Electronic Supplementary Information

One-pot Solvent-Free Reductive Amination of Aldehydes with a Solidified Amine

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Experimental Details

Materials. (S)-(-)-phenylethylamine was purchased from Lancaster, benzaldehyde was purchased from Hanawa, Platinum(Ⅳ) oxide hydrate (80~81% Pt) and Platinum 10% on activated carbon were purchased from Strem chemicals Inc., p-anisaldehyde,3-methoxybenzaldehyde, 2-furaldehyde, 3-furaldehyde, 1-naphthaldehyde, 2-methoxy-1-naphthaldehyde, 4-*tert*-butylbenzaldehyde, 4-(diphenylamino)benzaldehyde, N-Methyl-2-pyrrolecarboxaldehyde, 1-methylindole-3-carbaldehyde, 3-thiophenecarboxaldehyde, sodium borohydride, isobutyraldehyde, platinum on activated charcoal (Pt 5 wt%), trimethylacetaldehyde, cyclohexanecarboxaldehyde, cyclopentanecarboxaldehyde were purchased from Sigma-Aldrich, 3,4-dimethoxybenzaldehyde, 4-(dimethylamino)benzaldehyde were purchased from Acros, 3-fluorobenzaldehyde, 3-chlorobenzaldehyde, thiophene-2-carbaldehyde were purchased from TCI. All of the reagents were used without any further purification. Chiral amine carbamate salt **2** was prepared by previously reported method.[S1]

Instrumentation

All reactions were carried out in oven-dried glasswares with magnetic stirring. Reactions were monitored by thin layer chromatography (TLC) with 0.25 mm E. Merck pre-coated silica gel plates (60 F254). Visualization was accomplished with either UV light, or by immersion in solutions of ninhydrin followed by heating on a hot plate for about 10 s. Purification of reaction products was carried out by flash chromatography using Kieselgel 60 Art 9385 (230-400 mesh). Powder X-ray diffraction (XRD) data were collected using a Rigaku DMAX 2500 diffractometer (Cu Kα) operating at 40 kV and 150 mA. A Nicolet 205 instrument was used to measure infrared spectra. Melting point was measured with a SMP10-BIBBY. Thermogravimetric analysis (TGA) was performed with a TA Instrument TGA 2050 where temperature was increased by 10 ℃/min. GC/MS data were recorded on an Agilent 5973N and elemental analyses were obtained using a Carlo Erba EA1180 at the Organic Chemistry Research Center in Sogang University. ^{1}H NMR and ^{13}C NMR spectra in solution were recorded on a Varian 400-MHz Gemini operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C, and a Varian UNITY INOVA 500 at 500 MHz for ^{1}H and 125 MHz for ^{13}C, respectively. Chemical shifts are reported relative to TMS (δ = 0.0) for ^{1}H NMR and chloroform (δ = 77.16) for ^{13}C NMR. Data are reported as (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, sept = septet). Coupling constants are given in Hz. Ambiguous assignments were resolved

on the basis of standard one dimensional proton decoupling experiments. Optical rotations were obtained using a Rudolph Autopol III digital polarimeter and optical rotation data were reported as follows: $[\alpha]^{24}_{D}$ (concentration c = g/100 mL, solvent).

General procedure for the preparation of secondary amine using catalytic hydrogenation between solidified amine 2 and aldehydes 3

4-(dimethylamino)-benzaldehyde **3a** (149.2 mg, 1.00 mmol) was placed in a vial, the solidified amine **2** (143.2 mg, 0.500 mmol) was added and the vial warmed to 60 ^{o}C for 1 hour, then allowed to cool to room temperature. To the vial was added PtO_2 (4.3 mg), Pt/C (35.1 mg), or Pd/C (18.6 mg) and the hydrogenation proceeded at room temperature under 1 atm of H_2 for 17h. The crude product was purified by silica gel flash column chromatography (30% EA / 70% Hexane).

General procedure for the preparation of secondary amine using stoichiometric reduction between solidified amine 2 and aldehydes 3

4-(Dimethylamino)-benzaldehyde **3a** (149 mg, 1.00 mmol) was placed in a vial, the solidified amine **2** (143 mg, 0.50 mmol) was added, and the mixture was warmed to 60 ^{o}C for 1 hour, then allowed to cool to room temperature. To the mixture was added methanol (0.7 mL) and sodium borohydride (42 mg, 1.10 mmol) under air at room temperature. After 0.5h, the reaction mixture was diluted with ethyl acetate and treated with water. The organic layer was extracted from the aqueous layer using Pasteur pipette. The solvent of organic layer was removed in vacuo. The crude product was purified by silica gel flash column chromatography (30% EA / 70% Hexane).

Crystal growth of (*S,E*)-*N,N*-Dimethyl-4-(((1-phenylethyl)-imino)methyl)aniline 4a

For the growth of **4a** crystals, methylene chloride was added to the solid powder (252 mg) until the powder was completely dissolved at ambient temperature (1 mL total), followed by addition of hexane (1 mL) without mixing in a 5 mL vial. The resulting solution was carefully stored in the refrigerator for one day. Yellow crystals grew from the solution, which were separated by filtering and washing with pentane (3 × 3 mL).

X-ray crystallography. A single crystal of (*S,E*)-*N,N*-Dimethyl-4-(((1-phenylethyl)imino)methyl)aniline **4a** was selected by a nylon loop (Hampton Research Co.) placed on a handmade cooper plate, which was placed inside a liquid N_2 Dewar vessel at approximately -40 ºC and was mounted on a goniometer head in a N_2 cryostream. Data collections were carried out in a Bruker SMART AXS diffractometer equipped with a monochromator with a Mo Kα (λ = 0.71073 Å) incident beam. The charge-coupled device (CCD) data were integrated and scaled using the Bruker-SAINT software package, and the structure was solved and refined using SHEXTL V 6.12.[S2] Hydrogen atoms were located in the calculated positions. The crystal data for (*S,E*)-*N,N*-Dimethyl-4-(((1-phenylethyl)imino)methyl)aniline **4a**: $C_{17}H_{20}N_2$, Monoclinic, *P2(1)*, Z = 2, *a* = 8.5299(3), *b* = 6.0689(2) , *c* = 13.7293(5) Å, β = 91.554(2) °, *V* = 710.46(4) Å^3, μ = 0.070 mm^{-1}, ρ_{calcd} = 1.180 g/cm^3, R_1 = 0.0353, and wR_2 = 0.0930 for 3410 unique reflections and 175 variables. The crystallographic data for (*S,E*)-*N,N*-dimethyl-4-(((1-phenylethyl)imino)methyl)aniline **4a** are listed in Table S1, while Table S2 lists the selected bond distances and angles. CCDC-953131 for (*S,E*)-*N,N*-dimethyl-4-(((1-phenylethyl)imino)methyl)aniline **4a** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Table S1. Structural data for (*S,E*)-*N,N*-dimethyl-4-(((1-phenylethyl)imino)methyl)aniline **4a**

Empirical formula	$C_{17}H_{20}N_2$
Formula weight	252.35
Temperature (K)	100(2)
Wavelength (Å)	0.71073
Crystal system/space group	Monoclinic, *P2(1)*
Unit cell dimensions	
a (Å)	8.5299(3)
b (Å)	6.0689(2
c (Å)	13.7293(5)
α (°)	90
β (°)	91.554(2)
γ (°)	90
Volume (Å^3)	710.46(4)
Z	2
Calculated density (g/cm^{-3})	1.180
Absorption coefficient (mm^{-1})	0.070
Reflections collected	12394
Independent reflections [*R*(int)]	3410 [0.0399]

Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3410/1/175
Goodness-of-fit on F^2	0.641
Final R indices [$I > 2\text{sigma}(I)$]	$R_1 = 0.0353$, $wR_2 = 0.0930$
R indices (all data)	$R_1 = 0.0438$, $wR_2 = 0.1008$
Largest difference peak and hole (e/Å^3)	0.143 and −0.164

Table S2. Selected bond distances and bond angles (Å, °) (*S,E*)-*N,N*-dimethyl-4-(((1-phenylethyl)imino)methyl)aniline **4a**

Bond Distances (Å)	
N1-C7	1.4732(15)
N1-C9	1.2729(17)
N2-C13	1.3737(16)
N2-C16	1.455(2)
N2-C17	1.4497(19)
Bond Angles (°)	
C7-N1-C9	117.11(11)
C16-N2-C17	116.92(11)
C17-N2-C13	120.69(12)
C13-N2-C16	119.98(12)

Table S3. checkCIF/PLATON report

Structure factors have been supplied for datablock(s) chem260

No syntax errors found. CIF dictionary Interpreting this report

Datablock: chem260

```
Bond precision:  C-C = 0.0018 A          Wavelength=0.71073

 Cell:          a=8.5299(3)     b=6.0689(2)        c=13.7293(5)
                alpha=90        beta=91.554(2)     gamma=90
 Temperature:   100 K
```

