownish/yellow solid product remained. Mp 40 °C. Both the ^{13}C NMR and the ^{1}H NMR were of the crude products. ^{1}H NMR in d$_6$-acetone: δ 1.287-1.327(c), δ 2.870-2.946(c), δ 4.565(s), 7.155-7.303(c), 7.440-7.550(c), 7.848-7.980(c). Decoupled ^{13}C NMR in d$_6$-acetone: δ 36.742, δ 67.760(d, J=25.2Hz), δ 125.715(d, J=18.4 Hz), δ 127.452, δ

1.157(d, J=2.0 Hz), δ 2.560(t, J=2.0, 2.4 Hz), δ 7.025-7.166(c). Decoupled ^{13}C NMR in d_6-acetone: δ 209.743, δ 149.807, δ 133.377, δ 127.521, δ 125.548, δ 67.518, δ 52.847(c). IR peaks in THF: 1811.5 and 1644.7 cm^{-1}.

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COMPOUND III: η^5-benzothiophene, tin tri-n-butylcyclohexadienyl manganese tricarbonyl complex

0.0051 g (0.0000124 mol) (η^6–DBT)Mn(CO)$_3$BF$_4$, which had previously been dried, was added to a Schlenk tube equipped with a magnetic stirbar. The Schlenk tube was placed inside a -78 °C (acetone/dry ice bath) for an hour. The yellow powder was then placed under argon and 25 mL THF was added and the resulting solution was cooled for an hour at -78 °C. 5.50 mL (0.0011 mol) or 2.2 equivalent KNAP solution was added to this mixture. The solution changed color from light yellow to dark green immediately after the KNAP was added. After an hour stirring at -78 °C, the solution became a yellowish/brown color. 0.1345 mL (0.0005 mol) tri-n-butyl tin hydride was added by syringe. The solution immediately turned a dark brown color. The product was dried in vacuo at 0 °C for two hours, and then it was dried in vacuo overnight at room temperature. A brownish colored solid product was present. The solid product was redissolved in 15 mL THF and filtered by cannulation. The filtrate was dried by cannulation of argon from an empty Schlenk tube. The product was washed with petroleum ether and pumped dry in vacuo overnight. An oily brownish semisolid product was formed. Purification attempts were made by using a column filled with neutral alumina and pentane as the eluent under argon gas. The compound was dissolved into 5 mL THF before it was placed onto the column. Samples were collected in Schlenk tubes and dried in vacuo overnight. A reddish brown oil was present. In attempting to dry the

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COMPOUND IV: η^4-dibenzothiophene managnese tricarbonyl bis(triphenylphosphoranylidene)ammonium cation

0.0051 g (0.0000124 mol) (η^6–DBT)Mn(CO)$_3$BF$_4$, which had previously been dried, was added to a Schlenk tube equipped with a magnetic stirbar. The Schlenk tube was placed inside a -78 °C (acetone/dry ice bath) for an hour. The yellow powder was then placed under argon and 25 mL THF was added and the resulting solution was cooled for an hour at -78 °C. 5.50 mL (0.0011 mol) or 2.2 equivalent KNAP solution was added to this mixture. The solution changed color from light yellow to dark green immediately after the KNAP was added. After an hour stirring at -78 °C, the solution became a yellowish/brown color. Afterwards, 0.2870 g (0.0005 mol) [bis(triphenylphosphoranylidene)ammonium chloride] or PPNCl was dissolved in 20 mL THF in a separate Schlenk tube. The mixture was stirred for a half hour. The PPNCl solution was then cannulated into the Schlenk tube containing the KNAP, and (η^6-DBT)Mn(CO)$_3$BF$_4$ mixture. After stirring for an hour at -78 °C, the product turned a compound, the substance was washed with various solvents such as petroleum ether and methylene chloride. The oily substance was dried in vacuo for two days. The purified substance still remained a reddish brown colored oil. Both the ^{13}C NMR and the ^{1}H NMR were of the crude products. ^{1}H NMR in d_6-acetone: δ 0.899(t, J=7.20, 7.20 Hz), δ 0.956-1.102(c, J=8.0, 8.4, 4.8, 8.0, 8.0, 12.8, 8.4 Hz), δ 1.290-1.382(c, J=8.4, 7.2, 7.2, 7.2, 6.8 Hz), δ 1.479-1.620(c, J=7.6, 7.6, 7.6, 7.2, 8.0, 7.2, 10.8 Hz), δ 7.484-7.509(c, J=3.6, 3.2, 3.2 Hz), δ 7.881-7.904(c, J=3.6, 2.4, 3.2 Hz). ^{13}C NMR in d_6-acetone: δ 10.449, δ 13.817, δ 28.093, δ 54.810, δ 69.587, δ 127.633, δ 129.621, δ 211.774.

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dark brown color. The product was dried in vacuo at 0 °C for two hours, and then it was dried in vacuo overnight at room temperature. A brownish colored solid product was present. The solid product was redissolved in 15 mL THF and filtered by cannulation. The filtrate was dried by cannulation of argon gas from an empty Schlenk tube. The product was washed with petroleum ether and dried in vacuo overnight. A solid waxy brownish-red colored substance formed. Purification attempts were made by using a column filled with neutral alumina and pentane as the eluent, under argon gas. The compound was dissolved into 5 mL THF before it was placed onto the column. Samples were collected in Schlenk tubes and pumped dry in vacuo overnight. Yellow crystals were present but were not thoroughly dried. The substance was washed with various solvents such as petroleum ether and methylene chloride and pumped dry in vacuo for two days. The wet yellow crystals remained. Both the ^{13}C NMR and the ^{1}H NMR were of the crude products. ^{1}H NMR in d_6-acetone: δ 1.174-1.215(c), δ 1.291(t, J=12.4, 21.0 Hz), δ 2.145(t, J=6.8, 6.0 Hz), δ 2.604(t, J=5.6, 6.4 Hz), δ 7.674-7.840(c), δ 7.90275(d of d, J=9.6, 2.8 Hz). Decoupled ^{13}C NMR in d_6-acetone: δ 127.5685(d, J=48.4 Hz), δ 127.796, δ 131.1265(d, J=42.8 Hz), δ 131.786-132.28(c), δ 132.378-132.666(c). IR peaks in THF: 1725(vs) and 1775(m) cm^{-1}.

COMPOUND V

0.0051 g (0.0000124 mol) (η^6–DBT)Mn(CO)$_3$BF$_4$, which had previously been dried, was added to a Schlenk tube equipped with a magnetic stirbar. The Schlenk tube was dark brown color. The product was dried in vacuo at 0 °C for two hours, and then it was dried in vacuo overnight at room temperature. A brownish colored solid product was present. The solid product was redissolved in 15 mL THF and filtered by cannulation. The filtrate was dried by cannulation of argon gas from an empty Schlenk tube. The product was washed with petroleum ether and dried in vacuo overnight. A solid waxy brownish-red colored substance formed. Purification attempts were made by using a column filled with neutral alumina and pentane as the eluent, under argon gas. The compound was dissolved into 5 mL THF before it was placed onto the column. Samples were collected in Schlenk tubes and pumped dry in vacuo overnight. Yellow crystals were present but were not thoroughly dried. The substance was washed with various solvents such as petroleum ether and methylene chloride and pumped dry in vacuo for two days. The wet yellow crystals remained. Both the ^{13}C NMR and the ^{1}H NMR were of the crude products. ^{1}H NMR in d_6-acetone: δ 1.174-1.215(c), δ 1.291(t, J=12.4, 21.0 Hz), δ 2.145(t, J=6.8, 6.0 Hz), δ 2.604(t, J=5.6, 6.4 Hz), δ 7.674-7.840(c), δ 7.90275(d of d, J=9.6, 2.8 Hz). Decoupled ^{13}C NMR in d_6-acetone: δ 127.5685(d, J=48.4 Hz), δ 127.796, δ 131.1265(d, J=42.8 Hz), δ 131.786-132.28(c), δ 132.378-132.666(c). IR peaks in THF: 1725(vs) and 1775(m) cm^{-1}.

COMPOUND V

0.0051 g (0.0000124 mol) (η^6–DBT)Mn(CO)$_3$BF$_4$, which had previously been dried, was added to a Schlenk tube equipped with a magnetic stirbar. The Schlenk tube was

placed inside a -78 °C (acetone/dry ice bath) for an hour. The yellow powder was then placed under argon and 25 mL THF was added and the resulting solution was at hour -78 °C. 5.50 mL (0.0011 mol) or 2.2 equivalent KNAP solution was added to this mixture. The solution changed color from light yellow to dark green immediately after the KNAP was added. After an hour stirring at -78 °C, the solution became a yellowish/brown color. The product was dried in vacuo at 0 °C for two hours, and then it was dried in vacuo overnight at room temperature and stored in the refrigerator for two days. Under argon, 15 mL THF was added to the brownish colored solid product. Afterwards, 0.0090g (0.0004995 mol) deionized H_2O was placed inside 5 mL THF and the mixture was cannulated into the Schlenk tube containing the KNAP, and η^6-DBTMn(CO)$_3$BF$_4$ mixture. After stirring for an hour at -78 °C, the product turned a dark reddish brown color. It was then dried in vacuo inside a 0 °C bath for two hours and then at room temperature overnight. A brownish colored product was present. The brownish colored solid product was redissolved in 15 mL THF and filtered by cannulation. The filtrate was dried by cannulation of argon from an empty Schlenk tube. A reddish brown solid product was present. Mp 66 °C. ^{1}H NMR in d_6-acetone: δ 1.1525(q, J=1.6, 2.0, 1.6 Hz), δ 1.279(s), δ 1.8935(q, J=2.4, 2.0, 2.0 Hz), δ 1.978-1.994(c, J= 2.4, 2.0, 2.4, 2.0 Hz), δ 2.5605(q, J=2.0, 2.0, 2.4 Hz), δ 3.749(s), δ 7.481-7.517(c, J=2.8, 2.0, 1.2, 3.2, 2.0, 1.2, 2.0 Hz), δ 7.879-7.914(c, J=2.8, 2.0, 1.2, 2.8, 2.0, 1.2, 2.0 Hz). ^{13}C NMR in d_6-acetone: δ 54.857, δ 127.453, δ 129.531, δ 135.387, δ 211.729.

COMPOUND VI

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COMPOUND VI

Inside a glovebag filled with argon gas, 1.25 g (0.0036 mol) $Mo(CO)_3(C_2H_5CN)_3$ was placed inside a 250 mL three-necked flask with 2.31 g (0.0186 mol) P_4 and 102 mL xylene. The reaction was stirred at reflux (139 °C) for 15 hours. Afterwards, a cannula was used to transfer the xylene solution into a Schlenk tube and the remaining black solid material was placed inside a separate Schlenk tube and stored in the refrigerator. To the Schlenk tube containing the xylene solution, 240 mL dichloromethane was added by syringe. Two layers were immediately observed upon addition of the dichloromethane. The mixture was shaken for about 30 seconds. The mixture of solvents was pumped off overnight in vacuo and a white solid was present. The white solid was placed under argon gas which caused an immediate reaction with the white solid material. The solid released a whitish colored gas and changed color from white to a yellowish/orange color. Afterwards, 3x 50mL portions of pentane were added to the solid while it was cooling inside a -78 °C bath and a whitish colored gas was given off each time the pentane solution was cannulated into a separate Schlenk tube. Afterwards, the Schlenk tube containing the pentane solution was pumped off in vacuo overnight. A dark yellowish/white colored solid material was present. The product was again placed under argon which caused an immediate reaction. The solid changed color from a dark yellowish/white color to a light yellowish/white color and a gas was given off. The product was stored inside a refrigerator for about three months. White crystals formed inside the flask above the yellowish/white solid material. In attempting to do solubility tests on the solid material, a small amount was placed inside THF and a very strong reaction occurred which resulted in the solid material changing color from a yellow/white

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COMPOUND VII

Inside a glovebag filled with argon gas, 3.0829 g (0.0102 mol) $Cr(CO)_3(C_2H_5CN)_3$ was placed inside a 250 mL three-necked flask with 1.90 g (0.0153 mol) P_4 and 80 mL xylene. The reaction was stirred at reflux (139 °C) for 15 hours. Afterwards, a cannula was used to transfer the xylene solution into a separate Schlenk tube and the remaining black solid material was placed inside a separate Schlenk tube and stored in the refrigerator. To the Schlenk tube containing the xylene solution, 240 mL dichloromethane was added by syringe. Two layers were immediately observed upon addition of the dichloromethane. The mixture was shaken for about 30 seconds. The mixture of solvents was pumped off overnight in vacuo and a white solid was present. The white solid was placed under argon gas which caused an immediate reaction with the solid material. The solid released a whitish colored gas and changed color from white to a dark orange. Afterwards, 3x 50 mL portions of pentane were added to the solid while it was cooling inside a -78 °C bath and a whitish colored gas was given off each time the pentane solution was cannulated into a separate Schlenk tube. Afterwards, the Schlenk tube containing the pentane color to a dark orange color, accompanied by gas evolution. The product was determined to be pyrophoric when exposed to air. Both the ^{1}H NMR and the ^{13}C NMR were of the crude products. ^{1}H NMR in d_6-benzene: δ 0.267-0.299(c, J=6.8, 0.4, 0.8, 0.8 Hz), δ 0.887-0.958(c, J=28.9 Hz), δ 1.321-1.398(c, J=6.8, 8.0, 16.0 Hz). ^{13}C NMR in d_6-chloroform: δ 29.766, δ 30.934, δ 95.558, δ 206.828. ^{31}P NMR in deuterated chloroform: δ 64.082.

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COMPOUND VIII: η^5-pentaphenylphosphole tungsten tricarbonyl

Inside a 100 mL three-necked flask under argon, .2049 g (0.0004055 mol) $W(CO)_3(C_5H_5N)_3$ was placed along with .2773 g (0.0005976 mol) pentaphenylphosphole, and 60 mL m-xylene. The reaction was allowed to reflux at 96 °C for 9.5 hours. The solution changed from a light orange color to a dark brownish/yellow color. The product was dried in vacuo overnight. A greenish/brown colored solid was present. Both the ^{1}H NMR and the ^{13}C NMR were of the crude products. ^{1}H NMR in d_6-acetone: δ 6.927-6.956(c, J=2.4, 7.6, 1.6 Hz), δ 7.036-7.194(c, J=6.4, 8.4, 17.2, 22.4, 2.8, 6.0 Hz), δ 7.955-8.080(c). ^{13}C NMR in d_6-acetone: δ 69.692, δ 129.847, δ 131.880, δ 265.358. ^{31}P NMR in d-chloroform: δ 37.044. Mass spectrometry peaks: M/Z=732, (M/Z-CO) =704, [M/Z-2(CO)=676, [M/Z-(3CO) =648, $PC_4(C_6H_5)_5$=464, $-C_6H_5$=387, and -P=356. IR peaks m-xylene: 2075(m), 1975(m), 1946(vs) cm^{-1}.

solution was pumped off in vacuo overnight. A dark orange colored solid material was present. The product was again placed under argon which caused an immediate reaction. The solid remained a dark orange color as a gas was given off. The product was stored inside a refrigerator for about three months. White crystals formed inside the flask above the orange solid material. The product was determined to be pyrophoric when exposed to air. Both the ^{1}H NMR and the ^{13}C NMR were of the crude products. ^{1}H NMR in d$_6$-benzene: δ 0.285-0.302(c, J=2.0, 0.80, 0.80, 0.80, 0.80, 1.6 Hz), δ 0.550-0.580(c, J=7.6, 4.4 Hz), δ 0.895(s), δ 1.340-1.381(c, J=6.4, 10.0 Hz). ^{13}C NMR in d$_6$-chloroform: δ 1.069, δ 29.781, δ 30.972. ^{31}P NMR in d$_6$-benzene: δ 277.659.

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COMPOUND IX:

Inside a 100 mL three-necked flask under argon, 15 mL (0.1062 mol) (TFA) trifluoroacetic anhydride was cooled to 0 °C for 10 minutes and 2.0950 g (0.0114 mol) dibenzothiophene was added with stirring. 0.3589 g (.0016 mol) $Cr(CO)_6$ was added. The solution developed a gray color. Finally, 4 mL (8 M, 50% solution) HBF_4 was added. After 1 minute, the gray colored solution underwent an exothermic reaction, refluxing briefly despite the ice bath. After this occurred, the mixture was allowed to warm to room temperature and was refluxed at 75 °C for 5 hours. The reaction mixture turned a green color. The mixture was cooled and the solvent removed in vacuo. The greenish/yellow colored residue was then dissolved in 15 mL of 1:1 acetone/CH_2Cl_2, and the product was precipitated by cannulating ether into the vessel. The remaining solvent was cannulated out and discarded, and a beige colored precipitate was collected. The precipitate was redissolved in 15 mL acetone and the mixture was filtered through a medium fritted filter funnel. It was precipitated using diethyl ether. The remaining solvent was cannulated into a separate Schlenk tube and discarded while the beige product was pumped dry in vacuo and stored inside a Schlenk tube in the glovebox. Mp 85 °C. Both the ^{1}H NMR and the ^{13}C NMR were of the crude products. ^{1}H NMR in d$_6$-acetone: δ 0.928(s), δ 1.103(t, J=6.8, 7.2 Hz), δ 1.216(s), δ 1.2515(d, J=10.0), δ 1.849(s), δ 2.071-2.102(c, J=5.6, 1.6, 5.2 Hz), δ 2.631(s), δ 3.4035(q, J=7.20, 6.80, 7.20 Hz), δ 6.130(s), δ 7.476-7.535(c, J=2.4, 1.6, 3.2, 2.4, 1.6, 1.2, 2.0, 2.0, 2.8, 2.0, 2.4 Hz), δ 7.935-7.981(c, J=2.4, 3.6, 1.6,

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COMPOUND X:

Inside a 100 mL-three necked flask under argon, 0.2070 g (0.0004421 mol) $[Mn(\eta^6\text{-}C_6H_4(CH_3)_2(CO)_3]PF_6$, 0.3885 g (0.0008372 mol) pentaphenylphosphole, and 80 mL THF was added. The reaction was refluxed for two days using a variac and heating mantle set at 50 volts. The reaction was pumped dry in vacuo overnight. A bright yellow solid product was present. Both the ^1H NMR and the ^{13}C NMR were of the crude products. ^1H NMR in d_6-acetone: δ .197(d, J=5.6 Hz), δ .8035(q, J=49.6, 50.8, 29.6 Hz), δ 1.281(t, J=112.4, 47.6 Hz), δ 6.819-7.160(c, J=45.6, 8.0, 60.4, 6.8, 30.8, 33.2 Hz), δ 7.406-7.590(c, J=35.2 Hz). ^{31}P NMR in $CDCl_3$: δ 189.103.

COMPOUND XI and XII:

Inside a 100 mL three-necked flask under argon, 15 mL (0.1062 mol) (TFA) trifluoroacetic anhydride was cooled to 0 °C for 10 minutes. 2.0913 g (0.01135 mol) dibenzothiophene was added with stirring. 0.3763 g, (0.0009018 mol) $Mo(CO)_3(C_5H_5N)_3$ was added. The solution developed an orangish/brown color. Finally, 4 mL, (8 M, 50% solution) HBF_4 was added. After 1 minute, the orangish/brown colored solution underwent exothermic reaction, refluxing briefly despite the ice bath. After this occurred, the mixture was allowed to warm to room temperature and was refluxed at 74 °C for 5 hours. The reaction mixture turned a dark brownish/green color. The mixture was cooled

3.2, 0.8, 3.2, 3.6 Hz), δ 8.287-8.333(c, J=4.0, 3.2, 1.2, 2.4, 2.4, 2.8, 2.4 Hz). ^{13}C NMR in d_6-acetone: δ 121.812, δ 122.851, δ 124.672, δ 127.016, δ 135.603, δ 139.275.

