NEW FERROCENYL THIO AND ETHERS LIGANDS. PREPARATION, CHARACTERIZATION, AND THEIR PALLADIUM(II) AND PLATINUM(II) COMPLEXES AS CATALYSTS FOR SELECTIVE HYDROGENATION.

BY

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ABSTRACT

NEW FERROCENYL THIO AND SELENO ETHER LIGANDS. PREPARATION, CHARACTERIZATION, AND THEIR PALLADIUM(II) AND PLATINUM(II) COMPLEXES AS CATALYSIS FOR SELECTIVE HYDROGENATION.

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A series of previously unknown ferrocenyl thioethers $(C_5H_3\text{-}1\text{-}CH_2NMe_2\text{-}2\text{-}SR)Fe(C_5H_4\text{-}SR)$, R= Me, Et, n-Pr, i-Pr, n-Bu, s-Bu, t-Bu, i-Pentyl, Ph, Bz, 4-Tolyl and 4-Cl-Ph, have been prepared from the appropriate ferrocene precursors via dilithiation and reactions with RS-SR. The following techniques were used for characterization: ^1H, ^{13}C NMR, IR, MS and elemental analysis. The ferrocenylsulfide derivatives readily chelate with palladium(II) and platinum(II) chlorides to form the heterobimetallic complexes, $(C_5H_3\text{-}1\text{-}CH_2NMe_2\text{-}2\text{-}SR)Fe(C_5H_4\text{-}SR)PdCl_2$, R= Me, Et, n-Pr, i-Pr, Ph, Bz, 4-Tolyl, 4-Cl-Ph and $(C_5H_3\text{-}1\text{-}CH_2NMe_2\text{-}2\text{-}SR)Fe(C_5H_4\text{-}SR)$-

$PtCl_2$, R= Me, Ph, Bz, 4-Tolyl, 4-Cl-Ph. ^1H NMR spectra were obtained for these complexes, IR, MS, and elemental analysis data were also presented. The X-ray crystal structure of $(C_5H_3\text{-}1\text{-}CH_2NMe_2\text{-}2\text{-}SCH_3)Fe(C_5H_4\text{-}SCH_3)PdCl_2$ was also studied.

The chiral ferrocenylthioethers and selenoethers, (R,S)-$(C_5H_3\text{-}1\text{-}CHMeNMe_2\text{-}2\text{-}SR)Fe(C_5H_4\text{-}SR)$, R= Me, Et, n-Pr, i-Pr, n-Bu, s-Bu, t-Bu, i-Pentyl, Ph, Bz, 4-Tolyl, 4-Cl-Ph, (R,S)-$(C_5H_3\text{-}1\text{-}CHMeNMe_2\text{-}2\text{-}SeR)Fe(C_5H_4\text{-}SeR)$, R= Me, Ph, 4-Cl-Ph and (R,S)-$(C_5H_3\text{-}1\text{-}CHMeNMe_2\text{-}2\text{-}SeR)Fe(C_5H_5)$, R= Me, Ph, 4-Cl-Ph also have been prepared and their palladium(II) and platinum(II) complexes, (R,S)-$(C_5H_3\text{-}1\text{-}CHMeNMe_2\text{-}2\text{-}SR)Fe(C_5H_4\text{-}SR)PdCl_2$, R= Me, Et, n-Pr, i-Pr, Ph, Bz, 4-Tolyl, 4-Cl-Ph, (R,S)-$(C_5H_3\text{-}1\text{-}CHMeNMe_2\text{-}2\text{-}SR)Fe(C_5H_4\text{-}SR)PtCl_2$, R= Me, Ph, Bz, 4-Tolyl, 4-Cl-Ph, and (R,S)-$(C_5H_3\text{-}1\text{-}CHMeNMe_2\text{-}2\text{-}SeR)Fe(C_5H_4\text{-}SeR)$, R= Me, Ph, 4-Cl-Ph were prepared. The following techniques were used for the characterization: ^1H, ^{13}C NMR, IR, MS, and elemental analysis.

The palladium(II) ferrocenylsulfide complexes are good selective homogeneous and heterogeneous hydrogenation catalysts for reduction of dienes to monoenes at room temperature, and possible mechanisms are discussed in detail.

I would like to acknowledge the contribution of Professor Carl H. Brubaker, whose professional assistance and inspiration were indispensable.

I would also like to thank Dr. H. A. Eick, Dr. C. K. Chang and Dr. E. LeGoff for many helpful discussions and all the group members, A. A. Naiini, A. Hussein and C. H. Wang for the friendship.

Finally, I wish to express my deepest appreciation and thanks to my parents for their love, inspiration and understanding.

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INTRODUCTION

There has been intense interest and activity in asymmetric synthesis catalyzed by transition metal complexes with chiral ligands. [1-2] Although Emil Fischer mentioned asymmetric synthesis as early as 1894 [3] and Markwald [4] defined it ten years later, it was not until the mid-sixties that two developments offering very attractive approaches toward making such catalysts occured. The first catalyst was introduced by Wilkinson [5] and coworker, chlorotris-(triphenylphosphine)rhodium, 1 [$RhCl(PPh_3)_3$], and it exhibited amazing properties as a soluble hydrogenation catalyst for unhindered olefins.

$$CH_2{=}CH_2 + \underset{\mathbf{1}}{RhCl(PPh_3)_3} \xrightarrow{H_2} CH_3{-}CH_3$$

Homogeneous catalysts had been reported before, but this was the first one that compared in rates with the well-known heterogeneous counterparts. The other development was the discovery by Horner [6] in 1968 of methods for preparing optically active phosphine. The basic strategy was to replace the triphenylphosphine in Wilkinson's catalyst with a known asymmetric phosphine and hydrogenate a prochiral olefin.

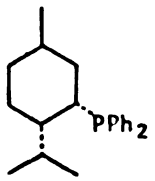
$$RCH{=}CR'R'' \xrightarrow[RhCl[(P(R_1R_2R_3)_3]]{H_2} RCH_2C^*R'R''(H)$$

The validity of this thinking was soon verified by using a rhodium complex of (S)-methylpropyl-phenylphosphine 2 to hydrogenate 2-phenylbutene to 2-phenylbutane in optical yield up to 8%.

The next major step was the discovery by Morrison that the ligand need not contain a chiral phosphorous atom. [7] Indeed, by using neomenthyldiphenylphosphine 3 (NMDPP) and rhodium, they obtained a suprising improvement in optical yield.

At about the same time, even more promising results were reported by Kagan and Dang. [8] Reasoning that stereoselectivity should be improved by conformational restriction around the metal, they have achieved great success with 2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis (diphenylphosphine)butane 4 (DIOP), which was prepared relatively easily from tartaric acid. The DIOP has been successfully applied in various kinds of catalytic asymmetric syntheses, e.g., hydrogenation of olefins [9-13] and ketones, [14,15] hydrosilylation of ketones [16-19] and imines, [9a] hydroformylation, [20-22] Grignard cross-coupling [23,24] and allylic alkylation.[25] The neomenthyldiphenyl-phosphine (NMDPP) [26,27] and its diasteromeric isomer 5 (MDPP), [27] introduced by Morrison et al., have been used for the hydrogenation of acrylic acids to give optical yield up

to 62%. [26,28] Meanwhile, they also examined a bisphosphine ligand 6 (CAMPHOS), which is derived from camphoric acid.[28]



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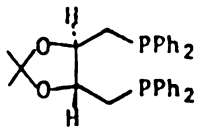

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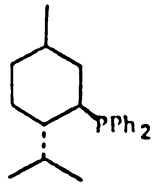

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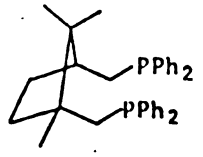

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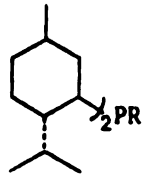
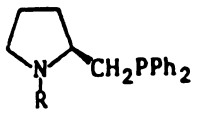
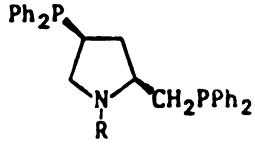
Dimethylphosphines 7 have been synthesized and used as chiral ligands for a nickel catalyzed cooligomerization of olefins. [29] Optically active amino acids, proline and hydroxyproline, have been employed as chiral sources of phosphine ligands. They are (S)-2-diphenylphosphinomethyl-pyrrolidine 8 [30] and (2S,4S)-4-diphenylphosphino-2-diphenyl-phosphinomethylpyrrolidines 9, [31] respectively, the latter even affording enantiomeric excess of 83-91% in the hydrogenation of α-acylamino cinnamic acids. 2-2'-bis (diphenylphosphinomethyl)-1,1'-binaphthyl 10 (NAPHOS) [32] whose chirality is due to binaphthyl axial chirality, has been prepared and used as a ligand in several transition metal complexes catalyzed asymmetric reactions.

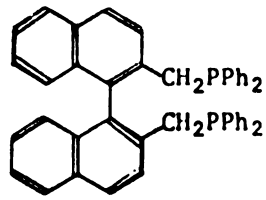




R=H, Me



R=H, $COOBu^t$



7 8 9 10

By this time, the requirements for efficient asymmetric catalysts were becoming clear. The crucial discoveries were:

a. Asymmetric catalysis could be accomplished in practical, optical yields by using metal complexes of phosphines chiral at the phosphorous or carbon center.

b. Best results were obtained when the catalytic complex was tightly structural. Thus, bidentate ligands, especially if conformationally restricted, were generally most desirable.

c. The best substrates were those with one or preferably more highly polar functional groups. Unfunctionalized alkanes gave poor optical yields. Subsequent work has concentrated on the exploitation of this breakthrough.

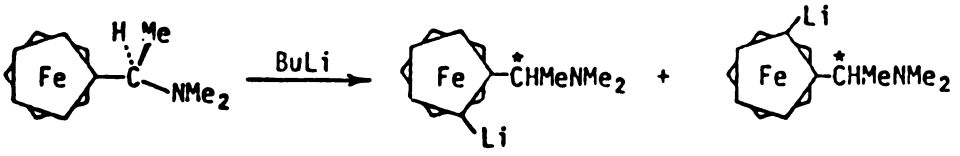
One of the most significant problems in studies on the catalytic asymmetric synthesis was to develop a chiral ligand that will enable the catalyst for a given reaction to be as efficient in stereoselectivity as possible, and considerable efforts have been devoted to searching for new chiral phosphine ligands. Since the catalytic action of

coordination complexes is related to the formation and the splitting of metal-substrate bonds, [33] the most efficient asymmetric synthesis should be achieved when complexes containing an "asymmetric" or "chiral" metal atom are used, [34-36] and would minimize the distance between the inducing asymmetric center and the asymmetric moiety being formed. Unfortunately, "chiral metal atoms" are generally not configurationally stable at room temperature, and only in a relatively few cases could complex, containing as the sole chirality center the metal atoms, be isolated as pure enantiomers. [37] In order to improve the configurational stability, tightly bonded ligands (such as the cyclopentadienyl group) must be used. [38] However, this generally lowers the catalytic activity of the complex by a great extent. Despite some interesting attempts, [39-41] conformational analysis of transition metal complexes is still in its infancy and very little is known about the electronic and steric effects on which the stability of diastereomeric organometallic complexes and their conformers are dependent.

In 1974, Kumada introduced a new type of phosphine ligands with planar chirality which arises from introduction of phosphino groups into the α-ferrocenylethyldimethylamino system [42] and their use as chiral ligands in some of the transition metal complex catalyzed asymmetric reactions.

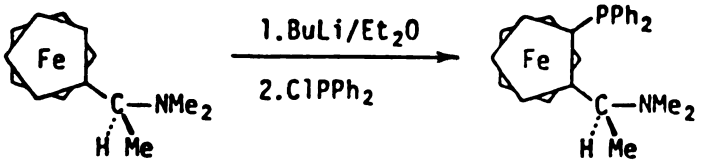
Chiral ferrocenylphosphines are readily prepared by way of lithiation of optically resolved α-ferrocenylethyl-di-

methylamine [FA], the lithiation of (R)-FA was previously reported by Ugi and coworkers [42] to proceed with high stereoselectivity to give preferentially (R)-α-[(R)-2-lithioferrocenyl]ethyldimethylamine.



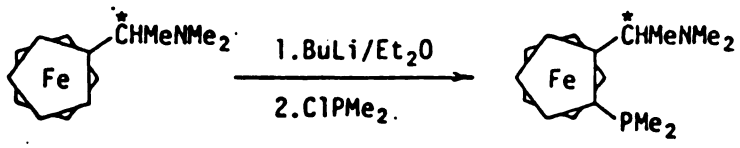
(R)-FA (R)-(R) (96%) (R)-(S) (4%)

Reaction of (S)-FA with a slight excess of butyllithium in ether, followed by treatment with chlorodiphenylphosphine to give a new type of phosphine chiral ligands, (S)-α-[(R)-2-diphenylphosphinoferrocenyl)ethyldimethylamine (PPFA).



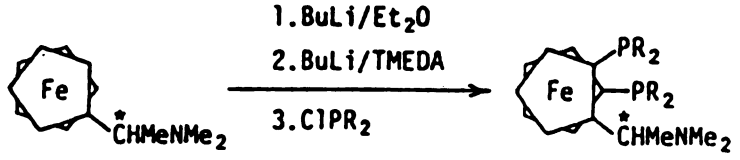
(S)-FA (S)-(R)-PPFA

Similarly, (R)-α-[(S)-2-dimethylphosphinoferrocenyl]-ethyldimethylamine (MPFA) was obtained in 31% yield with reaction of (R)-FA and chlorodimethylphosphine.



(*R*)-FA (*R*)-(*S*)-MPFA

The stepwise lithiation of (S)-FA with butyllithium in ether and then with butyllithium/ N,N,N′,N′-tetramethylethylenediamine (TMEDA) in ether led to the introduction of two diphenylphosphino groups, one onto each of the cyclopentadiene rings to give (S)-α-[(R)-1′,2-bis(diphenylphosphino]ethyldimethylamino (BPPFA) in 40% yield. [43] The analogous bis(dimethylphosphino) derivative (BMPFA) was also obtained similarly.



(*S*)-FA R=Ph, (*S*)-(*R*)-BPPFA
R=Me, (*S*)-(*R*)-BMPFA

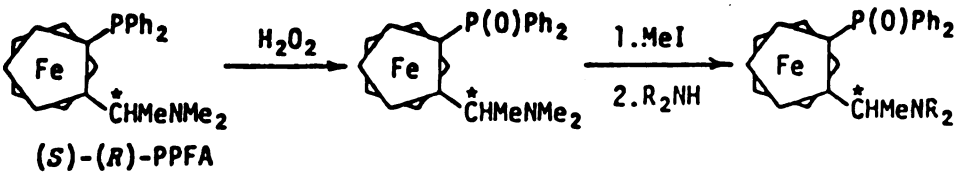
Kumada and coworker also tested some asymmetric hydrogenations [44] by use of several chiral ferrocenylphosphine ligands. (S)-(R)-BPPFA exerted an effective chiral influence in the hydrogenation of α-acetaminoacrylic acid substrate. In the presence of $[Rh(1,5\text{-hexadiene})Cl]_2$ and

(S)-(R)-BPPFA in a 1:2.4 ratio, the hydrogenation of α-acetamidoacrylic acid was completed in 20 hours at 50 atm initial hydrogen pressure and room temperature in 86-94%.

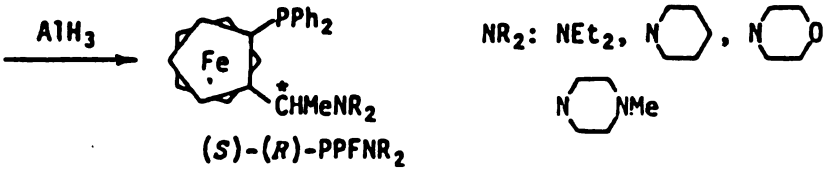
Also, various kinds of chiral ferrocenylphosphines, which have both planar and central elements of chirality and a functional group on the side chain, have been used as ligands for nickel or palladium complex catalyzed asymmetric cross-coupling reactions. Besides, asymmetric catalytic hydrosilylation of ketones [46,48] and asymmetric hydrogenation of prochiral carbonyl compounds were also examined by using some chiral ferrocenylphosphines as chiral ligands catalyzed with rhodium metal.

In their studies, Kumada ascribed the high ability of the chiral ferrocenylphosphines not only to their highly asymmetric structure, but also to the attractive interactions between functional groups on the substrate and on the chiral ligands coordinated to the transition metal catalyst. And it was found that the ferrocene planar chirality played a more important role than the central chirality. Also the dimethylamino group on the cyclopentadienyl ring is the first requisite for the high stereoselectivity. Furthermore, the stereoselectivity was not affected by introduction of substituents onto the diphenylphosphino group of the ligand, but was strongly affected by changing the steric bulkiness of the secondary amino group on the ferrocenylphosphine side chain.

One of the advantages of chiral ferrocenylphosphines was ascribed to easy replacement of the dimethylamino group in PPFA by other dialkylamino groups, achieved first by converting the phosphine to the phosphine oxide, then by quaternization of the nitrogen atom, followed by reaction with a secondary amine and finally by reduction with alane. The resulting diethylamino, piperidino, morpholino, and N-methylpiperazino derivatives have been thus prepared in 50-70% overall yield.

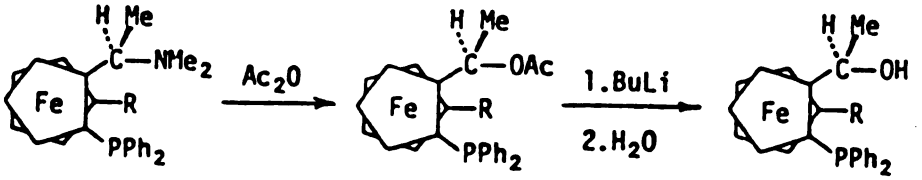


(*S*)-(*R*)-PPFA



(*S*)-(*R*)-PPFNR$_2$

Also, a hydroxy group could be introduced into the side chain of the chiral ferrocenylphosphines by the following scheme.



R=H	(*R*)-(*S*)-PPFA	(*R*)-(*S*)-PPFOAc	(*R*)-(*S*)-PPFOH
R=PPh$_2$	(*R*)-(*S*)-BPPFA	(*R*)-(*S*)-BPPFOAc	(*R*)-(*S*)-BPPFOH

These chiral phosphines are unique in that they all contain both planar and central elements of chirality and also a functional group such as amino or hydroxyl that can interact attractively with an appropriate functional center of the substrate which interacts with the chiral catalyst.

Results should be of interest in the dependence of structural influence on catalytic activity. However, catalytic properties for this kind of structurally different chiral ferrocenylphosphine ligands with transition metals have remained unknown since no such studies has been reported.

The investigation of asymmetric catalysis by transition metal complexes has been carried out up to now by using metal complexes containing chiral ligands. In Table 1 the use of the most common optically active ligands is reported. As shown in Table 1, the ligand most used in asymmetric catalysis is DIOP, less frequently used are phosphines containing chiral phosphorous atoms. [26,42] Nitrogen compounds, particularly alkaloids [49] and Schiff bases [50] have been used also with less encouraging results. As for the other types of ligands, phosphites [51] containing chiral groups and chiral alkoxy groups [52] also have some significance. There is increasing interest for the latter in particular. [53] Other asymmetric ligands which are seldom used are carboxylic acids, [54] amines, [55] amides, [56] ethers, [57] dioximes [58] and sulfoxides. [59] The highest extent of asymmetric induction has been obtained in hydrogenation when

Table 1. Optically active ligands most used for asymmetric catalytic reactions.[a,b]

Reaction \ Asymmetric Ligand	DIOP and analogous	$P^*(\;)(\;)$	$P(\;)(\;)-R^*$	$P(\;)(\;)-OR^*$	Ferrocenyl phosphines	Alcaloids	Shiff bases	Alkoxy groups
Reduction	20	13	5	1	2	9		1
Hyrdocarbonylation	12	3	2				1	
Hydrosilylation	11	13	2		1			
Cross-coupling	3				1			
Hydrovinylation			3					
Substitution (Si)	4							
Isomerization		1						1
Hydrogen shift							3	
Polymerization								3
Oligomerization			2					1
Dehydrogenation			3					
Carbenoid reaction							6	
Hydrogen transfer							2	
Dehydrohalogenation							1	
Hydroamination[c]				1				

[a] Figures correspond to the number of published papers in which the use of each asymmetric ligand has been described.
[b] Data are based on the most significant scientific papers and patents appeared up to the end of 1976.
[c] Addition of an hydrogen and a $-N^{R}_{R}$ group to a double bond.

DIOP [60] other than diphosphines, [61,62] phosphines containing chiral phosphorous atom [63] or ferrocenylphosphine [64] was used.

Up to now the choice of ligands has been mainly empirical. Yet, the experimental results so far obtained have told us little about structural features of a ligand that will bring the highest stereoselectivity in a given reaction, and all attempts to find relationships between ligand structures and extent of asymmetric induction obtainable in catalytic reactions have failed. [65]

Not many different transition metal complexes have been employed in the presence of chiral ligands to achieve asymmetric synthesis (see Table 2). All the elements of the first transition series, with the exception of Sc, Cr, Mn, have been used, and in Group VIII only Os has not found applications in asymmetric catalysis. The elements of Group IV to VII in the transition metal series seem to be less popular and only molybdenum has been used. Most of the metals have been chosen on the basis of their proven selectivity and higher catalytic activity in the corresponding non-asymmetric reactions. In the few cases investigated, an enhancement of the optical yield in the asymmetric catalytic synthesis has been achevied by decreasing the reaction temperature. [66] Potentially, all types of catalytic reactions in which metal complexes are used as the catalysts can be adapted for asymmetric syntheses. The large number of transition metals still not

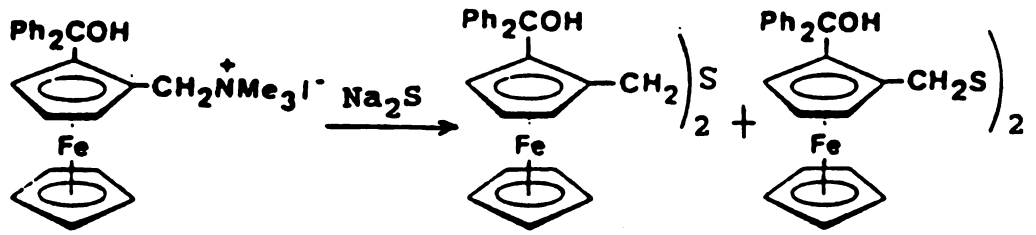
Table 2. Metals Used in Homogeneous Catalytic Asymmetric Reactions in Combination with Different Chiral Ligands

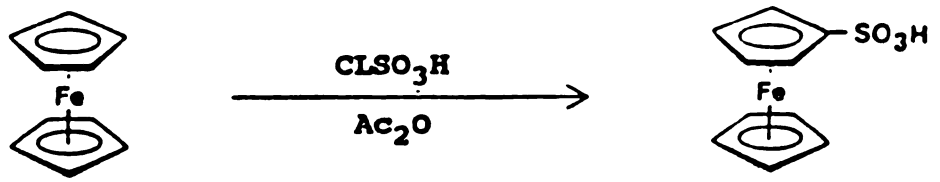
Reaction type \ Metal		Ti	V	Fe	Co	Ni	Cu	Mo	Ru	Rh	Pd	Ir	Pt
Hydrogenation of	C = C				X				X	X			X
	C = O				X				X	X		X	
	C = N								X	X			
Hydroformylation					X					X			X
Hydrocarboxylation											X		
Hydrosilylation of	C = C					X				X	X		X
	C = O									X			X
	C = N									X			
Hydrovinylation						X							
Cross-coupling						X					X		
Carbenoid reaction					X		X						
Polymerization		X		X		X							
Dehydrogenation									X	X			
Dehydrohalogenation					X								
Epoxidation			X					X					
Displacement reaction					X	X					X		
Isomerization of	P.O.				X								
	C = C	X				X			X				
	Strained H.C.									X			
	Allyl alcohols									X			
	Allyl amines				X								
Formation of	$\overset{*}{C}$ - O										X		
	$\overset{*}{C}$ - Br									X			
	$\overset{*}{C}$ - C	X				X	X				X		
	$\overset{*}{C}$ - N					X							
Hydrolysis of esters					X	X							
Acetoxylation of P.O.					X								

investigated and the large number of conceivable chiral ligands indicates that the field of asymmetric catalysis by transition metal complexes is a very fertile area, both from a theoretical and a practical point of view.

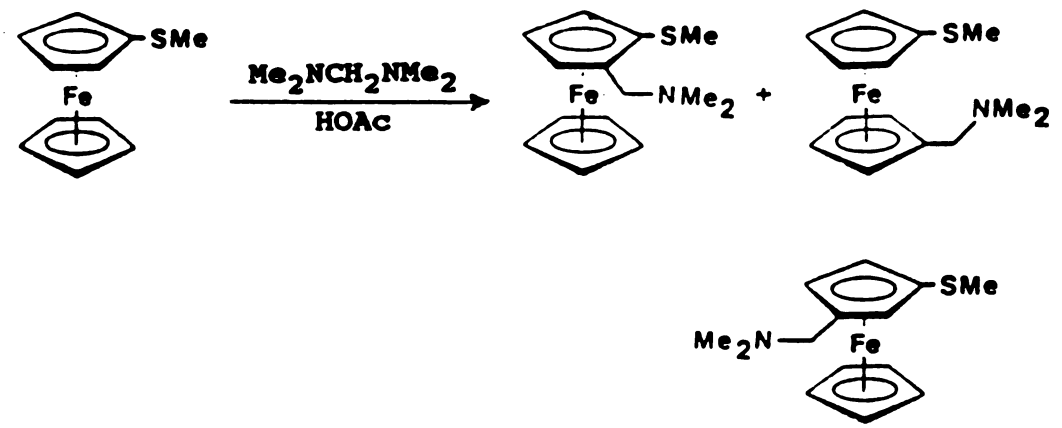
Until this point, only chiral phosphines or phosphine-amine combinations have provided satisfactory results. This is a severe limitation, for the synthesis of phosphines is not simple and the derived ligands, once obtained, are often sensitive, especially to oxidation by air. These considerations induced us to investigate some other type of chiral compounds, chiral ferrocenylsulfides, as potential ligands, and their complexes with transition metals as potential catalysts in some asymmetric synthesis reactions.

Some ferrocene derivatives with sulfur on side chains have been prepared before, but these were compounds of a nucleophilic or electrophilic substituent. Sulfur was introduced directly to a ferrocenyl ring via electrophilic sulfonation [67] 11.



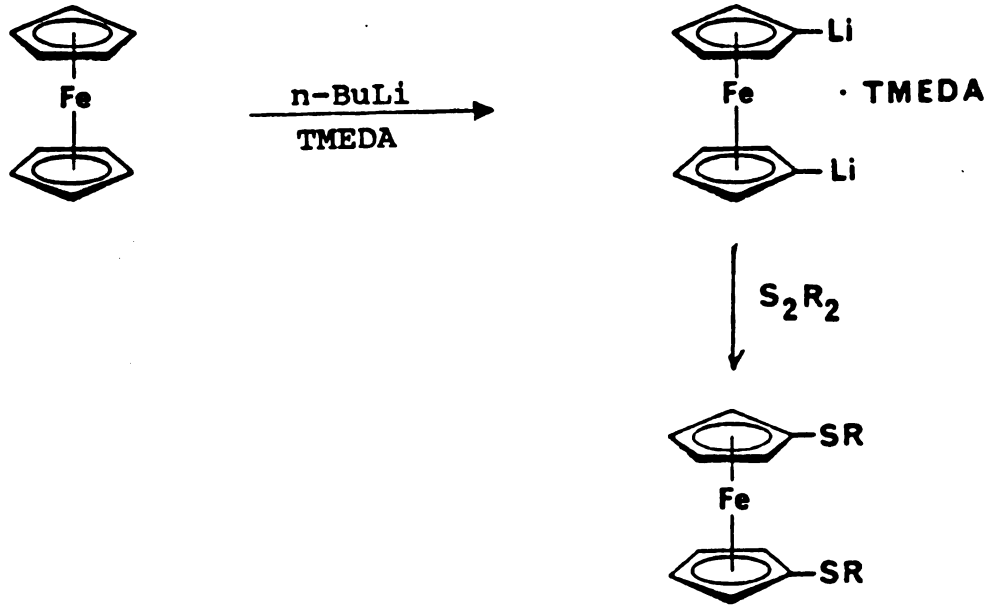


Sulfonic acid was converted first by PCl_3 to the sulfonyl chloride and reduced by $LiAlH_4$ then to the thiol. The thiol was converted to its methyl thioether. The methyl thioether was subjected to electrophilic substitution with bis(dimethylamino)methane. [68] However, these kinds of monosubstituted products were expected to obtain from the activating nature of the methylthio group.



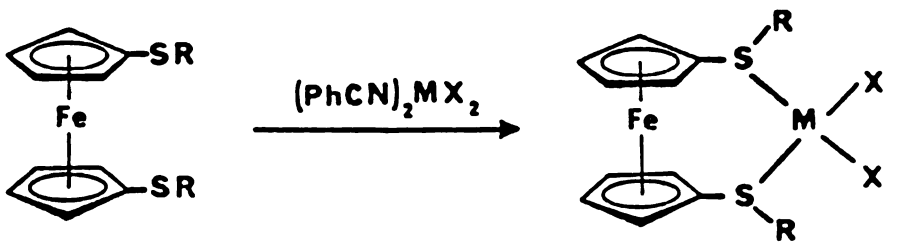
Very few thioether transition metal complexes have been reported as effective catalysts. $RhCl_3(S(C_2H_5)_2)_3$ was found to be effective in hydrogenation of maleic acid by James and Ng. [69] Also chiral sulfoxide ligands were active in asymmetric hydrogenation. [70]

Recently in this laboratory, [71] lithioferrocene and 1-1'-dilithioferrocene with various disulfides were found to give a series of ferrocenylsulfide derivatives, $Fe(C_5H_4SR)_2$, where R=Me, i-Pr, i-Bu, i-Pentyl, Ph and $PhCH_2$, by lithiation of ferrocene followed by reaction with appropriate disulfides. They are stable to oxidation but lack of any elements of planar and central chirality on the cyclopentadienyl ring.



R = Me, i-Pr, i-Bu, i-Pentyl
R = Ph, CH_2Ph

These ferrocenylsulfide derivatives readily chelate palladium and platinum halides to form ferrocenophane complexes, $Fe(C_5H_4SR)_2MX_2$, (R=Me, i-Pr, i-Bu, Ph, $PhCH_2$; M=Pd, Pt; X=Cl, Br).



M = Pd, Pt
X = Cl, Br
R = Me, i-Pr, i-Bu
Ph, CH_2Ph

Since the first appearance of ferrocene [74], dimethylaminomethylferrocene, [72] 1-dimethylaminoethylferrocene, [73] and bromoferrocene, [75] much effort has been expended on the reactions of their lithiation products.

Therefore, Brubaker and co-workers [76] continued to introduce the sulfide group onto the cyclopentadiene ring. By lithiation of dimethylaminomethylferrocene in ether solution, followed by reaction with appropriate disulfides, a series of structurally different substituent sulfide ligands, $(C_5H_5)Fe(C_5H_3\text{-}1\text{-}CH_2NMe_2\text{-}2\text{-}SR)$, R=Me, Et, n-Pr, i-Pr, n-Bu, s-Bu, i-Bu, t-Bu, i-Pentyl, Ph, Bz, 4-Tolyl, and 4-Cl-Ph, which possess planar chirality, were obtained. Similarly, the ferrocenylselenide ligands, $(C_5H_5)Fe(C_5H_3\text{-}CH_2NMe_2\text{-}2\text{-}SeR)$ (R=Me, Ph, 4-Cl-Ph), were also prepared. These ferrocenylselenide and ferrocenylsulfide derivatives readily chelate palladium and platinum dichloride to form the desired heterobimetallic complexes, $(C_5H_5)Fe(C_5H_3\text{-}1\text{-}CH_2NMe_2\text{-}2\text{-}SeR)PdCl_2$ and $(C_5H_5)Fe(C_5H_3\text{-}1\text{-}CH_2NMe_2\text{-}2\text{-}SR)PdCl_2$.

Through these studies, they found that the palladium ferrocenylsulfide complexes are good selective homogeneous and heterogeneous hydrogenation catalysts for the reduction of dienes to monoenes at room temperature and proposed a possible mechanism. [77] Lack of elemental chirality on ferrocenylsulfide and ferrocenylselenide ligands that have only planar chirality induced them to prepare other chiral ferrocenylthioethers and ferrocenylselenoethers ligands with both central and planar chirality which arise from introducing sulfide groups into the α-ferrocenylethyldimethylamine.

Later, a series of new chiral ferrocenylthioethers and selenoethers, (R,S)-$(C_5H_5)Fe(C_5H_3$-1-CHMeNMe$_2$-2-SR), R=Me, Et, n-Pr, i-Pr, n-Bu, s-Bu, t-Bu, i-Pentyl, Ph, Bz, 4-Tolyl, 4-Cl-Ph; (S,R)-$(C_5H_5)Fe(C_5H_3$-1-CHMeNMe$_2$-2-SeR), R=Me, Ph, 4-Cl-Ph were prepared in excellent yield by Brubaker and co-workers by lithiation of optically resolved α-ferrocenylethyldimethylamine, and treatment with appropriate disulfides and diselenides.

Similarly, complexes with palladium and platinum from chiral ferrocenylsulfide and ferrocenylselenide ligands also have been prepared. The chiral palladium ferrocenylsulfide and ferrocenylselenide complexes were found to be effective asymmetric Grignard cross-coupling agents. The palladium ferrocenylsulfide complexes catalyzed the formation of 4-phenyl-1-pentene from 1-phenyl-1-chloroethane and allylmagnesium chloride at 0^{o}C in high yield (> 95%). The

resulting configuration in all cases were S. The enantiomeric excess (e.e) ranged from 16.5 to 26.0 (S) and is much higher than those reported by Kellogg. [78] A mechanism of Grignard cross-coupling reaction for the chiral thioether-palladium was also proposed.

Up to this point, the whole framework of a new type of chiral ferrocenylsulfide and selenide ligands has been well developed by Brubaker. As an extension of this work, [79] we report preparations of a series of new chiral ferrocenyl-sulfide and selenide ligands with two sulfide or selenide substituents on each of the cycolpentadienyl rings, and their complexes with palladium and platinum metals as catalysts for some catalytically selective hydrogenation reactions.

The object of this research is the development of new chiral ligands and the investigation in the dependence of structurally different ligands on catalytic induction in asymmetric synthesis catalyzed by transition metal complexes.

EXPERIMENTAL

Air sensitive reagents were manipulated in prepurified argon or nitrogen. Standard schlenk-tube techniques and vacuum lines were employed. Where necessary a nitrogen-filled glovebox 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 by using neat films for liquid samples and Nujol mulls between CsI or KBr plates or in KBr pellets for solid samples. Mass spectra (MS) were obtained by means of a Finnigan 4021 instrument with INCOS data system. Optical rotations were measured with a Perkin-Elmer 141 polarimeter. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee. Gas chromatography (GC) was carried out by using a Hewlett-Packard 5880A instrument.

All melting points were determined by using a Thomas-Hoover capillary melting point apparatus and were corrected. Proton NMR spectra were obtained in chloroform-d_1 solution by use of a Bruker WM-250 spectrometer at 250 MHz. Chemical shifts are reported in ppm downfield from a tetramethyl-silane internal standard. Carbon-13 NMR (broadband proton decoupled and grated decoupled) were obtained by use of a Bruker WM-250 spectrometer at 62.9 MHz. A pulse width (PW) of 13 μs and a relaxation delay (RD) of 6s were generally employed.

All solvents used were A.C.S. reagent grade and were distilled by standard methods before use [80]. (R)-N,N-dimethyl-1-ferrocenylethylamine (R-1) was prepared according to Gokel and Ugi's procedure. [81] Dimethylaminomethylferrocene (12) was made by the standard method [82] or purchased. Bis(benzonitrile) complexes, $[(PhCN)_2MCl_2]$ where M = Pd, Pt, were prepared according to published procedures. [83] The hydrogenation substrate 1,3-cyclooctadiene was obtained from Columbian Carbon Co; 1,3-cyclohexadiene was obtained from Aldrich Chemical Co. These reagents were retreated by standard methods before use. Disulfides, diselenides and N,N,N',N'-tetramethylene-ethylenediamine (TMEDA) were purchased from Aldrich Chemical Company. A pressure bottle with gauge was used to perform hydrogenations.

A. Preparation of Ligands

1-Dimethylaminomethyl-2-1'-bis(methylthio)ferrocene (21, R=Me)

A solution of dimethylaminoethylferrocene (12, 2.43 g, 10 mmol) in 100 ml dry ether and 2.7 M n-BuLi in hexane (5.6 ml, 15 mmol) was mixed at -78°C under argon in a 250 ml round-bottomed flask. After the reaction mixture was stirred for 8 hr at room temperature, the reaction mixture was added to a solution of freshly distilled TMEDA (1.43 ml, 12 mmol) and n-BuLi (2.7 M, 5.6 ml, 15 mmol) in 50 ml dry ether at

-78°C and stirred for another 12 hr at room temperature. Then a solution of methyl disulfide (2.83 g, 30 mmol) in 20 ml dry ether was transferred into the reaction flask by syringe at -78°C, and stirred further 24 hr at room temperature. The reaction mixture was hydrolyzed with a cold saturated aqueous sodium hydrogen carbonate (30 ml) and filtered to remove any impurities. The resulting organic layer and ether extracts (50 ml) from the aqueous layer were combined, washed with ice water, dried over anhydrous sodium sulfate, concentrated in vacuum to give a dark oily residue which was chromatographed (60-200 mesh) on a silica gel column by gradient elution (hexane/ether). The product was obtained as a brown oil. Yield: 92%.

Anal. for $C_{15}H_{21}S_2NFe$
Calcd. C:53.73%, H:6.31%, Found C:54.14%, H:6.23%.

MS m/e (relative intensity): 335(M^+,100),320(M^+-Me,5),286 (M^+-SCH_3,6),276(M^+-Me-NMe_2,6),244(M^+-NMe_2-SCH_3,17),230(M^+-$NMe_2(CH_2)$-SCH_3,10),213(13),164(22),152(30),121(29),97(18), 91(21),58(Fe,66),56(Fe,47),44(NMe_2,32).

IR (neat, CsI), 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(antisymmetric ring-metal stretch) cm^{-1}.

^{1}H NMR (δ ppm), 2.18(s,6H,N$\underline{Me}_2$),2.25(s,3H,SC$\underline{H}_3$),2.26(s,3H, SC$\underline{H}_3$),3.24(d,1H,C$\underline{H}_2$N),3.55(d,1H,C$\underline{H}_2$N),4.09(m,2H,$\underline{H}_3$,$\underline{H}_4$,$\underline{H}_5$), 4.18(m,4H,$C_5\underline{H}_4$),4.28(m,1H,$\underline{H}_3$,$\underline{H}_4$,$\underline{H}_5$).

^{13}C NMR (δ ppm, in CD_3COCD_3), 19.3(q,S$\underline{C}H_3$),20.0(q,S$\underline{C}H_3$), 45.4(q,N$\underline{Me}_2$),57.4(d,$\underline{C}$HNMe$_2$),69.2(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),71.0(d,$\underline{C}'_2$,$\underline{C}'_5$) ,71.1(d,$\underline{C}'_2$,$\underline{C}'_5$),72.3(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),72.4(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),72.9(d, $\underline{C}'_3$,$\underline{C}'_4$),73.4(d,$\underline{C}'_3$,$\underline{C}'_4$),85.6(s,$\underline{C}'_1$),86.4(s,$\underline{C}_2$),88.2(s,$\underline{C}_1$).

1-Dimethylaminomethyl-2-1'-bis(ethylthio)ferrocene (22, R=Et)

The lithioferrocene was made by the same procedure as 21, (R=Me), by using 2.43 g (10 mmol) of dimethylaminoethyl-ferrocene (12), 100 ml dry ether, and 5.6 ml, 2.7 M solution of n-BuLi in hexane at -78°C. Then, the lithioferrocene solution was added a mixture of freshly distilled TMEDA (1.43 ml, 12 mmol) and n-BuLi (5.6 ml, 2.7 M, 15 mmol) in 50 ml dry ether at -78°C. After being stirred 12 hr at room temperature, ethyl disulfide (3.67 g, 30 mmol) was transferred into the reaction flask by syringe at -78°C and stirred for 24 hr. The reaction mixture was hydrolyzed with 30 ml of cold aqueous sodium bicarbonate and filtered off. The resulting organic layer and ether extracts from the aqueous layer were combined, washed with water and dried over Na_2SO_4. A dark brown residue was obtained after removal of solvent at reduced pressure, and was chromatographed on a silica gel column by gradient elution (hexane/ether) to give a brown oil. Yield: 89%.

Anal. for $C_{17}H_{25}S_2NFe$

Calcd. C:56.19%, H:6.93%, Found C:56.48%, H:6.93%.

MS m/e (relative intensity): 363(M^+,100),348(M^+-CH_3,5),334 ($M^+-C_2H_5$,7),318(M^+-3Me,16),302($M^+-SC_2H_5$,38),286(23),258(M^+-$NMe_2-SC_2H_5$,12),230(17),165(8),152(19),121(23),97(20),58 (31),56(19),44(12).

IR (neat, CsI), 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(antisymmetric ring-metal stretch) cm^{-1}.

^1H NMR (δ ppm), 1.12(t,3H,$\beta C\underline{H}_3$),1.19(t,3H,$\beta C\underline{H}_3$),2.16(s,6H, $N\underline{Me}_2$),2.53(q,2H,$SC\underline{H}_2$),2.60(m,1H,$SC\underline{H}_2$),2.64(m,1H,$SC\underline{H}_2$),3.20 (d,1H,$C\underline{H}_2N$),3.55(d,1H,$C\underline{H}_2N$),4.10(m,2H,$\underline{H}_3$,$\underline{H}_4$,$\underline{H}_5$),4.16(m,4H, $C_5\underline{H}_4$),4.29(m,1H,$\underline{H}_3$,$\underline{H}_4$,$\underline{H}_5$).

^{13}C NMR (δ ppm, in CD_3COCD_3), 15.5(q,$\beta\underline{C}H_3$),15.7(q,$\beta\underline{C}H_3$), 31.3(t,$S\underline{C}H_2$),31.9(t,$S\underline{C}H_2$),45.8(q,$N\underline{Me}_2$),58.0(d,$\underline{C}HNMe_2$),70.0 (d,d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),72.0(d,$\underline{C}'_2$,$\underline{C}'_5$),72.4(d,$\underline{C}'_2$,$\underline{C}'_5$),73.8(d,$\underline{C}_3$,$\underline{C}_4$, $\underline{C}_5$),75.4(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),76.0(d,$\underline{C}'_3$,$\underline{C}'_4$),76.3(d,$\underline{C}'_3$,$\underline{C}'_4$),82.7 (s,$\underline{C}'_1$),82.9(s,$\underline{C}_2$),89.5(s,$\underline{C}_1$).

1-Dimethylaminomethyl-2-1′-bis[(n-propyl)thio]ferrocene (23, R=n-Pr)

The lithioferrocene was made by the same procedure as 21, (R=Me), by using 2.43 g (10 mmol) of dimethylaminoethyl-ferrocene (12), 100 ml dry ether, and 5.6 ml, 2.7 M solution of n-BuLi in hexane at -78°C. Then, the lithioferrocene solution was added a mixture of freshly distilled TMEDA (1.43 ml, 12 mmol) and n-BuLi (5.6 ml, 2.7 M, 15 mmol) in 50 ml dry ether at -78°C. After being stirred 12 hr at room temperature, n-propyl disulfide (4.51 g, 30 mmol) was transferred into the reaction flask by syringe at -78°C and stirred for 24 hr. The reaction mixture was hydrolyzed with 30 ml of cold aqueous sodium bicarbonate and filtered off. The resulting organic layer and ether extracts from the aqueous layer were combined, washed with water and dried over Na_2SO_4. A dark brown residue was obtained after removal of solvent at reduced presure, and was chromatographed on a silica gel column by gradient elution (hexane/ether) to give a brown oil. Yield: 82%.

Anal. for $C_{19}H_{29}S_2NFe$
Calcd. C:58.30%, H:7.47%, Found, C:58.48%, H:7.53%.

MS m/e (relative intensity): 391(M^+,100),376(M^+-CH_3,3),346 (M^+-3Me,18),316(M^+-S(n-Pr),37),272(M^+-NMe_2-S(n-Pr),12),164 (13),152(17),121(17),97(18),58(40),56(17),44(28).

IR (neat, CsI), 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(antisymmetric ring-metal stretch) cm^{-1}.

^1H NMR (δ ppm), 0.88(t,3H,rC$\underline{H}_3$),0.95(t,3H,rC$\underline{H}_3$),1.46(m, 2H,βC$\underline{H}_2$),1.56(m,2H,βC$\underline{H}_2$),2.17(s,6H,N$\underline{Me}_2$),2.50(m,2H,SC$\underline{H}_2$), 2.56(m,1H,SC$\underline{H}_2$),2.64(m,1H,SC$\underline{H}_2$),3.21(d,1H,C$\underline{H}_2$N),3.55(d,1H, C$\underline{H}_2$N),4.08(m,2H,$\underline{H}_3$,$\underline{H}_4$,$\underline{H}_5$),4.17(m,4H,$C_5\underline{H}_4$),4.27(m,1H,$\underline{H}_3$,$\underline{H}_4$, $\underline{H}_5$).

^{13}C NMR (δ ppm, in CD_3COCD_3), 13.5(q,r$\underline{C}H_3$),13.6(q,r$\underline{C}H_3$), 23.4(t,$\beta\underline{C}H_2$),23.5(t,$\beta\underline{C}H_2$),39.1(t,S$\underline{C}H_2$),39.4(t,S$\underline{C}H_2$),45.5 (q,N$\underline{Me}_2$),57.5(d,$\underline{C}HNMe_2$),69.5(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),71.6(d,$\underline{C}'_2$,$\underline{C}'_5$),71. 9(d,$\underline{C}'_2$,$\underline{C}'_5$),73.3(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),74.8(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),75.3(d,$\underline{C}'_3$, $\underline{C}'_4$),75.7(d,$\underline{C}'_3$,$\underline{C}'_4$),82.8(s,$\underline{C}'_1$),82.9(s,$\underline{C}_2$),89.1(s,$\underline{C}_1$).

1-Dimethylaminomethyl-2-1′-bis[(i-propyl)thio]ferrocene (24, R=i-Pr).

The lithioferrocene was made by the same procedure as 21, (R=Me), by using 2.43 g (10 mmol) of dimethylaminoethyl-ferrocene (12), 100 ml dry ether, and 5.6 ml, 2.7 M solution of n-BuLi in hexane at -78°C. Then, the lithioferrocene solution was added a mixture of freshly distilled TMEDA (1.43 ml, 12 mmol) and n-BuLi (5.6 ml, 2.7 M, 15 mmol) in 50 ml dry ether at -78°C. After being stirred 12 hr at room temperature, i-propyl disulfide (4.51 g, 30 mmol) was

transferred into the reaction flask by syringe at -78°C and stirred for 24 hr. The reaction mixture was hydrolyzed with 30 ml of cold aqueous sodium bicarbonate and filtered off. The resulting organic layer and ether extracts from the aqueous layer were combined, washed with water and dried over Na_2SO_4. A dark brown residue was obtained after removal of solvent at reduced pressure, and was chromatographed on a silica gel column by gradient elution (hexane/ether) to give a brown oil. Yield: 81%.

Anal. for $C_{19}H_{29}S_2NFe$
Calcd. C:58.30%, H:7.47%, Found, C:58.54%, H:7.44%.

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^+-NMe_2-S(i-Pr), 12),230(10),195(13),164(15),152(23),121(20),97(24),88(12), 58(33),56(19),44(21).

IR (neat, CsI), 3097(ferrocene C-H stretch),2960-2765(alkyl C-H stretch),1449(ferrocene antisymmetric C-C stretch), 1260,1241(C-N stretch),835(C-H bend perpendicular to the plane of the Cp ring),652(S-C stretch),485(antisymmetric ring-metal stretch) cm^{-1}.

^1H NMR (δ ppm), 1.07(d,3H,$\beta C\underline{H}_3$),1.10(d,3H,$\beta C\underline{H}_3$),1.14(d, 3H,$\beta C\underline{H}_3$),1.18(d,3H,$\beta C\underline{H}_3$),2.16(s,6H,$N\underline{Me}_2$),2.81(h,1H,$SC\underline{H}$), 3.01(h,1H,$SC\underline{H}$),3.17(d,1H,$C\underline{H}_2N$),3.57(d,1H,$C\underline{H}_2N$),4.09(m,2H,$\underline{H}_3$, $\underline{H}_4$,$\underline{H}_5$),4.19(m,4H,$C_5\underline{H}_4$),4.32(m,1H,$\underline{H}_3$,$\underline{H}_4$,$\underline{H}_5$).

^{13}C NMR (δ ppm, in CD_3COCD_3), 22.8(q,βCH_3),23.2(q,βCH_3), 23.7(q,βCH_3),39.3(d,SCH),39.4(d,SCH),45.2(q,NMe_2),57.1 (d,C$HNMe_2$),69.3(d,C_3,C_4,C_5),71.7(d,C'_2,C'_5),72.1(d,C'_2, C'_5),73.2(d,C_3,C_4,C_5),76.1(d,C_3,C_4,C_5),76.6(d,C'_3,C'_4), 76.8(d,C'_3,C'_4),79.2(s,C'_1),80.6(s,C_2),89.5(s,C_1).

1-Dimethylaminomethyl-2-1'-bis[(n-butyl)thio]ferrocene (25, R=n-Bu)

The lithioferrocene was made by the same procedure as 21, (R=Me), by using 2.43 g (10 mmol) of dimethylaminoethyl-ferrocene (12), 100 ml dry ether, and 5.6 ml, 2.7 M solution of n-BuLi in hexane at -78°C. Then, the lithioferrocene solution was added a mixture of freshly distilled TMEDA (1.43 ml, 12 mmol) and n-BuLi (5.6 ml, 2.7 M, 15 mmol) in 50 ml dry ether at -78°C. After being stirred 12 hr at room temperature, n-butyl disulfide (5.35 g, 30 mmol) was transferred into the reaction flask by syringe at -78°C and stirred for 24 hr. The reaction mixture was hydrolyzed with 30 ml of cold aqueous sodium bicarbonate and filtered off. The resulting organic layer and ether extracts from the aqueous layer were combined, washed with water and dried over Na_2SO_4. A dark brown residue was obtained after removal of solvent at reduced pressure, and was chromatographed on a silica gel column by gradient elution (hexane/ether) to give a brown oil. Yield: 75%.

Anal. for $C_{21}H_{33}S_2NFe$

Calcd. C:60.13%, H:7.93%, Found, C:59.82%, H:7.71%.

MS m/e (relative intensity): 419(M^+,100),404(M^+-Me,3),374 (M^+-3Me,26),362(M^+-C_4H_9,8),330(M^+-S(n-Bu),44),318(M^+-NMe_2-C_4H_9,3),286(M^+-NMe_2-S(C_4H_9),9),164(15),152(20),121(19),97 (22),58(53),56(17),44(16).

IR (neat, CsI), 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(antisymmetric ring-metal stretch) cm^{-1}.

^1H NMR (δ ppm), 0.82(t,3H,$\delta C\underline{H}_3$),0.86(t,3H,$\delta C\underline{H}_3$),1.31(m,2H, $rC\underline{H}_2$),1.43(m,2H,$rC\underline{H}_2$),1.46(m,2H,$\beta C\underline{H}_2$),1.52(m,2H,$\beta C\underline{H}_2$),2.17 (s,6H,$N\underline{Me}_2$),2.53(m,2H,$SC\underline{H}_2$),2.60(m,1H,$SC\underline{H}_2$),2.66(m,1H,$SC\underline{H}_2$), 3.20(d,1H,$C\underline{H}_2N$),3.56(d,1H,$C\underline{H}_2N$),4.08(m,2H,$\underline{H}_3$,$\underline{H}_4$,$\underline{H}_5$),4.16(m, 4H,$C_5\underline{H}_4$),4.29(m,1H,$\underline{H}_3$,$\underline{H}_4$,$\underline{H}_5$).

^{13}C NMR (δ ppm, in CD_3COCD_3),13.9(q,$\delta\underline{C}H_3$),22.0(t,$r\underline{C}H_2$),22.1 (t,$r\underline{C}H_2$),32.0(t,$\beta\underline{C}H_2$),32.2(t,$\beta\underline{C}H_2$),36.6(t,$S\underline{C}H_2$),36.8 (t,$S\underline{C}H_2$),45.4(q,$N\underline{Me}_2$),57.3(d,$\underline{C}HNMe_2$),69.2(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),71.3 (d,$\underline{C}'_2$,$\underline{C}'_5$),71.6(d,$\underline{C}'_2$,$\underline{C}'_5$),73.1(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),74.5(d,$\underline{C}_3$,$\underline{C}_4$, $\underline{C}_5$),75.1(d,$\underline{C}'_3$,$\underline{C}'_4$),75.5(d,$\underline{C}'_3$,$\underline{C}'_4$),82.5(s,$\underline{C}'_1$),82.5(s,$\underline{C}_2$), 88.9(s,$\underline{C}_1$).

1-Dimethylaminomethyl-2-1'-bis[(sec-butyl)thio]ferrocene, (26, R=sec-Butyl)

The lithioferrocene was made by the same procedure as 21, (R=Me), by using 2.43 g (10 mmol) of dimethylaminoethyl-

ferrocene (12), 100 ml dry ether, and 5.6 ml, 2.7 M solution of n-BuLi in hexane at -78°C. Then, the lithioferrocene solution was added a mixture of freshly distilled TMEDA (1.43 ml, 12 mmol) and n-BuLi (5.6 ml, 2.7 M, 15 mmol) in 50 ml dry ether at -78°C. After being stirred 12 hr at room temperature, s-butyl disulfide (5.35 g, 30 mmol) was transferred into the reaction flask by syringe at -78°C and stirred for 24 hr. The reaction mixture was hydrolyzed with 30 ml of cold aqueous sodium bicarbonate and filtered off. The resulting organic layer and ether extracts from the aqueous layer were combined, washed with water and dried over Na_2SO_4. A dark brown residue was obtained after removal of solvent at reduced pressure, and was chromatographed on a silica gel column by gradient elution (hexane/ether) to give a brown oil. Yield: 59%.

Anal. for $C_{21}H_{33}S_2NFe$
Calcd. C:60.13%, H:7.93%, Found C:60.25%, H:7.79%.

MS m/e (relative intensity): 419(M^+,100),404(M^+-Me,6), 374 (M^+-3Me,36),362(M^+-C_4H_9,11),330(M^+-S(C_4H_9),49),318(M^+-NMe_2-C_4H_9,5),286(M^+-NMe_2-S(C_4H_9),14),164(18),152(32),121(20),97 (26),58(62),56(46),44(90).

IR (neat, CsI), 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 (antisymmetric ring-metal stretch) cm^{-1}.

^{1}H NMR (δ ppm), 0.87(t,3H,rC$\underline{H}_3$),0.97(t,3H,rC$\underline{H}_3$),1.10(d, 3H,βC$\underline{H}_3$),1.15(d,3H,βC$\underline{H}_3$),1.36(m,2H,βC$\underline{H}_2$),1.47(m,2H,βC$\underline{H}_2$), 2.17(s,6H,N$\underline{Me}_2$),2.57(h,1H,SC$\underline{H}$),2.83(h,1H,SC$\underline{H}$),3.20(d,1H, C$\underline{H}_2$N),3.56(d,1H,C$\underline{H}_2$N),4.12(m,2H,$\underline{H}_3$,$\underline{H}_4$,$\underline{H}_5$),4.19(m,4H,$C_5\underline{H}_4$), 4.31(m,1H,$\underline{H}_3$,$\underline{H}_4$,$\underline{H}_5$).

^{13}C NMR (Š ppm, in CD_3COCD_3),

1-Dimethylaminomethyl-2-1′-bis[(t-butyl)thio]ferrocene (27, R=t-Butyl)

The lithioferrocene was made by the same procedure as 21, (R=Me), by using 2.43 g (10 mmol) of dimethylaminoethyl-ferrocene (12), 100 ml dry ether, and 5.6 ml, 2.7 M solution of n-BuLi in hexane at -78°C. Then, the lithioferrocene solution was added a mixture of freshly distilled TMEDA (1.43 ml, 12 mmol) and n-BuLi (5.6 ml, 2.7 M, 15 mmol) in 50 ml dry ether at -78°C. After being stirred 12 hr at room temperature, t-butyl disulfide (5.35 g, 30 mmol) was transferred into the reaction flask by syringe at -78°C and stirred for 24 hr. The reaction mixture was hydrolyzed with 30 ml of cold aqueous sodium bicarbonate and filtered off. The resulting organic layer and ether extracts from the aqueous layer were combined, washed with water and dried over Na_2SO_4. A dark brown residue was obtained after removal of solvent at reduced pressure, and was chromatographed on a silica gel column by gradient elution (hexane/ether) to give a brown oil. Yield: 55.0%.

Anal. for $C_{21}H_{33}S_2NFe$

Calcd. C:60.13%, H:7.93%, Found C:60.59%, H:7.97%.

MS m/e (relative intensity): 419(M^+,21),374(M^+-3Me,72),361 (M^+-CH_2NMe_2,11),359(M^+-4Me,31),330(M^+-NMe_2-3Me,27),317(M^+-NMe_2-C_4H_9,6),286(M^+-NMe_2-S(C_4H_9),4),164(17),152(33),121(33), 58(44),56(19),44(17).

IR (neat, CsI), 3093(ferrocene C-H stretch),2967-2761(alkyl C-H stretch),1451(ferrocen 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(antisymmetric ring-metal stretch) cm^{-1}.

^1H NMR (δ ppm), 1.17(s,18H,$\beta C\underline{H}_3$),2.14(s,6H,$N\underline{Me}_2$),3.27(s,2H, $C\underline{H}_2N$),4.10(m,2H,$\underline{H}_3$,$\underline{H}_4$,$\underline{H}_5$),4.14(m,4H,$C_5\underline{H}_4$),4.19(m,1H,$\underline{H}_3$,$\underline{H}_4$, $\underline{H}_5$).

^{13}C NMR (δ ppm, in CD_3COCD_3), 31.0(s,$\beta\underline{C}$H3),37.2(s,S$\underline{C}$),44.9 (q,N$\underline{Me}$2),59.1(d,$\underline{C}H_2NMe_2$),69.8(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),70.9(d,$\underline{C}'_2$,$\underline{C}'_5$), 72.1(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),72.1(d,$\underline{C}'_3$,$\underline{C}'_4$),77.3(s,$\underline{C}'_1$),77.4(s,$\underline{C}_2$), 89.1(s,$\underline{C}_1$).

1-Dimethylaminomethyl-2-1′-bis[(i-pentyl)thio]ferrocene (28, R=i-Pentyl).

The lithioferrocene was made by the same procedure as 21, (R=Me), by using 2.43 g (10 mmol) of dimethylaminoethyl-ferrocene (12), 100 ml dry ether, and 5.6 ml, 2.7 M solution

of n-BuLi in hexane at -78°C. Then, the lithioferrocene solution was added a mixture of freshly distilled TMEDA (1.43 ml, 12 mmol) and n-BuLi (5.6 ml, 2.7 M, 15 mmol) in 50 ml dry ether at -78°C. After being stirred 12 hr at room temperature, i-pentyl disulfide (6.19 g, 30 mmol) was transferred into the reaction flask by syringe at -78°C and stirred for 24 hr. The reaction mixture was hydrolyzed with 30 ml of cold aqueous sodium bicarbonate and filtered off. The resulting organic layer and ether extracts from the aqueous layer were combined, washed with water and dried over Na_2SO_4. A dark brown residue was obtained after removal of solvent at reduced pressure, and was chromatographed on a silica gel column by gradient elution (hexane/ether) to give a brown oil. Yield: 78%.

Anal. for $C_{23}H_{37}S_2NFe$
Calcd. C:61.73%, H:8.33%, Found, C:62.00%, H:8.14%.

MS m/e (relative intensity): 447(M^+,84),432(M^+-Me,5),402 (M^+-3Me,30),376(M^+-C_5H_{11},11),344(M^+-SC_5H_{11},39),332(M^+-NMe_2-C_5H_{11},6),300(M^+-NMe_2-SC_5H_{11},8),164(24),152(29),149(44),121 (33),97(34),58(74),56(29),44(42).

IR (neat, CsI), 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(antisymmetric ring-metal stretch) cm^{-1}.

^{1}H NMR (δ ppm), 0.79(d,3H,δC$\underline{H}_3$),0.82(d,3H,δC$\underline{H}_3$),0.84(d,3H, δC$\underline{H}_3$),0.87(d,3H,δC$\underline{H}_3$),1.35(m,1H,rC$\underline{H}$),1.41(m,1H,rC$\underline{H}$),1.58 (m,2H,βC$\underline{H}_2$),1.63(m,2H,βC$\underline{H}_2$),2.16(s,6H,N$\underline{Me}_2$),2.54(m,2H,SC$\underline{H}_2$) ,2.64(m,1H,SC$\underline{H}_2$),2.71(m,1H,SC$\underline{H}_2$),3.20(d,1H,C$\underline{H}_2$N),3.57(d,1H, C$\underline{H}_2$N),4.08(m,2H,$\underline{H}_3$,$\underline{H}_4$,$\underline{H}_5$),4.17(m,4H,$C_5\underline{H}_4$),4.28(m,1H, $\underline{H}_3$,$\underline{H}_4$,$\underline{H}_5$).

^{13}C NMR (δ ppm, in CD_3COCD_3), 22.4(q,δ$\underline{C}H_3$),22.6(q,δ$\underline{C}H_3$), 22.8(q,δ$\underline{C}H_3$),27.4(d,r$\underline{C}$H),27.5(d,r$\underline{C}$H),34.9(t,β$\underline{C}H_2$),35.2(t, β$\underline{C}H_2$),39.2(t,S$\underline{C}H_2$),45.4(q,N$\underline{Me}_2$),57.3(d,$\underline{C}$HNMe$_2$),69.3(d,$\underline{C}_3$, $\underline{C}_4$,$\underline{C}_5$),71.4(d,$\underline{C}'_2$,$\underline{C}'_5$),71.7(d,$\underline{C}'_2$,$\underline{C}'_5$),73.2(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),74.5 (d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),75.0(d,$\underline{C}'_3$,$\underline{C}'_4$),75.6(d,$\underline{C}'_3$,$\underline{C}'_4$),82.6(s,$\underline{C}'_1$), 82.7(s,$\underline{C}_2$),89.1(s,$\underline{C}_1$).

1-Dimethylaminomethyl-2-1′-bis(phenylthio)ferrocene (29, R=Ph)

The lithioferrocene was made by the same procedure as 21, (R=Me), by using 2.43 g (10 mmol) of dimethylaminoethyl-ferrocene (12), 100 ml dry ether, and 5.6 ml, 2.7 M solution of n-BuLi in hexane at -78°C. Then, the lithioferrocene solution was added a mixture of freshly distilled TMEDA (1.43 ml, 12 mmol) and n-BuLi (5.6 ml, 2.7 M, 15 mmol) in 50 ml dry ether at -78°C. After being stirred 12 hr at room temperature, phenyl disulfide (6.55 g, 30 mmol) was transferred into the reaction flask through a cannula at -78°C and stirred for 40 hr. The reaction mixture was hydrolyzed with 30 ml of cold aqueous sodium bicarbonate and filtered off. The resulting organic layer and ether extracts

from the aqueous layer were combined, washed with water and dried over Na_2SO_4. A dark brown residue was obtained after removal of solvent at reduced pressure, and was chromatographed on a silica gel column by gradient elution (hexane/ether) to give a brown oil. The compound was obtained as a yellow crystal from the first band after two recrystallizations from acetone/hexane. yield: 74%, mp = 86-87°C.

Anal. for $C_{25}H_{25}S_2NFe$
Calcd. C:65.35%, H:5.48%, Found, C:65.49%, H:5.35%.

MS m/e (relative intensity): 459(M^+,100),444(M^+-Me,2),391 (21),363(8),350(M^+-SPh,42),335(13),306(M^+-NMe_2-SPh,38),230 (18),184(12),164(13),152(25),141(15),121(25),97(19),71(19), 58(36),44(18).

IR (neat, CsI), 3100(ferrocene C-H stretch),3075,3060,3020 (phenyl C-H stretch), 2975-2720(alkyl C-H stretch), 1441 (ferrocene antisymmetric C-C stretch),1182,1172(C-N stretch),835(C-H bend perpendicular to the plane of the Cp ring),620(S-C stretch),490(antisymmetric ring-metal stretch) cm^{-1}.

^1H NMR (δ ppm), 2.04(s,6H,N$\underline{Me}_2$),3.44(d,1H,C$\underline{H}_2$N),3.55(d,1H, C$\underline{H}_2$N),4.33(m,2H,$\underline{H}_3$,$\underline{H}_4$,$\underline{H}_5$),4.44(m,4H,$C_5\underline{H}_4$),4.60(m,1H,$\underline{H}_3$,$\underline{H}_4$,$\underline{H}_5$),7.02-7.19(m,10H,Ph).

