Supporting Information for

Selective Radical–Radical Cross–Couplings: Design of a Formal β-Mannich Reaction

Jenna L. Jeffrey,[†] Filip R. Petronijević[†] and David W. C. MacMillan*

Merck Center for Catalysis at Princeton University, Princeton, New Jersey 08544

*Corresponding author. E-mail: dmacmill@princeton.edu

Table of Contents

1. General Information.

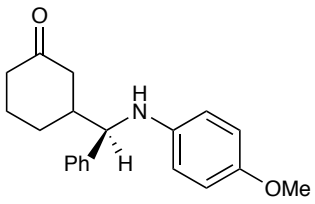
Commercial reagents were purified prior to use following the guidelines of Perrin and Armarego.[1] Solvents were purified by passage through columns of activated alumina, or according to the method of Grubbs.[2] Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator using a water bath. Chromatographic purification of products was accomplished using forced-flow column chromatography on ICN 60 32-64 mesh silica gel 63 according to the method of Still.[3] Thin-layer chromatography (TLC) was performed on Silicycle 0.25 mm silica gel F-254 plates. Visualization of the developed chromatogram was performed by fluorescence quenching or by anisaldehyde, ceric ammonium molybdate, or $KMnO_4$ stain. ^1H NMR spectra were recorded on a Bruker UltraShield Plus 500 MHz and are internally referenced to residual protio solvent signals. Data for ^1H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, dt = doublet of triplet, ddd = doublet of doublet of doublet, br = broad), coupling constant (Hz), integration. ^{13}C NMR spectra were recorded on a Bruker UltraShield Plus 500 (125 MHz) and data are reported in terms of chemical shift relative to $CDCl_3$ (77.0 ppm). IR spectra were recorded on a Perkin Elmer Paragon 1000 spectrometer and are reported in wavenumbers (cm^{-1}). High Resolution Mass spectra were obtained from the Princeton University Mass Spectral Facility.

2. Experimental Procedures

General β-Aminoalkylation Procedure A: A mixture of $Ir(ppy)_2(dtbbpy)PF_6$ (4.50 mg, 5.00 μmol, 0.005 equiv), DABCO (112 mg, 1.00 mmol, 1.00 equiv), imine (1.00 mmol, 1.00 equiv), cyclohexanone (520 μL, 5.00 mmol, 5.00 equiv), azepane (24.0 μL, 200 μmol, 0.200 equiv), trifluoroacetic acid (15.0 μL, 200 μmol, 0.20 equiv) and DMPU (1.33 mL) was placed in an 8 mL glass vial equipped with a magnetic stir bar and a nitrogen inlet. The mixture was subjected to three successive freeze-pump-thaw cycles. The vial was then sealed and placed 1 cm away from a blue LED strip cooled by a fan. The mixture was stirred and irradiated with blue LED light for 48 h. Upon completion, the reaction mixture was diluted with EtOAc (5 mL) and washed successively with brine (5 mL), water (5 mL) and brine (5 mL). The combined aqueous washings were extracted with EtOAc (2 x 5 mL). The combined organic extracts were dried (Na_2SO_4), filtered and concentrated *in vacuo*. Purification by flash column chromatography over silica gel (9:1–2:1 hexanes/EtOAc) afforded the pure product.

General Procedure B: A mixture of $Ir(ppy)_2(dtbbpy)PF_6$ (4.50 mg, 5.00 μmol, 0.005 equiv), DABCO (112 mg, 1.00 mmol, 1.00 equiv), imine (1.00 mmol, 1.00 equiv), ketone (5.00–10.0 mmol, 5.00–10.0 equiv), azepane (24.0–48.0 μL, 200–400 μmol, 0.20–0.40 equiv), trifluoroacetic acid (15.0 μL, 200 μmol, 0.20 equiv), lithium tetrafluoroborate (only where indicated, 94.0 mg, 1.00 mmol, 1.00 equiv) and DMPU (1.33 mL) was placed in an 8 mL glass vial equipped with a magnetic stir bar and a nitrogen inlet. The mixture was subjected to three successive freeze-pump-thaw cycles. The vial was then sealed and placed 1 cm away from a blue LED strip cooled by a fan. The mixture was stirred and irradiated with blue LED light for 48 h. Upon completion, the reaction mixture was diluted with EtOAc (5 mL) and washed successively with brine (5 mL), water (5 mL) and brine (5 mL). The combined aqueous washings were

extracted with EtOAc (2 x 5 mL). The combined organic extracts were dried over (Na_2SO_4), filtered and concentrated *in vacuo*. Purification by flash column chromatography over silica gel (9:1–2:1 hexanes/EtOAc) afforded the pure product.

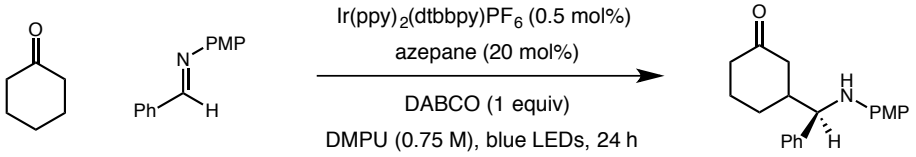


(±)-**18** 74% yield

3-(((4-Methoxyphenyl)amino)(phenyl)methyl)cyclohexan-1-one (18): Following General Procedure A, $Ir(ppy)_2(dtbbpy)PF_6$ (4.50 mg, 5.47 μmol, 0.005 equiv), DABCO (112 mg, 1.00 mmol, 1.00 equiv), imine (211 mg, 1.00 mmol, 1.00 equiv), cyclohexanone (0.52 mL, 5.0 mmol, 5.00 equiv), azepane (24.0 μL, 200 μmol, 0.200 equiv), trifluoroacetic acid (16 μL, 0.2 mmol, 0.2 equiv.), and DMPU (1.33 mL) provided the desired aminoketone (230 mg, 74%) in the form of a colorless oil as a mixture of diastereomers (1:1 ratio). Separation of the diastereomers was accomplished using flash column chromatography (silica gel, 4:1 hexanes/EtOAc). **IR** (film) 3385, 2936, 1704, 1618, 1510, 1451, 1347, 1233, 1178, 1125, 1067, 1035 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33–7.28 (m, 2 H), 7.27–7.19 (m, 3 H), 6.71–6.63 (m, 2 H), 6.50–6.43 (m, 2 H), 4.21 (d, *J* = 4.7 Hz, 0.54 H), 4.15 (d, *J* = 5.8 Hz, 0.36 H), 3.83 (brs, 1 H), 3.67 (s, 3 H), 2.63 (d, *J* = 12.3 Hz, 0.38 H), 2.42–1.96 (m, 6 H), 1.76 (d, *J* = 13.4 Hz, 0.47 H), 1.66–1.52 (m, 1 H), 1.52–1.34 (m, 1 H); **^{1}H NMR** (single diastereomer, 500 MHz, $CDCl_3$) δ 7.33–7.28 (m, 2 H), 7.27–7.19 (m, 3 H), 6.70–6.63 (m, 2 H), 6.49–6.45 (m, 2 H), 4.21 (d, *J* = 5.1 Hz, 1 H), 3.82 (brs, 1 H), 3.67 (s, 3 H), 2.40–1.99 (m, 7 H), 1.60 (dddd, *J* = 17.1, 13.8, 9.3, 4.4 Hz, 1 H), 1.52–1.42 (m, 1 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 211.2, 211.0, 152.1, 141.2, 141.0, 128.5 (2 C), 128.3, 127.3, 127.1 (2 C), 114.7 (2 C), 63.5, 62.9,

55.7, 45.5, 45.4, 45.1, 41.3 (2 C), 28.2, 27.7, 25.0 (2 C) ppm; **^{13}C NMR** (single diastereomer, 125 MHz, $CDCl_3$) δ 211.2, 152.0, 141.2, 141.0, 128.5, 128.3, 127.3, 127.1, 114.7 (2 C), 62.9, 55.6, 45.4, 45.1, 41.3, 27.7, 24.9 ppm; (HRMS (ESI) *m/z* calcd for $C_{20}H_{23}NO_2$ [$(M)^+$] 309.1729, found 309.1730.

Optimization Study

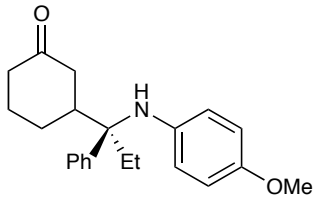


0.25 mmol (±)-**18**

cyclohexanone (equiv.)	(±)-18 (%)*
1	42
2	51
5	70

*% Yields calculated by ^{1}H NMR using an internal standard.

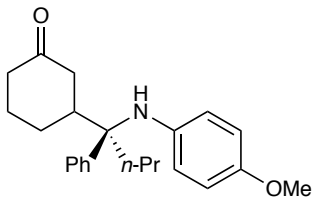
Table S1. Selected Optimization Study



(±)-**12** 79% yield

3-(1-((4-Methoxyphenyl)amino)-1-phenylpropyl)cyclohexan-1-one (**12):** Following General Procedure A, $Ir(ppy)_2(dtbbpy)PF_6$ (4.50 mg, 5.47 μmol, 0.005 equiv), DABCO (112 mg, 1.00 mmol, 1.00 equiv), imine (239 mg, 1.00 mmol, 1.00 equiv), cyclohexanone (0.52 mL, 5.00 mmol, 5.00 equiv), azepane (24.0 μL, 200 μmol, 0.20 equiv), trifluoroacetic acid (15 μL, 0.20 mmol, 0.2 equiv), and DMPU (1.33 mL) provided the desired aminoketone (265 mg, 79%) in the form of a colorless oil as an inseparable mixture of diastereomers (1:1). **IR** (film) 3377, 3054,

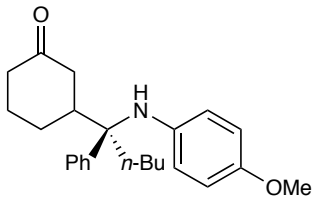
2959, 2880, 2831, 1709, 1618, 1510, 1462, 1380, 1348, 1304, 1266, 1236, 1179, 1136, 1112, 1039 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 7.9, 5.2 Hz, 2H), 7.43–7.29 (m, 3H, overlapping with solvent signal), 6.62 (dd, *J* = 8.7, 4.2 Hz, 2H), 6.31–6.23 (m, 2H), 3.70 (brs, 4H), 2.81 (dq, *J* = 13.8, 2.6 Hz, 0.5H), 2.58–2.49 (m, 0.5H), 2.39–1.95 (m, 7H), 1.85 (t, *J* = 13.5 Hz, 0.5H), 1.76 (t, *J* = 13.5 Hz, 0.5H), 1.68–1.54 (m, 1H), 1.10 (qd, *J* = 12.7, 3.1 Hz, 0.5H), 1.03–0.93 (m, 0.5H), 0.82–0.76 (m, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 212.5, 211.4, 151.8, 151.7, 141.2, 141.1, 139.6, 139.5, 128.3, 128.1, 127.9, 126.8, 116.7, 114.2 (2 C), 63.5, 63.4, 55.5, 46.2, 45.7, 43.5, 43.2, 41.1, 40.9, 26.0, 25.6, 25.1, 24.8, 23.6, 23.0, 7.1, 7.0 ppm; HRMS (ESI) *m/z* calcd for $C_{22}H_{28}NO_2$ [$(M+H)^+$] 338.2120, found 338.2120.



(±)-**13** 71% yield

3-(1-((4-Methoxyphenyl)amino)-1-phenylbutyl)cyclohexan-1-one (13): Following General Procedure A, $Ir(ppy)_2(dtbbpy)PF_6$ (4.50 mg, 5.00 μmol, 0.005 equiv), DABCO (112 mg, 1.00 mmol, 1.00 equiv), imine (253 mg, 1.00 mmol, 1.00 equiv), cyclohexanone (0.52 mL, 5.00 mmol, 5.00 equiv), azepane (24.0 μL, 200 μmol, 0.200 equiv), trifluoroacetic acid (16 μL, 0.20 mmol, 0.2 equiv.), and DMPU (1.33 mL) provided the desired aminoketone (250 mg, 71%) in the form of a beige foam as an inseparable mixture of diastereomers (1:1). **IR** (film) 3375, 3055, 2958, 2871, 2831, 1708, 1617, 1510, 1452, 1306, 1266, 1235, 1178, 1142, 1111, 1069, 1039 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 7.8, 5.4 Hz, 2H), 7.41–7.27 (m, 3H, overlapping with solvent signal), 6.62 (dd, *J* = 8.9, 4.1 Hz, 2H), 6.27 (t, *J* = 9.4 Hz, 1H), 3.78–3.54 (m, 4H), 2.84–2.76 (m, 0.5H), 2.54 (dd, *J* = 13.4, 2.9 Hz, 0.5H), 2.37–1.97 (m, 7H), 1.87 (t, *J* = 13.5 Hz,

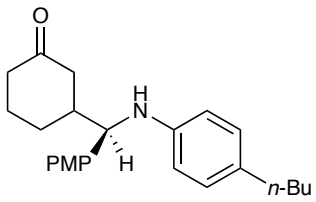
0.5H), 1.75 (t, *J* = 13.5 Hz, 0.5H), 1.67–1.53 (m, 1H), 1.36–1.20 (m, 2H), 1.12 (qd, *J* = 12.8, 3.1 Hz, 0.5H), 0.97 (qd, *J* = 12.9, 3.0 Hz, 0.5H), 0.83–0.76 (m, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 212.5, 211.4, 151.7 (2 C), 141.2, 141.1, 139.6, 139.5, 128.3, 128.1, 127.9, 126.8, 116.7, 114.2, 114.1, 63.5, 63.4, 55.5, 47.0, 46.5, 43.6, 43.3, 41.1, 40.9, 33.9, 33.3, 26.1, 25.7, 25.2, 24.8, 15.8, 15.7, 14.5, 14.4 ppm; HRMS (ESI) *m/z* calcd for $C_{23}H_{30}NO_2$ $[(M+H)^+]$ 352.2277, found 352.2276.



(±)-**14** 79% yield

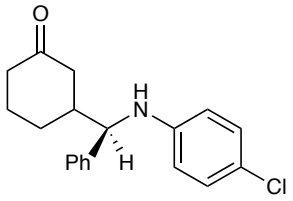
3-(1-((4-Methoxyphenyl)amino)-1-phenylpentyl)cyclohexan-1-one (**14**)**:** Following General Procedure A, $Ir(ppy)_2(dtbbpy)PF_6$ (4.50 mg, 5.00 μmol, 0.005 equiv), DABCO (112 mg, 1.00 mmol, 1.00 equiv), imine (267 mg, 1.00 mmol, 1.00 equiv), cyclohexanone (0.52 mL, 5.00 mmol, 5.00 equiv), azepane (24.0 μL, 200 μmol, 0.200 equiv), trifluoroacetic acid (16 μL, 0.20 mmol, 0.2 equiv.), and DMPU (1.33 mL) provided the desired aminoketone (290 mg, 79%) in the form of a colorless foam as an inseparable mixture of diastereomers (1:1). **IR** (film) 3377, 3056, 3031, 2955, 2933, 2869, 2831, 1709, 1617, 1510, 1465, 1445, 1379, 1347, 1305, 1267, 1236, 1179, 1136, 1111, 1069, 1039 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.50–7.42 (m, 4 H), 7.39–7.32 (m, 4 H), 7.29 (dt, *J* = 7.4, 3.6 Hz, 2 H), 6.58 (dd, *J* = 9.0, 3.9 Hz, 4 H), 6.28–6.18 (m, 4 H), 3.67 (overlapping s and brs, 8 H), 2.77 (dq, *J* = 13.8, 2.5 Hz, 1 H), 2.51 (dt, *J* = 13.7, 2.7 Hz, 1 H), 2.36–2.19 (m, 5 H), 2.19–1.93 (m, 9 H), 1.83 (t, *J* = 13.5 Hz, 1 H), 1.72 (t, *J* = 13.5 Hz, 1 H), 1.65–1.47 (m, 3 H), 1.31–1.02 (m, 9 H), 1.00–0.86 (m, 1 H), 0.76 (td, *J* = 6.8, 4.9 Hz, 6 H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 212.5, 211.5, 151.8 (2 C), 141.3, 141.2, 139.6, 139.5,

128.3, 128.1, 127.9, 126.8, 116.8 (2 C), 114.2 (2 C), 63.5, 63.4, 55.5, 47.0, 46.5, 43.6, 43.3, 41.1, 41.0, 31.1, 30.5, 26.2, 25.7, 25.2, 24.8, 24.6, 24.5, 22.8 (2 C), 13.9 ppm; HRMS (ESI) *m/z* calcd for $C_{24}H_{31}NO_2$ [$(M)^+$] 365.2355, found 365.2355.



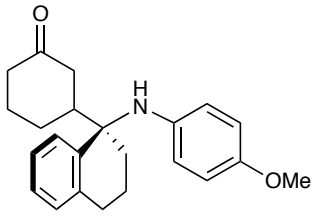
(±)-**19** 64% yield

3-(((4-Butylphenyl)amino)(4-methoxyphenyl)methyl)cyclohexan-1-one (19): Following General Procedure A, $Ir(ppy)_2(dtbbpy)PF_6$ (4.50 mg, 5.47 μmol, 0.005 equiv), DABCO (112 mg, 1.00 mmol, 1.00 equiv), imine (268 mg, 1.00 mmol, 1.00 equiv), cyclohexanone (0.52 mL, 5.0 mmol, 5.00 equiv), azepane (24.0 μL, 200 μmol, 0.200 equiv), acetic acid (12 μL, 0.2 mmol, 0.2 equiv.), and DMPU (1.33 mL) provided the desired aminoketone (231 mg, 64%) in the form of yellowish oil as an inseparable mixture of diastereomers (1:1 ratio). **IR** (film) 3388, 2953, 1707, 1614, 1247 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.19 (dd, 4 H, *J* = 9.8, 7.5 Hz), 6.90 (d, 4 H, *J* = 8.0 Hz), 6.86 (dd, 4 H, *J* = 8.7, 3.5 Hz), 6.51–6.41 (m, 4 H), 4.26–4.15 (m, 2 H), 3.79 (d, 6 H, *J* = 2.4 Hz), 2.62 (d, 1 H, *J* = 10.1 Hz), 2.44 (t, 4 H, *J* = 7.8 Hz), 2.39–2.01 (m, 12 H), 1.78 (s, 1 H), 1.59 (ddd, 3 H, *J* = 17.4, 8.7, 4.6 Hz), 1.49 (ddt, 5 H, *J* = 9.2, 7.6, 3.5 Hz), 1.38 (d, 1 H, *J* = 12.2 Hz), 1.37–1.23 (m, 5 H), 0.89 (t, 6 H, *J* = 7.3 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 211.3, 211.1, 158.7, 129.0 (2 C), 128.1, 113.9 (2 C), 62.3, 61.7, 55.2, 45.6, 45.3, 45.1, 41.3 (2 C), 34.6, 33.9, 28.0, 27.9, 25.0 (2 C), 22.3, 14.0 ppm; HRMS (ESI) *m/z* calcd for $C_{24}H_{32}NO_2$ 365.2355, found 365.2354.



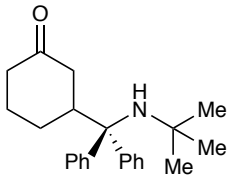
(±)-**20** 73% yield

3-(((4-Chlorophenyl)amino)(phenyl)methyl)cyclohexan-1-one (20): Following General Procedure A, $Ir(ppy)_2(dtbbpy)PF_6$ (4.50 mg, 5.47 μmol, 0.005 equiv), DABCO (112 mg, 1.00 mmol, 1.00 equiv), imine (216 mg, 1.00 mmol, 1.00 equiv), cyclohexanone (0.52 mL, 5.0 mmol, 5.00 equiv), azepane (24.0 μL, 200 μmol, 0.200 equiv), acetic acid (12 μL, 0.2 mmol, 0.2 equiv.), sodium acetate (164 mg, 5.0 mmol, 2.0 equiv.), water (10 μL, 0.50 mmol, 0.5 equiv.) and DMPU (1.33 mL) provided the desired aminoketone (229 mg, 73%) in the form of colorless oil as an inseparable mixture of diastereomers (1:1 ratio). **IR** (film) 3388, 2927, 1705, 1598, 1500, 1315 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31–7.24 (m, 4 H), 7.23–7.15 (m, 6 H), 6.96 (dd, 4 H, *J* = 8.9, 2.8 Hz), 6.41–6.35 (m, 4 H), 4.19 (d, 1 H, *J* = 5.3 Hz), 4.12 (d, 1 H, *J* = 6.1 Hz), 2.62–2.52 (m, 1 H), 2.38–2.28 (m, 2 H), 2.28–1.94 (m, 10 H), 1.70–1.67 (m, 1 H), 1.61–1.29 (m, 6 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 210.8, 210.7, 145.6, 145.5, 140.5, 140.2, 129.0, 128.9, 128.6 (2 C), 127.6, 127.1, 127.0, 122.2 (2 C), 114.5, 62.7, 62.2, 45.3 (2 C), 45.1, 45.0, 41.3, 41.2, 28.2, 27.8, 25.0, 24.9 ppm; HRMS (ESI) *m/z* calcd for $C_{20}H_{23}NO_2$ 313.1233, found 313.1238.



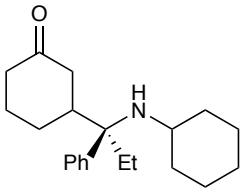
(±)-**15** 78% yield

3-(1-((4-Methoxyphenyl)amino)-1,2,3,4-tetrahydronaphthalen-1-yl)cyclohexan-1-one (15): Following General Procedure A, $Ir(ppy)_2(dtbbpy)PF_6$ (4.50 mg, 5.47 μmol, 0.005 equiv), DABCO (112 mg, 1.00 mmol, 1.00 equiv), imine (251 mg, 1.00 mmol, 1.00 equiv), cyclohexanone (0.52 mL, 5.0 mmol, 5.00 equiv), azepane (24.0 μL, 200 μmol, 0.200 equiv), trifluoroacetic acid (16 μL, 0.20 mmol, 0.2 equiv.), and DMPU (1.33 mL) provided the desired aminoketone in the form of a beige foam as an inseparable mixture of diastereomers (1:1 ratio, 271 mg, 78% yield). **IR** (film) 3392, 3058, 2944, 2873, 2832, 1708, 1615, 1510, 1485, 1448, 1347, 1302, 1235, 1179, 1134, 1115, 1038 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40 (ddd, *J* = 13.1, 7.5, 1.4 Hz, 1H), 7.12 (dddd, *J* = 12.5, 8.5, 6.6, 3.9 Hz, 3H), 6.61–6.55 (m, 2H), 6.33–6.26 (m, 2H), 3.74–3.45 (m, 4H), 2.85–2.65 (m, 2H), 2.57 (ddt, *J* = 13.9, 4.3, 2.3 Hz, 0.5H), 2.44–2.01 (m, 7H), 1.93–1.39 (m, 6H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 211.8, 211.4, 153.2, 152.9, 139.4, 139.2 (2 C), 139.1, 137.5, 137.4, 129.2, 129.1, 128.3, 128.2, 128.0, 126.6 (2 C), 125.8, 125.7, 119.8, 119.3, 114.1 (2 C), 59.5, 59.4, 55.4, 49.3, 49.0, 43.2, 42.9, 41.3, 29.9, 29.6, 29.2 (2 C), 26.1, 25.4, 25.1, 25.0, 20.0, 19.9 ppm; HRMS (ESI) *m/z* calcd for $C_{23}H_{28}NO_2$ $[(M+H)^+]$ 350.2120, found 350.2120.