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and the solvent removed in vacuo. The brown residue was then dissolved in 15 mL of 1:1 acetone/CH_2Cl_2, and the product was precipitated by cannulating ether into the vessel. The additional solvent was cannulated out and discarded, and the remaining beige colored precipitate was collected and redissolved in 15 mL acetone. The mixture was filtered through a medium fritted filter funnel and was precipitated using ether. The remaining solvent was cannulated into a separate Schlenk tube and discarded while the beigish colored product was dried in vacuo and stored in the glovebox. The crude product was dissolved in 5 mL benzene and placed on a neutral alumina column where the eluent used was benzene. Three bands present were collected off the column. They were blue, yellow, and brown. The product fractions were pumped dry in vacuo and stored in flasks under argon. The bands were analyzed by ^{1}H NMR and the brown and blue bands were suspected to be a newly synthesized products. ^{1}H NMR from the brown band compound XI in d_6-acetone: δ -0.157(s), δ 0.120-0.139(c), δ 0.683(s), δ 0.860-0.892(c), δ 0.121-0.1239(c), δ 1.457(s), δ 1.80-1.880(c), δ 2.402(s), δ 2.682(s), δ 6.080-6.120(c), δ 6.124-6.60(c), δ 7.355(c), δ 7.708(s), δ 8.042-8.078(c), δ 8.31-8.356(c), δ 8.52-8.57(c), δ 8.815(s), δ 8.882(t, J=7.6, 7.6 Hz), δ 9.1535(d, J=5.2 Hz). ^{1}H NMR from the blue band compound XII in d_6-acetone: δ -0.158-0.150(c), δ 0.08-0.146(c), δ 0.860-0.915(c), δ 0.124-0.141(c), δ 1.640(c), δ 2.32-2.35(c), δ 2.828(s), δ 3.9825(d, J=6.0 Hz), δ 7.357(t, J=1.2, 0.80 Hz).

CYCLIC VOLTAMMETRY OF (η^6-DBT)$Mn(CO)_3BF_4$

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Cyclic voltammetry was done inside the glovebox at room temperature. A three electrode cell was used with a silver/silver nitrate ($Ag/AgNO_3$) reference electrode, a platinum wire auxiliary electrode, and either a glassy carbon disk (GC), platinum disk (Pt), or gold disk (Au) working electrode. The working electrodes were polished with alumina and cleaned with ethanol.

The substrate (η^6-DBT)$Mn(CO)_3BF_4$ was made along with the $TBAPF_6$ the supporting electrolyte by established literature procedures.[3a, 18b] An (0.1 M) $TBAPF_6$/ acetonitrile solution was made and placed in a vial. Using a glassy carbon electrode, potential scans were run at a scan rate 200 mV/sec to get a background of the solution. Afterwards, (0.001 M) (η^6-DBT)$Mn(CO)_3BF_4$ was added to the vial. Using the glassy carbon electrode the solution was scanned at 200 mV/s. Ferrocene served as an internal standard. The potential for reduction of (η^6-DBT)$Mn(CO)_3BF_4$ is reported versus ferrocene/ferrocenium. The E^0=.124V, ΔE=80mV for ferrocene. For (η^6-DBT)$Mn(CO)_3BF_4$, -2.104 V=E_{pc}.

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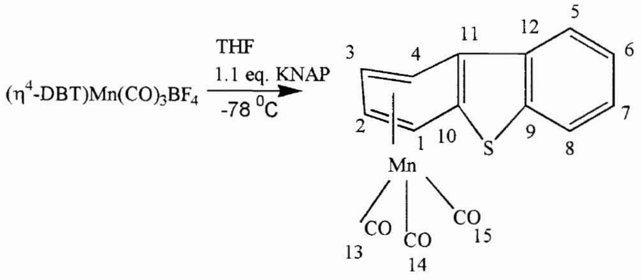
CHAPTER THREE

3.0 RESULTS and DISCUSSION

The reaction shown below outlines the synthesis of compound (I).



SCHEME 1: SYNTHESIS OF COMPOUND I

Addition of 1.1 equivalent of KNAP to (η^6-DBT)Mn$(CO)_3BF_4$ (which contains 18 electrons), results in the DBT ligand flipping from η^6 to η^4 coordination mode. We believe the product formed is a 17 electron species. Therefore, we are proposing compound I as a possible structure which adopts an η^4 bonding mode for the dibenzothiophene ring.[19a] Based on previously reported NMR data the Mn$(CO)_3$ moiety is not bonding with the naphthalene in the reduced products.[19b]

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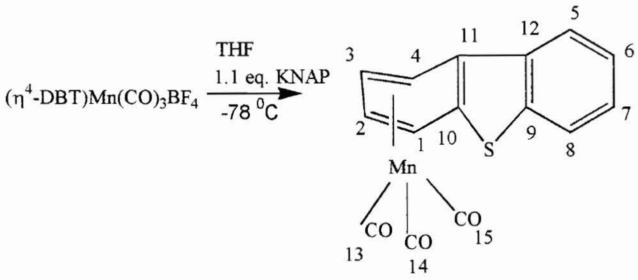

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Table 1

^{1}H NMR of Compound I

HYDROGEN NUMBER	δ	(m, J)
5-8	7.166-7.025	(c)
2, 3	2.560	(t, 2.0, 2.4 Hz)
1, 4	1.157	(d, 2.0 Hz)

Table 2

^{13}C NMR of Compound I

CARBON NUMBER	δ	(m, J)
13-15	209.735	(s)
11,12	149.807	(s)
9,10	133.38	(s)
5-8	125.55, 127.52	(s)
2,3	67.518	(s)
1,4	52.847	(c)

Tables 1 and 2, ^{1}H and ^{13}C NMR, are values obtained from the analysis of the unpurified crude product. Due to the wet state of the purified product and equipment problems, analysis was not done on the compound after attempts were made to purify the

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In Table 2, the carbons appearing at positions 13-15 at δ 209.735 form a singlet which is expected from the carbon bonding to the oxygen. Due to the strong electronegativity of oxygen, it is expected that this peak will have a strong downfield shift. The carbons at positions 5-8 show characteristics of the uncomplexed aromatic carbons containing a C=C appearing at δ 125.55 and δ 127.52 along with carbons 11-12 at 149.8, and carbons 9 and 10 at δ 133.38 which also may be shifted downfield due to the effects of the sulphur. Carbons 1 and 4 appear at δ 52.847 as a complex multiplet and carbons 2 and 3 appear at δ 67.518 as a singlet.[19c] These carbon peak assignments are characteristic of η^4 bonding.[20] In order to increase the signal-to-noise ratio, it became necessary to increase the time delay between pulses for the ^{13}C NMR experiment to 10.0 seconds per pulse.

In Table 1, one of the impurities which may be present is naphthalene whose peaks appear in the regions δ 7.489-7.520, and δ 7.885-7.917 as complex multiplets. Another suspected impurity is THF whose peaks appear at δ 2.0 and δ 3.685 as complex multiplets. The δ 2.0 peak may be covered by d_6-acetone.

In Table 2, the impurity THF whose peaks normally occur around δ 67 and δ 25 do not appear to be present in the carbon spectra of Compound I. The naphthalene peaks would material. In Table 1, the hydrogens appearing in compound 1 at positions 5-8 forming a complex multiplet in the region δ 7.166-7.026 are characteristic of an uncomplexed aromatic ring. The hydrogens appearing at positions 2 and 3 form a triplet at δ 2.560. The J constants are 2.0, and 2.4 Hz. The hydrogens appearing at positions 1 and 4 form a doublet at δ 1.157 with a J constant of 2.0 Hz.[19c] These proton shifts are characteristic for η^4 bonding.[20]

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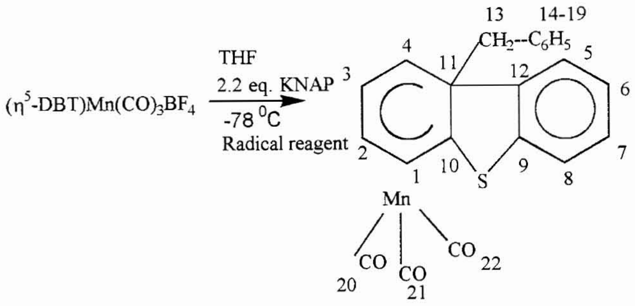
The reaction shown below outlines the synthesis of compound II:



SCHEME 2: SYNTHESIS OF COMPOUND II

Addition of 2.2 equivalents of KNAP to (η^6-DBT)Mn(CO)$_3$BF$_4$, (which contains 18 electrons), followed by electrophillic addition, results in the dibenzothiophene flipping from η^6 to η^5 coordination mode. We believe the product formed is an 18 electron species. The cyclohexadienyl ring contains is a six electron donor with an overall -1 charge. Each CO is a two electron donor. The manganese has an overall charge of +1 and is a six electron donor. We are proposing compound II as a possible structure which adopts an η^5 bonding mode for the dibenzothiophene ring.

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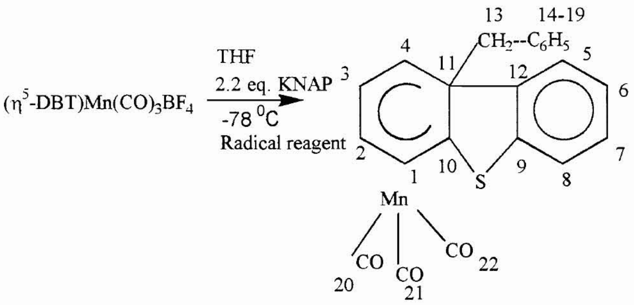

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Table 3

^{1}H NMR of Compound II

HYDROGEN NUMBER	δ	(m, J)
14-19	7.226	(c)
5,8 or 6,7	7.898, 7.502	(c)
1,4	1.287	(c)
2,3	4.565	(s)
13	2.907	(c)

Table 4

^{13}C NMR of Compound II

CARBON NUMBER	δ	(m, J)
20-22	209.863	(s)
14-19	125.715	(d, J=18.4 Hz)
13	36.742	(s)
11, 12	141.865	(s)
9, 10	133.612	(s)
5-8	127.452, 127.725,	(s)
	128.150, 128.347	(s)
1, 4	67.760	(d, J=25.2 Hz)
2, 3	not observable	

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Tables 3 and 4, ^{1}H and ^{13}C NMR, are values obtained from the analysis of crude product of compound II. In Table 3, the hydrogens appearing in compound II at positions 14-19 forming a complex multiplet in the region δ 7.226 have been assigned to the phenyl group which are characteristic for an aromatic ring. The hydrogens at positions 5-8 have been assigned to the two complex multiplets at δ 7.898, and δ 7.502 which exhibit aromatic character. The hydrogens at positions 1,4 were assigned to the CH stretches attached to C=C at δ 1.287. A complex multiplet is expected in this region due to the coupling of the CH's in the aromatic ring. The hydrogens at positions 2, 3 were assigned to the region at δ 4.565 forming a singlet, and the hydrogens at position 13 were assigned to the region δ 2.907 forming a complex multiplet due to coupling with the aromatic ring. These proton shifts are characteristic of η^5 coordination mode.[20]

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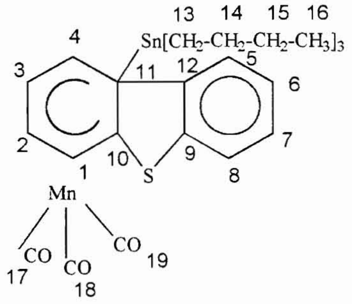
The impurities which may be present are THF and naphthalene. In the ^1H NMR, THF has peaks at δ 1.8 and δ 3.7. Naphthalene has peaks at δ 7.4-7.5 and δ 7.8 which are both complex multiplets. In the ^{13}C NMR, these impurities may appear at δ 67 and δ 25 for THF and δ 133, δ 127, and δ 125 which may be hidden due to overlapping carbon peaks.

The picture shown below represents a proposed structure for compound III:



SCHEME 3: STRUCTURE OF COMPOUND III

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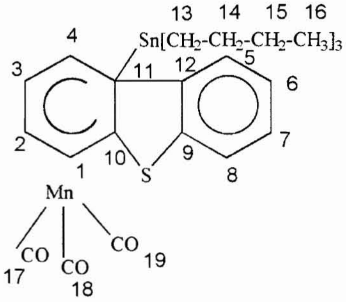

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Table 5

^{1}H NMR of Compound III

HYDROGEN NUMBER	δ	(m, J)
16	0.899	(t, J=7.20, 7.20 Hz)
15	1.290-1.382	(c)
14	1.479-1.620	(c)
13	0.956-1.102	(c)
6, 7	7.881-7.904	(c)
5, 8	7.484-7.509	(c)
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Table 6

^{13}C NMR for Compound III

CARBON NUMBER	δ
17-19	211.774
16	10.449
15	28.093
14	28.093
13	13.817
9-12	not observable
5-8	127.633, 129.621
2, 3	69.587
1, 4	54.810

Addition of 2.2 equivalents of KNAP to (η^6-DBT)Mn(CO)$_3$BF$_4$, (which contains 18 electrons), followed by electrophillic addition, results in the dibenzothiophene flipping from η^6 to η^5 coordination mode. We believe the product formed is an 18 electron species. Therefore, we are proposing this structure for compound III as a possible structure which adopts an η^5 bonding mode for the dibenzothiophene ring.

In Tables 5 and 6, the ^{1}H and ^{13}C NMR spectra were of the crude product. Attempts were made to purify the substance. Due to the wet purified substance and equipment problems, the purified substance was unable to be analyzed. In Table 5, the hydrogens appearing at position 16 were assigned to the region of δ 0.899 as a triplet(J=7.20, 7.20

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In Table 6, the carbons appearing at positions 17-19 in the region δ 211.774 were identified as the CO peaks. This downfield shift was expected due to the large electronegativity of oxygen. Carbons 9-12 were not observable at 1024 transients.[20] Carbons 5-8 appear in the aromatic regions δ 127.633, and δ 129.621 as expected. Carbons 2 and 3 appear in the region δ 69.587 while carbons 1 and 4 appear in the region δ 54.810. Carbons 16-13 appear as expected in the alkyl regions of the spectra and are assigned to the $(CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3)$ chain bonded to Sn.

The impurities which may be present are THF and naphthalene. In the ^1H NMR, THF has peaks at δ 1.8 and δ 3.7. It is possible that around δ 1.8 the THF peak is present; however, there is a very tiny peak which may indicate a trace of its presence. Naphthalene has peaks at δ 7.4-7.5 and δ 7.8 which are both complex multiplets and may be combined

Hz) which is the (CH$_3$)$_3$ portion of the structure. The hydrogens at position 15 appear in the region of δ 1.290-1.382 as a complex multiplet while the hydrogens at position 14 appear in the region δ 1.479-1.620 also as a complex multiplet. The hydrogens at position 13 appear in the region δ 0.956-1.102 as a complex multiplet while the hydrogens at positions 6 and 7 appear in the expected aromatic region δ 7.881-7.904 as a complex multiplet. The hydrogens at positions 5 and 8 appear in the expected aromatic region δ 7.484-7.509 while the hydrogens at positions 2 and 3 appear in the region δ 2.05 which overlaps with the solvent peak acetone. These hydrogens easily observed in CDCl$_3$ in the region δ 2.18 as a singlet. The hydrogen at positions 1 and 4 appear in the region δ 0.9 as an overlapping triplet(J=7.20, 7.20 Hz.) These hydrogen are easily identified using the solvent CDCl$_3$, and they appear in the region δ 0.986 as a complex multiplet.

In Table 6, the carbons appearing at positions 17-19 in the region δ 211.774 were identified as the CO peaks. This downfield shift was expected due to the large electronegativity of oxygen. Carbons 9-12 were not observable at 1024 transients.[20] Carbons 5-8 appear in the aromatic regions δ 127.633, and δ 129.621 as expected. Carbons 2 and 3 appear in the region δ 69.587 while carbons 1 and 4 appear in the region δ 54.810. Carbons 16-13 appear as expected in the alkyl regions of the spectra and are assigned to the (CH$_2$-CH$_2$-CH$_2$-CH$_3$) chain bonded to Sn.

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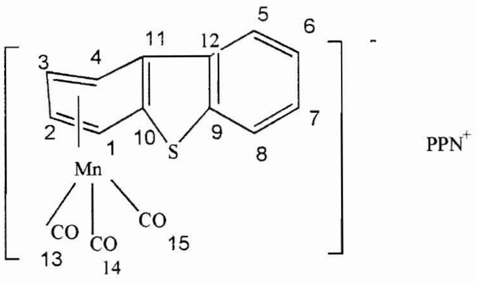
with the assigned peaks of the structure. In the ^{13}C NMR, these impurities may appear at δ 67 and δ 25 for THF which may be combined with the d$_6$-acetone. and δ 133, δ 127, and δ 125 which may be hidden due to overlapping carbon peaks or they may not be present at all.

The picture shown below represents a proposed structure for compound IV:



SCHEME 4: STRUCTURE OF COMPOUND IV

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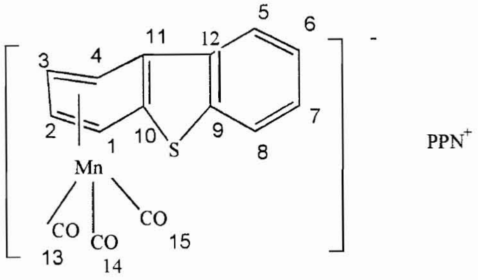

SCHEME 4: STRUCTURE OF COMPOUND IV

Table 7

^{1}H NMR of Compound IV

HYDROGEN NUMBER	δ	(m, J)
6, 7	7.90275	(d of d, J=9.6, 2.8 Hz)
5, 8	7.674-7.840	(c)
4	1.291	(t, J=12.4, 21.0 Hz)
3	2.604	(t, J=5.6, 6.4 Hz)
2	2.145	(t, J=6.8, 6.0 Hz)
1	1.174-1.215	(c)

In Table 7, the ^{1}H NMR spectra analysis was of the crude product. Purification was attempted and resulted in wet yellow crystals which were unable to be analyzed due to equipment problems and difficulty in drying the product. Addition of 2.2 equivalents of KNAP to (η^6-DBT)Mn(CO)$_3$BF$_4$, (which contains 18 electrons), results in the dibenzothiophene flipping from η^6 to η^4 coordination mode. We believe the product formed is an 18 electron species. Therefore, we are proposing this structure for compound IV as a possible structure which adopts an η^4 bonding mode for the dibenzothiophene ring.

In Table 7, the hydrogens 5-8 appearing in regions δ 7.90275(d of d, J=9.6, 2.8 Hz) and δ 7.674-7.840(c) are characteristic for aromatic rings.[20] Also appearing in the

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^{1}H NMR of Compound IV

HYDROGEN NUMBER	δ	(m, J)
6, 7	7.90275	(d of d, J=9.6, 2.8 Hz)
5, 8	7.674-7.840	(c)
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In Table 7, the hydrogens 5-8 appearing in regions δ 7.90275(d of d, J=9.6, 2.8 Hz) and δ 7.674-7.840(c) are characteristic for aromatic rings.[20] Also appearing in the aromatic region are carbon peaks which appear in the following regions: δ 132.378-132.666(c), δ 131.786-132.28 (c), δ 131.1265(d, J=42.8 Hz), δ 127.796, δ 127.5685(d, J=48.4 Hz).[20] The IR peaks for compound IV appeared 1725(vs) and 1775(m) cm^{-1}. These peaks represent the CO which are present at positions 13-15. Since the window of THF doesn't show aromatic peaks, our reaction was regulated by the shift of the CO stretches.[21] As the compound is reduced by 2.2 equivalents KNAP, this causes an expected shift of the CO peaks to lower wave numbers. In (η^6-DBT)-Mn(CO)$_3$BF$_4$, the IR peaks are present at 2077(s) and 2025(s, br) cm^{-1} compared to our product which has its peaks at 1725(vs), 1775 (m) cm^{-1}.[3a] This shift is a definite indicator that a reaction had occurred.[21]

An impurity which may be present is naphthalene whose peaks appear in the ^{1}H NMR at δ 7.4-7.5 and δ 7.8 and in the ^{13}C NMR at δ 133.39, δ 127.79, and δ 125.72. These peaks may be buried in with the product peaks in these regions.

