Catalytic Aza-Wittig Cyclisations for Heteroaromatic Synthesis

Alison E. McGonagle,[a] Stephen P. Marsden*,[a] and Ben McKeever[b]

a) School of Chemistry, University of Leeds, Leeds LS2 9JT, UK

b) AstraZeneca Process R&D, Charter Way, Silk Road Business Park, Macclesfield SK10 2NA, UK

Supporting information

General Experimental Methods

Toluene was distilled from sodium metal. Triethylamine was distilled from and stored over potassium hydroxide. All reactions were carried out under an atmosphere of dry nitrogen. Petroleum ether refers to the fraction boiling at 40-60°C. Column chromatography was carried out on Merck Kieselgel 60 (230-400 mesh). NMR spectra were recorded at 300 MHz (^{1}H nmr) and 75 MHz (^{13}C nmr). Chemical shifts are reported in parts per million relative to TMS and were referenced to residual protic solvent or solvent itself (^{1}H and ^{13}C nmr respectively). Coupling constants are reported in Hertz. Melting points were recorded on a Reichert hot stage apparatus and are uncorrected. Infra-red spectra were recorded as thin films on 5 mm NaCl plates.

SAFETY NOTICE: **CAUTION!** All azides should be treated as potentially explosive. Although we have not encountered any problems in the synthesis, handling, purification and use of the acyl azides, we recommend that all reactions and manipulations utilizing azides are carried out behind appropriate blast protectors, using glassware free from contamination by transition metals.

General procedure for formation of acid azides:

2'-Azidocarbonylbiphenyl-2-carboxylic acid methyl ester (precursor to 1a)

A solution of 2'-methoxycarbonyl-2-biphenyl carboxylic acid (400 mg, 1.6 mmol) in anhydrous acetone (4 ml) was treated at room temperature with anhydrous Et_3N (0.2 ml, 1.7 mmol) and DPPA (0.3 ml, 1.4 mmol). The reaction mixture was stirred under nitrogen and followed by IR to monitor DPPA disappearance (2170 cm^{-1}), and acyl azide formation (2133 cm^{-1}). After 15 h the reaction mixture was concentrated at room temperature. The residue was partitioned between EtOAc (25 ml) and sat. aq. $NaHCO_3$ (25 ml) and the aqueous layer was extracted with EtOAc (2 x 25 ml). The combined organic extracts were washed with sat. aq. $NaHCO_3$ soln. (50 ml), dried (Na_2SO_4) and concentrated at room temperature. The crude product was purified quickly by flash column chromatography (silica), eluting with CH_2Cl_2 to afford the title compound (317 mg, 72%) as a colourless oil; R_F= 0.3 (CH_2Cl_2); ν_{max} (NaCl/ film)/cm^{-1} 2133, 1726, 1698, 1228, 1182, 978, 754; ^1H NMR ($CDCl_3$) δ 3.70 (3H, s), 7.25 (1H, dd, *J*= 7.6, 0.9), 7.26 (1H, dd, *J*= 7.4, 1.0), 7.47-7.56 (2H, m), 7.59-7.68 (2H, m), 8.10 (2H, td, *J*= 7.7, 1.0); ^{13}C NMR ($CDCl_3$) δ 52.3, 127.8, 127.9, 129.4, 129.6, 130.5, 130.6, 131.0, 132.2, 133.3, 143.3, 144.4, 167.5, 173.1 (14 signals observed for 15 expected); HRMS (EI) Calcd. for $C_{15}H_{11}N_3O_3$ $[M]^+$ 281.0800; Found 281.0804.

2'-Azidocarbonyl-biphenyl-2-carboxylic acid ethyl ester (precursor to 1b)

Yield: 69%. R_F= 0.3 (CH_2Cl_2); ν_{max} (NaCl/ film)/cm^{-1} 2132, 1718, 1700, 1286, 1227, 1179, 977, 754; ^1H NMR ($CDCl_3$) δ 1.08 (3H, t, *J*= 7.2), 4.12 (2H, app. qd, *J*= 7.2, 0.8), 7.23-7.28 (2H, m), 7.46-7.54 (2H, m), 7.57-7.67 (2H, m), 8.07 (1H, dd, *J*= 7.8, 1.2), 8.12 (1H, dd, *J*= 7.7, 1.3); ^{13}C NMR ($CDCl_3$) δ 14.2, 61.1, 127.7, 127.9, 129.7, 130.0, 130.4, 130.5, 130.6, 131.0, 132.0, 133.2, 143.0, 144.6, 167.3, 173.0 ; HRMS (EI) Calcd. for $C_{16}H_{13}N_3O_3$ $[M]^+$ 295.0957; Found 295.0952.

