Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Electronic Supplementary Information for:

Nickel-catalyzed cross-coupling of O, N-chelated diarylborinates with aryl chlorides and mesylates

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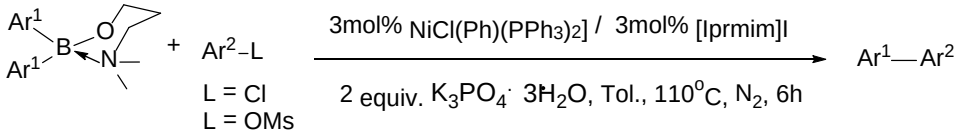
Contents

1. General information

All reactions were carried out under nitrogen by using standard Schlenk techniques unless otherwise stated. Commercially available chemicals were used as received. *trans*-NiCl(Ph)(PPh_3)$_2$, *trans*-NiCl(1-Nath)(PPh_3)$_2$, *trans*-NiCl(Ph)(PCy_3)$_2$, *trans*-NiCl(*o*-Tol)(PPh_3)$_2$, *trans*-NiCl(*o*-Tol)(PCy_3)$_2$, *trans*-NiCl(*o*-Tol)(dppf), $NiCl_2(PPh_3)_2$, 1a-1j, 4a-4g, 4a' , N-heterocyclic carbene precursors of [Bmim]Br, [Omim]Br, [diOim]Br, [diBim]Br, IMes·HCl, IPr·HCl, [Iprmim]I, [Ipreim]Br, [Iprbim]Br, [Mesmim]I, were prepared according to previously reported procedures. Column chromatograph was performed on 300-400 mesh silica gal. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 at ambient temperature. Chemical shifts in NMR are reported in ppm (δ), relative to the internal standard of tetramethylsilane (TMS). The signals observed are described as s (singlet), d (doublet), t (triplet), q (quartet), dd (double doublet), m (multiplets). The number of protons (n) for a given resonance is indicated as nH. Coupling constants are reported as *J* in Hz.

2. Typical procedure for cross-coupling



Under a N_2 atmosphere, to a 10 ml dry flask were added aryl chloride/mesylates (1 mmol), diarylborinates (0.65 mmol), NiCl(Ph)(PPh_3)$_2$ (3mol%), [Iprmim]I (3mol%), $K_3PO_4{\cdot}3H_2O$ (2 mmol), and dry toluene (5 ml). The mixture was stirred at 110℃ for a given time or monitored by TLC until the starting material was completely consumed. The reaction mixture was diluted with CH_2Cl_2 (15 ml), followed by washing with H_2O (3×10 ml). The organic layer was dried over Na_2SO_4, filtered, and evaporated under reduced pressure to give crude product, which was purified by column chromatography on silica gel to afford biaryl compounds.

3. Characterization data of biaryl compounds

4-Acetylbiphenyl 3aa[1] White solid (0.1904g, 97%), mp 121-123^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.4 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 7.6 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 1H), 2.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 145.8, 139.9, 135.9, 128.99, 128.95, 128.3, 127.3, 127.2, 26.7.

2-Acetylbiphenyl 3ab[2] Yellow oil (0.1668g, 85%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.49 (m, 2H), 7.43-7.38 (m, 5H), 7.34 (dd, *J* = 1.6, 7.6 Hz, 2H), 2.0 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.9, 140.9, 140.8, 140.5, 130.8, 130.3, 128.9, 128.7, 127.93, 127.91, 127.5, 30.5.

3-Acetylbiphenyl 3ac[2] Yellow oil (0.1766g, 90%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (t, *J* = 1.6 Hz, 1H), 7.92 (dd, *J* = 1.6, 8.0 Hz, 1H), 7.80-7.78 (m, 1H), 7.61(d, *J* = 7.2 Hz, 2H), 7.53 (t, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.40-7.36 (m, 1H); 2.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1, 141.7, 140.2, 137.6, 131.8, 129.1, 129.0, 127.9, 127.3, 127.0, 26.8.

Biphenyl-4-carbaldehyde 3ad[1] Yellow solid (**1a**/**2d** (0.1676g, 92%), **1a**/**4b** (0.1658g, 91%)), mp 57-58^{o}C; ^{1}H NMR

(400 MHz, $CDCl_3$) δ 10.05 (s, 1H), 7.95 (d, J = 8.4 Hz, 2H), 7.75 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 7.2 Hz, 2H), 7.48 (t, J = 7.6 Hz, 2H), 7.42 (t, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.9, 146.1, 138.7, 134.1, 129.2, 128.0, 127.4, 126.6, 126.3.

Methyl biphenyl-4-carboxylate 3ae[1] White solid (**1a**/**2e** (0.1974g, 93%), **1a**/**4c** (0.2059g, 97%)), mp 114-115^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 8.4 Hz, 2H), 7.67-7.61 (m, 4H), 7.47 (t, J = 7.2 Hz, 2H), 7.39 (t, J = 7.2 Hz, 1H), 3.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 145.6, 140.0, 130.1, 129.0, 128.9, 128.2, 127.3, 127.1, 52.2.

4-Nitrobiphenyl 3af[3] Yellow solid (0.1833g, 92%), mp 113-114^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, J = 8.8 Hz, 2H), 7.75-7.71 (m, 2H), 7.64-7.61 (m, 2H), 7.52-7.42 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 147.1, 138.8, 129.2, 129.0, 127.8, 127.4, 124.1.

2-Nitrobiphenyl 3ag[4] Yellow oi (0.1534g, 77%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, J = 1.2, 8.0 Hz, 1H), 7.63-7.59 (m, 1H), 7.49-7.39 (m, 5H), 7.33-7.30 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 137.4, 136.3, 132.4, 132.0, 128.7, 128.3, 128.2, 127.9, 124.1.

4-Methylbiphenyl 3ah[5] White solid (**1a**/**2h** (0.1598g, 95%), **1a**/**4d** (0.1615g, 96%)), mp 46-48^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, J = 1.6, 8.4 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 7.42 (t, J = 7.2 Hz, 2H), 7.31 (t, J = 7.6 Hz, 1H), 7.22 (d, J = 6.0 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.3, 138.5, 137.1, 129.6, 128.8, 127.1, 127.0, 21.2.

2-Methylbiphenyl 3ai[5] Colorless oil (**1a**/**2i** (0.1346g, 80%), **1a**/**4e** (0.1380g, 82%)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.38 (m, 2H), 7.34-7.30 (m, 3H), 7.26-7.22 (m, 4H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 135.4, 130.4, 129.9, 129.3, 128.2, 127.4, 126.9, 125.9, 20.6.

2,6-Dimethylbiphenyl 3aj[6] Colorless oil (0.0729g, 40%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (t, J = 7.2 Hz, 2H), 7.35-7.30 (m, 1H), 7.15-7.09 (m, 5H), 2.03 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 141.2, 136.1, 129.1, 128.5, 127.4, 127.1, 126.7, 21.0.

4-Methoxybiphenyl 3ak[1] White solid (**1a**/**2k** (0.1713g, 93%), **1a**/**4f** (0.1732g, 94%)), mp 88-89^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.51 (m, 4H), 7.40 (t, J = 8.0 Hz, 2H), 7.30 (t, J = 7.6 Hz, 1H), 6.97 (dd, J = 2.0, 6.8 Hz, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 140.9, 133.8, 128.8, 128.2, 126.8, 126.7, 114.3, 55.4.

2-Phenylanisole 3al[2] White solid, (0.1474g, 80%), mp 29-30^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.52 (m, 2H); 7.42-7.38 (m, 2H), 7.33-7.30 (m, 3H), 7.05-7.00(m, 2H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 138.6, 130.9, 130.7, 129.6, 128.7, 128.0, 127.0, 120.9, 111.2, 55.6.

1-(2'-Methylbiphenyl-4-yl)ethenone 3ca[5] Colourless oil (**1c**/**2a** (0.1598g, 76%), **1c**/**4a** (0.1619g, 77%)); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.01 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 7.30-7.21 (m, 4H), 2.65 (s, 3H), 2.27 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.0, 147.0, 140.8, 135.6, 135.2, 130.6, 129.52, 129.49, 128.2, 128.0, 126.0, 26.7, 20.4.

1-(3'-Methylbiphenyl-4-yl)ethenone 3da[5] White solid (**1d**/**2a** (0.1935g, 92%), **1d**/**4a** (0.1930g, 92%)), mp 50-61^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.01 (d, J = 8.4 Hz, 2H), 7.67 (d, J = 8.8 Hz, 2H), 7.42 (d, J = 8.8 Hz, 2H), 7.35 (t, J = 7.2 Hz, 1H), 7.21 (d, J = 7.6 Hz, 1H), 2.63 (s, 3H), 2.43 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 197.8, 146.0, 139.9, 138.6, 135.8, 129.0, 128.9, 128.0, 127.2, 124.4, 26.7, 21.6.

1-(4'-Methylbiphenyl-4-yl)ethenone 3ea[5] White solid (0.1914g, 91%), mp 118-120°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.0 Hz, 2H), 7.66 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 2.63 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 145.7, 138.3, 136.9, 135.6, 129.7, 129.0, 127.1, 126.9, 26.7, 21.2.

1-(4'-Methoxybiphenyl-4-yl)ethanone 3fa[1] White solid (**1f**/**2a** (0.2036g, 90%), **1f**/**4a**, (0.2082g, 92%)), mp 156-158°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 8.8 Hz, 2H), 6.99 (d, J = 8.8 Hz, 2H), 3.85 (s, 3H), 2.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 139.5, 135.4, 129.7, 128.9, 128.8, 128.3, 126.6, 114.4, 55.4, 26.6.

1-(2'-Methoxybiphenyl-4-yl)ethanone 3ga[1] White solid (**1g**/**2a** (0.1674g, 74%), **1g**/**4a,** (0.1788g, 79%)), mp 105-106°C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.00 (d, J = 8.8 Hz, 2H), 7.63 (d, J = 8.4 Hz, 2H), 7.38-7.32 (m, 2H), 7.07-6.99 (m, 2H), 3.82 (s, 3H), 2.63 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.0, 156.5, 143.6, 135.5, 130.7, 129.8, 129.5, 129.4, 128.1, 121.0, 111.3, 55.6, 26.7.

1-(4'-trifluoromethyl-4-yl)ethanone 3ha[7] White solid (**1h**/**2a** (0.1797, 68%), **1h**/**4a** (0.1982g 75%)), mp 122-123°C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.06 (d, J = 7.6 Hz, 2H), 7.73-7.68 (m, 6H), 2.65 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 197.6, 144.2, 143.4, 136.6, 130.2 (q, J = 32.4 Hz), 129.1, 127.6, 127.5, 125.9 (q, J = 3.8 Hz), 122.8, 26.7.

1-(4'-Fluorobiphenyl-4-yl)ethanone 3ia[8] White solid (**1i**/**2a** (0.2014g, 94%), **1i**/**4a** (0.2057g, 96%)), mp 108-109°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.4 Hz, 2H), 7.64-7.56 (m, 4H), 7.15 (t, J = 8.4 Hz, 2H), 2.63 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 163.0 (d, J = 246.5 Hz), 144.7, 136.0 (d, J = 3.4 Hz), 135.8, 129.0, 128.9, 127.1, 115.9 (d, J = 21.5 Hz), 26.7.

1-(3'-Fluorobiphenyl-4-yl)ethanone 3ja[8] White solid (0.1950g, 91%), mp 90-91°C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.04 (d, J = 8.4 Hz, 2H), 7.66 (d, J = 8.4 Hz, 2H)，7.48-7.40 (m, 2H), 7.36-7.32 (m, 1H), 7.14-7.08 (m, 1H), 2.65 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 197.7, 164.4, 162.0, 144.4, 142.1 (d, J = 7.7 Hz), 136.3, 130.5 (d, J = 8.5 Hz), 129.0, 127.2, 122.9 (d, J = 3.0 Hz), 114.6 (dd, J = 21 Hz, J = 85.6 Hz), 26.7.

4. References

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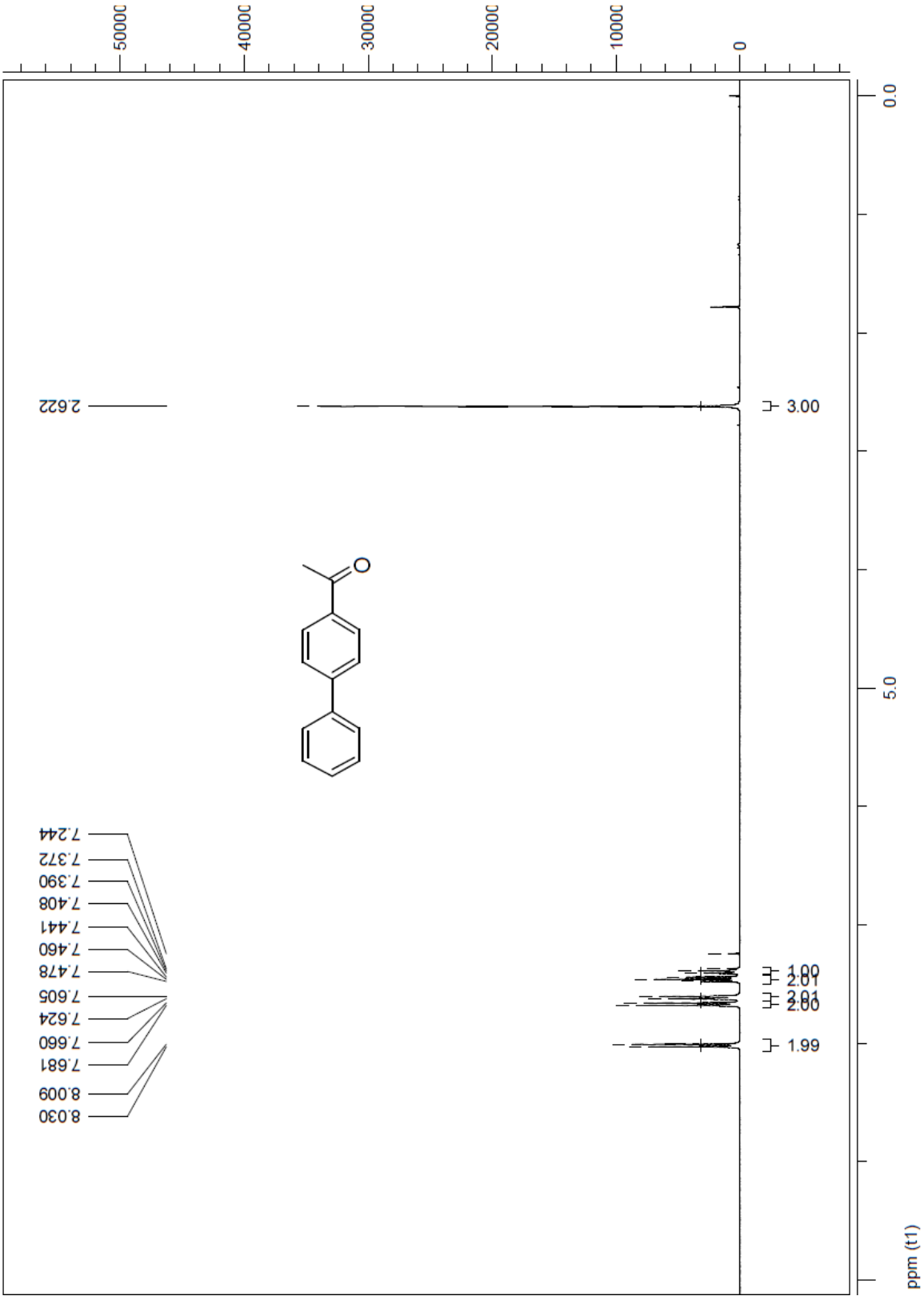
5. ^{1}H and ^{13}CNMR spectra of biaryl compounds

4-Acetylbiphenyl 3aa

^{1}H NMR



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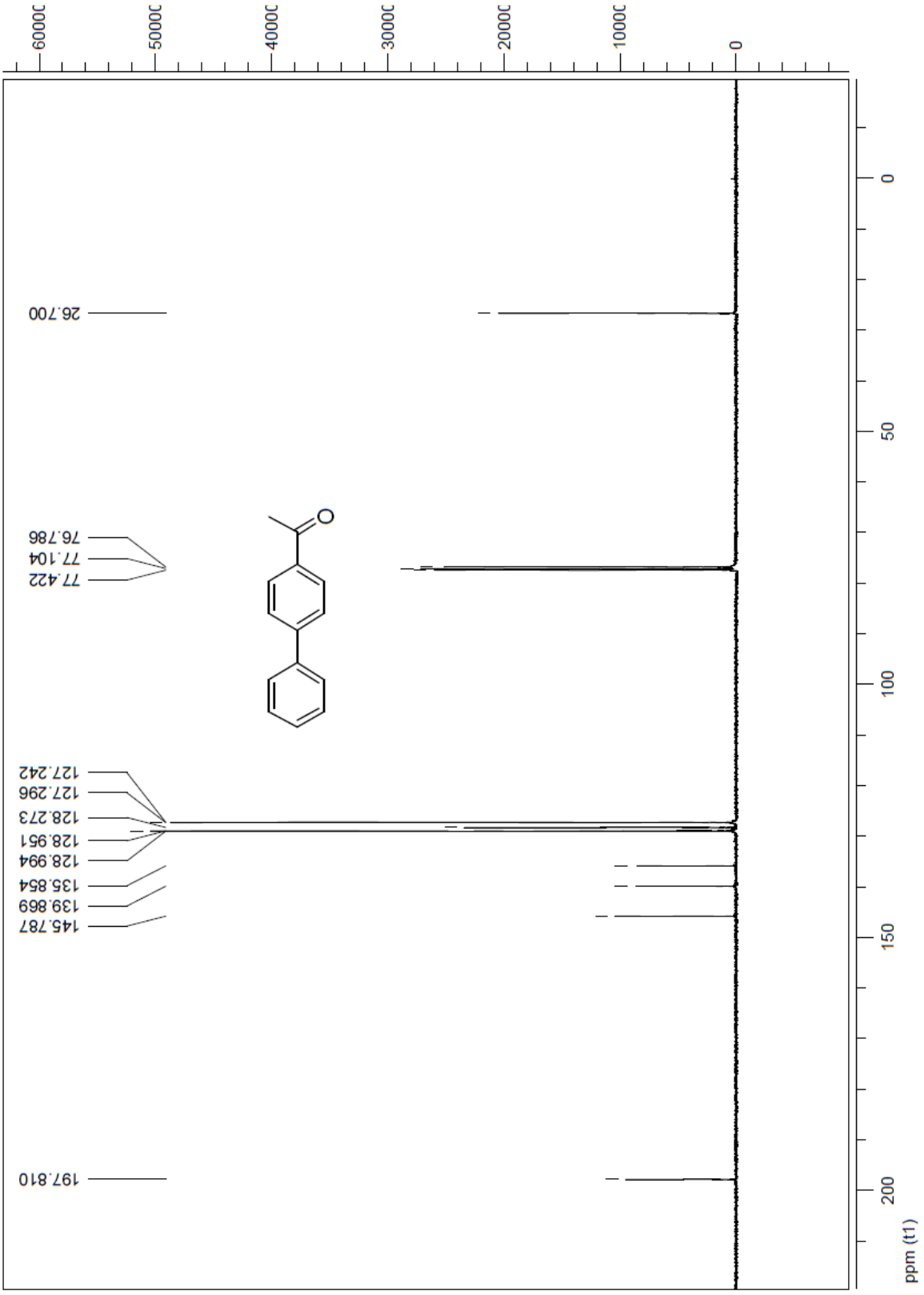
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1-(2’-Methylbiphenyl-4-yl)ethenone 3ca