For the reaction :

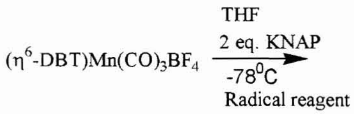
$$(\eta^6\text{-DBT})\mathrm{Mn(CO)_3BF_4} \xrightarrow[\text{-78}^0\text{C} \\ \text{Radical reagent}]{\text{THF} \\ \text{2 eq. KNAP}} \text{DECOMPOSITION}$$

SCHEME 5: ADDITION OF 1 EQUIVALENT H$_2$O AFTER 2 DAYS TO COMPOUND V

using deionized H$_2$O as the radical reducing agent. It is suspected that the 2 day lapse between the addition of 2.2 equivalents KNAP and then deionized H$_2$O resulted in decomposition. The ^{1}H and ^{13}C NMR spectra reported on the decomposition product. The starting material naphthalene seems to exist when comparing the ^{13}C NMR of the aromatic region are carbon peaks which appear in the following regions: δ 132.378-132.666(c), δ 131.786-132.28 (c), δ 131.1265(d, J=42.8 Hz), δ 127.796, δ 127.5685(d, J=48.4 Hz).[20] The IR peaks for compound IV appeared 1725(vs) and 1775(m) cm^{-1}. These peaks represent the CO which are present at positions 13-15. Since the window of THF doesn't show aromatic peaks, our reaction was regulated by the shift of the CO stretches.[21] As the compound is reduced by 2.2 equivalents KNAP, this causes an expected shift of the CO peaks to lower wave numbers. In (η^6-DBT)-$Mn(CO)_3BF_4$, the IR peaks are present at 2077(s) and 2025(s, br) cm^{-1} compared to our product which has its peaks at 1725(vs), 1775 (m) cm^{-1}.[3a] This shift is a definite indicator that a reaction had occurred.[21]

An impurity which may be present is naphthalene whose peaks appear in the ^1H NMR at δ 7.4-7.5 and δ 7.8 and in the ^{13}C NMR at δ 133.39, δ 127.79, and δ 125.72. These peaks may be buried in with the product peaks in these regions.

For the reaction :

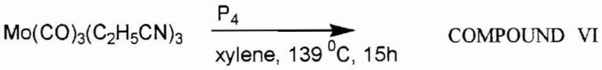


$$(\eta^6\text{-DBT})Mn(CO)_3BF_4 \xrightarrow[\substack{-78^0C \\ \text{Radical reagent}}]{\substack{\text{THF} \\ \text{2 eq. KNAP}}} \text{DECOMPOSITION}$$

SCHEME 5: ADDITION OF 1 EQUIVALENT H_2O AFTER 2 DAYS TO COMPOUND V

using deionized H_2O as the radical reducing agent. It is suspected that the 2 day lapse between the addition of 2.2 equivalents KNAP and then deionized H_2O resulted in decomposition. The ^1H and ^{13}C NMR spectra reported on the decomposition product. The starting material naphthalene seems to exist when comparing the ^{13}C NMR of the product to the starting material. Naphthalene peaks occur at δ 133.39, δ 127.79, and δ 125.72. THF may also be an impurity present at δ 1.85 and δ 3.8-3.9 in the ^1H NMR and in the ^{13}C NMR at δ 67 and δ 25. The ^1H NMR does display new peaks and the melting point of the product is 66-67 °C compared to the starting material naphthalene whose melting point is 80-82 °C indicating that some reaction may have occurred after the 2 equivalents of KNAP was added. After 2 days the deionized H_2O was added however decomposition of the intermediate product had occurred. Further analysis is necessary in order to determine the decomposition products.

For the reaction:



$$Mo(CO)_3(C_2H_5CN)_3 \xrightarrow[\text{xylene, 139 }^0C\text{, 15h}]{P_4} \text{COMPOUND VI}$$

SCHEME 6: SYNTHESIS OF COMPOUND VI

it is suspected that Compound VI was formed however, no structure has been determined. The ^1H and ^{13}C NMR are of the crude product. No attempts have been made to purify the product due to its pyrophoric nature. The ^1H NMR displays three complex multiplets which occur in the regions δ 0.267-0.299, δ 0.887-0.958, δ 1.321-1.398 which cannot be identified at this time. The ^{13}C NMR indicates peaks occurring at δ 29.766, δ 30.934, δ 95.558, and δ 206.828. The δ 206.828 peak is expected for the CO. The ^{31}P NMR indicates a peak occurring at δ 64.082. This compound was determined to be thermally unstable and pyrophoric because it reacts with air by burning, argon by smoking, and nitrogen by smoking making a detailed analysis and storage of compound VI extremely difficult. Further analysis is necessary to determine the exact structure of this compound.

product to the starting material. Naphthalene peaks occur at δ 133.39, δ 127.79, and δ 125.72. THF may also be an impurity present at δ 1.85 and δ 3.8-3.9 in the ^{1}H NMR and in the ^{13}C NMR at δ 67 and δ 25. The ^{1}H NMR does display new peaks and the melting point of the product is 66-67 °C compared to the starting material naphthalene whose melting point is 80-82 °C indicating that some reaction may have occurred after the 2 equivalents of KNAP was added. After 2 days the deionized H_2O was added however decomposition of the intermediate product had occurred. Further analysis is necessary in order to determine the decomposition products.

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SCHEME 6: SYNTHESIS OF COMPOUND VI

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In addition to the product , it is possible that the ^{1}H and ^{13} C NMR peaks represent the impurity propionitrile.

For the reaction:

$$Cr(CO)_3(C_2H_5CN)_3 \xrightarrow[\text{xylene, 139 }^0\text{C, 15h}]{P_4} \text{COMPOUND VII}$$

SCHEME 7: SYNTHESIS OF COMPOUND VII

it is suspected Compound VII was formed and no structure has been determined. The ^{1}H NMR and ^{13}C NMR spectra were of the crude product. No attempts were made to purify the product due to its pyrophoric nature. The ^{1}H NMR displays three complex multiplets along with a singlet which occur in the regions: δ 0.285-0.302(c), δ 0.550-0.580(c), δ 0.895(s), and δ 1.340-1.381(c). The ^{13}C NMR displays peaks occurring at δ 1.069, δ 29.781, and δ 30.972. The ^{31}P NMR displays a peak occurring at δ 277.659. This compound was determined to be thermally unstable because it reacts with air, nitrogen, and argon by smoking making storage of the compound and detailed analysis difficult. Further analysis is necessary to determine the exact structure of this compound.

A possible impurity for this compound, is propionitrile. Its peaks can be represented by those which are present in the alkyl region for the ^{1}H NMR.

In comparing the possible similarities in structures for compounds VI and VII, both have alkyl peaks occurring at δ .267-.299, δ .895-.958, and δ 1.321-1.398 which may attribute to both of them having the same structure. For compound VII, the peak occurring in the region δ .550-.580 may serve as an impurity. It should be noted that for Compound VII no peak was observed in the ^{13}C NMR in the CO region.

In addition to the product , it is possible that the ^{1}H and ^{13}C NMR peaks represent the impurity propionitrile.

For the reaction:

$$Cr(CO)_3(C_2H_5CN)_3 \xrightarrow[\text{xylene, 139 }^0\text{C, 15h}]{P_4} \text{COMPOUND VII}$$

SCHEME 7: SYNTHESIS OF COMPOUND VII

it is suspected Compound VII was formed and no structure has been determined. The ^{1}H NMR and ^{13}C NMR spectra were of the crude product. No attempts were made to purify the product due to its pyrophoric nature. The ^{1}H NMR displays three complex multiplets along with a singlet which occur in the regions: δ 0.285-0.302(c), δ 0.550-0.580(c), δ 0.895(s), and δ 1.340-1.381(c). The ^{13}C NMR displays peaks occurring at δ 1.069, δ 29.781, and δ 30.972. The ^{31}P NMR displays a peak occurring at δ 277.659. This compound was determined to be thermally unstable because it reacts with air, nitrogen, and argon by smoking making storage of the compound and detailed analysis difficult. Further analysis is necessary to determine the exact structure of this compound.

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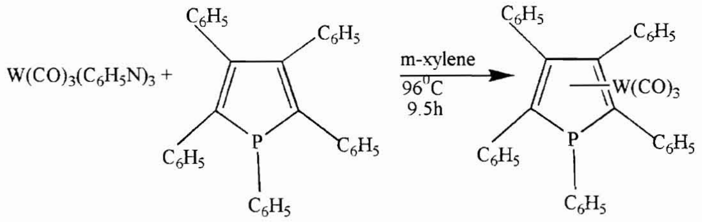
In comparing the possible similarities in structures for compounds VI and VII, both have alkyl peaks occurring at δ .267-.299, δ .895-.958, and δ 1.321-1.398 which may attribute to both of them having the same structure. For compound VII, the peak occurring in the region δ .550-.580 may serve as an impurity. It should be noted that for Compound VII no peak was observed in the ^{13}C NMR in the CO region.

For the reaction:



SCHEME 8: SYNTHESIS OF COMPOUND VIII

the product, tungsten tricarbonyl pentaphenylphosphole, is referred to in the experimental section as compound VIII. There are two possible ways that the pentaphenylphosphole ring could be coordinated to the W(CO)$_3$ moiety. The pentaphenylphosphole ring could coordinate through the two double bonds and the lone pair on phosphorus giving an 18 electron species, or only through the 2 double bonds giving a 16 electron species. The product was analyzed by mass spectrometry. The mass of the product, tungsten tricarbonyl pentaphenylphosphole, shows up at 732. The loss of one CO ligand is indicated by mass 704. The loss of the second CO ligand is indicated by mass 676, and the loss of the third CO ligand is indicated by mass 648. Pentaphenylphosphole is indicated by mass 464, the loss of a phenyl ring is indicated by mass 387, and the loss of the phosphorus atom is indicated by mass 356. The crude η^4-pentaphenylphosphole tungsten tricarbonyl product was analyzed by mass spectrometry, ^{1}H NMR, and ^{13}C NMR. The product appearing as compound VIII is a proposed structure based on the analysis of the crude product. The ^{13}C NMR spectra displays a peak appearing δ 265.358 which

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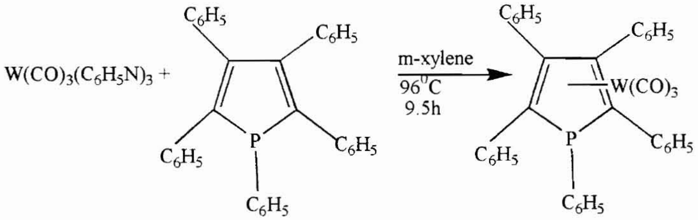

SCHEME 8: SYNTHESIS OF COMPOUND VIII

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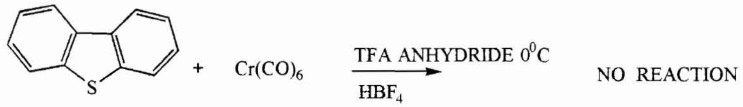
An impurity which may be present is *meta*-xylene, its peaks would occur in the aromatic region as complex multiplets and in the alkyl region of the spectra. They may be overlapped by the d_6-acetone.

For the reaction in attempting to synthesize compound IX,



SCHEME 9: SYNTHESIS OF COMPOUND IX

it is suspected that no reaction occurred. When comparing the ^{1}H NMR peaks of the final product to that of the starting material dibenzothiophene there was no change. The peak intensity and δ values were the same. Therefore, no reaction had occurred.

corresponds to the CO. In the aromatic region of the spectra, two peaks appear at δ 129.847, and δ 131.880 which make up the carbons which correspond to the phenyl rings. The 5-membered ring with the phosphorus corresponds with the peak at δ 69.692. These are alkene C's and not aromatic. The ^1H NMR spectra displays the aromatic protons in the regions δ 7.955-8.080(c), δ 7.036-7.194(c), and δ 6.927-6.956(c) which are assigned to the phenyl rings. The ^{31}P NMR displays a single phosphorus peak appearing in the area δ 37.044. The IR peaks of the final product appeared at 2075(m), 1975(m), and 1946(vs) cm^{-1}. These peaks represent the $(CO)_3$ portion of the structure.

An impurity which may be present is *meta*-xylene, its peaks would occur in the aromatic region as complex multiplets and in the alkyl region of the spectra. They may be overlapped by the d_6-acetone.

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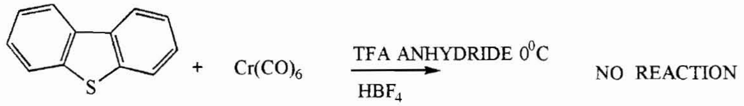

SCHEME 9: SYNTHESIS OF COMPOUND IX

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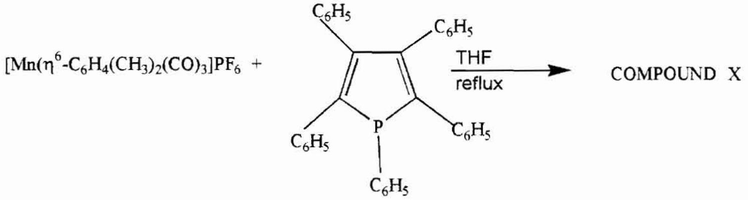
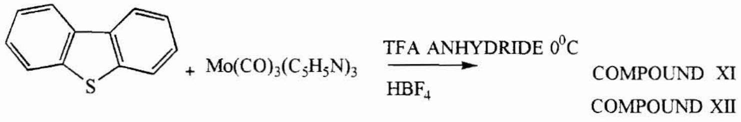
For the reaction:



SCHEME 10: SYNTHESIS OF COMPOUND X

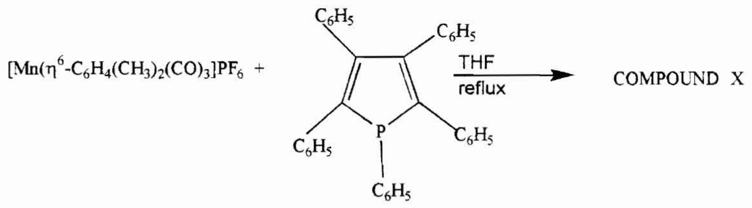
no actual product structure has been determined at this time. The ^1H NMR spectra displays peaks occurring at δ 0.197(d, J=5.6 Hz), δ .8035(q, J=49.6, 50.8, 29.6 Hz), δ 1.281(t, J=112.4, 47.6 Hz), δ 6.819-7.160(c) in the aromatic region, and δ 7.406-7.590(c) which also occurs in the aromatic region. ^{31}P NMR spectra displays one peak occurring at δ 189.103. Both of the starting materials contain a Phosphorus atom, however, now only one type of phosphorus peak is present in compound X. The peaks listed are new product peaks which do not appear in the starting materials. Further analysis is necessary to determine the exact structure of compound X. A possible impurity may be THF whose peaks occur at δ 2.8 and δ 3.8. A trace of this material may be present.

In the reaction:



SCHEME 11: SYNTHESIS OF COMPOUND XI AND XII

also referred to as compound XI and XII, two product bands (brown and blue) were collected from the column. When comparing the brown band to the Mo starting material, For the reaction:



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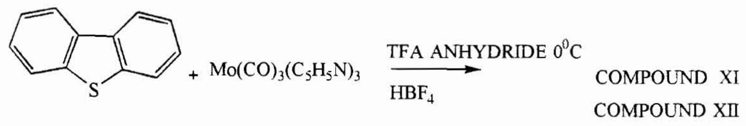
In the reaction:



SCHEME 11: SYNTHESIS OF COMPOUND XI AND XII

also referred to as compound XI and XII, two product bands (brown and blue) were collected from the column. When comparing the brown band to the Mo starting material,

there was no difference in peak intensity or δ values for the brown product compared to the starting material. Therefore the brown band is believed to be Mo(CO)$_3$(C$_5$H$_5$N)$_3$ since the ^{1}H NMR spectra displays δ 9.135(d), δ 8.882(t), and δ 7.355(c). When analyzing the blue band, one interesting peak appeared in the ^{1}H NMR spectra at δ 7.357(t). This peak is expected to be the solvent benzene which was used in the column. Temperature and time are two factors which may have contributed to the reaction failure. A higher reaction temperature with longer refluxing times may aide this reaction into synthesizing a product.

3.1 CYCLIC VOLTAMMETRY OF (η^6–DBT)Mn(CO)$_3$BF$_4$

The (η^6-DBT)Mn(CO)$_3$BF$_4$ complex was studied in acetonitrile at a range of scan rates. The working electrode(w) used was glassy carbon(GC). For the glassy carbon electrode, we observed an irreversible reduction at -2.104 V versus the ferrocene/ferrocenium couple. There was evidence of decomposition indicated by a change in color of the solution from yellow to green after electrochemical reduction.

3.2 Conclusion:

In summary, the reduction of (η^6-DBT)Mn(CO)$_3$BF$_4$ was accomplished by adding either 1.1 or 2.2 equivalents of KNAP. One equivalent of benzyl chloride, tributyltin hydride, and bis(triphenylphosphoranylidene)ammonium chloride was added to produce the new compounds. Compounds I, II, III, and IV share similar IR peaks which indicates that their structures are very similar.

The two phosphorus reactions dealing with Mo(CO)$_3$(C$_2$H$_5$CN)$_3$, and Cr(CO)$_3$(C$_2$H$_5$CN)$_3$ with P$_4$ produced thermally unstable products which are pyrophoric there was no difference in peak intensity or δ values for the brown product compared to the starting material. Therefore the brown band is believed to be $Mo(CO)_3(C_5H_5N)_3$ since the ^1H NMR spectra displays δ 9.135(d), δ 8.882(t), and δ 7.355(c). When analyzing the blue band, one interesting peak appeared in the ^1H NMR spectra at δ 7.357(t). This peak is expected to be the solvent benzene which was used in the column. Temperature and time are two factors which may have contributed to the reaction failure. A higher reaction temperature with longer refluxing times may aide this reaction into synthesizing a product.

3.1 CYCLIC VOLTAMMETRY OF $(\eta^6$–DBT)$Mn(CO)_3BF_4$

The $(\eta^6$-DBT)$Mn(CO)_3BF_4$ complex was studied in acetonitrile at a range of scan rates. The working electrode(w) used was glassy carbon(GC). For the glassy carbon electrode, we observed an irreversible reduction at -2.104 V versus the ferrocene/ferrocenium couple. There was evidence of decomposition indicated by a change in color of the solution from yellow to green after electrochemical reduction.

3.2 Conclusion:

In summary, the reduction of $(\eta^6$-DBT)$Mn(CO)_3BF_4$ was accomplished by adding either 1.1 or 2.2 equivalents of KNAP. One equivalent of benzyl chloride, tributyltin hydride, and bis(triphenylphosphoranylidene)ammonium chloride was added to produce the new compounds. Compounds I, II, III, and IV share similar IR peaks which indicates that their structures are very similar.

The two phosphorus reactions dealing with $Mo(CO)_3(C_2H_5CN)_3$, and $Cr(CO)_3(C_2H_5CN)_3$ with P_4 produced thermally unstable products which are pyrophoric due to their reactions with air, argon, nitrogen, and with solvents. Further analysis of these two products is necessary to determine their structures.

The two reactions dealing with pentaphenylphosphole which produced products tungsten tricarbonyl pentaphenylphosphole, and compound X appear to be air stable compounds. Further analysis is necessary to establish the actual structure of compound X.

The cyclic voltammetry of $(\eta^6$-DBT)$Mn(CO)_3BF_4$ was performed at various scan rates. An irreversible reduction wave was observed.

According to ^1H NMR, ^{13}C NMR, and ^{31}P NMR, proposed structural assignments were made for most crude products. For future projects, single crystals of the various products can be isolated and analyzed by x-ray diffraction. Cyclic voltammetry can be performed on the newly synthesized compounds possibly at varying temperatures.

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REFERENCES

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    b)Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*, Wiley: New York, **1980**, 229.

