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Applications of Ferrocenylsulfide-Based Catalysts in Selective Hydrogenations and Asymmetric Cross-coupling Reactions

presented by

Chun-Hsiung Wang

has been accepted towards fulfillment
of the requirements for

Ph. D. degree in Chemistry

Carl H. Brubaker Jr.
Major professor

Date July 15, 1991

APPLICATIONS OF FERROCENYLSULFIDE-BASED CATALYSTS IN SELECTIVE HYDROGENATIONS AND ASYMMETRIC CROSS-COUPLING REACTIONS

By

Chun-Hsiung Wang

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ABSTRACT

APPLICATIONS OF FERROCENYLSULFIDE-BASED CATALYSTS IN SELECTIVE HYDROGENATIONS AND ASYMMETRIC CROSS-COUPLING REACTIONS

By

Chun-Hsiung Wang

New chiral and achiral ferrocenylamine sulfides of the type $(C_5H_5)Fe(C_5H_3)[CH_2NR_2][SR']$, R=Et, *n*-Pr, R'= Me, Et, *p*-tolyl, *p*-chlorophenyl and (*R*,*S*)- or (*S*,*R*)-$(C_5H_5)Fe(C_5H_3)[CHMeNR_2][SR']$, R=Et, *n*-Pr, R'= Me, Et, *i*-Pr have been prepared by first converting corresponding 1-dimethylaminoethyl-2-alkylthio ferrocene to ferrocenylacetate derivatives followed by reaction with dimethylamine or di-*n*-propylamine. These compounds are air-stable and were characterized by spectroscopic techniques such as ^1H and ^{13}C NMR, infrared and mass spectroscopy as well as elemental analysis. These ferrocenylamine thioethers readily chelate palladium chloride to form the chiral and achiral heterobimetallic complexes, $(C_5H_5)Fe(C_5H_3)[CHR''NR_2][SR'][PdCl_2]$, (R=Et, *n*-Pr, R'=Me, Et, *p*-tolyl, *p*-chlorophenyl, R"=H), (R=Et, *n*-Pr, R'= Me, Et, *i*-Pr, R"=Me). ^1H NMR, IR, MS and elemental analyses were obtained for these complexes.

The catalytic applications of these complexes to the hydrogenation of conjugated-dienes and phenylacetylenes were examined. High chemo- and regioselectivities have been achieved with superior activities and 100% conversions in most cases.

A 1-2-disubstituted-ferrocenylsulfide ligand and it's palladium and platinum complexes were synthesized in order to compare the influence the substituents of the catalysts exerted on hydrogenations of conjugated-dienes. It reveals that both the amino- and sulfido-substituents have effects on the hydrogenation reaction. Changes in the amino group environment dominate. A plausible catalytic pathway is proposed for the hydrogenation of phenylacetylenes.

In situ rhodium catalysts were prepared by using chiral ferrocenylamine sulfide ligands to investigate the asymmetric induction of prochiral aminoacids. Reasonably good enantiomeric excess (ee) were obtained by measuring the optical rotations of the hydrogenated products on a polarimeter. A possible mechanism of asymmetric hydrogenation is proposed.

These new palladium complexes were also tested on the asymmetric Grignard cross-coupling reaction. Results have shown that the optical yields depended on the surroundings around the nitrogen atom within the catalysts.

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

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

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APPLICATIONS OF FERROCENYLSULFIDE-BASED CATALYSTS IN SELECTIVE HYDROGENATIONS AND ASYMMETRIC CROSS-COUPLING REACTIONS

INTRODUCTION

The preparation of enantiomerically pure compounds is of importance to chemists since for many pharmaceuticals, food additives, fragrances and agrochemicals, the desired biological properties are strongly related to a given absolute configuration. In many cases, the undesired enantiomer can provide side effects to the drug.[1]

The preparation of enantiomerically pure compounds can be divided into two categories:

(1). resolution of a racemic mixture

(2). asymmetric syntheses, which include stoichiometric- and catalytic asymmetric synthesis

Resolution is the oldest method and it has some disadvantage since the desired enantiomer cannot be obtained in more than 50% yield. However, it remains very useful if recycling of the undesired enantiomer and the resolving agent is possible. On the other hand, asymmetric synthesis makes possible preparation of a pure enantiomer from a prochiral starting material; 100% yield with respect to the starting material can often be achieved. Furthermore, by using a chiral catalyst, the efficiency can be increased dramatically since ideally only one molecule is required to carry out the reaction. This makes asymmetric catalysis very attractive because the required amount of chiral auxiliaries will be drastically decreased when compared to classical resolution process or to stoichiometric asymmetric synthesis.

The syntheses and applications of chiral catalysts in asymmetric syntheses have been of intense interest and activity. Spectacular progress has been made in the field of asymmetric catalysis by using homogeneous catalysts based on transition metal complexes modified by chiral ligands.[2-9] To date, the choice of ligands has been mainly empirical and all attempts to find relationships between ligand structure and extent of asymmetric induction obtainable in catalytic reactions have failed. However, several requirements have been found for efficient asymmetric catalysis. They are:

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

b. Best results are obtained when the catalytic complex is more stereorigid. Thus, bidentate ligands, especially if conformationally restricted, are generally most desirable.

c. The best substrates are those with one or preferably more highly polar functional groups. Unfunctionallized alkanes give poor optical yields.

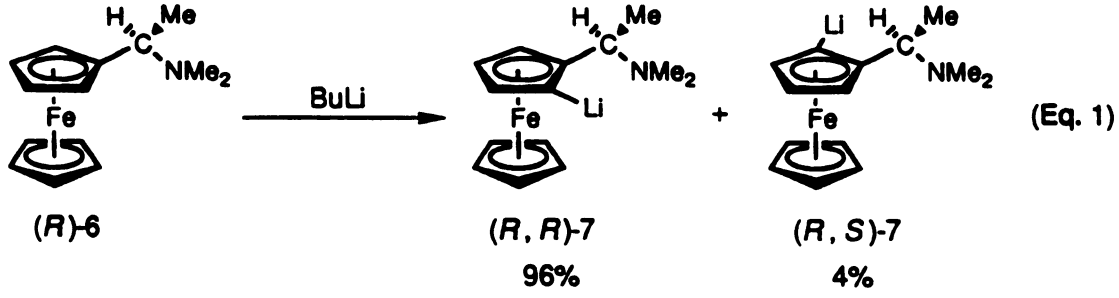
Many transition-metal complexes attached to the chiral chelating diphosphines have shown catalytic activities.[2-9] However, their stereodifferentiating ability can suffer due to their liability as complexing agents. For efficient transfer of asymmetry to a substrate to occur, the chiral ligand must be bound to the metal during the stereodifferentiating step. The η^5-cyclopentadienyl unit is therefore adopted because it bonds very strongly to transition metals. Moreover, it must be possible to modify the chiral ligands so that optimal catalyst-substrate matches can be achieved. Chiral ferrocenyl ligands with both planar and center chirality are of particular interest since they are able to fulfil these requirements.

The discovery of ferrocene in 1951[10] has led to a period of great endeavor in this field due to it's remarkable stability and

unusual reactivity. Since it behaves as an aromatic system[11], it readily undergoes a variety of aromatic substitution reactions such as acylation, alkylation, formylation, mercuration and sulfonation.[11,12] In many ways, the chemistry of ferrocene derivatives is very similar to that of benzene derivatives; however, important differences between them arise when the stereochemistry is considered.

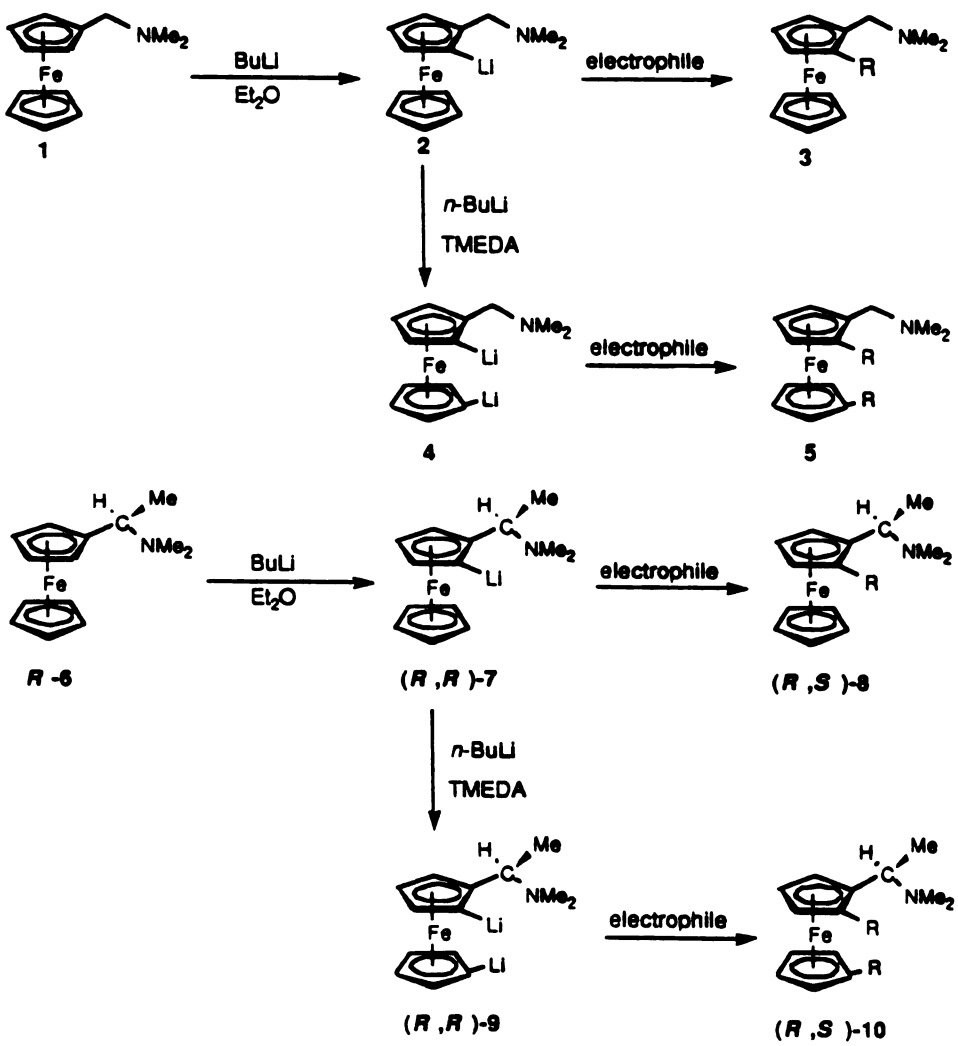
Unlike the benzenoid aromatic compounds, ferrocene derivatives possess planar chirality if one ring carries two different substituents.[13] Optical activity arises because there is no S_n axis.[14,15] Furthermore, the central element of chirality can be assessed by introducing a chiral center into the substituents. Thus, both planar and central chirality can be manifested in disubstituted ferrocenes.

Starting from [dimethylaminomethyl]ferrocene **1** and [1-(dimethylamino)ethyl] ferrocene **6**, a large number of 1,2-disubstituted ferrocenyl derivatives has been prepared by lithiation of **1** and **6** followed by treatment with various electrophiles. (Scheme 1) The chiral starting material **6** was first synthesized and resolved by Gokel and Ugi.[16] It was lithiated with *n*-butyllithium stereoselectively as shown in Eq.1.

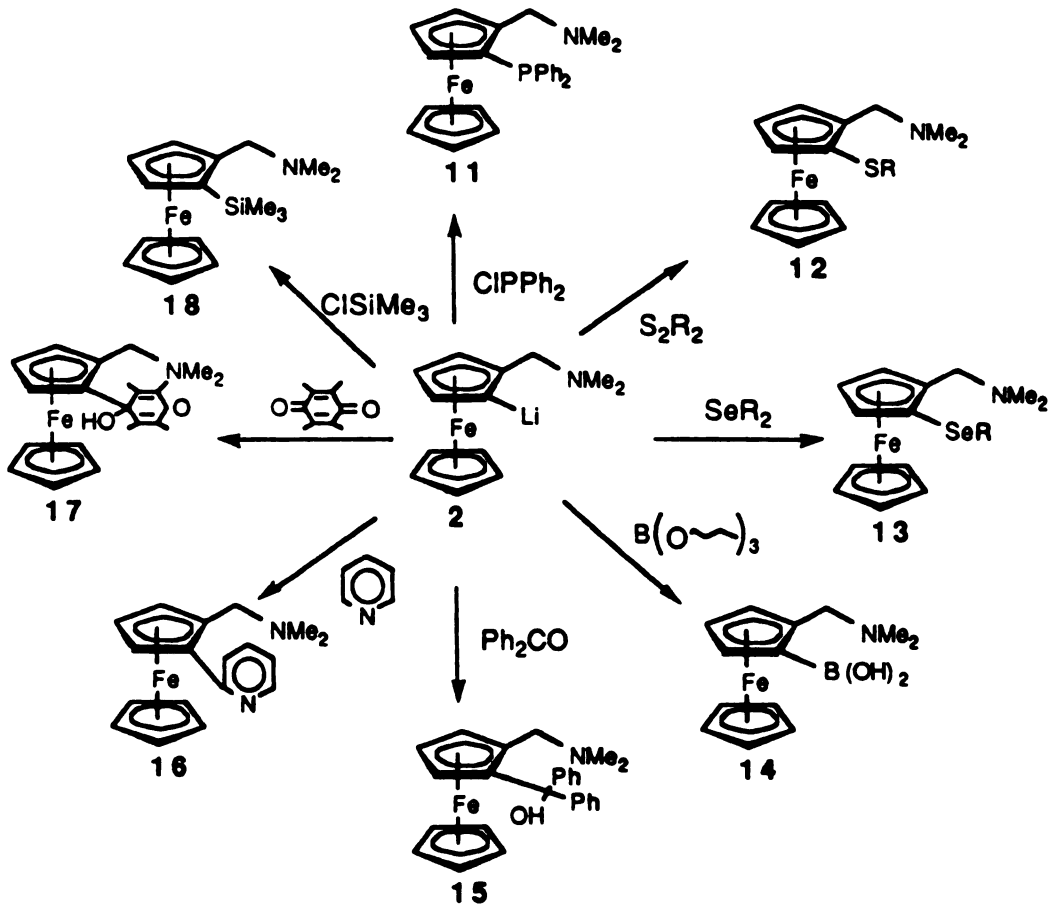


Scheme 2 shows a variety of products derived from the achiral lithiated product **2**. However, these derivatives possess no optical activities.

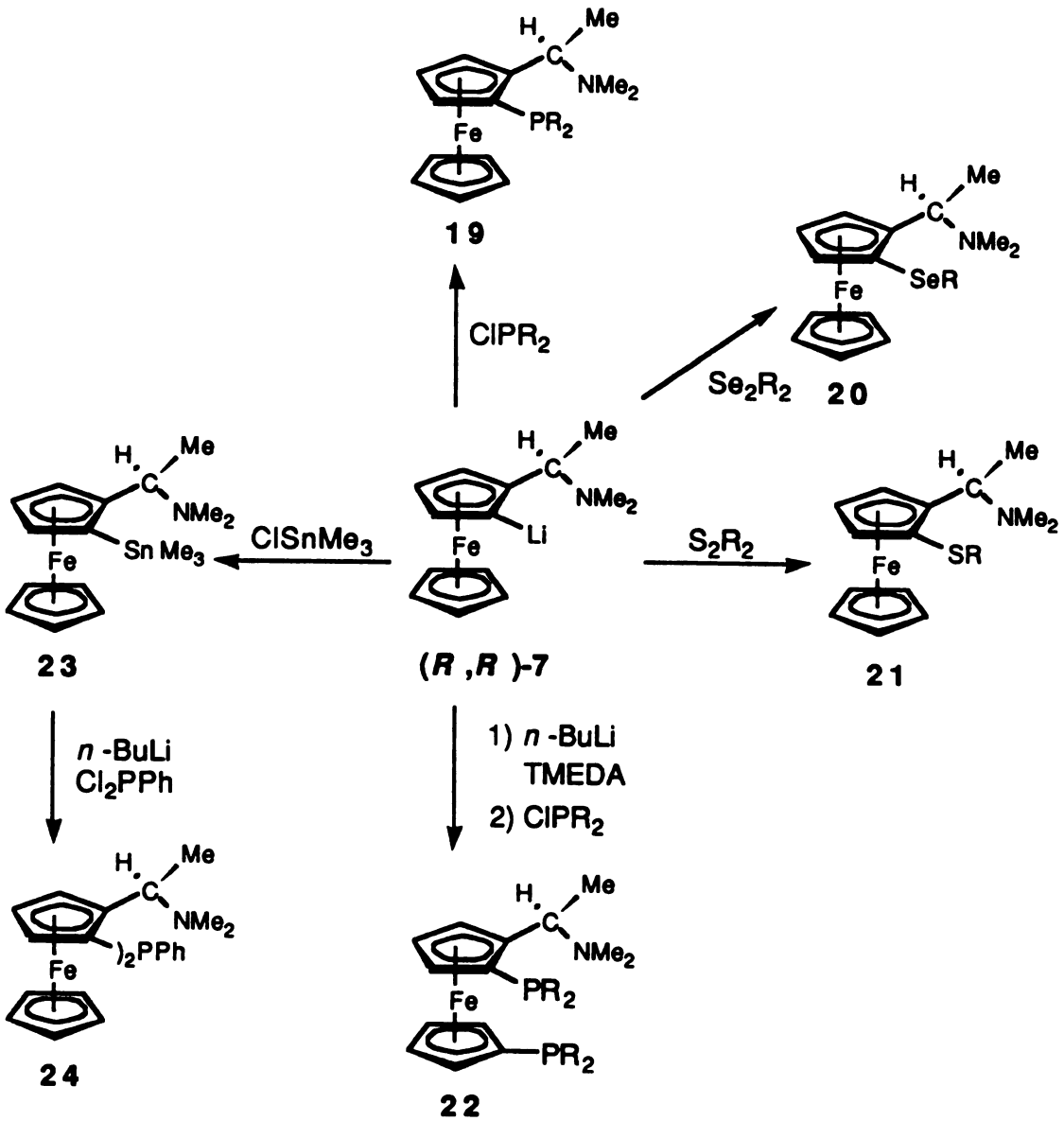
Numerous stereoisomers of **8** and **10** have been prepared[17-33] by the method shown in Scheme 1. Examples of the synthesis of these ferrocenyl compounds are depicted in Scheme 3. These ligands have been used extensively to prepare transition metal complexes found to be useful catalysts for asymmetric hydrogenation of olefins[32,34] and ketones[35], asymmetric hydrosilation of ketones[36], allylic alkylation[37], allylic amination[38], aldol condensation[39], and asymmetric Grignard cross-coupling reactions[40].


NMe2
Fe
BuLi
Et2O
Li
electrophile
R
1
2
3
n-BuLi
TMEDA
4
5
H
C
Me
R-6
(R,R)-7
(R,S)-8
(R,R)-9
(R,S)-10

Scheme 1


NMe2
PPh2
Fe
11
NMe2
SiMe3
Fe
18
ClSiMe3
ClPPh2
S2R2
NMe2
SR
Fe
12
NMe2
Fe HO
O
17
O
O
NMe2
Fe
Li
2
SeR2
NMe2
SeR
Fe
13
B(O~~)3
N
NMe2
Fe
N
16
Ph2CO
NMe2
B (OH) 2
Fe
14
NMe2
Ph
Ph
Fe
OH
15

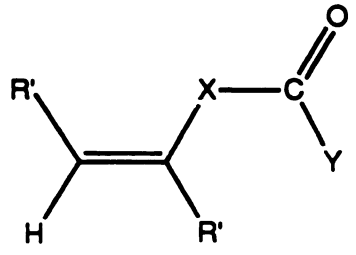
Scheme 2


H
Me
C
NMe2
PR2
Fe
19
ClPR2
Se2R2
SeR
20
Li
(R ,R)-7
ClSnMe3
Sn Me3
23
S2R2
SR
21
n -BuLi
Cl2PPh
24
1) n -BuLi
TMEDA
2) ClPR2
22

Scheme 3

Asymmetric Hydrogenation

The first asymmetric hydrogenation by homogeneous transition-metal catalysts were reported by Knowles and Horner and their co-workers in 1968.[41,42] They used methylphenylpropylphosphine as a chiral ligand with a rhodium catalyst and got 4-15% optical yields in asymmetric hydrogenation of prochiral olefins.[41] Since then, over 100 different ligands have been developed to obtain higher optical yields, mostly in rhodium-catalyzed asymmetric hydrogenations, and some phosphine ligands have been found very effective for hydrogenation of α-(acylamino) acrylic acids, producing α-amino acids of over 90% ee.[43,44] The high stereoselectivity attained has been shown to result from the characteristic structure of the olefin substrates as well as the chiral phosphine ligands.[45] Substrates that can be hydrogenated with high stereoselectivity have the following structural features:

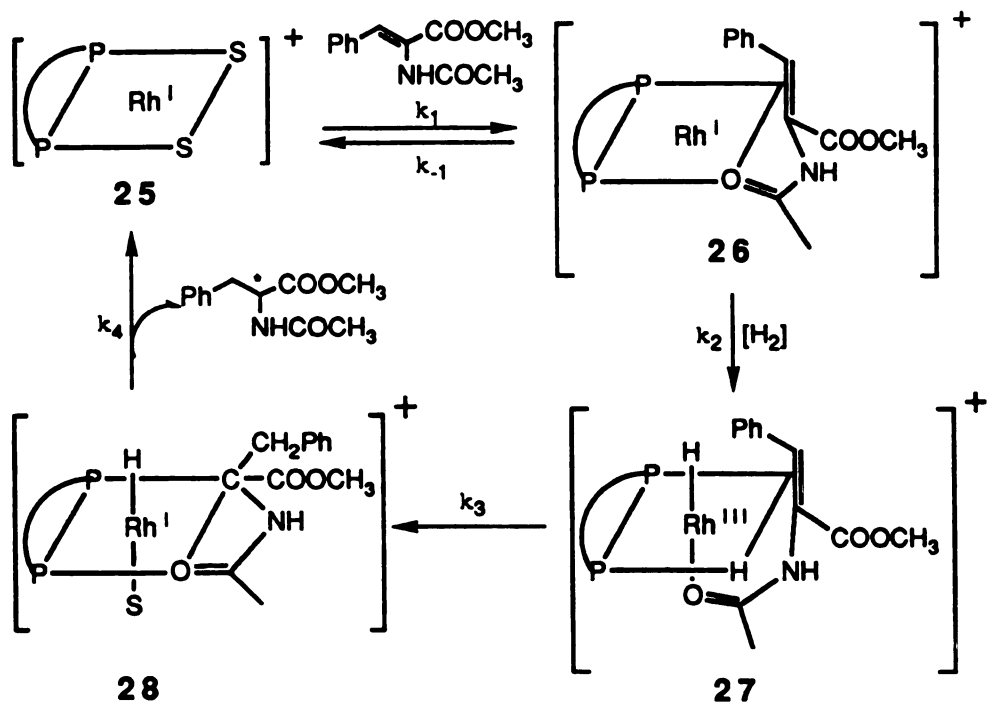


X = NH, O, CH_2
Y = R, OR

The substrate contains a carbonyl group three atoms removed from the double bond. This carbonyl group can coordinate with the rhodium, as well as the double bond, forming a chelated metal-substrate adduct in the diastereomeric transition states.[46] Thus, the stereoselectivity can be enhanced by making the diastereomeric transition state rigid.

Landis and Halpern have studied this hydrogenation both mechanistically and kinetically.[47] The metal-substrate adduct has

been intercepted and characterized by multinuclear NMR and X-ray crystallography.[48,49] The proposed catalytic mechanism is given in the following scheme.



Scheme 4

Chiral ferrocenyl phosphine-based rhodium catalysts have been reported to catalyze the hydrogenation of trisubstituted acrylicacids with up to 98.4% ee.[32] Yet, to date, few asymmetric hydrogenations with sulfur-based catalysts have been reported.[50] It is of great interest to investigate this hydrogenation with similar chiral ferrocenylsulfide ligands.

Homogeneous Selective Hydrogenation

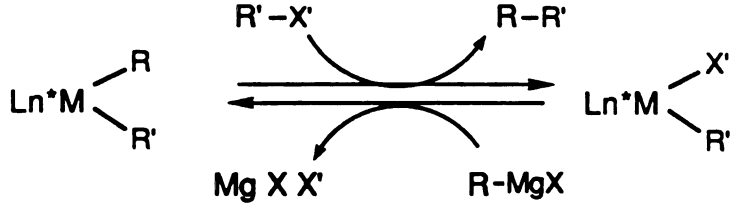
Organic substrate hydrogenation reactions, especially those involving olefins, have been thoroughly studied.[118-123] A large number of transition-metal complexes has been found to serve as "precatalyst" or "catalyst precursor" for catalytic hydrogenations. Though heterogeneous catalysts are usually more convenient for practical applications, homogeneous catalytic systems have been studied in a greater detail because: (a) A homogeneous system is more substrate selective than a heterogeneous system. Examples include exceptionally efficient asymmetric hydrogenation of prochiral olefins. This selectivity is the major advantage of a soluble catalyst. (b) Homogeneous systems usually perform at higher activities. (c) The catalysts can be modified easily. (d) Kinetic and mechanistic studies can be carried out more easily. On the other hand, the major disadvantages of homogeneous hydrogenation catalysts are: (a) their sensitivity to impurities (particularly traces of oxygen), (b) their tendency to cause olefin rearrangements, (c) the difficulty encountered in separating the product from the catalysts, and (d) the catalysts can seldom be recovered after reactions are complete.

The first example of homogeneous catalytic hydrogenation dates from 1938 by Calvin, who studied the reduction of benzoquinone by dissolved hydrogen.[51,52] However, it was not until the discovery of the effective "Wilkinson complex"-$RhCl(PPh_3)_3$[3-] [53] that the field of homogeneous catalysis really developed. A large number of similar transition metal complexes has been found to have high activity as well as excellent regio- or enantioselectivity. Examples include $RuCl_2(PPh_3)_3$[54], $RhH(CO)(PPH_3)_3$[55], $IrCl(CO)(PPh_3)_2$[56], and $[Co(CN)_5]^{3-}$. [57] Besides these mononuclear transition-metal complexes, bimetallic catalysts and metal clusters such as $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4$[58] and $Ni_4(\mu^3\text{-}\eta^2\text{-}RC{\equiv}CR)_3(CNR)_4$ [59] have been used in selective homogeneous hydrogenations.

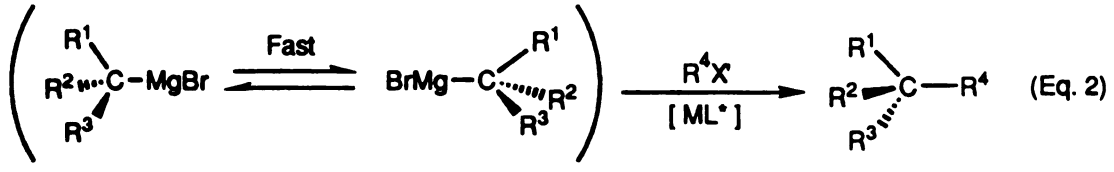
Recently in our laboratory, palladium ferrocenylamine sulfide catalysts have been applied in the selective hydrogenation of a variety of conjugated double bond systems with great success.[124,125]

Asymmetric Grignard Cross-coupling Reactions

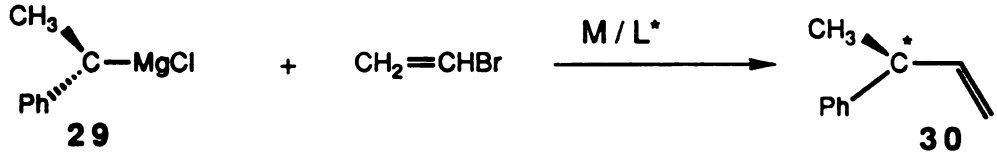
Carbon-carbon bond formation is of great importance in organic synthesis. The use of chiral transition metal catalysts for carbon-carbon bond formation is a most promising strategy, possessing the intrinsic advantages of catalytic asymmetric synthesis. An Asymmetric Grignard cross-coupling reaction was first described by Tamao and Kumada (1972) who used secondary alkyl Grignard reagents with organic halides catalyzed by nickel or palladium complexes.[68] The catalytic cycle proposed consists of a sequence of steps involving a diorganometal complex as an intermediate.[69,70] (Scheme 5) In this scheme L* is an optically active reagent that can bring about kinetic resolution of the Grignard reagent to form an optical active product.(Eq. 2)



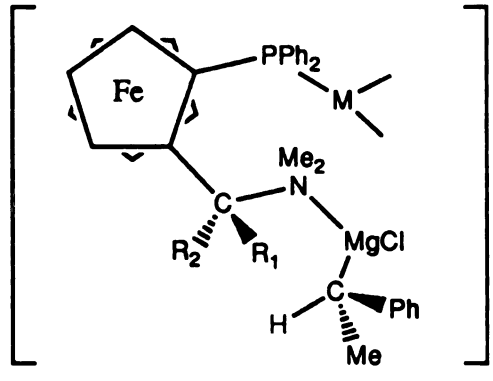
Scheme 5



The coupling reaction of (1-phenylethyl)magnesium chloride with vinyl bromide is, by far, the most extensively studied.[16,71](Eq. 3)

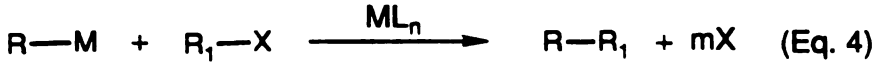


A diastereomeric transition state involving coordination of magnesium to a nitrogen atom was proposed for this reaction, as exemplified by **31**. It has been suggested that the amino group on the phosphine ligand is the first requisite for high stereoselectivity and that the surroundings of the nitrogen atom exert a strong effect on the stereoselectivity.[72]



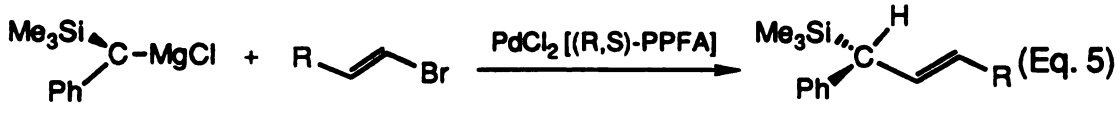
31

Organometallics other than Mg have been employed as Grignard reagents and in some cases give better optical yields. Examples such as Li[73], Al[74], B[75], Sn[76], Zr[77], Zn[78], Hg[79], etc. Eq. 4 exemplify these applications.



M = Ni , Pd
m = Mg, Li, Al, B, Sn, Zr, Zn, Hg
R1 = aryl, alkyl
X= Cl, Br, I, OR, SR, SeR, $OP(O)(OR)_2$

By modifying the alkyl group in the Grignard reagent with silyl groups, optical yield up to 95 % was obtained for the reaction of α-(trimethylsilyl)benzyl magnesium chloride with allylbromides.[80] (Eq. 5)

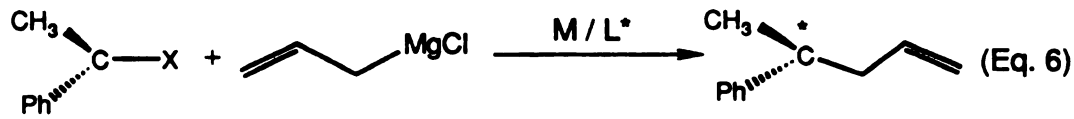


R = H, 95 % ee
R = Me, 85 % ee
R = Ph, 95 % ee

The allylsilanes are useful intermediates in organic synthesis, capable of reacting with a wide range of electrophiles in a regiospecific manner.[81] They can be used for the S_E' reactions to

produce various kinds of optically active compounds by an asymmetric induction provided by these optically active silanes.[80]

An alternative route to the preparation of the optically active products was described by Brubaker and co-workers by treating (1-chloroethyl)benzene with allylmagnesium chloride under the influence of chiral ferrocenylamine sulfide catalysts.[82,126] (Eq. 6)



(Eq. 6)

Optical yields obtained by this method were lower than those obtained by the previous method. (Eq. 3) The catalysts used were the air-stable ferrocenylamine sulfides of group 10 metal halides. The optical yield was found to be dependant on the environment of sulfur atom with more sterically encumbered ligands giving higher ee. Platinum and *in situ* nickel complexes gave better stereoselectivity than their palladium analogues.[126] As an extension of this work, we wish to investigate the influence of the amino substituents on this cross-coupling reaction.

The goal of this work was to modify the amino substituent on the ferrocenylamine thioether ligands; to prepare their palladium complexes and to test their catalytic activities as well as selectivities on hydrogenations of conjugated-dienes and phenylacetylenes. Their efficiencies were compared with those of other ferrocenylthioether complexes prepared previously in this laboratory.[82,83] The applications of the *in situ* prepared rhodium catalysts in asymmetric hydrogenation of prochiral aminoacids as well as the palladium catalysts in asymmetric Grignard cross-coupling of 1-chloroethylbenzene with allylmagnesium chloride were also investigated.

EXPERIMENTAL

Air-sensitive reagents were manipulated in a prepurified argon or nitrogen atmosphere by using standard Schlenk-ware techniques. All solvents were reagent grade and were distilled by standard methods.[84] Dimethylaminomethylferrocene, dialkyl disulfides and dialkylamines were purchased from Aldrich Chemical Company and used as received. (*R*)- and (*S*)-N,N-Dimethyl-1-ferrocenylethylamine was prepared and resolved by Ugi's procedure.[16] 1-Dimethylaminomethyl-2-alkylthioferrocene (**34,35**), (*R,S*)-1-(1-dimethylaminoethyl)-2-alkylthioferrocene ((***R,S***)-**48**,(***R,S***)-**49**) and (*S,R*)-1-(1-dimethylaminoethyl)-2-alkylthioferrocene ((***S,R***)-**47**) were prepared according to a reported procedure.[85]

Hydrogenation substrates were obtained from Aldrich Chemical Co., Alfa Products Co., Columbian Organic Chemical Co. or Columbian Carbon Co. and were purified by standard methods before use. The Grignard Cross-Coupling reagents, 1-phenylethylchloride and allylmagnesium chloride, were purchased from Aldrich Chemical Co.. The ^1H chiral shift reagent, Tris(d,d-dicampholylmethanato) europium(III) [Eu(dcm)$_3$] was purchased from Alfa Products.

^1H and ^{13}C NMR spectra in either chloroform-d_1 or acetone-d_6 were obtained by use of a Varian Gemini-300 spectrometer. 2D COSY spectra were obtained by using a Varian 500 MHz spectrometer. IR spectra were recorded by means of a Nicolet 740 FTIR spectrometer by using neat films between KBr plates for liquid samples and CsI pellets for solid samples. Mass spectra were obtained by use of a Finnigan 4000 instrument with an Incos data system at 70 eV. FAB mass spectra were obtained by using a Jeol JMS-HX110 Mass Spectrometer in a 3-Nitrobenzyl alcohol (NBA) matrix. Circular Dichroism measurements were obtained by a Jasco J-600 CD spectropolarimeter in a 1 cm cell by using $CHCl_3$ as solvent. Optical rotation measurement was performed on a Perkin Elmer 141 polarimeter. Melting points were determined by a Thomas-Hoover

capillary apparatus and are uncorrected. Gas chromatography was carried out by using a Hewlett-Packard 5880A instrument with a 25m GB-1 capillary column. Elemental analyses were performed by Galbraith Laboratories Inc. Knoxville, TN.

A. Preparation of ligands

a. Achiral ligands

(1). 1-Diethylaminomethyl-2-methylthioferrocene (**37**, R=Et, R'=Me, R"=H)

1-Dimethylaminomethyl-2-methylthioferrocene (**34**, 6 g, 20.8 mmol) was placed in a 100-mL round-bottomed flask equipped with a stirring bar and a reflux condenser. After addition of 64 mL acetic anhydride the mixture was heated at 100 °C for 2h. After reaction was complete, excess acetic anhydride was removed under reduced pressure. The crude product was chromatographed on an alumina gel column with hexane/CH_2Cl_2 as eluent. The yield was almost quantitative. A solution of 1 g (3.3 mmol) methylthioferrocenyl ethylacetate **36** and 3.1 mL diethylamine in 30 mL methanol was refluxed for 7 h. The solvent was removed and ether was added. The solution was washed with brine, dried over anhydrous magnesium sulfate, and evaporated. The residue was purified by column chromatography (silica, 10:1 hexane/ether) to give 0.67 g brown oil: yield 64%.

^{1}H NMR δ ppm (J in Hz) : 4.26 (d,C_5H_3); 4.08-4.11 (m,C_5H_3); 4.08 (s,Cp); 3.29-3.78 (dd,CH_2,13.0); 2.30-2.60 (m,αH,NEt_2); 1.00 (t,βH,NEt_2,7.0); 2.24 (s,SMe)

^{13}C NMR δ ppm : 87.4 (s,C_1); 83.4 (s,C_2); 72.0, 70.8, 67.1 (d,C_3,C_4,C_5); 70.0 (s,Cp); 51.0 (t,CH_2); 46.3 (t,αC,NEt_2); 11.7 (q,βC,NEt_2); 20.5(q,SMe)

IR (Nujol, KBr) cm^{-1} : 3093 (ferrocene C-H stretch); 2798-2973 (alkyl C-H stretch); 1448 (ferrocene antisymmetric C-H stretch); 1173,1194

(C-N stretch); 875 (C-H bending perpendicular to the plane of Cp ring); 534 (S-C stretch); 491 (antisymmetric ring-metal stretch)

MS m/e (relative intensity) : 317 (M^+, 11); 270 (M^+-SMe, 35); 245 (M^+-NEt_2, 89); 199 (M^+-SMe-NEt_2, 49); 121 (M^+-C_5H_3-SMe-CH_2NEt_2, 83); 56 (Fe, 100)

Elemental Analysis for $C_{16}H_{23}FeNS$ (Calc.) : C 60.12 (60.57); H 7.26 (7.09); N, 4.42 (4.43)

(2). 1-Diethylaminomethyl-2-ethylthioferrocene (**38**, R=Et, R'=Et, R"=H)

The procedure was the same as that for **37** except that 7.8 g 1-Dimethylaminomethyl-2-ethylthioferrocene (25.7 mmol) was used. The product after being chromatographed on silica gel gave 0.94 g yellow oil. Yield : 34%.

^1H NMR δ ppm (J in Hz) : 4.27 (d,C_5H_3); 4.08-4.12 (m,C_5H_3); 4.06 (s,Cp); 3.22-3.78 (dd,CH_2,13.1); 2.34-2.57 (m,αH,NEt_2); 0.98 (t,βH,NEt_2,7.1); 2.55-2.72 (m,αH,SEt); 1.14 (t,βH,SEt,7.4)

^{13}C NMR δ ppm : 88.4 (s,C_1); 80.3 (s,C_2); 74.1, 71.1, 67.4 (d,C_3,C_4,C_5); 69.9 (s,Cp); 51.0 (t,CH_2); 46.2 (t,αC,NEt_2); 11.6 (q,βC,NEt_2); 30.8 (t,αC,SEt); 20.5 (q,βC,SEt)

IR (Nujol, KBr) cm^{-1} : 3095 (ferrocene C-H stretch); 2796-2968 (alkyl C-H stretch); 1449 (ferrocene antisymmetric C-H stretch); 1175,1197 (C-N stretch); 818 (C-H bending perpendicular to the plane of Cp ring); 534 (S-C stretch); 500 (antisymmetric ring-metal stretch)

MS m/e (relative intensity) : 331 (M^+, 48); 270 (M^+-SEt, 34); 259 (M^+-NEt_2, 44); 199 (M^+-SEt-NEt_2, 18); 121 (M^+-C_5H_3-SEt-CH_2NEt_2, 43); 58 (100); 44 (62)

Elemental Analysis for $C_{17}H_{25}FeNS$ (Calc.) : C 61.76 (61.63); H 7.67 (7.60)

(3). 1-Diethylaminomethyl-2-(4-chlorophenyl)thioferrocene (**39**, R=Et, R'= 4-chlorophenyl, R"=H)

The procedure was the same as that for **37** except that 1.15 g 1-Dimethylaminomethyl-2-(4-chlorophenyl)thioferrocene (3.0 mmol) was used. The product after being chromatographed on silica gel gave yellow crystals. Mp. 91-92 °C. Yield : 20%.

^{1}H NMR δ ppm (J in Hz) : 4.30,4.40,4.45 (m,C_5H_3); 4.16 (s,Cp); 3.33-3.64 (dd,CH_2,13.6); 2.21-2.42 (m,αH,NEt_2); 0.85 (t,βH,NEt_2,7.1); 7.02-7.12 (m,Ph)

^{13}C NMR δ ppm : 90.4 (s,C_1); 76.6 (s,C_2); 76.2, 73.0, 69.6 (d,C_3,C_4,C_5); 70.9 (s,Cp); 51.7 (t,CH_2); 47.0 (t,αC,NEt_2); 12.1 (q,βC,NEt_2); 140.7, 130.8, 129.0, 128.7 (m,Ph)

IR (Nujol, KBr) cm^{-1} : 3096 (ferrocene C-H stretch); 2791-2963 (alkyl C-H stretch); 1455 (ferrocene antisymmetric C-H stretch); 1175,1197 (C-N stretch); 812 (C-H bending perpendicular to the plane of Cp ring); 545 (S-C stretch); 482 (antisymmetric ring-metal stretch)

MS m/e (relative intensity) : 413 (M^+, 18); 341 (M^+-NEt_2, 16); 270 (M^+-SPhCl, 24); 199 (M^+-SPhCl-NEt_2, 20); 121 (M^+-C_5H_3-SPhCl-CH_2NEt_2, 34); 85 (CH_2NEt_2,100)

Elemental Analysis for $C_{17}H_{23}ClFeNS$ (Calc.) : C 61.00 (60.98); H 5.85 (5.85)

(4). 1-Diethylaminomethyl-2-(4-methylphenyl)thioferrocene (**40**, R=Et, R'= 4-methylphenyl, R"=H)

The procedure was the same as that for **37** except that 8.0 g 1-Dimethylaminomethyl-2-(4-methylphenyl)thioferrocene (21.9 mmol) was used. The product after being chromatographed on silica gel gave brown crystals. Mp. 56 °C. Yield : 41%.

^{1}H NMR δ ppm (J in Hz) : 4.27,4.41,4.47 (m,C_5H_3); 4.15 (s,Cp); 3.44-3.66 (dd,CH_2,13.7); 2.33 (q,αH,NEt_2); 0.87 (t,βH,NEt_2,7.1); 6.92-7.04 (dd,Ph); 2.22 (s,Ph-CH_3)

^{13}C NMR δ ppm : 88.2 (s,C_1); 77.4 (s,C_2); 77.0, 71.5, 68.7 (d,C_3,C_4,C_5); 70.1 (s,Cp); 50.4 (t,CH_2); 46.1 (t,αC,NEt_2); 11.5 (q,βC,NEt_2); 136.9, 134.7, 129.2, 126.2 (m,Ph); 20.6 (q,Ph-CH_3)

IR (Nujol, KBr) cm^{-1} : 3095 (ferrocene C-H stretch); 2802-2969 (alkyl C-H stretch); 1451 (ferrocene antisymmetric C-H stretch); 1175,1199 (C-N stretch); 819 (C-H bending perpendicular to the plane of Cp ring); 543 (S-C stretch); 484 (antisymmetric ring-metal stretch)

MS m/e (relative intensity) : 393 (M^+, 28); 321 (M^+-NEt_2, 32); 270 (M^+-$SPhCH_3$, 46); 199 (M^+-$SPhCH_3$-NEt_2, 62); 121 (M^+-C_5H_3-$SPhCH_3$-CH_2NEt_2, 55); 85 (CH_2NEt_2,28); 58 (Et_2, 88); 40 (100)

Elemental Analysis for $C_{18}H_{26}FeNS$ (Calc.) : C 66.86 (67.17); H 7.11 (6.92)

(5). 1-Di-*n*-propylaminomethyl-2-methylthioferrocene (**41**, R=*n*-Pr, R'=Me, R"=H)

The procedure was the same as that for **37** except that 4.0 mL di-*n*-propylamine was used to react with the corresponding sulfidoferrocenyl ethylacetate. The product after being chromatographed on silica gel gave a yellow oil. Yield : 23%.

^1H NMR δ ppm (J in Hz) : 4.10,4.26 (d,C_5H_3); 4.07 (s,Cp); 3.26-3.78 (dd,CH_2,13.2); 2.17-2.43 (m,αH,NEt_2); 1.30-1.50 (m,βH,NEt_2); 0.81 (t,γH,7.3); 2.24 (s,SMe)

^{13}C NMR δ ppm : 87.4 (s,C_1); 83.3 (s,C_2); 72.1, 70.9, 67.1 (d,C_3,C_4,C_5); 69.8 (s,Cp); 55.5 (t,CH_2); 52.2 (t,αC,NEt_2); 20.0 (m,βC,NEt_2); 11.7 (q,γC,NEt_2); 20.4 (q,SMe)

IR (Nujol, KBr) cm^{-1} : 3095 (ferrocene C-H stretch); 2798-2958 (alkyl C-H stretch); 1457 (ferrocene antisymmetric C-H stretch); 1173,1187 (C-N stretch); 819 (C-H bending perpendicular to the plane of Cp ring); 528 (S-C stretch); 482 (antisymmetric ring-metal stretch)

MS m/e (relative intensity) : 345 (M^+, 19); 298 (M^+-SMe, 8); 245 (M^+-NPr_2, 100); 199 (M^+-SMe-NPr_2, 13); 121 (M^+-C_5H_3-SMe-CH_2NPr_2, 44); 56 (Fe, 100); 43 (C_3H_7, 88)

Elemental Analysis for $C_{18}H_{27}FeNS$ (Calc.) : C 62.21 (62.61); H 7.86 (7.88)

(6). 1-Di-*n*-propylaminomethyl-2-ethylthioferrocene (**42**, R=*n*-Pr, R'=Et, R"=H)

The procedure was the same as that for **37** except that 1.0 g ethylthioferrocenyl ethylacetate was used. The product after being chromatographed on silica gel gave a yellow oil. Yield : 55%.

^1H NMR δ ppm (J in Hz) : 4.11,4.28 (d,C_5H_3); 4.07 (s,Cp); 3.20-3.78 (dd,CH_2,13.2); 2.18-2.43 (m,αH,N-*n*-Pr_2); 1.32-1.50 (m,βH,N-*n*-Pr_2); 0.80 (t,γH,N-*n*-Pr_2,7.3); 2.53-2.77 (m,αH,SEt); 1.14 (t,βH,SEt,7.4)

^{13}C NMR δ ppm : 88.5 (s,C_1); 80.1 (s,C_2); 74.3, 71.3, 67.2 (d,C_3,C_4,C_5); 69.8 (s,Cp); 55.6 (t,CH_2); 52.5 (t,αC,NEt_2); 20.0 (m,βC,NEt_2); 11.7 (q,γC,NEt_2); 30.9 (t,αC,SEt); 14.5 (q,βC,SEt)

IR (Nujol, KBr) cm^{-1} : 3095 (ferrocene C-H stretch); 2798-2958 (alkyl C-H stretch); 1456 (ferrocene antisymmetric C-H stretch); 1172,1187 (C-N stretch); 819 (C-H bending perpendicular to the plane of Cp ring); 522 (S-C stretch); 478 (antisymmetric ring-metal stretch)

MS m/e (relative intensity) : 359 (M^+, 43); 298 (M^+-SEt, 29); 259 (M^+-N-*n*-Pr_2, 100); 199 (M^+-SEt-N-*n*-Pr_2, 13); 105 (14); 72 (53)

Elemental Analysis for $C_{19}H_{29}FeNS$ (Calc.) : C 62.83 (63.50); H 8.07 (8.07)

(7). 1-Di-*i*-propylaminomethyl-2-ethylthioferrocene (**43**, R=*i*-Pr, R'=Et, R"=H)

The procedure was the same as that for **37** except that 4.2 mL isopropylamine was used. The product after being chromatographed on silica gel gave a yellow oil. Yield : 52%.

^{1}H NMR δ ppm (J in Hz) : 4.08,4.28 (d,C_5H_3); 4.08 (s,Cp); 3.38-3.74 (dd,CH_2,13.5); 3.02 (m,αH,N-*i*-Pr_2); 1.00 (dd,βH,N-*i*-Pr_2,4.8); 2.50-2.73 (m,αH,SEt); 1.13 (t,βH,SEt,6.9)

^{13}C NMR δ ppm : 90.7 (s,C_1); 79.4 (s,C_2); 74.3, 71.5, 66.8 (d,C_3,C_4,C_5); 69.8 (s,Cp); 42.5 (t,CH_2); 46.6 (t,αC,N-*i*-Pr_2); 21.1,19.9 (m,βC,N-*i*-Pr_2); 31.0 (t,αC,SEt); 14.6 (q,βC,SEt)

IR (Nujol, KBr) cm^{-1} : 3095 (ferrocene C-H stretch); 2813-2964 (alkyl C-H stretch); 1457 (ferrocene antisymmetric C-H stretch); 1179,1200 (C-N stretch); 818 (C-H bending perpendicular to the plane of Cp ring); 533 (S-C stretch); 489 (antisymmetric ring-metal stretch)

MS m/e (relative intensity) : 359 (M^+, 6); 298 (M^+-SEt, 4); 259 (M^+-N-*i*-Pr_2, 47); 121 (M^+-SEt-CH_2N-*i*-Pr_2-C_5H_3, 26); 86 (N-*i*-Pr_2,44); 44 (100)

Elemental Analysis for $C_{19}H_{29}FeNS$ (Calc.) : C 63.18 (63.50); H 8.07 (8.07)

(8). 1-Di-*i*-butylaminomethyl-2-ethylthioferrocene (**44**, R=*i*-Bu, R'=Et, R"=H)

The procedure was the same as that for **37** except that 5.2 mL isobutylamine was used. The product after being chromatographed on silica gel gave a brown oil. Yield : 25%.

^{1}H NMR δ ppm (J in Hz) : 4.11,4.29 (d,C_5H_3); 4.06 (s,Cp); 3.17-3.69 (dd,CH_2,13.2); 1.93-2.14 (m,αH,N-*i*-Bu_2);1.71 (m,βH,N-*i*-Bu_2); 0.78-0.84 (dd,γH,N-*i*-Bu_2,6.5); 2.50-2.73 (m,αH,SEt); 1.15 (t,βH,SEt,7.4)

^{13}C NMR δ ppm : 88.2 (s,C_1); 80.0 (s,C_2); 74.2, 71.5, 67.3 (d,C_3,C_4,C_5); 69.8 (s,Cp); 53.5 (t,CH_2); 30.9 (t,αC,N-*i*-Bu_2); 26.2 (m,βC,N-*i*-Bu_2); 20.8,20.7(q,γC,N-*i*-Bu_2); 36.6 (t,αC,SEt); 26.2 (q,βC,SEt)

IR (Nujol, KBr) cm^{-1} : 3096 (ferrocene C-H stretch); 2795-2954 (alkyl C-H stretch); 1458 (ferrocene antisymmetric C-H stretch); 1171,1195 (C-N stretch); 820 (C-H bending perpendicular to the plane of Cp ring); 531 (S-C stretch); 492 (antisymmetric ring-metal stretch)

MS m/e (relative intensity) : 387 (M^+, 7); 326 (M^+-SEt, 1); 259 (M^+-CH_2N-*i*-Bu_2, 100); 121 (M^+-SEt-CH_2N-*i*-Bu_2-C_5H_3, 35); 56 (Fe,38); 41 (93)

Elemental Analysis for $C_{21}H_{33}FeNS$ (Calc.) : C 63.91 (65.11); H 8.31 (8.52)

(9). 1-Diphenylaminomethyl-2-*p*-chlorophenylthioferrocene (**45**, R=Ph, R'= *p*-chlorophenyl, R"=H)

The procedure was the same as that for **37** except that 1.0 g 1-Dimethylaminomethyl-2-(4-chlorophenyl)thioferrocene (21.9 mmol) and 0.5 g diphenylamine was used. The product after being chromatographed on silica gel gave brown crystals. Mp. 118 °C. Yield : 22%.

^1H NMR δ ppm (J in Hz) : 4.32,4.43,4.46 (m,C_5H_3); 4.06 (s,Cp); 4.54-5.09 (dd,CH_2,16.7); 6.87-6.93 (t,NPh_2); 6.94-6.99 (d,NPh_2,PhCl); 7.06-7.11 (d,PhCl); 7.06-7.12 (t,NPh)

^{13}C NMR δ ppm : 90.2 (s,C_1); 74.5 (s,C_2); 75.7, 72.3, 69.5 (d,C_3,C_4,C_5); 71.3 (s,Cp); 51.3 (t,CH_2); 149, 130.1, 122.3, 122.1 (m,NPh_2); 140.1, 131.1, 129.6, 128.1 (m,Ph-Cl)

IR (Nujol, KBr) cm^{-1} : 3017 (ferrocene C-H stretch); 1476,1497 (ferrocene antisymmetric C-H stretch); 1217,1256 (C-N stretch); 754 (C-H bending perpendicular to the plane of Cp ring); 698,670 (S-C stretch); 482 (antisymmetric ring-metal stretch)

MS m/e (relative intensity) : 509 (M^+, 53); 341 (M^+-NPh_2, 100); 306 (M^+-NPh_2-Cl, 10), 275 (M^+-NPh_2-Ph, 11); 249 (184 + C_5H_5, 14), 184 (M^+-CH_2NPh-SPhCl, 8); 121 (Fe+ C_5H_5, 8)

(10). 1-methylethylaminomethyl-2-methylthioferrocene (**46**, R=NMeEt, R'= Me, R"=H)

To 1 g (3.3 mmol) of **36** was added, via syringe, 20 mL 1.0 M HCl in diethylether at 0 °C.[147] The solution was allowed to warm to room temperature and stirred for a further 3h. The solvent was

removed by evacuation and a fresh 20 mL portion of dried ether was added to the residue. To this solution was added, via syringe, a mixture of 2.5 mL Methylethylamine in 20 mL ether at 0 °C. After being stirred for 3h, 10 mL of saturated aqueous $NaHCO_3$ was added. The resulting organic layer and ether extracts from the aqueous layer were combined, washed, dried and evaporated. The product was purified by column chromatography to give 0.22 g (65% overall yield) 1-methylethylaminomethyl-2-methylthioferrocene.

^1H NMR δ ppm (J in Hz) : 4.29 (d,2H,C_5H_3); 4.13 (m,1H,C_5H_3); 4.08 (s,Cp); 3.26-3.70 (dd,CH_2,12.9); 2.40 (dq,αH,NEt,7.2); 1.06 (t,βH,NEt,7.2); 2.15 (s, NMe); 2.24 (s,SMe)

^{13}C NMR δ ppm : 86.2 (s,C_1); 83.7 (s,C_2); 71.8, 70.6, 67.4 (d,C_3,C_4,C_5); 69.9 (s,Cp); 55.0 (t,CH_2); 51.0 (t,αC,NEt); 12.6 (q,βC,NEt); 41.2 (q,NMe); 20.3(q,SMe)

IR (Nujol, KBr) cm^{-1} : 3084 (ferrocene C-H stretch); 2781-2971 (alkyl C-H stretch); 1450 (ferrocene antisymmetric C-H stretch); 1175,1190 (C-N stretch); 809 (C-H bending perpendicular to the plane of Cp ring); 527 (S-C stretch); 492 (antisymmetric ring-metal stretch)

MS m/e (relative intensity) : 317 (M^+, 11); 270 (M^+-SMe, 35); 245 (M^+-NEt_2, 89); 199 (M^+-SMe-NEt_2, 49); 121 (M^+-C_5H_3-SMe-CH_2NEt_2, 83); 56 (Fe, 100)

b. Chiral ligands

(1). (*S*,*R*)-1-(1-Diethylaminoethyl)-2-methylthioferrocene ((*S*,*R*)-**50**,R=Et, R'=Me, R"=Me)

To 1.96 g (*S*,*R*)-1-(1-Dimethylaminoethyl)-2-methylthio ferrocene (6.47 mmol) was added 4.04 mL acetic anhydride; the mixture was heated at 50 °C for 2h. Excess acetic anhydride was removed under reduced pressure. The crude product was chromatographed on a silica gel column with hexane/CH_2Cl_2 as eluent to give 1.710 g (83.1% yield) methylthioferrocenyl ethylacetate. A solution of 0.93 g (2.0 mmol) methylthioferrocenyl ethylacetate in 2.5 mL methanol was added to 3.03 mL $HNEt_2$ and then stirred at room temperature for 24 h. The work up procedure was similar to that for the achiral ligands. The residue was purified by chromatography on a silica gel to give 0.44 g brown oil. Yield : 82%.

^1H NMR δ ppm (J in Hz) : 4.27,4.21,4.11 (m,C_5H_3); 4.07 (s,Cp); 4.25 (q,C<u>H</u>-CH_3,6.8); 1.27 (d,C<u>H</u>$_3$-CH,6.7); 2.22-2.54 (m,αH,NEt_2); 1.00 (t,βH,NEt_2,7.1); 2.29 (s,SMe)

^{13}C NMR δ ppm : 94.2 (s,C_1); 82.3 (s,C_2); 72.3, 68.0, 66.3 (d,C_3,C_4,C_5); 69.8 (s,Cp); 52.5 (d,<u>C</u>H-CH_3); 10.8 (q,CH-<u>C</u>H$_3$); 43.2 (t,αC,NEt_2); 14.2 (q,βC,NEt_2); 20.6 (q,SMe)

IR (Nujol, KBr) cm^{-1} : 3095 (ferrocene C-H stretch); 2808-2970 (alkyl C-H stretch); 1449 (ferrocene antisymmetric C-H stretch); 1176,1199 (C-N stretch); 818 (C-H bending perpendicular to the plane of Cp ring); 543 (S-C stretch); 509 (antisymmetric ring-metal stretch)

MS m/e (relative intensity) : 331 (M^+, 8); 258 (M^+-NEt_2, 66); 243 (M^+-Me-NEt_2, 31); 121 (M^+-C_5H_3-SMe-$CHCH_3NEt_2$, 72); 58 (Et_2, 100); 56 (Fe, 54)

Elemental Analysis for $C_{17}H_{25}FeNS$ (Calc.) : C 61.49 (61.63); H 7.46 (7.60)

(2). (*S*,*R*)-1-(1-Di-*n*-propylaminoethyl)-2-ethylthioferrocene ((*S*,*R*)-**51**, R=*n*-Pr, R'=Et, R"=Me)

The procedure was the same as that for (*S*,*R*)-**50** except that 4.0 mL Di-*n*-propylamine was used. The product after being chromatographed on silica gel gave a brown oil. Yield : 53%.