	Calculated	Reported
Volume	710.47(4)	710.46(4)
Space group	P 21	P2(1)
Hall group	P 2yb	?
Moiety	C17 H20 N2	?
Sum formula	C17 H20 N2	C17 H20 N2
Mr	252.35	252.35
Dx,g cm-3	1.180	1.180
Z	2	2
Mu (mm-1)	0.070	0.070
F000	272.0	272.0
F000’	272.09	
h,k,lmax	11,8,18	11,8,18
Nref	1922[3515]	3410
Tmin,Tmax	0.983,0.997	0.979,0.997
Tmin’	0.979	

```
Correction method= MULTI-SCAN

Data completeness= 1.77/0.97      Theta(max)= 28.290

R(reflections)= 0.0353( 2859)     wR2(reflections)= 0.1008( 3410)

S = 0.641                 Npar= 175
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The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B
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Alert level C

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_exptl_absorpt_process_details field. Absorption
correction given as multi-scan
GOODF01_ALERT_2_C The least squares goodness of fit parameter lies
           outside the range 0.80 <> 2.00
Goodness of fit given =                0.641
STRVA01_ALERT_4_C          Flack parameter is too small
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Alert level G

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study EXCEPT under VERY special conditions.
        It is preferred that Friedel data is merged in such cases. From the
CIF: _diffrn_reflns_theta_max                               28.29
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Completeness (_total/calc)          177.42% TEST3: Check
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Fraction of Friedel pairs measured    0.774
Are heavy atom types Z>Si present        no
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PLAT032_ALERT_4_G Std. Uncertainty on Flack Parameter Value High .     2.000
PLAT791_ALERT_4_G Note: The Model has Chirality at C7    (Verify)          S
PLAT916_ALERT_2_G Hooft y and Flack x Parameter values differ by .      4.30
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0 **ALERT level A** = Most likely a serious problem - resolve or explain
1 **ALERT level B** = A potentially serious problem, consider carefully
4 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
5 **ALERT level G** = General information/check it is not something unexpected

2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
2 ALERT type 2 Indicator that the structure model may be wrong or deficient
0 ALERT type 3 Indicator that the structure quality may be low
5 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special details" fields of the CIF. Check CIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

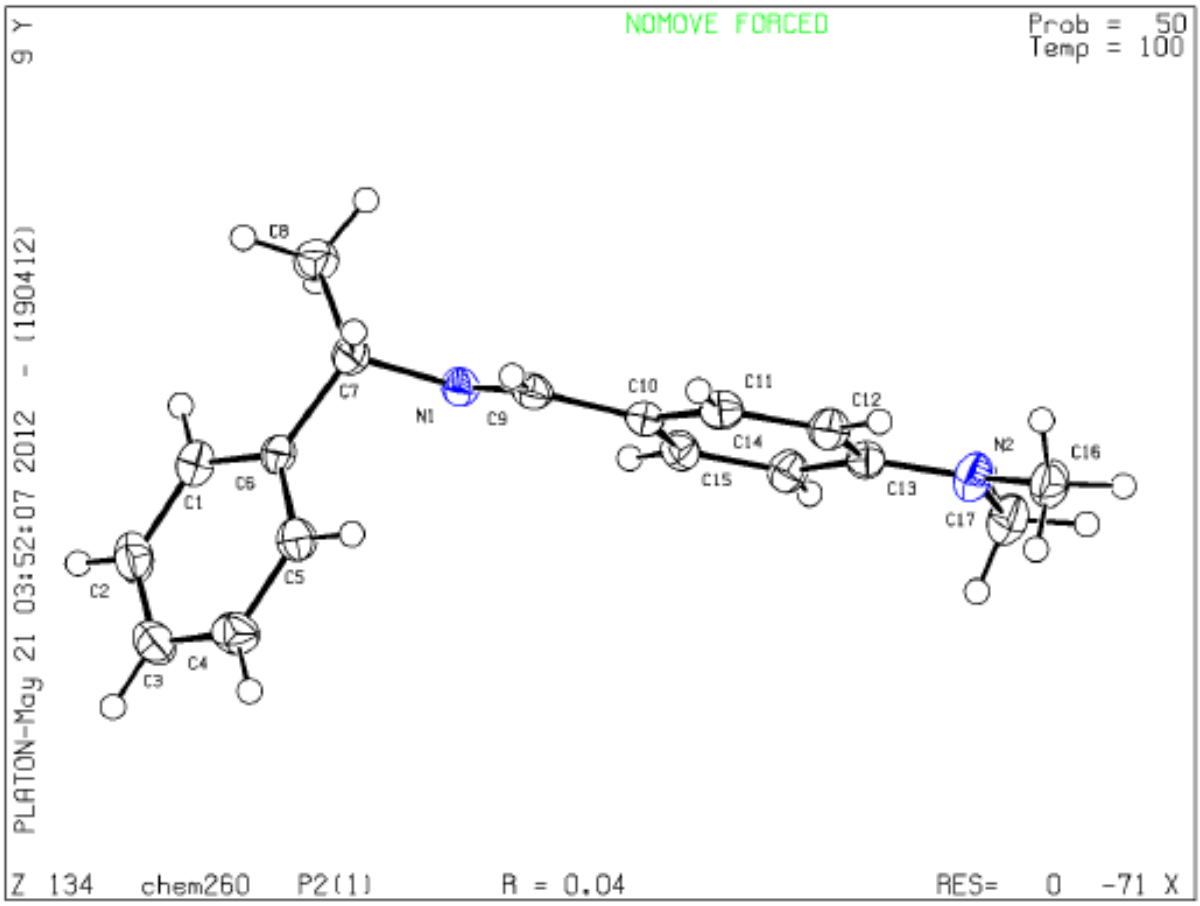
Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 19/04/2012; check.def file version of 14/04/2012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C3
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Analytical data of amines obtained from reductive amination between 2 and 3

(S)-1-Phenylethanaminium (S)-(1-phenylethyl)carbamate (2): white solid; mp N/A (totally sublimed at ~100 ^{o}C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13-7.31 (m, 9H), 6.44 (s, br, 2H) , 4.36-4.41 (m, 1H), 3.93-3.94 (d, 1H, *J* = 6.4 Hz) 1.31-1.33 (d, 3H, *J* = 6.4 Hz), 1.15-1.17 (d, 3H, *J* = 6.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 146.2, 143.8, 128.5, 128.2, 127.3, 126.3, 126.0, 125.8, 50.74, 50.52, 23.44; ν_{max} (powder)/cm^{-1} = 1621 (w) and 1554 (m) for ν(C=O); Anal. Calcd for $C_{17}H_{22}N_2O_2$: C, 71.30; H, 7.74; N, 9.78. found: C,71.23; H, 7.65; N, 9.89

Analytical data of amines obtained from the reductive amination reactions between 2 and aldehydes 3

(*S,E*)-*N,N*-Dimethyl-4-(((1-phenylethyl)imino)methyl)aniline (4a):[S3] pale yellow crystal; mp 87.7 ^{o}C; $[\alpha]^{24}_{D}$ +184 (*c* 1.00, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.64-7.66 (d, 2H, *J* = 8.5 Hz), 7.41-7.43 (d, 2H, *J* = 8 Hz), 7.30-7.33 (t, 2H, *J* = 7.5 Hz), 7.20-7.23 (m, 1H), 6.68-6.70 (d, 2H, *J* = 8.5 Hz), 4.46-4.49 (q, 1H, *J* = 6.5 Hz) 3.00 (s, 6H), 1.62 (br, s, 1H) 1.57-1.58 (d, 3H, *J* = 6.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.6, 152.3, 146.0, 129.8, 128.5, 126.9, 126.7, 125.0, 111.8, 69.6, 40.4, 25.0; Anal. Calcd for $C_{17}H_{20}N_2$: C, 80.91; H, 7.99; N, 11.10. found: C, 80.76; H, 7.86; N, 11.33; MS (EI^{+}) m/z = 252, 237, 221, 210, 193, 175, 165, 147, 134, 122, 105, 91, 77; GC-MS retention time Rt = 12.72 min.

(*S*)-*N,N*-Dimethyl-4-((1-phenylethylamino)methyl)aniline (5a): colorless oil; $[\alpha]^{24}_{D}$ +17.7 (*c* 0.015, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23-7.37 (m, 5H), 7.14-7.16 (d, 2H, *J*= 8.4 Hz), 6.70-6.72 (d, 2H, *J* = 8.8 Hz), 3.78-3.83 (q, 1H, *J* = 6.4 Hz), 3.55-3.58 (d, 1H, *J* = 12.8 Hz), 3.48-3.51 (d, 1H, *J* = 12.8 Hz), 2.93 (s, 6H), 1.34-1.36 (d, 3H, *J* = 6.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 145.8, 129.2, 128.7, 128.5, 127.0, 126.9, 112.8, 57.3, 51.1, 40.9, 24.6; Anal. Calcd. for $C_{17}H_{22}N_2$: C, 80.27; H, 8.72; N, 11.01. found: C, 80.31; H, 8.62; N, 10.86; MS (EI^{+}) m/z = 254, 149, 134, 118, 105, 91, 77; GC-MS retention time Rt = 12.20 min.

(*S*)-N-(3-Fluorobenzyl)-1-phenylethanamine (5b): colorless oil; $[\alpha]^{24}_{D}$ -26.9 (*c* 0.0067, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19-7.33 (m, 6H), 6.87-7.02 (m, 3H), 3.74-3.79 (q, 1H, *J* = 6.4 Hz), 3.60-3.64 (d, 1H, *J* = 14.0 Hz), 3.54-3.57 (d, 1H, *J* = 14.0 Hz), 1.34-1.35 (d, 3H, *J* = 6.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0 (d, $^{1}J_{C\text{-}F}$ =

244.1 Hz), 145.4, 143.5 (d, $^{3}J_{C\text{-}F}$ = 6.7 Hz), 129.9 (d, $^{3}J_{C\text{-}F}$ = 7.4 Hz), 128.6, 127.1, 126.7, 123.7, 129.8 (d, $^{2}J_{C\text{-}F}$ = 20.9 Hz), 113.7 (d, $^{2}J_{C\text{-}F}$ = 20.9 Hz); Anal. Calcd for $C_{15}H_{16}FN$: C, 78.57; H, 7.03; N, 6.11. found: C, 78.56; H, 6.98; N, 5.98. MS (EI^{+}) m/z = 229, 214, 152, 124, 109, 91, 77; GC-MS retention time Rt = 9.83 min.

(*S*)-N-(3-Chlorobenzyl)-1-phenylethanamine (5c): colorless oil; $[\alpha]^{24}_{D}$ -37.7 (*c* 0.0060, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13-7.34 (m, 9H), 3.75-3.80 (q, 1H, *J* = 6.4 Hz), 3.59-3.63 (d, 1H, *J* = 13.2 Hz), 3.53-3.57 (d, 1H, *J* = 13.2 Hz), 1.35-1.37 (d, 3H, *J* = 6.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4, 142.9, 134.3, 129.7, 128.6, 128.3, 127.2, 127.1, 126.7, 126.3, 57.7, 51.2, 24.6; Anal. Calcd for $C_{15}H_{16}ClN$: C, 73.31; H, 6.56; N, 5.70. found: C, 73.28; H, 6.61; N, 5.64. MS (EI^{+}) m/z = 245, 230, 168, 125, 105, 89, 77; GC-MS retention time Rt = 10.94 min.

(S)-1-Phenyl-N-(thiophen-3-ylmethyl)ethanamine (5d): colorless oil; $[\alpha]^{24}_{D}$ -28.6 (*c* 0.010, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.36 (m, 4H), 7.18-7.26 (m, 2H), 7.03 (s, 1H), 6.97-6.98 (d, 1H, *J* = 4.4 Hz), 3.75-3.80 (q, 1H, *J* = 6.4 Hz), 3.61(s, 2H), 1.33-1.35 (d, 3H, 6.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 141.7, 128.5, 127.7, 127.1, 126.7, 125,7, 121.4, 57.5, 46.7, 24.6; Anal. Calcd for $C_{13}H_{15}NS$: C, 71.84; H, 6.96; N, 6.44; S, 14.75. found: C, 71.80; H, 6.95; N, 6.44; S, 14.80. MS(EI^{+}) m/z = 216, 202, 140, 120, 112, 105, 97, 91, 85, 77; GC-MS retention time Rt = 10.58 min.

(S)-N-Benzyl-1-phenylethanamine (5e):[S4] colorless oil; $[\alpha]^{24}_{D}$ -38.3 (*c* 0.0073, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20-7.33 (m, 10H), 3.76-3.81 (q, 1H, *J* = 6.8 Hz), 3.62-3.65 (d, 1H, *J* = 12.8 Hz), 3.55-3.58 (d, 1H, *J* = 12.8 Hz), 1.33-1.35 (d, 3H, *J* = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.7, 140.8, 128.6, 128.5, 128.3, 127.1, 126.9, 126.8; Anal. Calcd for $C_{15}H_{17}N$: C, 85.26; H, 8.11; N, 6.63. found: C, 85.20; H, 8.10; N, 6.58. MS (EI^{+}) m/z = 196, 105, 91, 77, 65; GC-MS retention time Rt = 9.86 min.

(S)-N-(4-Methoxybenzyl)-1-phenylethanamine (5f):[S5] colorless oil; $[\alpha]^{24}_{D}$ -16.4 (*c* 0.0073, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.33 (d, 5H *J* = 4.8 Hz), 7.22-7.25 (q, 1H, *J* = 4 Hz), 6.27 (s, 1H), 6.07-6.08 (d, 1H, *J* = 2.4 Hz), 3.74-3.79 (q, 1H, *J* = 6.4 Hz), 3.63-3.66 (d, 1H, *J* = 14.4 Hz), 3.54-3.57 (d, 1H, *J* = 14.4 Hz), 1.33-1.35 (d, 3H, *J* = 6.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 145.1, 141.81, 128.6, 127.1, 126.8, 110.1, 106.9, 57.1, 44.1,

24.4; Anal. Calcd for $C_{16}H_{19}NO$: C, 79.63; H, 7.94; N, 5.80. found: C, 79.65; H, 7.96; N, 5.95. MS (EI+) m/z = 241, 226, 136, 121, 105, 91, 77, 65; GC-MS retention time Rt = 11.30 min.