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FIGURE S-1 ^{1}H NMR COMPOUND 1

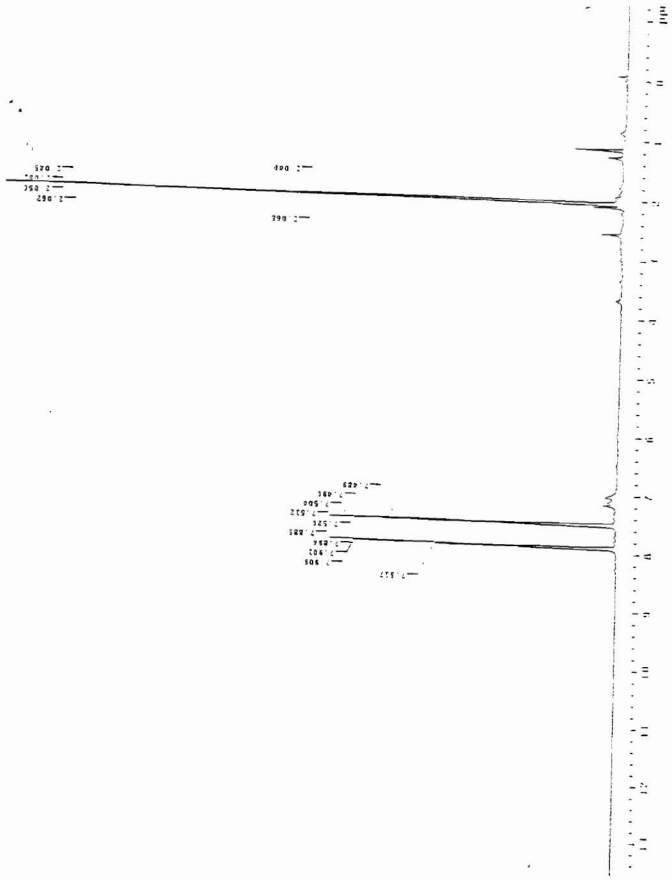


FIGURE S-1 ¹H NMR COMPOUND I

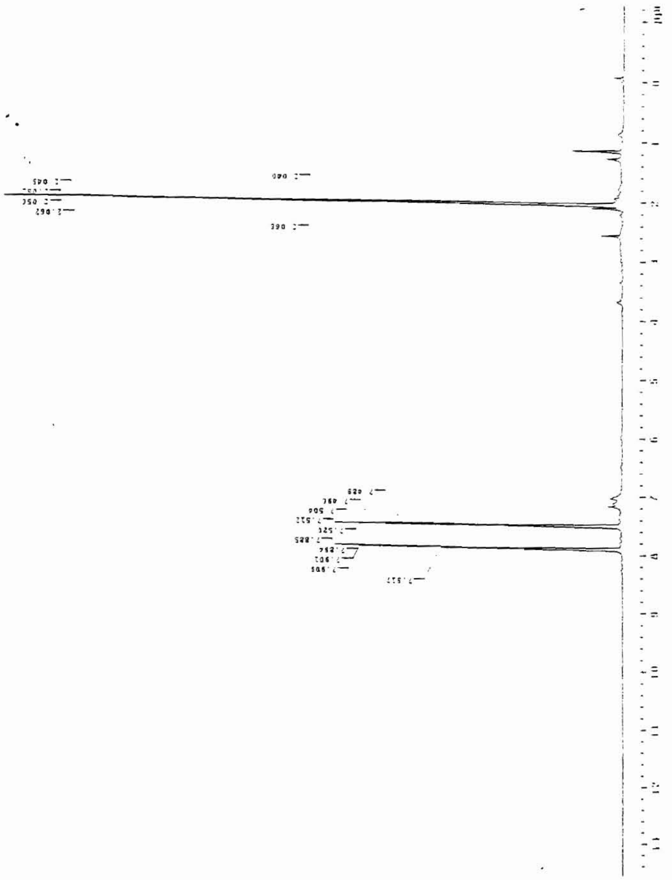


FIGURE S-2 ¹³C NMR COMPOUND I

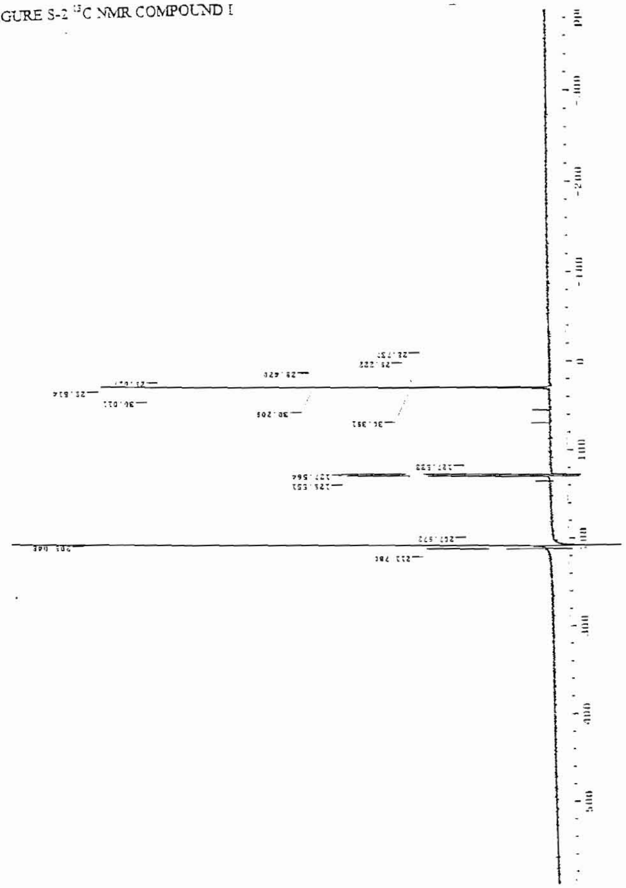


FIGURE S-2 ^{13}C NMR COMPOUND I

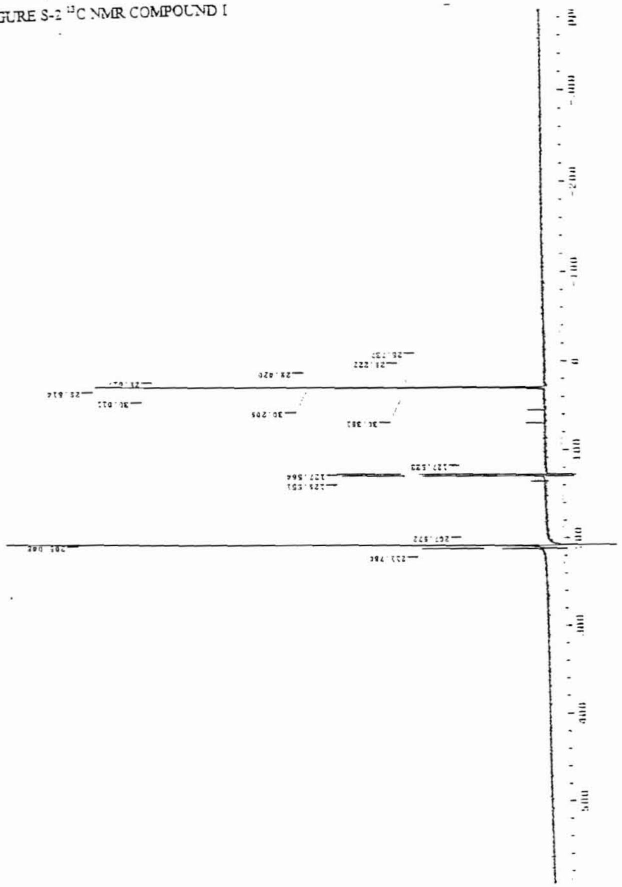


FIGURE S-3 ^{1}H NMR COMPOUND II

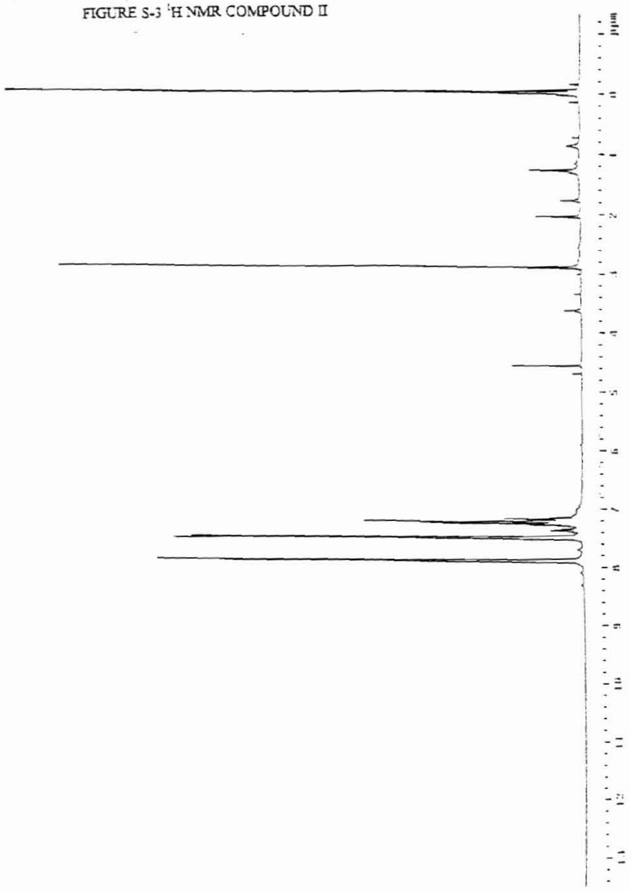
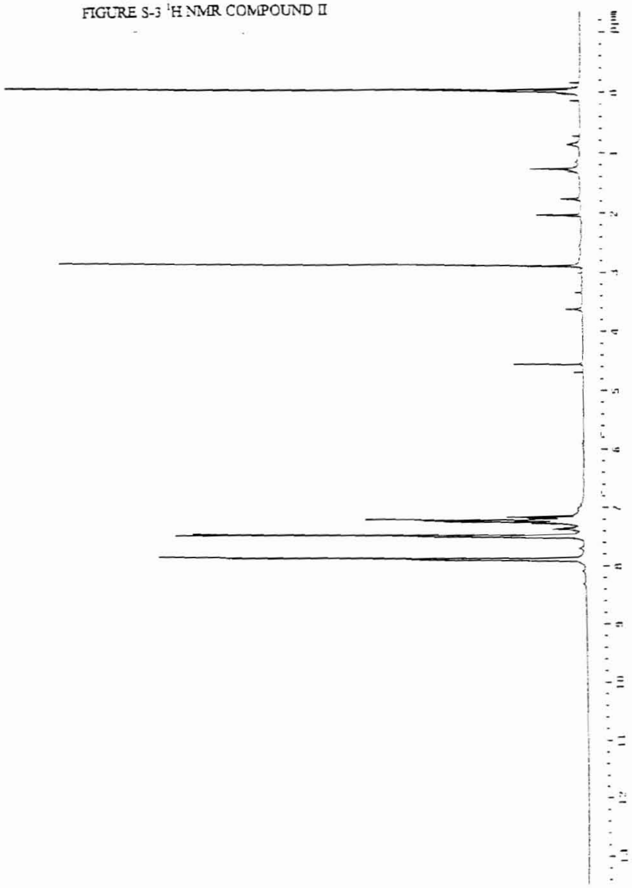


FIGURE S-3 ¹H NMR COMPOUND II



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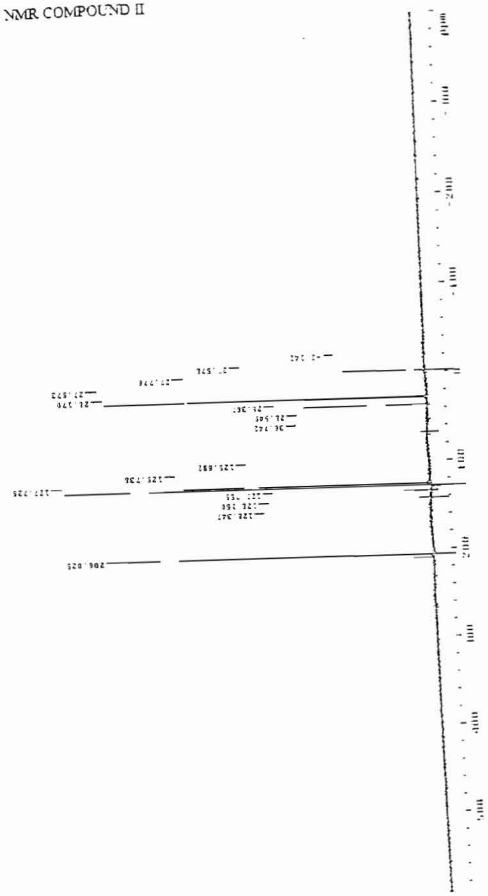


FIGURE S-4 ^{13}C NMR COMPOUND II

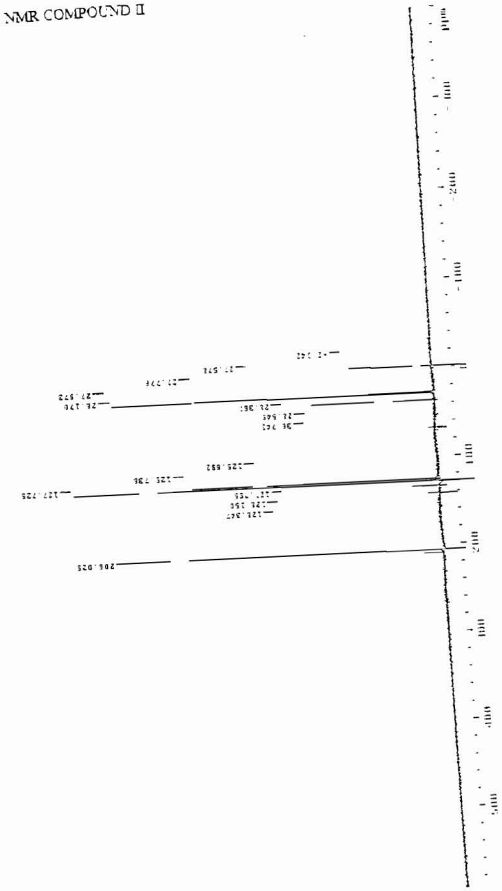


FIGURE S-5 ^{1}H NMR COMPOUND III

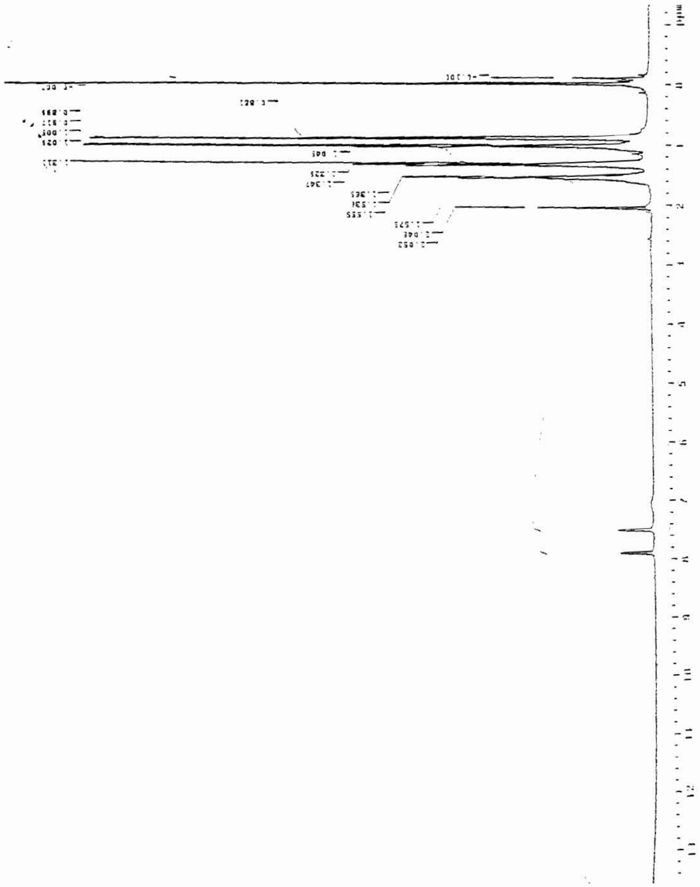


FIGURE S-5 ¹H NMR COMPOUND III

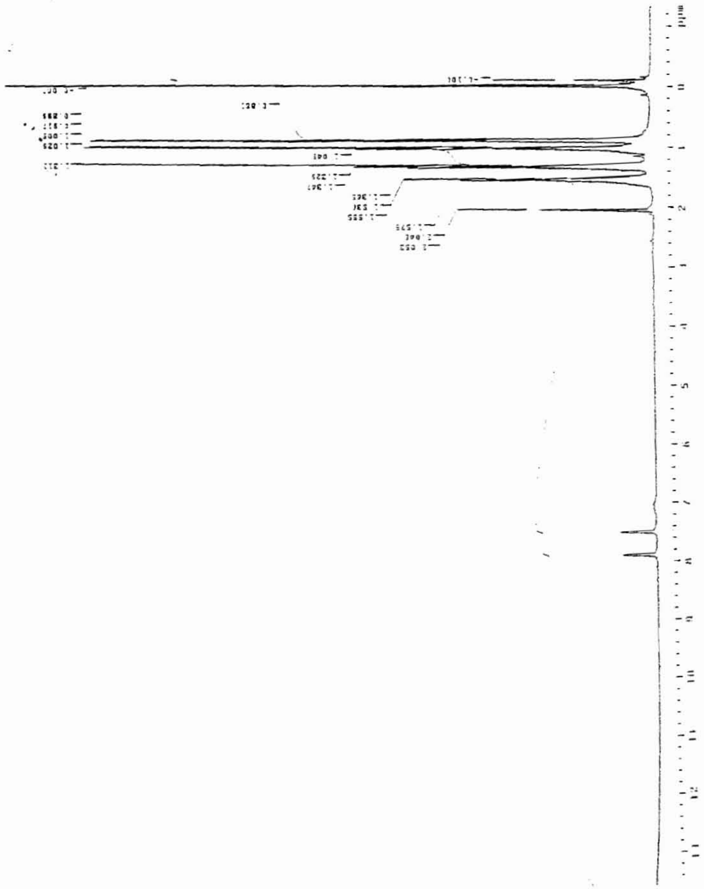


FIGURE S-6 ¹³C NMR COMPOUND III

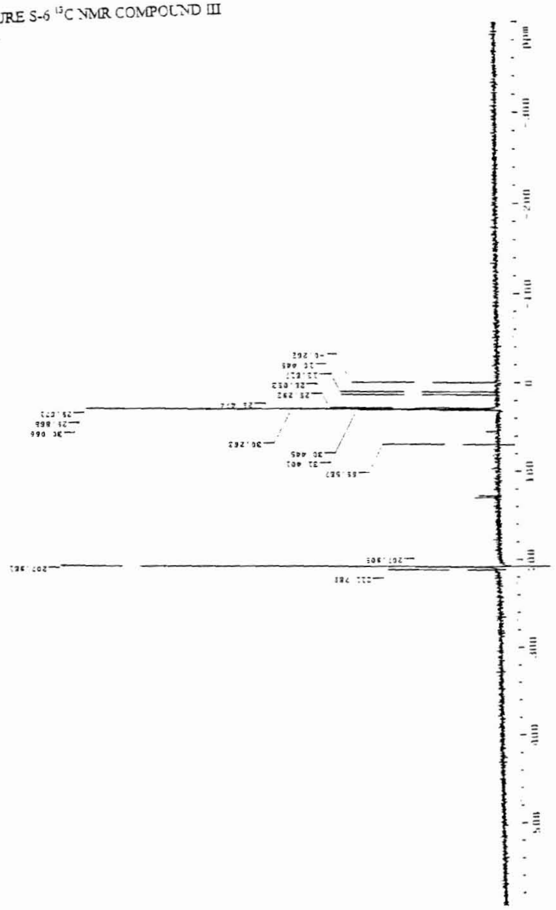


FIGURE S-6 ^{13}C NMR COMPOUND III

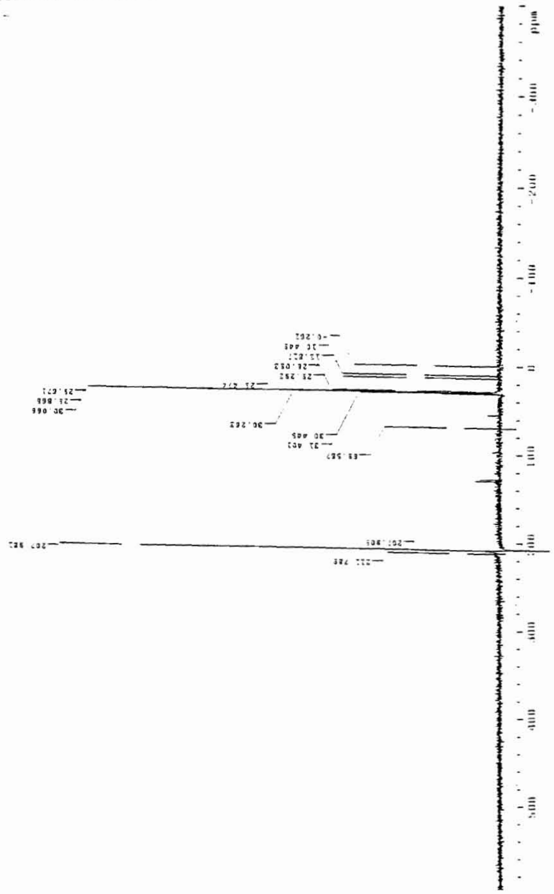
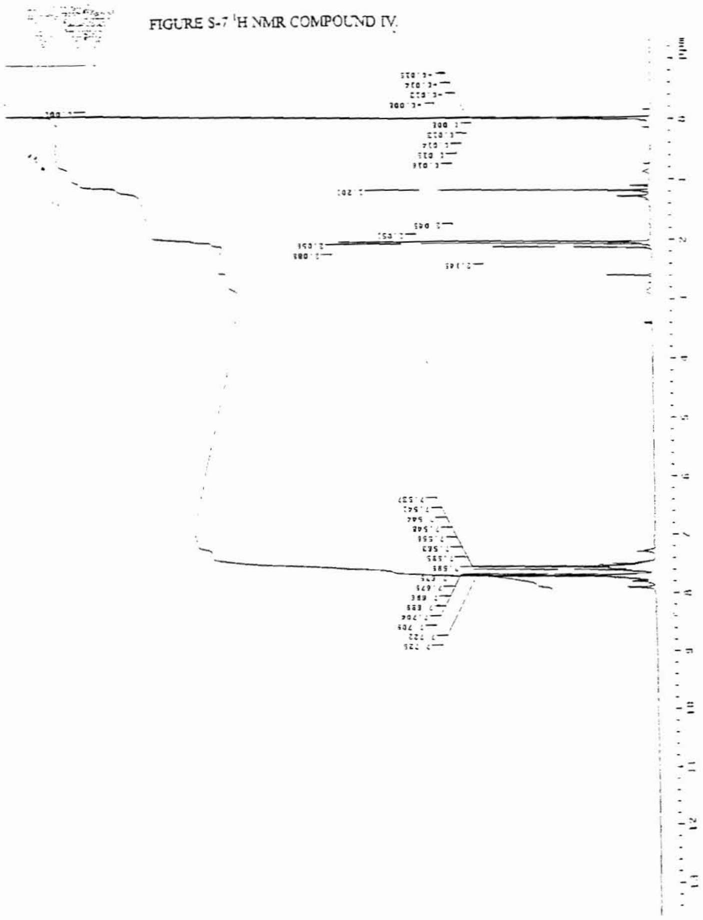


FIGURE S-7 ^{1}H NMR COMPOUND IV.