^{1}H NMR δ ppm (J in Hz) : 4.26,4.20,4.10 (m,C_5H_3); 4.06 (s,Cp); 4.16 (q,C<u>H</u>-CH_3); 1.27 (d,C<u>H</u>$_3$-CH,6.8); 2.18-2.38 (m,αH,N-*n*-Pr_2); 1.20-1.52 (m,βH,N-*n*-Pr_2,7.1); 0.73 (t,γH,N-*n*-Pr_2,7.1); 2.28 (s,SMe)

^{13}C NMR δ ppm : 94.1 (s,C_1); 82.7 (s,C_2); 71.6, 67.9, 66.3 (d,C_3,C_4,C_5); 69.8 (s,Cp); 53.2 (d,<u>C</u>H-CH_3); 11.8 (q,CH-<u>C</u>H$_3$); 52.5 (t,αC,N-*n*-Pr_2); 22.2 (t,βC,N-*n*-Pr_2); 10.8 (q,γC,N-*n*-Pr_2); 20.3 (q,SMe)

IR (Nujol, KBr) cm^{-1} : 3095 (ferrocene C-H stretch); 2808-2958 (alkyl C-H stretch); 1456 (ferrocene antisymmetric C-H stretch); 1174,1185 (C-N stretch); 818 (C-H bending perpendicular to the plane of Cp ring); 521 (S-C stretch); 512 (antisymmetric ring-metal stretch)

MS m/e (relative intensity) : 359 (M^+, 2); 258 (M^+-N-*n*-Pr_2, 100); 243 (M^+-Me-N-*n*-Pr_2, 50); 121 (M^+-C_5H_3-SMe-$CHCH_3$N-n-Pr_2, 69); 72 (86); 56 (Fe, 48); 43(C_3H_7, 50)

Elemental Analysis for $C_{19}H_{29}FeNS$ (Calc.) : C 62.85 (63.50); H 7.98 (8.07)

(3). (*R*,*S*)-1-(1-Diethylaminoethyl)-2-ethylthioferrocene ((*R*,*S*)-**52**, R=Et, R'=Et, R"=Me)

The procedure was the same as that for (*S*,*R*)-**50** except that (*R*,*S*)-1-(1-Dimethylaminoethyl)-2-ethylthioferrocene (6.47 mmol) was used. The product after being chromatographed on silica gel gave a brown oil. Yield : 64%

^{1}H NMR δ ppm (J in Hz) : 4.30,4.21,4.14 (m,C_5H_3); 4.07 (s,Cp); 4.24 (q,C<u>H</u>-CH_3,7.0); 1.26 (d,C<u>H</u>$_3$-CH,6.1); 2.26,2.47 (m,αH,NEt_2); 0.92 (t,βH,NEt_2,7.1); 2.60,2.90 (m,αH,SEt); 1.13 (t,βH,SEt,7.5)

^{13}C NMR δ ppm : 96.0 (s,C_1); 77.6 (s,C_2); 76.1, 68.4, 66.6 (d,C_3,C_4,C_5); 69.9 (s,Cp); 52.3 (d,$\underline{C}H$-CH_3); 10.2 (q,CH-$\underline{C}H_3$); 43.2 (t,αC,NEt_2); 14.3 (q,βC,NEt_2); 30.6 (t,αC,SEt); 14.3 (q,βC,SEt)

IR (Nujol, KBr) cm^{-1} : 3095 (ferrocene C-H stretch); 2806-2970 (alkyl C-H stretch); 1449 (ferrocene antisymmetric C-H stretch); 1175,1198 (C-N stretch); 819 (C-H bending perpendicular to the plane of Cp ring); 542 (S-C stretch); 509 (antisymmetric ring-metal stretch)

MS m/e (relative intensity) : 345 (M^+, 6); 272 (M^+-NEt_2, 30); 243 (M^+-Me-NEt_2, 29); 121 (M^+-C_5H_3-SMe-$CHCH_3NEt_2$, 68); 58 (Et_2, 100); 56 (Fe, 47)

Elemental Analysis for $C_{18}H_{27}FeNS$ (Calc.) : C 62.59 (62.61); H 7.98 (7.88)

(4). (*R*,*S*)-1-(1-Di-*n*-propylaminoethyl)-2-ethylthioferrocene ((*R*,*S*)-**53**, R=*n*-Pr, R'=Et, R"=Me)

The procedure was the same as that for (*R*,*S*)-**52** except that 4.0 mL Di-*n*-propylamine was used. The product after being chromatographed on silica gel gave a brown oil. Yield : 16%.

^1H NMR δ ppm (J in Hz) : 4.29,4.19,4.12 (m,C_5H_3); 4.06 (s,Cp); 4.15 (q,$C\underline{H}$-CH_3); 1.26 (d,$C\underline{H}_3$-CH,6.8); 2.13-2.38 (m,αH,N-*n*-Pr_2); 1.21,1.40 (m,βH,N-*n*-Pr_2,7.1); 0.72 (t,γH,N-*n*-Pr_2,7.3); 2.60,2.83 (m,αH,SEt); 1.13 (t,βH,SEt,7.4)

^{13}C NMR δ ppm : 95.1 (s,C_1); 78.9 (s,C_2); 74.6, 68.3, 66.6 (d,C_3,C_4,C_5); 69.9 (s,Cp); 53.1 (d,$\underline{C}H$-CH_3); 11.7 (q,CH-$\underline{C}H_3$); 52.6 (t,αC,N-*n*-Pr_2); 22.3 (t,βC,N-*n*-Pr_2); 10.5 (q,γC,N-*n*-Pr_2); 30.7 (t,αC,SEt); 14.4 (q,βC,SEt)

IR (Nujol, KBr) cm^{-1} : 3098 (ferrocene C-H stretch); 2809-2961 (alkyl C-H stretch); 1456 (ferrocene antisymmetric C-H stretch); 1173,1185 (C-N stretch); 820 (C-H bending perpendicular to the plane of Cp ring); 543 (S-C stretch); 505 (antisymmetric ring-metal stretch)

MS m/e (relative intensity) : 373 (M^+, 2); 272 (M^+-N-*n*-Pr_2, 40); 243 (M^+-Me-N-*n*-Pr_2, 32); 121 (M^+-C_5H_3-SEt-$CHCH_3$N-*n*-Pr_2, 50); 72 (100); 56 (Fe, 33)

Elemental Analysis for $C_{20}H_{31}FeNS$ (Calc.) : C 63.69 (64.34); H 8.22 (8.37)

(5). (*R*,*S*)-1-(1-Diethylaminoethyl)-2-isopropylthioferrocene ((***R*,*S*)-54**, R=Et, R'=*i*-propyl, R"=Me)

The procedure was the same as that for (***R*,*S*)-52** except that (*R*,*S*)-1-(1-Dimethylaminoethyl)-2-isopropylthioferrocene (7 mmol) was used. The product after being chromatographed on silica gel gave a brown oil. Yield : 26%

^{1}H NMR δ ppm (J in Hz) : 4.28,4.21,4.14 (m,C_5H_3); 4.06 (s,Cp); 4.24 (q,C<u>H</u>-CH_3,6.7); 1.24 (d,C<u>H</u>$_3$-CH,6.8); 2.19-2.30, 2.43-2.56 (m,αH,NEt_2); 0.89 (t,βH,NEt_2,7.1); 3.52 (m,αH,SEt); 1.15,1.05 (d,βH,SEt,6.5)

^{13}C NMR δ ppm : 96.0 (s,C_1); 77.6 (s,C_2); 76.1, 68.4, 66.7 (d,C_3,C_4,C_5); 69.9 (s,Cp); 52.2 (d,<u>C</u>H-CH_3); 9.70 (q,CH-<u>C</u>H$_3$); 43.2 (t,αC,NEt_2); 14.3 (q,βC,NEt_2); 38.2 (d,αC,S-*i*-Pr); 23.2,21.7 (q,βC,S-*i*-Pr)

IR (Nujol, KBr) cm^{-1} : 3096 (ferrocene C-H stretch); 2806-2963 (alkyl C-H stretch); 1451 (ferrocene antisymmetric C-H stretch); 1154,1169 (C-N stretch); 822 (C-H bending perpendicular to the plane of Cp ring); 542 (S-C stretch); 507 (antisymmetric ring-metal stretch)

MS m/e (relative intensity) : 359 (M^+, 4); 286 (M^+-NEt_2, 100); 243 (M^+-C_3H_7-NEt_2, 63); 121 (M^+-C_5H_3-S-*i*-Pr-CH-CH_3NEt_2, 56); 58 (Et_2, 55); 43 (C_3H_7, 74)

Elemental Analysis for $C_{19}H_{29}FeNS$ (Calc.) : C 63.67 (63.50); H 8.11 (8.07)

(6). (*R*,*S*)-1-(1-Di-*n*-propylaminoethyl)-2-isopropylthioferrocene
((*R*,*S*)-**55** ,R=*n*-Pr, R'= *i*-Pr, R"= Me)

The procedure was the same as that for (*R*,*S*)-**54** except that 4.0 mL Di-*n*-propylamine was used. The product after being chromatographed on silica gel gave a brown oil. Yield : 30%.

^{1}H NMR δ ppm (J in Hz) : 4.29,4.22,4.15 (m,C_5H_3); 4.06 (s,Cp); 4.19 (q,C<u>H</u>-CH_3,6.9); 1.27 (d,C<u>H</u>$_3$-CH,6.9); 2.14-2.40 (m,αH,N-*n*-Pr_2); 1.10-1.49 (m,βH,N-*n*-Pr_2,); 0.72 (t,γH,N-*n*-Pr_2,7.4); 3.42 (m,αH,S-*i*-Pr); 1.15,1.07 (d,βH,S-*i*-Pr,6.9)

^{13}C NMR δ ppm : 96.0 (s,C_1); 76.0 (s,C_2); 70.6, 68.7, 66.8 (d,C_3,C_4,C_5); 69.9 (s,Cp); 53.1 (d,<u>C</u>H-CH_3); 11.8 (q,CH-<u>C</u>H$_3$); 52.6 (t,αC,N-*n*-Pr_2); 22.3 (t,βC,N-*n*-Pr_2); 10.1 (q,γC,N-*n*-Pr_2); 38.2 (d,αC,S-*i*-Pr); 23.3,21.7 (q,βC,S-*i*-Pr)

IR (Nujol, KBr) cm^{-1} : 3098 (ferrocene C-H stretch); 2808-2961 (alkyl C-H stretch); 1453 (ferrocene antisymmetric C-H stretch); 1156,1171 (C-N stretch); 822 (C-H bending perpendicular to the plane of Cp ring); 542 (S-C stretch); 507 (antisymmetric ring-metal stretch)

MS m/e (relative intensity) : 387 (M^+, 2); 286 (M^+-N-*n*-Pr_2, 81); 243 (M^+-C_3H_7-N-*n*-Pr_2, 57); 178 (M+-C_5H_5-N-*n*-Pr_2-C_3H_7, 29); 121 (M^+-C_5H_3-S-*i*-Pr-CH-CH_3N-*n*-Pr_2, 97); 56 (Fe, 33); 43 (C_3H_7, 33)

Elemental Analysis for $C_{21}H_{33}FeNS$ (Calc.) : C 64.62 (65.11); H 8.22 (8.52)

c. Synthesis of Ferrocenylsulfide Ligand

1. 1-Methylthio-2-ethylthiomethylferrocene **56**.

To 1 g (3.3 mmol) of **36** was added, via syringe, 20 mL 1.0 M HCl in diethylether at 0 °C.[104] The solution was allowed to warm to room temperature and stirred for a further 3h. The solvent was removed by evacuation and a fresh 20 mL portion of dried ether was added to the residue. To this solution was added, via syringe, a mixture of 2.5 mL ethanethiol and 80 mg Na in 20 mL ether at 0 °C. After being stirred for 3h, 10 mL of saturated aqueous $NaHCO_3$ was added. The resulting organic layer and ether extracts from the aqueous layer were combined, washed, dried and evaporated. The product was purified by column chromatography to give 0.85 g (84% overall yield) 1-methylthio-2-ethylthiomethylferrocene **56**.

^1H NMR δ ppm (J in Hz) : 4.31,4.26,4.13 (m,C_5H_3); 4.10 (s,Cp); 3.53-3.81 (dd,CH_2,7.2); 2.52 (q,αH,SEt,7.1); 1.24 (t,βH,SEt,7.2); 2.25 (s,SMe)

^{13}C NMR δ ppm : 88.0 (s,C_1); 81.8 (s,C_2); 72.8, 69.3, 67.4 (d,C_3,C_4,C_5); 70.0 (s,Cp); 29.9 (t,CH_2); 26.2 (t,αC,SEt); 14.6 (q,βC,SEt); 20.9(q,SMe)

IR (Nujol, KBr) cm^{-1} : 3096 (ferrocene C-H stretch); 2820-2965 (alkyl C-H stretch); 1447 (ferrocene antisymmetric C-H stretch); 822 (C-H bending perpendicular to the plane of Cp ring); 532 (S-C stretch); 483 (antisymmetric ring-metal stretch)

Elemental Analysis for $C_{14}H_{18}FeS_2$ (Calc.) : C 54.77 (54.90); H 5.92 (5.92)

B. Preparation of palladium and platinum complexes

(1). 1-Diethylaminomethyl-2-methylthioferrocenyl Palladium Chloride (57, R=Me, R'=Et, R"=H)

To a benzene solution of 0.2 g $(PhCN)_2PdCl_2$ was added 0.17 g 1-Diethylaminomethyl-2-methylthioferrocene. The mixture was stirred overnight and the resulting red precipitate was collected by filtration and washed with cold benzene and ether to give 0.236 g product. Pure crystals were obtained by recrystallization from CH_2Cl_2/hexane. Mp. 154-156 °C; yield : 87% (based on $(PhCN)_2PdCl_2$)

^1H NMR δ ppm (J in Hz) : 4.52,4.41,4.32 (m,C_5H_3); 4.24 (s,Cp); 2.90,3.95 (d,CH_2,13.7); 3.87,3.28,2.67,2.30 (m,αH,NEt_2); 1.00,1.95 (t,βH,NEt_2,7.1); 2.75 (s,SMe)

IR (CsI pellet) cm^{-1} : 3088 (ferrocene C-H stretch); 2969-2932 (alkyl C-H stretch); 1458,1408 (ferrocene antisymmetric C-H stretch); 1108,1088 (C-N stretch); 833 (C-H bending perpendicular to the plane of Cp ring); 633 (S-C stretch); 494 (antisymmetric ring-metal stretch); 511 (Pd-N stretch); 322 (Pd-Cl stretch); 291 (Pd-S stretch)

MS m/e (relative intensity) : 317 (M^+-$PdCl_2$, 11); 270 (M^+-$PdCl_2$-SMe, 35); 245 (M^+-$PdCl_2$-NEt_2, 89); 199 (M^+-$PdCl_2$-SMe-NEt_2, 49); 121 (M^+-$PdCl_2$-C_5H_3-SMe-CH_2NEt_2, 83)

Elemental Analysis for $C_{16}H_{23}FeNSPdCl_2$ (Calc.) : C 38.82 (38.86); H 4.67 (4.69)

(2). 1-Diethylaminomethyl-2-ethylthioferrocenyl Palladium Chloride (58, R=Et, R'=Et, R"=H)

The procedure was the same as that for 57 except that 0.18 g 1-Diethylaminomethyl-2-ethylthioferrocene was used. The product after crystallization gave 0.181 g dark red crystals. Mp. 110-112 °C; yield : 65%.

^{1}H NMR δ ppm (J in Hz) : 4.53,4.40,4.34 (m,C_5H_3); 4.22 (s,Cp); 4.04,2.85 (d,CH_2,13.6); 3.90,3.20,2.60,2.20 (m,αH,NEt_2); 1.91,1.03 (t,βH,NEt_2,7.1); 3.40,3.20 (m,αH,SEt); 1.70 (t,βH,SEt,7.2)

IR (CsI pellet) cm^{-1} : 3081 (ferrocene C-H stretch); 2959,2924 (alkyl C-H stretch); 1454 (ferrocene antisymmetric C-H stretch); 1223,1152 (C-N stretch); 832 (C-H bending perpendicular to the plane of Cp ring); 612 (S-C stretch); 515 (Pd-N stretch); 328 (Pd-Cl stretch); 295 (Pd-S stretch)

FAB MS m/e (relative intensity) : 508 (M^+; 10); 436 (M^+-Cl_2,13); 331 (M^+-$PdCl_2$, 52); 259 (M^+-$PdCl_2$-NEt_2, 73); 121 (M^+-$PdCl_2$-C_5H_3-SEt-CH_2NEt_2, 60); 71 (NEt_2,63)

Elemental Analysis for $C_{17}H_{25}FeNSPdCl_2$ (Calc.) : C 39.74 (40.15); H 4.83 (4.95)

(3). 1-Diethylaminomethyl-2-(4-chlorophenyl)thioferrocenyl Palladium Chloride (**59**, R=Et, R'=4-chlorophenyl, R"=H)

The procedure was the same as that for **57** except that 0.23 g 1-Diethylaminomethyl-2-(4-chlorophenyl)thioferrocene was used. The product after crystallization gave 0.194 g brick red crystals. Mp. 135 °C; yield : 60%.

^{1}H NMR δ ppm (J in Hz) : 4.40,4.23,4.00 (m,C_5H_3); 4.10 (s,Cp); 4.64,2.96 (d,CH_2,13.6); 4.04,3.18,2.76,2.41 (m,αH,NEt_2); 1.96,1.06 (t,βH,NEt_2,7.1); 7.85,7.44 (m,Ph)

IR (CsI pellet) cm^{-1} : 3093 (ferrocene C-H stretch); 2931,2973 (alkyl C-H stretch); 1476 (ferrocene antisymmetric C-H stretch); 1096,1103 (C-N stretch); 829,808 (C-H bending perpendicular to the plane of Cp ring); 681 (S-C stretch); 491 (antisymmetric ring-metal stretch); 503 (Pd-N stretch); 329 (Pd-Cl stretch); 305 (Pd-S stretch)

MS m/e (relative intensity) : 413 (M^+-$PdCl_2$, 18); 341 (M^+-$PdCl_2$-NEt_2, 16); 270 (M^+-$PdCl_2$-SPhCl, 24); 199 (M^+-$PdCl_2$-SPhCl-NEt_2, 20); 121 (M^+-$PdCl_2$-C_5H_3-SPhCl-CH_2NEt_2, 34); 85 (CH_2NEt_2,100)

Elemental Analysis for $C_{17}H_{23}ClFeNSPdCl_2$ (Calc.) : C 42.26 (42.69); H 4.02 (4.06)

(4). 1-Diethylaminomethyl-2-(4-methylphenyl)thioferrocenyl Palladium Chloride (**60**, R=Et, R'=4-methylphenyl, R"=H)

The procedure was the same as that for **57** except that 0.22 g 1-Diethylaminomethyl-2-(4-methylphenyl)thioferrocene was used. The product after crystallization gave 0.222 g brick red crystals. Mp. 165-166 °C; yield : 71%.

^1H NMR δ ppm (J in Hz) : 4.38,4.22,4.15 (m,C_5H_3); 4.06 (s,Cp); 4.64,2.92 (d,CH_2,13.6); 4.06-3.95,3.18,2.75 (m,αH,NEt_2); 1.94,1.08 (t,βH,NEt_2,7.1); 7.83,7.26 (m,Ph); 2.37 (s,Ph-CH_3)

IR (CsI pellet) cm^{-1} : 3086 (ferrocene C-H stretch); 2924-2959 (alkyl C-H stretch); 1490 (ferrocene antisymmetric C-H stretch); 1081,1107 (C-N stretch); 804 (C-H bending perpendicular to the plane of Cp ring); 486 (antisymmetric ring-metal stretch); 497 (Pd-N stretch); 328 (Pd-Cl stretch); 302 (Pd-S stretch)

MS m/e (relative intensity) : 393 (M^+-$PdCl_2$, 28); 321 (M^+-$PdCl_2$-NEt_2, 32); 270 (M^+-$PdCl_2$-$SPhCH_3$, 46); 199 (M^+-$PdCl_2$-$SPhCH_3$-NEt_2, 62); 121 (M^+-$PdCl_2$-C_5H_3-$SPhCH_3$-CH_2NEt_2, 55); 85 (CH_2NEt_2,28); 58 (Et_2, 88); 40 (100)

Elemental Analysis for $C_{18}H_{26}FeNSPdCl_2$ (Calc.) : C 46.72 (46.32); H 4.96 (4.77)

(5). 1-Di-*n*-propylaminomethyl-2-methylthioferrocenyl Palladium Chloride (**61**, R=*n*-Pr, R'=Et, R"=H)

The procedure was the same as that for **57** except that 0.19 g 1-Di-*n*-propylaminomethyl-2-methylthioferrocene was used. The product after crystallization gave 0.195 g brick red crystals. Mp. 142-144 °C; yield : 68%.

^1H NMR δ ppm (J in Hz) : 4.51,4.38,4.32 (m,C_5H_3); 4.22 (s,Cp); 3.95,2.95 (d,CH_2,13.6); 3.73,3.08,2.47,2.13 (dt,αH,N-*n*-Pr_2);

3.21,1.98,1.65,1.37 (m,βH,N-*n*-Pr_2,7.1); 1.05,0.68 (t,γH,N-*n*-Pr_2,7.2); 2.73 (s,SMe)

IR (CsI pellet) cm^{-1} : 3093 (ferrocene C-H stretch); 2924,2959 (alkyl C-H stretch); 1462 (ferrocene antisymmetric C-H stretch); 1079,1107 (C-N stretch); 831 (C-H bending perpendicular to the plane of Cp ring); 518 (Pd-N stretch); 323 (Pd-Cl stretch); 295 (Pd-S stretch)

MS m/e (relative intensity) : 345 (M^+-$PdCl_2$, 19); 298 (M^+-$PdCl_2$-SMe, 8); 245 (M^+-$PdCl_2$-NPr_2, 100); 199 (M^+-$PdCl_2$-SMe-NPr_2, 13); 121 (M^+-$PdCl_2$-C_5H_3-SMe-CH_2NPr_2, 44); 56 (Fe, 100); 43 (C_3H_7, 88)

Elemental Analysis for $C_{18}H_{27}FeNSPdCl_2$ (Calc.) : C 41.79 (41.37); H 5.33 (5.17)

(6). 1-Di-*n*-propylaminomethyl-2-methylthioferrocenyl Palladium Chloride (**62**, R=*n*-Pr, R'=Et, R"=H)

The procedure was the same as that for **57** except that 0.20 g 1-Di-*n*-propylaminomethyl-2-methylthioferrocene was used. The product after crystallization gave 0.212 g dark red crystals. Mp. 127-128 °C; yield : 72%.

^1H NMR δ ppm (J in Hz) : 4.53,4.34 (m,C_5H_3); 4.21 (s,Cp); 4.06,2.90 (d,CH_2,13.7); 3.79,3.18,2.97,2.36 (dt,αH,N-*n*-Pr_2); 2.10-1.90,1.65-1.40 (m,βH,N-*n*-Pr_2,7.1); 1.04,0.68 (t,γH,N-*n*-Pr_2,7.4); 3.41,3.17 (m,αH,SEt); 1.69 (t,βH,SEt,7.2)

IR (CsI pellet) cm^{-1} : 3093 (ferrocene C-H stretch); 2924,2959 (alkyl C-H stretch); 1462 (ferrocene antisymmetric C-H stretch); 1082,1103 (C-N stretch); 820 (C-H bending perpendicular to the plane of Cp ring); 682 (S-C stretch); 518 (Pd-N stretch); 325 (Pd-Cl stretch); 296 (Pd-S stretch)

MS m/e (relative intensity) : 359 (M^+-$PdCl_2$, 43); 298 (M^+-$PdCl_2$-SEt, 29); 259 (M^+-$PdCl_2$-N-*n*-Pr_2, 100); 199 (M^+-$PdCl_2$-SEt-N-*n*-Pr_2, 13); 105 (14); 72 (53)

Elemental Analysis for $C_{19}H_{29}FeNSPdCl_2$ (Calc.) : C 42.81 (42.52); H 5.29 (5.45)

(7). 1-Ethylmethylaminomethyl-2-methylthio ferrocenyl palladium chloride (**63**, R=NMeEt, R'=Et, R"=H)

The procedure was the same as that for **57** except that 0.18 g 1-ethylmethylaminomethyl-2-ethylthioferrocene was used. The product after crystallization gave 0.181 g dark red crystals. Mp. 110-112 °C; yield : 65%.

^{1}H NMR δ ppm (J in Hz) : 4.48,4.40,4.34 (m,C_5H_3); 4.24 (s,Cp); 4.02,2.53 (d,CH_2,13.6); 3.97,2.13 (m,αH,NEt); 2.37 (s,αH,NMe) 1.90 (t,βH,NEt,7.0); 2.70 (s, SMe)

IR (CsI pellet) cm^{-1} : 3088 (ferrocene C-H stretch); 2971,2926 (alkyl C-H stretch); 1464,1414 (ferrocene antisymmetric C-H stretch); 1107 (C-N stretch); 837 (C-H bending perpendicular to the plane of Cp ring); 635 (S-C stretch); 513 (Pd-N stretch); 329 (Pd-Cl stretch); 295 (Pd-S stretch)

MS m/e (relative intensity) : 480 (M^+,5); 409 (M^+-Cl_2,13); 303 (M^+-$PdCl_2$, 100); 288 (M^+-$PdCl_2$-Me, 85); 231 (M^+-$PdCl_2$-NMeEt, 73); 136 (M^+-$PdCl_2$-C_5H_3-S-CH_2NMeEt, 100)

Elemental Analysis for $C_{17}H_{25}FeNSPdCl_2$ (Calc.) : C 39.74 (40.15); H 4.83 (4.95)

(8). 1-Methylthio-2-ethylthiomethylferrocenyl Palladium Chloride (**64**)

The procedure was the same as that for **57** except that 1-methylthio-2-ethylthiomethylferrocene was used. The product after crystallization gave 0.228 g brick red crystals. Mp. 180-185 °C; yield : 86%.

^{1}H NMR δ ppm (J in Hz) : 4.32,4.61 (m,C_5H_3); 4.49 (s,Cp); 3.54,3.66 (d,CH_2,13); 3.33 (q,αH,SEt,6); 1.61 (t,βH,SEt,6); 2.70 (s,SMe)

^{13}C NMR δ ppm : 88.0 (s,C_1); 81.8 (s,C_2); 72.8, 69.3, 67.4 (d,C_3,C_4,C_5); 70.0 (s,Cp); 29.9 (t,CH_2); 26.2 (t,αC,SEt); 14.6 (q,βC,SEt); 20.9(q,SMe)

IR (CsI pellet) cm^{-1} : 3086 (ferrocene C-H stretch); 2922,2960 (alkyl C-H stretch); 1450 (ferrocene antisymmetric C-H stretch); 833,818 (C-H bending perpendicular to the plane of Cp ring); 478 (antisymmetric ring-metal stretch); 325 (Pd-Cl stretch); 297 (Pd-S stretch); 241 (S-Pd-S bending)

Elemental Analysis for $C_{14}H_{18}FeS_2PdCl_2$ (Calc.) : C 34.33 (34.77); H 3.69 (3.75)

(9). 1-Methylthio-2-ethylthiomethylferrocenyl Platinum Chloride(**65**)

The procedure was the same as that for **64** except that 0.2 g bisbenzylnitrile platinum chloride was used. The product after crystallization gave 0.223 g yellow crystals. Mp. 213-214 °C; yield : 63%.

^1H NMR δ ppm (J in Hz) : 4.64,4.45,4.44 (m,C_5H_3); 4.50 (s,Cp); 3.84,3.68 (d,CH_2,13); 3.30 (q,αH,SEt,7.4); 1.58 (t,βH,SEt,7.4); 2.71 (s,SMe; J_{Pt-H}=21.7)

^{13}C NMR δ ppm : 88.0 (s,C_1); 81.8 (s,C_2); 72.8, 69.3, 67.4 (d,C_3,C_4,C_5); 70.0 (s,Cp); 29.9 (t,CH_2); 26.2 (t,αC,SEt); 14.6 (q,βC,SEt); 20.9(q,SMe)

IR (CsI pellet) cm^{-1} : 3086 (ferrocene C-H stretch); 2922,2960 (alkyl C-H stretch); 1450 (ferrocene antisymmetric C-H stretch); 833,818 (C-H bending perpendicular to the plane of Cp ring); 481 (antisymmetric ring-metal stretch); 324 (Pd-Cl stretch); 310 (Pd-S stretch); 244 (S-Pt-S bending)

Elemental Analysis for $C_{14}H_{18}FeS_2PtCl_2$ (Calc.) : C, 34.33 (34.77); H 3.69 (3.75)

(10). (*S*,*R*)-1-(1-Diethylaminoethyl)-2-methylthioferrocenyl Palladium Chloride ((*S*,*R*)-**66**, R=Et, R'=Me, R"=Me)

The procedure was the same as that for **57** except that 0.18 g (*S*,*R*)-1-(1-Diethylaminoethyl)-2-methylthioferrocene was used. The product after crystallization gave 0.252 g purple crystals. Mp. 142-143 °C; yield : 88%.

^{1}H NMR δ ppm (J in Hz) : 4.51,4.42 (m,C_5H_3); 4.30 (t,C_5H_3); 4.19 (s,Cp); 4.02 (q,C<u>H</u>-CH_3,6.6); 1.55 (d,C<u>H</u>$_3$-CH,6.8); 4.10,2.88,2.43 (m,αH,NEt_2); 1.97,1.09 (t,βH,NEt_2,7.1); 2.74 (s,SMe)

IR (CsI pellet) cm^{-1} : 3093 (ferrocene C-H stretch); 2931,2966 (alkyl C-H stretch); 1471,1452 (ferrocene antisymmetric C-H stretch); 1173,1258 (C-N stretch); 833 (C-H bending perpendicular to the plane of Cp ring); 680 (S-C stretch); 503 (Pd-N stretch); 337(Pd-Cl stretch); 315 (Pd-S stretch)

MS m/e (relative intensity) : 331 (M^+-$PdCl_2$, 8); 258 (M^+-$PdCl_2$-NEt_2, 66); 243 (M^+-$PdCl_2$-Me-NEt_2, 31); 121 (M^+-$PdCl_2$-C_5H_3-SMe-$CHCH_3NEt_2$, 72); 58 (Et_2, 100); 56 (Fe, 54)

Elemental Analysis for $C_{17}H_{25}FeNSPdCl_2$ (Calc.) : C 40.58 (40.15); H 4.92 (4.95)

(11). (*S*,*R*)-1-(1-Di-*n*-propylaminoethyl)-2-methylthioferrocenyl Palladium Chloride ((*S*,*R*)-**67**, R=*n*-Pr, R'=Me, R"=Me)

The procedure was the same as that for (*S*,*R*)-**66** except that 0.20 g (*S*,*R*)-1-(1-Di-*n*-propylaminoethyl)-2-ethylthioferrocene was used. The product after crystallization gave 0.262 g dark purple crystals. Mp. 130-131 °C; yield : 89%.

^{1}H NMR δ ppm (J in Hz) : 4.51,4.42,4.34 (m,C_5H_3); 4.19 (s,Cp); 4.01 (q,C<u>H</u>-CH_3,6.8); 1.55 (d,C<u>H</u>$_3$-CH,6.7); 3.96,2.34,2.19,1.64 (dt,αH,N-*n*-Pr_2); 3.32,2.34,1.91 (m,βH,N-*n*-Pr_2,7.1); 1.11,0.64 (t,γH,N-*n*-Pr_2,7.1); 2.73 (s,SMe)

IR (CsI pellet) cm^{-1} : 3077 (ferrocene C-H stretch); 2929,2970 (alkyl C-H stretch); 1474,1446 (ferrocene antisymmetric C-H stretch); 1172,1250 (C-N stretch); 833 (C-H bending perpendicular to the plane of Cp ring); 693 (S-C stretch); 478 (antisymmetric ring-metal stretch); 513 (Pd-N stretch); 317 (Pd-Cl stretch); 290 (Pd-S stretch)

MS m/e (relative intensity) : 359 (M^+, 2); 258 (M^+-$PdCl_2$-N-*n*-Pr_2, 100); 243 (M^+-$PdCl_2$-Me-N-*n*-Pr_2, 50); 121 (M^+-$PdCl_2$-C_5H_3-SMe-$CHCH_3N$-*n*-Pr_2, 69); 72 (86); 56 (Fe, 48); 43(C_3H_7,50)

Elemental Analysis for $C_{19}H_{29}FeNSPdCl_2$ (Calc.) : C 41.82 (42.52); H 5.33 (5.45)

(12). (*R*,*S*)-1-(1-Diethylaminoethyl)-2-ethylthioferrocenyl Palladium Chloride ((***R*,*S*)-68**, R=Et, R'=Et, R"=Me)

The procedure was the same as that for (***S*,*R*)-66** except that 0.19 g (*R*,*S*)-1-(1-Diethylaminoethyl)-2-ethylthioferrocene was used. The product after crystallization gave 0.226 g brick red crystals. Mp. 130-131 °C; yield : 79%.

^1H NMR δ ppm (J in Hz) : 4.54,4.42 (m,C_5H_3); 4.37 (t,C_5H_3); 4.18 (s,Cp); 4.08 (q,C<u>H</u>-CH_3,6.8); 1.54 (d,C<u>H</u>$_3$-CH,6.8); 2.71,2.34,1.80 (m,αH,NEt_2); 1.97,1.12 (t,βH,NEt_2,7.1); 3.36 (m,αH,SEt); 1.72 (t,βH,SEt,7.2)

IR (CsI pellet) cm^{-1} : 3086 (ferrocene C-H stretch); 2931,2973 (alkyl C-H stretch); 1448 (ferrocene antisymmetric C-H stretch); 1251 (C-N stretch); 828 (C-H bending perpendicular to the plane of Cp ring); 469 (antisymmetric ring-metal stretch); 516 (Pd-N stretch); 321 (Pd-Cl stretch); 287 (Pd-S stretch)

MS m/e (relative intensity) : 345 (M^+-$PdCl_2$, 6); 272 (M^+-$PdCl_2$-NEt_2, 30); 243 (M^+-$PdCl_2$-Me-NEt_2, 29); 121 (M^+-$PdCl_2$-C_5H_3-SMe-$CHCH_3NEt_2$, 68); 58 (Et_2, 100); 56 (Fe, 47)

Elemental Analysis for $C_{18}H_{27}FeNSPdCl_2$ (Calc.) : C 41.16 (41.37); H 5.15 (5.17)

(13). (*R*,*S*)-1-(1-Di-*n*-propylaminoethyl)-2-ethylthioferrocenyl Palladium Chloride ((***R*,*S*)-69**, R=*n*-Pr, R'=Et, R"=Me)

The procedure was the same as that for **(*S*,*R*)-66** except that 0.20 g (*R*,*S*)-1-(1-Di-*n*-propylaminoethyl)-2-ethylthioferrocene was used. The product after crystallization gave 0.166 g dark red crystals. Mp. 127 °C; yield : 55%.

^{1}H NMR δ ppm (J in Hz) : 4.52,4.39,4.36 (m,C_5H_3); 4.17 (s,Cp); 4.06 (q,C<u>H</u>-CH_3,6.8); 1.53 (d,$C\underline{H}_3$-CH,6.8); 3.98,2.50,2.14 (dt,αH,N-*n*-Pr_2); 2.29 (m,αH,N-*n*-Pr_2);3.32,2.29,1.92,0.95 (m,βH,N-*n*-Pr_2); 1.08,0.63 (t,γH,N-*n*-Pr_2,7.3); 3.32 (m,αH,SEt); 1.71 (t,βH,SEt,7.4)

IR (CsI pellet) cm^{-1} : 3081 (ferrocene C-H stretch); 2930,2957 (alkyl C-H stretch); 1457 (ferrocene antisymmetric C-H stretch); 1171,1248 (C-N stretch); 822 (C-H bending perpendicular to the plane of Cp ring); 512 (Pd-N stretch); 318 (Pd-Cl stretch); 299 (Pd-S stretch)

MS m/e (relative intensity) : 373 (M^+-$PdCl_2$, 2); 272 (M^+-$PdCl_2$-N-*n*-Pr_2, 40); 243 (M^+-$PdCl_2$-Me-N-*n*-Pr_2, 32); 121 (M^+-$PdCl_2$-C_5H_3-SEt-$CHCH_3$N-*n*-Pr_2, 50); 72 (100); 56 (Fe, 33)

Elemental Analysis for $C_{20}H_{31}FeNSPdCl_2$ (Calc.) : C 43.56 (43.62); H 5.61 (5.67)

(14). (*R*,*S*)-1-(1-Diethylaminoethyl)-2-isopropylthioferrocenyl Palladium Chloride ((***R*,*S*)-70**, R=Et, R'=*i*-propyl, R"=Me)

The procedure was the same as that for **(*S*,*R*)-66** except that 0.20 g (*R*,*S*)-1-(1-Diethylaminoethyl)-2-isopropylthioferrocene was used. The product after crystallization gave 0.241 g purple crystals. Mp. 123-124 °C; yield : 82%.

^{1}H NMR δ ppm (J in Hz) : 4.67,4.45 (m,C_5H_3); 4.41 (t,C_5H_3); 4.20 (s,Cp); 4.03 (q,C<u>H</u>-CH_3,6.6); 1.54 (d,$C\underline{H}_3$-CH,6.7); 2.62,2.37,1.83 (m,αH,NEt_2); 1.97,1.09 (t,βH,NEt_2,7.1); 4.20 (m,αH,S-*i*-Pr); 1.88,1.77 (t,βH,S-*i*-Pr,7.1)

IR (CsI pellet) cm^{-1} : 3093 (ferrocene C-H stretch); 2924,2973 (alkyl C-H stretch); 1448 (ferrocene antisymmetric C-H stretch); 1180,1247

(C-N stretch); 815 (C-H bending perpendicular to the plane of Cp ring); 470 (antisymmetric ring-metal stretch); 516 (Pd-N stretch); 318 (Pd-Cl stretch); 285 (Pd-S stretch)

MS m/e (relative intensity) : 359 (M^+-$PdCl_2$, 4); 286 (M^+-$PdCl_2$-NEt_2, 100); 243 (M^+-$PdCl_2$-C_3H_7-NEt_2, 63); 121 (M^+-$PdCl_2$-C_5H_3-S-*i*-Pr-$CHCH_3NEt_2$, 56); 58 (Et_2, 55); 43 (C_3H_7, 74)

Elemental Analysis for $C_{19}H_{29}FeNSPdCl_2$ (Calc.) : C 42.24 (42.52); H 5.47 (5.45)

(15). (*R*,*S*)-1-(1-Di-*n*-propylaminoethyl)-2-isopropylthioferrocenyl Palladium Chloride ((***R*,*S*)-71**, R=*n*-Pr, R'=*i*-Pr, R"=Me)

The procedure was the same as that for (***S*,*R*)-66** except that 0.21 g (*R*,*S*)-1-(1-Di-*n*-propylaminoethyl)-2-isopropylthioferrocene was used. The product after crystallization gave 0.223 g brick red crystals. Mp. 130 °C; yield : 72%.

^{1}H NMR δ ppm (J in Hz) : 4.65,4.42,4.40 (m,C_5H_3); 4.18 (s,Cp); 4.03 (m,C<u>H</u>-CH_3); 1.53 (d,C<u>H</u>$_3$-CH,6.8); 4.03,2.23,2.09 (dt,αH,N-*n*-Pr_2); 2.41.(m,αH,N-*n*-Pr_2); 2.41,1.87,0.81 (m,βH,N-*n*-Pr_2,); 1.07,0.61 (t,γH,N-*n*-Pr_2,7.1); 3.38 (m,αH,S-*i*-Pr); 1.87,1.76 (d,βH,S-*i*-Pr,7.1)

IR (CsI pellet) cm^{-1} : 3093 (ferrocene C-H stretch); 2930,2960 (alkyl C-H stretch); 1459 (ferrocene antisymmetric C-H stretch); 1170,1245 (C-N stretch); 817 (C-H bending perpendicular to the plane of Cp ring); 471 (antisymmetric ring-metal stretch); 514 (Pd-N stretch); 314 (Pd-Cl stretch); 286 (Pd-S stretch)

MS m/e (relative intensity) : 387 (M^+-$PdCl_2$, 2); 286 (M^+-$PdCl_2$-N-*n*-Pr_2, 81); 243 (M^+-$PdCl_2$-C_3H_7-N-*n*-Pr_2, 57); 178 (M^+-$PdCl_2$-C_5H_5-N-*n*-Pr_2-C_3H_7, 29); 121 (M^+-$PdCl_2$-C_5H_3-S-*i*-Pr-$CHCH_3$N-*n*-Pr_2, 97); 56 (Fe, 33); 43 (C_3H_7, 33)

Elemental Analysis for $C_{21}H_{33}FeNSPdCl_2$ (Calc.) : C 44.60 (44.67); H 5.84 (5.89)

C. General Procedure for Hydrogenation Reactions

The palladium catalysts (1.0 $X10^{-5}$ mol), 4.5 mL acetone and 3.725 $X10^{-3}$ mol substrate were added to a 100-mL pressure bottle equipped with a pressure gauge and a stirring bar. The bottle was evacuated and filled with H_2 several times, then fixed at 62 psi. The uptake of hydrogen was monitored by the pressure drop.

(1). 1,3-Cyclooctadiene

Following the general procedure, the products were distilled from the catalysts and analyzed by using ^1H NMR and GC. The 1,3-cyclooctadiene / cyclooctene ratio was determined by integration of the ^1H NMR in the olefin region. The (1,3-cyclooctadiene+cyclooctene) / cyclooctane ratio was determined by GC.

(2). Acrylic Acid

The hydrogenation product was distilled from the catalyst and analyzed by using ^1H NMR.

(3). Phenylacetylenes

Phenylacetylene, diphenylacetylene, bromophenylacetylene, methylphenylacetylene, and ethylphenylacetylene were used in the hydrogenations. The products were distilled from the catalysts and analyzed by using ^1H NMR.

(4). Asymmetric Hydrogenation of Aminoacids

The rhodium catalysts were prepared *in situ* by adding 20.4 mg $AgBF_4$ to 13.8 mg $[RhNBDCl]_2$ ($3x10^{-5}$ mol) in 4.5 mL methanol. After stirring under argon for 30 min, appropriate amount of ligands were added (ligand to metal ratio=1.05:1). One hour later the substrate ($2x10^{-3}$ mol) in 4.5 mL methanol was added quickly to the reaction mixture and the hydrogenation was performed as described.

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The products were worked up according to the reported procedure.[86] The conversion was determined by using ^{1}H NMR and optical purities were determined by checking the rotation on a polarimeter.[87]

D. Asymmetric Grignard Cross-Coupling Reaction

A 0.05 mmol sample of the appropriate catalyst was placed in a 100-mL round-bottom Schlenk flask which was then evacuated and filled with dry argon several times. After being cooled to -78 °C, 1.41 g (10.0 mmol) 1-phenylethyl chloride **31** in 20 mL dry ether was added via syringe to the flask which was then stirred for 2 h at room temperature. The reaction vessel was charged with 10 mL allylmagnesium chloride (2 M solution in THF) via syringe at -78 °C. The reaction mixture was stirred at room temperature for 36 h, then hydrolyzed with 10 mL 10% HCl. The organic layer and ether extracts from the aqueous layer were combined, washed first with saturated $NaHCO_3$ solution, then with water, dried over anhydrous $MgSO_4$ and evaporated to dryness. The product was chromatographed on a silica gel column to give 4-phenyl-1-pentene **32** (90-96% yield).

Oxidation of 4-phenyl-1-pentene to methyl-3-phenylbutyrate

The reported procedure[145] was followed : A 0.906 g sample (6.2 mmol) of 4-phenyl-1-pentene **32** was dissolved in 160 mL *t*-butyl alcohol. To this was added a solution of 2.48 g (18.0 mmol) K_2CO_3 in 120 mL of water and a solution of 10.26 g (48.0 mmol) sodium periodate and 1.26 g (8.0 mmol) $KMnO_4$ in 120 mL water. The solution was adjusted to pH 8.5 with 2N aqueous NaOH and stirred overnight. *t*-Butyl alcohol was evaporated under reduced pressure; then the aqueous solution was adjusted to pH 2.5 with concentrated HCl. Sodium bisulfite was added slowly until the solution become off-white. The aqueous solution was extracted twice with ether; these extracts were combined, washed, dried over anhydrous $MgSO_4$ and evaporated. A solution of the resulting acid (0.59 g, 3.5 mmol) and *p*-toluenesulfonic acid (80 mg) in 20 mL of MeOH was refluxed for 3 h, the solvent removed, and the residue extracted in ether. The ether solution was washed with 10% aqueous NaOH, dried over anhydrous

$MgSO_4$ and evaporated. The residue was distilled at 110-130 °C (2 mm) to give methyl-3-phenylbutyrate **33** (75-85%). A 90 mg sample of the chiral shift reagent, tris(d,d-dicampholylmethanato) europium(III), $Eu(dcm)_3$, was placed in an NMR tube under argon and 0.15 mL 1 M solution of methyl-3-phenylbutyrate **33** in $CDCl_3$ was added. The solution was diluted to 0.5 mL with $CDCl_3$ to 0.16 M in $Eu(dcm)_3$ and 0.3 M in methyl-3-phenylbutyrate. Argon was bubbled through the solution for one minute to eliminate oxygen; the NMR tube was then evacuated and sealed. The methyl ester proton of the two diastereomers gives two singlets; their ratio yields direct measurement to the enantiomeric excess.

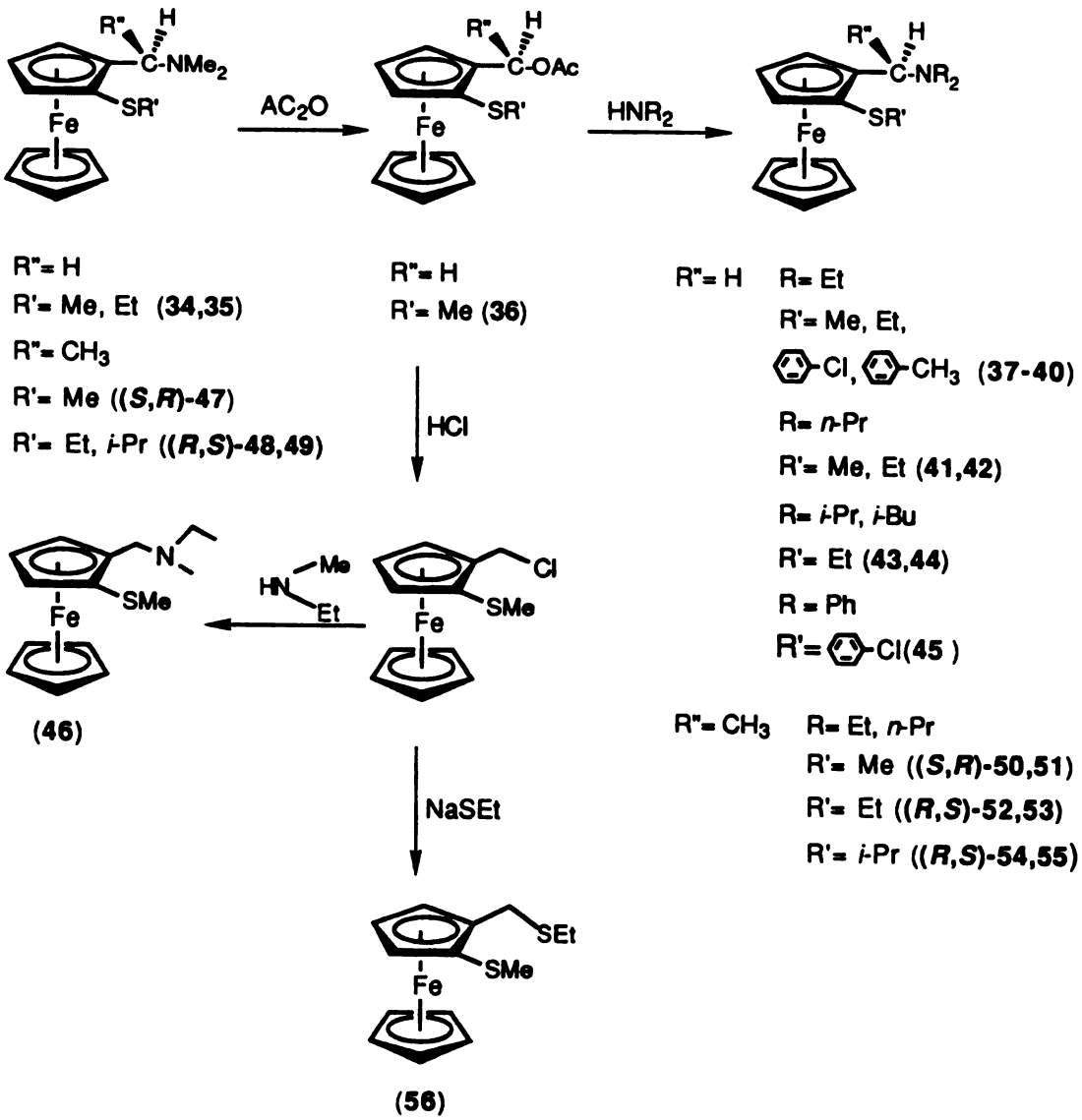
RESULTS AND DISCUSSION

A. Synthesis of Ferrocenylamine Catalysts

1. Synthesis and Characterization of Ferrocenylamine Ligands

(1). Ferrocenylamine Sulfides

The reactants, 1-Dimethylaminomethyl-2-alkylthioferrocene (**34,35**), (*R*,*S*)-1-(1-dimethylaminoethyl)-2-alkylthioferrocene ((***R***,***S***)-**48**,(***R***,***S***)-**49**) and (*S*,*R*)-1-(1-dimethylaminoethyl)-2-alkylthioferrocene ((***S***,***R***)-**47**), were prepared according to the reported procedure.[85] Dimethylaminoferrocenyl sulfides (**34,35**) were first converted to sulfidoferrocenyl ethylacetate, then react with diethylamine or di-*n*-propylamine to give diethylamino ferrocenyl sulfides (**37-40**) and di-*n*-propylaminoferrocenyl sulfides (**41,42**) , respectively.[17] The chiral ferrocenylamine sulfide ligands ((***S***,***R***)-**50**-(***R***,***S***)-**55**) were also prepared in this way with some modification (Scheme 6). All the ligands thus prepared are yellow to brown oils except when the thio substituents are 4-chlorophenylthio **39** and 4-tolylphenylthio **40**, which give yellow and brown crystals, respectively. The overall yield ranges from 20% to 85% dependent on the steric strain of the ligands.


R" H
C-NMe2
SR'
Fe
AC2O
C-OAc
HNR2
C-NR2
R"= H
R'= Me, Et (34,35)
R"= CH3
R'= Me ((S,R)-47)
R'= Et, i-Pr ((R,S)-48,49)
R"= H
R'= Me (36)
HCl
R"= H
R= Et
R'= Me, Et,
Cl, CH3 (37-40)
R= n-Pr
R'= Me, Et (41,42)
R= i-Pr, i-Bu
R'= Et (43,44)
R = Ph
R'= Cl(45)
R"= CH3
R= Et, n-Pr
R'= Me ((S,R)-50,51)
R'= Et ((R,S)-52,53)
R'= i-Pr ((R,S)-54,55)
N
SMe
Me
HN
Et
Cl
(46)
NaSEt
SEt
(56)

Scheme 6

The 300 MHz ^1H NMR data for the achiral and chiral ligands **37**-(***R*,*S*)-55** are tabulated in Tables 1 and 2; representative spectra are shown in Fig. 1 for achiral ligand 1-Diethylaminomethyl-2-ethyl thioferrocene (**38**) and in Fig. 2 for chiral ligand (*R*,*S*)-1-(1-Diethyl aminoethyl)-2-ethylthioferrocene, (***R*,*S*)-52**. In both cases, protons of the unsubstituted cyclopentadienyl ring appear as a singlet due to the free rotation around the Fe-Cp axis in ferrocene.[88] It is a good indication of single-ring substituted ferrocenes. Assignment of the substituted ring protons H_3, H_4, H_5 is difficult because of the ambiguous shielding or deshielding effects of the substituent.[89-91]

The aminomethylene and thiomethylene protons in compounds **38**, **42**, **44** and (***R*,*S*)-52** are diastereotopic and their signals show up as two multiplets due to the additional splitting of the neighboring protons. For the achiral ligands, a striking feature is the sensitivity of the chemical shift difference of the two diastereotopic methylene protons between the Cp ring and the amino substituent to the steric crowdedness at the β-carbons of both the amine and the thioether substituents (Tables 3, 4).

The variation in chemical shifts of the diastereotopic aminomethylene and thiomethylene protons are also related to each other to a smaller extent by the rotational hindrance of both groups. However, the transformation from achiral to chiral ligands produces a large change in the δ value; especially when the amino group is diethylamine. (Compare compounds **37**, **38**, (***S*,*R*)-50** and (***R*,*S*)-52**) This change indicates that the chiral methyl group imparts additional steric and/or electronic effect(s) to the ligands, and can be related to the extraordinarily fast rate of the hydrogenation of 1,3-cyclooctadiene to monoene as will be discussed later.