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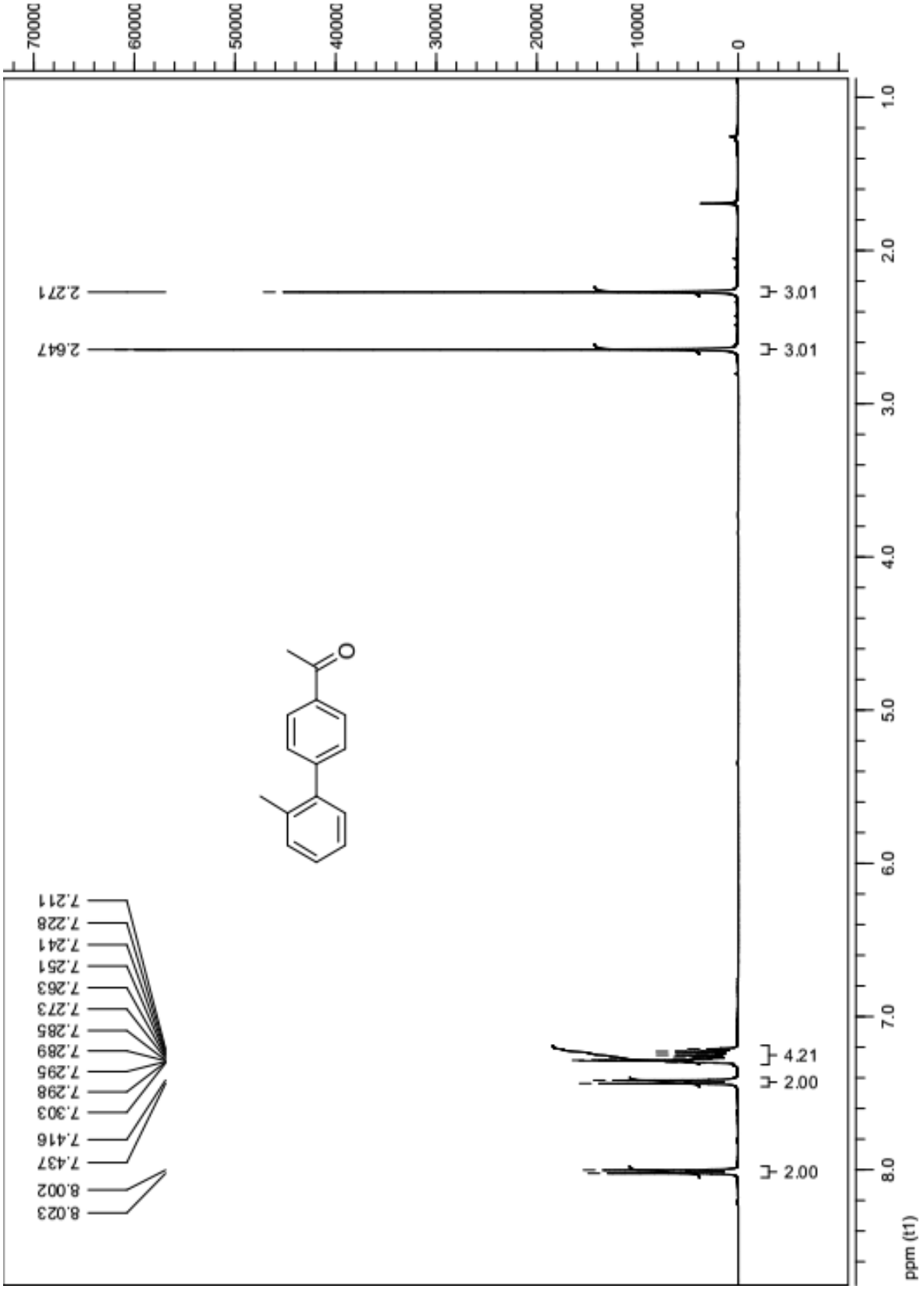

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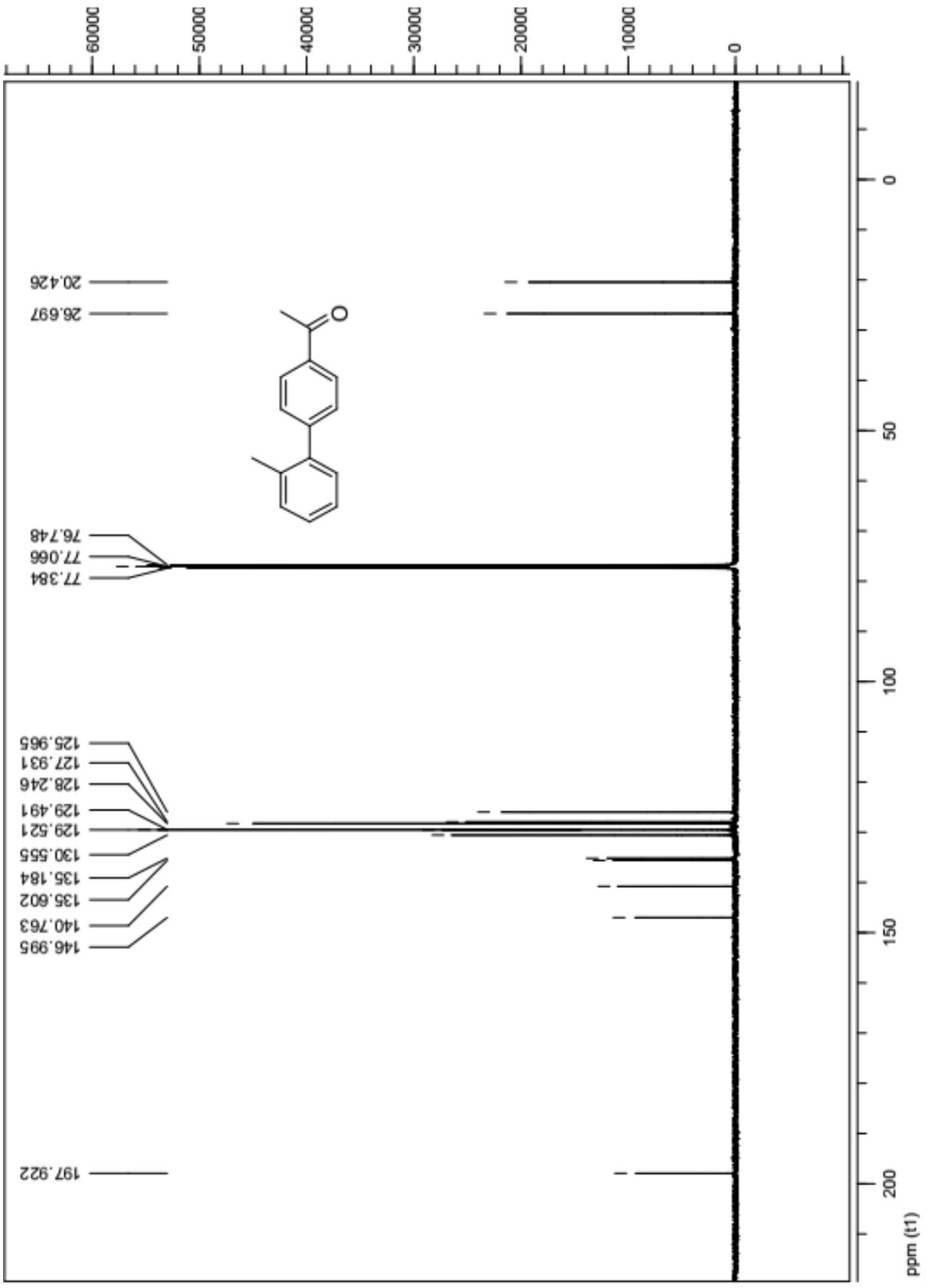
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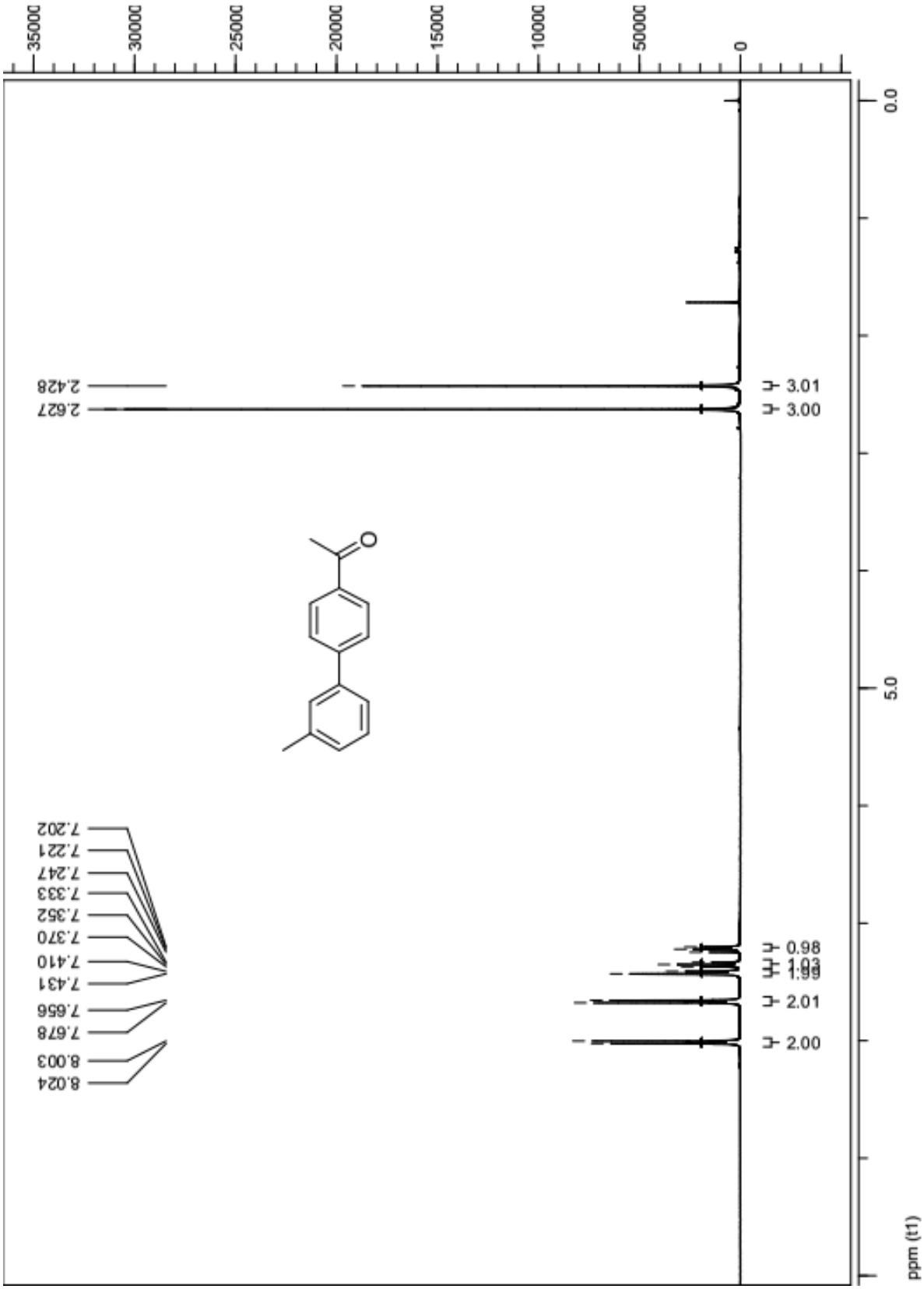

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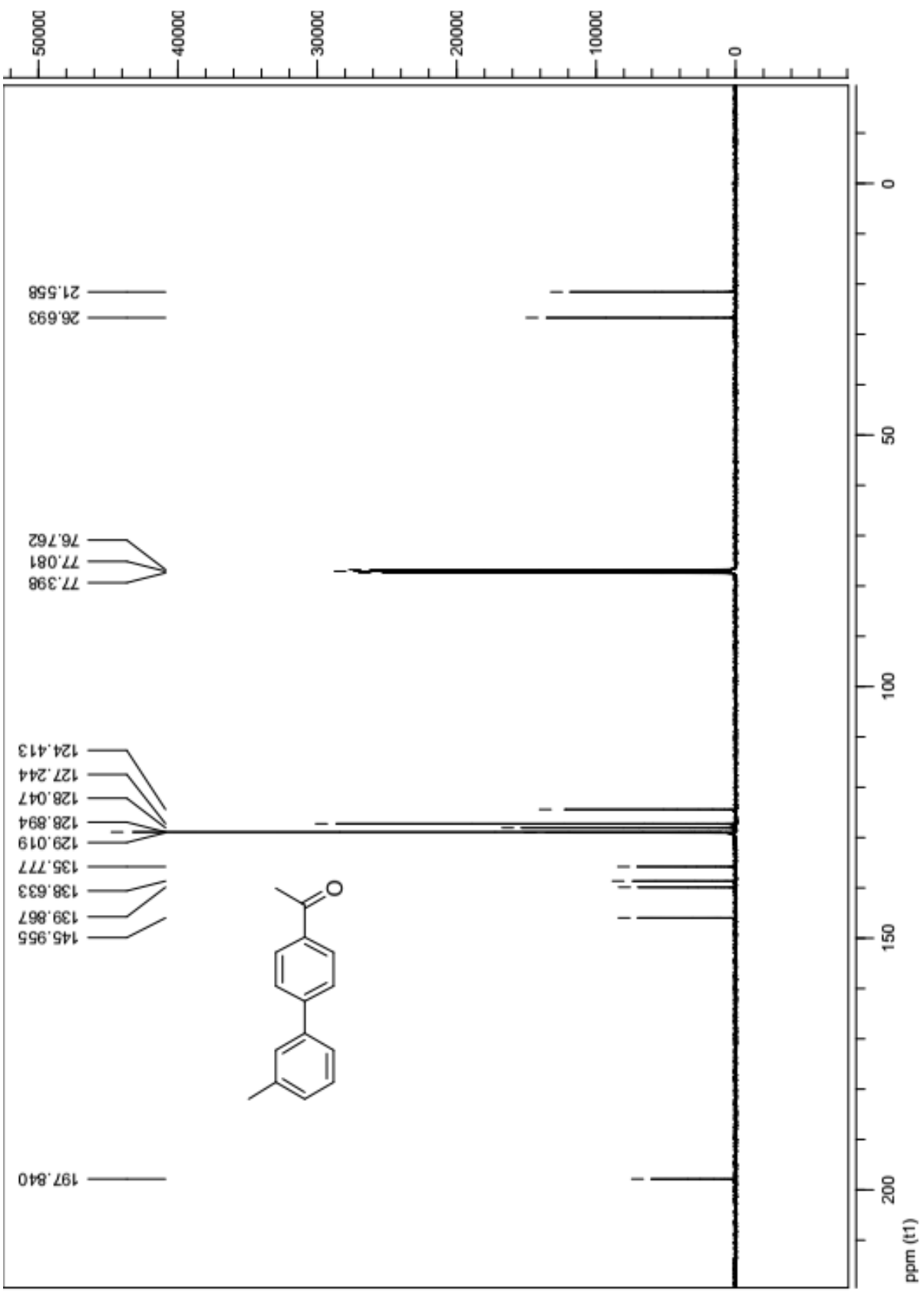
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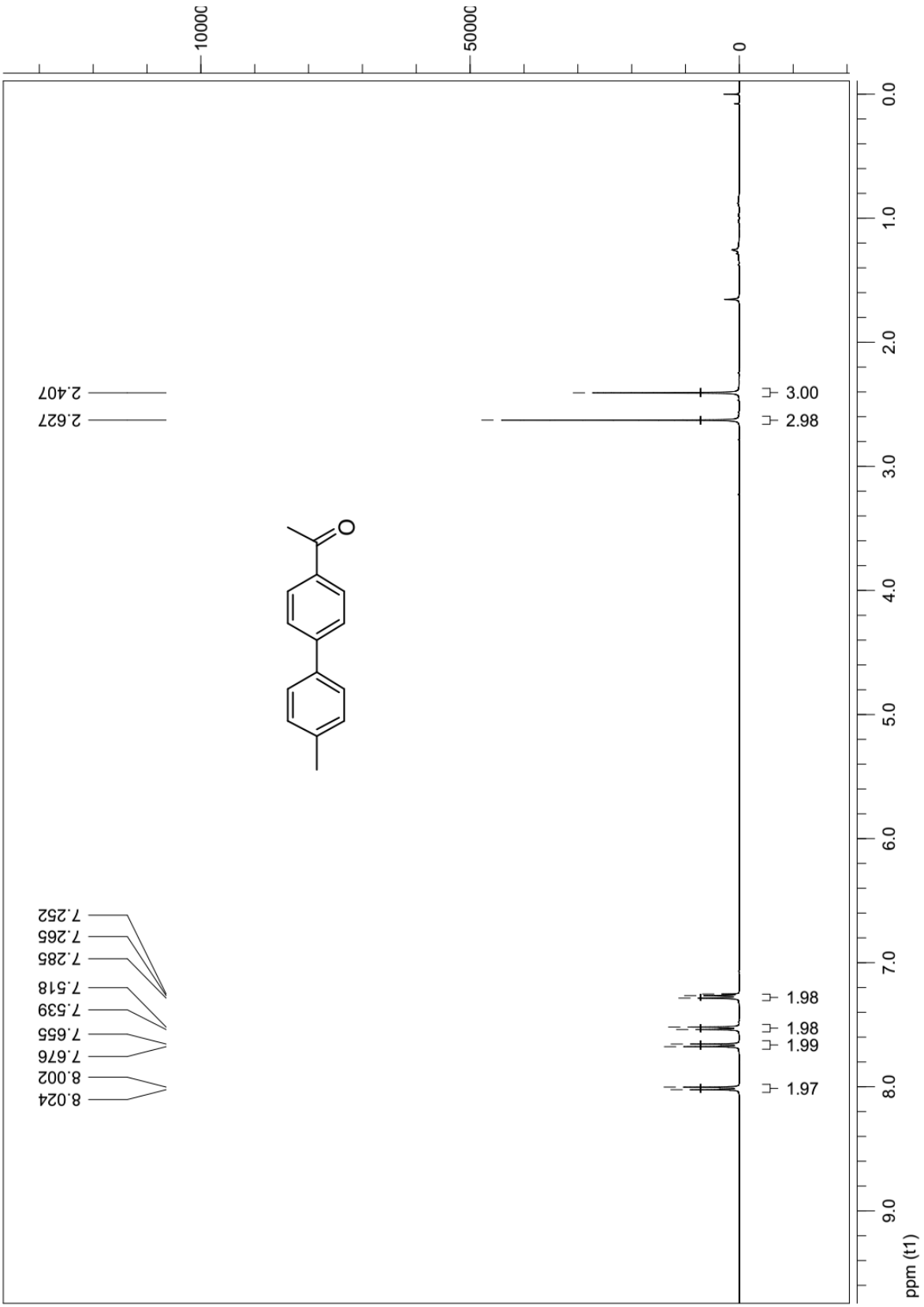
1-(4′-Methylbiphenyl-4-yl)ethenone 3ea

