Supporting Information

Hydrogen Bond Catalyzed Direct Reductive Amination of Ketones

Dirk Menche,* Jorma Hassfeld, Jun Li, Gerd Menche, Antje Ritter, Sven Rudolph

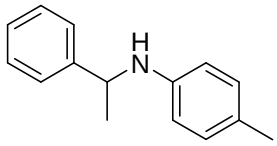
Gesellschaft für Biotechnologische Forschung mbH
Medzinische Chemie
Mascheroder Weg 1, D-38124 Braunschweig, Germany
Fax: (+)49531-6181-795
E-mail: dme05@gbf.de

General experimental procedure

A solution of acetophenone (**6**, 120 mg, 1.00 mmol) and *p*-anisidine (**7**, 123 mg, 1.00 mmol) in toluene (5 mL) was treated with the Hantzsch ester (**3**, 390 mg, 1.50 mmol), thiourea (**5b**, 7.60 mg, 0.100 mmol) and MS 5 Å (2.0 g) and the mixture was stirred 2 d at 50 °C under nitrogen. After filtration over celite, the solvent was evaporated and the residue purified by flash chromatography on silica gel (petroleum ether / diethylether = 8:1, 0.1% triethylamine) to give **8** (197 mg, 0.88 mmol, 88%).

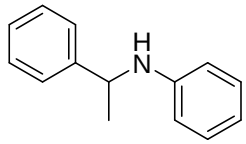
Spectroscopic data and copies of spectra for all new compounds

4-Methyl-*N*-(1-phenylethyl)-aniline (9)



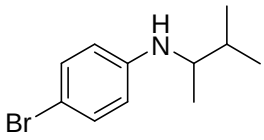
^{1}H NMR (400 MHz) δ 7.37 (d, *J*=7.6 Hz, 2 H) 7.31 (t, *J*=7.6 Hz, 2 H) 7.22 (t, *J*=7.1 Hz, 1 H) 6.90 (d, *J*=8.6 Hz, 2 H) 6.46 (d, *J*=8.6 Hz, 2 H) 4.46 (q, *J*=6.6 Hz, 1 H) 4.18 (br s, 1 H) 2.19 (s, 3 H) 1.52 (d, *J*=6.6 Hz, 3 H); ^{13}C NMR (100 MHz) δ 145.2, 144.8, 129.6, 128.6, 126.8, 126.7, 125.9, 113.7, 53.9, 24.8, 20.3; HRMS calculated for $C_{15}H_{18}N$ $[M+H]^{+}$: 212.1439, found: 212.1446.

_N_-(1-Phenylethyl)-aniline (10)



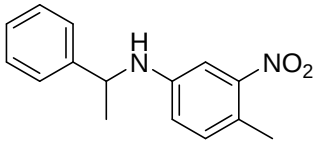
^{1}H NMR (300 MHz) δ ppm 7.29 - 7.43 (m, 4 H) 7.20 - 7.28 (m, 1 H) 7.11 (dd, *J*=8.5, 7.3 Hz, 2 H) 6.67 (tt, *J*=7.3, 1.0 Hz, 1 H) 6.55 (dd, *J*=8.7, 0.9 Hz, 2 H) 4.51 (q, *J*=6.7 Hz, 1 H) 4.19 (br s, 1 H) 1.54 (d, *J*=6.8 Hz, 3 H);^{13}C NMR (75MHz) δ 147.1, 145.1, 129.1, 128.6, 126.9, 125.8, 117.3, 113.4, 53.4, 24.9; HRMS calculated for $C_{14}H_{16}N$ $[M+H]^{+}$: 198.1283, found: 198.1288.

4-Bromo-_N_-(3-methylbutan-2-yl)-aniline (11)



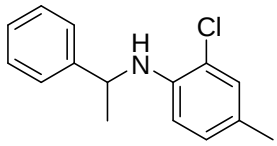
^{1}H NMR (300 MHz) δ 7.22 (d, *J*=8.9 Hz, 2 H) 6.45 (d, *J*=8.9 Hz, 2 H) 3.56 (br s, 1 H) 3.28 (dq, *J*=6.4, 5.1 Hz, 1 H) 1.81 (dsept, *J*=6.8, 5.1 Hz, 1 H) 1.09 (d, *J*=6.6 Hz, 3 H) 0.97 (d, *J*=6.8 Hz, 3 H) 0.91 (d, *J*=6.8 Hz, 3 H); ^{13}C NMR (75MHz) δ 146.8, 131.8, 114.6, 108.9, 53.6, 32.2, 19.0, 17.5, 16.4; HRMS calculated for $C_{11}H_{17}BrN$ $[M+H]^{+}$: 242.0544, found: 242.0551.

4-Methyl-3-nitro-_N_-(1-phenylethyl)-aniline (12)



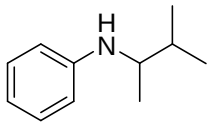
^{1}H NMR (400 MHz) δ ppm 7.29 - 7.38 (m, 4 H) 7.20 - 7.28 (m, 1 H) 7.13 (d, *J*=2.5 Hz, 1 H) 6.99 (d, *J*=8.1 Hz, 1 H) 6.63 (dd, *J*=8.6, 2.5 Hz, 1 H) 4.49 (q, *J*=6.6 Hz, 1 H) 4.40 (br s, 1 H) 2.39 (s, 3 H) 1.54 (d, *J*=7.1 Hz, 3 H); ^{13}C NMR (100 MHz) δ 149.6, 145.7, 143.9, 133.1, 128.8, 127.3, 125.8, 121.6, 118.2, 108.8, 53.7, 24.6, 19.4; HRMS calculated for $C_{17}H_{20}N_3O_2$ $[M+H+CH_3CN]^{+}$: 298.1556, found: 298.1550.

2-Chloro-4-methyl-*N*-(1-phenylethyl)-aniline (13)



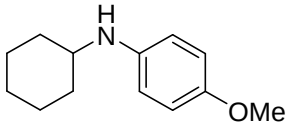
^{1}H NMR (400 MHz) δ 7.29 - 7.36 (m, 4 H) 7.17 - 7.27 (m, 1 H) 6.91 (d, *J*=8.1 Hz, 1 H) 6.56 (d, *J*=2.0 Hz, 1 H) 6.33 (dd, *J*=8.1, 2.5 Hz, 1 H) 4.45 (q, *J*=6.6 Hz, 1 H) 4.13 (br s, 1 H) 2.21 (s, 3 H) 1.51 (d, *J*=6.6 Hz, 3 H); ^{13}C NMR (100 MHz) δ 146.2, 144.7, 134.6, 131.2, 128.7, 127.0, 125.8, 124.3, 113.9, 112.1, 53.7, 24.7, 18.8; HRMS calculated for $C_{15}H_{17}ClN$ $[M+H]^{+}$: 246.1050, found: 246.1045.

***N*-(3-Methylbutan-2-yl)-aniline (14)**



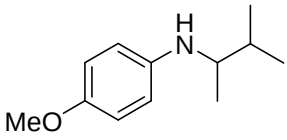
^{1}H NMR (300 MHz) δ ppm 7.25 (t, *J*=8.1 Hz, 2 H) 6.75 (td, *J*=7.3, 1.0 Hz, 1 H) 6.66 (dd, *J*=8.7, 0.9 Hz, 2 H) 3.52 (br s, 1 H) 3.43 (dq, *J*=6.5, 5.1 Hz, 1 H) 1.84 - 2.01 (m, 1 H) 1.19 (d, *J*=6.4 Hz, 3 H) 1.07 (d, *J*=7.0 Hz, 3 H) 1.01 (d, *J*=6.8 Hz, 3 H); ^{13}C NMR (75MHz) δ 147.8, 129.2, 116.6, 113.0, 53.4, 32.2, 19.1, 17.5, 16.5; HRMS calculated for $C_{11}H_{18}N$ $[M+H]^{+}$: 164.1439, found: 164.1438.

***N*-Cyclohexyl-4-methoxyaniline (15)**



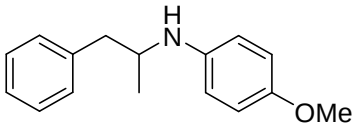
^{1}H NMR (300 MHz) δ ppm 6.76 (d, *J*=8.8 Hz, 2 H) 6.57 (d, *J*=8.8 Hz, 2 H) 3.74 (s, 3 H) 3.16 (tt, *J*=10.08, 3.77 Hz, 1 H) 3.08 (br s, 1 H) 2.10-1.99 (m, 2 H) 1.81-1.70 (m, 2 H) 1.69-1.59 (m, 1 H) 1.44-1.05 (m, 5 H); ^{13}C NMR (100 MHz) δ 151.9, 141.6, 114.9, 114.8, 55.8, 52.8, 33.6, 26.0, 25.0; HRMS calculated for $C_{13}H_{20}NO$ $[M+H]^{+}$: 206.1545, found: 206.1547.

4-Methoxy-*N*-(3-methylbutan-2-yl)-aniline (16)



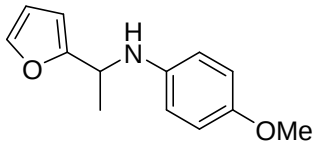
^{1}H NMR (300 MHz) δ 6.76 (d, *J*=9.0 Hz, 2 H) 6.58 (d, *J*=8.7 Hz, 2 H) 3.74 (s, 3 H) 3.24 (dq, *J*=6.0 Hz, 1 H) 1.75 - 1.93 (dsept, *J*=6.9, 4.9 Hz, 1 H) 1.07 (d, *J*=6.4 Hz, 3 H) 0.95 (d, *J*=7.2 Hz, 3 H) 0.90 (d, *J*=6.8 Hz, 3 H); ^{13}C NMR (75MHz) δ 152.0, 141.5, 115.1, 114.9, 55.8, 55.0, 31.9, 19.3, 17.3, 16.2; HRMS calculated for $C_{12}H_{19}NO$ $[M+H]^{+}$: 194.1545, found: 194.1546.

4-Methoxy-*N*-(1-phenylpropan-2-yl)-aniline (17)



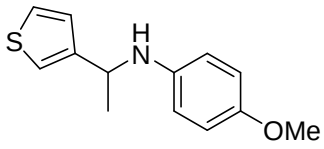
^{1}H NMR (400 MHz) δ 7.27 (t, *J*=7.4 Hz, 2 H) 7.23-7.13 (m, 3 H) 6.77 (d, *J*=9.0 Hz, 2 H) 6.57 (d, *J*=9.0 Hz, 2 H) 3.72 (s, 3 H) 3.66 (td, *J*=7.4, 6.1, 4.8 Hz, 1 H) 3.03 (br s, 1 H) 2.90 (dd, *J*=13.5, 4.8 Hz, 1 H) 2.65 (dd, *J*=13.5, 7.4 Hz, 1 H) 1.11 (d, *J*=6.1 Hz, 3 H); ^{13}C NMR (75MHz) δ 152.1, 141.4, 138.7, 129.4, 128.3, 126.2, 115.0, 115.0, 55.8, 50.4, 42.4, 20.3; HRMS calculated for $C_{16}H_{20}NO$ $[M+H]^{+}$: 242.1545, found: 242.1544.

***N*-(1-(Furan-2-yl)-ethyl)-4-methoxyaniline (18)**



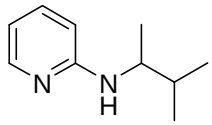
^{1}H NMR (400 MHz) δ 7.35 (d, *J*=2.0 Hz, 1 H) 6.78 (d, *J*=8.7 Hz, 2 H) 6.62 (d, *J*=8.7 Hz, 2 H) 6.30 (dd, *J*=3.0, 2.0 Hz, 1 H) 6.16 (d, *J*=3.6 Hz, 1 H) 4.57 (q, *J*=6.6 Hz, 1 H) 3.75 (s, 3 H) 3.60 (br s, 1 H) 1.56 (d, *J*=7.1 Hz, 3 H); ^{13}C NMR (400 MHz) δ 157.5, 152.5, 141.3, 141.2, 115.2, 114.8, 110.0, 105.0, 55.7, 48.4, 20.9; HRMS calculated for $C_{13}H_{16}NO_2$ $[M+H]^{+}$: 218.1181, found: 218.1178.