Table 1 300 MHz ^1H NMR Data for Compounds (37-46) in $CDCl_3$ at Room Temperature; δ ppm (Hz)

Compound	C_5H_5	C_5H_3	CH_2N	NR (SEt) αH	NR (SEt) βH	NR (SEt) γH	SR' αH	SR' βH	Ph	Ph-CH_3
37 (R=Et,R'=Me)	4.08 s	4.26 d 4.08-4.11 m	3.29-3.78 d,d (13.0)	2.30-2.60m	1.00 t (7.0)		2.24 s			
38 (R'=Et)	4.06 s	4.27 d 4.08-4.12 m	3.22-3.78 d,d (13.1)	2.34-2.57 m	0.98 t (7.1)		2.55-2.72 m	1.14 t (7.4)		
39 (R'=4-PhCl)	4.16 s	4.30, 4.40 4.45 m	3.33-3.64 d,d (13.6)	2.21-2.42 m	0.85 t (7.1)				7.02-7.12 m	
40 (R'=*p*-tolyl)	4.15 s	4.27, 4.41 4.47 m	3.44-3.66 d,d (13.7)	2.33 q (7.1)	0.87 t (7.1)				6.92-7.04 d,d	2.22 s
41 (R=*n*-Pr, R'=Me)	4.07 s	4.10 [a] 4.26 [b]	3.26-3.78 d,d (13.2)	2.17-2.43 m	1.30-1.50 m (7.3)	0.81 t (7.3)	2.24 s			
42 (R=*n*-Pr,) R'=Et)	4.07 s	4.11 [a] 4.28 [b]	3.20-3.78 d,d (13.2)	2.18-2.43	1.32-1.50	0.80 t (7.4)	2.53-2.77 m	1.14 t (7.4)		
43 (R=*i*-Pr, R'=Et)	4.08 s	4.08 [a]	3.38-3.74 d,d 4.28 [b]	3.02 m (13.5)	1.00 d,d (6.6)		2.50-2.77 m (4.8)	1.13 t (6.9)		
44 (R=*i*-Bu, R'=Et)	4.06 s	4.11 [a] 4.29 [b] m	3.17-3.69 d,d (13.2)	1.93-2.14 m	1.71 m	0.78-0.84 d,d (6.5)	2.50-2.73 m	1.15 t (7.4)		
45 (R=Ph, R'=4-PhCl)	4.06 s	4.46 t, 4.43 t	4.54-5.09 d d	6.87-6.93 t 7.06-7.12 t					6.97-6.99 d(ClPh) 7.06-7.11 d(ClPh)	

Table 1 Continued

Compound	C_5H_5	C_5H_3	CH_2N	NR (SEt) αH	NR (SEt) βH	NR (SEt) γH	SR' αH	SR' βH	Ph	Ph-CH_3
4 6 (R=NMeEt, R'=Me)	4.08 s	4.29 d, 4.13 t (12.9)	3.26-3.70 d d	2.40 d q(NEt) 2.15 s (NMe)	1.06 t (NEt) (7.2)			2.24 s		
5 6 (R=SEt, R'=Me)		4.10 s	4.13, 4.26 4.31 m	3.53-3.81 d,d (7.2)	2.52 q (7.1)	1.24 t (7.2)		2.25 s		

[a]1 H
[b]2H

Table 2 300 MHz ^{1}H NMR Data for Compounds ((*S*,*R*)-50-(*R*,*S*)-55) in $CDCl_3$ at Room Temperature; δ ppm (Hz)

Compound	C_5H_5	C_5H_3	CH-CH_3	CH_3-CH	NR αH	NR βH	NR γH	SR' αH	SR' βH
(*S*,*R*)-50 (R=Et,R'=Me)	4.07 s	4.11, 4.21 4.27 m	4.25 q (6.8)	1.27 d (6.7)	2.22-2.54[a] m	0.93 t (7.1)		2.29 s	
(*S*,*R*)-51 (R=*n*-Pr,R'=Me)	4.06 s	4.10, 4.20 4.26 m	4.16 q	1.27 d (6.8)	2.18-2.38[a] m	1.20-1.52[a] m	0.73 t (7.1)	2.28 s	
(*R*,*S*)-52 (R=Et,R'=Et)	4.07 s	4.14, 4.21 4.30 m	4.24 q (7.0)	1.26 d (6.1)	2.26[b] m 2.47[b] m	0.92 t (7.1)		2.60[c] m 2.91[c] m	1.13 t (7.5)
(*R*,*S*)-53 (R=*n*-Pr,R'=Et)	4.06 s	4.12, 4.19 4.29 m	4.15 q	1.26 d (6.8)	2.13-2.38[a] m	1.21[b] m 1.40[b] m	0.72 t (7.3)	2.60[b] m 2.83[b] m	1.13 t (7.4)
(*R*,*S*)-54 (R=Et,R'=*i*-Pr)	4.06 s	4.14, 4.21 4.28 m	4.24 q (6.7)	1.24 d (6.8)	2.19-2.30[b] m 2.43-2.56[b] m	0.89 t (7.1)		3.52 m	1.15,1.05 d (6.5)
(*R*,*S*)-55 (R=*n*-Pr,R'=*i*-Pr)	4.06 s	4.15, 4.22 4.29 m	4.19 q (6.9)	1.27 d (6.9)	2.14-2.40[a] m	1.10-1.49[a] m	0.72 t (7.4)	3.42 m	1.07, 1.15 d (6.9)

[a] 4 H
[b] 2 H
[c] 1 H

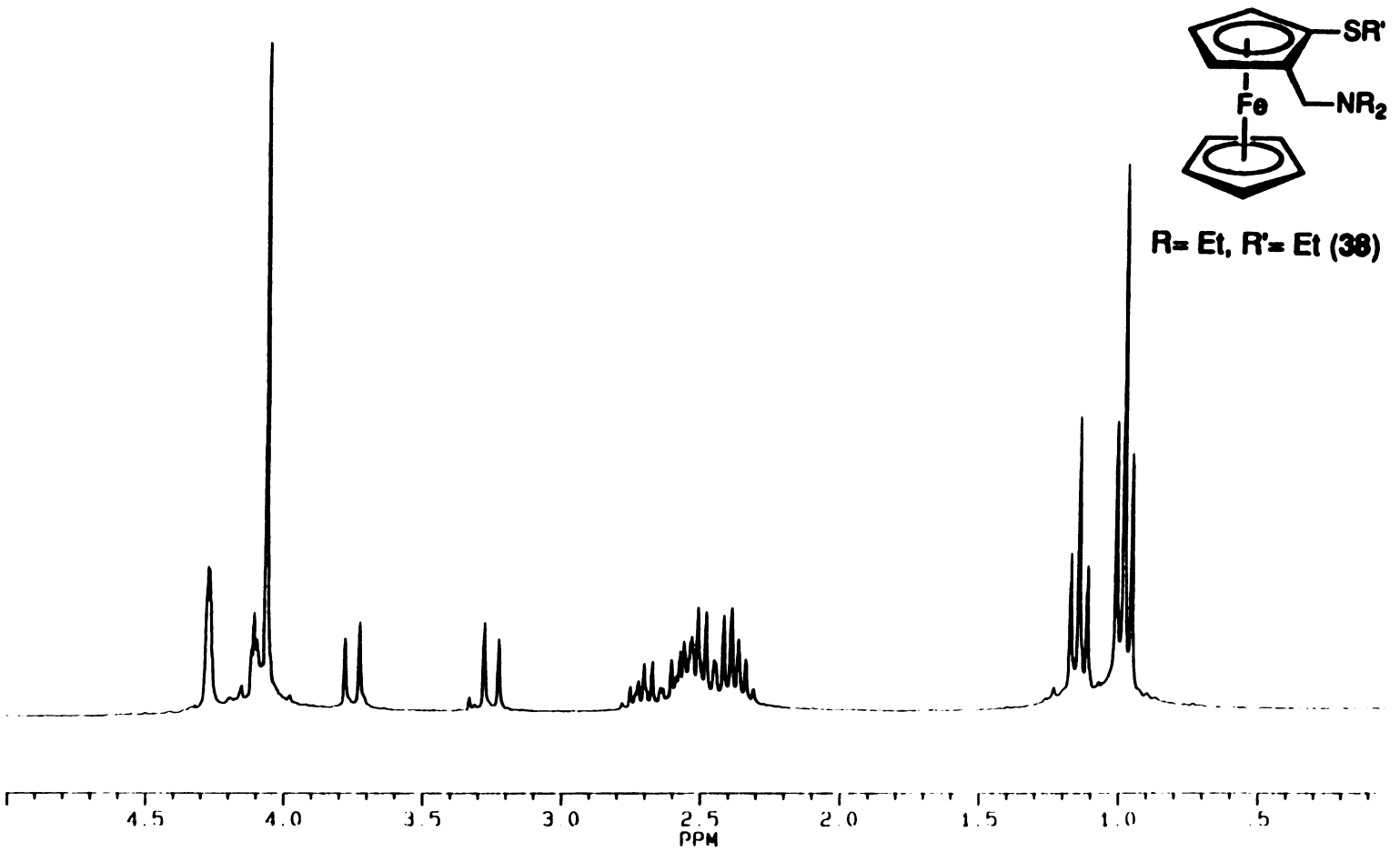


Figure 1. 300 MHz ^{1}H NMR spectrum of 38

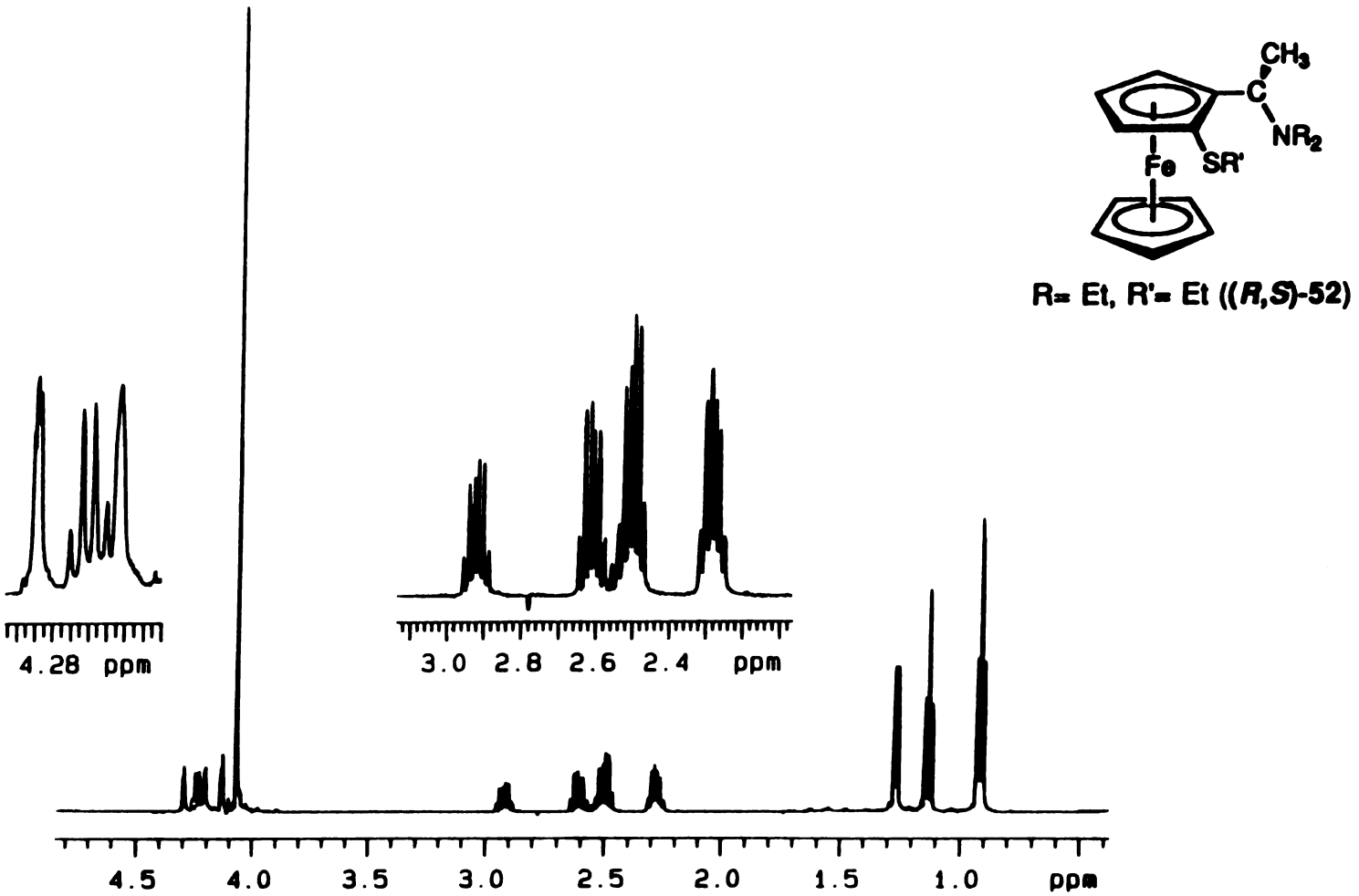


Figure 2. 300 MHz ^{1}H NMR spectrum of (*R,S*)-52

Table 3 Change in chemical shifts for achiral ferrocenylamine sulfides

Compound	NCH_2		$Cp\text{-}CH_2\text{-}N$		$S\text{-}CH_2$	
	δ	Δδ	δ	Δδ	δ	Δδ
37 (R=Et,R'=Me)	2.50, 2.43	0.07	3.75, 3.31	0.44	2.24 (SMe)	
38 (R'=Et)	2.50, 2.40	0.10	3.75, 3.25	0.50	2.70, 2.59	0.11
39 (R'=4-PhCl))	2.31	0	3.62, 3.36	0.26		
40 (R'=*p*-tolyl)	2.33	0	3.64, 3.46	0.18		
41 (R=*n*-Pr,R'=Me)	2.36, 2.26	0.10	3.76, 3.28	0.48	2.24 (SMe)	
42 (R=*n*-Pr,R'=Et)	2.36, 2.25	0.11	3.76, 3.22	0.54	2.69, 2.58	0.11
44 (R=*i*-Bu,R'=Et)	2.13, 2.09	0.04	3.67, 3.20	0.47	2.65, 2.58	0.07
46 (R=NMeEt,R'=Me)	2.41, 2.39	0.02	3.29, 3.68	0.39		
56 (R=SEt,R'=Me)	3.56, 3.79	0.23				
34[a] (R=Me,R'=Me)	3.57, 3.22	0.35			2.20 (SMe)	
35[b] (R=Me,R'=Et)	3.58, 3.19	0.39	2.61(m)	0.04		

[a] 1-(1-dimethylaminomethyl)-2-methylthioferrocene
[b] 1-(1-dimethylaminomethyl)-2-ethylthioferrocene

Table 4 Change in chemical shifts for chiral ferrocenylamine sulfides

Compound	N-CH_2		S-CH_2	
	δ	Δδ	δ	Δδ
(*S*,*R*)-50 (R=Et,R'=Me)	2.46, 2.31	0.15	2.29(SMe)	
(*S*,*R*)-51 (R=*n*-Pr,R'=Me)	2.28, 2.22	0.06	2.28(SMe)	
(*R*,*S*)-52 (R=Et,R'=Et)	2.48, 2.29	0.19	2.90, 2.63	0.27
(*R*,*S*)-53 (R=*n*-Pr,R'=Et)	2.31, 2.21	0.10	2.84, 2.61	0.22
(*R*,*S*)-54 (R=Et,R'=*i*-Pr)	2.49, 2.27	0.22	3.52 (S-C<u>H</u>) 1.15, 1.06 (SCC<u>H</u>3)	
(*R*,*S*)-55 (R=*n*-Pr,R'=*i*-Pr)	2.33; 2.20	0.13	3.42 (S-C<u>H</u>) 1.15,1.07 (SCC<u>H</u>3)	
(*R*,*S*)-48[a] (R=Me,R'=Me)	2.73, 2.63	0.10		

[a] (*R*, *S*)-1-methylthio-2-(1-dimethylaminoethyl)ferrocene, ref. 124

The 75.5 MHz ^{13}C NMR of achiral and chiral ferrocenylamine sulfides **37**- (***R,S***)-**55** are given in Tables 5 and 6, respectively. Tentative assignments of the chemical shifts for these compounds are made by comparison with similar studies[76,77,87] and by ^{13}C DEPT analyses. Typical off-resonance and DEPT ^{13}C NMR spectra for compound **37** are shown in Figs. 3 and 4 whereas spectra of other compounds are shown in the appendix.

In the off-resonance spectrum both the α- and β-carbons of diethylamino group at 46.3 and 11.7 ppm appear as singlets due to the fast inversion of the pyramidal nitrogen atom. The methylthio group appears at 20.5 ppm. C_1 was assigned at 87.4 ppm since it was a neighbor to a more electronegative element, S; whose inductive effect is more important than the resonance effect[100], thus C_1 appear at lower field than C_2 (83.4 ppm). The assignment of C_3, C_4 and C_5 was difficult due to complicated resonance and inductive effects of the sulfido and amino substituents.[100] The unsubstituted Cp signal appeared at 70 ppm as an intense peak.

The quaternary substituted carbons; C_1 and C_2 ; were not shown in the DEPT spectrum, whereas all other protonated carbons were detected. By adopting this pulse sequence in ^{13}C NMR, primary, secondary and tertiary carbons are easily identified.

The infrared data of compounds **37** - (***R,S***)-**55** listed in Tables 7 and 8 are assigned based on the available literature[93-101] and other ferrocenylamine sulfides reported previously.[82,83]

Two bands near 1000 and 1100 cm^{-1} are important features of ferrocene derivatives with unsubstituted rings. The C-S stretching bands appeared at 600-700 cm^{-1} and that for C-N stretching absorbed at about 1200 cm^{-1}. All other stretching, bending and breathing bands are generally consistent with the literature values.[93-101] Fig. 5 shows the spectrum for compound (***S,R***)-**50**.

Table 5 72.5 MHz ^{13}C NMR Spectra for ligands **37-46, 56**

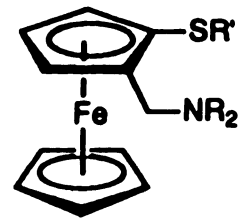
Compound	Cp	C_1	C_2	C_3,C_4,C_5	CH_2	NR (SEt)			SR'		Ph
						αC	βC	γC	αC	βC	
37	70	87.4	83.4	72.0, 70.8	51.0	46.3	11.7		20.5		
(R=Et,R'=Me)				67.1							
38	69.9	88.4	80.3	74.1, 71.1	51.0	46.2	11.6		30.8	14.5	
(R'=Et)				67.4							
39	70.9	90.4	76.6	76.2, 73.0	51.7	47.0	12.1				140.7,130.8
(R'=4-PhCl)				69.6							129.0, 128.7
40	70.1	88.2	77.4	77.0, 71.5	50.4	46.1	11.5				20.6, 136.9
(R'=*p*-tolyl)				68.7							134.7, 129.2, 126.6
41	69.8	87.4	83.3	72.1, 70.9	55.5	52.2	20.0	11.7	20.4		
(R=*n*-Pr,R'=Me)				67.1							
42	69.8	88.5	80.1	74.3, 71.3	55.6	52.5	20.0	11.7	30.9	14.5	
(R'=Et)				67.2							
43	69.8	90.7	79.4	74.3, 71.5	42.5	46.6	21.1		31.0	14.6	
(R=*i*-Pr,R'=Et)				66.8		19.9					
44	69.8	88.2	80.0	74.2, 71.5	53.5	30.9	26.2	20.8	36.6	26.2	
(R=*i*-Bu,R'=Et)				67.3			20.7				

Table 5 continued

4 5	71.3	90.2	74.5	75.7,72.3	51.3	149	130.1,	20.8		140.1,131.1
(R=Ph,R'=4-PhCl)				69.5			121.1,122.3			129.6,128.1
4 6	69.9	86.2	83.7	71.8, 70.6	55.0	51.0 (NEt)		12.6 (NEt)	20.3	
(R=NMeEt,R'=Me)				67.4		41.2 (NMe)				
5 6	70.0	88.0	81.8	72.8, 69.3	29.9	26.2	14.6	20.9		
(R=SEt,R'=Me)				67.4						

Table 6 72.5 MHz ^{13}C NMR Spectra for ligands (*S,R*)-50-(*R,S*)-55

Compound	Cp	C_1	C_2	C_3,C_4,C_5	$\underline{C}H$-CH_3	CH-$\underline{C}H_3$	NR			SR'	
							αC	βC	γC	αC	βC
(*S,R*)-50	69.8	94.2	82.3	72.3, 68.0	52.5	10.8	43.2	14.2		20.6	
(R=Et,R'=Et)				66.3							
(*S,R*)-51	69.8	94.1	82.7	71.6, 67.9	53.2	11.8	52.5	22.2	10.8	20.3	
(R=n-Pr,R'=Me)				66.3							
(*R,S*)-52	69.9	96.0	77.6	76.1, 68.4	52.3	10.2	43.2	14.3		30.6	14.3
(R=Et,R'=Et)				66.6							
(*R,S*)-53	69.9	95.1	78.9	74.6, 68.3	53.1	11.7	52.6	22.3	10.5	30.7	14.4
(R=n-Pr,R'=Et)				66.6							
(*R,S*)-54	69.9	96.0	77.6	76.1, 68.7	52.2	9.70	43.2	14.3		38.2	23.2
(R=Et,R'=*i*-Pr)				66.7				21.7			
(*R,S*)-55	69.9	96.0	76.0	70.6, 68.7	53.1	11.8	52.6	22.3	10.1	38.2	23.3
(R=*n*-Pr,R'=*i*-Pr)				66.8				21.7			



R= Et, R'= Me (37)

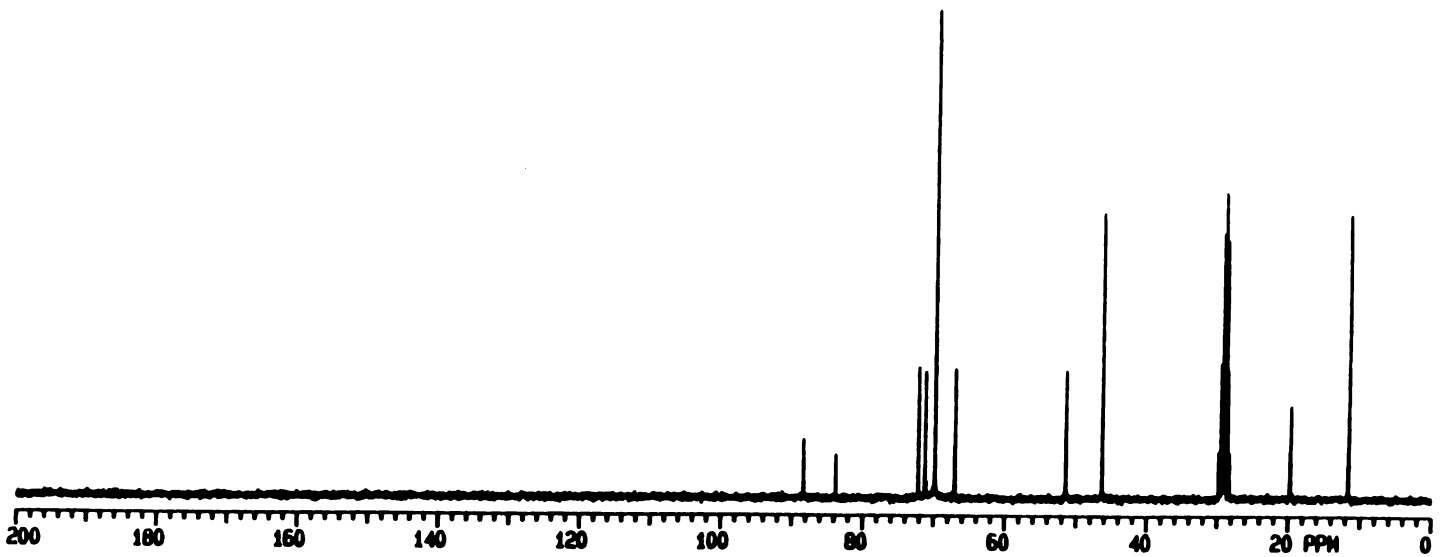


Figure 3. Broad band decoupled ^{13}C NMR spectrum of 37

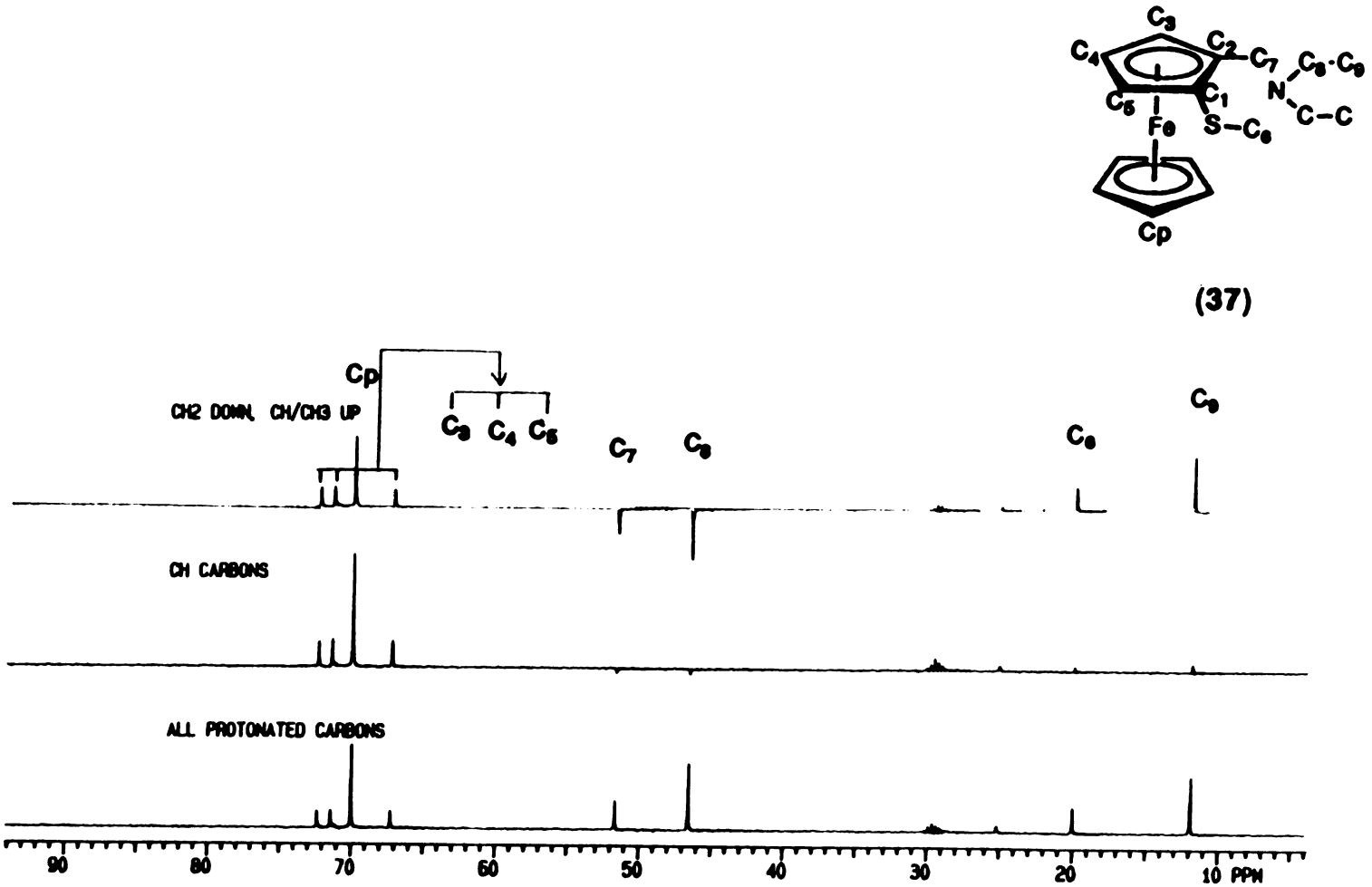


Figure 4. DEPT ^{13}C NMR spectrum of 37

Table 7 FTIR spectra of compounds **37-46,56**

Compound	Ferrocene C-H stretch	Alkyl C-H stretch	Ferrocene antisymmetric C-C stretch	C-N stretch	C-H bending ⊥ to the plane of Cp ring	S-C stretch	Antisymmetric ring-metal stretch
37	3093	2798-2973	1448	1173,1194	875	534	491
38	3095	2796-2968	1449	1175,1197	818	534	500
39	3096	2791-2963	1455	1175,1197	812	545	482
40	3095	2802-2969	1451	1175,1199	819	543	484
41	3095	2798-2958	1457	1173,1187	819	528	482
42	3095	2798-2958	1456	1172,1187	819	522	478
43	3095	2813-2964	1457	1179,1200	818	533	489
44	3096	2795-2954	1458	1171,1195	820	531	492
45	3017		1476	1256,1217	754	698,670	482
46	3084	2781-2971	1450	1190,1175	809	527	492
56	3096	2820-2965	1447	----------	822	532	483

Table 8 FTIR spectra of compounds **(*S*,*R*)-50-(*R*,*S*)-55**

Compound	Ferrocene C-H stretch	Alkyl C-H stretch	Ferrocene antisymmetric C-C stretch	C-N stretch	C-H bending ⊥ to the plane of Cp ring	S-C stretch	Antisymmetric ring-metal stretch
(*S*,*R*)-50	3095	2808-2970	1449	1176,1199	818	543	509
(*S*,*R*)-51	3095	2808-2958	1456	1174,1185	818	521	512
(*R*,*S*)-52	3095	2806-2970	1449	1175,1198	819	542	509
(*R*,*S*)-53	3098	2809-2961	1456	1173,1185	820	543	505
(*R*,*S*)-54	3096	2806-2963	1451	1154,1169	822	542	507
(*R*,*S*)-55	3098	2808-2961	1453	1156,1171	822	542	507

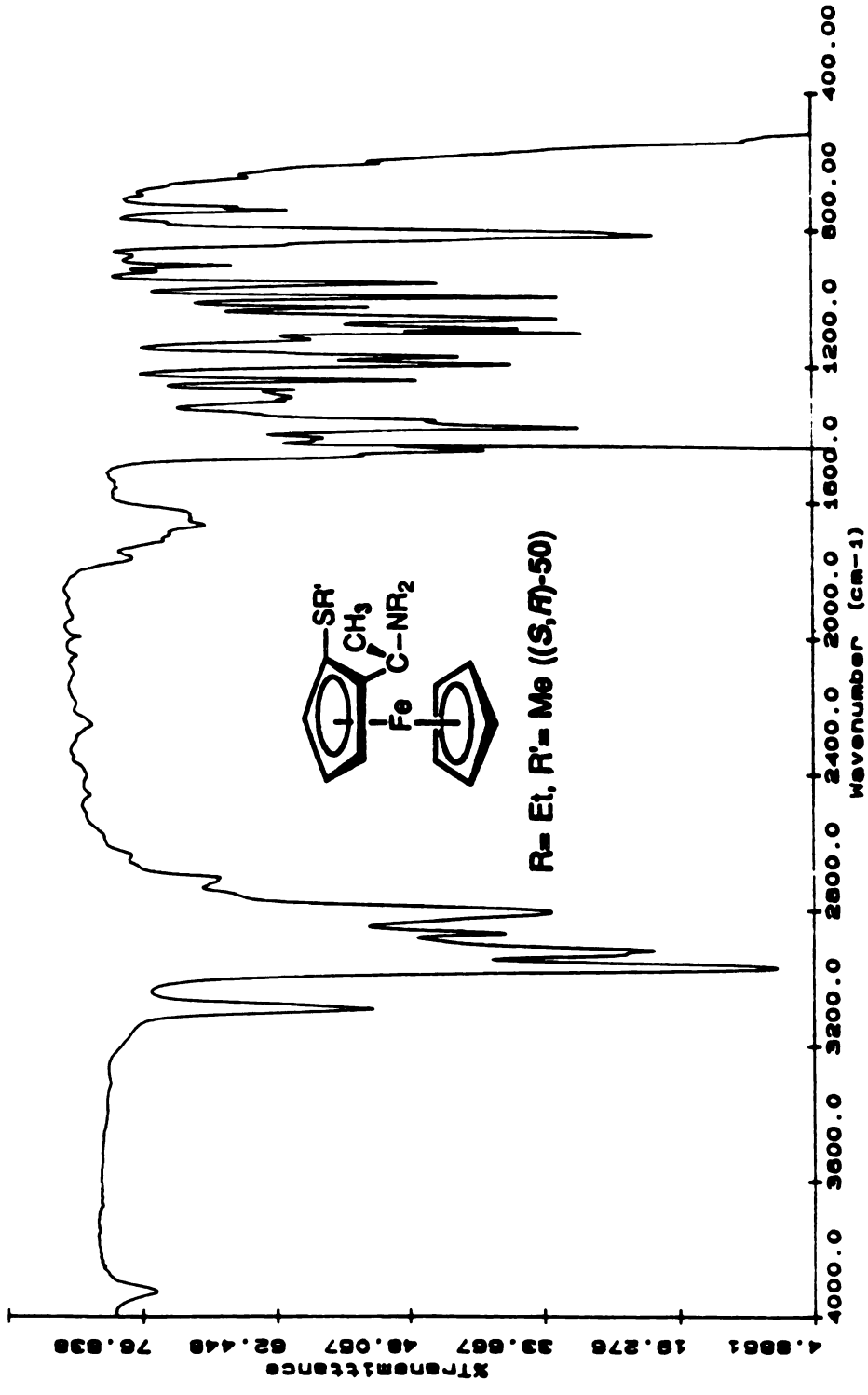


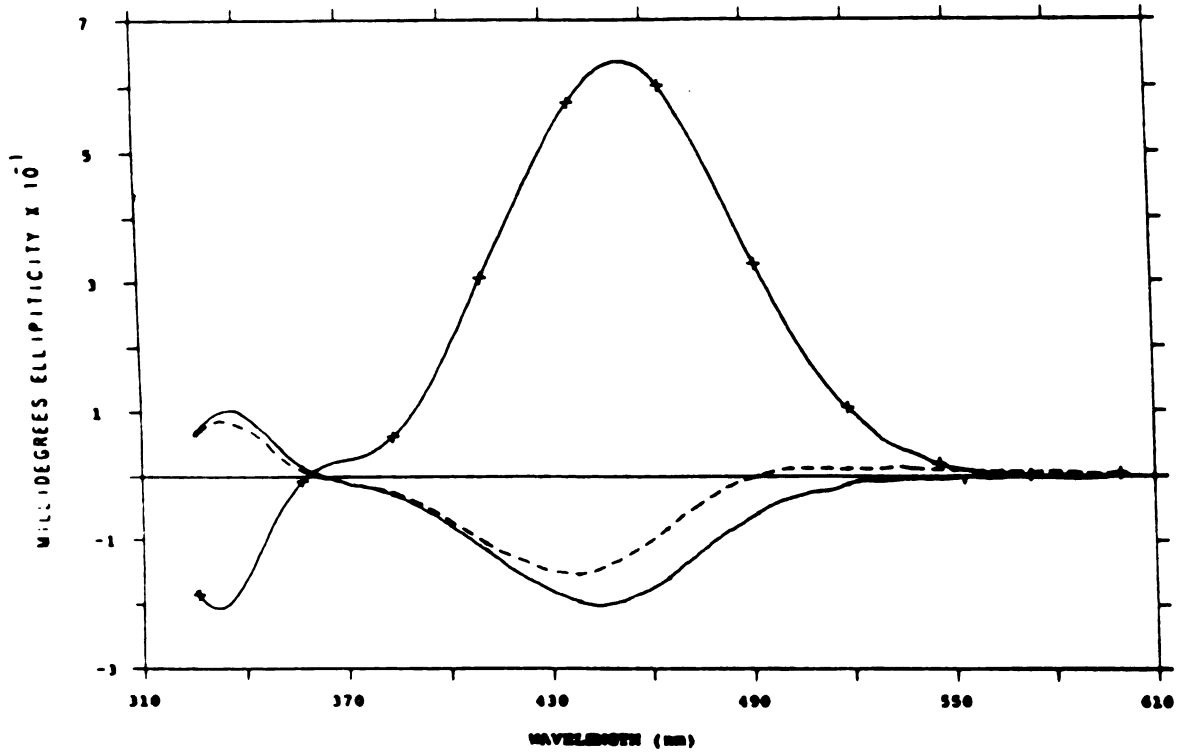
Figure 5. Mid IR spectrum of compound (*S,R*)-50

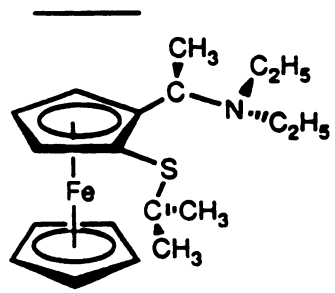
In the mass spectra molecular ion peaks are detected in all the compounds. For compounds **39** and **45** which contain Cl atoms, ^{37}Cl isotope peaks are also detected at M^++2. Other important fragments are M^+-CH_2NR_2, M^+-$CHCH_3NR_2$, M^+-SR', $CpFe^+$, Fe^+ and NR_2. The mass spectra are also shown in the appendix.

In order to assure the planar chirality of the chiral ligands, CD measurements were performed for some representative ligands. The CD spectra of compounds (*S*,*R*)-**51**, (*S*,*R*)-**52**, (*R*,*S*)-**54**, (*R*,*S*)-**55**, (*R*,*S*)-1-(1-dimethylaminoethyl)-2-phenylthioferrocene (*R*,*S*)-**81**, and (*S*,*R*)-1-(1-dimethylaminoethyl)-2-2'-(bismethylthio)ferrocene (*S*,*R*)-**82** are shown in Figs. 6 and 7.

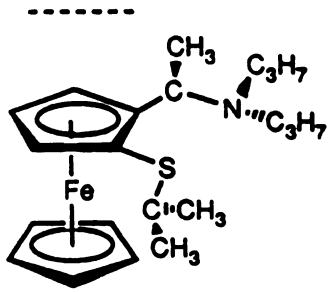
The absorption spectrum of ferrocene has two long wavelength bands at 325 and 440 nm assigned to d-d type transitions.[103] The CD spectra of chiral ferrocenylamine sulfides reveal optical activity arising from the planar chirality around these two absorption bands.

The assignments of planar chirality to these new ferrocenyl sulfides were made possible by comparison with known chiral ferrocenylphosphines.[15,17] (Fig. 8) The ferrocenylsulfides with planar chirality of *R* configuration (*S*,*R*)-**51**, (*S*,*R*)-**52** and (*S*,*R*)-**82**, all exhibit negative Cotton effects around 330-340 nm and positive ones around 440-450 nm, whereas negative Cotton effects are observed in the cases of (*R*,*S*)-**54**, (*R*,*S*)-**55** and (*R*,*S*)-**81** whose chiralities are *S*.

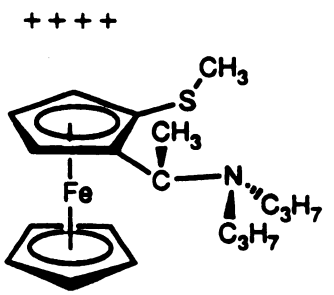




(*R*,*S*)-54

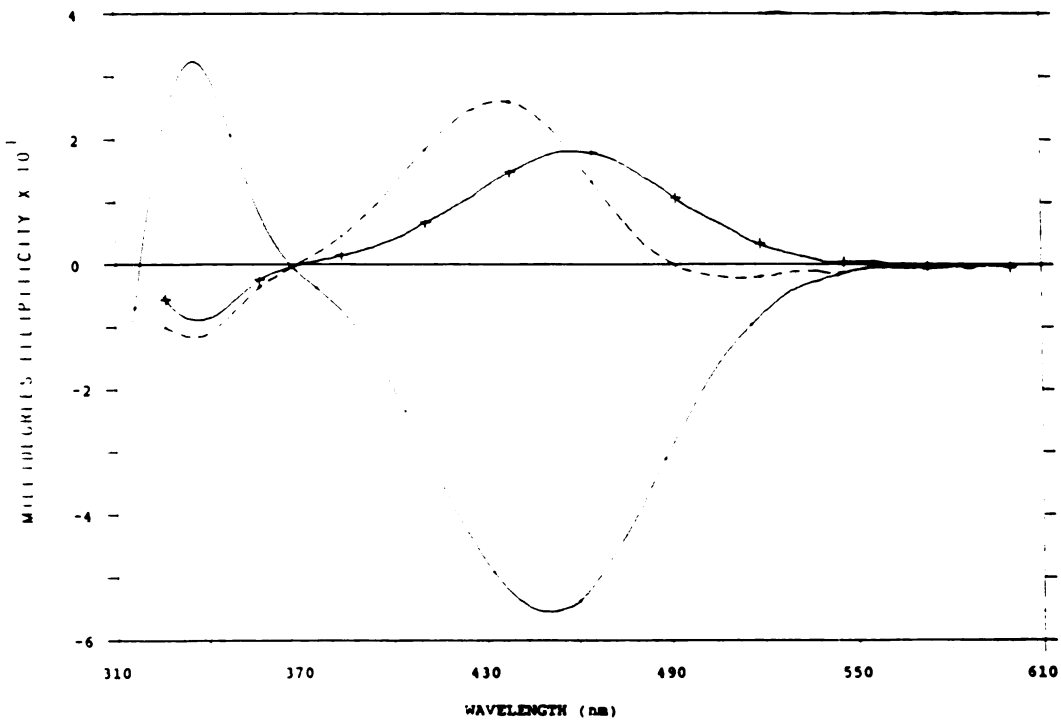


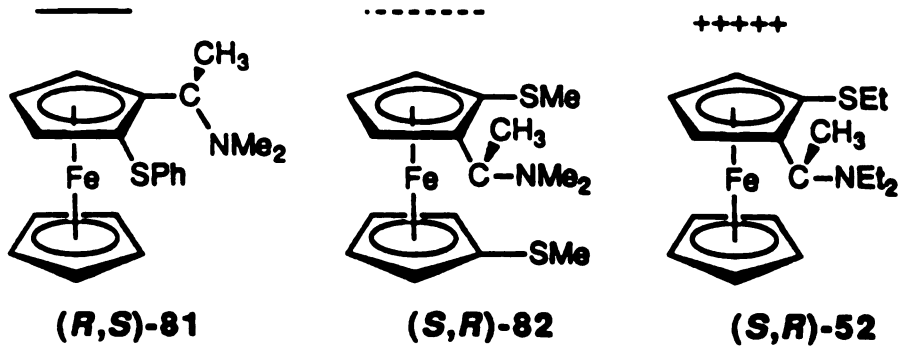
(*R*,*S*)-55



(*S*,*R*)-51

Figure 6. CD spectra of (*S*,*R*)-51, (*R*,*S*)-54 and (*R*,*S*)-55 in chloroform





(*R*,*S*)-81 (*S*,*R*)-82 (*S*,*R*)-52

Figure 7. CD spectra of (*S*,*R*)-52, (*S*,*R*)-82 and (*R*,*S*)-81 in chloroform

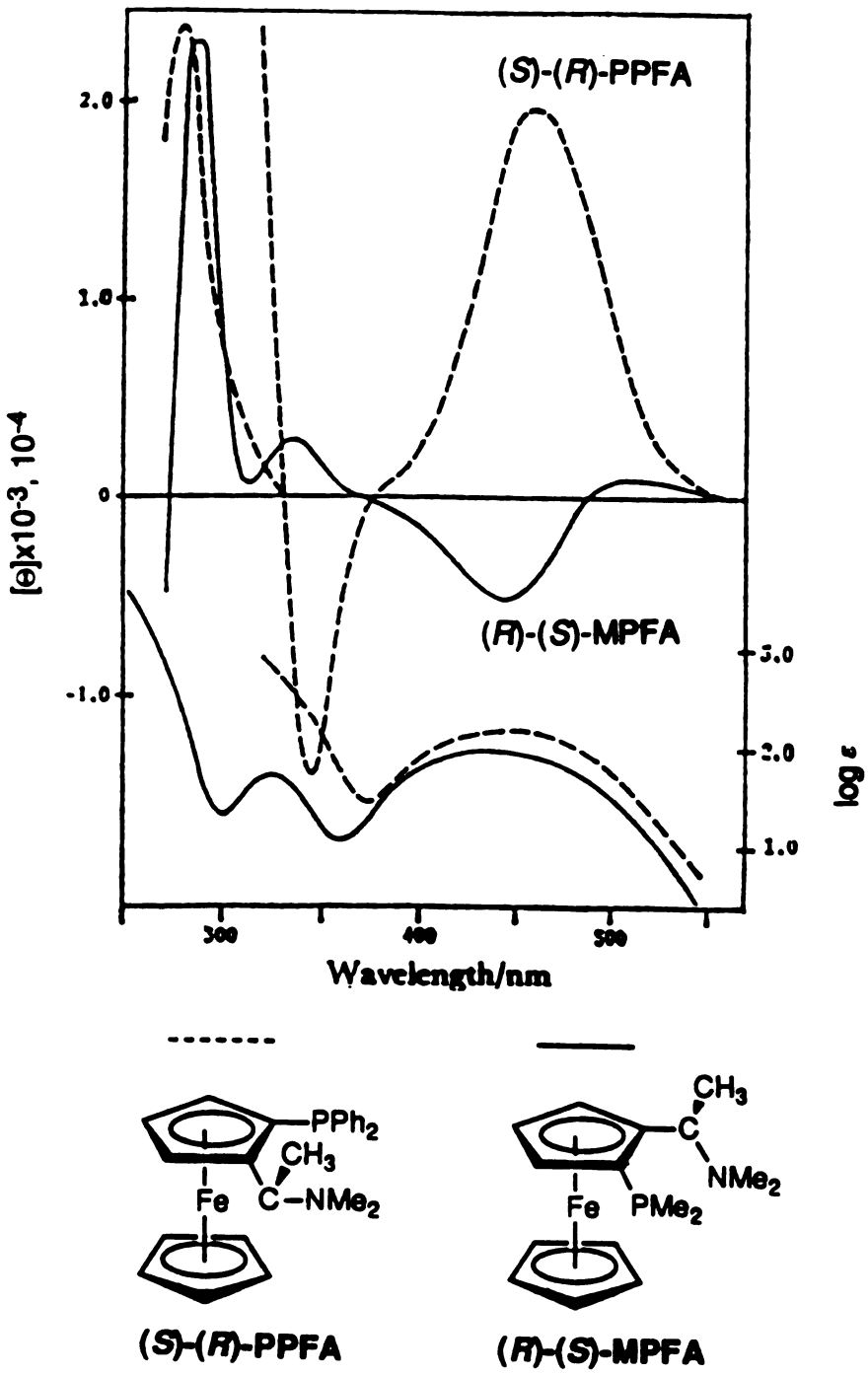


Figure 8. CD and UV spectra of (*S*,*R*)-PPFA and (*R*,*S*)-MPFA in chloroform

(2). Synthesis of Ferrocenyldisulfide Ligand

The 1,2-disubstituted ferrocenylsulfide ligand can be prepared by reacting the corresponding ferrocenyl ethylacetate with ethanethiol, but the yield is low (ca. 10-20%).

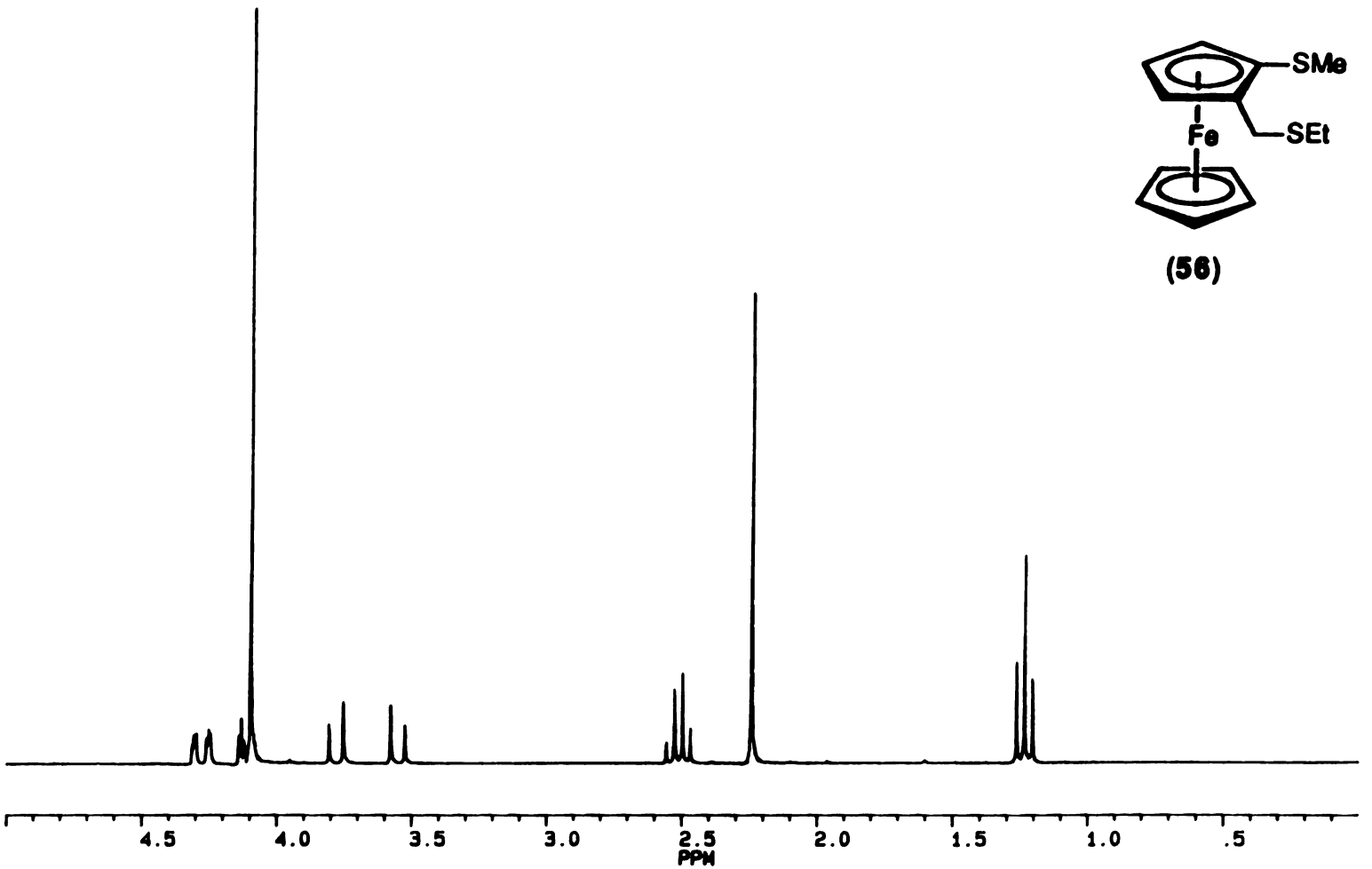
An alternative route was adopted and ligand **56** was generated *in situ* by first converting methylthioferrocenyl ethylacetate into halide, then stirring it with NaSEt.[104] The yield improved to 84%.

The ^{1}H NMR and off-resonance ^{13}C NMR are shown in Figs. 9 and 10. The two diastereotopic thiomethylene protons in the ethylthio group show a quartet which is different from those of the aminomethylene protons in the ethylamino group. The free rotation of the ethylthio group suggests that this ferrocenyl sulfide ligand is sterically more relaxed than those of ferrocenylamine sulfides.

The ^{13}C NMR spectrum assignment for the two thioether groups can be made by considering the different deshielding effect exerted by these two substituents. Thus, the unsubstituted Cp ring was assigned at 70.0 ppm, C_1 and C_2 at 88.0 and 81.8 ppm respectively; C_3, C_4, C_5 appeared at 72.8, 69.3, and 67.4 ppm; the methylthio group (C_6) at 20.9 ppm ; C_9 at 14.6 ppm.

Similar to the ^{13}C NMR assignments of the ferrocenylamine sulfide ligands, the methylene carbon (C_7) between the Cp ring and the sulfide substituent should appear at lower field than the thiomethylene carbon (C_8). So, C_7 was assigned at 29.9 and C_8 at 26.2 ppm.

An interesting feature arises if one compares the chemical shift of methylene carbons (C_7, C_8) in the ferroceneylamine sulfide series and compound **56**. The C_7 chemical shift in the former series appeared at around 50 ppm, but in compound **56** it appeared at around 30 ppm. Obviously, the more electronegative N atom pulls electron density from it's nearby carbon group more efficiently than does the less electronegative S atom; thus, the carbon groups near



(56)

Figure 9. 300 MHz ^{1}H NMR spectrum of **56**

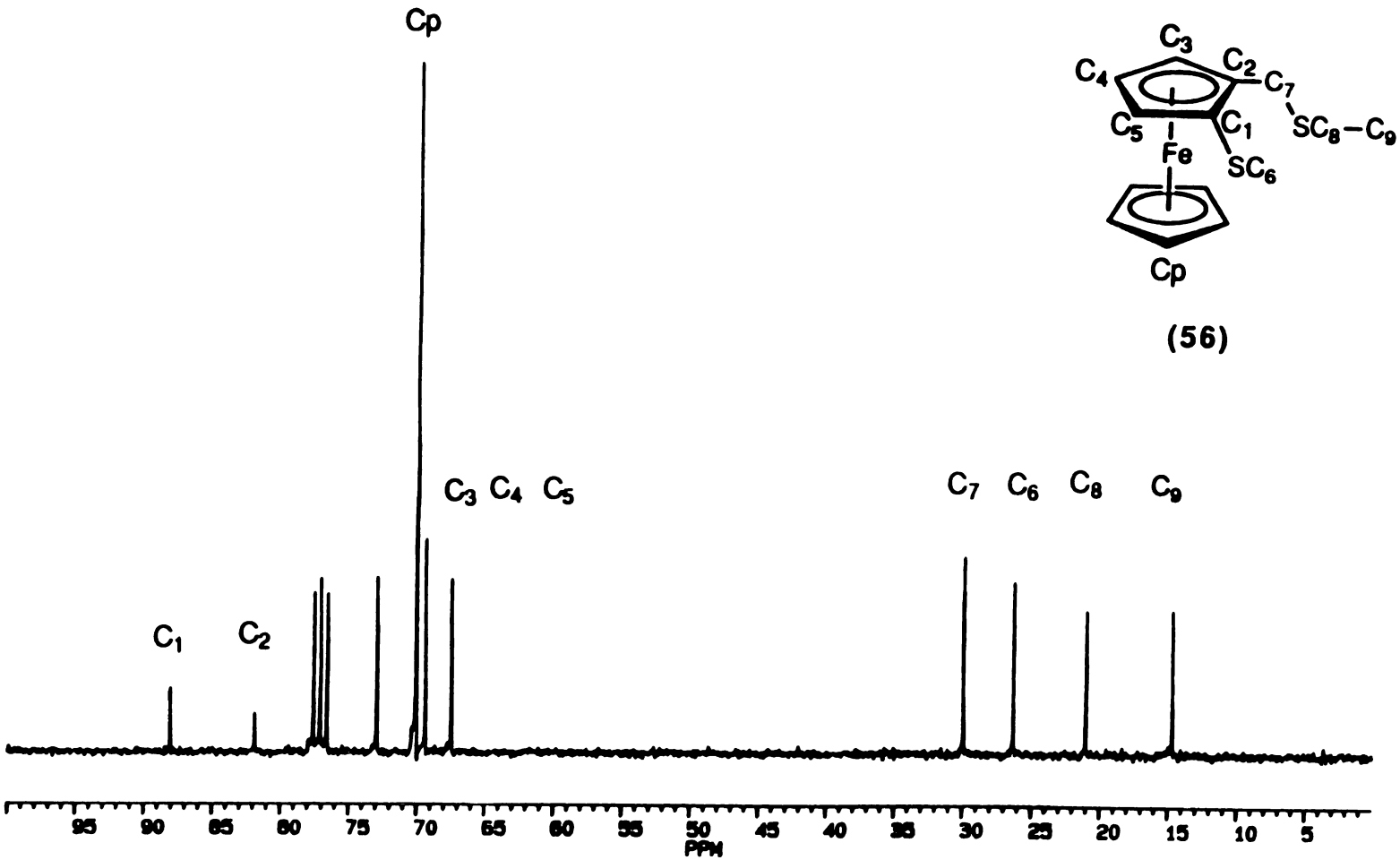
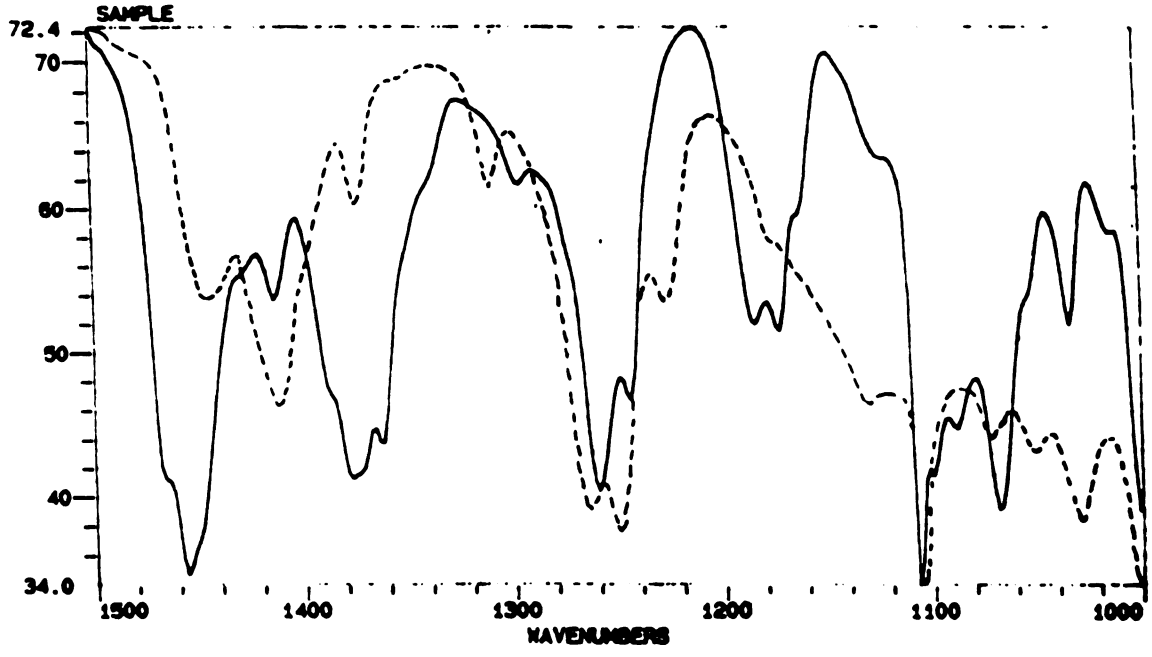


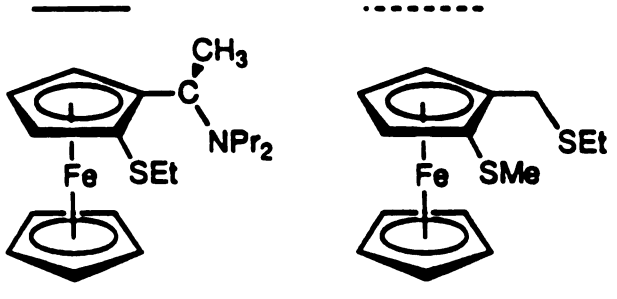
Figure 10. Broad band decoupled ^{13}C NMR spectrum of **56**

the S atom appear at higher field. The same argument holds for carbon C_8. The chemical shifts of C_9 appeared at about the same field (12-15 ppm), thus the inductive effect apparently influences only the nearby carbons (αC) significantly. The βC is less sensitive.[149(a)]

As expected, the IR C-N stretching bands around 1150-1190 cm^{-1} were not observed. (Fig. 11) Disappearance of C-N absorption in this region solidifies the C-N stretch assignment made in the ferrocenylamine sulfide ligands.

The mass spectrum is shown in Fig. 12. The molecular ion peak was observed again with a 43% relative intensity at M/e = 306; other important fragments include M^+-SEt (245), M^+-C_5H_5-Fe-C_5H_3 (124), Fe^+(56), $C5H5^+$(65).





(*R*,*S*)-53 (56)

Figure 11. Comparison of IR spectra of **56** and (*R*,*S*)-**53** in 1000 cm^{-1}-1500cm^{-1} region

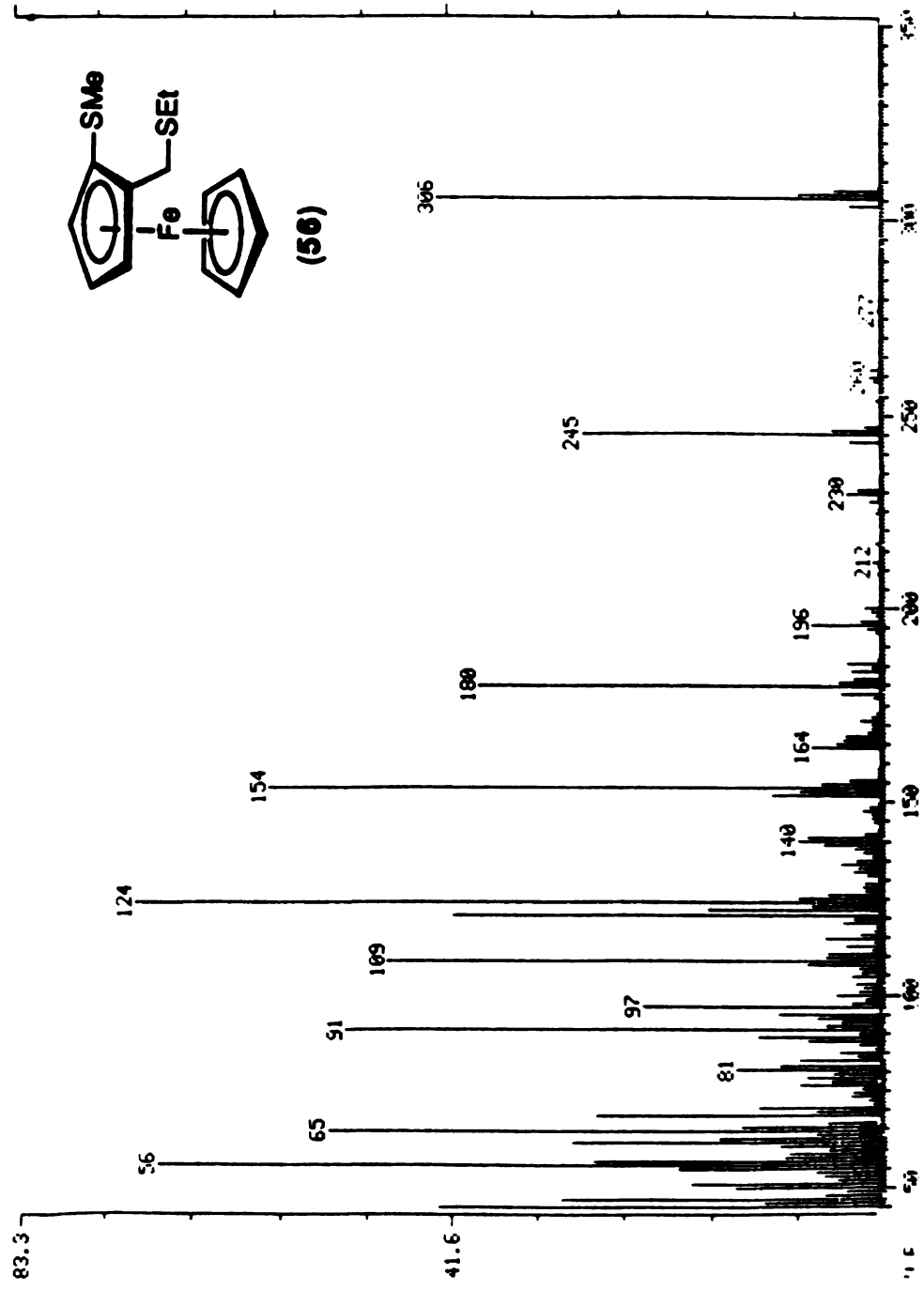


Figure 12. Mass spectrum of **56**

2. Preparation of Palladium and Platinum Complexes

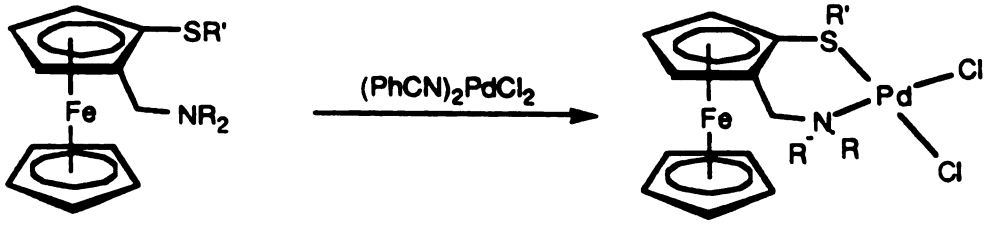
The procedure was similar to that used for preparation of other ferrocenylamine sulfide complexes reported previously;[82,83] however, shorter reaction times were employed, i.e., 8 h for palladium or 2 days for platinum complexes. Schemes 7,8 show the preparation of these heterobimetallic complexes.

These palladium complexes are soluble in polar organic solvents such as methylene chloride, chloroform, acetone and acetonitrile. The platinum complex is soluble in acetone and slightly soluble in the other three solvents. Pure samples can be obtained by recrystallization from either methylene chloride/hexane or acetone/ether. The catalysts obtained are stable for months without deterioration or decrease in catalytic activity.

Tables 9 and 10 show the 300 MHz ^{1}H NMR data for these achiral (**57-65**) and chiral complexes ((***R***,***S***)-**66**-(***R***,***S***)-**71**) respectively.

Since formation of the distorted six-member ring between the ligands and the metal chloride prohibited free inversion of the pyramidal N, the methyl region of the diethylamine group and that of the di-*n*-propylamine group appear as two triplets instead of the one present in the pure ligands. Donation of the lone pair electrons of the amino and thioether groups to palladium during complex formation causes the chemical shift of both groups to appear at lower field than did those of the free ligand. The thiomethylene and aminomethylene protons were assigned by 2D COSY experiments. A typical spectrum for achiral complex (***R***,***S***)-**68** is given in Fig. 13.

The two thiomethylene protons, for example, are assigned at δ=3.17 and 3.40 ppm since they are correlated with the methylthio group located at 1.70 ppm. The two sets of aminomethylene protons are assigned as follows : one set at 2.58 and 3.15 ppm is correlated to the methyl group at 1.04 ppm; the second set at 2.23 and 3.91 ppm is correlated to the methyl group at 1.91 ppm.