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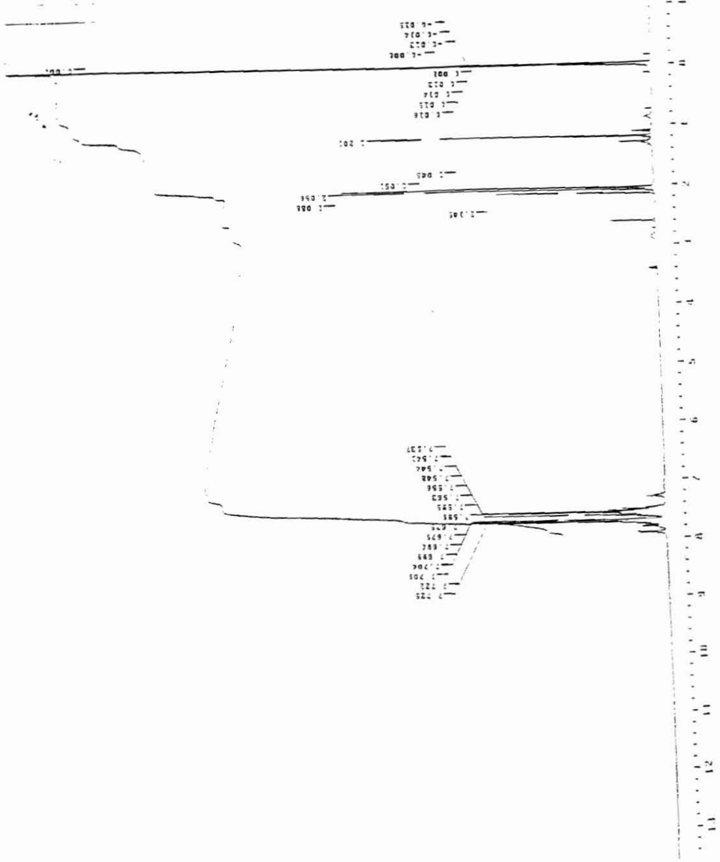
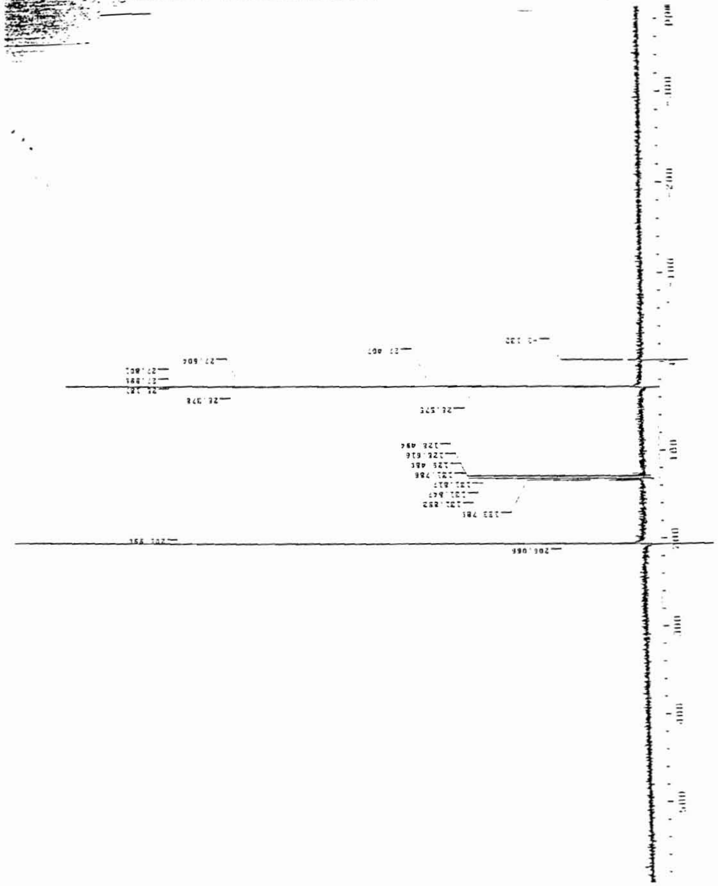


FIGURE S-8 ^{13}C NMR COMPOUND IV



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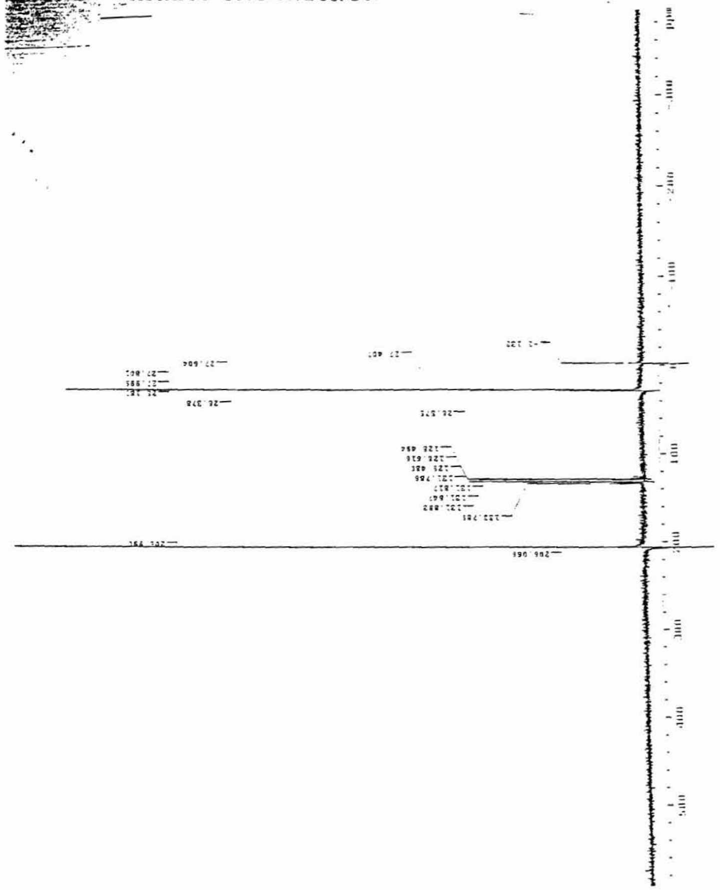