4-Methoxy-*N*-(1-(thiophen-3-yl)ethyl)-aniline (19)



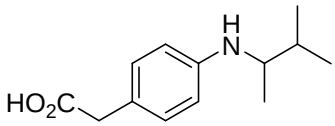
^{1}H NMR (300 MHz) δ 7.26 (dd, *J*=4.9, 3.0 Hz, 1 H) 7.12 (td, *J*=2.0, 1.2 Hz, 1 H) 7.06 (dd, *J*=5.1, 1.2 Hz, 1 H) 6.74 (d, *J*=9.0 Hz, 2 H) 6.54 (d, *J*=9.0 Hz, 2 H) 4.55 (q, *J*=6.6 Hz, 1 H) 3.72 (s, 3 H) 3.62 (br s, 1 H) 1.52 (d, *J*=6.6 Hz, 3 H); ^{13}C NMR (75MHz) δ 152.1, 146.8, 141.6, 126.1, 125.8, 120.0, 114.8, 114.8, 55.7, 50.3, 23.5; HRMS calculated for $C_{13}H_{16}NOS$: 234.0953, found: 234.0958.

***N*-(3-methylbutan-2-yl)-pyridin-2-amin (20)**

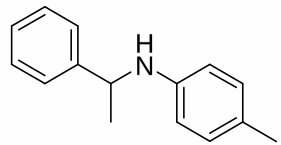


^{1}H NMR (300 MHz) δ 8.02 (dd, *J*=4.9, 0.9 Hz, 1 H) 7.38 (ddd, *J*=8.6, 6.9, 1.9 Hz, 1 H) 6.50 (ddd, *J*=7.0, 5.1, 0.9 Hz, 1 H) 6.34 (d, *J*=8.5 Hz, 1 H) 5.42 (br s, 1 H), 3.54 - 3.65 (ddq, *J*=8.9, 6.6, 5.1 Hz, 1 H) 1.81 (dsept, *J*=6.8, 5.1 Hz, 1 H) 1.12 (d, *J*=6.6 Hz, 3 H) 0.96 (d, *J*=6.9 Hz, 3 H) 0.92 (d, *J*=6.9 Hz, 3 H); ^{13}C NMR (75MHz) δ 158.4, 147.9, 137.6, 112.2, 106.7, 52.2, 32.9, 18.9, 18.0, 17.1; HRMS calculated for $C_{10}H_{17}N_2$ $[M+H]^+$: 165.1392, found: 165.1394.

2-(4-(3-Methylbutan-2-ylamino)-phenyl)-acetic acid (22)



^{1}H NMR (400 MHz) δ 7.05 (d, *J*=8.6 Hz, 2 H) 6.52 (d, *J*=8.1 Hz, 2 H) 6.29 (br s, 2 H), 3.50 (s, 2H), 3.30 (dq, *J*=6.3, 5.6 Hz, 1 H) 1.83 (dsept, *J*=6.8, 5.5 Hz, 1 H) 1.08 (d, *J*=6.6 Hz, 3 H) 0.95 (d, *J*=7.1 Hz, 3 H) 0.90 (d, *J*=7.1 Hz, 3 H); ^{13}C NMR (100 MHz) δ 177.7, 147.0, 130.2, 121.2, 113.2, 53.6, 32.3, 19.1, 17.5, 16.6; HRMS calculated for $C_{13}H_{20}NO_2$: 221.1494 $[M+H]^+$, found: 221.1480.


H
N

9

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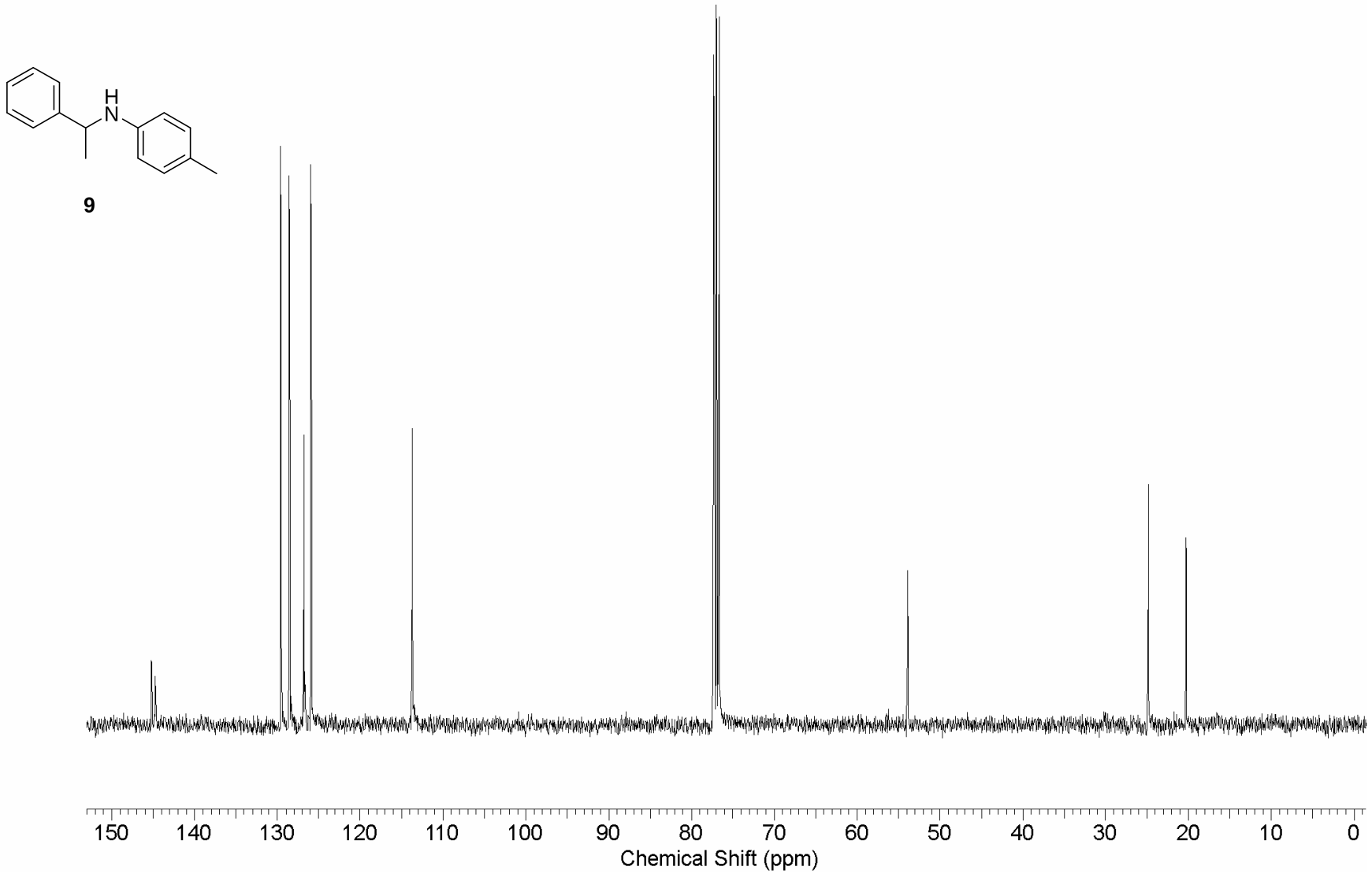
Chemical Shift (ppm)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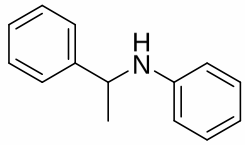
Chemical Shift (ppm)



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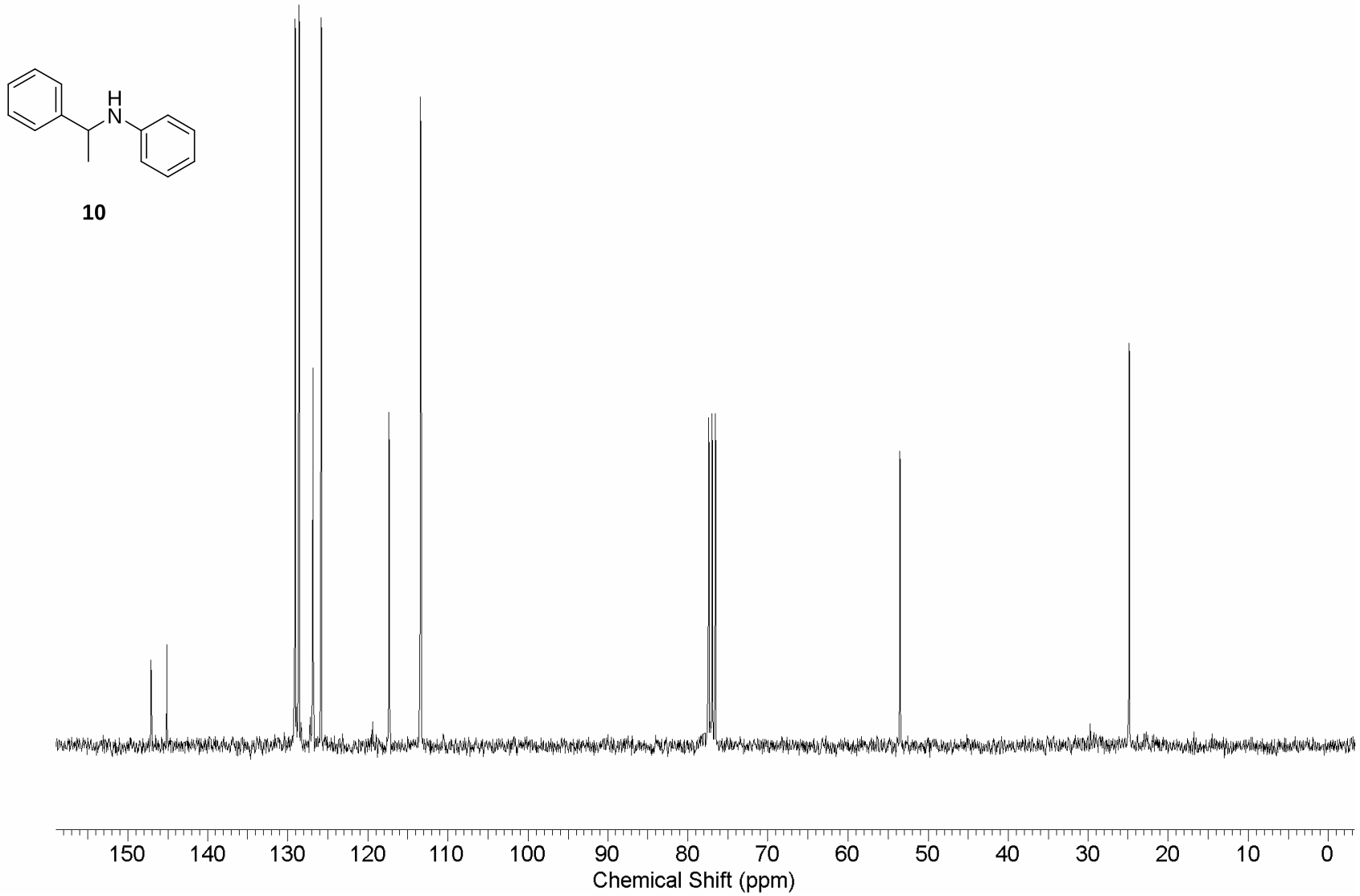
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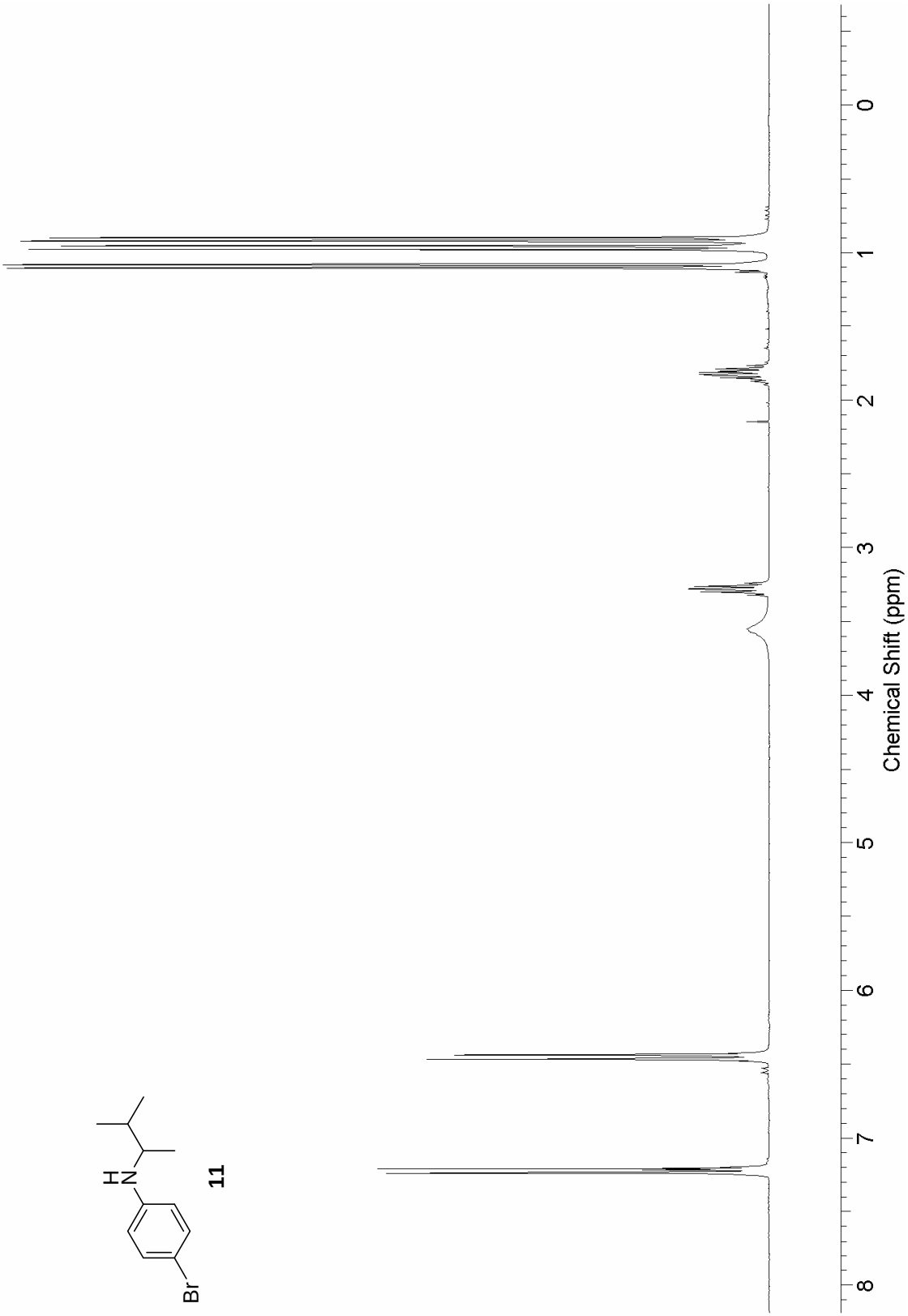
Chemical Shift (ppm)