^{1}H NMR



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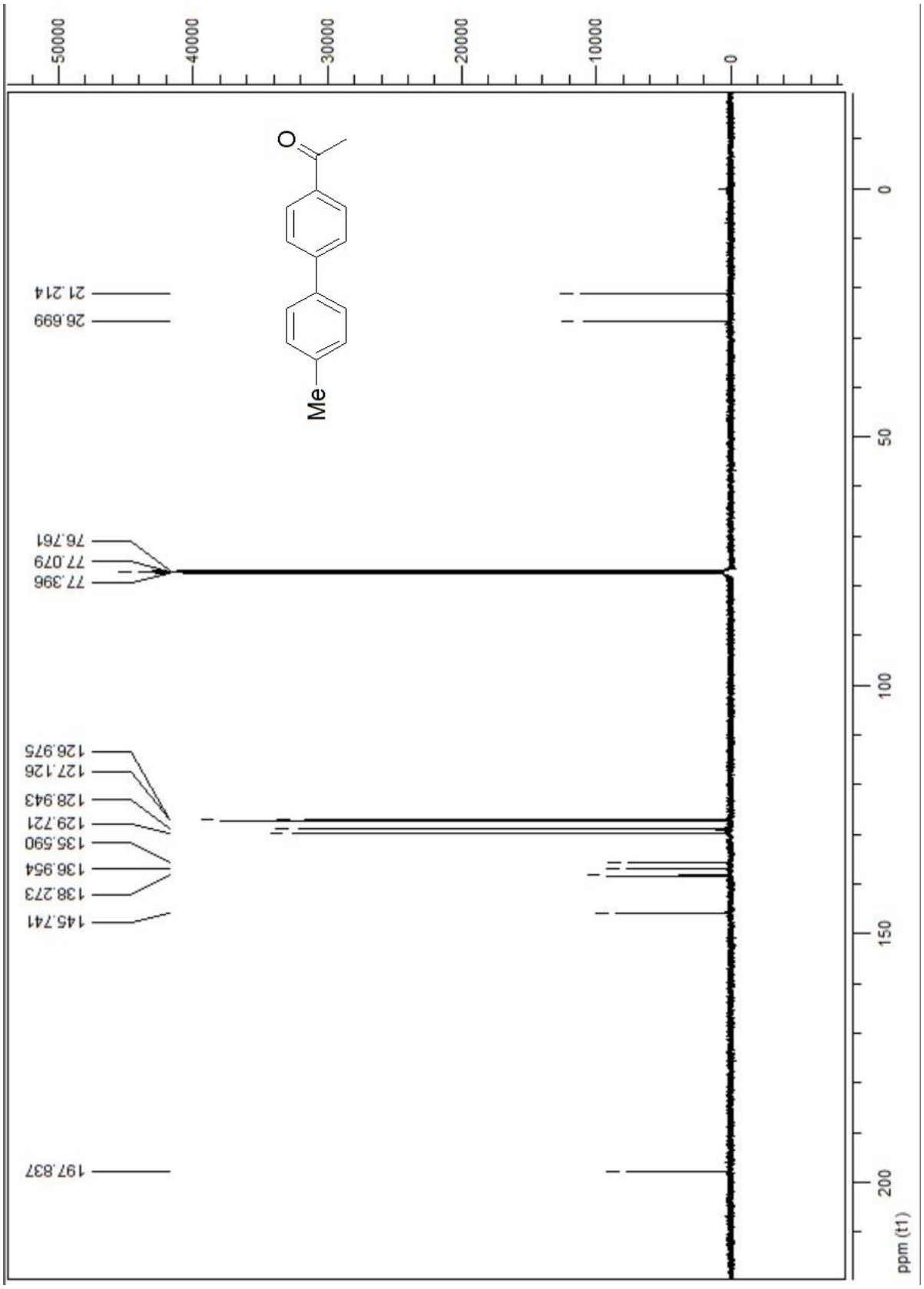
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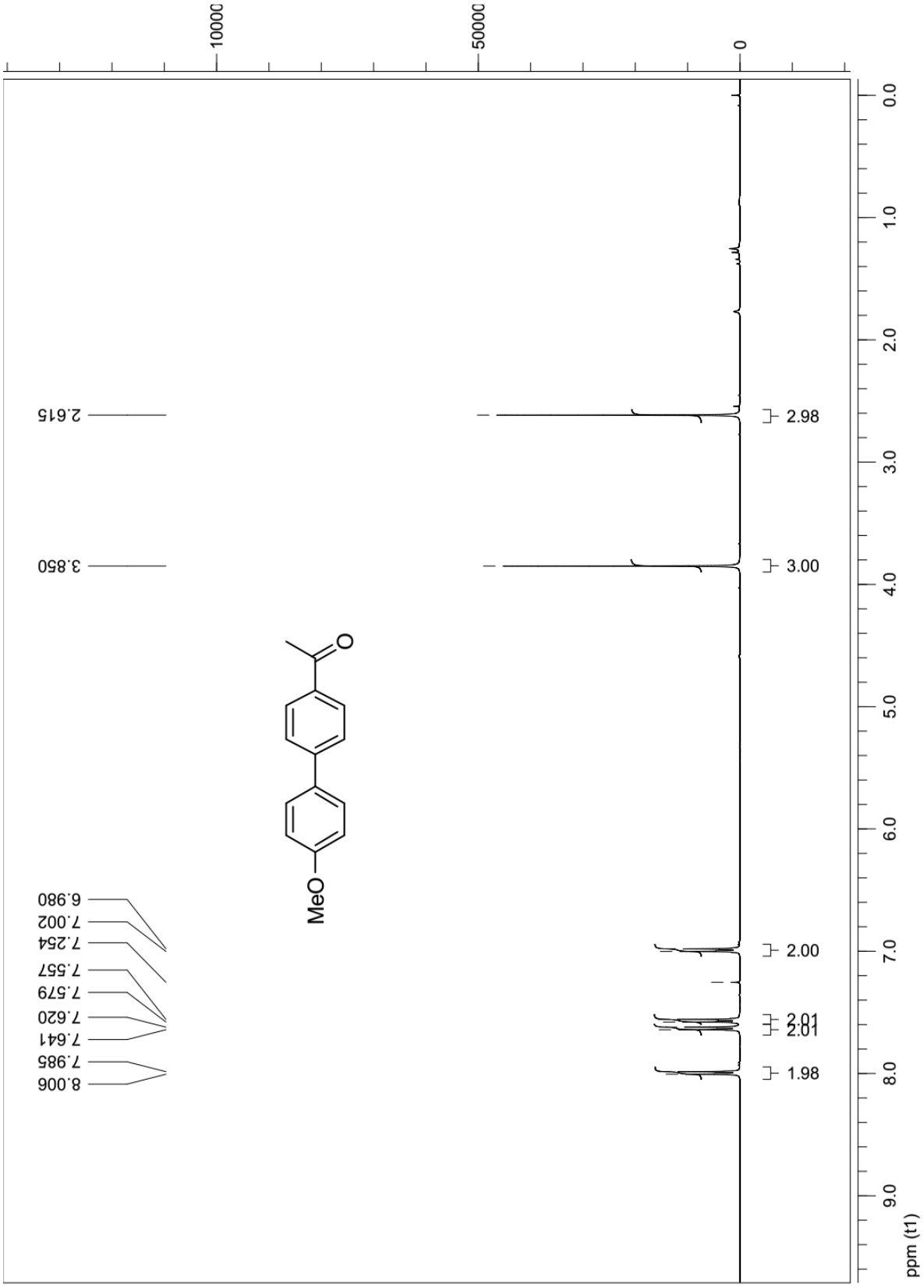
1-(4′-Methoxybiphenyl-4-yl)ethanone 3fa

^{1}H NMR



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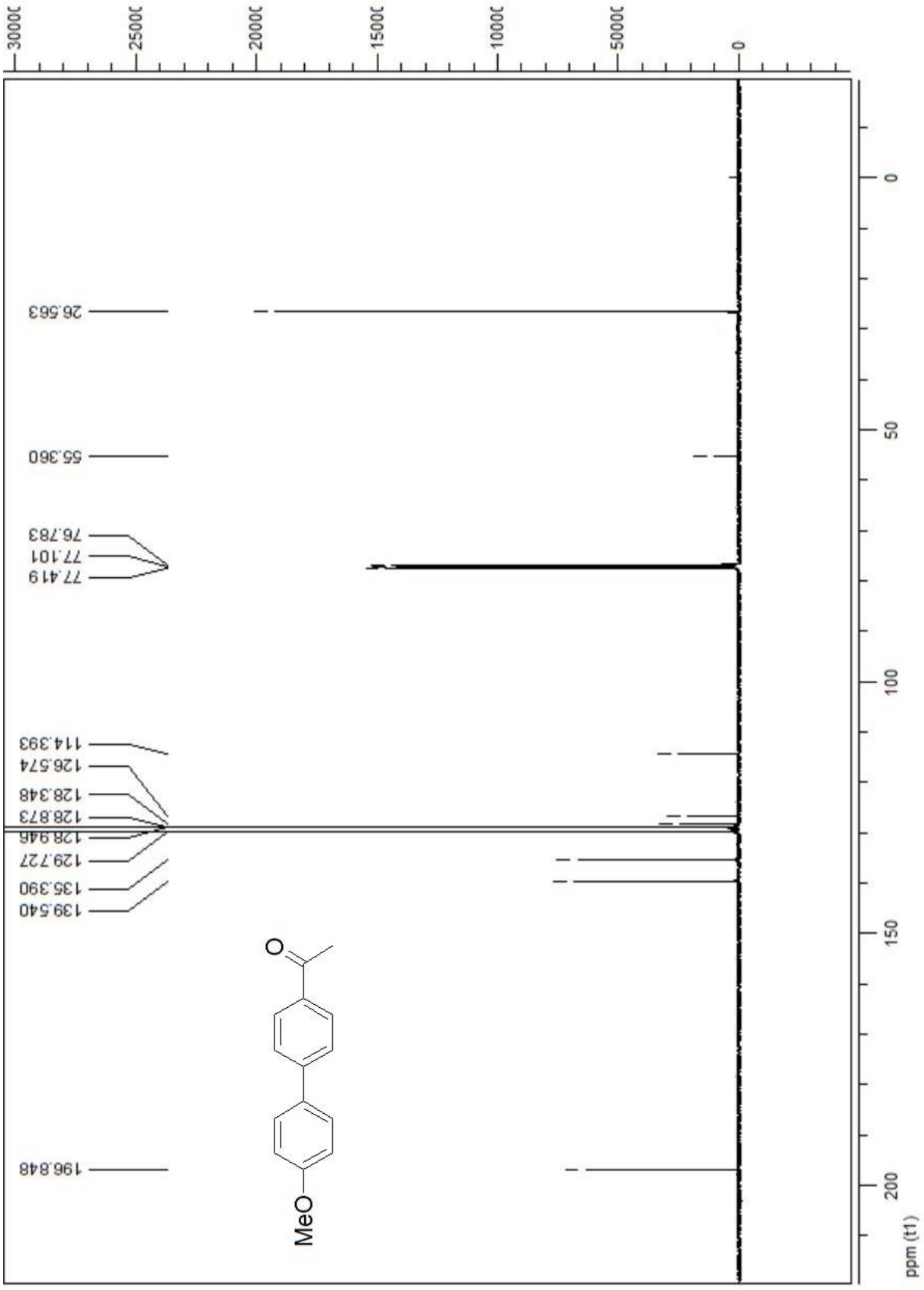
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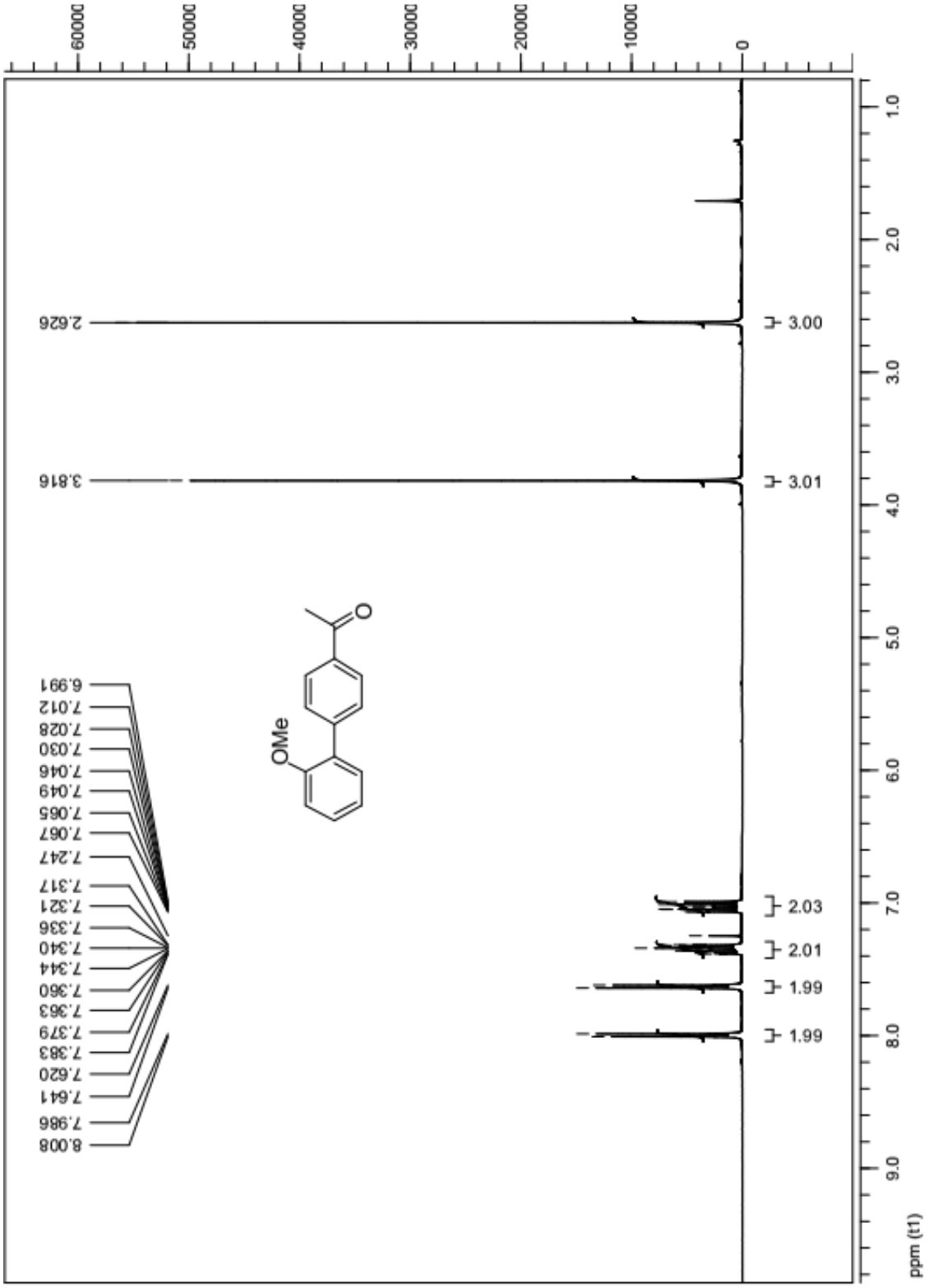
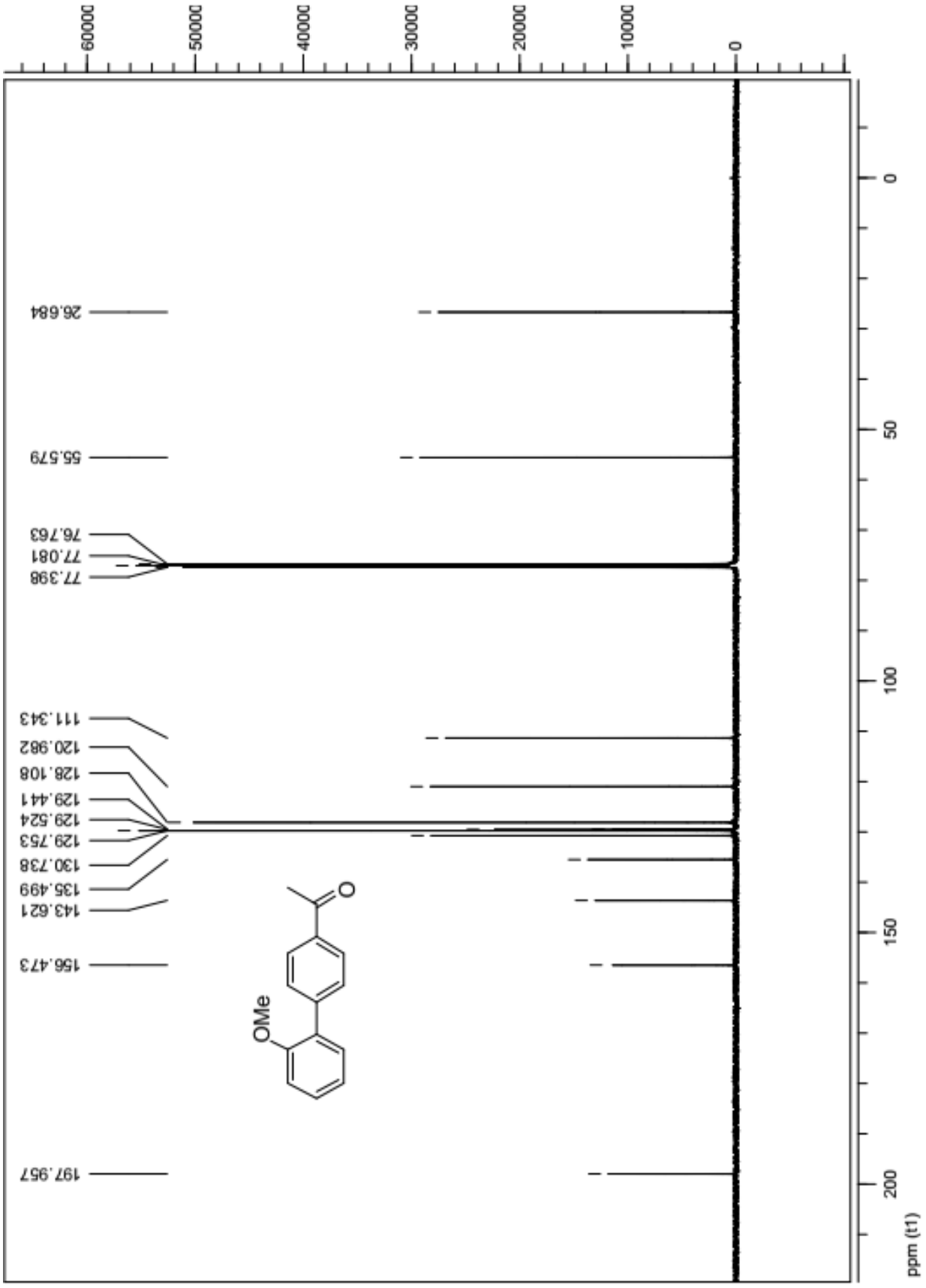
1-(2’-Methoxybiphenyl-4-yl)ethanone 3ga

^{1}H NMR



^{13}C NMR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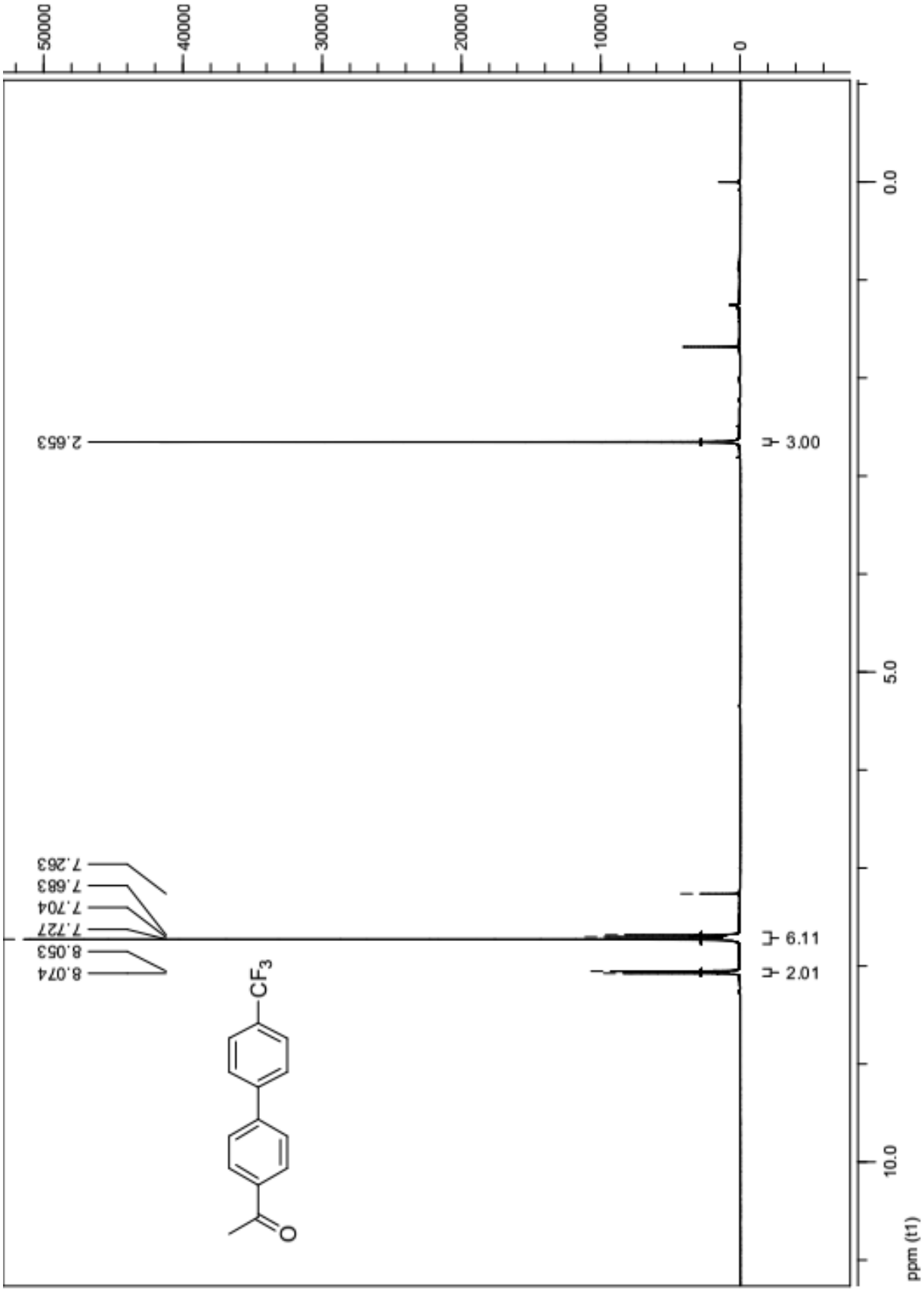
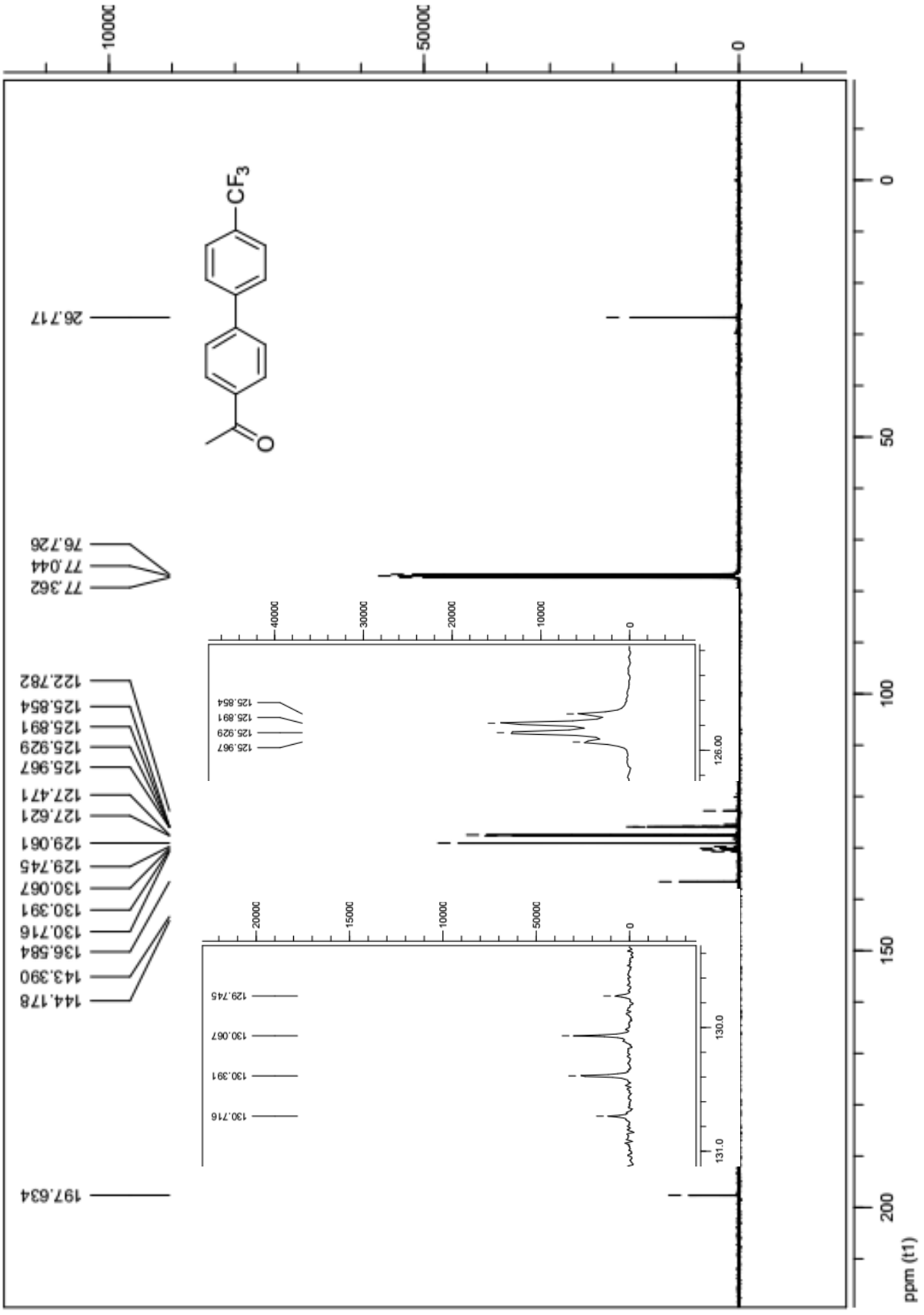
1-(4’-trifluoromethyl-4-yl)ethanone 3ha