^{13}C NMR (δ ppm, in CD_3COCD_3), 45.4(q,N$\underline{Me}_2$),56.9(d,$\underline{C}$HNMe_2), 71.3(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),73.4(d,$\underline{C}'_2$,$\underline{C}'_5$),73.6(d,$\underline{C}'_2$,$\underline{C}'_5$),74.1(d,$\underline{C}_3$,

$\underline{C}_4$,$\underline{C}_5$),77.1(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),77.4(d,$\underline{C}'_3$,$\underline{C}'_4$),77.5(d,$\underline{C}'_3$,$\underline{C}'_4$), 77.6(s,$\underline{C}'_1$),78.2(s,$\underline{C}_2$),90.0(s,$\underline{C}_1$),125.8(d,para Ph-$\underline{C}$),126.7 (d,ortho Ph-$\underline{C}$),127.4(d,ortho Ph-$\underline{C}$),129.2(d,meta Ph-$\underline{C}$),129.4 (d,meta Ph-$\underline{C}$),140.6(s,substituted Ph-$\underline{C}$),141.0(s,substituted Ph-$\underline{C}$).

1-Dimethylaminomethyl-2-1'-bis(benzylthio)ferrocene (30, R=Bz)

The lithioferrocene was made by the same procedure as 21, (R=Me), by using 2.43 g (10 mmol) of dimethylaminoethyl-ferrocene (12), 100 ml dry ether, and 5.6 ml, 2.7 M solution of n-BuLi in hexane at -78°C. Then, the lithioferrocene solution was added a mixture of freshly distilled TMEDA (1.43 ml, 12 mmol) and n-BuLi (5.6 ml, 2.7 M, 15 mmol) in 50 ml dry ether at -78°C. After being stirred 12 hr at room temperature, benzyl disulfide (7.38 g, 30 mmol) was transferred into the reaction flask through a cannula at -78°C and stirred for 40 hr. The reaction mixture was hydrolyzed with 30 ml of cold aqueous sodium bicarbonate and filtered off. The resulting organic layer and ether extracts from the aqueous layer were combined, washed with water and dried over Na_2SO_4. A dark brown residue was obtained after removal of solvent at reduced pressure, and was chromatographed on a silica gel column by gradient elution (hexane/ether). The compound was obtained as a brown oil. yield: 54%.

Anal. for $C_{27}H_{29}S_2NFe$

Calcd. C:66.52%, H:5.60%, Found C:66.59%, H:6.08%.

MS m/e (relative intensity): 487(M^+,100),472(M^+-Me,10),442 (M^+-3Me,37),366(M^+-NMe_2-C_6H_5,11),334(M^+-NMe_2-SBz,42),164 (14),152(22),121(38),91(23),58(27),56(44),44(78).

IR (neat, CsI), 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(antisymmetric ring-metal stretch) cm^{-1}.

^1H NMR (δ ppm), 2.19(s,6H,N$\underline{Me}_2$),2.98(d,1H,C$\underline{H}_2$N),3.78(d,H, C$\underline{H}_2$N),3.82(s,2H,SC$\underline{H}_2$),3.90(d,1H,SC$\underline{H}_2$),4.02(d,1H,SC$\underline{H}_2$),4.13-4.30(m,7H,$C_5\underline{H}_4$,$C_5\underline{H}_3$),7.14-7.32(m,8H,Ph).

^{13}C NMR (δ ppm, in CD_3COCD_3), 41.7(t,S$\underline{C}H_2$),42.4(t,S$\underline{C}H_2$),45.2 (q,NMe_2),57.4(d,$\underline{C}H_2$N),70.0(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),72.4(d,$\underline{C}'_2$,$\underline{C}'_5$),72.6 (d,$\underline{C}'_2$,$\underline{C}'_5$),72.9(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),74.8(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),75.9(d,$\underline{C}'_3$,$\underline{C}'_4$),76.1(d,$\underline{C}'_3$,$\underline{C}'_4$),82.3(s,$\underline{C}'_1$),82.6(s,$\underline{C}_2$),89.3(s,$\underline{C}_1$),126.3 (d,para Ph-$\underline{C}$),126.6(d,para Ph-$\underline{C}$),128.1(d,ortho Ph-$\underline{C}$),128.3 (d,ortho Ph-$\underline{C}$),128.9(d,meta Ph-$\underline{C}$),129.2(d,meta Ph-$\underline{C}$),138.6 (s,substituted Ph-$\underline{C}$),139.2(s,substituted Ph-$\underline{C}$).

1-Dimethylaminomethyl-2-1'-bis[(4-tolyl)thio]ferrocene (31, R=4-Tolyl)

The lithioferrocene was made by the same procedure as 21, (R=Me), by using 2.43 g (10 mmol) of dimethylaminoethyl-ferrocene (12), 100 ml dry ether, and 5.6 ml, 2.7 M solution

of n-BuLi in hexane at -78°C. Then, the lithioferrocene solution was added a mixture of freshly distilled TMEDA (1.43 ml, 12 mmol) and n-BuLi (5.6 ml, 2.7 M, 15 mmol) in 50 ml dry ether at -78°C. After being stirred 12 hr at room temperature, 4-tolyl disulfide (7.40 g, 30 mmol) was transferred into the reaction flask through a cannula at -78°C and stirred for 40 hr. The reaction mixture was hydrolyzed with 30 ml of cold aqueous sodium bicarbonate and filtered off. The resulting organic layer and ether extracts from the aqueous layer were combined, washed with water and dried over Na_2SO_4. A dark brown residue was obtained after removal of solvent at reduced pressure, and was chromatographed on a silica gel column by gradient elution (hexane/ether) to give a brown oil. The compound was obtained as a yellow crystal from the first band after two recrystallizations from acetone/hexane. yield: 78%, mp = 71-72°C.

Anal. for $C_{27}H_{29}S_2NFe$
Calcd. C:66.52%, H:5.60%, Found, C:66.43%, H:5.80%.

MS m/e (relative intensity): 487(M^+,100),472(M^+-Me,3),447 (19),419(17),364(M^+-S(Ph-CH_3),32),320(M^+-NMe_2-S(Ph-CH_3),33), 164(11),152(21),121(22),91(22),71(21),58(32),56(24),44(21).

IR (neat, CsI), 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(antisymmetric ring-metal stretch) cm^{-1}.

^1H NMR (δ ppm), 2.05(s,6H,N$\underline{Me}_2$),2.24(s,6H,Ph-C$\underline{H}_3$),3.43(d,1H, C$\underline{H}_2$N),3.51(d,1H,C$\underline{H}_2$N),4.30(m,2H,$\underline{H}_3$,$\underline{H}_4$,$\underline{H}_5$),4.39(m,4H,$C_5\underline{H}_4$), 4.53(m,1H,$\underline{H}_3$,$\underline{H}_4$,$\underline{H}_5$),6.95-7.06(m,8H,Ph).

^{13}C NMR (δ ppm, in CD_3COCD_3), 21.0(q,Ph-$\underline{C}H_3$),45.4(q,N$\underline{Me}_2$), 56.7(d,$\underline{C}$HNMe$_2$),71.0(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),72.9(d,$\underline{C}'_2$,$\underline{C}'_5$),73.3(d,$\underline{C}'_2$, $\underline{C}'_5$),73.8(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),76.6(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),77.1(d,$\underline{C}'_3$,$\underline{C}'_4$),77.2 (d,$\underline{C}'_3$,$\underline{C}'_4$),79.0(s,$\underline{C}'_1$),79.5(s,$\underline{C}_2$),89.5(s,$\underline{C}_1$),127.3(d,ortho Ph-$\underline{C}$),127.8(d,ortho Ph-$\underline{C}$),129.8(d,meta Ph-$\underline{C}$),130.0(d,meta Ph-$\underline{C}$),135.3(s,para Ph-$\underline{C}$),136.8(s,substituted Ph-$\underline{C}$),137.0 (s,substituted Ph-$\underline{C}$).

1-Dimethylaminomethyl-2-1′-bis[(4-chlorophenyl)thio]-ferrocene, (32, R=Ph-Cl)

The lithioferrocene was made by the same procedure as 21, (R=Me), by using 2.43 g (10 mmol) of dimethylaminoethyl-ferrocene (12), 100 ml dry ether, and 5.6 ml, 2.7 M solution of n-BuLi in hexane at -78°C. Then the lithioferrocene solution was added a mixture of freshly distilled TMEDA (1.43 ml, 12 mmol) and n-BuLi (5.6 ml, 2.7 M, 15 mmol) in 50 ml dry ether at -78°C. After being stirred 12 hr at room temperature, 4-chlorophenyl disulfide (8.65 g, 30 mmol) in 50 ml ether was transferred into the reaction flask through a cannula at -78°C and stirred for 40 hr. The reaction mixture was hydrolyzed with 30 ml of cold aqueous sodium

bicarbonate and filtered off. The resulting organic layer and ether extracts from the aqueous layer were combined, washed with water and dried over Na_2SO_4. A dark brown residue was obtained after removal of solvent at reduced pressure, and was chromatographed on a silica gel column by gradient elution (hexane/ether) to give a brown oil. The compound was obtained as a yellow crystal from the first band after two times recrystallizations from acetone/hexane. yield: 81%, mp = 75°C.

Anal. for $C_{25}H_{23}S_2NFeCl_2$
Calcd. C:56.83%, H:4.39%, Found, C:56.62%, H:4.35%.

MS m/e (relative intensity): 527(M^+,100),483(M^+-NMe_2,3),470 (M^+-CH_2NMe_2,3),384(M^+-S(C_6H_4Cl),55),340(M^+-NMe_2-S(C_6H_4Cl), 40),228(28),184(34),171(47),152(44),121(47),58(94),56(40), 44(31).

IR (neat, CsI), 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(antisymmetric ring-metal stretch) cm^{-1}.

^1H NMR (δ ppm), 2.04(s,6H,N$\underline{Me}_2$),3.44(s,2H,C$\underline{H}_2$N),4.37(m,2H, $\underline{H}_3$,$\underline{H}_4$,$\underline{H}_5$),4.45(m,4H,$C_5\underline{H}_4$),4.58(m,1H,$\underline{H}_3$,$\underline{H}_4$,$\underline{H}_5$),6.93-7.14 (m,8H,Ph).

^{13}C NMR (δ ppm, in CD_3COCD_3),45.3(q,N$\underline{Me}_2$),56.9(d,$\underline{C}$HNMe_2), 71.5(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),73.6(d,$\underline{C}'_2$,$\underline{C}'_5$),73.8(d,$\underline{C}'_2$,$\underline{C}'_5$),74.3(d,$\underline{C}_3$,

$\underline{C}_4$,$\underline{C}_5$),77.1(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),77.4(d,$\underline{C}'_3$,$\underline{C}'_4$),77.7(d,$\underline{C}'_3$,$\underline{C}'_4$),78.4 (s,$\underline{C}'_1$,$\underline{C}_2$),90.3(s,$\underline{C}_1$),128.1(d,ortho Ph-$\underline{C}$),128.9(d,ortho Ph-$\underline{C}$),129.1(d,meta Ph-$\underline{C}$),129.4(d,meta Ph-$\underline{C}$),131.1(s,para Ph-$\underline{C}$), 139.6(s,substituted Ph-$\underline{C}$),139.9(s,substituted Ph-$\underline{C}$).

(R)-1-(Dimethylamino)-ethylferrocene[(R)-1]

N,N-dimethyl-1-ferrocenylethylamine [($\underline{R}$)-1] was prepared and resolved by using ($\underline{R}$)-(+)tartaric acid as described by Ugi and coworkers [81]. The ($\underline{R}$)-(+)amine tartarate crystals were recovered from the mother liquor by treatment with diethylether and then recrystallized three times from 10:1\ acetone:water, allowing about 17 ml of solvent for each gram of salt. The tartarate salts were dissolved in 20% aqueous NaOH solution, extracted with diethyl ether and washed three times with water. The amine solutions were dried over anhydrous K_2CO_3 and evaporated to give a dark brown oil that partially solidified on cooling. $[\acute{A}]_D^{25}$+14.1° for ($\underline{R}$)-1-(dimethyl-amino)ethylferrocene [($\underline{R}$)-1].

MS m/e (relative intensity): 257(M^+,83),242(M^+-Me,95),213 (M^+-NMe_2,100),212(M^+-$HNMe_2$,36),121(FeCp,66),72($CHMeNMe_2$, 18),65(Cp,3),56(Fe,21),44(NMe_2,4).

^{1}H NMR (δ ppm), 4.11(m,4H,$C_5\underline{H}_4$),4.08(s,5H,Cp),3.60(q,J=6.8Hz ,1H,C$\underline{H}$),2.09(s,6H,N$\underline{Me}_2$),1.46(d,J=6.8Hz,3H,NC$\underline{H}CH_3$).

^{13}C NMR (δ ppm), 86.2(s,C_1),68.5(d,J=91Hz,$\underline{C}_2$,$\underline{C}_5$),67.7(d, J=88Hz,$\underline{C}$p),66.5(d,J=92.4Hz,$\underline{C}_2$,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),66.3(d,J=9.2Hz,

$\underline{C}_2$,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),65.9(d,J=91.4Hz,$\underline{C}_2$,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),57.8(d,J=67.3Hz, N$\underline{C}$H),40.2(q,J=47.4Hz,N$\underline{Me}_2$),14.8(q,J=42.9Hz,NCH$\underline{Me}$).

(R,S)-1-(1-Dimethylaminoethyl)-2-(methylseleno)ferrocene, (33, R=Me)

A hexane solution of n-BuLi (2.7 M, 2.16 ml, 5.83 mmol) was added to a solution of 1.50 g (5.84 mmol) (R)-1-(dimethylamino)ethylferrocene [(R)-1] in 60 ml dry ether at -78°C over a period of 20 min. The suspension was stirred for 12 hr at room temperature and cooled to -78°C, then 1.36 g (7.2 mmol) methyl diselenide was added dropwise over a 30 min period at -78°C. The reaction mixture was stirred under Ar for 24 hr at room temperature, and then refluxed for 12 hr to give a dark brown solution. Upon cooling to room temperature, the reaction mixture was slowly added to aqueous sodium bicarbonate and cooled in an ice-bath. The cloudy solution was then filtered. The resulting organic layer and ether extracts from the aqueous layer were combined, washed with ice water, dried over anhydrous $MgSO_4$, and concentrated in vacuo to afford a yellowish brown oil that was chromatographed on a silica gel column by gradient elution (hexane/ether/methylene chloride). The product was obtained as yellowish brown crystals after recrystallization from (acetone/hexane). Yield: 72.3%, mp = 74-75°C.

Anal. for $C_{15}H_{21}NFeSe$:
Calcd. C:51.48%, H:6.00%, Found C:51.56%, H:6.03%.

MS m/e (relative intensity): 351(M^+,64),336(M^+-Me,13),307 (M^+-NMe_2),306(M^+-$HNMe_2$,10),256(M^+-SeMe),226(M^+-$HNMe_2$-Se,6), 212(vinylferrocene,60),121(C_5H_5Fe,63),95(SeMe,9),72 ($HCMeNMe_2$,100),71($CMeNMe_2$,50),65(C_5H_5,14),56(Fe,61), 45 ($HNMe_2$,20),44(NMe_2,13).

IR (Nujol, CsI), 1176,1261 (C-N stretch),1090,1104 (asymmetric ring breathing),1000(ring-H bend parallel to ring),810(ring-H bend perpendicular to ring),497,526 (asymmetric ring tilt),450(asymmetric ring-Fe stretch) cm^{-1}.

^1H NMR (δ ppm), 1.36(d,3H,NCHC$\underline{H}_3$),2.10(s,6H,N$\underline{Me}_2$),2.12 (s,3H,SeC$\underline{H}_3$),3.91(q,1H,NC$\underline{H}$CH$_3$),4.08(s,5H,$C_5\underline{H}_5$),4.16(s,1H, $\underline{H}_3$,$\underline{H}_4$,$\underline{H}_5$),4.17(s,1H,$\underline{H}_3$,$\underline{H}_4$,$\underline{H}_5$),4.29(m,1H,$\underline{H}_3$,$\underline{H}_4$,$\underline{H}_5$).

^{13}C NMR (δ ppm, in CD_3COCD_3), 8.7(q,Se$\underline{C}H_3$),10.7(q,$\underline{C}H_3$CHN), 40.0(q,N$\underline{Me}_2$),57.7(d,CH$_3\underline{C}$HN),67.5(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),67.8(d,$\underline{C}_3$,$\underline{C}_4$, $\underline{C}_5$),70.3(d,C_5H_5),73.2(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),76.0(s,$\underline{C}_2$),94.2(s,$\underline{C}_1$).

(R,S)-1-(1-Dimethylaminoethyl)-2-(phenylseleno)ferrocene, (34, R=Ph)

A hexane solution of n-BuLi (2.7 M, 2.16 ml, 5.83 mmol) was added to a solution of 1.50 g (5.84 mmol) (R)-1-(dimethylamino)ethylferrocene [(R)-1] in 60 ml dry ether at -78°C over a period of 30 min. The suspension was stirred for 18 hr at 25°C and cooled to -78°C; then 1.80 g (5.83 mmol) phenyl diselenide in 40 ml ether was added dropwise over a 30 min period at -78°C. The reaction mixture was stirred under N_2 for 24 hr at room temperature, and then refluxed

for another 12 hr to give a dark brown solution. Upon cooling to room temperature, the reaction mixture was slowly hydrolyzed with aqueous sodium bicarbonate and cooled in an ice-bath; the cloudy solution was then filtered. The resulting organic layer and ether extracts from the aqueous layer were combined, washed with ice water, dried over anhydrous $MgSO_4$, and concentrated in vacuo to give a dark brown oil that was chromatographed on a silica gel column by gradient elution (hexane/ether/methylene chloride), giving the product as yellow crystals after two recrystallizations from (acetone/hexane). Yield: 73.0%, mp= 45-46^{o}C.

Anal. for $C_{20}H_{23}FeSeN$:
Calcd. C:58.28%, H:5.62%, Found C:58.28%, H:5.66%.

MS m/e (relative intensity): 412(M^+,7),397(M^+-Me,4),369(M^+-NMe_2,75),368(M^+-$HNMe_2$,90),367(M^+-3Me,35),342(5),288(M^+-$HNMe_2$-Se,25),212(vinylferrocene,19),165(54),152(28),121(C_5H_5Fe,77),72($HCMeNMe_2$,29),56(Fe,23),45($HNMe_2$,48),44(NMe_2,70).

IR (neat, CsI), 3091(ferrocene C-H stretch),3070-3060(phenyl C-H stretch),2952-2762(alkyl C-H stretch),1435(ferrocene antisymmetric C-C stretch),1255,1241(C-N stretch),818(C-H bend perpendicular to the plane of the Cp ring),510(Se-C stretch),463(antisymmetric ring-metal stretch) cm^{-1}.

^{1}H NMR (δ ppm), 1.47(d,3H,C$\underline{H}_3$CHN),1.98(s,6H,N$\underline{Me}_2$),3.92 (q,1H,$CH_3C\underline{H}N$),4.17(s,5H,$C_5\underline{H}_5$),4.32(m,2H,$\underline{H}_3$,$\underline{H}_5$),4.49(s,1H, $\underline{H}_4$),7.10-7.58(m,3H, meta,para-$\underline{H}$),7.40-7.43 (m,2H,ortho-$\underline{H}$).

^{13}C NMR (δ ppm, in CD_3COCD_3), 12.4(q,$\underline{C}H_3CH$),40.2(q,N$\underline{Me}_2$), 57.1(d,$CH_3\underline{C}H$),68.5(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),69.0(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),70.4 (d,$\underline{C}_5H_5$),72.6(s,$\underline{C}_2$),76.4(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),94.3(s,$\underline{C}_1$),126.1 (d,para Ph-$\underline{C}$),128.0(d,ortho Ph-$\underline{C}$),130.5(d,meta Ph-$\underline{C}$), 135.7(s,substituted Ph-$\underline{C}$).

(R,S)-1-(1-Dimethylaminoethyl)-2-(4-chlorophenyl)seleno-ferrocene, (35, R=4-chlorophenyl)

A hexane solution of n-BuLi (2.7 M, 2.16 ml, 5.83 mmol) was added to a solution of 1.50 g (5.84 mmol) of (R)-1-(dimethylamino)ethylferrocene [(R)-1] in 100 ml dry ether at -78°C. The suspension was stirred for 12 hr at room temperature and cooled to -78°C; then 2.22 g (5.83 mmol) 4-chlorophenyl diselenide in 60 ml dry ether was added dropwise over a 30 min period. The reaction mixture was stirred under N_2 for 24 hr at room temperature, giving an orange solution. After 12 hr refluxing under a N_2 flush, the mixture became a dark brown cloudy solution and was filtered. The filtrate was slowly added to aqueous sodium bicarbonate with cooling in an ice-bath and the cloudy solution was filtered again. The resulting organic layer and ether extracts from the aqueous layer were combined, washed with ice water, dried over anhydrous sodium sulfate and concentrated in vacuo to afford a dark brown oil that was

chromatographed on a silica gel column by gradient elution (hexane/ether/methylene chloride). The product was obtained as yellow crystals after recrystallization from acetone/hexane. Yield: 72.5%. mp= 92°C.

Anal. for $C_{20}H_{23}FeSeN$:
Calcd. C:53.78%, H:4.96%, Found C:53.81%, H:4.95%.

MS m/e (relative intensity): 447(M^+,78),432(M^+-Me,15),402 (M^+-NMe_2,60),322(M^+-$HNMe_2$-Se,14),212(23),165(55),149(76), 121(C_5H_5Fe,71),72($HCMeNMe_2$,60),65(C_5H_5,11),56(Fe,100),45 ($HNMe_2$,84),44(NMe_2,88).

IR (neat, CsI), 3090(ferrocene C-H stretch),3075-3030(phenyl C-H stretch),2950-2770(alkyl C-H stretch),1455(ferrocene antisymmetric C-C stretch),1255,1240(C-N stretch),815(C-H bend perpendicular to the plane of the Cp ring),518(Se-C stretch),495(antisymmetric ring-metal stretch) cm^{-1}.

^1H NMR (δ ppm), 1.37(d,3H,$C\underline{H}_3CHN$),1.94(s,6H,$N\underline{Me}_2$),3.88 (q,1H,$CH_3C\underline{H}N$),4.13(s,5H,$C_5\underline{H}_5$),4.28(m,2H,$\underline{H}_3$,$\underline{H}_5$),4.40(s,1H, $\underline{H}_4$),7.09(m,2H,ortho-$\underline{H}$),7.29(m,2H,meta-$\underline{H}$).

^{13}C NMR (δ ppm, in CD_3COCD_3), 11.2(q,$\underline{C}H_3CH$),40.0(q,$N\underline{Me}_2$), 57.4(d,$CH_3\underline{C}H$),69.1(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),69.4(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),70.7(d, $\underline{C}_5H_5$),72.0(s,$\underline{C}_2$),76.9(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),95.1(s,$\underline{C}_1$),129.0(d,ortho Ph-$\underline{C}$) ,132.2(d,meta Ph-$\underline{C}$),135.0(s,substituted Ph-$\underline{C}$).

(R,S)-1-Dimethylaminoethyl-2-1′-bis(methylthio)ferrocene, (36, R=Me)

A 2.7 M soultion of n-BuLi in hexane (3.0 ml, 8.1 mmol) was added to a solution of (R)-1-(Dimethylamino)ethylferrocene [(R)-1] (1.3 g, 5.1 mmol) in 100 ml dry ether at -78°C under argon in a 250 ml round-bottomed Schlenk flask equipped with a magnetic stirring bar. After the orange suspension reached room temperature it was stirred for 8 hr. Then, a solution of freshly distilled TMEDA (0.9 g, 7.5 mmol) and n-BuLi (3.0 ml, 8.1 mmol) in 50 ml dry ether was added to the reaction mixture at -78°C. After being stirred overnight at room temperature, the reaction mixture was added dropwise a solution of methyl disulfide (1.42 g, 15 mmol) in 20 ml ether over a 20 min period at -78°C. And the reaction was further stirred for 24 hr. The reaction mixture was hydrolyzed with cold saturated aqueous sodium bicarbonate (30 ml) and filtered. The resulting organic layer and ether extracts (50 ml) from the aqueous layer were combined, washed with ice water, dried over anhydrous $NaSO_4$, and concentrated in vacuo to give a dark oily residue that was chromatographed on a silica gel column by gradient elution (hexane/ether). The product was obtained as a brown oil. Yield 92%.

Anal. For $C_{16}H_{23}S_2NFe$:
Calcd. C:55.01%, H:6.64%, Found C:55.65%, H:6.80%.

MS m/e (relative intensity): 349(M^+,33),334(M^+-Me,13),304 (M^+-3Me,27),258((MeCH)$C_5H_3FeC_5H_4$(S-CH_3),42),242((CH)C_5H_3 FeC_5H_4(SCH_2),47),212(31),152(FeC_5H_4S,40),121(C_5H_3(CH_2NMe_2) ,65),72(MeCHN(CH_3)$_2$,100),56(Fe,78),44(-N(CH_3)$_2$,45).

IR (neat, CsI), 3095(ferrocene C-H stretch),2975-2778(alkyl C-H stretch),1441(ferrocene antisymmetric C-C stretch), 1267,1250(C-N stretch),827(C-H bend perpendicular to the plane of the Cp ring),652(S-C stretch),475(antisymmetric ring-metal stretch) cm^{-1}.

^1H NMR (δ ppm), 1.38(d,3H,C<u>H</u>$_3$CH),2.11(s,6H,N<u>Me</u>$_2$),2.24 (s,3H, SC<u>H</u>$_3$),2.29(s,3H,SC<u>H</u>$_3$),3.92(q,1H,C<u>H</u>$_3$CH),4.09(m,2H,<u>H</u>$_3$,<u>H</u>$_4$,<u>H</u>$_5$), 4.19(m,4H,C_5<u>H</u>$_4$),4.28(m,1H,<u>H</u>$_3$,<u>H</u>$_4$,<u>H</u>$_5$).

^{13}C NMR (δ ppm, in CD_3COCD_3), 10.7(q,<u>C</u>H_3CH),19.5(q,S<u>C</u>H_3), 19.6(q,S<u>C</u>H_3),40.0(q,N<u>Me</u>$_2$),56.0(d,CH_3<u>C</u>H),68.2(d,<u>C</u>$_3$,<u>C</u>$_4$,<u>C</u>$_5$), 68.8(d,<u>C</u>$_3$,<u>C</u>$_4$,<u>C</u>$_5$),71.0(d,<u>C</u>'$_2$,<u>C</u>'$_5$),72.2(d,<u>C</u>'$_2$,<u>C</u>'$_5$),72.3(d,<u>C</u>'$_3$, <u>C</u>'$_4$),73.1(d,<u>C</u>$_3$,<u>C</u>$_4$,<u>C</u>$_5$),84.6(s,<u>C</u>'$_1$),85.5(s,<u>C</u>$_2$),93.4(s,<u>C</u>$_1$).

<u>(R,S)-1-Dimethylaminoethyl-2-1'-bis(ethylthio)ferrocene (37, R=Et)</u>

The lithioferrocene was made by the same procedure as <u>36</u>, R=Me, by using 1.3 g (5.1 mmol) of (<u>R</u>)-1-(Dimethylamino)-ethylferrocene, 100 ml dry ether, and 3.0 ml (8.1 mmol) 2.7 <u>M</u> solution of <u>n</u>-BuLi in hexane at -78°C. Then, the lithioferrocene solution was added a mixture of freshly distilled TMEDA (0.9 g, 7.5 mmol) and <u>n</u>-BuLi (3.0 ml, 8.1 mmol) in 20 ml ether at -78°C. After being stirred overnight at room

temperature, ethyl disulfide (1.83 g, 15 mmol) was added by syringe at -78°C and the solution stirred for 24 hr. The reaction mixture was hydrolyzed with 30 ml of cold aqueous sodium bicarbonate and filtered off. The resulting organic layer and ether extracts from the aqueous layer were combined, washed with water and dried over Na_2SO_4. A dark brown residue was obtained after removal of solvent at reduced pressure, and was chromatographed on a silica gel column by gradient elution (hexane/ether) to give a brown oil. Yield 88%.

Anal. For $C_{18}H_{27}S_2NFe$:
Calcd. C:57.29%, H:7.21%, Found C:57.79%, H:7.50%.

MS m/e (relative intensity): 377(M^+,38),362(M^+-Me,14),332 (M^+-3Me,38),272((MeCH)$C_5H_3FeC_5H_4$(S-C_2H_5),33),242(47),212 (20),152(43),121(60),97(39),72(100),56(62),44(60).

IR (neat, CsI), 3095(ferrocene C-H stretch),2975-2780(alkyl C-H stretch),1443(ferrocene antisymmetric C-C stretch), 1265,1250(C-N stretch),830(C-H bend perpendicular to the plane of the Cp ring),652(S-C stretch),480(antisymmetric ring-metal stretch) cm^{-1}.

^1H NMR (δ ppm), 1.12(t,3H,βC$\underline{H}_3$),1.18(t,3H,βC$\underline{H}_3$),1.37(d,3H, C$\underline{H}_3$CH),2.10(s,6H,N$\underline{Me}_2$),2.54(q,2H,SC$\underline{H}_2$),2.65(m,1H,SC$\underline{H}_2$),2.78 (m,1H,sC$\underline{H}_2$),3.95(q,1H,CH_3C$\underline{H}$),4.08(m,2H,$\underline{H}_3$,$\underline{H}_4$,$\underline{H}_5$),4.19(m,4H, $C_5\underline{H}_4$),4.31(m,1H,$\underline{H}_3$,$\underline{H}_4$,$\underline{H}_5$).

^{13}C NMR (δ ppm, in CD_3COCD_3), 10.0(q,$\underline{C}H_3CH$),15.1(q,$\beta\underline{C}H_3$), 15.3(q,$\beta\underline{C}H_3$),30.4(t,$S\underline{C}H_2$),31.1(t,$S\underline{C}H_2$),40.0(q,$N\underline{Me}_2$),56.1 (d,$CH_3\underline{C}H$),68.8(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),69.6(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),71.8(d,$\underline{C}'_2$, $\underline{C}'_5$),72.0(d,$\underline{C}'_2$,$\underline{C}'_5$),75.1(d,$\underline{C}'_3$,$\underline{C}'_4$),76.3(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$), 81.5(s,$\underline{C}'_1$),81.7(s,$\underline{C}_2$),95.0(s,$\underline{C}_1$).

(R,S)-1-Dimethylaminoethyl-2-1'-bis[(n-propyl)thio]ferrocene (38, R=n-Pr)

The lithioferrocene was made by the same procedure as 36, R=Me, by using 1.3 g (5.1 mmol) of (R)-1-(Dimethylamino)-ethylferrocene, 100 ml dry ether, and 3.0 ml (8.1 mmol) 2.7 M solution of n-BuLi in hexane at -78°C. Then, the lithioferrocene solution was added a mixture of freshly distilled TMEDA (0.9 g, 7.5 mmol) and n-BuLi (3.0 ml, 8.1 mmol) in 20 ml ether at -78°C. After the solution had been stirred overnight at room temperature, propyl disulfide (2.26 g, 15 mmol) was added by syringe at -78°C and stirred for 24 hr. The reaction mixture was hydrolyzed with 30 ml of cold aqueous sodium bicarbonate and filtered off. The resulting organic layer and ether extracts from the aqueous layer were combined, washed with water and dried over Na_2SO_4. A dark brown residue was obtained after removal of solvent at reduced pressure, and was chromatographed on a silica gel column by gradient elution (hexane/ether) to give a brown oil. Yield 80%.

Anal. For $C_{20}H_{31}S_2NFe$:
Calcd. C:59.25%, H:7.71%, Found C:59.62%, H:7.82%.

MS m/e (relative intensity): 405(M^+,19),390(M^+-Me,8),360 (M^+-3Me,61),286((MeCH)$C_5H_3FeC_5H_4$(S-C_3H_7),48),242(92),152 (61),121(99),97(39),72(69),56(58),44(100).

IR (neat, CsI), 3095(ferrocene C-H stretch),2962-2779(alkyl C-H stretch),1441(ferrocene antisymmetric C-C stretch), 1267,1250(C-N stretch),829(C-H bend perpendicular to the plane of the Cp ring),653(S-C stretch),485(antisymmetric ring-metal stretch) cm^{-1}.

^1H NMR (δ ppm), 0.89(t,3H,rC$\underline{H}_3$),0.95(t,3H,rC$\underline{H}_3$),1.37(d,3H, C$\underline{H}_3$CH),1.46(m,2H,βC$\underline{H}_2$),1.58(m,2H,βC$\underline{H}_2$),2.10(s,6H,N$\underline{Me}_2$),2.50 (m,2H,SC$\underline{H}_2$),2.59(m,1H,SC$\underline{H}_2$),2.75(m,1H,SC$\underline{H}_2$),3.95(q,1H,C$\underline{H}_3$CH) ,4.09(m,2H,$\underline{H}_3$,$\underline{H}_4$,$\underline{H}_5$),4.18(m,4H,$C_5\underline{H}_4$),4.29(m,1H,$\underline{H}_3$,$\underline{H}_4$,$\underline{H}_5$).

^{13}C NMR (δ ppm, in CD_3COCD_3), 10.0(q,$\underline{C}H_3$CH),13.4(q,r$\underline{C}H_3$), 13.7(q,r$\underline{C}H_3$),23.2(t,β$\underline{C}H_2$),23.3(t,β$\underline{C}H_2$),38.6(t,S$\underline{C}H_2$),39.3 (t,S$\underline{C}H_2$),39.9(q,N$\underline{Me}_2$),56.1(d,$CH_3\underline{C}H$),68.7(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),69.5 (d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),71.7(d,$\underline{C}'_2$,$\underline{C}'_5$),71.9(d,$\underline{C}'_2$,$\underline{C}'_5$),75.0(d,$\underline{C}'_3$,$\underline{C}'_4$) ,75.8(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),81.7(s,$\underline{C}'_1$),82.0(s,$\underline{C}_2$),95.0(s,$\underline{C}_1$).

(R,S)-1-Dimethylaminoethyl-2-1′-bis[(i-propyl)thio]ferrocene (39, R=i-Pr)

The lithioferrocene was made by the same procedure as 36, R=Me, by using 1.3 g (5.1 mmol) of (R)-1-(Dimethylamino)-ethylferrocene, 100 ml dry ether, and 3.0 ml (8.1 mmol) 2.7 M solution of n-BuLi in hexane at -78°C. Then, the lithio-ferrocene solution was added a mixture of freshly distilled

TMEDA (0.9 g, 7.5 mmol) and n-BuLi (3.0 ml, 8.1 mmol) in 20 ml ether at -78°C. After the solution had been stirred overnight at room temperature, isopropyl disulfide (2.26 g, 15 mmol) was added by syringe at -78°C and stirred for 24 hr. The reaction mixture was hydrolyzed with 30 ml of cold aqueous sodium bicarbonate and filtered off. The resulting organic layer and ether extracts from the aqueous layer were combined, washed with water and dried over Na_2SO_4. A dark brown residue was obtained after removal of solvent at reduced pressure, and was chromatographed on a silica gel column by gradient elution (hexane/ether) to give a brown oil. Yield 82%.

Anal. For $C_{20}H_{31}S_2NFe$:
Calcd. C:59.25%, H:7.71, Found C:59.52%, H:7.83%.

MS m/e (relative intensity): 405(M^+,9),390(M^+-Me,3),360(M^+-3Me,19),286((MeCH)$C_5H_3FeC_5H_4$(S-C_3H_7),14),274(11),242(25),152(19),121(31),72(28),56(25),44(34).

IR (neat, CsI), 3095(ferrocene C-H stretch),2962-2778(alkyl C-H stretch),1440(ferrocene antisymmetric C-C stretch),1260,1250(C-N stretch),831(C-H bend perpendicular to the plane of the Cp ring),652(S-C stretch),485(antisymmetric ring-metal stretch) cm^{-1}.

^1H NMR (δ ppm), 1.06(d,3H,βC$\underline{H}_3$),1.09(d,3H,βC$\underline{H}_3$),1.13(d,3H,βC$\underline{H}_3$),1.16(d,3H,βC$\underline{H}_3$),1.29(d,3H,C$\underline{H}_3$CH),2.06(s,6H,N$\underline{Me}_2$),

2.78(h,1H,SC$\underline{H}$),3.17(h,1H,SC$\underline{H}$),3.94(q,1H,$CH_3C\underline{H}$),4.04(m,2H, $\underline{H}_3$,$\underline{H}_4$,$\underline{H}_5$),4.14(m,4H,$C_5\underline{H}_4$),4.29(m,1H,$\underline{H}_3$,$\underline{H}_4$,$\underline{H}_5$).

^{13}C NMR (δ ppm, in CD_3COCD_3), 9.2(q,$\underline{C}H_3CH$),23.0(q,$\beta\underline{C}H_3$), 23.6(q,$\beta\underline{C}H_3$),24.1(q,$\beta\underline{C}H_3$),39.3(d,S$\underline{C}$H),39.8(q,N$\underline{Me}_2$),56.1 (d,$CH_3\underline{C}$H),69.0(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),70.0(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),72.2(d,$\underline{C}'_2$,$\underline{C}'_5$) ,72.6(d,$\underline{C}'_2$,$\underline{C}'_5$),76.6(d,$\underline{C}'_3$,$\underline{C}'_4$),76.8(d,$\underline{C}'_3$,$\underline{C}'_4$),77.5 (d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),79.3(s,$\underline{C}'_1$),80.1(s,$\underline{C}_2$),96.2(s,$\underline{C}_1$).

(R,S)-1-Dimethylaminoethyl-2-1′-bis[(n-butyl)thio]ferrocene (40, R=n-Bu)

The lithioferrocene was made by the same procedure as 36, R=Me, by using 1.3 g (5.1 mmol) of (R)-1-(Dimethylamino)-ethylferrocene, 100 ml dry ether, and 3.0 ml (8.1 mmol) 2.7 M solution of n-BuLi in hexane at -78°C. Then, the lithioferrocene solution was added a mixture of freshly distilled TMEDA (0.9 g, 7.5 mmol) and n-BuLi (3.0 ml, 8.1 mmol) in 20 ml ether at -78°C. After the solution had been stirred overnight at room temperature, butyl disulfide (2.68 g, 15 mmol) was added by syringe at -78°C and stirred for 24 hr. The reaction mixture was hydrolyzed with 30 ml of cold aqueous sodium bicarbonate and filtered off. The resulting organic layer and ether extracts from the aqueous layer were combined, washed with water and dried over Na_2SO_4. A dark brown residue was obtained after removal of solvent at reduced pressure, and was chromatographed on a silica gel column by gradient elution (hexane/ether) to give a brown oil. Yield 79%.

Anal. For $C_{22}H_{35}S_2NFe$:

Calcd. C:60.96%, H:8.14%, Found C:61.13%, H:8.28%.

MS m/e (relative intensity): 433(M^+,25),418(M^+-Me,10),388 (M^+-3Me,58),300((MeCH)$C_6H_3FeC_6H_3S(C_4H_9)$,32),274(11),242 (66),152(40),121(44),97(36),72(94),56(36),44(77).

IR (neat, CsI), 3095(ferrocene C-H stretch),2962-2778(alkyl C-H stretch),1440(ferrocene antisymmetric C-C stretch), 1275,1250(C-N stretch),830(C-H bend perpendicular to the plane of the Cp ring),655(S-C stretch),482(antisymmetric ring-metal stretch) cm^{-1}.

^1H NMR (δ ppm), 0.83(t,3H,δC$\underline{H}_3$),0.88(t,3H,δC$\underline{H}_3$),1.37(d,3H, C$\underline{H}_3$CH),1.32(m,2H,rC$\underline{H}_2$),1.34(m,2H,rC$\underline{H}_2$),1.47(m,2H,βC$\underline{H}_2$), 1.53(m,2H,βC$\underline{H}_2$),2.10(s,6H,N$\underline{Me}_2$),2.53(m,2H,SC$\underline{H}_2$),2.64(m,1H, SC$\underline{H}_2$),2.77(m,1H,SC$\underline{H}_2$),3.93(q,1H,C$\underline{H}_3$CH),4.09(m,2H,$\underline{H}_3$,$\underline{H}_4$,$\underline{H}_5$), 4.18(m,4H,$C_5\underline{H}_4$),4.29(m,1H,$\underline{H}_3$,$\underline{H}_4$,$\underline{H}_5$).

^{13}C NMR (δ ppm, in CD_3COCD_3), 9.8(q,$\underline{C}H_3$CH),13.9(q,δ$\underline{C}H_3$), 22.0(t,r$\underline{C}H_2$),22.2(t,r$\underline{C}H_2$),32.1(t,β$\underline{C}H_2$),36.3(t,S$\underline{C}H_2$),37.0 (t,S$\underline{C}H_2$),39.9(q,N$\underline{Me}_2$),56.1(d,$CH_3\underline{C}$H),68.7($\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),69.5 (d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),71.3(d,$\underline{C}'_2$,$\underline{C}'_5$),71.9(d,$\underline{C}'_2$,$\underline{C}'_5$),74.9(d,$\underline{C}'_3$,$\underline{C}'_4$) ,75.9(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),81.3(s,$\underline{C}'_1$),82.2(s,$\underline{C}_2$),95.0(s,$\underline{C}_1$).

(R,S)-1-Dimethylaminoethyl-2-1'-bis[(sec-butyl)thio]-ferrocene, (41, R=sec-Bu)

The lithioferrocene was made by the same procedure as 36, R=Me, by using 1.3 g (5.1 mmol) of (R)-1-(Dimethylamino)-ethylferrocene, 100 ml dry ether, and 3.0 ml (8.1 mmol) 2.7 M solution of n-BuLi in hexane at -78°C. Then, the lithioferrocene solution was added a mixture of freshly distilled TMEDA (0.9 g, 7.5 mmol) and n-BuLi (3.0 ml, 8.1 mmol) in 20 ml ether at -78°C. After the solution had been stirred overnight at room temperature, sec-butyl disulfide (2.68 g, 15 mmol) was added by syringe at -78°C and stirred for 24 hr. The reaction mixture was hydrolyzed with 30 ml of cold aqueous sodium bicarbonate and filtered off. The resulting organic layer and ether extracts from the aqueous layer were combined, washed with water and dried over Na_2SO_4. A dark brown residue was obtained after removal of solvent at reduced pressure, and was chromatographed on a silica gel column by gradient elution (hexane/ether) to give a brown oil. Yield 76%.

Anal. For $C_{22}H_{35}S_2NFe$:
Calcd. C:60.96%, H:8.14%, Found C:61.19%, H:8.10%.

MS m/e (relative intensity): 433(M^+,17),418(M^+-Me,6),388 (M^+-3Me,35),300((MeCH)$C_5H_3FeC_5H_4$(S-C_4H_9),17),274(23),242 (50),152(43),121(49),72(63),56(40),44(75).

IR (neat, CsI), 3095(ferrocene C-H stretch),2970-2778(alkyl C-H stretch),1450(ferrocene antisymmetric C-C stretch), 1265,1250(C-N stretch),831(C-H bend perpendicular to the plane of the Cp ring),660(S-C stretch),480(antisymmetric ring-metal stretch) cm^{-1}.

^1H NMR (δ ppm), 0.85(t,3H,rC$\underline{H}_3$),0.92(t,3H,rC$\underline{H}_3$),1.03(d,3H ,βC$\underline{H}_3$),1.06(d,3H,βC$\underline{H}_3$),1.33(d,3H,C$\underline{H}_3$CH),1.42(m,2H,βC$\underline{H}_2$), 1.50(m,2H,βC$\underline{H}_2$),2.08(s,6H,N$\underline{Me}_2$),2.54(m,1H,SC$\underline{H}_2$),2.97(m,1H, SC$\underline{H}_2$),3.96(q,1H,CH$_3$C$\underline{H}$),4.09(m,2H,$\underline{H}_3$,$\underline{H}_4$,$\underline{H}_5$),4.19(m,4H,C$_5\underline{H}_4$), 4.30(m,1H,$\underline{H}_3$,$\underline{H}_4$,$\underline{H}_5$).

^{13}C NMR (δ ppm, in CD_3COCD_3), 9.4(q,$\underline{C}$H$_3$CH),12.1(q,r$\underline{C}$H$_3$), 12.6(q,r$\underline{C}$H$_3$),21.4(q,$\beta\underline{C}$H$_3$),22.0(q,$\beta\underline{C}$H$_3$),30.1(t,$\beta\underline{C}$H$_2$),30.4(t,β $\underline{C}$H$_2$),40.1(q,N$\underline{Me}_2$),46.4(d,S$\underline{C}$H),46.8(d,S$\underline{C}$H),56.4(d,CH$_3\underline{C}$H),69.3 (d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),70.4(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),72.5(d,$\underline{C}'_2$,$\underline{C}'_5$),73.0(d,$\underline{C}'_2$, $\underline{C}'_5$),77.0(d,$\underline{C}'_3$,$\underline{C}'_4$),77.2(d,$\underline{C}'_3$,$\underline{C}'_4$),77.7(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),80.2 (s,$\underline{C}'_1$),80.6(s,$\underline{C}_2$),96.5(s,$\underline{C}_1$).

(R,S)-1-Dimethylaminoethyl-2-1'-bis[(t-butyl)thio]ferrocene (42, R=t-Butyl)

The lithioferrocene was made by the same procedure as 36, R=Me, by using 1.3 g (5.1 mmol) of (R)-1-(Dimethylamino)-ethylferrocene, 100 ml dry ether, and 3.0 ml (8.1 mmol) 2.7 M solution of n-BuLi in hexane at -78°C. Then, the lithioferrocene solution was added a mixture of freshly distilled TMEDA (0.9 g, 7.5 mmol) and n-BuLi (3.0 ml, 8.1 mmol) in 20 ml ether at -78°C. After the solution had been stirred

overnight at room temperature, tert-butyl disulfide (2.68 g, 15 mmol) was added by syringe at -78°C and stirred for 24 hr. The reaction mixture was hydrolyzed with 30 ml of cold aqueous sodium bicarbonate and filtered off. The resulting organic layer and ether extracts from the aqueous layer were combined, washed with water and dried over Na_2SO_4. A dark brown residue was obtained after removal of solvent at reduced pressure, and was chromatographed on a silica gel column by gradient elution (hexane/ether) to give a brown oil. Yield: 54%.

Anal. for $C_{22}H_{35}S_2NFe$
Calcd. C:60.96%, H:8.14%, Found C:60.09%, H:8.15%.

MS m/e (relative intensity): 433(M^+,27),388(M^+-3Me,62),373 (M^+-4Me,21),361(M^+-CHMe-NMe_2,13),331(M^+-NMe_2-C_4H_9,30),299 (M+-NMe_2-SC_4H_9,7),274(12),242(45),152(37),121(39),72(92), 56(21),44(99).

IR (Nujol, CsI), 3081(ferrocene C-H stretch),2960-2770(alkyl C-H stretch),1450(ferrocene antisymmetric C-C stretch), 1260,1250(C-N stretch),839(C-H bend perpendicular to the plane of the Cp ring),640(S-C stretch),465(antisymmetric ring-metal stretch) cm^{-1}.

^1H NMR (δ ppm), 1.17(s,18H,$\beta C\underline{H}_3$),1.44(d,3H,$C\underline{H}_3CH$),2.06(s,6H, $N\underline{Me}_2$),3.62(q,1H,$C\underline{H}_3CH$),4.09(m,2H,$\underline{H}_3$,$\underline{H}_4$,$\underline{H}_5$),4.16(m,4H,$C_5\underline{H}_4$), 4.20(m,1H,$\underline{H}_3$,$\underline{H}_4$,$\underline{H}_5$).

^{13}C NMR (δ ppm, in CD_3COCD_3), 15.8(q,$\underline{C}H_3CH$),31.0(s,βCH_3), 40.7(q,$N\underline{Me}_2$),44.7(s,$S\underline{C}Me_3$),58.7(d,$CH_3\underline{C}H$),68.7(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$), 69.1(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),69.5(d,$\underline{C}'_2$,$\underline{C}'_5$),69.6(d,$\underline{C}'_2$,$\underline{C}'_5$),71.0(d,$\underline{C}'_3$, $\underline{C}'_4$),71.4(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),77.4(d,$\underline{C}'_1$),77.5(d,$\underline{C}_2$),89.4(s,C_1).

(R,S)-1-Dimethylaminoethyl-2-1'-bis[(i-pentyl)thio]ferrocene (43, R=i-Pentyl)

The lithioferrocene was made by the same procedure as 36, R=Me, by using 1.3 g (5.1 mmol) of (R)-1-(Dimethylamino)-ethylferrocene, 100 ml dry ether, and 3.0 ml (8.1 mmol) 2.7 M solution of n-BuLi in hexane at -78°C. Then, the lithioferrocene solution was added a mixture of freshly distilled TMEDA (0.9 g, 7.5 mmol) and n-BuLi (3.0 ml, 8.1 mmol) in 20 ml ether at -78°C. After the solution had been stirred overnight at room temperature, iso-pentyl disulfide (3.10 g, 15 mmol) was added by syringe at -78°C and stirred for 24 hr. The reaction mixture was hydrolyzed with 30 ml of cold aqueous sodium bicarbonate and filtered off. The resulting organic layer and ether extracts from the aqueous layer were combined, washed with water and dried over Na_2SO_4. A dark brown residue was obtained after removal of solvent at reduced pressure, and was chromatographed on a silica gel column by gradient elution (hexane/ether) to give a brown oil. Yield 76%.

Anal. For $C_{24}H_{39}S_2NFe$:
Calcd. C:62.46%, H:8.52%, Found C:62.73%, H:8.32%.

MS m/e (relative intensity): 461(M^+,68),446(M^+-Me,23),416 (M^+-3Me,63),314((MeCH)$C_5H_3FeC_5H_4$(S-C_5H_{11}),35),242(26),121 (22),72(92),56(15),44(22).

IR (neat, CsI), 3095(ferrocene C-H stretch),2980-2780(alkyl C-H stretch),1430(ferrocene antisymmetric C-C stretch), 1259,1245(C-N stretch),835(C-H bend perpendicular to the plane of the Cp ring),655(S-C stretch),475(antisymmetric ring-metal stretch) cm^{-1}.

^1H NMR (δ ppm), 0.80(d,3H,δC$\underline{H}_3$),0.81(d,3H,δC$\underline{H}_3$),0.84(d,3H ,δC$\underline{H}$3),0.85(d,3H,δC$\underline{H}_3$),1.37(d,3H,C$\underline{H}_3$CH),1.42(m,1H,rC$\underline{H}$), 1.61(m,1H,rC$\underline{H}$),2.10(s,6H,N$\underline{Me}_2$),2.52(m,2H,βC$\underline{H}_2$),2.54(m,2H, βC$\underline{H}_2$),2.58(m,2H,SC$\underline{H}_2$),2.75(m,1H,SC$\underline{H}_2$),2.79(m,1H,SC$\underline{H}_2$), 3.95(q,1H,CH_3C$\underline{H}$),4.09(m,2H,$\underline{H}_3$,$\underline{H}_4$,$\underline{H}_5$),4.18(m,4H,$C_5\underline{H}_4$), 4.29(m,1H,$\underline{H}_3$,$\underline{H}_4$,$\underline{H}_5$).

^{13}C NMR (δ ppm, in CD_3COCD_3), 9.7(q,$\underline{C}H_3$CH),22.4(q,δ$\underline{C}H_3$), 22.6(q,δ$\underline{C}H_3$),22.8(q,δ$\underline{C}H_3$),27.4(d,r$\underline{C}$H),27.7(d,r$\underline{C}$H),34.6(t, β$\underline{C}H_2$),35.3(t,β$\underline{C}H_2$),39.2(t,S$\underline{C}H_2$),39.9(q,N$\underline{Me}_2$),56.1(d,$CH_3\underline{C}$H), 68.8(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),69.6(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),71.7(d,$\underline{C}'_2$,$\underline{C}'_5$),71.9 (d,$\underline{C}'_2$,$\underline{C}'_5$),74.8(d,$\underline{C}'_3$,$\underline{C}'_4$),76.1(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),81.7(s,$\underline{C}'_1$), 82.4(s,$\underline{C}_2$),95.3(s,$\underline{C}_1$).

(R,S)-1-Dimethylaminoethyl-2-1'-bis(phenylthio)ferrocene (44, R=Ph)

The lithioferrocene was made by the same procedure as 36, R=Me, by using 1.3 g (5.1 mmol) of (R)-1-(Dimethylamino)-ethylferrocene, 100 ml dry ether, and 3.0 ml (8.1 mmol) 2.7

M solution of n-BuLi in hexane at -78°C. Then, the lithioferrocene solution was added a mixture of freshly distilled TMEDA (0.9 g, 7.5 mmol) and n-BuLi (3.0 ml, 8.1 mmol) in 20 ml ether at -78C. After the solution had been stirred overnight at room temperature, phenyl disulfide (3.28 g, 15 mmol) was added by syring at -78°C and stirred for 24 hr. The reaction mixture was hydrolyzed with 30 ml of cold aqueous sodium bicarbonate and filtered off. The resulting organic layer and ether extracts from the aqueous layer were combined, washed with water and dried over Na_2SO_4. A dark brown residue was obtained after removal of solvent at reduced pressure, and was chromatographed on a silica gel column by gradient elution (hexane/ether) to give a brown oil. The compound was obtained as yellow crystals from the first band after two recrystallization from acetone/hexane. yield: 77%. mp = 74-75°C.

Anal. for $C_{26}H_{27}S_2NFe$
Calcd. C:65.96%, H:5.75%, Found C:65.61%, H:5.77%

MS m/e (relative intensity): 473(M^+,12),458(M^+-Me,8),428(M^+-3Me,15),402(M^+-CHMe-NMe_2,4),320(M^+-NMe_2-SPh,11),305(M^+-NMe_2-Me-SPh,3),152(6),121(5),86(40),84(58),72(15),57(20),56(17),51(29),49(100),44(40).

IR (neat, CsI), 3095(ferrocene C-H stretch),3065,3050(phenyl C-H stretch),2975-2765(alkyl C-H stretch),1441(ferrocene antisymmetric C-C stretch),1268,1250(C-N stretch),830(C-H

bend perpendicular to the plane of the Cp ring),470 (antisymmetric ring-metal stretch) cm^{-1}.

^1H NMR (δ ppm), 1.47(d,3H,$C\underline{H}_3CH$),1.93(s,6H,$N\underline{Me}_2$),3.91(q,1H, $CH_3C\underline{H}$),4.30(m,2H,$\underline{H}_3$,$\underline{H}_4$,$\underline{H}_5$),4.41(m,4H,$C_5\underline{H}_4$),4.58(s,1H,$\underline{H}_3$,$\underline{H}_4$, $\underline{H}_5$),7.01-7.18(m,10H,$C_6\underline{H}_5$).

^{13}C NMR (δ ppm, in CD_3COCD_3), 12.1(q,$\underline{C}H_3CH$),40.2(q,$N\underline{Me}_2$), 56.4(d,$CH_3\underline{C}H$),70.7(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),70.9(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),73.8(d,$\underline{C}'_2$, $\underline{C}'_5$),73.9(d,$\underline{C}'_2$,$\underline{C}'_5$),77.5(d,$\underline{C}'_3$,$\underline{C}'_4$),78.1(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),79.1(s ,$\underline{C}'_1$),79.3(s,C_2),96.0(s,$\underline{C}_1$),125.7(d,para Ph-$\underline{C}$),125.9(d,para Ph-$\underline{C}$), 127.0(d,ortho Ph-$\underline{C}$),128.0(d,ortho Ph-$\underline{C}$),129.0(d,meta Ph-$\underline{C}$), 129.6(d,meta Ph-$\underline{C}$),141.3(s,substituted Ph-$\underline{C}$).

(R,S)-1-Dimethylaminoethyl-2-1'-bis(benzylthio)ferrocene (45, R=Bz)

The lithioferrocene was made by the same procedure as 36, R=Me, by using 1.3 g (5.1 mmol) of (R)-1-(Dimethylamino)-ethylferrocene, 100 ml dry ether, and 3.0 ml (8.1 mmol) 2.7 M solution of n-BuLi in hexane at -78°C. Then, the lithioferrocene solution was added a mixture of freshly distilled TMEDA (0.9 g, 7.5 mmol) and n-BuLi (3.0 ml, 8.1 mmol) in 20 ml ether at -78°C. After the solution had been stirred overnight at room temperature, benzyl disulfide (3.70 g, 15 mmol) was added by syringe at -78°C and stirred for 24 hr. The reaction mixture was hydrolyzed with 30 ml of cold aqueous sodium bicarbonate and filtered off. The resulting organic layer and ether extracts from the aqueous layer were

combined, washed with water and dried over Na_2SO_4. A dark brown residue was obtained after removal of solvent at reduced pressure, and was chromatographed on a silica gel column by gradient elution (hexane/ether). The product was obtained as a brown oil. Yield: 54%.

Anal. for $C_{28}H_{31}S_2NFe$
Calcd. C:67.06%, H:6.23%, Found C:66.95%, H:6.44%.

MS m/e (relative intensity): 501(M^+,24),486(M^+-Me,7),456(M^+-3Me,15),430(M^+-CHMe-NMe_2,24),334(40),378(M^+-SBz,5),243(21),187(14),179(11),155(13),121(14),91(18),72(98),56(23),44(21).

IR (neat, CsI), 3082(ferrocene C-H stretch),3060-3021(phenyl C-H stretch),2960-2775(alkyl C-H stretch),1450(ferrocene antisymmetric C-C stretch),1257,1248(C-N stretch),819(C-H bend perpendicular to the plane of the Cp ring),671(S-C stretch),470(antisymmetric ring-metal stretch) cm^{-1}.

^1H NMR (δ ppm), 1.36(d,3H,$C\underline{H}_3CH$),2.15(s,6H,$N\underline{Me}_2$),3.72(s,2H,$SC\underline{H}_2$),3.86(d,1H,$SC\underline{H}_2$),3.90(d,1H,$SC\underline{H}_2$),4.02(q,1H,$CH_3C\underline{H}$),4.12-4.31(m,7H,$C_5\underline{H}_4$,$C_5\underline{H}_3$),7.14-7.25(m,10H,Ph).

^{13}C NMR (δ ppm, in CD_3COCD_3), 9.04(q,$\underline{C}H_3CH$),40.0(q,$N\underline{Me}_2$),41.5(t,$S\underline{C}H_2$),42.2(t,$S\underline{C}H_2$),56.7(d,$CH_3\underline{C}H$),69.0(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),70.2(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),72.0(d,$\underline{C}'_2$,$\underline{C}'_5$),72.1(d,$\underline{C}'_2$,$\underline{C}'_5$),75.3(d,$\underline{C}'_3$,$\underline{C}'_4$),76.7(d,$\underline{C}'_3$,$\underline{C}'_4$),77.4(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),81.1(s,$\underline{C}'_1$),82.1(s,$\underline{C}_2$),96.1(s,$\underline{C}_1$),127.3(d,para Ph-$\underline{C}$),127.5(d,para Ph-$\underline{C}$),128.8(d,ortho Ph-$\underline{C}$),128.9(d,ortho Ph-$\underline{C}$),129.7(d,meta Ph-$\underline{C}$),129.9(d,meta Ph-$\underline{C}$),140.0(s,substituted Ph-$\underline{C}$).

(R,S)-1-Dimethylaminoethyl-2-1'-bis[(4-tolyl)thio]ferrocene (46, R=4-Tolyl)

The lithioferrocene was made by the same procedure as 36, R=Me, by using 1.3 g (5.1 mmol) of (R)-1-(Dimethylamino)-ethylferrocene, 100 ml dry ether, and 3.0 ml (8.1 mmol) 2.7 M solution of n-BuLi in hexane at -78°C. Then, the lithioferrocene solution was added a mixture of freshly distilled TMEDA (0.9 g, 7.5 mmol) and n-BuLi (3.0 ml, 8.1 mmol) in 20 ml ether at -78°C. After the solution had been stirred overnight at room temperature, p-tolyl disulfide (3.70 g, 15 mmol) was added by syringe at -78°C and stirred for 24 hr. The reaction mixture was hydrolyzed with 30 ml of cold aqueous sodium bicarbonate and filtered off. The resulting organic layer and ether extracts from the aqueous layer were combined, washed with water and dried over Na_2SO_4. A dark brown residue was obtained after removal of solvent at reduced pressure, and was chromatographed on a silica gel column by gradient elution (hexane/ether) to give a brown oil. The product was obtained as yellow crystals from the first band after two recrystallizations from acetone/hexane. yield: 72%. mp = 89-90°C.

Anal. for $C_{28}H_{31}S_2NFe$

Calcd. C:67.06%, H:6.23%, Found C:66.86%, H:6.21%.

MS m/e (relative intensity): 501(M^+,59),486(M^+-Me,22),456 (M^+-3Me,35),441(M^+-4Me,3),430(M^+-CHMe-NMe_2,19),334(66),378

(M^+-S(Ph-CH_3),3),243(18),187(17),179(12),155(14),153(25), 121(16),91(27),72(100),56(24),44(24).

IR (neat, CsI), 3150(ferrocene C-H stretch),3095,3080(phenyl C-H stretch),2970-2765(alkyl C-H stretch),1450(ferrocene antisymmetric C-C stretch),1275,1250(C-N stretch),847(C-H bend perpendicular to the plane of the Cp ring),470 (antisymmetric ring-metal stretch) cm^{-1}.

^1H NMR (δ ppm), 1.48(d,3H,C$\underline{H}_3$CH),1.95(s,6H,N$\underline{Me}_2$),2.24(s,6H, Ph-C$\underline{H}_3$),3.91(q,1H,CH_3C$\underline{H}$),4.29(m,2H,$\underline{H}_3$,$\underline{H}_4$,$\underline{H}_5$),4.37(m,4H, $C_5\underline{H}_4$),4.54(s,1H,$\underline{H}_3$,$\underline{H}_4$,$\underline{H}_5$),6.94-7.12(m,8H,Ph).

^{13}C NMR (δ ppm, in CD_3COCD_3), 12.3(q,$\underline{C}H_3$CH),20.8(q,$\underline{C}H_3$-Ph), 40.2(q,N$\underline{Me}_2$),56.2(d,$CH_3\underline{C}H$),70.4(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),70.6(d,$\underline{C}_3$,$\underline{C}_4$, $\underline{C}_5$),73.4(d,$\underline{C}'_2$,$\underline{C}'_5$),73.6(d,$\underline{C}'_2$,$\underline{C}'_5$),77.2(d,$\underline{C}'_3$,$\underline{C}'_4$),77.7(d, $\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),79.0(s, $\underline{C}'_1$),80.1(s,$\underline{C}_2$),95.4(s,$\underline{C}_1$),127.6(d,ortho Ph-$\underline{C}$),128.6(d,ortho Ph-$\underline{C}$),129.8(d,meta Ph-$\underline{C}$),130.3(d,meta Ph-$\underline{C}$),135.5(s,para Ph-$\underline{C}$),135.8(s,para Ph-$\underline{C}$),137.5(s, substituted Ph-$\underline{C}$).

(R,S)-1-Dimethylaminoethyl-2-1'-bis[(4-chlorophenyl)thio]-ferrocene, (47, R=4-Chlorophenyl)

The lithioferrocene was made by the same procedure as 36, R=Me, by using 1.3 g (5.1 mmol) of (R)-1-(Dimethylamino)-ethylferrocene, 100 ml dry ether, and 3.0 ml (8.1 mmol) 2.7 M solution of n-BuLi in hexane at -78°C. Then, the lithio-ferrocene solution was added a mixture of freshly distilled TMEDA (0.9 g, 7.5 mmol) and n-BuLi (3.0 ml, 8.1 mmol) in 20

ml ether at -78°C. After the solution had been stirred overnight at room temperature, Bis(p-chlorophenyl) disulfide (4.33 g, 15 mmol) was added by syringe at -78°C and stirred for 24 hr. The reaction mixture was hydrolyzed with 30 ml of cold aqueous sodium bicarbonate and filtered off. The resulting organic layer and ether extracts from the aqueous layer were combined, washed with water and dried over Na_2SO_4. A dark brown residue was obtained after removal of solvent at reduced pressure, and was chromatographed on a silica gel column by gradient elution (hexane/ether) to give a brown oil. The product was obtained as yellow crystals from the first band after two recrystallizations from acetone/hexane. yield: 76%. mp = 101-102°C.

Anal. for $C_{26}H_{25}S_2NFeCl_2$
Calcd. C:57.59%, H:4.65%, Found C:57.53%, H:4.67%.

MS m/e (relative intensity): 542(M^+,16),541(M^+-H,38),527(M^+-Me,27),497(M^+-3Me,21),470(M^+-CHMe-NMe_2,9),384(12),354(33),340(9),228(21),171(43),165(20),152(28),139(20),121(23),72(100),56(22),44(63).

IR (neat, CsI), 3100(ferrocene C-H stretch),3080-3045(phenyl C-H stretch),2975-2735(alkyl C-H stretch),1450(ferrocene antisymmetric C-C stretch),1275,1250(C-N stretch),850(C-H bend perpendicular to the plane of the Cp ring),455 (antisymmetric ring-metal stretch) cm^{-1}.

^{1}H NMR (δ ppm), 1.42(d,3H,C$\underline{H}_3$CH),1.93(s,6H,N$\underline{Me}_2$),3.90(q,1H, CH$_3$C$\underline{H}$),4.33(m,2H,$\underline{H}_3$,$\underline{H}_4$,$\underline{H}_5$),4.41(m,4H,C$_5\underline{H}_4$),4.53(m,1H,$\underline{H}_3$,$\underline{H}_4$, $\underline{H}_5$),6.93-7.13 (m,8H,Ph).