10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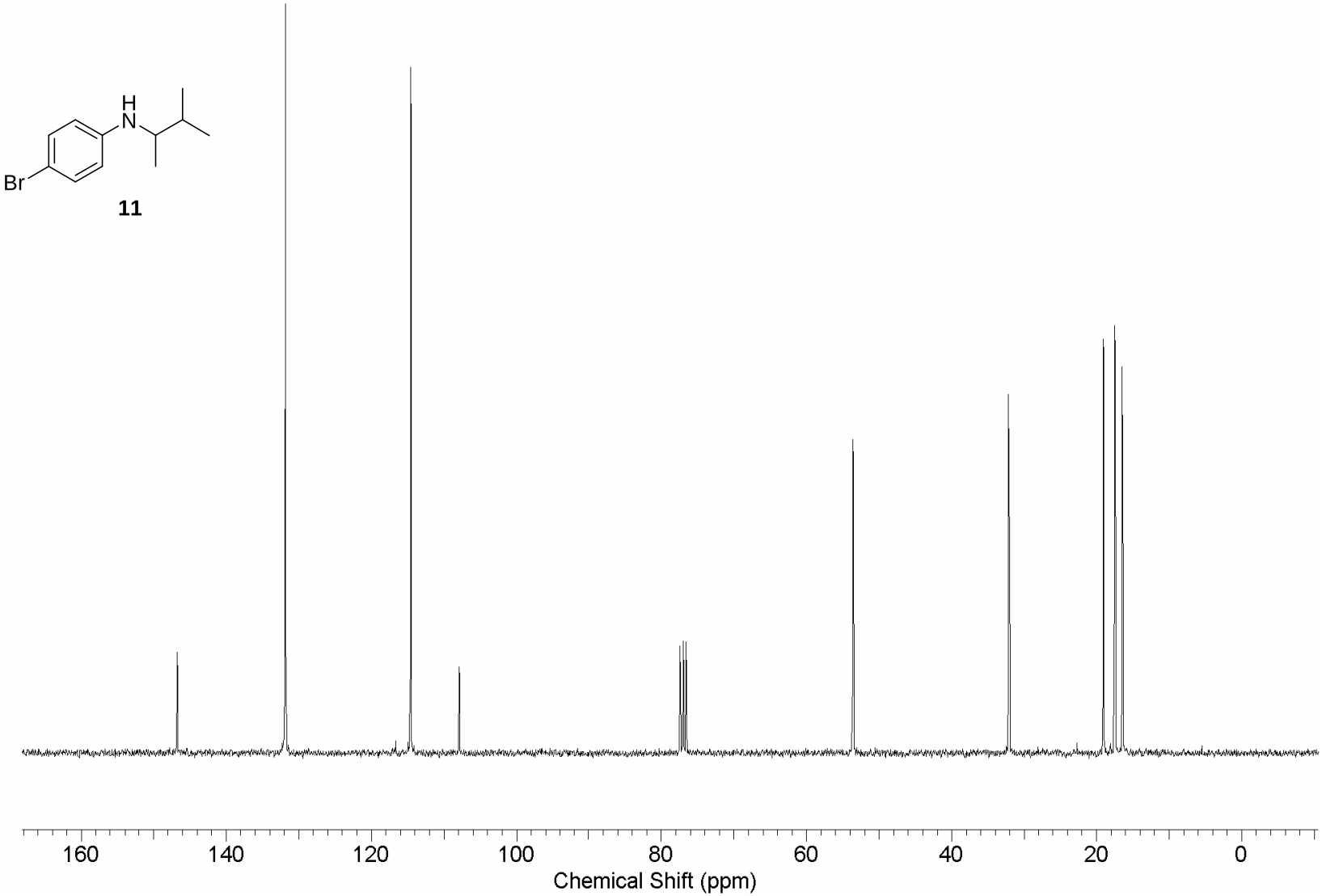
Chemical Shift (ppm)