(S)-N-(3-Methoxybenzyl)-1-phenylethanamine (5g):[S6] colorless oil; $[\alpha]^{24}_{D}$ -3.2 (*c* 0.0090, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18-7.33 (m, 6H), 6.75-6.85 (m, 3H), 3.76-3.81 (q, 1H, *J* = 6.4 Hz), 3.76 (s, 3H), 3.61-3.64 (d, 1H, *J* = 13.2 Hz), 3.53-3.57 (d, 1H, 13.2 Hz), 1.34-1.36 (d, 3H, 6.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 145.5, 142.3, 129.4, 128.5, 127.0, 126.8, 120.5, 113.7, 112.3, 57.5, 55.2, 51.6, 24.5; Anal. Calcd for $C_{16}H_{19}NO$: C, 79.63; H, 7.94; N, 5.80. found: C, 79.74; H, 7.90; N, 5.75. MS (EI^+) m/z = 240, 226, 164, 136, 121, 113, 105, 91, 77, 65; GC-MS retention time Rt = 11.19 min.

(S)-N-(Naphthalen-1-ylmethyl)-1-phenylethanamine (5h):[S7] colorless oil; $[\alpha]^{24}_{D}$ +13.9 (*c* 0.0067, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98-7.99 (d, 1H, *J* = 7.2 Hz), 7.82-7.84 (d, 1H, *J* = 7.6 Hz), 7.73-7.75 (d, 1H, *J* = 7.6 Hz), 7.34-7.50 (m, 8H), 7.28-7.30 (m, 1H), 4.07-4.10 (d, 1H, *J* = 13.2 Hz), 3.99-4.03 (d, 1H, *J* = 13.2 Hz), 3.89-3.94 (q, 1H, *J* = 6.4 Hz), 1.38-1.40 (d, 3H, *J* = 6.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.7, 136.3, 133.9, 131.9, 128.7, 128.6, 127.7, 127.1, 126.9, 126.2, 126.0, 125.6, 125.5, 123.9, 58.4, 49.6, 24.6; Anal. Calcd for $C_{19}H_{19}N$: C, 87.31; H, 7.33; N, 5.36. found: C, 87.34; H, 7.33; N, 5.27. MS (EI^+) m/z = 261, 246, 156, 141, 115, 105, 91, 77; GC-MS retention time Rt = 12.65 min.

(S)-N-((2-Methoxynaphthalen-1-yl)methyl)-1-phenylethanamine (5i): yellow oil; $[\alpha]^{24}_{D}$ +10.6 (*c* 0.011, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74-7.80 (m, 3H), 7.21-7.45 (m, 8H), 4.08-4.11 (d, 1H, *J* = 12.0 Hz), 4.03-4.00 (d, 1H, *J* = 12.0 Hz), 3.86-3.98 (m, 4H), 1.36-1.37 (d, 3H, 6.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 146.0, 133.3, 129.2, 129.0, 128.5, 128.4, 127.0, 126.6, 123.3, 123.2, 121.4, 113.1, 58.4, 56.4, 41.6, 24.8; Anal. Calcd for $C_{20}H_{21}NO$: C, 82.44; H, 7.26; N, 4.81; O, 5.49. found: C, 82.37; H, 7.14; N, 4.95. MS (EI^+) m/z = 291, 276, 260, 186, 171, 156, 141, 128, 115, 105, 91, 77; GC-MS retention time Rt = 13.36 min.

(S)-N-(4-tert-Butylbenzyl)-1-phenylethanamine (5j): colorless oil; $[\alpha]^{24}_{D}$ +4.6 (*c* 0.0056, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20-7.35 (m, 9H), 3.79-3.84 (q, 1H, *J* = 6.4 Hz), 3.60-3.63 (d, 1H, *J* = 13.2 Hz), 1.35-1.36 (d, 3H,

J = 6.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 125.8, 127.7, 128.5, 127.9, 127.0, 126.8, 125.4, 57.7, 51.4, 34.5, 31.5, 24.7; Anal. Calcd for $C_{19}H_{25}N$: C, 85.34; H, 9.42; N, 5.24. found: C, 85.27; H, 9.52; N, 5.12. MS (EI^+) m/z = 265, 252, 162, 147, 132, 117, 105, 91, 77, 65; GC-MS retention time Rt = 11.59 min.

(S)-N-((1-Methyl-1H-pyrrol-2-yl)methyl)-1-phenylethanamine (5k): colorless oil; $[\alpha]^{24}_D$ -14.1 (*c* 0.0064, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.38 (m, 5H) 6.54 (s, 1H), 5.97-6.02 (m, 2H), 3.78-2.82 (q, 1H, J = 6.4 Hz), 3.54-3.58 (d, 1H, J = 13.2 Hz), 3.55 (s, 3H), 3.49-3.52 (d, 1H, J = 13.2 Hz), 1.33-1.35 (d, 3H, J = 6.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.7, 131.4, 128.5, 127.0, 126.7, 122.2, 107.6, 106.5, 58.0, 43.5, 33.7, 24.5; Anal. Calcd for $C_{14}H_{18}N_2$: C, 78.46; H, 8.47; N, 13.07. found: C, 78.41; H, 8.34; N, 13.07. MS (EI^+) m/z = 214, 132, 120, 105, 94, 77; GC-MS retention time Rt = 10.00 min.

(S)-N-((1-Methyl-1H-indol-3-yl)methyl)-1-phenylethanamine (5l): yellow oil; $[\alpha]^{24}_D$ +3.6 (*c* 0.0047, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.56 (d, 1H, J = 8.0 Hz), 7.06-7.39 (m, 8H), 6.89 (s, 1H), 3.84-3.89 (q, 1H, J = 6.4 Hz), 3.80-3.83 (d, 1H, J = 13.2 Hz), 3.74-3.78 (d, 1H, J = 13.2 Hz), 1.34-1.36 (d, 3H, J = 6.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.8, 137.1, 128.5, 127.5, 127.2, 126.9, 126.8, 121.7, 119.1, 119.0, 113.7, 109.3, 57.8, 42.6, 32.6, 24.6; Anal. Calcd for $C_{18}H_{20}N_2$: C, 81.78; H, 7.63; N, 10.60. found: C, 81.78; H, 7.53; N, 10.50. MS (EI^+) m/z = 264, 159, 144, 132, 115, 106, 91, 77; GC-MS retention time Rt = 12.91 min.

(S)-N-(Furan-2-ylmethyl)-1-phenylethanamine (5m):[S8] colorless oil; $[\alpha]^{24}_D$ -68.7 (*c* 0.013, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.38 (m, 5H), 7.21-7.25 (dd, 1H, J = 4.0, 8.0 Hz), 6.26-6.27(d, 1H, J = 4.0 Hz), 6.07-6.08(d, 1H, J = 4.0 Hz), 3.74-3.79 (q, 1H, J = 6.4 Hz), 3.63-3.66 (d, 1H, J = 14.4 Hz), 3.54-3.57 (d, 1H, J = 14.4 Hz), 1.33-1.35 (d, 3H, J = 6.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 145.1, 141.8, 128.5, 127.1, 126.8, 110.1, 106.8, 57.1, 44.05, 24.4; Anal. Calcd for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96. found: C, 77.56; H, 7.37; N, 6.98. MS (EI^+) m/z = 201, 196, 186, 105, 96, 91, 81, 76, 53; GC-MS retention time Rt = 11.31 min.

(S)-N-(Furan-3-ylmethyl)-1-phenylethanamine (5n): yellow oil; $[\alpha]^{24}_D$ -35.5 (*c* 0.020, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21-7.34 (m, 7H), 6.33 (s, 1H), 3.77-3.82 (q, 1H, J = 6.4 Hz), 3.47 (s, 2H), 1.34-1.35 (d, 3H, J =

6.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4, 143.1, 139.8, 128.5, 127.0, 126.7, 124.2, 110.5, 57.5, 42.1, 24.4; Anal. Calcd for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96. found: C, 77.42; H, 7.45; N, 6.99. MS (EI^+) m/z = 200, 186, 120, 105, 96, 81, 53; GC-MS retention time Rt = 8.70 min.

(S)-2,2-Dimethyl-N-(1-phenylethyl)propan-1-amine (5o):[S9] yellow oil; $[\alpha]^{24}_D$ -55.6 (*c* 1.00, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29-7.33 (m, 4H), 7.20-7.24 (m, 1H), 3.68-3.72 (q, 1H, *J* = 6.5 Hz), 2.25-2.27 (d, 1H, *J* = 11 Hz), 2.12-2.14 (d, 1H, *J* = 11 Hz), 1.32-1.33 (d, 3H, *J* = 6.5 Hz), 0.88 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.7, 128.4, 126.7, 60.2, 59.1, 31.5, 27.9, 25.1; Anal. Calcd for $C_{13}H_{15}NO$: C, 81.61; H, 11.06; N, 7.32. found: C, 81.63; H, 11.05; N, 7.35. MS (EI^+) m/z = 191, 176, 134, 105, 91, 77; GC-MS retention time Rt = 10.11 min.

(S)-2-Methyl-N-(1-phenylethyl)propan-1-amine (5p):[S10] yellow oil; $[\alpha]^{24}_D$ -56.2 (*c* 1.00, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30-7.34 (m, 4H), 7.21-7.25 (m, 1H), 3.71-3.75 (q, 1H, *J* = 6.5 Hz), 2.32-2.35 (d of d, 1H, *J* = 11, 5, 6.5 Hz), 2.19-2.23 (d of d, 1H, *J* = 11.5, 7.5 Hz), 1.66-1.74 (heptet, 1H, *J* = 7.0 Hz), 1.34-1.35 (d, 3H, *J* = 6.5 Hz), 0.87-0.88(d of d, 6H, *J* = 6.5, 2.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.2, 128.5, 126.9, 126.7, 58.5, 56.0, 24.7, 20.9, 20.8; Anal. Calcd for $C_{13}H_{15}NO$: C, 81.30; H, 10.80; N, 7.90. found: C, 81.24; H, 10.71; N, 7.86. MS (EI^+) m/z = 177, 162, 134, 105, 91, 77; GC-MS retention time Rt = 9.91 min.

(S)-N-(Cyclohexylmethyl)-1-phenylethanamine (5q): yellow oil; $[\alpha]^{24}_D$ -30.6 (*c* 1.00, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30-7.35 (m, 4H), 7.21-7.24 (m, 1H), 3.70-3.74 (q, 1H, *J* = 6.5 Hz), 2.33-2.36 (d of d, 1H, *J* = 11.5, 6 Hz), 2.22-2.25 (d of d, 1H, *J* = 11.5, 7 Hz), 1.63-1.76 (m, 5H), 1.37-1.47 (m, 1H), 1.33-1.34 (d, 3H, *J* = 6.5 Hz), 1.09-1.30 (m 4H), 0.80-0.91 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.3, 128.5, 126.9, 126.7, 58.6, 54.8, 38.3, 31.7, 31.6, 26.8, 26.3, 26.2, 24.7; Anal. Calcd for $C_{13}H_{15}NO$: C, 82.70; H, 10.41; N, 6.89. found: C, 82.61; H, 10.44; N, 6.91. MS (EI^+) m/z = 203, 188, 134, 105, 91, 79, 41; GC-MS retention time Rt = 9.23 min.

(S)-N-(Cyclopentylmethyl)-1-phenylethanamine (5r): yellow oil; $[\alpha]^{24}_D$ -36.0 (*c* 1.00, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21-7.35 (m, 5H), 3.72-3.77 (q, 1H, *J* = 6.8 Hz), 2.43-2.47 (q, 1H, *J* = 6.8, 11.2 Hz), 2.30-2.34 (q, 1H, *J* = 7.2, 11.2 Hz), 1.32-1.33 (sept, 1H, *J* = 7.2 Hz), 1.68-1.78 (m, 2H), 1.47-1.58 (m, 4H), 1.34-1.35 (d, 3H, *J*

= 6.8 Hz), 1.06-1.12 (m, 2H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.2, 128.5, 126.9, 126.7, 58.7, 53.9, 40.3, 31.0, 25.4, 24.7; Anal. Calcd for $C_{13}H_{15}NO$: C, 82.89; H, 10.67; N, 6.44. found: C, 82.76; H, 10.77; N, 6.56. MS (EI^+) m/z = 217, 202, 134, 105, 91, 79, 55, 41; GC-MS retention time Rt = 9.94 min.

Fig. S1 ^{1}H NMR Spectrum of **2**.

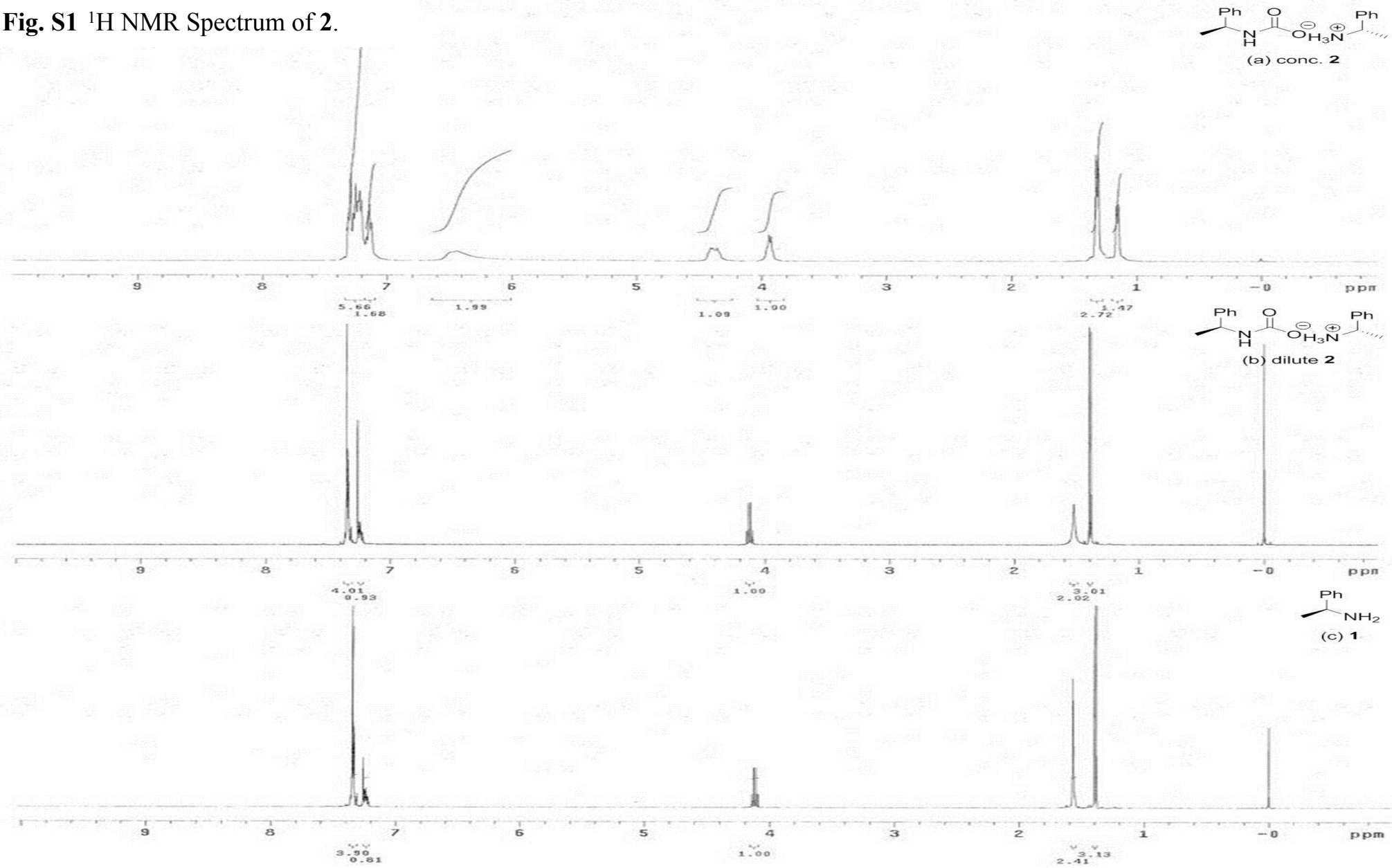


Fig. S2 ^{13}C NMR Spectrum of **2**.

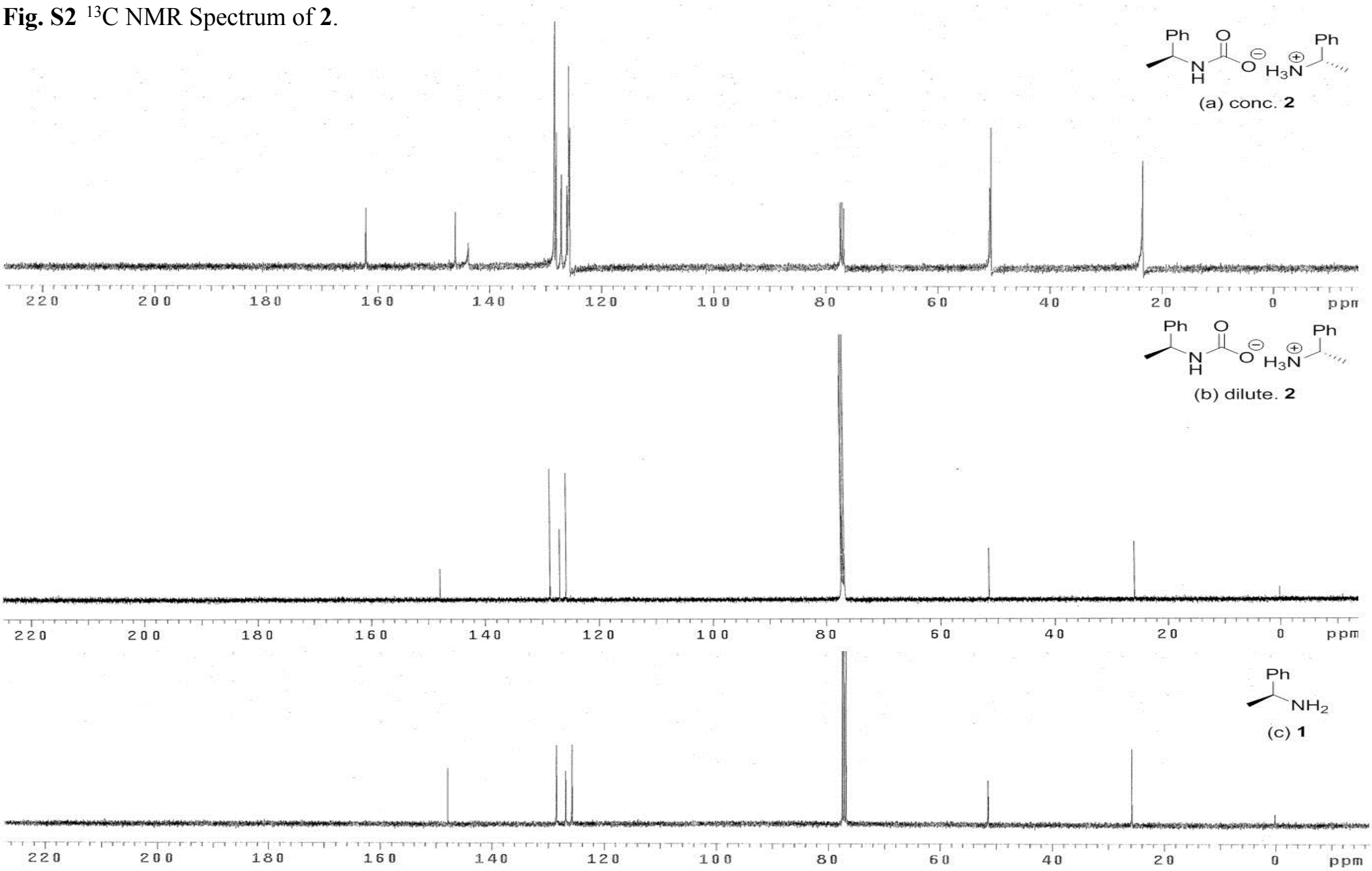


Fig. S3 TGA data of **2** : the temperature is increased by 10 °C per minute from 20 to 300 °C.

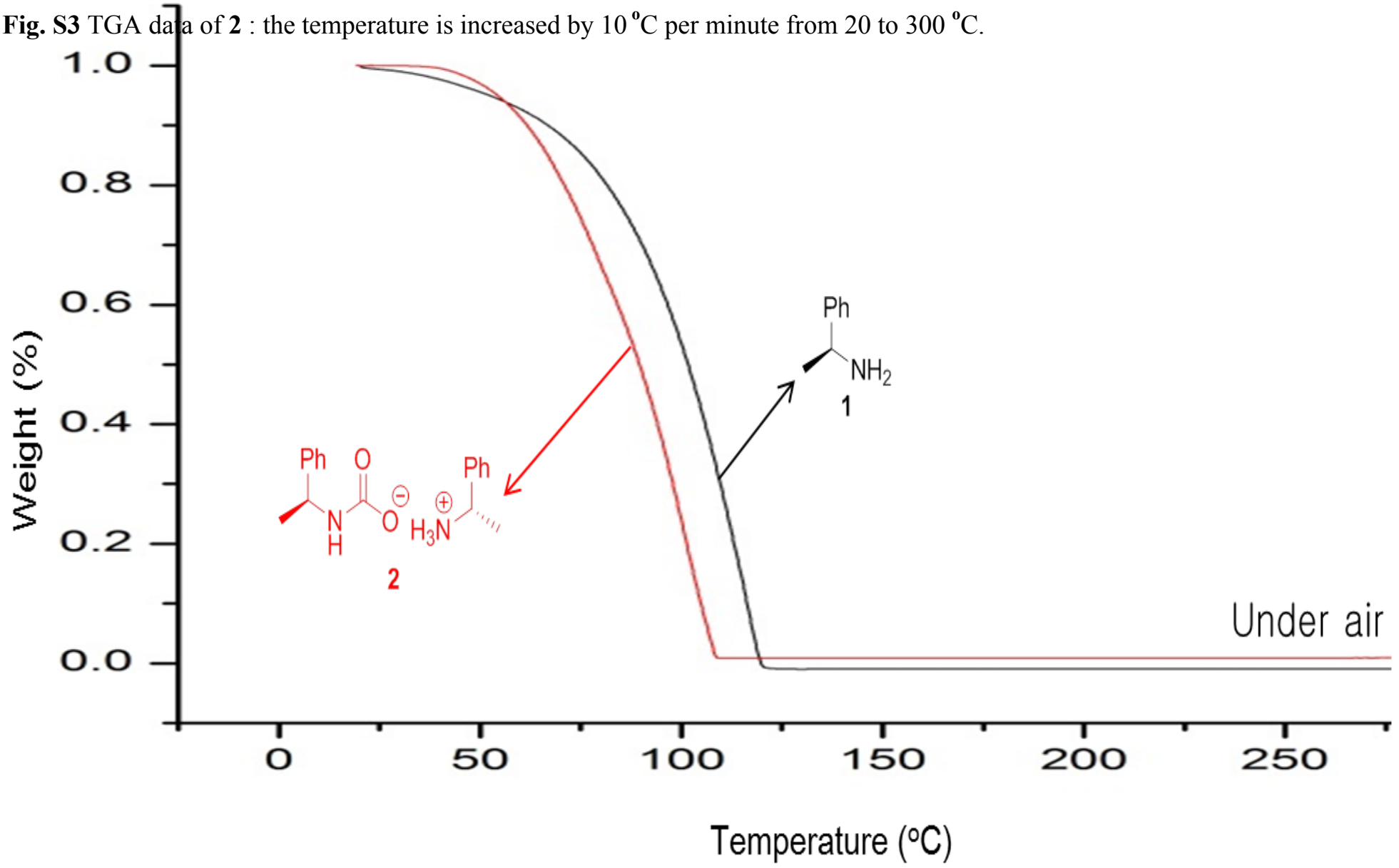


Fig. S4 (a) X-ray powder diffraction (XRD) pattern and (b) IR spectrum of **2**.

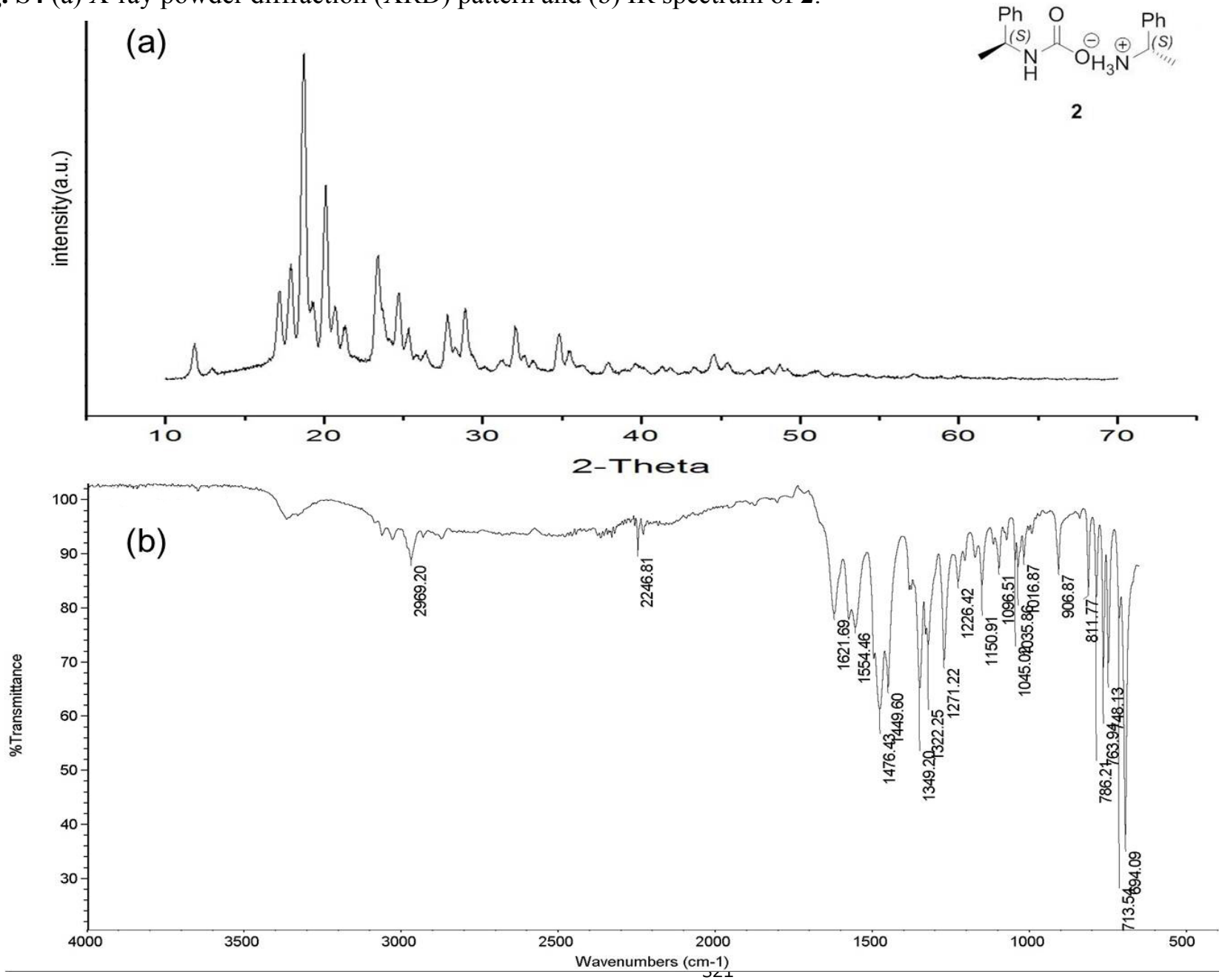


Fig. S5 ^{1}H NMR Spectrum of **4a.**

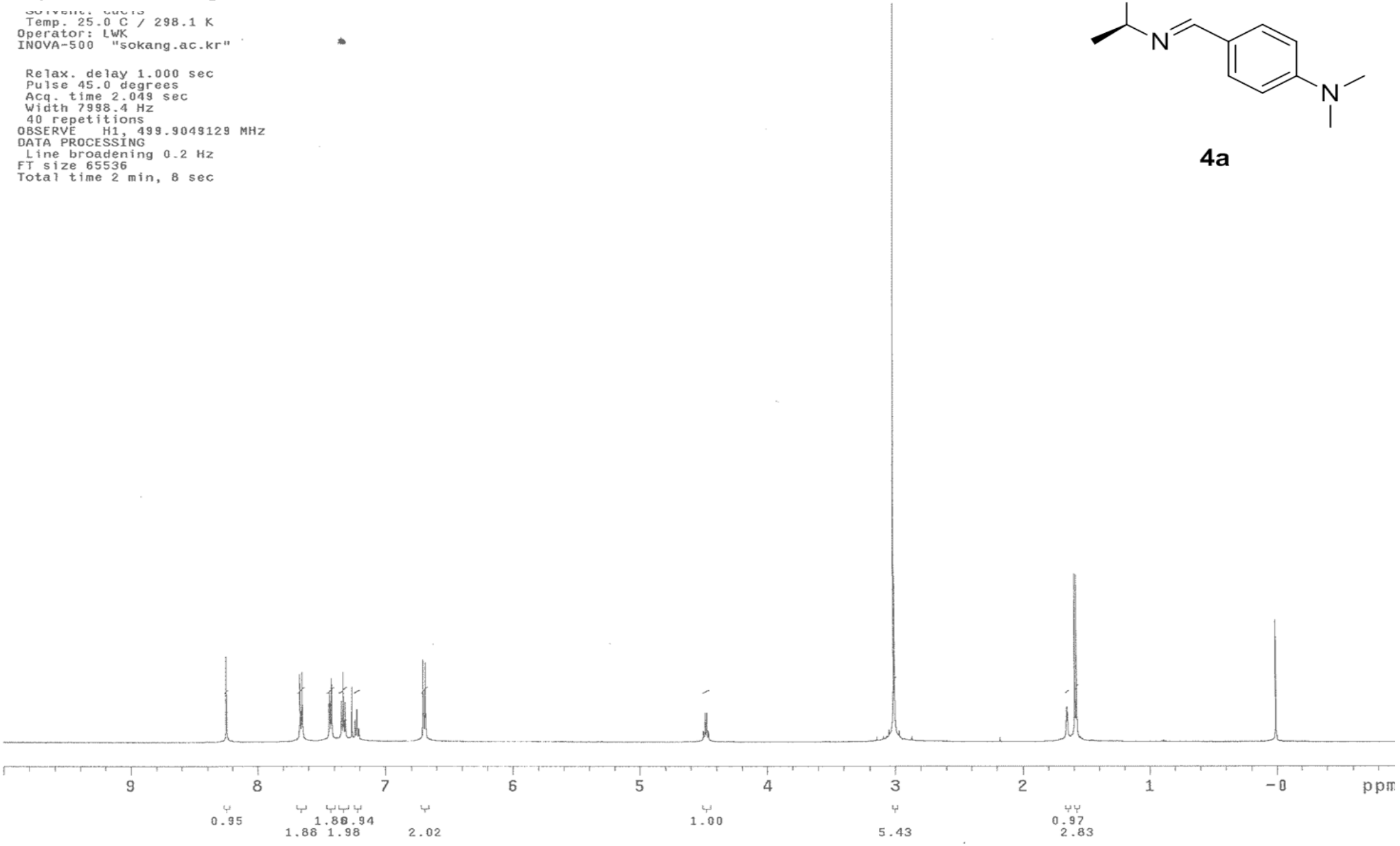


Fig. S6 ^{13}C NMR Spectrum of **4a.**

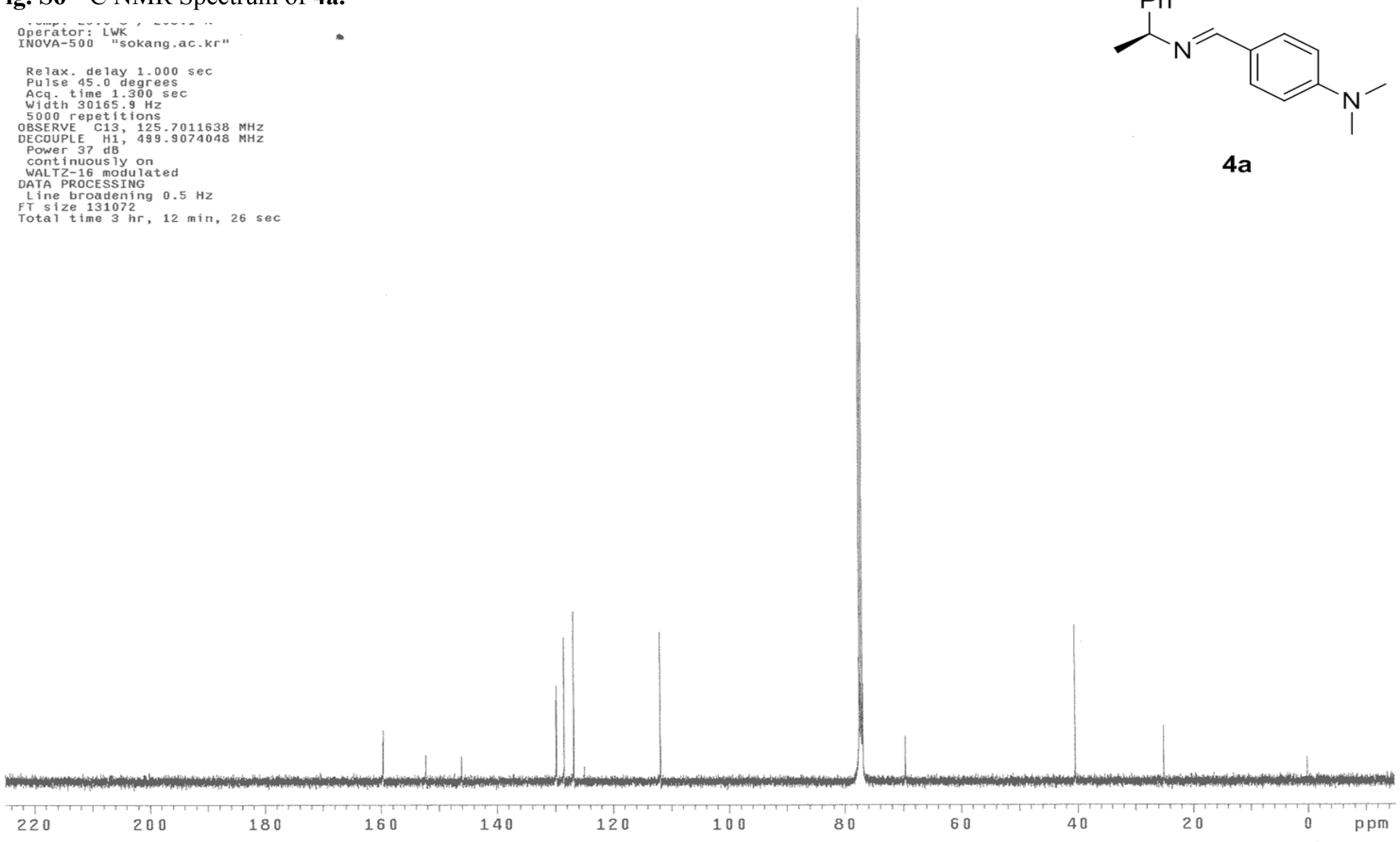
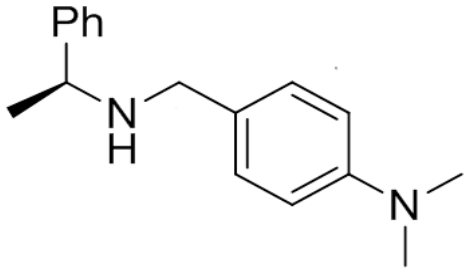
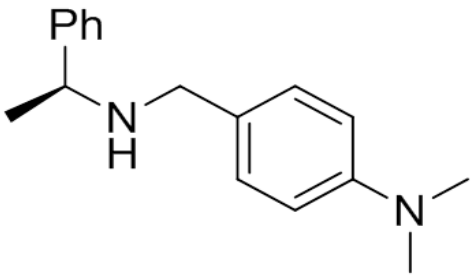


Fig. S7 ^{1}H NMR Spectrum of **5a.**



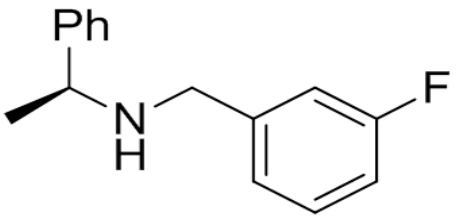
5a

Fig. S8 ^{13}C NMR Spectrum of **5a.**



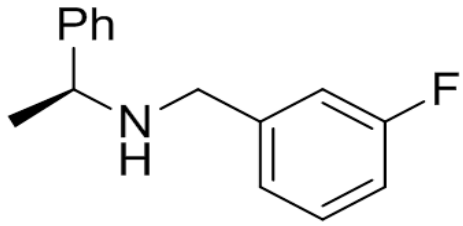
5a

Fig. S9 ^{1}H NMR Spectrum of **5b.**



5b

Fig. S10 ^{13}C NMR Spectrum of **5b.**



5b

