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**SYNTHESIS AND CHARACTERIZATION OF THREE SERIES OF NEW FERROCENYL AMINE
SULFIDE AND SELENIDE COMPLEXES OF GROUP 10 METALS AND THEIR APPLICATIONS TO
CATALYSIS AND ASYMMETRIC SYNTHESIS**

By

Ahmad Alavi Naiini

A DISSERTATION

**Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of**

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Department of Chemistry

1989

ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF THREE SERIES OF NEW FERROCENYL AMINE SULFIDE AND SELENIDE COMPLEXES OF GROUP 10 METALS AND THEIR APPLICATIONS TO CATALYSIS AND ASYMMETRIC SYNTHESIS

BY

Ahmad Alavi Nalini

Two series of new ferrocenyl amine sulfide and selenide ligands, (S,R)-[ER]C₅H₄FeC₅H₃[CHMeNMe₂][ER] and [ER]C₅H₄FeC₅H₃[CH₂NMe₂][ER] (E = S and Se; and R = Me, Et, n-Pr, i-Pr, n-Bu, sec-Bu, t-Bu, i-Pent, Ph, Bz, 4-tolyl, and 4-Cl-Ph) have been synthesized via lithiation of proper ferrocene precursors, first in the presence of ether and then TMEDA followed by treatment with appropriate disulfides and diselenides. These compounds, which are air stable, have been characterized by ¹H and ¹³C NMR, IR, MS, and elemental analysis. These ligands chelate platinum and palladium chloride to form the heterobimetallic complexes (S,R)-[ER]C₅H₄FeC₅H₃[CHMeNMe₂]-[ER][MCl₂] and [ER]C₅H₄FeC₅H₃[CH₂NMe₂][ER][MCl₂], (E = S and Se; R = Me, Et, n-Pr, i-Pr, Ph, Bz, 4-tolyl, and 4-Cl-Ph; M = Pd and Pt). A series of chiral platinum ferrocenyl amine sulfide, (R,S)-C₅H₃FeC₅H₃[CHMeNMe₂][SR][PtCl₂], (R = Me, Et, i-Pr, and Ph) have also been prepared by reaction of (PhCN)₂PtCl₂ and appropriate ferrocenyl amine thioether ligands. ¹H NMR, IR, MS and elemental analysis data were

obtained for the complexes. An x-ray structure of $[\text{SMe}] \text{C}_5\text{H}_4\text{FeC}_5\text{H}_3[\text{CH}_2\text{NMe}_2] \text{--} [\text{SMe}][\text{PdCl}_2]$ was determined .

High chemo- and regioselectivities have been achieved for the reduction of carbon-carbon double bonds of conjugated dienes and α - β unsaturated carbonyls, carboxylic acids, esters, amides, and nitriles by using new palladium ferrocenyl amine sulfide complexes.

Some platinum complexes, $\text{CpFeC}_5\text{H}_3[\text{CHMeNMe}_2][\text{SR}][\text{PtCl}_2]$; R = (Me, Et, i-Pr, Ph), were examined for their catalytic activities toward hydrogenation of 1,3-cyclooctadiene and it was found that they are far less active and selective than palladium analogs.

The reaction of NiCl_2 with chiral ligands $[\text{S,R}][\text{SR}]\text{C}_5\text{H}_4\text{FeC}_5\text{H}_3[\text{CHMeNMe}_2] \text{--} [\text{SR}]$, (R = Et, sec-Bu, Ph, and 4-Cl-Ph) produced in situ nickel complexes which are active catalysts for asymmetric Grignard cross-coupling reactions between allyl magnesium chloride and 1-phenyl-1-chloroethane.

The structure of $\text{CpFeC}_5\text{H}_3[\text{CH}_2\text{NMe}_2][\text{S-t-Bu}]$ was determined by an x-ray crystal structure study.

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DEDICATION

As this year marks the twentieth anniversary of my father's death, I would like to dedicate this thesis to him.

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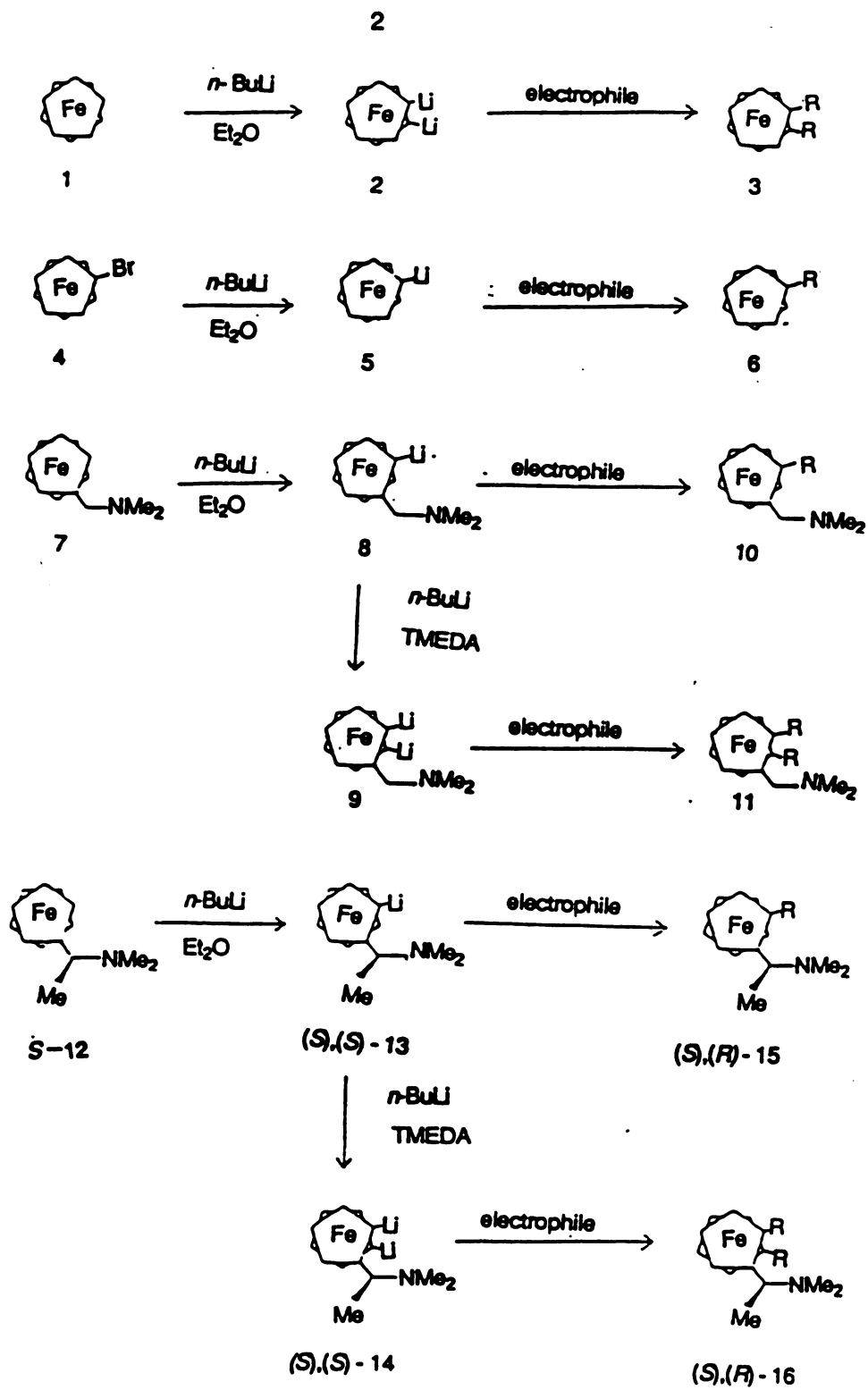
INTRODUCTION

INTRODUCTION

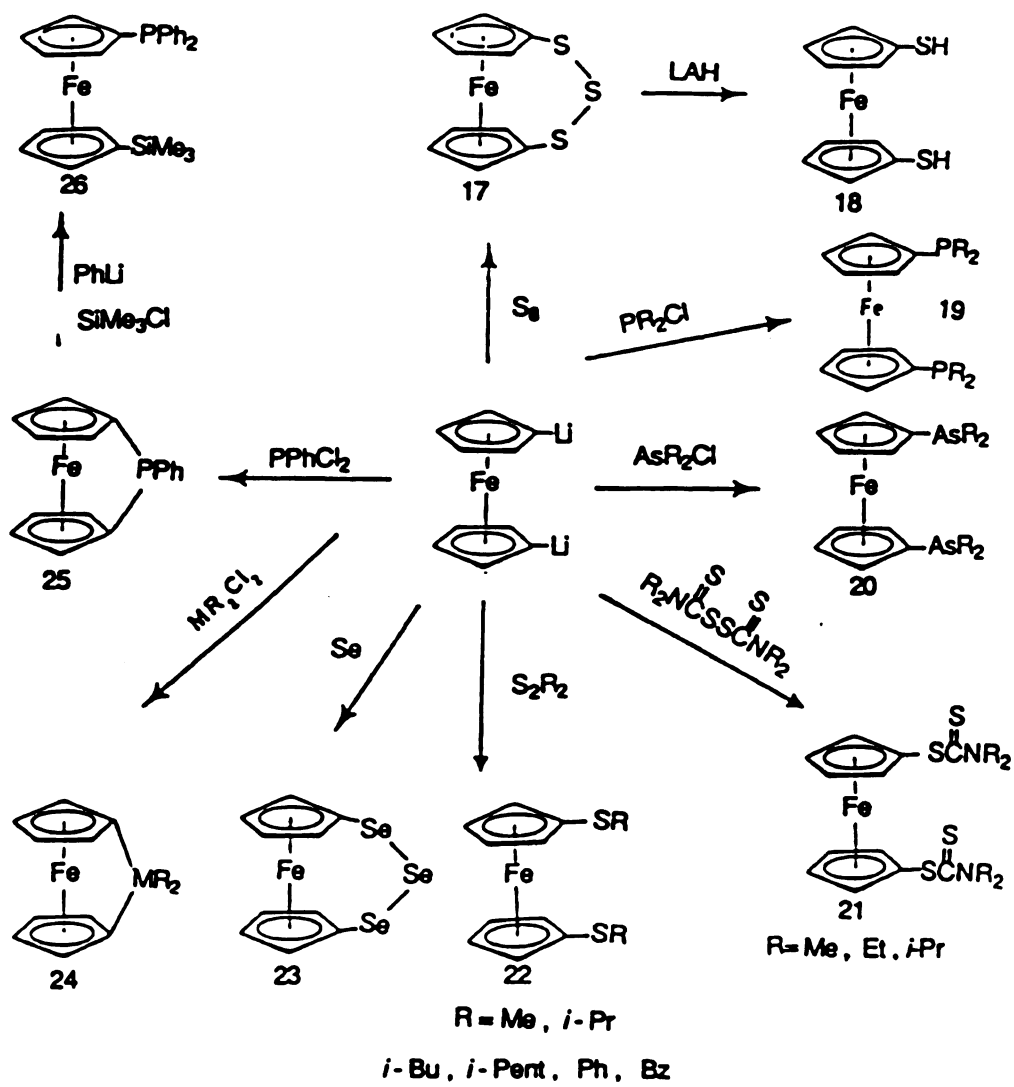
Since the first appearance of biscyclopentadienyliron(II) (ferrocene),¹ its chemistry has attracted much interest, mainly because of stability and unusual reactivity of ferrocene and its derivatives. The Cp (Cp = C₅H₅) rings display the chemistry of aromatic ring,⁵ however, ferrocene is more reactive than benzene toward electrophilic reagents and undergoes acylation, formylation, alkylation, mercuration, and sulfonation.² These substitution reactions are mostly electrophilic while electrophiles should not be able to oxidize iron or destroy the cyclopentadienyl ring-metal bond.

Reactive functional groups also can be introduced to the Cp ring via metallation. A large number of compounds have been synthesized by reaction of lithiation products 2, 5, 8, 9, 13, 14 (Scheme 1) of ferrocene 1, bromoferrocene 4, [(dimethylamino)methyl]ferrocene 7 and [1-(dimethylamino)ethyl]ferrocene 12 with different electrophiles. Among the various compounds derived from 1,1'-dilithioferrocene 2 are those where the electrophilic atom comes from group 14 (3, R=organic group³ and silyl group⁴), group 15 (3, R=AsMe₂, AsPh₂, PMe₂, PPh₂⁵ and P(*t*-Bu)₂⁶) and transition metals (3, R=AuPPh₃⁷ and Cu⁸). Compounds 6 (R=CO₂H, SiPh₃, SiMe₃, (Ph₂OH)⁹) have been synthesized via reaction of proper electrophiles with ferrocenyllithium 5¹⁰. Scheme 2 shows other reactions of compound 6. Electrophiles have been used to give 10 (R=PPh₂¹¹, SiMe₃¹², 2-Pyridyl¹³, ((OH)Ph₂¹⁴), Cl¹⁵ and B(OH)₂¹⁶ (Scheme 3). A wide variety of stereoisomers of 15 and 16 have been prepared¹⁷⁻³³ (Scheme 4). The resolution of 12 into its R and S enantiomers³⁴ let extensive studies of these compounds as chiral ligands in catalysis.

Lithiation of optically resolved N,N-dimethyl-1-ferrocenylethylamine 12, followed by treatment with chlorophosphines produce chiral ferrocenylphosphines.¹⁹ It



Scheme 1



Scheme 2



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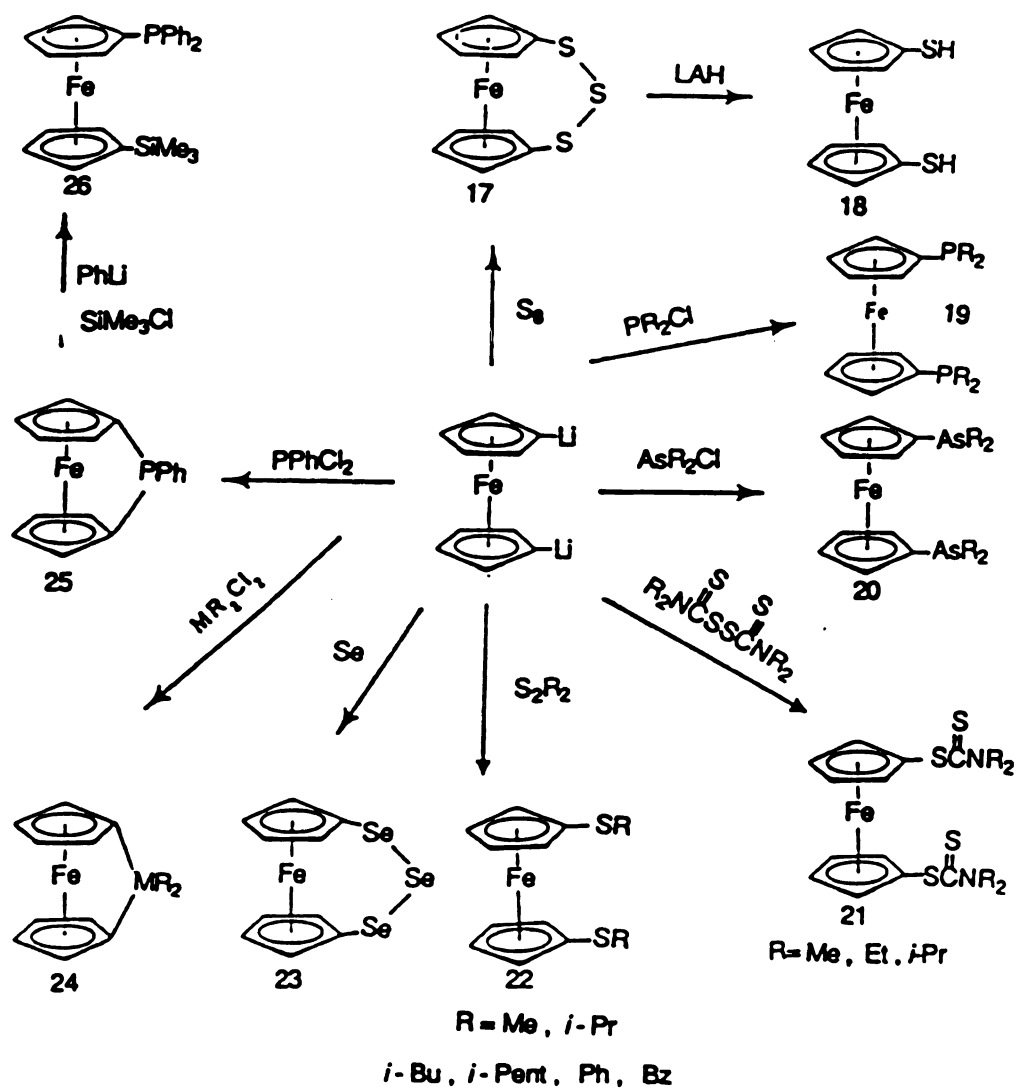


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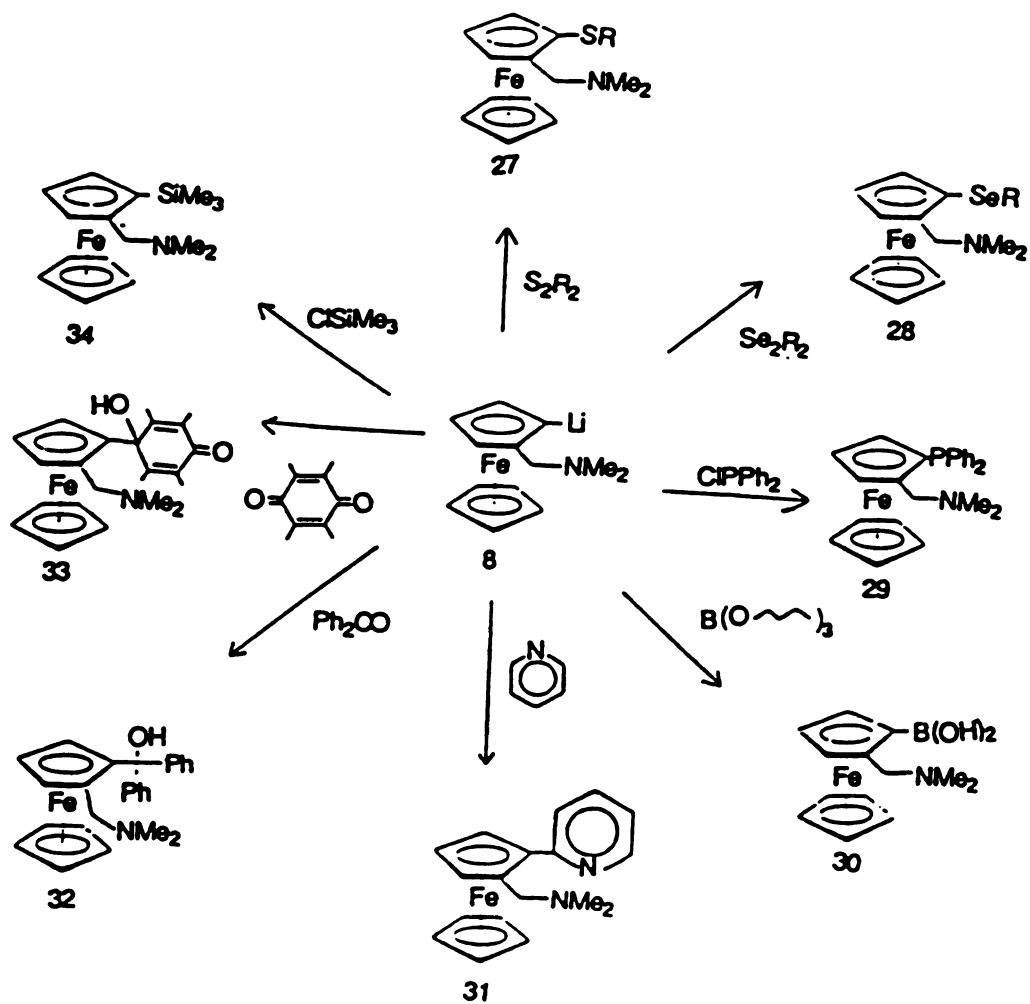
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Scheme 2



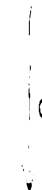
Scheme 3



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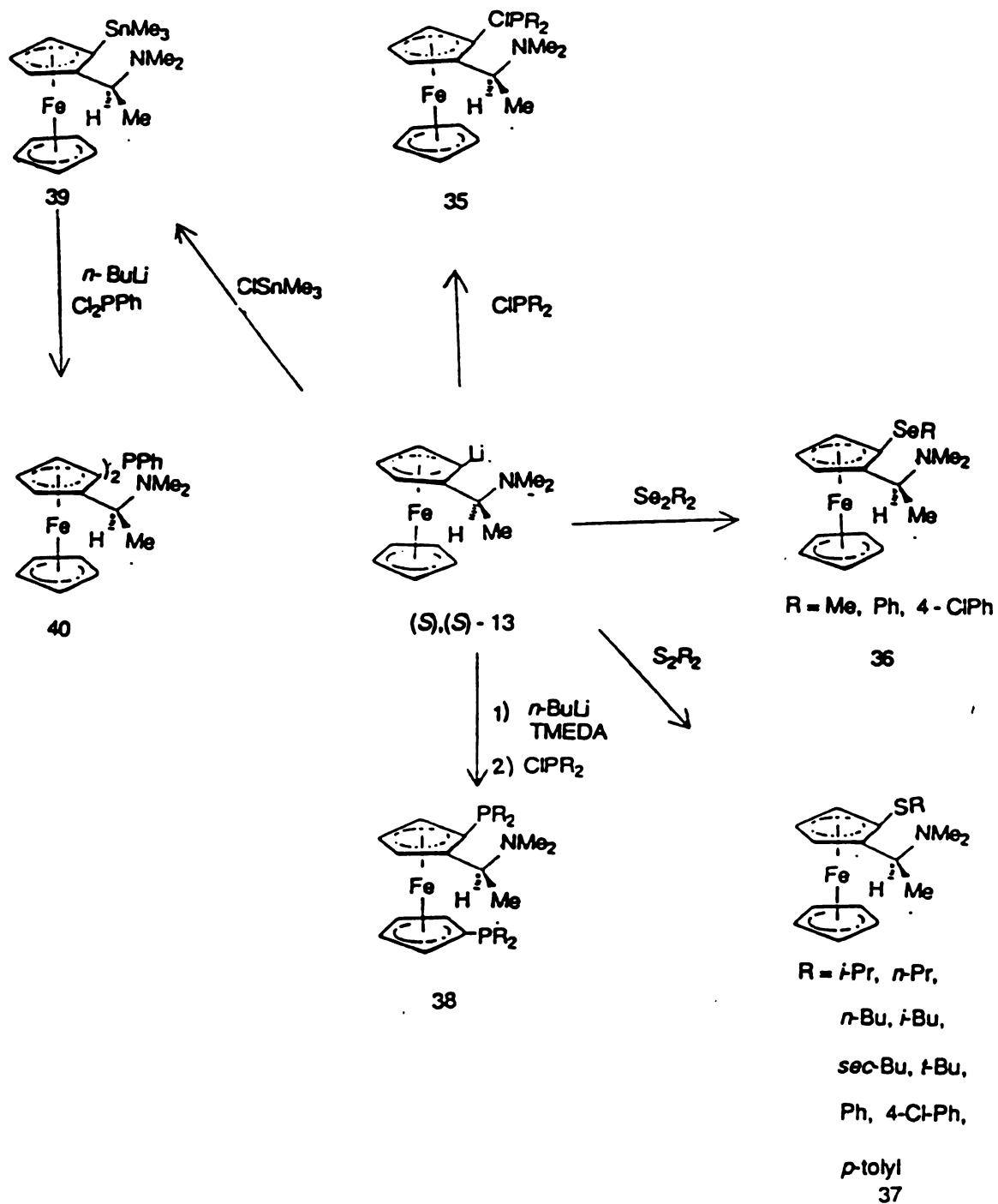
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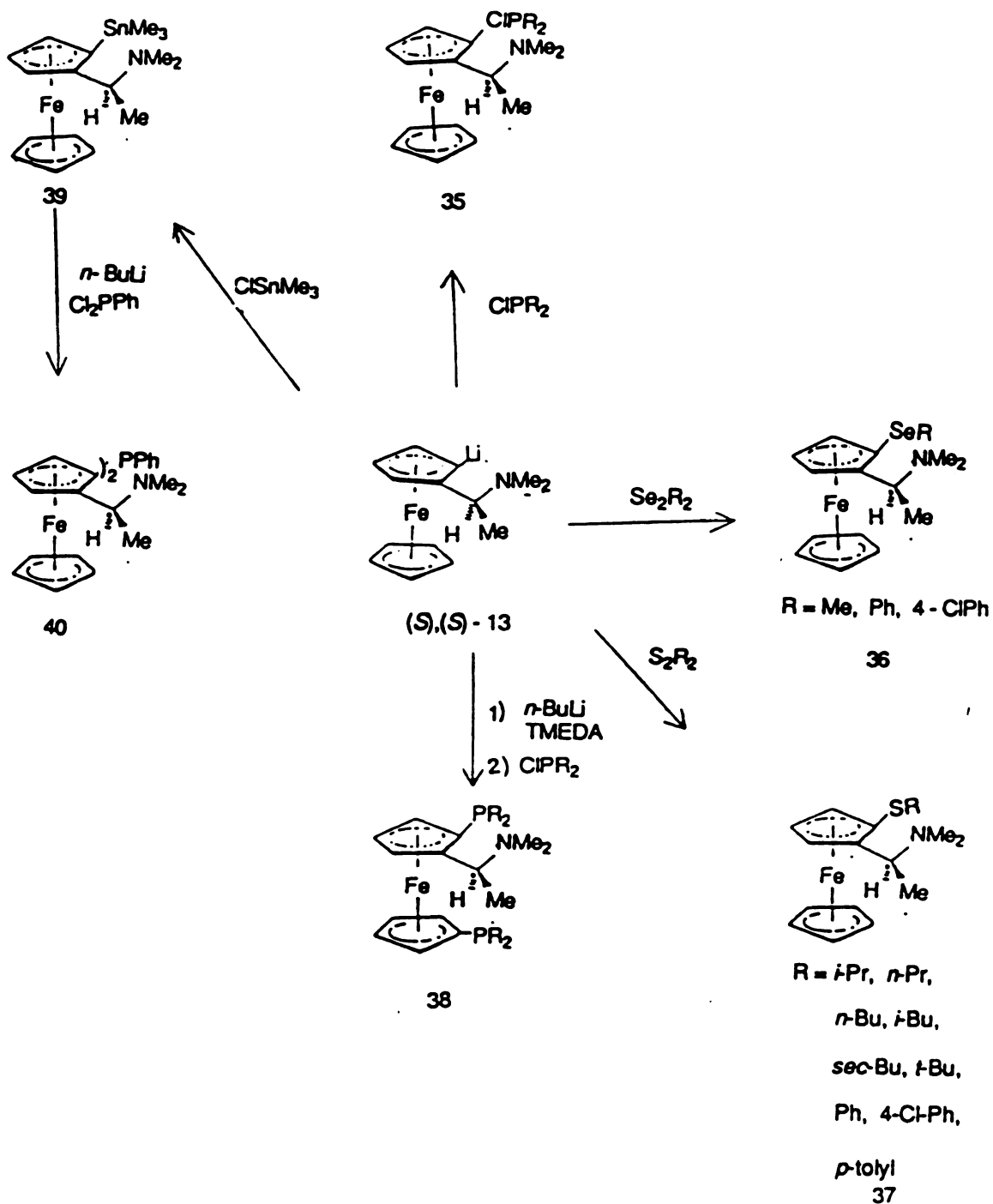
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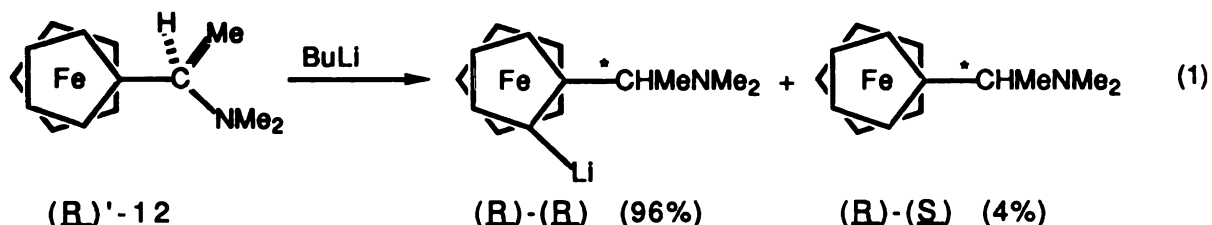


Scheme 4

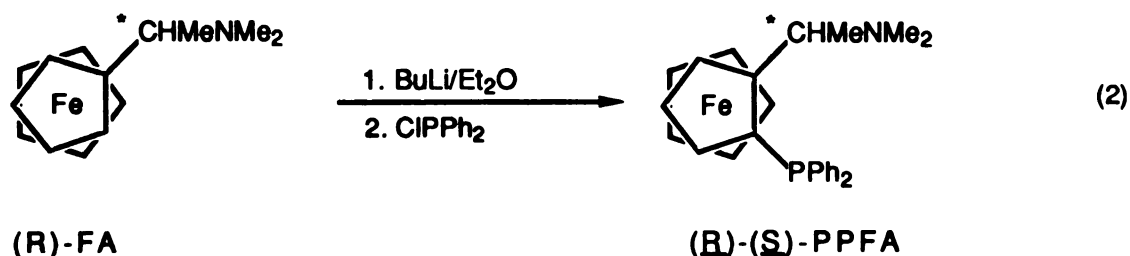


Scheme 4

It has been reported²⁶ that the lithiation of (*R*)-12 proceeds with high stereoselectivity to give mainly (*R*)- α -[(*R*)-2-lithioferrocenyl]ethyl dimethylamine.

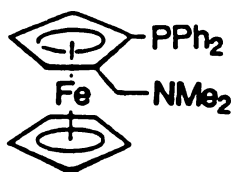


(*R*)-*N,N*-dimethyl[1-[(*S*)-2-(diPhenylPhosphino)ferrocenyl]]-amine[(*R*)-(*S*)-PPFA] has been synthesized by reaction of (*R*-7) with *n*-BuLi followed by introduction of chlorophosphines¹⁹, reaction 2.

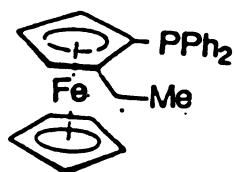


(*R*)-(*S*)-PPFA has planar chirality due to 1,2-unsymmetrically substituted ferrocene structure, central chirality and also a functional group. Kumada and co-workers have also synthesized other chiral ferrocenyl phosphines¹⁹, some of them are shown in Scheme 5. These ligands have been used extensively to prepare Pd, Pt, and Ni compounds which are useful catalysts in asymmetric hydrogenation of olefins,^{21,35} asymmetric hydrogenation of ketones,³⁶ asymmetric hydrosylation of ketones,¹⁷ and asymmetric Grignard cross-coupling reactions.^{18,37-42} Recently in this laboratory analogous ferrocenyl sulfide and selenide amine were prepared.⁴³⁻⁴⁸ Examples of these compounds are 21, 22 (Scheme 2), 27 (*R*=Me, Et, *n*-Pr, *i*-Pr, *n*-Bu, *i*-Bu, *i*-Pent, Ph, 4-ClPh, *p*-tolyl), 28 (*R*=Me, Ph, 4-ClPh) (Scheme 3), 36 and 37 (Scheme 4).

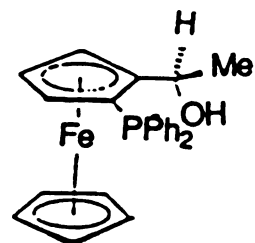
Scheme 6 and 7 show the preparation of Pd complexes of these ligands.



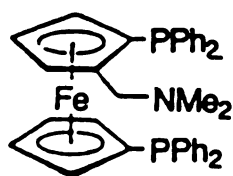
FcPN



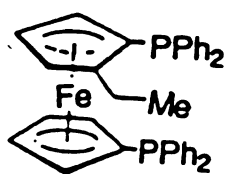
PPEF



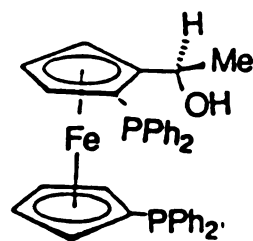
PPFOH



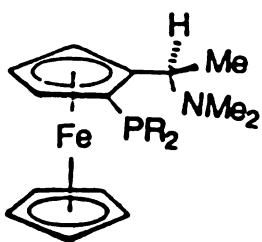
FcPPN



BPPEF

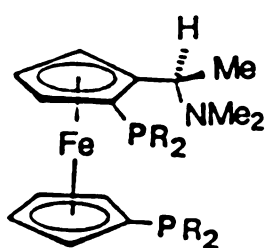


BPPFOH



R=Ph; PPFA

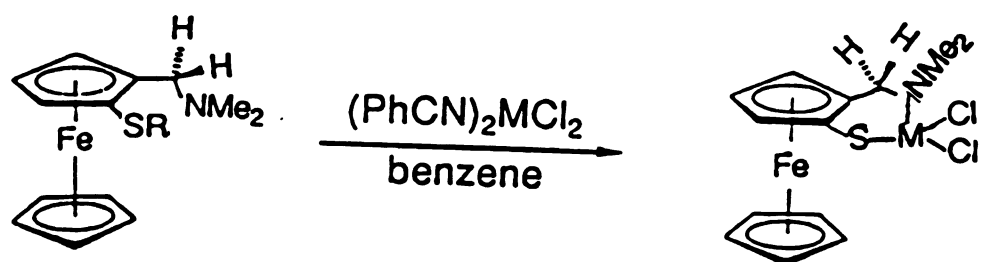
R=Ph; MPFA



R=Ph; BPPFA

R=Me; BMPFA

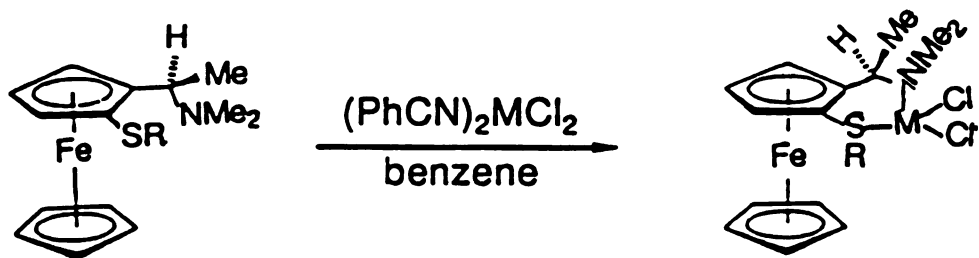
Scheme 5



M=Pd, R=Me

Et
i-Pr
n-Bu
i-Bu
t-Bu
i-Pent
 Ph
 Bz
 4-tolyl
 4-Cl-Ph

Scheme 6



$\text{M}=\text{Pd}$, $\text{R}=\text{Me}$
 $i\text{-Pr}$
 $n\text{-Pr}$
 $i\text{-Bu}$
 Ph
 $p\text{-tolyl}$
 4-Cl-Ph

Scheme 7

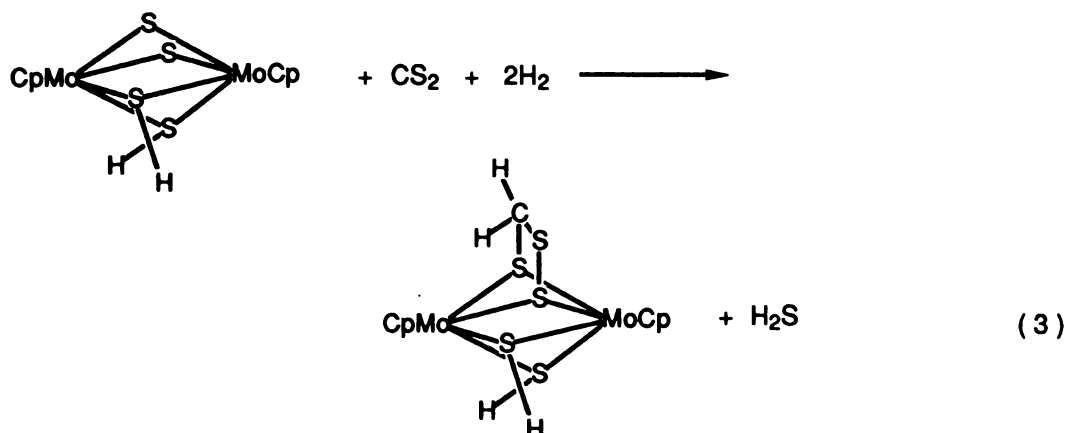


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Strong coordinating and absorptive properties of sulfur-containing complexes, cause them to block reactive metal sites and therefore act as poisons for noble metal catalysts.⁴⁹ However, interesting catalytic activities were displayed by many transition-metal sulfides.⁵⁰ Recently catalytic applications of transition-metal complexes with sulfide ligands have been reviewed.⁵¹ It has been found that under mild homogeneous conditions hydrogen can be activated by $(\text{CpMo})_2(\mu\text{-S})_2(\mu\text{-S}_2)$ to produce $(\text{CpMo})_2(\mu\text{-S})_2(\mu\text{-SH})_2$.⁵² The product was used as a catalyst for the formation of HD from a mixture of deuterium and hydrogen.⁵³ This sulfide complex also under mild conditions, catalyzed the hydrogenation of N=N bonds in azo compound to prepare the corresponding hydrazines.⁵² $(\text{CpMo}(\mu\text{-S}))_2\text{S}_2\text{CH}_2$ has similar catalytic activity and it has also catalyzed the hydrogenation of C=N bonds in isothiocyanate, isocyanates and imine to prepare thioformamides, formamides and amines.

Hydrogenolysis of elemental sulfur to give hydrogen sulfide has been achieved under 2-3 atm of hydrogen, by use of $[\text{Me}_n\text{CpMo}(\mu\text{-S})(\mu\text{-SH})]_2$ (Me=0, 1, 5).⁵³ It also has been found that $[(\text{Me}_5\text{Cp})\text{Mo}(\mu\text{-S})(\mu\text{-SH})]_2$ can be used as catalyst for the reduction of SO_2 in CHCl_3 at 75°C under 2.8 atm of H_2 .⁵⁴

Reduction of carbon disulfide to hydrogen sulfide and thioformaldehyde was achieved by use of catalytic amounts of $(\text{CpMo}(\mu\text{-S}))_2\text{S}_2\text{CH}_2$ (reaction 3) under 1-2



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of hydrogen at 70°C.⁵⁵ As it is shown in reaction 3, H₂CS has been stabilized by interaction with the sulfido ligand. This catalyst also has been used, under 2-3 atm of H₂, to convert bromoethylbenzene and β-bromostyrene to ethylbenzene.⁵⁶

Among various clusters that contain sulfide and have been examined for catalytic activity [Rh₁₇S₂(CO)₃₂]³⁻ is the largest. This cluster contains an antiprismatic arrangement of rhodium atoms. Two sulfide atoms are placed in an interlayer cavity (Figure 1).

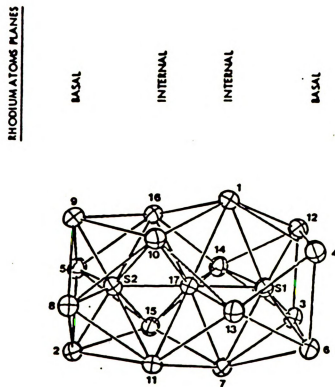


Figure 1. ORTEP diagram of [Rh₁₇(S)₂(CO)₃₂]³⁻ with the carbon monoxide ligands omitted.

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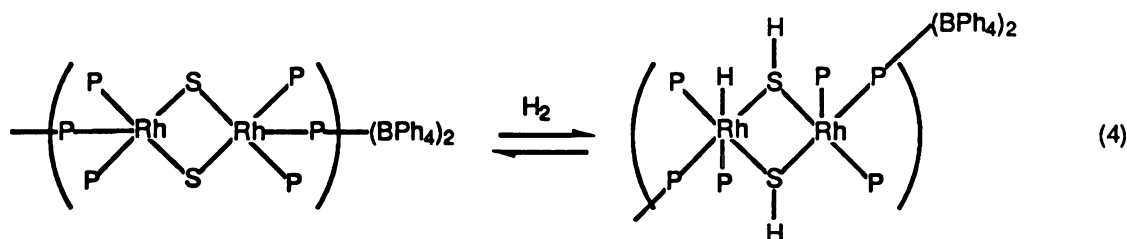
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Under 1 atm pressure of H_2 at $25^\circ C$ in THF, the reduction of phenylglyoxal to (2-hydroxyethyl)benzene have been achieved by use of this cluster as catalyst.⁵⁷ This cluster was also found to catalyze conversion of CO/H_2 (1 : 1) to give ethylene glycol and methanol in the presence of promoters and under much more vigorous conditions.^{58,59}

The complex $Ir_2(\mu-S)(CO)_2(dppm)_2$ where dppm is bis(diphenylphosphino)-methane), reacts with hydrogen molecule to produce $Ir_2H_2(\mu-S)(CO)_2(dpm)_2$.⁶⁰ Presence of both terminal and bridging hydride isomers were proved by characterization of products. At $80^\circ C$ and in toluene solution, olefins and acetylenes were hydrogenated by use of this hydride complex as a catalyst. H_2 has been activated by use of a dinuclear rhodium complex with bridging sulfide ligands (eq. 4).⁶¹



Reaction of $(\eta^3-2-CH_3C_3H_4)Pd$ and H_2S give $(\eta^3-2-CH_3C_3H_4Pd)_4S_2$ as the product.⁶² This tetranuclear palladium cluster has been used as a homogeneous catalyst, or catalyst precursor to hydrogenate 3-hexyne at ambient conditions.⁶³ Cis-3-hexene is the initial product but it is isomerized under reaction conditions. Mixed palladium-platinum and palladium-nickel clusters are insoluble in the reaction condition and show lower catalytic activity. $[Rh(C_2H_4)_2Cl_2]_2$ reacts with $Pt_2(\mu-S)_2(PPh_3)_4$ to give trinuclear complex $[(Ph_3P)_4Pt_2(\mu-S)_2Rh(C_2H_4)_2]PF_6$.⁶⁴ This complex was used as a catalyst for hydrogenation of cyclohexene, however, its catalytic activity under 1 atm pressure of hydrogen and $25^\circ C$ was almost 1/500 of the Wilkinson's catalyst.

$[Fe_4S_4Cl_4]^{2-}$, a tetranuclear iron cluster with sulfide ligands, has been used as a catalyst for hydrogenation of diphenylacetylene and cis- and trans-stilbene to the

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corresponding alkane in the presence of PhLi.⁶⁵ Related thiolate clusters such as $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}$ did not show such catalytic activity, therefore, it is believed that the lability of chloride ligands is important in this system. A mixture of $[\text{Fe}_4\text{S}_4\text{Cl}_4]^{2-}$ /PhLi also found to serve as a catalyst in the hydrogenation of octene to octanes. Furthermore, this system can selectively promote the reduction of terminal double bonds in dienes and monoenes.⁶⁶

The interesting catalytic activity of transition metal sulfides and also previous results obtained by Brubaker and co-workers, which showed some Pd complexes of ferrocenylamine sulfides are good catalysts for hydrogenation of dienes to monoenes^{45,48} under homogeneous and heterogeneous conditions and some have catalytic activity for asymmetric Grignard cross-coupling reactions,⁴⁷ led us to this work. The aim of this research was to prepare two new series of ferrocenylamine sulfide and selenide ligands and use them to prepare new complexes of the Ni triad. Investigation of catalytic activity of these previously unknown complexes and, also, their structural elucidation was carried out.

EXPERIMENTAL

EXPERIMENTAL

Air sensitive reagents were manipulated in a prepurified argon or nitrogen atmosphere. Standard Schlenk-ware techniques and a vacuum line was employed. Where necessary an argon-filled glove box was used for transfers.

Infrared spectra (IR) were obtained by use of a Perkin-Elmer 457 grating spectrophotometer or a Perkin-Elmer 599 grating spectrophotometer or a Nicolet 740 FT-IR spectrophotometer by using neat films of liquid samples, Nujol mulls between CsI plates or in KBr pellets for solid samples. Mass spectra (MS) were obtained by means of a Finnigan 4000 instrument with an Incos data system at 70 ev. Optical rotations were determined with a Perkin-Elmer 141 Polarimeter. ^1H and ^{13}C NMR were obtained by use of a Bruker WM-250 spectrometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Gas chromatography (GC) was carried out by using a Hewlett-Packard 5880, and a Varian 1400 instrument.

All melting points were determined by using a Thomas-Hoover capillary melting point apparatus and were uncorrected.

All solvents used were reagent grade and were distilled by standard methods.⁶⁷ (S)-N,N-dimethyl-1-ferrocenylethylamine(S-12) and (R)-N,N-dimethyl-1-ferrocenylethylamine(R-12) were prepared according to Ugi's procedure³⁴. Dimethylaminomethyl ferrocene, dialkyl and diaryl disulfides, dimethyl and diaryl diselenides and N,N,N',N'-tetramethylethylenediamine (TMEDA) were purchased from Aldrich Chemical Company. Bis (benzonitrile) complexes $[(\text{PhCN})_2\text{MCl}_2]$ where M=Pd and Pt, were prepared according to published procedures.^{68,69} All the hydrogenation substrates were obtained from Columbian Carbon Co., Columbian Organic Chemical Co. and Aldrich Chemical Co. These reagents were re-treated by standard methods before use. The Grignard cross-coupling substrate, 1-Phenylethyl chloride, was prepared as previously reported;⁷⁰ allylmagnesium chloride (2 M solution in THF) were obtained

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from Aldrich Chemical Co. The ^1H NMR chiral shift reagents, tris(d,d-dicampholymethanato)europium(III) $[\text{Eu}(\text{dcm})_3]$, was obtained from Alfa Products. A pressure bottle with a gauge was used to perform the hydrogenations.

X-ray structure determinations were performed by use of a Nicolet P3F computer controlled 4-circle diffractometer equipped with a graphite crystal incident beam monochromator.

A. Preparation of Ligands

**(R)-[1-(Dimethylamino)-ethyl]ferrocene[(R)-12] and
(S)-[1-(Dimethylamino)-ethyl]ferrocene[(S)-12].**

N,N-dimethyl-1-ferrocenylethylamine(12) was prepared and resolved by using (R)-(+)-tartaric acid by a modification of Ugi's procedure.³⁴ In the recrystallization of 1-ferrocenylethyl alcohol, a mixture of CH_2Cl_2 /heptane or CH_2Cl_2 /hexane was used in place of pure heptane and, consequently, a higher yield was achieved. The (R)-(+)-amine tartarate crystals were recovered from the mother liquor by treatment with diethylether and then recrystallized three times from 1:10 water:acetone, allowing about 17 mL of solvent for each g of salt. The (S)-(-)-amine tartarate crystals filtered off readily as previously reported.³⁴ The tartarate salts were dissolved in 20% aqueous NaOH solution and extracted with methylene chloride. The amine solution was dried over anhydrous K_2CO_3 and evaporated to give a dark brown oil that partially solidified on cooling. $[\alpha]_{\text{D}}^{25} -14.1^\circ$ for (S)-1-(dimethylamino)-ethylferrocene[(S)-12] and $[\alpha]_{\text{D}}^{25} +14.1$ for (R)-1-(dimethylamino)-ethylferrocene[(R)-12].

^1H NMR (δ ppm), 4.11(m, 4H, C_5H_4); 4.08(s, 5H, Cp); 3.60(q, $J=6.8\text{Hz}$, 1H, CH); 2.09(s, 6H, NMe_2); 1.46(d, $J=6.8\text{Hz}$, 3H, NHCH_3).

^{13}C NMR (δ ppm), 86.2(s, C_1); 68.5(d, $J=91\text{Hz}$, C_{2-5}); 67.7(d, $J=88\text{Hz}$, Cp); 66.5(d, $J=92.4\text{Hz}$, C_2 , C_3 , C_4 , C_5); 66.3(d, $J=9.2\text{Hz}$, C_2 , C_3 , C_4 , C_5); 65.9(d,

$J=91.4\text{ Hz}$, C_2 , C_3 , C_4 , C_5); $57.8(\text{d}, J=67.3\text{ Hz}, \text{NCH})$; $40.2(\text{q}, J=47.4\text{ Hz}, \text{NMe}_2)$; $14.8(\text{q}, J=42.9\text{ Hz}, \text{NCHMe})$.

MS m/e (relative intensity): 257(83, M^+), 242(95, $M^+-\text{Me}$), 213(100, $M^+-\text{NMe}_2$), 212(36, $M^+-\text{HNMe}_2$), 121(66, FeCp), 72(18, CHMeNMe_2), 65(3, Cp), 56(21, Fe), 44(4, NMe_2).

(S,R)-1-[1-(Dimethylamino)ethyl]-2,1'-bis(methylthio)-ferrocene.(43, R=Me)

The amine (S)-12 (1.3 g, 5.1 mmol) was dissolved in 75 mL dry ether and placed in a 200 mL round-bottomed Schlenk flask equipped with a side arm and rubber septum. The solution was cooled to -78°C and while being stirred, 3.0 mL (8.1 mmol) of a 2.7 M solution of $n\text{-BuLi}$ in hexane was added dropwise via a syringe. The orange suspension was allowed to reach room temperature and stirred overnight. Then, a solution of freshly distilled TMEDA (0.9 g, 7.5 mmol) and $n\text{-BuLi}$ (3.0 mL, 8.1 mmol) was added to the reaction mixture at -78°C . After being stirred for 8 more h at room temperature, to the reaction mixture was added dropwise, a solution of dimethyl disulfide (1.42 g, 15 mmol) at -78°C . The reaction mixture was allowed to reach room temperature and stirred under N_2 for an additional 24 h, after which saturated aqueous NaHCO_3 was added to the mixture. The resulting organic layer and ether extracts from the aqueous layer were combined, washed with cold water and dried over anhydrous Na_2SO_4 . Evaporation of the solvent gave a product mixture which was chromatographed on a silica gel column (hexane/ether) to give a brown oil: yield 90%.

^1H NMR (δ ppm), 4.26(m, 1H, H_3 , H_4 , H_5); 4.17(m, 4H, C_5H_4); 4.07(m, 2H, H_3 , H_4 , H_5); 3.90(q, $J=4.4$ Hz, 1H, CH_3CH); 2.28(s, 3H, SCH_3); 2.23(s, 3H, SCH_3); 2.09(s, 6H, NMe_2); 1.36(d, $J=4.4$ Hz, 3H, CH_3CH).

^{13}C NMR (δ ppm), 93.6(s, C_1); 85.9(s, C_2); 84.9(s, C^1_1); 73.2(d, C_5); 77.5(s, C^1_3 , C^1_4); 72.4(d, C^1_5); 71.1(d, C^1_2); 69.6(d, C_4); 68.4(d, C_3); 56.2(d, CHCH_3); 40.0 (q, NMe_2); 19.7(q, SCH_3); 19.6(q, SCH_3); 10.7(q, CH_3CH).

MS, m/e (relative intensity): 349(77, M^+), 334(24, M^+-Me), 304(38, M^+-3Me), 358(78, $\text{M}^+-\text{SMe}-\text{NMe}_2$), 72(100, MeCHNMe_2), 56(50, Fe), 44(25, NMe_2).

IR (neat, KBr disks) 3095 (ferrocene C-H stretch), 2970-2775 (alkyl C-H stretch), 1452 (ferrocene antisymmetric C-C stretch), 1265, 1249 (C-N stretch), 825 (C-H bend perpendicular to the plane of the Cp ring), 655 (S-C stretch), 491cm^{-1} (antisymmetric ring-metal stretch).

Anal. calcd. for $\text{C}_{16}\text{H}_{23}\text{S}_2\text{NFe}$: C, 55.01; H, 6.64. Found: C, 55.04; H, 6.61.

(S,R)-1-[1-(Dimethylamino)ethyl]-2,1'-bis(ethylthio)ferrocene (44, $\text{R}=\text{Et}$)

The amine (S)-12 (1.3 g, 5.1 mmol) was dissolved in 75 mL dry ether and placed in a 250 mL round-bottomed Schlenk flask equipped with a side arm and rubber septum. The suspension was cooled to -78°C and while being stirred 3.0 mL (8.1 mmol) $n\text{-BuLi}$ was added dropwise via a syringe. The orange suspension was allowed to reach room temperature and stirred overnight. A mixture of freshly distilled TMEDA (0.9 g, 7.5 mmol) and $n\text{-BuLi}$ (3.0 mL, 8.1 mmol) was then added to the reaction mixture at -78°C during a period of 10 min. After being stirred for 8 more h at room temperature, diethyl disulfide (1.83 g, 15 mmol) was added dropwise via a syringe at -78°C . The solution was allowed to reach room temperature and stirred under Ar for 36 h. After refluxing for 2 h, the reaction mixture was cooled and 30 mL of aqueous sodium bicarbonate was added. The organic layer was separated, dried and evaporated to give a brown oil. The oil was chromatographed on a silica gel by gradient elution (hexane/ether), to give a brown oil: yield 90%.

^1H NMR (δ ppm), 4.24(m, 1H, H_3 , H_4 , H_5); 4.16(m, 4H, C_5H_4); 4.05(m, 2H, H_3 , H_4 , H_5); 3.88(q, $J=6.8$ Hz, 1H, CH_3CH); 2.95(m, 1H, SCH_2); 2.65(m, 1H, SCH_2); 2.48(q, 2H, SCH_2); 2.04(s, 6H, NMe_2); 1.29(d, $J=6.8$ Hz, 3H, CH_3CH); 1.13(t, $J=7.5$ Hz, 3H, βCH_3); 1.06(t, $J=8.0$ Hz, 3H, βCH_3).

^{13}C NMR (δ ppm, CD_3COCD_3), 95.2(s, C_1); 82(s, C_2); 81.8(s, C_1); 76(d, C_3 , C_4 , C_5); 75.2(d, C_1 , C_5); 72.1(d, C_1 , C_5); 71.9(d, C_1 , C_5); 69.9(d, C_3 , C_4 , C_5); 68.8(d, C_3 , C_4 , C_5); 56.3(d, CH_3CH); 40.0(q, NMe_2); 31.2(t, SCH_2); 30.5(t, SCH_2); 15.3(q, βCH_3); 15.1(q, βCH_3); 10.1(q, CH_3CH).

MS m/e (relative intensity): 377(M^+ , 49), 362($\text{M}^+ - \text{Me}$, 19), 332($\text{M}^+ - 3\text{Me}$, 100), 152($\text{FeC}_5\text{H}_4\text{S}$, 33), 121($\text{C}_5\text{H}_3(\text{CH}_2\text{NMe}_2)$, 30), 72($\text{MeCHN}(\text{CH}_3)_2$, 33), 56(Fe , 24), 44(NMe_2 , 38).

IR (neat, KBr) 3095 (ferrocene C-H stretch), 2970-2775 (alkyl C-H stretch), 1452 (ferrocene antisymmetric C-C stretch), 1245, 1263 (C-N stretch), 837 (C-H bend perpendicular to the plane of the Cp ring), 655 (S-C stretch), 480 cm^{-1} (antisymmetric ring-metal stretch).

Anal. Calcd. for $\text{C}_{18}\text{H}_{27}\text{S}_2\text{NFe}$: C, 57.29; H, 7.21. Found: C, 57.38; H, 7.37.

(S,R)-1-[1-(Dimethylamino)ethyl]-2,1'-bis[(n-propyl)thio]-ferrocene (45, R = n-Pr)

A 2.7 M solution of n-BuLi in hexane (4.0 mL, 10.8 mmol) was added to a 10 mmol (2.55 g) (S)-[1-(Dimethylamino)ethyl]ferrocene in 100 mL dry ether at -78°C under Ar. The orange suspension was warmed to room temperature and stirred for 8 h. Then a solution of freshly distilled TMEDA (1.20 mL, 10.0 mmol) and n-BuLi (4.0 mL, 10.8 mmol) was added to the reaction mixture at -78°C . After being stirred overnight at room temperature, to the reaction mixture was added dropwise a solution of (4.52 g, 30 mmol) di(n-propyl) disulfide in 20 mL ether over a 20 min period at -78°C . The reaction mixture was stirred for 3 h at room temperature, then refluxed for

another 12 h. The workup is identical with that reported for 44, R-Et. The product was obtained as a brown oil: yield 83%.

^1H NMR (δ ppm), 4.31(m, 1H, H₃, H₄, H₅); 4.20(m, 4H, C₅H₄); 4.08(m, 2H, H₃, H₄, H₅); 3.94(q, J=6.8 Hz, 1H, CH₃CH); 2.80(m, 1H, SCH₂); 2.62(m, 1H, SCH₂); 2.52(m, 2H, SCH₂); 2.10(s, 6H, NMe₂); 1.58(m, 2H, β CH₂); 1.51(m, 2H, β CH₂); 1.30(d, J=6.8 Hz, 3H, CH₃CH); 0.98(t, J=7.6 Hz, 3H, γ CH₃); 0.91(t, J=7.6 Hz, 3H, γ CH₃).

^{13}C NMR (δ ppm, CD₃COCD₃), 95.0(s, C₁); 82.2(s, C₂); 82.1(s, C₁); 75.9(d, C₃, C₄, C₅); 75.1(d, C¹₃, C¹₄); 72.0(d, C¹₂, C¹₅); 71.9(d, C¹₂, C¹₅); 69.9(d, C₃, C₄, C₅); 68.9(d, C₃, C₄, C₅); 56.3(d, CH₃CH); 39.9(q, NMe₂); 39.4(t, SCH₂); 38.7(t, SCH₂); 23.4(t, β CH₂); 23.2(t, β CH₂); 13.7(q, γ CH₃); 13.5(q, γ CH₃); 10.0(q, CH₃CH).

MS m/e (relative intensity): 405(M⁺, 21), 390(M⁺-Me, 8), 360(M⁺-3Me, 100), 288(M⁺-S(C₃H₇)-NMe₂, 24), 242((CH)C₅H₃FeC₅H₄(SCH₂), 64), 152(FeC₅H₄S, 30), 72(MeCHNMe₂, 34), 56(Fe, 17), 44(NMe₂, 36).

IR (neat, Csl) 3095 (ferrocene C-H stretch), 2960-2770 (alkyl C-H stretch), 1455 (ferrocene antisymmetric C-C stretch), 1250, 1235 (C-N stretch), 826 (C-H bend perpendicular to the plane of the Cp ring), 655 (S-C stretch), 479 cm⁻¹ (antisymmetric ring-metal stretch). Anal. Calcd. for C₂₀H₃₁S₂NFe: C, 59.25; H, 7.71. Found: C, 59.31; H, 7.52.

(S,R)-1-[1-(Dimethylamino)ethyl]-2,1'-bis[(1-Propyl)thio]-ferrocene (46, R=L-Pr)

The procedure was the same as for 45, R=n-Pr, except that 4.52 g (30.0 mmol) of diisopropyl disulfide was used. The product was obtained as a brown oil: yield 80%.

^1H NMR (δ ppm), 4.34(m, 1H, H₃, H₄, H₅); 4.20(m, 4H, C₅H₄); 4.10(m, 2H, H₃, H₄, H₅); 3.94(q, J=6.8 Hz, 1H, CH₃CH); 3.20(h, 1H, SCH); 2.82(h, SCH);

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2.09(s, 6H, NMe₂); 1.33(d, q=6.8 Hz, 3H, CH₃CH); 1.19(d, J=6.9 Hz, 3H, βCH₃); 1.17(d, 3H, βCH₃); 1.12(d, 3H, βCH₃); 1.09(d, 3H, βCH₃).

¹³C NMR (δ ppm, CD₃COCD₃), 96.2(s, C₁); 80.3(s, C₂); 79.4(s, C¹₁); 77.6(d, C₃, C₄, C₅); 76.9(d, C¹₃, C¹₄); 76.8(d, C¹₃, C¹₄); 72.7(d, C¹₂, C¹₅); 72.3(d, C¹₂, C¹₅); 70.1(d, C₃, C₄, C₅); 69.1(d, C₃, C₄, C₅); 56.2(d, CH₃C₁H); 39.8(q, NMe₂); 39.4(d, SC₁H); 24.2(q, βC₁H₃); 23.6(q, βC₁H₃); 23.0(q, βC₁H₃); 9.2(q, C₁H₃CH).

MS m/e (relative intensity): 405(M⁺, 43), 390(M⁺-Me, 16), 360(M⁺-3Me, 100), 286(M⁺-S(C₃H₇)-NMe₂, 15), 242((CH)C₅H₃FeC₅H₄(SCH₂), 49), 152(FeC₅H₄S, 30), 72(MeCHNMe₂, 25), 56(Fe, 19), 44(NMe₂, 44).

IR (neat, KBr) 3095 (ferrocene C-H stretch), 2960-2775 (alkyl C-H stretch), 1455 (ferrocene antisymmetric C-C stretch), 1265-1250 (C-N stretch), 826 (C-H bend perpendicular to the plane of the Cp ring), 635 (S-C stretch), 455 cm⁻¹ (antisymmetric ring-metal stretch).

Anal. Calcd. for C₂₀H₃₁S₂NFe: C, 59.25; H, 7.71. Found: C, 59.53; H, 7.49.

(S,R)-1-[1-(Dimethylamino)ethyl]-2,1'-bis[(n-butyl)thio]ferrocene (47, R=n-Bu)

The amine (S)-12 (0.65 g, 2.55 mmol) was dissolved in 50 mL dry ether and placed in a 100 mL round-bottomed Schlenk flask equipped with a side arm and rubber septum. The suspension was cooled to -78°C and while being stirred 1.5 mL (4.05 mmol) n-BuLi was added dropwise via a syringe. The orange suspension was allowed to reach room temperature and stirred overnight. Then, to the reaction mixture was added a mixture of freshly distilled TMEDA (0.45 g, 3.75 mmol) and n-BuLi (1.5 mL, 4.05 mmol) at -78°C. After being stirred for 8 more h at room temperature, dibutyl disulfide (1.34 g, 7.5 mmol) was added dropwise via a syringe at -78°C. The solution was allowed to reach room temperature and stirred under Ar for 30 h. The work-up is

identical with that reported for 45(R= η -Pr). The product was obtained as a brown oil: yield 75%.

^1H NMR (δ ppm), 4.29(m, 1H, H₃, H₄, H₅); 4.16(m, 4H, C₅H₄); 4.07(m, 2H, H₃, H₄, H₅); 3.95(q, J=6.7 Hz, 1H, CH₃CH); 2.84(m, 1H, SCH₂); 2.61(m, 1H, SCH₂); 2.52(m, 1H, SCH₂); 2.08(s, 6H, NMe₂); 1.51(m, 2H, β CH₂); 1.47(m, β CH₂); 1.45(m, 2H, γ H); 1.40(m, 2H, γ H); 1.34(d, J=6.7 Hz, 3H, CH₃CH); 0.86(t, 3H, δ CH₃); 0.82(t, 3H, δ CH₃)

^{13}C NMR (δ ppm, CD₃COCD₃), 95.2(s, C₁); 82.5(s, C₂); 82.1(s, C₁); 75.9(d, C₃, C₄, C₅); 74.9(d, C¹₃, C¹₄); 71.9(d, C¹₂, C¹₅); 71.8(d, C¹₂, C¹₅); 69.9(d, C₃, C₄, C₅); 68.8(d, C₃, C₄, C₅); 56.3(d, CH₃CH); 39.8(q, NMe₂); 39.0(t, SCH₂); 36.3(t, SCH₂); 32.2(t, β CH₃); 22.3(t, γ CH₃); 22.0(t, γ CH₃); 13.8(q, δ CH₃); 9.8(q, CH₃CH).

MS m/e (relative intensity): 433(M⁺, 14), 418(M⁺-Me, 5), 388(M⁺-3Me, 100), 300(M⁺-S(C₄H₉)-NMe₂, 11), 242((CH)C₅H₃FeC₅H₄(SCH₂), 52), 152(FeC₅H₄S, 25), 72(MeCHNMe₂, 17), 56(Fe, 12), 44(NMe₂, 14)

IR (neat, CsI) 3095 (ferrocene C-H stretch), 2955-2775 (alkyl C-H stretch), 1455 (ferrocene antisymmetric C-C stretch), 1272, 1249 (C-N stretch), 828 (C-H bend perpendicular to the plane of the Cp ring), 655 (S-C stretch), 479 cm⁻¹ (antisymmetric ring-metal stretch).

Anal. Calcd. for C₂₂H₃₅S₂NFe: C, 60.96; H, 8.14. Found: C, 60.35; H, 7.93.

(S,R)-1-[1-(Dimethylamino)ethyl]-2,1'-bis[(sec-butyl)thio]-ferrocene (48, R=sec-Bu)

The procedure was the same as for 47 except 1.34 g (7.45 mmol) of di(sec-butyl) disulfide was used. Product was obtained as a brown oil: yield 73%.

^1H NMR (δ ppm), 4.34(m, 1H, H₃, H₄, H₅); 4.29(m, 4H, C₅H₄); 4.10(m, 2H, H₃, H₄, H₅); 3.98(q, J=6.8 Hz, 1H, CH₃CH); 3.04(m, 1H, SCH₂); 2.58(m, 1H,

SCH₂); 2.07(s, 6H, NMe₂); 1.52(m, 2H, βCH₂); 1.48(m, 2H, βCH₂); 1.36(d, J=6.8 Hz, 3H, CH₃CH); 1.15(d, J=6.9 Hz, 3H, βCH₃); 1.12(d, 3H, βCH₃); 0.95(t, 3H, γCH₃); 0.90(t, 3H, γCH₃).

¹³C NMR (δ ppm, CD₃COCD₃), 96.3(s, C₁); 80.9(s, C₂); 80.1(s, C₁); 77.9(d, C₃, C₄, C₅); 77.4(d, C₁₃, C₁₄); 77.2(d, C₁₃, C₁₄); 73.2(d, C₁₂, C₁₅); 72.6(d, C₁₂, C₁₅); 70.2(d, C₃, C₄, C₅); 69.5(d, C₃, C₄, C₅); 56.3(d, CH₃CH); 46.4(d, SCH); 46.2(d, SCH); 40.1(q, NMe₂); 30.3(t, βCH₂); 30.1(t, βCH₂); 22.2(q, βCH₃); 21.2(q, βCH₃); 12.6(q, γCH₃); 12.2(q, γCH₃), 9.5(q, CH₃CH).

MS m/e (relative intensity): 433(M⁺, 100), 418(M⁺-Me, 38), 388(M⁺-3Me, 68), 300(M⁺-SC₄H₉-NMe₂, 29), 242((CH)₅H₃FeC₅H₄(SCH₂), 22), 152(FeC₅H₅S, 14), 72(MeCHNMe₂, 30), 56(Fe, 7), 44(NMe₂, 4)

IR (neat, Csl) 3092 (ferrocene C-H stretch), 2960-2775 (alkyl C-H stretch), 1452 (ferrocene antisymmetric C-C stretch), 1265, 1249 (C-N stretch), 829 (C-H bend perpendicular to the plane of the Cp ring), 690 (S-C stretch), 450 cm⁻¹ (antisymmetric ring-metal stretch).

Anal. Calcd. for C₂₂H₃₅S₂NFe: C, 60.96; H, 8.14. Found: C, 61.13; H, 8.37.

(S,R)-1-[1-(Dimethylamino)ethyl]-2,1'-bis[(t-butyl)thio]ferrocene (49, R=t-Bu)

The procedure was the same as for 47 except 1.34 g (7.45 mmol) of di(t-butyl) disulfide was used. Product was obtained as a brown oil: yield 55%.

¹H NMR (δ ppm), 4.24(m, 1H, H₃, H₄, H₅); 4.19(m, 4H, C₅H₄); 4.13(m, 2H, H₃, H₄, H₅); 3.89(q, J=6.9 Hz, 1H, CH₃CH); 2.09(s, 6H, NMe₂); 1.30(d, J=6.9 Hz, 3H, CH₃CH); 1.22(s, 18H, βCH₃).

¹³C NMR (δ ppm, CD₃COCD₃), 89.5(s, C₁); 77.6(s, C₂); 77.5(s, C₁); 71.5(d, C₃, C₄, C₅); 71.2(d, C₁₃, C₁₄); 69.5(d, C₁₂, C₁₅); 69.4(d, C₁₂, C₁₅);

69.2(d, C₃, C₄, C₅); 68.6(d, C₃, C₄, C₅); 58.6(d, CH₃C₄H); 44.6(s, SCMe₃); 40.7(q, NMe₂); 31.1(q, βC₄H₃); 15.8(q, C₄H₃CH).

MS m/e (relative intensity): 433(M⁺, 69), 418(M⁺-Me, 45), 388(M⁺-3Me, 96), 300(M⁺-SC₄H₉-NMe₂, 30), 244 (100), 242((CH)₅C₅H₃FeC₅H₄(SCH₂), 23), 152(FeC₅H₄S, 19), 72(MeCHNMe₂, 7), 56(Fe, 20), 44(NMe₂, 28)

IR (neat, Csl) 3082 (ferrocene C-H stretch), 2963-2767 (alkyl C-H stretch), 1453 (ferrocene antisymmetric C-C stretch), 1262, 1251 (C-N stretch), 828 (C-H bend perpendicular to the plane of the Cp ring), 645 (S-C stretch), 462 cm⁻¹ (antisymmetric ring-metal stretch).

Anal. Calcd. for C₂₂H₃₅NFeS₂: C, 60.95; H, 8.14. Found: C, 61.71; H, 8.16.

(S,R)-1-[1-(Dimethylamino)ethyl]-2,1'-bis[(i-pentyl)thio]ferrocene (50, R=i-Pent)

A 2.7 M solution of n-BuLi in hexane (3 mL, 8.1 mmol) was added over a 30 min period to a solution of S-12 amine (1.3 g, 5.1 mmol) in 50 mL of dry ether under argon in a 250 mL round-bottomed Schlenk flask equipped with a magnetic stirring bar at -78°C. The suspension was stirred overnight at room temperature under Ar, and then a mixture of freshly distilled TMEDA (0.9 g, 7.5 mmol) and n-BuLi (3.0 mL, 8.1 mmol) was added via syringe at -78°C. After being stirred for one h, the reaction mixture was warmed to room temperature and stirred for 8 h. Then di(ipentyl) disulfide (3.10 g, 15 mmol) was added by syringe at -78°C and stirred for 36 more h. The mixture was slowly added to NaHCO₃(aq) and was cooled in an ice bath, and the cloudy solution was filtered. The resulting organic layer and ether extracts from the aqueous layer was combined, washed with ice water, dried over anhydrous Na₂SO₄, and concentrated in vacuo to afford a dark brown oil that was chromatographed on a silica gel column by gradient elution (hexane/ether). The product was obtained as a brown oil: yield 76%.

^1H NMR (δ ppm), 4.26(m, 1H, H₃, H₄, H₅); 4.19(m, 4H, C₅H₄); 4.06(m, 2H, H₃, H₄, H₅); 3.95(q, J=6.6 Hz, 1H, CH₃CH); 2.80(m, 1H, SCH₂); 2.76(m, 1H, SCH₂); 2.60(m, 2H, SCH₂); 2.55(m, 2H, β CH₂); 2.53(m, 2H, β CH₂); 2.08(s, 6H, NMe₂); 1.62(m, 1H, γ CH); 1.40(m, 1H, γ CH); 1.32(d, J=6.6 Hz, 3H, CH₃CH); 0.85(d, 3H, δ H); 0.83(d, 3H, δ H); 0.81(d, 3H, δ H); 0.79(d, 3H, δ H).

^{13}C NMR (δ ppm, CD₃COCD₃), 95.1(s, C₁); 82.6(s, C₂); 82.0(s, C₁); 76.1(d, C₃, C₄, C₅); 74.9(d, C₁₃, C₁₄); 71.9(d, C₁₂, C₁₅); 71.8(d, C₁₂, C₁₅); 69.7(d, C₃, C₄, C₅); 68.9(d, C₃, C₄, C₅); 56.3(d, CH₃CH); 39.9(q, NMe₂); 39.3(t, SCH₂); 35.4(t, β CH₂); 34.7(t, β CH₂); 27.8(d, γ CH); 27.5(d, γ CH); 22.7(q, δ CH₃), 22.5(q, δ CH₃); 22.4(q, δ CH₃); 9.7(q, CH₃CH).

MS m/e (relative intensity): 461(M⁺, 29), 446(M⁺-Me, 10), 416(M⁺-3Me, 96), 314(M⁺-SC₅H₁₁-NMe₂, 18), 242((CH)C₅H₃FeC₅H₄(SCH₂), 67), 152(FeC₅H₄S, 32), 72(MeCHNMe₂, 35), 56(Fe, 16), 44(NMe₂, 49)

IR (neat, CsI) 3095 (ferrocene C-H stretch), 2955-2778 (alkyl C-H stretch), 1460 (ferrocene antisymmetric C-C stretch), 1278, 1268 (C-N stretch), 829 (C-H bend perpendicular to the plane of the Cp ring), 652 (S-C stretch), 500 cm⁻¹ (antisymmetric ring-metal stretch).

Anal. Calcd. for C₂₄H₃₉S₂NFe: C, 62.46; H, 8.52. Found: C, 62.18; H, 8.13.

(S,R)-1-[1-(Dimethylamino)ethyl]-2,1'-bis(Phenylthio)ferrocene
(51, R=Ph)

A hexane solution of *n*-BuLi (2.7 M, 2.0 mL, 5.4 mmol) was added to a solution of 0.87 g (3.4 mmol) (S)-12 in 75 mL of dry ether at -78°C over a period of 30 min. The suspension was stirred for 12 h at 25°C then cooled to -78°C and a mixture of freshly distilled TMEDA (0.6 g, 5 mmol) and *n*-BuLi (2.0 mL, 5.4 mmol) was added dropwise over a 30 min period. The reaction mixture was stirred under Ar for 8 h and then diphenyl disulfide (2.19 g, 10 mmol) dissolved in 30 mL warm ether, was added

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dropwise via cannula to the orange suspension at -78°C . The reaction mixture was stirred under Ar for 30 h at 25°C and filtered. The filtrate was washed with H_2O , and the organic layer was separated and evaporated to give a brown oil. The oil was separated on a silica gel column by gradient elution (hexane/ether). The product was obtained as yellow crystals upon recrystallization from hexane/ CH_2Cl_2 : yield 80%.

^1H NMR (δ ppm), 7.05-7.20(m, 10H, C_6H_5); 4.60(m, 1H, H_3 , H_4 , H_5); 4.41(m, 4H, C_5H_4); 4.36(m, 2H, H_3 , H_4 , H_5); 3.90(q, $J=6.9$ Hz, 1H, CH_3CH); 1.93(s, 6H, NMe_2); 1.42 (d, $J=6.9$ Hz, 3H, CH_3CH).

^{13}C NMR (δ ppm, CD_3COCD_3), 141.5(s, substituted Ph C); 129.5(d, meta Ph C); 128.9(d, meta Ph C); 127.8(d, ortho Ph C); 126.8(d, ortho Ph C); 125.8(d, para Ph C); 125.6(d, para Ph C); 96.5(s, C_1); 79.3(s, C_2); 79.0(s, C_1); 78.0(d, C_3 , C_4 , C_5); 77.4(d, C_1^3 , C_1^4); 73.8(d, C_1^2 , C_1^5); 73.6(d, C_1^2 , C_1^5); 70.8(d, C_3 , C_4 , C_5); 70.5(d, C_3 , C_4 , C_5); 56.3(d, CH_3CH); 40.1(q, NMe_2); 11.9(q, CH_3CH).

MS m/e (relative intensity): 473(M^+ , 22), 458($\text{M}^+ - \text{Me}$, 10), 428($\text{M}^+ - 3\text{Me}$, 30), 402($\text{M}^+ - \text{CHMeNMe}_2$, 7), 320($\text{M}^+ - \text{NMe}_2 - \text{SPh}$, 35), 72(CHMeNMe_2 , 100), 56(Fe , 52), 44(NMe_2 , 47).

IR (Nujol, KBr) 3100 (ferrocene C-H stretch), 3065-3040 (phenyl C-H stretch), 2955-2755 (alkyl C-H stretch), 1462 (ferrocene antisymmetric C-C stretch), 1267, 1248 (C-N stretch), 849 (C-H bend perpendicular to the plane of the Cp ring), 475 cm^{-1} (antisymmetric ring-metal stretch).

Anal. Calcd. for $\text{C}_{26}\text{H}_{27}\text{S}_2\text{NFe}$: C, 65.96; H, 5.75. Found: C, 65.74; H, 5.92.

(S,R)-1-[1-(Dimethylamino)ethyl]-2,1'-bis(benzylthio)]ferrocene
(52, R=Bz)

The same procedure as 51 was followed except (2.47 g, 10 mmol) of dibenzyl disulfide was used. The product was obtained as a brown oil: yield 52%.

4.31 (q,

SOH₂)

C); 12

Ph C);

C5); 7

70.1 (d

SOH₂)

3), 43

stretch

stretch

Cp ring

(S, R)

(53,

disulfide

obtained

4H, C₂

Ph-CH₂

C); 135

Ph C);

^1H NMR (δ ppm), 7.13-7.27(m, 10H, Ph); 4.13-4.38(m, 7H, C_5H_4 , C_5H_3); 4.01(q, $J=6.8$ Hz, 1H, CH_3CH); 3.90(d, 1H, SCH_2); 3.85(d, 1H, SCH_2); 3.82(s, 2H, SCH_2); 2.14(s, 6H, NMe_2); 1.37(d, $J=6.8$ Hz, 3H, CH_3CH).

^{13}C NMR (δ ppm, CD_3COCD_3), 140.1(s, substituted Ph C); 129.8(d, meta Ph C); 129.7(d, meta Ph C); 129.0(d, ortho Ph C); 128.8(d, ortho Ph C); 127.7(d, para Ph C); 127.4(d, para Ph C); 96.3(s, C_1); 82.3(s, C_2); 81.0(s, C_1); 77.6(d, C_3 , C_4 , C_5); 76.6(d, C_1 , C_4); 75.5(d, C_1 , C_4); 72.0(d, C_2 , C_5); 71.9(d, C_2 , C_5); 70.1(d, C_3 , C_4 , C_5); 69.1(d, C_3 , C_4 , C_5); 56.5(d, CH_3CH); 42.0(t, SCH_2); 41.5(t, SCH_2); 40.1(q, NMe_2); 9.08(q, CH_3CH).

MS m/e (relative intensity): 501(M^+ , 14), 468($\text{M}^+ - \text{Me}$, 6), 458($\text{M}^+ - 3\text{Me}$, 3), 430($\text{M}^+ - \text{CH}(\text{Me})\text{NMe}_2$, 16), 72(CHMeNMe_2 , 95), 56(Fe , 35), 44(NMe_2 , 23).

IR (neat, KBr) 3085 (ferrocene C-H stretch), 3062-3020 (aryl C-H stretch), 2955-2780 (alkyl C-H stretch), 1455 (ferrocene antisymmetric C-C stretch), 1260, 1245 (C-N stretch), 820 (C-H bend perpendicular to the plane of the Cp ring), 675(S-C stretch), 470 cm^{-1} (antisymmetric ring-metal stretch).

(S,R)-1-[1-(Dimethylamino)ethyl]-2,1'-bis[(4-tolyl)thio]ferrocene (53, R=4-tolyl)

The procedure for 51 was repeated except 2.47 g (15 mmol) of di(4-tolyl) disulfide was used. After two recrystallizations from hexane/ CH_2Cl_2 , the product was obtained as yellow crystals: yield 75%, mp 86-87°C.

^1H NMR (δ ppm), 6.95-7.13(m, 8H, Ph); 4.55(m, 1H, H_3 , H_4 , H_5); 4.40(m, 4H, C_5H_4); 4.30(m, 2H, H_3 , H_4 , H_5); 3.91(q, $J=6.8$ Hz, 1H, CH_3CH); 2.24(s, 6H, Ph-CH_3); 1.95(s, 6H, NMe_2); 1.48(d, $J=6.8$ Hz, 3H, CH_3CH).