FIGURE S-9 ^{1}H NMR COMPOUND V

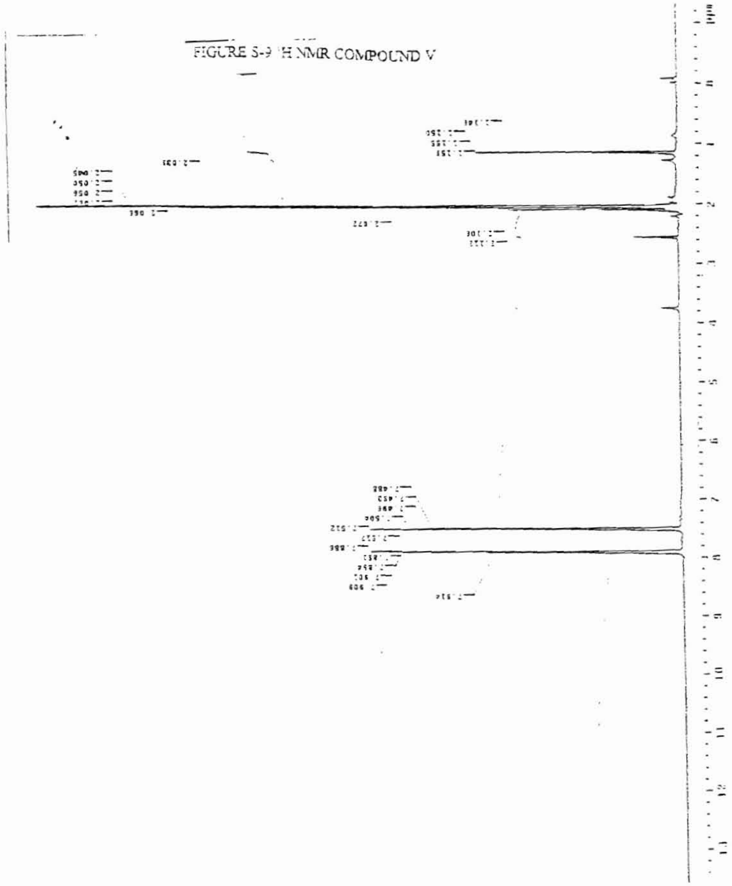


FIGURE S-9 ¹H NMR COMPOUND V

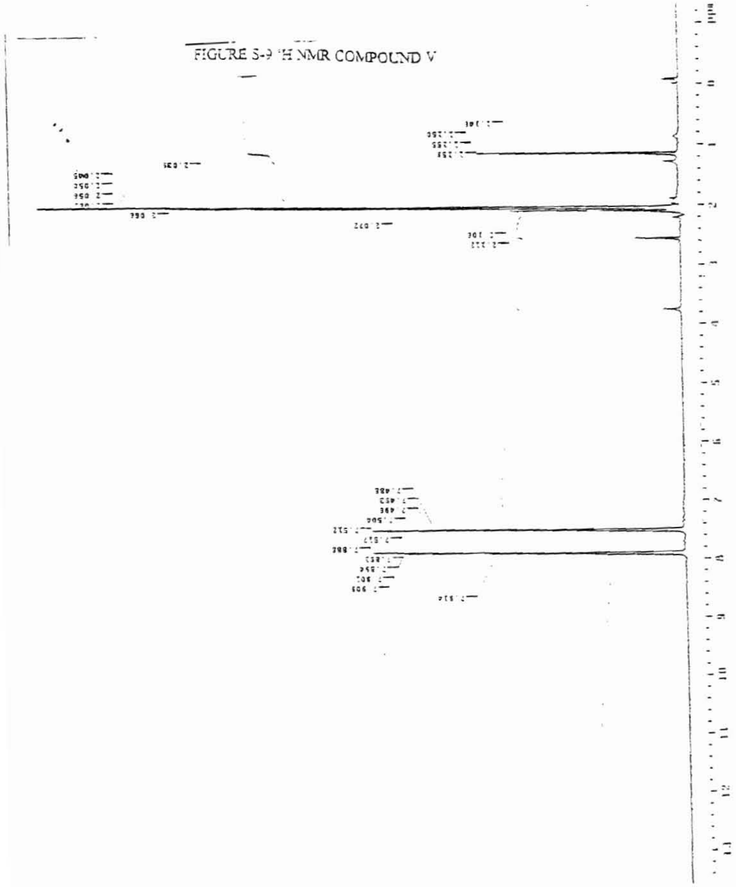


FIGURE S-10 ¹³C NMR COMPOUND V

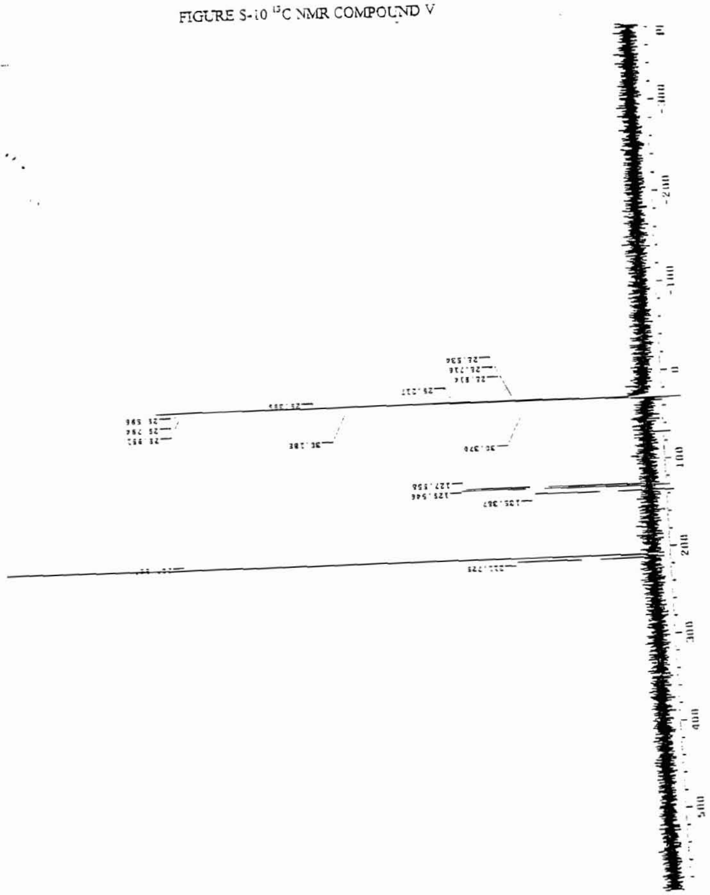


FIGURE S-10 ^{13}C NMR COMPOUND V

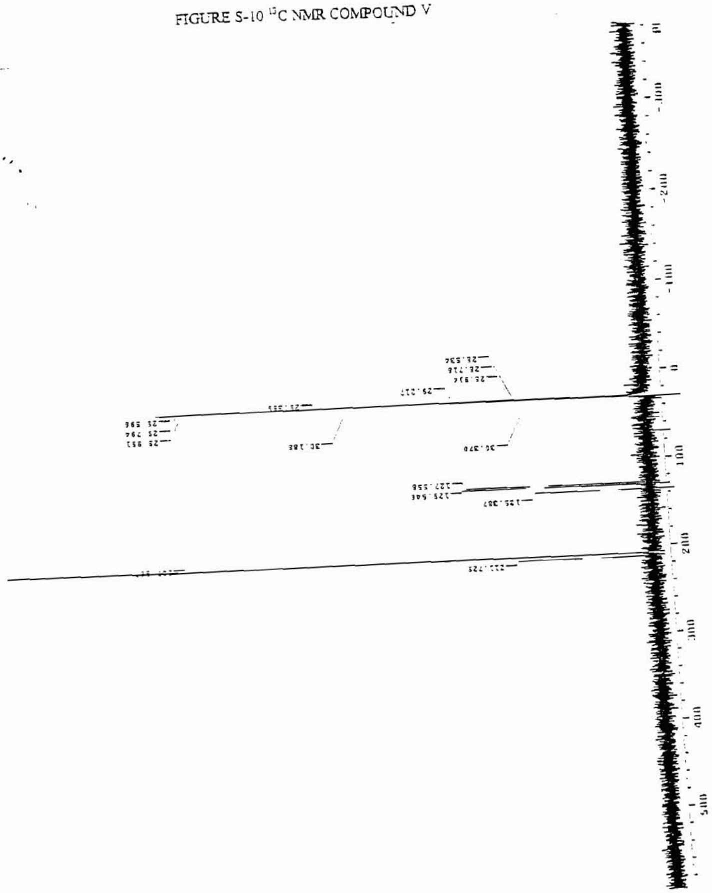


FIGURE S-11 ^{1}H NMR COMPOUND VI

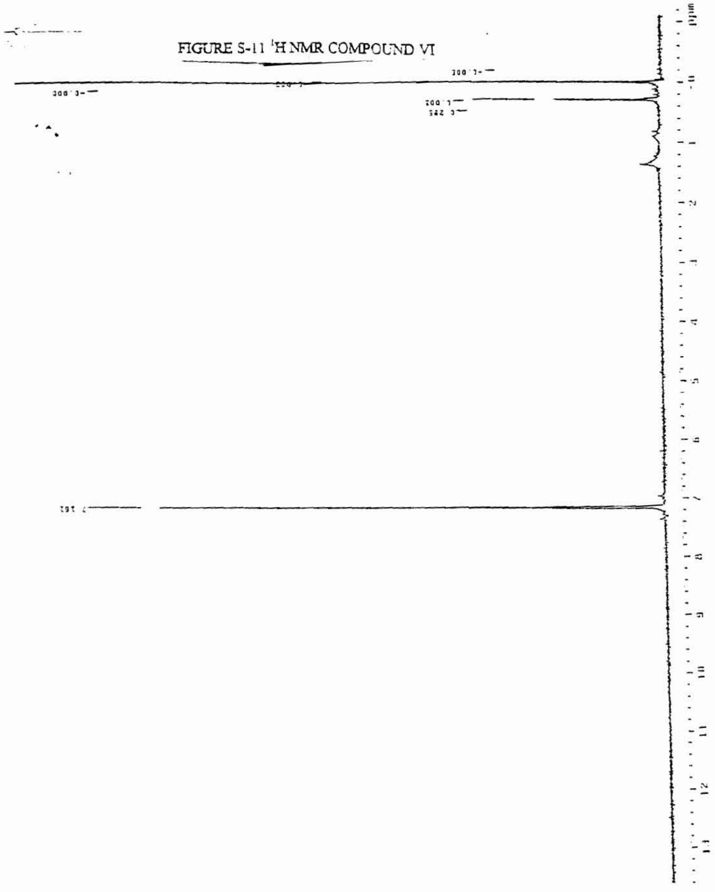


FIGURE S-11 ^{1}H NMR COMPOUND VI

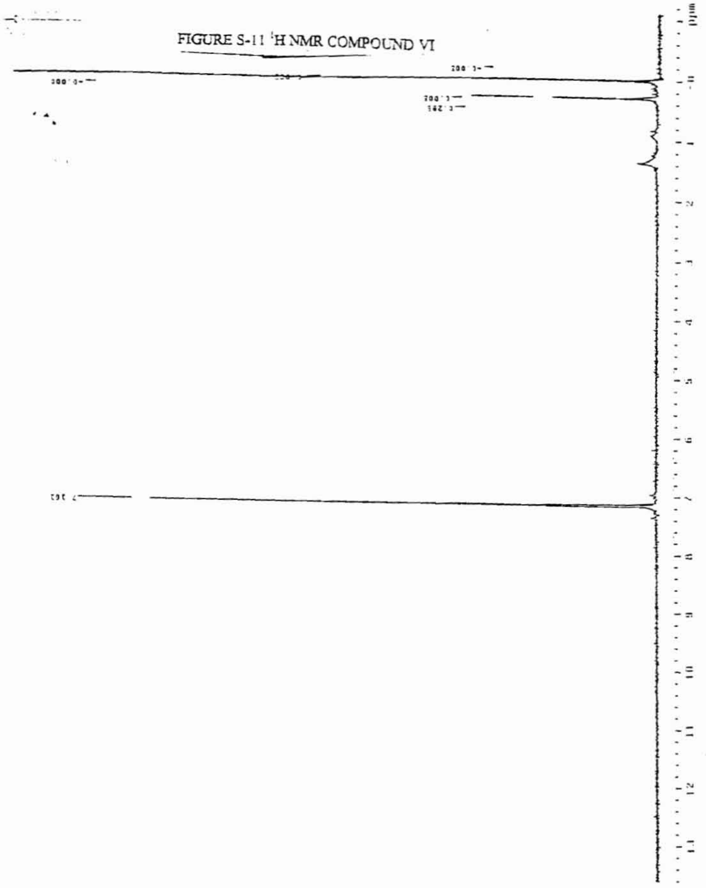


FIGURE S-12 ^{13}C NMR COMPOUND VI

FIGURE S-12 ^{13}C NMR COMPOUND VI

FIGURE S-13 ^{31}P NMR COMPOUND VI

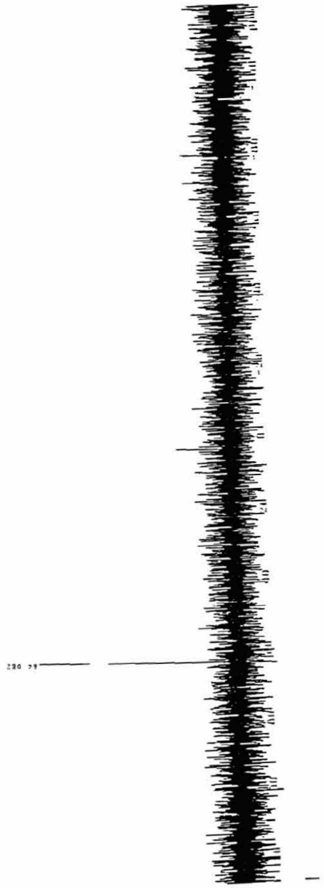


FIGURE S-13 ^{31}P NMR COMPOUND VI

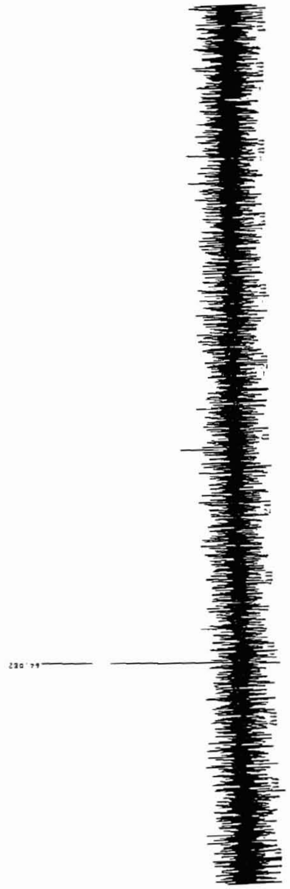


FIGURE S-14 ^{1}H NMR COMPOUND VII

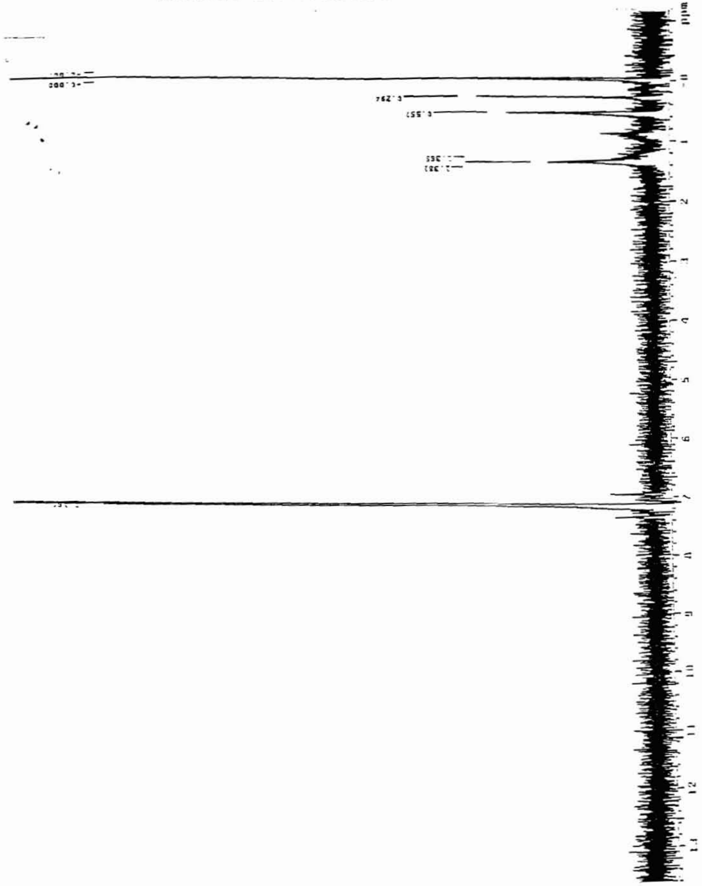


FIGURE S-14 ¹H NMR COMPOUND VII

FIGURE S-15 ¹³C NMR COMPOUND VII

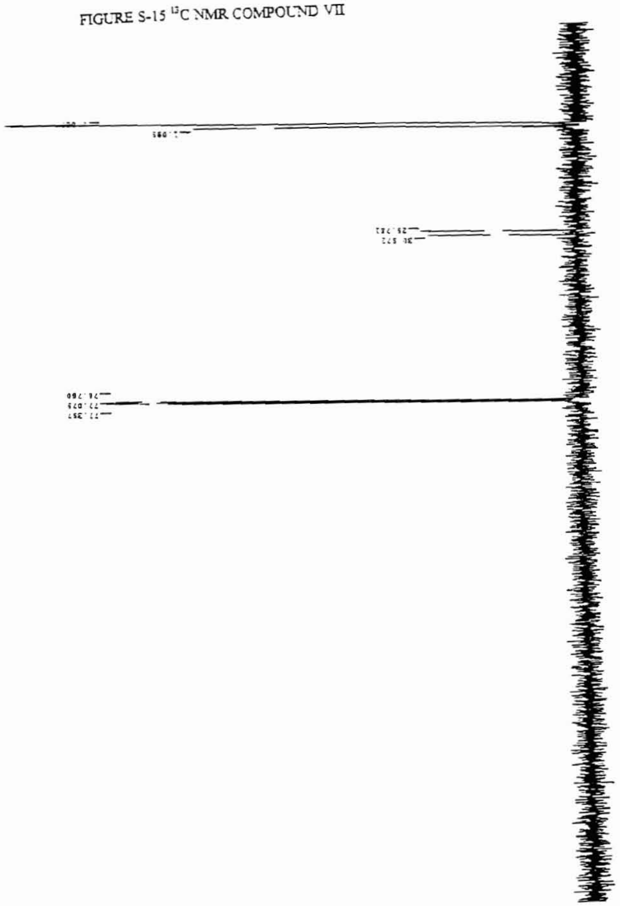


FIGURE S-15 ^{13}C NMR COMPOUND VII

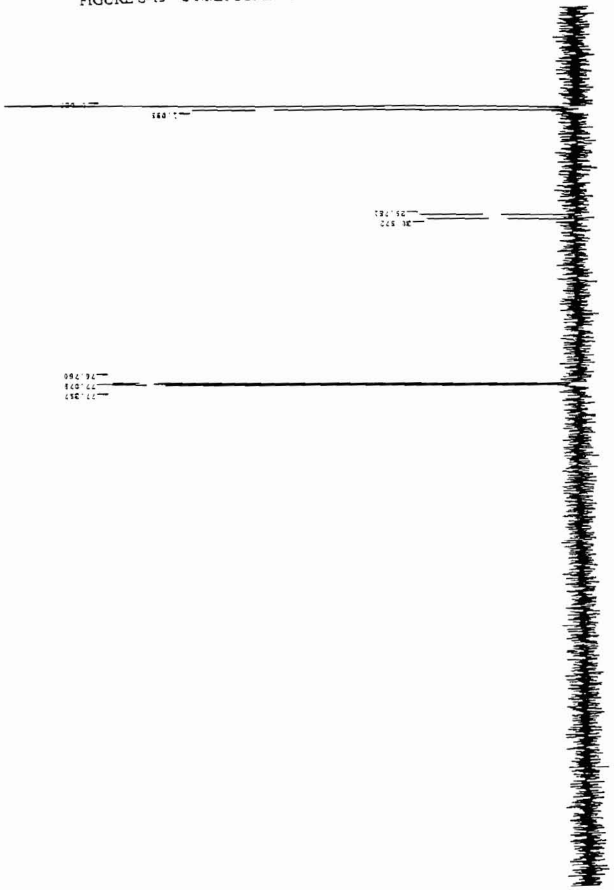


FIGURE S-16 ^{31}P NMR COMPOUND VII

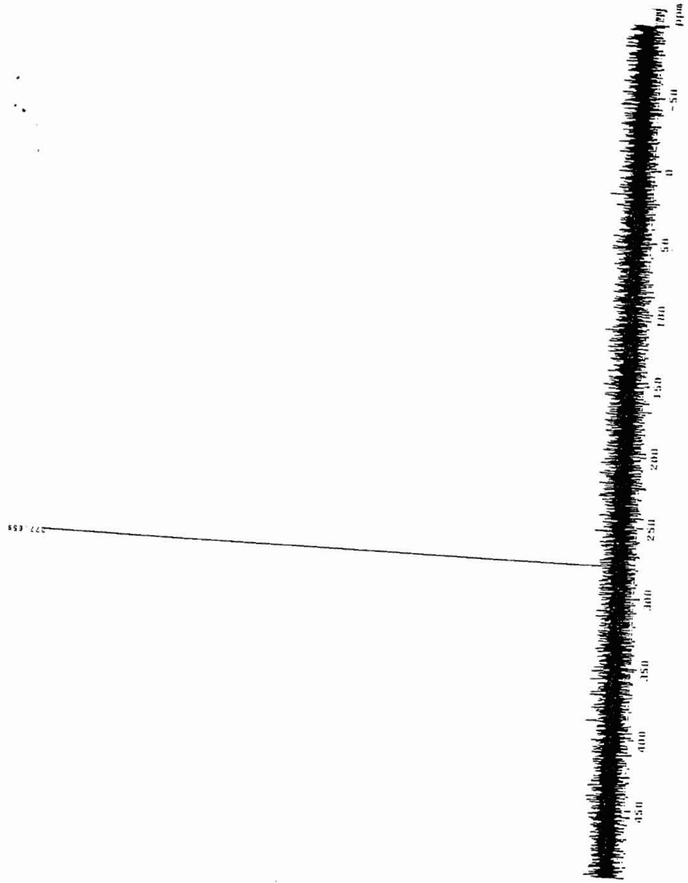
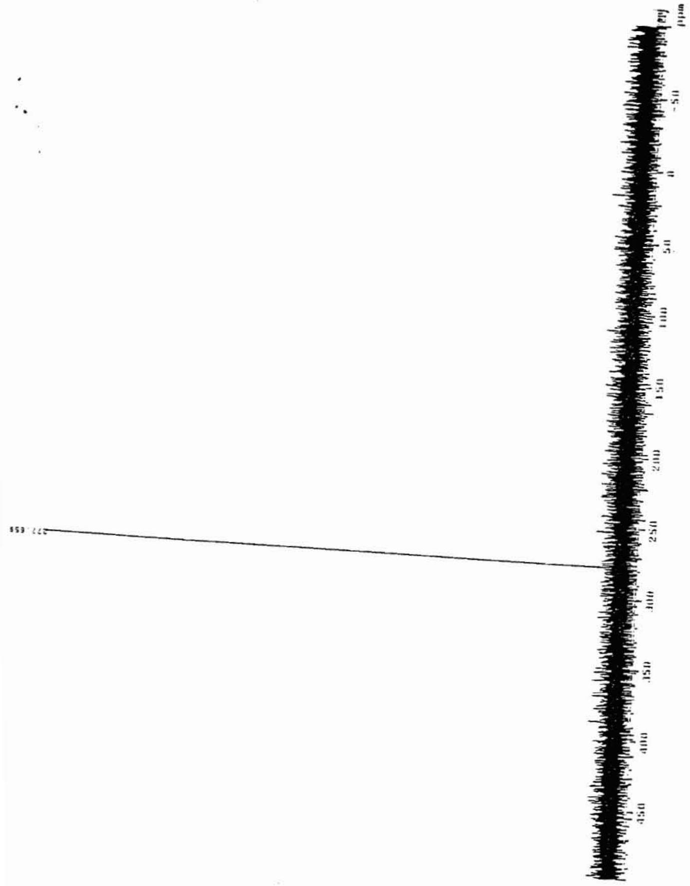


FIGURE S-16 ^{31}P NMR COMPOUND VII



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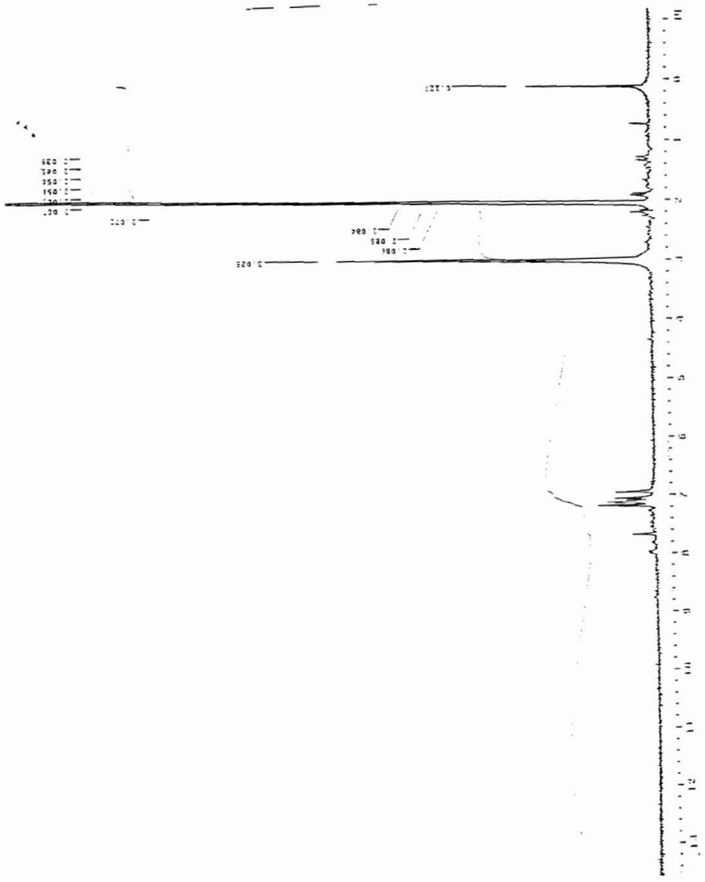


FIGURE S-17 ^{1}H NMR COMPOUND VIII

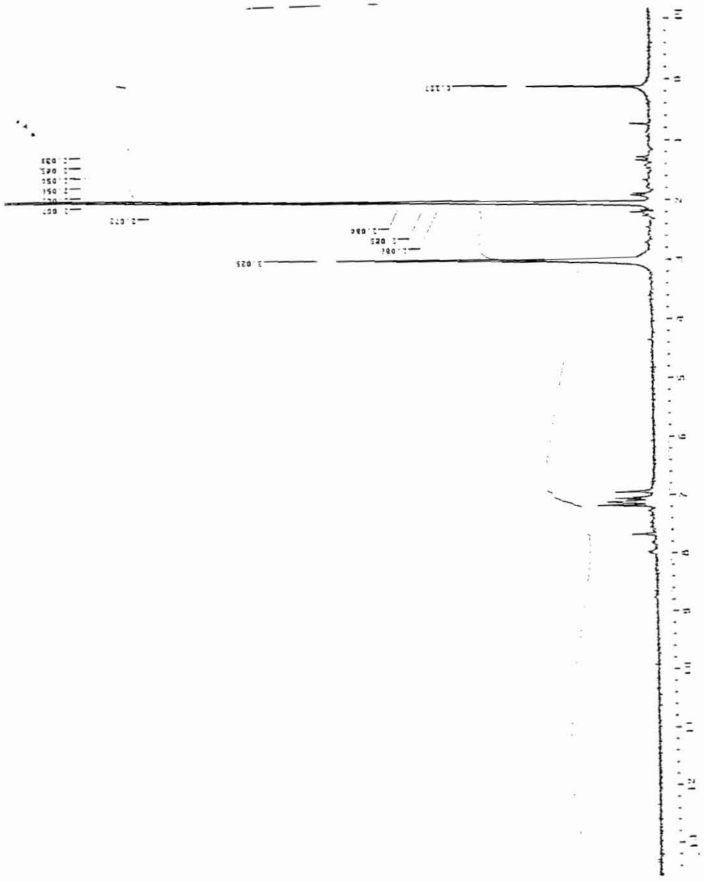


FIGURE S-18 ^{13}C NMR COMPOUND VIII

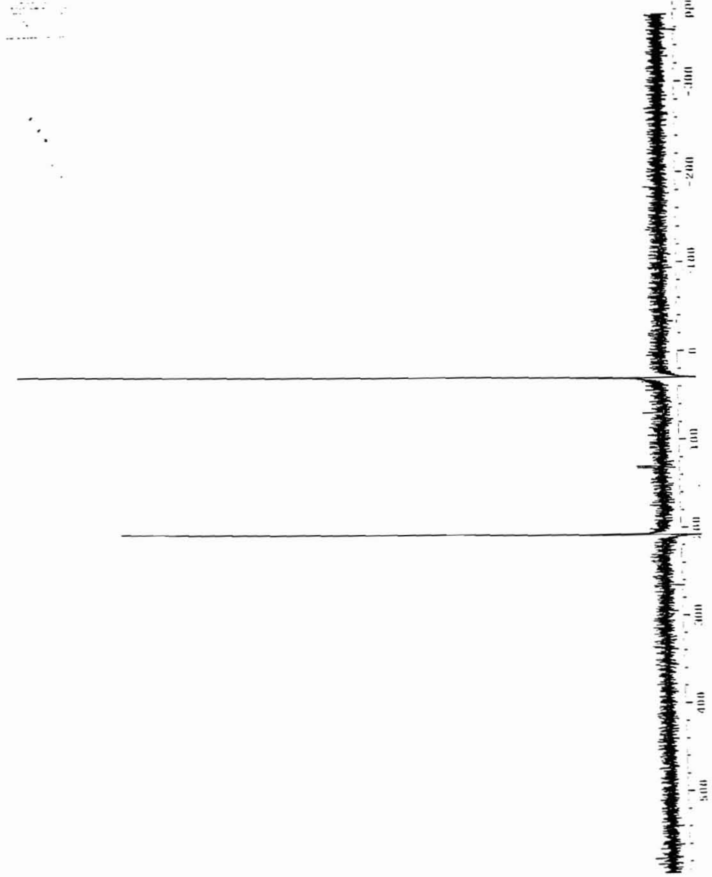


FIGURE S-18 ^{13}C NMR COMPOUND VIII

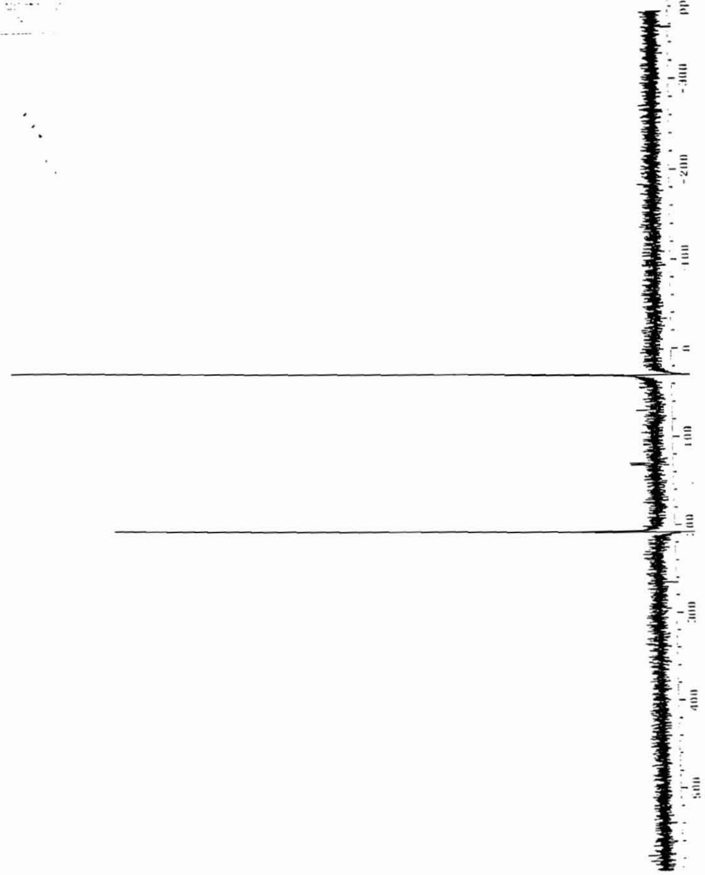
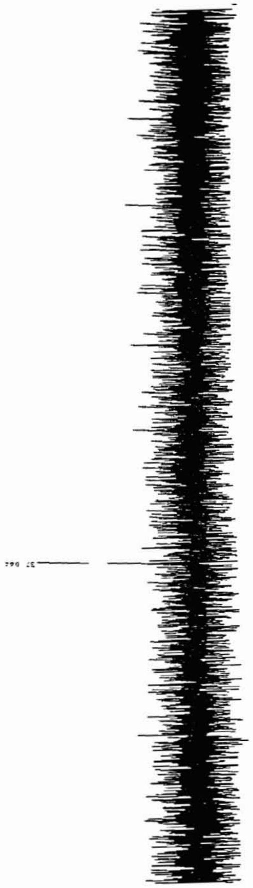