```
 Ambient temperature
Operator: LWK
VNMRS-400  "Varian-NMR"

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.300 sec
 Width 24509.8 Hz
 60 repetitions
OBSERVE  C13, 100.5127833 MHz
DECOUPLE  H1, 399.7344008 MHz
 Power 37 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 65536
Total time 38 min, 21 sec
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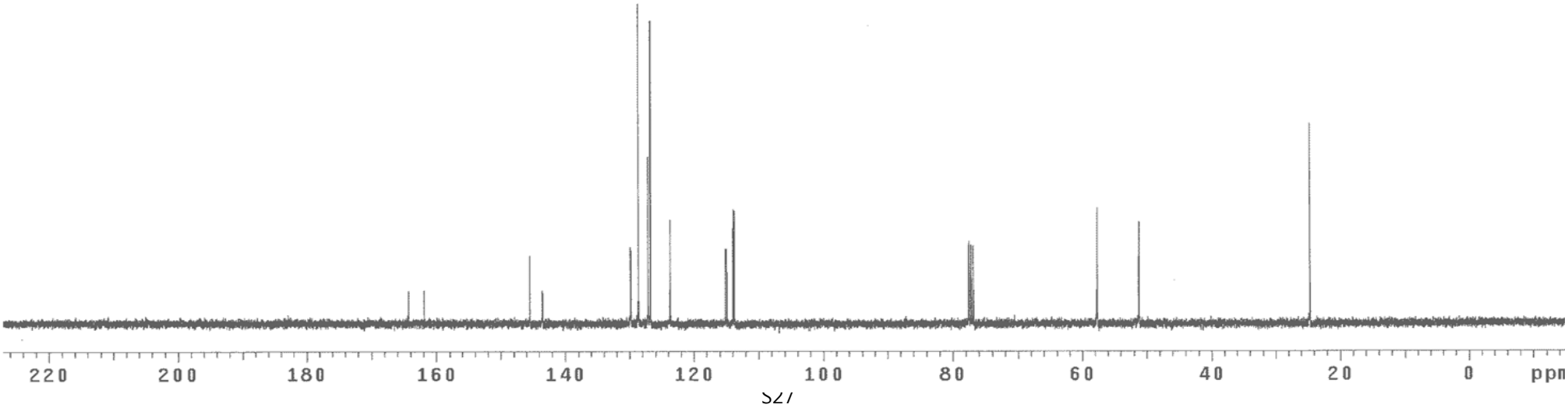

Fig. S11 ^{1}H NMR Spectrum of **5c.**

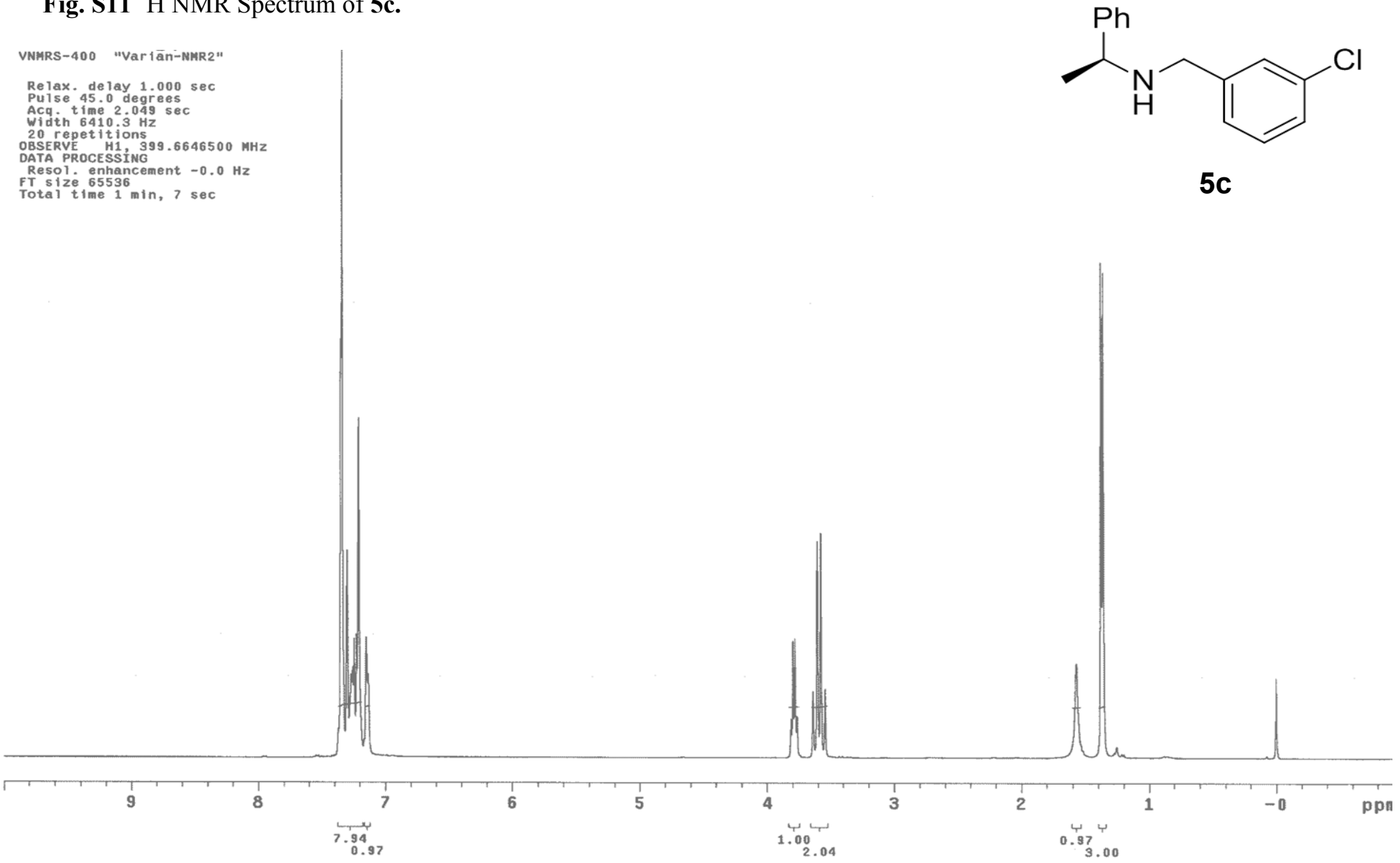

Fig. S12 ^{13}C NMR Spectrum of **5c.**

```
Pulse Sequence: s2pul
 Solvent: cdcl3
 Ambient temperature
Operator: LWK
VNMRS-400  "Varian-NMR"

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.300 sec
 Width 24509.8 Hz
 48 repetitions
OBSERVE  C13, 100.5127818 MHz
DECOUPLE  H1, 399.7344008 MHz
 Power 37 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 65536
Total time 38 min, 21 sec
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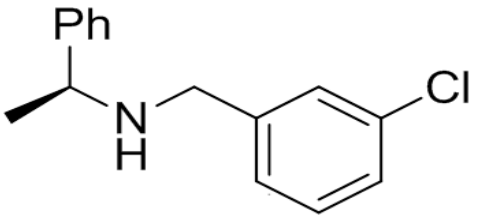

5c

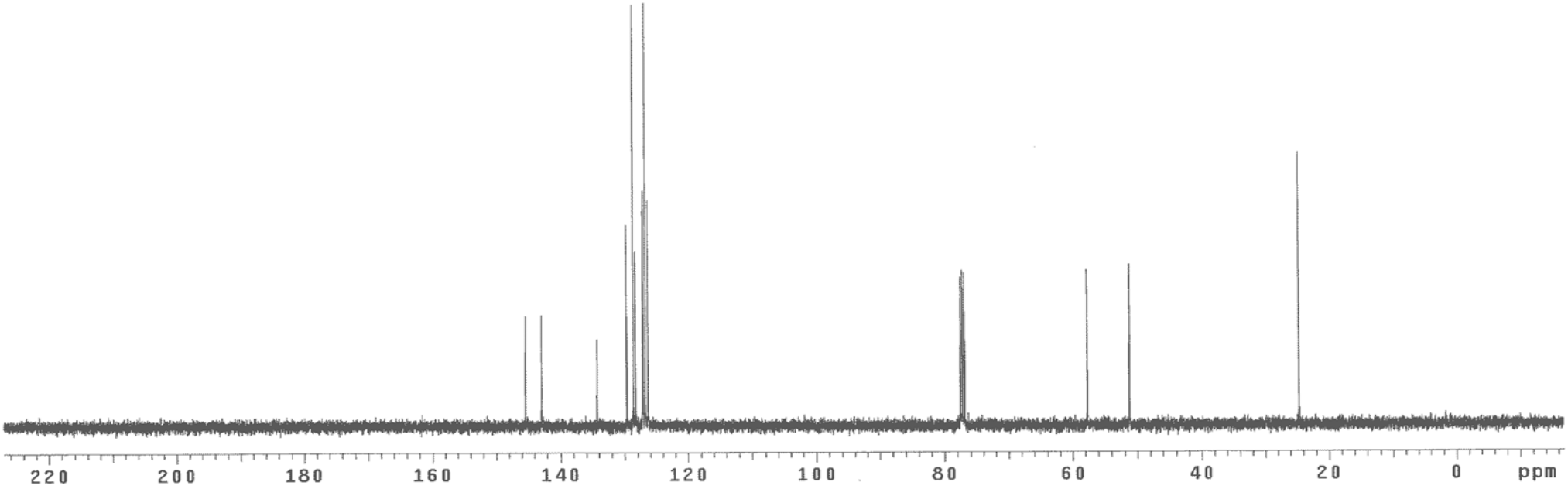

Fig. S13 ^{1}H NMR spectra of **5d.**

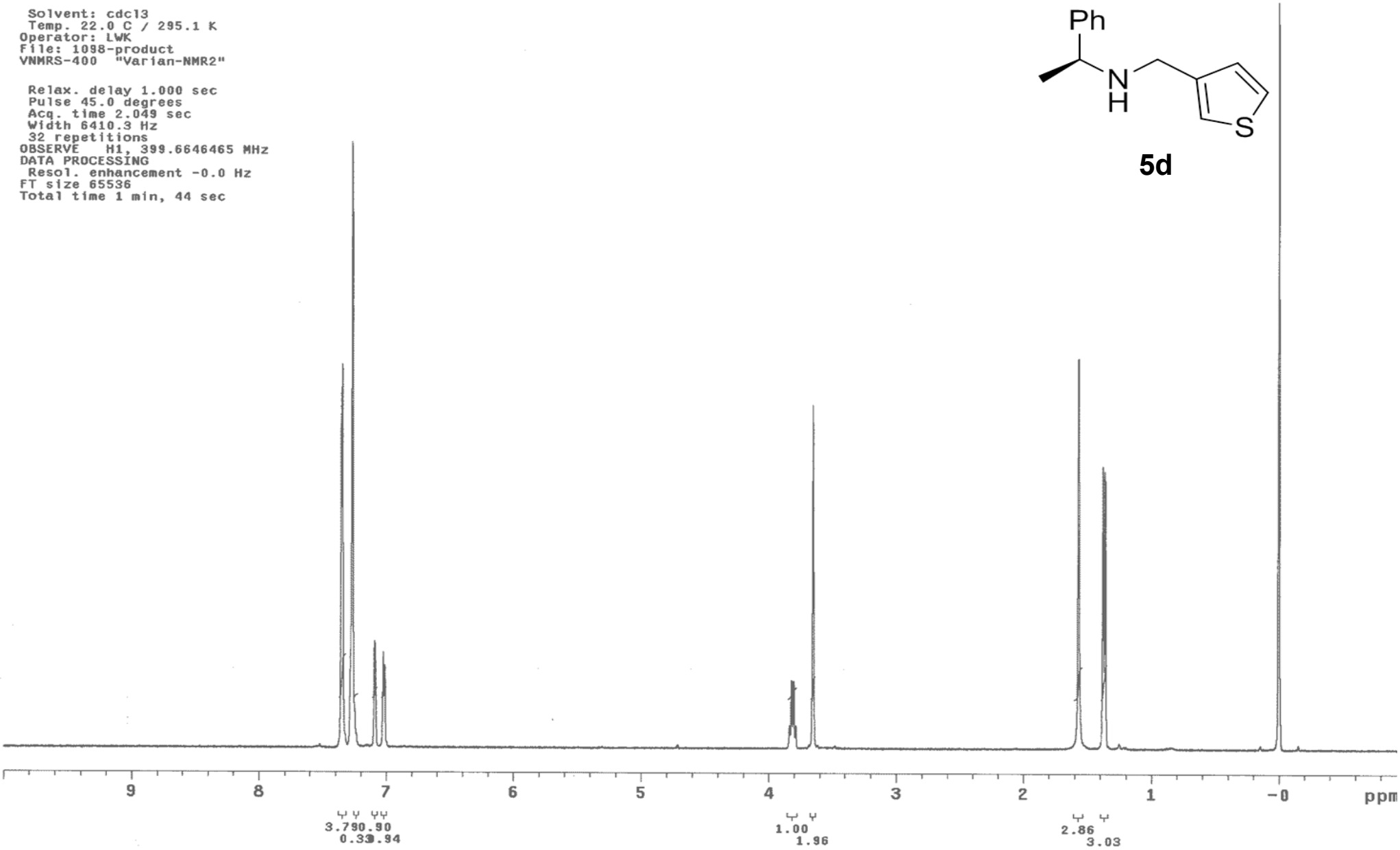

Fig. S14 ^{13}C NMR Spectrum of **5d.**

```
 Solvent: cdcl3
 Ambient temperature
Operator: LWK
VNMRS-400  "Varian-NMR"

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.300 sec
 Width 24509.8 Hz
 72 repetitions
OBSERVE  C13, 100.5127900 MHz
DECOUPLE  H1, 399.7344008 MHz
 Power 37 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 65536
Total time 38 min, 21 sec
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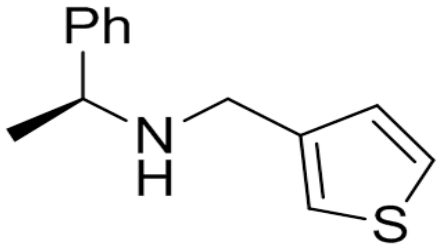