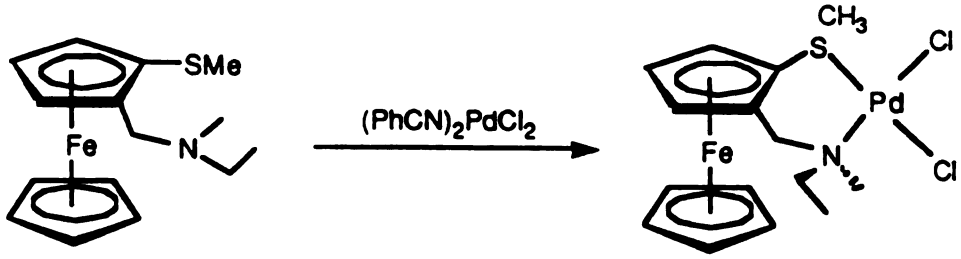


R=Et

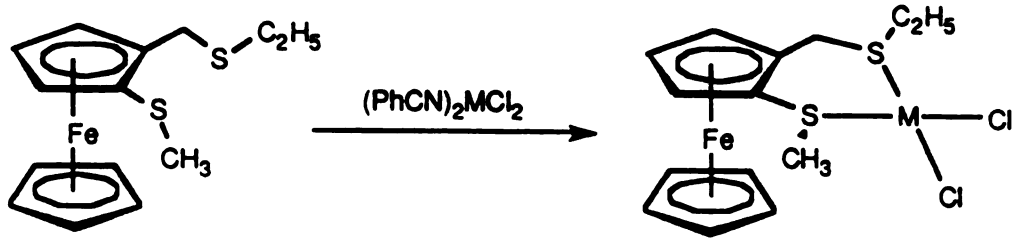
R'= Me,Et,  ,  **(57-60)**

R=*n*-Pr

R'= Me, Et **(61,62)**

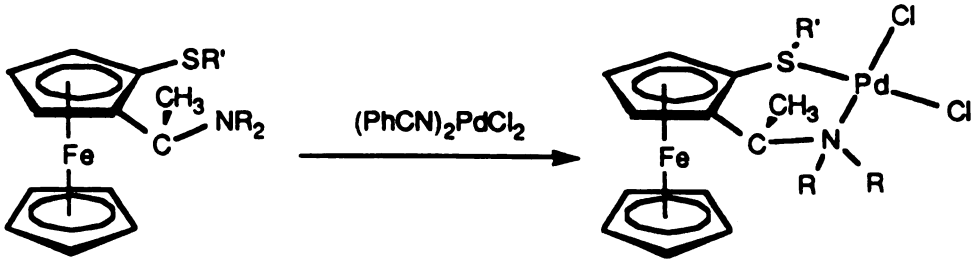


(63)



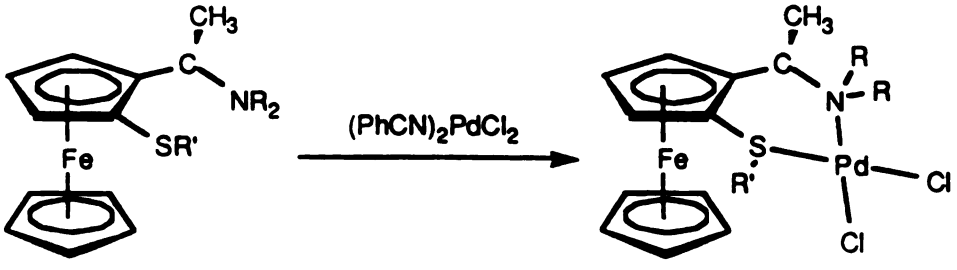
M=Pd **(64)**
M=Pt **(65)**

Scheme 7



R= Et,*n*-Pr

R'=Me ((***S,R***)-66,67)



R'= Et ((***R,S***)-68,69)

R'=*i*-Pr ((***R,S***)-70,71)

Scheme 8

Table 9 300 MHz ^{1}H NMR Data for Compounds (57-65) in $CDCl_3$ at Room Temperature; δ ppm (Hz)

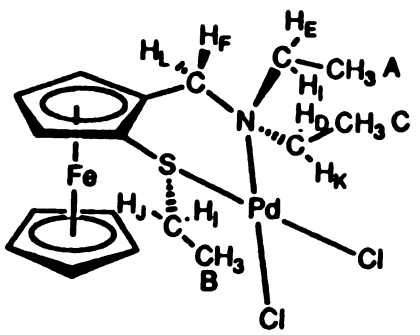
Compound	C_5H_5	C_5H_3	CH_2N	NR (SEt) αH	NR (SEt) βH	NR (SEt) γH	SR' αH	SR' βH	Ph	Ph-CH_3
5 7	4.24 s	4.32, 4.41	2.90 d (13.7)	2.30 m,2.67m	1.00 t (7.2)		2.75 s			
(R=Et,R'=Me)		4.52 m	3.95 d (13.7)	3.28 m,3.87m	1.95 t (7.0)					
5 8	4.22 s	4.34, 4.40	2.85 d (13.6)	2.20 m,2.60m	1.03 t (7.2)		3.20 m	1.70 t (7.2)		
(R=Et,R'=Et)		4.53 m	4.04 d (13.6)	3.20 m,3.90m	1.91 t (7.0)		3.40 m			
5 9	4.10 s	4.23, 4.40	2.96 d.(13.6)	2.41 m,2.76m	1.06 t.(7.2)				7.85[a]m	
(R'=4-PhCl)		4.00 m	4.64 d (13.6)	3.18 m,4.04m	1.96 t.(7.0)				7.44[a]m	
6 0	4.06 s	4.15, 4.22	2.92 d (13.6)	2.75 m,3.18m	1.08 t (7.1)					2.37
(R=*p*-tolyl)		4.38 m		3.95-4.06 [a]m	1.94 t (7.1)					
6 1	4.22 s	4.32, 4.38	2.95 d (13.5)	2.13dt,2.47dt	1.37 m,1.65 m	0.68 t (7.2)	2.73 s			
(R=n-Pr,R'=Me)		4.51 m	3.95 d (13.7)	3.08dt,3.73dt	1.98 m,3.21 m	1.05 t (7.2)				
6 2	4.21 s	4.34 [a]m	4.06 d (13.7)	2.36dt,2.97dt	1.40-1.65 [a]m	0.68 t (7.4)	3.17 [b]m	1.69 t (7.2)		
(R'=Et)		4.53 [b]m	2.90 d (13.7)	3.18dt,3.79dt	1.90-2.10 [a]m	1.04 t (7.4)	3.41 [b]m			
6 3	4.24 s	4.48, 4.40	4.02 d (13.0)	3.97 m, 2.13m	1.90 t (7.0)		2.70 s			
(R=NMeEt, R'=Me)		4.34 m	2.53 d (13.0)	2.37 s (NMe)						
64 (M=Pd)	4.49 s	4.51, 4.38	3.54 d (13.0)	3.33 q (6)	1.61 t (6)		2.70 s			
(R=SEt,R'=Me)		4.32 m	3.66 d (13.0)							
65 (M=Pt)	4.50 s	4.64, 4.45	3.84 d (13.0)	3.30 q (7.4)	1.58 t (7.4)		2.71 s			
(R=SEt,R'=Me)		4.44 m	3.68 d (13.0)				(Pt-H)=21.7 Hz			

[a]2H
[b]1H

Table 10 300 MHz ^{1}H NMR Data for Compounds ((*S*,*R*)-66-(*R*,*S*)-71)) in $CDCl_3$ at Room Temperature; δ ppm (Hz)

Compound	C_5H_5	C_5H_3	CH-CH_3	CH_3-CH	NR αH	NR βH	NR γH	SR' αH	SR' βH
(*S*,*R*)-66 (R=Et,R'=Me)	4.19 s	4.30 t 4.43 m 4.51 m	4.02 q (6.6)	1.55 d (6.8)	2.43[a] m 2.88[b] m 4.10[b] m	1.09 t (7.1) 1.97 t (7.1)		2.74 s	
(*S*,*R*)-67 (R=*n*-Pr,R'=Me)	4.19 s	4.34 t 4.42 m 4.51 m	4.01 q (6.8)	1.55 d (6.7)	1.64 dt 2.34 m 2.19 dt 3.96 dt	0.83 m 1.91 m 2.34 m 3.32 m	0.64 t (7.1) 1.11 t (7.1)	2.73 s	
(*R*,*S*)-68 (R=Et,R'=Et)	4.18 s	4.37 t 4.42 m 4.54 m	4.08 q (6.8)	1.54 d (6.8)	2.34[a] m 2.71[b] m 1.80[b] m	1.12 t (7.2) 1.97 t (7.1)		3.36 m	1.72 t (7.2)
(*R*,*S*)-69 (R=*n*-Pr,R'=Et)	4.17 s	4.36 m 4.39 m 4.52 m	4.06 q (6.8)	1.53 d (6.8)	2.14 d,t 2.29 m 2.50 d,t 3.98 d,t	0.95 m 1.92 m 2.29 m 3.32 m	0.63 t (7.2) 1.08 t (7.3)	3.32[b] m	1.71 t (7.2)
(*R*,*S*)-70 (R=Et,R'=*i*-Pr)	4.20 s	4.41 t 4.45 m 4.67 m	4.03 q (6.6)	1.54 d (6.7)	1.83[b] m 2.37[a] m 2.62[b] m	1.09 t (7.2) 1.97 t (7.1)		4.20 m	1.77 t (7.2) 1.88 t (7.0)
(*R*,*S*)-71 (R=*n*-Pr,R'=*i*-Pr)	4.18 s	4.40 m 4.42 m 4.65 m	4.03 m	1.53 d (6.8)	2.09 d,t 2.23 d,t 2.41 m 4.03 d,t	0.81[b] m 1.87 m 2.41 m	0.61 t (7.0) 1.07 t (7.1)	3.38 m	1.76 d (7.1) 1.87 d (7.0)

[a] 2H
[b] 1H



(58)

AUTOMATIC COSY ANALYSIS

	L	K	J	I	H	G	F	E	D	C	B	A	(ppm)
A						G		E					1 04
B			J	I									1 70
C		K							D				1 91
D		K								C			2 23
E						G						A	2 58
F	L												2 86
G			J					E				A	3 15
H													3 17
I											B		3 18
J						G					B		3 40
K									D	C			3 91
L							F						4 05

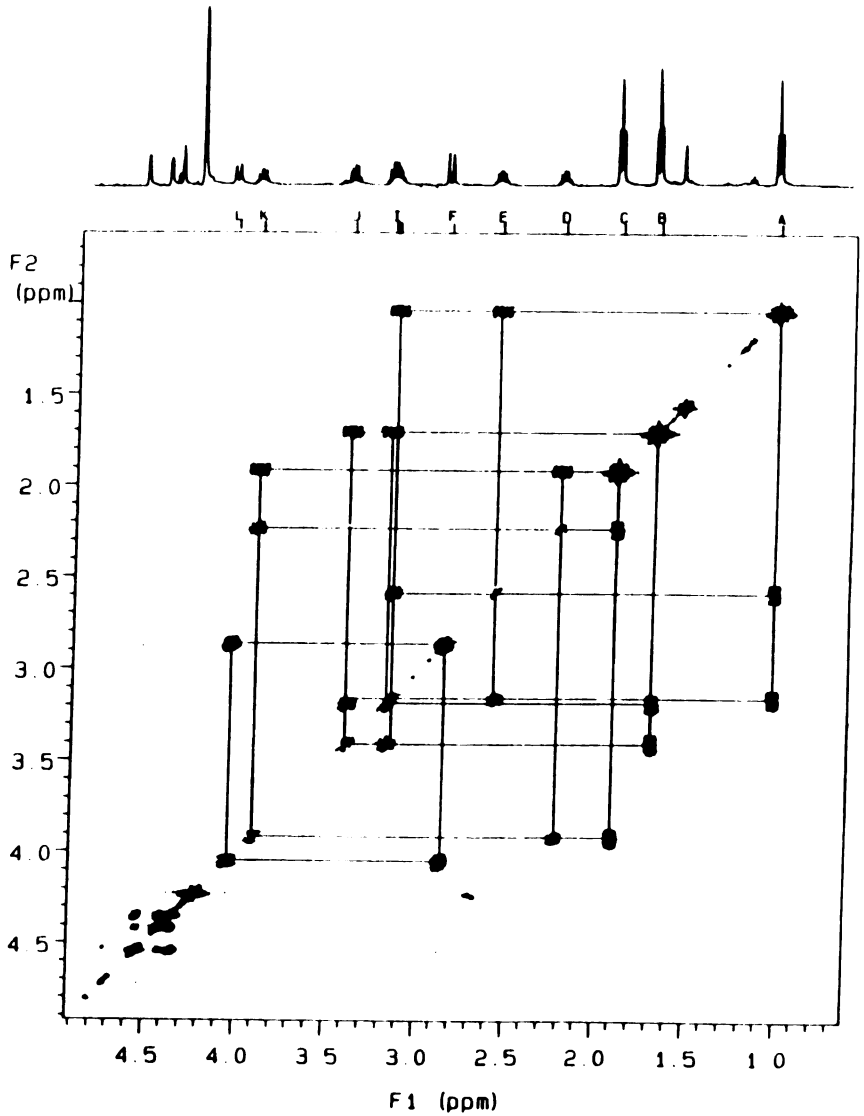


Figure 13. 2D COSY spectrum of 58

The chemical shifts of these four aminomethylene protons range from 2.23 to 3.91 ppm; apparently they experience very different chemical environments. This observation infers that some protons are closer to the metal center and some are more distant, with the closest proton appearing at higher field (it experienced the back donation of the electrons from the metal center). This consideration should also be true for the other moieties.

The ^1H NMR spectra for the 1,2-disubstituted ferrocenylsulfide palladium and platinum complexes are similar to those of the ferrocenyl-amine sulfide complexes. Again, the chemical shifts for both thioether groups are at lower field than those of the ligand. However, the two thiomethylene protons appear at the same chemical shift and appear as a broadened quartet. This observation is very different from that of the palladium ferrocenylamine sulfide complexes where the methylene protons appear at two distinct fields unless they are coincidentally collapsed at the same field. Perhaps the structure of the disulfide complexes are different from those of the amine-sulfide series and might exist as dimers instead of monomers.(Fig.14) In such a case the thiomethylene protons will be more sterically relieved and thus all methylene protons show only the first order spectrum. An X-ray crystallographic study of the platinum disulfide complex has been undertaken.

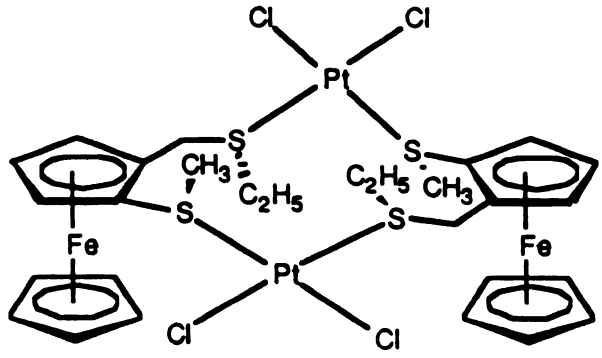


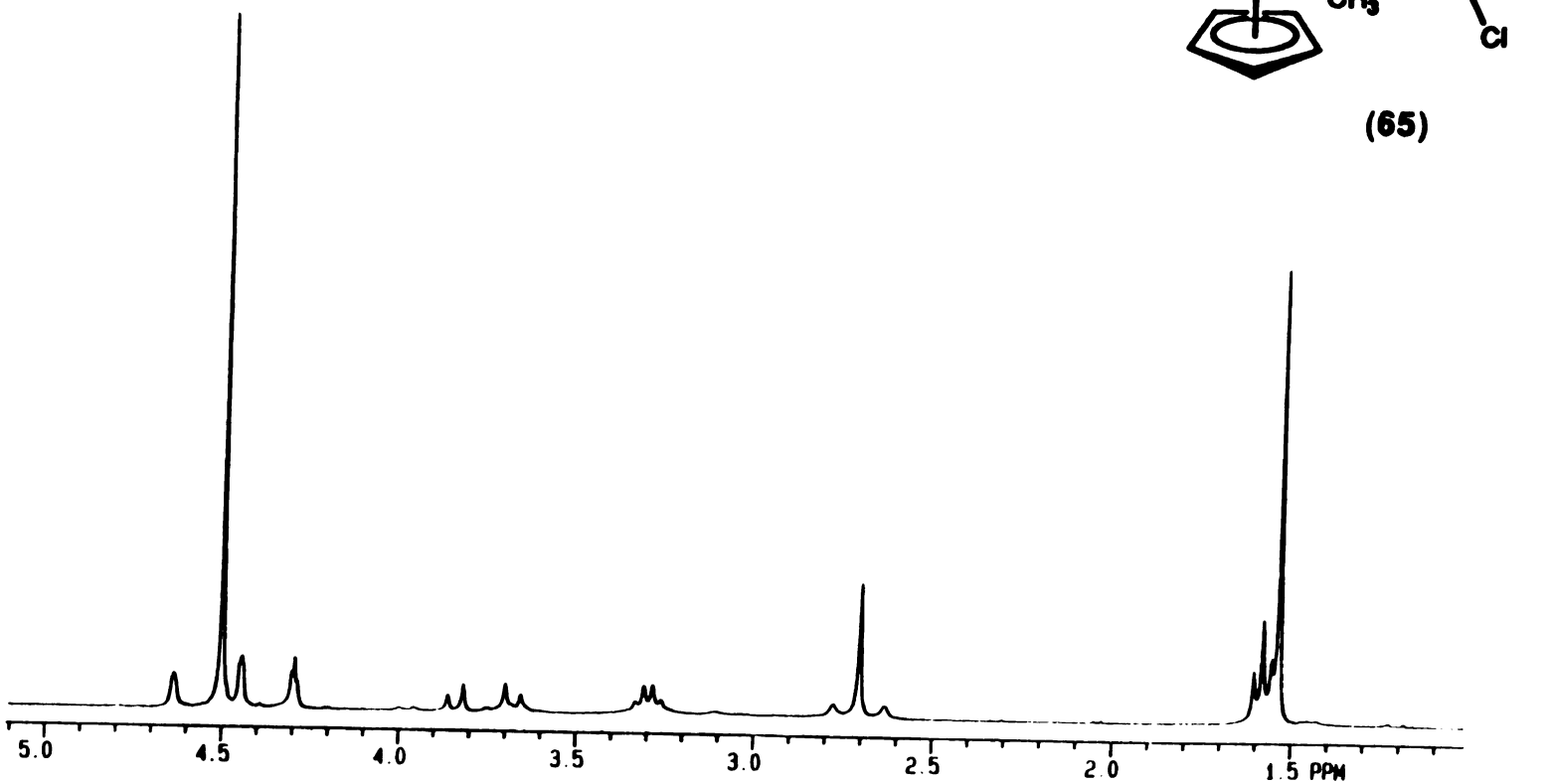
Fig. 14

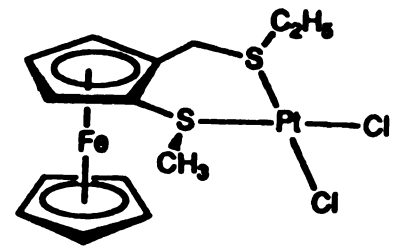
The ^{195}Pt-H coupling was observed in platinum compound **65** (Fig.15) with a Pt-H three-bond-coupling constant equal to 43.4 Hz, consistent with the literature value.[105-107] A comparison of the chemical shift of this compound with it's palladium analogue **64** indicates that the ethylthio group of both complexes appears at about the same field ($\Delta\Delta\delta$= -0.03 ppm), but the Cp-CH_2-N methylene protons appear at lower field ($\Delta\Delta\delta$= 0.22 ppm). This lower field shift may be due to a stronger inductive effect induced by the more electronegative platinum atom.

The infrared spectra of these palladium and platinum complexes are similar to those of the free ligands. The most important bands are the metal-chloride, metal-sulfur and metal-nitrogen stretching bands in the far IR region. The metal-S bands are often weak and occur close to those of the metal-halogen bands.[107] Thus, metal-sulfur and metal-halogen bands are assigned around 300-340 cm^{-1}. Metal-nitrogen stretching occurs at higher frequency, thus is assigned at around 500 cm^{-1}. These assignments are within the literature values.[108-116]

To assure the correctness of the assignments, far IR spectra of palladium and platinum ferrocenylsulfide complexes **64** and **65** were collected and compared with the palladium ferrocenylamine sulfide (**37**) as shown in Fig.16.

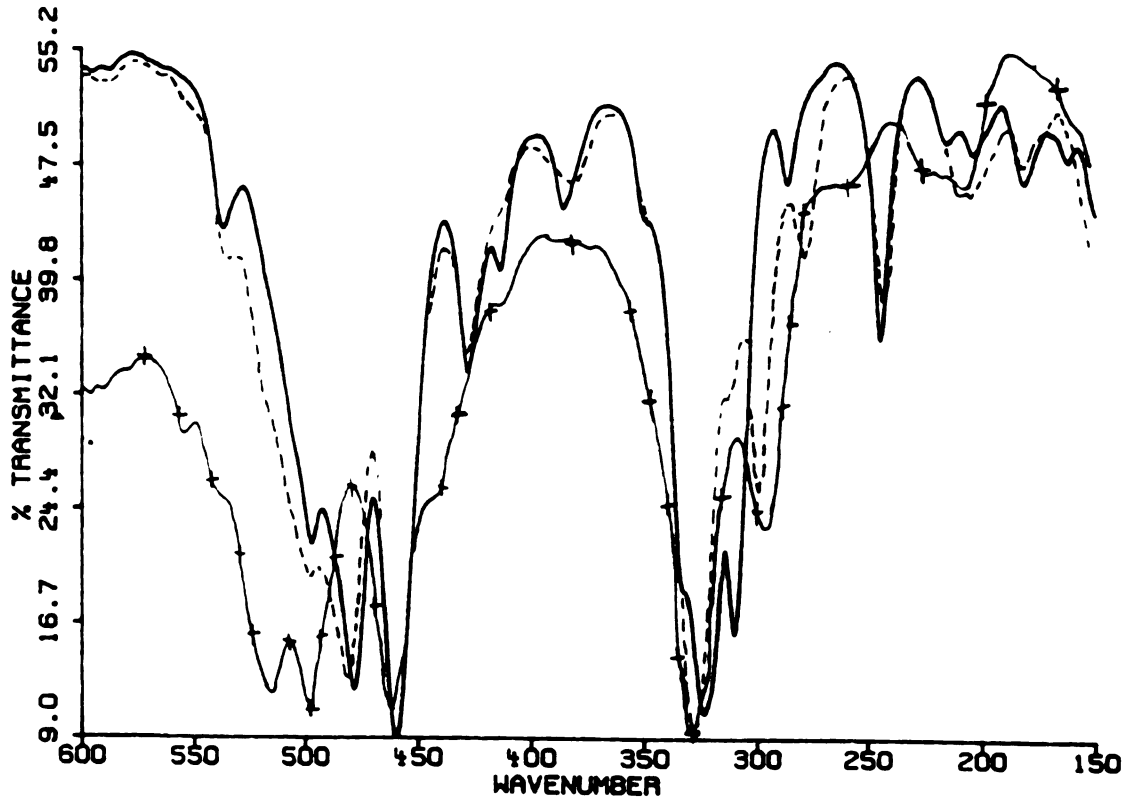
As one might expect, the Pd-N and Pt-N stretching bands around 510 cm^{-1} disappeared. One extra absorption found around 244 cm^{-1} in both disulfide complexes is probably due to the extra sulfur-metal-sulfur bending.[148] Clark and others[149] assigned this mode as M-S-C bending; however, this absorption was not found in the amine-sulfide complexes. A comparison of the structural differences between the amine-sulfide complexes and the sulfide-sulfide complexes indicates additional S-M-S bonds were formed by the latter; thus, assignment of this band as a S-M-S bending mode seems reasonable.





(65)

Figure 15. 300 MHz ^{1}H NMR spectrum of 65



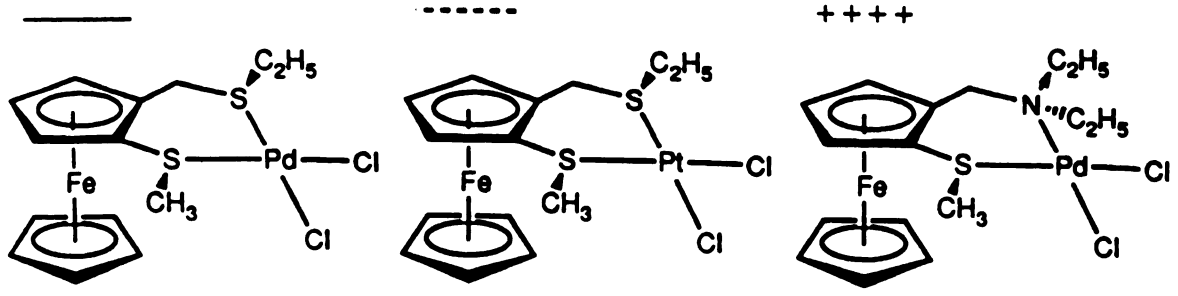


Figure 16. Comparison of far IR spectra of 57, 64 and 65

Since Pd-Cl and Pd-S absorbed at about the same region, it was difficult to assign them within the same series. However, by comparing the Pd-S and Pt-S absorptions one can clearly see the difference around the 300-340 cm^{-1} region. Since the Pt-S absorption occurred at higher wavenumbers than that of Pd-S ,[148] the former was assigned at 297 cm^{-1} and the latter at 310 cm^{-1}. On the other hand, the Pd-Cl absorption should be at 325 cm^{-1} and that of Pt-Cl at 324 cm^{-1}.

The far IR spectra for other complexes are collected in the appendix and the absorption frequencies of complexes **57**-(***R*,*S***)-**71** are listed in Table 11.

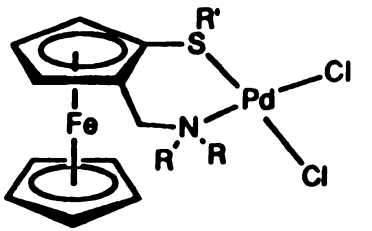
Due to the low volatility of these metal complexes, molecular ion peaks could not be detected by the conventional electron impact (EI) technique. However, the ligand ion peak was observed in these complexes and the fragmentations were similar to those of the free ligands.

The Fast Atom Bombardment (FAB) technique has been employed successfully to detect many inorganic molecules of low volatility.[117] By using NBA (3-nitrobenzyl alcohol) as a matrix, the molecular ion peaks for compounds **58**, **59** and (***R*,*S***)-**68** were detected. The FAB spectrum for compound **58** is shown in Fig. 17. The fragment patterns exhibit isotope effects. A computer simulation of the isotope intensity around the molecular ion region shows the same pattern as that of the sample. (Fig. 18) The major fragments of these complexes are listed in the experimental section.

The analytical data for these new ferrocenylamine sulfide and disulfide ligands as well as their metal complexes are collected in Tables 12 and 13.

Table 11 FTIR spectra of complexes **57-(*R*,*S*)-71**

Compound	Ring-Metal stretch	Pd-N stretch	M-Cl stretch	M-S stretch	S-M-S bending
57 (R=Et, R'=Me)	494	511	322	291	
58 (R=Et, R'=Et)	498	515	328	295	
59 (R=Et, R'=4-PhCl)	488	503	329	305	
60 (R=Et, R'=*p*-tolyl)	486	497	328	302	
61 (R=*n*-Pr, R'=Me)	499	518	323	295	
62 (R=*n*-Pr, R'=Et)	501	518	325	296	
64 (R=SEt, R'=Me)	480		328	295	241
65 (M=Pt)	478		324,285	310	244
(*S*,*R*)-66 (R=Et, R'=Me)	483	503	337	315	
(*S*,*R*)-67 (R=*n*-Pr, R'=Me)	490	513	317	290	
(*R*,*S*)-68 (R=Et, R'=Et)	501	516	321	287	
(*R*,*S*)-69 (R=*n*-Pr, R'=Et)	480	512	318	299	
(*R*,*S*)-70 (R=Et, R'=*i*-Pr)		516	318	285	
(*R*,*S*)-71 (R=*n*-Pr, R'=*i*-Pr)	486	514	314	286	



R= Et, R'= Et (58)

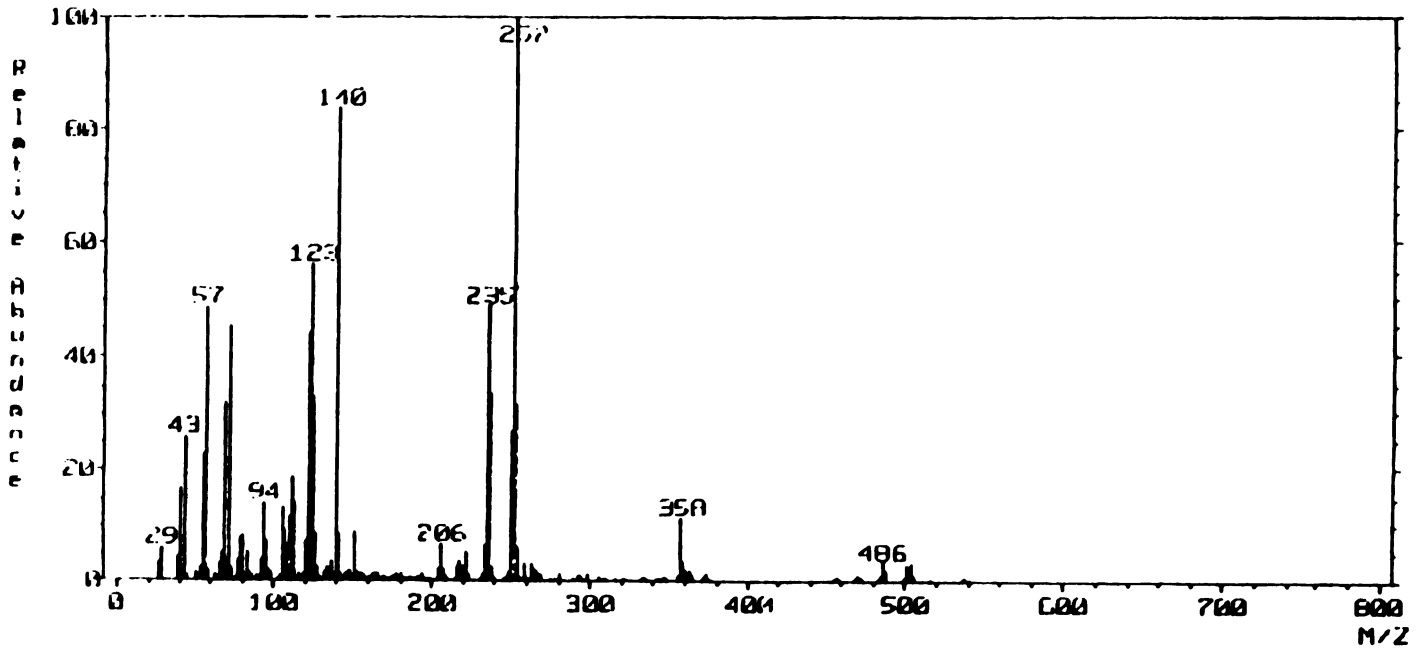
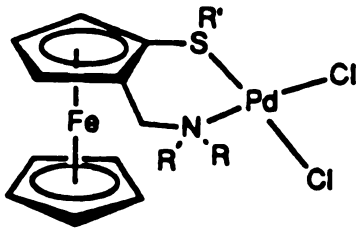


Figure 17. FAB mass spectrum of **58**



R= Et, R'= Et (58)

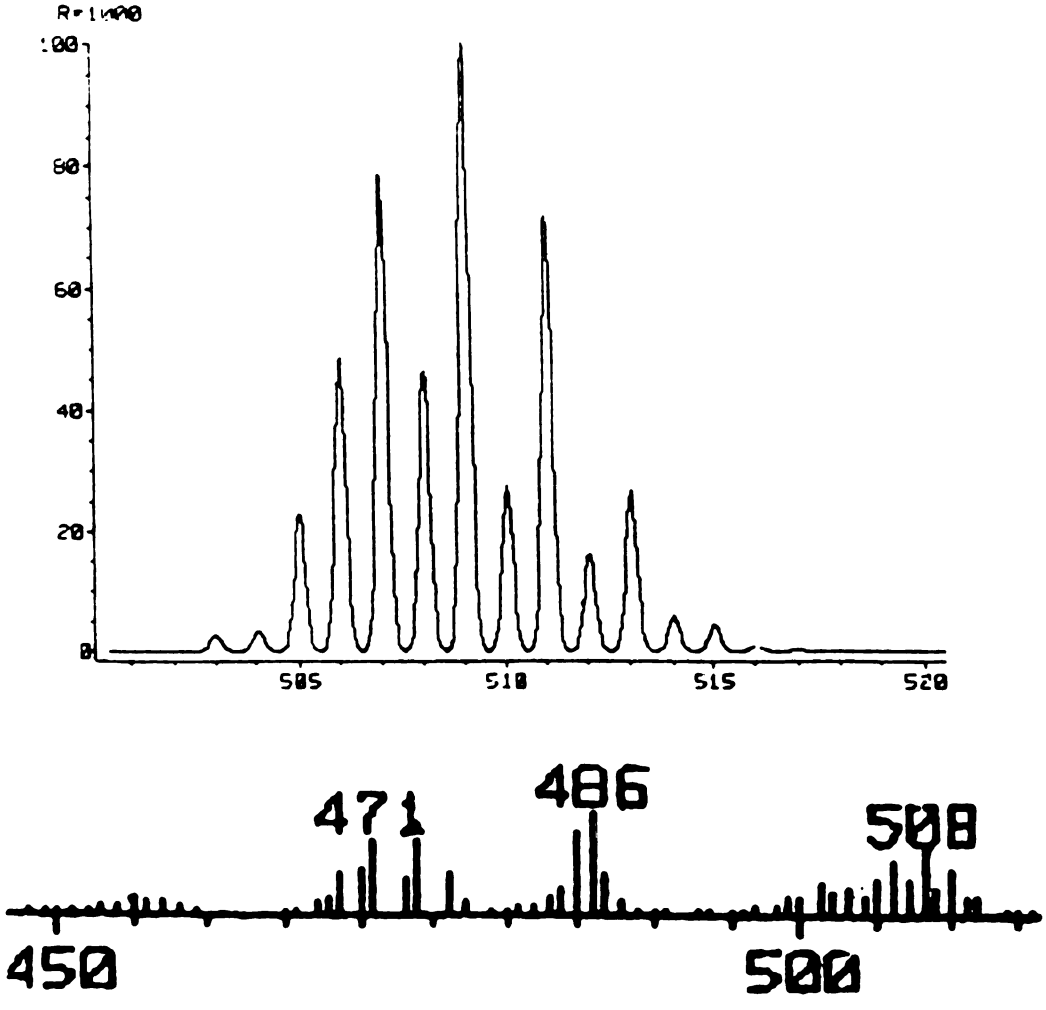


Figure 18. Comparsion of isotope patterns at the molecular ion region above: simulation, bottom: detected

Table 12 Analytical Data for Ligands[a] **37-56**.

Compound	Yield	Color	Analysis: found (calc.) (%)	
			C	H
37	65	yellow	60.12 (60.57)	7.09 (7.26)
38	34	yellow	61.76 (61.63)	7.67 (7.60)
39[b]	20	yellow	61.00 (60.98)	5.85 (5.85)
40[c]	41	brown	66.86 (67.17)	7.11 (6.92)
41	23	yellow	62.21 (62.61)	7.86 (7.88)
42	55	yellow	62.83 (63.50)	8.07 (8.07)
43	52	yellow	63.18 (63.50)	8.07 (8.07)
44	25	brown	63.91 (65.11)	8.31 (8.52)
46	84	yellow	54.77 (54.90)	5.92 (5.92)
(*S*,*R*)-50	82	brown	61.49 (61.63)	7.46 (7.60)
(*S*,*R*)-51	53	brown	62.85 (63.50)	7.98 (8.07)
(*R*,*S*)-52	64	brown	62.59 (62.61)	7.98 (7.88)
(*R*,*S*)-53	16	brown	63.69 (64.34)	8.22 (8.37)
(*R*,*S*)-54	26	brown	63.67 (63.50)	8.11 (8.07)
(*R*,*S*)-56	30	brown	64.62 (65.11)	8.22 (8.52)

[a] all ligands are oils except **39** and **40**.
[b] Mp. = 91-92 °C
[c] Mp. = 56 °C

Table 13 Yield, Melting Point, Color, and Analytical Data of Complexes **57-(*R*,*S*)-71**

Compound	Yield	Color	Mp.(°C)	Analysis: found (calc.) (%)	
				C	H
57	87	red	154-156	38.82 (38.86)	4.67 (4.69)
58	65	dark red	110-112	39.74 (40.15)	4.83 (4.95)
59	60	brick red	135	42.26 (42.69)	4.02 (4.06)
60	71	brick red	165-166	46.72 (46.32)	4.96 (4.77)
61	68	brick red	142-144	41.79 (41.37)	5.33 (5.17)
62	72	dark red	127-128	42.81 (42.52)	5.29 (5.45)
63	65	dark red	154-155	36.59 (37.46)	4.44 (4.37)
64	86	brick red	180-185	34.33 (34.77)	3.69 (3.75)
65	63	yellow	125	34.47 (34.18)	4.22 (4.22)
(*S*,*R*)-66	88	purple	142-143	40.58 (40.15)	4.92 (4.95)
(*S*,*R*)-67	89	dark purple	130-131	41.82 (42.52)	5.33 (5.45)
(*R*,*S*)-68	79	brick red	130-131	41.16 (41.37)	5.15 (5.17)
(*R*,*S*)-69	55	dark red	127	43.56 (43.62)	5.61 (5.67)
(*R*,*S*)-70	82	purple	123-124	42.24 (42.52)	5.47 (5.45)
(*R*,*S*)-71	72	brick red	130	44.60 (44.67)	5.84 (5.89)

B. Selective Hydrogenation

A large number of chiral and achiral ferrocenylamine sulfide catalysts prepared in this laboratory have been successfully employed in hydrogenations of double bonds with many functional groups.[124] By modifying the sulfido substituent(s) on either one or both cyclopentadiene rings of the ferrocenyl ligands [125,126], both regio- and stereo-selectivity approaching 100% were observed in several hydrogenations. Nevertheless, the effect of replacing the 1-dimethylamine group in the catalyst by other more bulky alkylamino groups has never been investigated. It was therefore decided to study these influences upon the hydrogenation reactions.

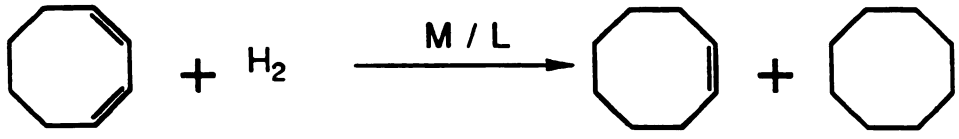
To exhibit catalytic activity, these compounds must have vacant coordination sites available to form reactive intermediates. Furthermore, catalytic activity of the transition-metal complexes is the result of a delicate balance of valence states and chemical bond strengths.[120] Too strong a bond between substrate (or hydrogen donor) and catalyst results in a stable complex which shows no catalytic effect. Similarly, reaction will not occur if the bonding between hydrogen donor and catalyst is too weak. Group 10 metal ferrocenylamine sulfide complexes have proven to be by far the most suitable catalysts for hydrogenations of conjugated-dienes to monoenes.

a. Homogeneous Hydrogenation of 1,3-Cyclooctadiene

The use of ferrocenylamine sulfide or selenide complexes to effect homogeneous and heterogeneous hydrogenation of a diene to a monoene has been reported previously.[83,127,128] The reaction rate was found to be related to steric and electronic effects exerted by the thioether substituents and both palladium and platinum ferrocenylamine selenide complexes were found ineffective for

homogeneous hydrogenation of 1,3-cyclooctadiene.[128] A possible explanation for this lack of catalytic activity resides in the metal-sulfur and metal-selenium bond strength. Breakage of the metal-sulfur bond is important to selective hydrogenation[127] and since the metal-selenium bond is stronger than the metal-sulfur bond, the palladium and platinum ferrocenylamine selenide complexes lack catalytic activity.

The hydrogenation was carried out in the presence of acetone. No hydrogen uptake was observed if CH_2Cl_2, CCl_4 or THF were used.[128] Dissociation of a metal-sulfur bond by acetone to form a catalyst-acetone intermediate followed by H_2 uptake may account for this observation.[127,129] Eq. 7 shows the selective hydrogenation of 1,3-cyclooctadiene.



(Eq. 7)

The catalytic activity of the new palladium catalysts (**57-(*R*,*S*)-71**) on the hydrogenation of 1,3-cyclooctadiene was examined and the results are presented in Tables 14-16.

The reaction products were 1,3-cyclooctadiene, cyclooctene, and cyclooctane. The ratios of 1,3-cyclooctadiene to cyclooctene were calculated by integration of the ^1H NMR spectrum of the products in the region between 5.5-5.9 ppm. As shown in Fig. 20 the olefinic protons of the diene appear at both 5.8 and 5.6 ppm, while the olefinic protons of the monoene show up at 5.6 ppm; thus the monoene to diene ratio was given by :

$$\text{monoene/diene} = (A5.6 - A5.8)/A5.8$$

where A is the integrated ^1H NMR area at the specified chemical shift. The ratio of (cyclooctadiene+cyclooctene) to cyclooctane were determined by GC with more than 0.7 min separation in retention time.

In general, the hydrogenation was carried out at a very efficient rate without an induction period; an exception was catalyst **57** which has a 2h induction time. The conversion is above 92 % and the selectivity ranges from 87.5 % to 99.9 % for the palladium ferrocenyl amine sulfide catalysts. The dependence of the hydrogenation on the catalysts is shown on Tables 14 and 15.

Increasing the steric bulkiness on both the amine and sulfide group increases the reaction rate with retention of yield and selectivity. In both achiral and chiral catalytic system, catalysts with the methylthio ligand (**57**, **64**, (*S*,*R*)-**66**, (*S*,*R*)-**67**) performed at a slower rate than those with other sulfide substituents; catalysts with the more bulky *n*-propylamine substituent also react more rapidly than those with an ethylamine group.

The rate enhancements obtained by replacing dimethylamine with diethylamine and di-*n*-propylamine is more obvious in the achiral catalytic system. In the chiral system it is difficult to observe this effect since reaction was complete within minutes. (Table 15) The rate enhancement for switching from an achiral to a chiral system and for replacing the dimethylamine with diethylamine and di-*n*-propylamine groups is due to the additional steric and/or electronic effect(s) exerted by these substituents. These effects probably contribute to : (a) the bond-breaking from the pre-catalyst (both Pd-N and Pd-S breakage are possible) to form an effective catalyst, and (b) the H_2 oxidative addition and HCl (or Cl_2) reductive elimination to give a *cis*-(substrate-metalhydride) intermediate. These are key steps for effective hydrogenation. The oxidative addition of H_2 to catalyst-substrate intermediate may be the rate-determining step since the hydrogenation of 1,3-cyclooctadiene is dependent on hydrogen pressure. (Table 16). Thus, by improving the

Table 14 Selective Hydrogenation of 1,3-cyclooctadiene [a] by Various Achiral Complexes, $(C_5H_5)Fe(C_5H_3)(CH_2NR_2)(SR')PdCl_2$ at 62 psi Hydrogen Pressure

Entry	Catalyst	Rx. Time	% Diene	% Monoene	% Alkane	Conversion (%)	Selectivity[b] (%)	Turnover rate (mol/mol·Pd·h)
1[c]	**57** (R=Et, R'=Me)	21 h	7.9	80.6	11.5	92.1	87.5	16.3
2	**58** (R'=Et)	41 min	3.0	93.8	3.2	97.0	96.7	528.8
3	**59** (R'=4-PhCl)	1 h	1.2	95.6	3.2	98.8	96.8	368.0
4	**60** (R'=*p*-tolyl)	18 min	4.7	91.9	3.4	95.3	96.4	1183.3
5	**61** (R=*n*-Pr, R'=Me)	2 h	4.7	92.4	2.9	95.3	97.0	177.5
6	**62** (R'=Et)	10 min	3.1	92.1	4.8	96.9	95.0	2165.7
7	**64** (R=SEt, R'=Me)	30 h	30.4	65.5	4.1	69.6	94.1	12.4

[a] $1.0X10^{-5}$ mol of catalyst, $3.725X10^{-3}$ mol of substrate, 4.5 mL acetone
[b] cyclooctene/ (cyclooctene + cyclooctane)
[c] with 2 h induction time

Table 15 Selective Hydrogenation of 1,3-cyclooctadiene[a] by Various Chiral Complexes, $(C_5H_5)Fe(C_5H_3)(CHMeNR_2)(SR')PdCl_2$ at 62 psi Hydrogen pressure

Entry	Catalysts	Rx. Time	% Diene	% Monoene	% Alkane	Conversion (%)	Selectivity[b] (%)	Turnover rate (mol/mol·Pd·h)
1	(*S*,*R*)-66 (R=Et, R'=Me)	2 h	0	90.7	9.3	100	90.7	186.3
2	(*S*,*R*)-67 (R=*n*-Pr)	47 min	6.3	90.8	2.9	93.7	96.9	445.5
3	(*R*,*S*)-68 (R=Et, R'=Et)	4 min	0	99.9	0.1	100	99.9	5587.5
4	(*R*,*S*)-69 (R=*n*-Pr)	2 min	0	98.1	1.9	100	98.1	11175.0
5	(*R*,*S*)-70 (R=Et,R'=*i*-Pr)	5 min	0	96.3	3.7	100	96.3	4470.0
6	(*R*,*S*)-71 (R=*n*-pr)	4 min	0	94.2	5.8	100	94.2	5587.5

[a] $1.0X10^{-5}$ mol of catalyst, $3.725X10^{-3}$ mol of substrate, 4.5 mL acetone

[b] cyclooctene/ (cyclooctene + cyclooctane)

Table 16 Hydrogenation of 1,3-cyclooctadiene,Effect of Pressure [a]

Entry	Pressure (psi)	Rx. Time	% Diene	% Monoene	% Alkane	Conversion (%)	Selectivity[b] (%)	Initial rate (mol/Pd·h·psi)
1	80	4 min	0	92.9	7.1	100	92.9	69.8
2	62	4 min	0	94.2	5.8	100	94.2	90.1
3	40	10 min	0	97.7	2.3	100	97.7	54.5
4	20	10 min	0	97.7	2.3	100	97.7	65.7

[a] 1.0×10^{-5} mol of (*R*,*S*)-68, 3.725×10^{-3} mol of substrate, 4.5 mL acetone at room temperature.
[b] cyclooctene/ (cyclooctene + cyclooctane)

efficacy of the bond-breaking step and the oxidative addition of H_2 the reaction rate can be increased.

The reaction rate for catalyst **64**, which bears two sulfide groups, was much slower than that for other catalysts with one sulfide and one amine group. A possible explanation for this behavior is stronger Pd-substrate bonding which results because the ethylthio group is not as bulky as the amine group; thus the reaction rate is reduced.

Attempts to investigate the influence on the catalytic activity of replacing 1-dimethylamine substituent by even more bulky di-*i*-propylamine, di-*i*-butylamine or diphenylamine failed. With the more bulky substituents the palladium complexes become inaccessible.

The effect of initial reaction pressure on the reaction time, yield and selectivity is shown in Table 16. The conversions were all 100% and selectivity decreased slightly as the pressure increased. This catalytic system has the best performance at 62 psi (entry 2); however, hydrogenation can still be carried out efficiently at 20 psi (ca. 1.4 atm).

To evaluate activities of new complexes reported here, catalysts **62** and **(*R*,*S*)-69** are compared with previously known Pd complexes (Table 17). The data for entries 4, 5, and 6 (complexes with one dimethylamine substituent and with sulfide substituent(s) at either one or both the two Cp rings) show hydrogenation activity about three orders of magnitude faster than that of the chelating bis(phosphine)[132] (entry 1) and about the same as that of the amine catalyst. (entry 2)[133] The activity of **(*R*,*S*)-69** is about five orders of magnitude faster than that of the chelating bis(phosphine) catalyst. Modified sulfido substituents show about the same activities (entries 4,5,6) while entries 7,8 show the difference in replacing the dimethylamine group with the di-*n*-propylamine group. Achiral catalyst **62** (entry 7) is 5 to 20 times as active as entries 4,5; chiral catalyst **(*R*,*S*)-69** is even more active (28-117 fold). Thus, we were

Table 17 Selective Homogeneous Hydrogenation of Dienes to Monoenes, Comparison of the Catalytic Activity

Entry	Initial Rate mol/mol.Pd·h·psi	Substrate	T°C	Metal	Solvent	Ref.
1	0.0011	1,4-cyclohexadiene	65	Pd^{2+}	toluene	130
2	3.45-5.52	isoprene	22	Pd^{0}	toluene	129
3	6.92	1,3-cyclooctadiene	27	Pd^{2+}	acetone	82
4	0.53	1,3-cyclooctadiene	27	Pd^{2+}	acetone	123
5	4.44	1,3-cyclooctadiene	27	Pd^{2+}	acetone	125
6	6.32	1,3-cyclooctadiene	27	Pd^{2+}	acetone	122
7	34.9	1,3-cyclooctadiene	27	Pd^{2+}	acetone	This work [a]
8	180.2	1,3-cyclooctadiene	27	Pd^{2+}	acetone	This work [b]

[a] $(C_5H_5)Fe(C_5H_3)(CH_2N\text{-}n\text{-}Pr_2)(SEt)PdCl_2$ (62)

[b] $(C_5H_5)Fe(C_5H_3)(CHMeN\text{-}n\text{-}Pr_2)(SEt)PdCl_2$ ((*R*,*S*)-69)

able to improve the activity of the ferrocenyl sulfide complexes by up to a factor of two by modifying amine substituents rather than sulfide substituents.

In this hydrogenation we have demonstrated that the chiral methyl group as well as the alkylamino group effectively influence the reaction rate. These new catalysts performed at high rate (up to 1.1×10^4 mol/mol·Pd·h) with retention in conversion and selectivity.

b. Hydrogenation of Acrylic Acid

Hydrogenation of acrylic acid was performed in a similar way to the above hydrogenation by using compounds **58**, **59**, (***R*,*S***)-**68**, (***R*,*S***)-**69** as catalysts. Results are presented in Table 18.

The conversions were all 100% with propionic acid as the sole product. Again, the chiral compounds catalyzed the reaction at a faster rate than achiral catalyst **58** and **59**. As can be seen from the table the catalytic abilities of these new compounds are comparable to those of other ferrocenylamine sulfide catalysts. It was therefore assumed that these new series of catalysts would be able to catalyze hydrogenations similar to those other ferrocenylamine sulfide catalysts do.[124] It should be noted that these new catalysts retain the same degree of selectivity and reactivity as do other similar ferrocenylamine sulfide catalysts.

Table 18 Hydrogenation of acrylic acid at 80 psi H_2 pressure[a]

Catalyst	Rx. time	Conversion	Turnover rate (mol/mol pd.h)	Ref.
58 (R=Et,R'=Et)	1 h	100 %	372.5	this work
59 (R'=4-PhCl)	1.33 h	100 %	280.1	this work
(***R,S***)-**68** (R=Et,R'=Et)	0.5 h	100 %	745.0	this work
(***R,S***)-**69** (R=*n*-Pr)	0.5 h	100 %	745.0	this work
(***S,R***)-**77**[b]	1 h	100 %	372.5	124
78[c] (R=Me,R'=*p*-tolyl)	1 h	100 %	372.5	124

[a] 3.725x 10^{-3} mol substrate, 1x10^{-5} mol catalyst, 4.5 mL acetone, room temperature, hydrogenation product: propionic acid

[b] (*S,R*)-1-dimethylaminoethyl-2-2'-*p*-tolylthioferrocenyl palladium chloride

[c] 1-dimethylaminomethyl-2-*p*-tolylthioferrocenyl palladium chloride

c. Hydrogenation of Phenylacetylenes

The selective hydrogenation of acetylenes to olefins is of great practical importance in connection with the problem of hydrotreating olefin cuts from petroleum to remove a compound with a triple bond, so that the olefins can be used in polymerization reactions. The majority of hydrogenations of acetylenes are carried out on heterogeneous catalytic systems[60] or on polymer-supported homogeneous catalysts. (homogeneous-heterogeneous catalysts)[61-67] Therefore, it should be interesting to investigate the activities and selectivity upon hydrogenation of phenylacetylenes by ferrocenyl thioether-based catalysts.

Several phenylacetylenes have been tested in this hydrogenation; substrates include phenylacetylene, diphenylacetylene, methylphenylacetylene, ethylphenylacetylene, and *t*-butylphenylacetylene. Reactions were either allowed to go to a totally hydrogenated alkane or were controlled at 8.5 psi pressure drop so that the alkyne was hydrogenated only to the alkene.

In general, phenylacetylene hydrogenation results parallel those of conjugated double bond hydrogenations; they are presented in Tables 19-20.

(1). Hydrogenation of Phenylacetylene to Ethylbezene

Table 19 shows hydrogenation results from uncontrolled reactions. Again, chiral catalysts (*S*,*R*)-**67** and (*R*,*S*)-**71** catalyze the reaction more efficiently than the achiral ones. Entries 3 and 5, in which the amino substituent dimethylamine in achiral complexes is replaced with diethylamine, show about a 2 fold rate increase; while changing diethylamine to di-*n*-propylamine enhanced the rate about 4 times (entries 1 and 4). A comparison of entries 1, 3 and 5 demonstrates that both the sulfido and the amino substituent influence the reaction rate, especially when the sulfido substituent is

Table 19 Hydrogenation of phenylacetylene to ethylbezene

Entry	Catalyst	Reaction time	%Alkene	%Alkyne	Turnover rate (mol/mol pd.h)
1	**58** (R=Et, R'=Et)	9 h	0	100	41.4
2	**59** (R=Et, R'=4-Cl-ph)	9 h	73.6	26.4	41.4
3	**60** (R=Et, R'=*p*-tolyl)	50 min	4.3	95.7	447.0
4	**62** (R=SEt, R'=Me)	2.25 h	0	100	165.6
5	**78**[b] (R=Me, R'=*p*-tolyl)	2 h	0	100	186.3
6	**(*S,R*)-67** (R=*n*-Pr, R'=Me)	23 min	0	100	971.7
7	**(*R,S*)-71** (R=*n*-Pr, R'=*i*-Pr)	22 min	0	100	1015.9
8	**(*S,R*)-77**[c]	12 h	0	100	31.0

[a] 3.725×10^{-3} mol substrate, 1×10^{-5} mol catalyst, 4.5 mL acetone at 80 psi H_2 pressure, room temperature

[b] 1-dimethylaminomethyl-2-*p*-tolylthioferrocenyl palladium chloride

[c] (*S,R*)-1-dimethylaminoethyl-2-2'-(bis-*p*-tolylthio)ferrocenyl palladium chloride

p-tolyl, which has a greater influence than any other sulfido group or any amino group. (For example, rate for entry 3 > entry 5 > entry 1)

One interesting feature arose when chiral catalyst (*S*,*R*)-**77** (entry 8) was used. This compound has two *p*-tolylthioether groups on both the ferrocenyl Cp rings. Yet, it showed no enhancement in the reaction rate, only a decrease in catalytic activity. It is possible that the additional *p*-tolylthioether group at the lower Cp ring inhibits formation of the substrate-metal adduct, a requirement for the catalytic reaction to take place. However, one cannot rule out the possibility that addition of the second thioether group to the ferrocenylamine catalyst changes the electronic character that produces decreased activity.

(2). Selective Hydrogenation of Phenylacetylene to Styrene

(a). Effect of Catalysts

The results for hydrogenation of phenylacetylene to styrene by a variety of ferrocenylsulfide catalysts are collected in Table 20. The reaction was controlled at 8 psi H_2 pressure drop, thus the phenylacetylene was expected to half-hydrogenate only to styrene. Chiral catalysts were not used in this hydrogenation since they catalyze the reaction so rapidly that to half-hydrogenate the substrate might be difficult. Results showed that selectivity to styrene can be achieved at about the 90% level with good conversion with compounds **57** and **58** as catalysts. It also showed that hydrogenations by less active catalysts gave better selectivities.

Attempts to enhance the selectivity by modifying the catalytic conditions (such as catalyst, H_2 pressure) were unsuccessful. Probably, in our catalytic system, hydrogenation of phenylacetylene to styrene and that of styrene to ethylbenzene are sequentially differentiable. Thus, styrene cannot be obtained alone in this system.

Table20 Hydrogenation of phenylacetylene to styrene: effect of catalysts

catalyst	reaction time	% alkene	% alkyne	conversion	selectivity	turnover rate (mol/mol pd.h)
57	24 h	89	11	100	89.0	15.5
58	2 h	88.4	10.3	98.7	89.6	367.7
59	1 h	80.4	14.0	94.4	85.2	351.6
60	32 min	80.7	9.8	90.5	89.2	623.0
62	1 h	83.8	8.7	92.5	90.6	344.6

[a] 3.725×10^{-3} mol substrate, 1×10^{-5} mol catalyst, 4.5 mL acetone at 80 psi H_2 pressure, room temperature, reactions were controlled at 8-8.5 psi pressure drop

To show how competitive these two reactions were, a separate experiment was carried out to hydrogenate styrene to ethylbezene at identical conditions. The result revealed that the turnover rate of the above reaction is about twice as fast as the rate of hydrogenation of phenylacetylene to styrene. Similar results were found by Muetterties, et al. in the hydrogenations of phenylacetylenes catalyzed by phosphine-based rhodium clusters.[134-137]

Since hydrogenation of phenylacetylene is very slow relative to the alkene hydrogenation sequence, the slow but selective hydrogenation of acetylene catalyzed by these palladium ferrocenyl catalysts can be rationalized by a much higher reactivity of the catalyst precursor or intermediate towards alkynes relative to alkene and to a different hydrogenation sequence for conversion of alkene to alkane.

Indeed, this is the case in our catalytic system. Phenylacetylene was added to complex (***R,S***)-**68** in approximately a 2 to 1 molar ratio in $CDCl_3$ at room temperature and the reaction was monitored by ^1H NMR. After about five minutes Pd-S and Pd-N bond-dissociation were observed. At the same time two new sets of signals were detected. Formation of the substrate-metal adduct was completed about one hour later. (see Fig.19) Addition of styrene to the same catalyst revealed no change in the spectrum after an 8 hour period. At this point it is clear that the greater affinity of phenylacetylene for the catalyst has a powerful influence on the selectivity.

We tried to profile the reaction coordinate by performing the reaction at 1 atm, but the reaction did not take place at such a low H_2 pressure.

(b). Solvent Effects

The influence of solvent upon hydrogenation of phenylacetylene was investigated under the same conditions and the results are shown in Table 21.

