To the Graduate Council:

I am submitting herewith a thesis written by Danny Rosario Martineau Jr. entitled " Silver Initiated Rearrangement of N-Chloroamines." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemistry.

Fred M. Schell, Major Professor

We have read this thesis
and recommend its acceptance:

Accepted for the Council:

Associate Vice Chancellor and
Dean of The Graduate School

SILVER INITIATED REARRANGEMENT OF N-CHLOROAMINES

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Danny Rosario Martineau Jr.

August 1997

DEDICATION

To my beautiful wife

Christie

for her patience and self sacrifice

and

To my friend

Timothy

who left this world with hopes and fears lifted to the Cross of Christ

and

To another friend

Michael

who now rests in the Shadow of The Almighty

ACKNOWLEDGEMENTS

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Abstract

Several secondary N-chloroamines were characterized by carbon-13 and proton NMR spectroscopy. The resulting chemical shifts were consistent with anticipated resonance and inductive effects exhibited by the compounds at hand. When allowed to stir for two days in the presence of silver tetrafluoroborate sealed under argon gas in the absence of light, two of the four N-chloroamines under investigation underwent rearrangement. The rearranged products were hydrolyzed upon work-up in a basic medium. The resulting anilines and elimination by-products were isolated by use of packed column chromatography. Separate syntheses of expected products were carried out to provide reference NMR spectra. Recovered compounds were also confirmed by mass spectroscopy and two dimensional NMR experiments.

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LIST OF SYMBOLS

bs	broad singlet
^{13}C	carbon-13 isotope
d	doublet
g	gram
^{1}H	hydrogen nucleus
hrs	hours
J	coupling constant
k	rate constant
L	liter
m	multiplet
M	molarity
mg	miligram
MHz	mega hertz
mL	mililiter
N	normality
NMR	nuclear magnetic resonance
pent	pentet
pH	hydronium ion concentration relative to water
ppm	parts per million
ps	pseudo

LIST OF SYMBOLS (continued)

q	quartet
R_f	ratio of fronts
s	singlet
t	triplet
TLC	thin layer chromatography
TMS	tetra methyl silane
v	volume
w	weight
Δ	difference of
δ	parts per million from TMS
ν	chemical shift measured in hertz
π	represents delocalized electrons in unsaturated systems

A Brief History on The Rearrangement of Nitrogen Containing Compounds

Organic reactions involving carbocations are well known and were accepted early in this century. However, prior to the nineteen sixties, there was very little investigation concerning possible nitrogen analogs of known trivalent electron-deficient carbocations . Such an analog, the divalent electron-deficient nitrogen species, has come to be known as a nitrenium ion. Figure 1 shows two nitrenium ions one might encounter.[1]

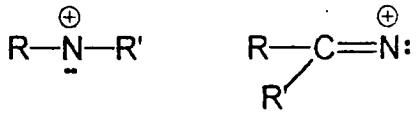


Figure 1. Examples of Nitrenium Ions

Stieglitz and coworker observed the rearrangement of triphenylmethylhydroxylamines (in the presence of phosphorus pentachloride), triphenylmethylchloroamines (in an alkaline medium) and triphenylmethyl azides (when exposed to heat). They however did not associate these reactions with a possible nitrenium ion intermediate. Stieglitz, instead, proposed that an univalent nitrogen derivative (a nitrene) was responsible for the observed rearrangements.[2] This view was not challenged until studies of *migration aptitudes* were performed by Newman and Hay (1953).[3] They varied the aryl substituents of triarylmethylhydroxlamines and compared the results to those seen by Stieglitz (his aryl group was simply phenyl). The tendencies observed were similar to those seen in studies of the pinacol rearrangement.

Roughly a decade later these types of rearrangements became the major focus of Gassman . He made the N-chloro derivative of 2-azabicyclo[2.2.2] octane, allowing it to reflux in a methanolic solution of silver nitrate to yield the product seen in Figure 2.[4]

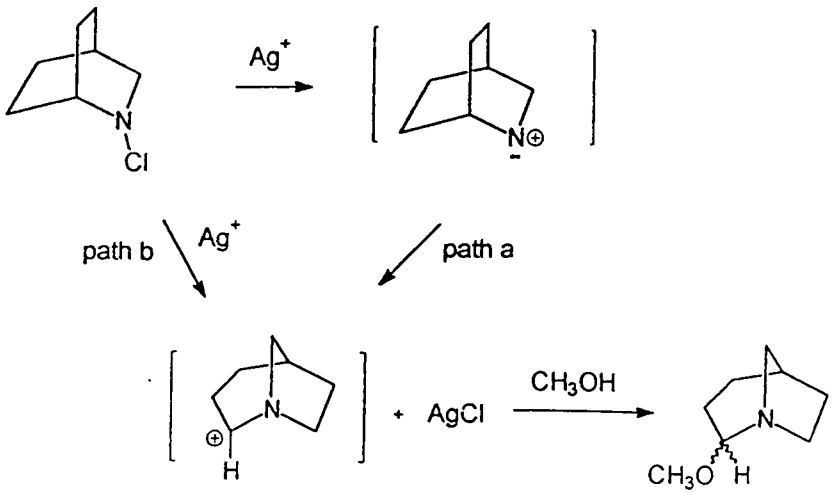


Figure 2. Rearrangement of N-Chloro-2-azabicyclo[2.2.2]octane

One can see how the formation of a nitrenium ion could be followed by an intramolecular 1,2- alkyl shift (path a), or a concerted scheme (path b), where the alkyl shift assists in the departure of the chloride anion. It can also be perceived in a *non-classical* fashion where the positive charge is delocalized as in Figure 3.

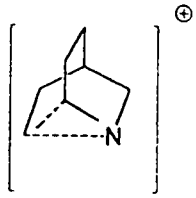
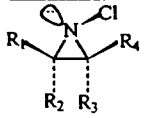
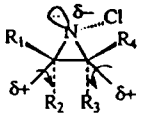


Figure 3. A Non-Classical Structure

It was known that the Woodward-Hoffmann symmetry rules were useful in predicting the products resulting from cyclopropyl cations upon electrocyclic ring opening. Applying this concept, Gassman's group did a study of the relative rates and the products (quaternary amine salts) which arose upon ring opening of several N-chloroazirines.[5] Table 1 shows how the changing of (R groups) affects the rate constant for the *disrotatory* openings.

Table 1. Ring Openings of Several N-chloroazirines

N-Chloroaziridine	Mode of ring opening	k_{rel}	Products
			
R_1,R_2,R_3 and R_4=H	I	1	2 HCH + NH_4Cl
R_1,R_2 and R_3=H ; R_4=CH_3	II	15	CH_3CH + HCH + NH_4Cl
R_1,R_2 and R_4=H ; R_3=CH_3	III	210	" " "
R_1 and R_3=H ; R_2 and R_4=CH_3	IV	1490	2 CH_3CH + NH_4Cl
R_1 and R_2=H ; R_3 and R_4=CH_3	V	1860	CH_3CH + HCH + NH_4Cl
R_1 and R_4=H ; R_2 and R_3=CH_3	VI	155,000	2 CH_3CH + NH_4Cl

The table also reflects the formation of hydrolyzed products. The hope was that the ring opening experiment would shed light on whether the "N-Cl" bond was cleaved in a heterolytic fashion. If we compare the transition states of compounds **I** and **II**, we see that the differing behavior is simply a reflection of the differing substitution on carbon, *i.e.* their relative stability as they become electron deficient, (2° more stable than 1°). The close relative rate constants of **IV** and **V** can be understood as two secondary centers reacting slightly less than in the case of a primary and tertiary center. However, comparison of **IV** and **VI** shows a tremendous difference. This is due to an increased steric strain in **IV** as one methyl group rotates inward. When the reaction was run in water, all the rates were higher than in methanol which is as they expected for a more polar medium. They concluded that heterolytic cleavage of the "N-Cl" bond had occurred.

It is very common for reactions of N-chloroamines to give back the free amine from which the N-chloro compound was derived. Gassman realized that he needed to address the concept of spin inversion in the presence of heavy atom (for the most part halogenated) solvents.[6] A nitrenium ion can assume either a singlet or triplet spin state; thus, it is a unique cation. In the heavy atom experiment, they anticipated the triplet state behavior to be more like a nitrogen radical cation than carbocation-like; thus, it should be a fine hydrogen abstractor as in the Hofmann-Loffler-Freytag reaction.[7] The data presented in Table 2 are a reflection of the reaction shown in Figure 4 run in several mixed solvents, some containing heavy atoms; also shown are the corresponding singlet to triplet spin state ratios.

Table 2. Singlet to Triplet State Ratios

Solvent	Singlet : Triplet Products
CH_3OH/C_6H_{14}	8.2
CH_3OH/CCl_4	0.22
$CH_3OH/p\text{-}Br_2C_6H_4$	1.7
$CH_3OH/CHCl_3$	0.064
$CH_3OH/CHBr_3$	0.022
CH_3OH/H_2O	11.2

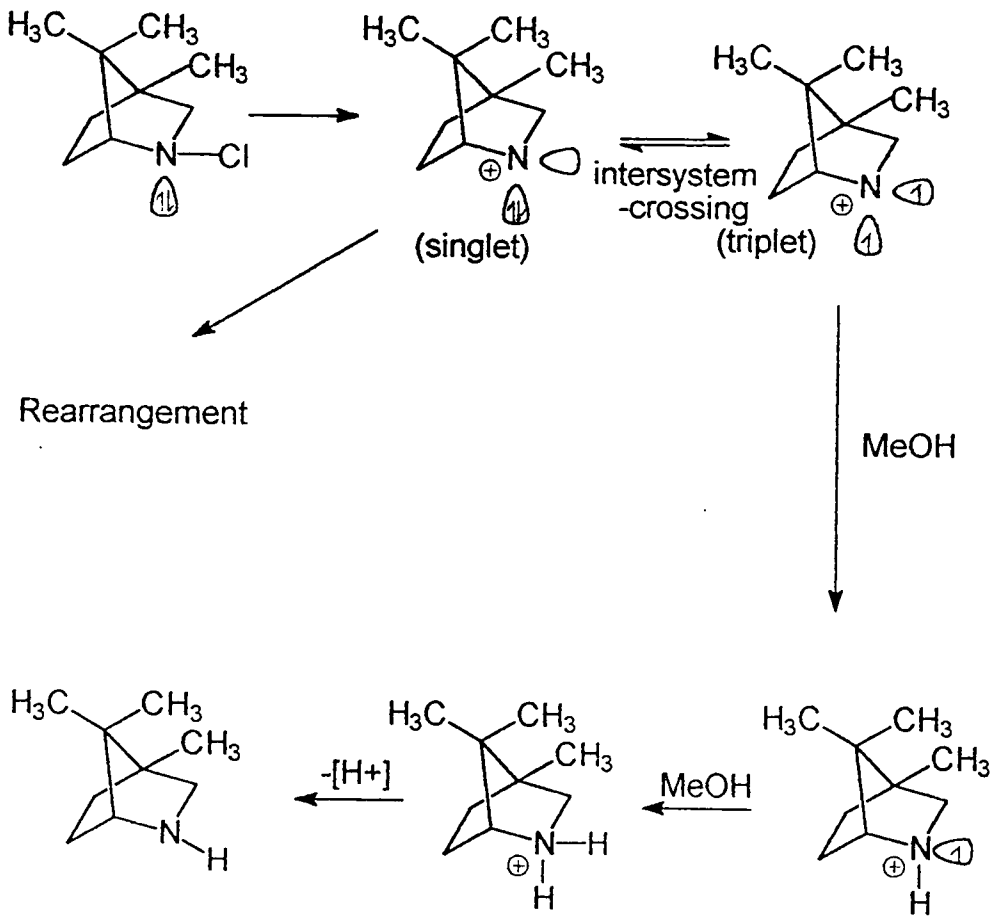


Figure 4. Singlet and Triplet State Intermediates

Examination of the data reveals that solvent polarity is not a dominating factor. The most polar (MeOH/water) and least polar (MeOH/hexane) solvents gave relatively similar singlet to triplet ratios. Gassman concluded that heavy atoms can induce spin inversion. In a later published review article, he addressed the claim that the slight difference in the two product ratios mentioned above may be due to dilution effects by noting that these effects would be much too small to explain the changes observed in the presence of halogenated solvents.[8] One may consider that the heavy atom experiment could have occurred via homolytic

cleavage of the "N-Cl" bond followed by hydrogen abstraction from one of the haloforms, but, the reaction was also run in carbon tetrachloride (where hydrogen abstraction is not available) and gave a similar ratio.

Edwards originally suggested a heterolytic path for the reaction in Figure 5. Later, he presented evidence for a homolytic process and suggested that transannular hydrogen abstraction by a nitrogen radical(s) may have been initiated by Ag(0). The intermediacy of amino radicals can be understood in light of the chain reactions shown in Figure 6.[9]

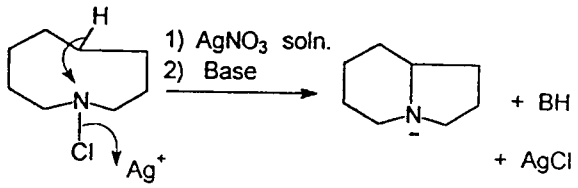


Figure 5. Heterolytic Mechanism of Rearrangement

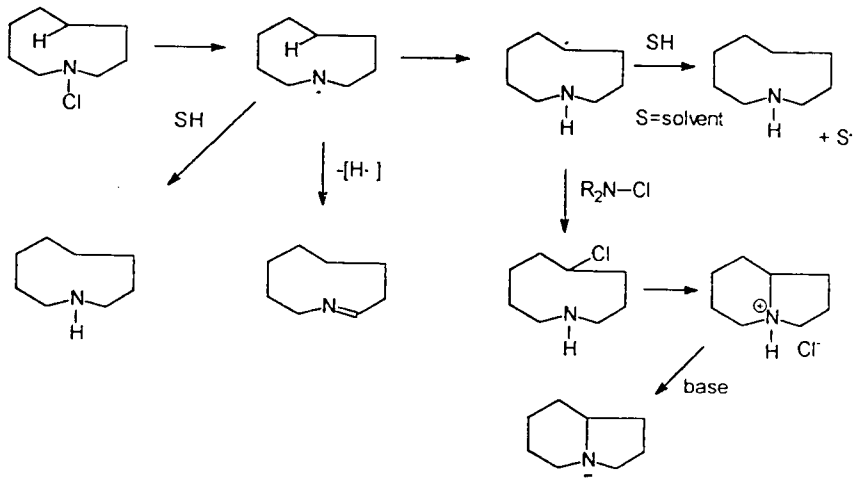


Figure 6. Homolytic Mechanism of Rearrangement

If trapping was done with amino radicals, why not trap the nitrenium ion? Fishbein and McClelland accomplished just that! Figure 7 shows a Bamberger rearrangement in which the intermediate nitrenium ion is trapped by the addition of azide (trapping with water is also shown). This trapping was confirmed by their assessment of the kinetic data and the fact that reaction with azide was found to occur near the limit of diffusion.[10] Recently, ion pairs which result from azide (or the solvent) and a nitrenium ion have also been trapped.[11]

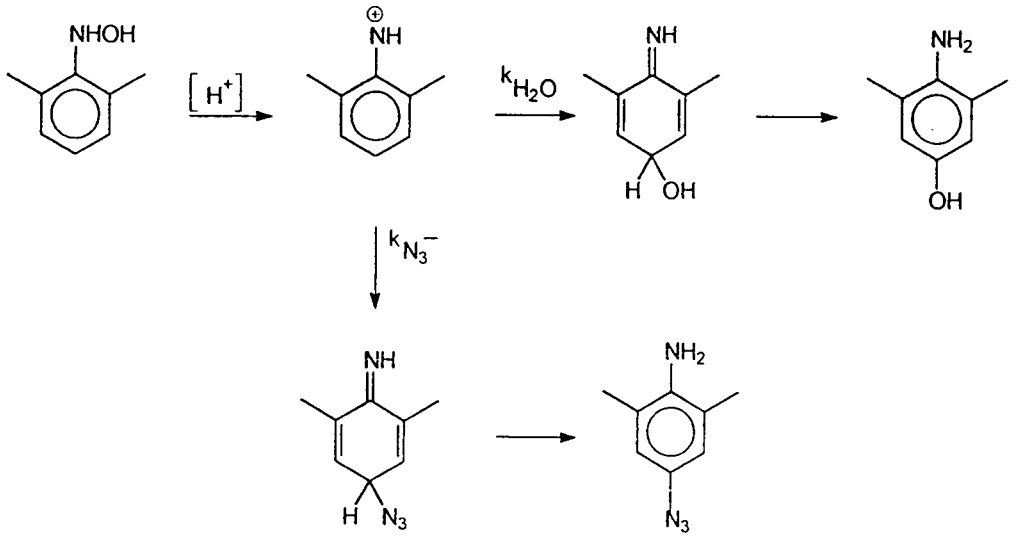


Figure 7. Trapping of the Nitrenium Ion

Ring expansion and contraction are very useful in the synthesis of natural products. Schell and Ganguly used several N-chloroamine models for the synthesis of alkaloids containing a bridgehead nitrogen. One of the compounds they studied was N-chloronortropane which upon reflux in a methanolic silver nirate solution underwent ring contraction. After work-up with sodium cyanoborohydride, pyrrolizidine (as seen in Figure 8) was isolated.[12]

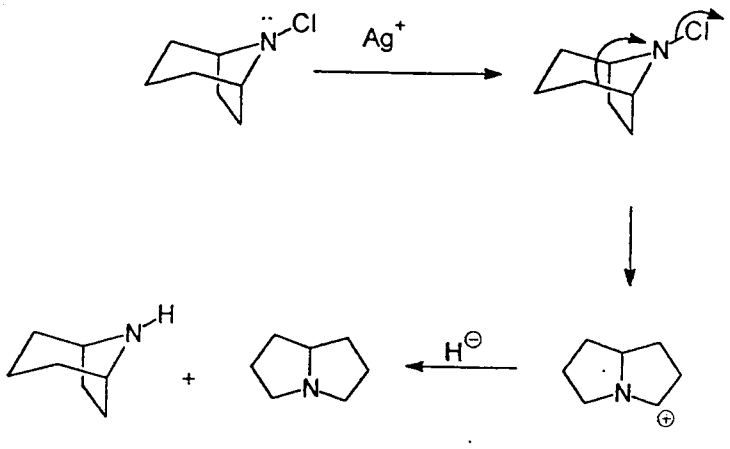


Figure 8. Rearrangement of N-chloro-nortropane

Although pyrrolizidine was present in a 35% yield, nortropane was also obtained in a 45% yield. Repeating the reaction in benzene and initiating with silver tetrafluoroborate proved to be superior. Mild work up with sodium borohyhride gave a near 90% yield of pyrrolizidine and very little nortropane. The same trends were observed for reactions with other fused ring systems, N-chlorogranatanine and N-chloro-*trans*-decahydroquinoline.

Just as N-chloroamines can be used to contract ring systems, they are also useful in ring expansions. Brown and Martineau synthesized the oxindole seen in Figure 9.[13] With the loss of the N-chloro substituent, one can imagine the expansion of the four- membered ring resulting in a stable tertiary carbocation. After reduction with sodium cyanoborohydride, a spiro indolopyrrolizidine results from ring expansion. Previously, there was a ring contraction during the formation of the oxindole. This contraction, however, did not involve the attack of a nitrogen atom. The overall result here is that a four and six membered rings have been replaced by two fused five- membered rings.

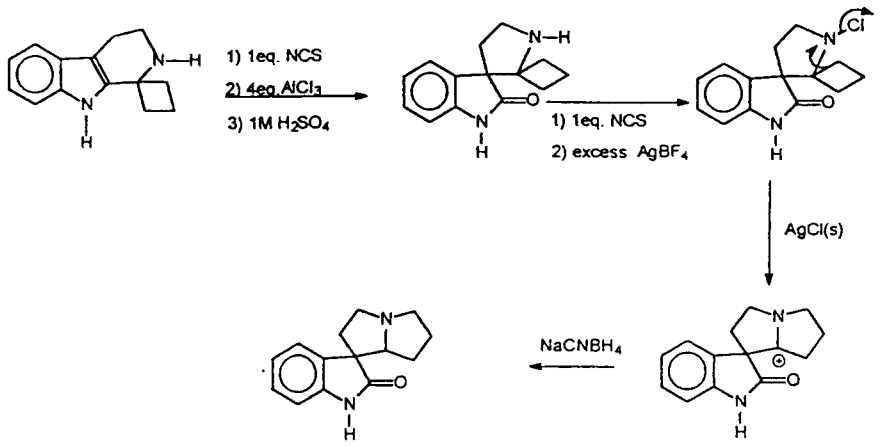


Figure 9. Rearrangement of an N-chloro-1,2,3,4-tetrahyrobetacarboline cyclobutyl spirocycle

Ring expansion has also been accomplished by the reaction of an N-chloroamine and a π-system. Gassman and associates demonstrated that in a polar medium (i.e. methanol or water) the reaction seen in Figure 10, for example, proceeds via a *π-route.* This π-route can be explained by the olefin attacking nitrogen with the loss of chlorine to give a nonclassical structure; collapse of the complex would then produce a desired azabicycle.[14]

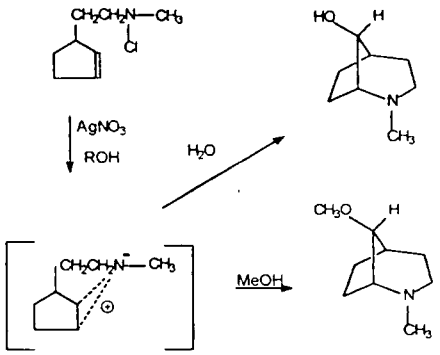


Figure 10. Rearrangement via a π-route

N-chloroamine type compounds have also been used in the formation of β-lactams . Wasserman and colleagues prepared the several hydroxyl amines listed in Table 3. Exposure of these materials to cyclopropanone followed by tosylation led to rearrangement. Although one could imagine the cyclopropyl group expansion assisting the departure of tosylate in a concerted fashion, their explanation is that a nitrenium ion forms to induce ring expansion (see Figure 11). Their choice of hydroxyl amines arose from biological interests. The resulting β-lactam in which the R group is isobutyl, contains all of the carbon atoms found in the fused 4,5 ring system of the penicillins.[15]

Table 3. Percent Yields for β-Lactams

HONHCH(CN)–R	Yield of β-Lactam
R= phenyl	43%
R= $CH_2CH_2CH_3$	45%
R= $CH(CH_3)_2$	41%
R= $CH_2CH_2CH_2CH_3$	40%
R= $CH_2CH(CH_3)_2$	45%

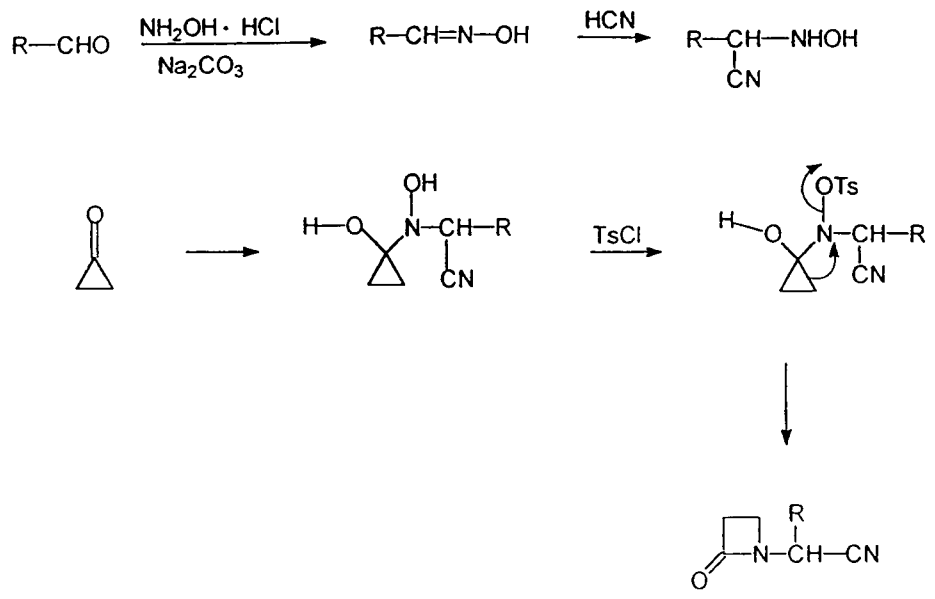


Figure 11. Synthesis of β-lactams

Although simple aliphatic secondary amines may not rearrange via a nitrenium ion intermediate, particular known species (*i.e. 4-aminobiphenyl and 2-aminofluorene*) are of biochemical interest since they bind to DNA.[16] Davidse and coworkers observed 2-fluorenyl- and 4-biphenylylacetylnitrenium ions and measured their lifetimes in an aqueous solution. Precursors **VIIa** and the N-chloride **VIIIb** were chosen giving rise to **IX** and **X** respectively (Figure 12).