^{1}H NMR



^{13}C NMR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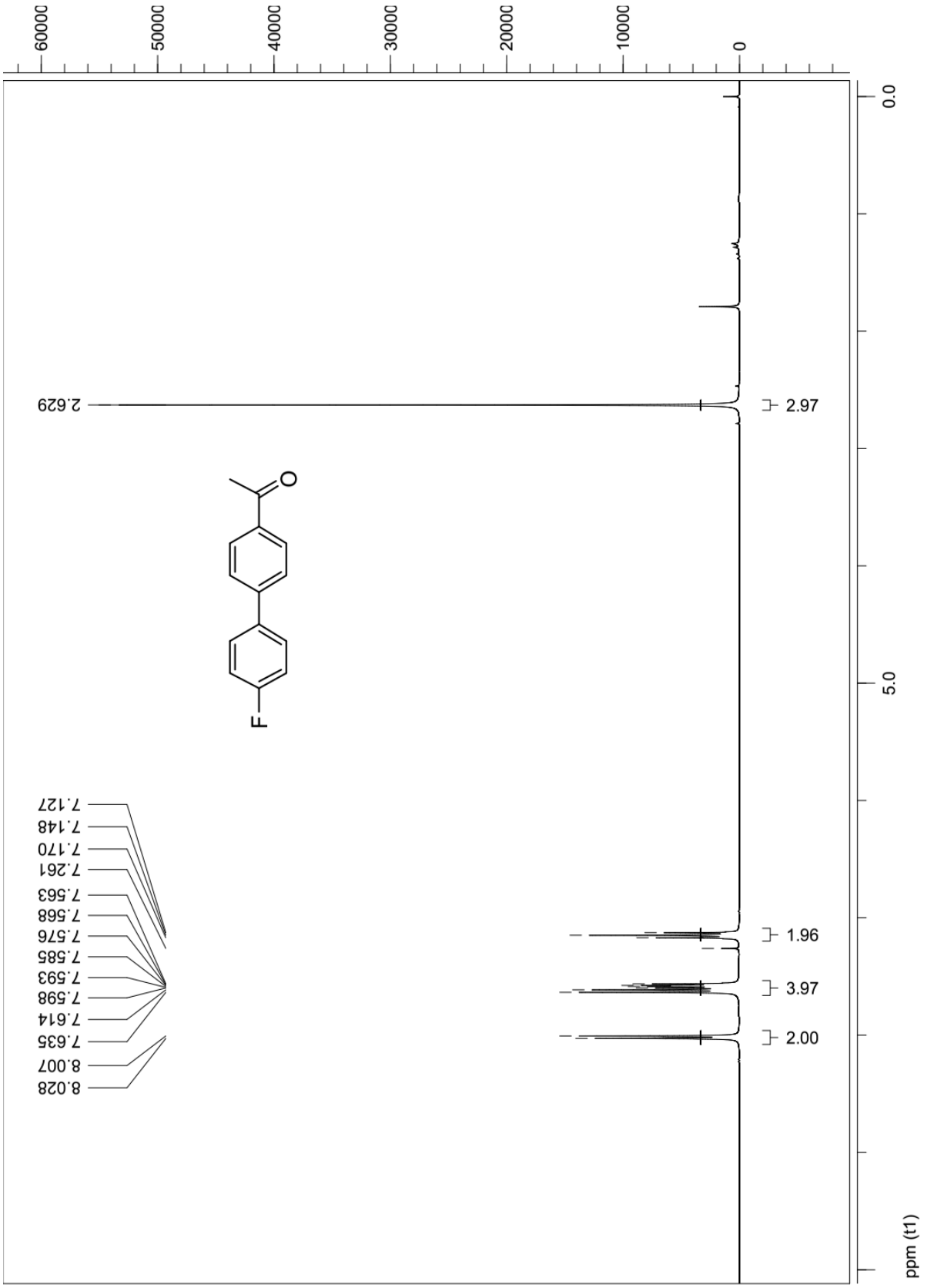
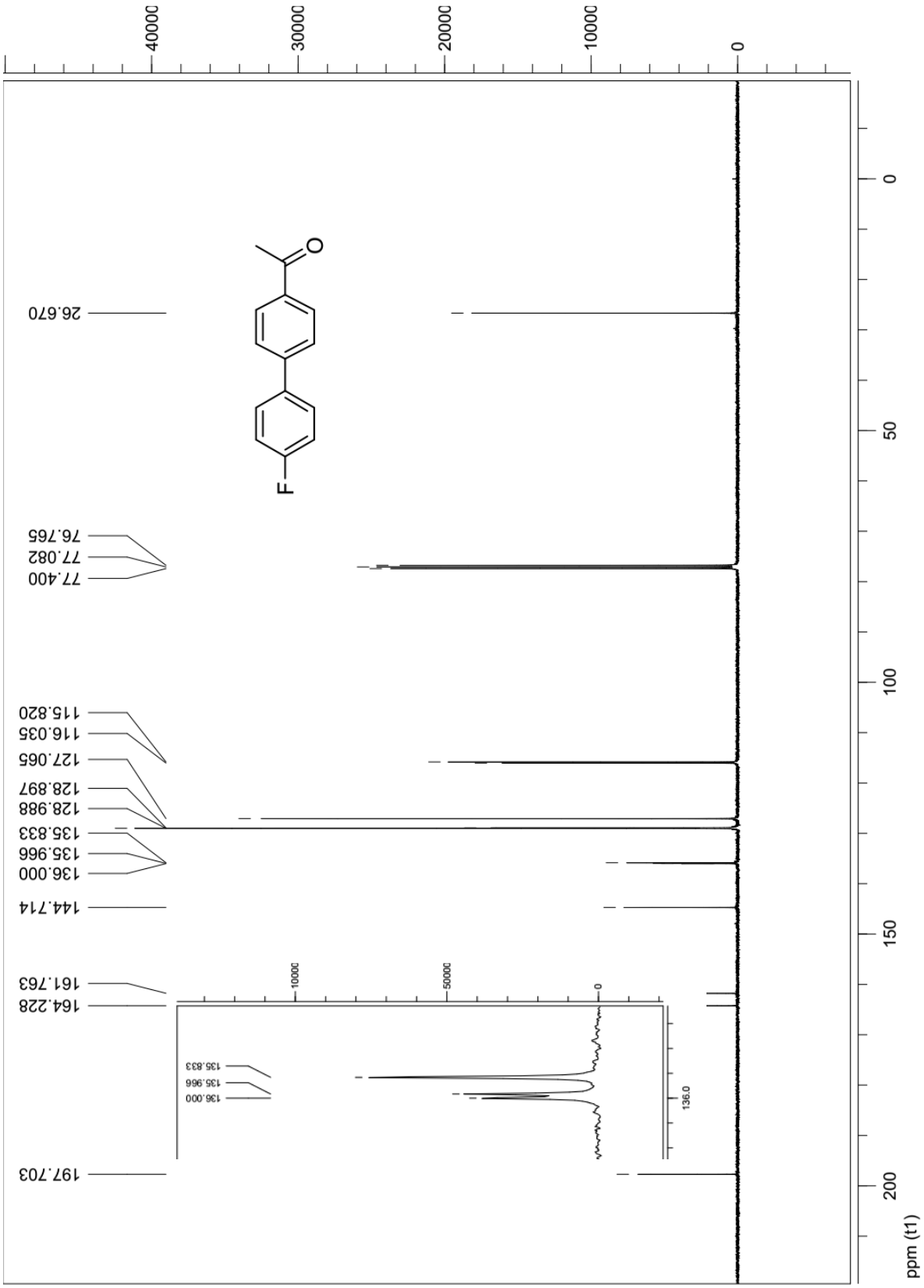
197.634
ppm (t1)

1-(4′-Fluorobiphenyl-4-yl)ethanone 3ia

^{1}H NMR

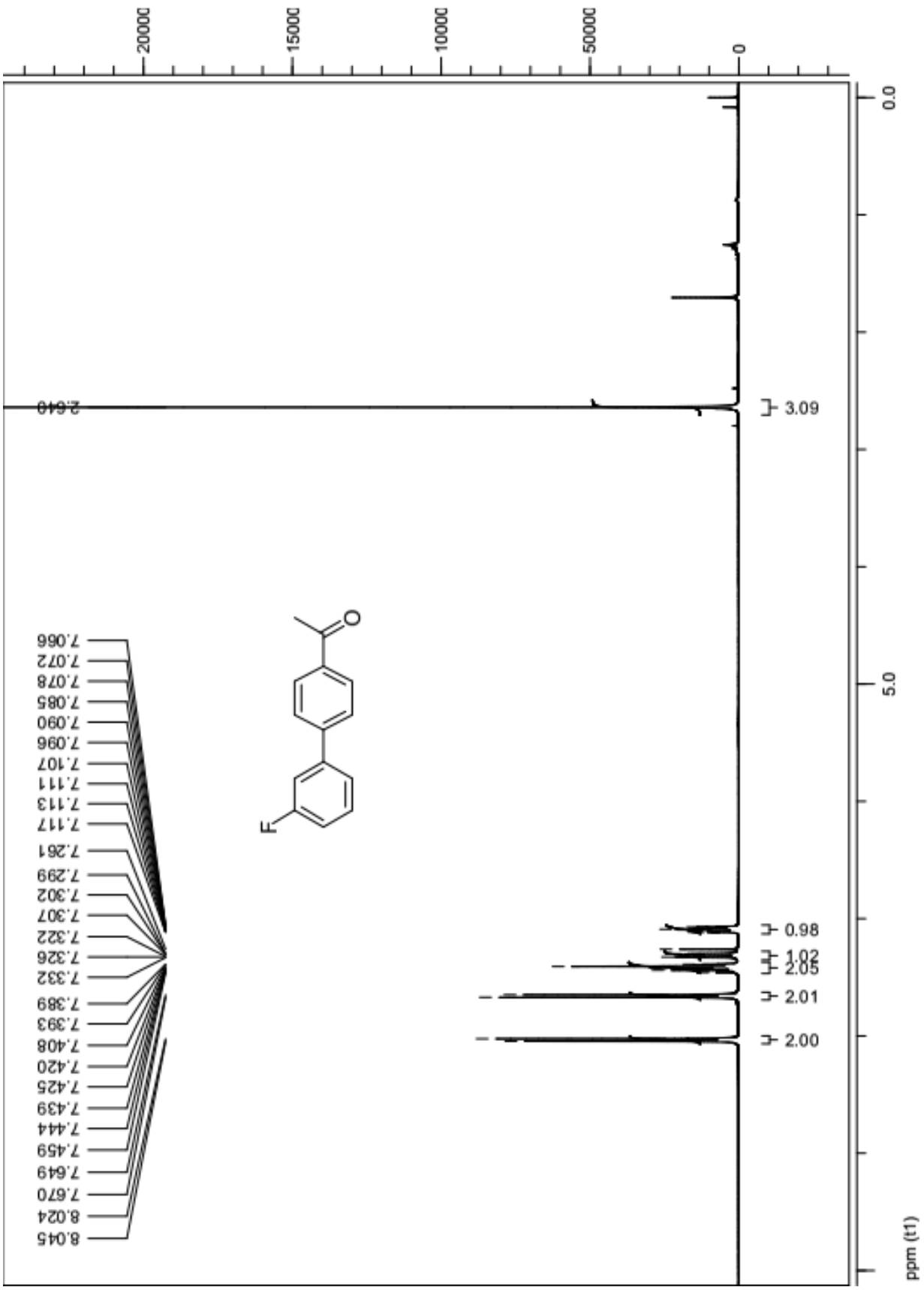


^{13}C NMR

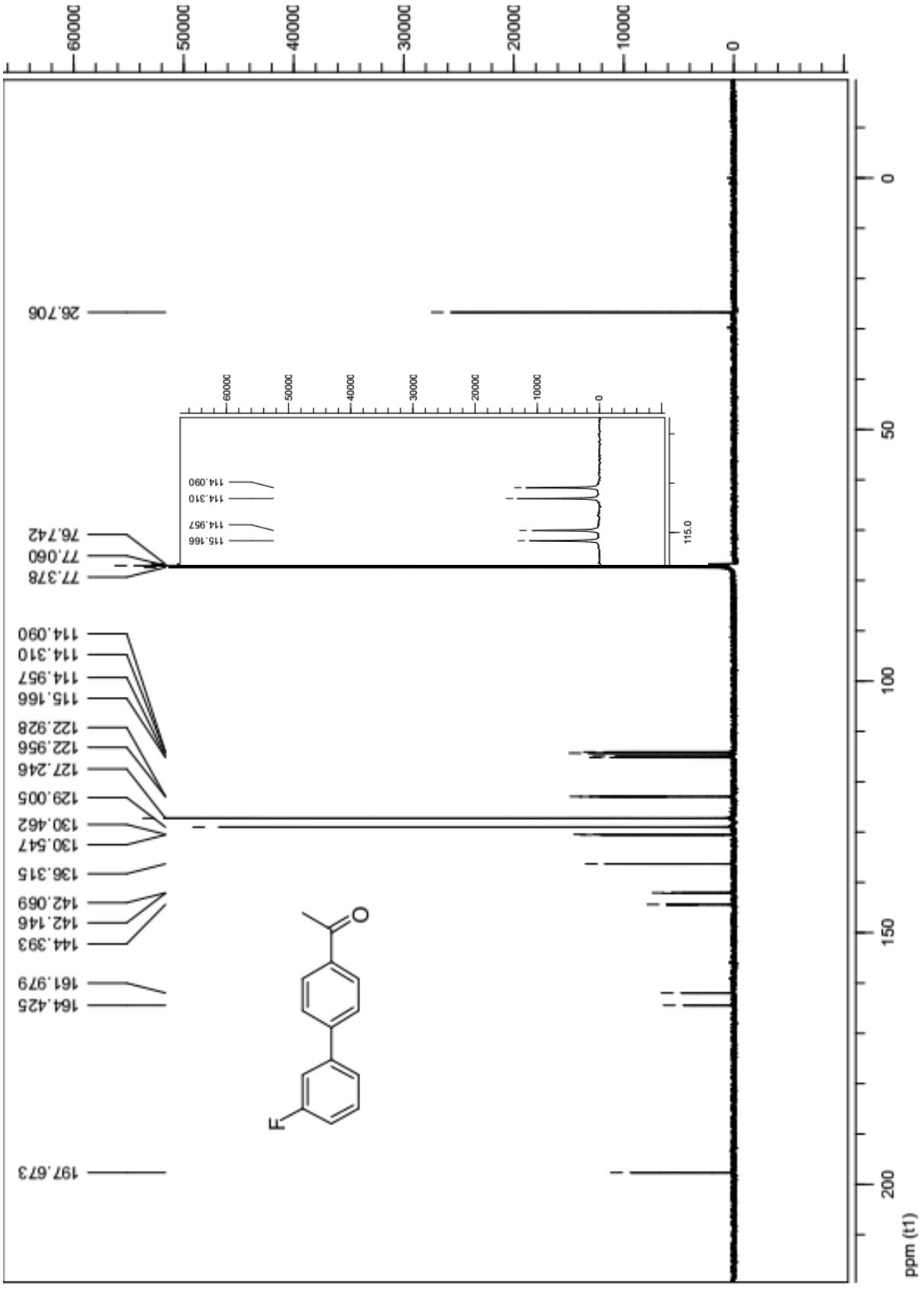

40000
30000
20000
10000
0
O
F
26.670
76.765
77.082
77.400
115.820
116.035
127.065
128.897
128.988
135.833
135.966
136.000
144.714
161.763
164.228
197.703
10000
5000
0
136.0
ppm (t1)
0
50
100
150
200