(±)-**17** 90% yield

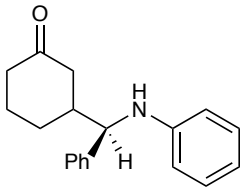
3-((*tert*-Butylamino)diphenylmethyl)cyclohexan-1-one (17): Following General Procedure A, $Ir(ppy)_2(dtbbpy)PF_6$ (4.50 mg, 5.47 μmol, 0.005 equiv), DABCO (112 mg, 1.00 mmol, 1.00 equiv), imine (237 mg, 1.00 mmol, 1.00 equiv), cyclohexanone (0.52 mL, 5.0 mmol, 5.00 equiv), azepane (24.0 μL, 200 μmol, 0.200 equiv), trifluoroacetic acid (16 μL, 0.20 mmol, 0.2 equiv.), and DMPU (1.33 mL) provided the desired aminoketone in the form of a white foam (303 mg, 90% yield). **IR** (film) 3339, 3084, 3056, 3021, 2953, 2865, 1711, 1598, 1489, 1446, 1361, 1346, 1313, 1264, 1221, 1157, 1105, 1065, 1030, 1002 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41 (brs, 4H), 7.32–7.22 (m, 6H), 2.96–2.79 (m, 2H), 2.37–2.16 (m, 2H), 2.05–1.92 (m, 2H), 1.69–1.51 (m, 3H), 0.8–0.62 (overlapping m and s, 10H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 212.9, 144.6, 143.9, 130.1, 128.3, 127.1, 126.9, 126.7, 68.2, 52.4, 45.6, 45.2, 41.4, 31.9, 27.9, 25.1 ppm; HRMS (ESI) *m/z* calcd for $C_{23}H_{30}NO$ [$(M+H)^+$] 336.2327, found 326.2330.



(±)-**16** 78% yield

3-(1-(Cyclohexylamino)-1-phenylpropyl)cyclohexan-1-one (16): Following General Procedure A, $Ir(ppy)_2(dtbbpy)PF_6$ (4.50 mg, 5.47 μmol, 0.005 equiv), DABCO (112 mg, 1.00 mmol, 1.00 equiv), imine (215 mg, 1.00 mmol, 1.00 equiv), cyclohexanone (0.52 mL, 5.0 mmol, 5.00 equiv), azepane (24.0 μL, 200 μmol, 0.200 equiv.) and DMPU (1.33 mL) provided the desired

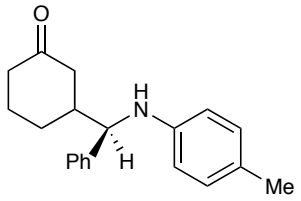
aminoketone (246 mg, 78%) in the form of colorless oil as an inseparable mixture of diastereomers (1:1). **IR** (film) 2925, 2651, 1712, 1447, 705 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.51 (dd, 4 H, *J* = 7.8, 2.5 Hz), 7.34 (dt, 4 H, *J* = 8.3, 7.8, 2.2 Hz), 7.27–7.25 (m, 2 H), 2.86 (dd, 1 H, *J* = 13.7, 2.7 Hz), 2.48–2.41 (m, 3 H), 2.36 (t, 4 H, *J* = 6.7 Hz), 2.30–2.21 (m, 2 H), 2.16 (dd, 1 H, *J* = 14.5, 7.2 Hz), 2.09–1.84 (m, 11 H), 1.79–1.63 (m, 8 H), 1.58–1.44 (m, 4 H), 1.31–1.02 (m, 12 H), 0.84 (dt, 6 H, *J* = 8.8, 7.3 Hz); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 213.4, 212.6, 143.1, 143.0, 128.2 (2 C), 127.3 (2 C), 126.4 (2 C), 64.1, 63.9, 50.8, 46.5, 46.2, 44.1, 43.6, 42.0, 41.3, 41.1, 36.9, 36.8, 36.3, 36.2, 27.0, 26.4, 26.0, 25.9, 25.4, 25.3, 24.9, 24.5, 8.0, 7.8 ppm; HRMS (ESI) *m/z* calcd for $C_{21}H_{32}NO$ 313.2406, found 313.2405.



(±)-**22** 57% yield

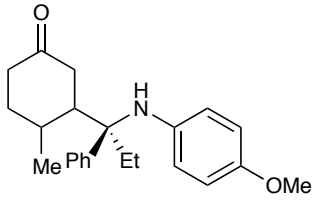
3-(Phenyl(phenylamino)methyl)cyclohexan-1-one (22): Following General Procedure A, $Ir(ppy)_2(dtbbpy)PF_6$ (4.50 mg, 5.47 μmol, 0.005 equiv), DABCO (112 mg, 1.00 mmol, 1.00 equiv), imine (181 mg, 1.00 mmol, 1.00 equiv), cyclohexanone (0.52 mL, 5.0 mmol, 5.00 equiv), azepane (24.0 μL, 200 μmol, 0.200 equiv), acetic acid (11.0 μL, 0.20 mmol, 0.20 equiv), and DMPU (1.33 mL) provided the desired aminoketone in the form of a colorless oil as an inseparable mixture of diastereomers (1:1 ratio, 160 mg, 57% yield). **IR** (film) 3389, 3084, 3054, 3026, 2935, 2864, 1706, 1602, 1502, 1452, 1430, 1372, 1347, 1316, 1264, 1228, 1179, 1155, 1123, 1077, 1065, 1029 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.34–7.20 (m, 10 H), 7.10–7.03 (m, 4 H), 6.64 (tt, *J* = 7.2, 1.9 Hz, 2 H), 6.55–6.48 (m, 4 H), 4.29 (d, *J* = 4.7 Hz, 0.66 H), 4.23 (d, *J* = 5.6 Hz, 1.32 H), 4.10 (brs, 2 H), 2.64 (dt, *J* = 10.1, 2.2 Hz, 1.31 H), 2.43–1.99 (m, 12 H),

1.81–1.70 (m, 1.5 H), 1.67–1.33 (m, 6 H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 211.1, 210.9, 147.0 (2 C), 141.0, 140.8, 129.1 (2 C), 128.5 (2 C), 128.3, 127.4, 127.3, 127.1, 127.0, 117.6, 117.5, 113.4, 62.6, 62.0, 445.4, 45.1 (2 C), 41.3, 41.2 28.2, 27.7, 25.0, 24.9 ppm; HRMS (ESI) *m/z* calcd for $C_{19}H_{22}NO$ [$(M+H)^+$] 280.1701, found 280.1703.



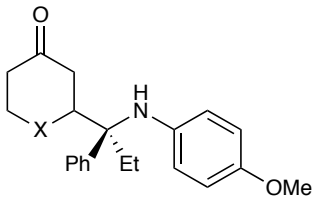
(±)-**21** 65% yield

3-(Phenyl(*p*-tolylamino)methyl)cyclohexan-1-one (21): Following General Procedure A, $Ir(ppy)_2(dtbbpy)PF_6$ (4.50 mg, 5.47 μmol, 0.005 equiv), DABCO (112 mg, 1.00 mmol, 1.00 equiv), imine (195 mg, 1.00 mmol, 1.00 equiv), cyclohexanone (0.52 mL, 5.0 mmol, 5.00 equiv), azepane (24.0 μL, 200 μmol, 0.200 equiv), trifluoroacetic acid (16 μL, 0.2 mmol, 0.2 equiv.), and DMPU (1.33 mL) provided the desired aminoketone (190 mg, 65%) in the form of colorless oil as an inseparable mixture of diastereomers (1:1 ratio). **IR** (film) 3391, 3024, 2922, 1703, 1512, 1315 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.34–7.25 (m, 10 H), 6.91 (dd, 4 H, *J* = 8.4, 2.7 Hz), 6.47 (dd, 4 H, *J* = 8.2, 2.9 Hz), 4.29 (d, 1 H, *J* = 4.4 Hz), 4.23 (d, 1 H, *J* = 5.4 Hz), 4.02 (br s, 2 H), 2.67–2.64 (m, 1 H), 2.42–2.31 (m, 3 H), 2.34–2.25 (m, 3 H), 2.20 (s, 6 H), 2.16–2.09 (m, 4 H), 1.79 (d, 1 H, *J* = 13.6 Hz), 1.69–1.38 (m, 6 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 211.2, 211.0, 144.8, 144.7, 141.2, 141.0, 129.6 (2 C), 128.5 (2 C), 127.3 (2 C), 127.1, 127.0, 113.5 (2 C), 62.8, 62.3, 45.5., 45.4, 45.2, 45.1, 41.3 (2 C), 28.2, 27.6, 25.0 (2 C), 20.3 ppm; HRMS (ESI) *m/z* calcd for $C_{20}H_{23}NO_2$ 313.1233, found 313.1238.



(±)-**23** 63% yield

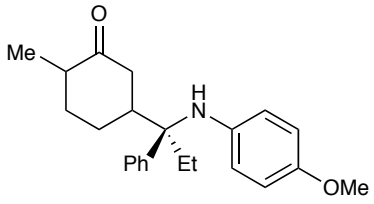
3-(1-((4-Methoxyphenyl)amino)-1-phenylpropyl)-4-methylcyclohexan-1-one (23): Following General Procedure B, $Ir(ppy)_2(dtbbpy)PF_6$ (4.50 mg, 5.00 μmol, 0.005 equiv), DABCO (112 mg, 1.00 mmol, 1.00 equiv), imine (239 mg, 1.00 mmol, 1.00 equiv), 4-methylcyclohexanone (1.23 mL, 10.0 mmol, 10.0 equiv), azepane (48.0 μL, 400 μmol, 0.40 equiv), trifluoroacetic acid (15.0 μL, 200 μmol, 0.20 equiv), $LiBF_4$ (94.0 mg, 1.00 mmol, 1.00 equiv) and DMPU (1.33 mL) provided the desired aminoketone (220 mg, 63%) in the form of a colorless oil as an inseparable mixture of diastereomers. **IR** (film) 3374, 2931, 2832, 1704, 1618, 1509, 1462, 1445, 1308, 1267, 1236, 1180, 1132, 1077, 1037 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.54–7.48 (m, 2 H), 7.33–7.27 (m, 3 H), 6.51 (d, *J* = 8.5 Hz, 2 H), 6.08 (d, *J* = 8.4 Hz, 2 H), 3.62 (s, 3 H), 3.52 (brs, 1 H), 2.89 (d, *J* = 14.3 Hz, 1 H), 2.43–2.34 (m, 2 H), 2.32–2.12 (m, 5 H), 1.78–1.69 (m, 2 H), 0.83 (t, *J* = 7.2 Hz, 3 H), 0.63 (d, *J* = 6.9 Hz, 3 H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 212.4, 151.7, 142.4, 139.6, 128.8, 127.9, 126.9, 116.4, 114.2, 62.5, 55.5, 49.7, 39.0, 36.4, 34.7, 27.8, 24.7, 12.1, 7.5 ppm; HRMS (ESI) *m/z* calcd for $C_{23}H_{30}NO_2$ [$(M+H)^+$] 352.2277, found 352.2278.



X = CMe_2 (±)-**24** 65% yield

3-(1-((4-Methoxyphenyl)amino)-1-phenylpropyl)-4,4-dimethylcyclohexan-1-one (24):

Following General Procedure B, $Ir(ppy)_2(dtbbpy)PF_6$ (4.50 mg, 5.47 μmol, 0.005 equiv), DABCO (112 mg, 1.00 mmol, 1.00 equiv), imine (239 mg, 1.00 mmol, 1.00 equiv), 4,4-dimethylcyclohexanone (883 mg, 7.00 mmol, 7.00 equiv), azepane (48.0 μL, 400 μmol, 0.400 equiv), trifluoroacetic acid (16 μL, 0.2 mmol, 0.2 equiv.), lithium tetrafluoroborate (94 mg, 1.00 mmol, 1.00 equiv) and DMPU (1.33 mL) provided the desired aminoketone in the form of colorless oil as an inseparable mixture of diastereomers (237 mg, 65% yield). **IR** (film) 3396, 2948, 2832, 1708, 1509, 1463, 1445, 1391, 1347, 1246, 1235, 1180, 1153, 1125, 1039 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.60–7.36 (m, 3 H), 7.36–7.22 (m, 7 H), 6.62–6.58 (m, 2 H), 6.57–6.53 (m, 1 H), 6.34–6.26 (m, 2 H), 6.24–6.16 (m, 1 H), 3.65 (overlapping singlets, 5 H), 2.57 (dq, *J* = 14.2, 7.0 Hz, 0.5 H), 2.38 (dq, *J* = 14.6, 7.3 Hz, 0.5 H), 2.29–2.10 (m, 2 H), 2.03 (dq, *J* = 14.2, 6.9 Hz, 1 H), 1.91 (s, 1 H), 1.57 (dd, *J* = 13.6, 5.4 Hz, 2 H), 1.43–1.32 (m, 5 H), 1.20 (s, 2 H), 0.81 (t, *J* = 7.2 Hz, 1.5 H), 0.73 (t, *J* = 7.2 Hz, 3 H), 0.33 (s, 1.5 H), 0.22 (s, 3 H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 212.9, 211.6, 152.0, 151.6, 142.9, 141.5, 139.5, 139.3, 128.2, 128.0, 127.2, 127.0, 117.2, 117.0, 114.3, 114.1, 65.5, 64.5, 55.5, 55.4, 52.4, 51.9, 44.5, 44.4, 40.7, 39.8, 38.0, 37.7, 35.2, 35.0, 31.5 (2 C), 30.4, 26.4, 25.3, 19.9, 19.3, 8.3, 7.0 ppm; HRMS (ESI) *m/z* calcd for $C_{24}H_{32}NO_2$ [$(M+H)^+$] 366.2433, found 366.2436.

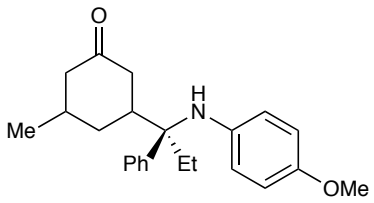


(±)-**25** 16% yield

5-(1-((4-Methoxyphenyl)amino)-1-phenylpropyl)-2-methylcyclohexan-1-one (25):

Following General Procedure A, $Ir(ppy)_2(dtbbpy)PF_6$ (4.50 mg, 5.47 μmol, 0.005 equiv), DABCO (112 mg, 1.00 mmol, 1.00 equiv), imine (239 mg, 1.00 mmol, 1.00 equiv), 2-

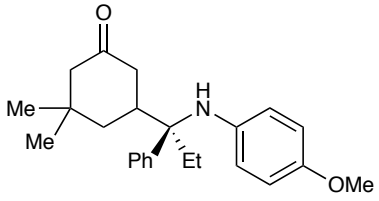
methylcyclohexanone (610 μL, 5.00 mmol, 5.00 equiv), pyrrolidine (17.0 μL, 0.20 mmol, 0.20 equiv), trifluoroacetic acid (16 μL, 0.2 mmol, 0.2 equiv.), and DMPU (1.33 mL) provided the desired aminoketone in the form of colorless oil as an inseparable mixture of diastereomers (54.9 mg, 16% yield). **IR** (film) 3379, 2931, 2872, 1704, 1619, 1509, 1446, 1376, 1305, 1267, 1236, 1179, 1137, 1078, 1036 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46–7.41 (m, 4 H), 7.36–7.31 (m, 4 H), 7.29–7.25 (m, 2 H), 6.60–6.53 (m, 4 H), 6.25–6.18 (m, 4 H), 3.65 (s, 3 H), 3.65 (s, 3 H), 3.63 (brs, 1 H), 3.58 (brs, 1 H), 2.76 (dt, *J* = 13.1, 2.9 Hz, 1 H), 2.49 (dt, *J* = 12.9, 3.0 Hz, 1 H), 2.30–2.22 (m, 3 H), 2.22–2.08 (m, 3 H), 2.08–2.00 (m, 5 H), 1.94 (dt, *J* = 13.0, 3.0 Hz, 1 H), 1.83–1.76 (m, 1 H), 1.34–1.22 (m, 3 H), 1.15 (qd, *J* = 12.8, 3.1 Hz, 1 H), 1.10–1.00 (m, 1 H), 0.96–0.90 (m, 6 H), 0.77 (t, *J* = 7.3 Hz, 6 H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 213.7, 212.5, 151.8, 151.7, 141.3, 141.2, 139.6, 139.5, 128.2, 127.9, 126.8, 116.8, 116.7, 114.2 (2 C), 63.6, 63.4, 55.5, 47.2, 46.7, 44.7, 44.5, 43.5, 43.1, 34.4, 34.1, 26.5, 26.0, 23.5, 23.2, 14.2, 14.1, 7.1, 7.0 ppm; HRMS (ESI) *m/z* calcd for $C_{23}H_{29}NO_2$ [M^+] 351.2198, found 351.2195.



(±)-**26** 72% yield

3-(1-((4-Methoxyphenyl)amino)-1-phenylpropyl)-5-methylcyclohexan-1-one (26): Following General Procedure B, $Ir(ppy)_2(dtbbpy)PF_6$ (4.50 mg, 5.00 μmol, 0.005 equiv), DABCO (112 mg, 1.00 mmol, 1.00 equiv), imine (239 mg, 1.00 mmol, 1.00 equiv), 3-methylcyclohexanone (1.23 mL, 10.0 mmol, 10.0 equiv), azepane (48.0 μL, 400 μmol, 0.40 equiv), trifluoroacetic acid (15.0 μL, 200 μmol, 0.20 equiv), $LiBF_4$ (94.0 mg, 1.00 mmol, 1.00 equiv) and DMPU (1.33 mL) provided the desired aminoketone (255 mg, 72%) in the form of a colorless oil as an inseparable

mixture of diastereomers. **IR** (film) 3377, 3055, 3032, 2956, 2881, 2831, 1708, 1618, 1599, 1510, 1461, 1445, 1381, 1361, 1297, 1266, 1236, 1180, 1156, 1132, 1112, 1075, 1038 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46–7.41 (m, 4 H), 7.38–7.31 (m, 4 H), 7.31–7.25 (m, 2 H), 6.60–6.53 (m, 4 H), 6.27–6.18 (m, 4 H), 3.67–3.51 (m, 8 H), 2.75–2.67 (m, 1 H), 2.48–2.40 (m, 1 H), 2.32–2.16 (m, 7 H), 2.15–2.03 (m, 3 H), 2.01–1.95 (m, 1 H), 1.95–1.88 (m, 1 H), 1.86–1.64 (m, 5 H), 1.35–1.26 (m, 1 H), 1.01–0.93 (m, 6 H), 0.81–0.74 (m, 6 H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 212.8, 212.2, 211.9, 211.2, 151.8 (2 C), 151.7, 141.2, 141.1, 141.0, 139.6, 139.5 (3 C), 128.2 (3 C), 127.9 (2 C), 126.9 (3 C), 116.8 (2 C), 116.7 (2 C), 114.2 (2 C), 63.5, 63.4 (3 C), 60.4, 55.5 (2 C), 49.4, 49.2, 47.3, 47.2, 45.0, 44.5, 43.4, 43.0, 42.8, 42.4, 40.3, 39.8, 34.8, 34.3, 32.9, 32.5, 31.8, 31.2, 29.2, 28.9, 23.5 (2 C), 23.3, 23.2, 22.5, 22.4, 19.5, 19.4, 14.2, 14.1, 7.1 (2 C), 7.0, 6.9 ppm; HRMS (ESI) *m/z* calcd for $C_{23}H_{30}NO_2$ [$(M+H)^+$] 352.2277, found 352.2276.

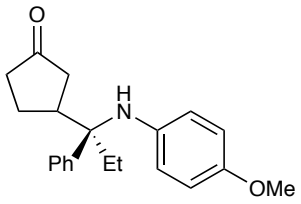


(±)-**27** 75% yield

5-(1-((4-Methoxyphenyl)amino)-1-phenylpropyl)-3,3-dimethylcyclohexan-1-one (27):

Following General Procedure B, $Ir(ppy)_2(dtbbpy)PF_6$ (4.50 mg, 5.00 μmol, 0.005 equiv), DABCO (112 mg, 1.00 mmol, 1.00 equiv), imine (239 mg, 1.00 mmol, 1.00 equiv), 3,3-dimethylcyclohexanone (1.39 mL, 10.0 mmol, 10.0 equiv), azepane (48.0 μL, 400 μmol, 0.40 equiv), trifluoroacetic acid (15.0 μL, 200 μmol, 0.20 equiv), $LiBF_4$ (94.0 mg, 1.00 mmol, 1.00 equiv) and DMPU (1.33 mL) provided the desired aminoketone (273 mg, 75%) in the form of a colorless solid as an inseparable mixture of diastereomers (1:1 ratio). **IR** (film) 2960, 2834, 1706, 1509, 1463, 1444, 1371, 1265, 1236, 1180, 1146, 1113, 1076, 1037 cm^{-1}; **^{1}H NMR** (500

MHz, $CDCl_3$) δ 7.48–7.41 (m, 4 H), 7.39–7.34 (m, 4 H), 7.31–7.26 (m, 2 H), 6.60–6.54 (m, 4 H), 6.26 (d, *J* = 9.0 Hz, 2 H), 6.21 (d, *J* = 9.0 Hz, 2 H), 3.71–3.52 (m, 8 H), 2.76–2.66 (m, 1 H), 2.48–2.39 (m, 1 H), 2.33–2.18 (m, 5 H), 2.18–2.08 (m, 1 H), 2.04–1.86 (m, 6 H), 1.76 (t, *J* = 13.2 Hz, 1 H), 1.70–1.62 (m, 2 H), 1.02 (s, 3 H), 1.00 (s, 3 H), 0.96–0.90 (m, 7 H), 0.80 (t, *J* = 7.3 Hz, 6 H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 212.4, 211.5, 151.8, 151.7, 141.1, 141.0, 139.5, 139.4, 128.2 (2 C) 127.9 (2 C), 126.8 (2 C), 116.8, 116.6, 114.1, 63.4, 55.4 (2 C), 54.1, 53.9, 42.7, 42.3, 41.3, 40.9, 39.3, 38.7, 34.5, 34.1, 32.2 (2 C), 26.0 (2 C), 23.6, 23.2, 7.0, 6.8 ppm; HRMS (ESI) *m/z* calcd for $C_{24}H_{31}NO_2$ [M^+] 365.2355, found 365.2355.