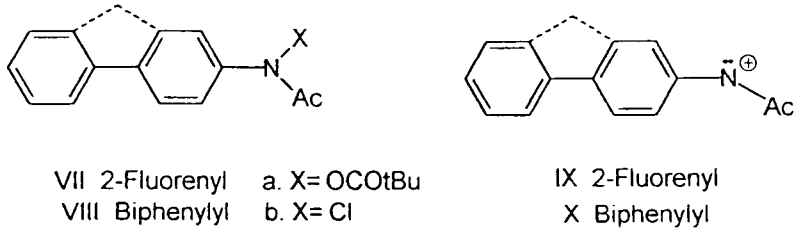


Figure 12. Biphenyl and 2-Flourenyl Systems

Using flash photolysis at an excitation of 248 nm resulted in an absorbance with a maximum wavelength near 450-460 nm in both cases. They proposed that the absorbance was due to the presence of **IX** and **X** based on the following:

(i) The trapping of ion pairs

(ii) The decays were consistent with cationic intermediates

(iii) The rate constant ratios (trapped with azide vs. water) for the decay of the nitrenium ions obtained directly with photolysis were similar to those seen in the sovolysis reactions performed

The latter of these observations is the most important because it demonstrates that the transient is identical with the ground-state intermediate.[17] They also point out that this makes a cation radical very unlikely for the identity of the observed intermediate. The carbenium ion seen in Figure 13 was found to react 100 times more rapidly than **IX** previously seen in Figure 12. This was unexpected because earlier studies comparing the same nitrenium ion with one containing a phenyl in place of the acetyl group, gave only a three-fold change.[18] The selectivities of arylnitrenium ions and benzylic cations have been used to infer relative kinetic stabilities .[19] However, this experiment marks the first time that kinetic stabilities were directly measured.

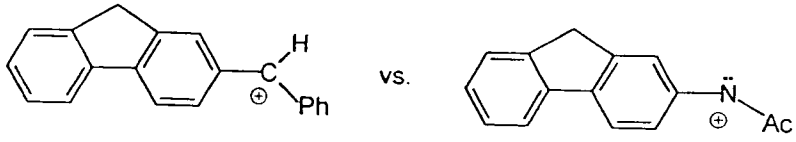


Figure 13. The 2-Flourenyl Intermediate and Carbon Analog

Throughout this discussion of N-chloroamines we have seen the progressive revelation and use of the nitrenium ion. It is not surprising that Stieglitz confused a nitrenium ion with a nitrene since a deprotonated nitrenium ion is a nitrene. Moreover, both species can have singlet or triplet spin states. The identity of the substituent on the nitrogen of the hydroxylamines used by Stiglitz was a hydrogen (R in Figure 14) and thus, unlike a carbon substituent, could be lost and regained during the course of the reaction.

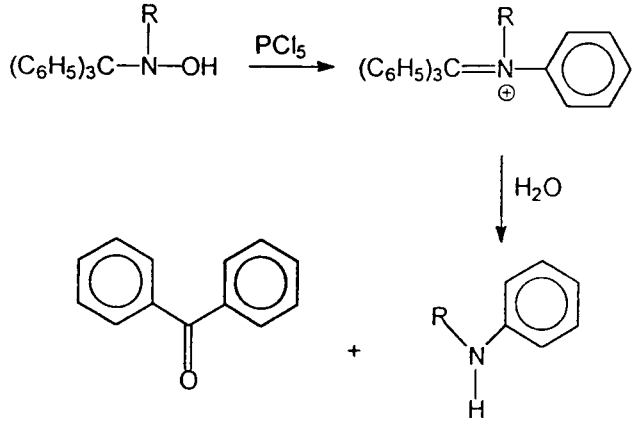


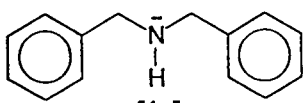
Figure 14. The Stieglitz Rearrangement

In summary, assessing the involvement of N-chloroamines in reactions is not always trivial. One may need to consider heterolytic vs. homolytic cleavage, solvent vs. silver initiation, σ vs. π routes. Dilution effects, spin states and/or amino radical formation may also need to be considered depending on the reaction at hand. Lastly, it is known that N-chloroamines are useful in synthesis, for changing the size of ring systems by promoting the migration of organic groups.

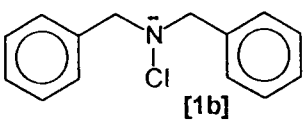
The Search for The Rearrangement of N-chloroamines

The purpose of the experiments which follow was to gain more insight as to the potential migration of aryl groups to the nitrogen center of selected secondary N-chloroamines.

In response to the claim by Edwards, Vocelle and ApSimon[9] that simple aliphatic nitrenium ions do not arise from N-chloroamine silver complexes, we began our studies with the rather simple dibenzyl amine **[1a]**. N-chloro-dibenzylamine **[1b]** was studied in the absence of light under two different conditions: stirring at room temperature and at reflux in the presence of silver tetrafluoroborate.



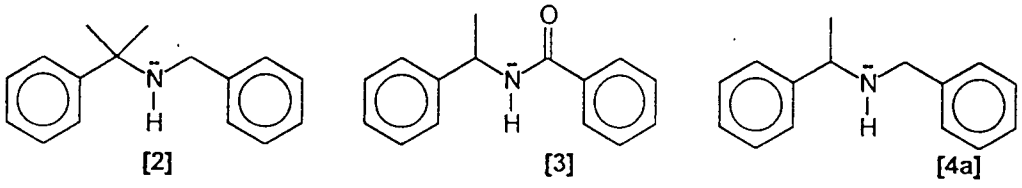
[1a]



[1b]

Each reaction was monitored using thin layer chromatography. When no more N-chloroamine was detected, the reaction was thought to have gone to completion. Disappearance of the N-chloroamine occurred more rapidly at reflux than at room temperature. After work up in base, NMR spectra were taken of the crude reaction mixture. These spectra revealed the parent amine and the presence of impurities. A sample of the reaction mixture was injected into a GC-Mass Spectrometer. The resulting chromatogram reflected the NMR spectra in that there was a peak of high abundance which gave the mass of the expected parent ion. Other peaks of very low natural abundance gave masses which did not correspond to the possible products one would expect from elimination or

rearrangement. It should be noted that at times known compounds did not give the mass of the parent ion. Spectra were obtained of the parent ion and fragments derived from it and these were used to assess the data at hand. Furthermore, it should be noted that sampling peaks at several different retention times often led to mass spectra of great similarity.



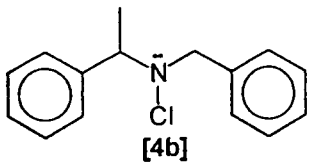
[2] [3] [4a]

Since our group[20] previously observed the rearrangement of N-chloro-N-benzyl-1-methyl-1-phenethylamine **[2;H=Cl]**, the possible rearrangement of N-chloro-N-benzyl-1-phenethylamine **[4a;H=Cl]** (spectra 7 and 8) was considered. The amide **[3]** from which the parent amine **[4a]** was derived contains a pseudo-pentet in the ^{1}H NMR (Spectrum 5) at 5.27 ppm. This is a consequence of the methine proton being split by the neighboring methyl protons and the proton attached to nitrogen. After reduction of the carbonyl group, only splitting of the methine proton by the methyl group occurs; thus, the ^{1}H NMR of **[4a]** (Spectrum 7) reveals a true quartet of one proton at 3.81 ppm. Spectrum 7 also contains a four line pattern of two protons at 3.62 ppm. This is an AB spin system with $\Delta\nu/J$ calculated to be ~1.11 using the following equation:

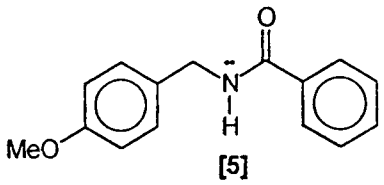
$(1\text{-}3) = (2\text{-}4) = \sqrt{(J^2 + \Delta\nu^2)}$; where 1 is the most deshielded resonance, and 4 is the least deshielded resonance

The centers of gravity ($\pm\Delta\nu/2$) here were calculated to be 959.75 and 945.25 Hz. The multiplet results from spin coupling of the geminal protons which are *diastereotopic* (chemically different) due to the presence of a stereogenic center. The ^{1}H NMR spectrum of **[4b]** (Spectrum 9) reveals that the AB system now has more AX character with $\Delta\nu/J$ calculated to be ~2.02 (an ideal AX system gives a ratio near 5). N-chloro-N-benzyl-1-phenethylamine **[4b]** was allowed to stir in the presence of silver tetrafluoroborate for one week both under reflux and at room temperature (reaction flasks were wrapped in aluminum foil). The reaction mixtures were monitored for the presence of unreacted N-chloroamine via TLC. Here, as with the previous reaction mixture, disappearance of the N-chloroamine occurred more rapidly while at reflux than at room temperature. Likewise, NMR spectra of the reaction mixture proved that it contained the parent amine and unknown contaminants. Mass spectra of selected peaks in the gas chromatograph gave the mass of the parent ion and assorted values which did not coincide with expected products. However, an attempt was made to isolate the observed impurities using a silica gel column and the following mobil phases: hexane, methylene chloride, chloroform and methanol. The parent amine was recovered from this column pure (confirmation by NMR).

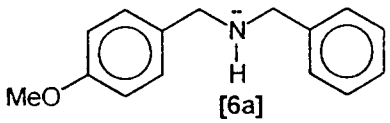
Next we considered an aryl system in which a substituent might aid aryl migration from the alpha carbon of nitrogen to the nitrogen center (a 1,2 shift). The *p*-anisyl system was chosen because the methoxy group is electron rich. The ^{1}H NMR spectrum of N-(*p*-methoxybenzyl)-benzamide **[5]** (Spectrum 11) reveals a doublet of two protons at 4.57 ppm. As seen with **[3]** the methylene protons here are split by the proton on nitrogen. Moreover, after reduction of the amide, the methylene protons appear as a singlet in Spectrum 13.



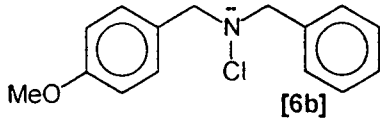
[4b]



[5]

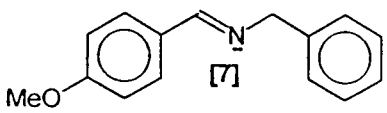


[6a]

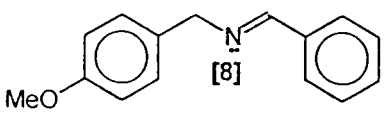


[6b]

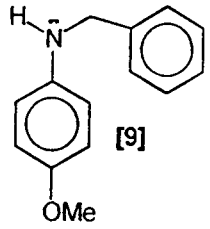
N-chloro-N-(*p*-methoxybenzyl)-benzylamine **[6b]** (spectrum 15 and 16) was dissolved in methylene chloride and allowed to stir in the dark at room temperature for 48 hrs in the presence of silver tetrafluoroborate. Aftter this period, no N-chloroamine was detected by TLC. Work-up in mild base (100 mL of a 1N sodium hydroxide solution) as with the previous compounds gave a crude reaction mixture. NMR spectra revealed the parent amine, chemical shifts in the imine region but no sign of the expected aniline. After injection of the sample into the GC-Mass Spectrometer, the most abundant peaks gave the parent ions of N-(*p*-methoxybenzyl)-benzylamine **[6a]**, N-(*p*-methoxybezylidene)-benzylamine **[7]**, N-benzylidene-*p*-methoxybenzylamine **[8]** and *p*-methoxy-N-benzylaniline **[9]**.



[7]

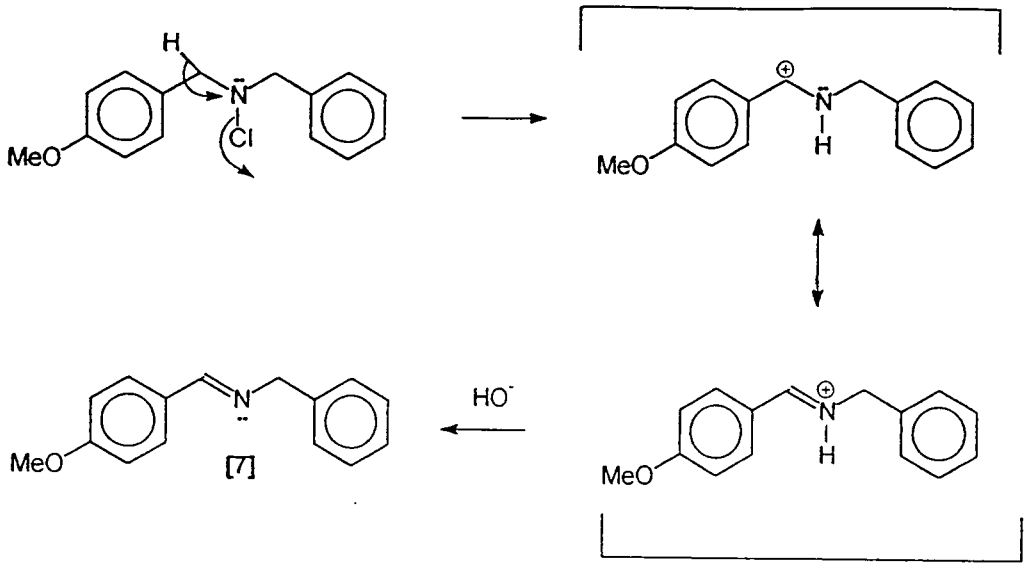


[8]



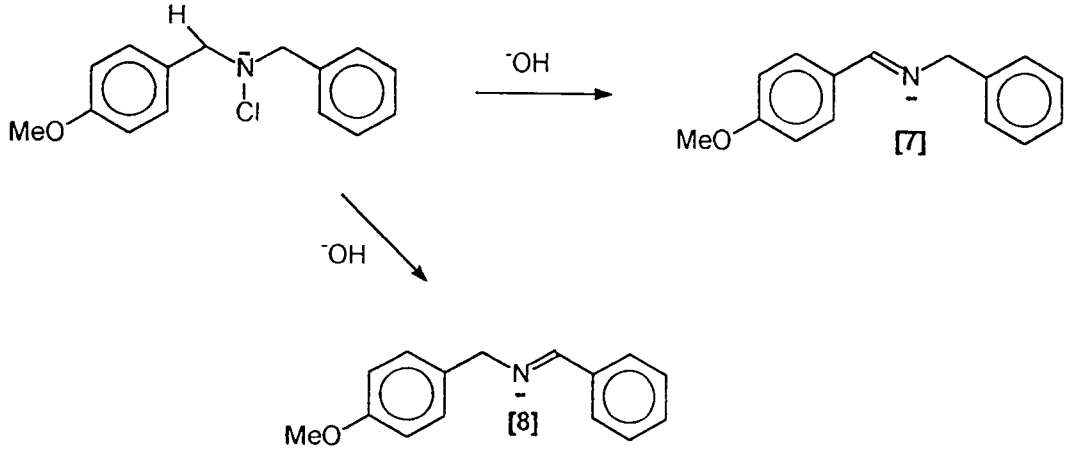
[9]

TLC revealed only two of the three spots when silica gel plates were eluted in methylene chloride. Likewise, only two spots were observed when silica gel plates were eluted with chloroform. How could this be? In retrospect, it is now understood that the aniline **[9]** elutes in pure methylene chloride whereas percentages of chloroform must be gradually added to set the imines (**[7]** and **[8]**) in motion. Consequently, if pure chloroform is added, the parent amine **[6a]** migrates with the imines (**[7]** and **[8]**). The gas chromatograph gave relative abundances consistent with the following percent yields: 35% of **[6a]** (spectra 13 and 14), 19% of **[7]** (spectra 17 and 18) and **[8]** (spectra 19 and 20), 16% of **[9]** (spectra 21 and 22) and 30% unaccounted for material. When the reaction was repeated under the same conditions but worked up in stronger base (100 mL of a 13%(w/v) sodium hydroxide solution), the following results, also confirmed by the gas chromatograph, were obtained: 40% of **[6a]** (spectra 13 and 14), 5% of **[7]** (spectra 17 and 18) and **[8]** (spectra 19 and 20), 18% of **[9]** (spectra 21 and 22) and 37% unaccounted for material. The same reaction run at reflux gave back only starting material even after only 24 hrs. One might consider Scheme 1 as a plausible mechanism for the origin of **[7]**; a hydride shift would leave a positive charge on carbon which could then be delocalized by the para-anisyl group.



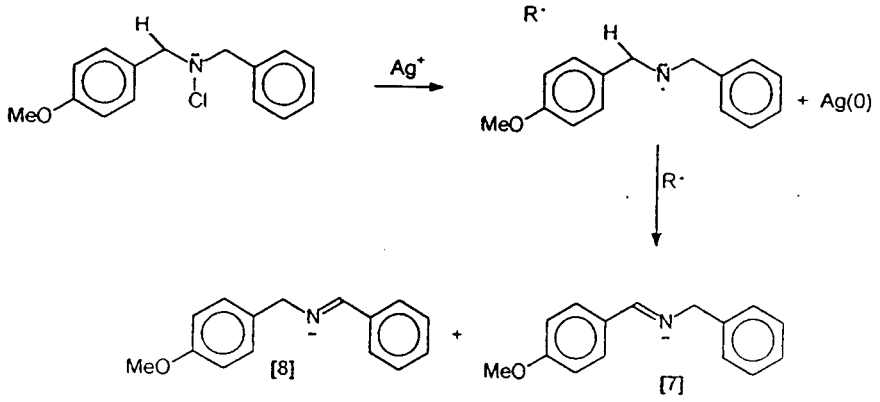
Scheme 1

Since hydride shifts were not seen in previous compounds one might consider E2 elimination of hydrogen chloride as seen in Scheme 2. Elimination can occur on either side of nitrogen.



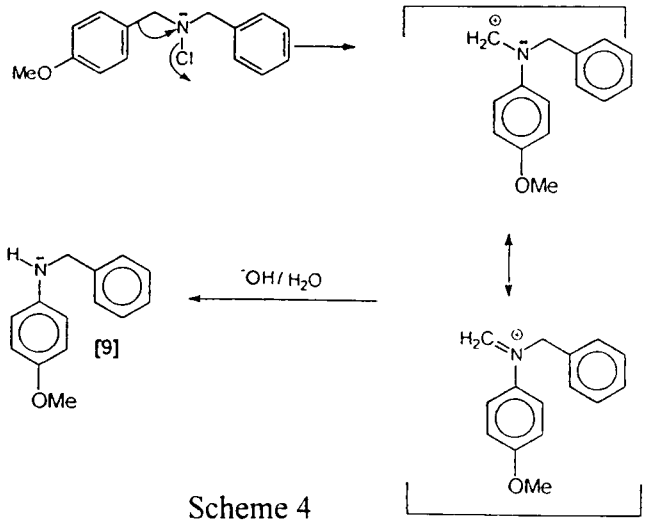
Scheme 2

Another alternative might be Scheme 3 which would occur with the homolytic cleavage of the N-Cl bond followed by hydrogen abstraction (this also can occur on both sides of nitrogen).



Scheme 3

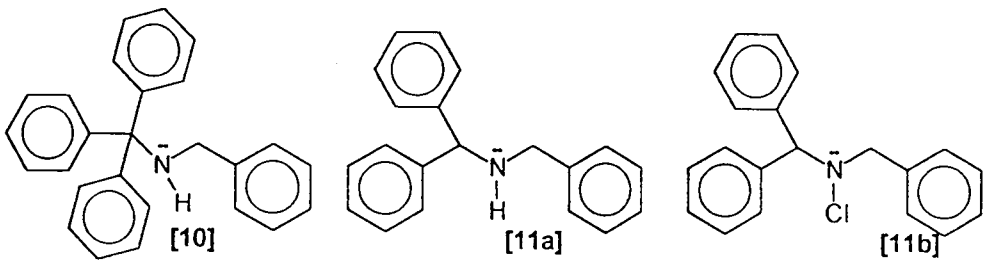
The formation of the aniline **[9]** (spectrum 21 and 22) can be explained by para-anisyl migration followed by hydrolysis as shown in Scheme 4. Two dimensional NMR spectra of **[9]** were also obtained to confirm the rearrangement (spectrum 23 and 24).



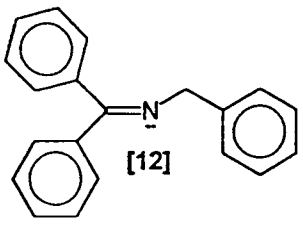
Scheme 4

Amino radicals may also be at work following the homolytic cleavage of the N-Cl bond as previously addressed. Imines **[7]** (spectra 17 and 18) and **[8]** (spectra 19 and 20), which may have arisen and the aniline **[9]** (spectra 21 and 22) were all separately synthesized by routes described in the experimental section. Spectra of these compounds were used as references for the compounds recovered.

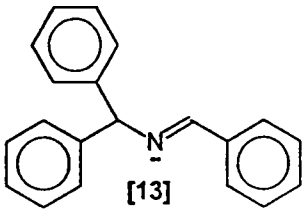
Since Stieglitz observed the rearrangement of N-(1,1,1-triphenylmethyl)-benzylamine **[10]** attention was directed to the possible rearrangement of N-benzyl-1-phenylbenzylamine **[11a]**.



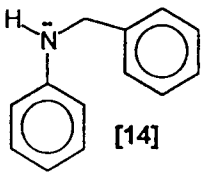
N-chloro-N-benzyl-1-phenylbenzylamine **[11b]** was dissolved in methylene chloride and allowed to stir in the dark at room temperature for 48 hrs in the presence of siver tetrafluoroborate. After this period, no N-chloroamine was detected by TLC. Work-up in strong base (100 mL of a 13% sodium hydroxide solution) gave a crude reaction mixture. NMR spectra revealed the presence of the following compounds: 30% of **[11a]** (spectra 25 and 26), 16% of **[14]** (spectra 29 and 30), 30% of benzaldehyde and 24% miscellaneous material of which a portion was unrecovered benzophenone (seen in the crude spectra 27 and 28). The expected imines (**[12]** and **[13]**) were not detected.