^{13}C NMR (δ ppm, in CD$_3$COCD$_3$),10.9(q,$\underline{C}$H$_3$CH),39.9(q,N$\underline{Me}_2$), 56.3(d,CH$_3\underline{C}$H),70.3(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),71.0(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),73.8(d,$\underline{C}'_2$, $\underline{C}'_5$),74.0(d,$\underline{C}'_2$,$\underline{C}'_5$),77.4(d,$\underline{C}'_3$,$\underline{C}'_4$),78.1(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),77.6 (d,$\underline{C}'_1$,$\underline{C}_2$),96.4(s,$\underline{C}_1$),128.2(d,ortho Ph-$\underline{C}$),128.8(d,ortho Ph-$\underline{C}$),129.2(s,para Ph-$\underline{C}$),129.5(s.para Ph-$\underline{C}$),130.9(d,meta Ph-$\underline{C}$),131.2(d,meta Ph-$\underline{C}$),140.3(s,substituted Ph-$\underline{C}$).

(R,S)-1-Dimethylaminoethyl-2-1'-bis(methylseleno)ferrocene (48, R=Me)

The lithioferrocene was made by the same procedure as 36, R=Me, by using 1.3 g (5.1 mmol) of (R)-1-(Dimethylamino)-ethylferrocene, 100 ml dry ether, and 3.0 ml (8.1 mmol) 2.7 M solution of n-BuLi in hexane at -78^{o}C. Then, the lithioferrocene solution was added a mixture of freshly distilled TMEDA (0.9 g, 7.5 mmol) and n-BuLi (3.0 ml, 8.1 mmol) in 20 ml ether at -78^{o}C. After the solution had been stirred overnight at room temperature, methyl diselenide (2.82 g, 15 mmol) was transferred into the reaction flask by syringe at -78^{o}C, stirred for 24 hours and then refluxed another 12 hr. Upon cooling to room temperature, the reaction mixture was hydrolyzed with 30 ml of cool aqueous sodium bicarbonate and filtered off. The resulting organic layer and ether extracts from the aqueous layer were combined, washed with water and dried over Na_2SO_4. A dark brown residue was obtained after

removal of solvent at reduced pressure, and was chromatographed on a silica gel column by gradient elution (hexane/benzene/ether) to give a brown oil. Yield: 69%.

Anal. for $C_{16}H_{23}Se_2FeN$
Calcd. C:43.37%, H:5.23%, Found C:43.85%, H:5.33%.

MS m/e (relative intensity): 443(M^+,9),428(M^+-Me,4),399(M^+-NMe_2,9),371(M^+-CHMe-NMe_2,6),349(M^+-$SeCH_3$,5),305(M^+-NMe_2-$SeCH_3$,7),290(53),288(36),212(29),152(39),121(16),89(20),72(63),44(100).

IR (neat, CsI), 3080(ferrocene C-H stretch),2961-2763(alkyl C-H stretch),1449(ferrocene antisymmetric C-C stretch), 1263,1242(C-N stretch),820(C-H bend perpendicular to the plane of the Cp ring),511(Se-C stretch),472(antisymmetric ring-metal stretch) cm^{-1}.

^1H NMR (δ ppm), 1.40(d,3H,$C\underline{H}_3CHN$),2.12(s,6H,$N\underline{Me}_2$),2.26(s,3H,$SeC\underline{H}_3$),2.30(s,3H,$SeC\underline{H}_3$),3.94(q,1H,$CH_3C\underline{H}N$),4.10(m,2H,$\underline{H}_3$,$\underline{H}_4$,$\underline{H}_5$),4.20(m,4H,$C_5\underline{H}_4$),4.30(m,1H,$\underline{H}_3$,$\underline{H}_4$,$\underline{H}_5$).

^{13}C NMR (δ ppm, in CD_3COCD_3), 8.56(q,$Se\underline{C}H_3$),9.30(q,$Se\underline{C}H_3$), 10.1(q,$\underline{C}H_3CHN$),39.8(q,$N\underline{Me}_2$),57.0(d,$CH_3\underline{C}H$),68.7(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$), 68.8(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),71.7(d,$\underline{C}'_2$,$\underline{C}'_5$),71.9(d,$\underline{C}'_2$,$\underline{C}'_5$),74.0(d,$\underline{C}_3$, $\underline{C}_4$,$\underline{C}_5$),75.0(d,$\underline{C}'_3$,$\underline{C}'_4$),77.0(s,$\underline{C}_2$,$\underline{C}'_1$),94.3(s,$\underline{C}_1$).

(R,S)-1-Dimethylaminoethyl-2-1'-bis(phenylseleno)ferrocene (49, R=Ph)

The lithioferrocene was made by the same procedure as 36, R=Me, by using 1.3 g (5.1 mmol) of (R)-1-(Dimethylamino)-ethylferrocene, 100 ml dry ether, and 3.0 ml (8.1 mmol) 2.7 M solution of n-BuLi in hexane at -78°C. Then, the lithioferrocene solution was added a mixture of freshly distilled TMEDA (0.9 g, 7.5 mmol) and n-BuLi (3.0 ml, 8.1 mmol) in 20 ml ether at -78°C. After the solution had been stirred overnight at room temperature, phenyl diselenide (4.68 g, 15 mmol) in 50 ml diethyl ether was added through a cannula at -78°C, stirred for 24 hr and then refluxed for 12 hr. Upon cooling to room temperature, the reaction mixture was hydrolyzed with 30 ml of cold aqueous sodium bicarbonate and filtered off. The resulting organic layer and ether extracts from the aqueous layer were combined, washed with water and dried over Na_2SO_4. A dark brown residue was obtained after removal of solvent at reduced pressure, and was chromatographed on a silica gel column by gradient elution (hexane/benzene/ether) to give a brown oil. Yield: 72%.

Anal. for $C_{26}H_{27}Se_2NFe$
Calcd. C:55.05%, H:4.80%, Found C:55.18%, H:4.97%.

MS m/s (relative intensity): 567(M^+,6),552(M^+-Me,3),523(M^+-NMe_2,15),368(M^+-SePh,11),288(12),197(13),165(51),152(32),141(57),121(11),72(55),56(49),44(100).

IR (neat, CsI), 3093(ferrocene C-H stretch),3072-3032(phenyl C-H stretch),2962-2762(alkyl C-H stretch),1438(ferrocene antisymmetric C-C stretch),1262,1240(C-N stretch),822(C-H bend perpendicular to the plane of the Cp ring),540(Se-C stretch),510(antisymmetric ring-metal stretch) cm^{-1}.

^{1}H NMR (δ ppm), 1.46(d,3H,$C\underline{H}_3CH$),1.97(s,6H,$N\underline{Me}_2$),3.93(q,1H, $CH_3C\underline{H}$),4.27(m,2H,$\underline{H}_3$,$\underline{H}_4$,$\underline{H}_5$),4.39(m,4H,$C_5\underline{H}_4$),4.52(m,1H,$\underline{H}_3$,$\underline{H}_4$, $\underline{H}_5$),7.14-7.43(m,10H,Ph).

^{13}C NMR (δ ppm, in CD_3COCD_3), 12.0(q,$\underline{C}H_3CH$),40.1(q,$N\underline{Me}_2$), 57.0(d,$CH_3\underline{C}H$),70.0(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),70.5(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),73.4(d,$\underline{C}'_2$, $\underline{C}'_5$),73.5(d,$\underline{C}'_2$,$\underline{C}'_5$),77.8($\underline{C}'_3$,$\underline{C}'_4$),78.0(d, $\underline{C}'_3$,$\underline{C}'_4$),78.1(d, $\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),79.2(s,$\underline{C}'_1$),80.2(s,$\underline{C}_2$),95.5(s,C_1),126.4(d,para Ph-$\underline{C}$),129.0(d,para Ph-$\underline{C}$),129.5(d,ortho Ph-$\underline{C}$),131.0(d,meta Ph-$\underline{C}$),135.2(s,substituted Ph-$\underline{C}$).

(R,S)-1-Dimethylaminoethyl-2-1'-bis[(4-chlorophenyl)seleno] ferrocene, (50, R=4-chlorophenyl)

The lithioferrocene was made by the same procedure as 36, R=Me, by using 1.3 g (5.1 mmol) of (R)-1-(Dimethylamino)-ethylferrocene, 100 ml dry ether, and 3.0 ml (8.1 mmol) 2.7 M solution of n-BuLi in hexane at -78°C. Then, the lithio-ferrocene solution was added a mixture of freshly distilled TMEDA (0.9 g, 7.5 mmol) and n-BuLi (3.0 ml, 8.1 mmol) in 20 ml ether at -78°C. After the solution had been stirred overnight at room temperature, 4-chlorophenyl diselenide (5.72 g, 15 mmol) in 50 ml ether was added through a cannula

at -78°C, stirred for 24 hr and then refluxed for 12 hr. Upon cooling to room temperature, the reaction mixture was hydrolyzed with 30 ml of cool aqueous sodium bicarbonate and filtered off. The resulting organic layer and ether extracts from the aqueous layer were combined, washed with water and dried over Na_2SO_4. A dark brown residue was obtained after removal of solvent at reduced pressure, and was chromatographed on a silica gel column by gradient elution (hexane/benzene/ether) to give a brown oil. The product was obtained as yellow crystals after recrystallization from (acetone/hexane). Yield: 69%. mp= 95-96°C.

Anal. for $C_{26}H_{25}Se_2NFeCl_2$
Calcd. C:49.09%, H:3.96%, Found C:49.32%, H:3.95%.

MS m/e (relative intensity): 636(M^+,4),591(M^+-3Me,33),402 (M^+-NMe_2-Se(Ph-Cl),3),290(11),165(54),152(35),139(42),89 (14),72(35),56(36),44(100).

IR (Nujol, CsI), 3093(ferrocene C-H stretch),3072-3028 (phenyl C-H stretch),2950-2762(alkyl C-H stretch),1457 (ferrocene antisymmetric C-C stretch),1268,1245(C-N stretch) ,812(C-H bend perpendicular to the plane of the Cp ring), 518(Se-C stretch),497(antisymmetric ring-metal stretch) cm^{-1}.

^1H NMR (δ ppm), 1.39(d,3H,$C\underline{H}_3CH$),1.96(s,6H,$N\underline{Me}_2$),3.92(q,1H, $CH_3C\underline{H}$),4.25(m,2H,$\underline{H}_3$,$\underline{H}_4$,$\underline{H}_5$),4.36(m,4H,$C_5\underline{H}_4$),4.46(s,1H,$\underline{H}_3$,$\underline{H}_4$, $\underline{H}_5$),7.10-7.30(m,8H,Ph).

^{13}C NMR (δ ppm, in CD_3COCD_3), 10.9(q,$\underline{C}H_3CH$),39.9(q,$N\underline{Me}_2$), 57.2(d,$CH_3\underline{C}H$),70.3(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),70.8(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),73.8(d,$\underline{C}'_2$, $\underline{C}'_5$),78.2(d,$\underline{C}'_3$,$\underline{C}'_4$),78.4(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),96.2(s,$\underline{C}_1$),129.0(d, ortho Ph-$\underline{C}$),129.7(d,ortho Ph-$\underline{C}$),131.2(d,meta Ph-$\underline{C}$),132.6 (d,meta Ph-$\underline{C}$),132.1(s,para Ph-$\underline{C}$),134.2(s,substituted Ph-$\underline{C}$),134.3(s,substituted Ph-$\underline{C}$).

B. Preparation of Metal Complexes

The complexes of $(C_5H_3\text{-}1\text{-}CH_2NMe_2\text{-}2\text{-}SR)Fe(C_5H_4\text{-}SR)PdCl_2$ (R=Me, Et, n-Pr, i-Pr, Ph, Bz, 4-Tolyl, 4-Chlorophenyl), $(C_5H_3\text{-}1\text{-}CH_2NMe_2\text{-}2\text{-}SR)Fe(C_5H_4\text{-}SR)PtCl_2$ (R=Me, Ph, Bz, 4-Tolyl, 4-Chlorophenyl), (R,S)-$(C_5H_3\text{-}1\text{-}CH(CH_3)NMe_2\text{-}2\text{-}SR)Fe(C_5H_4\text{-}SR)PdCl_2$ (R=Me, Et, n-Pr, i-Pr, Ph, Bz, 4-Tolyl, 4-Chlorophenyl) and (R,S)-$(C_5H_3\text{-}1\text{-}CH(CH_3)NMe_2\text{-}2\text{-}SR)Fe(C_5H_4\text{-}SR)PtCl_2$ (R=Me, Ph, Bz, 4-Tolyl, 4-Chlorophenyl) were prepared from benzene or methylene chloride solutions of the $(PhCN)PdCl_2$ or $(PhCN)PtCl_2$ and a slight excess of the ligands in an approximate 1:1.3 molar ratio. The reaction mixture was stirred under Ar at room temperature for 8 hr in the case of Pd complexes, and for 5 days in the case of Pt complexes. For the palladium complexes, the resulting precipitates were collected by suction, washed with cold benzene and then ether. The pure crystals were obtained after recrystallization from methylene chloride/hexane or acetonitrile/hexane. For the platinum complexes, the resulting precipitates were filtered off, washed with benzene followed by petroleum ether, and then recrystallized from acetone/hexane.

1-Dimethylaminomethyl-2-1′-bis(methylthio)ferrocene palladium(II) chloride (51)

The black crystals decomposed at 153°C.

Anal. for $C_{15}H_{21}S_2NFePdCl_2$:

Calcd. C:35.15%, H:4.13%, Found C:35.59%, H:4.13%.

MS m/e (relative intensity), 335(M^+-$PdCl_2$,21),320(M^+-$PdCl_2$-Me,3),305(M^+-$PdCl_2$-2Me,4),288(M^+-$PdCl_2$-SCH_3,10),152(8),121(10),97(8),62(9),58(22),56(14),44(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),324,318,298(Pd-S and Pd-Cl) cm^{-1}.

^1H NMR (δ ppm), 2.16(s,3H,$SC\underline{H}_3$),2.73(s,3H,$SC\underline{H}_3$),2.34 (s,3H, $N\underline{Me}_2$),2.70(d,1H,$C\underline{H}_2N$),3.09(s,3H,$N\underline{Me}_2$),3.89(d,1H,$C\underline{H}_2N$),4.26-4.45(m,7H,$C_5\underline{H}_4$,$C_5\underline{H}_3$).

1-Dimethylaminomethyl-2-1'-bis(ethylthio)ferrocene palladium(II) chloride (52)

The black crystals decomposed at 144-146°C.

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

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),286(11),258(19),230(21), 165(9),152(44),121(49),56(57),44(19).

IR (Nujol, CsI), 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),642(S-C stretch),476(ring-metal stretch),469(Pd-N),320-298(Pd-S and Pd-Cl) cm^{-1}.

^{1}H NMR (δ ppm), 1.14(t,3H,βC$\underline{H}_3$),1.67(t,3H,βC$\underline{H}_3$),2.30(s,3H, N$\underline{Me}_2$),2.58(q,2H,SC$\underline{H}_2$),2.73d,1H,C$\underline{H}_2$N),3.09(s,3H,N$\underline{Me}_2$),3.27(m, 1H,SCH$_2$),3.37(m,1H,SCH$_2$),4.02(d,1H,C$\underline{H}_2$N),4.38-4.52(m,7H, $C_5\underline{H}_4$,$C_5\underline{H}_3$).

1-Dimethylaminomethyl-2-1'-bis[(n-propyl)thio]ferrocene palladium(II) chloride (53)

Anal. for $C_{19}H_{29}S_2NFePdCl_2$
Calcd, C:40.13%, H:5.14%, Found C:40.10%, H:5.11%.

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),152(11),121(38), 97(27),56(7),44(30).

IR (Nujol, CsI), 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),637(S-C stretch),476(ring-metal),472(Pd-N),320-294(Pd-S and Pd-Cl) cm^{-1}.

1-Dimethylaminomethyl-2-1'-bis[(i-propyl)thio]ferrocene palladium(II) chloride (54)

The brown crystal decomposed at 131-132^{o}C.

Anal. for $C_{19}H_{29}S_2NFePdCl_2$
Calcd. C:40.13%, H:5.14%, Found C:40.33%, H:5.31%.

MS m/e (relative intensity): 391(M^+-$PdCl_2$,6),316(M^+-$PdCl_2$-S(i-Pr),6),272(M^+-$PdCl_2$-S(i-Pr),11),230(26),164(13),152(19), 97(21),56(49),44(67).

IR (Nujol, CsI), 3092(ferrocene C-H stretch),2970-2760 (alkyl C-H stretch),1428(ferrocene C-C stretch),1241,1176 (C-N stretch),829(C-H bend),637(S-C stretch),472(ring-metal stretch),476(Pd-N),322-300(Pd-S and Pd-Cl) cm^{-1}.

1-Dimethylaminomethyl-2-1'-bis(phenylthio)ferrocene palladium(II) chloride (55)

The brick-red crystals decomposed at 133°C.

Anal. for $C_{25}H_{25}S_2NFePdCl_2$
Calcd. C:47.16%, H:3.96%, Found C:46.99%, H:3.81%.

MS m/e (relative intensity), 459(M^+-$PdCl_2$,9),402(M^+-$PdCl_2$-CH_2NMe_2,3),350(M^+-$PdCl_2$-SPh,7),306(M^+-$PdCl_2$-SPh-NMe_2,8), 229(11),186(12),173(13),152(13),141(11),121(15),77(14), 58(28),44(26).

IR (Nujol, CsI), 3090(ferrocene C-H stretch),3080-3070 (phenyl C-H stretch),2950-2770(alkyl C-H stretch),1435 (ferrocene antisymmetric C-C stretch),1245,1181(C-N stretch),835(C-H bend perpendicular to the plane of Cp ring),640(S-C stretch),470(antisymmetric ring-metal stretch),460(Pd-N stretch),320-290(Pd-S and Pd-Cl stretch) cm^{-1}.

^1H NMR (δ ppm), 2.46(s,3H,N$\underline{Me}_2$),2.83(d,1H,C$\underline{H}_2$N),3.17(s,3H, N$\underline{Me}_2$),3.97(d,1H,C$\underline{H}_2$N),4.36-4.43(m,7H,$C_5\underline{H}_4$,$C_5\underline{H}_3$),[7.01-7.22(m),7.34-7.48(m),10H,Ph].

1-Dimethylaminomethyl-2-1′-bis(benzylthio)ferrocene palladium(II) chloride (56)

Anal. for $C_{27}H_{29}S_2NFePdCl_2$

Calcd. C:48.78%, H:4.40%, Found C:48.65%, H:4.43%

MS m/e (relative intensity): 487(M^+-$PdCl_2$,26),429(M^+-$PdCl_2$-NMe_2,32),364(M^+-$PdCl_2$-SBz,12),320(M^+-$PdCl_2$-NMe_2-SBz,9),243 (15),152(9),121(13),65(18),58(72),56(22),44(76).

IR (Nujol, CsI), 3102(ferrocene C-H stretch),3089-3033 (phenyl C-H stretch),2960-2780(alkyl C-H stretch),1430 (ferrocene antisymmetric C-C stretch),1244,1187(C-N stretch),831(C-H bend perpendicular to the plane of the Cp ring),640(S-C stretch),478(antisymmetric ring-metal stretch),472(Pd-N stretch),322-319(Pd-S and Pd-Cl stretch) cm^{-1}.

^1H NMR (δ ppm), 2.33(d,1H,$C\underline{H}_2N$),2.59(s,3H,$N\underline{Me}_2$),3.30(s,3H, $N\underline{Me}_2$),3.47(d,1H,$C\underline{H}_2N$),3.94-4.10(m,4H,$SC\underline{H}_2$-Ph),4.26-4.42 (m,7H,$C_5\underline{H}_4$,$C_5\underline{H}_3$),(7.14-7.25m,7.32-7.38m,10H,Ph).

1-Dimethylaminomethyl-2-1′-bis[(4-tolyl)thio]ferrocene palladium(II) chloride (57)

The brick-red crystals decomposed at 149°C.

Anal. for $C_{27}H_{29}S_2NFePdCl_2$

Calcd. C:48.78%, H:4.40%, Found C:48.91%, H:4.32%.

MS m/e (relative intensity), 487(M^+-$PdCl_2$,14),364(M^+-S(Ph-CH_3)-$PdCl_2$,10),320(M^+-$PdCl_2$-S(Ph-CH_3)-NMe_2,11),243(14),152(15),121(17),91(27),65(17),58(34),56(21),44(26).

IR (Nujol, CsI), 3100(ferrocene C-H stretch),3090-3025 (phenyl C-H stretch),2955-2775(alkyl C-H stretch),1430 (ferrocene antisymmetric C-C stretch),1243,1182(C-N stretch),831(C-H bend perpendicular to the plane of Cp ring),640(S-C stretch),477(antisymmetric ring-metal stretch),466(Pd-N stretch),326-315(Pd-S and Pd-Cl stretch) cm^{-1}.

^1H NMR (δ ppm), 2.24(s,3H,Ph-$C\underline{H}_3$),2.34(s,3H,Ph-$C\underline{H}_3$),2.43 (s,3H,$N\underline{Me}_2$),2.83(d,1H,$C\underline{H}_2N$),3.16(s,3H,$N\underline{Me}_2$),4.00(d,1H, $C\underline{H}_2N$),4.21-4.41(m,7H,$C_5\underline{H}_4$,$C_5\underline{H}_3$),[6.97-7.02(m),7.22-7.25 (m),8H,Ph].

1-Dimethylaminomethyl-2-1'-bis[(4-chlorophenyl)thio] ferrocene palladium(II) chloride (58)

The brick-red crystals decomposed at 151-152°C.

Anal. for $C_{25}H_{23}S_2NFePdCl_4$
Calcd. C:42.55%, H:3.29%, Found C:43.05%, H:3.31%.

MS m/e (relative intensity), 527(M^+-$PdCl_2$,10),483(M^+-$PdCl_2$-NMe_2,5),470(M^+-$PdCl_2$-CH_2NMe_2,6),384(M^+-$PdCl_2$-S(Ph-Cl),8), 340(M^+-$PdCl_2$-S(Ph-Cl)-NMe_2,7),263(9),184(13),171(17),152 (16),139(11),121(14),58(38),56(15),44(45).

IR (Nujol, CsI), 3090(ferrocene C-H stretch),3080-3060 (phenyl C-H stretch),2955-2770(alkyl C-H stretch),1428 (ferrocene antisymmetric C-C stretch),1245,1180(C-N stretch),832(C-H bend perpendicular to the plane of Cp ring),640(S-C stretch),475(antisymmetric ring-metal stretch),465(Pd-N stretch),321-300(Pd-S and Pd-Cl stretch) cm^{-1}.

^1H NMR (δ ppm), 2.44(s,3H,N$\underline{Me}_2$),2.83(d,1H,C$\underline{H}_2$N),3.16(s,3H, N$\underline{Me}_2$),4.05(d,1H,C$\underline{H}_2$N),4.16-4.43(m,7H,$C_5\underline{H}_4$,$C_5\underline{H}_3$),[6.94-6.97(m),7.13-7.17(m),7.39-7.42(m),8H,Ph].

1-Dimethylaminomethyl-2-1'-bis(methylthio)ferrocene platinum(II) chloride (59)

The yellow-flake crystals decomposed at 169-170^{0}C.

Anal. for $C_{15}H_{21}S_2NFePtCl_2$
Calcd. C:29.52%, H:3.47%, Found C:30.05%, H:3.86%.

MS m/e (relative intensity): 335(M^+-$PtCl_2$,100),276(M^+-$PtCl_2$-Me-NMe_2,42),244(M^+-$PtCl_2$-NMe_2-SCH_3,19),230(M^+-$PtCl_2$-NMe_2CH_2-SCH_3,9),212(11),164(20),152(19),91(22),58(34),56(49),44(96).

IR (Nujol, CsI), 3091(ferrocene C-H stretch),2957-2776 (alkyl C-H stretch),1428(ferrocene C-C stretch),1239,1178 (C-N stretch),830(C-H bend),638(S-C stretch),475(ring-metal stretch),476(Pt-N),319-297(Pt-S and Pt-Cl) cm^{-1}.

1-Dimethylaminomethyl-2-1′-bis(phenylthio)ferrocene platinum(II) chloride (60)

The yellow crystals decomposed at 180-182°C.

Anal. for $C_{25}H_{25}S_2NFePtCl_2$
Calcd. C:41.39%, H:3.47%, Found C:42.72%, H:3.66%.

MS m/e (relative intensity), 459(M^+-$PtCl_2$,100),416(M^+-$PtCl_2$-NMe_2,4),402(M^+-$PtCl_2$-CH_2NMe_2,3),350(M^+-$PtCl_2$-SPh,46),306(M^+-$PtCl_2$-NMe_2-SPh,45),229(23),196(11),185(13),173(32),152(17),141(17),121(17),78(24),58(26),44(15).

IR (Nujol, CsI), 3097(ferrocene C-H stretch),3083-3042 (phenyl C-H stretch),2971-2776(alkyl C-H stretch),1435 (ferrocene C-C stretch),1241,1191(C-N stretch), 835(C-H bend),637(S-C stretch),479(ring-metal stretch), 470(Pt-N),390,380,320,268(Pt-S and Pt-Cl) cm^{-1}.

1-Dimethylaminomethyl-2-1′-bis(benzylthio)ferrocene platinum(II) chloride (61)

Anal. for $C_{27}H_{29}S_2NFePtCl_2$
Calcd. C:43.04%, H:3.88%, Found C:43.10%, H:3.78%.

MS m/e (relative intensity): 487(M^+-$PtCl_2$,96),444(M^+-$PtCl_2$-NMe_2,12),364(M^+-$PtCl_2$-SBz,21),320(M^+-$PtCl_2$-NMe_2-SBz,32),188 (69),155(11),152(9),121(33),97(12),91(99),65(32),44(73).

IR (Nujol, CsI), 3093(ferrocene C-H stretch),3082-3069 (phenyl C-H stretch),1441(ferrocene C-C stretch),1246,1180

(C-N stretch),837(C-H bend),639(S-C stretch),466(ring-metal stretch),453(Pt-S),380,365,336,249(Pt-S and Pt-Cl) cm^{-1}.

1-Dimethylaminomethyl-2-1'-bis[(4-tolyl)thio]ferrocene platinum(II) chloride (62)

The yellow crystals decomposed at 190°C.

Anal. for $C_{27}H_{29}S_2NFePtCl_2$
Calcd. C:43.04%, H:3.88%, Found C:43.21%, H:3.92%.

MS m/e (relative intensity), 487(M^+-$PtCl_2$,35),444(M^+-$PtCl_2$-NMe_2,7),364(M^+-$PtCl_2$-S(Ph-CH_3),18),320(M^+-$PtCl_2$-S(Ph-CH_3)-NMe_2,19),188(50),155(19),152(11),97(11),91(100),65(27),44(72).

IR (Nujol, CsI), 3107(ferrocene C-H stretch),3093-3018 (phenyl C-H stretch),2960-2771(alkyl C-H stretch),1427 (ferrocene C-C stretch),1245, 1183(C-N stretch),832(C-H bend),645(S-C stretch),473(ring-metal stretch),468(Pt-N), 375,361,290,240(Pt-S and Pt-Cl) cm^{-1}.

1-Dimethylaminomethyl-2-1'-bis[(4-chlorophenyl)thio] ferrocene platinum(II) chloride (63)

The yellow-flake crystals decomposed at 208-210°C.

Anal. for $C_{25}H_{23}S_2NFePtCl_4$
Calcd. C:37.80%, H:2.92%, Found C:39.02%, H:2.98%.

MS m/e (relative intensity), 527(M^+-$PtCl_2$,85),484(M^+-$PtCl_2$-NMe_2,4),384(M^+-$PtCl_2$-S(Ph-Cl),57),340(M^+-$PtCl_2$-S(Ph-Cl)-NMe_2,47),263(33),228(35),208(55),184(45),171(63),152(51),121(29),77(38),56(34),44(100).

IR (Nujol, CsI), 3091(ferrocene C-H stretch),3079-3058 (phenyl C-H stretch),2941-2782(alkyl C-H stretch),1431 (ferrocene C-C stretch),1237, 1176(C-N stretch),830(C-H bend),635(S-C stretch),477(ring-metal stretch),468(Pt-N), 391,372,323,271(Pt-S and Pt-Cl) cm^{-1}.

(R,S)-1-(1-Dimethylaminoethyl)-2-(methylseleno)ferrocene palladium(II) chloride (64)

The brown crystals decomposed at 168-169°C.

Anal. for $C_{10}H_{21}NFeSePdCl_2$
Calcd. C:25.68%, H:4.49%, Found C:25.74%, H:4.42%.

MS m/e (relative intensity): 306(M^+-$HNMe_2$-$PdCl_2$,21),291(M^+-$PdCl_2$-Me-$HNMe_2$,45),226(M^+-$PdCl_2$-$HNMe_2$-Se,7),212(25),135(M^+-$PdCl_2$-C_5H_5Fe-SeMe,3),121(C_5H_5Fe,100),95(SeMe,12),72(9),66 (15),56(Fe,41),44(66).

IR (Nujol, CsI), 3098(ring-H stretch),2985,2945(alkyl C-H stretch),1476(methylene C-H scissoring),1456(methyl asymmetric C-H bend),1420,1378(methyl symmetric C-H bend),1252,1189(C-N stretch),1105(asymmetric ring breathing),1000(ring-H bend parallel to ring),832(ring-H

bend perpendicular to ring),516-535,494(asymmetric ring tilt),458(Pd-N stretch),324,302(Pd-Se,Pd-Cl stretch) cm^{-1}.

^1H NMR (δ ppm), 1.54(d,3H,$C\underline{H}_3CHN$),2.28(s,3H,$N\underline{Me}_2$),2.73(s,3H, $SeC\underline{H}_3$),3.25(s,3H,$N\underline{Me}_2$),3.85(q,1H,$CH_3C\underline{H}N$),4.23(s,5H,$C_5\underline{H}_5$), 4.39(m,1H,$\underline{H}_3$,$\underline{H}_5$),4.43(m,1H,$\underline{H}_4$),4.50(m,1H,$\underline{H}_3$,$\underline{H}_5$).

^{13}C NMR (δ ppm, in CD_2Cl_2), 10.7(q,$Se\underline{C}H_3$),16.6(q,$\underline{C}H_3CHN$), 41.4(q,$N\underline{Me}_2$),50.8(q,$N\underline{Me}_2$),65.9(d,$CH_3\underline{C}HN$),67.0(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$), 69.2(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),69.4(d,$\underline{C}_3$,$\underline{C}_4$,$\underline{C}_5$),71.6(d,$\underline{C}_5H_5$),70.5(s,$\underline{C}_2$), 88.4(s,$\underline{C}_1$).

(R,S)-1-(1-Dimethylaminoethyl)-2-(phenylseleno)ferrocene palladium(II) chloride (65)

The dark brown crystals decomposed at 163°C.

Anal. for $C_{20}H_{23}FeSeNPdCl_2$
Calcd. C:40.70%, H:3.90%, Found C:40.79%, H:3.95%.

MS m/e (relative intensity): 368(M^+-$PdCl_2$-$HNMe_2$,6),288(M^+-$PdCl_2$-$HNMe_2$-Se,3),212(28),157(SePh,11),135(M^+-$PdCl_2$-C_5H_5Fe-SePh,3),121(11),77(Ph,43),65(38),56(51),44(85).

IR (Nujol, CsI), 1580(phenyl C-C stretch),1250,1175(C-N stretch),1109,1030(asymmetric ring breathing),1000,903(ring-H parallel to ring),834(ring-H perpendicular to ring),744, 693(out-of-plane phenyl C-H bend),540,520,495(asymmetric ring tilt),469(Pd-N stretch),332,305(Pd-Se, Pd-Cl stretch) cm^{-1}.

(R,S)-1-(1-Dimethylaminoethyl)-2-[(4-chlorophenyl)seleno] ferrocene palladium(II) chloride (66)

Anal. for $C_{20}H_{22}FeSeCl_3N$

Calcd. C:38.46%, H:3.53%, Found C:39.65%, H:3.58%.

MS m/e (relative intensity):

IR (Nujol, CsI),

^1H NMR (δ ppm),

(R,S)-1-(1-Dimethylaminoethyl)-2-1'-bis(methylthio)ferrocene palladium(II) chloride (67)

The dark purple crystals decomposed at 146-148°C.

Anal. for $C_{16}H_{23}S_2NFePdCl_2$

Calcd. C:36.49%, H:4.40%, Found C:36.34%, H:4.78%.

MS m/e (relative intensity): 349(M^+-$PdCl_2$,44),304(M^+-$PdCl_2$-3Me,12),258(M^+-$PdCl_2$-NMe_2-SCH_3,23),242(13),232(15),212(39), 178(11),167(15),152(44),121(69),89(21),72(99),56(32),44(78).

IR (Nujol, CsI), 3091(ferrocene C-H stretch),2970-2850(alkyl C-H stretch),1455(ferrocene antisymmetric C-C stretch), 1255,1245(C-N stretch),837(C-H bend perpendicular to the plane of Cp ring),640(S-C stretch),475(antisymmetric ring-metal stretch),455(Pd-N stretch),332-299(Pd-S and Pd-Cl stretch) cm^{-1}.

^{1}H NMR (δ ppm), 1.52(d,3H,C$\underline{H}_3$CH),2.26(s,3H,SC$\underline{H}_3$),2.29(s,3H, N$\underline{Me}_2$),2.51(s,3H,SC$\underline{H}_3$),3.20(s,3H,N$\underline{Me}_2$),4.15(q,1H,CH$_3$C$\underline{H}$), 4.30-4.42(m,7H,C$_5\underline{H}_4$,C$_5\underline{H}_3$).

(R,S)-1-(1-Dimethylaminoethyl)-2-1′-bis(ethylthio)ferrocene palladium(II) chloride (68)

The brownish purple crystals decomposed at 136-137^{o}C.

Anal. for $C_{18}H_{27}S_2NFePdCl_2$
Calcd. C:38.98%, H:4.91%, Found C:38.66%, H:4.91%.

MS m/e (relative intensity): 377(M^+-$PdCl_2$,12),332(M^+-$PdCl_2$, 7),272(31),242(24),212(45),152(76),121(12),72(44),56(12),44(65).

IR (Nujol, CsI), 3103(ferrocene C-H stretch),2959-2760(aklyl C-H stretch),1427(ferrocene C-C stretch),1240,1178(C-N stretch),827(C-H bend),638(S-C stretch),476(ring metal stretch),470(Pd-N),319,301,288(Pd-S and Pd-Cl) cm^{-1}.

^{1}H NMR (δ ppm),

(R,S)-1-(1-Dimethylaminoethyl)-2-1′-bis[(n-propyl)thio] ferrocene palladium(II) dichloride (69)

The brown crystals decomposed at 148^{o}C.

Anal. for $C_{20}H_{31}S_2NFePdCl_2$
Calcd. C:41.22%, H:5.36%, Found C:41.44%, H:5.31%.

MS m/e (relative intensity): 405(M^+-$PdCl_2$,11),390(M^+-$PdCl_2$-

Me,9),360(M^+-$PdCl_2$-3Me,8),286(17),242(34),152(22),121(54), 97(28),72(23),56(75),44(85).

IR (Nujol, CsI), 3111(ferrocene C-H stretch),2964-2785 (aklyl C-H stretch),1428(ferrocene C-C stretch),1239,1190 (C-N stretch),825(C-H bend),638(S-C stretch),473(ring-metal stretch),472(Pd-N),320,301,287(Pd-S and Pd-Cl) cm^{-1}.

^1H NMR (δ ppm),

(R,S)-1-(1-Dimethylaminoethyl)-2-1'-bis[(i-propyl)thio] ferrocene palladium(II) chloride (70)

The brown crystals decomposed at 151°C.

Anal. for $C_{20}H_{31}S_2NFePdCl_2$
Calcd. C:41.22%, H:5.36%, Found C:42.23%, H:5.44%.

MS m/e (relative intensity): 405(M^+-$PtCl_2$,12),390(M^+-$PdCl_2$-Me, 5),360(M^+-$PdCl_2$-3Me,25),286(17),274(55),242(35),152(56), 121(61),72(44),44(13).

IR (Nujol, CsI), 3095(ferrocene C-H stretch),2970-2783 (aklyl C-H stretch),1445(ferrocene C-C stretch),1246,1190 (C-N stretch),826(ferrocene C-H bend),638(S-C stretch),475 (ring metal stretch),470(Pd-N), 319,289(Pd-S and Pd-Cl)cm^{-1}

^1H NMR (δ ppm),

(R,S)-1-(1-Dimethylaminoethyl)-2-1'-bis(phenylthio)ferrocene palladium(II) chloride (71)

The dark red crystals decomposed at 137-138°C.

Anal. for $C_{26}H_{27}S_2NFePdCl_2$
Calcd. C:47.99%, H:4.18%, Found C:47.43%, H:4.13%.

MS m/e (relative intensity): 473(M^+-$PdCl_2$,43),428(M^+-$PdCl_2$-3Me,12),402(M^+-$PdCl_2$-CHMe-NMe_2,11),302(M^+-$PdCl_2$-NMe_2-SPh,8), 152(42),121(23),84(13),72(16),57(21),56(42),49(78),44(76).

IR (Nujol, CsI), 3135(ferrocene C-H stretch),3101-3042 (phenyl C-H stretch),2972-2933(alkyl C-H stretch),1435 (ferrocene antisymmetric C-C stretch),1240,1172(C-N stretch),825(C-H bend perpendicular to the plane of Cp ring),645(S-C stretch),479(antisymmetric ring-metal stretch),440(Pd-N stretch),323-302(Pd-S and Pd-Cl stretch) cm^{-1}.

^1H NMR (δ ppm), 1.54(d,3H,$C\underline{H}_3CH$),2.33(s,3H,$N\underline{Me}_2$),3.28(s,3H, $N\underline{Me}_2$),4.11(q,1H,$CH_3C\underline{H}$),4.25-4.40(m,7H,$C_5\underline{H}_4$,$C_5\underline{H}_3$),[6.99-7.24 (m),7.44-7.53(m),10H,Ph].

(R,S)-1-(1-Dimethylaminoethyl)-2-1'-bis(benzylthio)ferrocene palladium(II) chloride (72)

Anal. for $C_{28}H_{31}S_2NFePdCl_2$
Calcd. C:49.54%, H:4.60%, Found C:49.47%, H:4.45%.

MS m/e (relative intensity): 501(M^+-$PdCl_2$,13),486(M^+-$PdCl_2$-Me,6),456(M^+-$PdCl_2$-3Me,3),430(M^+-$PdCl_2$-NMe_2-CHMe,11),378(M^+-$PdCl_2$-SBz,7),187(15),179(22),155(19),121(33),72(48),56(29),44(16).

IR (Nujol, CsI), 3090(ferrocene C-H stretch),3090-3035 (phenyl C-H stretch),2454-2876(alkyl C-H stretch),1427 (ferrocene antisymmetric C-C stretch),1252,1158(C-N stretch) ,832(C-H bend perpendicular to the plane of the Cp ring), 645(S-C stretch),476(antisymmetric ring-metal stretch), 461(Pd-N stretch),298-324(Pd-S and Pd-Cl stretch) cm^{-1}.

^1H NMR (δ ppm), 1.45(d,3H,$C\underline{H}_3CH$),2.34(s,3H,$N\underline{Me}_2$),3.30(s,3H, $N\underline{Me}_2$),3.96-4.16(m,4H,$SC\underline{H}_2$),4.20(q,1H,$CH_3C\underline{H}$),4.29-4.46(m,7H, $C_5\underline{H}_4$,$C_5\underline{H}_3$),(7.15-7.24m,7.25-7.36m,10H,Ph).

(R,S)-1-(1-Dimethylaminoethyl)-2-1'-bis[(4-tolyl)thio] ferrocene palladium(II) chloride (73)

The dark red crystals decomposed at 160-162°C.

Anal. for $C_{28}H_{31}S_2NFePdCl_2$
Calcd, C:49.54%, H:4.60%, Found C:49.89%, H:4.54%.

MS m/e (relative intensity): 501(M^+-$PdCl_2$,13),456(M^+-$PdCl_2$-3Me,6),430(M^+-$PdCl_2$-CHMe-NMe_2,11),378(M^+-S(Ph-CH_3),6),187 (29),179(11),155(24),121(29),91(35),72(66),56(49),44(73).

IR (Nujol, CsI), 3092(ferrocene C-H stretch),3081-3031 (phenyl C-H stretch),2962-2875(alkyl C-H stretch),1426 (ferrocene antisymmetric C-C stretch),1257,1251(C-N

stretch),833(C-H bend perpendicular to the plane of the Cp ring),645(S-C stretch),477(antisymmetric ring-metal stretch),462(Pd-N stretch),321-297(Pd-S and Pd-Cl stretch) cm^{-1}.

^1H NMR (δ ppm), 1.54(d,3H,$C\underline{H}_3CH$),2.24(s,3H,Ph-$\underline{CH}_3$),2.38(s, 3H,Ph-$C\underline{H}_3$),2.33(s,3H,$N\underline{Me}_2$),3.28(s,3H,$N\underline{Me}_2$),4.08(q,1H,$CH_3C\underline{H}$), 4.27-4.37(m,7H,$C_5\underline{H}_4$,$C_5\underline{H}_3$),[6.93-7.01(m),7.24-7.28(m),8H, Ph].

(R,S)-1-(1-Dimethylaminoethyl)-2-1'-bis[(4-chlorophenyl) thio]ferrocene palladium(II) chloride (74)

The black crystals decomposed at 157-159°C.

Anal. for $C_{26}H_{25}S_2NFePdCl_4$
Calcd. C:43.42%, H:3.50%, Found C:43.51%, H:3.55%.

MS m/e (relative intensity): 542(M^+-$PdCl_2$,43),527(M^+-$PdCl_2$-Me,9),470(M^+-$PdCl_2$-CHMe-NMe_2,6),384(13),354(21),340(7),171 (44),165(21),152(22),139(44),121(7),56(37),44(78).

IR (Nujol, CsI), 3112(ferrocene C-H stretch),3093-3029 (phenyl C-H stretch),2933-2871(alkyl C-H stretch),1427 (ferrocene antisymmetric C-C stretch),1253,1128(C-N stretch),831(C-H bend perpendicular to the plane of the Cp ring),643(S-C stretch),476(antisymmetric ring-metal stretch),460(Pd-N stretch),330-300(Pd-S and Pd-Cl stretch) cm^{-1}.

^{1}H NMR (δ ppm), 1.54(d,3H,CH_3CH),2.34(s,3H,NMe_2),3.29(s,3H, NMe_2),4.10(q,1H,CH_3CH),4.30-4.41(m,7H,C_5H_4,C_5H_3),[6.91-6.94 (m),7.13-7.16(m),7.33-7.46(m),8H,Ph].

(R,S)-1-(1-Dimethylaminoethyl)-2-1′-bis(methylseleno) ferrocene palladium(II) chloride (75)

Anal. for $C_{16}H_{23}Se_2NFePdCl_2$
Calcd. C:30.95%, H:3.74%, Found C,32.44%, H:3.79%.
IR,
^{1}H NMR (δ ppm), 1.54(d,3H,CH_3CH),2.13(s,3H,$SeCH_3$),2.27(s, 3H,NMe_2),2.38(s,3H,$SeCH_3$),3.19(s,3H,NMe_2),4.14(q,1H, CH_3CH),4.23-4.43(m,7H,C_5H_4,C_5H_3).

(R,S)-1-(1-Dimethylaminoethyl)-2-1′-bis(phenylseleno) ferrocene palladium(II) chloride (76)

The red crystals decomposed at 157-158°C.

Anal. for $C_{26}H_{27}Se_2NFePdCl_2$
Calcd. C:41.90%, H:3.66%, Found C:41.11%, H:3.92%.

MS m/e (relative intensity): 567(M^+-$PdCl_2$,13),523(M^+-$PdCl_2$-NMe_2,19),367(M^+-$PdCl_2$-NMe_2-SePh,9),348(3),286(5),229(7),212 (9),197(11),184(13),165(220,141(19),121(24),84(32),72(44),57 (32),49(21).

IR (Nujol, CsI),

^{1}H NMR (δ ppm), 1.56(d,3H,C$\underline{H}_3$CH),2.33(s,3H,N$\underline{Me}_2$),3.28(s,3H, N$\underline{Me}_2$),4.12(q,1H,CH$_3$C$\underline{H}$),4.33-4.57(m,7H,C$_5\underline{H}_4$,C$_5\underline{H}_3$),[7.15-7.25 (m),7.41-7.49(m),10H,Ph).

(R,S)-1-(1-Dimethylaminoethyl)-2-1'-bis[(4-chlorophenyl) seleno]ferrocene palladium(II) chloride (77)

The red crystals decomposed at 164-166^{o}C.

Anal. for $C_{26}H_{25}Se_2NFePdCl_4$
Calcd. C:38.35%, H:3.07%, Found C:38.39%, H:3.10%.

MS m/e (relative intensity): 636(M^+-$PdCl_2$,4),402(M^+-$PdCl_2$-NMe_2-Se(Ph-Cl),6),349(11),256(19),230(9),197(11),184(15), 121(55),84(39),72(100),56(45),44(96).

IR (Nujol, CsI), 3090(ferrocene C-H stretch),3087-3076 (phenyl C-H stretch),2889-2767(alkyl C-H stretch),1431 (ferrocene C-C stretch),1241,1178(C-N stretch),830(C-H bend),639(Se-C stretch),474(ring-metal stretch),465(Pd-N), 321-278(Pd-Se and Pd-Cl) cm^{-1}.

^{1}H NMR(δ ppm), 1.56(d,3H,C$\underline{H}_3$CH),2.32(s,3H,N$\underline{Me}_2$),3.33(s,3H, N$\underline{Me}_2$),4.19(q,1H,CH$_3$C$\underline{H}$),4.23-4.47(m,7H,C$_5\underline{H}_4$,C$_5\underline{H}_3$),(7.14-7.29m,7.36-7.50m,8H,Ph).

(R,S)-1-(1-Dimethylaminoethyl)-2-1'-bis(methylthio)ferrocene platinum(II) chloride (78)

The yellow-flake crystals decomposed at 166-168^{o}C.

Anal. for $C_{16}H_{23}S_2NFePtCl_2$

Calcd. C:31.23%, H:3.77%, Found C:31.01%, H:3.86%.

MS m/e (relative intensity): 349(M^+-$PtCl_2$,6),305(M^+-$PtCl_2$-NMe_2,7),258(M^+-$PtCl_2$-NMe_2-SCH_3,3),242(31),232(11),212(18),178(3),167(11),152(16),134(13),121(42),97(9),72(44),56(43),44(12).

IR (Nujol, CsI), 3093(ferrocene C-H stretch),2975-2841 (alkyl C-H stretch),1451(ferrocene C-C stretch),1254,1241 (C-N stretch),832(C-H bend),641(S-C stretch),472(ring-metal stretch),451(Pt-N),371, 360, 320, 271(Pt-S and Pt-Cl) cm^{-1}.

(R,S)-1-(1-Dimethylaminoethyl)-2-1'-bis(phenylthio) ferrocene platinum(II) chloride (79)

The yellow-flake crystals decomposed at 191-192°C.

Anal. for $C_{26}H_{27}S_2NFePtCl_2$
Calcd. C:42.23%, H:3.68%, Found C:42.29%, H:3.69%.

MS m/e (relative intensity): 473(M^+-$PtCl_2$,9),428(M^+-$PtCl_2$-3Me,4),402(4),348(5),286(3),229(7),197(11),165(17),141(7),121(9),97(21),84(23),72(45),57(49),49(100).

IR (Nujol, CsI), 3091(ferrocene C-H stretch),3085-3034(phenyl C-H stretch),2960-2871(alkyl C-H stretch),1425 (ferrocene C-C stretch),1258,1246(C-N stretch),829(C-H bend),647(S-C stretch),461(Pt-N),377,360,340,270(Pt-S and Pt-Cl) cm^{-1}.

(R,S)-1-(1-Dimethylaminoethyl)-2-1′-bis(benzylthio) platinum(II) chloride (80)

The yellow-flake crystals decomposed at 175°C.

Anal. for $C_{28}H_{31}S_2NFePtCl_2$
Calcd. C:43.82%, H:4.07%, Found C:43.97%, H:4.09%.

MS m/e (relative intensity): 501(M^+-$PtCl_2$,6),430(M^+-$PtCl_2$-CHMe-NMe_2,11),378(M^+-$PtCl_2$-SBz,5),334(12),244(12),187(15), 179(21),153(14),121(56),91(21),72(100),56(44),44(23).

IR (Nujol, CsI), 3098(ferrocene C-H stretch),3084-3031 (phenyl C-H stretch),2881-2459(alkyl C-H stretch),1425, 1257,1149(C-N stretch),829(C-H bend),651(S-C stretch),481, (ring-metal stretch),467(Pt-N),390,360,330,282(Pt-S and Pt-Cl) cm^{-1}.

(R,S)-1-(1-Dimethylaminoethyl)-2-1′-bis[(4-tolyl) thio]ferrocene platinum(II) chloride (81)

The yellow-flake crystals decomposed at 193-194°C.

Anal. for $C_{28}H_{31}S_2NFePtCl_2$
Calcd. C:43.82%, H:4.07%, Found C:43.61%, H:4.25%.

MS m/e (relative intensity): 501(M^+-$PtCl_2$,9),456(M^+-$PtCl_2$-3Me,6),378(M^+-$PtCl_2$-S(Ph-CH_3),7),334(13),319(3),100(6),287 (5),243(12),179(7),153(15),121(19),91(42),72(98),56(44), 44(29).

IR (Nujol, CsI), 3096(ferrocene C-H stretch),3084-3037 (phenyl C-H stretch),2971-2867(alkyl C-H stretch),1428 (ferrocene C-C stretch),1261,1257(C-N stretch),829(C-H bend),647(S-C stretch),475(ring-metal),469(Pt-N),375,367, 340,245(Pt-S and Pt-Cl) cm^{-1}.

^1H NMR (δ ppm), 1.58(d,3H,$C\underline{H}_3CH$),2.28(s,3H,Ph-$C\underline{H}_3$),2.40(s, 3H,$N\underline{Me}_2$),2.60(s,3H,Ph-$C\underline{H}_3$),3.34(s,3H,$N\underline{Me}_2$),4.10(m,1H, $CH_3C\underline{H}$),4.34-4.50(m,7H,$C_5\underline{H}_4$,$C_5\underline{H}_3$),(6.95-7.08m,7.22-7.30m, 8H,Ph).

(R,S)-1-(1-Dimethylaminoethyl)-2-1'-bis[(4-chlorophenyl) thio]ferrocene platinum(II) chloride (82)

The yellow-flake crystals decomposed at 210-212°C.

Anal. for $C_{26}H_{25}S_2NFePtCl_4$
Calcd. C:38.63%, H:3.12%, Found C:38.53%, H:3.02%.

MS m/e (relative intensity): 542(M^+-$PtCl_2$,5),497(M^+-$PtCl_2$-3Me,7),470(M^+-$PtCl_2$-CHMe-NMe_2,12),385(13),354(37),340(12), 228(22),171(44),152(62),139(39),121(44),72(100),56(24), 44(78).

IR (Nujol, CsI), 3101(ferrocene C-H stretch),3088-3028 (phenyl C-H stretch),2938-2875(alkyl C-H stretch),1430 (ferrocene antisymmetric C-C stretch),1255,1125(C-N stretch),830(C-H bend),645(S-C stretch),475(ring-metal stretch),465(Pt-N),385,371,339,245.(Pt-S and Pt-Cl) cm^{-1}.

C. CATALYTIC APPLICATIONS OF COMPLEXES.

a. Selective Hydrogenation in Conjugated 1,3-Cycloocta diene to Cyclooctene with Catalysts 51-58 and 67-74 in Organic Solvents.

The palladium complexes (2.0×10^{-5} mol), acetone (9.0 ml), and 1,3-cyclooctadiene (7.45×10^{-3} mol) were added into a 100 ml glass pressure bottle with a pressure gauge and stirring bar. The bottle was evacuated and filled with H_2 several times to a final pressure of 103 psi. After an induction period, usually 10 min., uptake of H_2 began immediately, and the hydrogenation continued slowly until the H_2 pressure remained invariant. The reaction normally ceased completely after 48 hr. In contrast, no hydrogen uptake was observed even after 3 days when platinum ferrocenylsulfides 60, 62 and 63 or palladium ferrocenyl-selenides 75-77 were used as hydrogenation catalysts. The procedures for the work-up of products involved the following steps; the solution was filtered, then the filtrate extracted twice with water, and the resulting organic layer dried over Na_2SO_4. The hydrogenation products were separated from the catalyst residues by distillation.

Most of the products identified by gas chromatography after the reaction were cyclooctene, cyclooctane and some reactant, 1,3-cyclooctadiene. The induction times, initial turnover rates, product ratios and selectivities are dependent on the catalysts used, and are shown in Table 14.

b. Solvent-Effects Studies in Hydrogenation of 1,3-cyclooctadiene to Cyclooctene with Catalysts 58 and 74.

The solvent effect was also studied with complexes 58 and 74. The complex (2.0 X 10^{-5} mol), 1,3-cyclooctadiene (7.45 X 10^{-3} mol) and different solvents (9.0 ml) were added into the pressure bottle. The solvents used are acetone, CH_2Cl_2, THF, pyridine, DMSO, and CH_3OH. In order to study the effect of added H_2O, it was added in acetone solvent only.
The same procedures for the sample work-up and the analysis of products were followed as part (a). Table 15 and Table 17 show the results of the solvent effect for the hydrogenation of 1,3-cyclooctadiene.

c. Additive-Effects Studies in Hydrogenation of 1,3-cyclooctadiene to Cyclooctene with Catalyst 74.

The complex 74 (2.0 X 10^{-5} mol), acetone (9.0 ml) and 1,3-cyclooctadiene (7.45 X 10^{-3} mol) with $AgNO_3$ (4.0 X 10^{-5} mol) as an additive were added into the pressure bottle. The work-up procedure was the same as part (a). Table 18 presents the results for the additive effect in the hydrogenation of 1,3-cyclooctadiene.

d. Selective Hydrogenation of 1,3-cyclohexadiene to Cyclohexene with Catalysts 55, 58, 71 and 74.

The complexes (2.0 X 10^{-5} mol), acetone (9.0 ml) and 1,3-cyclohexadiene (7.45 X 10^{-3} mol) were added into a 100 ml glass pressure bottle. The solution was milky suspension at the beginning, and then became a yellow clear as the reaction proceeded slowly. The hydrogenation was complete

after about 3 hr. The work-up procedures were followed as above.

RESULTS AND DISCUSSION

A. $(C_5H_3\text{-}1\text{-}CH_2NMe_2\text{-}2\text{-}SR)Fe(C_5H_4\text{-}SR)$, (R=Me, Et, n-Pr, i-Pr, n-Bu, s-Bu, t-Bu, i-Pentyl, Ph, Bz, 4-Tolyl, 4-Cl-Ph, (21-32).

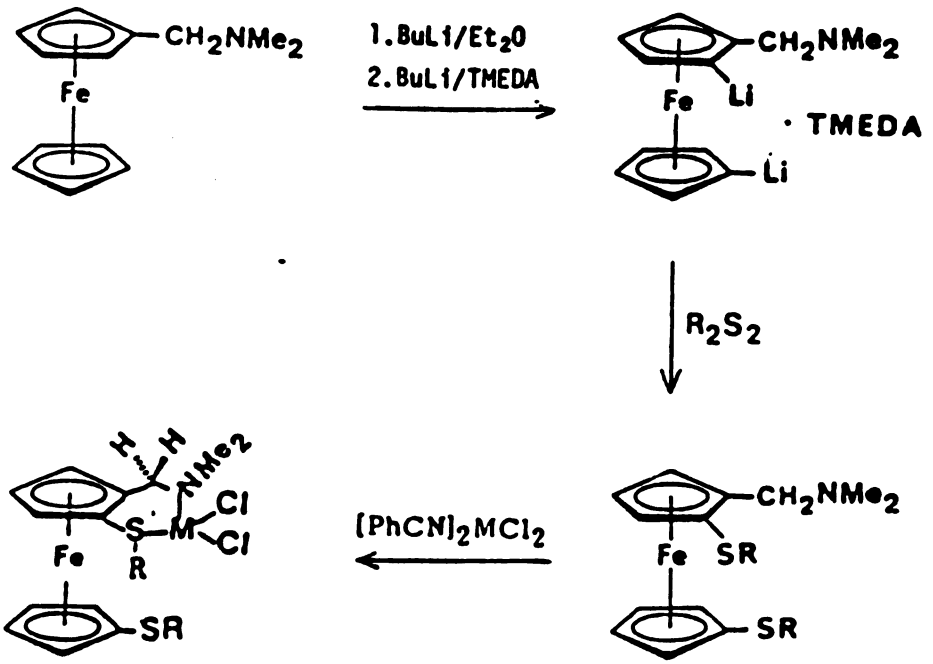
A series of monosubstituted ferrocenylsulfides $(C_5H_5)Fe(C_5H_3\text{-}1\text{-}CH_2NMe_2\text{-}2\text{-}SR)$, (R=Me, Et, n-Pr, i-Pr, n-Bu, s-Bu, i-Pentyl, Ph, Bz, 4-Tolyl and 4-Cl-Ph), and ferrocenylselenides $(C_5H_5)Fe(C_5H_3\text{-}1\text{-}CH_2NMe_2\text{-}2\text{-}SeR)$, (R=Me, Ph, 4-Cl-Ph), had been prepared in this laboratory, [71,76-79] by lithiation of dimethylaminomethylferrocene (12) in ether followed by reaction with appropriate disulfides and diselenides in high yields. Lithiation of dimethylaminomethylferrocene and ferrocene in the presence of N,N,N',N'-tetramethylethylenediamine (TMEDA) produces 1,1'-dilithioferrocene. [71] And it was expected that aminoferrocenylsulfides bearing two sulfide groups on each of the cyclopentadienyl ring could be prepared by the dilithiation of 1-dimethylaminomethylferrocene (12).

Indeed the stepwise lithiation of 1-dimethylaminomethylferrocene (12) with n-butyllithium in ether and then with n-butyllithium/TMEDA in the same solvent followed by reaction with the appropriate disulfides or diselenides led to the introduction of two thioether or selenoether groups, one onto each of the cyclopentadienyl rings to give various aminoferrocenylsulfide ligands, $(C_5H_3\text{-}1\text{-}CH_2NMe_2\text{-}2\text{-}SR)Fe$-

(C_5H_4-SR), (R=Me, Et, n-Pr, i-Pr, n-Bu, s-Bu, t-Bu, Ph, Bz, 4-Tolyl, 4-Cl-Ph), (21-32), in 55-92% yields (Figure 1).

The n-BuLi was not titrated, even though the procedure is available [71b] and aminoferrocenyllithium was also not isolated here, although isolation as a solid had been reported by Rausch et al, [84] but rather was prepared fresh for each reaction. The ferrocenylsulfide ligands contain planar elements of chirality due to the 1,2 disubstituted cyclopentadienyl ring and a functional group such as amino ($-NMe_2$). All the ligands thus prepared are brown oils, except when substituents are phenyl (29), 4-methyl-phenyl (31), and 4-chloro-phenyl (32), which are yellow to brown flaky crystals after recrystallization from acetone\hexane.

Table 3 shows 250 MHz ^1H NMR data for ferrocenylamino-thioethers (21-32). The most striking figure is the variable chemical shifts between the two diastereotopic protons of the aminomethylene group in the 2.98-3.78 ppm region as two distinct doublets. The same ^1H NMR figure of the aminomethylene protons had been observed in 1-dimethylamino-methyl-2-diphenylphosphinoferrocene. [85] The compounds with alkyl substituents, (21-28), at the position 2 on the cyclopentadienyl ring have larger chemical shift differences for two aminomethylene protons, and are very dependent on the steric crowding at the β-carbon of an alkyl group (30 > 24 > 28 > 25, 26 > 22 > 23 > 21 > 31 > 32, 27), the largest (0.80 ppm) for the R= benzyl substituent (30) and the smallest (0.0 ppm) for the R= t-butyl (27) and R= 4-Cl-Ph



M=Pd R= Me, (51).
Et, (52).
n-Pr, (53).
i-Pr, (54).
Ph, (55).
Bz, (56).
4-Tolyl, (57).
4-Cl-Ph, (58).

M=Pt R= Me, (59).
Ph, (60).
Bz, (61).
4-Tolyl, (62).
4-Cl-Ph, (63).

R= Me, (21).
Et, (22).
n-Pr, (23).
i-Pr, (24).
n-Butyl, (25).
s-Butyl, (26).
t-Butyl, (27).
i-Pentyl, (28).
Phenyl, (29).
Benzyl, (30).
4-Tolyl, (31).
4-Cl-Ph, (32).

Fgure 1. Synthetic routes for ferrocenylsulfide compouds, 21-32.

Table 3. 250 MHz ^1H NMR Data for $(C_5H_3\text{-}1\text{-}CH_2NMe_2\text{-}2\text{-}SR)Fe(C_5H_4\text{-}SR)$ in $CDCl_3$/TMS δ ppm, at room temperature.

						SR			
SR	Ph	C_5H_4	C_5H_3	CH_2N	NMe_2	αH	βH	γH	δH
21	-	4.18m	4.09m[a] 4.28m[b]	3.24d 3.55d	2.18s	2.25s 2.26s	-	-	-
22	-	4.16m	4.10m[a] 4.29m[b]	3.20d 3.55d	2.16s	2.53q[c] 2.60m[d] 2.64m[d]	1.12t 1.19t	-	-
23	-	4.17m	4.08m[a] 4.27m[b]	3.21d 3.55d	2.17s	2.50m[c] 2.56m[d] 2.64m[d]	1.32m 1.48m	0.88t 0.95t	-
24	-	4.19m	4.09m[a] 4.32m[b]	3.17d 3.57d	2.16s	2.81h 3.01h	1.07d 1.10d 1.14d 1.18d	-	-
25	-	4.16m	4.08m[a] 4.29m[b]	3.20d 3.56d	2.17s	2.53m[c] 2.60m[d] 2.66m[d]	1.46m 1.52m	1.31m 1.43m	0.82t 0.86t

Table 3 contiued.

26	-	4.19m	4.12m[a] 4.31m[b]	3.20d 3.56d	2.17s	2.57m 2.83m	1.10d[e] 1.15d[e] 1.36m[f] 1.47m[f]	0.87t 0.97t	-
27	-	4.14m	4.10m[a] 4.19m[b]	3.27s	2.14s	-	1.17s	-	-
28	-	4.17m	4.08m[a] 4.28m[b]	3.20d 3.57d	2.16s	2.54m[c] 2.64m[d] 2.71m[d]	1.58m 1.63m	1.35m 1.41m	0.79d 0.82d 0.84d 0.87d
29	7.02-7.19m	4.44m	4.33m[a] 4.60m[b]	3.44d 3.55d	2.04s	-	-	-	-
30	7.14-7.32m	4.13-4.30m		2.98d 3.78d	2.19s	3.82s[c] 3.90d[d] 4.02d[d]	-	-	-
31	6.95-7.06m	4.39m	4.30m[a] 4.53m[b]	3.43d 3.51d	2.05s	-	-	-	-
32	6.93-7.14m	4.45m	4.37m[a] 4.58m[b]	3.44s	2.04s	-	-	-	-

a=2H, b=1H, H_3, H_4, H_5; c=2H, d=1H; e=βCH_3, f=βCH_2.

(32) substituents. The compounds with aryl substituents (29 ,31, 32) have smaller differences (29 > 31 > 32) in diastereotopic chemical shifts due to one proton being more closer to the aromatic ring, and are found upfield because of the ring current effect. In the 4-Cl-phenyl (32) and t-butylthio (27) derivatives, Δ v/J = 0.0 (appear to overlap). These are the cases in which the outside peaks are small or nonexistent, respectively. The aminomethylene protons of (27), R= t-butyl and (32), R= 4-Cl-Ph appear as a singlet. The thiomethylene groups ($-SCH_2-R$) in compounds,22, 23, 25, 28 and 30, also diastereotopic, appear the variable chemical shift differences (0.02, 0.08, 0.06, 0.07 and 1.02 ppm for compounds 22, 23, 25, 28 and 30), and are also dependent on the steric crowding at the thiomethylene groups. However, the assignments of the substituted ring protons H_3, H_4 and H_5 in these compounds are difficult since a number of studies [86-89] of monosubstituted ferrocenes have shown that a single substituent may deshield or shield position 2 and 5, or position 3 and 4, in any combinations relative to ferrocene.