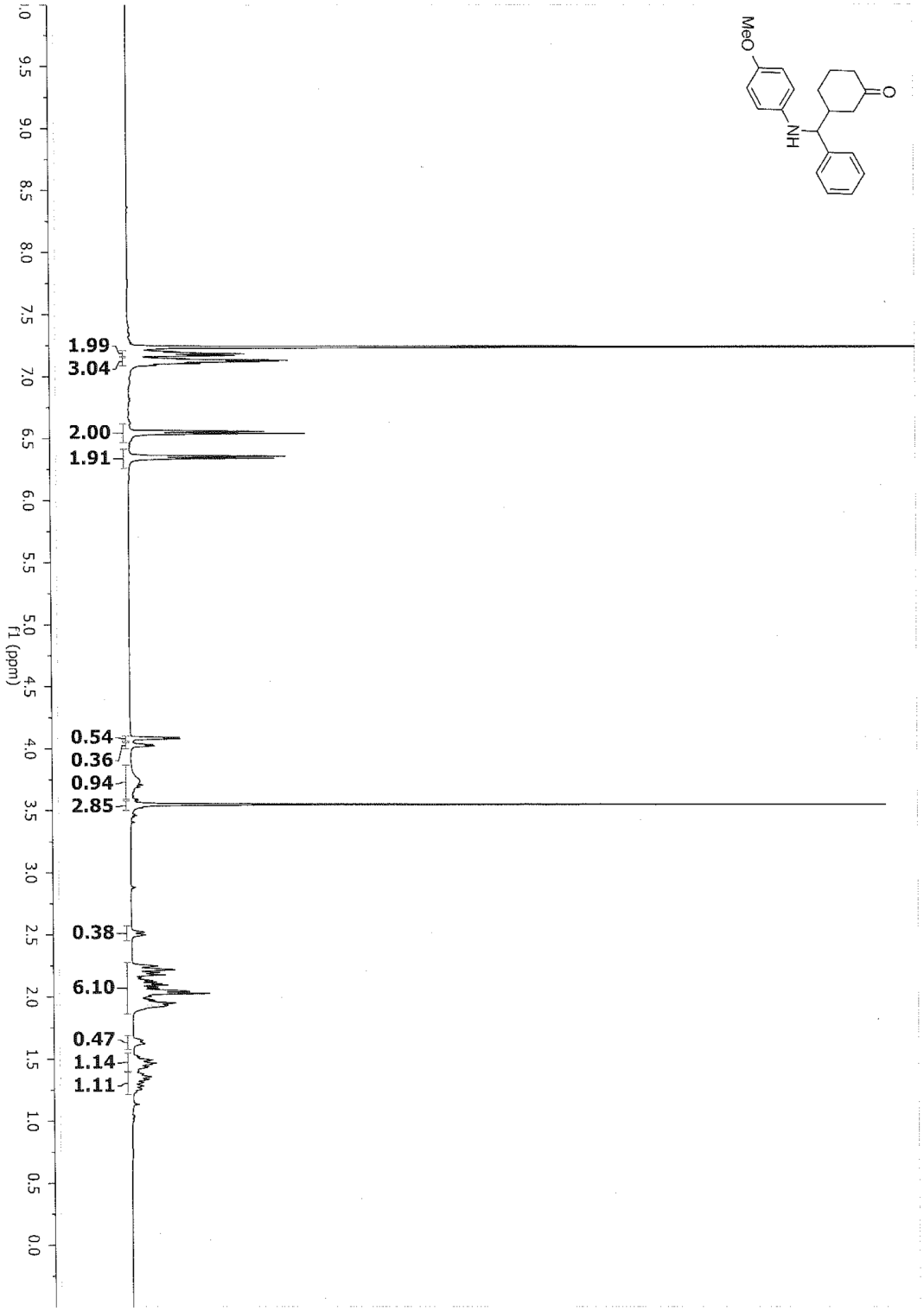


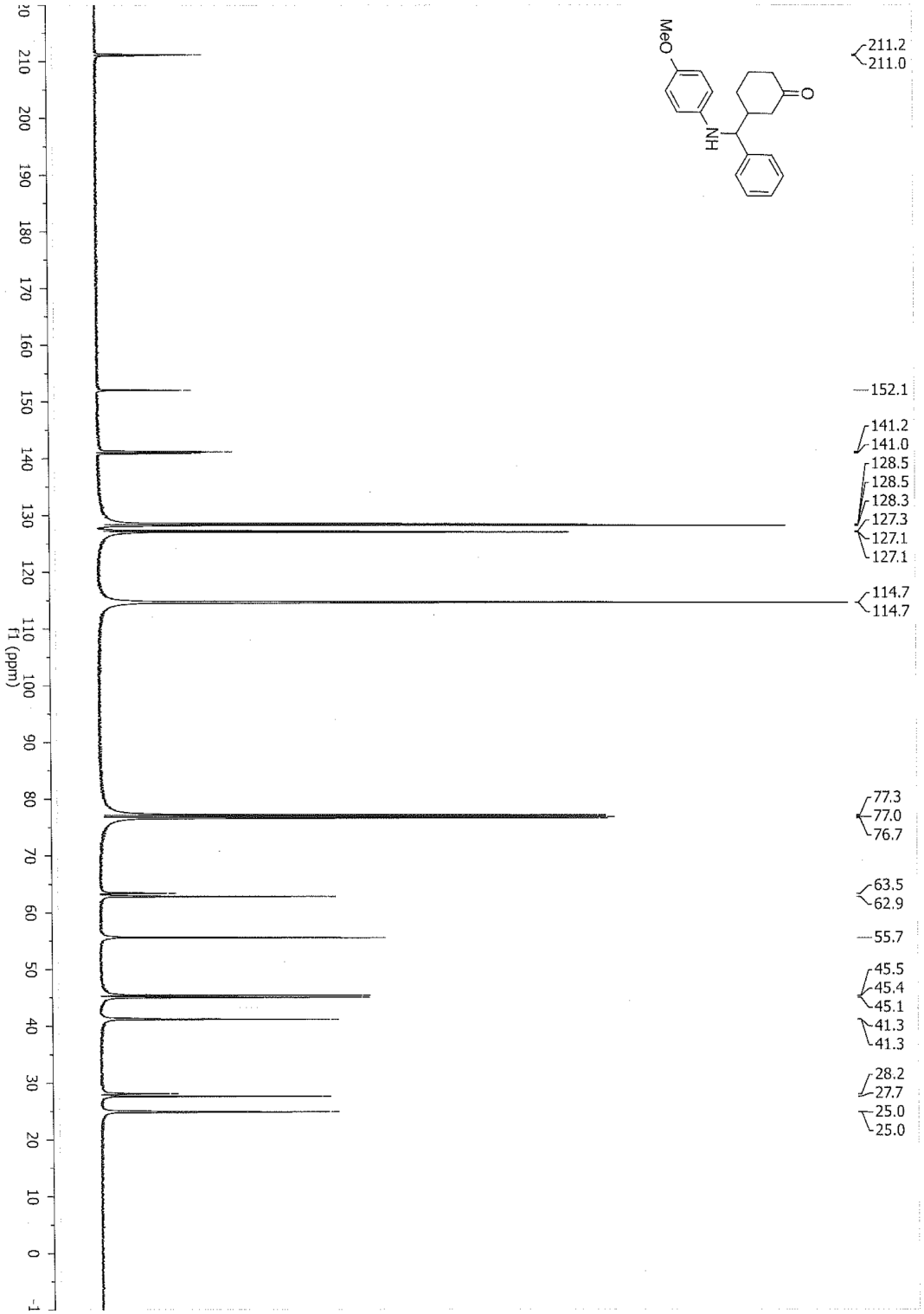
(±)-**28** 77% yield

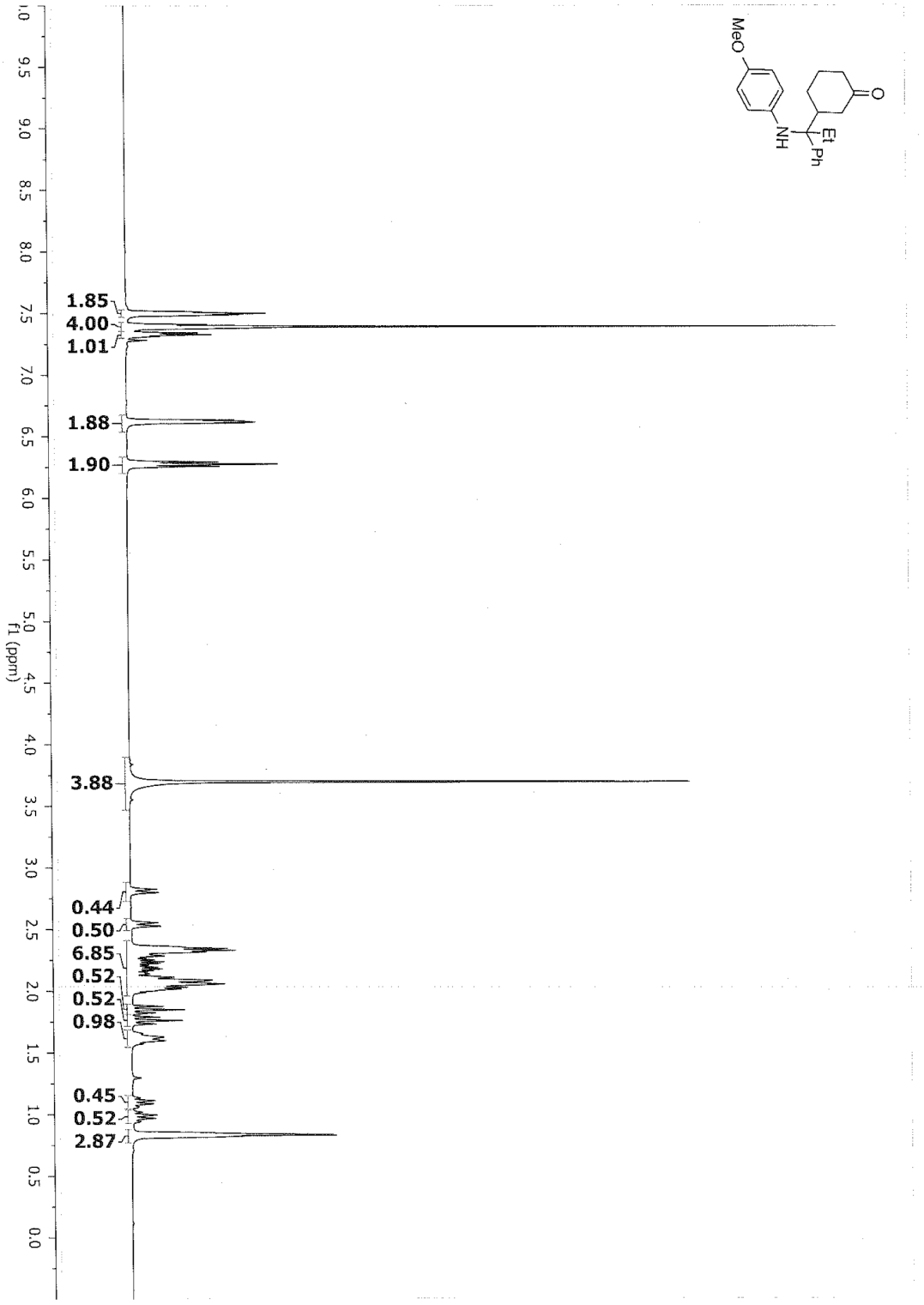
3-(1-((4-Methoxyphenyl)amino)-1-phenylpropyl)cyclopentan-1-one (28): Following General Procedure B, $Ir(ppy)_2(dtbbpy)PF_6$ (4.50 mg, 5.00 μmol, 0.005 equiv), DABCO (112 mg, 1.00 mmol, 1.00 equiv), imine (239 mg, 1.00 mmol, 1.00 equiv), cyclopentanone (0.89 mL, 10.0 mmol, 10.0 equiv), morpholine (35.0 μL, 400 μmol, 0.40 equiv), trifluoroacetic acid (15.0 μL, 200 μmol, 0.20 equiv), $LiBF_4$ (94.0 mg, 1.00 mmol, 1.00 equiv) and DMPU (1.33 mL) provided the desired aminoketone (248 mg, 77%) in the form of a colorless oil as an inseparable mixture of diastereomers (1:1 ratio). **IR** (film) 3382, 3054, 3030, 2967, 2900, 2831, 1740, 1511, 1462, 1444, 1403, 1380, 1351, 1297, 1237, 1207, 1175, 1142, 1114, 1036, 1001 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38–7.34 (m, 2H), 7.26–7.12 (m, 4H, overlapping with solvent peak), 6.47 (dd, *J* = 8.9, 5.7 Hz, 2H), 6.13 (dd, *J* = 11.1, 8.9 Hz, 2H), 3.72–3.50 (brs, 1H), 3.55 (d, *J* = 2.1 Hz, 3H), 2.55–2.44 (m, 1H), 2.34–1.99 (m, 4H), 1.98–1.88 (m, 3H), 1.84 (dd, *J* = 18.1, 12.0 Hz, 1H),

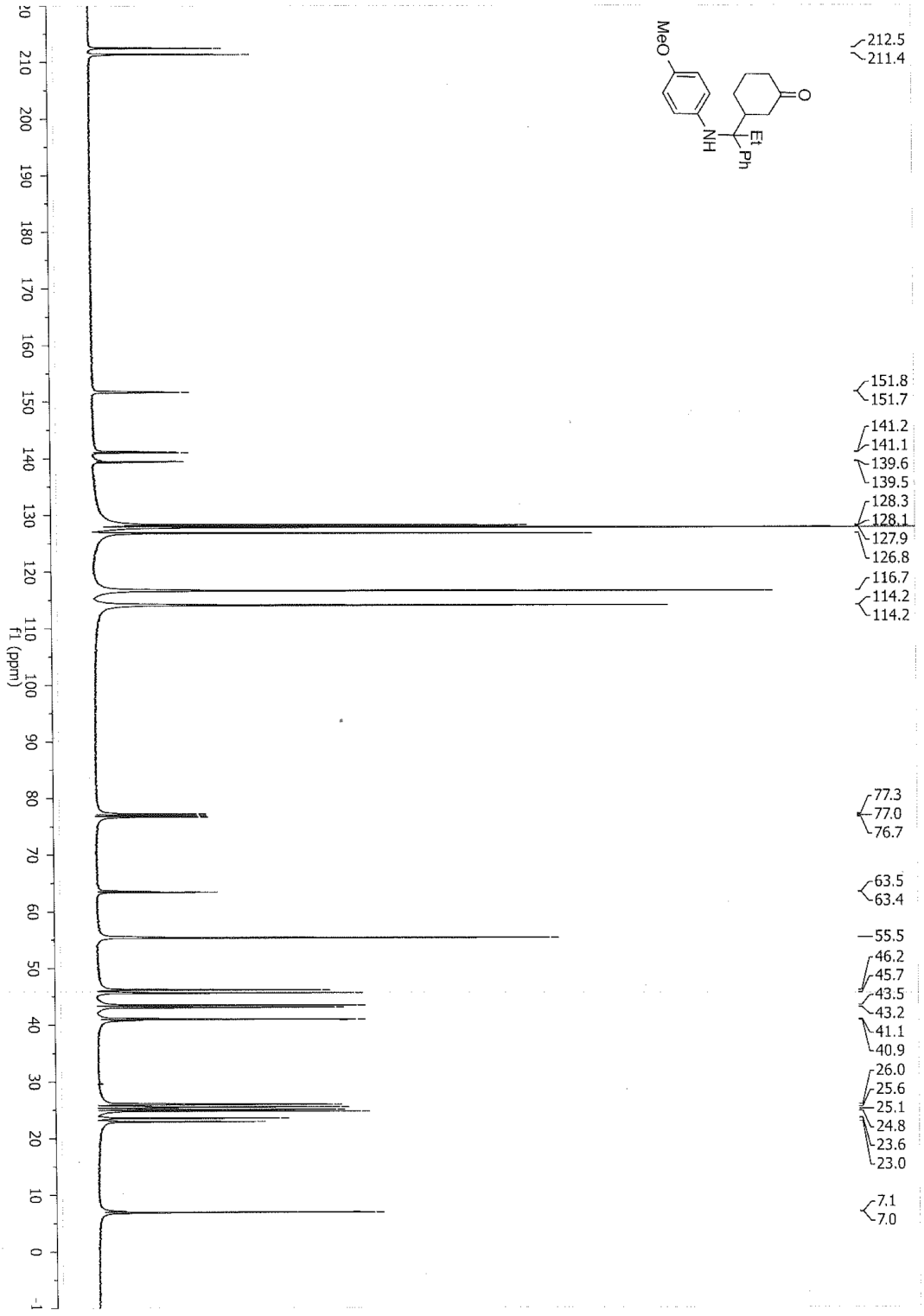
1.73 (dd, J = 17.8, 12.2 Hz, 1H), 1.45–1.26 (m, 1H), 0.90–0.82 (m, 3H) ppm; **^{13}C NMR** (125 MHz, $CDCl_3$) δ 218.0, 217.7, 151.8 (2 C), 141.1 (2 C), 139.4, 139.3, 128.3 (3 C), 128.1 (2 C), 127.0, 116.6, 116.5, 114.3, 114.2, 62.9, 62.6, 55.5, 45.1, 45.0, 40.6, 40.4, 38.3, 37.8, 25.7, 24.6, 23.9, 23.6, 7.4 (2 C) ppm; HRMS (ESI) *m/z* calcd for $C_{21}H_{25}NO_2$ [$(M)^+$] 323.1885, found 323.1885.