[12]



[13]



[14]

Unfortunately the GC-Mass spectrometer which had been used consistently prior to this point was under repair. However, unlike the first rearrangement observed, this reaction mixture contained the hydrolyzed by-product which confirms the formation of the aniline **[14]**. This is most likely due to the tendency of the hydrolyzed by-product of the first rearrangement, formaldehyde (more volatile than benzaldehyde) being lost when the solvent was removed *in vacuo*. Furthermore, the first aniline [9] was only detectible by mass spectroscopy whereas [14] was seen in the NMR spectra of the crude reaction mixture. As previously mentioned, Spectrum 28 reveals the presence of benzophenone which may have resulted if [11b] experienced a hydride shift followed by hydrolysis (as in Scheme 1). Although the preparation of [11a] involved the use of benzophenone, it is highly unlikely that this starting material would have survived the work-up conditions and column chromatography which preceded the rearrangement of [11b]. Consequently, no benzylamine was detected to support the idea of a hydride shift.

The rearrangement of N-(1,1,1-triphenylmethyl)-benzylamine [10] seen by Stieglitz gives a much higher yield than in the case of **[6a]**. This is because the two species have different motivating forces which result in rearrangement. In our case, **[6a]** was driven by electronic

bias which in turn induces a small degree of rearrangement. However, a driving force in **[10]** is the sum of the steric interactions amongst the phenyl substituents. Likewise, **[12a]** is also driven by steric forces, but much less than that of **[10]**. Although the aniline **[9]** was made by an easier method (as mentioned above) than our seemingly lengthy route which ends in a rearrangement, silver initiated rearrangement of N-chloro derivatives of particular natural product precursors may prove to be a short cut, especially in cases involving ring-expansion.

Experimental

General Preparatory Techniques

NMR spectra were acquired using a Bruker AC-250 spectrometer operating at 250 MHz for ^{1}H spectra and 62.88 MHz for ^{13}C spectra. All spectra were obtained in deuteriochloroform which contained tetramethylsilane (TMS). ^{1}H chemical shifts were referenced to TMS (δ 0.0 ppm) whereas ^{13}C chemical shifts were referenced to the center peak of deuterochloroform (δ 77.0 ppm). Routine mass spectra were obtained using an Hewlett-Packard 5890 GC/ 5970 MSD instrument.

Infrared spectra were obtained using a BIO-RAD FTS-7 Fourier Transform Infrared Spectrometer. Spectra were obtained as potassium bromide pellets. The percentage of compound crushed in anhydrous potassium bromide was between 1-2%.

Reaction flasks were cleaned with warm soap and water, rinsed with acetone and placed in an oven at 80°C. Chloroform and methylene chloride were distilled over diphosphorus pentoxide through a 65-cm Vigreux column. Tetrahydrofuran was distilled from sodium benzophenone ketyl while under argon gas. Methanol was stored over molecular sieves and absolute ethanol was distilled before use.

Thin layer chromatography (TLC) plates were prepared by dipping microscope slides into a slurry of chloroform and the stationary phase of choice. The stationary phases used (normal phase chromatography) were Merck Silica Gel G and Woelm Alumina G. The developed plates were stained using iodine vapor to visualize the results and obtain R_f-values.

Silver terafluoroborate, in brown plastic bottles, was stored in a glove box flooded with nitrogen gas. Other air-sensitive reagents like N-chlorosuccinimide and sodium borohydride were kept in a desiccator over calcium sulfate.

Preparation of N-(1-phenylethyl)benzmide [3]

The technique used was the Schotten-Baumann amide synthesis.[21] Methylbenzylamine (150 ml in the absence of solvent) was added to a 1L round-bottomed flask containing 500 mL of a 13%(w/v) sodium hydroxide solution. Excess (13%) benzoyl chloride was added drop wise with stirring and the reaction stirred at room temperature for 24 hrs. The solid material which resulted was washed with distilled water on a Büchner funnel. Recrystallization from absolute ethanol provided the purified product.

N-(1-phenylethyl)benzamide: ^{13}C NMR: δ 166.7 (C=O), 143.2, 134.7, 131.5, 128.8, 128.6, 127.5, 127.0, 126.3 (Aromatics), 49.3, 21.8. ^{1}H NMR: δ 7.75 (d, 2H), 7.33-7.25 (m, 8H), 6.92 (bs, N-H), 5.27 (ps-pent, 1H), 1.52 (t, 3H).

Preparation of N-(*p*-methoxybenzyl)-benzamide [5]

p-Methoxybenzylamine (8 g) was added to a 500 mL round-bottomed flask via a pipet in the absence of solvent. Two equivalents of a 13%(w/v) sodium hydroxide solution was added in excess with stirring. Excess benzoyl chloride (13%) was added dropwise with stirring. Stirring continued overnight and the resulting solid was washed with distilled water on a Büchner funnel. The amide was then recrystallized from methanol to give a pure sample.

N-(*p*-methyoxybenzyl)-benzamide: ^{13}C NMR: δ 167.2 (C=O), 159.1, 134.5, 131.5, 130.2, 129.3, 128.6, 126.9, 114.2 (Aromatics), 55.3, 43.6. ^{1}H NMR: δ 7.78 (d, 2H), 7.53-7.38

(m,3H), 7.28 (d, 2H), 6.88 (d,2H), 6.38 (bs, N-H), 4.57 (d, 2H), 3.80 (s, 3H).

Preparation of N-chlorodibenzylamine[1b]

Dibenzylamine (2 mL) was dissolved in a 500 mL round-bottomed flask charged with 100 mL of dry methylene chloride. N-chlorosuccinimide (1.2 equivalents) was added via a powder funnel and the contents stirred for one hour. After three extractions with equal volumes of sodium bicarbonate, the organic layer was dried over anhydrous sodium sulfate. The organic layer was transferred to a dry flask via a funnel and fluted filter paper. Thin layer chromatography was used to check the reaction. Removal of the solvent by the rotary evaporator was done with the water bath kept slightly below room temperature. The N-chloro compounds were never purified further but used directly in subsequent reactions.

Dibenzylamine: ^{13}C NMR: δ 140.3, 128.3, 128.1, 126.9 (Aromatics), 53.1. ^{1}H NMR: δ 7.35-7.20 (m, 10H), 3.79 (s, 4H), 1.64 (bs, N-H).

N-chlorodibenzylamine: ^{13}C NMR: δ 137.0, 129.0, 128.3, 127.8 (Aromatics), 67.1. ^{1}H NMR: δ 7.39-7.20 (m, 10H), 4.12 (s, 4H).

$AgBF_4$ treatment of N-chlorodibenzylamine [1b]

N-chlorodibenzylamine (340 mg) was dissolved in 350 mL of methylene chloride. The 500 mL round-bottomed flask was then wrapped in aluminum foil and placed in a glove box. One equivalent of silver tetrafluoroborate was added via a powder funnel. The mixture was allowed to stir and reflux in the dark, under argon gas for 5 days. TLC confirmed that the N-chloroamine was no longer present. A sodium hydroxide solution (100 mL , 1N) was added to the reaction mixture and it was allowed to stir for one hour. The contents were transferred to a separatory funnel along with distilled water rinses of the reaction flask.

After three extractions with methylene chloride, the organic layers were combined and set to dry over anhydrous sodium sulfate. The solution was poured through a celite pad under vacuum to remove remaining silver salts then filtered under gravity. After removal of solvent, NMR spectra revealed only the parent amine, dibenzylamine. No evidence for reaction or rearrangement was observed.

Preparation of N-benzyl-1-phenethylamine [4a]

A 1000 mL three-neck round-bottomed flask equipped with a condenser and gas inlet, a septum and a thermometer was charged with 300 mL of dry tetrahydrofuran. N-(1-phenylethyl)benzamide (5 g) was added via a powder funnel while stirring. After the amide was dissolved, 5 equivalents of borane-methyl sulfide (BMS) was added via a syringe such that the temperature of the mixture did not exceed 25°C. After stirring for 1.5 hrs. the solution was allowed to reflux under argon gas for 24 hrs. Thin layer chromatography was used to confirm that reduction of the amide had occurred. The flask was placed in an ice bath and 200 mL of methanol was added dropwise via an addition funnel while monitoring the temperature as above. The mixture was then allowed to stand at room temperature for 24 hrs. The reaction mixture was cooled to -2°C and hydrogen chloride gas was passed into the solution while keeping the temperature below 15°C. Addition of the acid was discontinued when the pH of the solution reached less than two. The solution was allowed to reflux for 24 hrs then cooled to give a slurry resembling rubber cement in color.[22] The solution was then stripped of organic solvents on a rotary evaporator. The remaining salt was recrystallized from methanol, dissolved in warm distilled water and basified in a separatory funnel with a 2%(w/v) potassium hydroxide solution. After addition of sodium

bicarbonate the solution was extracted three times with methylene chloride. The extractions were combined and dried over anhydrous potassium carbonate (preferred to magnesium sulfate because the lone pair electrons of nitrogen can attack magnesium). After transferring the organic layers to a dry flask through fluted filter paper, the solvent was removed to give the free amine.

N-benzyl-1-phenethylamine: ^{13}C NMR: δ 145.6, 140.7, 128.4, 128.3, 128.1, 126.9, 126.8, 126.7 (Aromatics), 57.5, 51.6, 24.5. ^{1}H NMR: δ 7.35-7.21(m, 10H), 3.81 (q, 1H), 3.62 (ps q, 2H), 1.67 (s, N-H), 1.37 (d, 3H).

Preparation of N-chloro-N-benzyl-1-phenethylamine [4b]

N-benzyl-1-phenethylamine (200 mg) was dissolved in methylene chloride in a 500 mL round-bottomed flask. N-chlorosuccinimide (1.2 equivalents) was added via a powder funnel and the mixture was allowed to stir for one hour. The contents were poured into a separatory funnel and extracted three times with sodium bicarbonate. The organic layer was dried over anhydrous sodium sulfate then filtered through fluted filter paper into a clean, dry flask. TLC confirmed the presence of the N-chloroamine. The solvent was then removed at room temperature *in vacuo*.

N-chloro-N-benzyl-1-phenethylamine: ^{13}C NMR: δ 141.7, 137.7, 128.8, 128.4, 128.2 (2C), 127.8, 127.5 (Aromatics), 68.8, 64.1, 19.5. ^{1}H NMR: δ 7.45-7.30 (m, 10H), 4.17 (q, 1H), 3.95 (ps q, 2H), 1.65 (d, 3H).

$AgBF_4$ treatment of N-chloro-N-benzyl-1-phenethylamine [4b]

Crude N-chloro-N-benzyl-1-phenethylamine (186 mg) was taken directly after it had been converted from the free base and dissolved in 300 mL of methylene chloride. The 500 mL

flask was then wrapped in aluminum foil and placed in a glove box flooded with nitrogen gas. Therein two equivalents of silver tetrafluoroborate was added via a powder funnel. The flask was then sealed under argon gas and allowed to stir in the dark at room temperature for one week, during which time the contents were monitored once a day by TLC. A sodium hydroxide solution (100 mL, 1N) was added to the reaction mixture and the reaction stirred for one hour. The solution was poured into a separatory funnel and portions of distilled water used to rinse the reaction flask were added to the aqueous layer. After three extractions with methylene chloride, the organic layers were combined and allowed to dry over anhydrous sodium sulfate. The organics were poured through a celite pad under vacuum then filtered under gravity through fluted filter paper. TLC revealed the presence of several compounds. The solution was concentrated *in vacuo* and after acquiring crude NMR spectra (which revealed the parent amine and traces of something in the aromatic region) the mixture was loaded onto a packed column (silica gel/ hexane). Various impurities eluted as percentages of methylene chloride, chloroform and methanol were added. All recovered impurities also contained the parent amine. When samples were analyzed using a GC-Mass Spectrometer, the chromatogram revealed an intense peak corresponding to the parent amine and peaks of low intensity possessing masses of no interest.

Preparation of N-(*p*-methoxybenzyl)-benzylamine [6a]

A 1000 mL three-neck round-bottomed flask equipped with a condenser and gas inlet, a septum and a thermometer was charged with 500 mL of dry tetrahydrofuran. N-(*p*-methoxybenzyl)-benzamide (9.5 g) was added via a powder funnel and allowed to stir until

the amide was dissolved. Borane-methyl sulfide was added through the septum via a syringe while the temperature of the mixture did not exceed 25°C.[22] The mixture stirred for 1.5 hrs and was allowed to reflux overnight. Thin layer chromatography was used to confirm the amide reduction. Methanol (200 mL) was added drop wise while an ice bath was used to keep the temperature of the mixture below 25°C. The mixture was allowed to stand at room temperature overnight. Hydrogen chloride gas was passed into the solution until a pH of 2 or less was obtained while the temperature did not exceed 15°C. The solution refluxed overnight under argon gas and was then stripped of solvent. The solid salt was then dissolved in boiling water and extracted three times with hexane and with methylene chloride. The salt was then basified with a 2% potassium hydroxide solution and extracted three times with chloroform. The solvent was evaporated to concentrate the resulting amine solution. The amine was loaded onto a packed column (alumina/methylene chloride). Following elution from the column, NMR spectra revealed remaining impurities. The amine was converted into the salt via hydrogen chloride gas as previously described. The recovered salt was recrystallized from chloroform, dissolved in boiling distilled water, basified and extracted as above. The resulting amine was proven pure by NMR spectra.

N-(*p*-methoxybenzyl)-benzylamine: ^{13}C NMR: δ 158.6, 140.2, 132.2, 129.3, 128.4, 128.2, 126.9, 113.8 (Aromatics), 55.2, 52.9, 52.5. 1H NMR: δ 7.34-7.24 (m, 7H), 6.87 (d, 2H), 3.80 (s,3H), 3.75 (s, 2H), 2.17 (s, 2H), 1.83 (bs, N-H).

Preparation of N-chloro-N-(*p*-methoxybenzyl)-benzylamine [6b]

N-(*p*-methoxybenzyl)-benzylamine (1 g) was dissolved in 200 mL of dry methylene chloride and allowed to stir in a 500 mL round-bottomed flask. N-chlorosuccinimide (1.2

equivalents) was added via a powder funnel and the reaction stirred for one hour. TLC revealed the presence of the N-chloroamine. The mixture was extracted three times with a saturated sodium bicarbonate solution. The organic layers were combined and dried over sodium sulfate, then poured through fluted filter paper under gravity. The sodium sulfate was rinsed with two 50 mL portions of methylene chloride and the rinses were poured through the filter paper. The combined solution was removed of solvent *in vacuo* and a sample was prepared for NMR analysis.

N-chloro-N-(*p*-methoxybenzyl)-benzylamine: ^{13}C NMR: δ 159.3, 137.2, 130.5, 130.2, 129.2, 128.4, 127.8, 114.3 (Aromatics), 66.8, 66.7, 55.3. ^{1}H NMR: δ 7.53-7.28 (m, 7H), 6.89 (d, 2H), 4.11 (s,3H), 4.09 (s,2H), 2.76 (s, 2H), 1.60 (bs, N-H).

$AgBF_4$ treatment of N-chloro-N-(*p*-methoxybenzyl)-benzylamine [6b]

The reaction flask containing the N-chloroamine solution previously described was immediately wrapped in aluminum foil and placed into a glove box where 2.5 equivalents of silver tetrafluoroborate was added via a powder funnel. The mixture was sealed under argon gas and allowed to stir in the dark for 48 hrs. TLC confirmed that no N-chloroamine remained. A sodium hydroxide solution (100 mL of a 13% solution) was added to the reaction flask and the reaction stirred for one hour. The contents were poured into a separatory funnel. Two 100 mL portions of 13% (w/v) sodium hydroxide were used to rinse the reaction flask then they were added to the separatory funnel. Three 100 mL portions of chloroform were used to rinse the reaction flask and extract the aqueous layer. The chloroform extracts were combined and dried over sodium sulfate. The sodium sulfate was rinsed with two 50 mL portions of chloroform. All extracts were combined and poured

through a celite pad. The solution was filtered under gravity and the solvent was removed *in vacuo*. NMR spectra of the crude mixture revealed the presence of the expected parent amine but also absorptions consistent with imines. Mass spectra of the mixture confirmed the structure of the parent amine **[6a]** and imines (elimination products **[7]** and **[8]**) and also the presence of the rearranged product, *p*-methoxy-N-benyzlaniline **[9]**. The crude solid was loaded onto a packed column (silica gel/methylene chloride). Although the parent amine and aniline products were isolated, the imines were inseparatable and eluted together. Furthermore, the retention times for the imines deviated by only a tenth of a second on the GC-Mass spectrometer. The recovered aniline was also characterized using two dimensional NMR techniques.

Preparation of N-benzylidene-*p*-methoxybenzylimine [8]

A 500 mL round-bottomed flask was charged with toluene and 1 mL of 4-methoxybenzylamine was added via a syringe. One equivalent of benzaldehyde was added along with a catalytic amount of *p*-toluene sulfonic acid and the solution stirred. The reaction flask was equipped with a Dean-Stark trap and a condenser with a gas inlet. The solution was allowed to reflux overnight under argon gas. The reaction mixture was allowed to cool and was filtered under gravity to remove the insoluble salt formed. NMR spectra revealed the expected imine and the presence of unreacted benzaldehyde. Most of the benzaldehyde was isolated and discarded by filtering the mixture through a pad of silica gel. The resulting NMR spectra were used as references to identify the imine which may have resulted upon elimination of hydrogen chloride from N-chloro-N-(*p*-methoxybenzyl)-benzylamine. Both the parent ion of the imine and a distinct fragmentation pattern were

revealed by mass spectrometry.

N-(*p*-methoxybenzylidene)-benzylimine: ^{13}C NMR: δ 161.4 (C=N), 136.1-125.2, 113.8 (Aromatics), 64.3, 55.1. ^{1}H NMR: δ 8.36 (s,1H), 7.39 (ps t, 2H), 7.27-7.15 (m, 5H), 6.86 (d, 2H), 4.76 (s, 2H), 3.78 (s, 3H).

Preparation of N-(*p*-methoxybenzylidene)-benzylimine [7]

A 500 mL round-bottomed flask was charged with toluene and 1 mL of benzyl amine was added via a syringe. One equivalent of *p*-anisaldehyde was added along with a catalytic amount of *p*-toluene sulfonic acid and the solution stirred. The reaction flask was equipped with a Dean-Stark trap and condenser with a gas inlet. The solution was allowed to reflux overnight under argon gas. The reaction mixture was allowed to cool and was filtered under gravity to remove the insoluble salt formed. NMR spectra revealed the imine and traces of starting materials. The imine was freed from the starting materials by filtering the mixture through a pad of silica gel. The resulting NMR spectra were used to identify the imine which may have resulted upon elimination of hydrogen chloride from N-chloro-N-(*p*-methoxybenzyl)-benzylamine. Both the parent ion of the imine and a distinct fragmentation pattern were revealed by mass spectrometry.

N-(*p*-methoxybenzylidene)-benzylimine: ^{13}C NMR: δ 161.3 (C=N), 139.6, 132.0, 129.8, 128.4, 127.9, 126.9, 125.3, 114.0 (Aromatics), 64.9, 55.3. ^{1}H NMR: δ 8.32 (s, 1H), 7.72 (d, 2H), 7.34-7.10 (m,5H), 6.92 (d, 2H), 4.79 (s, 2H), 3.84 (s, 3H).

Preparation of *p*-Methoxy-N-benzylaniline [9]

p-Anisidine (2.8g) was added to a 500 mL round-bottomed flask charged with toluene and allowed to stir until the solid was completely dissolved. One equivalent of

benzaldehyde was weighed and delivered to the solution via a pipet. A catalytic amount of *p*-toluene sulfonic acid was added and the flask was equipped with a Dean-Stark trap and a condenser with a gas inlet. The reaction mixture was allowed to reflux overnight under argon gas. The flask was allowed to cool and the contents were filtered under gravity. The toluene was removed using a rotary evaporator. The solid was redissolved in 200 mL of absolute ethanol and allowed to stir. Three equivalents of sodium borohydride was added in excess via a powder funnel.[23] The reaction mixture was allowed to reflux overnight. The solution was stripped of ethanol and the remaining solid was redissolved in chloroform. The solution was poured into a separatory funnel, extracted three times with a saturated sodium bicarbonate solution then allowed to dry over anhydrous sodium sulfate. The solution was filtered under gravity and the solvent removed *in vacuo*. The desired aniline was then isolated by filtering the mixture through a pad of silica gel. The resulting NMR spectra were used as references to identify the presence of the aniline which may have resulted upon rearrangement of N-chloro-N-(*p*-methoxybenzyl)-benzylamine. Both the parent ion of the aniline and a distinct fragmentation pattern were revealed by mass spectrometry.

p-Methoxy-N-benzylaniline: ^{13}C NMR: δ 152.1, 142.4, 139.9, 128.5, 127.5, 127.1, 114.9, 114.1 (Aromatics), 55.7, 49.2. ^{1}H NMR: δ 7.36-7.26 (m, 5H), 6.76 (d, 2H), 6.59 (d, 2H), 4.27 (s, 2H), 3.72 (s, 3H).

Preparation of N-benzyl-1-phenylbenzylamine [11a]:

Benzylamine (1 mL) was added to a 500mL round-bottomed flask containing toluene (200 mL) and allowed to stir. One equivalent of benzophenone was weighed and added with a catalytic amount of *p*-toluene sulfonic acid via a powder funnel. The flask was equipped

with a Dean-Stark trap and a condenser with a gas inlet. The reaction was allowed to reflux overnight under argon gas. The flask was allowed to cool and the contents were filtered under gravity. The toluene was removed using a rotary evaporator. The solid was then dissolved in absolute ethanol (250 mL) and allowed to stir. Three equivalents of sodium borohydride was added in excess via a powder funnel.[23] The reaction mixture was allowed to reflux overnight. Ethanol was removed via a rotary evaporator and the remaining solid was redissolved in chloroform. Hydrogen chloride gas was added to the flask until the pH of the solution reached less than two. The solution was extracted three times with 200 mL portions of hexane, then stripped of solvent. After recrystallization from chloroform, the salt was washed with cold chloroform on a Büchner funnel then redissolved in chloroform. The solution was poured into a separatory funnel, basified with a saturated sodium hydroxide solution, and extracted three times with fresh chloroform. The extracts were allowed to dry over anhydrous sodium sulfate, filtered under gravity and concentrated *in vacuo*. NMR spectra revealed the presence of the pure amine.

N-benzyl-1-phenylbenzylamine: ^{13}C NMR: δ 143.7, 140.2, 128.2, 128.1, 127.9, 127.1, 126.7, 126.6 (Aromatics), 66.2, 51.6. ^{1}H NMR: δ 7.41-7.07 (m, 15H), 4.82 (s,1H), 3.71 (s, 2H), 1.90 (s, N-H).

Preparation of N-chloro-N-benzyl-1-phenylbenzylamine [11b]:

N-benzyl-1-phenylbenzylamine (291 mg) was dissolved in a 500 mL round-bottomed flask charged with dry methylene chloride (200 mL). N-chlorosuccinimide (1.2 equivalents) was added via a powder funnel and the contents stirred for one hour. The solution was allowed to dry over anhydrous sodium sulfate and filtered under gravity into

a dry 500 mL round-bottomed flask. Thin layer chromatography confirmed the presence of the N-chloroamine.

$AgBF_4$ treatment of N-chloro-N-benzyl-1-phenylbenzylamine:

The flask containing the N-chloroamine solution previously mentioned was wrapped in aluminum foil and placed in a glove box. Silver tetrafluoroborate (2.5 equivalents) was added via a powder funnel. The flask was sealed under argon gas and the contents were allowed to stir in the absence of light for 48 hrs. Thin layer chromatography confirmed the disappearance of the N-chloroamine. A 13%(w/v) sodium hydroxide solution (100 mL) was added to the reaction mixture and allowed to stir for one hour. The contents were transferred to a separatory funnel along with distilled water rinse of the reaction flask. After three extractions with methylene chloride, the organic layers were combined, allowed to dry over anhydrous sodium sulfate and poured through a celite pad under vacuum. The solution was filtered under gravity and the solvent removed *in vacuo*. NMR spectra revealed the presence of N-benzyl1-phenylbenzylamine **[11a]** (spectra 25 and 26), N-benzylaniline **[14]** and benzaldeyde, the hydrolyzed by-product (both of which are present in spectra 27 and 28). There was no trace of the expected elimination products (**[12]** and **[13]**).