Figure 2 shows one of the typical 250 MHz ^1H NMR of ferrocenylsulfide derivatives, 25, R= n-butyl. The chemical shifts of the substituted ring protons H_3, H_4 and H_5 in 25 are 4.08 (2H) and 4.29 (1H) ppm, respectively. In comparison with the results of Dvoryantseva et al [90] and Slocum et al [86,88,89,91] the assignment at 4.14 ppm to the protons of the monosubstituted cyclopentadienyl ring ($-C_5H_4$) seems

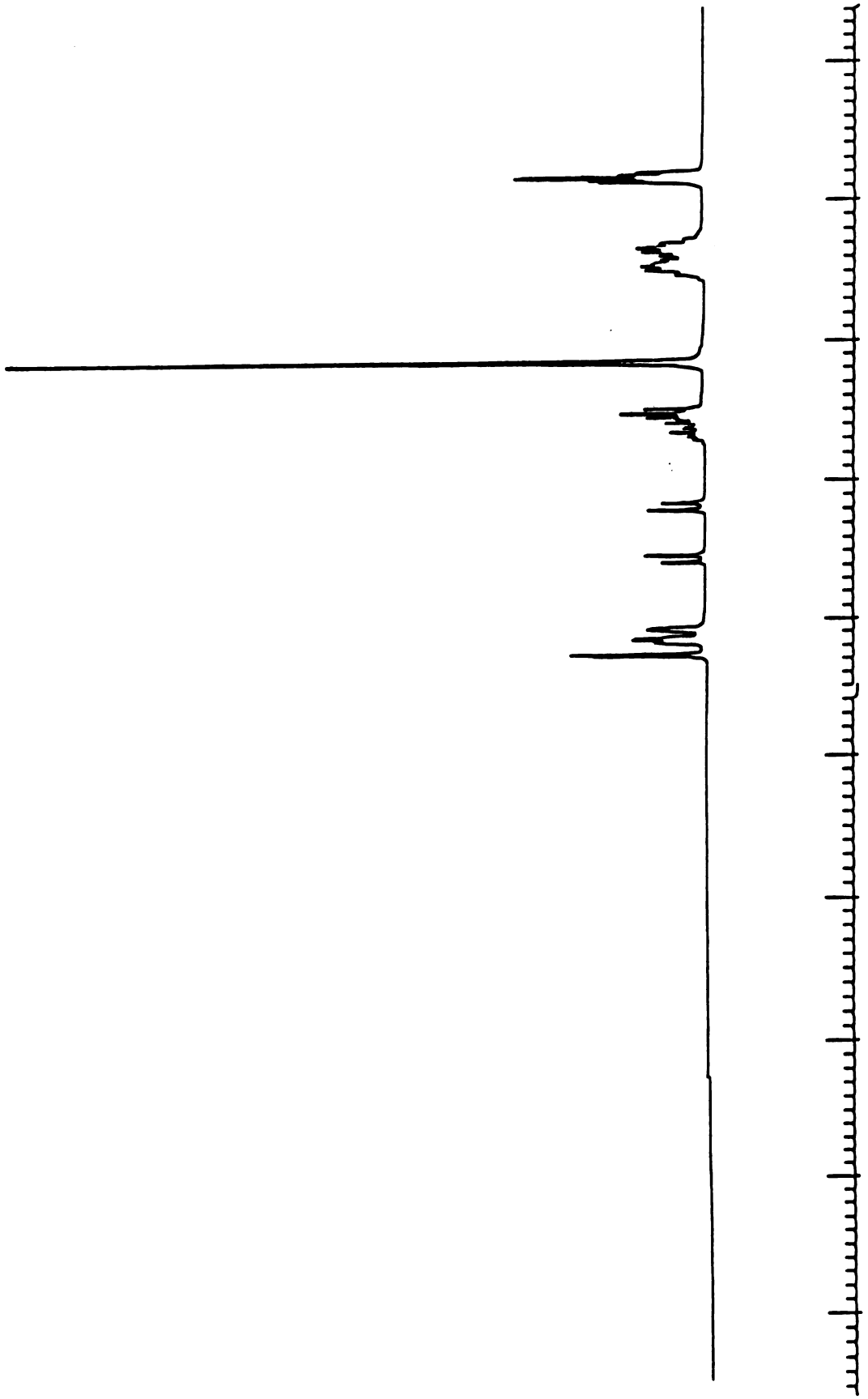


Figure 2. 250 MHz ^{1}H NMR spectrum of 25, R= n-Butyl.

reasonable, based on ^{1}H NMR integration. Lack of a sharp singlet around 4.00-4.20 ppm is complementary evidence that the ferrocenylsulfides are disubstituted instead of mono-substituted. Rausch and Siegel [87] have assigned the signals in the dimethylaminomethylferrocene (12) at 4.13 and 4.09 ppm to the $H_{2,5}$ and $H_{3,4}$, respectively, on the basis of deuterium labelling studies. The 2,5-positions of the monosubstituted ferrocenes except alkyl substituent [86-91] derivatives are sensitive to both deshielding by the inductive effect and shielding by the resonance effect of the electron-donating substituents. In the ferrocenyl tertiary amine thioethers, the deshielding by the inductive effect is stronger than the shielding by the resonance effect of the electron-donating substituents (such as -SR), especially for compounds with R = aryl groups, (29-32). The assignments of substituted ring protons shown in Table 3 are tentative, and deuteration studies must be employed to make unambiguous assignments.

Rotation [92] of the pyramidal $-NMe_2$ in these compounds is faster than the NMR time scale at room temperature, thus the two nitrogen methyls appear as a singlet around the 2.04-2.19 ppm region. However, the two methyls appear 1.75 and 2.04 ppm as a singlet in chiral aminoferrocenylphosphino [93] with -diphenyl and -dimethyl phosphine groups on each of the -Cp ring. The chemical shifts for different -SR substituents on the cyclopentadienyl ring show in the expected ranges of 0.70-3.50 ppm. Generally, the chemical

shifts of alkyl group follow as $\delta\underline{H} < \gamma\underline{H} < \beta\underline{H} < \alpha\underline{H}$. For example, in compound 26, R= sec-Butyl, $\beta C\underline{H}_3$ shows at a lower field than $\beta C\underline{H}_2$ as expected. In addition, the two terminal methyl groups on the -SR substituents, βCH_3 in 24 and $\check{S}CH_3$ in 28 are also diastereotopic, thus they appear as two well-separated distinct doublets.

^{13}C NMR spectroscopy is a sensitive tool for measuring the electron density distribution on the cyclopentadienyl ring in ferrocene. Substituents on the ring induce screening of the nuclei in two different ways, one due to magnetic anisotropy of the substituents and the second due to the electronic effect of the substituent that possess of both resonance and inductive components. The ^{13}C NMR data of the aminoferrocenylsulfides compounds (21-32) are given in Table 4. Suitably substituted derivatives do possess the diastereotopic carbons, such as compounds, 24, 26, and 28, which contain diastereotopic carbons βCH_3, βCH_3 and δCH3; would absorb at different chemical shifts.

One of typical ^{13}C NMR for compound 31, R= 4-tolyl, is shown in Figure 3. Assignments for these compounds are based on comparisons with some similar studies and off-resonance decoupled spectra. Since amine ($-CH_2NMe_2$) is a weakly electron-donating group, the inductive effect (deshielding is more sensitive at the 3,4-position) is a little larger than the resonance effect (shielding is more sensitive at the 2,5-position). The two methyls appear around 39.8-40.7 ppm. In contrast, the thio group (-SR) is an electron-

Table 4. ^{13}C NMR Data for $(C_5H_3\text{-}1\text{-}CH_2NMe_2\text{-}SR)Fe(C_5H_4\text{-}SR)$ in CD_3COCD_3/TMS, δ ppm, at room temperature.

SR	Ph	C_1	C_2 C_1'	C_3 C_4 C_5	$C_2'C_5'$	$C_3'C_4'$	CH_2N	NMe_2	SR			
									αC	βC	γC	δC
21	-	88.2	86.4 85.6	69.2 72.3 72.4	71.0 71.1	72.9 73.4	57.4	45.4	19.3 20.0	-	-	-
22	-	89.5	82.9 82.7	70.0 73.8 75.4	72.0 72.4	76.0 76.3	58.0	45.8	31.3 31.9	15.5 15.7	-	-
23	-	89.1	82.9 82.8	69.5 73.3 74.8	71.6 71.9	75.3 75.7	57.5	45.4	39.1 39.4	23.4 23.5	13.5 13.6	-
24	-	89.5	80.6 79.2	69.3 73.2 76.1	71.7 72.1	76.6 76.8	57.1	45.2	39.3 39.4	22.8 23.2 23.7	-	-
25	-	88.9	82.5 82.5	69.2 73.1 74.5	71.3 71.6	75.1 75.5	57.3	45.4	36.6 36.8	32.0 32.2	22.0 22.1	13.9
27	-	89.1	77.3 77.4	69.8 69.8 72.1	70.9 -	72.1	59.1	44.9	37.2	31.0	-	-

Table 4 contiued.

28	-		89.1	82.7	82.6	69.3	73.2	74.5	71.4	71.7	75.0 75.6	57.3	45.4	39.2	34.9 35.2	27.4 27.5	22.4 22.6 22.8
29	- 126.7 129.2 140.6	125.8[p] 127.4[o] 129.4[m] 141.0[s]	90.0	78.2	77.6	71.3	74.1	77.1	73.4	73.6	77.4 77.5	56.9	45.4	-	-	-	-
30	126.3 128.1 128.9 138.6	126.6[p] 128.3[o] 129.2[m] 139.2[s]	89.3	82.6	82.3	70.0	72.9	74.8	72.4	72.6	75.9 76.1	57.4	45.2	41.7 42.4	-	-	-
31	127.3 129.8 - 136.8	127.8[o] 130.0[m] 135.3[p] 137.0[s]	89.5	79.5	79.0	71.0	73.8	76.6	72.9	73.3	77.1 77.2	56.7	45.4	-	-	-	21.0
32	128.1 129.1 139.6	128.9[o] 129.4[m] 131.1[p] 139.9[s]	90.3	78.4	-	71.5	74.3	77.1	73.6	73.8	77.4 77.7	56.9	45.3	-	-	-	-

p; para, o; ortho, m; meta, and s; substituted carbons, respectively.

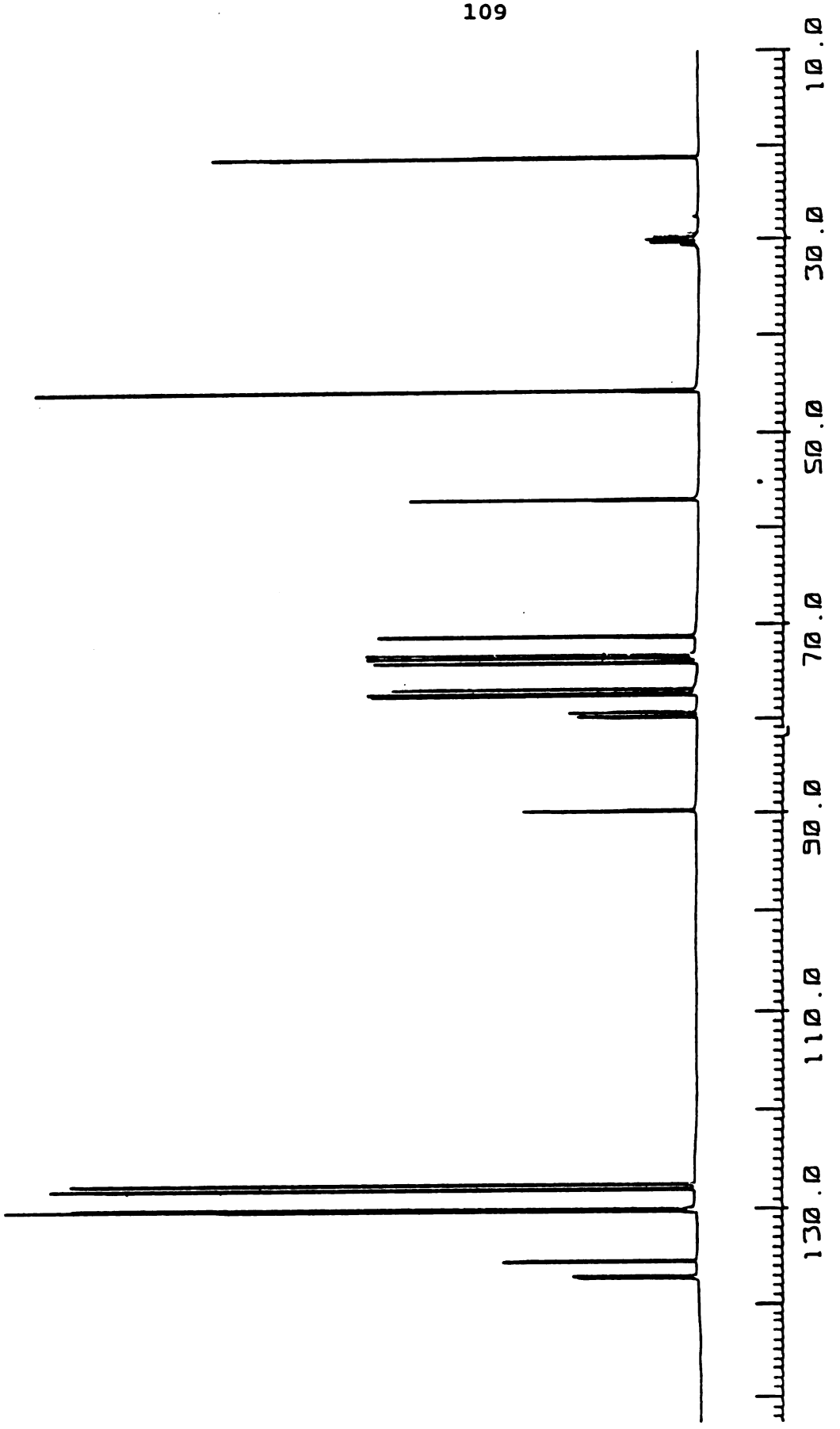


Figure 3. ^{13}C NMR spectrum of 31, R= 4-Tolyl.

donating substituent, and the inductive effect (deshielding is more sensitive at the 4,5-position) is stronger than the resonance effect (shielding is more senisitive at the 1,3-position). Therefore, it is not surprising that all carbons on -SR groups of ferrocenylsulfides appear at a lower chemical field than carbons on the amine group. For example, C_1 = 88.2 ppm but C_2 = 86.4 ppm in 21, R= Me, (ie. the chemical shield order is $C_1 > C_2$). To both carbons (C_2 and C_1,) that are bonded to both -SR substituents a set of signals, for example, at 86.4 and 85.6 ppm in 21, are assigned to C_2 and C_1,, and in the mean time these peaks (C_1, C_2 and C_1,) are the weakest peaks in the ^{13}C NMR spectra due to the long spin-lattice relaxation time of substituted carbons. The assignments for aromatic ring carbons (in Table 4) are tentative. Based on some studies [93-94], the chemical shifts in ^{13}C NMR must be C (substituted) > C (meta) > C (ortho) > C (para) for mono-substituted phenyl groups, and C (substituted) > C (para) > C (meta) > C (ortho) for 1,4-disubstituted phenyl groups. For compounds with di- substituted SR or SeR groups on each of the cyclopentadienyl ring, it is difficult to assign C_3, C_4 and C_5. Also C_2,, C_5, and C_3,, C_4, which are far away from the C_1 amino group ($-CH_2NMe_2$) in these compounds are assigned in a set based on the similarity of chemical environment (less affected by C_1 and C_2) and the number of signals on the ^{13}C NMR spectra. Consequently, the chemical shift for these ferrocenyl-

sulfides, 21-32, follows the order C(aromatic) > C_1 > C_2, C_1', and C_3', C_4' > C_2', C_5'. In contrast, the carbon assignments on aminomethylene group, $-CH_2NMe_2$, (signals at 56.9-58.0 ppm), nitrogen methyls, $-NMe_2$, (signals at 44.9-45.8 ppm) and all of carbons on the alkyl substituent (-SR) are clear. The carbons on the -SR groups also follow: αC > βC > γC > δC as in ^{13}C NMR spectra.

Most of the IR assignments were made based upon the available literature, [95-98] and are generally consistent with the alkyl, phenyl and ferrocenyl C-H or C-C bend stretches, and the C-N stretch was also observed. The adsorption band near 890 cm^{-1} would be indicative of 1,2-disubstitution (as opposed to 1,3-disubstitution), but actually are too weak to be diagnostic. Besides, the C-S and C-Se bonds should have stretches around 600-700 and 507-625 cm^{-1}, respectively, and ring-metal vibration is in the region of 500-450 cm^{-1}. Lack of two important bands [95] at 1000 and 1100 cm^{-1} in the infrared spectra of these ferrocenylsulfides (21-32) indicates that the absence of any cyclopentadienyl ring (unsubstituted ring) in these compounds. All IR data for these compounds are shown in the experimental section.

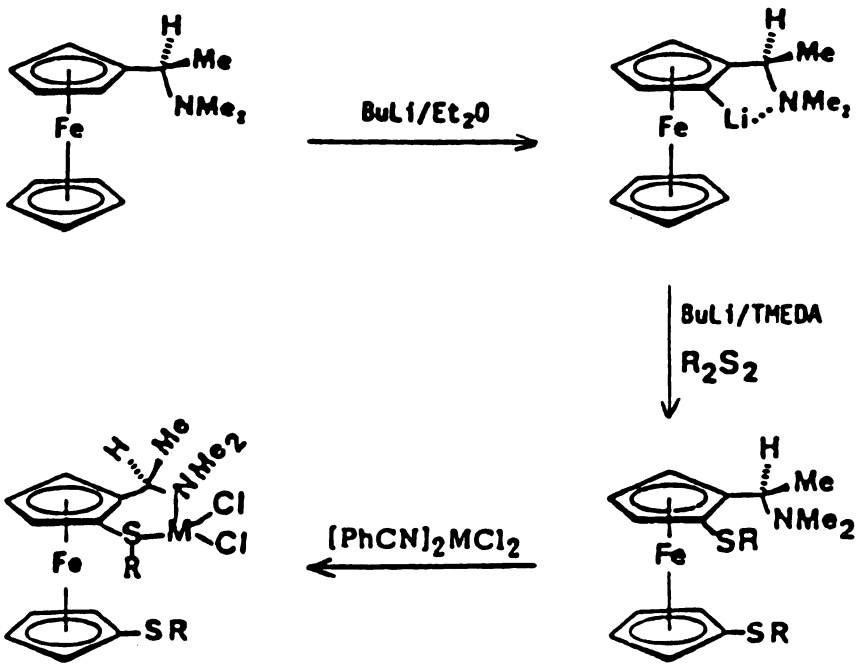
For the mass spectra the molecular-ion peaks for all of these ferrocenylsulfides are always observed with high intensities. Other important fragments included are M^+-Me, M^+-3Me, M^+-NMe_2, M^+-SR, M^+-NMe_2-SR, $-CH_2NMe_2$, Fe, -SR and

$-NMe_2$. Beside these major fragments, peaks consistent with the less abundant isotopes ^{54}Fe, ^{57}Fe, and ^{34}S were also detected.

B. (1), (R,S)-(C_5H_3-1-CHMeNMe$_2$-2-SR)Fe(C_5H_4-SR), (R=Me, Et, Pr, i-Pr, n-Bu, s-Bu, t-Bu, i-Pentyl, Ph, Bz, 4-Tolyl, 4-Cl-Ph), (36-47).

Chiral ferrocenylphosphine ligands which have a planar chiral center due to a 1,2-disubstituted cyclopentadienyl ring are highly effective ligands in transition metal catalyzed asymmetric synthesis. [24,27,32,43,44,64] Though few sulfides have been studied as ligands in metal complexes untill now, a series of previously unknown monosubstituted cyclopentadienyl ring, chiral ferrocenylsulfides, (R,S) or (S,R)-(C_5H_3-1-CHMeNMe$_2$-2-SR)Fe(C_5H_5), (R=Me, Et, n-Pr, i-Pr, n-Bu, s-Bu, t-Bu, i-Pentyl, Ph, Bz, 4-Tolyl and 4-Cl-Ph), and chiral ferrocenylselenides, (S,R)-(C_5H_3-1-CHMe$_2$NMe$_2$-2-SeR)Fe(C_5H_5), (R=Me, Ph and 4-Cl-Ph), had been prepared before from this laboratory. [77,79]

For the studies of the chiral ferrocenylsulfide compounds, the disubstituted chiral ferrocenylsulfides, (36-47), were prepared by using a synthesis procedure similar to that of the disubstituted ferrocenylsulfides, (21-32), as was discussed in part (a). Stepwise lithiation of (R)-1-(dimethylamino)ethylferrocene with n-BuLi in ether and then with n-BuLi\TMEDA followed by reaction with different disulfides gave the desired products, (R,S)-(C_5H_3-1-CHMe-NMe$_2$-2-SR)Fe(C_5H_4-SR), (R=Me, Et, n-Pr, i-Pr, n-Bu, s-Bu, t-Bu, i-Pentyl, Ph, Bz, 4-Tolyl and 4-Cl-Ph), (36-47), in 42-92% yields (Figure 4). The starting material, (R)-1-(dimethylamino)ethylferrocene, [(R)-1], was prepared



(R,S) Ligands

R= Me, (36).
Et, (37).
n-Pr, (38).
i-Pr, (39).
n-Butyl, (40).
s-Butyl, (41).
t-Butyl, (42).
i-Pentyl, (43).
Phenyl, (44).
Benzyl, (45).
4-Tolyl, (46).
4-Cl-Ph, (47).

M=Pd R= Me, (67).
Et, (68).
n-Pr, (69).
i-Pr, (70).
Ph, (71).
Bz, (72).
4-Tolyl, (73).
4-Cl-Ph, (74).

M=Pt R= Me, (78).
Ph, (79).
Bz, (80).
4-Tolyl, (81).
4-Cl-Ph, (82).

Figure 4. Synthetic routes for chiral ferrocenylsulfide compounds, 36-47.

according to Gokel and Ugi's procedure. [81] The lithiation of [(R)-1] was previously reported by Ugi and coworkers to proceed with high stereoselectivity to give preferentially (R)-[(R)-2-lithioferrocenyl]ethyldimethylamine.

These chiral compounds, 36-43 and 45, are all brown oils except 44, 46 and 47, which are yellow crystals after recrystallization from acetone/hexane. The quaternary ammonium salts of the general formula $[(C_5H_5)Fe(C_5H_4\text{-}CH_2\text{-}NMe_2CH_2R)^+X^-$, which were prepared in good yields by reaction of the corresponding alkyl halides with (dimethylaminomethyl)ferrocene even at low temperature, were reported by Nesmeyanov et al. [99-100] In order to avoid possibly obtaining these kinds of amine salts as a yellow powders instead of free amines, it is necessary to deprotonate the reaction mixture, by washing it with aqueous $NaHCO_3$ prior to a final column separation. Furthermore, to increase the yields of the chiral ferrocenyl tertiary amine thioethers, dry diethyl ether rather than halogenated organic solvents such as CH_2Cl_2, $CHCl_3$ or CCl_4 which produce salts, were always used as solvent in the entire synthesis, even though the starting material is very soluble in these halogenated solvents.

Table 5 presents ^1H NMR data for chiral ferrocenylsulfide compounds (36-47). The first (R) configuration refers to the asymmetric carbon atom on the amino group, $CHMeNMe_2$, whereas the second (S) configuration refers to the planar chirality element of 1,2-disubstituents on the

Table 5. 250 HMz ^{1}H NMR Data for (R,S)-(C_5H_3-1-CHMeNMe$_2$-2-SR)Fe(C_5H_4-SR) in CDCl TMS, δ ppm, at room temperature.

							SR			
SR	Ph	C_5H_4	C_5H_3	CHMe	NMe_2	CH_3CH	αH	βH	γH	δH
36	-	4.19m	4.09m[a] 4.28m[b]	3.92q	2.11s	1.38d	2.24s 2.29s	-	-	-
37	-	4.19m	4.08m[a] 4.31m[b]	3.95q	2.10s	1.37d	2.54q[c] 2.65m[d] 2.78m[d]	1.12t 1.18t	-	-
38	-	4.18m	4.09m[a] 4.29m[b]	3.95q	2.10s	1.37d	2.58m[c] 2.59m[d] 2.75m[d]	1.46m 1.58m	0.89t 0.95t	-
39	-	4.14m	4.04m[a] 4.29m[b]	3.94q	2.06s	1.29d	2.78h 3.17h	1.06d 1.09d 1.13d 1.16d	-	-
40	-	4.18m	4.09m[a] 4.29m[b]	3.93q	2.10s	1.37d	2.53m[c] 2.64m[d] 2.77m[d]	1.47m 1.53m	1.32m 1.34m	0.83t 0.88t

Table 5 contiued.

41	-	4.19m	4.09m[a] 4.30m[b]	3.96q	2.08s	1.33d	2.54m 2.97m	1.03d[e] 1.06d[e] 1.42m[f] 1.50m[f]	0.85t 0.92t	-
42	-	4.16m	4.09m[a] 4.20m[b]	3.62q	2.06s	1.44d	-	1.17s	-	-
43	-	4.18m	4.09m[a] 4.29m[b]	3.95q	2.10s	1.37d	2.58m[c] 2.75m[d] 2.79m[d]	2.52m 2.54m	1.42m 1.61m	0.80d 0.81d 0.84d 0.85d
44	7.01-7.18m	4.41m	4.30m[a] 4.58m[b]	3.91q	1.93s	1.47d	-	-	-	-
45	7.14-7.25m	4.12 - 4.31m		4.02q	2.15s	1.36d	3.72s[a] 3.86d[b] 3.90d[b]	-	-	-
46	6.94-7.12m	4.37m	4.29m[a] 4.54m[b]	3.91q	1.95s	1.48d	-	-	-	2.24
47	6.93-7.13m	4.41m	4.33m[a] 4.53m[b]	3.90q	1.93s	1.42d	-	-	-	-

a=2H, b=1H, H_1, H_2, H_3; c=2H, d=1H; e=βCH_3, f=βCH_2.

cyclopentadienyl ring. Basically, the structure of chiral ferrocenylaminosulfide (36-47), is similar to that of ferrocenylaminosulfide (21-32), except that one proton on the aminomethylene group was replaced by a methyl group. Thus, a doublet around 1.29-1.48 ppm and a quartet around 3.62-4.02 ppm could be easily assigned as a methyl group and a hydrogen atom on the chiral carbon center, respectively. The thiomethylene protons of the ($-SCH_2-R$) in some compounds (37, 38, 40, 43 and 45), also diastereotopic, appear in the variable chemical shift and have larger chemical shifts difference than a derivative that does not possess a chiral center (i.e. 22, 23, 25, 28 and 30). The differences are 0.13, 0.16, 0.07, 0.04 and 0.04 ppm for 37, 38, 40, 43 and 45, respectively. Two nitrogen methyls, also equivalent, appear around 1.93-2.11 ppm depending on the substituents on the cyclopentadienyl ring and also appear at a lower field than those derivatives (c.f. 2.04-2.18 ppm in 21-32) which do not possess a chiral carbon center because the $-CHMeNMe_2$ group is a stronger electron-donating group than the $-CH_2NMe_2$ group, which causes a lower chemical shift for chiral compounds. For example, a difference of 0.07, 0.06, 0.07, 0.10, 0.07, 0.09, 0.08, 0.06, 0.11, 0.04, 0.10 and 0.11 ppm in chemical shifts are observed for compounds (21-32) and (36-47) with the same -SR substituents on the cyclopentadienyl ring.

Figure 5 shows ^1H NMR for chiral ferrocenylsulfide 38, R= n-Pr. The chemical shifts of the substituted ring

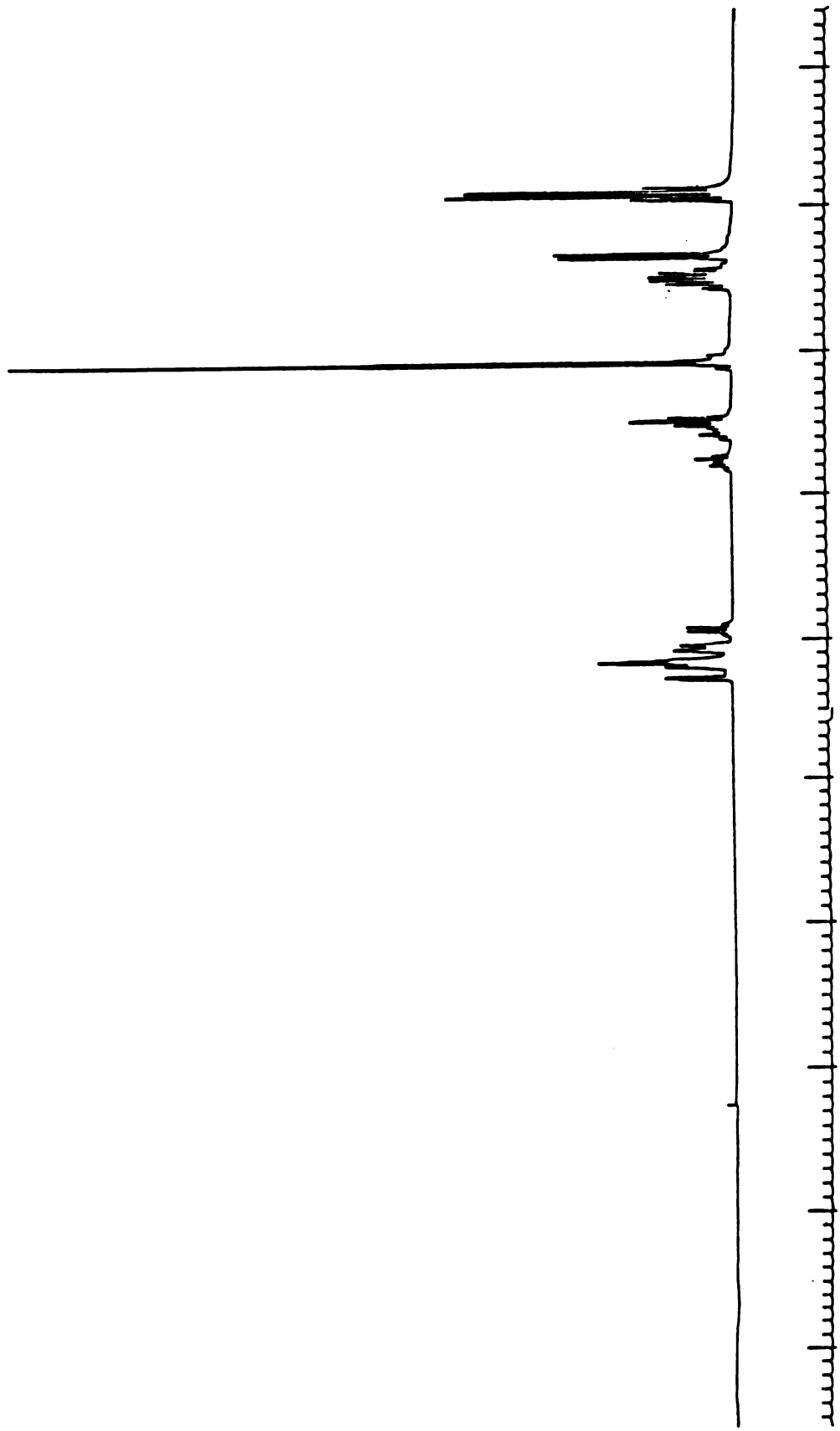


Figure 5. 250 MHz ^{1}H NMR spectrum of 38, R= n-Pr.

protons, H_3, H_4 and H_5 in (S,R)-1-(1-dimethylaminoethyl-2-phenylseleno)ferrocene [77-78] have been assigned as 4.48, 4.34 and 4.28 ppm, respectively. The assignments in chemical shifts of H_3, H_4 and H_5 for these chiral compounds, 36-47, are not possible due to a broad overlapped signal that must be caused by the electronic effects from the second -SR group on the cyclopentadienyl ring. The protons on the mono-substituted $-C_5H_4$ could be assigned to the broad signal around 4.16-4.41 ppm based on the integration of the ^1H NMR and comparisons with several known compounds.

The ^{13}C NMR spectra are similar to those in 21-32. The singlet at 9.2-15.8 ppm could be easily assigned to the methyl groups on the chiral carbon center. Compared to the compounds 21-32, assignments of signals at 39.9-40.7 ppm and 56.0-58.7 ppm to nitrogen methyls ($-NMe_2$) and the amino-methylene group ($-CHNMe_2$) appear certain and all appear at a lower field (compared with 21-32). The carbons on the SR substituents (such as αC, βC, γC and δC) and substituted cyclopentadienyl ring (C_1-C_5) all appear in the range of chemical shifts similar to those in compounds 21-32. The ^{13}C NMR data for chiral ferrocenylsulfide compounds 36-47 are given in Table 6. Figure 6 shows one typical ^{13}C NMR spectrum of compound 44, R= Ph.

The IR and mass spectra of chiral ferrocenylsulfide compounds, (36-47), are also similar to those of ferrocenylaminosulfides, (21-32). The high frequency bands at 3100-2860 cm^{-1} are assigned to C-H stretching. The strong

Table 6. ^{13}C NMR Data for (R,S)-(C_5H_3-1-CHMeNMe$_2$-2-SR)Fe(C_5H_4-SR) in CD_3COCD_3 / TMS, δ ppm, at room temperature.

SR	Ph	C_1	C_2, C_1'	C_3	C_4	C_5	C_2',C_5'	C_3',C_4'	CHMe	NMe2	CHMe	SR αC	SR βC	SR γC	SR δC
36	-	93.4	85.5 84.6	68.2	68.8	73.1	71.0 72.2	72.3	56.0	40.0	10.7	19.5 19.6	-	-	-
37	-	95.0	81.7 81.5	68.8	69.6	76.3	71.8 72.0	75.1	56.1	40.0	10.0	30.4 31.1	15.1 15.3	-	-
38	-	95.0	82.0 81.7	68.7	69.5	75.8	71.7 71.9	75.0	56.1	39.9	10.0	38.6 39.3	23.2 23.3	13.4 13.7	-
39	-	96.2	80.1 79.3	69.0	70.0	77.5	72.2 72.6	76.6 76.8	56.1	39.8	9.2	39.3	23.0 23.6 24.1	-	-
40	-	95.0	82.2 81.3	68.7	69.5	75.9	71.3 71.9	74.9	56.1	39.9	9.8	36.3 37.0	32.1	22.0 22.2	13.9
41	-	96.5	80.6 80.2	69.3	70.4	77.7	72.5 73.0	77.0 77.2	56.4	40.1	9.4	46.4 46.8	21.4 22.0 30.1 30.4	12.1 12.6	-

Table 6 contiued.

42	-		89.4	77.4	77.5	68.7	69.1	71.4	69.5	69.6	71.0	58.7	40.7	15.8	44.7	31.0	-	-
43	-		95.3	82.4	81.7	68.8	69.6	76.1	71.7	71.9	74.8	56.1	39.9	9.7	39.2	34.6 35.3	27.4 27.7 22.8	22.4 22.6
44	125.7 127.0 129.0	125.9[p] 128.0[o] 129.6[m] 141.3[s]	96.0	79.3	79.1	70.7	70.9	78.1	73.8	73.9	77.5	56.4	40.2	12.1	-	-	-	-
45	127.3 128.8 129.7	127.5[p] 128.9[o] 129.9[m] 140.0[s]	96.1	82.1	81.1	69.0	70.2	77.4	72.0	72.1	75.3 76.7	56.7 .	40.0	9.4	41.5 42.2	-	-	-
46	127.6 129.8 135.5	128.6o 130.3[m] 135.8[p] 137.5[s]	95.4	80.1	79.0	70.4	70.6	77.7	73.4	73.6	77.2	56.2	40.2	12.3	-	-	-	20.8
47	128.2 129.2 130.0	128.8[o] 129.5[p] 131.2[m] 140.3[s]	96.4	77.6	-	70.3	71.0	78.1	73.8	74.0	77.4	56.3	39.9	10.9	-	-	-	-

p; para, o; ortho, m; meta and s; substituted carbons, respectively.

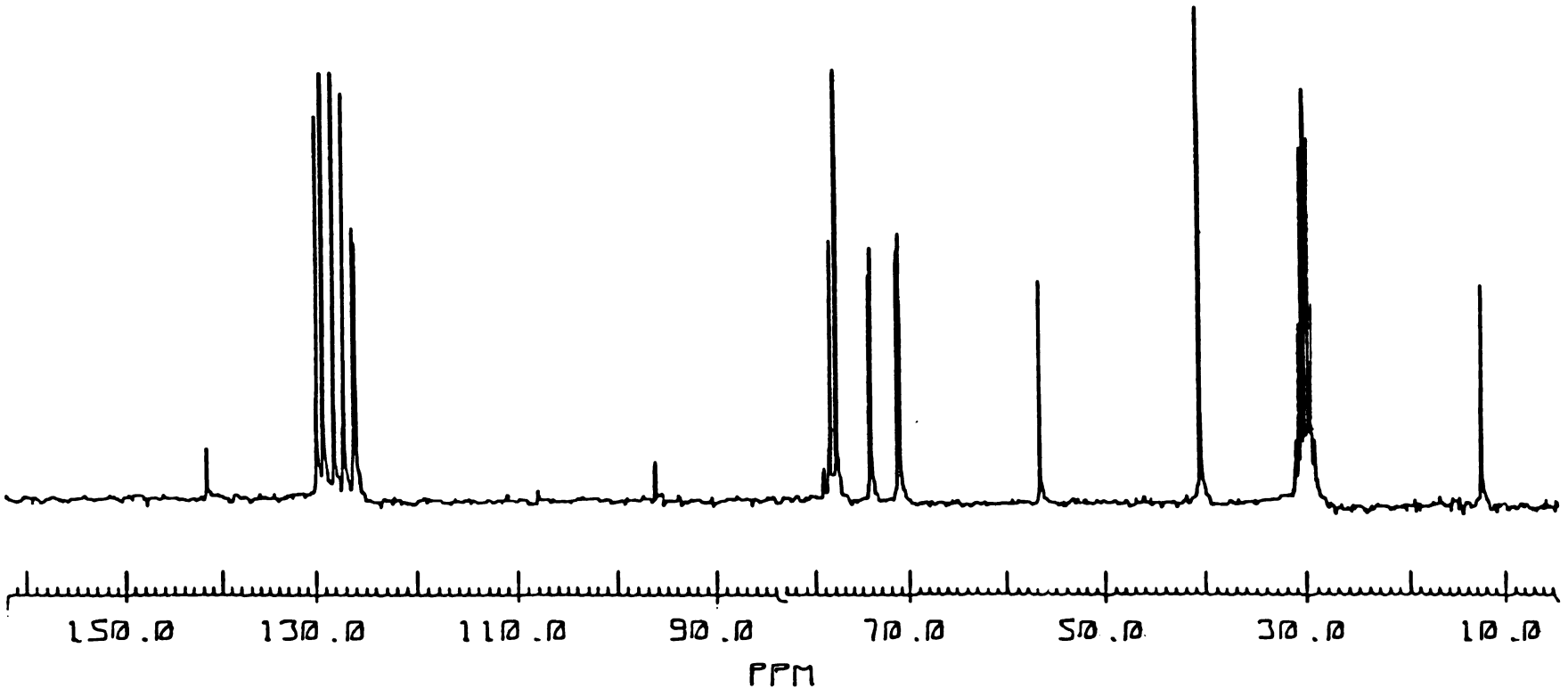


Figure 6. ^{13}C NMR spectrum of 44, R= Phenyl.

absorption bands around 1450-1380 cm^{-1} may be associated with alkyl C-H bend, whereas the broad band absorptions in the 500-450 cm^{-1} region may be associated with ring-metal vibrations such as asymmetric ring-metal tilt and asymmetric ring-metal stretches.

The mass spectrometric data refer to the experimental part. Some important fragments such as M^+, M^+-Me, M^+-SR, M^+-NMe_2-SR, SR (or SeR), Fe, NMe_2 and $CHMeNMe_2$ were obversed. In addition to these fragments, peaks consistent with the less abundant isotopes ^{54}Fe, ^{57}Fe and ^{34}S (or ^{82}Se, ^{78}Se, ^{77}Se and ^{76}Se) were present.

(2), (R,S)-(C_5H_3-1-CHMeNMe$_2$-2-SeR)Fe(C_5H_4-SeR), (R=Me, Ph, 4-Cl-Ph), (48-50), and (R,S)-(C_5H_3-1-CHMeNMe$_2$-2-SeR)Fe(C_5H_5), (R=Me, Ph,4-Cl-Ph), (33-35).

The element, selenium, is in the same group with sulfur, and has similar chemical properties. Sharpless [45] was the first one to make use of the organoselenium reagent, the phenyl selenide anion, in the conversion of epoxides into allylic alcohols. In addition, organoselenium anions are potential nucleophiles that exhibit a strong preference in reaction with soft acids. [47] When organoselenium species contain a good leaving group, they can serve as extremely reactive as soft electrophiles. [140] Thus in general, organoselenium moieties can be introduced into a variety of substrates in either a nucleophilic or an electrophilic sense, and once selenium is incorporated into a substrate, a number of options become available for subsequent functional group manipulations. Finally, most importantly, although most Se(II) species are stable toward β-elimination, their corresponding selenoxides undergo syn-eliminations at or below room temperature. [141] The β-elimination of selenoxides represent the mildest, general olein-forming reactions known thus far.

A series of chiral disubstituted ferrocenylselenide, 48-50, and monosubstituted ferrocenylselenide derivatives, 33-35, have also been synthesized similarly to those in ferrocenylsulfides, 21-32 and 36-47, as discussed in section A and B. Since the reactivity of a selenoether group toward

introduction onto the cyclopentadienyl ring is generally much less than that of the thioether group, it is necessary to reflux the solution instead of stir it in the synthesis of chiral ferrocenylselenides to achieve yields as high as those achieved in the sulfide derivatives.

Table 7 and Table 8 present ^1H NMR data for these chiral ferrocenylsulfides, 33-35 and 48-50. The resonance effect of a -SeR group is weaker than that of a -SR group due to the -SR group being a better electron-donating substituent and the inductive effect of a -SR group is stronger than that of a -SeR group due to the former's higher electronegativity. The inductive effect (deshielding is more sensitive at 4,5-positions) is larger than the resonance effect (shielding is more sensitive at 1,3-positions) in the case of -SeR and -SR substituted compounds. Therefore some conclusions can be drawn: (i) for -SeR substituted at position 2 of the ring, the inductive effect is much stronger than the resonance effect, whereas a -SR substituted at position 2 of the ring, the inductive effect is stronger than resonance effect, (ii) the inductive and resonance effects of a -SR substituent are stronger than those of a -SeR substituent. Based on the above generalizations, it is expected that the ^1H NMR of selenoethers would appear at the higher field of chemical shifts than those of thioethers. As shown in Table 7 and Table 8 the chemical shifts of $-NMe_2$ and $-CH_2N$ groups in compound, 49, when R= SePh appear at 2.16 and (3.55, 3.59)

Table 7. 250 MHz ^1H NMR for (R,S)-[(C_5H_3-1-CHMeNMe$_2$-ER)Fe(C_5H_4-ER)] in $CDCl_3$/TMS, δ ppm.

Compd.	ER	Ph	C_5H_4	C_5H_3	CH_3CH	NMe_2	CH_3CH	ER
36	SCH_3	-	4.19m 4.28m	4.09m	3.93q	2.11s	1.38d 2.29s	2.24s
48	$SeCH_3$	-	4.20m 4.30m	4.10m	3.95q	2.12s	1.40d 2.30s	2.26s
44	SPh	7.10-7.18m	4.41m 4.58m	4.30m	3.91q	1.93s	1.47d	-
49	SePh	7.14-7.43m	4.39m 4.52m	4.27m	3.93q	1.97s	1.46d	-
47	S(Ph-Cl)	6.93-7.13m	4.41m 4.53m	4.33m	3.90q	1.93s	1.42d	-
50	Se(Ph-Cl)	7.10-7.30m	4.36m 4.46m	4.25m	3.92q	1.96s	1.39d	-

Note: at room temperature.

Table 8. ^{13}C NMR Data for (R,S)-(C_5H_3-1-CHMeNMe$_2$-2-ER)Fe(C_5H_4-ER) in CD_3COCD_3/TMS, δ ppm, at room temperature.

ER	Ph	C_1	C_2C_1'	C_3	C_4	C_5	$C_2'C_5'$	$C_3'C_4'$	CHMe	NMe_2	CHMe	αC
SCH3	-	93.4	85.6 84.6	68.2	68.8	73.1	71.0 72.2	72.3	56.0	40.0	10.7	19.6
SeCH3	-	94.3	77.0	68.7	68.8	74.0	71.7 71.9	75.0	57.0	39.8	10.1	8.56 9.30
SPh	125.7 125.9^p 127.0 128.0^o 129.0 129.6^m - 141.3^s	96.0	79.3 79.1	70.7	70.9	78.1	73.8 73.9	77.5	56.4	40.2	12.1	-
SePh	126.4 129.0^p - 129.5^o - 131.0^m - 135.2^s	95.5	79.2	70.0	70.5	78.1	73.4 73.5	77.8 78.0	57.0	40.1	12.0	-
S(Ph-Cl)	128.2 128.8^o 129.2 129.5^m 130.9 131.2^p - 135.2^s	96.4	-	70.3	71.0	78.1	73.8 74.0	77.4	56.3	39.9	10.9	-
Se(Ph-Cl)	129.0 129.7^o 131.2 132.6^m - 132.1^p 134.2 134.3^s	96.2	-	70.3	7.08	78.2	73.8	78.2	57.2	39.9	10.9	-

p; para, o; ortho, m; meta and s; substituted carbons, respectively.

ppm, compared to the higher field, 2.04 and (3.44, 3.55) ppm values for compound, 44, when R= SPh. It seems reasonable to assign the chemical shifts in ^{13}C NMR (see Table 9 and Table 10) for compounds, 33-35, in the following order: $C_1 > C_2$ and $C_1 > C_5 > C_4 > C_5H_5 > C_3$ in -SeR, and $C_2 > C_1$ and C_1, $C_2 > C_5 > C_4 > C_5H_5 > C_3$ in -SR. The ^{13}C NMR data for chiral ferrocenylsulfides, 33-35 and 48-50 are given in Table 9 and Table 10.

The two most important peaks in the infrared spectra of these ferrocenylselenide monosubstituted compounds, 33-35, are the bands around 1000 and 1100 cm^{-1}. They obey the 9-10 rule, [95] expressed as follows. Ferrocene derivatives with an unsubstituted Cp ring show absorption near 9 μ (1100 cm^{-1}) due to an antisymmetric Cp ring breathing mode and near 10 μ (1000 cm^{-1}) due to the C-H bend parallel to the C_5H_5 ring, but those with both Cp rings substituted, like compounds, 48-50, do not exhibit such absorption peaks. The mass spectra of compounds, 33-35, 48-50, show molecular-ion peaks, expected fragments and smaller peaks consistent with isotopes ^{32}S, ^{76}Se, ^{78}Se, ^{82}Se, ^{54}Fe and ^{57}Fe.

Table 9. 250 MHz ^1H NMR data for $(C_5H_3\text{-}1\text{-}CH_2NMe_2\text{-}2\text{-}ER)Fe(C_5H_4\text{-}ER)$, in $CDCl_3$/TMS, δ ppm, at room temperature.

ER	Ph	$C_5\underline{H}_4$	$C_5\underline{H}_3$	$C\underline{H}_2N$	$N\underline{Me}_2$	$\alpha\underline{H}$
SCH_3	-	4.05m	3.95m[a] 4.14m[b]	3.08d 3.43d	2.05s	2.11s 2.13s
SPh	7.05-7.20m	4.45m	4.34m[a] 4.60m[b]	3.48d 3.50d	2.06s	-
SePh	7.30-7.42m	4.47m	4.39m[a] 4.63m[b]	3.55d 3.59d	2.16s	-
S(Ph-Cl)	6.94-7.18m	4.50m	4.41m[a] 4.60m[b]	3.31d 3.57d	2.04s	-
Se(Ph-Cl)	7.21-7.38m	4.48m	4.41m[a] 4.61m[b]	3.48d 3.57d	2.17s	-

a=2H, b=1H; H_3, H_4, H_5.

Table 10. ^{13}C NMR Data for $(C_5H_3\text{-}1\text{-}CH_2NMe_2\text{-}2\text{-}ER)Fe(C_5H_4\text{-}ER)$ in CD_3COCD_3/TMS, δ ppm, at room temperature.

ER	Ph		C_1	C_2C_1'	C_3	C_4	C_5	$C_2'C_5'$	$C_3'C_4'$	CHMe	NMe_2	αC
SCH3	-		88.2	86.4	69.2	72.3	72.4	71.0	72.9	57.4	45.4	19.3
				85.6				71.1	73.4			20.0
SPh	-	125.8^p	90.0	78.2	71.3	74.1	77.1	73.4	77.4	56.9	45.4	-
	126.7	127.4^o		77.6				73.6	77.5			
	129.2	129.4^m										
	140.6	141.0^s										
SePh	-	126.8^p	90.5	-	71.7	73.8	78.2	73.5	78.4	58.2	45.3	-
	129.6	129.8^o						73.7	78.5			
	129.9	130.7^m										
	-	141.9^s										
S(Ph-Cl)	128.1	128.9^o	90.3	78.4	71.5	74.3	77.1	73.6	77.4	56.9	45.3	-
	129.1	129.4^m						73.8	77.7			
	-	131.1^p										
	139.6	139.9^s										
Se(Ph-Cl)	129.5	129.8^o	90.8	-	71.9	74.0	78.2	73.7	78.4	58.1	45.3	-
	-	131.3^m						73.8	78.6			
	-	132.2^p										
	-	134.0^s										

p; para, o; ortho, m; meta and s; substituted carbons, respectively.

C. Palladium Complexes of (C_5H_3-1-CH_2NMe_2-2-SR)Fe(C_5H_4-SR), R=Me, Et, n-Pr, i-Pr, Ph, Bz, 4-Tolyl, 4-Cl-Ph, (51-58), and Platinum Complexes of (C_5H_3-1-CH_2NMe_2-2-SR)Fe(C_5H_4-SR), R=Me, Ph, Bz, 4-Tolyl, 4-Cl-Ph, (59-63).

Reaction of a benzene solution of the aminoferrocenylsulfides (21-24, 29-32) with bis(benzonitrile)palladium dichloride or platinum dichloride gave rise to the metal complexes 51-63. These heterobimetallic complexes are insoluble in benzene. The palladium aminoferrocenylsulfide complexes precipitated immediately upon mixing and the platinum complexes precipitated after the solution had been stirred for 5 days. The palladium complexes are soluble in polar organic solvents such as methylene chloride, chloroform, acetone and acetonitrile, except complex 51, R=Me, which is only soluble in acetonitrile. The platinum complexes are only slightly soluble in these solvents, but are extremely soluble in acetone. Pure samples could be obtained for palladium complexes as dark brown to red crystals by recrystallization from methylene chloride/hexane and for platnium complexes from acetone as yellow flaky crystals. 1-Dimethylaminomethyl-2-1'-bis(methylthio)-ferrocene palladium(II) dichloride, (51), used for X-ray structure studies, was recrystallized slowly from acetonitrile.

Table 11 presents the 250 MHz ^1H NMR data for the palladium aminoferrocenylsulfide complexes, (51, 52 and 55-58). NMR spectroscopy is an extremely valuable technique for

Table 11. 250 MHz ^1H NMR for complexes $[(C_5H_3\text{-}1\text{-}CH_2NMe_2\text{-}2\text{-}SR)Fe(C_5H_3\text{-}SR)]PdCl_2$, in $CDCl_3$/TMS, δ ppm.

Compd.	SR	Ph	C_5H_4, C_5H_3	NMe_2	CH_2NMe_2	SR
51	SCH3	-	4.26-4.45m	2.34s 3.09s	2.70d 3.89d	2.16s 2.73s
52	SEt	-	4.38-4.52m	2.30s 3.09s	2.73d 4.02d	1.14s[a] 1.67s[a] 2.58q[b] 3.27m[c] 3.37m[c]
55	SPh	7.01-7.22m 7.34-7.48m	4.36-4.43m	2.46s 3.17s	2.83d 3.97d	-
56	SBz	7.14-7.25m 7.32-7.38m	4.26-4.42m	2.59s 3.30s	2.33d 3.47d	3.94- 4.10m
57	S(Ph-CH_3)	6.97-7.02m 7.22-7.25m	4.21-4.41m	2.43s 3.16s	2.83d 4.00d	2.24s 2.34s
58	S(Ph-Cl)	6.94-7.17m 7.39-7.42m	4.16-4.43m	2.44s 3.16s	2.83d 4.05d	-

Note: a; CH_3, b; SCH_2, 2H, c; SCH_2, 1H. at room temperature.

determining the structure of the species in solution. It does, of course, depend on having nuclei that possess a nuclear spin. This means that not only can the protons present in thioethers and selenoethers ligands be studied but also the selenium (^{77}Se, natural abundance 7.5 %, has I=1/2). On the other hand the sulfur isotope ^{33}S with a nuclear spin of 3/2 and a natural abundance of only 0.74 %, is much less useful. Since the sulfur and selenium do not have nuclei that are suitable for nuclear quadrupole resonance studies [101], the only NQR results reported have used other nuclei present in the complex.

The aminoferrocenylsulfide ligands undergoe a significant change in the ^{1}H NMR spectra upon complexing with palladium chloride or platinum chloride. There are three possible coordination sites for palladium or platinum metal to coordinate, two sulfur and one nitrogen atom. Therefore the metal atom is expected to coordinate either to two sulfur atoms (structure I) leaving the amine group free, or to one sulfur and one nitrogen atom (structure II) forming a six-member ring rigid structure. Based on the differences in the structures of (I) and (II), we could easily distinguish these two complexes from the ^{1}H NMR spectra. In structure (I), the two nitrogen methyls are expected to appear as a singlet since the amine group is free (uncomplexed). In structure (II), the palladium atom coordinates to both the nitrogen and sulfur atoms, and the free rotation of the pyramidal nitrogen is inhibited by the

rigid six-member ring, thus the two nitrogen methyls are expected to appear at different chemical shifts as two distinctive singlets.

In addition, the chemical shifts of the two methyl groups in the $-NMe_2$ of the palladium aminoferrocenylsulfide complexes, (51-58), are more downfield than those in the corresponding free ligands. The splitting of the two nitrogen methyls is large since inversion of the pyramidal nitrogen in the metal complexes is inhibited by the rigid six-member ring structure. The same figure of the two methyls of $-NMe_2$ in the 2-dimethylaminoferrocenylpalladium chloride dimer had been observed before. Also large downfield shifts of the disubstituted cyclopentadienyl protons, H_3, H_4, and H_5 were observed (though they overlapped as a broad signal), probably because of either the magnetic anisotropy or the inductive effect of the metal chloride.

Figure 7 shows a typical ^1H NMR spectrum of the free ligand, 31, and its palladium complex, 57. As is illustrated in Figure 7 the two singlets at 2.43 and 3.16 ppm, which were compared with complex 55, are assigned to two nitrogen methyls instead of a singlet around 2.08 ppm in free ligand 31. The aminomethylene protons are assigned as two distinct doublets at 2.83 and 4.00 ppm, respectively. In contrast to a singlet at 2.26 ppm for the two methyls on the phenyl in the free ligand, they are split into two different singlets in the complex at 2.24 and 2.34 ppm, probably because one

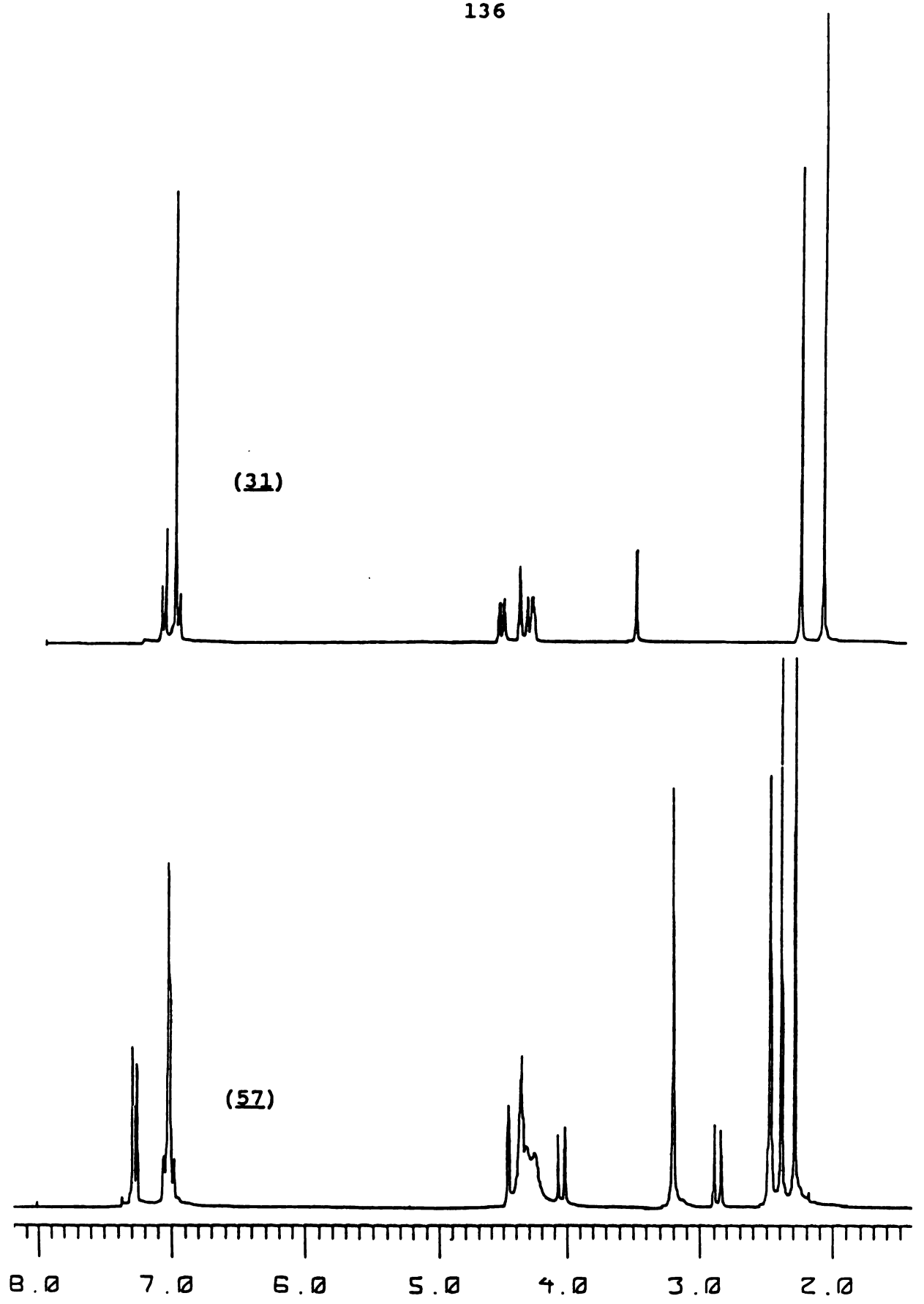


Figure 7. ^{1}H NMR spectrum of 31 and its palladium complex, 57, R= Phenyl.

-SR group bonds to metal palladium but the second -SR remains free. The protons on both cyclopentadienyl rings appear as a broad signal around 4.21-4.41 ppm. Unfortunately, ^{13}C NMR data for these complexes, 51-58, could not be obtained.

The use of infrared and Raman spectroscopy as techniques for determining structures is not as straightforward as X-ray diffraction for two reasons: (i) for complex polyatomic molecules of relatively low symmetry, more than one fundamental mode often contributes to a given band in the spectrum, (ii) in order to investigate the bonding between metals and ligands, it is generally necessary to carry out a detailed force field analysis, and this requires data from many isotopically substituted species. The metal-sulfur and metal-selenium bands are often weak and occur in the region of the spectrum similar to that of the metal-halogen bands of the halogen in the same period of the periodic table. Thus metal-sulfur vibrations occur around 300-340 cm^{-1} and metal-selenium vibrations around 200-240 cm^{-1}. The most important exceptions to the above generalizations are the thioether-bridged platinum(II) complexes, $(R_2S)_2Pt_2X_4$, where the metal-S stretching vibrations around 380-420 cm^{-1} reflect the much stronger metal-S bond when the thioethers are bridging rather than terminal [102] -- a result confirmed by X-ray diffraction. [103]

Another often used source of data concerning the nature of metal-ligand bonding is the influence of a ligand in the

trans position (often M-Cl) on the metal-ligand bonds, although complications [104,105] preclude any precise analysis of the trans influence results. However it can be stated that thioether or selenoether ligands generally show greater trans influence than nitrogen donors and smaller trans influence than teriary phosphines or arsines. [105] The individual metal-Cl and metal-N stretching modes of the complexes, 51-58, are given in the experimental part. The metal-N occurs at the higher frequency, around 460-475 cm^{-1}. As is illustrated in the IR spectra, replacing an -SR group by -SeR gives a larger drop in ν_{Pt-E} stretching vibrations for Pt(II) than Pd(II). Thus, whereas the relative Ð-bonding contribution in palladium(II) thioether or selenoether bonds increases in the order of Pd-S < Pd-Se, the order for platinum(II) appears to be anomalous, Pt-Se < Pt-S. The anomalously small Ð component in the Pt-Se bond is ascribed to a poor match between the relevant orbitals. The mass spectra have fragments consistent with those of the free ligands, except the absence of the parent peaks due to the weaker metal coordination bonds.

D. Palladium Complexes of (R,S)-(C_5H_3-1-CHMeNMe$_2$-2-SR)Fe (C_5H_4-SR), (R=Me, Et, n-Pr, i-Pr, Ph, Bz, 4-Tolyl, 4-Cl-Ph), (67-74), (R,S)-(C_5H_3-1-CHMeNMe$_2$-2-SeR)Fe(C_5H_4-SeR), (R=Me, Ph, 4-Cl-Ph), (75-77) and Platinum Complexes, (R=Me, Ph, Bz, 4-Tolyl, 4-Cl-Ph), (78-82).

Reaction of chiral (R,S)-(C_5H_3-1-CHMeNMe$_2$-2-SR)Fe(C_5H_4-SR), 36-47, or (R,S)-(C_5H_3-1-CHMeNMe$_2$-2-SeR)Fe(C_5H_4-SeR), (48-50), in benzene with palladium(benzonitrile) dichloride or platinum(benzonitrile) dichloride gave the expected metal complexes, 67-77 and 78-82. These heterobimetallic complexes are insoluble in benzene. Palladium complexes, 67-77, precipitated immediately after stirring the solution overnight, whereas platinum complexes, 78-82, were obtained after stirring the solution for 7 days.

The palladium complexes, dark red to burgundy, are highly soluble in organic solvents such as CH_2Cl_2, acetone, CH_3CN and $CHCl_3$, whereas platinum complexes which precipitated as yellow flaky crystals are only soluble in acetone. Pure samples were obtained after recrystallization from methylene chloride/ heptane for palladium complexes or from acetone for platinum complexes. The bimetallic complexes are sufficiently soluble in $CDCl_3$ to obtain ^1H NMR spectra.

The ^1H NMR data for the chiral palladium ferrocenyl-sulfides complexes, 67-74 and 75-77 are given in Table 12. The strong deshielding at the α-protons of the metal

Table 12. 250 MHz ^1H NMR for complexes (R,S)-[(C_5H_3-1-CHMeNMe_2-2-SR)Fe(C_5H_4-SR)]$PdCl_2$, in $CDCl_3$/TMS, δ ppm.

Compd.	SR	Ph	C_5H_4,C_5H_3	CH_3CH	NMe_2	CH_3CH	SR
67	SCH3	-	4.30-4.42m	4.15q	2.29s 3.20s	1.52d	2.26s 2.51s
71	SPh	6.99-7.24m 7.44-7.53m	4.25-4.40m	4.11q	2.33s 3.28s	1.54d	-
72	SBz	7.15-7.24m 7.25-7.36m	4.29-4.46m	4.20q	2.34s 3.30s	1.45d	3.96m 4.16m
73	S(Ph-CH_3)	6.93-7.01m 7.24-7.28m	4.27-4.37m	4.10q	2.33s 3.28s	1.54d	2.24s 2.38s
74	S(Ph-Cl)	6.91-7.16m 7.33-7.46m	4.30-4.41m	4.10q	2.34s 3.29s	1.54d	-

Note: at room temperature.

complexes is due to the magnetic anisotropy and the inductive effect of the metal halide and is also due to a little tilting of the cyclopentadienyl rings where the α-protons are farther from the shielding iron atom. [106] The chemical shift differences of the two methyl groups in the $-NMe_2$ of the chiral (R,S)-(C_5H_3-1-$CHMeNMe_2$-2-SR)Fe(C_5H_4-SR)-$PdCl_2$ complexes, 67-74, are larger than those of the (C_5H_3-1-CH_2NMe_2-2-SR)Fe(C_5H_4-SR)$PdCl_2$ complexes, 51-58, because a chiral center of the $-CHMeNMe_2$ group induces a different geometrical arrangement of the rigid six-member ring structure. The differences are 0.91, 0.95, 0.96, 0.95 and 0.96 ppm in chiral complexes, 67, 71-74, compared with 0.75, 0.71, 0.71, 0.73 and 0.72 ppm in complexes, 51, 55-58. The doublet at 1.45-1.52 ppm is assigned to the methyl group on the chiral center, $-CHMeNMe_2$, whereas the quartet at 4.10-4.15 ppm is assigned to the proton on the same chiral center depending on the substituents on the cyclopentadienyl ring, and they all have a downfield shift of 0.14, 0.07, 0.09, 0.06 and 0.12 ppm for the chiral methyl groups and of 0.14, 0.20, 0.18, 0.19 and 0.20 ppm for the protons on the same center in complexes, 67 and 71-74. Also, the protons on both cyclopentadienyl rings have a larger downfield shift than those in the free ligand, though they appear as a broad overlaping signal in the complexes instead of three well-separated broad peaks.