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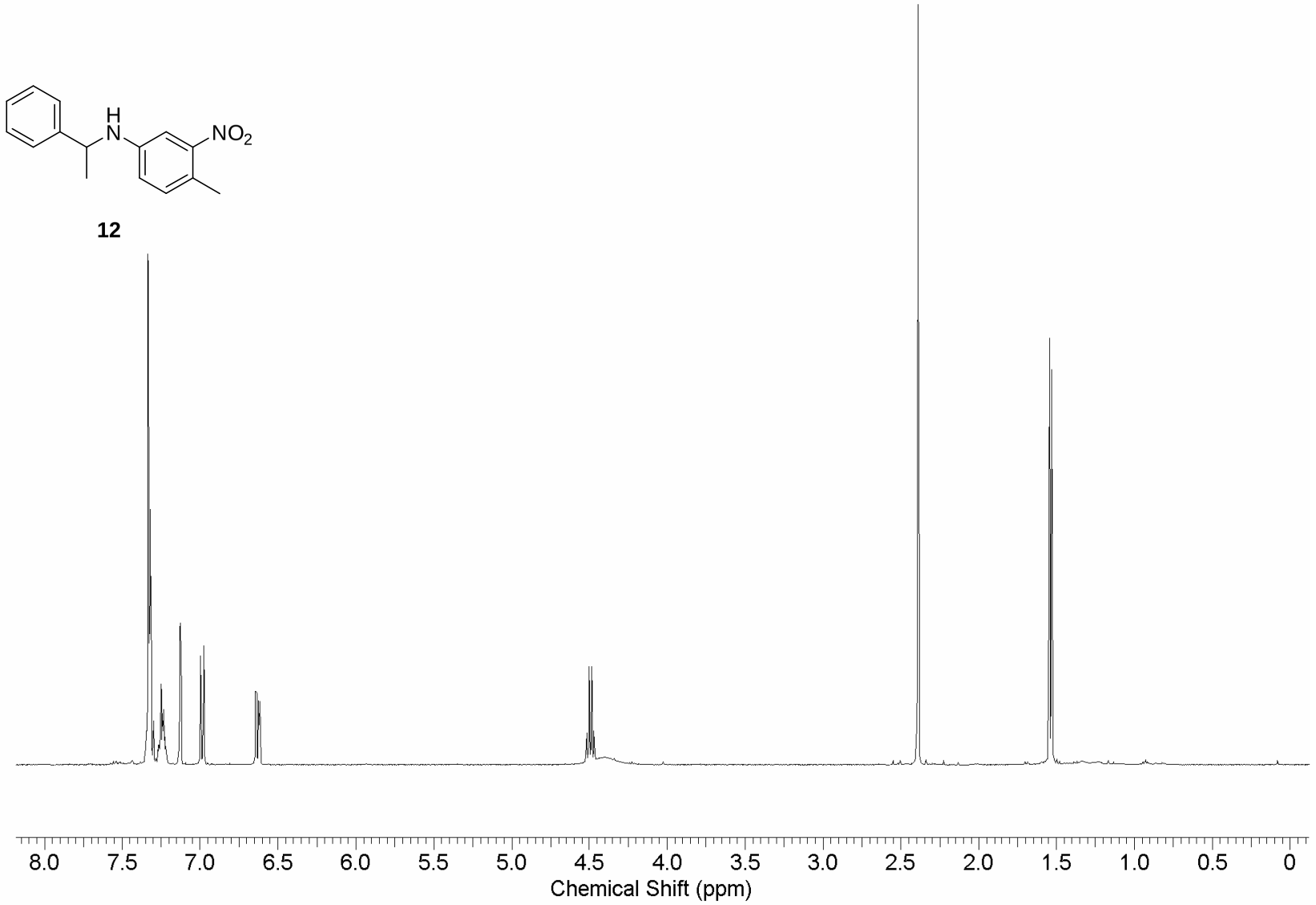
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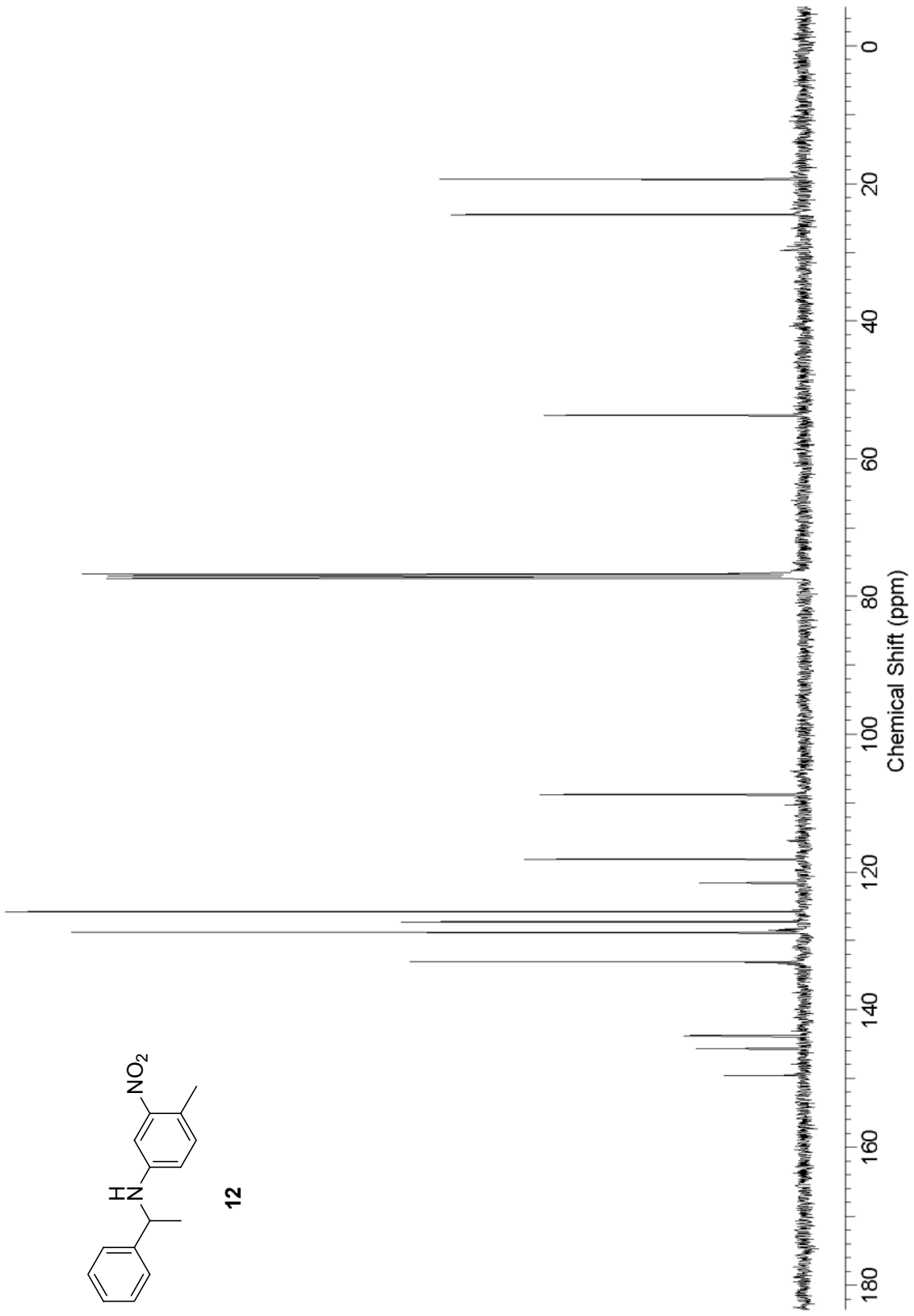
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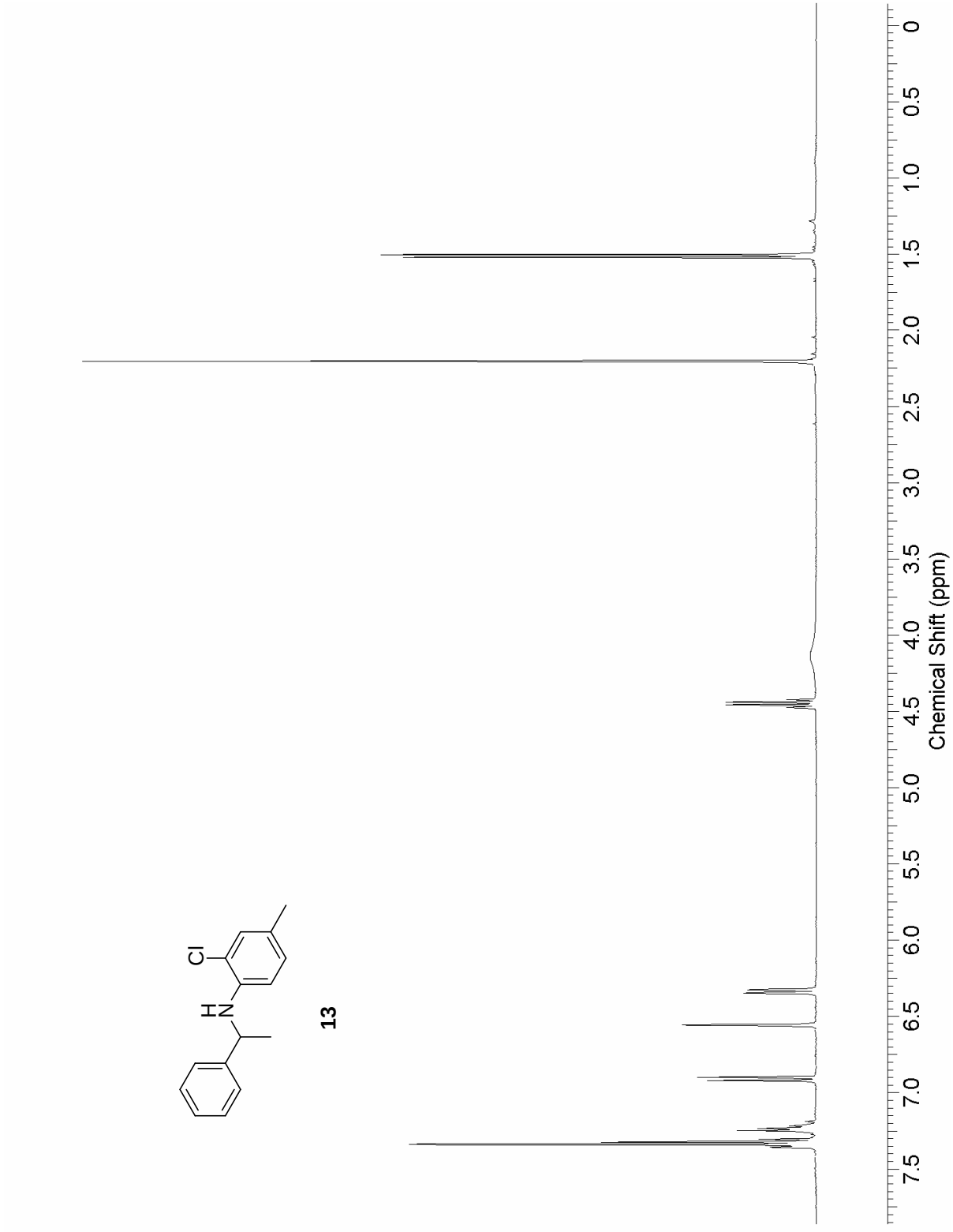
Chemical Shift (ppm)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1.0
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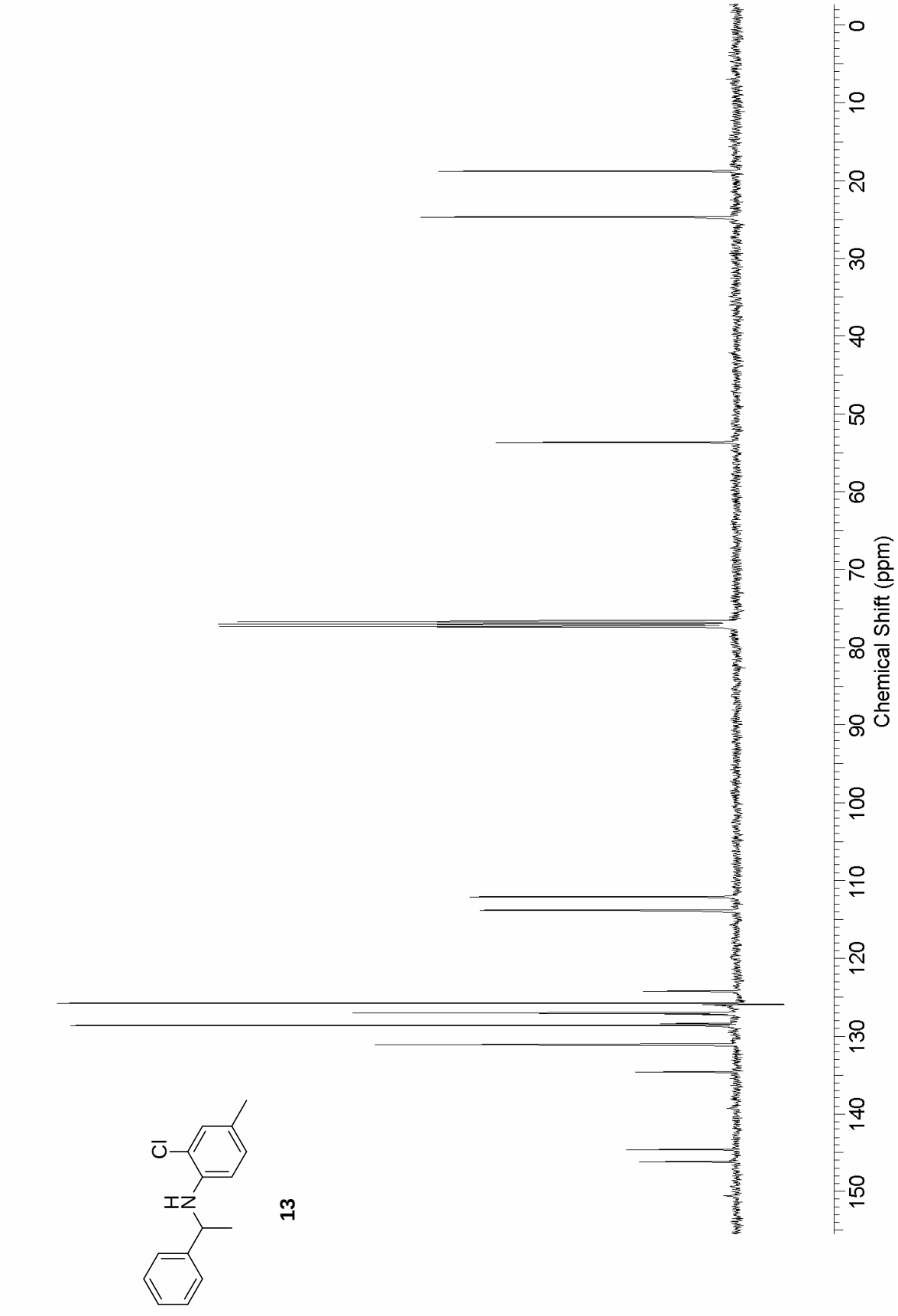
0
Chemical Shift (ppm)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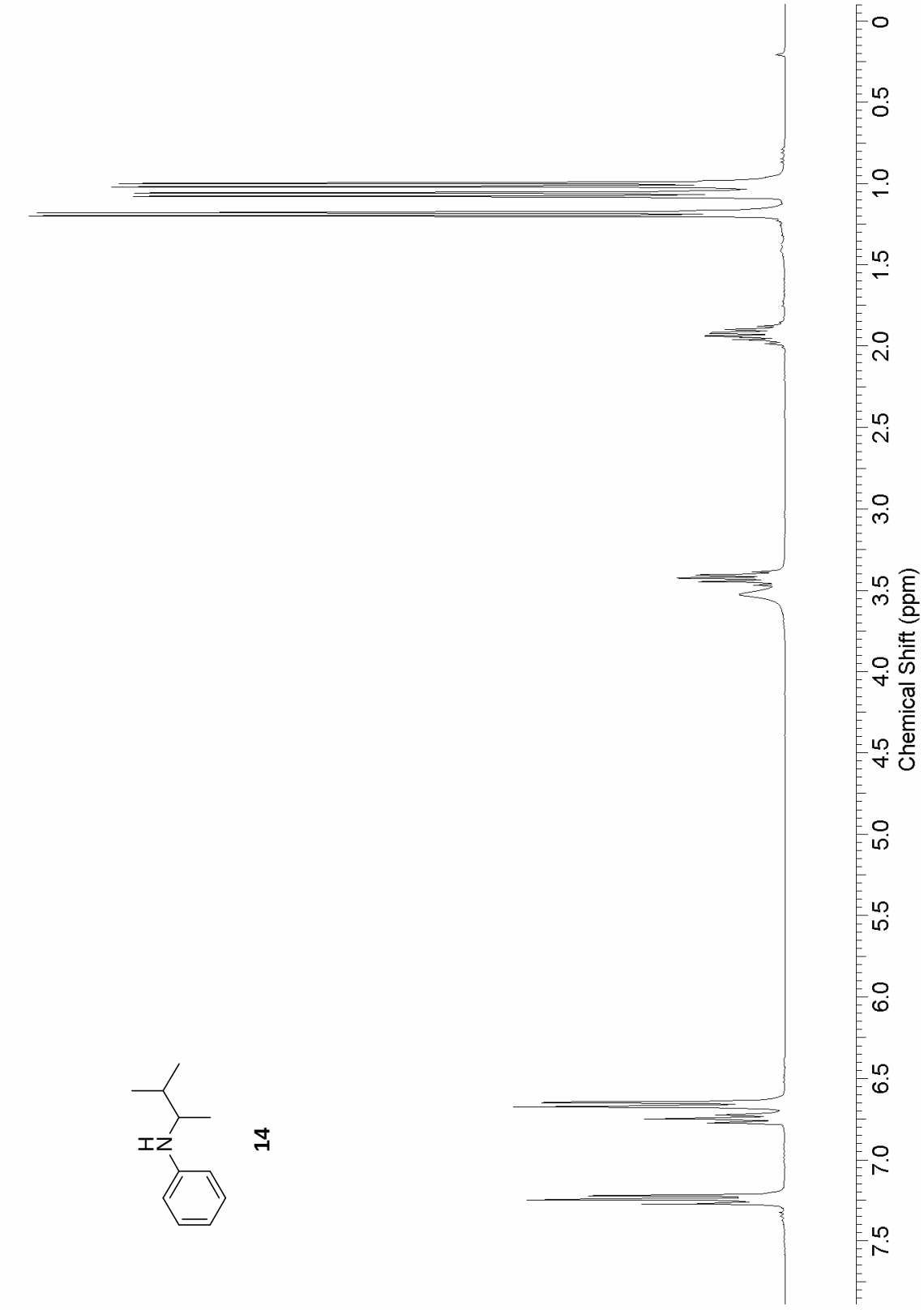
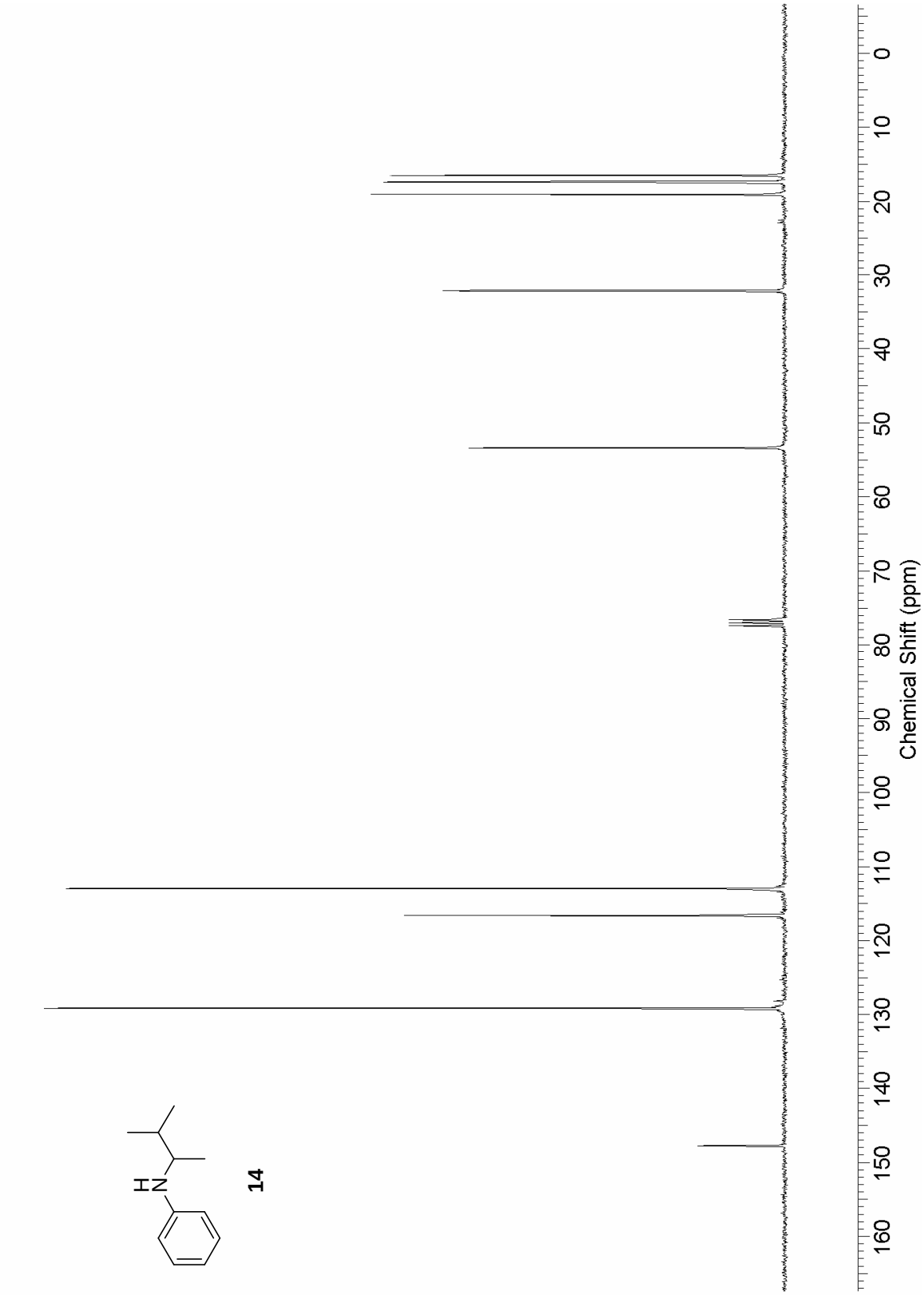
Chemical Shift (ppm)