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List of References

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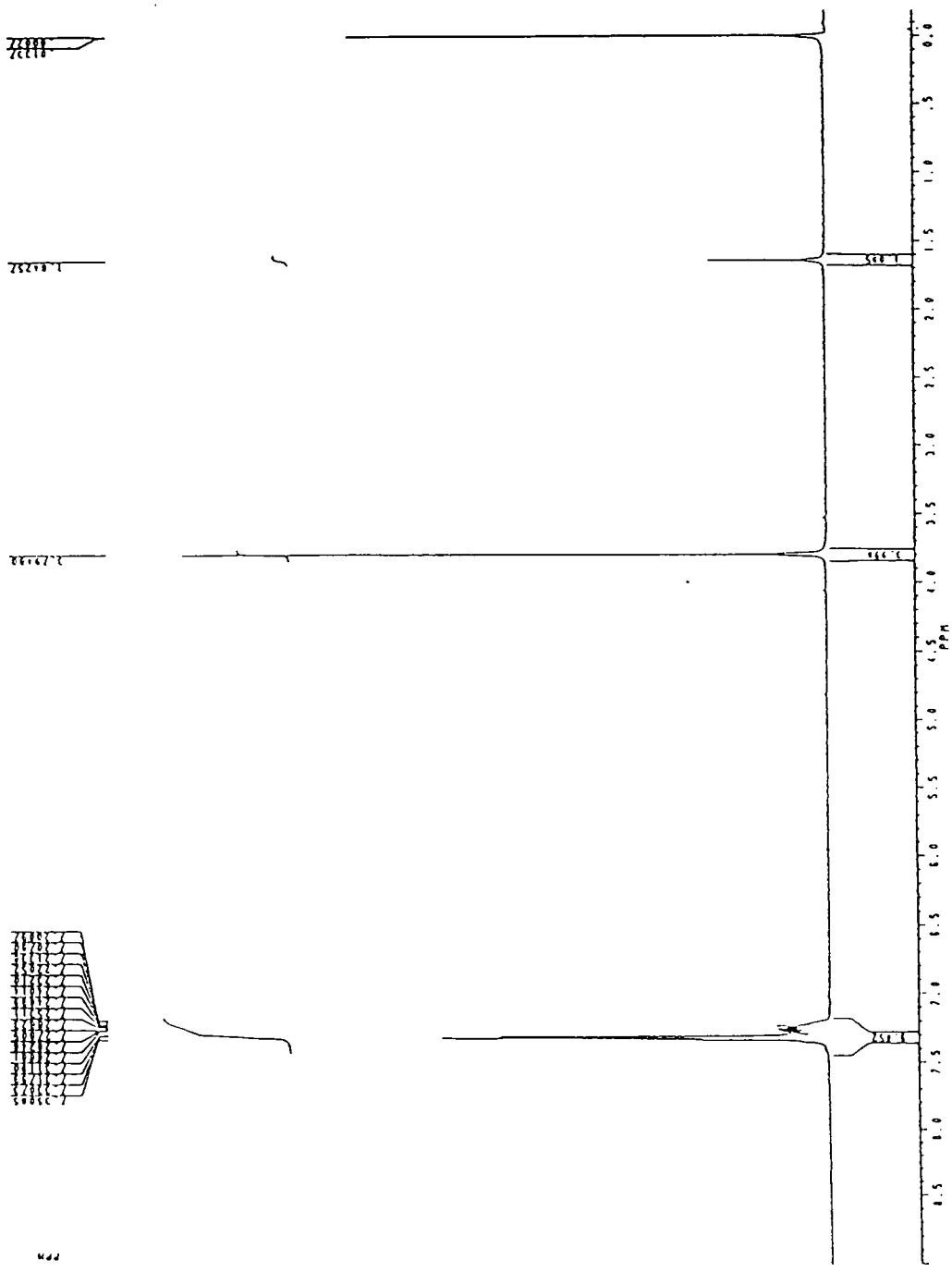
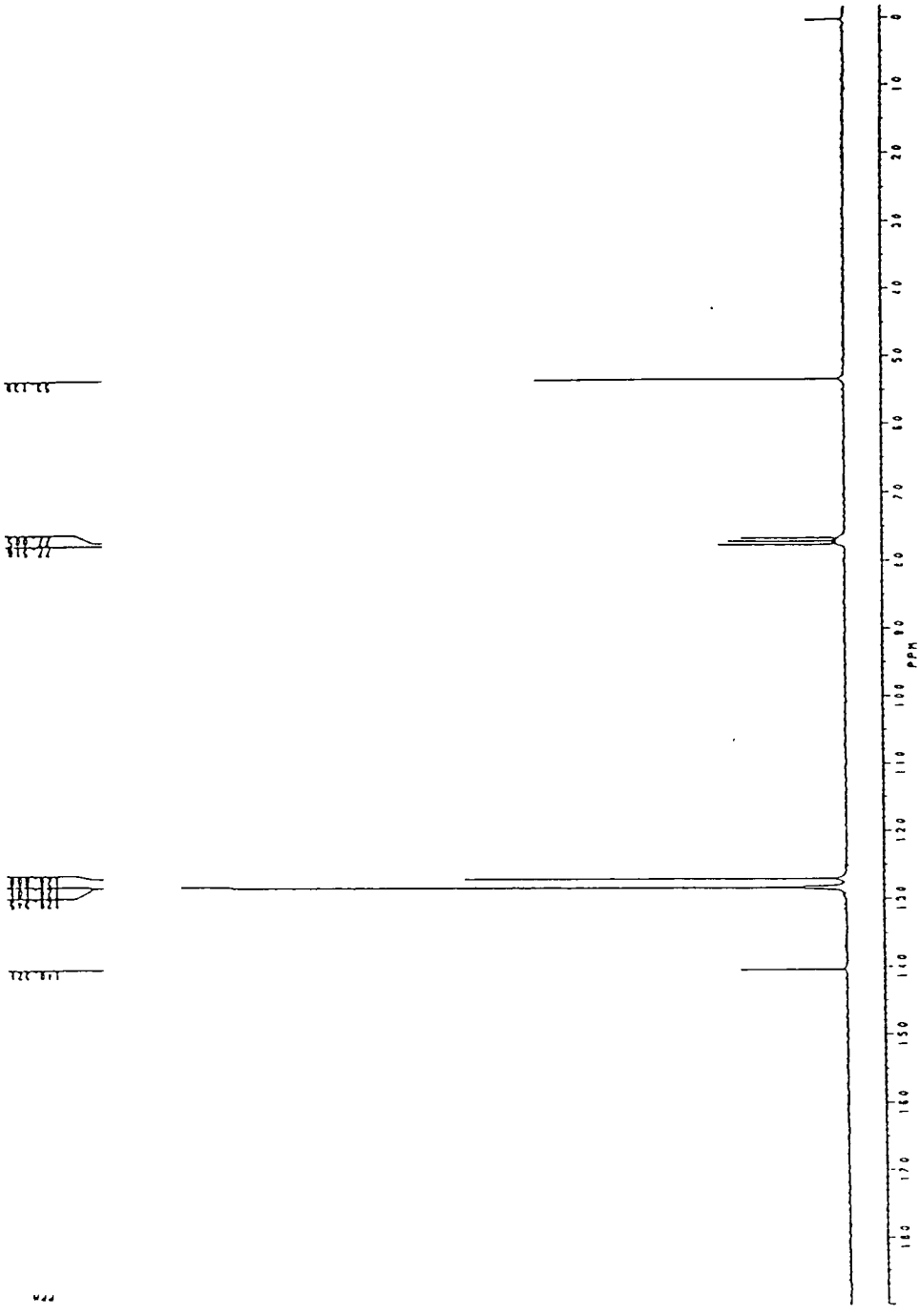
APPENDIX

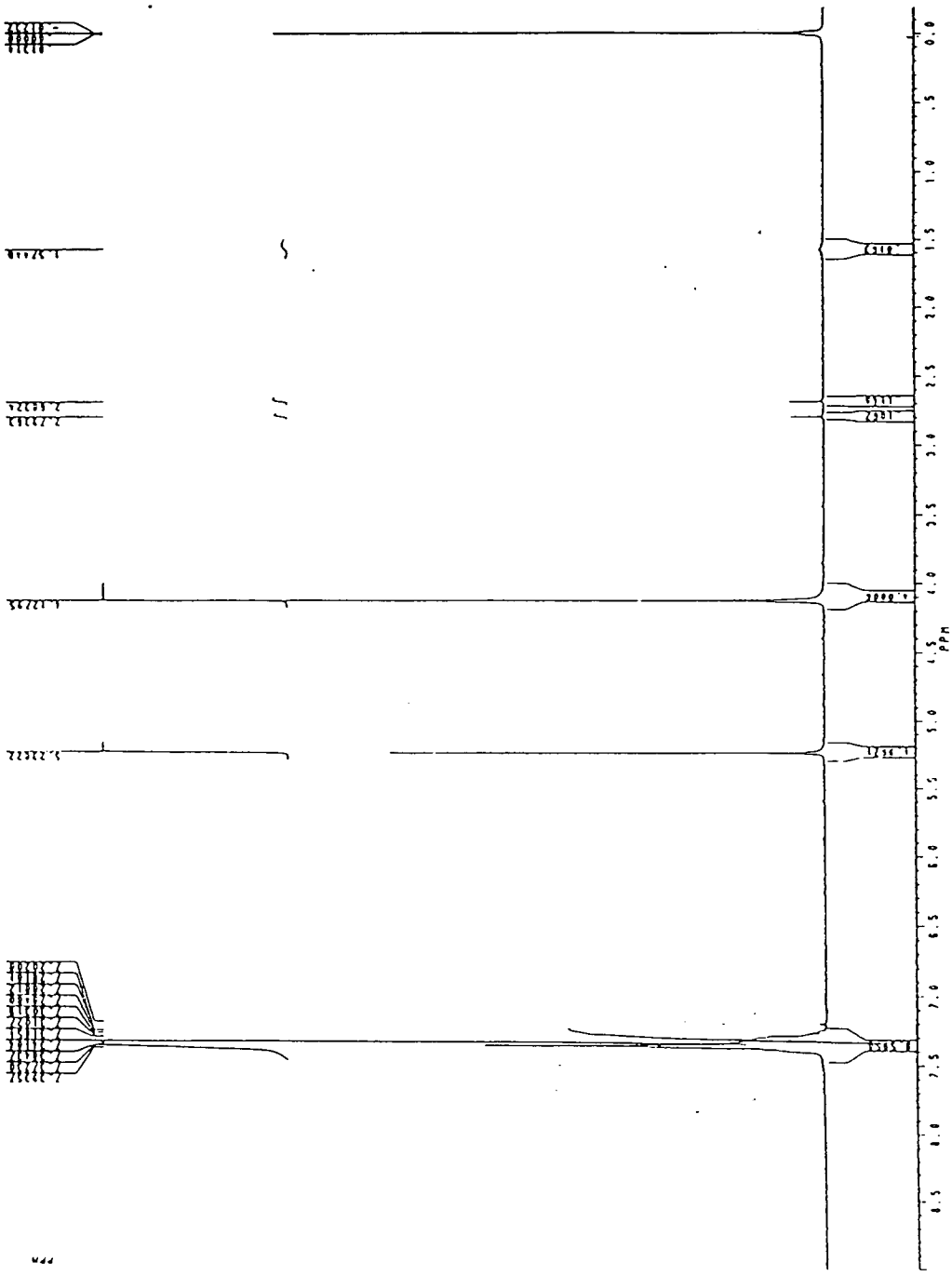
In the spectra that follow, signals due to solvent are present: chloroform at 7.26 ppm in the ^{1}H NMR and 77.2 ppm in the ^{13}C NMR; and methylene chloride at 5.29 ppm in the ^{1}H NMR and 53.3 in the ^{13}C NMR.



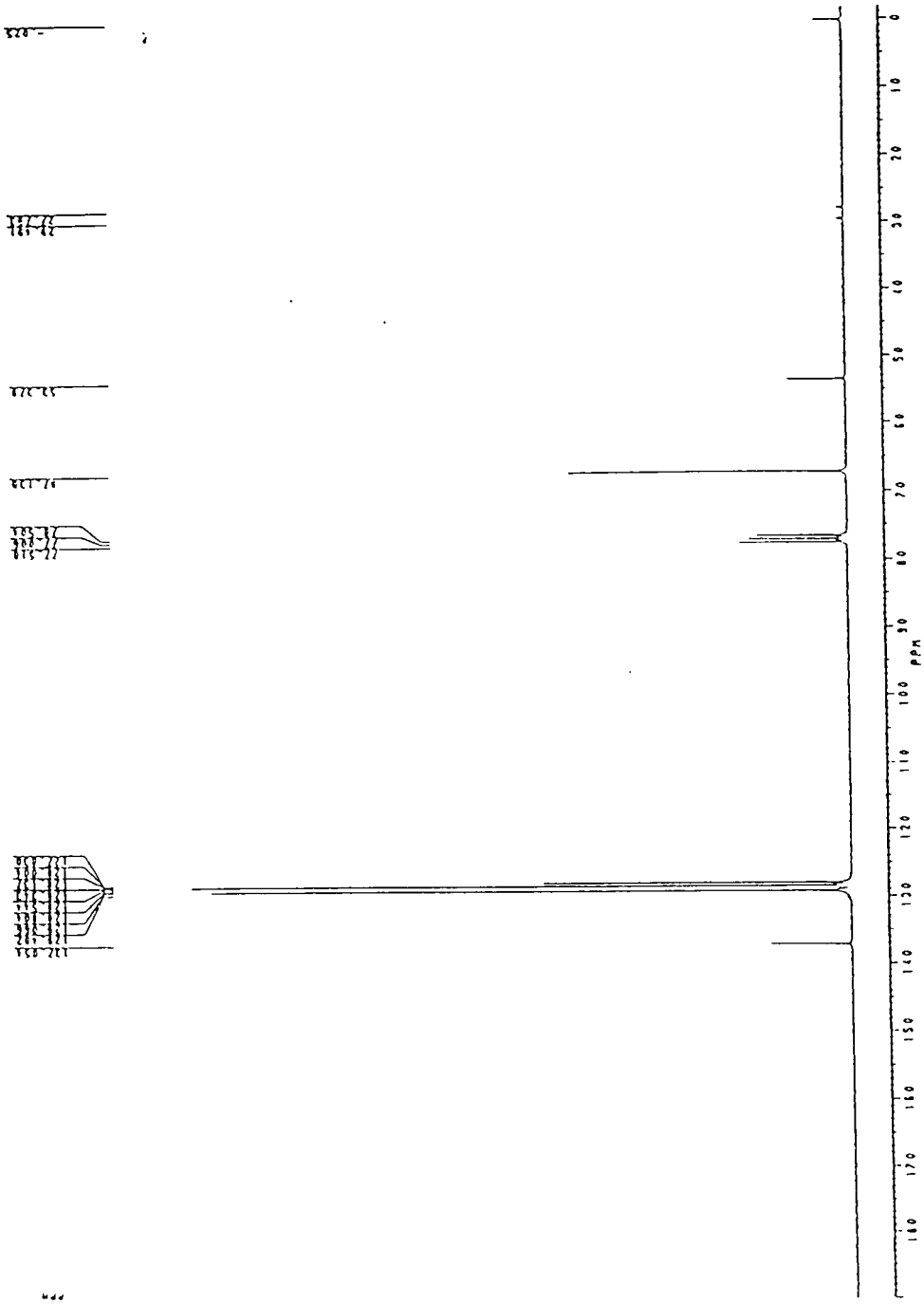
Spectrum 1: ^{1}H NMR spectrum of Dibenzylamine [1a]



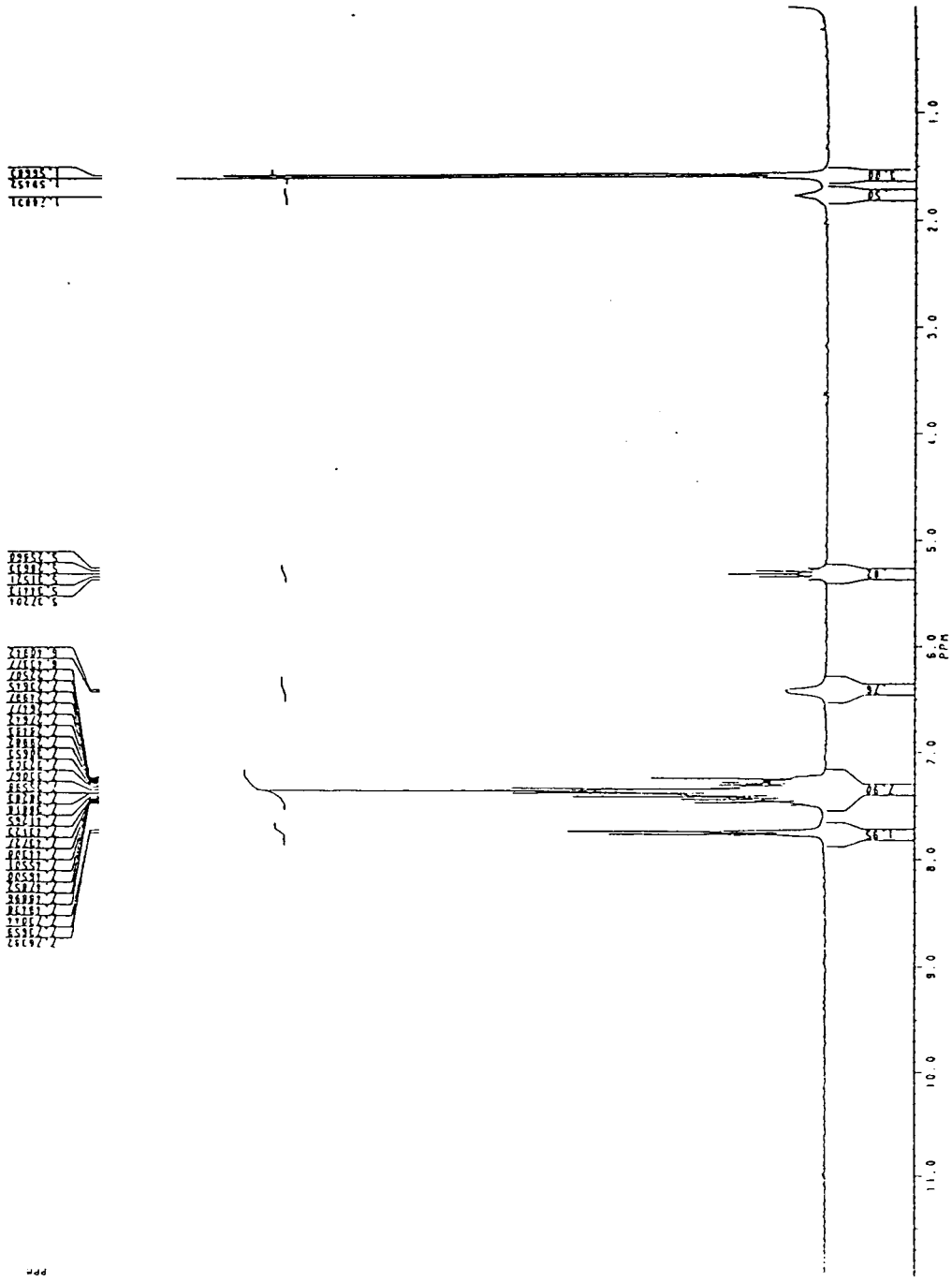
Spectrum 2: ^{13}C NMR spectrum of Dibenzylamine [1a]



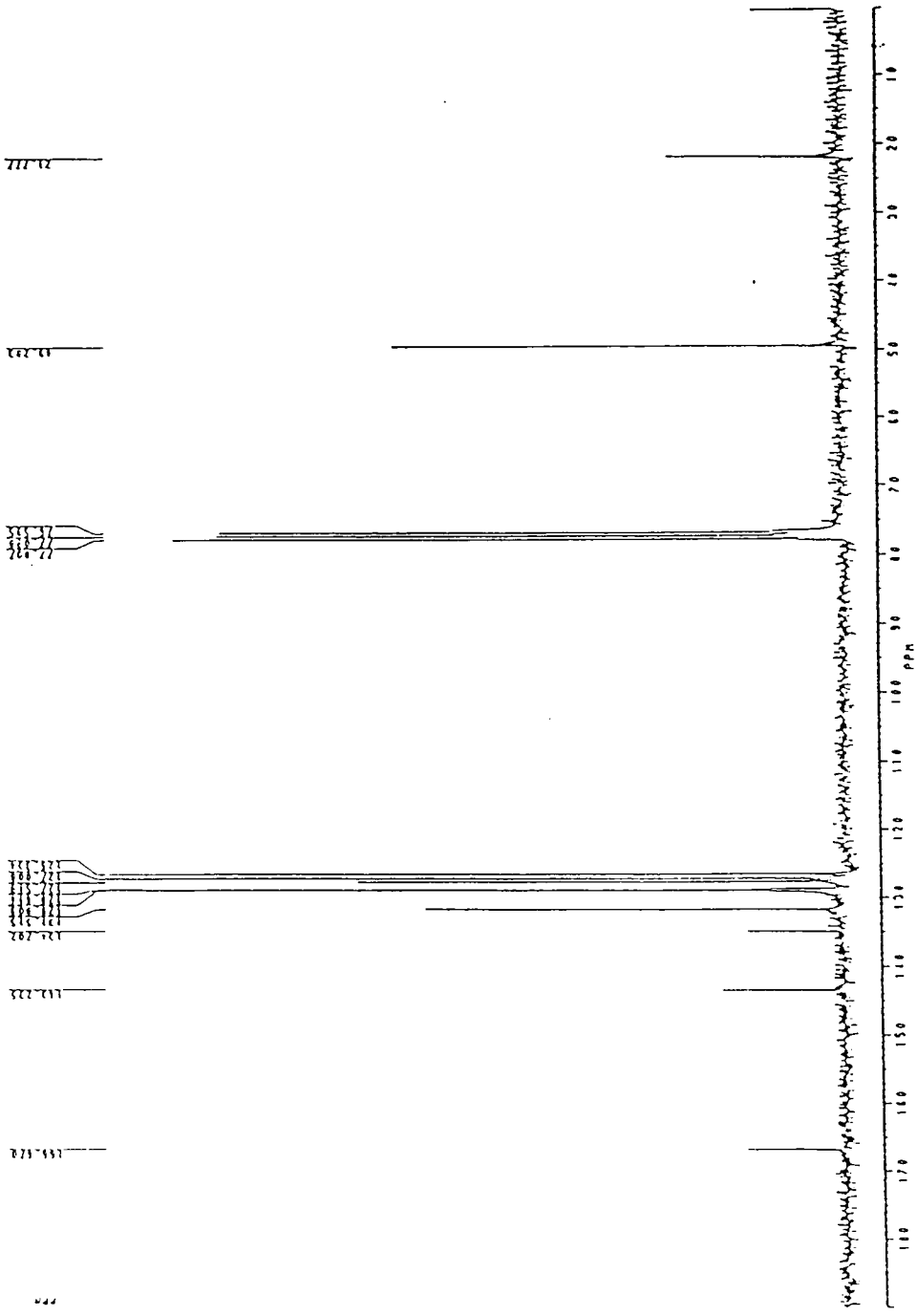
Spectrum 3: ^1H NMR spectrum of N-chlorodibenzylamine [1b]



