

Intramolecular alkene hydroaminations mediated by simple group 3 metal complexes: the development of non-lanthanocene-based catalysts
by Young Kwan Kim

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry
Montana State University
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Abstract:
Metallocene-based Group 3 metal complexes; lanthanocenes, have intrinsic problems for use as a universal catalysis. For example, preparations of most complexes are complicated, and most lanthanocenes are extremely sensitive to air and water and have structural limitation on variation.

The first application of non-metallocene-based Group 3 metal catalysts to intramolecular aminoalkene cyclizations has been achieved. Simple amido lanthanide complexes of the type Ln[N(TMS)2]3 (Ln = Y, Nd) have been found to be competent catalysts for this reaction, which have similar or superior activity in cyclization including diastereoselectivity to the lanthanocenes. Modification of the metal center in Ln [N(TMS)2]3 (Ln = Y, Nd, La) has been readily achieved by amine elimination in the presence of hindered chelating diamines, bis(thiophosphinic) amines, or bis(thioenamides) in situ, to provide new Group 3 amido chelates. These complexes have shown remarkably improved catalytic activities and stereoselectivities [e.g., 33:1 (trans/cis)\ in the cyclization of 2-aminohex-5-ene. An X-ray crystallographic structure of one of the bis(thiophosphinic amide)-based Group 3 metal complexes has been defined. Chiral lanthanide complexes have been implemented for enantioselective hydroamination reactions. The C2 symmetric catalysts exhibit good enantioselectivity in the cyclization of l-amino-2,2-dimethylpent-5-ene, as high as 66% enantiomeric excess at 10 °C.

These non-metallocene-based Group 3 metal complexes have shown superiority in terms of preparation, thermal stability, and catalytic activity over lanthanocenes in the hydroamination of aminoalkenes. In addition, the amido complexes should allow for a variety of ligand derivatives.

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To my father

To all of my family

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ABBREVIATIONS

n-BuLi	*n*-butyllithium
bp	boiling point
CaH_2	calcium hydride
CH_2Cl_2	methylene chloride
Cp*	1,2,3,4,5-pentamethylcyclopentadiene
DCC	*N,N'*-dicyclohexylcarbodiimide
DMF	dimethyl formamide
Et_3N	triethylamine
EtOH	ethanol
Et_2O	diethyl ether
HCl	hydrochloric acid
$LiAlH_4$	lithium aluminum hydride
$MgSO_4$	magnesium sulfate
mp	melting point
Ms	methanesulfonate
$NaHCO_3$	sodium bicarbonate
$NaBH_4$	sodium borohydride
NaOH	sodium hydroxide
NH_4Cl	ammonium chloride
$NH_2OH{\cdot}HCl$	hydroxylamine hydrochloride
Ph	phenyl
THF	tetrahydrofuran
TsCl	*p*-toluenesulfonyl chloride
Ts	*p*-toluenesulfonate

ABSTRACT

Metallocene-based Group 3 metal complexes; lanthanocenes, have intrinsic problems for use as a universal catalysis. For example, preparations of most complexes are complicated, and most lanthanocenes are extremely sensitive to air and water and have structural limitation on variation.

The first application of non-metallocene-based Group 3 metal catalysts to intramolecular aminoalkene cyclizations has been achieved. Simple amido lanthanide complexes of the type $Ln[N(TMS)_2]_3$ (Ln = Y, Nd) have been found to be competent catalysts for this reaction, which have similar or superior activity in cyclization including diastereoselectivity to the lanthanocenes. Modification of the metal center in $Ln[N(TMS)_2]_3$ (Ln = Y, Nd, La) has been readily achieved by amine elimination in the presence of hindered chelating diamines, bis(thiophosphinic) amines, or bis(thioenamides) in situ, to provide new Group 3 amido chelates. These complexes have shown remarkably improved catalytic activities and stereoselectivities [e.g., 33:1 (*trans/cis*)] in the cyclization of 2-aminohex-5-ene. An X-ray crystallographic structure of one of the bis(thiophosphinic amide)-based Group 3 metal complexes has been defined. Chiral lanthanide complexes have been implemented for enantioselective hydroamination reactions. The C_2 symmetric catalysts exhibit good enantioselectivity in the cyclization of 1-amino-2,2-dimethylpent-5-ene, as high as 66% enantiomeric excess at 10 °C.

These non-metallocene-based Group 3 metal complexes have shown superiority in terms of preparation, thermal stability, and catalytic activity over lanthanocenes in the hydroamination of aminoalkenes. In addition, the amido complexes should allow for a variety of ligand derivatives.

CHAPTER 1

INTRODUCTION

Among bond-forming processes, metal-catalyzed reactions are considered to be one of the most useful methods due to their unique efficiency and selectivity in molecular construction. Metal-catalyzed chemistry for the formation of carbon-carbon or carbon-hydrogen bonds has been well established by numerous studies.[1]

Many physiologically active substances contain carbon-oxygen or carbon-nitrogen bonds. The metal-catalyzed intramolecular hydroamination of carbon-carbon multiple bonds has come to be recognized as one of the most powerful methods for the synthesis of azacyclic intermediates.[2] However, organometallic-catalyzed formations of carbon-heteroatoms, particularly carbon-nitrogen bonds, are still rare.[2] In particular the efficient hydroamination of aliphatic alkenes remains among the most important challenges for catalysis research.

To date, various synthetic methods for the amination of C-C multiple bonds have been developed in two basic synthetic approaches, activation of nucleophilic amines and activation of electrophilic alkenes. Hydroamination via addition of nucleophilic amines to alkenes activated by groups such as keto, ester, nitrile, sulfoxide, and nitro[3] are generally useful for the synthesis of nitrogenous compounds. On the other hand, nonactivated alkenes are mostly promoted by late-transition metal complexes. An electrophilic transition metal complex such as Fe(II), Pd(II), Pt(II), Hg(II), Mo(II), or W(II) promotes

the electrophilicity of alkenes toward the nucleophilic attack of amines. In this case, however, a stoichiometric amount of metal complex is often required: because of the high affinity of amines to transition metals, they have tendency toward diplacement of coordinated alkenes rather than nucleophilic attack.[4]

The activation of amines can be accomplished by an alkali metal such as Li or Na, but the hydroamination frequently incurs a side reaction, especially polymerization.[2] Early- and late-transition metals also competently activate amines toward catalytic hydroamination reactions. Whereas early-transition metal activate amines via the formation of amido complex, late-transition metal activate amines via oxidative addition of the amine to the metal center, followed by insertion of the alkyne or alkene into the M-N bond.[5d] However, nucleophilic addition of the amine to alkyne or alkene activated by metal coordination, is also a possible pathway proposed for late-transition metal catalysis.[6] Recently, catalytic hydroamination using titanium,[7] rhodium,[5] palladium [5c, 6] and nickel,[8] have been reported. However, most of the reactions catalyzed by transition metals utilize 1,3-dienes, styrenes, aminoalkynes, aminoallenes or deactivatied nucleophiles such as anilines or sulfonamides to reduce the coordination strength of amine to metal cation.[9, 10] From a thermodynamic point of view, insertion of alkenes into the metal-nitrogen bond is more difficult due to approximately 29 kcal/mol and >35 kcal/mol less exothermic than that of allenes and alkynes, respectively.[11,12,13] In general, alkynes are more reactive than alkenes in metal catalyzed amination reactions because of

the sterically less hindred cylindrical π-system as well as more nucleophilic *sp*-hybridized C-atoms to be better π-donors.[14]

Of the variety of metal-based catalysts, complexes of lanthanide appear very well suited for effecting chemoselective, diastereoselective and enantioselective alkene hydroaminations under mild reaction conditions.[11,15] However, the development of lanthanide chemistry for hydroamination has progressed slowly and is in its initial stages today. Most of the complexes developed to date are metallocene-based and have various problems to overcome such as preparation of catalysts and stability with respect to thermal conditions and air. Overall, lanthanocenes have been quite limited in variety.

This dissertation describes the first non-metallocene-based Group 3 metal catalysts developed for hydroamination. In a historical context, the X-ray crystallographic structure of tetradentate ligand based complex **63** and the preliminary results that established its catalytic activity in aminoalkene hydroamination originally preceded the discovery of $Ln[N(TMS)_2]_3$ activity. These results were obtained by Professor Tom Livinghouse at Caltech. Since the detailed experiments on the simple amides were performed first, these results will be described prior to the discussion of the NPA series. Thus, the first part of this dissertation will discuss the catalytic activity of simple amido complexes for intramolecular alkene hydroaminations. The second section will describe dramatically improved catalytic activities as well as the diastereocontrol of Group 3 metals by coordination with non-metallocene bidentate ligands. Another type of non-metallocene-based Group 3 metal complex and its catalytic activities will be described in

the third section. In the last part, the catalyzed enantioselective hydroamination reaction will be discussed briefly.

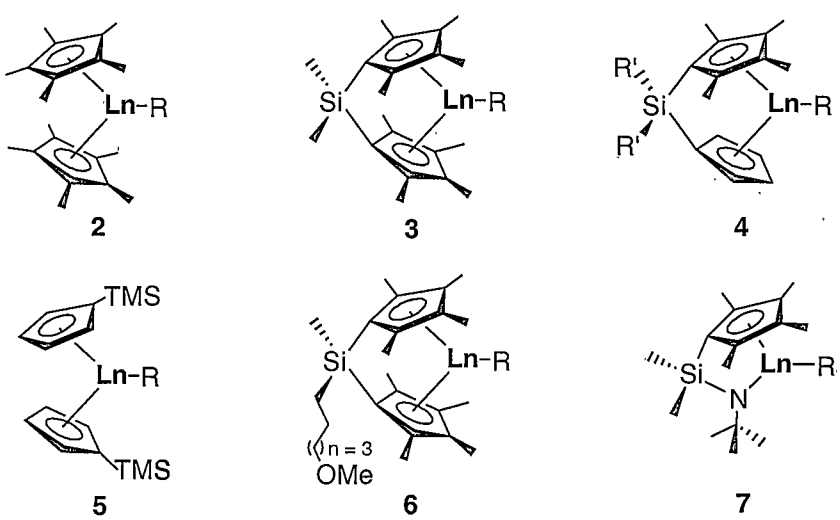
BACKGROUND

All *f*-block element ions, from $_{57}$La to $_{71}$Lu, have the trivalent oxidation state as their the most stable state. In the strict sense, scandium and yttrium are *d*-block elements, but these are generally classified with the lanthanides because of their chemical similarities, as is lanthanum that does not have a 4*f* electron.[16] Lanthanides and transition metals have quite different chemical properties. While transition metals, which characteristically have full *d*-type (*n*-1) orbitals, often result in a coordinate covalent bonding with a ligand, organolanthanide complexes have a mainly ionic character and behave as typical hard acids. Due to the lanthanide contraction of the 4*f* orbitals and the well-shielded environment by the 5*s* and 5*p* orbitals, the *f* orbitals have little interaction with ligand orbital resulting minimized ligand field stabilization effects (LFSE). The poor overlap with the ligand orbitals contributes to the predominantly ionic character, which causes the strong oxophilicity of the lanthanide cation. Furthermore, lanthanides have noticeably larger ionic radii and a greater flexibility in geometry and coordination numbers than transition metals, so their coordination numbers are usually eight, ten, or twelve.

Since three coordinate organolanthanides $[Ln\{N(TMS)_2\}_3]$ (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Ho, Y, Yb, Lu) (**1**), which are coordinatively highly unsaturated complexes, were synthesized by Bradley and co-workers in 1973,[17] many Group 3 complexes have been developed and their catalytic activity investigated for chemical reactions.[2, 18]

Organolanthanides are known to be among the most suitable catalysts for Ziegler-Natta-type polymerization.[19] In addition, organolanthanides exhibit unique characteristics as catalysts in hydrogenation,[19f,20] oligomerization,[21] hydroamination,[15c,22] hydrosilylation,[23] hydroboration,[24] and hydrophosphination.[25]

Although the first organolanthanide-catalyzed hydroamination reactions were described by Marks and co-workers in 1989,[22j] only nine types of catalysts have been reported to date. In the initial study, they used [Cp_2*LnR] (**2**), [Me_2 $SiCp*_2$LnR] (**3**) and [Et_2SiCp*CpLnR] (**4**) complexes, which have also proven their catalytic activity for polymerization, hydrogenation, and oligomerization.[19,20,21] Complexes **3** and **4** are sterically more open structures due to the silyl linkage and therefore have much higher



R = H, CH_3, $CH(TMS)_2$ or $N(TMS)_2$
R' = Me or Ethyl
Ln = Y, Lu, Sm, Nd, La

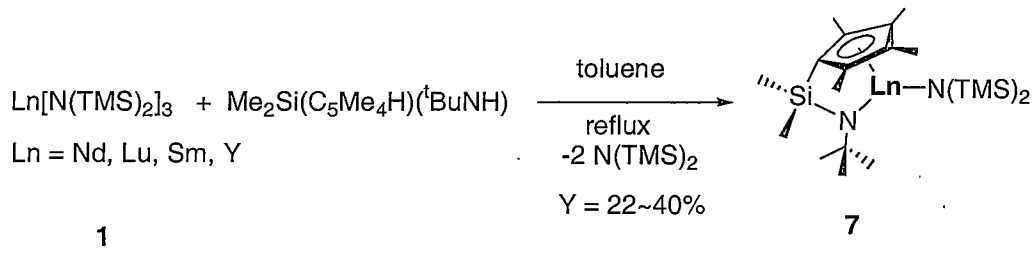
Figure 1. Catalysts Developed for Hydroamination

catalytic activity towards aminoalkene hydroaminations than [Cp_2*LnR] (**2**). Among this series of complexes (**2, 3** and **4**), [Et_2SiCp*CpLnR] (**4**) exhibits the highest activity.[22i]

The sterically bulky trimethylsilyl group has been introduced onto the cyclopentadienyl units to open the reactive metal center for interaction with olefins. The [$Cp^{TMS}{}_2$LnMe]$_2$ (Ln = Y, Sm, Nd) (**5**) complexes have shown excellent catalytic activity for 1,1-disubstituted aminoalkenes. However, the Cp^{TMS}-based complexes still have lower activity in the cyclization than the $Me_2SiCpCp$*-based complexes.[15c] Recently, a new series of constrained-geometry organolanthanide [Me_2SiCp*(t-BuN)LnR] (**7**) catalysts has been developed.[15b] These complexes afford significantly enhanced catalytic activity, with an increase in turnover numbers per hour of up to 30-fold over the Cp* ligand arrays. The silyl-linked amido cyclopentadienyl ligand [Me_2SiCp*(t-BuN)]$^{2-}$, which was originally developed for Sc,[26] makes a 12-electron [R = $CH(TMS)_2$] or 14-electron [R = $N(TMS)_2$] system complex by donating 8 electrons to the Group 3 metal. Accordingly, it makes electronically more unsaturated complexes than typical $Cp^*{}_2$LnR complexes which make a 14-electron [R = $CH(TMS)_2$] or 16-electron [R = $N(TMS)_2$] system. In addition, it has a sterically more favored structure for coordination of aminoalkenes.[22a]

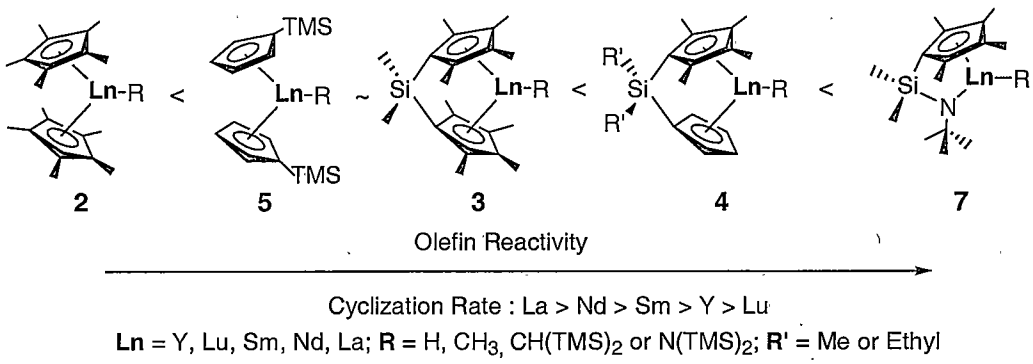
As with other lanthanocenes, however, the preparation of these complexes is very complicated and the synthetic yields are low (22-49%). Examples include Nd (24%), Lu (32%), Sm (22%) and Y (40%). As shown in Scheme 1, complex **7** is prepared using LnR_3 [R = $N(TMS)_2$] and Cp*HSiNHt-C_4H_9 at 110°C in toluene. However, to complete

the reaction, periodic removal of $HN(TMS)_2$ from the system, by evacuating the vessel to dryness, reintroducing solvent, and continuing heating, was required.



Scheme 1. Preparation of Lanthanocenes (7)

A methoxy group was introduced into $[MeO(CH_2)_5(Me)\ SiCp^*_2]YCH(SiMe_3)_2$ (**6**) to investigate the effect of a Lewis base.[20a] However, the methoxy group decreased the catalytic activity of the complex in both diastereocontrol and the rate of cyclization. For sterically less hindered simple aminoalkenes, the order of catalytic activity of the



Scheme 2. Relative Catalytic Activities Toward Hydroamination

lanthanocenes is **2** < **5** ~ **3** < **4** < **7** [15c,22a,h,i] (Scheme 2). However, for sterically more hindered aminoalkenes, such as 1,1-disubstituted and 1,2-disubstituted aminoalkenes, the lanthanocenes have different orders of activity dependent upon substrate. As summarized in Scheme 2, the rate of cyclization increases when the Cp* ligands are changed to the $Me_2SiCp^*_2$ system or when a lanthanide metal with a larger ionic radius is employed.[22h,i]

In addition to C_2 (**2**,**3** and **5**) and C_s-symmetric lanthanocenes (**7**), two types of chiral C_1-symmetric catalysts (**8**, **9**) have been utilized for the asymmetric aminoalkene hydroamination reaction (Figure 2). In both cases, a chiral auxiliary is introduced onto the cyclopentadienyl unit. Complex **8** (Ln = Sm) afforded up to 74% enantioselectivity at 30 °C (the turnover number, N_t (h^{-1}), is not available) in the cyclization of 1-amino-2,2-dimethylpen-5-ene.[22g] Chiral C_1-symmetric catalyst of the type $[Me_2Si(\eta^5\text{-OHF})(\eta^5\text{-}C_5H_3R^*)YN(SiMe_3)_2]$ (**9**) [OHF = octahydrofluorenyl; R* = (-)-mentyl] exhibits 67%

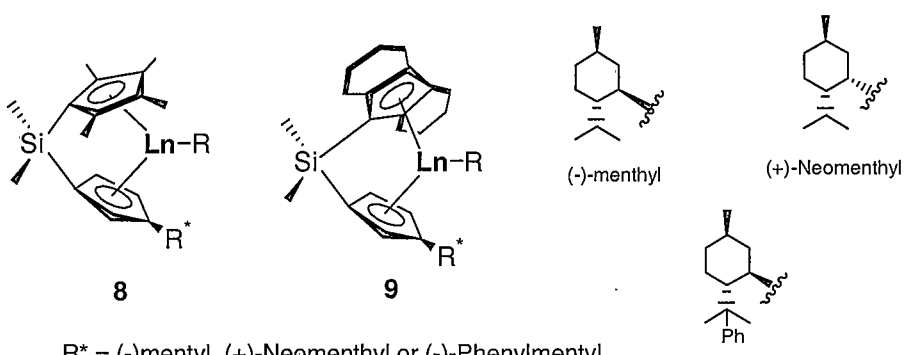
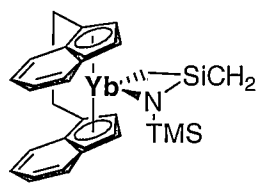


Figure 2. Asymmetric Catalysts for Hydroamination

(+) enantioselection at 25 °C [N_t (h^{-1}) = 2.1] in the cyclization of 1-amino-2,2-dimethylhex-5-ene to provide (+)-2,5,5-trimethylpiperidine.[27]

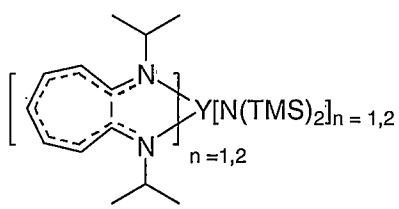
On the other hand, Broene and co-workers have explored a new ligand system other than the Cp* class in the intramolecular aminoalkene hydroamination reaction. Even though 1,2-bis (indenyl) ethane-derived lanthanocene **10** has moderate catalytic activity, it is more difficult to synthesize than the Cp* systems. In addition, it has no particular merits in the cyclization reactions.[28]



10

Figure 3. Another Type of Lanthanocene

Lately, as a substitution for the cyclopentadienyl unit, aminotroponiminates ([ATI]-), which are known to stabilize coordinatively unsaturated main group metal



11

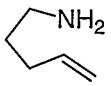
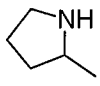
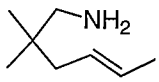
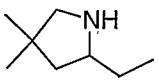
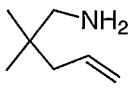
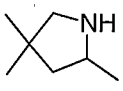
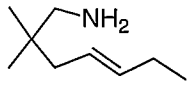
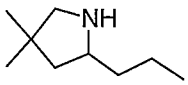
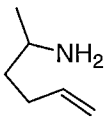
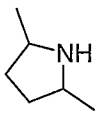
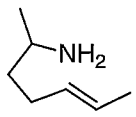
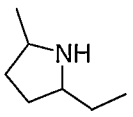
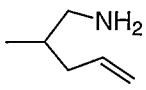
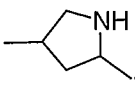
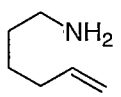
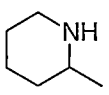
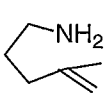
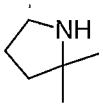
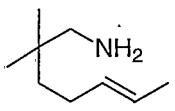
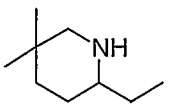
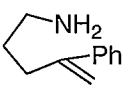
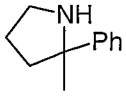
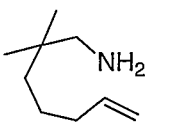
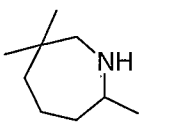
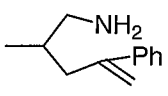
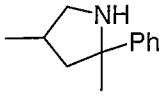
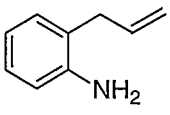
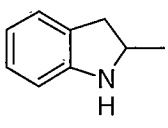
Figure 4. The First Non-metallocene-Based Early-Metal Catalysts for Hydroamination

complexes,[29] have been introduced for group 3[3a] and group 4 metals.[30] Roesky and co-workers have explored these complexes as the first non-metallocene-based Group 3 metal catalysts for intramolecular aminoalkyne hydroamination.[31] Unfortunately, the complexes have no catalytic activity for the aminoalkene cyclization reaction. These complexes have shown very little activity towards the hydroamination of aminoalkynes.

Various aminoalkene substrates have been examined for the generality and scope of the reaction catalyzed by organolanthanocenes. In this dissertation, the hydroamination reactions for aminoalkynes and aminoallenes are not reviewed. Using lanthanocene catalysts, the intramolecular alkene hydroamination reactions have created five-, six-, and seven-membered nitrogenous rings. The rates of cyclization of aminoalkenes are dependent on the ring size, in the order 5 > 6 >> 7. Even 1,1- (Table 1, Entries 5-7) and 1,2-disubstituted aminoalkenes (Table 1, Entries 8-10 and 12) lead to cyclization reactions. Among these substrates, 1,2-disubstituted aminoalkenes are the least reactive toward cyclization. Meanwhile, 2,2-dimethyl substituent on the aminoalkenes accelerates cyclization, through the Thorpe-Ingold effect,[32] when compared to unsubstituted substrates under similar conditions. On the other hand, organolanthanocene catalysts have shown 1000 times lower activity in the intermolecular hydroamination reaction than in the intramolecular version.[18,33] The scope of hydroamination reactions has been successfully expanded to bicyclic and bridged bicyclic amines. In some cases, however, the cyclization reactions require a larger catalyst loading, higher temperatures and longer

reaction times. For example, the preparation of 1-aza-2,2,5-trimethylbicyclo [3.3.0] octane was found to proceed with 41 mol% of $[Cp^{TMS}{}_2NdMe]_2$ (**5**) at 120 °C for seven days (yield 53%) [Table 2, Entry 3]. [15c]

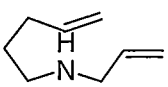
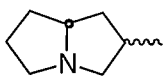
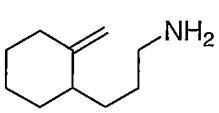
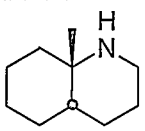
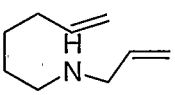
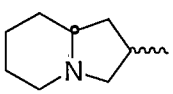
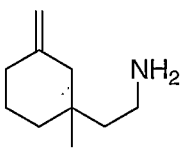
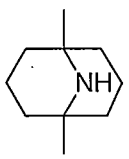
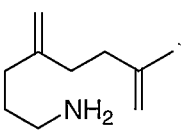
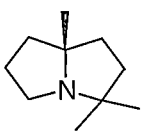
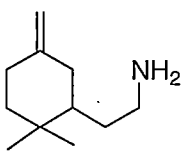
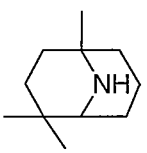
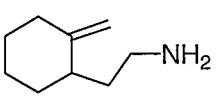
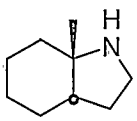
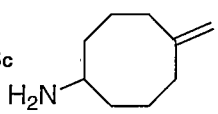
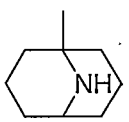
Table 1. Substrates Utilized for Hydroamination

Entry[ref.]	Substrate	Product	Entry[ref]	Substrate	Product
1[15d]			**8**[15q]		
2[15d]			**9**[5q]		
3[15d]			**10**[5q]		
4[15d]			**11**[22i]		
5[15c]			**12**[15a]		
6[15c]			**13**[15d]		
7[15c]			**14**[22i]		

Organolanthanide catalysis allows exquisite construction of nitrogenous natural products with high selectivity and efficiency. To date, two natural products have been

synthesized via organolanthanide-catalyzed intramolecular hydroamination by Molander and co-workers. A total synthesis of the alkaloid (-)-Pininol was performed in 10 steps with 19% overall yield to an enantiomeric purity in excess of 99.9+% using $Cp^*_2NdCH(TMS)_2$ (**2**).[34] This brief and efficient synthetic strategy has also been applied to the synthesis of MK-801. The potent anticonvulsant and neuroprotective agent MK-801[35] was synthesized with a 38% overall yield using the lanthanocene $[Cp^{TMS}NdMe]_2$ (**5**) for the hydroamination reaction.[36]

Table 2. Substates Utilized for Bicyclization

Entry[ref]	Substrate	Product	Entry[ref]	Substrate	Product
1[22c]			5[15c]		
2[22c]			6[15c]		
3[15c]			7[15c]		
4[15c]			8[15c]		

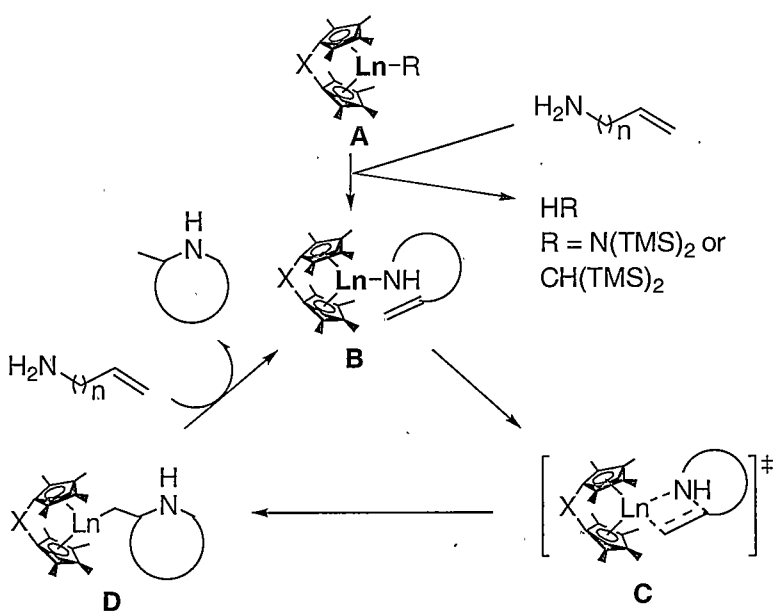


(-) Pinidinol MK 801

Figure 5. Natural Products Synthesized via Hydroamination

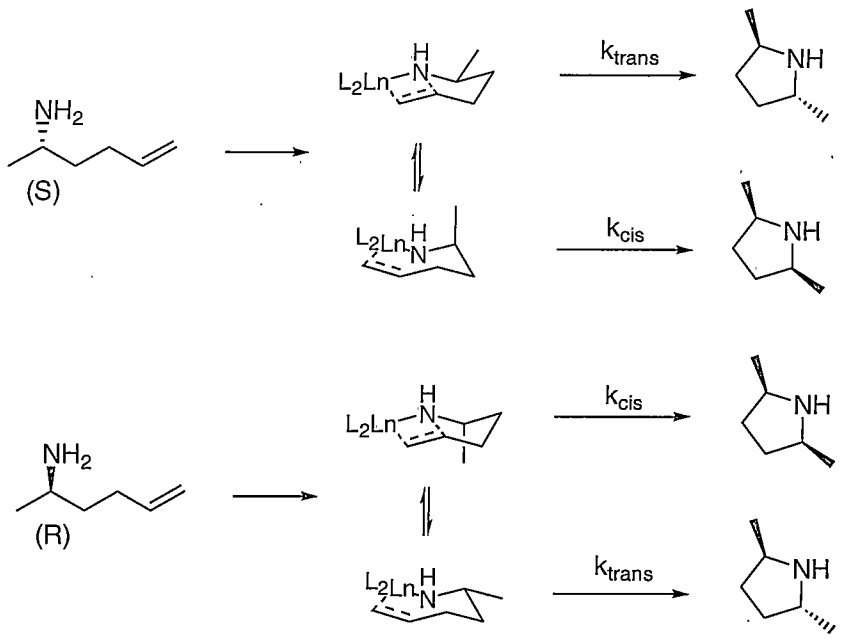
A characteristic feature of many lanthanide catalyzed reactions is the absence of accessible metal oxidation states for oxidative addition and reductive elimination processes. This implies that an addition is favorable for the reaction of alkenes/alkynes with the metal-nitrogen bond in catalytic hydroaminations. The proposed mechanism (Scheme 3),[2,22e,g,h] which is a similar process to the other catalytic cycles, has been

Scheme 3. Proposed Mechanism for Hydroamination of Aminoalkenes



established based on extensive kinetics studies.[22h] The precatalysts undergo rapid M-R bond metathesis by the amine. This protonolysis generates quantitative amido complexes or mixed amino-amide adducts as the resting state of the catalytic cycle (**B**).[22e,g] In the rate-determining step (**C**), the intramolecular olefin inserts into the M-N bond via a four-centered transition state has been proposed.[2,22h] This sterically demanding transition state creates a more sterically open lanthanide complex with a large-sized metal than with a small one. Accordingly, it will make a favorable olefin insertion into M-N bond and increase the reaction rate. Rapid protonolysis of the resulting M-C bond (**D**) by another amine regenerates the catalytically active Group 3 amido complex with liberation of the cyclic amine product. Kinetic analysis of the cyclization of aminoalkenes shows that the rate dependence is first-order in catalyst concentration and zero-order in substrate over at least three half-lives: $v = k[\text{catalyst}]^1[\text{substrate}]^0$.[2,2h]

The diastereoselectivity of products was rationalized based on the presumed catalyst-substrate steric interactions in the transition state (Scheme 4). In the case of 2-aminohex-5-ene (Table 1, Entry 3), the sterically more demanding axial methyl conformation may raise nonbonded interactions with the metal coordination sphere. So, a pseudo-chair seven-membered transition state favors an equatorial methyl conformation to afford the *trans* product. In comparison, 2-methylaminopent-4-ene (Table 1, Entry 4) is strerically less sensitive concerning diastereoselection by making a pseudo-chair seven-membered transition state, in which the methyl substituent is one more position distant from the sterically demanding metal center.



Scheme 4. Rationalization of Diastereoselectivity in the Cyclization

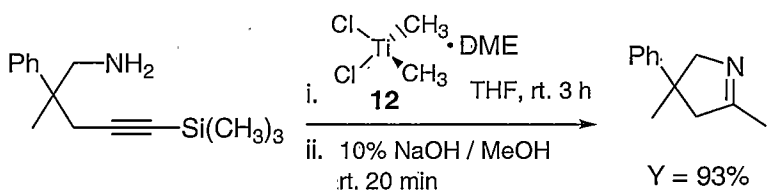
Even though organolanthanide-catalyzed intramolecular hydroamination reactions were initially explored using lanthanocenes, the complexes have several disadvantages to overcome. For example, preparation of precatalysts is complicated and the synthetic yields are generally low. In addition, most lanthanocenes are extremely sensitive to air and unstable with respect to temperature. Overall, lanthanocenes have structural limitations on variation for the further development of lanthanide chemistry

CHAPTER 2

INTRAMOLECULAR ALKENE HYDROAMINATIONS CATALYZED BY SIMPLE AMIDO DERIVATIVES OF THE GROUP 3 METALS

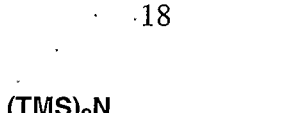
INTRODUCTION

Recently, the Livinghouse group has found that simple, non-metallocene-based Group 4 metal alkyls (**12**) have excellent activity towards aminoalkyne cyclizations (Scheme 5).[38]



Scheme 5. Aminoalkyne Cyclizations Mediated by Group 4 Metal Alkyl

Based on these results, preliminary studies toward the development of non-metallocene-based Group 3 metal catalysts were conducted by Professor Livinghouse that demonstrated catalytic activity for NPS-type Group 3 metal complexes and $Ln[N(TMS)_2]_3$ in aminoalkene hydroaminations. Subsequentially, we decided to first perform the detailed investigation with readily available $Ln[N(TMS)_2]_3$ complexes for the efficient development of non-metallocene Group 3 catalysts.



1

Figure 6. The First Three-Coordinated Lanthanide Complexes

The $Ln[N(TMS)_2]_3$ (**1**) species were the first three-coordinate lanthanide complexes and were prepared by Bradley and co-workers in 1973.[17] These complexes have an electronically unsaturated 12-electron system. As previously mentioned, over the last decade $Ln[N(TMS)_2]_3$ complexes were utilized only as starting materials for the preparation of organolanthanocenes via a tedious procedure, and the latter are more sensitive to air and thermally unstable than the $Ln[N(TMS)_2]_3$ complexes. Interestingly, the simple amido complexes $Ln[N(TMS)_2]_3$ were never investigated as catalysts for the intramolecular hydroamination reaction.

SYNTHESIS OF SUBSTRATES

Initially, six representative aminoalkenes (**15a-f**) were prepared according to literature procedures as shown in Schemes 6, 7, and 8. [15c,39] Among them, aminoalkenes **15c**,**d**,**e** and **f** were specifically assessed in diastereoselectivity studies.

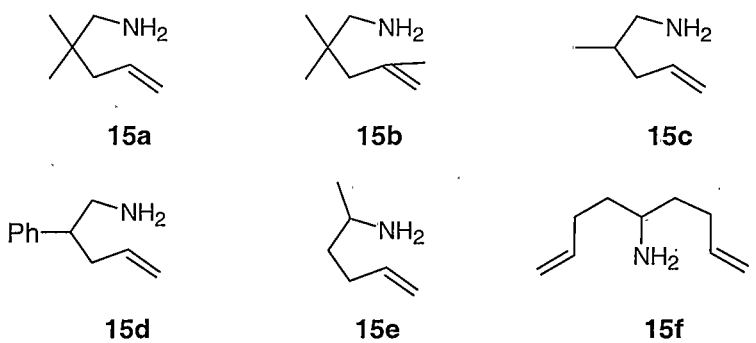
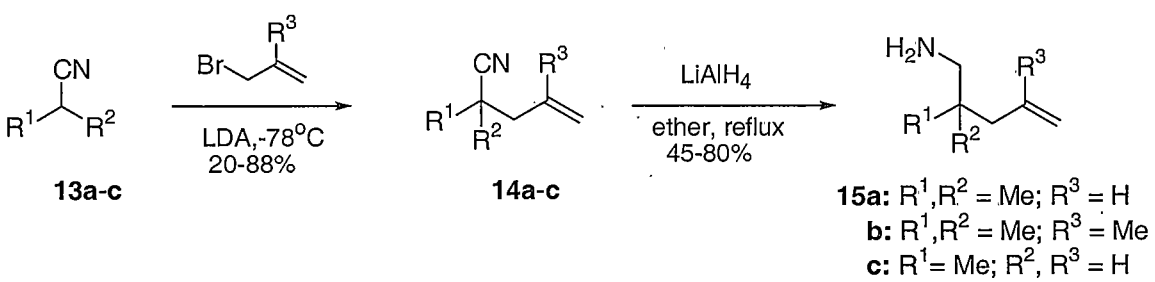


Figure 7. Aminoalkenes **15a-f**

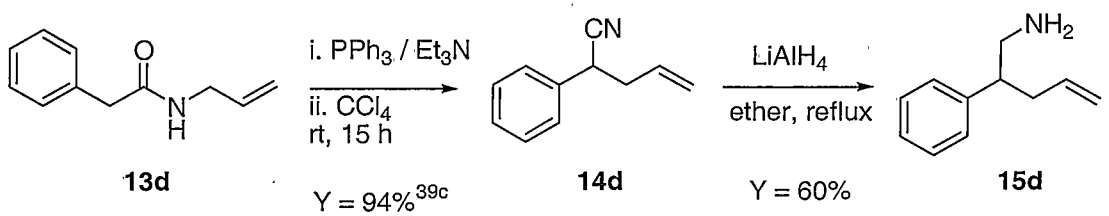
Aminoalkenes **15a-c** were prepared by the method described in Scheme 6. Various alkenyl halides were alkylated with lithiated nitriles generated by the reaction



Scheme 6. Synthesis of Aminoalkenes **15a**,**b**,**c**

with lithium diisopropylamine (LDA) at –78°C in 20-88% yield. The resulting nitriles **14a-c** were reduced with lithium aluminum hydride in ethyl ether followed by heating at reflux to provide the corresponding aminoalkenes **15a-c** in 45-80% yield.

As shown in Scheme 7, **14d** was prepared according to literature procedure [39c] from **13d** via a 3-Aza-Cope rearrangement. The nitrile **14d** was reduced by lithium aluminum hydride to provide the aminoalkene **15d** in 60% yield.



Scheme 7. Synthesis of Aminoalkene **15d**

2-Aminohex-5-ene **15e** and 1-but-3-enyl-pent-4-enylamine (**15f**) were prepared by the method described in Scheme 8. Treatment of **13e** or **13f** with two equivalents of hydroxylamine hydrochloride in ethanol/tetrahydofuran/water (4:2:1), followed by addition of sodium bicarbonate, afforded oxime **14e** or **14f** in 85% and 93% yield, respectively. Then, further conversion to aminoalkene **15e** or aminodiene **15f** was provided by the reduction with lithium aluminum hydride.

Scheme 8. Synthesis of Aminoalkenes **15e,f**

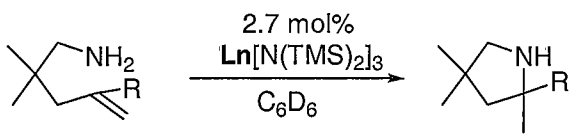
Each of these aminoalkenes was distilled from CaH_2 under an atmosphere of argon and stored in a dry box prior to hydroamination reactions.

INTRAMOLECULAR ALKENE HYDROAMINATIONS CATALYZED BY $Ln[N(TMS)_2]_3$

Our preliminary survey focused on the evaluation of $Y[N(TMS)_2]_3$ (**1a**) and $Nd[N(TMS)_2]_3$ (**1b**).[40] Among Group 3 metals, yttrium and neodymium were selected as representative smaller- and larger-sized lanthanides, respectively. The ionic radii of Y(III) and Nd (III) are1.040 Å and 1.123 Å, respectively, in 6-coordinate complexes.[41]

As revealed in Table 3 and Table 4, $Ln[N(TMS)_2]_3$ (**1**) complexes were shown to have excellent catalytic activity in intramolecular alkene hydroamination reactions. Aminoalkene **15a** cyclized smoothly to **16a** with 2.7 mol% of $Nd[N(TMS)_2]_3$ in C_6D_6 at 24°C in 4 h (>95 % yield), and with $Y[N(TMS)_2]_3$ at 24°C in 6 h. The size of the metal

Table 3. $Ln[N(TMS)_2]_3$ (**1**) Catalyzed Cyclization of Aminoalkenes **15a,b**



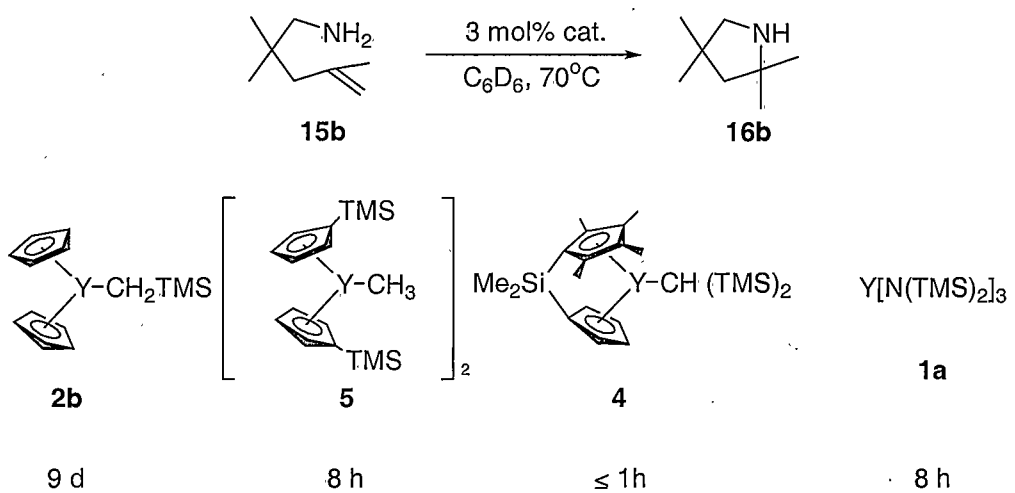
15a,b **16a,b**

	R	Ln	Temp (°C)	$t_{React.}$ [a]	Conv. [%] [b]
15a	H	**Y**	24	6 h	>95%
	H	**Nd**	24	4 h	>95%
15b	Me	**Y**	45	45 h	93 (80)[c]%
	Me	**Y**	70	8 h	94%[d]

[a] All reactions were conducted in C_6D_6. [b] Based on ^1H NMR integration. [c] Isolated yield as a *p*-toluenesulfonamide. [d] 3 mol% of catalyst was utilized.

did have an effect.[22h] The larger-metal neodymium complex furnished the cyclized product with a faster reaction rate than the smaller yttrium complex, which is in accord with the observations of the organolanthanocene-catalyzed cyclization.[22h]

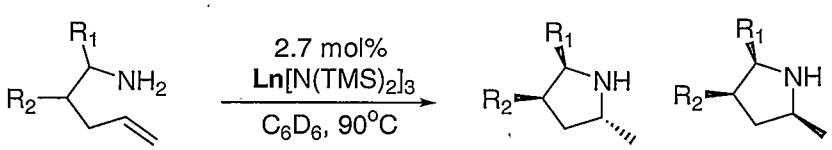
The simple amido Group 3 metal complexes exhibited excellent catalytic activities even with more hindered aminoalkenes such as **15b**. Aminoalkene **15b**, which has a protertiary center, was subjected to 3.0 mol% of $Y[N(TMS)_2]_3$ complex to afford 2,2-disubstituted pyrrolidine **16b** at 70°C in 8 h in 94% yield. On the other hand, cyclization using organolanthanocenes, Cp_2YCH_2TMS (**2b**), $[Cp^{TMS}{}_2YMe]_2$ (**5**) or $Me_2SiCpCp^*YCH(TMS)_2$ **4**, requires 9 d, 8 h, or $\leq$ 1 h, respectively,[15c] under the same reaction conditions (Scheme 9).



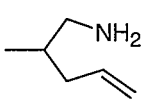
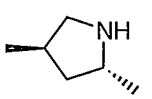
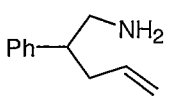
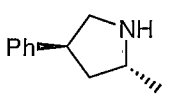
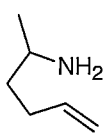
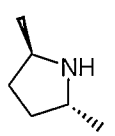
Scheme 9. Comparison of Catalytic Activities

The diastereocontrol of these $Ln[N(TMS)_2]_3$ complexes was investigated using aminoalkenes **15c,d,e** [Table 4]. In the case of **15e**, a highly diastereoselective cyclization was realized with $Y[N(TMS)_2]_3$ **1a** at 90°C to provide >95% yield in a ratio of 7:1 (*trans/cis*) in 6 d, whereas a 4:1 ratio of diastereoselectivity was obtained with $Nd[N(TMS)_2]_3$ **1b** at 90°C in 2 d. However, the cyclizations of C2-substituted aminoalkenes **15c** and **15d** proceeded with relatively low diastereoselectivity (1:1.7~2.2 = *trans/cis*). Moreover, the cyclization of aminoalkene **15c** and **15d** were insensitive to

Table 4. $Ln[N(TMS)_2]_3$ (**1**) Catalyzed Cyclization of Aminoalkenes **15c**, **d**, **e**



15c-e R_1, R_2 = H, Me or Ph **17c-e** **18c-e**

	Substrate	Ln	$t_{React.}$ [a]	Product	dr (*trans/cis*) [b]	Conv. (%) [b]
15c		**Y**	10 d	 + *cis*	1 : 2	>95
		Nd	7 d		1 : 2	>95
15d		**Y**	1.5 h	 + *cis*	1 : 1.7	95 (94)[c]
		Nd	1.5 h		1 : 2.2	>95
15e		**Y**	6 d	 + *cis*	7 : 1	94
		Nd	2 d		4 : 1	>95

[a] All reactions were conducted at 90°C. [b] Based on integration of the ^{1}H NMR spectrum; **17c** / **18c** : 0.81(d) / 0.90 (d) ppm; **17d** / **18d** : 1.02 (d) / 1.08 (d) ppm; **17e** / **18e** : 3.14 (septet) / 2.93 (m) ppm. [c] Isolated yield as a *p*-toluenesulfonamide.

the size of the metal in terms of cyclization rate and diastereoselectivity. Presumably, in sterically demanding transition states as shown in Figure 8 (**C**,**D**), the methyl or phenyl group of the aminoalkenes (**15c**,**d**) would be located far away from the metal center. Hence, the sterically hindered surrounding of the complex might less affect the diastereoselective cyclization of aminoalkenes (**15c**,**d**) than in the case of aminoalkene **15e** also shown in Figure 8 (**A**,**B**). Generally, the reaction rate was dependent on the metal size of the complex.

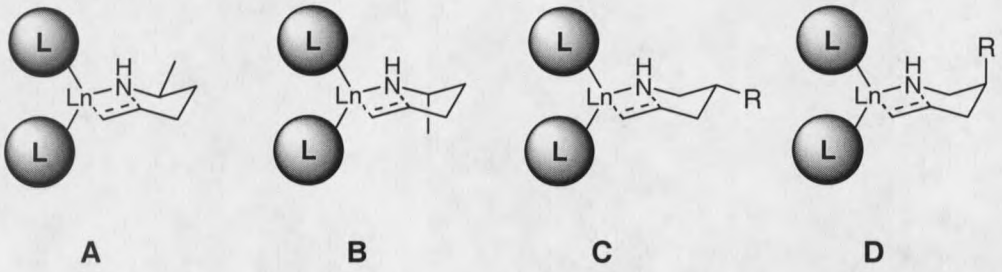
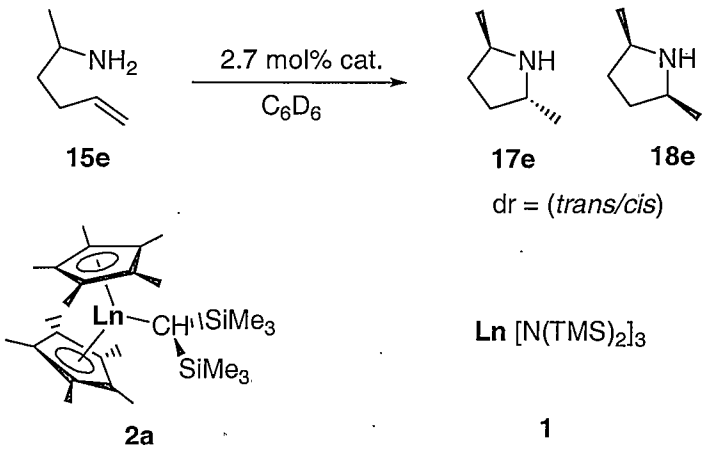


Figure 8. Rationalization of the Diastereoselectivity in the Cyclization of Aminoalkenes

The cyclization of **15d** proceeded notably faster than that of either **15c** or **15e**. The ancillary phenyl substituent in **15d** presumably accelerates the cyclization in a manner related to the Thorpe-Ingold effect.[32] In contrast, the sterically less hindered aminoalkene **15c** was cyclized very slowly. According to experimental observations, the aminoalkene formed a viscous solution with catalysts as soon as the substrate was added to the complex. The cyclization proceeded slowly only after it dissolved at 90°C.

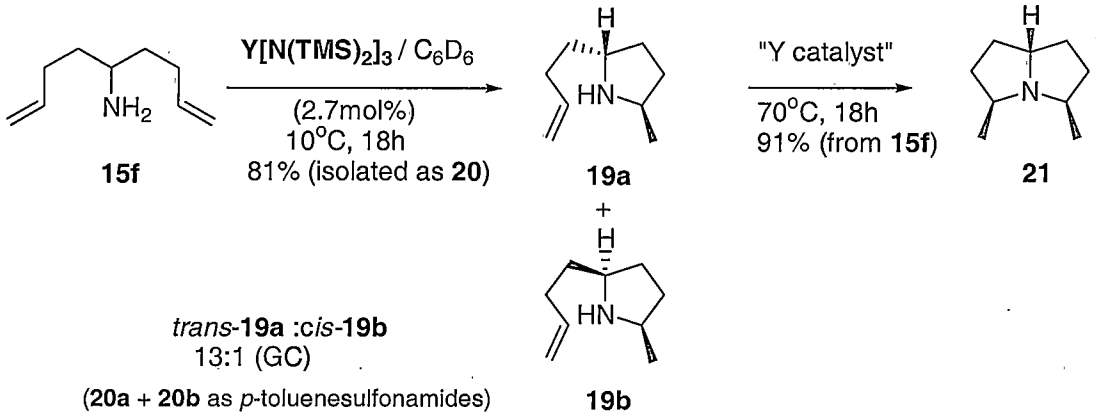
In comparison with the analogous aminoalkene cyclizations catalyzed by Group 3 metallocene complexes, $Cp^*_2LnCH(TMS)_2$ (**2b**) catalyzed the cyclization of **15e** to provide pyrrolidines (**17e, 18e**) with a 1:1.25 (Ln = Nd) and a 8:1 (Ln = Y) ratio of *trans /cis* diastereoselectivities at 25°C (Scheme 10), but reaction rates (N_t: turnover number) are not available.[22h]



Scheme 10. Comparison of Catalytic Activities

The simple amide Group 3 metal complexes have extended the scope of application by successful construction of a bicyclic compound. Aminodiene **15f** was subjected to 2.7 mol% of $Y[N(TMS)_2]_3$ (**1a**) in C_6D_6. As shown in Scheme 11, monocyclic compounds **19a** and **19b** were obtained with $Y[N(TMS)_2]_3$ at 10 °C over 18 h, then isolated to determine the ratio of diastereomers (**19a/19b** = 13:1 by G.C.) as a mixture of the corresponding *p*-toluenesulfonamides (**20a** and **20b**) in 81% yield.

Significantly, increasing the reaction temperature of **19a** and **19b** to 70 °C led to selective bicyclization of *trans*-**19a** to the expected pyrrolizine **21**[42] (91% overall yield) over 18 h. Under these conditions, *cis*-**19b** was inert toward cyclization and the corresponding pyrrolizine was not detected by ^{1}H NMR.



Scheme 11. Cataytic Activity of $Y[N(TMS)_2]_3$ in Bicyclizations

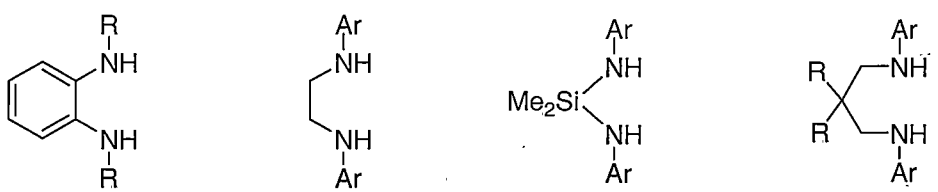
In summary, we have shown that simple amides of the type $Ln[N(TMS)_2]_3$ (**1**) display excellent catalytic activity in intramolecular alkene cyclizations. From this initial study, we have found that the reaction rates are affected more significantly by the structure of the substrate rather than by the metal size. Additionally, the $Ln[N(TMS)_2]_3$ complex has similar or superior activity in cyclization and diastereoselectivity to metallocene-based Group 3 complexes in several cases. Moreover, while metallocene-type catalysts have serious disadvantages in terms of their preparation and limited variety, the readily available non-metallocene-type catalysts $Ln[N(TMS)_2]_3$ should

provide a multitude of possible ligand variations. Significantly, this is the first application of non-metallocene-based Group 3 metal catalysis to intramolecular *aminoalkene* cyclization.

DRAMATIC RATE ENHANCEMENTS AND IMPROVED DIASTEREOSELECTIVITIES VIA CHELATING DIAMIDE COORDINATION

INTRODUCTION

Our development of non-metallocene-based Group 3 metal catalysts has allowed access to new types of complexes possessing bidentate ligands. It is well established that the catalytic activity of Group 3 metallocenes in aminoalkene hydroaminations is quite sensitive to steric perturbations surrounding the metal center.[15a,b,d] Thus, on the basis of electronic and steric factors and the pk_a value of protic amines, four categories of sterically hindered chelating diamide proligands were designed and synthesized.



22 **23** **24** **25**

Figure 9. Bidentate Proligands **22**, **23**, **24** and **25**

First, the bidentate proligands would lead to electronically and coordinatively unsaturated complexes with Group 3 metals. Presumably, a maximum of 12 electron and 3 coordination would be counted for **26-29** (Figure 10). In comparison, organo-lanthanocene **3** (Ln =Y) has an electron-deficient system with a maximum of 16 electrons

and is pseudo 7-coordinate,[57] but the electron deficiency is alleviated via an agostic interaction (Y···CH_3SiN-).[58a] Furthermore, complex **7** (Ln = Y) [58b] has a maximum of 14 electron and pseudo five-coordinate system[57] possessing an agostic interaction between yttrium and a methyl group (Y···CH_3SiN-).

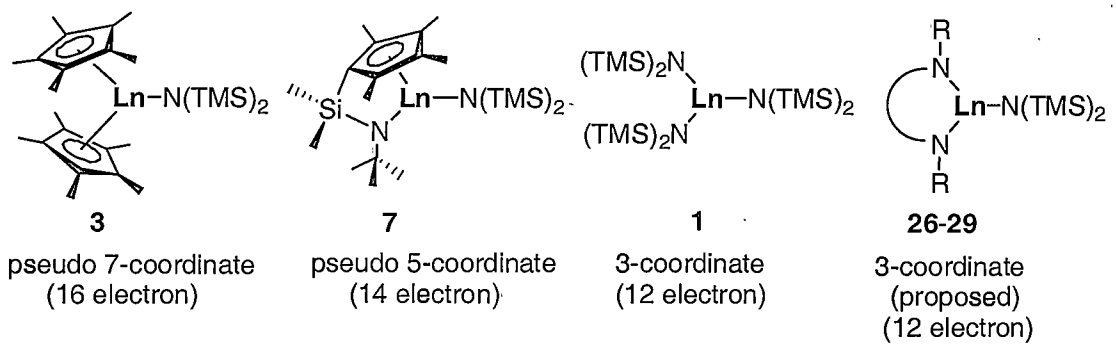
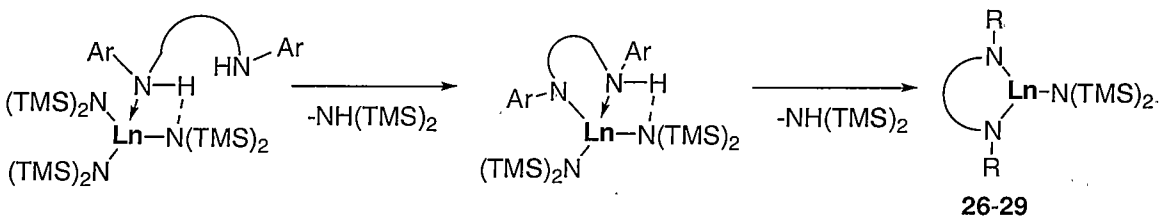


Figure 10. Coordinatively and Electronically Less Saturated Complexes

Second, the acidity of the amine is important for irreversible metallation, [39] and therefore feasible ligand exchange reactions. On the basis of the mechanism proposed by Anwander and co-workers,[43] it was assumed that the bidentate ligands would undergo Brőnsted-type acid-base reactions (Scheme 12). Proton transfer from the substrate to the amide nitrogen is the key step for a ligand exchange. After transfer of the "acidic" proton onto the amide nitrogen, dissociation of the protonated silylamine will occur. Sequential proton transfer would allow the second displacement of amine by the chelating ligand. Thus, the acidity of protic amine should be one of the crucial factors for a facile ligand exchange reaction.



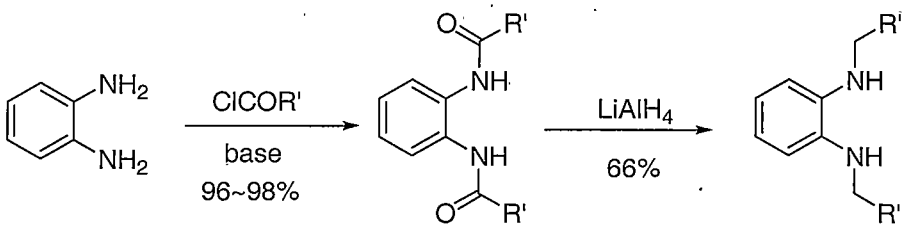
26-29

Scheme 12. Proposed Mechanism for Ligand Exchange Reaction

The sterically hindered and electronically less saturated chelating diamide complexes **26-29** might play an important role in altering the reactivity profile of Group 3 amido complexes.

SYNTHESIS OF PROLIGANDS

As shown in Scheme 13, ligands **22** were prepared according to a well-established literature procedure.[44] A solution of 1,2-phenylenediamine (**31**) in dichloromethane was treated with the requisite acyl chloride (2.1 equiv) via dropwise addition at 0 °C,

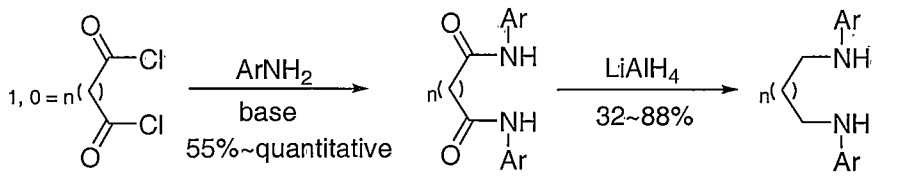


31 **32** **22**

Scheme 13. Synthesis of Proligands **22**

using triethylamine (2.5 equiv) as a scavenger for HCl. Then the bisamides (**32**) were reduced with lithium aluminum hydride to provide the corresponding proligands (**22**).

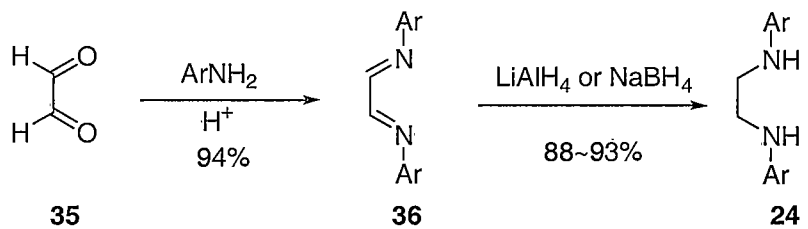
The diaryl derivatives were prepared via four different methods following a modified literature procedure.[45] First, as the most generally used method (Scheme 14),



33 **34** **23, 25b**

Scheme 14. Synthesis of Proligands **23** and **25b**

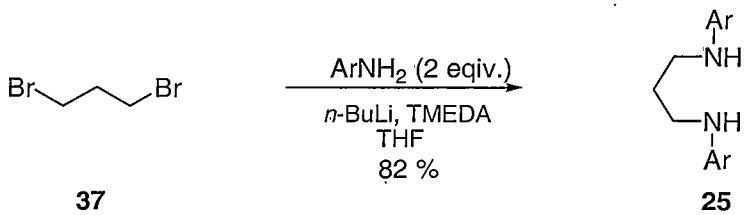
oxalyl chloride or malonyl dichloride (**33**) was subjected to a solution of aryl amine (2 equiv) containing triethylamine (2.5 equiv) in tetrahydrofuran at 0°C, and then the reaction mixture was allowed to stir at room temperature or heated at reflux depending on the aryl amine used. The resulting diaryl amides (**34**) were then reduced to diaryl amines (**23**) via conventional methods using lithium aluminum hydride. However, in the case of sterically hindered compounds such as the one having a 2-isopropylphenyl moiety, heating at reflux in tetrahydrofuran for several days was required. Second, as shown in Scheme 15, glyoxal (**35**) and a catalytic amount of formic acid were utilized for the condensation reaction with the aryl amine (2 equiv) in methanol to provide diimine intermediates at room temperature. The diaryl amine compounds (**24**) were prepared using the typical reduction method from the resulting diimines (**36**) with lithium



Scheme 15. Synthesis of Proligands **24**

aluminum hydride or sodium borohydride.[46] The diaryl diamine compounds were prepared via alternative procedures.[47] Aryl amines were lithiated (1.9 equiv) by *n*-butyllithium (1.9 equiv) in tetrahydrofuran at –78-22°C; then sequential addition of

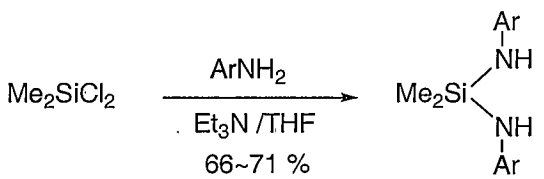
tetramethylethylenediamine (TMEDA) (1.9 equiv) and 1,3-dibromopropane (1 equiv) with stirring at room temperature afforded the corresponding diaryl amines (**25**).



37 **25**

Scheme 16. Synthesis of Proligands **25**

Finally, ligand **24** was readily prepared by heating at reflux a mixture of dichlorodimethylsilane and aryl amine (2 equiv) and triethylamine (2 equiv) in tetrahydrofuran (Scheme 17).

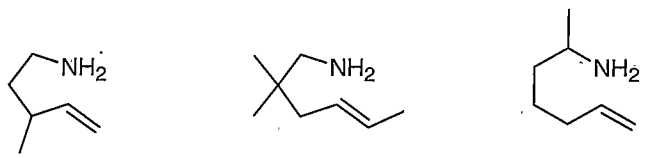


38 **24**

Scheme 17. Synthesis of Proligands **24**

SYNTHESIS OF SUBSTRATES

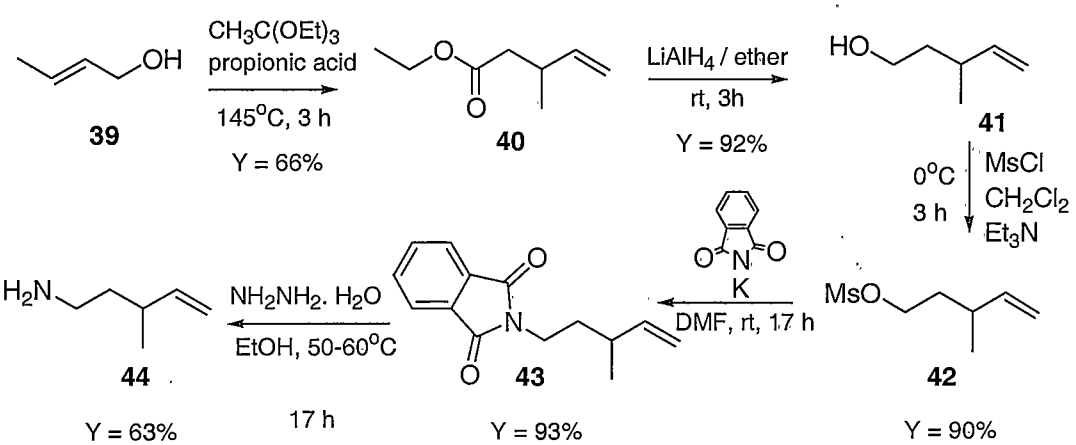
To investigate the scope of the catalysts derivered from the aforementioned amines, three more aminoalkenes **44**, **47** and **50** were prepared using literature procedures or slightly modified methods.[15a]



44 **47** **50**

Figure 11. Aminoalkenes **44**, **47** and **50**

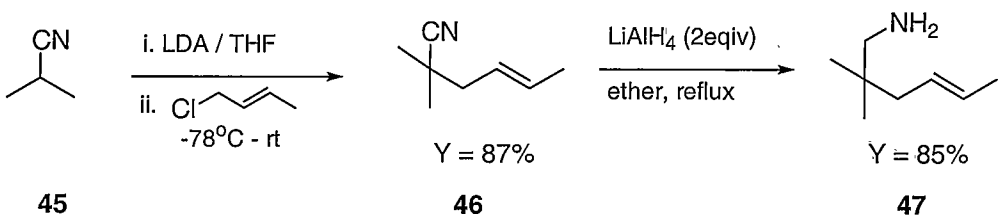
3-Methylpent-4-enylamine (**44**) was prepared from (*E*)-2-butene-1-ol in five steps (Scheme 18). The (*E*)-2-butene-1-ol (**39**) was transformed to ester **40** via the Johnson-Claisen rearrangement in the presence of triethyl orthoacetate at 145 °C in 66% yield.[48] The ester was reduced by lithium aluminum hydride to afford alcohol **41** in 92% yield,



Scheme 18. Synthesis of Aminoalkene **44**

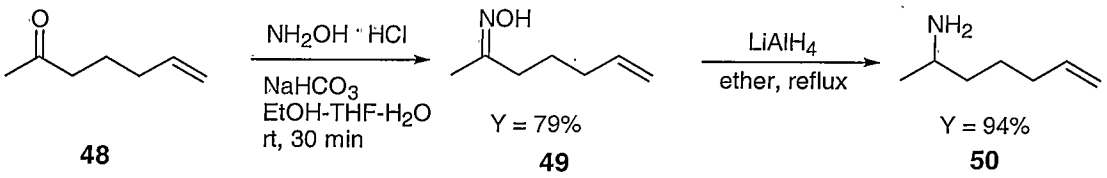
then the resulting alcohol was converted to sulfonate **44** in 90% yield. The Gabriel reaction of the sulfonate with potassium phthalimide, followed by treatment with hydrazine monohydrate in ethanol at 50-60 °C, produced aminoalkene **44** in 58% yield over two steps.

As shown in Scheme 19, isobutyronitrile (**45**) was lithiated by lithium diisopropylamine at –78°C, followed by addition of crotyl chloride to afford nitrile **46** in 87% yield. The resulting nitrile compound was reduced using lithium aluminum hydride to provide 1,2-disubstituted aminoalkene **47** in 85% yield.[15a] The aminoalkene **47** was found to contain 19% of the corresponding (**Z**)-isomer by ^{1}H-NMR.



Scheme 19. Synthesis of Aminoalkene (**47**)

Finally, 1-methylhex-5-enylamine (**50**) was synthesized from hept-6-en-2-one (**48**) via condensation with hydroxylamine, followed by reduction of the resulting oxime (**49**) using the typical method in 74% yield over two steps (Scheme 20).



48 **49** **50**

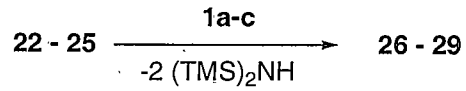
Scheme 20. Synthesis of Aminoalkene **50**

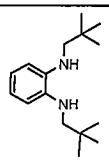
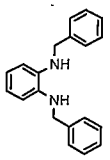
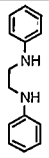
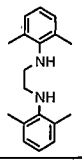
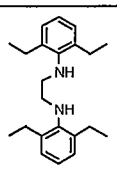
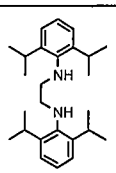
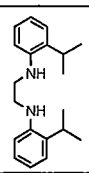
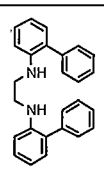
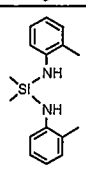
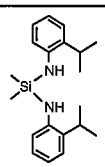
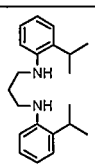
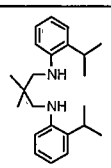
GENERATION OF GROUP 3 AMIDO COMPLEXES IN SITU

As revealed in Table 5, the ligand exchange reactions between the various ligands and $Ln[N(TMS)_2]_3$ (Ln = Y **1a**; Nd **1b**; La **1c**) were successful. The reaction between aryl amines and one equivalent of $Ln[N(TMS)_2]_3$ proceeded smoothly in <1 h ~ 15 days at 120°C. Metallation of the hindered diamines (**23**) via amine elimination was comparatively slow relative to **22**. On the other hand, the ligand exchange reactions were accelerated by increasing the temperature to 150 °C. As an example, the reaction between **1a** and **23h** required five days at 120 °C in C_6D_6, but the same reaction proceeded in only 5 h at 150 °C in toluene-d_8. Significantly, no decomposition of the amido complexes was observed even at these high temperatures. Therefore, these amido chelates have superb thermal stability as contrasted with the metallocene complexes synthesized by Marks and co-workers, that were partially decomposed and deactivated at 120°C.[15a]

The completion of ligand exchange was determined by ^1H NMR at the point when the TMS peak in $Ln[N(TMS)_2]_3$ disappeared by more than 90% and concomitantly there appeared a peak for free $HN(TMS)_2$ at 0.08 ppm.

Table 5. Generation of Group 3 Amido Complexes in Situ



	Proligands	$t_{Reac.}$ (120°C) [a]		Proligands	$t_{Reac.}$ (120°C) [a]
22a		**Y** : 15 min	**22b**		**Y** : 15 min
23a		**Y** : 10 d	**23b**		**Y** : 6 d **(b)** **Nd** : 2 d **(c)** **La** : 15 h **(d)**
23e		**Y** : 9 d **(e)** **Nd** : 5 d **(f)**	**23g**		**Y** : 23 d (8 d / 150 °C) [b]
23h		**Y** : 5 d **(h)** (5 h / 150°C) [b] **Nd** : 2 d **(i)** **La** : 15 h **(j)**	**23k**		**Y** : 12 h
24a		**Y** : 13 d	**24b**		**Y** : 2 d
25a		**Y** : 15 d	**25b**		**Y** : 13 d / 150 °C [b]

[a] All reactions were conducted in C_6D_6. [b] The reactions were conducted in Toluene-d_8

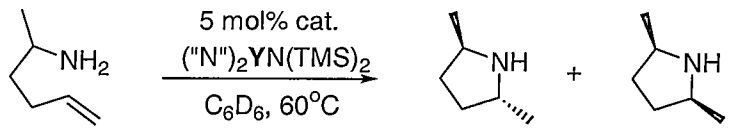
THE INTRAMOLECULAR HYDROAMINATION OF AMINOALKENE BY GROUP 3 AMIDO COMPLEXES GENERATED IN SITU

As part of our previous study,[39] we noted that the addition of representative aminoalkenes to catalytic quantities (2.7 mol%) of $Y[N(TMS)_2]_3$ (**1a**) or $Nd[N(TMS)_2]_3$ (**1b**) in C_6D_6 at 24°C resulted in the immediate and apparently quantitative liberation of $(TMS)_2NH$ with concomitant generation of the corresponding and presumably amine-ligated[50] amido complexes. The catalytic activity of these amido chelate complexes relative to $Y[N(TMS)_2]_3$ (**1a**) was first examined in the diastereoselective cyclization of the racemic aminoalkene (**15e**).

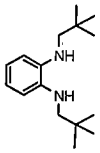
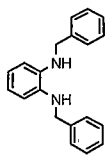
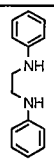
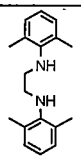
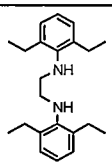
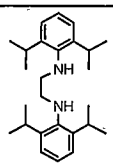
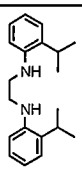
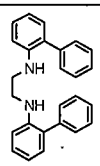
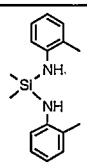
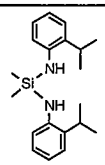
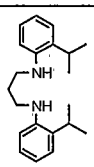
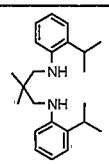
A compilation of reaction times and diastereoselectivities observed for the cyclization of aminoalkene **15e** in the presence of yttrium chelates **26-29** appears in Table 6. These Group 3 metal complexes prepared in situ exhibited dramatically increased catalytic activity in the hydroamination reaction and increased cyclization diastereoselectivity. [51]

Five-membered chelates **27b-h** derived from sterically hindered diamines **23b-h** are clearly superior in catalytic activity relative to complexes **26a,b**. Whereas the cyclization of **15e** to the pyrrolidines (**17e**, **18e**) in the presence of 5 mol% of $Y[N(TMS)_2]_3$ (**1a**) at 60 °C was extremely lethargic, requiring 31 days to reach 95% conversion (**17e/18e** = 9:1),[52] cyclization was >95% complete in 15 min at 60 °C in the presence of 5 mol% of **27h** (**17e/18e** = 19:1). Even though **27g** also had high catalytic activity towards cyclization, it provided somewhat lower diastereoselectivity than that of

Table 6. Catalyzed Cyclization of 2-Aminohex-5-ene (**15e**)



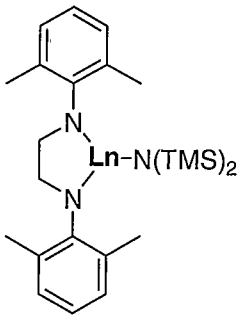
15e **17e** **18e**

Cat.	Ligands	$t_{Reac.}$ (60°C)[a] **d.r. (17e : 18e)**[b] **conv. (%)**[b]	Cat.	Ligands	$t_{Reac.}$ (60°C)[a] **d.r. (17e : 18e)**[b] **conv. (%)**[b]
26a		48 h (11 : 1) >95%	**26b**		240 h (10 : 1) 93%
27a		240 h (10 : 1) >95%	**27b**		70 min (19 : 1) >95%
27e		30 min (18 : 1) >95%	**27g**		15 min[c] (13 : 1) >95%
27h		15 min (19 : 1) >95%	**27k**		144 h (12 : 1) >95%
28a		11 h (19 : 1) >95%	**28b**		2 h (16 : 1) >95%
29a		42 h (11 : 1) >95%	**29b**		90 min (14 : 1) >95%

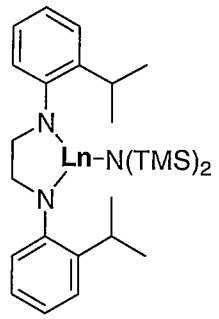
[a] All reactions were conducted at 60°C. [b] Based on integration of the ^{1}H NMR spectrum; **17e** / **18e** : 3.14 (septet) / 2.93 (m) ppm. [c] This reaction was conducted in toluene-d_8

similar type of proligands **27b**, **27e** and **27h**. In the case of **29b** compared with **29a**, the ancillary dimethyl group attached to propylenediamine backbone remarkably increased both cyclization rate (90 min in >95 % yield) and diastereoselectivity (**17e/18e** = 14:1).

The representative proligands **23b** and **23h**, and Group 3 metals, yttrium, neodymium, and lanthanum, were selected for the investigation of metal-size effect on the cyclization of aminoalkene **15e**. The ionic radii of Y(III), Nd (III) and La (III) are 1.040 Å, 1.123 Å and 1.172 Å, respectively, in 6-coordinate complexes.[40]



27b: Ln = Y
27c: Ln = Nd
27d: Ln = La



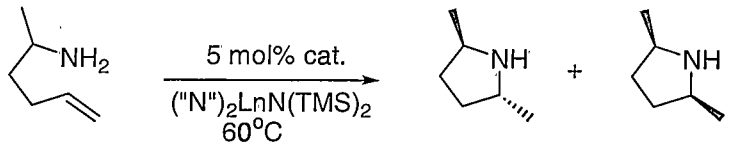
27h: Ln = Y
27 i: Ln = Nd
27 j: Ln = La

Scheme 21. Catalysts **27b-d**, **27h-j**

Interestingly, as shown in Table 7, these metal complexes exhibited unexpected results. In contrast to the case of organolanthanocenes, these non-metallocene complexes exhibited higher catalytic activity with the smaller Group 3 metals. That is, the order of the catalytic activity is Y > Nd > La. Presumably, the larger metal is more available for

ligation by substrate **15e**, with the consequence that catalytic activity may be reduced.

Table 7. Catalyzed Cyclization of 2-Aminohex-5-ene (**15e**)

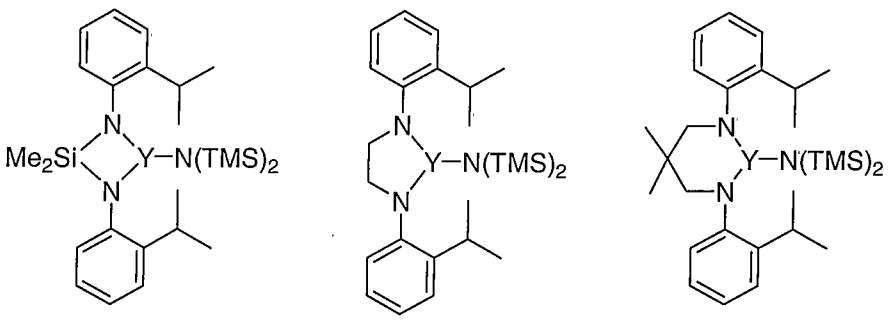


15e **17e** **18e**

Entry	Complex	Ln	$t_{React.}$ [a]	d.r. (17e : 18e) [b]	Conv. [%] [b]
1	**27b**	Y	70 min	19 : 1	>95%
2	**27h**	Y	15 min	19 : 1	>95%
3	**27c**	Nd	2 h	13 : 1	>95%
4	**27 i**	Nd	6 h	13 : 1	>95%
5	**27d**	La	13 h	11 : 1	>95%
6	**27 j**	La	9 h	10 : 1	>95%

[a] All reactions were conducted at 60°C. [b] Based on integration of the ^{1}H NMR spectrum; **17e** / **18e** : 3.14 (septet) / 2.93 (m) ppm.

As shown in Scheme 22, opening of the coordination sphere at yttrium using diamines **24**, which create four-membered chelates with metals, [53] resulted in catalysts (e.g., **28b**) that possess lower activity (**17e/18e** = 16:1, 2 h at 60°C in >95% yield) when compared with **27h** (**17e/18e** = 19:1, 15 min at 60°C in >95% yield). Six-membered chelates (e.g., **29b**) reminiscent of the zirconium complexes reported by McConville[54] are comparatively inferior in terms of activity as well as stereoselectivity (**17e/18e** = 13:1, 90 min at 60°C in >95% yield) to **27h**.



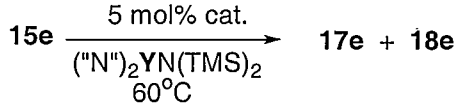
28b | **27h** | **29b**

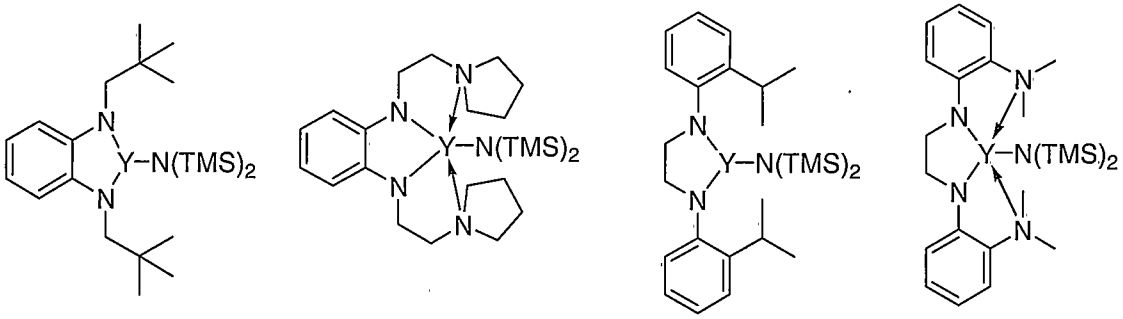
t = 2 h
17e/18e = [16 : 1]

15 min
[19 :1]

90 min
[13 : 1]

Scheme 22. Hydroamination by Catalyst **28b, 27h** or **29b**





26a | **30** | **27h** | **31**

48 h / 60°C
(11 : 1) >95%

84 h / 60°C
(19 : 1) >95%

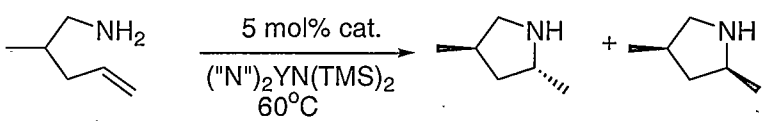
15 min / 60°C
(19 : 1) >95%

17 h / 60°C
(7 : 1) >95%

Scheme 23. Catalyzed Cyclization of 2-Aminohex-5-ene (**15e**)

The incorporation of secondary ligating domains, as in complex **30**, resulted in a decreased conversion rate but improved diastereoselectivity (**17e/18e** = 19:1, 84 h at 60°C in >95% yield) when compared to chelate structures such as **26a** that possess simple alkyl substituents. However, in diaryl amine complex **31**, the secondary ligating moiety gave a significant negative effect on both reaction rate and diastereoselectivity to provide 7:1 (**17e/18e**) ratio of diastereoslectivity at 60°C in >95% yield in 17 h.

Table 8. Catalyzed Cyclization of 2-Methylaminohex-4-ene (**15c**)



15c **17c** **18c**

Complex	$t_{React.}$ [a]	d.r. (17c : 18c) [b]	Conv. [%] [b]
27b	120 h	1 : 1.4	>95%
27e	61 h	1 : 1.5	>95 % (99)[c]
27h	40 h	1 : 1.3	>95%

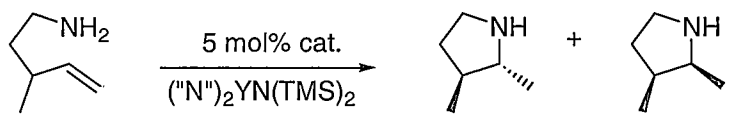
[a] All reactions were conducted at 60°C in C_6D_6. [b] Based on integration of the ^{1}H NMR spectrum; **17c** / **18c** : 0.81(d) / 0.90 (d) ppm. [c] Isolated yield as phosphonamides.

In a study to obtain an estimate of the substrate control of diastereoselectivity leading to the formation of substituted pyrrolidines, aminoalkene **15c** was subjected to cyclization in the presence of 5 mol% of **27b, 27e** and **27h**. As observed in the case of $Ln[N(TMS)_2]_3$, the cyclization of **15c** proved less selective, providing pyrrolidines **17c**

and **18c** with a *trans/cis* ratio of only 1:1.3~1.5. In the case of cyclization with **27e**, the resulting amines were isolated as the corresponding phosphonamides in 99% yield to confirm the stereochemistry (Table 8).[55]

As shown in Table 9, aminoalkene **44** was cyclized by **27e** to 2,3-disubstituted pyrrolidines **51a** and **51b.** Although higher temperatures were required to complete the cyclization, the reaction furnished a diastereomeric ratio of 9:1 at 120°C in >95% yield. In addition, the pyrrolidines **51a** and **51b** were isolated as the corresponding *p*-toluenesulfonamides in 81% yield. In this case, the complex **27e** formed a slurry with the substrate during the hydroamination reaction. Presumably, the sterically less hindered aminoalkene **44** ligated the complex **27e** to form a heterogeneous mixture solution, which may have reduced effective catatytic activity in cyclization.

Table 9. Catalyzed Cyclization of 3-Methylaminohex-4-ene (**44**)



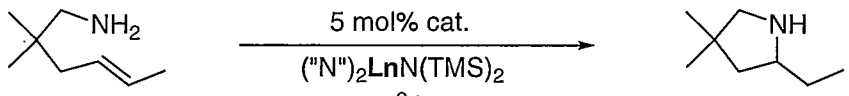
44 **51a** **51b**

Complex	Temp. (°C)	$t_{React.}$ [a]	d.r. (51a : 51b)[b]	Conv. [%][b]
27e	60	7 d	13 : 1	49%
	90	5 d	10 : 1	76%
	120	14 h	9 : 1	>95% (81)[c]

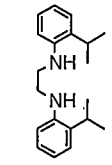
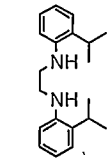
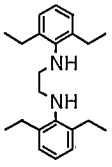
[a]All reactions were conducted in toluene-d_8. [b]based on integration of the ^{1}H NMR spectrum; **51a / 51b** : 1.01 (d) / 0.75 (d) ppm. [c] Isolated as a *p*-toluenesulfonyl amide.

1,2-Disubstituted alkenes have been shown to be the least reactive carbon-carbon double bonds toward intramolecular hydroamination studied thus far.[15a] Despite this, aminoalkene **47** was efficiently converted into pyrrolidine **52** at 125 °C over 12, 11 and 6.5 hours in the presence of 5 mol% of **27e**, **27h** and **27i**, respectively (Table 10). These results are noteworthy as the catalytic activities of these first-generation Group 3 chelates are comparable, and in the case of **27e**, superior to those of the sensitive and less accessible metallocene complexes described by Marks and co-workers (Scheme 24).[15a]

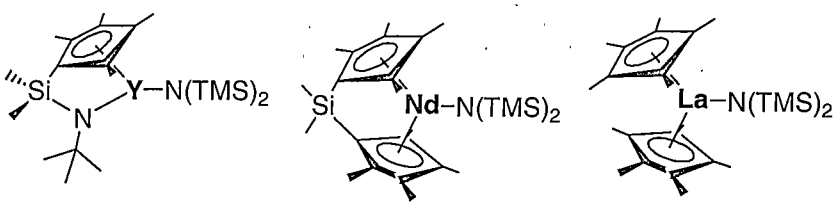
Table 10. Catalyzed Cyclization of 2,2-Dimethylaminohex-4-ene (**47**)



47 **52**

Complex	Proligand	Ln	t_{Reac} [a]	Yield [b]
27h		Y	12 h	>95%
27i		Nd	11 h	>95%
27e		Nd	6.5 h	>95%

[a]All reactions were conducted in toluene-d_8. [b] Based on integration of the ^{1}H NMR spectrum

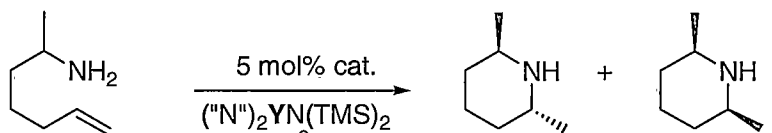


3.3 mol% Y (19 h / >95%) | 5.0 mol% Nd (19 h / >95%) | 4.8 mol% La (12 h / >95%)

Scheme 24. Lanthanocene-Catalyzed Cyclization of **47**

Complexes **26a** and **27b,e,h** were next examined for the diastereoselective cyclization of aminoalkene **50** to piperidines **53a** and **53b** (Table 11). Although these reactions were slower and less stereoselective than those involving aminoalkene **15e**,

Table 11. Catalyzed Cyclization of 2-Aminohept-6-ene (**50**)



50 **53a** **53b**

Complex	$t_{React.}$ [a]	d.r. (53a : 53b) [b]	Conv. [%] [b]
26a	10 h	1 : 4	>95%
27b	45 min	1 : 4	>95%
27e	<15 min	1 : 4	>95%
27h	100 min	1 : 5	>95%

[a] All reactions were conducted at 120°C. [b] Based on integration of the ^{1}H NMR spectrum; **53a/53b**: 2.95 (m) / 2.46 (m) ppm.

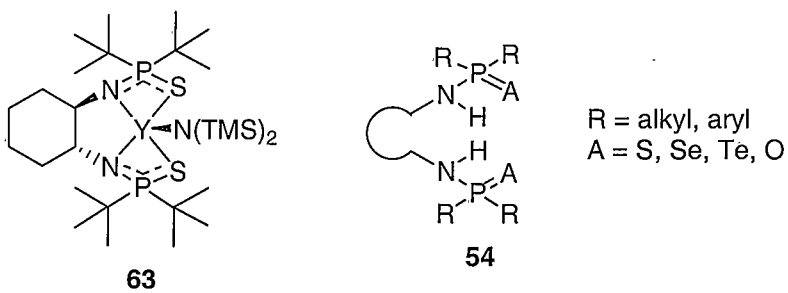
similar trends in catalytic activity were observed, with **27b,e,h** showing the highest activities. The notable activity of complex **27e** as compared to **27b** or **27h** in this transformation further emphasizes the sensitivity of intramolecular aminoalkene hydroaminations to steric perturbations within the ligand domain.

In summary, we have demonstrated that the modification of the metal center in $Ln[N(TMS)_2]_3$ (Ln = Y, Nd) is readily achieved by amine elimination in the presence of hindered chelating diamines, in situ, to provide new Group 3 metal chelates. In addition, the complexes have shown substantially improved catalytic activities and stereoselectivities in intramolecular aminoalkene hydroamination. In contrast to organolanthanocenes, these amido complexes normally exhibited the greatest activity with yttrium, and are robust at high temperatures. [15a]

TETRADENTATE LIGAND-BASED GROUP 3 METAL COMPLEXES: CHELATING (THIO, SELENO, TELLURO)PHOSPHORANMIDE LIGANDS

INTRODUCTION

As part of a more general study of the non-metallocene-based Group 3 metal complexes, we designed a new type of proligand possessing an ancillary chelating moiety based on the informative X-ray crystallographic structure of **63** (Figure 12).



63 **54**

Figure 12. Complex **63** and Tetradentate Proligands

Recently, some NPA ligand systems were introduced into transition metal complexes.[56] However, there have been remarkably few investigations concerning the catalytic activity of NPA type (A = S, Se, Te and O) ligand-based complexes for organic synthesis.

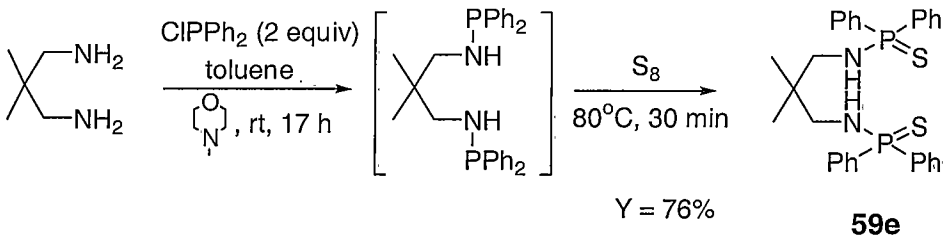
NPA ligand systems would afford electronically unsaturated maximum 16-electron system complexes, which are common in organolanthanocenes.[57] By employing NPA systems possessing acidic proton amines, the limitations in the selection of the

ancillary group will be reduced even when compared to the diaryl diamine ligands described in the second section of this dissertation. To investigate the chelating effect of the ancillary atom, Group 16 elements (A = S, Se, Te and O) were selected as components in the NPA systems. It is well known that sulfur and selenium have high coordination abilities toward cationic metal centers and have large van der Waals radii [41,55] (S: 1.80 Å; Se: 1.90 Å). Tellurium also has a large van der Waals radius (2.06 Å). The order of electronegativity is inversely related to radius (e.g., Pauling electronegativity S: 2.58; Se: 2.55 and Te: 2.1 Pauling units [41].

Based on these properties, we expected that these new types of proligands could play a special role for the formation of non-metallocene-based Group 3 metal complexes, which might possess good catalytic activity for reactions of synthetic interest.

SYNTHESIS OF PROLIGANDS

As a representative example of the preparation of NPA-type (A = S, Se, Te) ligands, compound **59e** was prepared by a modified literature procedure as shown in Scheme 25.[58] 2,2-Dimethylpropane-1,3-diamine was treated with chlorodiphenyl-phosphine in toluene, using 4-methylmorpholine as the base. The resulting white precipitate was rapidly filtered with care being taken to minimize exposure to air, and the



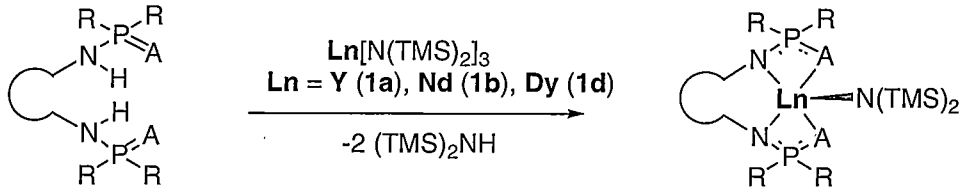
Scheme 25. Synthesis of Proligand **59e**

cake was leached with dry toluene. Sulfur, selenium or tellurium was then added in portions to the reaction mixture (exothermic). The reaction mixture was heated to 80 °C with stirring for 30 min under argon. The crude product was subsequently recrystallized from methylcyclohexane. For some other proligand cases, *N,N*-diisopropylethylamine was used instead of 4-methylmorpholine as the HCl scavenger.

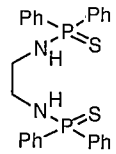
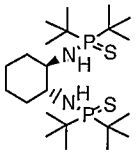
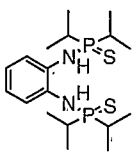
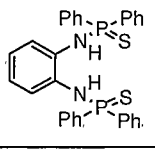
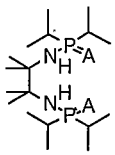
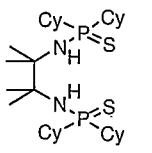
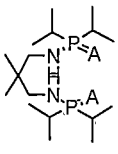
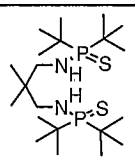
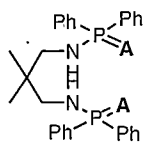
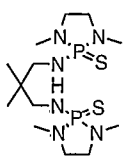
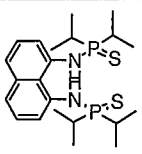
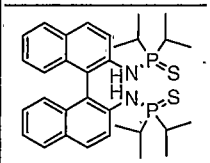
GERERATION OF TETRADENTATE LIGAND-BASED GROUP 3 COMPLEXES IN SITU

As shown in Table 12, the reactions between $Ln[N(TMS)_2]_3$ (Ln = Y **1a**; Nd **1b**; Dy **1d**) and proligands **55-61** proceeded more rapidly than in the cases involving the diaryl ethylenediamine backbone proligand described in the previous section. Presumably the NPA systems, which possess more acidic protons than diamines, resulted in accelerated ligand exchange reactions with $Ln[N(TMS)_2]_3$. In particular, incorporation of an aromatic moiety as an inductively electron-withdrawing group within the NPA backbone allowed for much faster reactions than those with alkyl moieties. Most of the proligands (**55**, **77b**, **59e**, **60** and **61**) containing the aromatic group, except **57a**, underwent the ligand exchange reaction within 15 min. On the other hand, the sterically bulky and electron-donating moiety in proligand **59g** retarded the ligand exchange reaction. Unexpectedly, the **59a** ligand exhibited a very fast metal incorporation, even though it has an electron-donating alkyl moiety as the ancillary group.

Table 12. Generation of Tetradentate Ligand-Based Group 3 Metal Complexes



55-61 **62-68**

	Proligands	$t_{Reac.}$ (120°C)[1]		Proligands	$t_{Reac.}$ (120°C)
55		< 30 min	**56**		13 h
57a		4 h	**57b**		< 15 min
58 a,d		**S** : 10 d **(Y)** (a) : 10 d **(Dy)**[2] (b) : 45 min **(Nd)** (c) **Se** : 9 d **(Y)** (d)	**58e**		10 d
59 a-c		**S** : < 30 min (a) **Se** : < 15 min (b) **Te** : < 15 min (c)	**59d**		2 d
59 e,f		**S** : 10 min (e) **O** : < 15 min / rt (f)	**59g**		2 d
60		< 15 min	**61**		< 15 min

[1] All reactions were conducted in C_6D_6 at 120°C; [2] At 150°C (toluene-d_8)

X-RAY CRYSTALLOGRAPHIC STUDIES

In the case of **63**, colorless crystals were successfully grown in toluene under a nitrogen atmosphere, and X-ray diffraction data were collected at a low temperature. The structure of complex **63** is shown below (Figure 13). As expected, X-ray analysis has exhibited that two ancillary chelating sulfurs are bonded to the cationic metal and the yttrium atom is slightly out of the square plane resulting in a slightly distorted square pyramidal geometry (Figure 14).

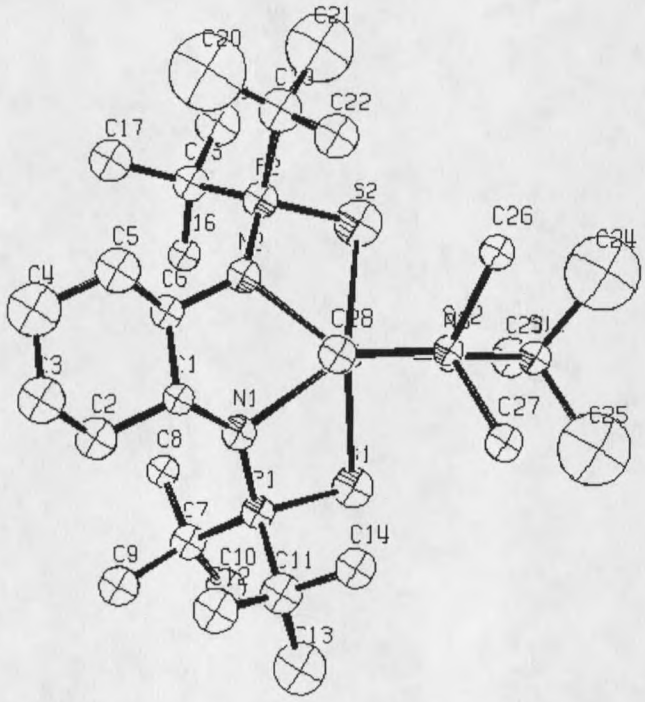
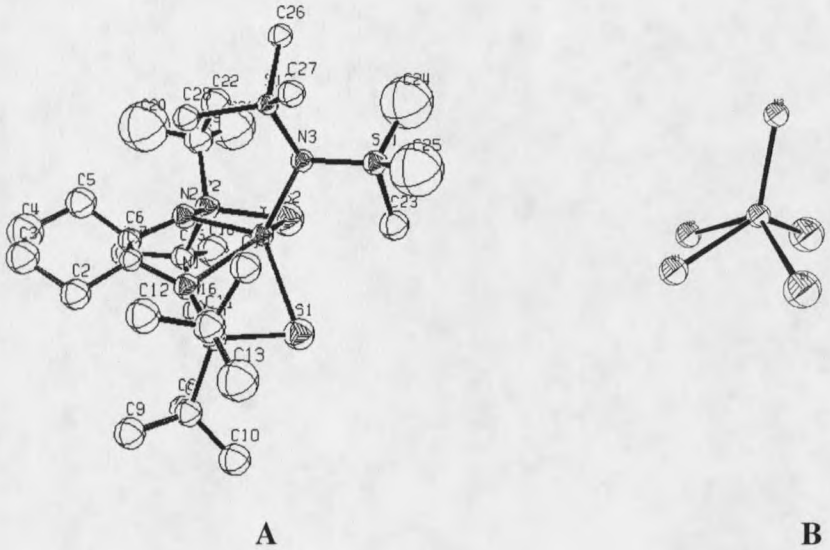


Figure 13. View from Perpendicular Angle to Square Plane (S1-N1-N2-S2) of **63**



A **B**

Figure 14. (A) View from an Acute Angle to Square Plane (S1-N1-N2-S2) of **63**
(B) Simplified Structure of **A**

Significantly, this less coordinated chelate is very unusual among organolanthanide complexes, since eight, ten, or twelve coordination numbers are normally found in the lanthanides due to their large metal size. On the other hand, all organolanthanide complexes that are utilized for hydroamination contain a cyclopentadieneyl (Cp^*) group and thus have a coordination number pseudo 5 or 7, forming a 14- or 16-electron system.[18]

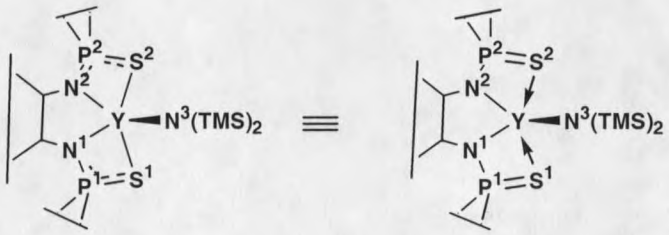


Figure 15. Core Structure of **63**

X-ray analysis revealed that the bond lengths between Y--S(1) [2.7409 (11) Å] and Y--S(2) [2.7179 (11) Å] as well as between Y--N(1) [2.314 (3) Å] and Y--N(2) [2.309 (3) Å] are a little different, which implies that complex **63** has a distorted geometry. The bond length of Y--N(3) [2.234 (3) Å] is significantly shorter than those of Y--N(1) [2.314 (3) Å] and Y--N(2) [2.309 (3) Å]. Whereas the electron densities of N(1) and N(2) are delocalized to the NPS system by resonance, the localized lone pair electrons on N(3) are presumably donated by a π-dative bond to the electronically unsaturated yttrium atom.[59] That is, the stong bond would be due to the additional π-donation from the filled N(3) *p* orbital to vacant Y *d* orbital (Figure 16) as well as the N(3)-Y σ-bond.[60]

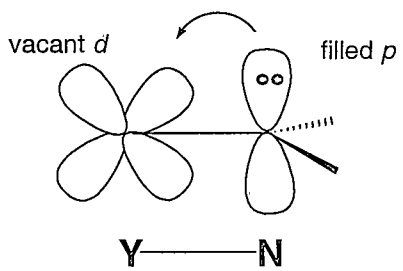


Figure 16. Electron Donation from the Filled *p* Orbital of N to the Empty *d* Orbital of Y

In comparison with organolanthanocenes, the bond length of Y--N(3) [2.234 (3) Å] **63** is shorter than that of $Cp^*_2YN(SiMe_3)_2$ (**2**) [Y--$(SiMe_3)_2$: 2.274 (5) Å and 2.253 (5) Å], which has two independent molecules in the asymmetric unit,[59] and that of [$Cp^*Si(Me_2)N$-*t*-C_4H_9)]$YN(SiMe_3)_2$ **7**, [Y--$N(SiMe_3)_2$: 2.255 (8) Å].[60] In the case of **7**, a

strong bonding by the ligand [Y--N(*t*-C_4H_9)($SiMe_2Cp^*$): 2.184 (7) Å] might make a sterically more hindered metal center.

The comparatively shorter bond length of Y--N(3) **63** may imply that the metal yttrium is electronically and coordinatively more deficient, and that it has a more opened ligand environment.

Complex **63** is electronically unsaturated and has a maximum of 16-electrons if we count five electrons for each NPS system, three electrons from the nitrogen of bis(trimethylsilyl)amide and three electrons for yttrium. Even though electron counting for [(Cp*)$Si(Me_2)$-N-*t*-C_4H_9)]$YN(TMS)_2$ (**7**) and Cp*$LnN(TMS)_2$ (**2**) affords maximum

Table 13. Selected Bond Lengths [Å] and Angles [°] for **63**

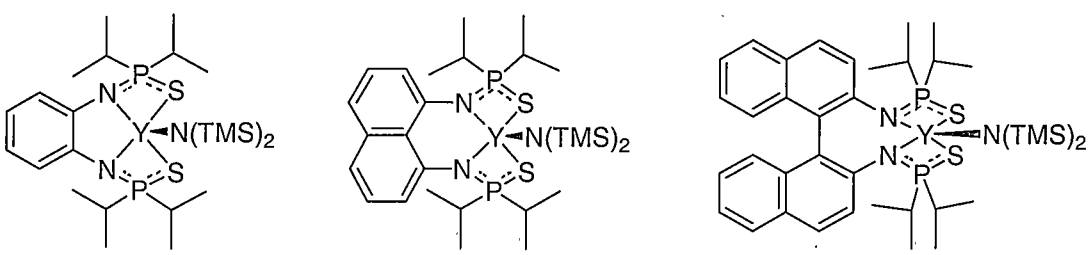
Y-N(3) 2.234(3)	S(2)-Y-S(1) 118.76(4)
Y-N(1) 2.314(3)	N(3)-Y-P(2) 115.67(8)
Y-N(2) 2.309(3)	N(1)-Y-P(2) 96.80(8)
Y-S(2) 2.7179(11)	N(2)-Y-P(2) 29.95(7)
Y-S(1) 2.7409(11)	S(2)-Y-P(2) 39.93(3)
Y-P(2) 3.1280(10)	S(1)-Y-P(2) 135.25(3)
Y-P(1) 3.1566(10)	N(3)-Y-P(1) 116.26(8)
Y-Si(1) 3.2474(11)	N(1)-Y-P(1) 28.94(7)
	N(2)-Y-P(1) 98.93(7)
N(3)-Y-N(1) 120.86(11)	S(2)-Y-P(1) 137.04(4)
N(3)-Y-N(2) 115.71(11)	S(1)-Y-P(1) 39.51(3)
N(1)-Y-N(2) 71.36(10)	P(2)-Y-P(1) 119.97(3)
N(3)-Y-S(2) 105.53(8)	N(3)-Y-Si(1) 29.58(7)
N(1)-Y-S(2) 128.84(8)	N(1)-Y-Si(1) 139.02(8)
N(2)-Y-S(2) 69.88(7)	N(2)-Y-Si(1) 136.06(8)
N(3)-Y-S(1) 107.88(8)	S(2)-Y-Si(1) 92.11(3)
N(1)-Y-S(1) 67.94(7)	S(1)-Y-Si(1) 92.78(3)
N(2)-Y-S(1) 131.14(8)	P(2)-Y-Si(1) 120.50(3)
S(2)-Y-S(1) 118.76(4)	P(1)-Y-Si(1) 119.53(3)
N(3)-Y-P(2) 115.67(8)	

14-electron and 16-electron systems respectively, the agostic interaction between yttrium and H—CH_2Si might compensate for electron deficiency. Furthermore, the large bond angle of S(1)-Y-S(2) [118.76 (4)°] in **63** may make the access of the substrate aminoalkenes to the unsaturated metal center favorable for hydroamination and other reactions of interest.

THE INTRAMOLECULAR HYDROAMINATION OF AMINOALKENES BY TETRADENTATE-LIGAND-BASED GROUP 3 METAL COMPLEXES GENERATED IN SITU

As with the bidentate ligands described in the second section, the NPA ligands increased the catalytic activity along with the cyclization diastereoselectivity observed for intramolecular hydroaminations.