^{13}C NMR (δ ppm, CD_3COCD_3), 136.8(s, substituted Ph C); 136.0(d, para Ph C); 135.3(s, para Ph C); 130.0(d, meta Ph C); 129.8(d, meta Ph C); 127.8(d, ortho Ph C); 127.3(d, ortho Ph C); 95.4(s, C_1); 79.7(s, C_2); 79.1(s, C_1); 77.7(d, C_3 , C_4 ,

C₅); 77.2(d, C¹₃, C¹₄); 73.6(d, C¹₂, C¹₅); 73.4(d, C¹₂, C¹₅); 70.6(d, C₃, C₄, C₅); 70.4(d, C₃, C₄, C₅); 56.9(d, CH₃CH); 45.4(q, NMe₂); 20.9(q, CH₃Ph); 12.3(q, CH₃CH).

MS m/e (relative intensity): 501(M⁺, 19), 786(M⁺-Me, 7), 456(M⁺-3Me, 100), 179(42), 153(54), 121(31), 72(CHMeNMe₂, 94), 56(Fe, 50), 44(NMe₂, 71).

IR (Nujol, KBr) 3100 (ferrocene C-H stretch), 3085-3045 (phenyl C-H stretch), 2980-2741 (alkyl C-H stretch), 1460 (ferrocene antisymmetric C-C stretch), 1260, 1235 (C-N stretch), 811 (C-H bend perpendicular to the plane of the Cp ring), 470 cm⁻¹ (antisymmetric ring-metal stretch).

Anal. Calcd. for C₂₈H₃₁S₂NFe: C, 67.06; H, 6.27. Found: C, 67.20; H, 6.20.

(S,R)-1-[1-(Dimethylamino)ethyl]-2,1'-bis[(4-Cl-Ph)thio]-ferrocene (54, R=4-Cl-Ph)

The same procedure as 51 was followed except 2.88 g (10 mmol) of bis(4-Cl-Ph) disulfide was used. Upon recrystallization from hexane/CH₂Cl₂, the product was obtained as yellow crystals: yield 81%, mp 114-116°C.

¹H NMR (δ ppm), 6.98-7.11(m, 8H, Ph); 4.56(m, 1H, H₃, H₄, H₅); 4.42(m, 4H, C₅H₄); 4.35(m, 2H, H₃, H₄, H₅); 3.92(q, J=6.8 Hz, 1H, CH₃CH); 1.97(s, 6H, NMe₂); 1.42(d, J=6.8 Hz, 3H, CH₃CH).

¹³C NMR (δ ppm, CD₃COCD₃), 139.9(s, substituted Ph C); 131.1(d, meta Ph C); 130.8(d, meta Ph C); 129.5(s, para Ph C); 129.2(s, para Ph C); 128.8(d, ortho Ph C); 128.2(d, ortho Ph C); 96.4(s, C₁); 79.4(s, C¹₁, C₂); 78.1(d, C₃, C₄, C₅); 77.4(d, C¹₃, C¹₄); 74.0(d, C¹₂, C¹₅); 73.8(d, C¹₂, C¹₅); 71.0(d, C₃, C₄, C₅); 70.7(d, C₃, C₄, C₅); 56.3(d, CH₃CH); 39.9(q, NMe₂); 10.8(q, CHCH₃).

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SeCH₃);

MS m/e (relative intensity): 543(M⁺, 16), 541(16), 528(M⁺-Me, 5), 526(9), 498(M⁺-3Me, 5), 496(6), 72(CHMeNMe₂, 100), 56(Fe, 13), 44(NMe₂, 14).

IR (Nujol, KBr) 3100 (ferrocene C-H stretch), 3085-3045 (aryl C-H stretch), 2980-2740 (alkyl C-H stretch), 1460 (ferrocene antisymmetric C-C stretch), 1260, 1235 (C-N stretch), 811 (C-H bend perpendicular to the plane of the Cp ring), 470 cm⁻¹ (antisymmetric ring-metal stretch).

Anal. Calcd. for C₂₆H₂₅S₂NFeCl₂: C, 57.59; H, 4.65. Found: C, 57.47; H, 4.60.

(S,R)-1-[1-(Dimethylamino)ethyl]-2,1'-bis(methylseleno)ferrocene (55, R=Me)

A 2.7 M solution of *n*-BuLi in hexane (3.0 mL, 8.1 mmol) was added to a 1.3 g (5.1 mmol) (S)-[1-(Dimethylamino)ethyl]ferrocene in 100 mL dry ether at -78°C under Ar. The orange suspension was warmed to room temperature and stirred for 8 h. Then, a solution of freshly distilled TMEDA (0.9 g, 7.5 mmol) and *n*-BuLi (3 mL, 8.1 mmol) was added to the reaction mixture at -78°C. After being stirred overnight at room temperature, to the reaction mixture was added dropwise a solution of dimethyl diselenide (2.82 g, 15 mmol) in 20 mL ether over a 20 min period at -78°C. The reaction mixture was stirred for 12 h at room temperature under Ar. After being refluxed for 24 h, the reaction mixture was cooled and then 30 mL of saturated aqueous NaHCO₃ was added. The resulting organic layer and ether extracts from the aqueous layer were combined, washed twice with ice water, dried over anhydrous Na₂SO₄, and evaporated to give a dark oily residue. The oil was chromatographed on silica gel by eluting first with hexane and then with CH₂Cl₂ to give a brown oil: yield 82%.

¹H NMR (δ ppm), 4.24(m, 1H, H₃, H₄, H₅); 4.17(m, 4H, C₅H₄); 4.07(m, 2H, H₃, H₄, H₅); 3.96(q, J=6.8 Hz, 1H, CH₃CH); 2.12(s, 3H, SeCH₃); 2.11(s, 3H, SeCH₃); 2.07(s, 6H, NMe₂); 1.33(d, J=6.8 Hz, 3H, CH₃CH).

^{13}C NMR (δ ppm, CD_3COCD_3), 94.4(s, C_1); 77.1(s, C_2 , C'_1); 75.0(d, C_3 , C_4); 74.2(d, C_3 , C_4 , C_5); 71.9(d, C'_2 , C'_5); 71.6(d, C'_2 , C'_5); 68.7(d, C_3 , C_4 , C_5); 68.7(d, C_3 , C_4 , C_5); 59.1(d, CH_3CH); 39.8(q, NMe_2); 10.2(q, CH_2); 9.32(q, SeCH_3); 8.62(q, SeCH_3).

MS m/e (relative intensity): 443(M^+ , 27), 441(11), 428($\text{M}^+ - \text{Me}$, 6), 398($\text{M}^+ - 3\text{Me}$, 24), 397(14), 396(15), 349($\text{M}^+ - \text{SeMe}$, 8), 305($\text{M}^+ - \text{SeMe} - \text{NMe}_2$, 11), 304(28), 212(26), 149(23), 72(CHMeNMe_2 , 42), 56(Fe , 50), 44(NMe_2 , 34).

IR (neat, Csl) 3078 (ferrocene C-H stretch), 2961-2765 (alkyl C-H stretch), 1449 (ferrocene antisymmetric C-C stretch), 1265, 1240 (C-N stretch), 820 (C-H bend perpendicular to the plane of the Cp ring), 511 (Se-C stretch), 470 cm^{-1} (antisymmetric ring-metal stretch).

Anal. Calcd. for $\text{C}_{16}\text{H}_{23}\text{Se}_2\text{FeN}$: C, 43.37; H, 5.23. Found: C, 43.51; H, 5.23.

(S,R)-1-[1-(Dimethylamino)ethyl]-2,1'-bis(phenylseleno)ferrocene (56, R=Ph)

A hexane solution of $n\text{-BuLi}$ (2.7 M, 3 mL, 8.1 mmol) was added to a solution of 1.3 g (5.1 mmol) S-(12) in 100 mL of dry ether at -78°C over a period of 30 min. The suspension was stirred for 12 h at 25°C and cooled to -78°C , and then a mixture of freshly distilled TMEDA (0.9 g, 7.5 mmol) and $n\text{-BuLi}$ (3.0 mL, 8.1 mmol) was added via a syringe. The reaction mixture was stirred under Ar overnight and then 4.86 g (15 mmol) of diphenyl diselenide in 40 mL dry ether was added through a cannula at -78°C over a period of 30 min. The reaction mixture was stirred under Ar for 30 h and then refluxed for 10 more h. Upon cooling, saturated aqueous NaHCO_3 was added and the resulting organic layer and ether extracts of aqueous layer were combined. After drying and evaporation of solvent, the resulting product mixture was chromatographed on a

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silica gel column (hexane/ether). The product was obtained as yellow crystals upon recrystallization from CH_2Cl_2 /hexane: yield 76%, mp 57-58°C.

^1H NMR (δ ppm), 7.11-7.36(m, 10H, Ph); 4.50(m, 1H, H_3 , H_4 , H_5); 4.34(m, 4H, C_5H_4); 4.26(m, 2H, H_3 , H_4 , H_5); 3.92(q, $J=6.7$ Hz, 1H, CH_3CH); 1.96(s, 6H, NMe_2); 1.44(d, $J=6.7$ Hz, 3H, CH_3CH).

^{13}C NMR (δ ppm, CD_3COCD_3), 135.0(s, substituted Ph); 130.8(d, meta Ph C); 129.9(d, ortho Ph C); 128.8(d, para Ph C); 126.7(d, para Ph C); 95.8(s, C_1); 80.7(s, C_2); 79.6(s, C^1_1); 78.4(d, C_3 , C_4 , C_5); 78.2(d, C^1_3 , C^1_4); 78.0(C^1_3 , C^1_4); 73.9(d, C^1_2 , C^1_5); 73.7(d, C^1_2 , C^1_5); 70.8(d, C_3 , C_4 , C_5); 70.1(d, C_3 , C_4 , C_5); 56.9(d, CH_3CH); 40.9(q, NMe_2); 11.8(q, CHCH_3).

MS m/e (relative intensity): 569(M^+ , 2), 567(2), 368($\text{M}^+ - \text{SePh}$, 3), 167(10), 166(24), 165(65), 153(28), 152(42), 72(CHMeNMe_2 , 52), 56(Fe , 56), 44(NMe_2 , 100).

IR (Nujol, KBr) 3092 (ferrocene C-H stretch), 3072-2041 (phenyl C-H stretch), 2965-2765(alkyl C-H stretch), 1447 (ferrocene antisymmetric C-C stretch), 1260, 1241 (C-N stretch), 828 (C-H bend perpendicular to the plane of the Cp ring), 540 (Se-C stretch), 510 cm^{-1} (antisymmetric ring-metal stretch).

Anal. Calcd. for $\text{C}_{26}\text{H}_{27}\text{Se}_2\text{NFe}$: C, 55.05; H, 4.80. Found: C, 54.19; H, 4.74.

(S,R)-1-[1-(Dimethylamino)ethyl]-2,1'-bis[(4-Cl-Ph)-seleno]ferrocene (57, R=4-Cl-Ph)

The same procedure for 56 was followed except 5.72 g, 15 mmol of bis(4-Cl-Ph) diselenide was used. The product after two recrystallizations from CH_2Cl_2 /hexane was obtained as yellow crystals: yield 65%, mp 92-93°C.

^1H NMR (δ ppm), 7.14-7.35(m, 8H, Ph); 4.63(m, 1H, H_3 , H_4 , H_5); 4.38(m, 4H, C_5H_4); 4.29(m, 2H, H_3 , H_4 , H_5); 3.92(q, $J=6.8$ Hz, 1H, CH_3CH); 1.97(s, 6H, NMe_2); 1.39(d, $J=6.8$ Hz, 3H, CH_3CH).

^{13}C NMR (δ ppm, CD_3COCD_3), 134.6(s, substituted Ph); 132.8(s, para Ph C); 132.4(d, meta Ph C); 132.3(d, meta Ph C); 129.8(d, ortho Ph C); 129.2(d, ortho Ph C); 96.1(s, C₁); 78.3(d, C₃, C₄, C₅); 78.2(d, C¹₃, C¹₄); 73.8(d, C¹₂, C¹₅); 70.9(d, C₃, C₄, C₅); 70.5(d, C₃, C₄, C₅); 57.4(d, CH₃CH); 39.9(q, NMe₂); 10.8(q, CH₂CH₃).

MS m/e (relative intensity): 637(M⁺, 5), 635(6), 592(M⁺-3Me, 42), 590(51), 402(M⁺-NMe₂-Se(PhCl), 9), 72(CHMeNMe₂, 68), 56(Fe, 23), 44(NMe₂, 100).

IR (Nujol KBr) 3105 (ferrocene C-H stretch), 3080-3030 (aryl C-H stretch), 2955-2765(alkyl C-H stretch), 1447 (ferrocene antisymmetric C-C stretch), 1265, 1241 (C-N stretch), 817 (C-H bend perpendicular to the plane of the Cp ring), 511 (Se-C stretch), 470 cm^{-1} (antisymmetric ring-metal stretch).

Anal. Calcd. for $\text{C}_{26}\text{H}_{25}\text{Se}_2\text{NFeCl}_2$: C, 49.09; H, 3.96. Found: C, 49.61; H, 3.99.

1-[(Dimethylamino)methyl]-2,1'-bis(methylthio)ferrocene (58, R=Me)

A 2.7 M solution of n -BuLi in hexane (4.0 mL, 10.8 mmol) was added to a 10 mmol solution of [(dimethylamino)ethyl]ferrocene (2.43 g) in 100 mL dry ether at -78°C under Ar. The orange suspension was warmed to room temperature and stirred for 8 h. Then, a solution of freshly distilled TMEDA (1.20 mL, 10.0 mmol) and n -BuLi (4.0 mL, 10.8 mmol) was added to the reaction mixture at -78°C . After being stirred overnight at room temperature, to the reaction mixture was added dropwise a solution of dimethyl disulfide (2.83 g, 30 mmol) in 20 mL dry ether over a 20 min period at 78°C . The reaction mixture was stirred for 3 h at room temperature, then refluxed for another 12 h. Then, it was hydrolyzed with a cold saturated aqueous NaHCO_3 solution (40 mL). The resulting organic layer and ether extracts from the aqueous layer were combined, washed with ice water, dried over anhydrous Na_2SO_4 , and concentrated in

vacuum to give a dark oily residue which was chromatographed on a silica gel column by gradient elution (hexane/ether). The product was obtained as a brown oil: yield 92%.

^1H NMR (δ ppm), 4.28(m, 1H, H₃, H₄, H₅); 4.18(m, 4H, C₅H₄); 4.09(m, 2H, H₃, H₄, H₅); 3.55(d, J=12.1 Hz, 1H, CH₂N); 3.24(d, J=12.1 Hz, 1H, CH₂N); 2.26(s, 3H, SCH₃); 2.25(s, 3H, SCH₃); 2.18(s, 6H, NMe₂).

^{13}C NMR (δ ppm, CD₃COCD₃), 88.2(s, C₁); 86.4(s, C₂); 85.6(s, C¹₁); 73.4(d, C¹₃, C¹₄); 72.9(d, C¹₃, C¹₄); 72.4(d, C₃, C₄, C₅); 72.3(d, C₃, C₄, C₅); 71.1(d, C¹₂, C¹₅); 71.0(d, C¹₂, C¹₅); 69.2(d, C₃, C₄, C₅); 57.4(t, CHNMe₂); 45.4(q, NMe₂); 20.0(q, SCH₃); 19.3(q, SCH₃).

MS m/e (relative intensity): 335(M⁺, 100), 320(M⁺-Me, 5), 286(M⁺-SCH₃, 6), 244(M⁺-NMe₂-SCH₃, 17), 230(M⁺-NMe₂(CH₃)-SCH₃, 10), 213(13), 164(22), 152(30), 56(Fe, 47), 44(NMe₂, 32).

IR (neat Csl) 3097 (ferrocene C-H stretch), 2925-2762 (alkyl C-H stretch), 1420 (ferrocene antisymmetric C-C stretch), 1269, 1259 (C-N stretch), 819 (C-H bend perpendicular to the plane of the Cp ring), 640 (S-C stretch), 480 cm⁻¹ (antisymmetric ring-metal stretch).

Anal. Calcd. for C₁₅H₂₁S₂NFe: C, 53.73; H, 6.31. Found: C, 54.14; H, 6.23.

1-[(Dimethylamino)methyl]-2,1'-bis(ethylthio)ferrocene (59, R=Et)

Procedure was the same as 58 except 3.67 g (30 mmol) diethyl disulfide was used. The product was obtained as a brown oil.

^1H NMR (δ ppm), 4.29(m, 1H, H₃, H₄, H₅); 4.16(m, 4H, C₅H₄); 4.10(m, 2H, H₃, H₄, H₅); 3.55(d, 1H, CH₂N); 3.20(d, CH₂N); 2.64(m, 1H, SCH₂); 2.60(m, 1H, SCH₂); 2.53(q, 2H, SCH₂); 2.16(s, 6H NMe₂); 1.19(t, 3H, β CH₃); 1.12(t, 3H, β CH₃).

^{13}C NMR (δ ppm, CD₃COCD₃), 89.5(s, C₁); 82.9(s, C₂); 82.7(s, C¹₁); 76.3(d, C¹₃, C¹₄); 76.0(d, C¹₃, C¹₄); 75.4(d, C₃, C₄, C₅); 73.8(d, C₃, C₄, C₅);

72.4(d, C¹₂, C¹₅); 72.0(d, C¹₂, C¹₅); 70.0(d, C₃, C₄, C₅); 58.0(t, $\underline{\text{C}}\text{H}_2\text{NMe}_2$); 48.8(q, NMe₂); 31.9(t, $\text{S}\underline{\text{C}}\text{H}_2$); 31.3(t, $\text{S}\underline{\text{C}}\text{H}_2$); 15.7(q, βCH_3); 15.5(q, βCH_3).

MS m/e (relative intensity): 363(M⁺, 100), 348(M⁺-Me, 5), 334(M⁺-Et, 7), 318(M⁺-3Me, 16), 302(M⁺-SC₂H₅, 38), 286(23), 258(M⁺-NMe₂-SC₂H₅, 12), 230(17), 165(8), 152(19), 121(23), 97(20), 58(31), 56(Fc, 19), 44(NMe₂, 31).

IR (neat, Csl) 3095 (ferrocene C-H stretch), 2972-2763 (alkyl C-H stretch), 1430 (ferrocene antisymmetric C-C stretch), 1260, 1249 (C-N stretch), 828 (C-H bend perpendicular to the plane of the Cp ring), 630 (S-C stretch), 482 cm⁻¹ (antisymmetric ring-metal stretch).

Anal. Calcd. for C₁₇H₂₅S₂NFe: C, 56.19; H, 6.93. Found: C, 56.48; H, 6.93.

1-[(Dimethylamino)methyl]-2,1'-bis[(*n*-propyl)thio]ferrocene (60, R = *n*-Pr)

Procedure was the same as 58 except 4.51 g (30 mmol) di(*n*-propyl) disulfide was used. The product was obtained as a brown oil: yield 82%.

¹H NMR (δ ppm), 4.27(m, 1H, H₃, H₄, H₅); 4.17(m, 4H, C₅H₄); 4.08(m, 2H, H₃, H₄, H₅); 3.55(d, J=12.7 Hz, 1H, $\underline{\text{C}}\text{H}_2\text{N}$); 3.21(d, J=12.7 Hz, 1H, $\underline{\text{C}}\text{H}_2\text{N}$); 2.64(m, 1H, SCH₂); 2.56(m, 1H, SCH₂); 2.50(m, 2H, SCH₂); 2.17(s, 6H NMe₂); 1.56(m, 2H, βCH_2); 1.46(m, 2H, βCH_2); 0.95(t, 3H, γCH_3); 0.88(t, 3H, γCH_3).

¹³C NMR (δ ppm, CD₃COCD₃), 89.1(s, C₁); 82.9(s, C₂); 82.8(s, C¹₁); 75.7(d, C¹₃, C¹₄); 75.3(d, C¹₃, C¹₄); 74.8(d, C₃, C₄, C₅); 73.3(d, C₃, C₄, C₅); 71.9(d, C¹₂, C¹₅); 71.6(d, C¹₂, C¹₅); 69.5(d, C₃, C₄, C₅); 57.5(t, $\underline{\text{C}}\text{H}_2\text{NMe}_2$); 45.5(q, NMe₂); 39.4(t, $\text{S}\underline{\text{C}}\text{H}_2$); 39.1(t, $\text{S}\underline{\text{C}}\text{H}_2$); 23.5(t, βCH_2); 23.4(t, βCH_2); 13.6(q, γCH_3); 13.5(q, γCH_3).

MS m/e (relative intensity): 391(M⁺, 100), 376(M⁺-Me, 3), 346(M⁺-3Me, 18), 316(M⁺-S(n-Pr), 37), 272(M⁺-NMe₂-S(n-Pr), 12), 164(13), 152(17), 58(40), 56(Fe, 17), 44(NMe₂, 28).

IR (neat, Csl) 3095 (ferrocene C-H stretch), 2962-2764 (alkyl C-H stretch), 1448 (ferrocene antisymmetric C-C stretch), 1260, 1240 (C-N stretch), 829 (C-H bend perpendicular to the plane of the Cp ring), 649 (S-C stretch), 481 cm⁻¹ (antisymmetric ring-metal stretch).

Anal. Calcd. for C₁₉H₂₉S₂NFe: C, 58.30; H, 7.47. Found: C, 58.48; H, 7.53.

1-[(Dimethylamino)methyl]-2,1'-bis[(i-propyl)thio]ferrocene (61, R = i-Pr)

The procedure for 58 was followed except 4.51 g (30 mmol) of di(isopropyl) disulfide was used. Product was obtained as a brown oil: yield 81%.

¹H NMR (δ ppm), 4.32(m, 1H, H₃, H₄, H₅); 4.19(m, 4H, C₅H₄); 4.09(m, 2H, H₃, H₄, H₅); 3.57(d, J=12.8 Hz, 1H, CH₂N); 3.17(d, J=12.8 Hz, 1H, CH₂N); 3.01(h, 1H, SCH); 2.81(h, 1H, SCH); 2.16(s, 6H, NMe₂); 1.18(d, J=8.8 Hz, 3H, βCH₃); 1.14(d, J=6.8 Hz, βCH₃); 1.10(d, J=8.8 Hz, 3H βCH₃); 1.07(d, J=6.8 Hz, 3H, βCH₃).

¹³C NMR (δ ppm, CD₃COCD₃), 89.5(s, C₁); 80.6(s, C₂); 79.2(d, C¹₁); 76.8(d, C¹₃, C¹₄); 76.6(d, C¹₃, C¹₄); 76.1(d, C₃, C₄, C₅); 73.2(d, C₃, C₄, C₅); 72.1(d, C¹₂, C¹₅); 71.7(d, C¹₂, C¹₅); 69.3(d, C₃, C₄, C₅); 57.1(t, CH₂NMe); 45.2(q, NMe₂); 39.4(d, SC₂H₂); 39.3(d, SC₂H); 23.7(q, βCH₃); 23.2(q, βCH₃); 22.8(q, βCH₃).

MS m/e (relative intensity): 391(M⁺, 100), 376(M⁺-Me, 6), 346(M⁺-3Me, 24), 316(M⁺-S(i-Pr), 39), 304(21), 272(M⁺-NMe₂-S(i-Pr), 12), 230(10), 195(13), 164(15), 121(20), 56(Fe, 19), 44(NMe₂, 21).

IR (neat, Csl) 3097 (ferrocene C-H stretch), 2960-2765 (alkyl C-H stretch), 1449 (ferrocene antisymmetric C-C stretch), 1260, 1241 (C-N stretch),

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R:

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835 (C-H bend perpendicular to the plane of the Cp ring), 652 (S-C stretch), 485 cm^{-1} (antisymmetric ring-metal stretch).

Anal. Calcd. for $\text{C}_{19}\text{H}_{29}\text{S}_2\text{NFe}$: C, 58.30; H, 7.47. Found: C, 58.54; H, 7.44.

**1-[(Dimethylamino)methyl]-2,1'-bis[(*n*-butyl)thio]ferrocene (62,
R=*n*-Bu)**

The procedure for 58 was followed except 5.35 g (30 mmol) di(*n*-butyl) disulfide was used. The product was obtained as a brown oil: yield 75%.

^1H NMR (δ ppm), 4.29(m, 1H, H_3 , H_4 , H_5); 4.15(m, 4H, C_5H_4); 4.08(m, 2H, H_3 , H_4 , H_5); 3.56(d, $J=12.7$ Hz, 1H, CH_2N); 3.20(d, $J=12.7$ Hz, d, 1H, CH_2N); 2.66(m, 1H, SCH_2); 2.60(m, 1H, SCH_2); 2.53(m, 2H, SCH_2); 2.17(s, 6H, NMe_2); 1.52(m, 2H, βCH_2); 1.46(m, 2H, βCH_2); 1.43(m, 2H γCH_2); 1.31(m, 2H, γCH_2); 0.86(t, 3H, δCH_3); 0.82(t, 3H, δCH_3).

^{13}C NMR (δ ppm, CD_3COCD_3), 88.9(s, C_1); 82.5(s, C_2); 82.4(s, C^1_1); 75.5(d, C^1_3 , C^1_4); 75.1(d, C^1_3 , C^1_4); 74.5(d, C_3 , C_4 , C_5); 73.1(d, C_3 , C_4 , C_5); 71.6(d, C^1_2 , C^1_5); 71.3(d, C^1_2 , C^1_5); 69.2(d, C_3 , C_4 , C_5); 57.3(t, CH_2NMe_2); 54.4(q, NMe_2); 36.8(t, SCH_2); 36.6(t, SCH_2); 32.2(t, βCH_2), 32.0(t, βCH_2); 22.1(t, γCH_2); 22.0(t, γCH_2); 13.9(q, δCH_3).

MS m/e (relative intensity): 419(M^+ , 100), 404(M^+-Me , 3), 374(M^+-3Me , 26), 362($\text{M}^+-(\text{n-Bu})$, 8), 330($\text{M}^+-\text{S}(\text{n-Bu})$, 44), 318($\text{M}^+-\text{NMe}_2-(\text{n-Bu})$, 3), 286($\text{M}^+-\text{NMe}_2-\text{S}(\text{n-Bu})$, 9), 164(15), 121(19), 56(Fe, 17), 44(NMe_2 , 16).

IR (neat, Csl) 3095 (ferrocene C-H stretch), 2996-2768 (alkyl C-H stretch), 1442 (ferrocene antisymmetric C-C stretch), 1275, 1261 (C-N stretch), 830 (C-H bend perpendicular to the plane of the Cp ring), 635 (S-C stretch), 480 cm^{-1} (antisymmetric ring-metal stretch).

Anal. Calcd. for $\text{C}_{21}\text{H}_{33}\text{S}_2\text{NFe}$: C, 60.13; H, 7.93. Found: C, 59.82; H, 7.71.

**1-[(Dimethylamino)methyl]-2,1'-bis[(sec-butyl)thio]ferrocene (63,
R=sec-Butyl)**

The procedure was the same as for 58, except 5.35 g (30 mmol) of di(sec-butyl) disulfide was used. The product was obtained as a brown oil: yield 59%.

^1H NMR (δ ppm), 4.31(m, 1H, H₃, H₄, H₅); 4.19(m, 4H, C₅H₄); 4.12(m, 2H, H₃, H₄, H₅); 3.56(d, 1H, CH₂N); 3.20(d, 1H, CH₂N); 2.83(h, 1H, SCH); 2.57(h, 1H, SCH); 2.17(s, 6H, NMe₂); 1.47(m, 2H, β CH₂); 1.36(m, 2H, β CH₂); 1.15(d, 3H, β CH₃); 1.10(d, 3H, β CH₃); 0.97(t, 3H γ CH₃); 0.87(t, 3H, γ CH₃).

MS m/e (relative intensity): 419(M⁺, 100), 404(M⁺-Me, 6), 374(M⁺-3Me, 36), 362(M⁺-(sec-Bu), 11), 330(M⁺-S(sec-Bu), 49), 318(M⁺-NMe₂-(sec-Bu), 5), 286(M⁺-NMe₂-S(sec-Bu), 14), 164(18), 121(20), 56(Fe, 46), 44(NMe₂, 90).

IR (neat, Csl) 3094 (ferrocene C-H stretch), 2998-2770 (alkyl C-H stretch), 1444 (ferrocene antisymmetric C-C stretch), 1276, 1263 (C-N stretch), 829 (C-H bend perpendicular to the plane of the cyclopentadienyl ring), 636 (S-C stretch), 480 cm⁻¹ (antisymmetric ring-metal stretch).

Anal. Calcd. for C₂₁H₃₃S₂NFe: C, 60.13; H, 7.93. Found: C, 60.25; H, 7.79.

**1-[(Dimethylamino)methyl]-2,1'-bis[(t-butyl)thio]ferrocene (64,
R=t-Bu)**

The procedure was the same as for 58, except 5.35 g (30 mmol) of di(t-butyl) disulfide was used. The product was obtained as a brown oil: yield 55%.

^1H NMR (δ ppm), 4.19(m, 1H, H₃, H₄, H₅); 4.14(m, 4H, C₅H₄); 4.10(m, 2H, H₃, H₄, H₅); 3.27(s, 2H, CH₂N); 2.14(s, 6H, NMe₂); 1.17(s, 18H, β CH₃).

^{13}C NMR (δ ppm, CD₃COCD₃), 89.1(s, C₁); 77.4(s, C₂); 77.3(s, C¹₁); 72.1(d, C¹₃, C¹₄); 72.1(d, C₃, C₄, C₅); 70.9(d, C¹₂, C¹₅); 69.8(d, C₃, C₄, C₅); 59.1(t, α CH₂NMe₂); 44.9(q, NMe₂); 37.2(s, S-C); 31.0(q, β CH₃).

MS m/e (relative intensity): 419(M^+ , 21), 374(M^+ -3Me, 72), 361(M^+ -CH₂NMe₂, 11), 359(M^+ -4Me, 31), 330(M^+ -NMe₂-3Me, 27), 317(M^+ -NMe₂-(*i*-Bu), 6), 286(M^+ -NMe₂-S(*i*-Bu), 4), 164(17), 121(33), 56(Fe, 19), 44(NMe₂, 17).

IR (neat, CsI) 3093 (ferrocene C-H stretch), 2967-2761 (alkyl C-H stretch), 1451 (ferrocene antisymmetric C-C stretch), 1231, 1222 (C-N stretch), 822 (C-H bend perpendicular to the plane of the Cp ring), 620 (S-C stretch), 470 cm⁻¹ (antisymmetric ring-metal stretch).

Anal. Calcd. for C₂₁H₃₃S₂NFe: C, 60.13; H, 7.93. Found: C, 60.59; H, 7.97.

1-[(Dimethylamino)methyl]-2,1'-bis[(*i*-Pent)thio]ferrocene (65, R=*i*-Pent)

The procedure was the same for 58 except 6.19 g (30 mmol) of di(*i*-pentyl) disulfide was used. The product was obtained as a brown oil: yield 78%.

¹H NMR (δ ppm), 4.28(m, 1H, H₃, H₄, H₅); 4.17(m, 4H, C₅H₄); 4.08(m, 2H, H₃, H₄, H₅); 3.57(d, J=12.7 Hz, CH₂N); 3.20(d, J=12.7 Hz, 1H, CH₂N); 2.71(m, 1H, SCH₂); 2.64(m, 1H, SCH₂); 2.54(m, 2H, SCH₂); 2.16(s, 6H, NMe₂); 1.63(m, 2H, βCH₂); 1.58(m, 2H, βCH₂); 1.41(m, 1H, γCH); 1.35(m, 1H, γCH); 0.87(d, J=3.8 Hz, 3H δCH₃); 0.84(d, J=2.6 Hz, 3H, δCH₃); 0.82(d, J=3.8 Hz, 3H, δCH₃); 0.79(d, J=2.6 Hz, 3H, δCH₃).

¹³C NMR (δ ppm, CD₃COCD₃), 89.1(s, C₁); 82.7(s, C₂); 82.6(s, C¹₁); 76.6(d, C¹₃, C¹₄); 75.0(d, C¹₃, C¹₄); 74.5(d, C₃, C₄, C₅); 73.2(d, C₃, C₄, C₅); 71.7(d, C¹₂, C¹₅); 71.4(d, C¹₂, C¹₅); 69.3(d, C₃, C₄, C₅); 57.3(t, CH₂NMe₂); 45.4(q, NMe₂); 39.2(t, SCH₂); 35.2(t, βCH₂); 34.9(t, βCH₂); 27.5(d, γCH); 27.4(d, γCH); 22.8(q, δCH₃); 22.6(q, δCH₃); 22.4(q, δCH₃).

MS m/e (relative intensity): 447(M^+ , 84), 432(M^+ -Me, 5), 402(M^+ -3Me, 30), 376(M^+ -(*i*-Pent), 11), 344(M^+ -S(*i*-Pent), 39), 332(M^+ -NMe₂-(*i*-Pent),

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6), 300(M^+ -NMe₂-S(l-Pent), 8), 164(24), 149(44), 97(34), 56(Fe, 29), 44(NMe₂, 42).

IR (neat, Csl) 3090 (ferrocene C-H stretch), 2955-2762 (alkyl C-H stretch), 1441 (ferrocene antisymmetric C-C stretch), 1272, 1260 (C-N stretch), 835 (C-H bend perpendicular to the plane of the Cp ring), 649 (S-C stretch), 478 cm⁻¹ (antisymmetric ring-metal stretch).

Anal. Calcd. for C₂₃H₃₇S₂NFe: C, 61.73; H, 8.33. Found: C, 62.00; H, 8.14.

1-[(Dimethylamino)methyl]-2,1'-bis(phenylthio)ferrocene (66, R=Ph)

The same procedure was used as for 58 except 6.55 g (30 mmol) diphenyl disulfide was used. The product was obtained as yellow crystals after two recrystallizations from CH₂Cl₂/hexane: yield 74%. mp 86-87°C.

¹H NMR (δ ppm), 7.02-7.19(m, 10H, Ph); 4.60(m, 1H, H₃, H₄, H₅); 4.44(m, 4H, C₅H₄); 4.33(m, 2H, H₃, H₄, H₅); 3.55(d, 1H, CH₂N); 3.44(d, 1H, CH₂N); 2.04(s, 6H, NMe₂).

¹³C NMR (δ ppm, CD₃COCD₃), 141.0(s, substituted Ph C); 140.6(s, substituted Ph C); 129.4(d, meta, Ph C); 129.2(d, meta Ph C); 127.4(d, ortho Ph C); 126.7(d, ortho Ph C); 125.8(d, para Ph C); 90.0(s, C₁); 78.2(s, C₂); 77.6(s, C¹₁); 77.5(d, C¹₃, C¹₄); 77.4(d, C¹₃, C¹₄); 77.1(d, C₃, C₄, C₅); 74.1(d, C¹₃, C¹₄); 73.6(d, C¹₂, C¹₅); 73.4(d, C¹₂, C¹₅); 71.3(d, C₃, C₄, C₅); 56.9(t, CH₂NMe₂); 45.4(q, NMe₂).

MS m/e (relative intensity): 459(M^+ , 100), 444(M^+ -Me, 2), 391(21), 350(M^+ -SPh, 42), 306(M^+ -NMe₂-SPh, 38), 230(18), 152(25), 121(25), 71(19), 58(36), 44(NMe₂, 18).

IR (neat, Csl) 3100 (ferrocene C-H stretch), 3075, 3060, 3020 (phenyl C-H stretch), 2975-2720 (alkyl C-H stretch), 1441 (ferrocene antisymmetric C-C

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stretch), 1182, 1172 (C-N stretch), 835 (C-H bend perpendicular to the plane of the Cp ring), 620 (S-C stretch), 490 cm^{-1} (antisymmetric ring-metal stretch).

Anal. Calcd. for $\text{C}_{25}\text{H}_{25}\text{S}_2\text{NFe}$: C, 65.35; H, 5.48. Found: C, 65.49; H, 5.35.

1-[(Dimethylamino)methyl]-2,1'-bis(benzylthio)ferrocene (67, R=Bz)

The procedure was the same as 58 except 7.38 g (30 mmol) dibenzyl disulfide was used. The product was obtained as a brown oil: yield 54%.

^1H NMR (δ ppm), 7.14-7.32(m, 8H, Ph); 4.13-4.30(m, 7H, C_5H_4 , C_5H_3); .4.02(d, $J=2.7$ Hz, 1H SCH_2); 3.90(d, $J=2.7$ Hz, SCH_2); 3.82(s, 2H, SCH_2); 3.78(d, $J=12.5$ Hz, CH_2N); 2.98(d, $J=12.5$ Hz, 1H, CH_2N); 2.19(s, 6H, NMe_2).

^{13}C NMR (δ ppm, CD_3COCD_3), 139.2(s, substituted Ph C); 138.6(s, substituted Ph C); 129.2(d, meta Ph C); 128.9(d, meta Ph C); 128.3(d, ortho Ph C); 128.1(d, ortho Ph C); 126.6(d, para Ph C); 126.3(d, para Ph C); 89.3(s, C_1); 82.6(s, C_2); 82.3(s, C^1_1); 76.1(d, C^1_3 , C^1_4); 75.9(d, C^1_3 , C^1_4); 74.8(d, C_3 , C_4 , C_5); 72.9(d, C_3 , C_4 , C_5); 72.6(d, C^1_2 , C^1_5); 72.4(d, C^1_2 , C^1_5); 70.0(d, C_3 , C_4 , C_5); 57.4(t, CH_2N); 45.2(q, NMe_2); 42.4(t, SCH_2); 41.7(t, SCH_2).

MS m/e (relative intensity): 487(M^+ , 100), 472(M^+-Me , 10), 442(M^+-3Me , 37), 366($\text{M}^+-\text{NMe}_2\text{-Bz}$, 11), 334($\text{M}^+-\text{NMe}_2\text{-SBz}$, 42), 164(14), 121(38), 58(27), 56(Fe, 44), 44(NMe_2 , 78).

IR,(neat, Csl) 3098 (ferrocene C-H stretch), 3080, 3025 (phenyl C-H stretch), 2962-2760 (alkyl C-H stretch), 1451 (ferrocene antisymmetric C-C stretch), 1258, 1327 (C-N stretch), 820 (C-H bend perpendicular to the plane of the Cp ring), 620 (S-C stretch), 475 cm^{-1} (antisymmetric ring-metal stretch).

Anal. Calcd. for $\text{C}_{27}\text{H}_{29}\text{S}_2\text{NFe}$: C, 66.52; H, 5.60. Found: C, 66.59; H, 6.08.

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**1-[(Dimethylamino)methyl]-2,1'-bis[(4-tolyl)thio]ferrocene (68,
R=4-tolyl)**

Procedure was the same as 58 except 7.40 g (30 mmol) di(4-tolyl) disulfide was used. The product was obtained as yellow crystals after two recrystallizations from acetone/hexane: yield 78%. mp 71-72°C.

¹H NMR (δ ppm), 6.95-7.06(m, 8H, Ph); 4.53(m, 1H, H₃, H₄, H₅); 4.39(m, 4H, C₅H₄); 4.30(m, 2H, H₃, H₄, H₅); 3.51(d, J=2.0 Hz, 1H CH₂N); 3.43(d, J=2.0 Hz, 1H, CH₂N); 2.24(s, 6H, PhCH₃); 2.05(s, 6H, NMe₂).

¹³C NMR (δ ppm, CD₃COCD₃), 137.0(s, substituted Ph C); 136.8(s, substituted Ph C); 135.3(s, para Ph C); 130.3(d, meta Ph C); 129.8(d, meta Ph C); 127.8(d, ortho Ph C); 127.3(d, ortho Ph C); 89.5(s, C₁); 79.5(s, C₂); 79.0(s, C¹₁); 77.2(d, C¹₃, C¹₄); 77.1(d, C¹₃, C¹₄); 76.6(d, C₃, C₄, C₅); 73.8(d, C₃, C₄, C₅); 73.3(d, C¹₂, C¹₅); 72.9(d, C¹₂, C¹₅); 71.0(d, C₃, C₄, C₅); 56.7(t, CH₂NMe₂); 45.4(q, NMe₂); 21.0(q, PhCH₃).

MS m/e (relative intensity): 487(M⁺, 100), 472(M⁺-Me, 3), 447(19), 419(17), 364(M⁺-S(4-tolyl), 32), 320(M⁺-NMe₂-S(4-tolyl), 33), 152(21), 121(22), 91(22), 56(Fe, 24), 44(NMe₂, 21).

IR (Nujol, KBr) 3100 (ferrocene C-H stretch), 3090, 3080 (phenyl C-H stretch), 2970-2765 (alkyl C-H stretch), 1442 (ferrocene antisymmetric C-C stretch), 1260, 1270 (C-N stretch), 849 (C-H bend perpendicular to the plane of the Cp ring), 620 (S-C stretch), 460 cm⁻¹ (antisymmetric ring-metal stretch).

Anal. Calcd. for C₂₇H₂₉S₂NFe: C, 66.52; H, 5.60. Found: C, 66.43; H, 5.80.

**1-[(Dimethylamino)methyl]-2,1'-bis[(4-Cl-Ph)thio]ferrocene (69,
R = 4-Cl-Ph)**

The procedure was the same as 58 except 8.53 g bis(4-Cl-Ph) disulfide was used. The product was obtained as yellow crystals after recrystallization from CH₂Cl₂/hexane: yield 81%. mp 75°C.

¹H NMR (δ ppm), 6.93-7.14(m, 8H, Ph); 4.58(m, 1H, H₃, H₄, H₅); 4.45(m, 4H, C₅H₄); 4.37(m, 2H, H₃, H₄, H₅); 3.44(s, 2H, CH₂NMe₂); 2.04(s, 6H, NMe₂).

¹³C NMR (δ ppm, CD₃COCD₃), 139.9(s, substituted Ph C); 139.6(s, substituted Ph C); 131.1(s, para Ph C); 129.4(d, meta Ph C); 129.1(d, meta Ph C); 128.9(d, ortho Ph C); 128.1(d, ortho Ph C); 90.3(s, C₁); 78.4(s, C¹₁, C₂); 77.7(d, C¹₃, C¹₄); 77.4(d, C¹₃, C¹₄); 77.1(d, C₃, C₄, C₅); 74.3(d, C₃, C₄, C₅); 73.8(d, C¹₂, C¹₅); 73.6(d, C¹₂, C¹₅); 71.5(d, C₃, C₄, C₅); 56.9(t, CH₂NMe₂); 45.3(q, NMe₂).

MS m/e (relative intensity): 529(69), 528(M⁺, 37), 527(100), 384(M⁺-S(PhCl), 55), 340(M⁺-NMe₂-S(PhCl), 40), 58(CH₂NMe₂, 94), 44(NMe₂, 31).

IR (Nujol, KBr) 3095 (ferrocene C-H stretch), 3082, 3055 (phenyl C-H stretch), 2970-2760 (alkyl C-H stretch), 1450 (ferrocene antisymmetric C-C stretch), 1185, 1170 (C-N stretch), 815 (C-H bend perpendicular to the plane of the Cp ring), 620 (S-C stretch), 475 cm⁻¹ (antisymmetric ring-metal stretch).

Anal. Calcd. for C₂₅H₂₃S₂NFeCl₂: C, 56.83; H, 4.39. Found: C, 56.62; H, 4.35.

**1-[(Dimethylamino)methyl]-2,1'-bis(phenylseleno)ferrocene (70,
R = Ph)**

The procedure was the same as for 58 except 9.36 g of diphenyl diselenide was used. Upon two recrystallizations from CH₂Cl₂/hexane, the product was obtained as yellow crystals: yield 79%. mp 60-61°C.

^1H NMR (δ ppm), 7.30-7.42(m, 10H, Ph); 4.63(m, 1H, H₃, H₄, H₅); 4.47(m, 4H, C₅H₄); 4.39(m, 2H, H₃, H₄, H₅); 3.59(d, 1H, CH₂NMe₂); 3.55(d, 1H, CH₂NMe₂); 2.16(s, 6H, NMe₂).

^{13}C NMR (δ ppm, CD₃COCD₃), 141.9(s, substituted Ph C); 130.7(d, meta Ph C); 129.9(d, meta Ph C); 129.8(d, ortho Ph C); 129.6(d, ortho Ph C); 126.8(d, para Ph C); 90.5(s, C₁); 78.5(d, C¹₃, C¹₄); 78.4(d, C¹₃, C¹₄); 78.2(d, C₃, C₄, C₅); 73.8(d, C₃, C₄, C₅); 73.7(d, C¹₂, C¹₅); 71.7(d, C₃, C₄, C₅); 58.2(t, CH₂NMe₂); 45.3(q, NMe₂).

MS m/e (relative intensity): 555(53), 553(M⁺, 56), 398(33), 276(M⁺-C₅H₃-CH₂NMe₂-SePh, 13), 58(CH₂NMe₂, 85), 44(NMe₂, 31).

IR (Nujol, KBr) 3100 (ferrocene C-H stretch), 3055(aryl C-H stretch), 2970-2760 (alkyl C-H stretch), 1470 (ferrocene antisymmetric C-C stretch), 1253, 1238 (C-N stretch), 841 (C-H bend perpendicular to the plane of the Cp ring), 540 (Se-C stretch), 510 cm⁻¹ (antisymmetric ring-metal stretch).

Anal. Calcd. for C₂₅H₂₅NSe₂Fe: C, 54.25; H, 4.55. Found: C, 54.19; H, 4.74.

1-[(Dimethylamino)methyl]-2,1'-bis(4-Cl-Ph)seleno]ferrocene (71, R=4-Cl-Ph)

The procedure was the same as for 58 except 11.43 g (30 mmol) of bis(4-Cl-Ph) diselenide was used. After two recrystallizations from CH₂Cl₂/hexane, the product was obtained as yellow crystals: yield 67%. mp 96-98°C.

^1H NMR (δ ppm), 7.21-7.38(m, 8H, Ph); 4.61(m, 1H, H₃, H₄, H₅); 4.48(m, 4H, C₅H₄); 4.41(m, 2H, H₃, H₄, H₅); 3.57(d, 1H, CH₂NMe₂); 3.48(d, CH₂NMe₂); 2.17(s, 6H, NMe₂).

^{13}C NMR (δ ppm, CD₃COCD₃), 134.0(s, substituted Ph C); 132.2(s, para Ph C); 131.3(d, meta Ph C); 129.8(d, ortho Ph C); 129.5(d, ortho Ph C); 90.8(s, C₁);

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78.6(d, C¹₃, C¹₄); 78.4(d, C¹₃, C¹₄); 78.2(d, C₃, C₄, C₅); 74.0(d, C₃, C₄, C₅);
73.7(d, C¹₂, C¹₅); 71.9(d, C₃, C₄, C₅); 58.1(t, CH₂NMe₂); 45.3(q, NMe₂).

MS m/e (relative intensity): 624(20), 623(22), 622(M⁺, 9), 621(19),
434(7), 432(20), 390(M⁺-Se(PhCl)-NMe₂, 6), 380(M⁺-Se(PhCl)-CH₂NMe₂, 8),
58(CH₂NMe₂, 100), 44(NMe₂, 38).

IR (Nujol, KBr) 3105 (ferrocene C-H stretch), 3050, 3043 (aryl C-H stretch), 2975-2759 (alkyl C-H stretch), 1460 (ferrocene antisymmetric C-C stretch), 1260, 1235 (C-N stretch), 812 (C-H bend perpendicular to the plane of the Cp ring), 540 (Se-C stretch), 490 cm⁻¹ (antisymmetric ring-metal stretch).

Anal. Calcd. for C₂₅H₂₃Cl₂NSe₂Fe: C, 48.13; H, 3.72. Found: C, 48.57; H, 3.89.

B. Preparation of Metal Complexes

The complexes (S,R)-[ER][C₅H₄]Fe[CHMeNMe₂][ER][MCl₂] and [ER][C₅H₄]Fe[CH₂NMe₂][ER][MCl₂] where E=S, Se, R=Me, Et, *i*-Pr, Ph, Bz, 4-tolyl, and 4-Cl-Ph, and M=Pd and Pt, and CpFeC₅H₃[CHMeNMe₂][SR][PtCl₂] where R=Me, Et, *i*-Pr, and Ph were prepared from a benzene solution of the (PhCN)₂PdCl₂ (0.1g) or (PhCN)₂PtCl₂ (0.2g) and a slight excess of ligand in an approximate 1 : 1.2 molar ratio. The reaction mixture was stirred for 8 h in the case of Pd complexes, and for 8 days in the case of Pt complexes. The resulting precipitates were collected by filtration, washed with cold benzene and petroleum ether. The pure crystals were obtained by recrystallization from CH₂Cl₂/hexane or acetone.

**(S,R)-[1-[1-(Dimethylamino)ethyl]-2,1'-bis(methylthio)ferrocene]-
Palladium(II) chloride (72)**

The general procedure was followed by using amine thioether 43 and $(\text{PhCN})_2\text{PdCl}_2$. The product was obtained as dark purple crystals: yield 90%. mp 157-158°C (dec).

^1H NMR (δ ppm), 4.31-4.45(m, 7H, C_5H_4 , C_5H_3); 4.14(q, $J=4.3$ Hz, 1H, CH_3CH); 3.21(s, 3H, NMe_2); 2.52(s, 3H, SMe_2); 2.29(s, 3H, NMe_2); 2.26(s, 3H, SMe); 1.53(d, $J=4.3$ Hz, 3H, CH_3CH).

MS m/e (relative intensity): 349(M^+-PdCl_2 , 40), 304($\text{M}^+-\text{PdCl}_2-\text{NMe}_2-\text{SCH}_3$, 15), 72(CHMeNMe_2 , 100), 56(Fe , 27), 44(NMe_2 , 72).

IR (Nujol, CsI) 3097 (ferrocene C-H stretch), 2973-2854 (alkyl C-H stretch), 1449 (ferrocene C-C stretch), 1261, 1247 (C-N stretch), 841 (S-C stretch), 456 (ring-metal stretch), 452(Pd-N stretch), 389, 374, 326, 269, 218 cm^{-1} (Pd-S and Pd-Cl stretch).

Anal. Calcd. for $\text{C}_{16}\text{H}_{23}\text{S}_2\text{NFePdCl}_2$: C, 36.49; H, 4.40. Found: C, 36.67; H, 4.22.

**(S,R)-[1-[1-(Dimethylamino)ethyl]-2,1'-bis(phenylthio)ferrocene]-
Palladium(II) chloride (73)**

The general procedure was followed by using amine thioether 51 and $(\text{PhCN})_2\text{PdCl}_2$. The product was obtained as dark purple crystals: yield 87%. mp 142-143°C(dec).

^1H NMR (δ ppm), (7.43-7.51 and 6.98-7.25)(m, 10H, Ph); 4.26-4.41(m, 7H, C_5H_4 , C_5H_3); 4.11(q, $J=6.6$ Hz, 1H, CHCH_3); 3.29(s, 3H, NMe_2); 2.34(s, 3H, NMe_2); 1.55(d, $J=6.6$ Hz, CH_3CH).

MS m/e (relative intensity): 473(M⁺-PdCl₂, 13), 428(M⁺-PdCl₂-3Me, 15), 402(M⁺-PdCl₂-CHMeNMe₂, 13), 320(M⁺-PdCl₂-NMe₂-SPh, 8), 72(CHMeNMe₂, 18), 56(Fe, 24); 44(NMe₂, 100).

IR (Nujol, Csl) 3096 (ferrocene C-H stretch), 3079-3041 (aryl C-H stretch), 2969-2849 (alkyl C-H stretch), 1448 (ferrocene C-C stretch), 1261, 1239 (C-N stretch), 836 (C-H bend perpendicular to the plane of the Cp ring), 641 (S-C stretch), 469 (Pd-N stretch), 378, 360, 321, 231, 217 cm⁻¹ (Pd-S and Pd-Cl stretch).

Anal. Calcd. for C₂₆H₂₇S₂NFePdCl₂: C, 47.99; H, 4.18. Found: C, 48.01; H, 4.51.

(S,R)-[1-[1-(Dimethylamino)ethyl]-2,1'-bis(benzylthio)ferrocene]-Palladium(II) chloride (74)

The general procedure was followed by using thioether 52. The product was obtained as dark purple crystals: yield 74%. mp 172-174°C(dec).

¹H NMR (δ ppm), 7.15-7.34(m, 10H, Ph); 4.29-4.44(m, 7H, C₅H₄, C₅H₃); 4.21(q, J=6.6 Hz, 1H, CHCH₃); 3.94-4.13(m, 4H, CH₂Ph); 3.32(s, 3H, NMe₂); 2.35(s, 3H, NMe₂); 1.46(d, J=6.6 Hz, 3H, CHCH₃).

MS m/e (relative intensity): 501(M⁺-PdCl₂, 14), 428(M⁺-PdCl₂-Me, 5), 456(M⁺-PdCl₂-3Me, 3), 430(M⁺-PdCl₂-CHMeNMe₂, 13), 378(M⁺-PdCl₂-SBz, 9), 72(CHMeNMe₂, 56), 56(Fe, 25), 44(NMe₂, 18).

IR (Nujol, Csl) 3095 (ferrocene C-H stretch), 3078-3038 (aryl C-H stretch), 2880-2455 (alkyl C-H stretch), 1425 (ferrocene C-C stretch), 1251, 1160 (C-N stretch), 835 (C-H bend perpendicular to the plane of the Cp ring), 643 (S-C stretch), 475(antisymmetric ring-metal stretch, 463(Pd-N stretch), 381, 361, 323, 235, 219 cm⁻¹ (Pd-S and Pd-Cl stretch).

Anal. Calcd. for C₂₈H₃₁S₂NFePdCl₂: C, 49.54; H, 4.60. Found: C, ; H, .

(S,R)-[1-[1-(Dimethylamino)ethyl]-2,1'-bis[(4-tolyl)-thio]ferrocene]Palladium(II) chloride (75)

The general procedure was followed by using amine thioether **53** and $(\text{PhCN})_2\text{PdCl}_2$. The product was obtained as red crystals: yield 85%. mp 163-165°C(dec).

^1H NMR (δ ppm), 6.92-7.27(m, 8H, Ph); 4.24-4.40(m, 7H, C_5H_4 , C_5H_3); 4.10(q, $J=6.7$ Hz, 1H, CHCH_3); 3.30(s, 3H, NMe_2); 2.39(s, 3H, PhCH_3); 2.36(s, 3H, NMe_2); 2.26(s, 3H, PhCH_3); 1.55(d, $J=6.7$ Hz, 3H, CHCH_3).

MS m/e (relative intensity): 501(M^+-PdCl_2 , 12), 456($\text{M}^+-\text{PdCl}_2-3\text{Me}$, 7), 430($\text{M}^+-\text{PdCl}_2-\text{CHMeNMe}_2$, 14), 378(M^+-SPhMe , 8), 72(CHMeNMe_2 , 71), 56(Fe, 43), 44(NMe_2 , 79).

IR (Nujol, CsI) 3093 (ferrocene C-H stretch), 3076-3035 (aryl C-H stretch), 2959-2871 (alkyl C-H stretch), 1430 (ferrocene C-C stretch), 1260, 1249 (C-N stretch), 829 (C-H bend perpendicular to the plane of the Cp ring), 644 (S-C stretch), 481(antisymmetric ring-metal stretch), 459(Pd-N stretch), 377, 369, 321, 236, 218 cm^{-1} (Pd-S and Pd-Cl stretch).

Anal. Calcd. for $\text{C}_{28}\text{H}_{31}\text{S}_2\text{NFePdCl}_2$: C, 49.54; H, 4.60. Found: C, 49.64; H, 4.76.

(S,R)-[1-[1-(Dimethylamino)ethyl]-2,1'-bis[(4-Cl-Ph)thio]ferrocene]Palladium(II) chloride (76)

The general procedure was followed by using amine thioether **54** and $(\text{PhCN})_2\text{PdCl}_2$. The product was obtained as black crystals: yield 90%. mp 154-155°C(dec).

^1H NMR (δ ppm), 6.95-7.49(m, 8H, Ph); 4.30-4.42(m, 7H, C_5H_4 , C_5H_3); 4.13(q, $J=6.5$ Hz, CHCH_3); 3.29(s, 3H, NMe_2); 2.34(s, 3H, NMe_2); 1.56(d, $J=6.5$ Hz, 3H, CHCH_3).

MS m/e (relative intensity): 543(16), 541(16), 528(5), 526(6), 470(M^+ -PdCl₂-CHMeNMe₂, 7), 72(100, 56(Fe, 13), 44(NMe₂, 13).

IR (Nujol, Csl) 3099 (ferrocene C-H stretch), 3089-3031 (aryl C-H stretch), 2931-2869 (alkyl C-H stretch), 1430 (ferrocene C-C stretch), 1249, 1130 (C-N stretch), 829 (C-H bend perpendicular to the plane of the Cp ring), 645 (S-C stretch), 480(antisymmetric ring-metal stretch), 459(Pd-N stretch), 379, 365, 331, 235, 221 cm⁻¹ (Pd-S and Pd-Cl stretch).

Anal. Calcd. for C₂₆H₂₅S₂NFePdCl₂: C, 43.42; H, 3.50. Found: C, 43.39; H, 3.66.

(S,R)-[1-[1-(Dimethylamino)ethyl]-2,1'-bis(Phenylthio)ferrocene]-Platinum(II) chloride (77)

The general procedure was followed by using (PhCN)₂PtCl₂ and amine thioether 51. The product was obtained as yellow crystals: yield 61%. mp 188-190°C(dec).

MS m/e (relative intensity): 473(M^+ -PtCl₂, 9), 428(M^+ -PtCl₂-3Me, 6), 402(M^+ -PtCl₂-CHMeNMe₂, 3), 72(CHMeNMe₂, 51).

IR (Nujol, Csl) 3093 (ferrocene C-H stretch), 3085-3100 (aryl C-H stretch), 2958-2869 (alkyl C-H stretch), 1425 (ferrocene C-C stretch), 1261, 1247 (C-N stretch), 831 (C-H bend perpendicular to the plane of the Cp ring), 649(S-C stretch), 459(antisymmetric ring-metal stretch), 381, 359, 340, 268 cm⁻¹ (Pt-N, Pt-Cl and Pt-S stretch).

Anal. Calcd. for C₂₆H₂₇S₂NFePtCl₂: C, 42.23; H, 3.68. Found: C, 41.97; H, 3.64.

**(S,R)-[1-[1-(Dimethylamino)ethyl]-2,1'-bis(benzylthio)ferrocene]-
Platinum(II) chloride (78)**

The general procedure was followed by using $(\text{PhCN})_2\text{PtCl}_2$ and amine thioether 52. The product was obtained as yellow crystals: yield 49%. mp 179-181°C(dec).

MS m/e (relative intensity): 501($\text{M}^+ - \text{PtCl}_2$, 7), 430($\text{M}^+ - \text{PtCl}_2 - \text{CHMeNMe}_2$, 13), 378($\text{M}^+ - \text{PtCl}_2 - \text{SBz}$, 7), 72(CHMeNMe_2 , 100), 56(Fe, 46), 44(NMe_2 , 21).

IR (Nujol, Csl) 3100, 3085-3029, 2879-2760, 1425, 1281, 1151, 830, 655, 479, 466, 389, 362, 335, 279.

Anal. Calcd. for $\text{C}_{28}\text{H}_{31}\text{S}_2\text{NFePtCl}_2$: C, 43.82; H, 4.07. Found: C, 44.01; H, 4.11.

**(S,R)-[1-[1-(Dimethylamino)ethyl]-2,1'-bis[(4-tolyl)thio]-
ferrocene]Platinum(II) chloride (79)**

The general procedure was followed by using $(\text{PhCN})_2\text{PtCl}_2$ and amine thioether 53. The product was obtained as yellow crystals: yield 62%. mp 190-191°C(dec).

MS m/e (relative intensity): 501($\text{M}^+ - \text{PtCl}_2$, 8), 456($\text{M}^+ - \text{PtCl}_2 - 3\text{Me}$, 5), 379($\text{M}^+ - \text{PtCl}_2 - \text{SPhMe}$, 9), 72(CHMeNMe_2 , 100), 56(Fe, 47), 44(NMe_2 , 24).

IR (Nujol, Csl) 3101, 3085-3040, 2969-2871, 1430, 1263, 1259, 832, 651, 475, 466, 376, 369, 339, 247.

Anal. Calcd. for $\text{C}_{28}\text{H}_{31}\text{S}_2\text{NFePtCl}_2$: C, 43.82; H, 4.07. Found: C, 43.98; H, 4.21.

**(S,R)-[1-[1-(Dimethylamino)ethyl]-2,1'-bis(phenylseleno)-
ferrocene]Palladium(II) chloride (80)**

The general procedure was followed by using $(\text{PhCN})_2\text{PdCl}_2$ and amine selenoether 55. The product was obtained as purple crystals: yield 93%. mp 141-142°C(dec).

^1H NMR (δ ppm), 7.14-7.50(m, 10H, Ph); 4.35-4.60(m, 7H, C_5H_4 , C_5H_3); 4.13(q, 1H, CHCH_3); 3.29(s, 3H, NMe_2); 2.35(s, 3H, NMe_2); 1.56(d, 3H, CHCH_3).

MS m/e (relative intensity): 567(M^+ - PdCl_2 , 15), 523(M^+ - PdCl_2 - NMe_2 , 23), 367(M^+ - PdCl_2 - NMe_2 -SePh, 8), 72(CHMeNMe_2 , 51).

IR (Nujol, CsI) 3095, 3081-3072, 2881-2772, 1430, 1245, 1181, 837, 631, 472, 466, 341, 323, 278, 212.

Anal. Calcd. for $\text{C}_{26}\text{H}_{27}\text{Se}_2\text{NFePdCl}_2$: C, 41.90; H, 3.66. Found: C, 40.90; H, 3.63.

(S,R)-[1-[1-(Dimethylamino)ethyl]-2,1'-bis[(4-Cl-Ph)-seleno]ferrocene]Palladium(II) chloride (81)

The general procedure was followed by using $(\text{PhCN})_2\text{PdCl}_2$ and amine selenoether 57. The product was obtained as red crystals: yield 71%. mp 161-163°C(dec).

^1H NMR (δ ppm), 7.17-7.47(m, 8H, Ph); 4.23-4.47(m, 7H, C_5H_4 , C_5H_3); 4.17(q, 1H, CHCH_3); 3.37(s, 3H NMe_2); 2.27(s, 3H, NMe_2); 1.56(d, 3H, CHCH_3).

MS m/e (relative intensity): 636(M^+ - PdCl_2 , 6), 402(M^+ - PdCl_2 - NMe_2 -Se(PhCl), 10); 72(CHMeNMe_2 , 100), 56(Fe, 50), 44(q, NMe_2 , 88).

IR (Nujol, CsI) 3092, 3081-3072, 2871-2777, 1429, 1245, 1171, 828, 636, 471, 462, 351, 323, 298, 279, 217.

Anal. Calcd. for $\text{C}_{26}\text{H}_{25}\text{Se}_2\text{NFePdCl}_2$: C, 38.53; H, 3.07. Found: C, 38.63; H, 3.10.

(S,R)-[1-[1-(Dimethylamino)ethyl]-2,1'-bis(phenylseleno)-ferrocene]Platinum(II) chloride (82)

The general procedure was followed by using $(\text{PhCN})_2\text{PtCl}_2$ and amine selenoether **56**. The product was obtained as yellow crystals: yield 81%. mp 171-173°C(dec).

MS m/e (relative intensity): 524(47), 522(48), 368(5), 290(15), 288(11), 286(10), 154(28), 158(38), 141(45), 121(10), 44(100).

IR (Nujol, CsI) 1439, 1251, 1174, 834, 630, 480, 354, 344, 313, 286, 259, 253 cm^{-1} .

Anal. Calcd. for $\text{C}_{26}\text{H}_{27}\text{Se}_2\text{NFePtCl}_2$: C, 37.50; H, 3.27. Found: C, 37.50; H, 3.17.

[1-[(Dimethylamino)methyl]-2,1'-bis(methylthio)ferrocene]-Palladium(II) chloride (83)

The general procedure was followed except amine thioether **58** and $(\text{PhCN})_2\text{PdCl}_2$ were used. The product was obtained as deep red crystals: yield 87%. mp 153°C(dec).

^1H NMR (δ ppm), 4.26-4.45(m, 7H, C_5H_4 , C_5H_3); 3.89(d, $J=12.7$ Hz, 1H, CH_2NMe_2); 3.09(s, 3H, NMe_2); 2.73(s, 3H, SCH_3); 2.70(d, $J=12.7$ Hz, 1H, CH_2NMe_2); 2.34(s, 3H, NMe_2); 2.16(s, 3H, SCH_3).

MS m/e (relative intensity): 335(M^+-PdCl_2 , 21), 320($\text{M}^+-\text{PdCl}_2-\text{Me}$, 3), 305($\text{M}^+-\text{PdCl}_2-2\text{Me}_2$, 4), 288($\text{M}^+-\text{PdCl}_2-\text{SCH}_3$, 10), 58(CH_2NMe_2 , 22), 56(Fe , 14), 44(q, NMe_2 , 66).

IR (Nujol, CsI) 3111 (ferrocene C-H stretch), 2960-2765 (alkyl C-H stretch), 1429 (ferrocene C-C stretch), 1239, 1186 (C-N stretch), 827 (S-C stretch), 474 (ring-metal stretch), 468 (Pd-N stretch), 324, 318, 298 cm^{-1} (Pd-S and Pd-Cl stretch).

Anal. Calcd. for $C_{15}H_{21}S_2NFePdCl_2$: C, 35.15; H, 4.13. Found: C, 35.59; H, 4.13.

**[1-[(Dimethylamino)methyl]-2,1'-bis(ethylthio)ferrocene]-
Palladium(II) chloride (84)**

The general procedure was followed by using $(PhCN)_2PdCl_2$ and amine thioether 59. The product was obtained as black crystals: yield 59%. mp 144-146°C(dec).

1H NMR (δ ppm), 4.38-4.52(m, 7H, C_5H_4 , C_5H_3); 4.02(d, $J=12.8$ Hz, 1H, CH_2NMe_2); 3.37(m, 1H, SCH_2); 3.27(m, 1H, SCH_2); 3.09(s, 3H NMe_2); 2.73(d, $J=12.8$ Hz, 1H, CH_2NMe_2); 2.58(q, 2H, SCH_2); 2.30(s, 3H, NMe_2); 1.67(t, 3H, βCH_3); 1.14(t, 3H, βCH_3).

MS m/e (relative intensity): 363(M^+-PdCl_2 , 7), 334($M^+-PdCl_2-C_2H_5$, 5), 302($M^+-PdCl_2-SC_2H_5$, 11), 56(Fe, 57), 44(NMe_2 , 19).

IR (Nujol, Csl) 3110 (ferrocene C-H stretch), 2959-2760 (alkyl C-H stretch), 1427 (ferrocene C-C stretch), 1243, 1184 (C-N stretch), 827 (C-H bend perpendicular to the plane of Cp ring), 642 (S-C stretch), 476 (ring-metal stretch), 469 (Pd-N stretch), 320-298 cm^{-1} (Pd-S and Pd-Cl stretch).

Anal. Calcd. for $C_{17}H_{25}S_2NFePdCl_2$: C, 37.77; H, 4.66. Found: C, 37.65; H, 4.55.

**[1-[(Dimethylamino)methyl]-2,1'-bis[(n-propyl)thio]ferrocene]-
Palladium(II) chloride (85)**

The general procedure was followed and $(PhCN)_2PdCl_2$ and ferrocenylamine sulfide 60 were used. The product was obtained as purple crystals: yield 63%. mp 151-152°C(dec).

MS m/e (relative intensity): 391(M^+-PdCl_2 , 11), 316($M^+-PdCl_2-S(n-Pr)$, 22), 272($M^+-PdCl_2-NMe_2-S(n-Pr)$, 7), 56(Fe, 7), 44(NMe_2 , 30).

IR (Nujol, Csl) 3110 (ferrocene C-H stretch), 2959-2770 (alkyl C-H stretch), 1432 (ferrocene C-C stretch), 1238, 1182 (C-N stretch), 828 (C-H bend perpendicular to the plane of Cp ring), 637 (S-C stretch), 476 (ring-metal stretch), 472 (Pd-N stretch), 320-294 cm^{-1} (Pd-S and Pd-Cl stretch).

Anal. Calcd. for $\text{C}_{19}\text{H}_{29}\text{S}_2\text{NFePdCl}_2$: C, 40.13; H, 5.14. Found: C, 40.10; H, 5.11.

**[1-[(Dimethylamino)methyl]-2,1'-bis[(1-propyl)thio]ferrocene]-
Palladium(II) chloride (86)**

The brown crystals decomposed at 131-132°C.

MS m/e (relative intensity): 391($\text{M}^+ - \text{PdCl}_2$, 6), 316($\text{M}^+ - \text{PdCl}_2 - \text{S}(\text{i-Pr})$, 6), 272($\text{M}^+ - \text{PdCl}_2 - \text{S}(\text{i-Pr})$, 11), 56(Fe, 49), 44(NMe_2 , 67).

IR (Nujol, Csl) 3092, 2970-2760, 1428, 1241, 1176, 829, 637, 476, 472, 322-300 cm^{-1} .

Anal. Calcd. for $\text{C}_{19}\text{H}_{29}\text{S}_2\text{NFePdCl}_2$: C, 40.13; H, 5.14. Found: C, 40.33; H, 5.31.

**[1-[(Dimethylamino)methyl]-2,1'-bis(Phenylthio)ferrocene]-
Palladium(II) chloride (87)**

The general procedure was followed except $(\text{PhCN})_2\text{PdCl}_2$ and amine thioether 66 were used. The product was obtained as brick-red crystals: yield 85%. mp 133°C(dec).

^1H NMR (δ ppm), 7.01-7.48(m, 10H, Ph); 4.36-4.43(m, 7H, C_5H_4 , C_5H_3); 3.97(d, $J=12.5$ Hz, 1H, CH_2NMe_2); 3.17(s, 3H, NMe_2); 2.83(d, $J=12.5$ Hz, 1H, CH_2NMe_2); 2.46(s, 3H, NMe_2).

MS m/e (relative intensity): 459(M^+ -PdCl₂, 9), 402(M^+ -PdCl₂-CH₂NMe₂, 3), 350(M^+ -PdCl₂-SPh, 7), 306(M^+ -PdCl₂-SPh-NMe₂, 8), 58(CH₂NMe₂, 28), 44(NMe₂, 26).

IR (Nujol, Csl) 3090, 3080-3070, 2950-2770, 1435, 1245, 1181, 835, 640, 470, 460, 379, 365, 330, 240, 225.

Anal. Calcd. for C₂₅H₂₅S₂NFePdCl₂: C, 47.16; H, 3.98. Found: C, 46.99; H, 3.81.

**[1-[(Dimethylamino)methyl]-2,1'-bis(benzylthio)ferrocene]-
Palladium(II) chloride (88)**

The general procedure was followed by using (PhCN)₂PdCl₂ and amine thioether 67. The product was obtained as purple crystals: yield 82%. mp 161-163°C(dec).

¹H NMR (δ ppm), 7.14-7.3(m, 10H, Ph); 4.26-4.42(m, 7H, C₅H₄, C₅H₃); 3.94-4.10(m, 4H, SCH₂Ph); 3.47(d, J=12.8 Hz, 1H, CH₂NMe₂); 3.30(s, 3H, NMe₂); 2.59(s, 3H, NMe₂); 2.33(d, J=12.8 Hz, 1H, CH₂NMe₂).

MS m/e (relative intensity): 478(M^+ -PdCl₂, 26), 429(M^+ -PdCl₂-NMe₂, 32), 364(M^+ -PdCl₂-SBz, 12), 320(M^+ -PdCl₂-NMe₂-SBz, 9), 58(CH₂NMe₂, 72), 44(NMe₂, 76).

IR (Nujol, Csl) 3102, 3089-3033, 2960-2780, 1430, 1244, 1187, 831, 640, 478, 472, 378, 364, 245, 218 cm⁻¹.

Anal. Calcd. for C₂₇H₂₉S₂NFePdCl₂: C, 48.78; H, 4.40. Found: C, 48.65; H, 4.43.

**[1-[(Dimethylamino)methyl]-2,1'-bis[(4-tolyl)thio]ferrocene]-
Palladium(II) chloride (89)**

The general procedure was followed by using (PhCN)₂PdCl₂ and amine thioether 68. The product was obtained as brick-red crystals: yield 79%. mp 149°C(dec).

^1H NMR (δ ppm), 6.97-7.25(m, 8H, Ph); 4.21-4.41(m, 7H, C_5H_4 , C_5H_3); 4.00(d, $J=12.7$ Hz, 1H, CH_2NMe_2); 3.16(s, 3H, NMe_2); 2.83(d, $J=12.7$ Hz, 1H, CH_2NMe_2); 2.43(s, 3H, NMe_2); 2.34(s, 3H, PhCH_3); 2.24(s, 3H, PhCH_3).

MS m/e (relative intensity): 478($\text{M}^+ - \text{PdCl}_2$, 14), 364($\text{M}^+ - \text{S}(\text{PhCH}_3) - \text{PdCl}_2$, 10), 320($\text{M}^+ - \text{PdCl}_2 - \text{S}(\text{PhCH}_3) - \text{NMe}_2$, 11), 58(CH_2NMe_2 , 34), 56(Fe, 21), 44(NMe_2 , 26).

IR (Nujol, CsI) 3100, 3090-3025, 2955-2775, 1430, 1243, 1182, 831, 640, 477, 466, 371, 363, 328, 239, 221 cm^{-1} .

Anal. Calcd. for $\text{C}_{27}\text{H}_{29}\text{S}_2\text{NFePdCl}_2$: C, 48.78; H, 4.40. Found: C, 48.41; H, 4.32.

[1-[(Dimethylamino)methyl]-2,1'-bis[(4-Cl-Ph)thio]-ferrocene]Palladium(II) chloride (90)

The general procedure was followed by using $(\text{PhCN})_2\text{PdCl}_2$ and amine thioether 69. The product was obtained as brick-red crystals: yield 93%. mp 151-152°C(dec).

^1H NMR (δ ppm), 6.94-7.42(m, 8H, Ph); 4.16-4.43(m, 7H, C_5H_4 , C_5H_3); 4.05(d, $J=12.8$ Hz, 1H, CH_2NMe_2); 3.16(s, 3H, NMe_2); 2.83(d, $J=12.8$ Hz, 1H, CH_2NMe_2); 2.24(s, 3H, NMe_2).

MS m/e (relative intensity): 527($\text{M}^+ - \text{PdCl}_2$, 10), 483($\text{M}^+ - \text{PdCl}_2 - \text{NMe}_2$, 5), 470($\text{M}^+ - \text{PdCl}_2 - \text{CH}_2\text{NMe}_2$, 6), 384($\text{M}^+ - \text{PdCl}_2 - \text{S}(\text{PhCl})$, 8), 340($\text{M}^+ - \text{PdCl}_2 - \text{S}(\text{PhCl}) - \text{NMe}_2$, 7), 58(CH_2NMe_2 , 38), 56(Fe, 15), 44(NMe_2 , 45).

IR (Nujol, CsI) 3090, 3080-3060, 2955-2770, 1428, 1245, 1180, 823, 640, 475, 465, 321-300 cm^{-1} .

Anal. Calcd. for $\text{C}_{25}\text{H}_{23}\text{S}_2\text{NFePdCl}_2$: C, 42.55; H, 3.29. Found: C, 43.05; H, 3.31.

**[1-[(Dimethylamino)methyl]-2,1'-bis(methylthio)ferrocene]-
Platinum(II) chloride (91)**

The general procedure was followed by using (PhCN)₂PtCl₂ and amine thioether 58. The product was obtained as yellow crystals: yield 63%. mp 169-170°C(dec).

MS m/e (relative intensity): 335(M⁺-PtCl₂, 100), 276(M⁺-PtCl₂-Me-NMe₂, 42), 244(M⁺-PtCl₂-NMe₂-SMe, 19), 230(M⁺-PtCl₂-CH₂NMe₂-SMe, 9), 58(CH₂NMe₂, 34), 56(Fe, 49), 44(NMe₂, 96).

IR (Nujol, Csl) 3091, 2957-2776, 1428, 1239, 1178, 830, 638, 475, 476, 319-297 cm⁻¹.

Anal. Calcd. for C₁₅H₂₁S₂NFePtCl₂: C, 29.52; H, 3.47. Found: C, 30.05; H, 3.86.

**[1-[(Dimethylamino)methyl]-2,1'-bis(phenylthio)ferrocene]-
Platinum(II) chloride (92)**

The general procedure was followed by using (PhCN)₂PtCl₂ and amine thioether 66. The product was obtained as yellow crystals: yield 56%. mp 180-182°C(dec).

MS m/e (relative intensity): 459(M⁺-PtCl₂, 100), 416(M⁺-PtCl₂-NMe₂, 4), 402(M⁺-PtCl₂-CH₂NMe₂, 3), 350(M⁺-PtCl₂-SPh, 46), 306(M⁺-PtCl₂-NMe₂-SPh, 45), 58(CH₂NMe₂, 26), 44(NMe₂, 15).

IR (Nujol, Csl) 3097, 3083-3042, 2971-2776, 1435, 1241, 1191, 835, 637, 479, 470, 390, 380, 320, 268 cm⁻¹.

Anal. Calcd. for C₂₅H₂₅S₂NFePtCl₂: C, 41.39; H, 3.47. Found: C, 42.72; H, 3.66.

[1-[(Dimethylamino)methyl]-2,1'-bis(benzylthio)ferrocene]-**Platinum(II) chloride (93)**

The general procedure was followed by using (PhCN)₂PtCl₂ and amine thioether

67. The product was obtained as yellow crystals: yield 49%. mp 176-178°C(dec).

MS m/e (relative intensity): 487(M⁺-PtCl₂, 96), 444(M⁺-PtCl₂-NMe₂, 12), 364(M⁺-PtCl₂-SBz, 21), 320(M⁺-PtCl₂-NMe₂-SBz, 32), 44(NMe₂, 73).

IR (Nujol, Csl) 3093, 3082-3069, 1441, 1246, 1180, 837, 639, 446, 453, 380, 365, 336, 249 cm⁻¹.

Anal. Calcd. for C₂₇H₂₉S₂NFePtCl₂: C, 43.04; H, 3.88. Found: C, 43.10; H, 3.78.

[1-[(Dimethylamino)methyl]-2,1'-bis[(4-tolyl)thio]ferrocene]-**Platinum(II) chloride (94)**

The general procedure was followed by using (PhCN)₂PtCl₂ and amine thioether

68. The product was obtained as yellow crystals: yield 58%. mp 190°C(dec).

MS m/e (relative intensity): 487(M⁺-PtCl₂, 35), 444(M⁺-PtCl₂-NMe₂, 7), 364(M⁺-PtCl₂-S(PhMe), 18), 320(M⁺-PtCl₂-S(PhMe)-NMe₂, 19), 44(NMe₂, 72).

IR (Nujol, Csl) 3107, 3093-3018, 2960-2771, 1427, 1245, 1183, 832, 645, 473, 468, 375, 361, 290, 240 cm⁻¹.

Anal. Calcd. for C₂₇H₂₉S₂NFePtCl₂: C, 43.04; H, 3.88. Found: C, 43.21; H, 3.92.

[1-[(Dimethylamino)methyl]-2,1'-bis[(4-Cl-Ph)thio]ferrocene]-**Platinum(II) chloride (95)**

The general procedure was followed by using (PhCN)₂PtCl₂ and amine thioether

69. The product was obtained as yellow crystals: yield 65%. mp 208-210°C(dec).

MS m/e (relative intensity): 527(M^+ -PtCl₂, 85), 484(M^+ -PtCl₂-NMe₂, 4), 384(M^+ -PtCl₂-S(PhCl), 57), 340(M^+ -PtCl₂-S(PhCl)-NMe₂, 47), 56(Fe, 34), 44(NMe₂, 100).

IR (Nujol, Csl) 3091, 3079-3058, 2941-2782, 1431, 1237, 1176, 830, 635, 477, 468, 391, 372, 323, 271 cm⁻¹.

Anal. Calcd. for C₂₅H₂₃S₂NFePtCl₄: C, 37.80; H, 2.92. Found: C, 39.02; H, 2.98.

**[1-[(Dimethylamino)methyl]-2,1'-bis(Phenylseleno)ferrocene]-
Palladium(II) chloride (96)**

The general procedure was followed by using (PhCN)₂PdCl₂ and amine selenoether 71. The product was obtained as dark-red crystals: yield 90%. mp 128-129°C(dec).