Figure 8 shows one of the typical ^1H NMR spectrum of the chiral ferrocenylsulfide ligands, 46, and its palladium

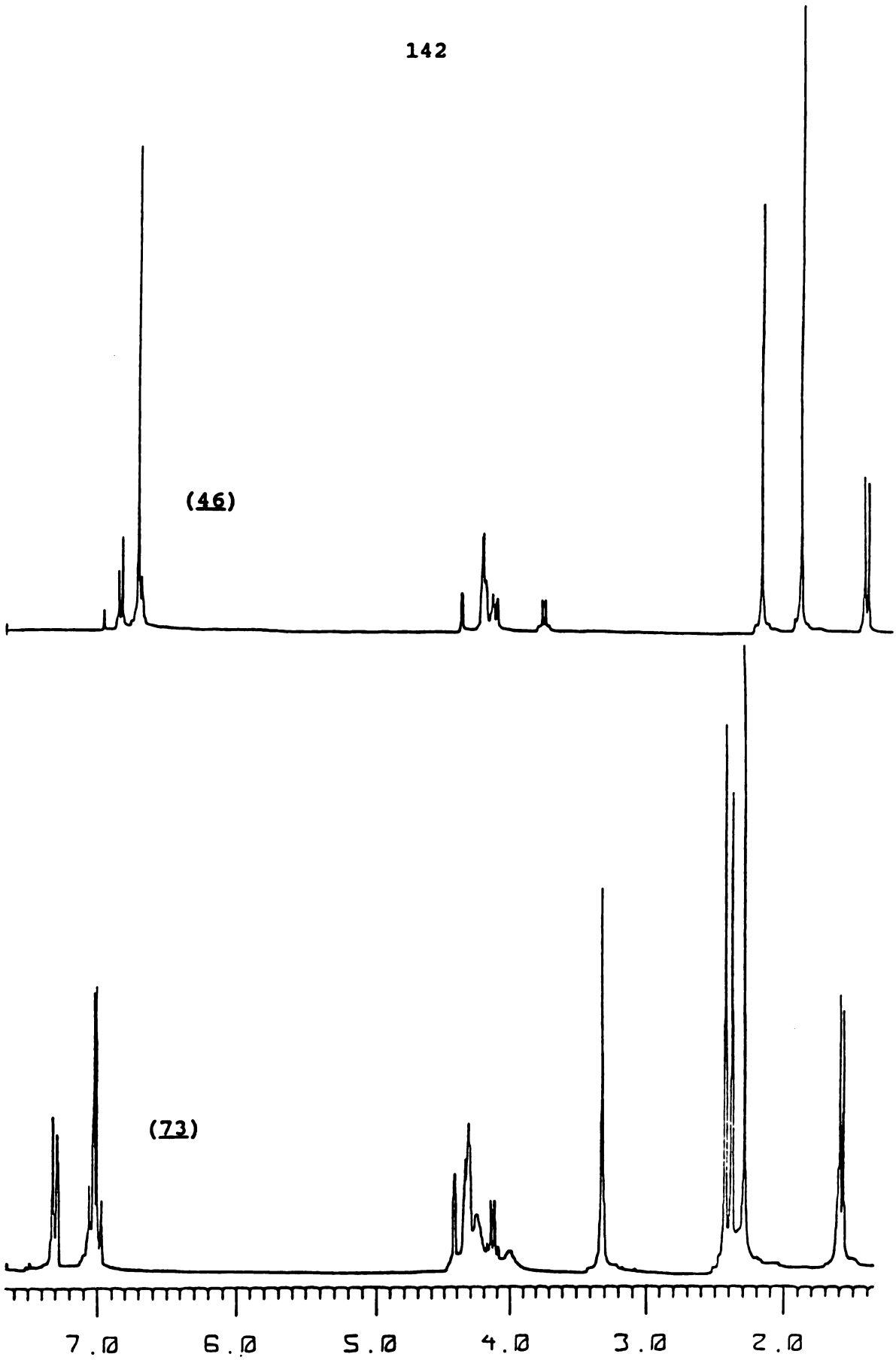


Figure 8. ^{1}H NMR spectrum of 46 and its palladium complex, 73, R= 4-Tolyl.

complex, 73. Unfortunately ^{13}C NMR for these metal complexes could not be otained. Earlier studies [79] from this laboratory showed that the ^{1}H NMR spectra of the chiral (R,S)-1-(1-dimethylaminoethyl)-2-(arylthio)ferrocene palladium dichloride were very temperature dependent. Results showed that these difference are due to the variable rates of pyramidal sulfur inversion -- breaking the Pd-S bond and reforming it with the other configuration at the sulfur atom. Inversion at a coordinated thioether site was first demonstrated in $PtCl_2$(2,5-dithia-hexane), for which the two sets of triplets of the methyl protons coalesce to a single triplet above 95^0C. [107] Much of the work in this field [107-117] determines coalescene temperatures of the palladium and platinum complexes, indicative that the inversion is not a dissociative-associative mechanism.

A simplistic view of the mechanism generally proposed [111] is the displacement at the central metal ion of the lone pair of the thioether or selenoether used in the M-S or M-Se bonds by the lone pair, which is not involved in the bonding via a planar intermediate in which the sulfur or selenium atom remains pyramidal. Ease of exchange between free and coordinated ligands is in the order $TeEt_2 >> SeEt_2 > SEt_2$, as are the relative energy barriers. [113-115] This suggests to us that the Pd-S bond is the weakest bonds at the square planar palladium atom in the complex, and more importantly it is useful as an explanation of the reaction mechanism in selective hydrogenation of 1,3-cyclooctadiene with these

complexes as catalysts. S-dealkylation was first reported in 1883 [118] for the S-demethylation of dimethyl thioether by $PtCl_2$. However, the subject was neglected until the 60s when it was found [119-120] that 8-(methylthio)-quinoline complexed as a neutral ligand toward palladium(II) and platinum(II). However, S-dealkylation was not observed in this work as it was with similar complexes, as a matter of fact attempted to S-dealkylation in these metal complexes led to decomposition. All of the analyses of the metal complexes, 51-82, support their structures and are not like various reported dimers, [121] or with only Pd-N chelation.

The IR and mass spectra for these metal chiral ferrocenyl sulfide complexes, 67-74, 78-82, are generally similar to those of metal complexes, 51-63, discussed in section (C).

E. X-ray structure studies of 1-dimethylaminomethyl-2-1'-bis(methylthio)ferrocene Palladium Dichloride (51).

For the palladium or platinum complexes of thioether and selenoether, the observed metal-S or metal-Se bond lengths are shorter than expected on the basis of the sums of the covalent radii, an observation that has often led to the suggestion that these M-S bonds, together with the Pd-Se bond where the same is also found, involve some Đ back-donation from metal to sulfur or selenium.

In all the complexes the bond angles about sulfur and selenium are approximately tetrahedral, consistent with the presence of one lone pair of electrons in an orbital that can be roughly described as sp^3. Distortions from the ideal tetrahedral angle would be expected and are indeed found where the metal and sulfur and selenium atoms form part of a ring. Most M-S-C angles lie below rather than above the tetrahedral angle, an observation that can be attributed, probably either to the large steric effect of a lone pair or to less complete involvement of the s orbital in hybridization. [104]

The crystal structures of 1-1'-bis(iso-butylthio)-ferrocene palladium dichloride (95) and (R,S)-1-(1-dimethyl-amino)-2-(methylthio)ferrocene palladium dichloride (96) have been determined in this laboratory. [77] The palladium atom coordinates to both sulfur atoms in complex 95, and to both nitrogen and sulfur atoms in complex 96. In both complexes the environment of the palladium atom is described

as square planar with two cis chlorines and two sulfur atoms, in 95, and one nitrogen and one sulfur atom, in 96, respectively. Some other similar palladium ferrocenylphosphine complexes, [$PdCl_2$(PPFA)] (97) [122] and [$PdCl_2$(BPPFA)] (98), [123] were reported by Kumada and coworkers. Crystal structure analysis of chiral phosphine transition metal complexes has proved to be a useful tool in the elucidation of the mechanism of stereocontrol in catalytic asymmetric reactions, especially in the rhodium-catalyzed hydrogenation of enamide precursors of amino acids. [124] Kumada also proposed that the high efficiency of the $PdCl_2$(DPPF) catalyst could be ascribed to its large P-Pd-P angle and small Cl-Pd-Cl angle. [125]

In order to understand the structural and the catalytic properties of the disubstituted metal ferrocenylsulfide complexes, the X-ray crystal structure of complex, 51, was also examined in detail.

F. Selective Hydrogenation of Conjuated Dienes to Monoenes with Metal Complexes in Organic Solvents at Room Temperature.

The hydrogenation of olefins has been studied extensively, perhaps more than any other reactions catalyzed by soluble metal complexes. [124b-124d,126] This intensive study seems anomalous because soluble catalysts are seldom used for olefin hydrogenation in industry or in organic synthesis. Heterogeneous catalysts are ususally more active and more convenient for practical applications such as the hydrogenation of cyclododecatriene to cyclododecane or of dicyanobutene to adiponitrile. The sole commercial use of a soluble catalyst for olefin hydrogenation is the reduction of an unsaturated amino acid to a precursor of the drug L-dopa. Even though this operation is conducted on a small scale, it is interesting because it involves asymmetric induction through use of an optically active catalyst. This selectivity is the major advantage of a soluble catalyst. The best studied soluble catalyst for olefin hydrogenation is Wilkinson's catalyst $RhCl(PPh_3)_3$.

Generally, the most active catalysts are to be found in the salts and complexes of Rh, Ru and Pd. The catalytic activity of the transition-metal salts and complexes is the result of a delicate balance of valence states and strengths of chemical bonds. [127] Too strong a bond between the hydrogen donor and the transition metal results in stable compounds showing no catalytic activity. Similarly, there is

no catalytic activity if reaction between the hydrogen donor and the transition element cannot occur. The activity of the catalyst depends on the existence of free coordination sites on the central metal or on the possibility of producing a vacant site by loss of a ligand. Therefore, the coordination number of the metal complex should be less than the maximum possible, or for saturated complexes, the ligand-metal bond strength should be such that dissociation is possible or that ligand displacement by a solvent, hydrogen donor, or substrate hydrogen acceptor can occur.

In 1967, $PtCl_2(SPh_2)_2$ was found to be selective for the hydrogenation of dienes to monoenes in the presence of $SnCl_2$ [128]. Treatment of $PdCl_2$ or Na_2PdCl_4 with tertiary amines resulted in an active selective catalyst. [129] The same was true of $PdCl_2$ when treated with 2,2'-bipyridine and $NaBH_4$. [130] The thioether-rhodium complex, $RhCl_3(SEt)_3$, was used in the hydrogenation of the maleic acid. [69,131-132]

(a) Selective Hydrogenation of Conjuated 1,3 Cyclooctadiene to Cyclooctene with Complexes (51-53, 55-58, 67-69, 71-74).

The palladium aminoferrocenylsulfide complexes have been used as catalysts for reduction of 1,3-cyclooctadiene to cyclooctene in various solvents at room temperature. Hydrogenation of 1,3-cyclooctadiene occurred fast in acteone at 103 psi initial hydrogen pressure as shown in Table 14. This is a homogeneous system without any H_2O or reducing agents, and reaction proceeded at a normal rate (turnover rate from 79.0 to 722.4 mol/mol pd.h). The conversions and selectivities in all cases were fairly high, up to 100% and 96.8%., respectively. The original red solution became yellow clear with some black precipate, probably palladium metal, as time passed, but the solution remained homogeneous. The principal products at the end of reaction was cyclooctene with some cyclooctane. The percentages of products were determined by gas chromatography. The ratio of (cyclooctadiene + cyclooctene) to cyclooctane were separated by more than 0.7 min. in the GC. spectrum, and the ratio of 1,3-cyclooctadiene to cyclooctene was determined by 250 MHz ^1H NMR as shown in Figure 9.

The chemical shifts of the central and outer olefinic protons of the diene appear around 5.8 and 5.6 ppm, respectively, while that of the monoene is near 5.6 ppm. Therefore, the ratio of monoene to diene is calculated by following equation.

Table 14. Hydrogenation of 1,3-Cyclooctadiene[a] with 55-58 -- Effect of Catalysts[b].

Catalyst /$PdCl_2$	Solvent[c]	Turnover Rate	Conver. (%)	Products(%) Monoene	Alkane	Select. (%)
SPh	acetone	363.4	100	93.8	7.22	93.8
SBz	acetone	79.3	100	92.8	7.20	92.0
S(Ph-CH_3)	acetone	390.3	100	88.6	11.4	88.6
S(Ph-Cl)	acetone	722.4	100	96.8	3.19	96.8

a: 7.45×10^{-3} mole of substrate. b: catalyst = [(C_5H_3-1-CH_2NMe_2-2-SR)Fe(C_5H_4-SR)]$PdCl_2$, 2×10^{-5}mole, at room temperature, 103 psi initial pressure. c: 9 ml of solvent.

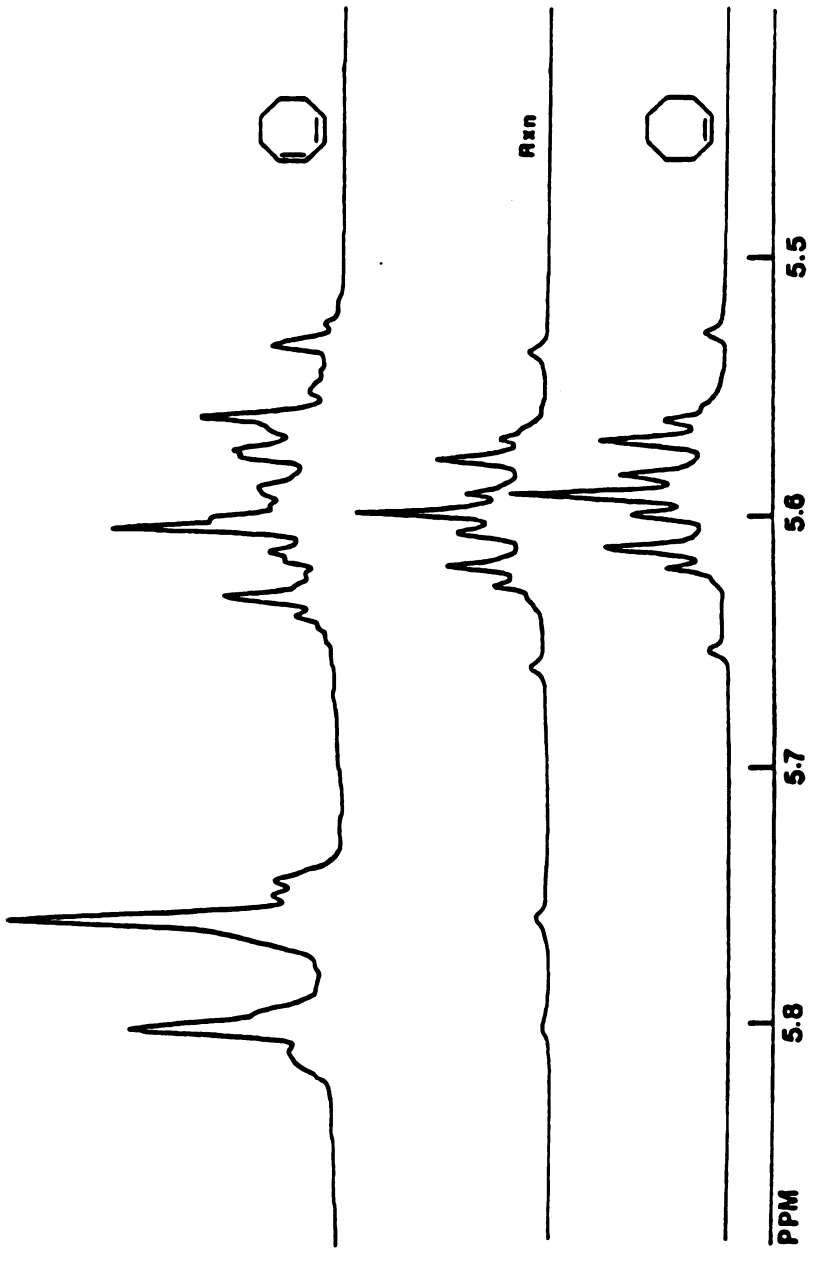


Figure 9. Olefinic region of 250 MHz ^{1}H NMR of 1,3-cyclooctadiene(top), the mixture of 1,3-cyclooctadiene and cyclooctene(middle), and cyclooctene(bottom).

$$\frac{\text{Monoene}}{\text{Diene}} = \frac{\text{Area(5.6)-Area(5.8)}}{\text{Area(5.8)}}$$

In Table 14. it is apparent that the turnovers rate are dependent on the catalytic activity of the different complexes. The more the steric crowding and electron-withdrawing of the substituents on the cyclopentadienyl, the more favorable the selective hydrogenation. The hydrogenation reaction failed when palladium selenide or platinum sulfide were used as catalysts, suggestive that the breakeage of the metal-sulfide bond (or metal-selenide) may be a key step for the catalytic hydrogenation since the Pd-Se or Pt-S bond is stronger than the Pd-S bond in these catalysts. Table 15 shows the solvent effect of the hydrogenation reaction using complex, 58, as catalyst. The conversion and selectivity reduced when H_2O was added to the acetone or when reaction was carried out in a stronger coordinating solvent such as THF. However, the catalyst still remained active in a weaker solvent such as CH_2Cl_2, an observation which had not been observed before in this laboratory with the similar ferrocenylsulfide palladium catalysts.

The same hydrogenation reaction was examined by using chiral ligand complexes, 67-69 and 71-74 with acetone as solvent. Conversions in all cases were 100%. The turnover rates, percentages of monoene and selectivities are strongly dependent on the different substituent groups on the

Table 15. Hydrogenation of 1,3-Cyclooctadiene[a] with Catalyst 58 -- Effect of Solvents[b].

Catalyst /$PdCl_2$[c]	Solvent	Turnover Rate	Conver. (%)	Products(%) Monoene	Alkane	Select. (%)
S(Ph-Cl)	acetone	722.4	100	96.8	3.19	96.8
"	acetone/ H_2O	141.8	82.0	76.5	5.50	93.2
"	THF	383.8	62.6	60.4	2.13	96.6
"	CH_2Cl_2	178.7	80.0	79.5	0.47	99.4

a: 7.45×10^{-3} mole of substrate. b: 9 ml of solvent. c: catalyst = $[(C_5H_3\text{-}1\text{-}CH_2NMe_2\text{-}2\text{-}SR)Fe(C_5H_4\text{-}SR)]PdCl_2$, R=4-Cl-Ph, 2×10^{-5}mole, at room temperature, 103 psi initial pressure.

cyclopentadienyl ring; i.e. different catalysts. The percentage of monoene and selectivity were both 100% for complex, 68, R = Et. There does not seem to be any relationship between catalytic activity and the different complexes used as catalysts based upon the data in Table 16.

Failure of the hydrogenation reactions using chiral palladium selenide or platinum sulfide complexes was observed again as mentioned before. Meanwhile, the solvent effect, using complex 74 as catalyst, was also studied in detail as shown in Table 17. In a stronger solvent, such as pyridine, catalytic activity for the conversion was reduced dramatically, down to 7.23%; however, selectivity remained 100%. Our results indicate that the significance of the solvent lies mainly in its tendency to coordinate. Strongly coordinating solvents inhibit the catalytic activity, whereas weakly coordinating ones do not.

Results obtained from the hydrogenation in different solvents suggest the following increasing order of catalyst-solvent interaction: CH_2Cl_2 < $(CH_3)_2CO$ < THF < pyridine. This roughly parallels the order of increasing coordinating efficiency of the solvents. Monoene yields ranged from 92.2% in methylene chloride to 7.23% in pyridine for chiral palladium complex catalysts. Metal-solvent interactions may range from weak dipole-dipole interaction or solvent cage formation to chemical bonding or coordination, as in pyridine. This could be confirmed by 250 MHz ^1H NMR spectra;

Table 16. Hydrogenation of 1,3-Cyclooctadiene[a] with Catalysts 67-69, 71-74 and 79 -- Effect of Catalysts[b].

Catalyst /$PdCl_2$	Solvent[c]	Turnover Rate	Conver. (%)	Products(%) Monoene	Alkane	Select. (%)
SCH_3	acetone	45.7	100	95.5	4.48	95.5
SC_2H_5	acetone	9.7	100	100	0.0	100
S(n-Pr)	acetone	18.3	100	92.3	7.70	92.3
SPh	acetone	114.5	100	86.4	13.6	86.4
SBz	acetone	62.4	100	89.7	10.3	89.7
S(Ph-CH_3)	acetone	291.9	100	84.6	15.4	84.6
S(Ph-Cl)	acetone	645.1	100	91.6	8.43	91.6
SPh/Pt[d]	acetone	-	-	No H_2 Uptake		-
SePh/Pd	acetone	-	-	No H_2 Uptake		-

a: 7.45×10^{-3} mole of substrate. b: catalyst = [(R,S)-(C_5H_3-1-$CHMeNMe_2$-2-SR)Fe(C_5H_4-SR)]$PdCl_2$, 2×10^{-5}mole, at room temperature, 103 psi initial pressure. c: 9 ml of solvent. d: platinum complex.

Table 17. Hydrogenation of 1,3-Cyclooctadiene[a] with 74 -- Effect of Solvents[b].

Catalyst /$PdCl_2$[c]	Solvent	Turnover Rate	Conver. (%)	Products(%) Monoene	Alkane	Select. (%)
S(Ph-Cl)	acetone	645.1	100	91.6	8.43	91.6
"	acetone/ H_2O	254.0	81.2	75.3	5.90	92.3
"	THF	371.6	95.0	84.6	10.4	89.1
"	pyridine	82.1	7.23	7.23	0.0	100
"	CH_2Cl_2	165.6	93.8	92.2	1.55	98.3

a: 7.45×10^{-3} mole of substrate. b: 9 ml of solvent. c: catalyst =[(R,S)-(C_5H_3-1-$CHMeNMe_2$-2-SR)Fe(C_5H_4-SR)]$PdCl_2$, 2×10^{-5}mole, at room temperature, 103 psi initial pressure.

the chemical shifts of the complex-coordinated pyridine have a larger downfield shift than free pyridine.

Not suprisingly, both conversion and selectivity were a function of the additives employed. With $AgNO_3$ added in acetone, the turnover rate and conversion decreased but selectivity increased somewhat (up to 100%). In anhydrous acetone solvent, the Ag^+ slowly scavenges the Cl^- from the hydrogenation cycle and inhibits the enhanced hydrogenation of the cyclooctene to cyclooctane. However, with added $AgNO_3$ and H_2O in acetone the Ag^+ ion precipitates immediately all of the Cl^- from the palladium complexes into the aqueous phase, which causes reduction of the catalytic activity of the complexes. In some cases the hydrogenation completely failed, depending on the order adding of $AgNO_3$ and H_2O into the system (see Table 18). Futhermore, the effect of a formation of a hydroxo bond at the palladium atom due to the hydrolysis reaction can not be excluded [133]. The quaternary ammonium salts may precipitate and act as the catalyst, or a Pd^{2+} hydroxide species dissociated from the thioether may precipitate.

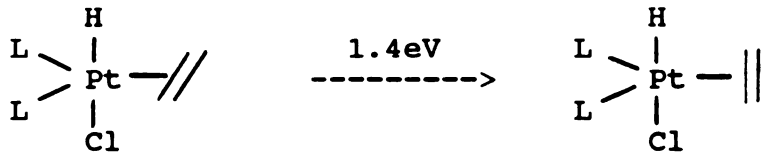
The insertion of olefins and acetylene into Pd-H and Pt-H bonds have been studied extensively. [134-135] It has generally been accepted that the formation of the metal-hydrido bond and its reaction with unsaturated compounds are one of the key steps in the overall reactions [136]. Thorn and Hoffmann have carried out a detailed theoretical analysis of the reaction of ethylene with trans-$(H_3P)_2Pt(H)Cl$. [137] They

Table 18. Hydrogenation of 1,3-Cyclooctadiene[a] with 74 -- Effect of Additives[b]

Catalyst /$PdCl_2$[c]	Solvent/ Additive	Turnover Rate	Conver. (%)	Products(%) Monoene	Alkane	Select. (%)
S(Ph-Cl)	acetone	645.1	100	91.6	8.43	91.6
"	acetone+ $AgNO_3$[d]	134.1	22:5	22.5	0.0	100
"	acetone+ $AgNO_3$[d] H_2O[e] 3	74.2	14.53	14.5	0.0	100

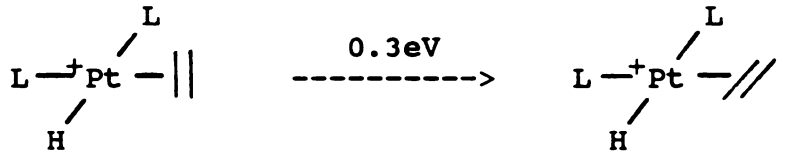
a: 7.45×10^{-3} mole of substrate. b: 9 ml of solvent. c: catalyst [(R,S)-(C_5H_3-1-CHMeNMe_2-2-SR)Fe(C_5H_4-SR)]$PdCl_2$, 2×10^{-5} mole, at room temperature, 103 psi initial pressure. d: 4×10^{-5} mmol. e: 2×10^{-4} mole.

found that the ground state of the five-coordinate complex **A** could not be transformed readily into configuration **B** (with coplanar ethylene and hydride ligands) as required for insertion.



A **B**

In contrast, they found that the perpendicular ethylene in a four-coordinate complex **C** could easily rotate to give the coplanar complex **D** and insertion (the normal preference for a perpendicular orientation is apparently the result of steric and not electronic factors).[138-139]



C **D**

They therefore proposed that the insertion of olefins into the Pt-H bonds of planar complexes proceeded via a four-coordinate (with the olefin replacing a ligand and achieving a coordination site cis to the hydride) rather than a five-coordinate entity (with no ligand loss prior to

coordination and insertion of the olefin). Thorn and Hoffmann also suggested that their results should extend to acetylenes and to Pd-C and Pt-C sigma bonds, and thus that olefin and acetylene insertions into Pd-C and Pt-C bonds should also prefer four-coordinate mechanisms over five-coordinate ones.

Figure 10 presents a possible mechanistic scheme for the homogeneous selective hydrogenation of 1,3-cycloocta-diene. The hydrogenation proceeded either from 100 via four-coordinate intermediates, 105, 106, 107, and 108, then back to 100 having a cycle, or from 100 via five-coordinate intermediates, 110, 107 and 109 then back to 100. Although an analysis of ^{195}Pt NMR chemical shifts in a range of complexes according to Ramsey's equation has led to the suggestion that the covalency of platinum(II)-ligand bonds increases in the order $NMe_3 << Cl^- < C_2H_4 < Me_2SO$, $SMe_2 < PMe_3 < SeMe_2 < AsMe_3 < SbMe_3 < TeMe_2 < I^-$. Breakage of Pd-S, but not Pd-N or Pd-Cl bonds was supported by many experimental results: (1) X-ray studies show the length of the Pd-S bond is longer than that of Pd-N or Pd-Cl bonds, suggestive that the Pd-S bond might be the weakest, (2) all palladium selenide or platinum sulfide complexes used as catalysts in acetone could be recovered completely after failure of the hydrogenation reaction and would explain that breakage of the Pd-S bond should be the first step in the mechanism since Pd-Se or Pt-S is stronger than Pd-S and (3) the variable temperature ^1H NMR spectra of complexes showed

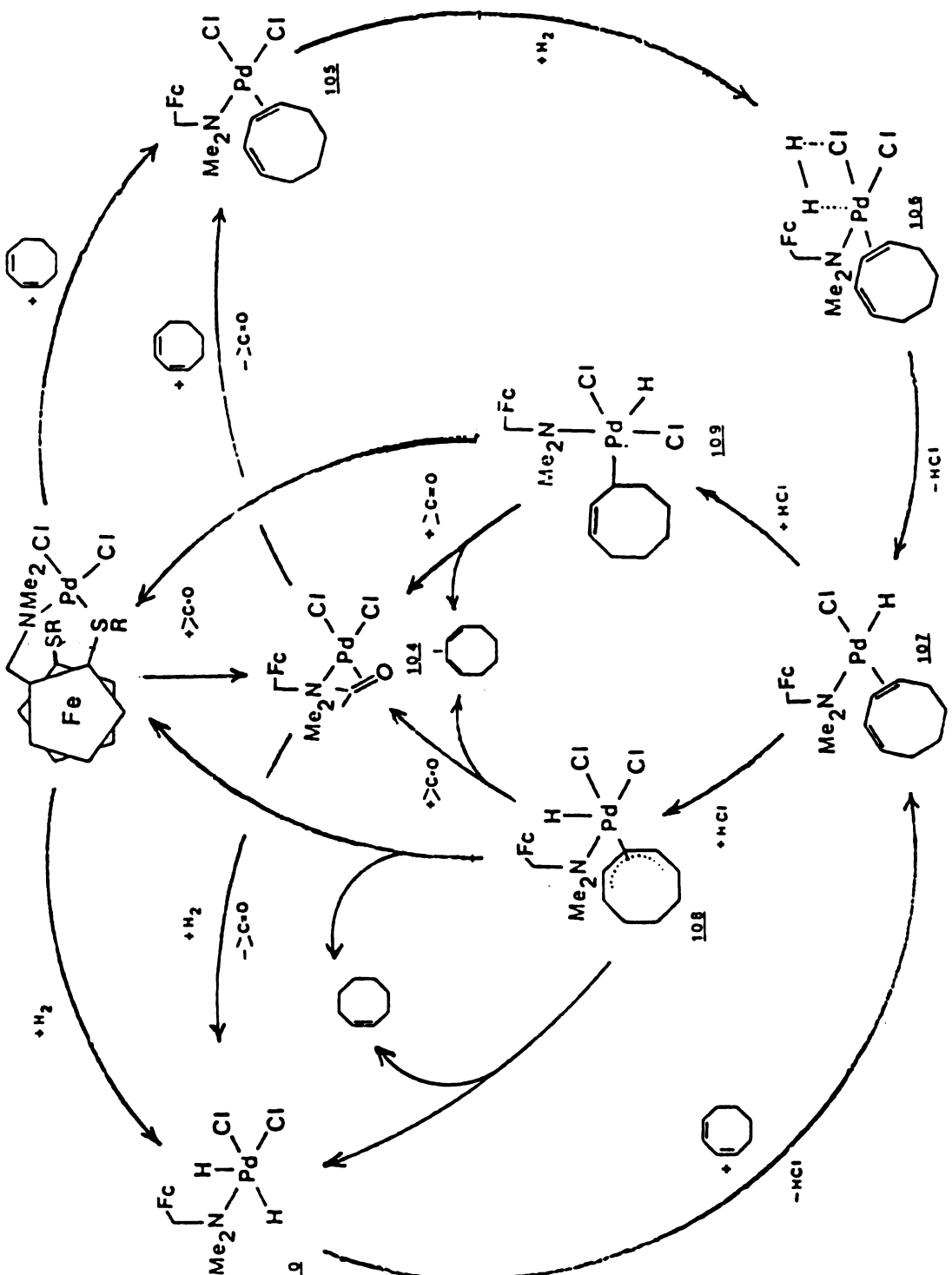


Figure 10. Possible mechanisms of the homogeneous selective hydrogenation of 1,3-cyclooctadiene through a four-coordination intermediate, Fc-; 2,1'-dialkylthio-ferrocenyl.

that even at room temperature the pyramidal sulfur inversion in two different conformational structures could occur by breaking the Pd-S bond and reforming it with the other configuration at sulfur.

The insertion of olefin into the Pd-H bond of planar complex 107 proceeds via a four-coordinate intermediate, and then takes up a HCl molecule to form a five-coordinate trigonal bipyramid (TBP), 109, or rearrange to a five-coordinate square pyramid (SP), 108. The cycle passing 109 is less probable than that passing 108 since the Đ-allylic metal intermediate (108) is more reactive than δ-allylic metal intermediate (109). The cycle from 110 to 107, the homolytic fission of hydrogen, would involve unlikely oxidation of palladium(II) to palladium(IV). As a matter of fact, reduction to palladium metal was always observed during the reaction.

In order to understand the possible source of hydrogen for the formation of the metal hydride complex, the hydrogenation was tried in different conditions: (a) under H_2 with acetone as solvent, (b) under H_2 without solvent, (c) under Ar with solvent and (d) under Ar without solvent. The hydrogenation took place only in (a) and (b) with different degrees of conversions. This shows that, while molecular hydrogen and substrate may supply hydride ions, the solvent cannot be a significant source of hydrogen, at least under the high hydrogen pressure. One may expect that if solvent is not used in the hydrogenation, the monoene

yield will be reduced, was demonstrated with complex 55. When this complex was used as a catalyst, the monoene percentage dropped about half from 93% to 49%. In addition, the possibility of binuclear catalysis in the diene hydrogenation has not been excluded.

(b). Selective Hydrogenation of Conjugated 1,3-Cyclohexadiene to Cyclohexene with Complexes (55, 58, 71, 74).

The selective hydrogenation of 1,3-cyclohexadiene in acetone at room temperature and a 103 psi initial hydrogen pressure with complexes as catalysts was also examined in detail. Similarly, the products, cyclohexene and cyclohexane, were analyzed by gas chromatography and ^{1}H NMR as discussed before. In Table 19 the turnover rate, induction time, and selectivities are dependent on different substituents on the cyclopentadienyl ring, whereas the percentages of cyclohexene and selectivities in all cases were much higher than those in the hydrogenation of 1,3-cyclooctadiene. It is evident from the preceding results that observed rates and products in hydrogenations catalyzed by palladium complexes depend on the ligands, the oxidation state of the central metal atom, substrates, solvents and other constituents of reaction mixtures. Of these, the nature of substrates appears to be most important and, in fact, determines the relative effect of other variables. Therefore, it can be assumed that the complexing of the substrate is an important step in the reaction sequences. It is evident that open-chain olefins are more likely to assume the proper arrangement for bonding to the metal than cyclic ones. Thus, open-chain dienes such as 1,7-octadiene are hydrogenated much faster than cyclic dienes such as 1,5-cyclooctadiene. It is also reflected in the general

Table 19. Hydrogenation of 1,3-Cyclohexadiene[a] with 55, 58, 71 and 74 -- Effect of Catalysts.

Catalyst /$PdCl_2$	Solvent	Turnover Rate	Conver. (%)	Products(%) Monoene	Alkane	Select. (%)
SPh[c]	acetone	475.5	100	95.9	4.14	95.9
S(Ph-Cl)[c]	acetone	665.5	100	94.8	5.16	94.8
SPh[d]	acetone	249.5	100	97.0	3.05	97.0
S(Ph-Cl)[d]	acetone	248.3	100	95.7	4.31	95.7

a: 7.45×10^{-3}mole of substrate in 9 ml acetone. b: 2×10^{-5}mole catalysts. c:$(C_5H_3\text{-}1\text{-}CH_2NMe_2\text{-}2\text{-}SR)Fe(C_5H_4\text{-}SR)PdCl_2$. d:(R,S)-$(C_5H_3\text{-}1\text{-}CHMeNMe_2\text{-}2\text{-}SR)Fe(C_5H_4\text{-}SR)PdCl_2$, at room temperature, 103 psi initial pressure.

observation that the rate of isomerization is much greater than the rate of hydrogenation.

APPENDIX

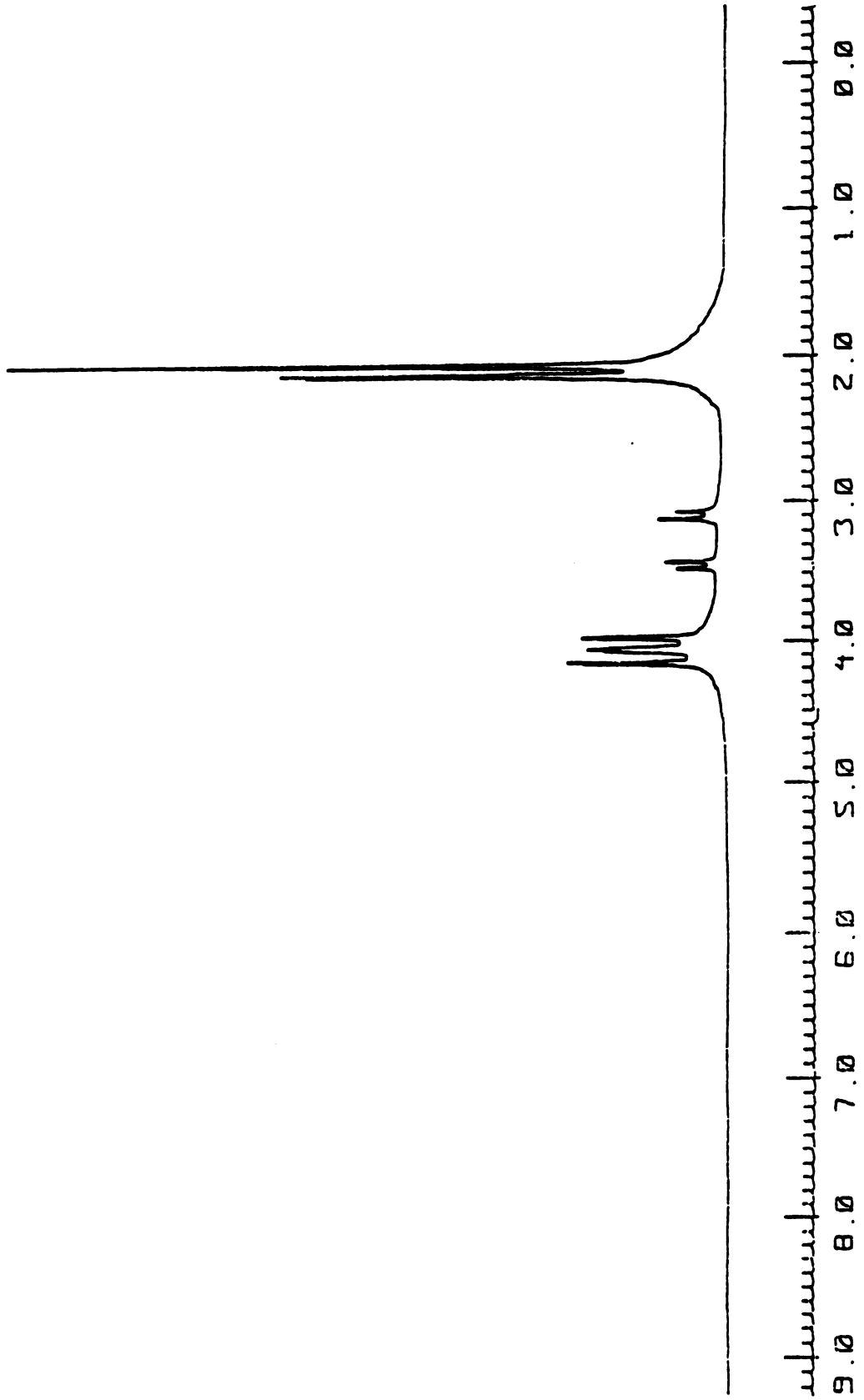


Figure 11. ^{1}H NMR spectrum of 21, R= Me.

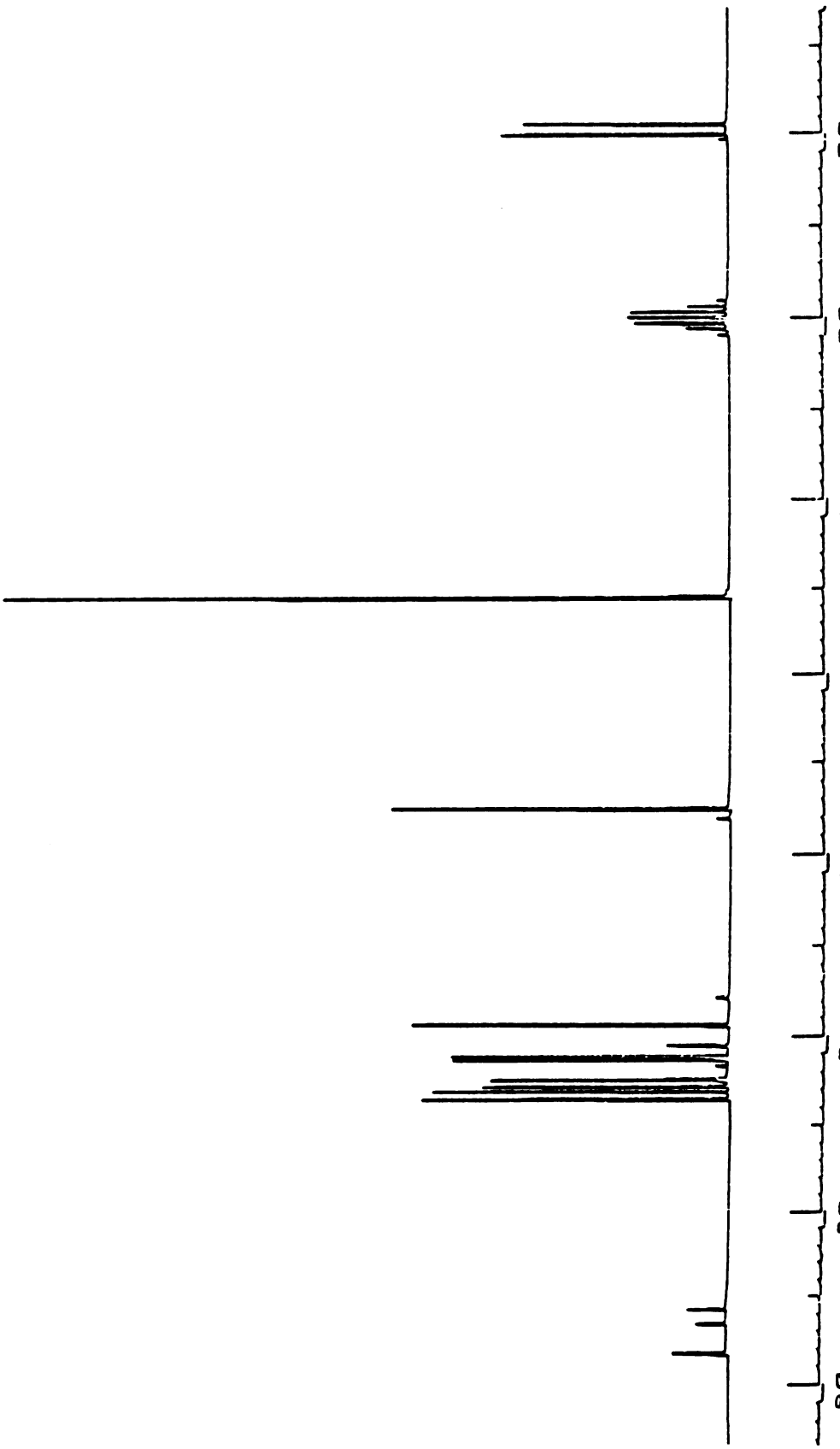


Figure 12. ^{13}C NMR spectrum of 21, R= Me.

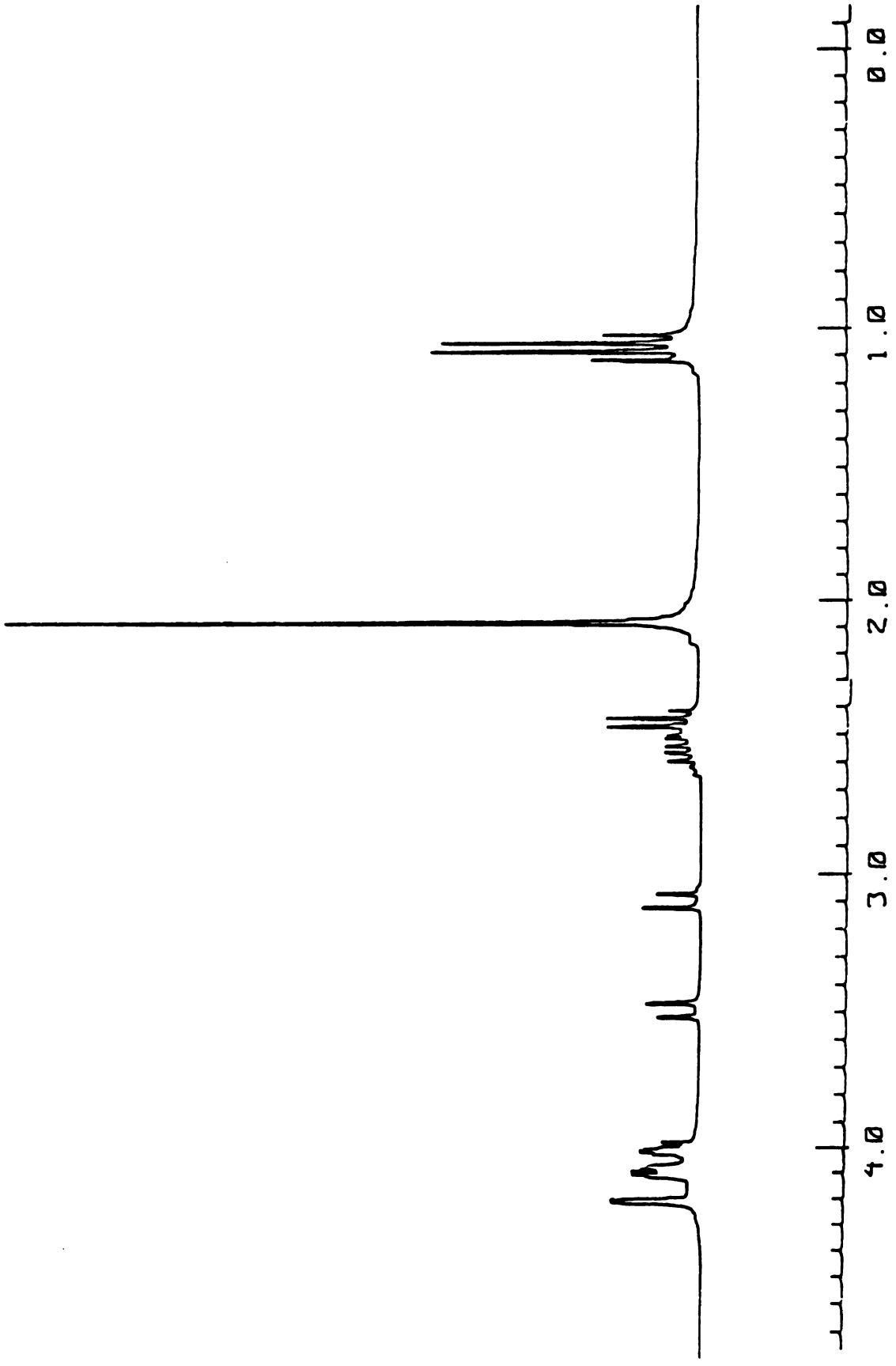


Figure 13. ^{1}H NMR spectrum of 22, R= Et.

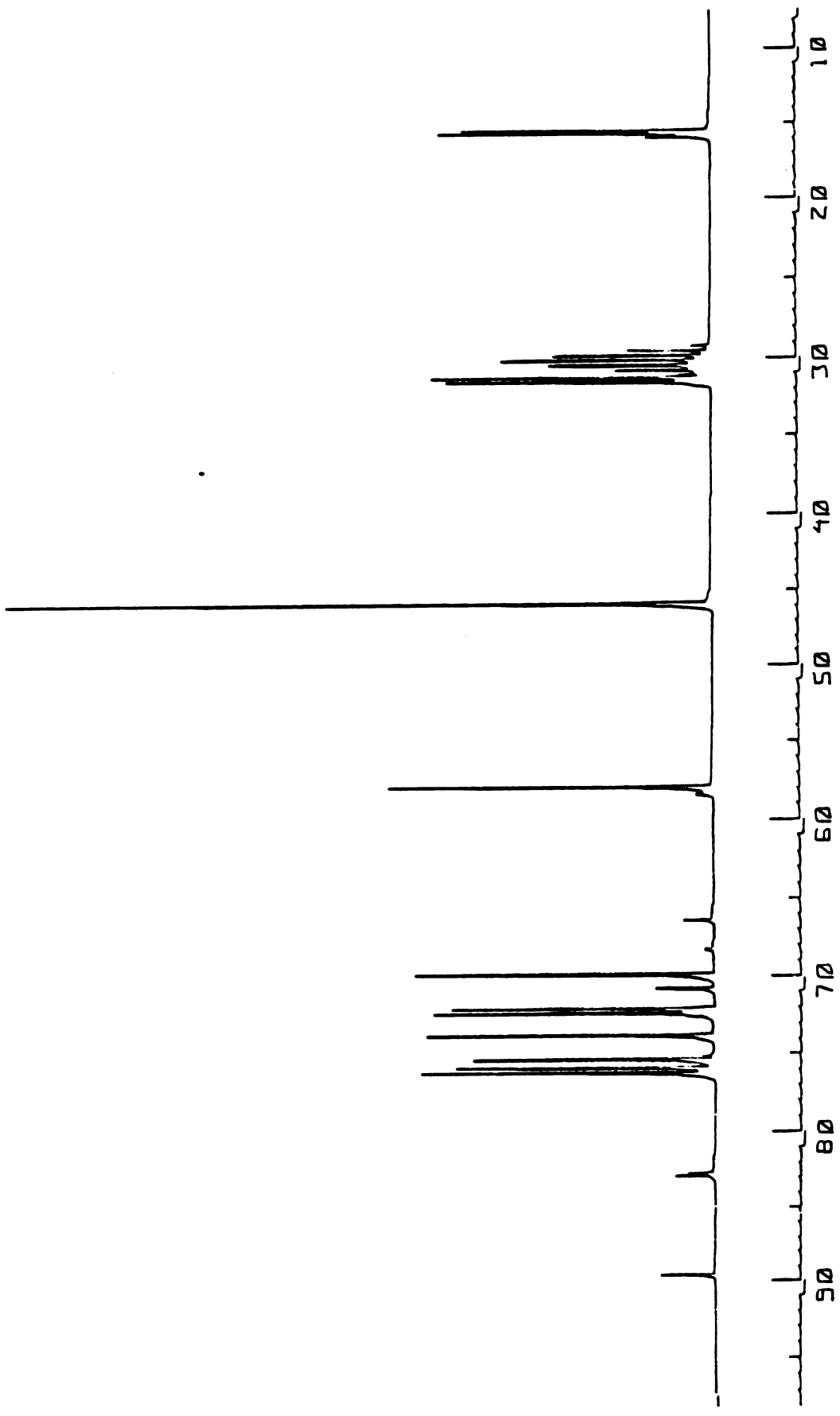


Figure 14. ^{13}C NMR spectrun of 22, R= Et.

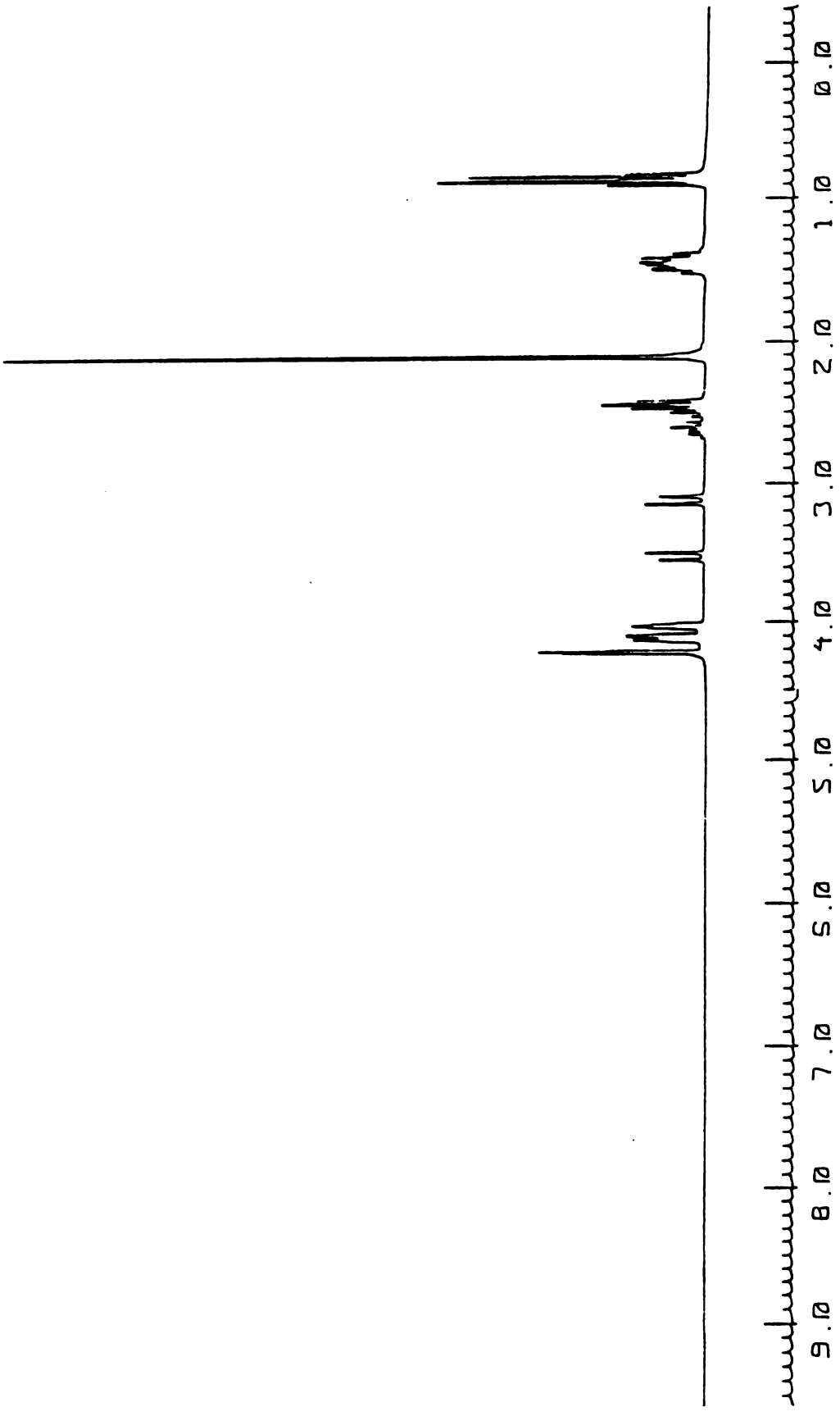


Figure 15. ^{1}H NMR spectrum of 23, R= n-Pr.

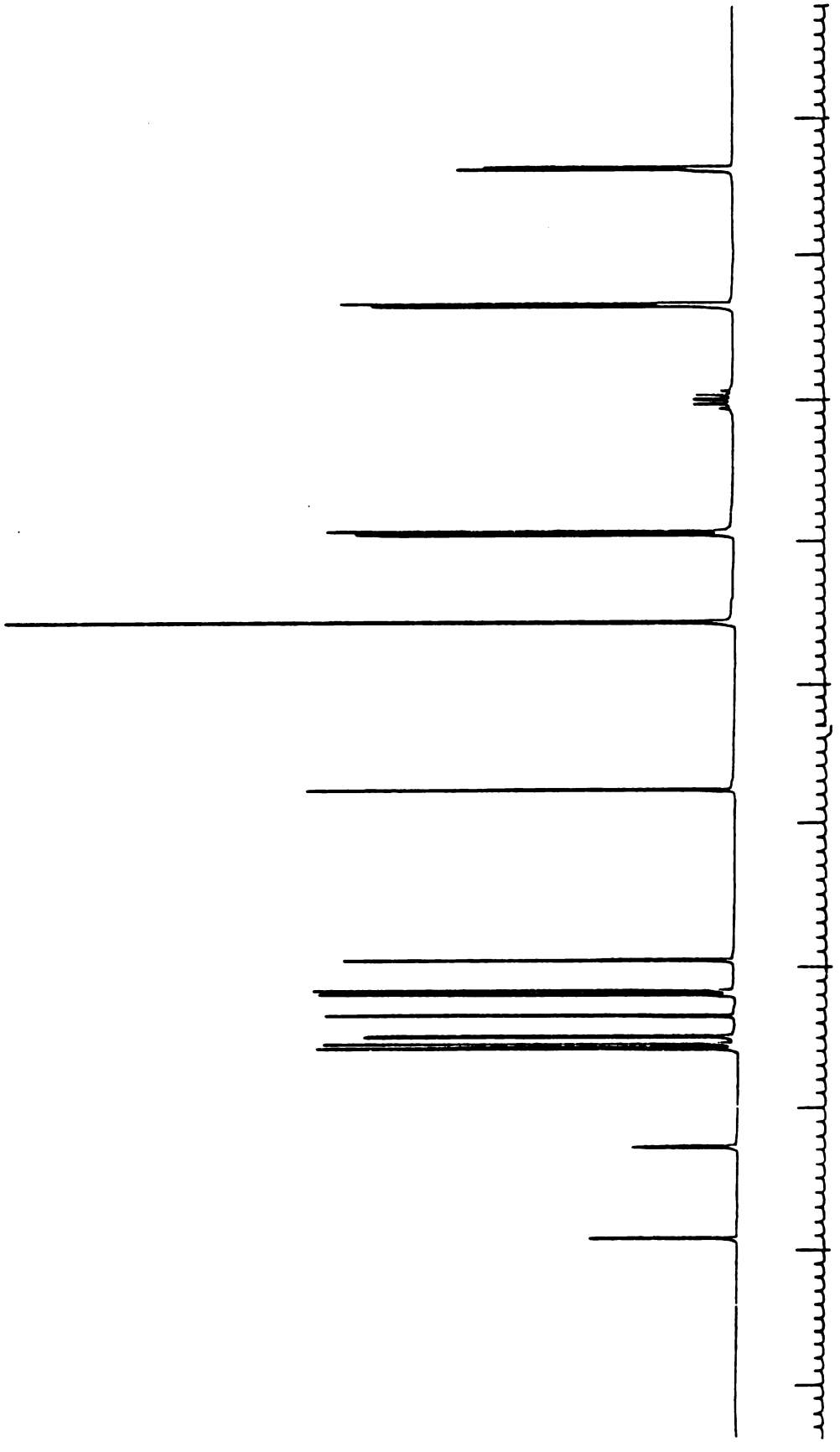


Figure 16. ^{13}C NMR spectrum of 23, R= n-Pr.

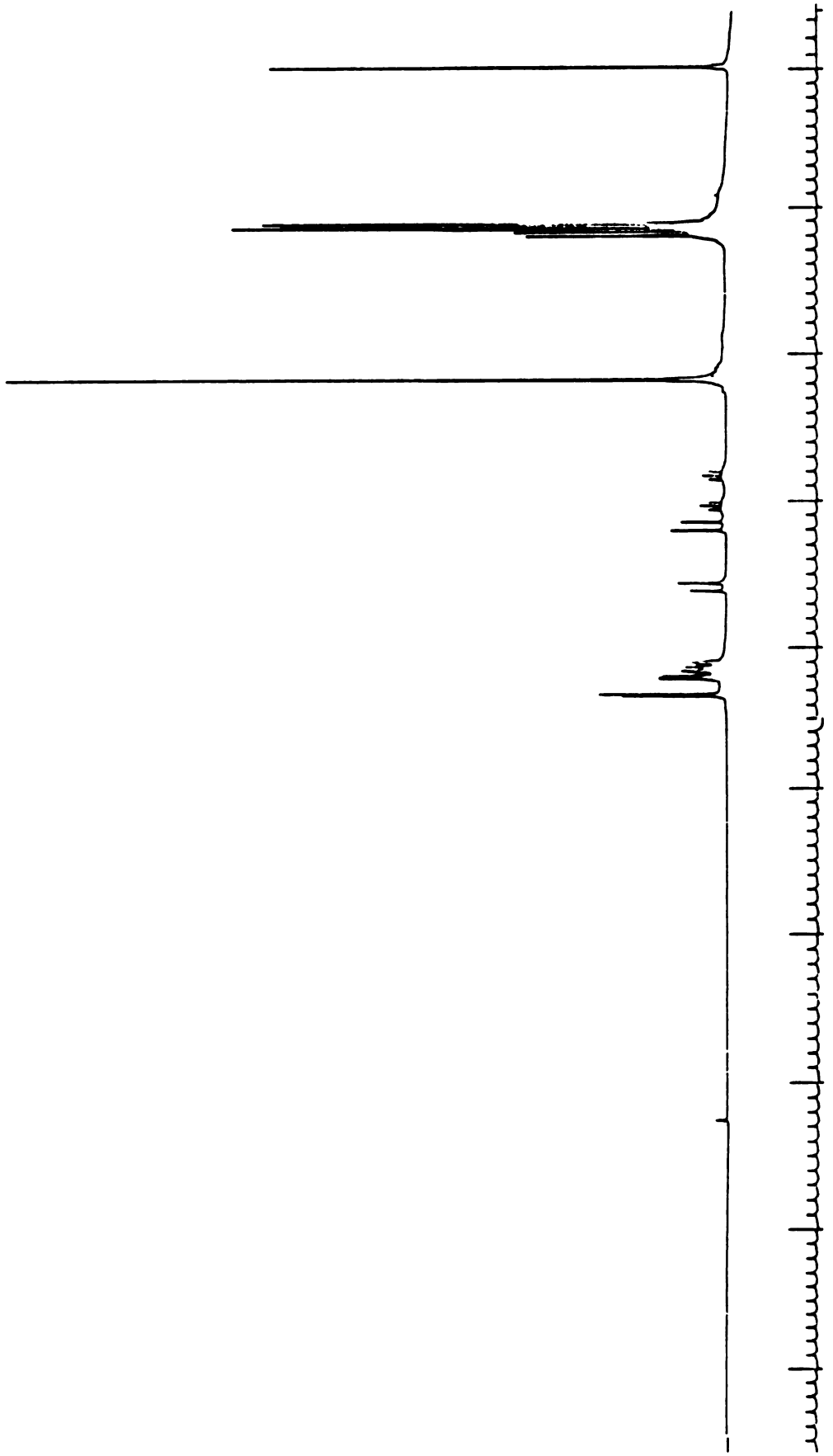


Figure 17. ^{1}H NMR spectrum of 24, R= i-Pr.

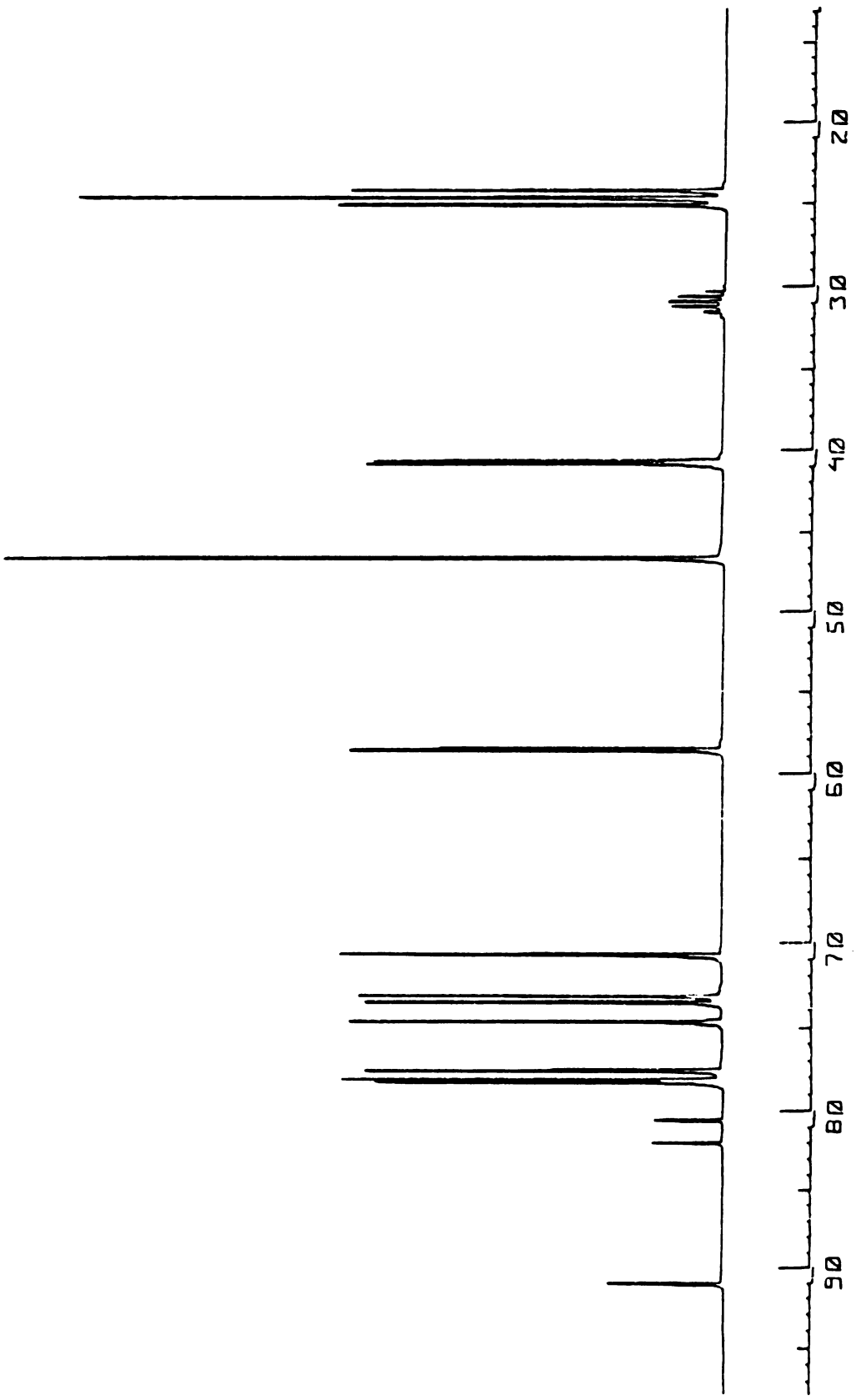


Figure 18. ^{13}C NMR spectrum of 24, R= i-Pr.