Our study of NPA ligand based Group 3 metal-catalyzed intramolecular alkene hydroaminations focused on the cyclization of 2-amino-hex-6-ene (**15e**) (Table 14). As a study of chelating size effect, three types of complexes (**64a**, **67** and **68**) were examined. These complexes have a *5*,4,4-; a *6*,4,4-; and a *7*,4,4-membered coordination ring, respectively, as shown in Scheme 26. Complex **64a** catalyzed the hydroamination reaction of **15e** to provide a 9:1 (*trans*/*cis*) ratio of diasteroselectivity at >95% yield in 3 h at 60°C. However, complex **67** having a *6*,4,4-membered ring coordination, gave



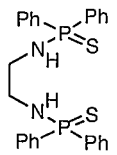
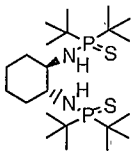
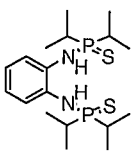
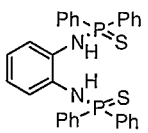
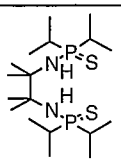
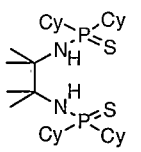
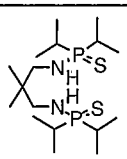
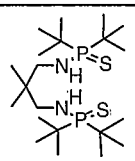
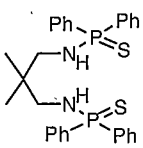
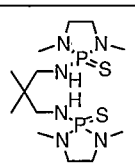
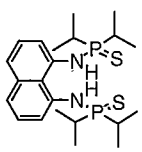
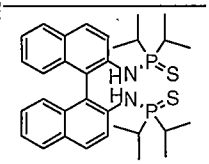
64a **67** **68**

3 h (9 : 1) 60 h (10 :1) 2 h (16 :1)

Scheme 26. Cyclization of **15e** Catalyzed by **64a**, **67** or **68**

Table 14. Catalyzed Cyclization of 2-Aminohex-5-ene (**15e**)

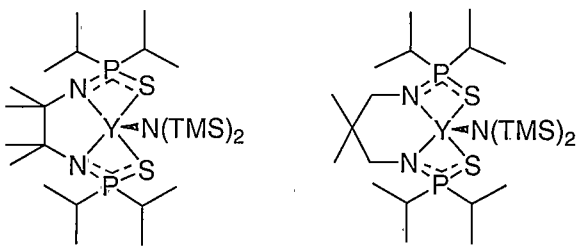
15e **17e** **18e**

Cat.	Proligands	$t_{Reac.}$ (60°C)[a] d.r. (17e : 18e) conv. [%][b]	Cat.	Proligands	$t_{Reac.}$ (60°C)[a] d.r. (17e : 18e) conv. [%][b]
62		17 h (6 :1) >95%	**63**		15 h (8 :1) >95%
64a		3 h (9 :1) >95%	**64b**		22 h (7 :1) >95%
65a		15 min (13 :1) >95%	**65e**		40 min (12 :1) >95%
66a		1 h (7 :1) >95%	**66d**		4.5 h (8 :1) >95%
66e		2 h (9 :1) >95%	**66g**		3.5 h (7 :1) >95%
67		60 h (10 :1) >95%	**68**		2 h (16 :1) >95%

[a] All reactions were conducted at 60°C. [b] Based on integration of the ^{1}H NMR spectrum; **17e / 18e** : 3.14 (septet) / 2.93 (m) ppm.

significantly decreased catalytic activity in terms of the cyclization rate (60 h, >95%), but diastereoselectivity was slightly improved to 10:1 (*trans/cis*). On the other hand, complex **68** exhibited remarkably improved cyclization diastereoselectivity (16:1) with a somewhat enhanced cyclization rate (2 h, >95%) when compared with **64a**.

Based on the informative X-ray analysis of complex **63**, complex **67**, having a rigid naphthalene-1,8-diamine backbone, might generate a sterically more shielded motif due to the reduced S-Y-S bond angle and the N-Y-N bond angle. In contrast, complex **68** might form a significantly distorted square pyramidal geometry due to the tortional angle between the naphthalene rings. Presumably, the twisted bisnaphthalenediamine backbone results in a much larger N-Y-N bond angle, which should lead to the opening of the S-Y-S bond angle. The wide bond angle of S-Y-S should make it feasible to accommodate sterically demanding substrates, and the distorted geometry generated should improve the diastereoselectivity of cyclization.



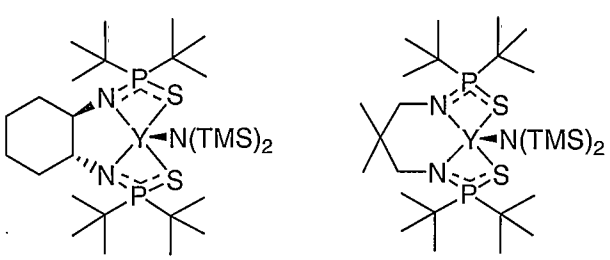
65a
15 min
(13 :1)

66a
1 h
(7 :1)

Scheme 27. Cyclization of **15e** Catalyzed by **65a** or **66a**

Various types of proligands that generate a distorted chelate geometry were complexed with Group 3 metals. Surprisingly, the rate of cyclization was dramatically accelerated using complex **65a** containing the ligand 2,3-dimethyl-2,3-diaminobutane. In the presence of 5 mol% of **65a**, the cyclization was >95% completed in 15 min at 60°C with high diastereoselectivity (*trans* /*cis* = 13:1), similar to the case of complex **68**.

It was observed that the complexes possessing sterically bulky and flexible ligand backbones, exhibited better catalytic activities in terms of reaction rate than rigid ligand-based catalysts. Compared to the rigid naphthalene backbone of complex **67**, for example, utilizing the flexible and sterically bulky 2,2-dimethylpropanediamine (complex **66a**) led to a 60-fold increase in the cyclization rate under identical reaction conditions. Furthermore, 2,2-dimethylpropanediamine complex **66d**, which has a more flexible ligand diamine backbone, showed higher activity in the rate of cyclization of aminoalkene than complex **63**, which has a *trans* cyclohexane-1,2-diamine backbone.



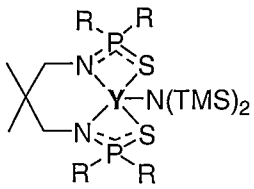
63
15 h
(8 :1)

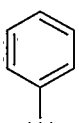
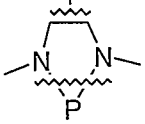
66d
4.5 h
(8 :1)

Scheme 28. Cyclization of **15e** Catalyzed by **63** or **66d**

The effect of the ancillary group on phosphorus was investigated by exploring steric and electronic factors. Replacement of the isopropyl moiety of **66a** with a *t*-butyl group as a sterically bulkier group to afford **66d** reduced the activity of the catalyst, but led to a modest improvement in diasteroselectivity [e.g., 7:1 to 8:1 (**17e/18e**)]. Using a more electronically donating group, a *N,N'*-dimethylethylenediamine moiety, in complex **66g** also decreased the catalytic activity of the complex. Furthermore, complex **66e**, which contains an electron-withdrawing phenyl group in the ligand, resulted in reduced

Table 15. Catalyzed Cyclization of 2-Aminohex-5-ene (**15e**)



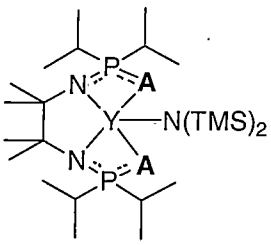
Cat.	R	$t_{React.}$ [a]	d.r. (17e : 18e)[b]	Conv. [%] [c]
66a		1 h	7 : 1	>95%
66d		4.5 h	8 : 1	>95%
66e		2 h	8 : 1	>95%
66g		3.5 h	7 : 1	>95%

[a] All reactions were conducted at 60°C. [b] Based on integration of the 1H NMR spectrum; **17e/18e** : 3.14 (septet) / 2.93 (m) ppm..

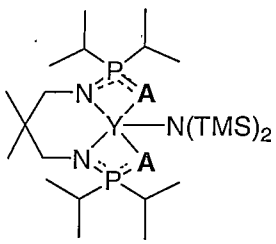
catalytic activity of the complex (**66e**). The observed substituent effects on phosphorus indicate that both electron withdrawing and electron donating groups as compared with isopropyl, deactivate the catalytic activity of complexes toward the hydroamination reaction.

The X-ray structure of complex **63** has shown that the ancillary sulfur is strongly bonded to yttrium, $Y\text{-}S_1$ [2.7409 (11) Å], $Y\text{-}S_2$ [2.7179 (11) Å]. These above results show that the catalysts possessing chelating sulfur exhibited excellent cyclization activities. Accordingly, the chelate effect of the ancillary atom was subsequently investigated by incorporation of representative atoms of Group 16 elements (i.e., selenium and tellurium) into the NPA ligand systems, as a replacement for sulfur [Table 15]. Selenium and tellurium have bigger van der Waals radii (Se: 1.90 Å, Te: 2.06 Å) than sulfur (S: 1.80 Å), and the selenium atom exhibits high coordination ability toward electronically deficient metal centers as does sulfur.[54a] In the case of complex **66b**, the replacement of sulfur by selenium resulted in a much improved diastereoselectivity ratio: it provided an 11:1 ratio of *trans* to *cis* isomers, without the decrease in reaction rate (1 h, >95% yield). In contrast, the incorporation of tellurium into the ligand system resulted in reduction of the catalytic activity of complex **66c**, while the diastereoselectivity was increased to provide a 12:1 ratio of *trans* to *cis* isomers. In the case of complex **65d**, however, incorporation of the larger-sized selenium instead of sulfur into the proligand **58d** resulted in a decreased rate of cyclization with no improvement in diastereoselectivity.

Table 16. Catalyzed Cyclization of 2-Aminohex-5-ene (**15e**)



A = S : **65a**
Se:**65b**



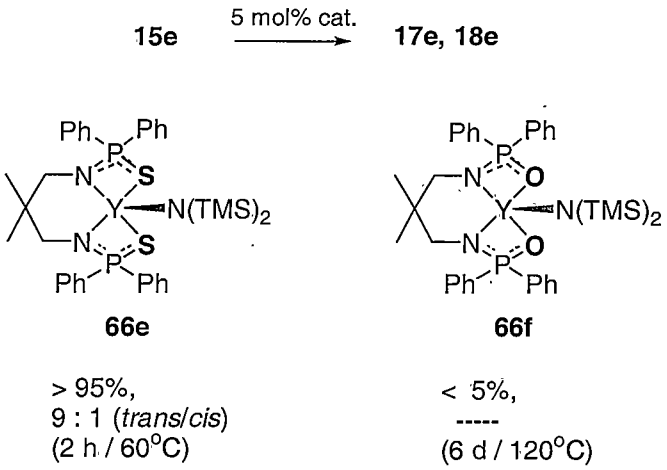
A = S : **66a**
Se:**66b**
Te: **66c**

15e —5 mol% cat., 60°C→ **17e** + **18e**

Complex	Ln	A	$t_{React.}$ [a]	d.r. (17e : 18e)[b]	Conv. [%] [b]
65a	Y	**S**	15 min	13 : 1	>95%
65d		**Se**	1 h	13 : 1	>95%
66a		**S**	1 h	7 : 1	>95%
66b	Y	**Se**	1 h	11 : 1	>95%
66c		**Te**	2 h	12 : 1	>95%

[a]All reactions were conducted at 60°C. [b]Based on integration of the ^{1}H NMR spectrum; **17e/18e** : 3.14 (septet) / 2.93 (m) ppm.

As expected, the catalytic activity of complex **66f** that possesses an oxygen bound to phosphorus was extremely suppressed. Even at a higher temperature (120 °C), the cyclization proceeded less than 5% for six days. Probably the strong ligation of oxygen to the metal center resulting from the extreme oxophilicity of the lanthanides resulted in an electronically and sterically unfavored complex for the hydroamination reaction.



Scheme 29. Cyclization of **15e** Catalyzed by **66e** or **66f**

Since proligand **58a** that provided complexes **65a**, **65b** and **65c** was shown to possess a superior level of catalytic efficiency in both cyclization rate and diastereocontrol, this ligand domain was selected for further exploration.

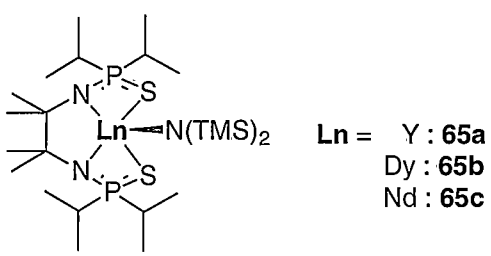
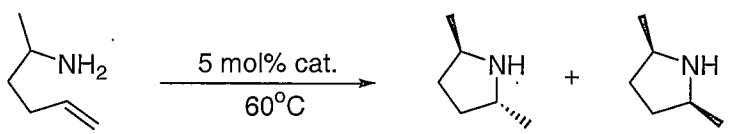


Figure 17. Complexes **65a**, **65b** and **65c**

It is well established that organolanthanocenes possessing a larger-sized metal exhibit higher levels of catalytic activity in the cyclization of aminoalkenes. In contrast

to this trend, incorporation of a larger-sized metal (e.g., Nd), resulting in **65c**, diminished the observed catalytic efficiency (>95% conv., 6:1 dr, 45 min t_{react}) (Table 17). Additionally, even with the similar sized dysprosium (1.052 Å),[41] the catalytic activity of **65b** was notably retarded to afford only 41% conversion with a 10:1 ratio of diastereoselectivity after 15 min. In this case, the yield and diasteroselectivity were determined after separation of the product from the catalyst via vacuum transfer because of the strong paramagnetism of dysprosium, which caused substantial line broadening in the ^{1}H NMR spectrum.

Table 17. Catalyzed Cyclization of 2-Aminohex-5-ene (**15e**)



15e **17e** **18e**

Complex	Ln	$t_{React.}$ [a]	d.r. (17e : 18e) [b]	Conv. [%] [b]
65a	**Y**	15 min	13 : 1	>95%
65b	**Dy**	15 min	10 : 1	41%
65c	**Nd**	45 min	6 : 1	>95%

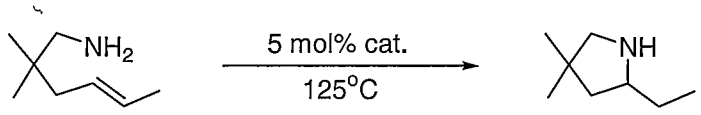
[a]All reactions were conducted at 60°C. [b]Based on integration of the ^{1}H NMR spectrum;**17e / 18e** : 3.14 (septet) / 2.93 (m) ppm.

Furthermore, reproducibility of these new Group 3 metal catalysis in the hydroamination reaction of aminoalkenes was confirmed by showing successful results

on a preparative scale. That is, the hydroamination reaction of 2-aminohex-6-ene (1 mmol scale) utilizing 5 mol% of complex **66a**, provided a 7/1 ratio of diastereomers in 75min at 60 °C, and the resulting amine was isolated as hydrochloride salt form quantitatively.

Our efforts to investigate non-metallocene-based Group 3 metal catalysts for intramolecular alkene hydroamination subsequently focused on the cyclization of the1,2-disubstituted aminoalkene **47** (Table 18). As was noted in the previous section, 1,2-disubstituted aminoalkenes are the most lethargic substrates for lanthanide-catalyzed hydroaminations explored to date. When 2,2-dimethylaminohex-4-ene **47** was subjected to 5 mol% of the catalyst **65a**, the cyclization proceeded at a reasonable rate at 125°C to afford >95% of cyclized compound **52** in 14 h.

Table 18. Catalyzed Cyclization of 2,2-Dimethylaminohex-4-ene (**47**)



47 **52**

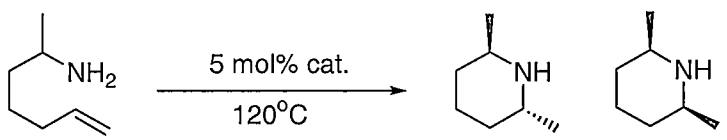
Complex	Ln	$t_{React.}$ [a]	Conv. [%] [b]
65a	**Y**	14 h	>95%
65b	**Dy**	14 h	78%
65c	**Nd**	15 h	>95%

[a]All reactions were conducted at 125°C. [b]Based on integration of the ^{1}H NMR spectrum.

In accordance with the trend of NPA systems to metal-size effects, neodymium complex **65c** provided a slightly reduced cyclization rate (>95% yield, 15 h). In addition, the utilization of the covalently "smaller" dysprosium complex **65b** led to a much slower hydroamination reaction (78% yield, 14 h) when compared to yttrium complex **65a**.

The scope of the hydroamination reaction using this representative NPS-type complex was expanded by the successful construction of a six-membered ring. These reactions were performed using 2-aminohept-6-ene (**50**) with 5 mol% of complex **65a-c** at 120 °C. Using complex **65a** the cyclization was completed in 1 h to afford a 4:1 (*cis/ trans*) ratio of diastereoselectivity. Meanwhile, with the larger sized metal complex **65c**, the rate of cyclization was decreased to provide >95% of conversion in two hours, but the diastereoselectivity between **53a** and **53b** was increased somewhat to 6:1.

Table 19. Catalyzed Cyclization of 2-Aminohept-6-ene (**50**)



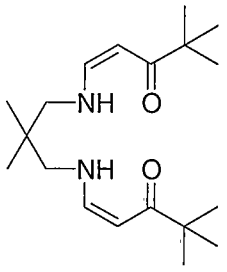
50 **53a** **53b**

Complex	Ln	$t_{React.}$ [a]	d.r. (53a : 53b) [b]	Conv. [%] [b]
65a	**Y**	1 h	1 : 4	>95%
65b	**Dy**	1 h	1 : 5	9%
65c	**Nd**	2 h	1 : 6	>95%

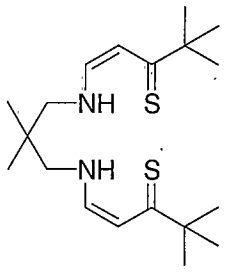
[a]All reactions were conducted at 120°C. [b]Based on integration of the ^{1}H NMR spectrum; **53a / 53b**: 2.95 (m) / 2.46 (m) ppm.

Clearly, these results indicate that the metal-size effect in NPS systems leads to reversal of the observed trends when compared to organolanthanocenes in cyclization rate and diastereoselectivity. Moreover, dysprosium complex **65b** that contains a metal of similar size to yttrium exhibits very low cyclization activity so as to afford only 9% conversion to product **53a,b** in one hour, albeit with a slightly increased ratio of **53a** to **53b** (5:1).

Another class of tetradentate ligands (i.e., **69a** and **69b**), which have N-C=C-C=S conjugated systems were attached to yttrium. The proligands **69a** and **69b** would afford electronically unsaturated maximum 16-electron complexes related to the preceeding NPA ligand-based complexes.



69a

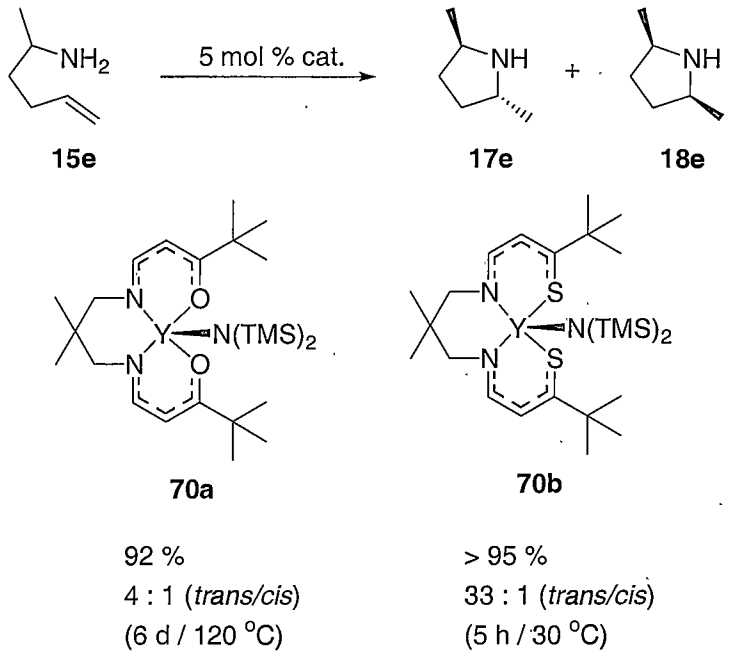


69b

Figure 18. Proligands **69a** and **69b**

Unlike the case of complex **66f** (p 67) that also possesses oxygen within the ligand system, complex **70a** exhibited weak catalytic activity in the cyclization of aminoalkene **15e** to give 92% conversion at 120 °C over 6 days with 4:1 *trans/cis* ratio of

diastereoselectivity. In contrast, the yttrium complex **70b** exhibits remarkably high catalytic activity in terms of diastereoselectivity (*17e/18e = 33:1*) at 30 °C in >95% yield over 5 h. The complex **70b** was found to posses limited stability in the presence of the substrate amine at 60 °C or higher. As revealed in Table 20, complex **70b** completely lost catalytic activity at 60 °C after 2 h to afford only 29% conversion. Furthermore, at higher temperatures (e.g., 150 °C) the preformed complex **70b** did not exhibit any catalytic activity in the cyclization of aminoalkene **15e**, presumably as a consequence of rapid amine mediated degradation.



Scheme 30. Catalyzed Hydroamination of aminoalkene **15e**

Table 20. Thermal Stability of Complex **70b**

15e $\xrightarrow{\text{5 mol\% cat.}}$ **17e + 18e**

Complex	Temp (°C)	$t_{React.}$	d.r. (17e : 18e)[a]	Conv. [%] [a]
70b	30°C	5 h	33 : 1	>95 %
	60°C	2 h	N.A.	29 %
	120°C	2 h	-	-

[a]Based on integration of the ^{1}H NMR spectrum;**17e / 18e** : 3.14 (septet) / 2.93 (m) ppm.

In summary, we have confirmed by X-ray analysis that the NPS-type complex has a pentacoordinated pseudo-square pyramidal geometry. Notably, introducing the NPA binding system spectacularly enlarges the scope of structural variation in the ligand. The initially developed NPA-type catalysts have shown excellent efficiency in the intramolecular aminoalkene hydroamination with a broad variety of substrates. In addition, a new type of complex **70b** exhibited outstanding catalytic activity in terms of diasteroselectivity in the cyclization of aminoalkene, though it has limited stability at temperature. We have also found that these complexes clearly exhibit different behaviors with respect to metal size than the conventional lanthanocene complexes. We have also shown that the non-metallocene Group 3 metal complexes have superior catalytic efficiency as well as chemical and physical properties when compared to lanthanocenes.

ENANTIOSELECTIVE CATALYTIC HYDROAMINATION REACTIONS BY GROUP 3 METAL COMPLEXES

INTRODUCTION

The vast number of naturally occurring bioactive organic compounds are enantiopure. Moreover, enantiopure products are playing an increasingly important role in the drug industry. Since the development of chiral rhodium-phosphine complexes for enantioselective hydrogenation [61] and the discovery of the proline-catalyzed Robinson annulation [62] around 1970, a number of powerful synthetic catalysts have been developed for the synthesis of highly enantioenriched compounds.[63]

For the synthesis of enantiomerically pure heterocycles, amino acids have been the most extensively used as chiral building blocks. Despite their versatility, amino acids are quite limited in structural diversity. In terms of efficiency and utility, catalytic enantioselective hydroamination would be one of the most desirable methods for the synthesis of nitrogenous compounds. However, only a few catalysts based on iridium,[64] palladium,[65] and lanthanocenes[22g,27] have been developed so far for enantioselective hydroamination.

In early-transition metal chemistry, C_1 symmetric organolanthanide *ansa*-metallocene catalysts of the type $[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3R^*)Ln(SiMe_3)_2]$ (**8**) [R* = (-)-mentyl, (+)-neomentyl, (-)-phenylmentyl; Ln = La, Nd, Sm, Y, Lu; E = CH, N] and $[Me_2Si(\eta^5\text{-}OHF)(\eta^5\text{-}C_5H_3R^*)LnN(SiMe_3)_2]$ (**9**) [OHF = octahydrofluorenyl; R* =

(-)-mentyl; Ln = Sm, Y, Lu] have been developed for the enantioselective and diastereoselective intramolecular hydroamination of aminoalkenes. Catalyst (Ln = Sm) **8** cyclized 2,2-dimethylaminopent-4-ene to give 2,4,4-trimethylpyrrolidine with 53% enantiomeric excess at 25 °C (turnover frequency N_t = 84 h^{-1}) and 74% enantiomeric excess at –30 °C (the turnover frequency, N_t, is not available due to extremely slow cyclization rate).

As discussed in the Background section of this dissertation, only four chiral ligands have been developed so far. This suggests that the preparation of chiral ligands is like exceptionally tricky. Moreover, in the case of lanthanocene complexes some epimerization of catalyst is observed during the asymmetric cyclization of aminoalkene due to weak coordination of the Cp moiety to the metal center.[27]

As an initial study for the development of non-metallocene Group 3 catalysts for enantioselective aminoalkene hydroamination, we surveyed several ligand classes with

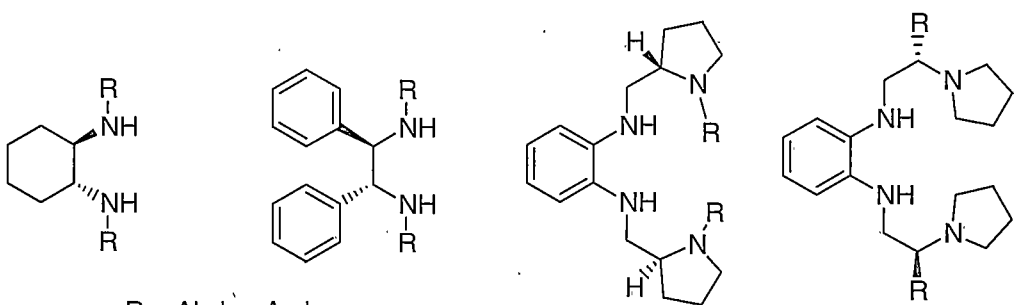
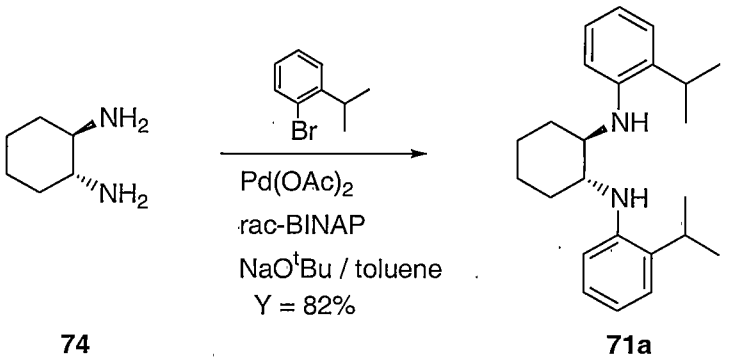


Figure 19. Asymmetric Proligands **71,72,73a-c**

two distinct strategies. These were being introduction of chirality at the ligand diamine backbone and the incorporation of an asymmetric secondary chelating moiety to the achiral diamine backbone.

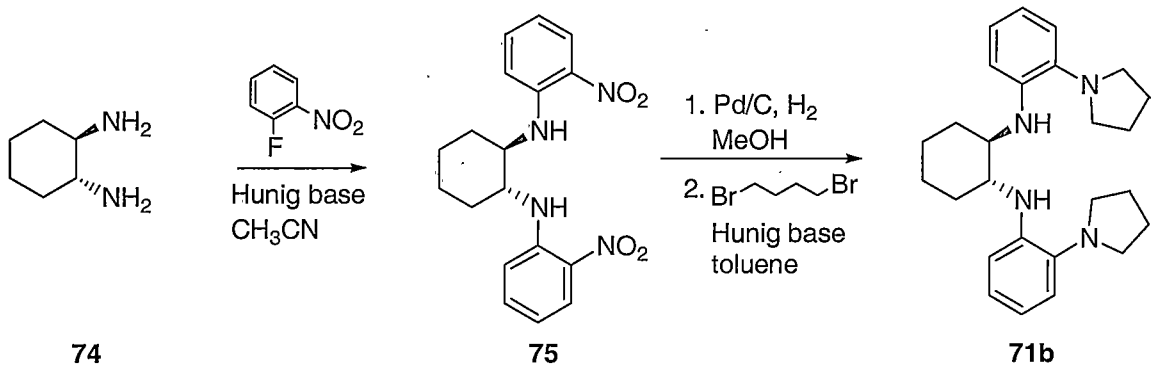
SYNTHESIS OF ASYMMETRIC PROLIGANDS

Proligand **71a** was readily prepared using a palladium-catalyzed amination reaction between (1*R*,2*R*)-diaminocyclohexane and 1-bromo-2-isopropylbenzene in 82% yield.



Scheme 31. Synthesis of Proligand **71a**

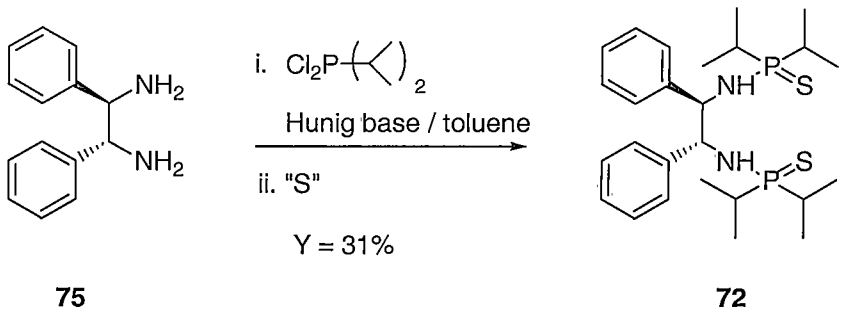
Alternatively, (1*R*,2*R*)-diaminocyclohexane (74) was coupled with 1-fluoro-2-nitrobenzene in the presence of *N*,*N*-diisopropylethylamine as an HF scavenger to



Scheme 32. Synthesis of Proligand **71b**

provide intermediate **75** in 64% yield. Compound **75** was reduced to the corresponding amine in 98% yield by the typical reducing condition using Pd/C catalyst under a hydrogen atmosphere, and treatment with 1,4-dibromobutane in the presence of *N,N*-diisopropyl-ethylamine provided **71b** in 59% yield.

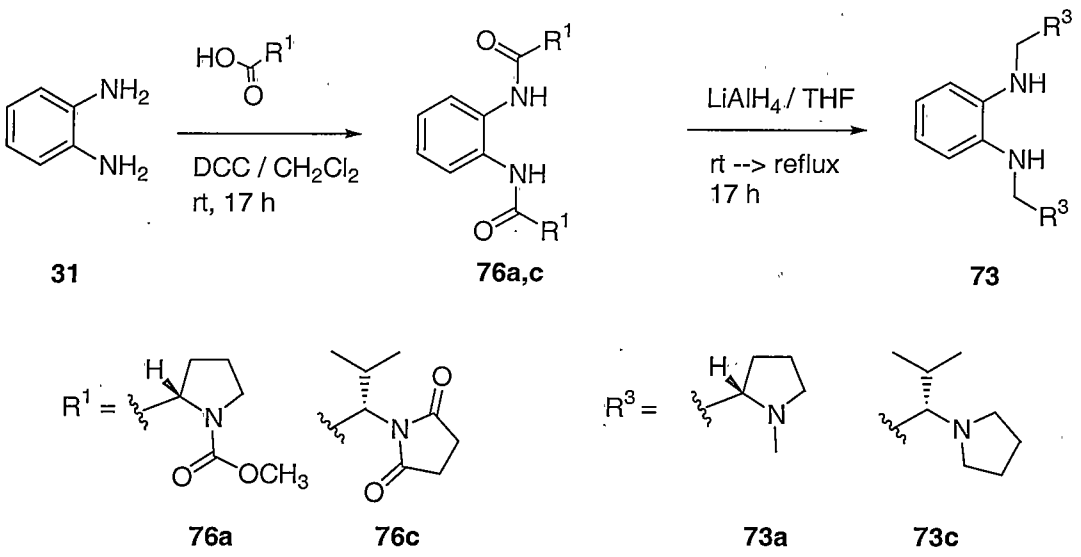
Proligand **72** was prepared by following the standard method described in the third section of this dissertation in 31% yield.



75 **72**

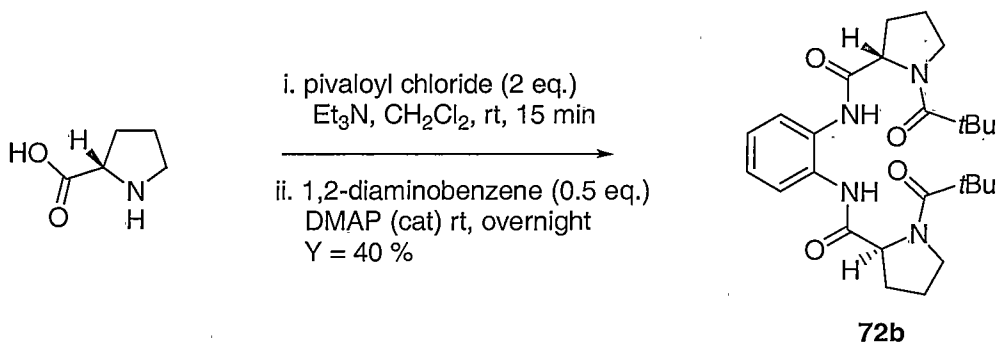
Scheme 33. Synthesis of Proligand **72**

Readily available enantiopure amino acids were utilized as chiral pool sources for the preparation of asymmetric ligands. The incorporation of asymmetric moieties onto the1,2-phenylenediamine backbone was achieved by using *N,N'*-dicyclohexyl-carbodiimide (DCC), followed by $LiAlH_4$ reduction to provide a variety of diastereo- and enantiomerically pure proligands (**73a-c**).[66(a)] Enantiomeric excesses (ee) of proligands were determined by intergration of the ^1H NMR spectrum using (S)-(+)- and (*R*)-(-)-*O*-acetylmandelic acid (2.2 equiv) in $CDCl_3$.[85]



Scheme 34. Synthesis of Proligands **73a**, **73b**

Proligand **73c** was prepared by the coupling of 1,2-phenylenediamine with the mixed anhydride of proline and trimethylacetic acid generated in situ, in the presence of *N,N*-dimethylaminopyridine (DMAP) catalyst in 40% yield. The amide intermediate (**76c**) was reduced to **73c** using $LiAlH_4$ in 19% yield.



Scheme 35. Synthesis of Intermediate **76c** for Proligand **73c**

ENANTIOSELECTIVE INTRAMOLECULAR HYDROAMINATION: ASYMMETRIC CATALYSIS WITH GROUP 3 METAL AMIDO COMPLEXES

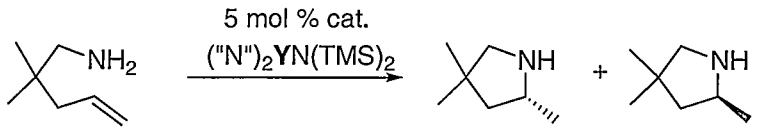
Our initial study of chiral ligand-based catalytic enantioselective intramolecular aminoalkene hydroaminations focused on the cyclization of 2,2-dimethylaminopent-4-ene to 2,4,4-trimethylpyrrolidine. A compilation of reaction times and enantioselectivities observed in the reaction appears in Table 21. Like achiral complexes, chiral complexes were conveniently generated in situ at 120 °C or 150 °C in benzene-d_6 or toluene-d_8. Enantiomeric excesses (ee) and absolute configurations of 2,4,4-trimethylpyrrolidine (**16-R** or **16-S**) were determined by measuerment of opitical rotation[22g] and intergration of the ^{1}H NMR spectrum using (*R*)-(-)-*O*-acetylmandelic acid (1.2 equiv) in $CDCl_3$.[85]

We have found that the secondary ligating moiety in the ligand system exhibits an important role in the enantioselective control of aminoalkene hydroamination. While complex **77** catalyzed the cyclization of aminoalkene without any enantioselectivity in the error range (0% enantiomeric excess, at 25 °C / 3 h), an analogous complex **78** possessing the ancillary ligating tertiary amine moiety into the ligand exhibit 17% enantiomeric excess at 25 °C in 57 h. Incorporation of the secondary ligating moiety in the ligand system as in complex **57**, however, resulted in significantly reduced cyclization rates.

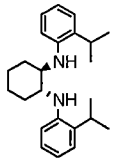
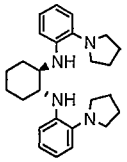
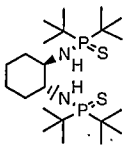
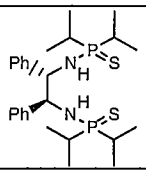
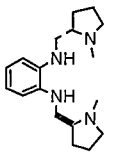
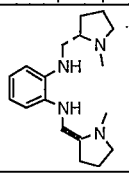
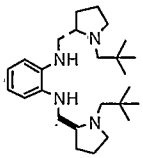
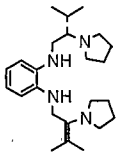
On the other hand, complex **80** exhibit greatly increased enantioselectivity in the catalytic cyclization of aminoalkene to provide 56% enantiomeric excess (-) in >95% yield in 22 h at 25 °C. As expected, the enantioselectivity was somewhat improved at 10

°C to provide 66% enantiomeric excess (-) in >95% yield in seven days. Apparently, the location of the chiral center significantly influences the enantioselection of the catalyst toward aminoalkene hydroamination.

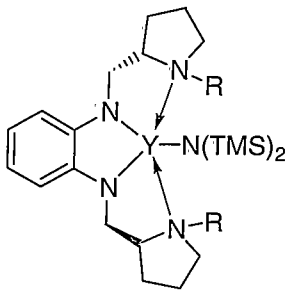
Table 21. Catalyzed Asymmetric Hydroamination of Aminoalkene **15e**



15a **16-(*R*)** **16-(*S*)**

Cat.	Proligands	$t_{Reac.}$ / Temp. (°C) ee[a] (config) [b] conv. (%)[c]	Cat.	Proligands	$t_{Reac.}$ / Temp. (°C) ee[a] (config) [b] conv. (%)[c]
77		3 h / 25°C 0% >95%	**78**		57 h / 25°C 17% (*S*)-(+) >95%
63		5 d / 25°C 13% (*S*)-(+) >95%	**79**		4 h / 25°C 22 % (*S*)-(+) >95%
80		22 h / 25°C 56% (*R*)-(-) >95%	**80**		7 d / 10°C 66% (*R*)-(-) >95%
81		12 d / 25°C 5.4% (*R*)-(-) >95%	**82**		34 h / 25°C 10% (*R*)-(-) >95%

[a] Based on integration of the ^{1}H NMR spectrum using (*R*)-(-)-*O*-acetylmandelic acid; 3.14 (m, 1H), 1H for **16-(*R*)**; 2.93 (m, 3H), 1H for **16-(*R*)** and 2H for **16-(*S*)**. [b] $[\alpha]^{20}_D$ = -24.3° for (*R*)-(-)-2,4,4-trimethylpyrrolidine.[22g]



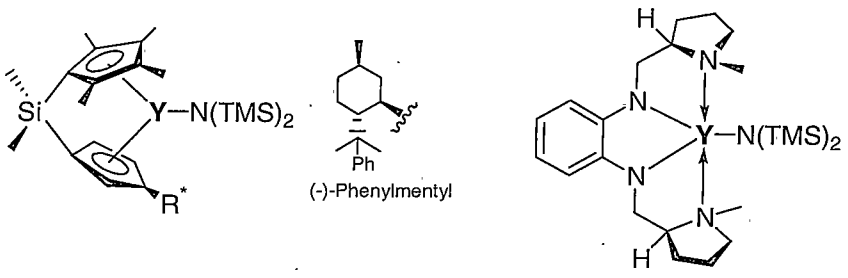
R = -CH_3 (**80**) : 56% ee/25°C/22 h

-$CH_2C(CH_3)_3$(**81**) : 5.4% ee/25°C/12 d

Scheme 36. Substituent Effect on Enantioselective Hydroamination

The ancillary effect of an alkyl group substituted at the pyrrolidine moiety was investigated by exploring its steric contribution. Replacement of the methyl group with a neopentyl group as a sterically bulkier moiety to afford **81**, significantly reduced the catalytic activity of the complex in both reaction rate (12 d / 25 °C, >95% conversion) and enantioselectivity (5.4% enantiomeric excess). The bulkier neopentyl group probably inhibits effective chelating of the chiral pyrrolidine moiety to the metal center.

In comparison to organolanthanocenes under analogous reaction conditions (Scheme 37), yttrium complex **8**, which is bound to the best chiral ligand in the series of organolanthanides, catalyzed the asymmetric cyclization of **15a** to (*S*)-(+)-2,4,4-trimethylpyrrolidines **16** in 56% enantiomeric excess at 25 °C, but with a very low turnover frequency (8 h^{-1}).



8

56% ee (*S*)-(+)
8 N_t (h^{-1}) / 25°C

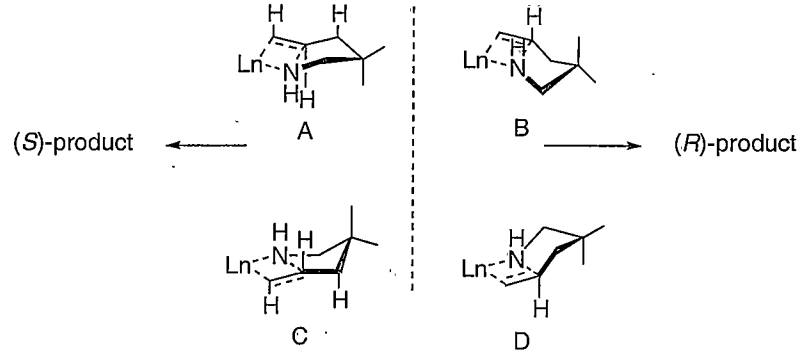
80

56% ee (*R*)-(-)
22 h / 25°C

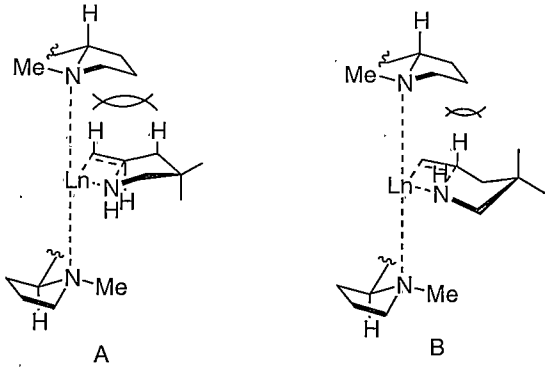
Scheme 37. Comparison of Catalytic Asymmetric Aminoalkene Hydroaminations

The stereochemistry of product can be rationalized on the basis of presumed catalyst-substrats steric interactions at the transition state. In the pseudo-chair seven menbered transition states (Scheme 38), **A** and **C** give (*S*)-product in the cyclization of 2,2-dimethylaminopent-4-ene, whereas **B** and **D** provide (*R*)-product. The stereoselection of chiral C_2 symmetric complex **80** catalyst in the formation of (*R*)-(-)-2,4,4-trimethylpyrrolidines **16** can be expained on the basis of the transition state (Scheme 39). Whereas the transition state **A** involves unfavored interaction between diaxial hydrogens (H_a-C3,H_a-C5) and the sterically bulky proline moiety, the conformation of **B** has only one axial hydrogen (H_a-C4), which is faced on the upper proline moiety. So, two transition states, **B** and **D**, which avoid the steric conflict between the hydrogens at C3 and C5 and the proline moieties (upper one for **B** and lower one for **D**), give preference

for a pseudo-chair seven membered transition state. Thus, the enantioselective hydroamination reaction catalyzed by **80** predominately gives (*R*)-product via the more sterically favorable transition states, **B** or **D** (Scheme 38), as is consistent with the observed results. The difference in activation free energy ($\Delta G^{\ddagger}$) for the formation of (*R*)-2,4,4-trimethylpyrrolidine versus (*S*)-enantiomer from 2,2-dimethylaminopent-4-ene was calculated as -0.75 kcal/mol (56% ee at 25 °C) and -0.89 kcal/mol (66% ee at 10 °C), respectively.



Scheme 38. Pseudo-Chair Seven Membered Transition States in the Cyclization of 2,2-Dimethylaminopent-4-ene by **80**



Scheme 39. Rationalization of the Enantionslectivity in the Cyclization of 2,2-Dimethyl-aminopent-4-ene by **80**

In summary, we have found that the Group 3 metal complexes possessing ligands that have an asymmetric center in the ancillary group provide higher enantioselectivites in the cyclization of a representative aminoalkene than those one that have a chiral center in the diamine backbone. Moreover, these readily available amido complexes have shown good enantioselectivity in the aminoalkene hydroamination reaction, as high as 66% ee at 10 °C. These early results have provided critical clues for the design of chiral Group 3 metal catalysts for asymmetric aminoalkene hydroamination.

CONCLUSION

We have developed the first non-metalocene-based Group 3 metal catalysts for the hydroamination of aminoalkenes. The simple amido complexes, $Ln[N(TMS)_2]_3$ (Ln = Y, Nd), display high catalytic activity for the cyclization of various aminoalkenes. Specifically, $Y[N(TMS)_2]_3$ has been used to catalyze a sequential aminodiene bicyclization with high diastereocontol, resulting in the construction of a pyrrolizidine nucleus in one step. Modification of the Ln(III) center in $Ln[N(TMS)_2]_3$ is readily achieved, in situ, using sterically hindered chelating diamines. The complexes generated in this manner exhibited substantially improved catalytic activity as well as stereoselectivity in the cyclization of representative aminoalkenes. In addition, X-ray crystallographic analysis has shown that complex **63** possessing a NPS-type ligand has a pseudo-square pyramidal geometry. In addition to an extraordinary catalytic activity of complex **70b** in diastereoselective cyclization of aminoalkene, a series of the NPA (A = S, Se, Te) ligand-based Group 3 complexes also provide high catalytic activities and good diastereocontrol. Futhermore, the study described herein provides the first examples of readily available Group 3 metal complexes as non-metallocene-based catalysts for asymmetric aminoalkene hydroamination. Significantly, these readily accessible non-metallocene-based complexes are superior to lanthanocenes in terms of preparation, enhanced thermal stability and high possible ligand variability. These studies therefore

constitute an important contribution to the development of Group 3 metal catalysts for aminoakene hydroamination.

CHAPTER 3

EXPERIMENTAL

GENERAL INFORMATION

Melting points were obtained using a Met-Temp II apparatus equipped with a digital thermometer and are uncorrected. Infrared spectra were recorded on a Perkin Elmer model 1600 FT-IR. Infrared spectra of solids were obtained by standard KBr pellet procedures or by dissolving the material in a highly volatile solvent then depositing on a NaCl plate and evaporation the solvent under reduced pressure.

^{1}H NMR spectra were recorded on a Bruker DPX-300 (300 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the residual protic solvent resonance as the internal standard (chloroform: δ 7.24 ppm; benzene: δ 7.15 ppm; toluene: δ 6.98 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, bs = broad singlet, app = apparent), integration, coupling constants (in Hz), and assignments. ^{13}C NMR spectra were recorded on a Bruker DRX-300 (75 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent as the internal standard ($CDCl_3$: δ 77.0 ppm; C_6D_6: 128.0 ppm). $^{1}H\{^{31}P\}$ NMR spectra were recorded on a Bruker DPX-300 (300 MHz) spectrometer with complete phosphorus decoupling. $^{31}P\{^{1}H\}$ NMR spectra were recorded on a Bruker DPX-300 (121 MHz) spectrometer with complete proton decoupling. Mass spectra were obtained on a VG 70E

series mass spectrometer, under electron impact conditions at 70 eV or chemical ionization, and on a Bruker Biflex-III Time-of-Flight (TOF) mass spectrometer operated in reflectron mode using Matrix Assisted Laser Desorption Ionization (MALDI). Analytical thin layer chromatography was performed on Polygram® SIL G/UV_{254} 1.25 mm silica gel plates with a fluorescent indicator. Flash chromatography was performed on Merck silica gel 60. Solvents for extraction and flash chromatography were reagent grade. All experiments for hydroamination reactions were carried out under an argon atmosphere using standard anaerobic methods. Group 3 metal complexes were manipulated under an argon atmosphere in a glove box. Under argon atmosphere, benzene-d_6 and toluene-d_8, and aminoalkenes were distilled from Na and CaH_2 respectively, and stored at –30 °C in a glove box. The reagents $Ln[N(TMS)_2]_3$ (Ln = Y, Nd, La, Dy) were prepared according to the literature procedures.[67]

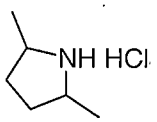
GENERAL PROCEDURE FOR INTRAMOLECULAR AMINOALKENE HYDROAMINATION REACTION

Method A: In an argon-filled glove box, $Ln[N(TMS)_2]_3$ (9×10^{-6} mol) and the corresponding aminoalkene (3.2×10^{-4} mol) were introduced into an NMR tube (J. Young) equipped with a teflon screw cap, and C_6D_6 (0.7 mL) was added. The reaction mixture was then maintained at the indicated temperature until alkene hydroamination was completed.

Method B: In an argon-filled glove box, $Ln[N(TMS)_2]_3$ (1.6 x 10^{-5} mol) and the appropriate ligands (1.6 x 10^{-5} mol) were introduced into an NMR tube (J. Young) equipped with a teflon screw cap, and C_6D_6 or toluene-d_8 (0.7 mL) was added. The homogeneous reaction mixture was heated to 120 °C (C_6D_6) or 150 °C (toluene-d_8) to effect ligand exchange as indicated by the disappearance of $Ln[N(TMS)_2]_3$ with concomitant generation of free $(TMS)_2NH$. The appropriate aminoalkene (3.2 x 10^{-4} mol) was added to the resulting complex and the reaction mixture was subsequently heated at 60, 120 or 125 °C in an oil bath.

PREPARATIVE SCALE REACTION

2,5-Dimethylpyrrolidine hydrochloride (**HCl·17e, HCl·18e**)[72a]



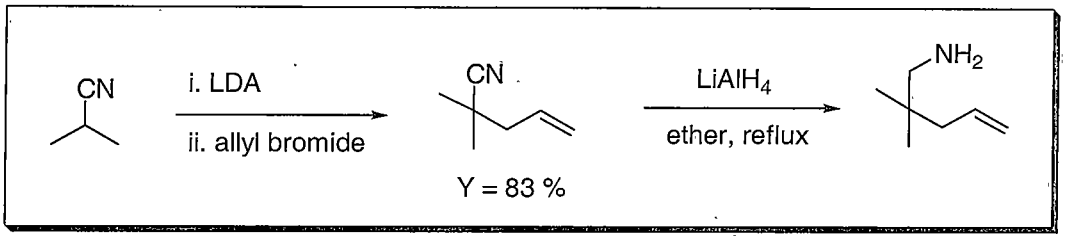
In an argon-filled glove box, $Y[N(TMS)_2]_3$ (28.5 mg, 5 x 10^{-5} mol) and *N,N'*-bis(*P,P*-diisopropylthiophosphinyl)-2,2-dimethyl-1,3-propanediamine (**59a**) (19.9 mg, 5 x 10^{-5} mol) were introduced into an NMR tube (J. Young) equipped with a teflon screw cap, and C_6D_6 (2.2 mL) was added. The homogeneous reaction mixture was heated to 120 °C for 1h to effect ligand exchange as indicated by the disappearance of $Y[N(TMS)_2]_3$ with concomitant generation of free $(TMS)_2NH$. 1-Methylpent-4-enylamine (**15e**) (99 mg, 1 mmol) was added to the resulting complex and the reaction mixture was subsequently heated at 60 °C in an oil bath for 75 min. The resulting products were

separated from catalyst via vacuum transfer, then added slowly to a HCl solution in MeOH (3 mL) at 0 °C which was prepared by addition of acetyl chloride (0.2 mL) to MeOH at 0 °C. The solvent was evaporated in vacuo to afford 135 mg (quantitative) the target product as a white solid.

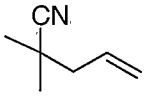
The spectrum is consistant with the data in literature. See reference for separated spectrum of *trans* and *cis*, respectively. [[72a] Katritzky, A. R.; Cui, X-L, Yang, B.; Steel, P. J. *J. Org. Chem.* 1999, *64*, 1979-1985]

^{1}HNMR (500 MHz, $CDCl_3$); (*trans*/*cis* = 9 : 1) (*trans* only): $\delta = 9.54$ (bs, 2H, NH_2^+Cl), 3.79 (m, 2H, CH), 2.18 (m, 2H, C*H*H), 1.66 (m, 2H, CH*H*), 1.49 (d, $J = 7.0$ Hz, 6H, CH_3) ppm ; ^{13}C NMR (125 MHz, $CDCl_3$) *trans*: $\delta = 54.84$, 32.23, 18.16 ppm; *cis*: $\delta = 56.11$, 30.78, 17.92 ppm.

SYNTHESIS OF AMINOALKENES AND CYCLIZED PRODUCTS



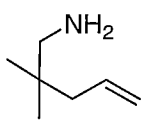
2,2-Dimethylpent-4-enenitrile (**14a**) [39b]



Isobutyronitrile (5 g, 72 mmol) was added dropwise to a solution of LDA at – 78 °C which was prepared by addition of *n*-BuLi (2.54 M, 31 mL, 79.2 mmol) to diisopropyl amine (11.0 mL, 79.2 mmol) in THF (120 mL) at 0 °C, and the solution was allowed to stir at this temperature for 2 h. Allyl bromide (7.5 mL, 86.4 mmol) in THF (30 mL) was added over a period of 5-10 min, the reaction mixture was stirred at –78 °C for 3 h, and then allowed to warm to room temperature with stirring overnight. The reaction mixture was quenched by addition of H_2O (2 mL) and Et_2O (200 mL) was added, then warmed to room temperature and washed with 1N HCl aqueous solution (2 x 20 mL). The aqueous solution was extracted with Et_2O (3 x 10 mL). The combined organic phase was dried (anhydrous $MgSO_4$), filtered, and concentrated in vacuo. The residue was distilled at 146-148 °C to afford 6.5 g (83%) of the title compound. (R_f = 0.38 $_{KMnO4}$, 5% ethyl acetate in *n*-hexane).

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.85 (m, 1H, -CH=), 5.20 (bd, J = 9.3 Hz, 1H, =C*H*H), 5.17 (bd, J = 16.5 Hz, 1H, =CH*H*), 2.26 (d, J = 7.2 Hz, 2H, CH_2), 1.32 (s, 6H, CH_3) ppm ; ^{13}C NMR (75 MHz, $CDCl_3$): δ 132.15, 124.66, 119.84, 45.03, 32.12, 26.17 ppm ; IR (neat): ν 3081.9, 2980.6, 2936.5, 1643.7, 1469.8, 925.0 cm^{-1}; LRMS (EI): m / z (relative intensity) 109 (M^+, 95), 94 (16), 68 (100).

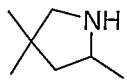
2,2-Dimethylaminopent-4-ene (**15a**) [39b]



This compound was prepared in a fashion analogous to **15e** (p.104) utilizing 2,2-dimethylpent-4-enenitrile (5.9 g, 54 mmol), $LiAlH_4$ (4.2 g, 108 mmol) and Et_2O (250 mL) (bp = 123-125 °C).

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.78 (m, 1H, -CH=), 4.99 (m, 2H, $=CH_2$), 2.43 (s, 2H, CH_2N), 1.94 (d, J = 7.5 Hz, CH_2), 1.23 (bs, 2H, NH_2), 0.82 (s, 6H, CH_3) ppm ; ^{13}C NMR (75 MHz, $CDCl_3$): δ 135.36, 116.89, 52.71, 44.02, 34.91, 24.60 ppm; IR (neat): ν 3380.0, 3304.3, 3074.2, 2955.8, 1638.4, 1470.1, 912.5 cm^{-1}; LRMS (EI): m / z (relative intensity) 113 (M^+, <0.1), 112 (0.8), 98 (37), 55 (100).

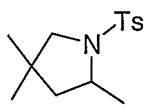
2,4,4-Trimethylpyrrolidine (**16a**) [22g]



This spectrum is consistant with the data in literature. [[22g] Giardello, M. A.; Conticello, V. P.; Brard, L.; Gagné, M. R.; Marks, T. J. *J. Am. Chem. Soc.* 1994, *116,* 10241].

^{1}H NMR (300 MHz, C_6D_6): δ 3.08 (m, 1H, NCH), 2.64 (app d, NC*H*H), 2.48 (app d, NCH*H*), 1.47 (dd, *J* = 12.3, 6.9 Hz, 1H, C*H*H), 1.12 (bs, 1H, NH), 1.05 (d, *J* = 6.3 Hz, 3H, CH_3), 0.98 (s, 3H, CH_3), 0.96 (m, 1H, CH*H*), 0.92 (s, 3H, CH_3) ppm.

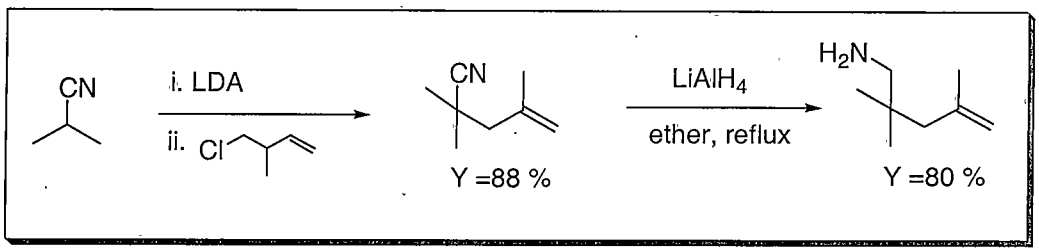
N-(*p*-Tolylsulfonyl)-2,4,4-trimethylpyrrolidine (**Ts-16a**)



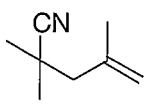
This compound was prepared in a fashion analogous to **20** (p.109) utilizing 2,4,4-trimethylpyrrolidine (**16a**).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.69 (d, *J* = 8.2 Hz, 2H, ArH), 7.27 (d, *J* = 8.2 Hz, 2H, ArH), 3.61 (m, 1H, NCH), 3.13 (d, *J* = 10.2 Hz, 1H, NC*H*H), 3.03 (dd, *J* = 10.2, 0.9 Hz, 1H, NCH*H*), 2.39 (s, 3H, CH_3), 1.70 (ddd, *J* = 12.6, 7.2, 0.9 Hz, 1H, C*H*H), 1.38 (d, *J* = 6.0 Hz, 3H, CH_3), 1.37 (m, 1H, *CHH*), *1*.0 (s, 3H, CH_3), 0.53 (s, 3H, CH_3) ppm ; ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.06, 135.25, 129.43, 127.42, 61.44, 55.92, 48.86, 37.12,

26.54, 25.86, 22.69, 21.47 ppm ; LRMS (EI): m / z (relative intensity) 267 (M^+, 7), 252 (100), 155 (58), 91 (61).



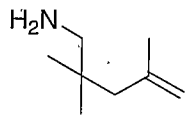
2,2,4-Trimethylpent-4-enenitrile (**14b**) [15c]



This compound was prepared in a fashion analogous to **14a** (p.92) utilizing isobutyronitrile (4.5 g, 65 mmol), THF (10 mL), diisopropylamine (10 mL, 71.5 mmol), *n*-BuLi, 2.54 M (28 mL, 71.5 mmol) and 1-chloro-3-methyl-2-butene (21 mL, 195 mmol) to give 7.1 g (88%) of **14b**, $R_f = 0.56$ $_{KMnO4}$ (10% ethyl acetate in *n*-hexane).

^{1}H NMR (300 MHz, $CDCl_3$): δ 4.95 (d, *J* = 1.5 Hz, 1H, =C*H*H), 4.81 (d, *J* = 1.5 Hz, 1H, =CH*H*), 2.23 (s, 2H, CH_2), 1.88 (s, 3H, CH_3), 1.34 (s, 6H, CH_3) ppm ; ^{13}C NMR (75 MHz, $CDCl_3$): δ 140.55, 125.41, 116.09, 48.49, 31.26, 27.03, 23.69 ppm ; IR (neat): ν 3078.3, 2978.0, 1643.0 cm^{-1}; LRMS (EI): m / z (relative intensity) 123 (M^+, 15), 108 (19), 55 (100);

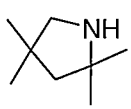
2,2,4-Trimethylaminopent-4-ene (**15b**) [15c]



This compound was prepared in a fashion analogous to **15e** (p.104) utilizing 2,2,4-trimethylpent-4-enenitrile (6 g, 48.7 mmol), $LiAlH_4$ (3.7 g, 97.4 mmol) and Et_2O (90 mL) to give 4.97 g (80%) of **15b**. [Purification by distillation at 147-148 °C].

^1H NMR (300 MHz, $CDCl_3$) δ 4.81 (bs, 1H, =C*H*H), 4.61 (bs, 1H, =CH*H*), 2.44 (s, 2H, CH_2), 1.91 (s, 2H, CH_2N), 1.74 (s, 3H, CH_3), 0.98 (bs, 2H, NH_2), 0.84 (s, 6H, CH_3) ppm ; ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.41, 114.10, 53.25, 47.11, 35.52, 25.29, 25.18 ppm ; IR (neat): ν 3386.0, 3313.6, 3072.3, 2953.7, 1640.0, 1471.6, 1373.8, 890.4 cm^{-1} ; LRMS (EI): m / z (relative intensity) 127 (M^+, <0.1), 128 (<0.1), 112 (23), 71 (63), 55 (100).

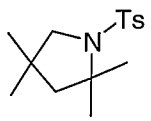
2,2,4,4-Tetramethylpyrrolidine (**16b**) [15c]



This spectrum is consistant with the data in literature. [[15c] Molander, G. A.; Dowdy, E. D. *J. Org. Chem.* 1998, *63,* 8983].

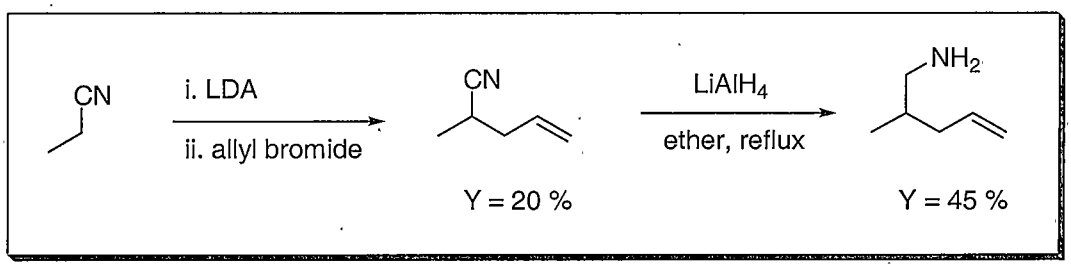
^1H NMR (300 MHz, C_6D_6): δ 2.60 (d, *J* = 7.2 Hz, 2H, NCH_2), 1.29 (s, 2H, CH_2), 1.09 (s, 6H, CH_3), 0.95 (s, 6H, CH_3) ppm.

N-(*p*-Tolylsulfonyl)-2,2,4,4-tetramethylpyrrolidine (**Ts-16b**) [68]

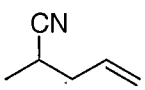


This compound was prepared in a fashion analogous to **20** (p.109) utilizing 2,2,4,4-tetramethylpyrrolidine (**16b**). This spectrum is consistant with the data in literature. [[68]Tamaru, Y.; Hojo, M,; Higashimura, H.; Yoshida, Z.-i. *J. Am. Chem. Soc.* 1988, *110*, 3994].

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.71 (d, J = 8.1 Hz, 2H, ArH), 7.25 (d, J = 8.1 Hz, 2H, ArH), 3.04 (s, 2H, CH_2), 2.39 (s, 3H, $PhCH_3$), 1.67 (s, 2H, CH_2), 1.47 (s, 6H, CH_3), 1.01 (s, 6H, CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.51, 138.09, 129.18, 127.25, 65.44, 61.12, 56.80, 36.02, 29.75, 27.31, 21.37 ppm; HRMS calcd for $C_{15}H_{23}NO_2S^+$ 281.1449, found 281.1442.



2-Methylpent-4-enenitrile (**14c**) [39b]

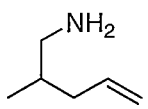


This compound was prepared according to the procedure in literature by utilizing propionitrile (10 mL, 0.14 mol), diisopropylamine (19.6 mL, 0.14 mol), *n*-BuLi (2.54 M,

55 mL, 0.14 mol) and allyl bromide (12.1 mL, 0.14 mol) to give 2.67 g (20%) of **14c**. [Purification by distillation using Vigreux column at 139 °C].

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.78 (m, 1H, -CH=), 5.16 (m, 2H, $=CH_2$), 2.65 (m, 1H, CHCN), 2.30 (app bs, 2H, CH_2), 1.29 (d, J =7.2 Hz, 3H, CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 132.94, 122.43, 118.91, 37.85, 25.29, 17.37 ppm ; LRMS (EI): m / z (relative intensity) 95 (M^+, 100), 80 (12), 53 (61).

2-Methylaminohex-4-ene (**15c**) [39b]

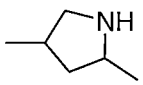


This compound was prepared in a fashion analogous to **15e** (p.104) utilizing 2-methylpent-4-enenitrile (**14c**) (2.67 g, 28 mmol), $LiAlH_4$ (2.1 g, 56 mmol) and Et_2O (110 mL) to give 1.5 g (54%) of **15c**. [Purification by distillation at 100-101 °C (lit.[6] 115-116 °C); d = 0.791].

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.76 (ddt, J = 17.1, 10.2, 7.2 Hz, -CH=), 5.00 (m, 2H, $=CH_2$), 2.61 (dd, J = 12.6, 6.0 Hz, 1H, NC*H*H), 2.46 (dd, J = 12.6, 6.9 Hz, 1H, NCH*H*), 2.11 (m, 1H, C*H*H), 1.87 (m, 1H, CH*H*), 1.53 (app octet, 1H, CH), 1.27 (bs, 2H, NH_2), 0.88 (d, J = 6.6 Hz, 3H, CH_3) ppm ; ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.10, 115.79, 47.97, 38.87, 36.23, 17.25 ppm; IR (neat): ν 3371.8, 3296.3, 3075.2, 2955.8, 2906.9,

1639.5, 1460.9, 908.3 cm^{-1}; LRMS (EI): m / z (relative intensity) 99 (M^+, 0.8), 98 (3.3), 82 (36), 56 (100).

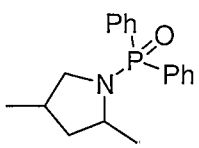
2,4-Dimethylpyrrolidine (**17c**,**18c**) [7d]



See the reference for separated spectrum of *cis* and *trans*. [[7d] Pugin, B.; Venanzi, L. *J. Organometallic Chem.* 1981, *214*, 125.

^1H NMR (300 MHz, C_6D_6): (*cis* / *trans* mixture): δ 3.05-2.87 (m, 1.7H), 2.43 (m, 0.7H), 2.24 (m, 0.4H), 2.01-1.79 (m, 1.4H), 1.26 (app t, 1H), 1.03 (2d, 3H), 0.66 (m, 1H) ; *cis*: 0.90 (d, J = 6.6 Hz, 2H, CH_3); *trans*: 0.81 (d, J = 6.9 Hz, 1H, CH_3) ppm.

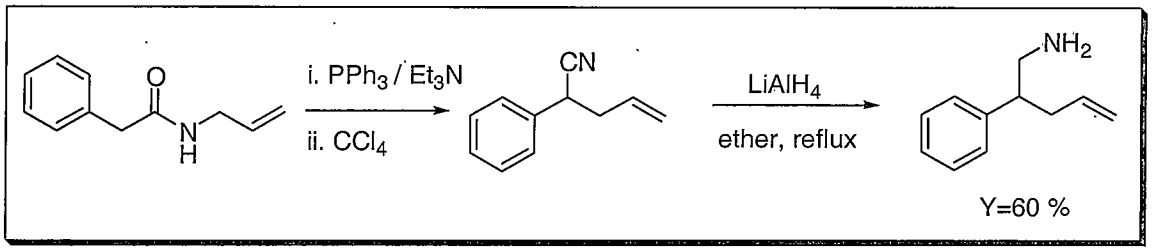
N-Diphenylphosphinoyl-2,4-dimethylpyrrolidine (**Ph_2PO-17c**, **Ph_2PO-18c**) [55]



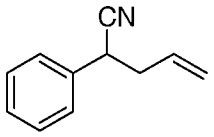
The phosphinoylation was accomplished by using the literature procedure. This spectrum is consistant with the data in literature. [[55] Besev, M.; Engman, L. *Org. Lett.* 2000, 2, 1589]. See the reference for separated spectrum of *cis* and *trans*.

^1H NMR (300 MHz, $CDCl_3$): (*cis* / *trans* mixture): δ 7.9-7.6 (m, 4H), 7.45-7.21 (m, 6H), 3.73 (m, 1H), 3.20 (m, 1H), 2.62 (m, 0.33H), 2.42-2.10 (m, 1.67H), 1.62 (m, 0.33H), 1.03

(m, 0.66H); *trans*: 0.94 (d, J = 6.3 Hz, 2H, CH_3), 0.93 (d, J = 6.6 Hz, 2H, CH_3) ; *cis*: 0.91 (d, J = 6.0 Hz, 1H, CH_3), 0.89 (d, J = 5.7 Hz, 1H, CH_3) ppm. LRMS (EI): m / z (relative intensity) 299 (M^+, 3), 284 (97), 201 (100), 98 (80).



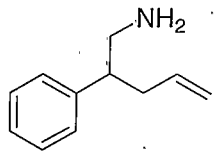
2-Phenylpent-4-enenitrile (**14d**)



This compound was prepared according to the procedure in literature by utilizing *N*-allyl-2-phenylacetamide[39] (8.7 g, 0.05 mol), PPh_3 (27.4 g, 0.105 mol), Et_3N (20.7 mL, 0.15 mol) and CCl_4 (14.4 mL, 0.15 mol). [Purification by distillation at 63-64 °C / 0.05 torr]. This spectrum is consistant with the data in literature.[39]

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.33 (m, 5H, ArH), 5.78 (ddt, J = 14.1, 9.9, 7.2 Hz, 1H, -CH=), 3.83 (t, J = 7.2 Hz, 1H, CH), 2.62 (m, 2H, CH_2) ppm;

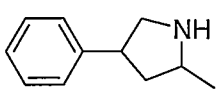
2-Phenylaminopent-4-ene (**15d**) [39d]



This compound was prepared in a fashion analogous to **15e** (p.104) utilizing 2-phenylpent-4-enenitrile (**14d**) (3g, 19 mmol) and $LiAlH_4$ (1.4g, 38 mmol) in Et_2O (60 mL) to give 1.85 g (60%) of **15d**. [Purification by distillation at 203-204 °C].

^1H NMR (300 MHz, $CDCl_3$): δ 7.25 (m, 5H, ArH), 5.67 (ddt, *J* = 17.1, 10.2, 7.2 Hz, 1H, -CH=), 4.97 (bd, *J* = 17.1 Hz, =C*H*H), 4.92 (bd, *J* = 10.2 Hz, 1H, =CH*H*), 2.95 (dd, *J* = 12.6, 5.7 Hz, 1H, NC*H*H), 2.83 (dd, *J* = 12.6, 8.7 Hz, 1H, NCH*H*), 2.67 (app quintet, 1H, -CH-), 2.36 (m, 2H, CH_2), 1.32 (bs, 2H, NH_2) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.03, 136.55, 128.46, 127.90, 126.44, 116.04, 49.39, 47.44, 38.30 ppm ; IR (neat): ν 3370.6, 3294.9, 3061.8, 2919.4, 1639.6, 1601.2, 1493.5, 1452.5, 913.3, 701.0 cm; LRMS (EI): m / z (relative intensity) 161 (M^+, 3), 160 (25), 146 (7), 91 (100).

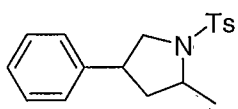
2-Methyl-4-phenylpyrrolidine (**17d**,**18d**) [68]



This spectrum is consistant with the data in literature. [[68] Cignarella, G.; Barlocco, D.; Landriani, L.; Pinna, G. A.; Andriuoli, G.; Dona, G. *Farmaco* 1991, *46*, 527]

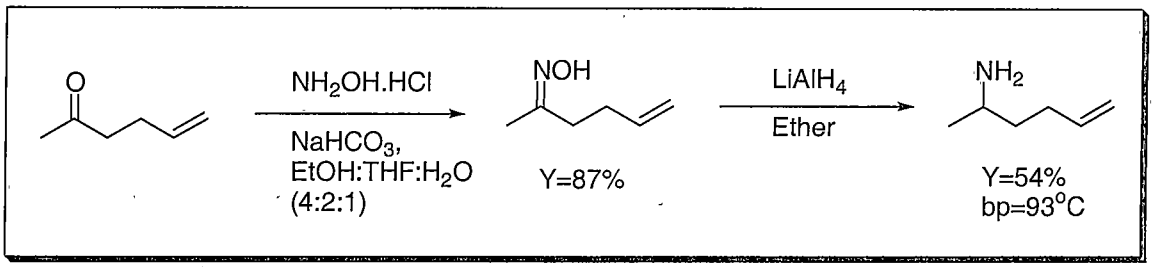
^{1}H NMR (300 MHz, C_6D_6): (*cis/trans* mixture): δ 7.21-7.03 (m, 5H), 3.23-2.67 (m, 3.6H), 2.72 (app q, 0.4H), 2.05 (m, 0.47H), 1.80 (m, 0.6H), 1.52 (m, 0.6H), 1.24 (m, 0.6H); *cis*: 1.08 (d, J = 6.0 Hz, 1.9H, CH_3); *trans*: 1.02 (d, J = 6.3 Hz, 1.1H, CH_3) ppm.

N-(*p*-Tolylsulfonyl)-2-methyl-4-phenylpyrrolidine (**Ts-17d**,**Ts-18d**)

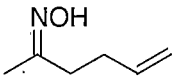


This compound was prepared in a fashion analogous to **20** (p.109) utilizing 2-methyl-4-phenylpyrrolidine (**17d**,**18d**)

^{1}H NMR (300 MHz, $CDCl_3$): (*cis* / *trans* mixture); only major peaks (*cis*): δ 7.69 (d, J = 8.4 Hz, 2H, ArH), 7.0 (d, J = 8.4 Hz, 2H, ArH), 6.94 (m, 5H, ArH), 3.71 (m, 2H, NCH_2), 3.27 (app t, 1H, NCH), 2.56 (m, 1H, PhCH), 2.36 (s, 3H, $PhCH_3$), 2.26 (m, 1H, C*H*H), 1.61 (m, 1H, CH*H*), 1.39 (d, J = 6.3 Hz, 3H, CH_3) ppm ; ^{13}C NMR (75 MHz, $CDCl_3$): (*cis* / *trans* mixture); only major peaks (*cis*): δ 143.33, 139.76, 139.56, 135.18, 129.66, 128.50, 127.35, 126.86, 56.96, 54.99, 42.83, 42.09, 22.58, 21.45 ppm ; HRMS calcd for $C_{18}H_{21}NO_2S^+$ 315.1293, found 315.1279.



Hex-5-en-2-one oxime (**14e**) [70]

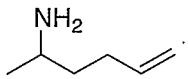


To a solution of hex-5-en-2-one (3 g, 30.6 mmol) in 30 mL of EtOH:THF:H_2O (4:2:1, by volume) was added hydroxylamine hydrochloride, $NH_2OH{\cdot}HCl$ 4.25 g (61.2 mmol), followed by sodium bicarbonate, $NaHCO_3$ (5.14 g, 61.2 mmol) at 0 °C. The reaction mixture was stirred for 30 min at room temperature. After concentration, the resedue was diluted with 20 mL of ethyl acetate, washed with water (3 mL x 3) followed by brine solution (3 mL). The resultant solution was dried (anhydrous $MgSO_4$), filtered, and concentrated in vacuo. The crude product was distilled to afford 3.22 g (93%) of title compound **14e**. [$R_f = 0.35_{KMnO4,}$ two times were developed with 10% ethyl acetate in n-hexane].

^{1}H NMR (300 MHz, $CDCl_3$): (*E*/*Z* mixture): δ 9.03 (bs, 1H, OH), 5.78 (m, 1H, -CH=), 5.02 (m, 2H, =CH_2), 2.45 (t, *J* = 7.2 Hz, 0.6 H, CH_2), 2.26 (app s, 3.4 H, CH_2), 1.86 (s, 1.8 H, CH_3), 1.85 (s, 1.2 H, CH_3) ppm ; ^{13}C NMR (75 MHz, $CDCl_3$): (*E*/*Z* mixture): δ 157.87, 137.41, 137.19, 115.33, 115.18, 105.36, 35.17, 30.29, 29.42, 27.87, 19.93, 13.53

ppm ; IR (neat): ν 3240.2, 3078.6, 2917.8, 1663.1, 1641.7, 1446.1, 914 cm^{-1}; LRMS (EI): m / z (relative intensity) 113 (M^+, 10), 98 (37), 55 (100)

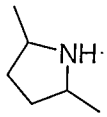
2-Aminohex-5-ene (**15e**) [39a]



To a suspension of $LiAlH_4$ (2.07 g, 47 mmol) in 60ml of dry Et_2O at 0 °C was added dropwise hex-5-en-2-one oxime (**14e**) (3 g, 26.5 mmol). After refluxing for 3 h, the reaction mixture was cooled to 0°C and carefully quenched via sequential addition of H_2O (2 mL), 15% NaOH (2 mL) and H_2O (4 mL). The mixture was stirred for 2 h at room temperature, and anhydrous $MgSO_4$ (5 g) was added. The suspension was filtered. The filter cake was leached with Et_2O and concentrated by distillation using Vigreux column. The residue was purified by distillation at 92-93 °C to afford 1.66 g (63%) of title compound **15e**.

^1H NMR (300 MHz, $CDCl_3$): δ 5.79 (ddt, *J* = 17.1, 10.2, 6.6, Hz, 1H, -CH=), 4.98 (bd, *J* = 17.1 Hz, 1H, =C*H*H), 4.92 (bd, *J* = 10.2 Hz, 1H, =CH*H*), 2.87 (sextet, *J* = 6.3 Hz, 1H, CH), 2.07 (m, 2H, CH_2), 1.38 (m, 2H, CH_2), 1.16 (bs, 2H, NH), 1.03 (d, *J* = 6.3 Hz, 3H, CH_3) ppm ; ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.62, 114.43, 46.44, 39.23, 30.73, 23.92 ppm ; IR (neat): ν 3356.9, 3286.1, 3076.4, 2958.1, 2923.6, 1640.2, 1453.6, 909.6 cm^{-1}; LRMS (EI): m / z (relative intensity) 99 (M^+, 1.6), 98 (6.5), 84 (37), 67 (100).

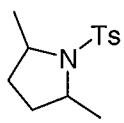
2,5-Dimethylpyrrolidine (**17e**,**18e**) [22h]



This spectrum is consistant with the data in literature. [[22h] Gagne, M. R.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* 1992, *114*, 275. [71] Harding, K.E.; Burks, S.R. *J. Org. Chem.* 1981, *46*, 3920]. See the references for separated spectrum of *cis* and *trans*.

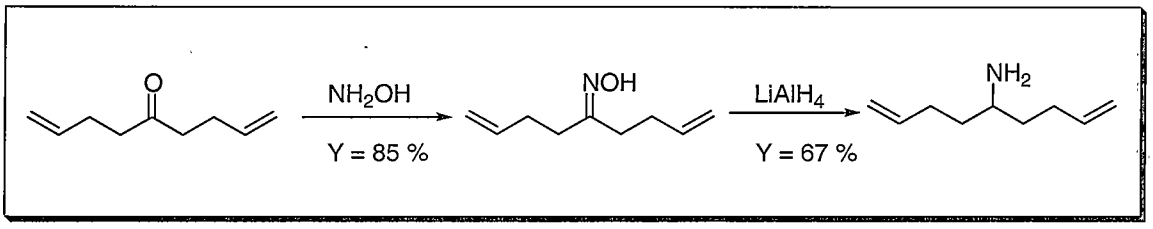
^{1}H NMR (300 MHz, C_6D_6): (*cis* / *trans* mixture), only major peaks (*trans*) based on the spectrum in reference: δ 3.14 (septet, J = 6.3 Hz, 2H, NCH), 1.75 (m, 2H, C*H*H), 1.07 (m, 2H, CH*H*), 0.99 (d, J = 6.3 Hz, 3H, CH_3), 0.86 (bs, 1H, NH); *cis* (only one of methyl peaks): δ 2.93 (m, NCH) ppm.

N-(p-Tolylsulfonyl)-2,5-dimethylpyrrolidine (**Ts-17e**, **Ts-18e**) [72b]

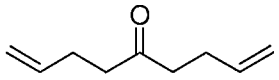


This compound was prepared in a fashion analogous to **20** (p.109) utilizing 2,5-dimethyl-pyrrolidine (**17e**,**18e**). This spectrum is consistant with the data in literature. [[72b] Baeckvall, J.-E.; Schink, H. E.; Renko, Z. D. *J. Org. Chem.* 1990, *55*, 826]. See the reference for separated spectrum of *cis* and *trans*.

^{1}H NMR (300 MHz, $CDCl_3$): (*cis* / *trans* mixture); only major peaks (*trans*) based on the spectrum in reference: δ 7.71(d, *J* = 7.9 Hz, 2H, ArH), 7.23 (d, *J* = 7.9 Hz, 2H, ArH), 3.99 (quintet, *J* = 6.3 Hz, 2H, NCH), 2.38 (s, 3H, CH_3), 2.08 (m, 2H, C*H*H), 1.50 (m, 2H, CH*H*), 1.16 (d, *J* = 6.3 Hz, 6H, CH_3) ppm ; ^{13}C NMR (75 MHz, $CDCl_3$) (*cis* / *trans* mixture), only major peaks (*trans*) based on the spectrum in reference: δ 142.52, 139.72, 129.34, 126.92, 57.54, 31.13, 21.41, 21.27 ppm ; LRMS (EI): m / z (relative intensity) 253 (M^+, 4), 238 (100), 155 (69), 91 (64).



Nona-1,8-dien-5-one (**13f**) [39e]



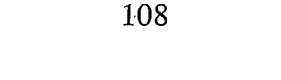
This compound was prepared via slightly modified literature procedure.[39e] To a solution of *N'*-isopropylidene-*N,N*-dimethylhydrazine [39e] (4.73g, 47 mmol) in THF (200 mL) was added dropwise *n*-BuLi (2.54 M, 20.5 mL, 52 mmol) and the reaction mixture was allowed to stir at 0 °C for 30 min. To the reaction mixture was added allyl bromide (4.5 mL, 51.7 mmol) and the resultant solution was stirred at room temperature for 2 h. This procedure was repeated by dropwise addition of *n*-BuLi (2.54 M, 20.5 mL, 52

mmol) to the above reaction mixture, followed by stirring at 0 °C for 30 min. To the reaction mixture was added allyl bromide (4.5 mL, 51.7 mmol) and the resultant solution was stirred at room temperature for 2 h. After dilution with ether (100 mL), the mixture was washed with saturated NH_4Cl and brine solution. The organic layer was dried (anhydrous $MgSO_4$), filtered, and evaporated in vacuo over ice-water bath.

The residue was added to a solution of 10% aqueous HCl: CH_2Cl_2 (1:2, v/v) and the resultant was stirred for 20 min. The heterogeneous mixture was separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 15 mL). The organic phase was dried (anhydrous $MgSO_4$), filtered, and evaporated in vacuo. The residue was purified by column chromatography on silica gel (10% ethyl acetate in *n*-hexane for elution) to furnish 2.6 g (40%) of the title compound **13f**.

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.78 (ddt, J = 16.8, 10.2, 6.3 Hz, 2H, -CH=), 5.00 (bd, J = 16.8 Hz, 2H, =C*H*H), 4.96 (bd, J = 10.2 Hz, 2H, =CH*H*), 2.49 (t, J = 7.3 Hz, 4H, $COCH_2$), 2.30 (app q, 4H, CH_2) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 209.29, 137.07, 115.18, 41.83, 27.68 ppm; LRMS (EI): m / z (relative intensity) 138 (M^+, 0.4), 83 (44), 55 (100).

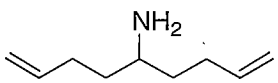
Nona-1,8-dien-5-one oxime (**14f**) [39f]



This compound was prepared in a fashion analogous to **14e** (p.103) utilizing nona-1,8-dien-5-one (2.66 g, 19 mmol), $NH_2OH \cdot HCl$ (4.01 g, 57 mmol), $NaHCO_3$ (4.85 g, 57 mmol) and 30 mL of EtOH : THF : H_2O (4 : 2 : 1, by volume) mixture to give 2.5 g (85%) of **14f**. [Purification by column chromatography on silica gel (15% ethyl acetate in *n*-hexane for elution); $R_f = 0.36$ $_{KMnO4}$].

^1H NMR (300 MHz, $CDCl_3$): (*E* / *Z*): δ 9.28 (bs, 1H, NOH), 5.81 (m, 2H, -CH=), 5.01 (m, 4H, $=CH_2$), 2.43 (t, J = 7.5 Hz, 2H, CH_2), 2.27 (bs, 6H, CH_2) ppm ; ^{13}C NMR (75 MHz, $CDCl_3$): (*E* / *Z*): δ 160.29, 137.53, 137.36, 115.24, 115.13, 33.57, 30.14, 29.53, 27.12 ppm; IR (neat): ν 3250.1, 3077.4, 2920.2, 1641.7, 1446.0, 994.6, 911.9 cm^{-1}; LRMS (EI): m / z (relative intensity) 153 (M^+, 0.8), 152 (6), 136 (72), 55 (100).

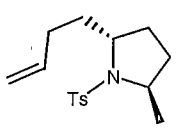
1-But-3-enylpent-4-enylamine (**15f**)



This compound was prepared in a fashion analogous to **15e** (p.104) utilizing nona-1,8-dien-5-one oxime (2.45 g, 16 mmol), $LiAlH_4$ (1.25 g, 32 mmol) and Et_2O (70 mL) to give 1.5 g (67%) of **15f**.

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.80 (ddt, J = 16.8, 10.2, 6.6 Hz, 2H, -CH=), 5.01 (bd, J = 16.8 Hz, 2H, =C*H*H), 4.93 (bd, J = 10.2 Hz, 2H, =CH*H*), 2.72 (m, 1H, CH), 2.13 (m, 4H, CH_2), 1.50 (m, 2H, CH_2), 1.34 (m, 2H, CH_2), 1.18 (bs, 2H, NH_2) ppm ; ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.64, 114.50, 50.22, 37.21, 30.44 ppm ; IR (neat): ν 3367.0, 3292.6, 3075.7, 2918.9, 2849.8, 1639.8, 1450.0, 994, 909 cm^{-1}; LRMS (EI): m / z (relative intensity) = 139 (M^+, <0.1), 138 (1), 84 (100)

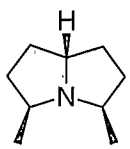
N-(*p*-Tolylsulfonyl)-2-but-3-enyl-5-methylpyrrolidine (**20**)



REPRESENTATIVE METHOD FOR SULFONYLATION: The reaction mixture, which was completely cyclized to 2-but-3-enyl-5-methylpyrrolidine (0.32 mmol) by catalyst $Y[N(TMS)_2]_3$, was diluted with CH_2Cl_2 (1 mL) followed by addion of pyridine (79 μL) and TsCl (77 mg, 4 μmol) at 0 °C. After stirring for 2 h, the reaction mixture was diluted with CH_2Cl_2 (15 mL) and washed with 1N HCl (2 x 3 mL). The organic layer was dried ($MgSO_4$), filtered, and concentrated in vacuo. The residue was subjected to column chromatography on silica gel (5% ethyl acetate / *n*-hexane for elution) to give 82 mg (81.3%) of the title compound **20** as colorless solid. The ratio of *trans*:*cis* was determined by GC analysis to be 13 : 1.

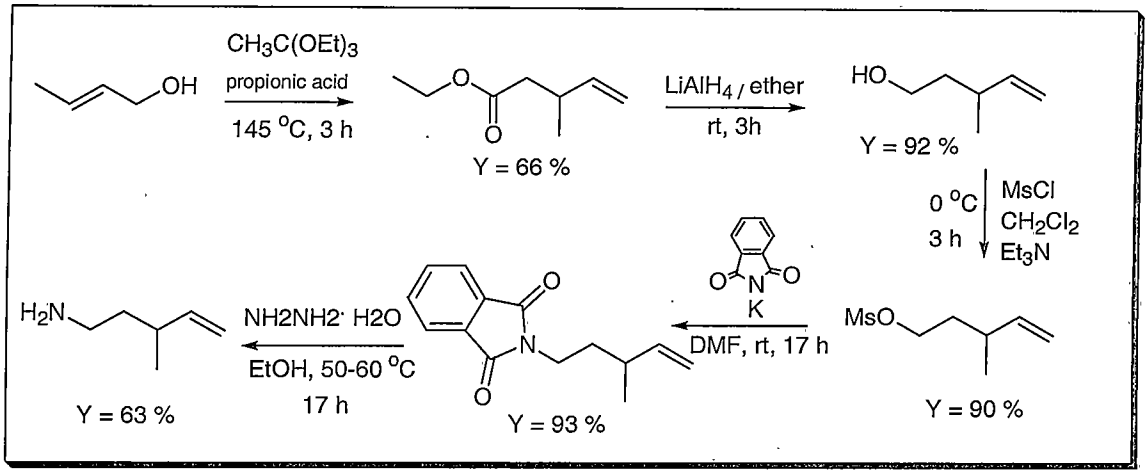
^{1}H NMR (300 MHz, $CDCl_3$): (*trans* / *cis* mixture = 13/1), only major peaks (*trans*): δ 7.65 (d, *J* = 8.4 Hz, 2H, ArH), 7.18 (d, *J* = 8.4 Hz, 2H, ArH), 5.68 (m, 1H, -CH=), 4.89 (m, 2H), 3.96 (app quintet, 1H, NCH), 3.76 (m, 1H, NCH), 2.33 (s, 3H, CH_3), 1.95 (m, 5H), 1.60 (m, 1H), 1.45-1.20 (m, 2H), 1.10 (d, *J* = 6.3 Hz, 3H, CH_3) ppm ; ^{13}C NMR (75 MHz, $CDCl_3$) (*cis* / *trans* mixture), only major peaks (*trans*): δ 142.54, 139.62, 137.73, 129.34, 126.89, 114.77, 59.95, 56.33, 33.11, 31.35, 30.49, 27.65, 21.39, 20.86 ppm ; HRMS (EI): calcd for $C_{16}H_{23}NO_2S^+$ 293.1449, found 293.1445.

3,5-Dimethylhexahydropyrrolizine (**21**) [39f]

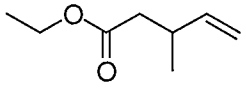


See the reference for separated spectrum of *cis* and *trans*. [[39f] Ciganek, E. *J. Org. Chem.* 1995, *60*, 5803]

^{1}H NMR (300 MHz, C_6D_6): (mixture of monocyclized *cis*-**20**): only the peaks of the title compound based on the spectrum in the reference for **21** and the spectrum of the monocyclized *cis*-**20**; δ 3.64 (quintet, *J* = 6.9 Hz, 1H, CH), 2.65 (m, 2H, CH), 1.79 (m, 4H, CH_2), 1.40 (m, 2H, C*H*H), 1.21 (m, 2H, CH*H*), 1.15 (d, *J* = 6.3 Hz, 6H, CH_3) ppm ; ^{13}C NMR (75 MHz, C_6D_6): δ 65.54, 61.63, 35.83, 32.79, 22.79 ppm.



3-Methylpent-4-enoic acid ethyl ester (**40**) [73]

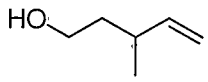


This compound was prepared according to the method in literature.[73] The mixture of crotyl alcohol (5 g, 69.3 mmol) and trietyl orthoacetate (20 g, 0.13 mol) in the presence of propionic acid (0.2 g) was heated at 145 °C oil bath for 3 h with distillation to remove the resulting ethyl alcohol. After cooling to room temperature, the reaction mixture was diluted with Et_2O (40 mL), washed with 2N HCl, H_2O, and dried over anhydrous $MgSO_4$. After filtration, the organic phase was evaporated in vacuo over ice-water bath, and purified by distillation at 142-143 °C to give 6.5 g (66%) of the title compound **40**.

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.74 (ddd, J = 17.4, 10.2, 7.2 Hz, 1H, -CH=), 5.00 (bd, J = 17.4 Hz, 1H, =C*H*H), 4.93 (bd, J = 10.2 Hz, 1H, =CH*H*), 4.10 (q, J = 7.2 Hz, 2H, CH_2), 2.65 (septet, J = 7.2 Hz, 1H, -CH-), 2.32 (dd, J = 14.7, 7.2 Hz, 1H, -CH*H*-), 2.22 (dd, J =

14.7, 7.2 Hz, 1H, -C*H*H-), 1.22 (t, J = 7.2 Hz, 3H, CH_3), 1.03 (d, J = 7.2 Hz, 3H, CH_3) ppm.

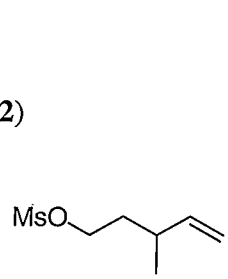
3-Methylpent-4-en-1-ol (**41**) [73]



This compound was prepared according to the procedure in literature.[73] To a suspension of $LiAlH_4$ (1.1 g, 28.1 mmol) in diethyl ether (50 mL) was added dropwise 3-methylpent-4-enoic acid ethyl ester (**40**) (2 g, 14.06 mmol) dissolved in Et_2O (10 mL) at room temperature, then the mixture was stirred for 3 h. After the typical work-up, the residue was distilled at 55-57 °C / 11 torr to provide 1.3 g (92%) of the title compound **41**. [R_f = 0.27 $_{KMnO4}$ (20% ethyl acetate in *n*-hexane).

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.76(ddd, J = 17.1, 10.2, 6.9 Hz, 1H, -CH=), 4.99 (bd, J = 17.1 Hz, 1H, =C*H*H), 4.93 (bd, J = 10.2 Hz, =CH*H*), 3.65 (t, J = 6.6 Hz, 2H, CH_2O), 2.28 (septet, J = 6.9 Hz, 1H, -CH-), 1.57 (app q, 2H, CH_2), 1.47 (bs, 1H, OH), 1.00 (d, J = 6.9 Hz, 3H, CH_3) ppm ; ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.23, 113.07, 61.21, 39.30, 34.87, 20.38 ppm; IR (neat): ν 3331.3, 2961.1, 2874.3, 1639.7, 1454.2, 1417.3, 1373.5, 1052.5, 995.7, 911.7 cm^{-1}; LRMS (EI): m / z (relative intensity) 100 (M^+, <0.1), 82 (18), 67 (100), 55 (52).

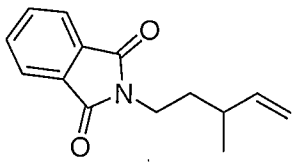
3-Methylpent-4-enyl-1-mesylate (**42**)



To a solution of 3-methylpent-4-en-1-ol (**41**) (2.8 g, 28 mmol) in CH_2Cl_2 (110 mL) at 0 °C was added triethylamine (7.8 mL, 55.9 mmol), methansulfonyl chloride (3.5 g, 30.8 mmol), then the mixture was stirred at 0 °C for 3 h. The reaction mixture was diluted with CH_2Cl_2 (30 mL), washed with H_2O (3 x 5 mL), dried over anhydrous $MgSO_4$. After filteration, the solvent was evaporated in vacuo. The residue was purified by bulb to bulb distillation at 60 °C / 1.5 torr to furnish 4.5 g (90%) of the title compound **42**. R_f= 0.23 $_{KMnO4}$ (20% ethyl acetate in *n*-hexane)

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.62 (m, 1H, -CH=), 5.00 (m, 2H, $=CH_2$), 4.22 (m, 2H, OCH_2), 2.97 (s, 3H, SCH_3), 2.31 (septet, *J* = 6.6 Hz, -CH-), 1.73 (m, 2H, CH_2), 1.03 (d, *J* = 6.6 Hz, 3H, CH_3) ppm ; ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.53, 114.34, 68.36, 37.33, 35.42, 34.34, 20.23 ppm ; IR (neat): ν 2965.6, 1640.5, 1358.9, 1175.3, 974.9, 942.4 cm^{-1}; LRMS (EI): m / z (relative intensity) 178 (M^+, <0.01), 82 (17), 69 (100).

N-(3-Methylpent-4-enyl)phthalimide (**43**)



To a solution of 3-methylpent-4-enyl-1-mesylate (**42**) (1.46 g, 8.2 mmol) in DMF (75 mL) was added potassium phtalimide (1.3 g, 7.0 mmol), then the mixture was stirred at room temperature for overnight. The reaction mixture was diluted with ethyl acetate (100 mL) and washed with H_2O (5 x 5 mL). The organic phase was dried (anhydrous $MgSO_4$), filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (20% ethyl acetate in *n*-hexane for elution) R_f = 0.36 anisaldehyde to furnish 1.5 g (93%) of the title compound **43**.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.81 (m, 2H, ArH), 7.67 (m, 2H, ArH), 5.70 (ddd, *J* = 17.1, 10.2, 6.9 Hz, 1H, -CH=), 5.01 (bd, *J* = 17.1 Hz, 1H, =C*H*H), 4.93 (bd, *J* = 10.2 Hz, 1H, =C*H*H), 3.65 (m, 2H, NCH_2), 2.18 (septet, *J* = 6.9 Hz, 1H, -CH-), 1.66 (app q, 2H, -CH_2-), 1.04 (d, *J* = 6.9 Hz, 3H, CH_3) ppm ; ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.36, 143.18, 133.81, 132.19, 123.11, 113.55, 36.38, 35.72, 34.80, 20.19 ppm ; IR (neat): ν 3466.9, 3076.4, 2961.0, 2869.2, 1769.6, 1713.7, 1392.4, 722.0 cm^{-1}; LRMS (EI): m / z (relative intensity) 229 (M^+, 10), 200 (31), 160 (100)

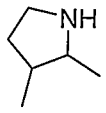
3-Methylaminohex-4-ene (**44**) [74]

To a solution of *N*-(3-methylpent-4-enyl)phthalimide (**43**) (4g, 17 mmol) in ethyl alcohol (100 mL) was added hydrazine monohydrate (0.85 mL, 17 mmol), then the mixture was heated at 50~60 °C for overnight. After cooling to room temperature, the reaction mixture was filtered and the filtercake was washed with ethyl alcohol (3 x 10 mL). To the organic phase was added *c*-HCl (7 mL) and the solution was evaporated in vacuo. To the resulting white solid was added CH_2Cl_2 (200 mL), KOH pellets (3 g), and H_2O (3 mL). After stirring for 10 min, the organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phase was dried (KOH pellet), filtered, and concentrated in vacuo over ice-water bath. The residue was distilled at 109-110 °C to furnish 1.05 g (63%) of the title compound **44**.

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.59 (ddd, J = 17.7, 10.2, 7.5 Hz, 1H, -CH=), 4.86 (bd, J = 17.7 Hz, 1H, =CH*H*), 4.82 (bd, J = 10.2 Hz, 1H, =C*H*H), 2.59 (t, J = 6.9 Hz, 2H, NCH_2), 2.12 (septet, J = 6.9 Hz, 1H, CH), 1.34 (q, J = 6.9 Hz, 2H, CH_2), 1.06 (bs, 2H, NH_2), 0.90 (d, J = 6.9 Hz, 3H, CH_3) ppm ; ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.31, 112.62, 40.56, 40.11, 35.56, 20.29 ppm; IR (neat): ν 3299.2, 3076.4, 2960.9, 2924.6, 1639.6,

1462.0, 910.7 cm^{-1}; LRMS (EI): m / z (relative intensity) 99 (M^+, 1), 98 (5), 84 (25), 67 (74), 56 (100).

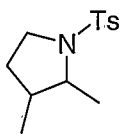
2,3-Dimethylpyrrolidine (**51**) [75]



See the reference for separated spectrum of *cis* and *trans*. [[75] Barbry, D.; Hasiak, B.; Couturier, D. *Magn. Reson. Chem.* 1990, *28*, 560]

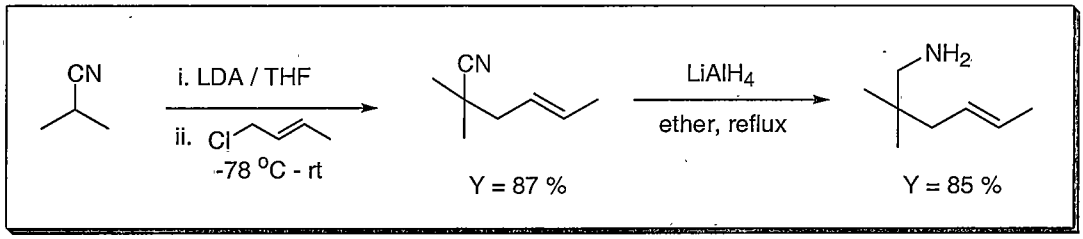
^1H NMR (300 MHz, toluene-d_8): (*cis* / *trans* mixture); only major peaks (*trans*) based on the spectrum in reference: δ 2.79 (m, 2H, NCH_2), 2.37 (m, 1H, NCH), 1.81 (m, 1H, C*H*H), *1*.20 (m, 2H, C*H*H, CH), 1.01 (d, J = 6.3 Hz, 3H, CH_3), 0.87 (d, J = 6.3 Hz, CH_3); *cis* (only one of methyl groups): 0.75 (d, J = 6.9 Hz, CH_3) ppm.

N-(*p*-Tolylsulfonyl)-2,3-dimethylpyrrolidine (**Ts-51**) [76]

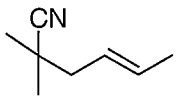


This compound was prepared in a fashion analogous to **20** (p.109) but utilizing 2,3-dimethylpyrrolidine (**51**). This spectrum is consistant with the data in literature [[76]

Nagashima, H.; Ozaki, N.; Ishii, M.; Seki, K.; Masayoshi Washiyama, M.; Itoh, K. *J. Org. Chem.* 1993, *58*, 464]. See the reference for separated spectrum of *cis* and *trans*. ^{1}H NMR (300 MHz, $CDCl_3$): (*cis* / *trans* mixture); only major peaks (*trans*) based on the spectrum in reference: δ 7.68 (d, *J* = 8.1 Hz, 2H, ArH), 7.27 (d, *J* = 8.1 Hz, 2H, ArH), 3.32 (m, 2H, NCH_2), 3.08 (quintet, *J* = 6.1 Hz, 1H, NCH), 2.39 (s, 3H, CH_3), 1.89-1.70 (m, 2H, CH_2), 1.31 (d, *J* = 6.1 Hz, 3H, CH_3), 1.08 (m, 1H, CH), 0.65 (d, *J* = 6.9 Hz, 3H, CH_3) ; *cis* (only one of methyl peaks): 0.85 (d, *J* = 6.6 Hz) ppm. LRMS (EI): m / z (relative intensity) 253 (M^+, 7), 238 (100), 155 (77), 91 (82).



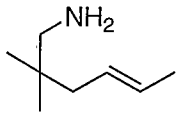
2,2-Dimethylhex-4-enenitrile (**46**) [15a]



This compound was prepared in a fashion analogous to **14a** (p.92) utilizing isobutyronitrile (3.8 g, 55 mmol) in THF (91 mL), diisopropylamine (8.5 mL, 60.5 mmol), *n*-BuLi (2.59 M, 23.3 mL, 60.5 mmol), (*E*)-2-butene-1-ol (5.9 mL, 60.5 mmol) and THF (20mL) to give 5.9 g (87%) of **46**. [Purification by distillation at 60~65 °C / 30 torr; R_f = 0.58 $_{KMnO4}$ (20% ethyl acetate in *n*-hexane)]

^{1}H NMR (300 MHz, $CDCl_3$): (*E* / *Z* mixture, 19% *Z* form) δ 5.59-5.42 (m, 2H, CH=CH), 2.25 (d, *J* = 7.5 Hz, 0.28H, CH_2), 2.15 (d, *J* = 6.9 Hz, 1.82H, CH_2), 1.67 (dd, *J* = 6.0, 0.9 Hz, 2.16H, CH_3), 1.61 (d, *J* = 6.9 Hz, 0.84H, CH_3), 1.27 (s, 6H, CH_3) ppm ; ^{13}C NMR (75 MHz, $CDCl_3$): (*E* / *Z* mixture), *E* only: δ 130.63, 124.98, 124.72, 43.94, 32.48, 26.17, 17.94 ppm ; IR (neat): ν 2977.2, 2936.0, 1453.8, 1369.3, 969.6 cm^{-1}; LRMS (EI): m / z (relative intensity) 123 (M^+, 5), 69 (61), 55 (100).

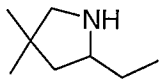
2,2-Dimethylaminohex-4-ene (**47**) [15a]



This compound was prepared in a fashion analogous to **15e** (p.104) utilizing 2,2-dimethylhex-4-enenitrile (**46**) (5 g, 40.6 mmol), $LiAlH_4$ (3.08 g, 81.2 mmol) and Et_2O (30 mL) to give 4.4 g (85%) of **47**. [Purification by distillation at 150-152 °C]

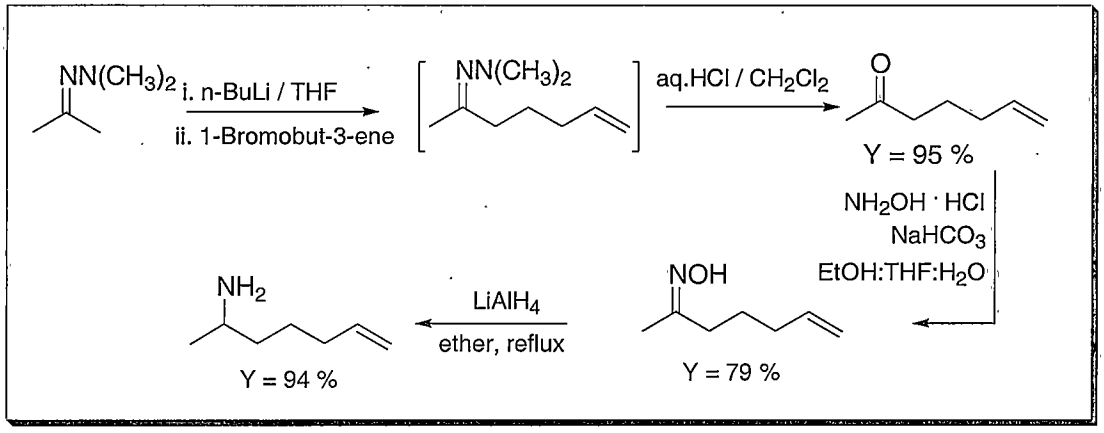
^{1}H NMR (300 MHz, $CDCl_3$): (*E* / *Z* mixture, 19% *Z* form): δ 5.41 (m, 2H, CH=CH), 2.44 (s, 0.38H, CH_2), 2.40 (s, 1.62H, CH_2), 1.94 (d, *J* = 7.5 Hz, 0.38H, CH_2), 1.86 (m, 1.62H, CH_2), 1.63 (dd, *J* = 3.6, 0.9 Hz, 2.43H, CH_3), 1.59 (d, *J* = 6.0 Hz, 0.57H, CH_3), 1.23 (bs, 2H, NH), 0.85 (s, 1.14H, CH_3), 0.83 (s, 4.86H, CH_3) ppm ; ^{13}C NMR (75 MHz, $CDCl_3$): (*E* / *Z* mixture), *E* only: δ 127.59, 127.23, 52.65, 42.62, 35.01, 24.62, 17.99 ppm ; IR (neat): ν 3328.2, 3304.6, 2957.4, 1573.8, 1470.0, 1366.0, 1315.8, 968.2 cm^{-1}; LRMS (EI): m / z (relative intensity) 127 (M^+, 1.6), 110 (26), 55 (100).