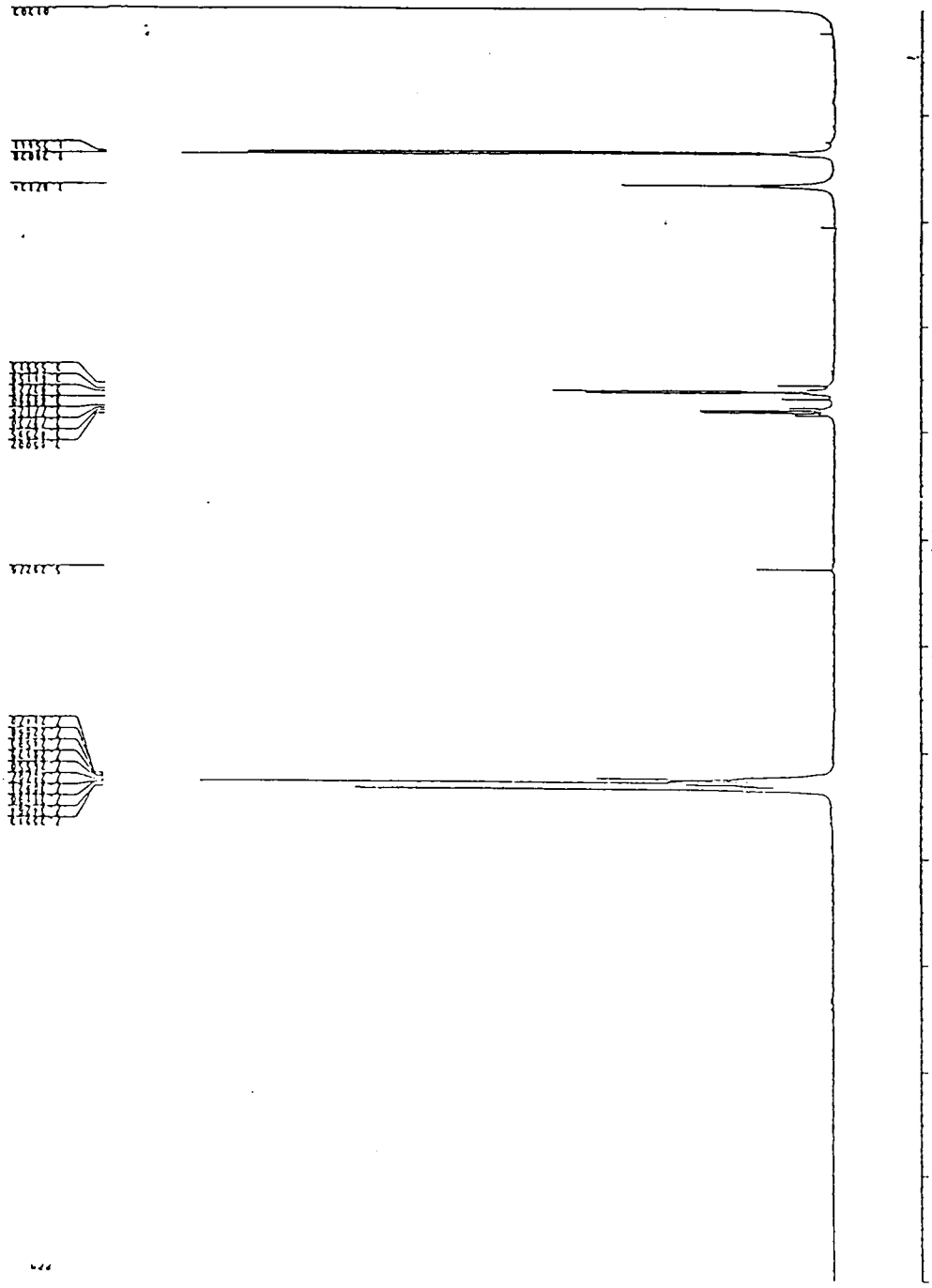
Spectrum 4: ^{13}C NMR spectrum of N-chlorodibenzylamine [1b]



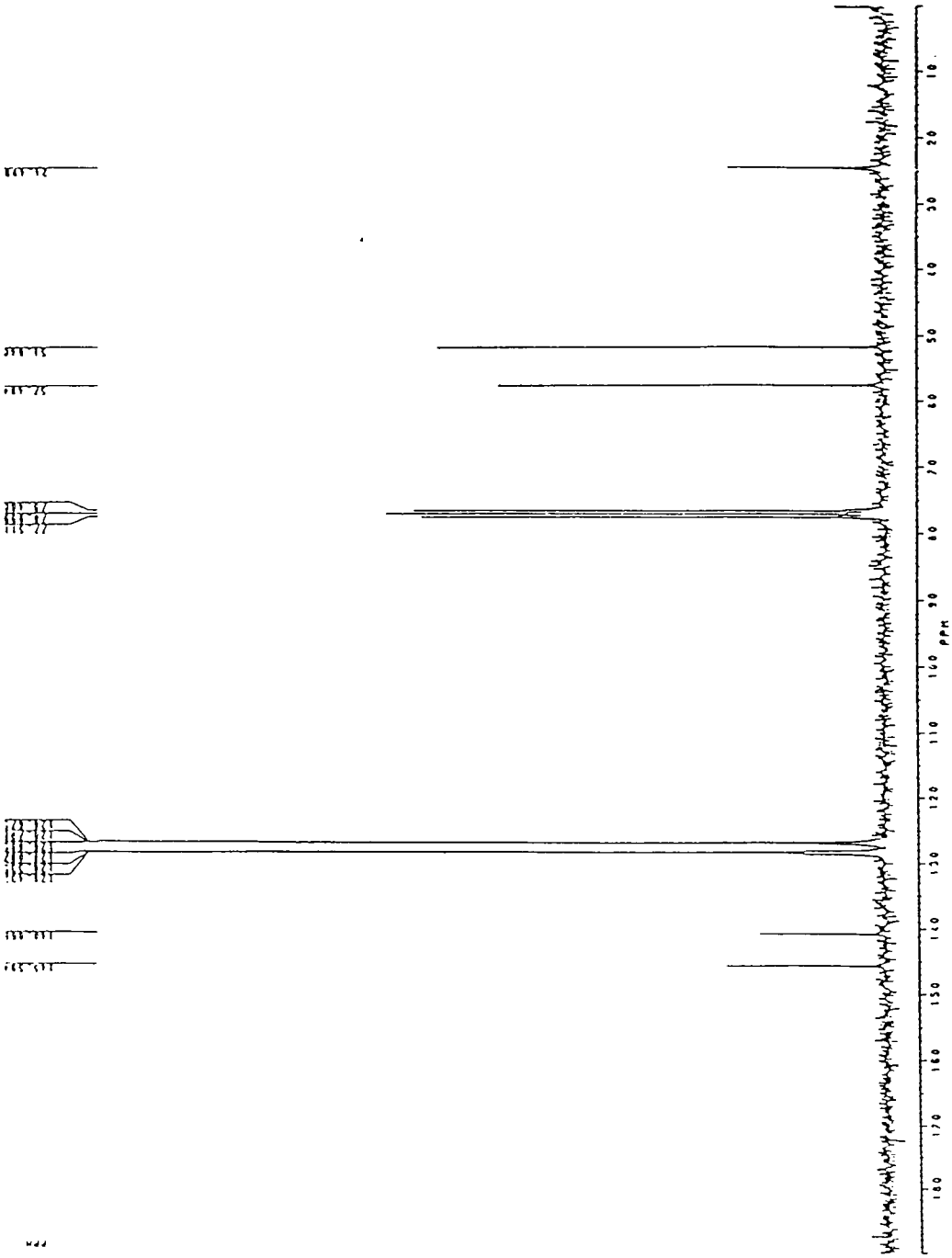
Spectrum 5: ^{1}H NMR spectrum of N-(1-phenylethyl)benzamide **[3]**



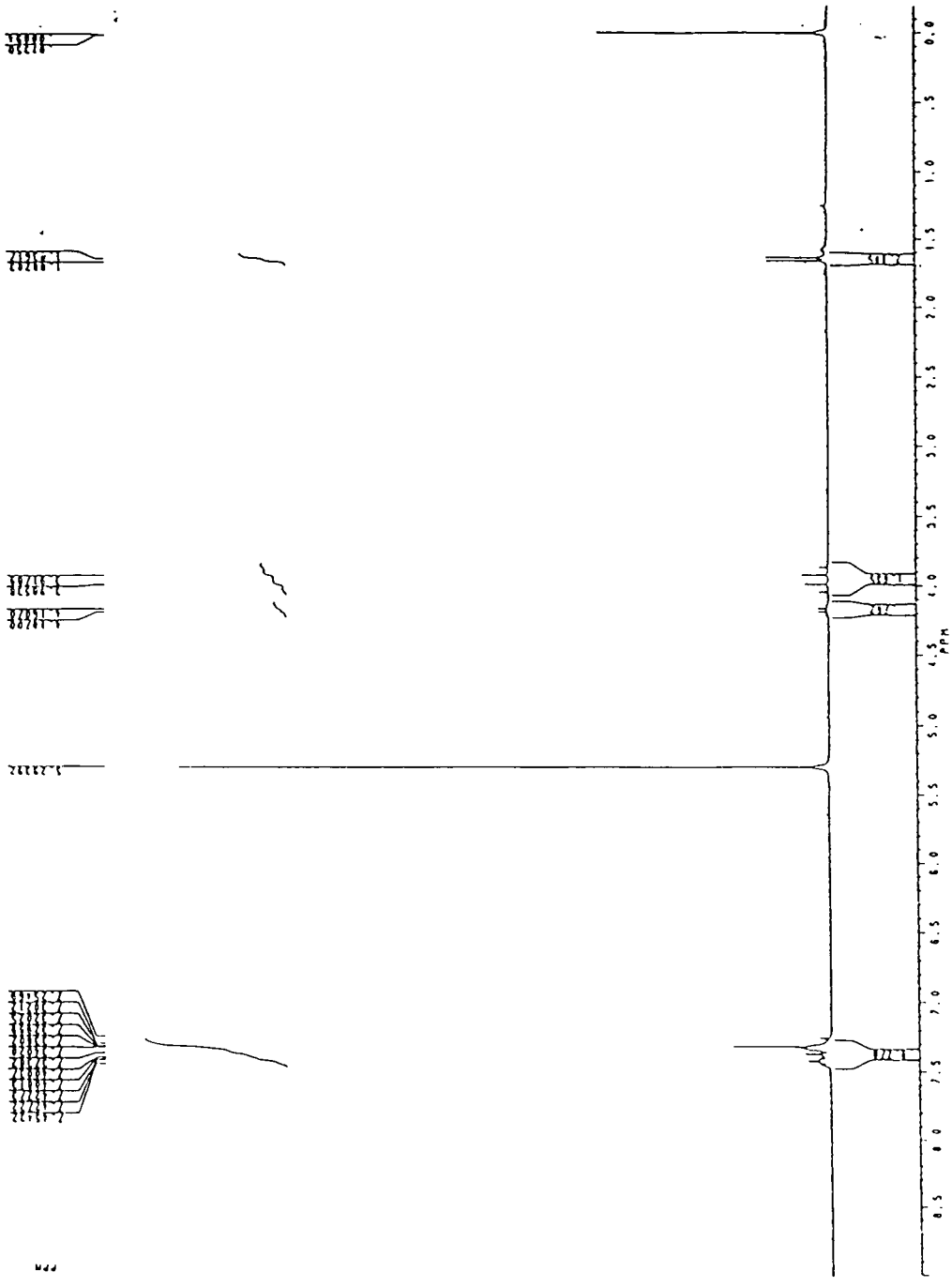
Spectrum 6: ^{13}C NMR spectrum of N-(1-phenylethyl)benzamide **[3]**



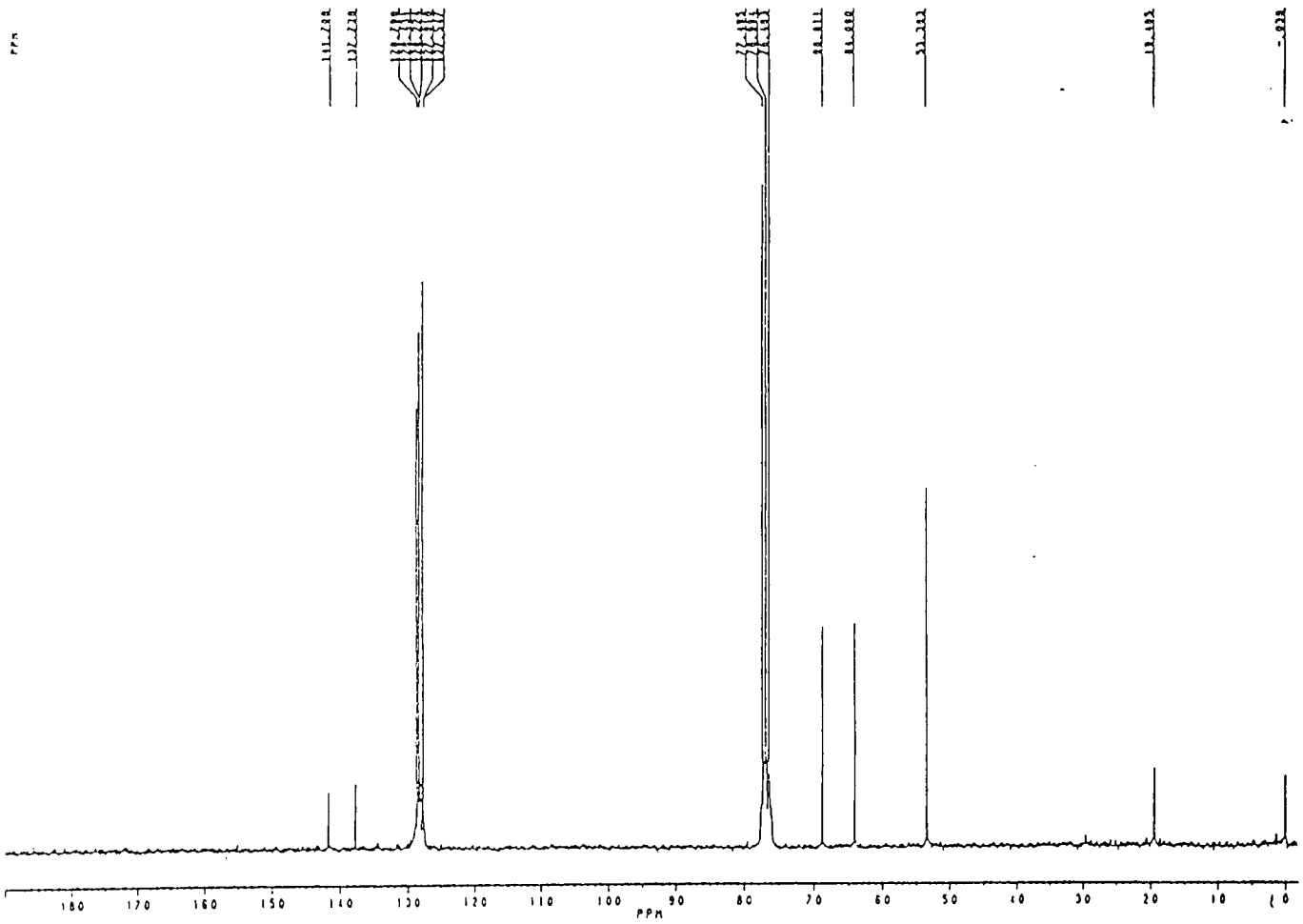
Spectrum 7: ^{1}H NMR spectrum of N-benzyl-1-phenethylamine **[4a]**



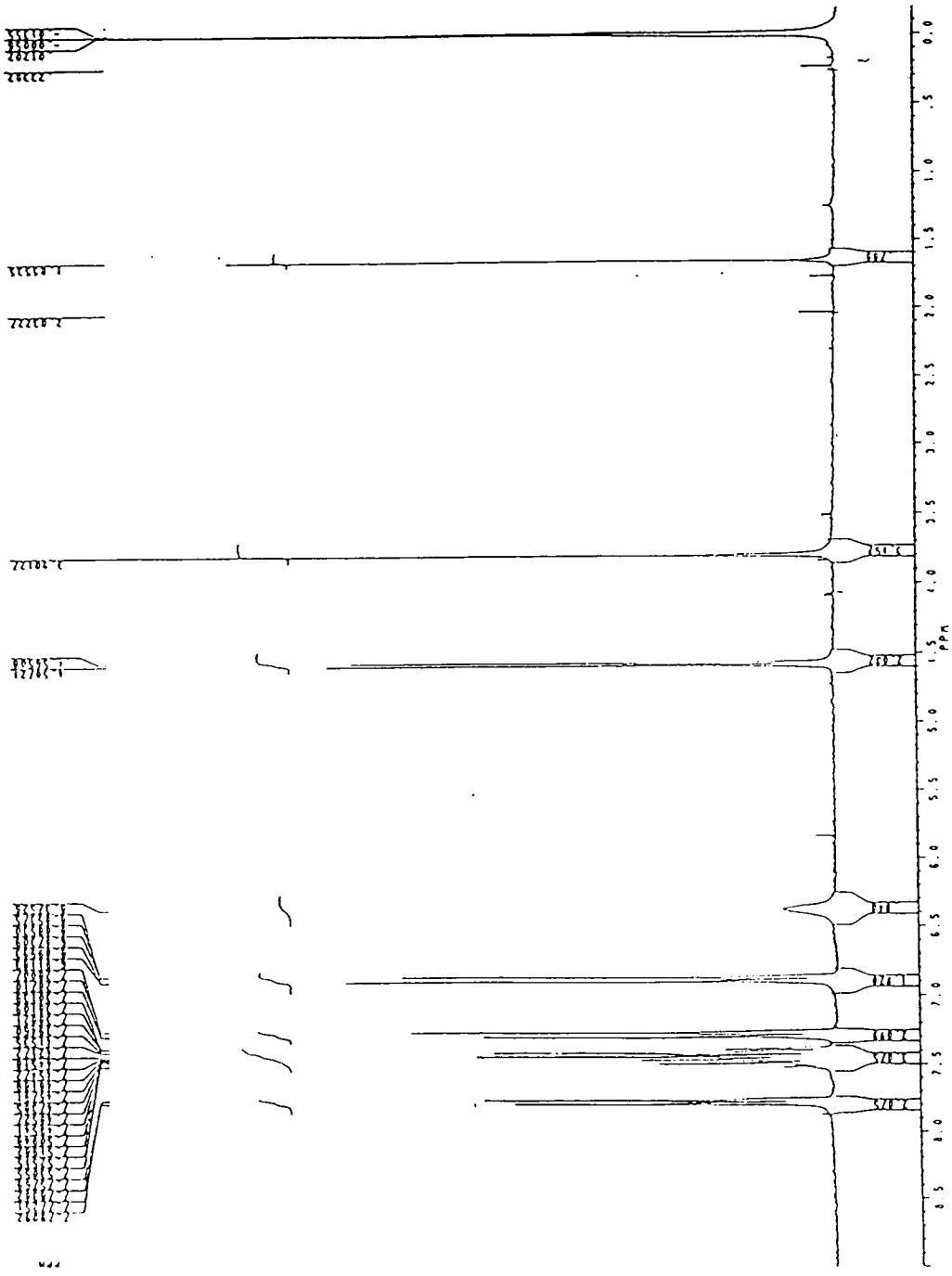
Spectrum 8: ^{13}C NMR spectrum of N-benzyl-1-phenethylamine **[4a]**



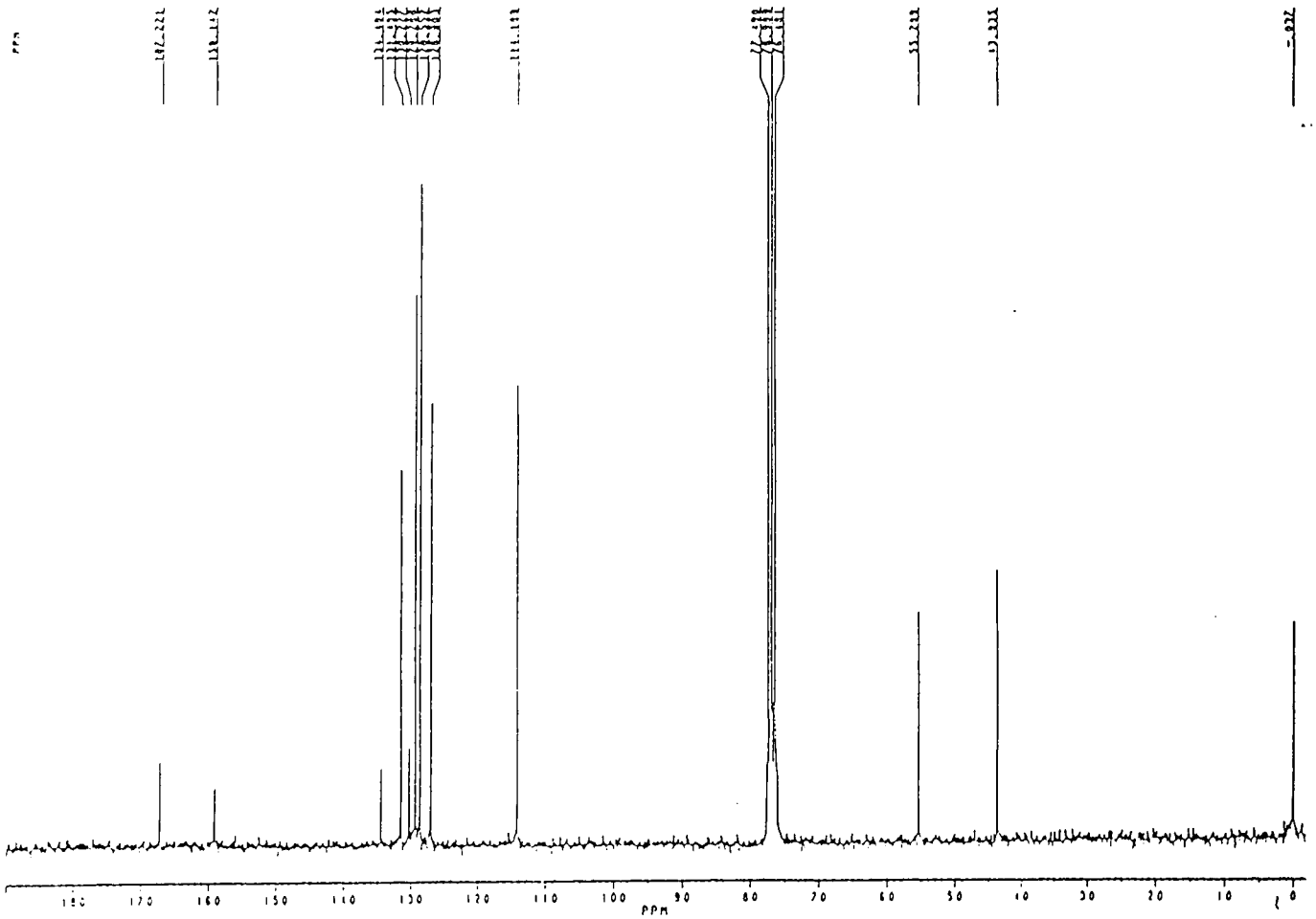
Spectrum 9: ^{1}H NMR spectrum of N-chloro-N-benzyl-1-phenethylamine **[4b]**