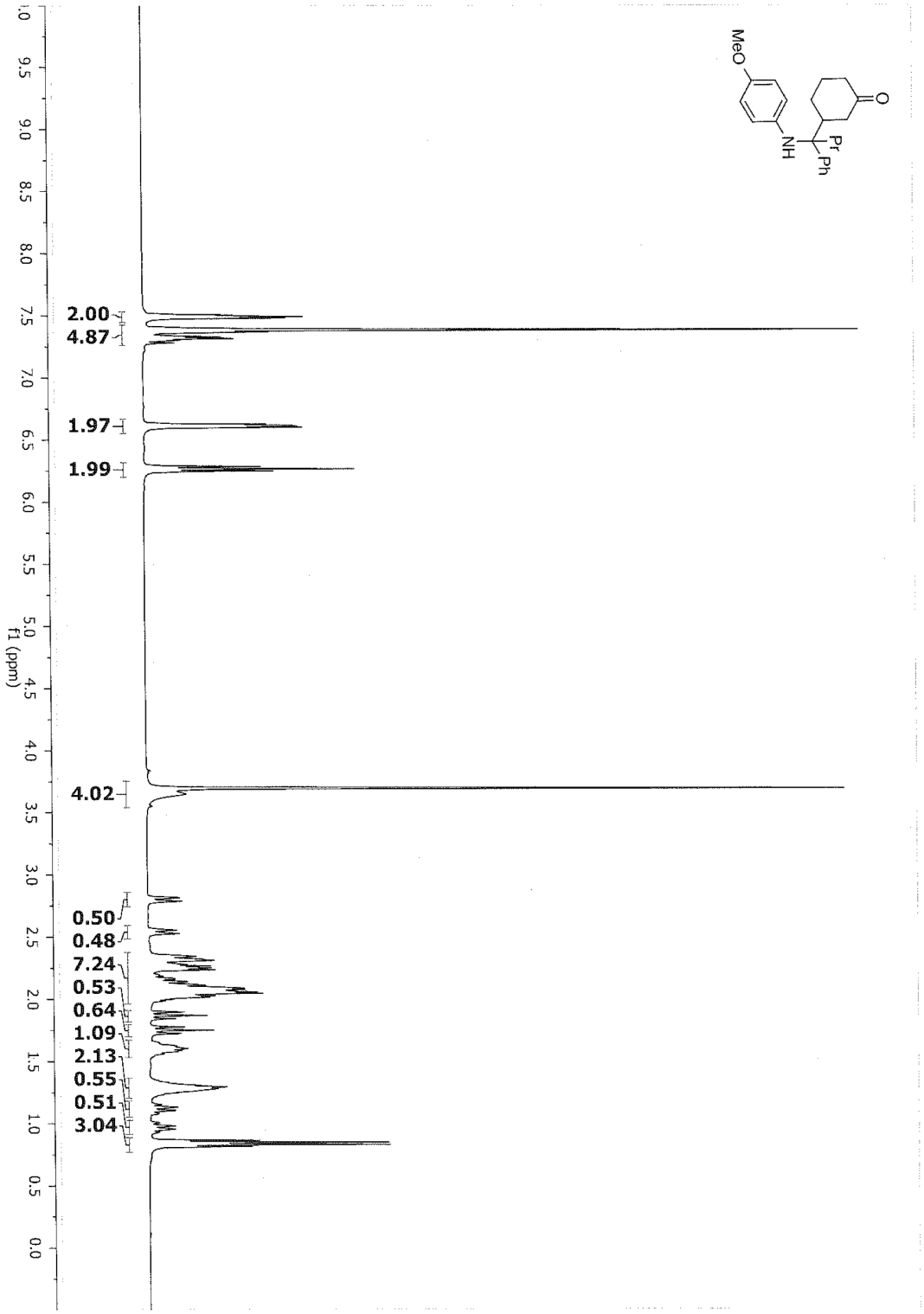
3. Spectral Data

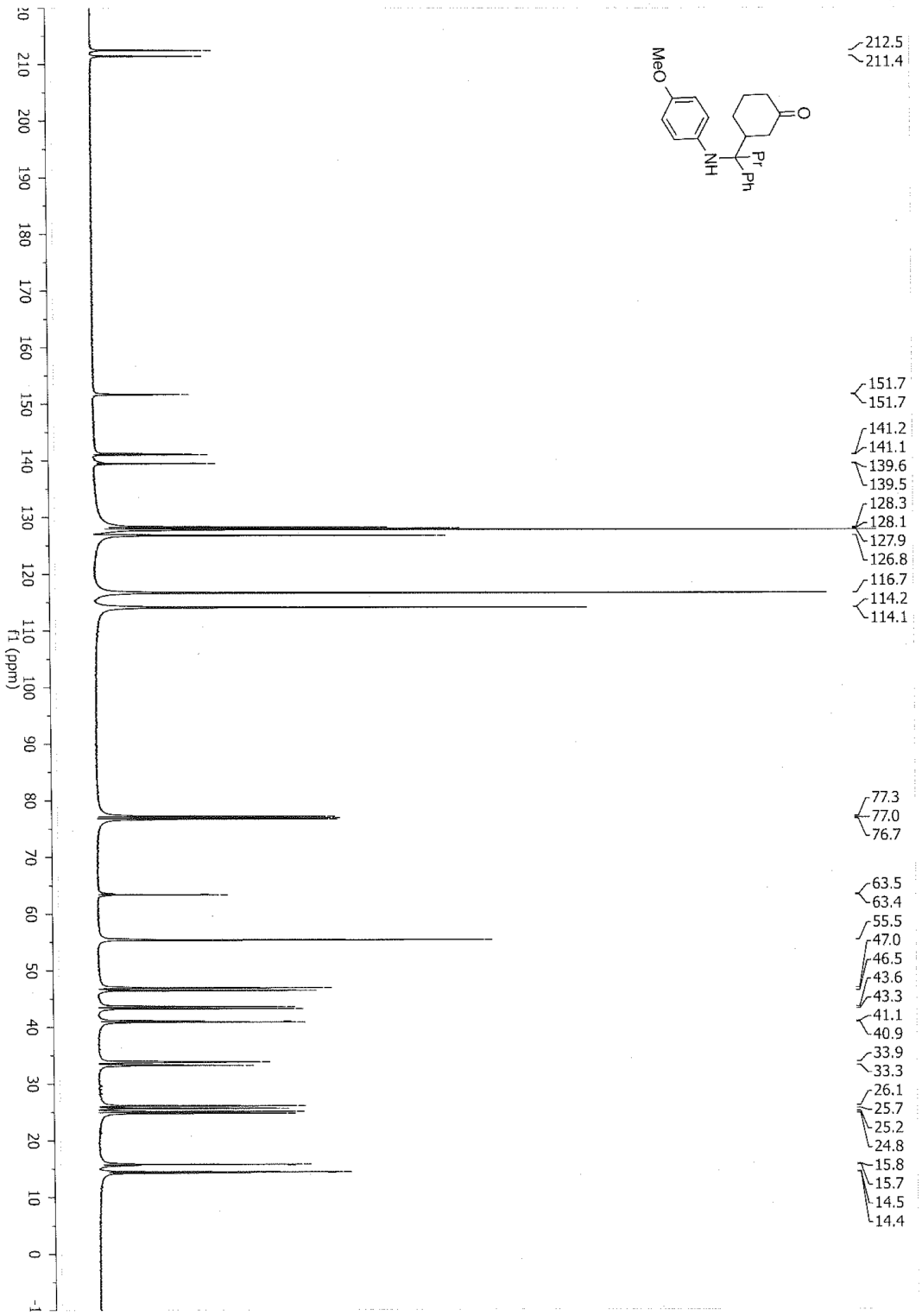


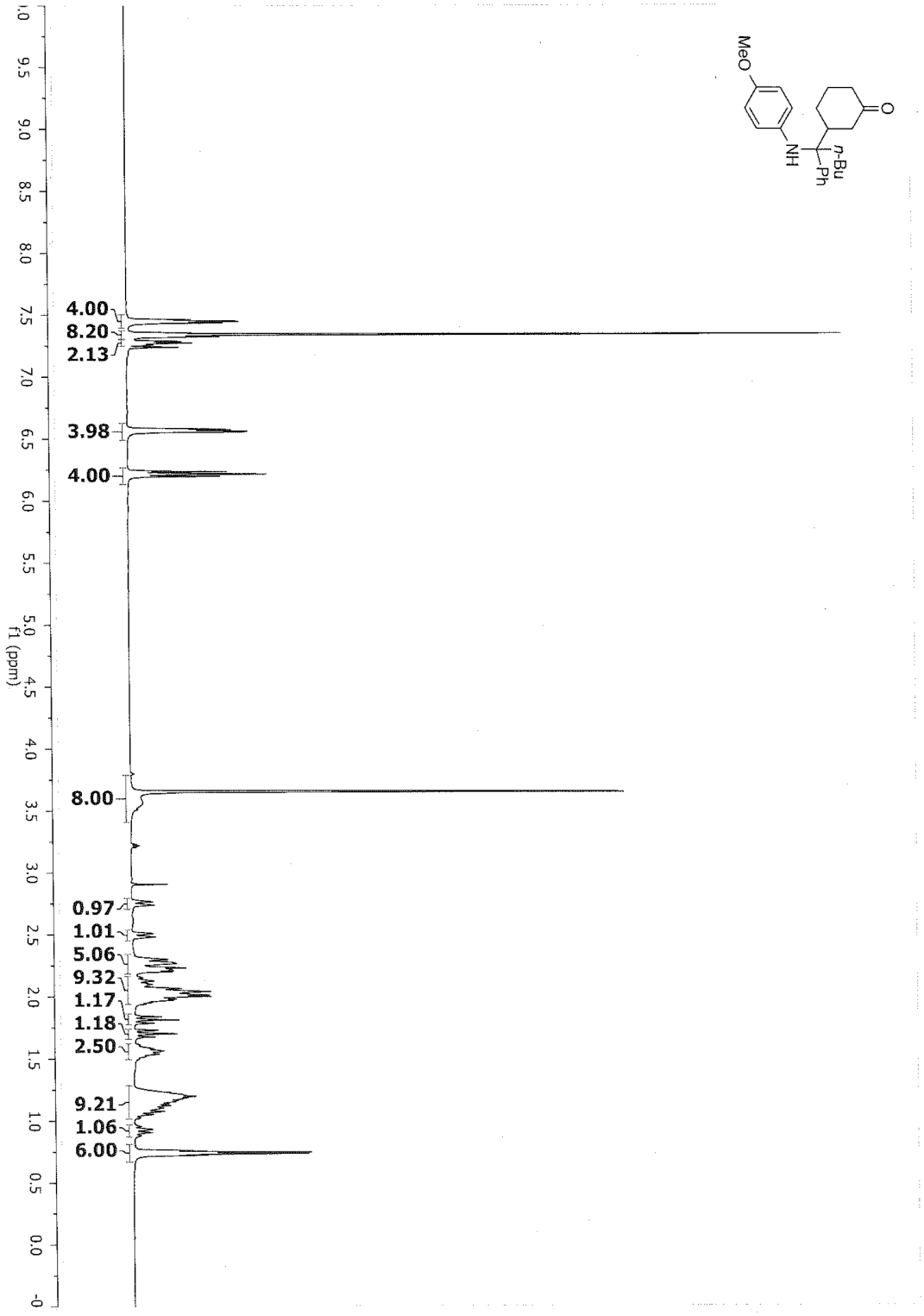

MeO
NH
O
211.2
211.0
152.1
141.2
141.0
128.5
128.5
128.3
127.3
127.1
127.1
114.7
114.7
77.3
77.0
76.7
63.5
62.9
55.7
45.5
45.4
45.1
41.3
41.3
28.2
27.7
25.0
25.0
f1 (ppm)

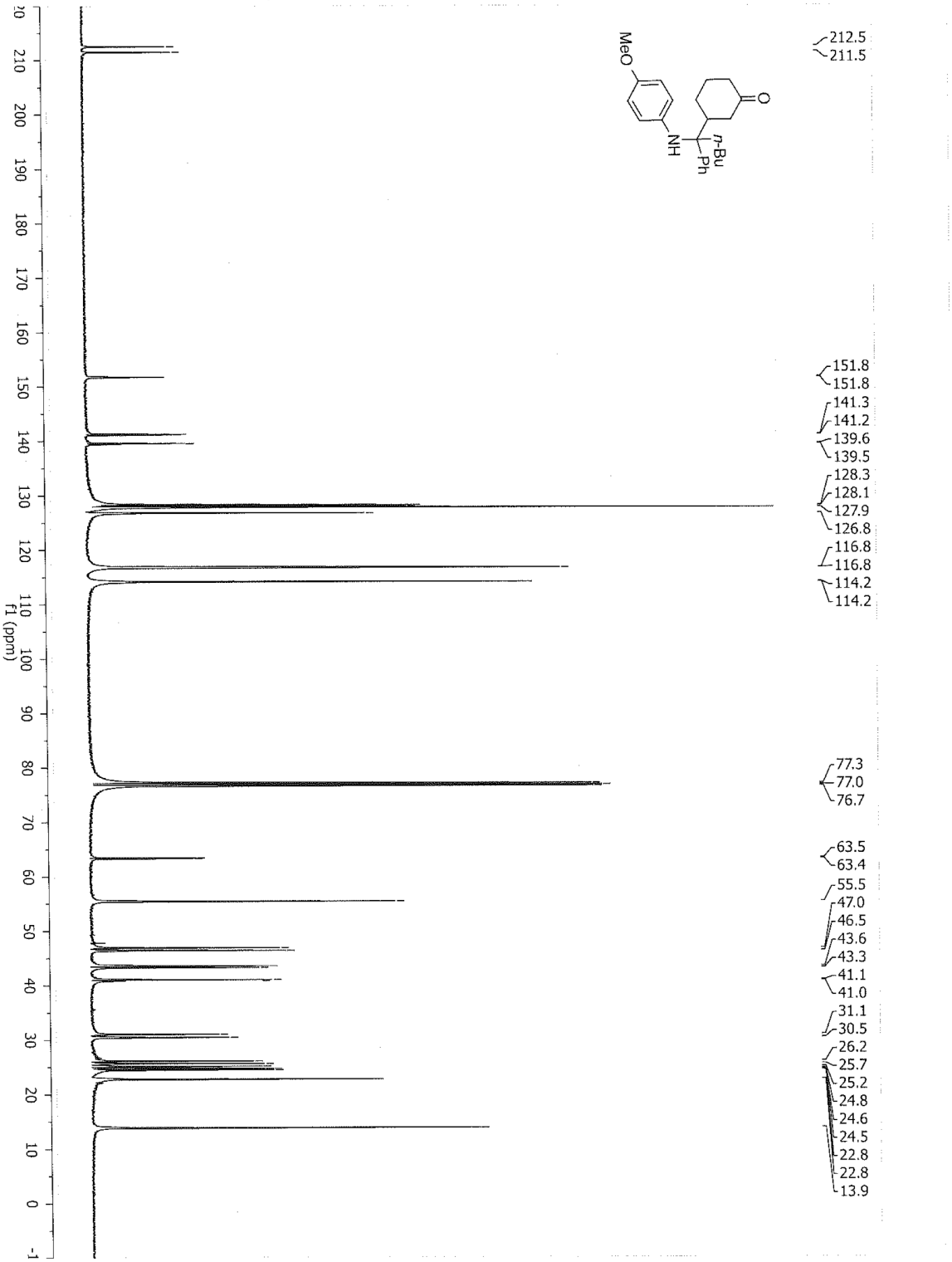

MeO
NH
Et
Ph
O
1.85
4.00
1.01
1.88
1.90
3.88
0.44
0.50
6.85
0.52
0.52
0.98
0.45
0.52
2.87
f1 (ppm)

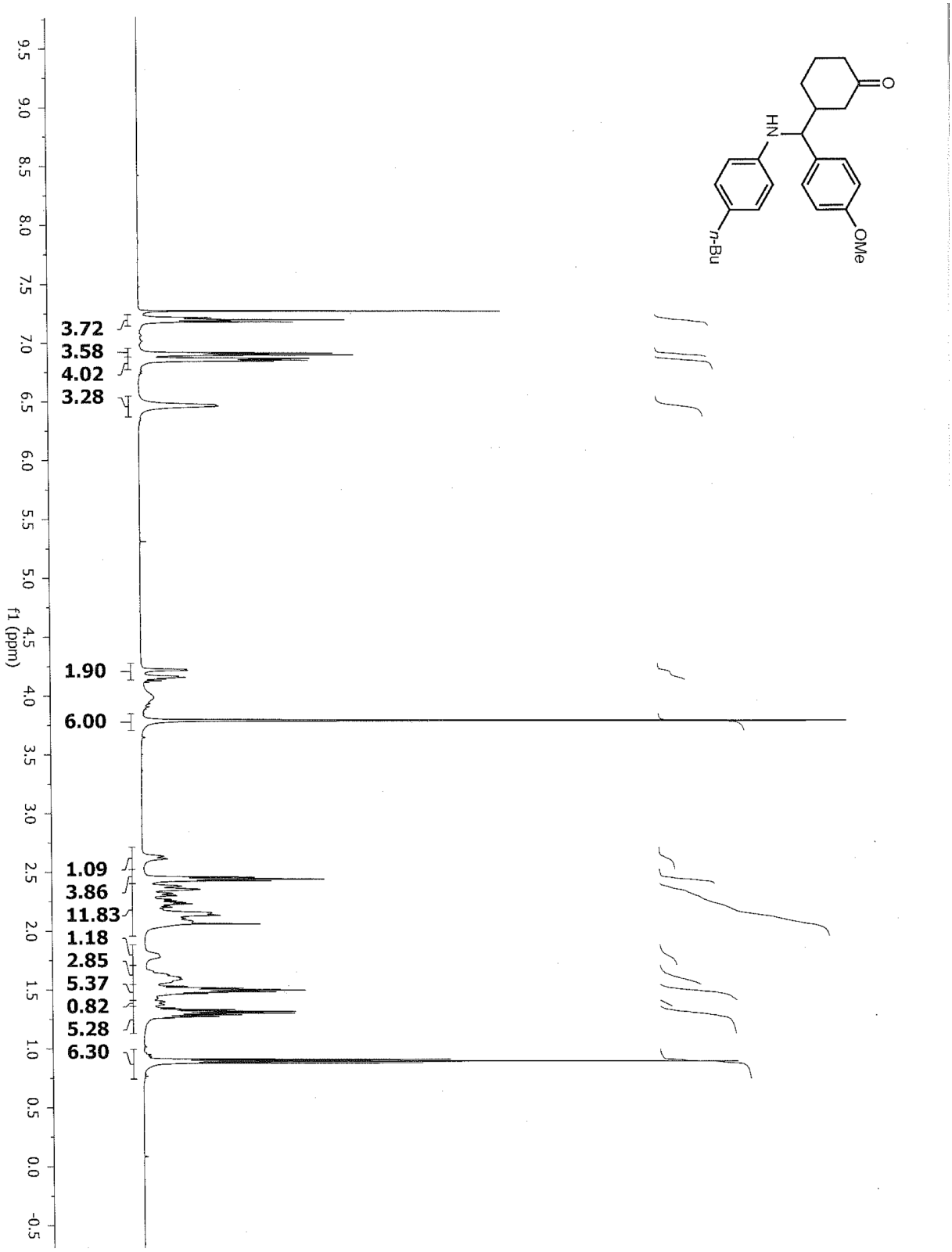

MeO
NH
Et
Ph
O
212.5
211.4
151.8
151.7
141.2
141.1
139.6
139.5
128.3
128.1
127.9
126.8
116.7
114.2
114.2
77.3
77.0
76.7
63.5
63.4
55.5
46.2
45.7
43.5
43.2
41.1
40.9
26.0
25.6
25.1
24.8
23.6
23.0
7.1
7.0
f1 (ppm)

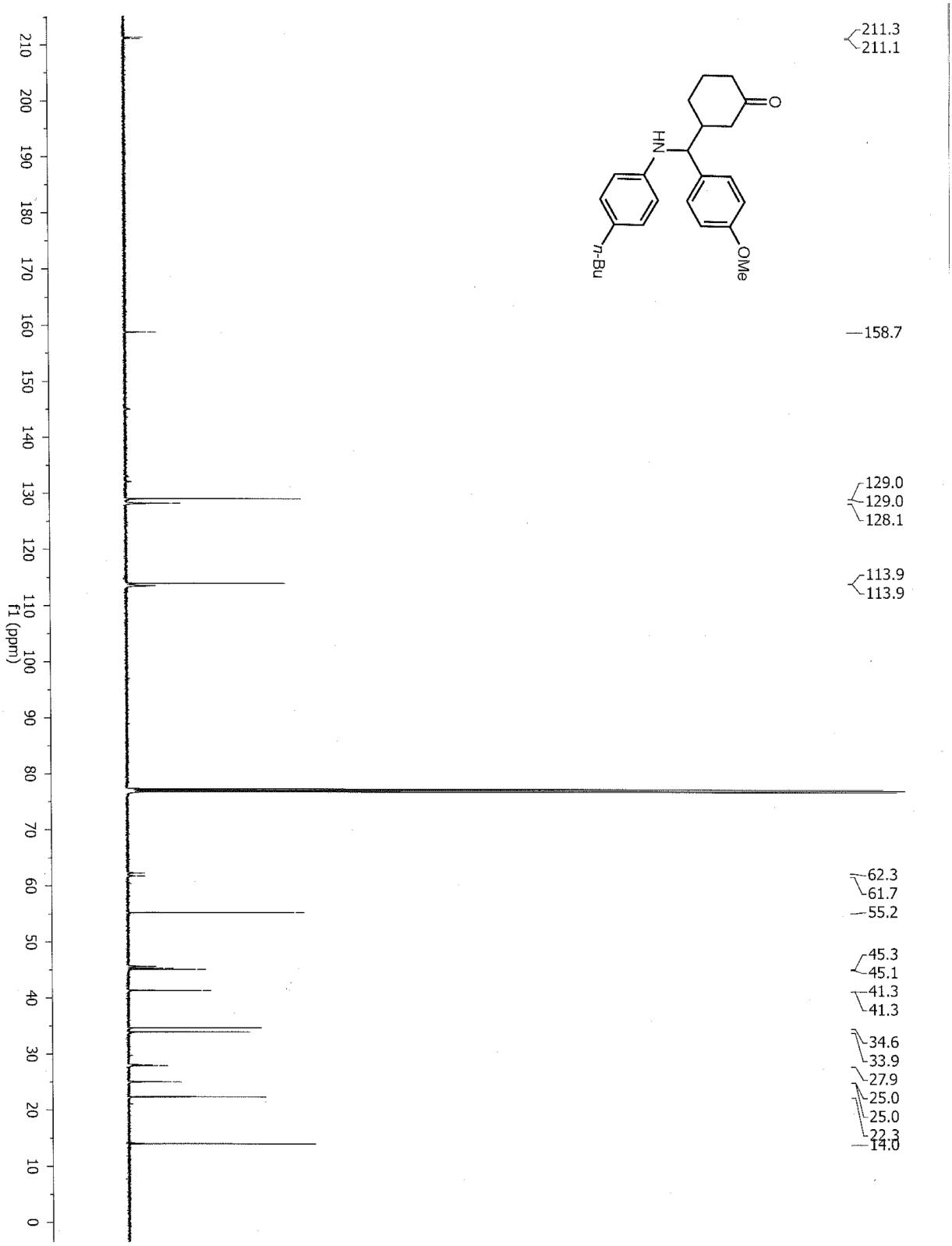

MeO
NH
Pr
Ph
O
2.00
4.87
1.97
1.99
4.02
0.50
0.48
7.24
0.53
0.64
1.09
2.13
0.55
0.51
3.04
f1 (ppm)

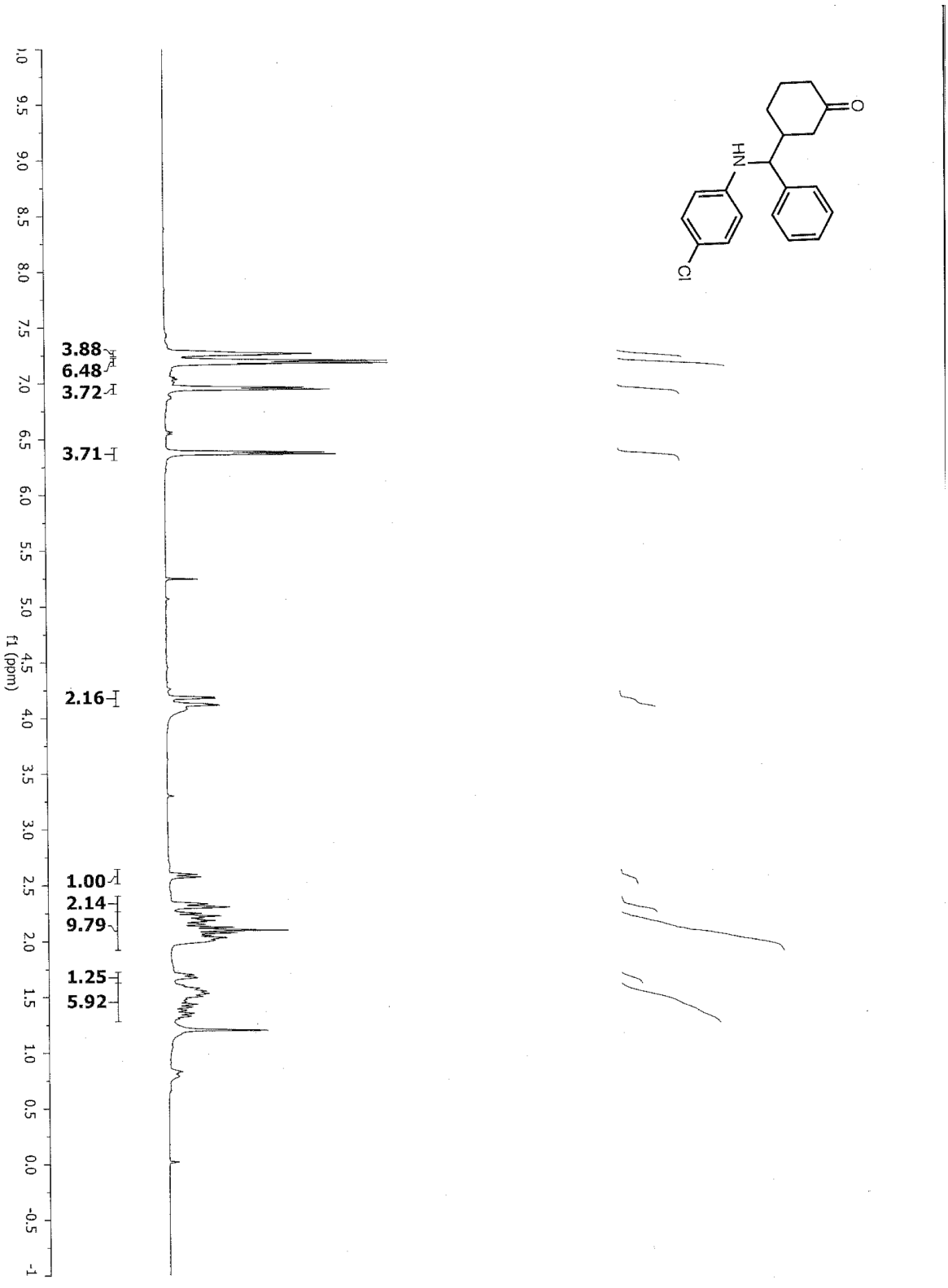

MeO
NH
Pr
Ph
O
212.5
211.4
151.7
151.7
141.2
141.1
139.6
139.5
128.3
128.1
127.9
126.8
116.7
114.2
114.1
77.3
77.0
76.7
63.5
63.4
55.5
47.0
46.5
43.6
43.3
41.1
40.9
33.9
33.3
26.1
25.7
25.2
24.8
15.8
15.7
14.5
14.4
f1 (ppm)

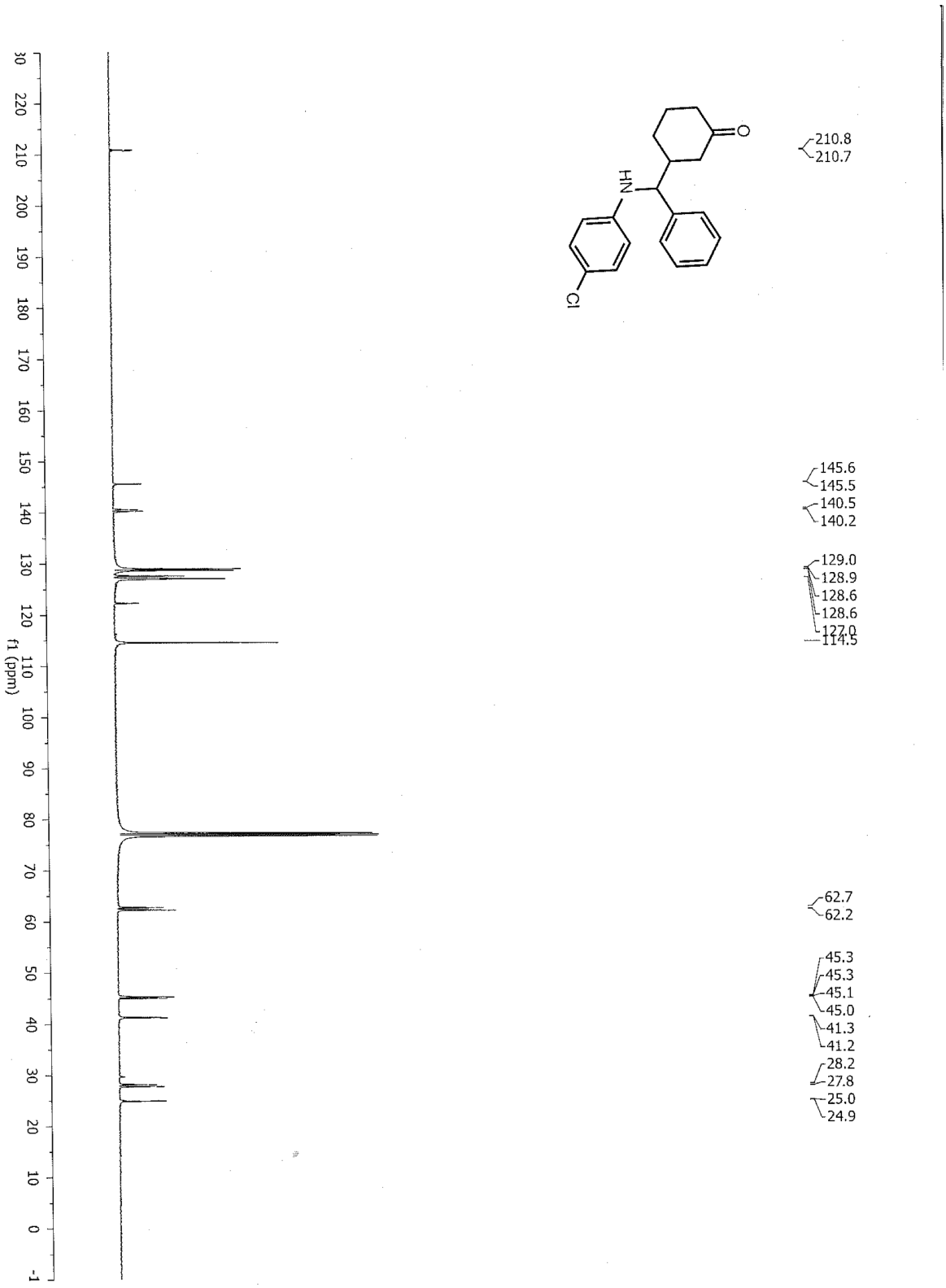

MeO
NH
n-Bu
Ph
O
4.00
8.20
2.13
3.98
4.00
8.00
0.97
1.01
5.06
9.32
1.17
1.18
2.50
9.21
1.06
6.00
f1 (ppm)