5d

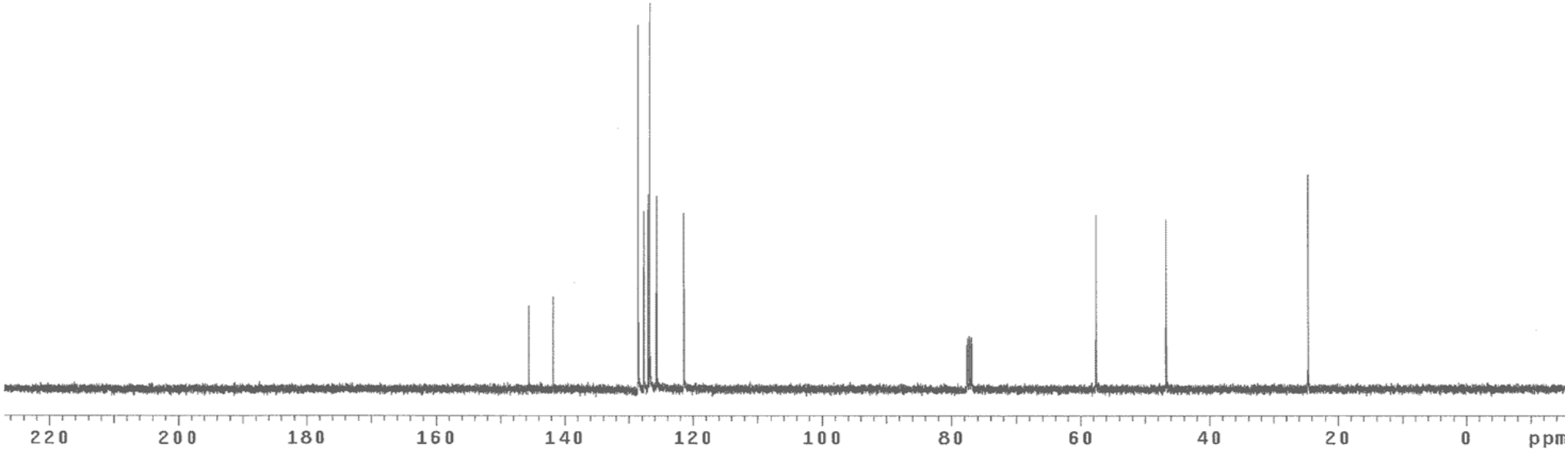

Fig. S15 ^{1}H NMR Spectrum of **5e.**

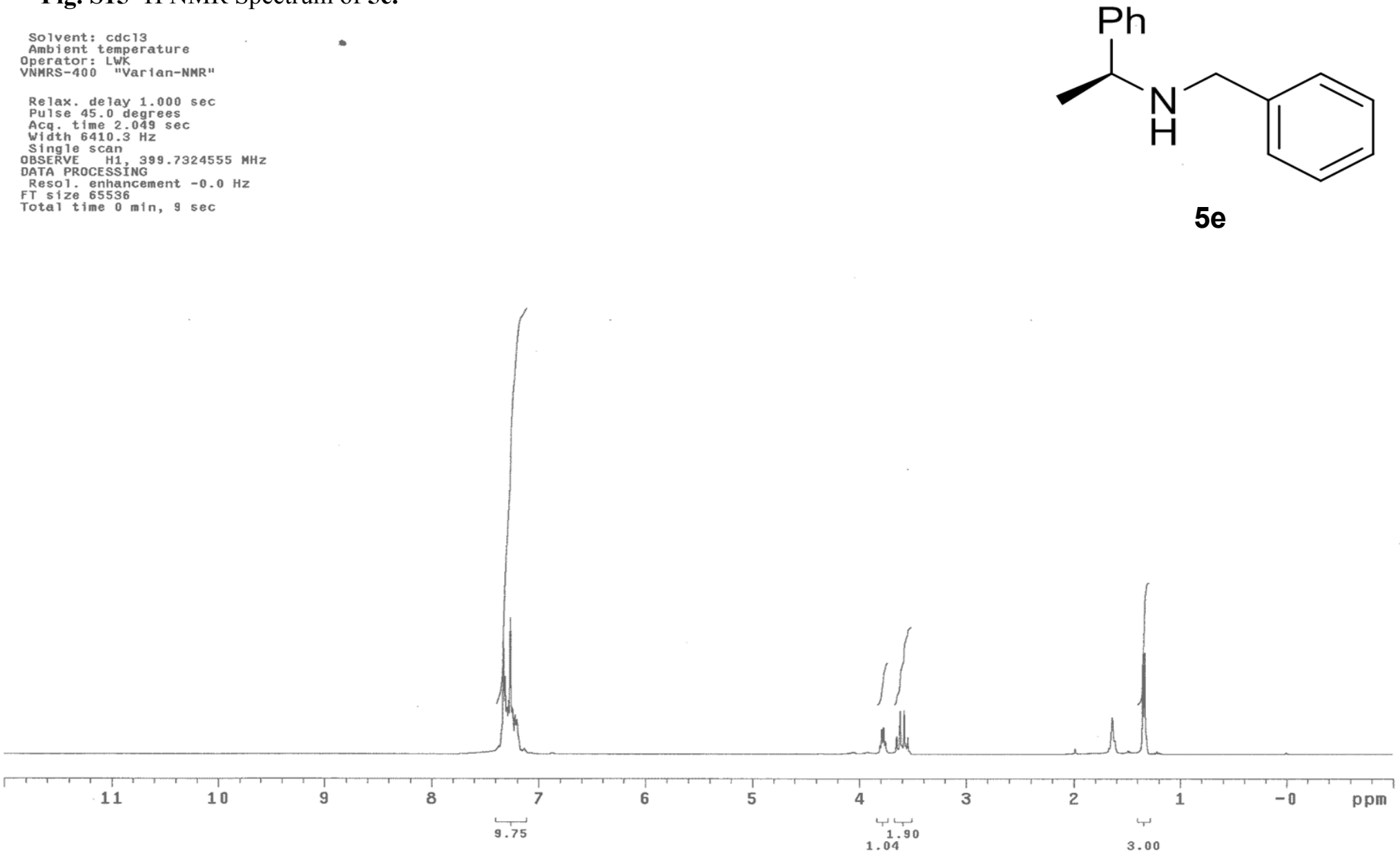

Fig. S16 ^{13}C NMR Spectrum of **5e.**

```
 Solvent: cdcl3
 Ambient temperature
Operator: LWK
VNMRS-400  "Varian-NMR"

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.300 sec
 Width 24509.8 Hz
 64 repetitions
OBSERVE   C13, 100.5127833 MHz
DECOUPLE  H1, 399.7344008 MHz
 Power 37 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 65536
Total time 38 min, 21 sec
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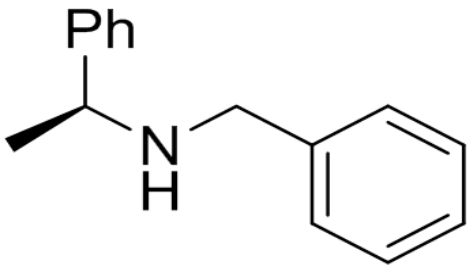


5e

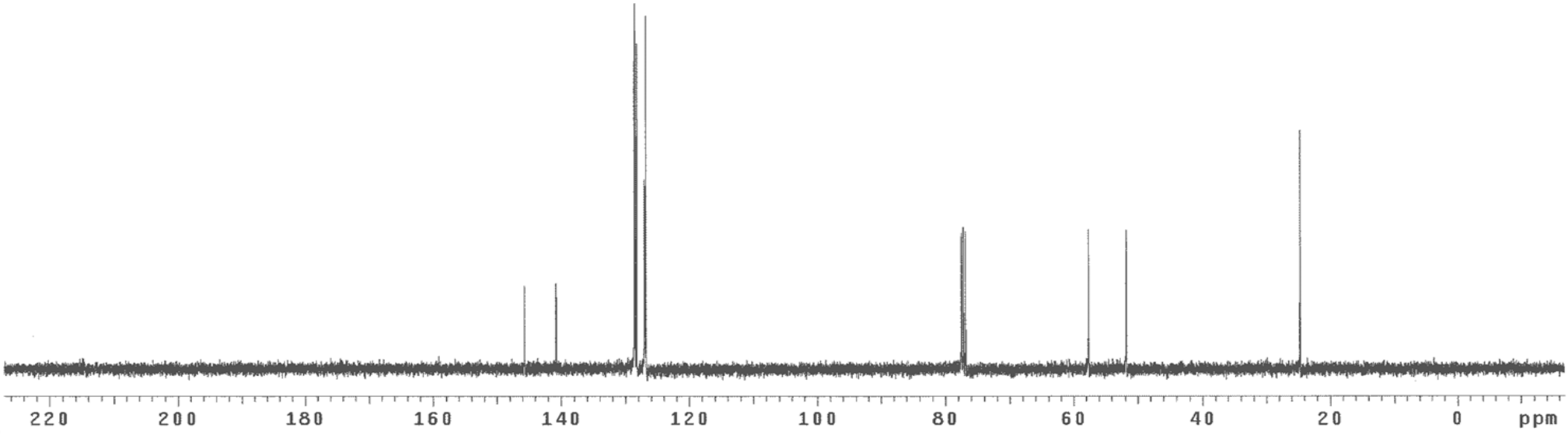
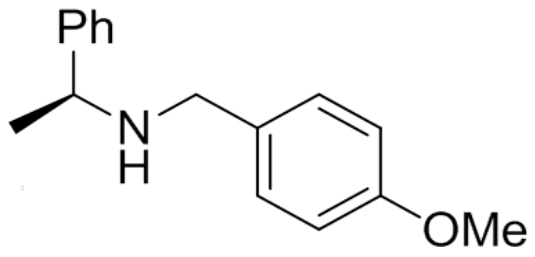


Fig. S17 ^{1}H NMR Spectrum of **5f.**

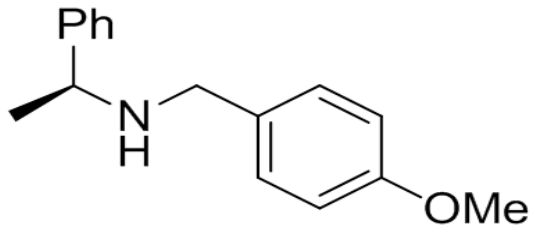


5f

Fig. S18 ^{13}C NMR Spectrum of **5f.**

```
Pulse Sequence: s2pul
 Solvent: cdcl3
 Ambient temperature
Operator: LWK
VNMRS-400  "Varian-NMR"

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.300 sec
 Width 24509.8 Hz
 48 repetitions
OBSERVE  C13, 100.5127915 MHz
DECOUPLE  H1, 399.7344008 MHz
 Power 37 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 65536
Total time 38 min, 21 sec
```



5f

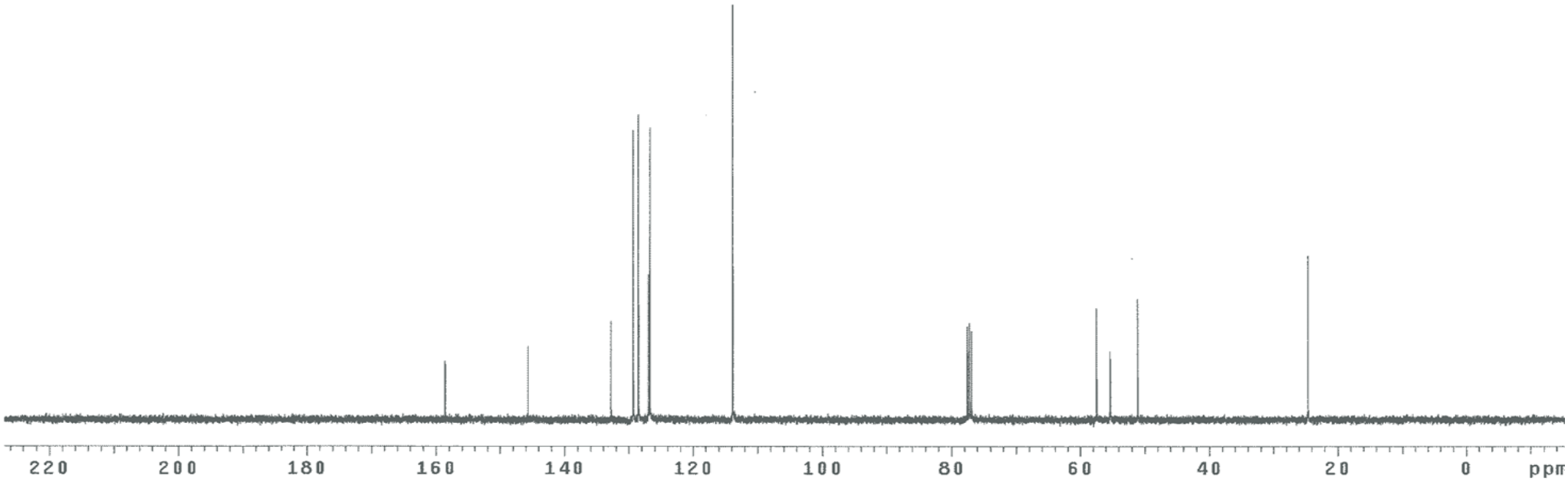


Fig. S19 ^{1}H NMR Spectrum of **5g.**

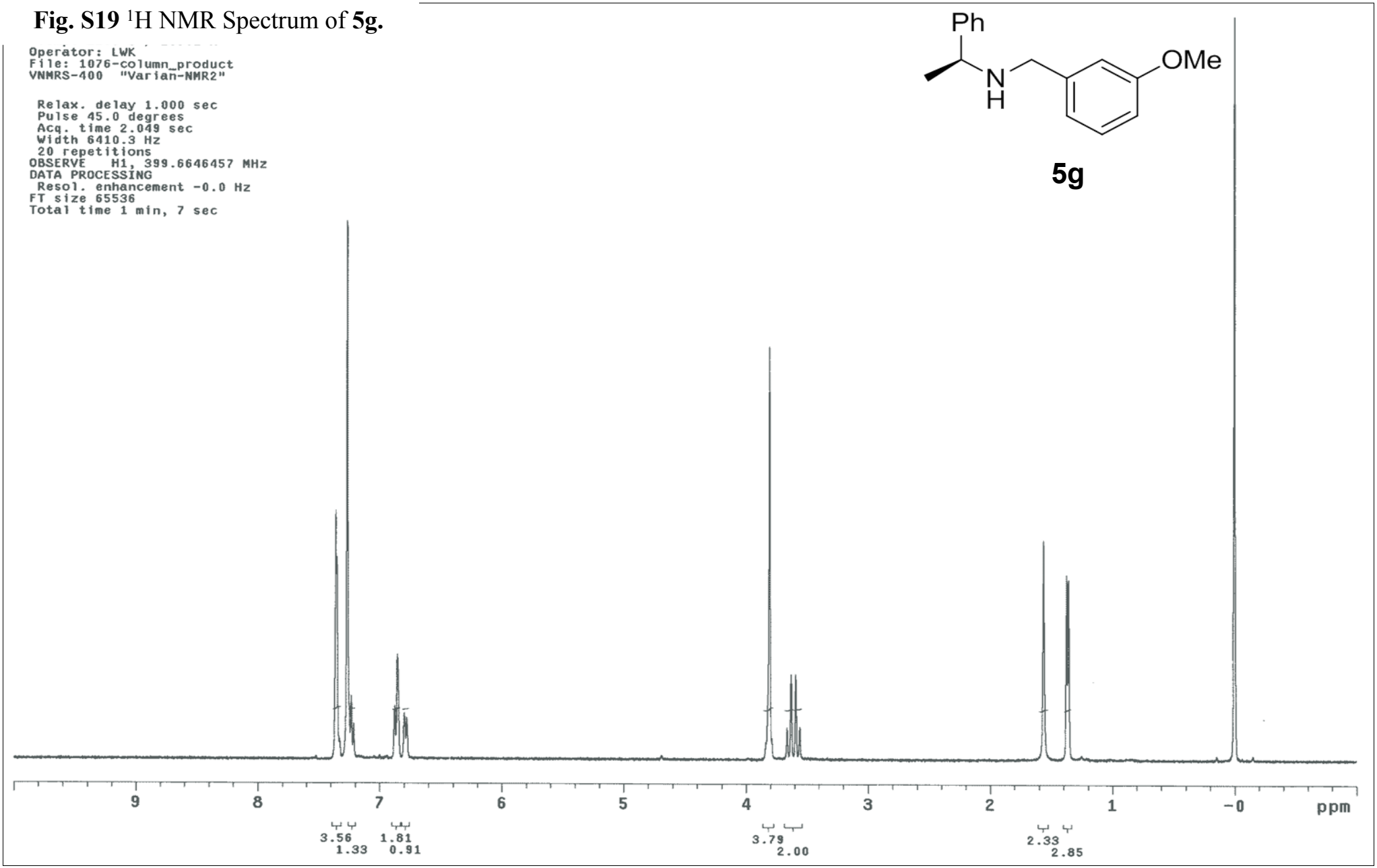
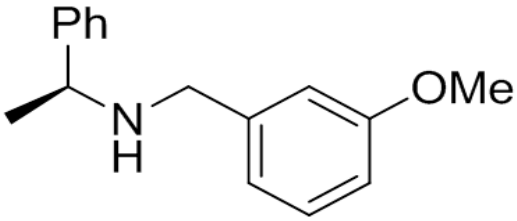


Fig. S20 ^{13}C NMR Spectrum of **5g.**



5g

```
 Solvent: cdcl3
 Ambient temperature
Operator: LWK
VNMRS-400  "Varian-NMR"

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.300 sec
 Width 24509.8 Hz
 40 repetitions
OBSERVE  C13, 100.5127878 MHz
DECOUPLE  H1, 399.7344008 MHz
 Power 37 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 65536
Total time 38 min, 21 sec
```

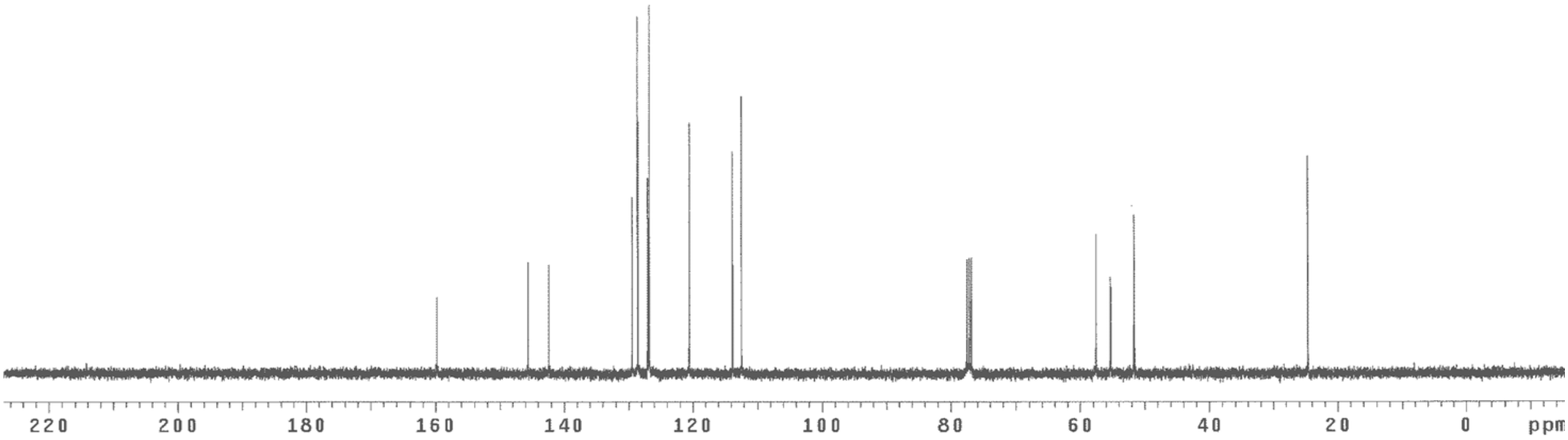


Fig. S21 ^{1}H NMR Spectrum of **5h.**

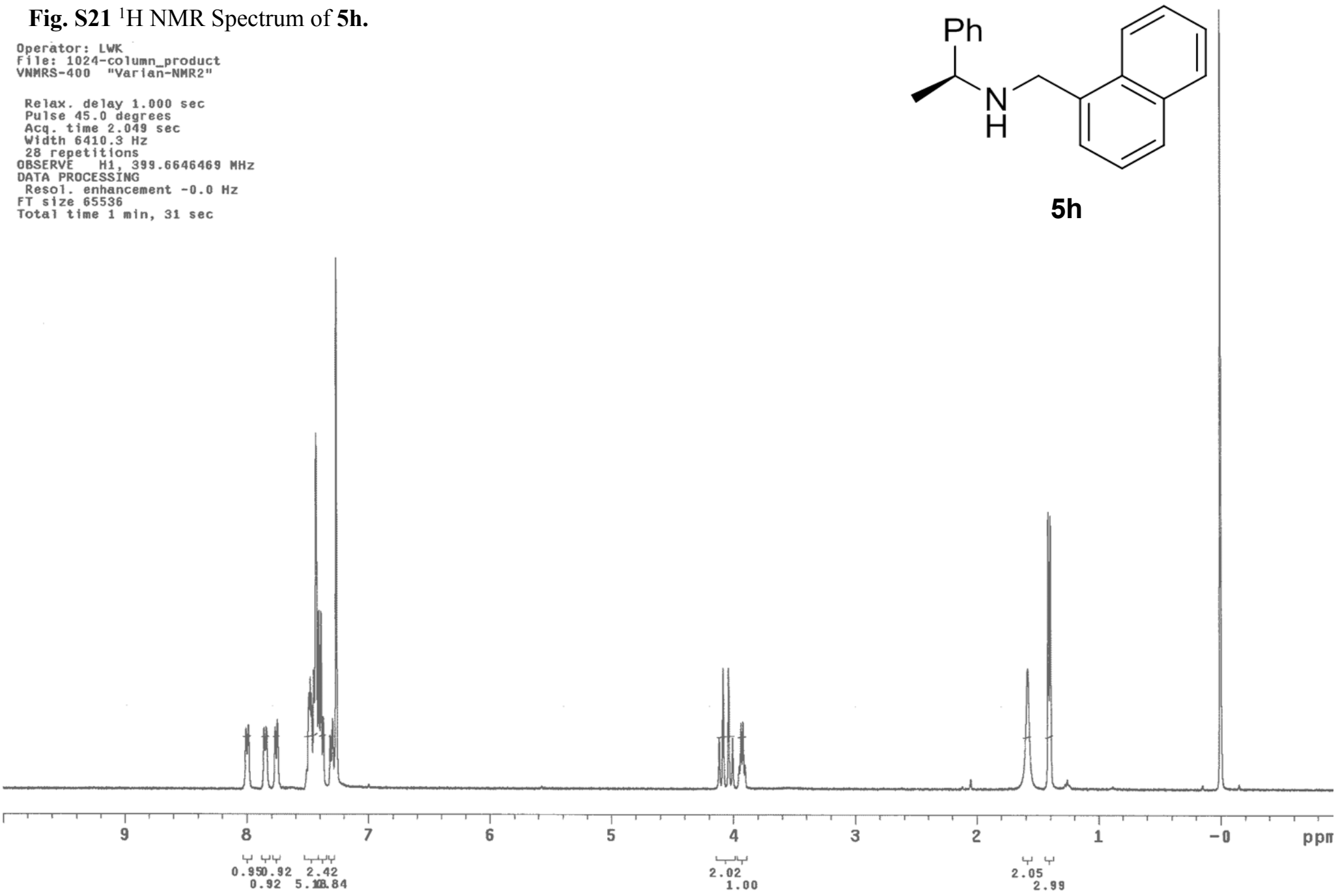
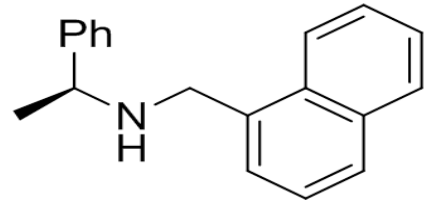


Fig. S22 ^{13}C NMR Spectrum of **5h.**



5h

```
 Ambient temperature
Operator: LWK
VNMRS-400  "Varian-NMR"

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.300 sec
 Width 24509.8 Hz
 80 repetitions
OBSERVE  C13, 100.5127960 MHz
DECOUPLE  H1, 399.7344008 MHz
 Power 37 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 65536
Total time 38 min, 21 sec
```

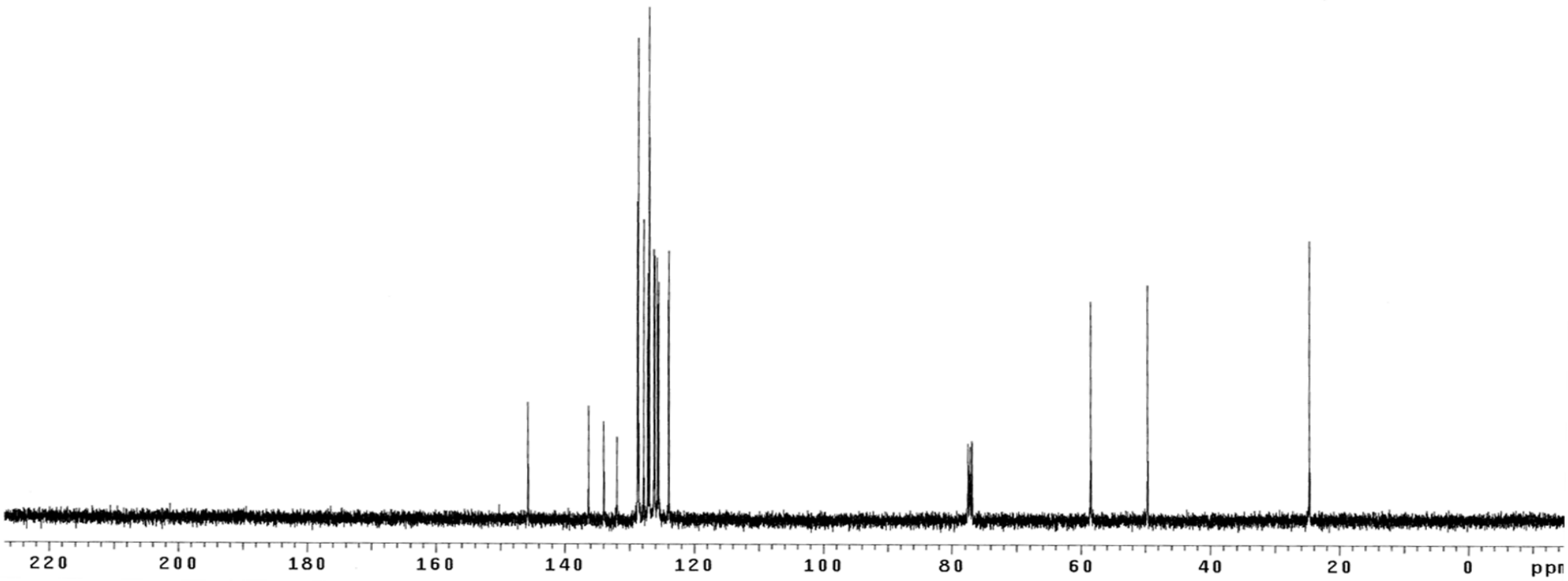
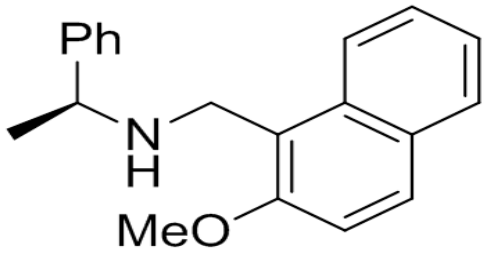


Fig. S23 ^{1}H NMR Spectrum of **5i.**

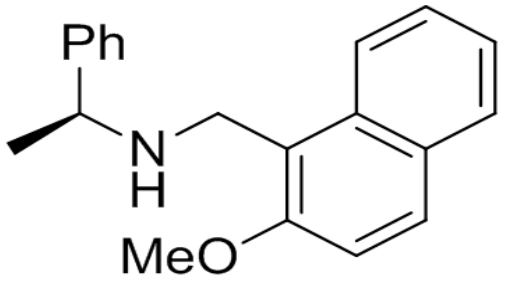


5i

Fig. S24 ^{13}C NMR Spectrum of **5i.**