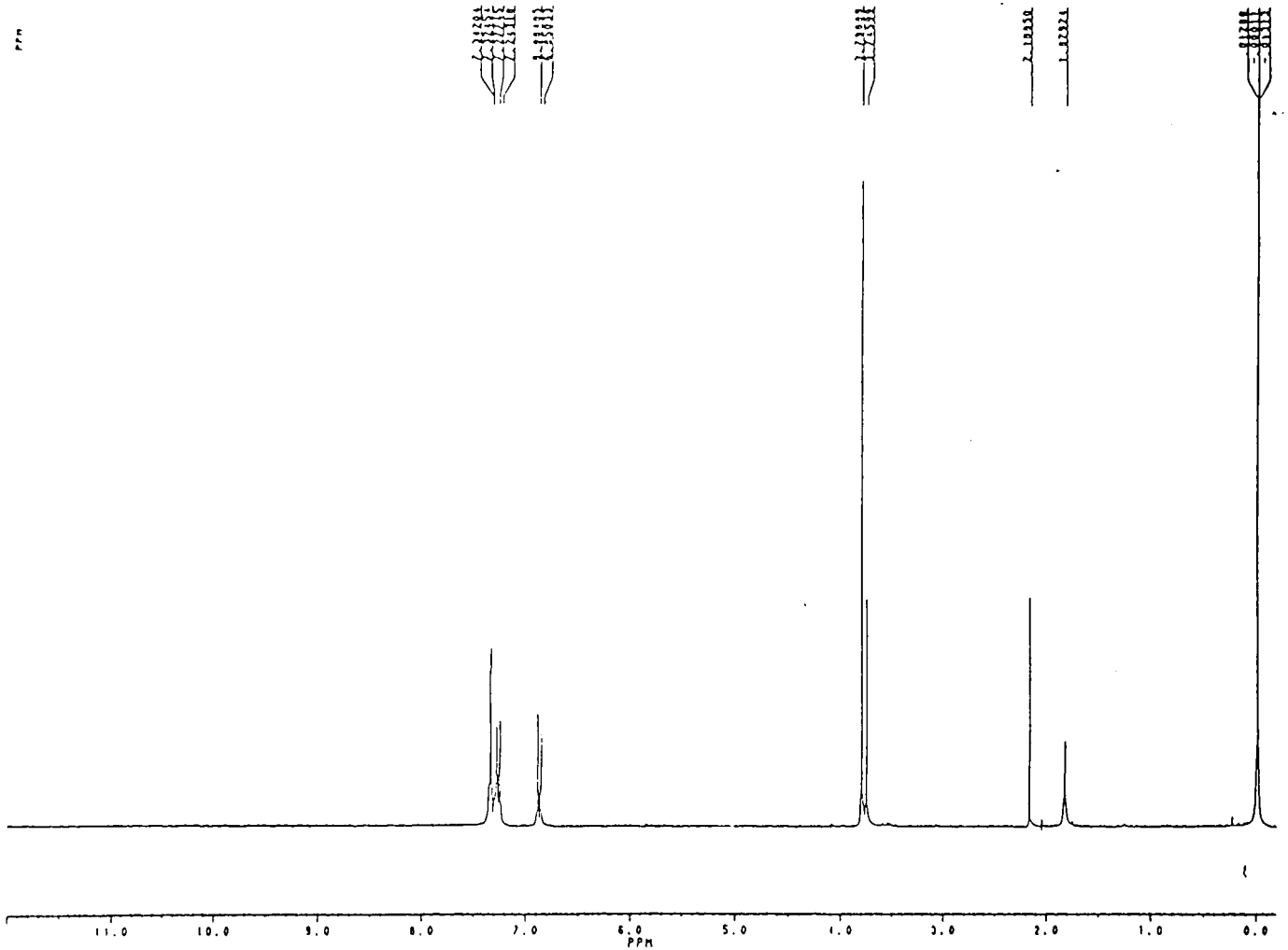
Spectrum 10: ^{13}C NMR spectrum of N-chloro-N-benzyl-1-phenethylamine **[4b]**



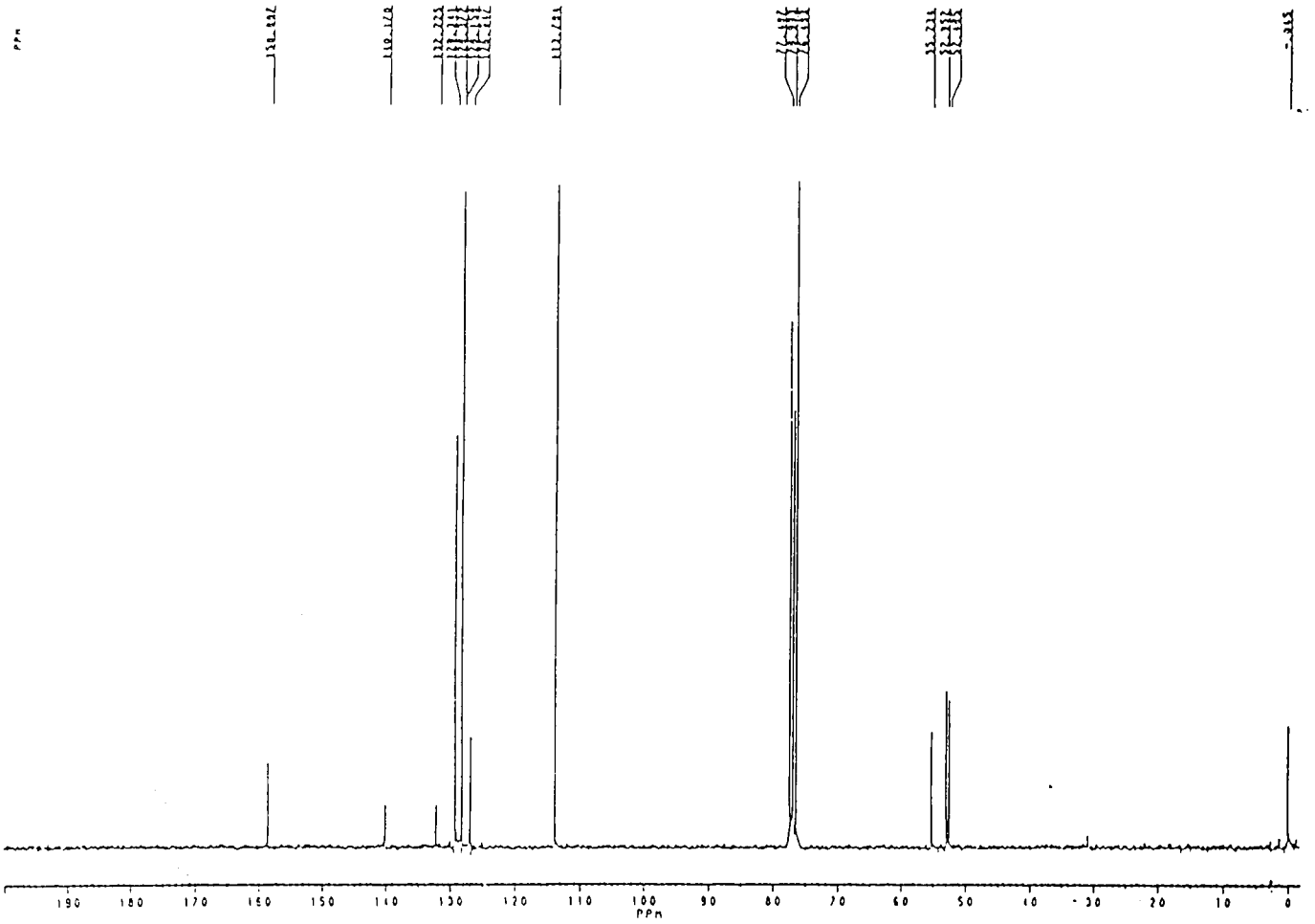
Spectrum 11: ^{1}H NMR spectrum of N-(*p*-methoxybenzyl)-benzamide **[5]**



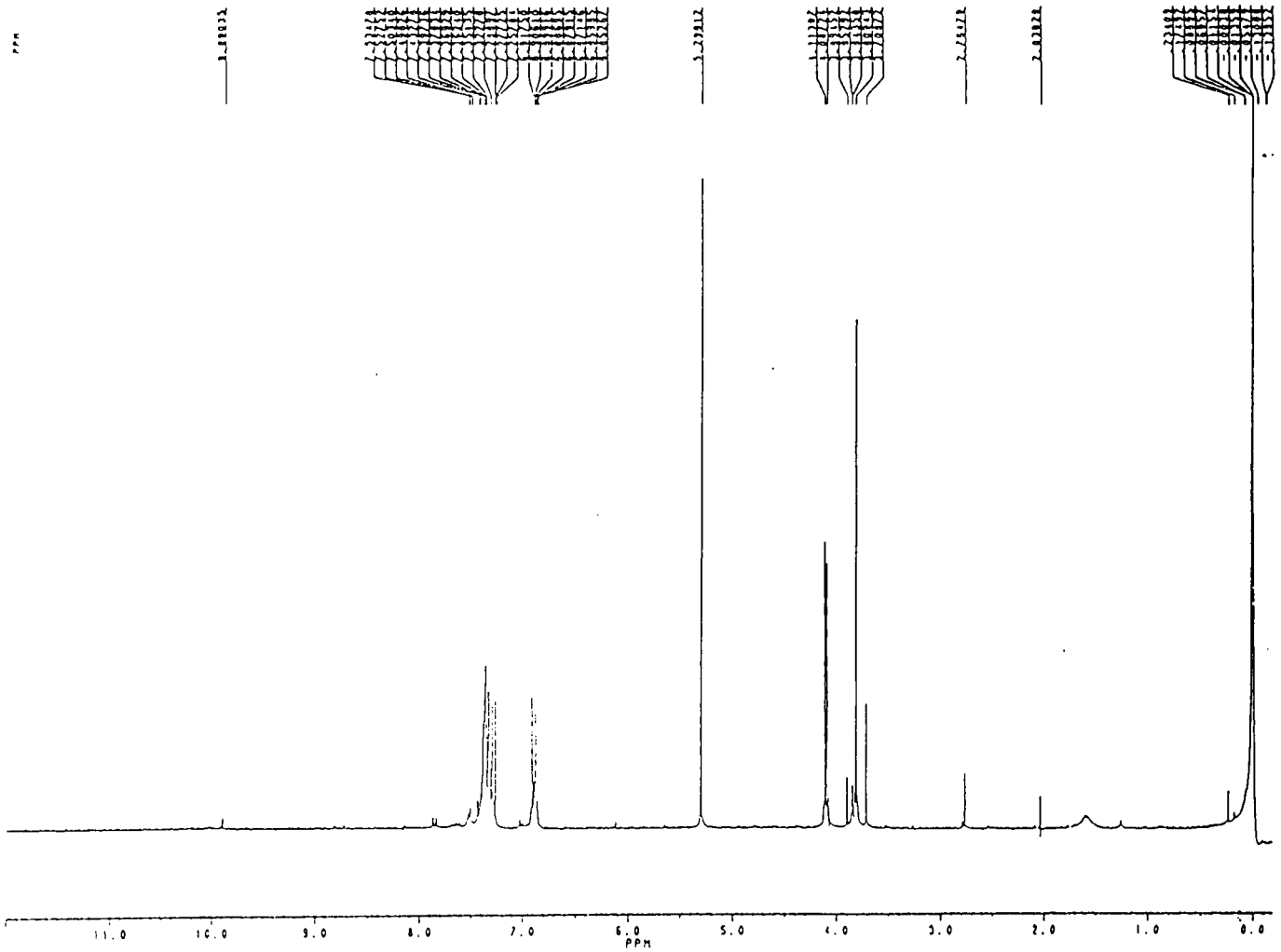
Spectrum 12: ^{13}C NMR spectrum of N-(*p*-methoxybenzyl)-benzamide **[5]**



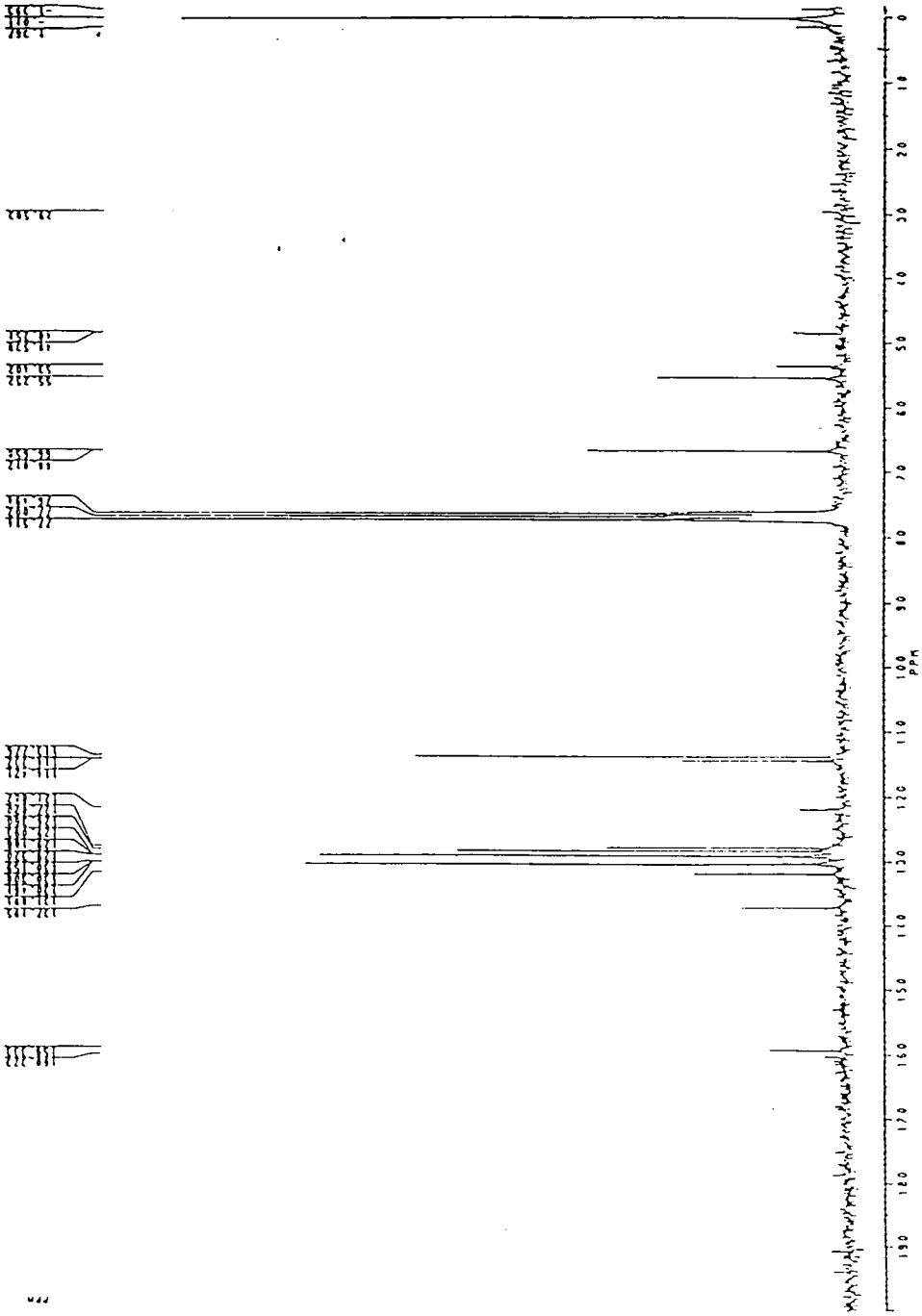
Spectrum 13: ^{1}H NMR spectrum of N-(*p*-methoxybenzyl)-benzylamine **[6a]**



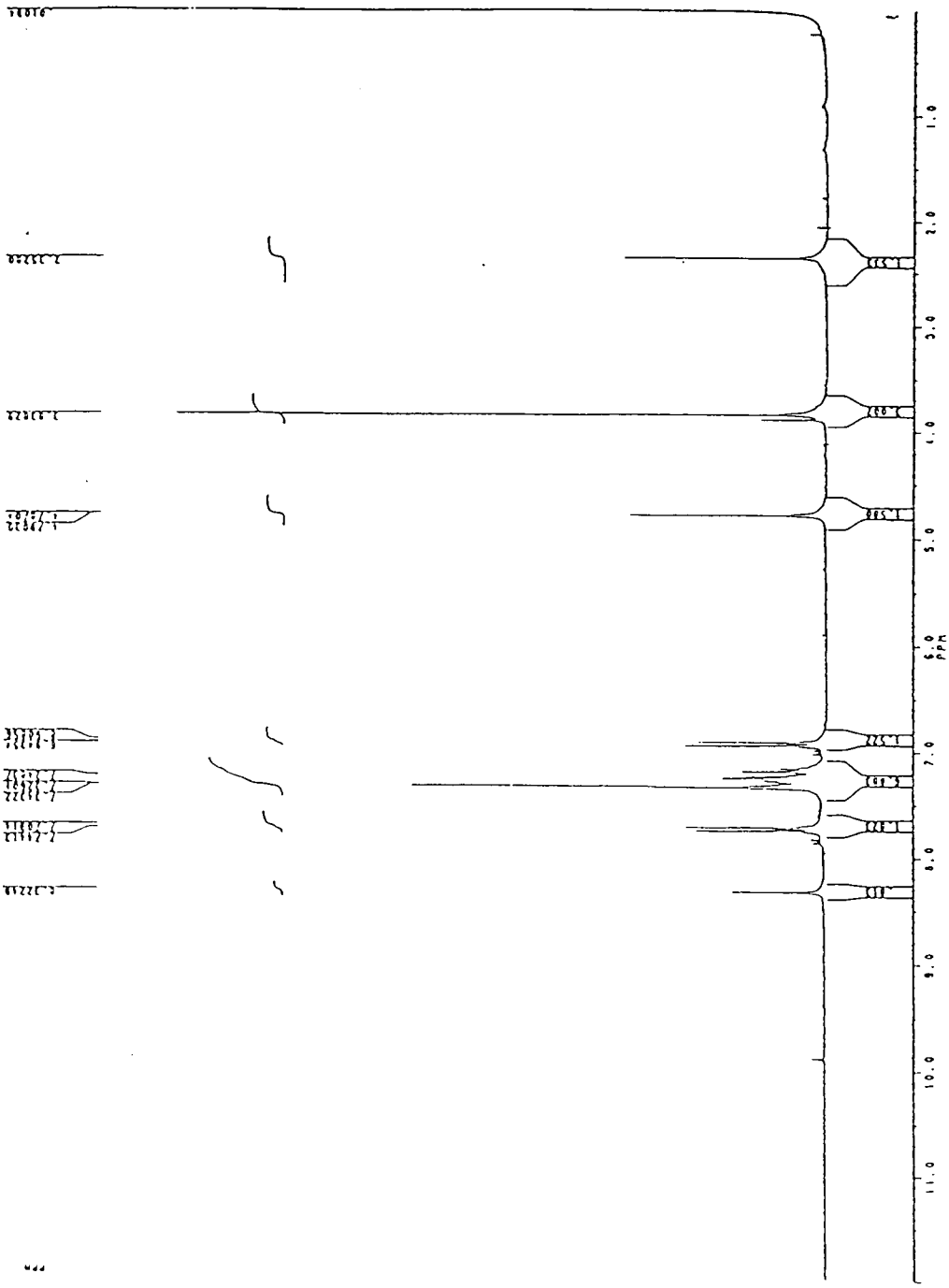
Spectrum 14: ^{13}C NMR spectrum of N-(*p*-methoxybenzyl)-benzylamine **[6a]**



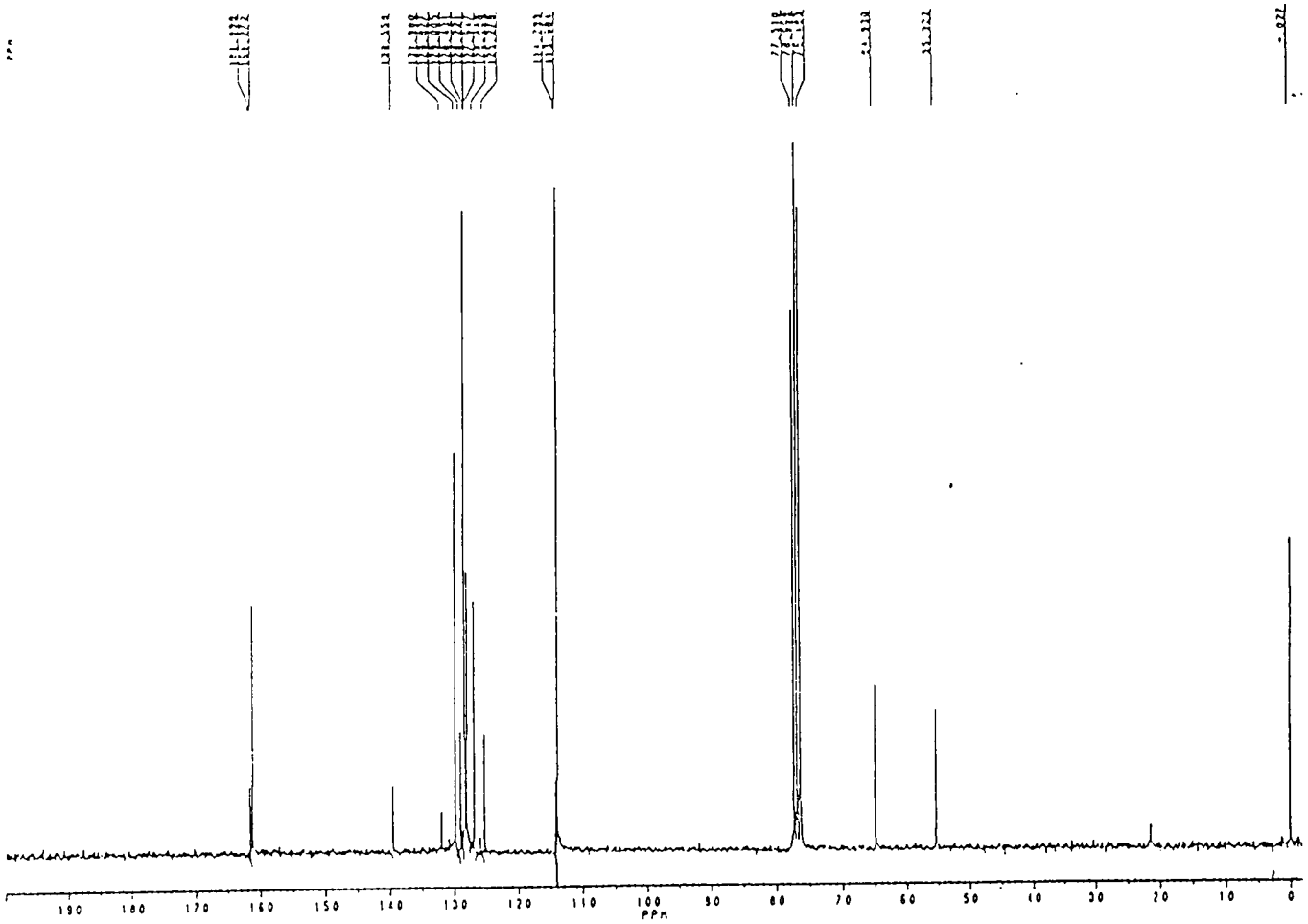
Spectrum 15: ^{1}H NMR spectrum of N-chloro-N-(*p*-methoxybenzyl)-benzylamine **[6b]**