1-(3’-Fluorobiphenyl-4-yl)ethanone 3ja

^{1}H NMR

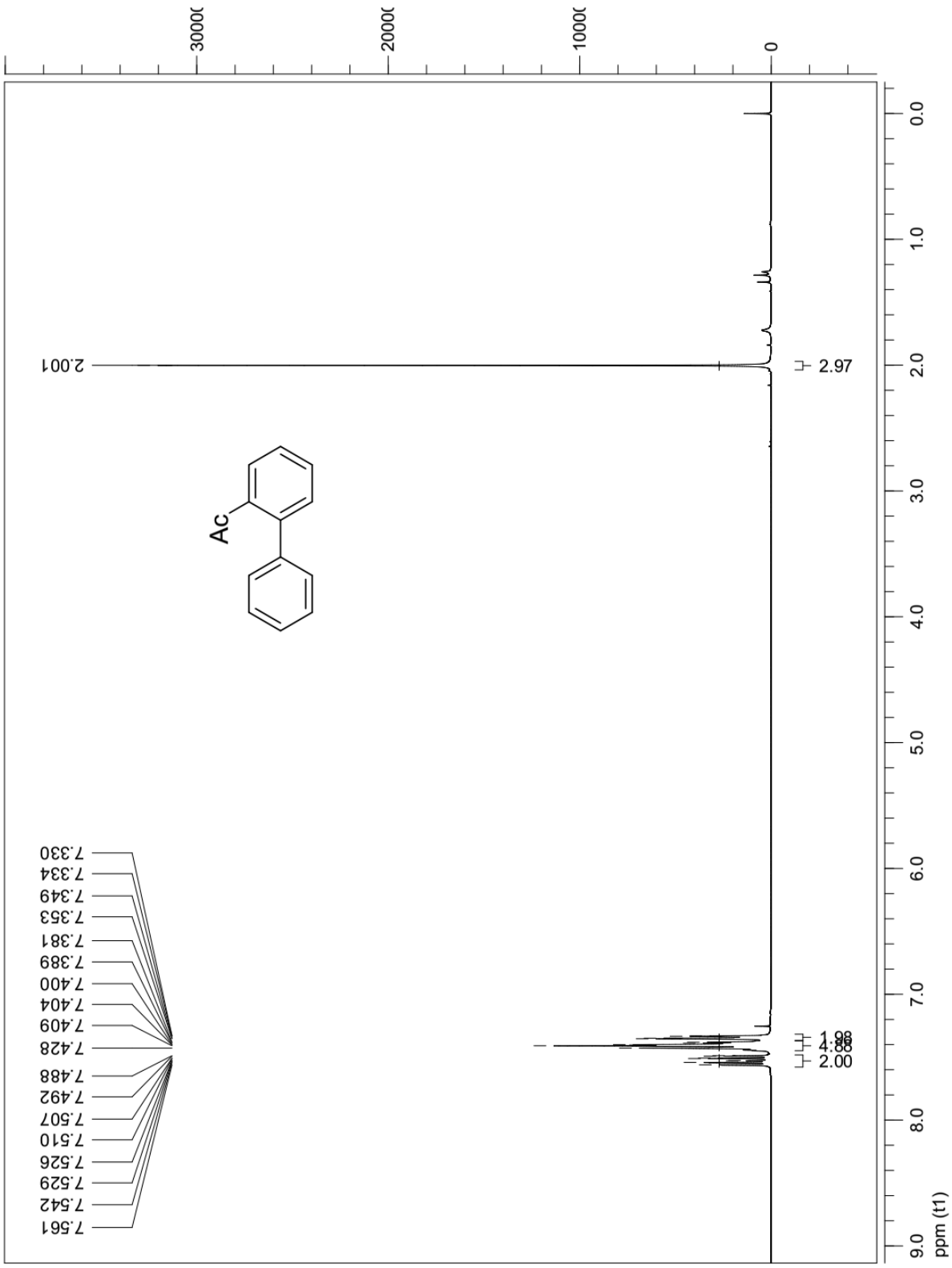


^{13}C NMR

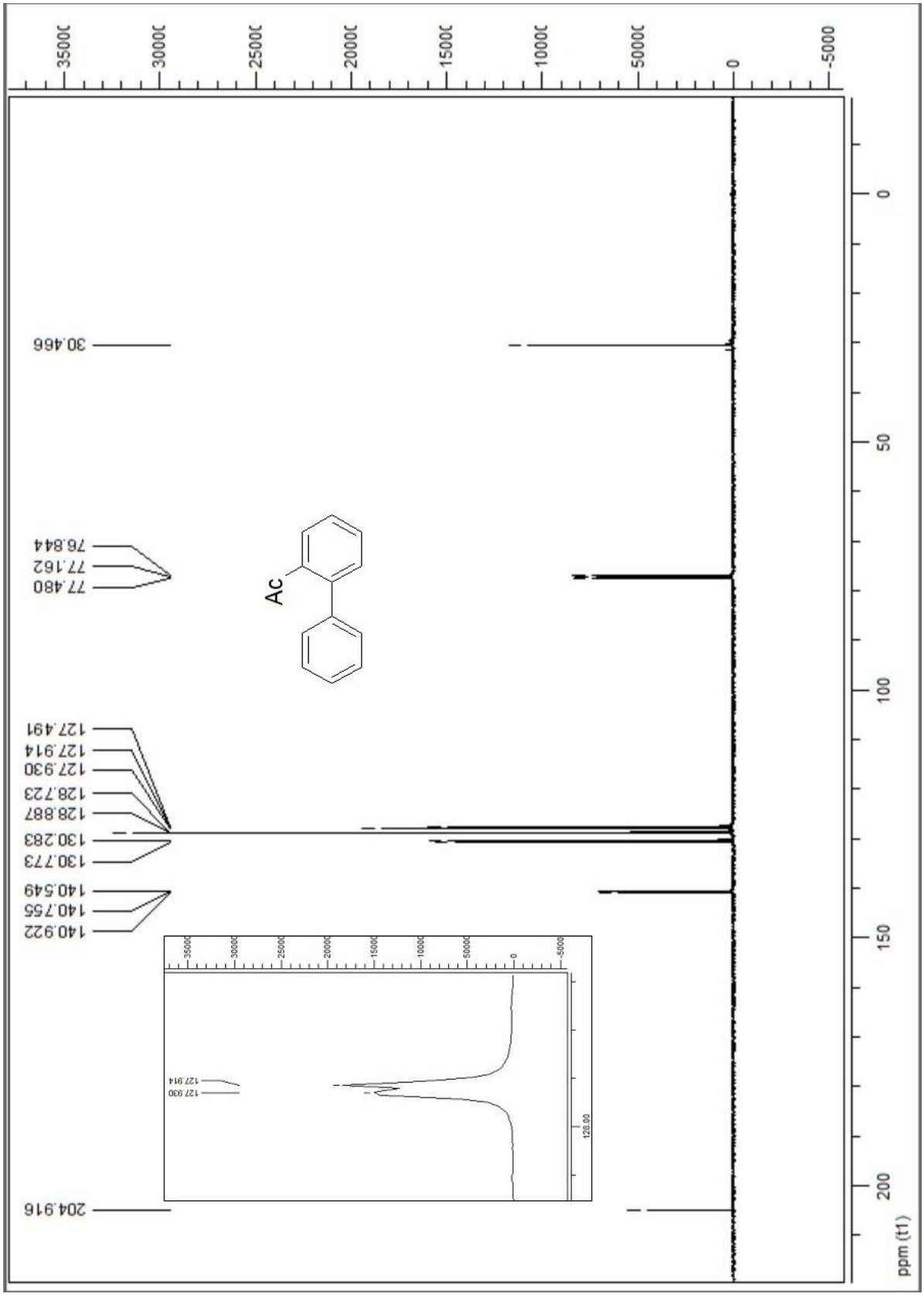

26.706
76.742
77.060
77.378
114.090
114.310
114.957
115.166
122.928
122.956
127.246
129.005
130.462
130.547
136.315
142.069
142.146
144.393
161.979
164.425
197.673
F
O
ppm (t1)

2-Acetylbiphenyl 3ab

^{1}H NMR

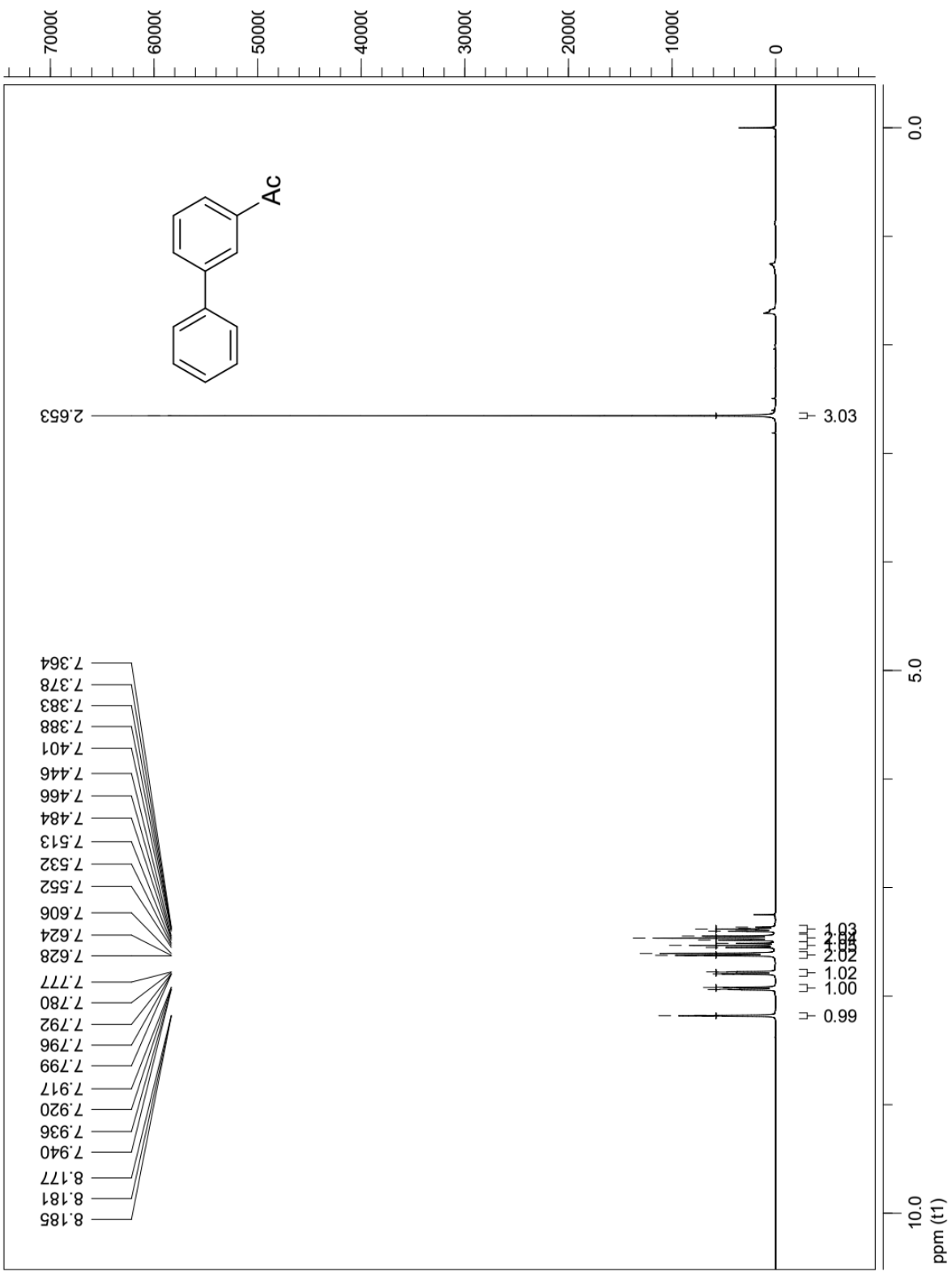


^{13}C NMR

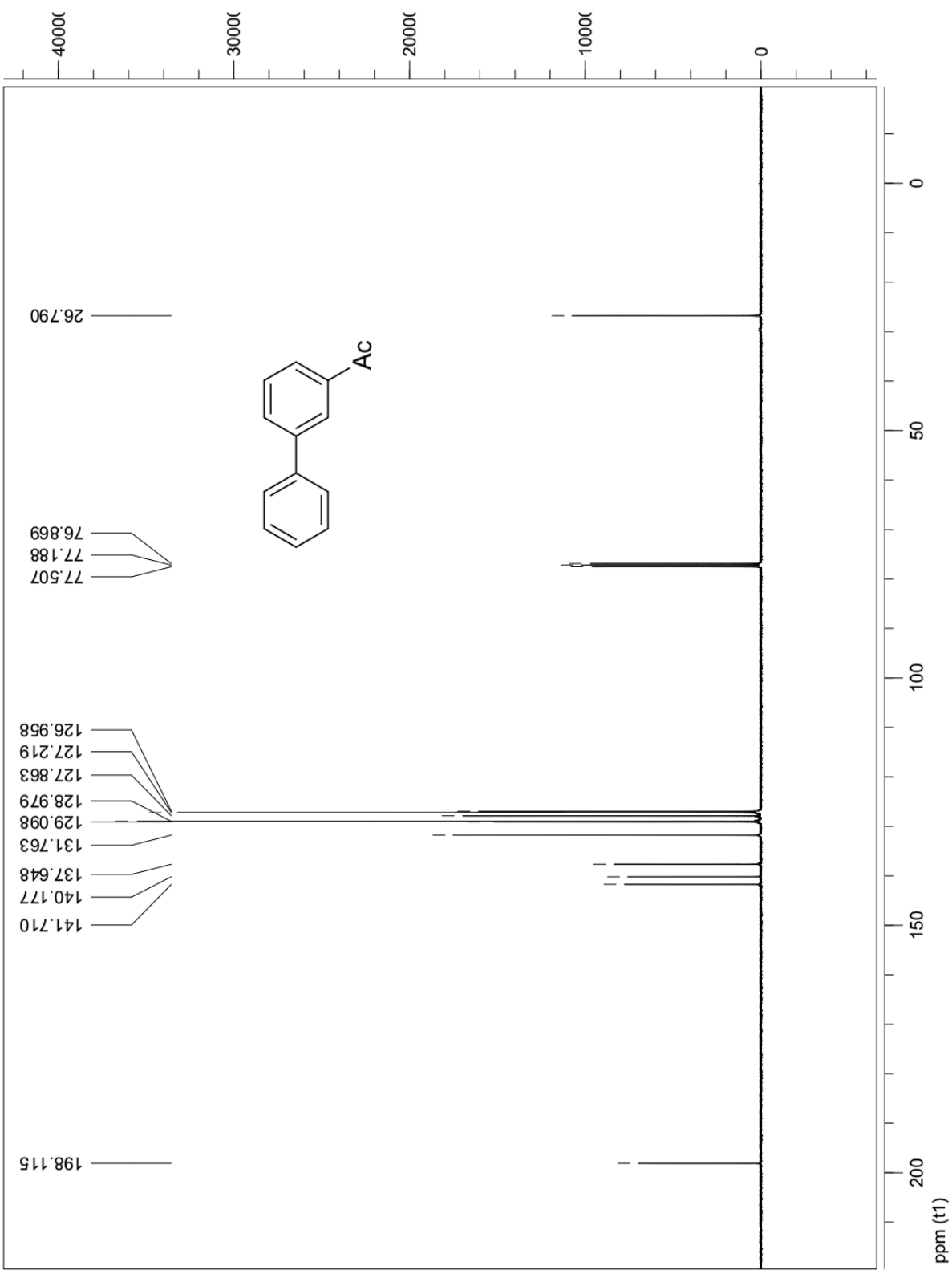

30.466
76.844
77.162
77.480
Ac
127.491
127.914
127.930
128.723
128.887
130.283
130.773
140.549
140.755
140.922
204.916
ppm (t1)

3-Acetylbiphenyl 3ac

^{1}H NMR

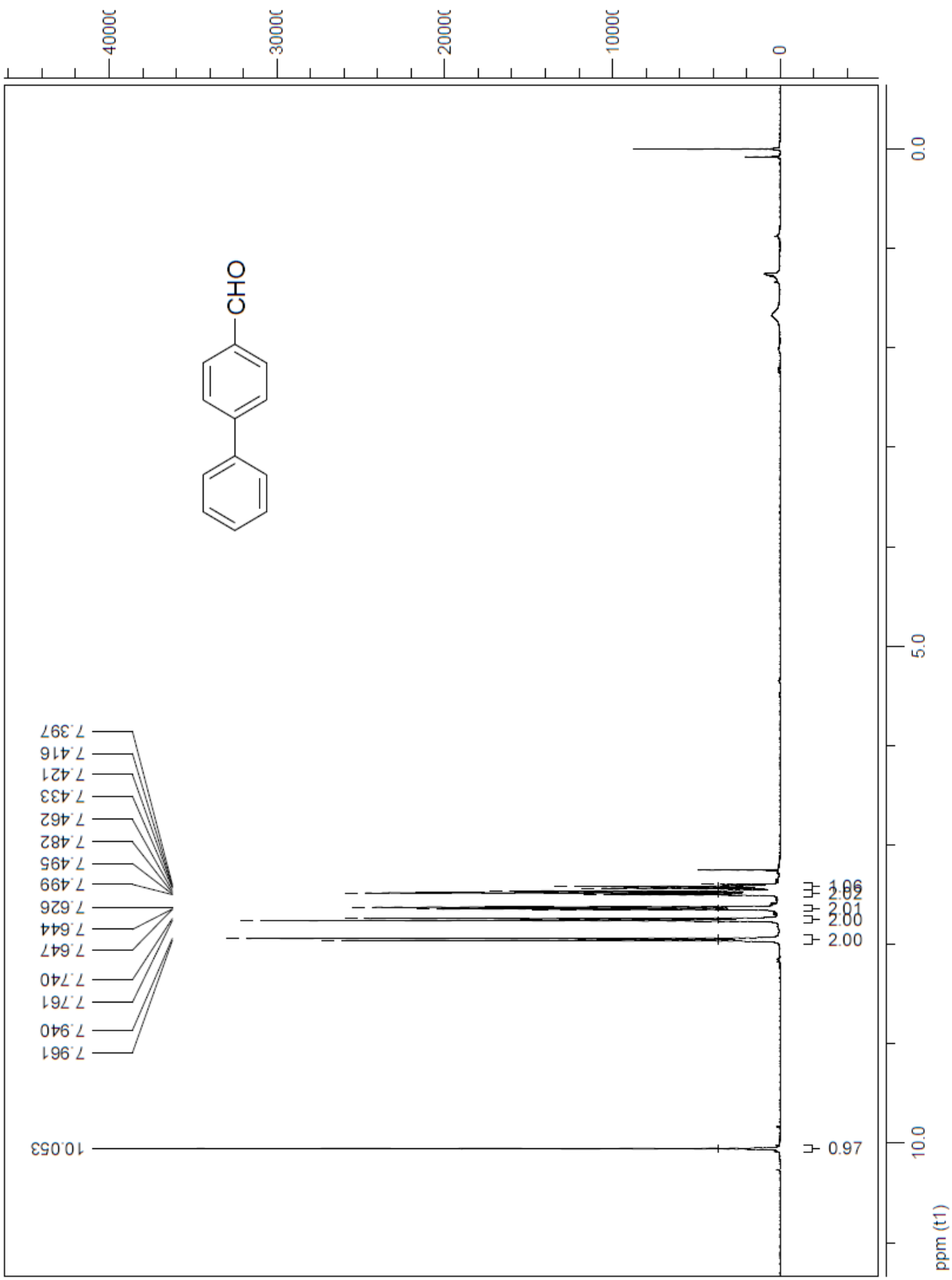


^{13}C NMR

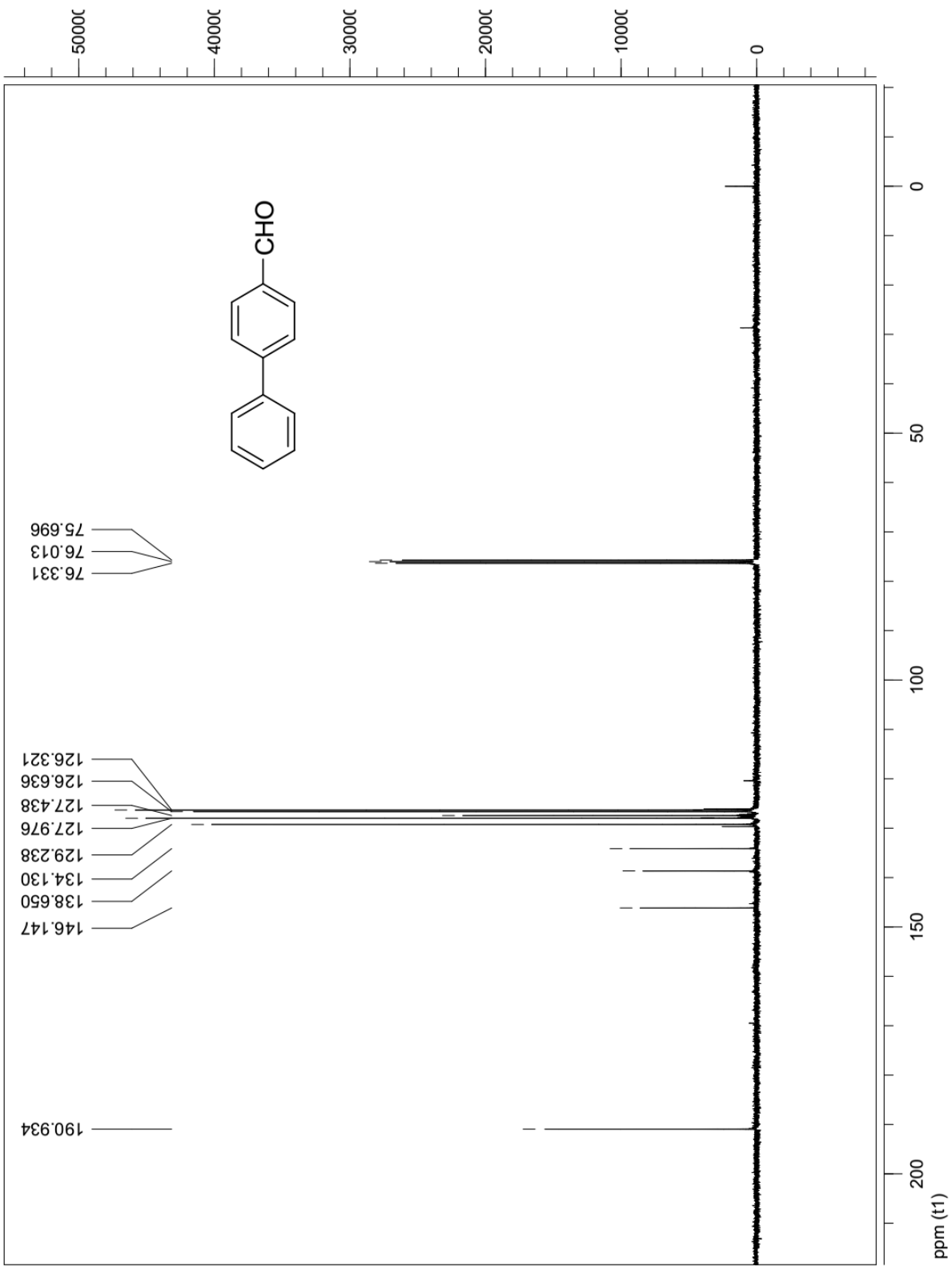

4000
3000
2000
1000
0
26.790
76.869
77.188
77.507
126.958
127.219
127.863
128.979
129.098
131.763
137.648
140.177
141.710
198.115
Ac
0
50
100
150
200
ppm (t1)