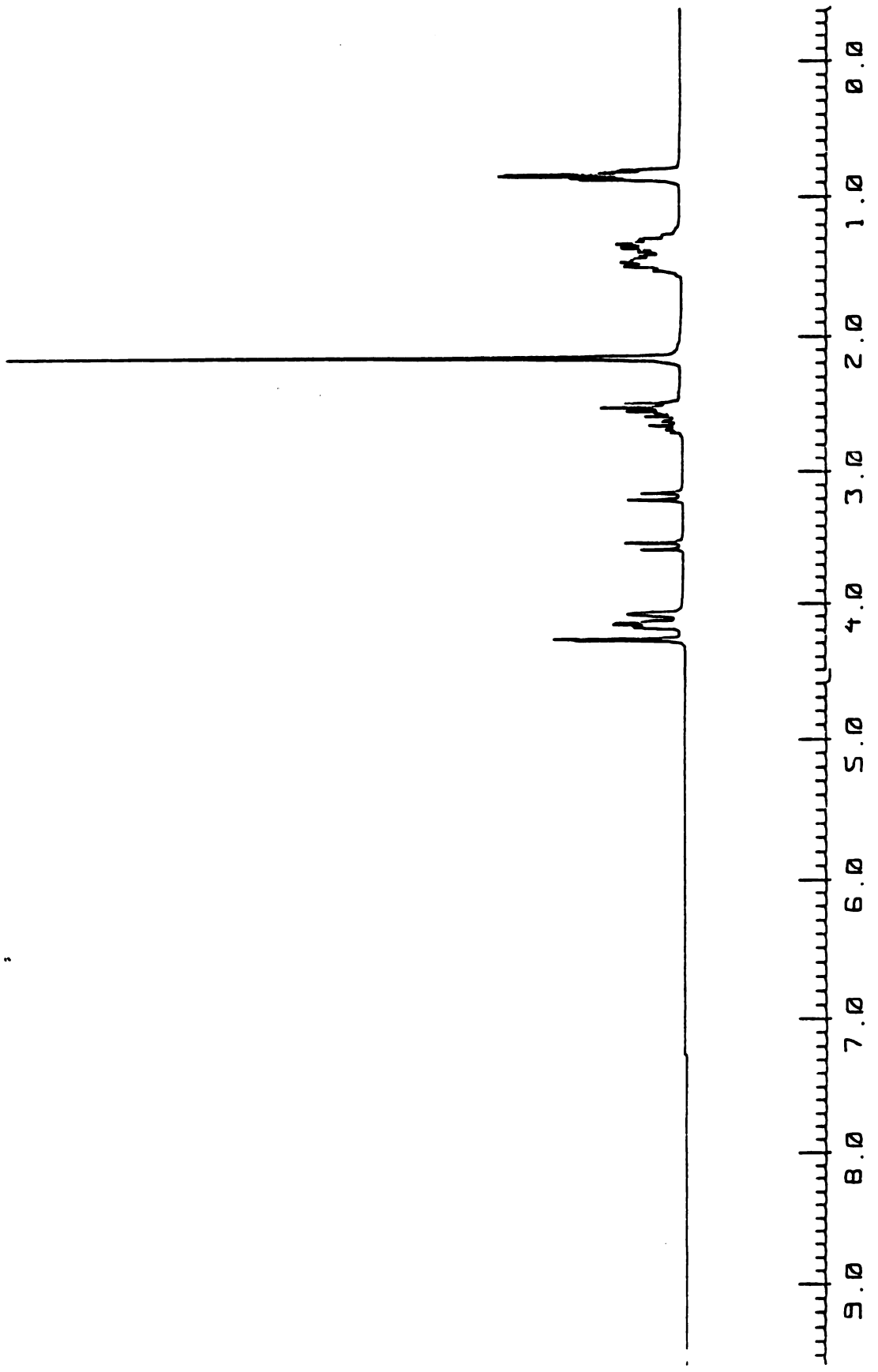


Figure 19. ^{1}H NMR spectrum of 25, R= n-Butyl.

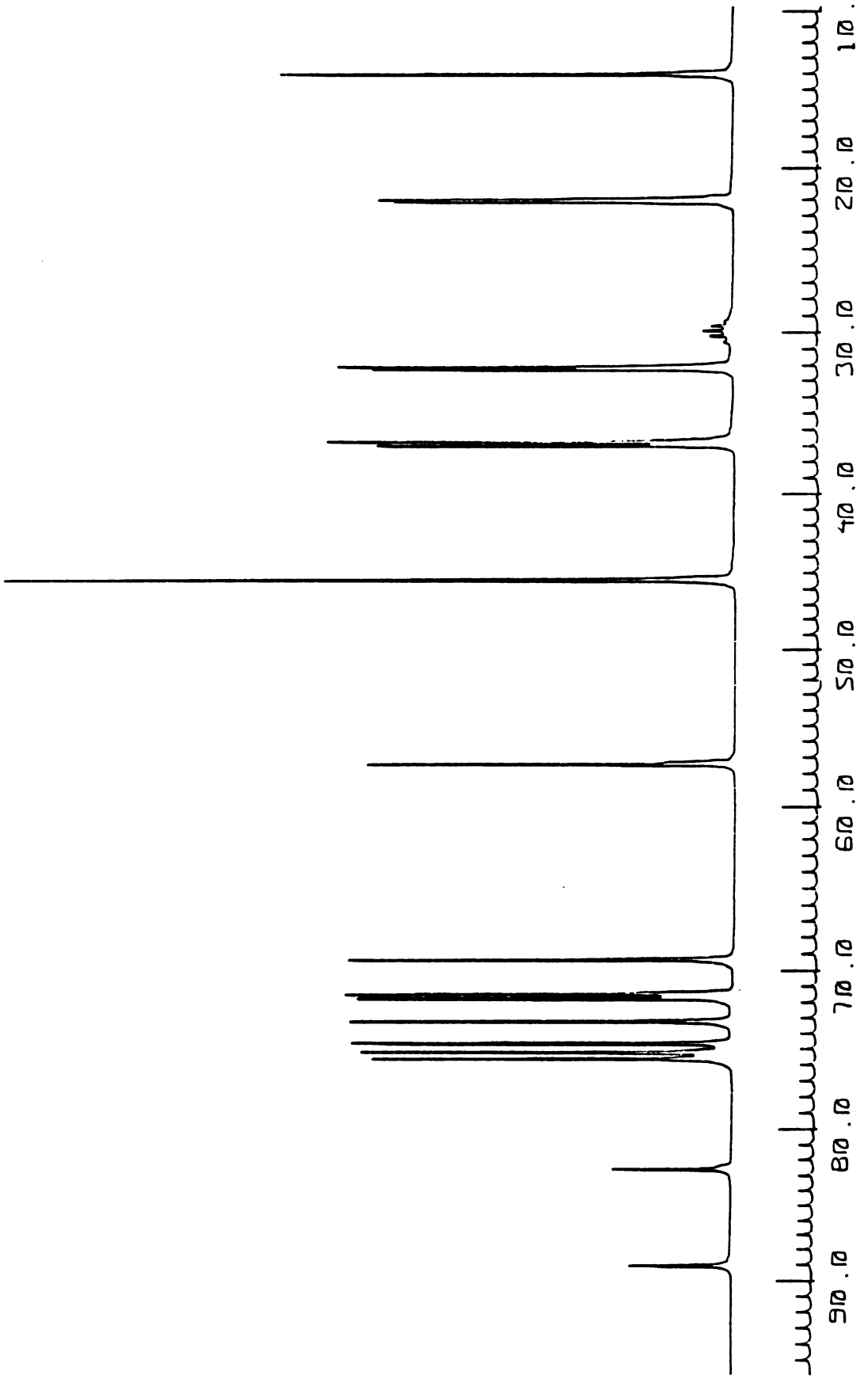


Figure 20. ^{13}C NMR spectrum of 25, R= n-Butyl.

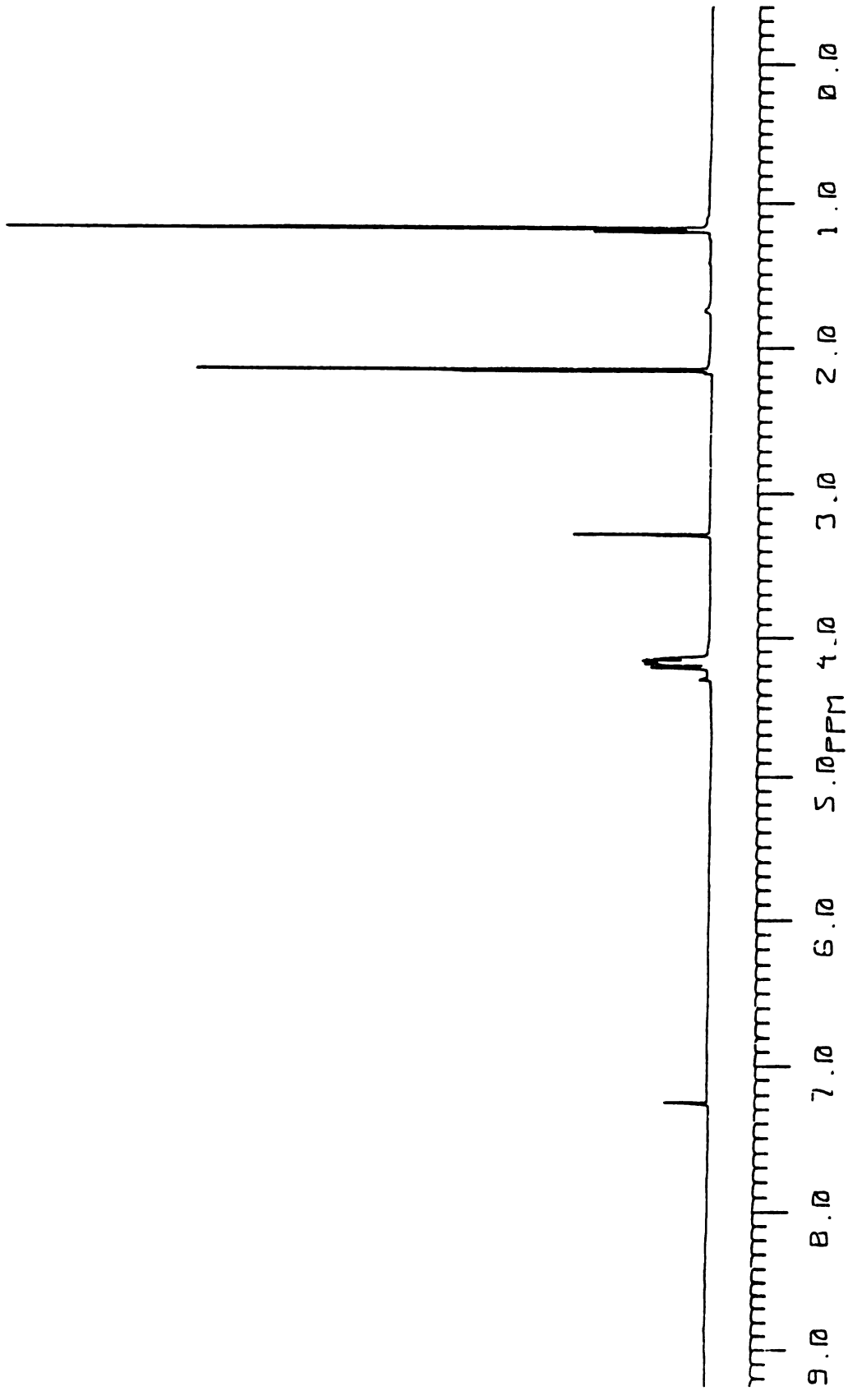


Figure 21. ^{1}H NMR spectrum of 27, R= t-Butyl.

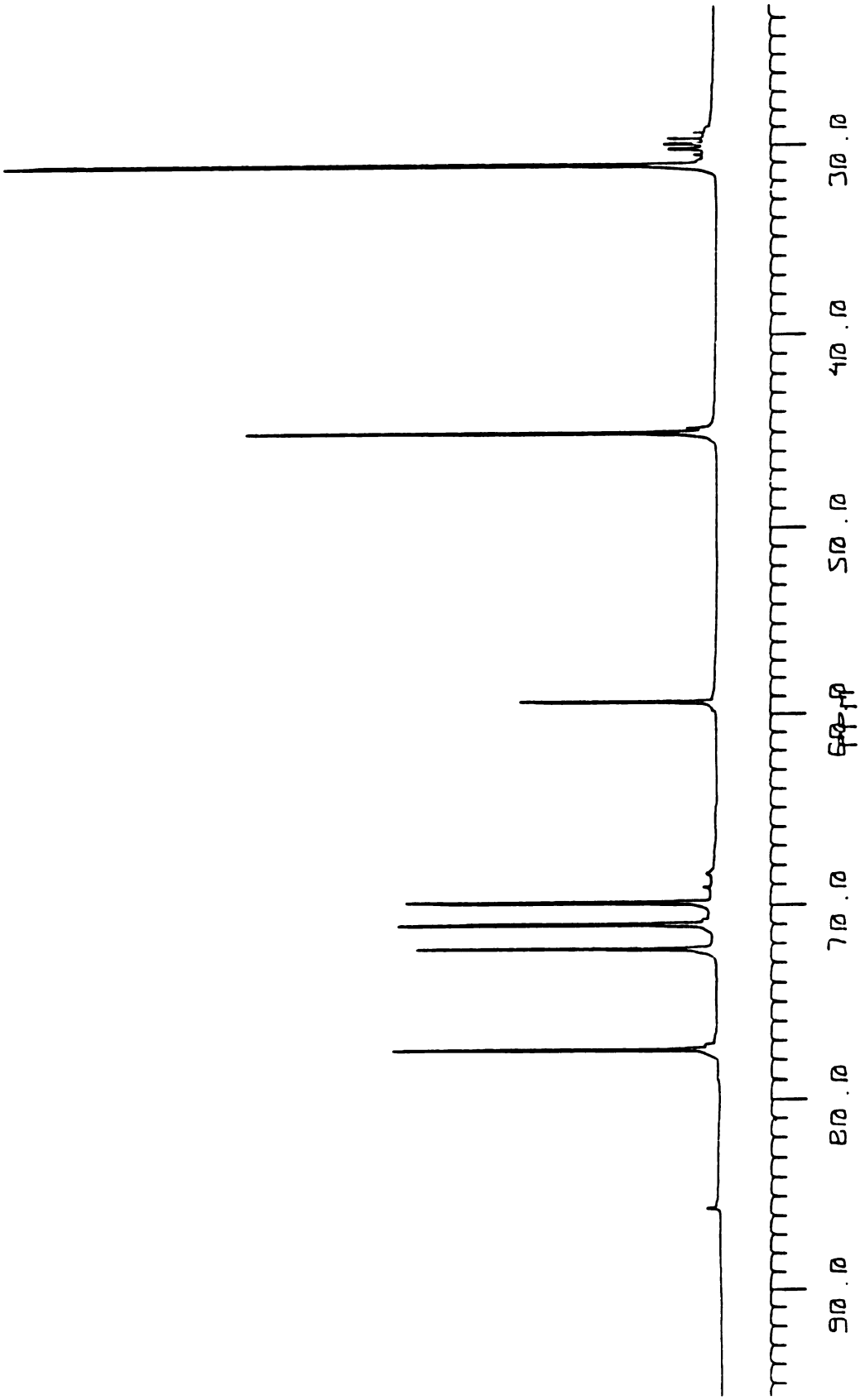


Figure 22. ^{13}C NMR spectrum of 27, R= t-Butyl.

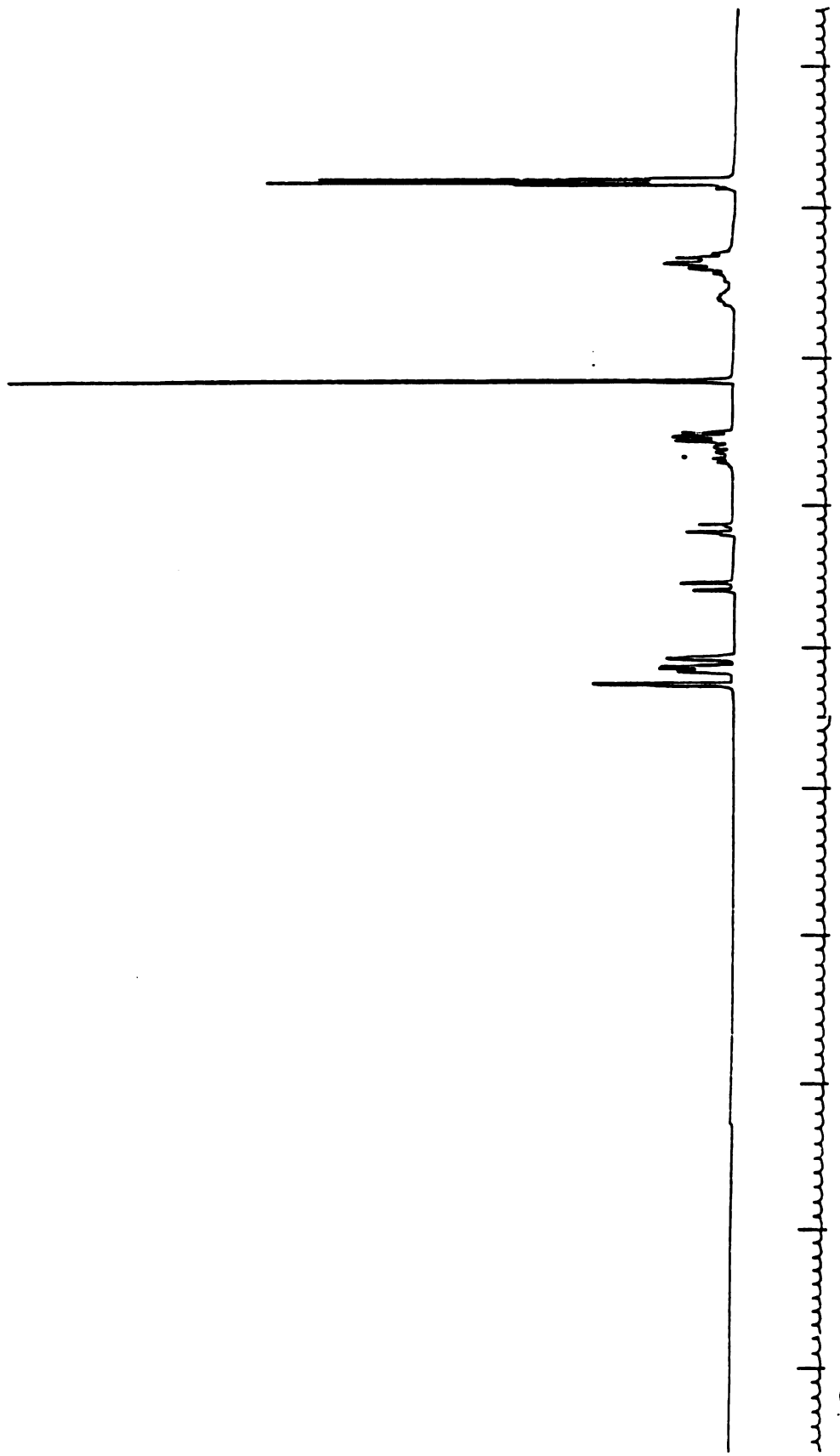


Figure 23. ^{1}H NMR spectrum of 28, R= i-Pentyl.

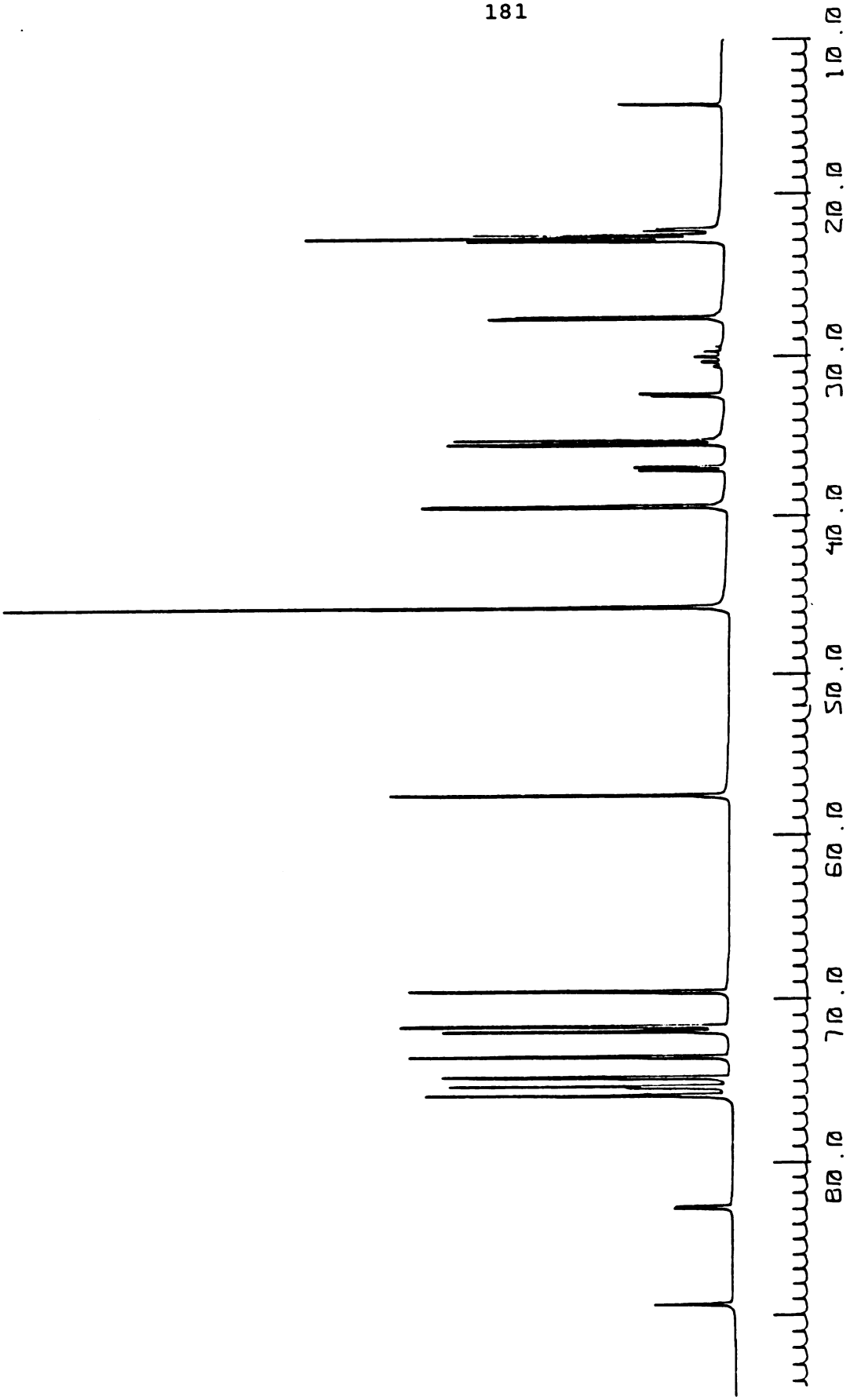


Figure 24. ^{13}C NMR spectrum of 28, R= i-Pentyl.

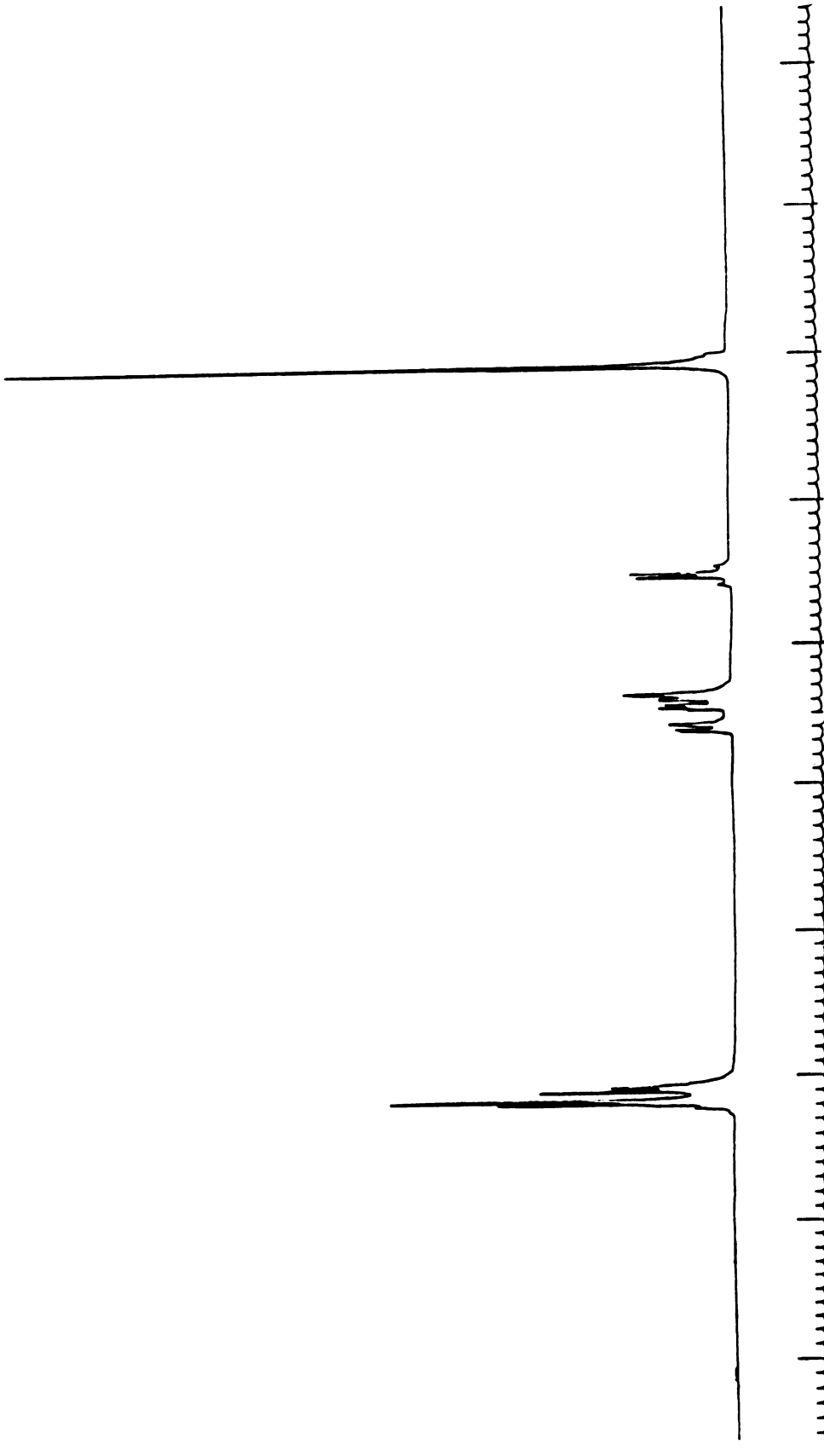


Figure 25. ^{1}H NMR spectrum of 22, R= Phenyl.

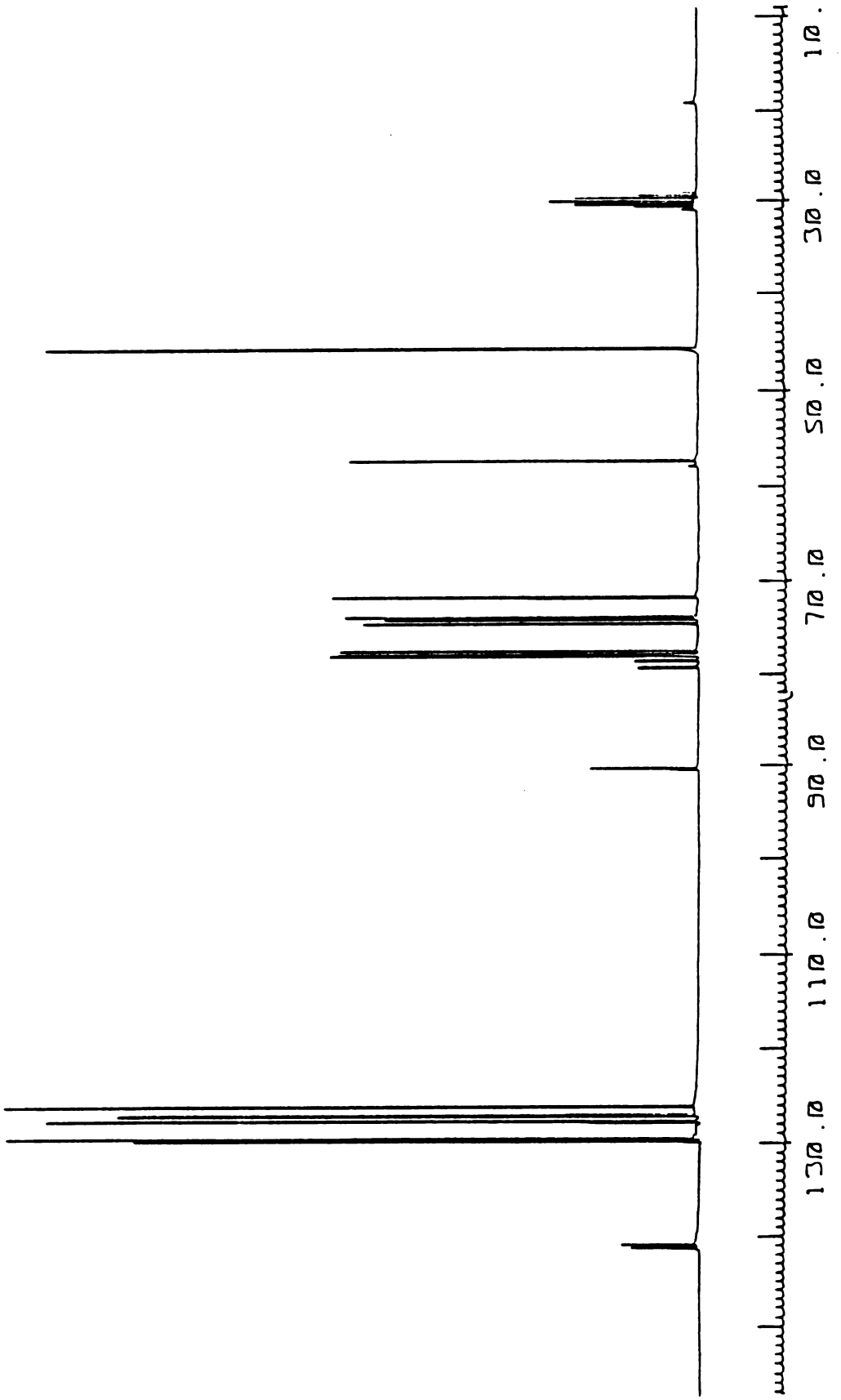


Figure 26. ^{13}C NMR spectrum of 29, R= Phenyl.

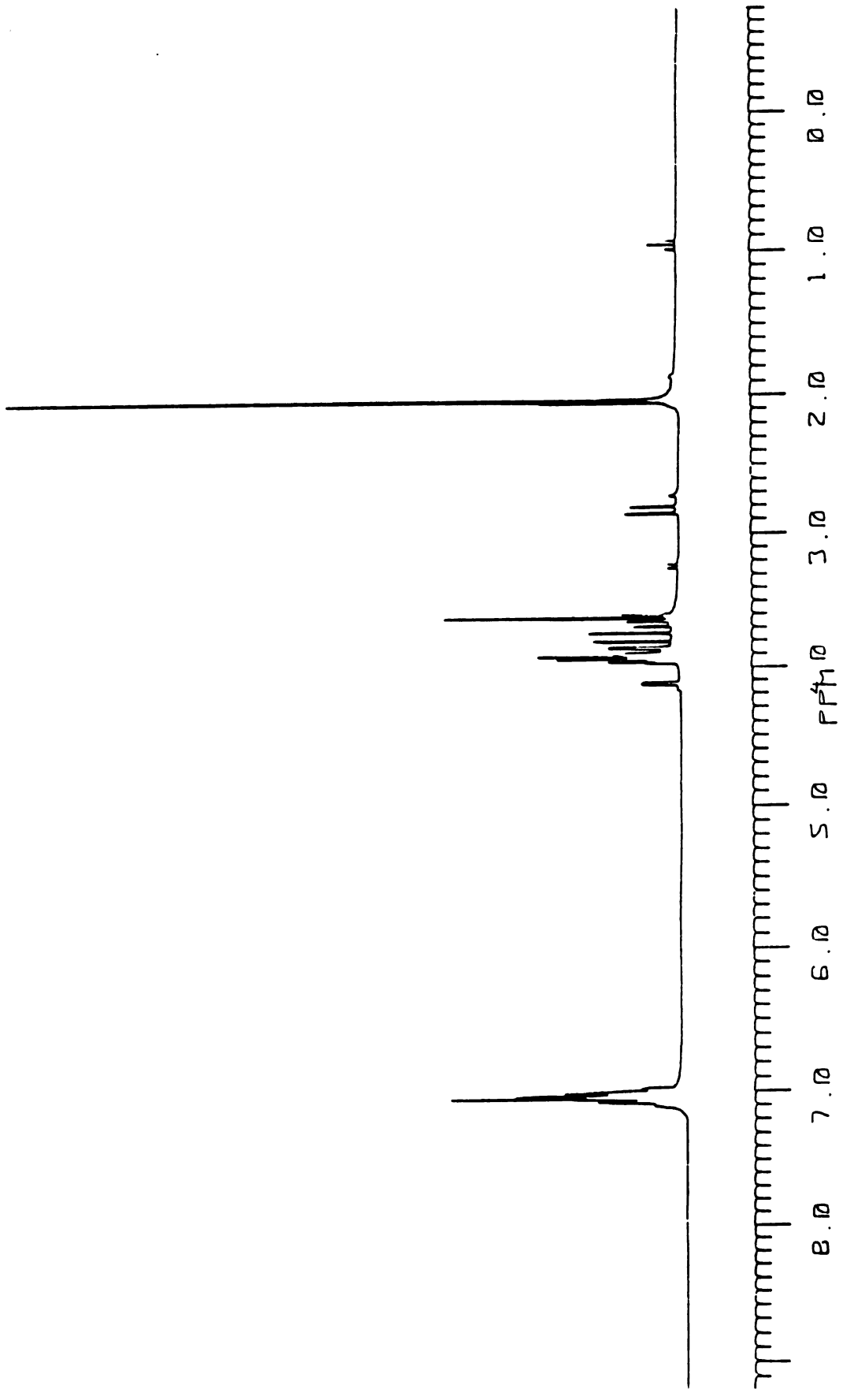


Figure 27. ^{1}H NMR spectrum of 30, R= Benzyl.

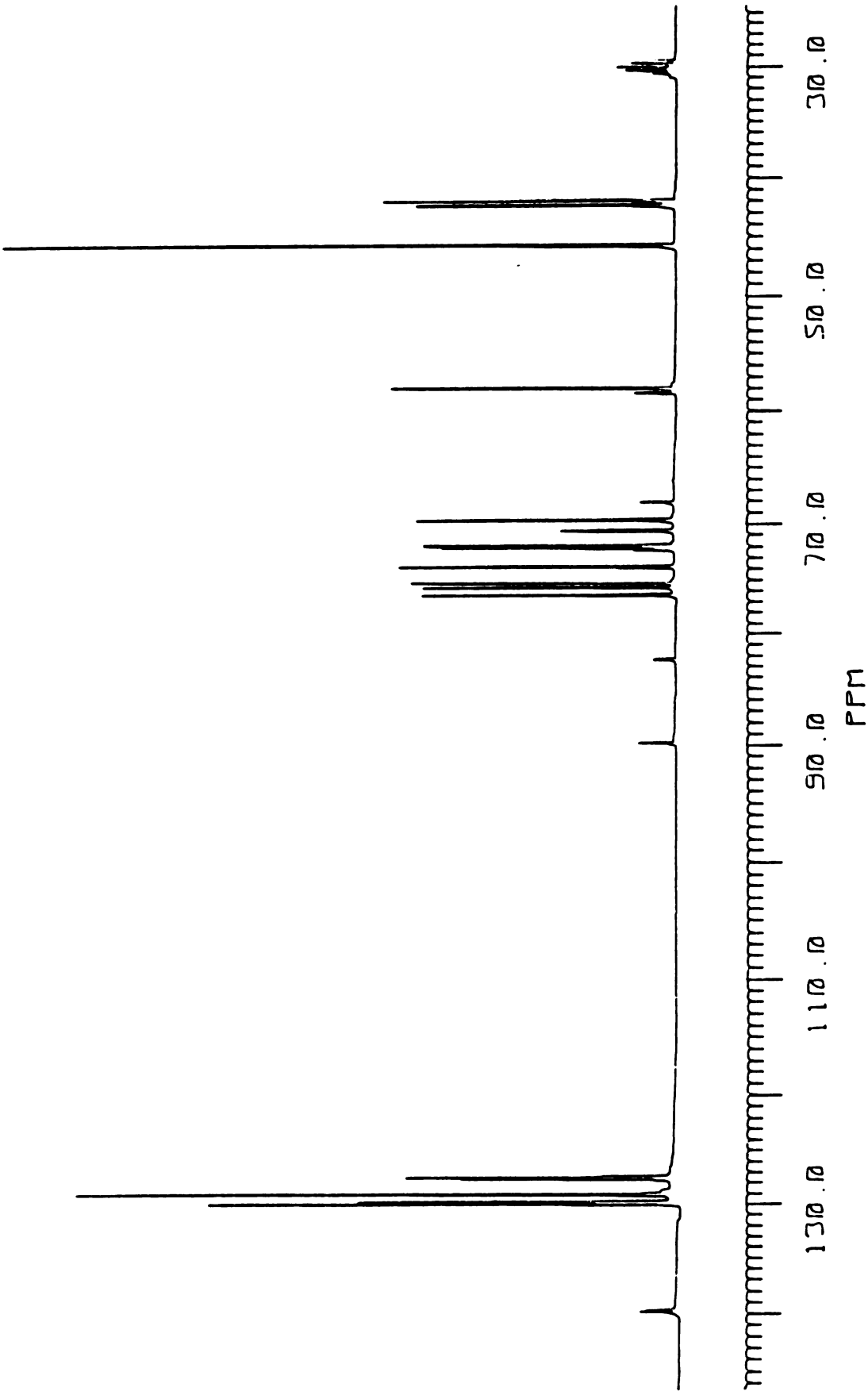


Figure 28. ^{13}C NMR spectrum of 30, R= Benzyl.

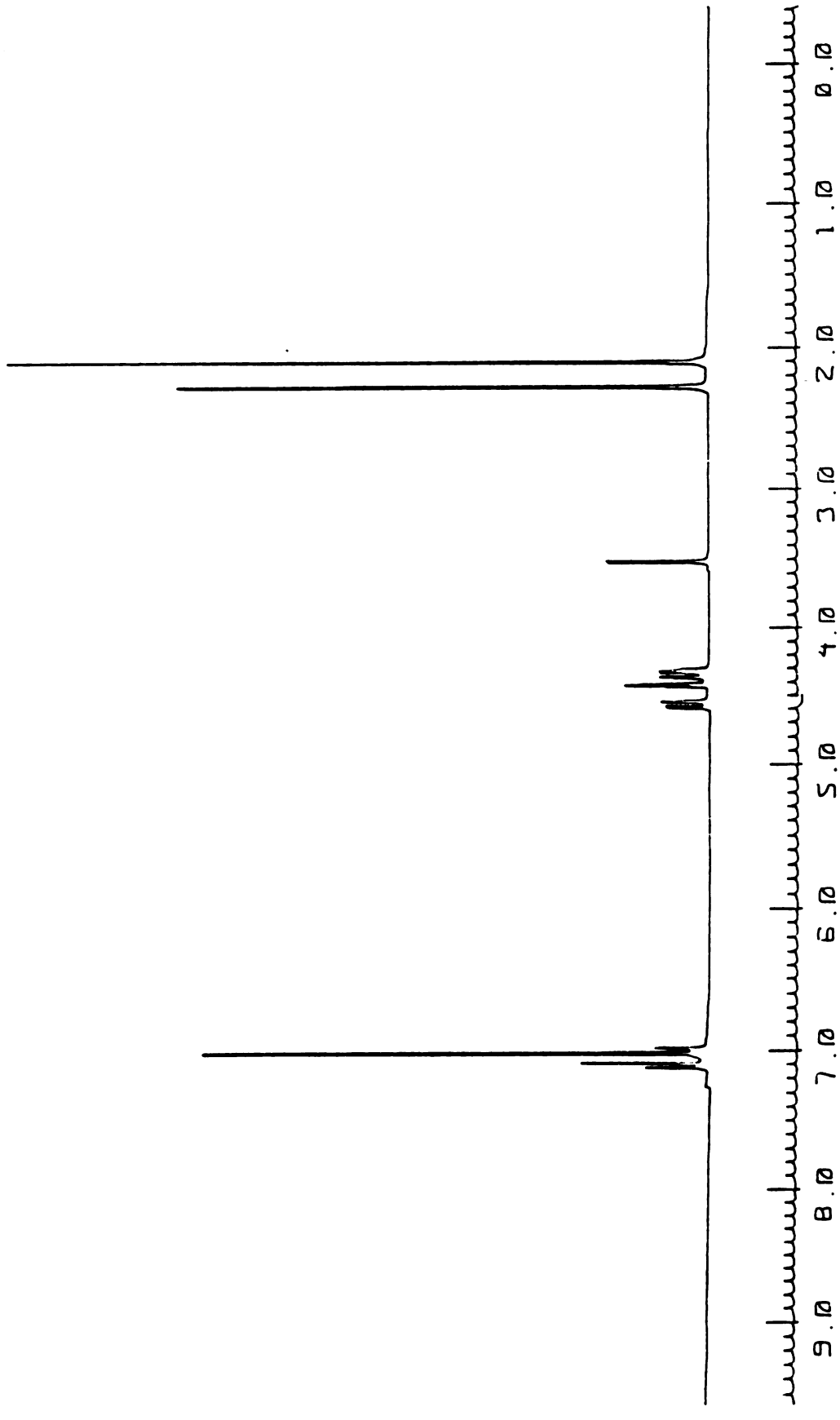


Figure 29. ^{1}H NMR spectrum of 31, R= 4-Tolyl.

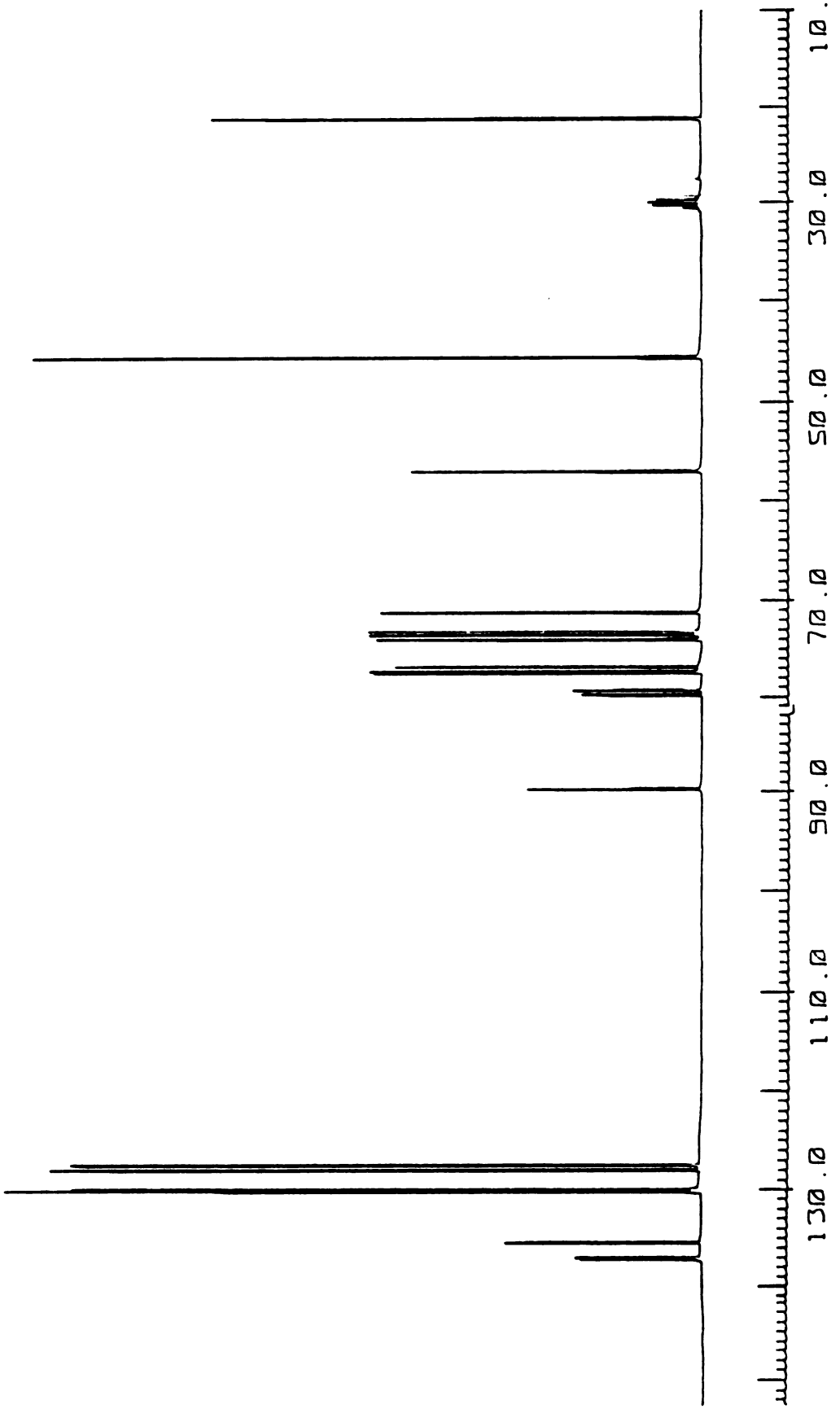


Figure 30. ^{13}C NMR spectrum of 31, R= 4-Tolyl.

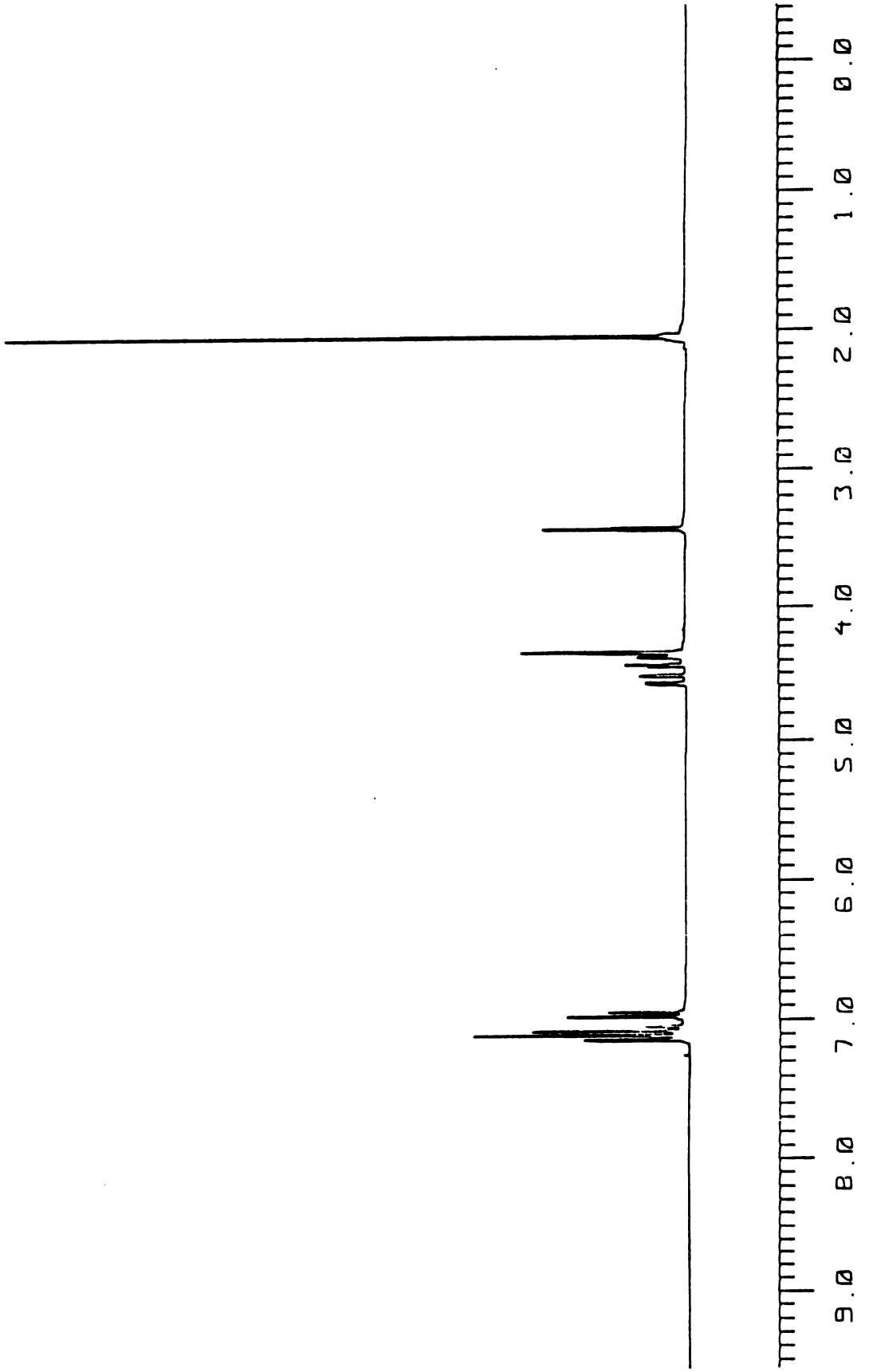


Figure 31. ^{1}H NMR spectrum of 32, R= 4-Cl-Ph.

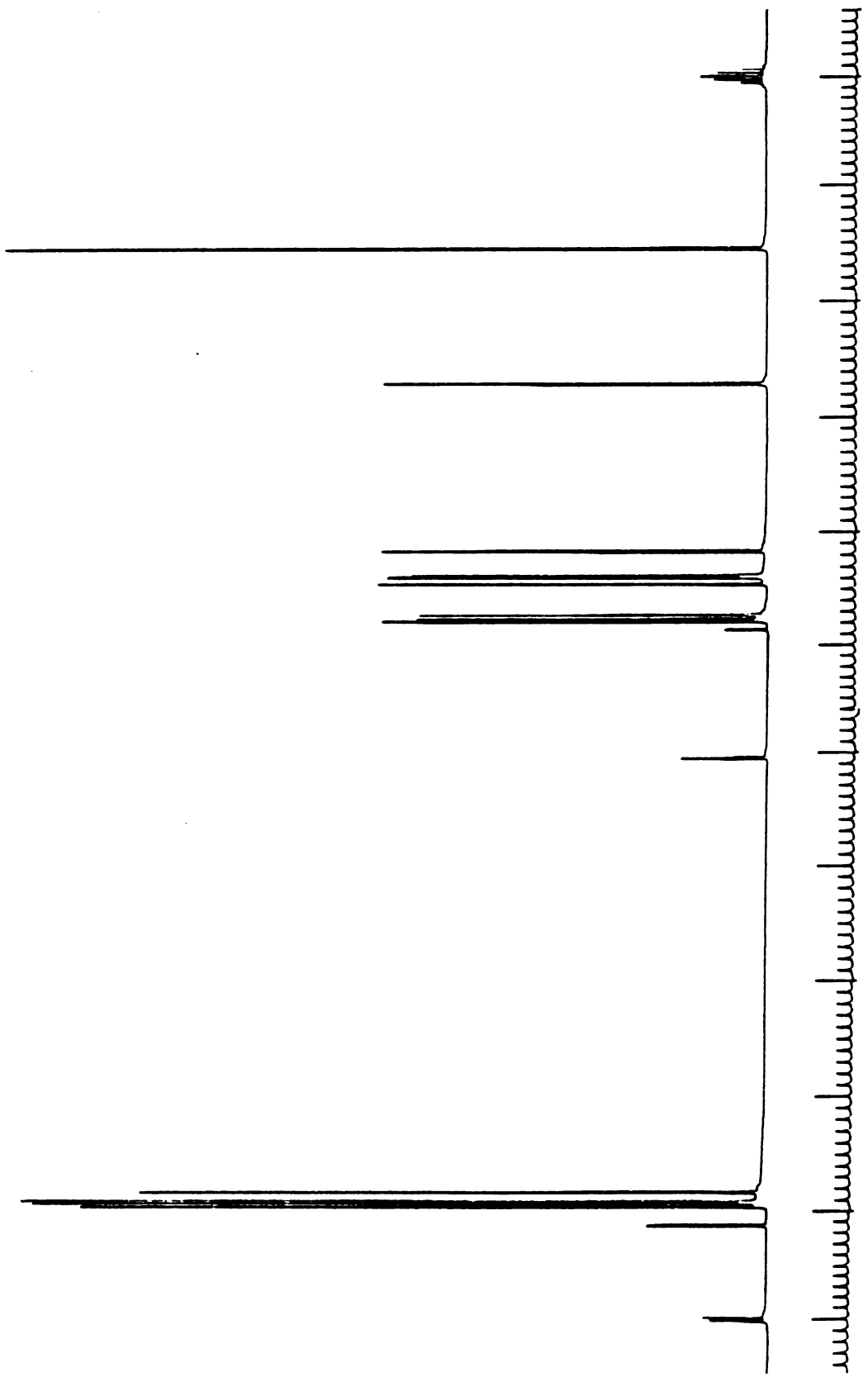


Figure 32. ^{13}C NMR spectrum of 32, R= 4-CL-Ph.

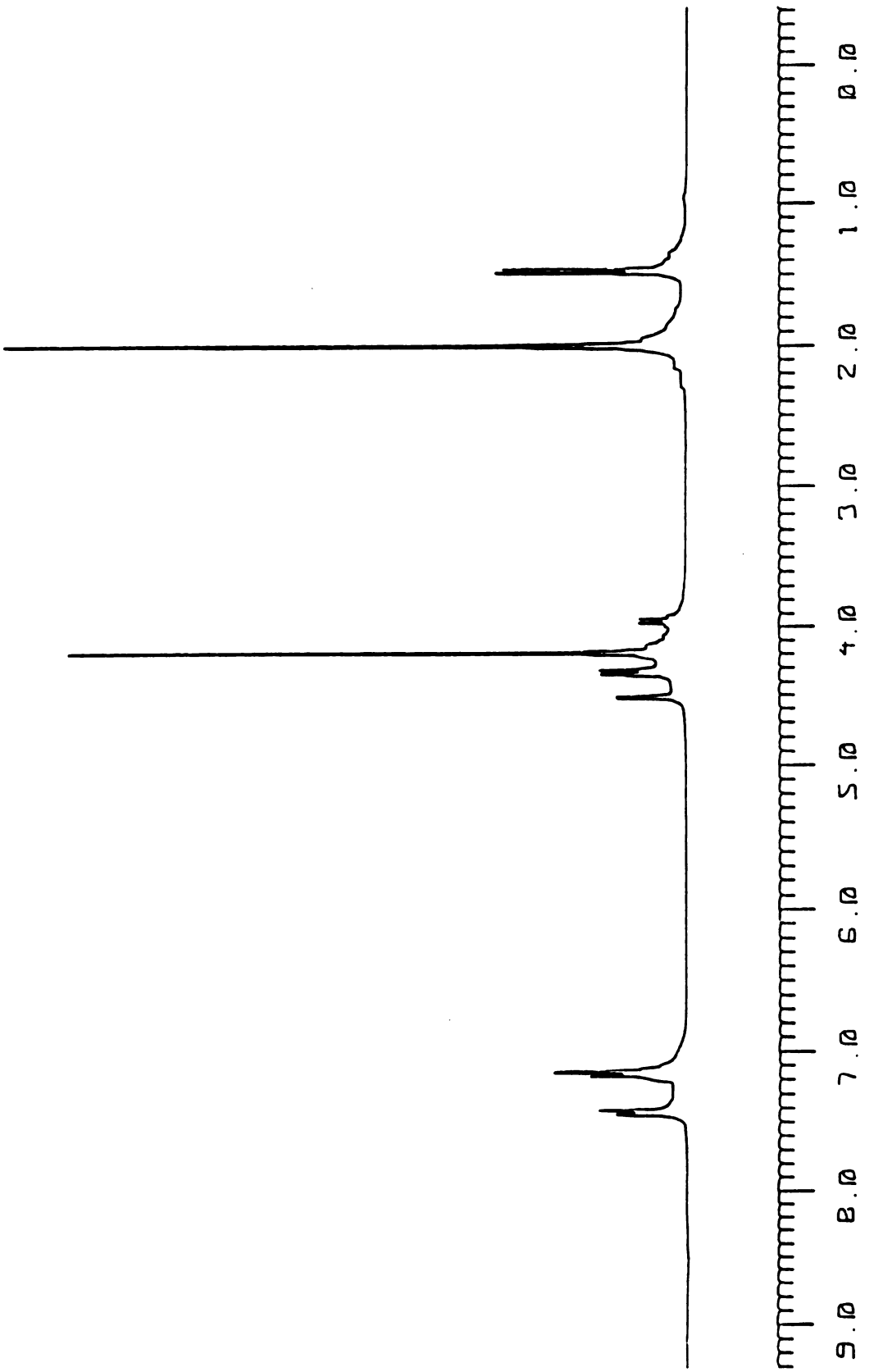


Figure 33. ^{1}H NMR spectrum of 34, R= Phenyl.

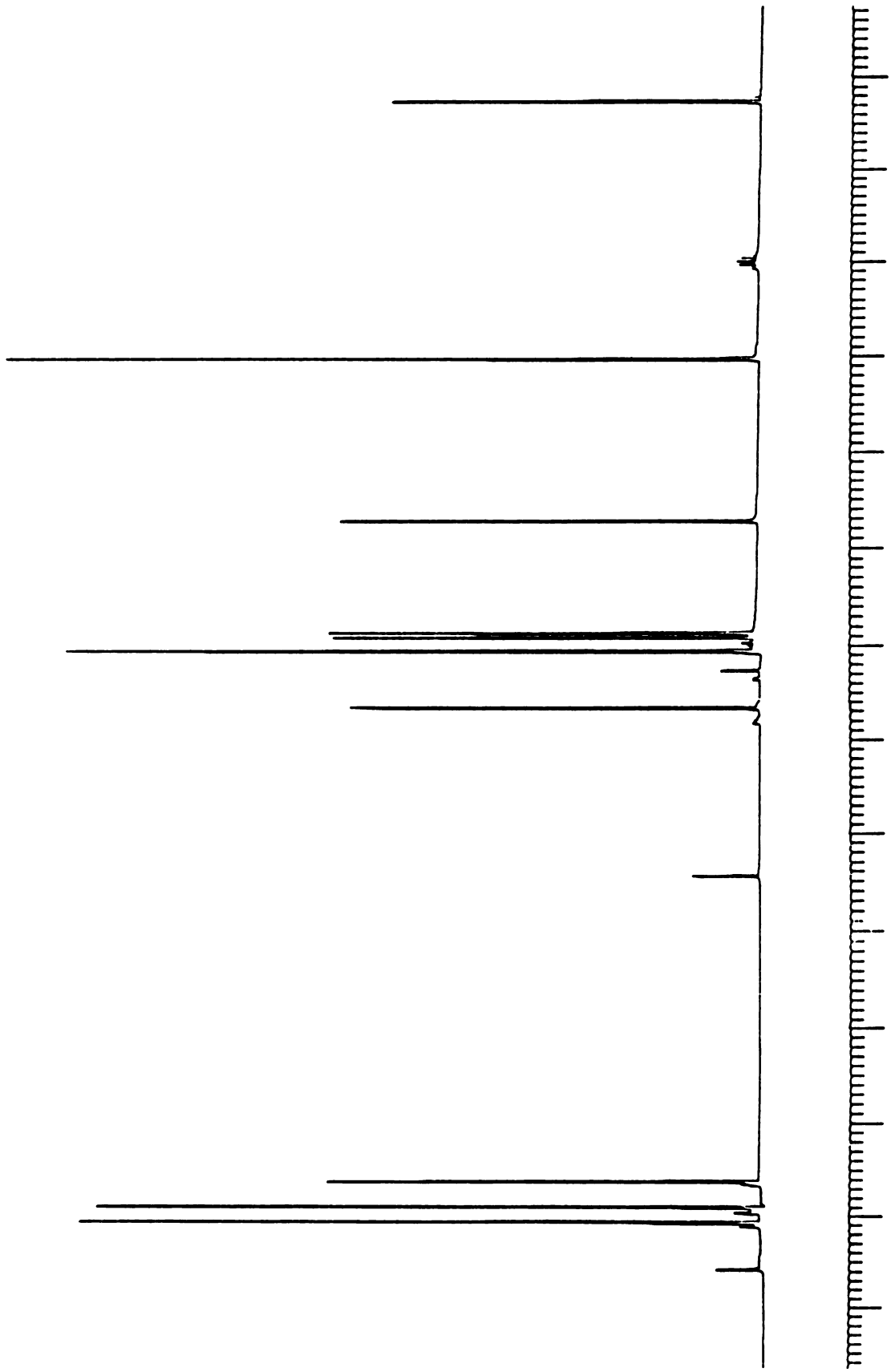


Figure 34. ^{13}C NMR spectrum of 34, R= Phenyl.

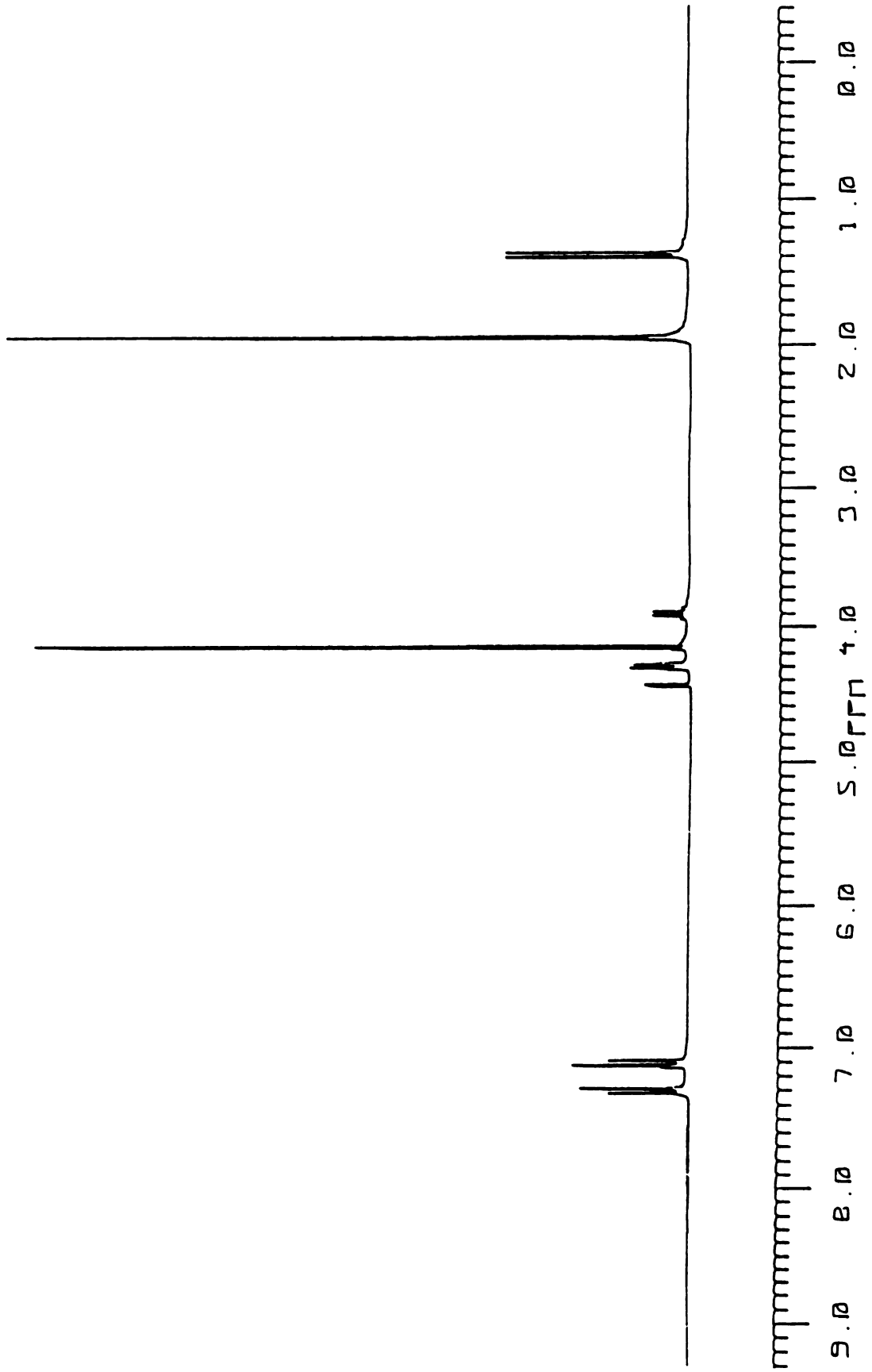


Figure 35. ^{1}H NMR spectrum of 35, R= 4-Cl-Ph.