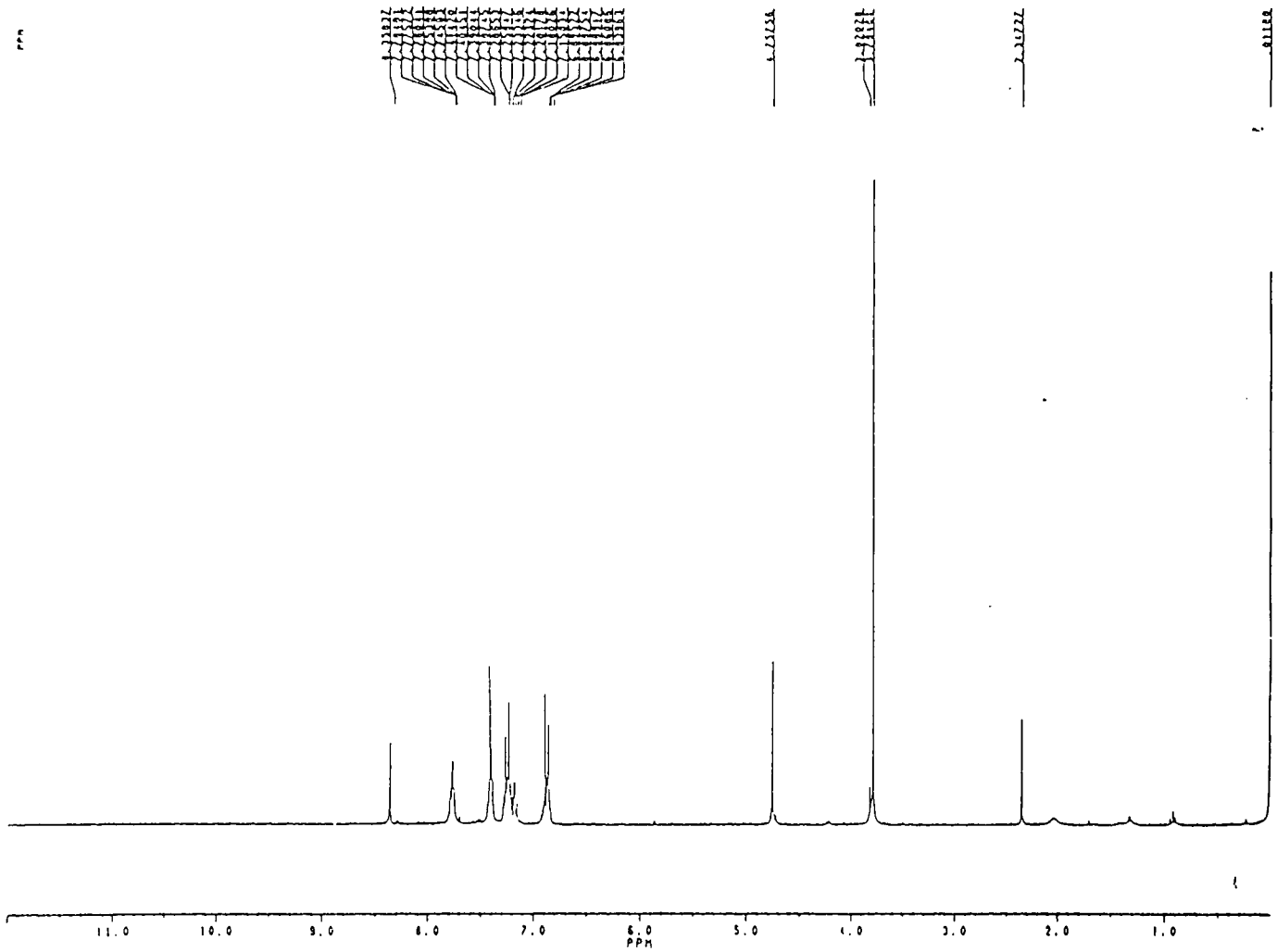
Spectrum 16: ^{13}C NMR spectrum of N-chloro-N-(*p*-methoxybenzyl)-benzylamine [6b]



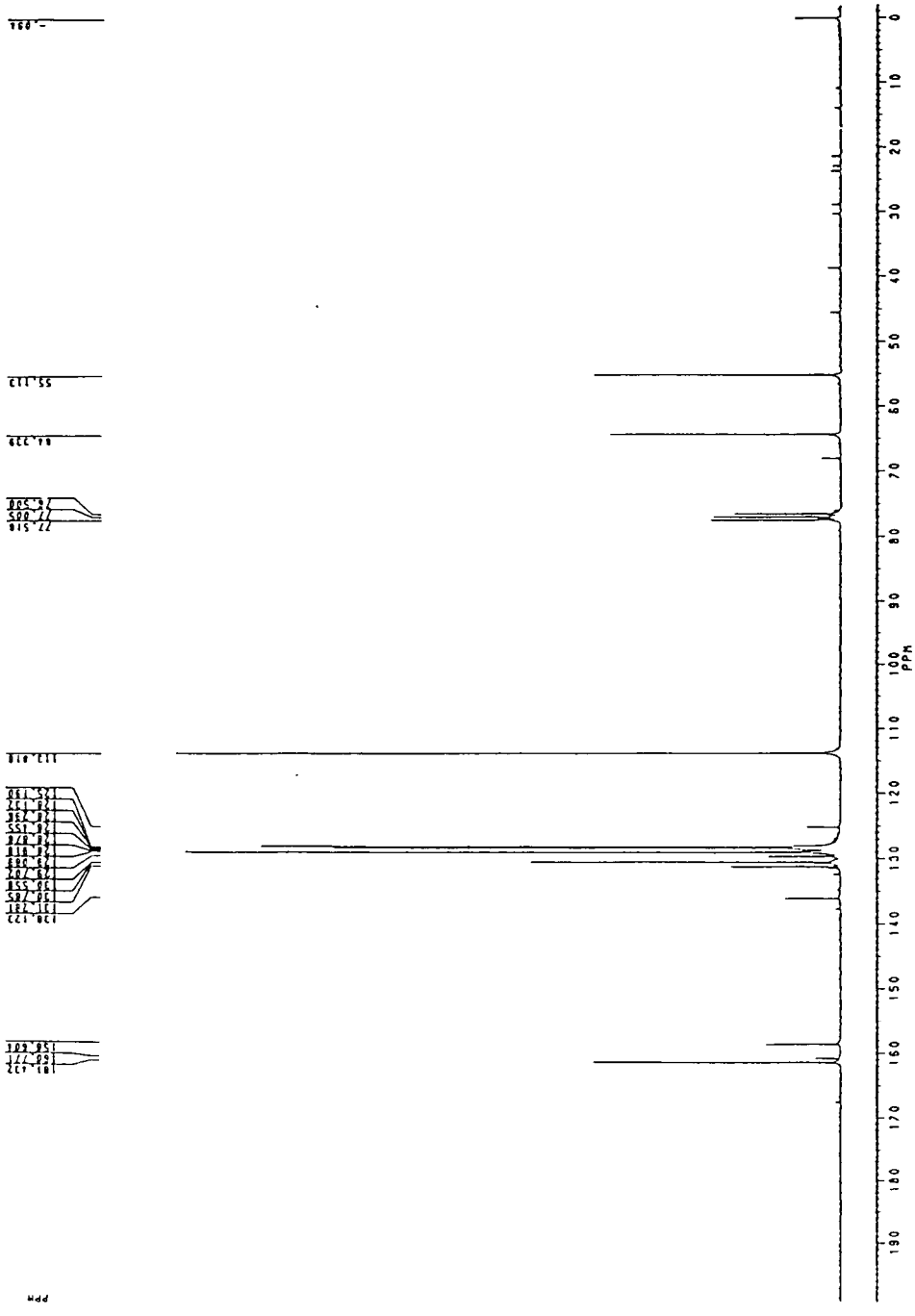
Spectrum 17: ^{1}H NMR spectrum of N-(*p*-methoxybezylidene)-benzylimine [7]



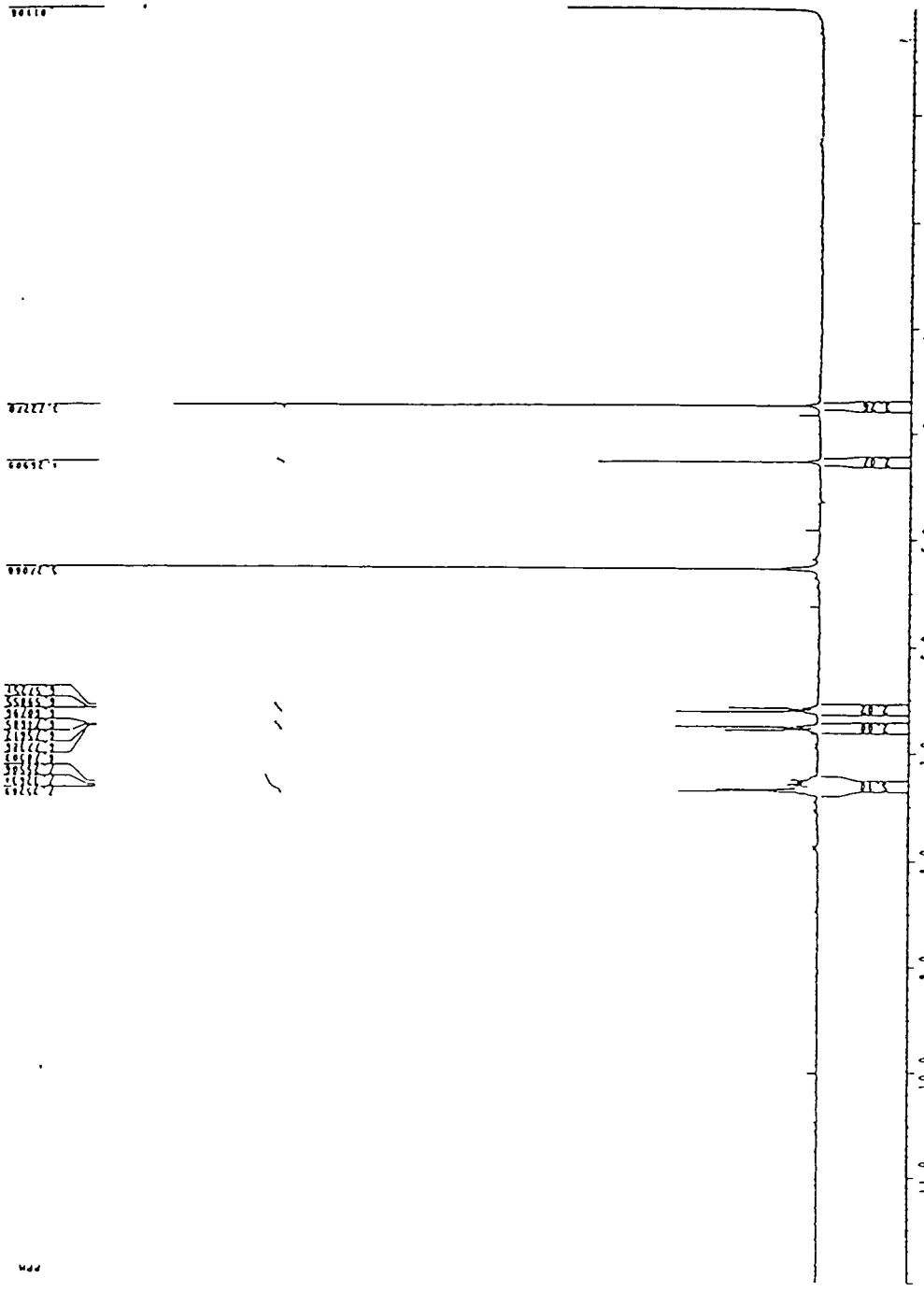
Spectrum 18: ^{13}C NMR spectrum of N-(*p*-methoxybenzylidene)-benzylimine [7]



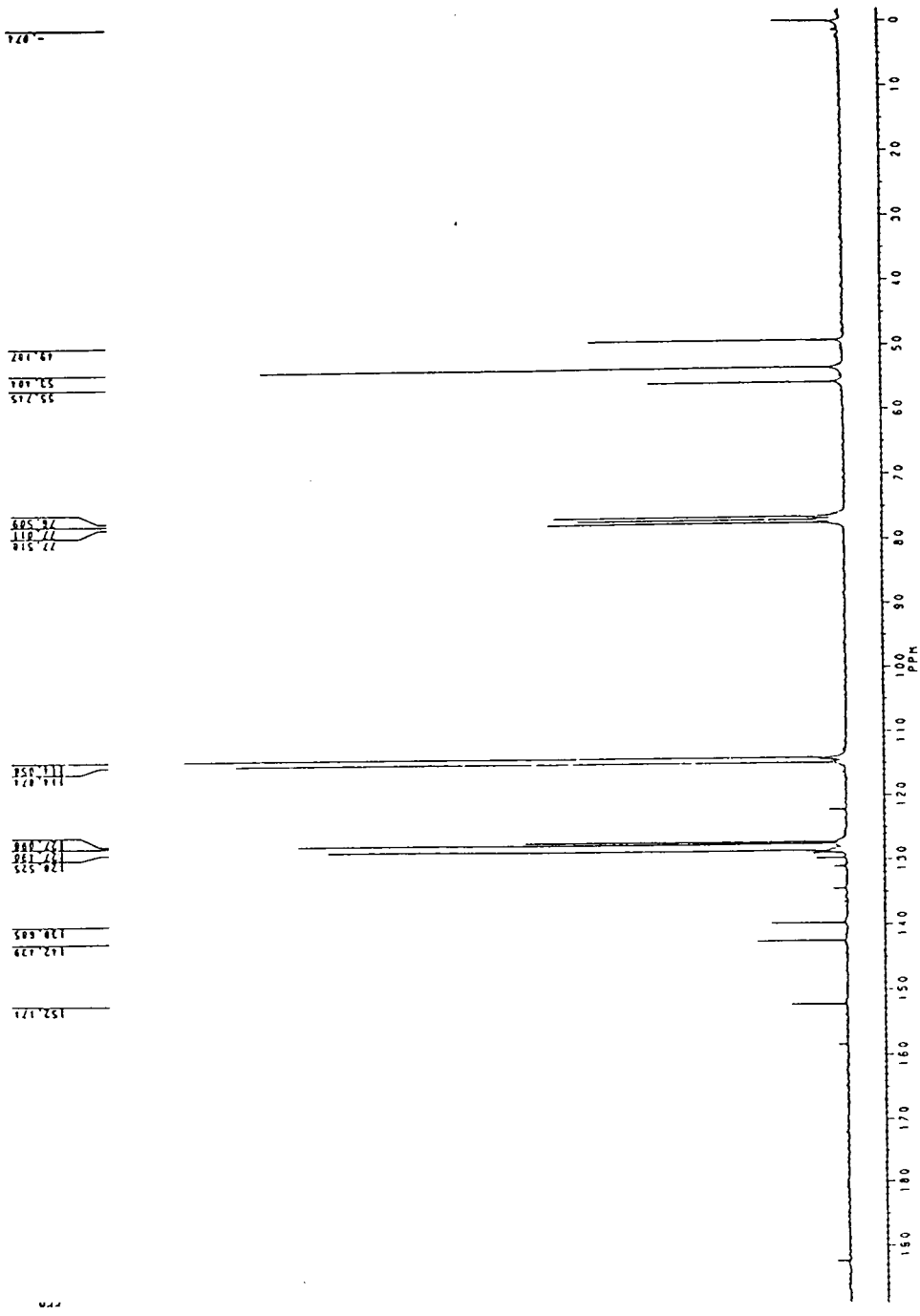
Spectrum 19: ^{1}H NMR spectrum of N-benzylidene-*p*-methoxybenzylimine **[8]**



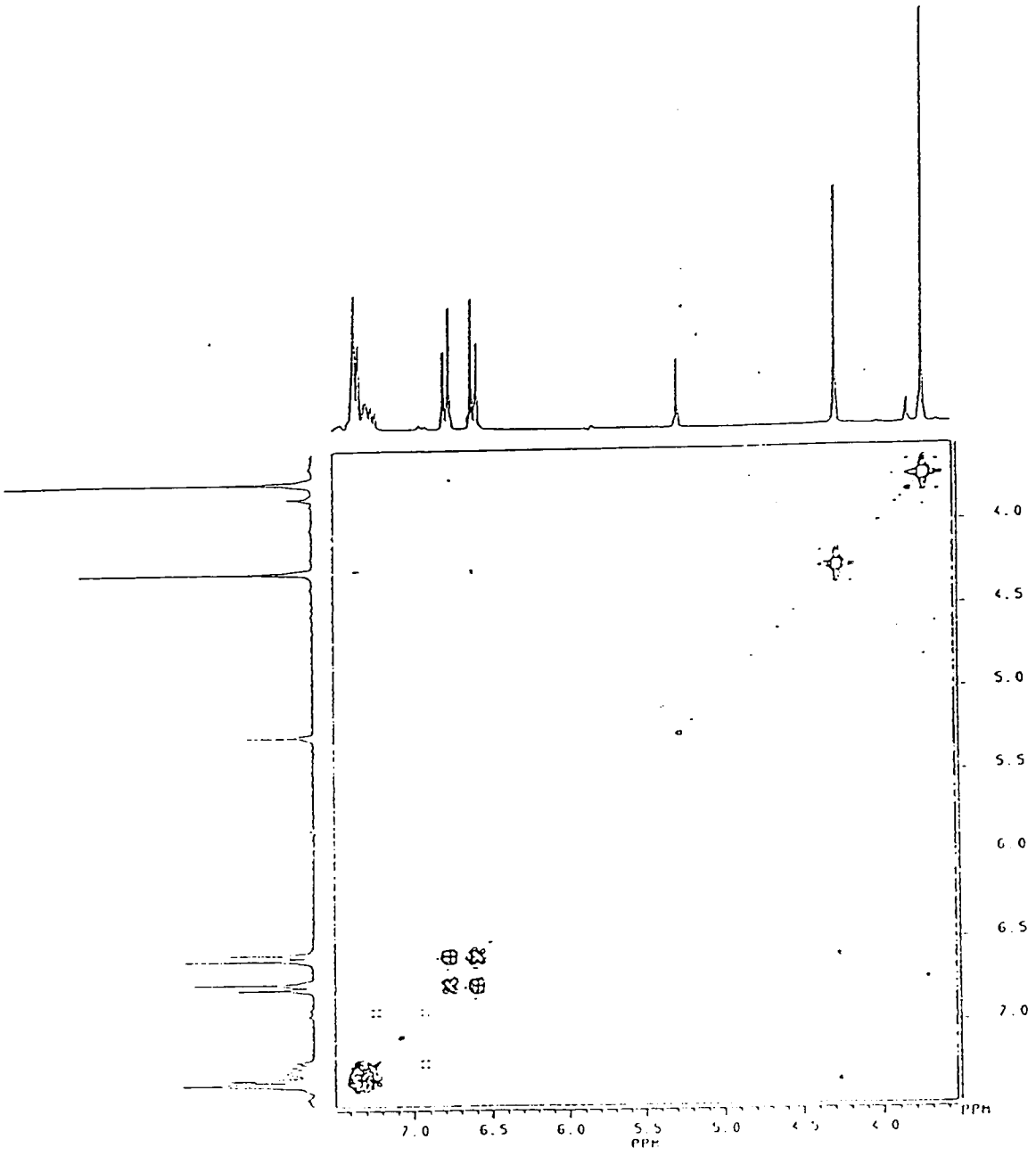
Spectrum 20: ^{13}C NMR spectrum of N-benzylidene-p-methoxybenzylimine [8]



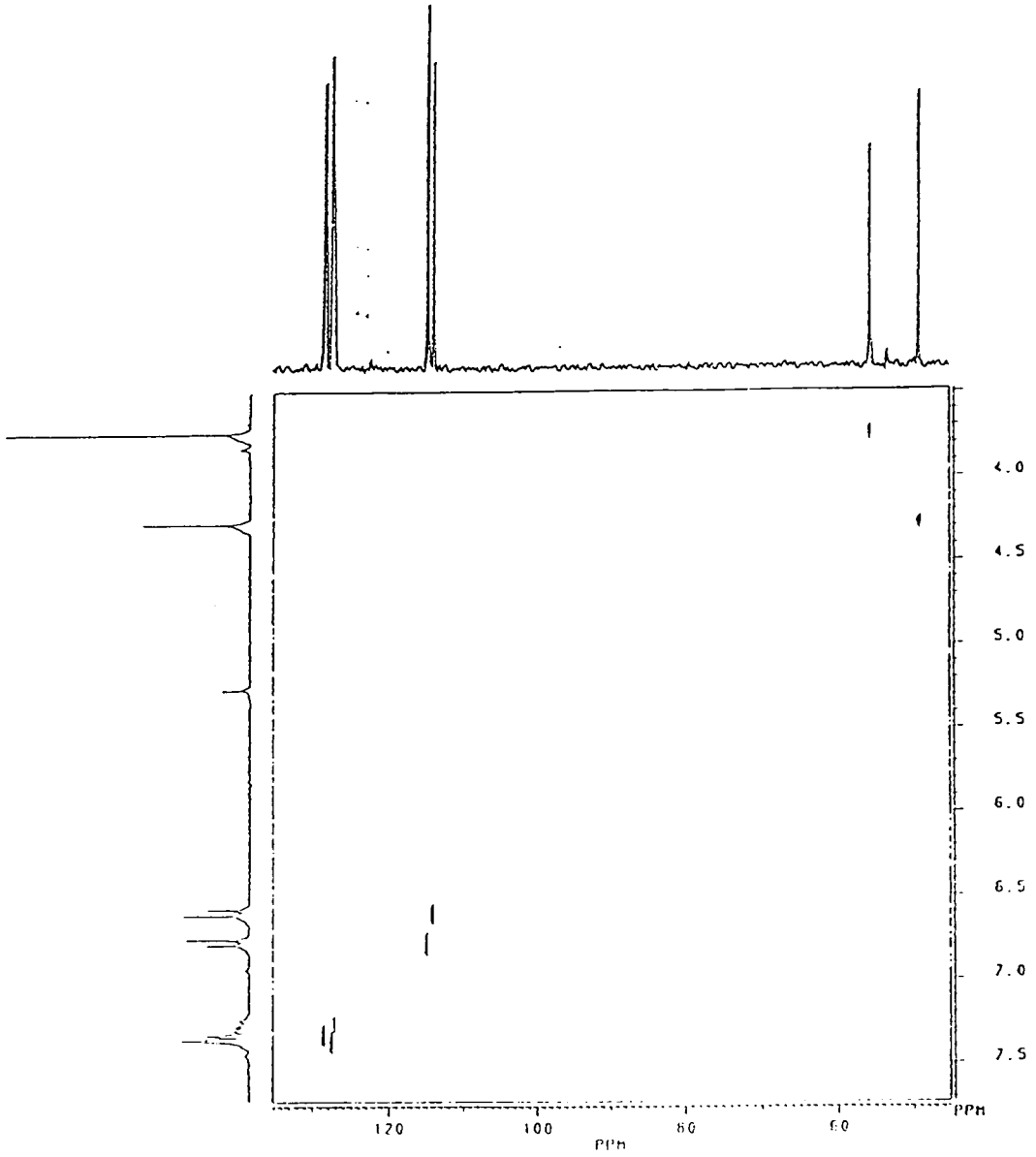
Spectrum 21: ^{1}H NMR spectrum of *p*-methoxy-N-benzylaniline [9]