Biphenyl-4-carbaldehyde 3ad

^{1}H NMR

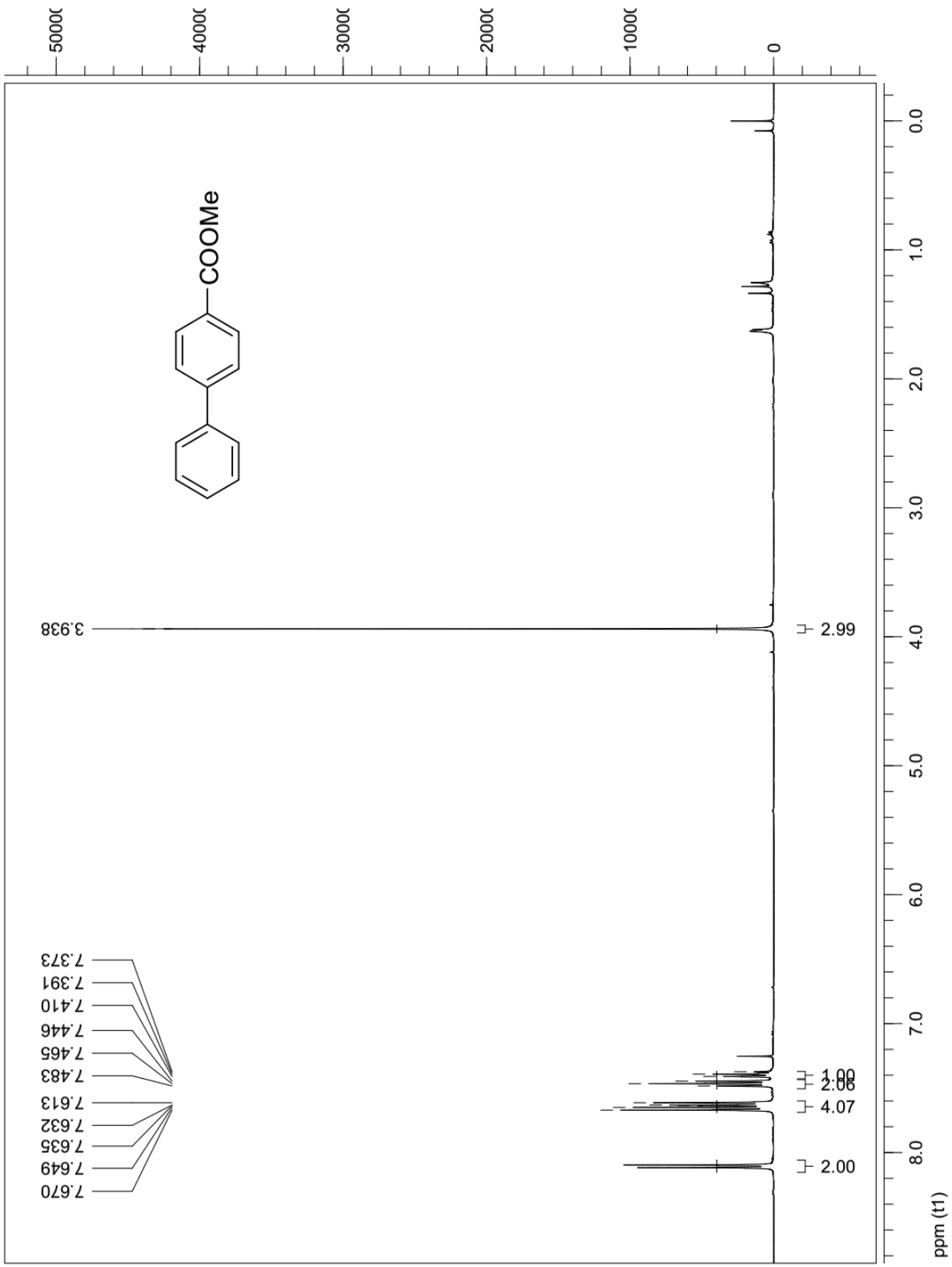


^{13}C NMR

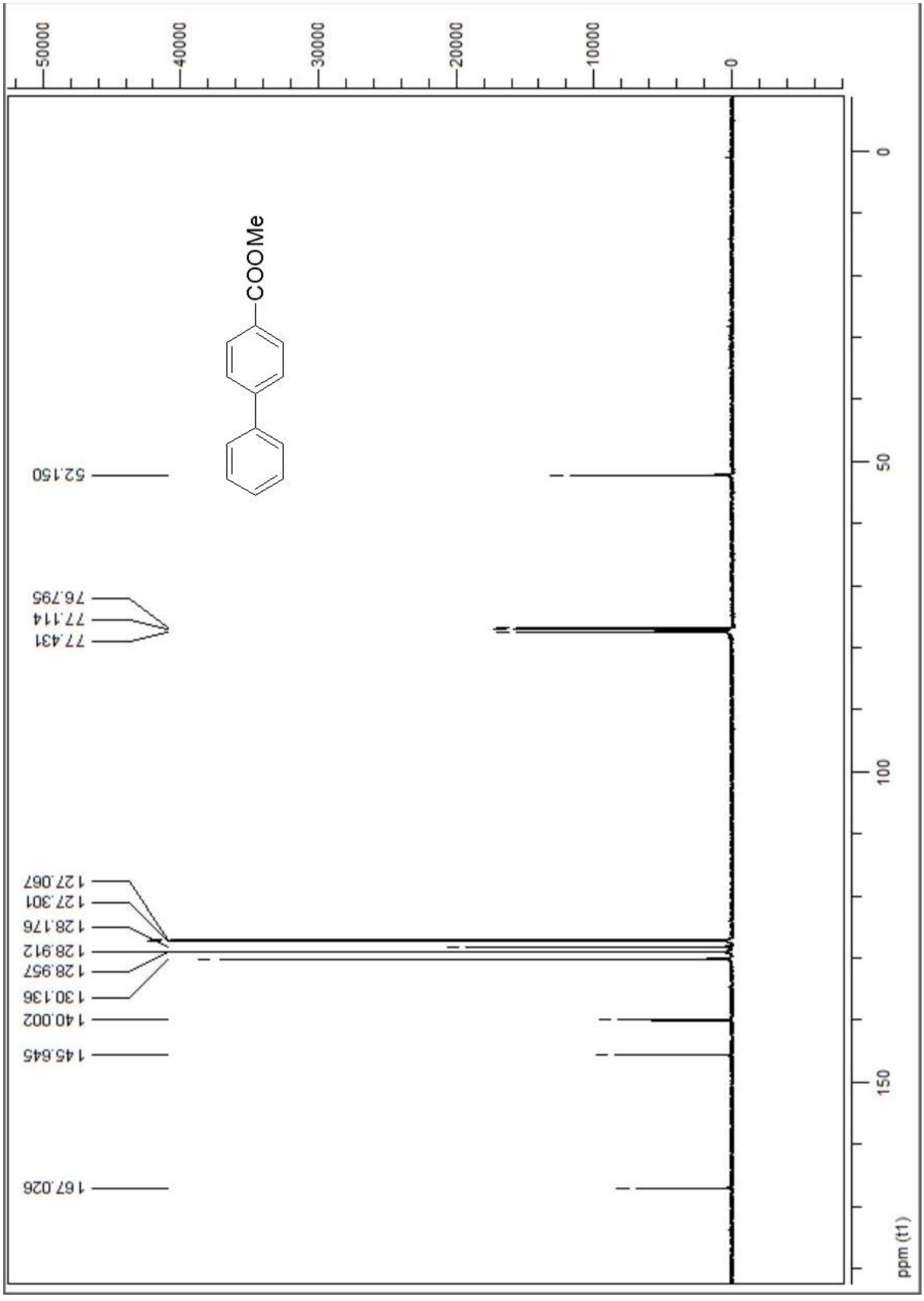

CHO
190.934
146.147
138.650
134.130
129.238
127.976
127.438
126.636
126.321
76.331
76.013
75.696
ppm (t1)

Methyl biphenyl-4-carboxylate 3ae

^{1}H NMR

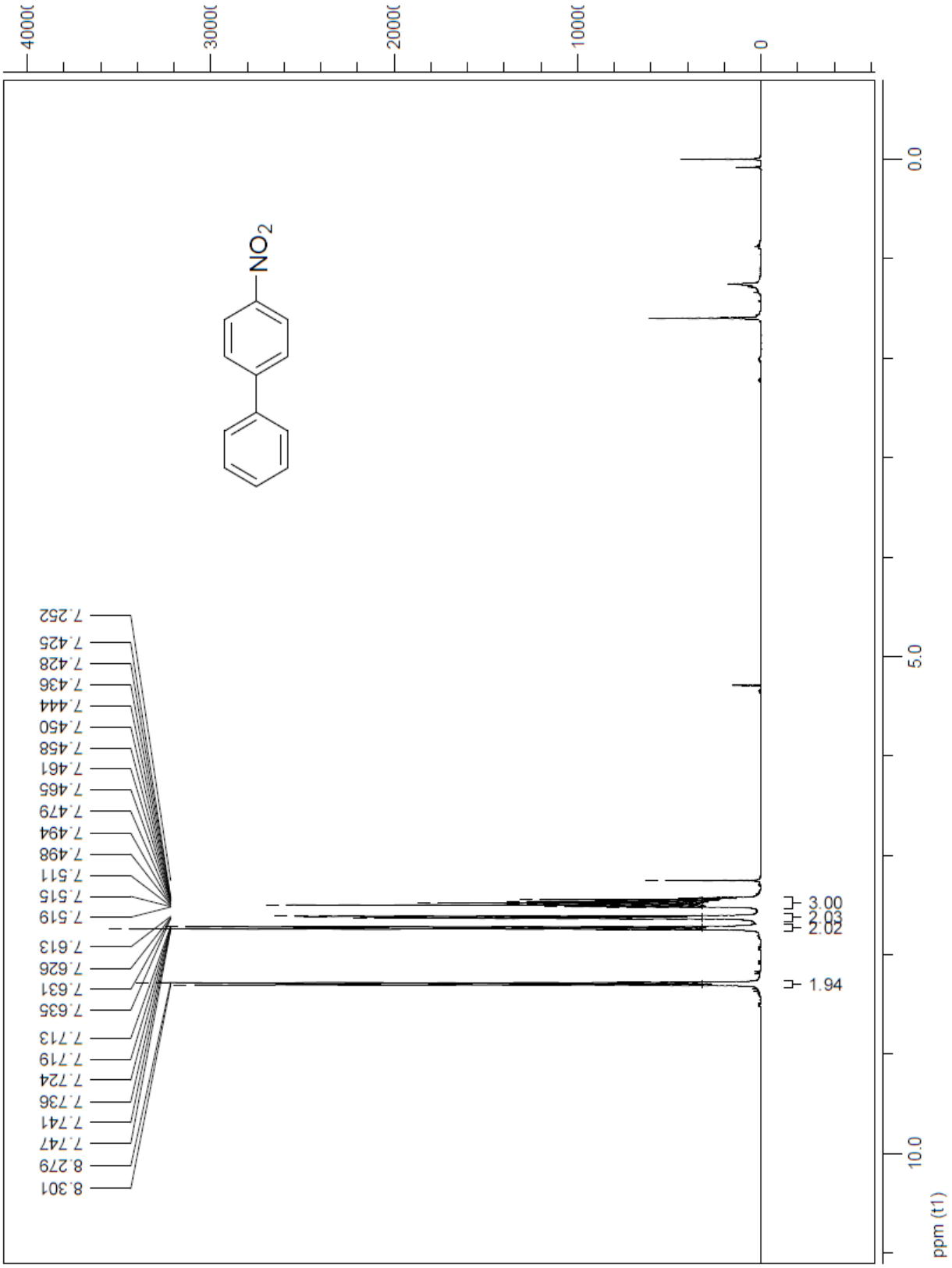


^{13}C NMR

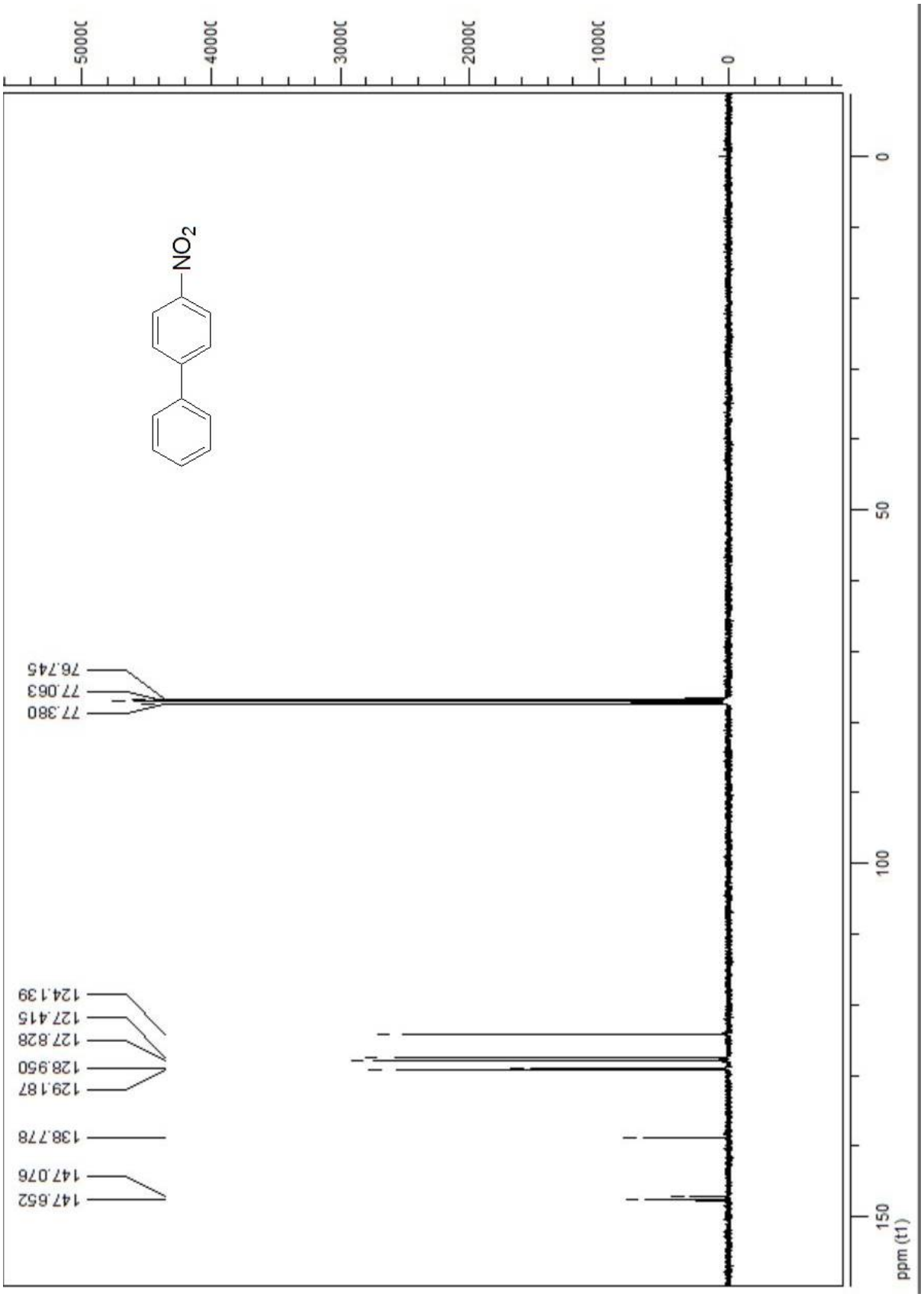

COOMe
52.150
76.795
77.114
77.431
127.067
127.301
128.176
128.912
128.957
130.136
140.002
145.645
167.026
ppm (t1)

4-Nitrobiphenyl 3af

^{1}H NMR

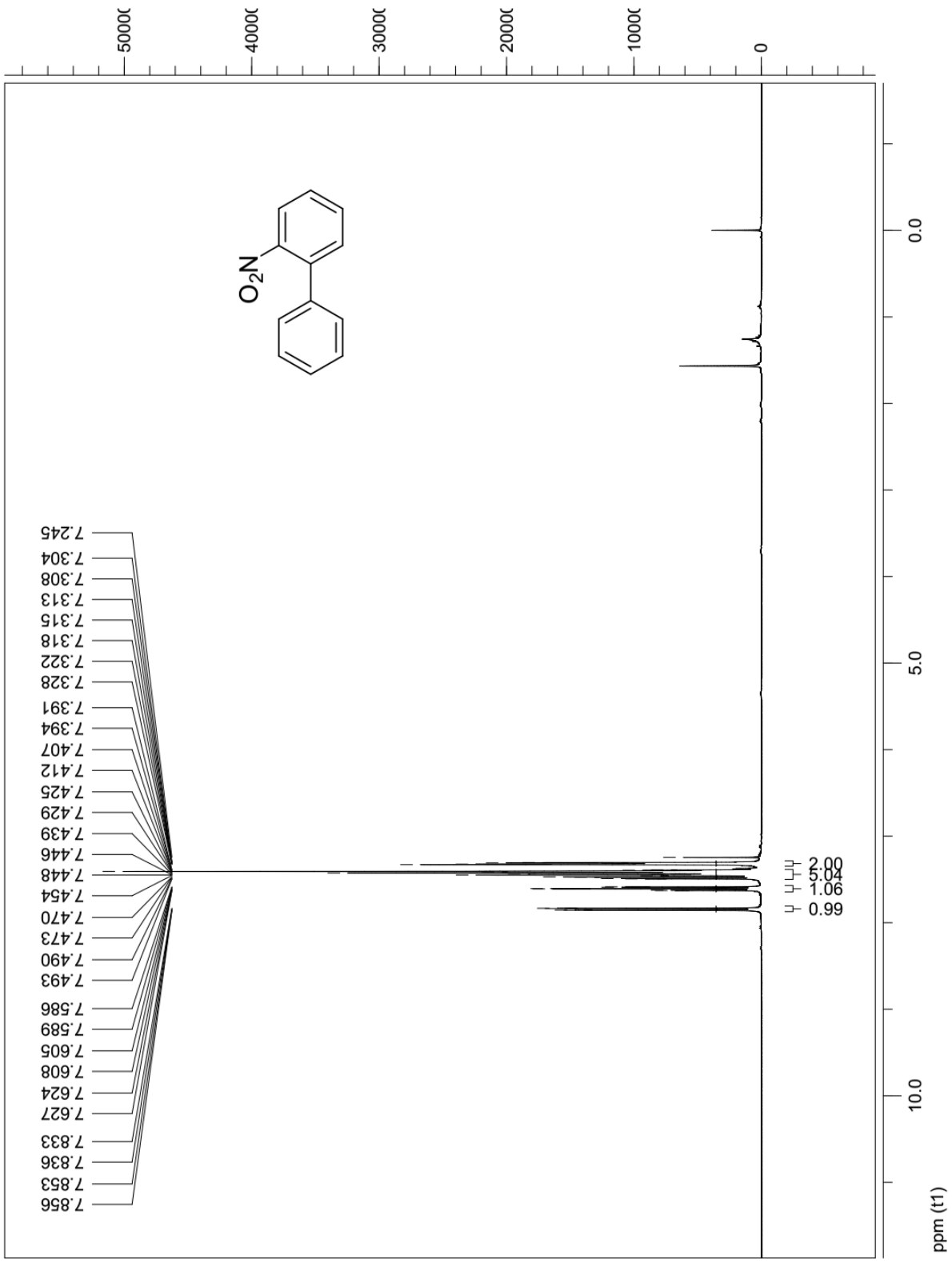


^{13}C NMR

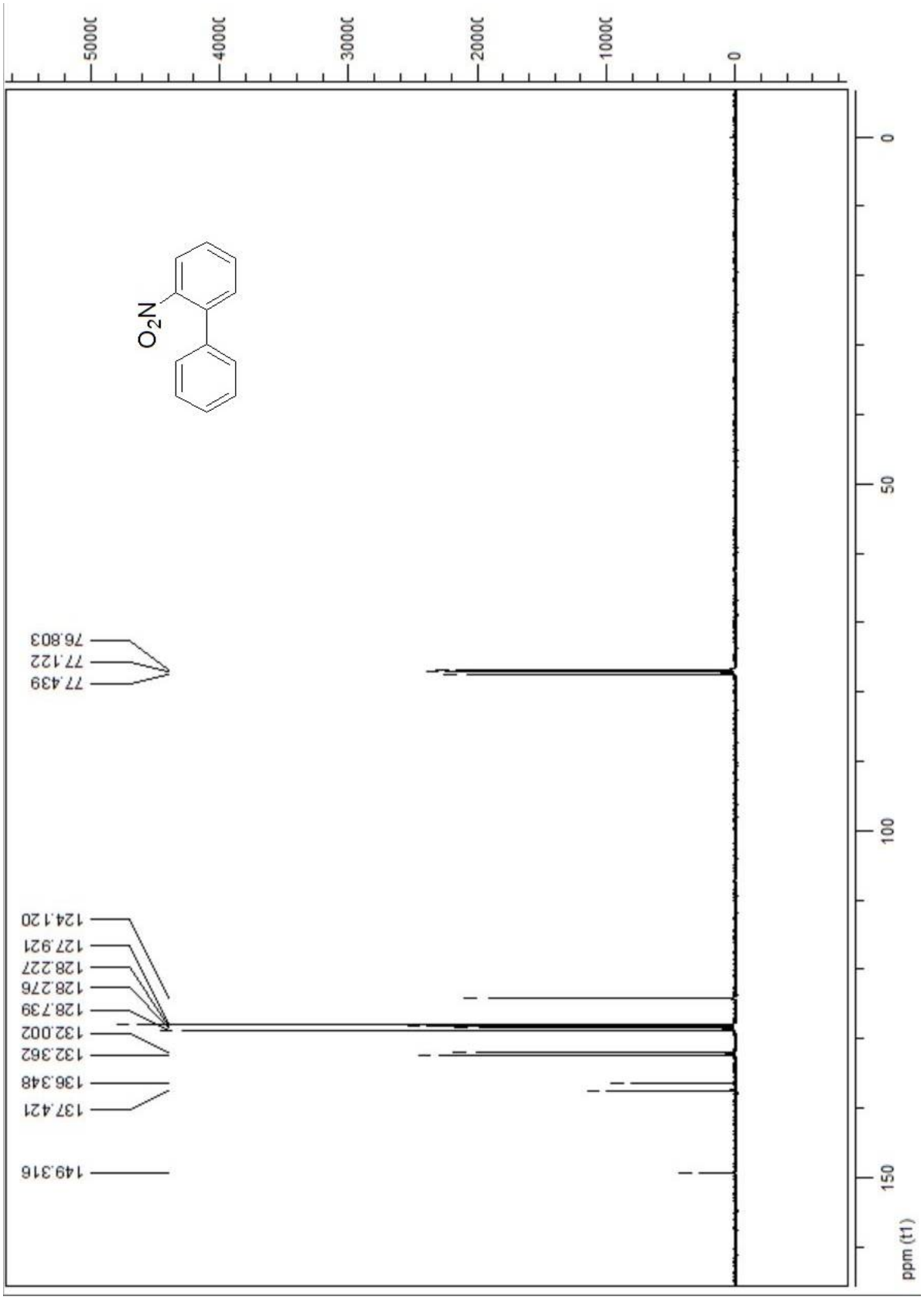

NO2
147.652
147.076
138.778
129.187
128.950
127.828
127.415
124.139
77.380
77.063
76.745
ppm (t1)