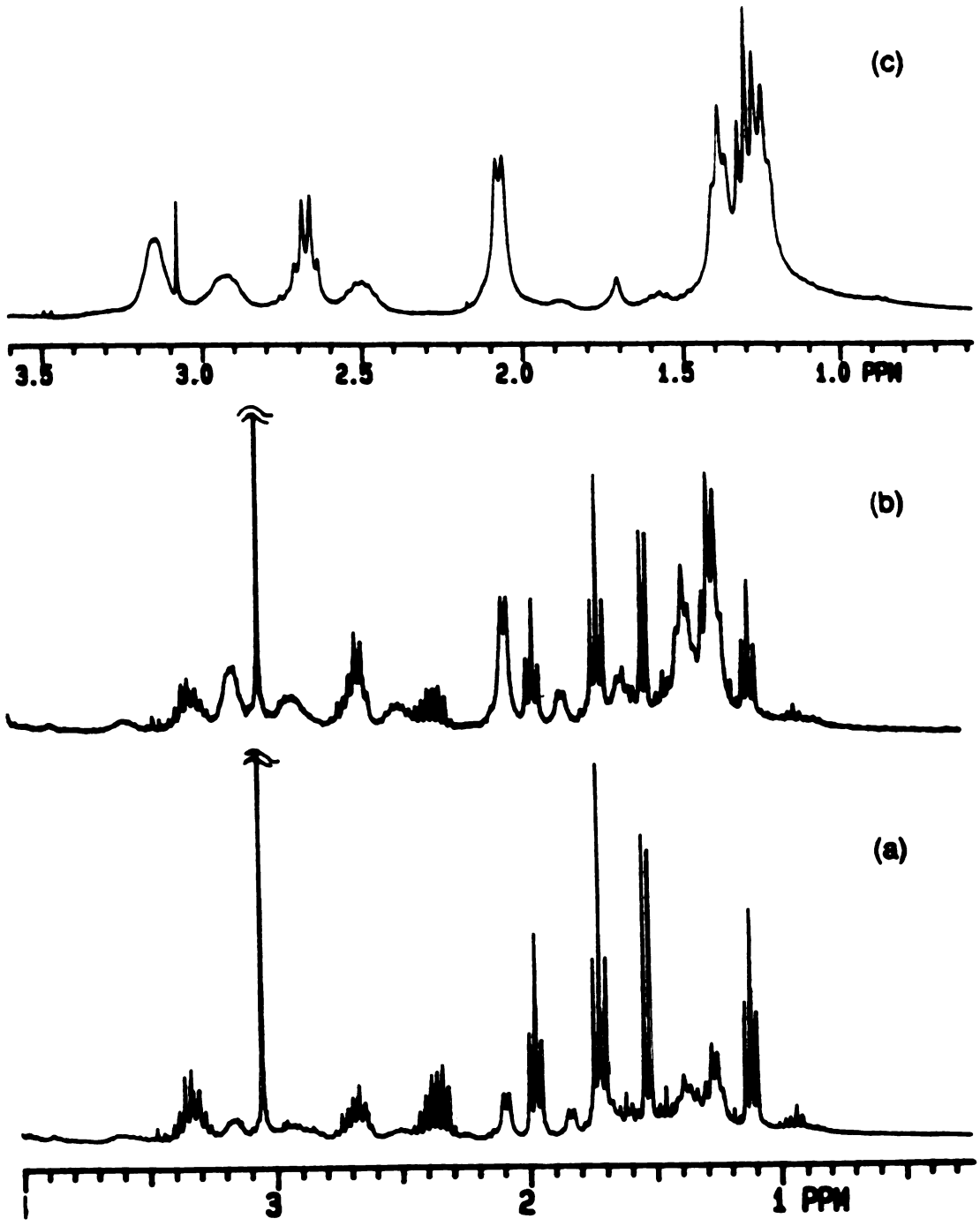


Figure 19. Phenylacetylene + (*R,S*)-68, (a) 5 min (b) 30 min (c) 1 h

Table 21 Hydrogenation of phenylacetylene to styrene[a] : effect of solvents

solvent	reaction time	% alkene	% alkyne	conversion	selectivity	turnover rate (mol/mol pd.h)
acetone	1 h	88.4	10.3	98.7	89.6	367.7
THF	22 h	90.2	5.8	96.0	94.0	16.3
CH_3CN	24 h	89.3	4.7	94.0	95.0	14.6
CH_3CN	31 h	91.0	9.0	100.0	91.0	12.0
CH_2Cl_2[b]	24 h					

[a] 3.725x 10^{-3} mol substrate, 1x10^{-5} mol catalyst **58**, 4.5 mL acetone at 80 psi H_2 pressure, room temperature,
reactions were controlled at 8-8.5 psi pressure drop

[b] reaction incomplete, only 2.5 psi pressure drop was observed

Consistent with the hydrogenation of 1,3-cyclooctadiene, initiation of the hydrogenation sequence required polar solvents again in this case to create a vacant coordination site. CH_2Cl_2 is inadequate since it is not a good coordinating solvent. Among those polar solvents employed in this hydrogenation, acetone again is the best choice, though its selectivity is slightly lower than that of others. Since the faster reaction rate (thus the higher turnover rate) may compensate for the slight loss in selectivity, acetone was adopted as solvent in this hydrogenation.

(c). Selective Hydrogenation of Disubstituted Acetylenes

Because phenylacetylene was selectively hydrogenated successfully, a series of phenylacetylenes was investigated under either controlled or fully hydrogenated conditions. Results are shown in Table 22. Compare entries 1 and 4; here the chiral catalysts (***R***,***S***)-**68** no longer possess higher activity than achiral catalyst **62**. Instead, (***R***,***S***)-**68** is 1/7 as fast as **62**. Again, as in the catalytic hydrogenation of phenylacetylene, the 1-1'-Cp ring disubstituted catalyst (***R***,***S***)-**77** requires a longer time to complete the reaction. It takes about twice as long to hydrogenate diphenylacetylene as to hydrogenate phenylacetylene.

Recall that in hydrogenations of the less sterically hindered phenylacetylenes the chiral methyl group exerts a powerful influence on rate enhancement. In this case, besides the inherent affinity of the substrate to the catalyst, one also must consider the steric bulkiness of both entities. Thus the most steric hindered chiral 1-1'-disubstituted catalyst takes the longest time to complete the reaction. Yet, because of it's stereorigidity, it also yielded the best selectivity among the catalysts tried.

The chiral catalyst (***R***,***S***)-**68**, which is considered more bulky than (***R***,***S***)-**79**, but less crowded than (***R***,***S***)-**77**, performed at a moderate rate. We see that in order to obtain good selectivity and

Table 22 Hydrogenation of diphenylacetylene [a]

Catalyst	% *cis*-stilbene	% *trans*-	% Bibenzyl	Rx. time	Conversion	Selectivity
62 (R=*n*-Pr, R'=Et)	29	7	64	2 h	100	36[d]
(*R,S*)-**77**[b]	71	0	29	26.5 h	100	71[d]
79[c] (R=Et, R'=*i*-Pr)	45	0	55	1.5 h	100	45[d]
(*R,S*)-**68** (R=Et, R'=Et)	31	0	69	15 h	100	31[d]
58 (R=Et, R'=Et)	54	6	40	1 h	100	60[e]
62 (R=*n*-Pr, R'=Et)	33	7.5	59.5	1 h	100	40.5[e]

[a] 3.725x 10^{-3} mol substrate, 1x10^{-5} mol catalyst, 4.5 mL acetone at 80 psi H_2 pressure, room temperature

[b] (*R, S*)-1-(1-dimethylaminoethyl)-2-2'-bis-*p*-tolylthioferrocenyl palladium chloride

[c] 1-dimethylaminomethyl-2-*i*-propylthioferroceneyl palladium chloride

[d] selectivity toward stilbene

[e] reaction were controlled at 8.5 psi pressure drop, selectivity toward bibenzyl

high activity a detailed balance of the electronic and steric effects must be matched.

Results of hydrogenation of methylphenylacetylene, ethylphenylacetylene, and *t*-butylphenylacetylene are presented in Tables 23 and 24.

In general, hydrogenation rates of these acetylenes are : 1-phenyl-1-propyne > phenylacetylene = diphenylacetylene > 1-phenyl-1-butyne, whereas for *t*-butylphenylacetylene, only less bulky catalysts (*R*,*S*)-**79** were able to carry out the hydrogenation to a small extent (11%) after a 12.5 h hydrogenation time. For other more hindered catalysts no hydrogenation uptake was observed. The possible reason may be that the bulky *t*-butylphenylacetylene prohibits formation of metal-substrate adduct. Thus, the more sterically crowded the substrate, the longer the reaction time. The rate of hydrogenation of diphenylacetylene is about equal to that of phenylacetylene and faster than that of ethylphenylacetylene, probably due to it's planar character. The selectivities toward alkene formations for the hydrogenation of diphenylacetylene, 1-phenyl-1-propyne are lower than that of phenylacetylene.

An attempt to rationalize the selectivity simply on the basis of substrate bulkiness was unsuccessful (Table 25). Several factors are thought to influence the selectivity and are summarized in section (e).

(d). Proposed Mechanism for Hydrogenation of Phenylacetylenes

The proposed catalytic cycle is shown in Scheme 9. The first step involves formation of the active metal-substrate adduct **72** by binding of H_2 and phenylacetylene to the catalyst precursor **71**. It is not clear at this moment whether absorption of H_2 or addition of substrate to the catalyst occurs first. The release of HCl (or Cl2) gas was detected by the color change of litmus paper during the catalysis. A piece of blue litmus paper was attached on the reaction

Table 23 Hydrogenation of methylphenylacetylene[a]

Catalyst	% propenyl benzene	% propyl benzene	reaction time	% conversion	selectivity
59	12	88	58 min	100	88.0[c]
60	15	85	1 h	100	85.0[c]
(*S*,*R*)-66	39	61	1 h	100	61.0[c]
(*R*,*S*)-68	0	100	32 min	100	100.0[c]
(*R*,*S*)-71	0	100	33 min	100	100.0[c]
(*R*,*S*)-79[b]	27	73	43 min	100	73.0c
58	53	26	30 min	79	67.2[d]
59	19	59	21 min	78	24.4[d]
60	78	22	16 min	100	78.0[d]
(*R*,*S*)-68	73	27	27 min	100	73.0[d]

[a] 3.725×10^{-3} mol substrate, 1×10^{-5} mol catalyst, 4.5 mL acetone at 80 psi H_2 pressure, room temperature

[b] 1-dimethylaminomethyl-2-*i*-propylthioferroceneyl palladium chloride

[c] selectivity toward propylbenzene

[d] reaction were controlled at 8-8.5 psi pressure drop, selectivity toward propenylbenzene

Table 24 Hydrogenation of ethylphenylacetylene and *t*-butylphenylacetylene[a]

substrate	catalyst	%alkyne	% alkene	%alkane	Rx. time	conversion
$PhC{\equiv}CC_2H_5$	**58**	62.7	34.8	2.5	14 h	37.3
	62	39.8	50.7	9.5	21 h	60.2
	(*R*,*S*)-68	88.8	11.1	0.1	26.5 h	11.2
	80[b]	97.6	2.4	0	24 h	2.4
$PhC{\equiv}CC_4H_9$	**(*R*,*S*)-79**[c]	0	89.0	11.0	12.5 h	11.0
	58	no reaction				
	64	no reaction				
	(*R*,*S*)-68	no reaction				

[a] 3.725×10^{-3} mol substrate, 1×10^{-5} mol catalyst, 4.5 mL acetone at 80 psi H_2 pressure, room temperature

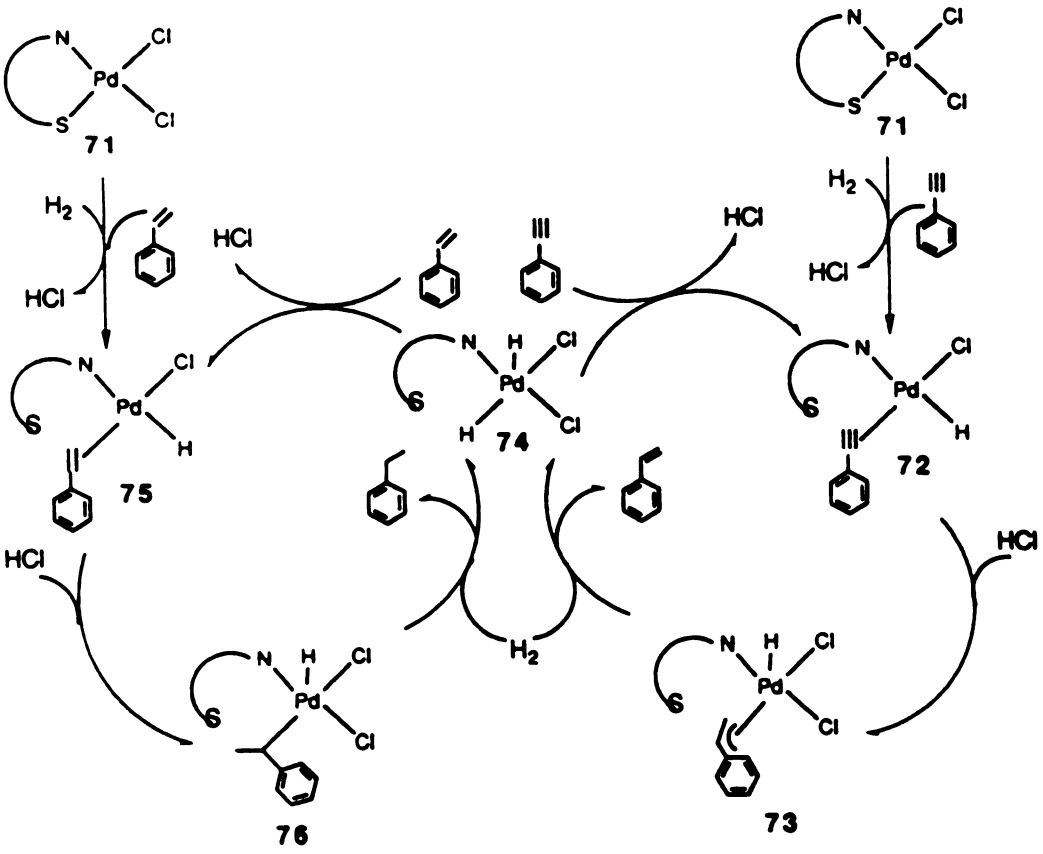
[b] 1-dimethylaminomethyl-2-methylthioferroceneyl palladium chloride

[c] 1-dimethylaminomethyl-2-*i*-propylthioferroceneyl palladium chloride

Table 25 Hydrogenation of phenylacetylenes by using **58** as catalyst[a]

substrate	% alkene	% alkane	Rx. time	conversion	selectivity
PhC≡CH	88.4	10.3	2 h	98.7	89.6
PhC≡CPh	60.0	40.0	1 h	100	60.0
$PhC{\equiv}CCH_3$	52.8	25.8	30 min	78.6	67.2
$PhC{\equiv}CC_2H_5$	34.8	2.5	14 h	37.3	93.3
$PhC{\equiv}CC_4H_9$	no Rx.				

[a] 3.725×10^{-3} mol substrate, 1×10^{-5} mol catalyst, 4.5 mL acetone at 80 psi H_2 pressure, room temperature, selectivity toward alkenes



Scheme 9 Proposed mechanism for hydrogenation of phenylacetylene

tube about 3 inches above the solution level to avoid possible interference from the contents of the solution. During the reaction the color of the litmus paper changed gradually from blue to pink - an indication of evolution of an acidic gas. The hydrogen insertion followed by oxidative addition of HCl to **72** then proceeds to give **73**. The H atom in **73** added to H-phenylacetylene to form styrene and another mole of H_2 oxidatively added to the catalyst to form a common intermediate **74**, which can bind with either phenylacetylene or styrene, and continue the hydrogenation.

The catalytic pathway for the hydrogenation of styrene on the left hand side of the catalytic cycle is much the same as that of phenylacetylene. Thus, intermediates **75** and **76** were formed during the catalytic process and the hydrogenated product - ethylbenzene- was released after the oxidative addition of H_2 to **76** to form intermediate **74** again. Since formation of phenylacetylene-catalyst adduct **72** is more favored than formation of styrene-catalyst adduct **75**; i.e., the catalytic cycle for phenylacetylene reduction is more predominant than that for styrene reduction ; it is not difficult to rationalize why high selectivity can be obtained even though the rate of hydrogenation of styrene is faster than that of phenylacetylene.

(e) Concluding Remarks:

Among those acetylenes tested for hydrogenation reactions phenylacetylene shows the highest selectivity. Hydrogenation of 1-phenyl-1-butyne also shows high selectivity during the early stage of hydrogenation. (see Table 25, entries 1 and 4) However, the conversion and the turnover rate are rather low in comparison to phenylacetylene. In summary, the factors that influence the rate and the selectivities to the half-hydrogenated products are:

(1). the relative ease of substrate-Pd bond formation. (which include the affinity of the substrate to the metal center and the steric interaction between them)

(2). the relative rates of hydrogenation from triple bond to double bonds and from double to single bonds

(3). the hydrogenations of alkynes to alkenes and of alkenes to alkanes may involve different catalytic pathway.

As stated in an earlier section, the catalytic activity of the transition-metal complexes is the result of a delicate balance of valence states and bond strengths. The hydrogenation of acetylenes by palladium ferrocenylsulfide catalysts is a good example of a catalytic system that falls in this category.

C. Asymmetric Hydrogenation of Aminoacid Precursors

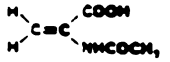
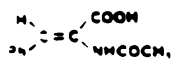
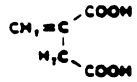
Asymmetric hydrogenation of aminoacid precursors have been documented since the 1970's. Soluble catalysts have been employed in these hydrogenations since they can be better defined than heterogeneous catalysts, and in such complexes it is often easy to vary widely the steric and electronic environment of the catalytically active site in order to optimize both the chemical and optical yields of an asymmetric synthesis. To date, enantiomeric excess of up to 99% have been achieved by using chiral phosphine-based rhodium catalysts.[138,139] Among those hydrogenations with high ee values, chiral chelating phosphines have been adopted in most cases.

Asymmetric hydrogenation of aminoacid precursors by ferrocenylphosphines as chirality inducing units were reported by Kumada and co-workers[18,101] and Cullen et al..[21] Their results showed that cationic rhodium ferrocenylphosphine complexes were able to carry out this asymmetric hydrogenation as effectively as the chelating phosphine-based rhodium catalysts.

Though chiral sulfides usually yield lower enantiomeric excess than do chiral phosphines[50], ferrocenylsulfides possess superior air stability. We wished to investigate the catalytic activities of these ferrocenylsulfides on aminoacid precursor hydrogenations.

The asymmetric hydrogenation of α-acetamidoacrylic acid, α-acetamidocinnamic acid and itaconic acid were performed by using cationic rhodium ferrocenylamine sulfide catalysts prepared *in situ.* Enantiomeric excess was determined by a Perkin Elmer 141 polarimeter. The asymmetric hydrogenation of these prochiral substrates are depicted in Eqs. 8 and 9. Results are shown in Table 26.

Table 26 Asymmetric hydrogenation of aminoacid precursors[a] by *in situ* rhodium catalysts

substrate	ligand	reaction time	[α] obs.	% ee	Conf.
	(*R*,*S*)-**53**	36 min	16.5	24.8[g]	R
	(*S*,*R*)-**83**[b]	1.33 h	14.2	21.4[g]	R
	(*S*,*R*)-**84**[c]	2.5 h	14.4	21.7[g]	R
	(*R*,*S*)-**85**[d]	19 min	11.3	17.0[g]	R
	(*R*,*S*)-**52**	3 h	14.9	37.2[h]	S
	(*R*,*S*)-**53**	1 h	10.3	25.7[h]	S
	(*R*,*S*)-**84**[b]	2 h	12.0	29.9[h]	S
	(*R*,*S*)-**52**	1 h	2.7	15.6[i]	R
	(*R*,*S*)-**53**	0.25 h	2.1	12.4[i]	R
	(*R*,*S*)-**54**	0.5 h	2.9	17.1[i]	R
	(*R*,*S*)-**68**[e]	1.66 h	-0.8	4.7[i]	S
	(*R*,*S*)-**70**[e]	0.5 h	0	0	
	(*R*,*S*)-**68**[f]	no H_2 uptake			

a 7.55x10^{-3} mol substrate, 3.0x10^{-5} mol $[RhNBDCl]_2$, 11.7 mg $AgBF_4$, 7.0x10^{-5} mol ligands, 9 mL methanol, catalysts prepared *in situ*, hydrogenation run at 60 psi H_2 pressure, room temperature

b (*S*,*R*)-1-(1-dimethylaminomethyl)-2-methylthioferrocene

c (*S*,*R*)-1-(1-di-*n*-propylaminomethyl)-2-phenylthioferrocene

d (*R*,*S*)-1-1'-(bis-*t*-butylthio)-2-(1-dimethylaminomethyl)ferrocene

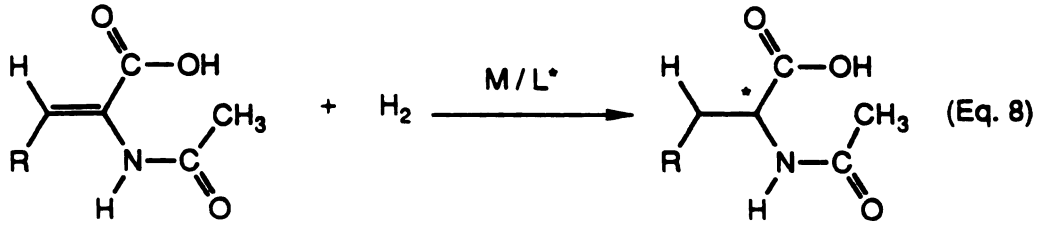
e Palladium complex

f Nickel complex

g N-acetyl(*R*)alanine: $[\alpha]_D$= + 66.5° (C=2, H_2O)

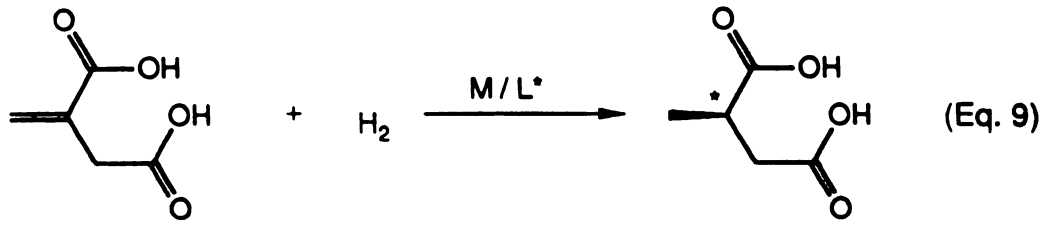
h N-acetyl(*S*)phenylalanine: $[\alpha]_D$= +40.1° (C=1, MeOH)

i *R*-methylsuccinic acid : $[\alpha]_D$= +17.0° (C=4.41, EtOH)



R = H, α-acetamidoacrylic acid
R = Ph, α-acetamidocinnamic acid

R = H, N-actylalanine
R = Ph, N-acetylphenylalanine

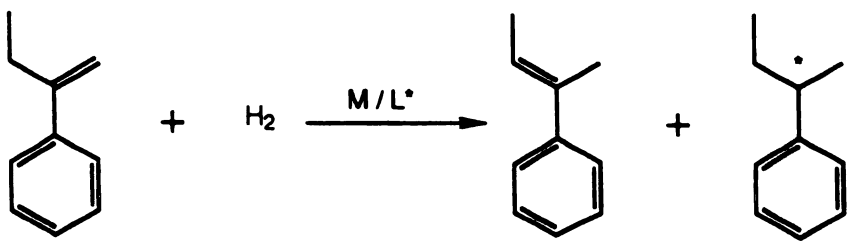


Hydrogenation of α-acetamidocinnamic acid to N-acetylphenylalanine by *in situ* catalysts (***R***,***S***)-**52**, (***R***,***S***)-**53** and (***S***,***R***)-**84** give ee values at 37.2%, 25.7% and 29.9% , respectively. Hydrogenations of α-acetamidoacrylic acid and itaconic acid yield somewhat lower ee's. The higher ee for the former hydrogenation can be rationalized by noting that α-acetamidocinnamic acid is more sterically encumbered than itaconic acid, thus the α-acetamidocinnamic acid-catalyst adduct possess better diastereoselectivity. A similar observation was found in other catalytic systems with phosphine-based rhodium catalysts.[87,140,141]

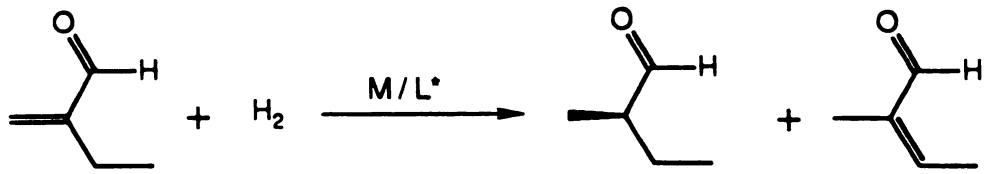
Modifications of both the amino and sulfido substituents or addition of a second sulfido substituent to the unsubstituted Cp ring did not alter the ee significantly. A comparison of the optical yields of these aminosulfide-based catalysts with those of the aminophosphine-based analogues shows that chiral phosphine catalysts do yield better results(entries 7 and 14). The higher ee's

obtained for the phosphine complexes can be attributed to the increased stereorigidity, which is an important factor for achieving high optical yields from the reduction of prochiral substrates.[138,141]

In the ferrocenyl phosphine catalyst (the chiral phosphine unit possess two phenyl groups), it is suggested that these phenyl groups, as well as the functional group requirements on the substrate, play central roles in the induction of the asymmetry.[86,142,144] For example, attempts to asymmetrically hydrogenate α-ethylstyrene and 2-ethylacrolein were unsuccessful. The former reaction gave 2-phenylbutane with no optical yield and an isomerized product, 2-phenyl-2-butene. The latter hydrogenation gave 69% 2-methylbutyaldehyde with no ee and another isomerized product as shown in Eqs. 10 and 11. The lack of asymmetric induction in these two cases shows the requisite of a carbonyl group three atoms away to the double bond to cooperatively (with the double bond) bond to the catalyst to form a stereorigid intermediate and thus induce high asymmetry.



(Eq. 10)



(Eq. 11)

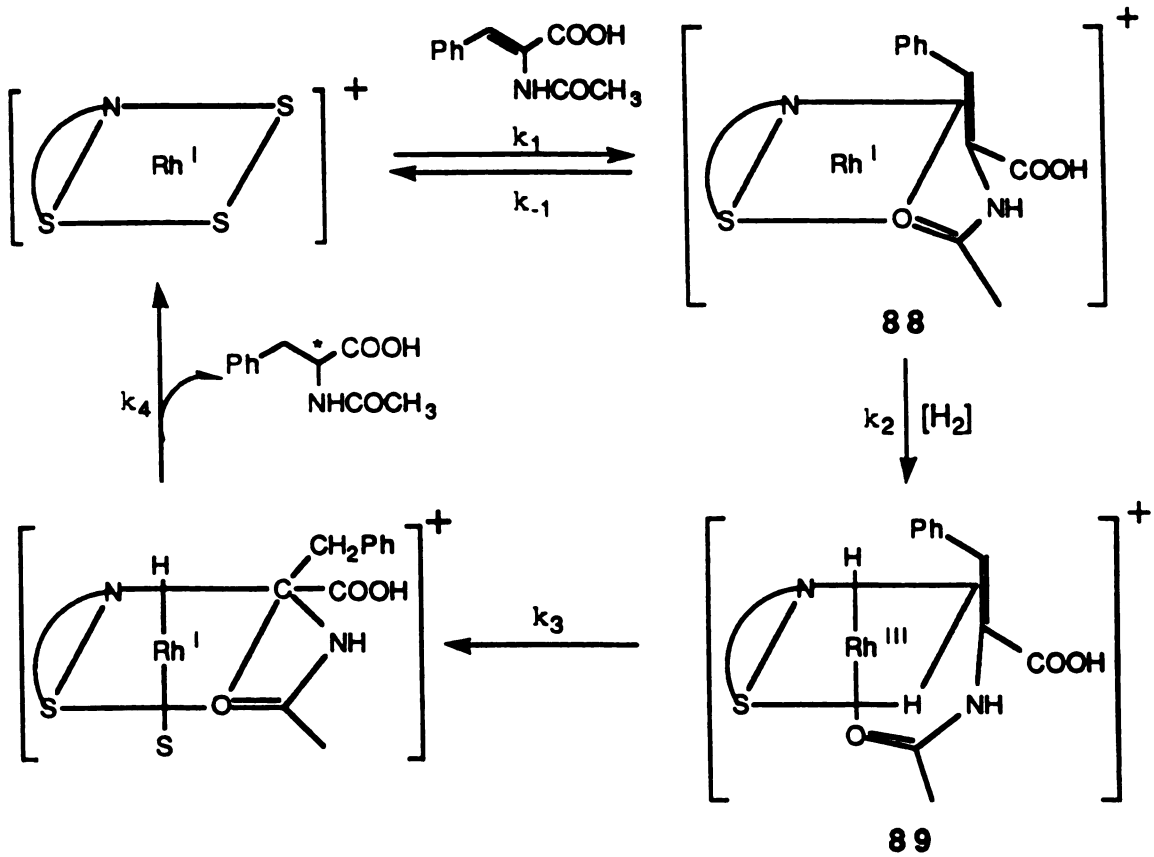
69 % 22 %

Attempts to employ ferrocenyl palladium complexes as catalysts in the reduction of α-acetamidoacrylic and α-acetamido-cinnamic acid was not successful. Yet, complexes (***R***,***S***)-**68** and (***R***,***S***)-**70** do hydrogenate itaconic acid, though the optical yields were low. It gives 4.7% ee in one case and no enantiomeric excess at all in other case (Table 26, entries 11 and 12). It is apparent that the course of hydrogenation should be different from that of the rhodium catalytic system since there are not as many coordination sites available as in the case of rhodium catalyst. Perhaps the reaction pathways will be similar to the reduction of the conjugated double bonds where chemoselective and regioselective reactions dominate.

In situ ferrocenyl nickel complexes were also tested in the hydrogenation of itaconic acid (entry 13). No hydrogenation uptake was observed after one day, presumably because no vacant coordination site is available for effective substrate-catalyst adduct formation for the further hydrogenations.

Proposed Mechanism

Based on the previous mechanistic study of asymmetric hydrogenation of prochiral aminoacids catalyzed by cationic rhodium ferrocenylphosphine complexes[23], the active catalytic species is probably $[(N\text{-}S)Rh(solvent)_2]^+$, where (N-S) stands for ferrocenylamine sulfide ligands bonded to rhodium through N and S atoms. The hydrogenation then proceeds as sketched in Scheme 10.



Scheme 10 Proposed mechanism for asymmetric hydrogenation

According to this mechanism, substrate was added to the rhodium solvate to form a square planar intermediate **88** in which the substrate bonded to rhodium through the acylcarbonyl and the olefin.[23,45,143] The cis-addition of hydrogen to the catalyst then occurred with the metal center rearranging to form an octahedral intermediate **89**. Insertion of a hydrogen atom into the substrate then proceeded in steps (3) and (4) to form the aminoacid and to continue the catalytic cycle. However, the other plausible catalytic pathway via a hydride intermediate $[(N\text{-}S)Rh(H)_2(solvent)_x]^+$ rather than the simple solvate cannot be ruled out.[23,50]

Concluding Remarks

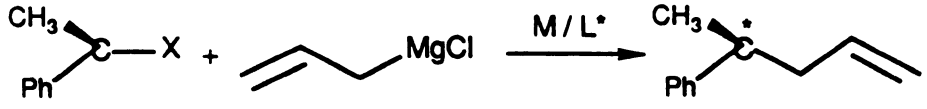
Several factors may influence the enantioselectivity of an asymmetric synthesis, such as the catalyst stereorigidity, substrate structures, solvents, temperature, and hydrogenation pressures. For the hydrogenation of prochiral aminoacids the stereorigidity and structures of substrates play the center role in the induction of asymmetry. More stereorigid chelating phosphine-based rhodium catalysts induce higher ee than the sulfide analogues. Furthermore, the effective substrates are characterized by the presence of a neighboring polar binding site (an acylamino substituent) as well as the reactive olefin site. These two binding sites can affect the anchoring of the substrate to the catalyst through chelation, thus better stereoselectivity can be achieved. Though, to date, the choice of chiral ligands (as well as the asymmetric catalysts) is still empirical. The opportunities, via molecular engineering, to achieve high optical yield are unlimited. This type of chemistry should remain a very fruitful frontier full of promise.

D. Asymmetric Grignard Cross-Coupling Reaction

The asymmetric cross-coupling reaction of 1-chloroethylbenzene with allylmagnesium chloride using group 10 metal ferrocenylsulfide catalysts has been studied in this laboratory. [126,127] It was found that ferrocenylsulfide catalysts with thioether substituents on both cyclopentadiene rings gave better enantiomeric excess than the monosubstituted analogues. Increasing the steric crowdedness of the thioether substituents also increases the optical yield.

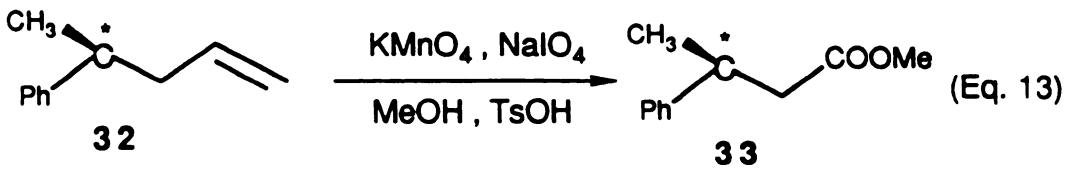
As an extension of this work, we intended to investigate the efficacy of asymmetric synthesis upon replacement of the dimethylamine substituent with the more bulky diethylamine and di-*n*-propylamine groups.

The Grignard cross-coupling reaction shown in Eq. 12 was studied by using different palladium ferrocenylamine sulfide complexes. The chemical yields of all reactions exceeded 90%, and optical yields varied depending on the catalysts used. The cross-coupling product, 4-phenyl-1-pentene, was oxidized with potassium permanganate and sodium periodate as reported previously.[145] The optical rotation of the resulting acid is strongly affected by small quantities of impurities; therefore it is usually converted to the methyl ester (Eq. 13) and the optical yields were determined by ^1H NMR spectroscopy with the chiral shift reagent, $Eu(dcm)_3$.[146]



(Eq. 12)

32



(Eq. 13)

As shown in Fig. 20 for the ^1H NMR spectrum of methyl-3-phenylbutyrate, the methyl ester proton signal splits into two singlets for the two diastereomers. Integration of these two singlets reflects directly the optical yield of the coupling product. The procedure was used previously by Kumada and co-workers, who assigned the higher field signal for the *S* enantiomer of methyl-3-phenylpropionate.[147] Increasing the shift reagent concentration deshielded the chemical shift δ of the methyl ester proton signal and increased the enantiomeric shift difference $\Delta\Delta\delta$. The best concentrations of the chiral shift reagent and the substrate were 0.27 M and 0.5 M in $CDCl_3$ respectively, where the $\Delta\Delta\delta$ was large enough for the integration of the appropriate signals.

Results of this asymmetric synthesis are tabulated in Table 27. Modifying the sulfide substituents did not influence the optical yields greatly. However, by replacing the dimethylamine group with diethylamine and di-*n*-propylamine, the ee decreased from 26 to 13.4 and 5.8 (entries 7, 1 and 2). Furthermore, unlike the catalytic system with the dimethylamine group where the absolute configuration of the coupling product was dependent on the configuration of the catalyst used, the (*R*,*S*)-catalysts gave ***S*** **-33**, while the (*S*,*R*)-catalysts gave ***R*** **-33**. In the case of diethylamine and di-*n*-propylamine substituents, the coupling reaction gave only R product regardless of the catalyst configuration. These observations were also found in the ferrocenylphosphine-based nickel catalytic system PPFA/$NiCl_2$.[76] Obviously, the steric bulkiness of the amino substituent has a powerful effect on the stereoselectivity. Replacing the chloro functional group with a bromo group in the substrate didn't change the optical yield significantly.

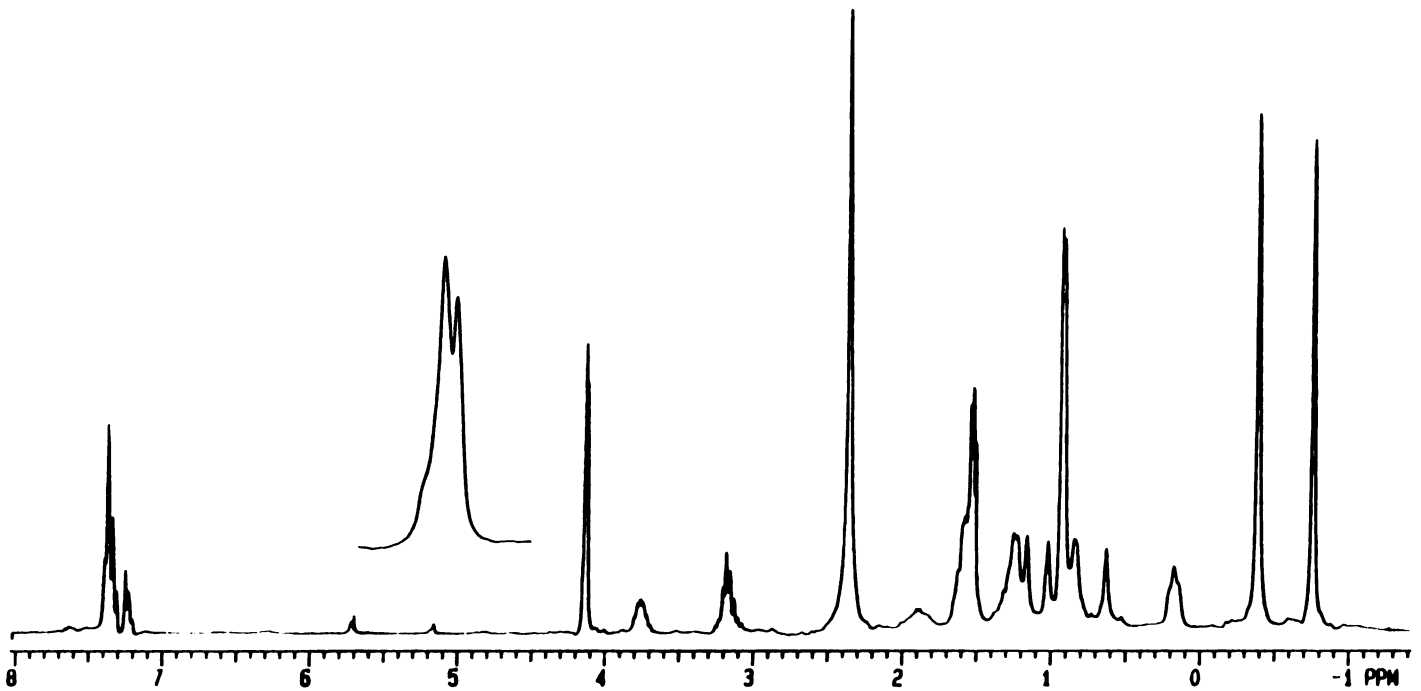


Figure 20. ^1H NMR spectra of (*R*)- and (*S*)-methylphenyl butyrate in the presence of chiral shift reagents $Eu(dcm)_3$

Table 27 Asymmetric Gringard cross-coupling of chloroethylbenzene with allylmagnesium chloride by new chiral ferrocenylamine sulfide catalysts[a]

catalyst	% optical yield	Conf.
(*S,R*)-66 (R=Et,R'=Me,X=Cl)	13.4	R
(*S,R*)-67 (R=*n*-Pr,R'=Me)	5.8	R
(*R,S*)-69 (R=*n*-Pr,R'=Et)	11.8	R
(*R,S*)-70 (R=Et,R'=*i*-Pr)	10.0	R
(*R,S*)-71 (R=*n*-Pr,R'=*i*-Pr)	12.8	R
(*R,S*)-71[b] (X=Br)	8.6	R
(*S,R*)-79[c] (R=Me,R'=Me,X=Cl)	26.0	R
(*S,R*)-83[c] (R=Me,R'=*i*-Pr)	31.0	R

[a] 10 mmol 1-phenylethylchloride, 20 mmol allylmagnesium chloride, 36 h at room temperature
[b] using bromoethylbenzene as halide source
[c] Ref. 124

It is not clear at this moment why increasing the steric bulkiness of the amino substituent should reduce the optical yield. However, based on the available data, the amino group on the ferrocenyl ligand is most important for high stereoselectivity and the nitrogen atom environment exerts a strong effect on the asymmetric induction.

APPENDIX

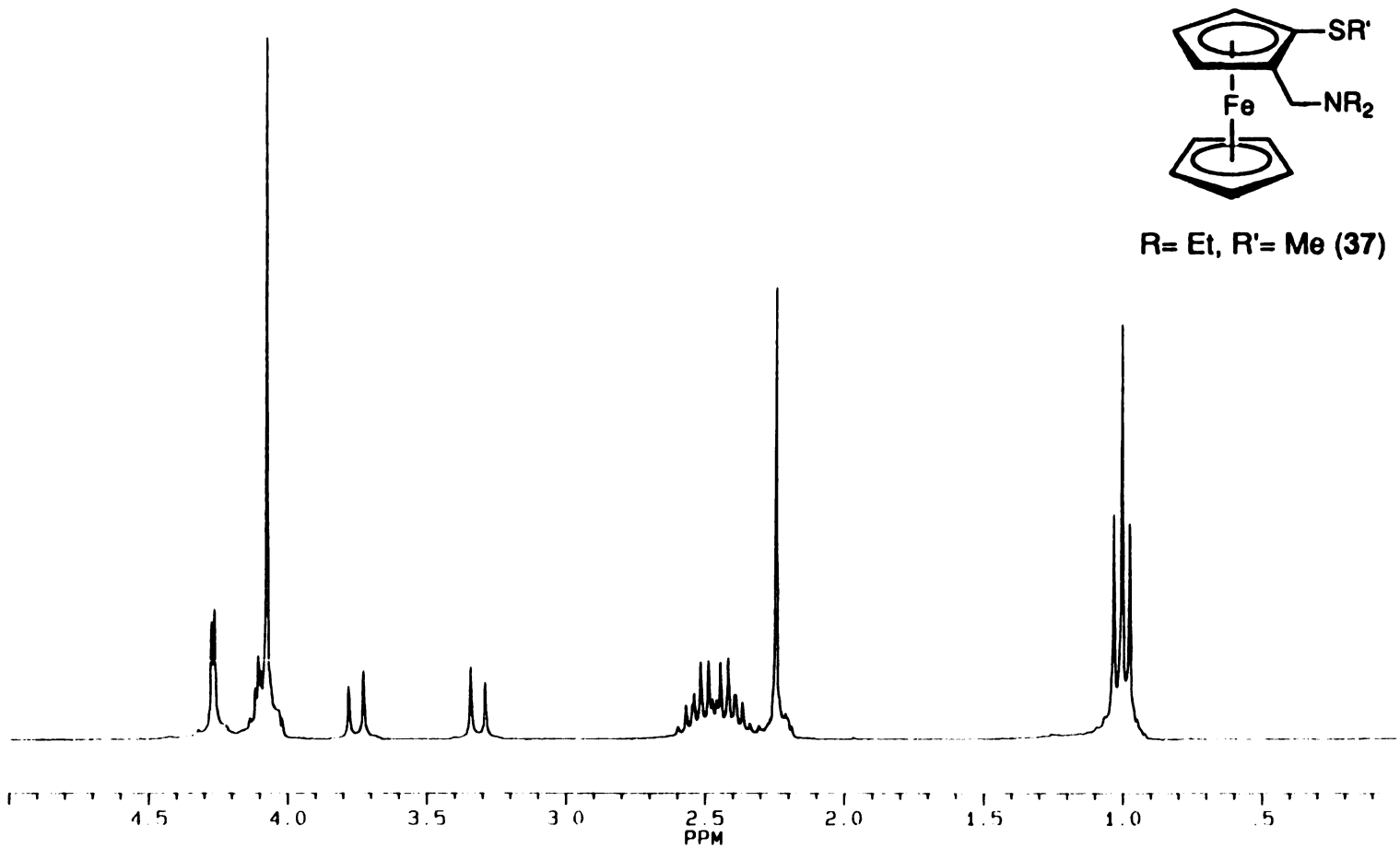
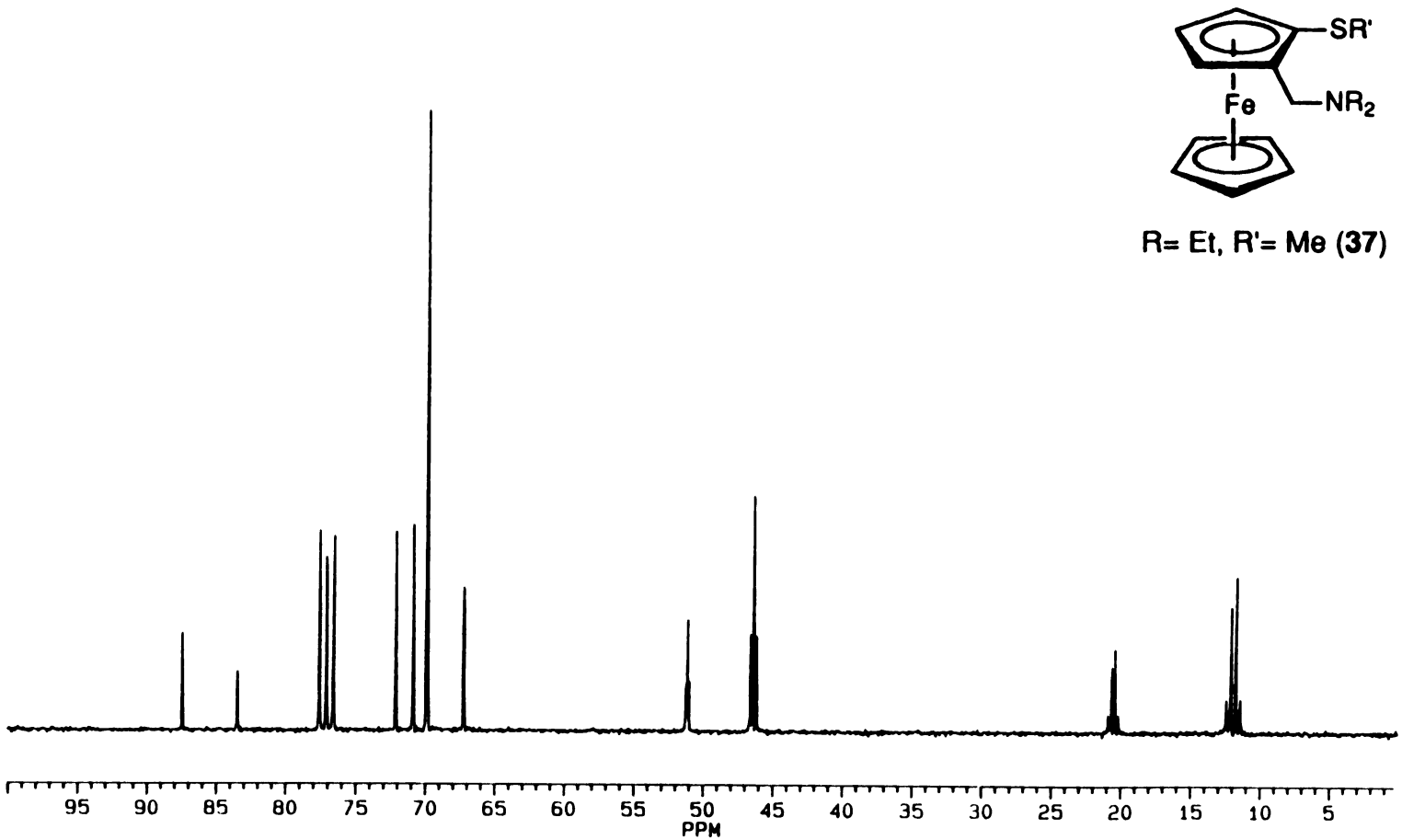


Figure 21. 300 MHz ^{1}H NMR spectrum of **37**



R= Et, R'= Me (37)

Figure 22. Off-resonance decoupled ^{13}C NMR spectrum of 37

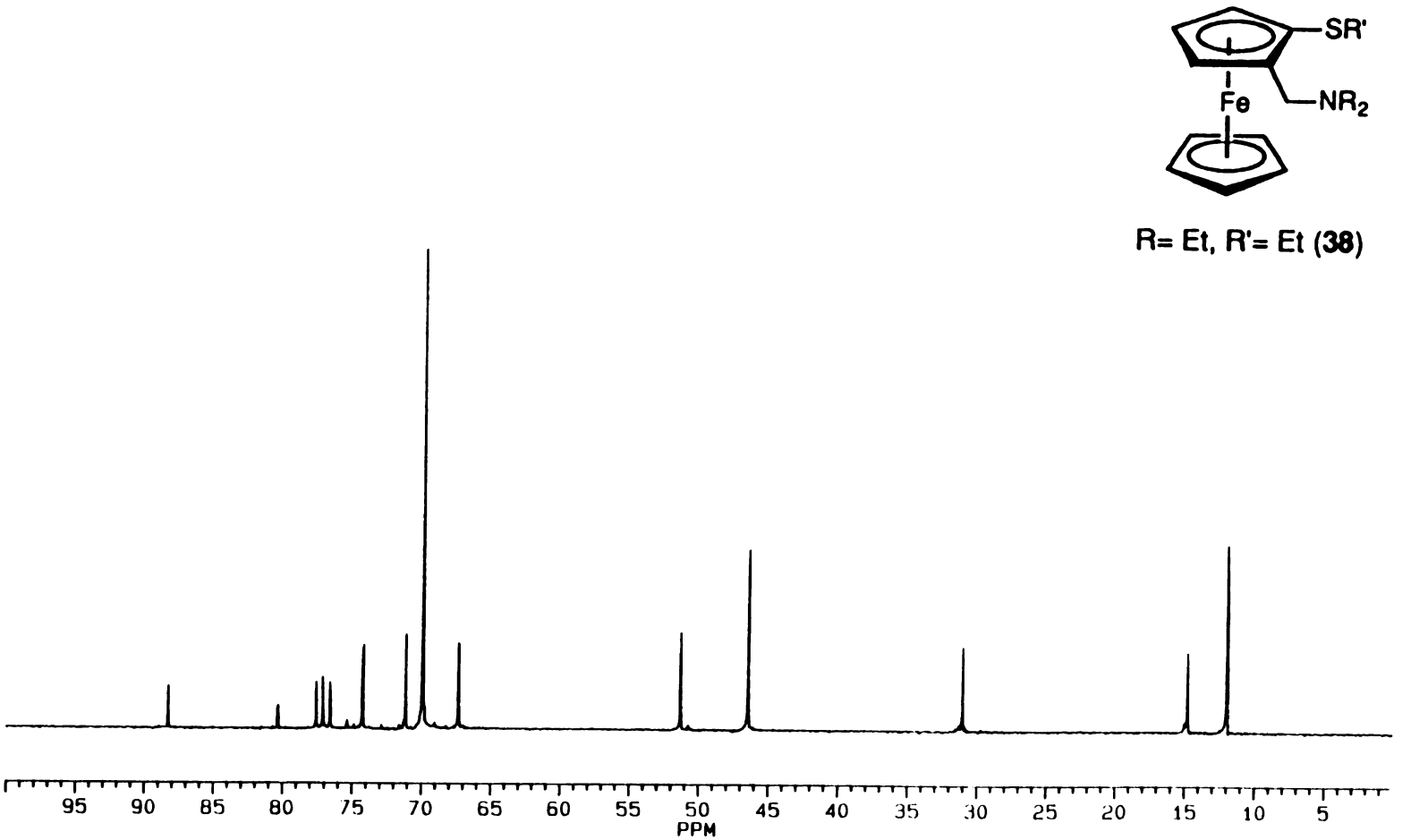


Figure 23. Broad band decoupled ^{13}C NMR spectrum of 38

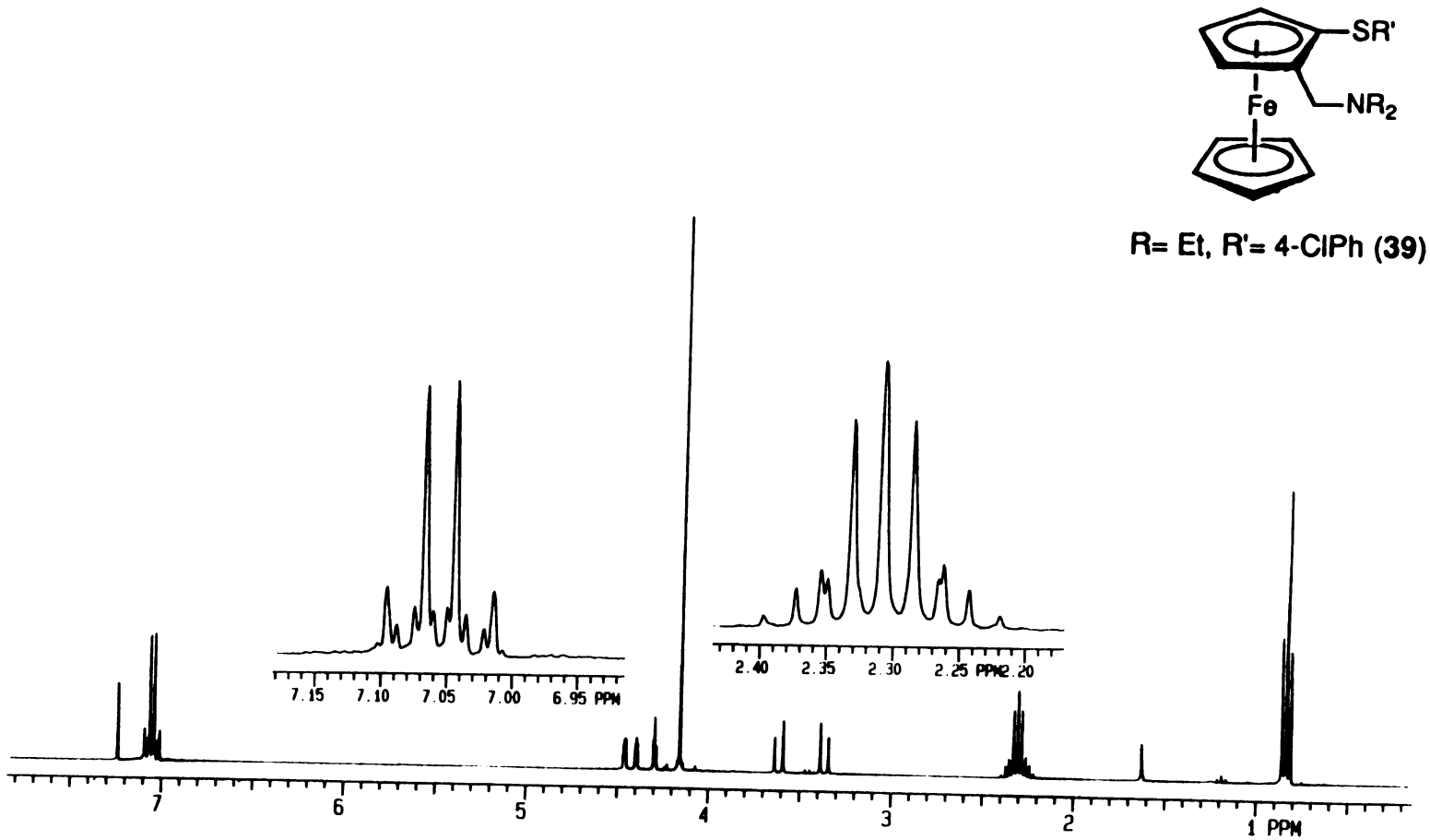


Figure 24. 300 MHz ^{1}H NMR spectrum of **39**

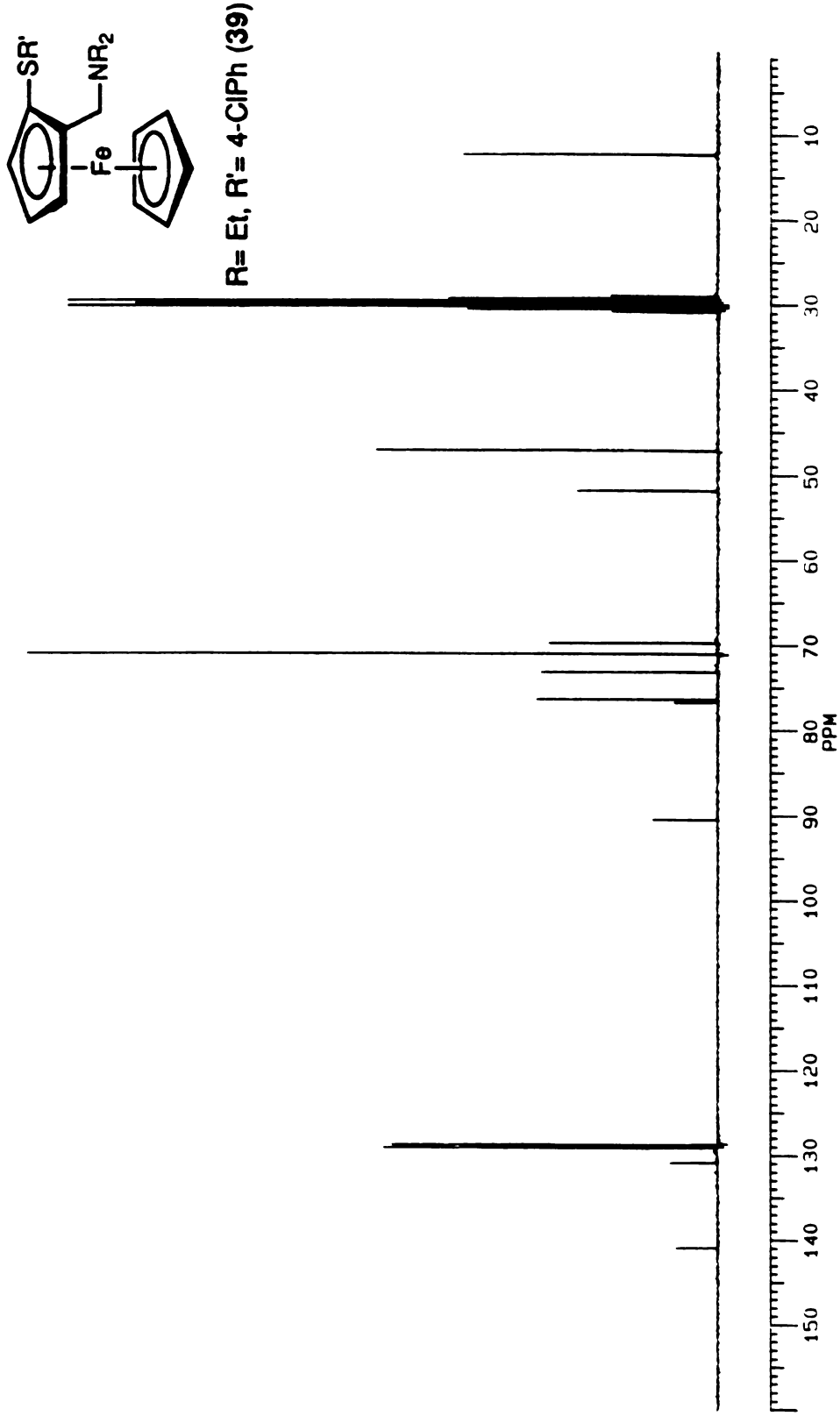
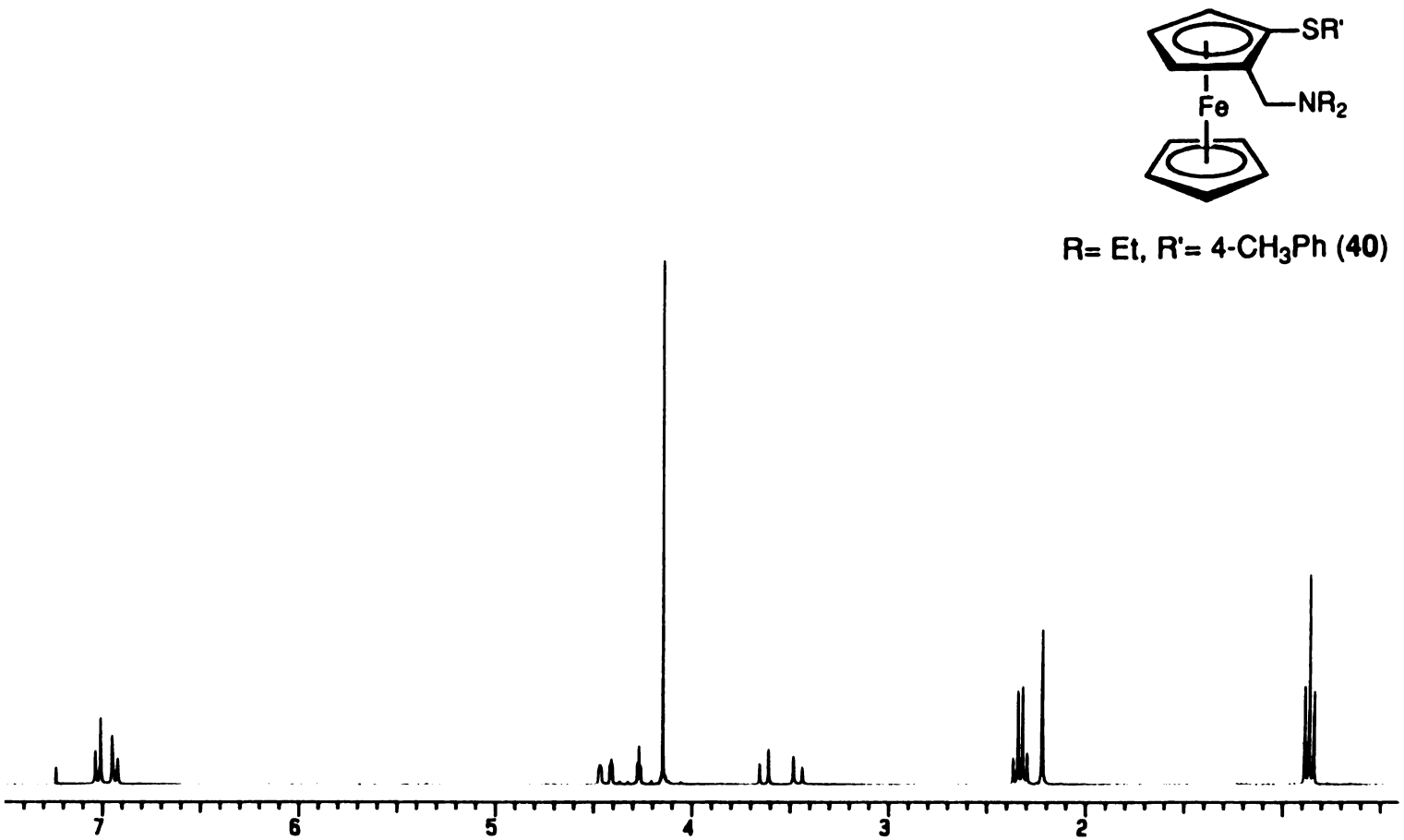
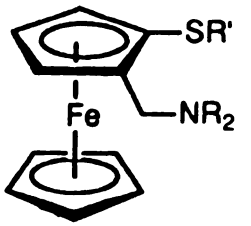