FIGURE S-19 ^{31}P NMR COMPOUND VIII



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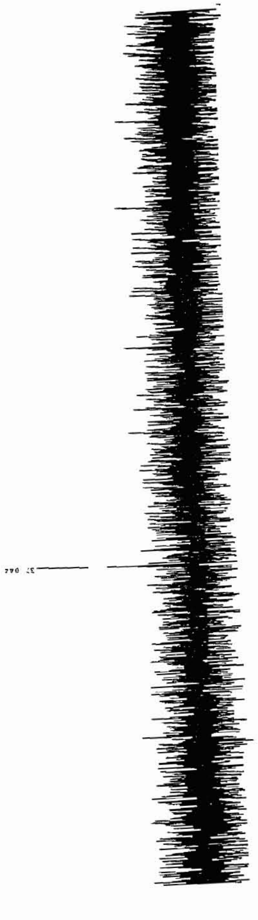

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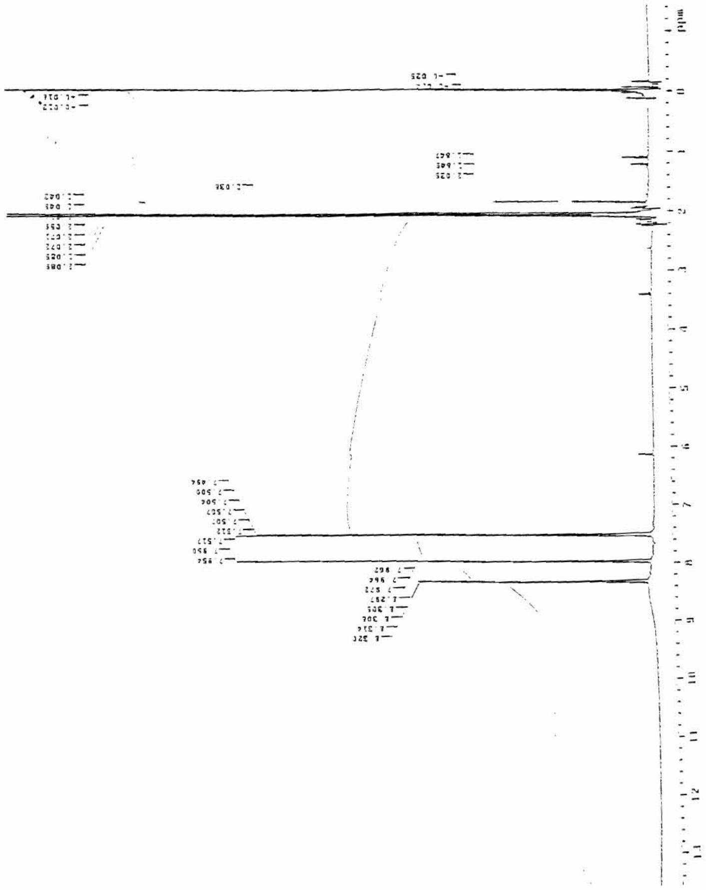