2-Nitrobiphenyl 3ag

^{1}H NMR

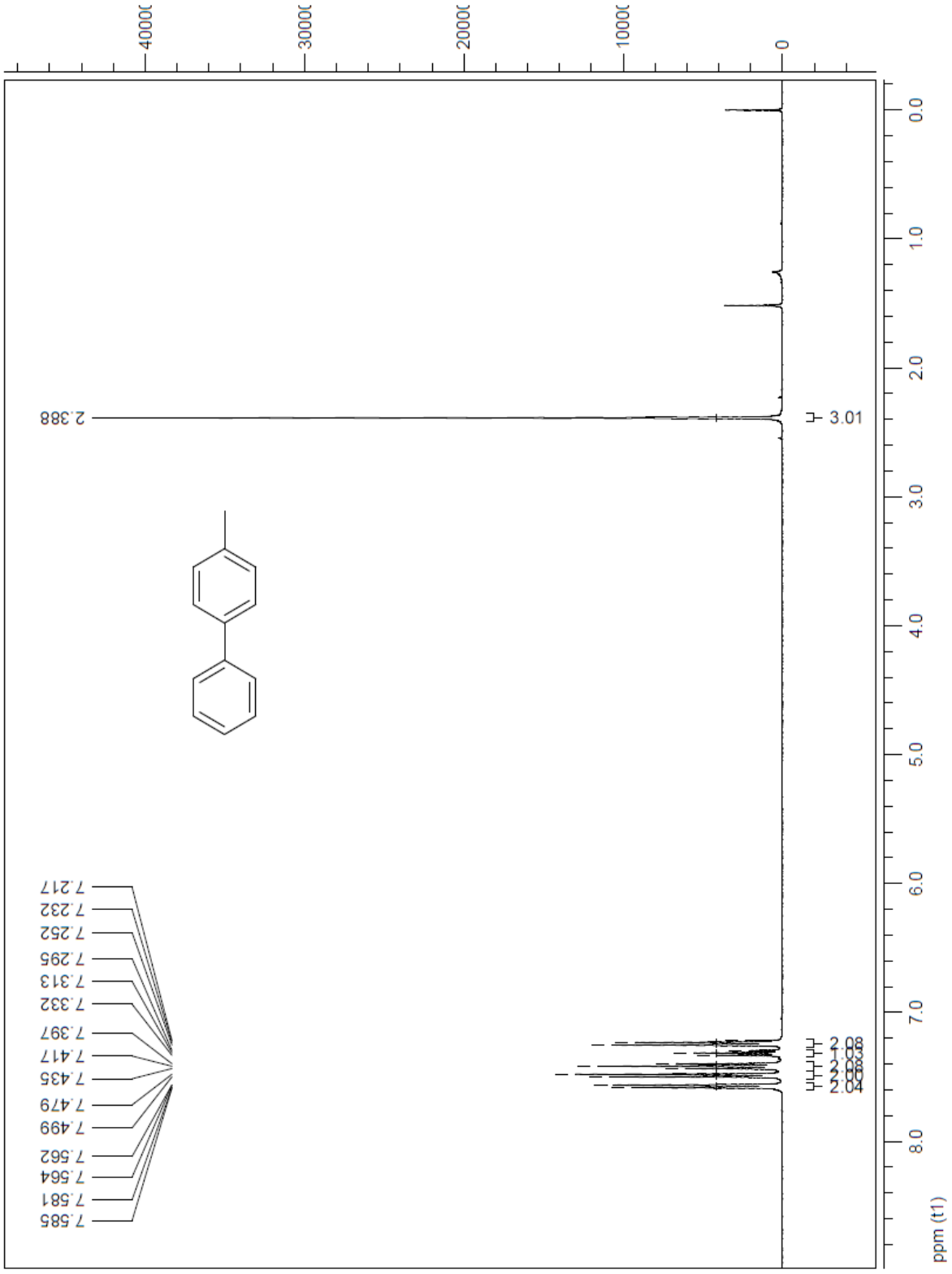


^{13}C NMR

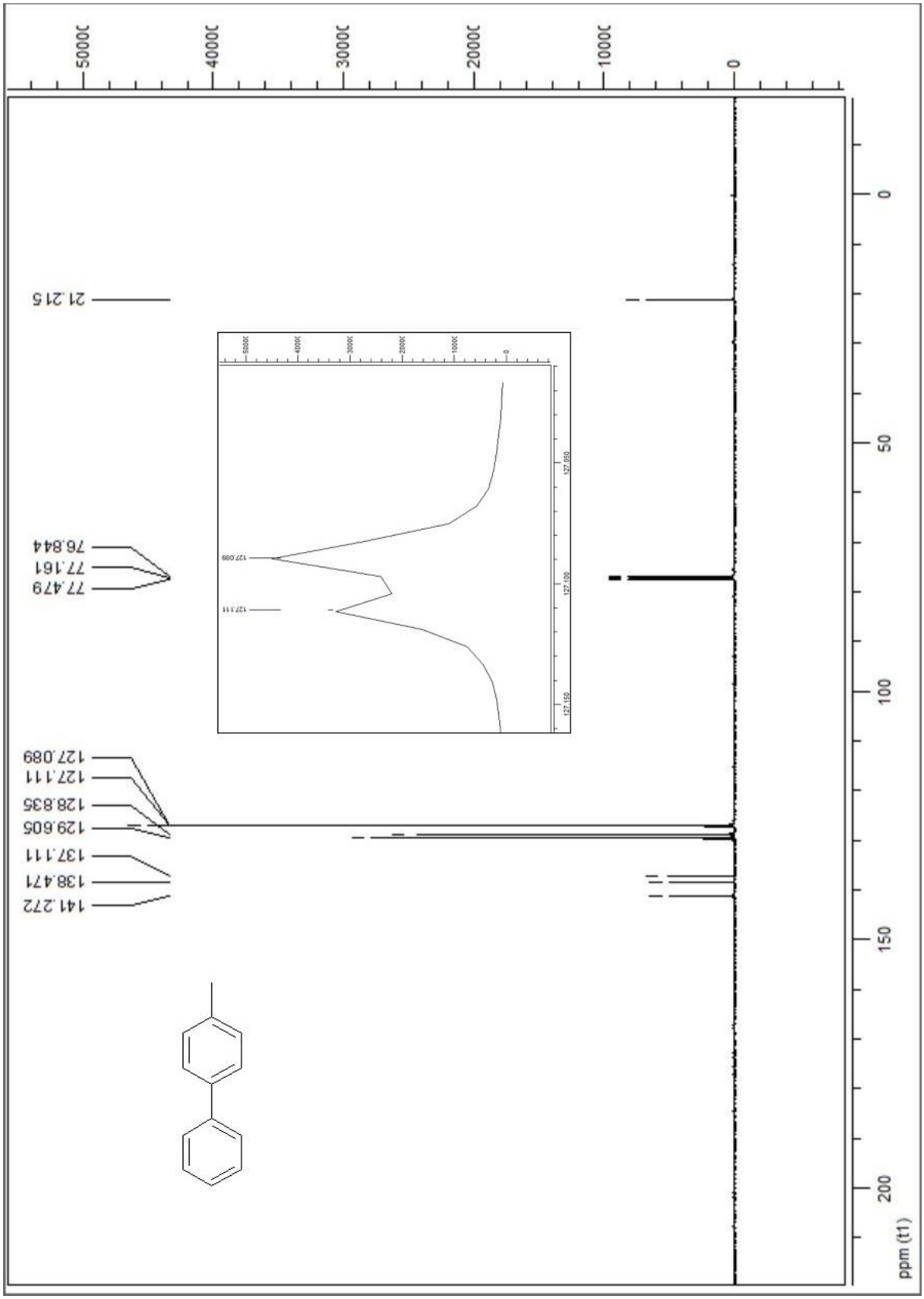

O2N
76.803
77.122
77.439
124.120
127.921
128.227
128.276
128.739
132.002
132.362
136.348
137.421
149.316
ppm (t1)

4-Methylbiphenyl 3ah

^{1}H NMR

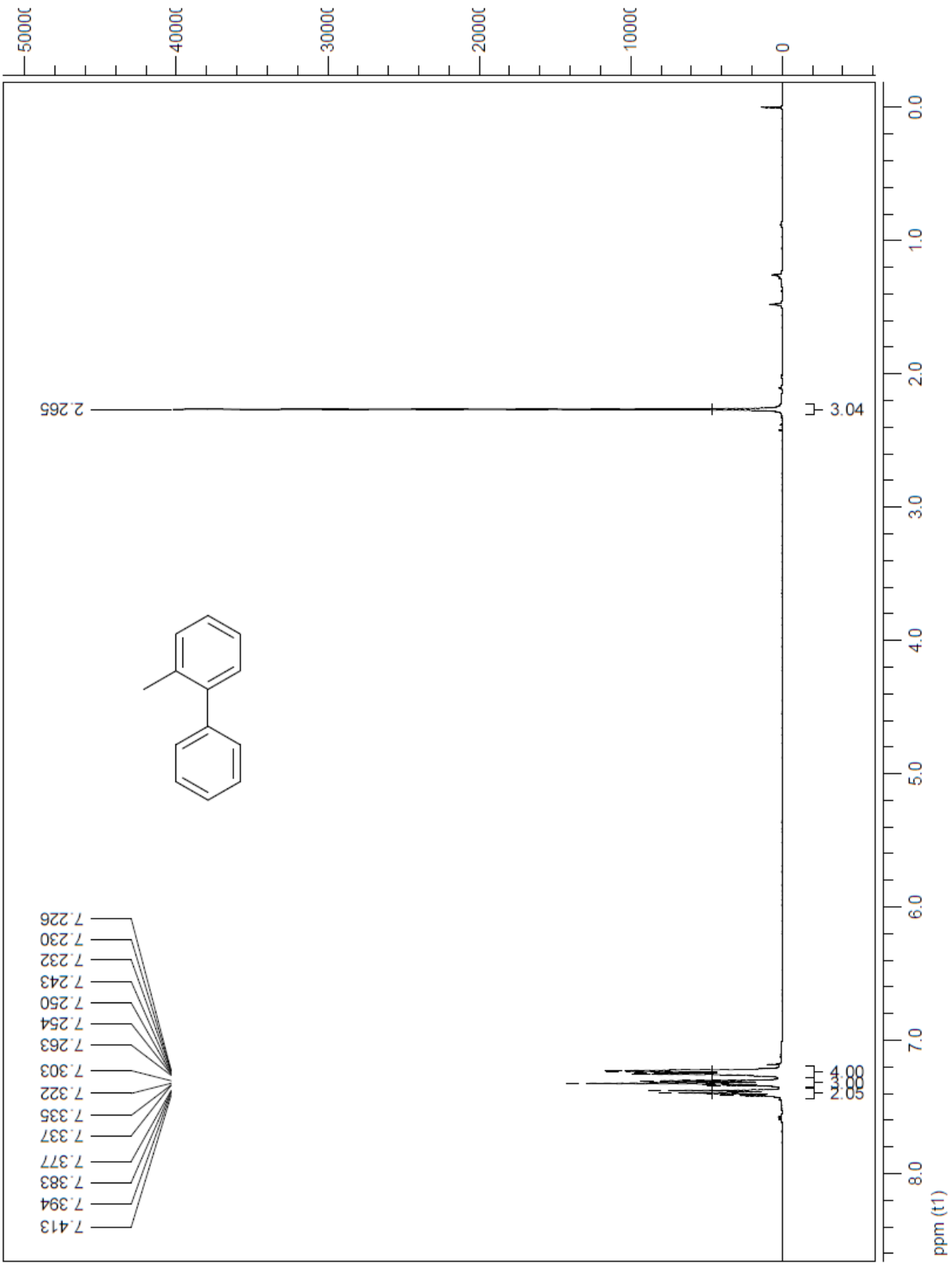


^{13}C NMR

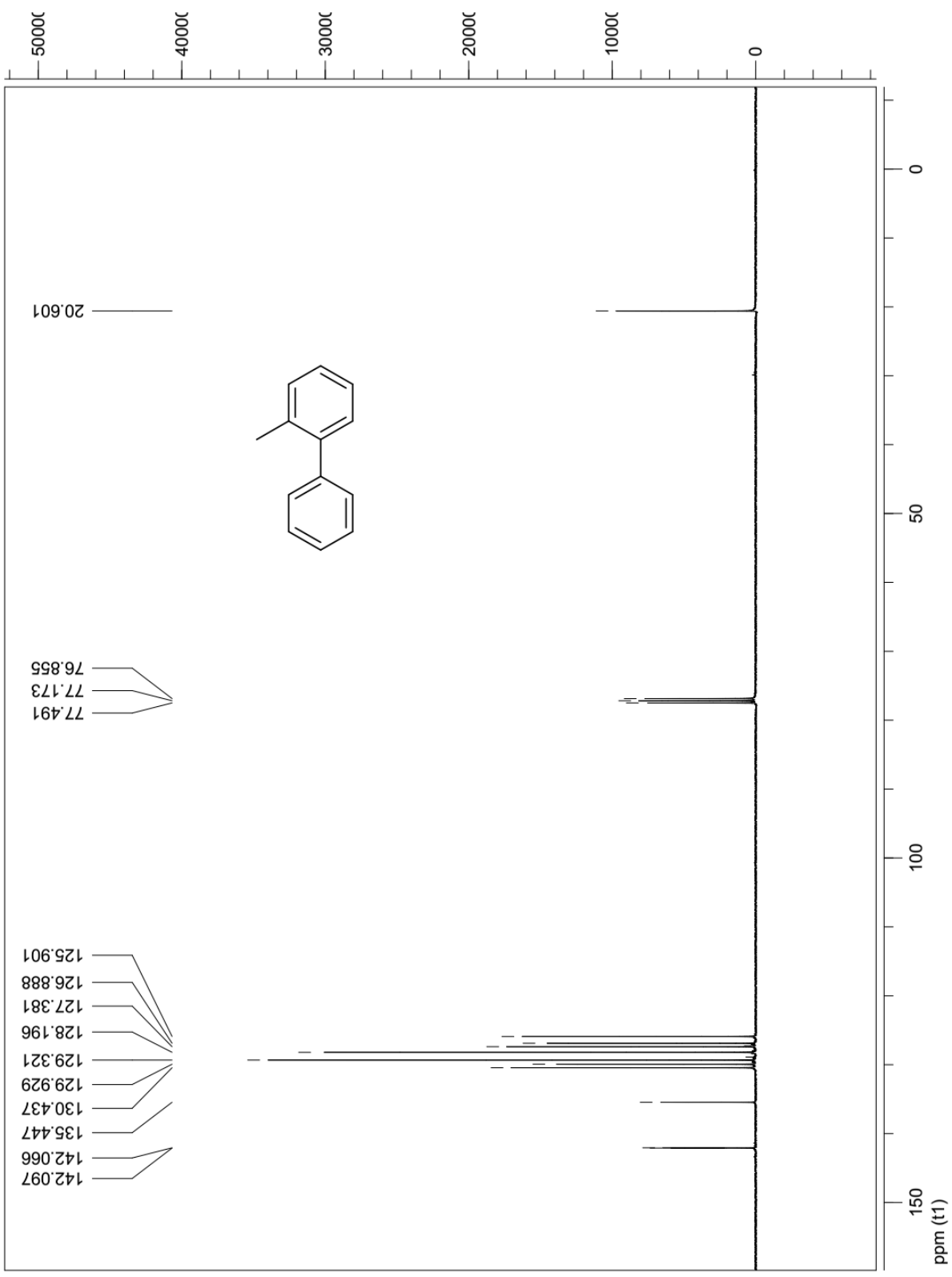

21.215
76.844
77.161
77.479
127.089
127.111
128.835
129.605
137.111
138.471
141.272
ppm (t1)