14


Chemical Shift (ppm)
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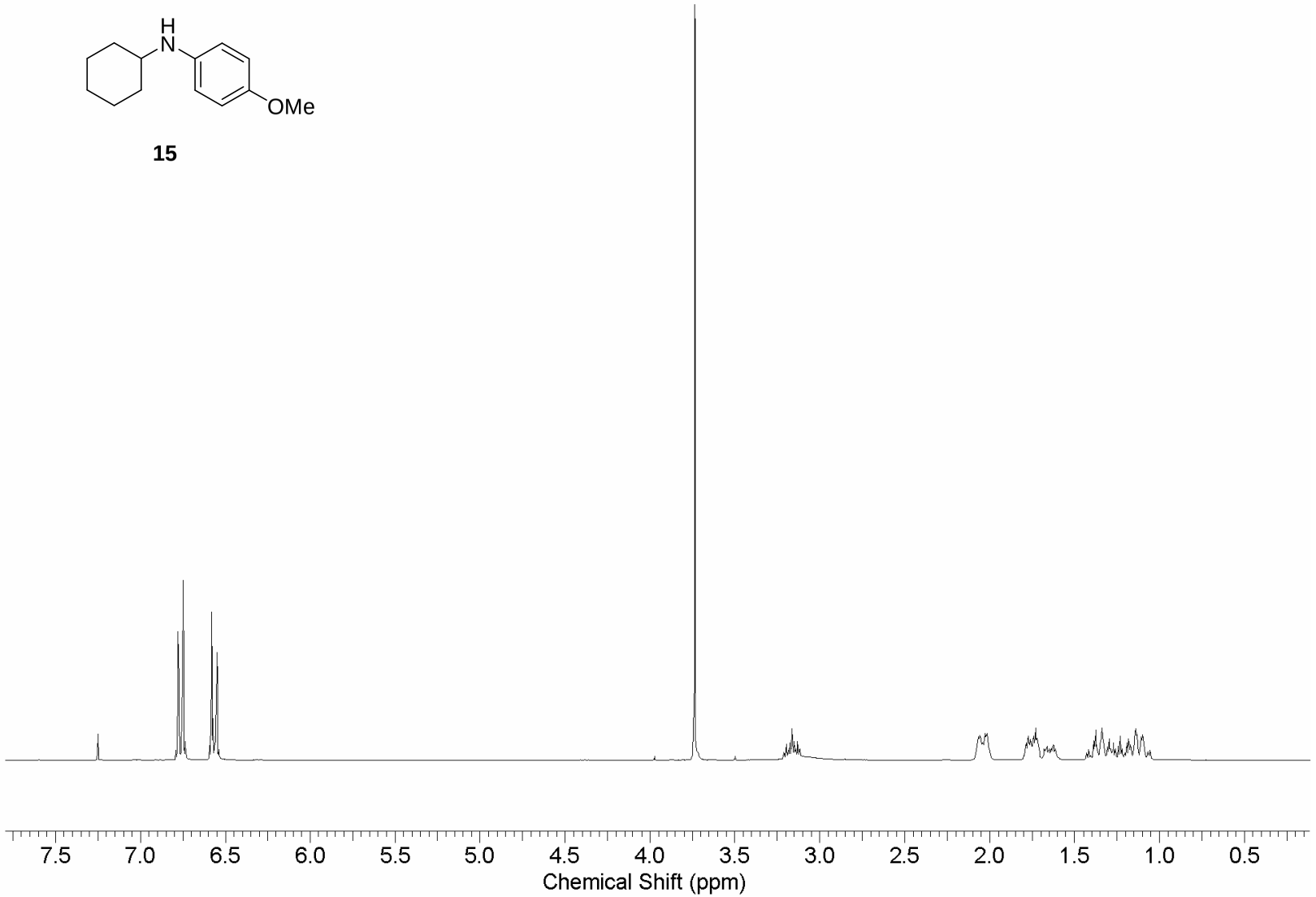
H
N