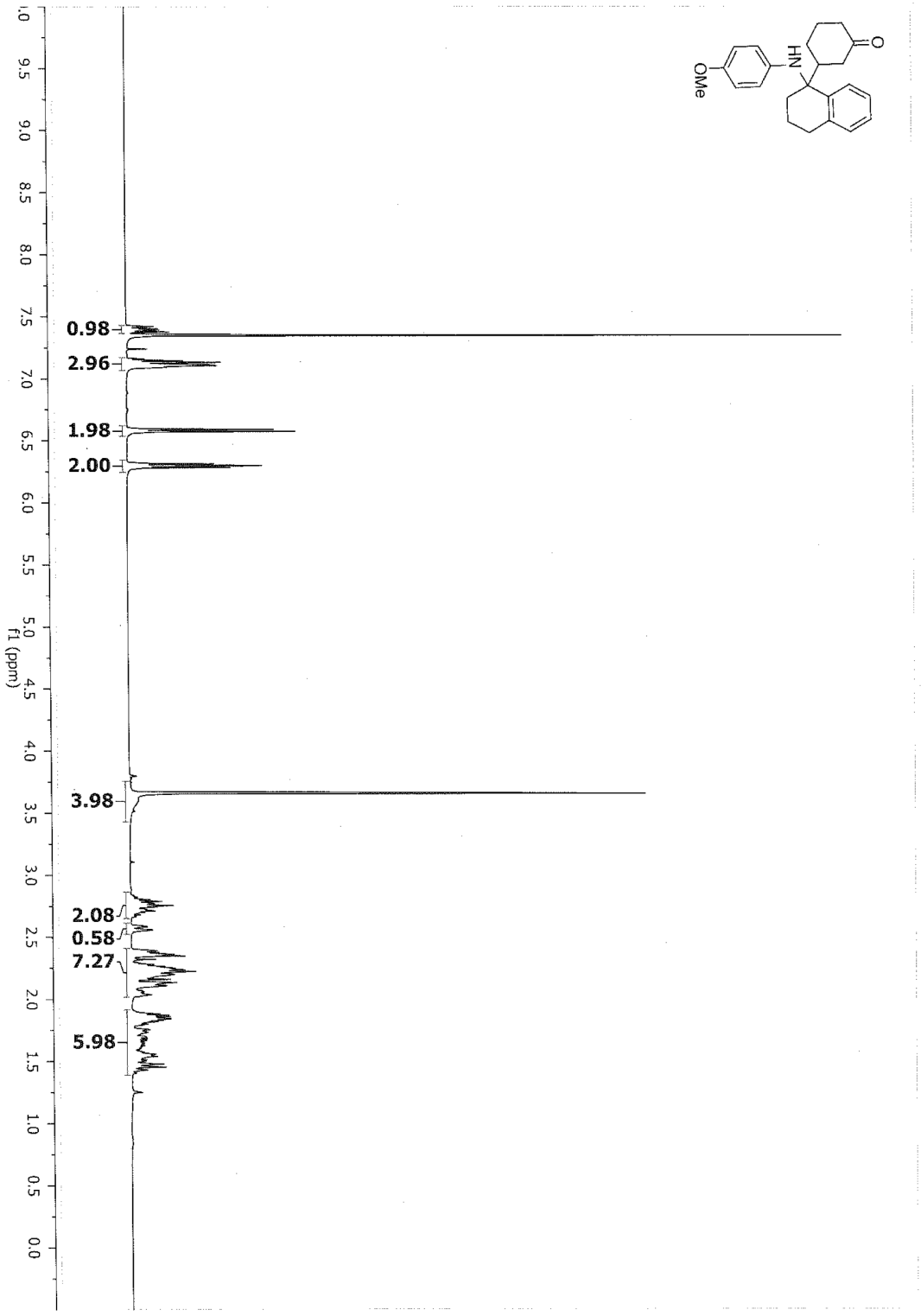

MeO
NH
n-Bu
Ph
O
212.5
211.5
151.8
151.8
141.3
141.2
139.6
139.5
128.3
128.1
127.9
126.8
116.8
116.8
114.2
114.2
77.3
77.0
76.7
63.5
63.4
55.5
47.0
46.5
43.6
43.3
41.1
41.0
31.1
30.5
26.2
25.7
25.2
24.8
24.6
24.5
22.8
22.8
13.9
f1 (ppm)

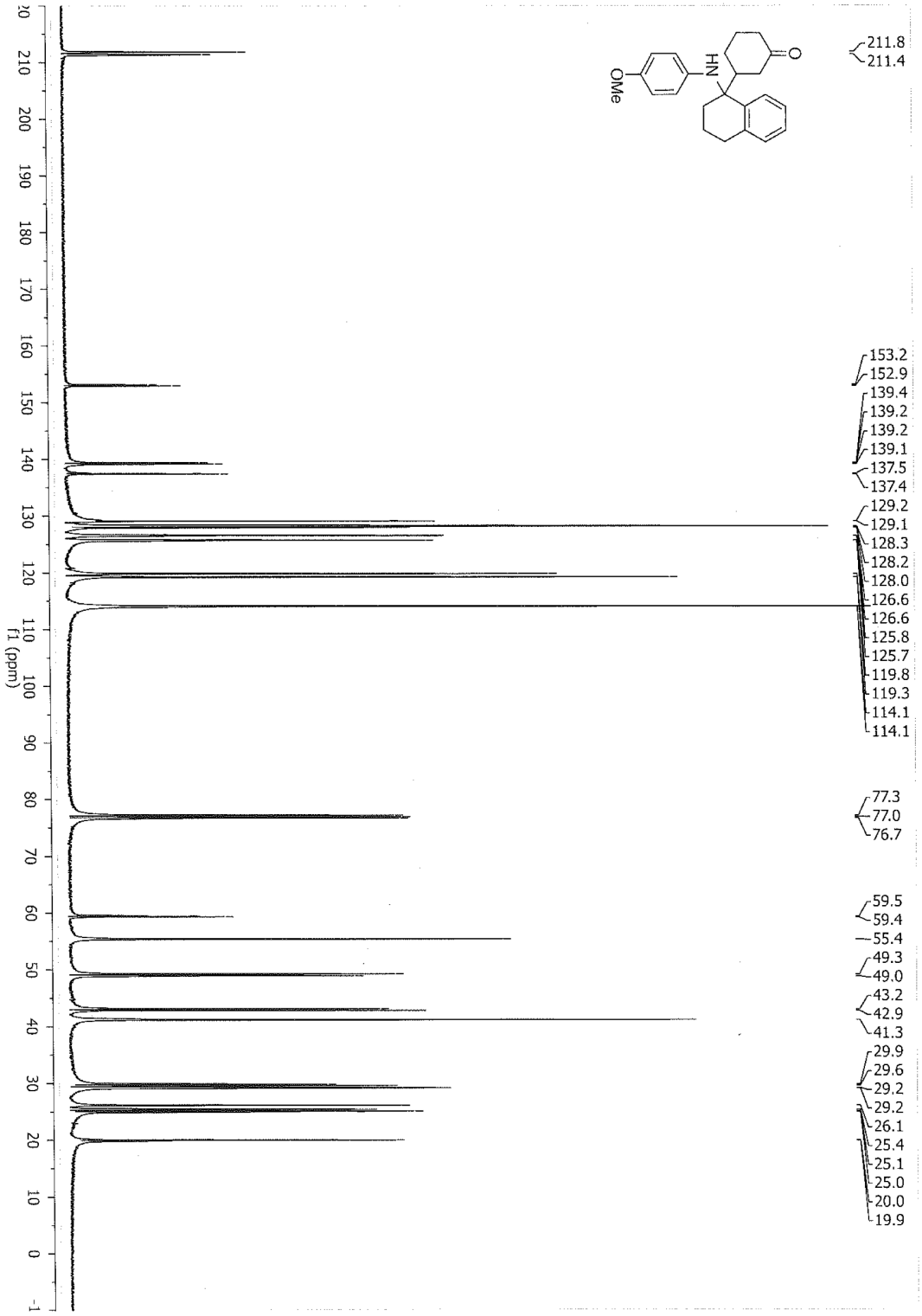

O
HN
n-Bu
OMe
3.72
3.58
4.02
3.28
1.90
6.00
1.09
3.86
11.83
1.18
2.85
5.37
0.82
5.28
6.30
f1 (ppm)

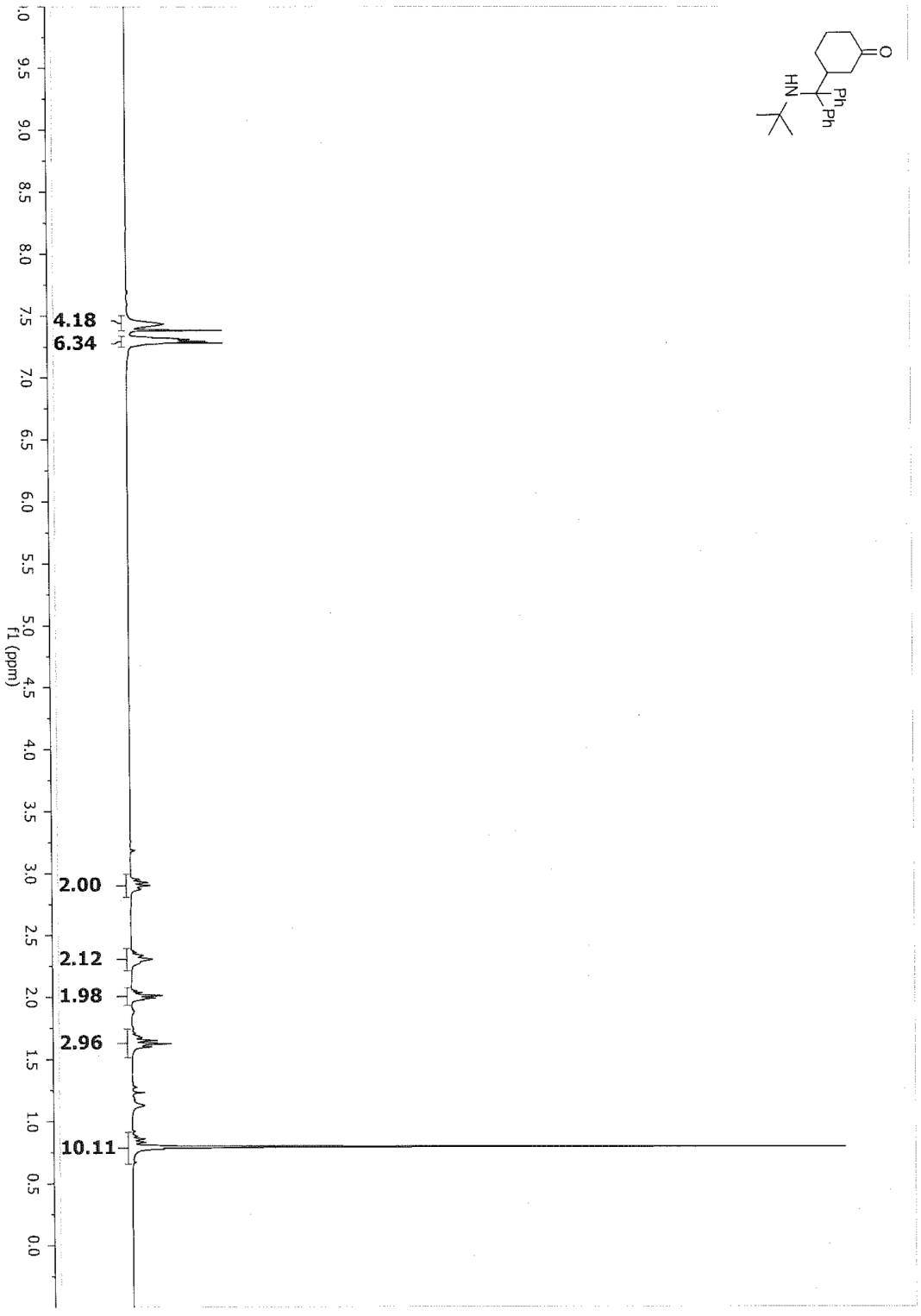

211.3
211.1
158.7
129.0
129.0
128.1
113.9
113.9
62.3
61.7
55.2
45.3
45.1
41.3
41.3
34.6
33.9
27.9
25.0
25.0
22.3
14.0
HN
O
n-Bu
OMe
f1 (ppm)

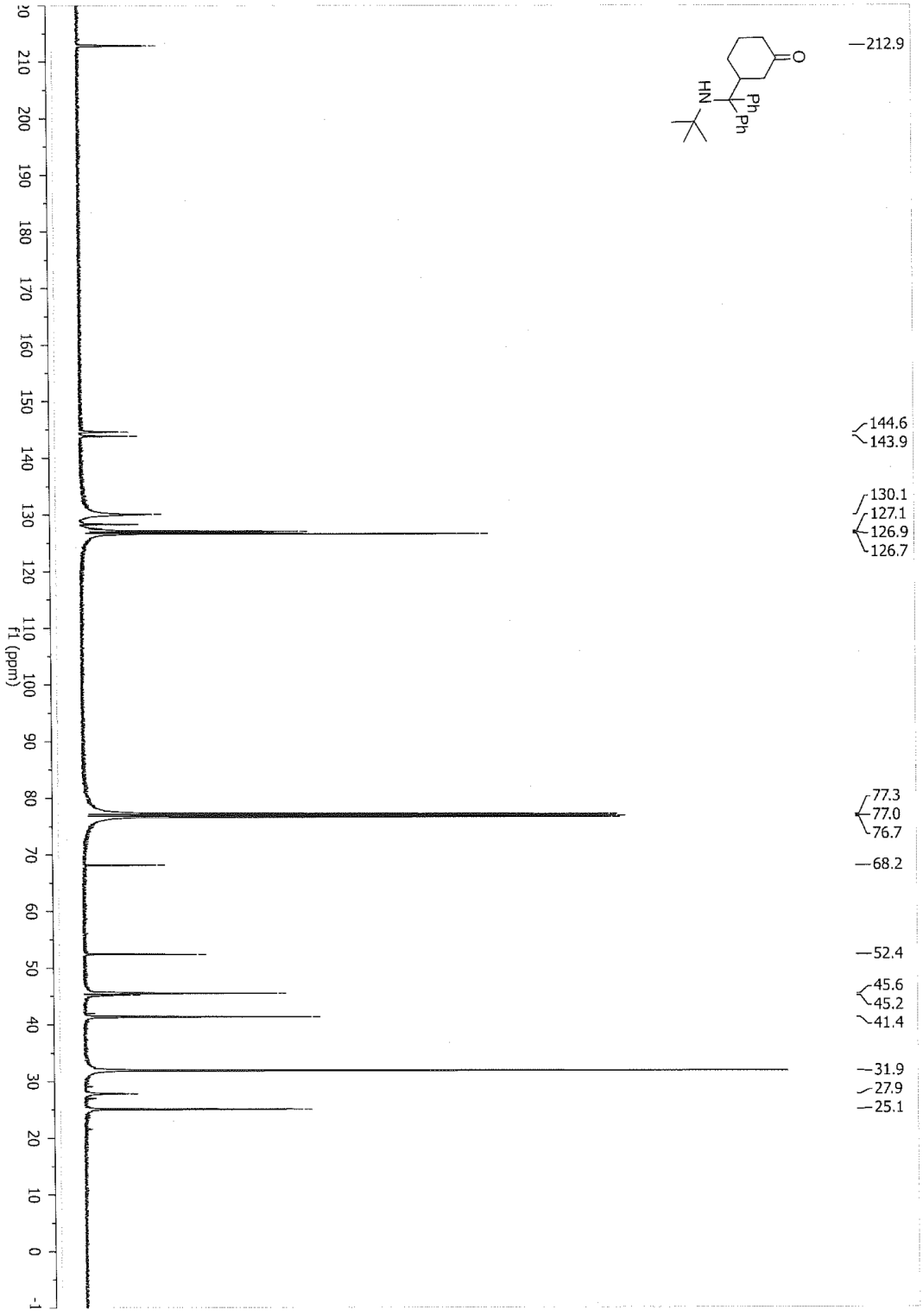

O
HN
Cl
3.88
6.48
3.72
3.71
2.16
1.00
2.14
9.79
1.25
5.92
f1 (ppm)

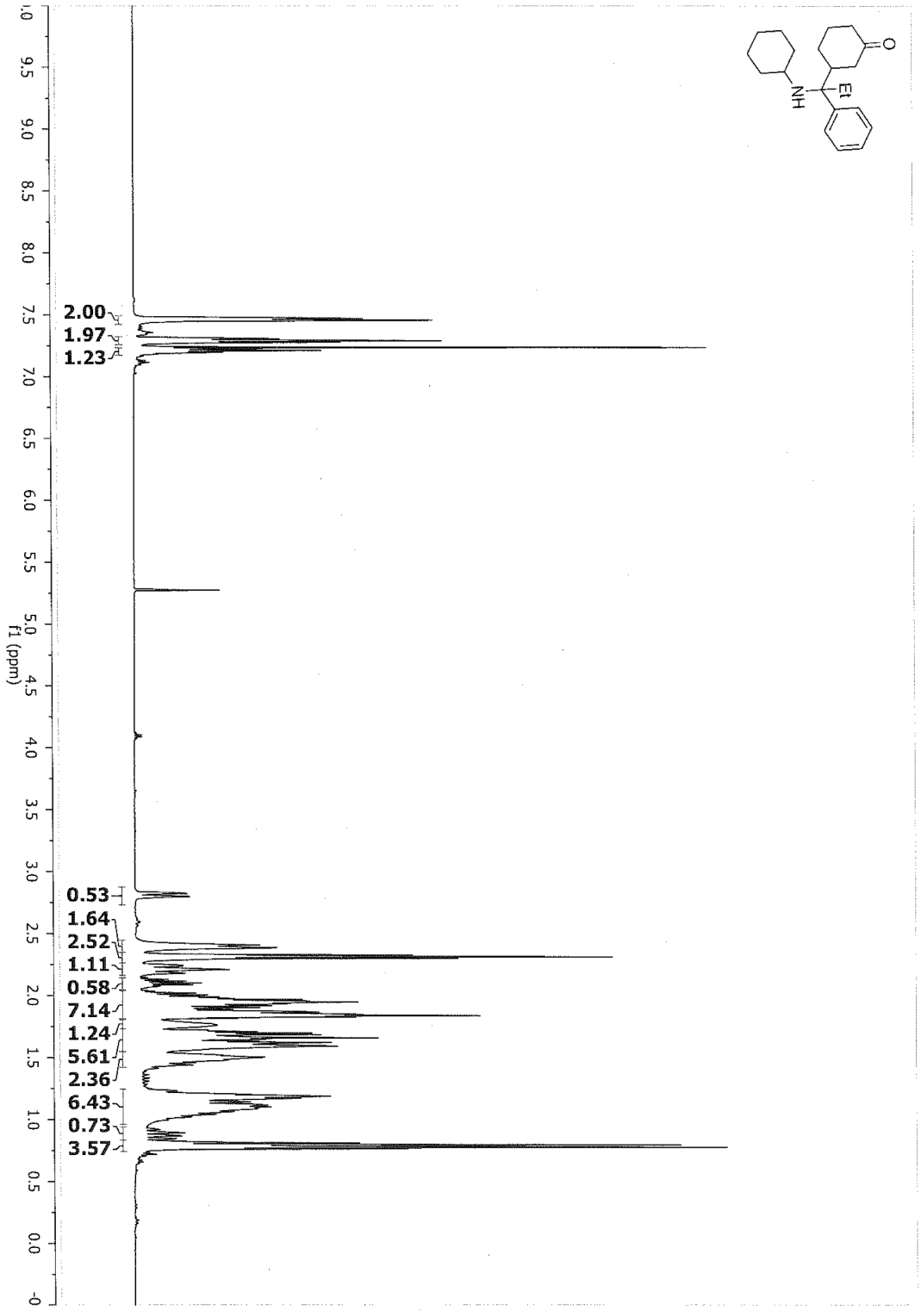

O
HN
Cl
210.8
210.7
145.6
145.5
140.5
140.2
129.0
128.9
128.6
128.6
127.0
114.5
62.7
62.2
45.3
45.3
45.1
45.0
41.3
41.2
28.2
27.8
25.0
24.9
f1 (ppm)