Figure 25. Broad band decoupled ^{13}C NMR spectrum of **39**



R= Et, R'= 4-CH_3Ph (**40**)

Figure 26. 300 MHz ^{1}H NMR spectrum of **40**



R= Et, R'= 4-CH_3Ph (**40**)

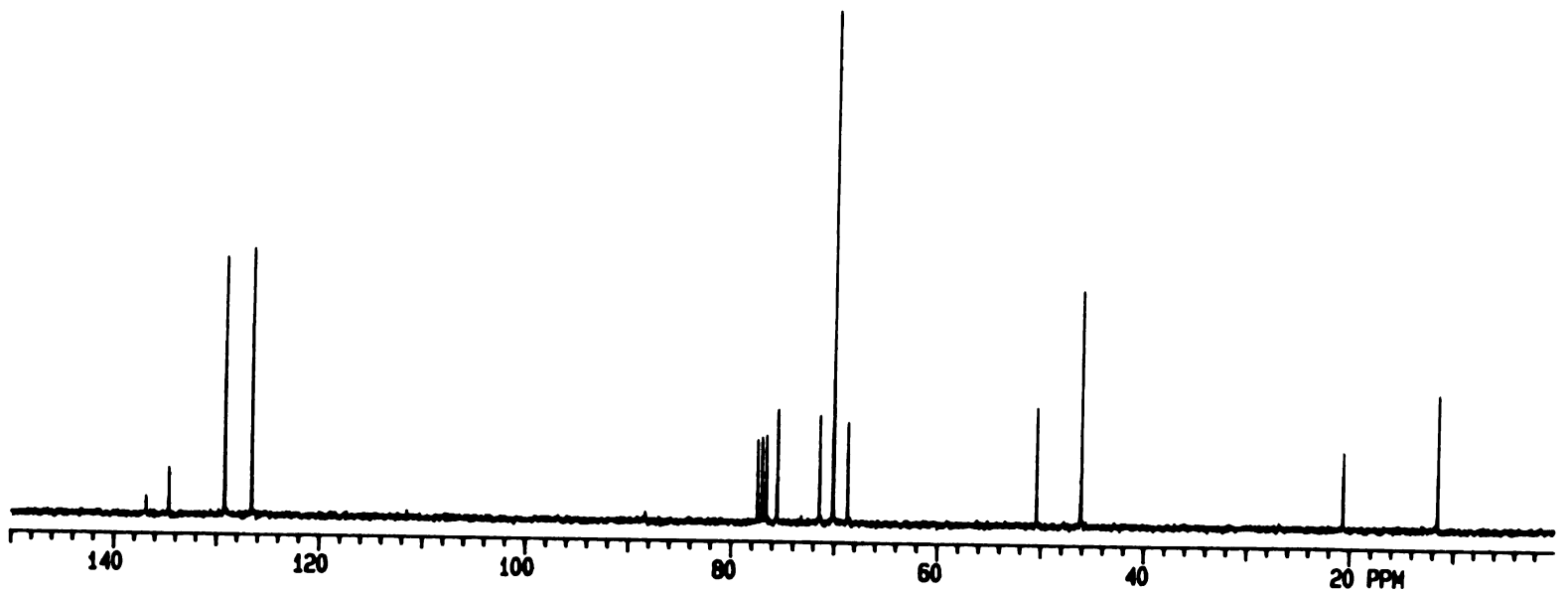


Figure 27. Broad band decoupled ^{13}C NMR spectrum of **40**

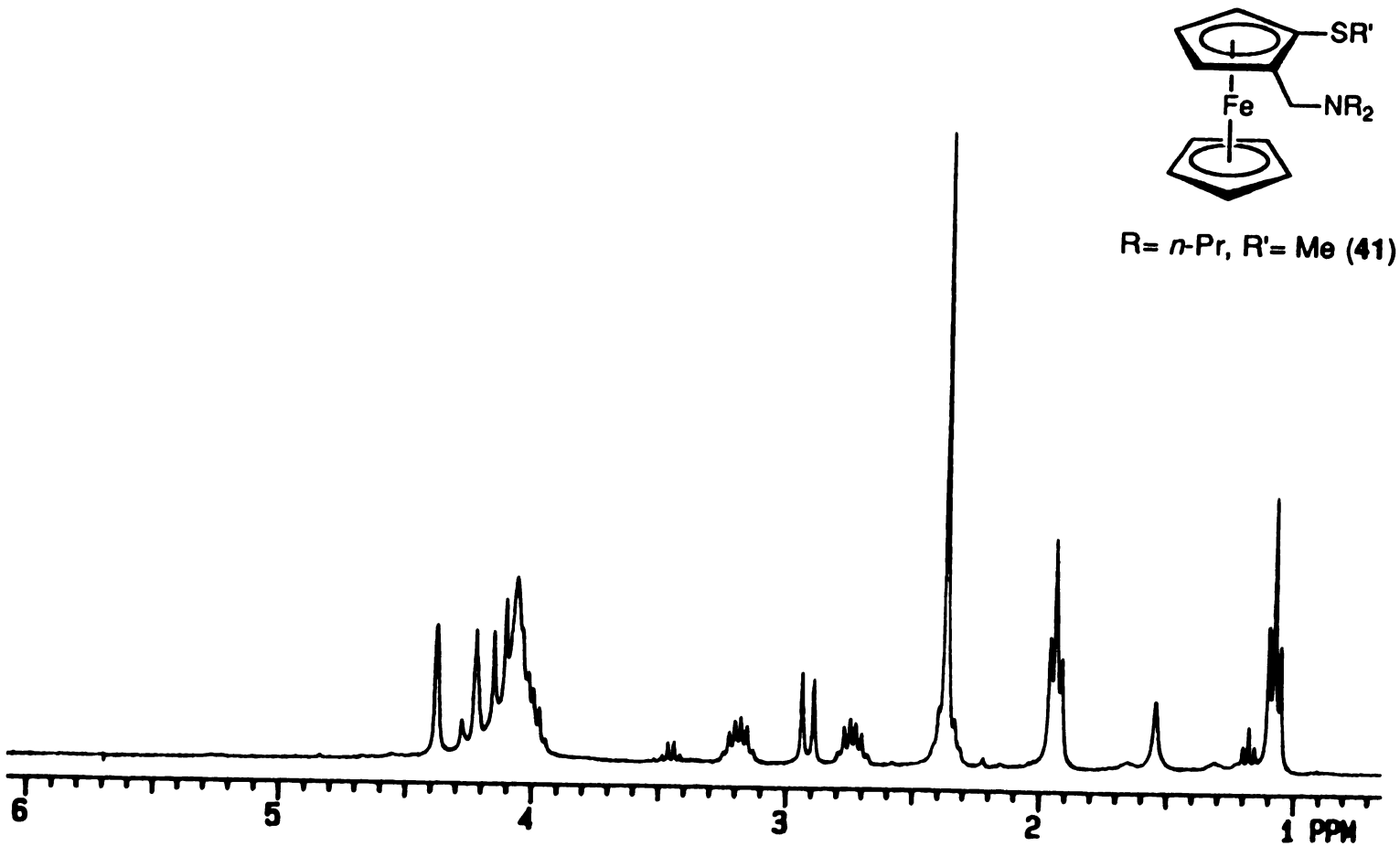
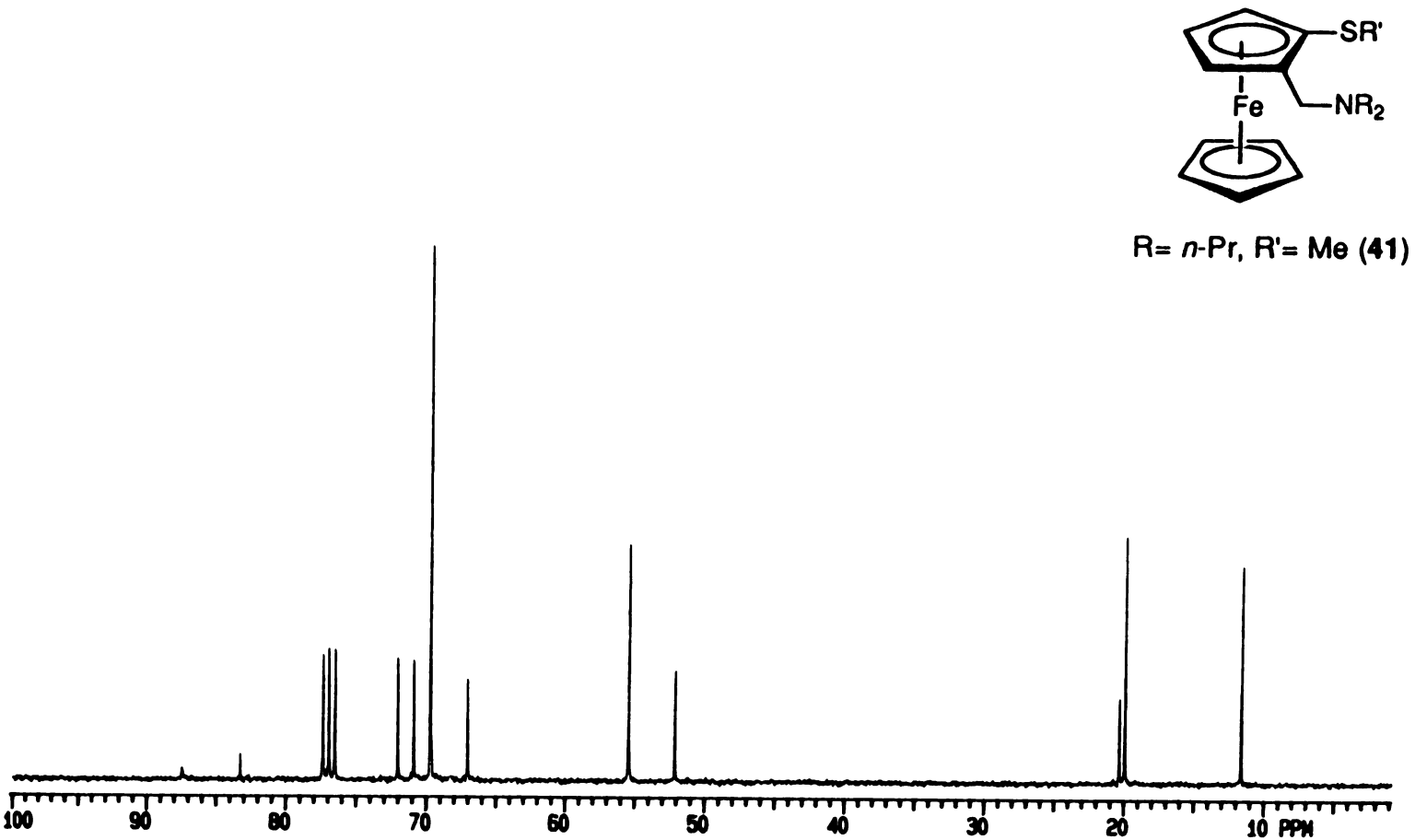


Figure 28. 300 MHz ^{1}H NMR spectrum of **41**



R= *n*-Pr, R'= Me (**41**)

Figure 29. Broad band decoupled ^{13}C NMR spectrum of **41**

R= *n*-Pr, R'= Me (**41**)

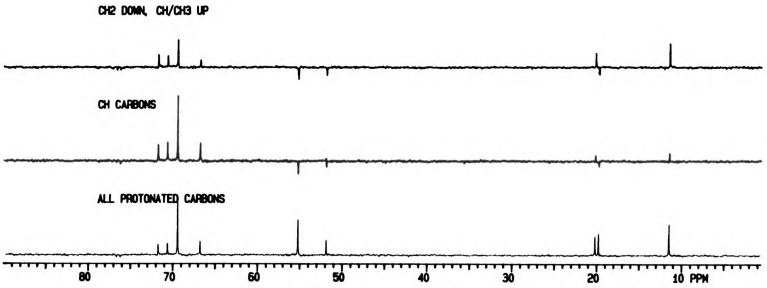


Figure 30. DEPT ^{13}C NMR spectrum of **41**

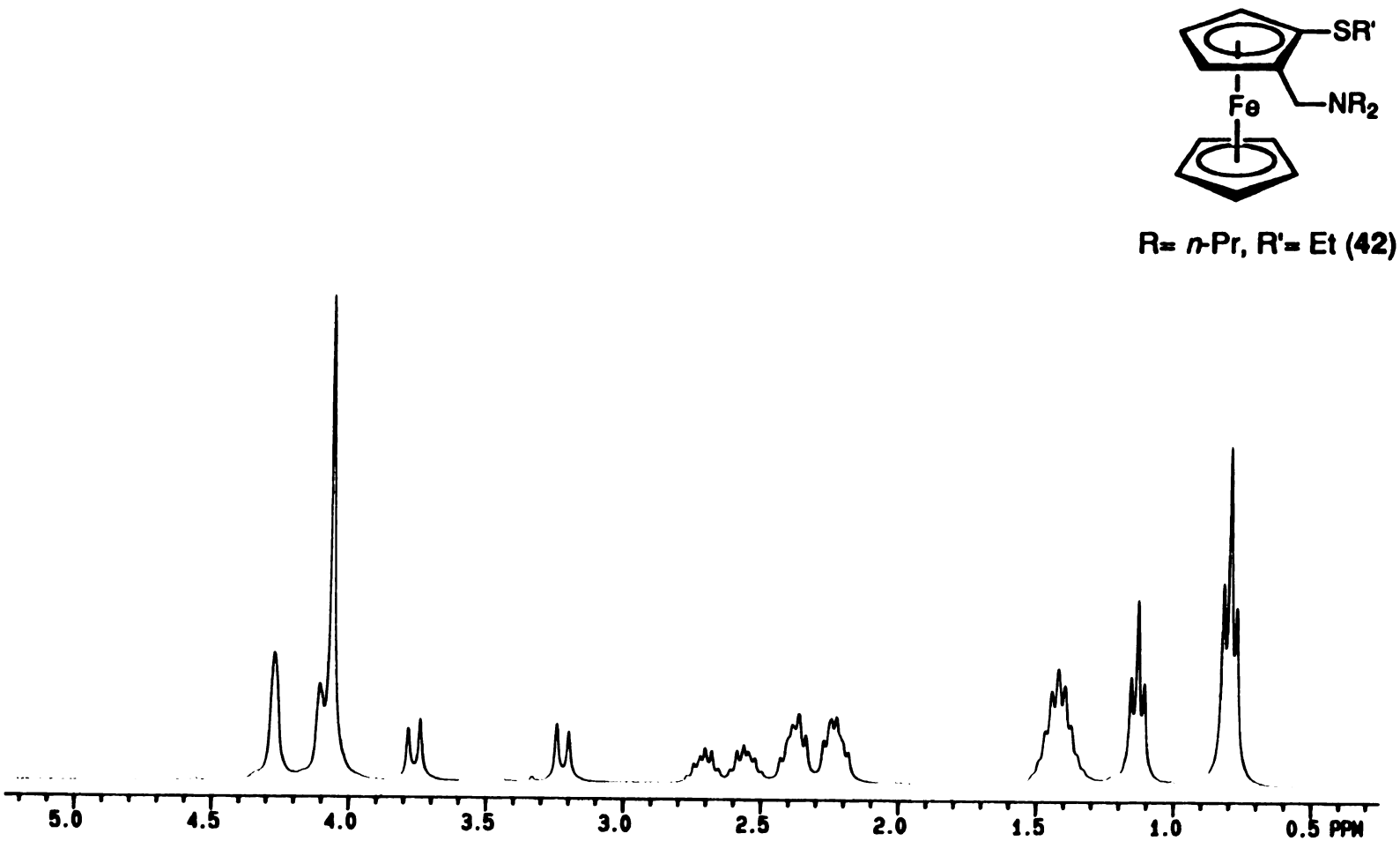


Figure 31. 300 MHz ^{1}H NMR spectrum of **42**

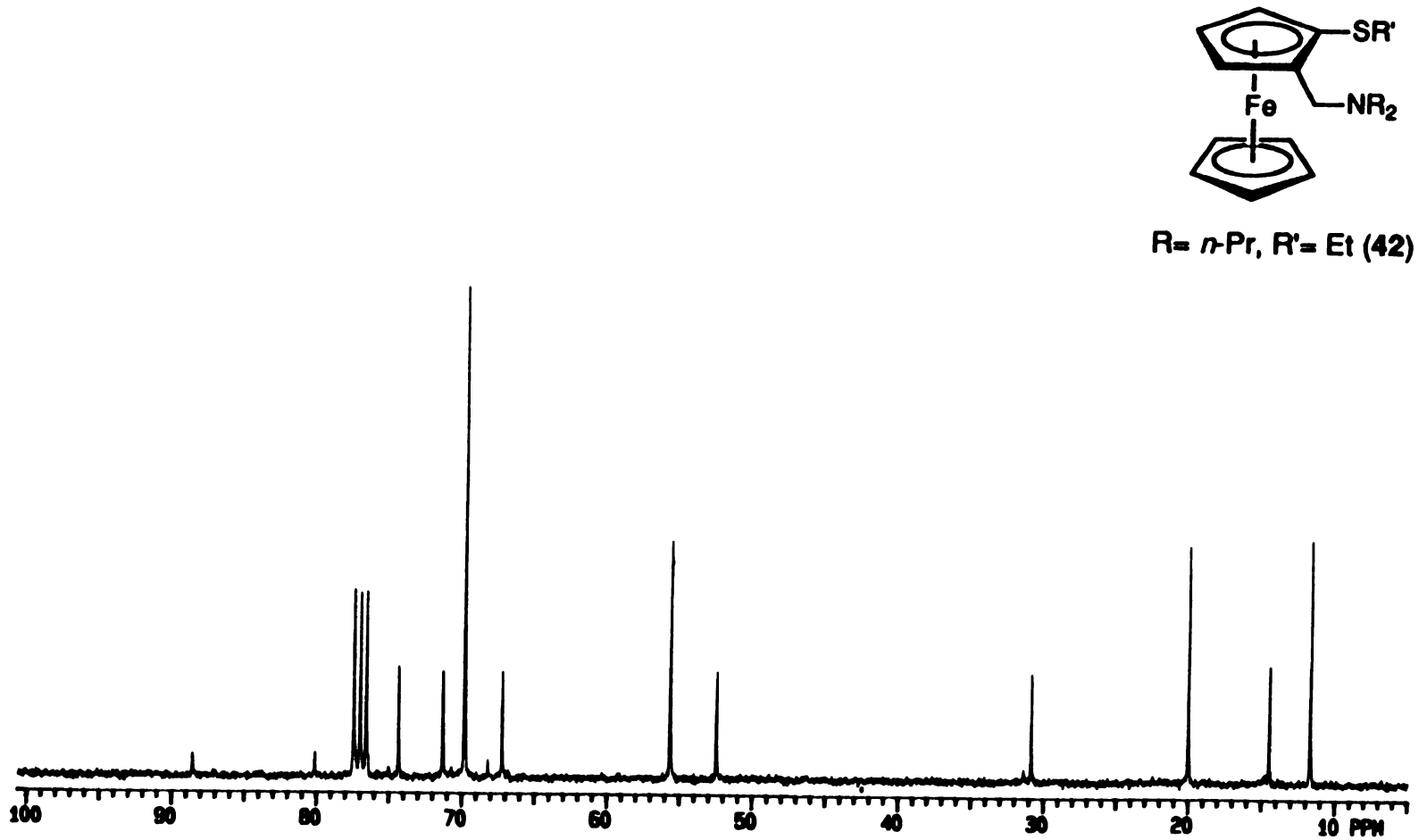


Figure 32. Broad band decoupled ^{13}C NMR spectrum of **42**

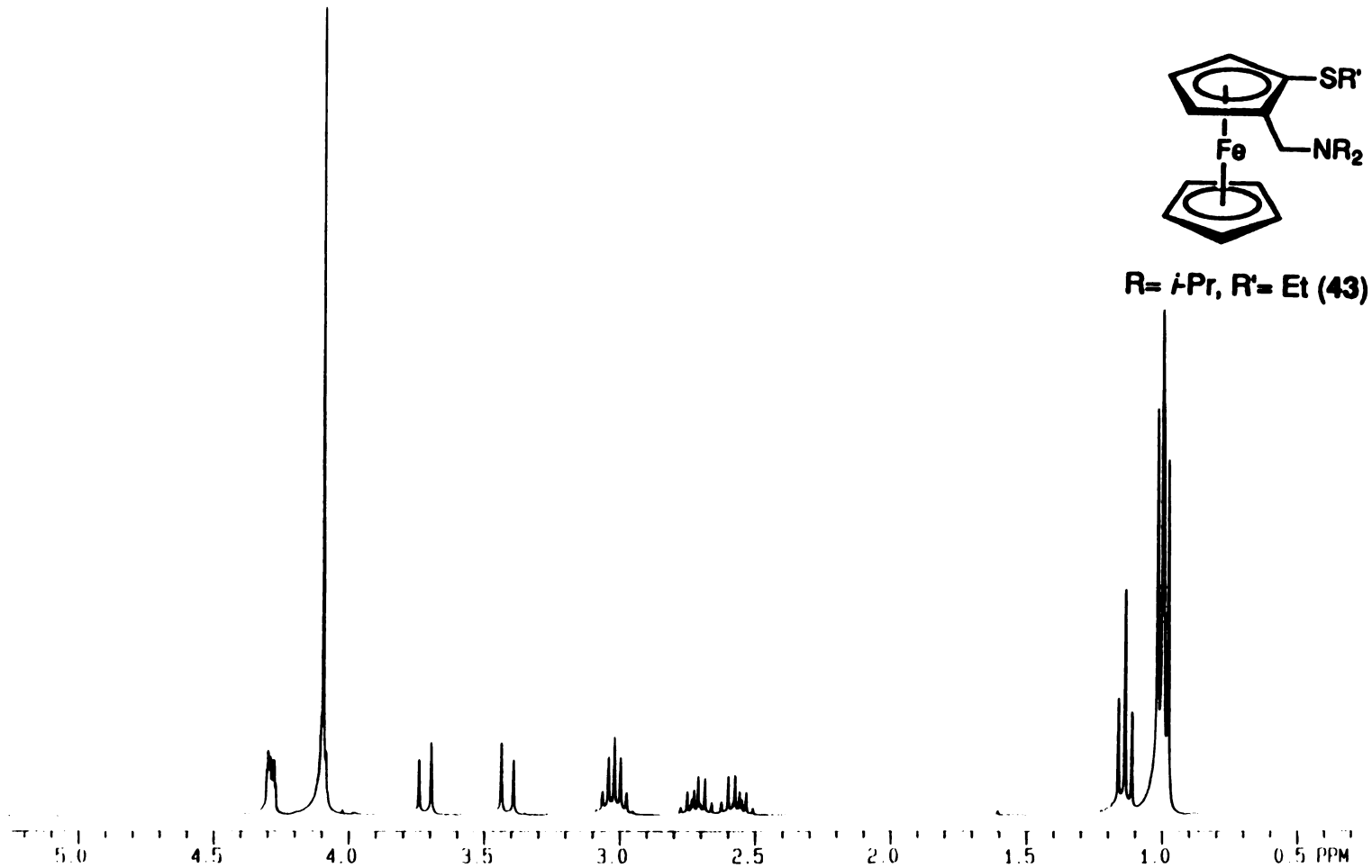


Figure 33. 300 MHz ^{1}H NMR spectrum of 43

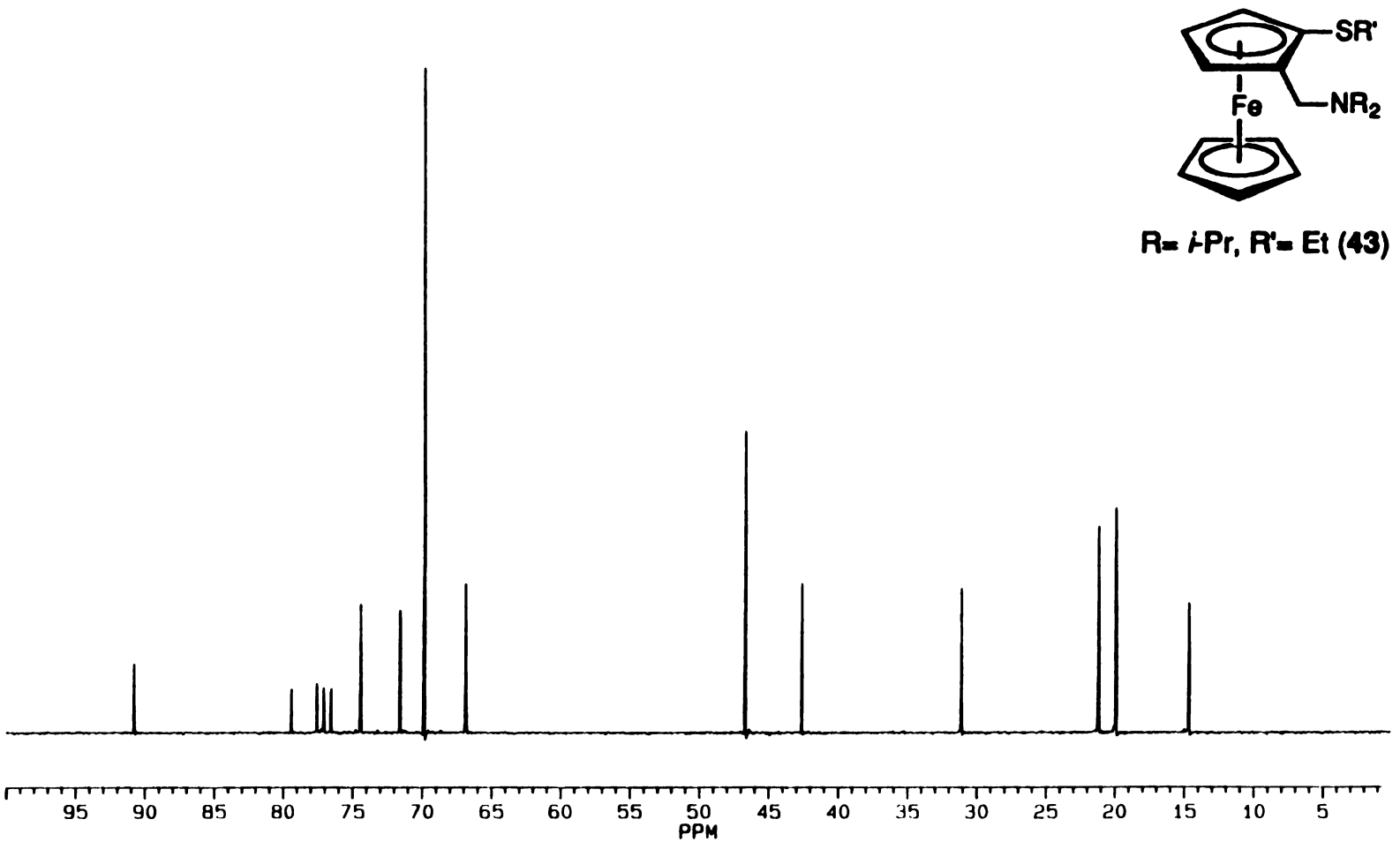
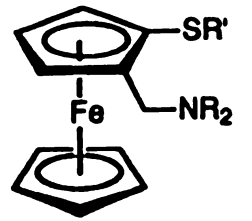


Figure 34. Broad band decoupled ^{13}C NMR spectrum of **43**



R= *i*-Bu, R'= Et (**44**)

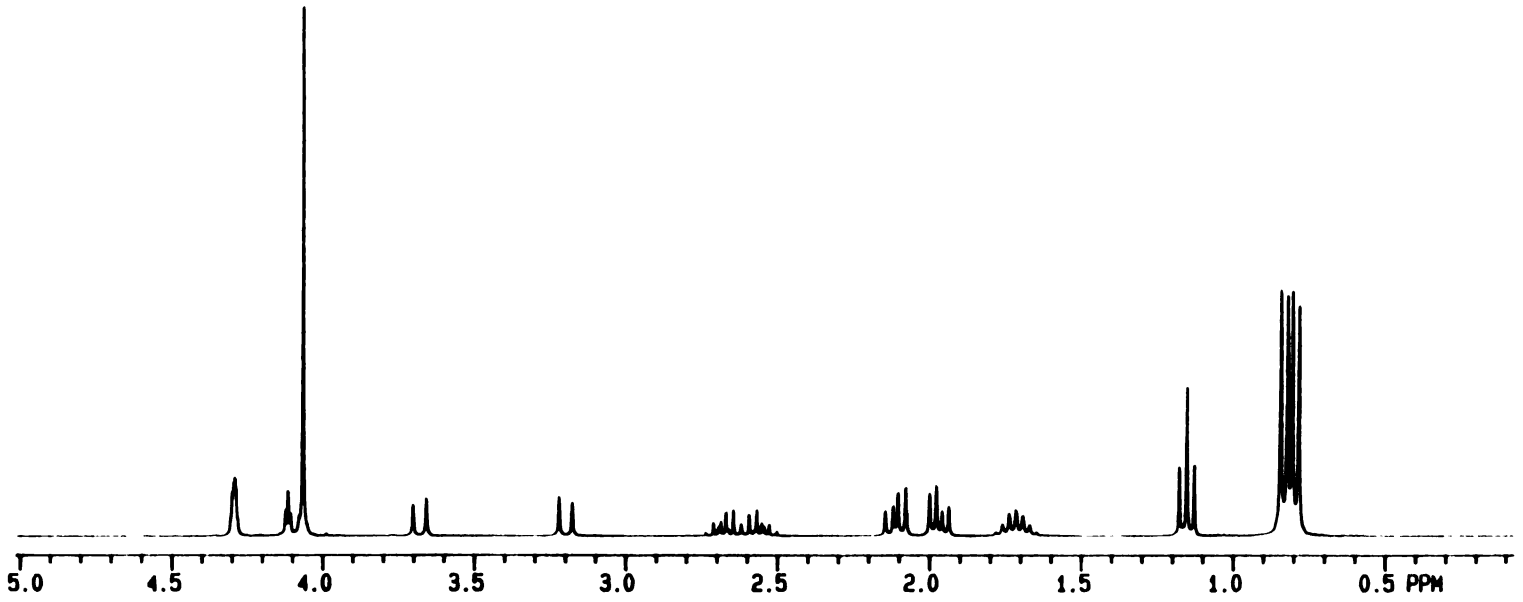
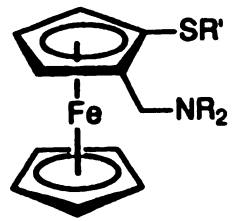


Figure 35. 300 MHz ^{1}H NMR spectrum of **44**



R= *i*-Bu, R'= Et (**44**)

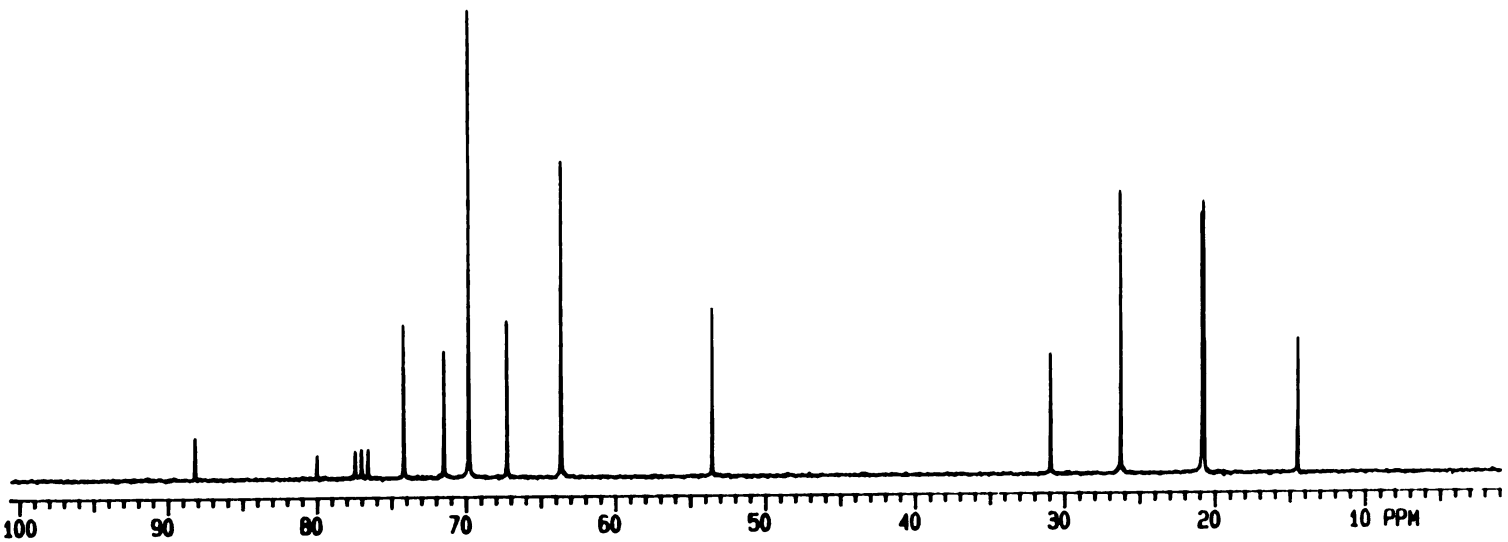


Figure 36. Broad band decoupled ^{13}C NMR spectrum of **44**

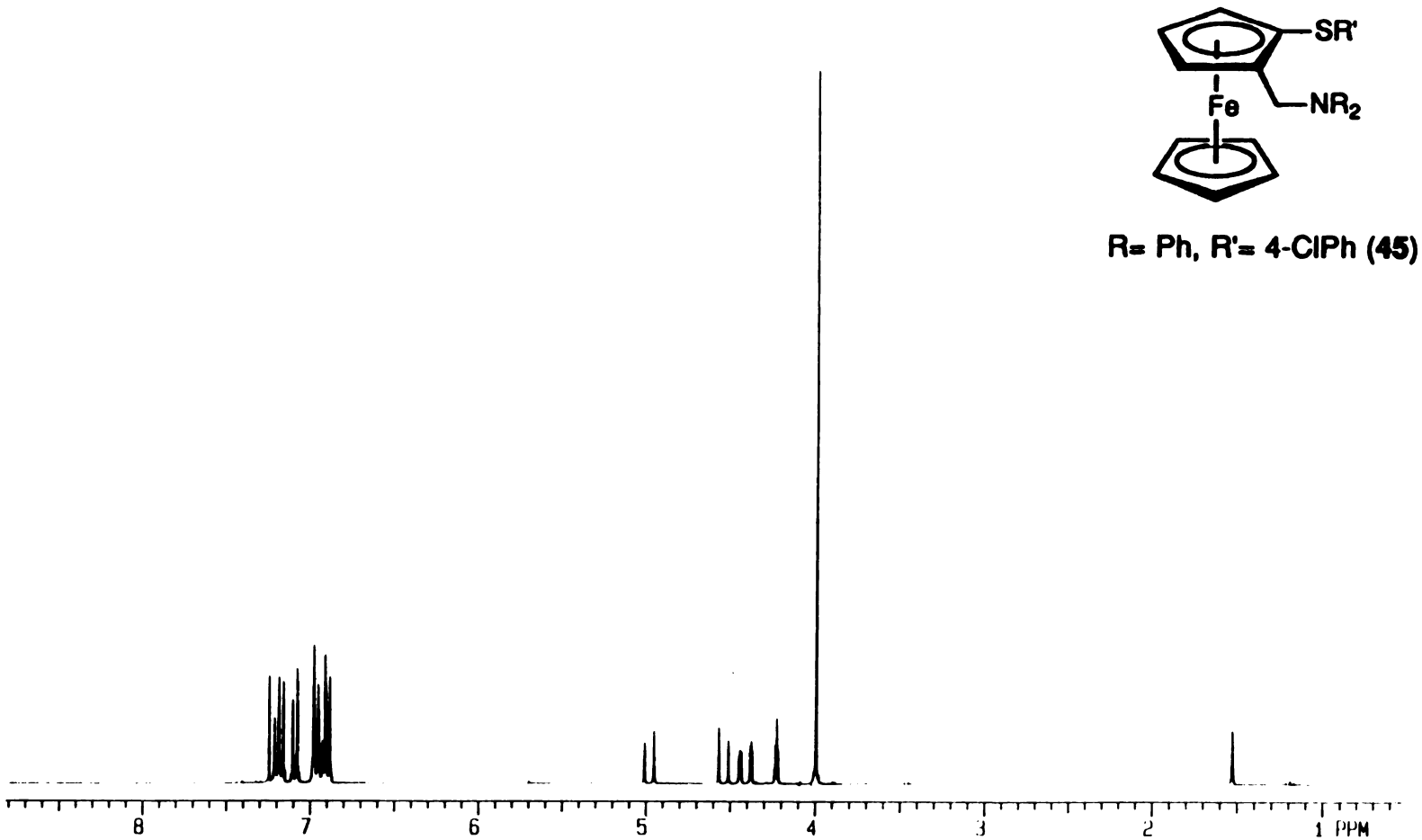


Figure 37. 300 MHz ^{1}H NMR spectrum of **45**

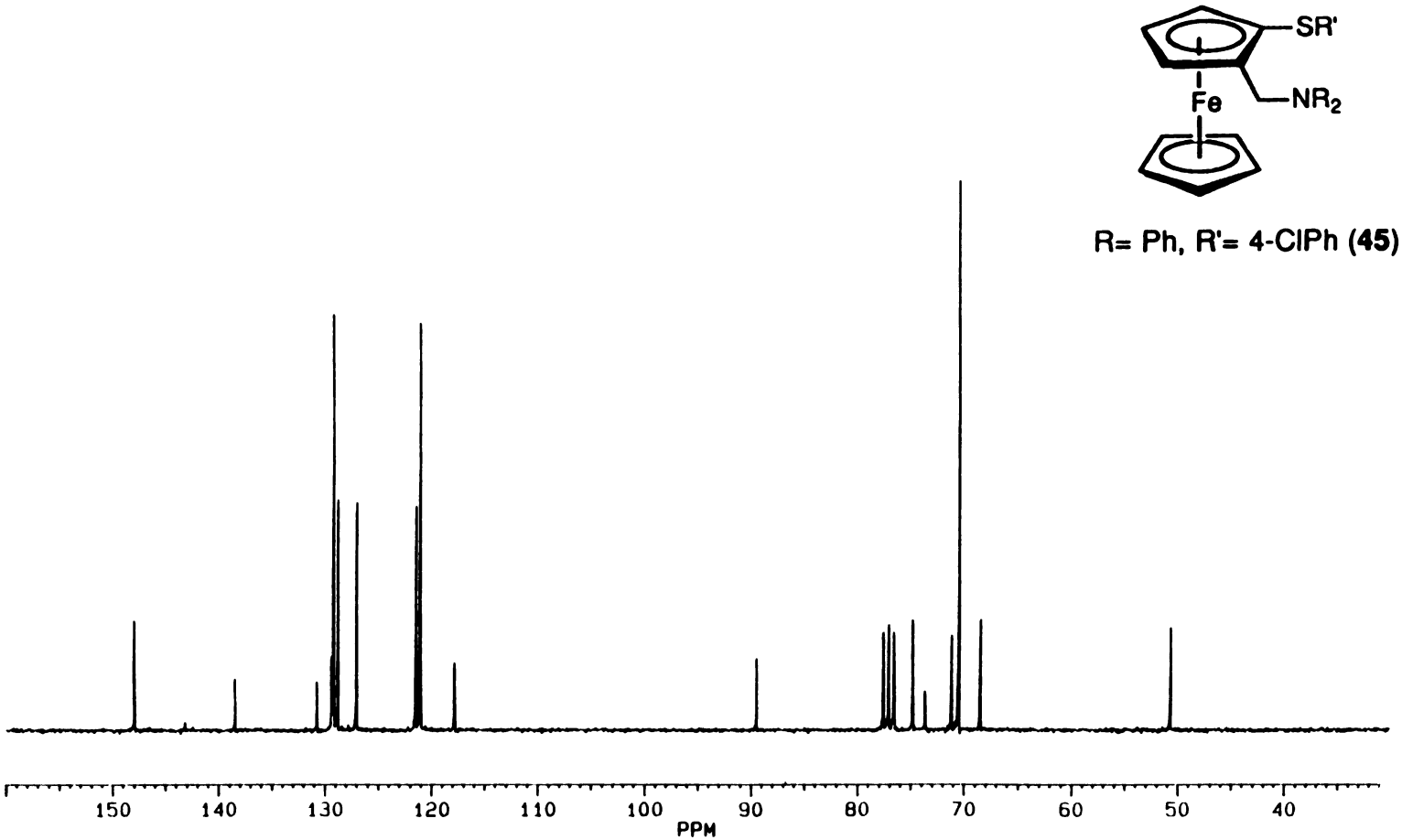
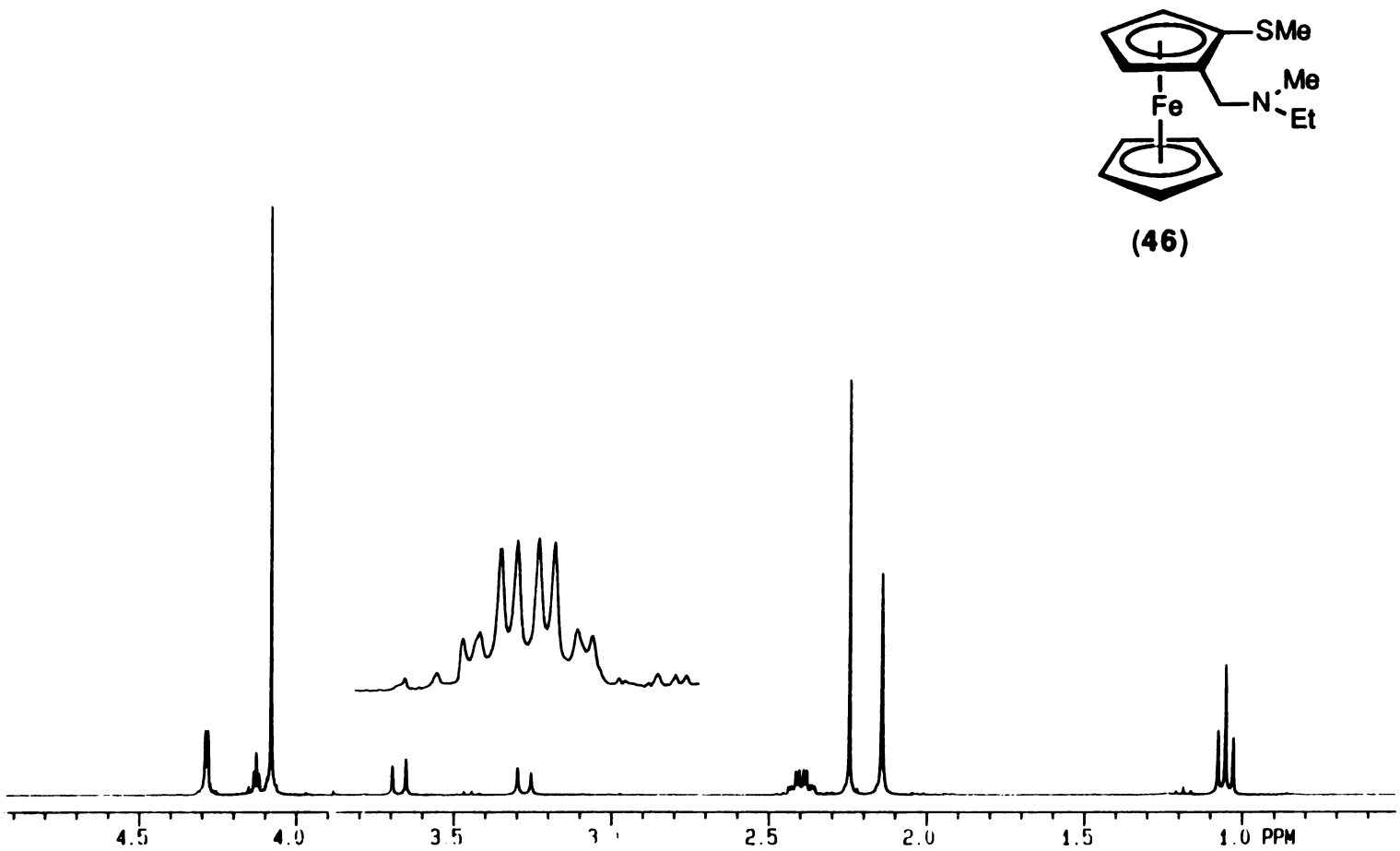


Figure 38. Broad band decoupled ^{13}C NMR spectrum of 45



(46)

Figure 39. 300 MHz ^{1}H NMR spectrum of **46**

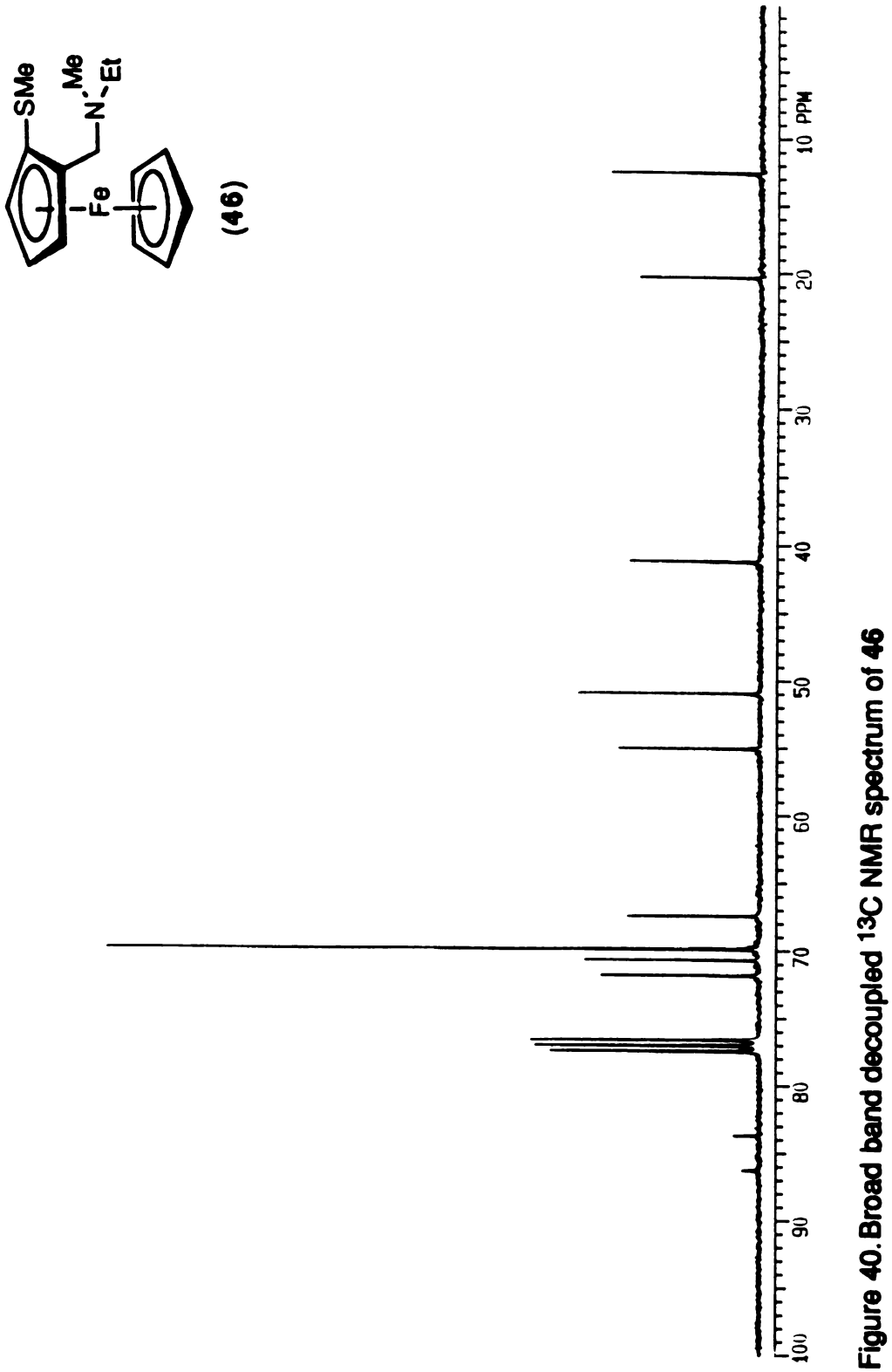
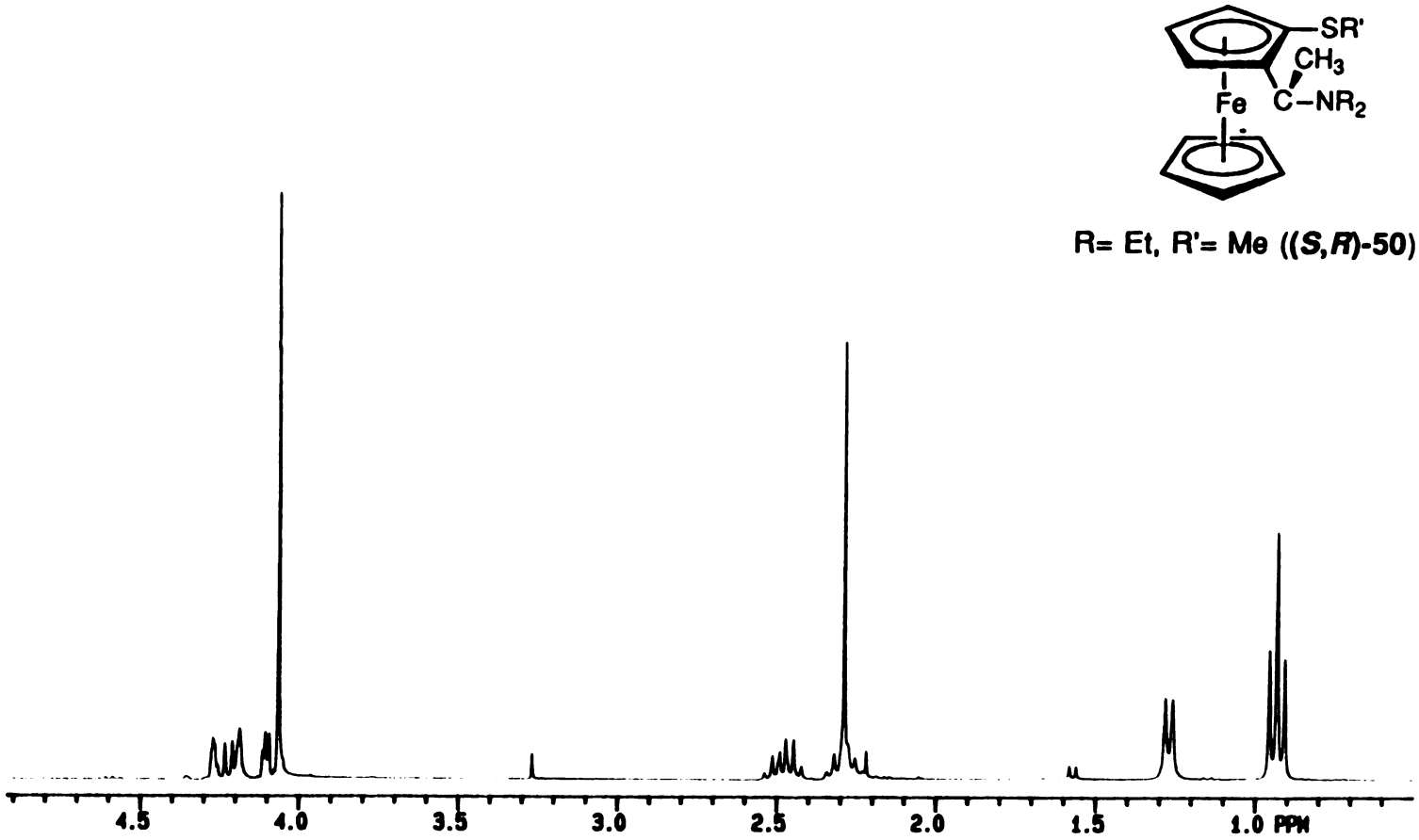


Figure 40. Broad band decoupled ^{13}C NMR spectrum of **46**



R= Et, R'= Me ((*S*,*R*)-50)