```
 Solvent: cdcl3
 Ambient temperature
Operator: LWK
VNMRS-400  "Varian-NMR"

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.300 sec
 Width 24509.8 Hz
 80 repetitions
OBSERVE  C13, 100.5127908 MHz
DECOUPLE  H1, 399.7344008 MHz
 Power 37 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 65536
Total time 38 min, 21 sec
```



5i

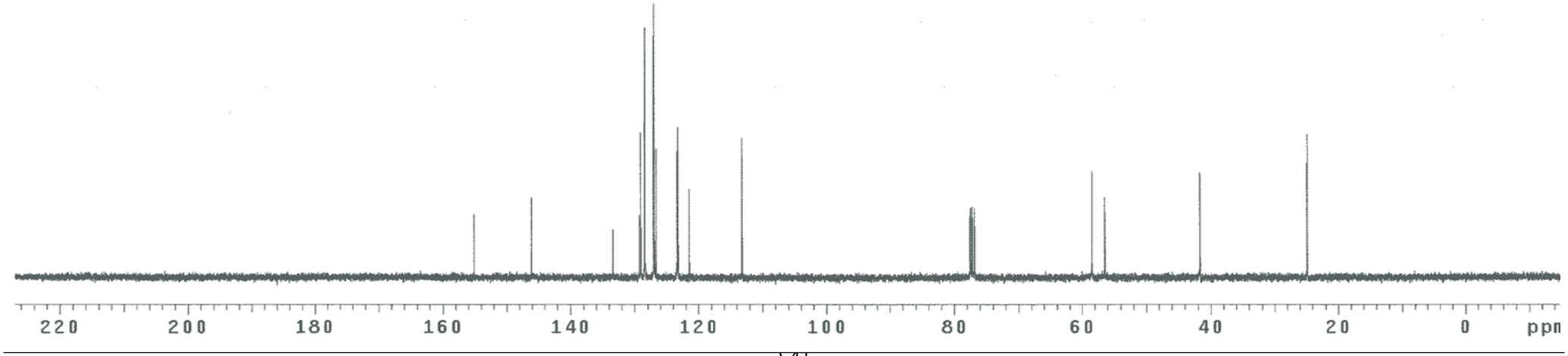
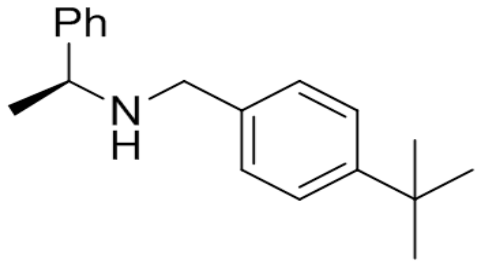


Fig. S25 ^{1}H NMR Spectrum of **5j.**



5j

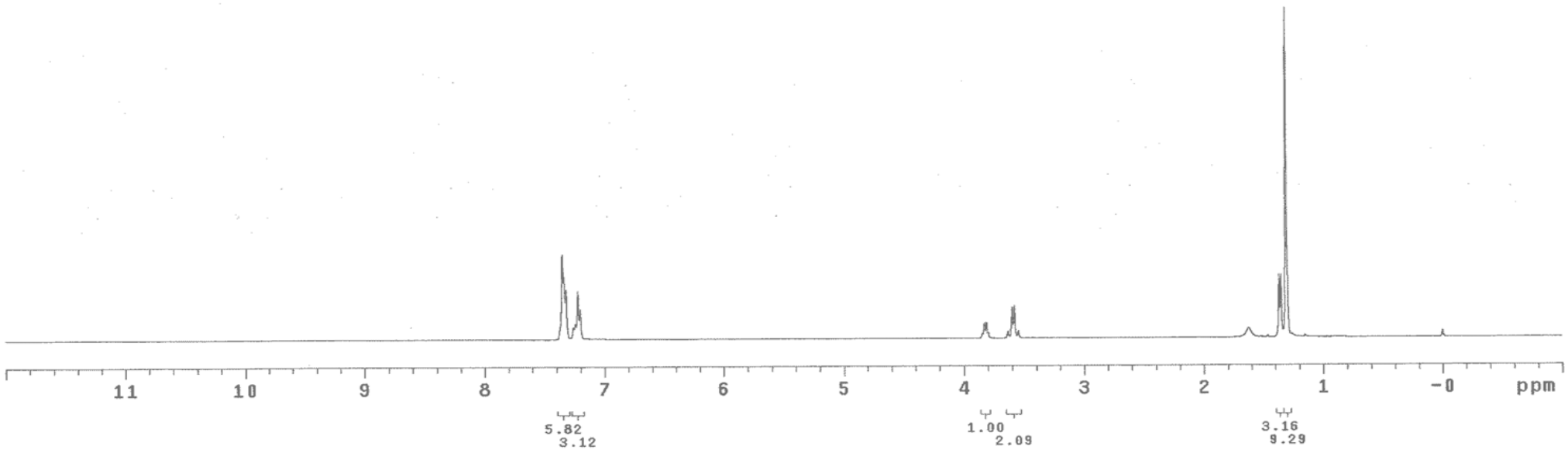
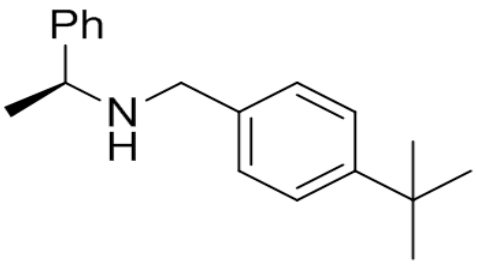


Fig. S26 ^{13}C NMR Spectrum of **5j.**

```
 Solvent: cdcl3
 Ambient temperature
Operator: LWK
VNMRS-400  "Varian-NMR"

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.300 sec
 Width 24509.8 Hz
 64 repetitions
OBSERVE  C13, 100.5127825 MHz
DECOUPLE  H1, 399.7344008 MHz
 Power 37 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 65536
Total time 38 min, 21 sec
```



5j

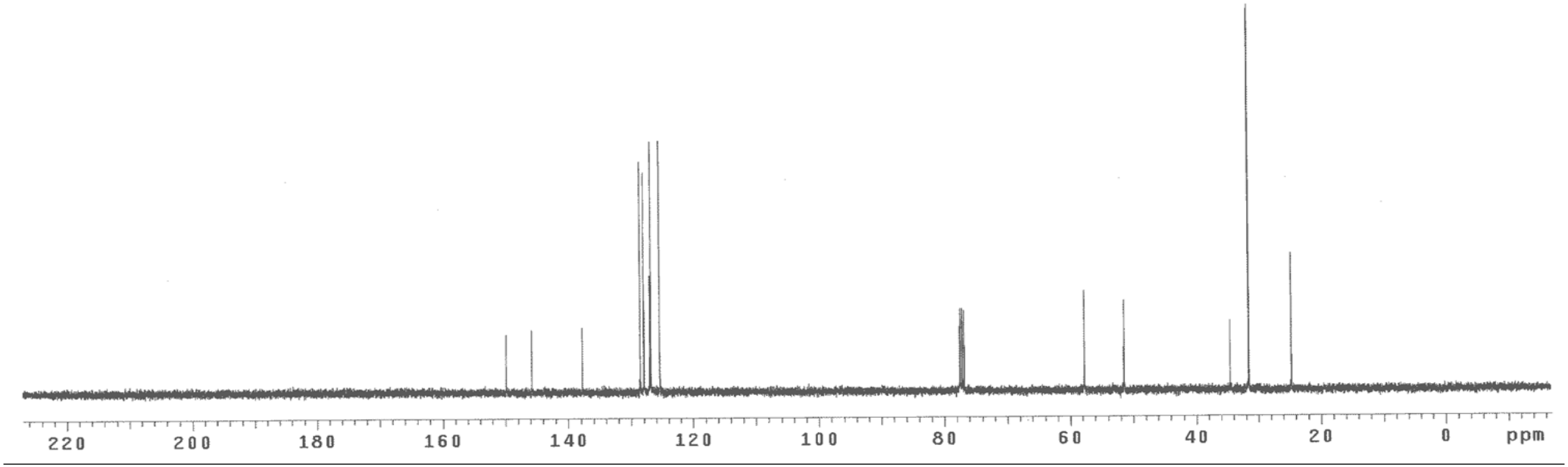
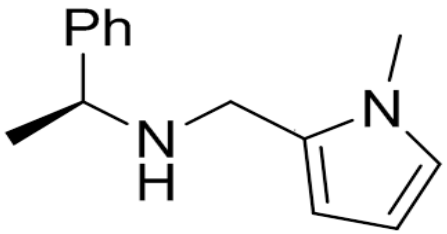


Fig. S27 ^{1}H NMR Spectrum of **5k.**



5k

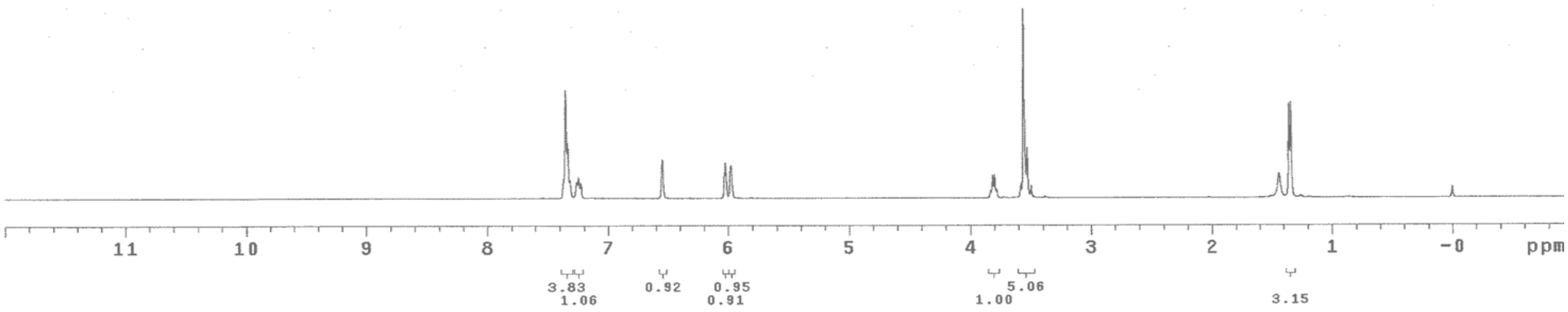
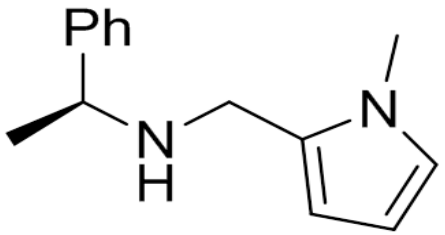


Fig. S28 ^{13}C NMR Spectrum of **5k.**



5k

```
 Solvent: cdcl3
 Ambient temperature
Operator: LWK
VNMRS-400  "Varian-NMR"

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.300 sec
 Width 24509.8 Hz
 60 repetitions
OBSERVE  C13, 100.5127938 MHz
DECOUPLE  H1, 399.7344008 MHz
 Power 37 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 65536
Total time 38 min, 21 sec
```

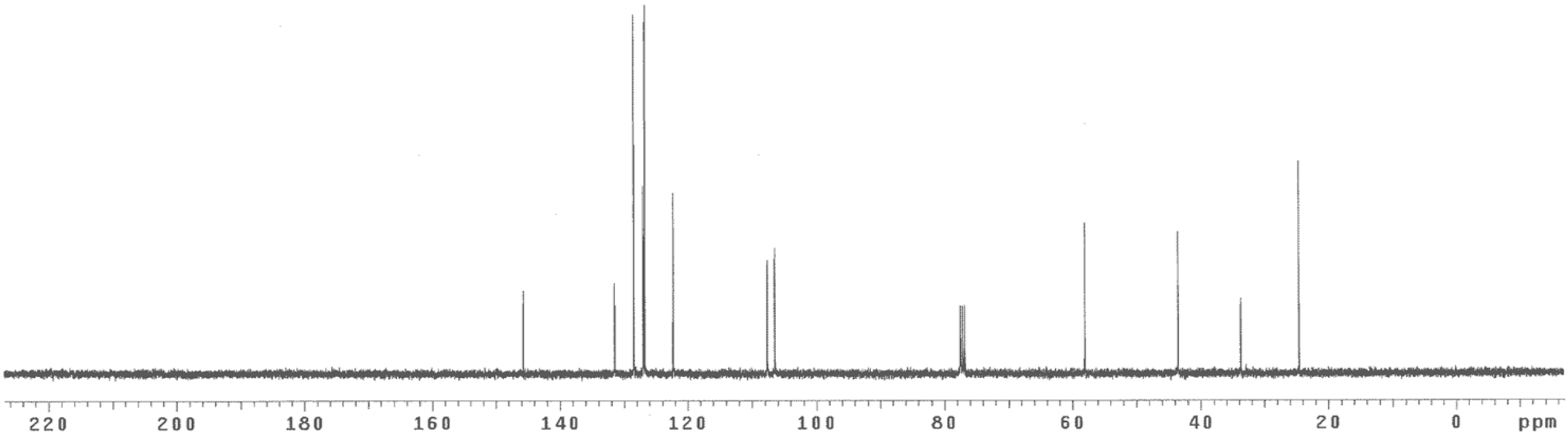
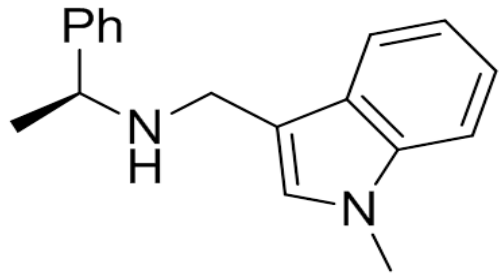


Fig. S29 ^{1}H NMR Spectrum of **5l.**



5l

```
 Solvent: cdcl3
 Ambient temperature
Operator: LWK
VNMRS-400  "Varian-NMR"

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 2.049 sec
 Width 6410.3 Hz
 Single scan
OBSERVE    H1, 399.7324565 MHz
DATA PROCESSING
 Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min, 9 sec
```

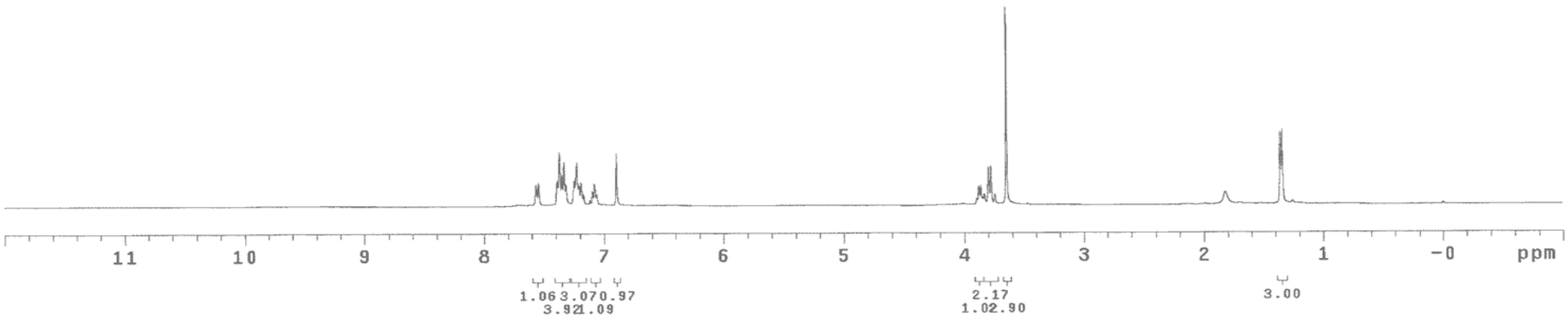
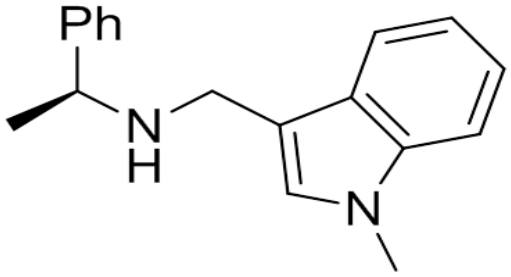


Fig. S30 ^{13}C NMR Spectrum of **5l.**

```
 Solvent: cdcl3
 Ambient temperature
Operator: LWK
VNMRS-400  "Varian-NMR"