2-Ethyl-4,4-dimethylpyrrolidine (**52**) [15a]

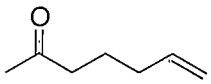


This spectrum is consistant with the data in literature [[15a] Ryu, J.-S.; Marks, T. J.; McDonald, F. E. *Org. Lett.*, 2001, *3*, 3091].

^{1}H NMR (300 MHz, C_6D_6): δ 2.87 (m 1H, NCH), 2.60 (dd, J = 9.9, 5.7 Hz, 1H, NC*H*H), 2.46 (dd, J = 9.9, 6.9 Hz, 1H, NCH*H*), 1.50-1.17 (m, 4H, CH_2), 0.98 (s, 3H, CH_3), 0.91 (s, 3H, CH_3), 0.87 (t, J = 7.5 Hz, 3H, CH_3) ppm.



ept-6-en-2-one (**48**) [49a]

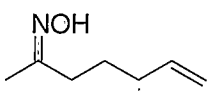


To a solution of *N'*-isopropylidene-*N,N*-dimethylhydrazine [77] (2 g, 20 mmol) in THF (50 mL) at 0 °C was slowly added *n*-BuLi (2.51 M, 7.96 mL, 20 mmol) and the mixture was stirred for 40 min. To the reaction mixture was added dropwise 1-bromide-3-pentene (2.21 mL, 22 mmol), then the mixture was stirred at the same temperature for 2 h. After dilution with Et_2O (30 mL), the mixture was washed with saturated NH_4Cl and brine solution. The organic layer was dried ($MgSO_4$), filtered and concentrated in vacuo over ice-water bath to afford 2.55 g (96%) of *N,N*-dimethyl-*N'*-(1-methylhex-5-enylidene) hydrazine [R_f = 0.19 $_{KMnO4}$ (40% ethyl acetate in *n*-hexane)]. This compound was utilized for next reaction without further purification.

To a heterogeneous solution of 10% aqueous HCl (30 mL) and CH_2Cl_2 (50 mL) was added *N,N*-dimethyl-*N'*-(1-methylhex-5-enylidene)hydrazine (2.5 g, 16.2 mmol), then the mixtuer was stirred at room temperature overnight. After separation of organic phase, the aqueous phase was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic solution was dried (anhydrous $MgSO_4$), filtered, and concentrated in vacuo. The residue was purified via column chromatography on silica gel [9% ethyl ether in *n*-pentane for elution (R_f = 0.24 $_{KMnO4}$)] to furnish 1.8 g (99%) of **48**.

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.73 (ddt, J = 17.1, 10.2, 6.6 Hz, 5.01~4.93 (m, 2H, $=CH_2$), 2.40 (t, J = 7.2 Hz, 2H, CH_2), 2.10 (s, 3H, CH_3), 2.03 (app q, 2H, CH_2), 1.64 (quintet, J = 7.2 Hz, 2H, CH_2) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 208.87, 137.91, 115.19, 42.80, 32.99, 29.91, 22.75 ppm ; IR (neat): ν 2925.2, 1715.2, 1364.8, 1163.1, 913.0 cm^{-1}; LRMS (EI): m / z (relative intensity) 112 (M^+, 11), 97 (14), 58 (100).

Hept-6-en-2-one oxime (**49**) [49b]

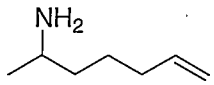


This compound was prepared in a fashion analogous to **14e** (p.103) utilizing hept-6-en-2-one (**48**) (2.1 g, 19 mmol), $NH_2OH \cdot HCl$ (3.9 g, 57 mmol), $NaHCO_3$ (4.7 g, 57 mmol) and EtOH:THF:H_2O (50 mL) to give 1.88 g (79%) of **49**. [R_f (*E/Z* oxime mixture) = 0.36 and 0.28 $_{KMnO4}$ (20% ethyl acetate in *n*-hexane)].

^{1}H NMR (300 MHz, $CDCl_3$): (*E/Z* mixture): δ 5.77(m, 1H, -CH=), 5.05 – 4.94 (m, 2H, CH_2), 2.36 (t, J = 7.5 Hz, 0.5H, CH_2), 2.18 (t, J =7.5 Hz, 1.5H, CH_2), 2.05 (app sextet, 2H, CH_2), 1.86 (s, 2H, CH_3), 1.85 (s, 1H, CH_3), 1.59 (quintet, J = 7.5 Hz, 2H, CH_2) ppm ; ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.73, 158.33, 138.02, 115.02, 35.20, 33.67, 33.13, 28.12, 25.40, 24.72, 19.85, 13.42 ppm ; IR (neat): ν 3236.0, 3077.4, 2927.3, 1663.8,

1640.6, 1456.0, 1439.6, 912.5 cm^{-1} ; LRMS (EI): m / z (relative intensity) 127 (M^+, 91), 112 (70), 55 (100).

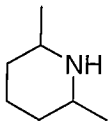
2-Aminohept-6-ene (**50**)



To a stirred suspension of $LiAlH_4$ (1g, 28 mmol) in dry Et_2O (60 mL) was added hep-6-en-2-one oxime (**49**) [5] (1.8 g, 14 mmol) dropwise at room temperature. After heating at reflux overnight, the reaction mixture was cooled to 0 °C and carefully quenched via sequential addition of H_2O (2 mL), 15% aqueous NaOH (2 mL) and H_2O (4 mL). The mixture was subsequently stirred at room temperature for 2h and anhydrous $MgSO_4$ (3 g) was added. The suspension was filtered and the filtrate was concentrated in vacuo. The residue was distilled at 101-103 °C to afford 1.5 g (94%) of the title compound **50**.

^1H NMR (300 MHz, $CDCl_3$): δ 5.79 (ddt, J = 17.1, 10.2, 6.6 Hz, 1H, -CH=), 4.97 (m, 2H, $=CH_2$), 2.86 (sextet, J = 6.3 Hz, 1H, CH), 2.04 (q, J = 6.3 Hz, 2H, $-CH_2-$), 1.46-1.32 (m, 6H, $-CH_2-$, NH_2), 1.03 (d, J = 6.3 Hz, 3H, CH_3) ppm ; ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.83, 114.46, 46.88, 39.64, 33.81, 25.74, 23.97 ppm ; IR (neat): ν 3354.3, 3278.1, 3075.9,2956.6, 2926.4, 2856.9, 1822.6, 1640.2, 1584.9, 1458.8, 1373.6, 994.9, 909.8 cm^{-1} ; HRMS (CI, NH_3): exact mass calcd for $[C_7H_{15}N+H]^+$ 114.1283, found 114.1283.

2,6-Dimethylpiperidine (**53**) [78]

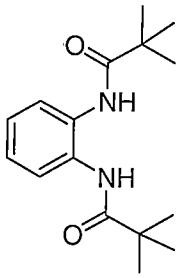


See the reference for spectrum of *trans* compound. The *cis* compound is commercial available from Aldrich. [[78a] For *trans*: Freville, S.; Bonin, M.; Celerier, J.-P.; Husson, H.-P.; Lhommet, G.; Quirion, J. –C.; Thuy, V. M. *Tetrahedron* 1997, *53*, 8447, [78b] For *cis*: aldrich reagent]

^{1}H NMR (300 MHz, C_6D_6): (*cis* / *trans* mixture); *trans*: (NCH peaks only): δ 2.95 (m. 2H. NCH); only major peaks (*cis*) based on the spectrum of commercial available *cis* compound: δ 2.46 (m, 2H, NCH), 1.65 (m, 1H, C*H*H), 1.40 (m, 2H, CH_2), 1.09 (m, 1H, CH*H*), 0.95 (d, J = 6.3 Hz, 6H, CH_3), 0.72 (bs, 1H, NH) ppm.

SYNTHESIS OF PROLIGANDS

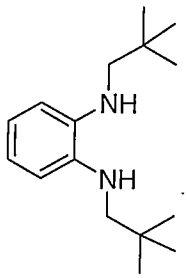
N,N'-Bis-*tert*-butylacetyl-1,2-phenylenediamine (**32a**) [44a]



To a solution of 1,2-phenylenediamine (0.3 g, 2.77 mmol) and triethylamine (0.97 mL, 6.92 mmol), dichloromethane (10 mL) at 0 °C was added dropwise trimethylacetyl chloride [99% pure, (0.724 mL, 5.82 mmol)]. The reaction mixture was stirred at room temperature overnight. The mixture was diluted with dichloromethane (20 mL), then washed with H_2O (10 mL), 1N HCl (5 mL) and saturate $NaHCO_3$ (5 mL). The organic phase was dried (anhydrous $MgSO_4$), filtered, and concentrated in vacuo to afford 0.8 g (92%) of **32a** as a white solid. $R_f = 0.59$ (50% ethyl acetate in *n*-hexane).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.14 (bs, 2H, NH), 7.21 (m, 2H, ArH), 7.03 (m, 2H, ArH), 1.17 (s, 18 H, CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 177.96, 131.00, 125.85, 125.76, 39.30, 27.61 ppm; IR (KBr): ν 3301.9, 2964.3, 1656.3, 1515.5, 747.6 cm^{-1}; LRMS (EI): m / z (relative intensity) 276 (M^+, 43), 219 (35), 135 (63), 57 (100).

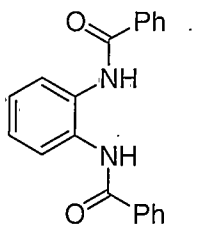
N,N'-Bis-(2,2-dimethylpropyl)-1,2-phenylenediamine (**22a**) [44b]



This compound was prepared in a fashion analogous to **23h** (p.135) utilizing *N,N'*-bis-*tert*-butylacethyl-1,2-phenylenediamine (**32a**)

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.75 (m, 2H, ArH), 6.70 (m, 2H, ArH), 3.6-3.2 (bs, 2H, NH), 2.83 (s, 4H, CH_2), 1.02 (s, 18H, CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.23, 119.24, 112.21, 56.46, 31.44, 27.82, ppm; IR (KBr):v 3311.2, 3062.1, 2953.9, 2864.5, 1600.0, 1519.8, 1472.0, 1253.2 1129.8, 736.7 cm^{-1}; LRMS (EI): m / z (relative intensity) 248 (M^+, 29), 191 (100), 121 (76).

N,N'- Bis-1,2-Phenylenebenzamide (**32b**) [44c]

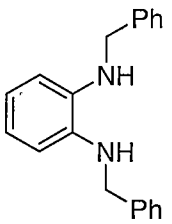


This compound was prepared in a fashion analogous to **32a** (p.125) 1,2-phenylenediamine [98% pure, (1 g, 9.06 mmol)], benzoyl chloride (2.3 mL, 19.9 mmol),

Et_3N (3.2 mL, 22.6 mmol), CH_2Cl_2 (30 mL) to give 2.8 g (98%) of **32b** as a white solid. mp = 276-277 °C

^1H NMR (300 MHz, DMSO-d_6): δ 10.04 (bs, 2H, NH), 7.91 (d, J = 6.9 Hz, 4H, ArH), 7.63 (m, 2H, ArH), 7.52 (m, 6H, ArH), 7.25 (m, 2H, ArH) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ 166.32, 135.03, 132.72, 132.17, 129.43, 128.35, 126.73, 126.43 ppm ; IR (KBr): ν 3271.4, 1656.6, 1526.5, 1498.1, 1310.3, 712.9 cm^{-1};

N,N'-Bis-benzyl-1,2-phenylendiamine (**22b**) [44c]

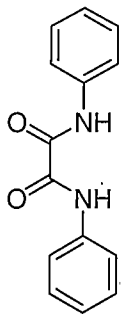


This compound was prepared in a fashion analogous to **23h** (p.135) utilizing *N,N'*-bis-1,2-phenylenebenzamide (**32b**) (1 g, 3.16 mmol), $LiAlH_4$ (0.371 g, 9.48 mmol) and THF (70 mL) to give 0.6 g (66%) of **22b**. [Purification by bulb to bulb distillation at 140 °C / 0.05 torr; $R_f = 0.25_{uv}$ (5% ethyl acetate in *n*-hexane); pale yellow oil].

^1H NMR (300 MHz, $CDCl_3$): δ 7.30 (m, 10H, ArH), 6.72 (m, 4H, ArH), 4.21 (s, 4H, CH_2), 3.74 (bs, 2H, NH) ppm; ^{13}H NMR (75 MHz, $CDCl_3$); δ 139.36, 137.09, 128.59, 127.83, 127.26, 119.49, 112.10, 48.83 ppm ; IR (neat): ν 3364.9, 3059.8, 3027.9, 2840.5,

1598.5, 1513.7, 1451.6, 1259.7, 737.7 cm^{-1}; LRMS (EI): m / z (relative intensity) 288 (M^+, 28), 197 (100), 91 (61).

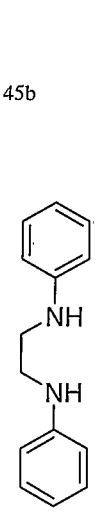
N,N'-Diphenyloxalamide (**34a**) [45a]



This compound was prepared in a fashion analogous to **32a** (p.125) utilizing oxalyl chloride (1.39 g, 10.9 mmol), aniline (4.1 g, 43.8 mmol) and CH_2Cl_2 (70 mL) to give 2.6 g of **34a** quantitatively. [Purification by acid-base work-up and washing the resulting solid with *n*-hexane; brownish solid;].

^1H NMR (300 MHz, $CDCl_3$): δ 1.96 (bs, 2H, NH), 7.66 (d, J = 7.5 Hz, 4H, ArH), 7.39 (t, J = 7.5 Hz, 4H, ArH), 7.20 (t, J = 7.5 Hz, 2H, ArH) ppm ; ^{13}C NMR (75 MHz, DMSO-d_6): δ 158.59, 137.64, 128.74, 124.61, 120.43 ppm ; IR (KBr): ν 3304.3, 1666.2, 1596.1, 1531.1, 1440.0, 753.9 cm^{-1}; LRMS (EI): m / z (relative intensity) 240 (M^+, 100), 120 (26), 93 (62).

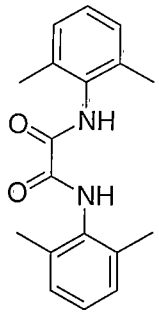
N,N'-Diphenylethane-1,2-diamine (**23a**) [45b]



This compound was prepared in a fashion analogous to **23h** (p.135) utilizing *N,N'*-diphenyloxalamide (**34a**) (2 g, 8.32 mmol), $LiAlH_4$ (0.63 mg, 16.6 mmol) and THF (30 mL) to give 0.8 g (45%) of **23a**. [Purification by bulb to bulb distillation at 135 °C / 1 torr; R_f = 0.3 (20% ethyl acetate in *n*-hexane); white solid].

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.18 (m, 4H, ArH), 6.73 (t, *J* = 7.5 Hz, 2H, ArH), 6.65 (d, *J* = 7.8 Hz, 4H, ArH), 3.95 (bs, 2H, NH), 3.39 (s, 4H, CH_2) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.88, 129.34, 117.94, 113.11, 43.34 ppm ; IR (KBr):*ν* 3417.8, 3049.2, 2945.0, 2866.2, 1597.6, 1514.0, 1341.7, 1264.4, 754.4 cm^{-1}; LRMS (EI): m / z (relative intensity) 212 (M^+, 19), 106 (100), 77 (36).

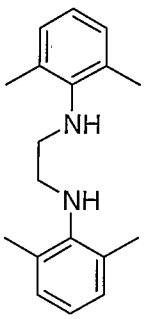
N,N'-Bis-(2,6-dimethylphenyl)oxalamide (**34b**) [46a]



This compound was prepared in a fashion analogous to **32a** (p.125) utilizing oxalyl chloride (1 g, 7.9 mmol), 2,6-dimethylaniline (2.1 g, 17.4 mmol), Et_3N (2.6 mL, 19.0 mmol) and THF (40 mL) to give 2.28 g (97.6%) of **34b**. [Purification by acid-base work-up; $R_f = 0.27_{uv}$, 20% ethyl acetate in *n*-hexane); white solid (mp = 235-237 °C)].

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.82 (bs, 2H, NH), 7.13 (m, 6H, ArH), 2.27(s, 12H) ppm ; ^{13}H NMR (75 MHz, $CDCl_3$): δ 158.05, 134.94, 132.27, 128.36, 127.86, 18.40 ppm; IR (KBr): 3282.8, 2976.4, 2921.8, 1668.5, 1498.4 cm^{-1}; LRMS (EI): m / z (relative intensity) 296 (M^+, 40), 268 (11), 148 (42), 121 (100).

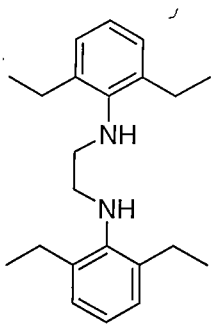
N,N'-Bis(2,6-dimethylphenyl)ethane-1,2-diamine (**23b**) [46a]



This compound was prepared in a fashion analogous to **34h** (p.135) utilizing *N,N'*-bis(2,6-dimethylphenyl)oxalamide (**34b**) (1.5g, 5.06 mmol), $LiAlH_4$ (380 mg, 13.5 mmol), THF (30 mL) to give 0.7 g (51.5%) of **23b**. [Purification by prep TLC coated by silica gel, 20% ethyl acetate in *n*-hexane for elution; $R_f = 0.31_{uv}$ (CH_2Cl_2 : EtOAc = 40 : 1); white solid].

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.99 (d, J = 7.2 Hz, 4H, ArH), 6.82 (t, J = 7.2 Hz, 2H, ArH), 3.20 (s, 4H, CH_2), 2.29 (s, 12H, CH_3) ppm; ^{13}H NMR (75 MHz, $CDCl_3$): δ 129.54, 128.92, 128.40, 122.18, 48.82, 18.57 ppm; IR (KBr): 3487.5, 2919.9, 1593.4, 1472.7, 1256.0, 1213.5, 1097.5, 763.2 cm^{-1}; LRMS (EI): m / z (relative intensity) 268 (M^+, 11), 249 (12), 134 (100).

N,N'-Bis(2,6-diethylphenyl)ethylenediamine (**23e**) [46a]

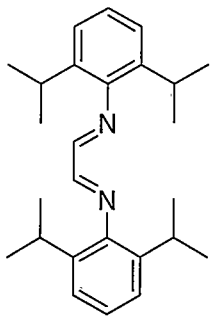


To a solution of glyoxal (1.14 mL, 9.85 mmol) and 2,6-diethylaniline [98% pure, (3 g, 19.7 mmol)] in MeOH (6 mL) was added 2 drops of formic acid, and stirred at room temperature overnight. The reaction mixture was concentrated in vacuo, and then the crude compound was directly used for next reaction without further purification; R_f = 0.32 (10% ethyl acetate in *n*-hexane)]

The crude compound dissolved in THF (5 mL) was added dropwise to a suspension of $LiAlH_4$ (750 mg, 19.7 mmol) in THF (80 mL), and then heated at reflux for 1h. The reaction mixture was cooled to 0 °C and carefully quenched via sequential addition of H_2O (1 mL), 15% aqueous NaOH (1 mL) and H_2O (2 mL). The mixture was stirred at room temperature for 1 h, and anhydrous $MgSO_4$ (2 g) was added, followed by filtration and concentration of the filtrate in vacuo. The residue was purified by distillation (bp = 139-140 °C / 1 torr) to provide 2.8 g (Y = 88%) of the title compound **23e**. R_f = 0.67 (20% ethyl acetate in *n*-hexane)].

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.97 (m, 4H, ArH), 6.88 (m, 2H, ArH), 3.32 (bs, 2H, NH), 3.10 (s, 4H, NCH_2), 2.62 (q, J = 7.5 Hz, 8H, CH_2), 1.16 (t, J = 7.5 Hz, 12H, CH_3) ppm; ^{13}H NMR (75 MHz, $CDCl_3$): δ 144.85, 136.45, 126.72, 122.91, 50.54, 24.45, 14.88 ppm; IR (neat): 3366.9, 2963.4, 2871.1, 1591.9, 1453.9, 1256.3, 1200.1, 1109.9, 754.0 cm^{-1} ; LRMS (EI): m / z (relative intensity) 324 (M^+, 14), 162 (100), 147 (29), 132 (24).

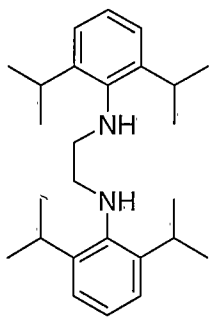
N, N'-Bis(2,6-diisopropylphenyl)-1,4-diazadine (**36g**) [46b]



To a solution of glyoxal (40% in H_2O, 300 μL, 2.6 mmol), and 2,6-diisopropylaniline (1 g, 5.2 mmol), in methanol (4 mL) was added 2 drops of formic acid, and stirred at room temperature for 2 h. The resulting solid was collected by filtration and washed with MeOH (2 mL) to provide 0.92 g (94%) of the title compound. For a high quality of compound, the product was purified by recrystallization in methyl alcohol to afford 606 mg (62%) of **36g** as a bright yellowish crystal (needle type). [R_f = 0.77 (20% ethyl acetate in *n*-hexane); mp = 106-107 °C].

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.09 (bs, 2H, CH=N), 7.16 (m, 6H, ArH), 2.92 (septet, J = 6.9 H, 2H, CH), 1.19 (d, J = 6.9 Hz, 24H, CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.09, 147.99, 136.70, 125.11, 123.16, 28.03, 23.37 ppm ; IR (KBr): ν 3062.1, 2960.7, 1625.7, 1464.0, 1435.3, 1175.8, 761.9 cm^{-1}; LRMS (EI): m / z (relative intensity) 376 (M^+, ≤ 0.1), 333 (100).

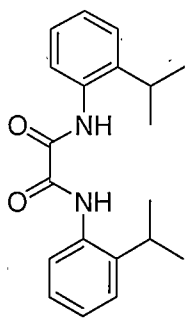
N,N'-Bis-(2,6-diisopropylphenyl)ethane-1,2-diamine (**23g**) [46c]



To a solution of *N, N'*-bis(2,6-diisopropylphenyl)-1,4-diazadine (**36g**) (500 mg, 1.33 mmol) in EtOH (15 ml) was added portionwise $NaBH_4$ (200 mg, 5.32 mmol) for 10 min at room temperature, then stirred overnight. The solution was concentrated in vacuo, diluted with EtOAc (20 ml), washed with H_2O (5 ml x 3) and dried over anhydrous $MgSO_4$. After filteration, the solvents were evaporated in vacuo. The residue was subjected to column chromatography on silica gel (5% ethyl acetate in *n*-hexane for elution) to give 468 mg (93%) of the title compound **23g** as a white solid. (mp = 98-99 °C).

^{1}H NMR ($CDCl_3$, ppm): δ 7.11 (m, 6H, ArH), 3.36 (septet, J = 6.9 Hz, 4H, CH), 3.35 (bs, 2H, NH), 3.16 (s, 4H, CH_2), 1.25 (d, J = 6.9 Hz, 24H, CH_3) ppm; ^{13}H NMR (CDCl3, ppm); δ 143.25, 142.45, 123.85, 123.59, 52.26, 27.76, 24.24 ppm ; LRMS (EI): m / z (relative intensity) 380 (M^+, 10), 190 (100), 160 (32).

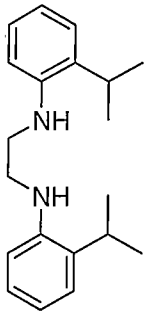
N,N'-Bis-(2-isopropylphenyl)oxalamide (**34h**)



To a solution of 2-isopropyl aniline [97% pure, (2.4 g, 17.4 mmol)] and triethylamine (2.6 ml, 19 mmol) in THF (60 mL) at 0 °C was added dropwise oxalyl chloride (1g, 7.9 mmol). The reaction mixture was stirred overnight, then refluxed for 1h. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate (50 ml), and then washed with H_2O (20 ml), 1N HCl (10 ml) and sat. $NaHCO_3$ (10 ml). The organic layer was dried (anhydrous $MgSO_4$), filtered, and evaporated in vacuo to provide 2.5 g (quantitative) of the title compound **34h** as a white solid [R_f = 0.54 (20% ethyl acetate in *n*-hexane); mp = 179.3-181.0 °C]

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.49 (bs, 2H, NH), 8.03 (dd, J = 7.8, 1.8 Hz, 2H, ArH), 7.28 (m, 6H, ArH), 3.13 (septet, J = 6.6 Hz, 2H, CH), 1.30 (d, J = 6.6 Hz, 12H, ArH) ppm ; ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.95, 139.21, 132.86, 126.63, 126.37, 125.91, 122.14, 28.09, 22.89 ppm ; IR (KBr): ν 3307.3, 2957.7, 1665.7, 1512.3, 756.1, 704.2 cm^{-1} ; LRMS (EI): m / z (relative intensity) 324 (M^+, 63), 162 (100).

N,N'-Bis(2-isopropylphenyl)ethane-1,2-diamine (**23h**)

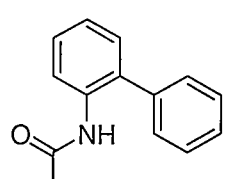


N,N'-Bis(2-isopropylphenyl)oxalamide (**34h**) (2.0 g, 6.16 mmol) was reduced by addition to $LiAlH_4$ (0.47 g, 12.3 mmol) in THF (30 mL) at room temperature and then heating the resulting mixture at reflux overnight. The reaction mixture was cooled to 0 °C and carefully quenched via sequential addition of H_2O (0.5 mL), 15% aqueous NaOH (0.5 mL) and H_2O (1 mL). The mixture was stirred at room temperature for 2h, and anhydrous $MgSO_4$ (1 g) was added. After filteration, the solvent was evaporated in vacuo. The residue was purified by preparative TLC coated by silica gel, 20% ethyl acetate in *n*-

hexane for elution, $R_f = 0.47_{uv}$) to afford 1 g (55%) of the title compound **23h** as a white solid (mp = 47-48 °C).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.15 (m, 4H, ArH), 6.76 (m, 4H, ArH), 4.03 (bs, 2H, NH), 3.50 (s, 4H, CH_2), 2.85 (septet, J = 6.9 Hz, 2H, CH), 1.22 (d, J = 6.9 Hz, 12H, CH_3) ppm ; ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.59, 132.78, 126.76, 125.09, 117.95, 110.78, 43.54, 27.18, 22.32 ppm ; IR (KBr): ν 3421.3, 2959.5, 2867.5, 1602.3, 1582.1, 1504.7, 1449.1, 1305.6, 1256.8, 744.7 cm^{-1}; HRMS (CI, NH_3): exact mass calcd for $[C_{20}H_{28}N_2+H]^+$ 297.2331, found 297.2368.

N,N'-Bis-biphenyl-2-yloxalamide (**34k**)

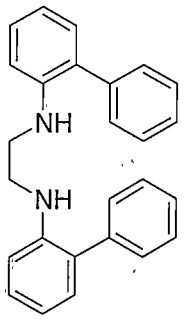


This compound was prepared in a fashion analogous to **32a** (p.125) utilizing oxalyl chloride (0.26 g, 2.95 mmol), 2-aminobiphenyl (1 g, 5.91 mmol), 4-methylmorpholine (1.4 mL, 13.0 mmol) and CH_2Cl_2 (15 mL) to give 0.78 g (67%) of **34k**. [Purification by trituration with 30% ethyl acetate in *n*-hexane and washing with

small amount of ethyl acetate; R_f = 0.64 (20% ethyl acetate in *n*-hexane, uv); white solid (mp = 239-240 °C)]

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.53 (bs, 2H, NH), 8.36 (d, *J* = 8.1 Hz, 2H, ArH), 7.54~7.18 (m, 16H, ArH) ppm ; ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.32, 137.19, 133.25, 132.86, 130.37, 129.26, 129.16, 128.41, 128.38, 125.28, 120.28 ppm ; IR (KBr):*v* 3335.5, 3067.3, 1690.8, 1583.8, 1516.4, 1447.5, 756.5, 697.5 cm^{-1}; LRMS (EI): m / z (relative intensity) 392 (M^+, 100), 281 (14), 196 (68).

N,N'-Bis-biphenyl-2-ylethane-1,2-diamine (**23k**)

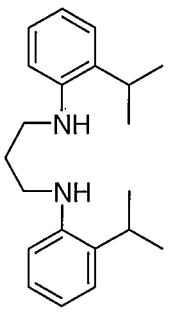


This compound was prepared in a fashion analogous to **23h** (p.135) utilizing *N,N'*-bisbiphenyl-2-yloxalamide (**34k**) (0.8 g, 20.4 mmol), $LiAlH_4$ (0.154 g, 40.8 mmol) and THF 20 mL to give 640 mg (86%) of **23k**. [Purification by column chromatography on silica gel, 5% ethyl acetate in *n*-hexane for elution); white solid (mp = 114-115 °C)]

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40~7.18 (m, 12H, ArH), 6.77 (t, *J* = 7.5 Hz, 2H, ArH), 6.69 (d, *J* = 7.5 Hz, 4H, ArH), 4.13 (bs, 2H, NH), 3.31 (s, 4H, CH_2) ppm; ^{13}H NMR (75

MHz, $CDCl_3$): δ 144.59, 139.18, 130.36, 129.23, 128.89, 128.70, 128.00, 127.25, 117.43, 110.49, 43.11 ppm; IR (KBr): 3408.9, 3054.2, 2851.8, 1602.1, 1506.3, 1489.2, 1435.0, 1314.5, 1282.0, 747.8 cm^{-1}; HRMS (EI): exact mass calcd for $[C_{26}H_{24}N_2]^+$ 364.1939, found 364.1936.

N,N'-Bis-(2-isopropylphenyl)propane-1,3-diamine (**25a**) [79]

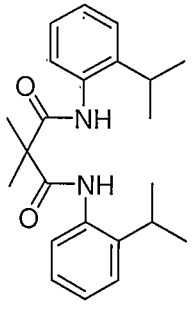


This compound was prepared according to literature procedure[47] utilizing 1,3-dibromopropane (1.31 mL, 12.9 mmol), 2-isopropylaniline (3.5 g, 25 mmol), *n*-BuLi (2.59 M, 9.99 mL, 25 mmol), tetramethylethylenediamine (TMEDA) (3.9 mL, 25 mmol) and THF (20 mL) to give 3.3 g (82%) of **65a**. [Purification by column chromatography on silica gel, R_f = 0.36 (10% ethyl acetate in *n*-hexane); yellowish oil].

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.12 (m, 4H, ArH), 6.75 (t, *J* = 7.5 Hz, 2H, ArH), 6.67 (d, *J* = 8.1 Hz, 2H, ArH), 3.87 (bs, 2H, NH), 3.31 (t, *J* = 6.6 Hz, 4H, CH_2N), 2.84 (septet, *J* = 6.9 Hz, 2H, CH), 2.05 (septet, *J* = 6.6 Hz, 2H, CH_2), 1.23 (d, *J* = 6.9 Hz, 12H, CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.73, 132.36, 126.74, 124.97, 117.55, 110.58, 42.51,

29.41, 27.17, 22.35 ppm ; IR (KBr): ν 3450.0, 2958.7, 1602.4, 1505.8, 1444.0, 742.6 cm^{-1}; LRMS (EI): m / z (relative intensity) 310 (M^+, 27), 174 (20), 146 (70), 132 (100).

N,N'-Bis(2-isopropylphenyl)-2,2-dimethylmaloamide (**34**$_{-25b}$)

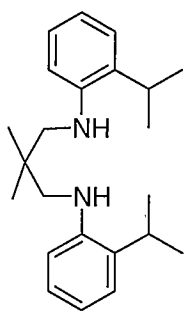


A mixture of 2,2-dimethylmalonic acid (1.16 g, 7.06 mmol) and thionyl chloride (10 mL) was heated at refluxe for 2h. The mixture was concentrated in vacuo to remove volatile materials. To the residue was sequentially added CH_2Cl_2 (30 mL), 4-methyl morpholine (3.4 mL, 31.02 mmol) and 2-isopropyl aniline (1.91 g, 14.1 mmol) at 0 °C, then stirred for 2h at room temperature. The mixture was diluted with CH_2Cl_2 (20 mL), and then washed with 1N HCl, sat. $NaHCO_3$ and brine solution. The organic layer was dried (anhydrous $MgSO_4$), filtered, evaporated in vacuo to provide 1.8 g (70%) of the title compound **34**$_{-25b}$. The resulting compound was used for next reaction without further purification. [White solid (mp = 152-154 °C)]

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.49 (bs, 2H, NH), 7.73 (t, J = 7.5 Hz, 2H, ArH), 7.29 ~7.17 (m, 6H, ArH), 3.00 (septet, J = 6.6 Hz, 2H, CH), 1.72 (s, 6H, CH_3), 1.22 (d, J = 6.6

Hz, 12H, CH_3) ppm ; ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.98, 140.32, 133.89, 126.39, 126.11, 125.59, 24.08,50.76, 28.09, 24.31, 22.86 ppm ; IR (KBr): *v* 3322.3, 2974.8, 1651.4, 1519.1, 754.0 cm^{-1}; LRMS (EI): m / z (relative intensity) 366 (M^+, 8), 205 (18), 162 (100).

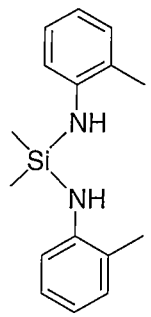
N,N'-Bis(2-isopropylphenyl)-2,2-dimethylpropane-1,3-diamine (**25b**)



This compound was prepared in a fashion analogous to **32a** (p.125) utilizing *N,N'*-bis(2-isopropylphenyl)-2,2-dimethylmaloamide (**34-25b**) (1 g, 2.73 mmol), $LiAlH_4$ (207 mg, 5.46 mmol) to give 300 mg (32%) of **25b** as a colorless oil.

^1H NMR (300 MHz, $CDCl_3$): δ 7.15 (m, 4H, ArH), 7.75 (m, 4H, ArH), 4.03 (bs, 2H, NH), 3.16 (s, 4H, CH_2), 2.85 (septet, *J* = 6.9 Hz, 2H, CH), 1.27 (d, *J* = 6.9 Hz, 12H, CH_3), 1.20 (s, 6H, CH_3) ppm ; ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.32, 132.48, 126.74, 124.88, 117.48, 110.71, 53.83, 35.15, 27.37, 24.67, 22.24 ppm ; IR (neat): *v* 3322.6, 2974.3, 1651.7, 1519.1, 1290.5, 1254.1, 754. cm^{-1} ; HRMS (EI): exact mass calcd for $[C_{23}H_{34}N_2]^+$ 338.2722, found 338.2718.

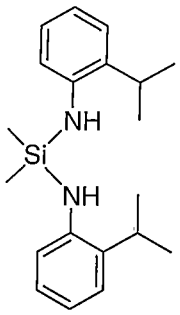
Bis[(2-methyl)phenylamino]dimethylsilane (**24a**)



To a stirred solution of 2-methylaniline (3 mL, 28 mmol) and Et_3N (3.9 mL, 28 mmol) in THF (30 mL) was added dichlorodimethylsilane (1.7 mL, 14 mmol) dropwise at 0 °C. The mixture was stirred at room temperature for 30 min and then heated at reflux for 1h. The mixture was diluted with ethyl acetate (50 mL), washed with water, dried over anhydrous $MgSO_4$. After filteration, the solvents were evaporated in vacuo. Purification of the residue by bulb-to-bulb distillation (120-125 °C / 0.02 torr) afforded 2.5 g (66%) of the title compound **24a** as a white solid (mp = 56-57 °C).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.00 (m, 6H, ArH), 6.67 (td, J = 7.2, 1.5 Hz, 2H, ArH), 3.53 (bs, 2H, NH), 2.16 (s, 6H, $ArCH_3$), 0.45 (s, 6H, $Si(CH_3)_2$) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.49, 130.46, 126.92, 124.02, 118.32, 115.42, 17.82, -0.883 ppm; IR (KBr): ν 3202, 2961.0, 1622.3, 1496.5, 1256.6, 1062.8, 904.0, 870.8, 198.9, 750.0 cm^{-1}

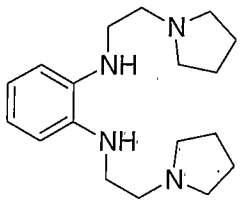
Bis[(2- isopropyl)phenylamino]dimethylsilane (**24b**)



To a stirred solution of 2-isopropylaniline [97% pure, (3 mL, 22.5 mmol)], Et_3N (3.8 mL, 27 mmol) and DMAP (274 mg, 2.2 mmol) in 1,2-DME (30 mL) was added dichlorodimethylsilane (1.37 mL, 11.2 mmol) dropwise at 0 °C. The reaction mixture was stirred at room temperature for 30 min and then heated at reflux overnight. The mixture was diluted with ethyl acetate (50 mL), washed with water and dried over anhydrous $MgSO_4$. After filteration, the solvent were evaporated in vacuo. Purification of the residue by distillation (120-125 °C / 0.02 torr) afforded 2.6 g (70.5%) of the title compound **24b** as a colorless oil.

^{1}H NMR (300 MHz, acetone-d_6): δ 7.07 (m, 4H, ArH), 6.86 (m, 2H, ArH), 6.76 (m, J = 7.2 Hz, 2H, ArH), 4.3 (bs, 2H, NH), 3.12 (septet, J = 6.9 Hz, 2H, CH), 1.17 (d, J = 6.9 Hz, 12H, CH_3), 0.41 (s, 6H, $Si(CH_3)_2$) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.13, 134.24, 126.37, 125.36, 118.75, 116.41, 27.51, 22.46, -0.80 ppm ; IR (neat): ν 3372.5, 3063.1, 2960.2, 1620.1, 1495.5, 1453.9, 1293.6, 1256.2, 906.9, 873.7, 747.4 cm^{-1}.

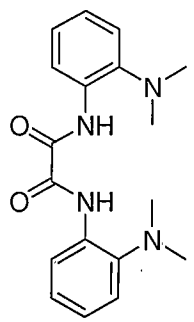
N,N'-Bis(2-pyrrolidin-1-ylethyl)-1,2-phenylenediamine (**30**)



This compound was prepared in a fashion analogous to **32a** (p.125) and **23h** (p.136) utilizing (2-oxo-1-pyrrolidinyl)acetyl chloride [80]

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.75 (dd, J = 5.7, 3.6 Hz, 2H, ArH), 6.64 (dd, J = 5.7, 3.6 Hz, 2H, ArH), 3.88 (bs, 2H, NH), 3.19 (app d, 4H, NCH_2), 2.77 (t, J = 6.3 Hz, 4H, NCH_2), 2.54 (m, 8H, NCH_2), 1.78 (m, 8H, CH_2) ppm; ^{13}H NMR (75 MHz, $CDCl_3$): δ 137.47, 118.78, 111.36, 55.15, 54.09, 43.12, 23.52 ppm; IR (KBr): v 3322.2, 2959.9, 2794.5, 1691.1, 1599.3, 1517.3, 1441.3, 1256.8, 1145.5, 732.8 cm^{-1}; HRMS (EI): exact mass calcd for $[C_{18}H_{30}N_4]^+$ 302.2470, found 302.2474.

N,N'-Bis(2-dimethylaminophenyl)oxalamide (**34**$_{-31}$)

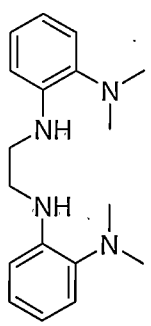


This compound was prepared in a fashion analogous to **32a** (p.125) utilizing oxalyl chloride (466 mg, 3.67 mmol), *N,N*-dimethyl-1,2-phenylenediamine [81] (1 g, 7.34

mmol), 4-methylmorpholine (1.8 mL, 16.1 mmol) and CH_2Cl_2 (15 mL) to give 0.66 g (55%) of **34**$_{31}$. [Purification by trituration with *n*-hexane; R_f = 0.61 (20% ethyl acetate in *n*-hexane); pale orange-yellowish solid (mp = 174-175 °C)].

^{1}H NMR (300 MHz, $CDCl_3$): δ 10.49 (bs, 2H, NH), 8,41 (m, 2H, ArH), 7.23 (m, 2H, ArH), 7.14 (m, 4H, ArH), 2.70 (s, 12H, CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.64, 144.14, 131.76, 125.14, 124.76, 120.23, 119.33, 44.75 ppm ; IR (KBr): *ν* 3313.8, 2947-2784.8, 1680.0, 1513.4, 1453.7, 941.3 cm^{-1} ; LRMS (EI): m / z (relative intensity) 326 (M^+, 15), 308 (87), 163 (100).

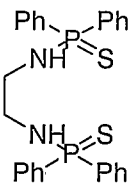
N,N'-Bis[(2-dimethylamino)phenyl]ethane-1,2-diamine (**31**)



This compound was prepared in a fashion analogous to **23h** (p.135) utilizing *N,N'*-bis(2-dimethylaminophenyl)oxalamide (**34**$_{31}$) (0.63 g, 1.93 mmol), $LiAlH_4$ (0.15 g, 3.86 mmol) and THF (15 mL) to give 370 mg (64%) of **31**. [$R_f = 0.25_{uv}$, 10% ethyl acetate in *n*-hexane; pale yellowish oil]

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.00 (m, 4H, ArH), 6.68 (m, 4H, ArH), 4.93 (bs, 2H, NH), 3.43 (s, 4H, CH_2), 2.60 (s, 12H, CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.05, 140.44, 124.65, 119.09, 116.73, 109.91, 43.83, 43.19 ppm ; IR (neat): ν 3338.3, 2936.1, 2823.5, 2781.6, 1597.4, 1508.0, 1452.8, 739. 8 cm^{-1}; HRMS (EI): exact mass calcd for $[C_{18}H_{26}N_4]^+$ 298.2157, found 298.2152.

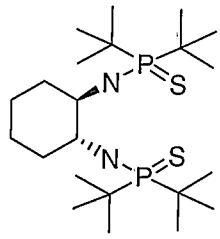
N,N'-Bis(*P,P*-diphenylthiophosphinyl)ethylenediamine (**55**) [56]



This compound was prepared in a fashion analogous to **59e** (p.155) utilizing chlorodiphenylphosphine and ethylene diamine. [Purification by column chromatography on silica gel, 20% ethyl acetate in *n*-hexane for elution, R_f = 0.2$_{uv}$; mp = 153-155 °C].

^{1}H{^{31}P} NMR (300 MHz, $CDCl_3$): δ 7.93 (d, J = 6.9 Hz, 8H, ArH), 7.41 (m, 12H, ArH), 3.24 (bs, 2H, NH), 3.14 (s, 4H, CH_2) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 133.85 (d, $J_{c\text{-}p}$ = 102 Hz), 131.68 (d, $J_{c\text{-}p}$ = 2.8 Hz), 131.54 (d, $J_{c\text{-}p}$ = 11.1 Hz), 128.44 (d, $J_{c\text{-}p}$ = 12.8 Hz), 42.08 (d, $J_{c\text{-}p}$ = 6.5 Hz) ppm; ^{31}P{^{1}H} (121 MHz, $CDCl_3$): δ 60.80 ppm ; IR (KBr): ν 3367.6, 3269.1, 1437.0, 1105.3, 1082.6, 714.6 cm^{-1}; HRMS (EI): exact mass calcd for $[C_{26}H_{26}N_2P_2S_2]^+$ 492.1012, found 492.1008.

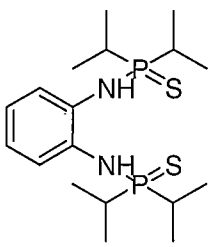
(1*R*,2*R*)-*N*,*N*'-Bis(*P*,*P*-di-*tert*-butylthiophosphinyl)cyclohexanediamine (**56**)



This compound was prepared in a fashion analogous to **59e** (p.155) utilizing chlorodi-*tert*-butyl phosphine and (1*R*,2*R*)-1,2-diaminocyclohexane. mp = 157-158 °C

$^{1}H\{^{31}P\}$ NMR (300 MHz, $CDCl_3$): δ 3.52 (bs, 2H, NH), 2.24 (app d, 2H, NCH), 1.85 (m, 4H, CH_2), 1.45 (m, 4H, CH_2), 1.29 (s, 36 H, CH_3) ppm ; ^{13}C NMR (75 MHz, $CDCl_3$): δ 52.85, 40.47 (d, $J_{c\text{-}p}$ = 40.48), 39.00 (d, $J_{c\text{-}p}$ = 53.62 Hz), 30.62, 27.64, 27.44, 21.06 ppm ; $^{31}P\{^{1}H\}$ (121 MHz, $CDCl_3$): δ 96.02 ppm ; IR (KBr): ν 3413.0, 3246.1, 2932.0, 1474.2, 671.2 cm^{-1}; HRMS (EI): exact mass calcd for $[C_{22}H_{48}N_2P_2S_2]^+$ 466.2734, found 466.2724.

N,*N*'-Bis(*P*,*P*-diisopropylthiophosphinyl)-1,2-phenylenediamine (**57a**) [56]

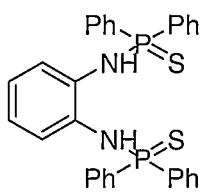


This compound was prepared in a fashion analogous to **59e** (p.155) utilizing chloropdiisopropylphosphine and 1,2-phenylenediamine [Purification by column

chromatography on silica gel, 20% ethyl acetate in *n*-hexane for elution, R_f= 0.31_{uv}; mp = 114~115 °C]

$^1H\{^{31}P\}$ NMR (300 MHz, $CDCl_3$): δ 7.34 (dd, J = 6.0, 3.6 Hz, 2H, ArH), 6.98 (dd, J = 6.0, 3.6 Hz, 2H, ArH), 5.30 (bs, 2H, NH), 2.33 (septet, J = 6.9 Hz, 4H, CH), 1.26 (d, J = 6.9 Hz, 12H, CH_3), 1.25 (d, J = 6.9 Hz, 12H, CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 134.76, 126.05, 124.65, 29.87 (d, $J_{c\text{-}p}$ = 61.7 Hz, P-$C(CH_3)_2$), 16.73 (d $J_{c\text{-}p}$ = 2.7 Hz), 16.55 ppm; $^{31}P\{^1H\}$ (121 MHz, $CDCl_3$): δ = 87.54 ppm; IR (KBr): ν 3201.3, 2960.9, 2871.4, 1595.3, 1496.9, 1388.7, 1288.6, 941.8, 676.4 cm^{-1}; HRMS (EI): exact mass calcd for $[C_{18}H_{34}N_2P_2S_2]^+$ 404.1638, found 404.1630.

N,N'-Bis(*P,P*-diphenylthiophosphinyl)-1,2-phenylenediamine (**57b**)

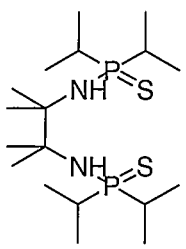


This compound was prepared in a fashion analogous to **59e** (p.155) 1,2-phenylenediamine (0.54 g, 5 mmol), *N,N*-diisopropylethylamine (2.09 mL, 12 mmol) and chlorodiphenylphosphine (1.79 mL, 10 mmol) in dichloromethane (30 mL), followed by the addition of sulfur (0.34 g, 10.5 mmol) to give 1.9 g (70%) of **57b**. [Purification by column chromatography on silica gel, 30% *n*-hexane in CH_2Cl_2 for elution, R_f = 0.6_{uv}

(40% ethyl acetate in *n*-hexane); mp = 204-205 °C; recrystallization from methylcyclohexane].

$^{1}H\{^{31}P\}$ NMR (300 MHz, $CDCl_3$): δ 7.94 (d, J = 7.8 Hz, 8H, ArH), 7.52 - 7.34 (m, 4H, ArH), 7.42 (d, J = 7.8 Hz, 8H, ArH), 6.92 (m, 2H, ArH), 6.79 (m, 2H, ArH), 5.78 (bs, 2H, NH) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 133.89, 133.47 (d, $J_{c\text{-}p}$ = 94.5 Hz), 131.96 (d, $J_{c\text{-}p}$ = 2.4 Hz), 131.73 (d, $J_{c\text{-}p}$ = 11.3 Hz), 128.57 (d, $J_{c\text{-}p}$ = 13.1 Hz), 125.54 (d, $J_{c\text{-}p}$ = 3.4 Hz), 124.96 ppm; $^{31}P\{^{1}H\}$ (121 MHz, $CDCl_3$): δ 57.41 ppm ; IR (KBr): ν 3310.7, 1595.9, 1498.7, 1435.7, 1294.6, 1103.6, 713.0 cm^{-1}; HRMS (EI): exact mass calcd for $[C_{30}H_{26}N_2P_2S_2]^+$ 540.1012, found 540.0996.

N,N'-Bis(*P,P*-diisopropylthiophosphinyl)-2,3-dimethyl-2,3-butanediamine (**58a**)

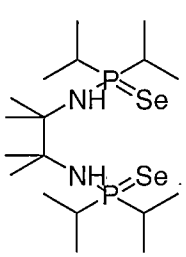


This compound was prepared in a fashion analogous to **59e** (p.155) utilizing 2,3-dimethyl-2,3-diaminobutane (0.29 g, 2.5 mmol), 4-methylmorpholine (0.66 mL, 6 mmol) and chlorodiisopropylphosphine (0.8 mL, 5 mmol) in toluene (15.5 mL) at 70 °C, followed by the addition of sulfur (0.17 g, 5.25 mmol) to give 440 mg (43%) of **58a**.[

Purification by column chromatography on silica gel, CH_2Cl_2 for elution, $R_f = 0.22$ (I_2); mp = 147-148 °C].

$^1H\{^{31}P\}$ NMR (300 MHz, $CDCl_3$): δ 2.69 (bs, 2H, NH), 2.19 (septet, J = 6.9 Hz, 4H, CH), 1.44 (s, 12H, CH_3), 1.22 (d, J = 6.9 Hz, 12H, CH_3), 1.19 (d, J = 6.9 Hz, 12H, CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 62.54 (d, $J_{c\text{-}p}$ = 5.0 Hz), 31.45 (d, $J_{c\text{-}p}$ = 67.3 Hz), 25.01, 17.22, 16.54 ppm; $^{31}P\{^1H\}$ (121 MHz, $CDCl_3$): δ 83.59 ppm; IR (KBr): ν 3319.9, 3240.3, 2961.2, 1458.8, 1420.8, 1135.9, 1021.5, 690.2 cm^{-1}; HRMS (EI): exact mass calcd for $[C_{18}H_{42}N_2P_2S_2]^+$ 412.2264, found 412.2256.

N,N'-Bis(*P,P*-diisopropylselenophosphinyl)-2,3-dimethyl-2,3-butanediamine (**58d**)

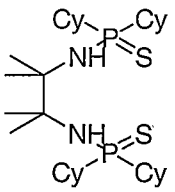


This compound was prepared in a fashion analogous to **59e** (p.155) utilizing 2,3-dimethyl-2,3-diaminobutane (0.2 g, 1.7 mmol), *N,N*-diisopropylethylamine (1.35 mL, 7.65 mmol) and chloropdiisopropylhosphine (0.55 mL, 3.4 mmol) in toluene (6 mL). Following the addition of selenium (0.29 g, 3.57 mmol) the reaction mixture was heated at reflux for 2 h to provide 690 mg (79%) of **58d**. [Purification by column

chromatography on silica gel, 20% ethyl acetate in *n*-hexane for elution, $R_f = 0.25_{uv}$; mp = 167-169 °C].

$^1H\{^{31}P\}$ NMR (300 MHz, $CDCl_3$): δ 2.62 (bs, 2H, NH), 2.27 (septet, J = 7.2 Hz, 4H, CH), 1.47 (s, 12H, CH_3), 1.23 (d, J = 7.2 Hz, 12H, CH_3), 1.20 (d, J = 7.2 Hz, 12H, CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 63.08, 31.84 (d, $J_{c\text{-}p}$ = 54.3 Hz), 24.95, 17.71, 16.86 ppm ; $^{31}P\{^1H\}$ (121 MHz, $CDCl_3$): δ 80.16 ppm (side band due to ^{31}P-^{77}Se: d, J = 71.38 Hz); IR (KBr): ν 3310.2, 3224.2, 2961.8, 1463.7, 1134.2, 1020.9, 629.8 cm^{-1}; HRMS (EI): exact mass calcd for $[C_{18}H_{42}N_2P_2Se_2]^+$ 506.1167, found 506.1167.

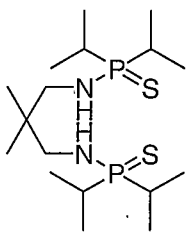
N,N'-Bis(*P,P*-dicyclohexylthiophosphinyl)-2,3-dimethyl-2,3-butanediamine (**58e**)



This compound was prepared in a fashion analogous to **59e** (p.155) utilizing 2,3-dimethyl-2,3-diaminobutane (0.29 g, 2.5 mmol), *N,N*-diisopropylethylamine (1.96 mL, 11.25 mmol) and chlorodicyclohexylphosphine (1.16 g, 5 mmol) in dichloromethane (7.5 mL) by heating at reflux for 2 days, followed by the addition of sulfur (0.17 g, 5.25 mmol) to furnish 1.19 g (83%) of **58e**. [Purification by column chromatography on silica gel, 30% *n*-hexane in CH_2Cl_2 for elution, R_f = 0.15(I_2); mp = 146-148 °C; recrystallization from methylcyclohexane].

$^{1}H\{^{31}P\}$ NMR (300 MHz, $CDCl_3$): δ 2.65 (bs, 2H, NH), 1.99–1.67 (m, 26H, CH_2, CH), 1.43 (s, 12H, CH_3), 1.43–0.82 (m, 18H, CH_2) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 62.49 (d, $J_{c\text{-}p}$ = 5.1 Hz), 26.88, 26.78 (d, $J_{c\text{-}p}$ = 3.9 Hz), 26.59 (d, $J_{c\text{-}p}$ = 3.0 Hz), 26.39, 26.00, 25.01 ppm; $^{31}P\{^{1}H\}$ (121 MHz, $CDCl_3$): δ 76.74 ppm; IR (KBr): ν 3296.4, 3195.6, 2928.8, 2850.2, 1447.7, 1392.0, 1201.5, 1133.5, 1021.1, 996.6, 730.2, 612.1 cm^{-1}; HRMS (EI): exact mass calcd for $[C_{30}H_{58}N_2P_2S_2]^+$ 572.3516, found 572.3508.

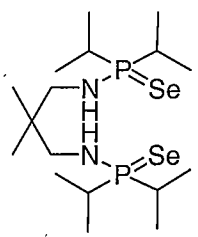
N,N'-Bis(*P,P*-diisopropylthiophosphinyl)- 2,2-dimethyl-1,3-propanediamine (**59a**).



This compound was prepared in a fashion analogous to **59e** (p.155) utilizing 2,2-dimethyl-propane-1,3-diamine (0.3 g, 2.5 mmol), *N,N*-diisopropylethylamine (1.96 mL, 11.25 mmol) and chlorodiisopropylphosphine (0.8 mL, 5 mmol) in dichloromethane (7.5 mL), followed by the addition of sulfur (0.17 g, 5.25 mmol) to give quantitative yield of **59a**. [Purification by column chromatography on silica gel, 20% ethyl acetate in *n*-hexane for elution; R_f = 0.23 (I_2); mp = 143-144 °C ; recrystallization from methylcyclohexane].

$^1H\{^{31}P\}$ NMR (300 MHz, $CDCl_3$): δ 2.86 (s, 4H, CH_2), 2.63 (bs, 2H, NH), 2.10 (septet, J = 6.9 Hz, 4H, CH), 1.17 (d, J = 6.9 Hz, 12H, CH_3), 1.16 (d, J = 6.9 Hz, 12H, CH_3) ppm ; ^{13}C NMR (75 MHz, $CDCl_3$): δ 46.91, 36.91 (t, $J_{c\text{-}p}$ = 6.0 Hz), 30.23 (d, $J_{c\text{-}p}$ = 61.6 Hz), 23.58, 16.51, 16.24 (d, $J_{c\text{-}p}$ = 2.7 Hz) ppm; $^{31}P\{^1H\}$ (121 MHz, $CDCl_3$): δ 90.06 ppm; IR (KBr): ν 3324.3, 3207.0, 2974.0, 1446.5, 1073.8, 829.8, 708.4 cm^{-1}; HRMS (EI): exact mass calcd for $[C_{17}H_{40}N_2P_2S_2]^+$ 398.2108, found 398.2097.

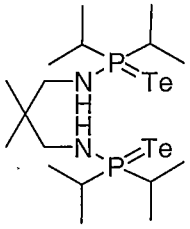
N,N'-Bis(*P,P*-diisopropylselenophosphinyl)-2,2-dimethyl-1,3-propanediamine (**58b**)



This compound was prepared in a fashion analogous to **59e** (p.155) utilizing 2,2-dimethylpropane-1,3-diamine (0.3 mL, 2.5 mmol), *N,N*-diisopropylethylamine (1.96 mL, 11.25 mmol) and diisopropylchlorophosphine (0.8 mL, 5 mmol) in toluene (7.5 mL) at 70 °C, followed by the addition of selenium (0.4 g, 5.24 mmol) to give 1 g (81%) of **58b**. [Purification by column chromatography on silica gel, from CH_2Cl_2 : *n*-hexane (1 : 7) to CH_2Cl_2 for gradient elution; R_f = 0.26_{uv}, (CH_2Cl_2); m.p. = 156-157 °C; recrystallization from methylcyclohexane].

$^{1}H\{^{31}P\}$ NMR (300 MHz, $CDCl_3$): δ 2.87 (s, 4H, CH_2), 2.70 (bs, 2H, NH), 2.15 (septet, J = 6.9 Hz, 4H, CH), 1.20 (d, J = 6.9 Hz, 12H, CH_3), 1.14 (d, J = 6.9 Hz, 12H, CH_3), 0.83 (s, 6H, CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 48.15, 36.99 (t, $J_{c\text{-}p}$ = 6.0 Hz), 30.68 (d, $J_{c\text{-}p}$ = 53.0 Hz, P-CH), 23.62, 17.12, 16.55 (d, $J_{c\text{-}p}$ = 2.4 Hz) ppm; $^{31}P\{^{1}H\}$ (121 MHz, $CDCl_3$): δ 91.63 ppm (side band due to ^{31}P-^{77}Se: d, J = 718.7 Hz) ; IR (KBr): ν 3289.9, 3185.6, 2857.9, 2867.2, 1454.8, 1421.6, 1262.8, 1092.2, 820.4 cm^{-1}; HRMS (EI): exact mass calcd for $[C_{17}H_{40}N_2P_2Se_2]^+$ 492.1011, found 492.1015.

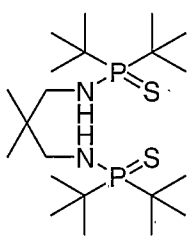
N,N'-Bis(*P,P*-diisopropyltellurophosphinyl)- 2,2-dimethyl-1,3-propanediamine (**59c**)



This compound was prepared in a fashion analogous to **59e** (p.155) utilizing 2,2-dimethylpropane-1,3-diamine (0.3 g, 2.5 mmol), *N,N*-diisopropylethylamine (1.96 mL, 11.25 mmol) and chlorodiisopropylphosphine (0.8 mL, 5 mmol) in toluene (7.5 mL) at 70 °C, followed the addition of tellurium (0.67 g, 5.25 mmol) to give 520 mg (35%) of **59c** as a gray solid. [Purification by column chromatography on silica gel, 20% ethyl acetate in *n*-hexane for elution, R_f = 0.31_{uv}; mp = 165-167 °C].

$^1H\{^{31}P\}$ NMR (300 MHz, $CDCl_3$): δ 2.81 (d, J = 7.2 Hz, 4H, CH_2), 2.37 (t, J = 7.2 Hz, 2H, NH), 2.10 (septet, J = 6.9 Hz, 4H, CH), 1.16 (d, J = 6.9 Hz, 12H, CH_3), 1.12 (d, J = 6.9 Hz, 12H, CH_3), 0.85 (s, 6H, CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 51.00, 37.22 (t, $J_{c\text{-}p}$ = 6.0 Hz), 31.46 (d, $J_{c\text{-}p}$ = 42.1 Hz), 23.76, 18.53, 17.31 (d, $J_{c\text{-}p}$ = 2.5 Hz) ppm ; $^{31}P\{^1H\}$ (121 MHz, $CDCl_3$): δ 69.89 ppm (side band due to ^{31}P-^{125}Te: d, J = 1794.55 Hz); ; IR (KBr): ν 3269.0, 3161.9, 2954.2, 2864.3, 1458.3, 1419.5, 1242.4, 1080.5, 1074, 8, 816.7, 668.6 cm^{-1}; HRMS (EI): exact mass calcd for $[C_{17}H_{40}N_2P_2Te_2]^+$ 589.0776, found 589.0765.

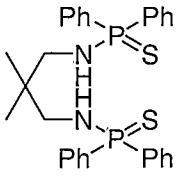
N,N'-Bis(*P,P*-di-tert-butylthiophosphinyl)- 2,2-dimethyl-1,3-propanediamine (**59d**)



This compound was prepared in a fashion analogous to **59e** (p.155) utilizing 2,2-dimethylpropane-1,3-diamine (0.3 g, 2.5 mmol), *N,N*-diisopropylethylamine (1.96 mL, 11.25 mmol) and chloro-di-*tert*-butylphosphine [96% pure, (0.99 mL, 5 mmol)] in dichloromethane (7.5 mL), followed by the addition of sulfur (0.17 g, 5.25 mmol) to furnish 770 mg (68%) of **59d**. [Purification by column chromatography on silica gel, 30% *n*-hexane in CH_2Cl_2 for elution, R_f = 0.22 (I_2); mp = 198-199 °C; recrystallization from methylcyclohexane].

$^{1}H\{^{31}P\}$ NMR (300 MHz, $CDCl_3$): δ 2.93 (bs, 6H, CH_2, NH), 1.32 (s, 18H, CH_3), 1.29 (s, 18H, CH_3), 0.84 (s, 6H, CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 47.83, 40.34 (d, $J_{c\text{-}p}$ = 53.8 Hz), 37.43 (t, $J_{c\text{-}p}$ = 3.8 Hz), 27.78, 23.68 ppm; $^{31}P\{^{1}H\}$ (121 MHz, $CDCl_3$): δ 98.98 ppm ; IR (KBr): *v* 3327.5, 3226.2, 2947.4, 2906.4, 1477.8, 1093.2, 806.4, 668.7 cm^{-1}; HRMS (EI): exact mass calcd for $[C_{21}H_{48}N_2P_2S_2]^+$ 454.2734, found 454.2723.

N,N'-Bis(*P,P*-diphenylthiophosphinyl)-2,2-dimethyl-1,3-propanediamine (**59e**)



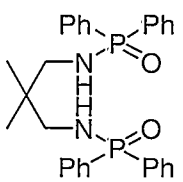
To a solution of 2,2-dimethylpropane-1,3-diamine (0.6 mL, 5 mmol) and 4-methylmorpholine (1.3 mL, 12 mmol) in toluene (25 mL) was added chloro-diphenylphosphine (1.8 mL, 10 mmol) dissolved in toluene (25 mL) dropwise with stirring at 0 °C. The reaction mixture was allowed to attain room temperature and stirred overnight.

The resulting white precipitate was rapidly filtered with care being taken to minimize exposure to air and the filter cake was leached with dry toluene (2 x 3 mL). Sulfur (0.337 g, 10.5 mmol) was then added in portions (exothermic) to the resulting mixture. The reaction mixture was heated to 80 °C with stirring for 30 min under argon. After cooling to room temperature, the mixture was concentrated in vacuo. The residue

was purified by column chromatography on silica gel [CH_2Cl_2 for elution, $R_f = 0.22_{uv}$ (20% ethyl acetate in *n*-hexane)], to afford 2.03 g (76%) of the title compound **59e** as a white solid (mp = 132-133 °C). The product was recrystallized from methylcyclohexane for utilization as a ligand.

$^1H\{^{31}P\}$ NMR (300 MHz, $CDCl_3$): δ 7.89 (d, J = 5.7 Hz, 8H, ArH), 7.39 (m, 12H, ArH), 3.14 (bs, 2H, NH), 2.85 (s, 4H, CH_2), 0.89 (s, 6H, CH_3) ppm ; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 134.35 (d, $J_{c\text{-}p}$ = 101.25 Hz), 131.58, 131.44, 128.47 (d, $J_{c\text{-}p}$ = 12.75), 49.95, 35.72 (t, $J_{c\text{-}p}$ = 7.7 Hz), 23.88 ppm; $^{31}P\{^1H\}$ (121 MHz, $CDCl_3$): δ 61.30 ppm; IR (KBr): ν 3192.1, 2956.4, 1477.5, 1437.1, 1411.2, 1299.8, 1105.0, 1060.6, 716.7 cm^{-1}; HRMS (EI): exact mass calcd for $[C_{29}H_{32}N_2P_2S_2]^+$ 534.1482, found 534.1477.

N,N'-Bis(*P,P*-diphenylphosphinoyl)-2,2-dimethyl-1,3-propanediamine (**59f**)

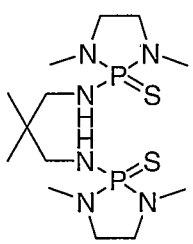


To a solution of 2,2-dimethylpropane-1,3-diamine (0.3 mL, 2.5 mmol) and *N,N*-diisopropylethylamine (1.96 mL, 11.25 mmol) in CH_2Cl_2 (7.5 mL) was added chlorodiphenylphosphine (0.95 mL, 5 mmol) dropwise with stirring at 0 °C. The reaction mixture was allowed to attain room temperature and stirred for 2h. After the typical work-up, the residue was purified by recrystallization, which involved the addition of

methylcyclohexane to a solution of crude compound dissolved in a minimum amount of CH_2Cl_2 to provide 1.2 g (96%) of the title compound. mp = 194-195 °C

$^1H\{^{31}P\}$ NMR (300 MHz, $CDCl_3$): δ 7.82 (app d, J = 6.6 Hz, 8H, ArH), 7.49-7.37 (m, 12H, ArH), 4.08 (bs, 2H, NH), 2.83 (d, J = 5.4 Hz, 4H, CH_2), 0.86 (6H, CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 132.93 (d, $J_{c\text{-}p}$ = 127.05 Hz), 131.92 (d, $J_{c\text{-}p}$ = 9.75 Hz), 131.77 (d, $J_{c\text{-}p}$ = 1.87 Hz), 128.49 (d, $J_{c\text{-}p}$ = 12.45 Hz), 47.93, 36.06, 23.59 ppm; $^{31}P\{^1H\}$ (121 MHz, $CDCl_3$): δ 25.79 ppm; IR (KBr): ν 3177.8, 2956.8, 2668.4, 1437.8, 1187.8, 1124.0, 723.8, 557.4 cm^{-1}; HRMS (EI): exact mass calcd for $[C_{29}H_{32}N_2O_2S_2]^+$ 502.1939, found 502.1954.

N,N'-Bis(1,3-dimethyl-2-thio-[1,3,2]diazaphospholidinyl)-2,2-dimethyl-1,3-propanediamine (**59g**)

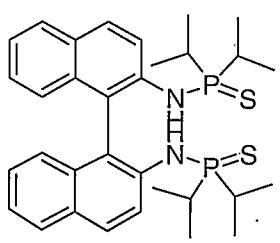


This compound was prepared in a fashion analogous to **59f** (p.156) utilizing 2,2-dimethylpropane-1,3-diamine (0.11g, 1.1 mmol), *N,N*-diisopropylethylamine (0.45 mL, 2.6 mmol) and 2-chloro-1,3-dimethyl-[1,3,2]diazaphosphoridine-2-sulfide[82] (400 mg, 2.2 mmol) in 1,2-dichloroethane (5 mL) at 100 °C to provide 310 mg (72%) of **59g**.

[Purification by column chromatography on silica gel, 30% ethyl acetate in *n*-hexane for elution, $R_f = 0.14_{KMnO4}$; mp = 134-136 °C; recrystallization from methylcyclohexane].

$^1H\{^{31}P\}$ NMR (300 MHz, $CDCl_3$): δ 3.29 (m, 6H, CH_2), 3.00 (m, 4H, CH_2), 2.60 (s, 6H, NCH_3), 2.58 (s, 6H, NCH_3), 2.66-2.47 (m, 4H, CH_2, NH), 0.77 (s, 6H, CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 47.96 (d, $J_{c\text{-}p}$ =5.4 Hz), 47.82 (d, $J_{c\text{-}p}$ = 9.6 Hz), 35.38 (t, $J_{c\text{-}p}$ = 6.0 Hz), 32.00 (d, $J_{c\text{-}p}$ = 5.6 Hz), 23.39 ppm; $^{31}P\{^1H\}$ (121 MHz, $CDCl_3$): δ 76.41 ppm ; IR (KBr): *ν* 3294.7 2922.0, 2860.0, 1470.1, 1412.1, 1259.2, 1226.6, 1165.0, 1099.9, 1035.7, 943.6, 844.5, 745.0, 704.1 cm^{-1}; HRMS (EI): exact mass calcd for $[C_{13}H_{32}N_6P_2S_2]^+$ 398.1605, found 398.1590.

N,N'-Bis(*P,P*-diisopropylthiophosphinyl)binaphthyl-2,2'-diamine (**61**)

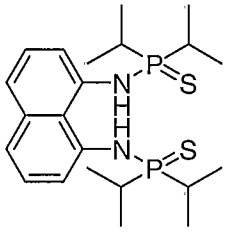


This compound was prepared in a fashion analogous to **59e** (p.155) utilizing (±)-[1,1']binaphthyl-2,2'-diamine (0.71 g, 2.5 mmol), 4-methylmorpholine (0.66 mL, 6 mmol) and chlorodiisopropylphosphine (0.8 mL, 5 mmol) in toluene (7.5 mL) at 70 °C, followed by the addition of sulfur (0.17 g, 5.25 mmol) to secure 0.75 g (52%) of **61**. [Purification by column chromatography on silica gel, 30% CH_2Cl_2 in *n*-hexane for

elution, $R_f = 0.54_{uv}$ (20% ethylacetate in *n*-hexane); mp = 159-160 °C; recrystallization from methylcyclohexane]

$^1H\{^{31}P\}$ NMR (300 MHz, $CDCl_3$): δ 8.30 (d, J = 9.0 Hz, 2H, ArH), 7.90 (d, J = 9.0 Hz, 2H, ArH), 7.84 (d, J = 7.8 Hz, 2H, ArH), 7.32 (m, 2H, ArH), 7.23 (m, 2H, ArH), 7.06 (d, J = 8.4 Hz, 2H, ArH), 4.30 (bs, 2H, NH), 1.93 (app octet, 4H, CH), 1.04 (d, J = 7.2 Hz, 6H, CH_3), 0.93 (d, J = 7.5 Hz, 6H, CH_3), 0.85 (d, J = 7.2 Hz, 6H, CH_3), 0.80 (d, J = 7.5 Hz, 6H, CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 139.33, 132.88, 129.52, 129.24, 128.32, 127.25, 124.23, 119.89, 117.28 (d, $J_{c\text{-}p}$ = 6.7 Hz), 31.62 (d, $J_{c\text{-}p}$ = 61.4 Hz), 30.32 (d, $J_{c\text{-}p}$ = 62.4 Hz), 16.28, 16.18 (d, $J_{c\text{-}p}$ = 2.1 Hz), 16.04 (d, $J_{c\text{-}p}$ = 2.9 Hz) ppm ; $^{31}P\{^1H\}$ (121 MHz, $CDCl_3$): δ 83.53 ppm ; IR (KBr): ν 347.8, 3329.5, 2963.6, 1617.9, 1591.1, 1463.6, 1407.3, 1278.0, 1244.4, 995.2, 820.1, 737.2 cm^{-1}; HRMS (EI): exact mass calcd for $[C_{32}H_{42}N_2P_2S_2]^+$ 580.2264, found 580.2267.

N,N'-Bis(*P,P*-diisopropylthiophosphinyl)-1,8-diaminonaphthalene (**60**)

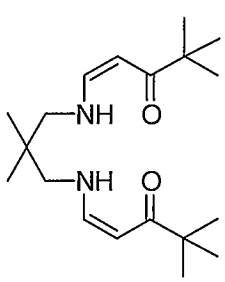


This compound was prepared in a fashion analogous to **59e** (p.155) utilizing naphthalene-1,8-diamine (0.4 g, 2.5 mmol), 4-methylmorpholine (0.66 mL, 6 mmol) and

chlorodiisopropylphosphine (0.8 mL, 5 mmol) in toluene (7.5 mL) at 70 °C, and then addition of sulfur (0.17 g, 5.25 mmol). [Yield = 35% (400 mg); Purification by column chromatography on silica gel, 10% ethyl acetate in *n*-hexane for elution, $R_f = 0.29_{uv}$; mp = 155-57 °C; recrystallization from methylcyclohexane]

$^1H\{^{31}P\}$ NMR (300 MHz, $CDCl_3$): δ 7.56 (d, J = 7.8 Hz, 2H, ArH), 7.53 (d, J = 7.8 Hz, 2H, ArH), 7.30 (t, J = 7.8 Hz, 2H, ArH), 2.61 (septet, J = 6.3 Hz, 4H, CH), 1.23 (d, J = 6.3 Hz, 12 H, CH_3), 1.16 (d, J = 6.3 Hz, 12H, CH_3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 136.78, 136.19, 125.56, 125.52, 121.04 (d, $J_{c\text{-}p}$ = 3.5 Hz), 29.55 (d, $J_{c\text{-}p}$ = 60.3 Hz), 17.10, 16.91 (d, $J_{c\text{-}p}$ = 2.5 Hz) ppm; $^{31}P\{^1H\}$ (12 MHz, $CDCl_3$): δ 90.27 ppm; IR (KBr): ν 3187.9, 2969.7, 1578.0, 1458.9, 1409.8, 1272.4, 889.2 cm^{-1}; HRMS (EI): exact mass calcd for $[C_{22}H_{36}N_2P_2S_2]^+$ 454.1795, found 454.1797.

N,N'-Bis(4,4-dimethylpent-1-ene-3-onyl)-2,2-dimethyl-1,3-propanediamine (**69a**)

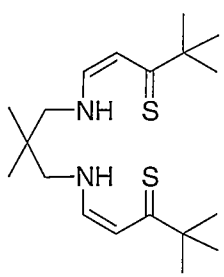


To a stirred solution of 2,2-dimethyl-5-hydroxy-4-penten-3-one (1.38 g, 10 mmol) in 1,2-DME (12 mL) was added a solution of 2,2-dimethyl-1,3-propanediamine (501 mg, 5 mmol) in 1,2-DME (3 mL) dropwise at 0 °C. The reaction mixture was allowed to

warm to room temperature, then stirred at this temperature overnight. The solvent was removed in vacuo and the residue was recrystallized from heptane to provide the title compound (1.14 g, 71 %). mp = 56-57 °C

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.93 (bs, 2H, NH), 6.64 (dd, J = 12.3, 7.6 Hz, 2H, NCH=), 5.15 (d, J = 7.6 Hz, 2H, =CH-), 2.96 (d, J = 6.6 Hz, 4H, NCH_2), 1.11 (s, 18H, CH_3), 0.91 (s, 6H, CH_3) ppm ; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 206.57, 153.91, 89.34, 57.15, 41.58, 36.54, 27.68, 22.86ppm; IR (KBr): ν = 3287.2 (bs), 2962.5, 1633.3, 1572.4, 1486.1, 1102.4 cm^{-1} ; HRMS (MALDI / TOF): exact mass calcd for $[C_{19}H_{34}N_2O_2 + H]^+$ 323.2698, found 323.2674.

N,N'-Bis(4,4-dimethylpent-1-ene-3-thionyl)-2,2-dimethyl-1,3-propanediamine (**69b**)

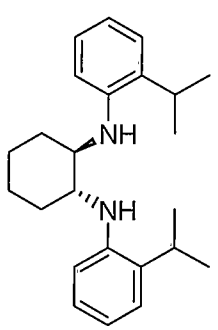


A 10 mL round bottomed flask equipped with a magnetic stirring bar, argon inlet and septum was charged with the above bis(enamide) (**69a**) (322 mg, 1.0 mmol) and Lawesson's reagent (485 mg, 1.2 mmol). The flask was immersed in an ice bath and 1,2-DME (5 mL) was added by syringe. The resulting suspension was stirred at 0 °C for 1 h during which time the solids dissolved to afford an orange solution. The reaction mixture

was diluted with ether (25 mL), extracted with 1 % aqueous NaOH (2 x 20 mL) and washed with brine (15 mL). The solvents were evaporated and the residue was purified by chromatography on silica gel (5 % ethyl acetate–hexane for elution) followed by recrystallization from heptane to furnish the title compound (223 mg, 63 %) as orange crystals. mp = 104-105 °C

^{1}H NMR (300 MHz, C_6D_6): δ = 6.51 (dd, J = 12.9, 7.6 Hz, 2H, NCH=), 6.09 (d, J = 7.6 Hz, 2H, =CH-), 2.68 (d, J = 6.3 Hz, 4H, NCH_2), 1.14 (s, 18H, CH_3), 0.47 (s, 6H, CH_3) ppm ; ^{13}C NMR (75 MHz, C_6D_6): δ = 227.36, 155.13, 106.64, 56.90, 46.59, 35.03, 31.59, 22.65 ppm ; IR (KBr): ν = 3450, 2959.7, 1617.3, 1497.3, 1270.6, 1123.7, 990.0, 800.9 cm^{-1}; HRMS (MALDI / TOF): exact mass calcd for $[C_{19}H_{34}N_2S_2 + H]^+$ 355.2241, found 355.2251.

(1*R*,2*R*)-*N*,*N*'-Bis(2-isopropylphenyl)-1,2-cyclohexanediamine (**71a**)

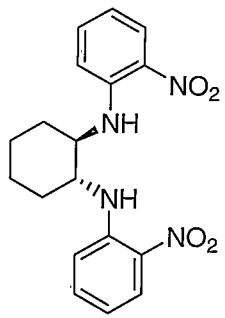


An round bottom flask with magnetic stir bar was charged with palladium acetate, $Pd(OAc)_2$ (97 % pure, 20.2 mg, 8.76 x 10^{-5}), *rac*-BINAP (98% pure, 111 mg, 1.75 x 10^{-4}

mmol) and sodium tert-butoxide, t-BuOK (97 % purity, 521 mg, 5.25 mmol), then evacuated and backfilled with argon. After addition of toulene (12 mL), the mixture was stirred at room temperature for 20 min., followed by addition of (1*R*,2*R*)-(-)-diaminocyclohexane [Enantiomeric purity: 99% ee GLC by Aldrich] (200 mg, 1.75 mmol) and 1-bromo-2-isopropylbenzene (732 mg, 3.68 mmol) sequently. The reaction mixture was then heated at 100 °C for 4 days. The reaction mixture was purified by column chromatography on silica to afford 438 mg (Y = 82%) of the title compound. The value of enantionmeric excess (99% ee) was determined based on the enantiomeric purity of (1*R*,2*R*)-(+)-1,2-diphenylethylenediamine purchased from Aldrich

^{1}H (300MHz, $CDCl_3$) δ 7.07 (m, 4H, ArH), 6.70 (m, 4H, ArH), 3.84 (bs, 2H, NH), 3.30 (m, 2H, NCH), 2.66 (septet, *J* = 6.9 Hz, 2H, CH), 2.34 (m, 2H, CH_2), 1.74 (m, 2H, CH_2), 1.40 (m, 2H, CH_2), 1.21 (m, 2H, CH_2), 1.13 (d, *J* = 6.9 Hz, 3H, CH_3), 1.08 (d, *J* = 6.9 Hz, 3H, CH_3) ppm; ^{13}C NMR (300 MHz, $CDCl_3$) δ 144.33, 133.15, 126.59, 125.28, 117.44, 111.09, 57.68, 32.56, 26.97, 24.55, 22.42, 22.28 ppm; HRMS (EI): exact mass calcd for $[C_{24}H_{34}N_2]^+$ 350.2721, found 350.2717.

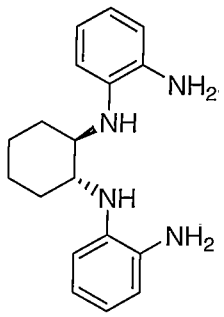
(1*R*,2*R*)-*N*,*N*'-Bis(2-nitrophenyl)-1,2-cyclohexanediamine (**75a**)



To a solution of (1*R*,2*R*)-(-)-diaminocyclohexane [Enantiomeric purity: 99% ee GLC by Aldrich] (0.5 g, 4.38 mmol) and *N*,*N*-diisopropylethylamine (1.8 mL, 10.5 mmol) in CH_3CN (5 mL) was added 1-fluoro-2-nitrobenzene [99% pure, (1 mL, 9.64 mmol)]. The reaction mixture was heated at reflux with stirring overnight under argon. After complete reaction, the reaction mixture was cooled to room temperature. The resulting solid was collected by filteration, then purified by washing the solid with *n*-hexane to afford 1 g (64%) of **75a**.

^{1}H NMR (300MHz, $CDCl_3$) δ 8.11 (bd, J = 6.3 Hz, 2H, NH), 7.91 (dd, J = 8.7, 1.5 Hz, 2H, ArH), 7.25 (app t, 2H, ArH), 6.92 (d, J = 8.7 Hz, 2H, ArH), 6.49 (app t, 2H, ArH), 3.69 (m, 2H, NH), 2.18 (m, 2H, CH_2), 1.86 (m, 2H, CH_2), 1.49 (m, 4H, CH_2) ppm; ^{13}C NMR (300 MHz, $CDCl_3$) δ 144.86, 135.95, 131.68, 126.63, 115.41, 113.75, 56.36, 32.01, 24.24 ppm; HRMS (EI): exact mass calcd for $[C_{18}H_{20}N_4O_4]^+$ 356.1484, found 356.1492.

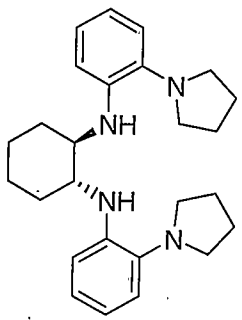
(1*R*,2*R*)-*N*,*N*'-Bis(2-aminophenyl)-1,2-cyclohexanediamine (**75b**)



To a solution of (1*R*,2*R*)-*N*,*N*'-bis(2-nitrophenyl)-1,2-cyclohexanediamine (**75a**) (0.5 g, 1.40 mmol) in MeOH (20 mL) was added 5% Pd/C (40 mg). The mixture was stirred under H_2 pressure (30 psi) using a Parr appratus for overnight. filteration, the solvent was evaporated in vacuo to afford 410 mg (98%) of **75b**. The resulting product was directly used for next reaction without further purification. R_f = 0.45 (20% ethyl acetate in *n*-hexane)

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.81-6.67 (m, 8H, ArH), 3.6-3.2 (bs, 6H, NH, NH_2), 3.21 (m, 2H, NCH), 2.35 (m, 2H, CH_2), 1.76 (m, 2H, CH_2), 1.38 (m, 2H, CH_2), 1.15 (m, 2H, CH_2) ppm; ^{13}C NMR (300 MHz, $CDCl_3$): δ 136.46, 135.80, 120.09, 119.25, 116.57, 113.61, 57.58, 32.35, 24.86 ppm; IR (KBr) *v* 3380.3, 3306.1, 3199.9, 2928.7, 2852.9, 1597.9, 1504.5, 1453.4, 1268.5, 737.2 cm^{-1}; HRMS (EI): exact mass calcd for $[C_{18}H_{24}N_4]^+$ 296.2000, found 296.2005.

(1*R*,2*R*)-*N*,*N*'-Bis(2-pyrrolidine-1-ylphenyl)-1,2-cyclohexanediamine (**71b**)

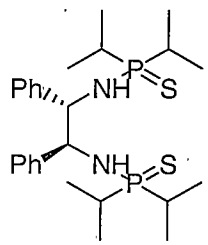


This compound was prepared via slightly modified literature procedure.[83] A solution of *N*,*N*'-bis(2-aminophenyl)cyclohexane-1,2-diamine (200 mg, 0.67 mmol, 1,3-dibromopropane (161 μL, 1.34 mmol), and *N*,*N*-diisopropylethylamine (560 μL, 3.2 mmol) in 3 mL of toluene was heated at 110 °C. When the reaction was completed, the reaction mixture diluted with ethyl acetate (10 mL), washed with water (2 x 2 mL) and dried over $MgSO_4$. After filteration, the solvent was evapotrated in vacuo. The residue was purified by column chromatography on silica (5% ethyl acetate in *n*-hexane for elution). An undesired volatile substance, which was not separable by column chromatography, was removed by evaporation using Schelenk vacuum line at 60 °C / 0.05 torr. (Yield = 59%, 160 mg). The value of enantionmeric excess (99% ee) was determined based on the enantiomeric purity of (1*R*,2*R*)-(+)-1,2-diphenylethylenediamine purchased from Aldrich.

^{1}H NMR (250 MHz, benzene-d_6) δ 7.03 (m, 4H, ArH), 6.74 (m, 4H, ArH), 4.88 (bs, 2H, NH), 3.18 (m, 2H, NCH), 2.80 (m, 8H, NCH_2), 2.21 (m, 2H, CH_2), 1.48 (m, 10H, CH_2),

1.15 (m, 4H, CH_2) ppm; ^{13}C NMR (250 MHz, benzene-d_6) δ 143.83, 137.68, 124.64, 119.21, 116.93, 110.48, 57.66, 51.44, 32.90, 24.83, 24.18 ppm; IR (KBr) *v* 3324.1, 2929.4, 2811.3, 1596.3, 1505.9, 736.2 cm^{-1}; HRMS (EI): exact mass calcd for $[C_{26}H_{36}N_4]^+$ 404.2939, found 404.2950.

(1*R*,2*R*)-*N*,*N*'-Bis(*P*,*P*-diisopropylthiophosphinyl)-1,2-diphenylethylenediamine (**72**)

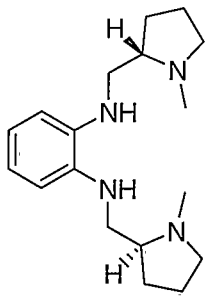


This compound was prepared in a fashion analogous to **59e** (p.155) utilizing (1*R*,2*R*)-(+)-1,2-diphenylethylenediamine [Enantiomeric purity: 99% ee GLC by Aldrich] (97% pure, 100 mg, 4.57 x 10^{-4} mol), chlorodiisopropylphophine (145 μL, 9.14 x 10^{-4} mol) and 4-methylmorpoline (120 μL, 1.1 mmol) in toluene (3 mL), followed by the addition of sulfur (15 mg, 4.8 x 10^{-4} mol) to give 73 mg (31%) of **72**. [Purification by column chromatography on silica gel (CH_2Cl_2 for elution, $R_f = 0.29_{uv}$); mp = 153-154 °C]. The value of enantionmeric excess (99% ee) was determined based on the enantiomeric purity of (1*R*,2*R*)-(+)-1,2-diphenylethylenediamine purchased from Aldrich

$^1H\{^{31}P\}$ NMR (250 MHz, $CDCl_3$) δ 7.09 (m, 6H, ArH), 6.87 (m, 4H, ArH), 4.44 (m, 2H, NCH), 4.05 (bs, 2H, NH), 2.40 (septet, *J* = 7.2 Hz, 2H, CH), 1.81 (septet, *J* = 7.2 Hz, 2H,

CH), 1.40 (d, J = 7.2 Hz, 6H, CH_3), 1.27 (d, J = 7.2 Hz, 6H, CH_3), 0.91 (d, J = 7.2 Hz, 6H, CH_3), 0.90 (d, J = 7.2 Hz, 3H, CH_3), 0.81 (d, J = 7.2 Hz, 6H, CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.60, 128.14, 127.79, 127.03, 61.22, 31.62 ($J_{c\text{-}p}$ = 63 Hz), 29.29 ($J_{c\text{-}p}$ = 61 Hz), 17.28, 17.22, 16.83, 16.49 ppm; ^{31}P (250 MHz, $CDCl_3$): δ 91.86 ppm; IR (KBr) ν 3321.9, 2963.2, 2670.9, 1456.1, 1066.0, 700.1 cm^{-1}; HRMS (CI): exact mass calcd for $[C_{26}H_{42}N_2P_2S_2+H]^+$ 509.2342, found 509.2334.

N,N'-Bis[(2*S*)-1-methylpyrrolidine-2-ylmethyl]-1,2-phenylenediamine (**73a**)

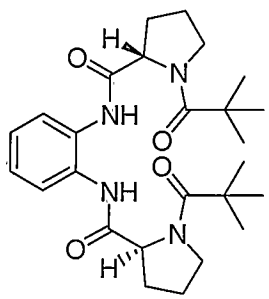


This compound was prepared in a fashion analogous to **32a** (p.124) and **23h** (p. 135) utilizing (2*S*)-pyrrolidine-1,2-dicarboxylic acid 1-methyl ester.[84] [Purification using preparative TLC coated by alumina (neutral) (ethyl acetate for elution)]. The value of enantiomeric excess (> 95% ee) was determined by ^1H NMR technique using (*S*)-(+)- and (*R*)-(-)-*O*-acetylmandelic acid.[85]

^1H NMR (300 MHz, $CDCl_3$): δ 6.73 (m, 2H, ArH), 6.06 (m, 2H, ArH), 3.94 (bs, 2H, NH), 3.07 (m, 6H, NCH_2, NCH), 2.53 (m, 2H, NC*H*H), 2.35-2.2 (m, 2H, NCH*H*), 2.31 (s, 6H, CH_3), 1.98-1.83 (m, 8H, CH_2) ppm; ^{13}C NMR (300 MHz, $CDCl_3$): δ 137.82,

118.37, 110.40, 64.18, 57.73, 45.28, 40.47, 29.05, 23.32 ppm; IR (KBr) ν 3325.8, 2938.5, 2842.4, 2789.1, 1600.2, 1522.8, 1438.1, 727.3 cm^{-1}; HRMS (EI): exact mass calcd for $[C_{18}H_{30}N_4]^+$ 302.2470 , found 302.2475.

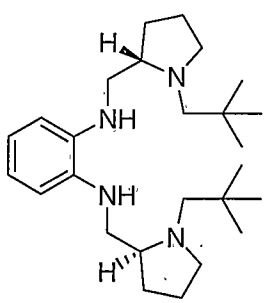
N,N'-Bis[(2*S*)-1-(2,2-dimethylpropionyl)pyrrolidine-2-ylacetyl)-1,2-phenylenediamine (**76b**)



To a soultion of (*L*)-proline (1g, 8.68 mmol) and triethylamine (2.4 mL, 17.4 mmol) in CH_2Cl_2 (20 mL) at 0 °C was added dropwise trimethylacetyl chloride (2.1 mL, 17.4 mmol), then stirred at room temperature for 15 min. After the addition of 1,2-phenylenediamine (470 mg, 4.34 mmol) and 4-dimethylaminopyridine (5 mg), the reaction mixture was allowed to attain room temperature and stirred overnight. The reaction mixture was diluted with CH_2Cl_2 (20 mL), washed with 10% HCl, washed with saturated $NaHCO_3$ and dried over $MgSO_4$. After filteration, the solvent was evaporated in vacuo. The residue was purified by subjection to column chromatography on silica gel (80% ethyl acetate in *n*-hexane for elution, $R_f = 0.23_{uv}$), to provide 822 mg (40%) of **76c**.

^{1}H NMR (250 MHz, $CDCl_3$) δ 8.76 (bs, 2H, NH), 7.52 (m, 2H, ArH), 7.07 (m, 2H, ArH), 4.70 (t, J = 5.8 Hz, 2H, NCH), 3.71 (m, 4H, NCH_2), 2.1-2.0 (m, 6H, CH_2), 1.90 (m, 2H, CH_2), 1.20 (s, 18H, CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.30, 172.03, 130.26, 125.63, 125.10, 62.60, 48.64, 38.90, 27.36, 27.09, 26.10 ppm; IR (KBr) ν 3245.8, 2971.7, 1703.3, 1605.2, 1539.0, 1410.6, 1172.3, 755.2 cm^{-1}; HRMS (EI): exact mass calcd for $[C_{26}H_{38}N_4O_4]^+$ 470.2893, found 470.2900.

N,N'-Bis[(2*S*)-1-(2,2-dimethylpropyl)pyrrolidine-2-ylmethyl]-1,2-phenylenediamine (**73b**)

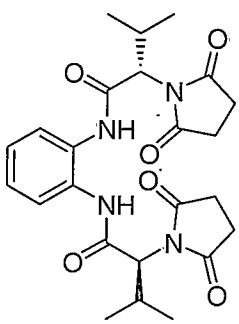


This compound was prepared in a fashion of **23h** (p.135) utilizing **76b** (800mg, 1.7 mmol), $LiAlH_4$ (0.5 g, 13.6 mmol) in THF 30 mL, followed by heating at reflux overnight to give 270 mg (19%) of **73b**. [Purification by column chromatography on silica gel (10% methanol in CH_2Cl_2 for elution)]. The value of enantionmeric excess (> 95 % ee) was determined by ^{1}H NMR technique using (*S*)-(+)- and (*R*)-(-)-*O*-acetylmandelic acid. [85]

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.70 (m, 2H, ArH), 6.55 (m, 2H, ArH), 4.17 (bs, 2H, NH), 3.30 (m, 2H, NC*H*H), 3.01 (s, 4H, NCH_2), 2.80 (m, 2H, NCH*H*), 2.42 (app d,

NC*H*H), 2.30 (app q, 2H, NCH), 2.14 (app d, NCH*H*), 2.0-1.7 (m, 8H, CH_2), 0.82 (s, 18H, CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.05, 117.86, 109.57, 68.39, 65.05, 58.20, 44.92, 32.45, 28.59, 27.76, 24.90 ppm; IR (KBr) *v* 3305.8, 2950.3, 2808.4, 1603.1, 1519.1, 1435.1, 1361.3, 1259.4, 1109.2, 731.9 cm^{-1}; HRMS (EI): exact mass calcd for $[C_{26}H_{46}N_4]^+$ 414.3722, found 414.3724.

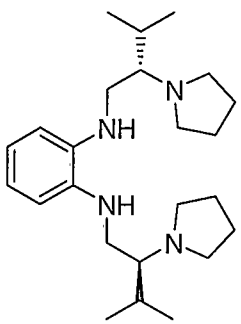
N,N-Bis[2-(2,5-dioxopyrrolidin-1-yl)-2-(*S*)-isopropylacetyl]-1,2-phenylenediamine (**76c**)



To a solution of 1,2-phenylenediamine (540 mg, 5.02 mmol) and (2*S*)-2-(2,5-dioxopyrrolidin-1-yl)-3-methyl-butyric acid (2 g, 10 mmol) in CH_2Cl_2 (30 mL) at 0 °C was added dropwise DCC (2.07 g, 10 mmol) in CH_2Cl_2 (5 mL). The mixture was allowed to attain room temperature with stirring for overnight. The resulting solid was fillered off, wased with 5% HCl and saturated $NaHCO_3$ solution sequently. The organic phase was dired ($MgSO_4$), filtered, and evaporated in vacuo. The crude was subjected to column chromatography on silica gel (ethyl acetate for elution) to give 250 mg (10%) of **76c**.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.75 (bs, 2H, NH), 7.55 (dd, J = 5.5, 3.5 Hz, 2H, ArH), 7.16 (dd, J = 5.5, 3.5 Hz, 2H, ArH), 4.38 (d, J = 11.0 Hz, 2H, NCH), 2.81-2.74 (m, 2H, CH), 2.78 (s, 8H, CH_2), 1.12 (d, J = 7.0 Hz, 6H, CH_3), 0.84 (d, J = 7.0 Hz, 6H, CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.64, 167.20, 129.63, 126.31, 63.01, 28.05, 26.77, 25.51, 20.14, 19.36 ppm; IR (KBr) ν 3292.6, 2966.7, 1704.4, 1538.0, 1389.3, 1102.1, 755.7 cm^{-1}; HRMS (EI): exact mass calcd for $[C_{24}H_{30}N_4O_6]^+$ 470.2165, found 470.2180.

N,N'-Bis[(2*S*)-2-isopropyl-2-pyrrolidinylethyl]-1,2-phenylenediamine (**73c**)



This compound was prepared in a fashion of **23h** (p.135) utilizing *N,N*-bis[(2*S*)-2-(2,5-dioxopyrrolidin-1-yl)-2-isopropylacetyl]-1,2-phenylenediamine (**76c**) (200 mg, 0.42 mmol) and $LiAlH_4$ (130 mg, 3.4 mmol) in THF (20 mL). Purification using preparative TLC coated by alumina (neutral) (10% ethyl acetate in *n*-hexane for elution) funished 20 mg (12%) of **73c**. The value of enantiomeric excess (> 95% ee) was determined by ^{1}H NMR technique using (*S*)-(+)- and (*R*)-(-)-*O*-acetylmandelic acid. [85]

^{1}H NMR (500 MHz, benzene-d_6): δ 7.04 (dd, J = 5.5, 3.5 Hz, 2H, ArH), 6.70 (dd, J = 5.5, 3.5 Hz, 2H, ArH), 4.22 (bs, 2H, NH), 3.05 (m, 4H, NCH_2), 2.37 (m, 8H, NCH_2), 2.13 (app q, 2H, NCH), 1.91 (app octet, 2H, CH), 1.55 (app s, 8H, CH_2), 1.12 (d, J = 5.0 Hz, 6H, CH_3), 0.92 (d, J = 5.0 Hz, 6H, CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.97, 118.55, 109.80, 66.81, 50.85, 42.23, 30.16, 23.57, 20.95, 18.32 ppm; HRMS (EI): exact mass calcd for $[C_{24}H_{42}N_4]^+$ 386.3409, found 386.3398.