¹H NMR (δ ppm), 7.01-7.48(m, 10H, Ph); 4.36-4.43(m, 7H, C₅H₄, C₅H₃); 3.97(d, J=13 Hz, 1H, CH₂NMe₂); 3.17(s, 3H, NMe₂); 2.83(d, J=13 Hz, 1H, CH₂NMe₂); 2.46(s, 3H, NMe₂).

IR (Nujol, Csl) 3100, 3070, 3050, 3020, 2975-2820, 1460, 1290, 1190, 1180, 811, 550, 480, 392, 382, 342, 241 cm⁻¹.

Anal. Calcd. for C₂₅H₂₅NSeFePdCl₂: C, 41.04; H, 3.49. Found: C, 41.17; H, 3.50.

**(R,S)-[1-[1-(Dimethylamino)ethyl]-2-(methylthio)ferrocene]-
Platinum(II) chloride (97)**

The general procedure was followed by using (PhCN)₂PtCl₂ and (R,S)-CpFe[C₅H₃][CHMeNMe₂][SMe]. The product was obtained as yellow crystals: yield 82%. mp 181-183°C(dec).

^1H NMR* (δ ppm), 4.47(m, 1H, H₃, H₄, H₅); 4.35(m, 1H, H₃, H₄, H₅); 4.31(m, 1H, H₃, H₄, H₅); 4.21(s, 5H, Cp); 3.47(q, J= Hz, 1H, NCHNMe); 3.34(s, 3H, NMe₂); 2.71(s, 3H, SMe); 2.45(s, 3H, NMe₂); 1.55(d, J= Hz, 3H, NCHCH₃).

MS m/e (relative intensity): 303(M⁺-PtCl₂, 1), 258(M⁺-PtCl₂-3Me, 6), 121(FeCp, 3), 44(NMe₂, 100).

IR (Nujol, Csl) 520, 475, 385, 360, 330, 305, 295, 275, 250, 220 cm⁻¹.

Anal. Calcd. for C₁₅H₂₁NSPtCl₂Fe: C, 31.64; H, 3.72. Found: C, 31.43; H, 3.67.

**(R,S)-[1-[1-(Dimethylamino)ethyl]-2-(ethylthio)ferrocene]-
Platinum(II) chloride (98)**

The general procedure was followed by using (PhCN)₂PtCl₂ and (R,S)-CpFe[C₅H₃][CHMeNMe₂][SEt]. The product was obtained as yellow crystals: yield 78%. mp 177-179°C(dec).

^1H NMR (δ ppm), 4.51(m, 1H, H₃, H₄, H₅); 4.34(m, 2H, H₃, H₄, H₅); 4.19(s, 5H, Cp); 3.98(q, J= Hz, 1H, CHMe); 3.69(q, 1H, SCH₂); 3.44(q, 1H, SCH₂); 3.32(s, 3H, NMe₂); 2.45(s, 3H, NMe₂); 1.66(d, J= Hz, 3H, CHMe); 1.23(t, 3H, SCH₂Me).

MS m/e (relative intensity): 317(M⁺-PtCl₂, 3), 302(M⁺-PtCl₂-Me, 1), 273(M⁺-PtCl₂-NMe₂, 4), 272(M⁺-PtCl₂-HNMe₂, 16), 121(FeCp, 4), 44(NMe₂, 100).

IR (Nujol, Csl) 505, 478, 467, 458, 421, 372, 339, 315, 249, 228cm⁻¹.

Anal. Calcd. for C₁₆H₂₃NSPtCl₂Fe: C, 32.95; H, 3.97. Found: C, 32.58; H, 3.72.

* For coupling between ^{195}Pt and ^1H see Chapter III (Results and Discussion).

**(R,S)-[1-[1-(Dimethylamino)ethyl]-2-[(1-Propyl)thio]ferrocene]-
Platinum(II) chloride (99)**

The general procedure was followed by using $(\text{PhCN})_2\text{PtCl}_2$ and (R,S)- $\text{CpFe}[\text{C}_5\text{H}_3][\text{CHMeNMe}_2][\text{S-i-Pr}]$: yield 85%. mp 176-178°C(dec).

^1H NMR (δ ppm), 4.73-4.39(m, 3H, H_3 , H_4 , H_5); 4.26(s, 5H, Cp); 3.60(m, 1H, SCHMe_2); 3.47(q, 1H, NCHMe); 3.34(s, 3H, NMe_2); 2.45(s, 3H, NMe_2); 1.77(d, NCHMe); 1.57(d, 3H, βCH_3); 1.23(d, 3H, βCH_3).

MS m/e (relative intensity): 331($\text{M}^+ - \text{PtCl}_2$, 1), 316($\text{M}^+ - \text{PtCl}_2 - \text{Me}$, 1), 288($\text{M}^+ - \text{PtCl}_2 - \text{HNMe}_2$, 17), 244($\text{M}^+ - \text{PtCl}_2 - \text{CHMeNMe}_2$, 8), 121(FeCp , 5), 44(NMe_2 , 100).

IR (Nujol, Csl) 503, 471, 405, 390, 349, 317, 305, 225, 210 cm^{-1} .

Anal. Calcd. for $\text{C}_{17}\text{H}_{25}\text{NSPtCl}_2\text{Fe}$: C, 34.18; H, 4.22. Found: C, 34.08; H, 4.31.

**(R,S)-[1-[1-(Dimethylamino)ethyl]-2-(Phenylthio)ferrocene]-
Platinum(II) chloride (100)**

The general procedure was followed by using $(\text{PhCN})_2\text{PtCl}_2$ and (R,S)- $\text{CpFe}[\text{C}_5\text{H}_3][\text{CHMeNMe}_2][\text{SPh}]$. The product was obtained as yellow crystals: yield 68%. mp 175-176°C(dec).

^1H NMR (δ ppm), 7.15-7.57(m, 5H, Ph); 4.23-4.35(m, 3H, H_3 , H_4 , H_5); 4.20(s, 5H, Cp); 3.77(q, 1H, NCHMe); 3.42(s, 3H, NMe_2); 2.52(s, 3H, NMe_2); 1.53(d, 3H, NCHMe).

MS m/e (relative intensity): 320($\text{M}^+ - \text{PtCl}_2 - \text{HNMe}_2$, 3), 212($\text{M}^+ - \text{PtCl}_2 - \text{SPh} - \text{NMe}_2$, 3), 77(C_6H_5 , 3), 65(C_5H_5 , 9), 44(NMe_2 , 26).

IR (Nujol, Csl) 500, 475, 450, 438, 330, 310, 250, 230, 215 cm^{-1} .

Anal. Calcd. for $\text{C}_{20}\text{H}_{23}\text{FeSNPtCl}_2$: C, 38.05; H, 3.67. Found: C, 36.59; H, 3.57.

C. Grignard cross-coupling reaction of allylmagnesium chloride to 4-phenyl-1-pentene using NiCl_2 and ligand 44, 48, 51, and 54.

NiCl_2 (0.0499 mmol, 0.0065 g) was placed in a 100 mL round-bottomed Schlenk flask equipped with a stirring bar and a septum. The vessel was evacuated and filled with Ar several times. 10 mL dry ether was added to the flask to dissolve NiCl_2 and then 0.0499 mmol of appropriate ligand was added and the reaction mixture was stirred for 2 h. Upon being cooled to -78°C 1.41 g (10.0 mmol) 1-Phenylethyl chloride in 20 mL dry ether was added dropwise and stirred for 2 h at room temperature before allylmagnesium chloride (20 mmol, 10 mL of a 2 M solution in THF) being added via syringe at -78°C . The reaction mixture was allowed to warm to 0°C , stirred for 40 h and hydrolyzed with 10% HCl. The organic layer and ether extracts from the aqueous layer were combined, washed with saturated NaHCO_3 solution and water, and dried over Na_2SO_4 . Evaporation of solvent and chromatography on a silica gel column (hexane/ether) gave 96-97.5% of 4-Phenyl-1-Pentene.

Conversion of 4-Phenyl-1-Pentene to methyl 3-Phenylbutyrate.

The procedure is identical with that reported before.⁷¹ A solution of 2.48 g (18.0 mmol) K_2CO_3 in 120 mL of water and a solution of 10.26 g (48 mmol) of sodium periodate and 1.26 g (8 mmol) of KMnO_4 in 120 mL of water was added to a solution of 4-Phenyl-1-Pentene (0.906 g, 6.2 mmol) in 160 mL tert-butyl alcohol. Aqueous NaOH (2N) was added dropwise until the PH of solution was 8.5. After being stirred overnight, tert-butyl alcohol was removed under reduced pressure. The solution was adjusted to PH 2.5 by dropwise addition of concentrated HCl. Then sodium bisulfite was added until the solution became off-white. The solution was extracted twice with ether, then extracts were combined, dried over K_2CO_3 and concentrated. A solution of acid (0.590 g, 3.5 mmol) and p-toluenesulfonic acid (80 mg) in 20 mL of methanol was

refluxed for 3 h. Upon the solvent being removed, the residue was taken up in ether. Then, the reaction mixture was washed with 10% aqueous NaOH, dried over anhydrous K_2CO_3 , evaporated, and distilled [100-120°C (0.01 mm)] to give methyl 3-Phenylbutrate (70-87%).

1H NMR (δ ppm), 7.16-7.45(m, 5H, Ph); 3.61(s, 3H, OCH_3); 3.28(sex, J = 7.0Hz, 1H, $CHPhMe$); 2.63(dd, $J_{gem}=15Hz$, $J_{vic}=8Hz$, 1H, CH_2CH); 2.53(dd, $J_{gem}=15Hz$, $J_{vic}=8Hz$, 1H, CH_2CH); 1.29(d, J=7.0Hz, 3H, $CHCH_3$).

D. Selective Hydrogenation of Conjugated Dienes to Olefins.

7.45×10^{-3} mol of substrate, 9 mL acetone and 2×10^{-5} mol catalysts were added to a 100 mL pressure bottle equipped with stirring bar. The bottle filled and evacuated at least 3 times with hydrogen before it was filled at a determined pressure. At the end of each experiment the initial turnover rate, product analysis and selectivity were determined.

E. X-ray Structural Determination

1. [1-[(Dimethylamino)methyl]]-2-(t-butylthio)-ferrocene]Palladium chloride ⁷² (101)

A summary of data collection and crystallographic parameters for compound 101 is given in Table 1.

**2. [1-[(Dimethylamino)methyl]-2,1'-bis(methylthio)-
ferrocene]Palladium(II) chloride (83)**

A summary of data collection and crystallographic parameters for compound 83 is given in Table 2.

Table 1

X-ray Structure Determination for [1-(dimethylamino)methyl]-2-(1-butylthio)ferrocene]palladium dichloride (101)

Formula:	C₁₇H₂₅Cl₂FeNPdS
F.W.:	508.61
Crystal:	
color:	purple red
size:	0.20x0.20x0.35 mm
mounting:	glass capillary, random orientation
density:	1.75 g/cm³ (calc)
Radiation:	MoKα, (λ = 0.71073Å)
Instrument:	Nicolet P3F diffractometer
Unit cell:	
no. reflns:	1 8
2θ range:	30 < 2θ < 39
temperature:	23(1)°C
system:	orthorhombic
space group:	P2₁2₁2₁
a:	7.818(1)Å
b:	14.336(3)Å
c:	17.235(3)Å
Volume:	1931.7(5)Å
Data collection:	
scan type:	θ-2θ
scan rate:	2°/min (in 2θ)
scan range (°):	2.10 + (2θ(Kα₂) - 2θ(Kα₁))
max. 2θ:	50°
total data:	3 177

Table 1. Continued

unique data:	3153
Absorption correction:	
coefficient:	20.6 cm ⁻¹ (for MoK α)
type:	empirical, based on psi-scans
range:	0.933 to 1.000, average = 0.981
Structure solution:	
method:	Patterson heavy-atom, Pd atom located, other non-
H atoms	from succeeding difference maps
Structure refinement:	
method	full-matrix least-squares
minimization:	$\Sigma w(F_o - F_c)^2$
weight, w:	1.0 for observed reflections
H-atoms:	riding on carbon atom
scat. factors:	Cromer and Waber ⁷³
$\Delta f'$ and $\Delta f''$:	Cromer ⁷³
observed data:	2591 with $I > 3\sigma(I)$
parameters:	208
convergence:	largest $\delta/\sigma < 0.37$
R factors:	$R_1 = \Sigma F_o - F_c / \Sigma F_o = 0.046$
	$R_2 = (\Sigma w(F_o - F_c)^2 / \Sigma w F_o^2)^{1/2} = 0.053$
e.s.d.o.u.w.:	2.38
computer:	VAX 11/750
program system:	SDP/VAX ⁷⁴

Table 2

X-ray Structure Determination for [1-[(Dimethylamino)methyl]-2,1'-bis(methylthio)ferrocene]palladium(II) chloride (83)

Formula:	$C_{15}H_{21}Cl_2FePdNS_2$
F.W.:	512.62
Crystal:	
color:	deep red
size:	0.04x0.36x0.60 mm
mounting:	glass capillary, random orientation
density:	1.90 g/cm ³ (calc)
Radiation:	MoK α , (λ = 0.71073Å)
Instrument:	Nicolet P3F diffractometer
Unit cell:	
no. reflns:	18
2 θ range:	20 < 2 θ < 25
temperature:	24(1)°C
system:	orthorhombic
space group:	P2 ₁ /c
a:	11.567(2)Å
b:	11.675(2)Å
c:	13.270(2)Å
Volume:	1792.1(4)Å ³
Data collection:	
scan type:	θ -2 θ
scan rate:	3°/min (in 2 θ)
scan range (°):	2.00 + (2 θ (K α_2) - 2 θ (K α_1))
max. 2 θ :	50°
total data:	3329

Table 2. Continued

unique data:	3006
Absorption correction:	
coefficient:	23.2 cm ⁻¹ (for MoK α)
type:	empirical, based on psi-scans
range:	0.933 to 1.000, average = 0.996
Structure solution:	
method:	Patterson heavy-atom, Pd atom located, other non-
H atoms	from succeeding difference maps
Structure refinement:	
method	full-matrix least-squares
minimization:	$\Sigma w(F_o - F_c)^2$
weight, w:	1.0 for observed reflections
H-atoms:	riding on carbon atom
scat. factors:	Cromer and Waber ⁷³
$\Delta f'$ and $\Delta f''$:	Cromer ⁷³
observed data:	2742 with $I > 3\sigma(I)$
parameters:	200
convergence:	largest $\delta/\sigma < 0.37$
R factors:	$R_1 = \Sigma F_o - F_c / \Sigma F_o = 0.084$
	$R_2 = (\Sigma w(F_o - F_c)^2 / \Sigma w F_o^2)^{1/2} = 0.105$
e.s.d.o.u.w.:	5.59
computer:	VAX 11/750
program system:	SDP/VAX ⁷⁴

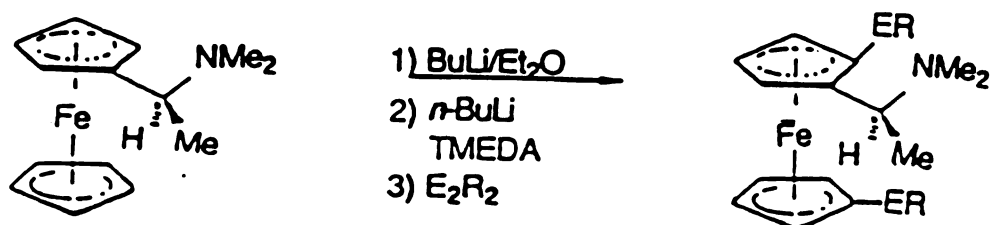
RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

1. Preparation of Ligands

a.1 Synthesis of (S,R)-[ER]C₅H₄FeC₅H₃[CHMeNMe₂][ER] (E = S, R = Me, Et, n-Pr, i-Pr, n-Bu, t-Bu, sec-Bu, i-Pent, Ph, Bz, 4-tolyl, and 4-Cl-Ph and E = Se, R = Me, Ph, and 4-Cl-Ph) (43-57).

A series of previously unknown ferrocenyl amine sulfide and selenide ligands (S,R)[ER]C₅H₄FeC₅H₃[CHMeNMe₂][ER] where E = S, Se and R = Me, Et, n-Pr, i-Pr, n-Bu, sec-Bu, t-Bu, i-Pent, Ph, Bz 4-tolyl and 4-Cl-Ph were prepared via lithiation of (S)-[1-(dimethylamino)ethyl]ferrocene, first in the presence of ether and then TMEDA, followed by treatment with appropriate disulfides or diselenides as it is shown in Scheme 8. (S)-[1-(dimethylamino)ethyl]ferrocene 12 was prepared according to Ugi's procedure³⁴ and was resolved by using (R)-(+)-tartaric acid. At the first step (S)-12 was lithiated by use of n-BuLi in ether to give 96% of (S)-(S)-13 (Scheme 1)²⁵ further lithiation in the presence of TMEDA and then reaction with suitable dialkyl or diaryl disulfides or diselenides produced the (S)-(R) amines 43-57. It has been shown that it is necessary to wash the products by use of aqueous NaHCO₃ solution in order to enhance the yield.⁷⁵ Without using NaHCO₃ the yields of the ferrocenyl amines with one sulfide substituent were between 0.1% to 45%⁷⁶ while yields were considerably higher when the reaction mixtures were washed.⁷⁵ In the former case the products were obtained as yellow powders,⁷⁶ possibly because the products were salts of the amine. Ether was always used as the solvent in the synthesis of these ligands, and halogenated organic solvents such as CH₂Cl₂, CHCl₃ and CCl₄ were avoided to prevent the possible production of quaternary ammonium salts such as those reported by Nesmayanov and co-workers.^{77,78} The separation was carried out by chromatography on silica gel column. The products in most cases were obtained as



E=S R=Me(43)
 Et(44)
 n-Pr(45)
 i-Pr(46)
 n-Bu(47)
 s-Bu(48)
 t-Bu(49)
 i-Pent(50)
 Ph(51)
 Bz(52)
 4-tolyl(53)
 4-Cl-Ph(54)

E=Se R=Me(55)
 Ph(56)
 4-Cl-Ph(57)

Scheme 8

brown oils, but for compounds **51**, **53**, **54**, **56**, and **57** after several recrystallizations from CH₂Cl₂/hexane the products were obtained as yellow crystals. Compounds **43-57** all have two elements of chirality, namely, central and planar chirality (due to two different substituents in one Cp ring).⁷⁹ These ligands also have an amine as a functional group. The presence of the elements of chirality and functional group is essential for a ligand if it is to be used in asymmetric synthesis.⁸⁰

a.2 ¹H NMR of Compounds 43-57

Table 3 presents ¹H NMR data of compounds **43-57**. Figures 2 and 3 also show ¹H NMR of [S-*i*-Pr]C₅H₄FeC₅H₃[CHMeNMe₂][S-*i*-Pr] and [SPh]C₅H₄FeC₅H₃[CHMeNMe₂][SPh] which are typical examples. An important feature of these spectra is the diastereotopic nature of S-CH₂ protons. The non-isochronicity of these protons is due to the chirality of the ligands and they appear at different positions with their proper multiplicity. However, sometimes the total number of peaks are fewer than that expected due to the overlap of some peaks. The two methyl groups of NMe₂ are also diastereotopic and, therefore, non equivalent. They give only one signal because of rapid inversion at the N-atom. This phenomenon was also observed by other workers.⁸¹ The upfield chemical shifts for the NMe₂ protons are due to the ring current effect. It is difficult to assign substituted Cp ring protons with absolute certainty. ¹H NMR studies⁸²⁻⁸⁴ have proved that any substituent may shield or deshield either positions 2 and 5 or 3 and 4, in any combination relative to ferrocene. Here, we have assigned the position of Cp ring protons by comparison with previous results⁴⁵⁻⁴⁸ and by integration of clearly separated peaks.

a.3 ¹³C NMR of Compounds 43-57

Carbon-13 NMR data are presented in Table 4. Figures 4 and 5 also show ¹³C NMR spectra of [S-*i*-Pr]C₅H₄FeC₅H₃[CHMeNMe₂][S-*i*-Pr] and [S-Ph]C₅H₄FeC₅H₃[CHMeNMe₂][S-Ph] respectively. All of these compounds have central and planar elements of chirality and C₁ symmetry. Consequently, groups such as

Table 3

250 MHz ^1H NMR Data for (S,R)-[ER] $\text{C}_5\text{H}_4\text{FeC}_5\text{H}_3[\text{CHMeNMe}_2]\text{[ER]}$ in CDCl_3 at Room Temperature: δ ppm (J, Hz)

SR

Compound	Ph	C_5H_4	C_5H_3	CHMe	NMe_2	CHMe	αH	βH	γH	δH
(<u>S</u> , <u>R</u>)-43, E=S, R=Me		4.17 m	4.26 m ^a 4.07 m ^b	3.90 q (4)	2.09 s	1.36 d' (4)	2.28 s			
							2.23 s			
(<u>S</u> , <u>R</u>)-44, E=S; R=Et		4.16 m	4.24 m ^a 4.05 m ^b	3.88 q (7)	2.04 s	1.29 d (7)	2.95 m ^a	1.13 t		
							2.65 m ^a	1.06 t		
							2.48 q ^b			
(<u>S</u> , <u>R</u>)-45, E=S; R= η -Pr		4.20 m	4.31 m ^a 4.08 m ^b	3.94 q (7)	2.10 s	1.30 d (7)	2.80 m ^a	1.58 m ^b	0.98 t	
							2.62 m ^a	1.52 m ^b	0.91 t	
							2.52 m ^b			
(<u>S</u> , <u>R</u>)-46, E=S; R=i-Pr		4.20 m	4.34 m ^a 4.10 m ^b	3.94 q (7)	2.09 s	1.33 d (7)	3.20 h	1.19 d		
							2.82 h	1.17 d		
								1.12 d		
								1.09 d		
(<u>S</u> , <u>R</u>)-47, E=S; R= η -Bu		4.16 m	4.29 m ^a 4.07 m ^b	3.95 q (7)	2.08 s	1.34 d (7)	2.84 m ^a	1.51 m ^b	1.45 m ^b	0.86 t
							2.61 m ^a	1.47 m ^b	1.40 m ^b	0.82 t
							2.52 m ^b			
(<u>S</u> , <u>R</u>)-48, E=S; R= ξ -Bu		4.22 m	4.34 m ^a 4.10 m ^b	3.98 q (7)	2.07 s	1.36 d (7)	3.04 m ^a	1.52 m ^b	0.95 t	
							2.58 m ^a	1.48 m ^b	0.90 t	
								1.15 d		
								1.12 d		

Table 3 Continued

Compound	Ph	C ₅ H ₄	C ₅ H ₃	CHMe	NMe ₂	CHMe	SR			
							αH	βH	γH	δH
(S,R)-49, E=S; R=i-Bu		4.19 m	4.24 m ^a 4.13 m ^b	3.89 q (7)	2.09 s	1.30 d (7)	1.22 s			
(S,R)-50, E=S; R=i-Pent		4.19 m	4.26 m ^a 4.06 m ^b	3.95 q (7)	2.08 s	1.32 d (7)	2.80 m ^a 2.76 m ^a 2.60 m ^b	2.55 m ^b 2.53 m ^b	1.62 m ^a 1.40 m ^a 0.81 d 0.79 d	
(S,R)-51, E=S; R=Ph	7.05-7.20 m	4.40 m	4.60 m ^a 4.36 m ^b	3.90 q (7)	1.93 s	1.42 d (7)				
(S,R)-52, E=S; R=Bz	7.13-7.27 m	4.13 - 4.38 m		4.01 q (7)	2.14 s	1.37 d (7)	3.90 d ^a 3.85 d ^a 3.82 s ^b			
(S,R)-53, E=S; R=4-tolyl	6.95 -7.13 m	4.40 m	4.55 m ^a 4.30 m ^b	3.91 q (7)	1.95 s	1.48 d (7)	2.24 ^c			
(S,R)-54, E=S; R=4-chlorophenyl	6.98 -7.11 m	4.42 m	4.56 m ^a 4.35 m ^b	3.92 q (7)	1.97 s	1.42 d (7)				
(S,R)-55, E=Se; R=Me		4.17 m	4.24 m ^a 4.07 m ^b	3.96 q (7)	2.07 s	1.33 d (7)	2.12 s 2.11 s			
(S,R)-56, E=Se; R=Ph	7.11-7.36 m	4.34 m	4.50 m ^a 4.26 m ^b	3.92 q (7)	1.96 s	1.44 d (7)				

Table 3 Continued

Compound	Ph	C ₅ H ₄	C ₅ H ₃	CHMe	NMe ₂	CHMe	SR			
							αH	βH	γH	δH
(S,E)-57, E=Se; R=4-chlorophenyl	7.14-7.35 m	4.38 m 4.29 m ^b	4.63 m ^a	3.92 q (7)	1.97 s	1.39 d (7)				
a ¹ H, b ² H, cPh-CH ₃										

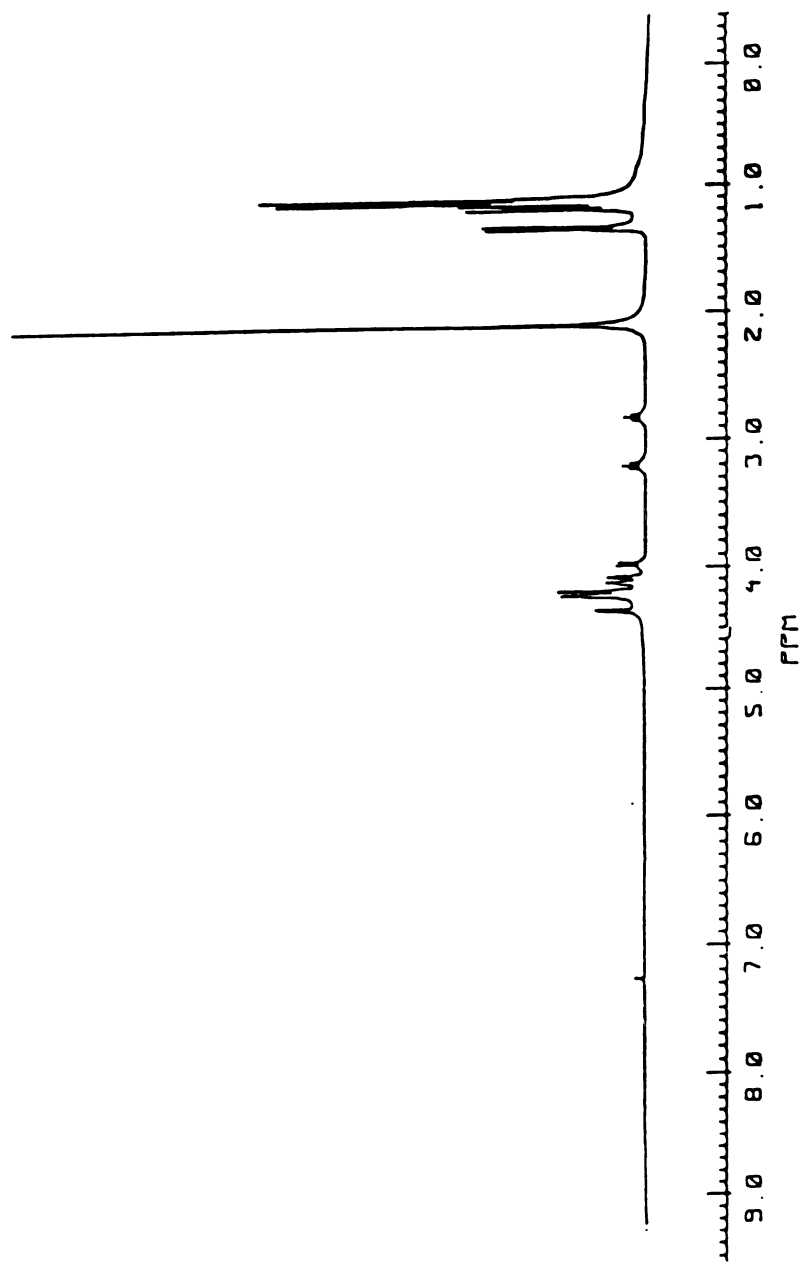


Figure 2. ^1H NMR spectrum of compound 46 (R = *i*-Pr)

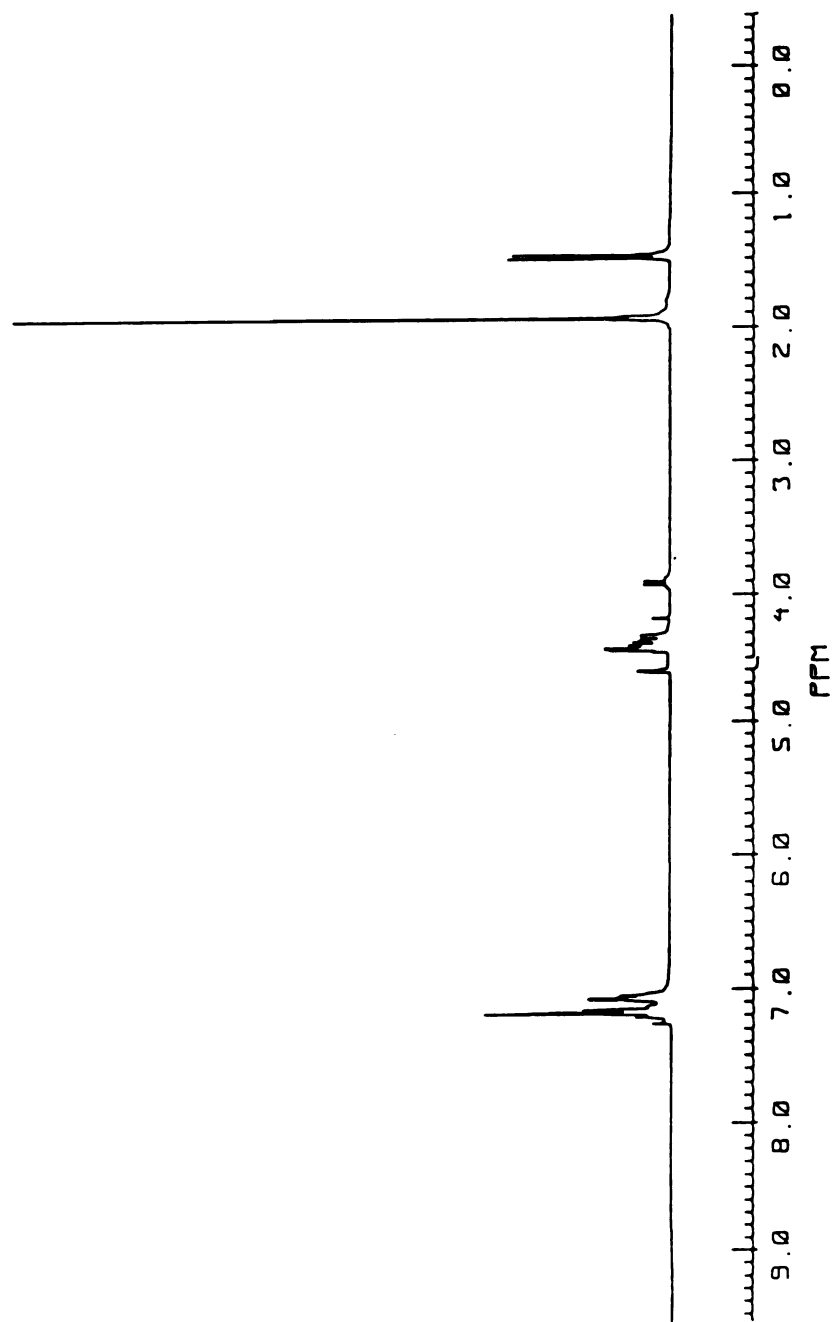


Figure 3. ^1H NMR spectrum of 51 (R = Ph)

Table 4
250 MHz Gated Decoupled ^{13}C NMR Data for (S,E)-[ER] $[\text{C}_9\text{H}_4\text{FeC}_5\text{H}_3(\text{CHMeNMe}_2)\text{ER}]$ in CD_3COCD_3 at Room Temperature: δ ppm.

Compound	Ph	C ₁	C ₂	C ¹ ₁	C ₃ , C ₄ , C ₅	C ¹ ₂ C ¹ ₅	C ¹ ₃ C ¹ ₄	CHMe	NMe ₂ CHMe	αC	SR		
											βC	γC	δC
(S,E)-43, E-S; R=Me		93.6	85.9	84.9	68.4, 69.6, 73.2	72.4	77.5 71.1	56.2	40.0 10.7	19.7	19.6		
(S,E)-44, E-S; R=Et		95.2	82.0	81.8	76, 76.9, 68.8	72.1	75.2	56.3	40.0 10.1	31.2 15.3			
(S,E)-45, E-S; R=n-Pr		95.0	82.2	82.1	75.9, 69.9, 68.9	72.0	75.1 71.9	56.3	39.9 10.0	39.4 23.4 13.7	30.5 15.1		
(S,E)-46, E-S; R=i-Pr		96.2	80.3	79.4	77.6, 70.1, 69.1	72.7	76.9 72.3	56.2 76.8	39.8 9.2	39.4 24.2			23.6 23.0
(S,E)-47, E-S; R=n-Bu		95.2	82.5	82.1	75.9, 69.9, 68.8	71.9	74.9 71.8	56.3	39.8 9.8	39.0 32.2 22.3 13.8	36.3		22.0
(S,E)-48, E-S; R=sec-Bu		96.3	80.9	80.1	77.9, 70.2, 69.5	73.2	77.4 72.6	56.3 77.2	40.1 9.5	46.4 30.3 12.6	46.2 30.1 12.2		
(S,E)-49, E-S; R=i-Bu		89.5	77.6	77.5	71.5, 69.2, 68.6	69.5	71.2 69.4	58.6	40.7 15.8	44.6 31.1			
(S,E)-50, E-S; R=i-Pent		95.1	82.6	82.0	76.1, 69.7, 68.9	71.9	74.9 71.8	56.3	39.9 9.7	39.3 35.4 27.8 22.7	34.7 27.5		22.5 22.4

Table 4 Continued

Compound	Ph	C ₁	C ₂	C _{1'}	C ₃ , C ₄ , C ₅	C ₁₂ , C ₁₃	C ₁₃ , C ₁₄	C ₁₅ , Me	NMe ₂	CH ₂	89		
											αC	βC	γC
(S,E)-51, E-S; R-Ph	141.5 ^s , 129.5 ^m 128.9 ^m , 127.8 ^m 128.8 ^o , 125.8 ^p 125.6 ^p	98.5	79.3	79.0	78, 70.8, 70.5	73.8	77.4	58.3 73.8	40.1	11.9			
(S,E)-52, E-S; R-Bz	140.1 ^s , 129.8 ^m 129.7 ^m , 129.0 ^o 128.8 ^o , 127.7 ^p 127.4 ^p	98.3	82.3	81.0	77.6, 70.1, 69.1	72.0	78.6	58.5 71.9	40.1 75.5	9.08	42.0		41.5
(S,E)-53, E-S; R-p-tolyl	138.8 ^s , 136.0 ^p 135.3 ^p , 130 ^m 129.8 ^m , 127.8 ^o 127.4 ^o	95.4	79.7	79.1	77.7, 70.6, 70.4	73.6	77.2	58.9 73.4	45.4	12.3			20.9 ^a
(S,E)-54, E-S; R-4-chlorophenyl	139.9 ^s , 131.1 ^m 130.8 ^m , 129.5 ^p 129.2 ^p , 128.8 ^o 128.2 ^o	98.4	79.4	79.4	78.1, 71.0, 70.7	74.0	77.4	58.3 43.8	39.9	10.8			
(S,E)-55, E-Se; R-Me		94.4	77.1	77.1	74.2, 68.7, 68.6	71.9	73.0	59.1 71.6	39.8	10.2	9.32		8.62
(S,E)-56, E-Se; R-Ph	135.0 ^s , 130.8 ^m 129.9 ^o , 128.8 ^p 128.7 ^p	95.8	80.7	79.6	78.4, 70.8, 70.1	73.9	78.2	58.9 73.7	40.9 78.0	11.8			

Table 4 Continued

Compound	Ph	C ₁	C ₂	C ¹ ₁	C ₃ , C ₄ , C ₅	C ¹ ₂ C ¹ ₅	C ¹ ₃ C ¹ ₄	CH-Me	NMMe ₂ CH-Me	SR			
										αC	βC	γC	δC
(S,B)-51, E-S; R-Ph	141.5 ^s , 129.5 ^m 128.9 ^m , 127.8 ^m 128.9 ^o , 125.8 ^p 125.6 ^p	98.5	79.3	79.0	78, 70.8, 70.5	73.8	77.4	56.3 73.6	40.1 11.9				
(S,B)-52, E-S; R-Bz	140.1 ^s , 129.8 ^m 129.7 ^m , 129.0 ^o 128.8 ^o , 127.7 ^p 127.4 ^p	98.3	82.3	81.0	77.6, 70.1, 69.1	72.0	76.6	56.5 71.9	40.1 9.08 75.5	42.0		41.5	
(S,B)-53, E-S; R-p-tolyl	138.8 ^s , 136.0 ^p 135.3 ^p , 130 ^m 129.8 ^m , 127.8 ^o 127.4 ^o	95.4	79.7	79.1	77.7, 70.8, 70.4	73.6	77.2	56.9 73.4	45.4 12.3				20.9 ^a
(S,B)-54, E-S; R-4-chlorophenyl	139.9 ^s , 131.1 ^m 130.8 ^m , 129.5 ^p 129.2 ^p , 128.8 ^o 128.2 ^o	98.4	79.4	79.4	78.1, 71.0, 70.7	74.0	77.4	56.3 43.8	39.9 10.8				
(S,B)-55, E-Se; R-Me		94.4	77.1	77.1	74.2, 68.7, 68.6	71.9	73.0	59.1 71.6	39.8 10.2	9.32		8.62	
(S,B)-56, E-Se; R-Ph	135.0 ^s , 130.8 ^m 129.9 ^o , 128.8 ^p 128.7 ^p	95.8	80.7	79.6	78.4, 70.8, 70.1	73.9	78.2	56.9 73.7	40.9 11.8 78.0				

Table 4 Continued

[illegible]

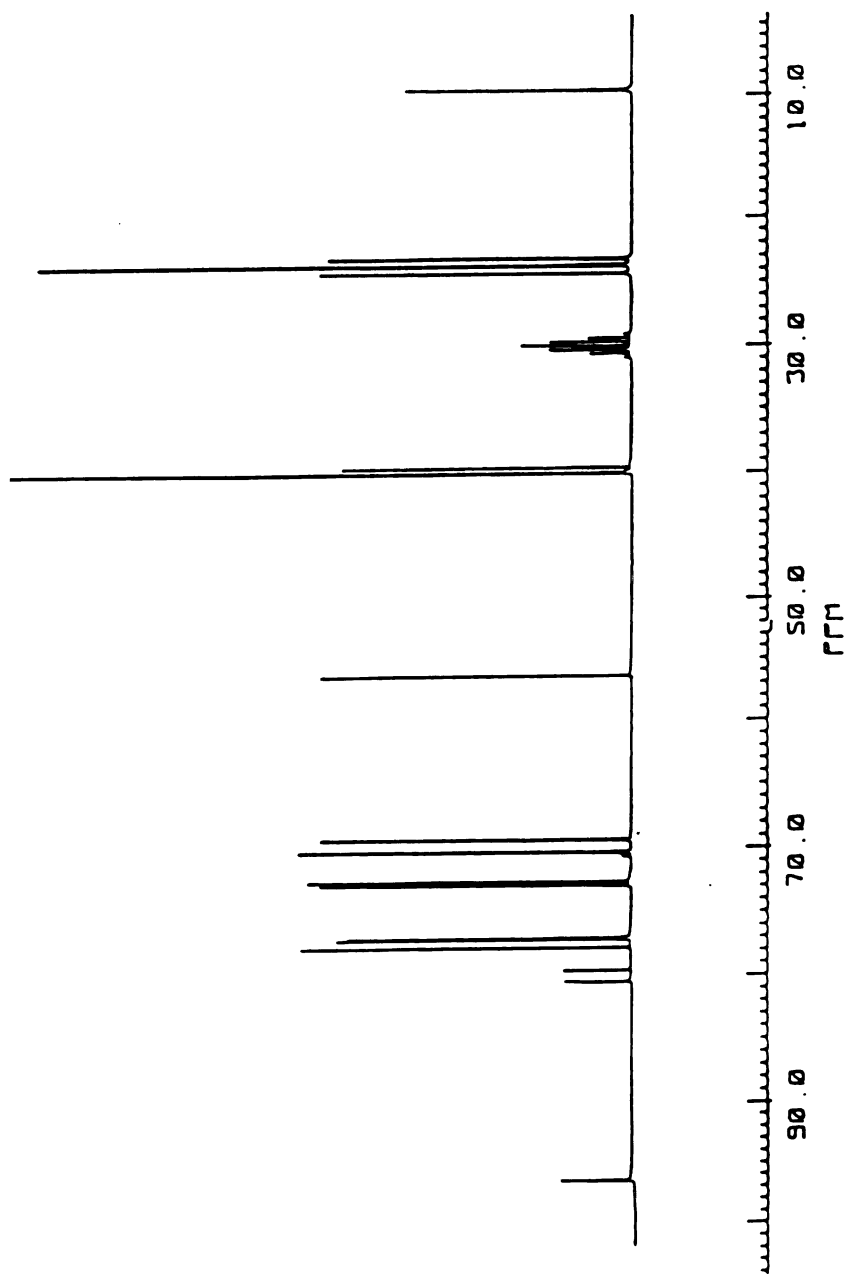


Figure 4. Gated decoupled ^{13}C NMR spectrum of 46 ($\text{R} = i\text{-Pr}$)

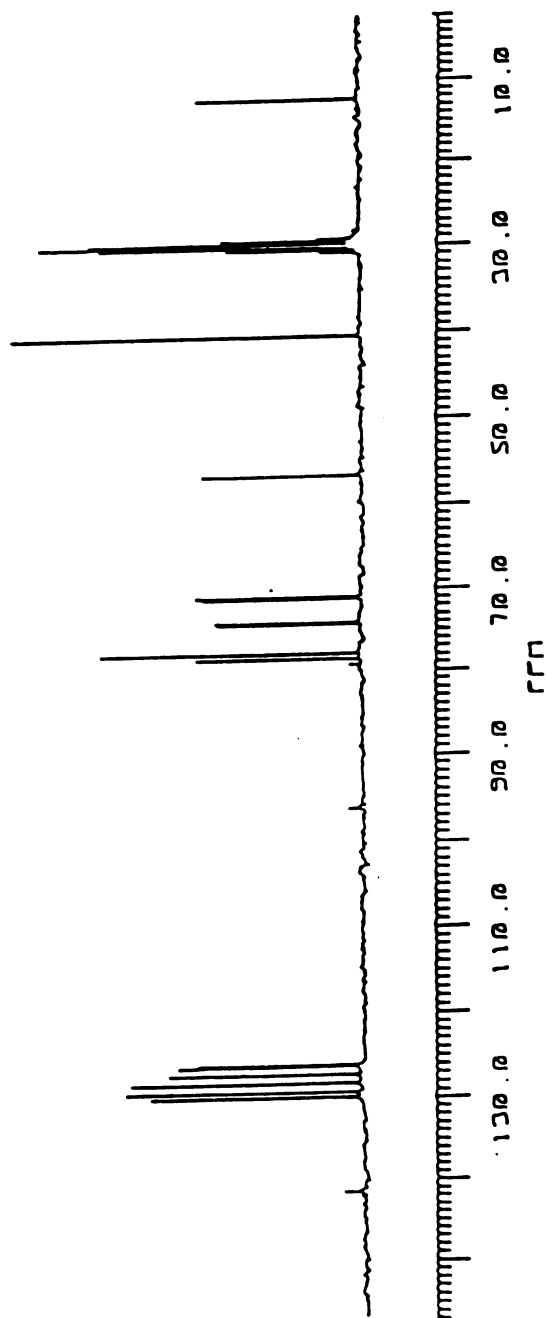


Figure 5. Gated decoupled ^{13}C NMR spectrum of compound 51(R = Ph)

isopropyl methyls are diastereotopic and appear at different positions. Due to fast inversion of nitrogen in the NMe_2 , the two methyl groups appear at the same chemical shift. On the basis of deuterium-labeling studies, Koridze⁸⁵ and co-workers have assigned the signals in methoxy-ferrocene. Such labeling studies were not performed in this work, so most of the assignments here are tentative. Nevertheless, the assignment of C_1 , C_2 and C^1_1 in Cp rings are reasonable. The chemical shifts of C_2 and C^1_1 reflect the inductive and field effects of the substituents ($-\text{SR}$) and ($-\text{SeR}$) and they should be close to each other. Therefore, with the exception of the aryl carbons, the most down field peaks are due to carbon C_1 . Two adjacent peaks in region 77-83 ppm belong to C^1_1 and C_2 . The assignment of the other carbons of the Cp rings is difficult, and based on comparison with previous results.⁴⁵⁻⁴⁸

a.4 Infrared (IR) Spectra of Compounds 43-57

The IR data are presented in the experimental section. A few examples of IR spectra are also shown in the appendix, and Figure 6 shows IR spectra of compound 46. An inspection of these data shows that some frequencies are common to all the chiral ferrocenyl amine compounds 43-57. The assignment of these frequencies are tentative and based on comparison with the vibrational spectra of ferrocene² and its derivatives.⁸⁶ The observed bands around $3150\text{-}2750\text{ cm}^{-1}$ are assigned to C-H stretching frequency. The band around 1450 cm^{-1} is attributed to the ferrocene antisymmetric C-C stretch while absorption around $1220\text{-}1280\text{ cm}^{-1}$ could be associated with the C-N stretch. The bands around $620\text{-}655\text{ cm}^{-1}$ are assigned to the S-C stretch while that of $510\text{-}550\text{ cm}^{-1}$ may be associated with the Se-C stretch. The broad band absorptions in the region of $500\text{-}470\text{ cm}^{-1}$ may be attributed to the ring-metal vibrations such as an asymmetric ring-metal stretch or an asymmetric ring-metal tilt. Absorption near 890 cm^{-1} is indicative of 1,2-(as opposed to 1,3-) disubstitution of the Cp ring. This is an excellent tool to distinguish between the two different substituent patterns in cases of acetyl, alkyl and aryl ferrocenyl compounds.⁸⁷⁻⁹⁰

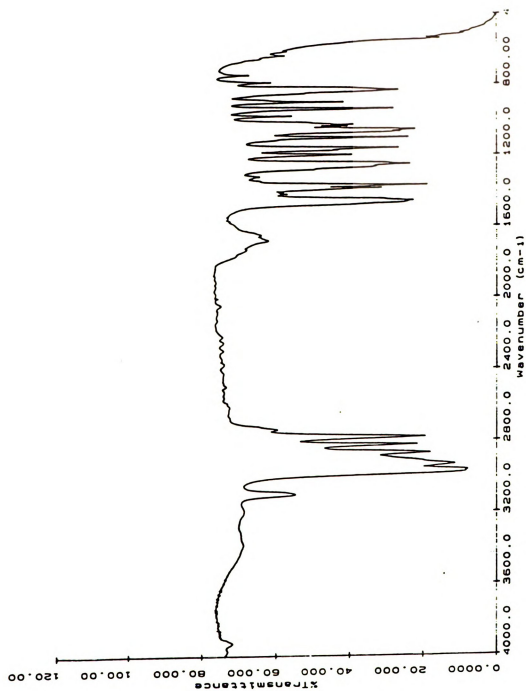


Figure 6. IR spectrum of 46 (R = i-Pr)

a.5 Mass Spectra of Compounds 43-57

Mass spectra (MS) data of compounds 43-57 are given in the experimental section. Figure 7 shows mass spectrum for compound 46, which serves as a typical example. For compounds 43-57 the molecular ion peaks have high intensity. Other observed peaks are M^+-NMe_2-SR , $CHMeNMe_2$, Fe , $SR(SeR)$ and NMe_2 . Aside from these major fragments, smaller peaks consistent with isotopes ^{34}S , ^{54}Fe , ^{57}Fe , ^{76}Se , ^{78}Se , and ^{82}Se were also observed.

b.1 Synthesis of $[ER]C_5H_4FeC_5H_3[CH_2NMe_2][ER]$ ($E = S, R = Me, Et, n\text{-}Pr, i\text{-}Pr, n\text{-}Bu, sec\text{-}Bu, i\text{-}Bu, i\text{-}Pent, Ph, Bz, 4\text{-}tolyl, \text{ and } 4\text{-}Cl\text{-}Ph$ and $E = Se, R = Ph, \text{ and } 4\text{-}Cl\text{-}Ph$) (58-71)

A series of hitherto unknown ferrocenyl amine sulfides and selenides $[ER]C_5H_4FeC_5H_3[CH_2NMe_2][ER]$ where $E = S$ and Se and $R = Me, Et, n\text{-}Pr, i\text{-}Pr, n\text{-}Bu, sec\text{-}Bu, i\text{-}Bu, i\text{-}Pent, Ph, 4\text{-}tolyl, \text{ and } 4\text{-}Cl\text{-}Ph$ were prepared via lithiation of [(dimethylamino)methyl]ferrocene first in the presence of ether and then TMEDA followed by treatment with appropriate disulfides or diselenides as it is shown in Scheme 9. The products were deprotonated by use of sodium hydrogen carbonate before separation by column chromatography as mentioned in Part 1.a.1 of this section. The yields are generally high, between 90% to 52%. The yield for sulfide ligands are higher than those of the selenides. Some by-products with only one substituted Cp ring, $CpFeC_5H_3[CH_2NMe_2][SeR]$ were found in the case of the selenide ligands. The separation of these by-products was difficult because of their close R_f with the main products in all TLC solvent systems. For each of the selenide ligands, column chromatography was repeated at least three times. The same problem was observed when $S_2(t\text{-}Bu)_2$ was allowed to react with 9, because $i\text{-}Bu$ is a bulky group and it is difficult to introduce two $s\text{-}i\text{-}Bu$ groups with one in each Cp ring. The yield in this case was only 55%. It is interesting to note that all attempts to synthesize 1,1'-bis($i\text{-}butylthio$)ferrocene have

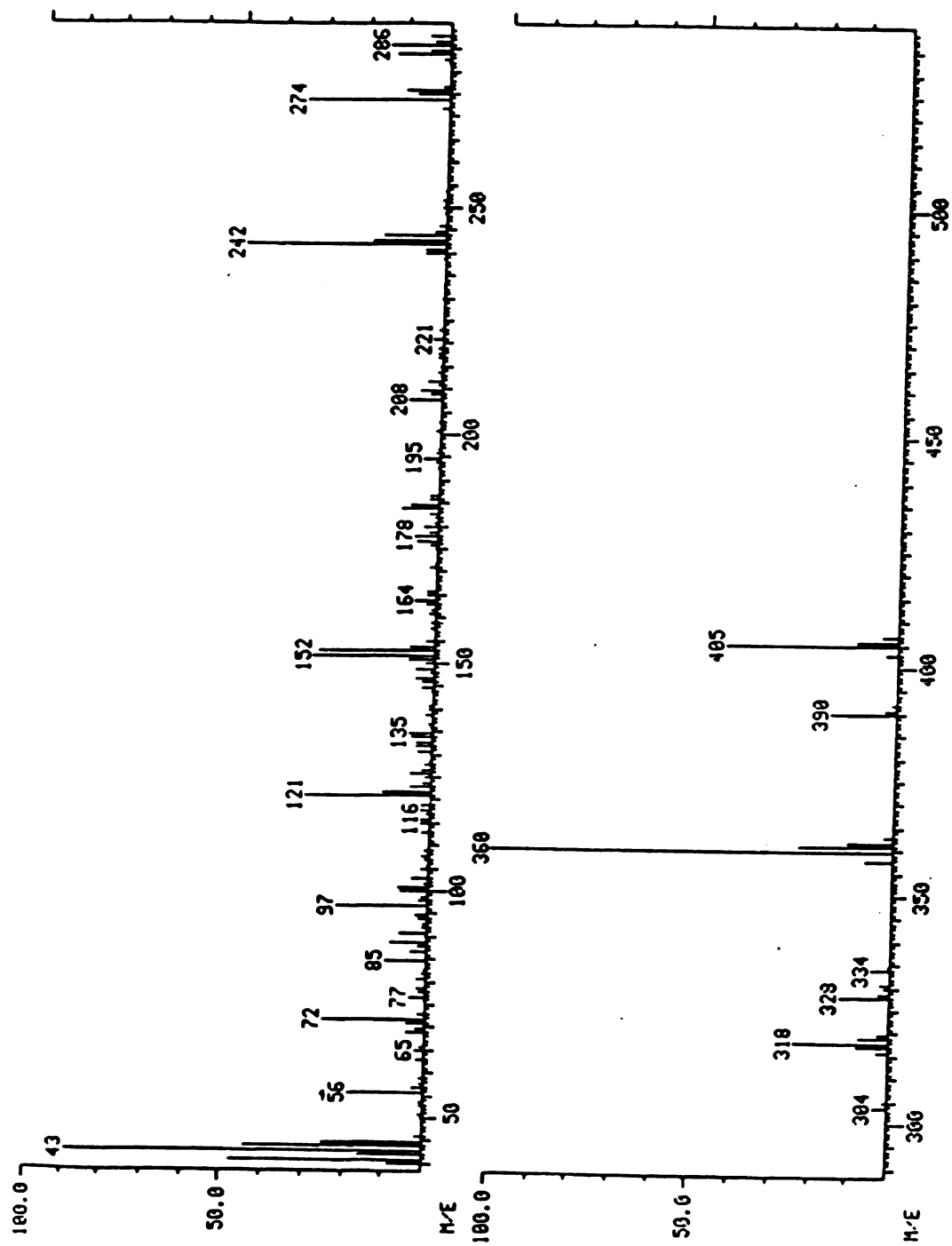
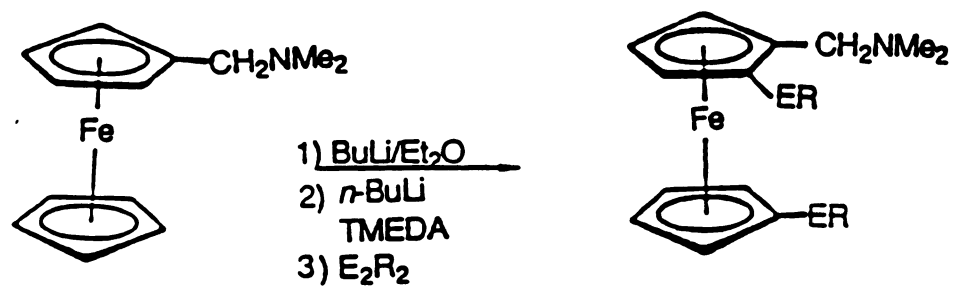


Figure 7. Mass spectrum of compound 46 (R = i-Pr)



E=S R=Me(58)
 Et(59)
 n-Pr(60)
 i-Pr(61)
 n-Bu(62)
 s-Bu(63)
 t-Bu(64)
 i-Pent(65)
 Ph(66)
 Bz(67)
 4-tolyl(68)
 4-Cl-Ph(69)

E=Se R=Ph(70)
 4-Cl-Ph(71)

Scheme 9

failed.⁹¹ However, [1-(dimethylamino)-methyl]-2-*i*-butylthio ferrocene, which has only one *i*-butyl sulfide substituent, was prepared and the yield was 52.5%.⁹²

Compounds 58-65 and 67 were obtained as brown oils while ligands 66, 68, 69, 70 and 71 were crystallized by use of a CH₂Cl₂/hexane mixture. These compounds lack central chirality but they all have a planar element of chirality due to two different substituents in one Cp ring.² However, the products here are racemic mixtures.

Kumada and co-workers¹⁹ resolved ferrocenyl amine phosphines analogs and used them as well as ligands with both central and planar chirality (analogs to 43-57) for asymmetric Grignard cross coupling reactions and found that the ferrocene planar chirality is more important than the carbon central chirality.³⁷ Such resolution was not performed here. The investigation of the regioselectivity of Pd complexes of these ligands was emphasized in this work. The mono and dilithio substituted 8 and 9 (Scheme 1) were not isolated here but rather were prepared fresh for each reaction. However, Rausch and co-workers reported isolation and characterization of 1,1'-

Dilithioferrocene, 2TMEDA, ferrocenyllithium, TMEDA, and 2-

lithio[(dimethylamino)methyl]ferrocene as air-sensitive solids.⁹⁸ Ligands 58-71 are air-stable and they have been characterized by ¹H NMR, ¹³C NMR, IR, MS and elemental analysis

b.2 ¹H NMR of Compounds 58-71

Table 5 presents ¹H NMR data for ligands 58-71. Figures 8-10 show ¹H NMR spectra of compounds 61(R = *i*-Pr) and 64(R = *i*-Bu) and 66(R = Ph). The large chemical shift between the two diastereotopic protons of the amino-methylene group in the 3-4 ppm region for many of these compounds is an important feature of their ¹H NMR spectra. For example, the value of $\Delta\nu/J$ ⁹⁴ for ligand 61 (Figure 8) is 6 so there are two clearly defined doublets. These chemical shift differences are variable and depend on the nature of the R group. Compounds with alkyl sulfide substituents generally have larger chemical shift differences than those with aryl substituents,

Table 5
250 MHz ^1H NMR Data for $[\text{ER}]\text{C}_5\text{H}_4\text{FeC}_5\text{H}_3[\text{CH}_2\text{NMe}_2][\text{ER}]$ in CDCl_3 at Room Temperature: δ ppm (J , Hz)

Compound	Ph	C_5H_4	C_5H_3	CH_2N	NMe ₂	SR				Ph-CH ₃
						αH	βH	γH	δH	
58, E=S, R=Me		4.18 m	4.09 m ^a	3.24 d (12)	2.18 s	2.25 s				
			4.28 m ^b	3.65 d (12)		2.26 s				
59, E=S; R=Et		4.16 m	4.10 m ^a	3.20 d (12)	2.16 s	2.53 q ^a	1.12 t			
			4.29 m ^b	3.55 d (12)		2.60 m ^b	1.19 t			
						2.64 m ^b				
60, E=S; R= η -Pr		4.17 m	4.08 m ^a	3.21 d (12)	2.17 s	2.50 m ^a	1.32 m	0.88 t		
			4.27 m ^b	3.55 d (12)		2.56 m ^a	1.48 m	0.95 t		
61, E=S; R= η -Pr		4.19 m	4.09 m ^a	3.17 d (9)	2.16 s	2.81 h	1.07 d			
			4.32 m ^b	3.57 d (9)		3.01 h	1.10 d			
							1.14 d			
							1.18 d			
62, E=S; R= η -Bu		4.16 m	4.08 m ^a	3.20 d (13)	2.17 s	2.53 m ^a	1.46 m	1.31 m	0.82 t	
			4.29 m ^b	3.56 d (13)		2.60 m ^b	1.52 m	1.43 m	0.86 t	
						2.66 m ^b				
63, E=S; R= ξ -Bu		4.19 m	4.12 m ^a	3.20 d	2.17 s	2.57 m	1.10 d	0.87 t		
			4.13 m ^b	3.56 d		2.83 m	1.15 d	0.97 t		
64, E=S; R= ι -Bu		4.14 m	4.10 m ^a	3.27 s	2.14 s		1.36 m			
			4.19 m ^b				1.47 m			
							1.17 s			

Table 5 Continued

Compound	Ph	C ₅ H ₄	C ₅ H ₃	CH ₂ N	NMe ₂	SR				Ph-CH ₃
						αH	βH	γH	δH	
65, E=S; R=i-Pent		4.17 m	4.08 m ^a	3.20 d (13)	2.16 s	2.54 m ^a	1.58 m	1.35 m	0.79 d	
			4.28 m ^a	3.57 d (13)		2.64 m ^b	1.63 m	1.41 m	0.82 d	
						2.71 m ^b			0.84 d	
66, E=S; R=Ph	7.02-7.19 m	4.44 m	4.33 m ^a	3.44 d	2.04 s					
			4.60 m ^b	3.55 d						
67, E=S; R=Bz	7.14-7.32 m	4.13 -4.30 m		2.98 d (3)	2.19 s	3.82 s ^a				
				3.78 d (3)		3.90 d ^b				
						4.02 d ^b				
68, E=S; R=p-tolyl	6.95-7.06 m	4.39 m	4.30 m ^a	3.43 d (2)	2.05 s					2.24 s
			4.53 m ^b	3.51 d (2)						
69, E=S; R=4-chlorophenyl	6.93-7.17 m	4.45 m	4.37 m ^a	3.44 s	2.04 s					
			4.58 m ^b							
70, E=Se; R=Ph	7.30-7.42 m	4.47 m	4.63 m ^a	3.55 d	2.16 s					
			4.39 m ^b	3.55 d						
71, E=Se; R=4-chlorophenyl	7.21-7.38 m	4.48 m	4.61 m ^a	3.57 d	2.17 s					
			4.41 m ^b	3.48 d						

a₁H, b₂H

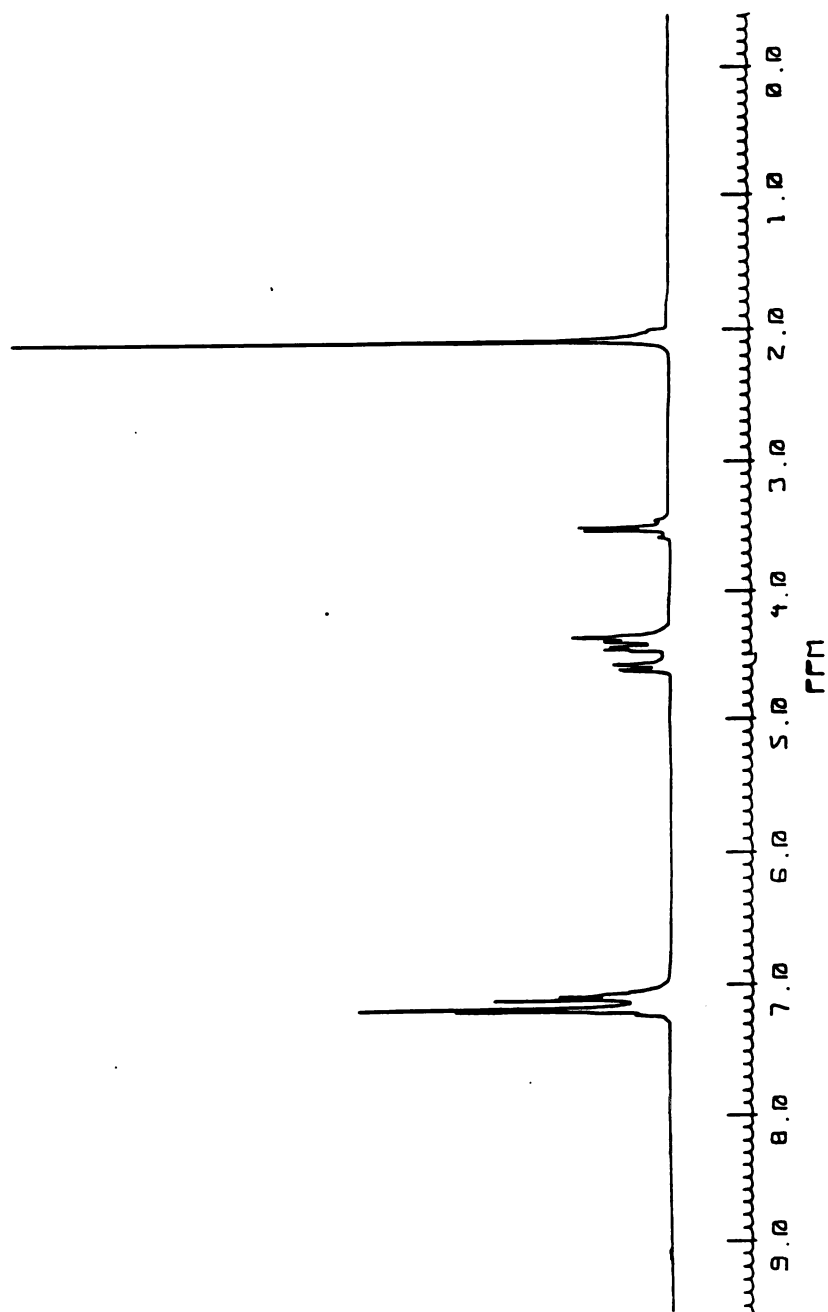


Figure 10. ^1H NMR spectrum of 66 (R = Ph)

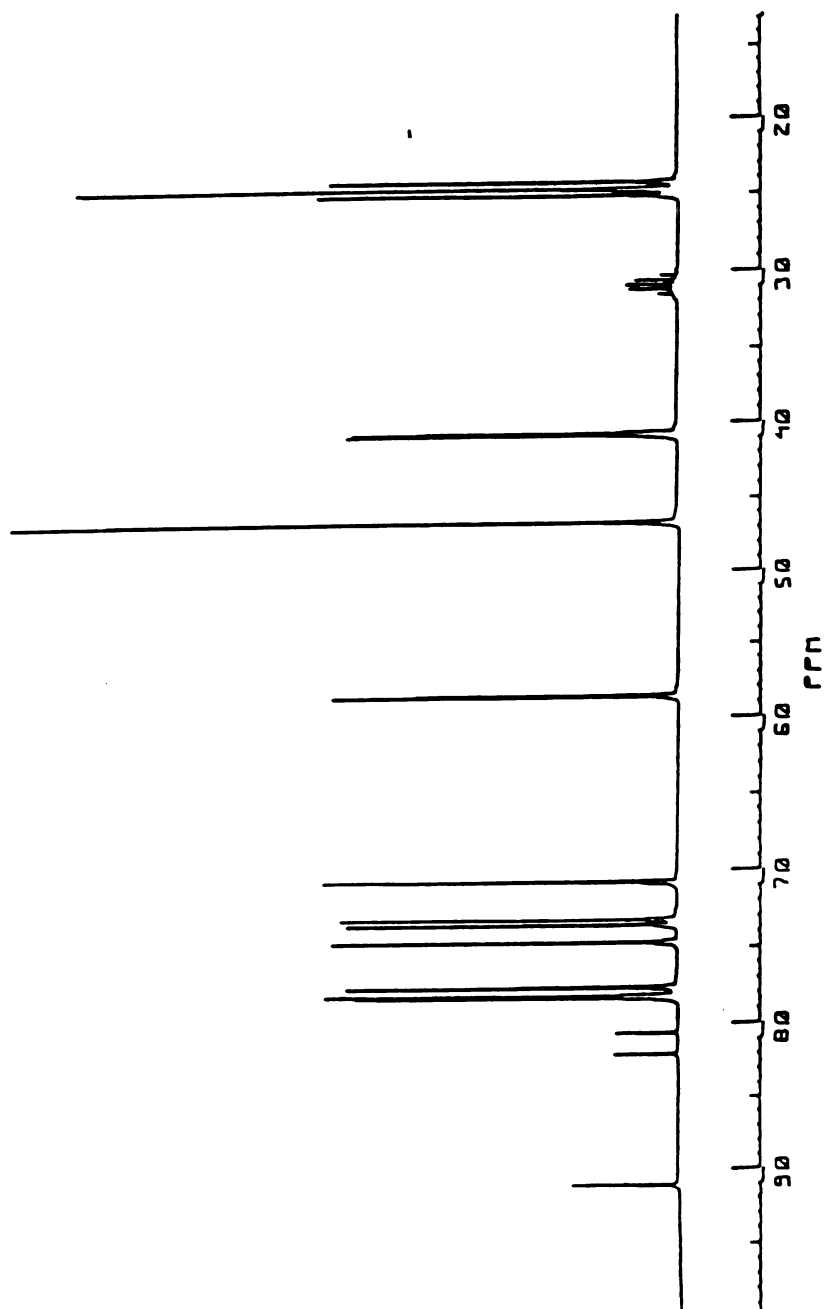


Figure 11. Gated decoupled ^{13}C NMR spectrum of compound 61 ($\text{R} = i\text{-Pr}$)

(compare Figure 8 with Figure 10). Chemical shift differences in ligands with alkylthio groups depend on the steric crowding at β -carbon of the alkyls. The largest chemical shift difference have been observed for ligand 67(R = Bz) and the smallest for compound 64(R = *i*-Bu) and 67(R = 4-Cl-Ph) for which $\Delta\nu/J = 0.0$ and the two signals overlap (Figure 9). The compounds with aryl substituents have smaller chemical shift differences between their aminomethylene protons, possibly because one proton is close to aromatic ring and the effect of ring current on that proton force two peaks to be close to each other. The thiomethylene groups (SCH_2 -) are also diastereotopic and the two methylene protons with their proper multiplicity are present at different chemical shifts. The nitrogen methyls appear as singlets in the 1.99-2.16 ppm range because the inversion of the pyramidal N of NMe_2 is faster than the NMR time scale at room temperature. The assignment of Cp protons is difficult and require deuteration studies. Such studies were not performed here. The assignments in Table 5 are based on the integration of different peaks and the previous results obtained in this laboratory,⁴⁵⁻⁴⁸ and the results of Ovoryantesva.⁹⁵

The chemical shifts for different protons of R in -SR or -SeR (R = alkyl) appear at 0.70-3.50 ppm which is the expected region for alkyl sulfide and selenide substituents. Protons closer to S and Se have lower chemical shifts so $\alpha\text{H} > \beta\text{H} > \gamma\text{H} > \delta\text{H}$ (Table 5). Comparison of Tables 3 and 5 reveals the following interesting points. 1. The spectra of compounds 43-57 basically are similar to those of 58-71 except that because of the existence of the $\text{CH}_2\text{MeNMe}_2$ substituent in the first series, there is a doublet around 1.38-1.45 ppm and a quartet around 3.62-4.04 ppm while in the second series, because of the existence of CH_2NMe_2 group with two diastereotopic methylene protons there exist two doublets which sometimes are completely distinguishable and sometime overlap to produce only a singlet. 2. The diastereotopic thiomethylene protons in the second series (compounds 58-71) have chemical shift differences similar to those of the first group (compounds 43-57). 3. The protons of the NMe_2 methyls in

the second series appear at lower chemical shifts (2.04-2.18) relative to first series (1.91-2.13 ppm) because Me of CHMeNMe₂ is more electron donating relative to H of -CH₂NMe₂. Some ¹H NMR spectra of these series are shown in the appendix.

b.3 ¹³C NMR of Compounds 58-71

Carbon-13 NMR data of compounds 58-71 are presented in Table 6. Figures 11 and 12 show ¹³C NMR spectra of compounds 61 and 66, respectively. A few other examples of ¹³C NMR spectra can be found in the appendix. All of these ligands have planar chirality and C₁ symmetry.² Consequently, groups such as isopropyl methyls (Figure 11) are diastereotopic and appear at different positions. Due to fast inversion of two methyl groups in the NMe₂ these two non-equal groups appear at the same chemical shift. The assignment of Cp carbons is tentative. ¹³C NMR spectroscopy is a sensitive tool for measuring the electron density on the Cp rings of ferrocene. Each substituent can have two different effects. 1. Magnetic anisotropy of the substituent, 2. electronic effects of the substituent which encompasses both resonance and inductive components. Unambiguous assignment requires labeling studies such as those performed by Koridze and co-workers.⁸⁵ Nevertheless, the assignments of C₁, C₂ and C¹₁ in Cp rings are reasonable. The chemical shifts of C₂ and C¹₁ reflect the magnetic anisotropy and the electronic effects of the substituents (-SR) and (-SeR), which should be similar. Therefore, the most downfield peaks (except aryl carbon signals) are due to the carbon C₁ and the two adjacent peaks in the region 77-83 ppm belong to C¹₁ and C₂. A comparison with other results obtained in this laboratory⁴⁵⁻⁴⁸ is the basis for the assignment of the other peaks. A quick look at tables 4 and 6 shows a general agreement between the ¹³C NMR spectra for the two series, except that the first series has one more signal for the same (-SR) or (-SeR), because (CHMeNMe₂) has 3 signals while (CH₂NMe₂) has only 2 signals.

Table 6
250 MHz Gated Decoupled ^{13}C NMR Data for $[\text{Er}(\text{C}_5\text{H}_4\text{FeC}_5\text{H}_3(\text{CH}_2\text{NMe}_2)\text{ER})]$ in CD_3COCD_3 at Room Temperature: δ ppm.

Compound	Ph	C ₁	C ₂	C ¹ ₁	C ₃ , C ₄ , C ₅	C ¹ ₂ , C ¹ ₃ , C ¹ ₄	C ¹ ₅	CH ₂ N	NMe ₂	SR			
										αC	βC	γC	δC
58, E-S; R=Me		88.2	86.4	85.6	79.4, 72.3, 69.2	71.1 71.0	73.4 72.9	57.4	45.4	20.0 19.3			
59, E-S; R=Et		89.5	82.9	82.7	75.4, 73.8, 70.0	72.4 72.0	76.3 76.0	58.0	45.8	31.9 31.3	15.7 15.5		
60, E-S; R=Q-Pr		89.1	82.9	82.8	74.5, 73.3, 69.5	71.9 71.6	75.7 75.3	57.5	45.4	39.4 39.1	23.5 23.4	13.6 13.5	
61, E-S; R=I-Pr		89.5	80.6	79.2	76.1, 73.2, 69.3	72.1 71.7	76.8 76.0	57.1	45.2	39.4 39.3	23.7 23.2		22.8
62, E-S; R=Q-Bu		88.9	82.5	82.5	74.5, 73.1, 69.2	71.6 71.3	75.5 75.1	57.3	45.4	36.8 36.6	32.2 32.0	22.1 22.0	13.9
64, E-S; R=I-Bu		89.1	77.3	77.4	72.1, 69.8, 69.8	70.9	72.1	59.1	44.9	37.2	31.0		
6, E-S; R=I-Pent		89.1	82.7	82.6	74.5, 73.2, 69.3	71.7 71.4	75.6 75.0	57.3	45.4	39.2	35.2	27.5	22.8
											34.9	27.4	22.6
66, E-S; R=Ph	141.0 ^a , 140.6 ^b 129.4 ^m , 129.2 ^m 127.4 ^o , 126.7 ^o 125.8 ^p	90.0	78.2	77.6	77.1, 74.1, 71.3	73.6 73.4	77.5 77.4	56.9	45.4				22.4

Table 6
250 MHz Gated Decoupled ^{13}C NMR Data for $[\text{Er}(\text{C}_5\text{H}_4\text{FeC}_5\text{H}_3(\text{CH}_2\text{NMe}_2))\text{Er}]$ in CD_3COCD_3 at Room Temperature: δ ppm.

Compound	Ph	C ₁	C ₂	C _{1'}	C ₃ , C ₄ , C ₅	C ¹ ₂ , C ¹ ₅	C ¹ ₃ , C ¹ ₄	CH ₂ N	NMe ₂	SR			
										αC	βC	γC	δC
58, E-S; R=Me		88.2	86.4	85.6	79.4, 72.3, 69.2	71.1 71.0	73.4 72.9	57.4	45.4	20.0 19.3			
59, E-S; R=Et		89.5	82.9	82.7	75.4, 73.8, 70.0	72.4 72.0	76.3 76.0	58.0	45.8	31.9 31.3	15.7 15.5		
60, E-S; R=i-Pr		89.1	82.9	82.8	74.5, 73.3, 69.5	71.9 71.6	75.7 75.3	57.5	45.4	39.4 39.1	23.5 23.4	13.6 13.5	
61, E-S; R=i-Pr		89.5	80.6	79.2	76.1, 73.2, 69.3	72.1 71.7	76.8 76.0	57.1	45.2	39.4 39.3	23.7 23.2		22.8
62, E-S; R=i-Bu		88.9	82.5	82.5	74.5, 73.1, 69.2	71.6 71.3	75.5 75.1	57.3	45.4	36.8 36.6	32.2 32.0	22.1 22.0	13.9
64, E-S; R=i-Bu		89.1	77.3	77.4	72.1, 69.8, 69.8	70.9	72.1	59.1	44.9	37.2	31.0		
6, E-S; R=i-Pent		89.1	82.7	82.6	74.5, 73.2, 69.3	71.7 71.4	75.6 75.0	57.3	45.4	39.2	35.2 34.9	27.5 27.4	22.8 22.6 22.4
66, E-S; R=Ph	141.0 ^a , 140.6 ^b 129.4 ^m , 129.2 ^m 127.4 ^o , 126.7 ^o 125.8 ^p	90.0	78.2	77.6	77.1, 74.1, 71.3	73.6 73.4	77.5 77.4	56.9	45.4				

Table 6 Continued

Compound	Ph	C1	C2	C1'	C3, C4, C5	C12, C15	C13, C14	CH ₂ N	NMe2	SR		
										αC	βC	γC
. E-S; R-Bz	139.2 ^s , 138.6 ^s	89.3	82.8	82.3	74.8, 72.9, 70.0	72.6	75.9	57.4	45.2	41.7		
	129.2 ^m , 128.9 ^m					72.4		78.1			42.4	
	128.3 ^o , 128.1 ^o											
	128.6 ^p , 128.3 ^p											
68, E-S; R-4-tolyl	137.0 ^s , 136.8 ^s	89.5	79.5	79.0	76.8, 73.8, 71.0	73.3	77.2	58.7	45.4			21.0 ^a
	135.3 ^p , 130.0 ^m					72.9	77.1					
	129.8 ^m , 127.8 ^o											
	127.3 ^o											
69, E-S; R-4-chlorophenyl	139.9 ^s , 139.6 ^s	90.3	78.4	78.4	77.1, 74.3, 71.5	73.8	77.7	58.9	45.3			
	131.1 ^p , 129.4 ^m					73.6	77.4					
	129.1 ^m , 128.9 ^o											
	128.1 ^o											
70, E-Se; R-Ph	141.9 ^s , 130.7 ^m	90.5	78.5	78.5	78.2, 73.8, 71.7	73.7	78.4	58.2	45.3			
	129.9 ^m , 129.8 ^o											
	129.6 ^o , 126.8 ^p											
71, E-Se; R-4-chlorophenyl	134.0 ^s , 132.2 ^p	90.8	78.6	78.6	78.2, 74.0, 71.9	73.7	78.4	58.1	45.3			
	131.3 ^m , 129.8 ^o											
	129.5 ^o											

s=substituted; m=meta; o=ortho; p=para; ^aPhCH₃

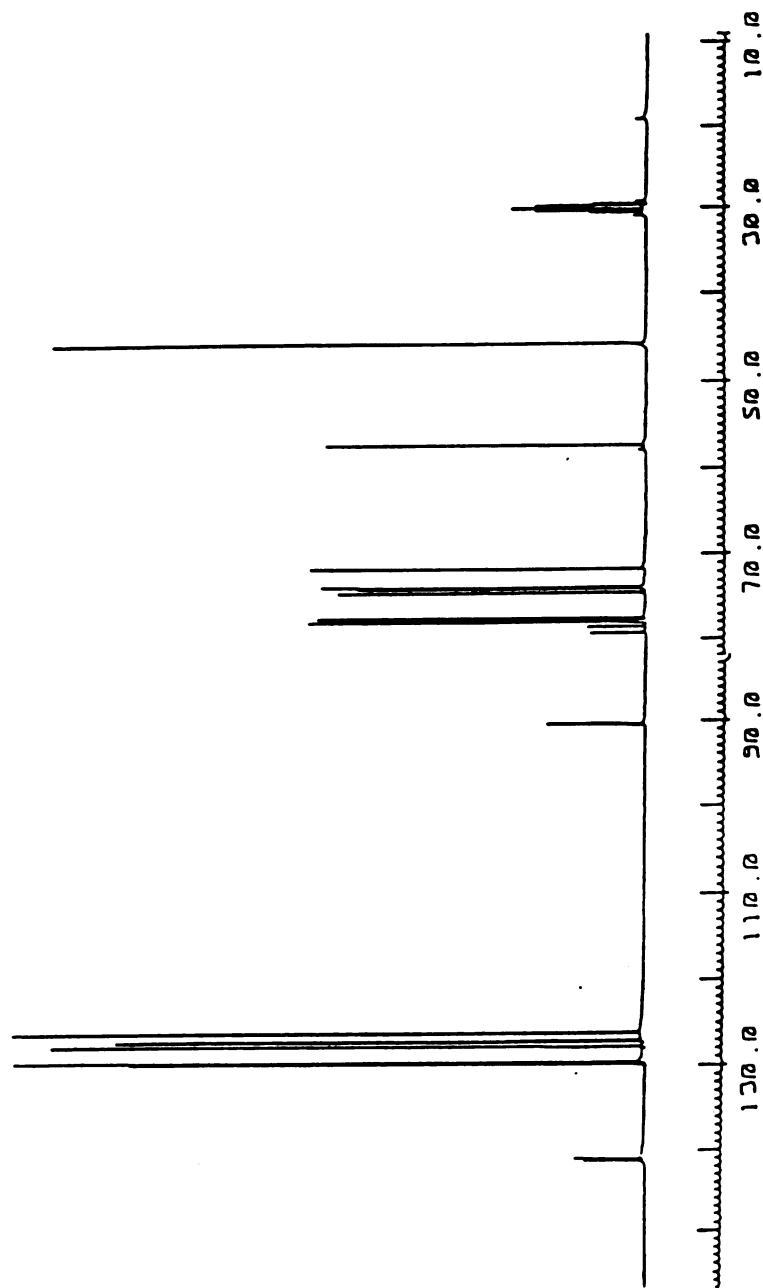


Figure 12. Gated decoupled ^{13}C NMR spectrum of compound 66 (R = Ph)

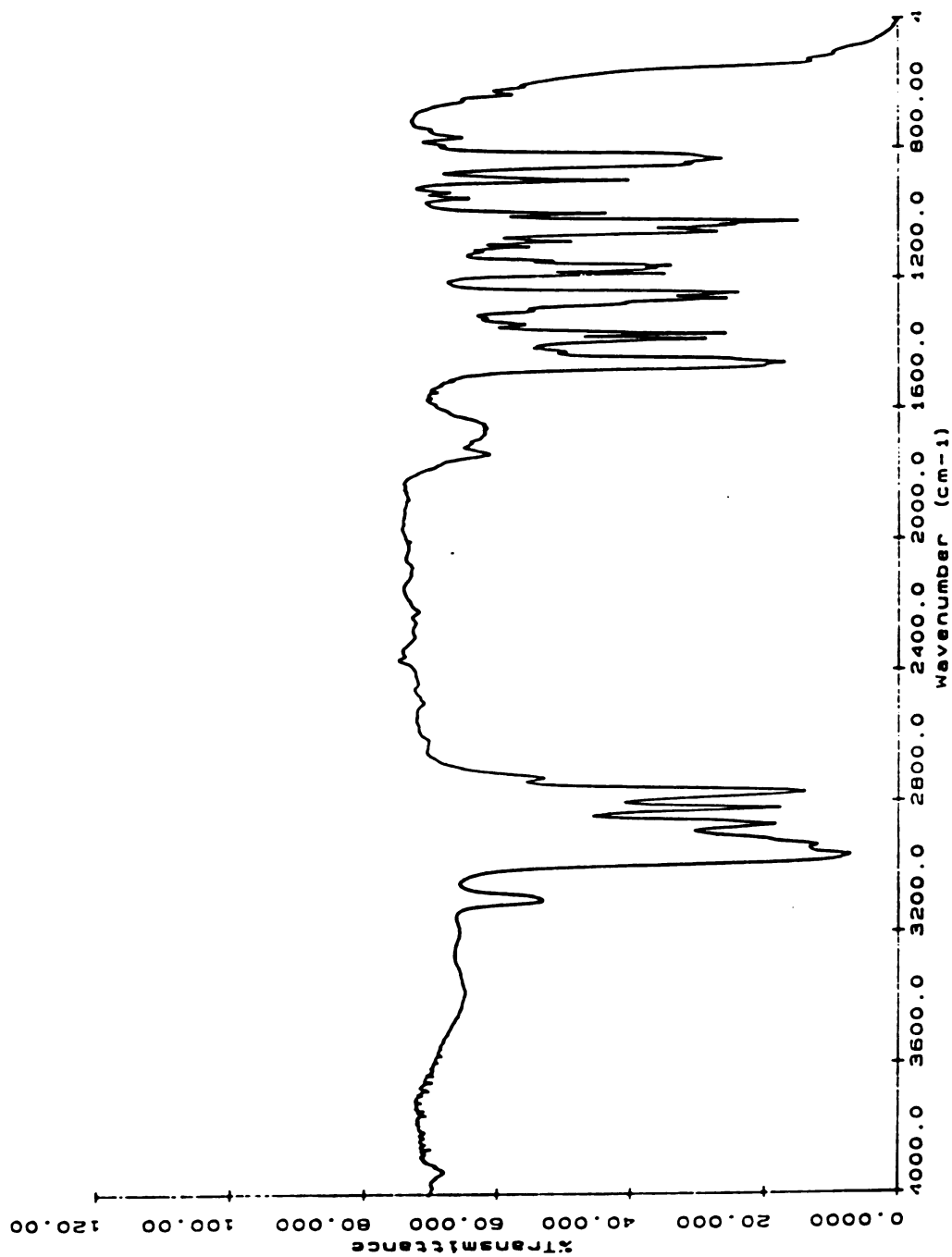


Figure 13. IR spectrum of compound 61 (R = i-Pr)

b.4 Infrared (IR) and Mass Spectra for Compounds 58-71

IR spectra of these series are very similar to those of 43-57. Figure 13 shows the IR for ligands 61 ($R = i\text{-Pr}$). Comparison of this figure and Figure 6 reveals this similarity and the reader is referred to Part 1.a.4 for the detailed discussion of Infrared spectra. A few IR spectra of this series are shown in the appendix.