2'-Azidocarbonylbiphenyl-2-carboxylic acid isopropyl ester (precursor to 1c)

Yield: 72%. R_F= 0.4 (CH_2Cl_2); ν_{max} (NaCl/ film)/cm^{-1} 2132, 1711, 1704, 1440, 1286, 1227, 976, 754; ^{1}H NMR ($CDCl_3$) δ 1.01, (3H, d, *J*= 6.2), 1.09 (3H, d, *J*= 6.2), 5.00 (1H, septet, *J*= 6.3), 7.25 (2H, td, *J*= 7.6, 1.2), 7.50 (1H, dd, *J*= 7.7, 1.3), 7.51 (1H, dd, *J*= 7.7, 1.5), 7.55-7.65 (2H, m), 8.09 (2H, td, *J*= 8.0, 1.4); ^{13}C NMR ($CDCl_3$) δ 21.9, 68.5, 127.7, 127.9, 128.8, 129.8, 130.4, 130.5, 131.0, 131.8, 133.2, 142.7, 144.8, 166.9, 172.9 (15 signals observed for 17 expected); HRMS (EI) Calcd. for $C_{17}H_{15}N_3O_3$ $[M]^+$ 309.1113; Found 309.1114.

2'-Azidocarbonyl-biphenyl-2-carboxylic acid diethyl amide (precursor to 1d)

Yield: 71%. R_F= 0.4 (Et_2O); ν_{max} (NaCl/ film)/cm^{-1} 2133, 1695, 1628, 1429, 1228, 979; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.69-0.78 (3H, m), 0.87 (3H, t, *J*= 7.0), 2.63-3.61 (4H, br. m), 7.13-7.57 (7H, m), 7.94 (1H, d, *J*= 7.7); ^{13}C NMR ($CDCl_3$) δ 12.4, 14.2, 38.5, 42.6, 126.6, 128.2, 128.6, 130.3, 130.8, 132.9, 141.4 (7 Ar signals observed for 12 expected), 170.1, 173.6; HRMS (EI) Calcd. for $C_{18}H_{17}N_2O_2$ $[M–N_2–H]^+$ 293.1290; Found 293.1293.

2'-Azidocarbonyl-biphenyl-2-carboxylic acid piperidinyl amide (precursor to 1e)

Yield: 63%. R_F= 0.4 (Et_2O); ν_{max} (NaCl/ film)/cm^{-1} 2132, 1697, 1627, 1443, 1227, 979, 750; ^{1}H NMR ($CDCl_3$) δ 1.08-1.59 (6H, br. m), 2.88-3.51 (4H, br. m), 7.11-7.70 (7H, m), 7.93 (1H, d, *J*= 7.8); ^{13}C NMR ($CDCl_3$) δ 24.6, 25.0, 25.9, 42.7, 48.1, 125.0, 126.0, 127.6, 128.2, 128.3, 128.7, 129.0, 129.1, 129.4, 130.8, 132.9, 141.5, 169.1, 169.4; HRMS (EI) Calcd. for $C_{19}H_{17}N_2O_2$ $[M–N_2–H]^+$ 305.1290; Found 305.1281.

2-Benzoyloxybenzoyl azide (precursor to 4a)

Yield: 70%. mp = 73-75ºC (dec.); R_F= 0.5 (CH_2Cl_2); ν_{max} (NaCl/ film)/cm^{-1} 2136, 1741, 1696, 1595, 1489, 1233, 1094, 911; ^{1}H NMR ($CDCl_3$) δ 7.27 (1H, d, *J*= 8.2), 7.37 (1H, td, *J*= 7.3, 0.8), 7.53 (2H, t, *J*= 7.7), 7.63-7.70 (2H, m), 8.07 (1H, dd, *J*= 7.9, 1.5), 8.24 (2H, dd, *J*= 7.4, 1.3); ^{13}C NMR ($CDCl_3$)

δ 124.1, 124.8, 126.6, 129.0, 129.7, 130.8, 132.2, 134.1, 135.6, 151.5, 165.6, 170.6; HRMS (EI) Calcd. for $C_{14}H_9N_3O_3$ $[M]^+$ 267.0644; Found 267.0653.

2-(4-Fluorobenzoyloxy)benzoyl azide (precursor to 4b)

Yield: 91%. mp = 87-88ºC (dec.); R_F= 0.5 (CH_2Cl_2); ν_{max} (NaCl/ film)/cm^{-1} 2137, 1743, 1697, 1600, 1506, 1262, 1233, 1063, 982; ^{1}H NMR ($CDCl_3$) δ 7.22 (2H, t, *J*= 8.7), 7.27 (1H, dd, *J*= 8.1, 0.9), 7.39 (1H, td, *J*= 7.7, 1.0), 7.69 (1H, td, *J*= 7.8, 1.7), 8.08 (1H, dd, *J*= 8.0, 1.5), 8.24-8.29 (2H, dd, *J*= 8.9, 5.4); ^{13}C NMR ($CDCl_3$) δ 115.9 (d, *J*= 22.2), 123.6, 124.3, 125.6, 126.4, 131.8, 133.0 (d, *J*= 9.3), 135.3, 151.0, 164.6, 166.1 (d, *J*= 276.2), 170.3; HRMS (EI) Calcd. for $C_{14}H_8FN_3O_3$ $[M]^+$ 285.0550; Found 285.0542.