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APPENDICES

APPENDIX A

X-RAY CRYSTALLOGRAPIC ANALYSIS FOR **63**

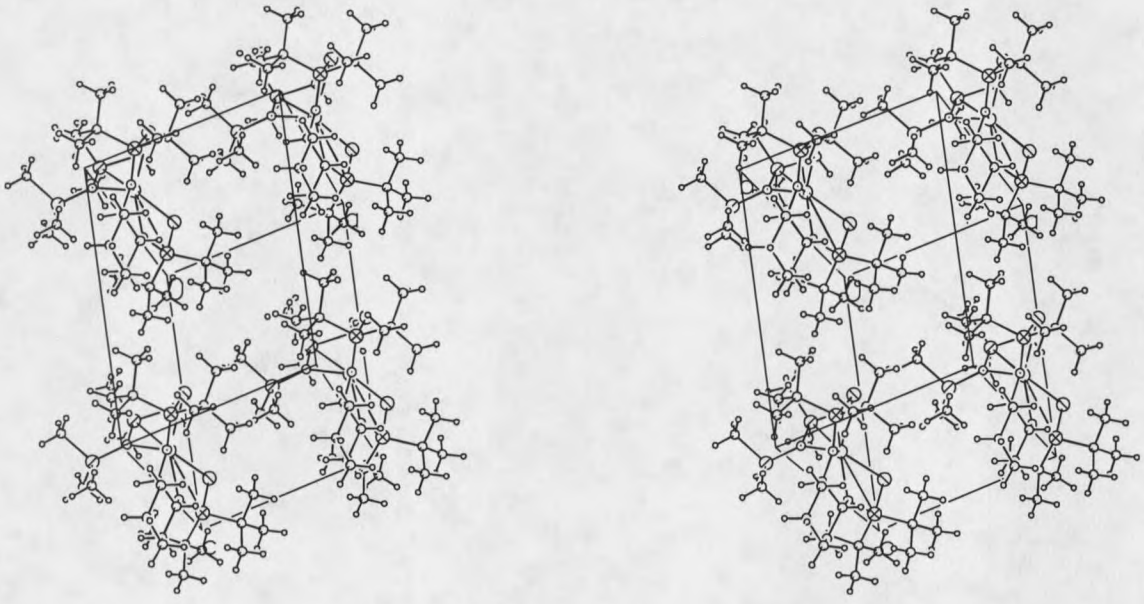


Figure 20. Unit Cell of **63**

Table 22. Crystal Data and Structure Refinement for **63**

Empirical formula	$C_{28}H_{64}N_3P_2S_2Si_2Y$
Formula weight	713.97
Crystallization Solvent	Toluene
Crystal Habit	Chunk
Crystal size	0.33 x 0.20 x 0.15 mm^3
Crystal color	Colorless

DATA COLLECTION

Preliminary Photos	Rotation	
Type of diffractometer	CCD area detector	
Wavelength	0.71073 Å MoKα	
Data Collection Temperature	98(2) K	
θ range for 9280 reflections used in lattice determination	2.60 to 27.81°	
Unit cell dimensions	a = 8.6504(8) Å b = 11.4334(10) Å c = 11.4503(10) Å	α= 113.1150(10)° β= 104.540(2)° γ = 102.616(2)°
Volume	942.13(15) $Å^3$	
Z	1	
Crystal system	Triclinic	
Space group	P1	
Density (calculated)	1.258 Mg/m^3	
F(000)	382	
Data collection program	Bruker SMART	
θ range for data collection	2.07 to 28.18°	
Completeness to θ = 28.18°	93.4 %	
Index ranges	$-11 \le h \le 11, -15 \le k \le 14, -15 \le l \le 15$	
Data collection scan type	ω scans at 7 ϕ settings	
Data reduction program	Bruker SAINT v6.1	

DATA COLLECTION-CONTINUED

Reflections collected	16489
Independent reflections	8311 [R_{int}= 0.0510]
Absorption coefficient	1.828 mm^{-1}
Absorption correction	None
Max. and min. transmission (theory)	0.7736 and 0.5812

STRUCTURE SOLUTION AND REFINEMENT

Structure solution program	SHELXS-97 (Sheldrick, 1990)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	8311 / 3 / 367
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	1.407
Final R indices [I>2σ(I), 7476 reflections]	R1 = 0.0427, *w*R2 = 0.0805
R indices (all data)	R1 = 0.0477, *w*R2 = 0.0813
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.000
Average shift/error	0.000
Absolute structure parameter	-0.039(3)
Largest diff. peak and hole	0.935 and -0.389 e.$Å^{-3}$

SPECIAL REFINEMENT DETAILS

Refinement of F^2 against ALL reflections. The weighted R-factor (wR) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Table 23. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **63**. U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Y	9752(1)	2617(1)	7647(1)	24(1)
P(1)	11032(1)	5385(1)	7577(1)	27(1)
P(2)	10996(1)	2515(1)	10406(1)	28(1)
Si(1)	7179(2)	-116(1)	4837(1)	36(1)
Si(2)	5213(1)	1306(1)	6335(1)	30(1)
S(1)	11298(1)	3683(1)	6289(1)	38(1)
S(2)	11168(2)	1165(1)	8688(1)	46(1)
N(1)	10441(4)	4950(3)	8602(3)	27(1)
N(2)	10186(4)	3480(3)	9944(3)	25(1)

TABLE 23-CONTINUDED

N(3)	7107(4)	1197(3)	6188(3)	26(1)
C(1)	9971(5)	5544(3)	9807(4)	23(1)
C(2)	10616(5)	7086(4)	10665(4)	32(1)
C(3)	9838(6)	7492(4)	11745(4)	39(1)
C(4)	10197(7)	6836(4)	12654(4)	44(1)
C(5)	9686(6)	5297(4)	11795(4)	34(1)
C(6)	10514(5)	4950(3)	10758(4)	25(1)
C(7)	13198(6)	6766(4)	8362(5)	40(1)
C(8)	14309(6)	6528(4)	9443(5)	50(1)
C(9)	13164(6)	8220(4)	9034(5)	50(1)
C(10)	14027(6)	6666(5)	7306(5)	61(2)
C(11)	9360(6)	5742(4)	6516(4)	37(1)
C(12)	8774(6)	6823(5)	7385(5)	50(1)
C(13)	9936(7)	6151(5)	5521(5)	59(1)
C(14)	7790(6)	4414(5)	5680(5)	56(1)
C(15)	13229(6)	3401(4)	11721(4)	39(1)
C(16)	14282(6)	4147(5)	11174(5)	57(1)
C(17)	13374(6)	4438(5)	13142(4)	55(1)
C(18)	14007(7)	2376(5)	11909(5)	63(2)
C(19)	9515(6)	1479(4)	10879(4)	41(1)
C(20)	9470(11)	2259(5)	12270(7)	112(3)
C(21)	9955(9)	271(6)	10882(8)	90(2)
C(22)	7780(8)	957(8)	9782(8)	136(4)
C(23)	9420(6)	57(5)	5053(5)	63(2)
C(24)	6145(11)	-1832(5)	4606(9)	133(4)
C(25)	6195(10)	-160(8)	3157(5)	116(3)
C(26)	3970(5)	-137(4)	6511(5)	45(1)
C(27)	3789(6)	1352(5)	4830(4)	49(1)
C(28)	5612(5)	2905(4)	7883(4)	40(1)

Table 24. Bond lengths [Å] and angles [°] for **63**

Y-N(3)	2.234(3)	P(1)-N(1)	1.592(3)
Y-N(1)	2.314(3)	P(1)-C(11)	1.870(4)
Y-N(2)	2.309(3)	P(1)-C(7)	1.887(4)
Y-S(2)	2.7179(11)	P(1)-S(1)	2.0315(13)
Y-S(1)	2.7409(11)	P(2)-N(2)	1.612(3)
Y-P(2)	3.1280(10)	P(2)-C(19)	1.878(4)
Y-P(1)	3.1566(10)	P(2)-C(15)	1.874(4)
Y-Si(1)	3.2474(11)	P(2)-S(2)	2.0332(13)

TABLE 24-CONTINUDED

Si(1)-N(3)	1.708(3)	C(13)-H(13B)	0.9800
Si(1)-C(24)	1.851(5)	C(13)-H(13C)	0.9800
Si(1)-C(23)	1.847(5)	C(14)-H(14A)	0.9800
Si(1)-C(25)	1.874(6)	C(14)-H(14B)	0.9800
Si(2)-N(3)	1.715(3)	C(14)-H(14C)	0.9800
Si(2)-C(28)	1.864(4)	C(15)-C(16)	1.521(6)
Si(2)-C(27)	1.877(5)	C(15)-C(18)	1.530(6)
Si(2)-C(26)	1.874(4)	C(15)-C(17)	1.545(6)
N(1)-C(1)	1.482(4)	C(16)-H(16A)	0.9800
N(2)-C(6)	1.484(4)	C(16)-H(16B)	0.9800
C(1)-C(2)	1.522(5)	C(16)-H(16C)	0.9800
C(1)-C(6)	1.527(5)	C(17)-H(17A)	0.9800
C(1)-H(1)	0.9426	C(17)-H(17B)	0.9800
C(2)-C(3)	1.518(5)	C(17)-H(17C)	0.9800
C(2)-H(2A)	0.9428	C(18)-H(18A)	0.9800
C(2)-H(2B)	0.9428	C(18)-H(18B)	0.9800
C(3)-C(4)	1.514(6)	C(18)-H(18C)	0.9800
C(3)-H(3A)	0.9602	C(19)-C(22)	1.504(7)
C(3)-H(3B)	0.9602	C(19)-C(20)	1.505(7)
C(4)-C(5)	1.531(5)	C(19)-C(21)	1.511(6)
C(4)-H(4A)	0.9489	C(20)-H(20A)	0.9800
C(4)-H(4B)	0.9489	C(20)-H(20B)	0.9800
C(5)-C(6)	1.504(5)	C(20)-H(20C)	0.9800
C(5)-H(5A)	0.9521	C(21)-H(21A)	0.9800
C(5)-H(5B)	0.9521	C(21)-H(21B)	0.9800
C(6)-H(6)	0.8781	C(21)-H(21C)	0.9800
C(7)-C(8)	1.520(6)	C(22)-H(22A)	0.9800
C(7)-C(10)	1.534(6)	C(22)-H(22B)	0.9800
C(7)-C(9)	1.545(5)	C(22)-H(22C)	0.9800
C(8)-H(8A)	0.9800	C(23)-H(23A)	0.9800
C(8)-H(8B)	0.9800	C(23)-H(23B)	0.9800
C(8)-H(8C)	0.9800	C(23)-H(23C)	0.9800
C(9)-H(9A)	0.9800	C(24)-H(24A)	0.9800
C(9)-H(9B)	0.9800	C(24)-H(24B)	0.9800
C(9)-H(9C)	0.9800	C(24)-H(24C)	0.9800
C(10)-H(10A)	0.9800	C(25)-H(25A)	0.9800
C(10)-H(10B)	0.9800	C(25)-H(25B)	0.9800
C(10)-H(10C)	0.9800	C(25)-H(25C)	0.9800
C(11)-C(12)	1.529(5)	C(26)-H(26A)	0.9800
C(11)-C(13)	1.539(6)	C(26)-H(26B)	0.9800
C(11)-C(14)	1.540(6)	C(26)-H(26C)	0.9800
C(12)-H(12A)	0.9800	C(27)-H(27A)	0.9800
C(12)-H(12B)	0.9800	C(27)-H(27B)	0.9800
C(12)-H(12C)	0.9800	C(27)-H(27C)	0.9800
C(13)-H(13A)	0.9800	C(28)-H(28A)	0.9800
		C(28)-H(28B)	0.9800

TABLE 24-CONTINUDED

C(28)-H(28C)	0.9800	N(2)-P(2)-Y	45.65(10)
N(3)-Y-N(1)	120.86(11)	C(19)-P(2)-Y	121.62(15)
N(3)-Y-N(2)	115.71(11)	C(15)-P(2)-Y	125.48(14)
N(1)-Y-N(2)	71.36(10)	S(2)-P(2)-Y	59.10(4)
N(3)-Y-S(2)	105.53(8)	N(3)-Si(1)-C(24)	115.1(2)
N(1)-Y-S(2)	128.84(8)	N(3)-Si(1)-C(23)	110.19(17)
N(2)-Y-S(2)	69.88(7)	C(24)-Si(1)-C(23)	105.7(3)
N(3)-Y-S(1)	107.88(8)	N(3)-Si(1)-C(25)	113.1(2)
N(1)-Y-S(1)	67.94(7)	C(24)-Si(1)-C(25)	106.5(4)
N(2)-Y-S(1)	131.14(8)	C(23)-Si(1)-C(25)	105.7(3)
S(2)-Y-S(1)	118.76(4)	N(3)-Si(1)-Y	40.20(10)
N(3)-Y-P(2)	115.67(8)	C(24)-Si(1)-Y	128.4(3)
N(1)-Y-P(2)	96.80(8)	C(23)-Si(1)-Y	70.00(14)
N(2)-Y-P(2)	29.95(7)	C(25)-Si(1)-Y	124.5(3)
S(2)-Y-P(2)	39.93(3)	N(3)-Si(2)-C(28)	110.37(17)
S(1)-Y-P(2)	135.25(3)	N(3)-Si(2)-C(27)	112.09(18)
N(3)-Y-P(1)	116.26(8)	C(28)-Si(2)-C(27)	106.5(2)
N(1)-Y-P(1)	28.94(7)	N(3)-Si(2)-C(26)	113.03(17)
N(2)-Y-P(1)	98.93(7)	C(28)-Si(2)-C(26)	106.9(2)
S(2)-Y-P(1)	137.04(4)	C(27)-Si(2)-C(26)	107.6(2)
S(1)-Y-P(1)	39.51(3)	P(1)-S(1)-Y	81.35(4)
P(2)-Y-P(1)	119.97(3)	P(2)-S(2)-Y	80.96(4)
N(3)-Y-Si(1)	29.58(7)	C(1)-N(1)-P(1)	138.8(2)
N(1)-Y-Si(1)	139.02(8)	C(1)-N(1)-Y	114.0(2)
N(2)-Y-Si(1)	136.06(8)	P(1)-N(1)-Y	106.35(13)
S(2)-Y-Si(1)	92.11(3)	C(6)-N(2)-P(2)	128.8(2)
S(1)-Y-Si(1)	92.78(3)	C(6)-N(2)-Y	118.7(2)
P(2)-Y-Si(1)	120.50(3)	P(2)-N(2)-Y	104.40(13)
P(1)-Y-Si(1)	119.53(3)	Si(1)-N(3)-Si(2)	122.03(18)
N(1)-P(1)-C(11)	112.81(18)	Si(1)-N(3)-Y	110.22(15)
N(1)-P(1)-C(7)	115.56(18)	Si(2)-N(3)-Y	127.73(15)
C(11)-P(1)-C(7)	112.0(2)	N(1)-C(1)-C(2)	118.9(3)
N(1)-P(1)-S(1)	102.88(11)	N(1)-C(1)-C(6)	109.3(3)
C(11)-P(1)-S(1)	107.27(13)	C(2)-C(1)-C(6)	108.2(3)
C(7)-P(1)-S(1)	105.26(14)	N(1)-C(1)-H(1)	106.6
N(1)-P(1)-Y	44.71(10)	C(2)-C(1)-H(1)	106.6
C(11)-P(1)-Y	115.25(14)	C(6)-C(1)-H(1)	106.6
C(7)-P(1)-Y	132.75(15)	C(1)-C(2)-C(3)	110.8(3)
S(1)-P(1)-Y	59.14(4)	C(1)-C(2)-H(2A)	109.5
N(2)-P(2)-C(19)	111.78(18)	C(3)-C(2)-H(2A)	109.5
N(2)-P(2)-C(15)	114.73(17)	C(1)-C(2)-H(2B)	109.5
C(19)-P(2)-C(15)	112.9(2)	C(3)-C(2)-H(2B)	109.5
N(2)-P(2)-S(2)	104.75(11)	H(2A)-C(2)-H(2B)	108.1
C(19)-P(2)-S(2)	106.12(14)	C(4)-C(3)-C(2)	111.4(3)
C(15)-P(2)-S(2)	105.64(14)	C(4)-C(3)-H(3A)	109.3
		C(2)-C(3)-H(3A)	109.3

TABLE 24-CONTINUED

C(4)-C(3)-H(3B)	109.3	C(12)-C(11)-C(13)	109.7(4)
C(2)-C(3)-H(3B)	109.3	C(12)-C(11)-C(14)	106.5(4)
H(3A)-C(3)-H(3B)	108.0	C(13)-C(11)-C(14)	108.8(4)
C(3)-C(4)-C(5)	111.0(3)	C(12)-C(11)-P(1)	112.6(3)
C(3)-C(4)-H(4A)	109.4	C(13)-C(11)-P(1)	112.5(3)
C(5)-C(4)-H(4A)	109.4	C(14)-C(11)-P(1)	106.5(3)
C(3)-C(4)-H(4B)	109.4	C(11)-C(12)-H(12A)	109.5
C(5)-C(4)-H(4B)	109.4	C(11)-C(12)-H(12B)	109.5
H(4A)-C(4)-H(4B)	108.0	H(12A)-C(12)-H(12B)	109.5
C(6)-C(5)-C(4)	111.8(3)	C(11)-C(12)-H(12C)	109.5
C(6)-C(5)-H(5A)	109.2	H(12A)-C(12)-H(12C)	109.5
C(4)-C(5)-H(5A)	109.2	H(12B)-C(12)-H(12C)	109.5
C(6)-C(5)-H(5B)	109.2	C(11)-C(13)-H(13A)	109.5
C(4)-C(5)-H(5B)	109.2	C(11)-C(13)-H(13B)	109.5
H(5A)-C(5)-H(5B)	107.9	H(13A)-C(13)-H(13B)	109.5
N(2)-C(6)-C(5)	115.6(3)	C(11)-C(13)-H(13C)	109.5
N(2)-C(6)-C(1)	110.2(3)	H(13A)-C(13)-H(13C)	109.5
C(5)-C(6)-C(1)	108.9(3)	H(13B)-C(13)-H(13C)	109.5
N(2)-C(6)-H(6)	107.3	C(11)-C(14)-H(14A)	109.5
C(5)-C(6)-H(6)	107.3	C(11)-C(14)-H(14B)	109.5
C(1)-C(6)-H(6)	107.3	H(14A)-C(14)-H(14B)	109.5
C(8)-C(7)-C(10)	107.9(4)	C(11)-C(14)-H(14C)	109.5
C(8)-C(7)-C(9)	109.5(4)	H(14A)-C(14)-H(14C)	109.5
C(10)-C(7)-C(9)	107.8(4)	H(14B)-C(14)-H(14C)	109.5
C(8)-C(7)-P(1)	106.1(3)	C(16)-C(15)-C(18)	108.0(4)
C(10)-C(7)-P(1)	111.7(3)	C(16)-C(15)-C(17)	108.8(4)
C(9)-C(7)-P(1)	113.7(3)	C(18)-C(15)-C(17)	108.0(4)
C(7)-C(8)-H(8A)	109.5	C(16)-C(15)-P(2)	106.8(3)
C(7)-C(8)-H(8B)	109.5	C(18)-C(15)-P(2)	111.1(3)
H(8A)-C(8)-H(8B)	109.5	C(17)-C(15)-P(2)	114.1(3)
C(7)-C(8)-H(8C)	109.5	C(15)-C(16)-H(16A)	109.5
H(8A)-C(8)-H(8C)	109.5	C(15)-C(16)-H(16B)	109.5
H(8B)-C(8)-H(8C)	109.5	H(16A)-C(16)-H(16B)	109.5
C(7)-C(9)-H(9A)	109.5	C(15)-C(16)-H(16C)	109.5
C(7)-C(9)-H(9B)	109.5	H(16A)-C(16)-H(16C)	109.5
H(9A)-C(9)-H(9B)	109.5	H(16B)-C(16)-H(16C)	109.5
C(7)-C(9)-H(9C)	109.5	C(15)-C(17)-H(17A)	109.5
H(9A)-C(9)-H(9C)	109.5	C(15)-C(17)-H(17B)	109.5
H(9B)-C(9)-H(9C)	109.5	H(17A)-C(17)-H(17B)	109.5
C(7)-C(10)-H(10A)	109.5	C(15)-C(17)-H(17C)	109.5
C(7)-C(10)-H(10B)	109.5	H(17A)-C(17)-H(17C)	109.5
H(10A)-C(10)-H(10B)	109.5	H(17B)-C(17)-H(17C)	109.5
C(7)-C(10)-H(10C)	109.5	C(15)-C(18)-H(18A)	109.5
H(10A)-C(10)-H(10C)	109.5	C(15)-C(18)-H(18B)	109.5
H(10B)-C(10)-H(10C)	109.5	H(18A)-C(18)-H(18B)	109.5
		C(15)-C(18)-H(18C)	109.5

TABLE 24-CONTINUED

H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(22)-C(19)-C(20)	110.3(6)
C(22)-C(19)-C(21)	108.3(5)
C(20)-C(19)-C(21)	105.8(5)
C(22)-C(19)-P(2)	105.1(3)
C(20)-C(19)-P(2)	114.3(3)
C(21)-C(19)-P(2)	112.9(3)
C(19)-C(20)-H(20A)	109.5
C(19)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(19)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(19)-C(21)-H(21A)	109.5
C(19)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(19)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(19)-C(22)-H(22A)	109.5
C(19)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(19)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
Si(1)-C(23)-H(23A)	109.5
Si(1)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
Si(1)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
Si(1)-C(24)-H(24A)	109.5
Si(1)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
Si(1)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
Si(1)-C(25)-H(25A)	109.5
Si(1)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
Si(1)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
Si(2)-C(26)-H(26A)	109.5
Si(2)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
Si(2)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5
Si(2)-C(27)-H(27A)	109.5
Si(2)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
Si(2)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
Si(2)-C(28)-H(28A)	109.5
Si(2)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5
Si(2)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5

Table 25. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **63.**

	x	y	z	U_{iso}
H(1)	8770(50)	5244(13)	9477(14)	27
H(2A)	10328(9)	7475(12)	10091(16)	38
H(2B)	11820(30)	7421(11)	11094(12)	38
H(3A)	10299(13)	8460(30)	12299(15)	47
H(3B)	8620(30)	7224(8)	11305(12)	47
H(4A)	9578(19)	7015(7)	13240(19)	52
H(4B)	11380(40)	7221(12)	13209(18)	52
H(5A)	10010(10)	4921(12)	12386(17)	41
H(5B)	8480(40)	4898(12)	11334(13)	41
H(6)	11620(50)	5361(19)	11210(20)	30
H(8A)	15481	7175	9833	75
H(8B)	14305	5597	9023	75
H(8C)	13857	6659	10171	75
H(9A)	12653	8315	9724	75
H(9B)	12482	8386	8331	75
H(9C)	14333	8883	9472	75
H(10A)	15169	7369	7758	91
H(10B)	13321	6799	6586	91
H(10C)	14119	5766	6898	91
H(12A)	9743	7687	7954	74
H(12B)	8338	6532	7976	74
H(12C)	7867	6945	6784	74
H(13A)	8975	6217	4912	88
H(13B)	10326	5462	4974	88
H(13C)	10875	7034	6043	88
H(14A)	7496	4087	6297	84
H(14B)	8052	3725	5004	84
H(14C)	6821	4587	5209	84
H(16A)	13780	4784	11009	86
H(16B)	14288	3486	10314	86
H(16C)	15457	4650	11847	86
H(17A)	12777	3957	13536	82
H(17B)	12856	5092	13044	82
H(17C)	14582	4922	13747	82
H(18A)	15218	2852	12507	94
H(18B)	13898	1690	11016	94
H(18C)	13402	1931	12326	94
H(20A)	8946	2937	12264	169
H(20B)	10638	2721	12958	169
H(20C)	8797	1630	12494	169
H(21A)	10927	578	11725	135
H(21B)	10255	-162	10087	135

TABLE 25-CONTINUDED

H(21C)	8967	-385	10834	135
H(22A)	6984	261	9859	204
H(22B)	7860	559	8879	204
H(22C)	7364	1710	9892	204
H(23A)	10020	929	5123	95
H(23B)	9446	-688	4261	95
H(23C)	9984	22	5889	95
H(24A)	6560	-1841	5480	200
H(24B)	6425	-2501	3924	200
H(24C)	4904	-2063	4292	200
H(25A)	6592	760	3262	174
H(25B)	4947	-496	2863	174
H(25C)	6531	-765	2468	174
H(26A)	3477	-968	5627	67
H(26B)	3051	80	6804	67
H(26C)	4733	-278	7195	67
H(27A)	4434	2051	4667	73
H(27B)	2814	1567	5022	73
H(27C)	3374	463	4016	73
H(28A)	6387	2942	8695	60
H(28B)	4527	2923	7990	60
H(28C)	6131	3691	7777	60

Table 26. Anisotropic displacement parameters ($Å^2 x\ 10^4$) for **63.** The anisotropic displacement factor exponent takes the form: $-2p^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Y	284(2)	201(2)	189(2)	57(2)	61(2)	79(2)
P(1)	350(6)	255(5)	242(5)	127(4)	139(5)	113(5)
P(2)	394(6)	224(5)	226(5)	109(4)	85(5)	146(5)
Si(1)	332(7)	251(6)	307(6)	2(5)	98(5)	47(5)
Si(2)	248(6)	343(6)	262(6)	118(5)	81(5)	88(5)
S(1)	547(7)	339(6)	334(6)	138(5)	270(6)	197(5)
S(2)	726(8)	378(6)	290(6)	112(5)	154(6)	381(6)
N(1)	370(19)	174(15)	232(16)	67(13)	123(15)	104(14)
N(2)	359(18)	200(15)	196(15)	85(13)	80(14)	129(14)
N(3)	288(18)	214(16)	220(16)	77(13)	77(14)	78(14)
C(1)	290(20)	219(18)	184(18)	105(15)	98(16)	91(16)
C(2)	500(30)	260(20)	260(20)	150(17)	160(20)	189(19)
C(3)	610(30)	230(20)	310(20)	95(18)	170(20)	200(20)
C(4)	810(30)	280(20)	270(20)	109(19)	260(20)	250(20)
C(5)	560(30)	290(20)	290(20)	178(18)	220(20)	220(20)
C(6)	330(20)	161(17)	201(19)	53(15)	67(17)	78(16)
C(7)	410(30)	370(20)	440(30)	200(20)	190(20)	130(20)
C(8)	340(30)	410(30)	580(30)	170(20)	70(20)	90(20)
C(9)	510(30)	310(20)	610(30)	210(20)	220(30)	60(20)
C(10)	540(30)	550(30)	790(40)	310(30)	400(30)	130(30)
C(11)	510(30)	410(20)	290(20)	222(19)	150(20)	230(20)
C(12)	590(30)	610(30)	420(30)	300(20)	160(20)	360(30)
C(13)	850(40)	700(40)	460(30)	420(30)	310(30)	380(30)
C(14)	470(30)	550(30)	510(30)	280(30)	-40(20)	100(20)
C(15)	410(30)	380(20)	320(20)	160(20)	30(20)	190(20)
C(16)	350(30)	720(30)	600(30)	350(30)	40(20)	170(30)
C(17)	570(30)	490(30)	390(30)	130(20)	-10(20)	200(30)
C(18)	690(40)	620(30)	510(30)	270(30)	0(30)	370(30)
C(19)	570(30)	290(20)	440(30)	250(20)	180(20)	160(20)
C(20)	1750(70)	440(40)	1370(70)	300(40)	1260(60)	200(40)
C(21)	1430(60)	650(40)	1340(60)	820(40)	840(50)	630(40)
C(22)	570(40)	1640(70)	1840(80)	1490(70)	-100(50)	-300(40)
C(23)	510(30)	540(30)	460(30)	-120(20)	220(30)	110(30)
C(24)	1650(70)	320(30)	2270(90)	360(40)	1560(70)	290(40)
C(25)	1540(70)	1620(70)	310(30)	190(40)	340(40)	1080(60)
C(26)	320(20)	480(30)	480(30)	190(20)	170(20)	70(20)
C(27)	370(30)	640(30)	450(30)	260(20)	120(20)	220(20)
C(28)	370(20)	430(20)	380(20)	150(20)	170(20)	170(20)

APPENDIX B

^{1}H, ^{13}C AND ^{31}P SPECTRA FOR SUBSTRACTES, CYCLIZED PRODUCTS AND LIGANDS

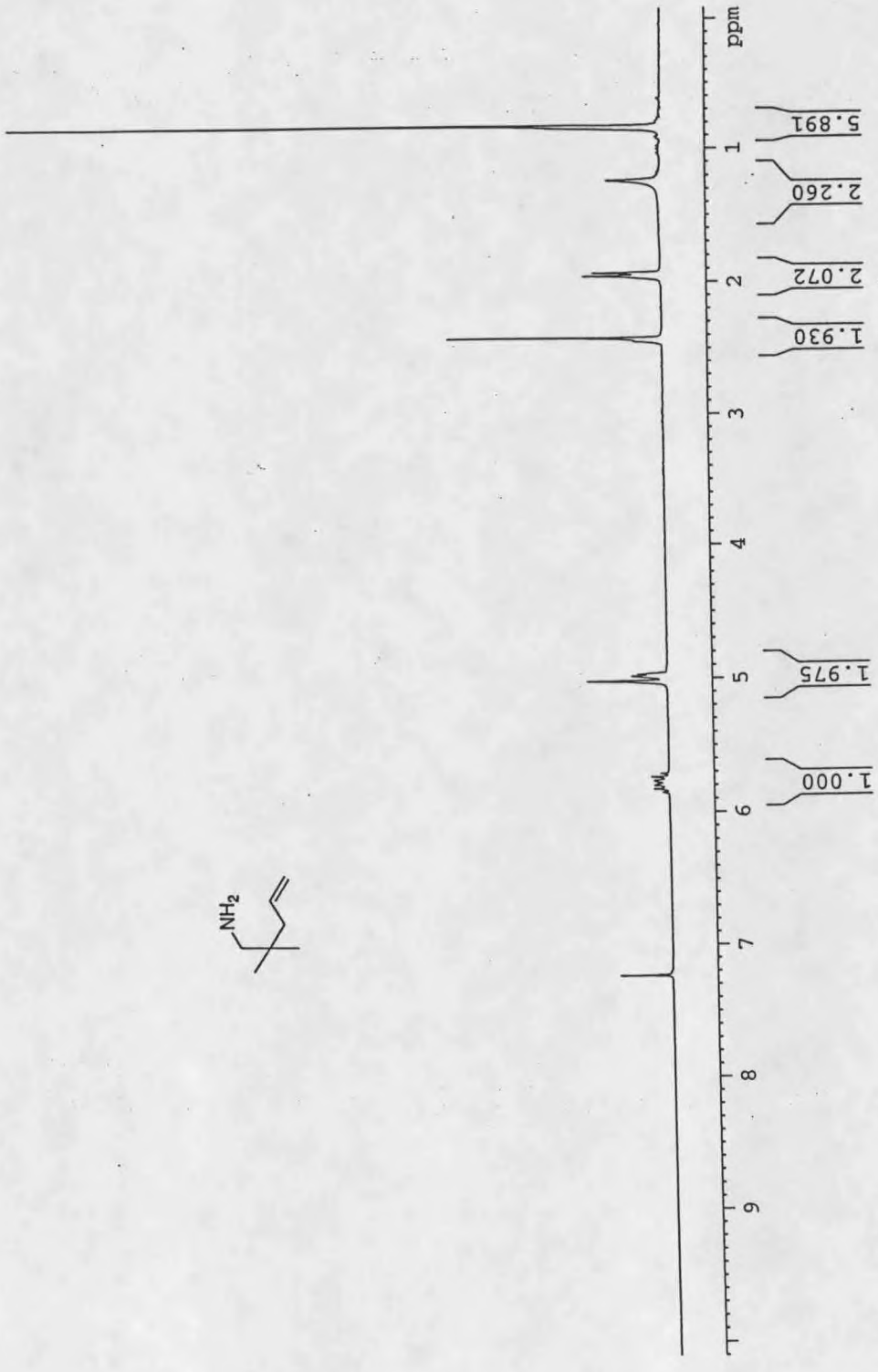


Figure 21. ^{1}H NMR Spectrum of 2,2-Dimethylaminopent-4-ene (**15a**)

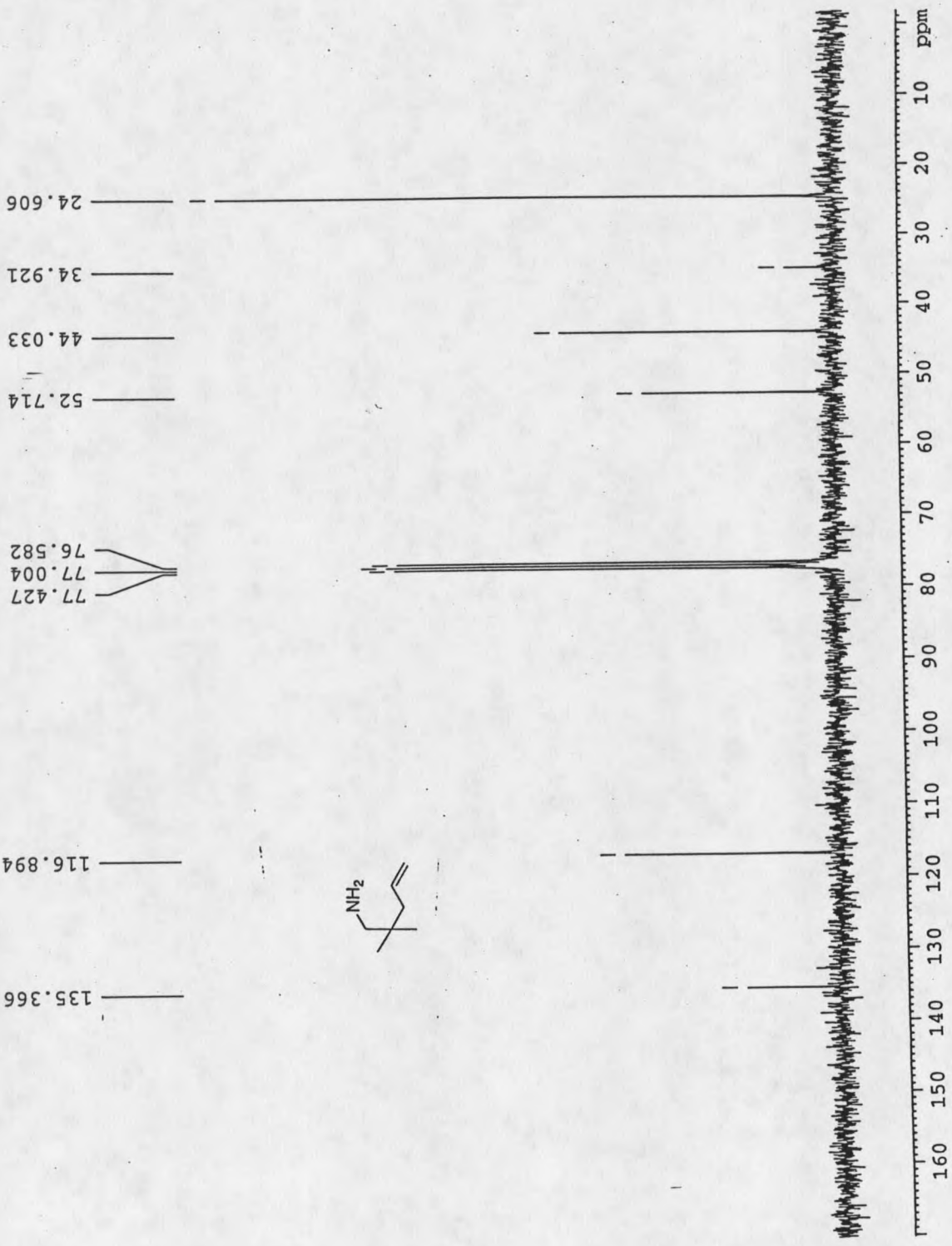


Figure 22. ^{13}C NMR Spectrum of 2,2-Dimethylaminopent-4-ene (**15a**)



Figure 23. ^{1}H NMR Spectrum of 2,4,4-Trimethylpyrrolidine (**16a**)

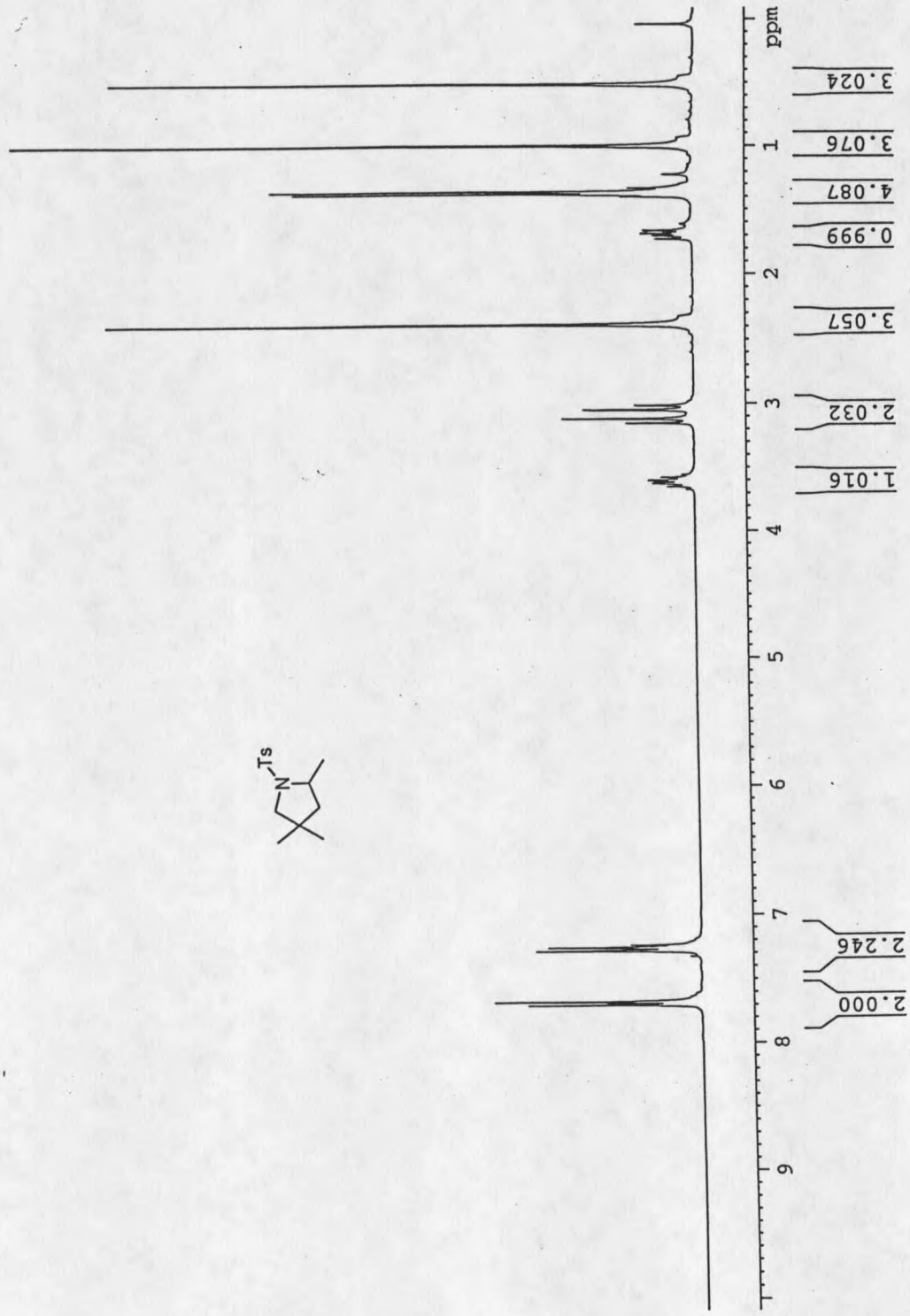


Figure 24. ^{1}H NMR Spectrum of *N*-(*p*-Tolylsulfonyl)-2,4,4-trimethylpyrrolidine (**Ts-16a**)

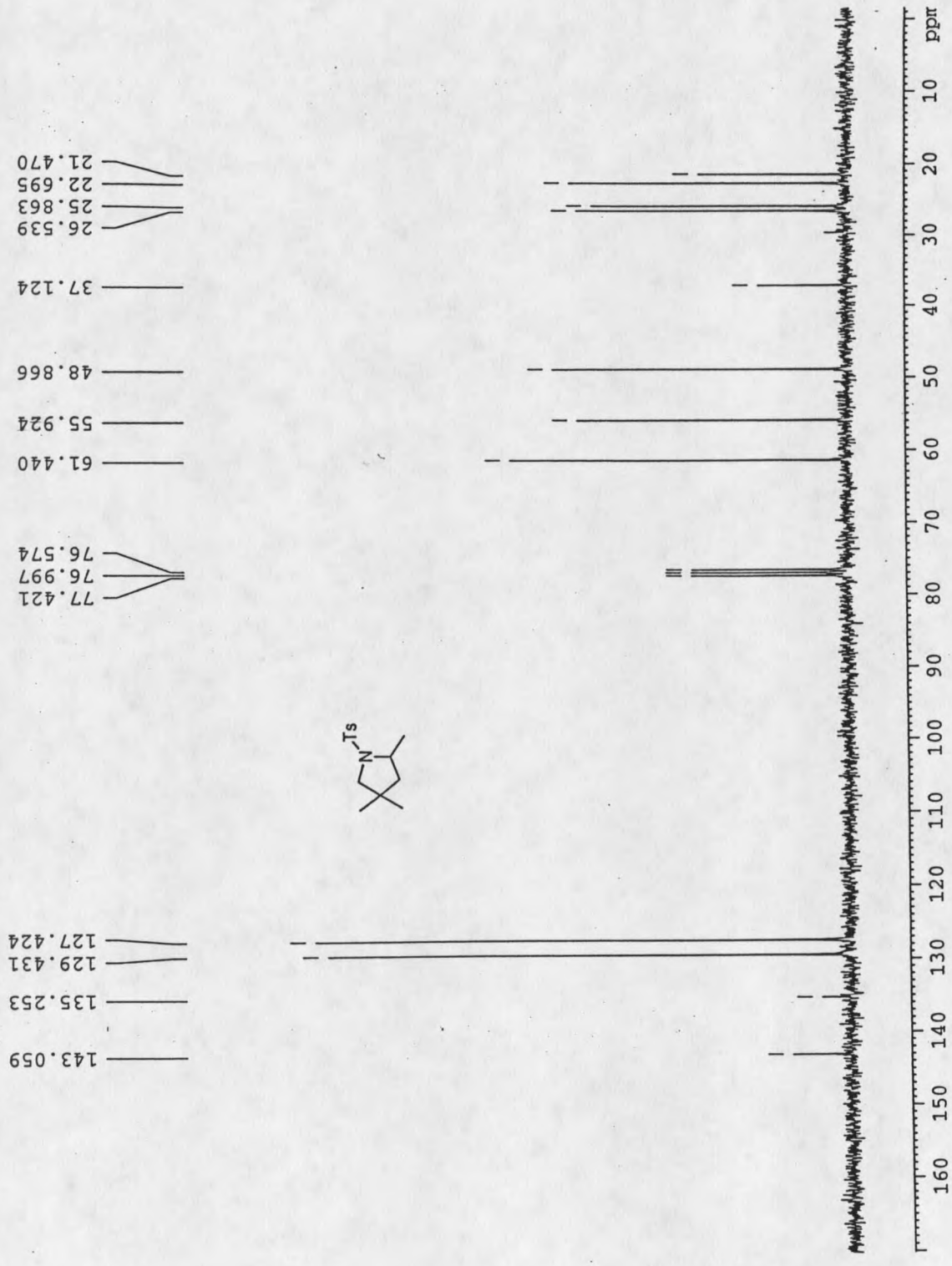


Figure 25. ^{13}C NMR Spectrum of *N*-(*p*-Tolylsulfonyl)-2,4,4-trimethylpyrrolidine (**Ts-16a**)

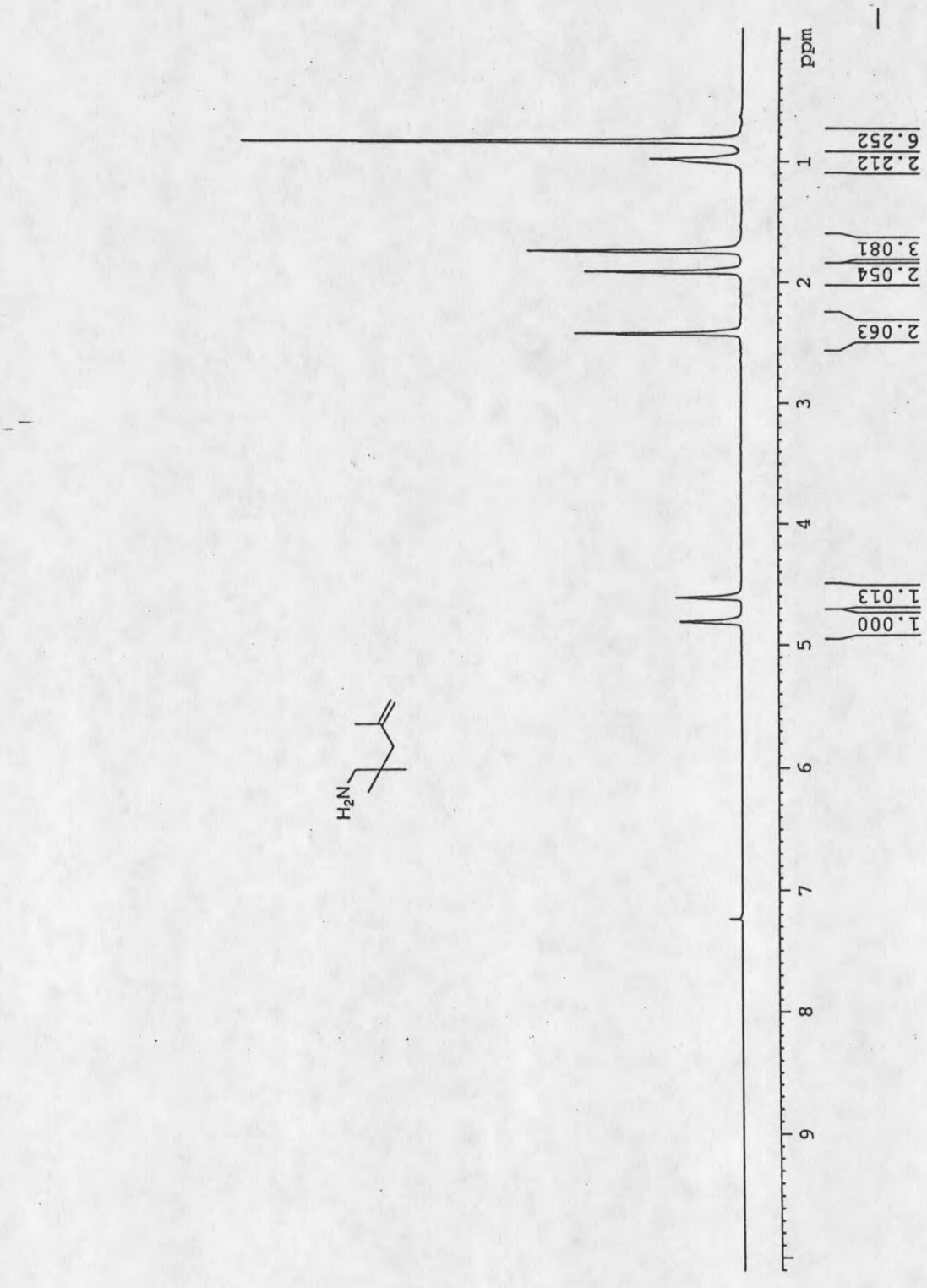


Figure 26. ^{1}H NMR Spectrum of 2,2,4-Trimethylaminopent-4-ene (**15b**)

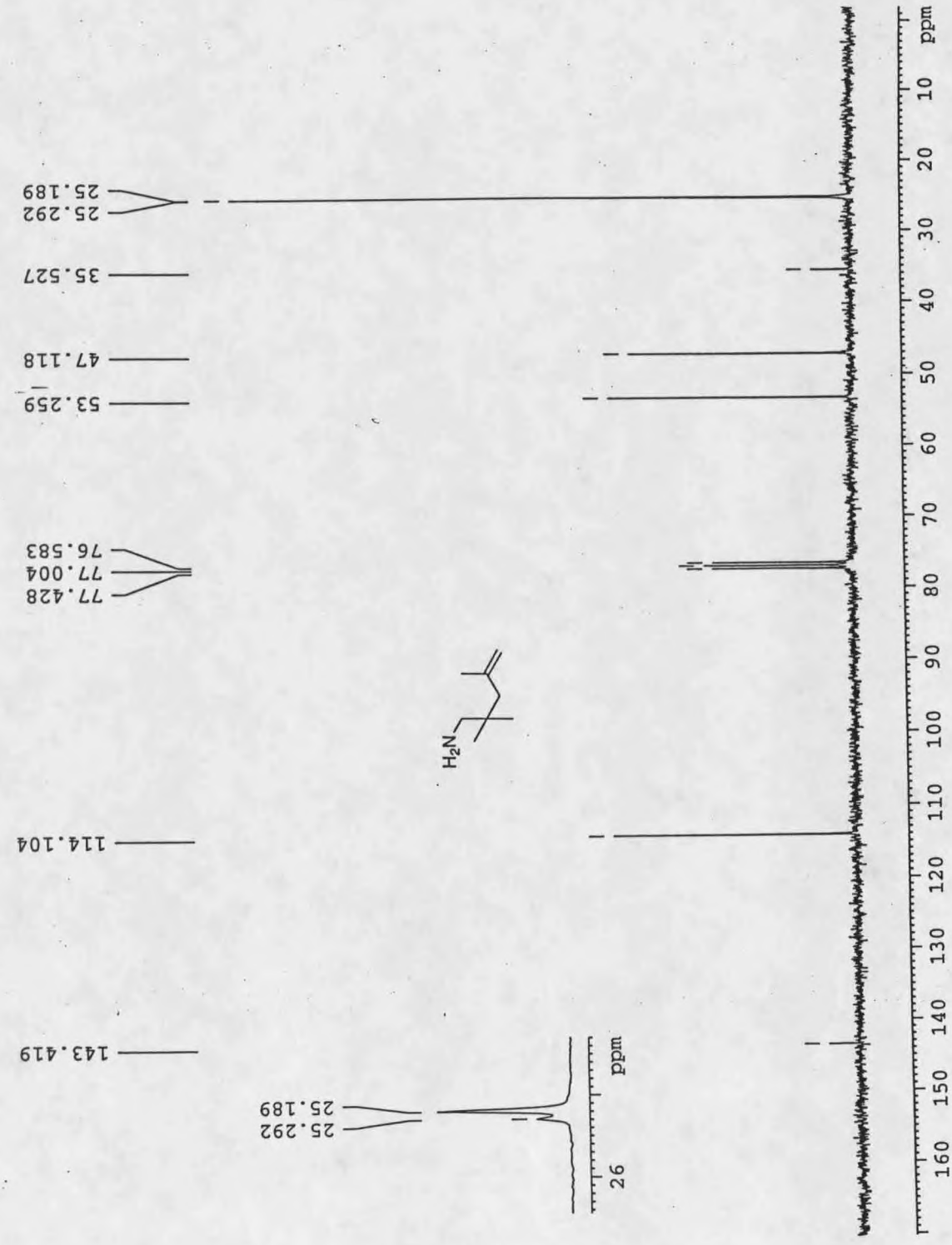


Figure 27. ^{13}C NMR Spectrum of 2,2,4-Trimethylaminopent-4-ene (**15b**)

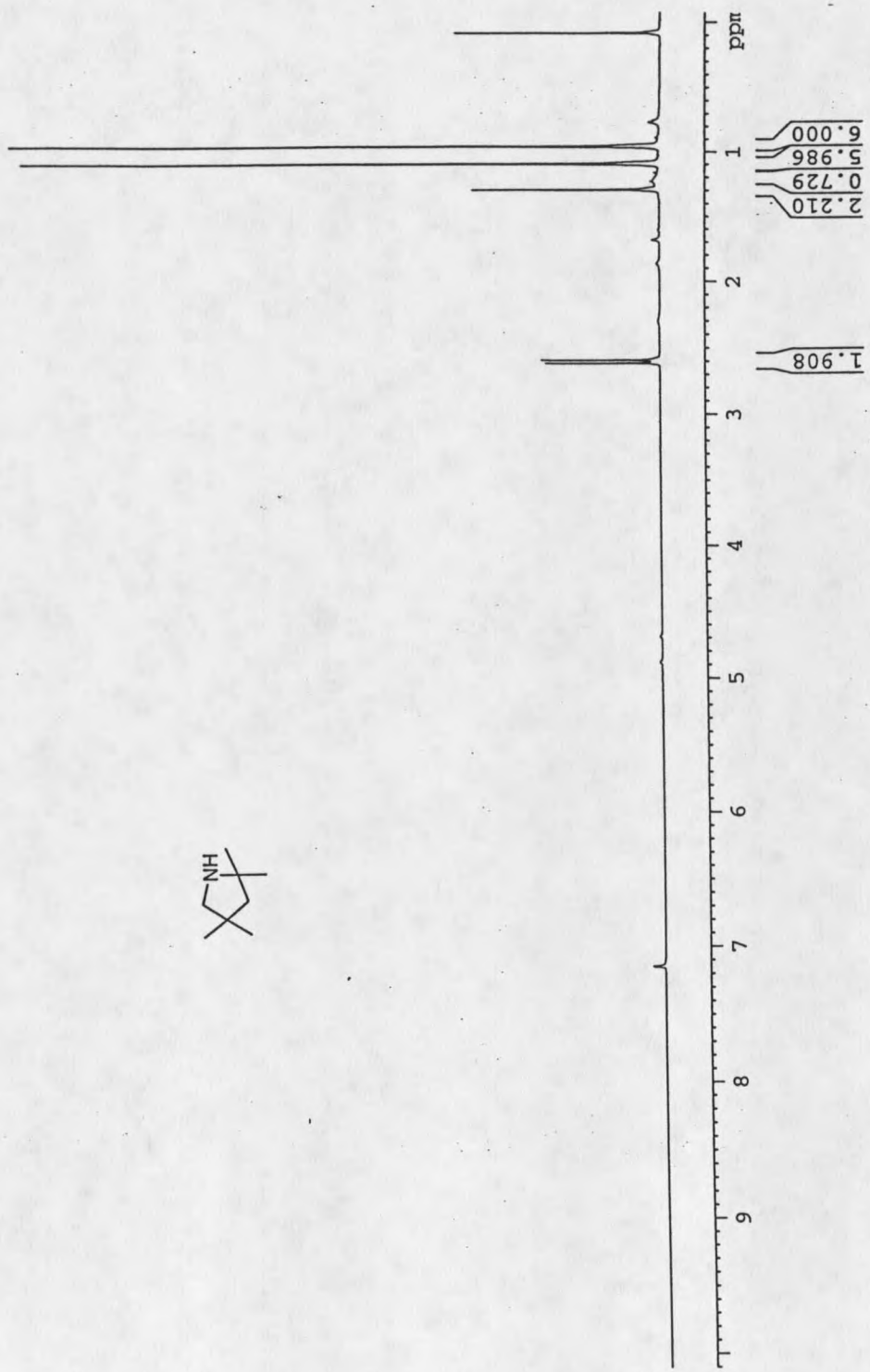


Figure 28. ^{1}H NMR Spectrum of 2,2,4,4-Tetramethylpyrrolidine (**16b**)

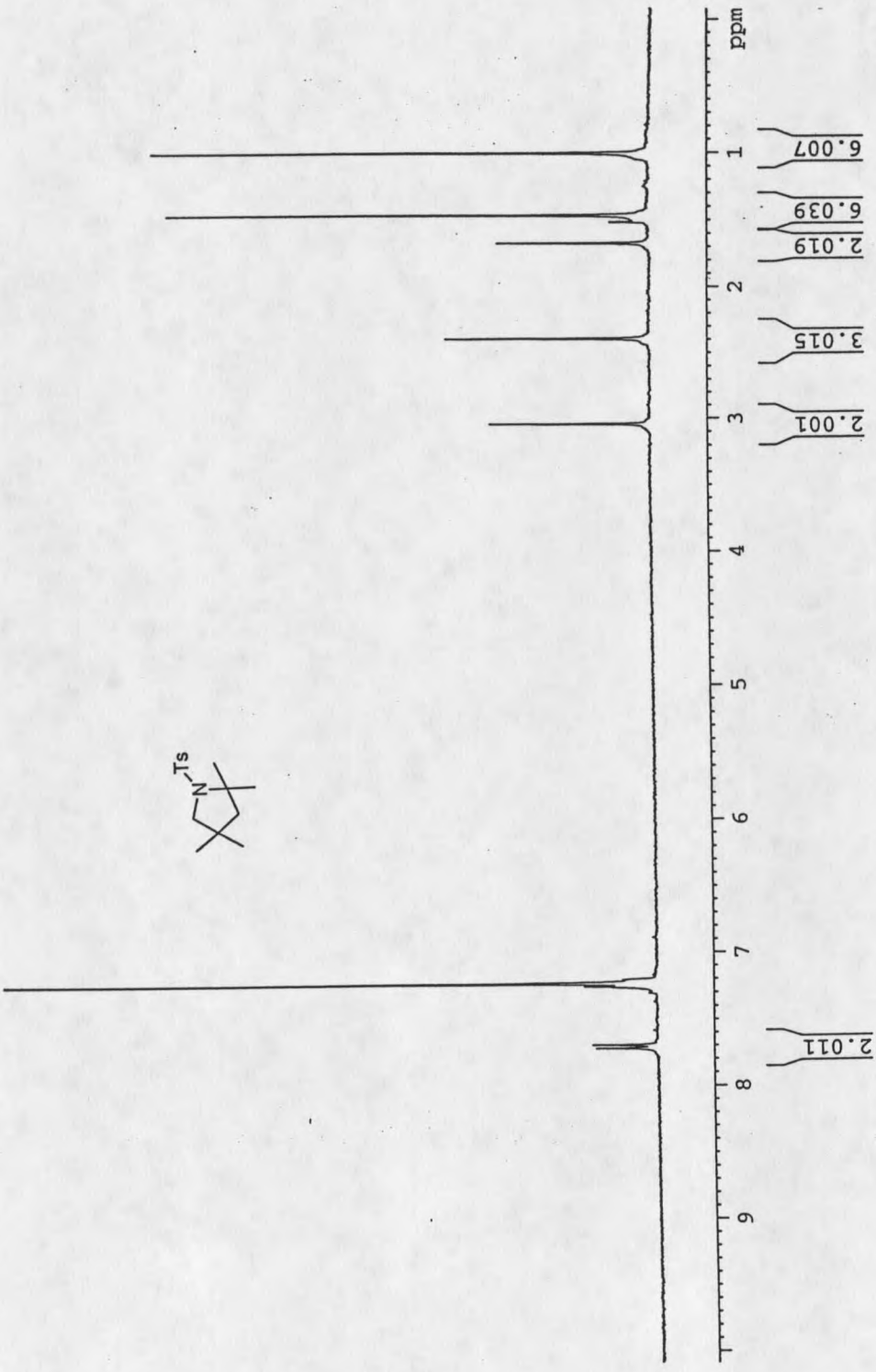


Figure 29. ^{1}H NMR Spectrum of *N*-(*p*-Tolylsulfonyl)-2,2,4,4-tetramethylpyrrolidine (**Ts-16b**)

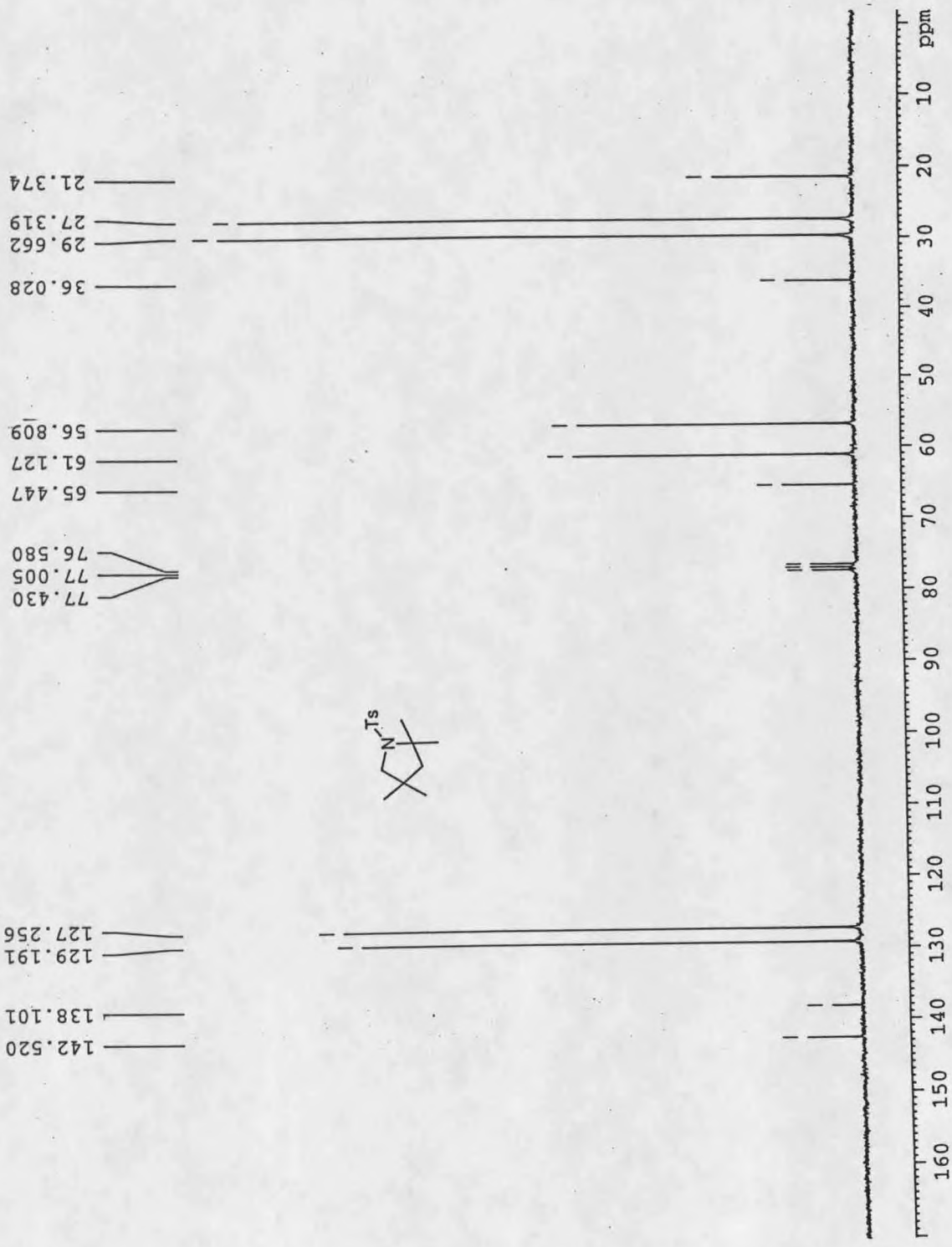


Figure 30. ^{13}C NMR Spectrum of *N*-(*p*-Tolylsulfonyl)-2,2,4,4-tetramethylpyrrolidine (**Ts-16b**)

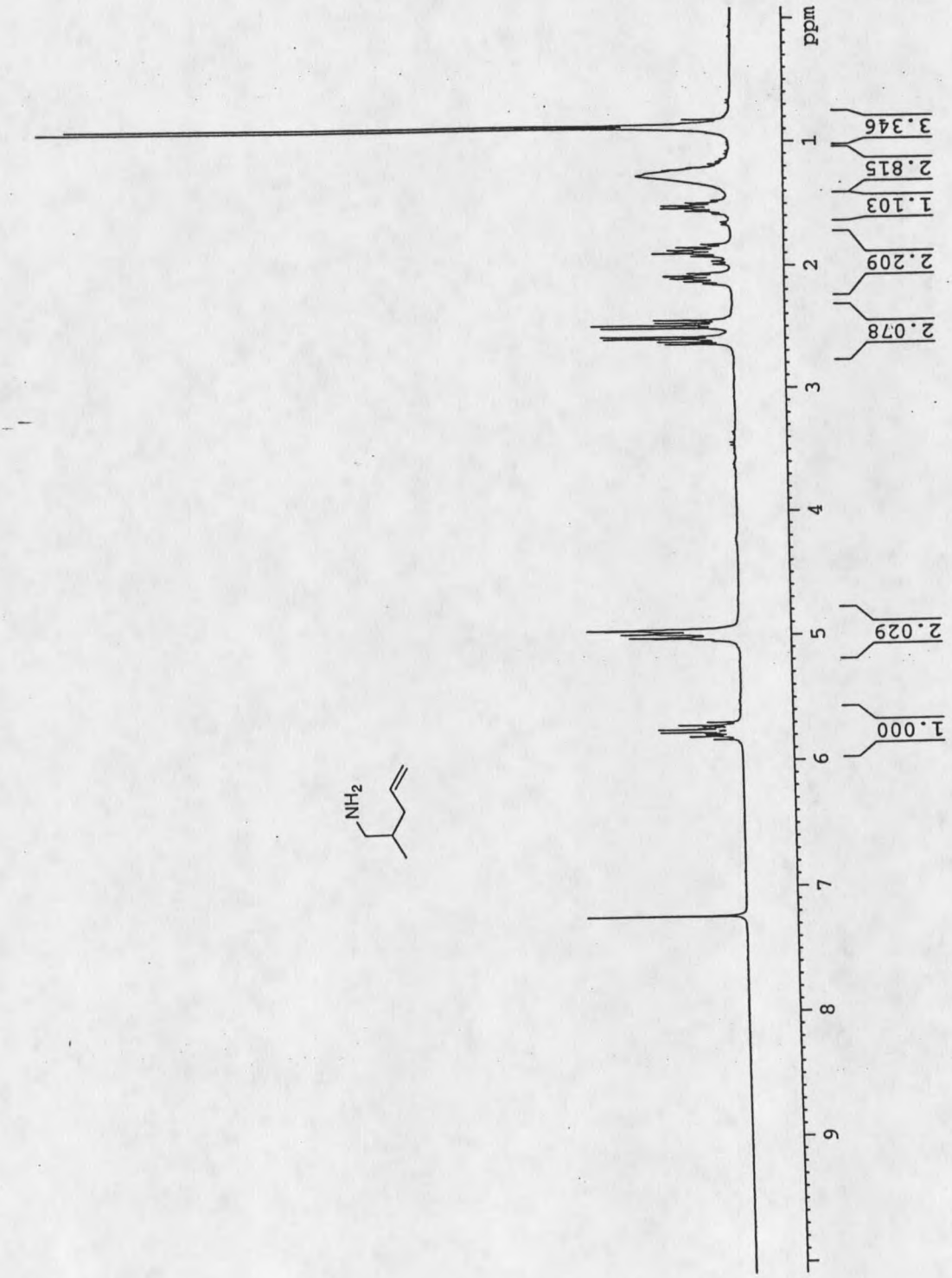


Figure 31. ^{1}H NMR Spectrum of 2-Methylaminohex-4-ene (**15c**)

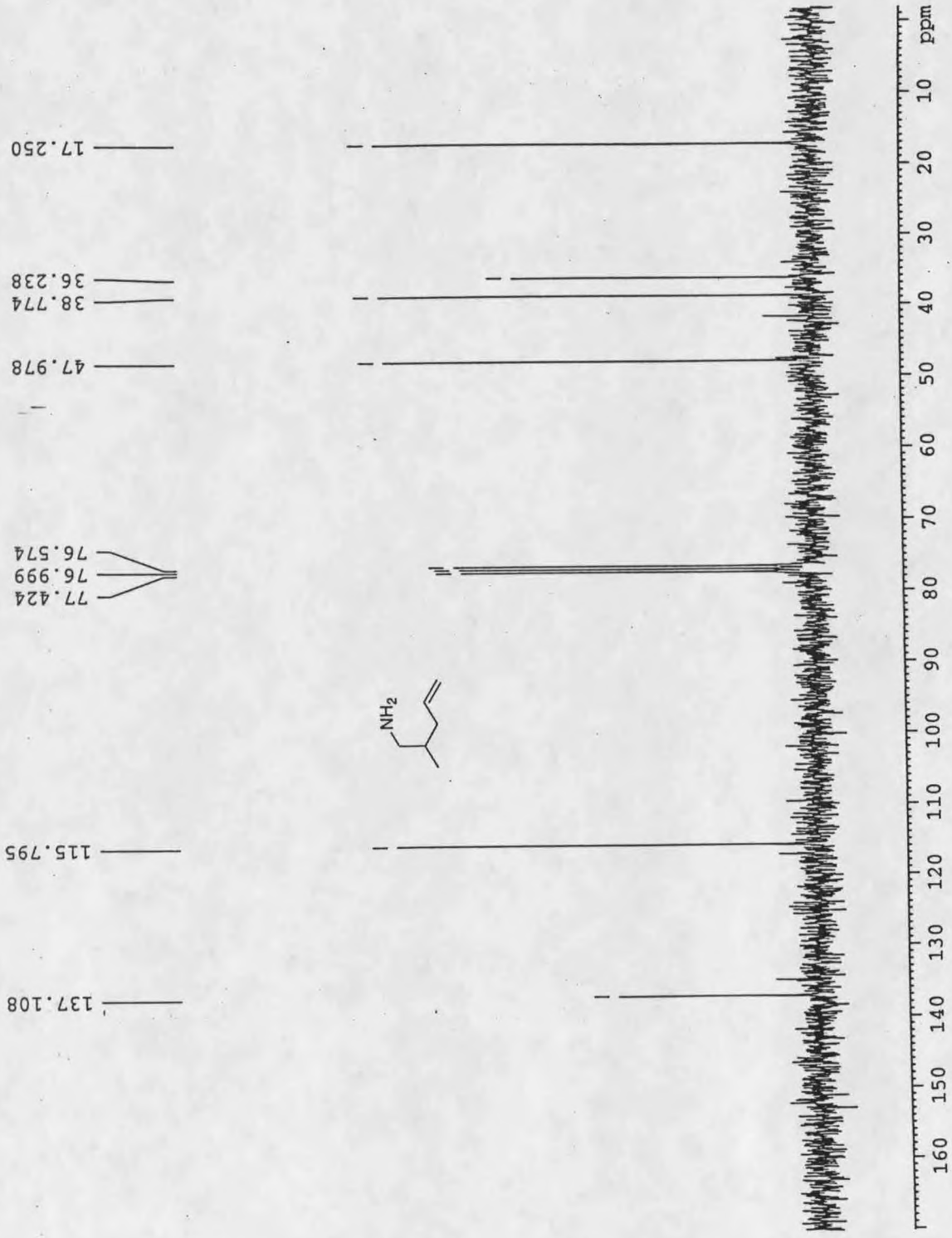


Figure 32. ^{13}C NMR Spectrum of 2-Methylaminohex-4-ene (**15c**)

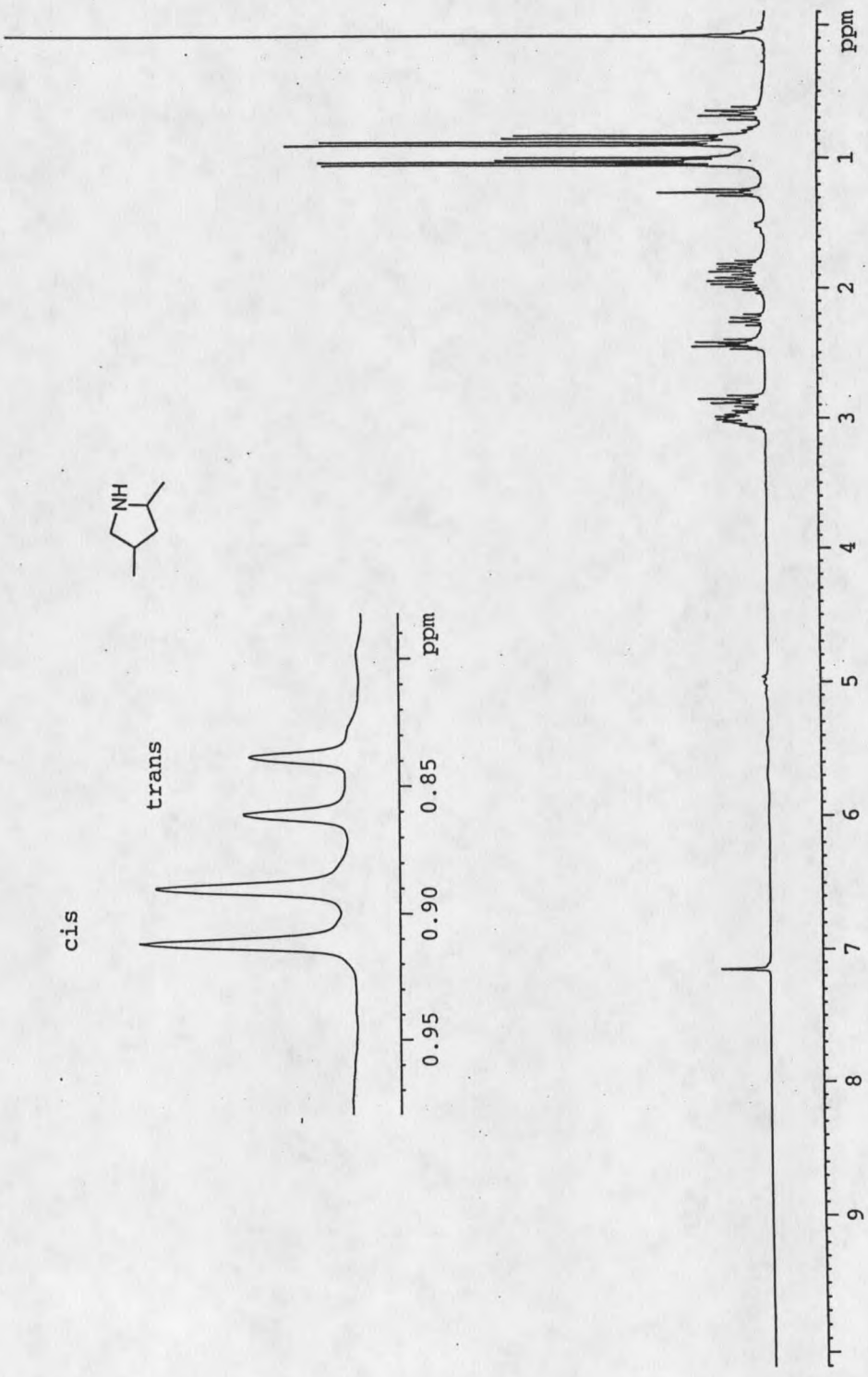


Figure 33. ^{1}H NMR Spectrum of 2,4-Dimethylpyrrolidine (**17c**,**18c**)

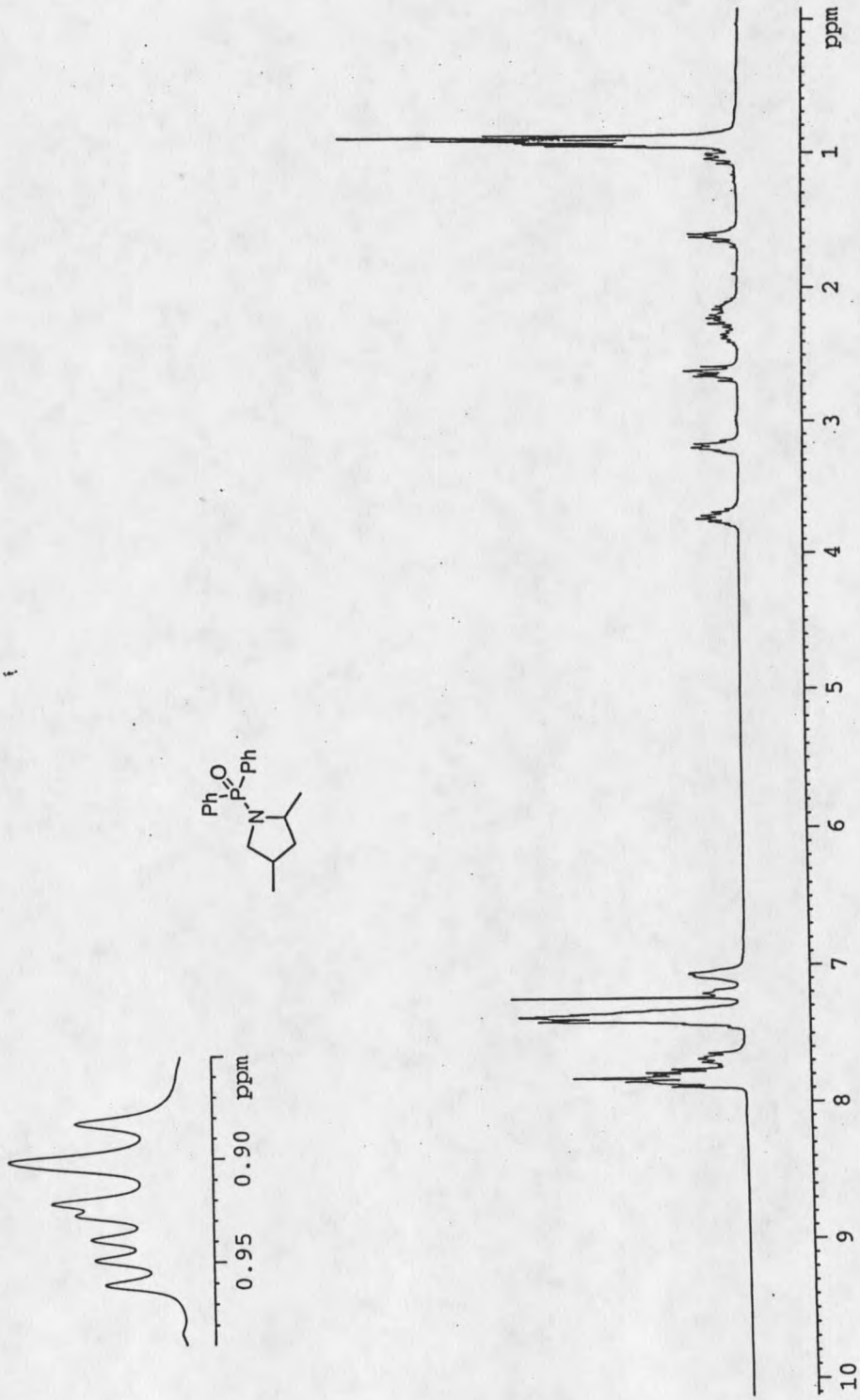


Figure 34. ^{1}H NMR Spectrum of *N*-Diphenylphosphinoyl-2,4-dimethylpyrrolidine (**Ph_2PO-17c**, **Ph_2PO-18c**)

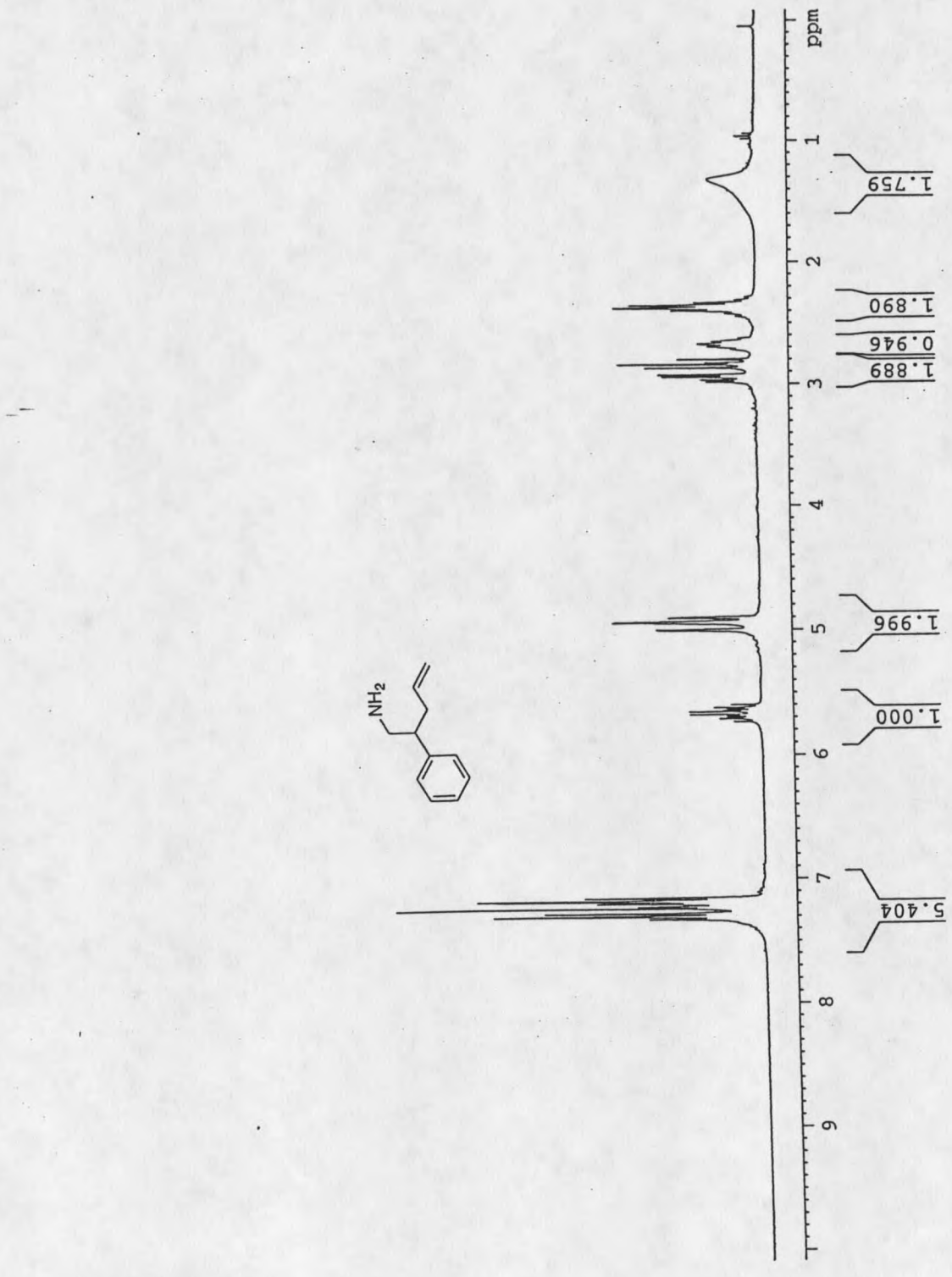


Figure 35. ^{1}H NMR Spectrum of 2-Phenylaminopent-4-ene (**15d**)

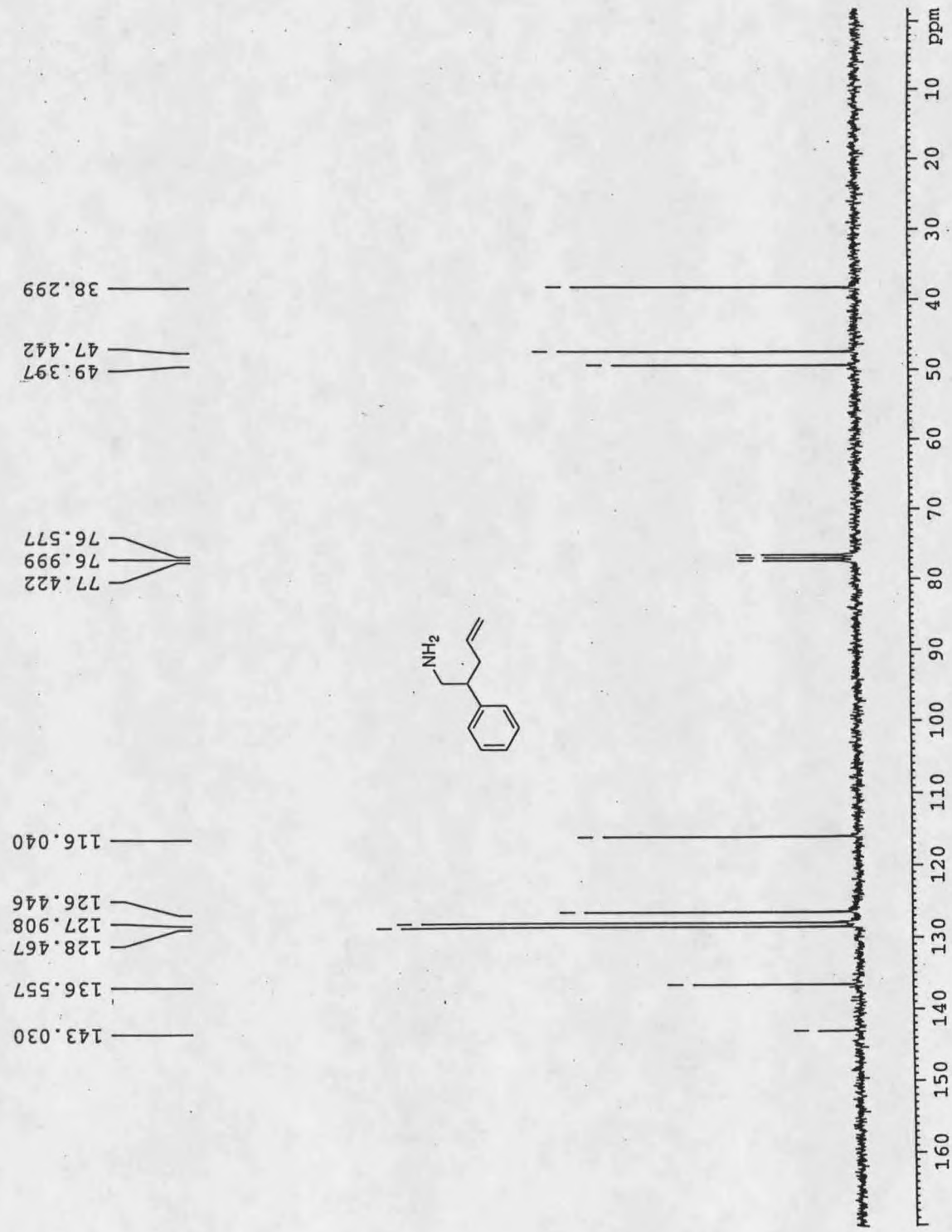


Figure 36. ^{13}C NMR Spectrum of 2-Phenylaminopent-4-ene (**15d**)

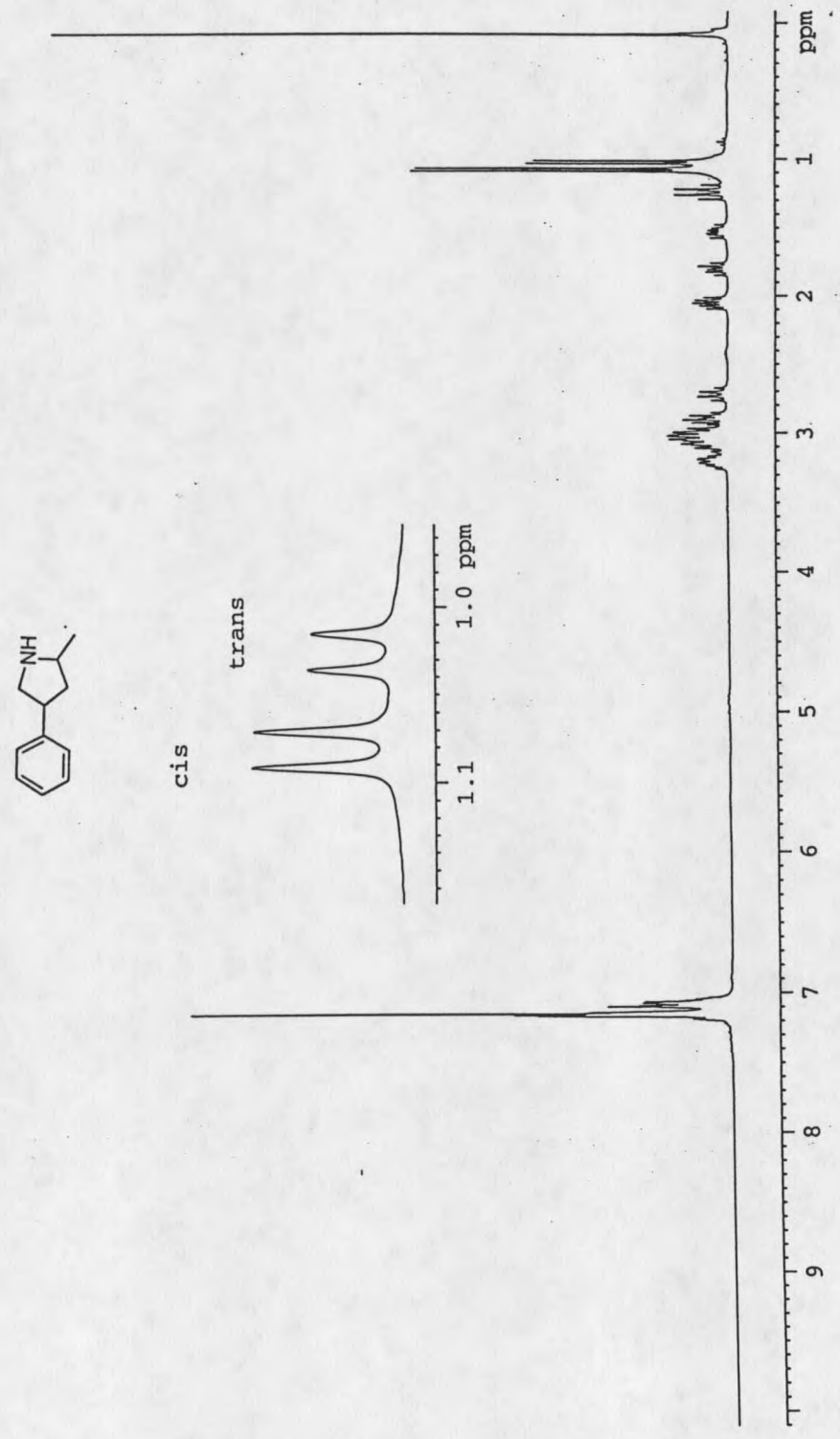


Figure 37. ^{1}H NMR Spectrum of 2-Methyl-4-phenylpyrrolidine (**17d**,**18d**)

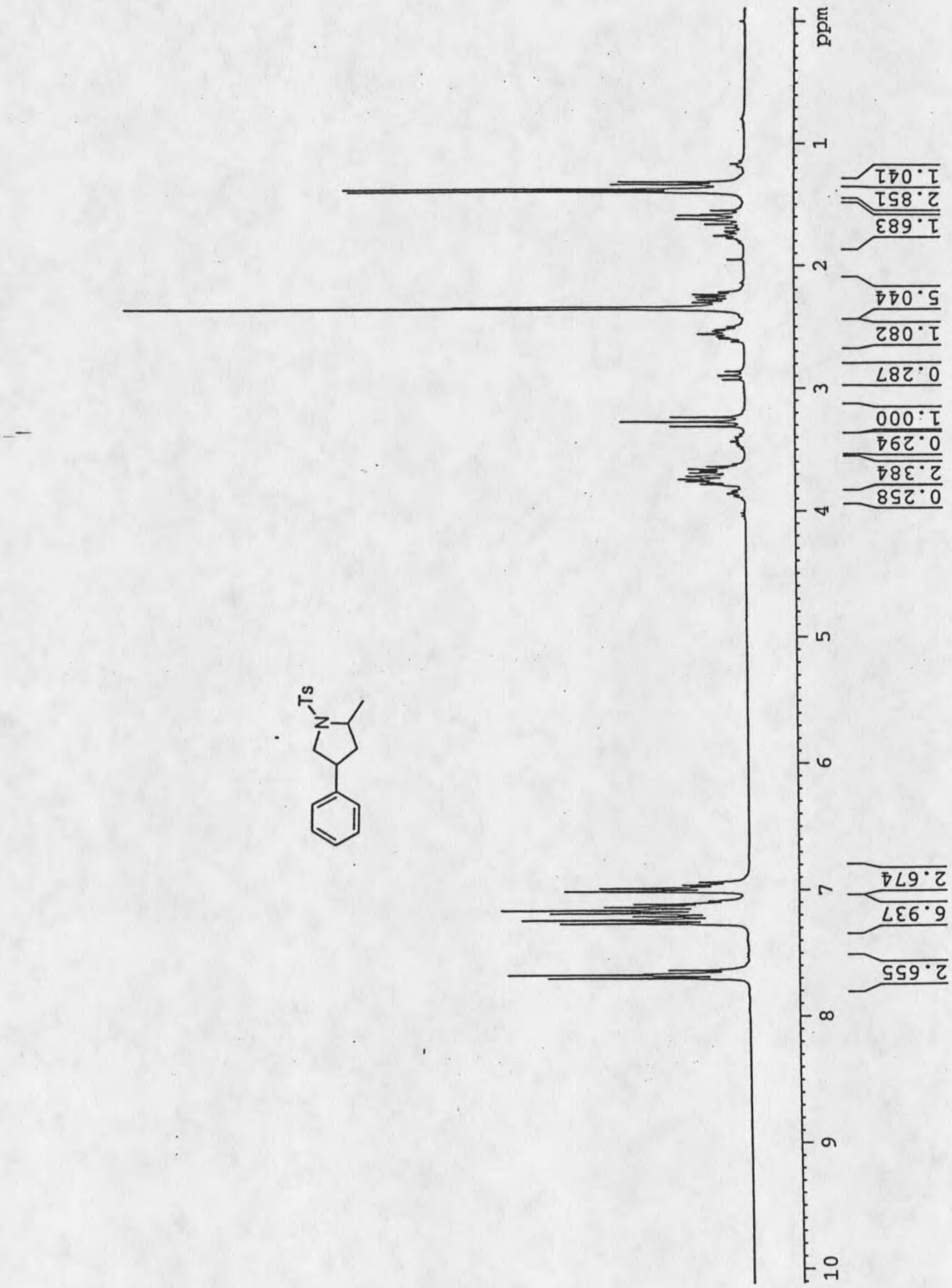


Figure 38. ^{1}H NMR Spectrum of *N*-(*p*-Tolylsulfonyl)-2-methyl-4-phenylpyrrolidine (**Ts-17d**,**Ts-18d**)

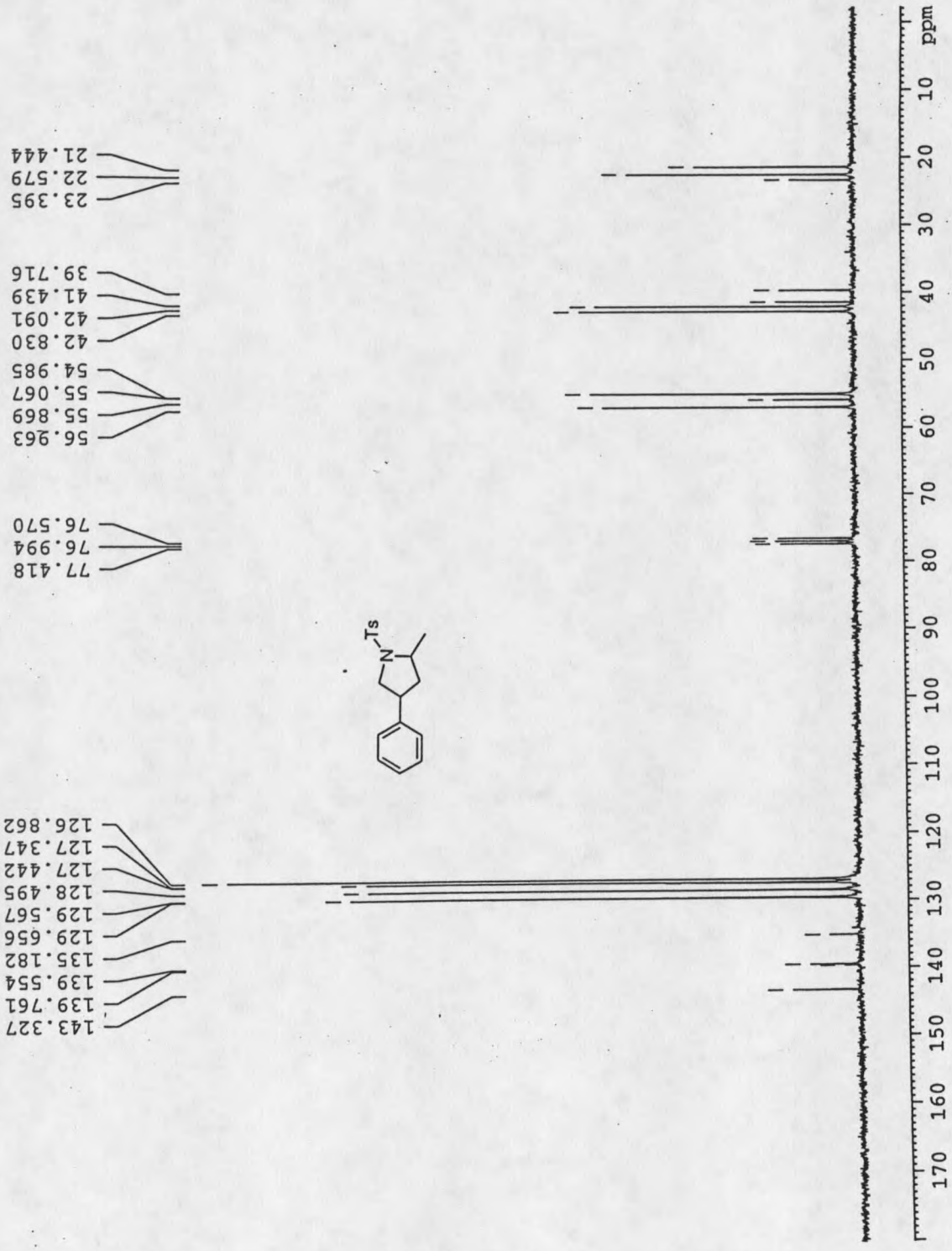


Figure 39. ^{1}3C NMR Spectrum of *N*-(*p*-Tolylsulfonyl)-2-methyl-4-phenylpyrrolidine (**Ts-17d,Ts-18d**)

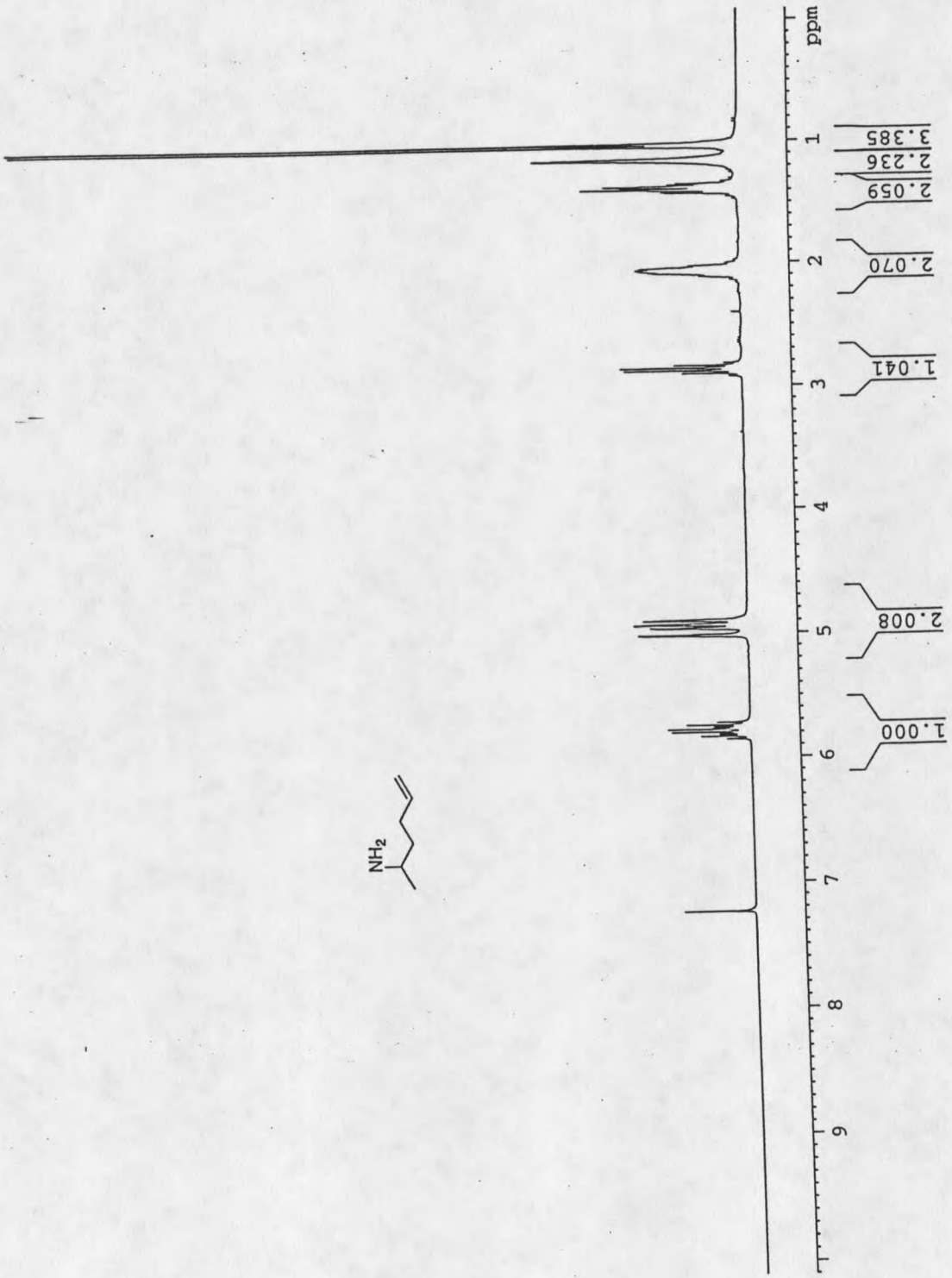


Figure 40. ^{1}H NMR Spectrum of 2-Aminohex-5-ene (**15e**)

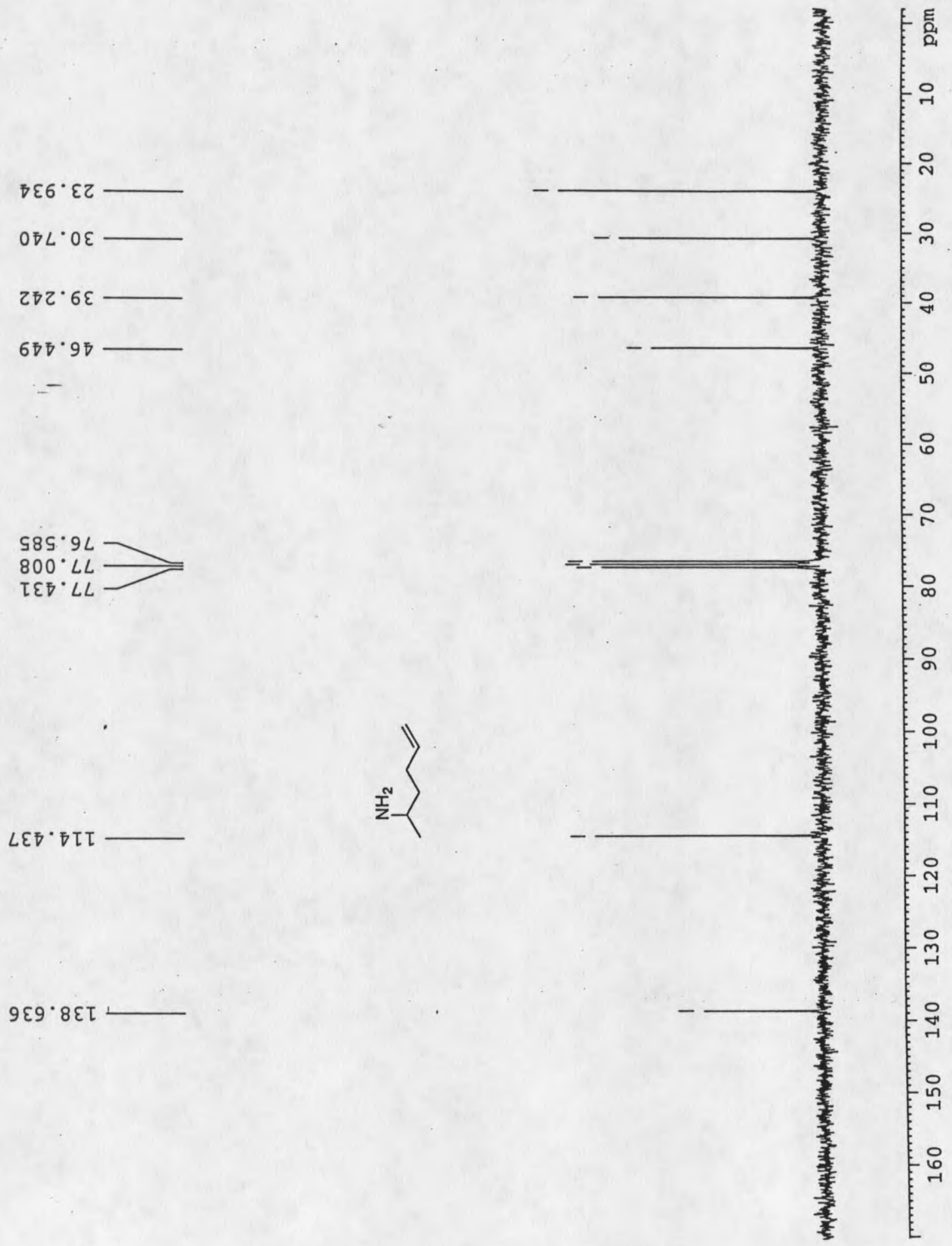


Figure 41. ^{13}C NMR Spectrum of 2-Aminohex-5-ene (**15e**)

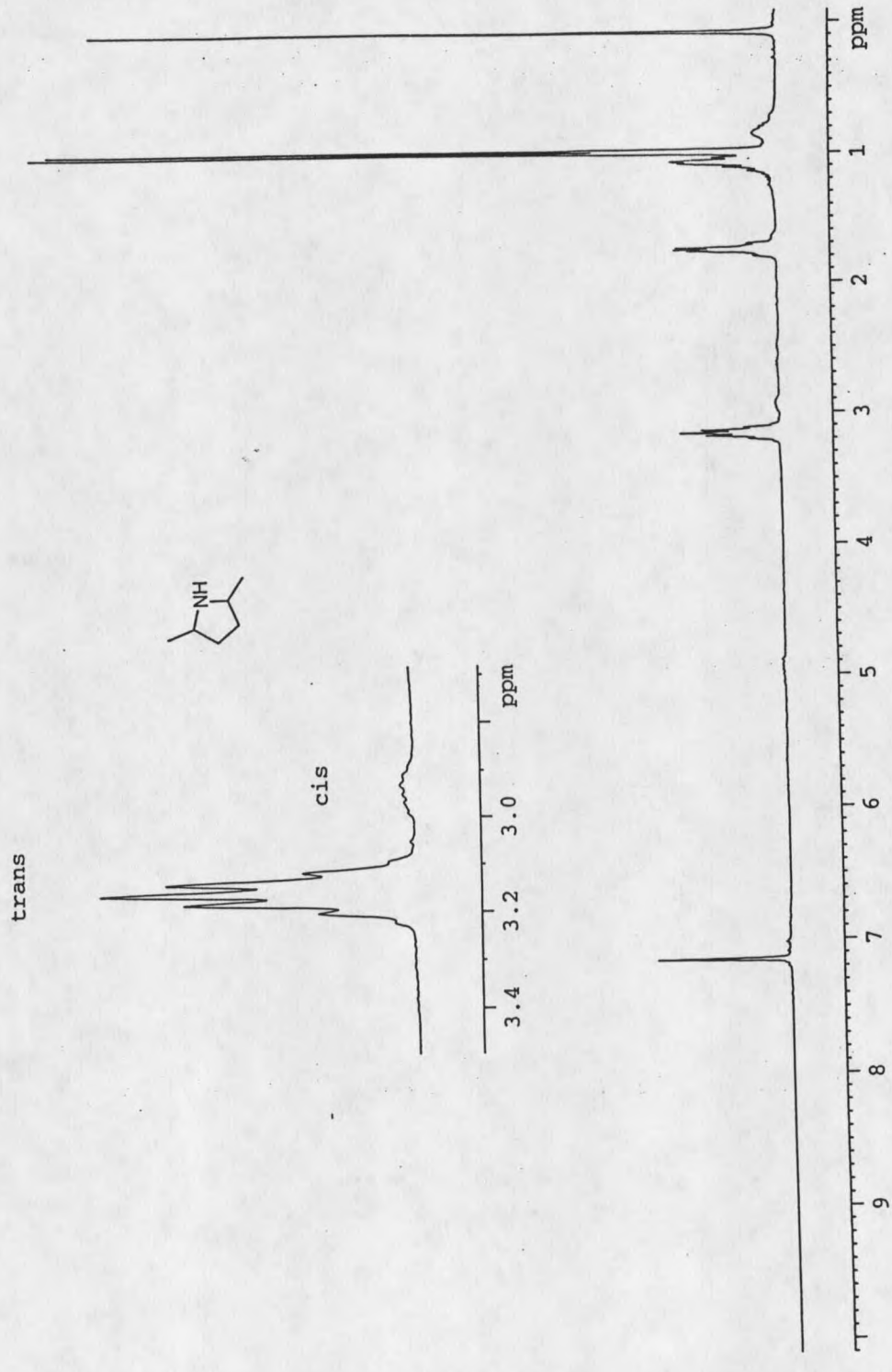


Figure 42. ^{1}H NMR Spectrum of 2,5-Dimethylpyrrolidine (**17e**,**18e**)

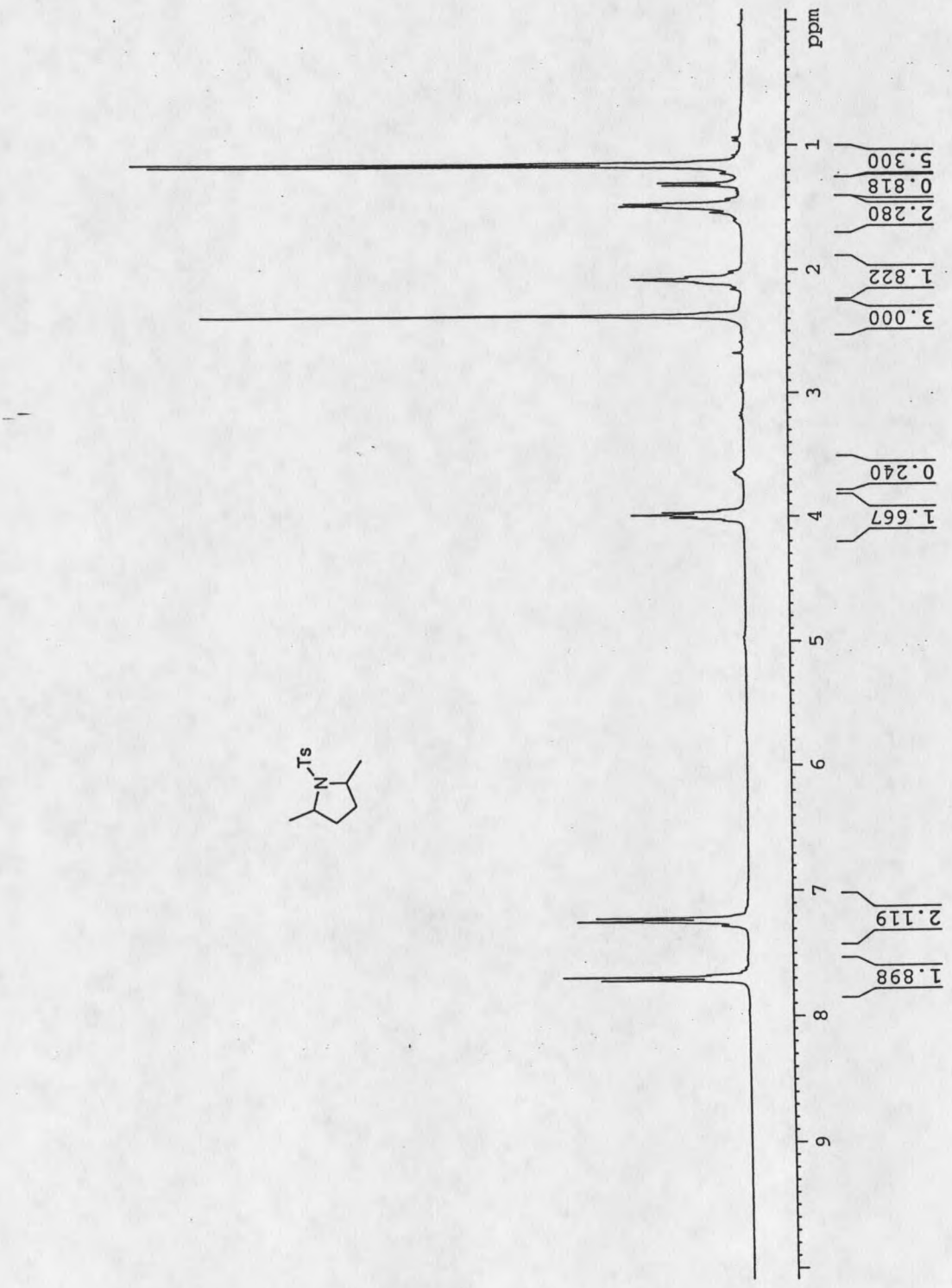


Figure 43. ^{1}H NMR Spectrum of *N*-(*p*-Tolylsulfonyl)-2,5-dimethylpyrrolidine (**Ts-17e, Ts-18e**)

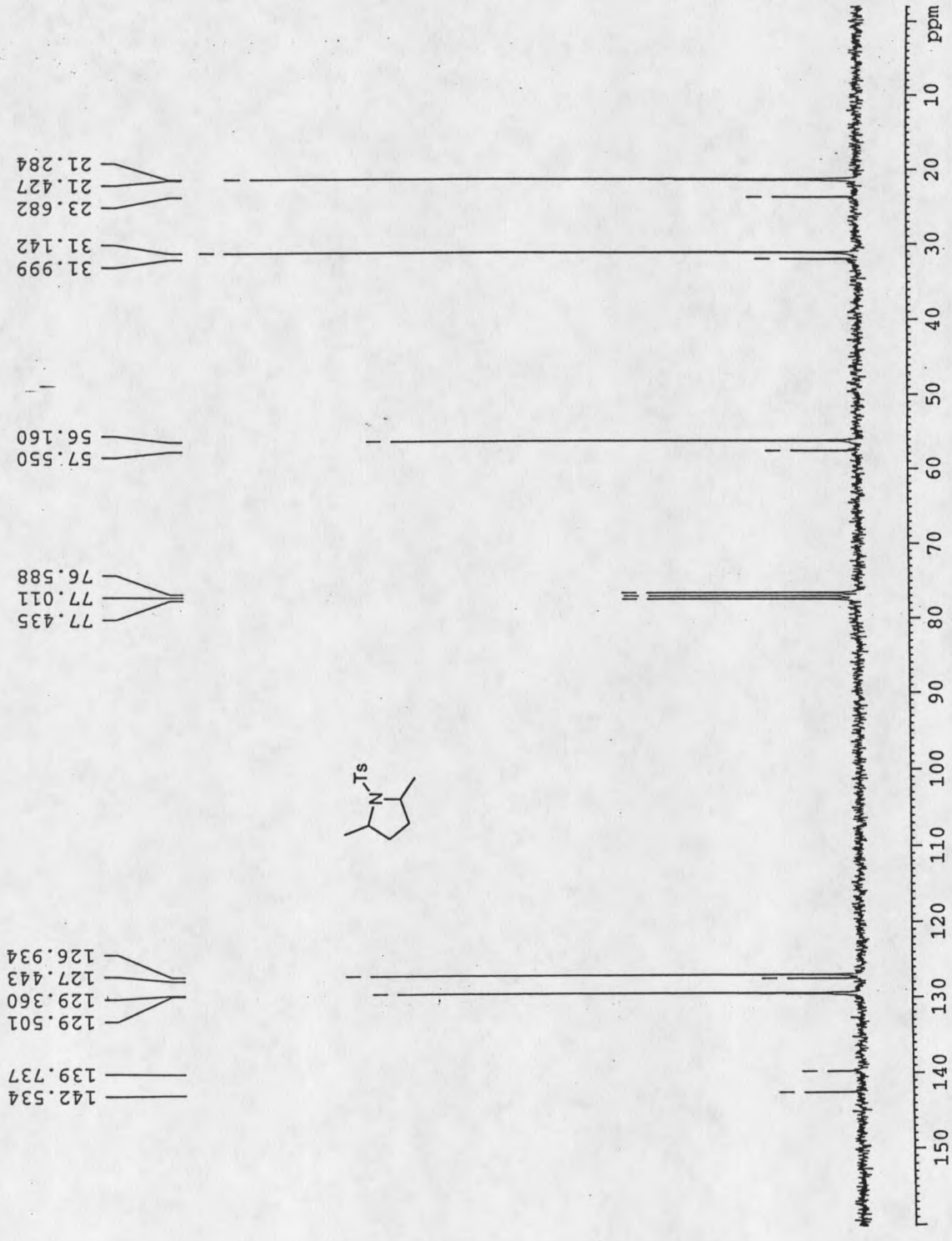


Figure 44. ^{1}H NMR Spectrum of *N*-(*p*-Tolylsulfonyl)-2,5-dimethylpyrrolidine (**Ts-17e, Ts-18e**)