14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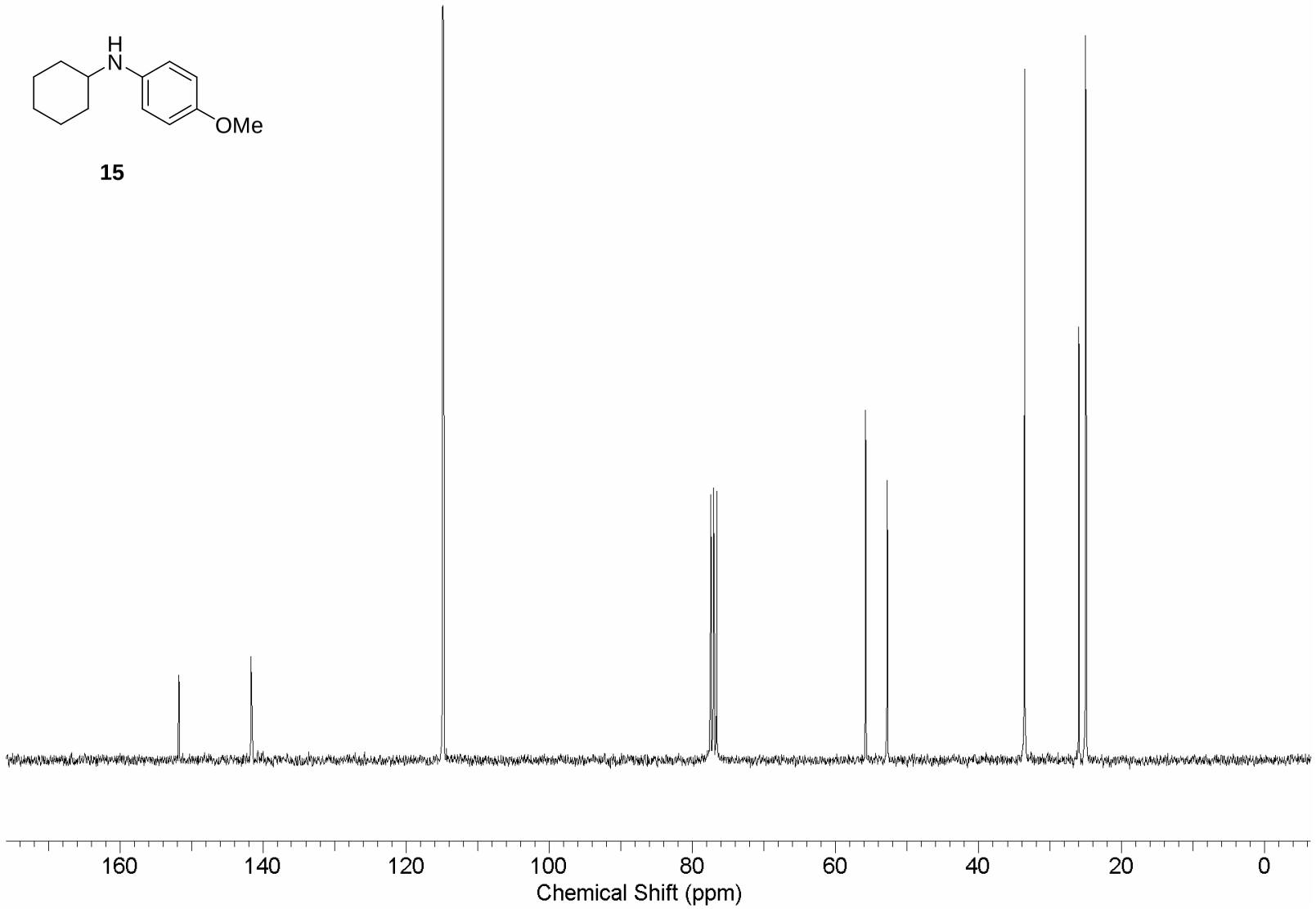
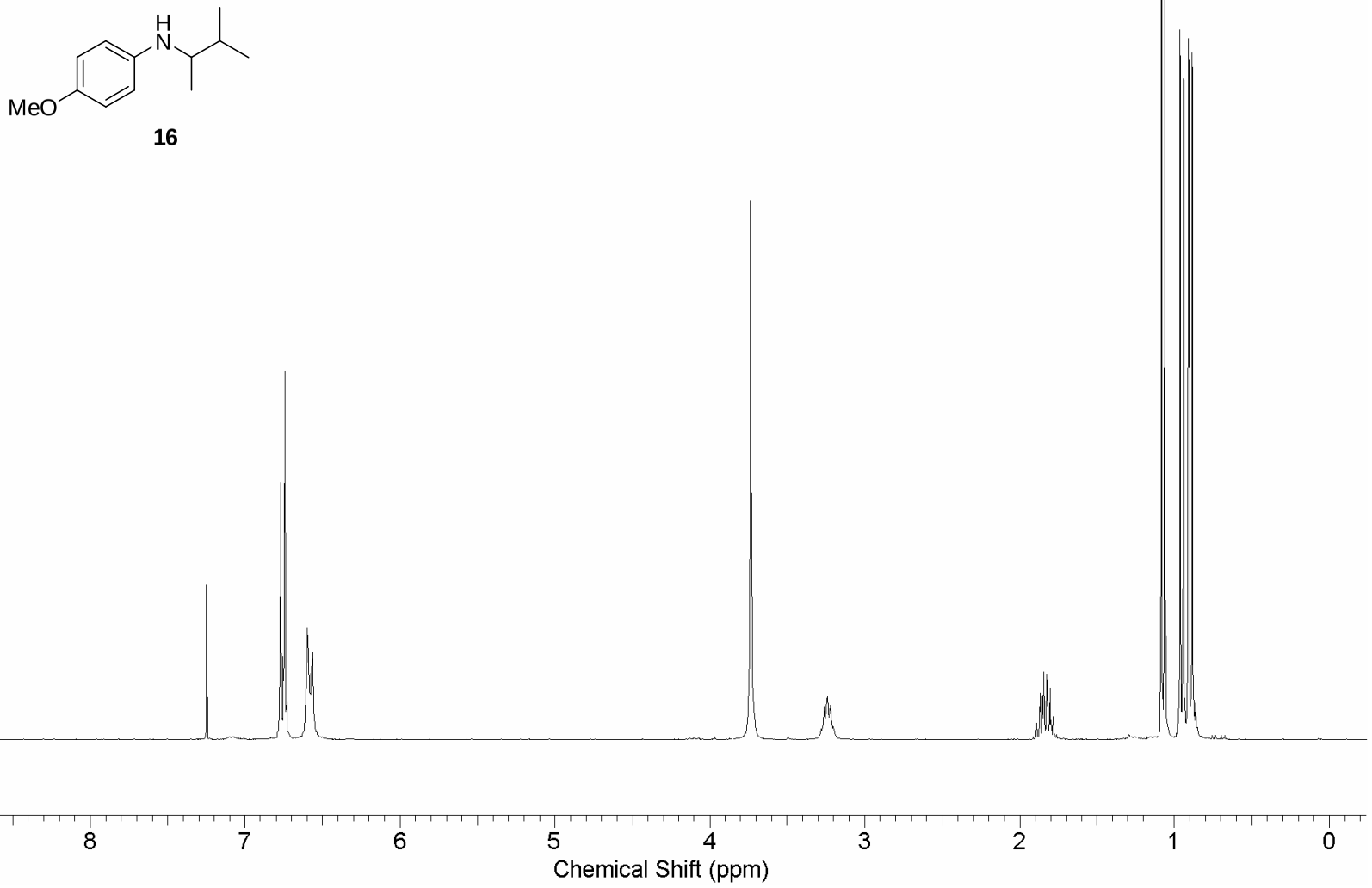
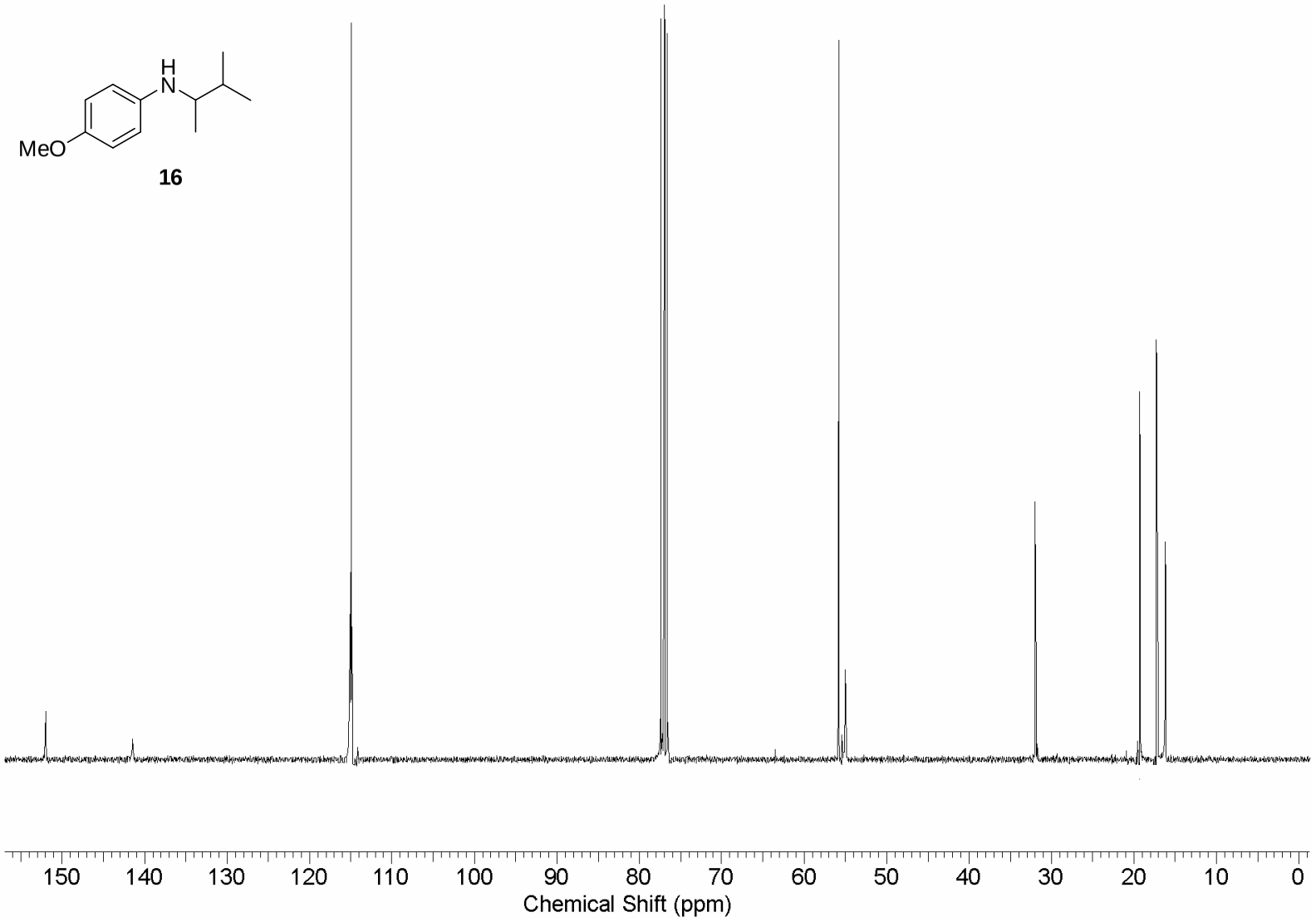
1.5
1.0
0.5
Chemical Shift (ppm)