Mass spectra of these complexes generally show molecular ion (M^+), ($M^+ - 15$ or $M^+ - \text{Me}$), ($M^+ - 45$ or $M^+ - 3\text{Me}$), ($M^+ - \text{SR}$), ($M^+ - \text{SR} - \text{CH}_2\text{NMe}_2$), CH_2NMe_2 (58), Fe (56), NMe (44). Smaller peaks consistent with isotopes ^{34}S , ^{54}Fe , ^{57}Fe , ^{76}Se , ^{78}Se , ^{82}Se are also observed. Figure 14 shows mass spectra of ligand 61 ($R = i\text{-Pr}$).

2. Preparation of Complexes

a.1 Synthesis of Palladium and Platinum Complexes (S,R)-

$[\text{ER}]\text{C}_5\text{H}_4\text{FeC}_5\text{H}_3[\text{CHMeNMe}_2][\text{ER}][\text{MCl}_2]$ ($M = \text{Pd}$, $E = \text{S}$, $R = \text{Me}$, Ph , Bz , 4-tolyl , and 4-Dc-Ph ; $M = \text{Pt}$, $E = \text{S}$, $R = \text{Ph}$, Bz , 4-tolyl ; $M = \text{Pd}$, $E = \text{Se}$, $R = \text{Ph}$, and 4-Cl-Ph ; $M = \text{Pt}$, $E = \text{Se}$, $R = \text{Ph}$) (72-82)

Complexes 72-82 were prepared via treatment of appropriate benzene solution of chiral ferrocenyl amine sulfide and selenide ligands with bis(benzonitrile)palladium or platinum chloride, $(\text{PhCN})_2\text{MCl}_2$ ($M = \text{Pt}$, Pd) according to Scheme 10. The resulting heterobimetallic products are insoluble in benzene. Precipitation of the products occur after a few hours (3-8) in the case of palladium and after 2-7 days in the case of platinum. The palladium complexes are soluble in acetone and other polar solvents such as methylene chloride and chloroform, but the Pt complexes are not soluble in any common solvents. They are only slightly soluble in acetone. Analytically pure complexes of palladium were obtained by recrystallization from acetone or mixed solvent systems of methylene chloride/hexane.

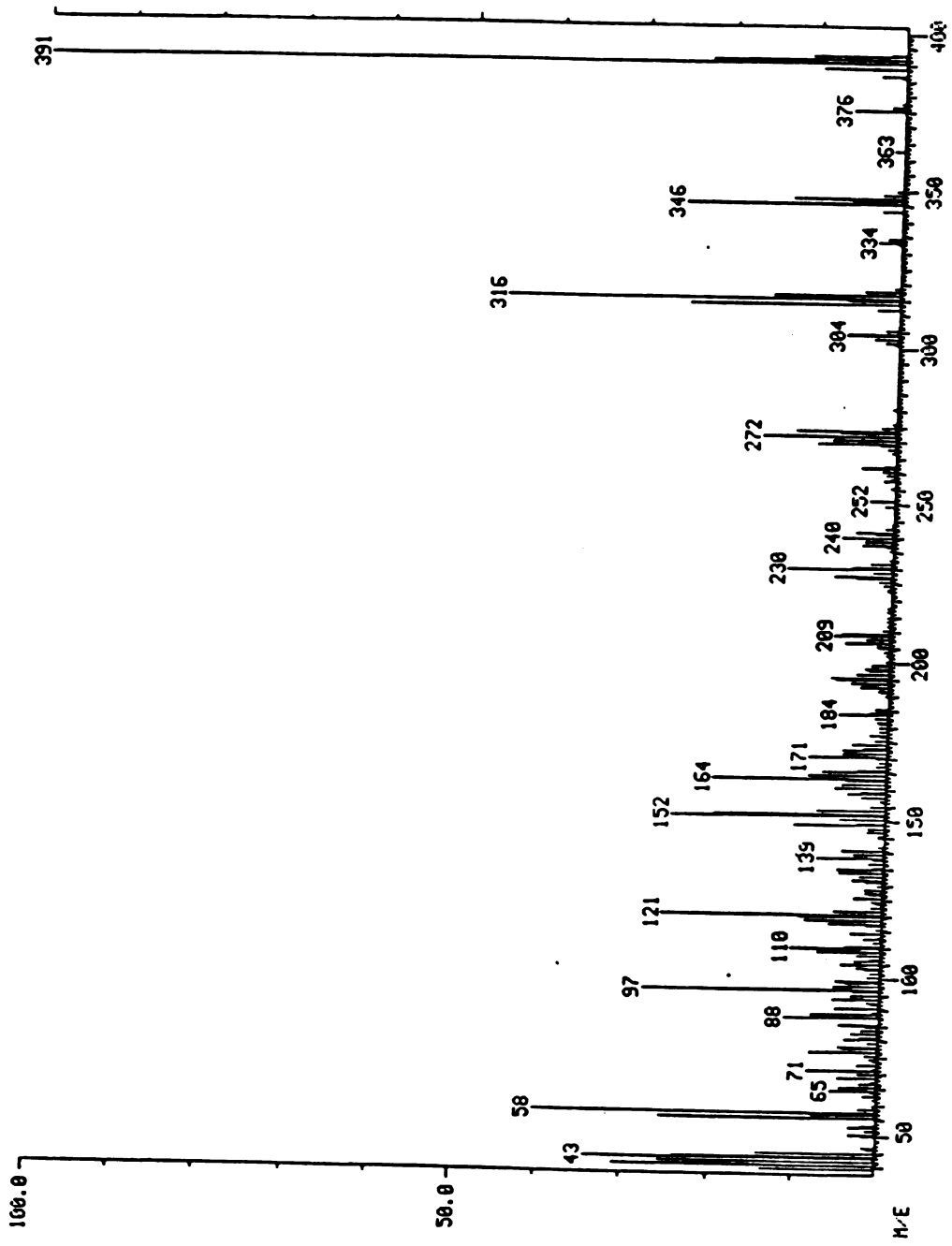
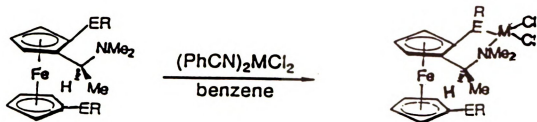


Figure 14. Mass spectrum of compound 61 (R = i-Pr)



$\text{E}=\text{S}$, $\text{M}=\text{Pd}$, $\text{R}=\text{Me}$ (72)
 Ph (73)
 Bz (74)
 4-tolyl (75)
 4-Cl-Ph (76)

$\text{M}=\text{Pt}$, $\text{R}=\text{Ph}$ (77)
 Bz (78)
 4-tolyl (79)

$\text{E}=\text{Se}$, $\text{M}=\text{Pd}$, $\text{R}=\text{Ph}$ (80)
 $\text{R}=4\text{-Cl-Ph}$ (81)

$\text{M}=\text{Pt}$, $\text{R}=\text{Ph}$ (82)

a.2 ^1H NMR of Heterobimetallic Complexes 72-82

The 250 MHz ^1H NMR data for the chiral palladium complexes are presented in Table 7. Because the platinum complexes are almost insoluble in all common solvents, obtaining solution NMR for them was almost impossible and they were characterized by elemental analysis, mass spectra and infrared spectra. Figure 15 shows the free ligand (S,R)-[S-4-tolyl]C₅H₄FeC₅H₃[CHMeNMe₂][S-4-tolyl] **53** versus complex **75** which was obtained by complexation of free ligand **53** with the adduct of palladium dichloride. This comparison is very important for deducing the striking differences between the free and complexed compounds. It is also helpful to understand the structure of bi-metallic complexes. One important feature of complexed ligands is the downfield shift of all signals because of either magnetic anisotropy or the inductive effect of the metal chloride. Also, in the free ligands, two non-equivalent methyl groups of S-Ph-Me accidentally appear at the same chemical shift while in the palladium complex **75** they are separated by 0.2 ppm and both signals are downfield relative to free ligand. The most striking difference in the ^1H NMR spectra of the complexed ligand relative to the free ligand is the observed chemical shift of the methyl groups in NMe₂. Sokolov, et al. had observed in the 2-dimethylaminomethylferrocenyl palladium chloride dimer, there were two signals for the two methyl groups of NMe₂.⁹⁶ Here, the same splitting pattern was observed. This is a very important and helpful observation in understanding the structure of these compounds. Chiral ligands **43-57** have three coordination sites, one N atom and two S atoms (or Se atoms). Therefore, there are three possible structures as shown in Scheme 11. The structure of PdCl₂[(S)-(R)-BPPFA] has been reported by Kumada and co-workers⁹⁷ (Figure 16). In that complex, palladium is coordinated to the two phosphine atoms, rather than coordinated by a phosphine and a nitrogen atom. However, the appearance of two methyl groups of NMe₂ at two different chemical shifts rule out the existence of similar structure for the analogous, ferrocenyl amine sulfide and selenide complexes. Structure C of Scheme 11 cannot be ruled out without further

Table 7

250 MHz ¹H NMR Data for (S,B)-[ER]C₅H₄FeC₅H₃[CHMeNMe₂][ER][PdCl₂] in CDCl₃ at Room Temperature: δ ppm (J, Hz)

Compound	Ph	C ₅ H ₄ , C ₅ H ₃	CH ₃ CH	NMe ₂	CH ₃ CH	Ph-CH ₃	S-CH ₂ -Ph or S-Me
72, E=S, R=Me		4.31-4.35 m	4.14 q (4)	3.21 s 2.29 s	1.53 d (4)		2.52 s 2.26 s
73, E=S; R=Ph	7.43-7.51 m 6.98-7.25 m	4.26-4.41 m	4.11 q (7)	3.29 s 2.34 s	1.55 d (7)		
74, E=S; R=Bz	7.15-7.34 m	4.29-4.44 m	4.21 q (7)	3.32 s 2.35 s	1.46 d (7)		3.94-4.13 m
75, E=S; R=4-tolyl	6.92-7.27 m	4.24-4.40 m	4.10 q (7)	3.30 s 2.36 s	1.55 d (7)	2.39 s 2.26 s	
76, E=S; 4-chlorophenyl	6.95-7.49 m	4.30-4.42 m	4.13 q(7)	3.29 s 2.34 s	1.56 d (7)		
80, E=Se; R=Ph	7.14-7.50 m	4.35-4.60 m	4.13 q	3.29 s 2.33 s	1.56 d		
81, E=Se; R=4-chlorophenyl	7.17-7.47 m	4.23-4.74 m	4.17 q	3.37 s 2.27 s	1.56 d		

a₁H, b₂H

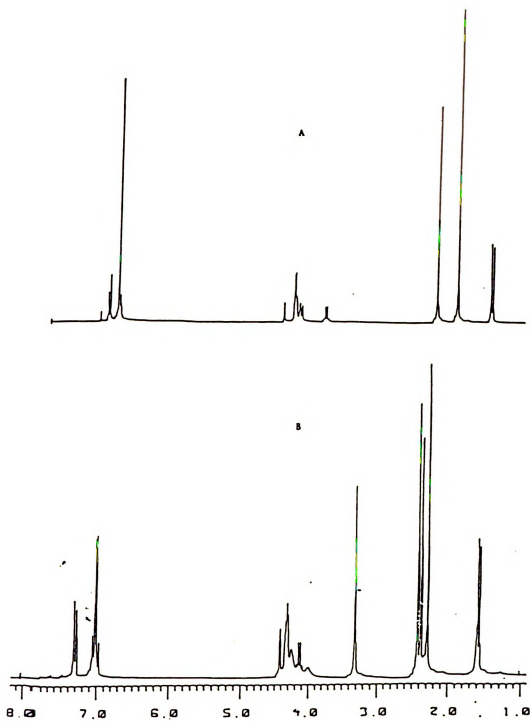
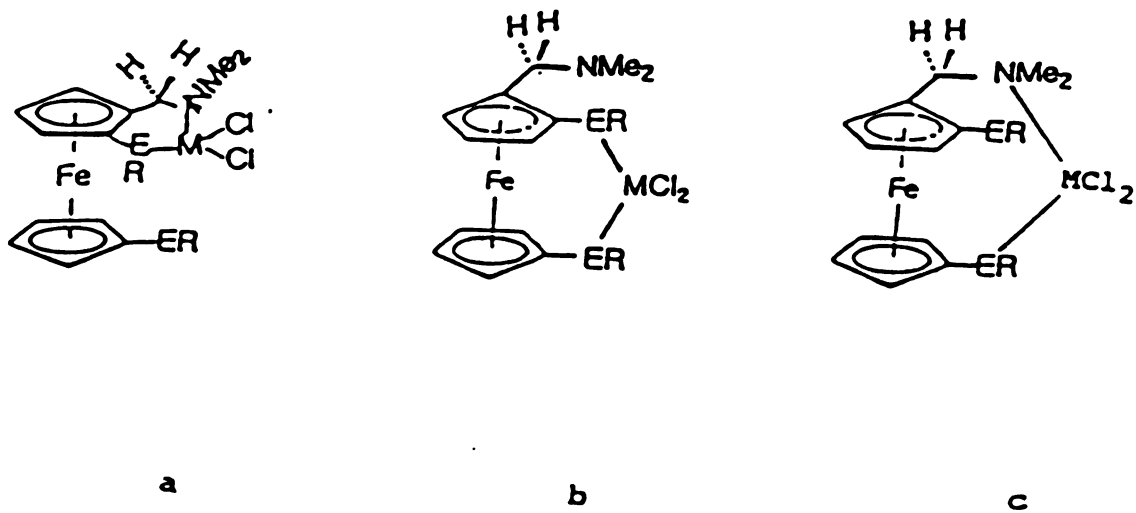


Figure 15. A) ^1H NMR spectrum of compound 53
B) ^1H NMR spectrum of complex 75



Scheme 11

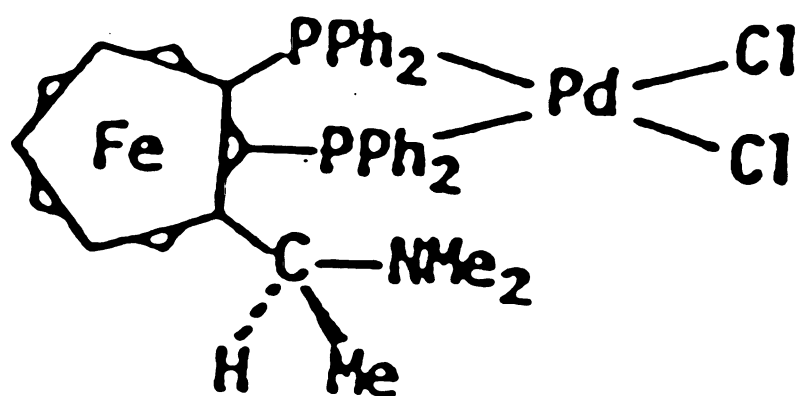


Figure 16. Structure of $\text{PdCl}_2[(S,R)\text{-BPPFA}]$

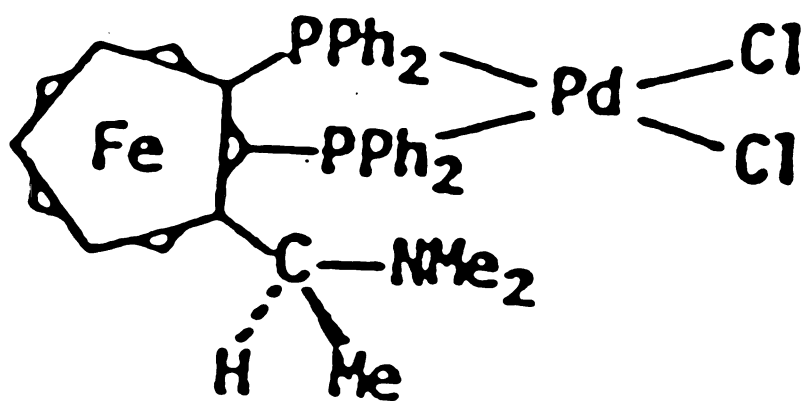


Figure 16. Structure of $\text{PdCl}_2[(\text{S,R})\text{-BPPFA}]$

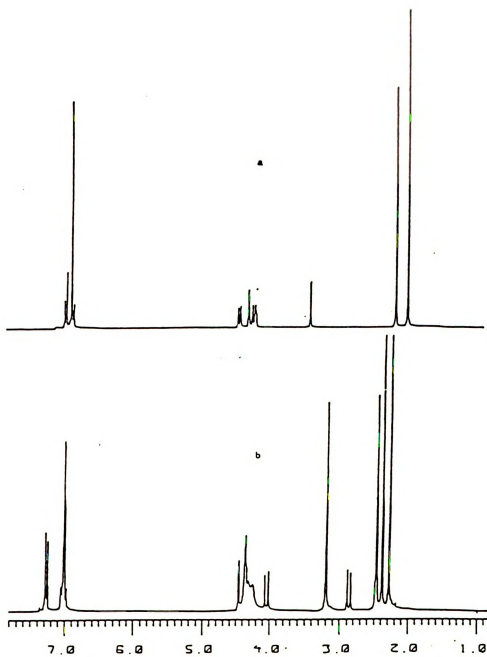


Figure 17. a) ^1H NMR spectrum of ligand **68**
b) ^1H NMR spectrum of complex **69**

investigation. As it will be shown, the structure of $[\text{SMe}][\text{C}_5\text{H}_4]\text{Fe}[\text{C}_5\text{H}_3]-[\text{CH}_2\text{MeNMe}_2][\text{SMe}][\text{PdCl}_2]$ was investigated by X-ray diffraction analysis and it confirmed the structure a (Scheme 11). From the above discussions it can be concluded that in the metal complexes the chemical shifts of the two methyl groups in NMe_2 are different and much more downfield than those of the corresponding free ligands. The inversion of the bipyramidal N of these metal complexes are prevented by the presence of rigid 6-membered ring complexes (a. Scheme 11).

a.3 Infrared Spectra (IR) of Chiral Complexes (72-82)

The infrared data for complexes 72-82 are given in the experimental part. A comparison of these data and those of the free ligands shows that the most striking difference can be found in the low frequency region because of the presence of metal-ligand vibrations. IR data for several complexes are given in Table 8. These data clearly show that metal-S bands are very close to metal-Cl bands and it is often very difficult to distinguish one from the other. So here the bands around $231\text{-}389\text{ cm}^{-1}$ are attributed to the Pd-Cl or Pd-S bands. The Pd-N and Pt-N stretches occur in region $460\text{-}500\text{ cm}^{-1}$ and at 630 cm^{-1} respectively. As was emphasized earlier, the complexes 72-82 have C^1 symmetry and in these kinds of molecules often more than one fundamental mode contributes to a given peak.¹⁰⁷ Thus these assignments are tentative, however, all data in Table 8 and also other values in the literature confirm them.¹⁰⁸⁻¹¹³

Table 8

Metal-N, Metal-Cl, and Metal-S Stretching Modes in Some Pd and Pt Sulfide Complexes

Compound	ν , cm^{-1}	Stretching Mode	Reference
7 2	492 389,374 326,269	Pd-N Pd-Cl, Pd-S	This work
7 3	469 378,360 321,231	Pd-N Pd-Cl, Pd-S	This work
7 7	649 381,359 340,268	Pt-N Pt-S and Pt-Cl	This work
7 8	651 376,369 339,247	Pt-N Pt-S and Pt-Cl	This work
(PhSC ₃ H ₆ SPh)PdCl ₂	278,262 323,308	Pd-Cl Pd-S	98
PdL ₂ Cl ₂ ^a	480	Pd-N	99
[PdCl ₂ (RN=CH-CH=NR)]	325 337,330	Pd-Cl Pd-Cl	100
[PdCl ₂ (Py-2-CH=NR)]	330,338	Pd-Cl	100
Pd(PhSCH ₂ CH ₂ SPh)Cl ₂	315,296	Pd-Cl	101
Pt(PhSCH ₂ CH ₂ SPh)Cl ₂	315,302	Pt-Cl	101
Pd(PhSCH=CHSPh)Cl ₂	318,298	Pd-Cl	101
Pt(PhSCH=CHSPh)Cl ₂	316,300	Pt-Cl	101
Pd ₂ Cl ₄ (SMe ₂)	340	Pd-S	102
[Pd(S ₃ N) ₂]	374,319	Pd-S	103
[Pt(S ₃ N) ₂]	329	Pt-S	103
Pd(PhS) ₂ (diars)	363,317	Pd-S	104
Pt(dto) ₂ ²⁻	340	Pt-S	105 ^b

Table 8 Continued

Compound	ν , cm^{-1}	Stretching Mode	Reference
$\text{PtL}_2^1\text{Cl}_2^c$	565	Pt-N	106
	325	Pt-S	
$[\text{Pt}(\text{L}^1-\text{H})_2]$	530,746	Pt-N	106
	330	Pt-S	

^a L =2-picolyI-p-nitrophenyl

^bdto=dithionalato complex

^c $\text{L}^1=\text{NH}_2\text{NHC}(=\text{S})\text{SMe}$

b. Synthesis and Characterization of Palladium and Platinum

Complexes $[\text{ER}]\text{C}_5\text{H}_4\text{FeC}_5\text{H}_3[\text{CH}_2\text{NMe}_2][\text{ER}][\text{MCl}_2]$ ($\text{M} = \text{Pd}$, $\text{E} = \text{S}$,
 $\text{R} = \text{Me}$, Et , $n\text{-Pr}$, $i\text{-Pr}$, Ph , Bz , 4-tolyl , and 4-Cl-Ph ; $\text{M} = \text{Pt}$, $\text{E} =$
 S , $\text{R} = \text{Me}$, Ph , Bz , 4-tolyl , and 4-Cl-Ph ; $\text{M} = \text{Pd}$, $\text{E} = \text{Se}$, $\text{R} = \text{Ph}$)
(83 - 96)

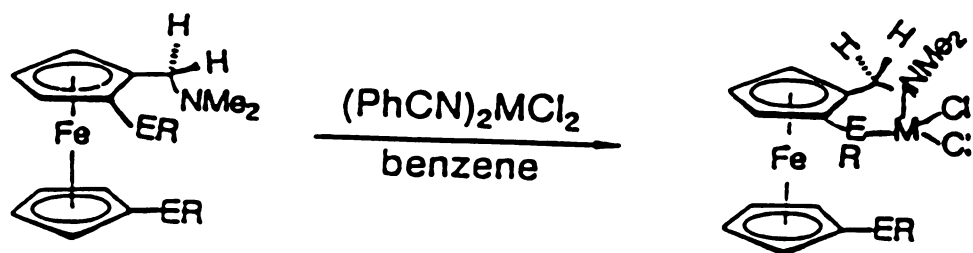
The new heterobimetallic complexes 83-96 were prepared by reaction of bis(benzonitrile) adducts of palladium and platinum chloride with appropriated ferrocenyl amine sulfide or selenide ligands as discussed in Part 2.a.1 of this section (Scheme 12). These complexes have a planar element of chirality due to two different substituents in the 1,2 positions of one Cp ring² but the product was obtained as a racemic mixture.

250 MHz ¹H NMR data for these complexes are shown in Table 9. Also Figure 17 shows the comparison between free ligand $[\text{S-4-tolyl}]\text{C}_5\text{H}_4\text{FeC}_5\text{H}_3[\text{CH}_2\text{NMe}_2][\text{S-4-tolyl}]$ 68 and its palladium complex 89. The non-isochronicity of the two methyl groups of NMe₂ (Figure 16b) is strong evidence for coordination of that group to the metal as a consequence of a higher energy barrier for inversion at the nitrogen atom.

Structure of [1-(Dimethylamino)methyl]-2,1'-bis(methylthio)-ferrocene Palladium(II) dichloride (83)

Atomic parameters are listed in Table 10 and 11 and selected bond lengths and bond angles are given in Tables 12, and 13. A drawing showing the atom labeling and thermal ellipsoids is given in Figure 18 and a stereographic packing diagram is given in Figure 19.

The carbon-carbon distances in the cyclopentadienyl ring vary from 1.35 (2) Å to 1.48 (3) Å averaging at 1.41 (3) Å. This is a typical value for ferrocene. The bond angles within two Cp-rings (C-C-C) change from 105(2)° to 111(2)° with an average of 108(2)° which is the typical value for the angle of a regular planar pentagon.



$\text{E}=\text{S}$, $\text{M}=\text{Pd}$, $\text{R}=\text{Me}$ (83)
 Et (84)
n-Pr (85)
i-Pr (86)
 Ph (87)
 Bz (88)
 4-tolyl (89)
 4-Cl-Ph (90)

$\text{M}=\text{Pt}$, $\text{R}=\text{Me}$ (91)
 Ph (92)
 Bz (93)
 4-tolyl (94)
 4-Cl-Ph (95)

$\text{E}=\text{Se}$, $\text{M}=\text{Pd}$, $\text{R}=\text{Ph}$ (96)

Scheme 12

Table 9

250 MHz ^1H NMR Data for $[\text{SR}][\text{C}_5\text{H}_4\text{FeC}_5\text{H}_3[\text{CH}_2\text{NMe}_2][\text{SR}][\text{PdCl}_2]$ in CDCl_3/TMS at Room Temperature; δ , ppm (J, Hz)

Compound	Ph	C_5H_4 , C_5H_3	CH_2NMe_2	CH_2NMe_2	CH_2NMe_2	PhCH_3	SR	
							αH or $\text{S-CH}_2\text{Ph}$	βH
83, E = S; R = Me		4.26-4.45 m	3.89 d (12.7) 2.70 d (12.7)	3.09 s 2.34 s			2.73 s	
							2.16 s	
84, E = S; R = Et		4.38-4.52 m	4.02 d (12.8) 2.73 d (12.8)	3.09 s 2.30 s			3.37 m ^a	1.67 t
							3.27 m ^a	1.14 t
87, E = S; R = Ph	7.01-7.48 m	4.36-4.43 m	3.97 d (12.5) 2.83 d (12.5)	3.17 s 2.46 s			2.58 q ^b	
88, E = S; R = Bz	7.14-7.30 m	4.26-4.42 m	3.47 d (12.8) 2.33 d (12.8)	3.30 s 2.59 s			3.94-4.10	
89, E = S; R = 4-tolyl	6.97-7.25 m	4.21-4.41 m	4.00 d (12.7) 2.83 d (12.7)	3.16 s 2.43 s		2.24 s 2.34 s		
90, E = S; R = 4-CIPh	6.94-7.42 m	4.16-4.43 m	4.05 d (12.8) 2.83 d (12.8)	3.16 s 2.24 s				

a 1H

b 2H

-1-1

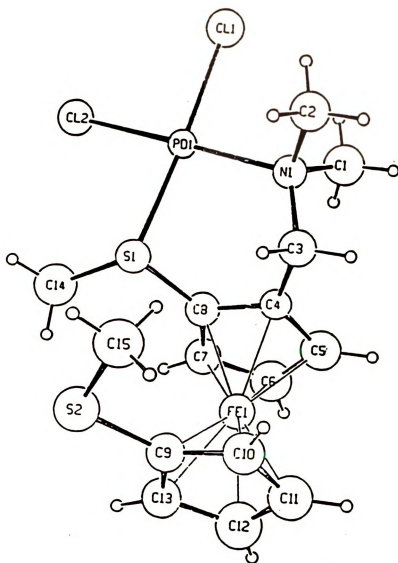


Figure 18. The molecular structure and the numbering of the atoms of 83

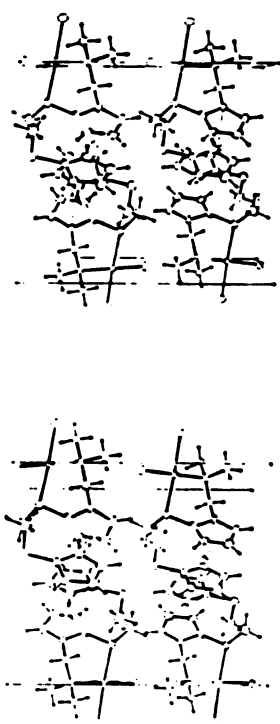


Figure 19. Stereographic packing diagram of 83

Table 10.
Positional Parameters and
Their Estimated Standard Deviations for
[1-[(Dimethylamino)methyl]-2,1'-bis(methylthio)ferrocene]-
Palladium(II) Chloride (83)

Atom	x	y	z	B(Å ²)
Pd1	-0.00381(9)	0.07699(9)	0.13725(8)	2.16(2)
Fe1	0.3796(2)	0.5121(2)	-0.2072(2)	3.22(5)
C11	-0.2012(4)	0.1096(4)	0.1597(4)	4.08(9)
C12	-0.0070(4)	0.2026(4)	0.0033(3)	3.55(8)
S1	0.1860(3)	0.0392(3)	0.1070(3)	2.90(7)
S2	0.4198(4)	-0.1420(5)	0.0622(4)	4.6(1)
N1	-0.001(1)	-0.031(1)	0.2701(9)	2.7(2)
C1	-0.037(2)	0.038(2)	0.357(1)	4.3(4)
C2	-0.088(1)	-0.126(1)	0.253(1)	3.7(3)
C3	0.110(1)	-0.089(1)	0.293(1)	3.4(3)
C4	0.202(1)	0.002(1)	0.310(1)	2.5(3)
C5	0.258(2)	0.045(2)	0.396(1)	4.1(4)
C6	0.332(2)	0.137(2)	0.365(1)	4.6(4)
C7	0.319(1)	0.148(2)	0.261(1)	3.6(3)
C8	0.243(1)	0.070(1)	0.225(1)	3.5(3)
C9	0.454(1)	-0.120(2)	0.190(1)	3.5(3)
C10	0.422(1)	-0.180(2)	0.276(1)	4.0(4)
C11	0.476(2)	-0.135(2)	0.361(1)	4.5(4)
C12	0.544(2)	-0.043(2)	0.329(2)	5.4(5)
C13	0.534(1)	-0.033(2)	0.219(1)	3.8(4)
C14	0.264(2)	0.139(2)	0.032(1)	4.9(4)
C15	0.306(2)	-0.241(2)	0.073(1)	4.9(4)

Anisotropically refined atoms are given in the form of
the isotropic equivalent thermal parameter defined as:

$$(4/3) * [a^2 * B(1,1) + b^2 * B(2,2) + c^2 * B(3,3) \\ + ab(\cos \gamma) * B(1,2) + ac(\cos \beta) * B(1,3) \\ + bc(\cos \alpha) * B(2,3)]$$

Table 11.
General Temperature Factor Expressions - U's - for
[1-[(Dimethylamino)methyl]-2,1'-bis(methylthio)ferrocene]-
Palladium(II) Chloride (83)

Name	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
Pd1	0.027(1)	0.026(1)	0.029(1)	0.000(0)	0.001(0)	0.001(1)
Fe1	0.039(1)	0.042(1)	0.041(1)	0.003(1)-0.006(1)		0.001(1)
C11	0.040(2)	0.055(2)	0.059(2)	0.007(2)-0.002(2)		0.008(2)
C12	0.053(2)	0.045(2)	0.037(2)	0.007(2)-0.003(2)		0.011(2)
S1	0.040(2)	0.035(2)	0.035(2)-0.001(2)		0.005(2)	0.002(2)
S2	0.058(3)	0.066(3)	0.051(2)	0.003(2)	0.005(2)-0.006(2)	
N1	0.040(6)	0.033(6)	0.028(6)-0.002(5)		0.005(5)-0.000(5)	
C1	0.07(1)	0.06(1)	0.035(9)	0.013(9)	0.003(8)-0.005(8)	
C2	0.041(8)	0.054(9)	0.045(9)-0.013(8)-0.004(7)			0.006(8)
C3	0.046(8)	0.039(8)	0.043(8)	0.005(7)	0.002(7)	0.008(7)
C4	0.033(7)	0.032(7)	0.032(7)-0.004(6)-0.003(6)			0.005(6)
C5	0.06(1)	0.05(1)	0.045(9)	0.010(9)-0.008(8)-0.006(8)		
C6	0.05(1)	0.07(1)	0.06(1)	-0.007(9)-0.009(9)-0.01(1)		
C7	0.034(8)	0.047(9)	0.057(9)-0.004(8)-0.009(7)-0.005(8)			
C8	0.053(8)	0.048(9)	0.034(8)	0.008(8)	0.020(7)	0.008(7)
C9	0.034(8)	0.050(9)	0.049(9)	0.004(8)	0.000(7)-0.006(8)	
C10	0.040(8)	0.048(9)	0.06(1)	0.018(8)	0.006(8)-0.003(9)	
C11	0.05(1)	0.06(1)	0.06(1)	0.018(9)-0.002(9)		0.002(9)
C12	0.08(1)	0.05(1)	0.07(1)	-0.01(1)	-0.02(1)	-0.01(1)
C13	0.048(9)	0.045(9)	0.053(9)-0.000(8)-0.001(8)			0.010(8)
C14	0.07(1)	0.06(1)	0.06(1)	-0.00(1)	0.01(1)	0.01(1)
C15	0.08(1)	0.05(1)	0.06(1)	0.01(1)	-0.02(1)	-0.00(1)

The form of the anisotropic thermal parameter is:

$$\exp[-2\pi^2\{h^2a^2U(1,1) + k^2b^2U(2,2) + l^2c^2U(3,3) + 2hkabU(1,2) + 2hlacU(1,3) + 2klbcU(2,3)\}]$$

where a, b, and c are reciprocal lattice constants.

Table 11.
General Temperature Factor Expressions - U's - for
[1-[(Dimethylamino)methyl]-2,1'-bis(methylthio)ferrocene]-
Palladium(II) Chloride (83)

Name	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
Pd1	0.027(1)	0.026(1)	0.029(1)	0.000(0)	0.001(0)	0.001(1)
Fe1	0.039(1)	0.042(1)	0.041(1)	0.003(1)	-0.006(1)	0.001(1)
C11	0.040(2)	0.055(2)	0.059(2)	0.007(2)	-0.002(2)	0.008(2)
C12	0.053(2)	0.045(2)	0.037(2)	0.007(2)	-0.003(2)	0.011(2)
S1	0.040(2)	0.035(2)	0.035(2)	-0.001(2)	0.005(2)	0.002(2)
S2	0.058(3)	0.066(3)	0.051(2)	0.003(2)	0.005(2)	-0.006(2)
N1	0.040(6)	0.033(6)	0.028(6)	-0.002(5)	0.005(5)	-0.000(5)
C1	0.07(1)	0.06(1)	0.035(9)	0.013(9)	0.003(8)	-0.005(8)
C2	0.041(8)	0.054(9)	0.045(9)	-0.013(8)	-0.004(7)	0.006(8)
C3	0.046(8)	0.039(8)	0.043(8)	0.005(7)	0.002(7)	0.008(7)
C4	0.033(7)	0.032(7)	0.032(7)	-0.004(6)	-0.003(6)	0.005(6)
C5	0.06(1)	0.05(1)	0.045(9)	0.010(9)	-0.008(8)	-0.006(8)
C6	0.05(1)	0.07(1)	0.06(1)	-0.007(9)	-0.009(9)	-0.01(1)
C7	0.034(8)	0.047(9)	0.057(9)	-0.004(8)	-0.009(7)	-0.005(8)
C8	0.053(8)	0.048(9)	0.034(8)	0.008(8)	0.020(7)	0.008(7)
C9	0.034(8)	0.050(9)	0.049(9)	0.004(8)	0.000(7)	-0.006(8)
C10	0.040(8)	0.048(9)	0.06(1)	0.018(8)	0.006(8)	-0.003(9)
C11	0.05(1)	0.06(1)	0.06(1)	0.018(9)	-0.002(9)	0.002(9)
C12	0.08(1)	0.05(1)	0.07(1)	-0.01(1)	-0.02(1)	-0.01(1)
C13	0.048(9)	0.045(9)	0.053(9)	-0.000(8)	-0.001(8)	0.010(8)
C14	0.07(1)	0.06(1)	0.06(1)	-0.00(1)	0.01(1)	0.01(1)
C15	0.08(1)	0.05(1)	0.06(1)	0.01(1)	-0.02(1)	-0.00(1)

The form of the anisotropic thermal parameter is:

$$\exp[-2\pi^2\{h^2a^2U(1,1) + k^2b^2U(2,2) + l^2c^2U(3,3) + 2hkabU(1,2) + 2hlacU(1,3) + 2klbcU(2,3)\}]$$

where a, b, and c are reciprocal lattice constants.

Table 12.
Bond Distances (in Angstroms) for
[1-[(Dimethylamino)methyl]-2,1'-bis(methylthio)ferrocene]-
Palladium(II) Chloride (83)

Atom1	Atom2	Distance
Pd1	Cl1	2.335(4)
Pd1	Cl2	2.305(4)
Pd1	S1	2.277(4)
Pd1	N1	2.164(12)
S1	C8	1.74(2)
S1	C14	1.78(2)
S2	C9	1.76(2)
S2	C15	1.76(2)
N1	C1	1.47(2)
N1	C2	1.51(2)
N1	C3	1.50(2)
C3	C4	1.52(2)
C4	C5	1.41(2)
C4	C8	1.45(2)
C5	C6	1.44(3)
C6	C7	1.39(3)
C7	C8	1.35(2)
C9	C10	1.39(3)
C9	C13	1.42(2)
C10	C11	1.38(3)
C11	C12	1.41(3)
C12	C13	1.48(3)

Numbers in parentheses are estimated standard deviations
in the least significant digits.

Table 13.
Bond Angles (in Degrees) for
[1-[(Dimethylamino)methyl]-2,1'-bis(methylthio)ferrocene]-
Palladium(II) Chloride (83)

Atom1 -----	Atom2 -----	Atom3 -----	Angle -----
C11	Pd1	C12	89.0(2)
C11	Pd1	S1	176.6(2)
C11	Pd1	N1	89.9(4)
C12	Pd1	S1	89.9(2)
C12	Pd1	N1	175.9(3)
S1	Pd1	N1	91.3(3)
Pd1	S1	C8	99.3(6)
Pd1	S1	C14	117.6(7)
C8	S1	C14	100.6(9)
C9	S2	C15	100.5(9)
Pd1	N1	C1	109.(1)
Pd1	N1	C2	107.3(9)
Pd1	N1	C3	116.2(9)
C1	N1	C2	109.(1)
C1	N1	C3	110.(1)
C2	N1	C3	105.(1)
N1	C3	C4	108.(1)
C3	C4	C5	133.(1)
C3	C4	C8	120.(1)
C5	C4	C8	107.(1)
C4	C5	C6	107.(2)
C5	C6	C7	107.(2)
C6	C7	C8	111.(2)
S1	C8	C4	118.(1)

Table 13. Bond Angles (Continued) for
[1-[(Dimethylamino)methyl]-2,1'-bis(methylthio)ferrocene]-
Palladium(II) Chloride (83)

Atom1 -----	Atom2 -----	Atom3 -----	Angle -----
S1	C8	C7	134.(1)
C4	C8	C7	108.(1)
S2	C9	C10	131.(1)
S2	C9	C13	120.(1)
C10	C9	C13	109.(2)
C9	C10	C11	111.(2)
C10	C11	C12	107.(2)
C11	C12	C13	109.(2)
C9	C13	C12	105.(2)

Numbers in parentheses are estimated standard deviations
in the least significant digits.

The Pd-S bond length is 2.277(4) Å which compares favorably with the sum of the covalent radii (2.35 Å)¹¹⁴ and suggests very limited π bonding in the Pd-S bond. There is no trans bond lengthening effect for the Pd-Cl bond trans to sulfur atom. The average value for the Pd-Cl distances is 2.32 (4) Å comparing favorably with the sum of the Pauling covalent radii, 2.31 Å.¹¹⁴ Pd is in a square planar environment with two chlorine ions cis to each other. The Cl-Pd-Cl bond angle is 89.0(2)° and the S-Pd-N bond angle is 91.3(3)°.

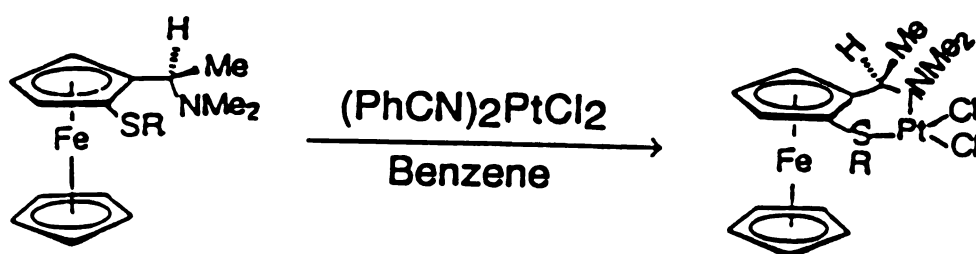
The structure of (Ph₃P)PdFe(C₅H₄S)₂ with two chelating thiolate groups has been reported.¹¹⁵ The presence of a weak Fe-Pd dative bond was proposed for this heterobimetallic complex on the basis of a Fe-Pd distance of 2.878 (1) Å. Such interaction between Pd and Fe does not exist here.

The two cyclopentadienyl rings are eclipsed and are almost parallel; the dihedral angle between two Cp rings is 1.54°.

The most striking feature of the structure of complex 83 is the coordination of the Pd atom to S and N atoms of the same ring which confirm structure a Scheme 11. An X-ray diffraction study of PdCl₂(S,R-BPPFA) (Scheme 5) was carried out by Hayashi and co-workers (Figure 16).⁹⁷ In that complex Pd has square planar geometry with two cis chlorine and two phosphorus atoms, and the nitrogen atom is not bound to palladium. The difference between the structures of palladium ferrocenyl amine sulfides and phosphine analogs is very interesting and this maybe an important reason for observed differences in the catalytic activities of these two classes of complexes.

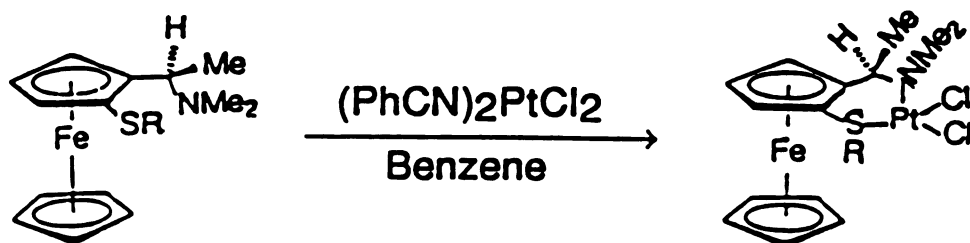
c. Synthesis and Characterization of Platinum Complexes (R,S)-CpFe[CHMeNMe₂][SR][PtCl₂] (R = Me, Et, *i*-Pr, and Ph) (97-100)

Complexes 97-100 were prepared from benzene solution of 0.1 g of (PhCN)₂PtCl₂ and the appropriate ferrocenylamine sulfide ligands in 1 : 1.1 molar ratio (Scheme 13). The reaction mixture was stirred at 35°-45°C for 7 days. The resulting



R=Me (97)
Et (98)
***i*-Pr (99)**
Ph (100)

Scheme 13



R=Me (97)
Et (98)
***i*-Pr (99)**
Ph (100)

Scheme 13

precipitates were filtered, washed with benzene, then with petroleum ether and recrystallized from CH_2Cl_2 /hexane by slow evaporation. Yields, ^1H NMR (without coupling to ^{195}Pt), IR, MS, melting point and elemental analysis of these compounds were reported in the experimental section. The most striking feature of NMR is coupling of ^{195}Pt to protons of dimethylamino groups. Table 14 shows the coupling constants of ^{195}Pt and the neighboring protons of different Pt complexes. ^{195}Pt ($I = 1/2$) has a natural abundance of 33% and has roughly the same relative sensitivity as the ^{13}C nucleus. It has been found¹¹⁵ that $^3J(^{195}\text{Pt}^1\text{H})$ in platinum complexes with PMe_3 and other analog ligands are between 15-57 Hz. Table 14 shows that here $^3J(^{195}\text{Pt}^1\text{H})$ values are in the range 28.4-51.9 which compares favorably with the results reported before.¹¹⁶ Figure 20 shows the NMR spectra for compound (R,S)- $\text{CpFe}[\text{CHMeNMe}_2]\text{-}[\text{SMe}][\text{PtCl}_2]$ 97

3. Catalytic Applications of Complexes

a. Selective Hydrogenation of Conjugated Double Bonds

a.1 Selective Hydrogenation of Cyclooctadiene by Use of Complexes 97-100

The selective hydrogenation of dienes to monoenes has been well documented. Catalytic systems include, for example, $[\text{Co}(\text{CN})_5^{3-}]$ ¹¹⁷ and $[\text{PdCl}(\text{PPh}_3)(\eta^3\text{-allyl})]$.¹¹⁸ Selective hydrogenation of 1,3- and 1,5- cyclooctadiene to cyclooctene has been achieved by ruthenium(0)polyolefin complexes.¹¹⁹ A similar behavior is shown by $\text{Ni}(\text{acac})_2$ in the presence of $\text{Al}_2\text{Et}_3\text{Cl}_3$ and PPh_3 .¹²⁰ Novel homogeneous and mineral supported, nitrogen containing palladium compounds were also used as catalysts in this process.^{121,122} The other catalytic systems used for selective hydrogenation of 1,3-cyclooctadiene are as follows: Zirconium(III) complexes containing chelated $\text{ZrCH}_2\text{PPh}_3$,¹²³ untreated and prereduced copper chromite at 140°C and 1 atm pressure,¹²⁴ colloidal palladium in Poly(η -vinyl-2-pyrrolidone) at 30°C and atmospheric H_2 pressure,¹²⁵ and polymer membranes containing 200 Å Ni particles on active carbon.¹²⁶ This catalyst is 4 times as active as Raney nickel with 90%

Table 14

Coupling Constant (Hz) of ^{195}Pt With The Neighboring
Protons; δ , ppm (Hz)

Compound	NCH_3	SCH_3
9 7	2.45 (28.9) 3.34 (28.9)	2.71 (51.9)
9 8	2.45 (30.4) 3.32 (29.5)	
9 9	2.45 (29.6) 3.34 (29.7)	
1 0 0	2.52 (29.8) 3.42 (29.9)	

selectivity for monoene (vs. 50% for Raney nickel).¹²⁶ Selective hydrogenation of polyenes is of practical importance; in particular, the hydrogenation of cyclopentadienes to cyclopentene has been a subject of a number of patents.¹²⁷

It has been shown that homogeneous hydrogenation of 1,3-cyclooctadiene to cyclooctene in acetone by using palladium ferrocenyl amine sulfide catalysts resulted in high chemical yields (up to 100%) and improved selectivity of the product.⁴⁸ All attempted homogeneous hydrogenation by using catalysts 97-100 failed. Table 15 shows that the hydrogenation of cyclooctadiene to cyclooctene in the presence of catalyst 98 can occur only if a mixture of acetone and water is used as the solvent. In the absence of any solvent, or in the presence of acetone or CH₂Cl₂, and THF, no hydrogen uptake was observed. A possible explanation for the different behavior of platinum and palladium ferrocenyl amine is as follows; Pt-S bonds are stronger than Pd-S bonds and as has been demonstrated,⁴⁸ breakage of Pd-S bonds could be important to the selective hydrogenation of the 1,3-cyclooctadiene. It should be noted here that palladium ferrocenyl amine selenide complexes also failed to have catalytic activity under the same conditions, because Pd-Se bonds are stronger than Pd-S bonds. The addition of water to acetone caused the catalyst to precipitate. The reaction was performed under heterogeneous conditions and gave fairly good results as it is shown in Table 16.

The heterogeneous reactions may proceed via hydrolysis of a Pd-Cl bond. Table 17 shows an example of the effect of pressure in hydrogenation. As shown, a minimum of 80 psi initial H₂ pressure was required to effect an appreciable hydrogenation by using a platinum ferrocenyl amine sulfide 98 as a catalyst. Palladium analogs required as low as 61 psi initial H₂ pressure for excellent results.⁴⁸ In order to evaluate catalytic activity of Pt complexes, catalyst 97 is compared with previously known Pt complexes (Table 18). A comparison of this catalyst with the entries 2 and 3 shown that although platinum catalysts reported here are considerably slower than the palladium analogs,⁴⁸ they are one order of magnitude faster than those reported by Bailar and co-

Table 15
Hydrogenation of 1,3-cyclooctadiene, Effect of Solvent^a

Catalyst	Solvent	Conversion (%)	Turnover Rate mol/mol pt.hr	Induction Time (h)	Products		
					Cyclooctene (%)	Cyclooctane (%)	Selectivity ^b (%)
CpFeC ₅ H ₃ [CHMeNMe ₂][SEt][PtCl ₂] 98	9 mL acetone	no H ₂ uptake					
	9 mL acetone + 2 mL water	49.1	3.64	6	15.9	32.2	32.38
	9 mL CH ₂ Cl ₂	no H ₂ uptake					
	9 mL THF	no H ₂ uptake					
	without solvent	no H ₂ uptake					

^a 2.0x10⁻⁵ mol of catalyst, 7.45x10⁻³ mol of substrate, at room temperature initial hydrogen pressure of 104 psi

^b cyclooctene/(cyclooctene + cyclooctane)

Table 16

Heterogeneous Hydrogenation of 1,3-cyclooctadiene^a

Catalyst	Conversion (%)	Turnover Rate mol/mol pt h	Induction Time(h)	Products		
				Cyclooctene (%)	Cyclooctane (%)	Selectivity ^b (%)
CpFeC ₅ H ₃ [CHMeNMe ₂][SMe][PtCl ₂] 97	77.6	11.01	3	27.9	49.7	35.95
CpFeC ₅ H ₃ [CHMeNMe ₂][SEt][PtCl ₂] 98	49.1	3.64	6	15.9	32.2	32.38
CpFeC ₅ H ₃ [CHMeNMe ₂][S-i-Pr][PtCl ₂] 99	18.2	1.39	8.5	9.3	8.9	51.10
CpFeC ₅ H ₃ [CHMeNMe ₂][SPh][PtCl ₂] 100	82.9	4.6	3.5	26.2	56.7	31.60

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^a 9 mL acetone, 2 mL water, 2.0x10⁻⁵ mol of catalyst, 7.45x10⁻³ mol of substrate, at room temp., initial hydrogen pressure of 104 psi.

^b cyclooctene/(cyclooctene + cyclooctane)

Table 17

Hydrogenation of 1,3-cyclooctadiene, effect of pressure^a

Catalyst	Pressure (psi)	Conversion (%)	Turnover Rate (mol/mol pt.hr)	Induction Time (h)	Products		
					Cyclooctene (%)	Cyclooctane (%)	Selectivity ^b (%)
CpFeC ₅ H ₃ [CHMeNMe ₂][SEt][PtCl ₂] 98	104	49.1	3.64	6	15.9	32.2	32.38
"	80	41.8	7.07	7.5	4.7	37.5	10.29
"	61	no H ₂ uptake					

^a 9.0 mL acetone + 2 mL water, 2.0x10⁻⁵ mol catalyst, 7.45x10⁻³ mol of substrate, room temperature.^b cyclooctene/(cyclooctene + cyclooctane).

Table 18

Selective hydrogenation of dienes to monoenes

Initial Rate mol/mol of Pd (Pt)/h/psi	Substrate	T,°C	Metal	Solvent	Additive	Reference
0.106	1,3-COD	27	Pt ²⁺	acetone	water	This work ^a
0.0114	1,5-COD	90	Pt ²⁺	CH ₂ Cl ₂	SnCl ₂	128
0.0154	1,4-cyclohexadiene	90	Pt ²⁺	CH ₂ Cl ₂	SnCl ₂	128

^a CpFeC₅H₃[CHMeNMe₂][SMe][PtCl₂] 97

workers.¹²⁸ It should be mentioned here that the compounds present after each hydrogenation reaction were 1,3-cyclooctadiene, cyclooctene and cyclooctane. The (1,3-cyclooctadiene-cyclooctene) : cyclooctane was determined by GC. The 1,3-cyclooctadiene : cyclooctene ratios were determined by integration of the ¹H NMR in the olefinic region. The outer olefinic protons of the diene and the olefinic protons of the monoene appear around 5.6 ppm. While the central protons of the diene appear at 5.8 ppm. The ratio of monoene to diene is therefore given by:

$$\frac{\text{Monoene}}{\text{Diene}} = \frac{A_{5.6} - A_{5.8}}{A_{5.8}}$$

A = The area of ¹H NMR peaks which are obtained by integration.

Figure 21 shows how the H₂ pressure is changed by time. In this case, catalyst 98 CpFeC₅H₃[SEt][PtCl₂] was used and initial H₂ pressure was 80 psi. During the first 30 min the pressure was constant and then it increased possibly because Cl₂ or HCl gas was produced. After being constant for a few hours the pressure dropped until the completion of the reaction. The rate of pressure decrease rate was almost constant throughout the course of the reaction.

a.2 Selective Hydrogenation of Cyclooctadiene by Use of Complexes 72-96

After it was found that platinum ferrocenyl amine sulfide complexes are far less active and selective than palladium analogs for the hydrogenation of cyclooctadiene, the catalytic activities of complexes 72-96 were investigated. In comparison with the catalysts reported by Shen⁴⁸ and Okoroafor⁷⁵ these complexes have an additional sulfide or selenide substituent in the second Cp rings. Kumada and co-workers show that existence of the second phosphine groups in the second Cp rings can effect the catalytic activities of ferrocenyl amine phosphine analogs. Table 19 shows the results of the hydrogenation of cyclooctadiene by use of some of the above complexes as selective catalysts.

Table 19

Selective Hydrogenation of 1,3-cyclooctadiene^a With Various Complexes in Acetone^b at Room Temperature and 104 psi Initial H₂ Pressure

Catalyst ^c	Conversion (%)	Induction Time (h)	Turnover Rate (mol/mol cat. hr)	Products			Selectivity ^d (%)
				Cyclooctene (%)	Cyclooctane (%)	Cyclooctene (%)	
[SR]C ₅ H ₄ FeC ₅ H ₃ [CHMeNMe ₂][SR][PdCl ₂] R = Me 72 R = Ph 73 R = 4-tolyl 75 R = 4-Cl-Ph 76	100	42.5	17.26	96.67	3.33	9.67	130
	96.2	0	114.46	84.5	3.8	86.8	
	98.6	0	464.75	91.88	6.75	93.1	
	100	0	684.17	96.75	3.25	96.7	
[SPH]C ₅ H ₄ FeC ₅ H ₃ [CHMeNMe ₂][SPH][PtCl ₂] 77	No hydrogen uptake						
[SePh]C ₅ H ₄ FeC ₅ H ₃ [CHMeNMe ₂][SePh][PdCl ₂] 80	No hydrogen uptake						
[SR]C ₅ H ₄ FeC ₅ H ₃ [CH ₂ NMe ₂][SR][PdCl ₂] R = Ph 87 R = Bz 88 R = 4-tolyl 89 R = 4-Cl-Ph 90	100	0	363.4	93.8	7.22	93.8	
	100	0	79.3	92.80	7.20	92.8	
	100	0	390.3	88.60	11.40	88.6	
	100	0	722.4	96.81	3.19	96.81	

^a 7.45x10⁻³ mol of substrate

^b 9 mL acetone

^c 2.0x10⁻⁵ mol of catalyst

^d selectivity = cyclooctene/(cyclooctene + cyclooctane)

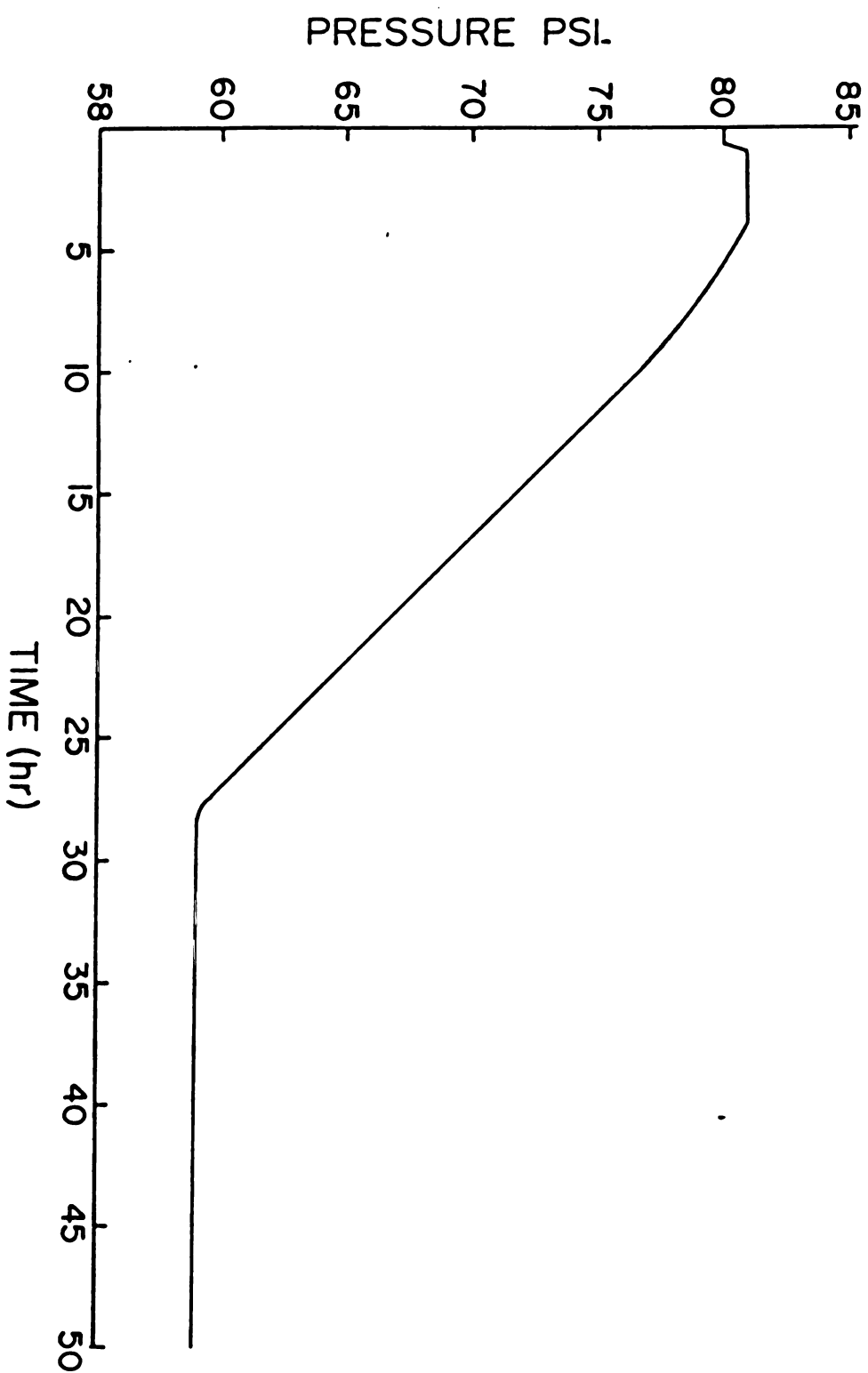


Figure 21.

Heterogeneous selective hydrogenation of 1,3-cyclooctadiene in acetone/water solvent system at room temperature and 80 psi initial H_2 pressure by using complex 98.

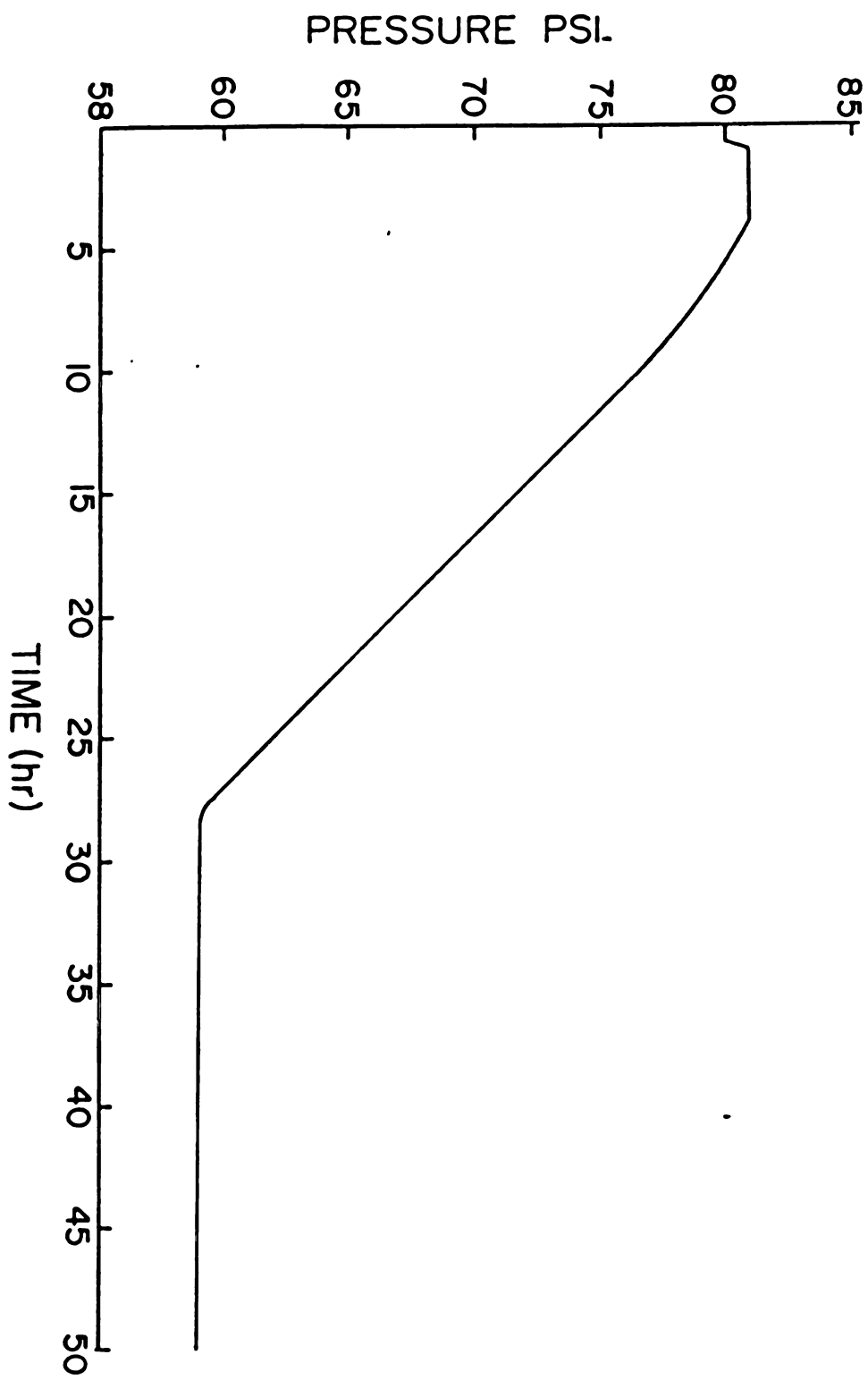


Figure 21.

Heterogeneous selective hydrogenation of 1,3-cyclooctadiene in acetone/water solvent system at room temperature and 80 psi initial H₂ pressure by using complex 98.

Again, no hydrogen uptake was observed when a complex with Pd-Se or Pt-S bond was used. When complexes **72**, **73**, **75**, **76**, **87**, **88**, **89** with Pd-S bonds were used hydrogenation reactions were performed in high conversion (for most of the cases 100%), high turnover rate and excellent selectivity. The best result was obtained when $[S(4\text{-Cl-Ph})]C_5H_4FeC_5H_3[CH_2NMe_2][S(4\text{-Cl-Ph})]PdCl_2$ **90** was used as a catalyst. In this case the conversion is 100%, turnover rate is 722.4 mol/mol cat. h and selectivity is 96.81%. This catalyst is comparable with the other state of the art catalysts for selective hydrogenation of cyclooctadiene to cyclooctene. It will be shown later that this catalyst is also very effective for selective reduction of the other conjugated double bonds. When catalyst **73** $SPh[C_5H_4FeC_5H_3[CHMeNMe_2][SPh][PdCl_2]$ was used the conversion was 96.2% and selectivity was 86.8%. Figure 22 shows how the selectivity of the reaction has been changed with the time. The percentage of cyclooctadiene, cyclooctene, and cyclooctane throughout the reaction can be determined by use of this figure. It is interesting that both cyclooctene and cyclooctane are formed in the beginning of the reaction but the rate of production of cyclooctene is much faster than that of cyclooctane. The selectivity gradually was reduced and after a while it remained almost constant. Figure 23 shows the olefinic region of 1H NMR spectra of products after 3.5 h, 2.5 h, and 0.5 h. Figure 24 shows how H_2 pressure is changed when catalyst **90** is used for the hydrogenation of cyclooctadiene. Table 20 shows the effect of different solvents in the hydrogenation of cyclooctadiene when complex **90** was used as a catalyst. These data clearly show that hydrogenation reactions are solvent dependant. The best results were obtained when acetone was used as the solvent. Lower turnover rate and conversion were observed when THF, CH_2Cl_2 , or a mixture of 9 mL acetone and 2 mL water were used as solvents. The selectivities for all the cases were very high. It should be noted that when the solvent was acetone, THF, or CH_2Cl_2 homogeneous mixtures were obtained but when a mixture of water and acetone was used Pd catalyst was precipitated and the reaction was performed under heterogeneous

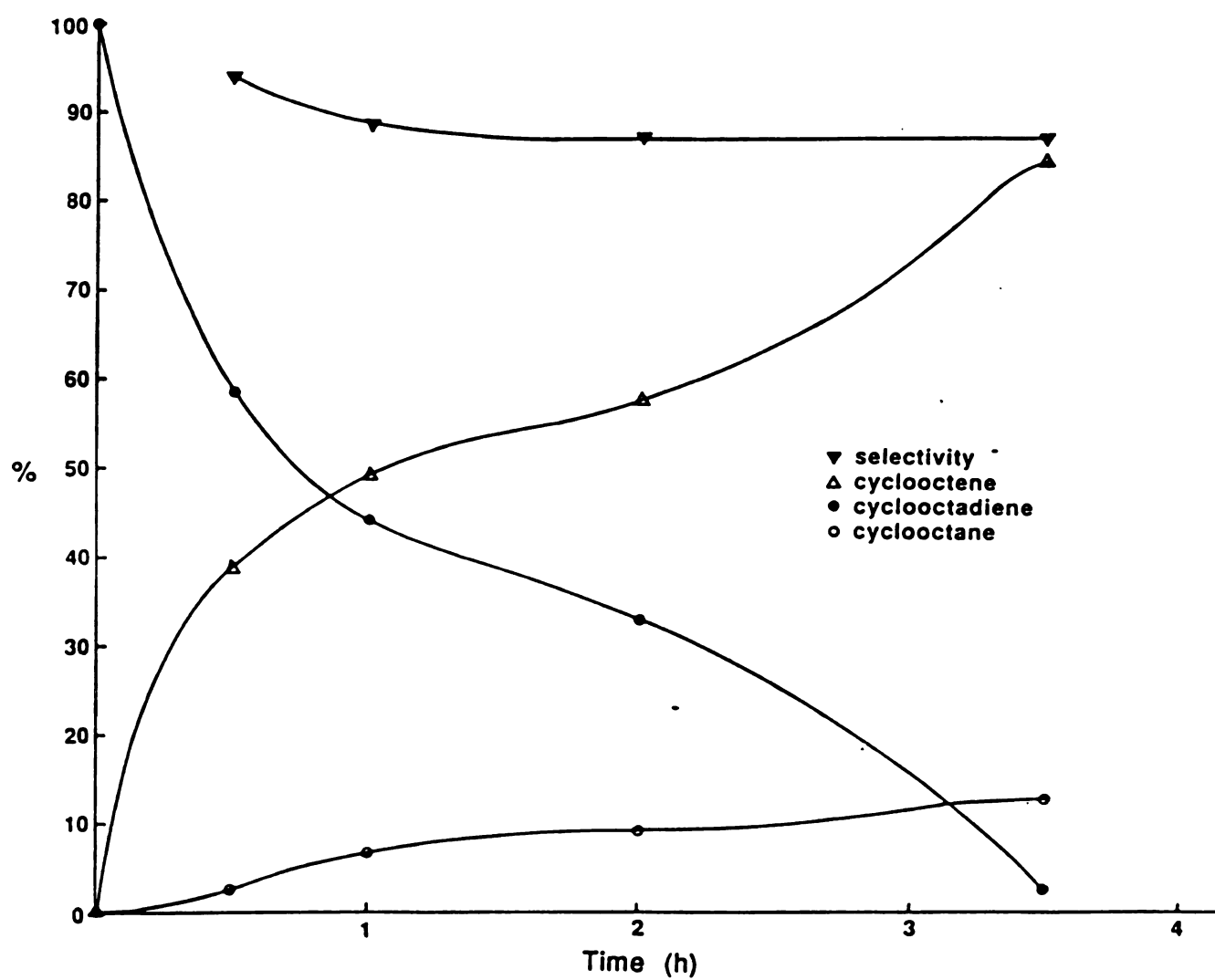


Figure 22. Selective reduction of 1,3-cyclooctadiene at room temperature and 104 psi initial H₂ pressure by using complex 73

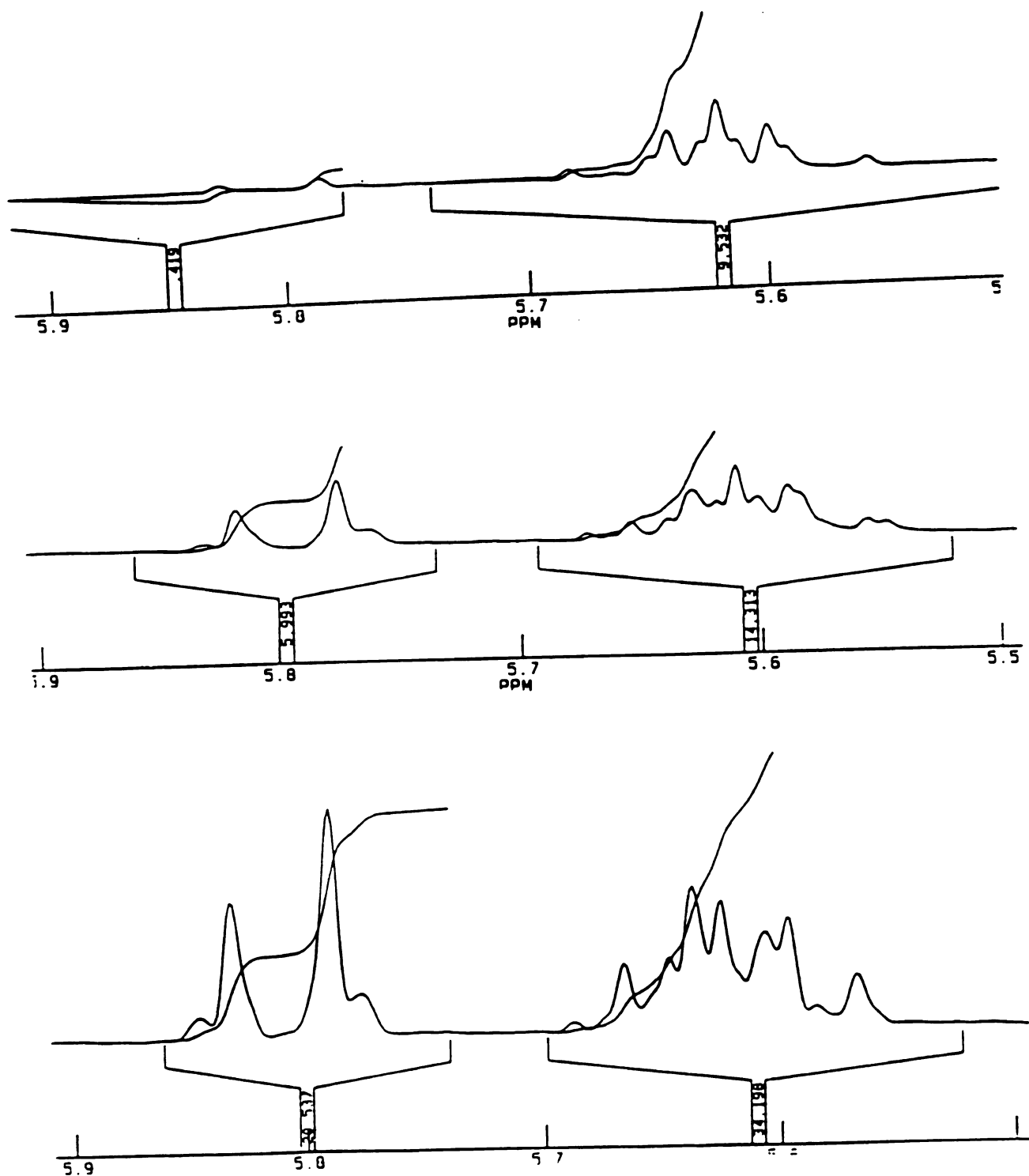


Figure 23. Olefinic region of ^1H NMR spectra of products of hydrogenation of 1,3-cyclooctadiene-at room temperature and 104 psi initial H_2 pressure after 3.5 h (above), 2.5 h (middle) and 0.5 h (below).