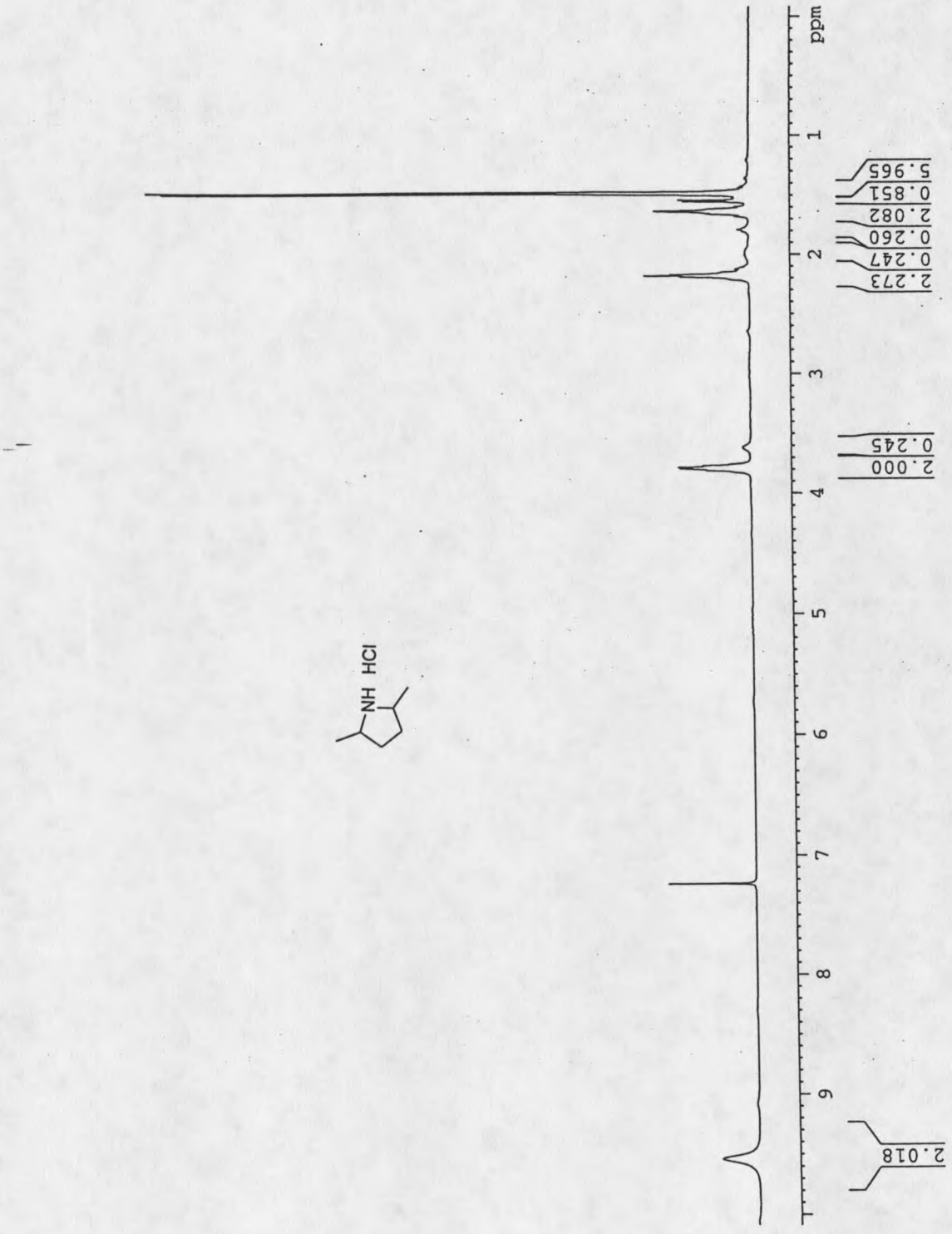


Figure 45. ^{1}H NMR Spectrum of 2,5-Dimethylpyrrolidine hydrochloride (**HCl·17e**, **HCl·18e**)

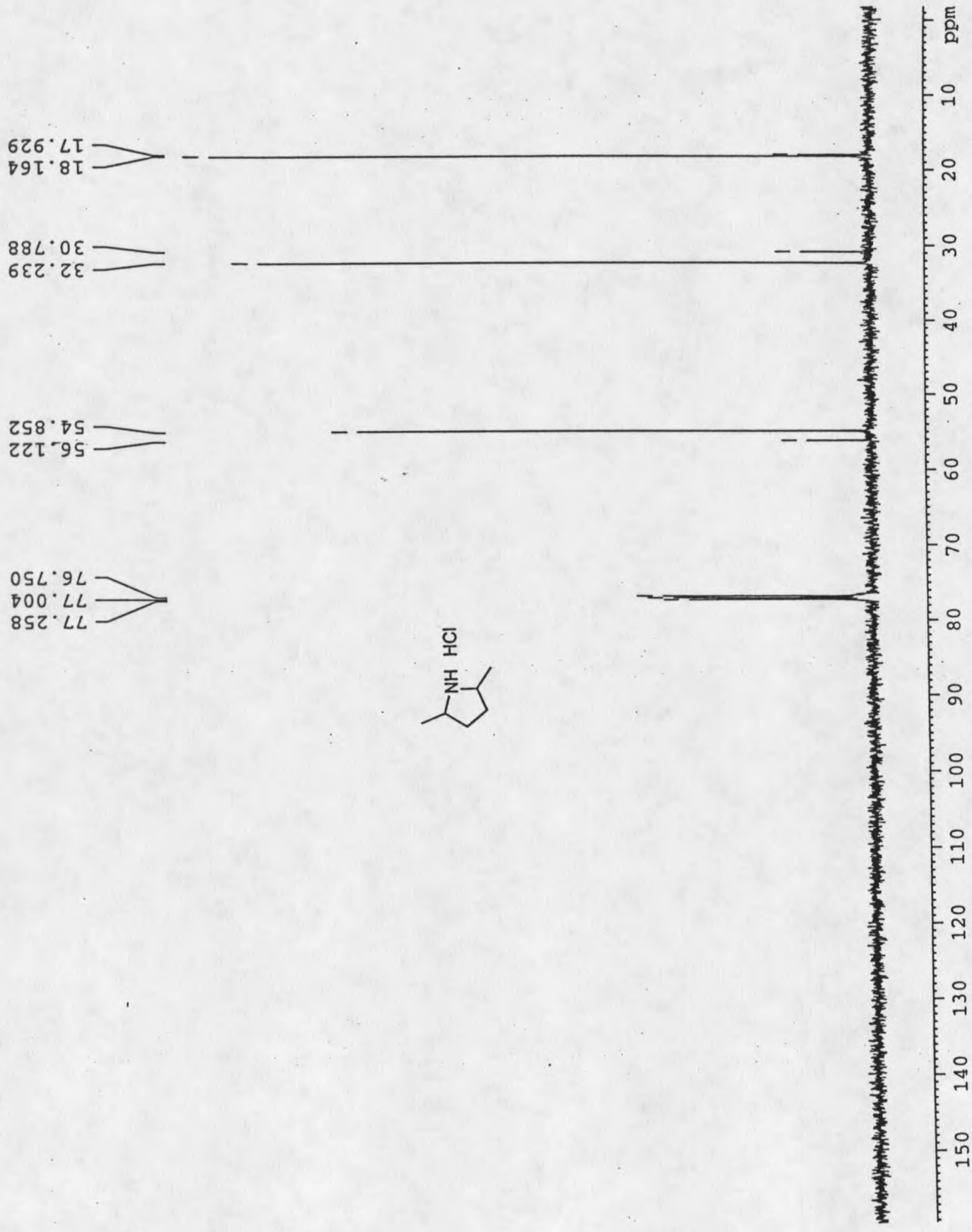


Figure 46. ^{13}C NMR Spectrum of 2,5-Dimethylpyrrolidine hydrochloride (**HCl·17e**, **HCl·18e**)

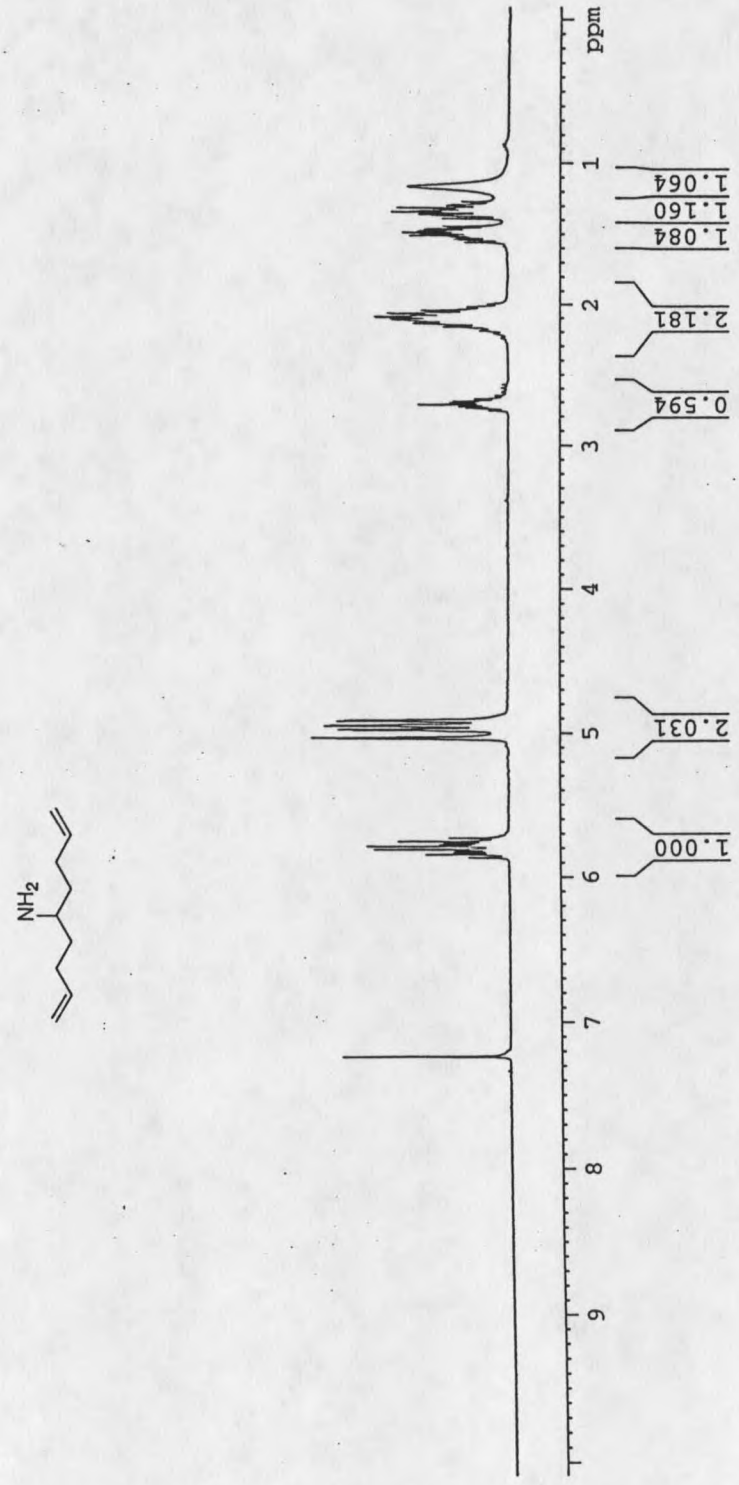


Figure 47. ^{1}H NMR Spectrum of 1-But-3-enylpent-4-enylamine (**15f**)

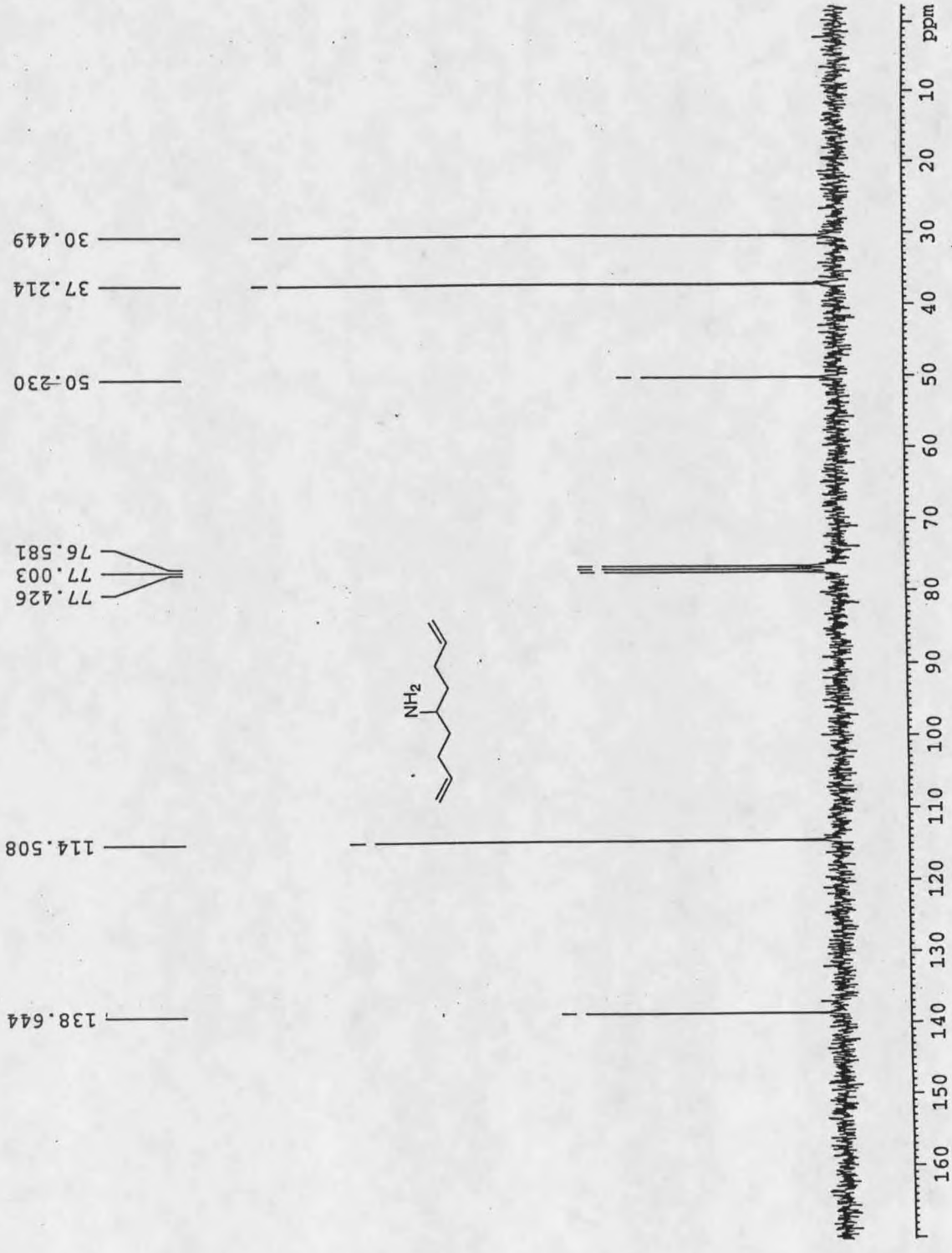


Figure 48. ^{13}C NMR Spectrum of 1-But-3-enylpent-4-enylamine (**15f**)

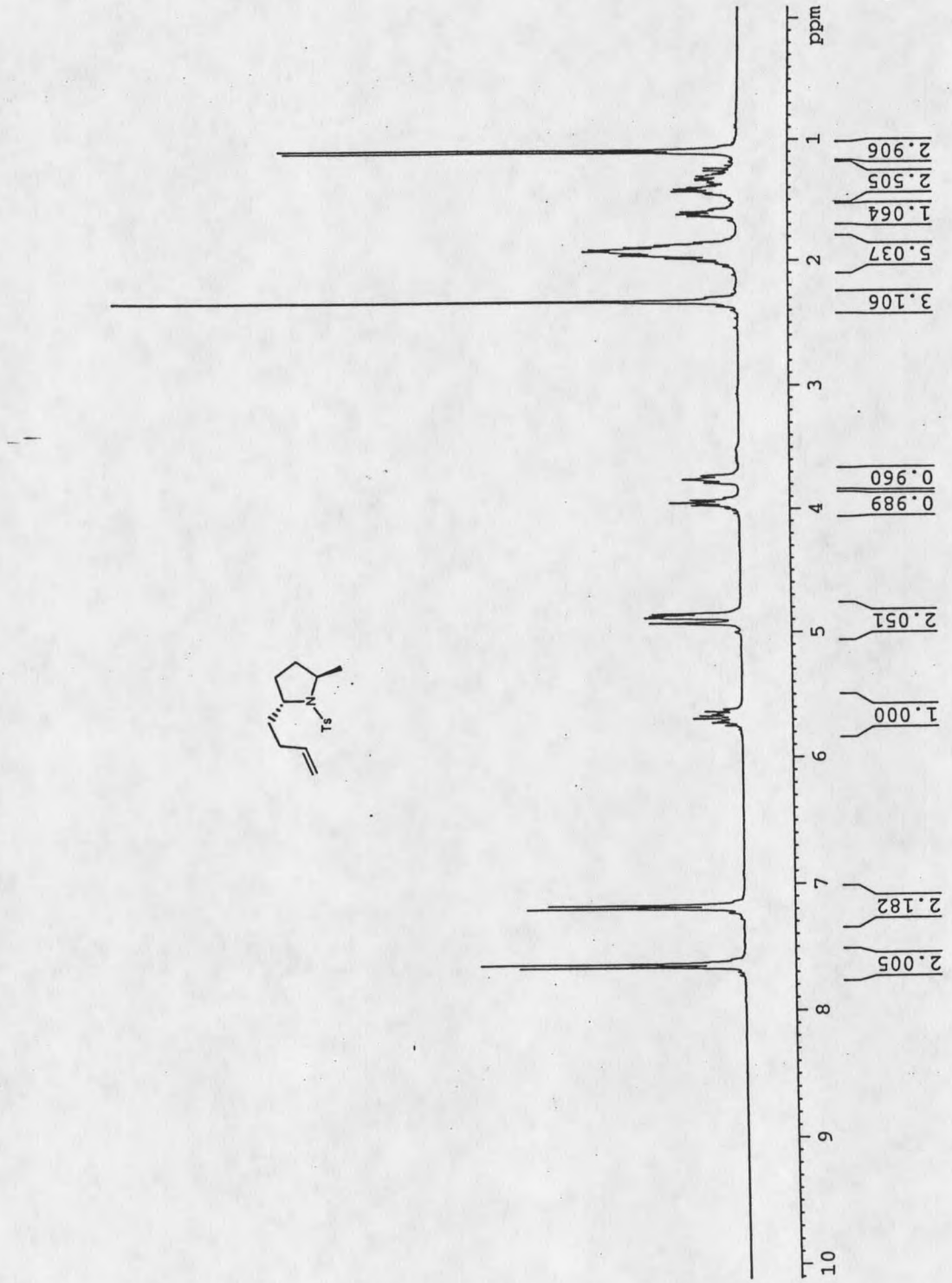


Figure 49. ^{1}H NMR Spectrum of *N*-(*p*-Tolylsulfonyl)-2-but-3-enyl-5-methylpyrrolidine (**20**)

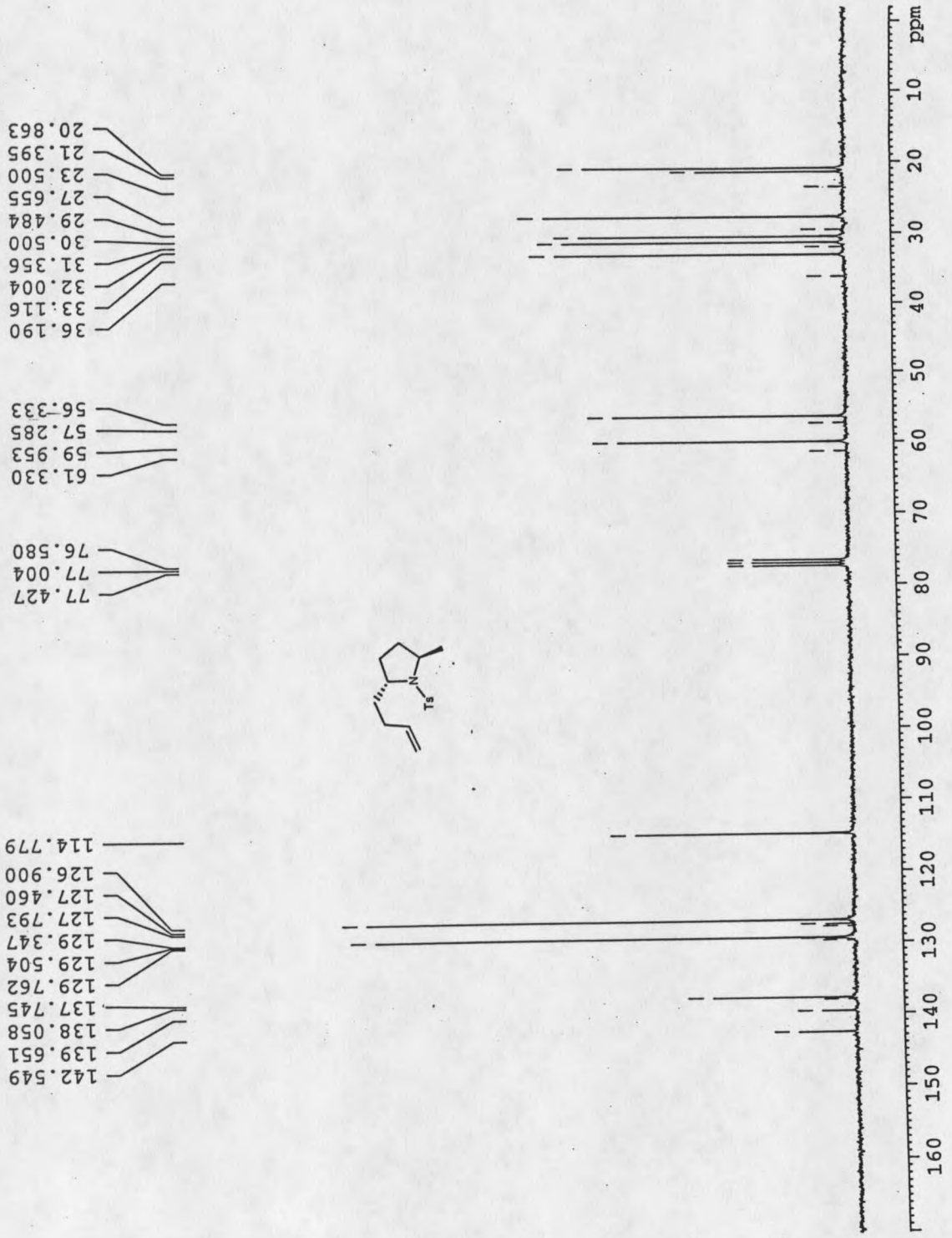


Figure 50. ^{13}C NMR Spectrum of *N*-(*p*-Tolylsulfonyl)-2-but-3-enyl-5-methylpyrrolidine (**20**)

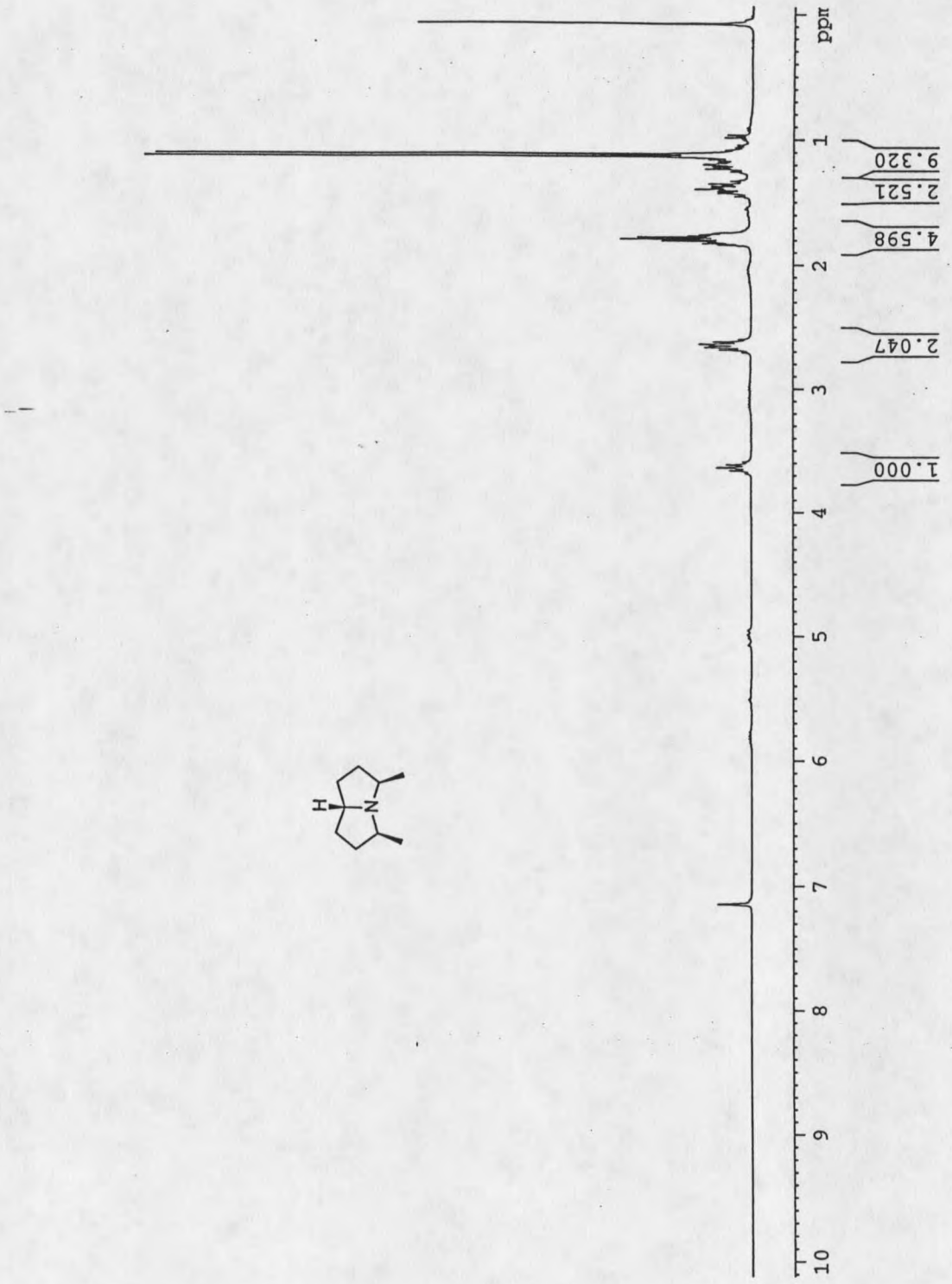


Figure 51. ^{1}H NMR Spectrum of 3,5-Dimethylhexahydropyrrolizine (**21**)

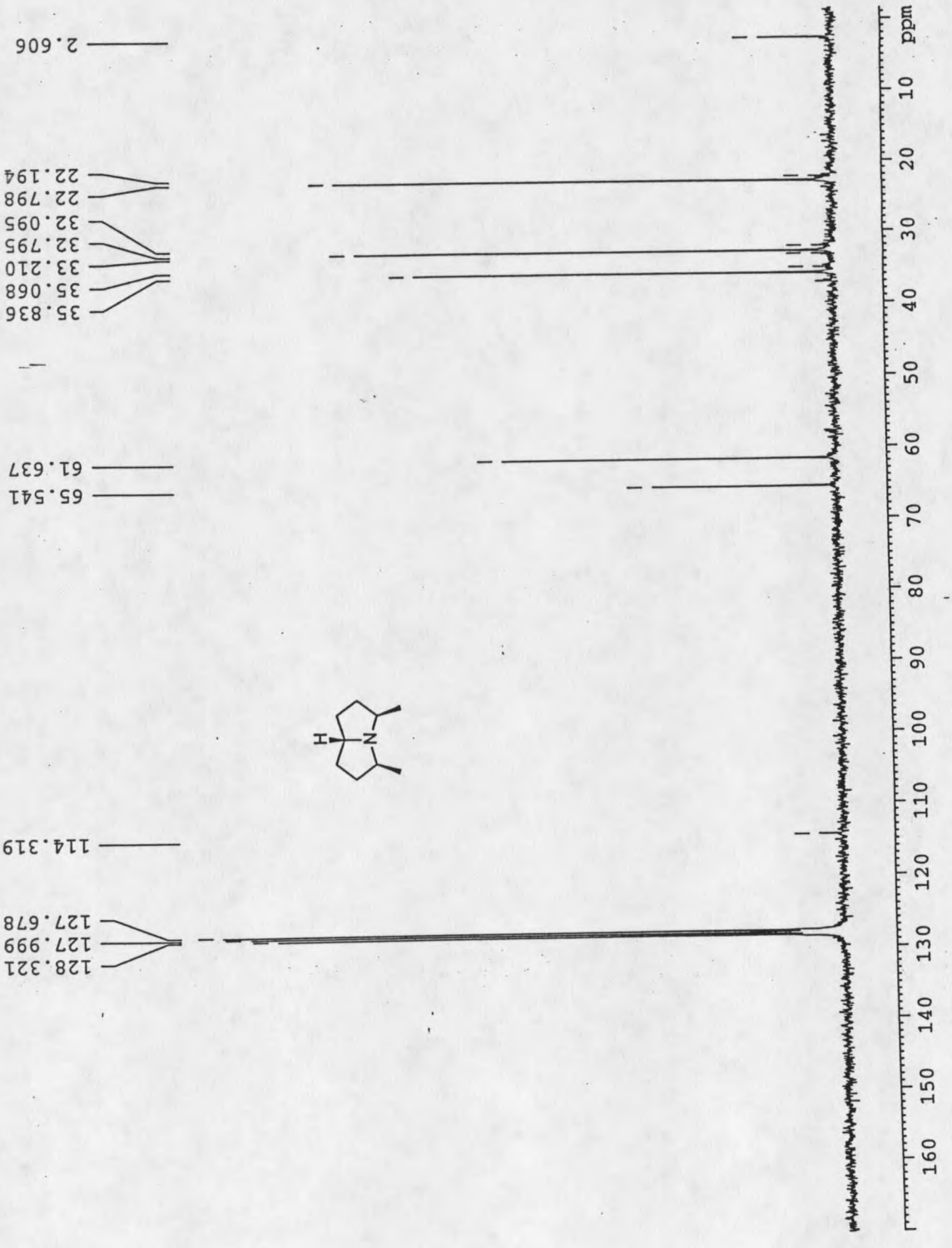


Figure 52. ^{1}3C NMR Spectrum of 3,5-Dimethylhexahydropyrrolizine (**21**)

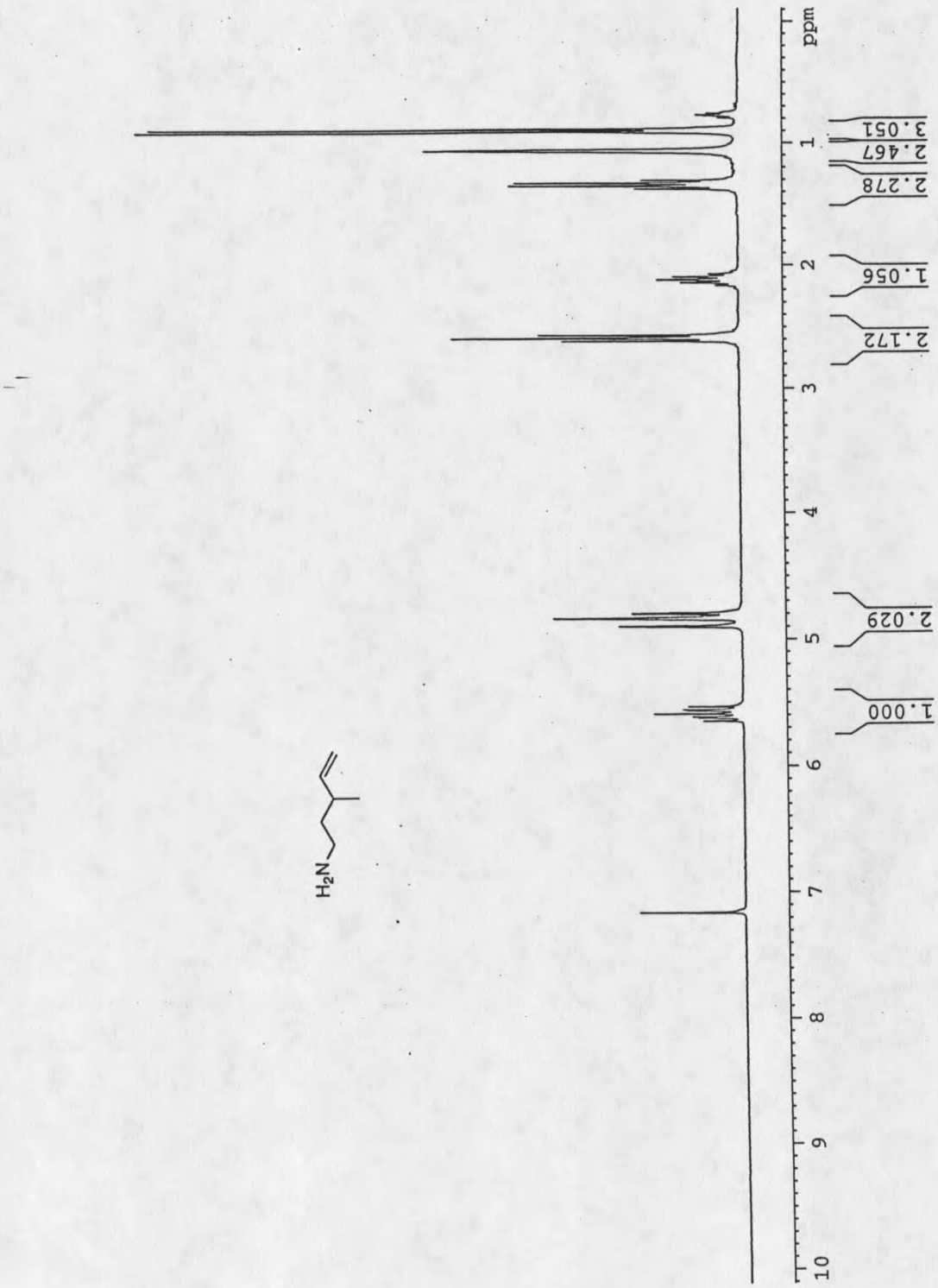


Figure 53. ^{1}H NMR Spectrum of 3-Methylaminohex-4-ene (**44**)

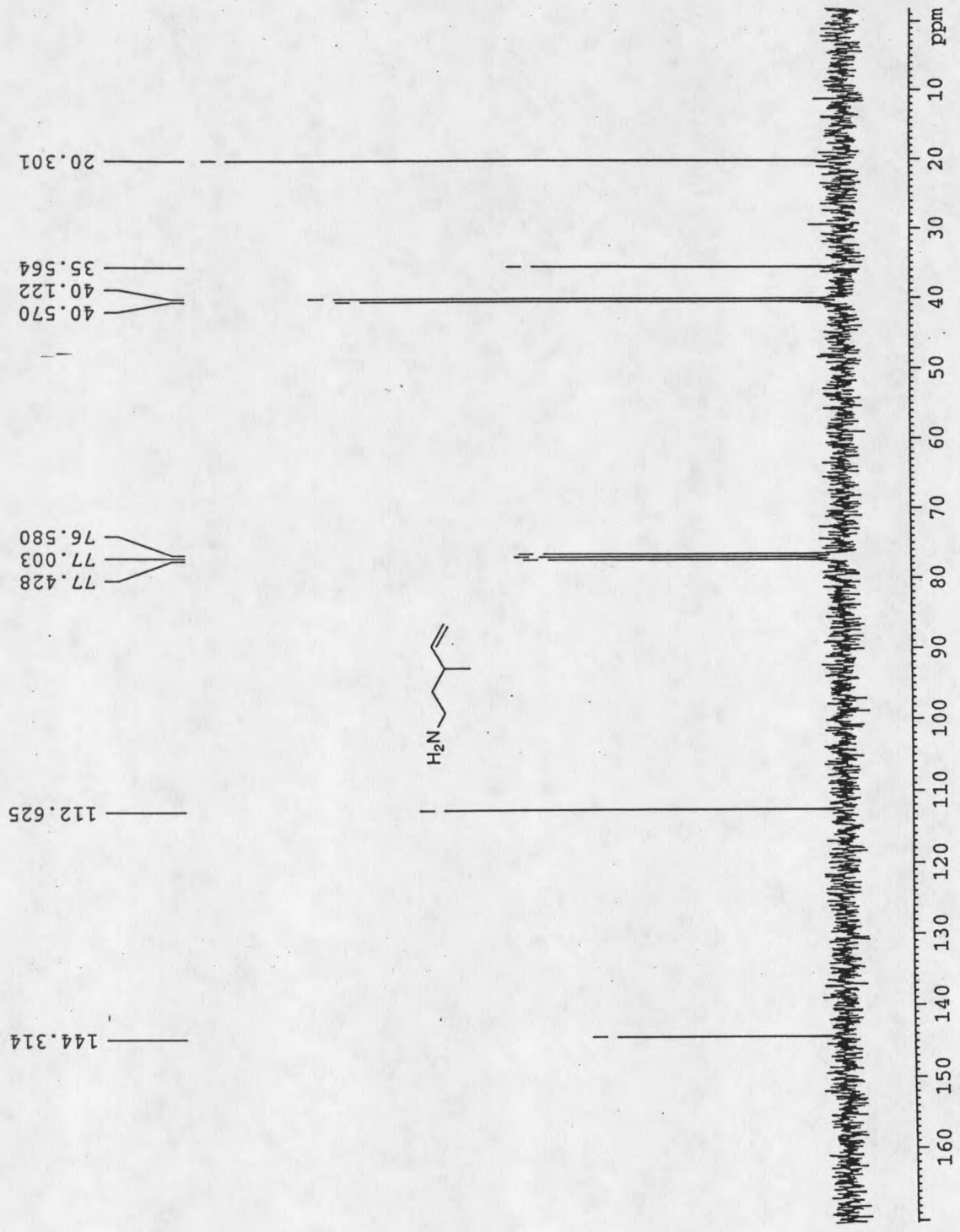


Figure 54. ^{13}C NMR Spectrum of 3-Methylaminohex-4-ene (**44**)

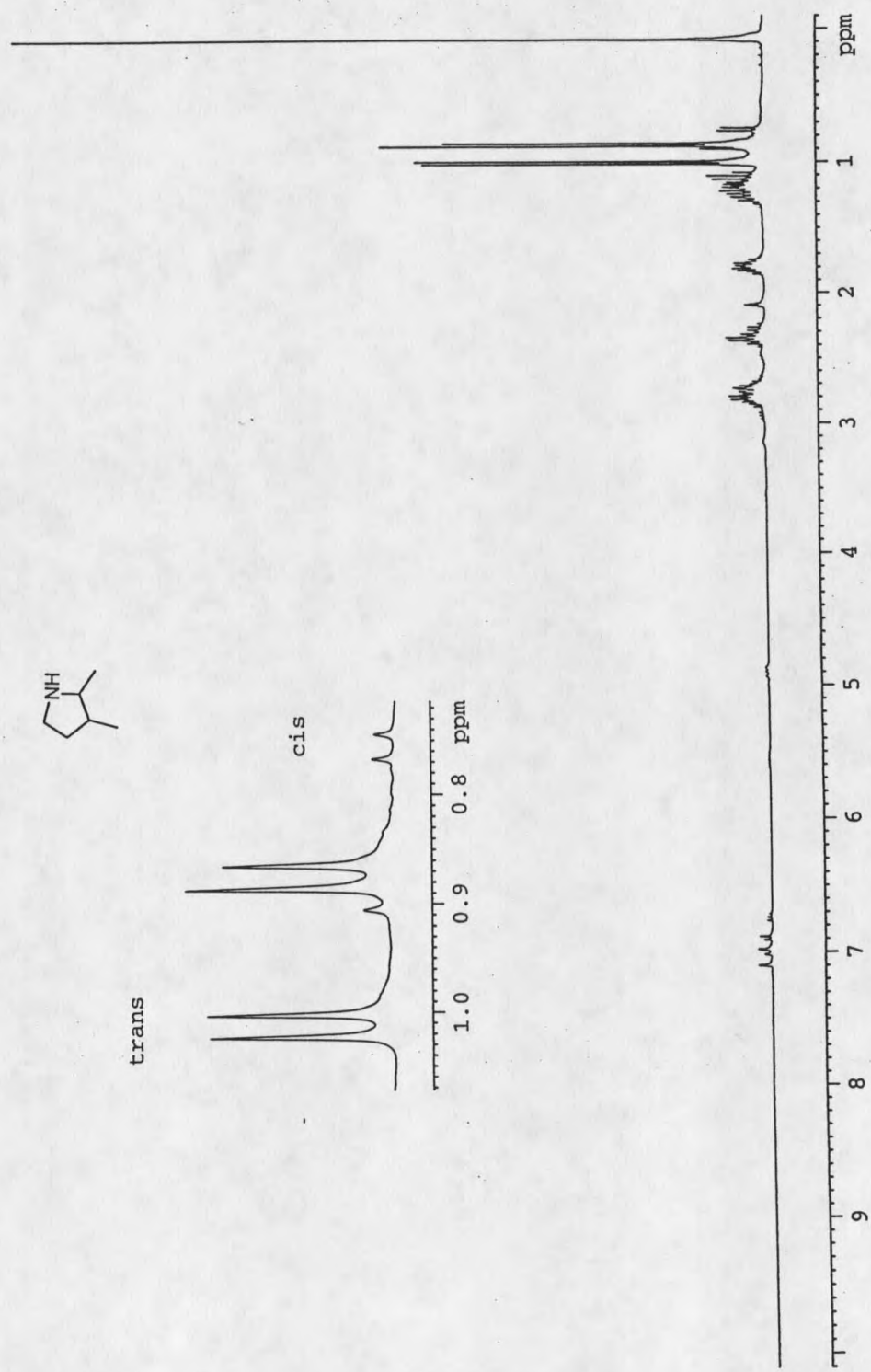


Figure 55. ^{1}H NMR Spectrum of 2,3-Dimethylpyrrolidine (**51**)

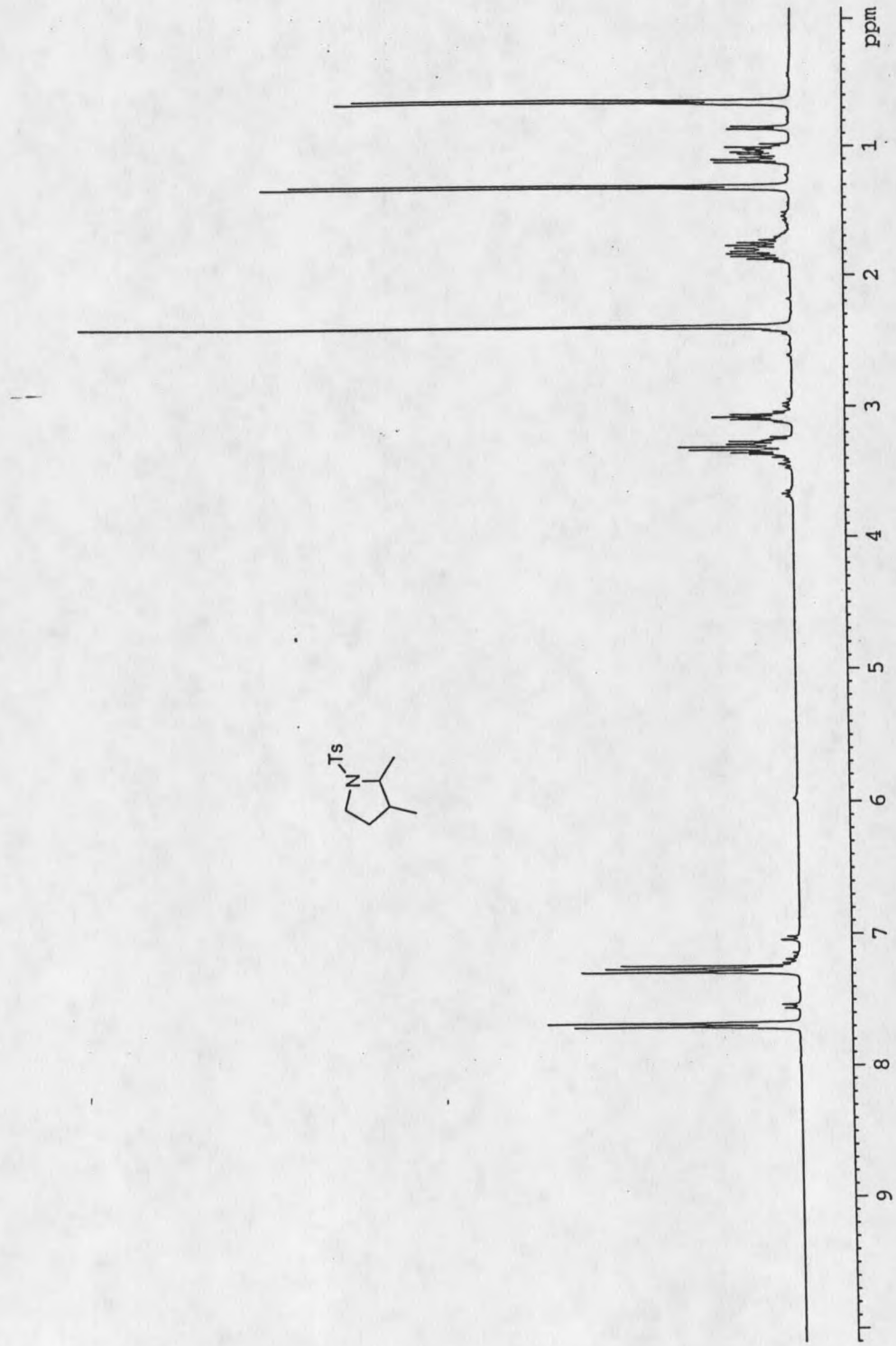


Figure 56. ^{1}H NMR Spectrum of *N*-(*p*-Tolylsulfonyl)-2,3-dimethylpyrrolidine (**Ts-51**)

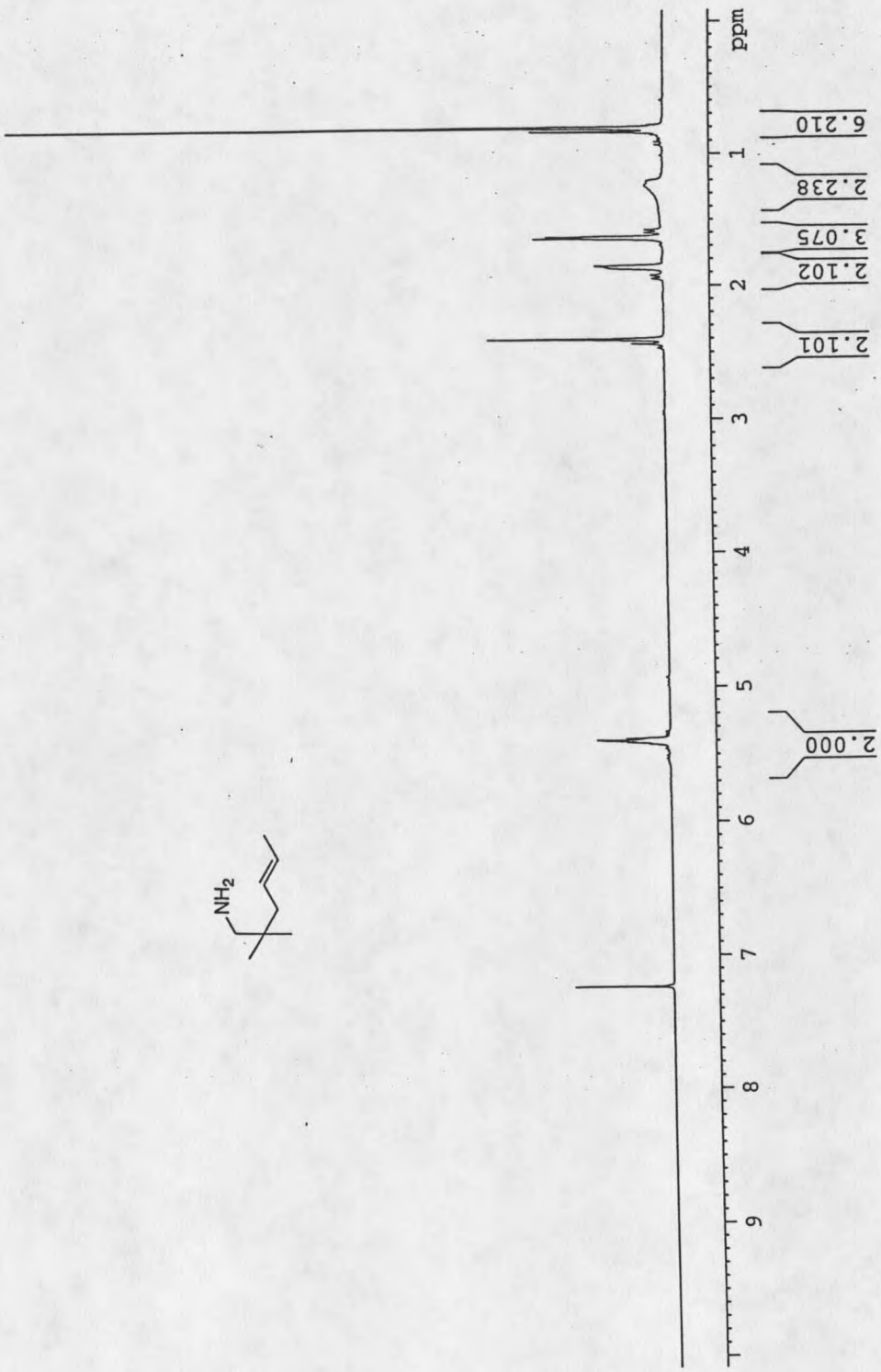


Figure 57. ^{1}H NMR Spectrum of 2,2-Dimethylaminohex-4-ene (**47**)

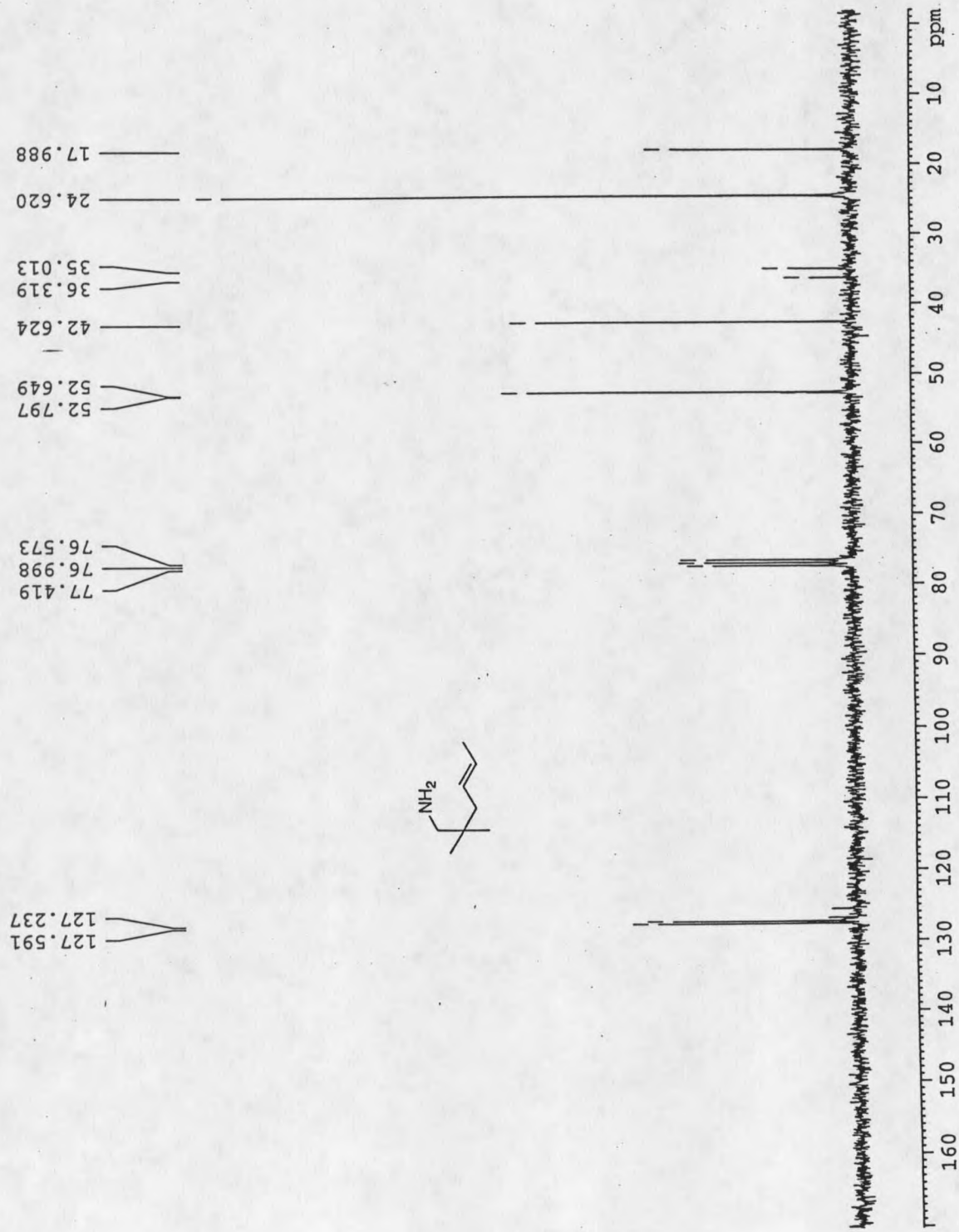


Figure 58. ^{13}C NMR Spectrum of 2,2-Dimethylaminohex-4-ene (**47**)

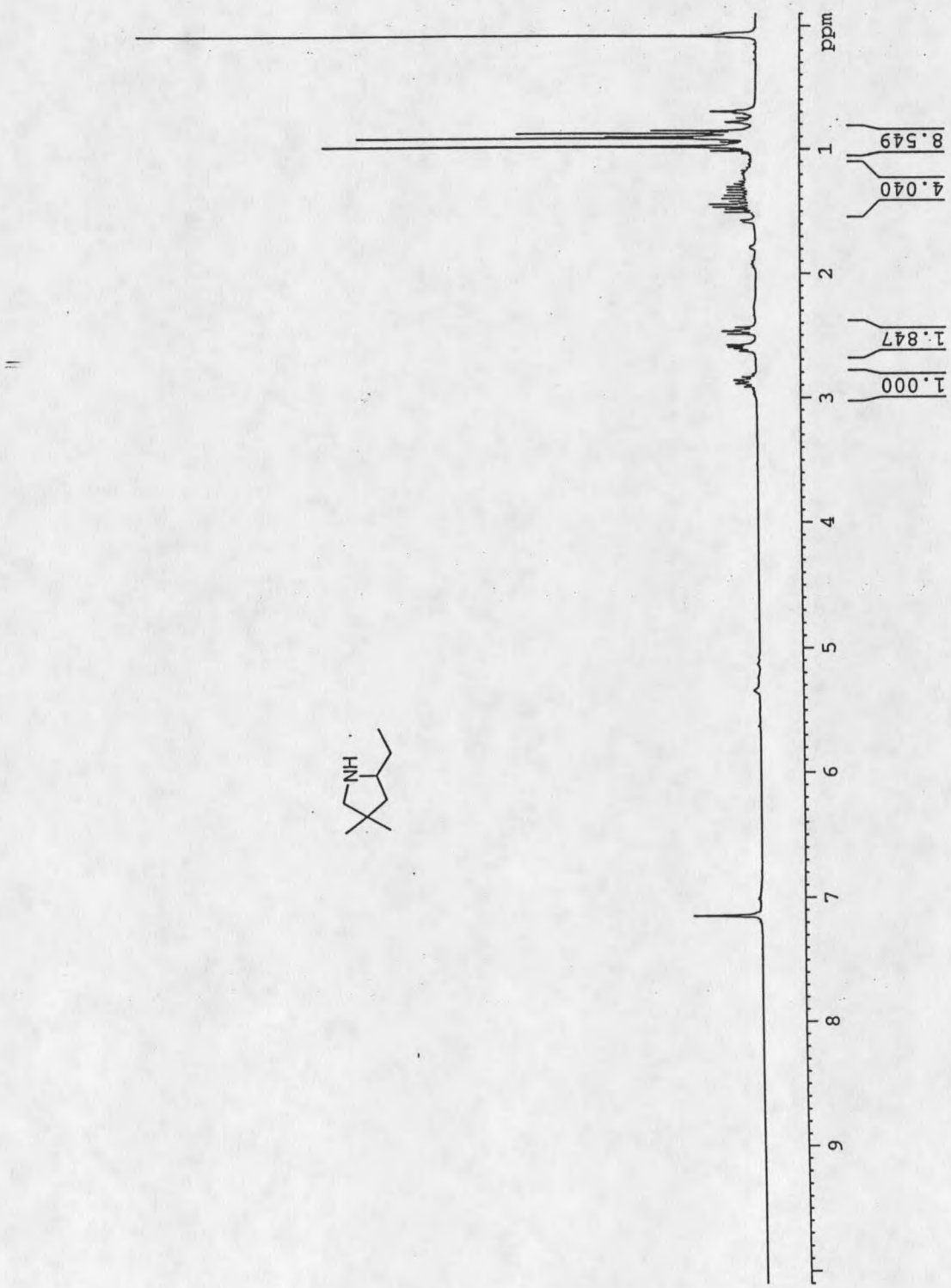


Figure 59. ^{1}H NMR Spectrum of 2-Ethyl-4,4-dimethylpyrrolidine (**52**)

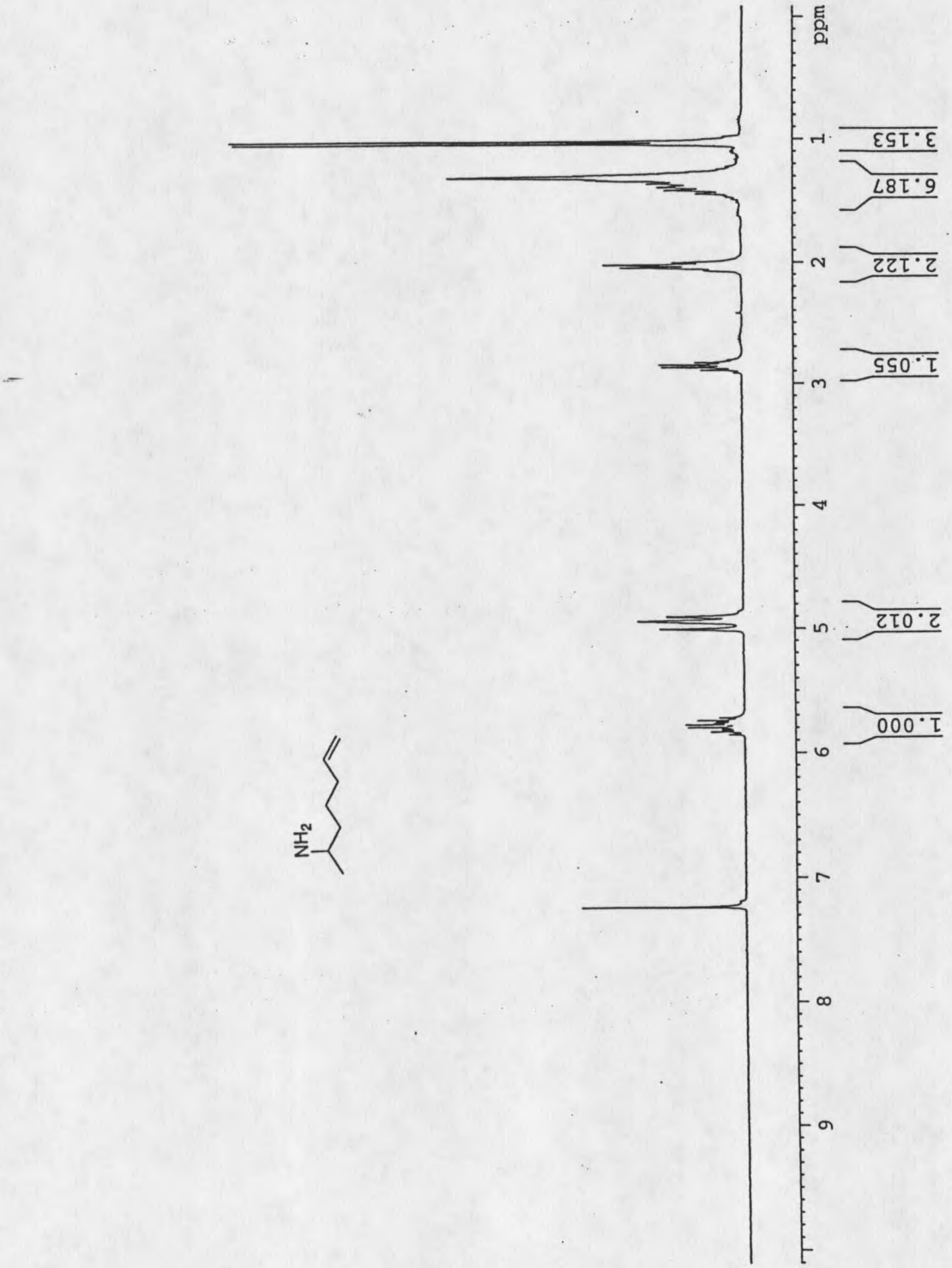


Figure 60. ^{1}H NMR Spectrum of 2-Aminohept-6-ene (**50**)

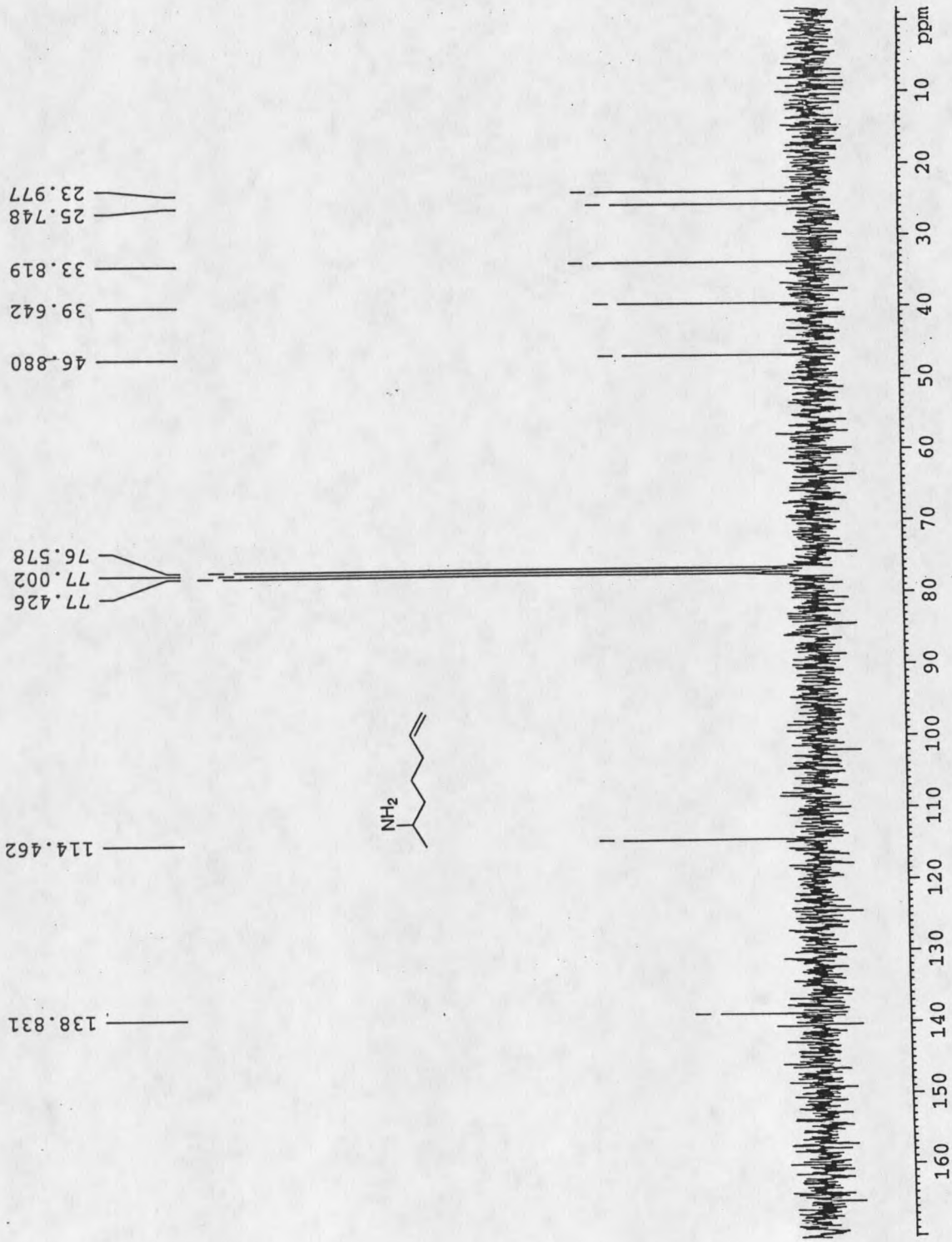


Figure 61. ^{13}C NMR Spectrum of 2-Aminohept-6-ene (**50**)

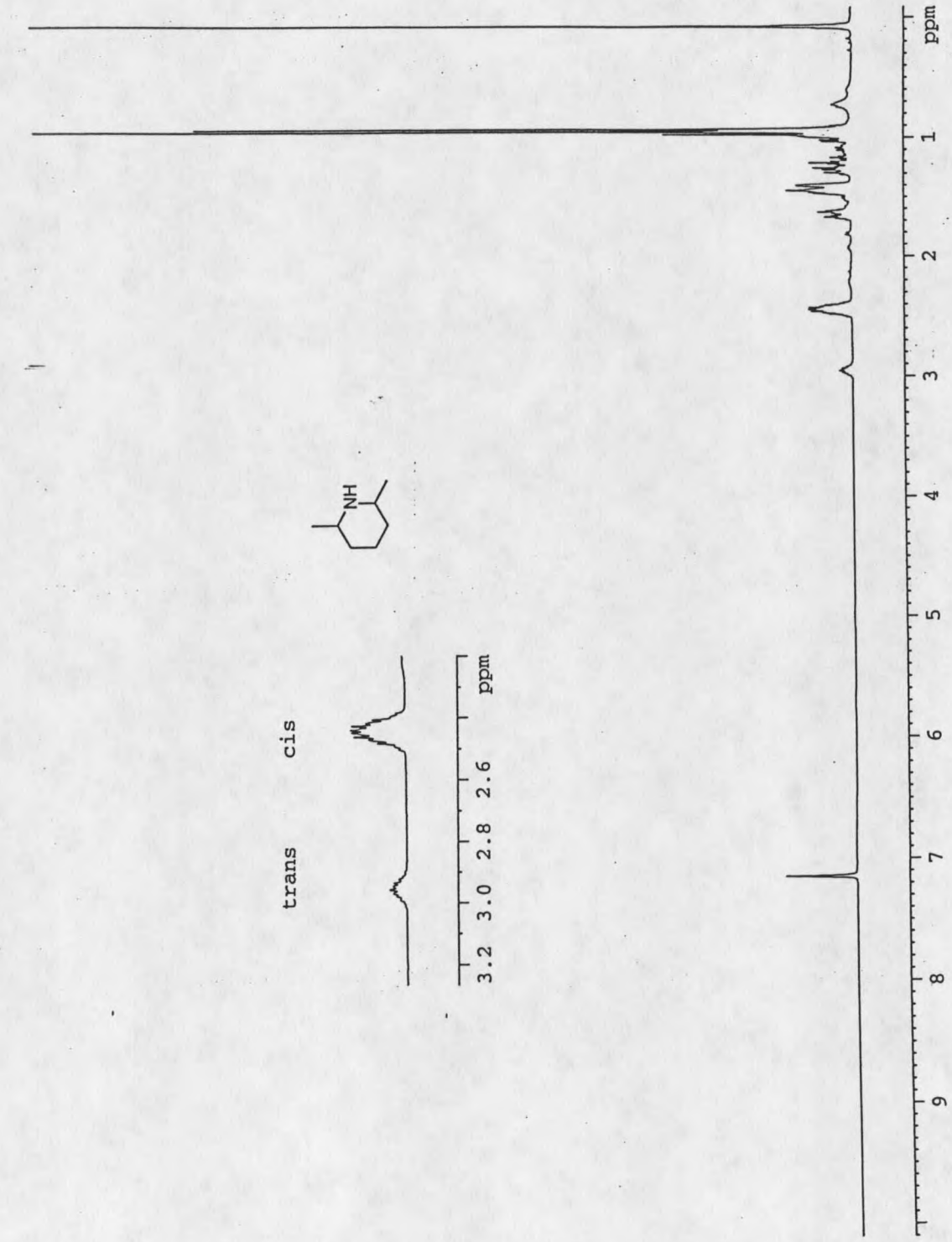


Figure 62. ^{1}H NMR Spectrum of 2,6-Dimethylpiperidine (**53**)

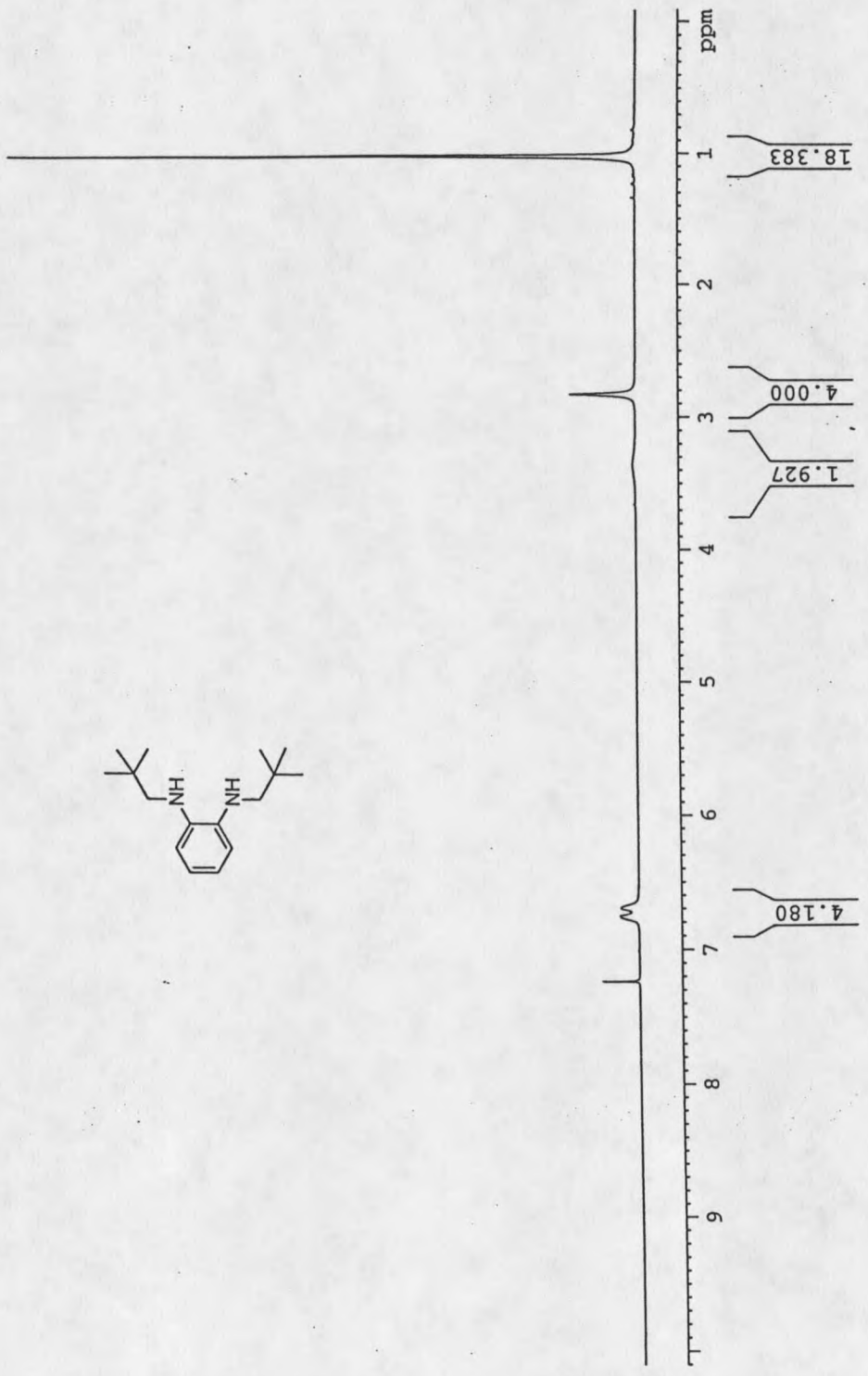


Figure 63. ^{1}H NMR Spectrum of *N,N'*-Bis-(2,2-dimethylpropyl)-1,2-phenylenediamine (**22a**)

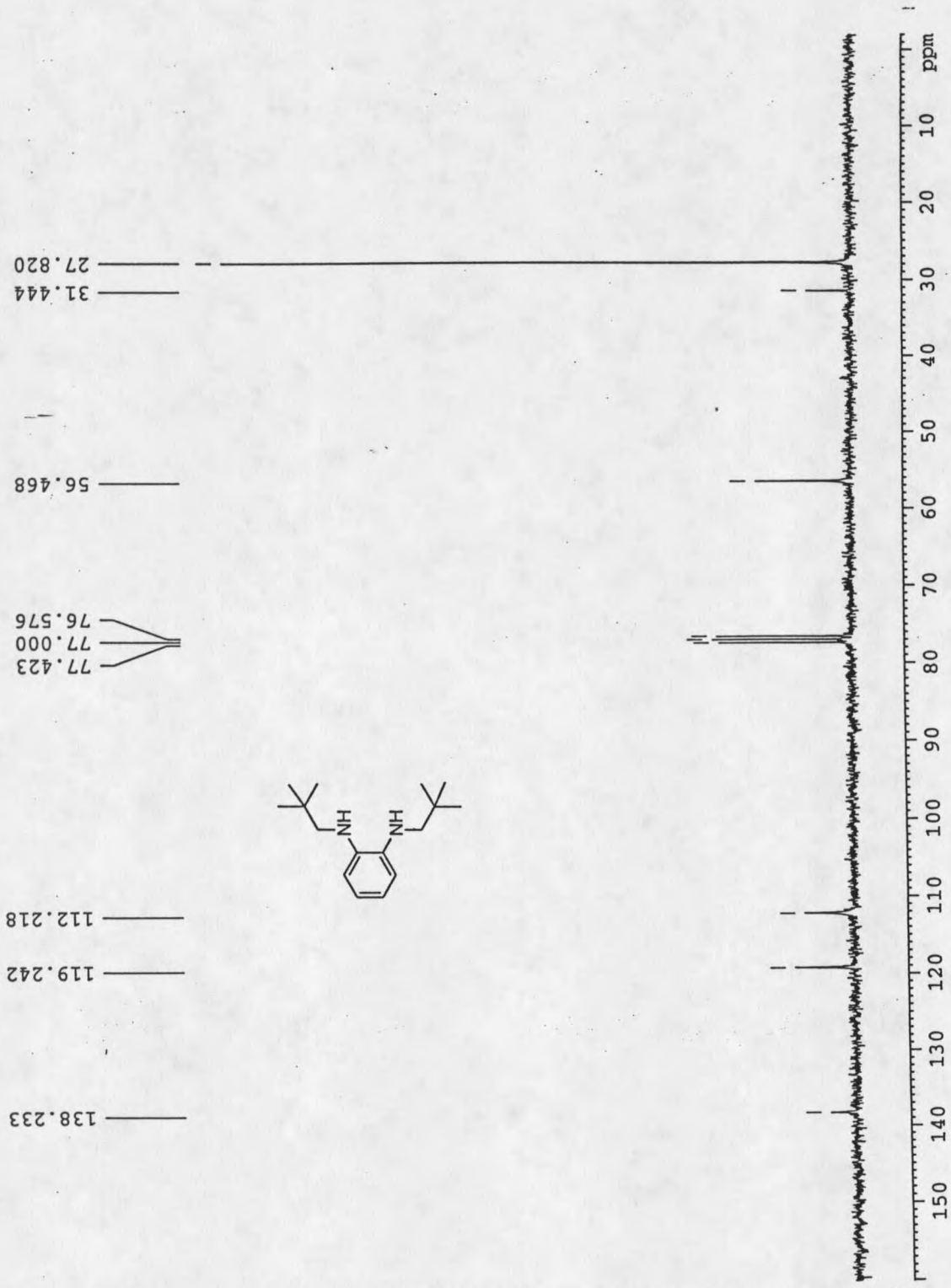


Figure 64. ^{13}C NMR Spectrum of *N,N'*-Bis-(2,2-dimethylpropyl)-1,2-phenylenediamine (22a)

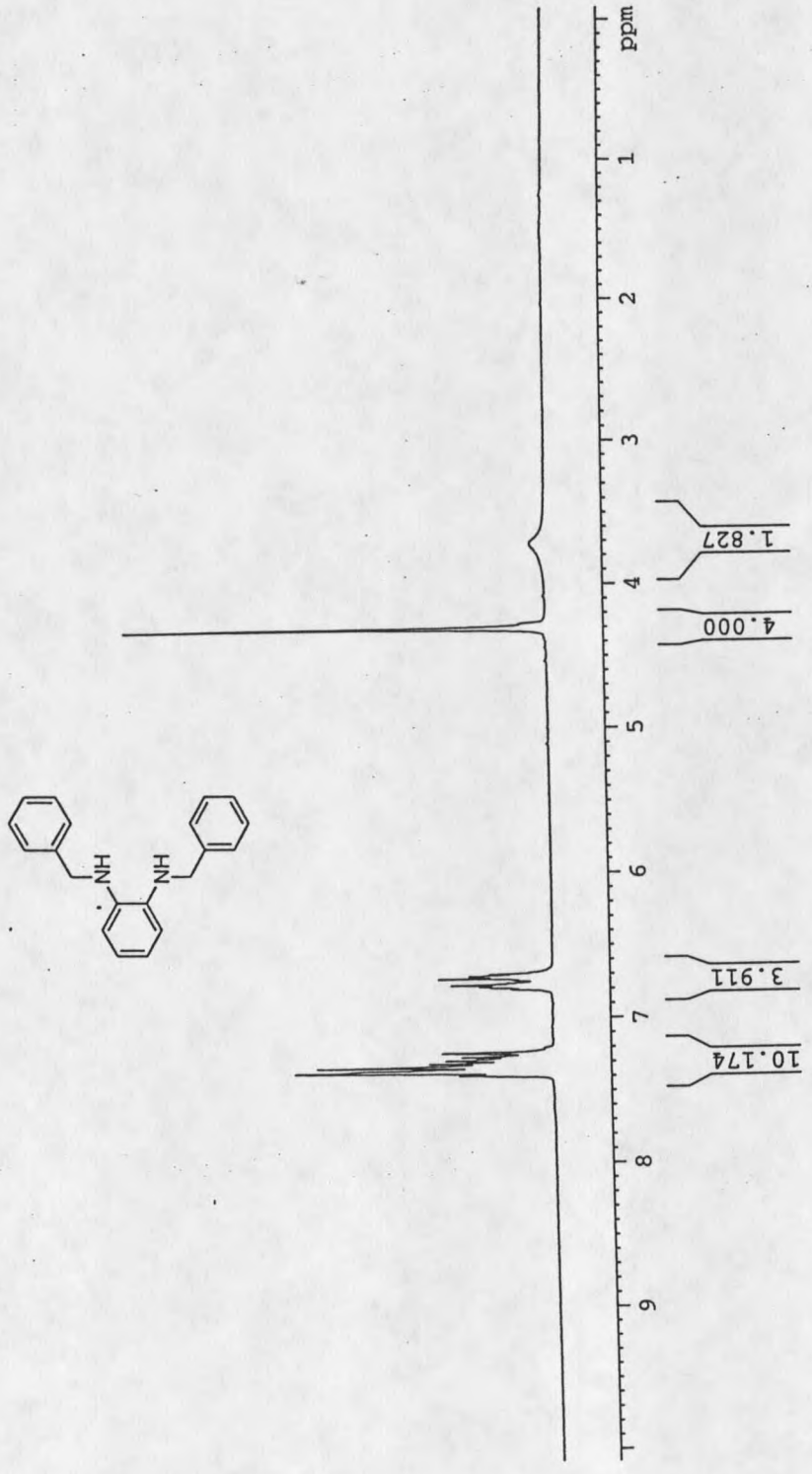


Figure 65. ^{1}H NMR Spectrum of N,N'-Bis-benzyl-1,2-phenylendiamine (**22b**)

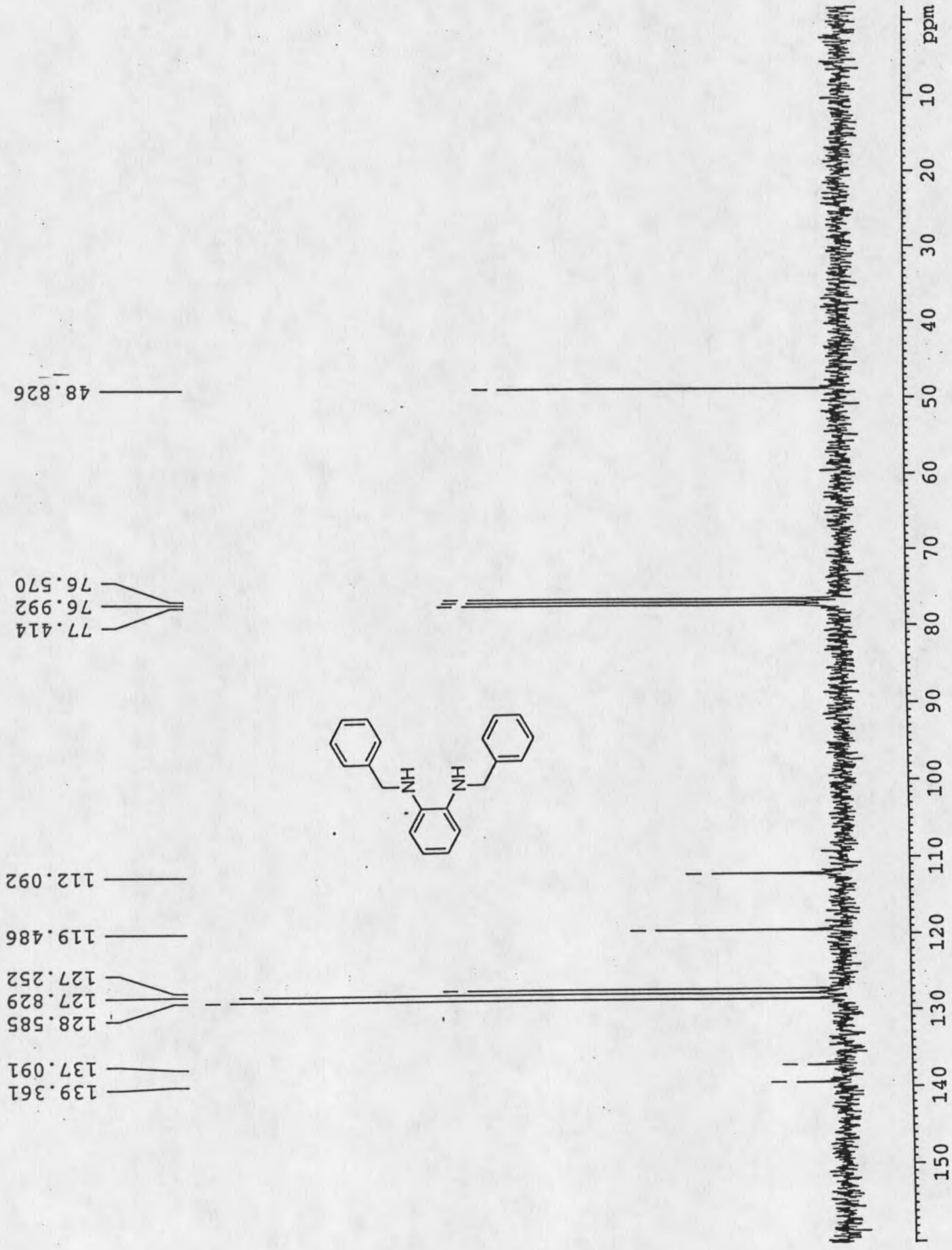


Figure 66. ^{13}C NMR Spectrum of N,N'-Bis-benzyl-1,2-phenylendiamine (**22b**)

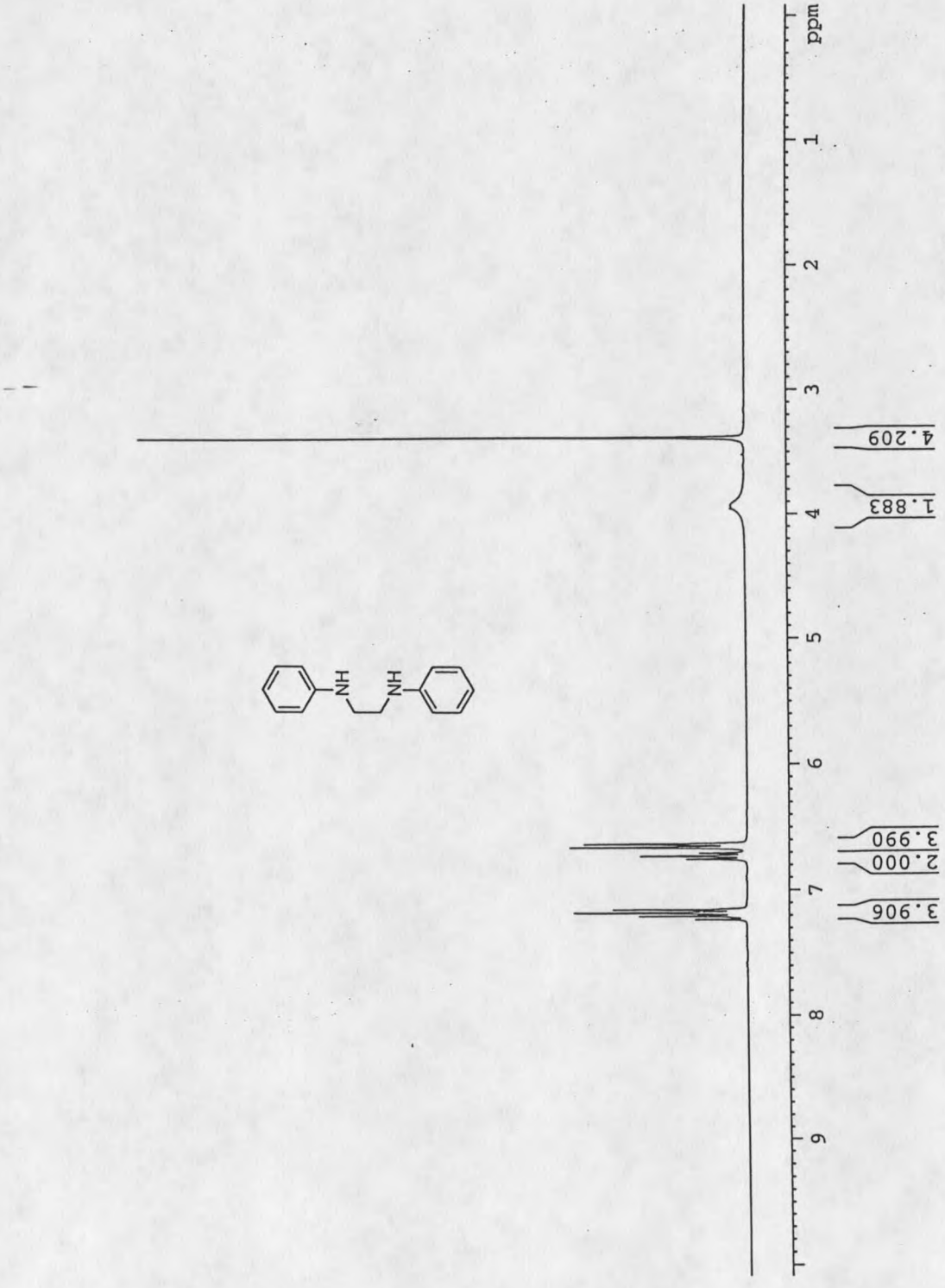


Figure 67. ^{1}H NMR Spectrum of N,N'-Diphenylethane-1,2-diamine (**23a**)

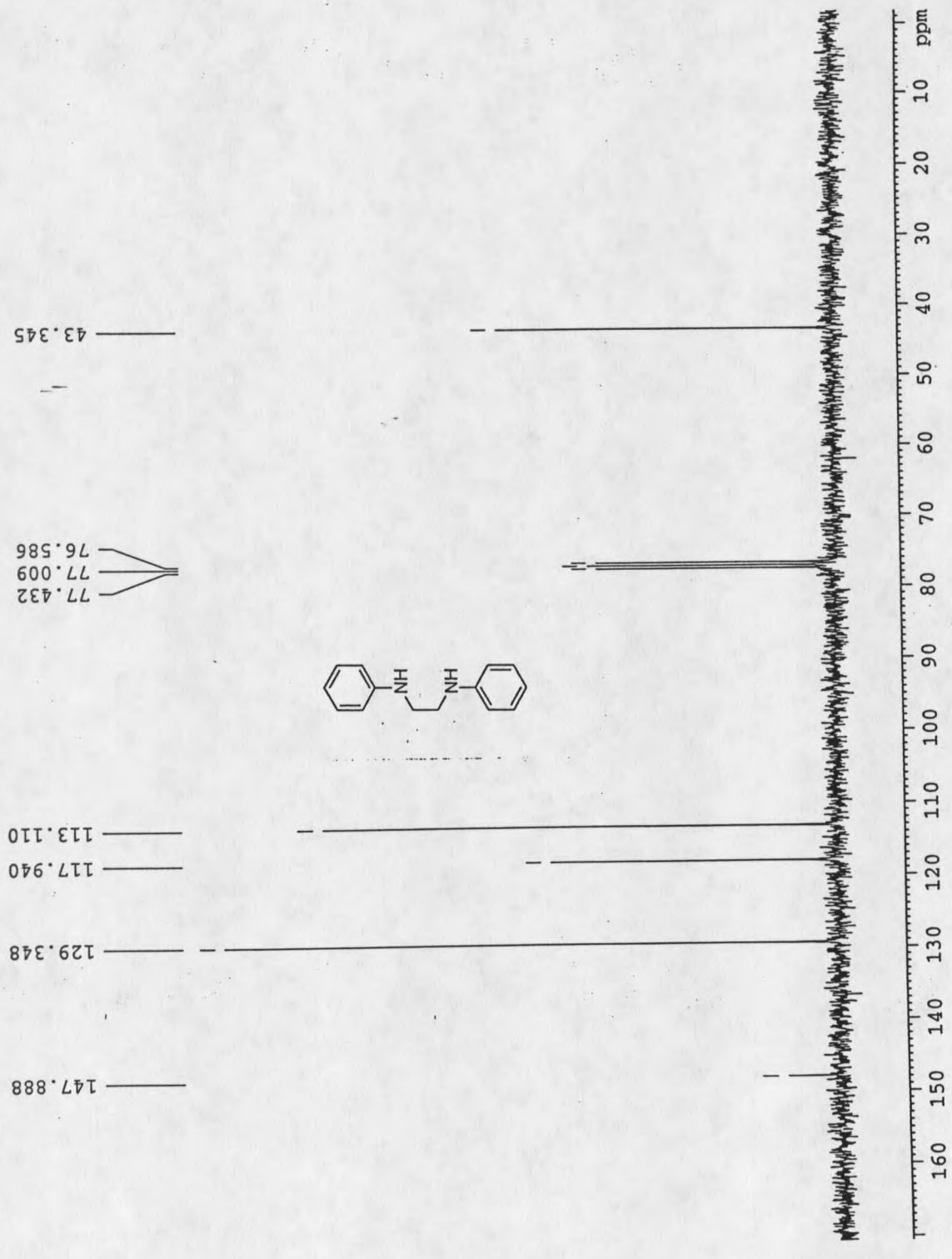


Figure 68. ^{13}C NMR Spectrum of *N,N'*-Diphenylethane-1,2-diamine (**23a**)

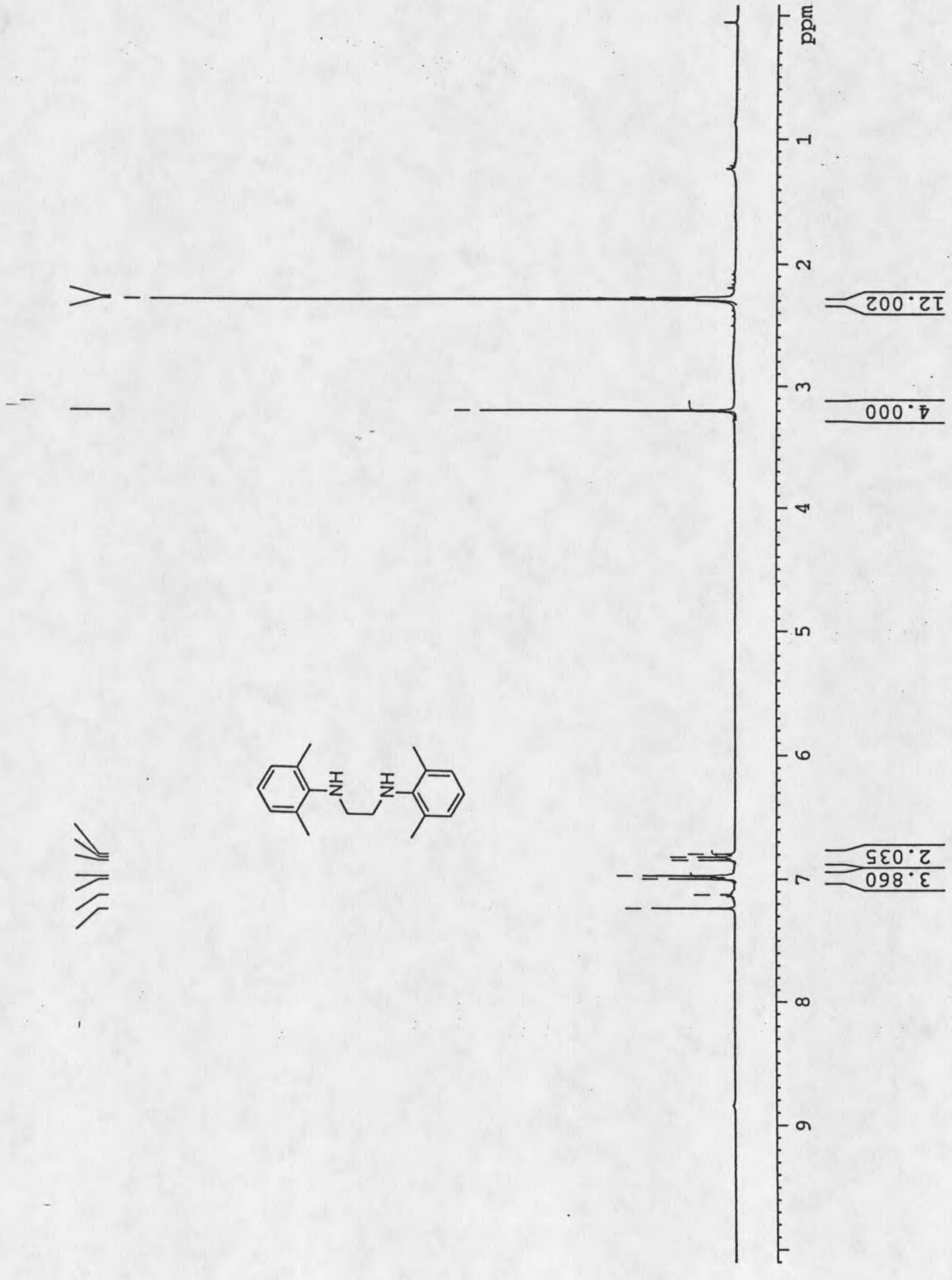


Figure 69. ^{1}H NMR Spectrum of *N,N'*-Bis(2,6-dimethylphenyl)ethane-1,2-diamine (**23b**)

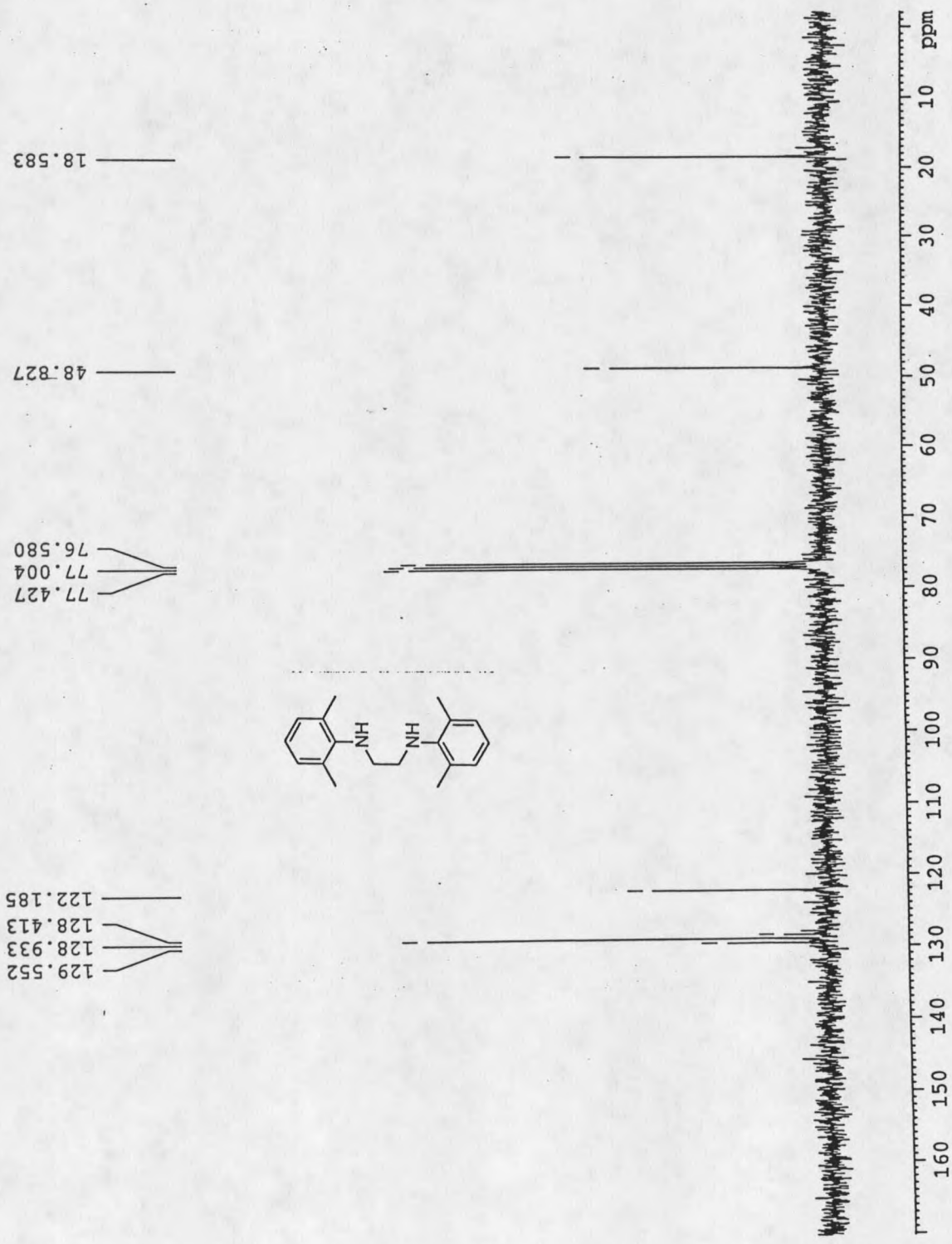


Figure 70. ^{13}C NMR Spectrum of *N,N'*-Bis(2,6-dimethylphenyl)ethane-1,2-diamine (**23b**)

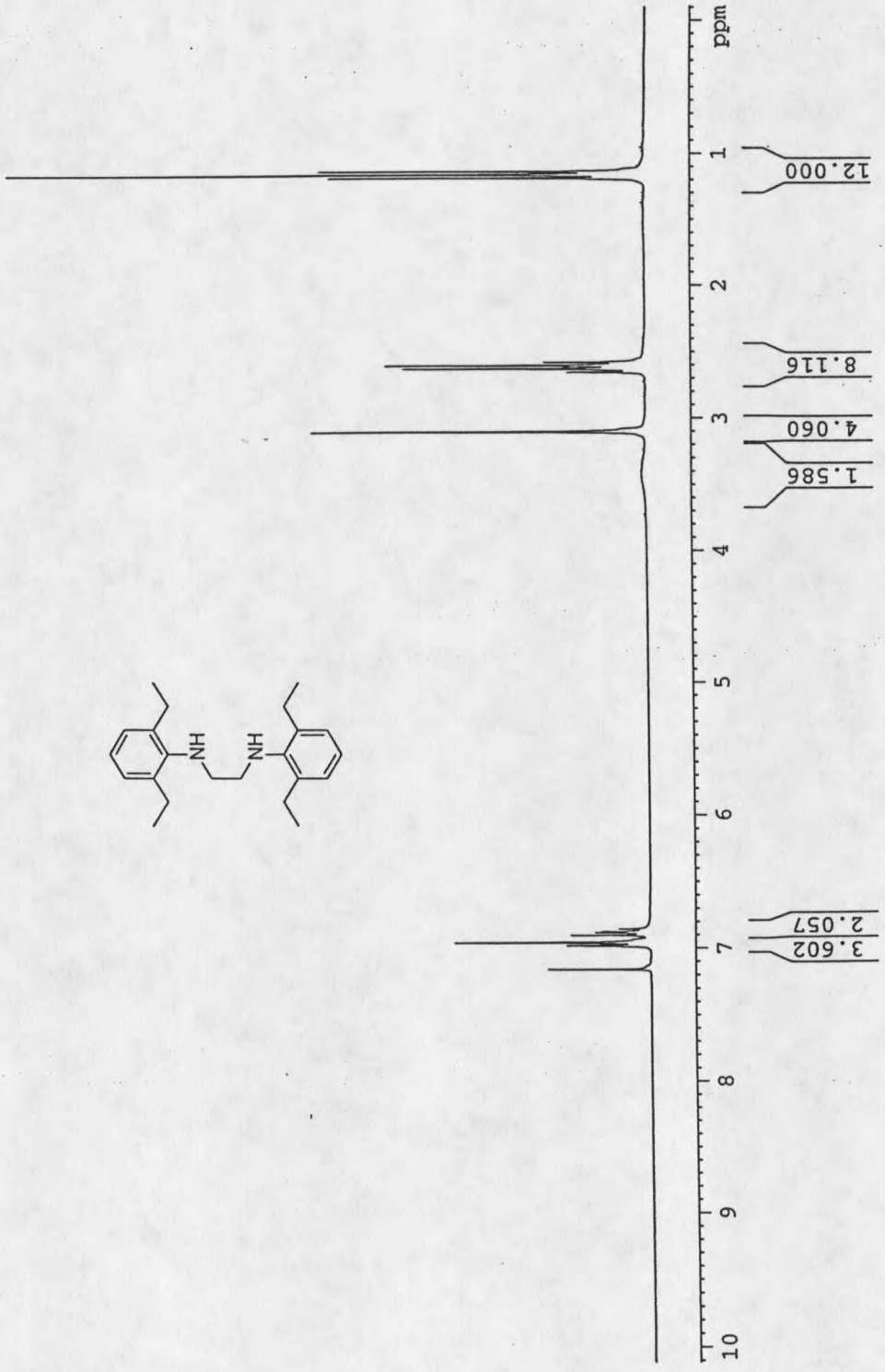


Figure 71. ^{1}H NMR Spectrum of *N,N'*-Bis(2,6-diethylphenyl)ethylenediamine (**23e**)

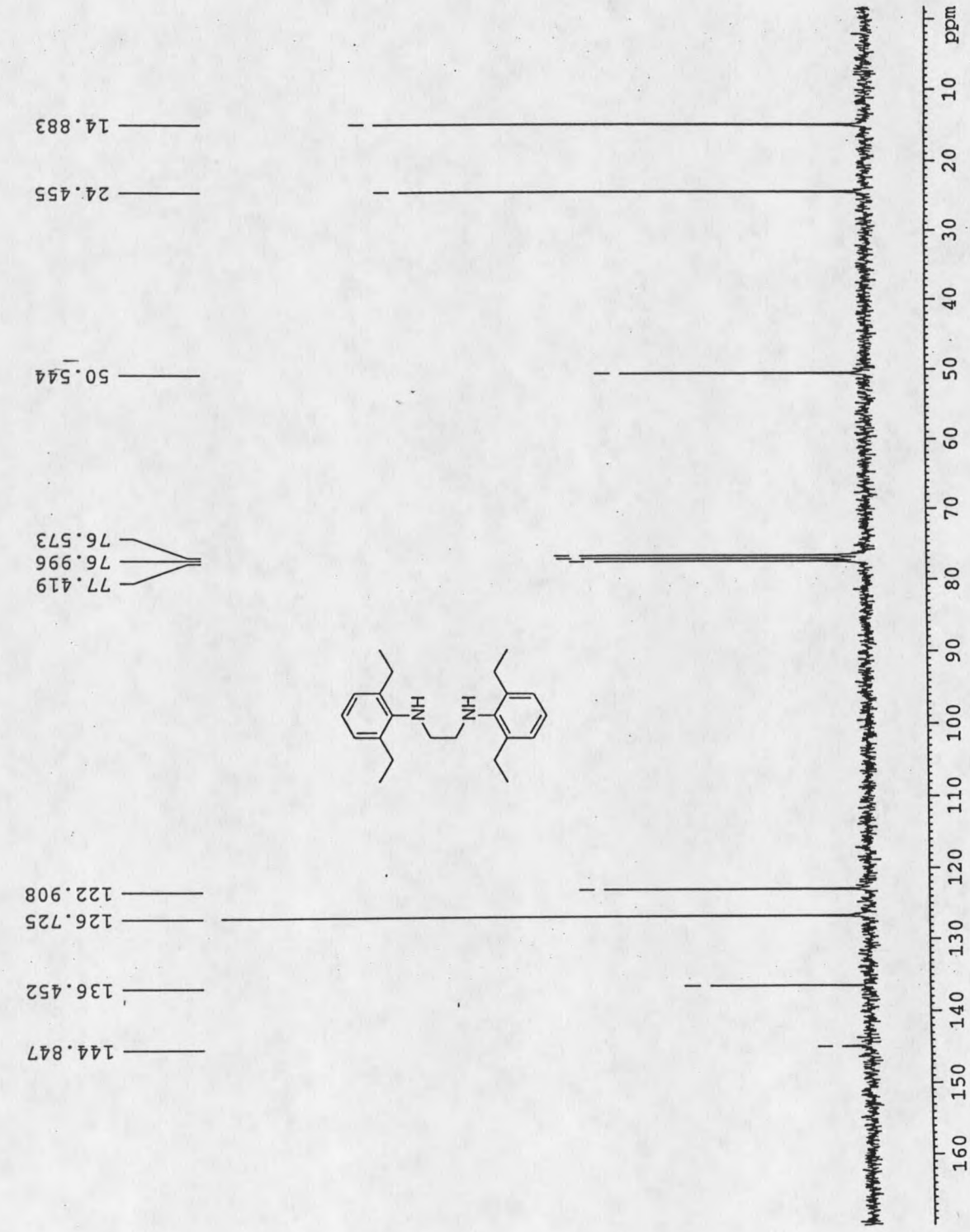


Figure 72. ^{13}C NMR Spectrum of *N,N'*-Bis(2,6-diethylphenyl)ethylenediamine (**23e**)