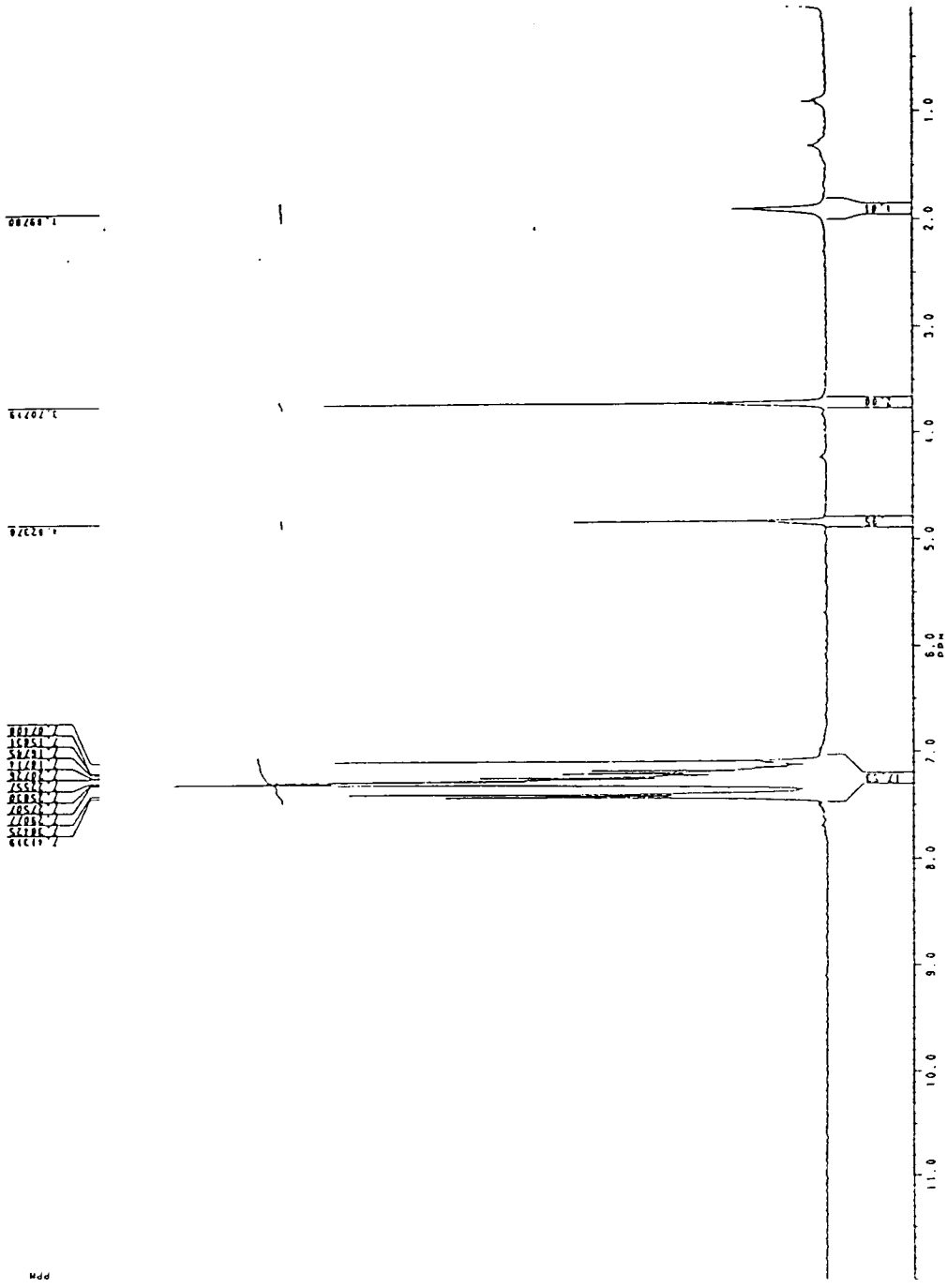
Spectrum 22: ^{13}C NMR spectrum of *p*-methoxy-N-benzylaniline [9]



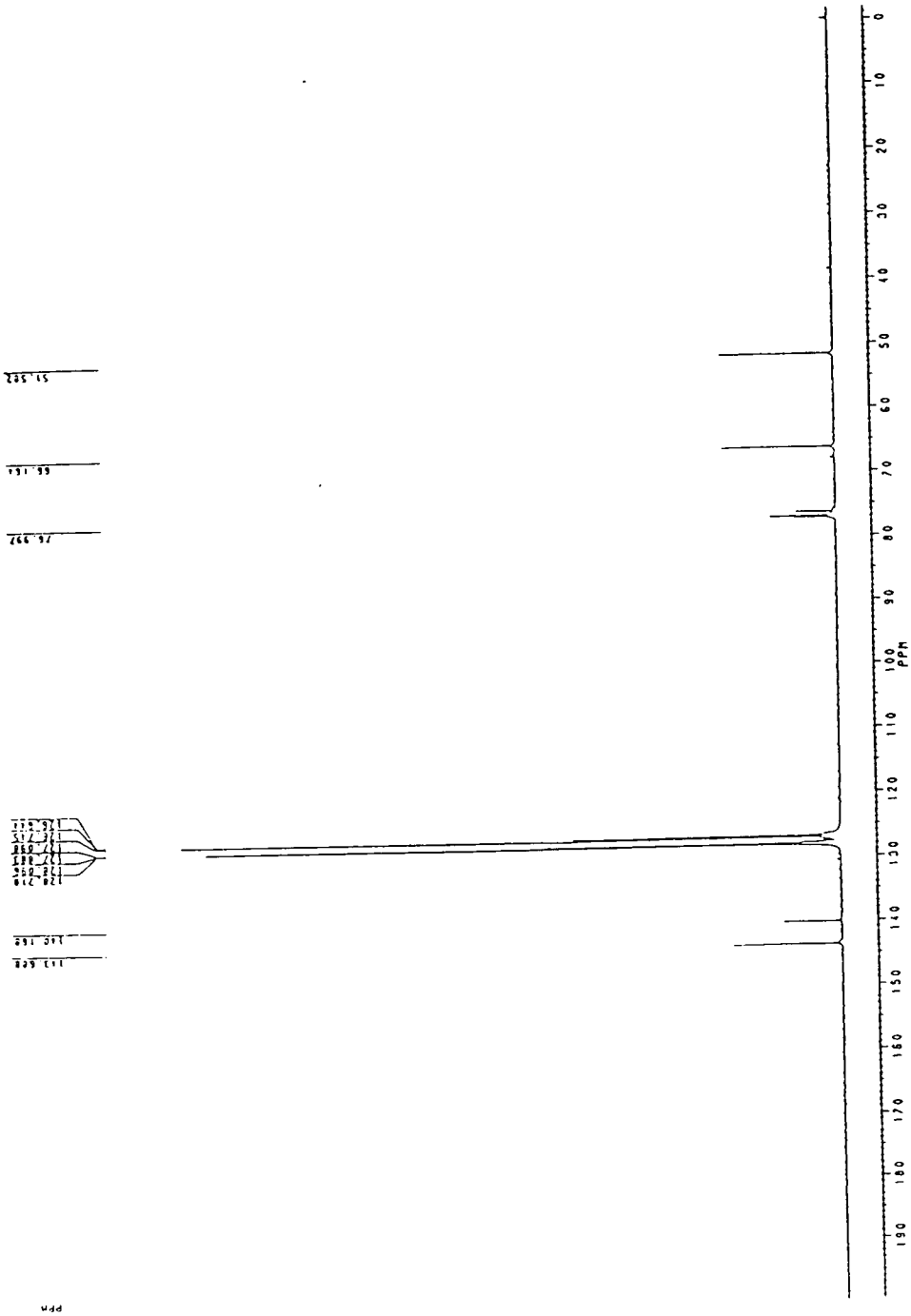
Spectrum 23: 2-Dimensional COSY spectrum of *p*-methoxy-N-benzylaniline [9]



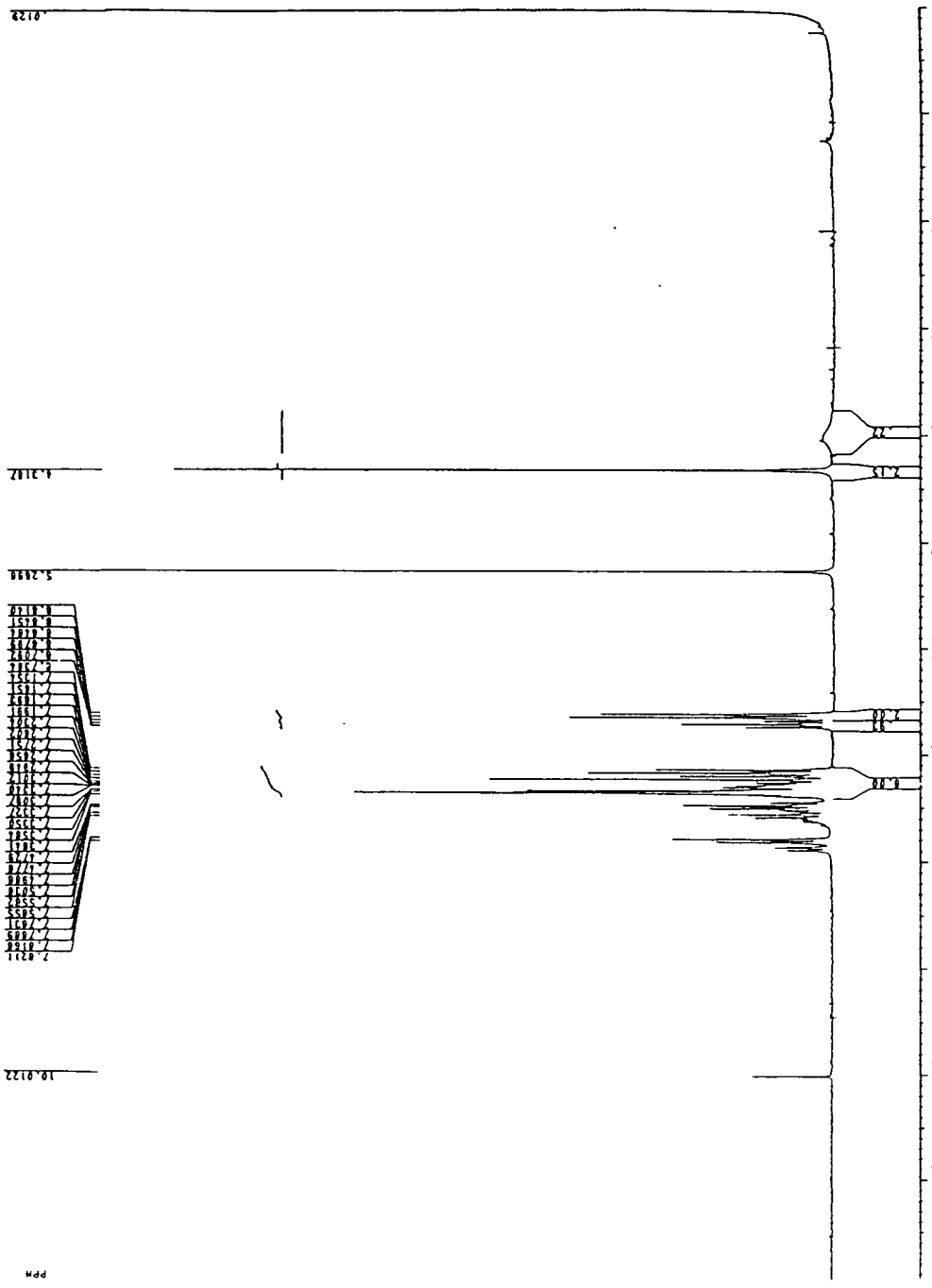
Spectrum 24: 2-Dimensional HETCOR spectrum of *p*-methoxy-N-benzylaniline **[9]**



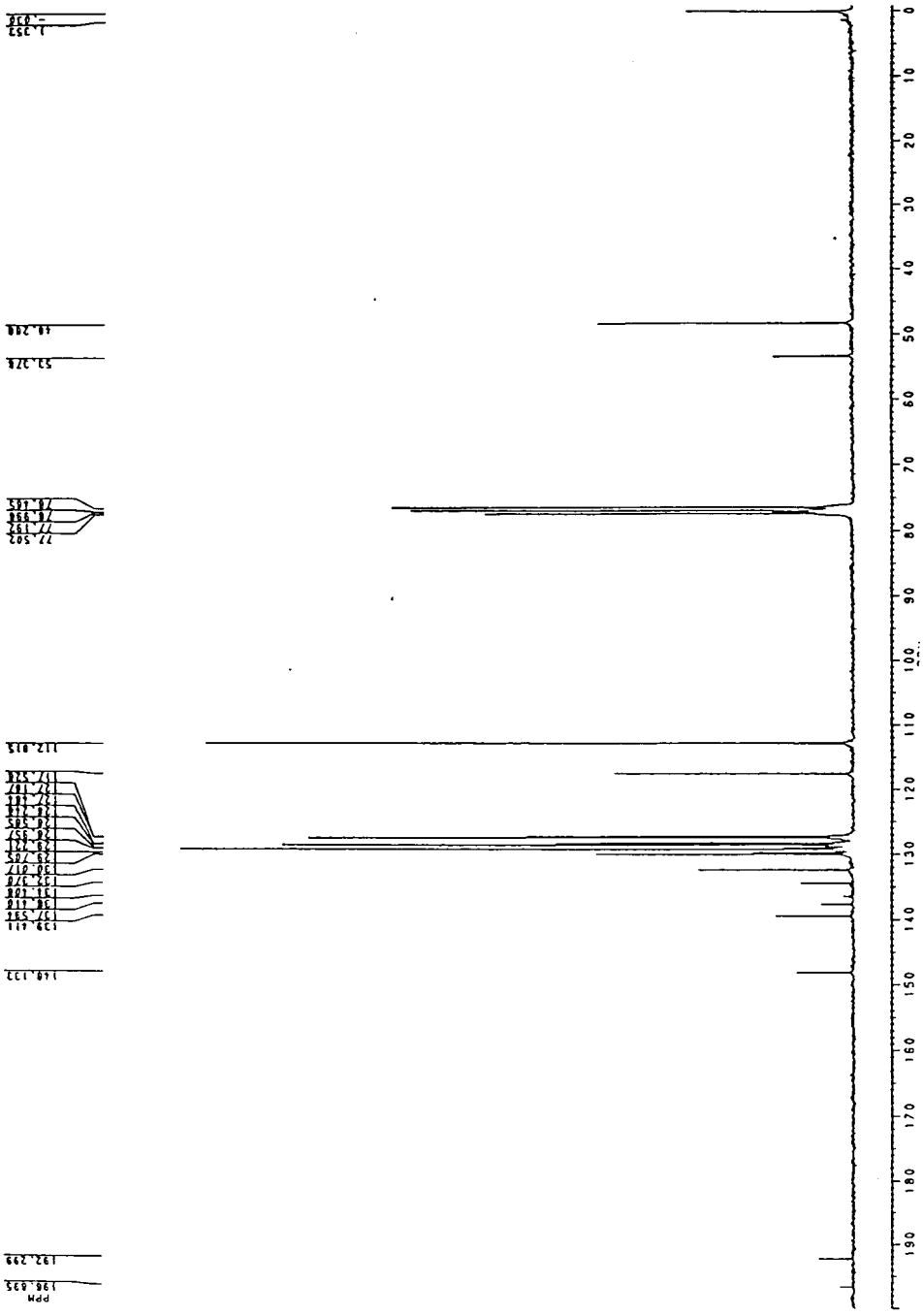
Spectrum 25: ^1H NMR spectrum of N-benzyl-1-phenylbenzylamine [11a]



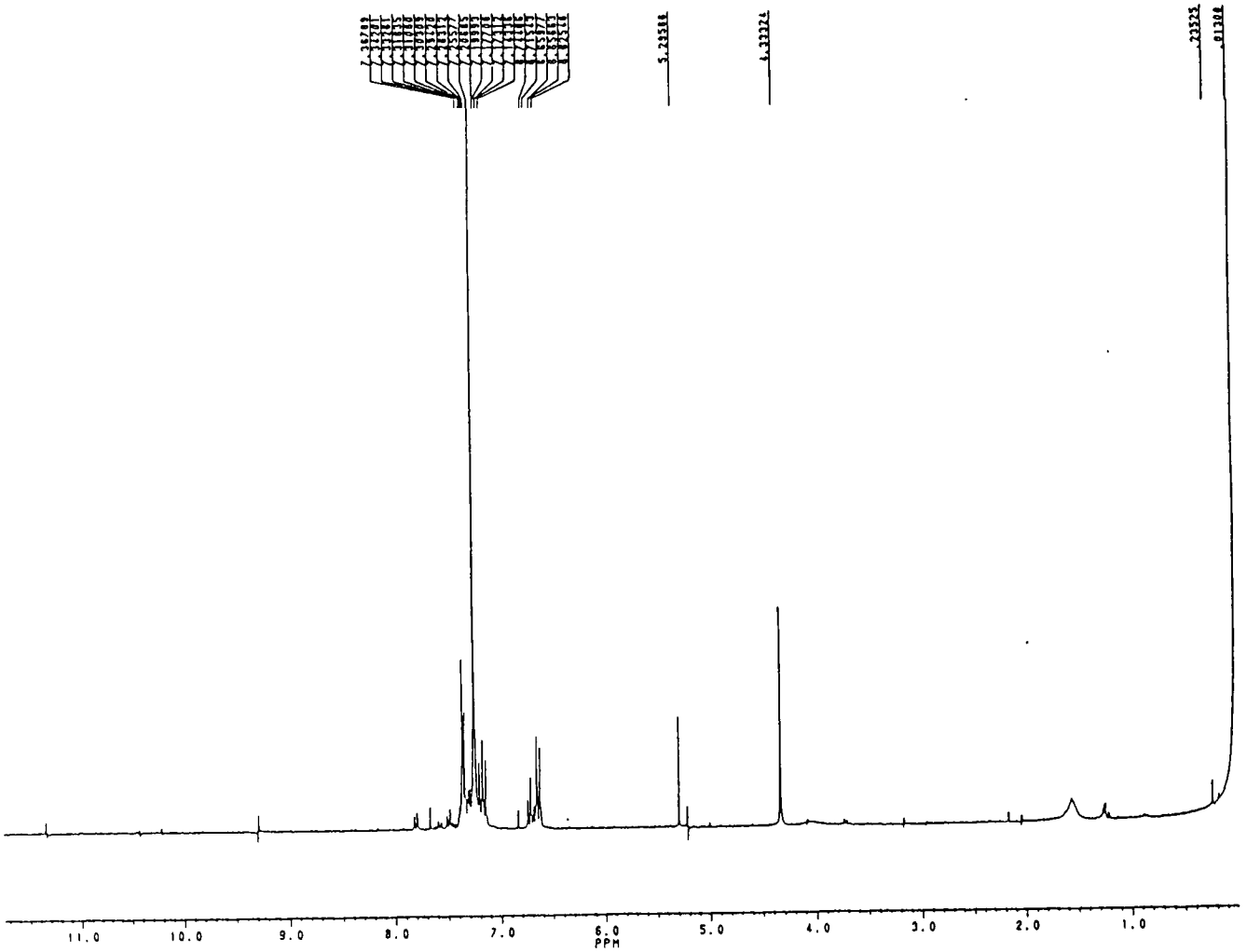
Spectrum 26: ^{13}C NMR spectrum of N-benzyl-1-phenylbenzylamine [11a]



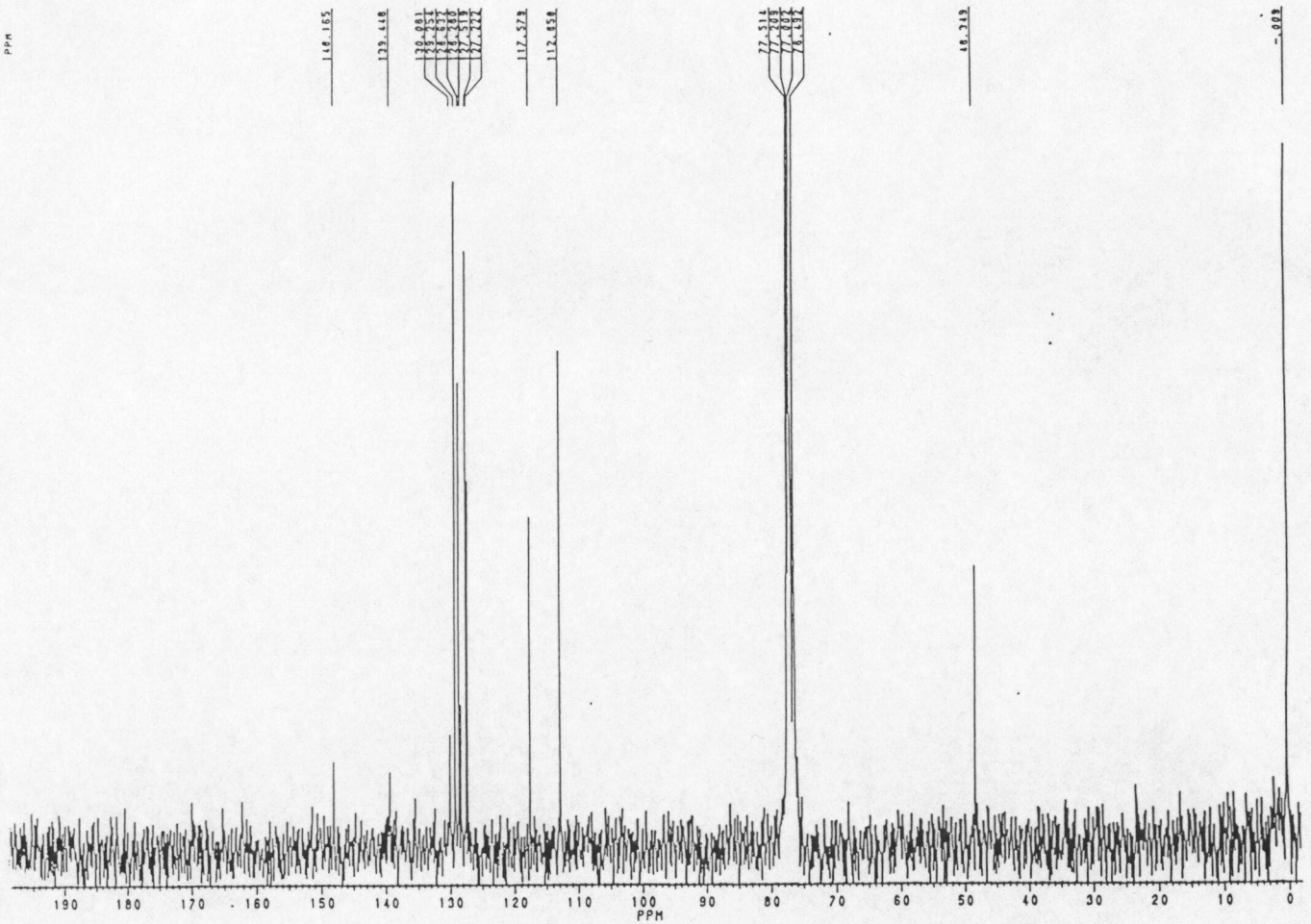
Spectrum 27: ^{1}H NMR spectrum of N-benzylaniline **[14]** (crude)



Spectrum 28: ^{13}C NMR spectrum of N-benzylaniline [14] (crude)



Spectrum 29: ^{1}H NMR spectrum of N-benzylaniline **[14]** (purified)



Spectrum 30: ^{13}C NMR spectrum of N-benzylaniline **[14]** (purified)

VITA

Danny R. Martineau Jr., son of Danny R. Martineau and Kathleen Macrina, was born in Willimantic, Connecticut on January 2, 1969. He graduated from Windham High School in Willimantic, Connecticut in June 1987. Two weeks after graduation he entered the U.S. Air Force and obtained a trade as an electronic technician while assigned to the 20th Tactical Fighter Wing, Upper Heyford, England. Dan was honorably discharged from the Air Force in July 1991. In the fall of 1991, the author entered Lee College in Cleveland, Tennessee. He graduated *cum laude* in May 1995 with a Bachelor of Science in Chemistry. In the fall of 1995, he entered graduate school at the University of Tennessee where he served as a teaching assistant and helped to maintain the chemistry stockroom.

Dan is married to Christie Martin of Green, Ohio and currently resides in Knoxville. After graduation, Dan may pursue a career in industry or continue his military career as an officer in the U.S. Coast Guard and teach after retirement.