Selective Hydrogenation of cyclooctadiene by use of
[S(4-ClPh)]C₅H₄FeC₅H₃[CH₂NMe₂][S(4-ClPh)][PdCl₂]

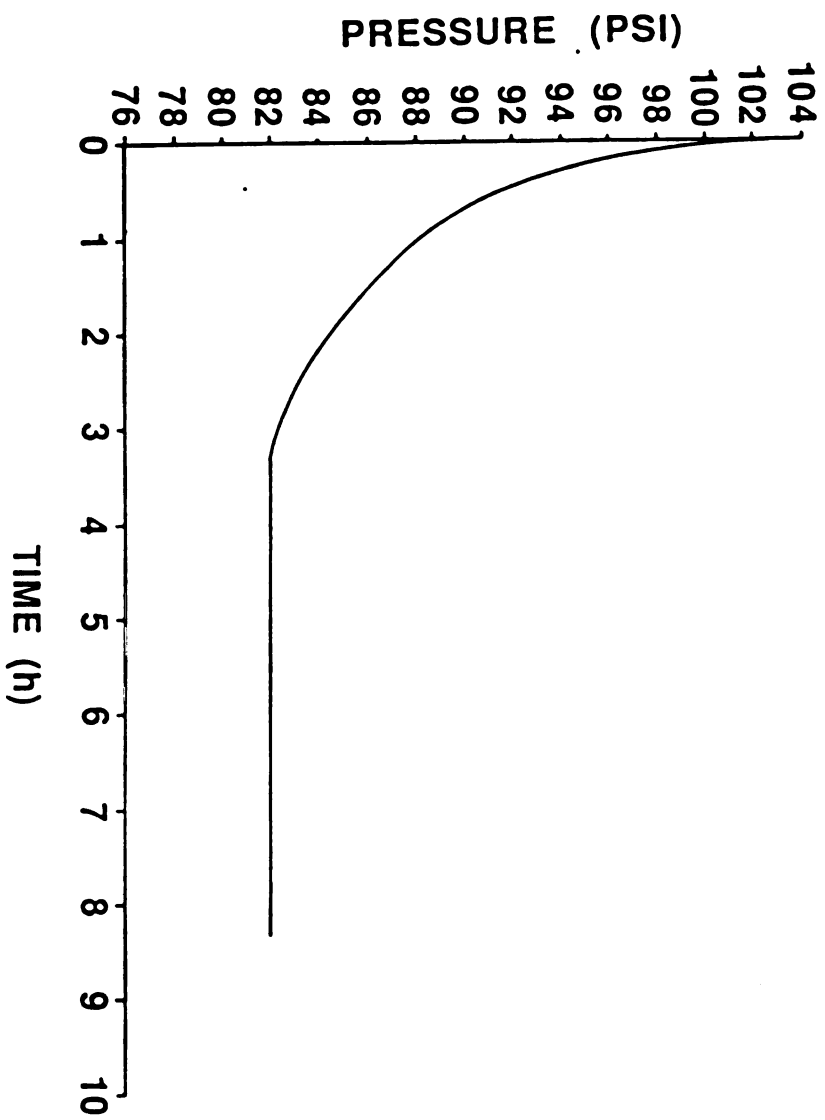


Figure 24

Table 20

Effect of Solvents^a in Selective Hydrogenation of 1,3-cyclooctadiene^b at Room Temperature and 104 psi Initial H₂ Pressure

Catalyst ^c	Solvent	Conversion (%)	Turnover Rate (mol/mol cat. h)	Products		
				Cyclooctene (%)	Cyclooctane (%)	Selectivity ^d (%)
[S(4-CIPh)]C ₅ H ₄ FeC ₅ H ₃ [CH ₂ NMe ₂] [S(4-CIPh)][PdCl ₂] 90	acetone	100	722.4	96.8	3.19	96.8
	THF	62.8	383.8	60.4	2.13	96.6
	CH ₂ Cl ₂	80.0	178.7	79.5	0.47	99.4
	acetone/water ^e	82.0	141.8	76.5	5.50	93.2

^a 9 mL solvent (except entry 4)^b 7.45x10⁻³ mol of substrate^c 2x10⁻⁵ mol of catalyst^d selectivity = cyclooctene/(cyclooctene + cyclooctane)^e 9 mL acetone + 2 mL water

conditions. A similar behavior was observed for Pt complexes with different solvents as was discussed before.

a.3 Selective Hydrogenation of 1,3-cyclohexadiene

Table 21 shows the results of hydrogenation of 1,3-cyclohexadiene by use of catalysts **73**, **76**, **87**, and **90** in the presence of acetone as solvent. In all cases the conversions were 100% and there was no induction time. Turnover rates were fairly high from 152.8 to 665.17 mol/mol cat. h. The selectivities were high and in the case of catalyst **73**, 96.7% selectivity was achieved. A comparison between the hydrogenation reactions catalyzed by complexes **73** and **76** reveals that the turnover rate is far higher in the latter reaction while the selectivity is higher in the former case. Also, the turnover rate is higher for catalyst **90** with two 4-chlorophenylthio substituents than for **87** with two phenylthio substituents while the selectivity is almost equal for both catalysts. Comparison of data in Tables 19 and 21 shows that the results of hydrogenation depend on the substrates. For the same catalyst when substrate changes from 1,3-cyclooctadiene to 1,3-cyclohexadiene both turnover rate and selectivity were changed.

a.4 Selective Hydrogenation of 2,3-dimethyl-1,3-butadiene.

Upon being found that new palladium ferrocenyl amine sulfide complexes are active catalysts for selective hydrogenations of cyclic conjugated substrates, we decided to investigate the hydrogenation of acyclic substrates with conjugated double bonds. Table 22 shows the results of hydrogenation of 2,3-dimethyl-1,3-butadiene. The major product in all cases is 2,3-dimethyl-2-butene and this shows that not only hydrogenation but also isomerization has occurred in this process. Preparation and characterization of compounds **102-105** (Table 22) have been reported⁹² but their catalytic activities remained unknown. In order to investigate the effect of second aryl or alkylthio substituent in the second Cp ring these complexes have been used along with new compounds in hydrogenation of several substrates. A direct comparison between

Table 21

Selective Hydrogenation of 1,3-cyclohexadiene^a With Various Complexes in Acetone^b At Room Temperature and 104 psi Initial H₂ Pressure

Catalyst ^c	Conversion (%)	Induction Time (h)	Turnover Rate (mol/mol cat. hr)	Products		
				Cyclohexene (%)	Cyclohexane (%)	Selectivity ^d (%)
[SR]C ₅ H ₄ FeC ₅ H ₃ [CHMeNMe ₂][SR][PdCl ₂] R = Ph 73 R = 4-Cl-Ph 76	100	0	152.8	96.7	3.3	96.7
	100	0	544.2	89.2	10.8	89.2
[SR]C ₅ H ₄ FeC ₅ H ₃ [CH ₂ NMe ₂][SR][PdCl ₂] R = Ph 87 R = 4-Cl-Ph 90	100	0	475.53	95.9	4.1	95.9
	100	0	665.17	94.8	5.6	94.8

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^a 7.45x10⁻³ mol of substrate

^b 9 mL acetone

^c 2.0x10⁻⁵ mol of catalyst

^d selectivity = cyclohexene/(cyclohexene + cyclohexane)

Table 22

Selective Hydrogenation of 2,3-dimethyl-1,3-butadiene at Room Temperature^a

Catalyst	Induction Time (h)	Initial Turnover Rate (mol/mol Pd h)	 (%)	 (%)	 (%)	 (%)
(<u>S</u> , <u>B</u>)-[SMe]C ₅ H ₄ FeC ₅ H ₃ [CHMeNMe ₂][SMe][PdCl ₂] (72)	0.5	85.1	0.2	35.1	49.5	15.2
(<u>S</u> , <u>B</u>)-[S-(4-tolyl)]C ₅ H ₄ FeC ₅ H ₃ [CHMeNMe ₂][S-(4-tolyl)][PdCl ₂] (75)	0.5	496.6	0.1	18.6	74.8	6.5
(<u>S</u> , <u>B</u>)-[S-(4-Cl-Ph)]C ₅ H ₄ FeC ₅ H ₃ [CHMeNMe ₂][S-(4-Cl-Ph)][PdCl ₂] (76)	0.1	160.8	0.9	24.9	73.3	0.9
[SMe]C ₅ H ₄ FeC ₅ H ₃ [CH ₂ NMe ₂][SMe][PdCl ₂] (83)	15	9.4	0.1	15.6	73.9	10.4
[S-(4-tolyl)]C ₅ H ₄ FeC ₅ H ₃ [CH ₂ NMe ₂][S-(4-tolyl)][PdCl ₂] (89)	1	252.1	0.5	28.1	66.2	5.2
(<u>S</u> , <u>B</u>)-C ₅ H ₅ FeC ₅ H ₃ [CHMeNMe ₂] [SMe][PdCl ₂] (102) ^b	1	50.6	0	33.3	52.1	14.6
(<u>S</u> , <u>B</u>)-C ₅ H ₅ FeC ₅ H ₃ [CHMeNMe ₂] [S-(4-tolyl)][PdCl ₂] (103) ^b	0.2	542.9	0.4	9.3	70.1	20.2
C ₅ H ₅ FeC ₅ H ₃ [CH ₂ NMe ₂] [SMe][PdCl ₂] (104) ^b	1	575.7	0	43.9	47.3	8.8
C ₅ H ₅ FeC ₅ H ₃ [CH ₂ NMe ₂] [S-(p-tolyl)][PdCl ₂] (105) ^b	1	274.5	0.2	16.5	61.2	22.1

^a80 psi initial pressure of H₂, 4.5cc acetone, 2.37x10⁻³ mol substrate, and 1x10⁻⁵ mol catalyst.

complex **72** with two methylthio substituents and **102** with only one methylthio shows similar results. Although the induction time has been reduced by half and initial turnover rate increased by ca. 60% after introduction of the second methyl sulfide group in the second Cp ring but the percentage of products are close in the both cases. It is very interesting and somehow surprising that addition of the second methylthio substituent to the unsubstituted Cp ring of the chiral complex $(S,R)\text{CpFeC}_5\text{H}_3[\text{CHMeNMe}_2][\text{SMe}][\text{PdCl}_2]$ dramatically changes its catalytic activity toward hydrogenation of 2,3-dimethyl-1,3-butadiene (compare entries 4 and 8, Table 22). The induction time is increased by a factor of 15 and also initial turnover rate decreased by a factor of 50. On the other hand, higher selectivity was achieved by use of the catalyst **63**. Conversion for all investigated catalysts were more than 99% and initial turnover rate reached to 575.7 mol/mol Pd. h, however, the selectivity was not as good as for the other substrates (cyclooctadiene and cyclohexadiene). The best results were obtained by use of $(S,R)\text{-[S(4-tolyl)]C}_5\text{H}_4\text{Fe[CHMeNMe}_2][\text{S(4-tolyl)]}[PdCl_2]$ **75**. The conversion, selectivity and, the initial turnover rate were 99.9%, 74.8%, and 49.66 (mol/mol Pd h) respectively.

The (2,3-dimethylbutane + 2,3-dimethyl-1-butene):2,3-dimethyl-2-butene:2,3-dimethyl-1,3-butadiene ratios were determined by GC. The 2,3-dimethylbutane:2,3-dimethyl-1-butene ratios were obtained by integration of appropriate peaks in ^1H NMR. The starting materials, 2,3-dimethyl-1,3-butadiene, shows a singlet at 1.9 ppm for 6 methyl protons and a doublet at 5 ppm for 4 olefinic protons while 2,3-dimethyl-2-butene shows only one singlet at 1.6 ppm in the proton NMR spectra. On the other hand, ^1H NMR spectra of 2,3-dimethyl-1-butene has a peak at 4.6 ppm for two olefinic protons which is completely distinguishable from the doublet of the starting material. There is also a doublet at 0.9 ppm for 6 protons of terminal methyls. ^1H NMR spectra of 2,3-dimethylbutane also shows a doublet at 0.9 ppm for 12 methyl protons and a

multiplet for the other 2 protons at 1.4 ppm. Therefore, it may be concluded that the ratios of 2,3-dimethylbutane: 2,3-dimethyl-1-butene can be obtained by:

$$\frac{\text{2,3-dimethylbutane}}{\text{2,3-dimethyl-1-butene}} = \frac{A_{0.9-3}A_{4.5} / 2}{A_{4.5}}$$

a.5 Selective Hydrogenation of 3-methyl-1,3-pentadiene.

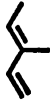
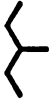
Table 23 shows the results of hydrogenation of 3-methyl-1,3-pentadiene by use of 8 different palladium ferrocenyl amine sulfides as catalysts. The solvent in all cases was acetone and the initial H₂ pressure was 80 psi. The existence of two double bonds in two different environments is the interesting point about this substrate. The last three substrates, cyclooctadiene, cyclohexadiene, and 2,3-dimethyl-1,3-butadiene all have two equivalent double bonds, therefore, only one initial monoene product was obtained. However, in the case of 2,3-dimethyl-1,3-butadiene the initial product was isomerized. Here, there is a competition between the terminal and internal double bonds. It is not surprising that the terminal double bond has been hydrogenated much faster than the other double bond and 3-methyl-2-pentene was obtained as the major product. The selectivities and the conversions both are high and reached to 94.8% and 100% respectively. These results also show that introduction of second sulfide substituent at the unsubstituted Cp ring effects the conversions and the selectivities. However, these effects are not always parallel (compare results of entries 1 and 4 versus results of entries 3 and 6).

a.6 Selective Hydrogenation of Double and Triple Bonds Conjugated to Aromatic Rings.

Table 24 presents the results for the hydrogenation of styrene, 4-vinylpyridine, and phenylacetylene. These reactions were all performed under homogeneous conditions by using acetone as a solvent and in all cases quantitative yields were observed. Hydrogenation of styrene was much faster than 4-vinylpyridine and phenylacetylene. When catalyst 75 was used for hydrogenation of both styrene and 4-phenylpyridine,

Table 23

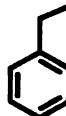
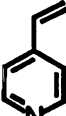
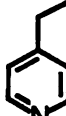
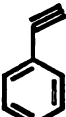
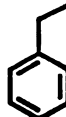
Selective Hydrogenation of 3-methyl-1,3-pentadiene at Room Temperature^a

Catalyst	 (%)	 (%)	 (%)	 (%)	Conversion (%)	Selectivity (%)
(<u>S</u> , <u>R</u>)-[SMe]C ₅ H ₄ FeC ₅ H ₃ [CHMeNMe ₂][SMe][PdCl ₂] (72)	0	6.2	85.1	8.7	100	85.1
(<u>S</u> , <u>R</u>)-[S-(4-tolyl)]C ₅ H ₄ FeC ₅ H ₃ [CHMeNMe ₂][S-(4-tolyl)][PdCl ₂] (75)	12.9	4.00	82.4	0.7	87.1	94.6
[SMe]C ₅ H ₄ FeC ₅ H ₃ [CH ₂ NMe ₂][SMe][PdCl ₂] (83)	2.6	15.3	78.2	3.9	97.4	80.2
[S-(4-tolyl)]C ₅ H ₄ FeC ₅ H ₃ [CH ₂ NMe ₂][S-(4-tolyl)][PdCl ₂] (89)	10.0	7.9	81.7	0.4	90.0	90.5
(<u>S</u> , <u>R</u>)-C ₅ H ₅ FeC ₅ H ₃ [CHMeNMe ₂][SMe][PdCl ₂] (102)	1.0	9.1	86.2	3.7	99.0	87.1
(<u>S</u> , <u>R</u>)-C ₅ H ₅ FeC ₅ H ₃ [CHMeNMe ₂][S-(p-tolyl)][PdCl ₂] (103)	21.1	3.8	74.8	0.3	78.9	94.8
C ₅ H ₅ FeC ₅ H ₃ [CHMeNMe ₂] [SMe][PdCl ₂] (104)	0.2	2.7	83.2	13.9	99.8	83.4
C ₅ H ₅ FeC ₅ H ₃ [CH ₂ NMe ₂] [S-(4-tolyl)][PdCl ₂] (105)	0	4.5	80.7	14.8	100	80.7

^a80 psi initial pressure of H₂, 4.5 cc acetone, 2.375x10⁻³ mol substrate, and 1x10⁻⁵ mol catalyst

Table 24

Selective Hydrogenation of Styrene, 4-vinylpyridine, and phenylacetylene.^a

Entry	Catalyst ^b	Starting Material	Time (h)	Product	Yield (%)
1	7 5		2		>99
2	8 3	"	12	"	>99
3	8 9	"	0.25	"	>99
4	10 4	"	0.25	"	>99
5	10 5	"	0.25	"	>99
6	7 5		14		>99
7	8 9	"	17	"	>99
8	10 4	"	15	"	>99
9	7 5		12		>99
10	10 5	"	2	"	>99

^a Room temperature, 80 psi initial pressure of H₂, 4.5 mL acetone 2.375x10⁻³ mol substrate, and 1x10⁻⁵ mol catalyst.

^b 75 : (S,R)-[S-(4-tolyl)]C₅H₄FeC₅H₃[CHMeNMe₂][S-(4-tolyl)][PdCl₂]
 83 : [SMe]C₅H₄FeC₅H₃[CHMeNMe₂][SMe][PdCl₂]
 89 : [S-(4-tolyl)]C₅H₄FeC₅H₃[CH₂NMe₂][S-(4-tolyl)][PdCl₂]
 104 : C₅H₅FeC₅H₃[CH₂NMe₂][SMe][PdCl₂]
 105 : C₅H₅FeC₅H₃[CH₂NMe₂][S-(4-tolyl)][PdCl₂]

Table 25

Chemoselective Hydrogenation of Carbon-Carbon Double Bonds of α - β Unsaturated Carbonyls, Aldehydes, Carboxylic Acids, Esters, Nitriles, and Anides

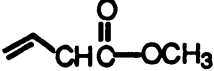
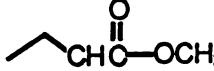
Entry	Catalyst ^b	Starting Material	Time (h)	Product	Yield (%)
1	7 2		8		>99
2	7 5	"	0.5	"	>99
3	8 3	"	8	"	>99
4	8 9	"	10	"	>99
5	10 2	"	0.5	"	>99
6	10 3	"	0.5	"	>99
7	10 4	"	10	"	>99
8	10 5	"	1	"	>99
9	7 2		2		>99
10	10 4	"	9	"	>99
11	10 5	"	12	"	>97
12	7 5		1.2		>99
13	8 9	"	1	"	>99
14	10 4	"	3	"	>99
15	10 5	"	1	"	>99
16	7 5		0.75		>99
17	8 9	"	0.75	"	>99
18	10 4	"	1	"	>99
19	10 5	"	0.1	"	>99
20	7 5		3		>99

Table 25 Continued

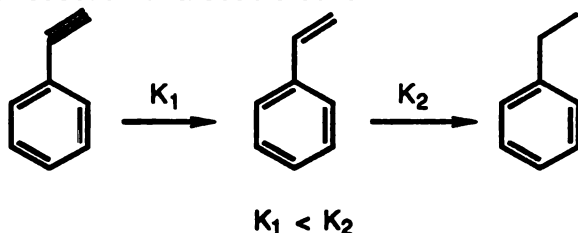
Entry	Catalyst ^b	Starting Material	Time (h)	Product	Yield (%)
21	89		1		>99
22	104	"	0.25	"	>99
23	104c	"	0.5	"	>99
24	105	"	0.25	"	>99
25	75		0.1		>99
26	105	"	0.5	"	>99

^a Room temperature, 80 psi initial pressure of H₂, 4.5 mL acetone, 2.375x10⁻³ mol substrate, and 1x10⁻⁵ mol catalyst.

^b 72 : (S,R)-[SMe]C₅H₄FeC₅H₃[CHMeNMe₂][SMe][PdCl₂]
 75 : (S,R)-[S-(4-tolyl)]C₅H₄FeC₅H₃[CHMeNMe₂][S-(4-tolyl)][PdCl₂]
 83 : [SMe]C₅H₄FeC₅H₃[CHMeNMe₂][SMe][PdCl₂]
 89 : [S-(4-tolyl)]C₅H₄FeC₅H₃[CH₂NMe₂][SMe][PdCl₂]
 102 : (S,R)-C₅H₄FeC₅H₃[CHMeNMe₂][SMe][PdCl₂]
 103 : (S,R)-C₅H₄FeC₅H₃[CHMeNMe₂][S-(4-tolyl)][PdCl₂]
 104 : C₅H₅FeC₅H₃[CH₂NMe₂][SMe][PdCl₂]
 105 : C₅H₅FeC₅H₃[CH₂NMe₂][S-(4-tolyl)][PdCl₂]

^c 4.75x10⁻³ mol substrate

styrene was hydrogenated 7 times faster than 4-vinylpyridien. In the case of catalyst 68 this ratio was 68:1. A reasonable explanation is that 4-phenylpyridine has two coordination sites, the double bond and the nitrogen atom. Thus, some of the active sites of the catalysts were coordinated to the nitrogen atom and consequently the turnover rate was decreased. It has been reported that the use of pyridiene as the solvent in homogeneous reduction of cyclooctadiene in the presence of a ferrocenyl amine sulfide catalyst resulted in lowering the turnover rate and poor yield (7.2%).^{129,130} The reason is that again the pyridine nitrogen solvent competes with double bonds of the substrate for coordination to active sites of the catalyst. Styrene also was hydrogenated much faster than phenylacetylene and indicates that reduction of a triple bond to a double bond is slower than the reduction of a double bond.



a.7 Chemoselective Hydrogenation of Carbon-Carbon Double Bonds Conjugated to Different Functional Groups.

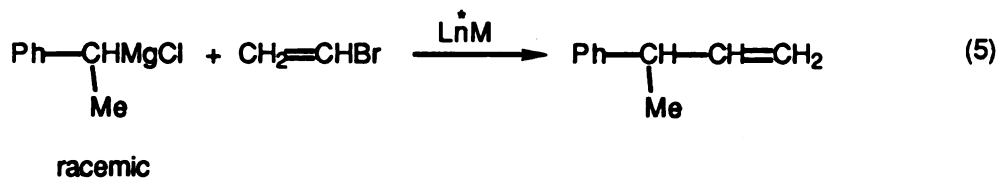
Chemo- and regioselective reduction of carbon-carbon double bonds is of importance in organic synthesis. Boron¹³¹ and transition metal hydrides (e.g. iron,¹³² rhodium,¹³⁴ cobalt,¹³⁵ aluminum,¹³⁶ palladium,¹³⁷ and nickel¹³⁸ hydrides) are frequently used in stoichiometric amounts.

By using different palladium ferrocenyl amine sulfide complexes, chemoselective reduction of carbon-carbon double bonds conjugated to different functional groups have been investigated. As shown in Table 25, short reaction times and quantitative yields are two important aspects of all of these reactions. Hydrogenation of vinylmethylketone was carried out by use of 8 different catalysts (entries 1-8) and it was found that ethylmethylketone is the only product for all of these reactions. Not even traces of

1-buten-3-ol  or 2-butanol  was found. The reaction time was varied between 0.5-10 h and in most cases it was slower for the catalysts with two sulfide substituents than those with only one. Hydrogenation of acrylaldehyde (entries 9-11), acrylic acid (entries 12-15), methyl acrylate (entries 16-19), acrylonitrile (entries 20-24) and acrylamide (entries 25-26) were also investigated and in all the cases it was only the carbon-carbon double bond that was hydrogenated. As shown in Table 25, when 2.375×10^{-3} mol acrylamide was hydrogenated by use of 1×10^{-5} mol catalyst 104, $\text{CpFeC}_5\text{H}_3[\text{CH}_2\text{NMe}_2][\text{SMe}]\text{-}[\text{PdCl}_2]$, the reaction was completed in ca. 15 min and when 4.75×10^{-3} mol acrylamide was used the reaction was ended in ca. 30 min. This shows that the turnover rate of this reaction remained constant throughout the reaction.

b. Asymmetric Grignard Cross-Coupling Reactions.

Asymmetric carbon-carbon bond formation is of great interest for the preparation of chiral molecules, and frequently novel chiral transition-metal catalysts have been used for this purpose.^{80,139} In 1973, the first asymmetric Grignard cross-coupling reaction catalyzed by a nickel complex was reported.¹⁴⁰ The asymmetric coupling of vinyl halides with Grignard reagents by use of chiral nickel or palladium complexes of ferrocenyl phosphines has been extensively investigated^{42,141} and spectacularly successful results have been achieved (equation 5). the



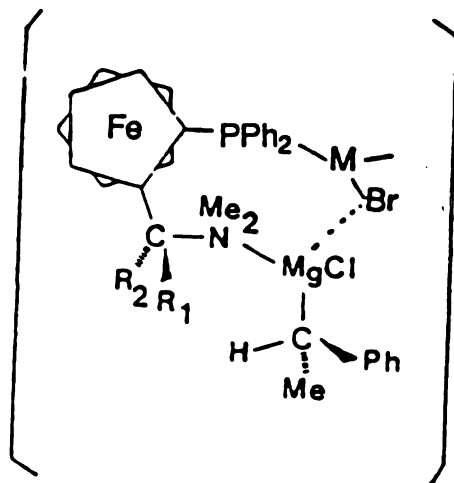
enantioselective step in the catalytic cycle was the transmetallation reaction and the

Table 26

Asymmetric Grignard Cross-Coupling Reactions Using Chiral Nickel
Ferrocenyl Amine Sulfide Catalysts

Catalyst	Chemical Yield Configuration (%)	e.e. (%)	
(S,R)-[SR]C ₅ H ₄ FeC ₅ H ₃ [CHMeNMe ₂] [SR]/NiCl ₂			
R = Et	97.5	21.2	R
R = <u>sec</u> -Bu	96	23.2	R
R = Ph	96	22.5	R
R = 4-Cl-Ph	96.5	27.7	R

most important intermediate of the reaction was the diastereomeric transition state shown below.



The transmetalation step must be slow compared to the equilibrium of the Grignard reagent to keep a racemic mixture, because the optical purity of the coupling product is not affected by the degree of conversion of the Grignard reagent.

It was shown that the ferrocene chirality plays the major role in this asymmetric reaction and chirality at the carbon bearing the amino function does not influence the optical purity of the products. However, it should be reminded that the coordination of magnesium of the Grignard reagent to the amine group is the first requisite for achieving high enantioselectivity.

Reaction of NiCl_2 with chiral ligands **44**, **48**, **51**, and **54** produced in situ nickel complexes that are active catalysts for asymmetric Grignard cross coupling reactions between allylmagnesium chloride and 1-phenyl-1-chloroethane (equation 6).

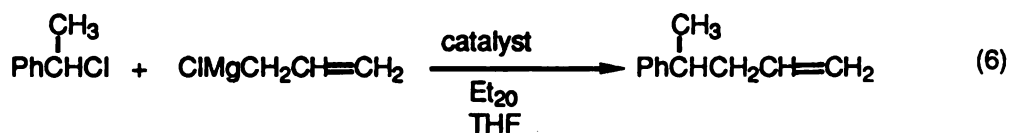


Table 26 shows the chemical and optical yields of these reactions. The chemical yields were very high for all four investigated complexes (96%-97.5%) and fairly good optical yields were achieved (21.2%-27.7%). The yields are much higher than those

reported by Kellog¹⁴² and slightly better than those reported by Okoroafor.⁴⁷ The proposed mechanism is shown in Figure 25 which is based on the Grignard cross-coupling reaction mechanism postulated by Kumada^{18b} and co-workers for nickel phosphineferrocenyl amine catalysts. Although all attempts for isolation of nickel/ferrocenyl amine sulfide failed, but because of similarity of the results obtained here and those obtained by use of Pd analogs,¹⁴³ we assume that nickel complexes have the same structures as the palladium complexes.

It has been shown that the optical rotation of the 4-phenyl-1-pentene was strongly affected by small amounts of impurities.⁴¹ Moreover, products were racemized and it was difficult to determine the optical purity by use of a polarimeter. The enantiomeric excess of the products was determined by use of ¹H NMR spectroscopy in the presence of a chiral shift reagent, tris(d,d-dicampholylmetanato)europium(III) (Eu(dcm)₃) after the alkene was converted into the methylester.¹⁴⁴ Figures 26 and 27 show the dependency of the chemical shift (δ), and the enantiomeric shift difference ($\Delta\delta$) on the concentration of the chiral shift reagent and the temperature at a constant concentration of the substrate (0.5 M) in chloroform-d₁. At room temperature and without addition of the chiral shift reagent there is only one singlet for the methyl protons of the methylester. However, the signal separates into two distinct singlets after addition of the shift reagent. Upon increasing the concentration of shift reagent the signal was shifted downfield and $\Delta\delta$ was increased. The enantiomeric excess was clearly determined when concentration of the shift reagent reached 0.27 M. It has been reported by Kumada⁴¹ that the signal of (S)-methyl-3-phenyl propionate appears at a higher field than that of the R enantiomer. Therefore, here we also attribute the higher field signals to S enantiomer. In all cases the resulting product has R configuration, the configuration of ferrocene chirality. However, we cannot deduce any conclusion from this observation.

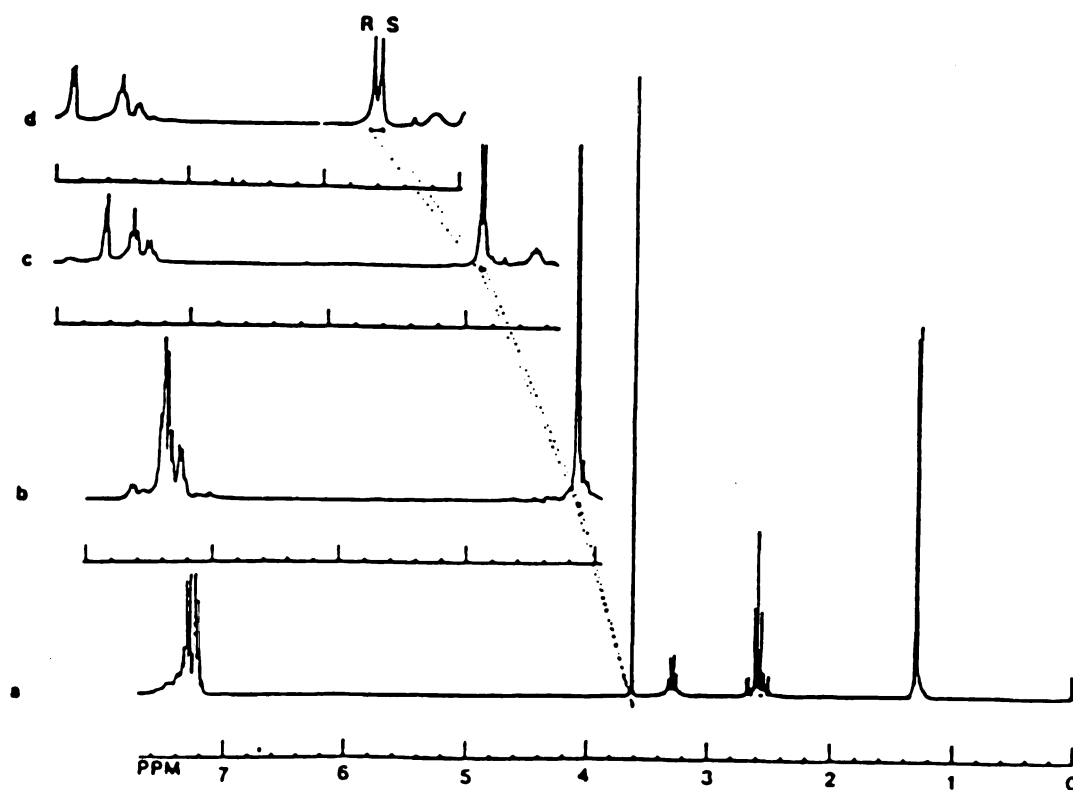


Figure 26. ^1H NMR spectra of (R) and (S)-methyl-3-butyrate in the presence of increasing concentrations of chiral shift reagent $\text{Eu}(\text{dcm})_3$. The concentration of substrate in these spectra is 0.5 M in CDCl_3/TMS , and that of $\text{Eu}(\text{dcm})_3$ is (a) 0.0 M, (b) 0.09 M, (c) 0.18 M, and (d) 0.27 M.

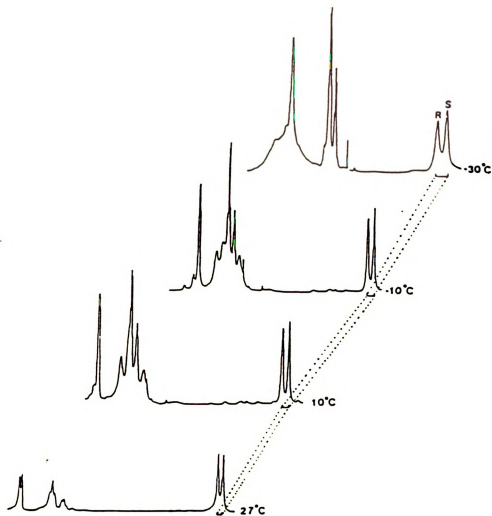


Figure 27. The magnitudes of $\Delta\Delta\delta$ increase for methyl 3-phenylbutyrate with decreasing temperature in the presence of chiral shift reagent, $\text{Eu}(\text{dcm})_3$. The concentration of substrate and chiral shift reagent in CDCl_3/TMS are 0.5 and 0.27 M, respectively

4. Structure of [1-[(Dimethylamino)methyl]-2-(*t*-Butylthio)ferrocene]Palladium dichloride (101)

Atomic parameters are listed in Table 27 and 28 and selected bond lengths and angles are given in Tables 29 and 30 respectively; a drawing showing the atom labeling and thermal ellipsoid is given in Figure 28, a stereographic packing diagram is given in Figure 29 and a stereographic view of the complex is given in Figure 30.

The palladium atom is in a square-planar environment where the sulfur and nitrogen atoms of the ligand chelate to the palladium. The Fe-C distances range from 2.017(9) to 2.084(9)Å, with an average value of 2.046(22)Å, comparing favorably with those of (*R,S*)-CpFeC₅H₃[CHMeNMe₂][SMe][PdCl₂].⁴⁷ The C-C distances in the cyclopentadienyl rings range from 1.37(2) to 1.436(13)Å, with an average value of 1.409(6)Å; these values are typical for ferrocene. The bond lengths to Pd closely approximate the sum of the Pauling covalent radii;¹¹⁴ Pd-S observed at 2.312(2)Å, compared with 2.35Å; Pd-Cl observed average 2.303(3)Å, compared with 2.31Å; and Pd-N observed at 2.147(7)Å, compared with 2.16Å.

The most striking angular feature of the complex is the obtuse S-Pd-N angle of 100.2(2)° that can be attributed, in part, to steric crowding caused by the bulky *t*-butyl group. Cullen¹⁴⁵ has observed an analogous effect by *t*-butyl substituents in ferrocene-bridged bis(tertiaryphosphine) complexes of Rh.

The two cyclopentadienyl rings are eclipsed and are slightly tilted with respect to each other; the dihedral angle is 8.0.

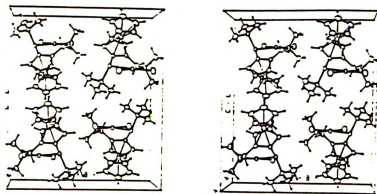


Figure 29. Stereographic packing diagram of complex 101 (ORTEP, 20% probability ellipsoids). The c-axis is vertical, the b-axis is horizontal and the a-axis is normal to the page.

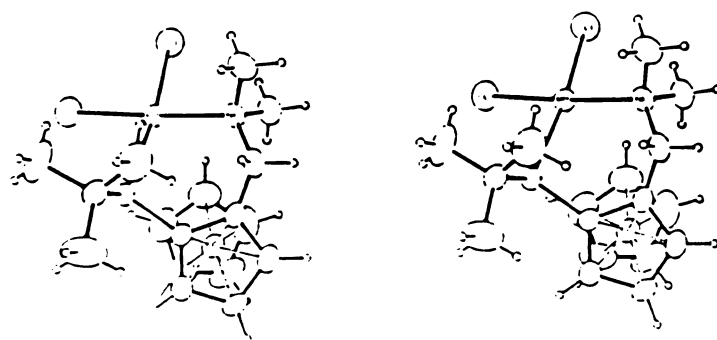


Figure 30. Stereographic view of complex 101 (ORTEP, 50% probability ellipsoids).

Table 27

Positional Parameters and
Their Estimated Standard Deviations for
[1-[(Dimethylamino)methyl]-2-(t-butylthio)ferrocene]palladium
dichloride

Atom	x	y	z	B(Å ²)
Pd1	0.51669(7)	0.20158(5)	0.16807(4)	2.425(9)
Fe1	0.7763(2)	0.2623(1)	0.35287(8)	2.80(2)
C11	0.3293(3)	0.0774(2)	0.1569(2)	4.51(6)
C12	0.2871(3)	0.2996(2)	0.1539(2)	4.47(6)
S1	0.6636(3)	0.3400(2)	0.1855(1)	2.41(4)
N1	0.7229(9)	0.1035(5)	0.1788(5)	3.0(2)
C1	0.689(1)	0.0331(7)	0.2410(7)	3.9(2)
C2	0.736(1)	0.0537(7)	0.1017(6)	4.0(2)
C3	0.897(1)	0.1438(6)	0.1953(6)	3.0(2)
C5	0.906(1)	0.2188(6)	0.2536(6)	2.6(2)
C6	1.018(1)	0.2231(6)	0.3180(6)	3.3(2)
C7	1.020(1)	0.3159(6)	0.3493(6)	3.3(2)
C8	0.904(1)	0.3691(7)	0.3034(6)	2.9(2)
C9	0.836(1)	0.3108(6)	0.2464(5)	2.4(1)
C10	0.548(1)	0.1938(9)	0.3742(6)	4.4(2)
C11	0.670(2)	0.172(1)	0.4304(8)	5.5(3)
C12	0.718(2)	0.257(1)	0.4668(7)	5.8(3)
C13	0.627(2)	0.328(1)	0.4331(7)	5.1(3)
C14	0.524(1)	0.291(1)	0.3760(6)	4.8(2)
C15	0.756(1)	0.3889(7)	0.0957(6)	3.1(2)
C16	0.854(2)	0.3186(9)	0.0483(6)	5.0(3)
C17	0.605(2)	0.422(1)	0.0475(7)	5.4(3)
C18	0.868(2)	0.4685(9)	0.1170(8)	6.3(3)

Anisotropically refined atoms are given in the form of
the isotropic equivalent thermal parameter defined as:

$$(4/3) * [a^2 * B(1,1) + b^2 * B(2,2) + c^2 * B(3,3) \\ + ab(\cos \gamma) * B(1,2) + ac(\cos \beta) * B(1,3) \\ + bc(\cos \alpha) * B(2,3)]$$

Table 28

General Temperature Factor Expressions - U's - for
[1-((Dimethylamino)methyl)-2-(t-butylthio)ferrocene]palladium
dichloride

Name	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
Pd1	0.0176(2)	0.0337(2)	0.0409(3)	-0.0009(3)	0.0015(3)	-0.0003(3)
Fe1	0.0266(5)	0.0428(6)	0.0371(6)	-0.0035(6)	-0.0011(5)	0.0060(6)
C11	0.032(1)	0.050(1)	0.089(2)	-0.015(1)	-0.003(1)	0.007(2)
C12	0.0227(8)	0.058(1)	0.089(2)	0.009(1)	-0.006(1)	-0.002(2)
S1	0.0235(8)	0.0286(9)	0.039(1)	0.0034(8)	-0.0033(8)	0.0010(9)
N1	0.023(3)	0.030(3)	0.062(5)	0.002(3)	-0.002(4)	-0.004(4)
C1	0.036(5)	0.034(5)	0.079(7)	-0.002(4)	-0.003(5)	0.010(5)
C2	0.039(5)	0.047(5)	0.067(7)	0.005(5)	0.007(5)	-0.019(5)
C3	0.020(4)	0.032(4)	0.063(6)	0.003(3)	0.008(4)	0.006(4)
C5	0.019(3)	0.034(4)	0.048(5)	-0.000(3)	-0.002(3)	0.010(4)
C6	0.024(3)	0.042(4)	0.058(5)	0.002(4)	-0.002(4)	0.014(4)
C7	0.025(3)	0.046(5)	0.054(5)	-0.011(4)	-0.013(4)	0.007(4)
C8	0.029(4)	0.035(4)	0.048(5)	-0.001(4)	-0.003(4)	0.008(4)
C9	0.021(3)	0.033(4)	0.037(4)	-0.001(4)	-0.001(3)	0.002(4)
C10	0.040(5)	0.070(6)	0.057(6)	-0.022(5)	0.017(4)	-0.001(6)
C11	0.064(7)	0.070(7)	0.076(7)	0.009(7)	0.018(7)	0.032(6)
C12	0.047(6)	0.12(1)	0.051(6)	-0.016(8)	-0.011(5)	0.009(8)
C13	0.060(6)	0.080(8)	0.053(6)	-0.021(6)	0.023(5)	-0.021(6)
C14	0.032(4)	0.093(8)	0.058(6)	0.011(7)	0.019(4)	0.004(7)
C15	0.037(4)	0.038(4)	0.043(5)	-0.006(4)	-0.009(4)	0.011(4)
C16	0.064(7)	0.080(8)	0.044(5)	0.001(7)	0.011(6)	0.017(6)
C17	0.046(6)	0.096(9)	0.064(7)	0.010(7)	-0.008(6)	0.038(6)
C18	0.090(8)	0.074(7)	0.074(8)	-0.049(6)	-0.001(8)	0.009(7)

The form of the anisotropic thermal parameter is:

$$\exp[-2\pi^2\{h^2a^2U(1,1) + k^2b^2U(2,2) + l^2c^2U(3,3) + 2hkabU(1,2) + 2hlacU(1,3) + 2klbcU(2,3)\}]$$

where a, b, and c are reciprocal lattice constants.

Table 29

Bond Distances (in Angstroms) for
[1-((Dimethylamino)methyl)-2-(t-butylthio)ferrocene]palladium
dichloride

Atom1	Atom2	Distance
Pd1	C11	2.314(3)
Pd1	C12	2.292(3)
Pd1	S1	2.312(2)
Pd1	N1	2.147(7)
Fe1	C5	2.084(9)
Fe1	C6	2.062(9)
Fe1	C7	2.053(9)
Fe1	C8	2.017(10)
Fe1	C9	2.017(9)
Fe1	C10	2.069(11)
Fe1	C11	2.041(13)
Fe1	C12	2.017(12)
Fe1	C13	2.042(12)
Fe1	C14	2.055(10)
S1	C9	1.756(8)
S1	C15	1.846(10)
N1	C1	1.496(14)
N1	C2	1.513(14)
N1	C3	1.503(11)
C3	C5	1.472(13)
C5	C6	1.418(13)
C5	C9	1.434(12)
C6	C7	1.436(13)

Table 29 Continued

Atom1	Atom2	Distance
-----	-----	-----
C7	C8	1.423(13)
C8	C9	1.397(13)
C10	C11	1.40(2)
C10	C14	1.41(2)
C11	C12	1.42(2)
C12	C13	1.38(2)
C13	C14	1.37(2)
C15	C16	1.51(2)
C15	C17	1.52(2)
C15	C18	1.48(2)

Numbers in parentheses are estimated standard deviations
in the least significant digits.

Table 30

Bond Angles (in Degrees) for
[1-[(Dimethylamino)methyl]-2-(t-butylthio)ferrocene]palladium
dichloride

Atom1 -----	Atom2 -----	Atom3 -----	Angle -----
C11	Pd1	C12	88.1(1)
C11	Pd1	S1	170.29(9)
C11	Pd1	N1	88.8(2)
C12	Pd1	S1	82.93(9)
C12	Pd1	N1	176.8(2)
S1	Pd1	N1	100.2(2)
Pd1	S1	C9	104.7(3)
Pd1	S1	C15	114.3(3)
C9	S1	C15	107.0(4)
Pd1	N1	C1	111.9(6)
Pd1	N1	C2	106.6(6)
Pd1	N1	C3	116.3(5)
C1	N1	C2	108.8(7)
C1	N1	C3	106.4(8)
C2	N1	C3	106.6(7)
N1	C3	C5	116.9(7)
C3	C5	C6	126.6(8)
C3	C5	C9	126.4(8)
C6	C5	C9	105.3(8)
C5	C6	C7	109.9(8)
C6	C7	C8	106.4(8)
C7	C8	C9	108.3(8)
S1	C9	C5	124.3(7)

Table 30 Continued

Atom1 -----	Atom2 -----	Atom3 -----	Angle -----
S1	C9	C8	124.8(7)
C5	C9	C8	110.1(8)
C11	C10	C14	108.(1)
C10	C11	C12	107.(1)
C11	C12	C13	109.(1)
C12	C13	C14	109.(1)
C10	C14	C13	108.(1)
S1	C15	C16	113.5(7)
S1	C15	C17	106.0(7)
S1	C15	C18	108.4(8)
C16	C15	C17	107.9(9)
C16	C15	C18	110.(1)
C17	C15	C18	111.(1)

Numbers in parentheses are estimated standard deviations
in the least significant digits.

Table 30 Continued

Atom1 -----	Atom2 -----	Atom3 -----	Angle -----
S1	C9	C8	124.8(7)
C5	C9	C8	110.1(8)
C11	C10	C14	108.(1)
C10	C11	C12	107.(1)
C11	C12	C13	109.(1)
C12	C13	C14	109.(1)
C10	C14	C13	108.(1)
S1	C15	C16	113.5(7)
S1	C15	C17	106.0(7)
S1	C15	C18	108.4(8)
C16	C15	C17	107.9(9)
C16	C15	C18	110.(1)
C17	C15	C18	111.(1)

Numbers in parentheses are estimated standard deviations
in the least significant digits.

APPENDIX

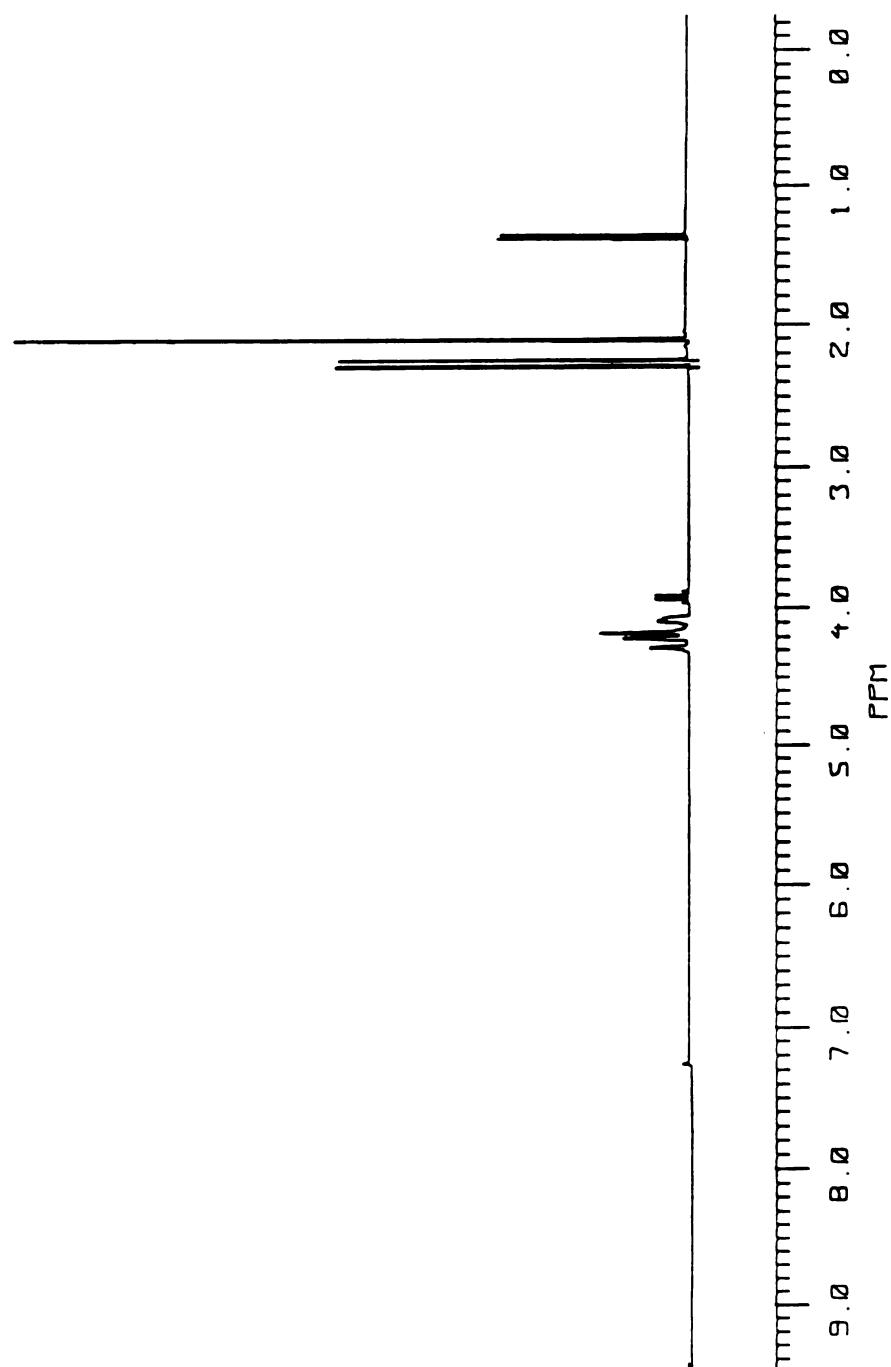


Figure 31. ^1H NMR spectrum of compound 43 (R = Me)

Figure 32. Gated decoupled ^{13}C NMR of compound 43 ($R = \text{Me}$)

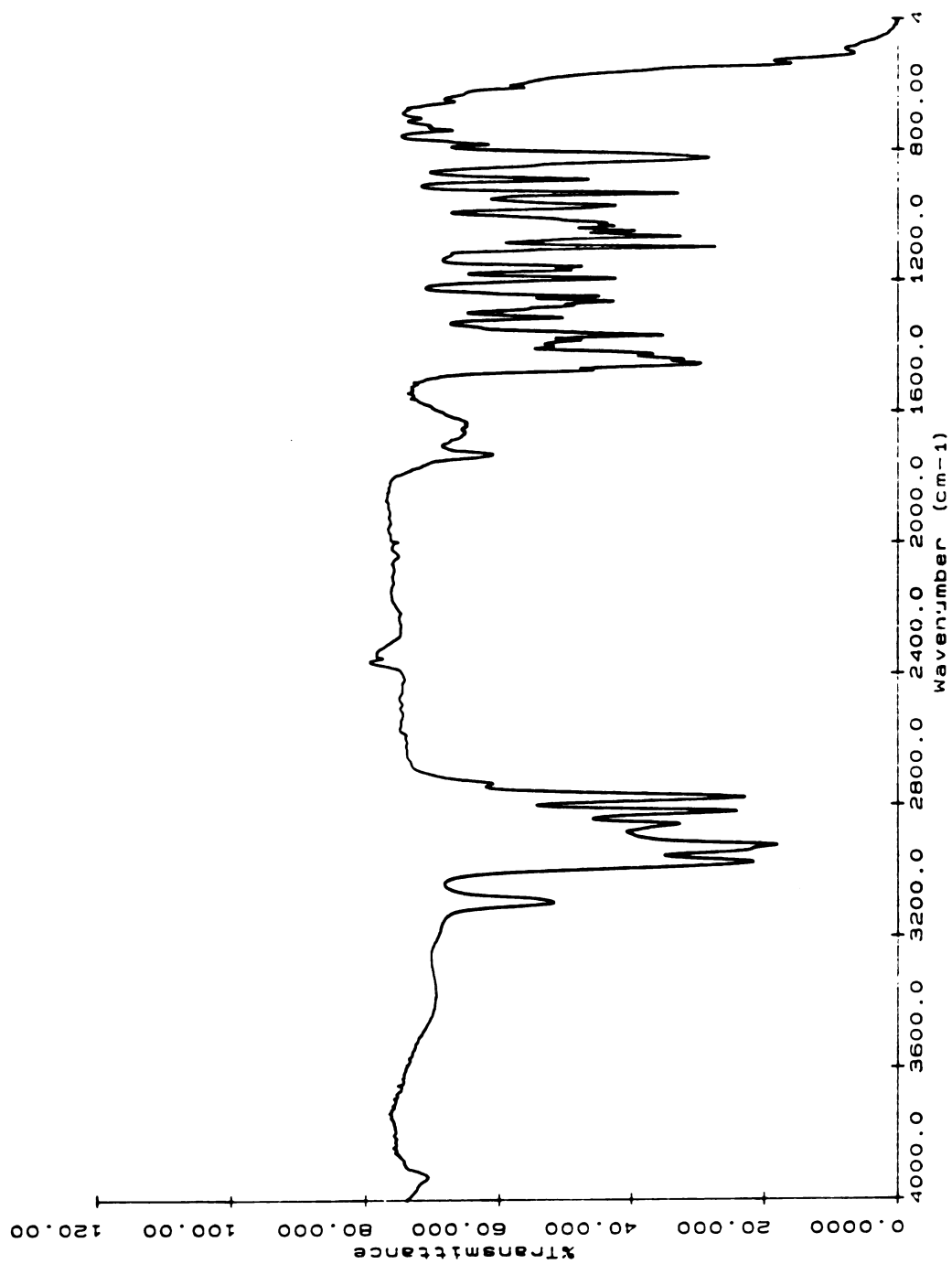


Figure 33. IR spectrum of compound 43 (R = Me)

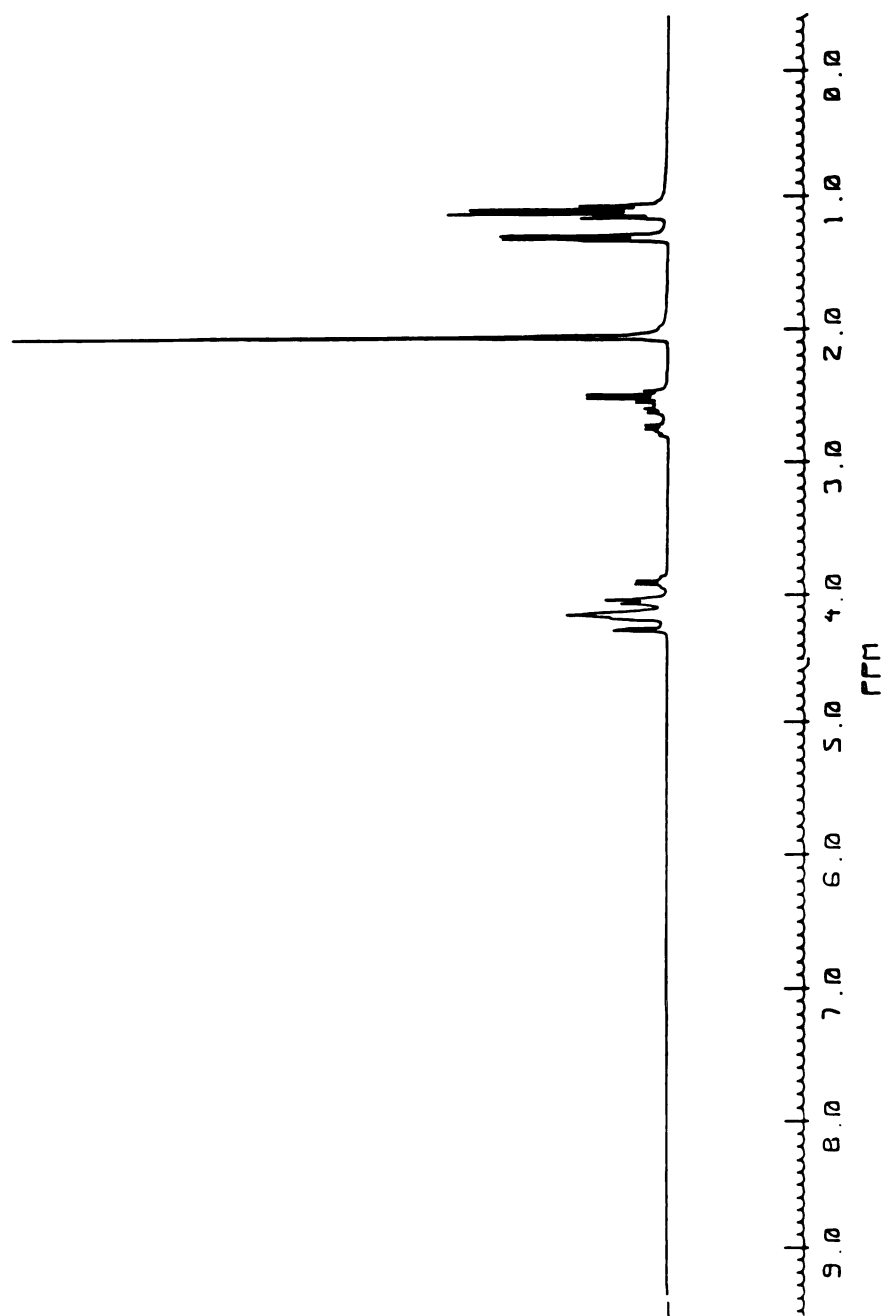


Figure 34. ^1H NMR spectrum of compound 44 (R = Et)

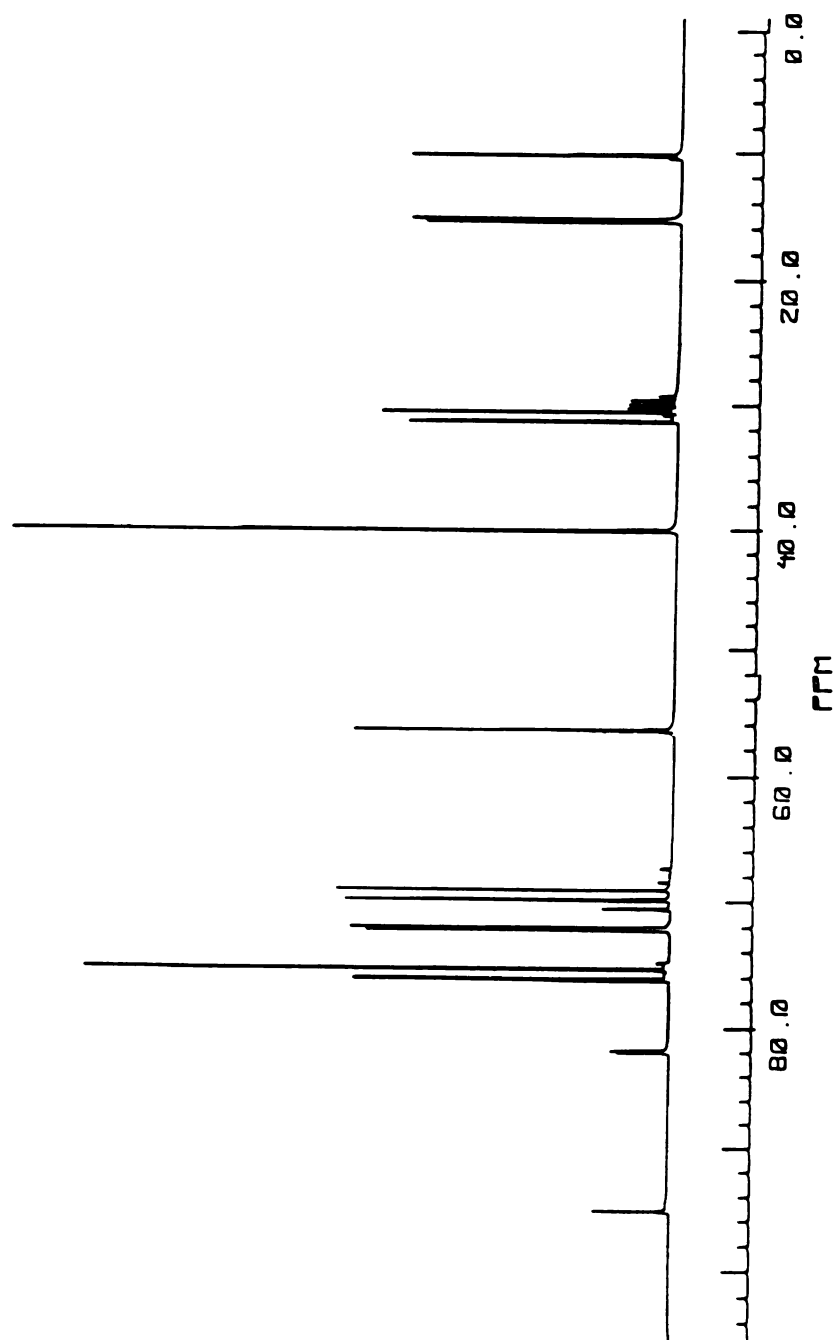


Figure 35. Gated decoupled ^{13}C NMR of compound 44 (R = Et)

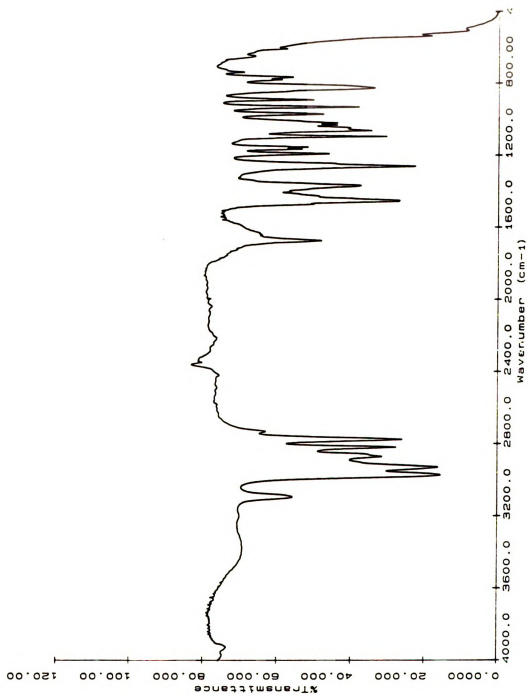


Figure 36. IR spectrum of compound 44 (R = Et)

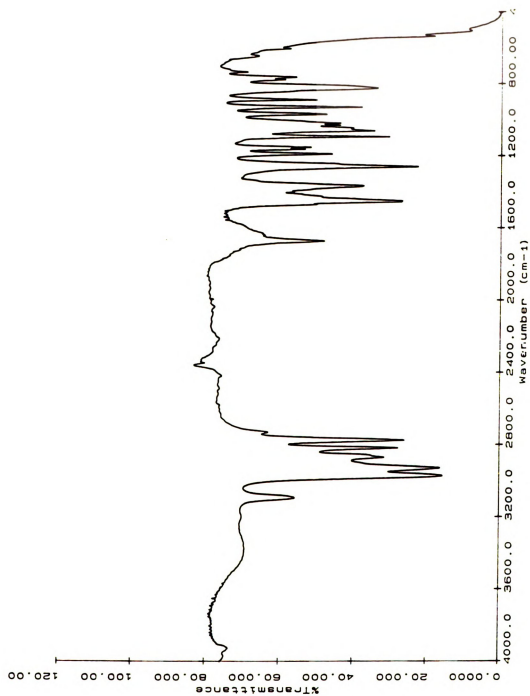


Figure 36. IR spectrum of compound 44 (R = Et)

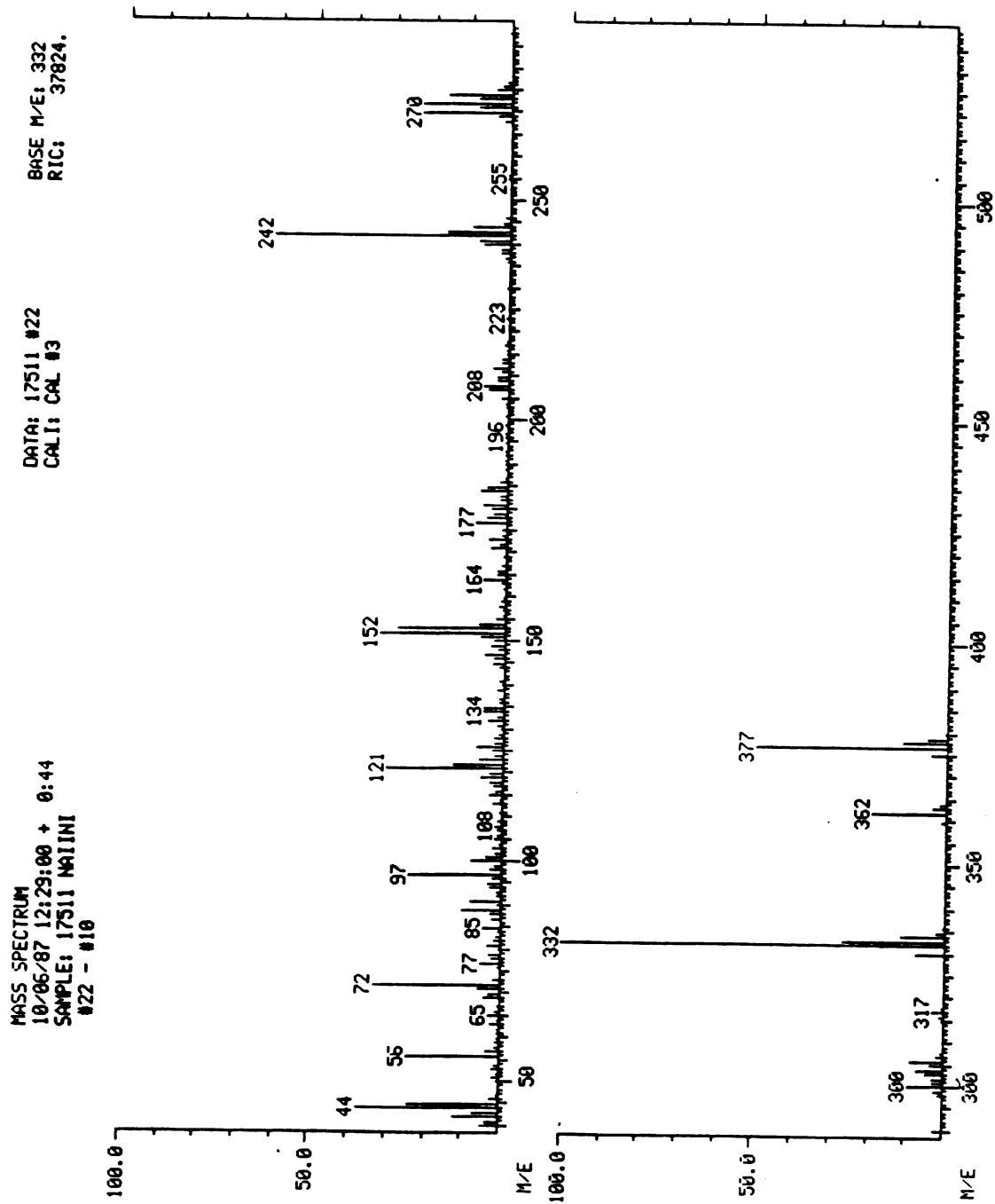


Figure 37. Mass spectrum of compound 44 (R = Et)

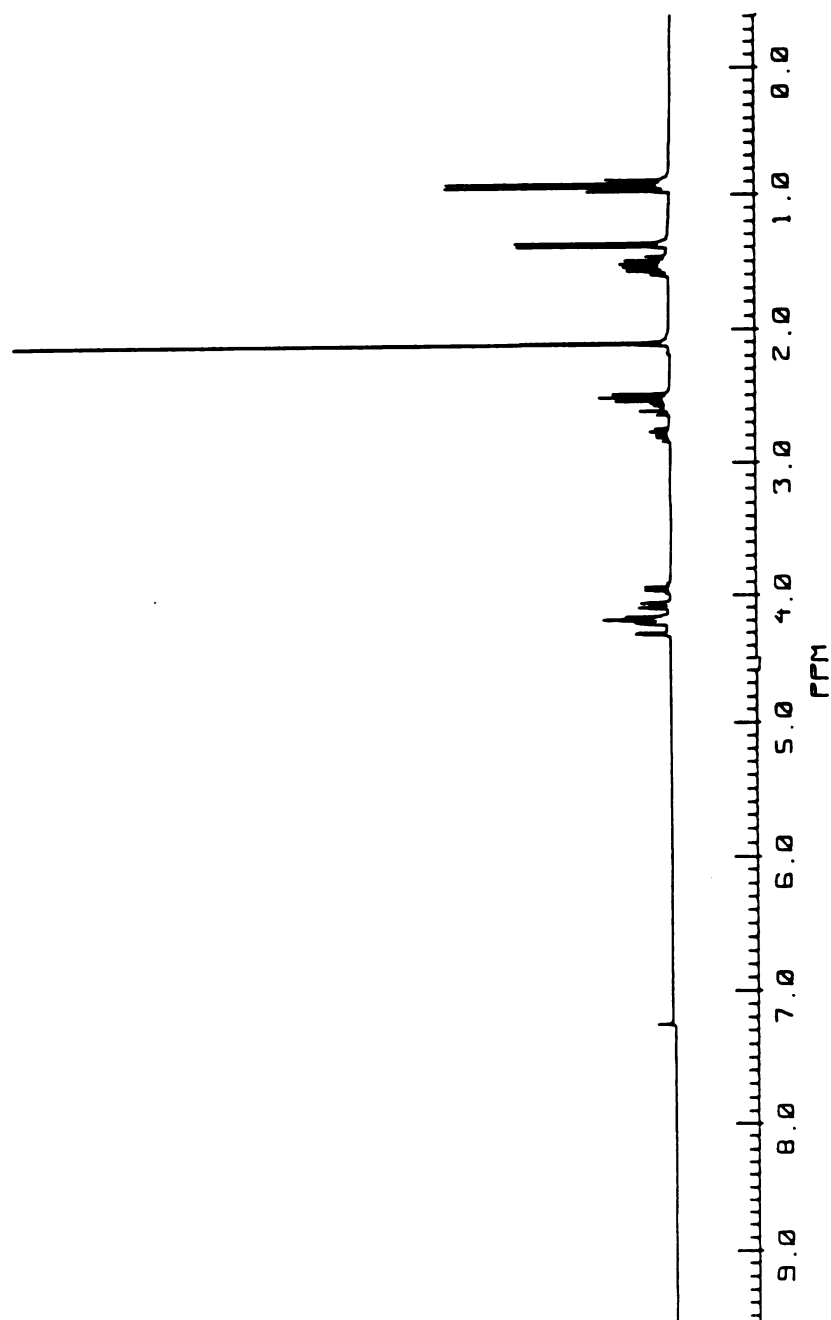


Figure 38. ^1H NMR spectrum of compound 45 (R = n-Pr)

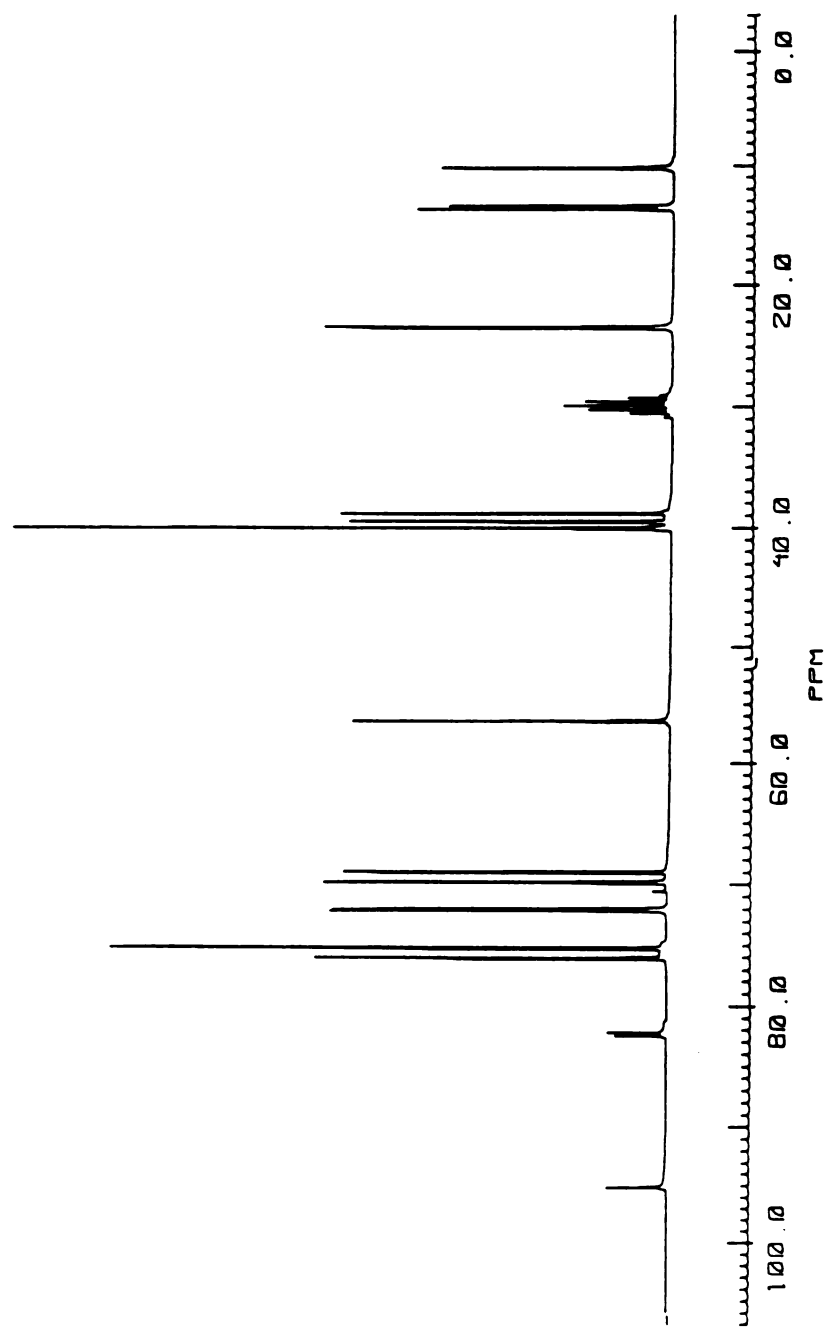


Figure 39. Gated decoupled ^{13}C NMR of compound 45 ($\text{R} = \text{n-Pr}$)

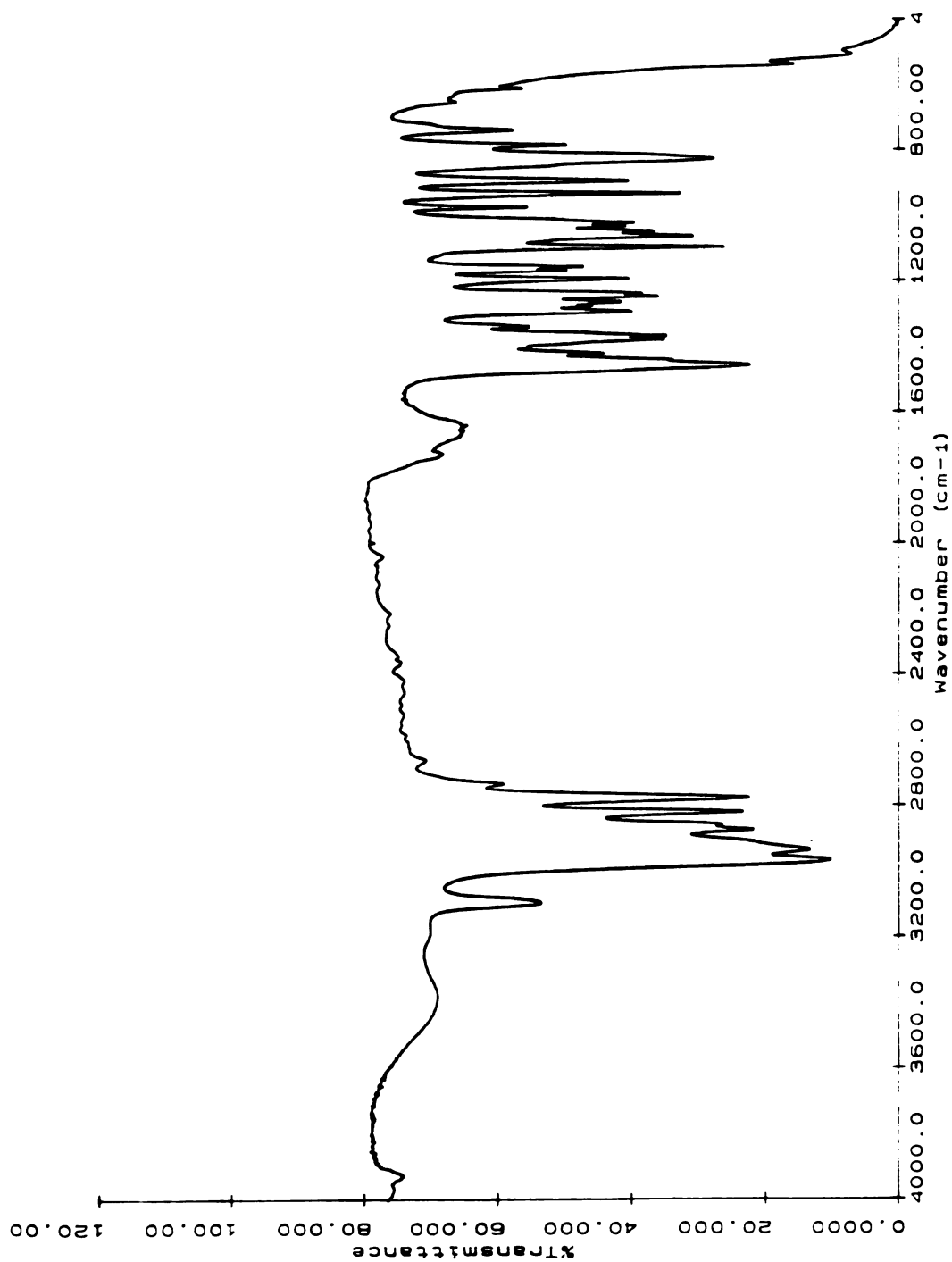


Figure 40. IR spectrum of compound **45** (R = n-Pr)

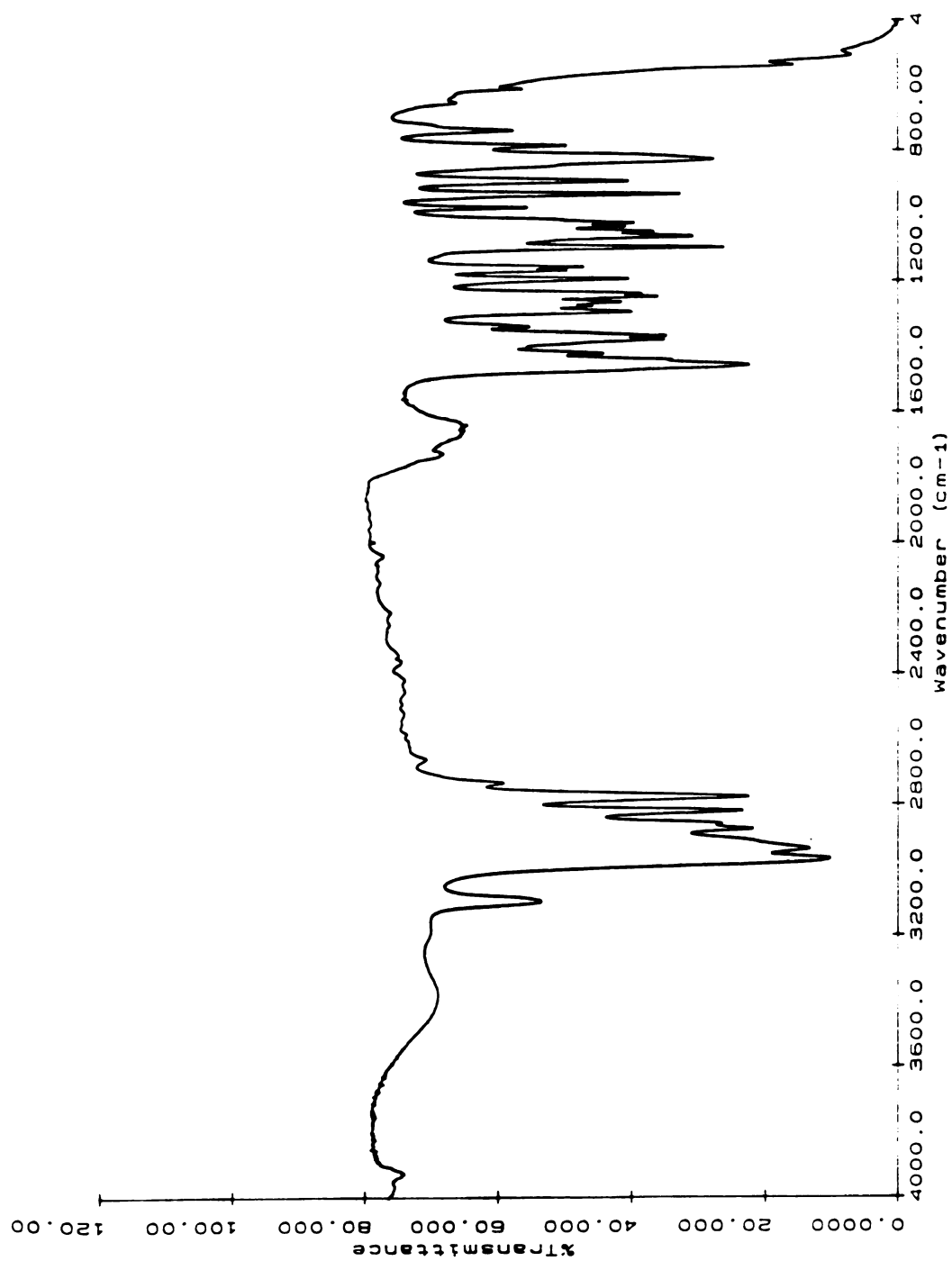


Figure 40. IR spectrum of compound 45 (R = n-Pr)