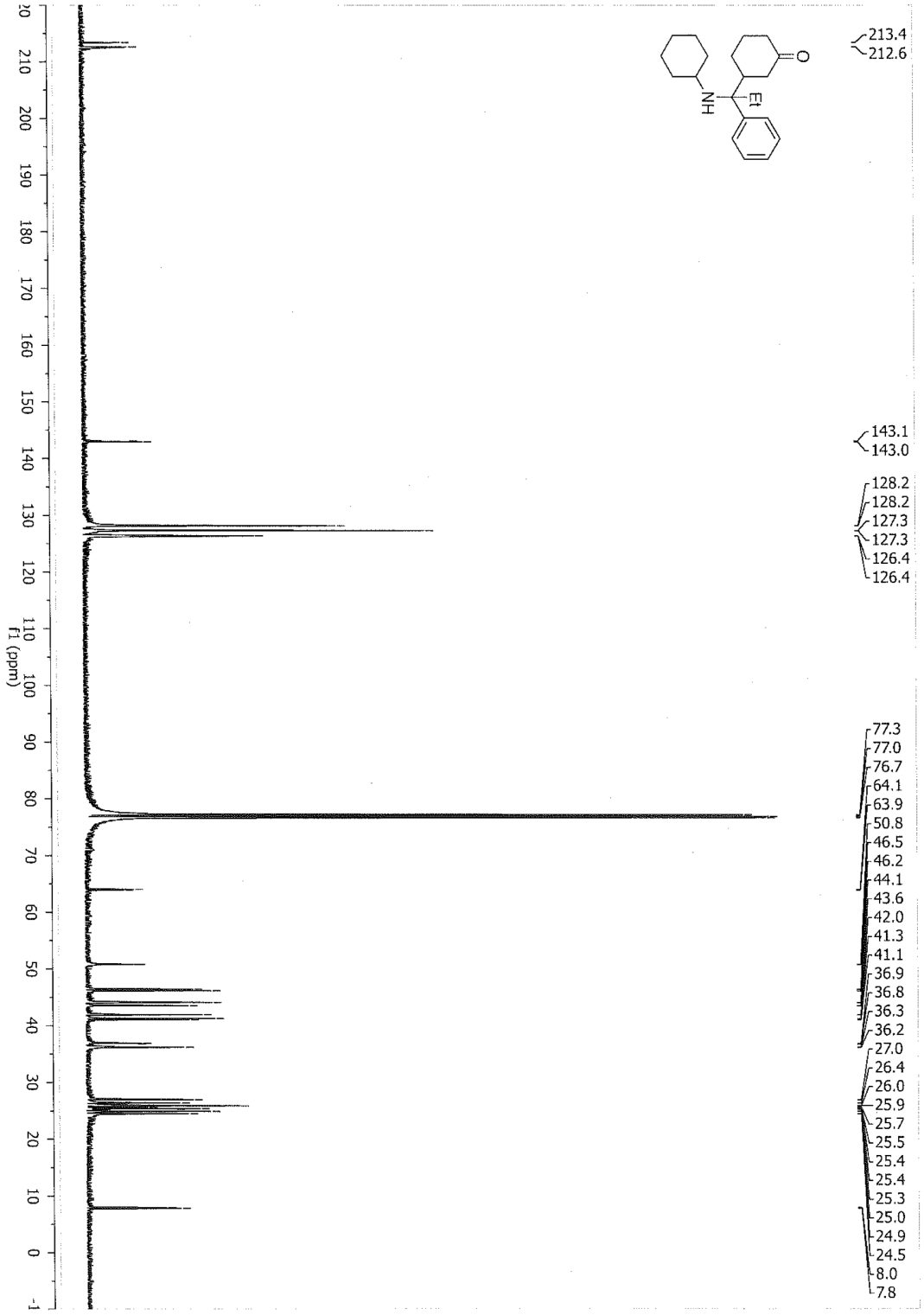

HN
O
OMe
0.98
2.96
1.98
2.00
3.98
2.08
0.58
7.27
5.98
f1 (ppm)

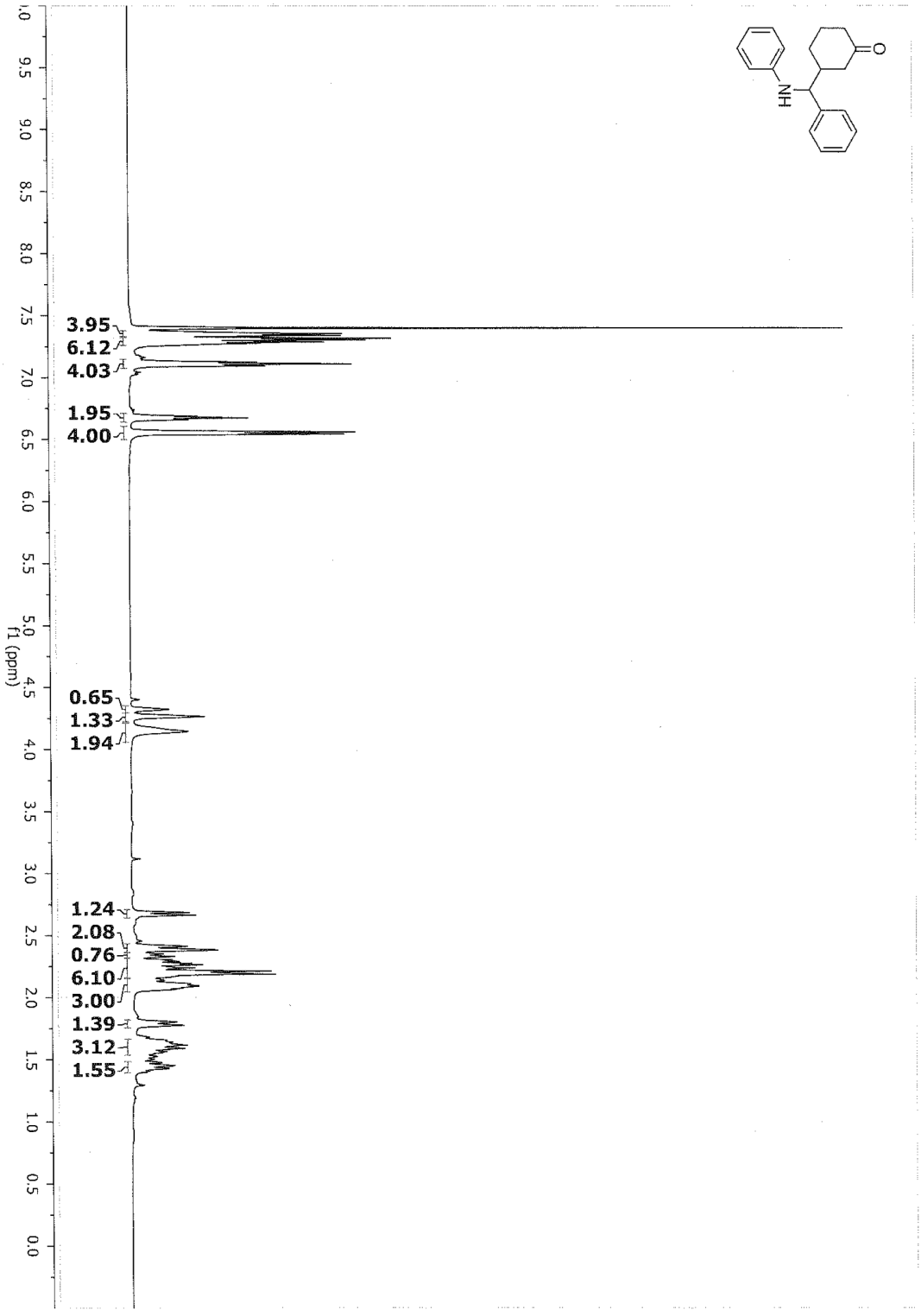

OMe
HN
O
211.8
211.4
153.2
152.9
139.4
139.2
139.2
139.1
137.5
137.4
129.2
129.1
128.3
128.2
128.0
126.6
126.6
125.8
125.7
119.8
119.3
114.1
114.1
77.3
77.0
76.7
59.5
59.4
55.4
49.3
49.0
43.2
42.9
41.3
29.9
29.6
29.2
29.2
26.1
25.4
25.1
25.0
20.0
19.9
f1 (ppm)

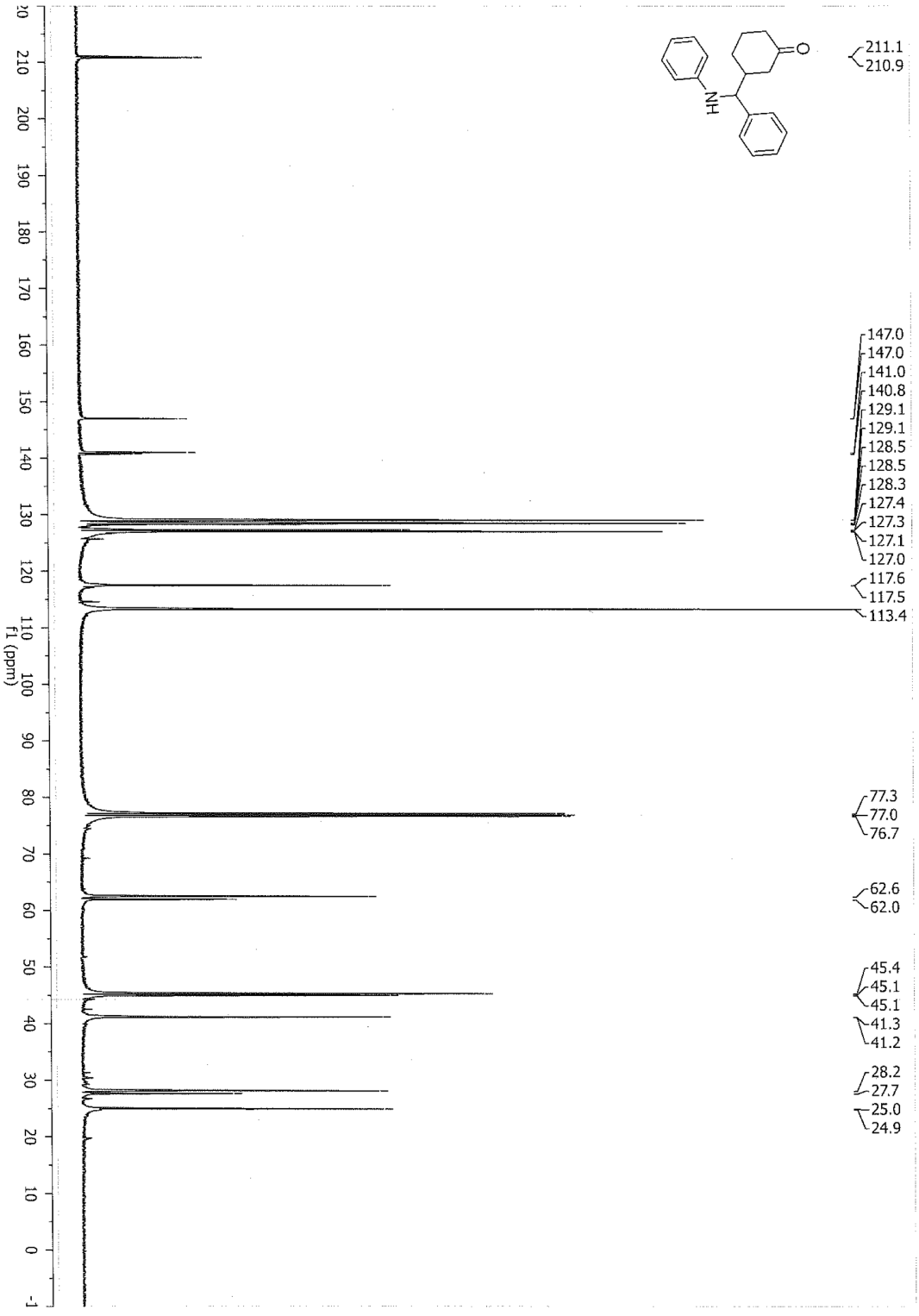

4.18
6.34
2.00
2.12
1.98
2.96
10.11
f1 (ppm)
HN
Ph
Ph
O

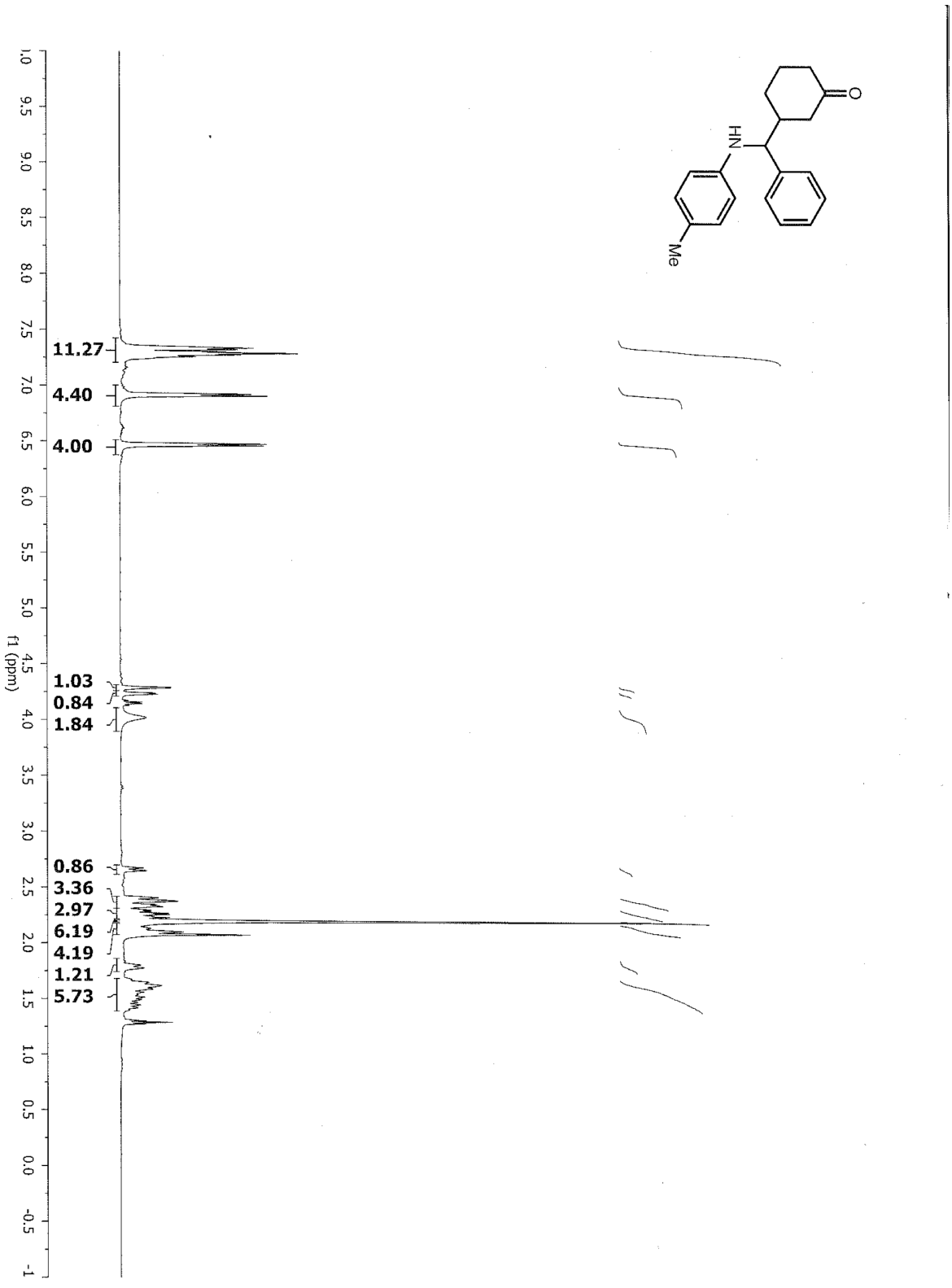

212.9
144.6
143.9
130.1
127.1
126.9
126.7
77.3
77.0
76.7
68.2
52.4
45.6
45.2
41.4
31.9
27.9
25.1
HN
Ph
Ph
O
f1 (ppm)

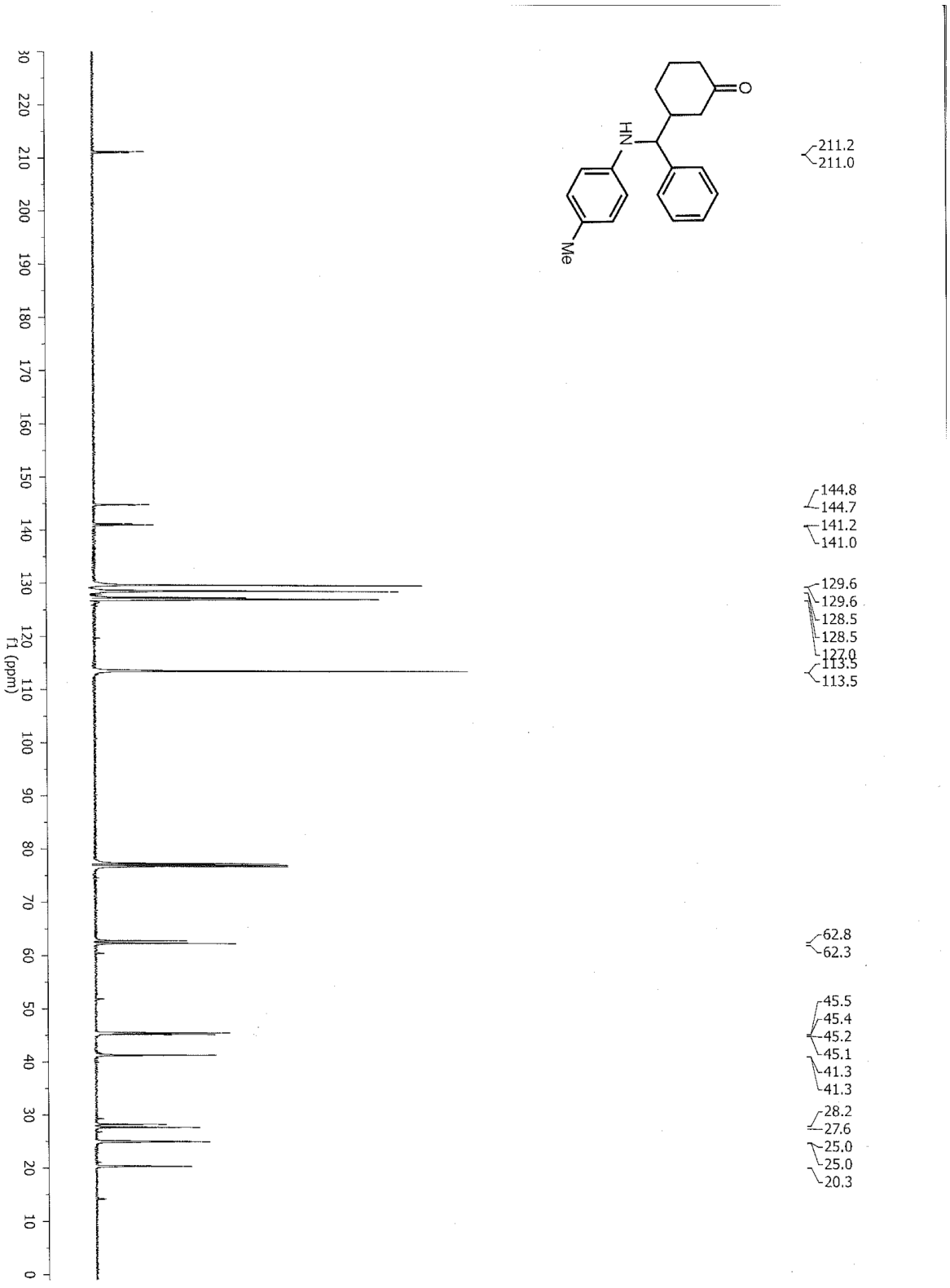

2.00
1.97
1.23
0.53
1.64
2.52
1.11
0.58
7.14
1.24
5.61
2.36
6.43
0.73
3.57
f1 (ppm)
NH
Et
O

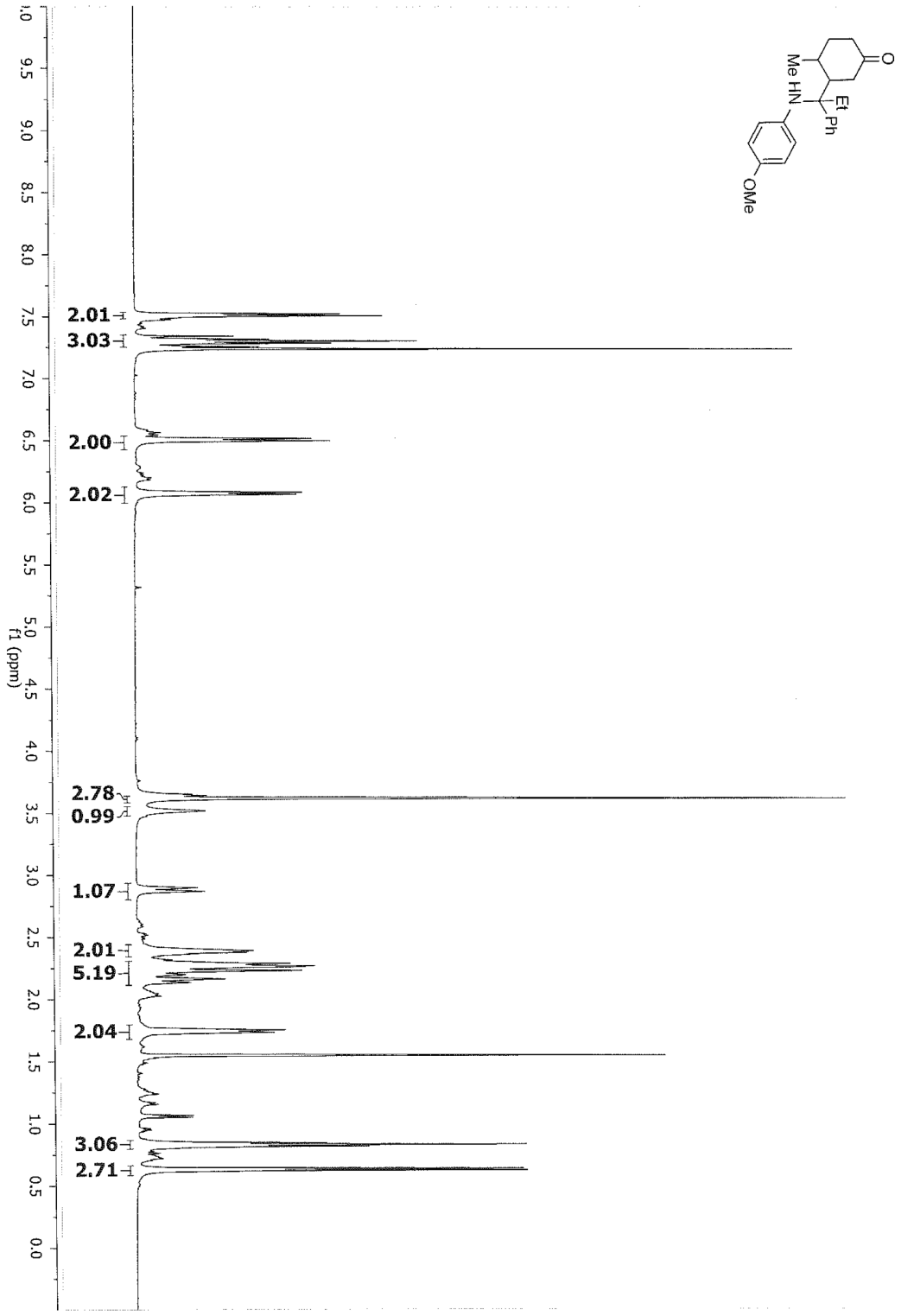

213.4
212.6
143.1
143.0
128.2
128.2
127.3
127.3
126.4
126.4
77.3
77.0
76.7
64.1
63.9
50.8
46.5
46.2
44.1
43.6
42.0
41.3
41.1
36.9
36.8
36.3
36.2
27.0
26.4
26.0
25.9
25.7
25.5
25.4
25.4
25.3
25.0
24.9
24.5
8.0
7.8
NH
Et
O
f1 (ppm)