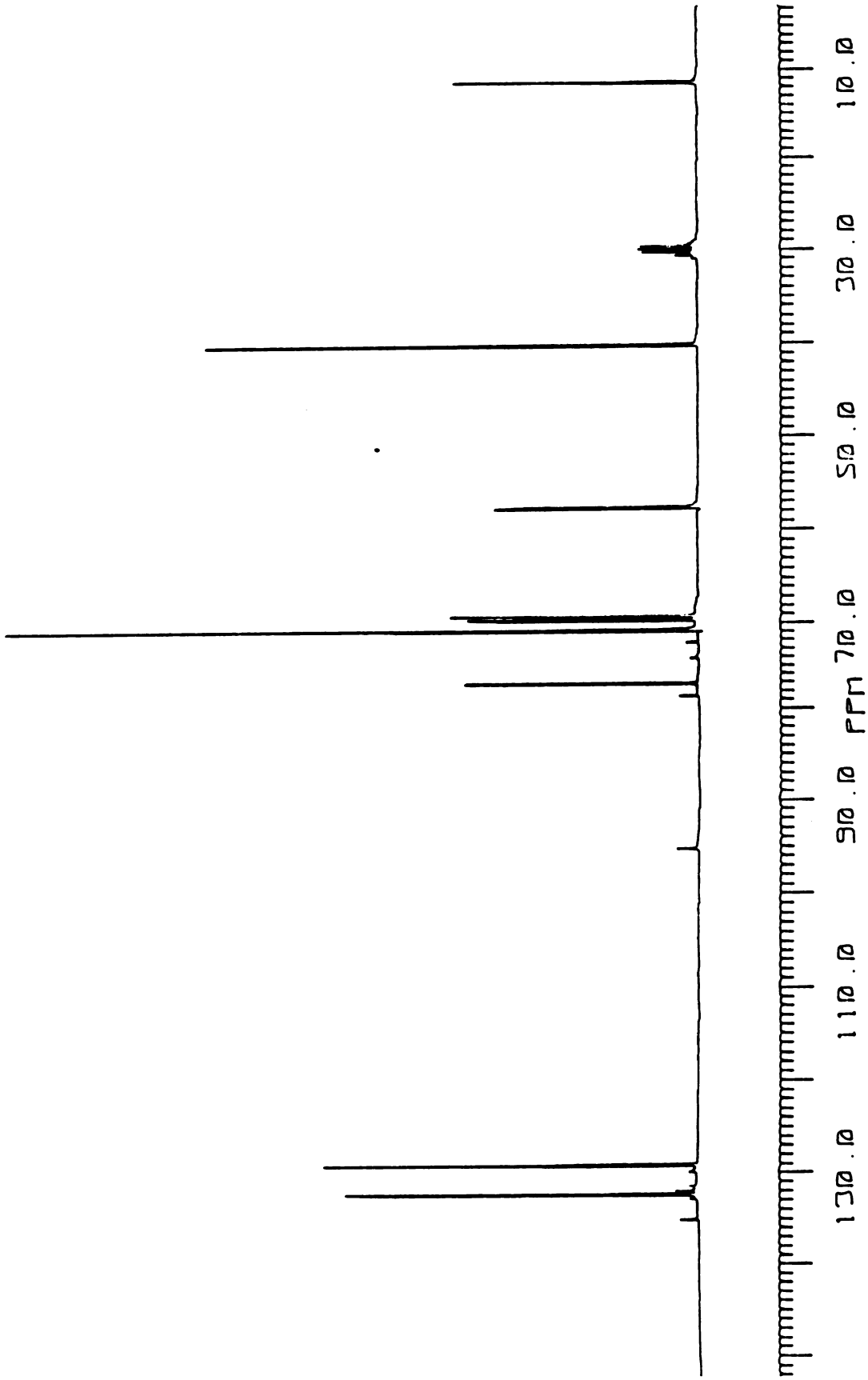


Figure 36. ^{13}C NMR spectrum of 35, R= 4-Cl-Ph.

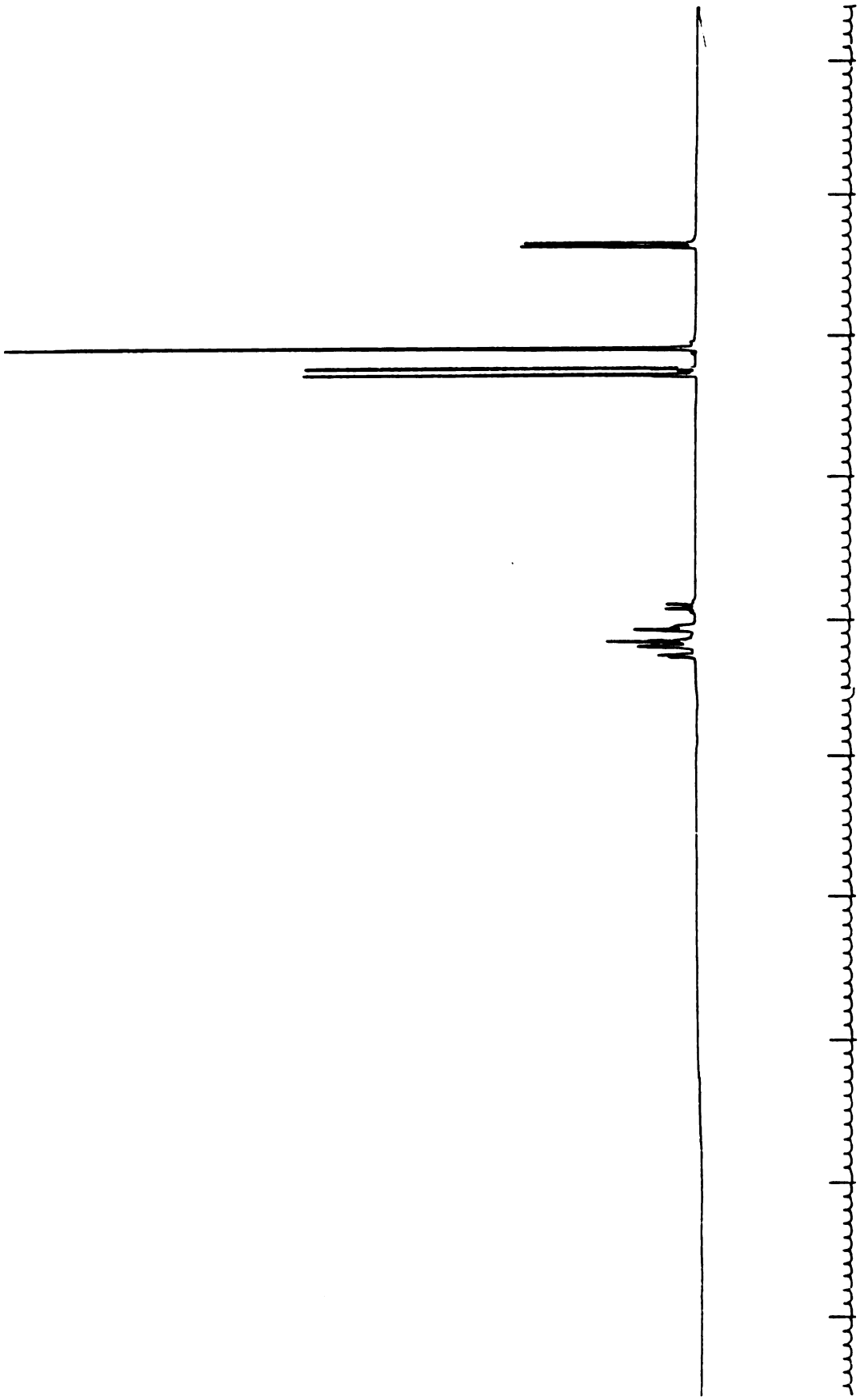


Figure 37. ^{1}H NMR spectrum of 36, R= Me.

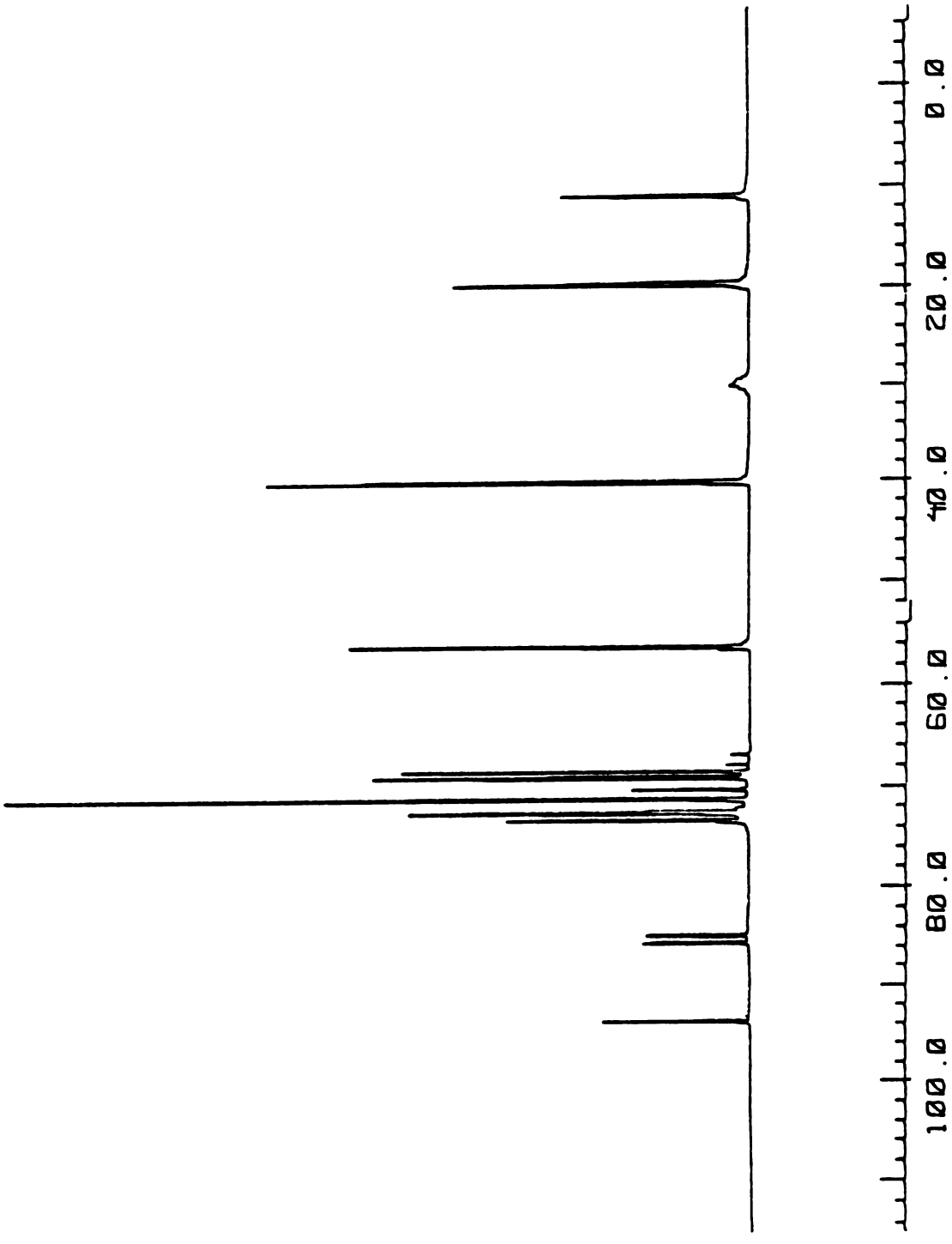


Figure 38. ^{13}C NMR spectrum of 36, R= Me.

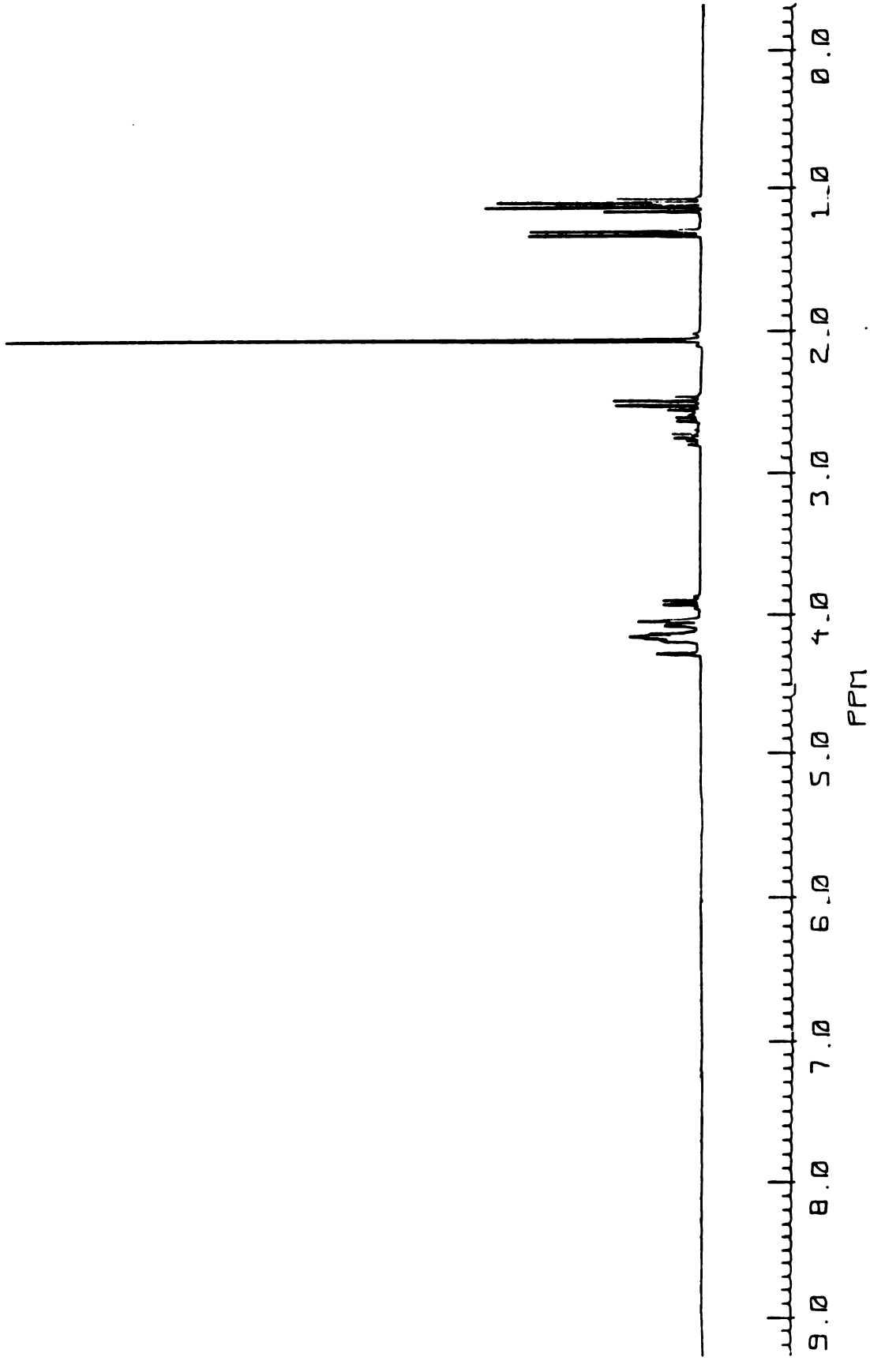


Figure 39. ^{1}H NMR spectrum of 37, R= Et.

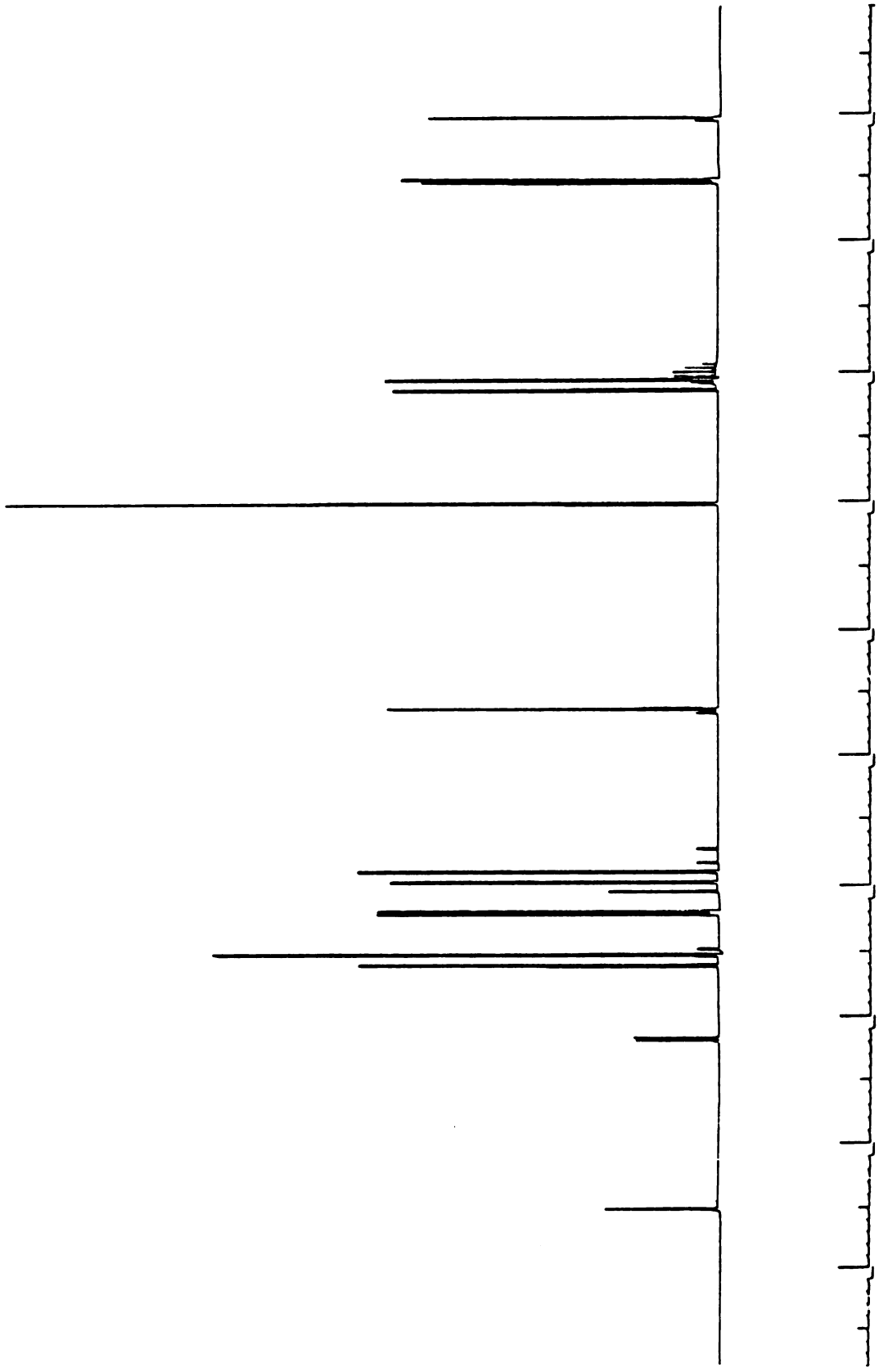


Figure 40. ^{13}C NMR spectrum of 37, R= Et.

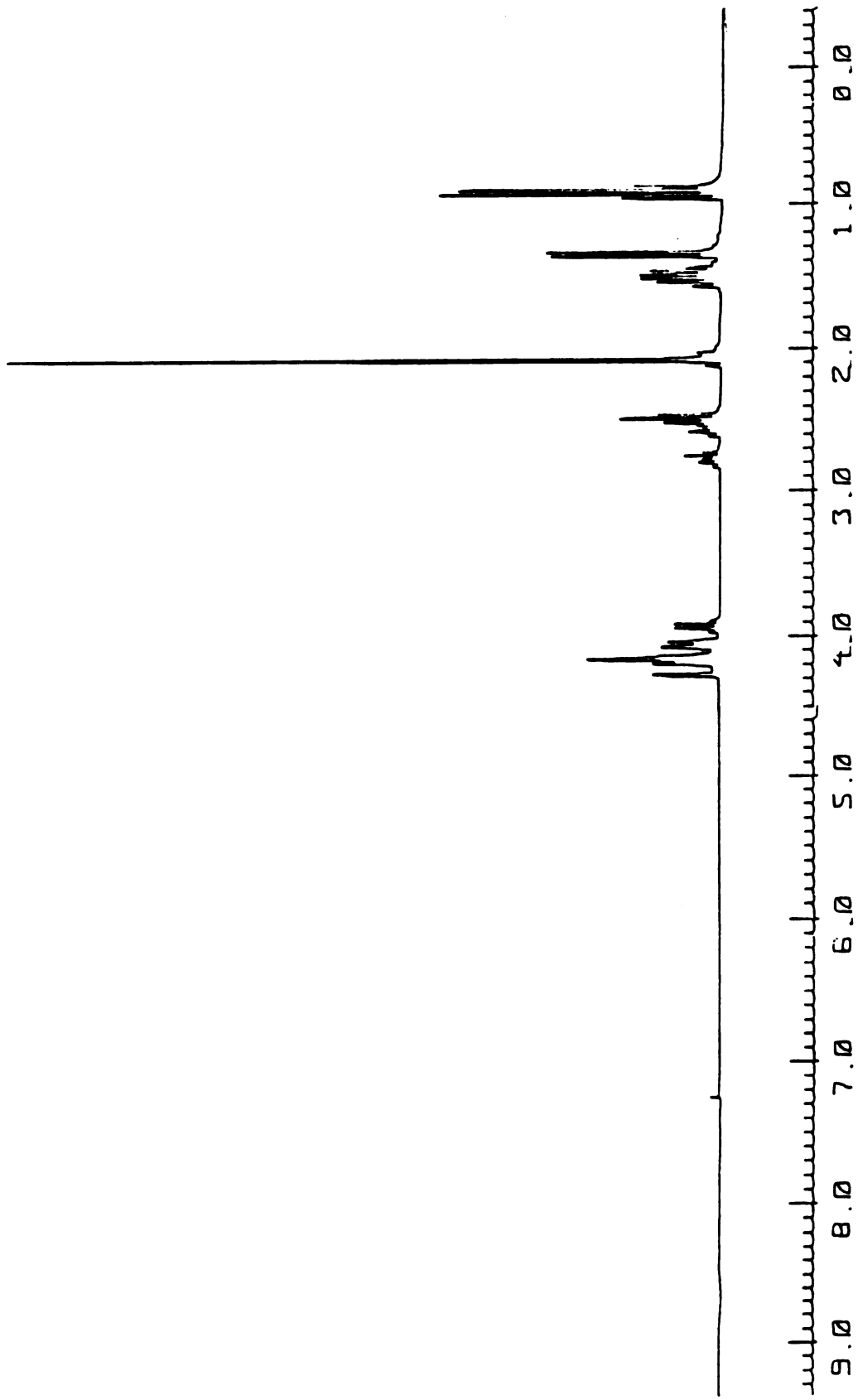


Figure 41. ^{1}H NMR spectrum of 38, R= n-Pr.

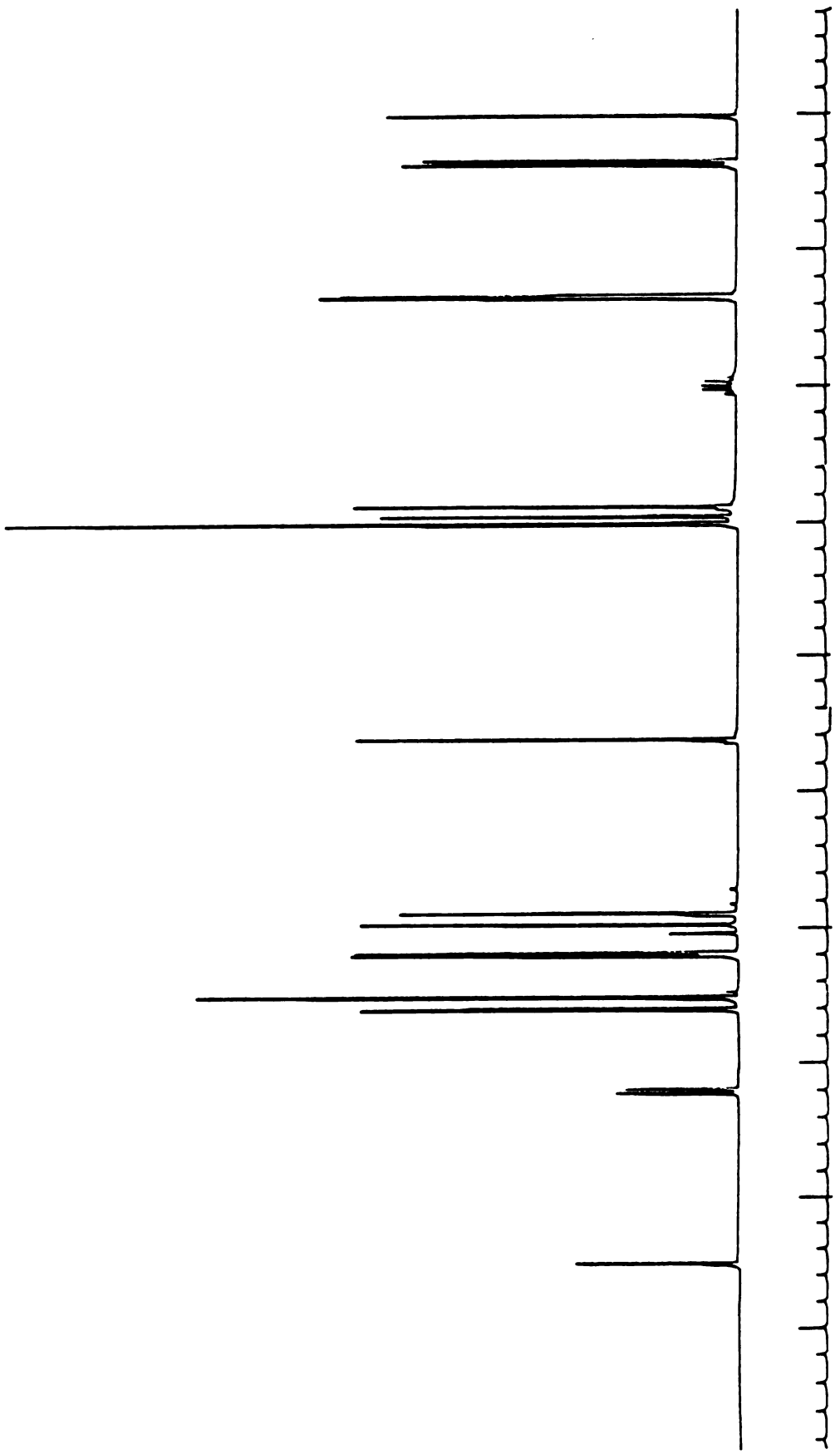


Figure 42. ^{13}C NMR spectrum of 38, R= n-Pr.

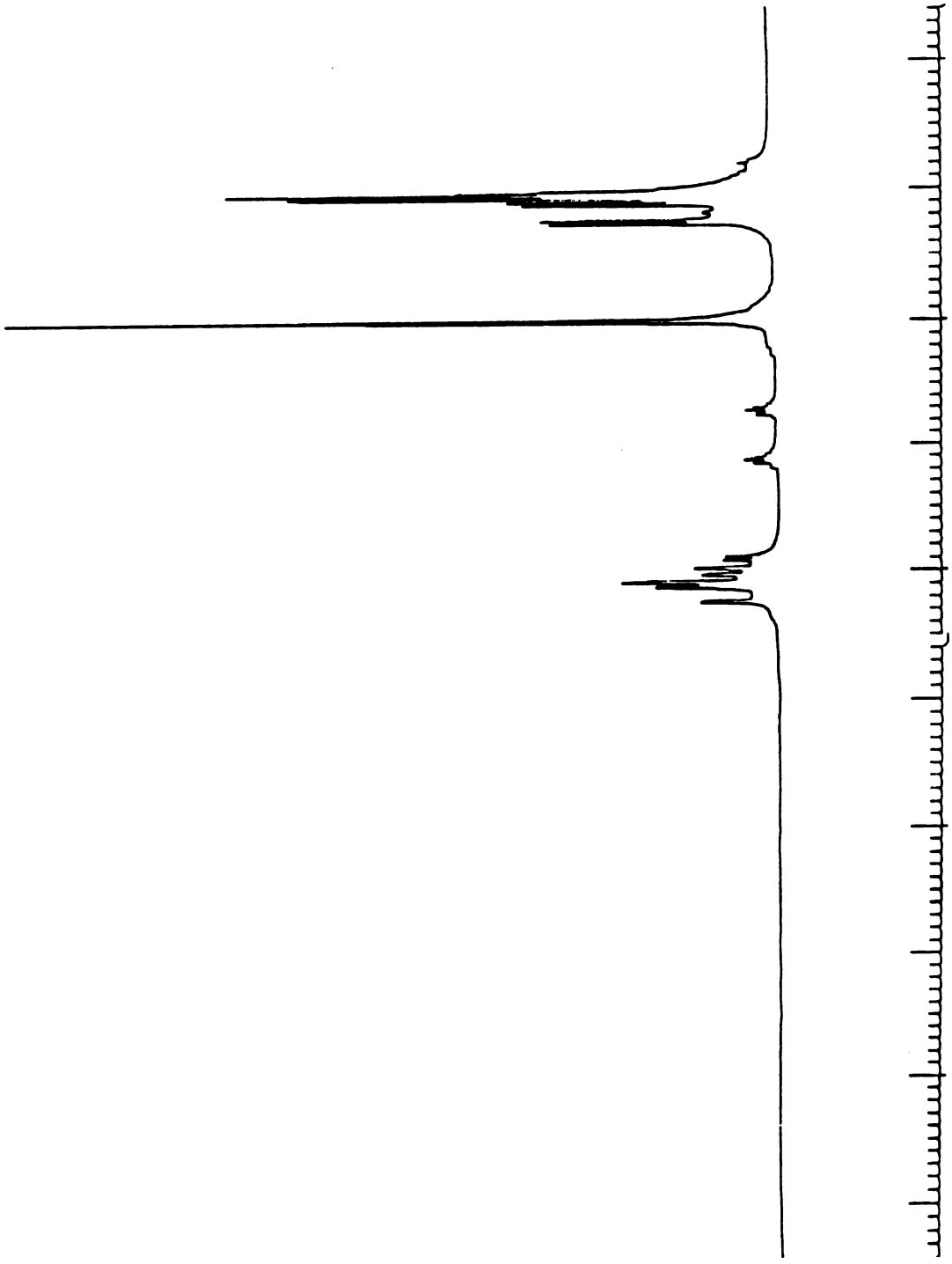


Figure 43. ^{1}H NMR spectrum of 39, R= i-Pr.

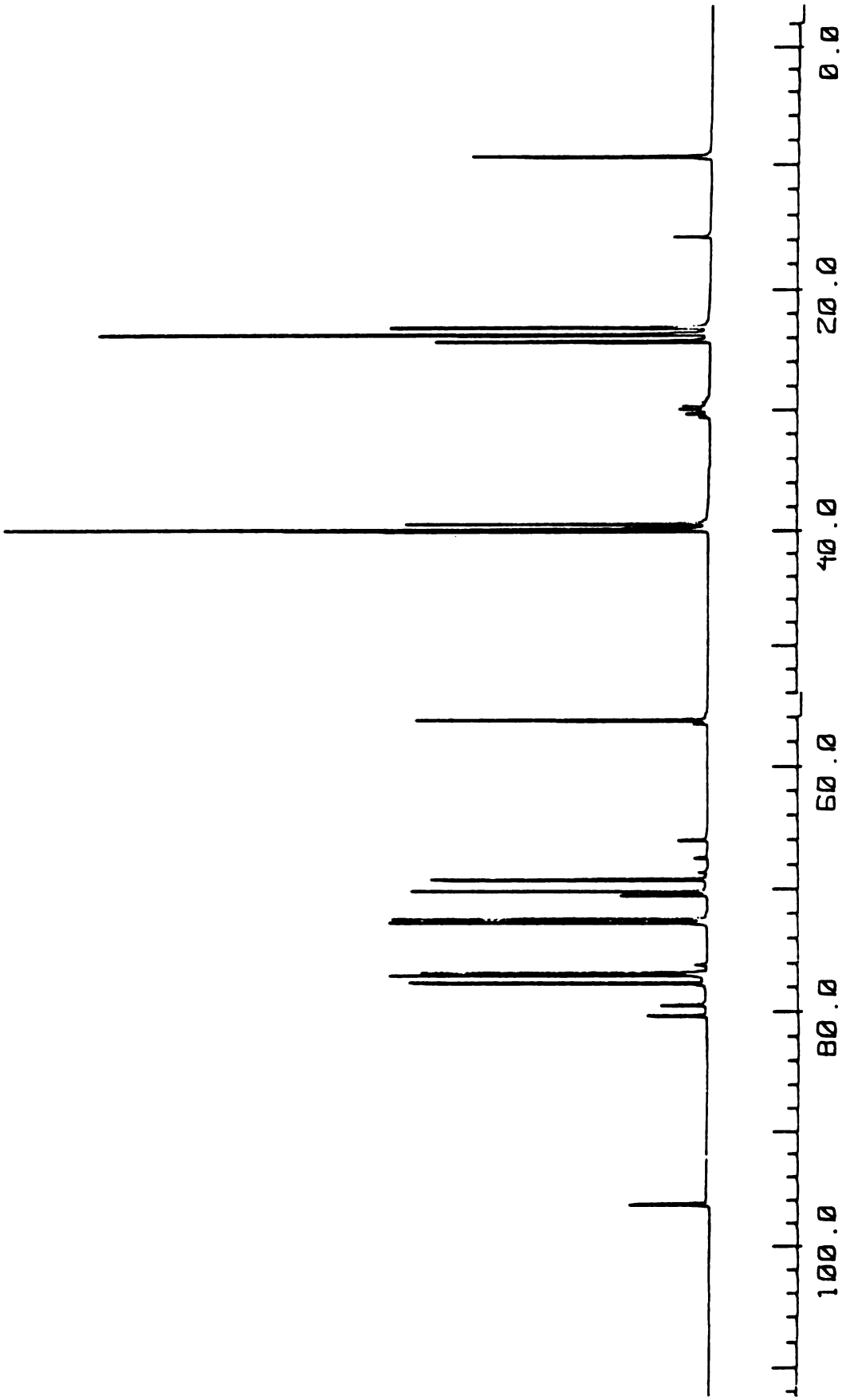


Figure 44. ^{13}C NMR spectrum of 39, R= i-Pr.

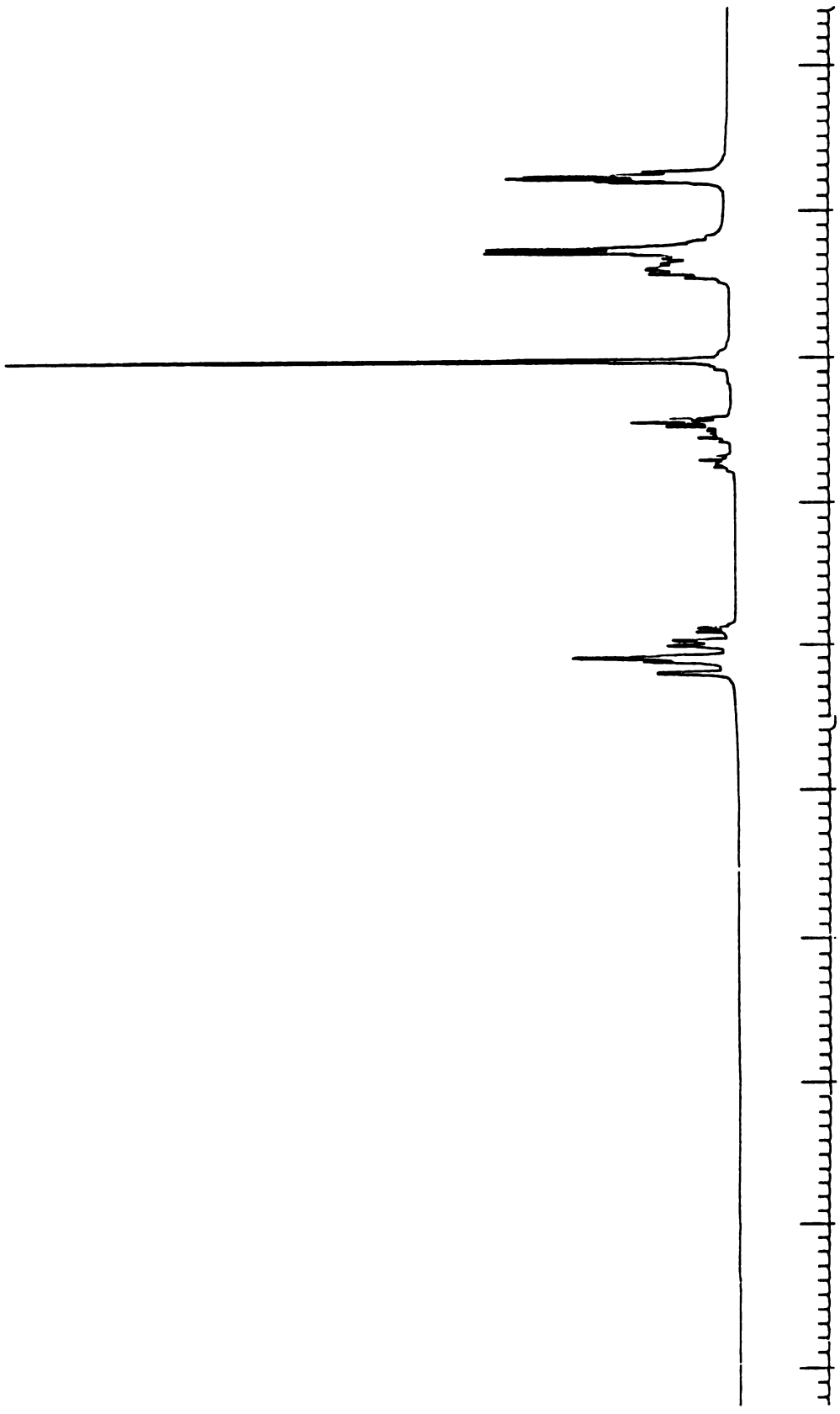


Figure 45. ^{1}H NMR spectrum of 40, R= n-Butyl.

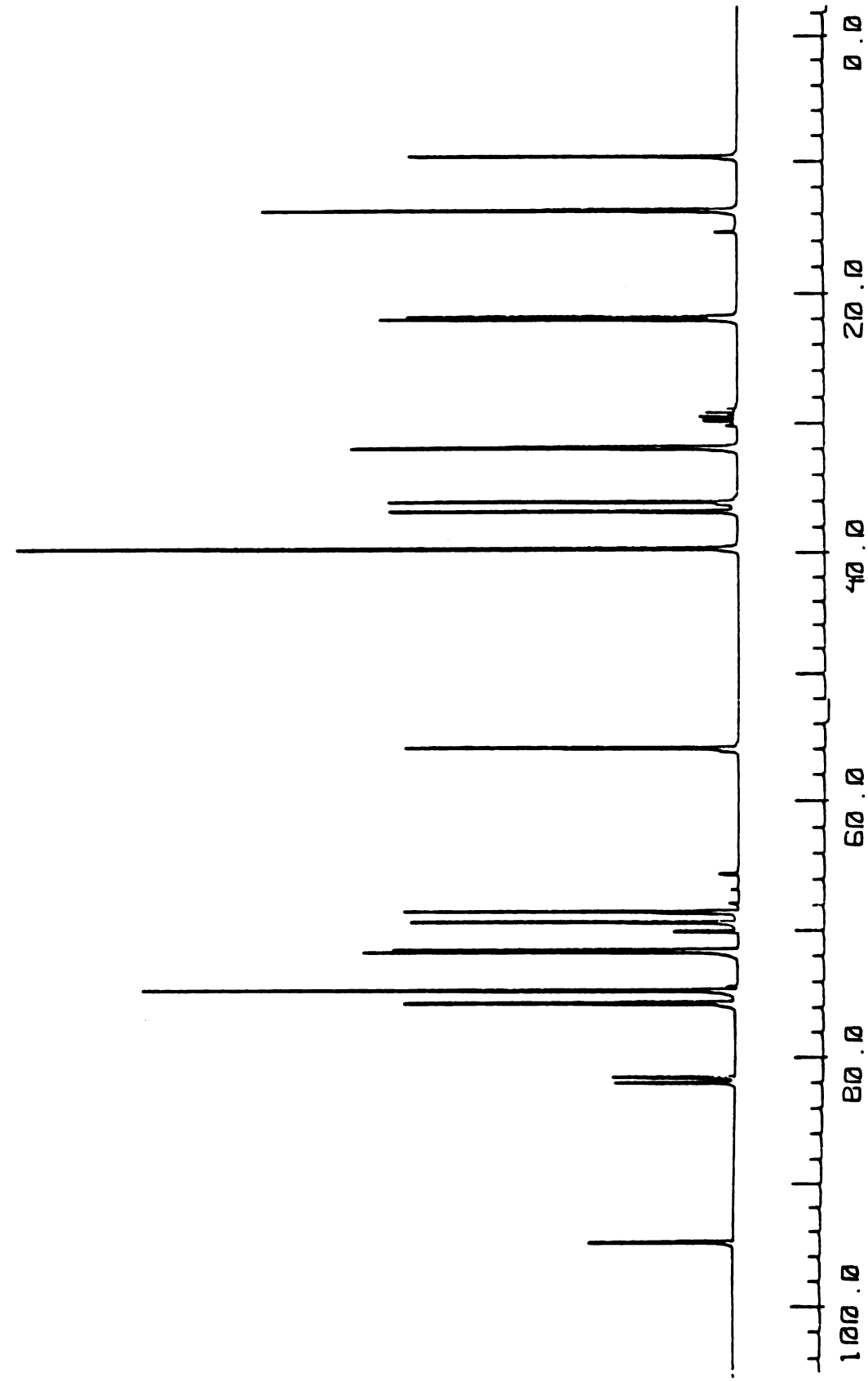


Figure 46. ^{13}C NMR spectrum of 40, R= n-Butyl.

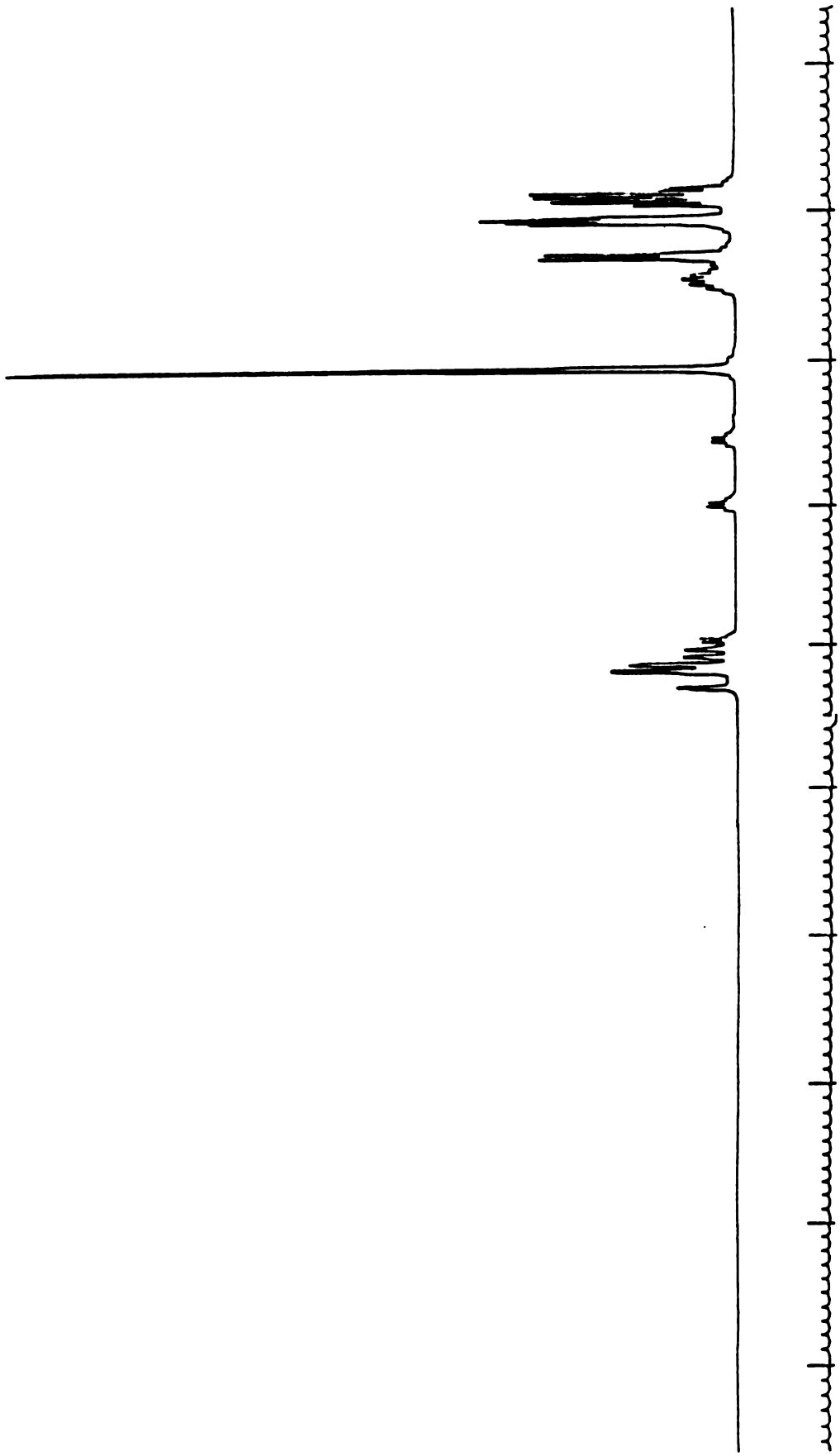


Figure 47. ^{1}H NMR spectrum of **41**, R= s-Butyl.

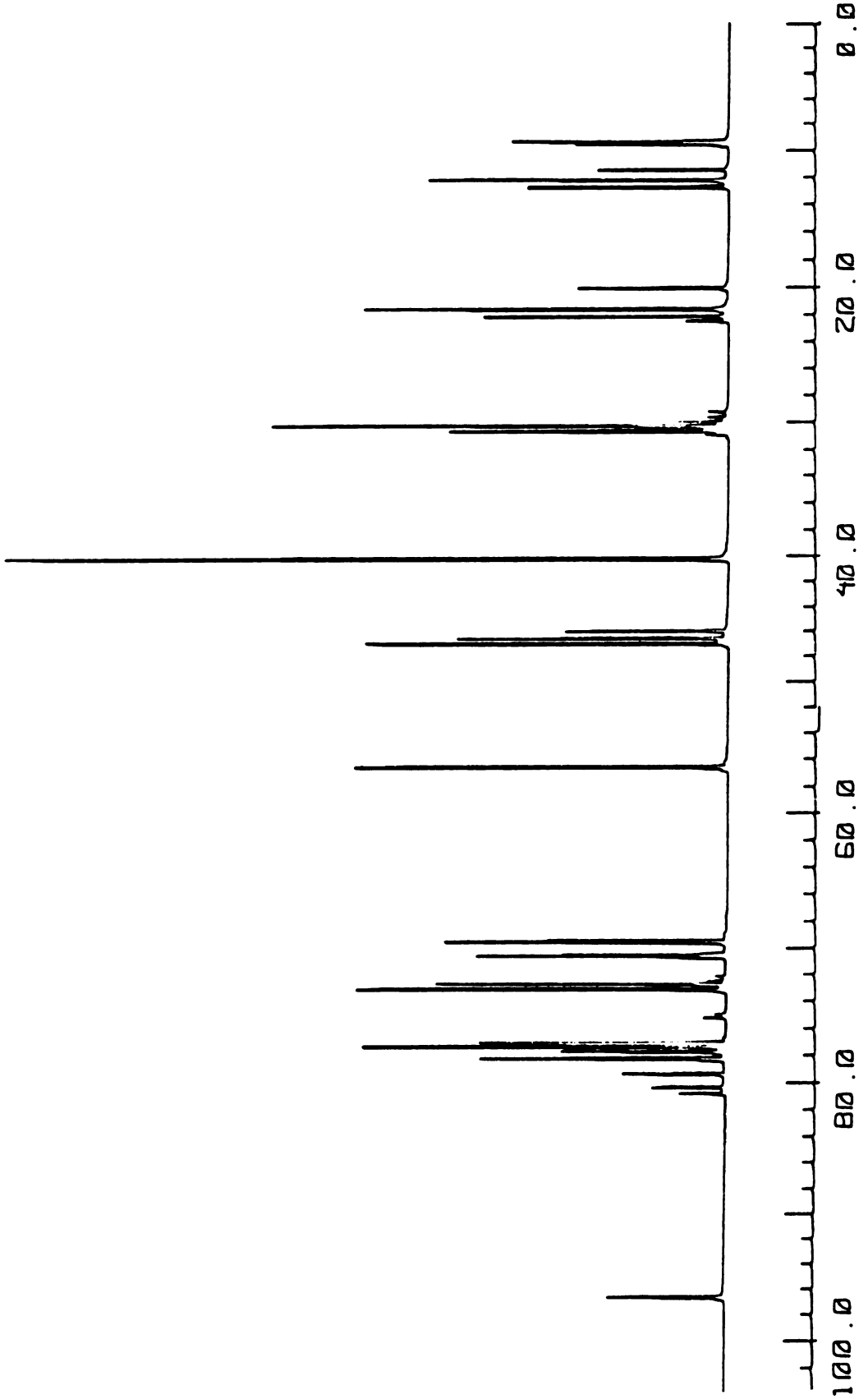


Figure 48. ^{13}C NMR spectrum of 41, R= s-Butyl.

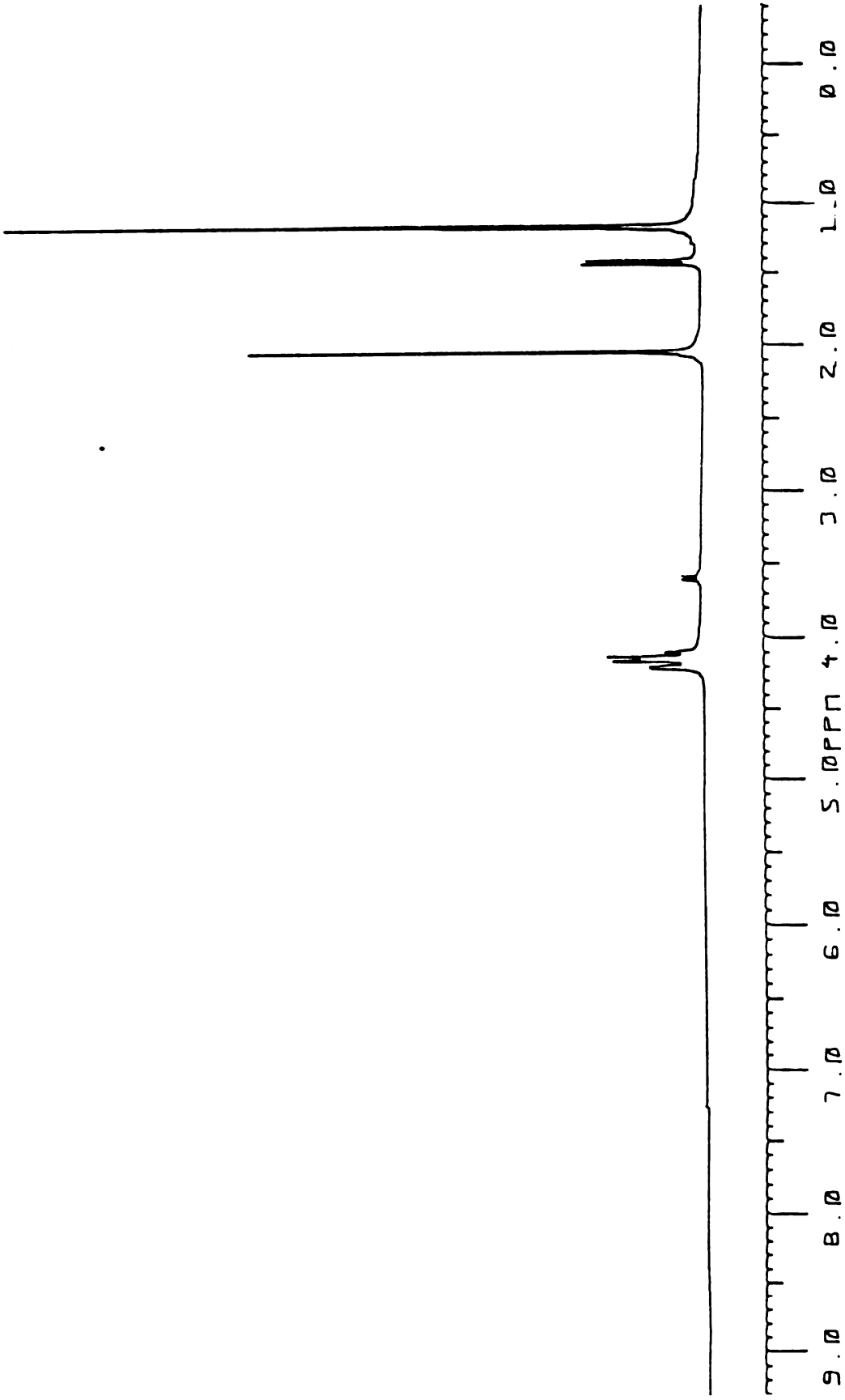


Figure 49. ^{1}H NMR spectrum of 42, R= t-Butyl.

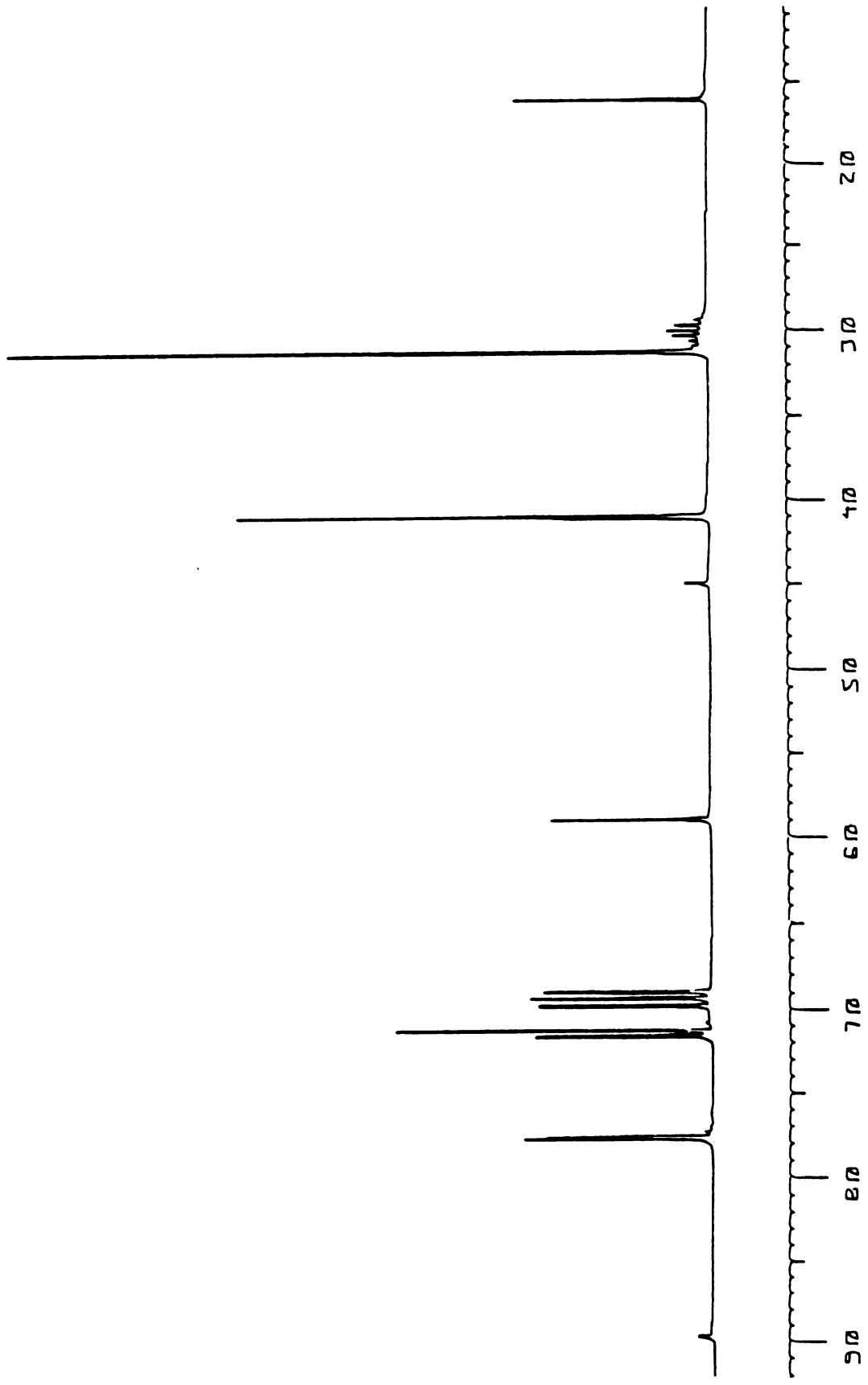


Figure 50. ^{13}C NMR spectrum of 42, R= t-Butyl.

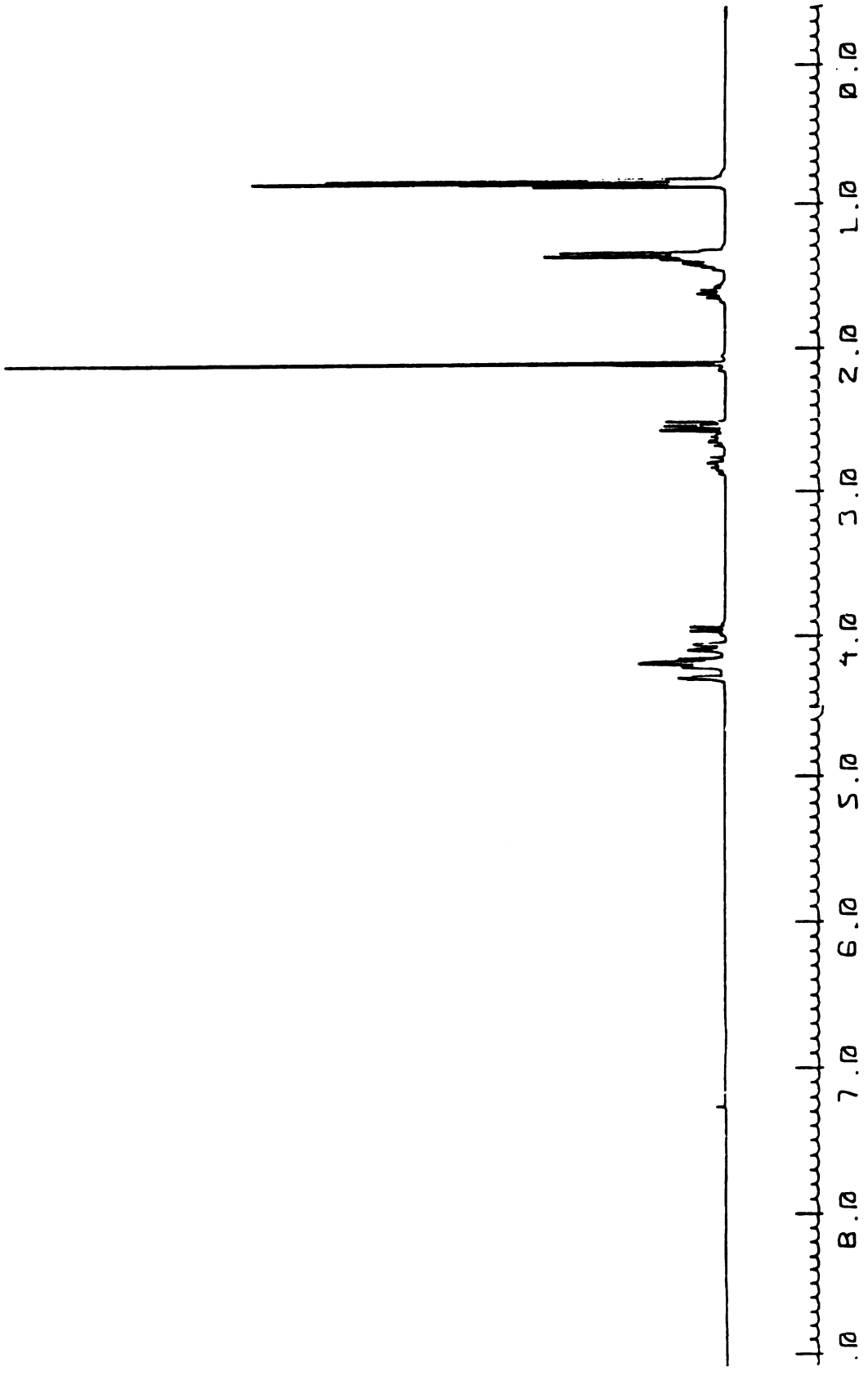


Figure 51. ^{1}H NMR spectrum of 43, R= i-Pentyl.

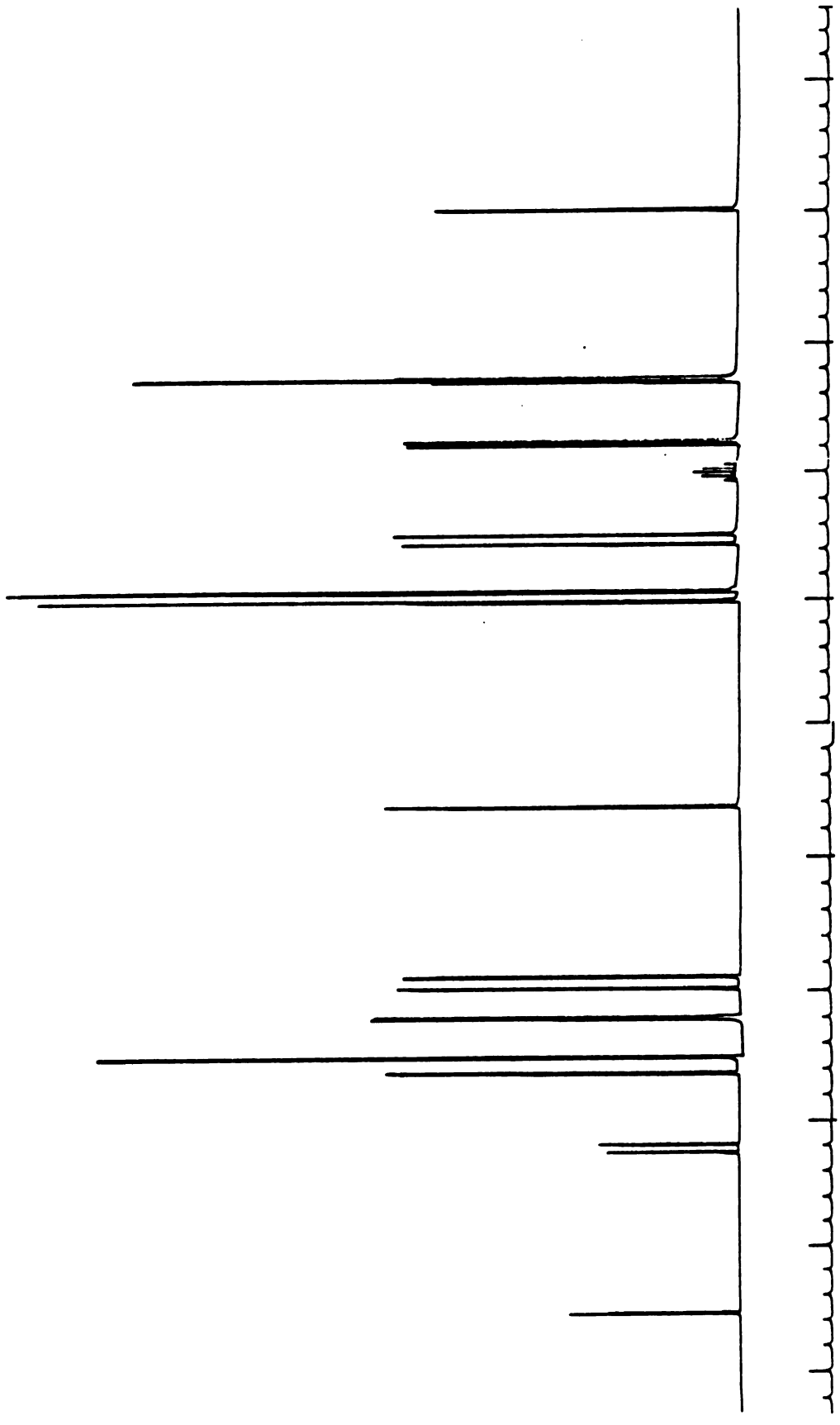


Figure 52. ^{13}C NMR spectrum of 43, R= i-Pentyl.

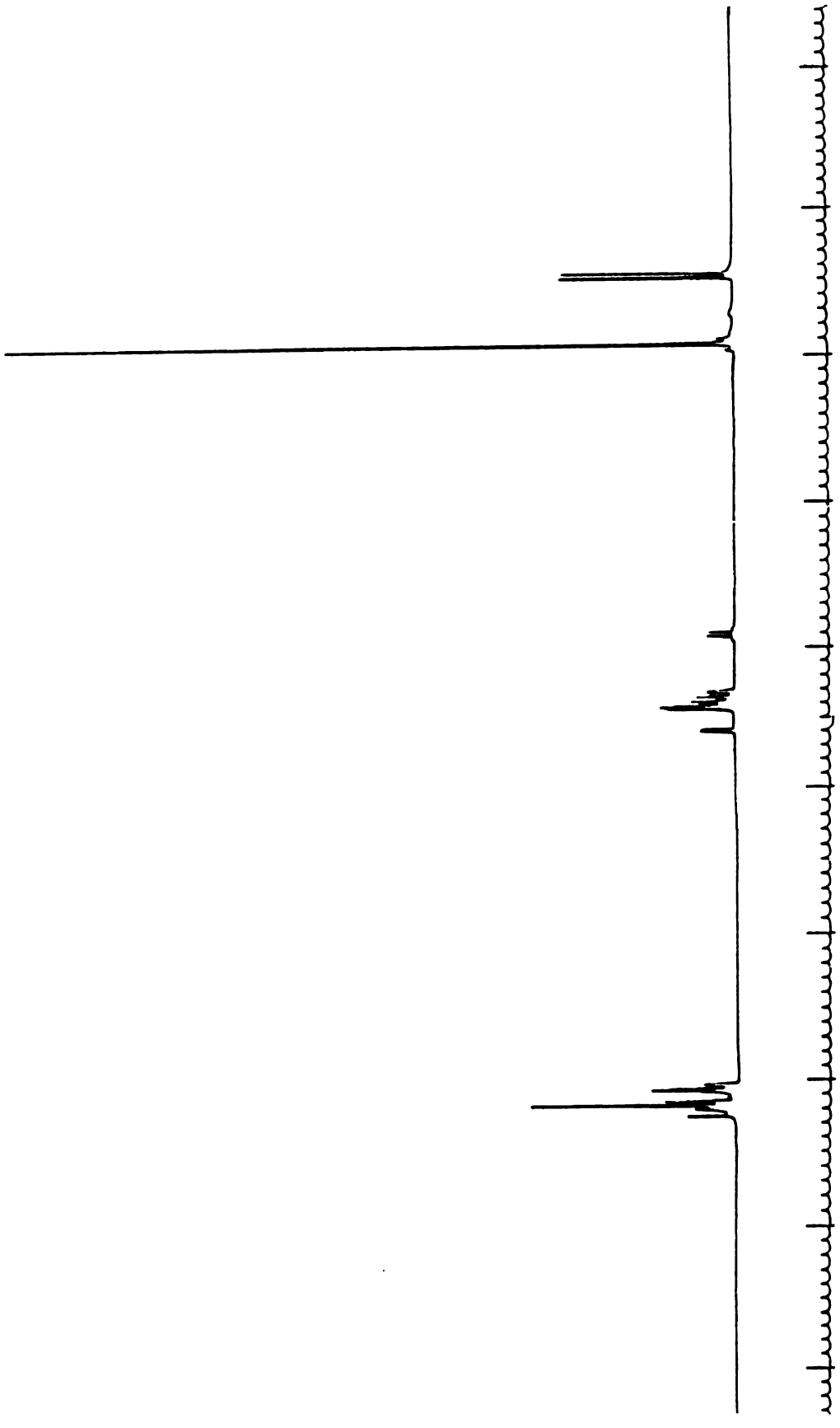


Figure 53. ^{1}H NMR spectrum of 44, R= Phenyl.