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.300 sec
 Width 24509.8 Hz
 40 repetitions
OBSERVE  C13, 100.5127960 MHz
DECOUPLE  H1, 399.7344008 MHz
 Power 37 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 65536
Total time 38 min, 21 sec
```



5l

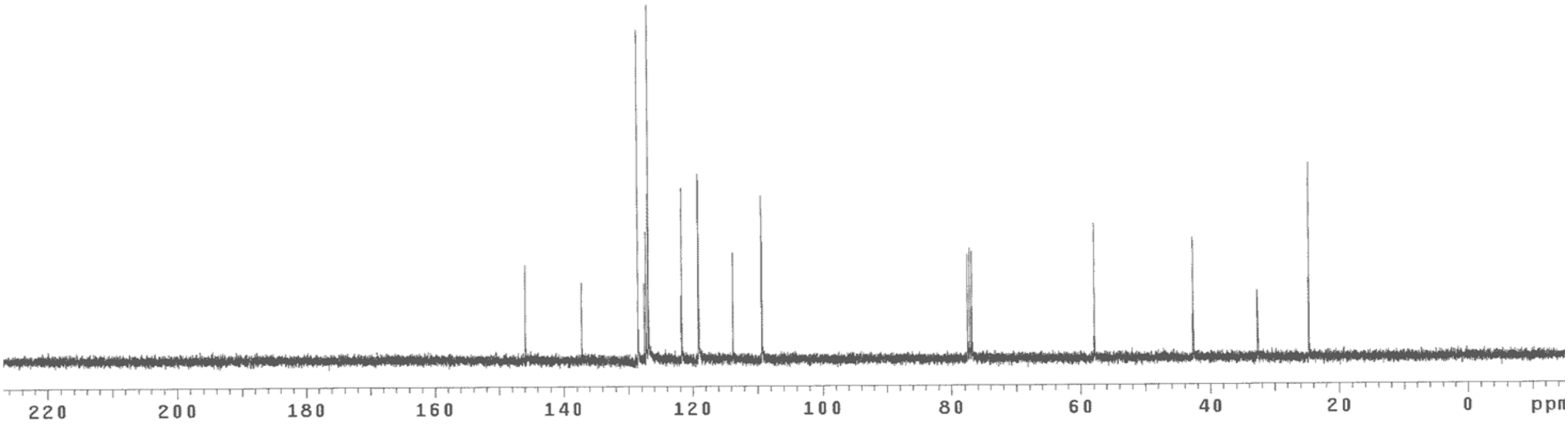


Fig. S31 ^{1}H NMR Spectrum of **5m.**

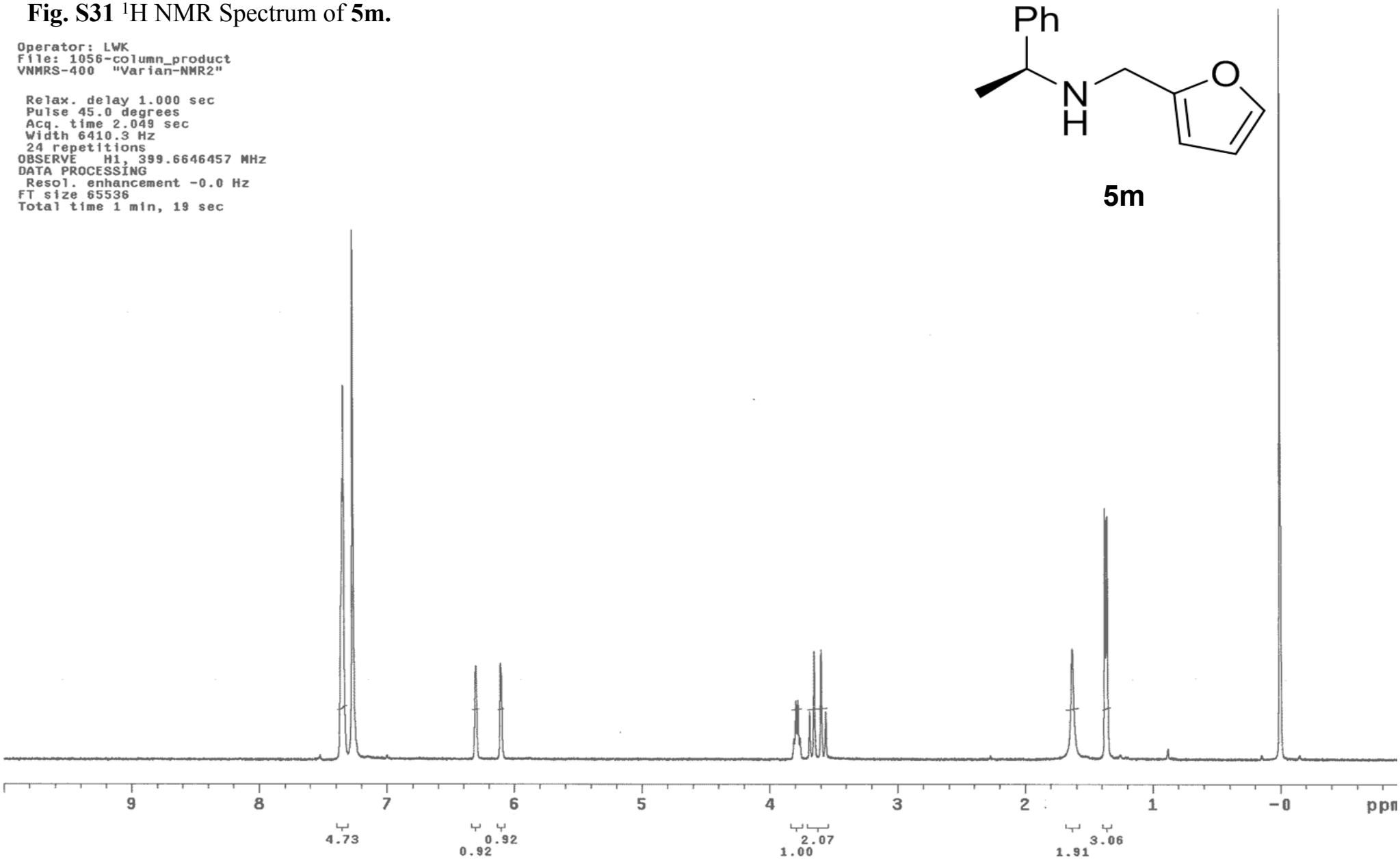
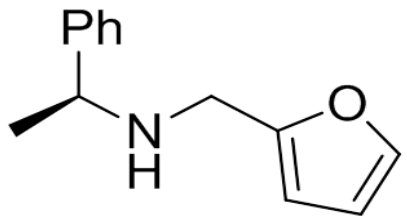


Fig. S32 ^{13}C NMR Spectrum of **5m.**



5m

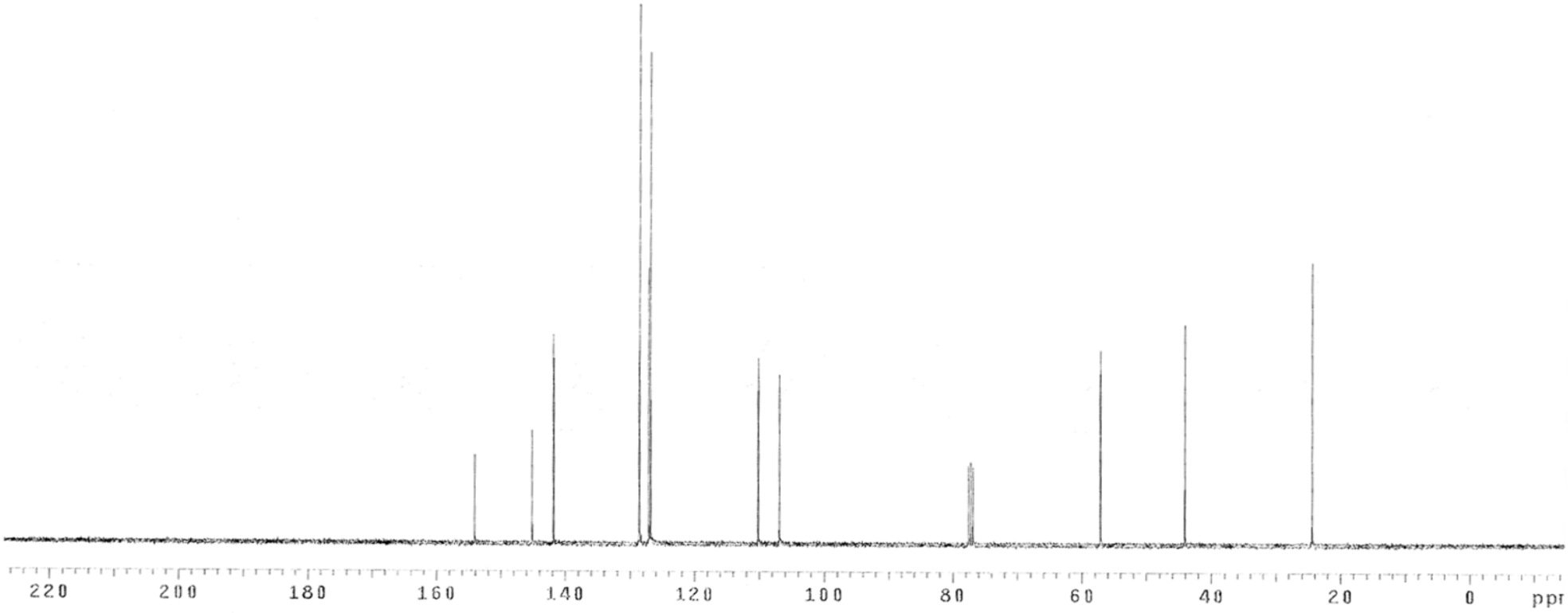
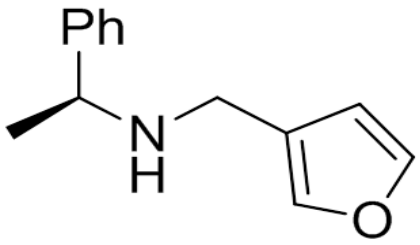


Fig. S33 ^{1}H NMR Spectrum of **5n.**



5n

```
 Solvent: cdcl3
 Ambient temperature
Operator: LWK
VNMRS-400  "Varian-NMR"