2-Methylbiphenyl 3ai

^{1}H NMR

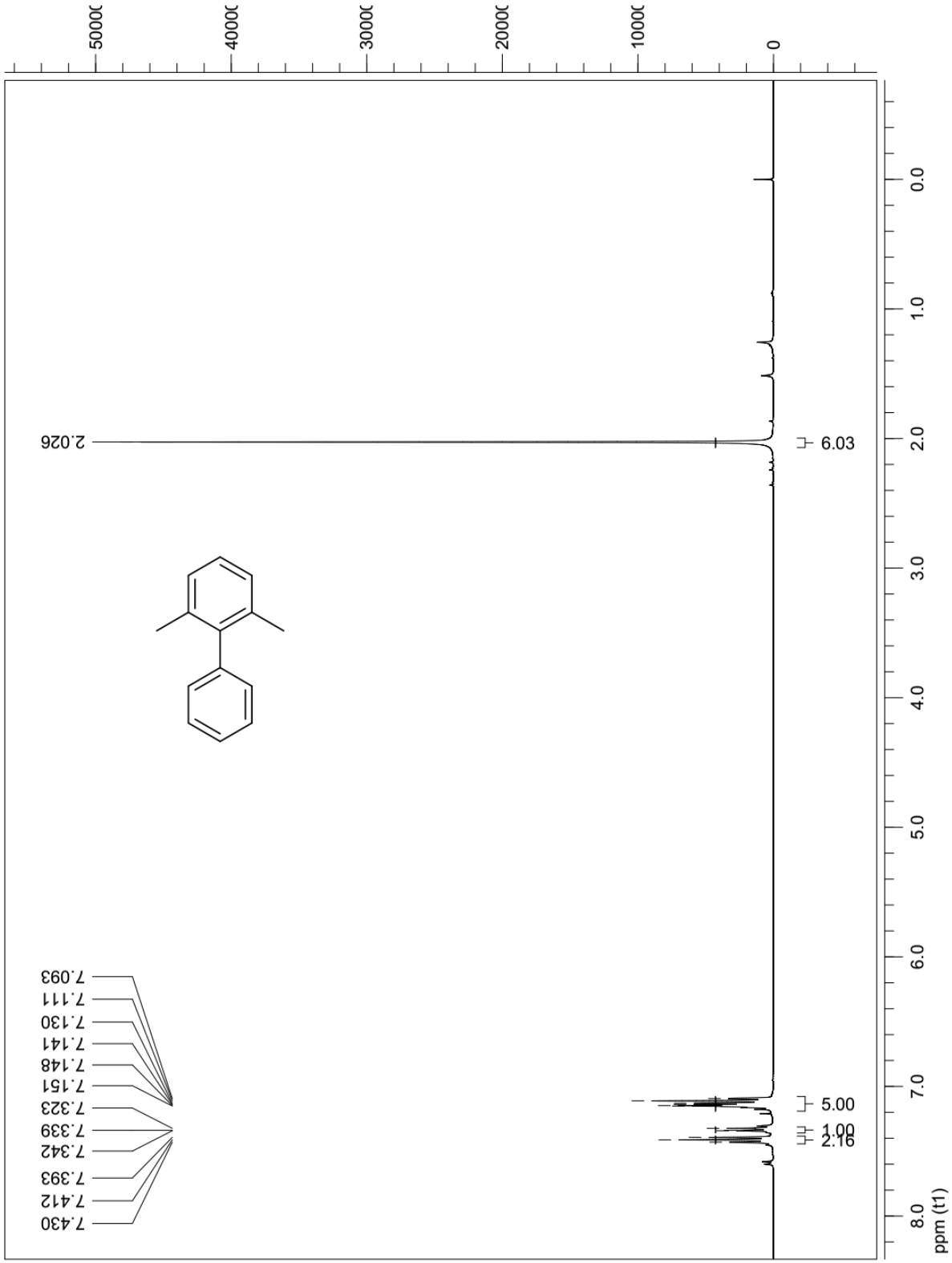


^{13}C NMR

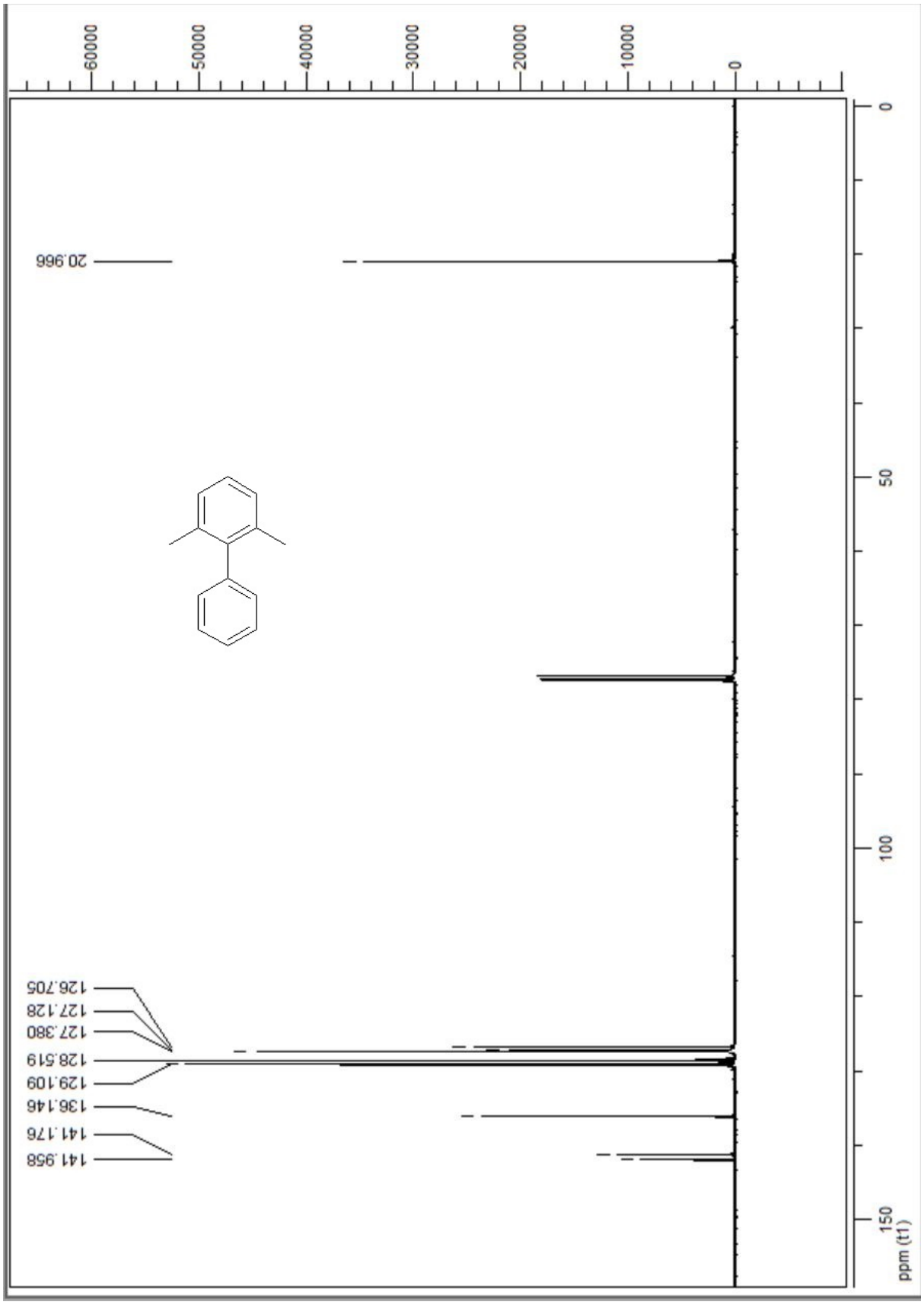

20.601
76.855
77.173
77.491
125.901
126.888
127.381
128.196
129.321
129.929
130.437
135.447
142.066
142.097
ppm (t1)

2,6-Dimethylbiphenyl 3aj

^{1}H NMR

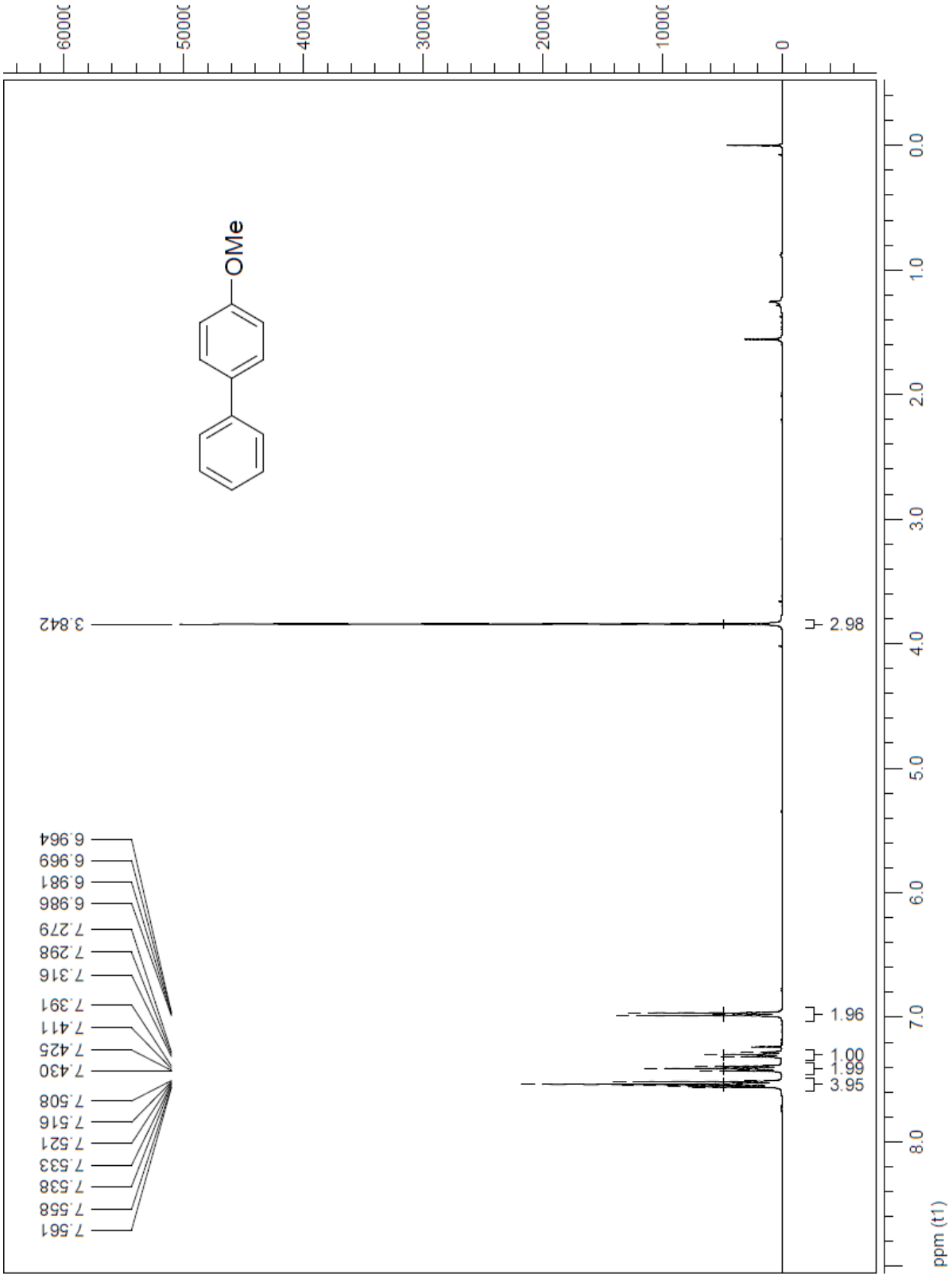


^{13}C NMR

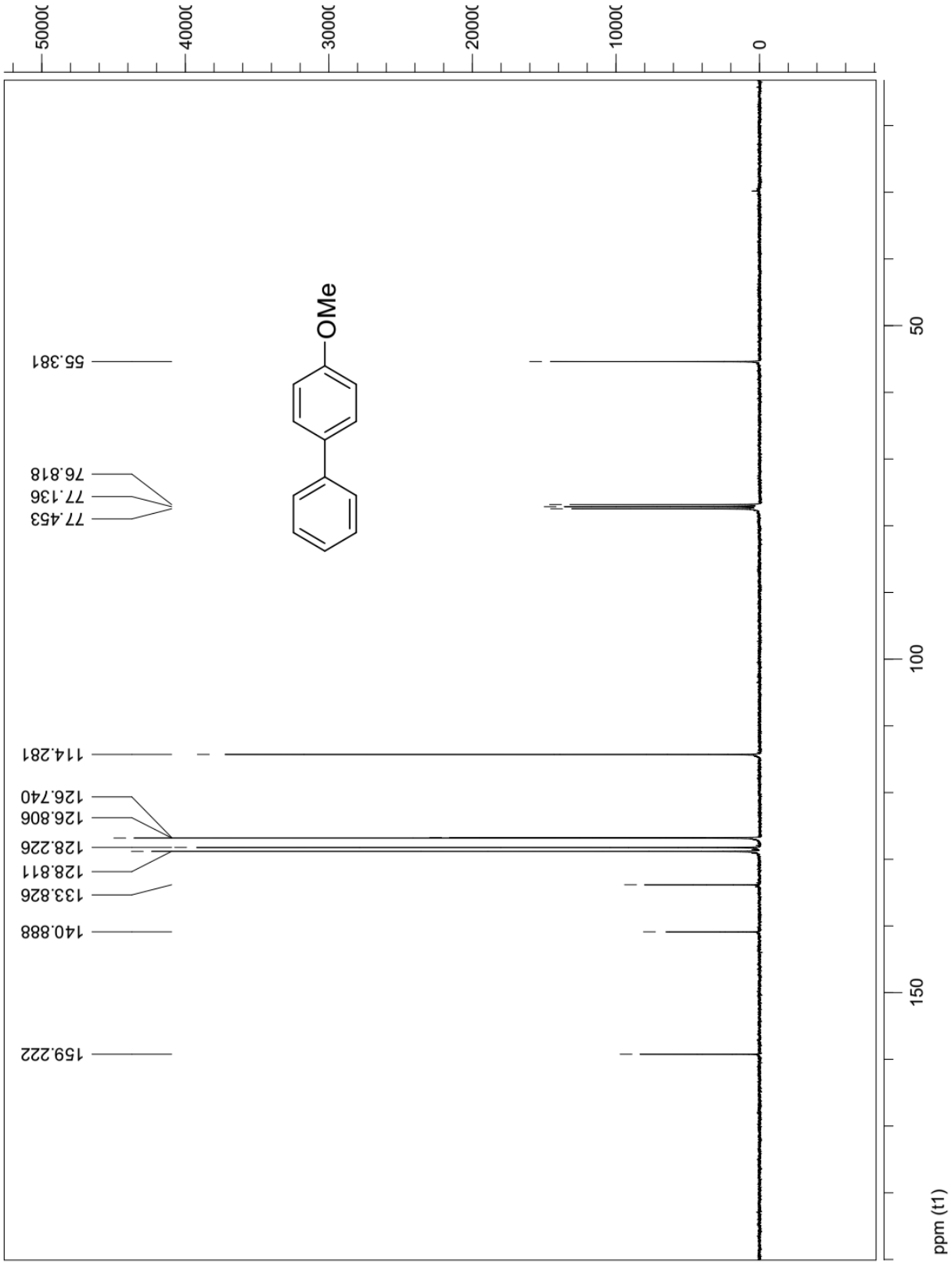

60000
50000
40000
30000
20000
10000
0
20.966
126.705
127.128
127.380
128.519
129.109
136.146
141.176
141.958
0
50
100
150
ppm (t1)

4-Methoxybiphenyl 3ak

^{1}H NMR

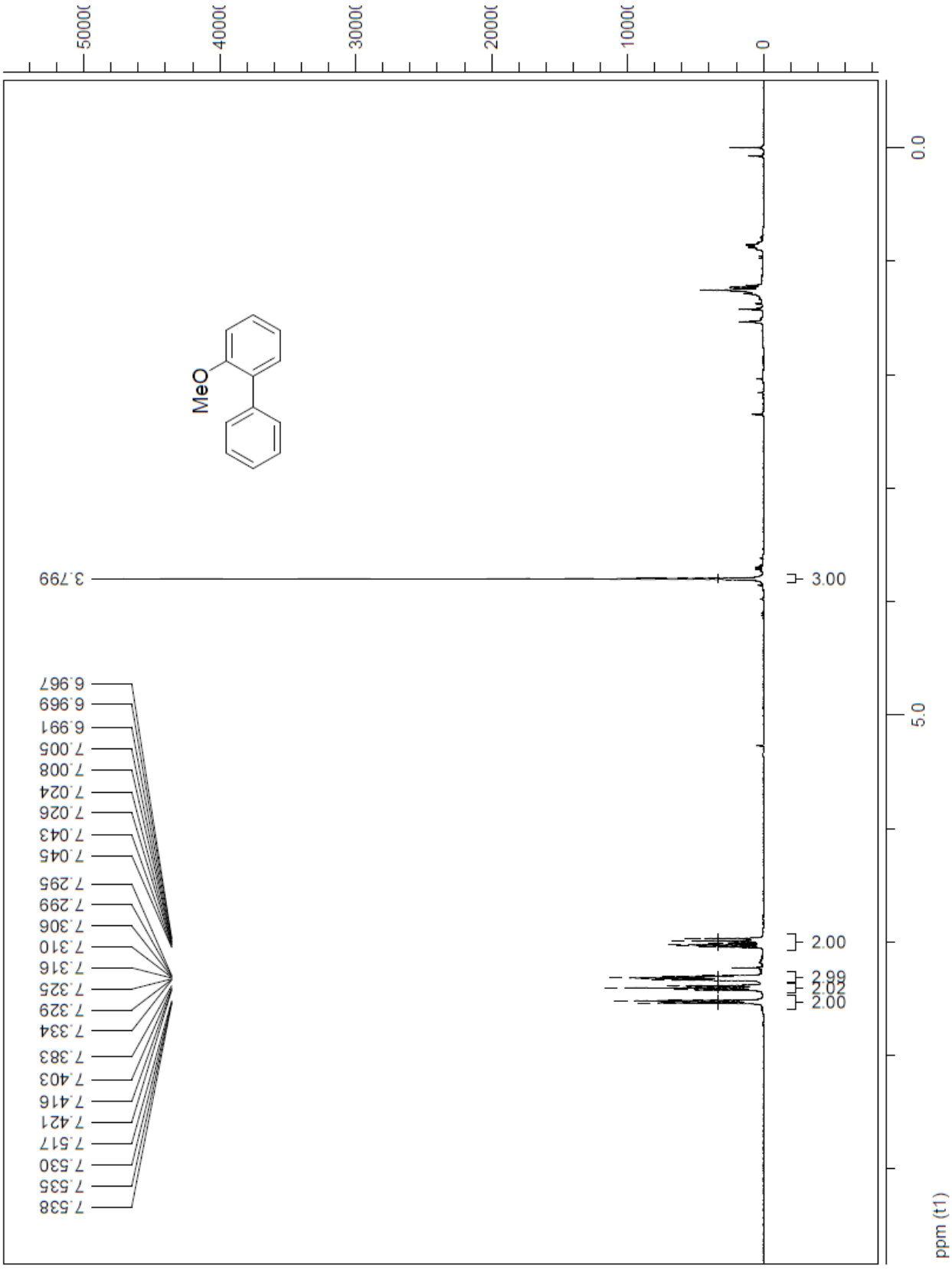


^{13}C NMR

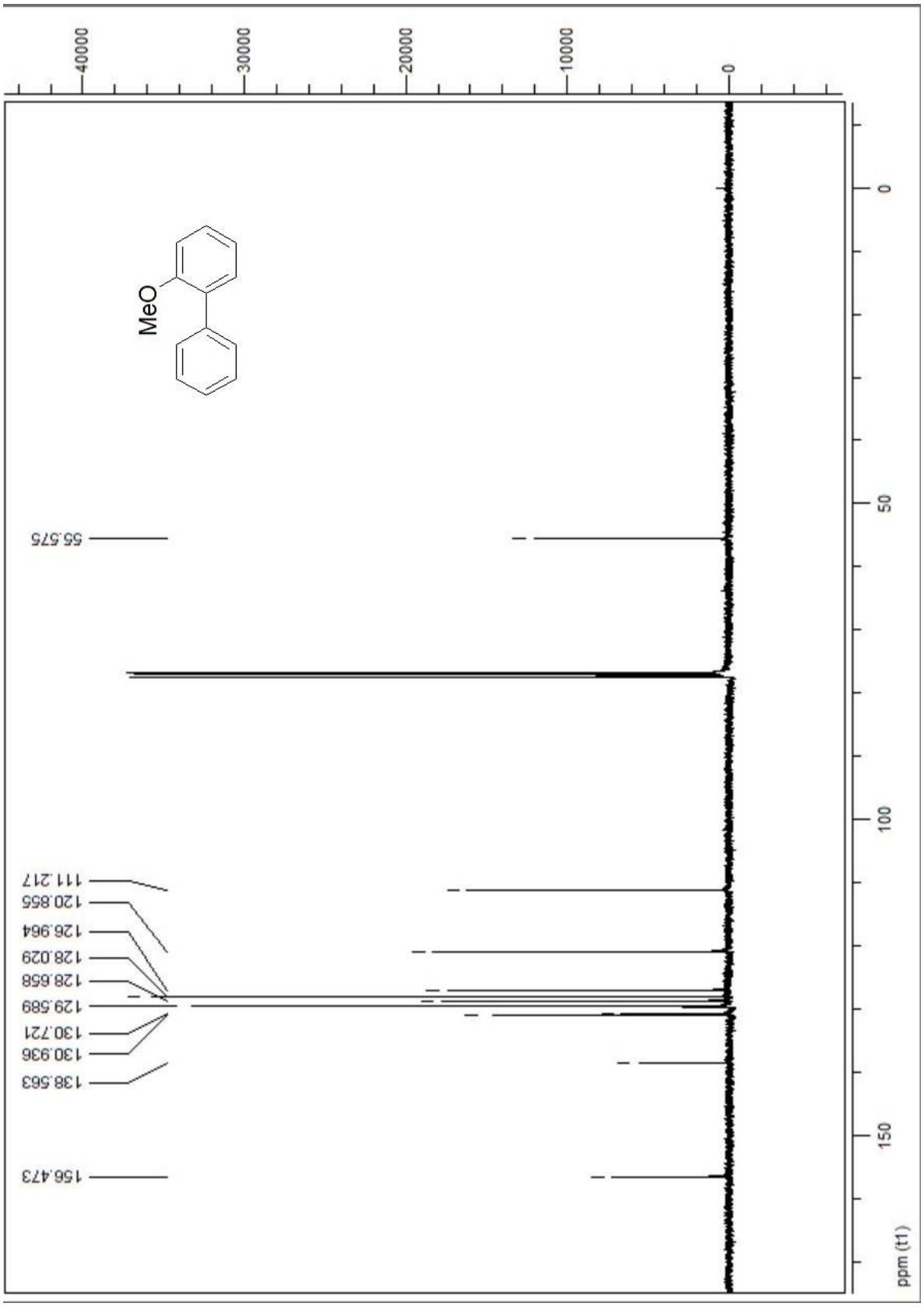

OMe
55.381
76.818
77.136
77.453
114.281
126.740
126.806
128.226
128.811
133.826
140.888
159.222
ppm (t1)

2-Phenylanisole 3al

^{1}H NMR



^{13}C NMR


40000
30000
20000
10000
0
MeO
55.575
111.217
120.855
126.964
128.029
128.658
129.589
130.721
130.936
138.563
156.473
0
50
100
150
ppm (t1)