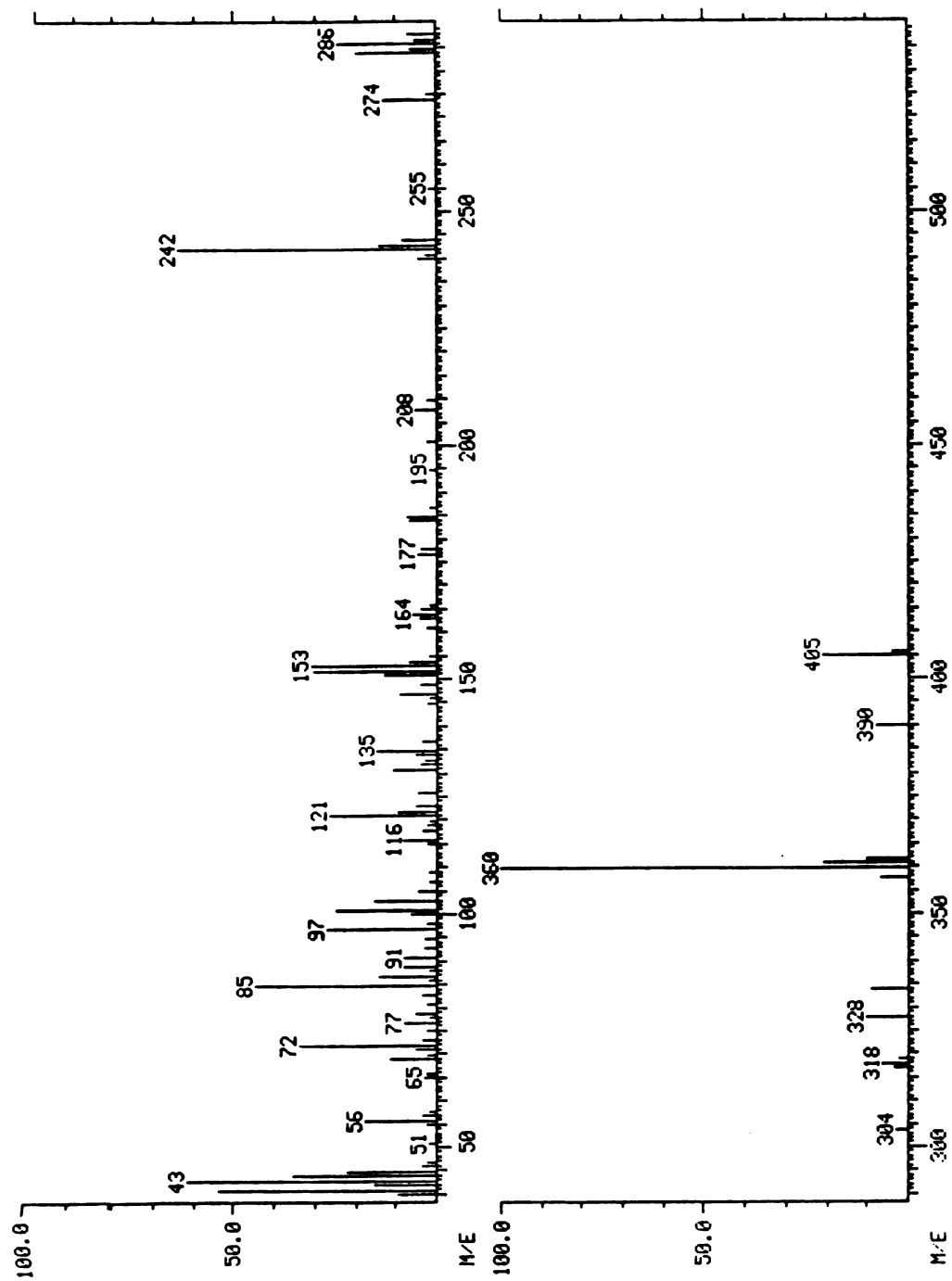


Figure 41. Mass spectrum of compound 45 (R = D-Pr)

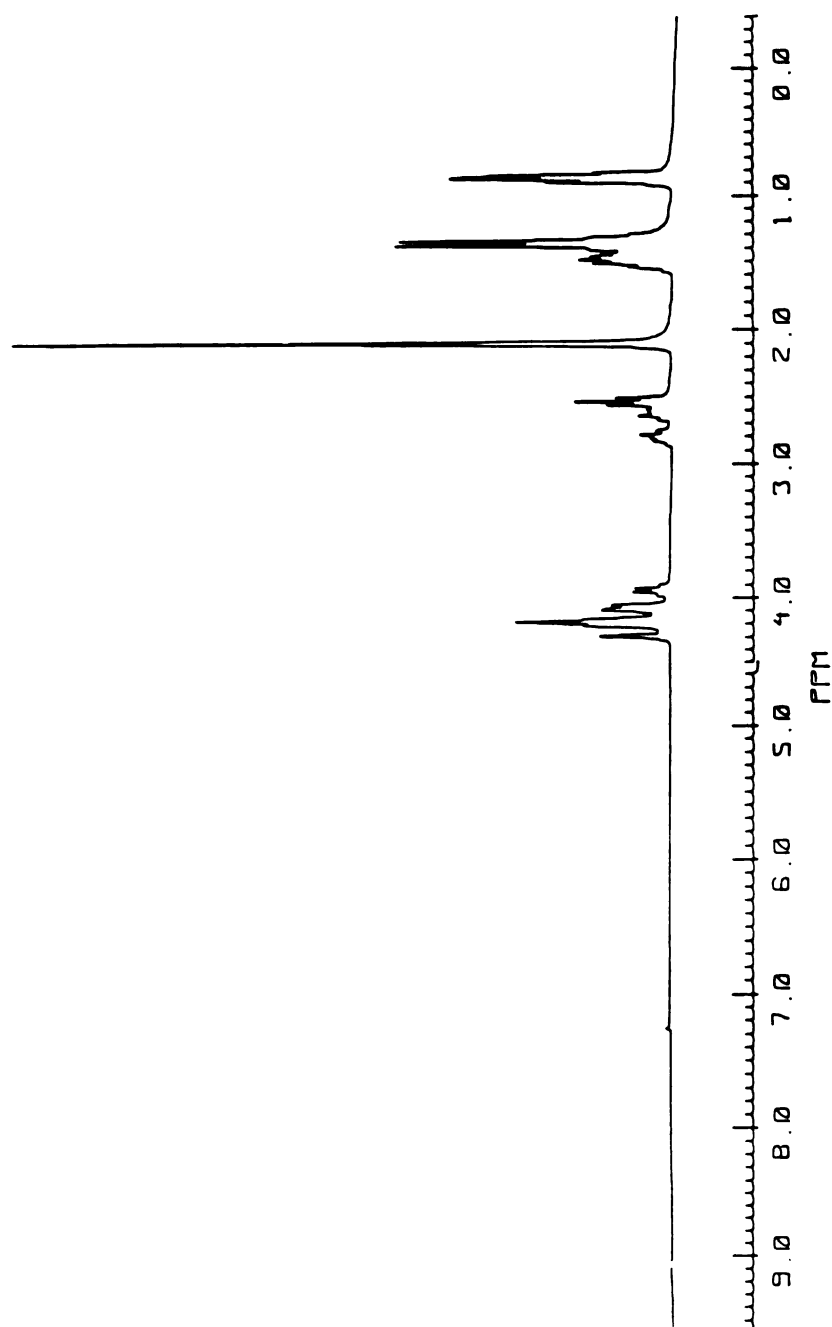


Figure 42. ^1H NMR spectrum of compound 47 (R = n-Bu)

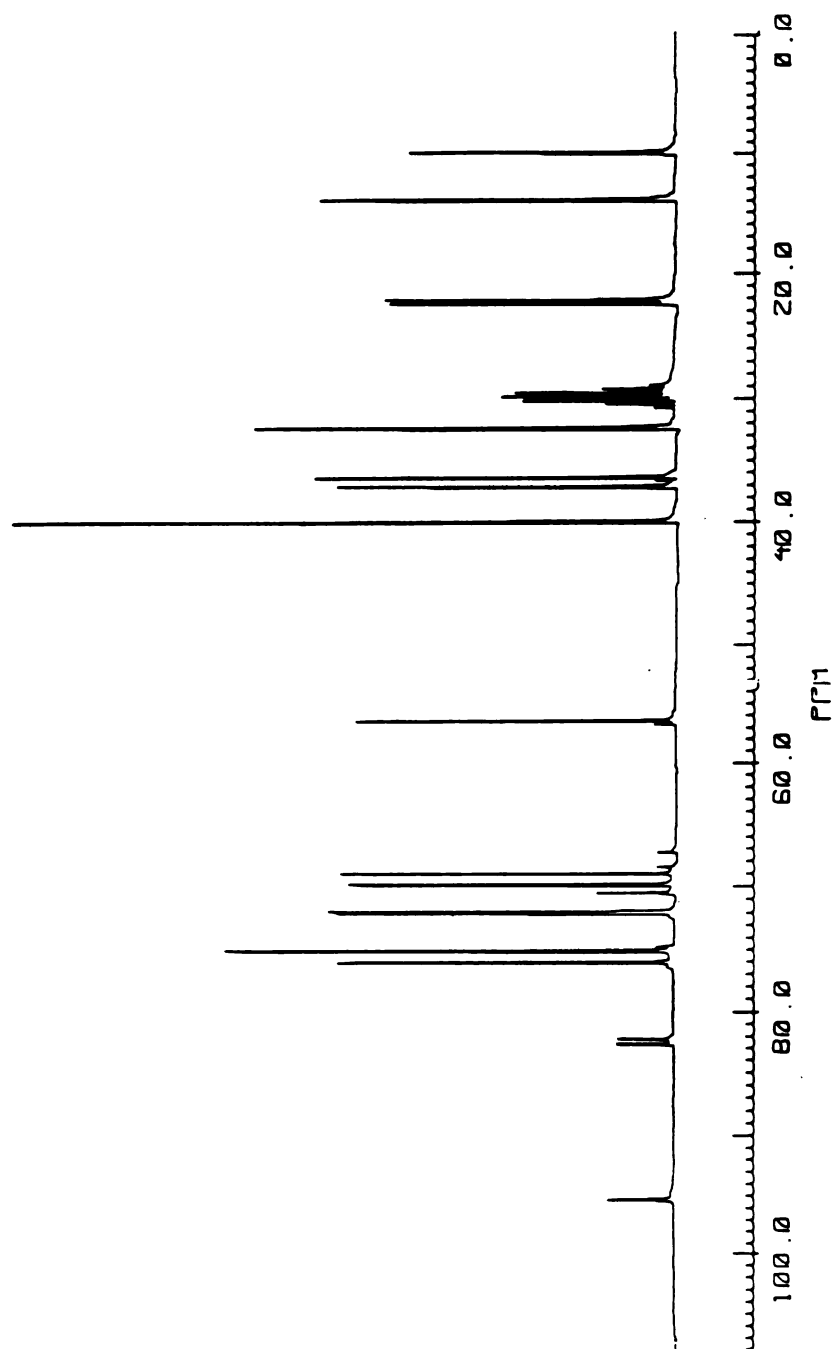


Figure 43. Gated decoupled ^{13}C NMR of compound 47 (R = n-Bu)

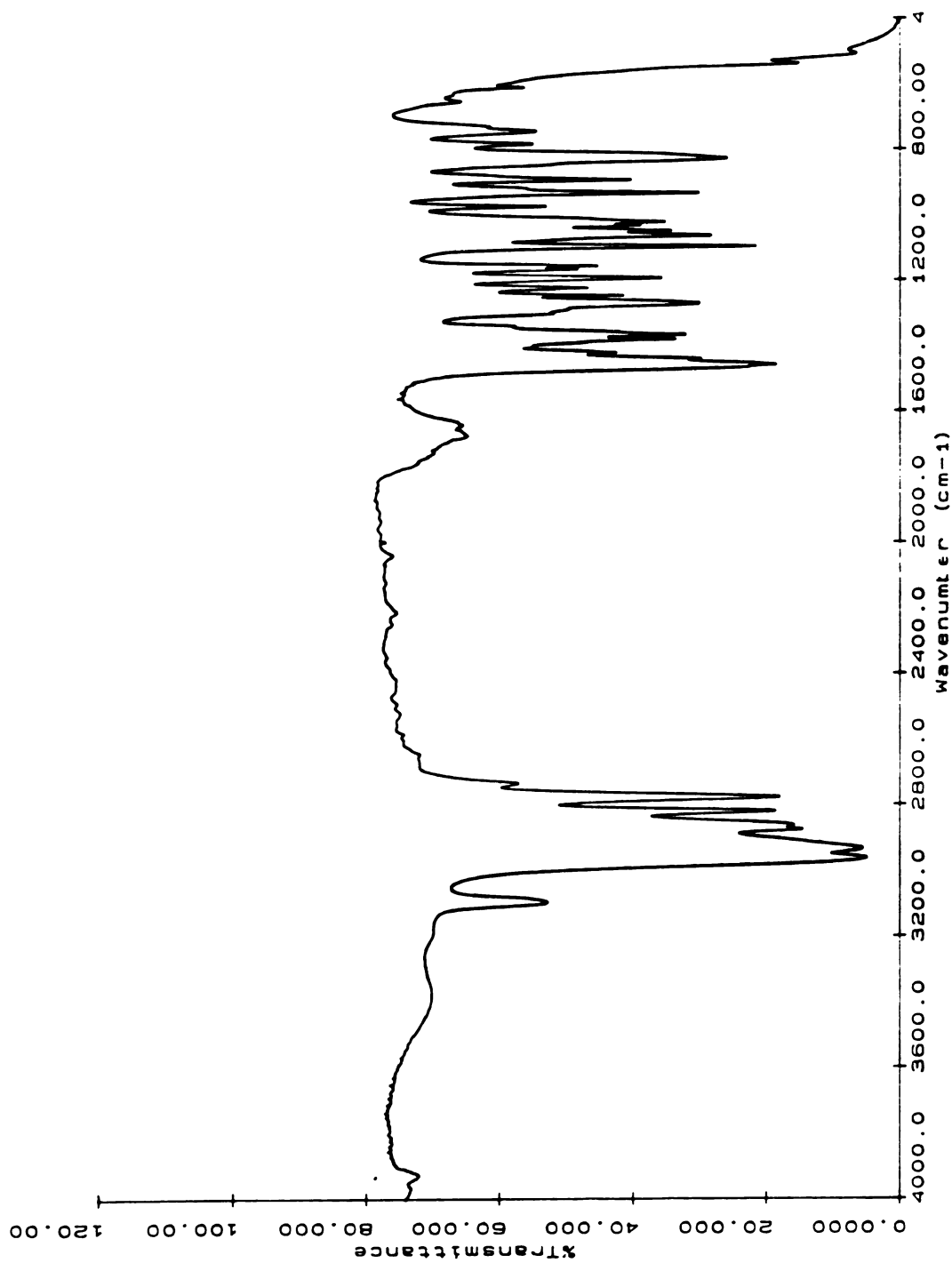


Figure 44. IR spectrum of compound 47 (R = n-Bu)

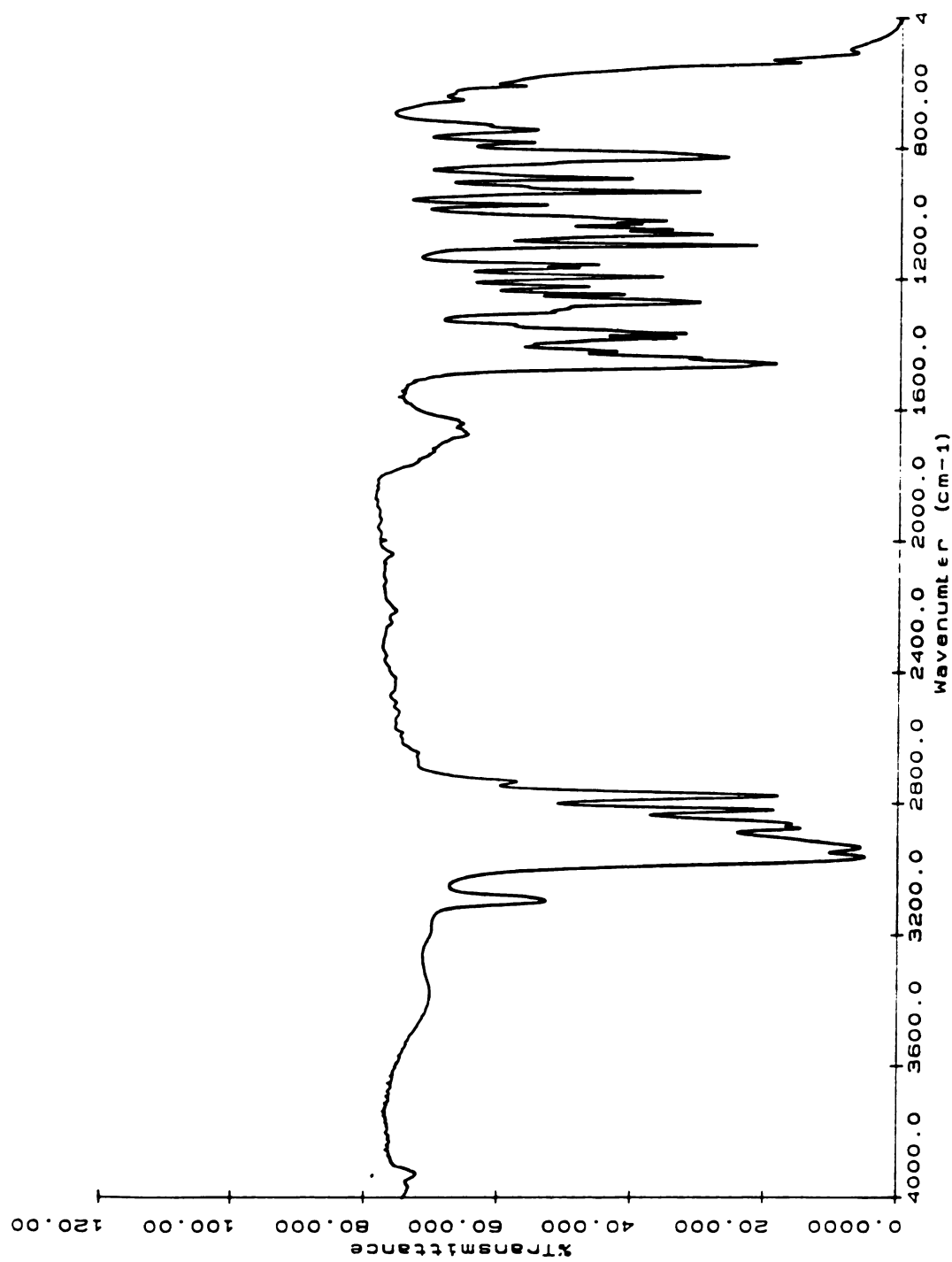


Figure 44. IR spectrum of compound 47 (R = n-Bu)

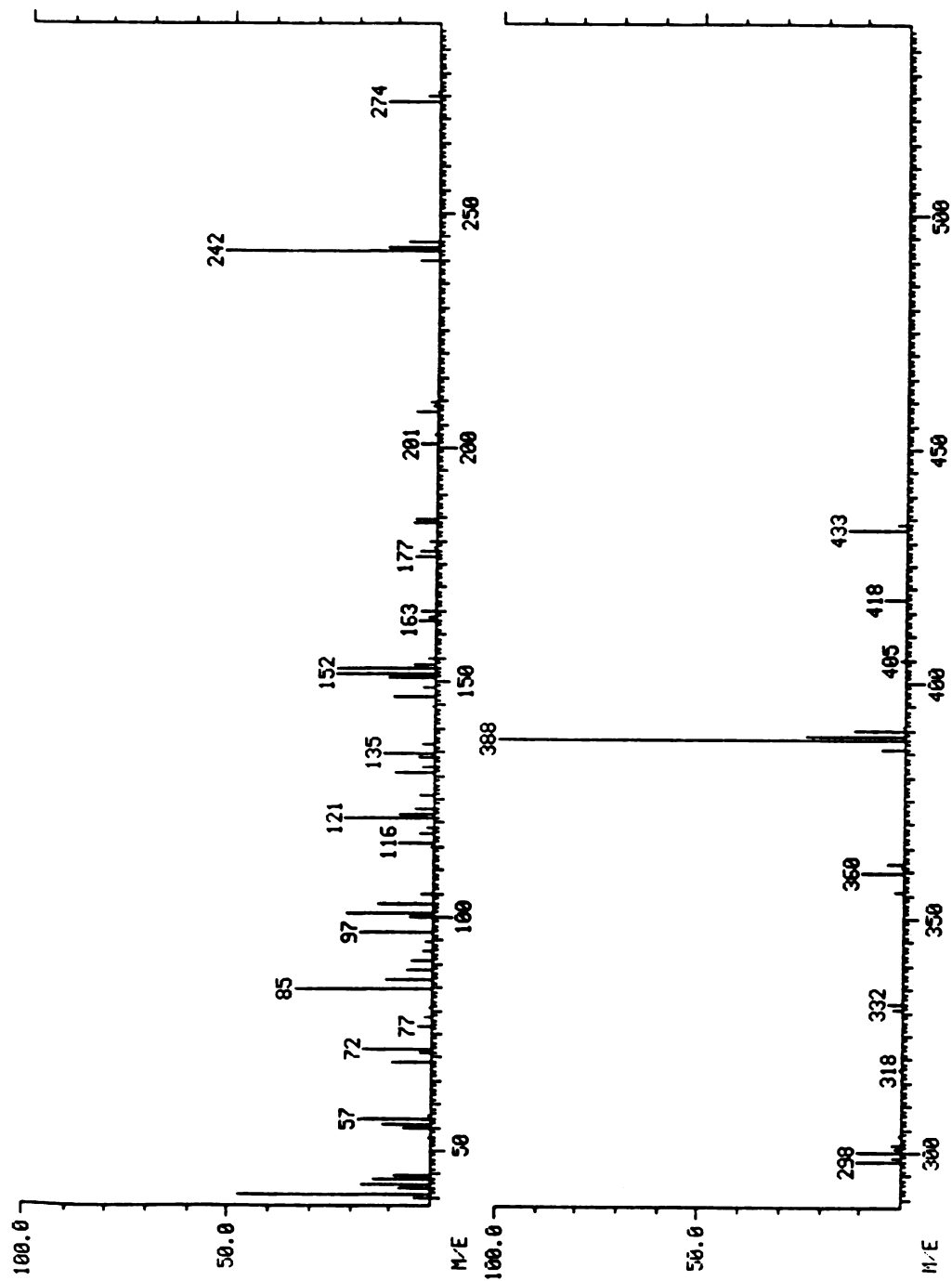


Figure 45. Mass spectrum of compound 47 (R = n-Bu)

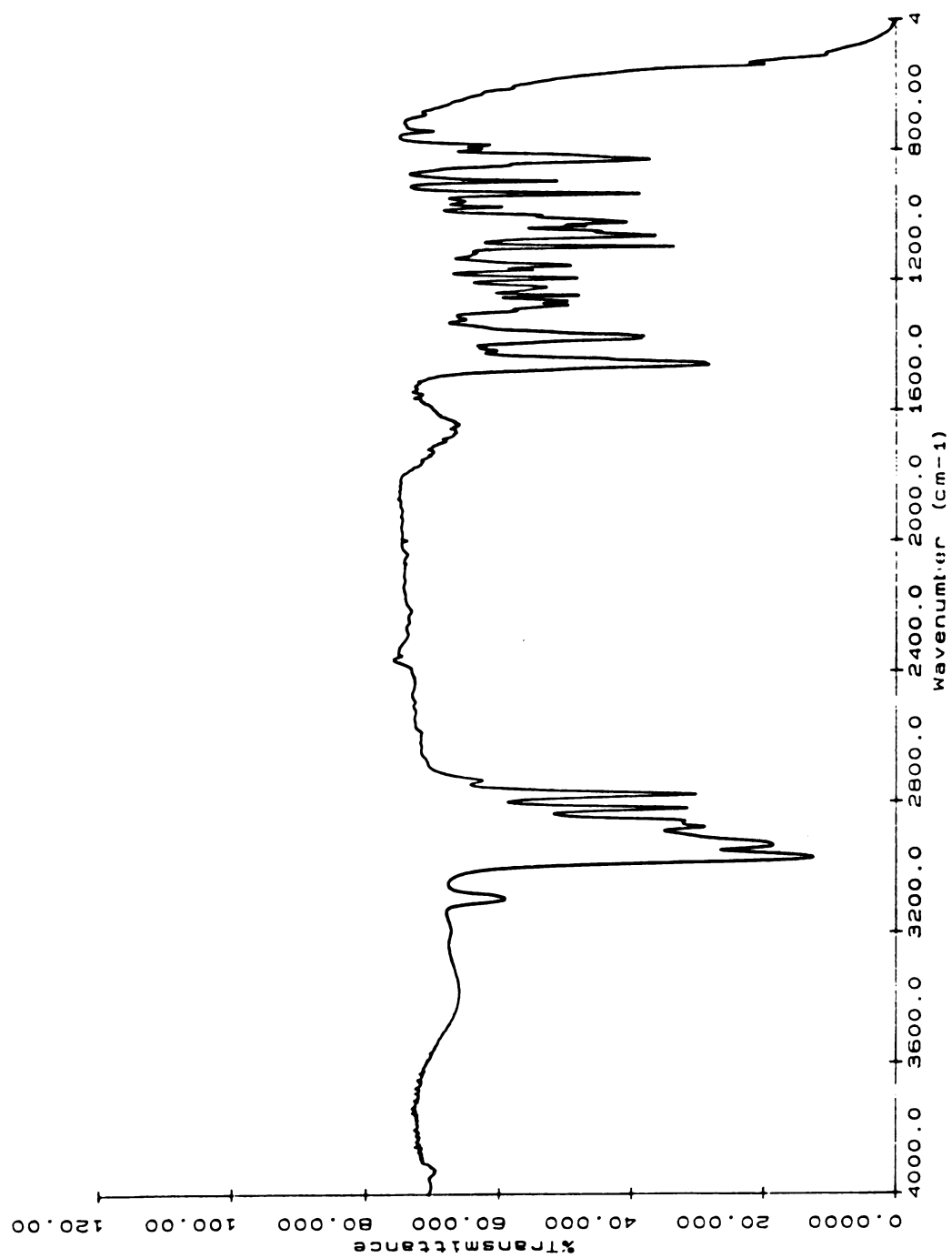


Figure 46. IR spectrum of compound 48 (R = sec-Bu)

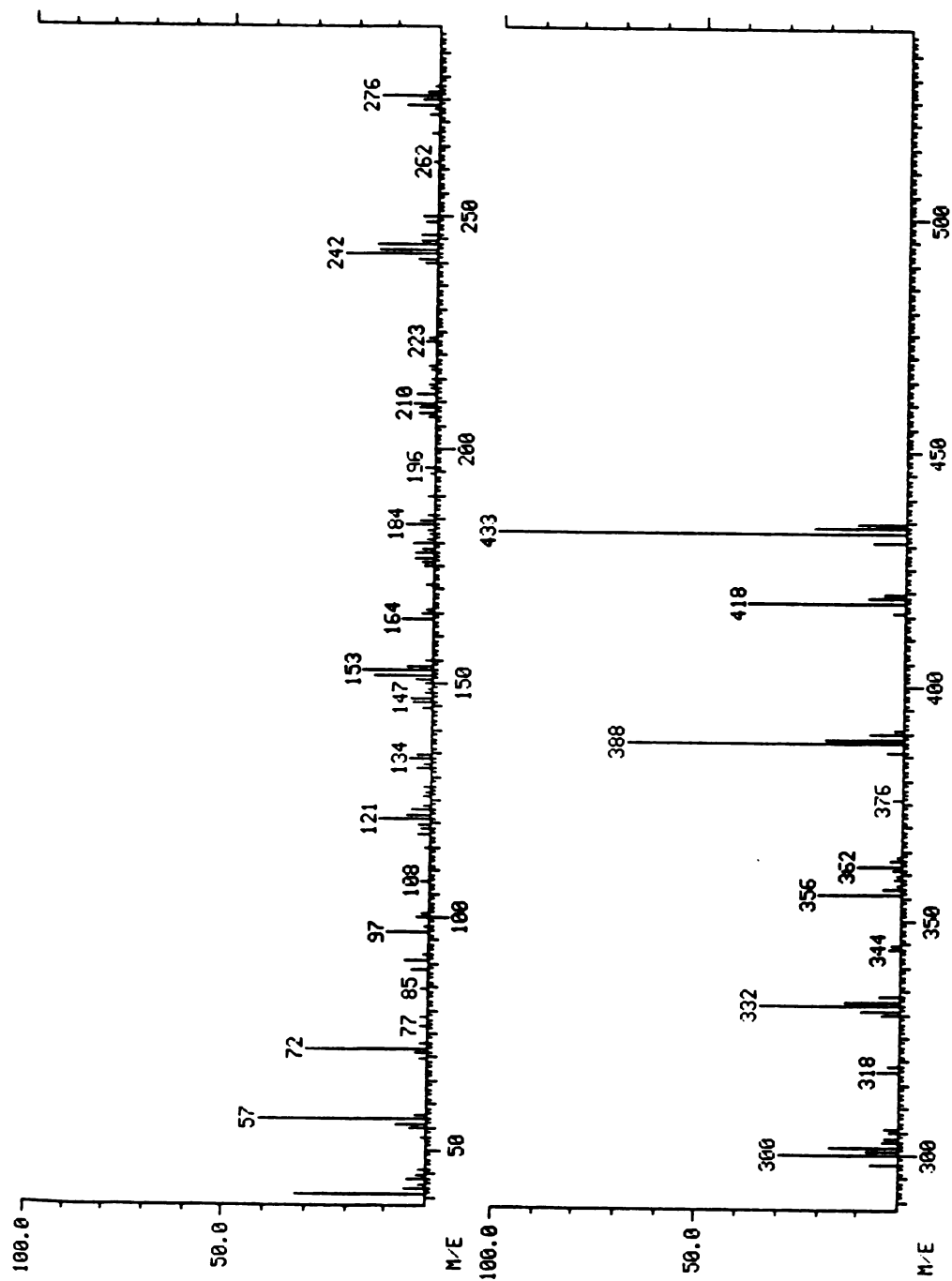


Figure 47. Mass spectrum of compound 48 (R = sec-Bu)

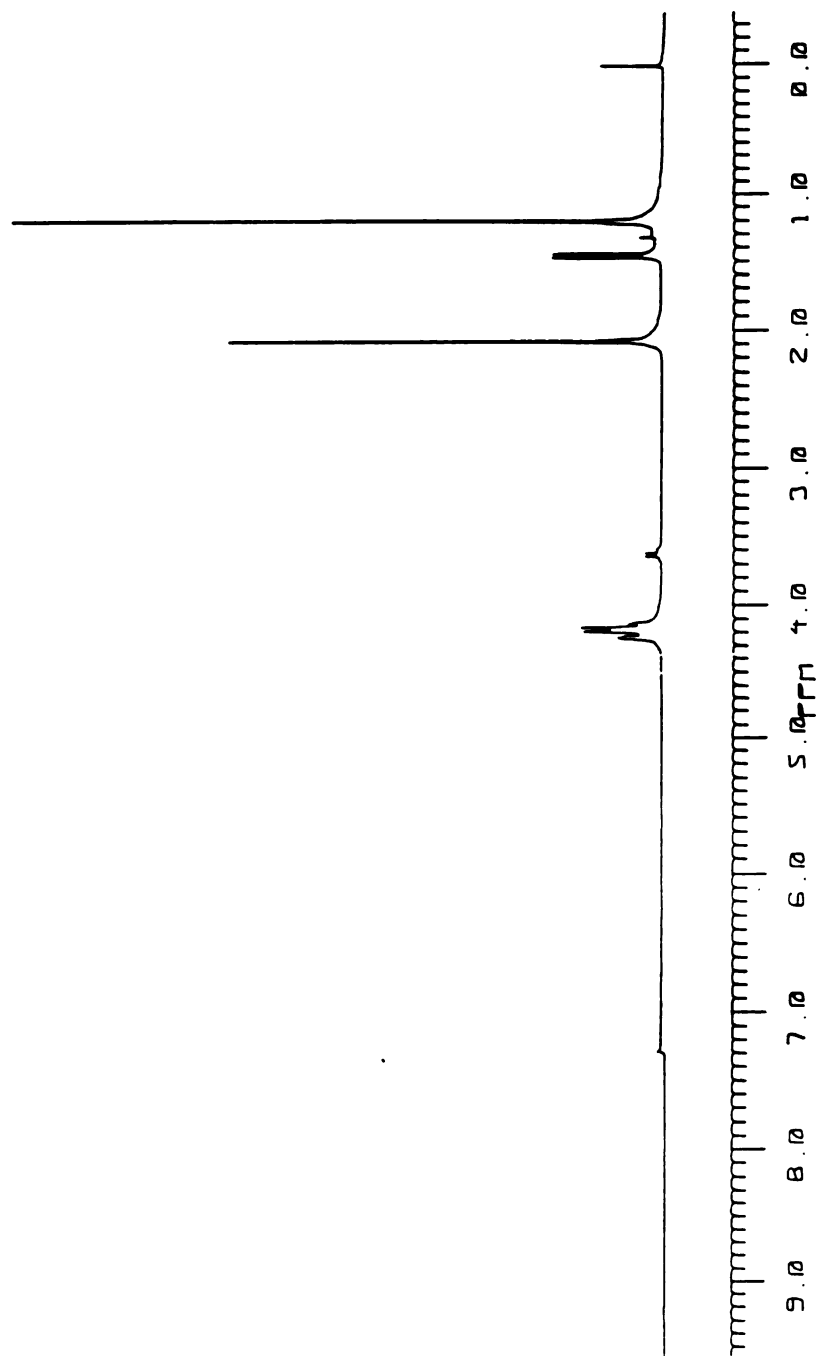


Figure 48. ^1H NMR spectrum of compound 49 (R = *t*-Bu)

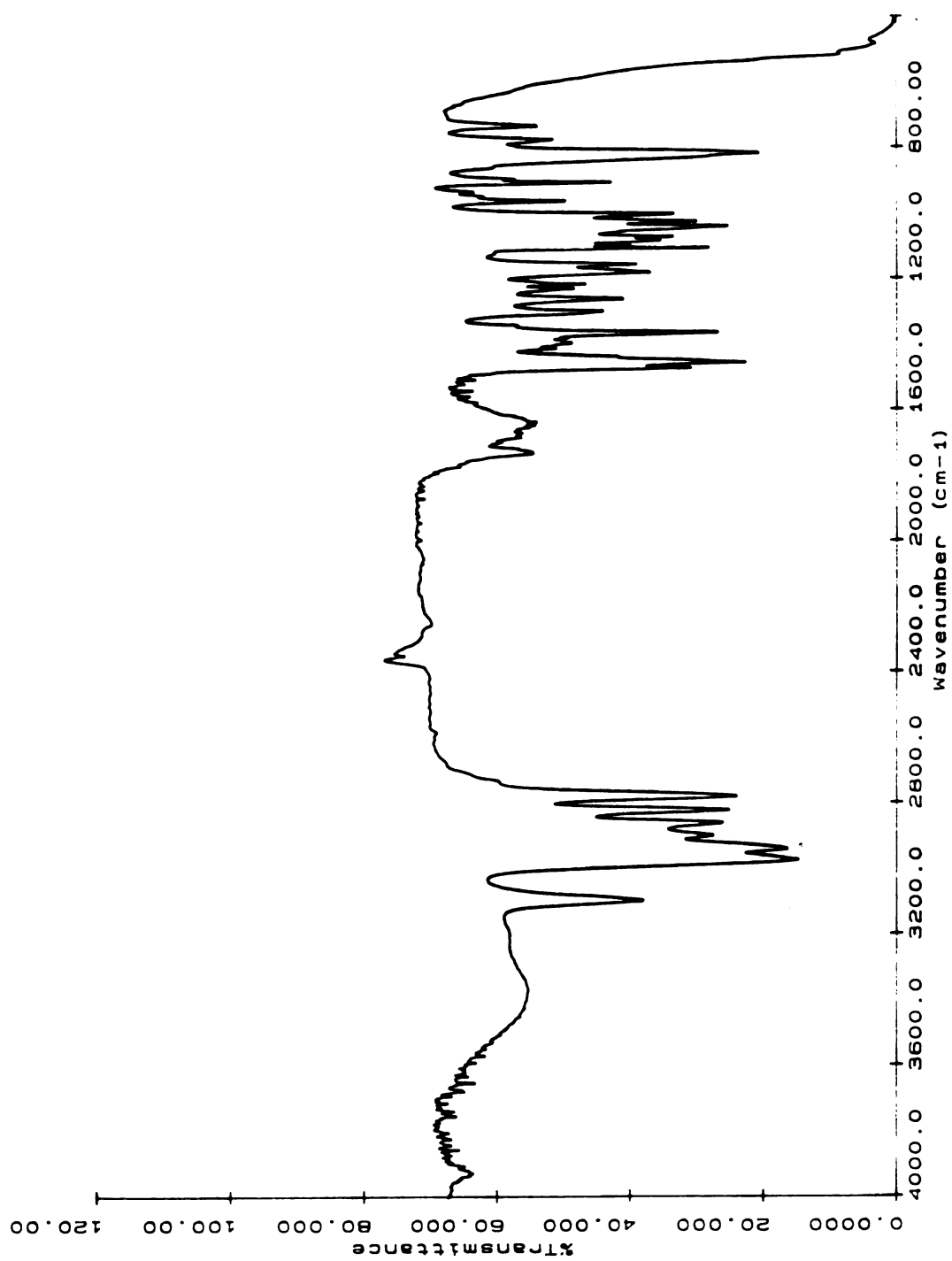


Figure 49. IR spectrum of compound 49 (R = t-Bu)

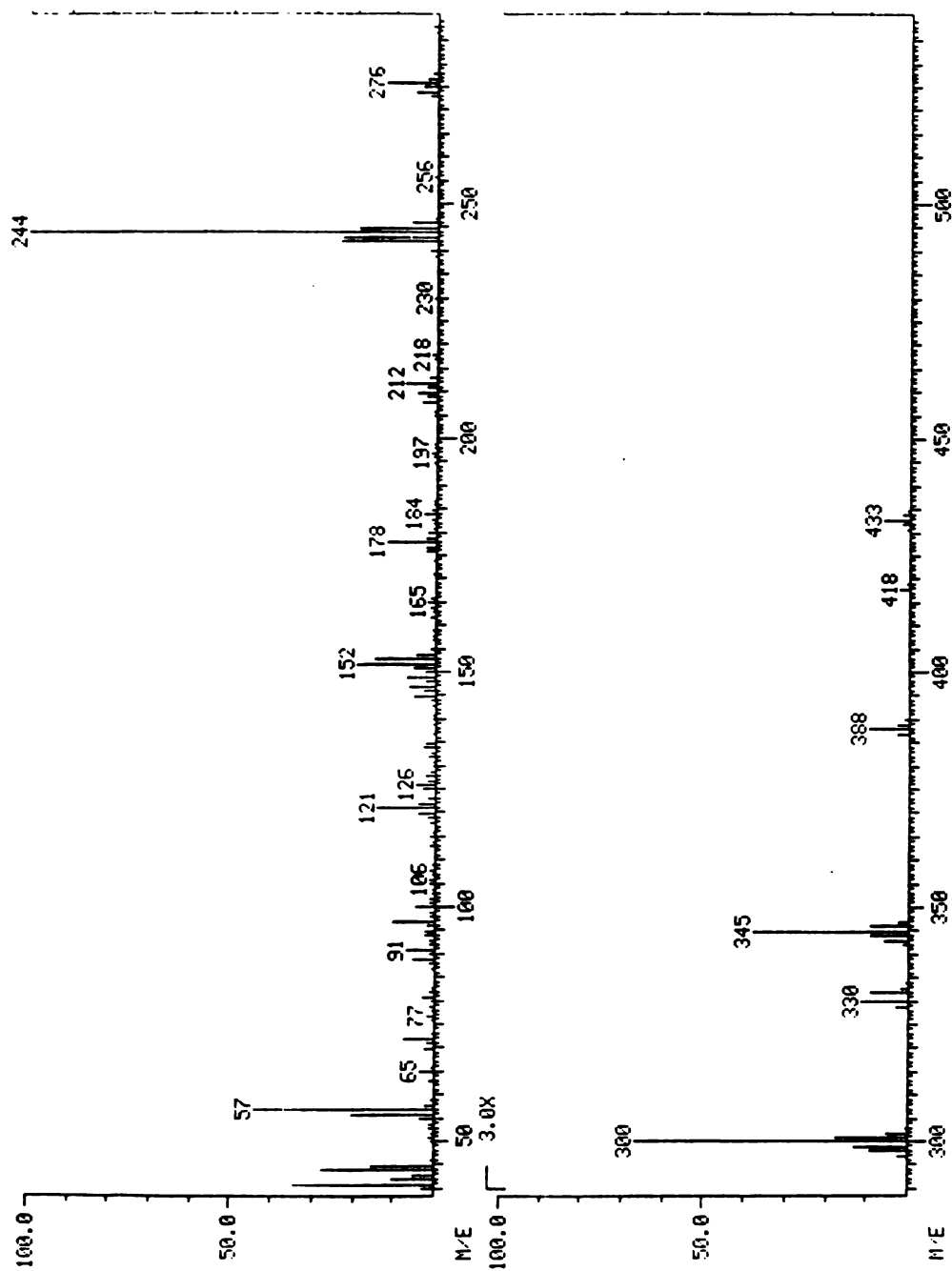


Figure 50. Mass spectrum of compound 49 (R = t-Bu)

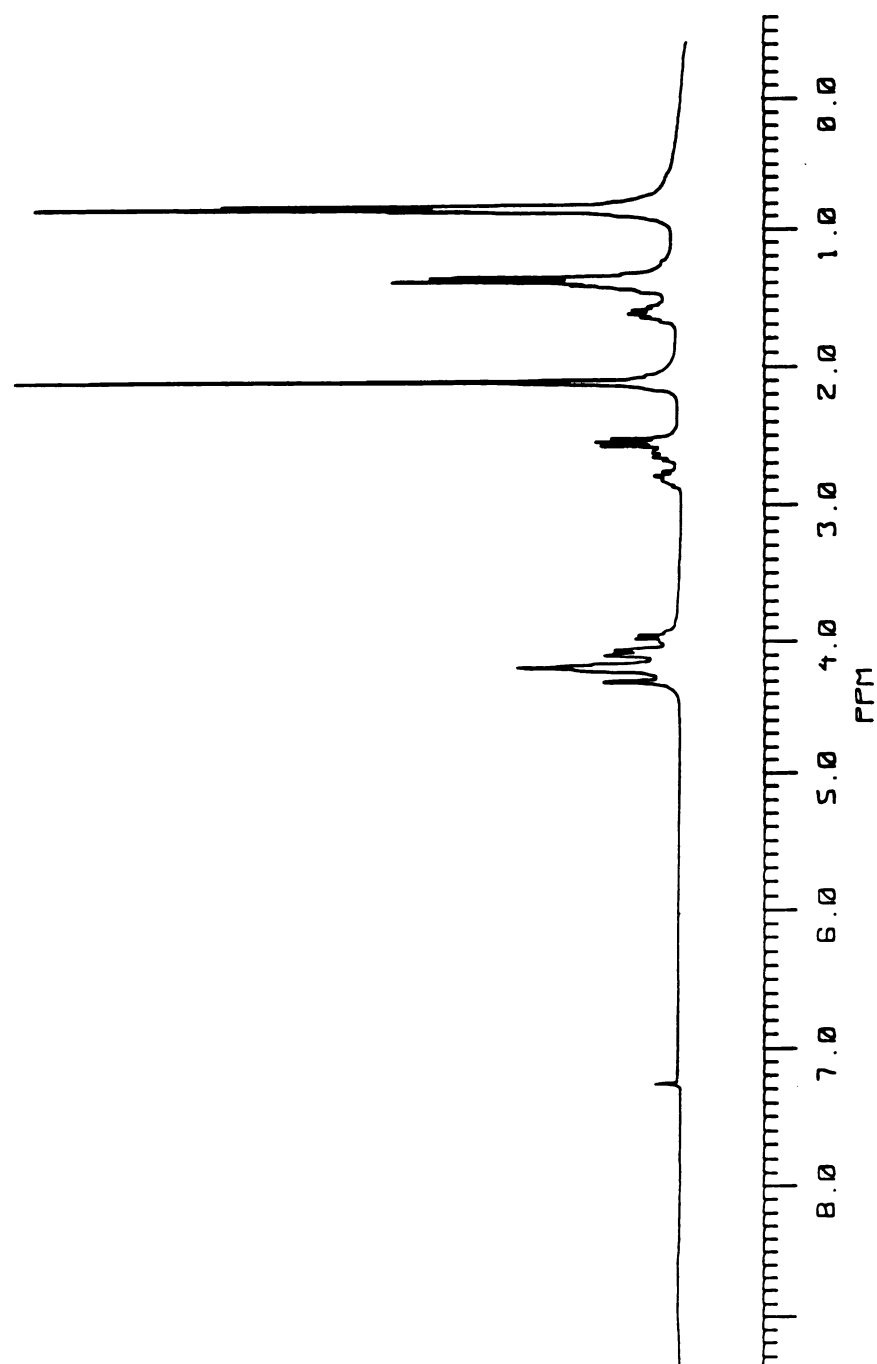


Figure 51. ^1H NMR spectrum of compound 50 (R = i-pentyl)

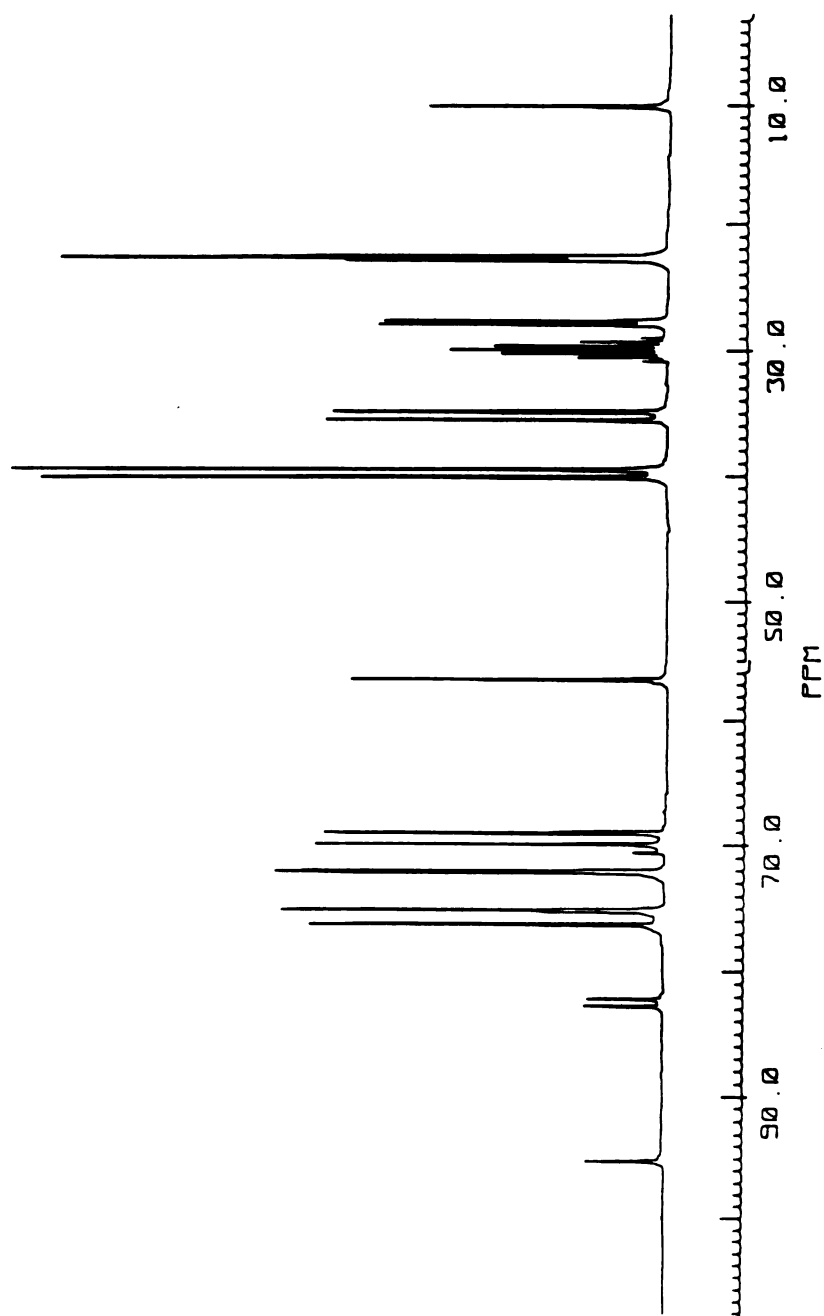


Figure 52. Gated decoupled ^{13}C NMR of compound 50 ($\text{R} = i\text{-pentyl}$)

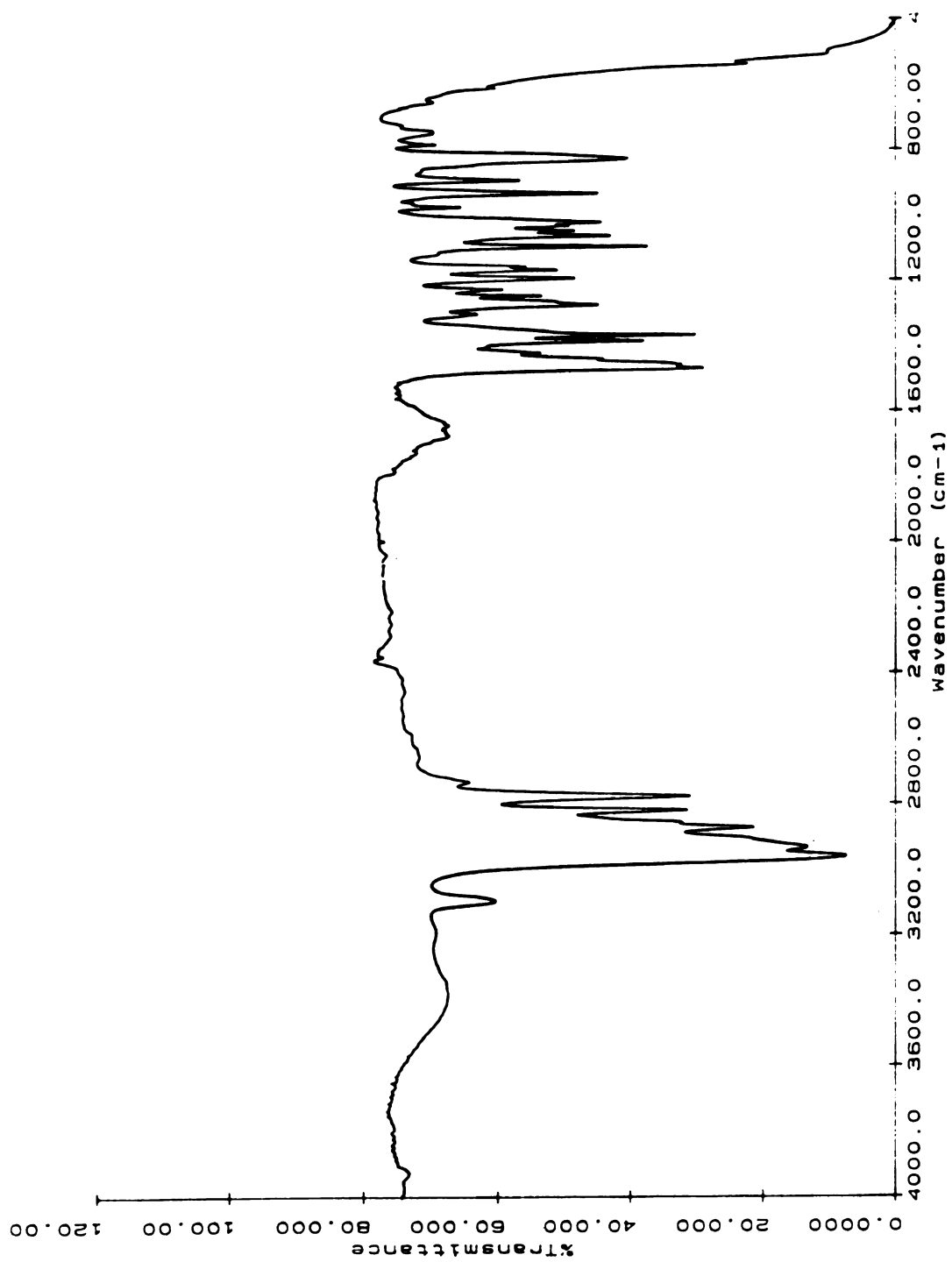


Figure 53. IR spectrum of compound 50 (R = i-pentyl)

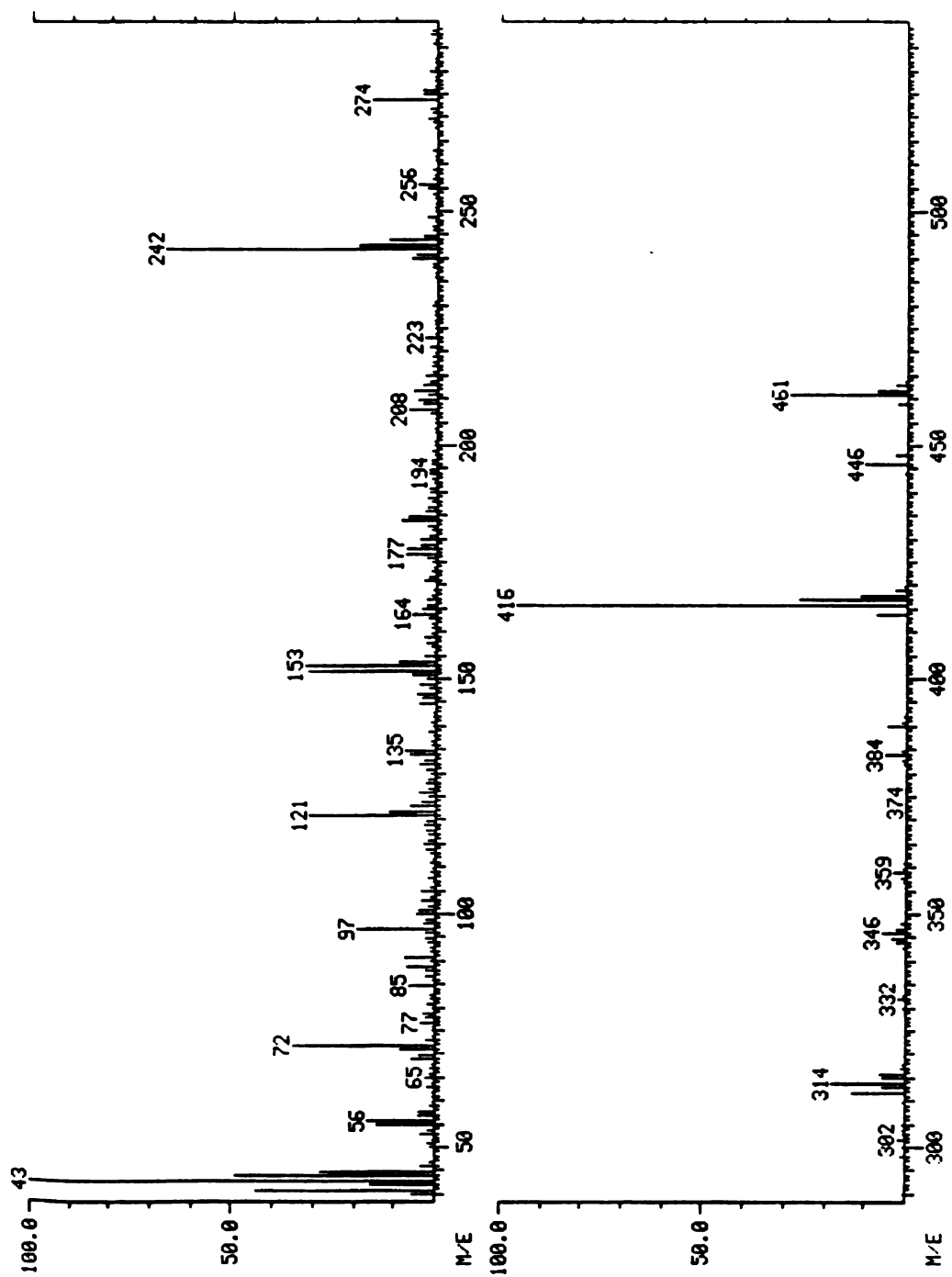


Figure 54. Mass spectrum of compound 50 (R = i-pentyl)

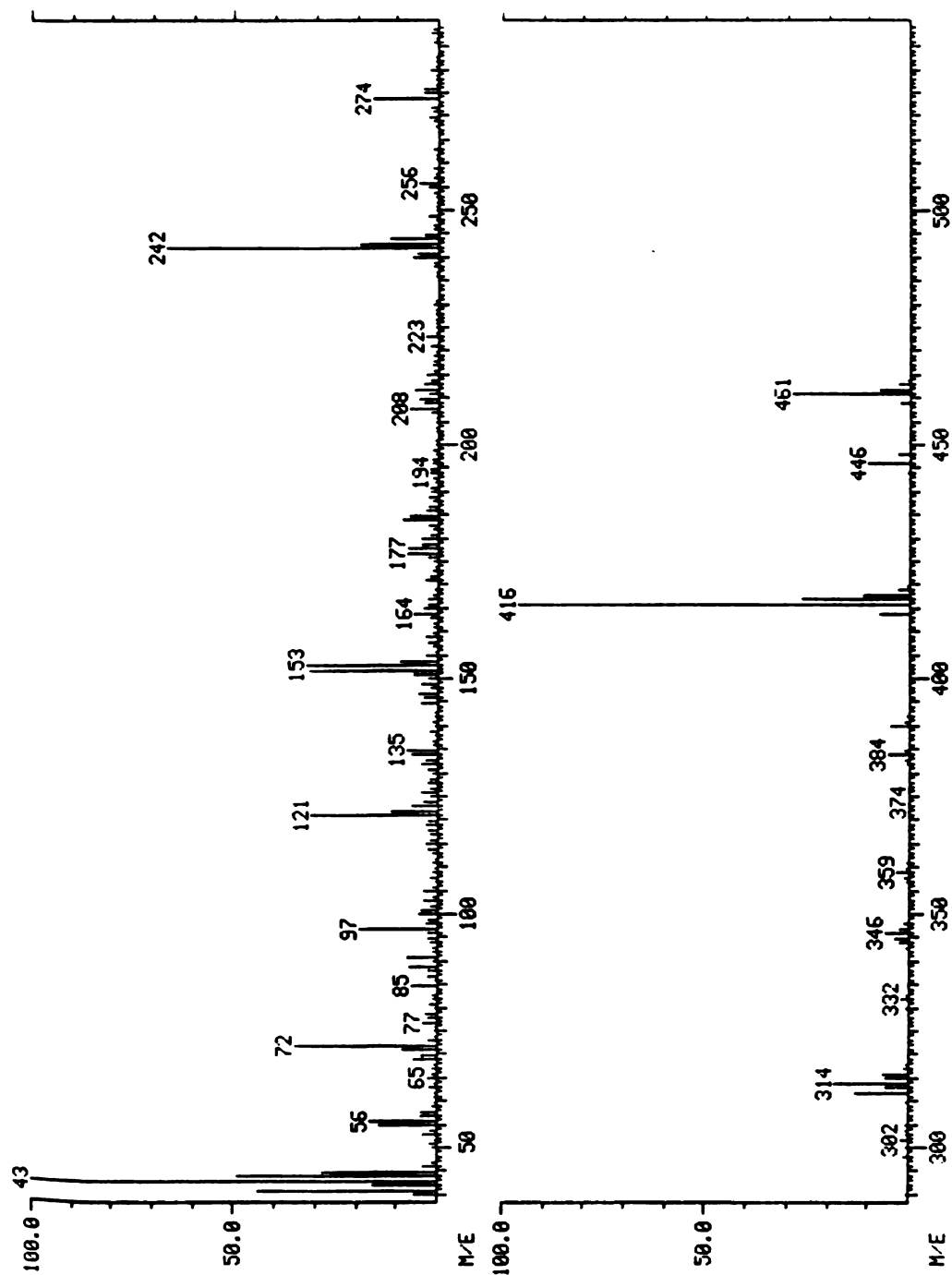


Figure 54. Mass spectrum of compound 50 (R = i-pentyl)

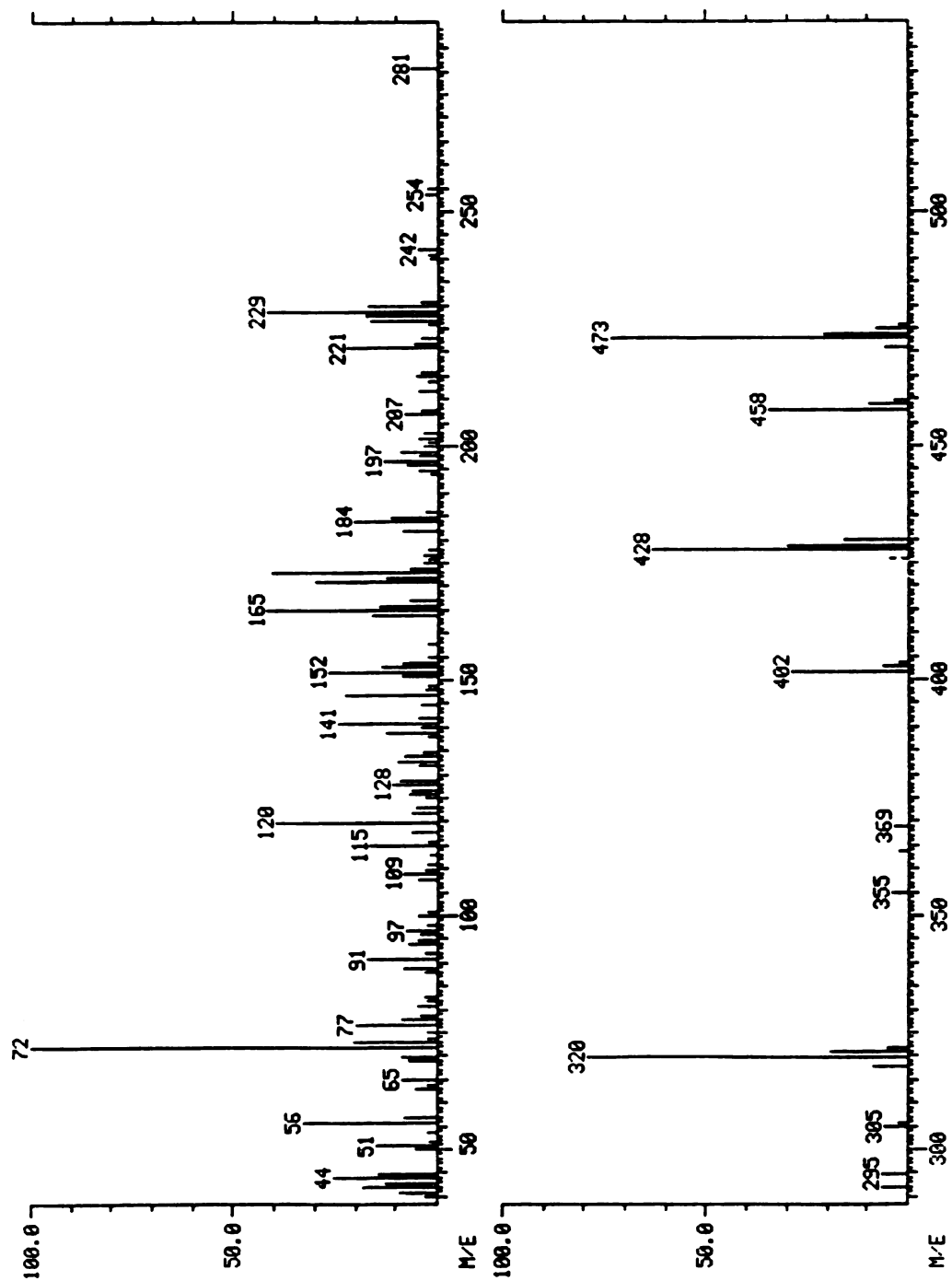


Figure 55. Mass spectrum of compound 51 (R = Ph)

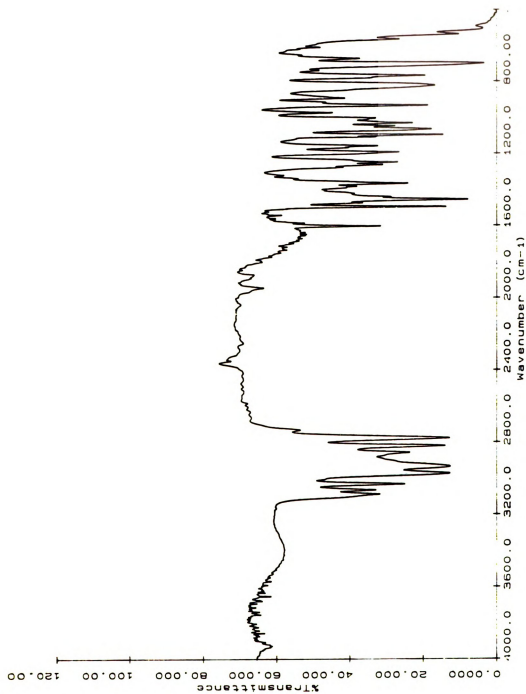


Figure 56. IR spectrum of compound **52** (R = Bz)

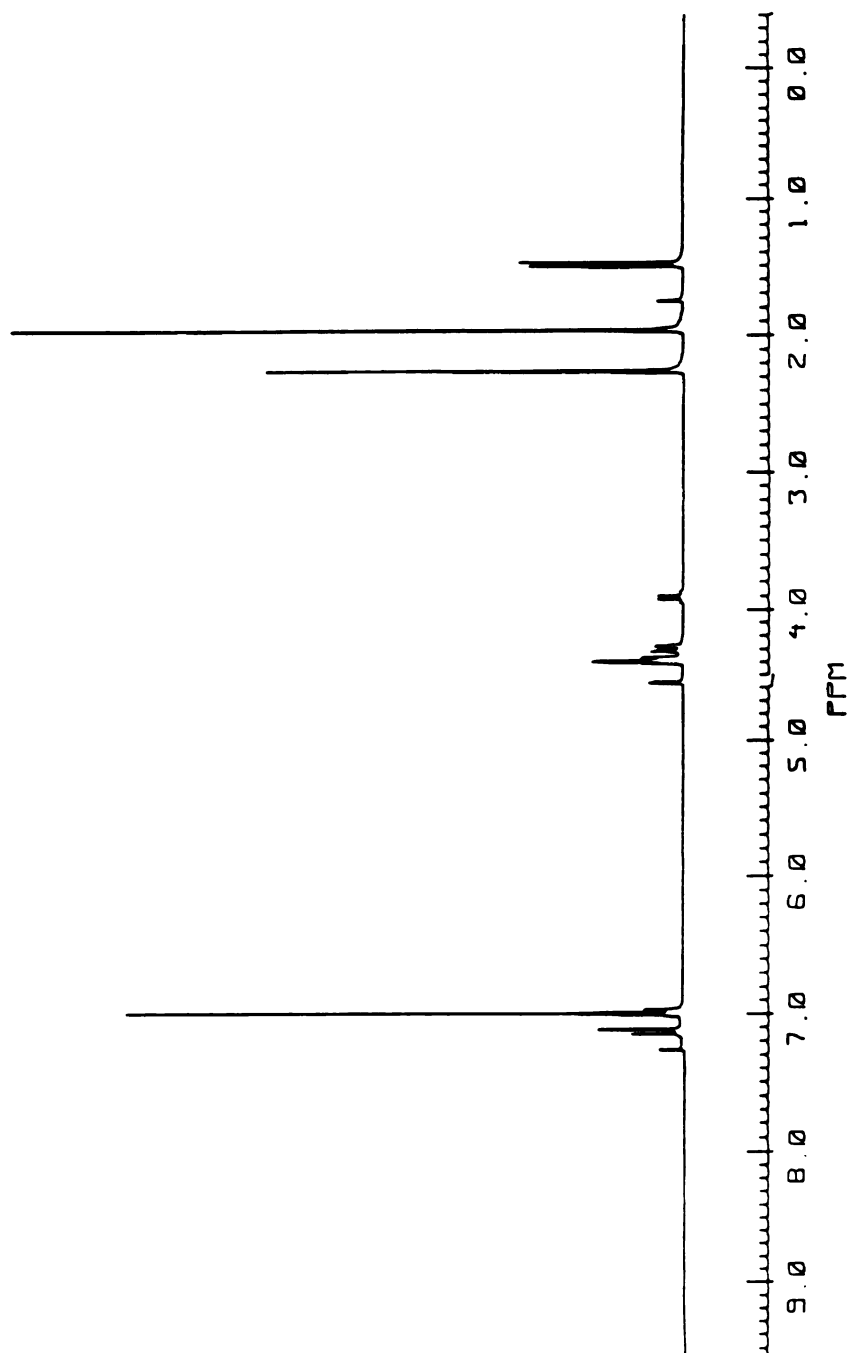


Figure 57. ^1H NMR spectrum of compound 53 (R = 4-tolyl)

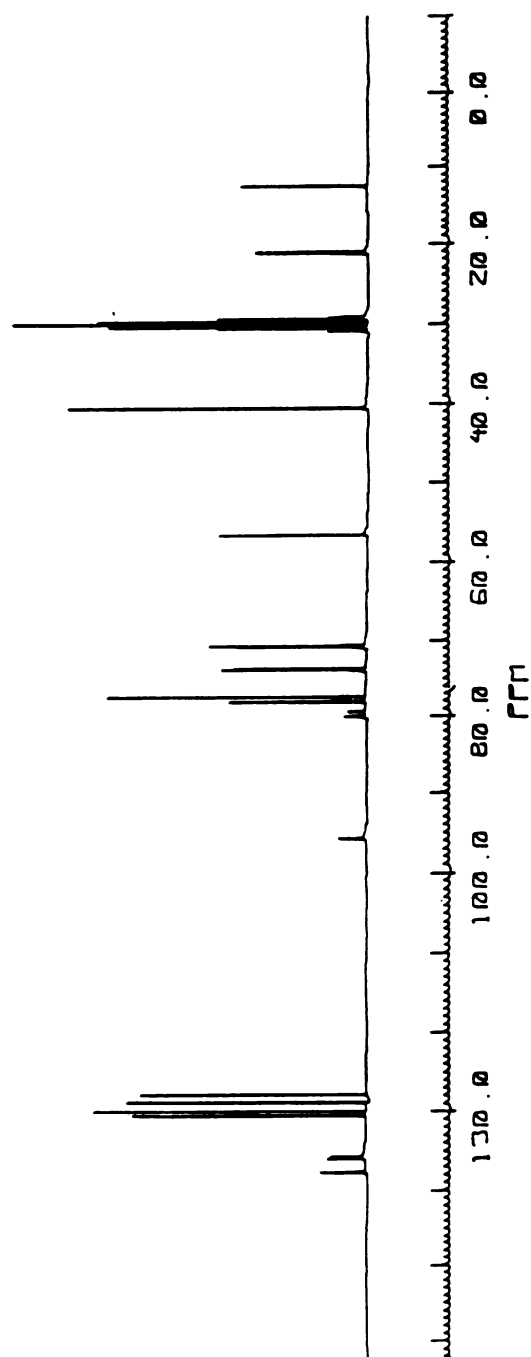


Figure 58. Gated decoupled ^{13}C NMR of compound 53 ($\text{R} = 4\text{-tolyl}$)

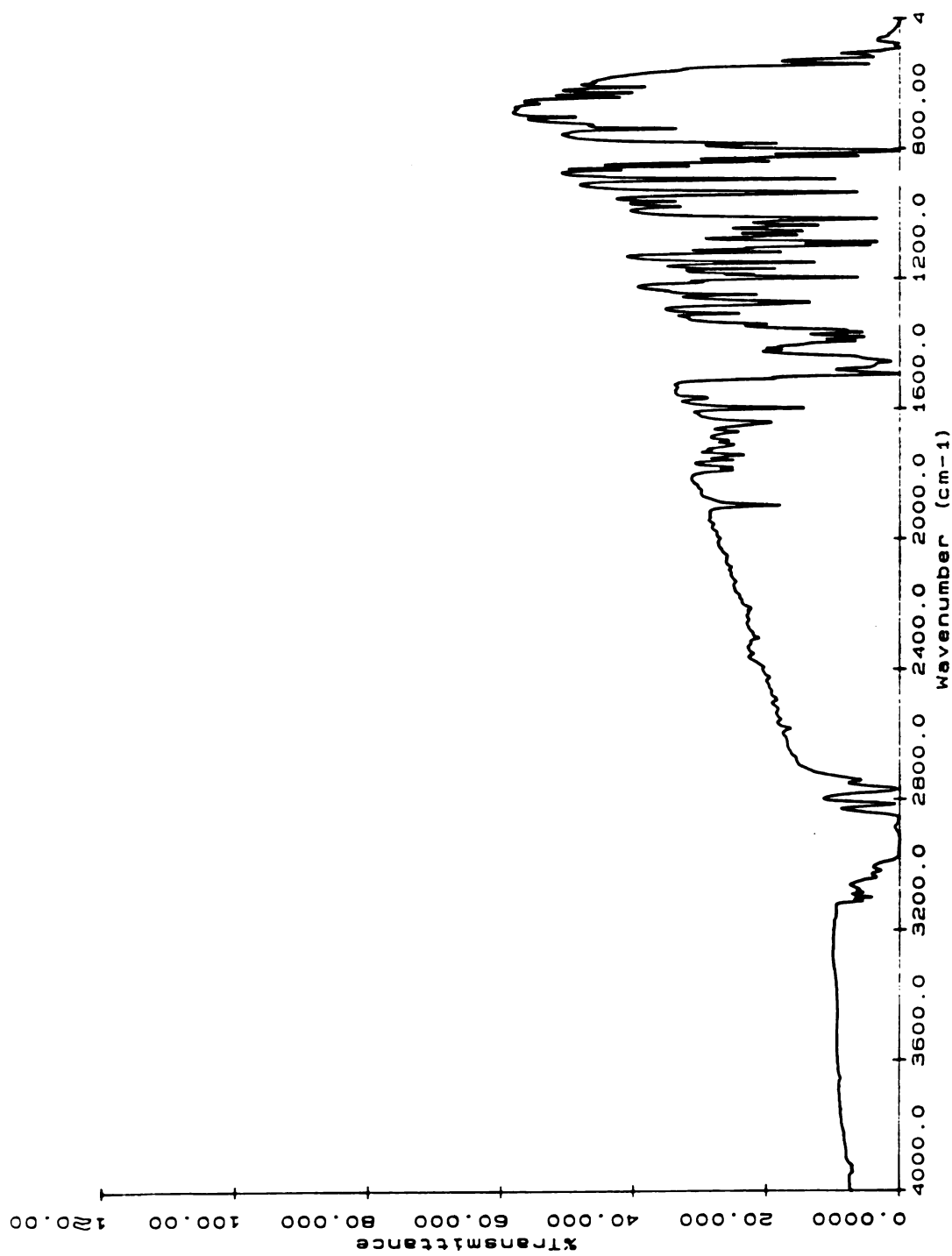


Figure 59. IR spectrum of compound 53 (R = 4-tolyl)

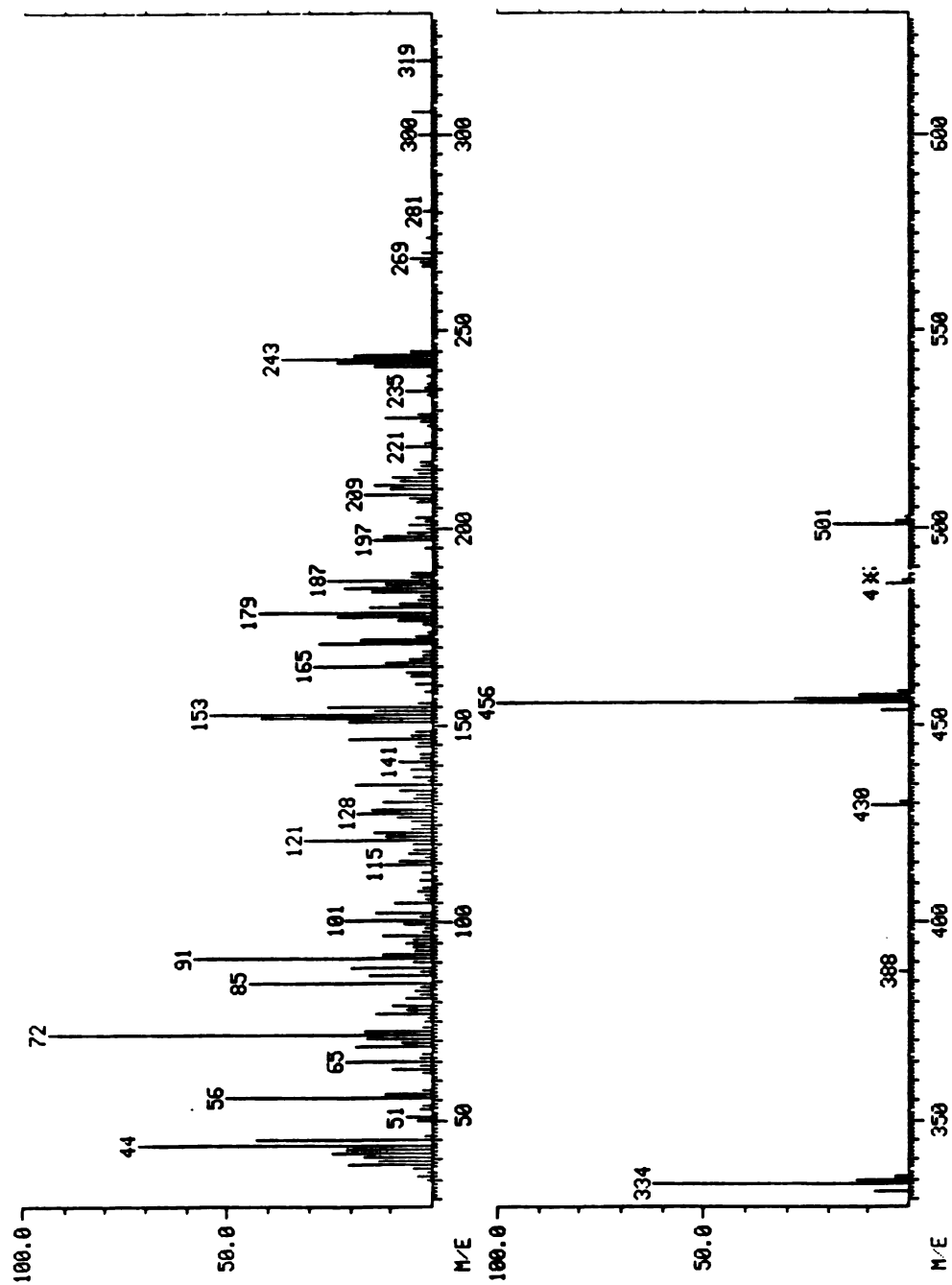


Figure 60. Mass spectrum of compound 53 (R = 4-tolyl)