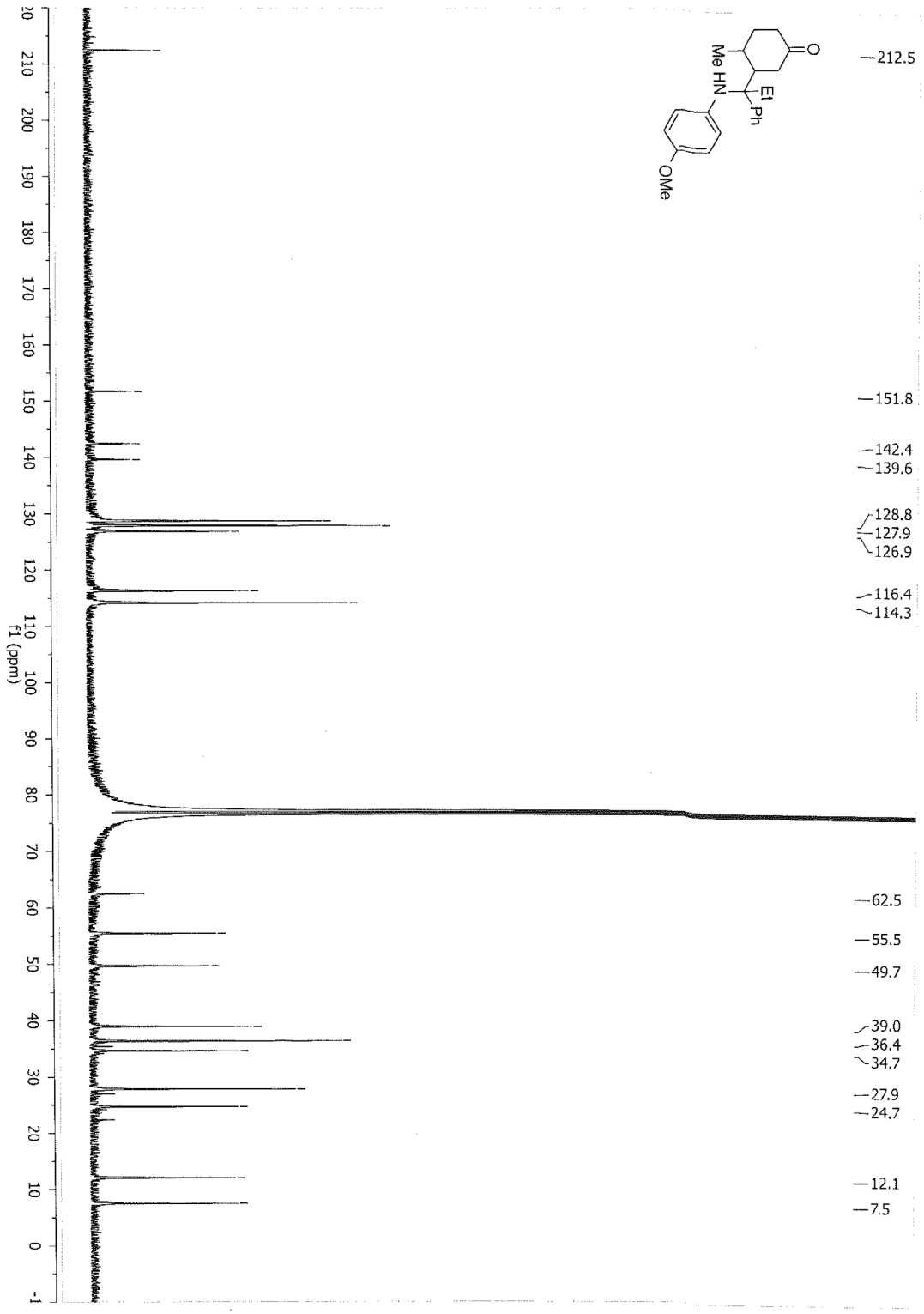

3.95
6.12
4.03
1.95
4.00
0.65
1.33
1.94
1.24
2.08
0.76
6.10
3.00
1.39
3.12
1.55
f1 (ppm)
NH
O

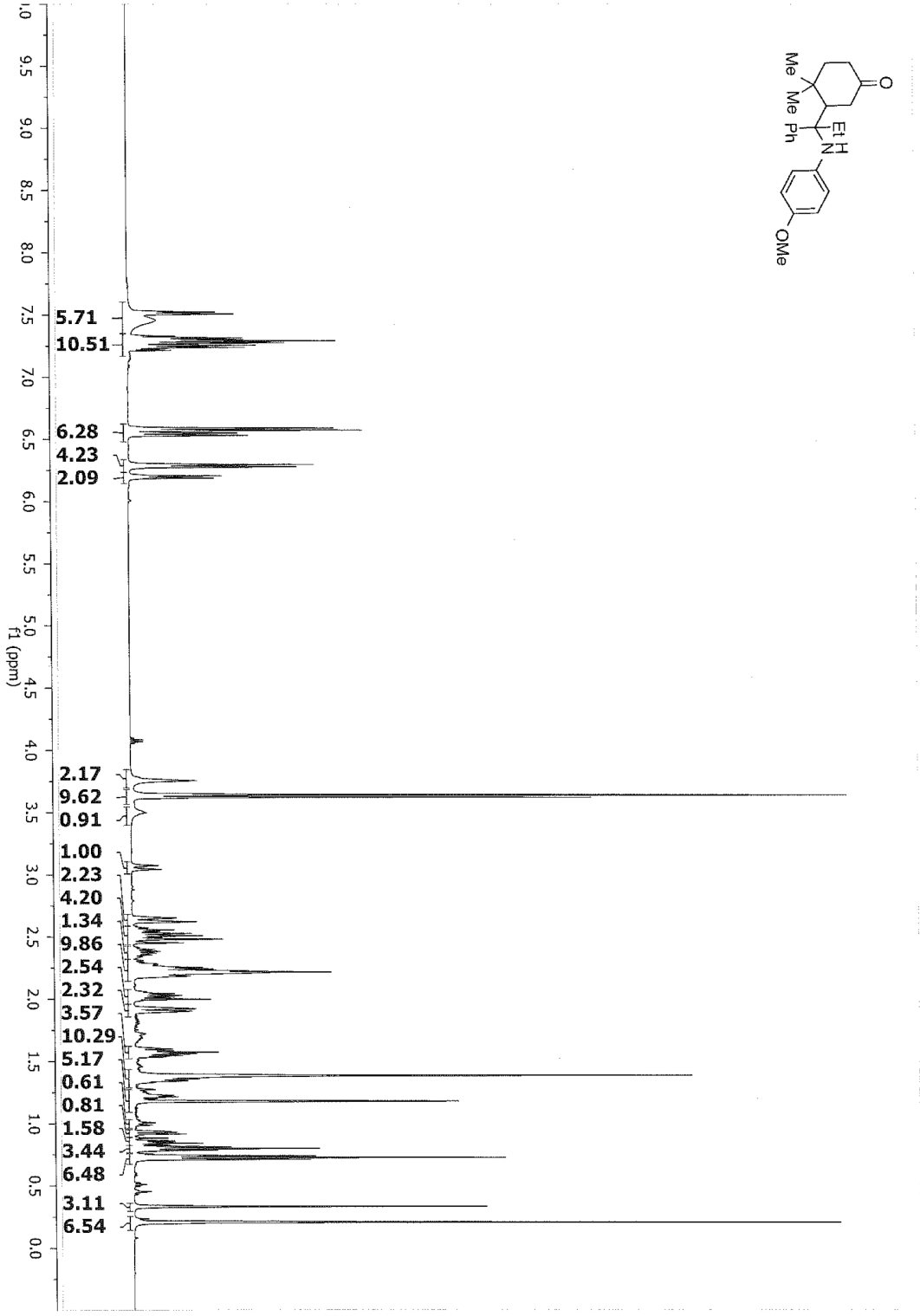

211.1
210.9
147.0
147.0
141.0
140.8
129.1
129.1
128.5
128.5
128.3
127.4
127.3
127.1
127.0
117.6
117.5
113.4
77.3
77.0
76.7
62.6
62.0
45.4
45.1
45.1
41.3
41.2
28.2
27.7
25.0
24.9
f1 (ppm)

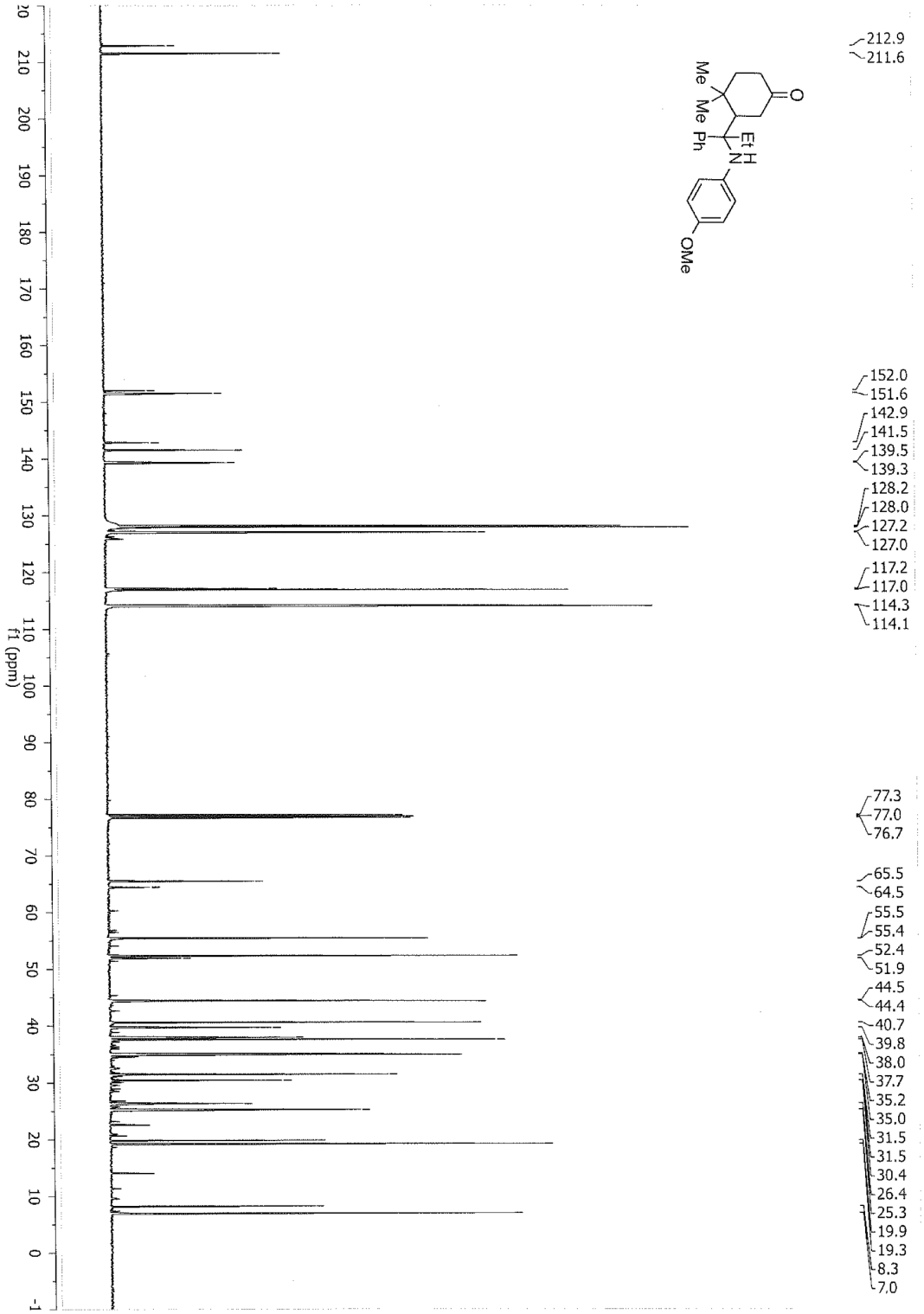

11.27
4.40
4.00
1.03
0.84
1.84
0.86
3.36
2.97
6.19
4.19
1.21
5.73
f1 (ppm)
HN
O
Me

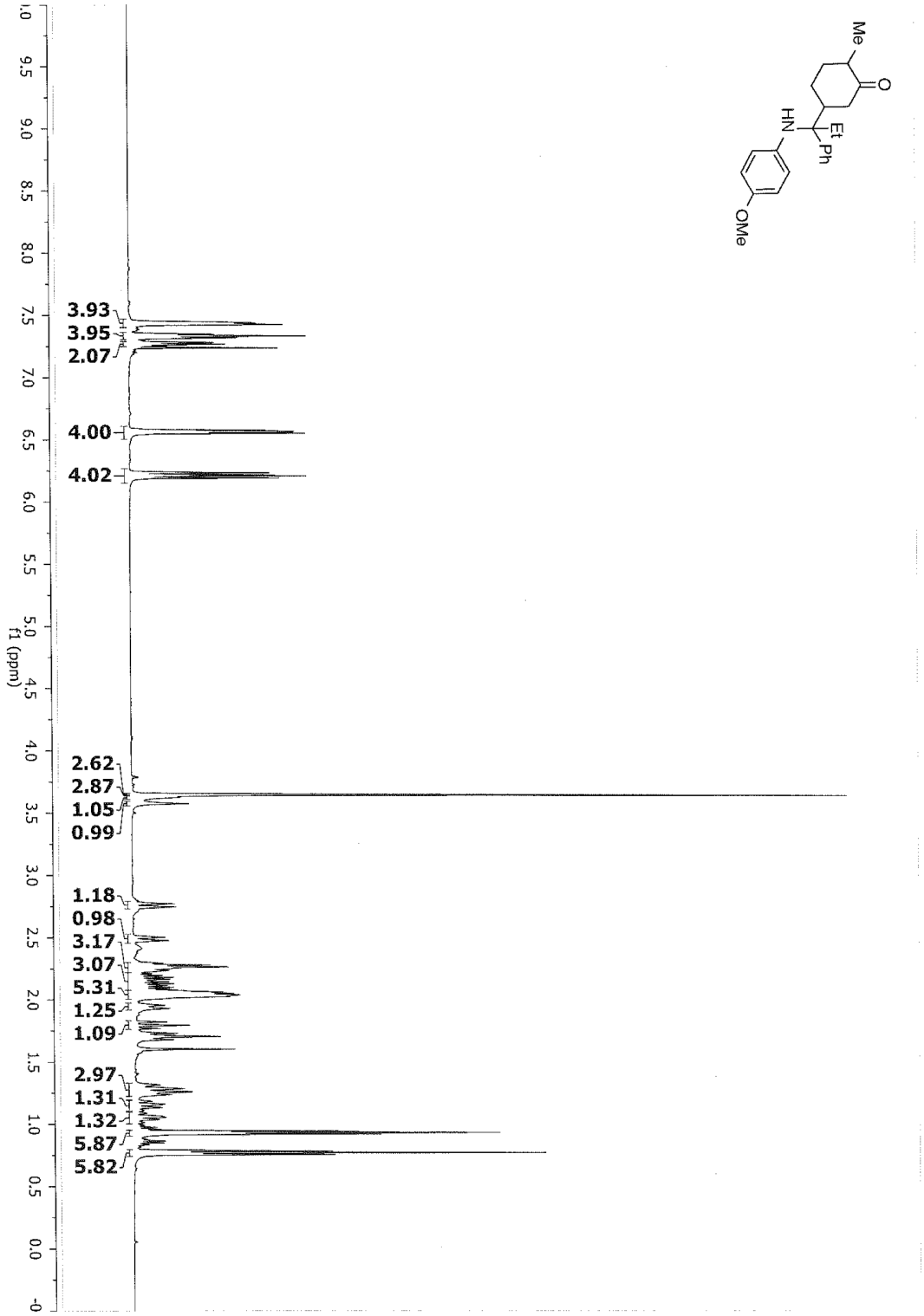

HN
O
Me
211.2
211.0
144.8
144.7
141.2
141.0
129.6
129.6
128.5
128.5
127.0
113.5
113.5
62.8
62.3
45.5
45.4
45.2
45.1
41.3
41.3
28.2
27.6
25.0
25.0
20.3
f1 (ppm)

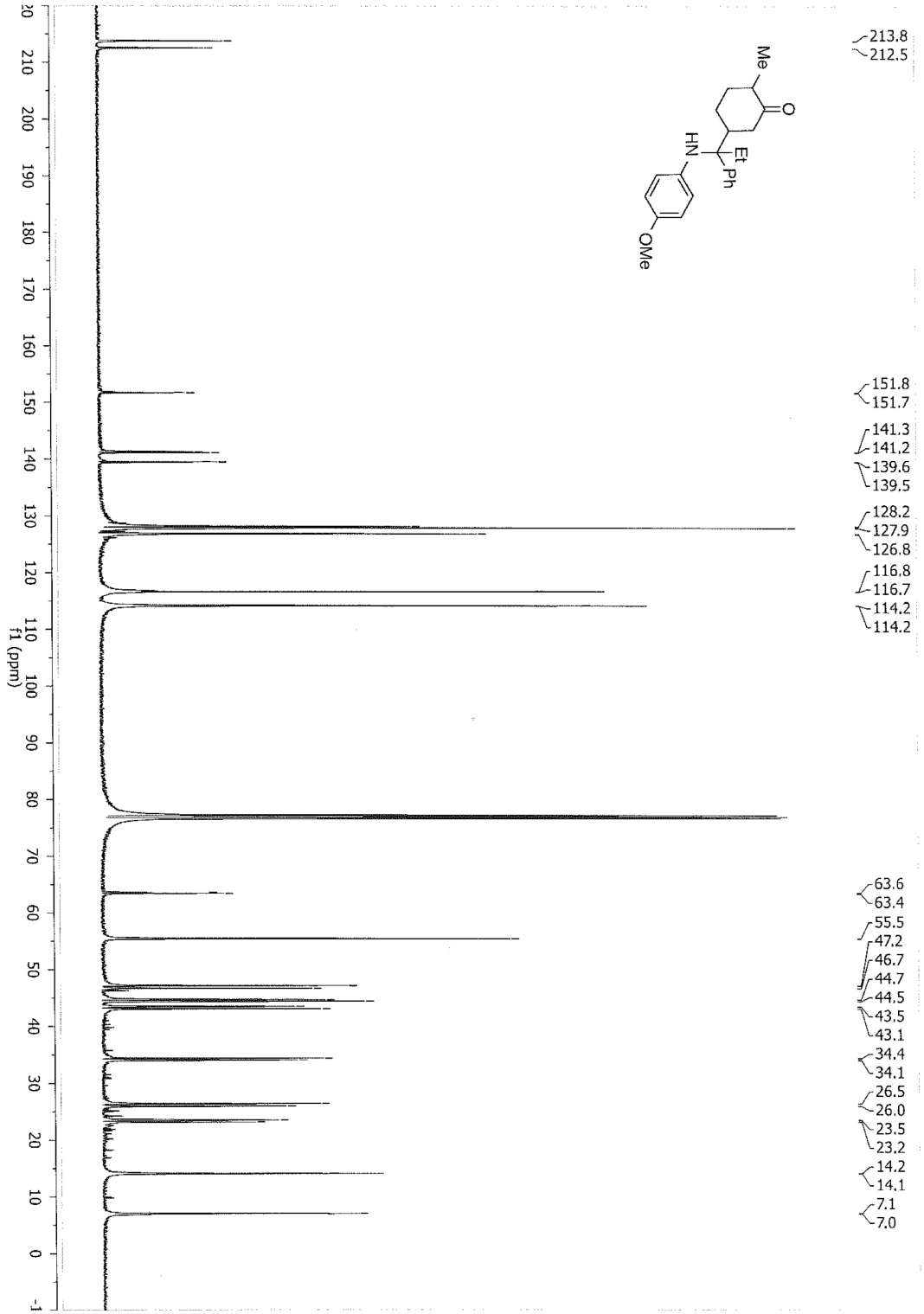

Me HN
Et
Ph
OMe
O
2.01
3.03
2.00
2.02
2.78
0.99
1.07
2.01
5.19
2.04
3.06
2.71
f1 (ppm)

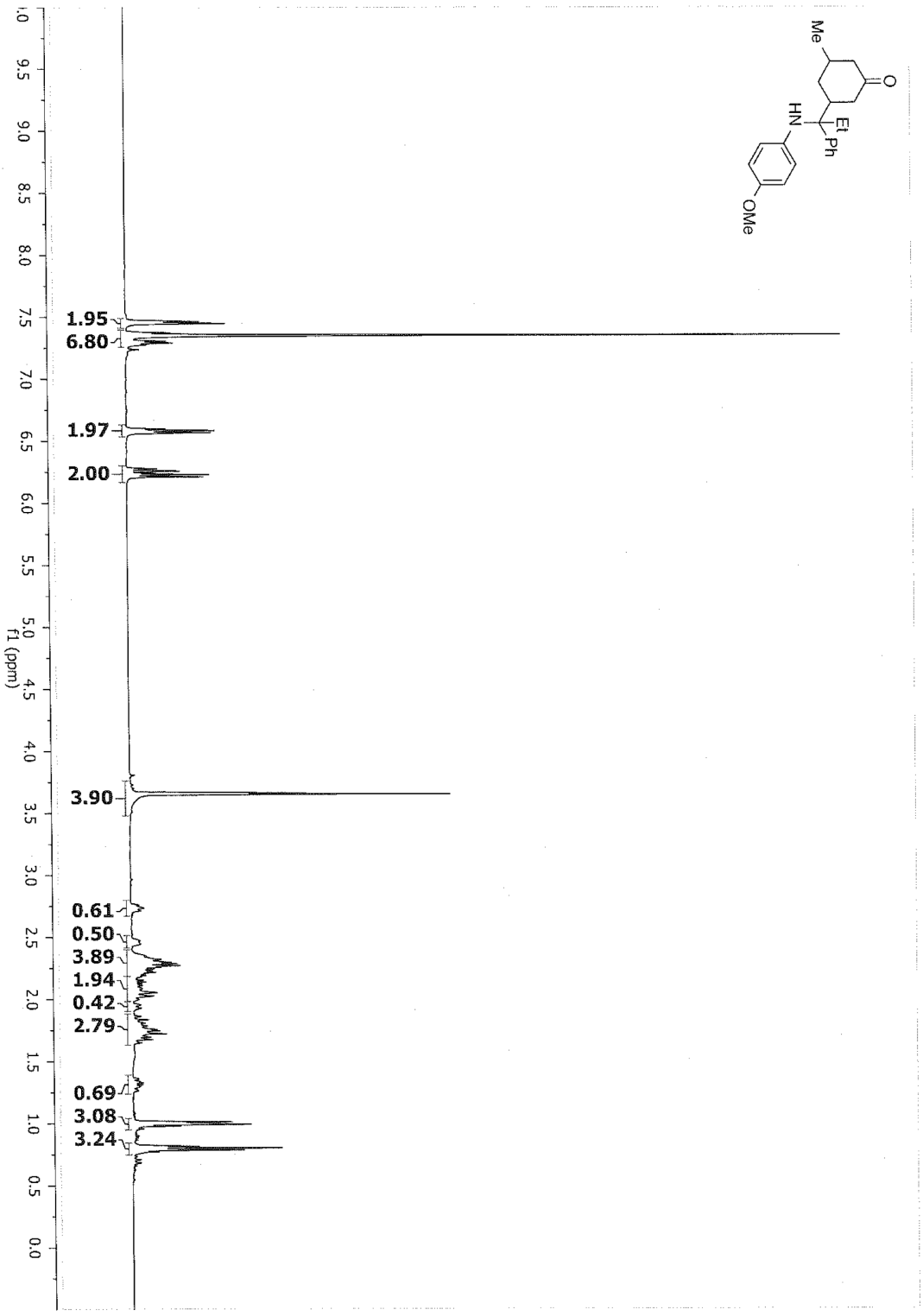

212.5
151.8
142.4
139.6
128.8
127.9
126.9
116.4
114.3
62.5
55.5
49.7
39.0
36.4
34.7
27.9
24.7
12.1
7.5
Me HN
Et
Ph
OMe
O
f1 (ppm)