Figure 41. 300 MHz ^{1}H NMR spectrum of (*S*,*R*)-50

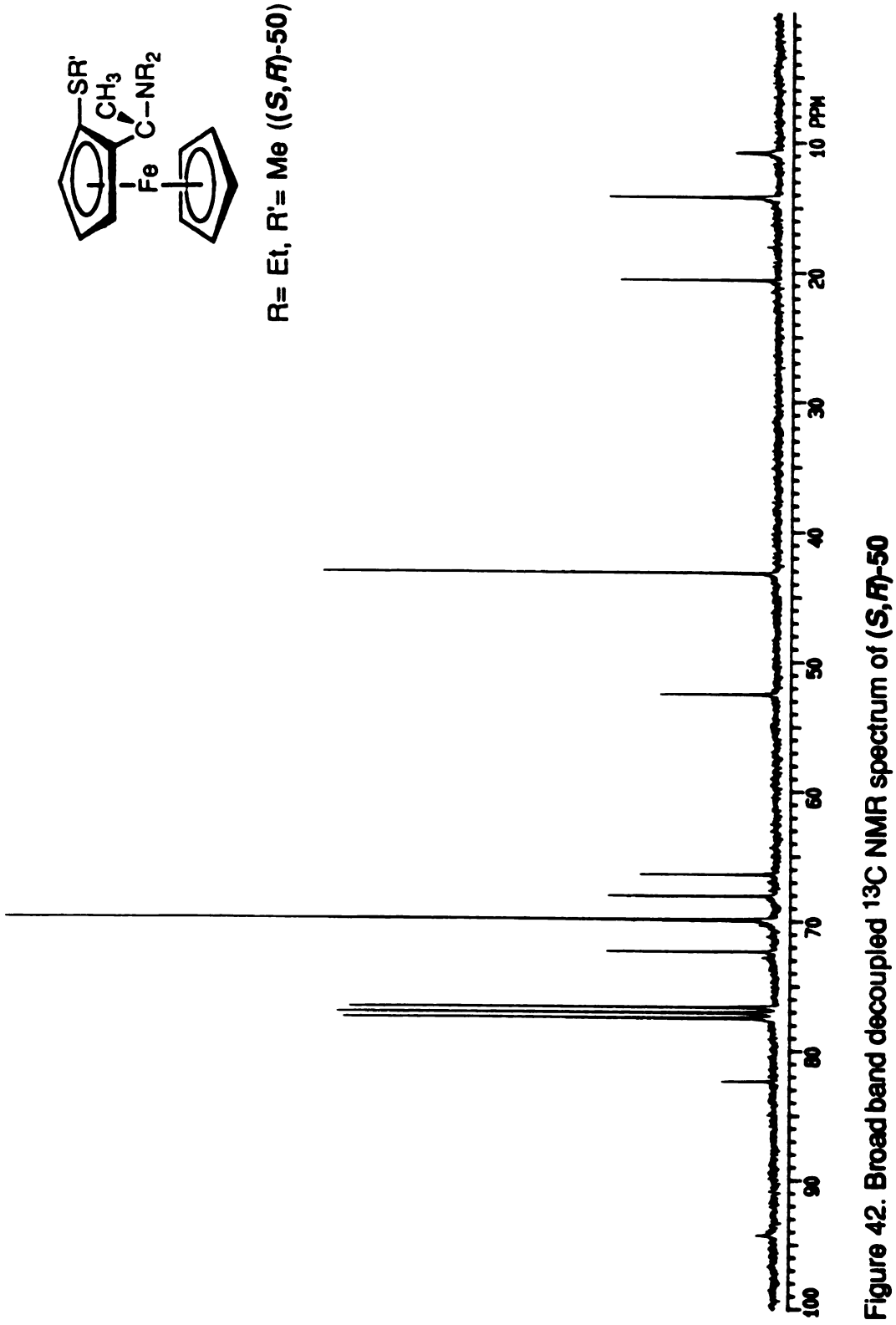


Figure 42. Broad band decoupled ^{13}C NMR spectrum of (*S,R*)-50

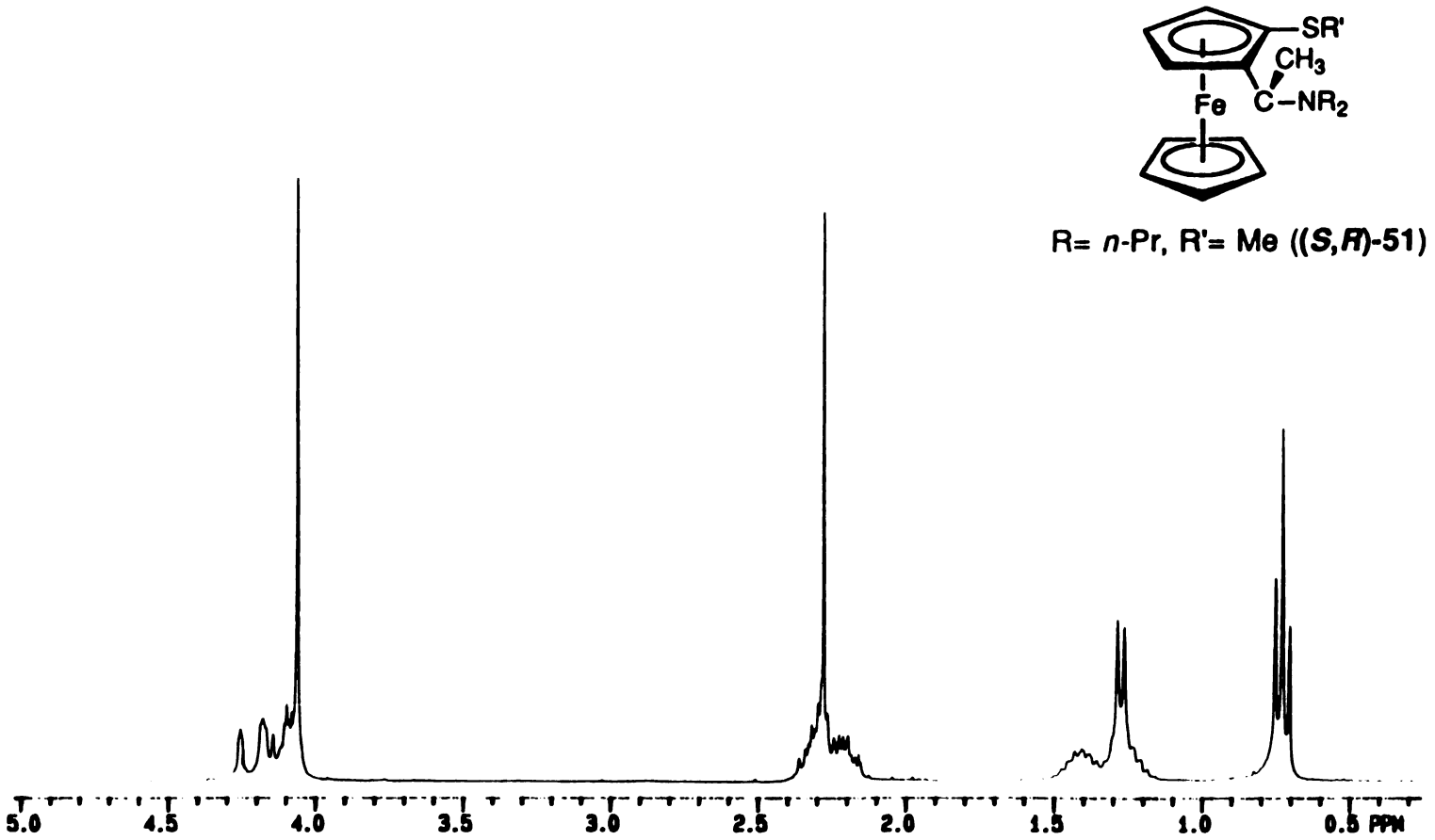


Figure 43. 300 MHz ^{1}H NMR spectrum of (*S*,*R*)-51

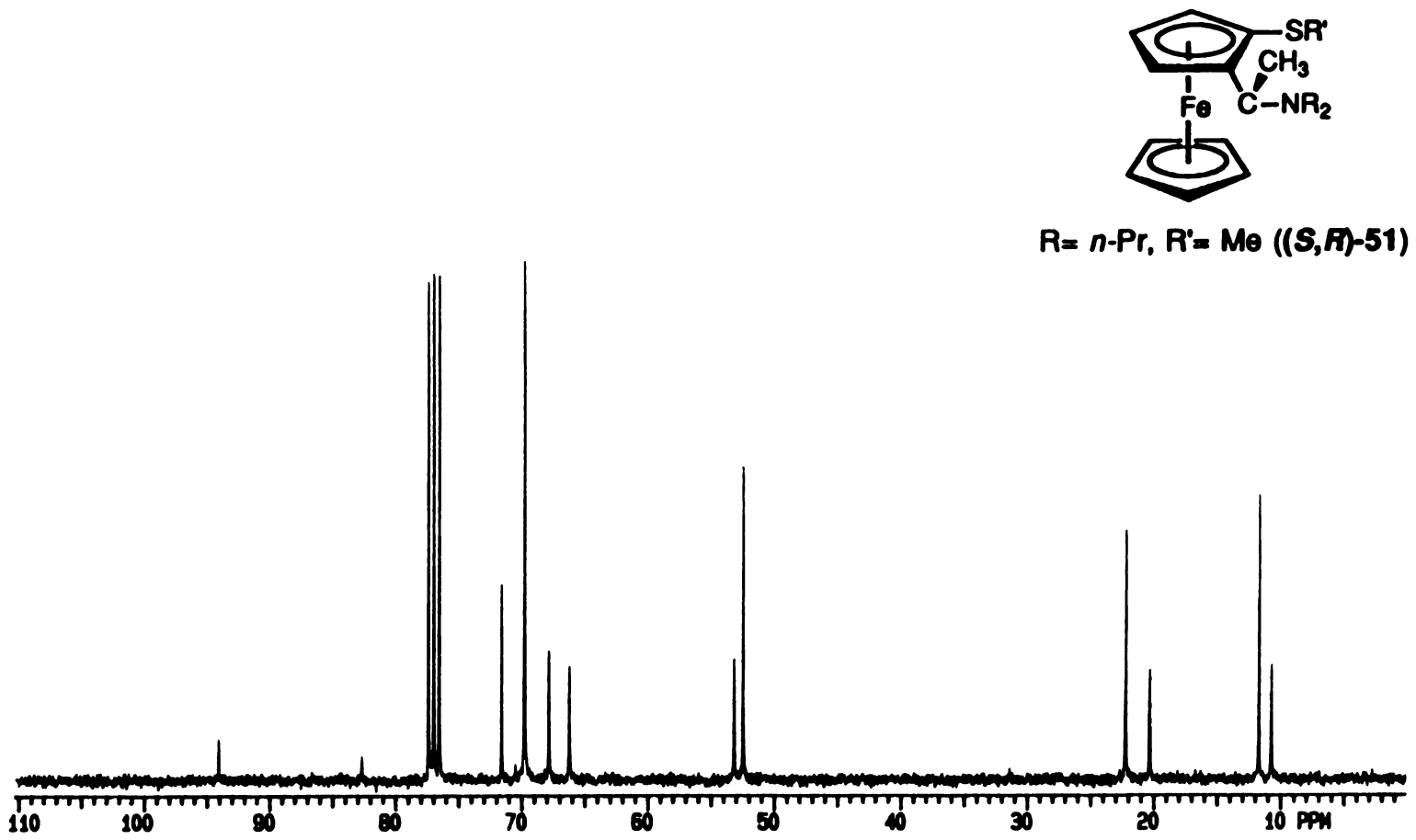
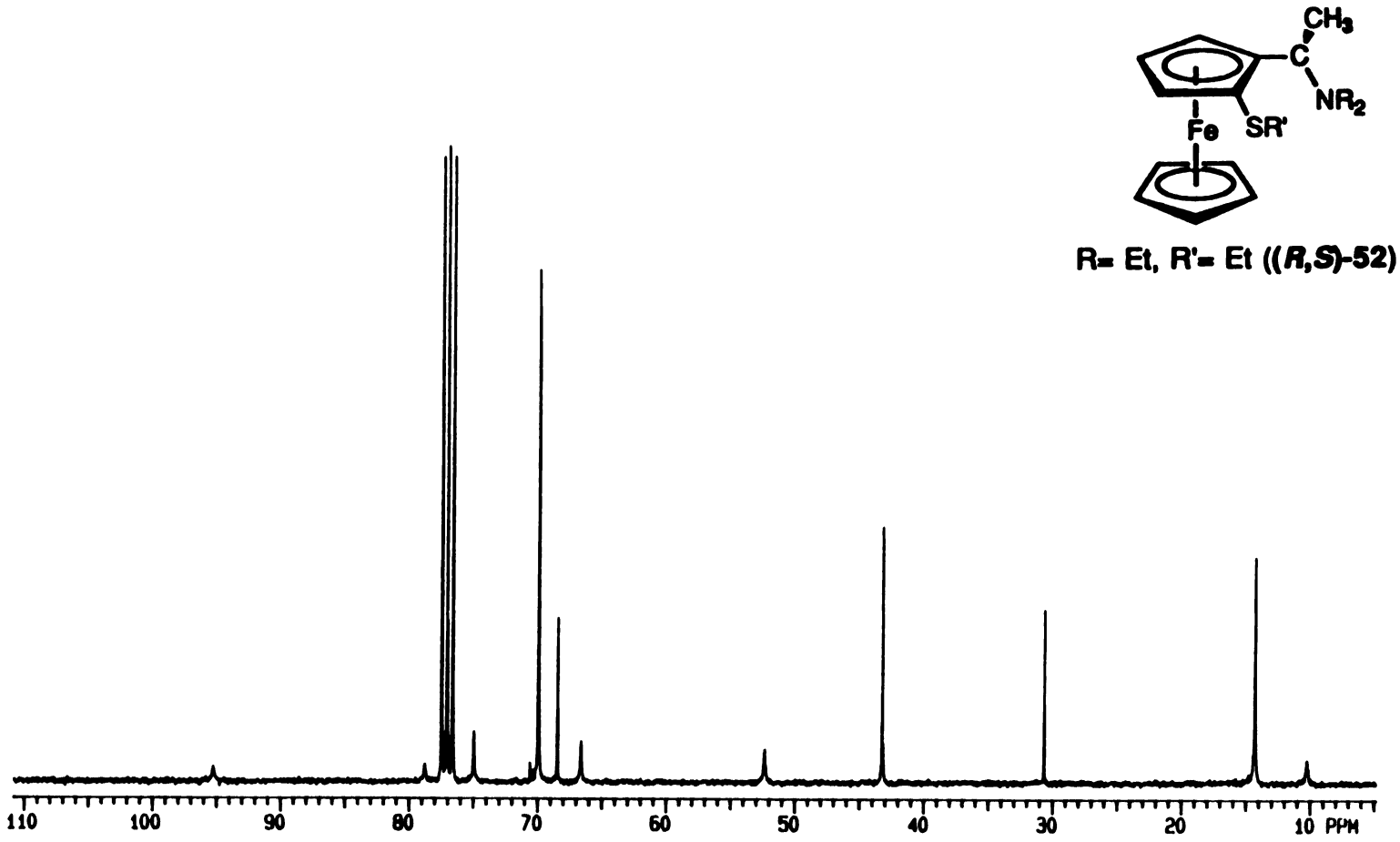


Figure 44. Broad band decoupled ^{13}C NMR spectrum of (*S,R*)-51



R= Et, R'= Et ((*R*,*S*)-52)

Figure 45. Broad band decoupled ^{13}C NMR spectrum of (*R*,*S*)-52

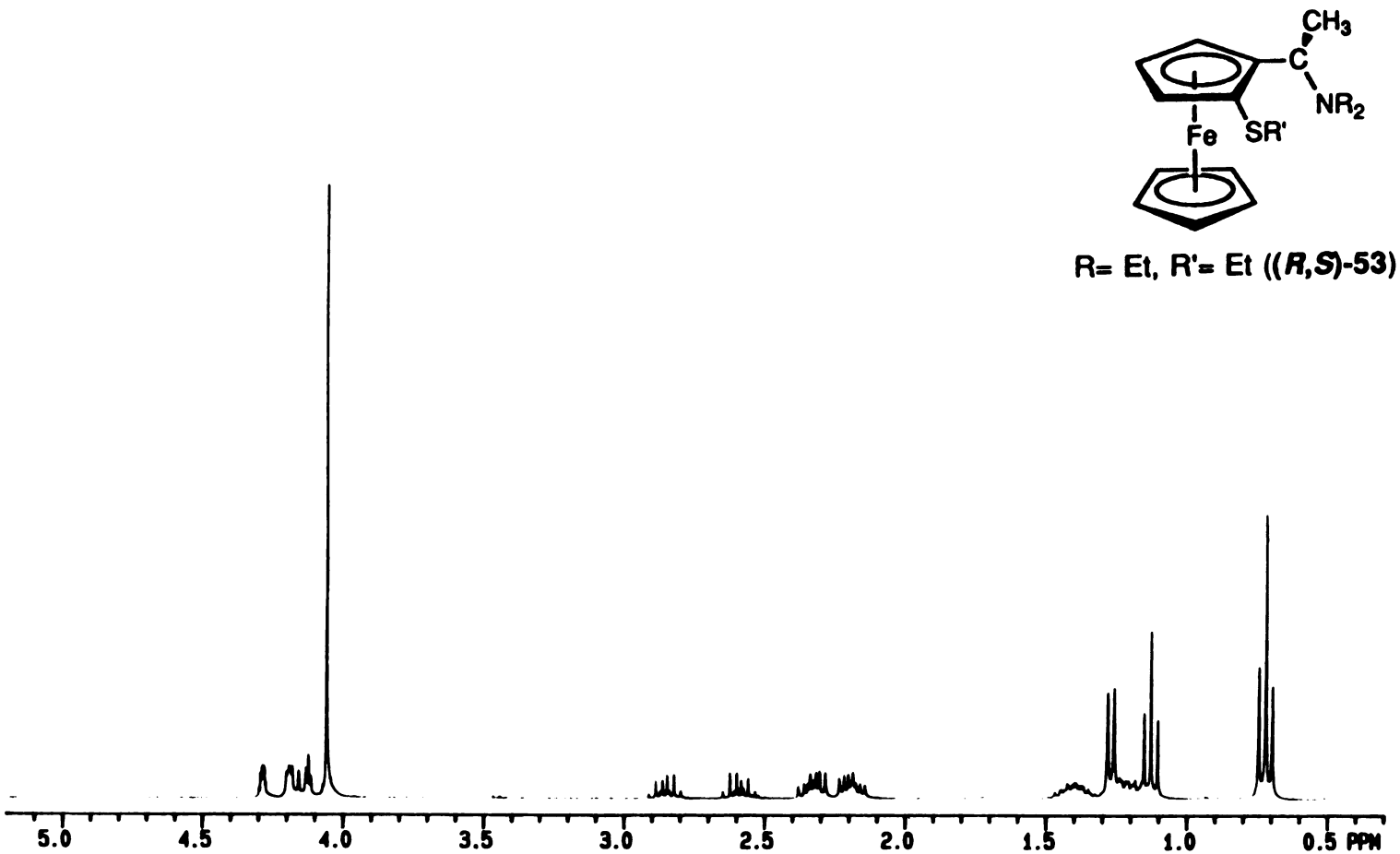
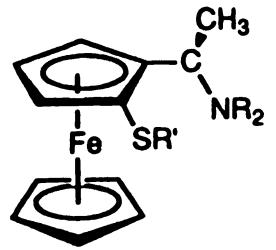


Figure 46. 300 MHz ^{1}H NMR spectrum of (*R,S*)-53



R= Et, R'= Et ((*R,S*)-53)

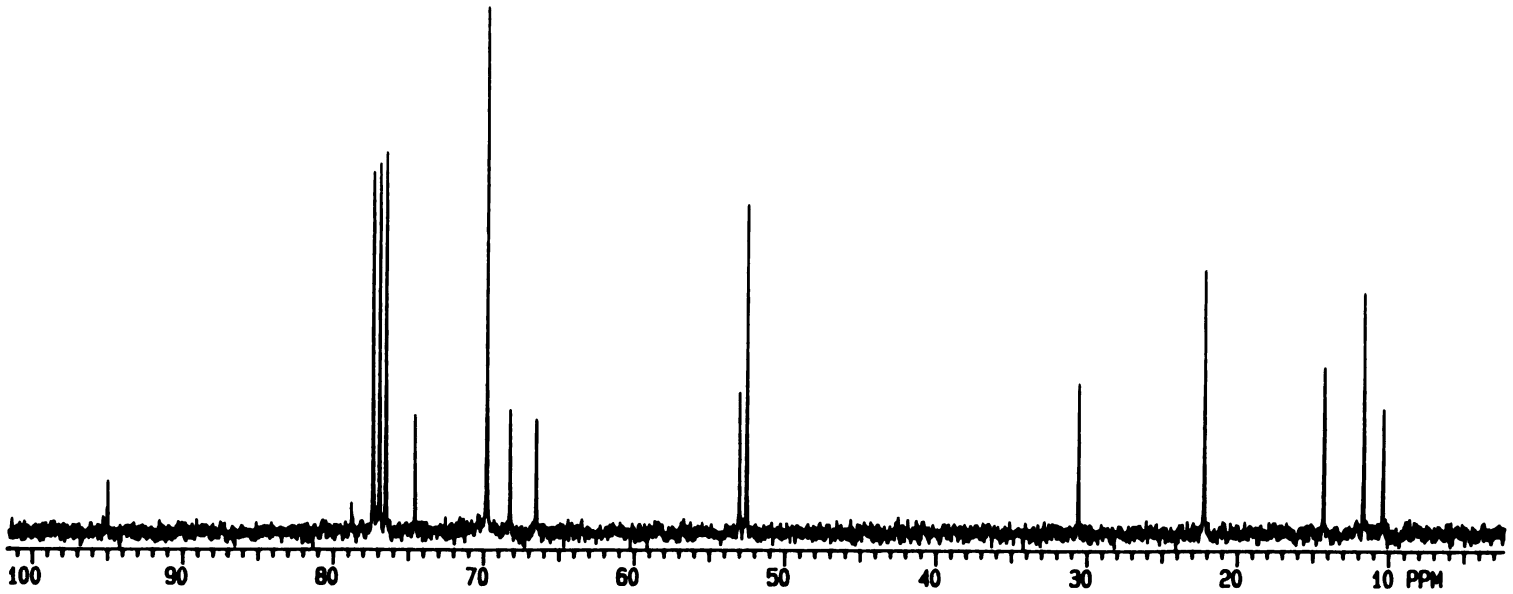
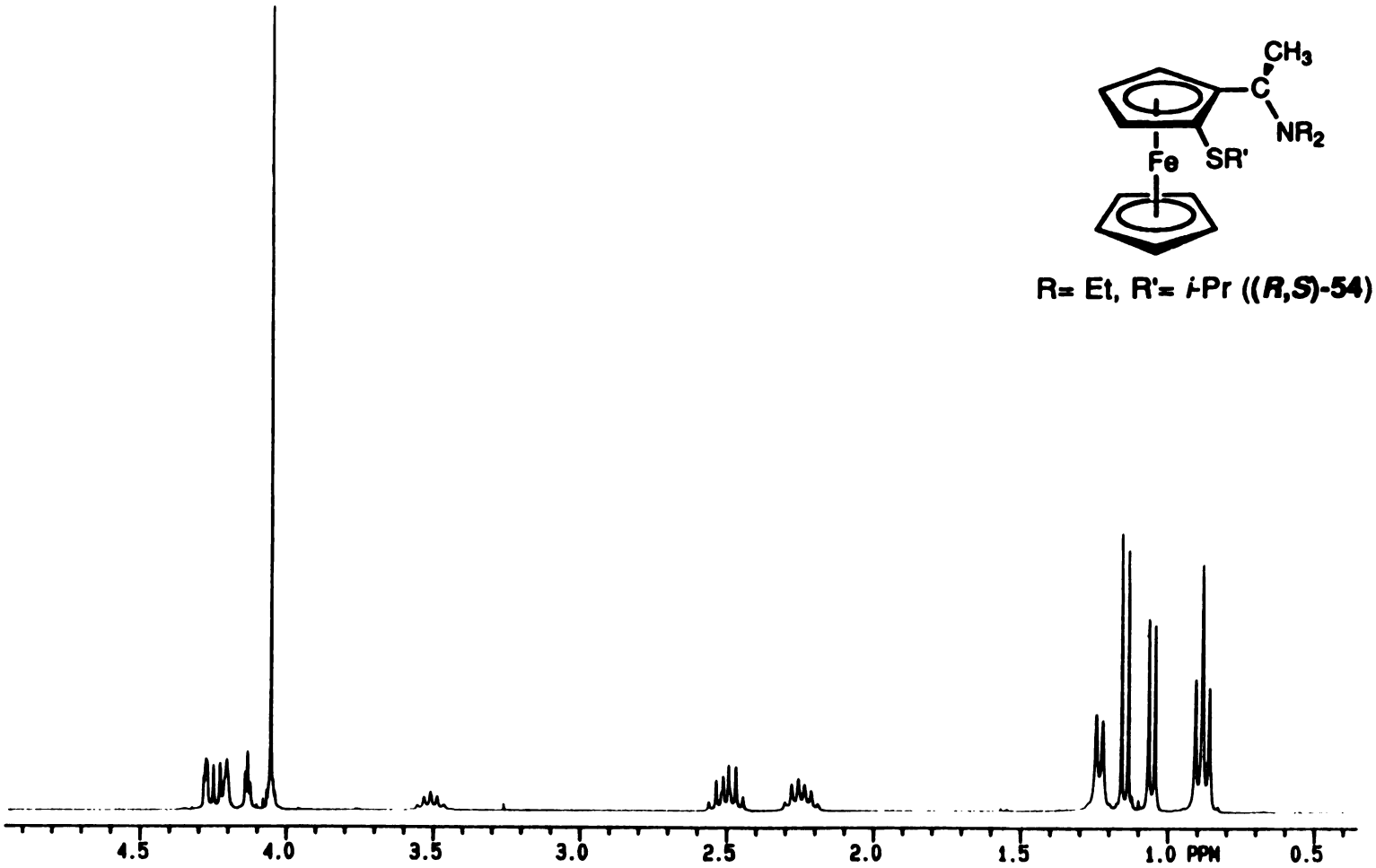


Figure 47. Broad band decoupled ^{13}C NMR spectrum of (*R,S*)-53



R= Et, R'= *i*-Pr ((*R*,*S*)-54)

Figure 48. 300 MHz ^{1}H NMR spectrum of (*R*,*S*)-54

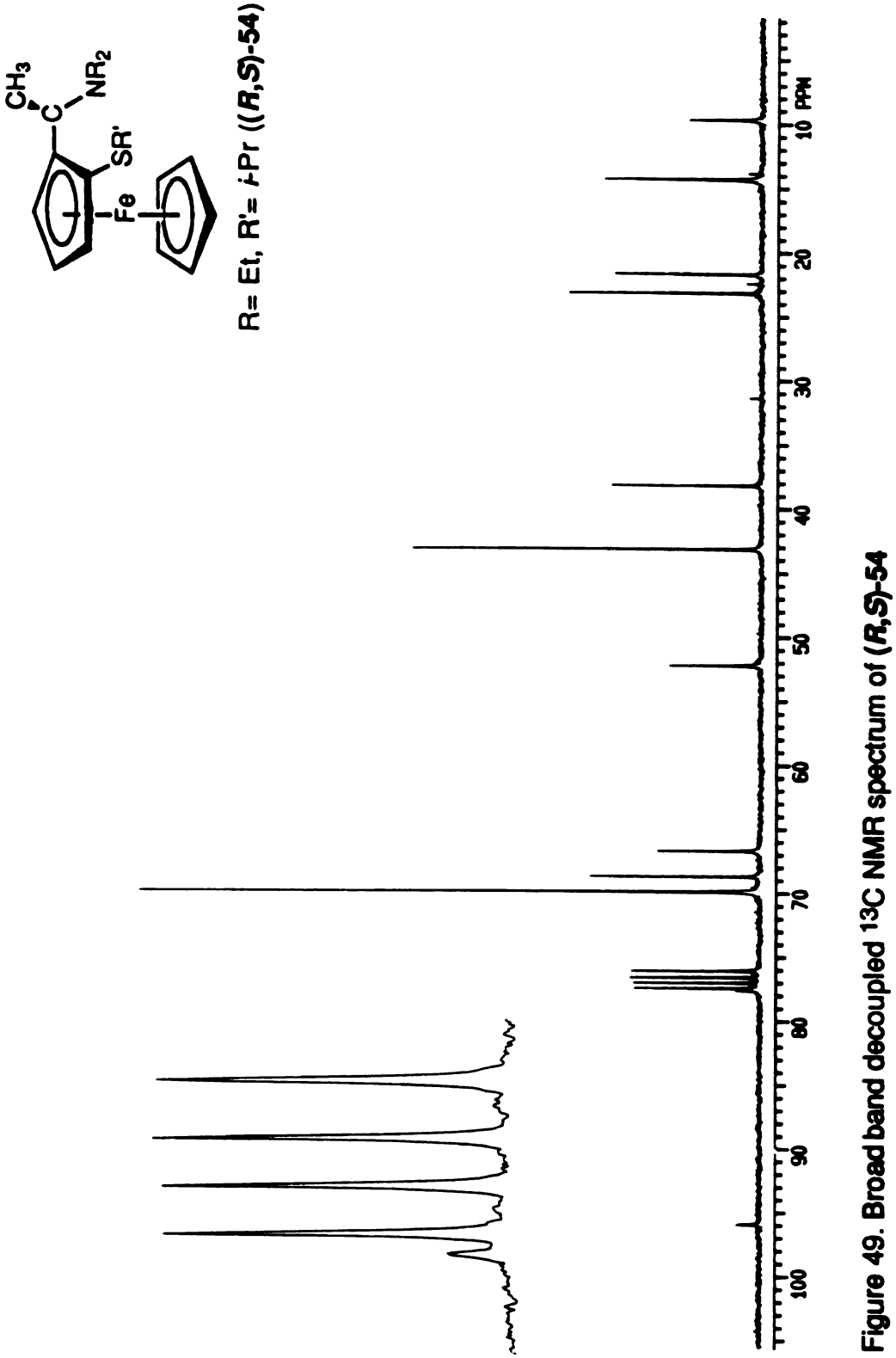


Figure 49. Broad band decoupled ^{13}C NMR spectrum of (*R,S*)-54

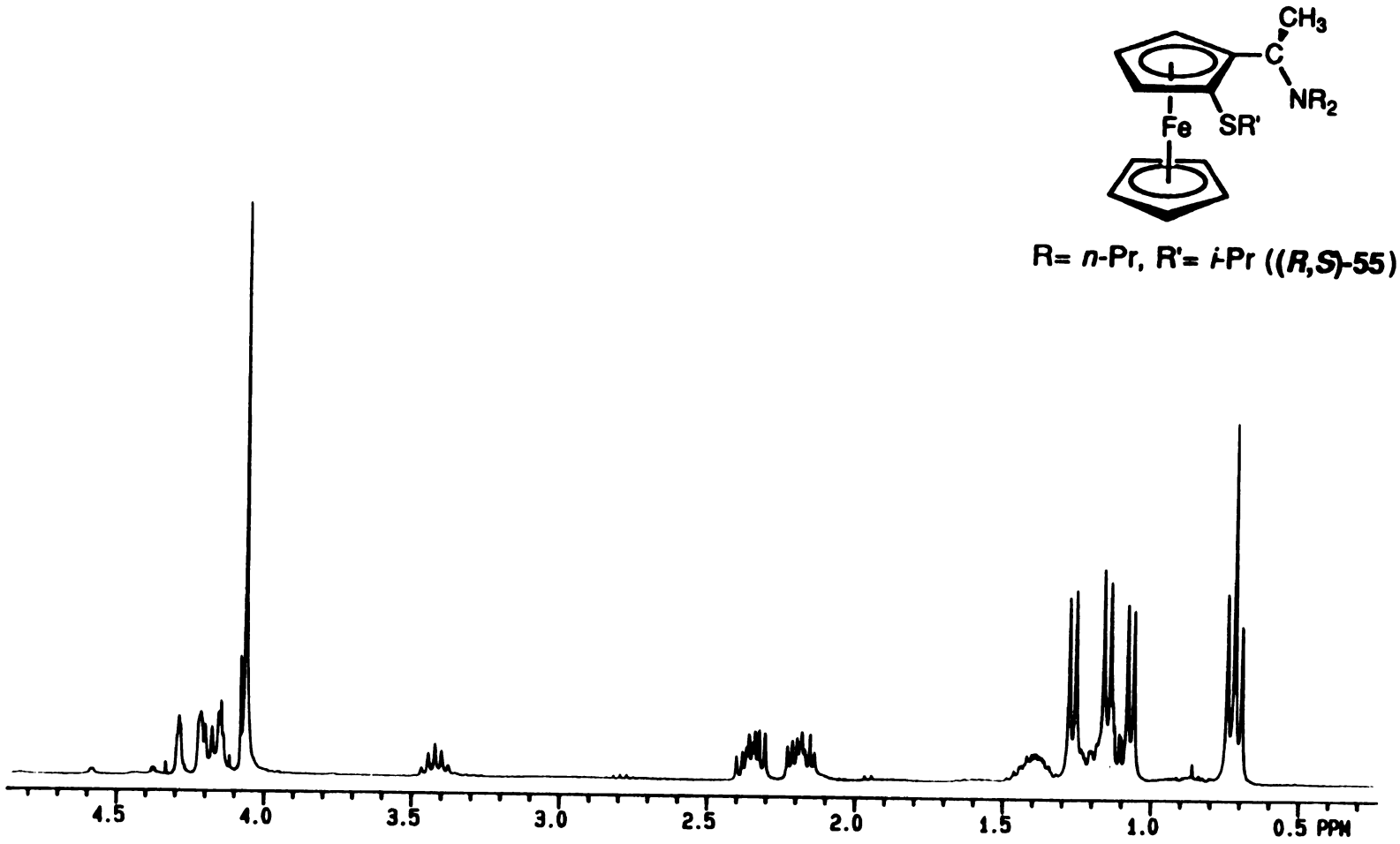


Figure 50. 300 MHz ^{1}H NMR spectrum of (*R,S*)-55

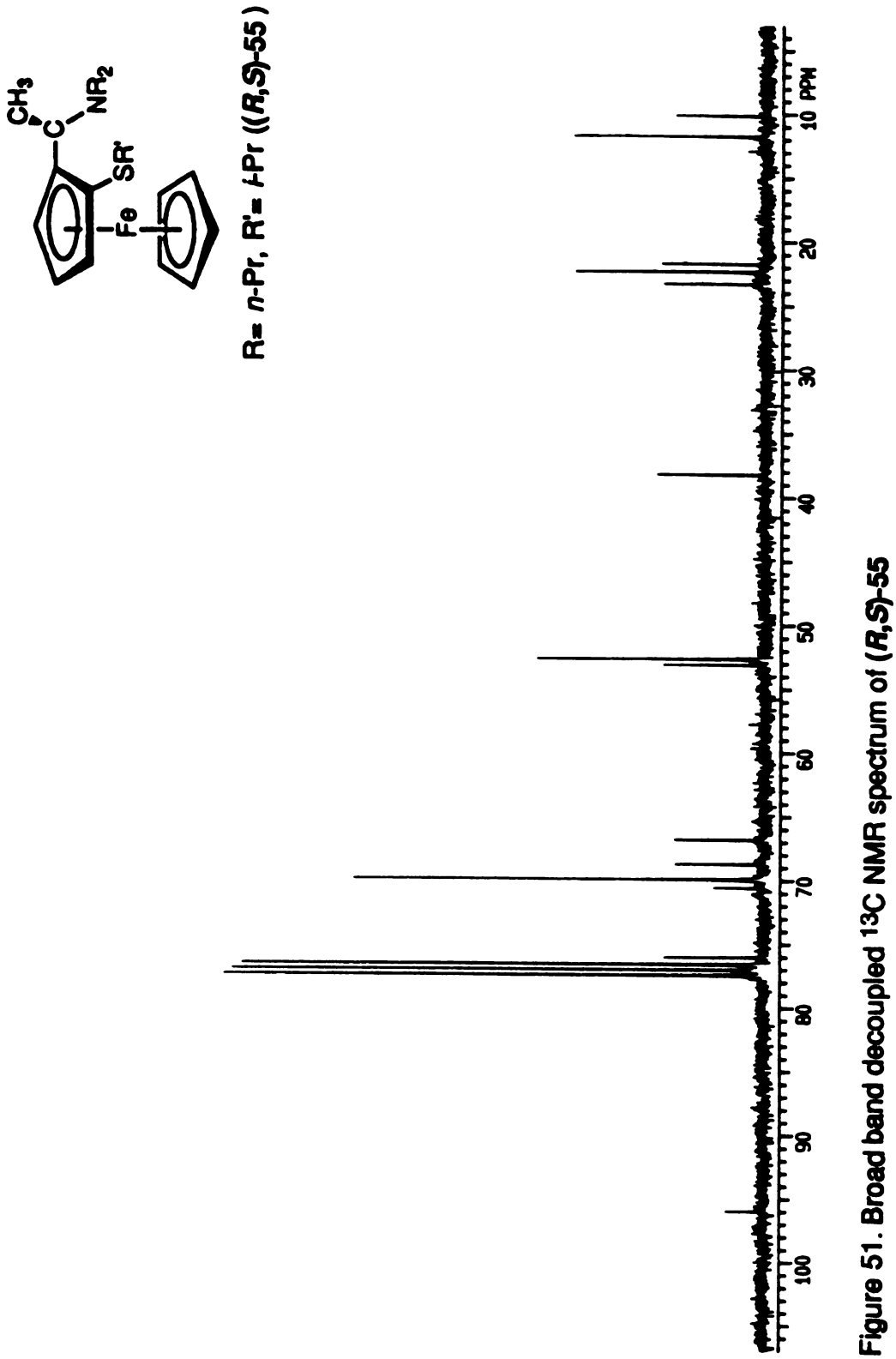


Figure 51. Broad band decoupled ^{13}C NMR spectrum of (*R,S*)-55

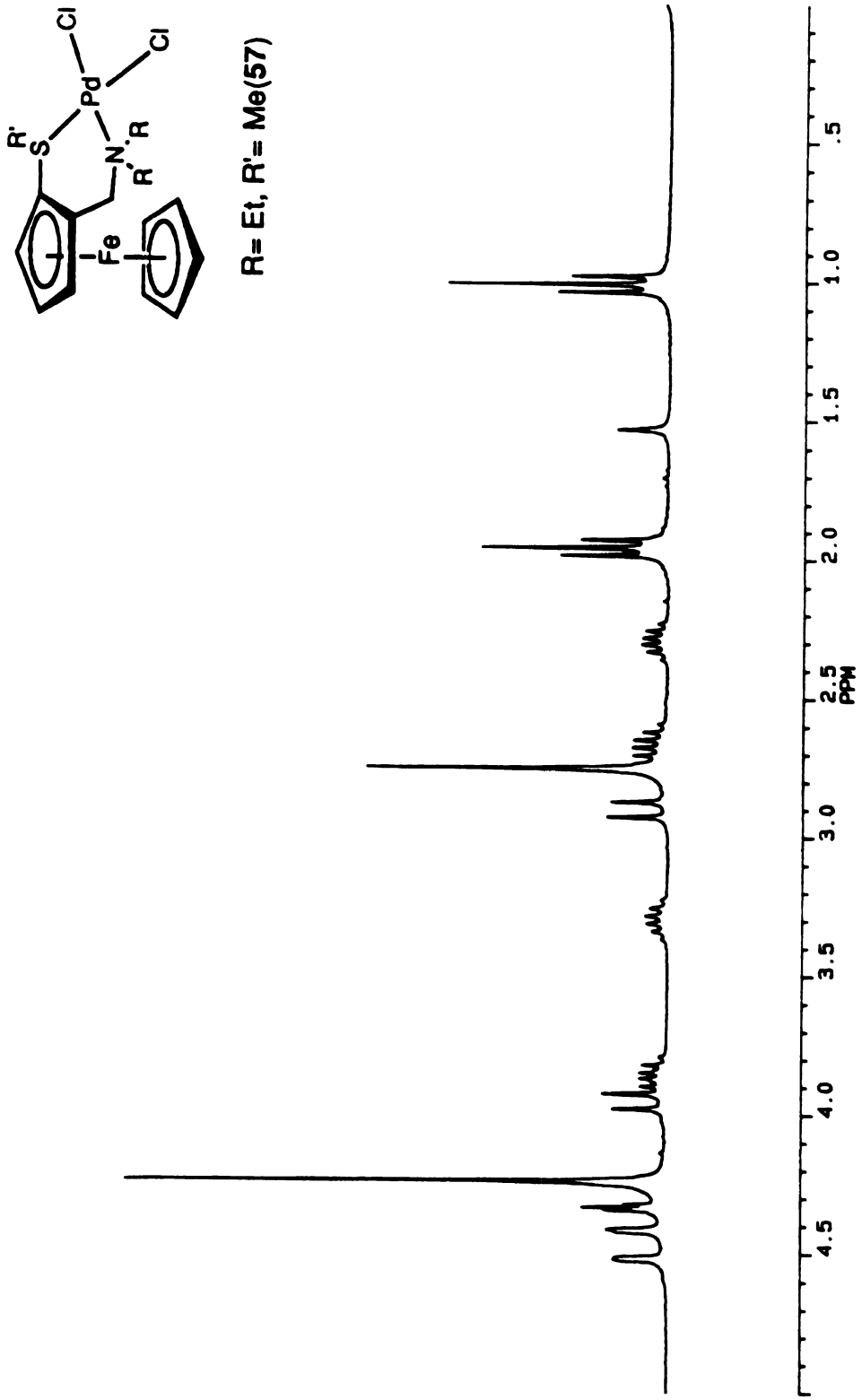
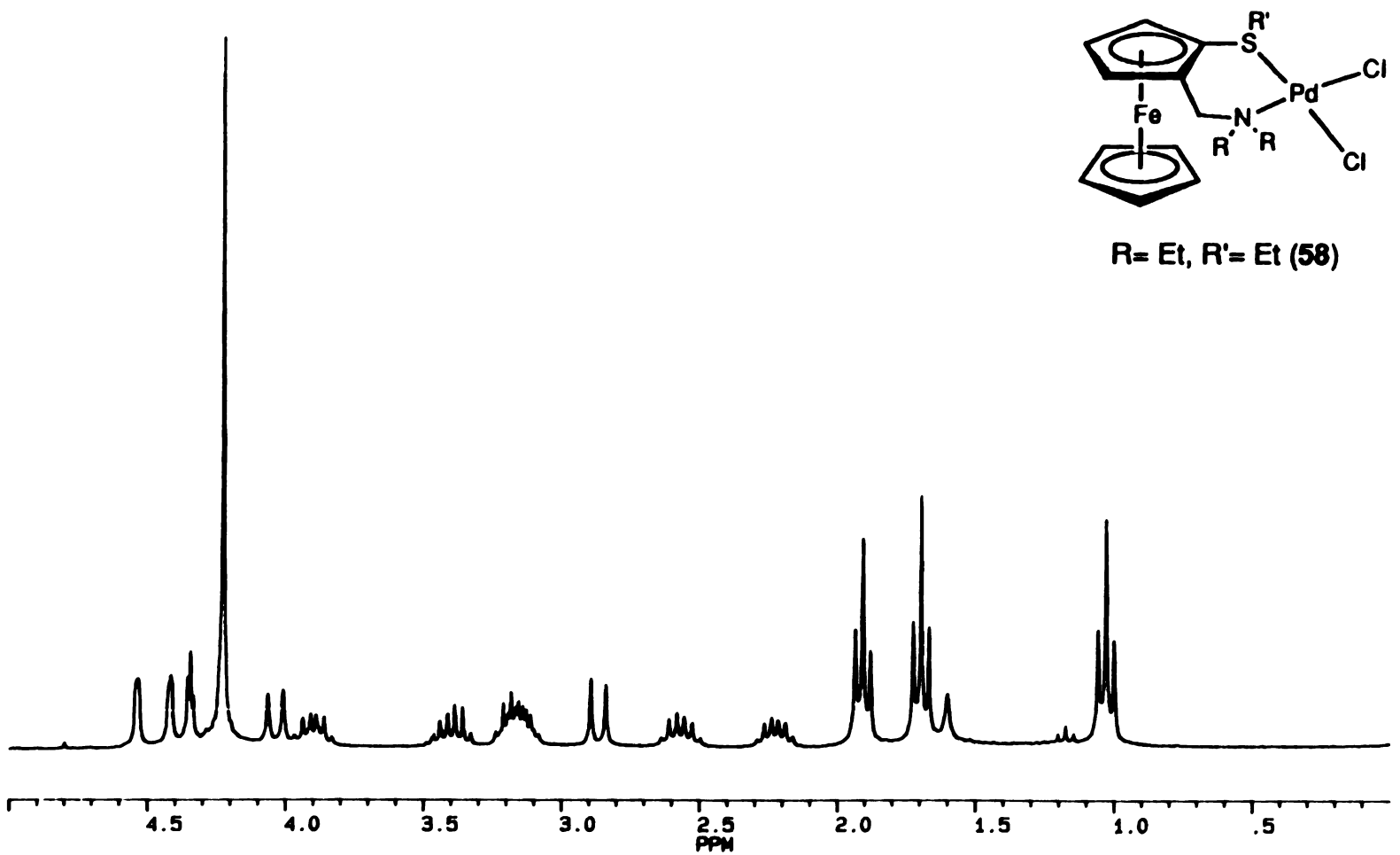
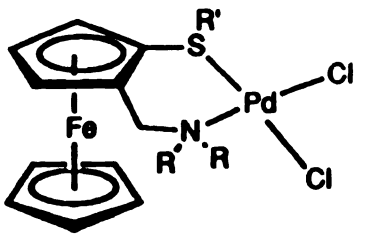


Figure 52. 300 MHz ^{1}H NMR spectrum of **57**



R= Et, R'= Et (**58**)

Figure 53. 300 MHz ^{1}H NMR spectrum of **58**



R= Et, R'= 4-CH_3Ph (60)

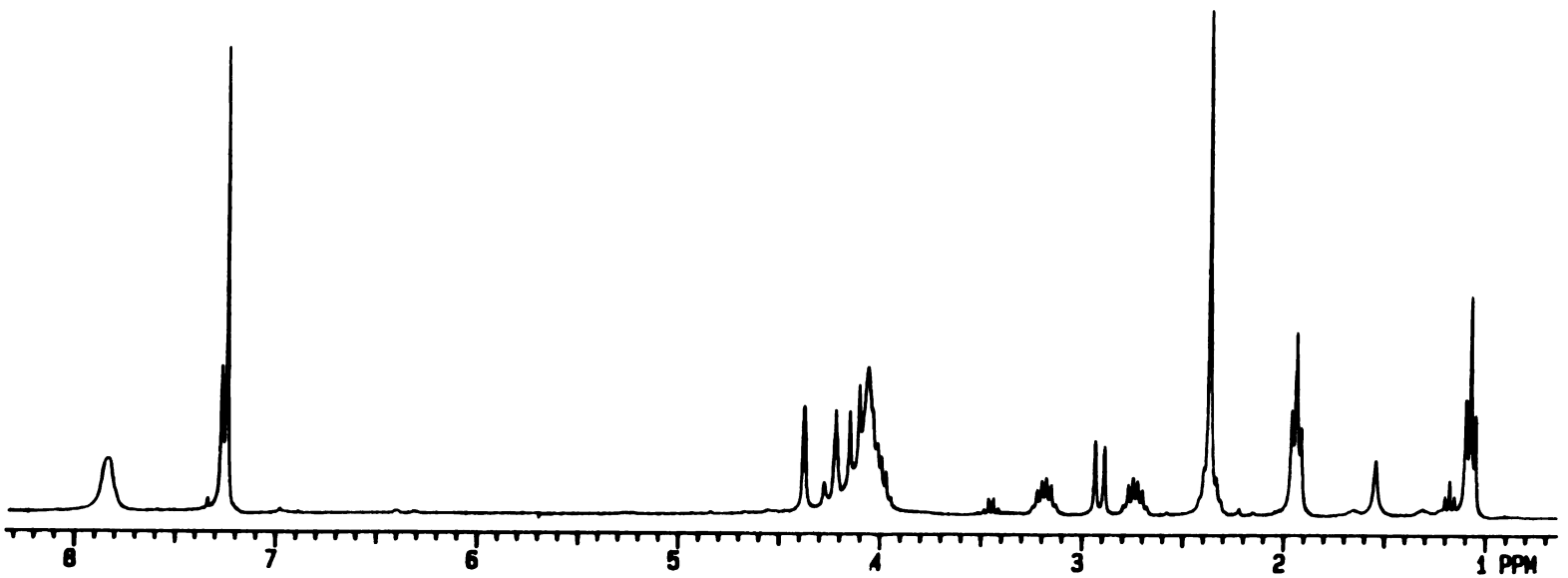


Figure 54. 300 MHz ^{1}H NMR spectrum of 60

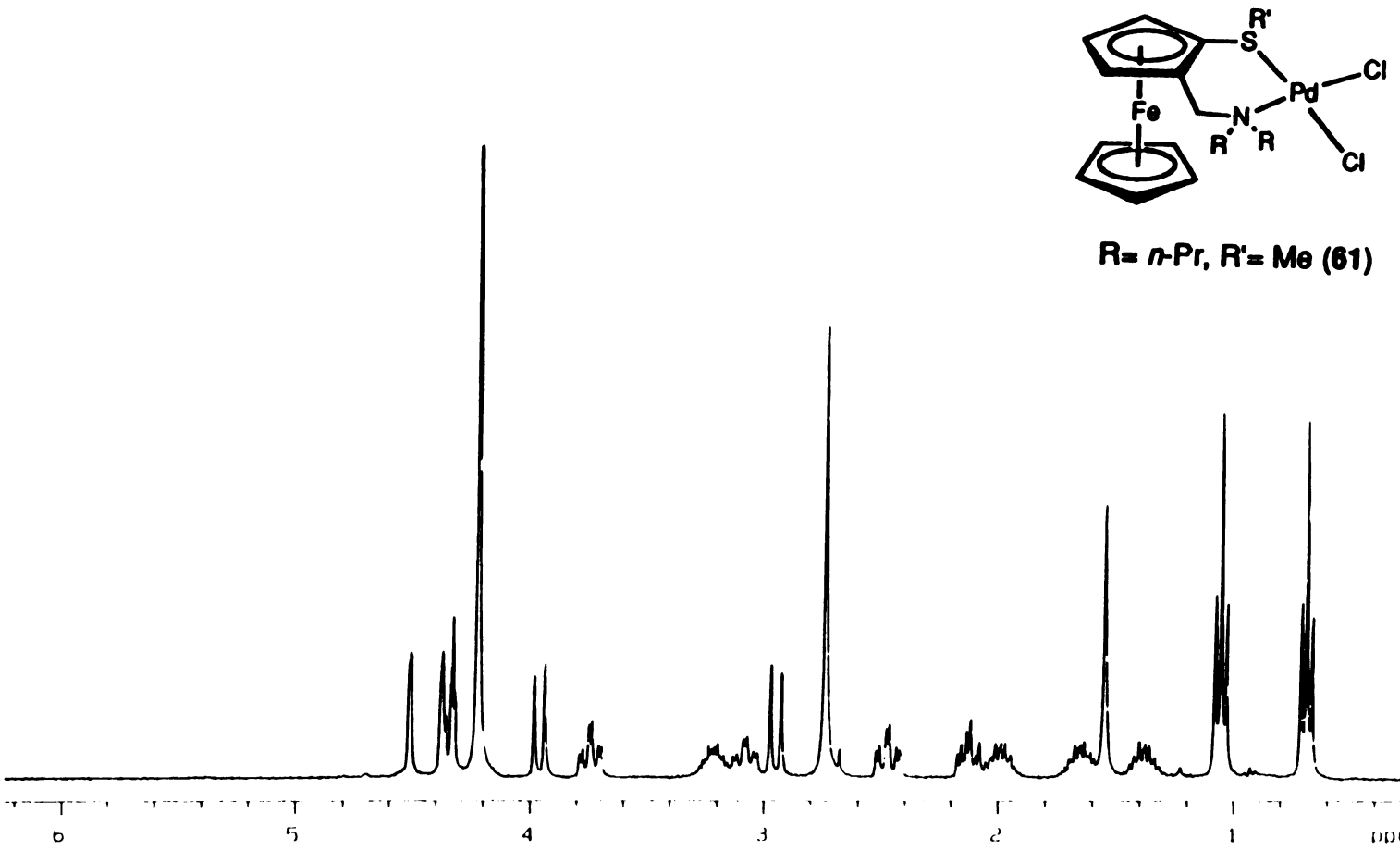
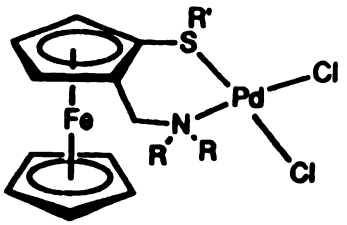


Figure 55. 300 MHz ^{1}H NMR spectrum of 61



R= *n*-Pr, R'= Et (62)

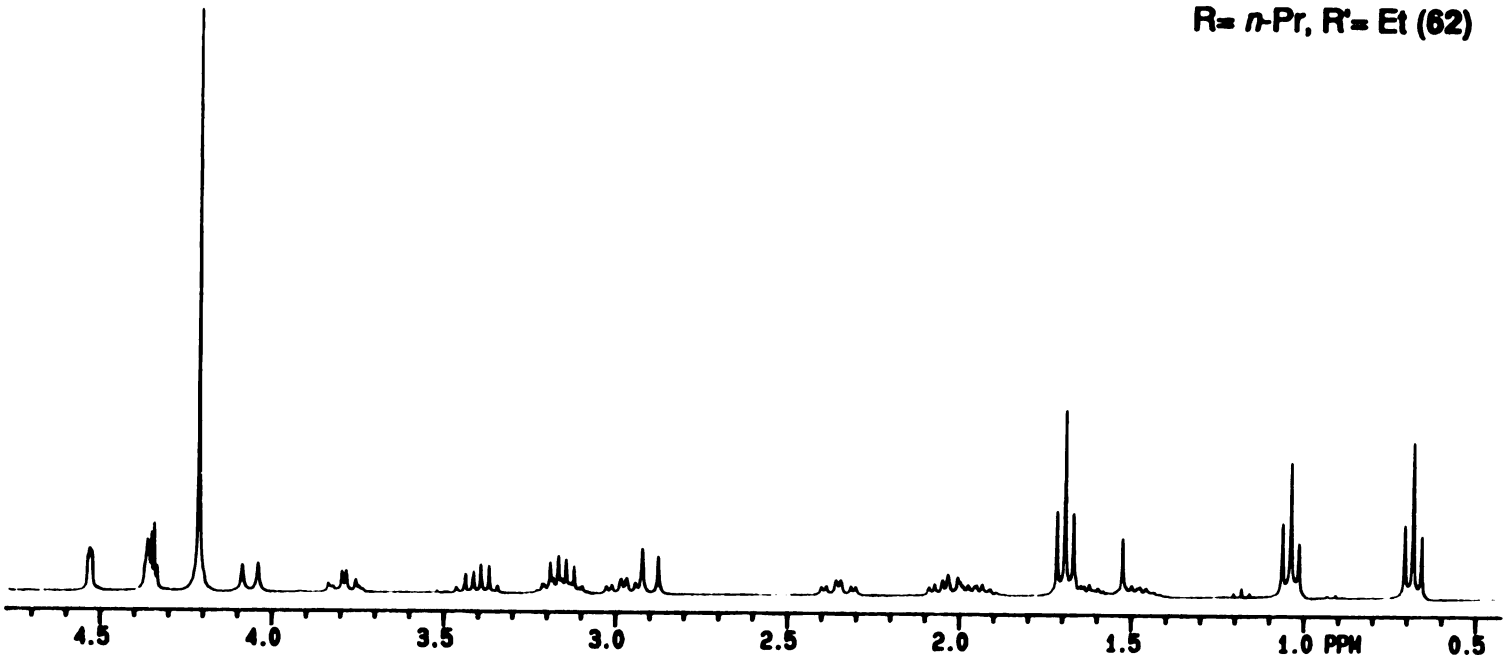
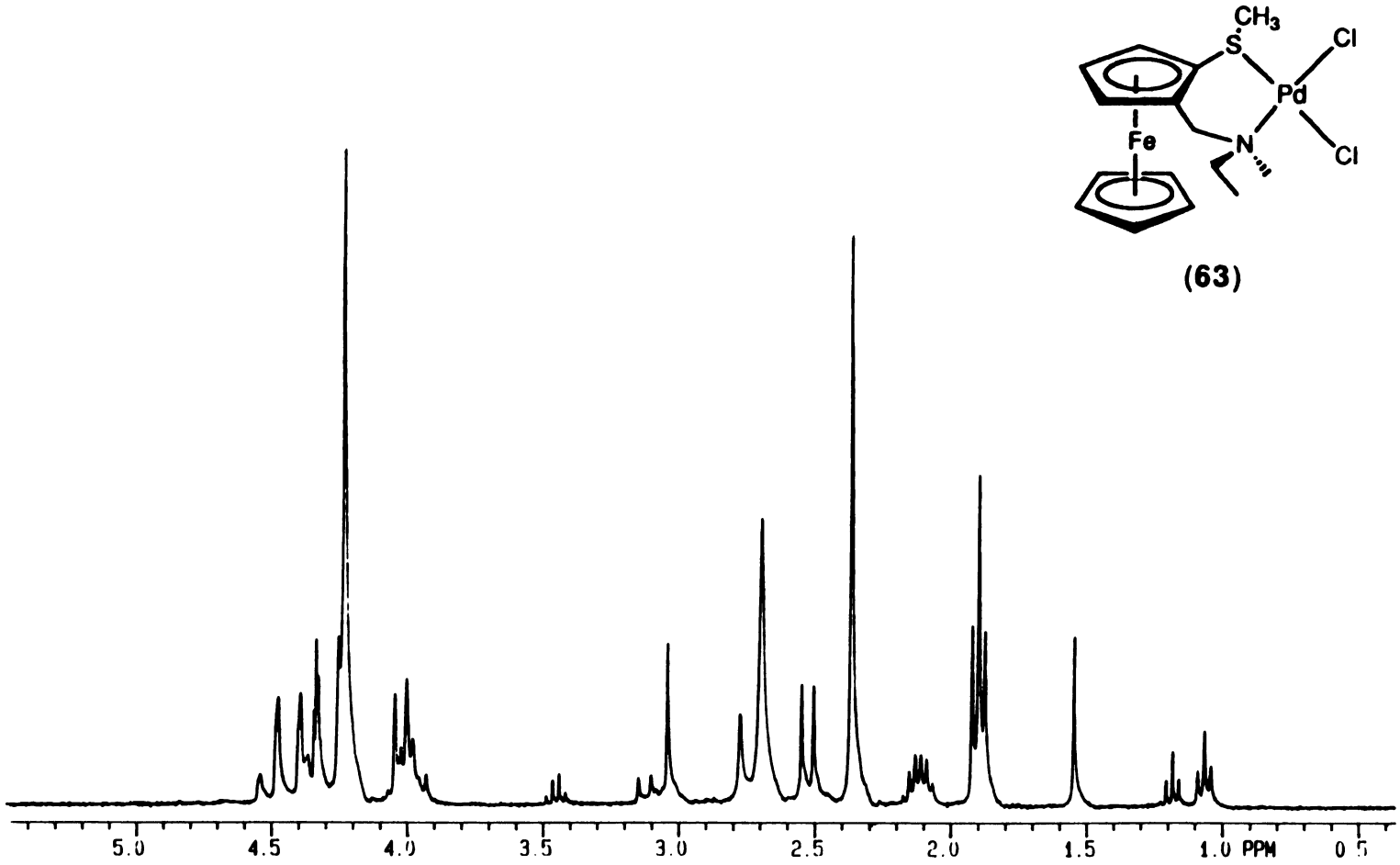
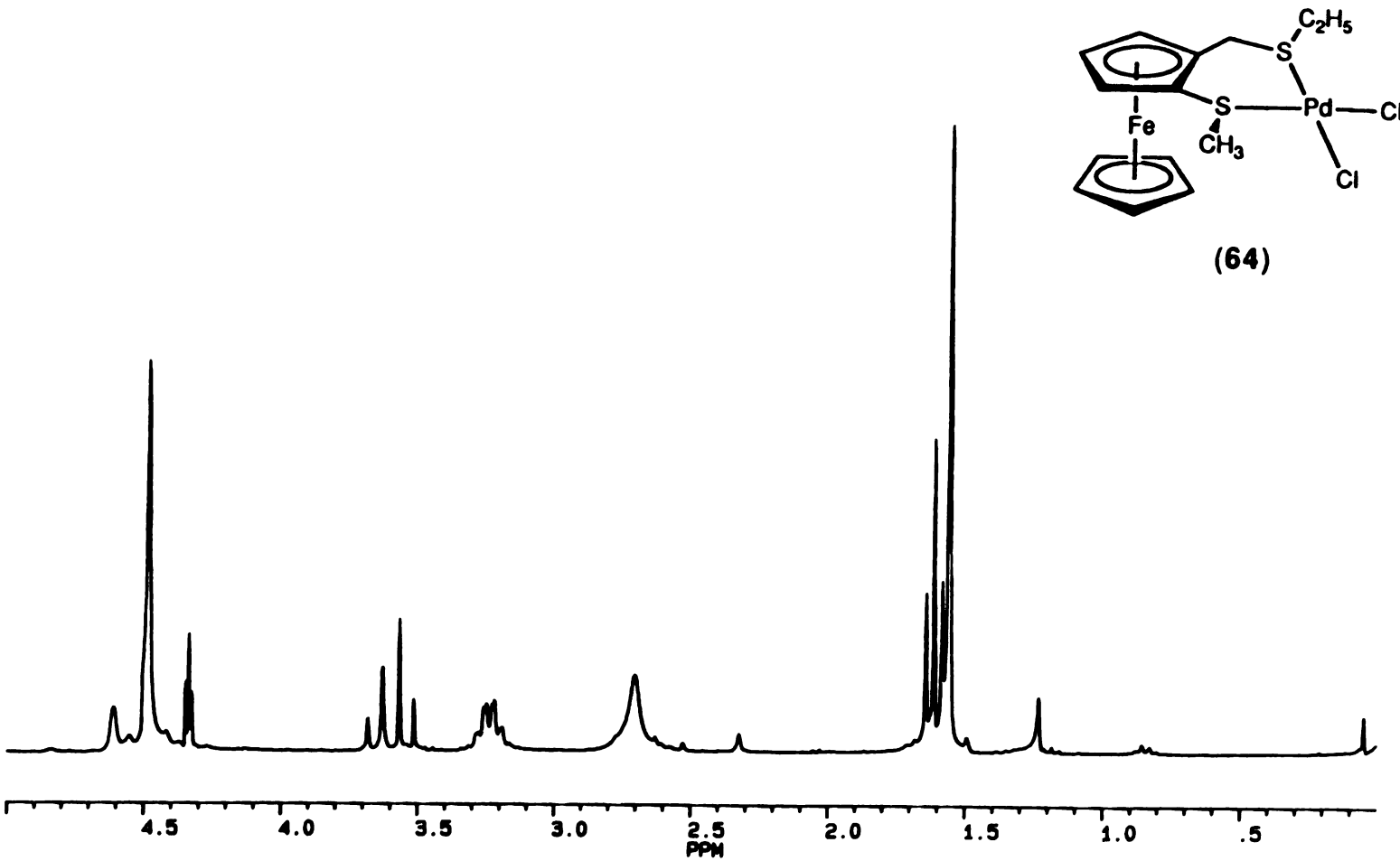


Figure 56. 300 MHz ^{1}H NMR spectrum of 62



(63)

Figure 57. 300 MHz ^{1}H NMR spectrum of **63**



(64)