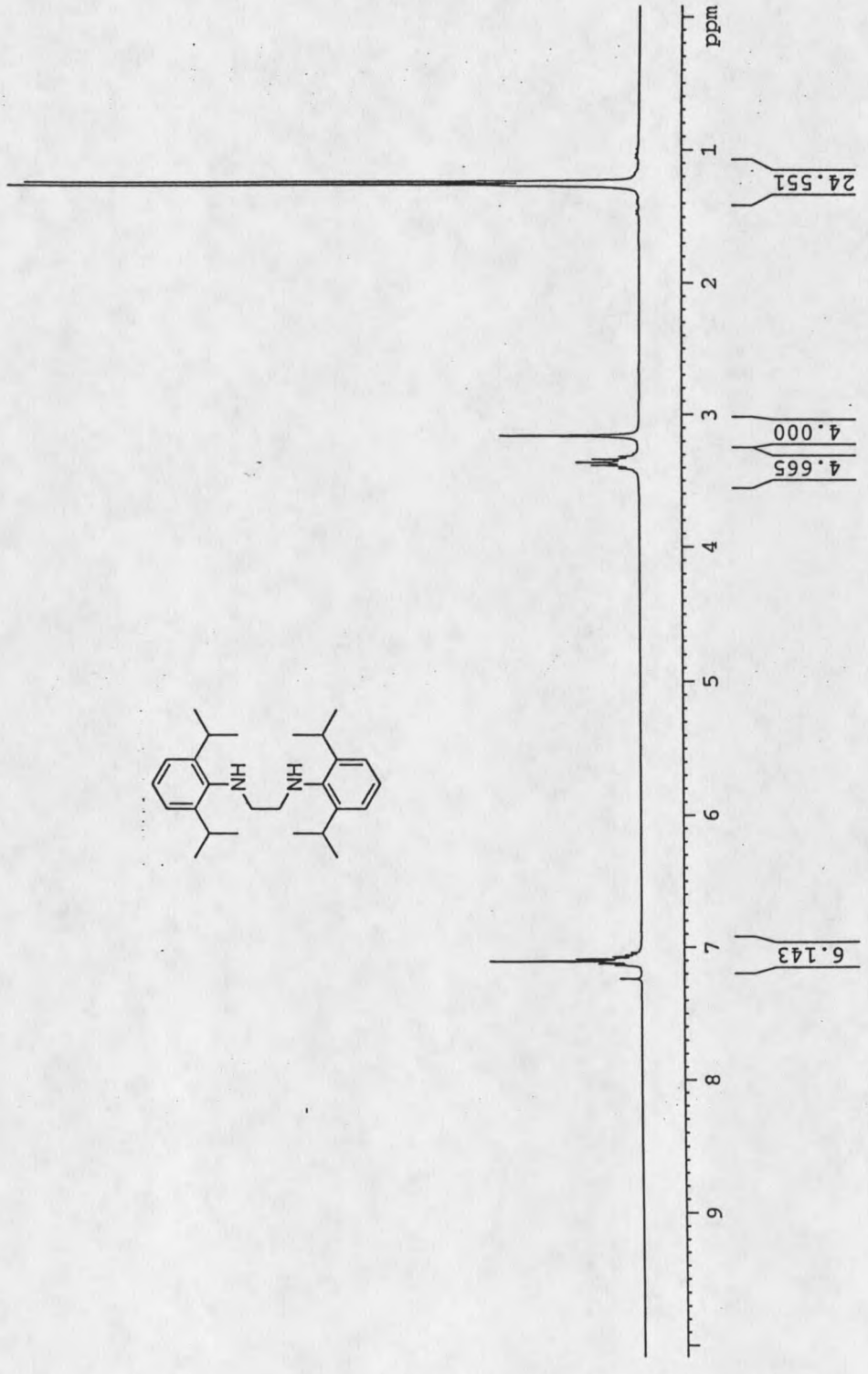


Figure 73. ^{1}H NMR Spectrum of *N,N'*-Bis-(2,6-diisopropylphenyl)ethane-1,2-diamine (**23g**)

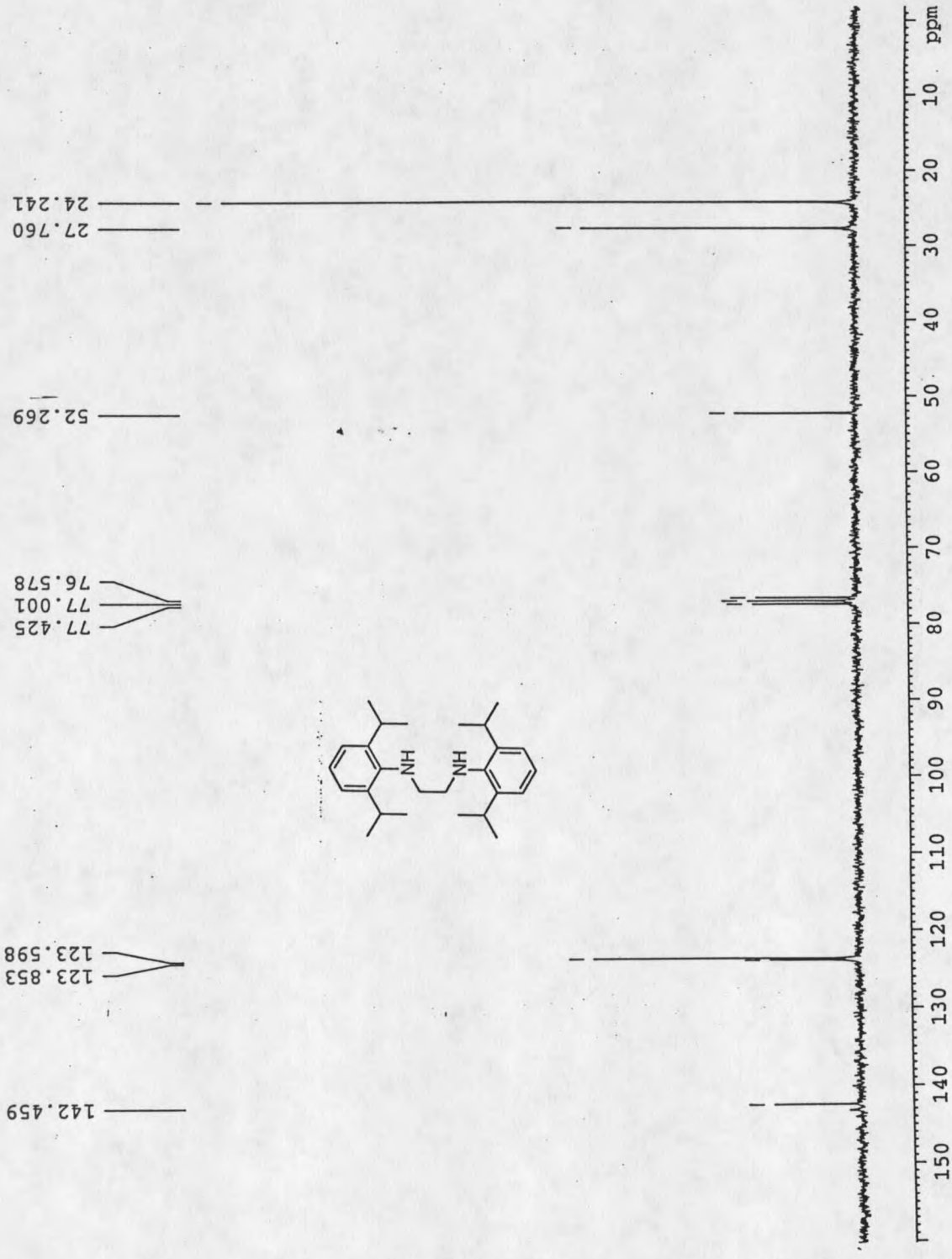


Figure 74. ^{13}C NMR Spectrum of *N,N'*-Bis-(2,6-diisopropylphenyl)ethane-1,2-diamine (**23g**)

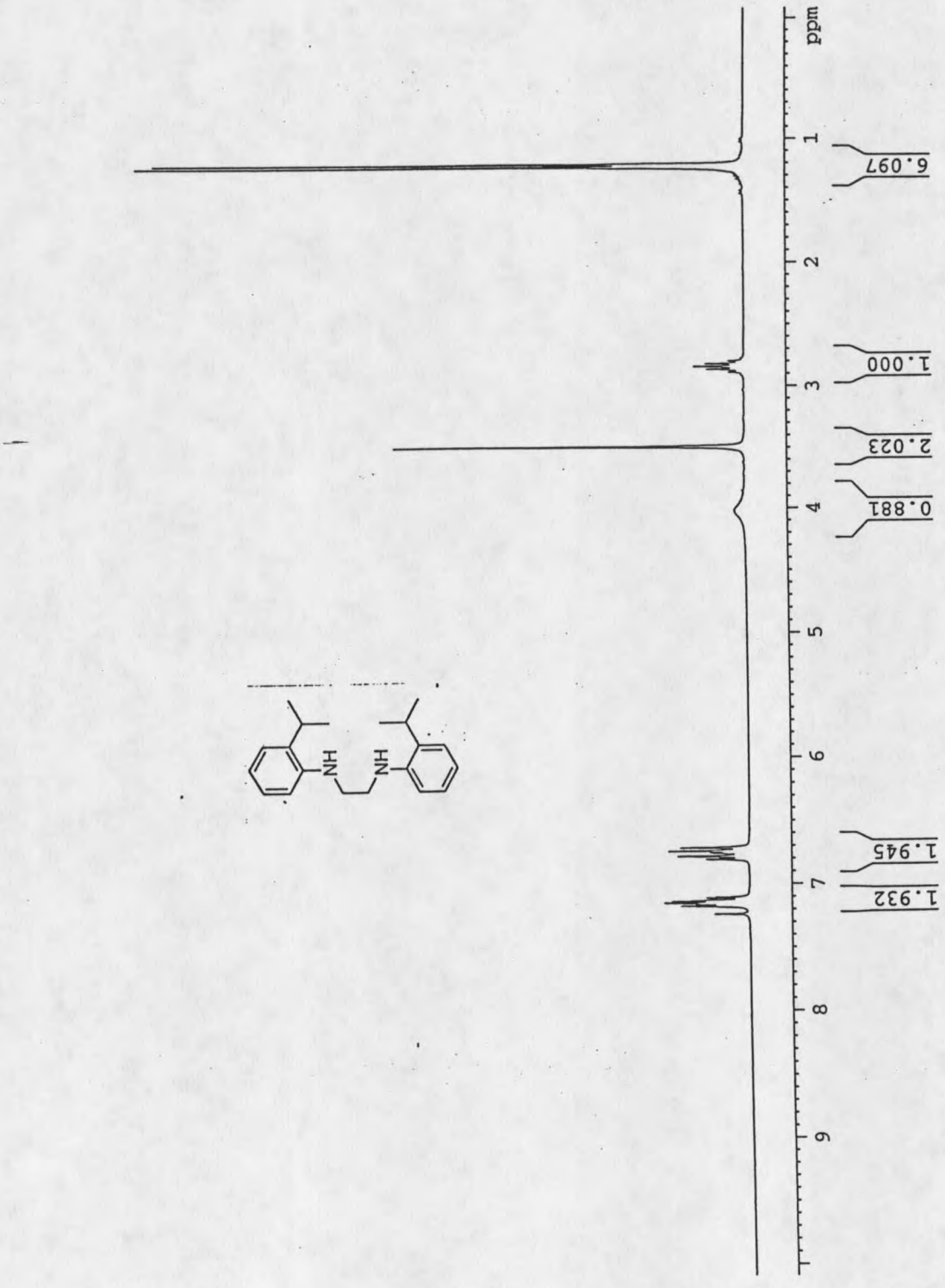


Figure 75. ^{1}H NMR Spectrum of *N,N'*-Bis(2-isopropylphenyl)ethane-1,2-diamine (**23h**)

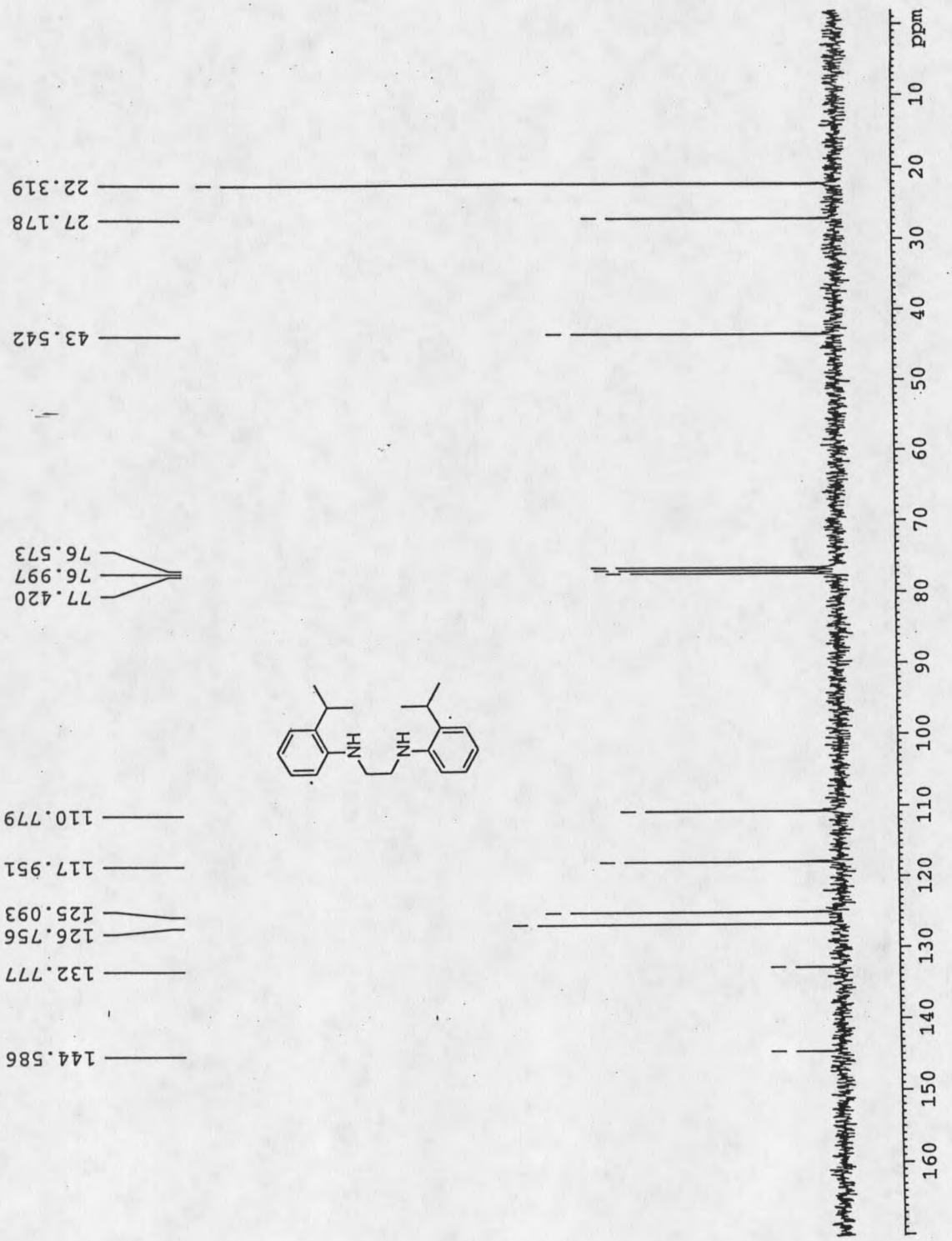


Figure 76. ^{13}C NMR Spectrum of *N,N'*-Bis(2-isopropylphenyl)ethane-1,2-diamine (**23h**)

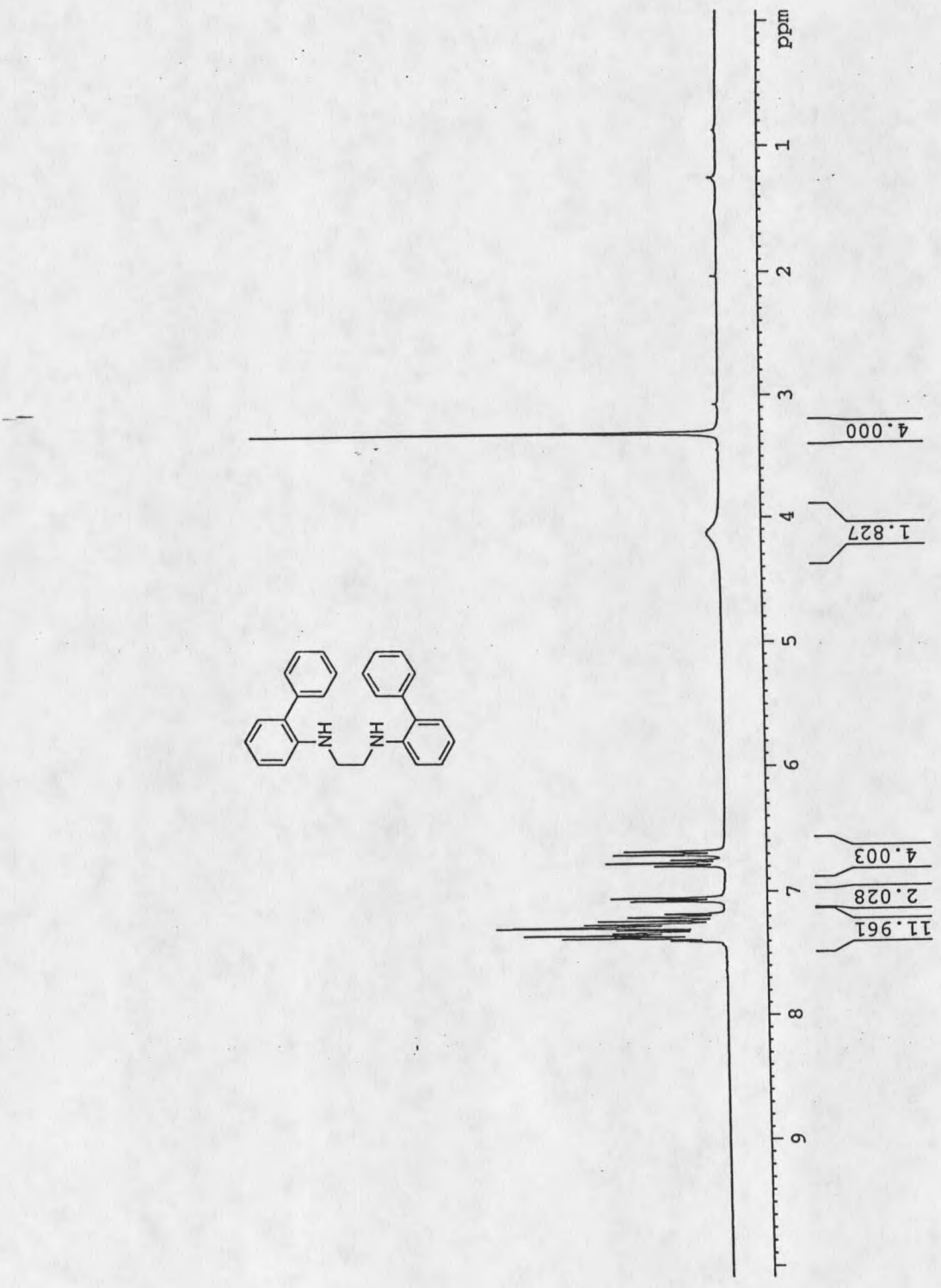


Figure 77. ^{1}H NMR Spectrum of N,N'-Bis-biphenyl-2-ylethane-1,2-diamine (**23k**)

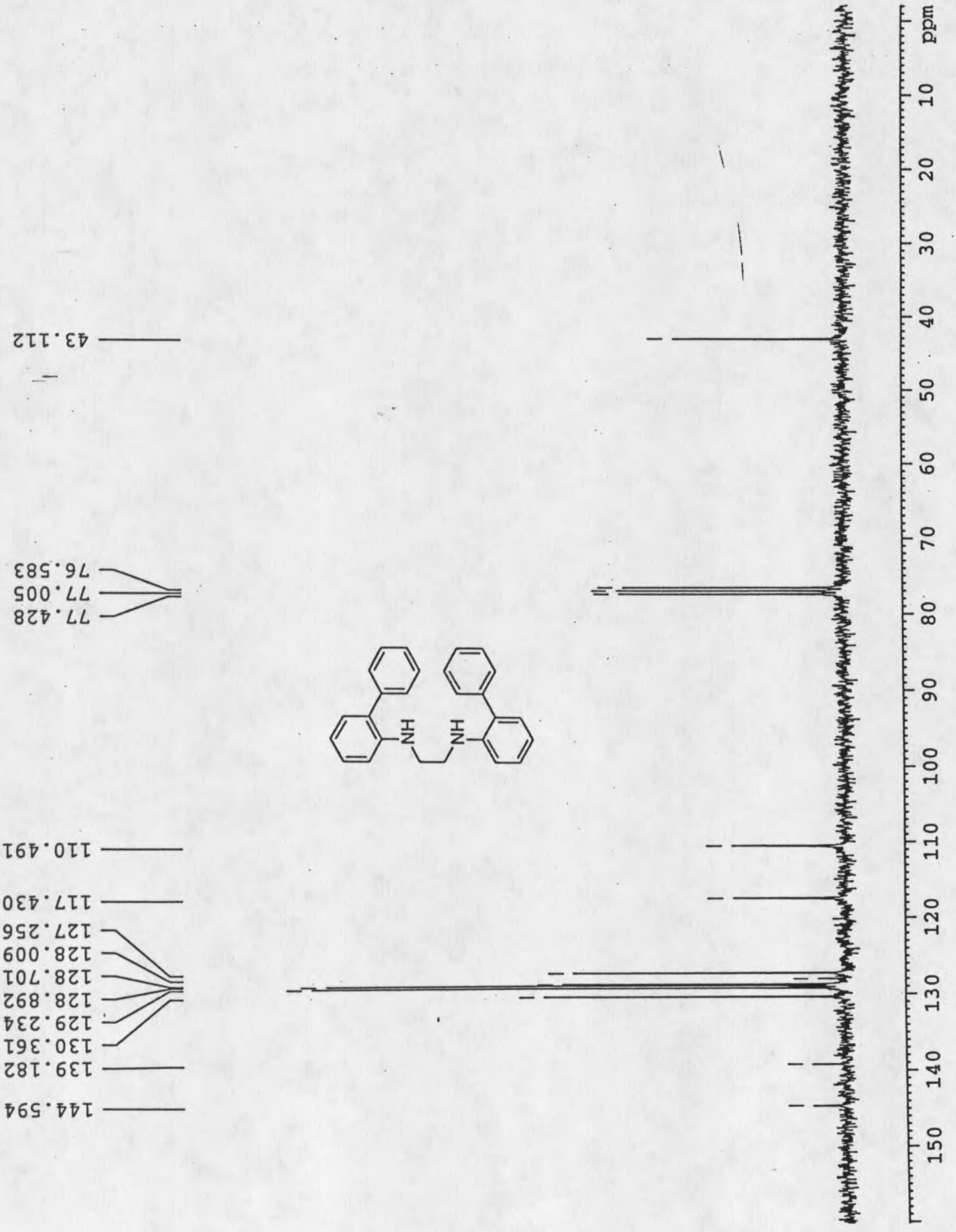


Figure 78. ^{13}C NMR Spectrum of *N,N'*-Bis-biphenyl-2-ylethane-1,2-diamine (**23k**)

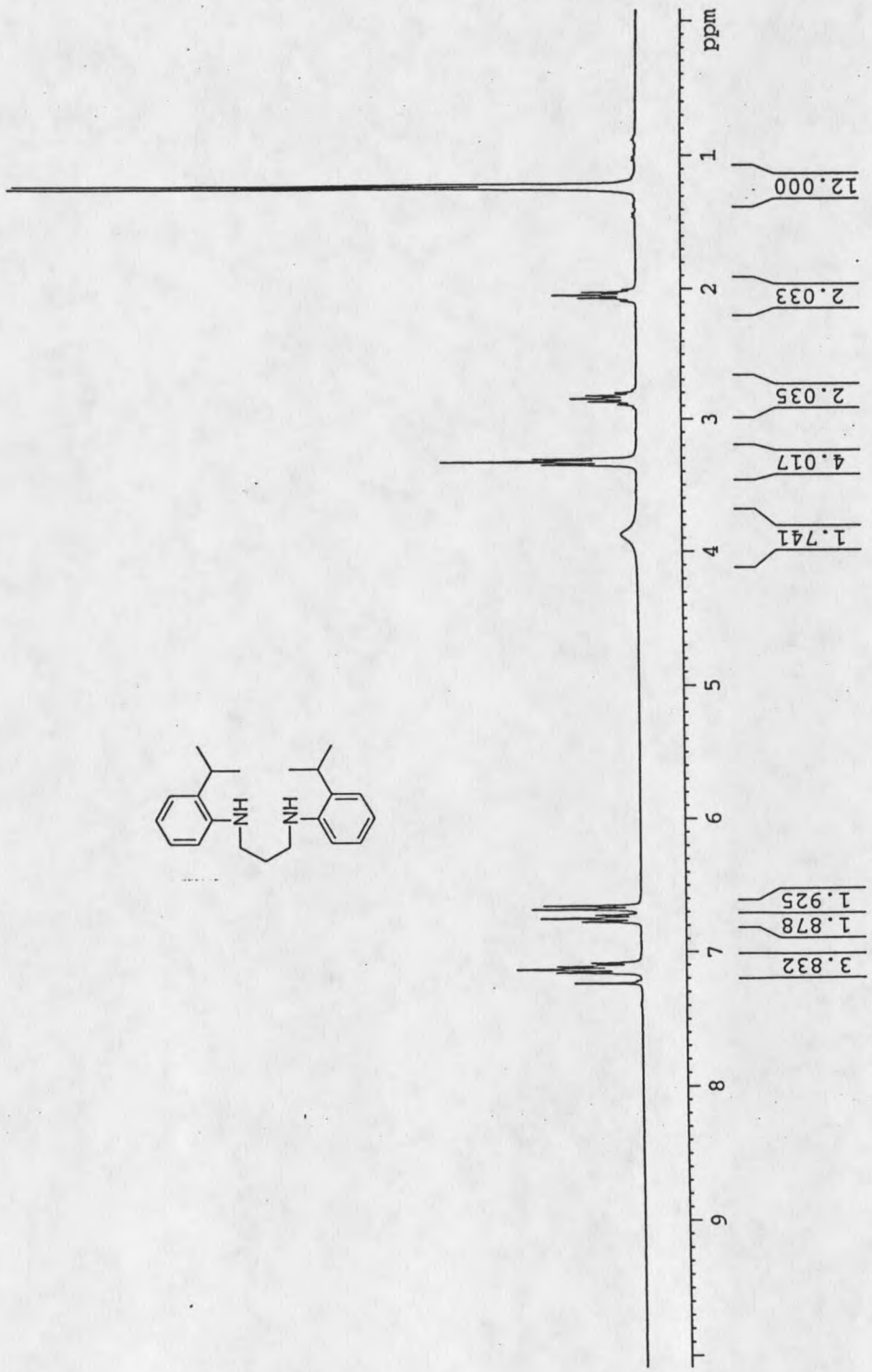


Figure 79. ^{1}H NMR Spectrum of *N,N'*-Bis-(2-isopropylphenyl)propane-1,3-diamine (**25a**)

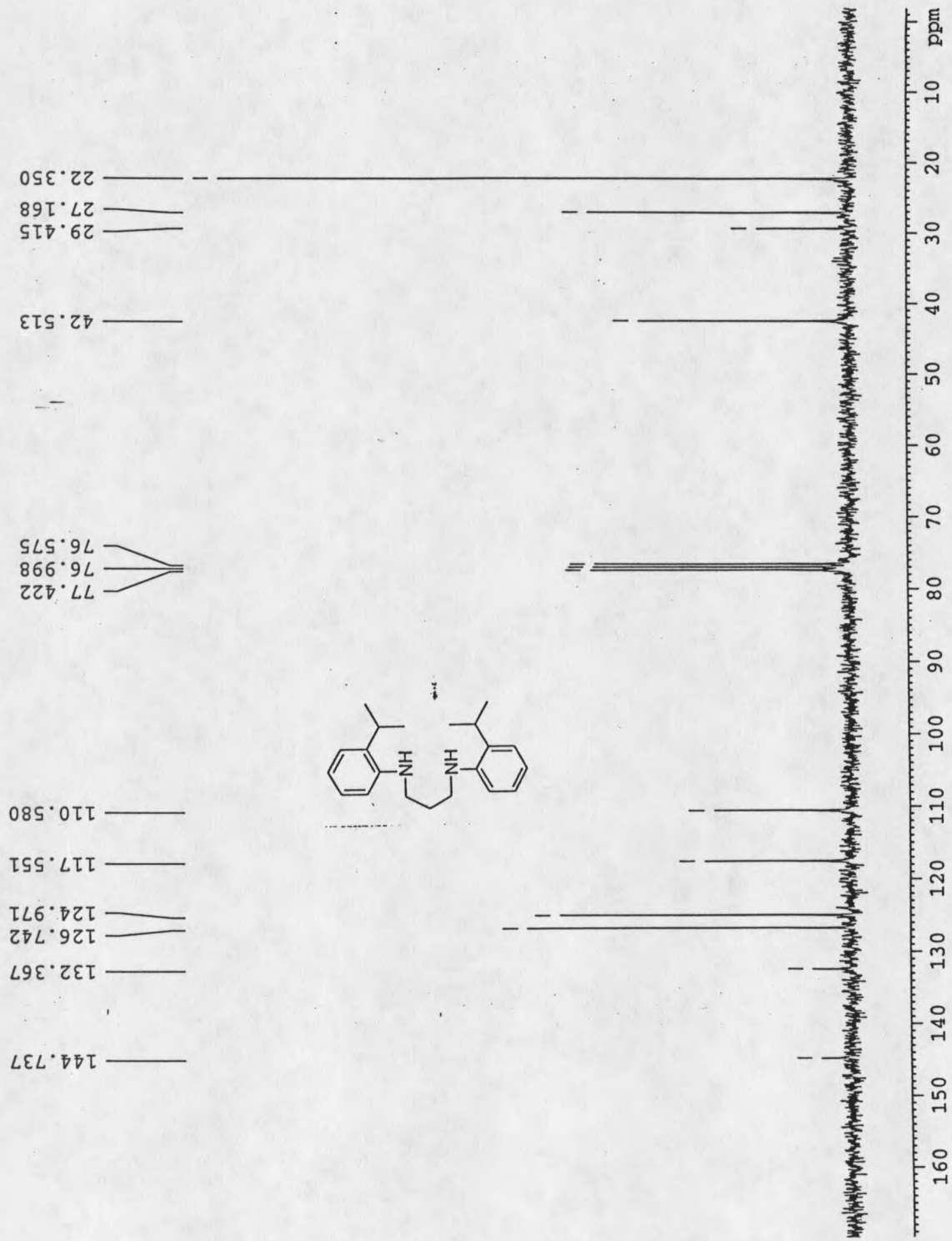


Figure 80. ^{13}C NMR Spectrum of *N,N'*-Bis-(2-isopropylphenyl)propane-1,3-diamine (**25a**)

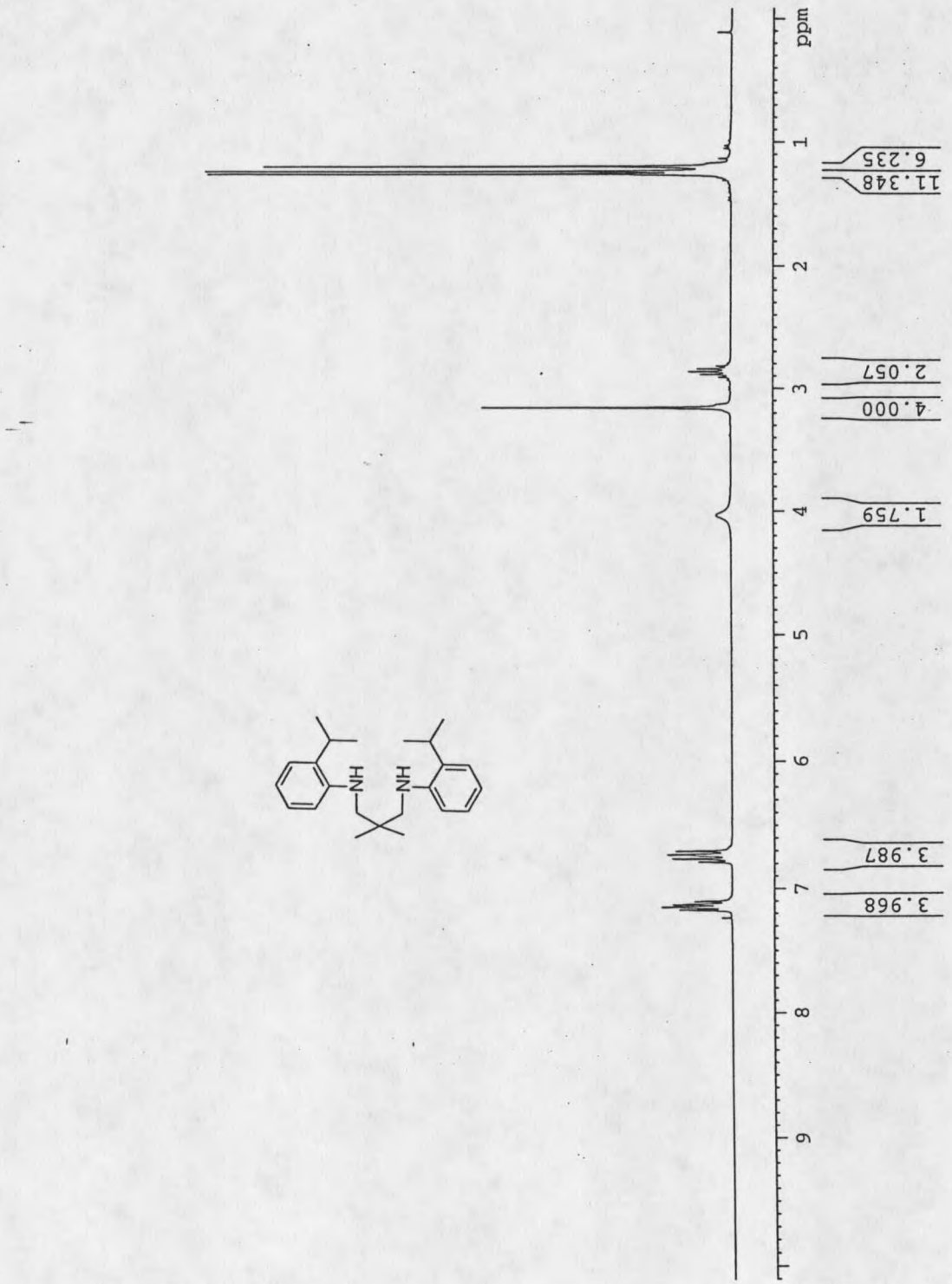


Figure 81. ^{1}H NMR Spectrum of *N,N'*-Bis(2-isopropylphenyl)-2,2-dimethylpropane-1,3-diamine (**25b**)

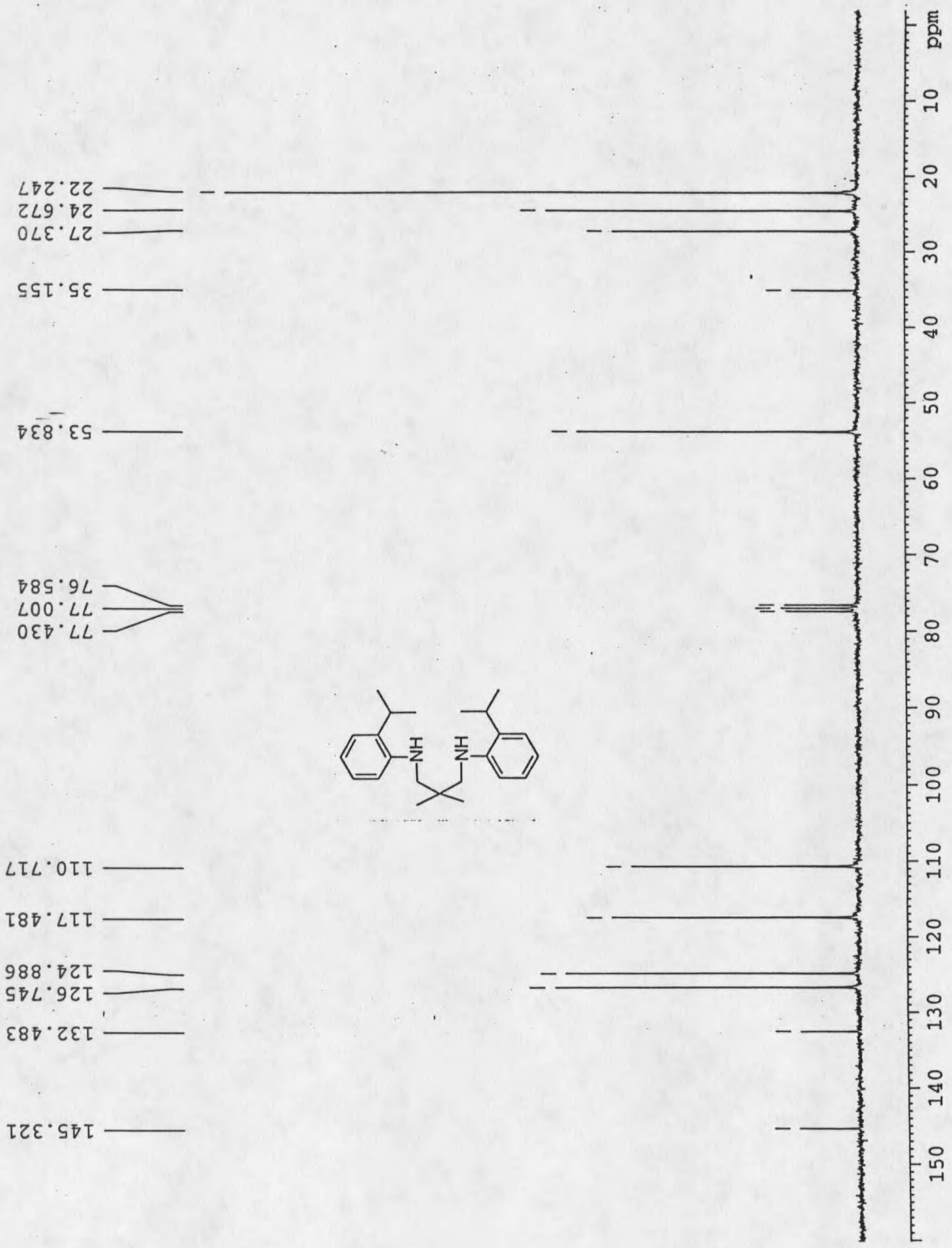


Figure 82. ^{13}C NMR Spectrum of *N,N'*-Bis(2-isopropylphenyl)-2,2-dimethylpropane-1,3-diamine (**25b**)

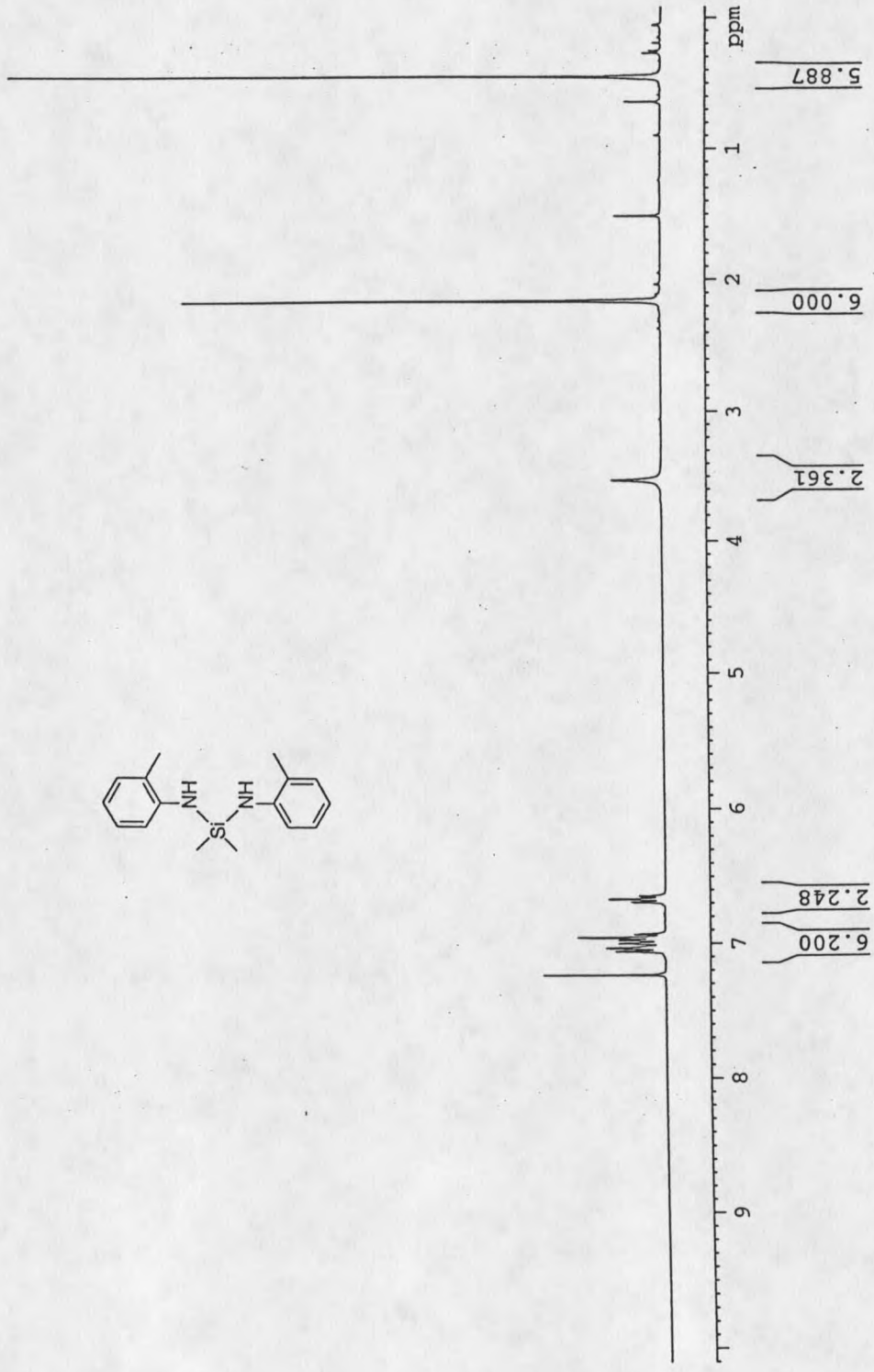


Figure 83. ^{1}H NMR Spectrum of Bis[(2-methyl)phenylamino]dimethylsilane (**24a**)

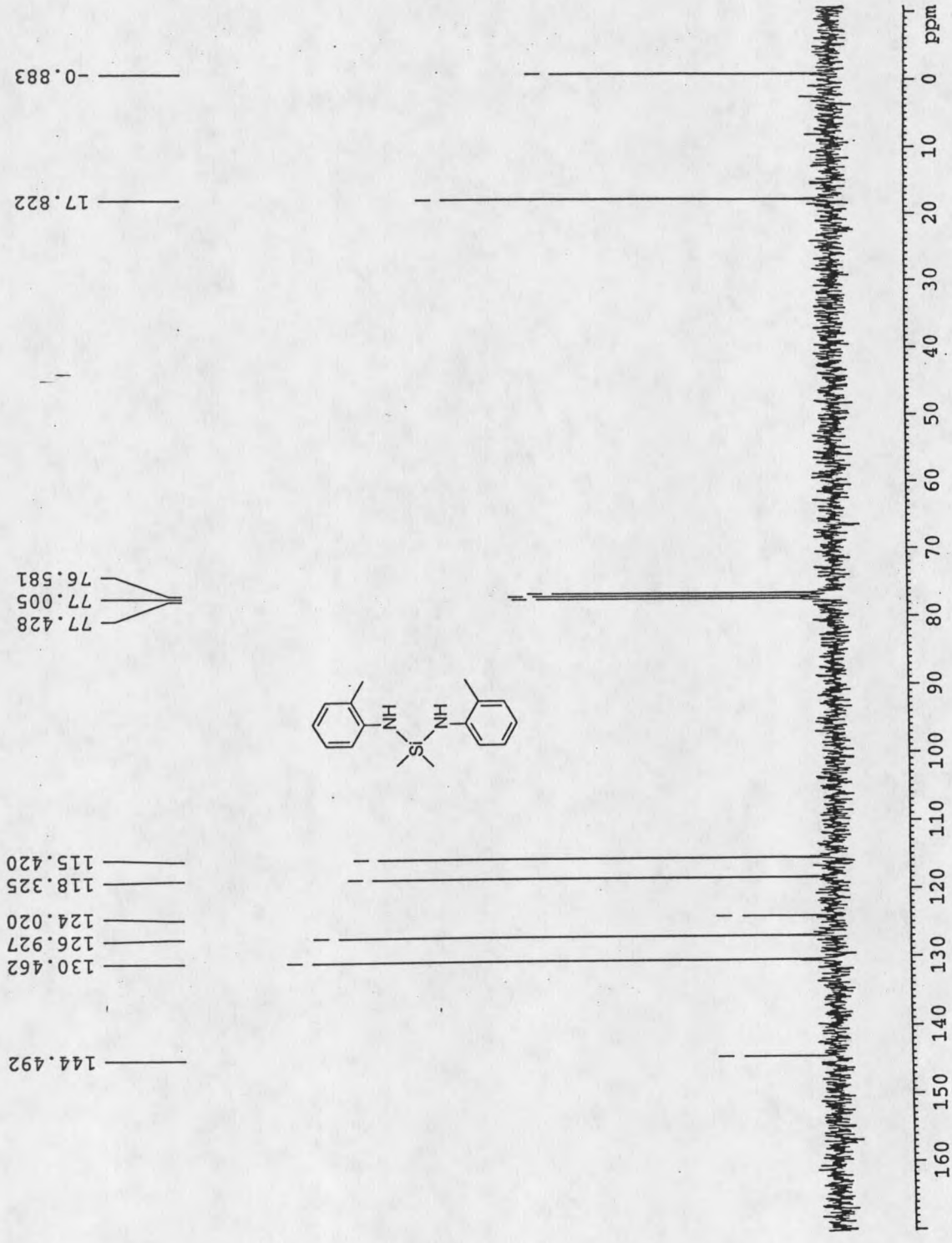


Figure 84. ^{13}C NMR Spectrum of Bis[(2-methyl)phenylamino]dimethylsilane (**24a**)

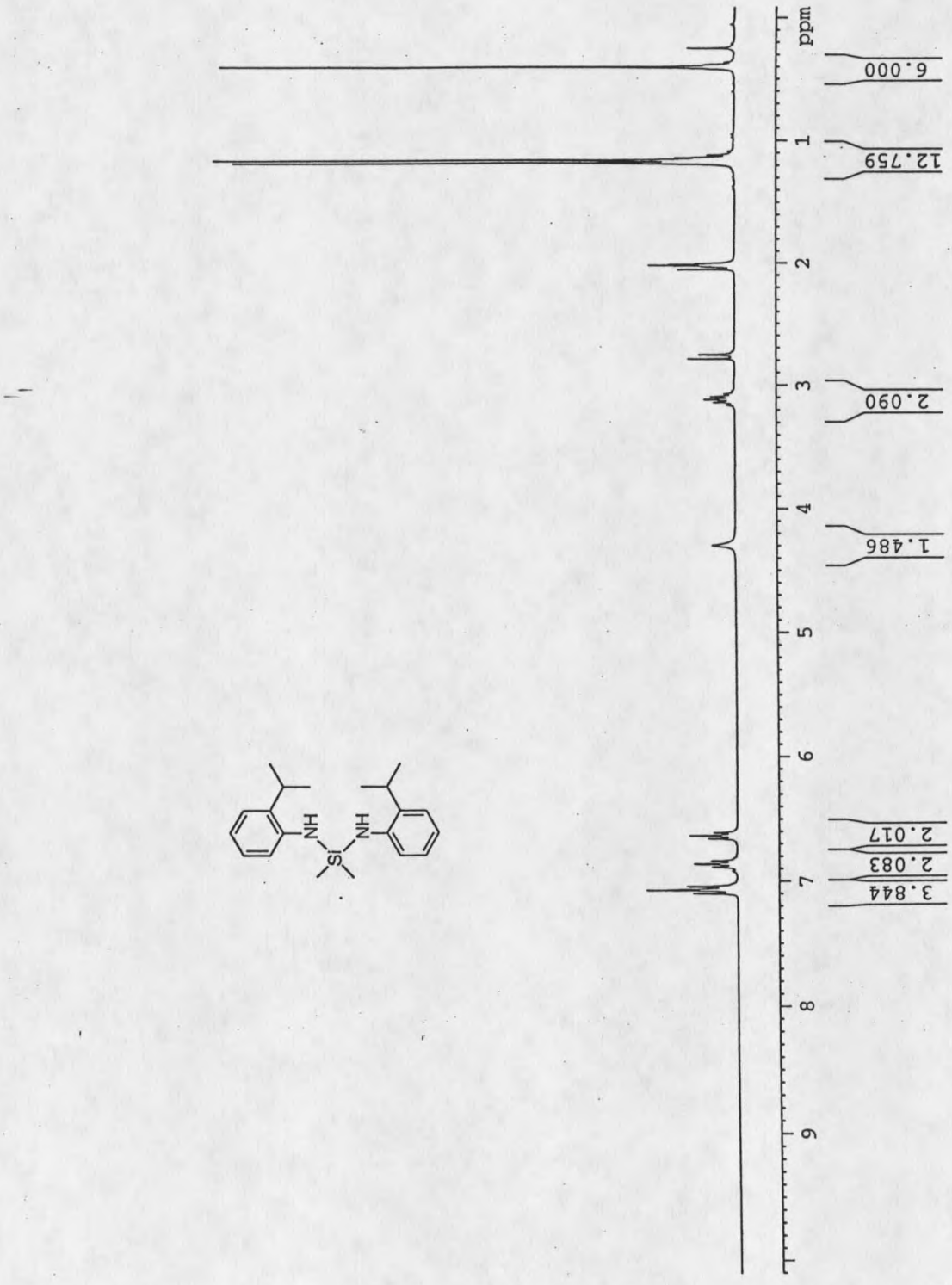


Figure 85. ^{1}H NMR Spectrum of Bis[(2- isopropyl)phenylamino]dimethylsilane (**24b**)

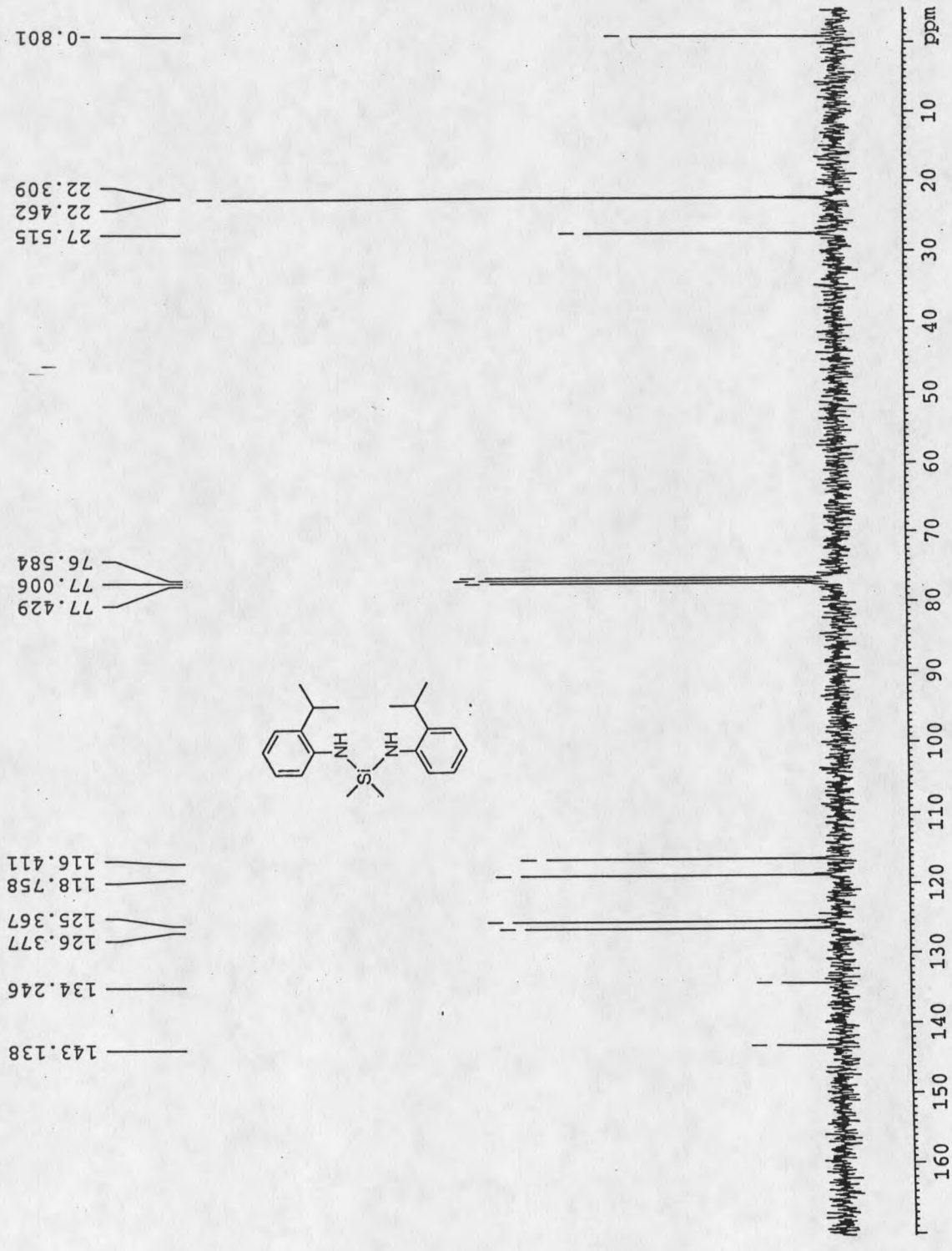


Figure 86. ^{13}C NMR Spectrum of Bis[(2- isopropyl)phenylamino]dimethylsilane **(24b)**

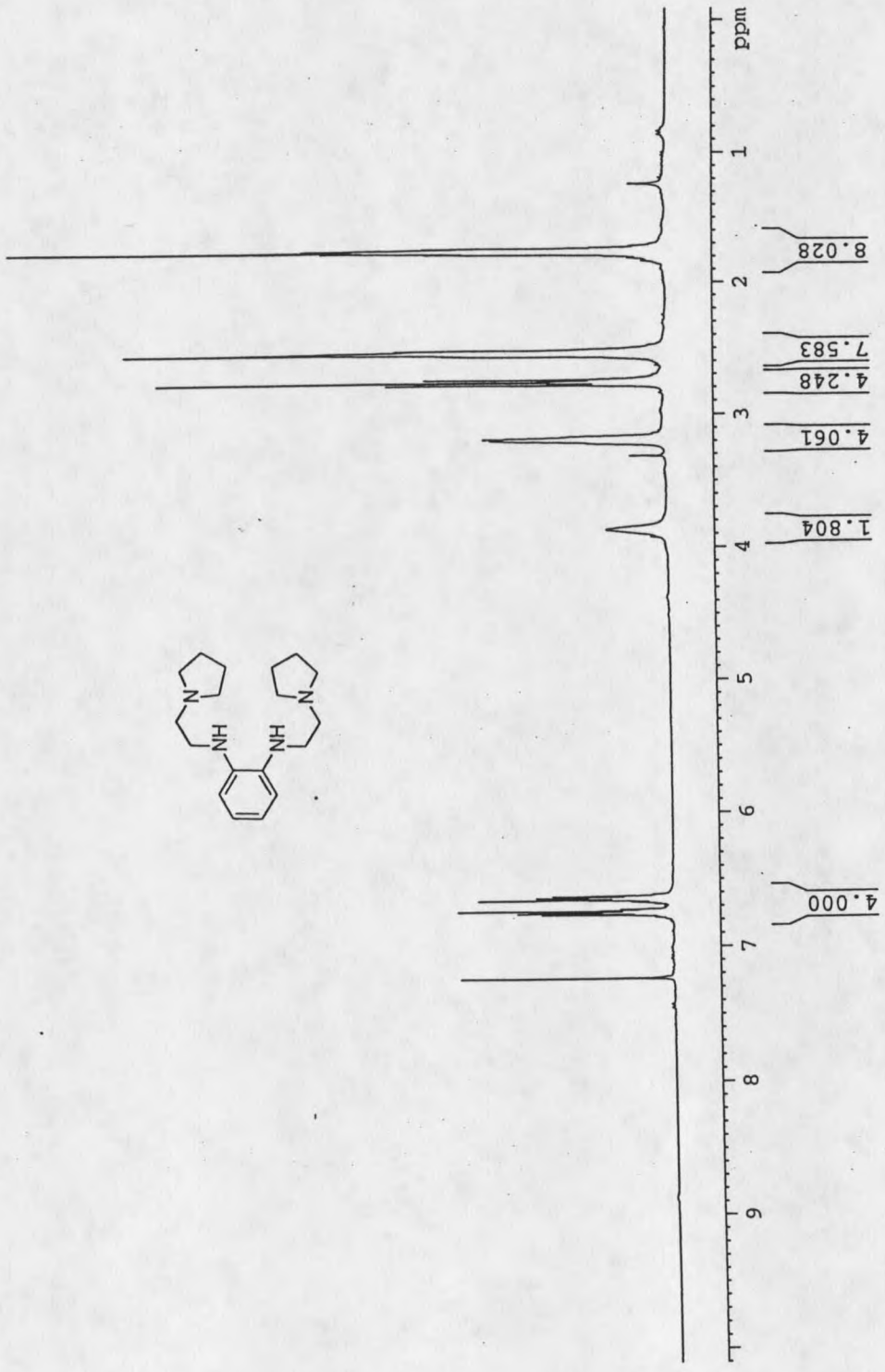


Figure 87. ^{1}H NMR Spectrum of *N,N'*-Bis(2-pyrrolidin-1-ylethyl)-1,2-phenylenediamine (**30**)

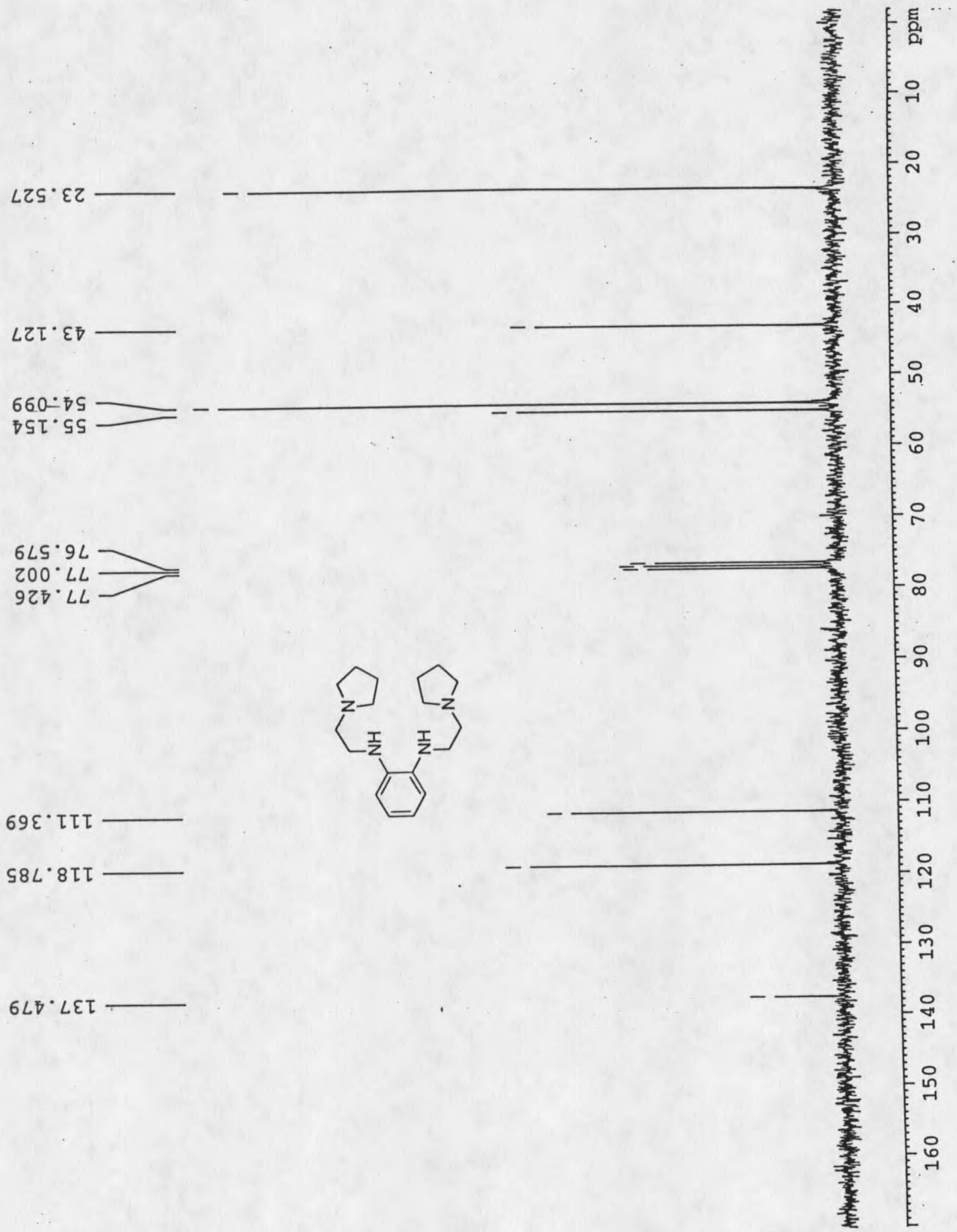


Figure 88. ^{13}C NMR Spectrum of *N,N'*-Bis(2-pyrrolidin-1-ylethyl)-1,2-phenylenediamine (**30**)

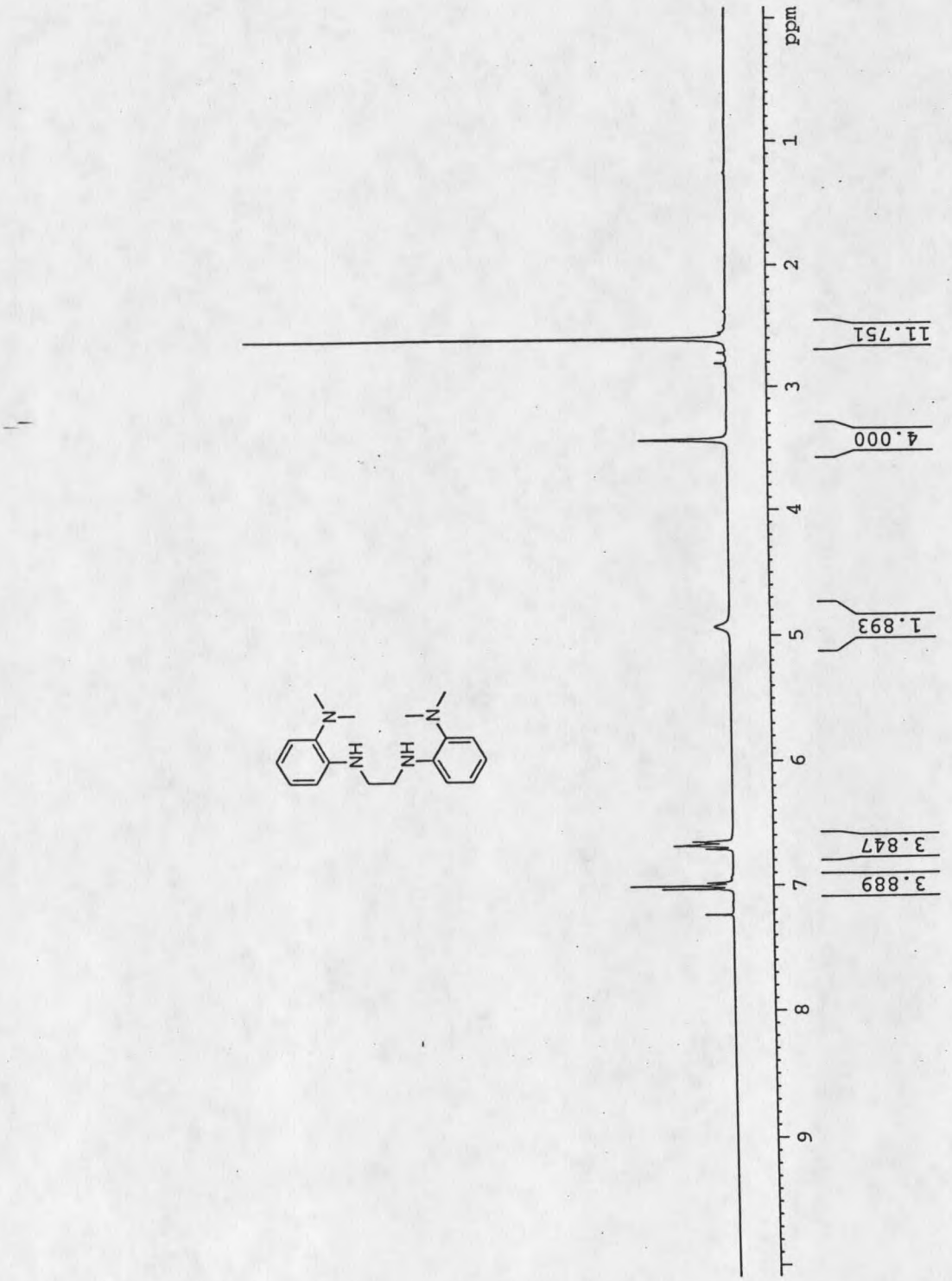


Figure 89. ^{1}H NMR Spectrum of *N,N'*-Bis[(2-dimethylamino)phenyl]ethane-1,2-diamine (**31**)

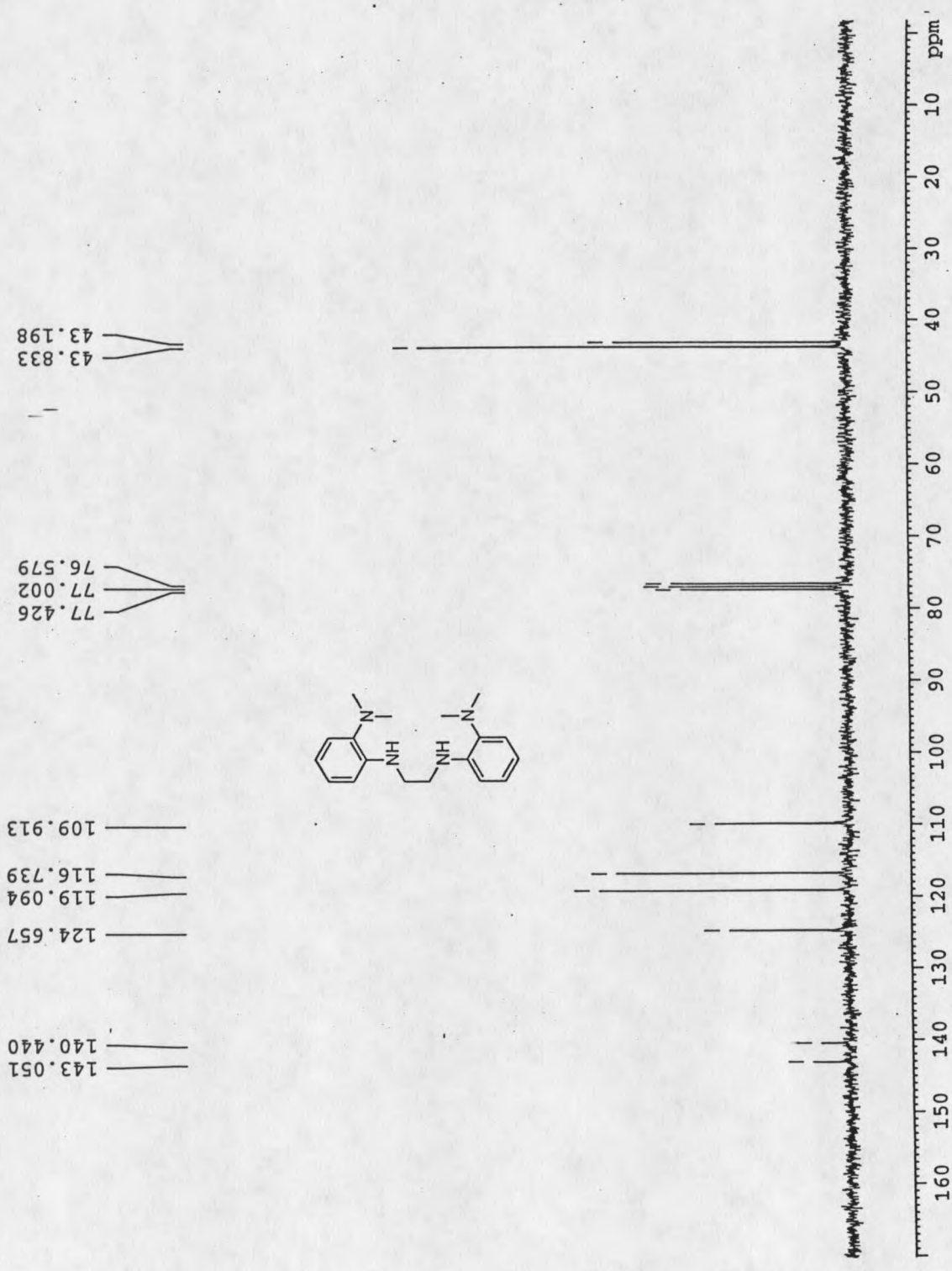


Figure 90. ^{13}C NMR Spectrum of *N,N'*-Bis[(2-dimethylamino)phenyl]ethane-1,2-diamine (**31**)

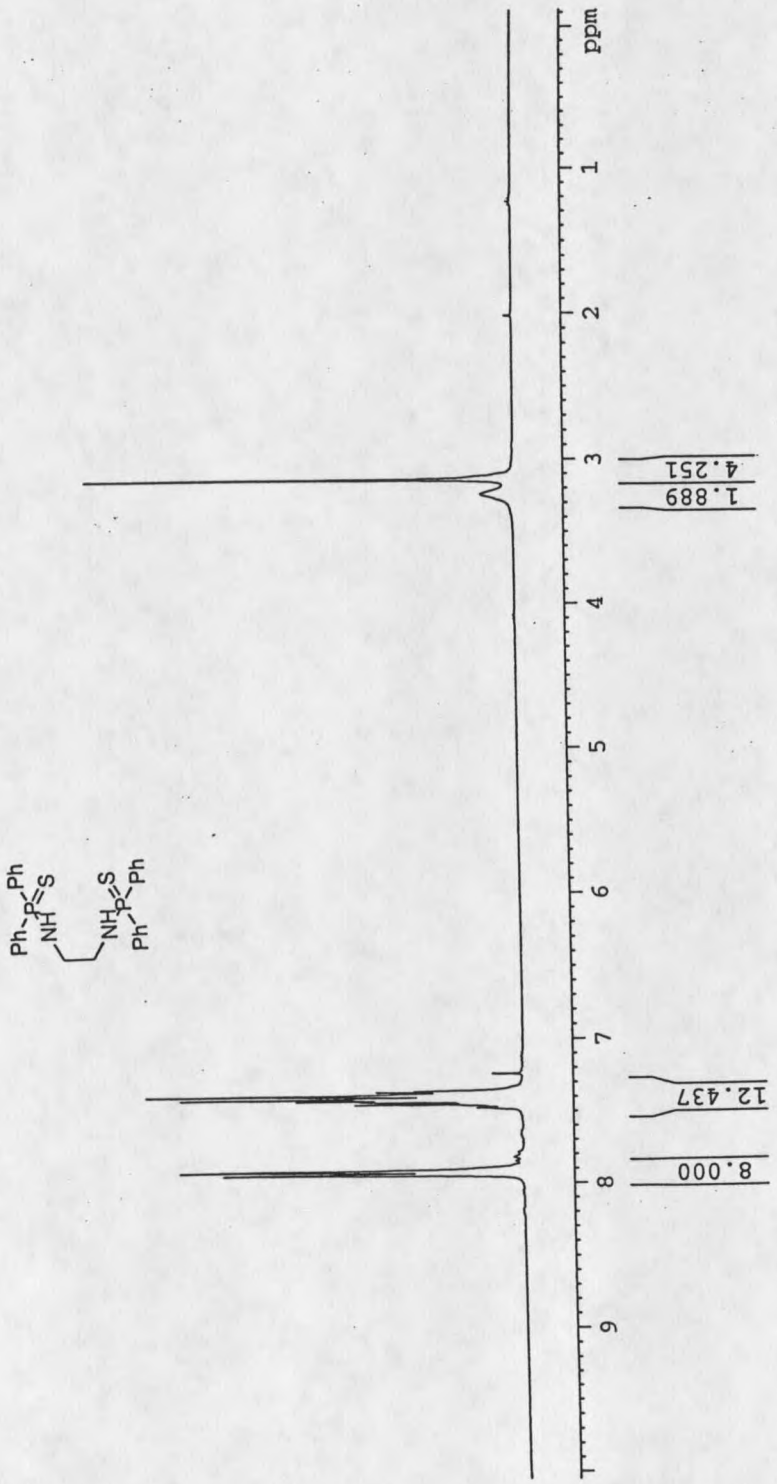


Figure 91. $^{1}H\{^{31}P\}$ NMR Spectrum of *N,N'*-Bis(*P,P*-diphenylthiophosphinyl)ethylenediamine (**55**)

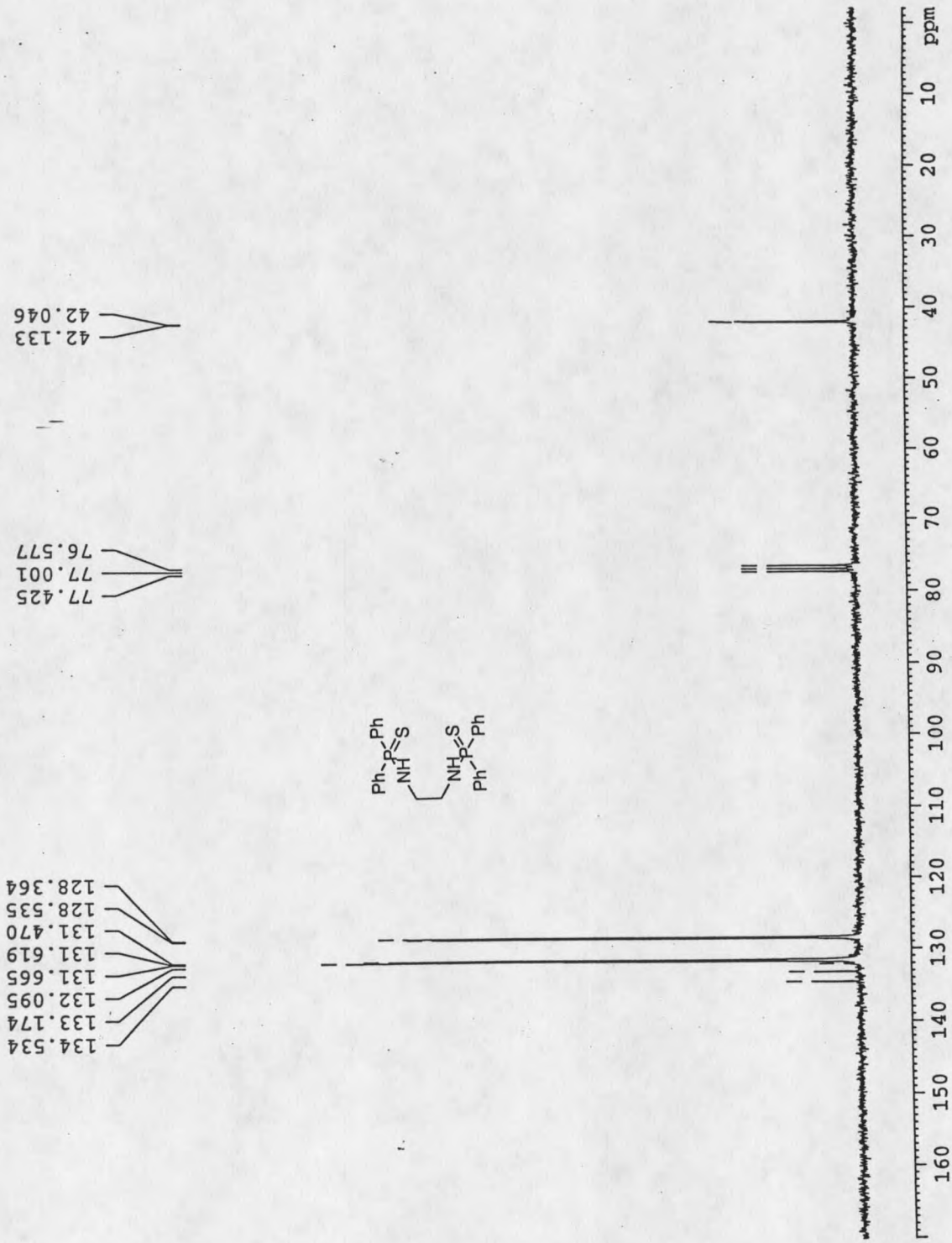


Figure 92. ^{13}C NMR Spectrum of *N,N'*-Bis(*P,P*-diphenylthiophosphinyl)ethylenediamine (**55**)

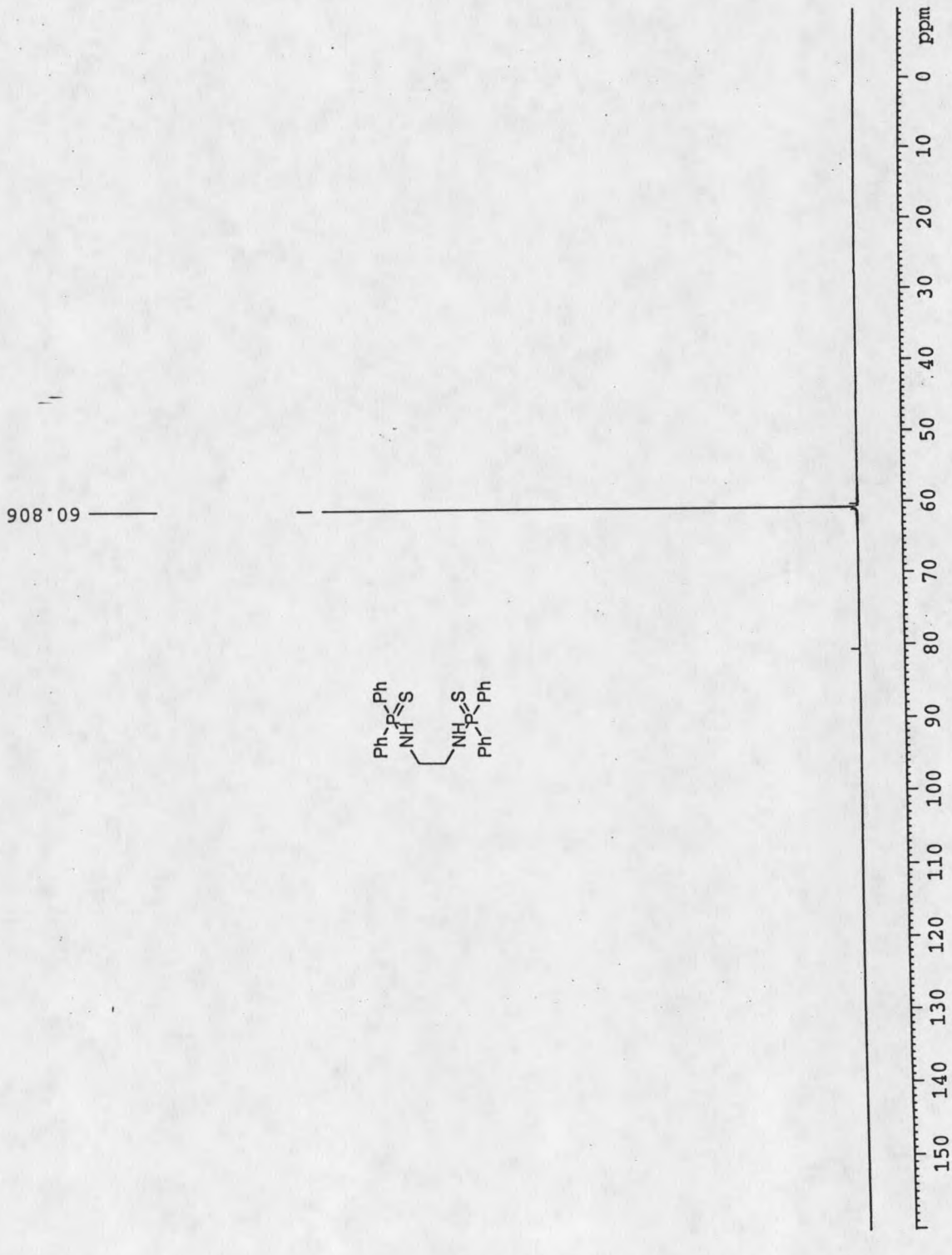


Figure 93. $^{31}P\{H\}$ NMR Spectrum of *N,N'*-Bis(*P,P*-diphenylthiophosphinyl)ethylenediamine (**55**)

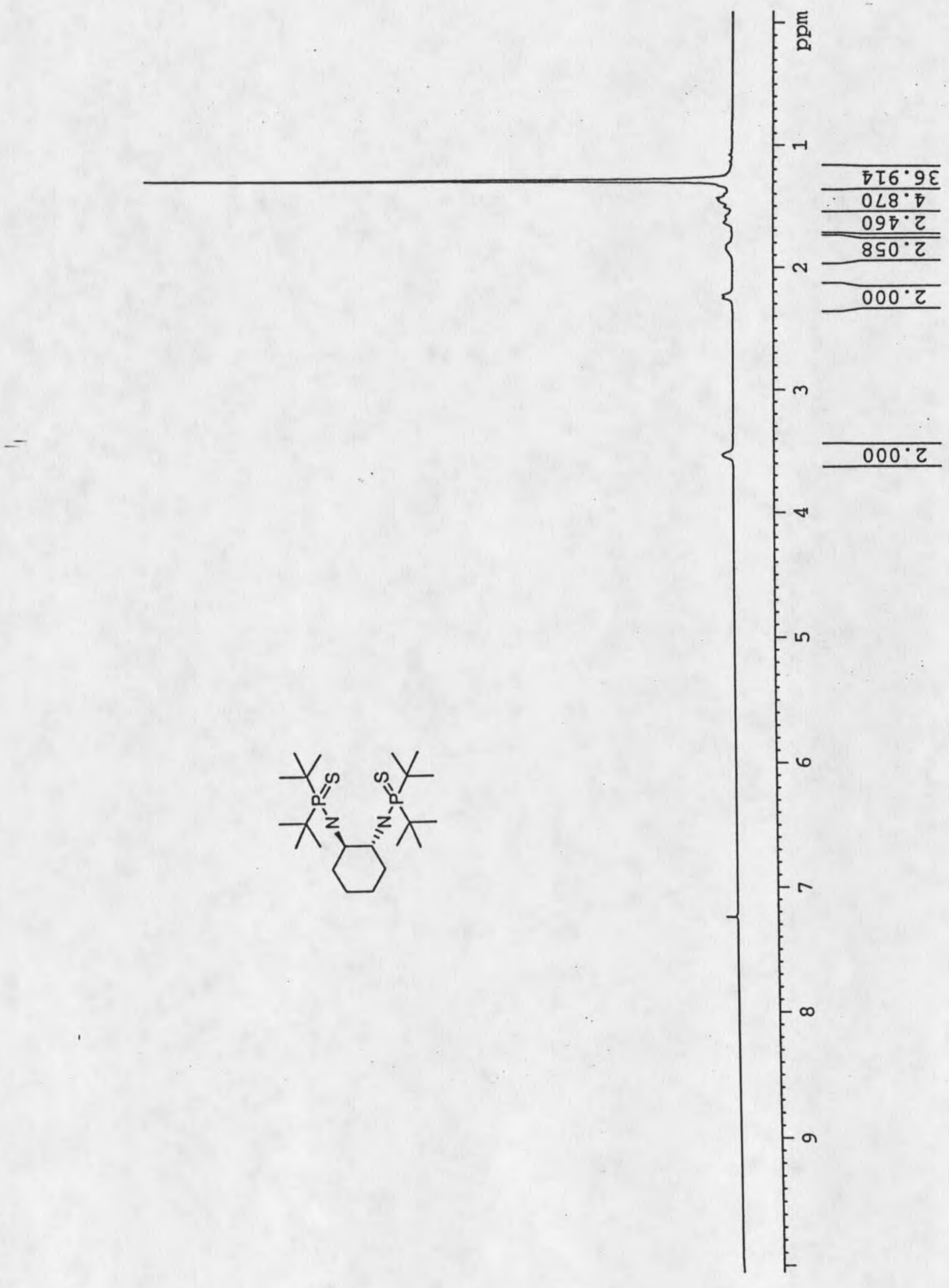


Figure 94. $^{1}H\{^{31}P\}$ NMR Spectrum of (1*R*,2*R*)-*N*,*N*′-Bis(*P*,*P*-di-*tert*-butylthio-phosphinyl)-cyclohexanediamine (**56**)

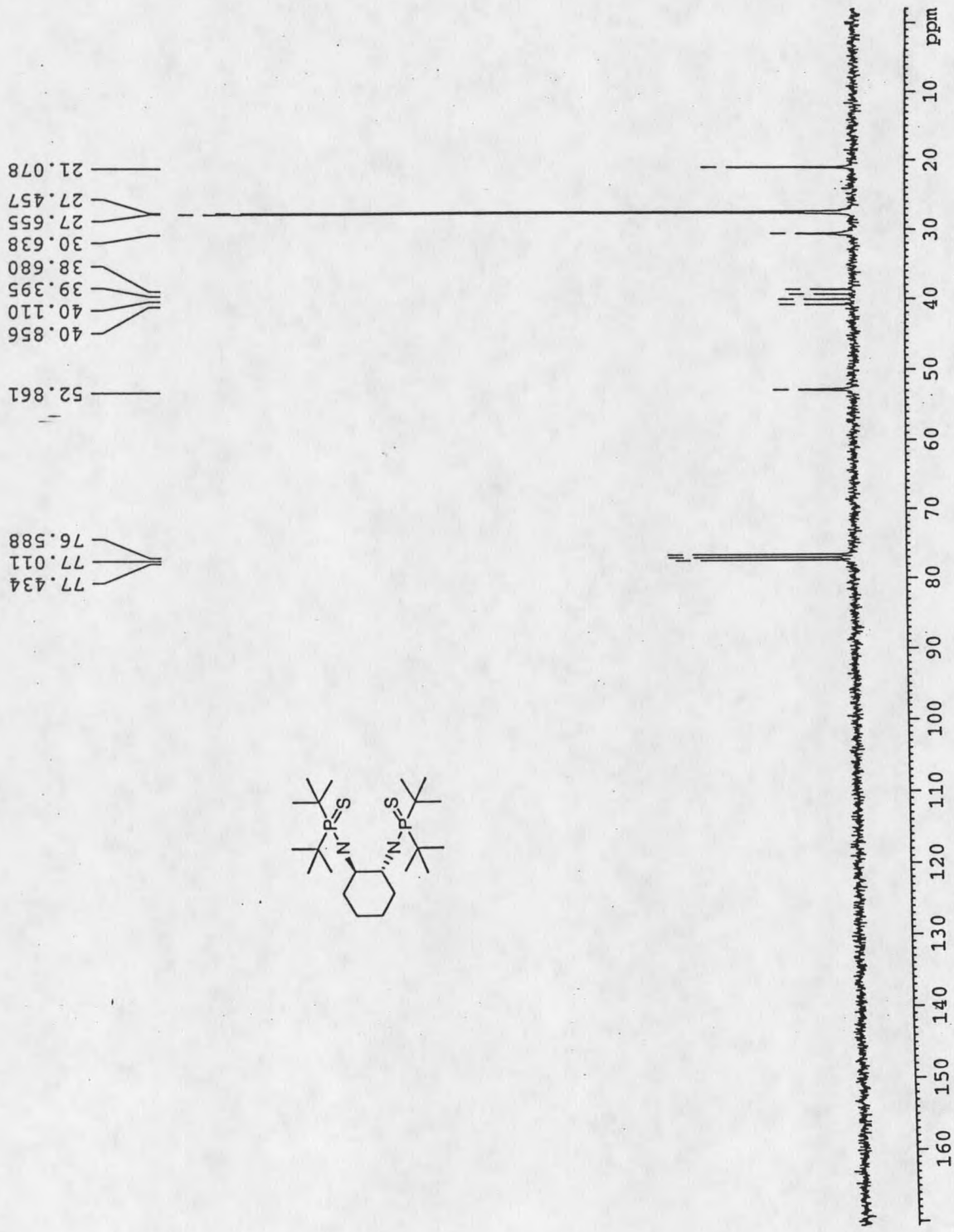


Figure 95. ^{13}C NMR Spectrum of (1*R*,2*R*)-*N*,*N'*-Bis(*P*,*P*-di-*tert*-butylthiophosphinyl)-cyclohexanediamine (**56**)

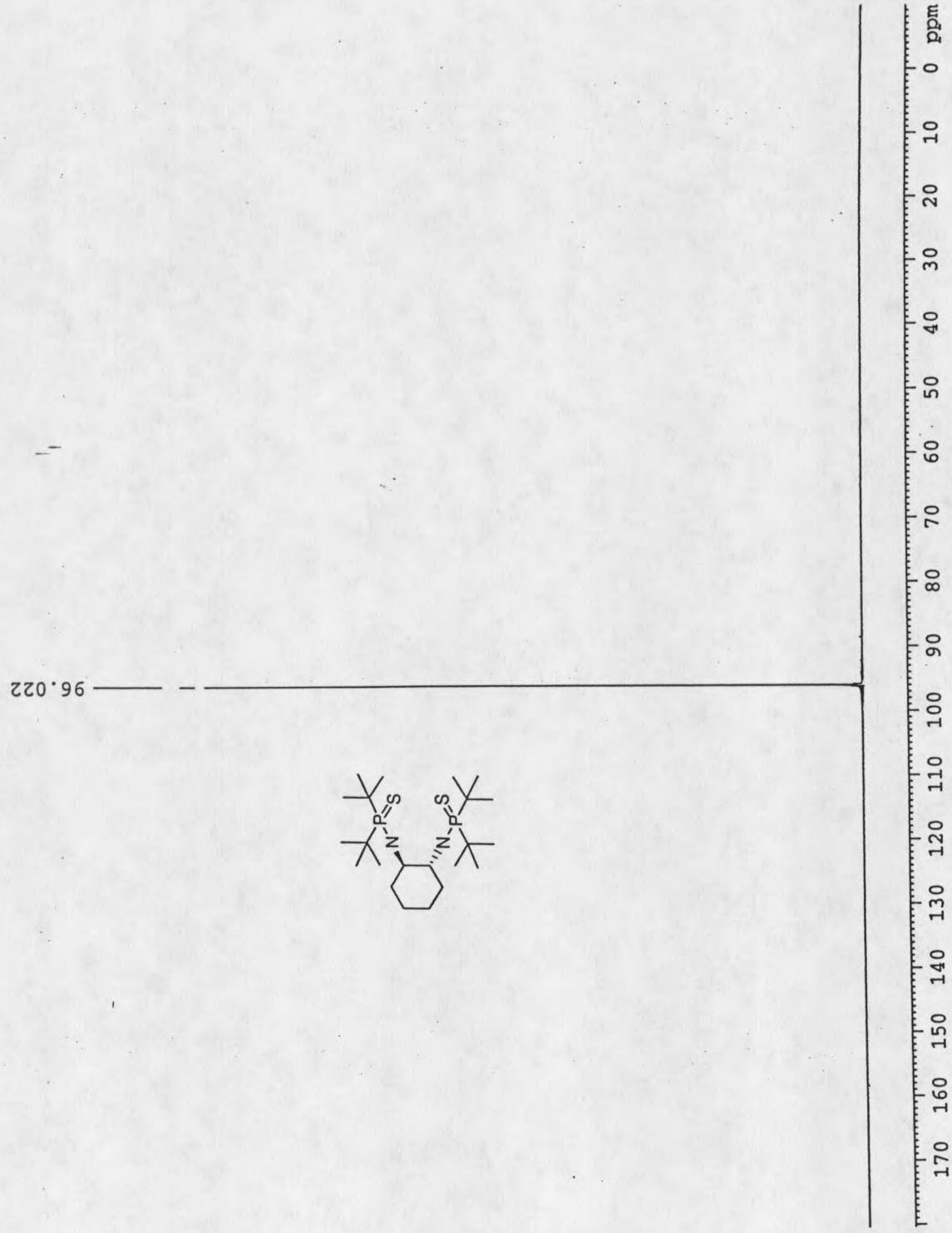


Figure 96. $^{31}P\{H\}$ NMR Spectrum of (1*R*,2*R*)-*N*,*N*'-Bis(*P*,*P*-di-*tert*-butylthiophosphinyl)-cyclohexanediamine (**56**)

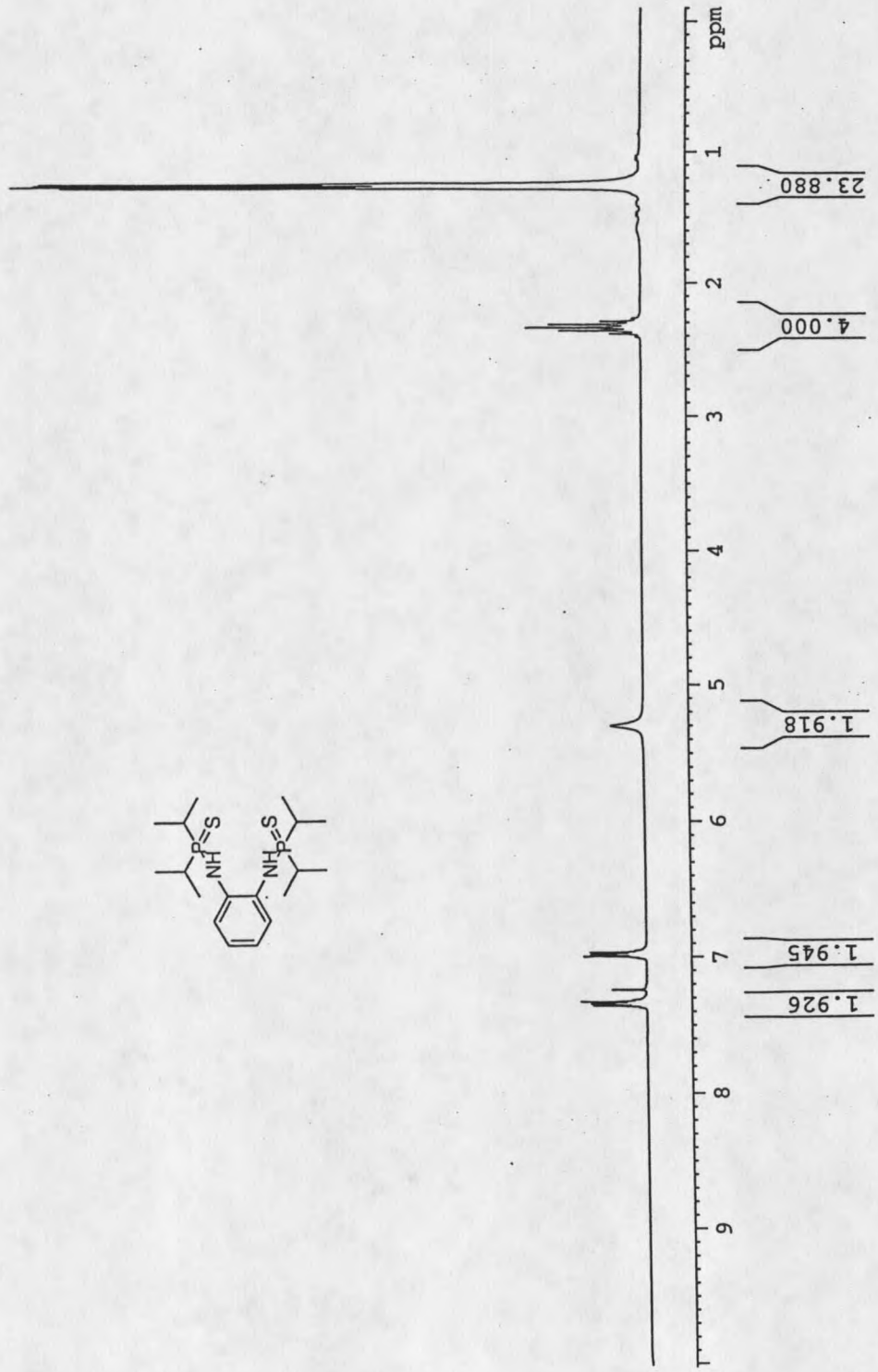


Figure 97. $^{1}H\{^{31}P\}$ NMR Spectrum of *N,N'*-Bis(*P,P*-diisopropylthiophosphinyl)-1,2-phenylenediamine (**57a**)

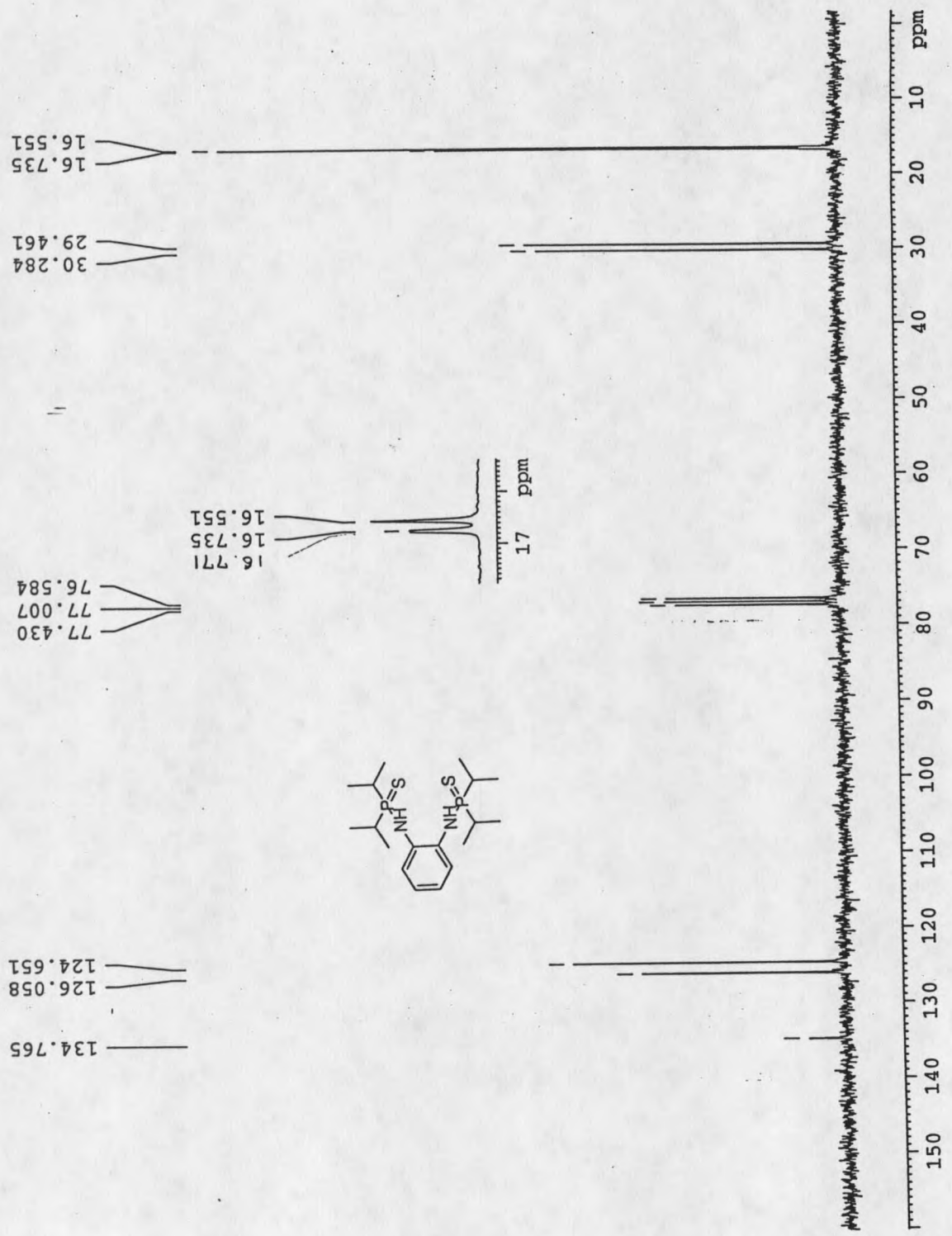


Figure 98. ^{13}C NMR Spectrum of *N,N'*-Bis(*P,P*-diisopropylthiophosphinyl)-1,2-phenylenediamine (**57a**)

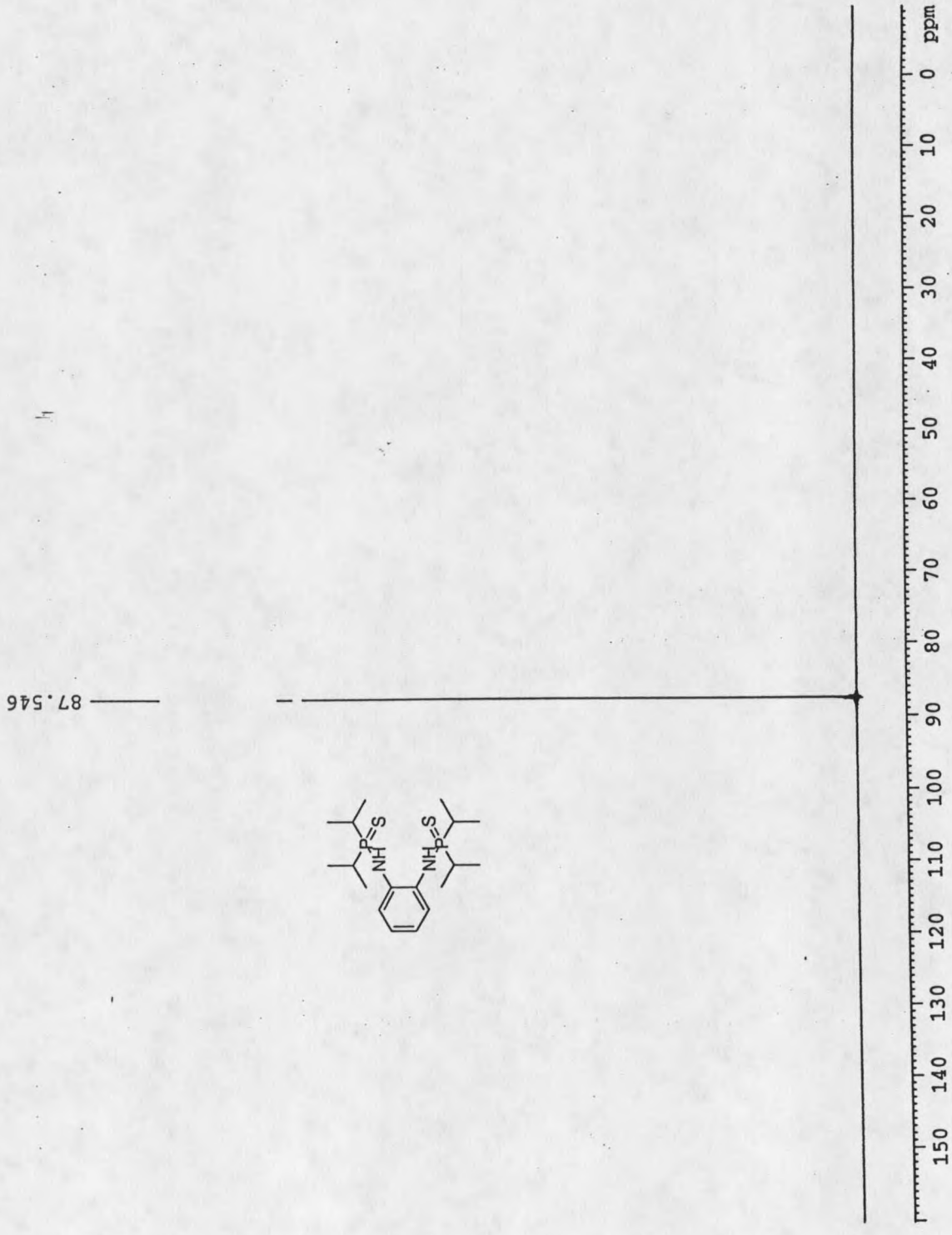


Figure 99. $^{31}P\{H\}$ NMR Spectrum of *N,N'*-Bis(*P,P*-diisopropylthiophosphinyl)-1,2-phenylenediamine (**57a**)

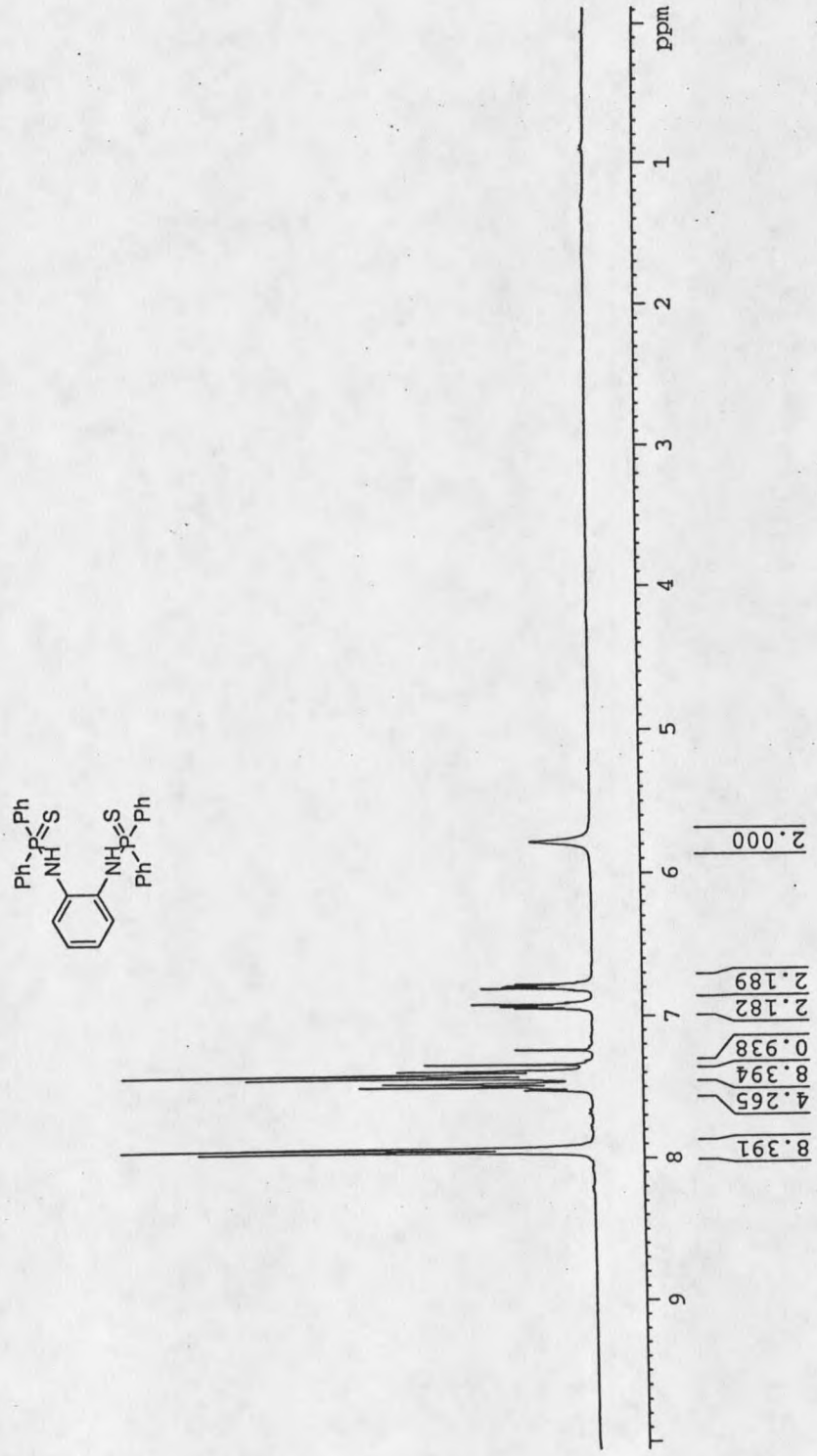


Figure 100. $^{1}H\{^{31}P\}$ NMR Spectrum of *N,N'*-Bis(*P,P*-diphenylthiophosphinyl)-1,2-phenylenediamine (**57b**)