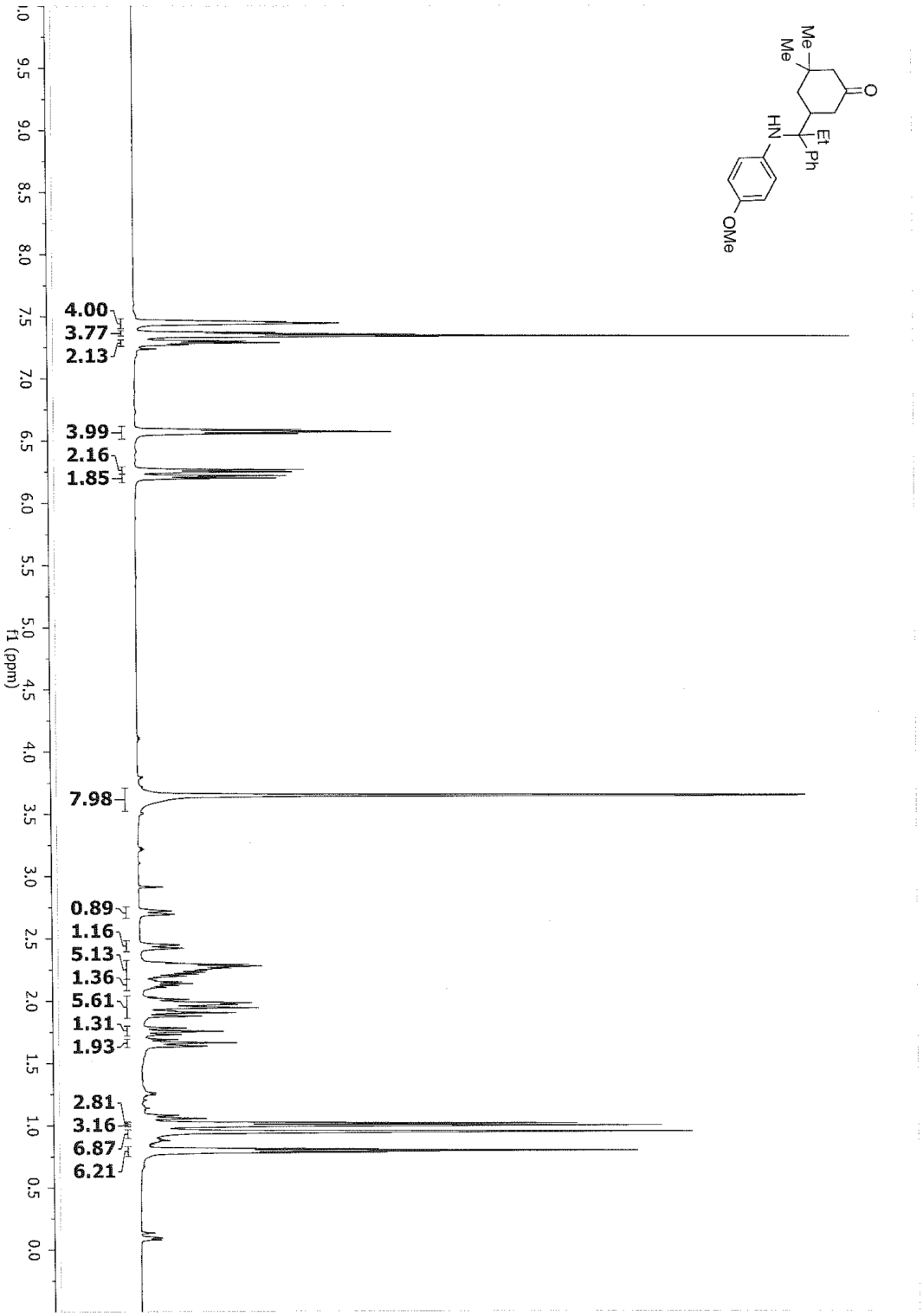

Me
Me
Ph
Et
H
N
O
OMe
5.71
10.51
6.28
4.23
2.09
2.17
9.62
0.91
1.00
2.23
4.20
1.34
9.86
2.54
2.32
3.57
10.29
5.17
0.61
0.81
1.58
3.44
6.48
3.11
6.54
f1 (ppm)

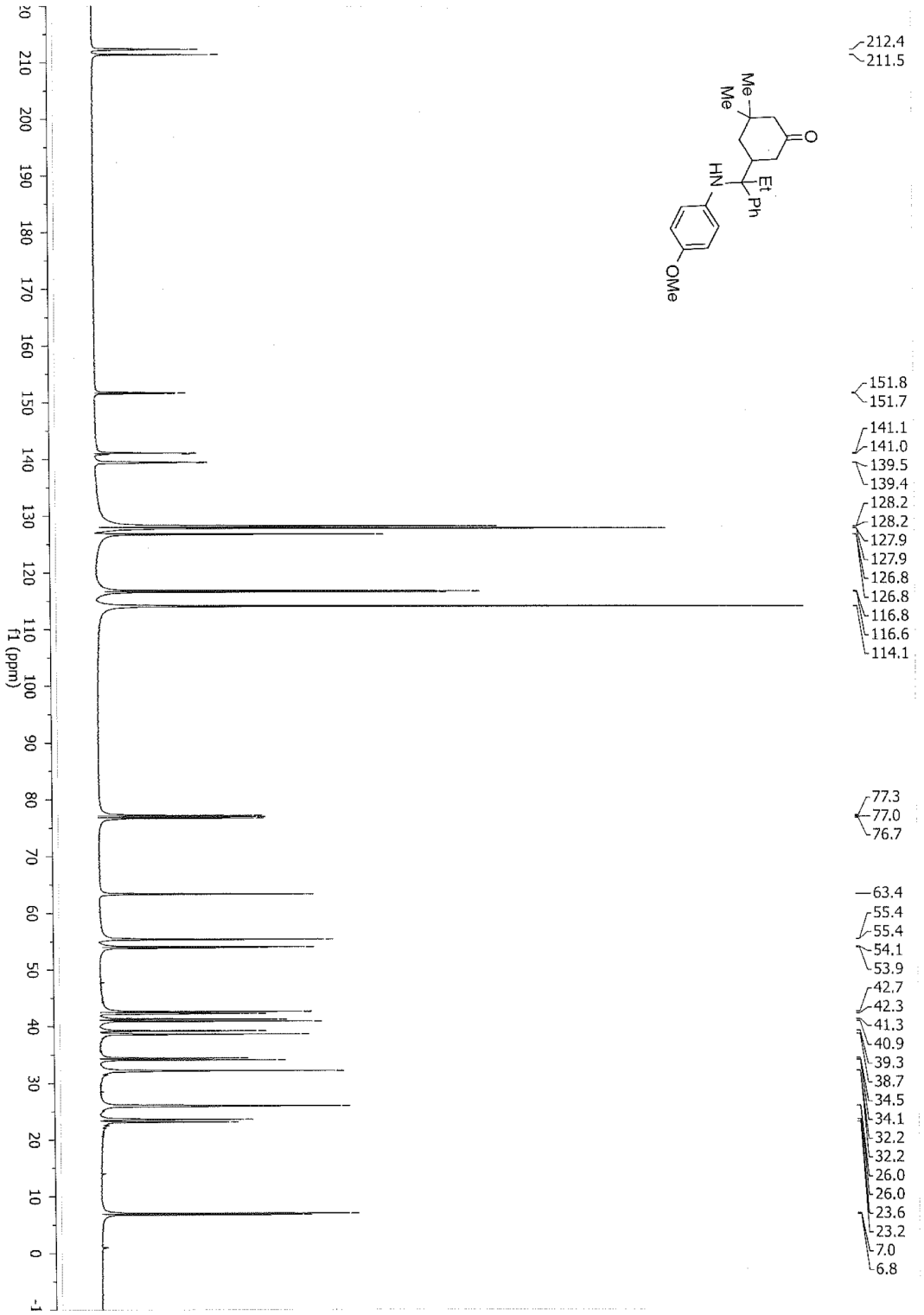

212.9
211.6
152.0
151.6
142.9
141.5
139.5
139.3
128.2
128.0
127.2
127.0
117.2
117.0
114.3
114.1
77.3
77.0
76.7
65.5
64.5
55.5
55.4
52.4
51.9
44.5
44.4
40.7
39.8
38.0
37.7
35.2
35.0
31.5
31.5
30.4
26.4
25.3
19.9
19.3
8.3
7.0
f1 (ppm)
Me
Me
Ph
Et
H
N
O
OMe

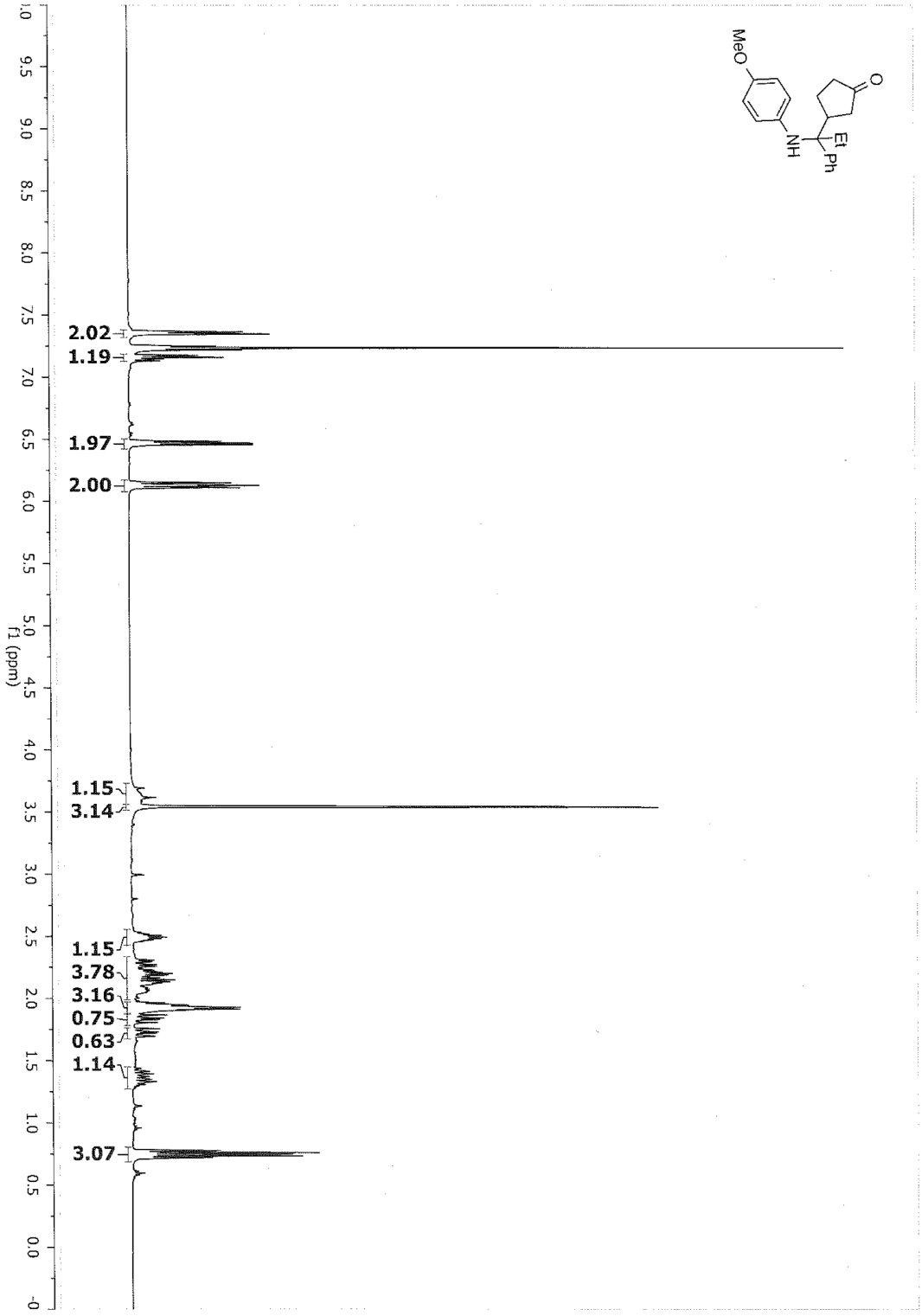

Me
O
HN
Et
Ph
OMe
3.93
3.95
2.07
4.00
4.02
2.62
2.87
1.05
0.99
1.18
0.98
3.17
3.07
5.31
1.25
1.09
2.97
1.31
1.32
5.87
5.82
f1 (ppm)

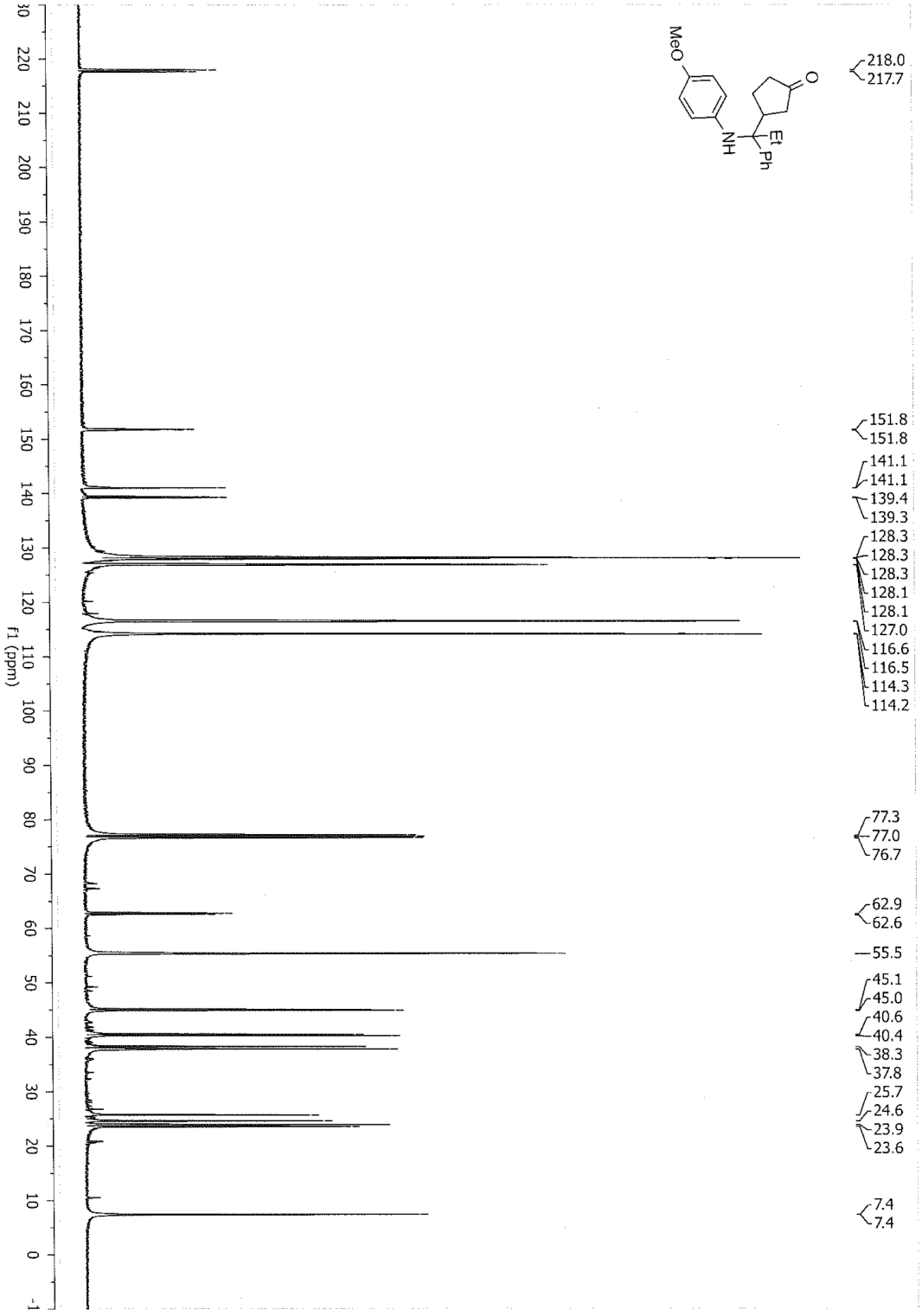

Me
O
HN
Et
Ph
OMe
213.8
212.5
151.8
151.7
141.3
141.2
139.6
139.5
128.2
127.9
126.8
116.8
116.7
114.2
114.2
63.6
63.4
55.5
47.2
46.7
44.7
44.5
43.5
43.1
34.4
34.1
26.5
26.0
23.5
23.2
14.2
14.1
7.1
7.0
f1 (ppm)


Me
O
HN
Et
Ph
OMe
1.95
6.80
1.97
2.00
3.90
0.61
0.50
3.89
1.94
0.42
2.79
0.69
3.08
3.24
f1 (ppm)


Me
Me
O
HN
Et
Ph
OMe
4.00
3.77
2.13
3.99
2.16
1.85
7.98
0.89
1.16
5.13
1.36
5.61
1.31
1.93
2.81
3.16
6.87
6.21
f1 (ppm)


212.4
211.5
151.8
151.7
141.1
141.0
139.5
139.4
128.2
128.2
127.9
127.9
126.8
126.8
116.8
116.6
114.1
77.3
77.0
76.7
63.4
55.4
55.4
54.1
53.9
42.7
42.3
41.3
40.9
39.3
38.7
34.5
34.1
32.2
32.2
26.0
26.0
23.6
23.2
7.0
6.8
Me
Me
O
HN
Et
Ph
OMe
f1 (ppm)


MeO
NH
Et
Ph
O
2.02
1.19
1.97
2.00
1.15
3.14
1.15
3.78
3.16
0.75
0.63
1.14
3.07
f1 (ppm)


MeO
NH
Et
Ph
O
218.0
217.7
151.8
151.8
141.1
141.1
139.4
139.3
128.3
128.3
128.3
128.1
128.1
127.0
116.6
116.5
114.3
114.2
77.3
77.0
76.7
62.9
62.6
55.5
45.1
45.0
40.6
40.4
38.3
37.8
25.7
24.6
23.9
23.6
7.4
7.4
f1 (ppm)

4. Stern–Volmer Emission Quenching Data

Emission intensities were recorded using a Perkin Elmer LS50 luminescence spectrophotometer. All $Ir(ppy)_2(dtbbpy)PF_6$ solutions were excited at 450 nm and the emission intensity was collected at 525-675 nm. In a typical experiment, to a $3.0 \bullet 10^{-5}$ M solution of $Ir(ppy)_2(dtbbpy)PF_6$ in DMPU was added the appropriate amount of quencher in a screw-top 1.0 cm quartz cuvette. After degassing the sample with a stream of argon for 10 minutes, the emission of the sample was collected.

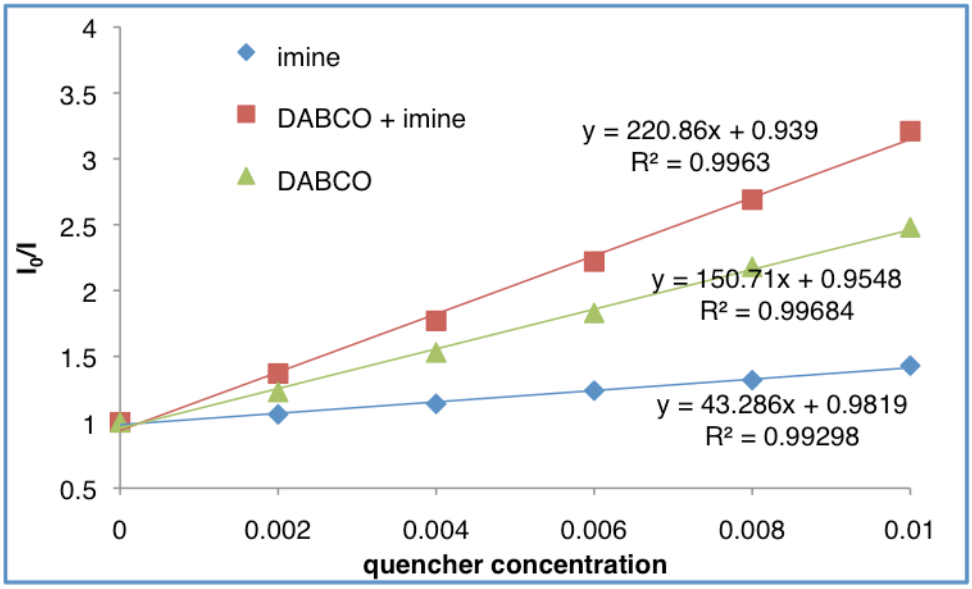


Figure 1. $Ir(dtbbpy)(ppy)_2PF_6$ emission quenching with DABCO, (*E*)-*N*-(4-methoxyphenyl)-1-phenylmethanimine (imine), or a mixture of DABCO and imine.

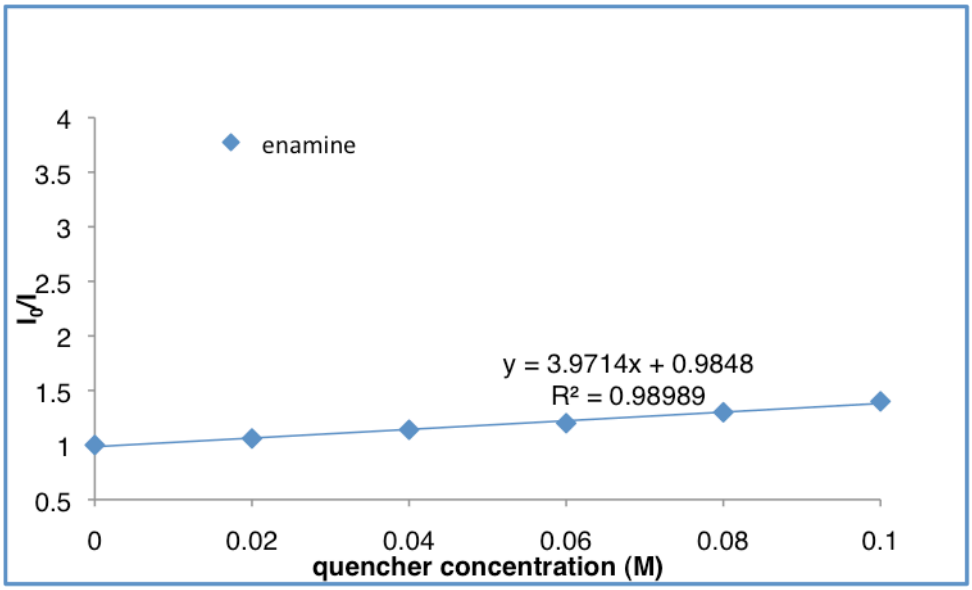


Figure 2. $Ir(dtbbpy)(ppy)_2PF_6$ emission quenching with enamine **5**.

5. References Cited

[1] Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals, 3rd ed.* Pergamon Press: Oxford, 1988.

[2] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. Safe and Convenient Procedure for Solvent Purification. *Organometallics* **1996**, *15*, 1518–1520.

[3] Still, W. C.; Kahn, M. A.; Mitra, J. Rapid Chromatographic Technique for Preparative Separations with Moderate Resolution. *J. Org. Chem.* **1978**, *43*, 2923–2925.