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 2.049 sec
 Width 6410.3 Hz
 Single scan
OBSERVE   H1, 399.7324192 MHz
DATA PROCESSING
 Resol. enhancement -0.0 Hz
FT size 65536
Total time 0 min, 9 sec
```

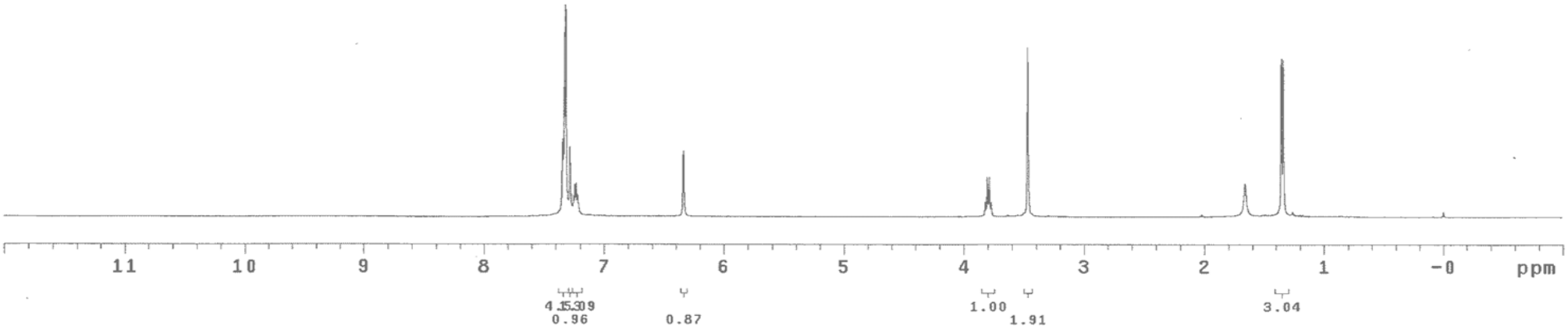
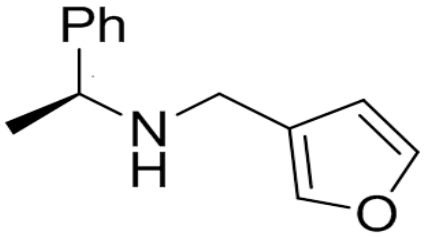


Fig. S34 ^{13}C NMR Spectrum of **5n.**



5n

Fig. S35 ^{1}H NMR Spectrum of **5o.**

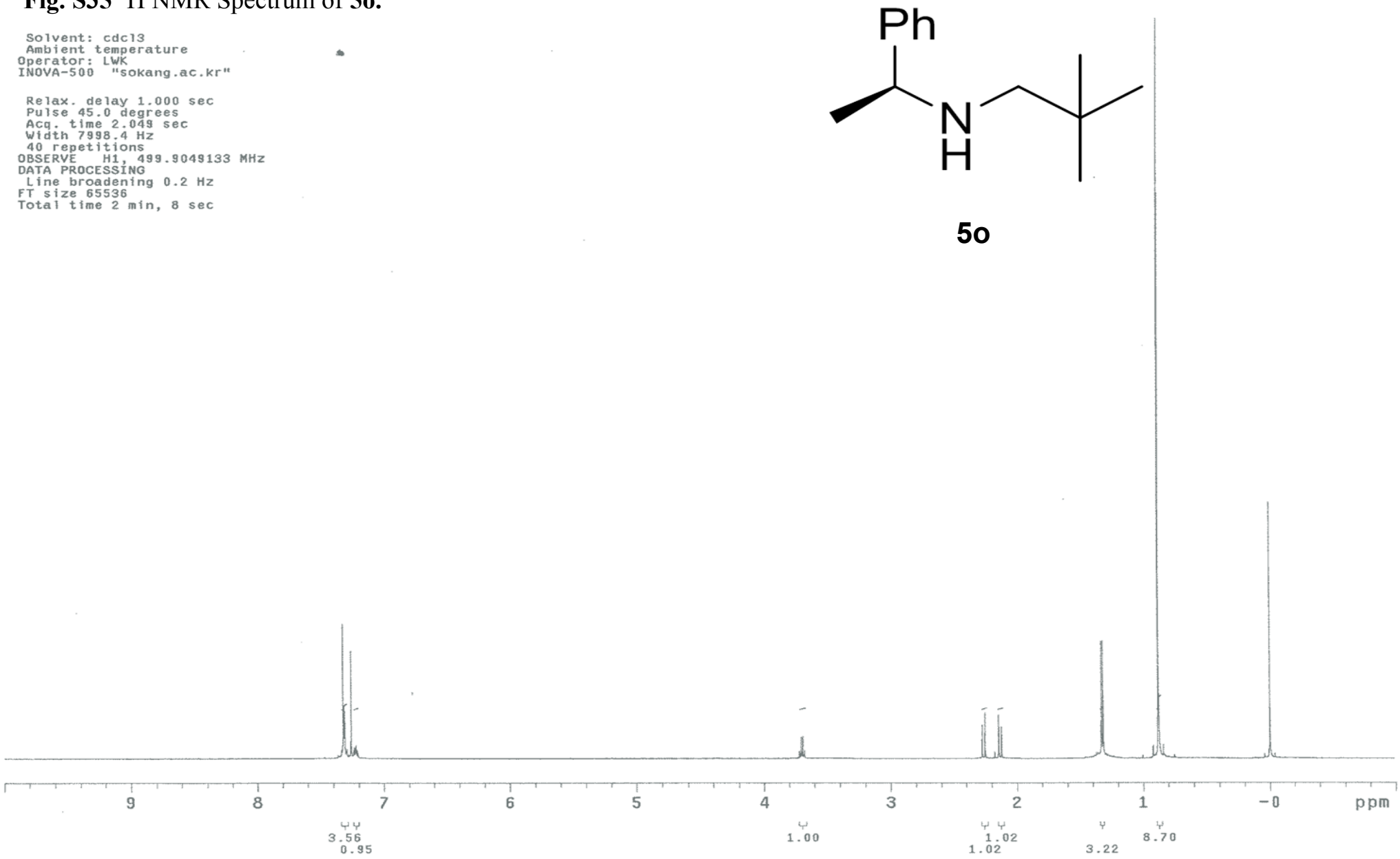
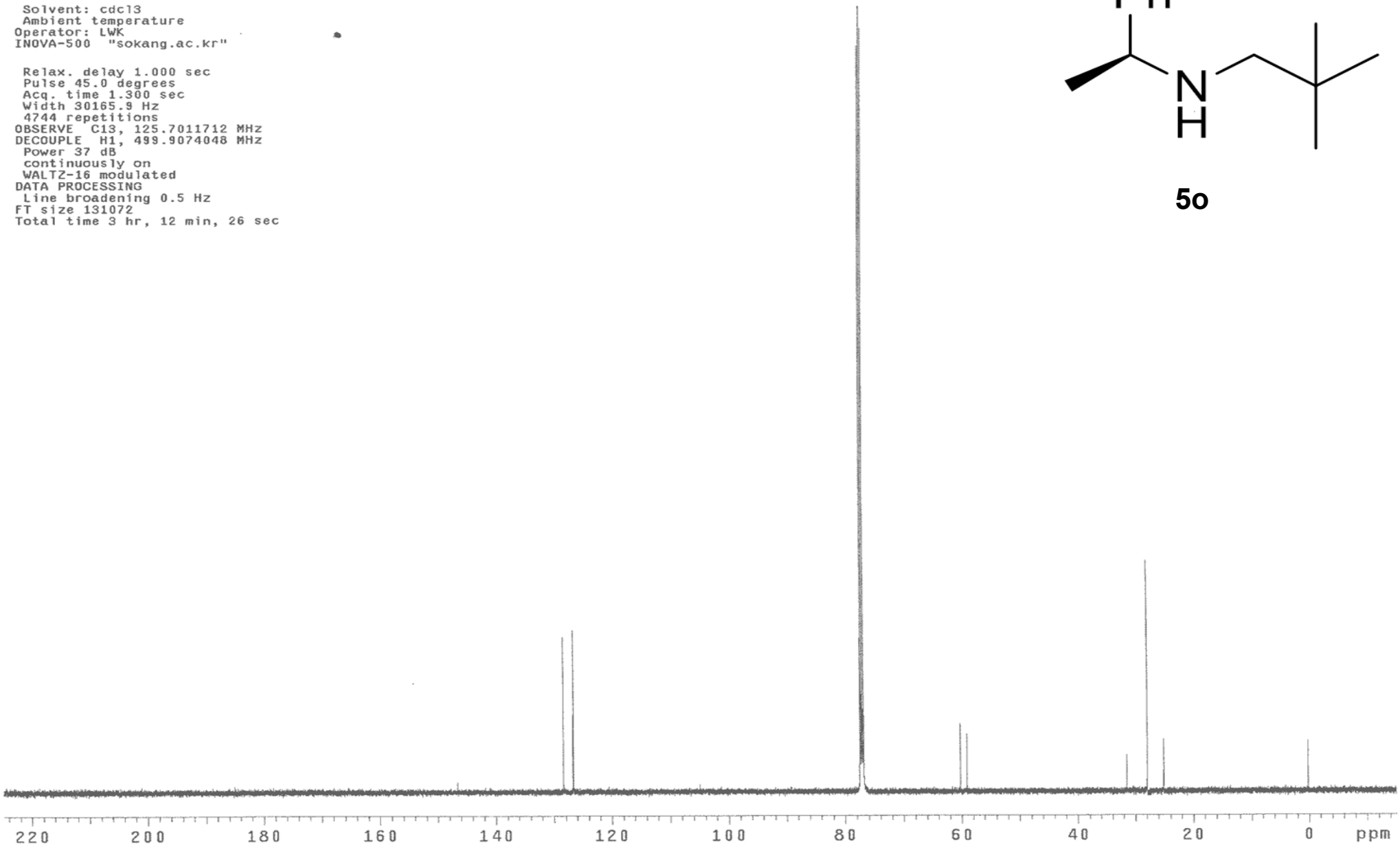


Fig. S36 ^{13}C NMR Spectrum of **5o.**



5o

Fig. S37 ^{1}H NMR Spectrum of **5p.**

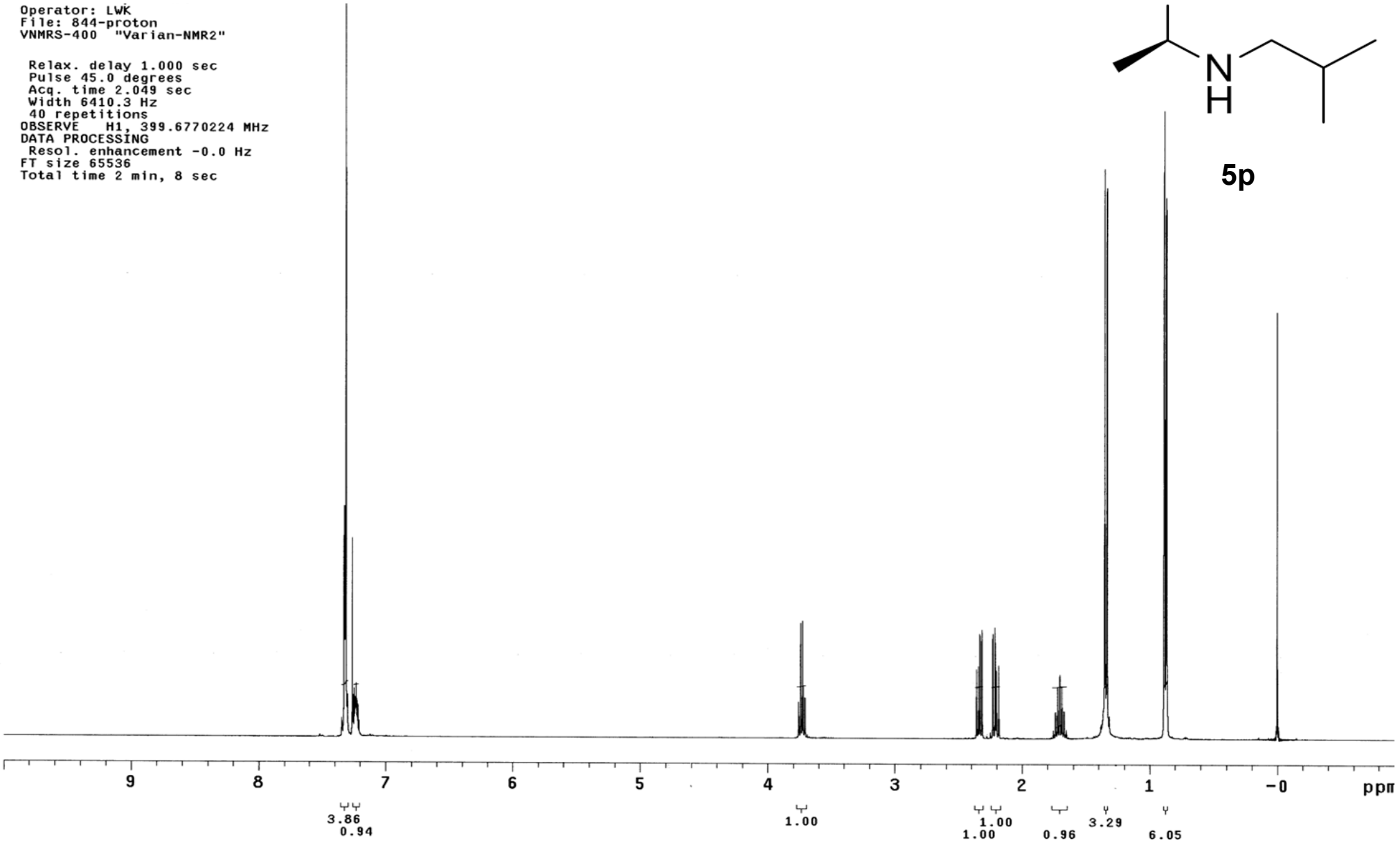


Fig. S38 ^{13}C NMR Spectrum of **5p.**

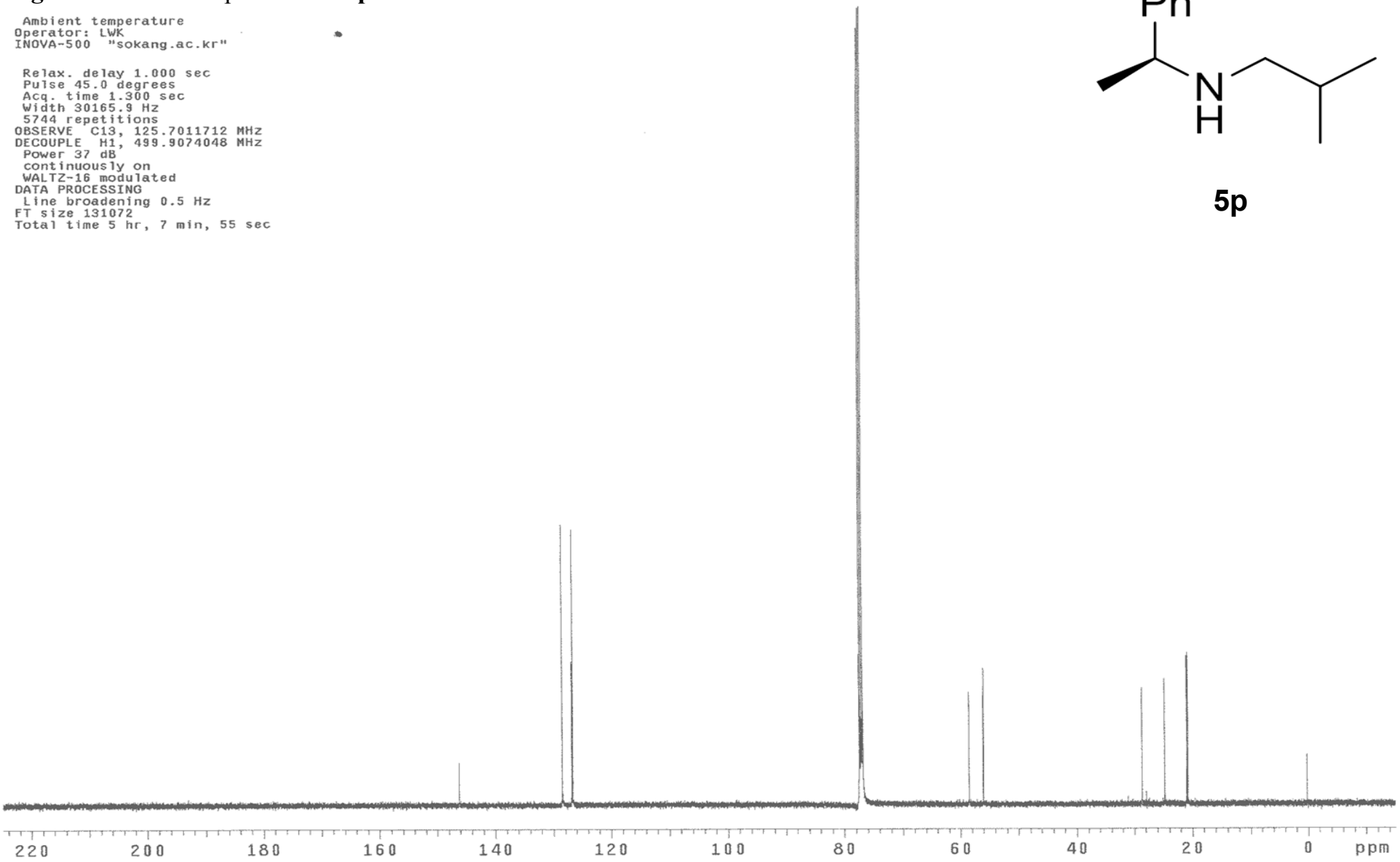


Fig. S39 ^{1}H NMR Spectrum of **5q.**

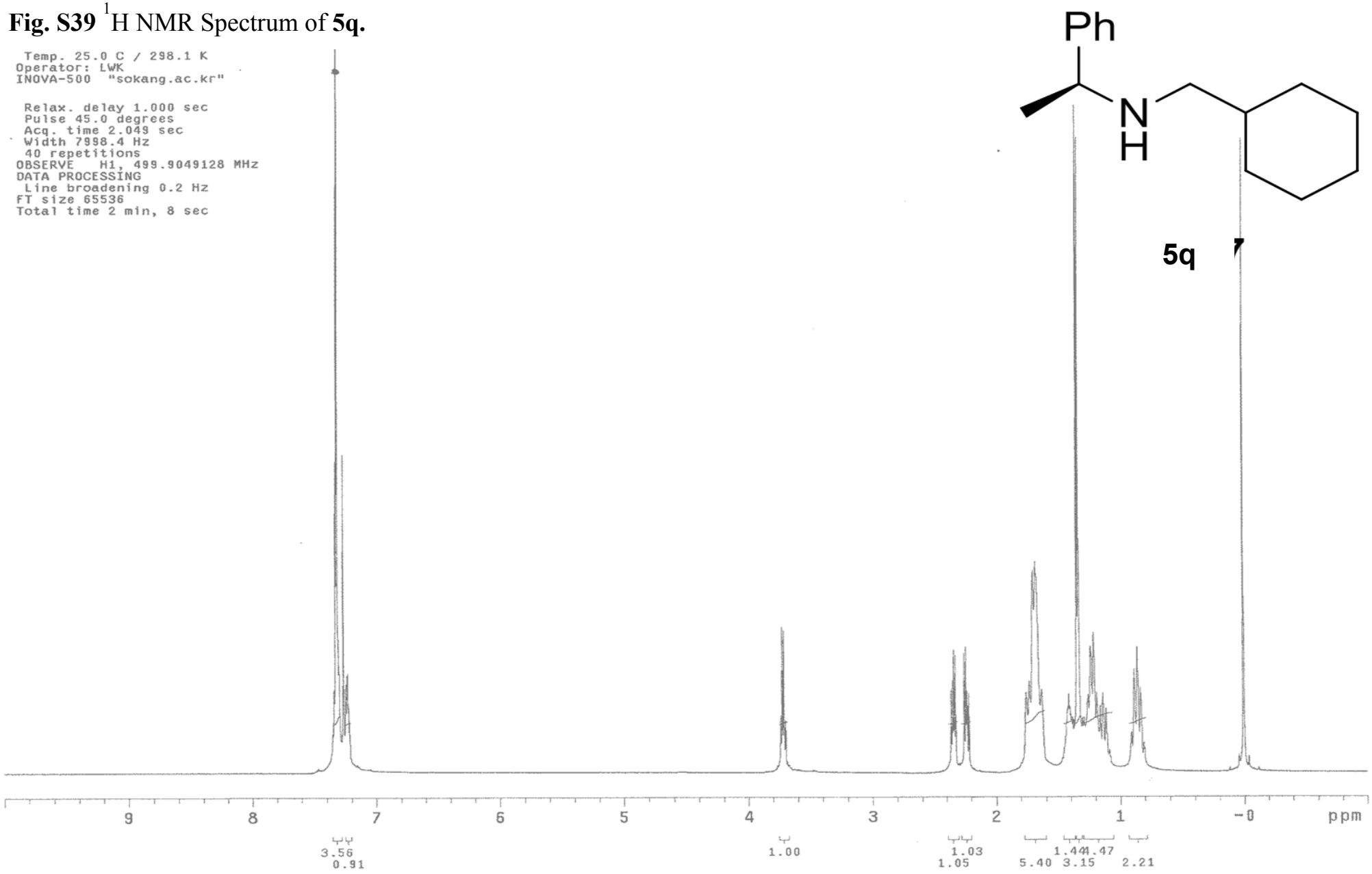


Fig. S40 ^{13}C NMR Spectrum of **5q.**

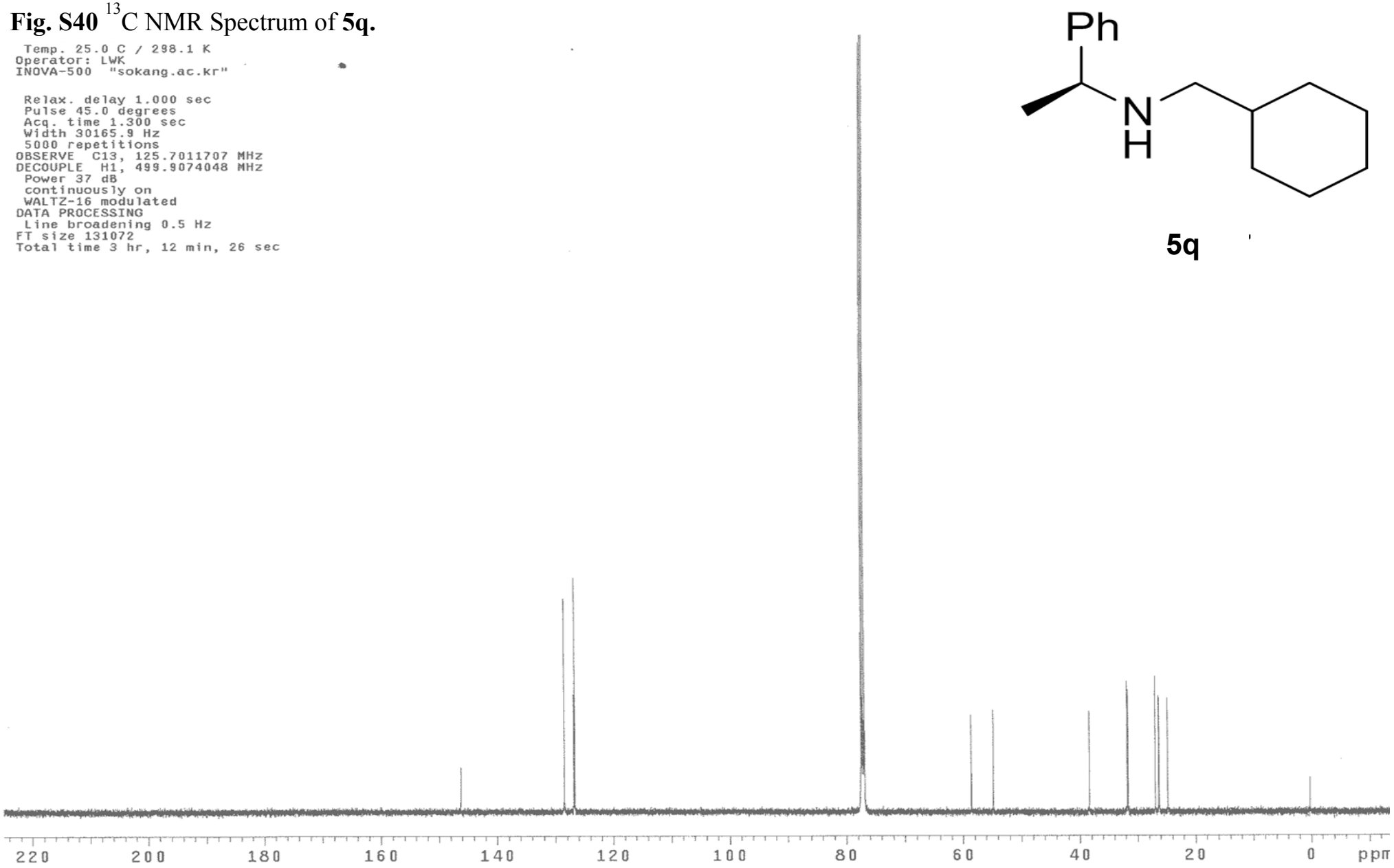


Fig. S41 ^{1}H NMR Spectrum of **5r.**

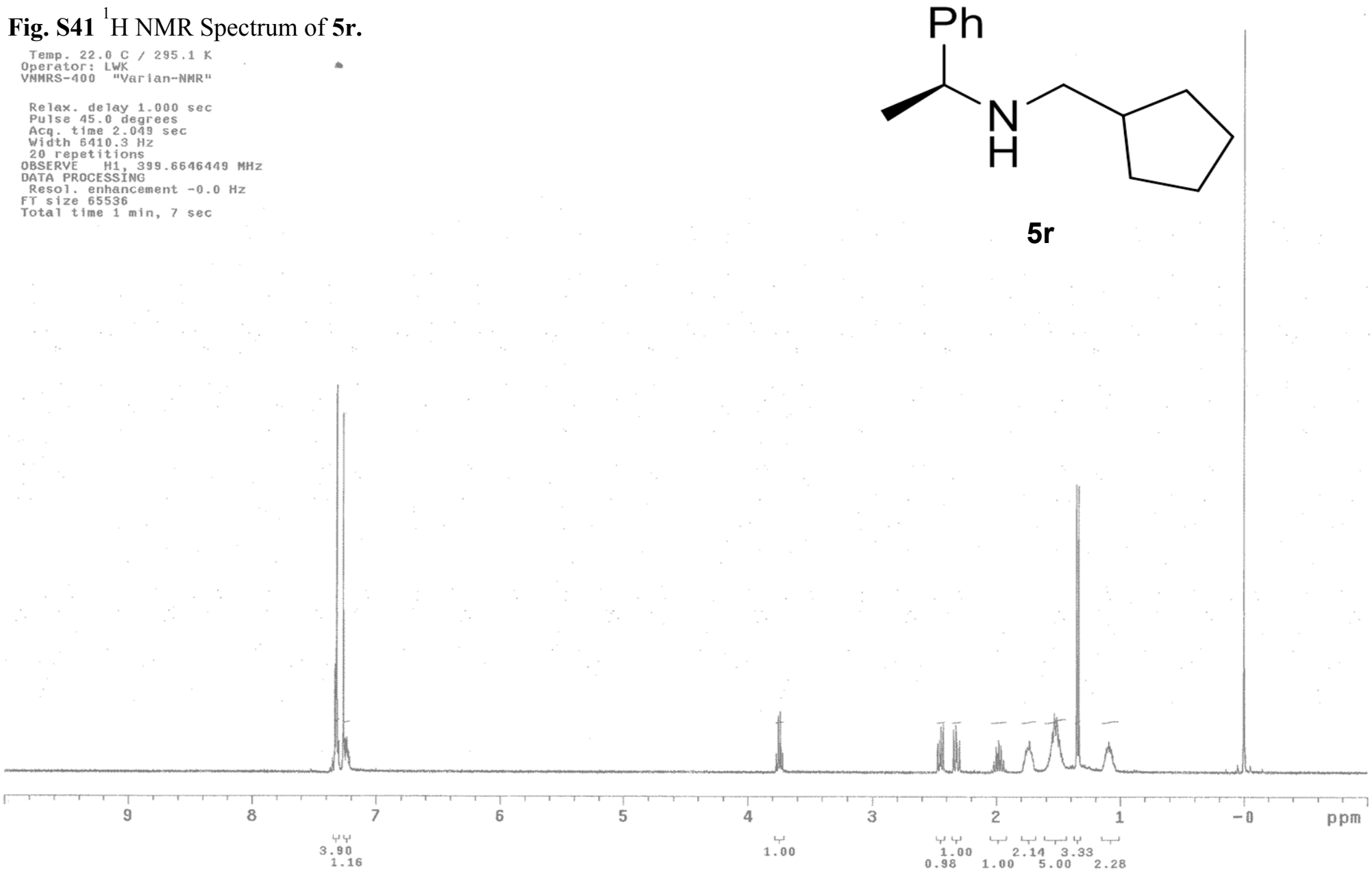
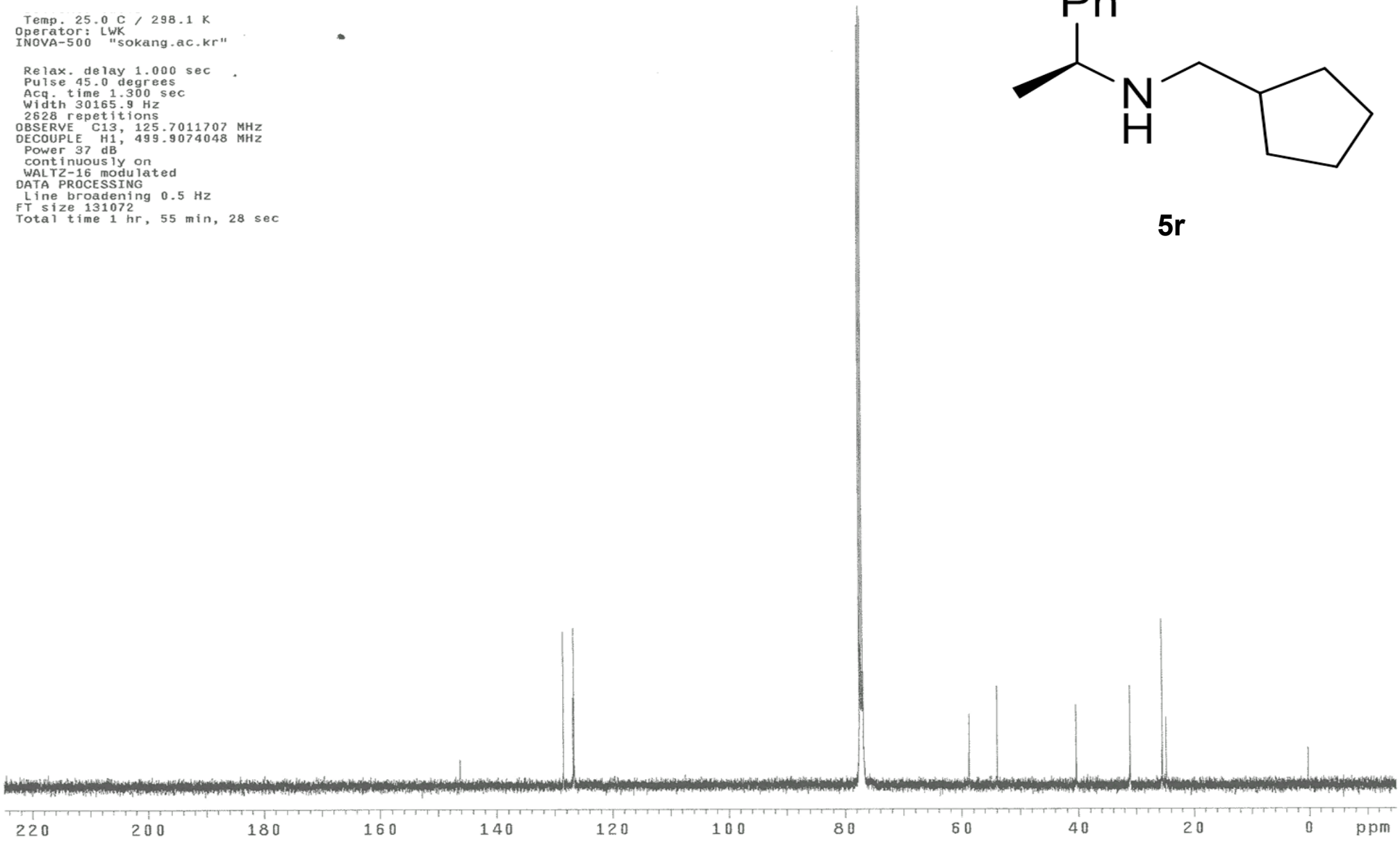


Fig. S42 ^{13}C NMR Spectrum of **5r.**



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