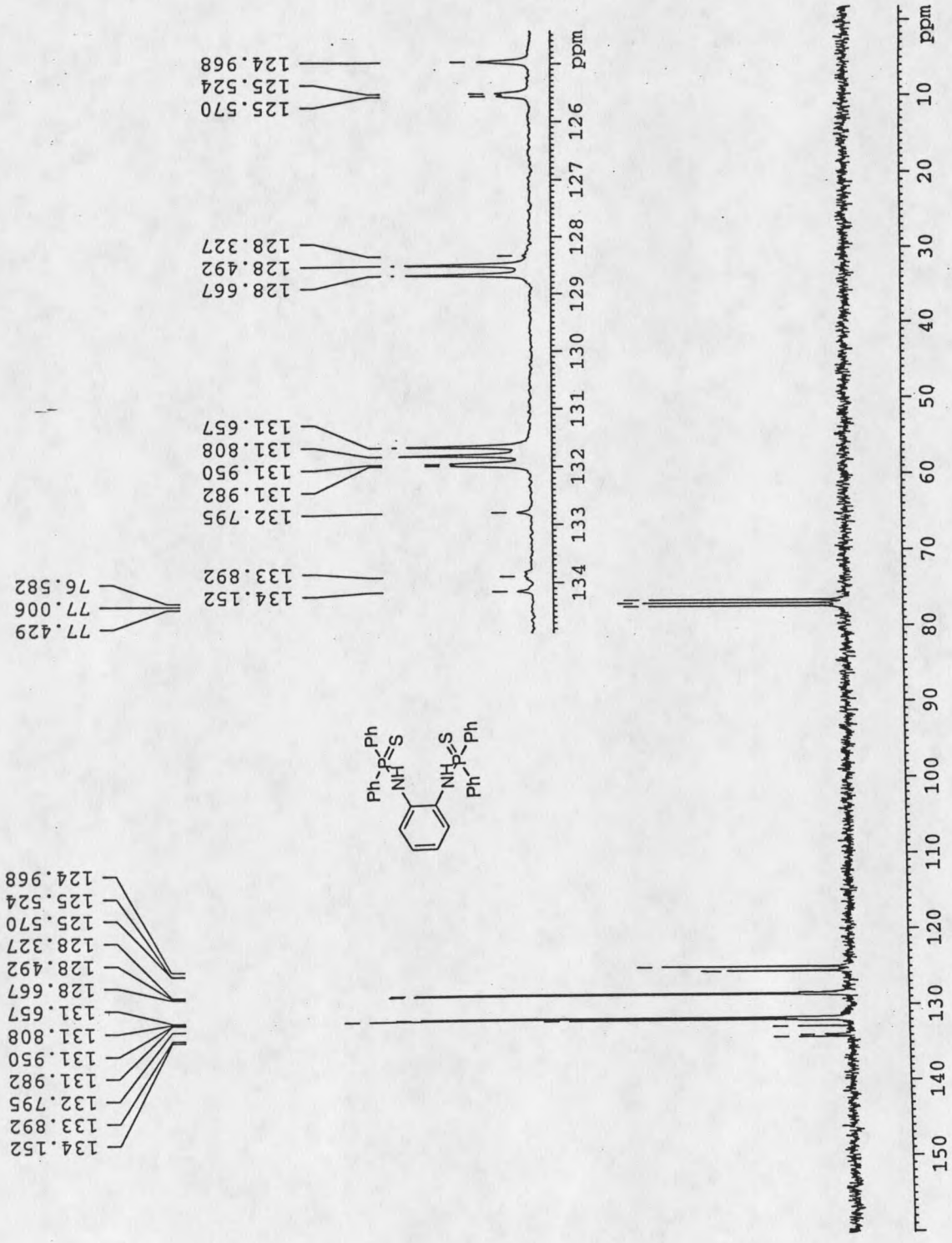


Figure 101. ^{13}C NMR Spectrum of *N,N'*-Bis(*P,P*-diphenylthiophosphinyl)-1,2-phenylenediamine (**57b**)

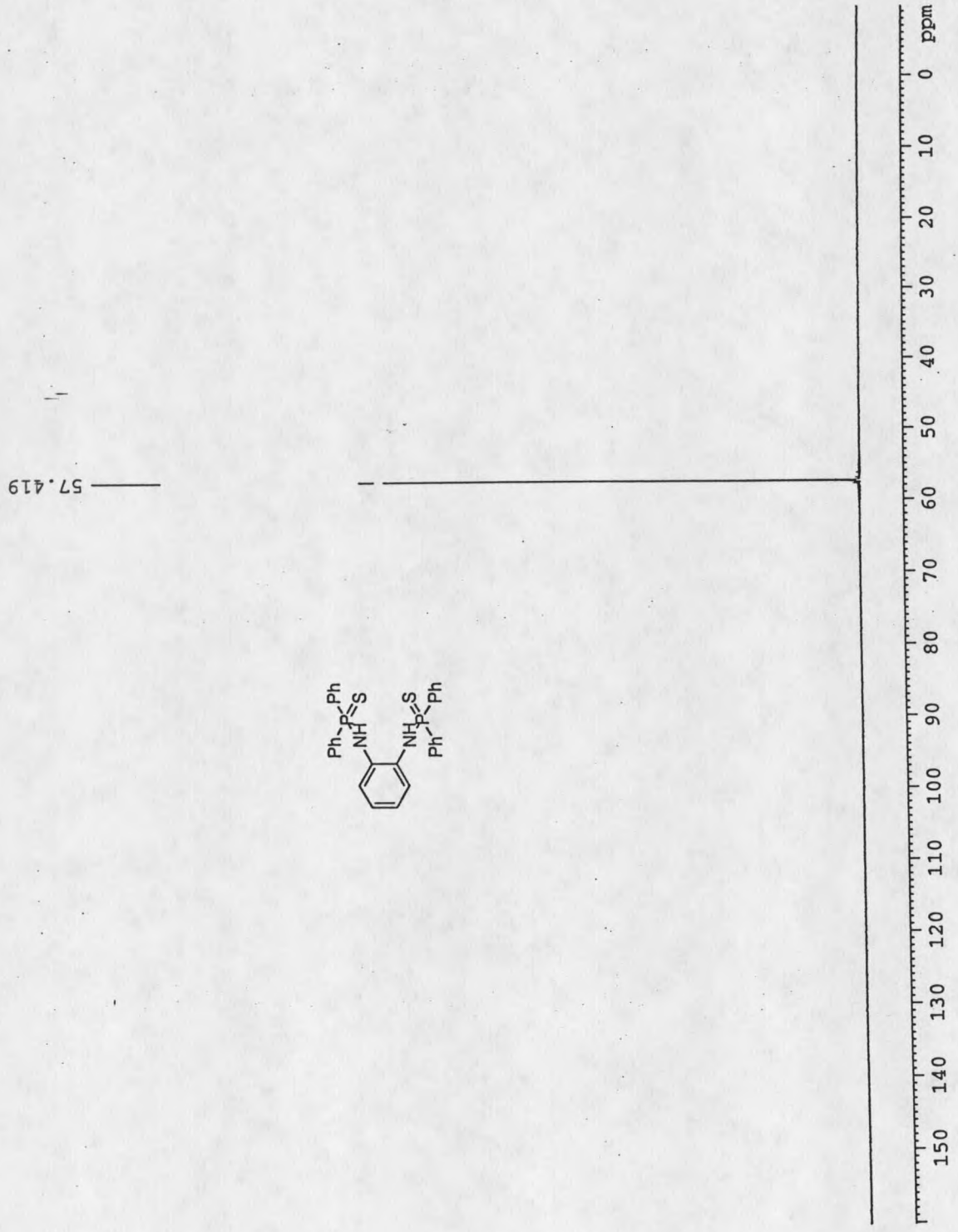


Figure 102. $^{31}P\{H\}$ NMR Spectrum of *N,N'*-Bis(*P,P*-diphenylthiophosphinyl)-1,2-phenylenediamine (**57b**)

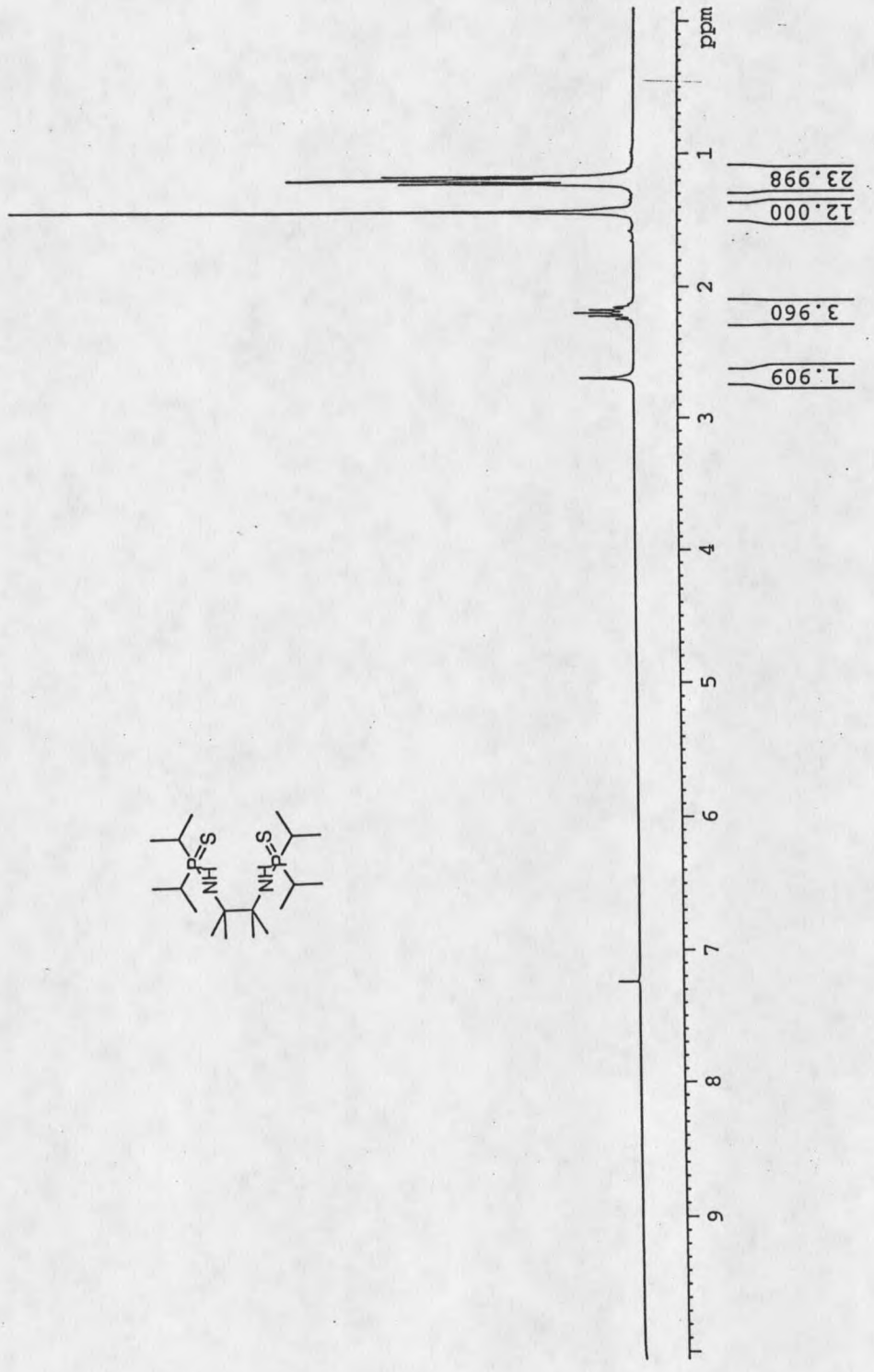


Figure 103. $^{1}H\{^{31}P\}$ NMR Spectrum of *N,N'*-Bis(*P,P*-diisopropylthiophosphinyl)-2,3-dimethyl-2,3-butanediamine (**58a**)

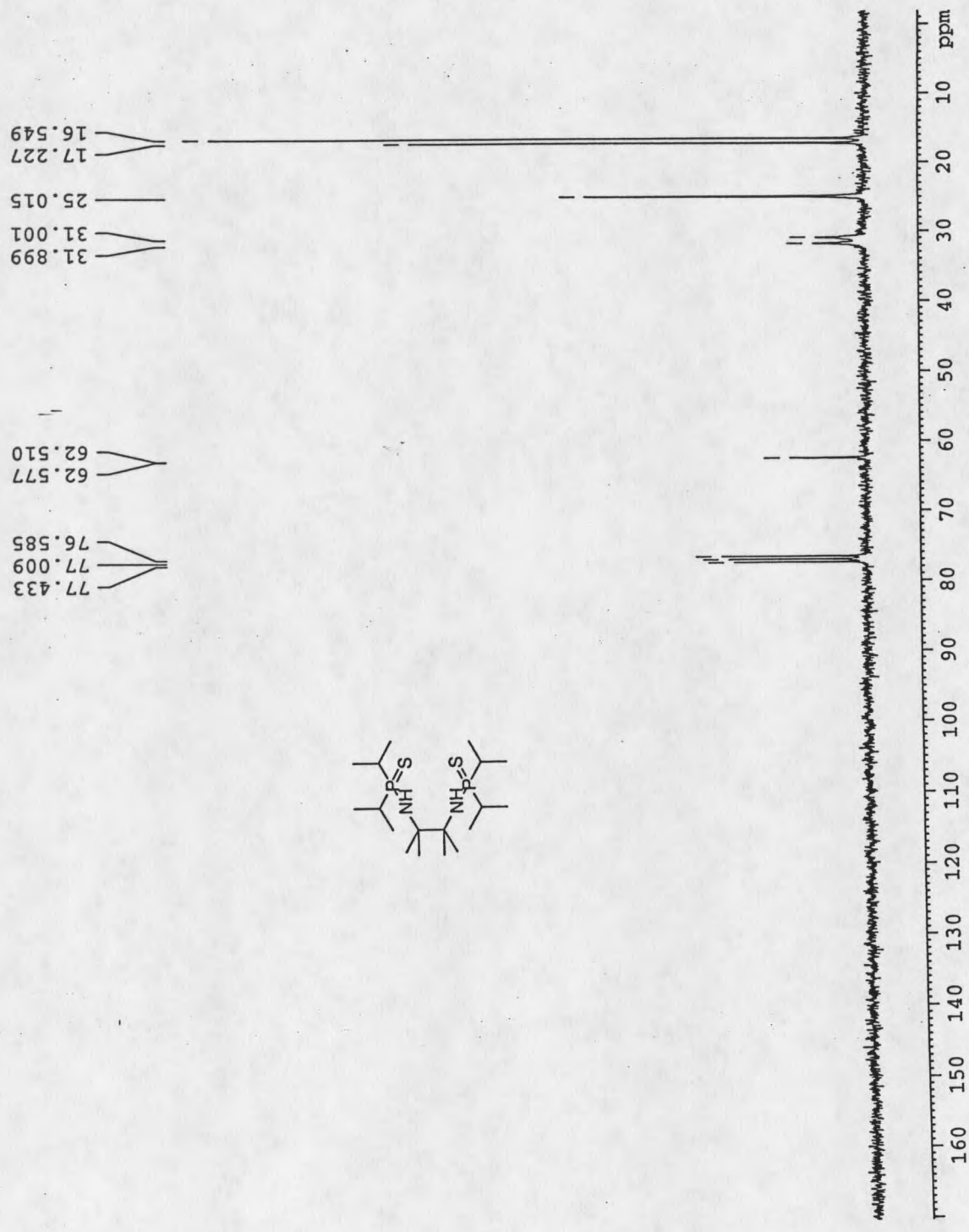


Figure 104. ^{13}C NMR Spectrum of *N,N'*-Bis(*P,P*-diisopropylthiophosphinyl)-2,3-dimethyl-2,3-butanediamine (**58a**)

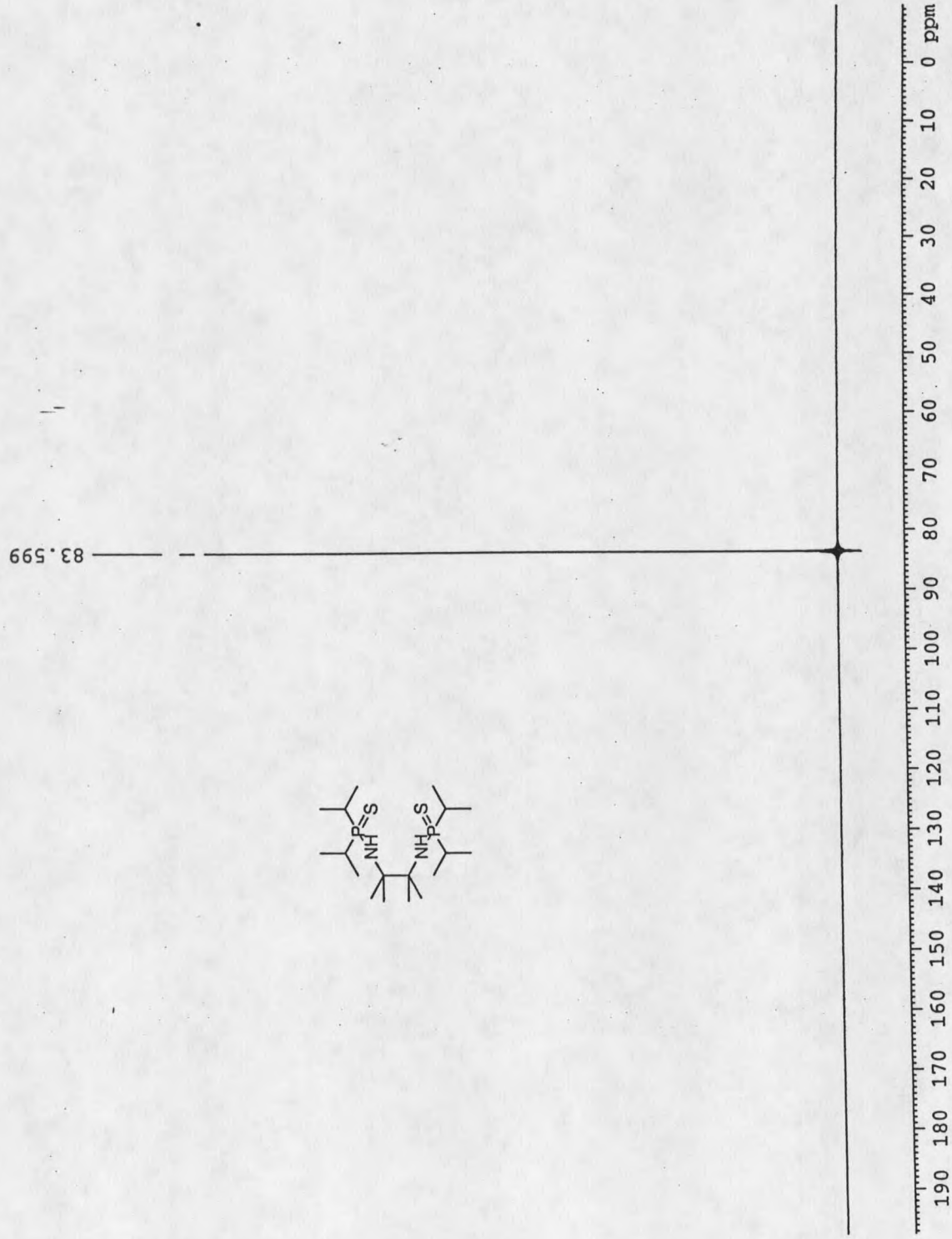


Figure 105. $^{31}P\{H\}$ NMR Spectrum of *N,N'*-Bis(*P,P*-diisopropylthiophosphinyl)-2,3-dimethyl-2,3-butanediamine (**58a**)

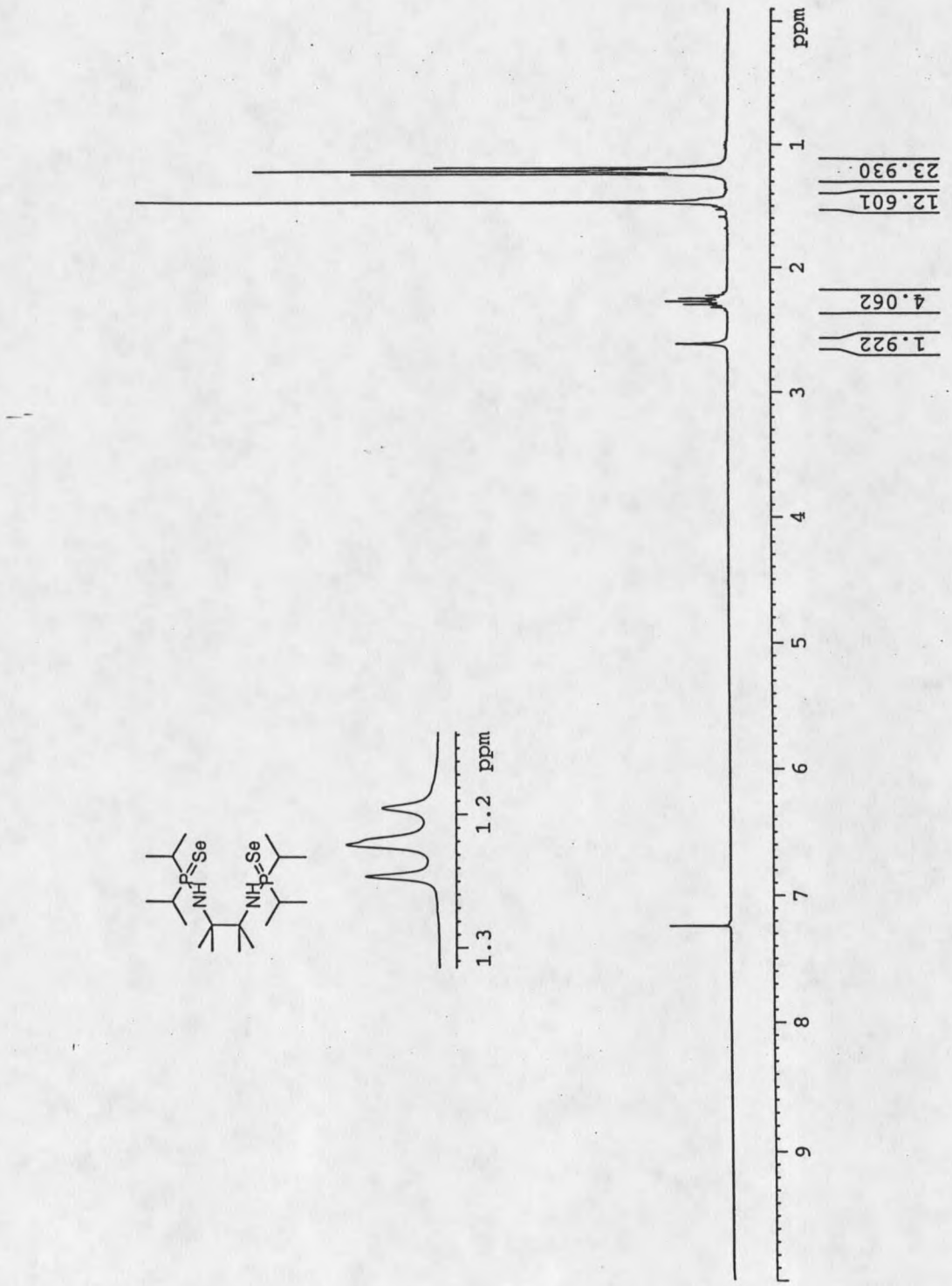


Figure 106. $^{1}H\{^{31}P\}$ NMR Spectrum of *N,N'*-Bis(*P,P*-diisopropylselenophosphinyl)-2,3-dimethyl-2,3-butanediamine (**58d**)

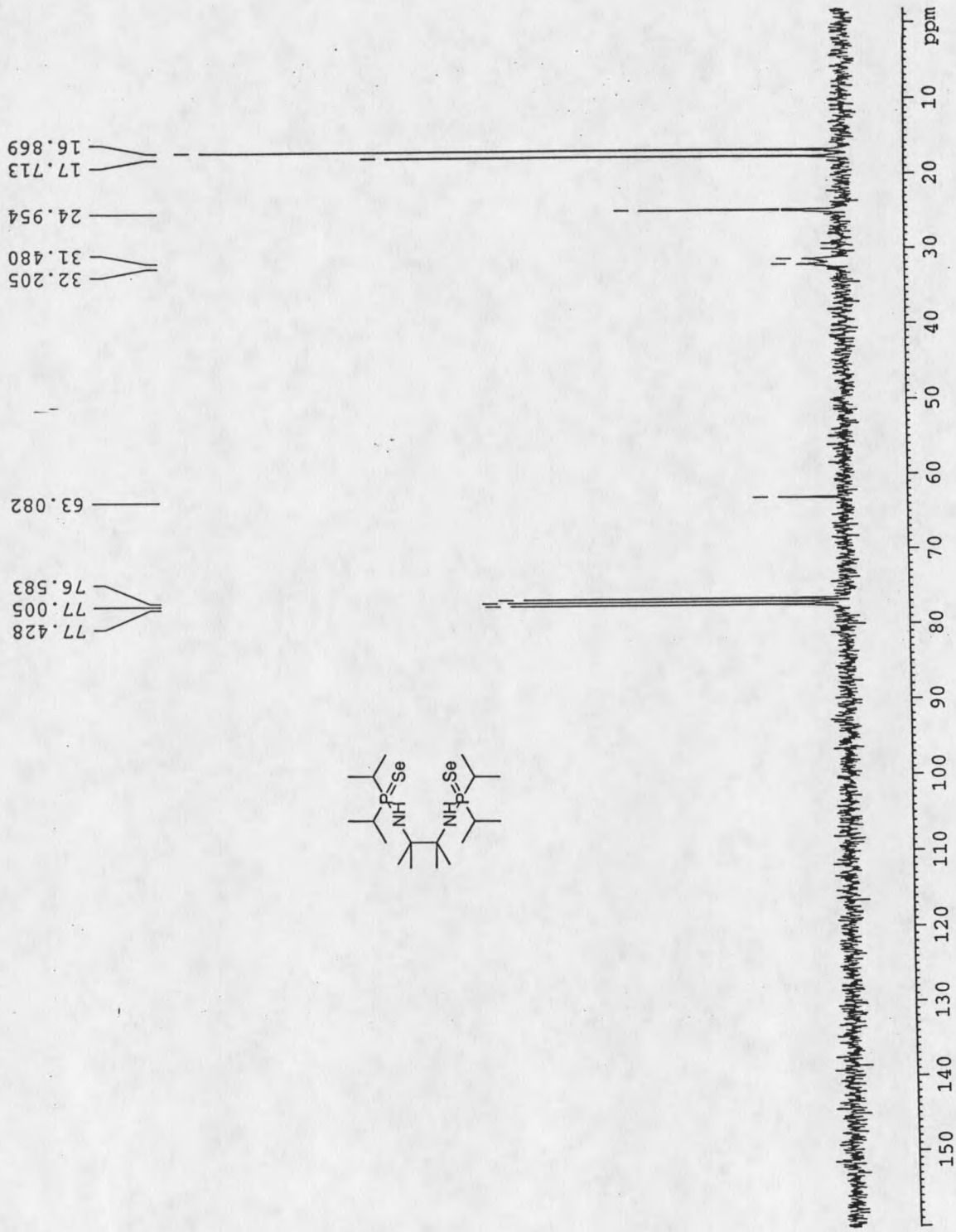


Figure 107. ^{13}C NMR Spectrum of *N,N'*-Bis(*P,P*-diisopropylselenophosphinyl)-2,3-dimethyl-2,3-butanediamine (**58d**)

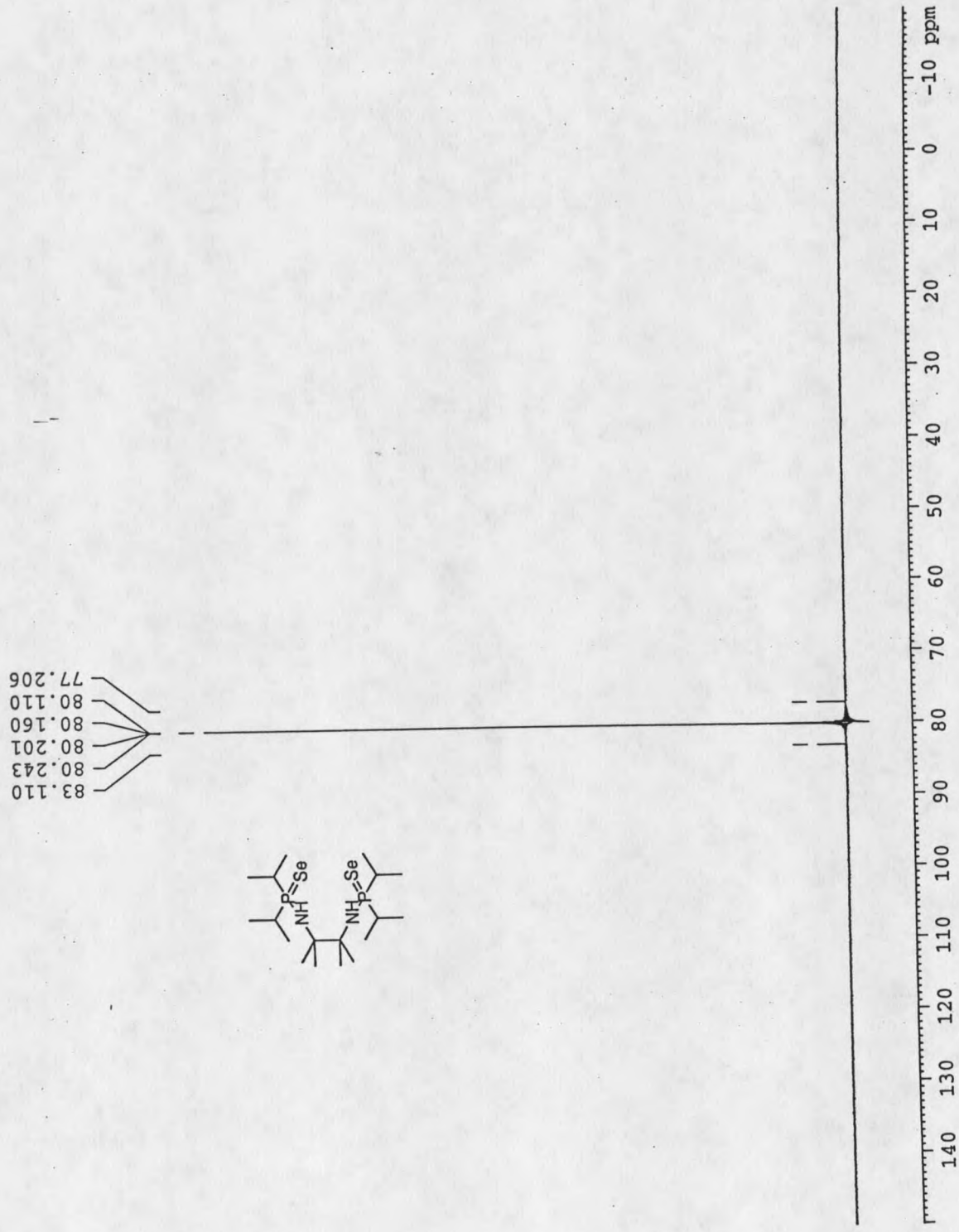


Figure 108. $^{31}P\{H\}$ NMR Spectrum of *N,N'*-Bis(*P,P*-diisopropylselenophosphinyl)-2,3-dimethyl-2,3-butanediamine (**58d**)

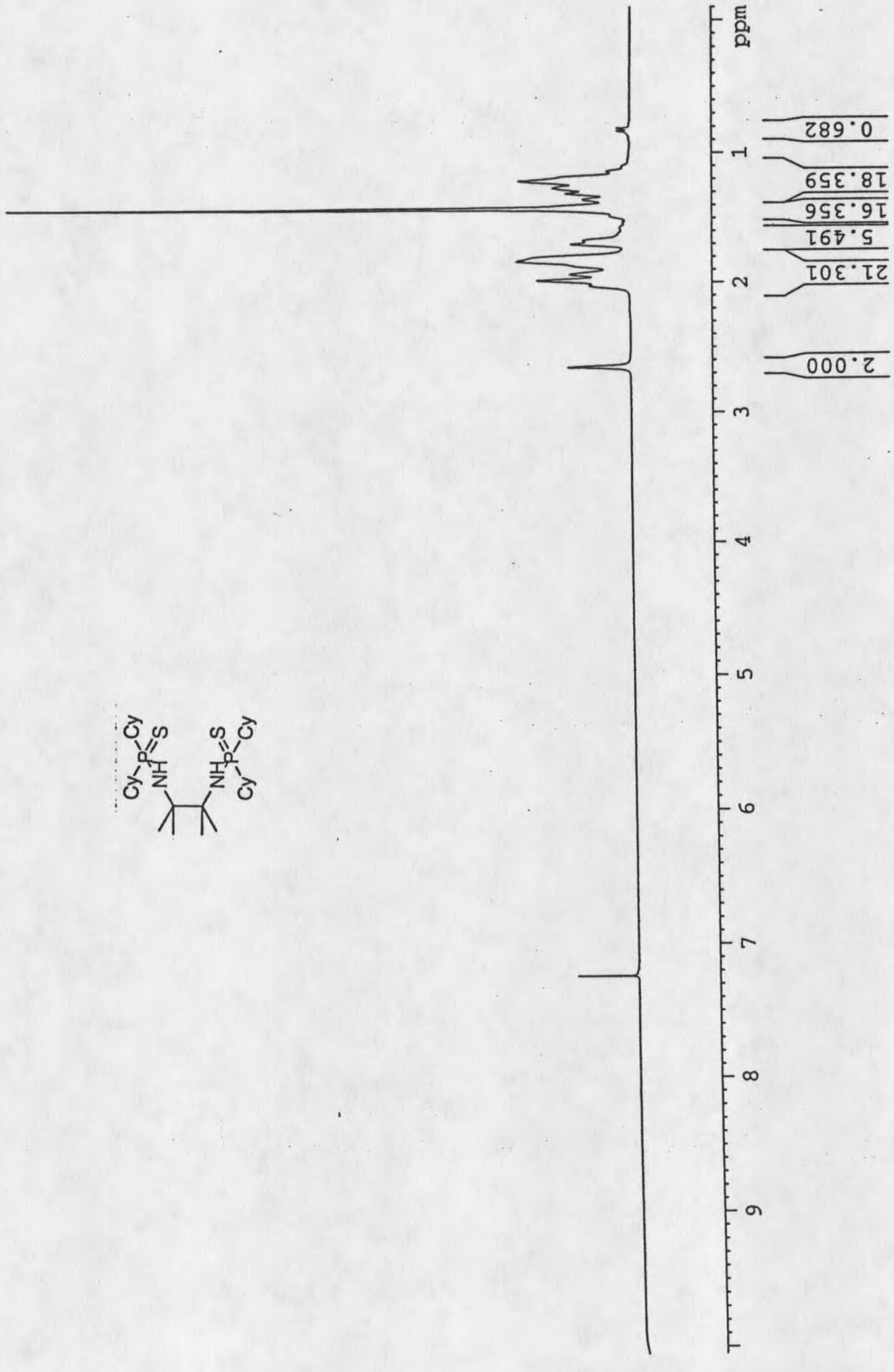


Figure 109. $^{1}H\{^{31}P\}$ NMR Spectrum of *N,N'*-Bis(*P,P*-dicyclohexylthiophosphinyl)-2,3-dimethyl-2,3-butanediamine (**58e**)

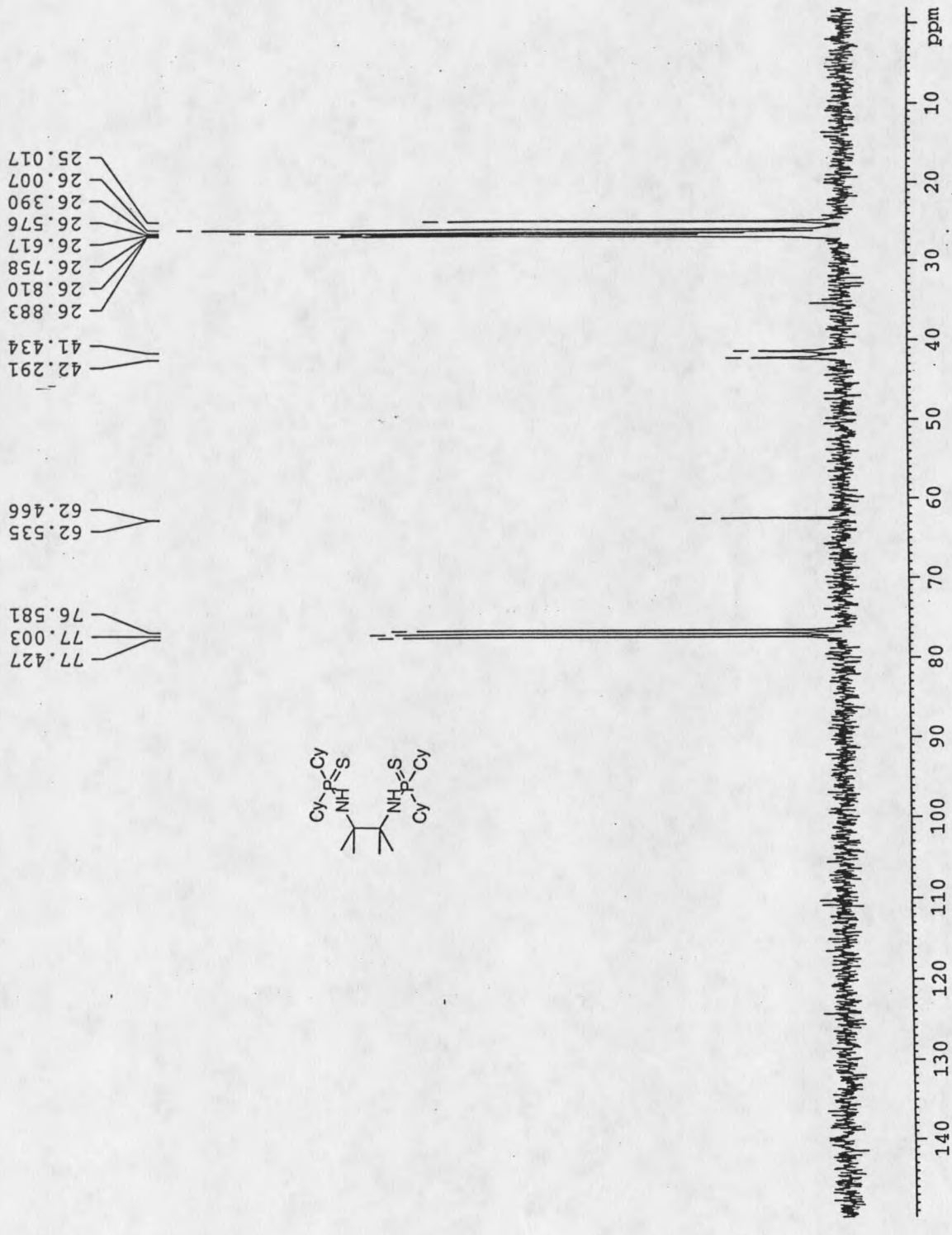


Figure 110. ^{13}C NMR Spectrum of *N,N'*-Bis(*P,P*-dicyclohexylthiophosphinyl)-2,3-dimethyl-2,3-butanediamine (**58e**)

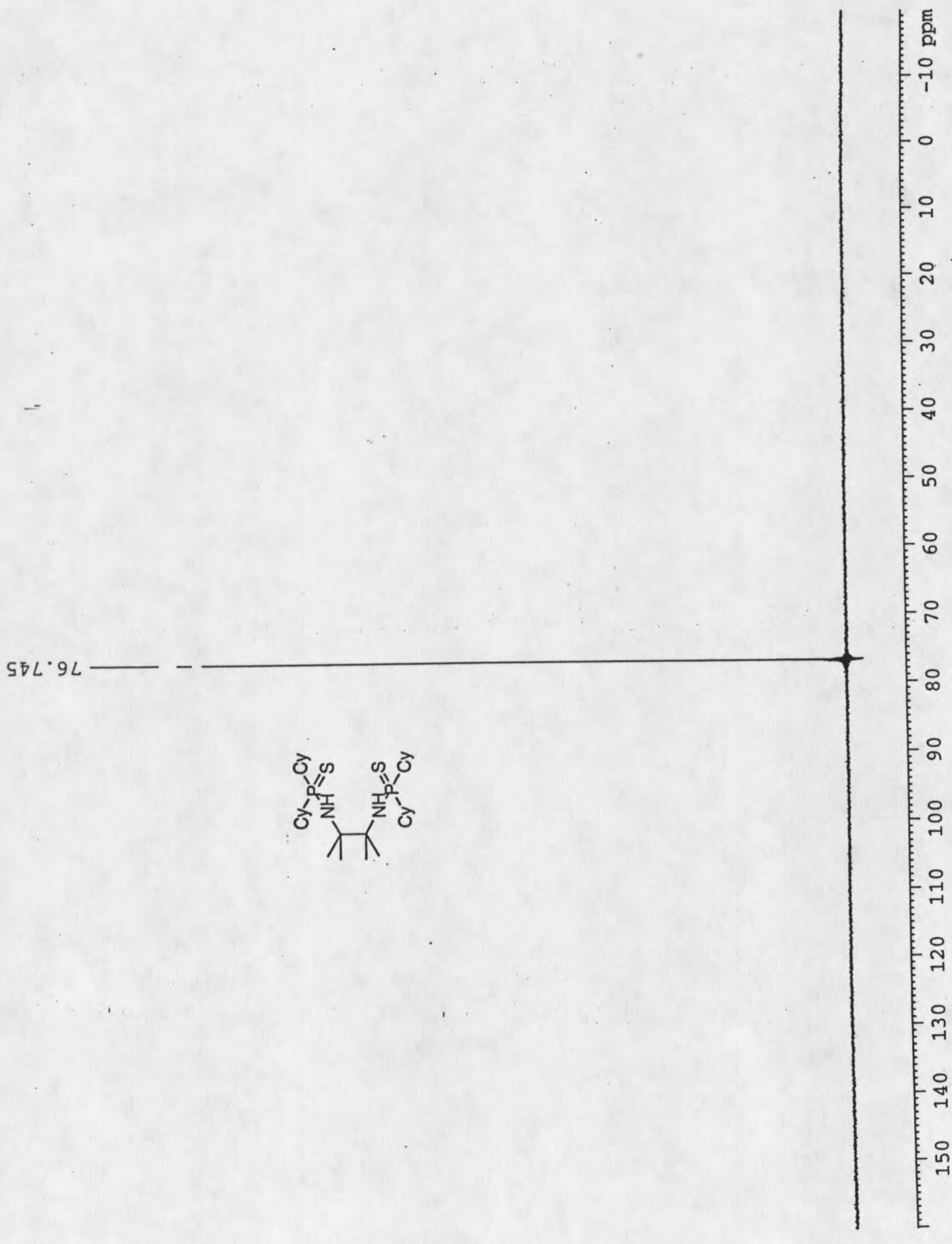


Figure 111. $^{31}P\{H\}$ NMR Spectrum of *N,N'*-Bis(*P,P*-dicyclohexylthiophosphinyl)-2,3-dimethyl-2,3-butanediamine (**58e**)

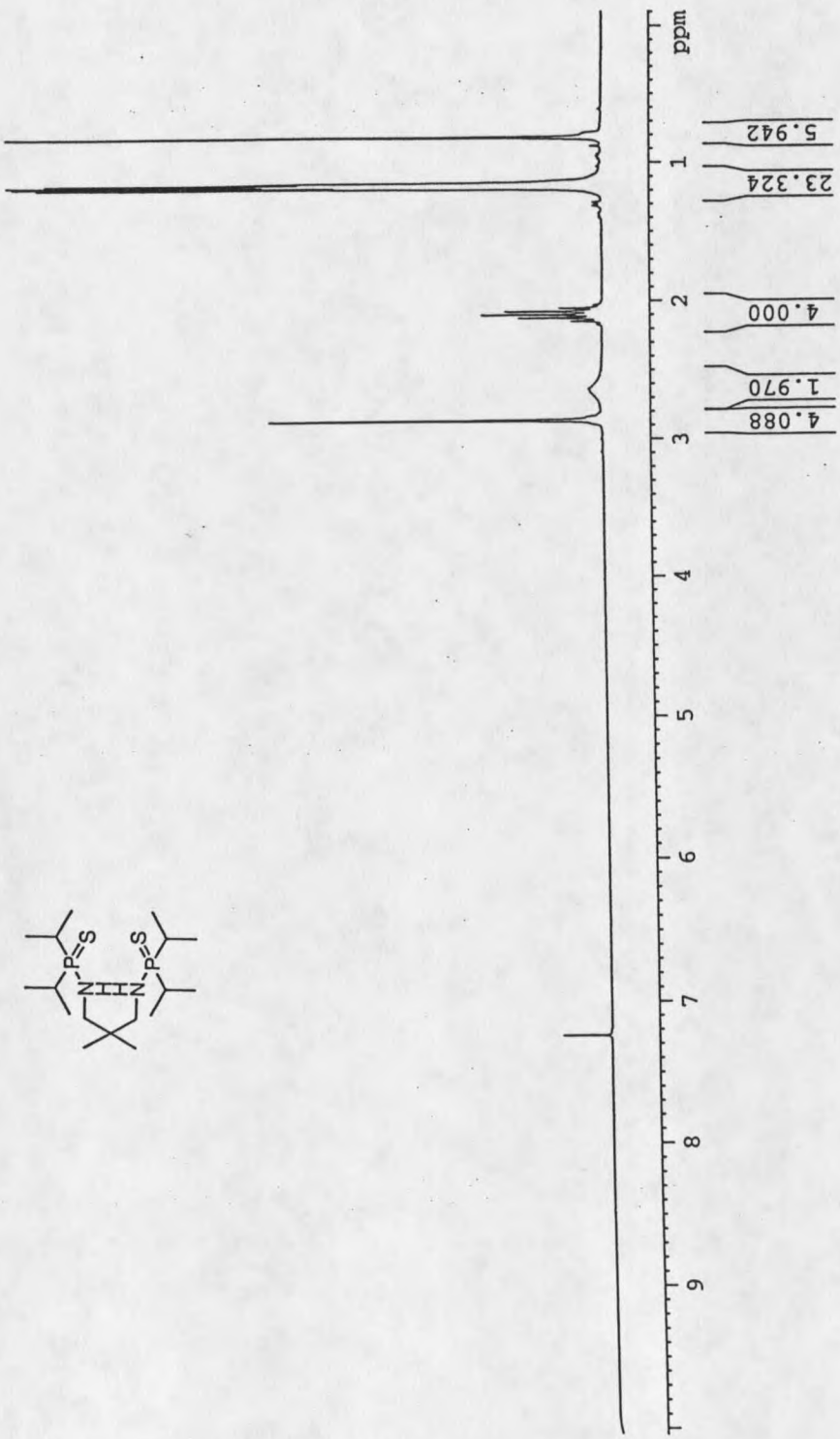


Figure 112. $^{1}H\{^{31}P\}$ NMR Spectrum of *N,N'*-Bis(*P,P*-diisopropylthiophosphinyl)-2,2-dimethyl-1,3-propanediamine (**59a**)

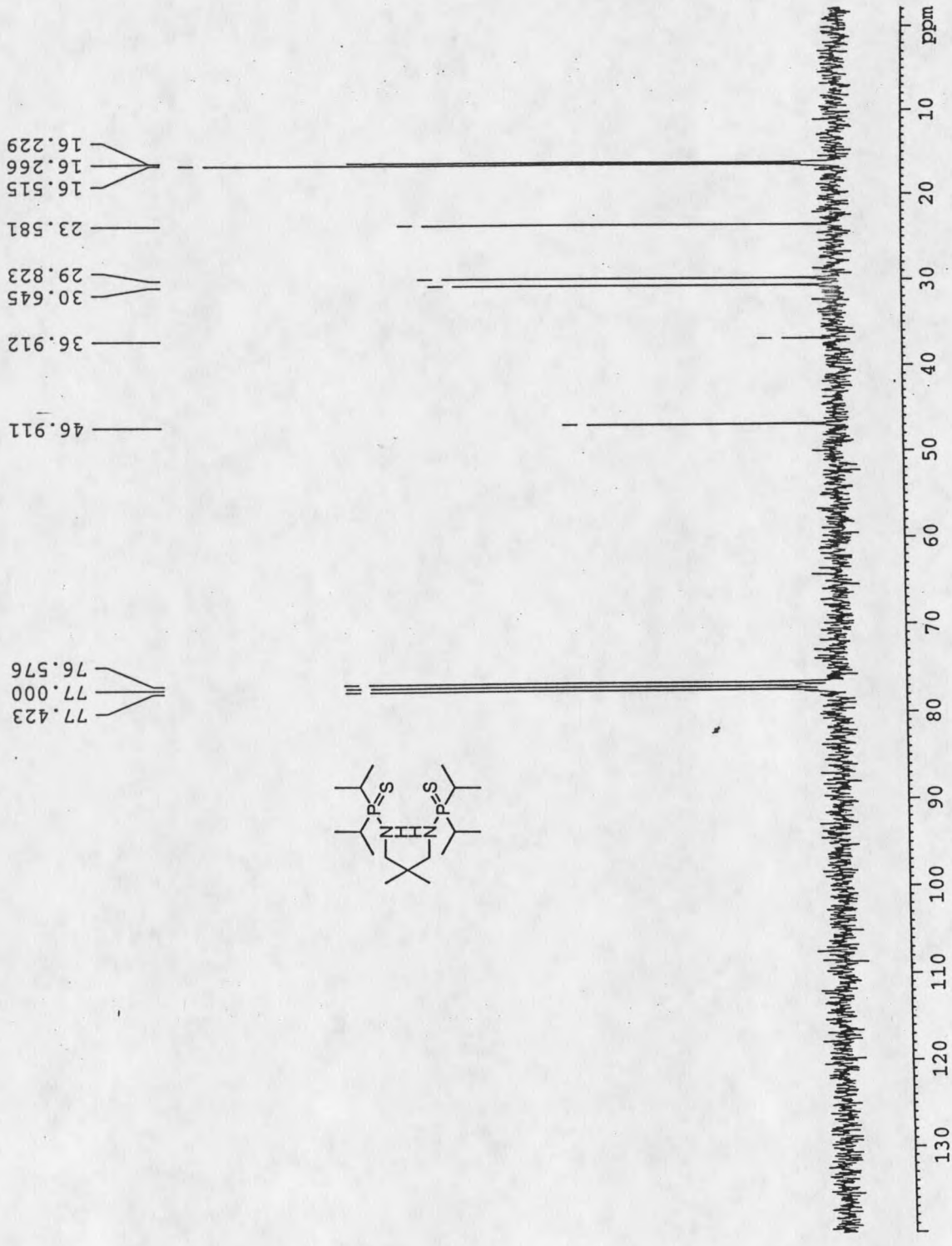


Figure 113. ^{13}C NMR Spectrum of *N,N'*-Bis(*P,P*-diisopropylthiophosphinyl)- 2,2-dimethyl-1,3-propanediamine (**59a**)

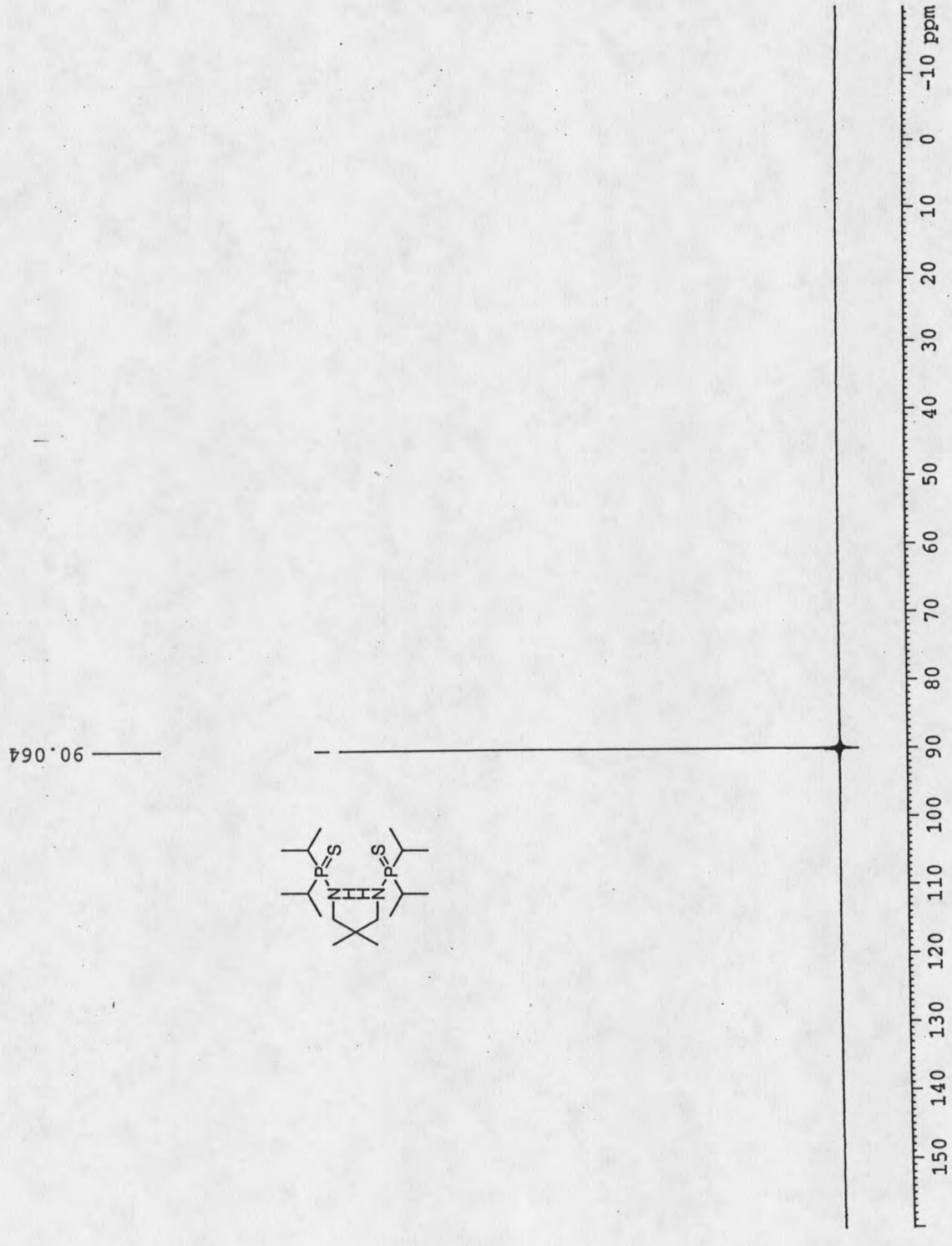


Figure 114. $^{31}P\{H\}$ NMR Spectrum of *N,N'*-Bis(*P,P*-diisopropylthiophosphinyl)- 2,2-dimethyl-1,3-propanediamine (**59a**)

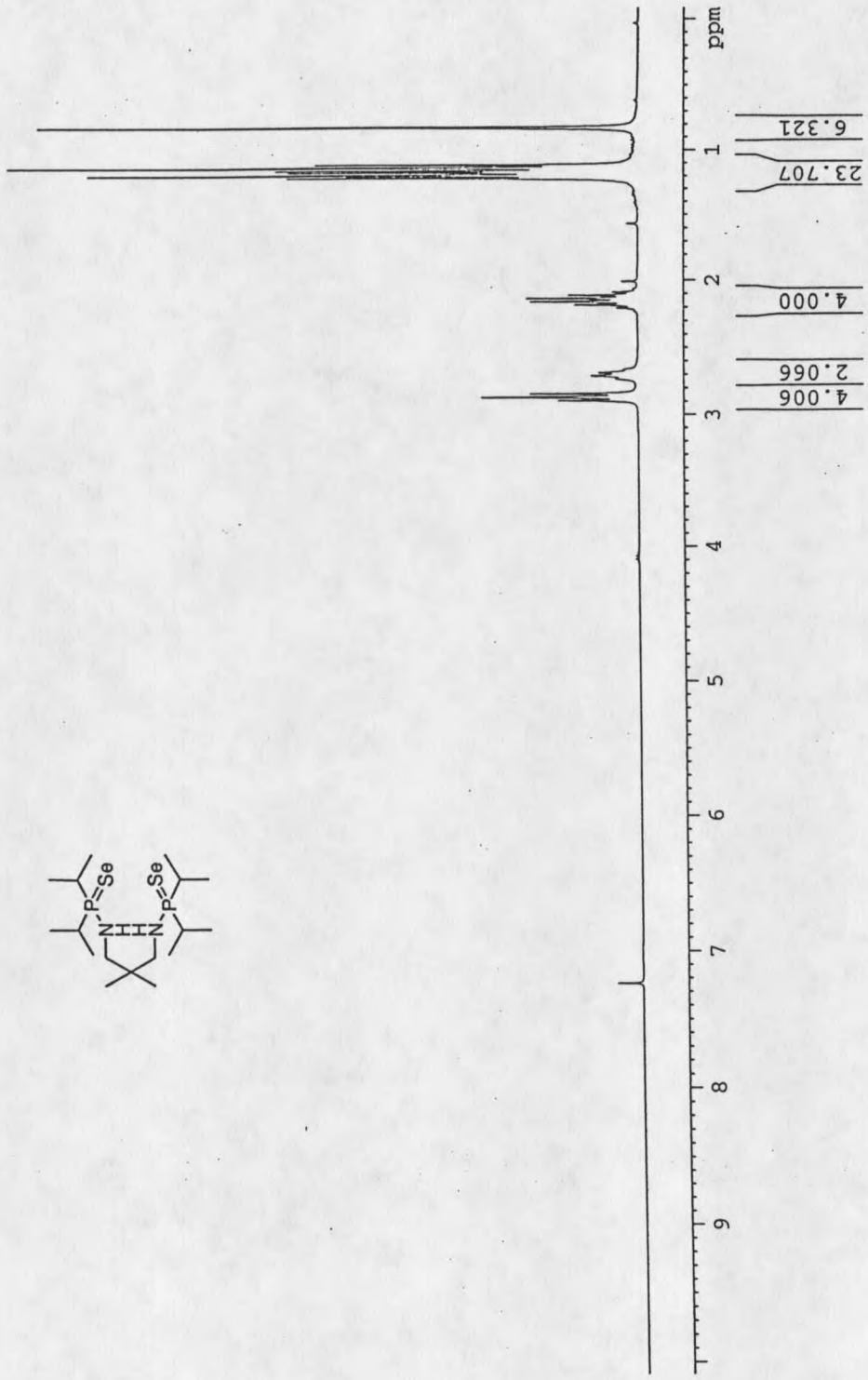


Figure 115. $^{1}H\{^{31}P\}$ NMR Spectrum of *N,N'*-Bis(*P,P*-diisopropylselenophosphinyl)-2,2-dimethyl-1,3-propanediamine (**58b**)

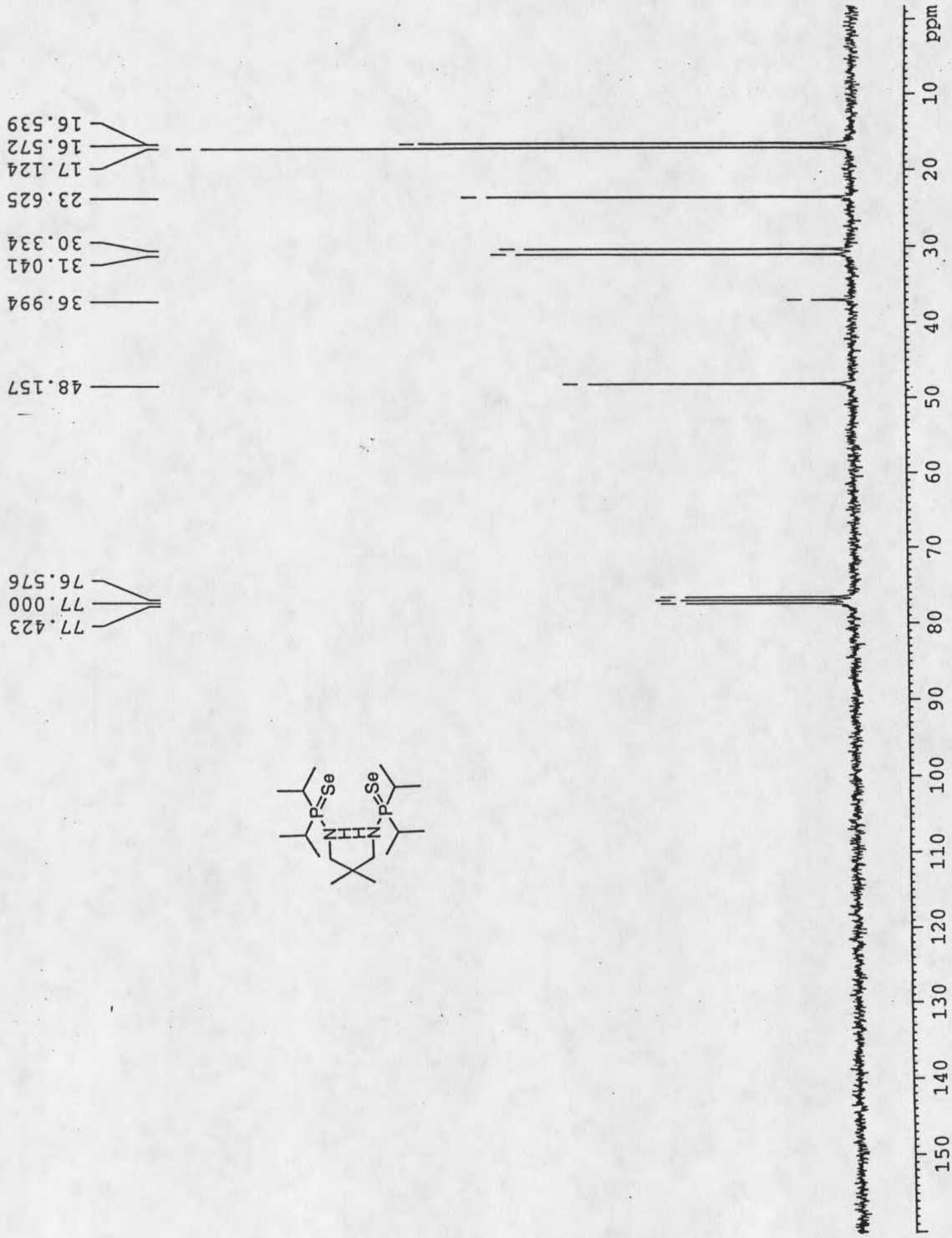


Figure 116. ^{13}C NMR Spectrum of *N,N'*-Bis(*P,P*-diisopropylselenophosphinyl)-2,2-dimethyl-1,3-propanediamine (**58b**)

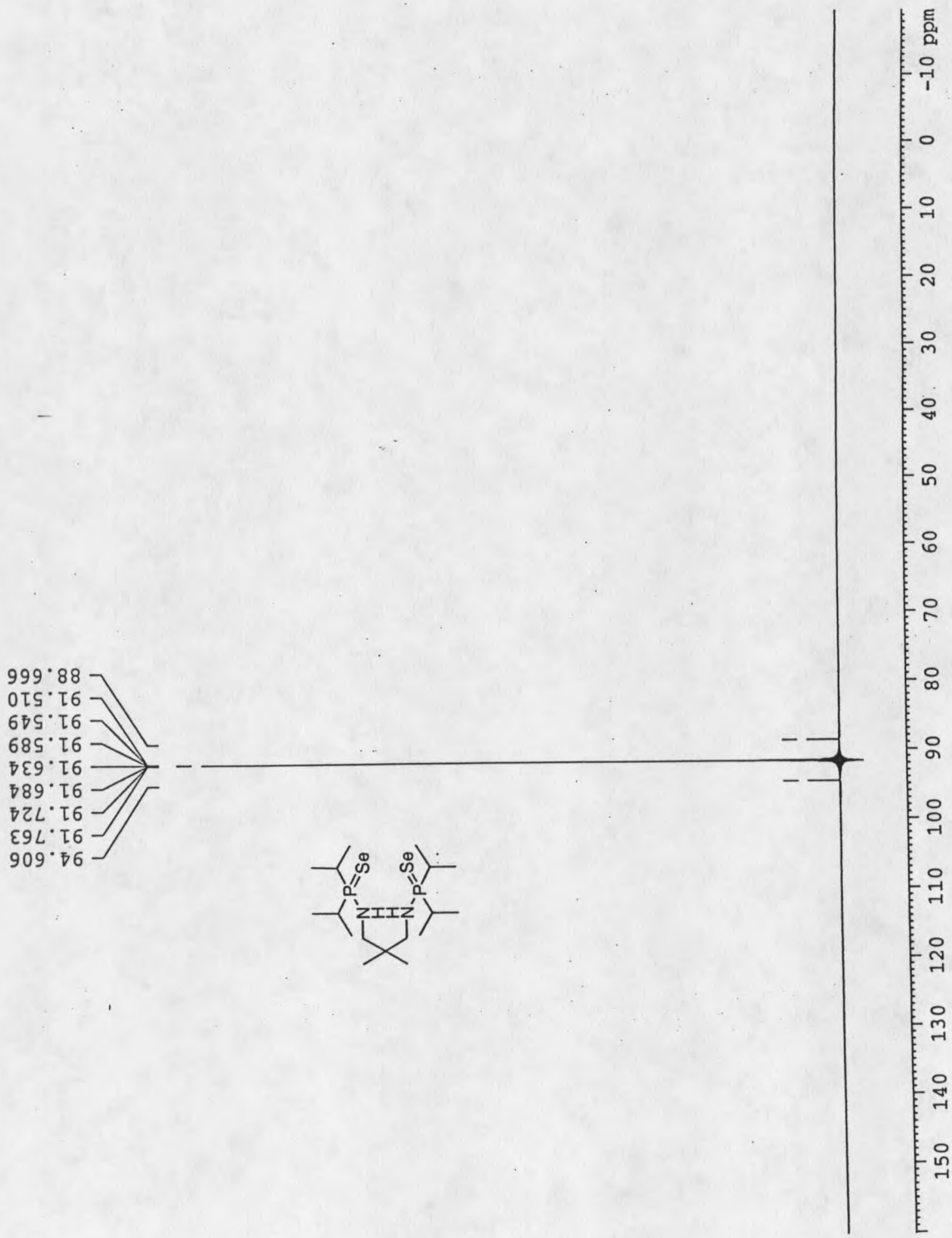


Figure 117. $^{31}P\{H\}$ NMR Spectrum of *N,N'*-Bis(*P,P*-diisopropylselenophosphinyl)-2,2-dimethyl-1,3-propanediamine (**58b**)

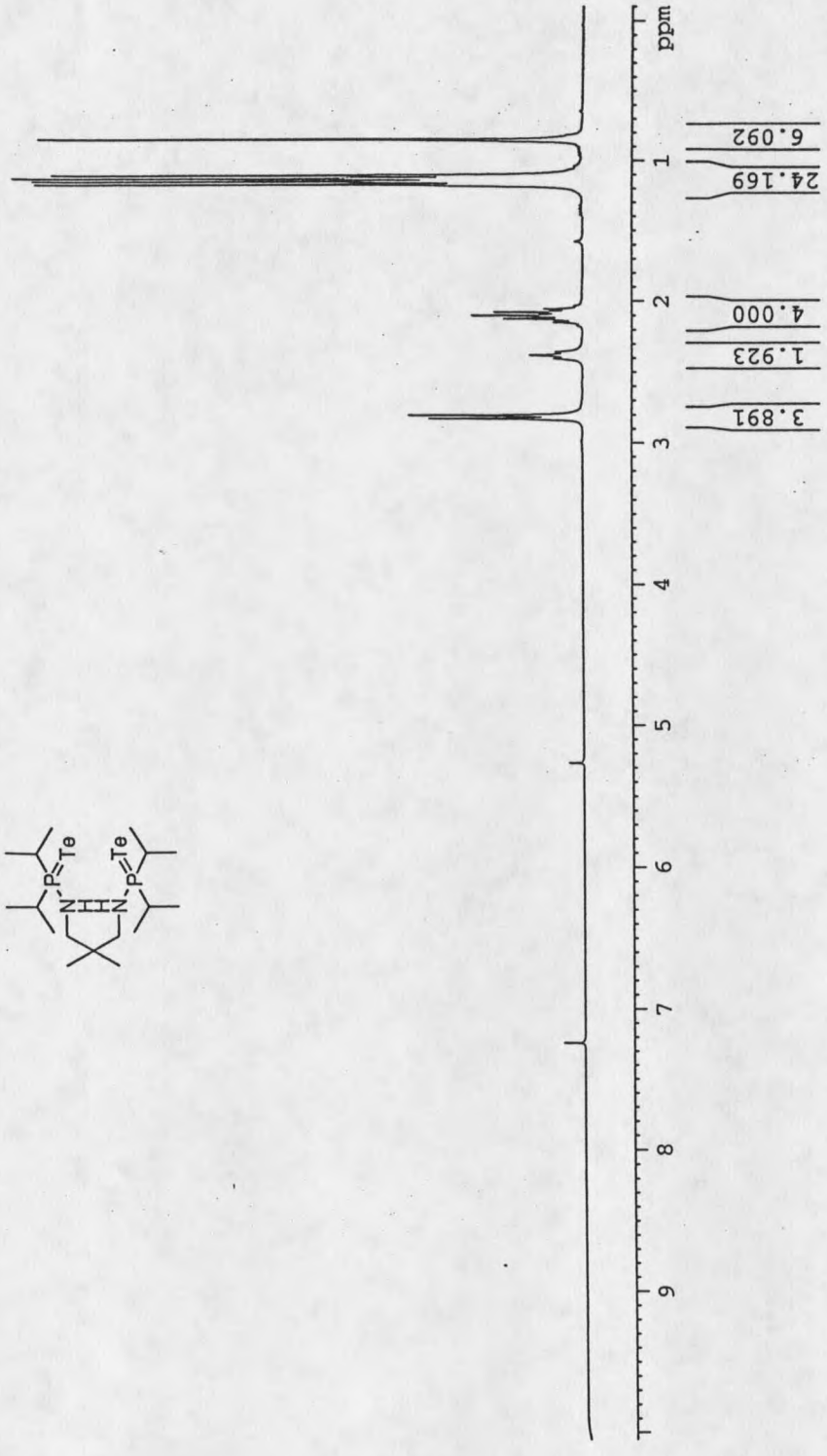


Figure 118. $^{1}H\{^{31}P\}$ NMR Spectrum of *N,N'*-Bis(*P,P*-diisopropyltellurophosphinyl)-2,2-dimethyl-1,3-propanediamine (**59c**)

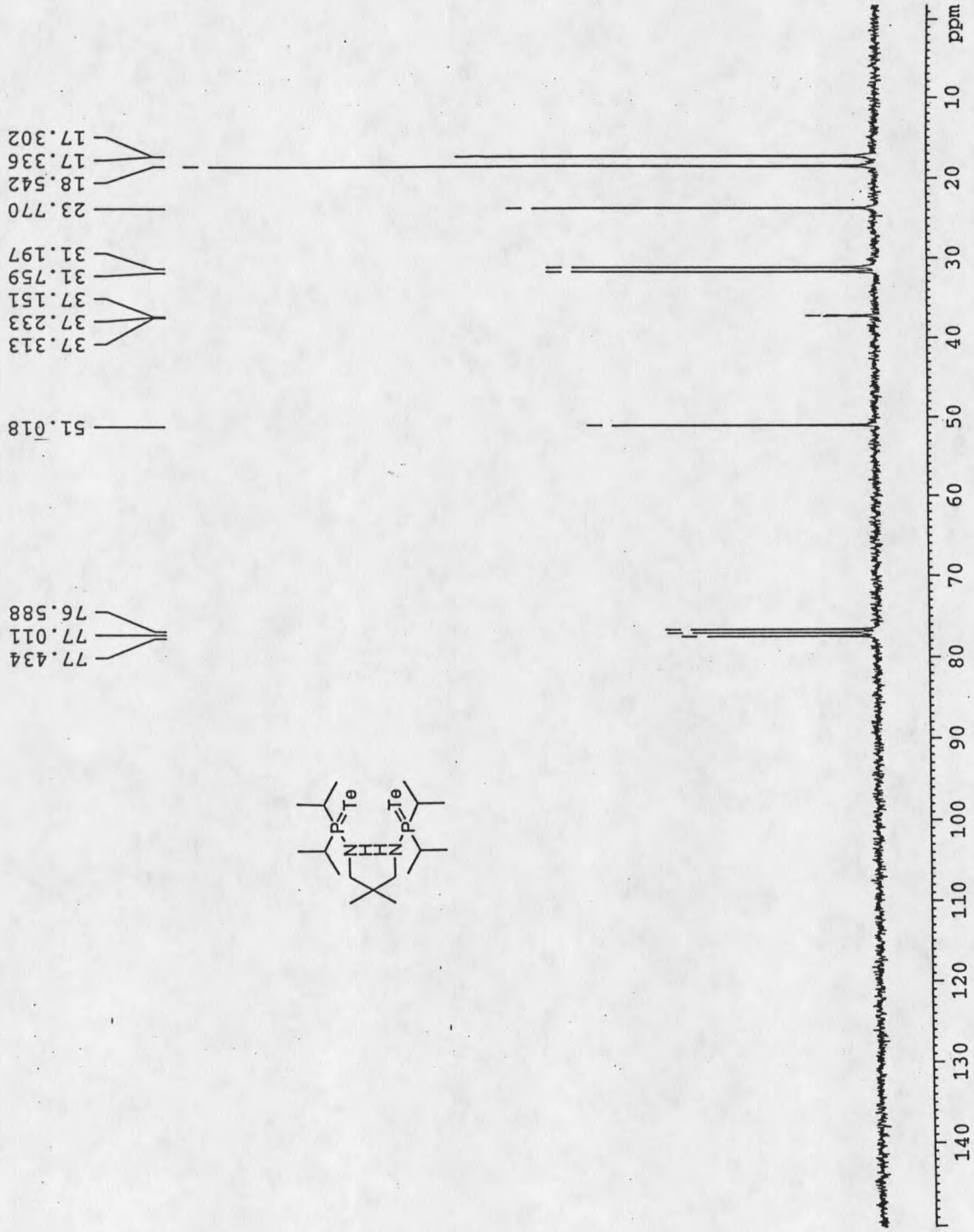


Figure 119. ^{13}C NMR Spectrum of *N,N'*-Bis(*P,P*-diisopropyltellurophosphinyl)- 2,2-dimethyl-1,3-propanediamine (**59c**)

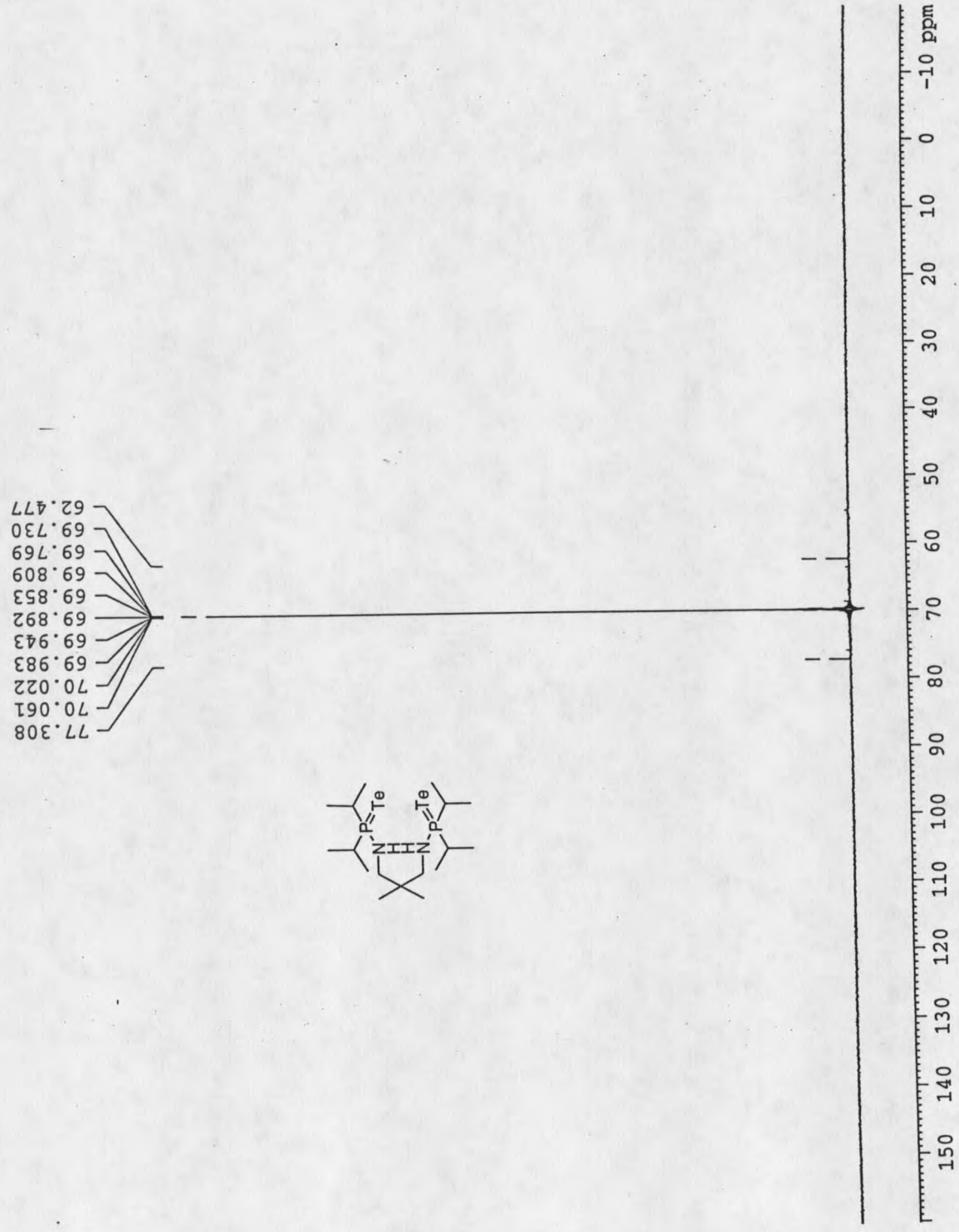


Figure 120. $^{31}P\{H\}$ NMR Spectrum of *N,N'*-Bis(*P,P*-diisopropyltellurophosphinyl)-2,2-dimethyl-1,3-propanediamine (**59c**)

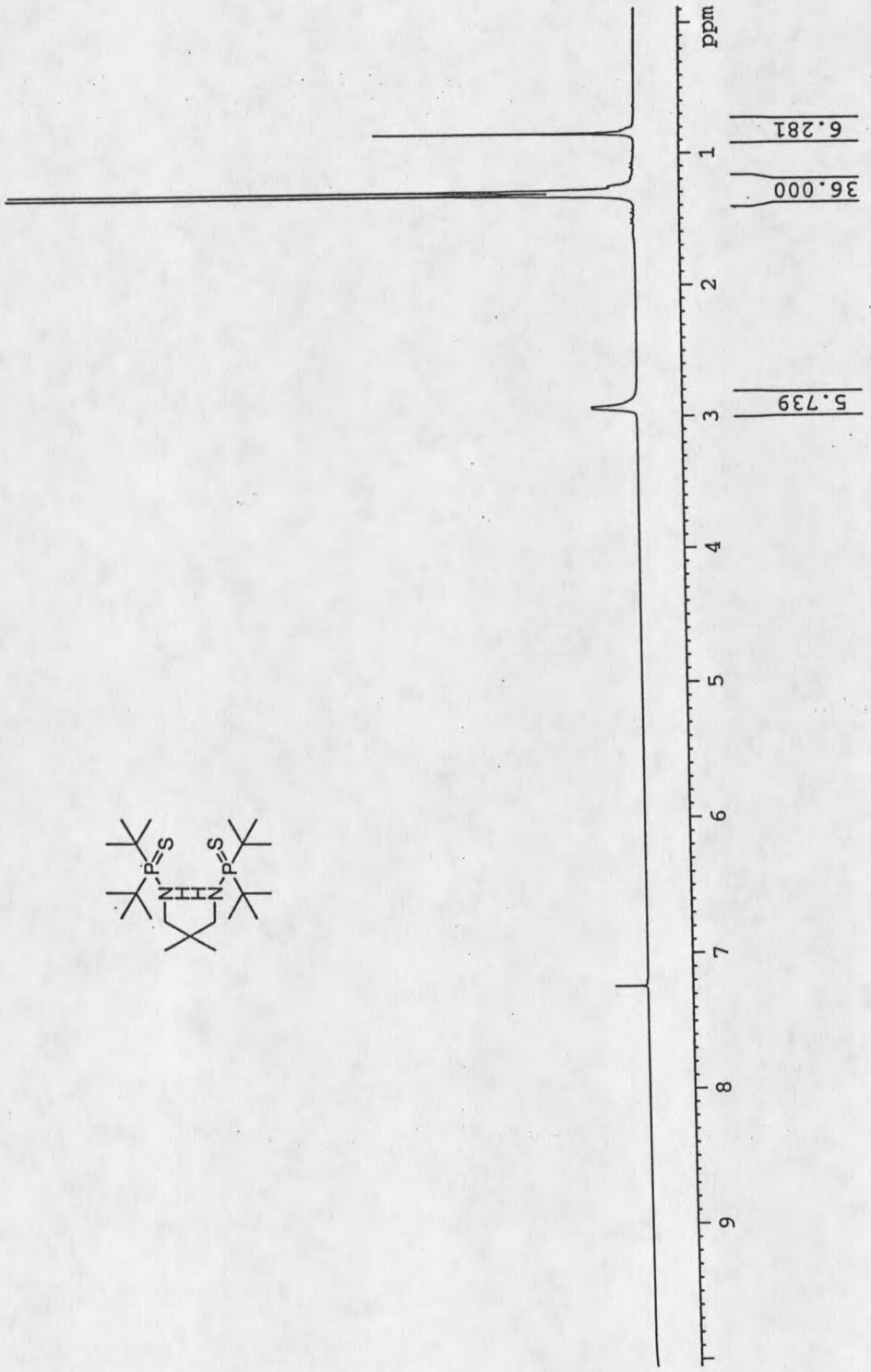


Figure 121. $^{1}H\{^{31}P\}$ NMR Spectrum of *N,N'*-Bis(*P,P*-di-tert-butylthiophosphinyl)- 2,2-dimethyl-1,3-propanediamine (**59d**)

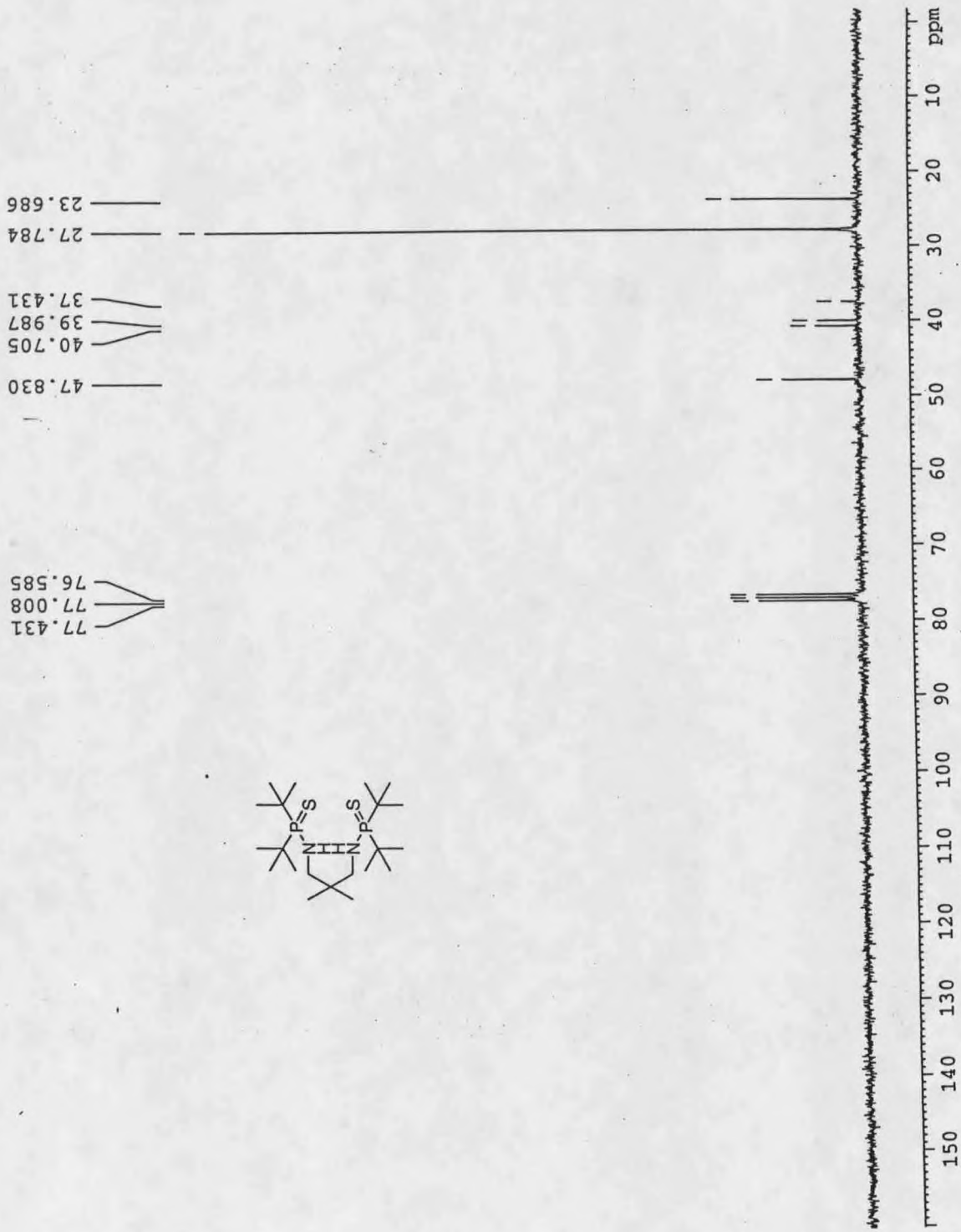


Figure 122. ^{13}C NMR Spectrum of *N,N'*-Bis(*P,P*-di-tert-butylthiophosphinyl)- 2,2-dimethyl-1,3-propanediamine (**59d**)

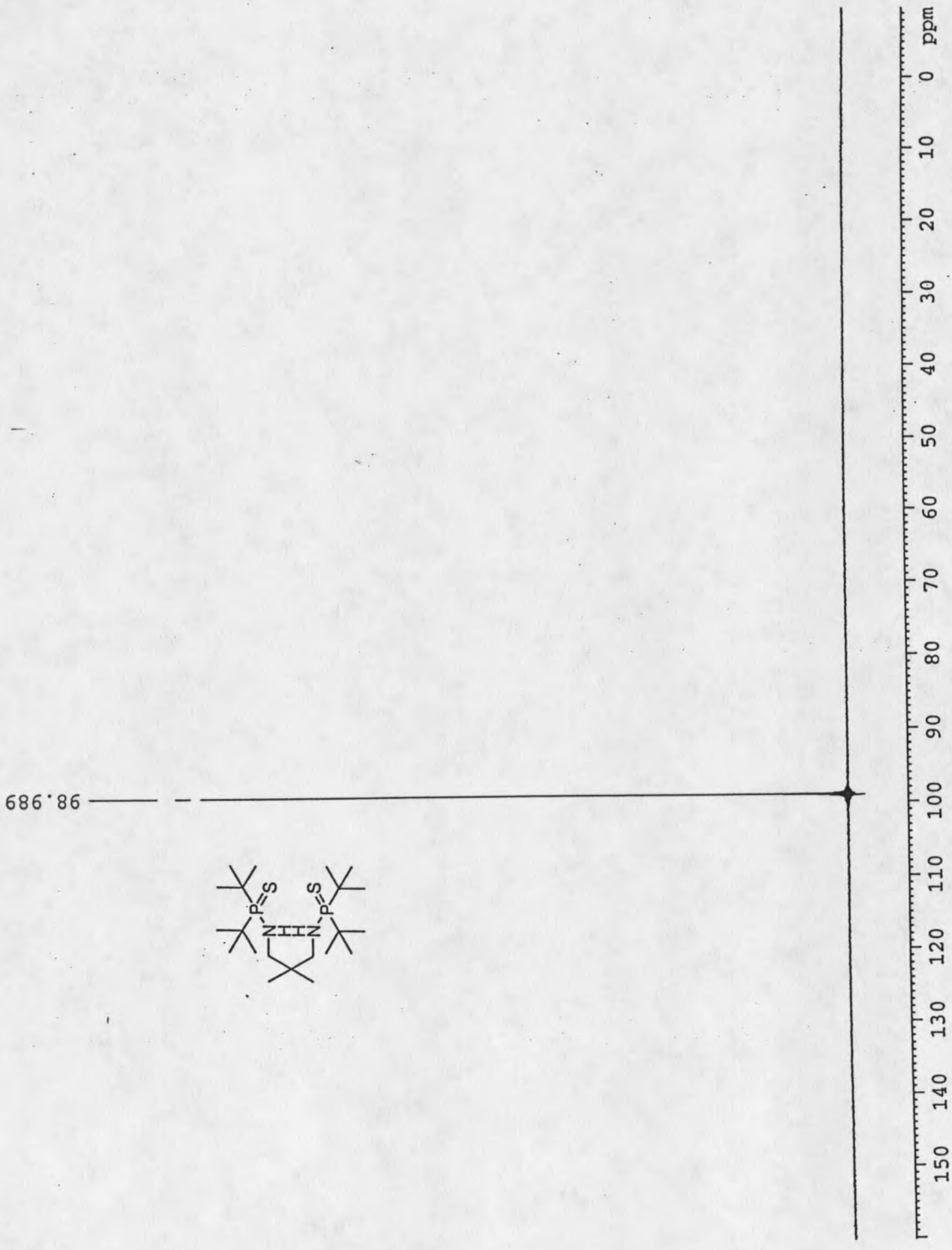


Figure 123. $^{31}P\{H\}$ NMR Spectrum of *N,N'*-Bis(*P,P*-di-tert-butylthiophosphinyl)- 2,2-dimethyl-1,3-propanediamine (**59d**)

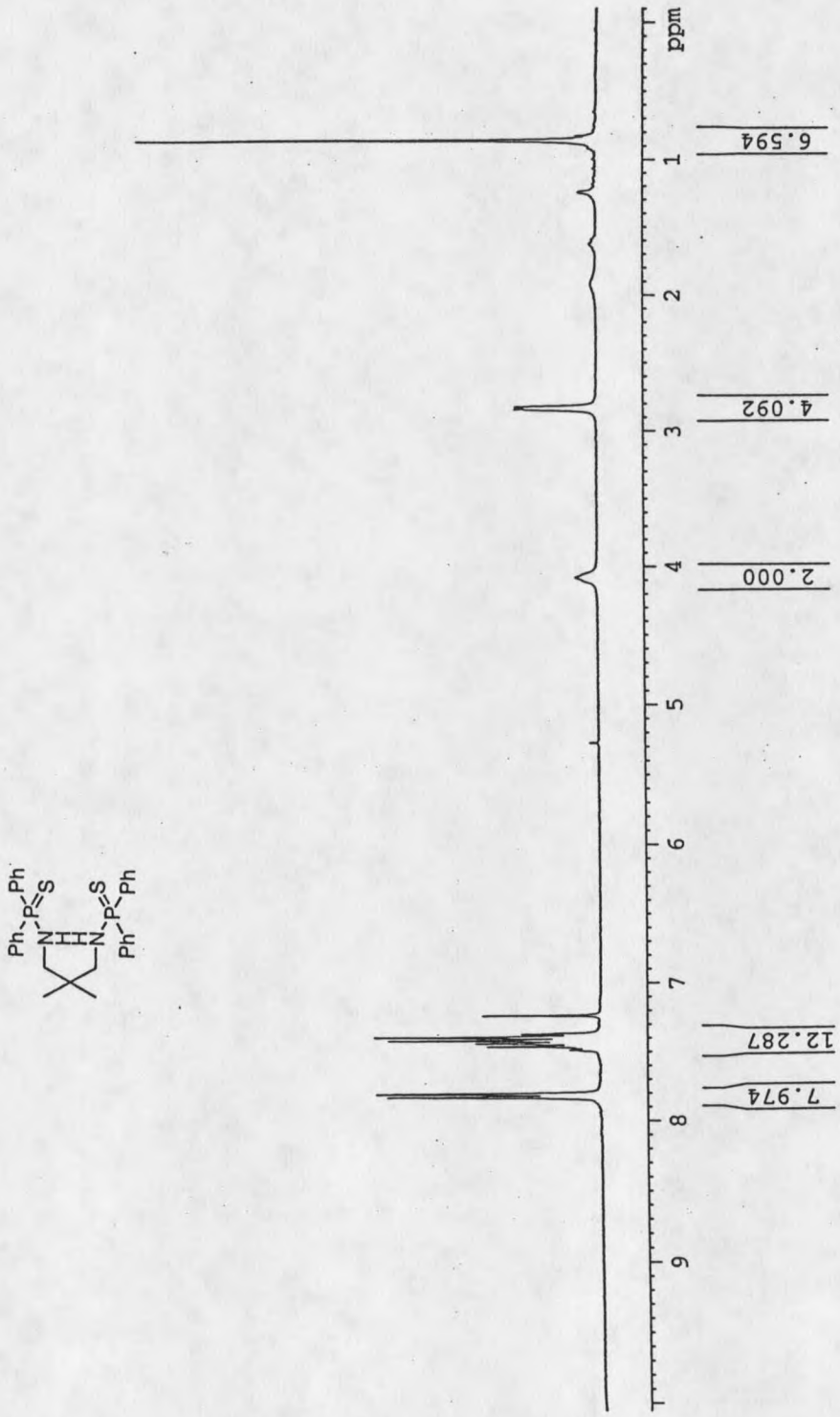


Figure 124. $^{1}H\{^{31}P\}$ NMR Spectrum of *N,N'*-Bis(*P,P*-diphenylthiophosphinyl)-2,2-dimethyl-1,3-propanediamine (**59e**)

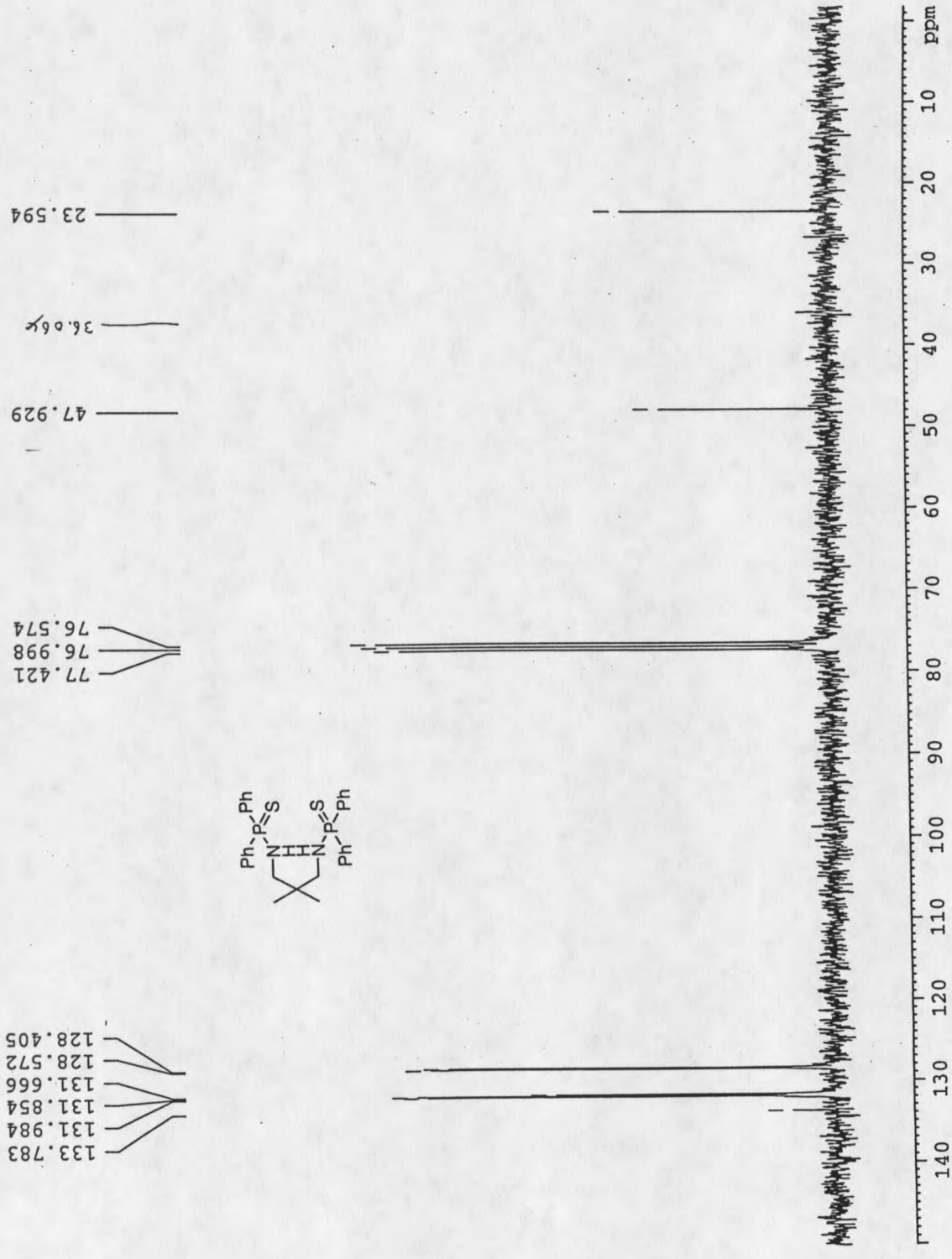


Figure 125. ^{13}C NMR Spectrum of *N,N'*-Bis(*P,P*-diphenylthiophosphinyl)-2,2-dimethyl-1,3-propanediamine (**59e**)

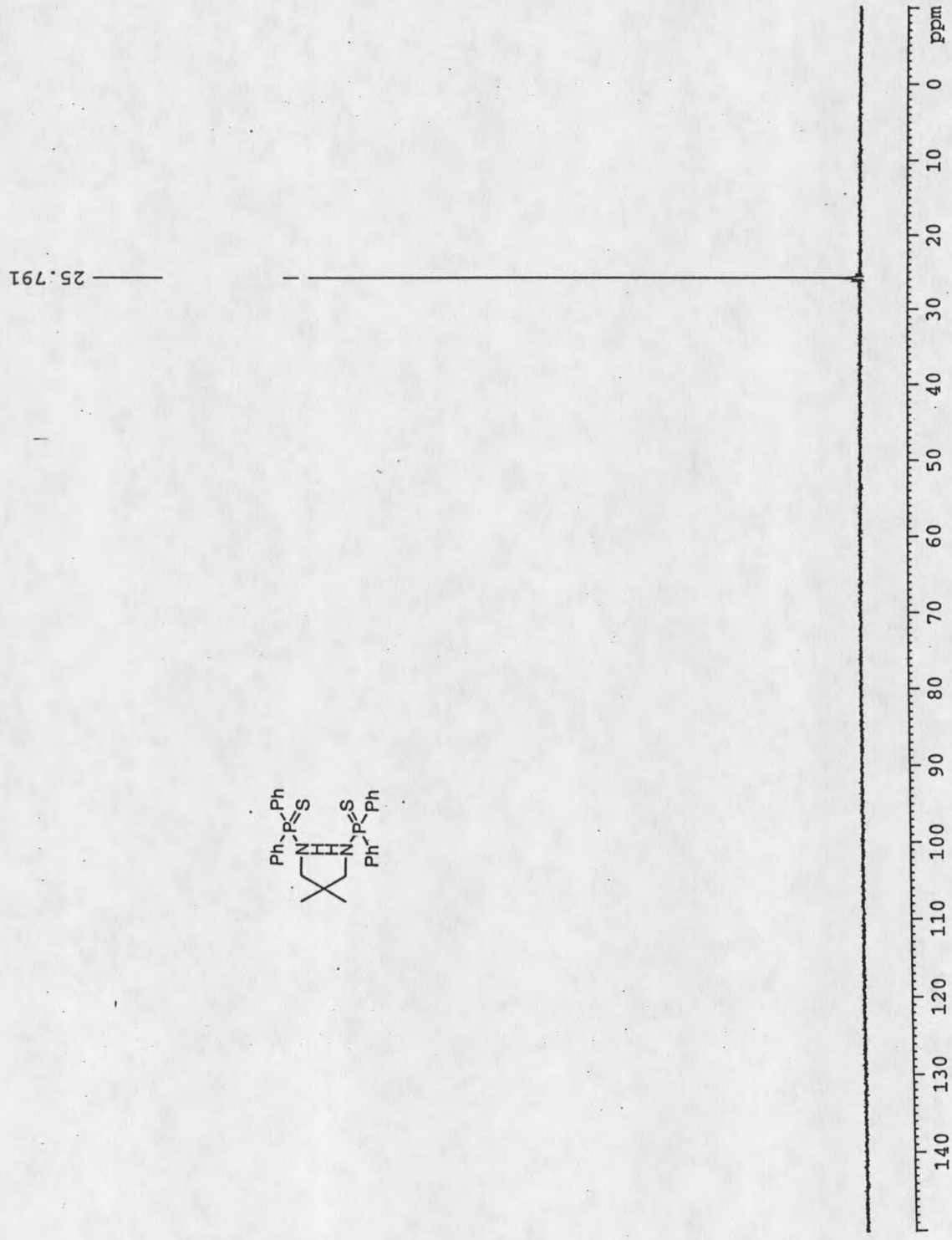


Figure 126. $^{31}P\{H\}$ NMR Spectrum of *N,N'*-Bis(*P,P*-diphenylthiophosphinyl)-2,2-dimethyl-1,3-propanediamine (**59e**)

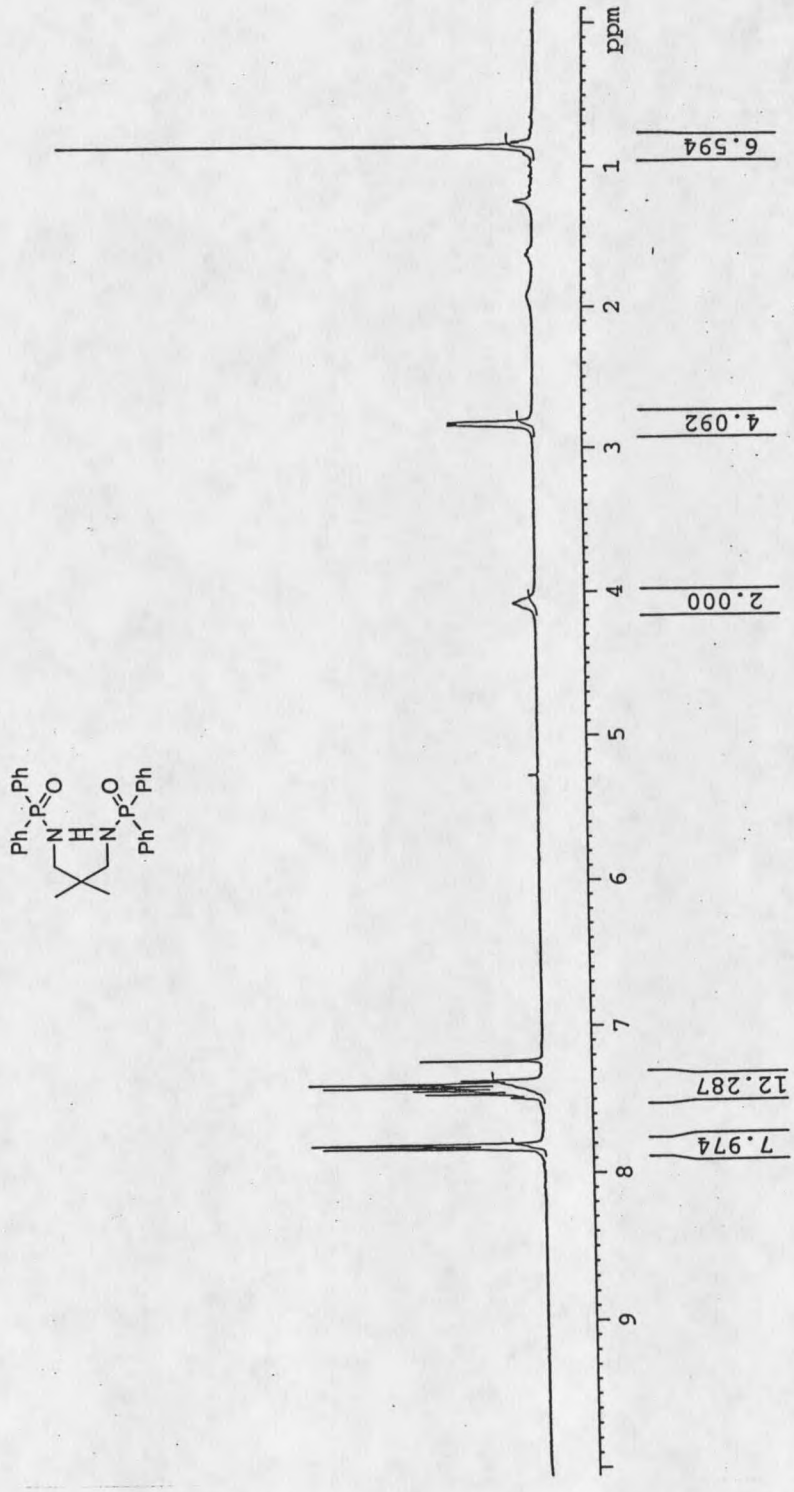


Figure 127. $^{1}H\{^{31}P\}$ NMR Spectrum of *N,N'*-Bis(*P,P*-diphenylphosphinoyl)-2,2-dimethyl-1,3-propanediamine (**59f**)

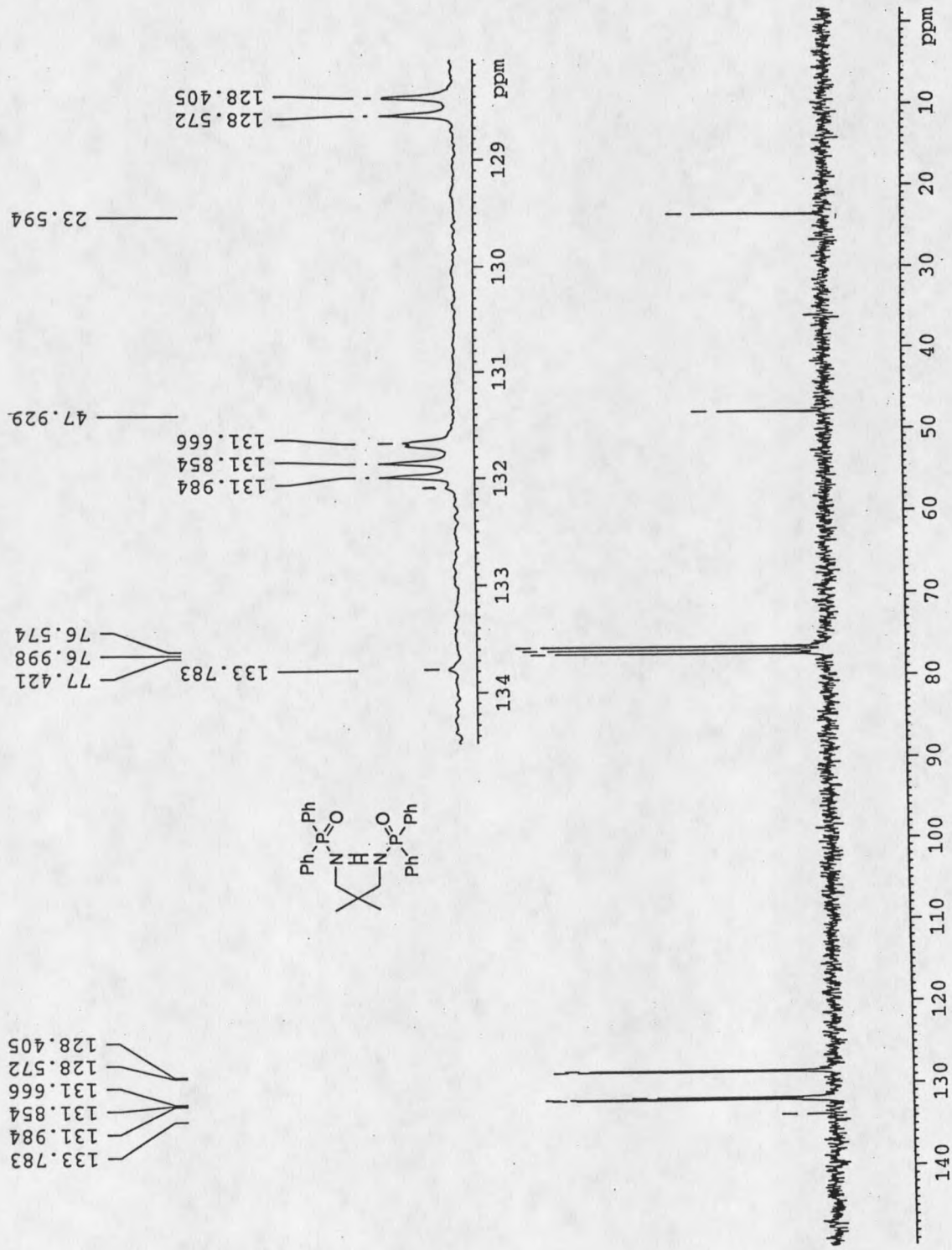


Figure 128. ^{13}C NMR Spectrum of *N,N'*-Bis(*P,P*-diphenylphosphinoyl)-2,2-dimethyl-1,3-propanediamine (**59f**)