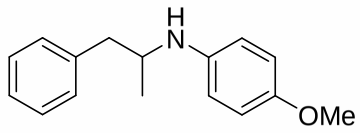
15



15

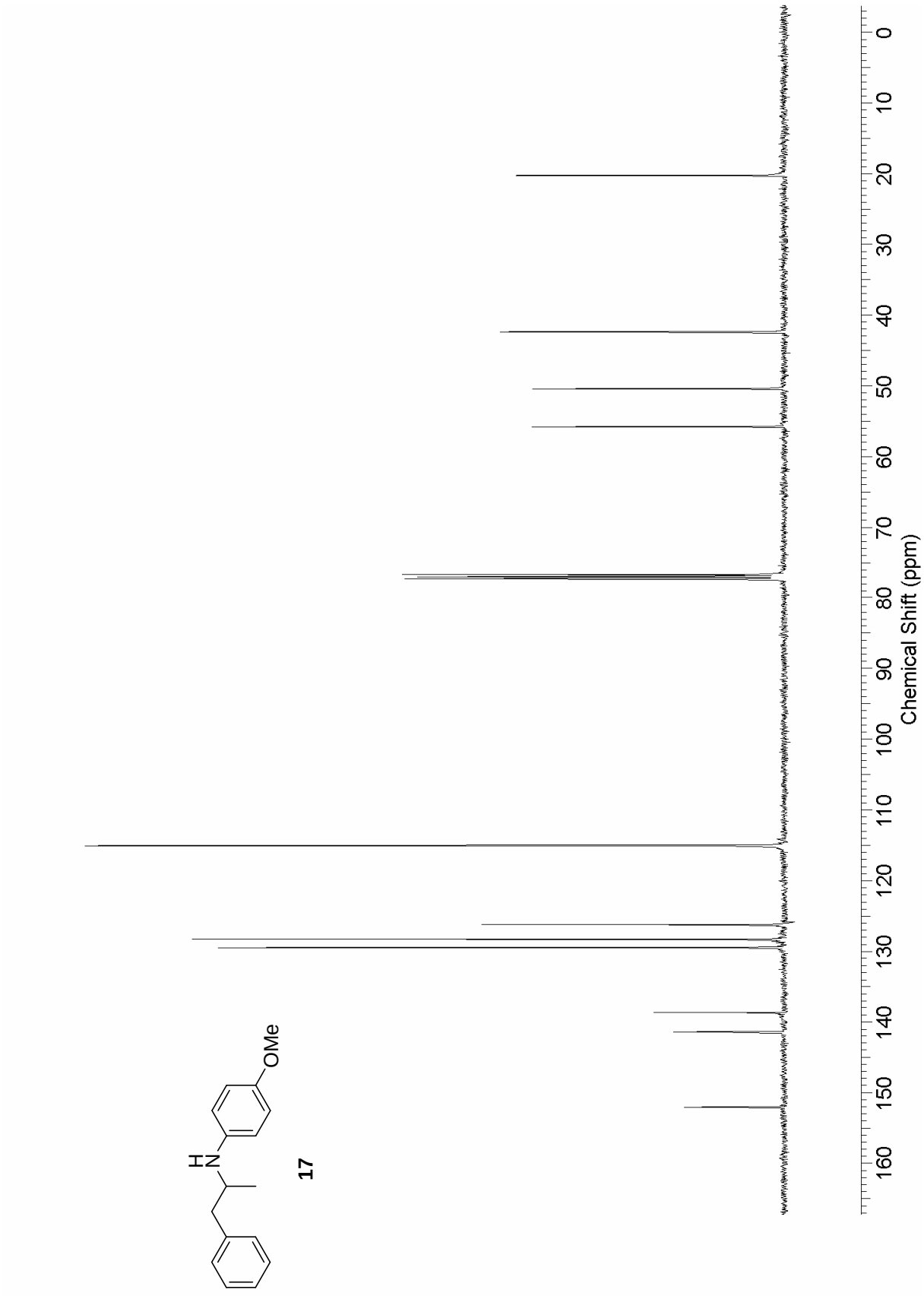

MeO
H
N
16
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

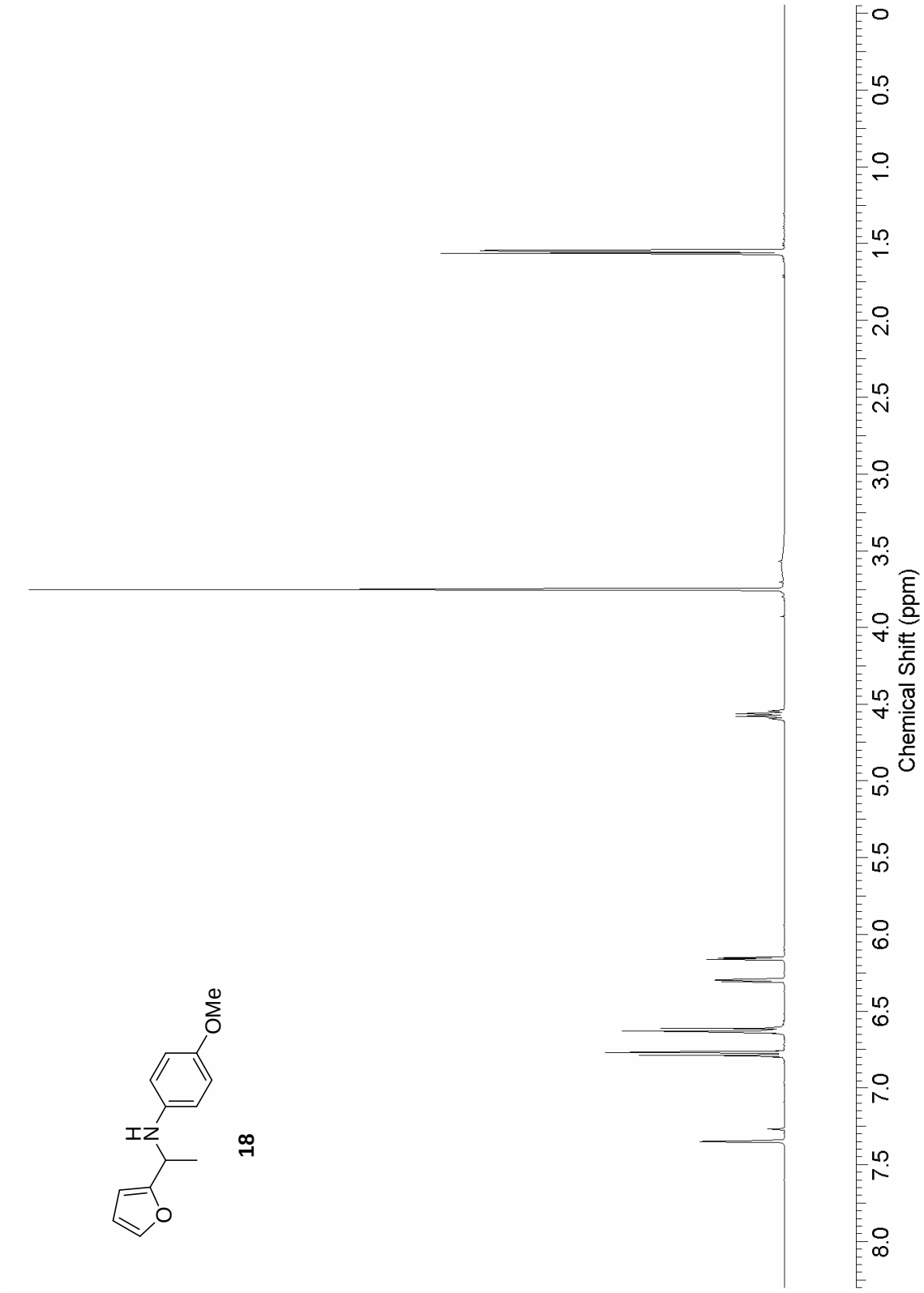

H
N
MeO
16
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

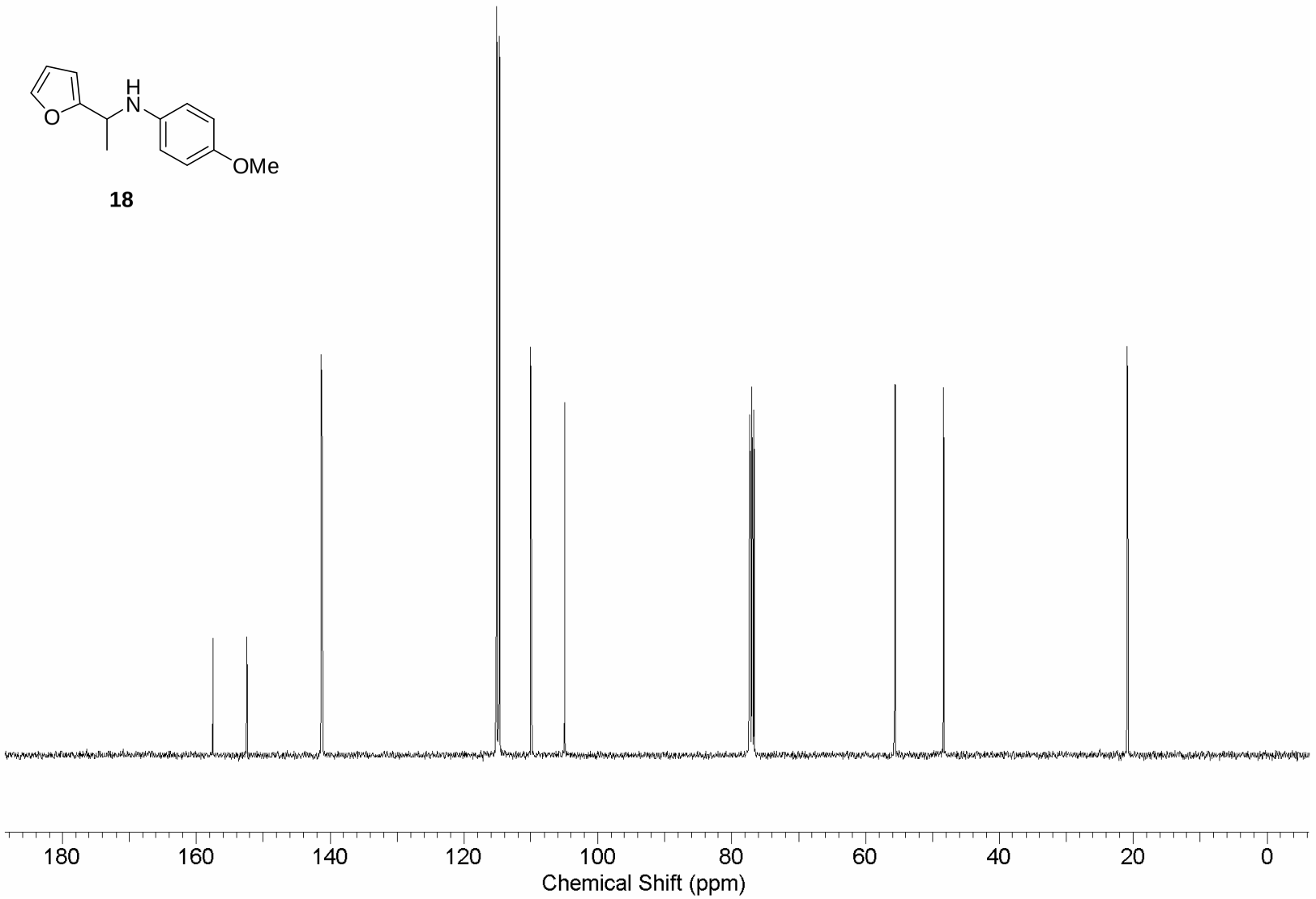

H
N
OMe

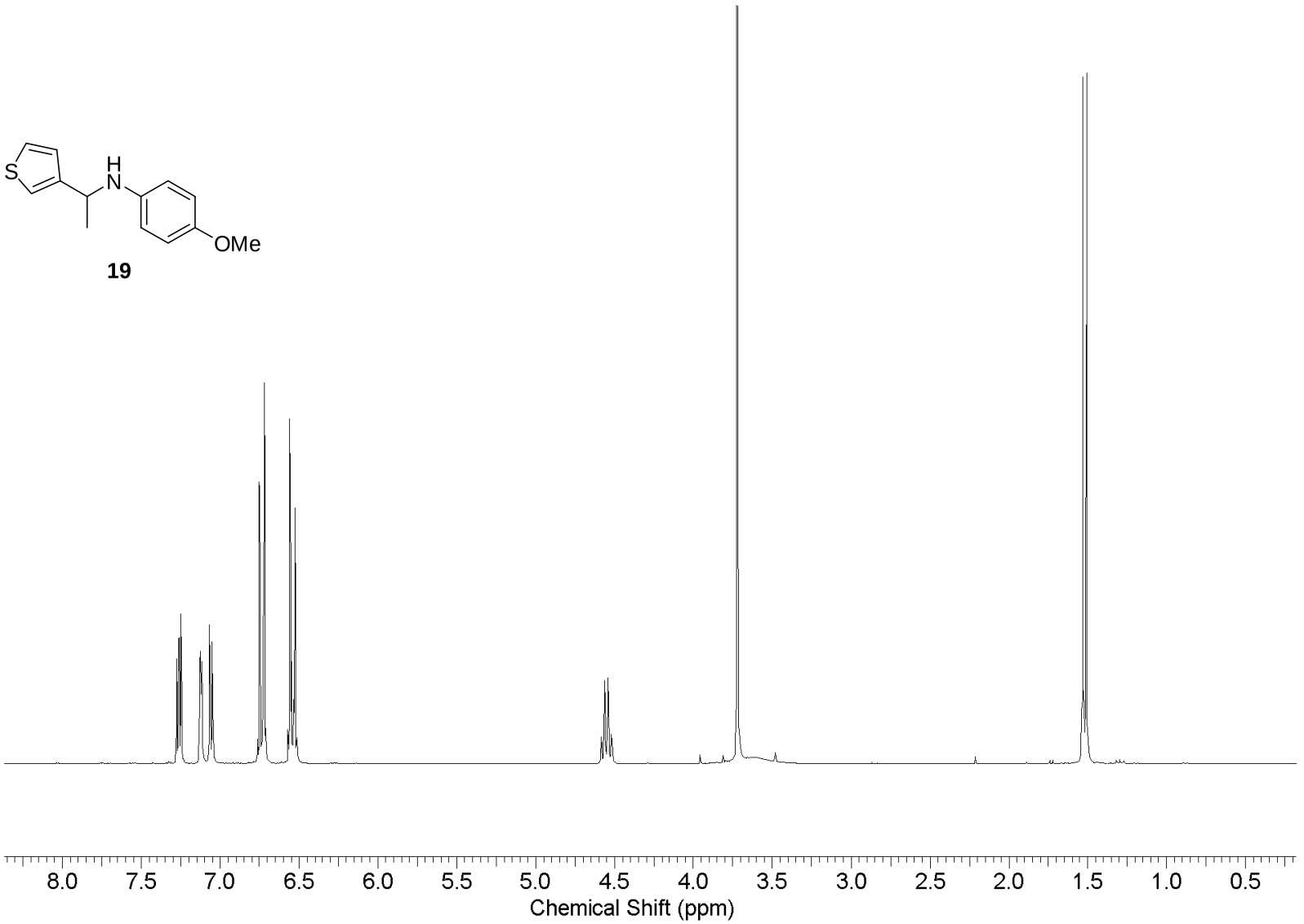
17

8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

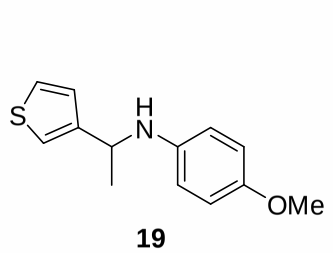

OMe
H
N
17
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
Chemical Shift (ppm)