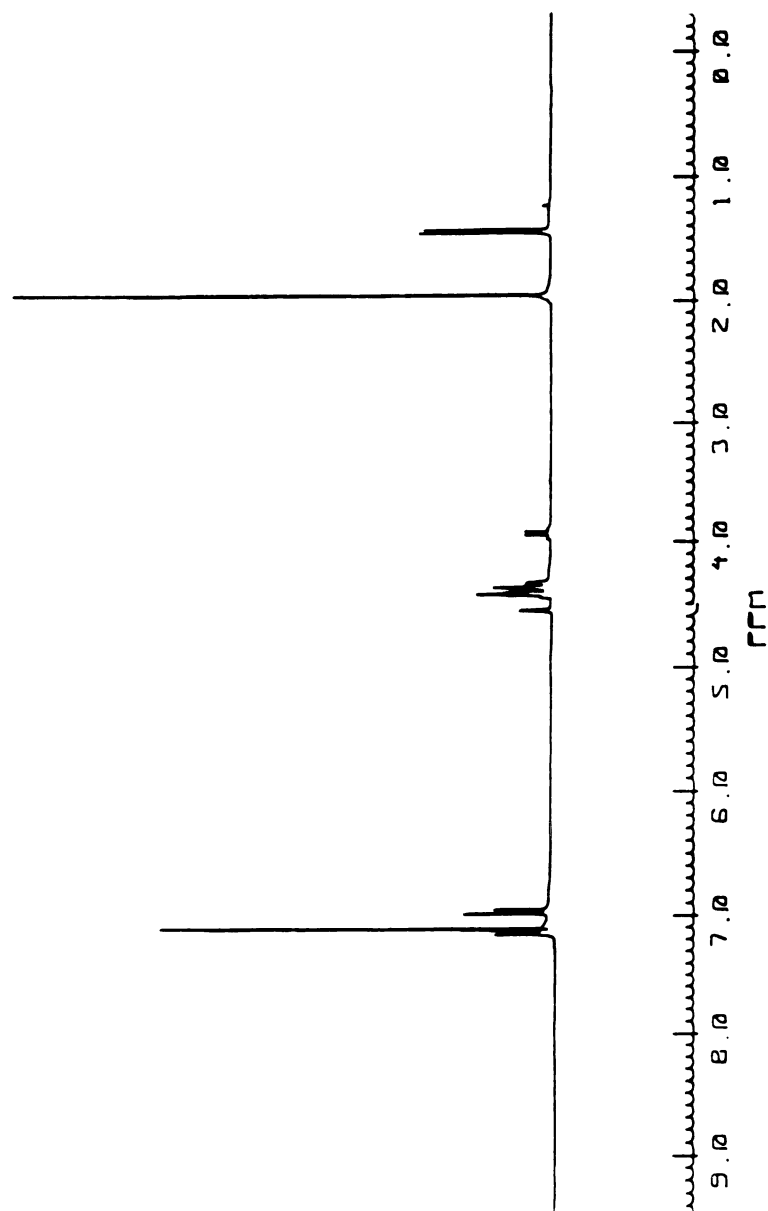


Figure 61. ^1H NMR spectrum of compound 54 (R = 4-Cl-Ph)

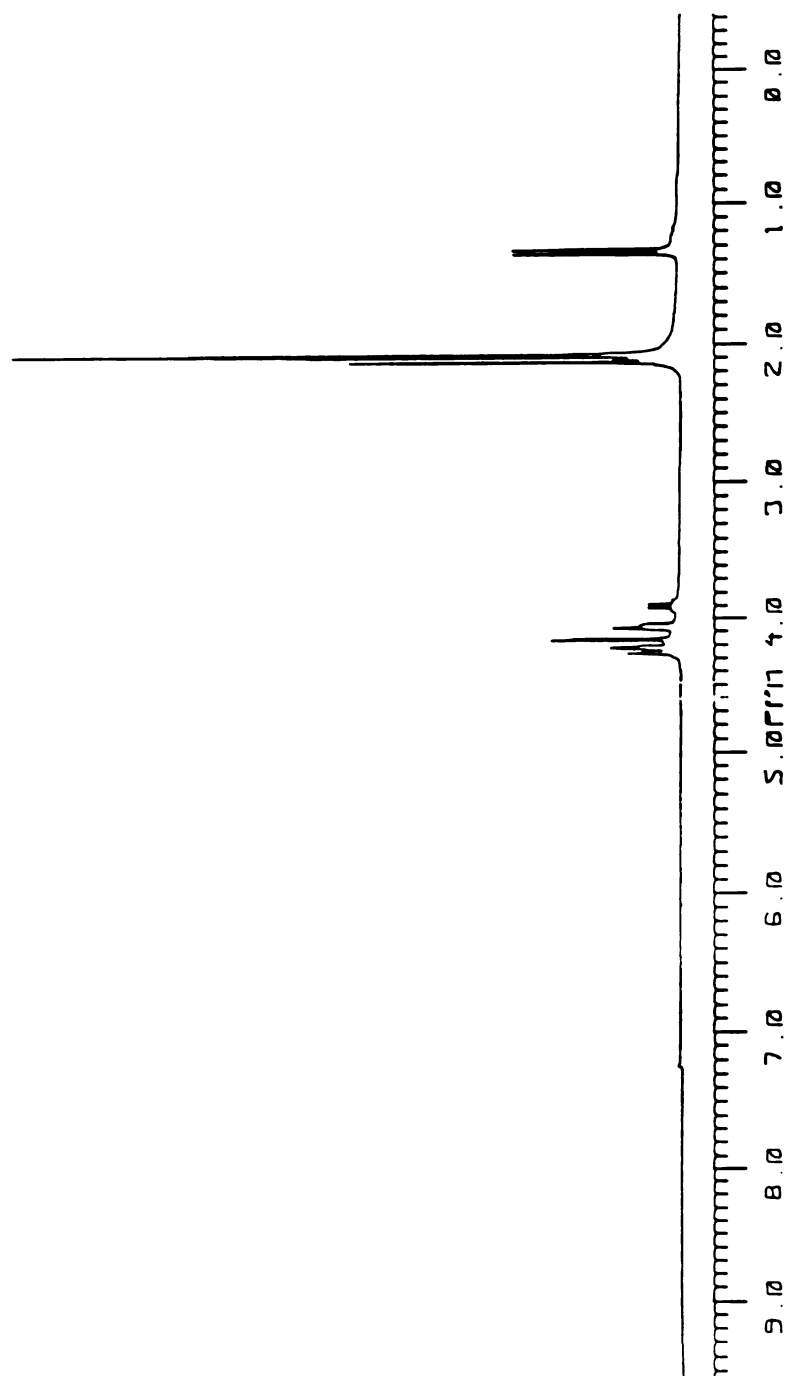


Figure 62. ^1H NMR spectrum of compound 55 (R = Me)

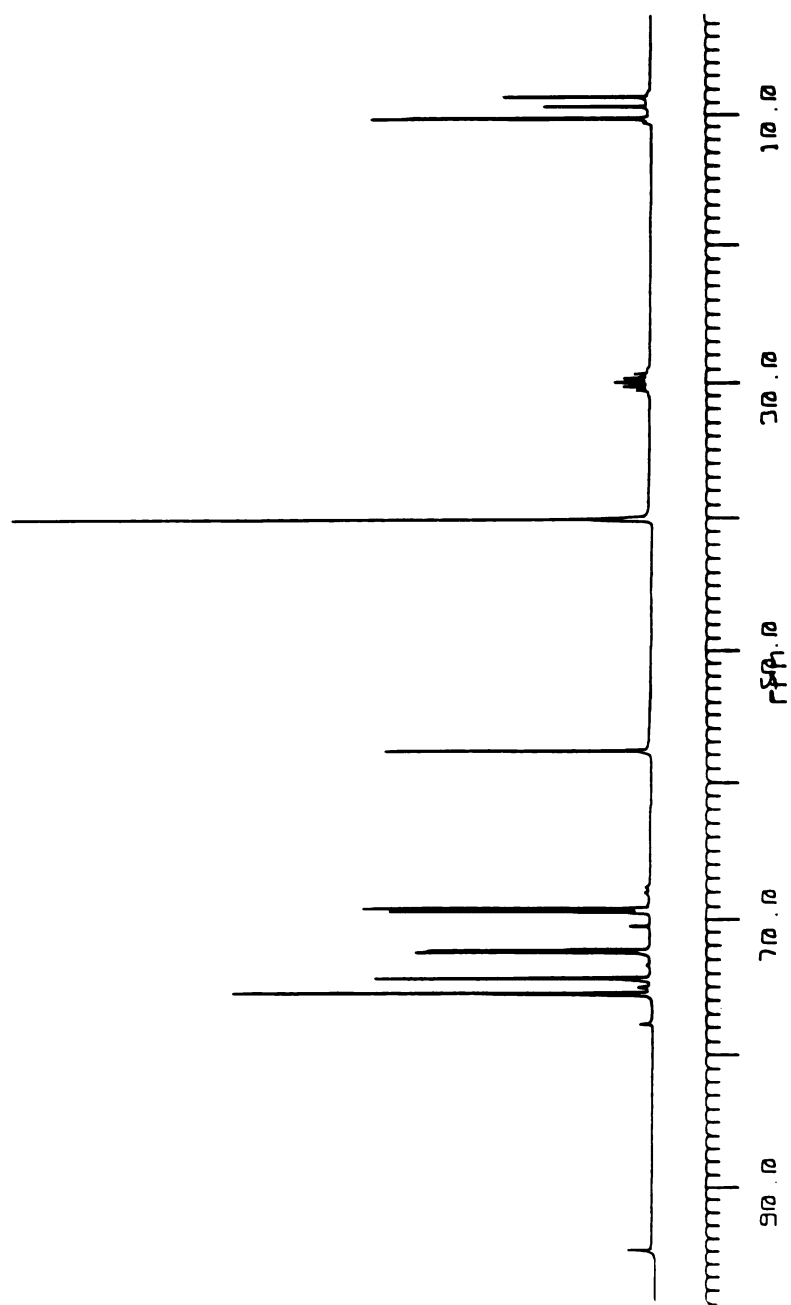


Figure 63. Gated decoupled ^{13}C NMR of compound 55 ($\text{R} = \text{Me}$)

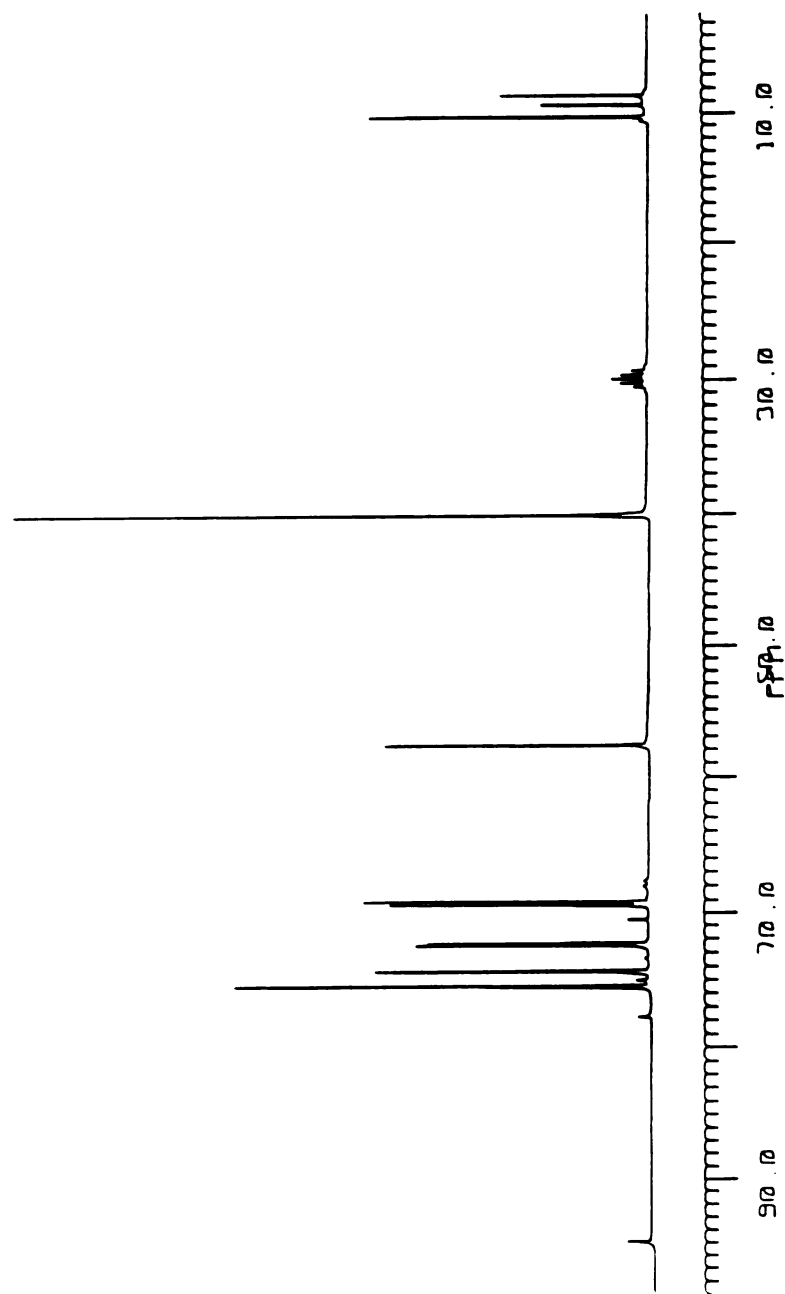


Figure 63. Gated decoupled ^{13}C NMR of compound 55 (R = Me)

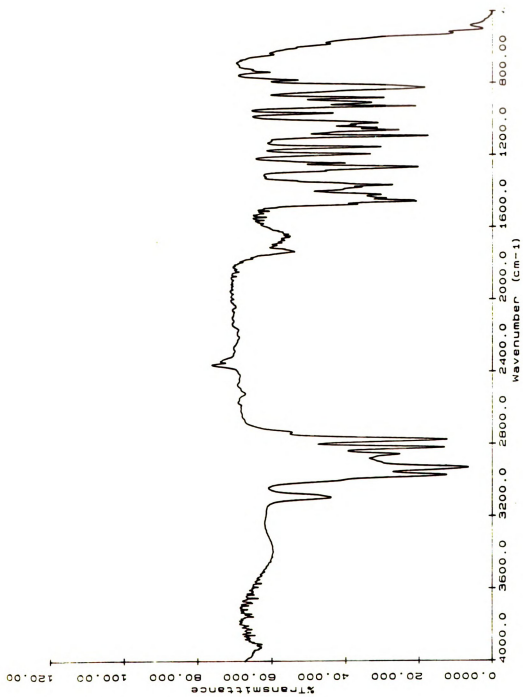


Figure 64. IR spectrum of compound 55 (R = Me)

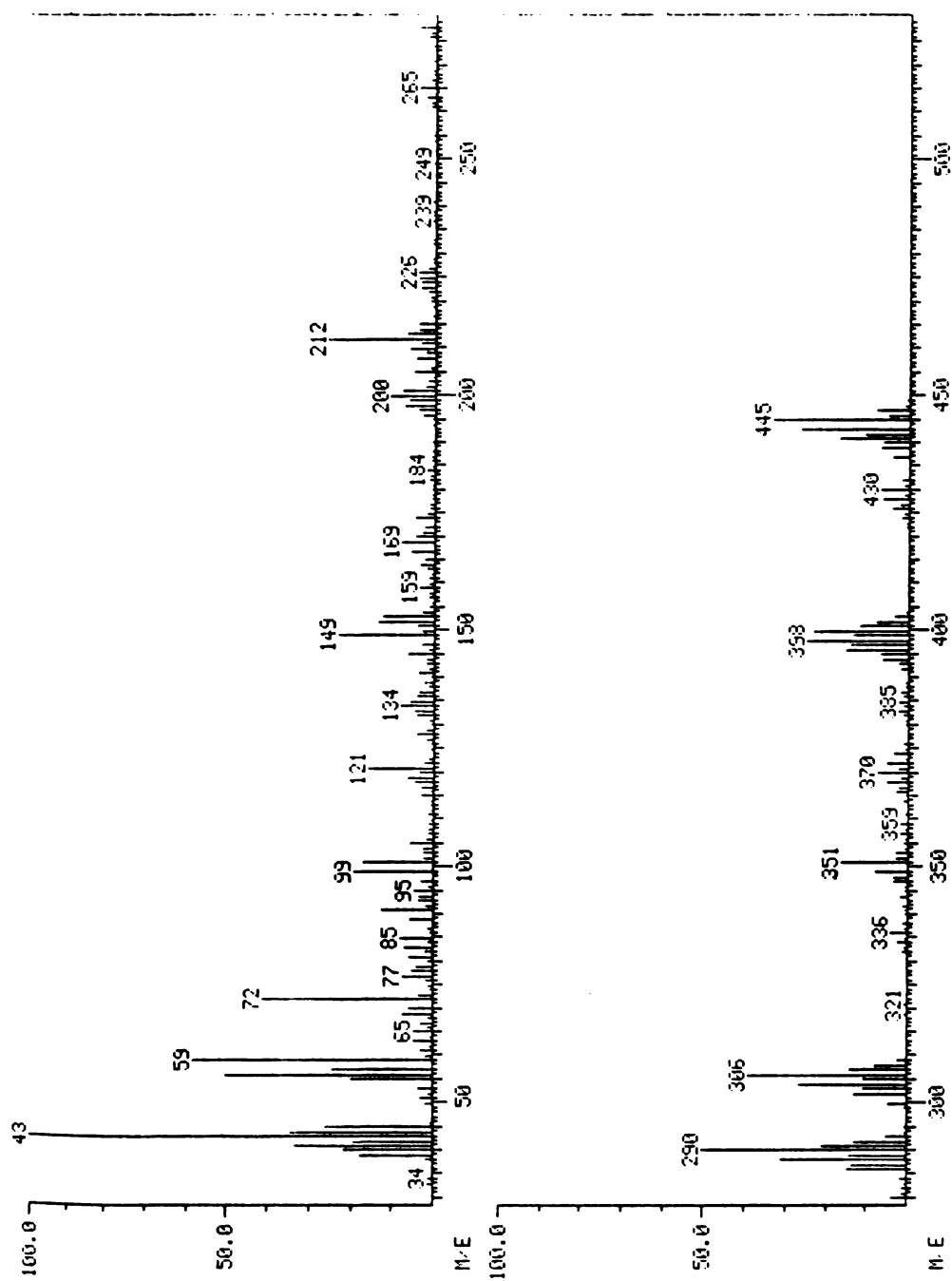


Figure 65. Mass spectrum of compound 55 (R = Me)

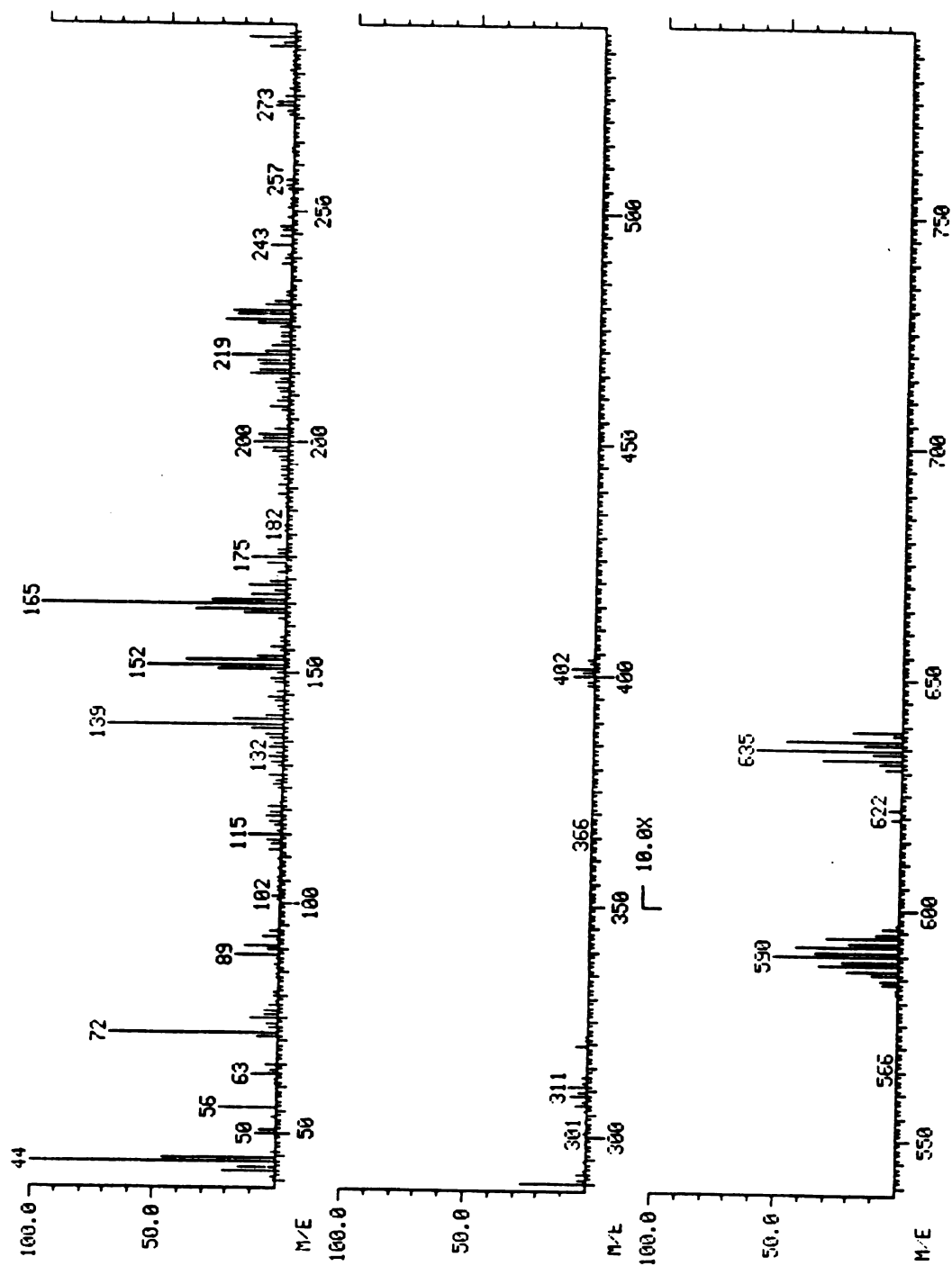


Figure 66. Mass spectrum of compound 57 (R = 4-Cl-Ph)

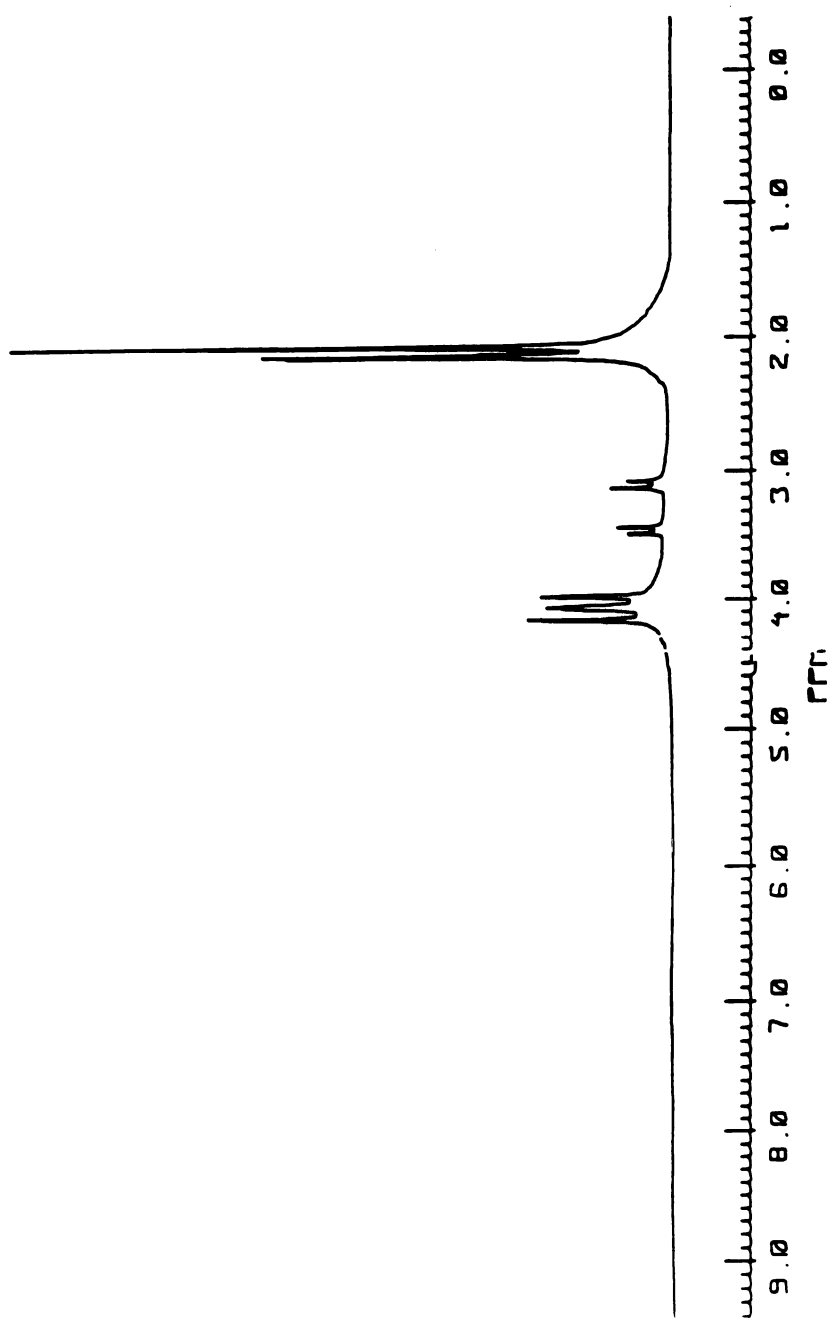


Figure 67. ^1H NMR spectrum of compound 58 (R = Me)

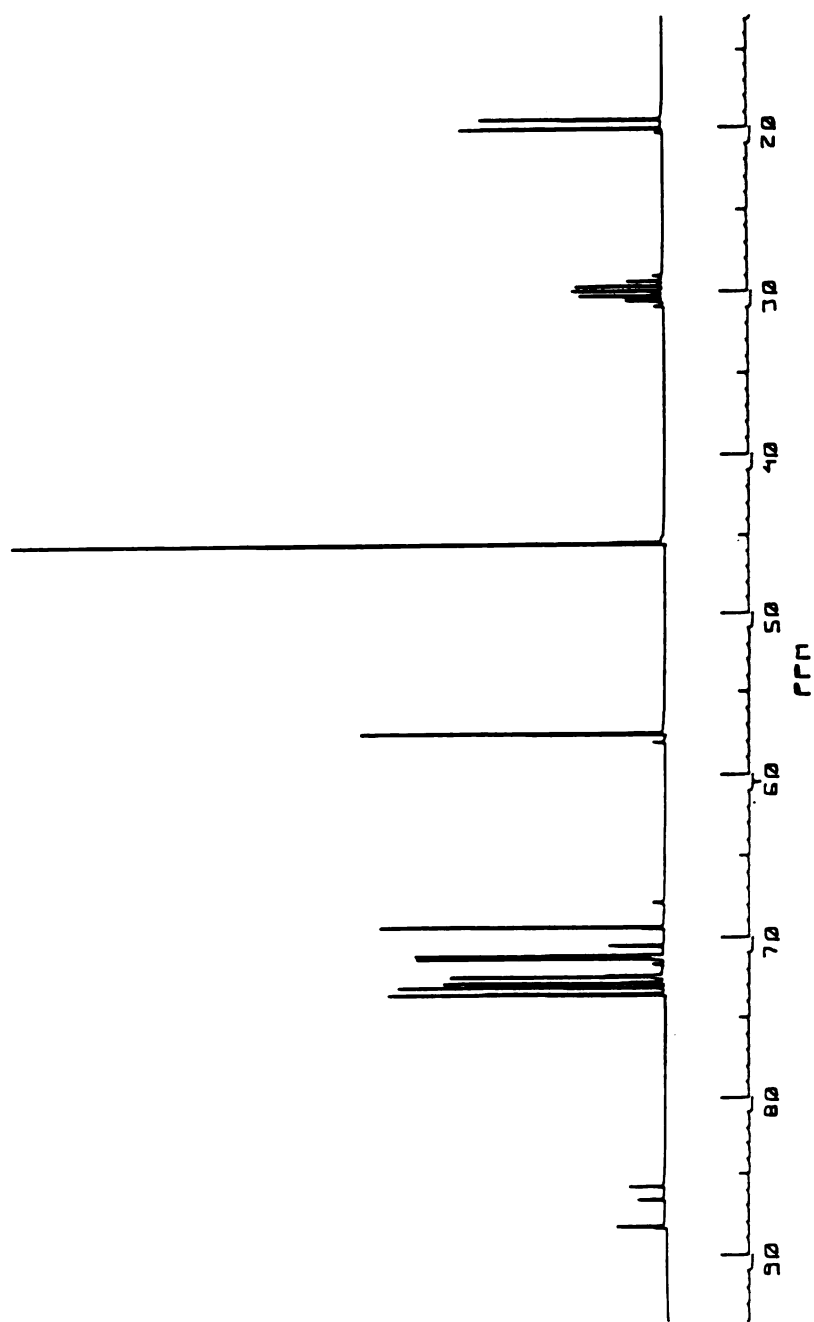


Figure 68. Gated decoupled ^{13}C NMR of compound 58 (R = Me)

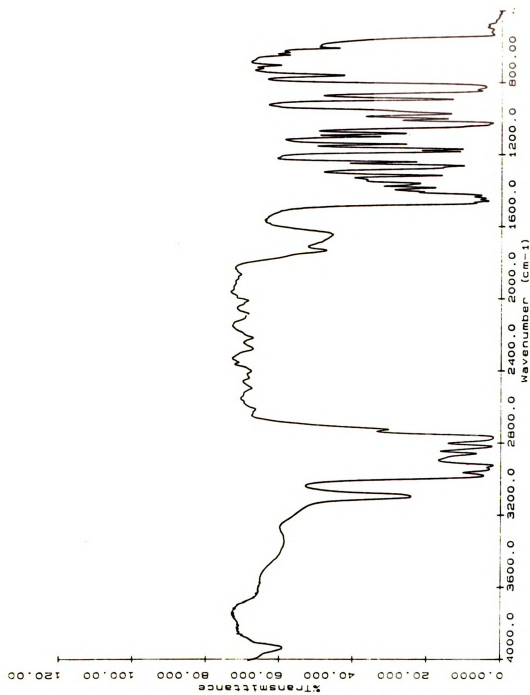


Figure 69. IR spectrum of compound **58** (R = Me)

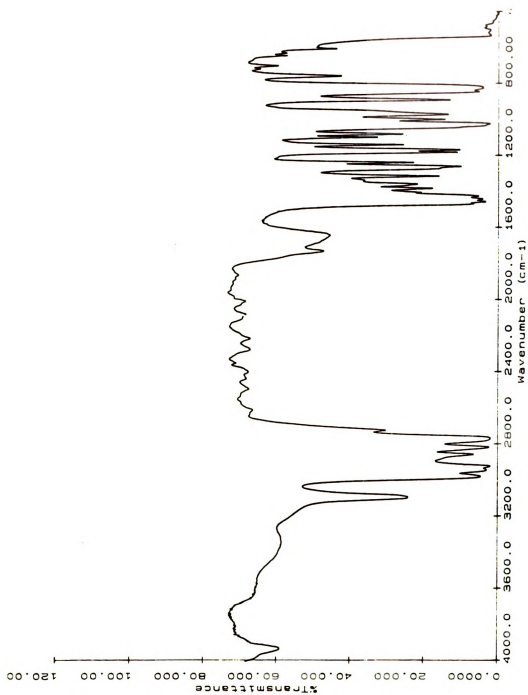


Figure 69. IR spectrum of compound 58 (R = Me)

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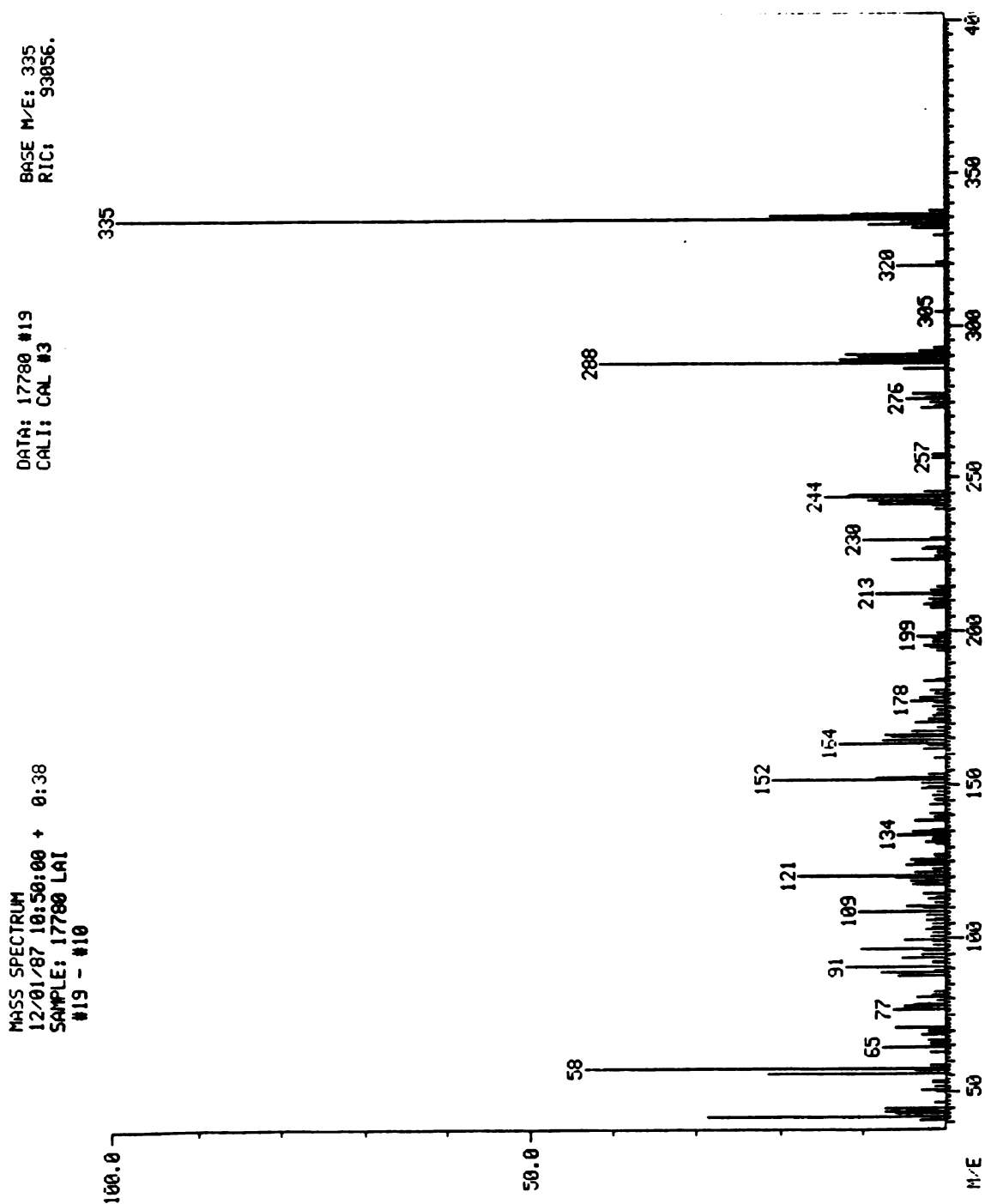


Figure 70. Mass spectrum of compound 58 (R = Me)

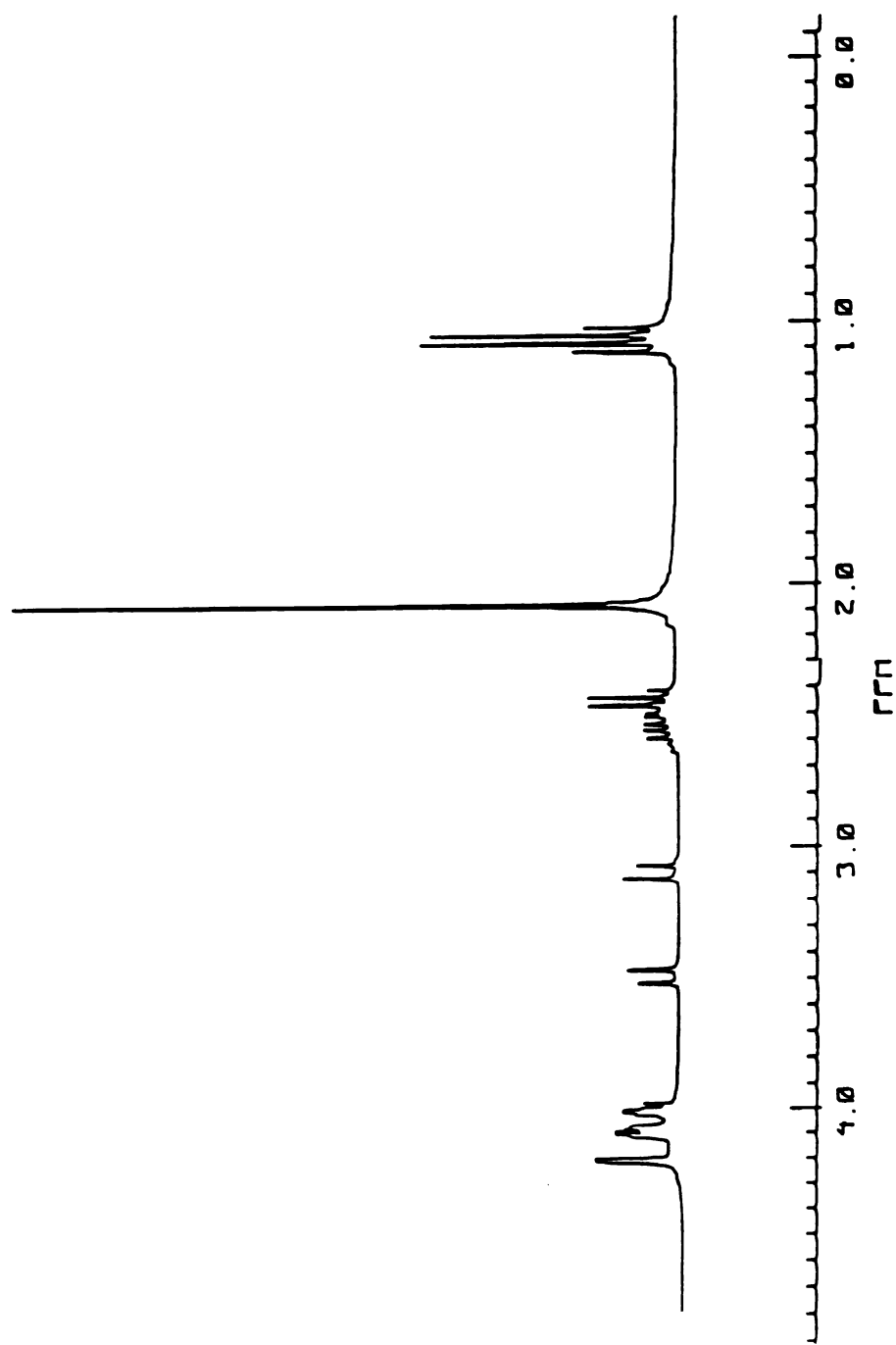


Figure 71. ^1H NMR spectrum of compound 59 (R = Et)

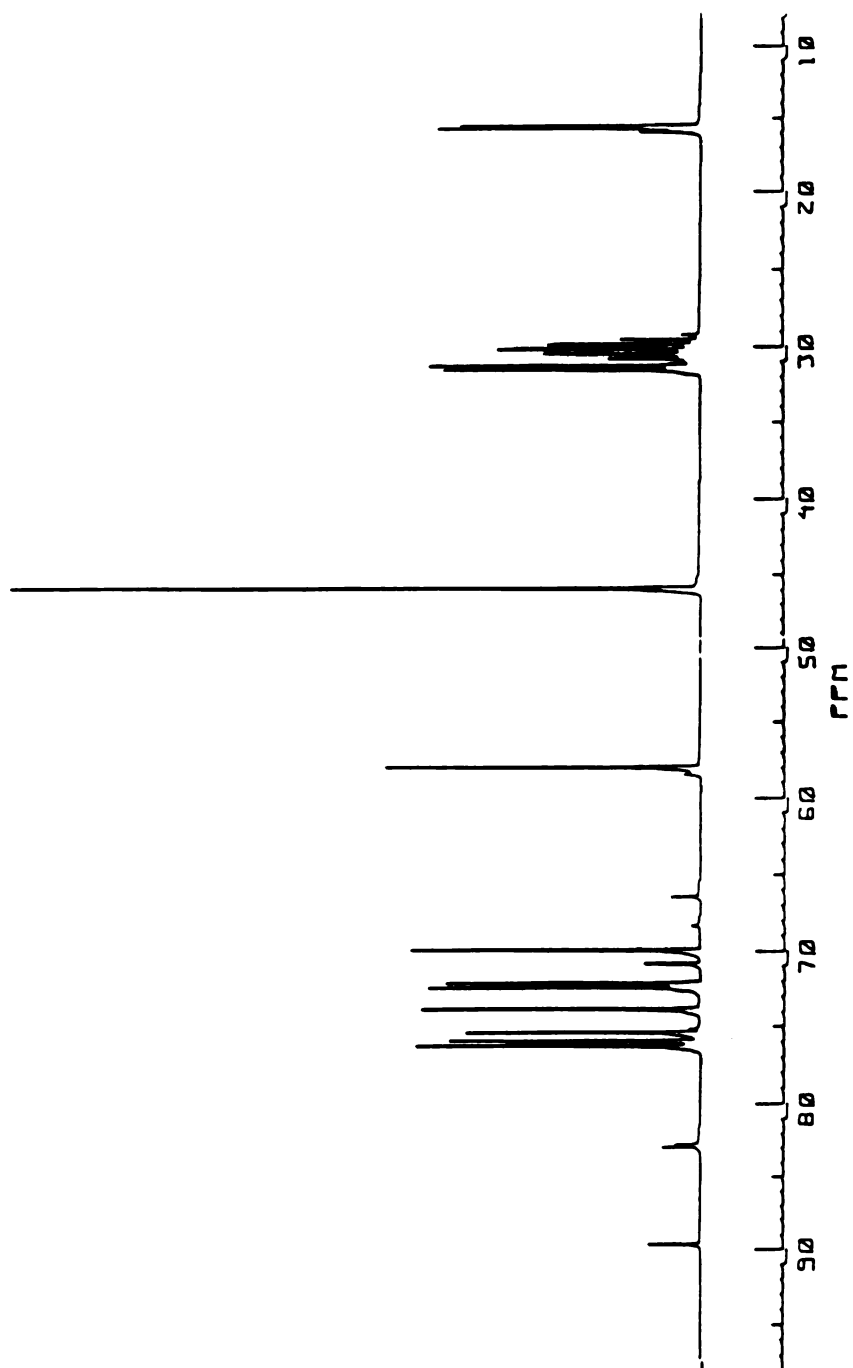


Figure 72. Gated decoupled ^{13}C NMR of compound 59 (R = Et)

CH2 S-Ethyl 31 May 88 08:15:03

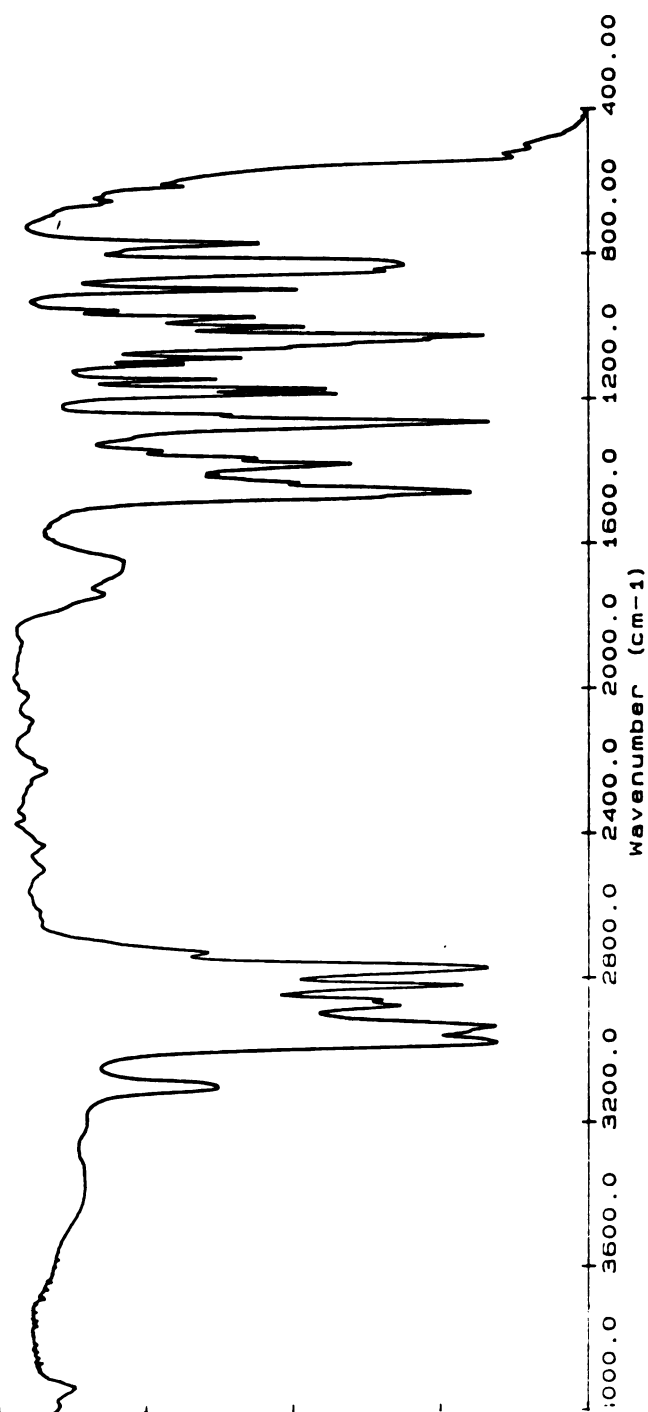


Figure 73. IR spectrum of compound 59 (R = Et)

100.0

20.3

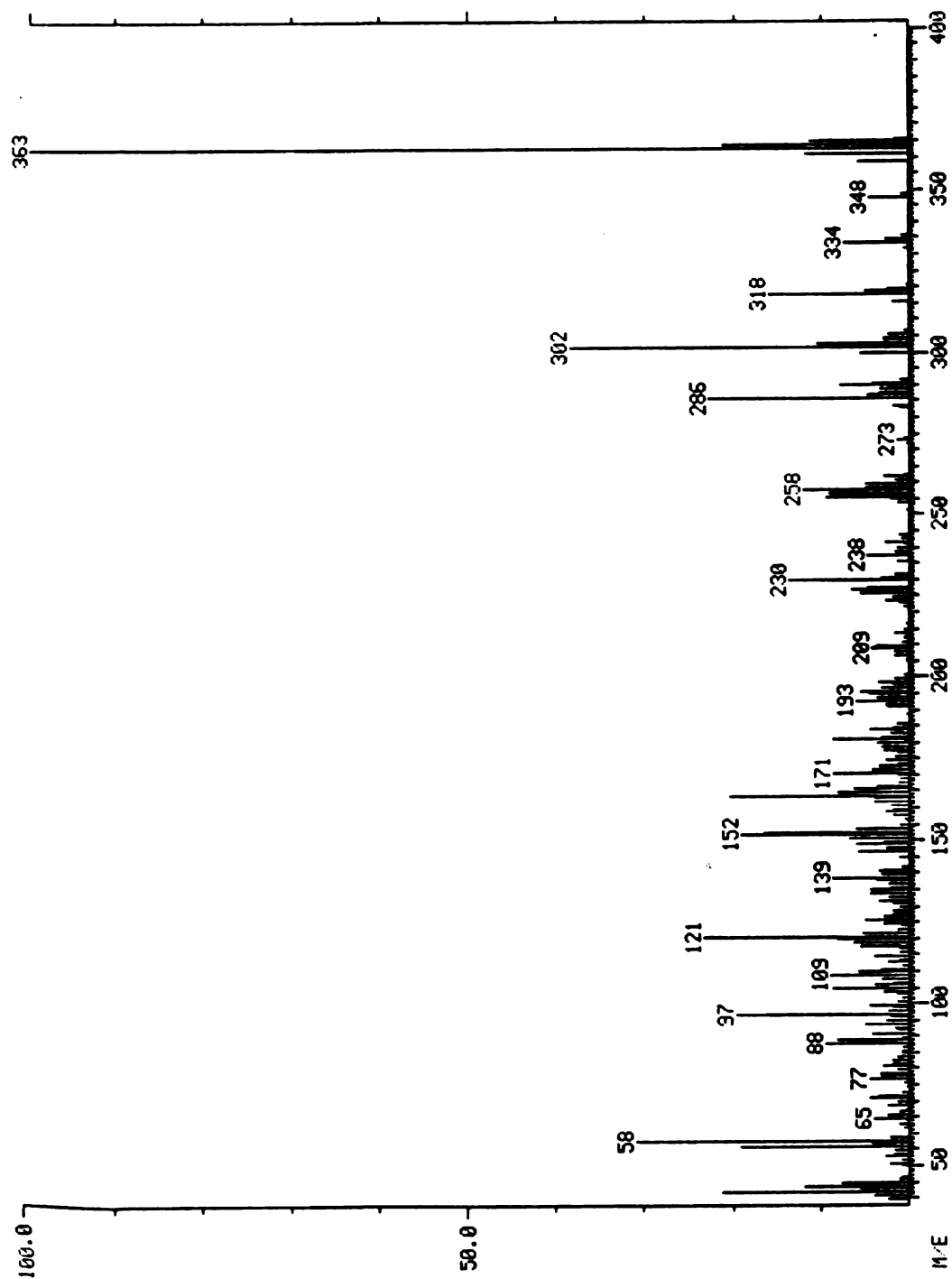


Figure 74. Mass spectrum of compound 59 (R = Et)

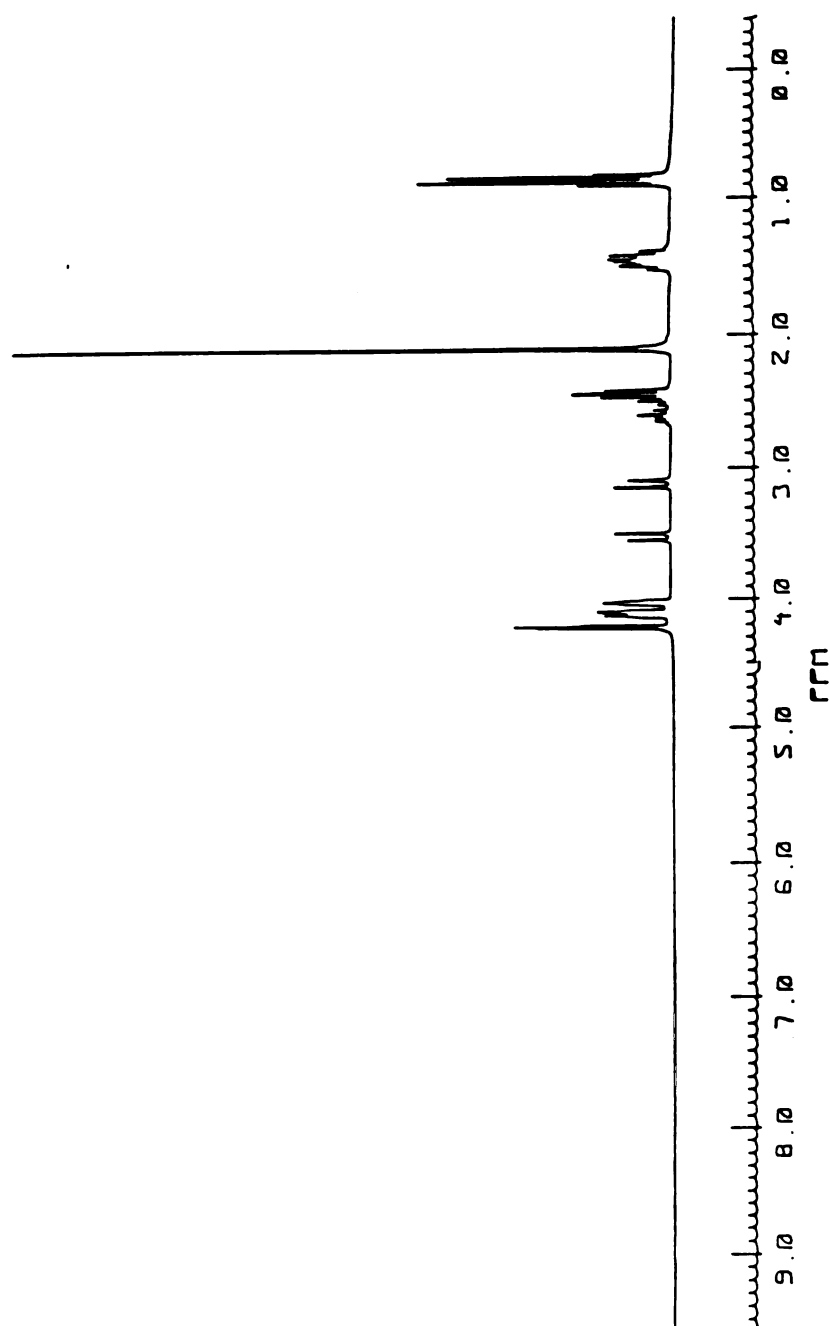


Figure 75. ^1H NMR spectrum of compound 60 (R = n-Pr)

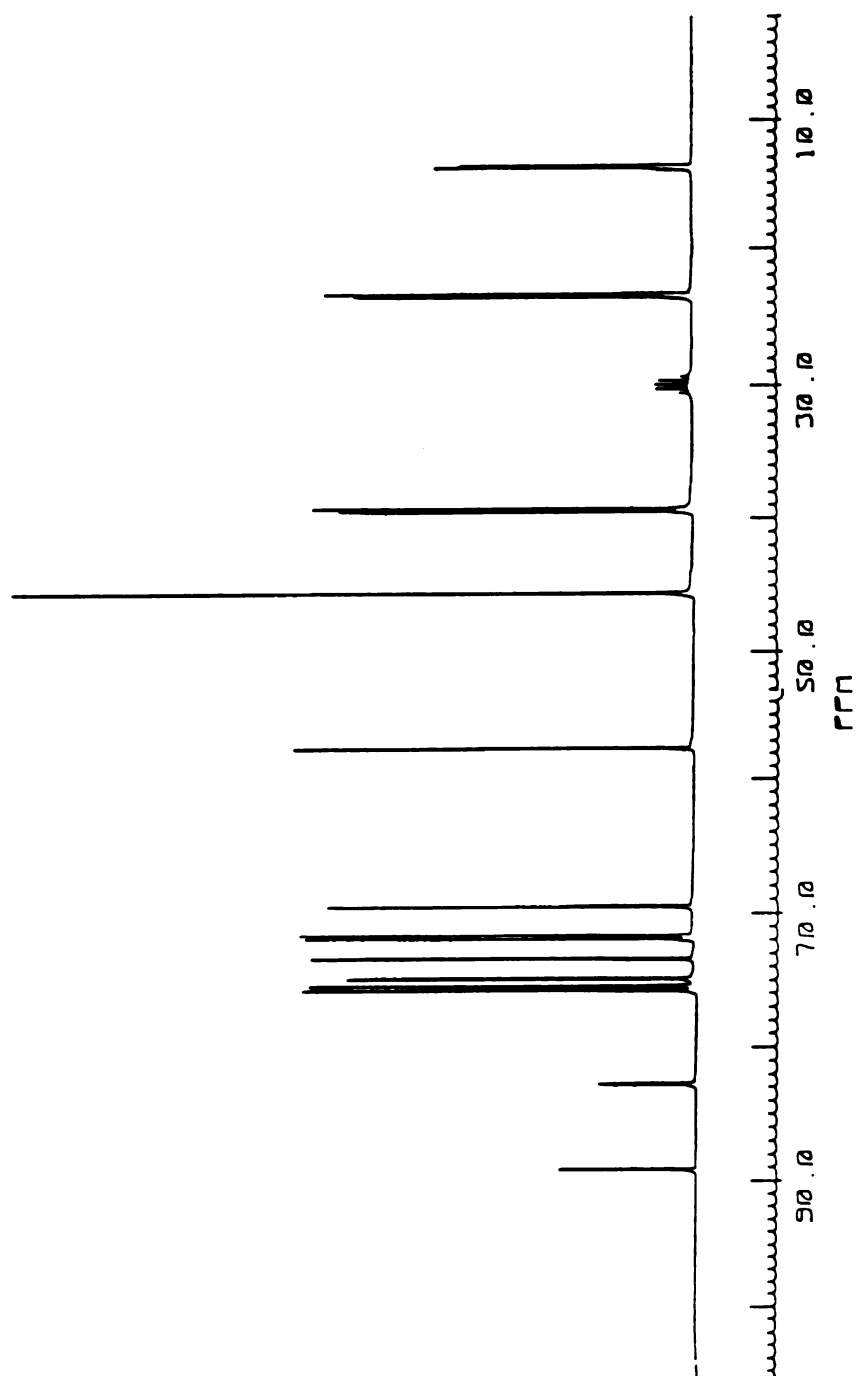


Figure 76. Gated decoupled ^{13}C NMR of compound 60 ($\text{R} = \text{n-Pr}$)

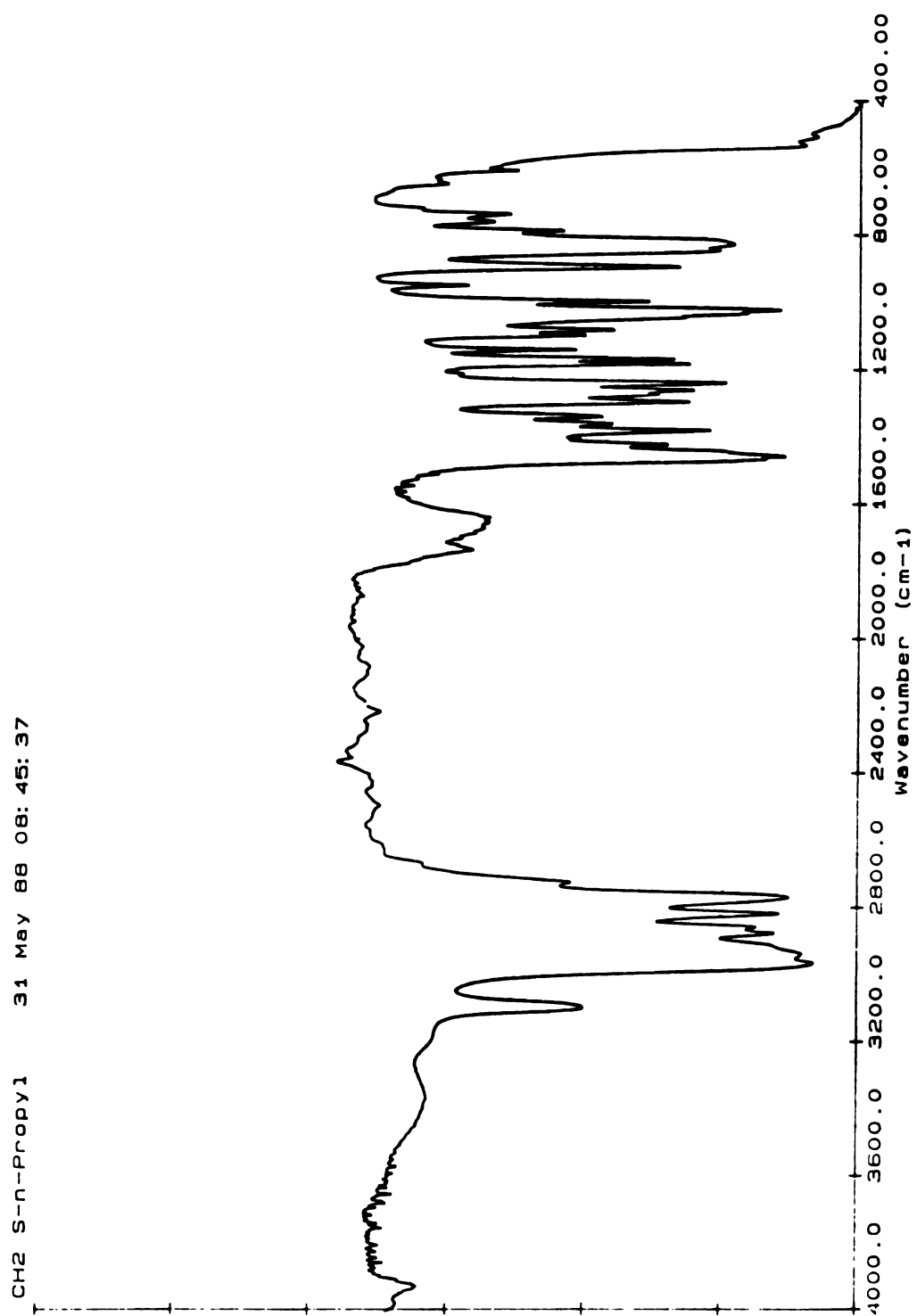


Figure 77. IR spectrum of compound 60 (R = n-Pr)

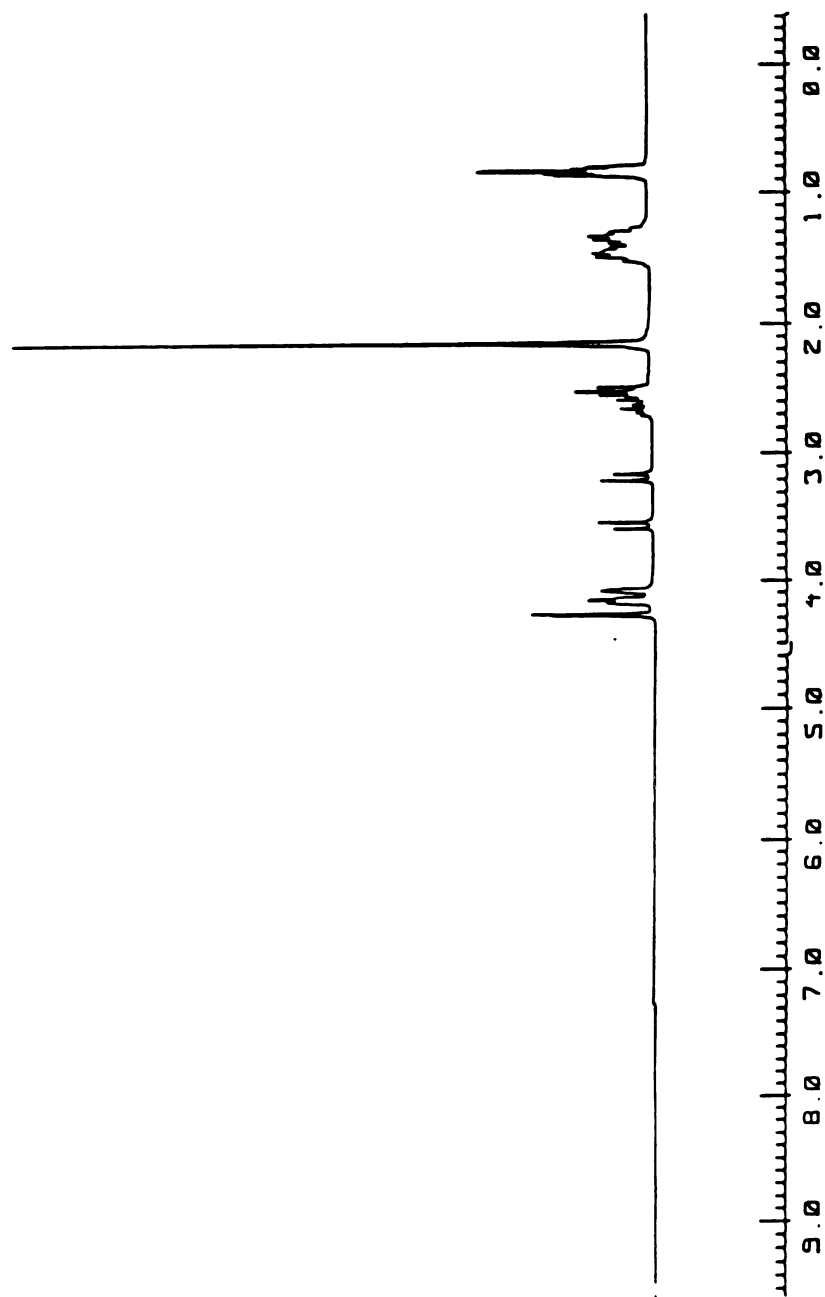


Figure 78. ^1H NMR spectrum of compound 62 (R = n-Bu)

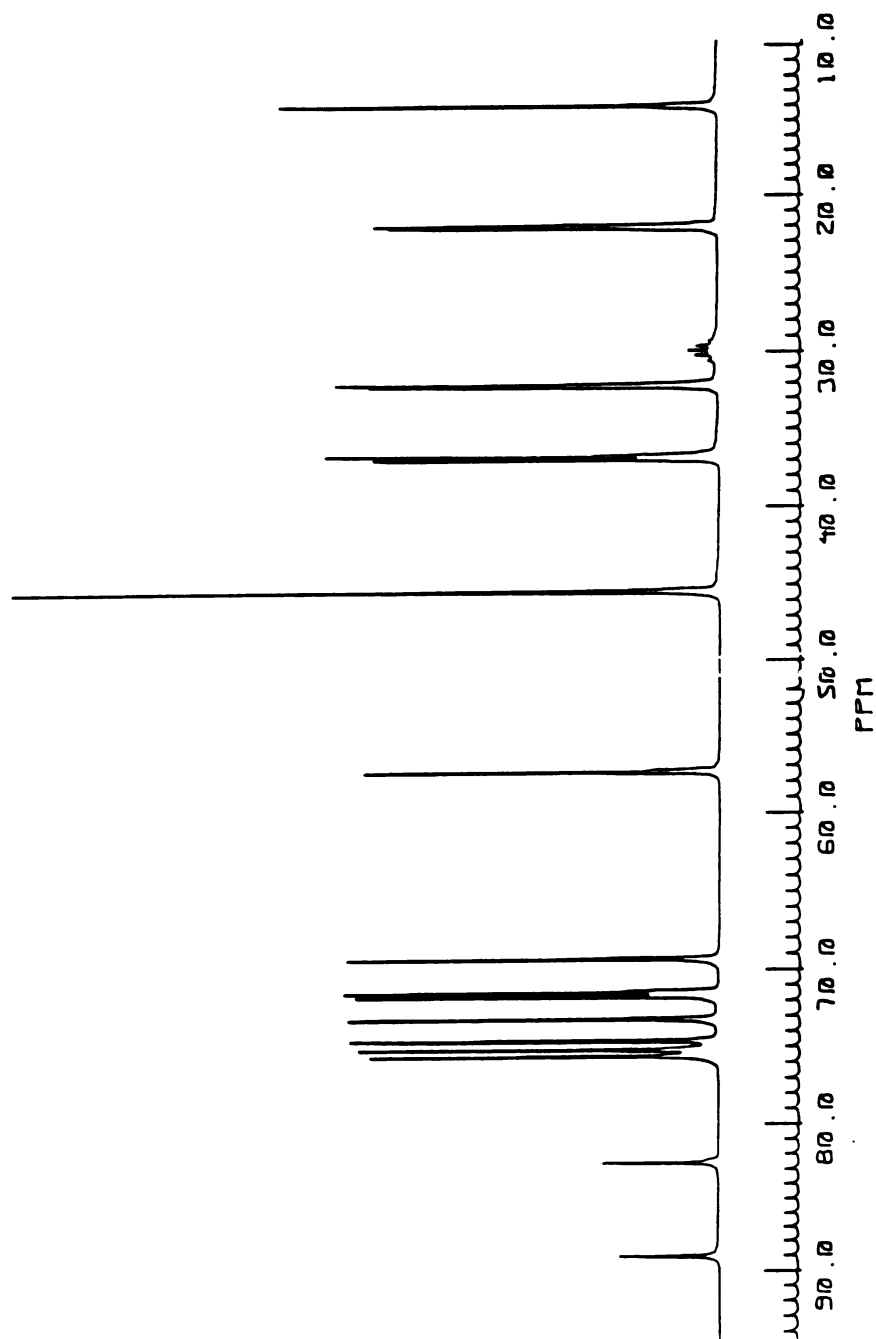


Figure 79. Gated decoupled ^{13}C NMR of compound 62 (R = n-Bu)

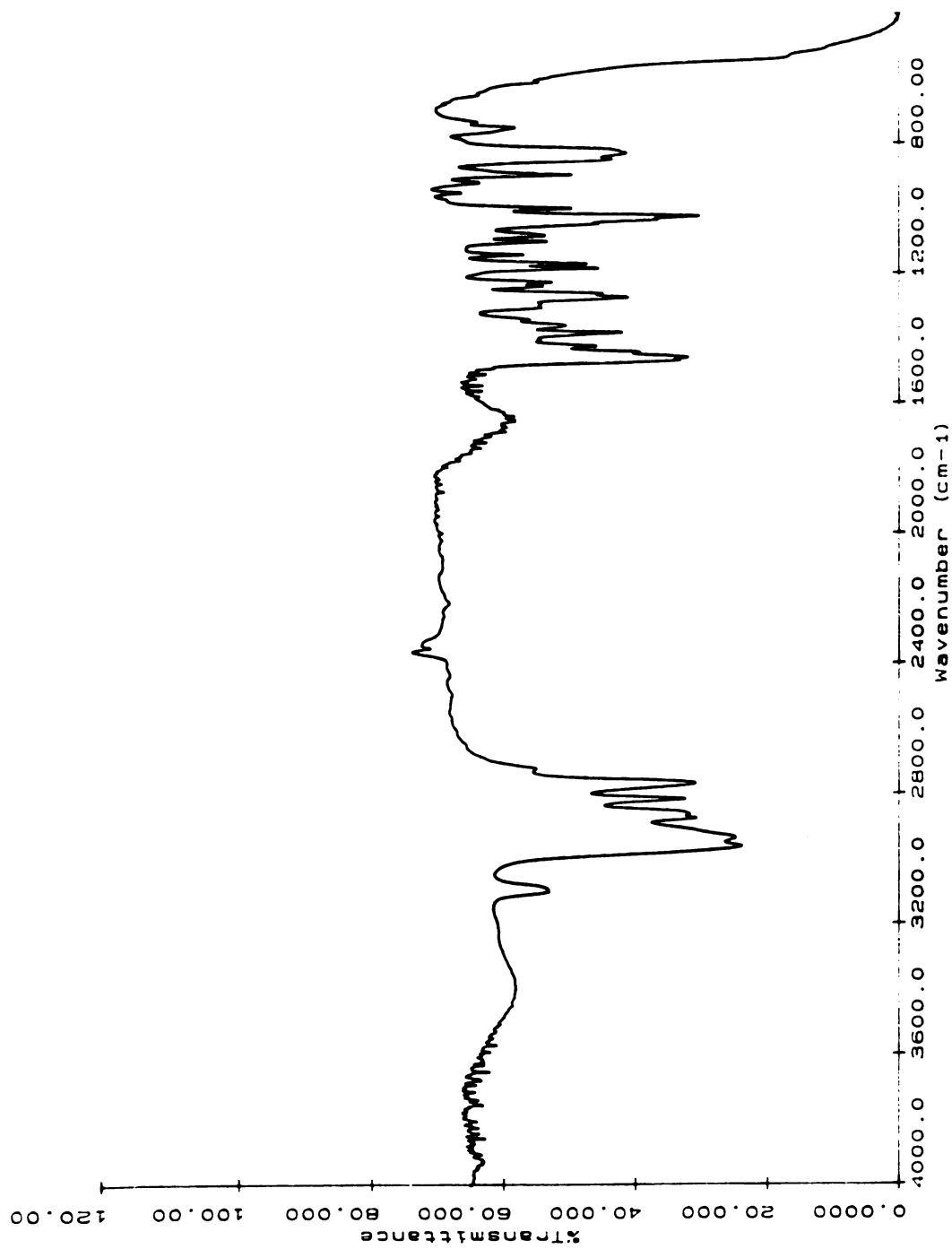


Figure 80. IR spectrum of compound 62 (R = n-Bu)

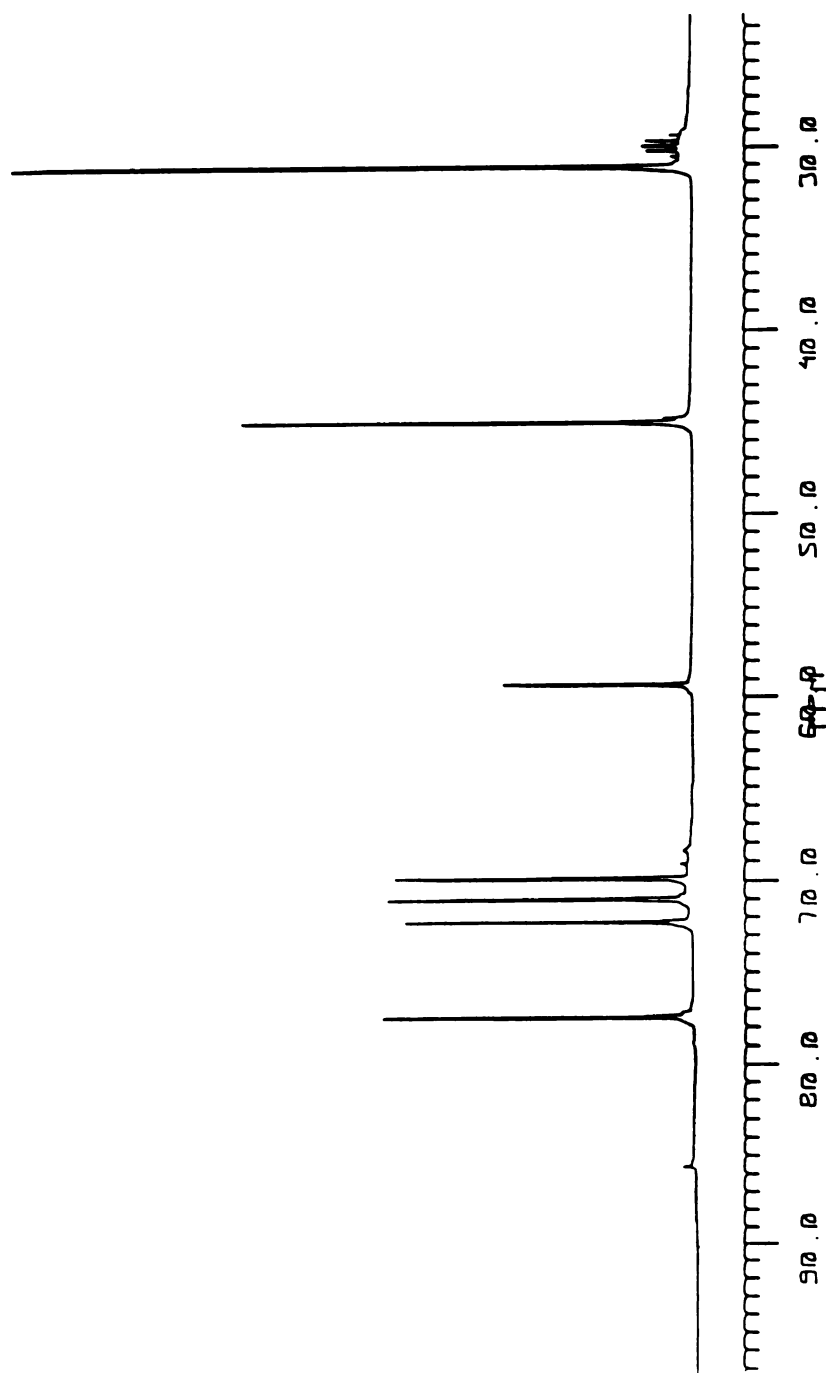


Figure 81. Gated decoupled ^{13}C NMR of compound 64 (R = t-Bu)

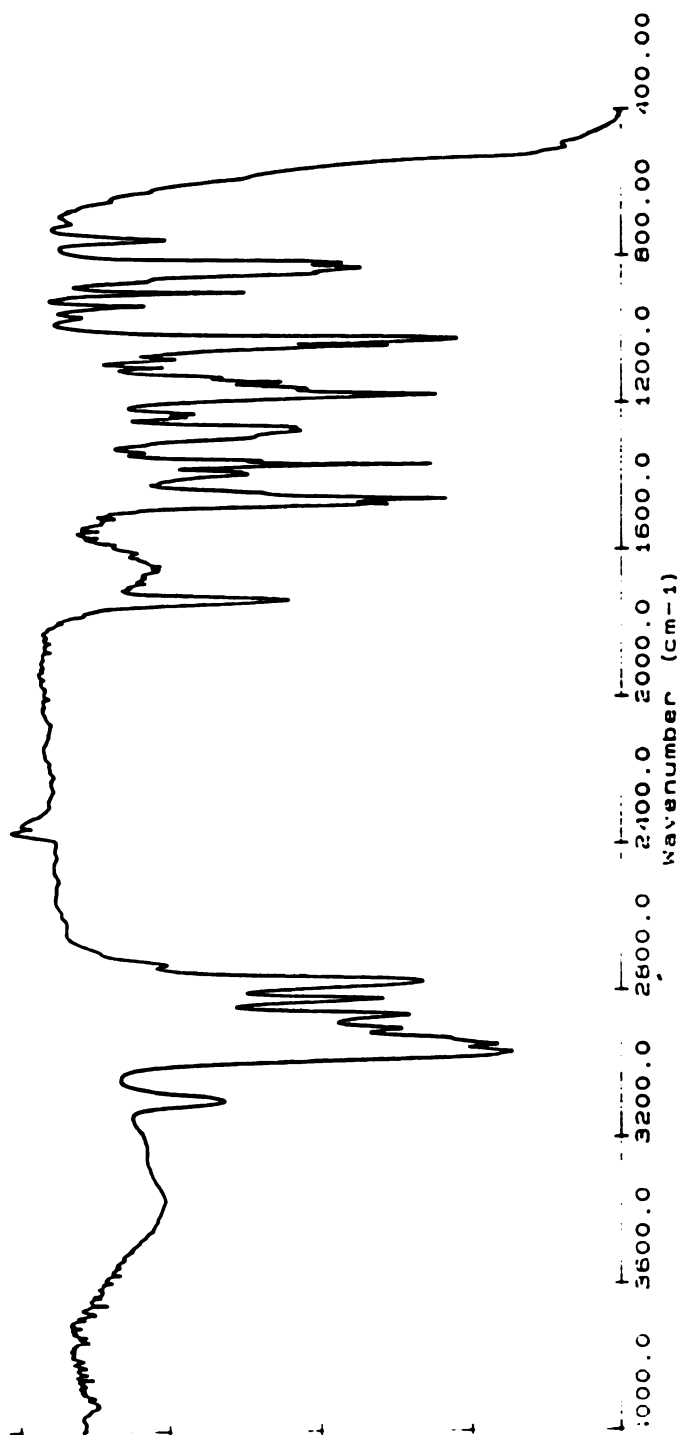


Figure 82. IR spectrum of compound 64 (R = i-Bu)