Figure 58. 300 MHz ^1H NMR spectrum of 64

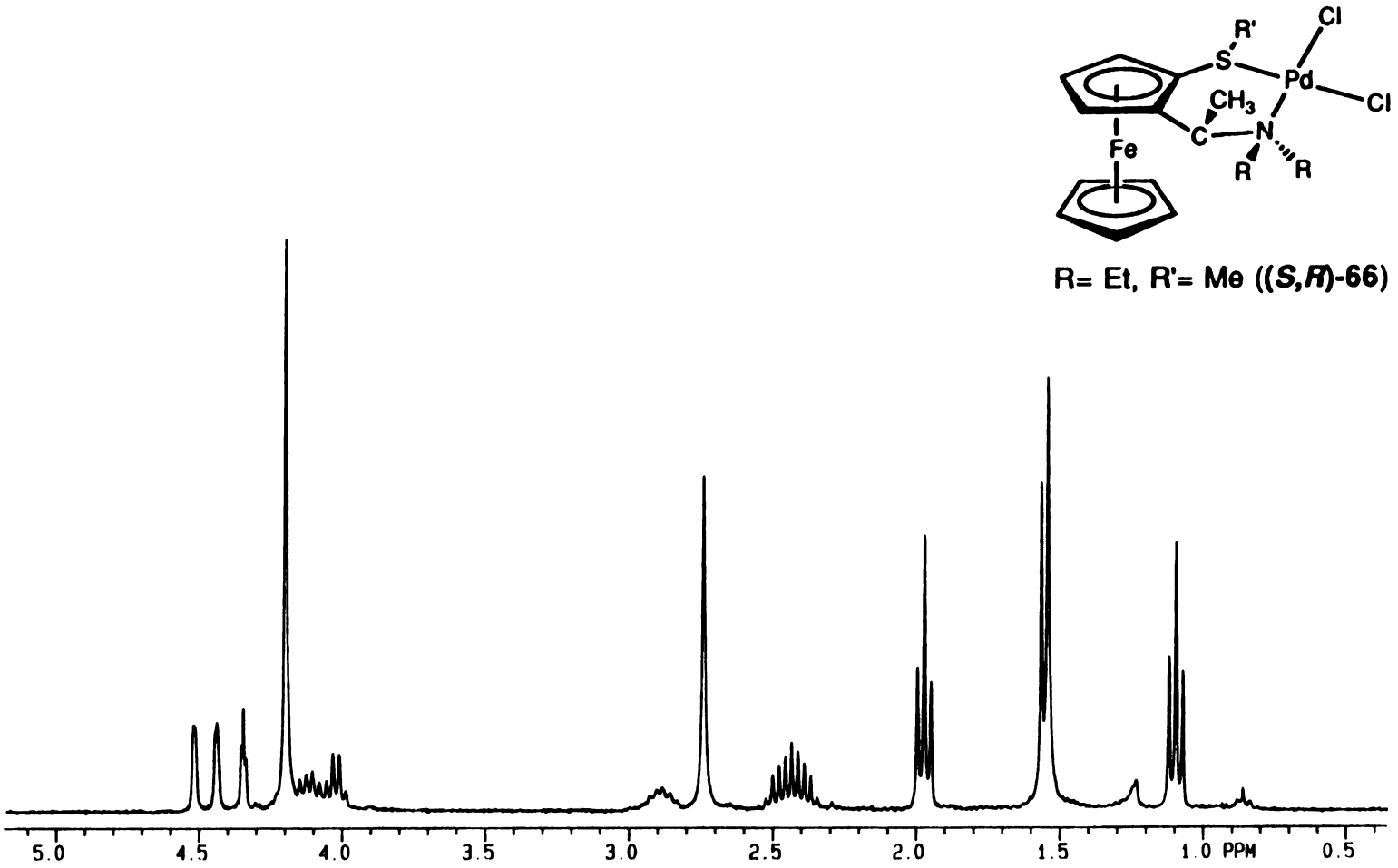
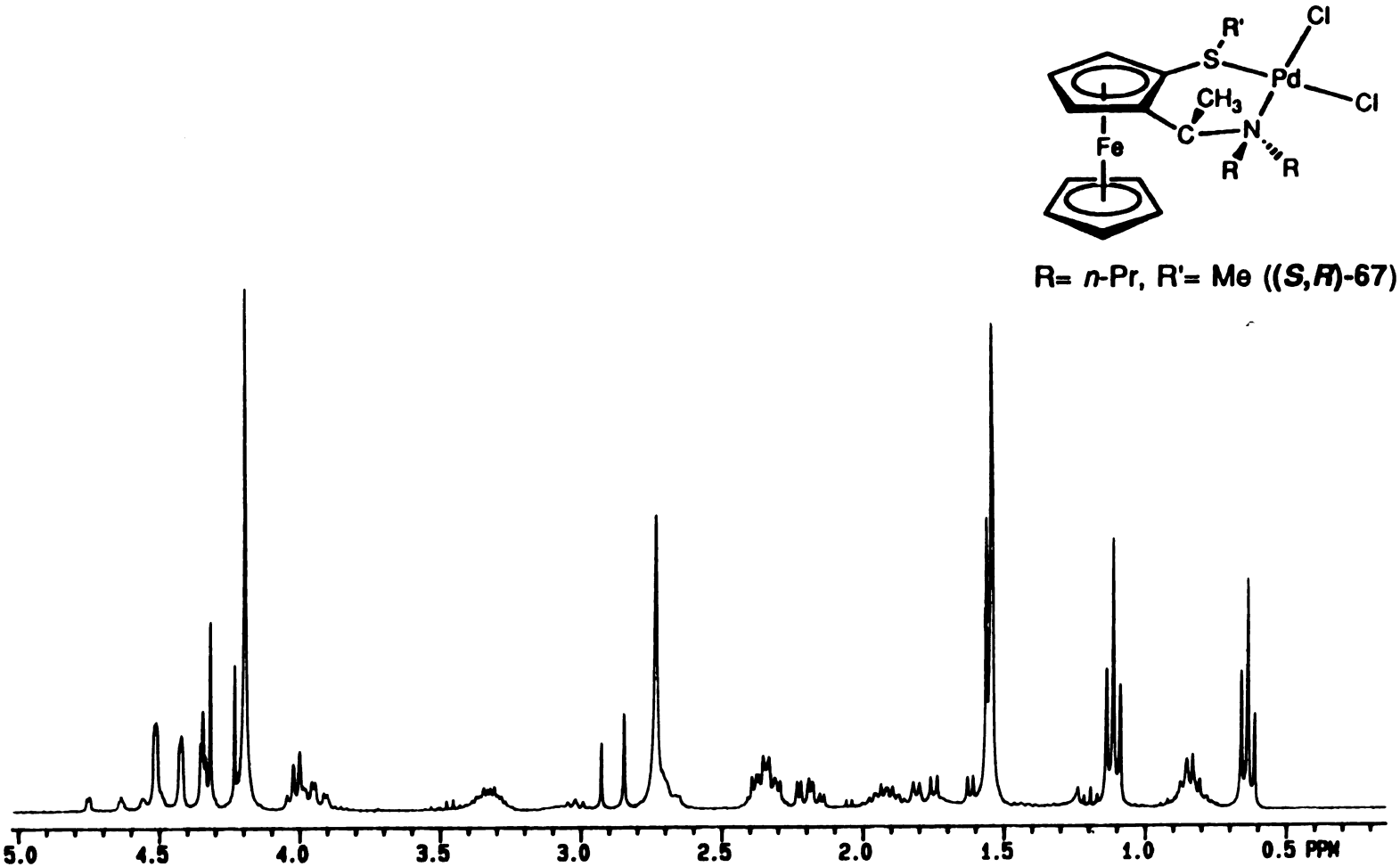
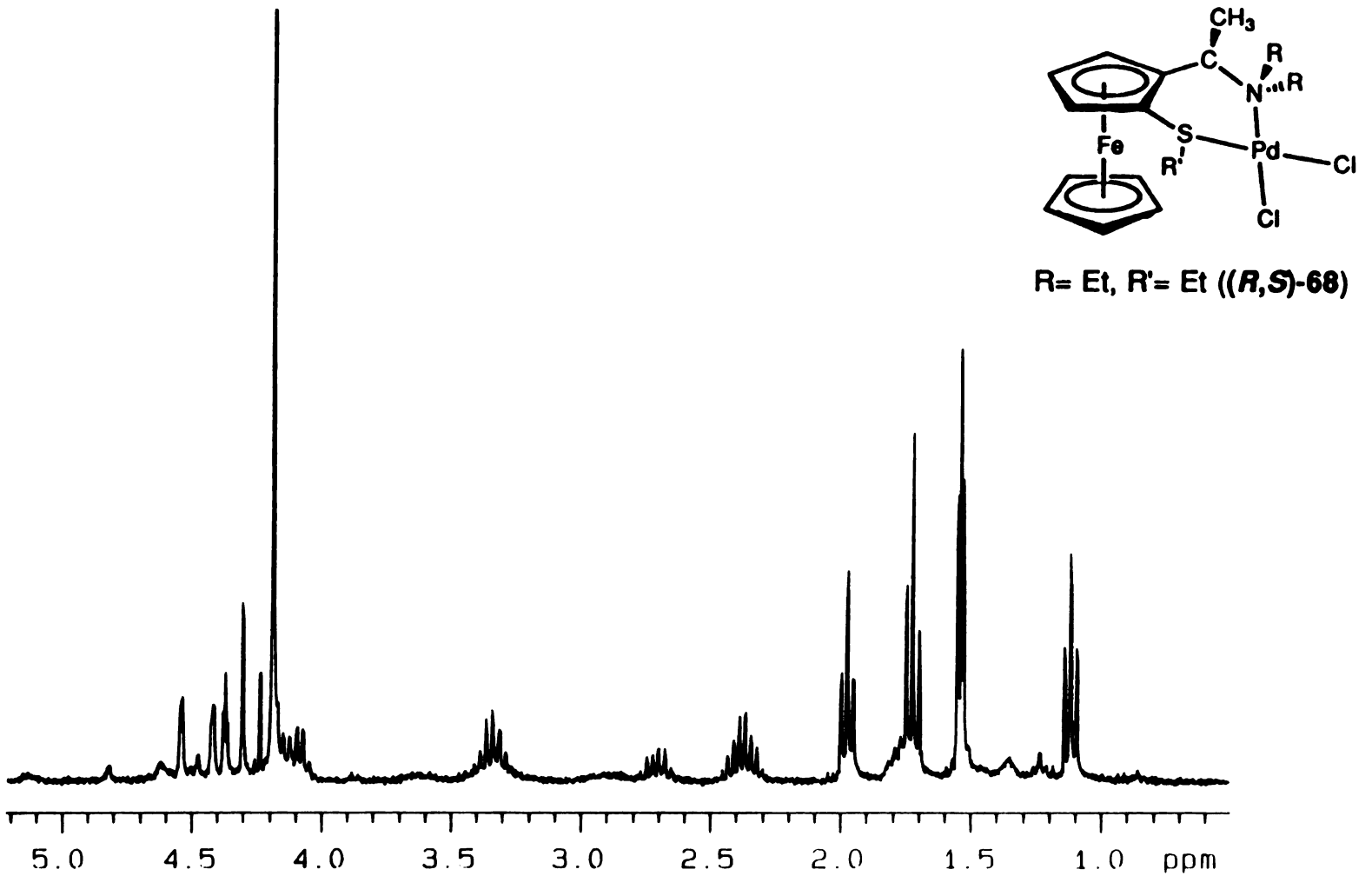


Figure 59. 300 MHz ^{1}H NMR spectrum of (*S,R*)-66



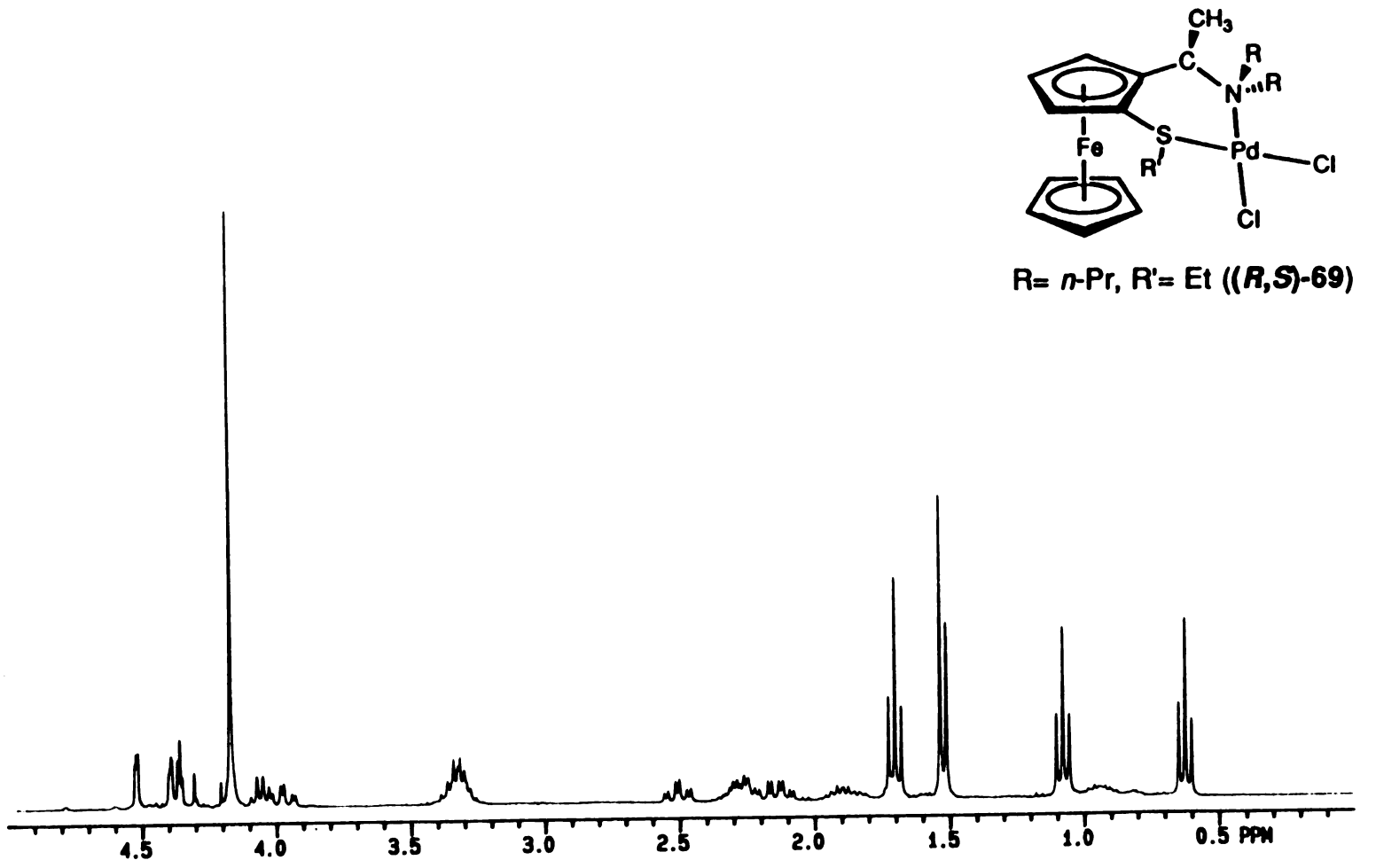
R= *n*-Pr, R'= Me ((*S*,*R*)-67)

Figure 60. 300 MHz ^{1}H NMR spectrum of (*S*,*R*)-67



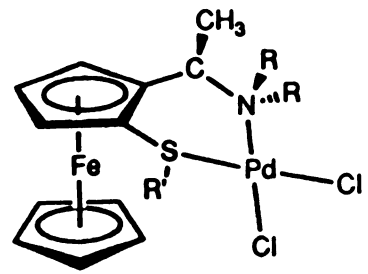
R= Et, R'= Et ((*R*,*S*)-68)

Figure 61. 300 MHz ^{1}H NMR spectrum of (*R*,*S*)-68



R= *n*-Pr, R'= Et ((*R*,*S*)-69)

Figure 62. 300 MHz ^{1}H NMR spectrum of (*R*,*S*)-69



R= Et, R'= *i*-Pr ((*R*,*S*)-70)

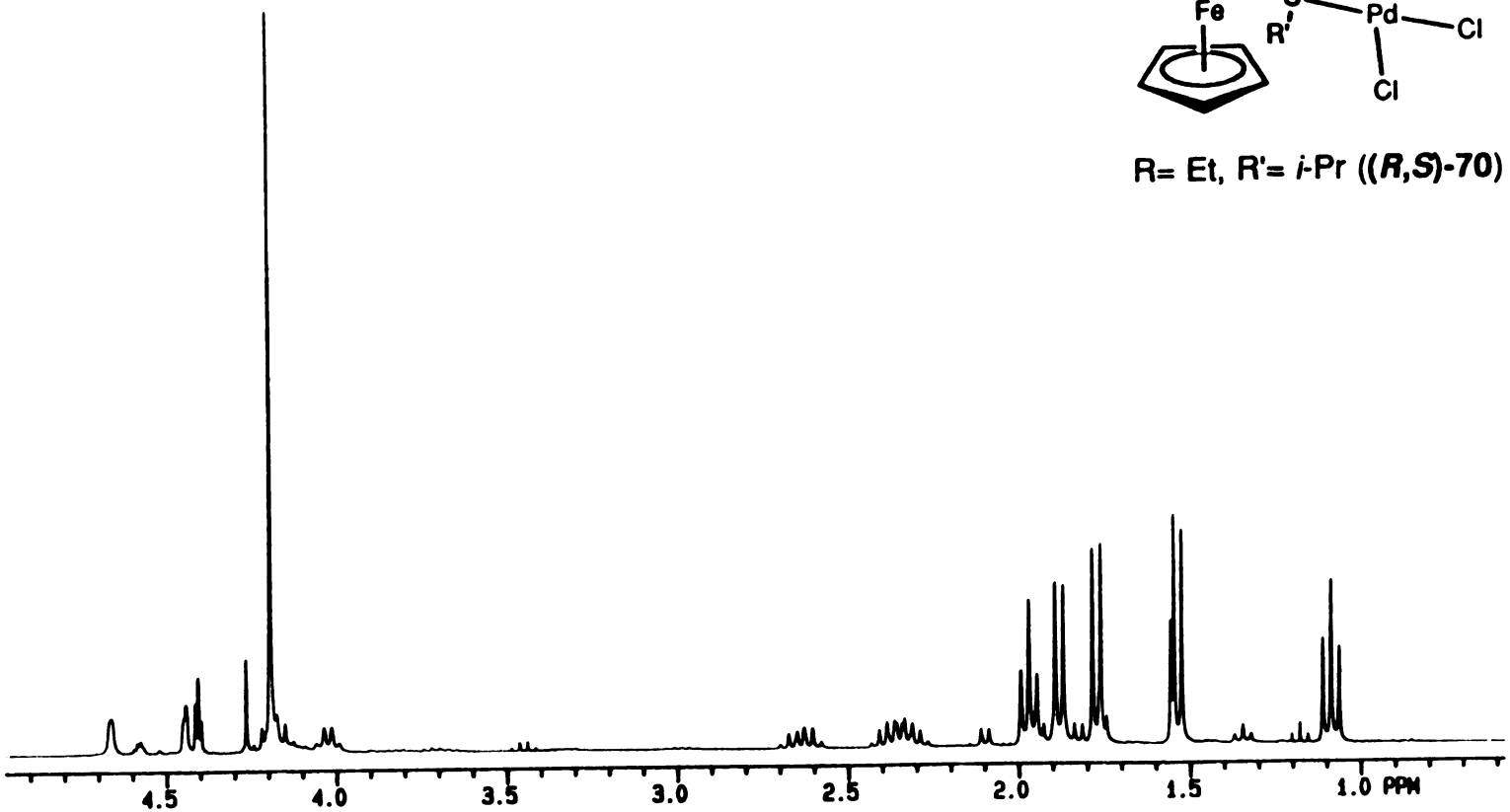
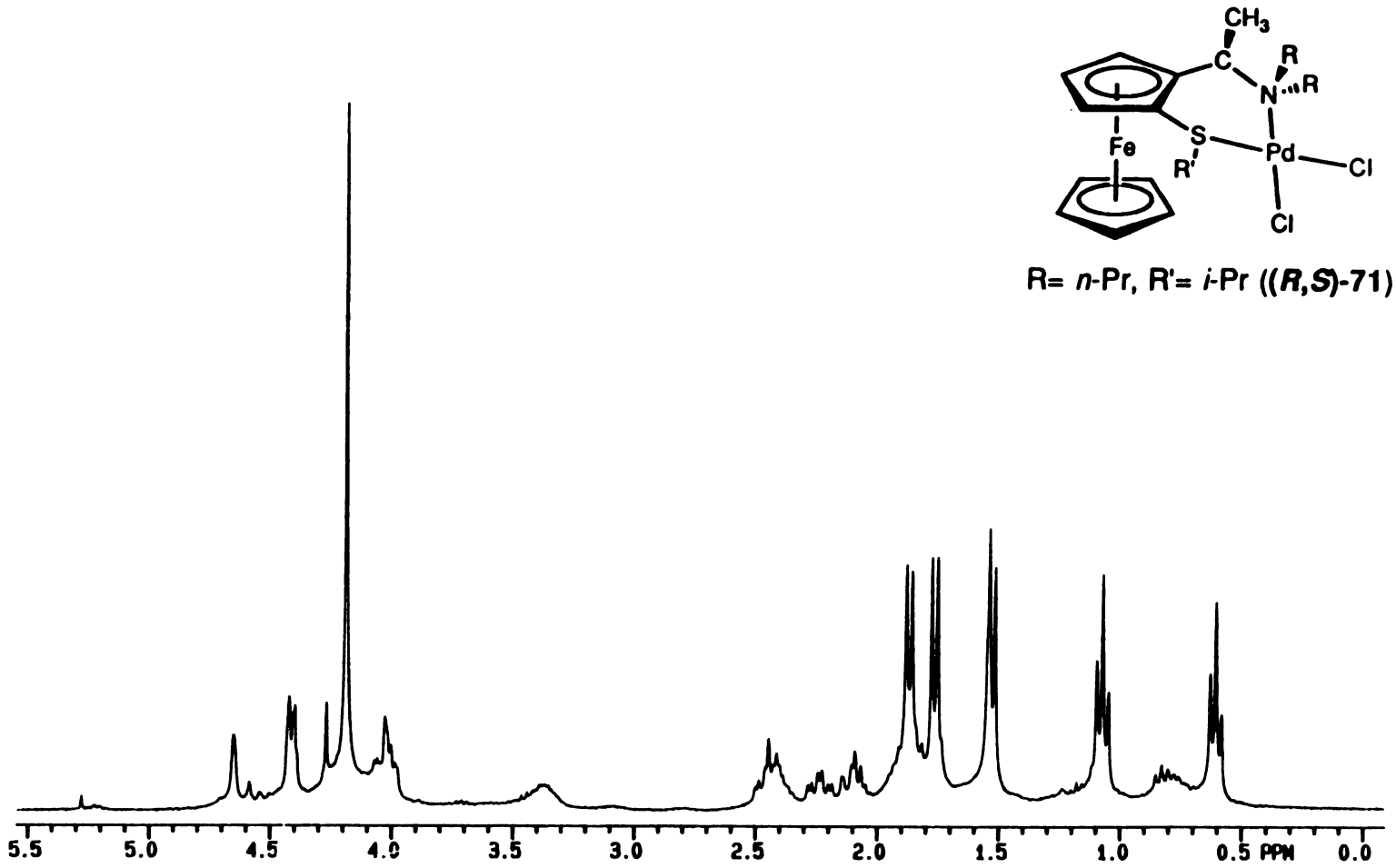


Figure 63. 300 MHz ^{1}H NMR spectrum of (*R*,*S*)-70



R= *n*-Pr, R'= *i*-Pr ((*R*,*S*)-71)

Figure 64. 300 MHz ^{1}H NMR spectrum of (*R*,*S*)-71

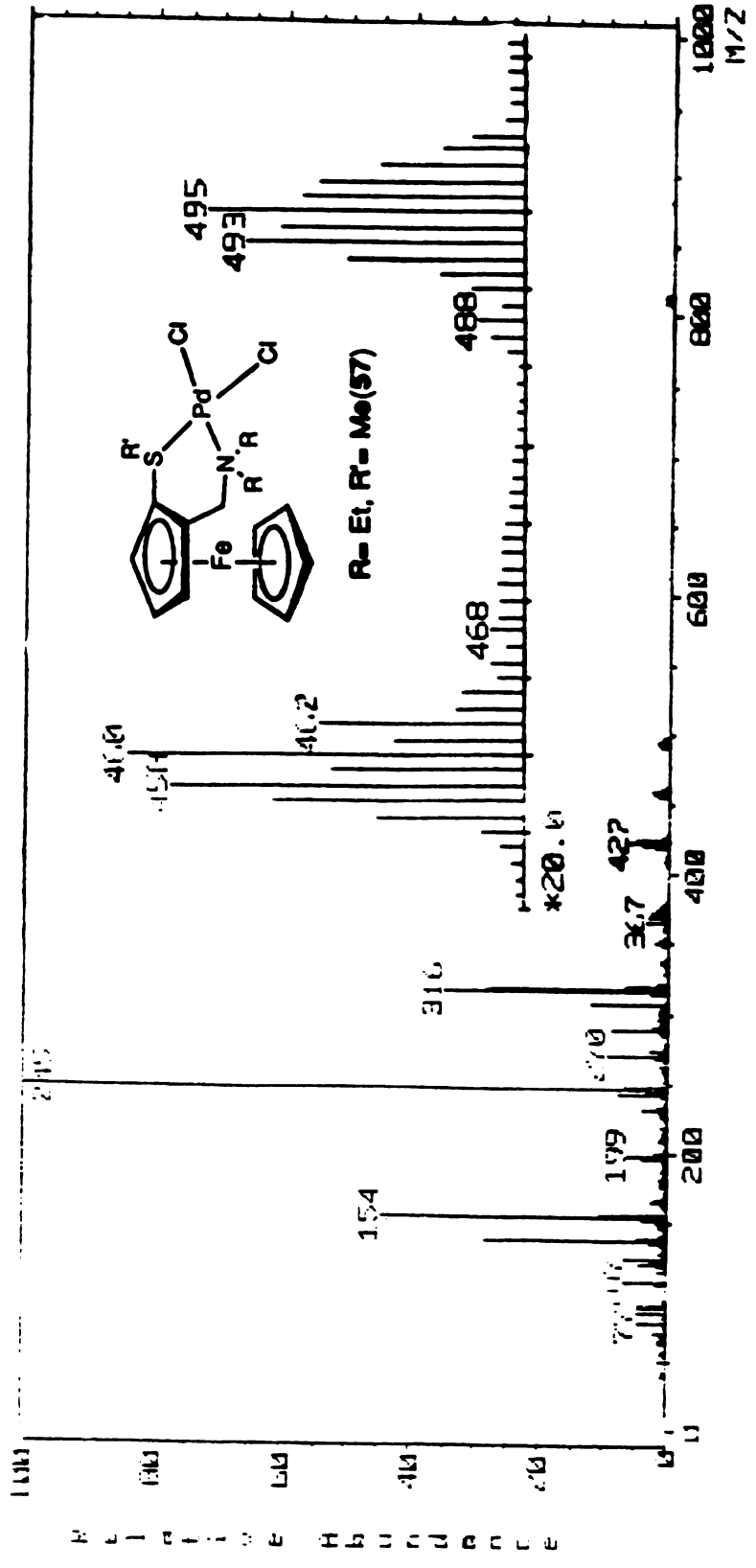


Figure 65. FAB Mass spectrum of complex 57

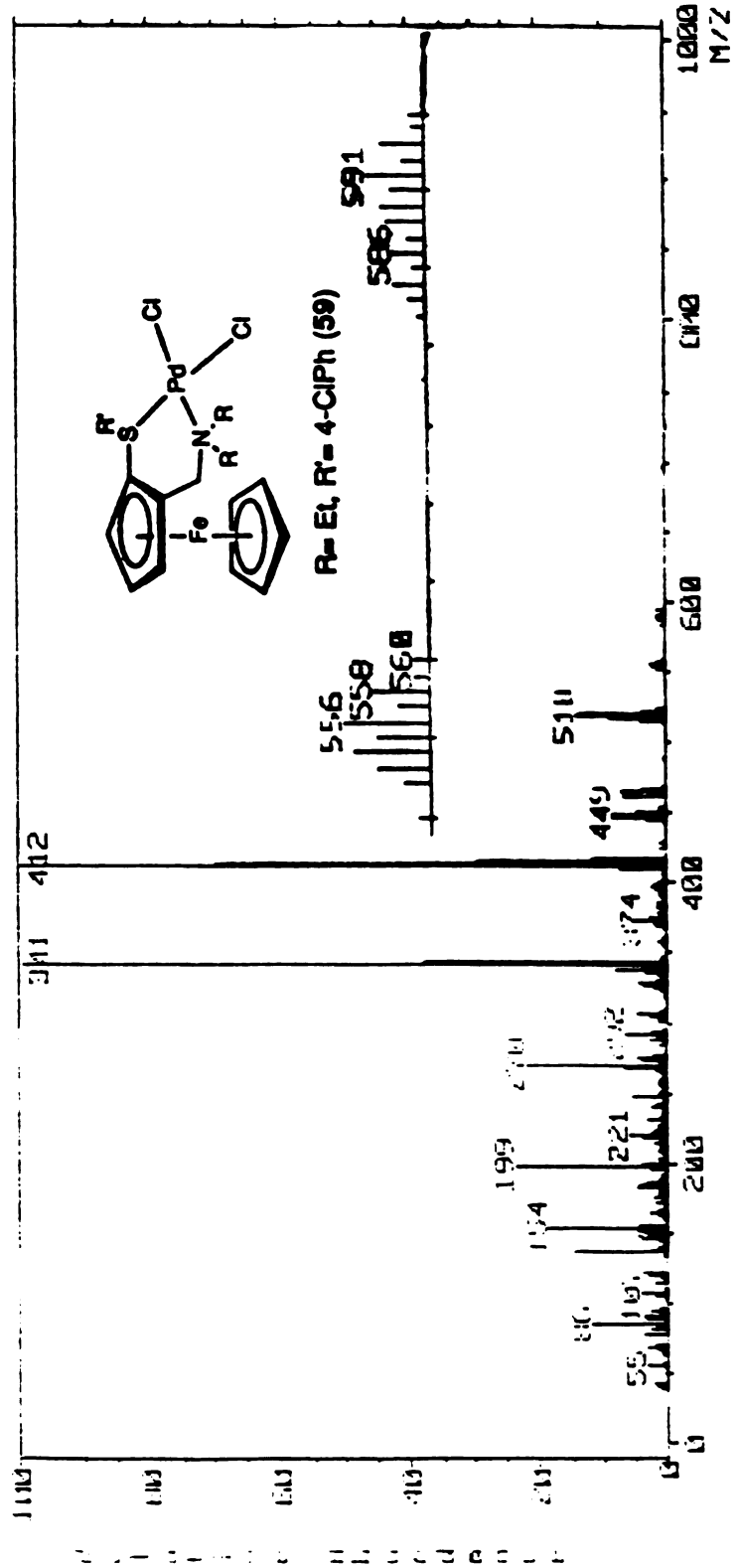


Figure 66. FAB Mass spectrum of complex 59

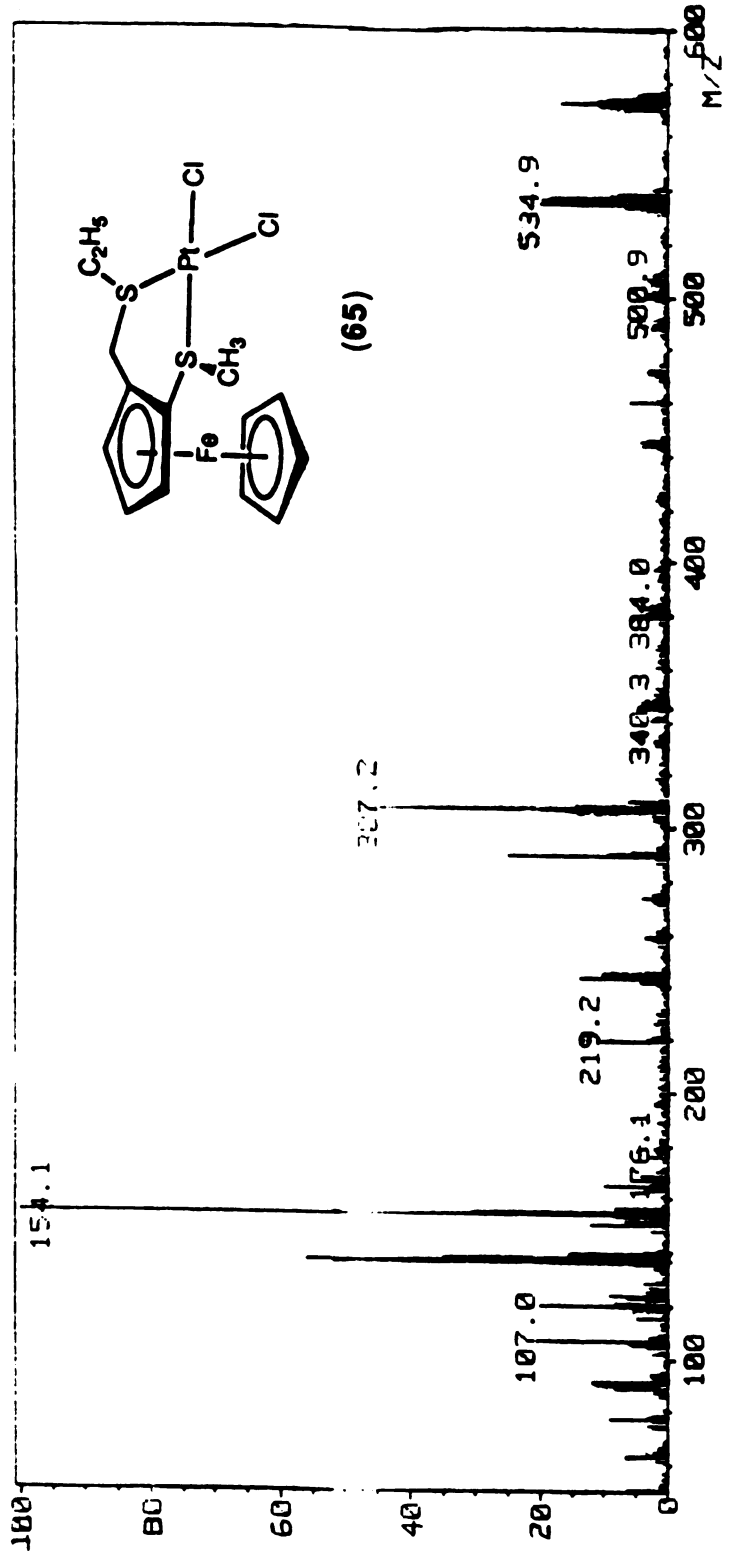


Figure 67. FAB Mass spectrum of complex **65**

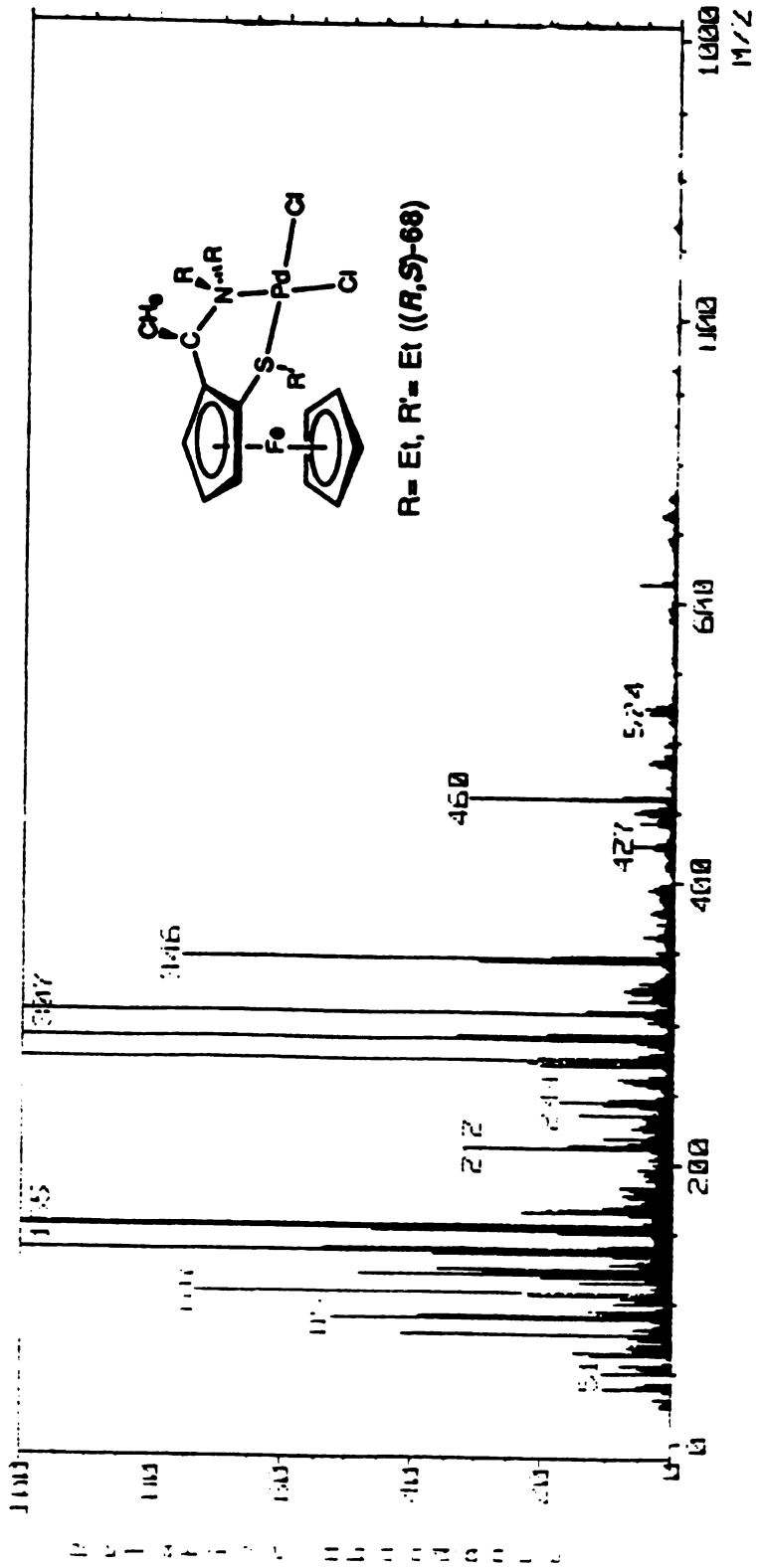


Figure 68. FAB Mass spectrum of complex (*R,S*)-68

REFERENCES

REFERENCES

1. Kagan, H. B. *Bull. Soc. Chim. Fr.* **1988**, *5*, 846.

2. Koenig, K. E. *Asymmetric Synthesis* ; Morrison J. D. Ed. ; Academic; New York, **1984**, Vol 5 , P1.

3. (a). Kagan, H. B. and Fiaud, J. C. *Topics in Stereochemistry*, Ed by Eliel E. L. and Allinger, N. L., Wiley-Interscience, New York **1978**, *Vol. 10* P. 175. (b). Bosnich, B. *Asymmetric Catalysis* Kluwer Academic Publishers, Boston, MA., **1986**

4. Morrison, J. D. and Mosher, H. S. *Asymmetric Organic Reactions* Prentice-Hall, Englewood Cliffs, New Jersey, **1971**

5. Scott, J. W. and Valentine, D. Jr. *Science* **1974**, *184*, 943.

6. Valentine, D. Jr. and Scott, J. W. *Synthesis* **1978**, 329.

7. Takaya, H.; Ohta, T.; Sayo, N.; Kumobayashi, H.; Akutagawa, S.; Ioue, S.; Kasahara, I., and Noyori, R. *J. Am. Chem. Soc.* **1987**, *109*, 1596.

8. Bosnich, B. and Fryzuk, M. D. *Topics in Inorganic and Organometallic Stereochemistry* Ed. by Geoffroy, G. Wiely-Interscience, New York, **1981** P.119.

9. Pearce, R. *Catalysis* **1978**, *2*, 176.

10. (a). Kealy, T. J. and Pauson, P. L. *Nature* **1951**, *168*, 1039. (b). Miller, S. A.; Tebboth, J. A., and Tremaine, J. F. *J. Am. Chem. Soc.* **1952** , *74*, 632.

11. Rosenblum, M. , *Chemistry of the Iron Group Metallocenes, Part I.* Wiely, New York, **1965**.

12. Wilkinson, G. ; Stone, F. G. A. ; Abel., E. W. *Comprehensive Organometallic Chemistry* Pergamon Press, New York, **1982**.

13. Schlogl, K. *Top. Stereochem.* **1967**, *1*, 39.

14. Mislow, K. *Introduction to Stereochemistry* Benjamin, Inc., New York, **1966**.

15. Ugi, I.; Marquarding, D.; Klusacek, H.; Grokel, G., and Gillespie, P. *Angew. Chem. Int. Ed.* **1970**, *9*, 703.

16. Gokel, G. W. and Ugi, I. K. *J. Chem. Educ.* **1972**, *49*, 294.

17. Hayashi, T.; Yamamoto, K.; Kumada, M. *Tetrahedron Lett.* **1974**, 4405.

18. Hayashi, T.; Tajika, M.; Tamao, K.; Kumada, M. *J. Am. Chem. Soc.* **1976**, *98*, 3718.

19. Hayashi, T.; Mise, T.; Fukushima, M.; Kagotani, M.; Nagashima, N.; Hamada, Y.; Matasumoto, A.; Kawakawi, S.; Konishi, M.; Yamamoto, K.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1138.

20. Cullen, W. R.; Yeh, E.-S. *J. Organomet. Chem.* **1977**, *139*, C13.

21. Cullen, W. R.; Einstein, F.W.B.; Huang, C.-H.; Willis, A. C.; Yeh, E.-S. *J. Am. Chem. Soc.* **1980**, *102*, 988.

22. Cullen, W. R.; Woolins, J. D. *Coord. Chem. Rev.* **1981**, *39*,1.

23. Cullen, W. R.; Woolins, J. D. *Can. J. Chem.* **1982**, *60*, 1793.

24. Bulter, I. R.; Cullen, W. R.; Reglinski, J.; Rettig, S. J.; *J. Organomet. Chem.* **1983**, *249*, 183.

25. Marquarding, D.; Klusacek, H.; Gokel, G.; Hoffman, P.; Ugi, I. *J. Am. Chem. Soc.* **1970**, *92*, 5389.

26. Gokel, G.; Hoffman, P.; Klusacek, H.; Ugi, I. *Angew..Chem. Int. Ed.* **1970**, *9*, 64.

27. Valkovich, P. B.; Gokel, G.; Ugi, I. K. *Tetrahedron Lett.* **1973**, 2947.

28. Battelle, L. F.; Bau, R.; Gokel, G. W.; Oyakowa, R. T.; Ugi, I. K. *J. Am. Chem. Soc.* **1973**, *95*, 482.

29. Stuber, S.; Ugi, I. *Synthesis* **1973**, 309.

30. Knowles, W. S. *Acc. Chem. Res.* **1983**, *16*, 106.

31. Yamamoto, K.; Wakatsuki, J.; Sugimoto, R. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1132.

32. Hayashi, T.; Norio, K.; Yoshihito, I. *J. Am. Chem. Soc.* **1987**, *109*, 7876.

33. Hayashi, T.; Yamamoto, A.; Ito, Y. *J. Chem. Soc. Chem. Commun.* **1986**, 1090.

34. Hayashi, T.; Kanehira, K. and Kumada, M. *Tetrahedron Lett.* **1981**, *22*, 4417.

35. Hayashi, T.; Katsumura, A.; Konishi, M.; Kumada, M. *Tetrahedron Lett.* **1979**, 425.

36. Hayashi, T.; Yamamoto, A.; Hagihara, T.; Ito, Y. *Tetrahedron Lett.* **1986**, *27*, 191.

37. (a) Hayashi, T.; Yamamoto, A.; Hagihara, T. *J. Organomet. Chem.* **1986**, *51*, 723. (b) Hayashi, T.; Yamamoto, A.; Ito, Y. *Chem. Lett.* **1987**, 177.

38. Hayashi, T.; Yamamoto, A.; Ito, Y.; Nishioka, E.; Miura, H.; Yanagi, K. *J. Am. Chem. Soc.* **1989**, *111*, 6301.

39. Hayashi, T. *Pure. Appl. Chem.* **1988**, *60*, 7.

40. Hayashi, T.; Hayashizahi, K.; Kiyai, Y.; Ito, Y. *J. Am. Chem. Soc.* **1988**, *110*, 8153.

41. Knowles, W. S.; Sabacky, M. *J. Chem. Soc. Chem. Commun.* **1968**, 1445.

42. Horner, L.; Siegel, H.; Buthe, H. *Angew.Chem. Int. Ed.* **1968**, *7*, 942.

43. Caplar, V.; Comisso, G.; Sunjic, V. *Synthesis* **1981**, 85.

44. Merril, R. E. *Asymmetric Synthesis Using Chiral Phosphine Ligands* Reaction Design Corporation Inc.; Hillside, NJ, **1979**.

45. Chan, A. S. C.; Pluth, J. J.; Halpern, J. *J. Am. Chem. Soc.* **1980**, *102*, 5952 and references therein.

46. Brown, J. M.; Chaloner, P. A. *J. Chem. Soc. Chem. Commun.* **1980**, *344* and references therein.

47. Landis, C. R.; Halpern, J. *J. Am. Chem. Soc.* **1987**, *109*, 1746.

48. Chan, A. S. C.; Pluth, J. J.; Halpern, J. *Inorg. Chim. Acta.* **1979**, *37*, L477.

49. Chan, A. S. C.; Halpern, J. *J. Am. Chem. Soc.* **1980**, *102*, 838.

50. (a) James, B. R.; McMillan, R. S. *Can. J. Chem.* **1977**, *55*, 3927. (b) James, B. R.; Morris, R. H.; Reimer, K. J. *Can. J. Chem.* **1977**, *55*, 2353. (c) James, B. R.; McMillan, R. S.; Reimer, K. J. *J. Mol. Catal.* **1976**, *1*, 439.

51. Calvin, M. *Trans. Faraday Soc.* **1938**, *34*, 1181.

52. Calvin, M. *J. Am. Chem. Soc.* **1939**, *61*, 2230.

53. Jardine, F. H. *J. Chem. Soc. A.* **1966**, 1711.

54. Fahey, D. R. in *Catalysis in Organic Synthesis* Academic Press, **1976**.

55. D'Aniello, M. J., Jr. and Barefield, E. K. *J. Am. Chem. Soc.* **1978**, *100*, 1474.

56. (a) Vaska, L.; Rhodes, R. E. *J. Am. Chem. Soc.* **1965**, *87*, 4970. (b) Eberhardt, G. G.; Vaska, L. *J. Catal.* **1967**, *8*, 183.

57. Harmon, R. E.; Gupta, S. K.; Brown, J. D. *Chem. Rev.* **1973**, *73*, 21.

58. Slater, S.; Muetterties, E. L. *Inorg. Chem.* **1980**, *19*, 3337.

59. Muetterties, E. L.; Band, E.; Kokorin, A.; Pretzer, W. R.; Thomas, M. G. *Inorg. Chem.* **1980**, *19*, 1552.

60. James, M. K.; Colin, J. S. *Tetrahedron Lett.* ,**1988**, *29*, 5545.

61. (a) Carturan, G.; Cocoo, G.; Facchin, G; Navazio, G. *J. Mol. Catal.* **1984**, *26*, 375.

62. Shuikina, L. P. and Frolov, V. M. *Kinet. Katal.* **1981**, *22*, 177.

63. McGown, W. T.; Kemball, C.; Whan, D. A. and Scurrel, M. S. *J. Chem. Soc. Faraday Trans. 1* **1977**, *73*(4), 632.

64. Cherkashin, G. M.; Shuikina, L. P.; Pareango, O. P. and Frolov, V. M *Kinet. Katal.* **1986**, *26*, 1110.

65. Kung, H. H. and Burwell, R. L., Jr. *J. Catal.* **1980**, *62*, 11.

66. Nayak, S. D.; Mahadevan, V. and Srinivasan, M. *J. Catal.* **1985**, *92*, 327.

67. Shuikina, L. P.; El'natanova, A. I.; Kovaleva, L. S.; Parenago, O. P. and Frolov, V. M. *Kinet. Katal.* **1981**, *22*, 177.

68. (a) Corriu, R. J. P.; Masse, J. P. *J. Chem. Soc. Chem. Commun.* **1972**, 144. (b) Tamao, K.; Kumada, M. *Organometallic Reactions and Synthesis* Becker, E. I.; Tsutsui, M. Eds. Plenum: New York, **1977**.

69. Tamao, K.; Sumitani, K.; Kiso, Y.; Zembaayashi, M.; Fujioka, A.; Kodama, S.; Nakajima, I.; Minato, A.; Kumada, M. *Bull Chem. Soc. Jpn.* **1976**, *49*, 1958.

70. Morrel, D. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1975**, *97*, 7262.

71. Hayashi, T.; Konish, M.; Fukushima, M.; Mise, T.; Kagotani, M.; Tajika, M.; Kumada, M. *J. Am. Chem. Soc.* **1982**, *104*, 180.

72. Hayashi, T.; Kumada, M. *Acc. Chem. Res.* **1982**, *15*, 395.

73. Negishi, E. *Acc. Chem. Res.* **1982**, *15*, 340.

74. Mole, T.; Jeffery, E. A. *Organoaluminum Compounds* Elsevier: Amsterdam, **1972**.

75. (a) Brown, H. C. *Hydroboration*; Benjamin: New York, **1962**. (b) Miyaura, N.; Yamada, K. *J. Chem. Soc. Chem. Commun.* **1979**, 867. (c) Miyaura, N.; Yamada, K.; Suzuki, A. *Tetrahedron Lett.* **1979**, 3437. (d) Miyaura, N.; Suginome, H.; Suzuki, A. *Tetrahedron Lett.* **1981**, *22*, 127. (e) Mikhailov, B. M.; Bubnov, Y. N. *Organoboron Compounds In Organic Synthesis* OPA: Amsterdam, **1984**.

76. (a) Kosugi, M.; Sasazawa, K.; Shimizu, Y.; Migita, T. *Chem. Lett.* **1977**, 301. (b) Milstein, D.; Stille, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 4992.

77. (a) Wailes, P. C.; Weigold, H.; Bell, A. P. *J. Organomet. Chem.* **1971**, *27*, 373. (b) Hart, D. W.; Blakburn, T. F.; Schwartz, J. *J. Am. Chem.*

Soc. **1975**, *97*, 679. (c) For a review see: Schwartz, J. *J. Organomet. Chem. Lib.* **1976**, *1*, 641.

78. Hayashi, T.; Hagihara, T.; Katsuro, Y.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 363.

79. Tamao, K.; Kumada, M. *Organometallic Reactions and Synthesis* Becker, E. I.; Tsutsui, M. Eds. Plenum: New York, **1977**, *Vol. 1.*, P.119.

80. Hayashi, T.; Konishi, M; Ito, H.; Kumada, M. *J. Am. Chem. Soc.* **1982**, *104*, 4962.

81. (a) Hosomi, A.; Sakurai, H. *Tetrahedron Lett.* **1976**, 1295. (b) Fleming, I.; Au-Yeung, B.-w. *Tetrahedron* **1981**, *37*, 13. (c) Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761.

82. (a) Okoroafor, M. O.; Ward, D. L. and Brubaker, C. H. Jr. *Organometallics*, **1988**, *7*, 1504. (b) Honeychuck, R. V.; Okoroafor, M. O.; Shen, L.-H. and Brubaker, C. H. Jr. *Organometallics*, **1986**, *5*, 482.

83. (a) Shen, L.-H. ; Okoroafor, M. O. and Brubaker, C. H. Jr. *Organometallics*, **1988**, *7*, 825. (b) Lai, C. K.; Naiini, A. A. and Brubaker, C. H. Jr. *Inorg. Chim. Acta.* **1989**, *164*, 205.

84. Gordon, A. J. and Ford, P. A. *The Chemist's companion*, Wiley, New York, **1972**, P. 445.

85. Hartley, F. R. *The Chemistry of Palladium and Platinum*, Wiley, New York, **1973**, P. 462.

86. Riley, D. P. and Shumate, R. E. *J. Org. Chem.* **1980**, *45*, 5187.

87. Amma, J. P. and Stille, J. K. *J. Org. Chem.* **1982**, *47*, 468.

88. Rossenblum, N.; Woodward, R. B. *J. Am. Chem. Soc.* **1958**, *80*, 5443.

89. Rausch, M. D.; Siegel, A. *J. Organomet. Chem.* **1976** , *17*, 117.

90. Slocum, D. W.; Ernst, C. R. *Adv. Organomet. Chem.* **1972**, *10*, 79.

91. Slocum, D. W.; Ernst, C. R. *Adv. Organomet. Chem. Rev. A.* **1970**, *6*, 337.

92. Koridze, A. A.; Petrovskii, P. V.; Fedin, E. I. Izv. *Akad. Nauk. SSSR Ser. Khim.* **1974**, 2156.

93. Jain, S. C. and Rivest, R. *J. Inorg. Nucl. Chem.* **1970**, *32*, 1579.

94. Marr, G. and Hunt, T. *J. Chem. Soc. (C)* **1969**, 1070.

95. (a) Sollott, G. P. and Howard, E. Jr. *J. Org. Chem.* **1962**, *27*, 4034. (b) Sollott, G. P.; Mertowoy, H. E.; Portnoy, S. and Sneed, J. L. *ibid.* **1963**, *28*, 1090.

96. (a) Kumada, M. *Pure. Appl. Chem.* **1980**, *52*, 669. (b) Hayashi, T.; Konishi, M.; Tokota, K.-I. and Kumada, M. *Chem. Comm.* **1981**, 313.

97. Hughes, O. R. and Unruh, J. D. *J. Mol. Catal.* **1981**, *12*, 71.

98. Unruh, J. D. and Christensen, J. R. *J. Mol. Catal.* **1982**, *14*, 19.

99. Honeychuck, R. V., Ph.D. Thesis, Michigan State University, East Lansing, MI. **1984**

100. Shen, L.-H., Ph.D. Thesis, Michigan State University, East Lansing, MI. **1985**.

101. Hayashi, T.; Mise, T.; Mitachi, S.; Yamamoto, K.; Kumada, M. *Tetrahedron Lett.* **1976**, 1133.

102. Bailey, R. T.; Lippincott, E. R. *Spectrochim. Acta.* **1965**, *21*, 389.

103. Rosenblum, M. *Chemistry of The Iron Group Metallocenes* Wiely-Interscience, New York, **1965**, P. 40.

104. Vinod, T. K. Ph. D. Thesis , University of Victoria, Victoria BC, Canada, **1986**.

105. Goggin, P. L.; Goodfellow, R. J.; Knight, J. R.; Norton, M. G.; Taylor, B. F. *J. Chem. Soc. Dalton. Trans.* **1973**, 2220.

106. Seyferth, D.; Hames, B. W.; Rucker, T. G.; Gowle, M.; Dickson, R. S. *Organometallics*, **1983**, *2*, 472.

107. Murray, S. G.; Hartley, F. R. *Chem. Rev.* **1981**, *81*, 365.

108. Plusec, J.; Westland, A. D. *J. Chem. Soc.* **1965**, 5371.

109. El-Dissouky, A.; Refaat, L. S. *Inorg. Chim. Acta.* **1984**, *87*, 213.

110. Crociani, B.; DiBianca, F. *Inorg. Chim. Acta.* **1988**, 253.

111. Hartley, F. R.; Murray, S. G.; Levason, W.; Soutter, H. E.; McAuliffe, C. A. *Inorg. Chim. Acta.* **1979**, *35*, 265.

112. Goggin, P. L.; Goodfellow, R. J.; Haddock, S. R.; Reed, F. J. S.; Smith, J. G.; Thomas, K. M. *J. Chem. Soc. Dalton. Trans.* **1972**, 1904.

113. Woolins, J. D.; Grinter, R.; Johnson, M. K.; Thomson, A. J. *J. Chem. Soc. Dalton. Trans.* **1980**, 1910.

114. Roundhill, D. M. *Inorg. Chem.* **1980**, *19*, 553.

115. Czernuzewicz, R. S.; Nakamoto, K.; Strommen, D. P. *Inorg. Chem.* **1980**, *19*, 793.

116. Battistoni, C.; Giuliani, A. M.; Paparazzo, E.; Tarli, F. *J. Chem. Soc. Dalton. Trans.* **1984**, 1293.

117. (a) Lyon, P. A. Ed. *Desorption Mass Spectrometry* ACS Symposium Series **1985**. (b) Ackermann, B. L. Ph.D. Thesis, Michigan State University, East Lansing, MI. **1986**.

118. James, B. R. *Homogeneous Hydrogenation* Wiley, New York, **1979**.

119. Nakamura, A.; Tsutsui, M. *Principles and Applications of Homogeneous Catalysis* Wiley, New York, **1980**.

120. Masters, C. *Homogeneous Transition-metal Catalysis* Chapman and HallLtd. New York **1981**.

121. James, B. R. in *Advances in Organometallic Chemistry* **1979**, *Vol. 17*, P. 319.

122. Parshall, G. W. *Homogeneous Catalysis* Wiley, New York, **1980**.

123. Faller, J. W. *Homogeneous Catalysis with Metal Phosphine Complexes*; Pigolet, L. H. Ed.; Plenum: New York, **1983**, Chapter 2.

124. (a) Naiini, A. A., Ph.D. Thesis, Michigan State University, East Lansing, MI. **1989**. (b) Ali, H. M., Ph.D. Thesis, Michigan State University, East Lansing, MI. **1990**.

125. Lai, C. K.; Naiini, A. A. and Brubaker,C. H. Jr., *Inorganica Chimica Acta*, **1989**, *164*, 205.

126. Ali, H. M. and Brubaker,C. H. Jr., *J. Mol. Catal.* **1990**, *60*, 331.

127. Okoroafor, M. O.; Shen,L.-H.; Honeychuck, R. V. and Brubaker,C. H. Jr. *Organometallics*, **1988**, *7*, 1297.

128. Naiini, A. A.; Okoroafor, M. O and. Brubaker, C. H. Jr., *J. Mol. Catal.* **1989**, *54*, L27 and references therein.

129. Tolman, C. A. *Chem. Soc. Rev.*, **1972**, *1*, 337.

130. Collman, J. P.; Hegedus, L. S.; Norton, J. R. and Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, University Science, Mill Valley, CA. **1987**, P. 531.

131. Atwood, J. D. *Inorganic and Organometallic Reaction Mechanisms*, Brooks/Cole , Monterey , CA., **1985**, P. 200.

132. Stern, E. W. and Maples,P. K. *J. Catal.*, **1972**, *27*, 120.

133. Frolov, V. M.; Parenago, O. P ; Bondarenko, G. N.; Kovaleva, L. S.; El'natanova, A. I.; Shuikina, L. P.;Cherkashin, G. M. and Mirskaya, E. Y. *Kinet. Katal.*, **1981**, *22*, 1356.

134. Muetterties, E. L. *Catal. Rev.- Sci. Eng.* **1981**, *23*, 69.

135. Sivak, A. J. and Muetterties, E. L. *J. Am. Chem. Soc.* **1979**, *101*, 4878.

136. Muetterties, E. L. *J. Organomet. Chem.* **1980**, *200*, 177.

137. Burch, R. R.; Shusterman, A. J.; Muetterties, E. L.; Teller, R. G. and Williams, J. M. *J. Am. Chem. Soc.* **1983**, *105*, 3546.

138. Kagan, H. B. and Fiaud, J. C. *Top. Stereochem.* **1978**, *10*, 175.

139. Apsimon, J. W. and Seguin, R. P. *Tetrahedron* **1979**, *35*, 2797.

140. Fiorini, M. and Giongo, G. M. *J. Mol. Catal.* **1980**, *7*, 411.

141. Kyba, E. P.; Davis, R. E.; Juri, P. N. and Shirley, K. R. *Inorg. Chem.* **1981**, *20*, 3616.

142. (a) MacNeil, P. A.; Roberts, N. K. and Bosnich, B. *J. Am. Chem. Soc.* **1981**, *103*, 2273. (b) Ball, R. G. and Payne, N. C. *Inorg. Chem.* **1977**, *16*, 1187.

143. Vineyard, B. D.; Knowles, W. S. and Sabacky, M. J. *J. Mol. Catal.* **1983**, *19*, 159.

144. Kagan, H. B. *Pure Appl. Chem.* **1975**, *43*, 401.

145. Spencer, H. K.; Hill, R. K. *J. Org. Chem.* **1976**, *41*, 2485.

146. McCreary, M. D.; Lewis, D. W.; Wernick, D. L.; Whitsides, G. M. *J. Am. Chem. Soc.* **1974**, *96*, 1038.

147. Hayashi, T.; Konish, M.; Fukushima, M.; Kanehira, K.; Hioki, T.; Kumada, M. *J. Org. Chem.* **1976**, *41*, 2485.

148. (a) Allkins, J. and Hendra, P. J. *J. Chem. Soc. (A)* **1967**, 1325. (b) Adams, D. M. and Chandler, P. J. *J. Chem. Soc. (A)* **1969**, 588.

149. (a) Allen, E. A. and Wilkinson, W. Spectrochimica. Acta. 1972, 28 A, 725. (b) Aires, B. E.; Fergusson, J. E.; Howarth, D. T. and Miller, J. M. *J. Chem. Soc. (A)* **1971**, 1144. (c) Clark, R. J. H.; Natile, G.; Belluco, U.; Cattalini, L. and Filippin, C. *J. Chem. Soc. (A)* **1970**, 659.