OMe
H
N
O
18
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

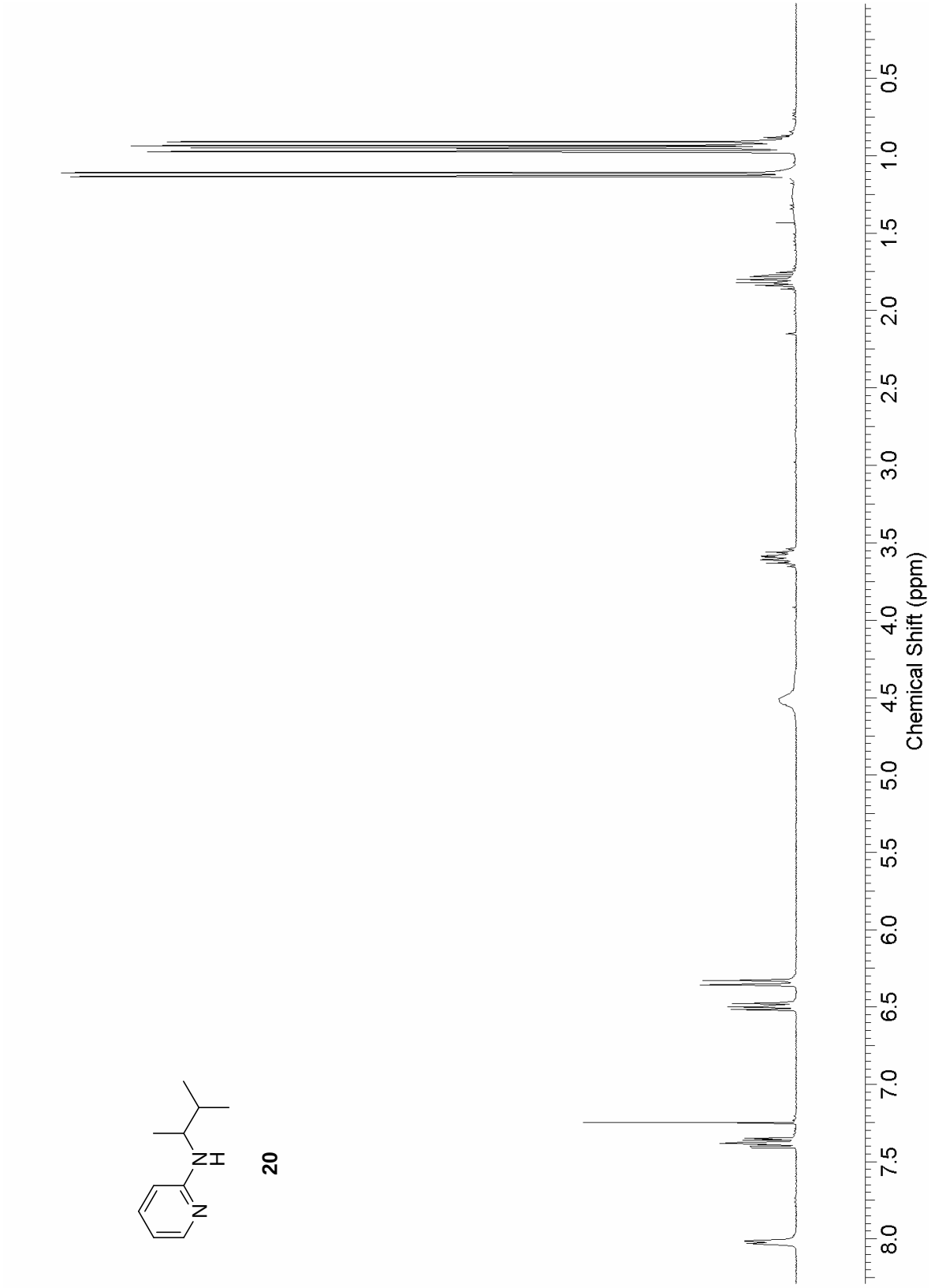

H
N
O
OMe
18
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

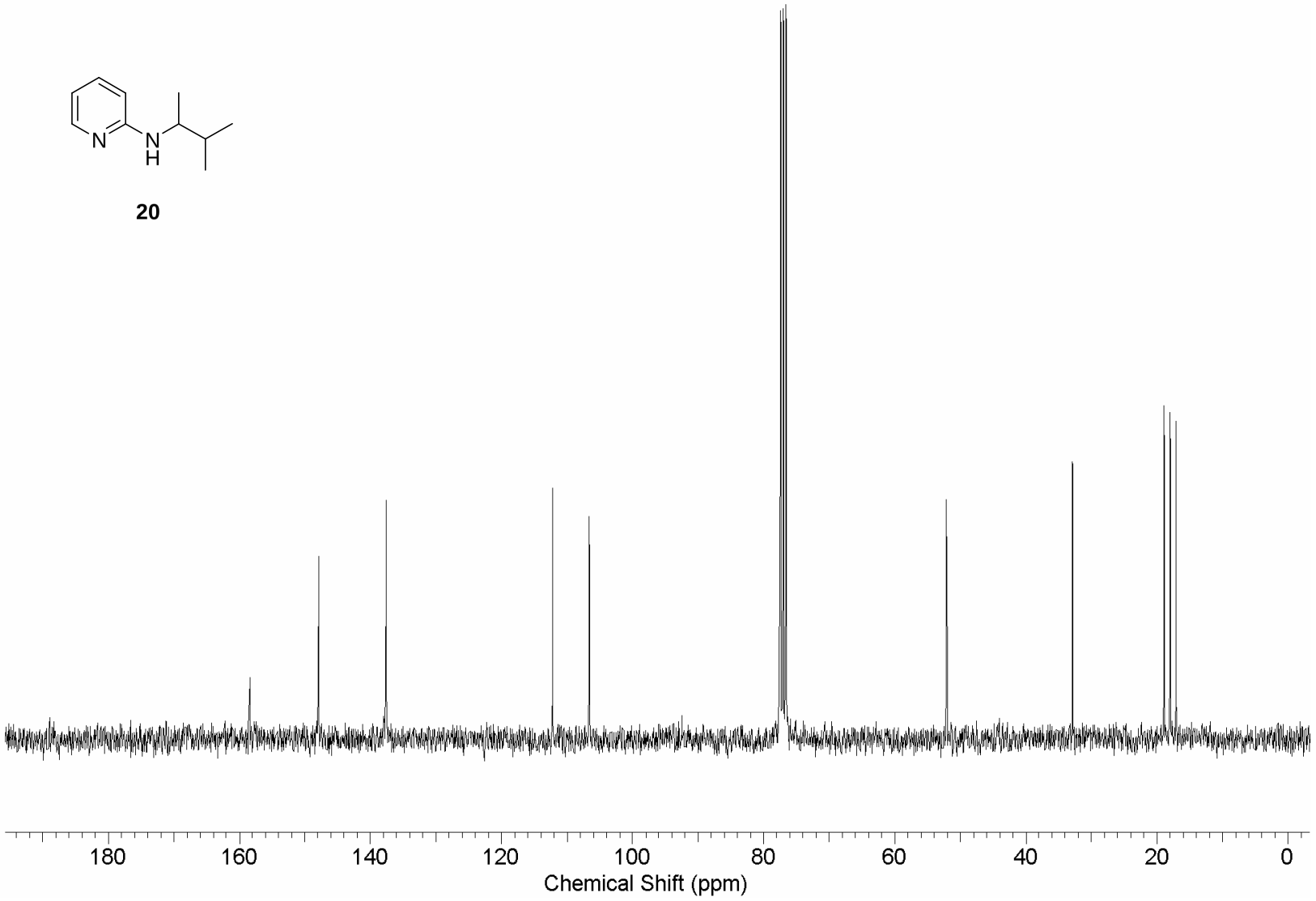

S
H
N
OMe
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)

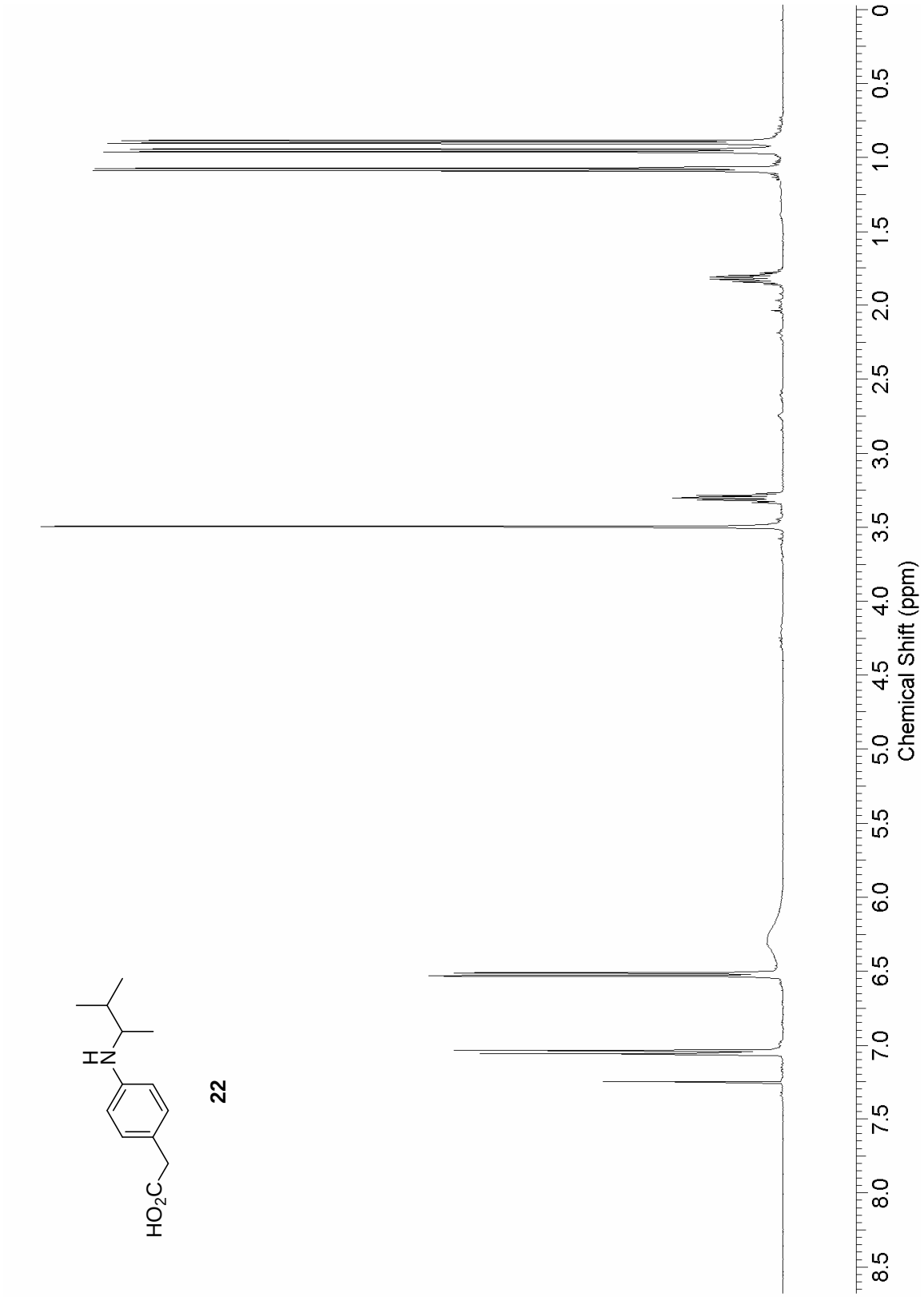
19



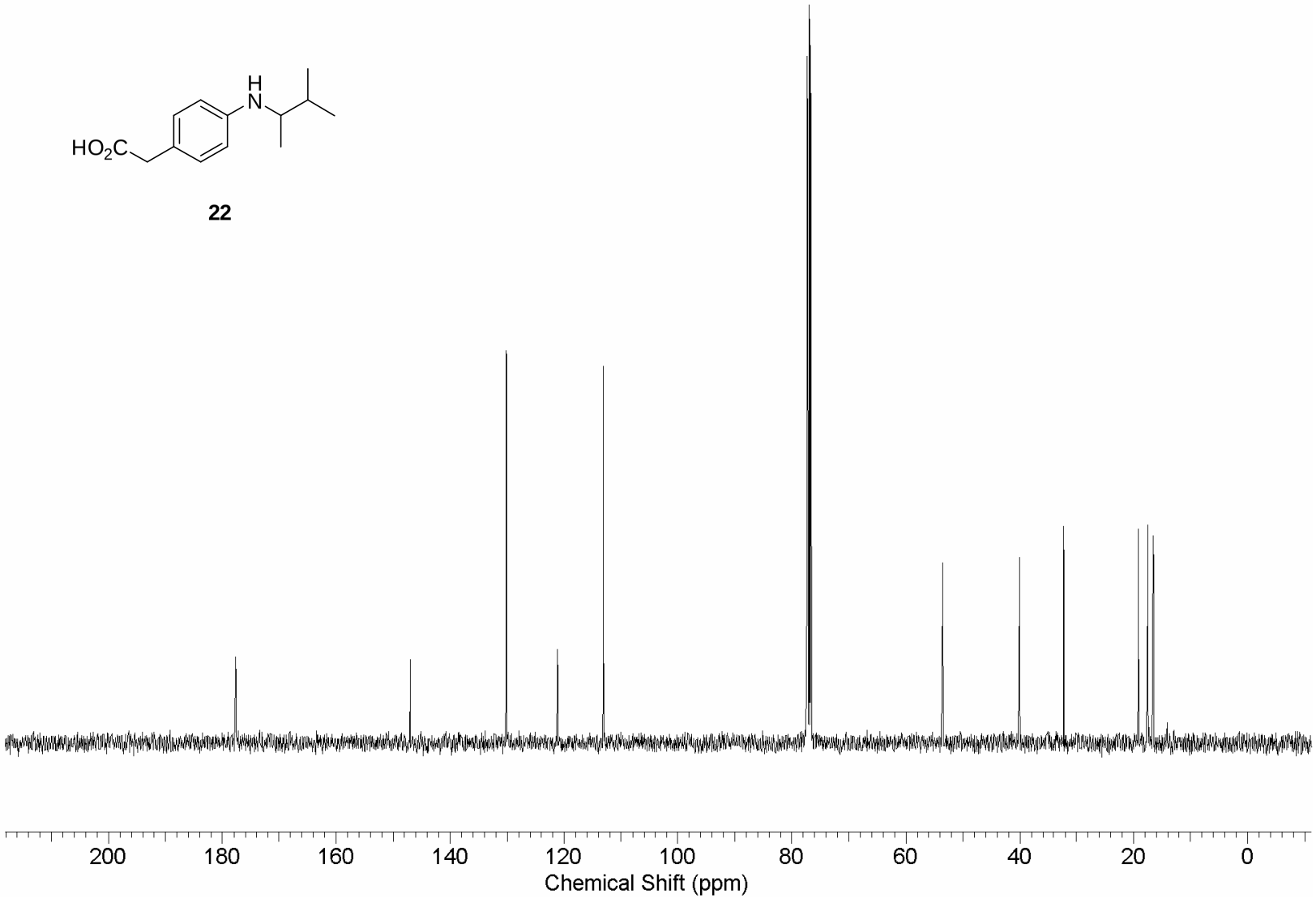
19


N
H
N
20
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)


N
N
H
20
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


HO2C
H
N
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

22


HO2C
H
N
22
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)