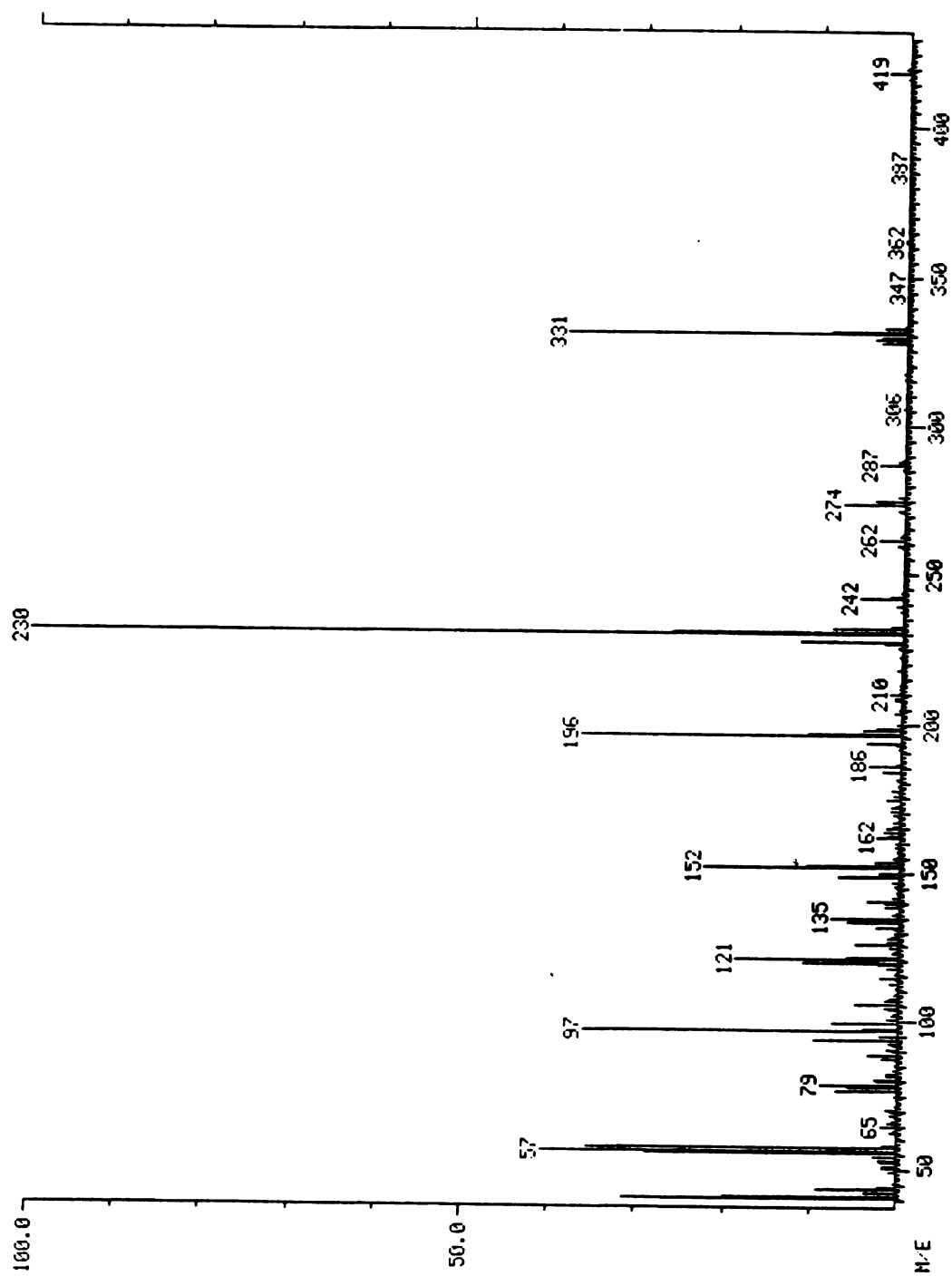


Figure 83. Mass spectrum of compound 64 (R = t-Bu)

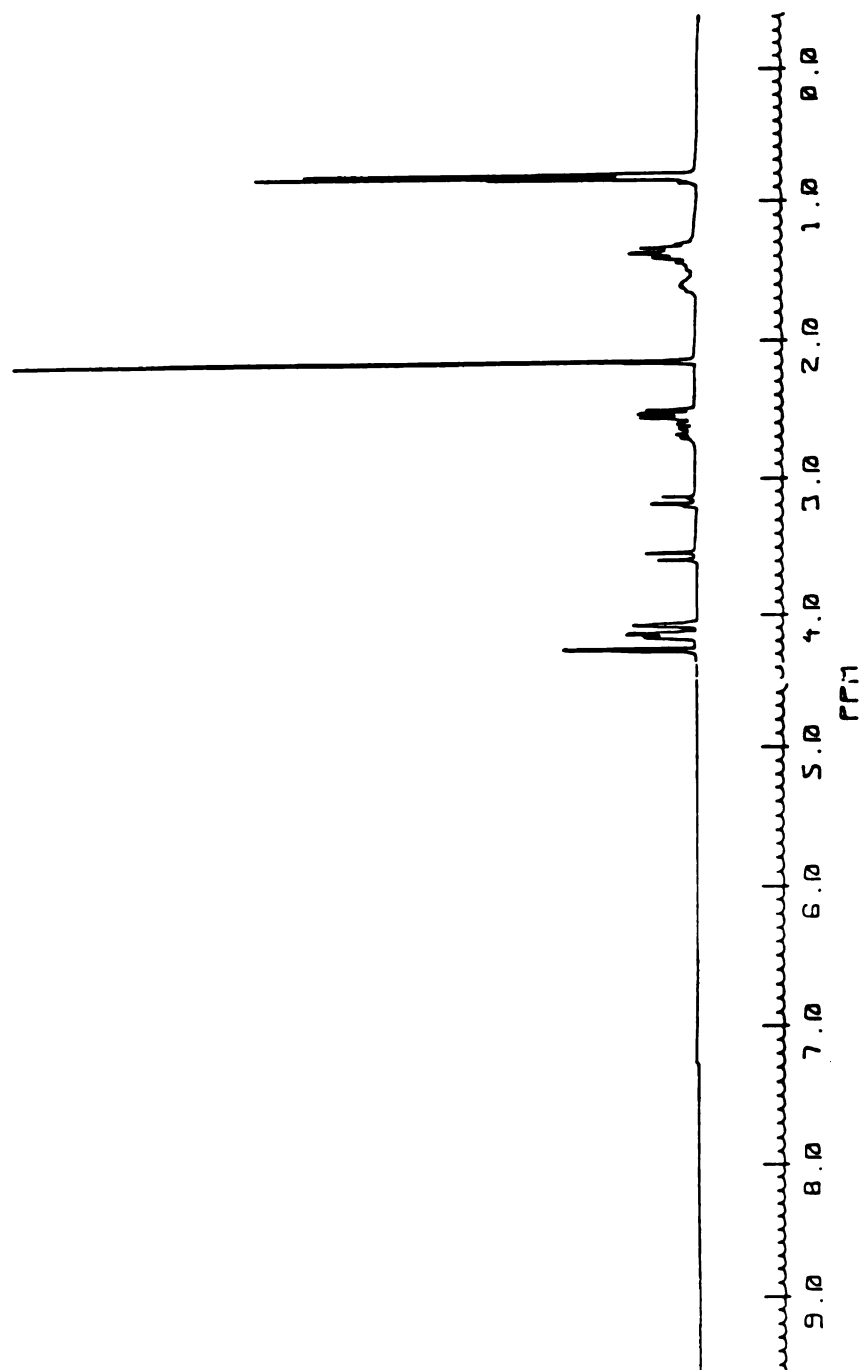


Figure 84. ^1H NMR spectrum of compound 65 (R = i-pentyl)

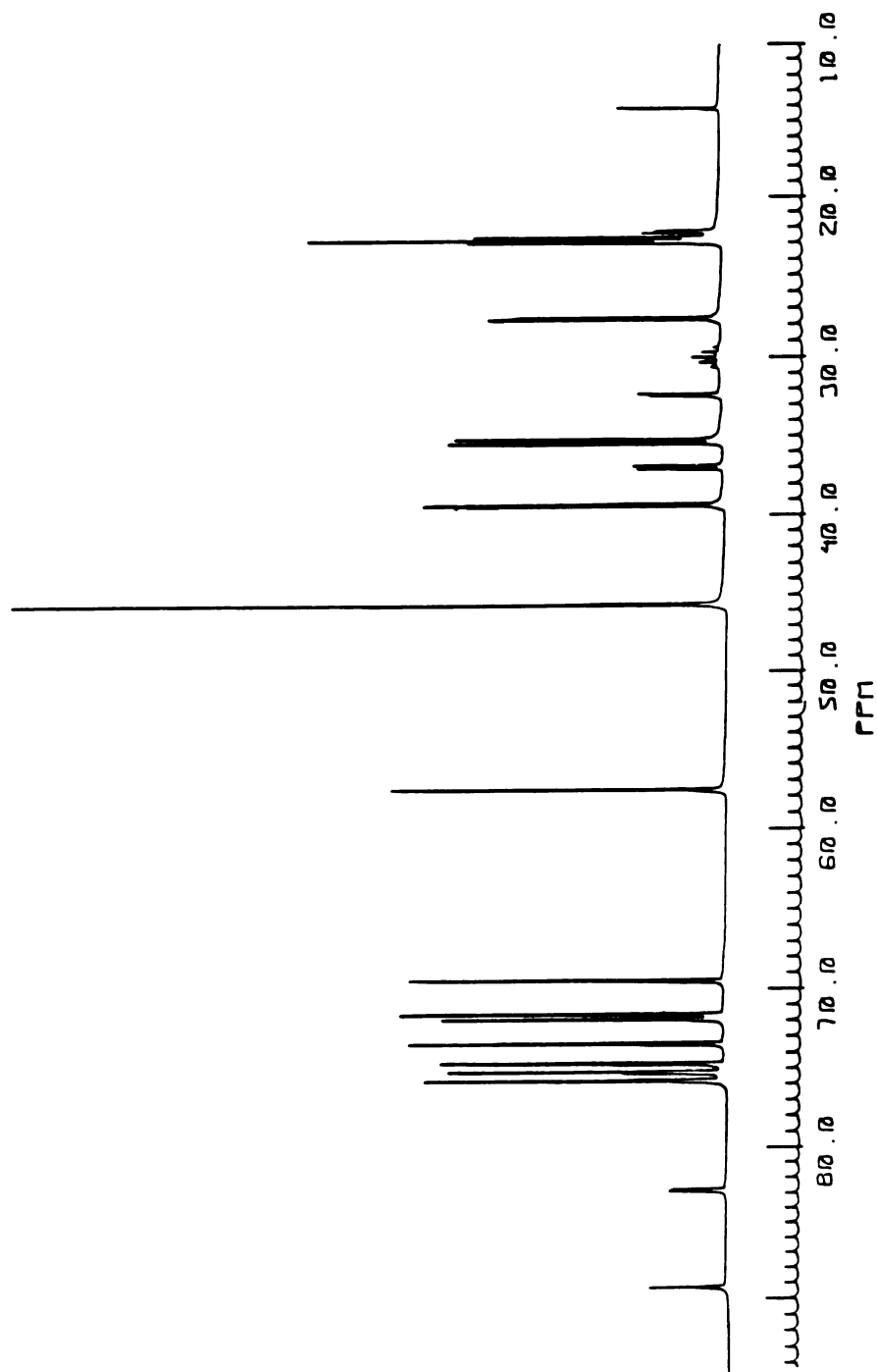


Figure 85. Gated decoupled ^{13}C NMR of compound 65 (R = i-pentyl)

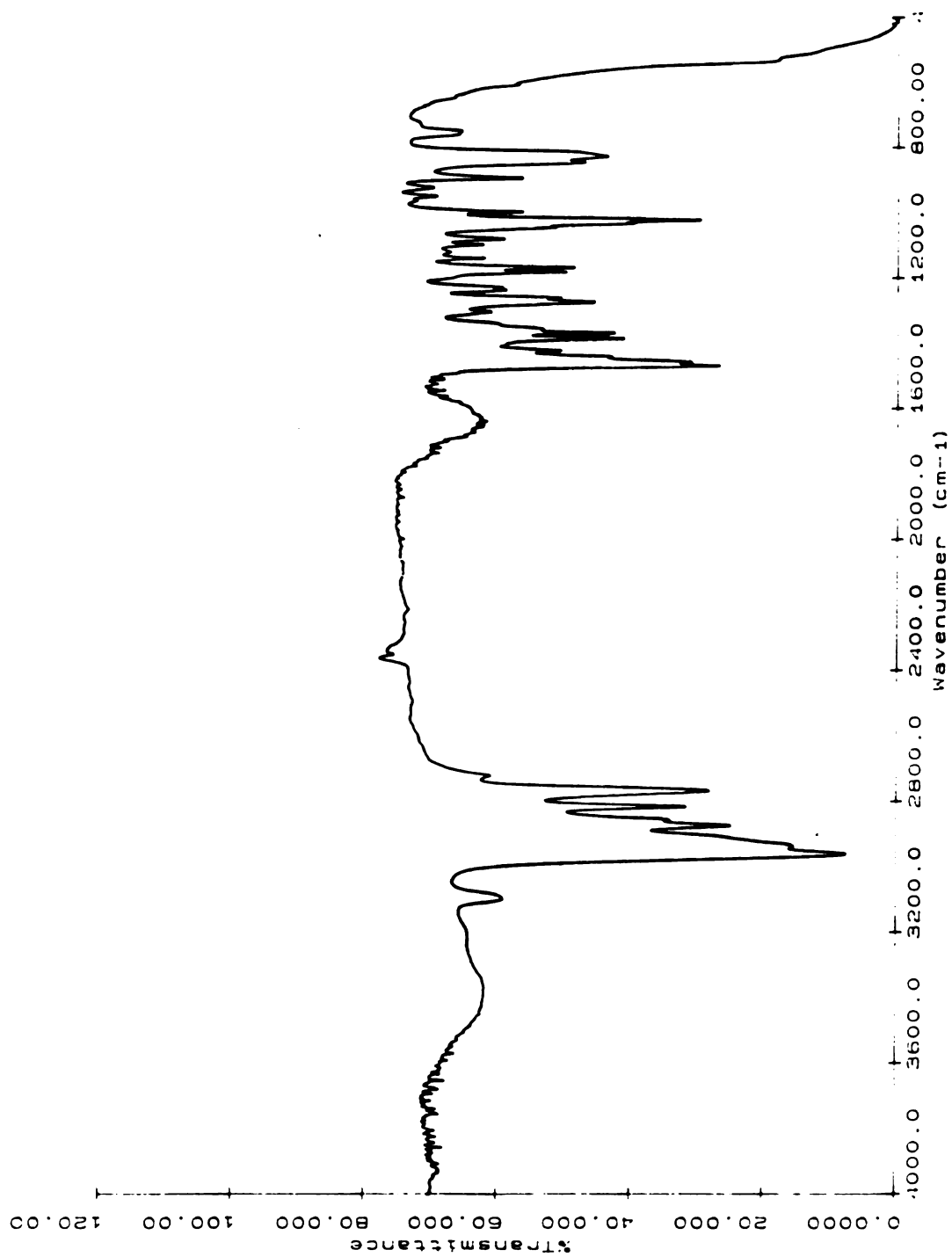


Figure 86. IR spectrum of compound **65** (R = i-pentyl)

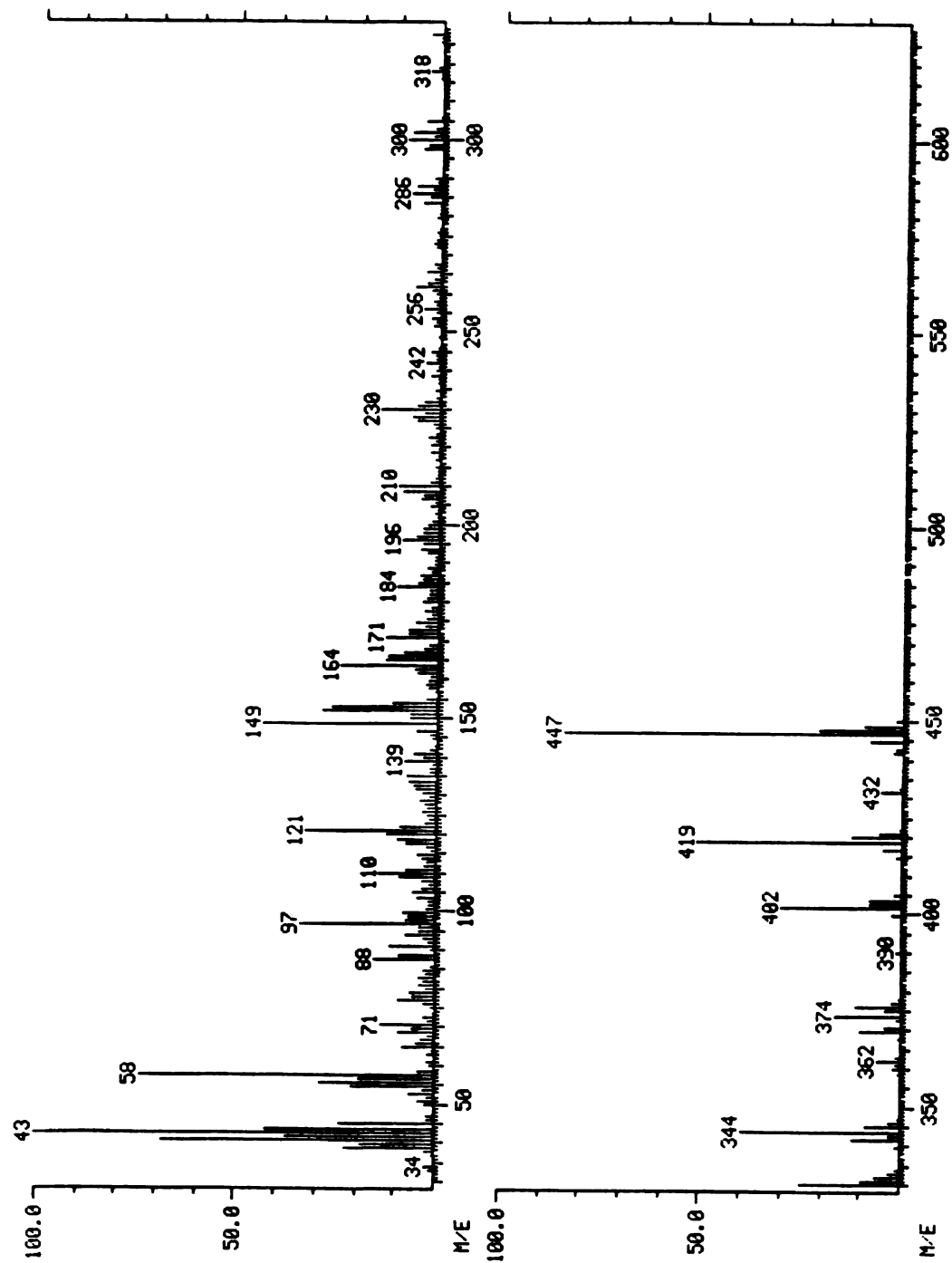


Figure 87. Mass spectrum of compound 65 (R = i-pentyl)

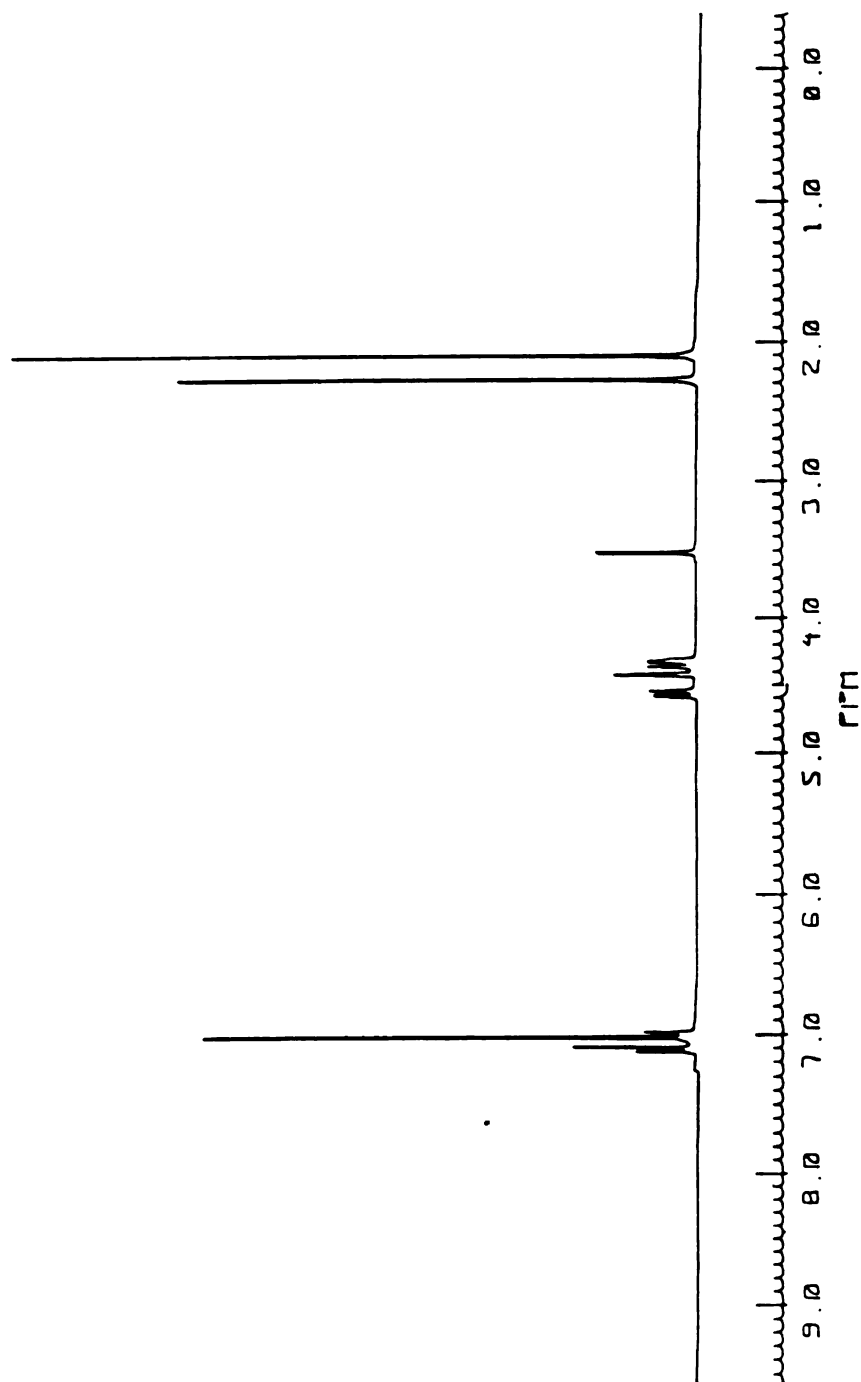


Figure 88. ^1H NMR spectrum of compound 68 (R = 4-tolyl)

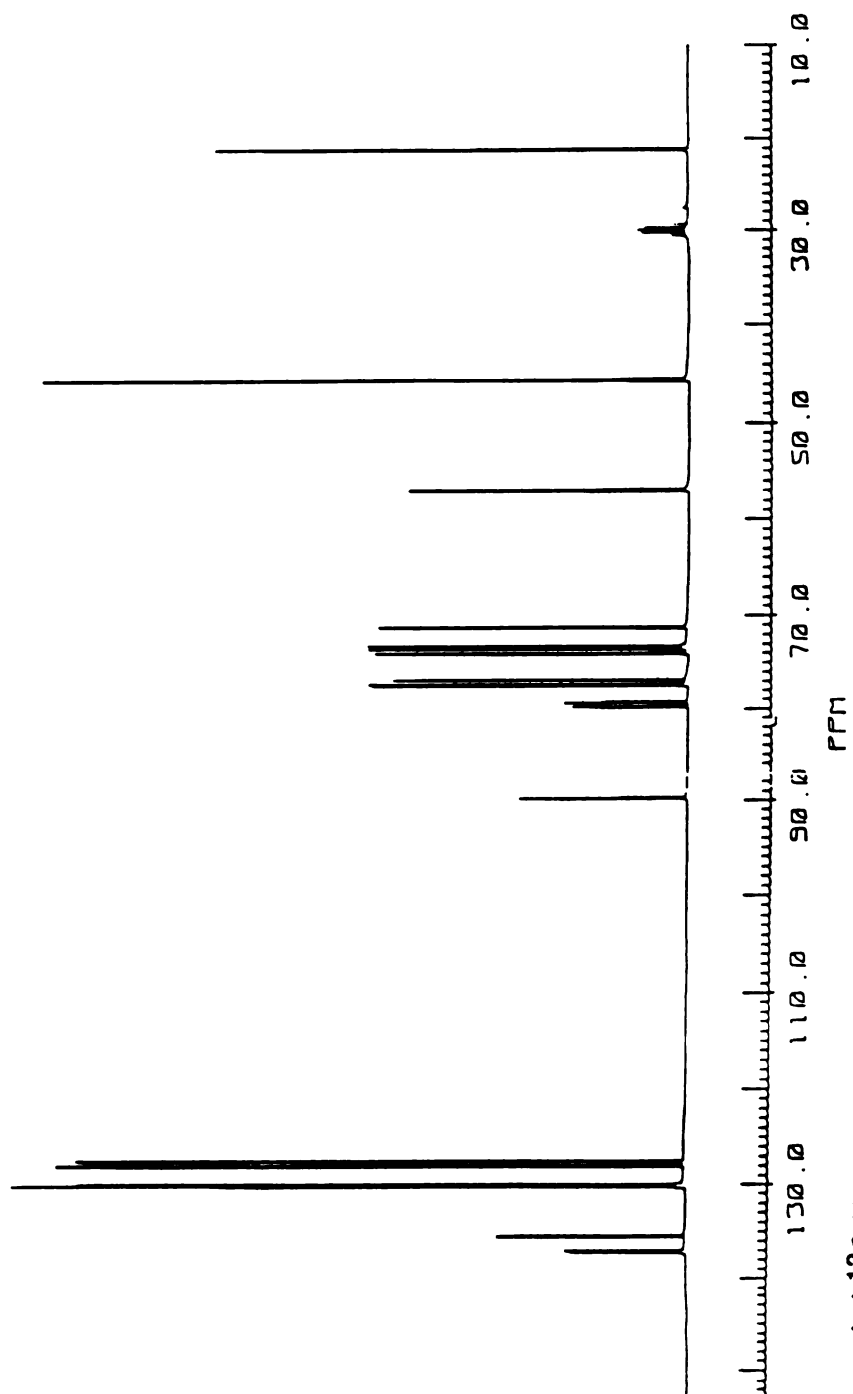


Figure 89. Gated decoupled ^{13}C NMR of compound 68 ($\text{R} = 4\text{-tolyl}$)

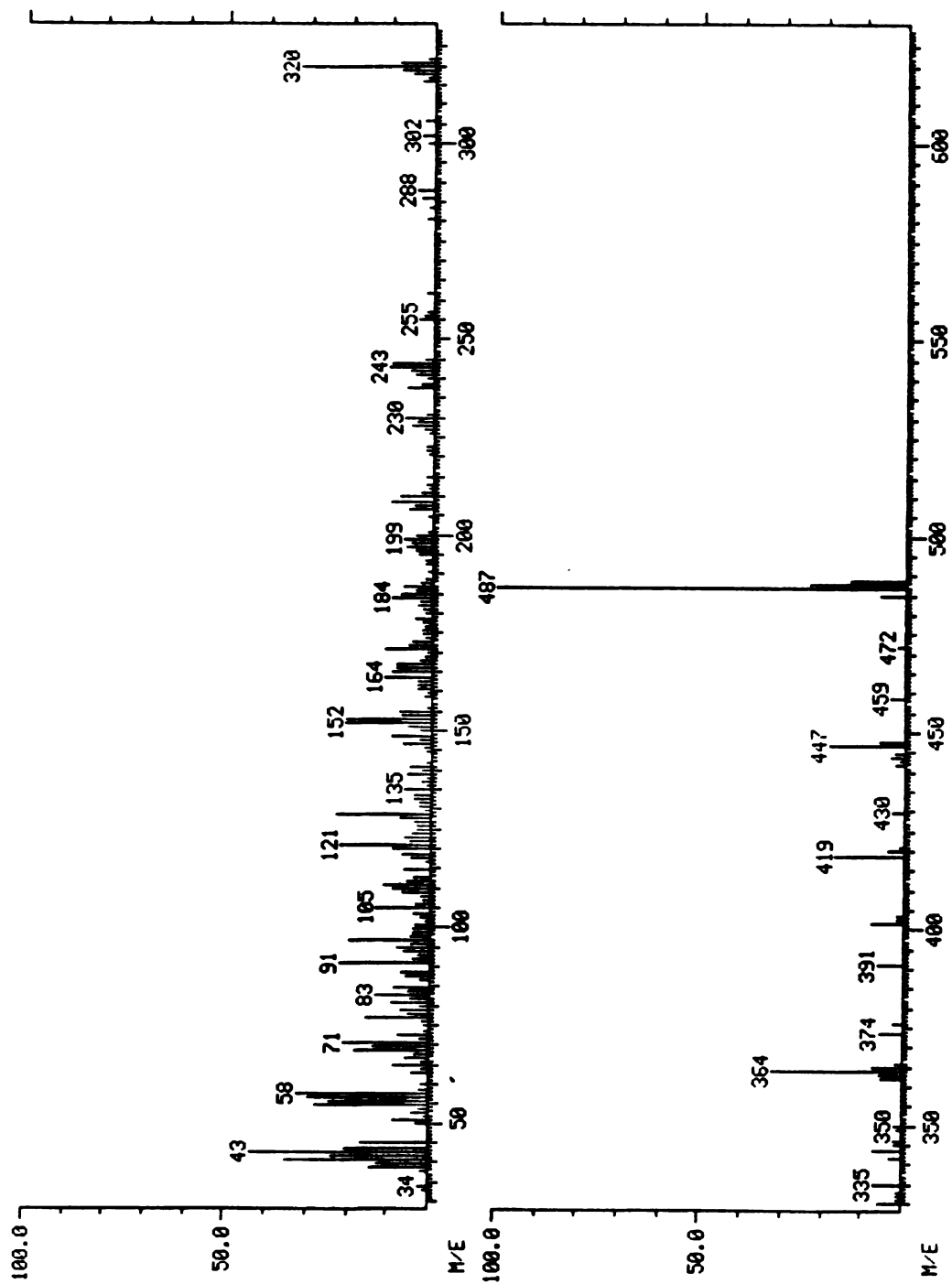


Figure 90. Mass spectrum of compound 68 (R = 4-tolyl)

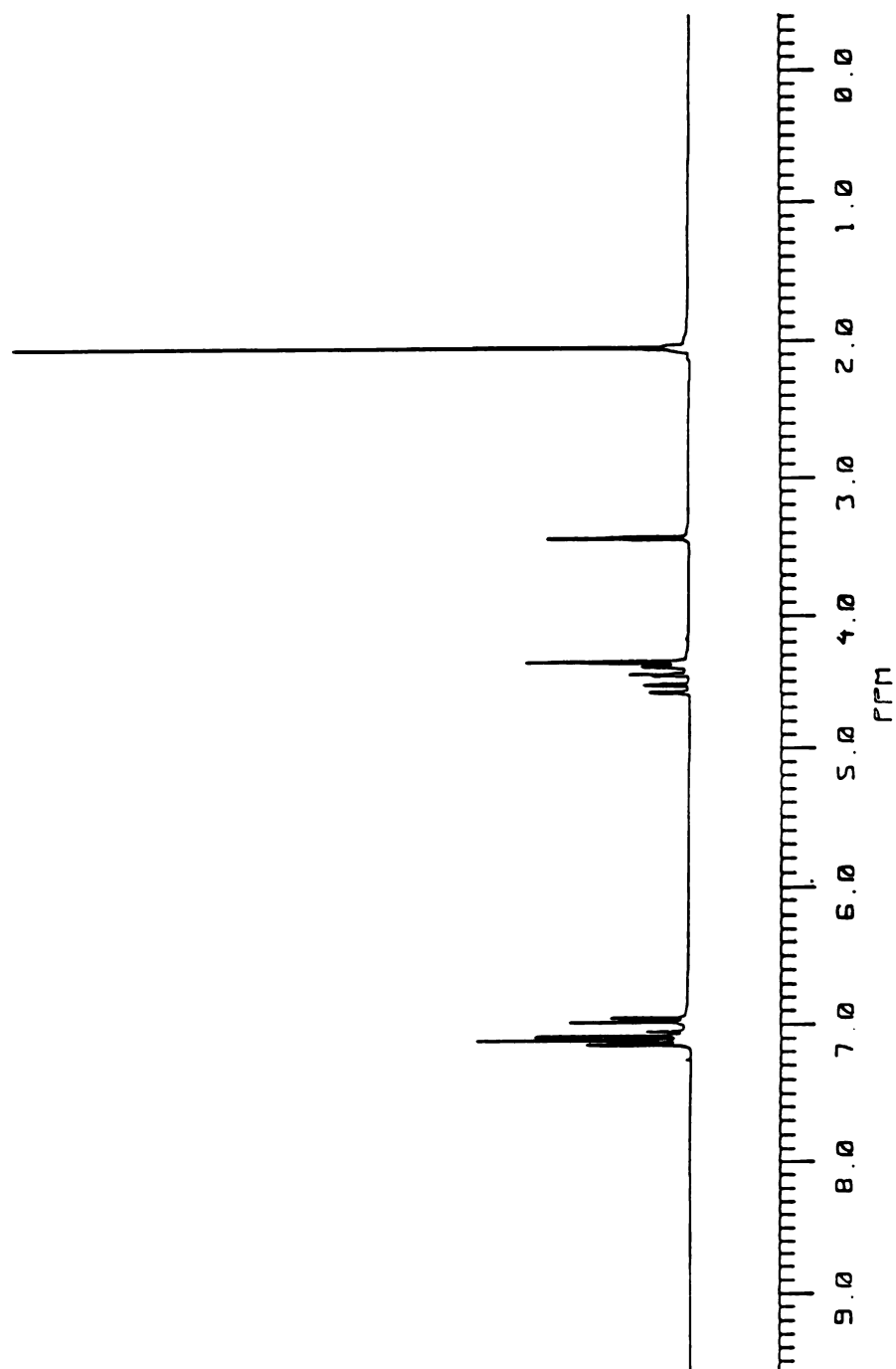


Figure 91. ^1H NMR spectrum of compound 69 (R = 4-Cl-Ph)

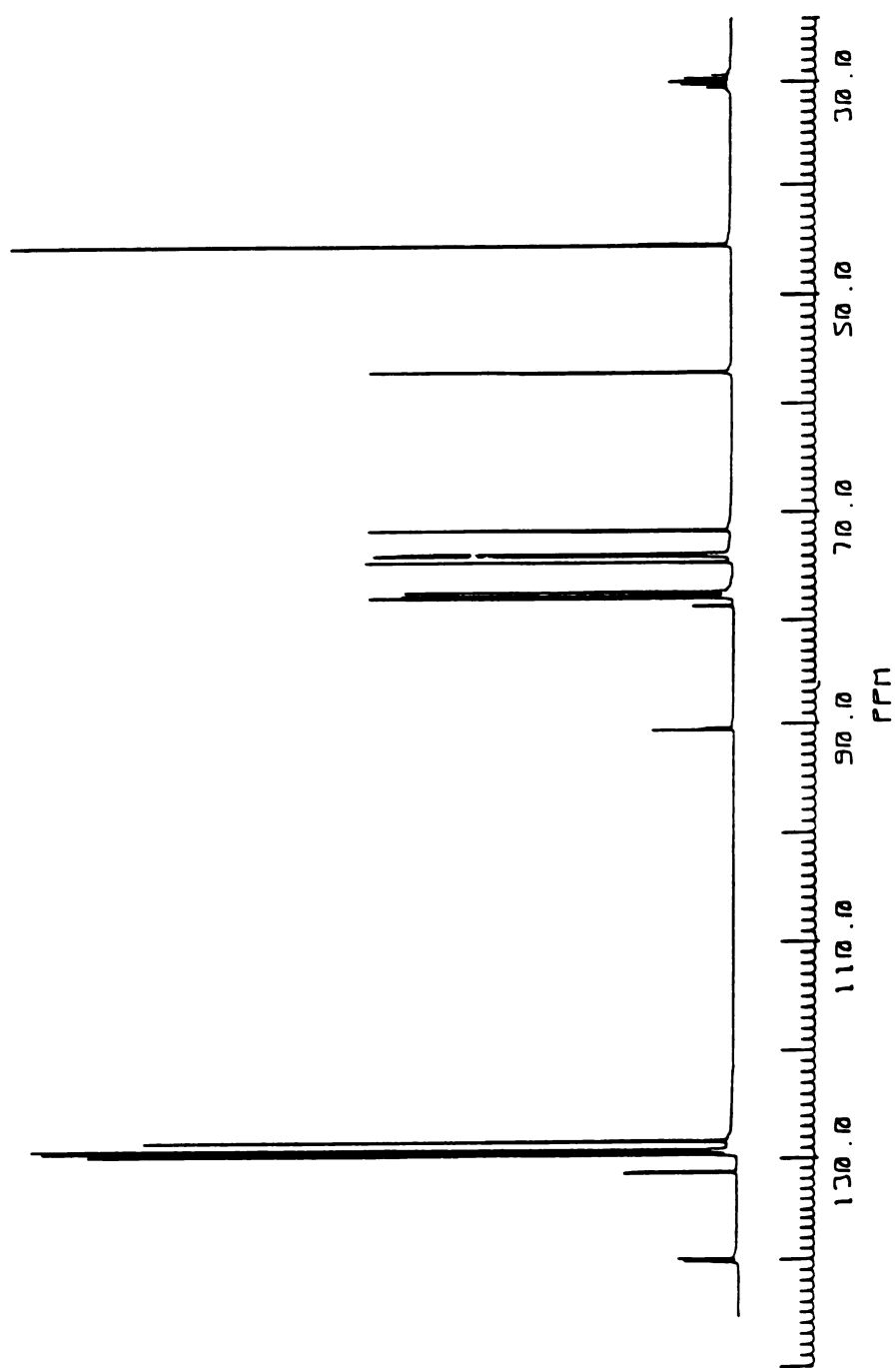


Figure 92. Gated decoupled ^{13}C NMR of compound 69 (R = 4-Cl-Ph)

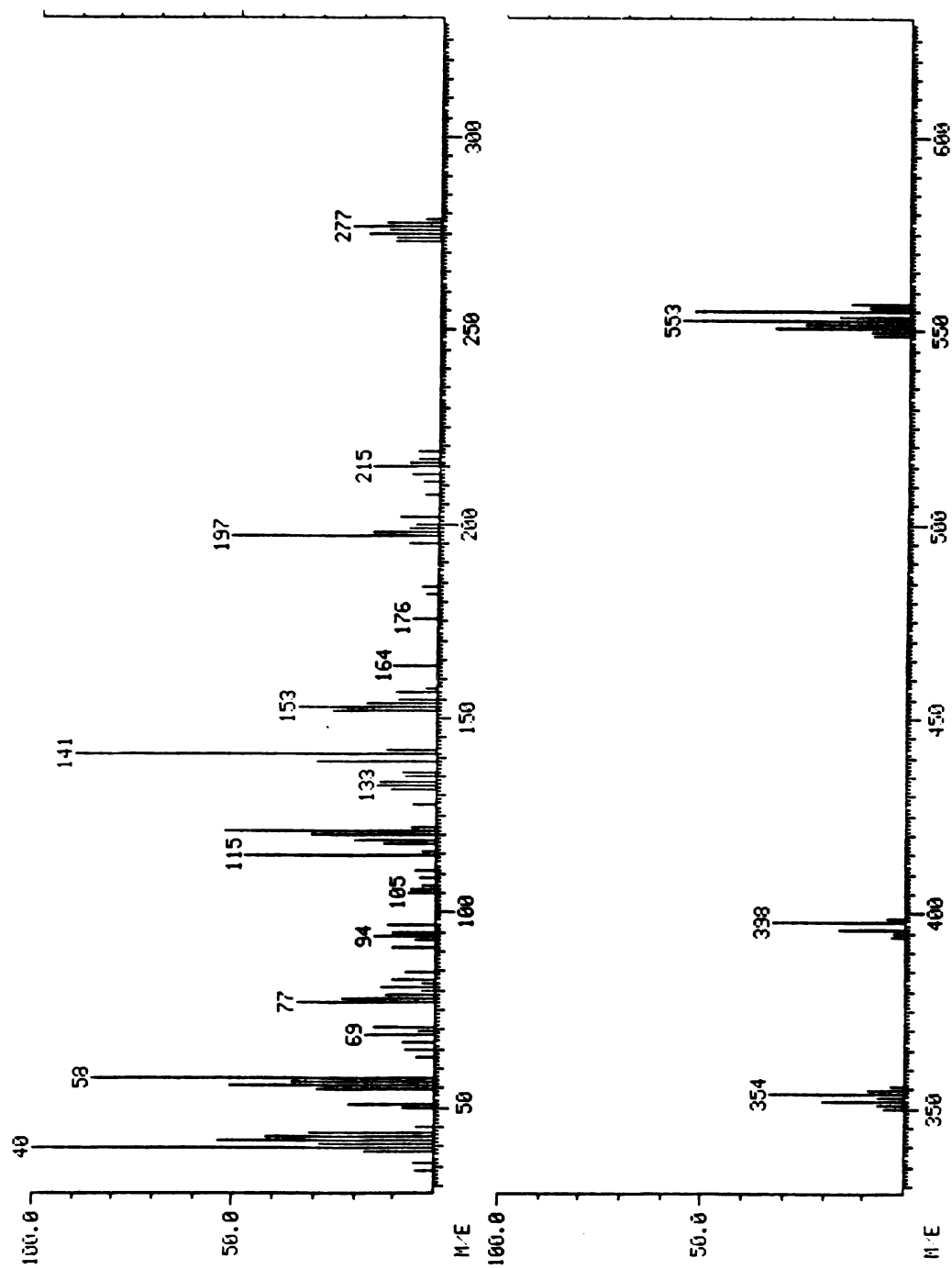


Figure 93. Mass spectrum of compound 70 (R = Ph)

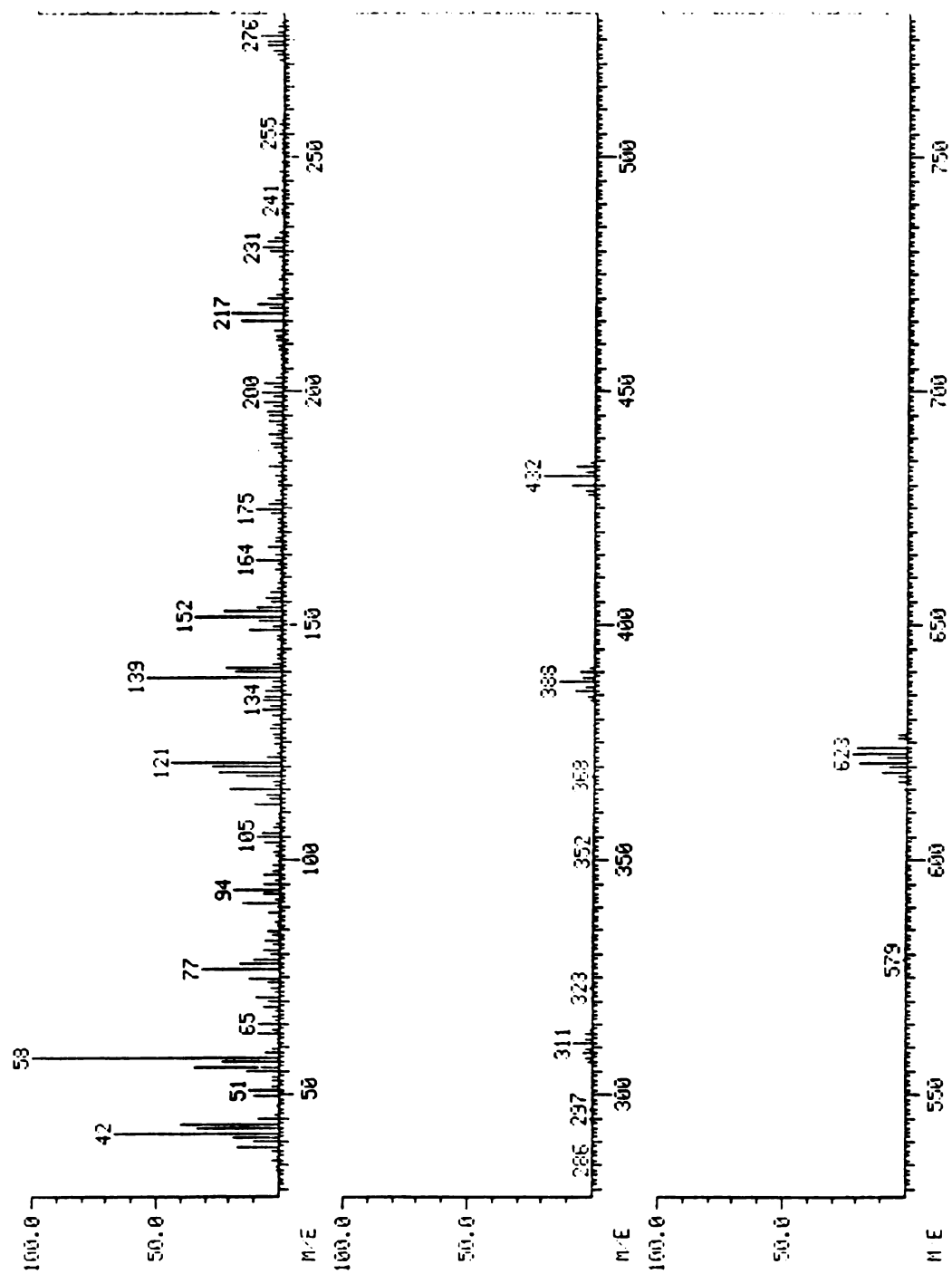


Figure 94. Mass spectrum of compound 71 (R = 4-Cl-Ph)

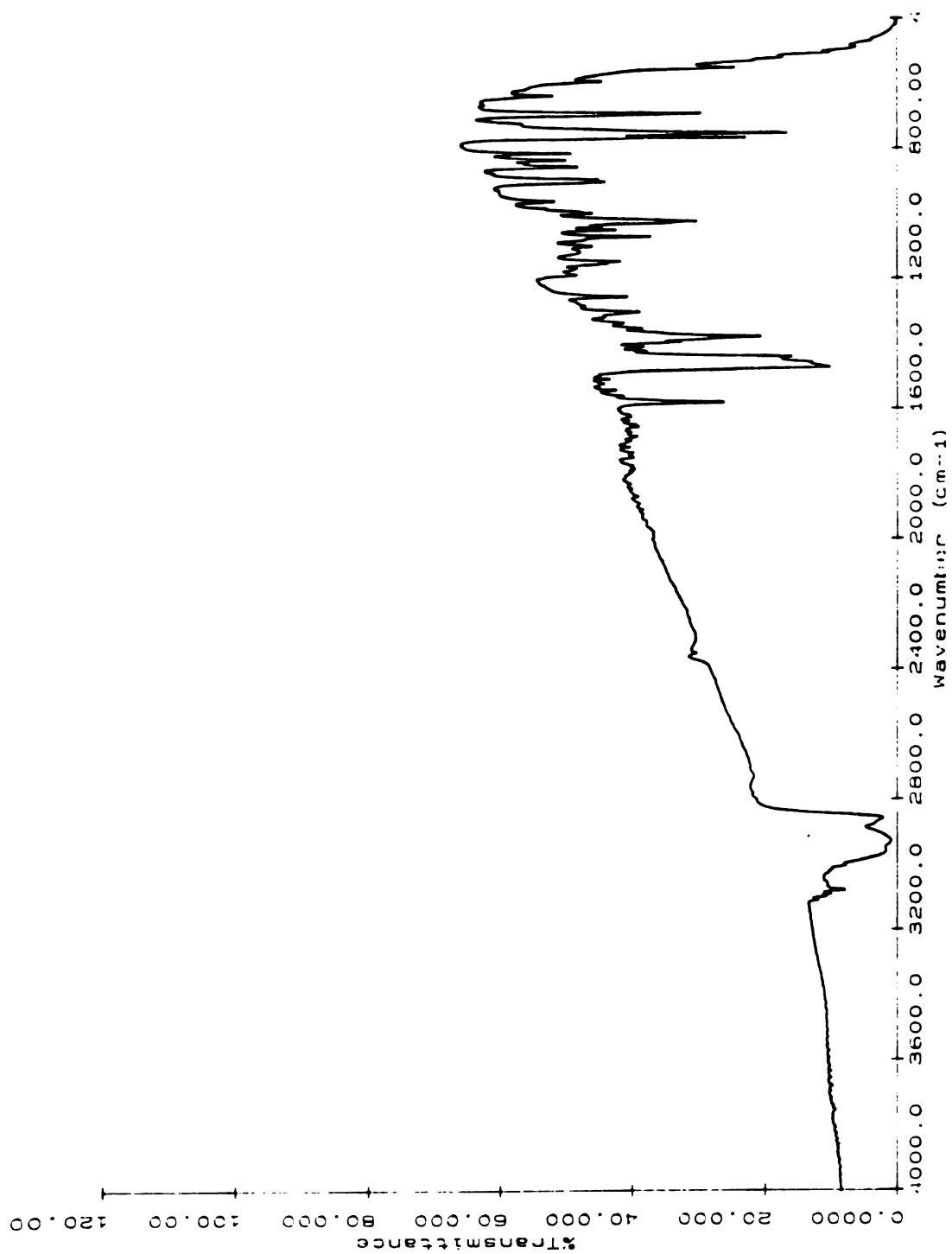


Figure 95. IR spectrum of compound 73 (R = Ph)

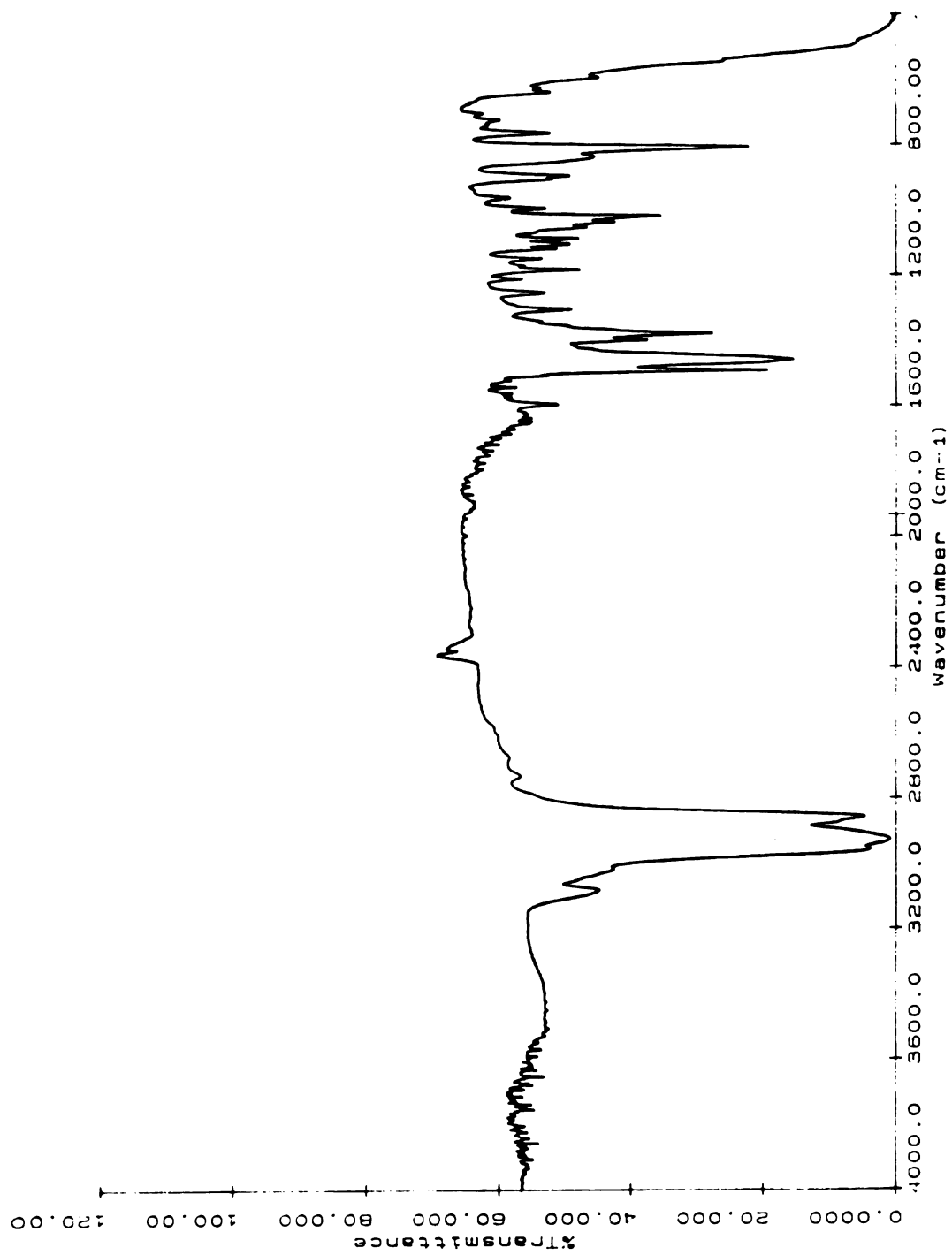


Figure 96. IR spectrum of compound 75

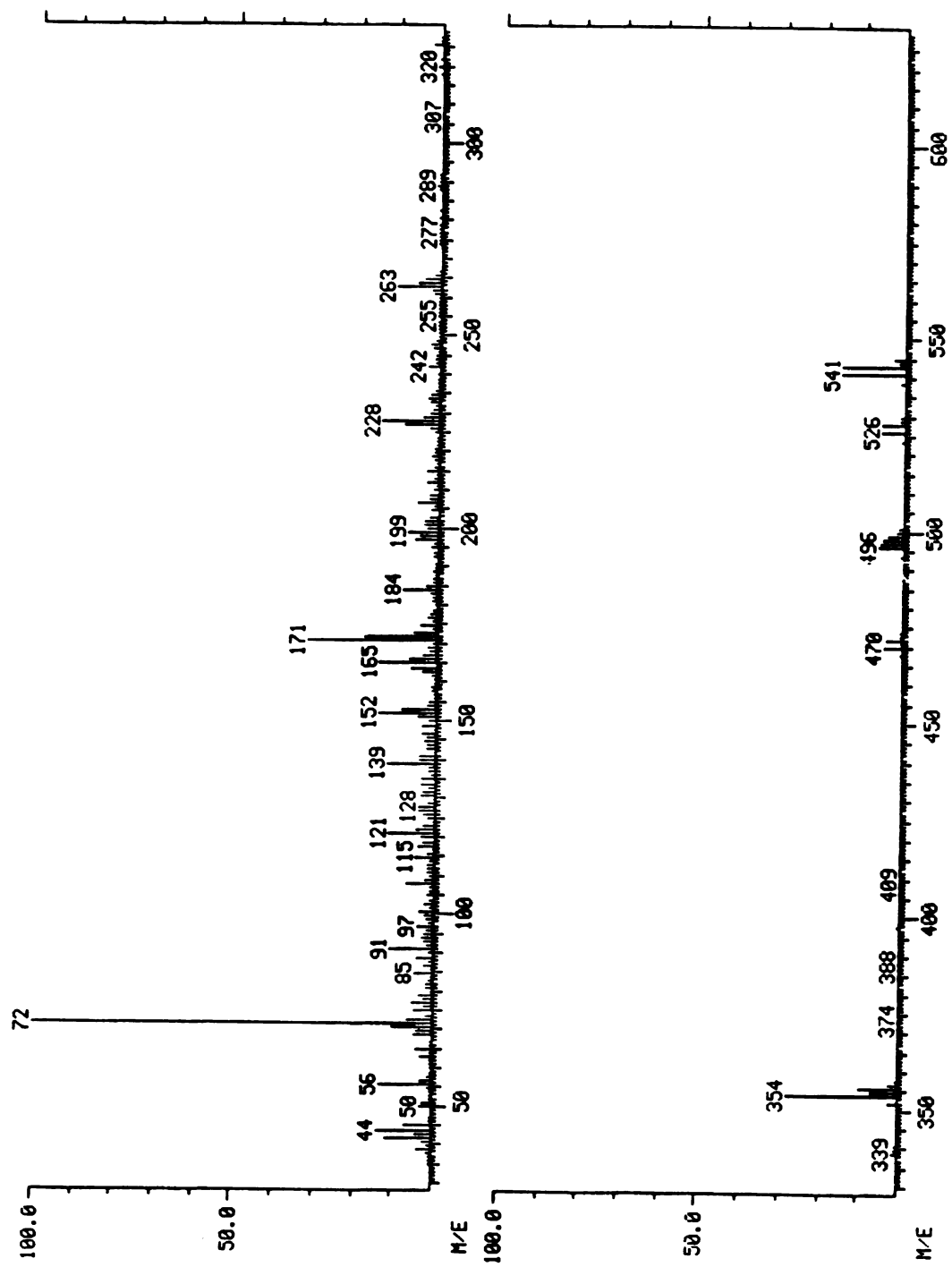


Figure 97. Mass spectrum of compound 76 (R = 4-Cl-Ph)

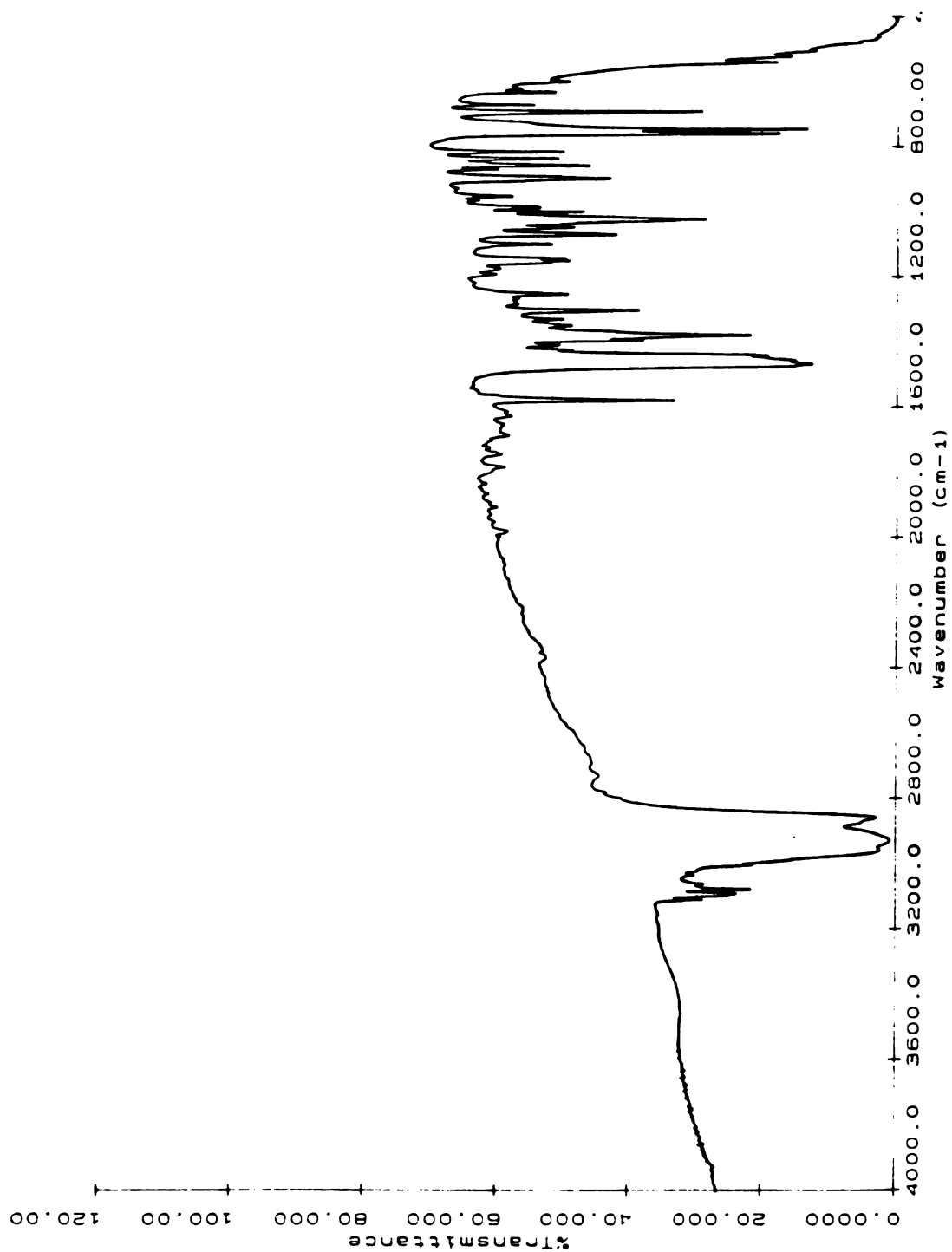


Figure 98. IR spectra of compound 82

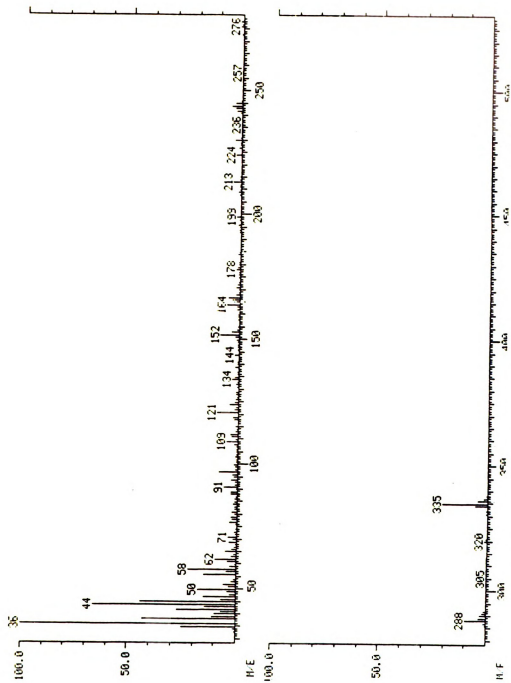


Figure 99. Mass spectrum of compound 83 (R = Me)

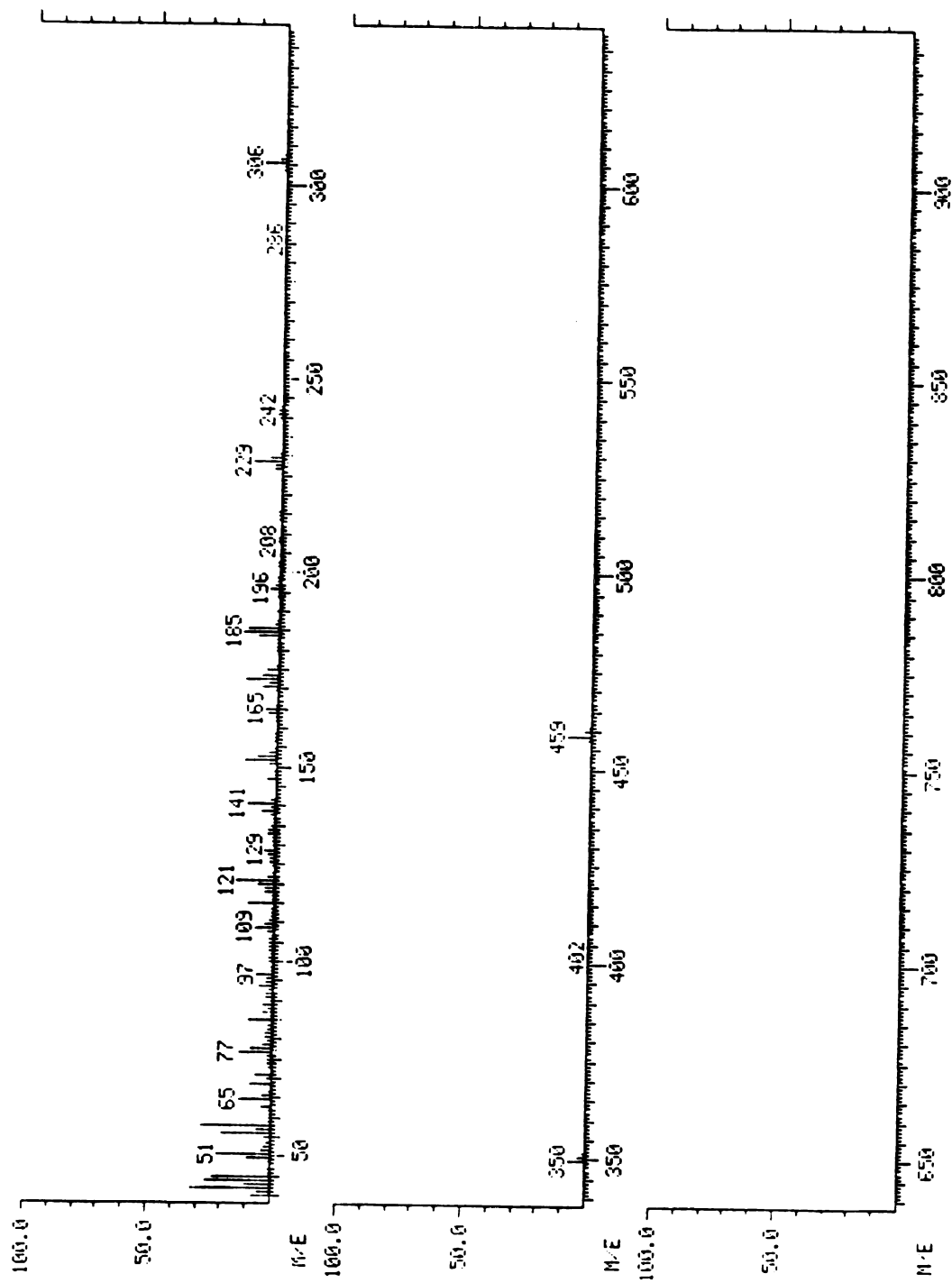


Figure 100. Mass spectrum of compound 87 (R = Ph)

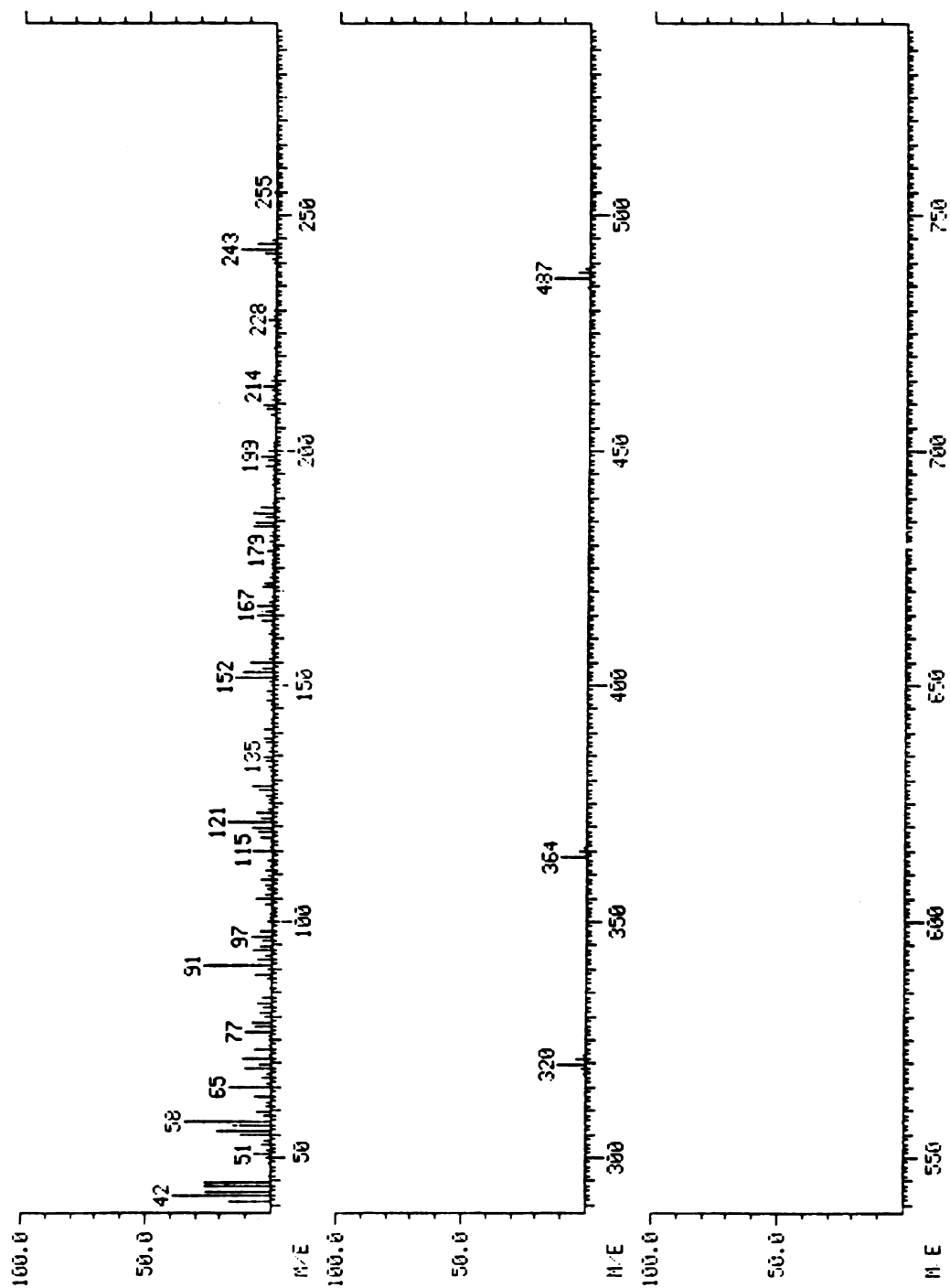


Figure 101. Mass spectrum of compound 89 (R = 4-tolyl)

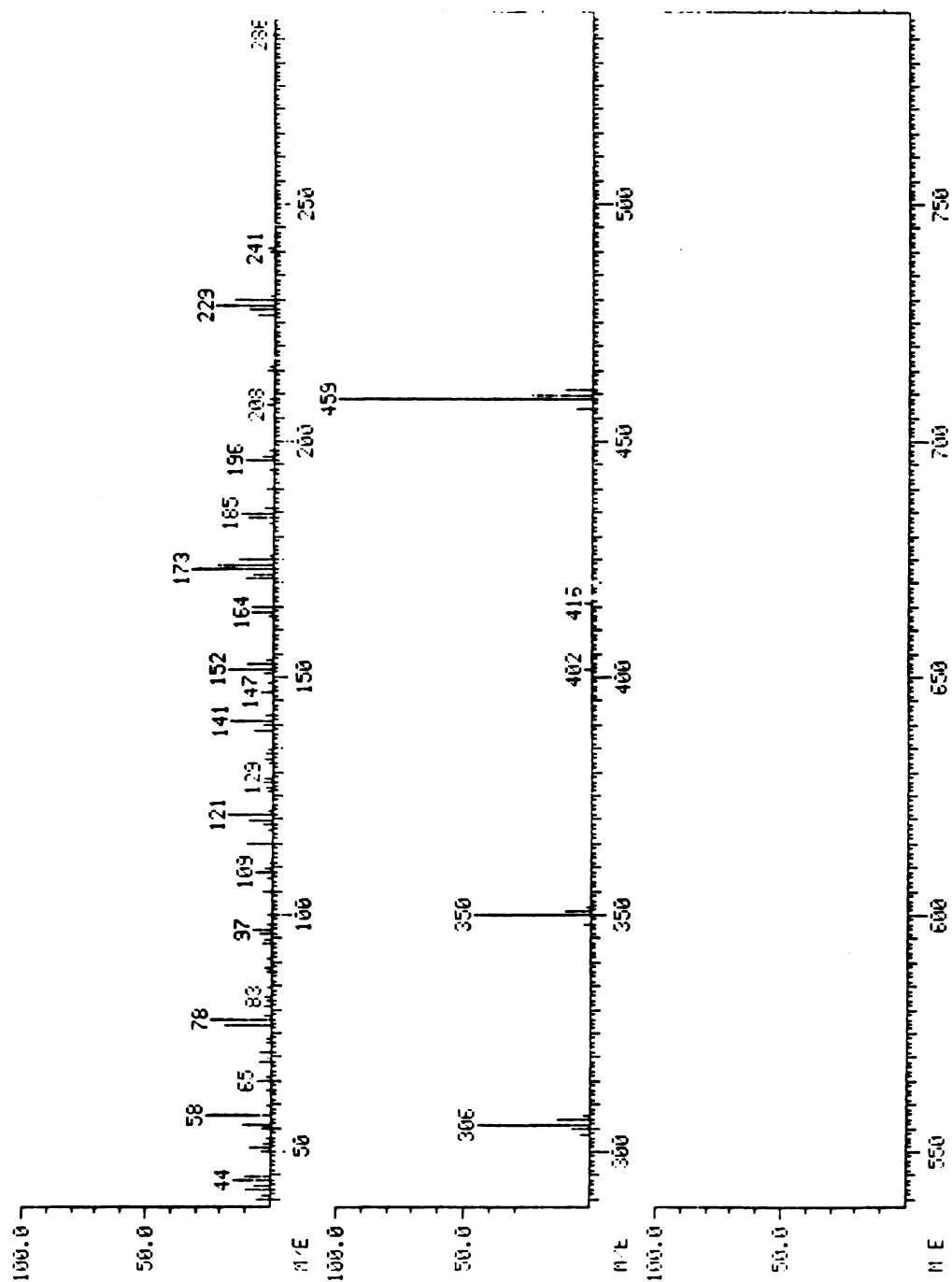


Figure 102. Mass spectra of compound 92 (R = Ph)

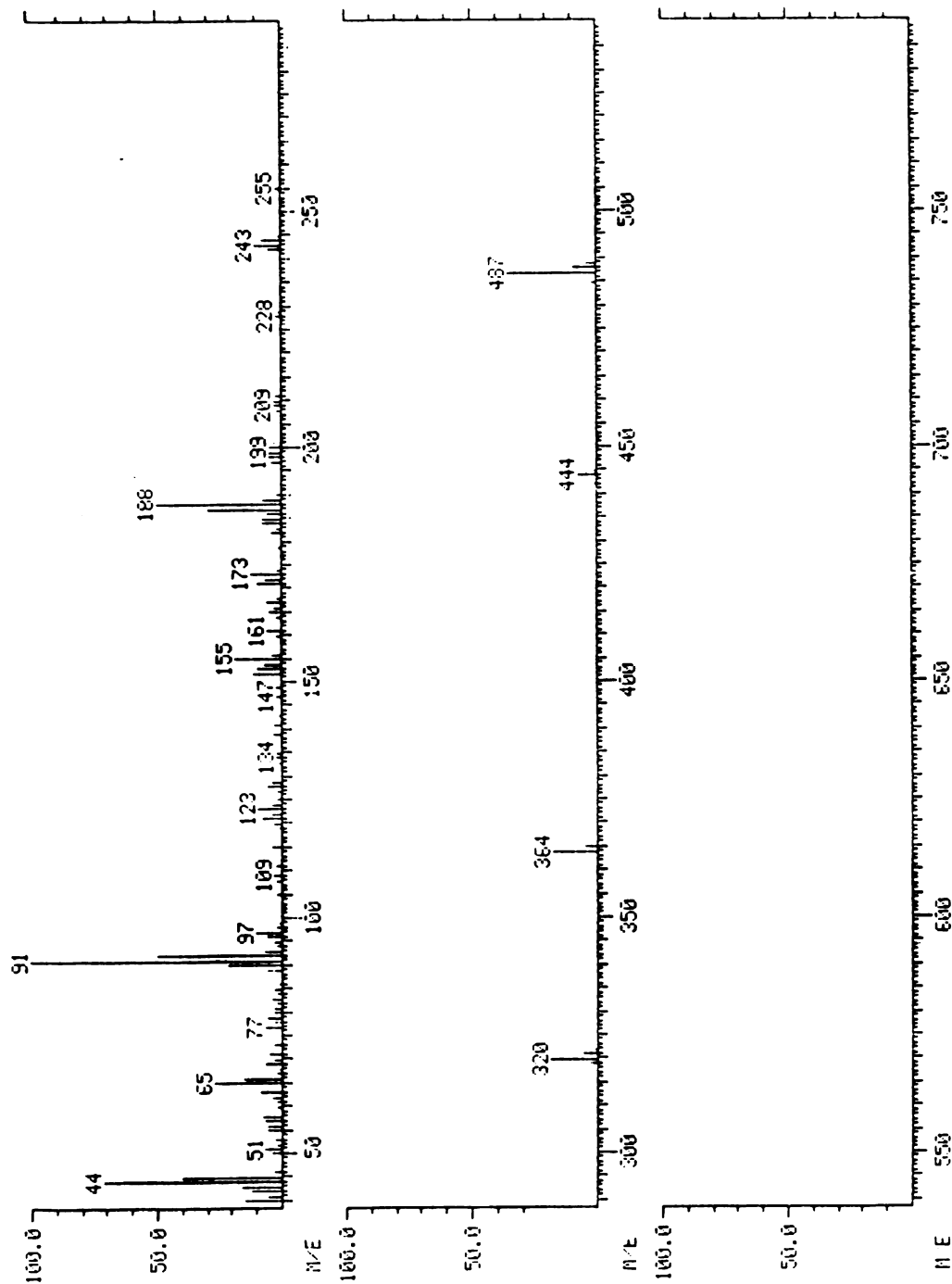


Figure 103. Mass spectrum of compound 95 (R = 4-tolyl)

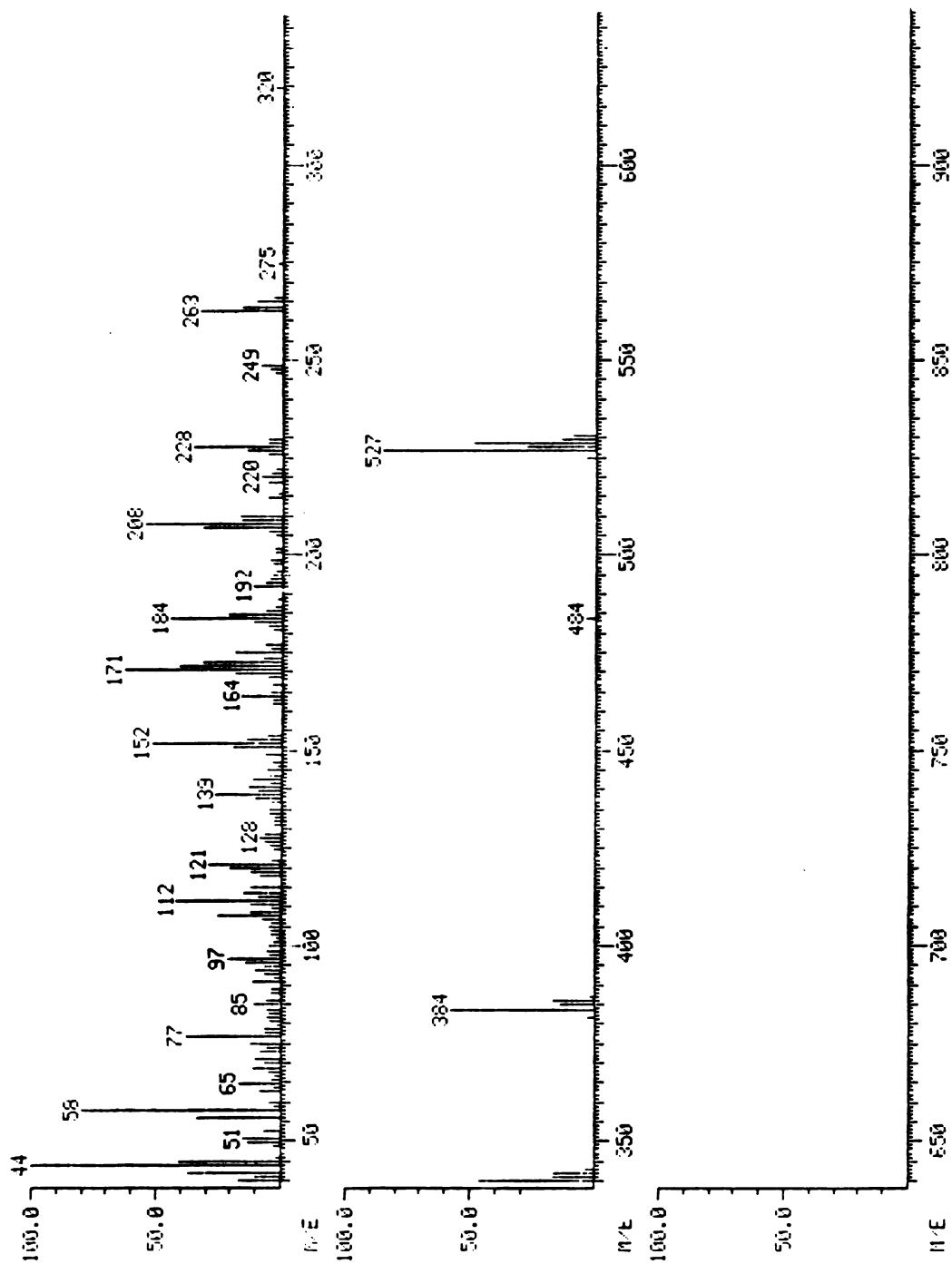


Figure 104. Mass spectra of compound 95 (R = 4-Cl-Ph)

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