FIGURE S-20 ¹H NMR COMPOUND IX

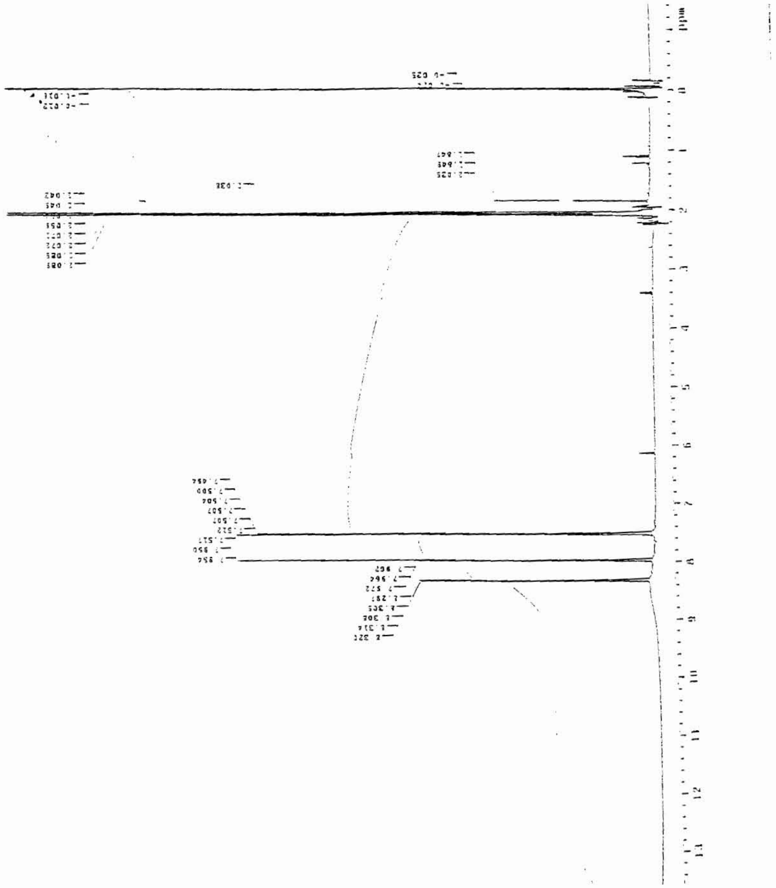

FIGURE S-21 ¹³C NMR COMPOUND IX

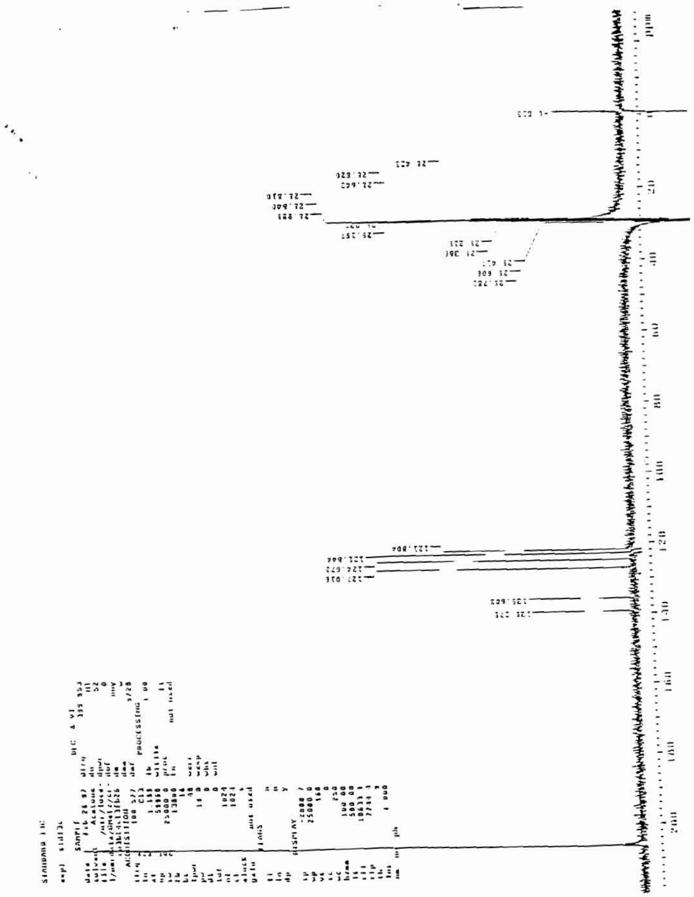

FIGURE S-21 ^{13}C NMR COMPOUND IX

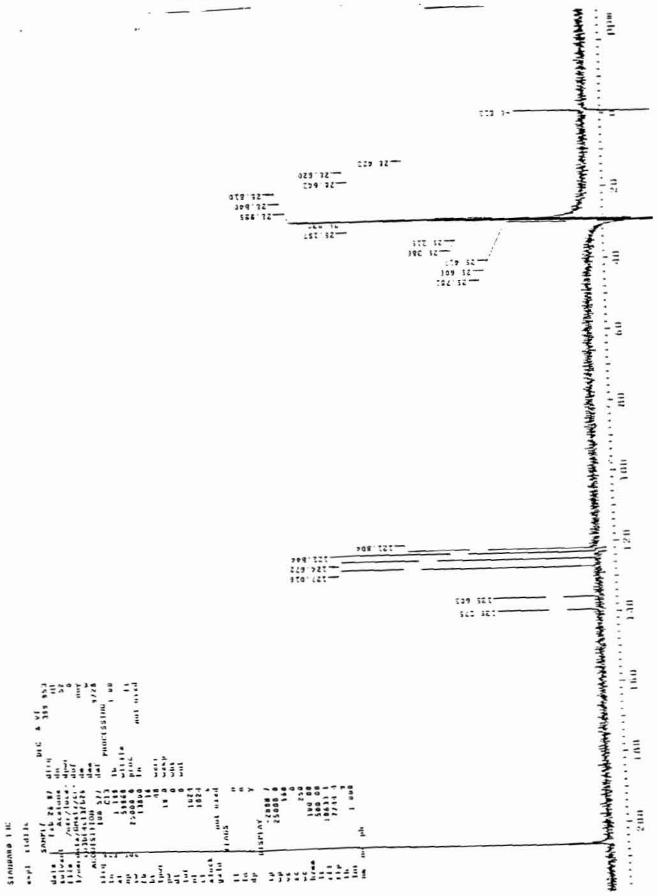

FIGURE S-22 ^{1}H NMR COMPOUND X

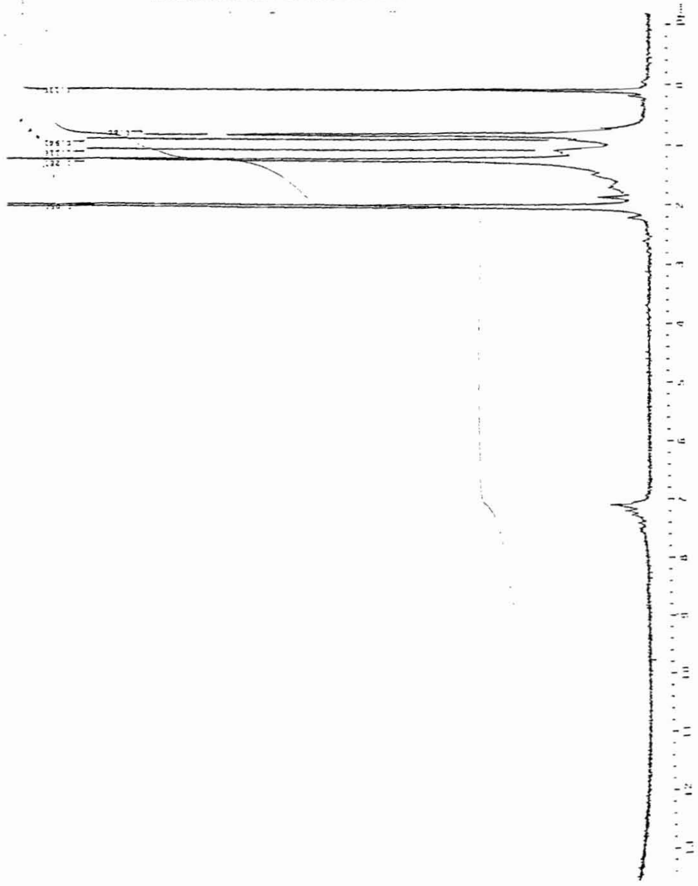

FIGURE S-22 ¹H NMR COMPOUND X

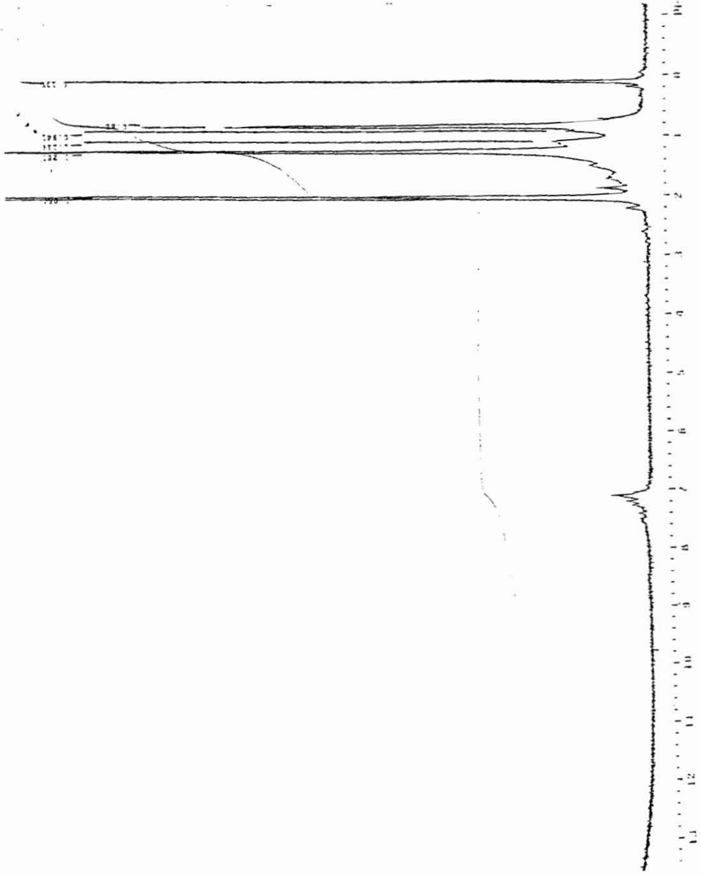

FIGURE S-23 ³¹P NMR COMPOUND X

FIGURE 5-23 ^{31}P NMR COMPOUND X

FIGURE 5-24 ^{1}H NMR COMPOUND XI BROWN BAND

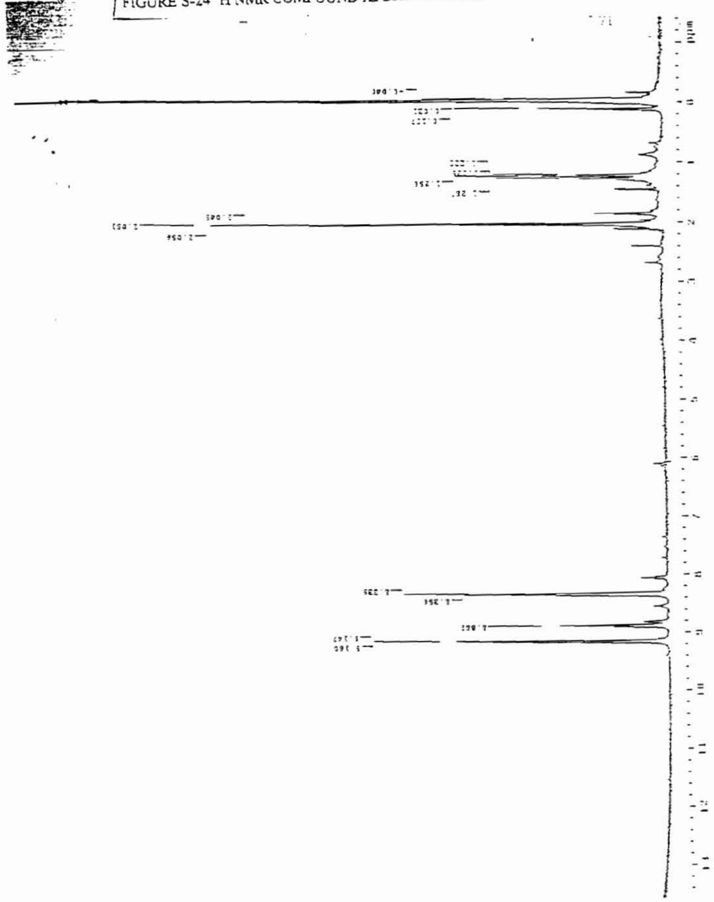

FIGURE S-24 ¹H NMR COMPOUND XI BROWN BAND

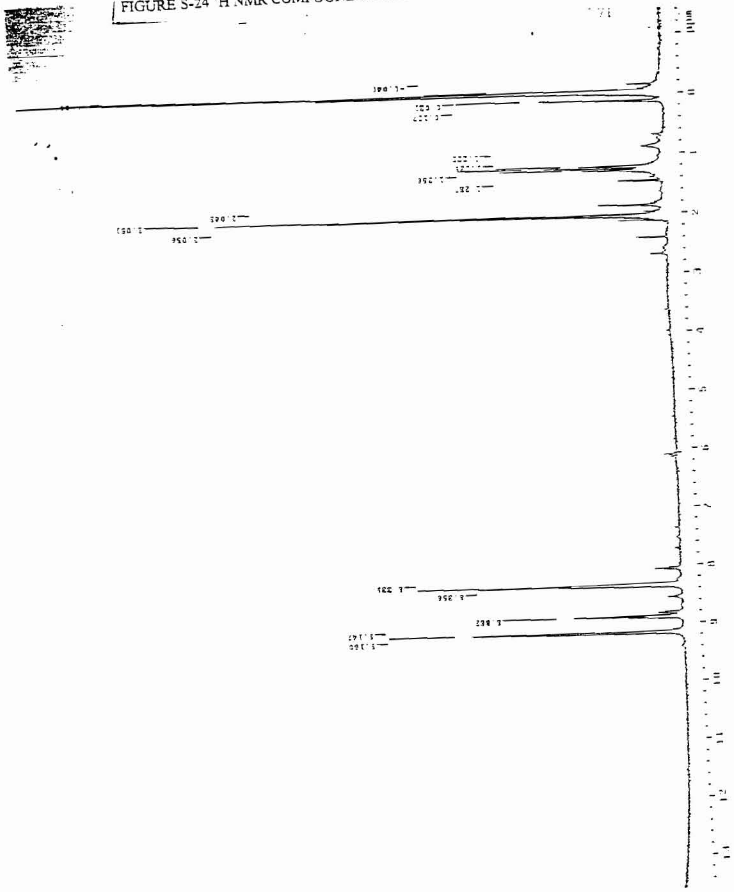

FIGURE S-25 ¹H NMR COMPOUND XII BLUE BAND

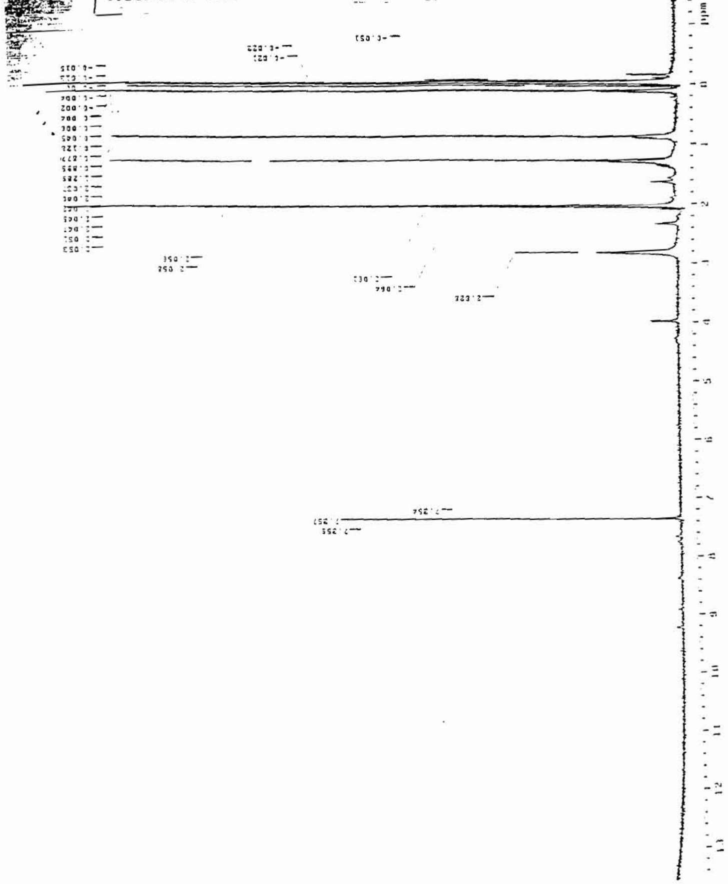

FIGURE S-25 ^{1}H NMR COMPOUND XII BLUE BAND

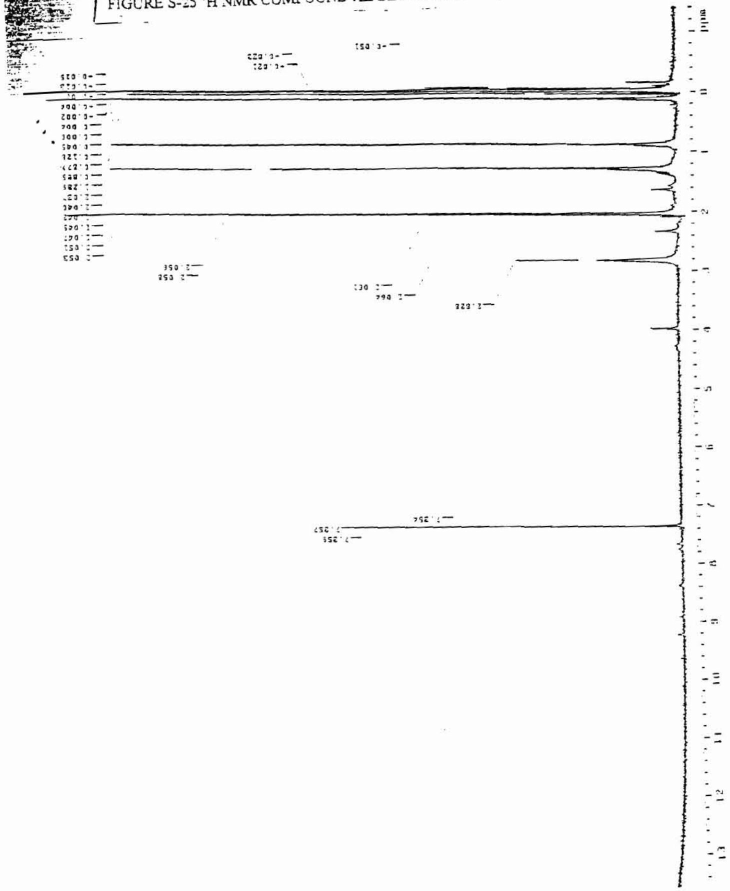

FIGURE S-26 MASS SPEC OF COMPOUND VIII

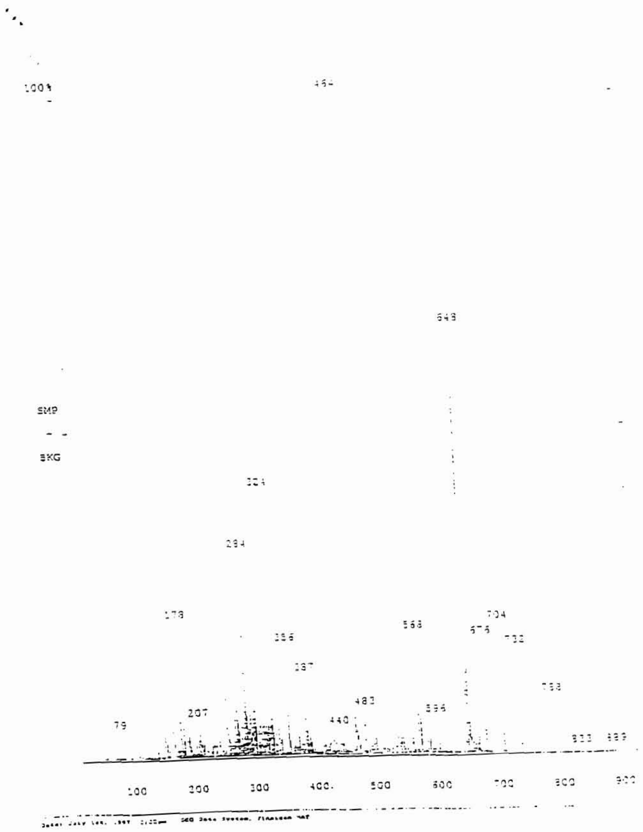

FIGURE S-26 MASS SPEC OF COMPOUND VIII

FIGURE S-27 IR COMPOUND VIII
(AFTER 9.5 HOURS)

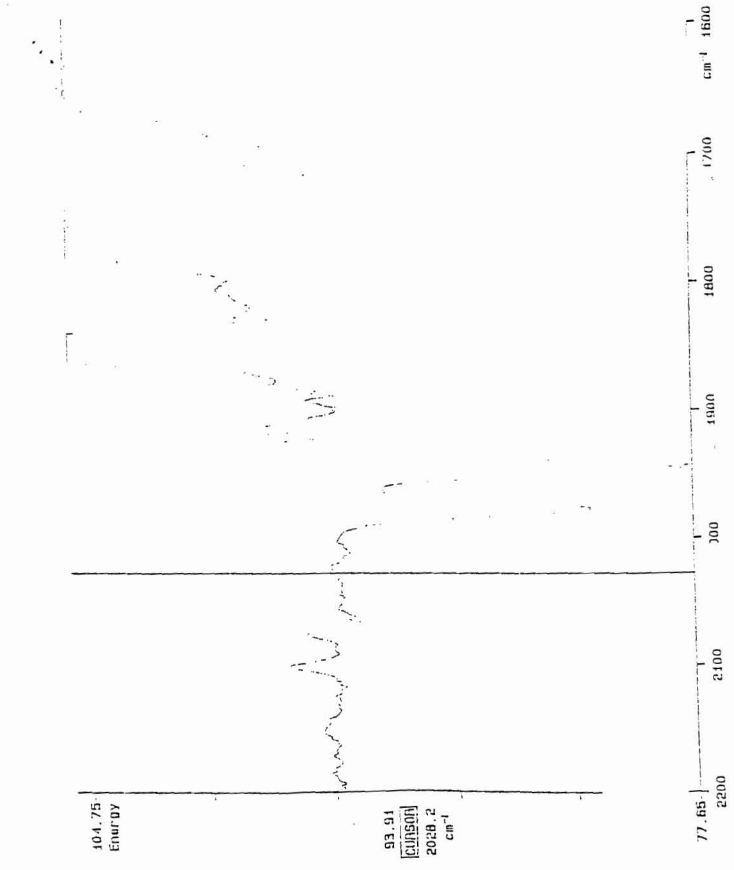

FIGURE S-27 IR COMPOUND VIII
(AFTER 9.5 HOURS)

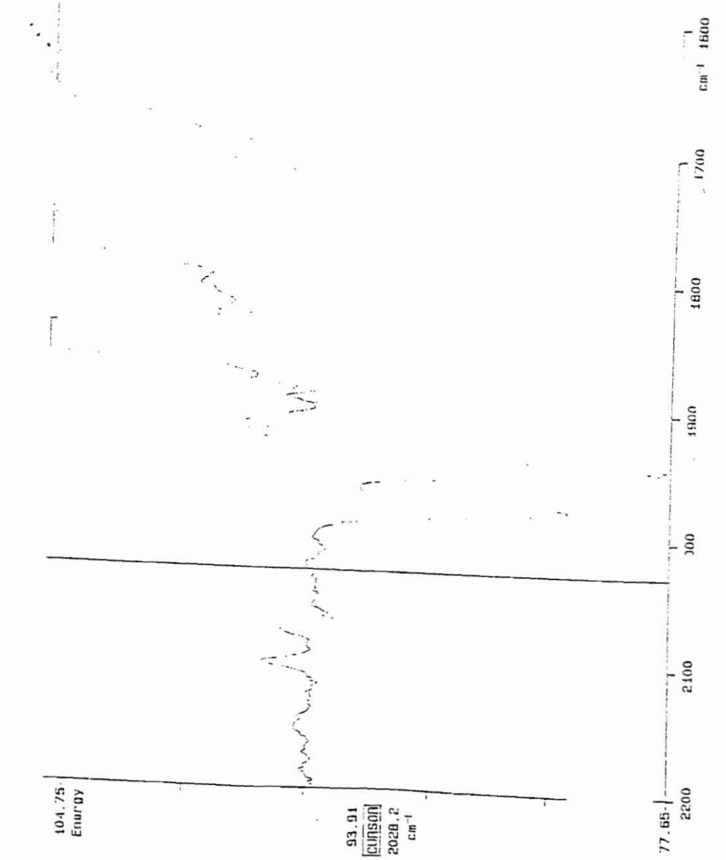

FIGURE S-28 IR COMPOUND VIII
(AFTER 4.5 HOURS)

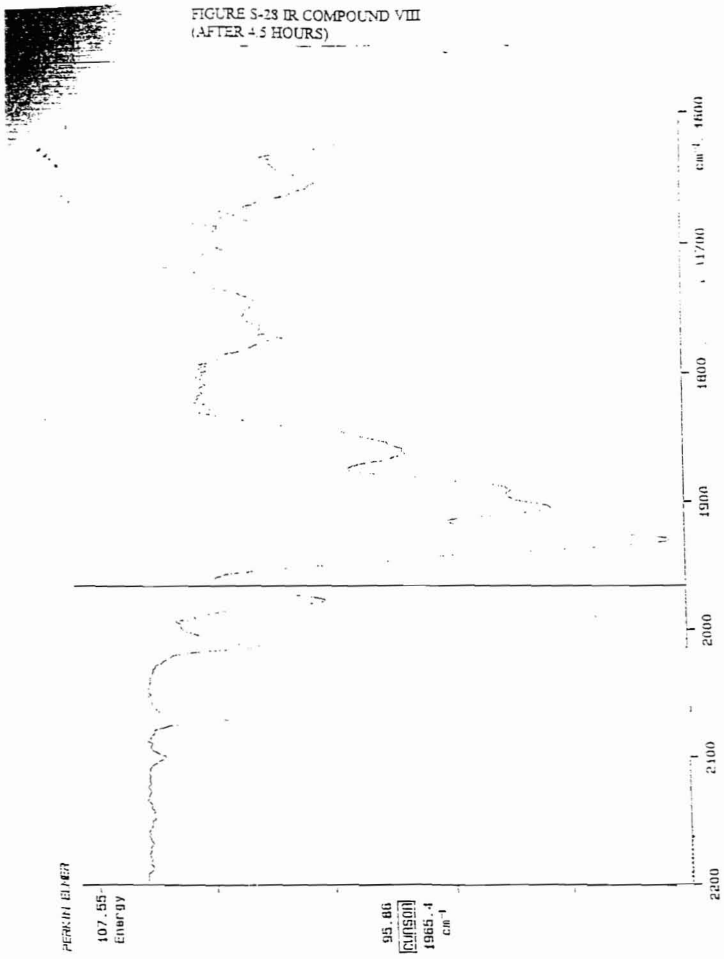

FIGURE S-28 IR COMPOUND VIII
(AFTER 4.5 HOURS)

FIGURE S-29 IR COMPOUND IV

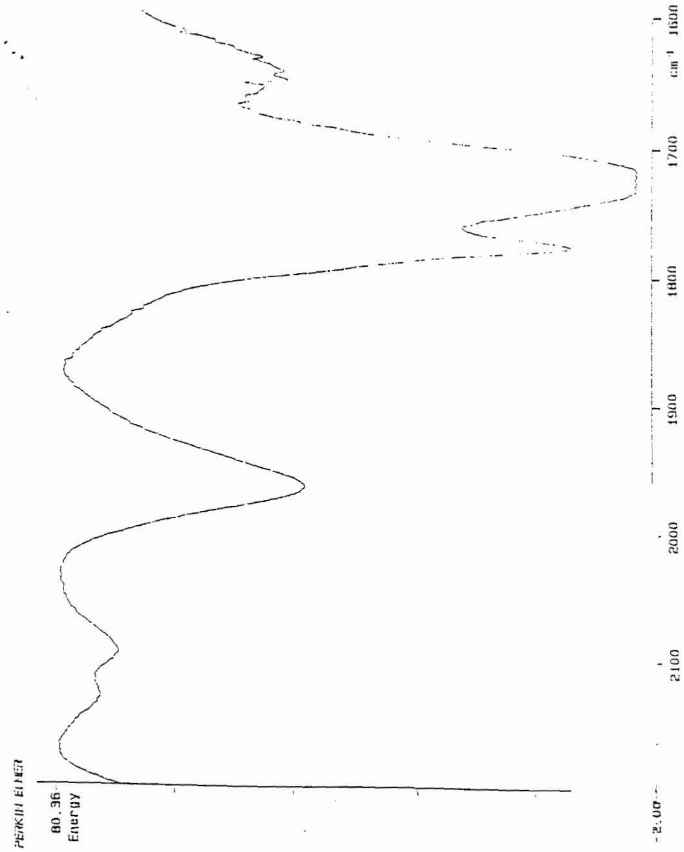

FIGURE S-29 IR COMPOUND IV

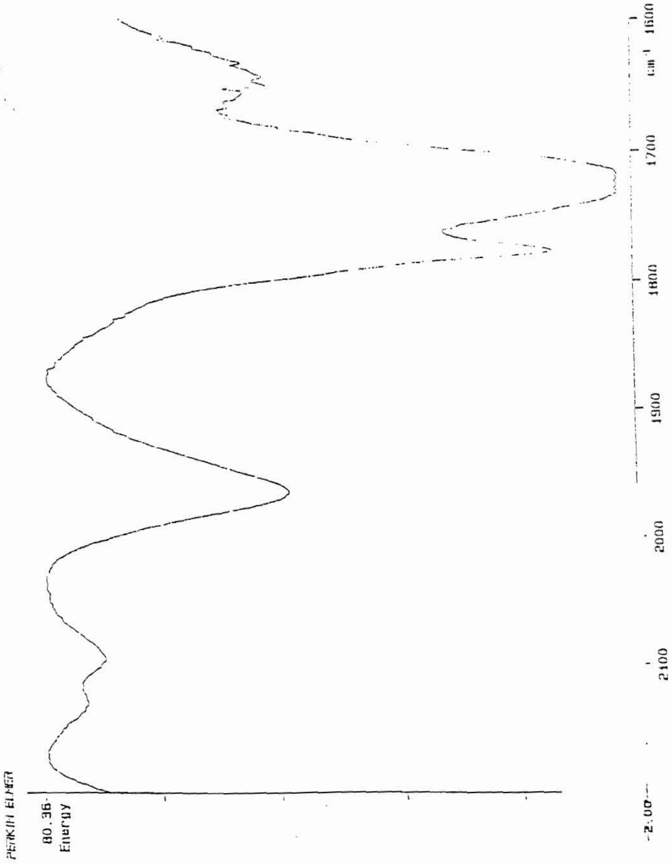

FIGURE S-30 IR COMPOUND II

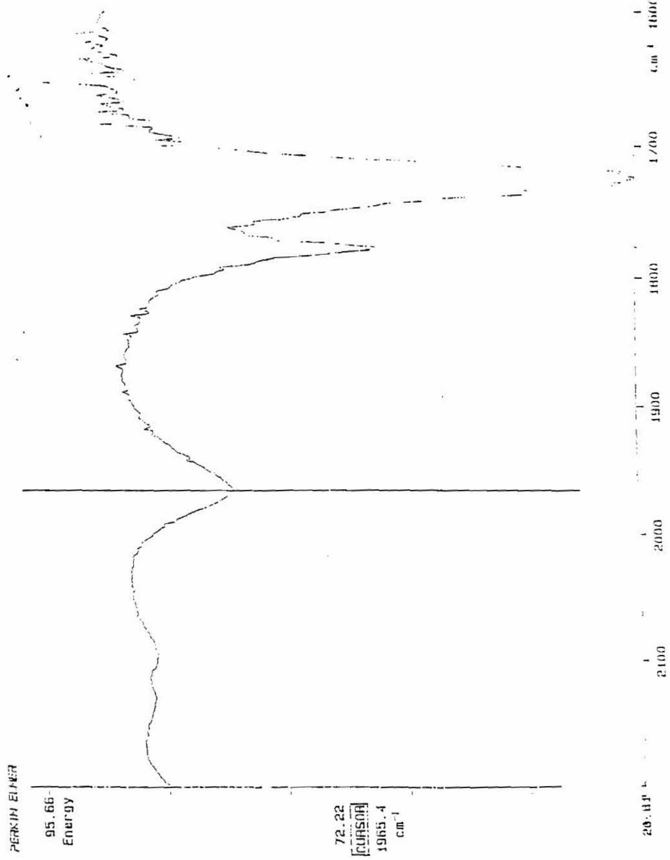

FIGURE S-30 IR COMPOUND II

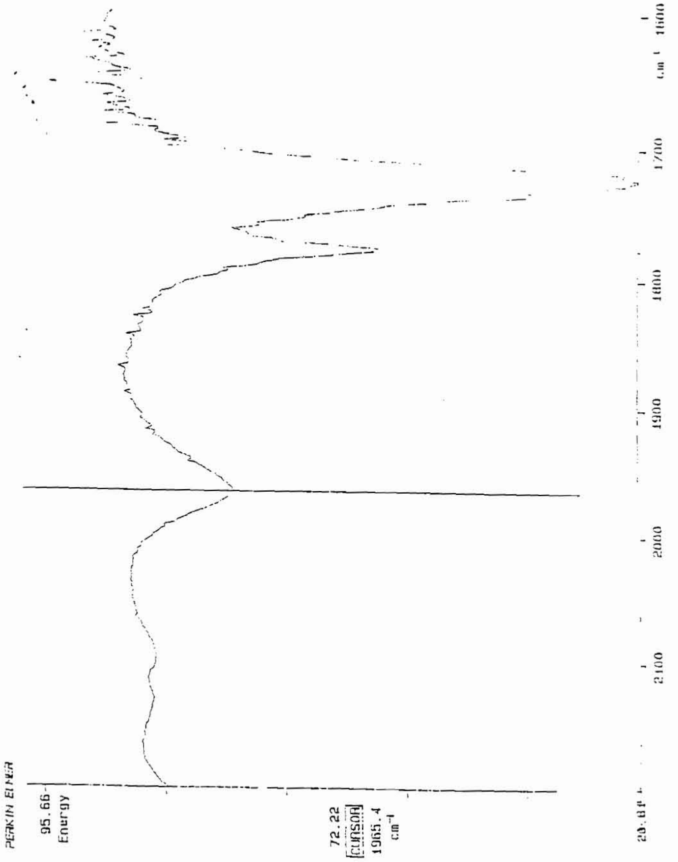

FIGURE S-31 CYCLIC VOLTAMMETRY OF
OF (η^5-DBT)Mn(CO)$_3$BF$_4$ GC .1 V/s