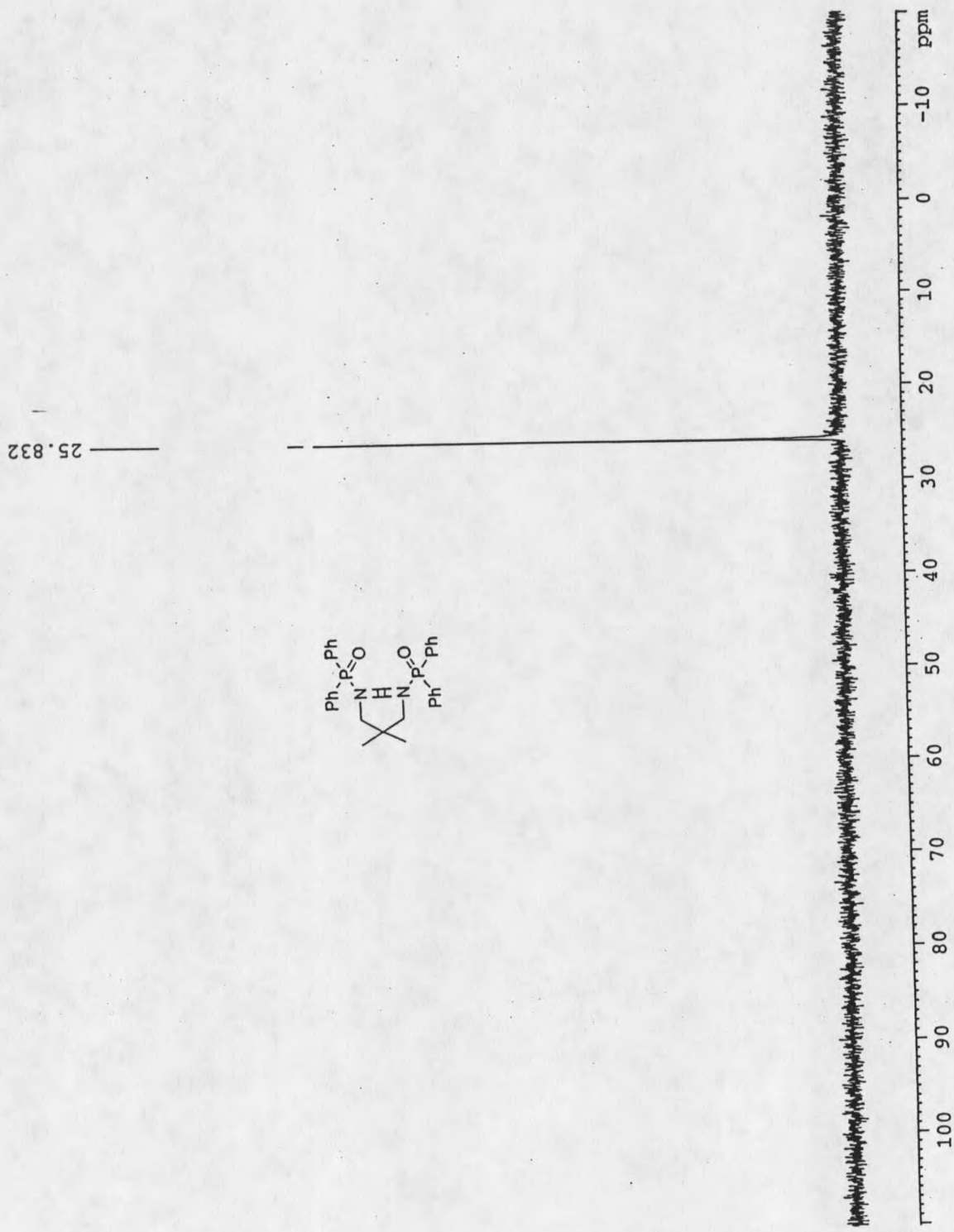


Figure 129. $^{31}P\{H\}$ NMR Spectrum of *N,N'*-Bis(*P,P*-diphenylphosphinoyl)-2,2-dimethyl-1,3-propanediamine (**59f**)

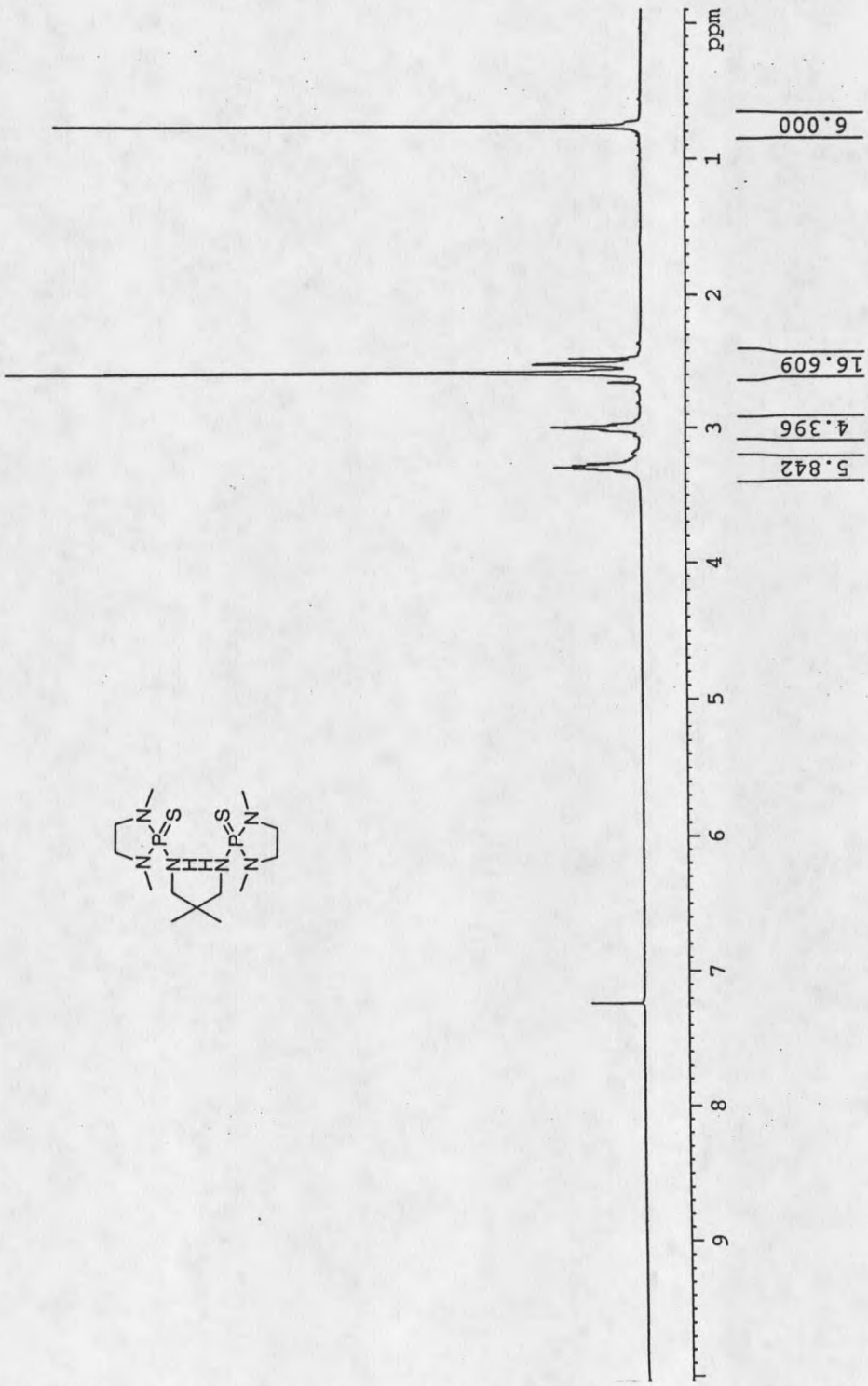


Figure 130. $^{1}H\{^{31}P\}$ NMR Spectrum of *N,N'*-Bis(1,3-dimethyl-2-thio-[1,3,2] diazaphospho-lidinyl)-2,2-dimethyl-1,3-propanediamine (**59g**)

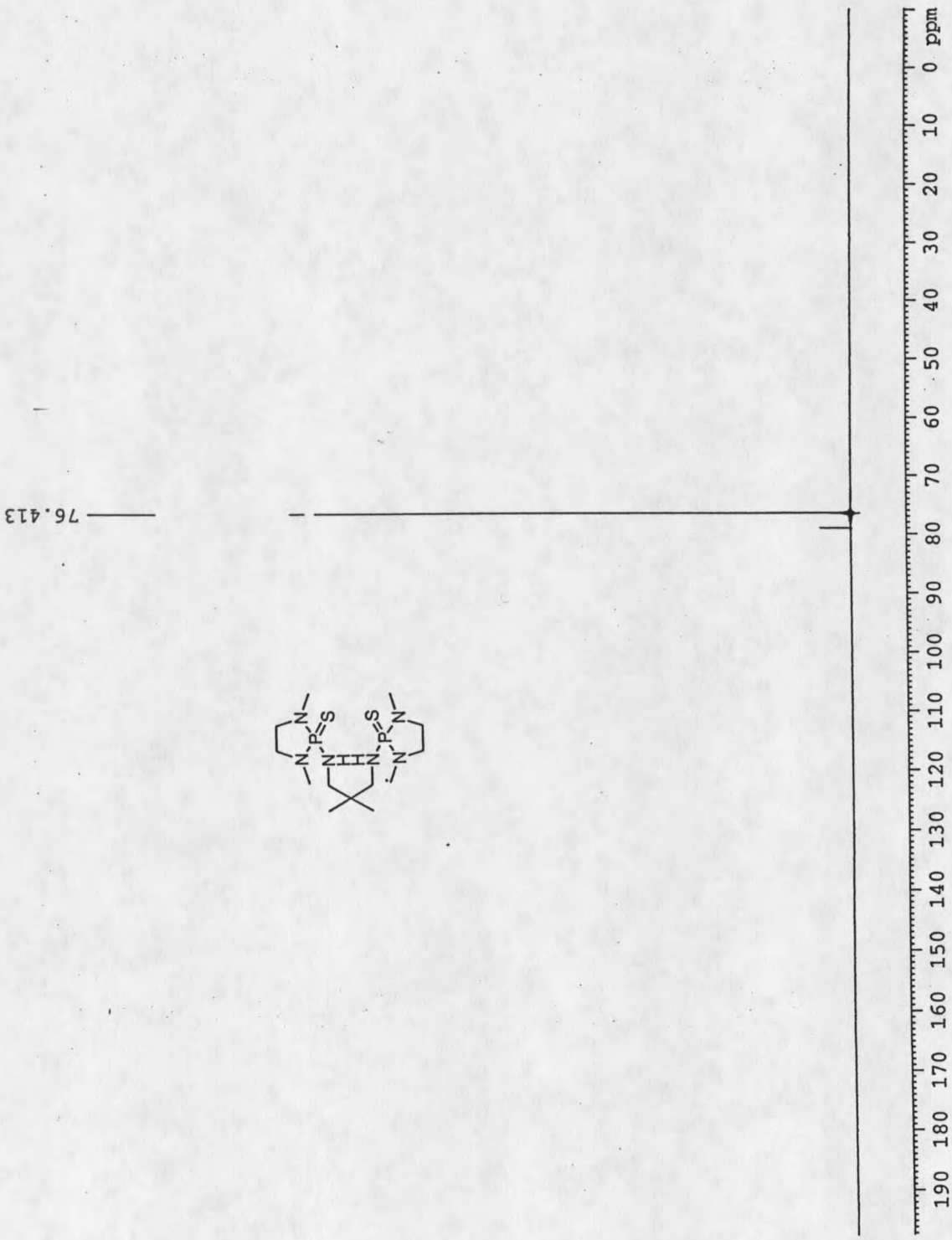


Figure 131. ^{13}C NMR Spectrum of *N,N'*-Bis(1,3-dimethyl-2-thio-[1,3,2]diazaphospholidinyl)-2,2-dimethyl-1,3-propanediamine (**59g**)

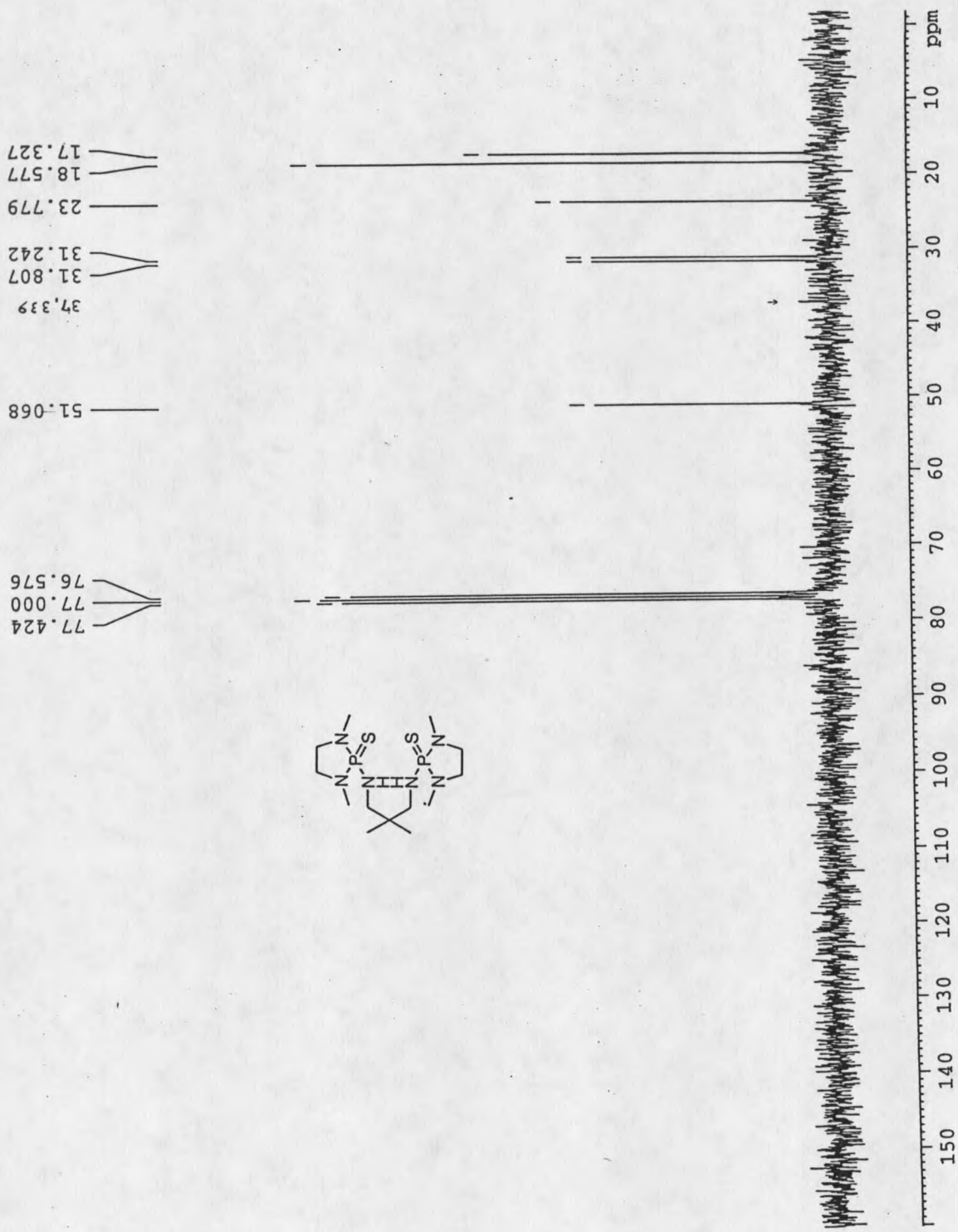


Figure 132. $^{31}P\{H\}$ NMR Spectrum of *N,N'*-Bis(1,3-dimethyl-2-thio-[1,3,2] diaza-phospholidinyl)-2,2-dimethyl-1,3-propanediamine (**59g**)

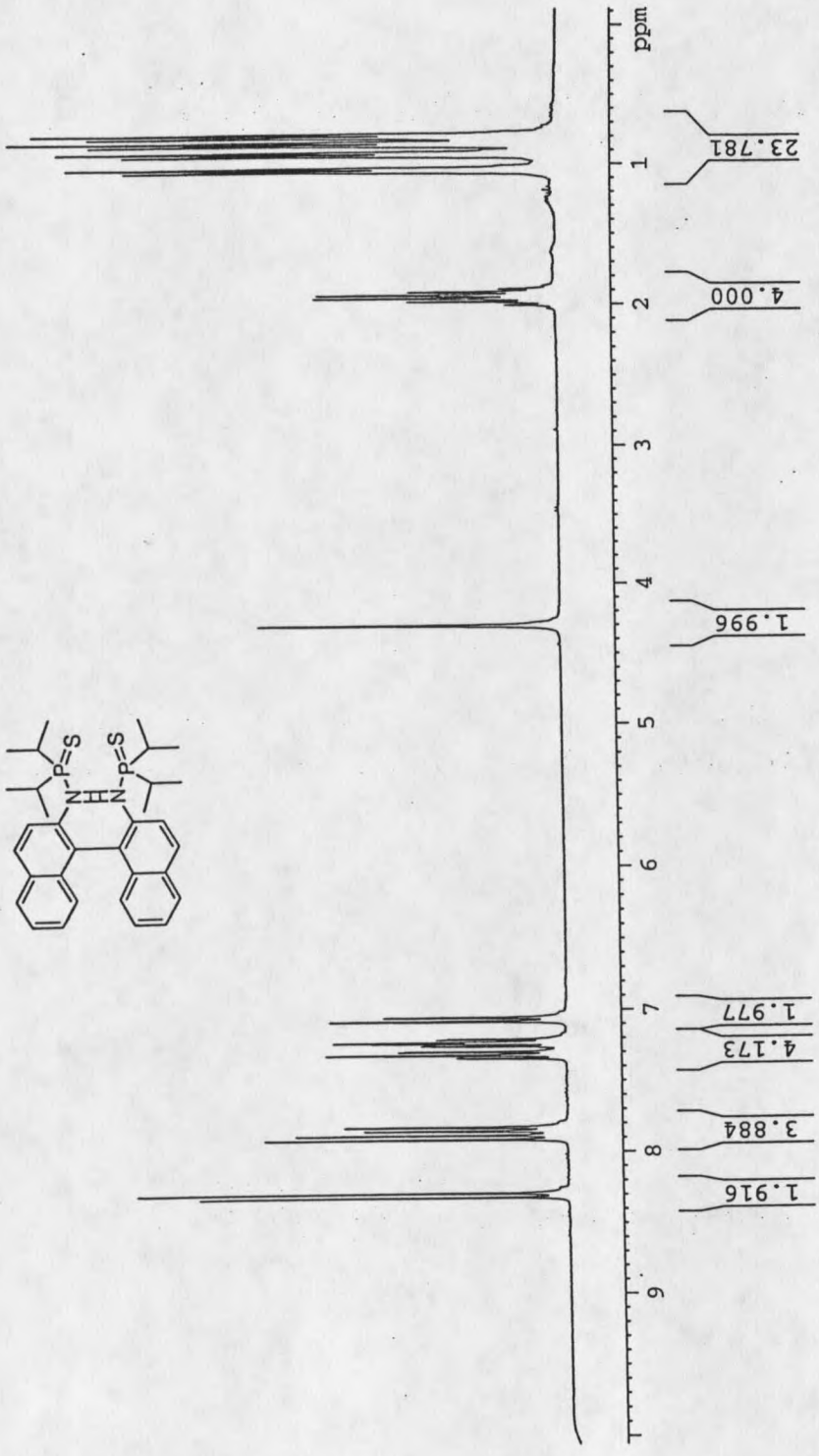


Figure 133. $^{1}H\{^{31}P\}$ NMR Spectrum of *N,N'*-Bis(*P,P*-diisopropylthiophosphinyl) binaphthyl-2,2'-diamine (**61**)

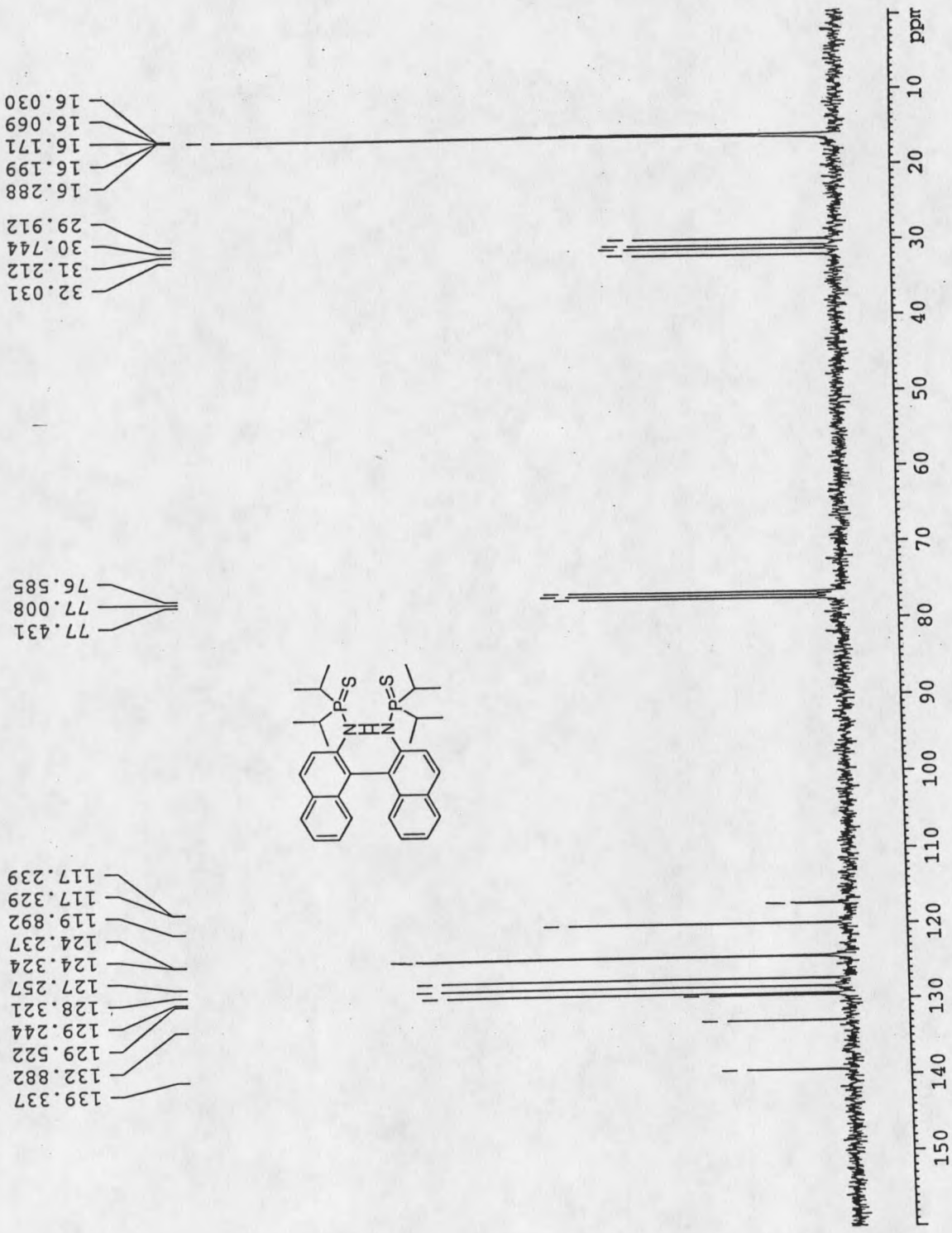


Figure 134. ^{13}C NMR Spectrum of *N,N'*-Bis(*P,P*-diisopropylthiophosphinyl)binaphthyl-2,2'-diamine (**61**)

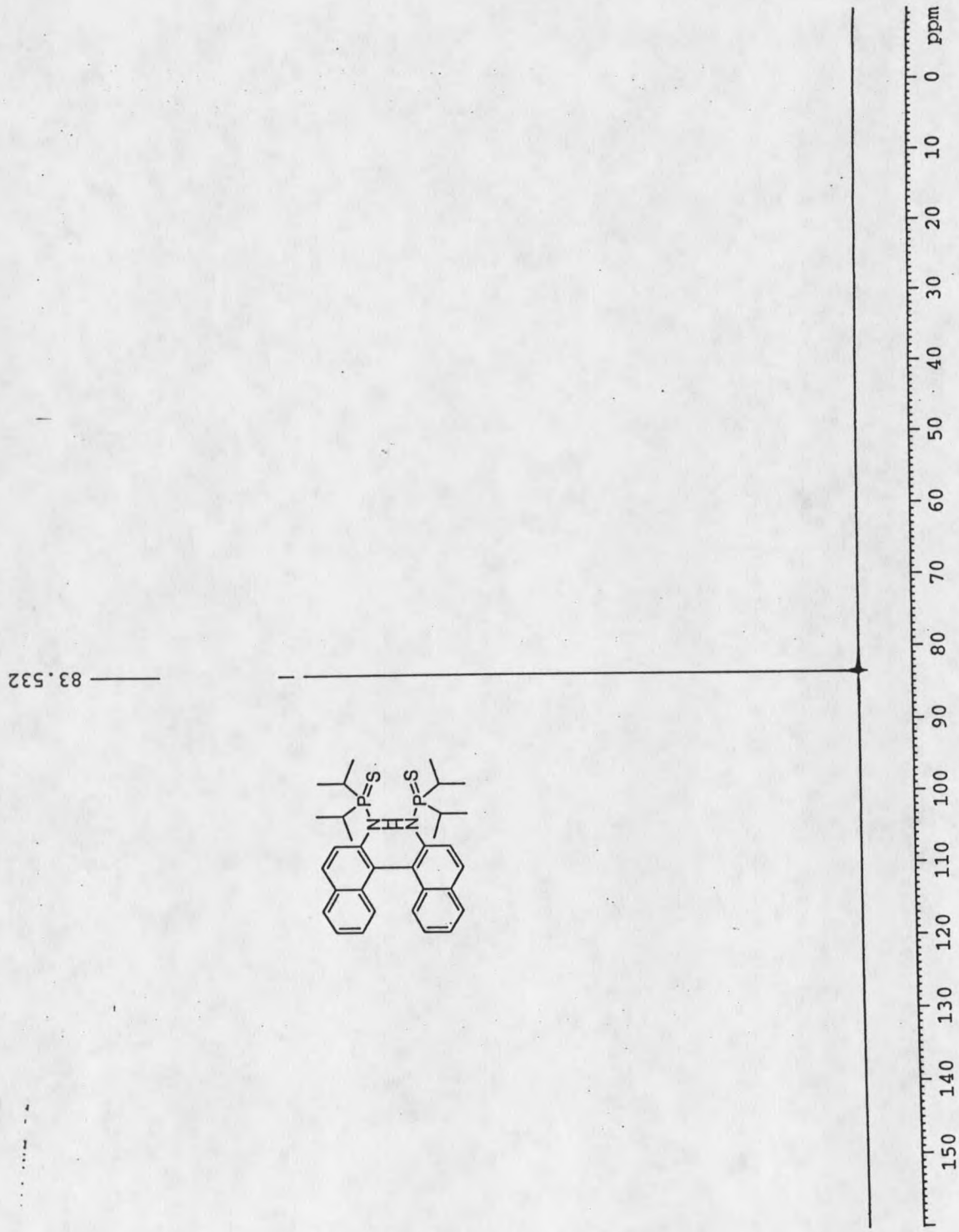


Figure 135. $^{31}P\{H\}$ NMR Spectrum of *N,N'*-Bis(*P,P*-diisopropylthiophosphinyl) binaphthyl-2,2'-diamine (**61**)

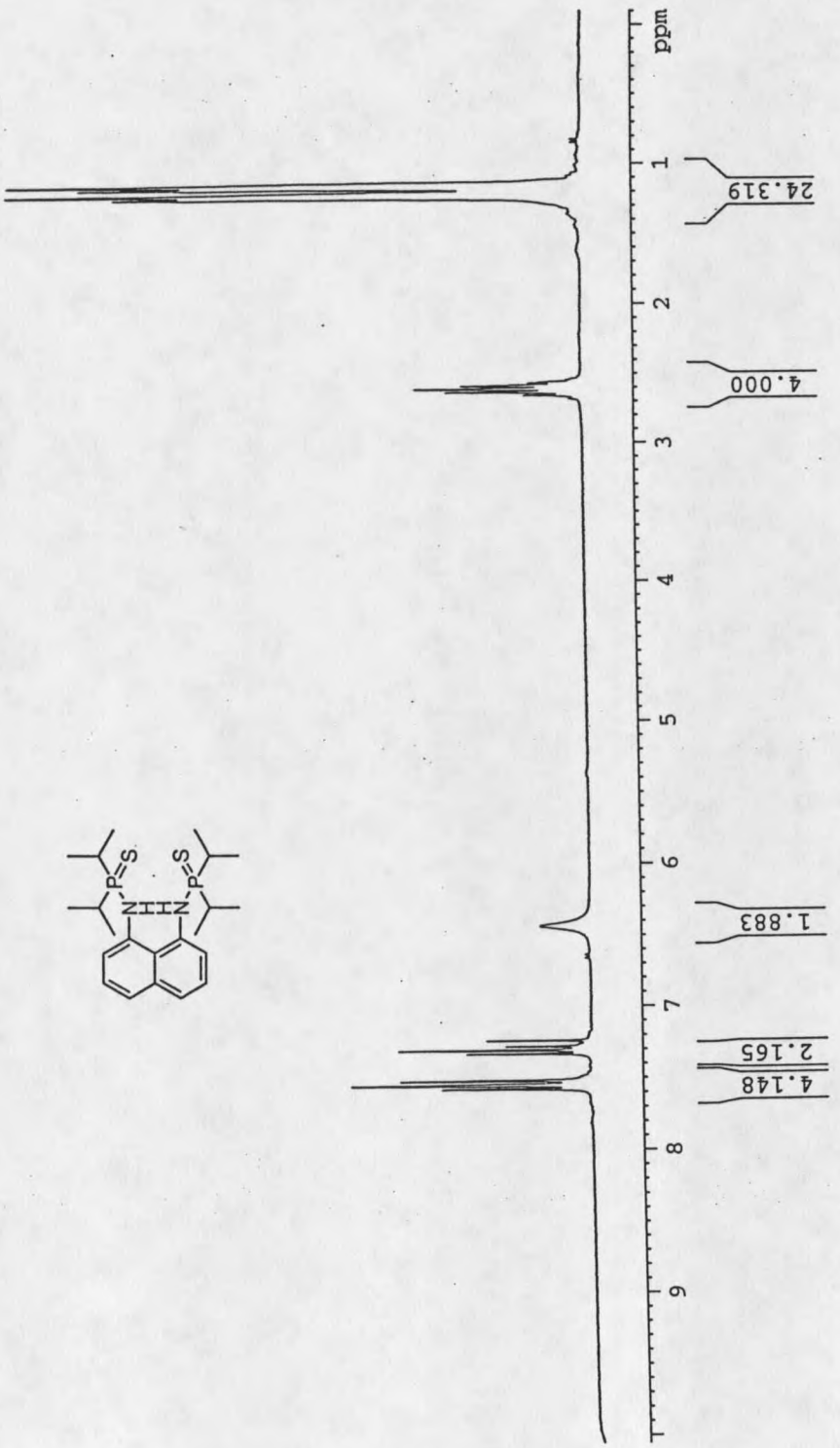


Figure 136. $^{1}H\{^{31}P\}$ NMR Spectrum of *N,N'*-Bis(*P,P*-diisopropylthiophosphinyl)-1,8-diaminonaphthalene (**60**)

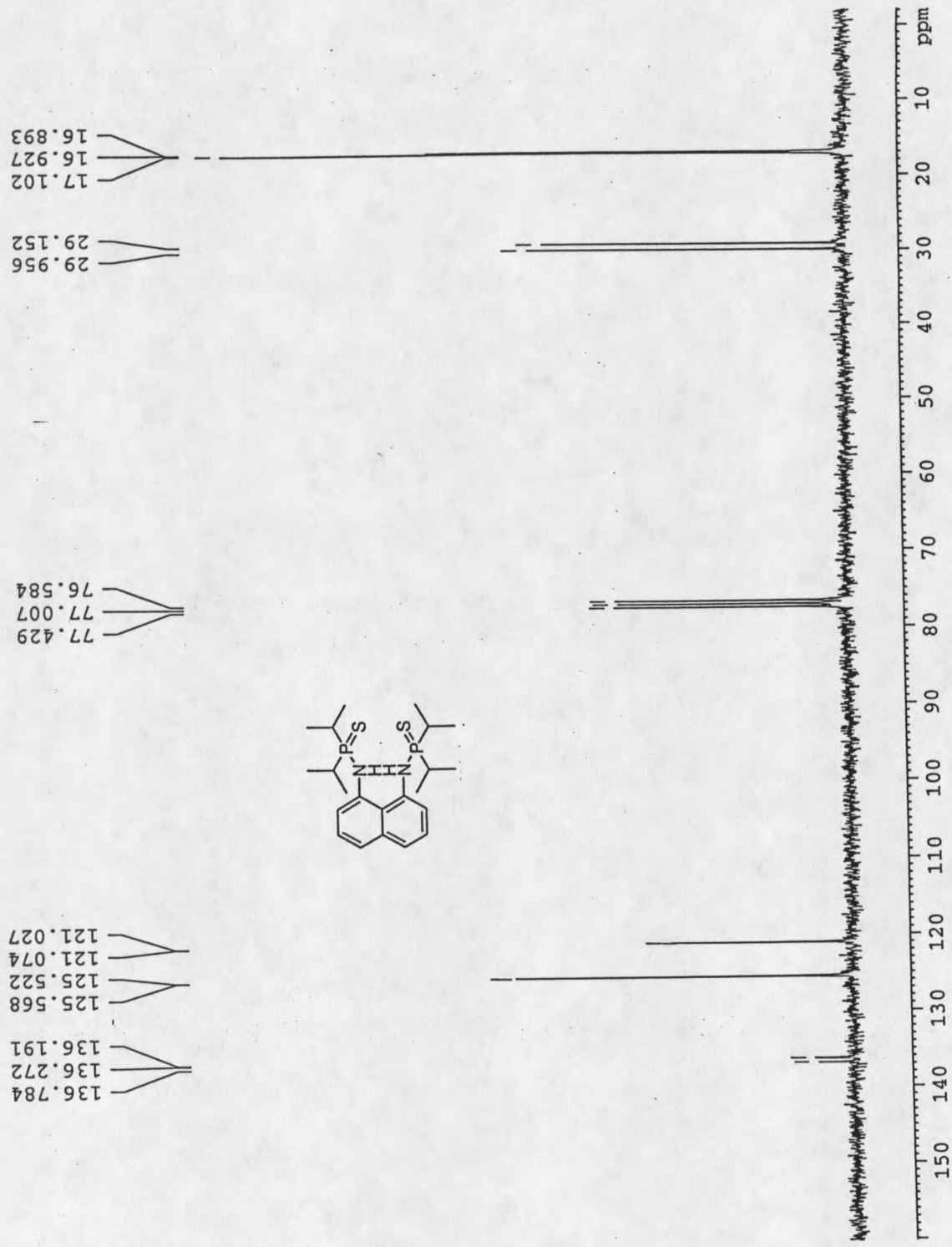


Figure 137. ^{13}C NMR Spectrum of *N,N'*-Bis(*P,P*-diisopropylthiophosphinyl)-1,8-diaminonaphthalene (**60**)

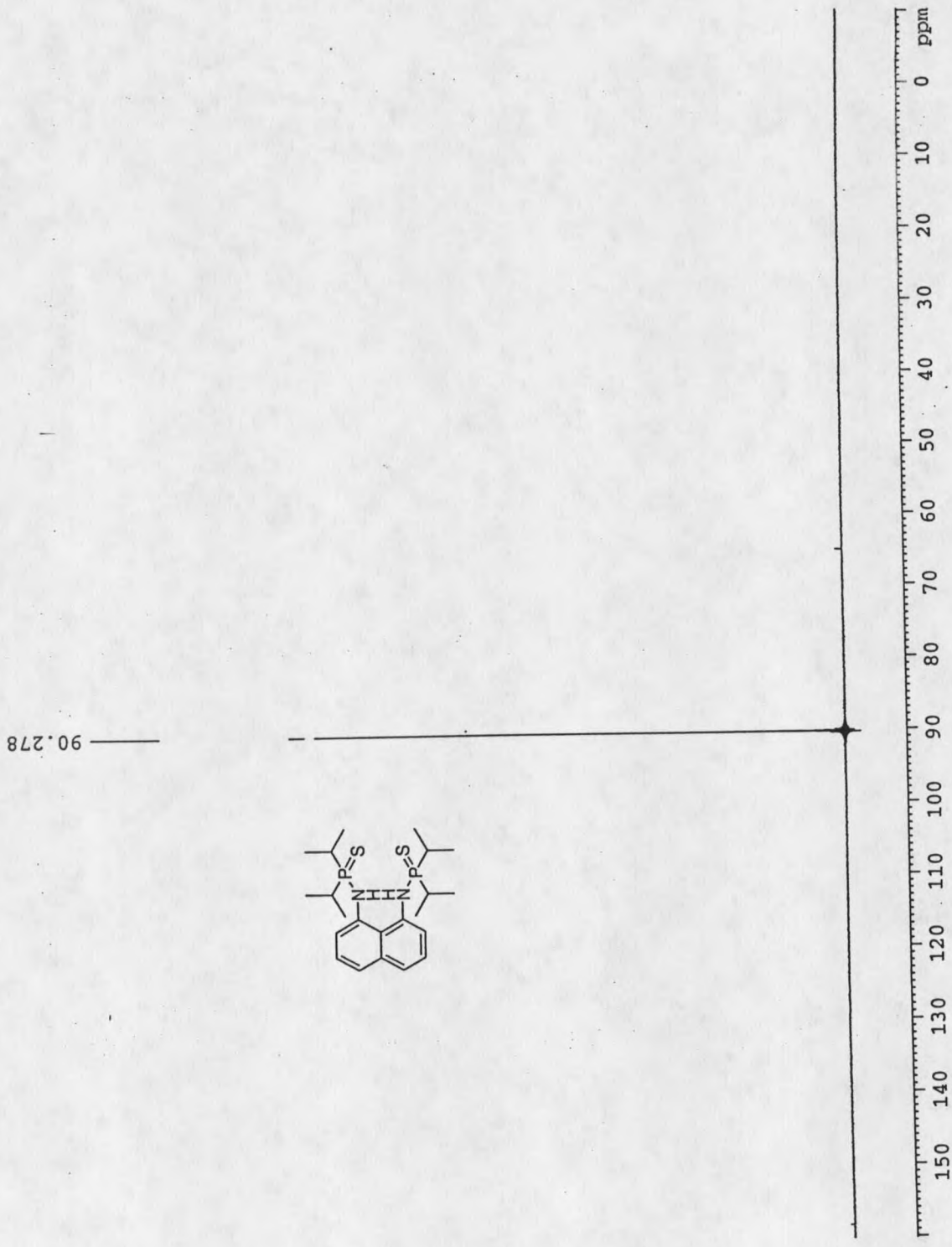


Figure 138. $^{31}P\{H\}$ NMR Spectrum of *N,N'*-Bis(*P,P*-diisopropylthiophosphinyl)-1,8-diaminonaphthalene (**60**)

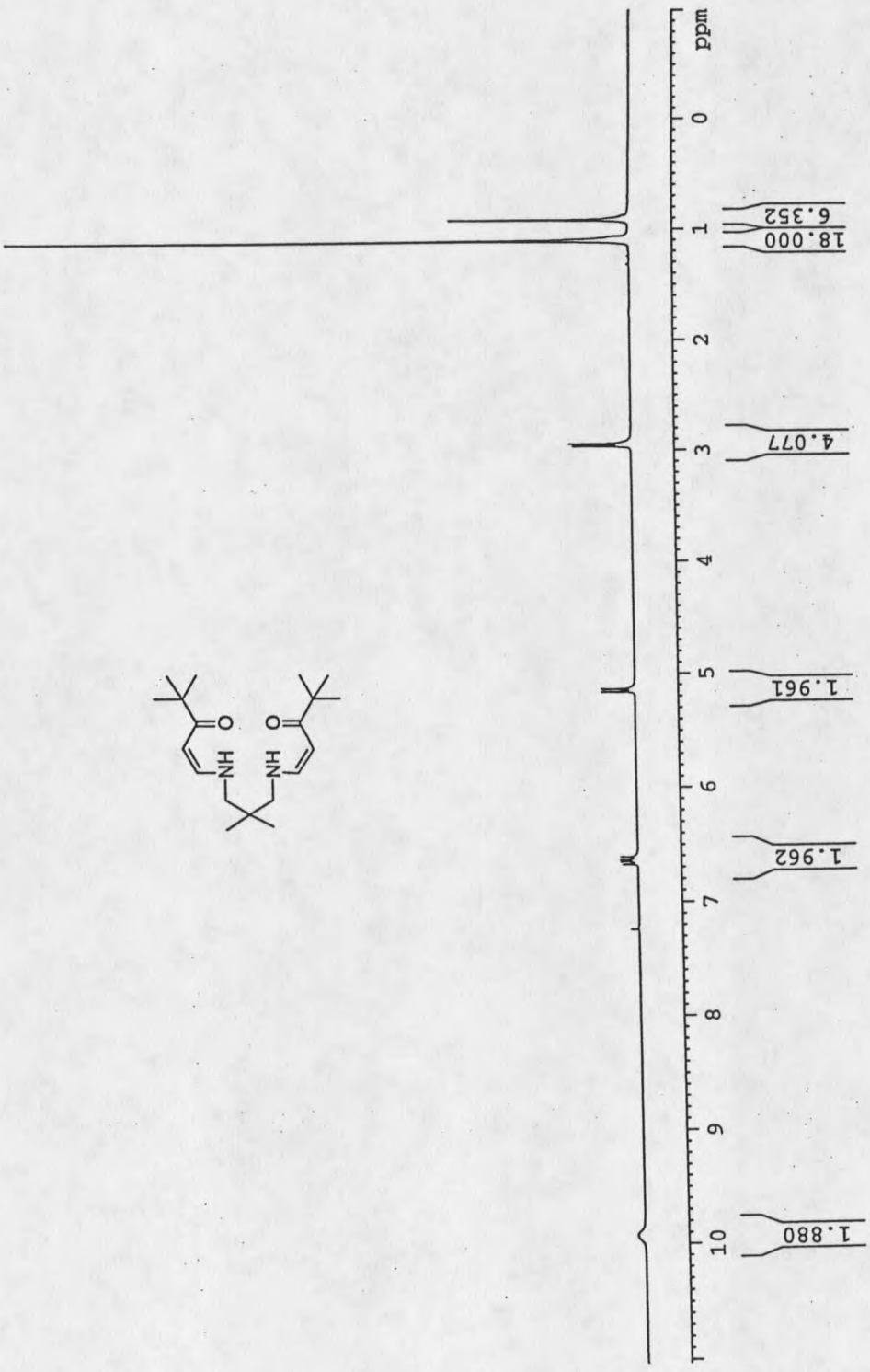


Figure 139. ^{1}H NMR Spectrum of *N,N'*-Bis(4,4-dimethylpent-1-ene-3-onyl)-2,2-dimethyl-1,3-propanediamine (**69a**)

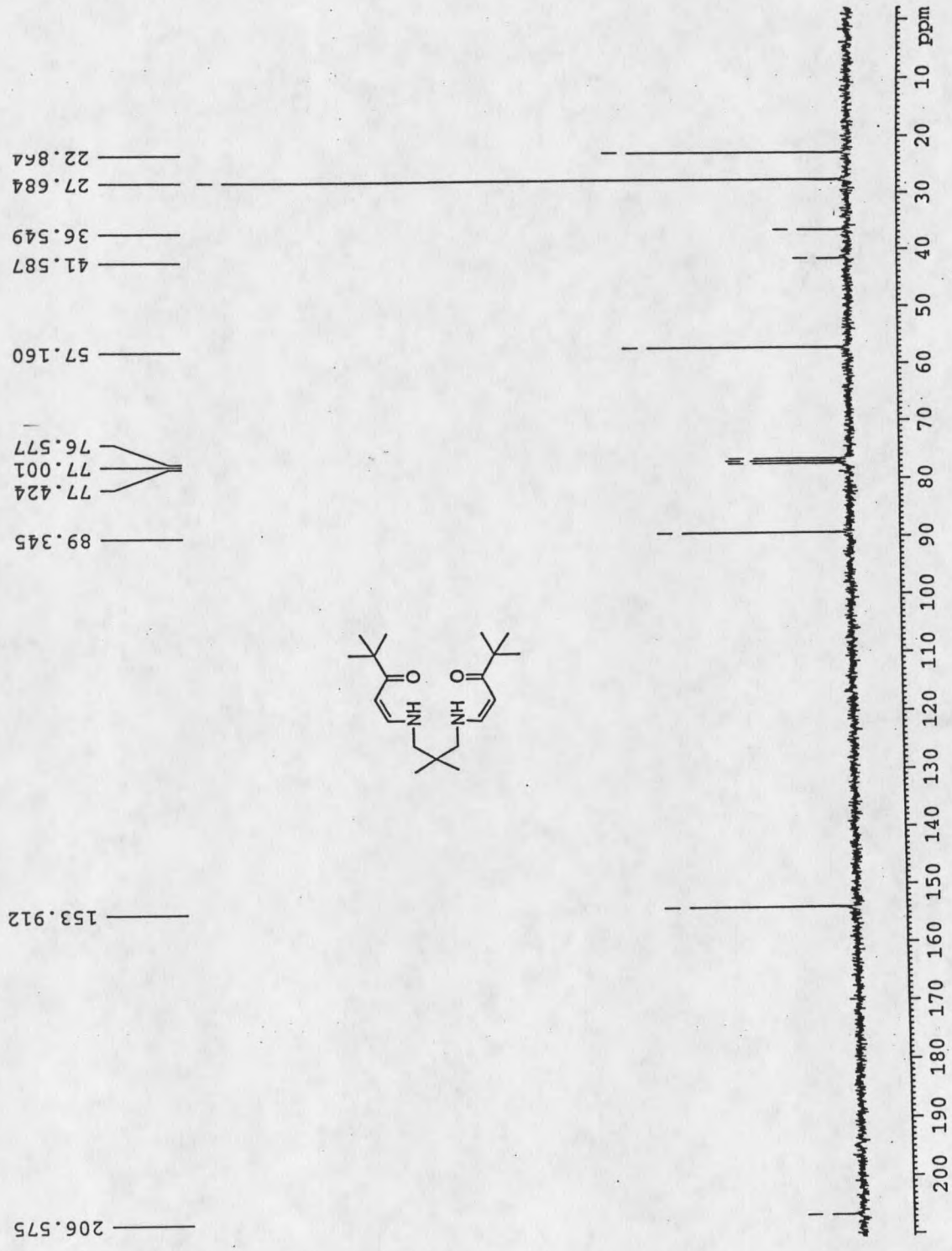


Figure 140. ^{13}C NMR Spectrum of *N,N'*-Bis(4,4-dimethylpent-1-ene-3-onyl)-2,2-dimethyl-1,3-propanediamine (**69a**)

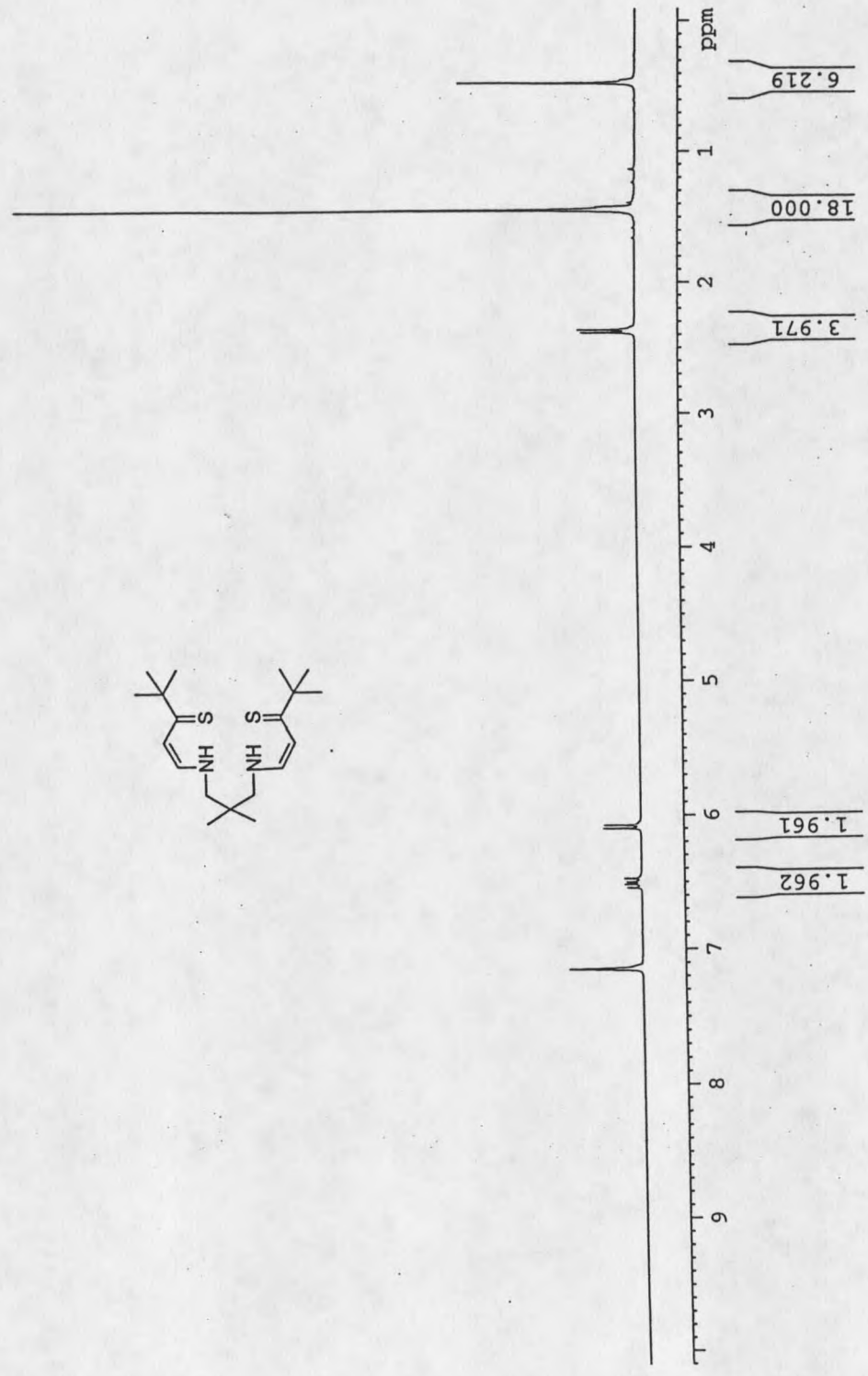


Figure 141. ^{1}H NMR Spectrum of *N,N'*-Bis(4,4-dimethylpent-1-ene-3-thionyl)-2,2-dimethyl-1,3-propanediamine (**69b**)

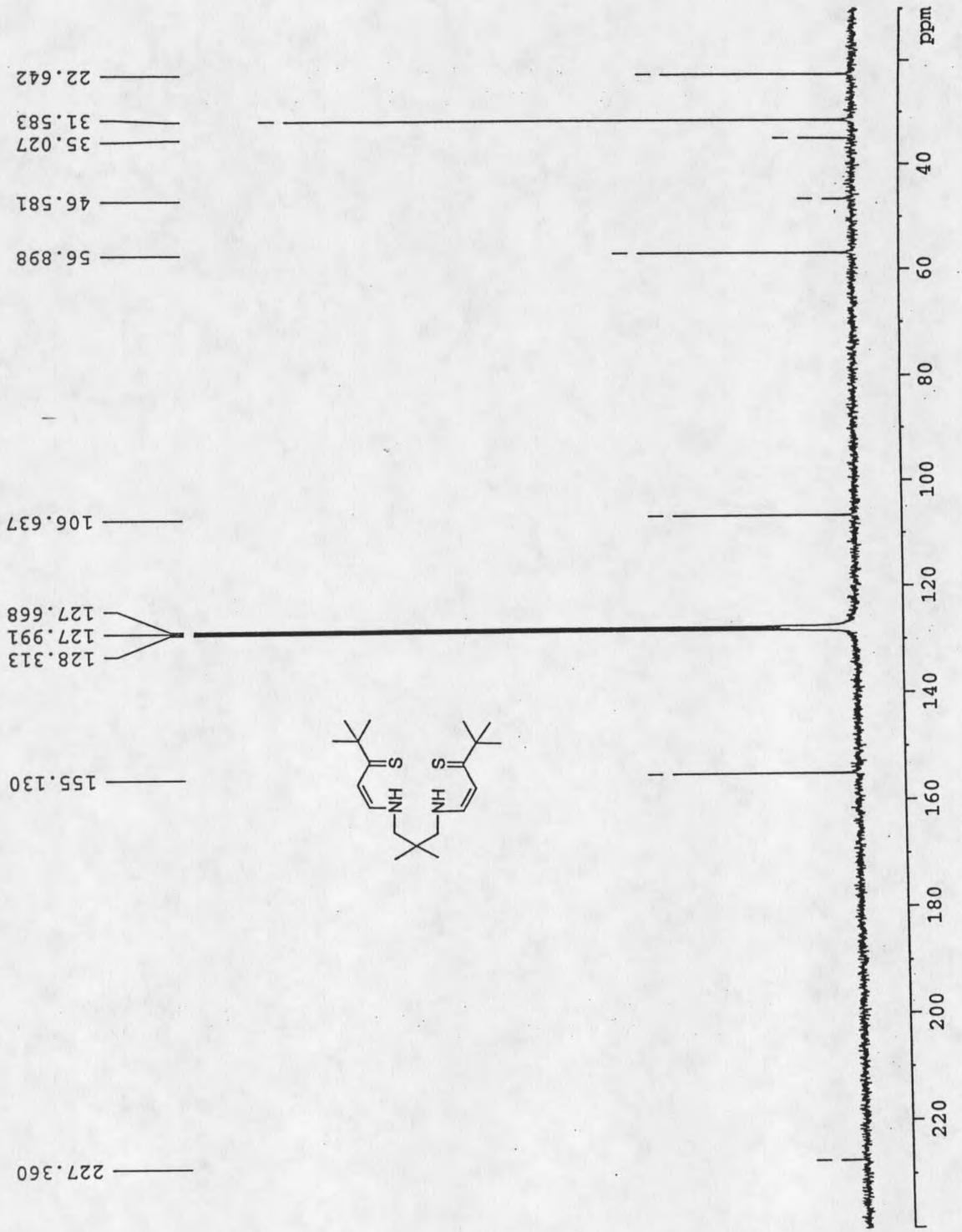


Figure 142. ^{13}C NMR Spectrum of *N,N'*-Bis(4,4-dimethylpent-1-ene-3-thionyl)-2,2-dimethyl-1,3-propanediamine (**69b**)

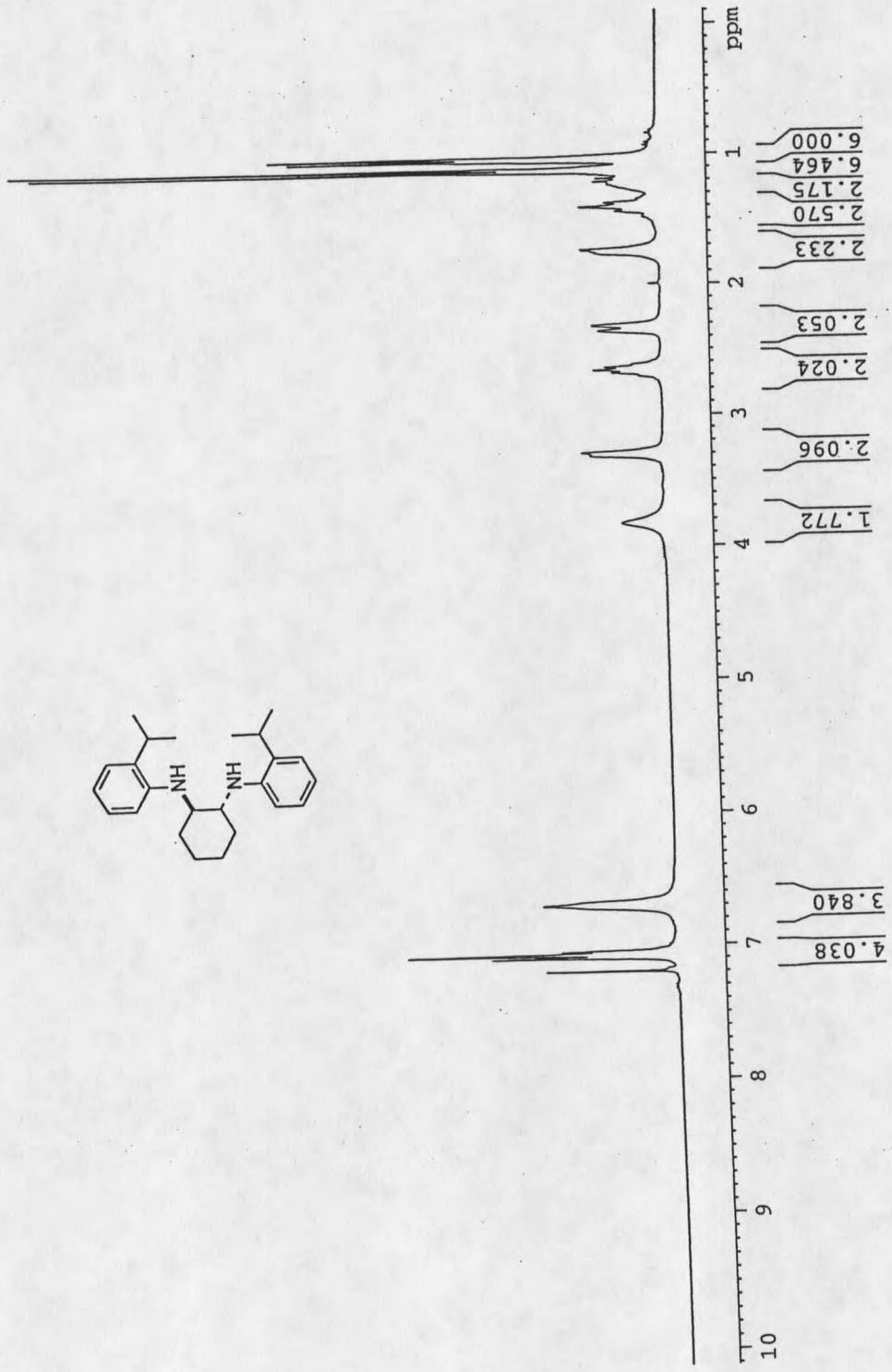


Figure 143. ^{1}H NMR Spectrum of (1*R*,2*R*)-*N*,*N*'-Bis(2-isopropylphenyl)-1,2-cyclohexanediamine (**71a**)

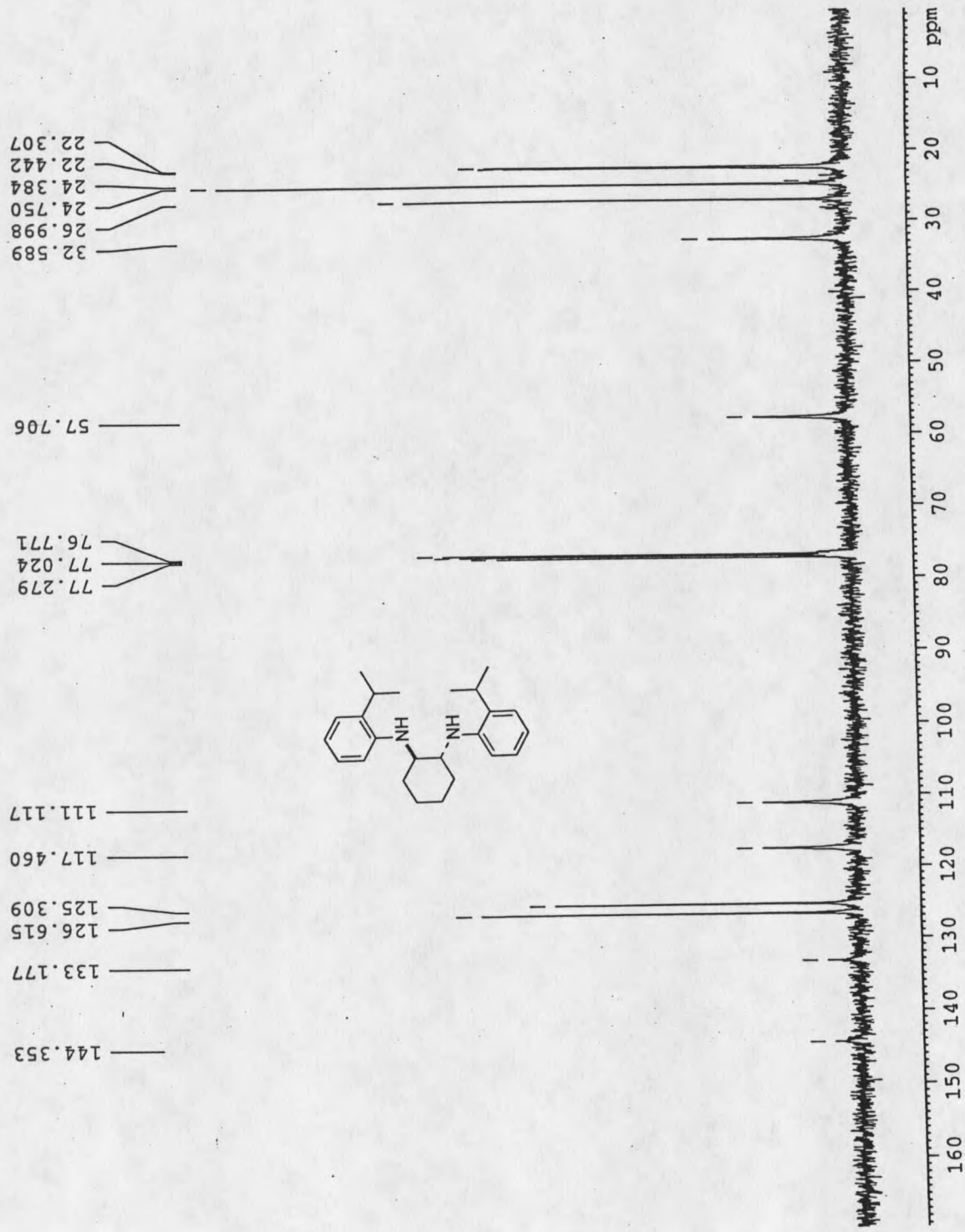


Figure 144. ^{13}C NMR Spectrum of (1*R*,2*R*)-*N*,*N*'-Bis(2-isopropylphenyl)-1,2-cyclohexanediamine (**71a**)

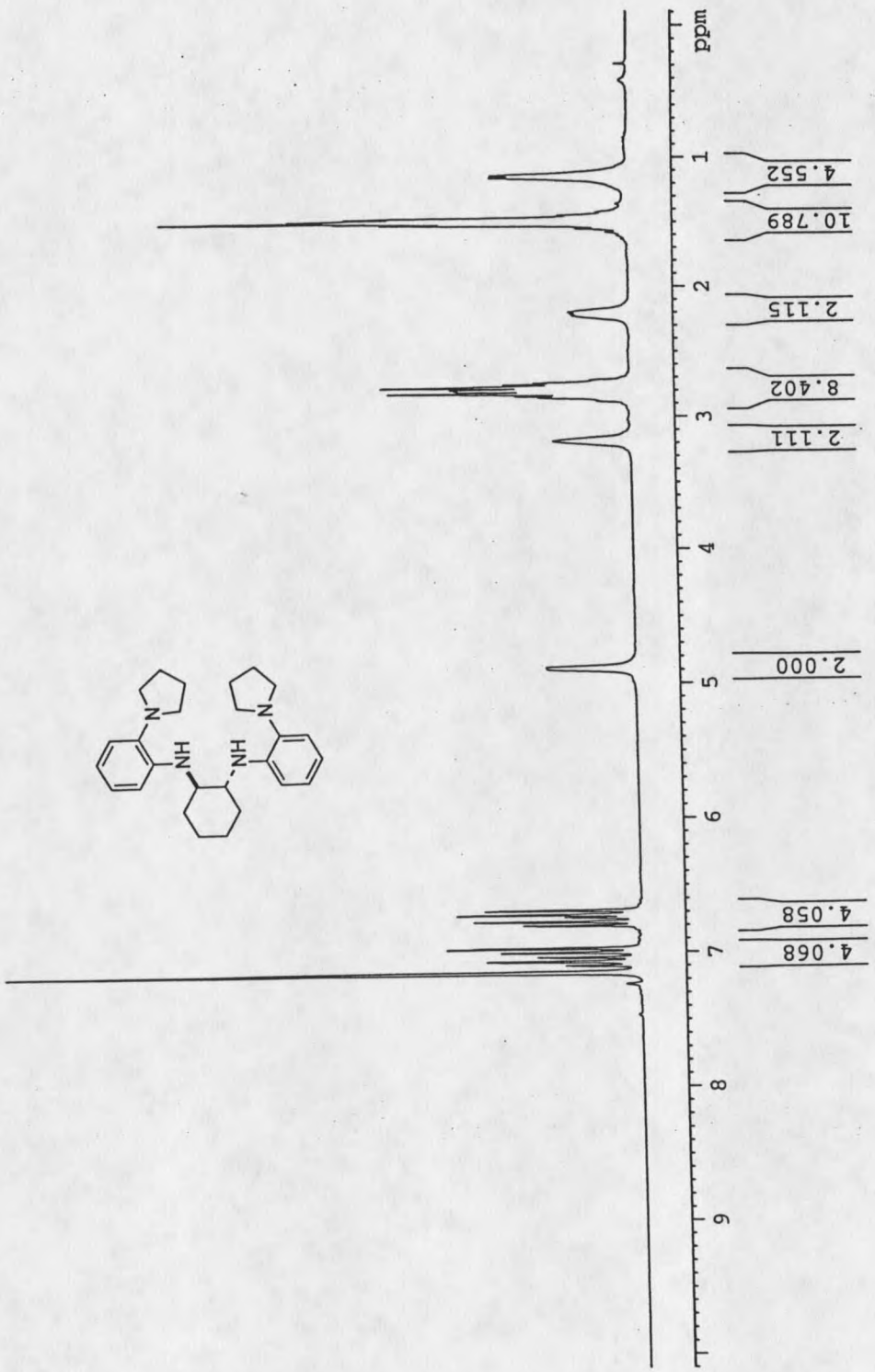


Figure 145. ^{1}H NMR Spectrum of (1*R*,2*R*)-*N*,*N*'-Bis(2-pyrrolidine-1-ylphenyl)-1,2-cyclohexanediamine (**71b**)

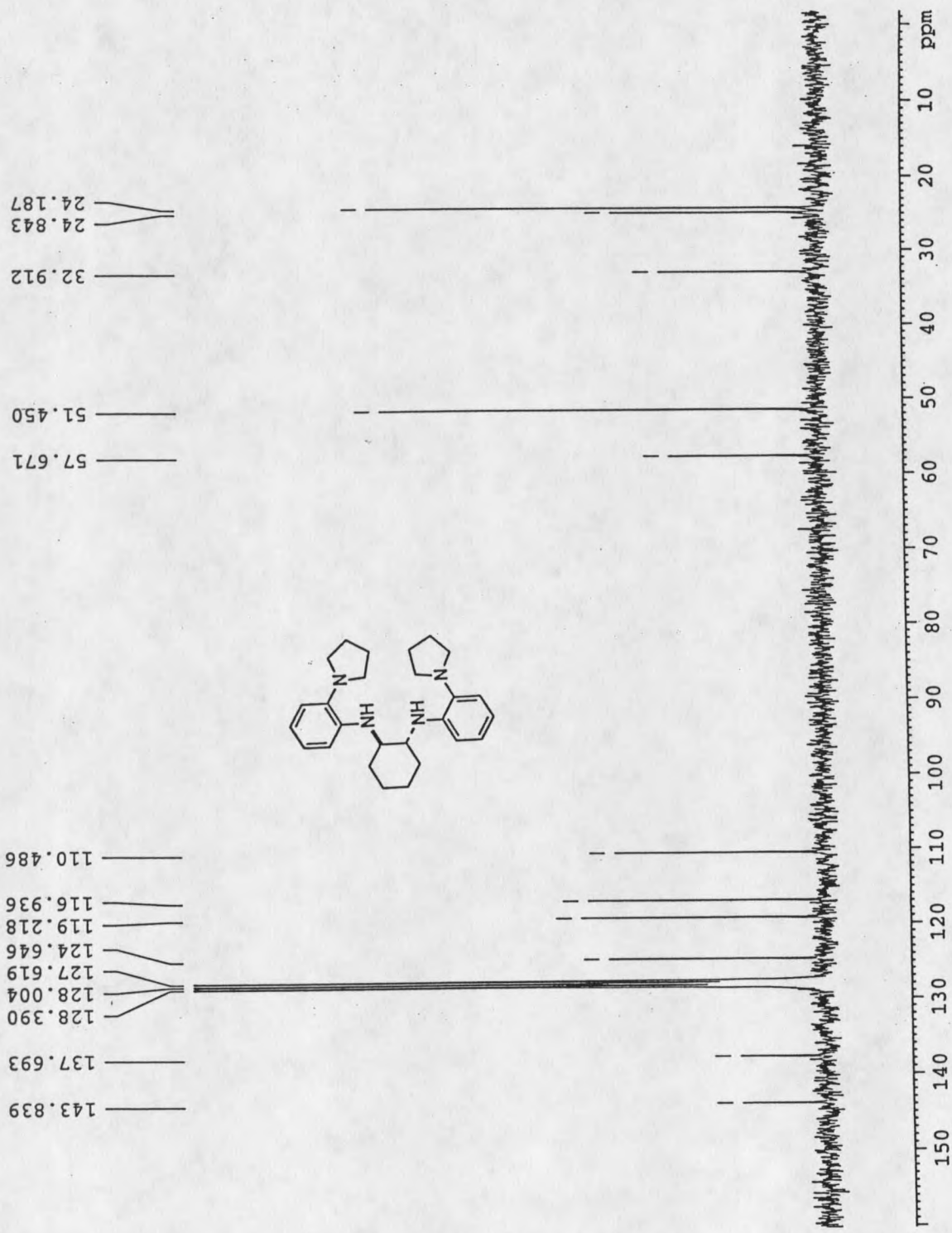


Figure 146. ^{13}C NMR Spectrum of (1*R*,2*R*)-*N*,*N'*-Bis(2-pyrrolidine-1-ylphenyl)-1,2-cyclohexanediamine (**71b**)

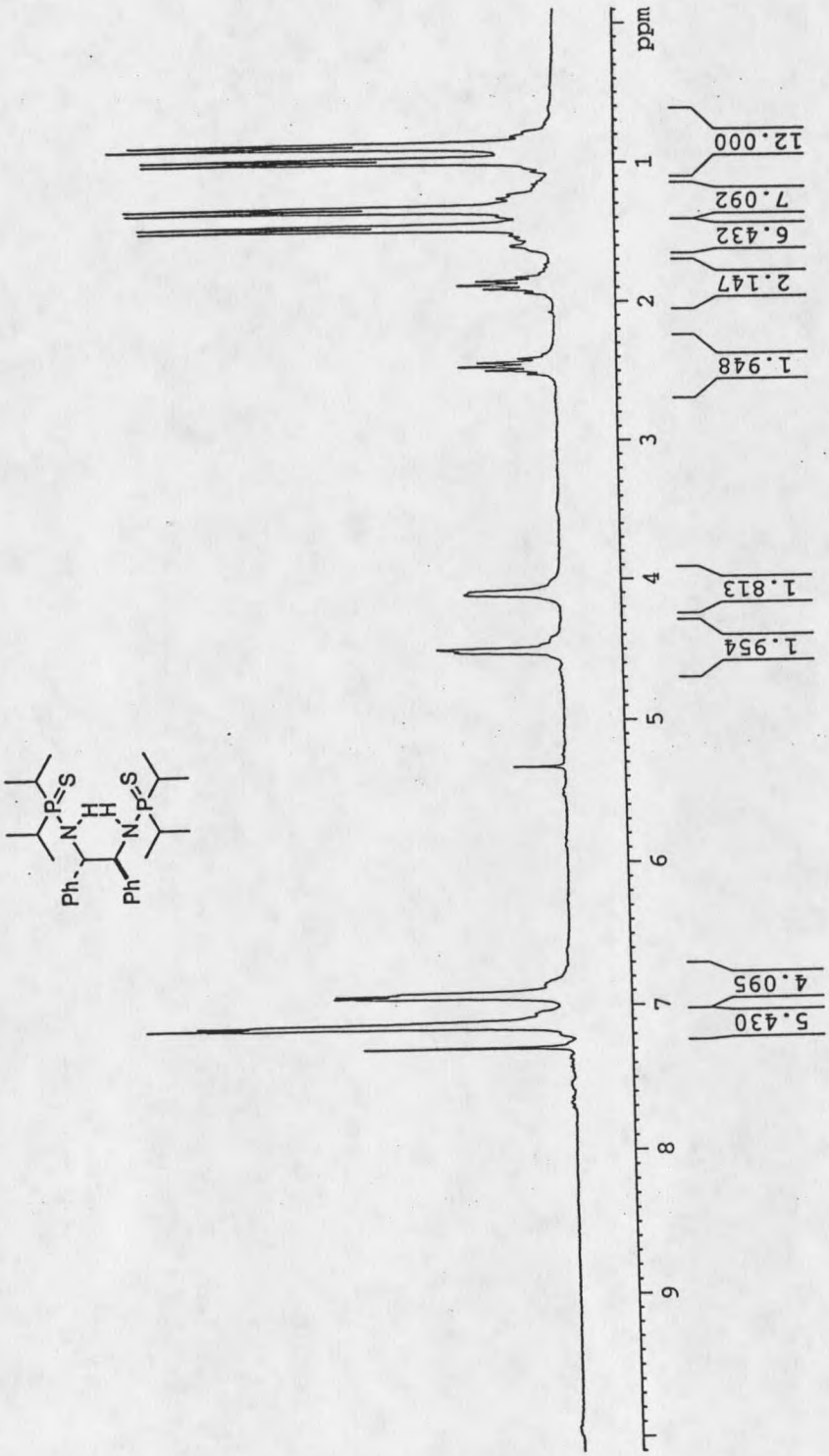


Figure 147. $^{1}H\{^{31}P\}$ NMR Spectrum of (1*R*,2*R*)-*N*,*N*'-Bis(*P*,*P*-diisopropylthiophosphinyl)-1,2-diphenylethylenediamine (**72**)

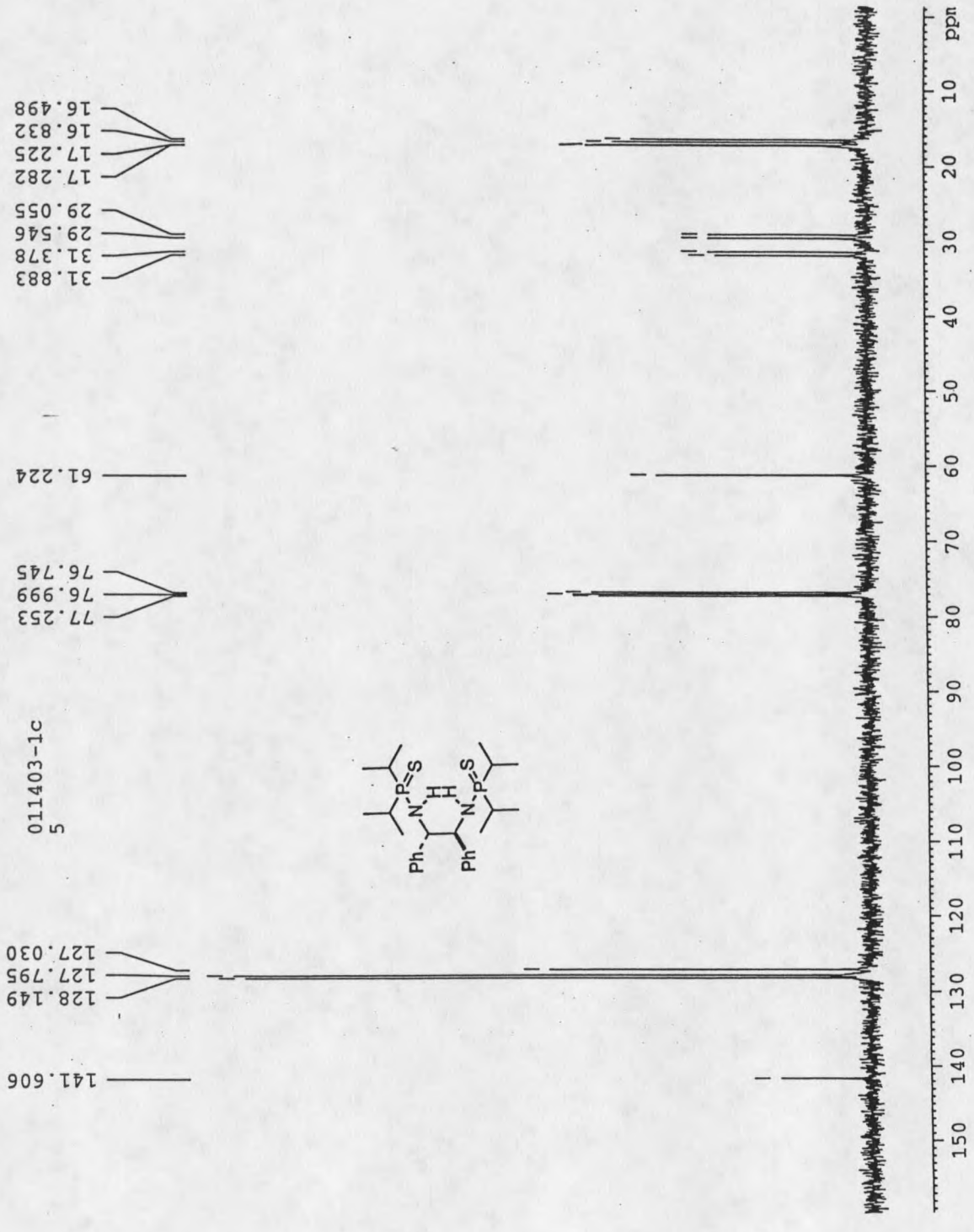


Figure 148. ^{13}C NMR Spectrum of (1*R*,2*R*)-*N,N'*-Bis(*P,P*-diisopropylthiophosphinyl)-1,2-diphenylethylenediamine (**72**)

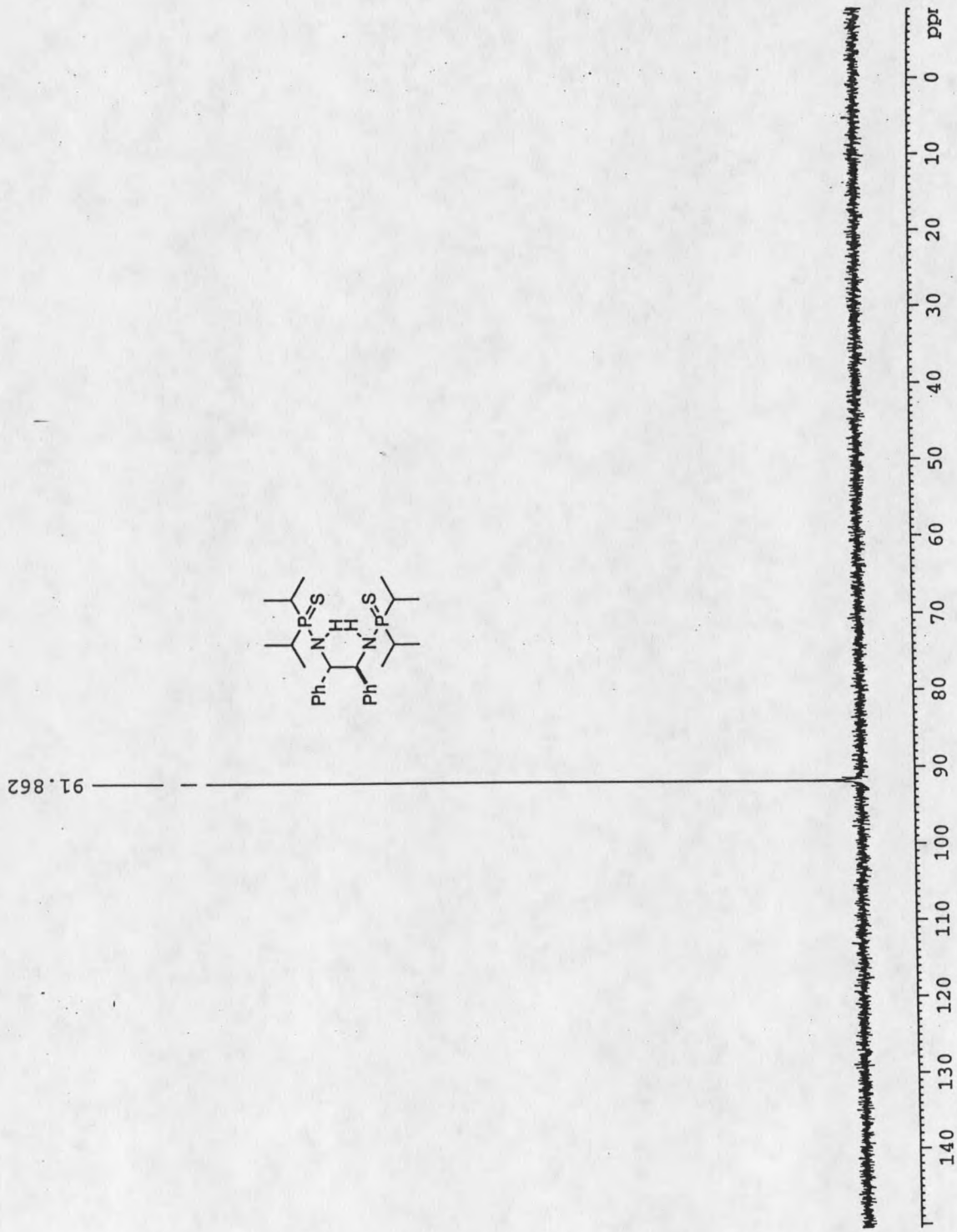


Figure 149. $^{31}P\{^{1}H\}$ NMR Spectrum of (1*R*,2*R*)-*N,N'*-Bis(*P,P*-diisopropylthiophosphinyl)-1,2-diphenylethylenediamine (**72**)

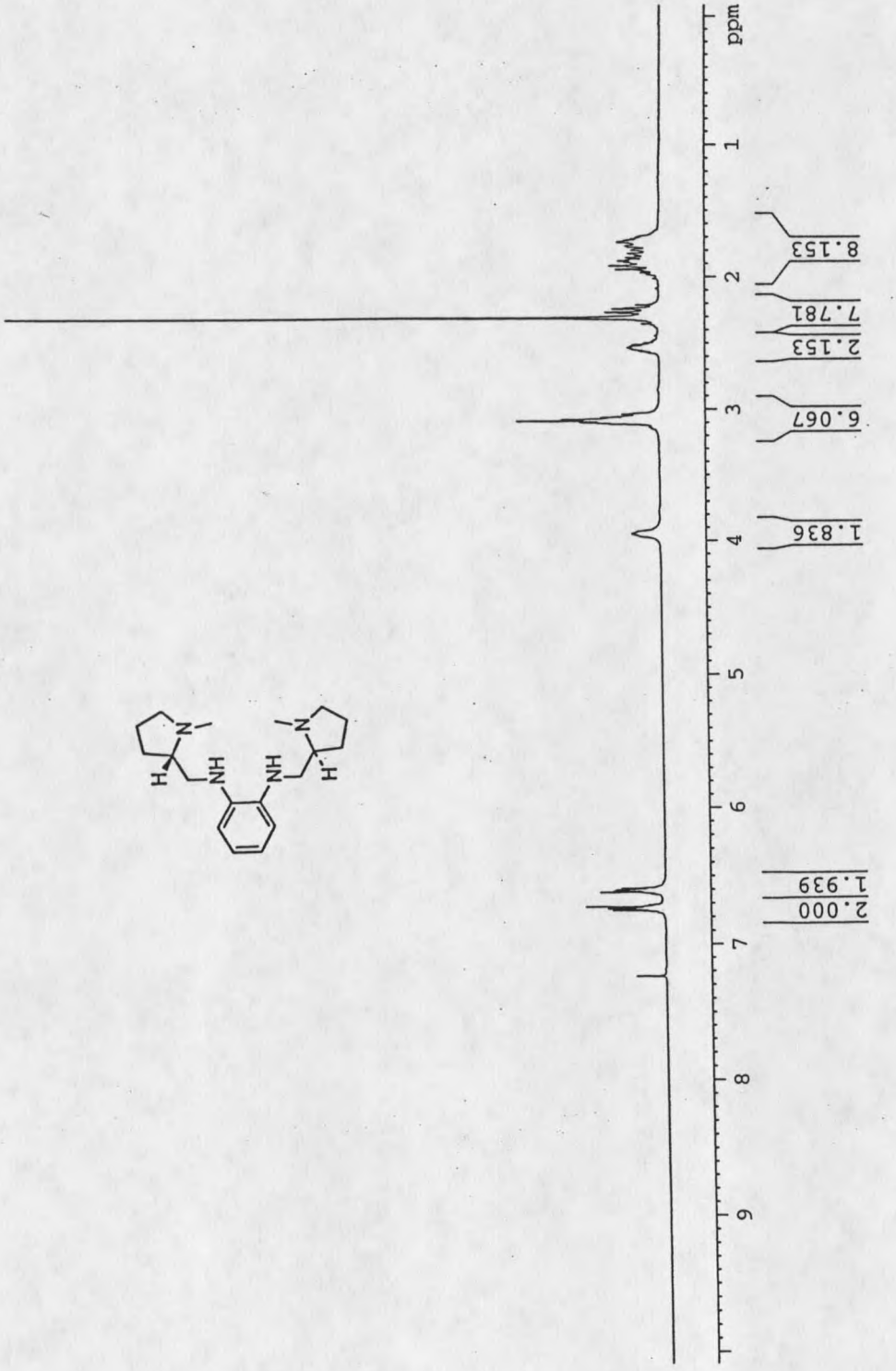


Figure 150. ^{1}H NMR Spectrum of *N,N'*-Bis[(2*S*)-1-methylpyrrolidine-2-ylmethyl]-1,2-phenylenediamine (**73a**)

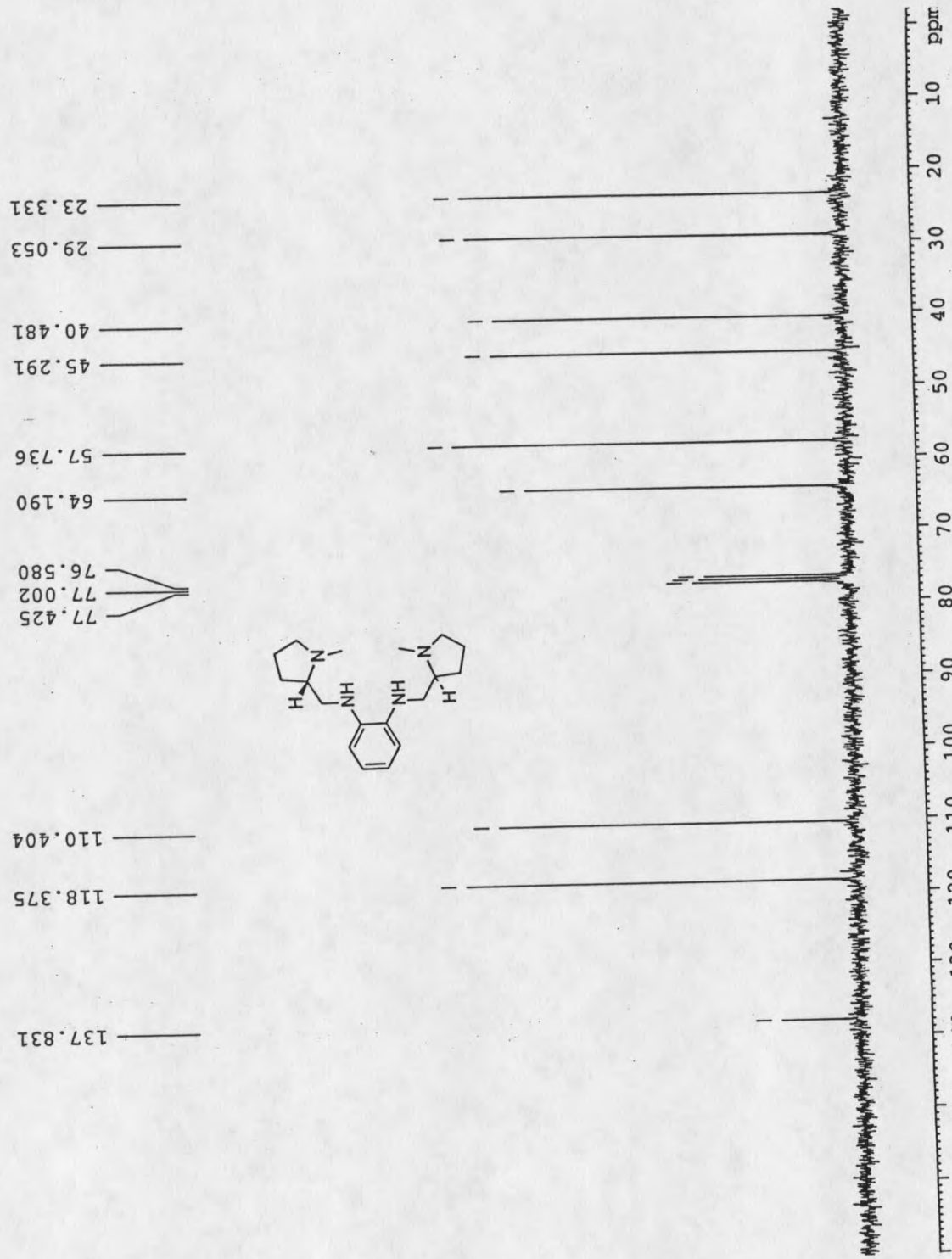


Figure 151. ^{13}C NMR Spectrum of *N,N'*-Bis[(2*S*)-1-methylpyrrolidine-2-ylmethyl]-1,2-phenylenediamine (**73a**)

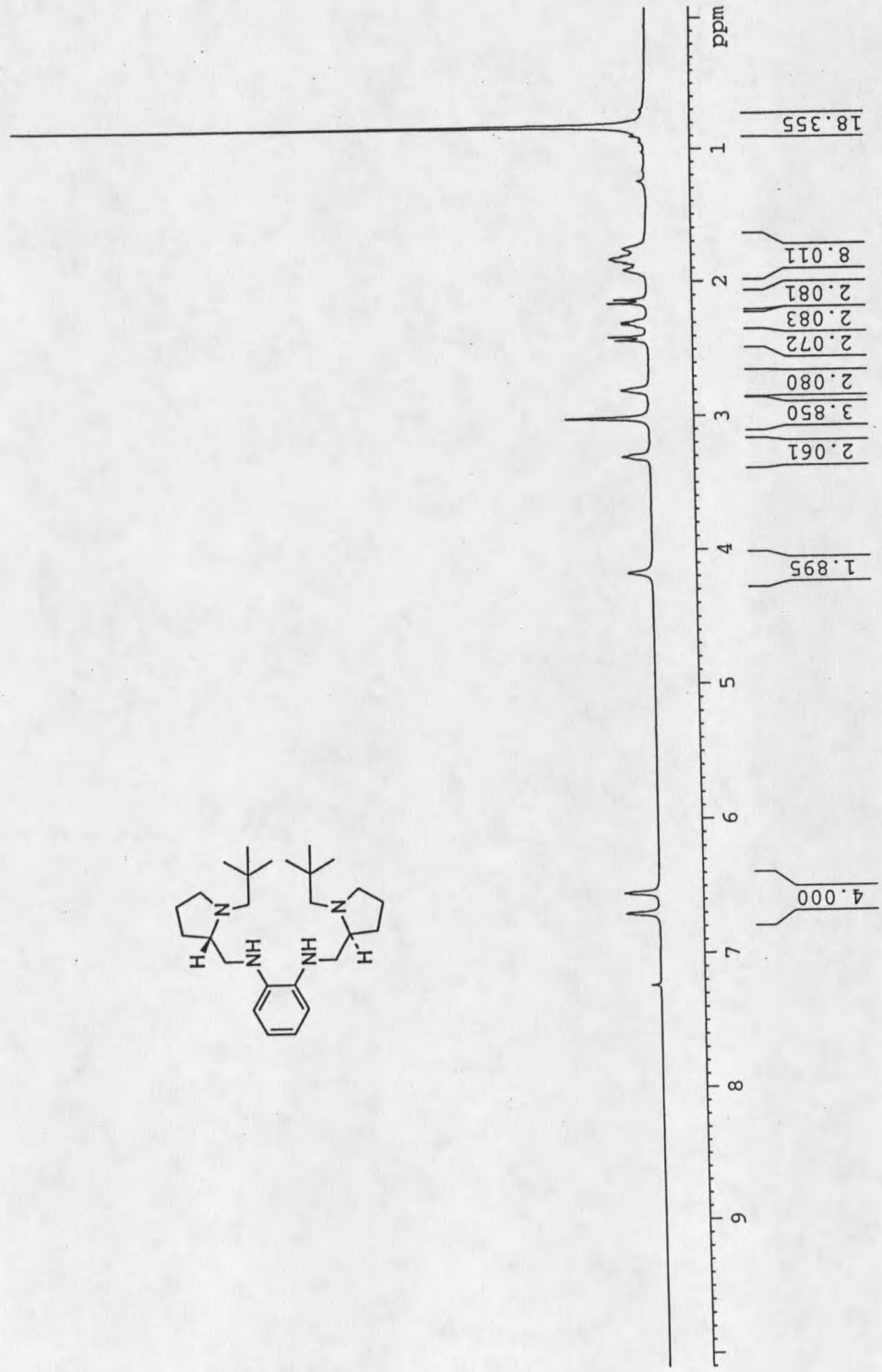


Figure 152. ^{1}H NMR Spectrum of *N,N'*-Bis[(2*S*)-1-(2,2-dimethylpropyl)pyrrolidine-2-ylmethyl]-1,2-phenylenediamine (**73b**)

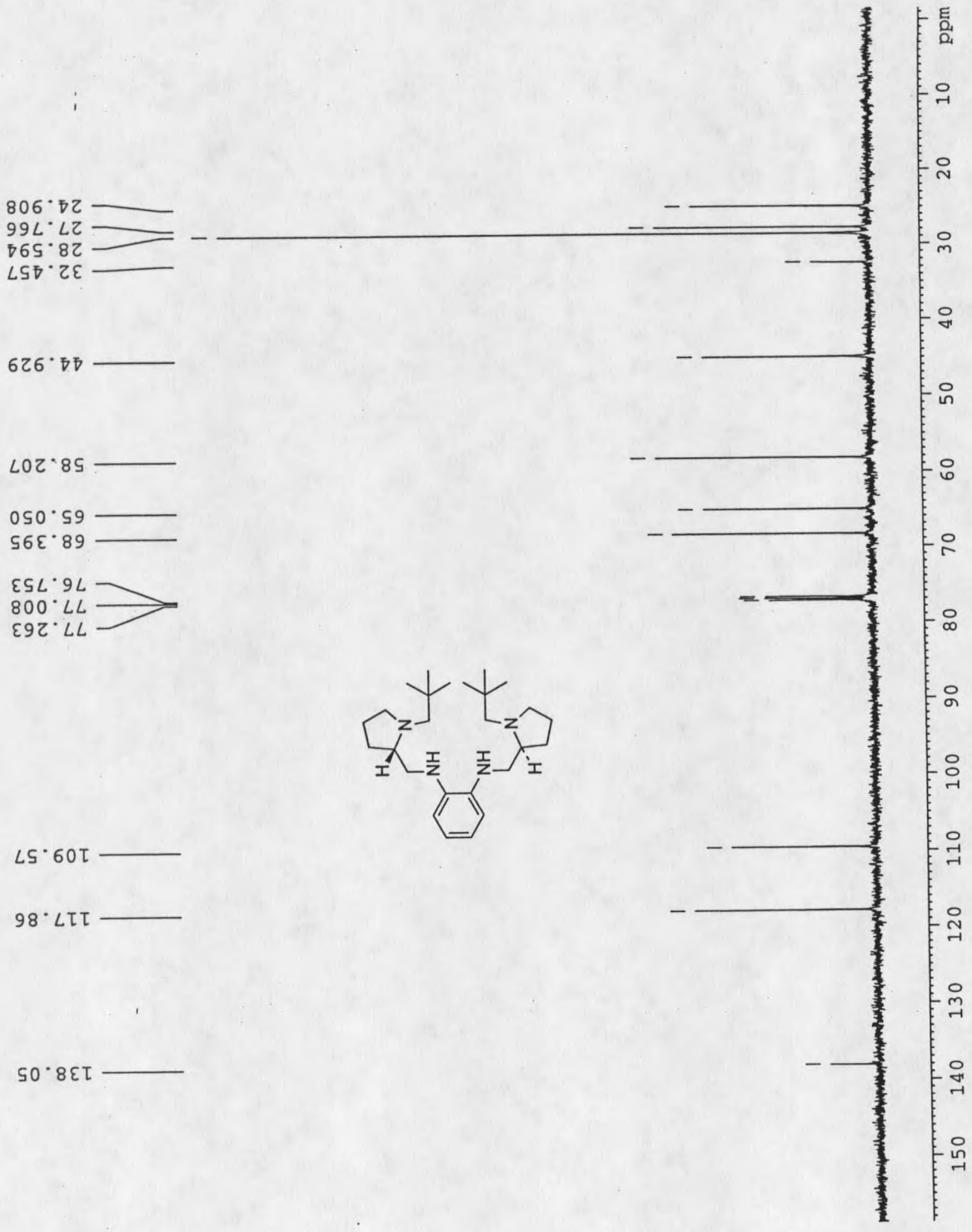


Figure 153. ^{13}C NMR Spectrum of *N,N'*-Bis[(2*S*)-1-(2,2-dimethylpropyl)pyrrolidine-2-ylmethyl]-1,2-phenylenediamine (**73b**)

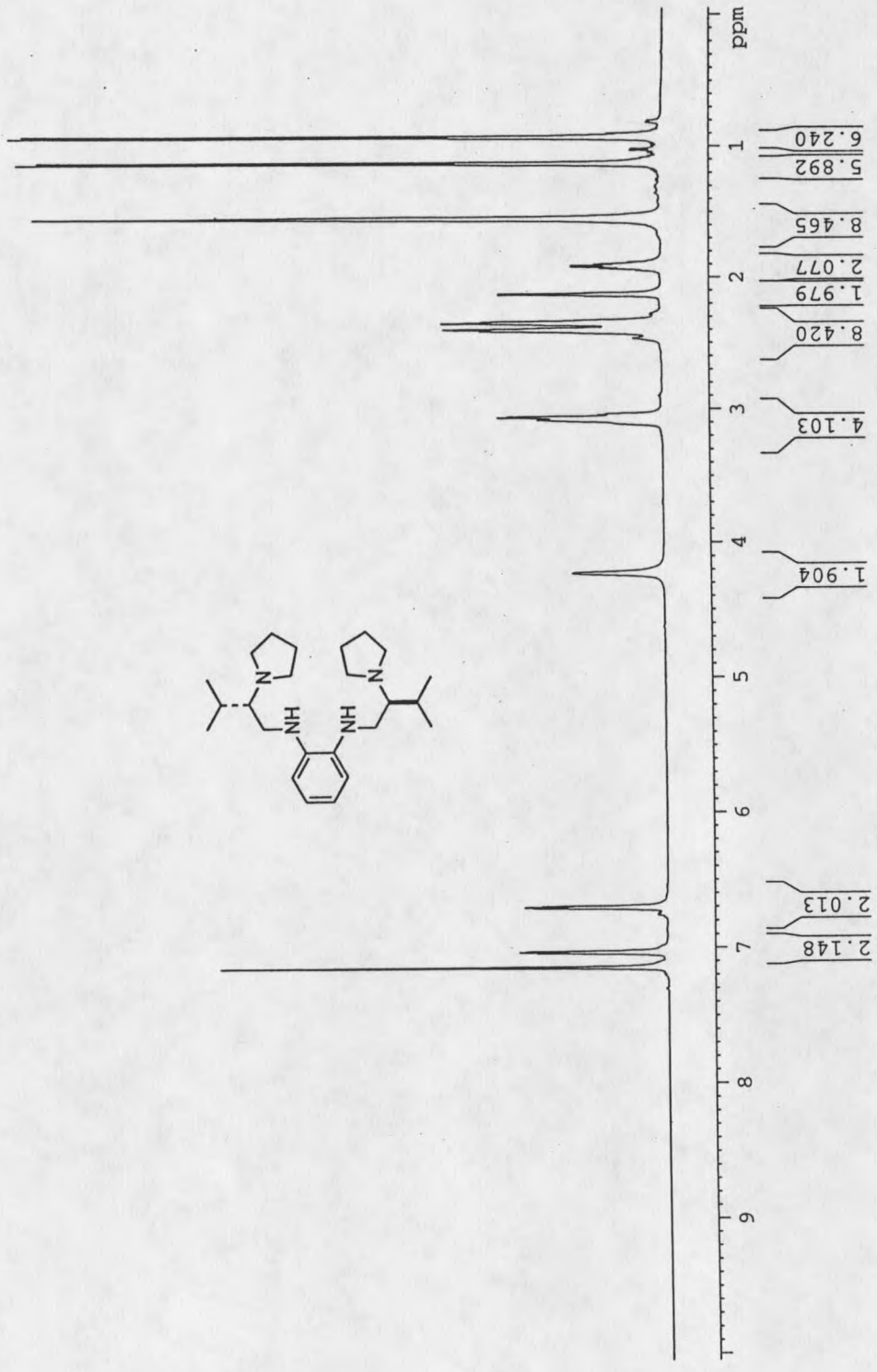


Figure 154. ^{1}H NMR Spectrum of *N,N'*-Bis[(2*S*)-2-isopropyl-2-pyrrolidinylethyl]-1,2-phenylenediamine (**73c**)

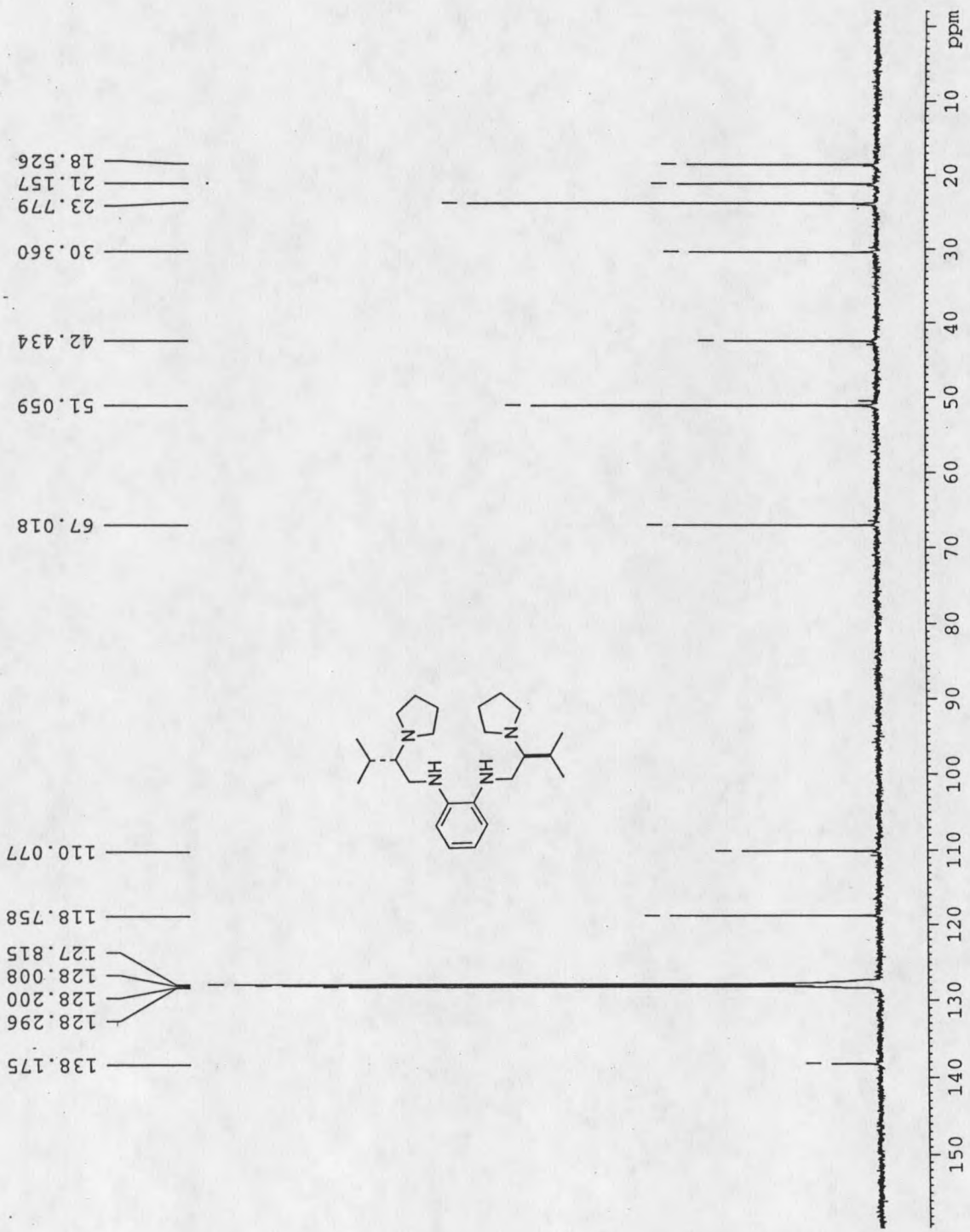


Figure 155. ^{13}C NMR Spectrum of *N,N'*-Bis[(2*S*)-2-isopropyl-2-pyrrolidinylethyl]-1,2-phenylenediamine (**73c**)

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