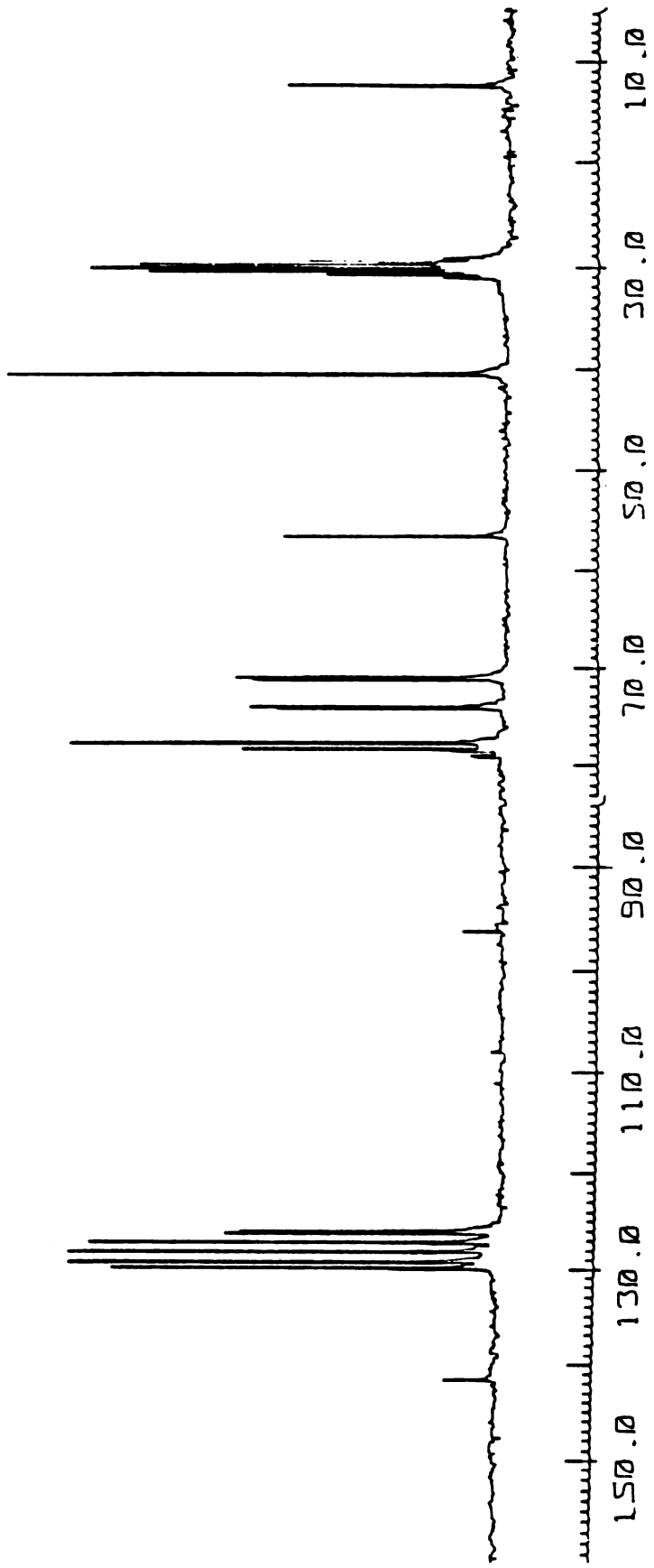


Figure 54. ^{13}C NMR spectrum of 44, R= Phenyl.

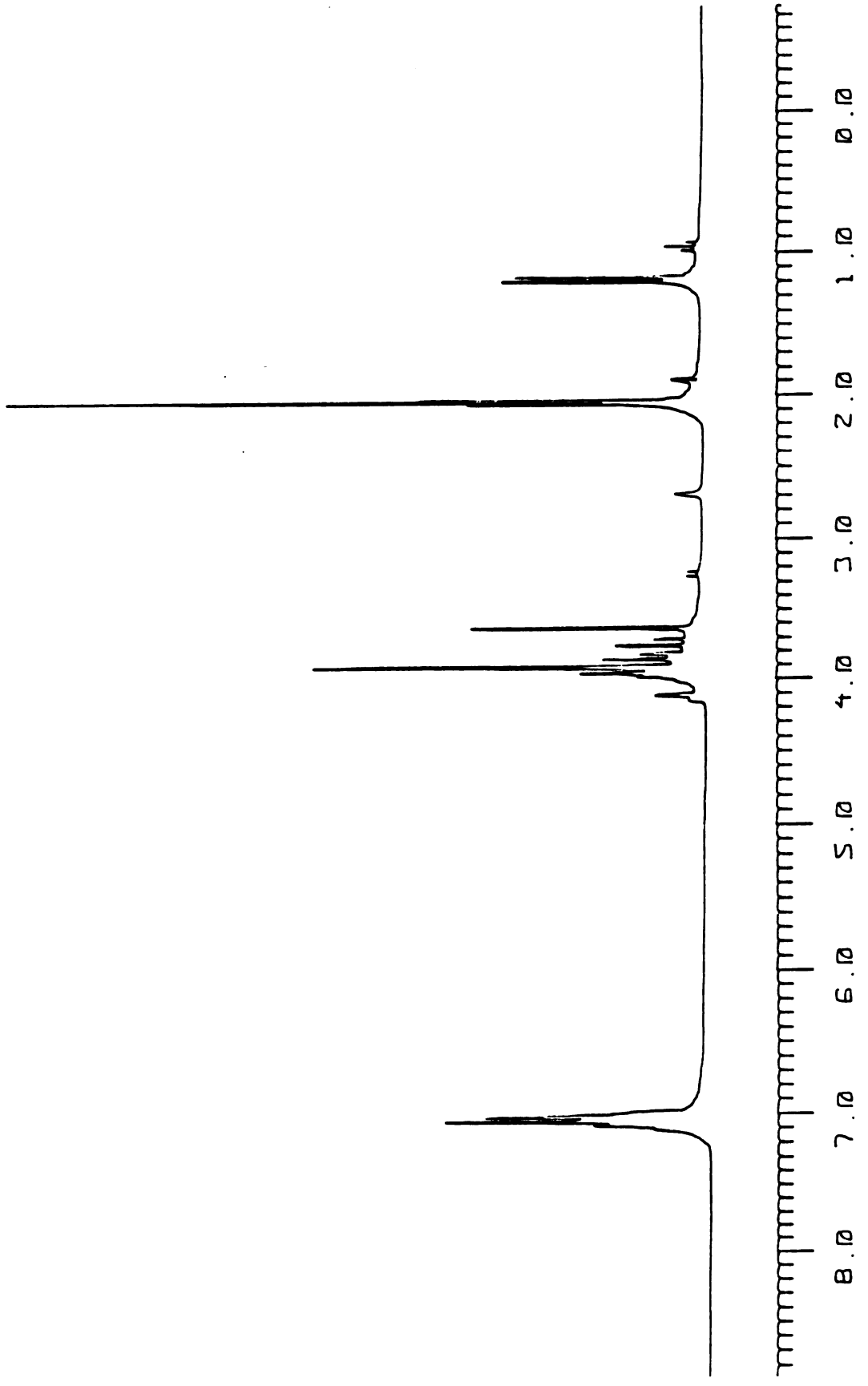


Figure 55. ^{1}H NMR spectrum of 45, R= Benzyl.

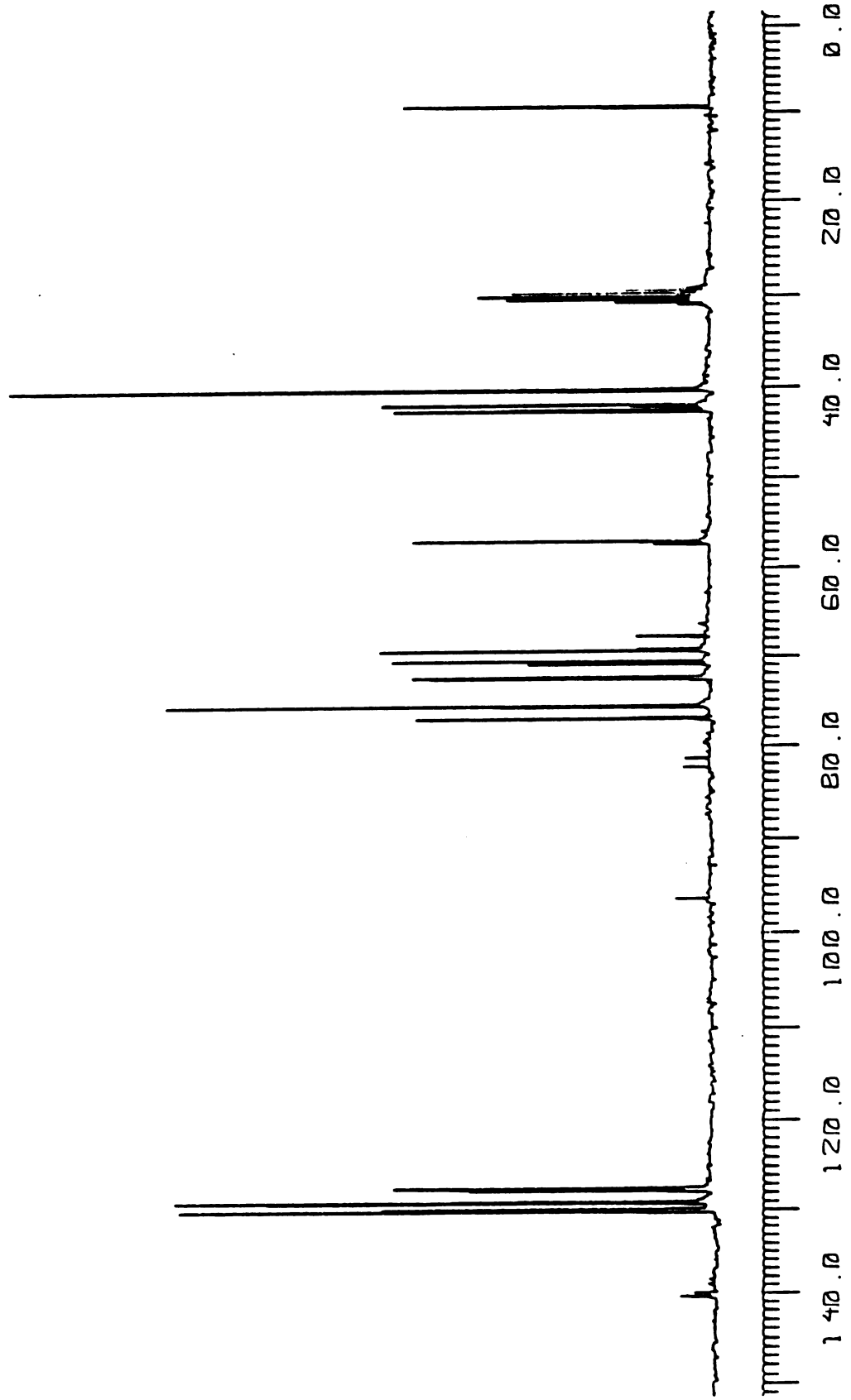


Figure 56. ^{13}C NMR spectrum of 45, R= Benzyl.

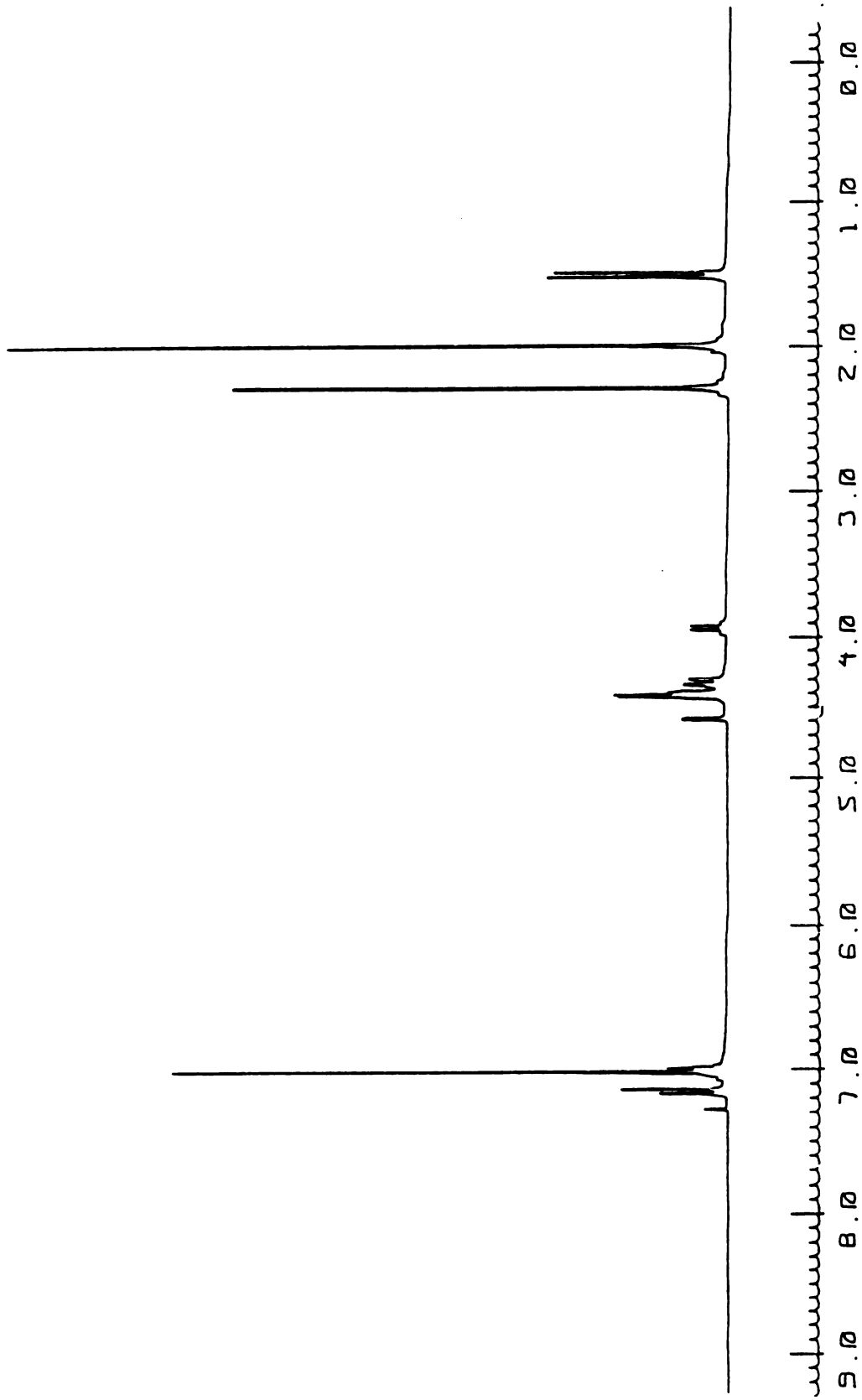


Figure 57. ^{1}H NMR spectrum of 46, R= 4-Tolyl.

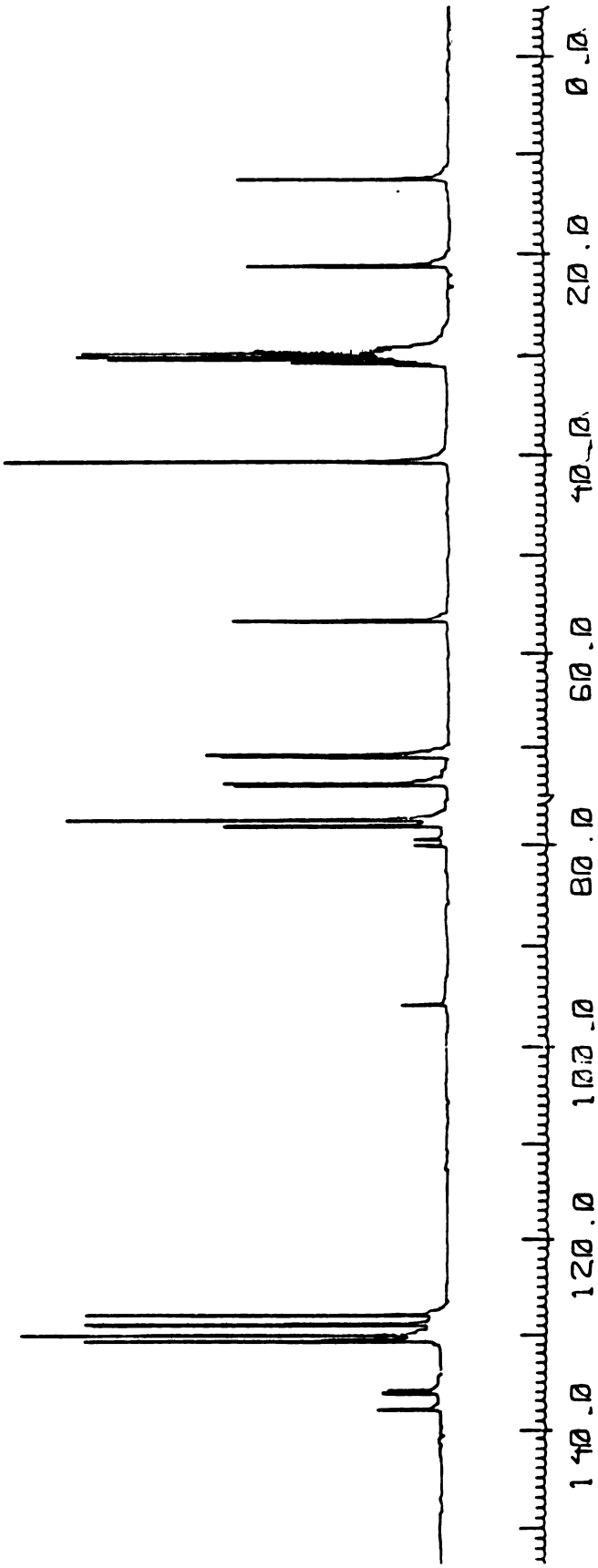


Figure 58. ^{13}C NMR spectrum of 46, R= 4-Tolyl.

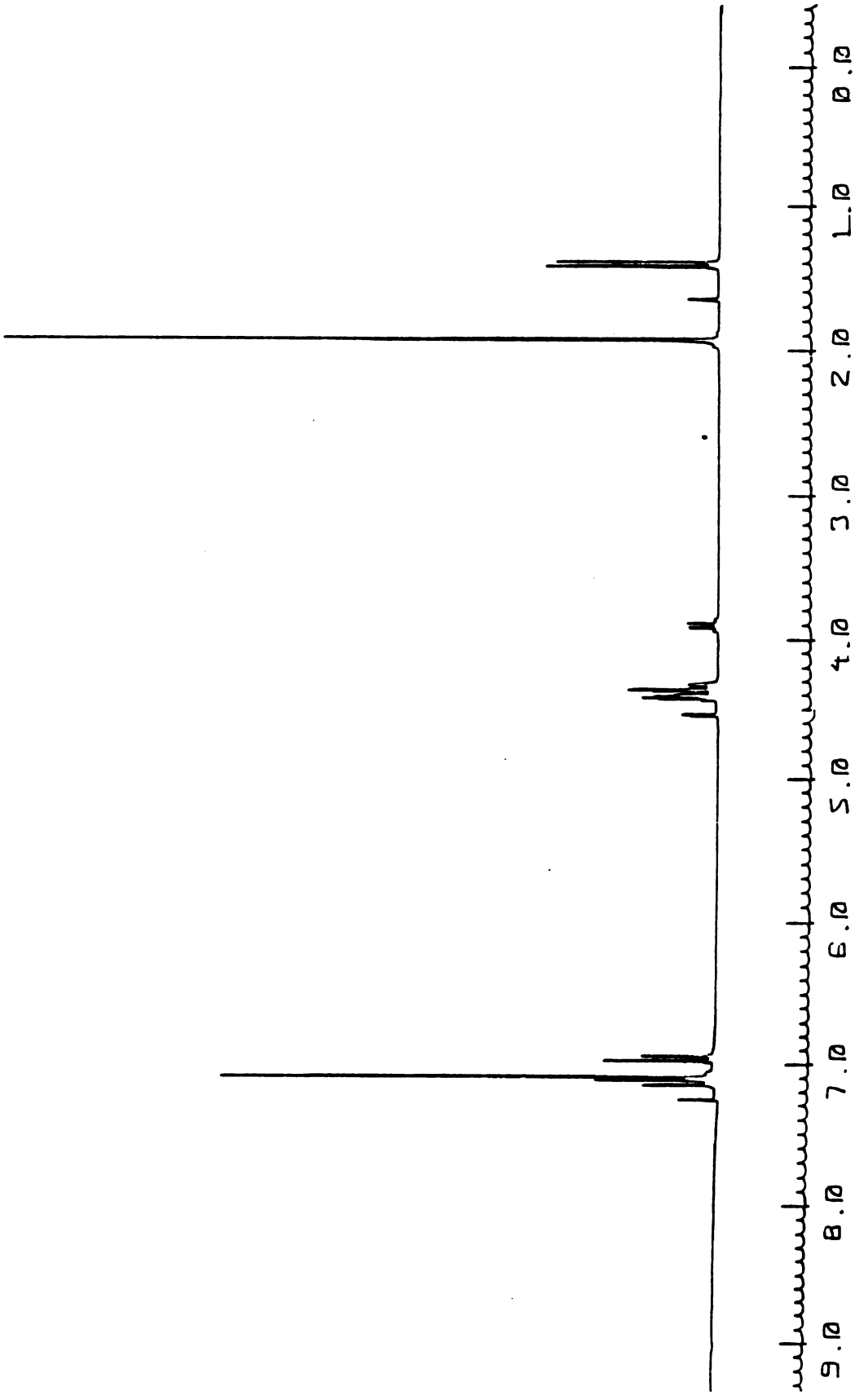


Figure 59. ^{1}H NMR spectrum of 47, R= 4-Cl-Ph.

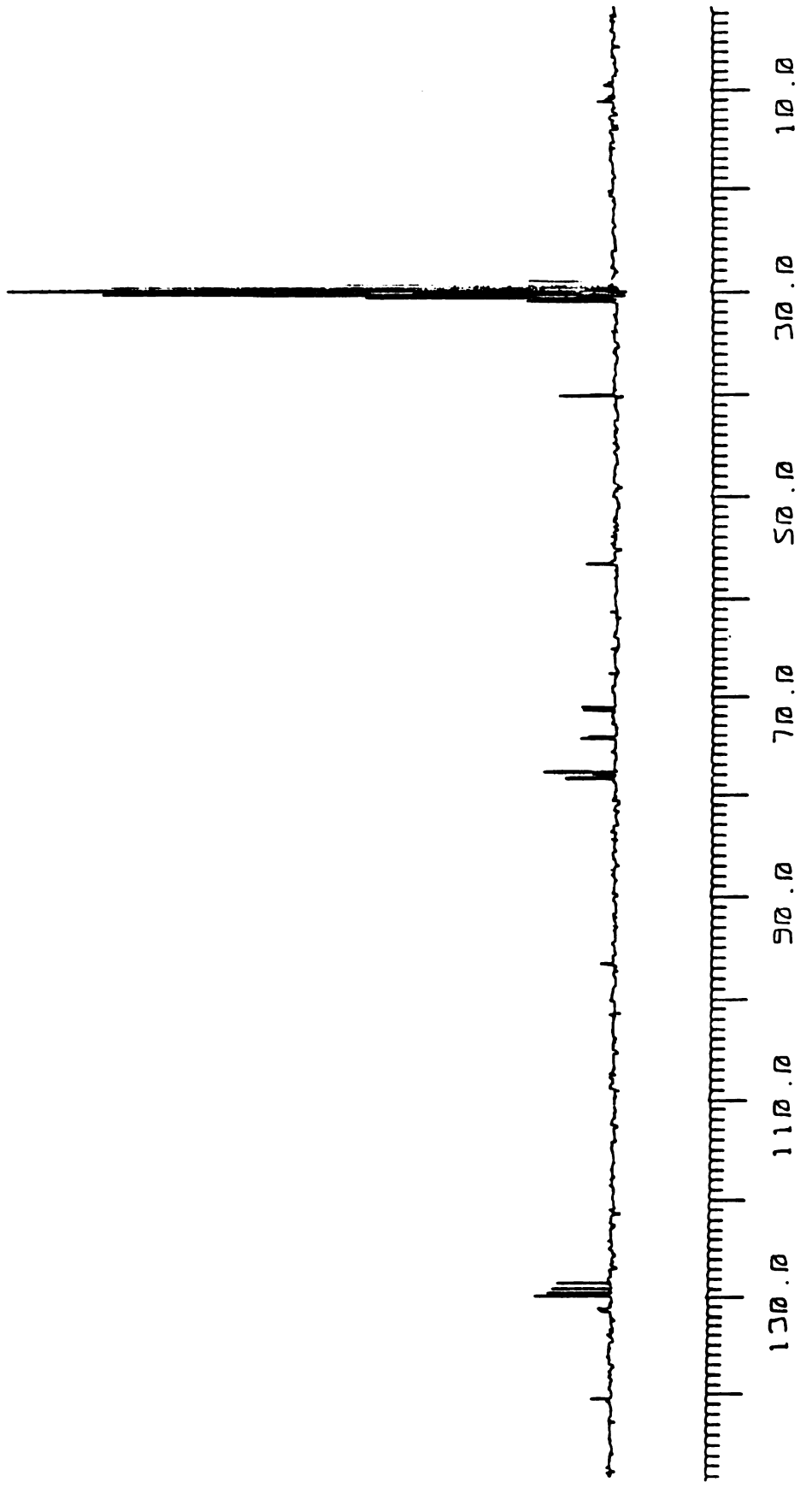


Figure 60. ^{13}C NMR spectrum of 47, R= 4-Cl-Ph.

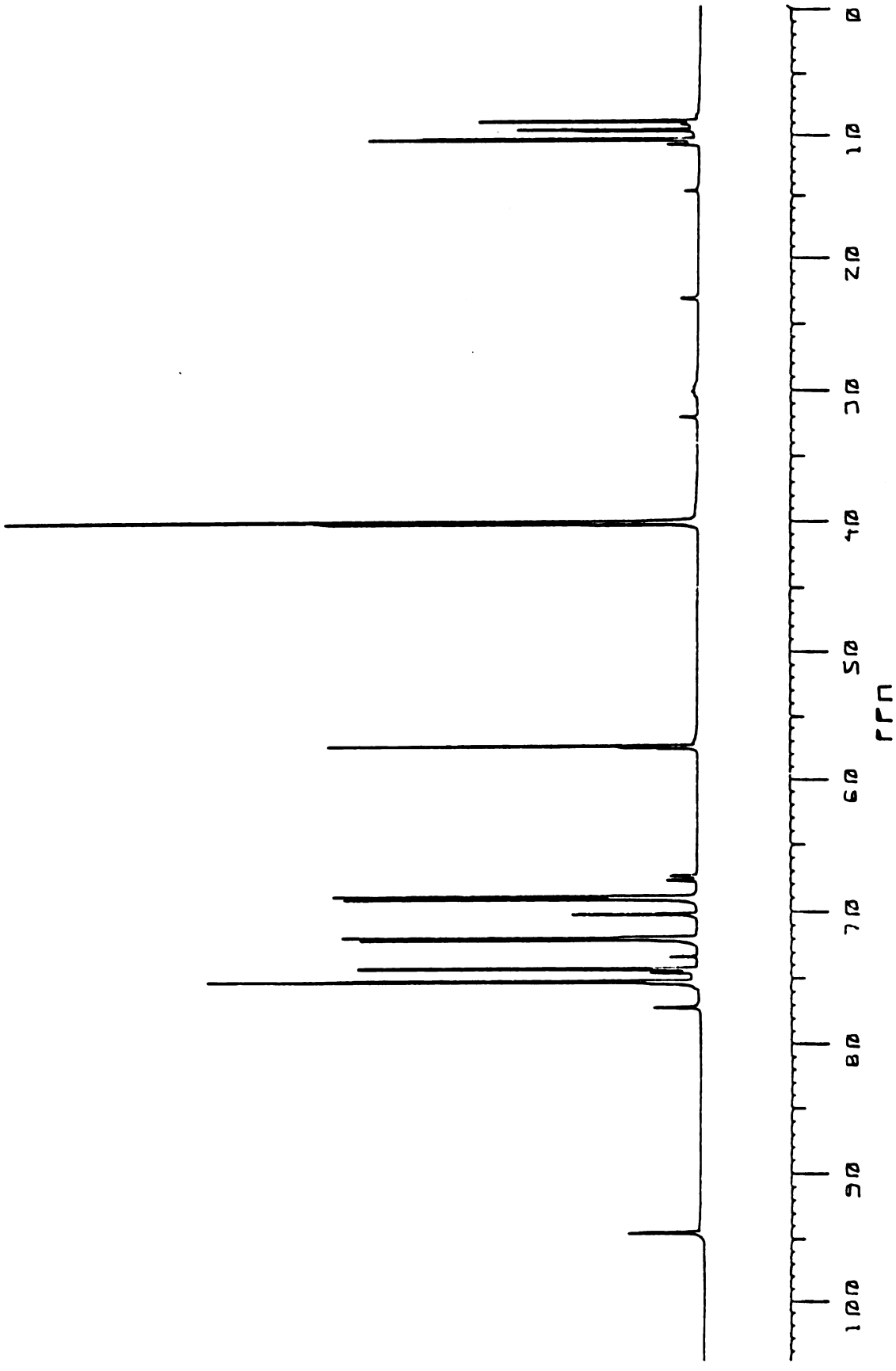


Figure 61. ^{13}C NMR spectrum of 48, R= Me.

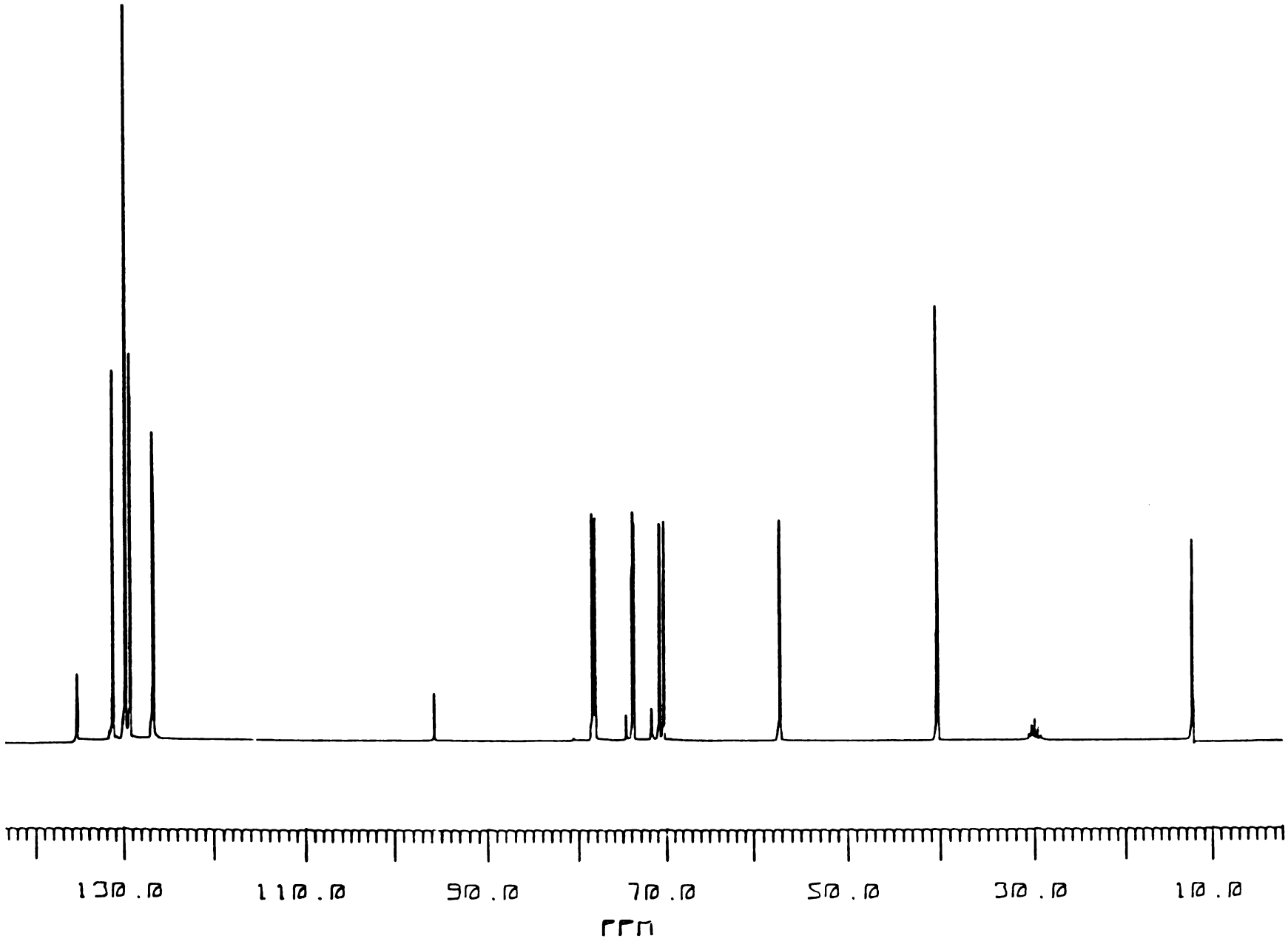


Figure 62. ^{13}C NMR spectrum of 49, R= Phenyl.

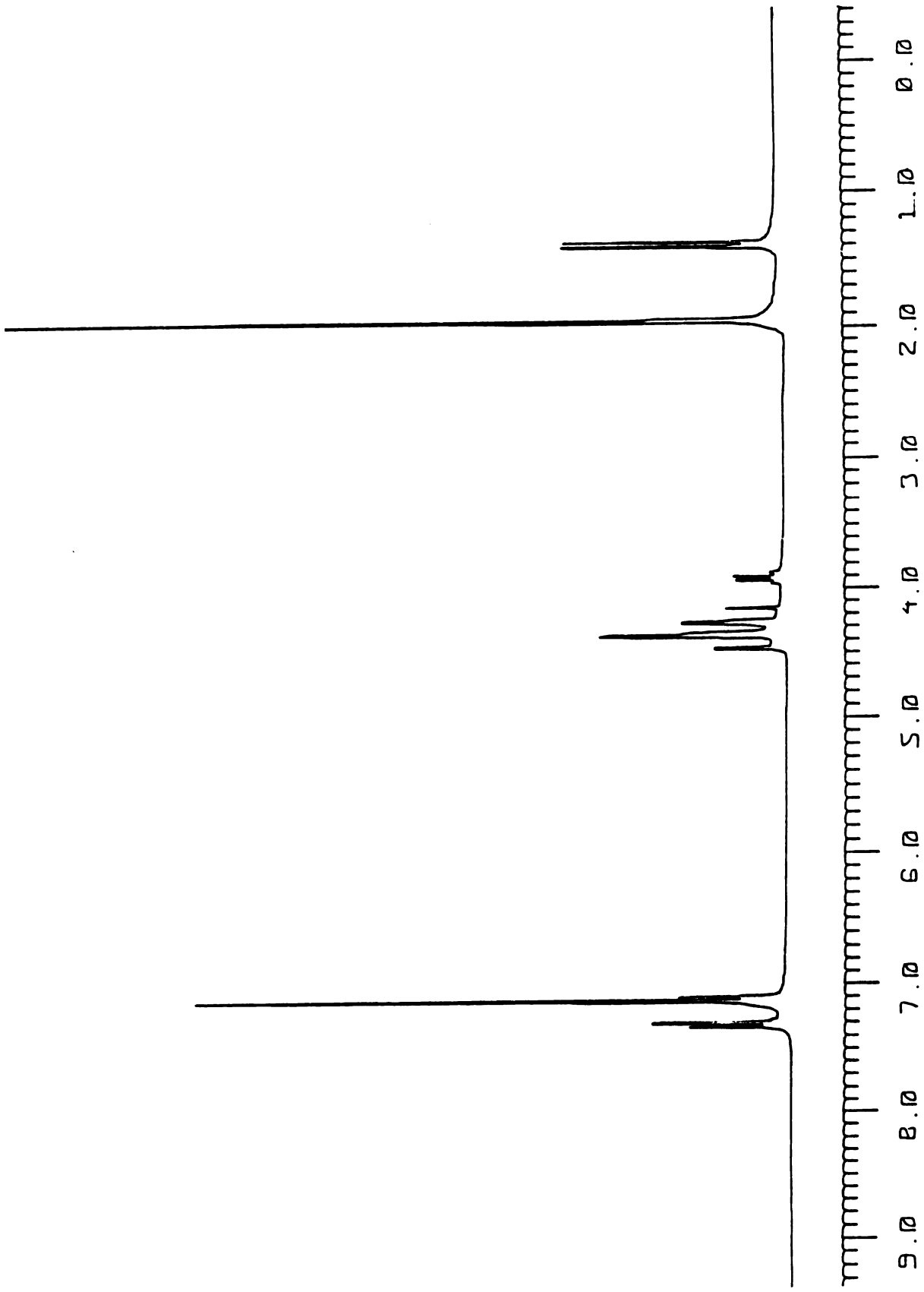


Figure 63. ^{1}H NMR spectrum of 50, R= 4-Cl-Ph.

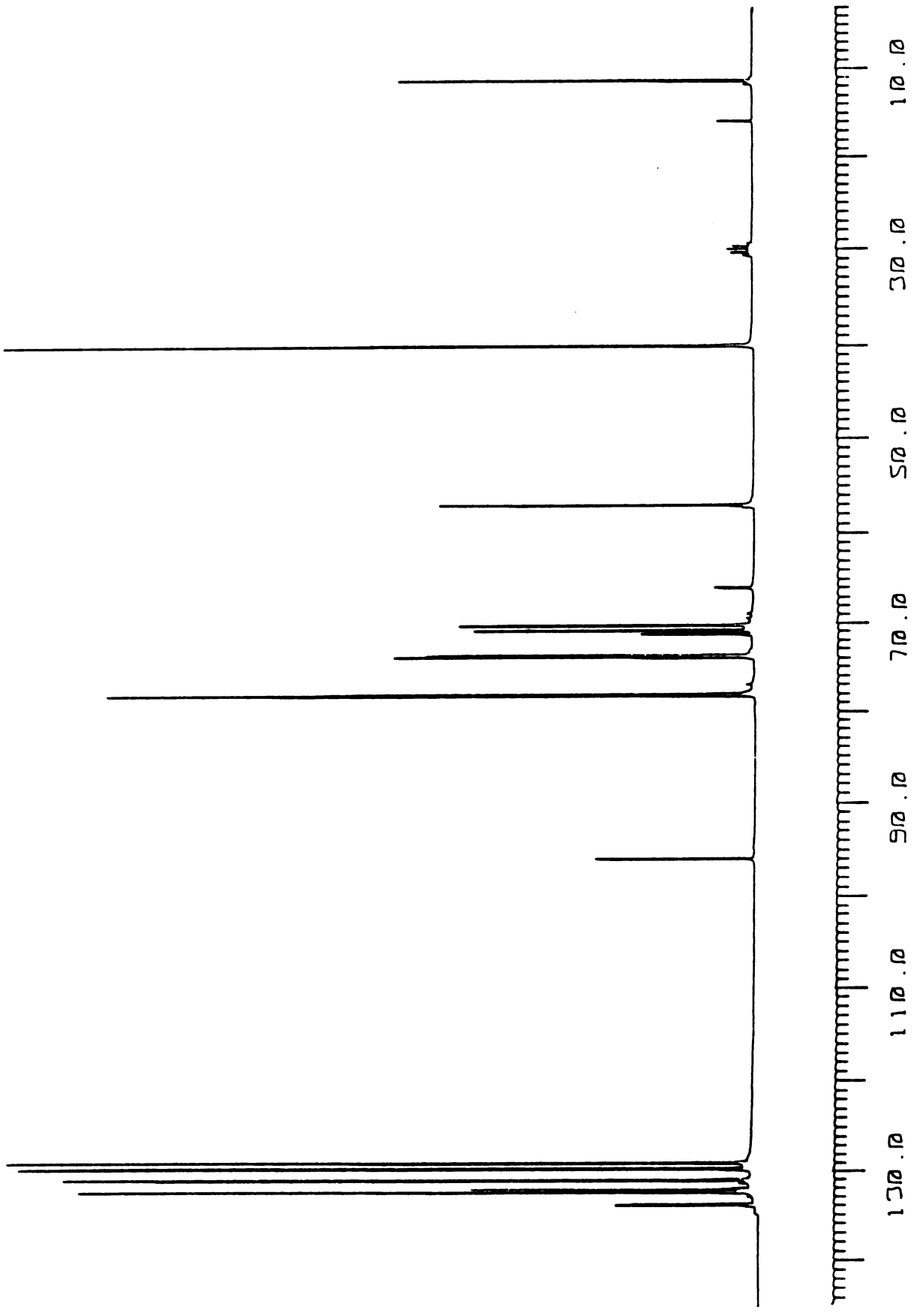


Figure 64. ^{13}C NMR spectrum of 50, R= 4-Cl-Ph.

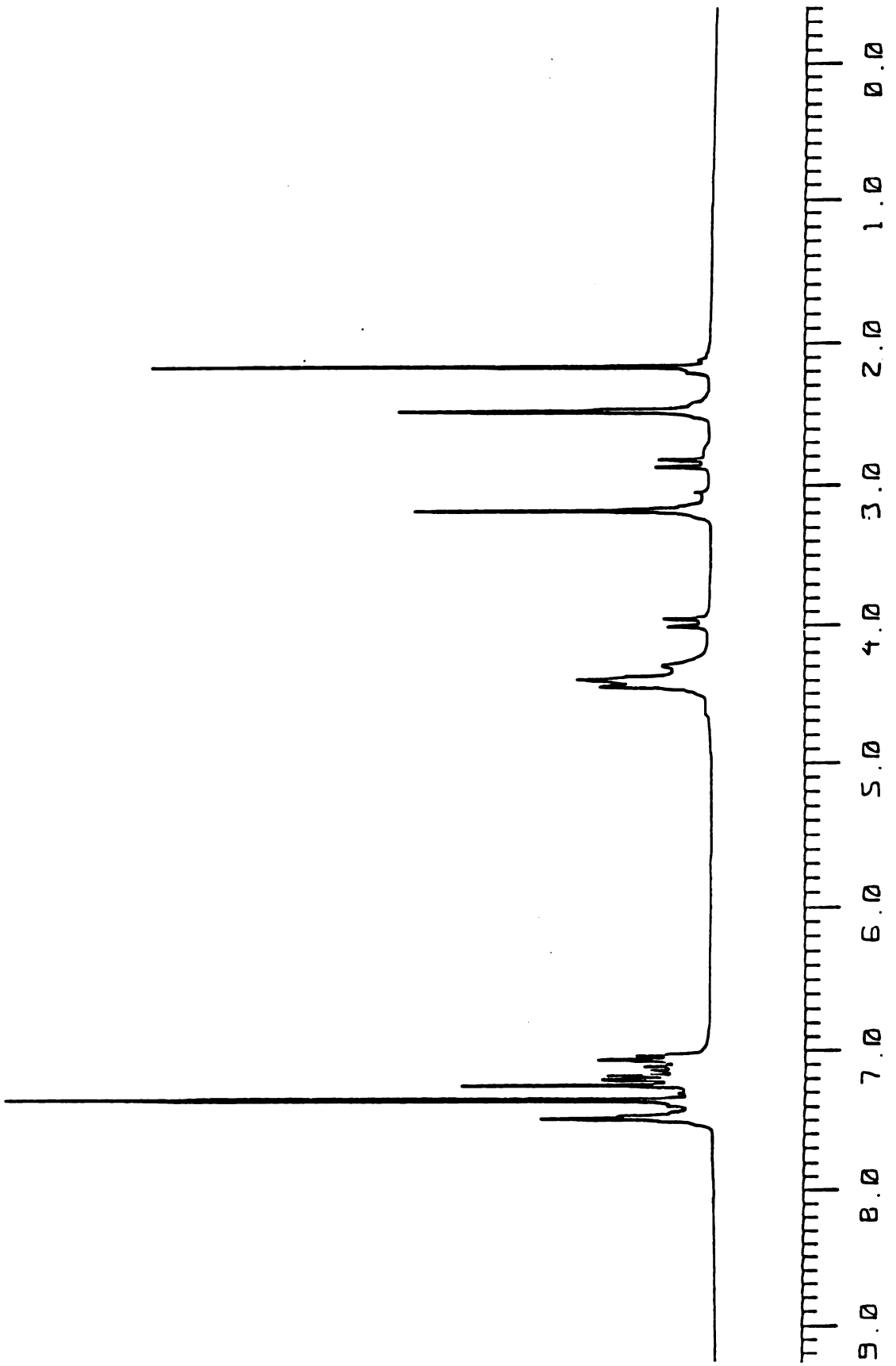


Figure 65. ^{1}H NMR spectrum of 55, R= Phenyl.

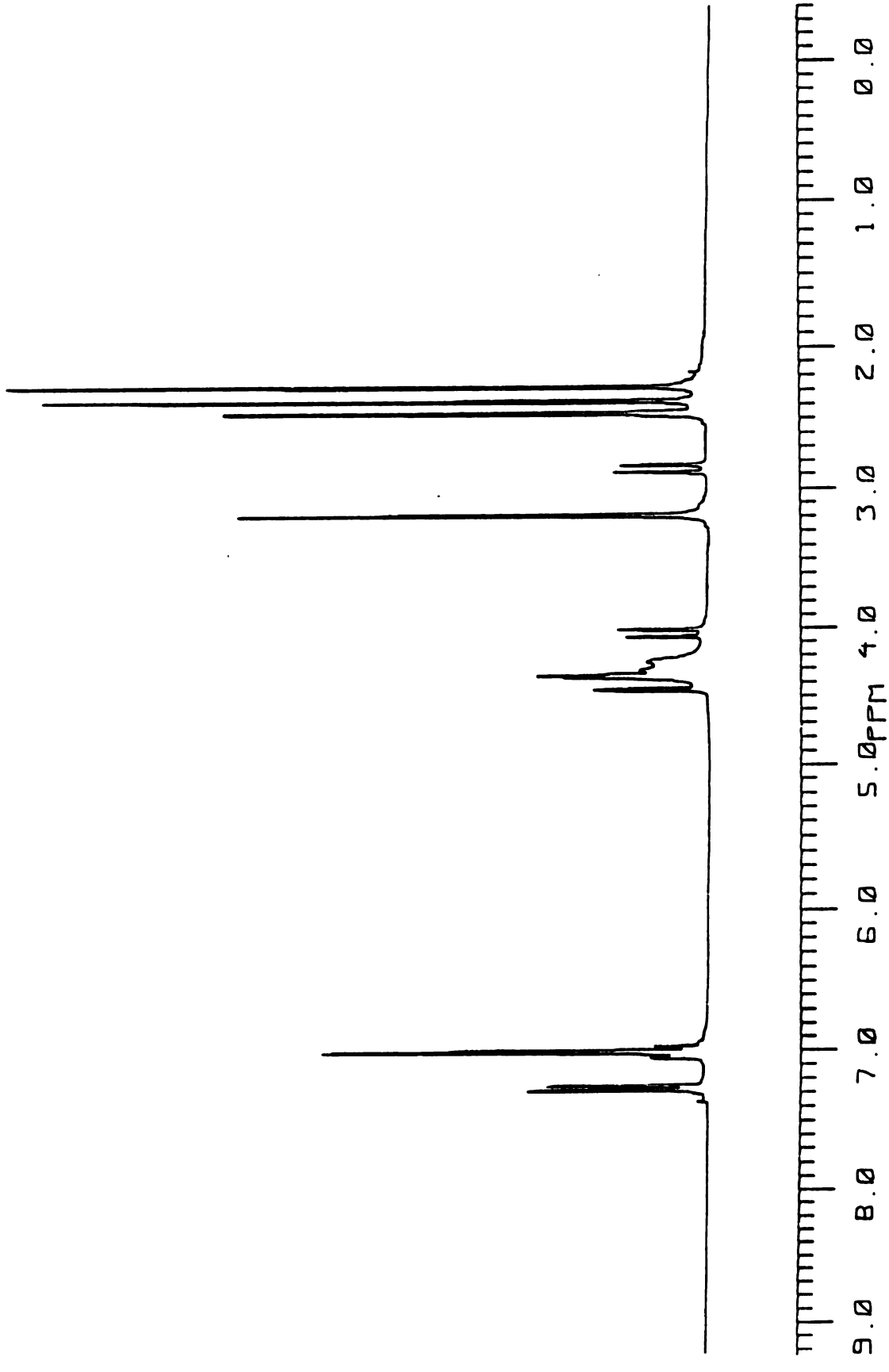


Figure 66. ^{1}H NMR spectrum of 5Z, R= 4-Tolyl.

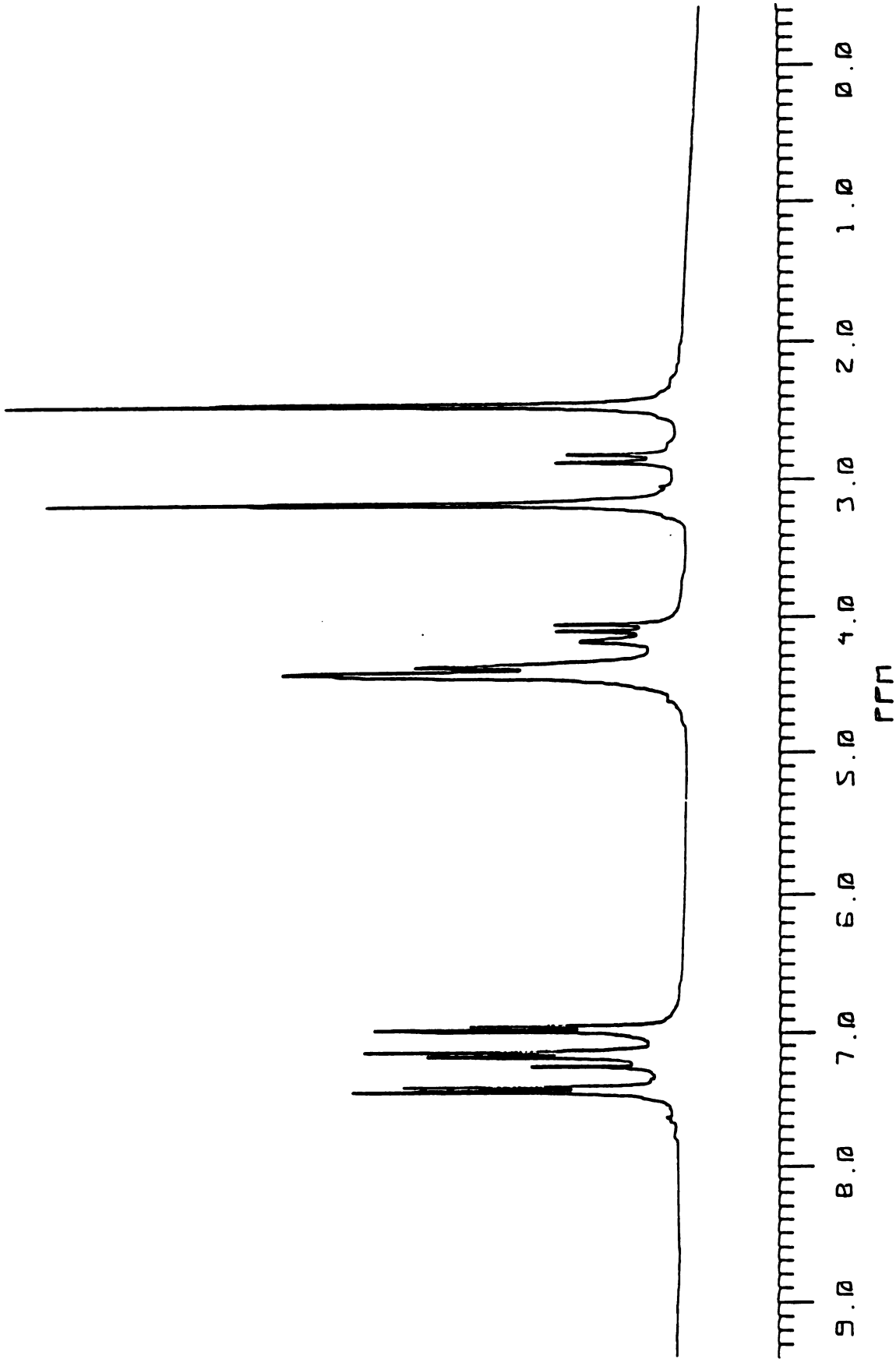


Figure 67. ^{1}H NMR spectrum of 58, R= 4-Cl-Ph.

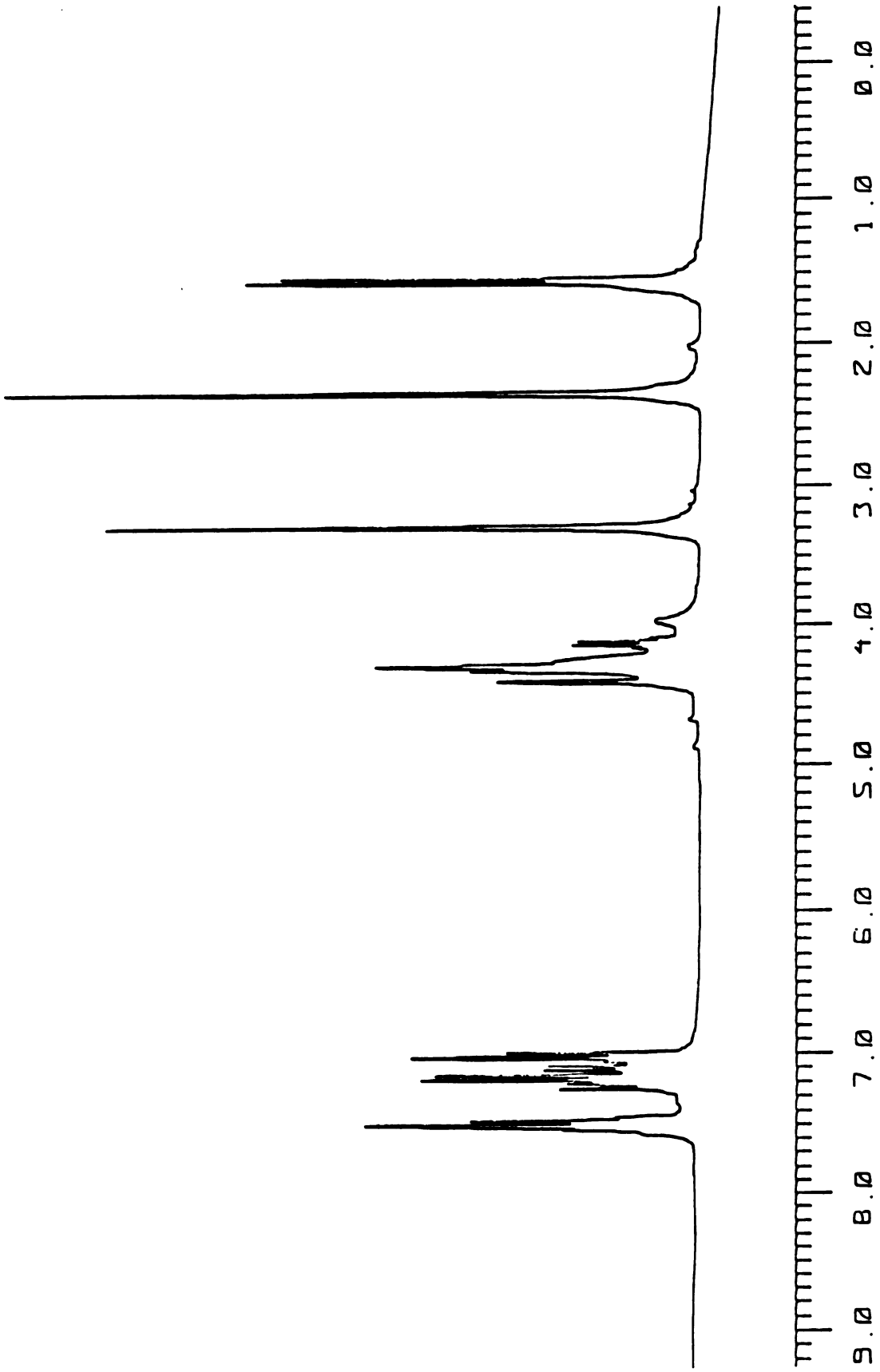


Figure 68. ^{1}H NMR spectrum of 71, R= Phenyl.

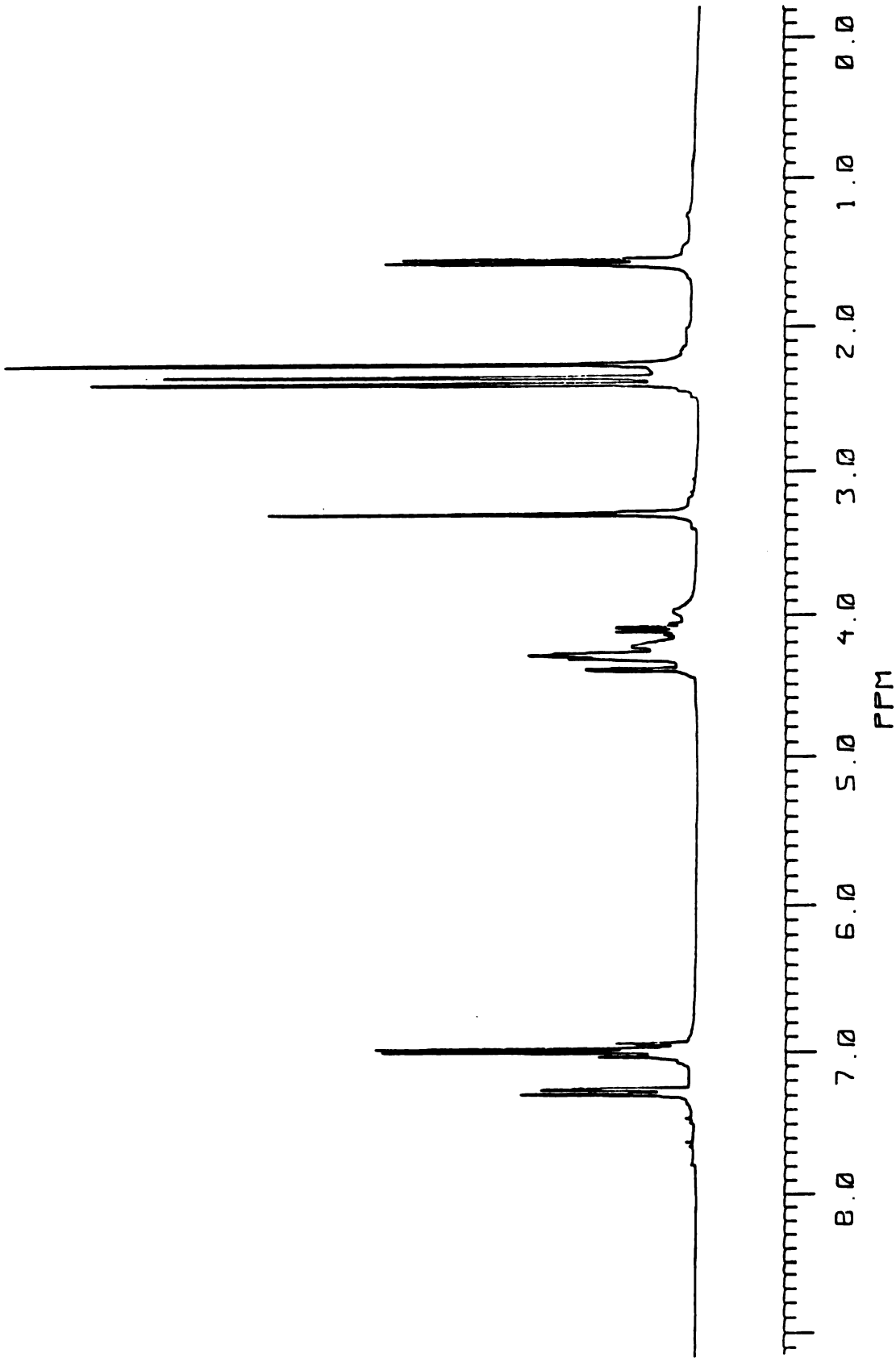


Figure 69. ^{1}H NMR spectrum of 73, R= 4-Tolyl.

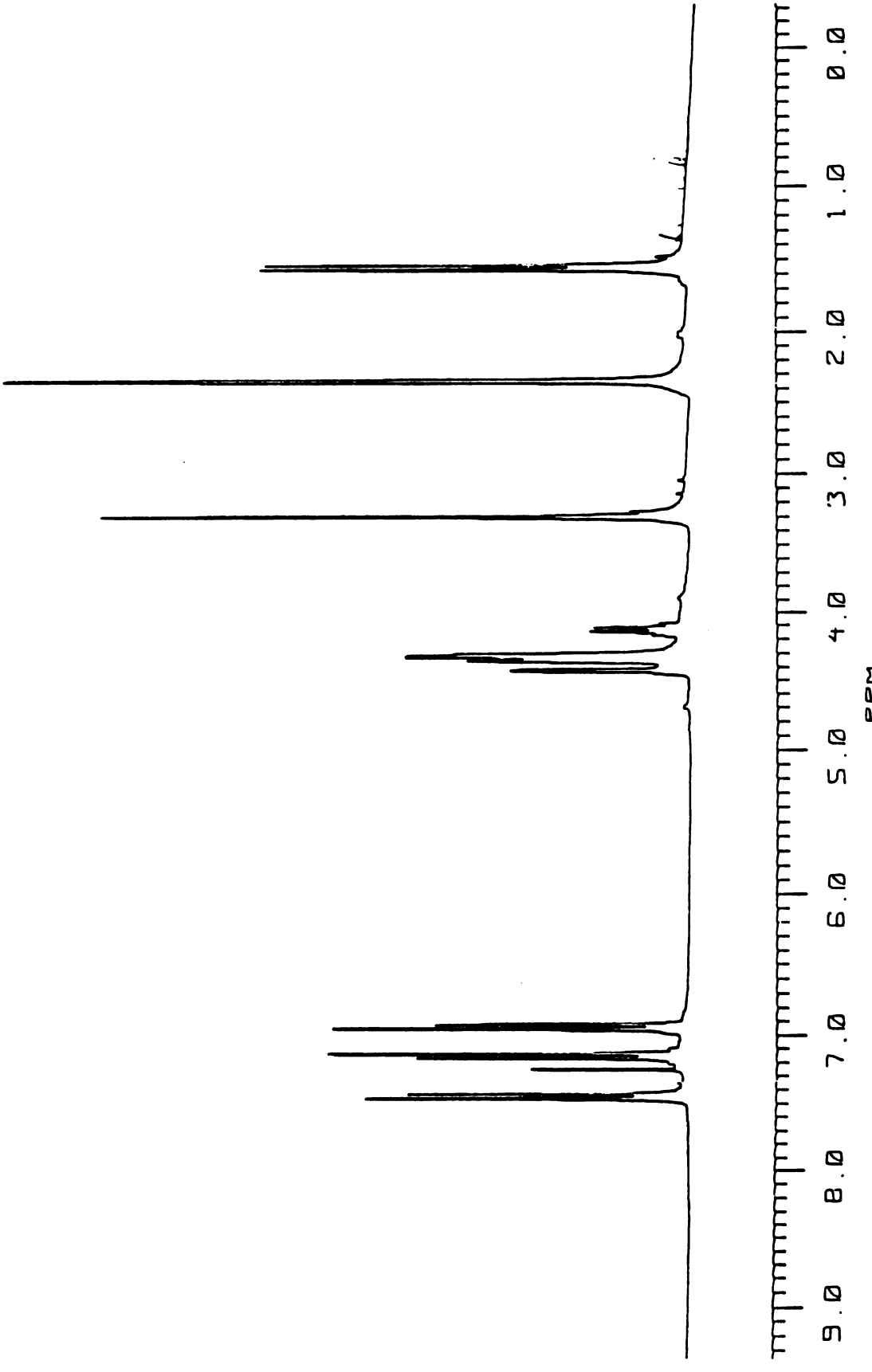


Figure 70. ^{1}H NMR spectrum of 74, R= 4-Cl-Ph.

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