2-(4-Methoxybenzoyloxy)benzoyl azide (precursor to 4c)

Yield: 78%. mp = 64-66ºC (dec.); R_F= 0.4 (1: 1 Et_2O: Petrol); ν_{max} (NaCl/ film)/cm^{-1} 2136, 1733, 1605, 1511, 1256, 1167, 1093, 911; ^{1}H NMR ($CDCl_3$) δ 3.91 (3H, s), 7.02 (2H, d, *J*= 8.7), 7.27 (1H, d, *J*= 8.2), 7.37 (1H, td, *J*= 7.7, 0.8), 7.67 (1H, td, *J*= 7.8, 1.5), 8.06 (1H, dd, *J*= 7.9, 1.5), 8.20 (2H, d, *J*= 9.0); ^{13}C NMR ($CDCl_3$) δ 54.5, 113.0, 120.6, 122.8, 123.5, 125.0, 130.7, 131.5, 134.1, 150.2, 163.0, 163.9, 169.3; HRMS (EI) Calcd. for $C_{15}H_{11}N_3O_4$ $[M]^+$ 297.0750; Found 297.0758.

2-(2'-Furoyloxy)benzoyl azide (precursor to 4d)

Yield: 82%. R_F= 0.4 (CH_2Cl_2); ν_{max} (NaCl/ film)/cm^{-1} 2137, 1745, 1695, 1593, 1488, 1292, 1235, 1091, 912; ^{1}H NMR ($CDCl_3$) δ 6.63 (1H, dd, *J*= 3.5, 1.8), 7.27 (1H, d, *J*= 7.9), 7.38 (1H, td, *J*= 7.7, 0.8), 7.45 (1H, d, *J*= 3.6), 7.64-7.72 (2H, m), 8.06 (1H, dd, *J*= 7.9, 1.5); ^{13}C NMR ($CDCl_3$) δ 112.8, 120.4, 124.1, 124.8, 126.9, 132.2, 135.7, 144.2, 147.8, 150.5, 157.1, 170.6; HRMS (EI) Calcd. for $C_{12}H_7N_3O_4$ $[M]^+$ 257.0437; Found 257.0436.

2-Acetoxybenzoyl azide (precursor to 4e)

Yield: 69%. R_F= 0.5 (CH_2Cl_2); ν_{max} (NaCl/ film)/cm^{-1} 2137, 1767, 1695, 1594, 1237, 1094, 912; ^{1}H NMR ($CDCl_3$) δ 2.39 (3H, s), 7.14 (1H, dd, *J*= 7.9, 0.8), 7.33 (1H, td, *J*= 7.7, 0.9), 7.63 (1H, td, *J*=7.7, 1.6), 7.98 (1H, dd, *J*= 7.9, 1.5); ^{13}C NMR ($CDCl_3$) δ 21.5, 123.7, 124.6, 126.6, 132.1, 135.7, 151.3, 170.1, 170.7; HRMS (EI) Calcd. for $C_9H_7N_3O_3$ $[M]^+$ 205.0487; Found 205.0481.

2-(Heptanoyloxy)benzoyl azide (precursor to 4f)

Yield: 82%. R_F= 0.5 (CH_2Cl_2); ν_{max} (NaCl/ film)/cm^{-1} 2131, 1763, 1695, 1604, 1489, 1234, 1095, 912; ^{1}H NMR ($CDCl_3$) δ 0.92 (3H, t, *J*= 6.8), 1.32-1.49 (6H, m), 1.79 (2H, quintet, *J*= 7.5), 2.66 (2H, t, *J*= 7.6), 7.12 (1H, d, *J*= 8.0), 7.32 (1H, t, *J*= 7.7), 7.62 (1H, td, *J*= 7.7, 1.3), 8.01 (1H, dd, *J*= 7.8, 1.4); ^{13}C NMR ($CDCl_3$) δ 13.0, 21.5, 23.4, 27.8, 30.5, 33.2, 123.2, 125.0, 125.4, 130.6, 134.2, 149.9, 169.3, 171.3; HRMS (EI) Calcd. for $C_{14}H_{17}N_3O_3$ $[M]^+$ 275.1270; Found 275.1259.

2-(2'-Methylpentanoyloxy)benzoyl azide (precursor to 4g)

Yield: 85%. R_F= 0.5 (CH_2Cl_2); ν_{max} (NaCl/ film)/cm^{-1} 2136, 1758, 1699, 1604, 1489, 1233, 1094, 912; ^{1}H NMR ($CDCl_3$) δ 0.99 (3H, t, *J*= 7.3), 1.35 (3H, d, *J*= 6.9), 1.39-1.63 (3H, m), 1.82-1.94 (1H, m), 2.80 (1H, sextet, *J*= 6.9), 7.10 (1H, dd, *J*= 8.2, 1.0), 7.32 (1H, td, *J*= 7.7, 1.0), 7.62 (1H, td, *J*= 7.7, 1.6), 8.00 (1H, dd, *J*= 7.8, 1.7); ^{13}C NMR ($CDCl_3$) δ 14.4, 17.0, 20.8, 35.9, 39.7, 124.6, 126.4, 126.8, 132.0, 135.4, 151.4, 170.6, 175.6; HRMS (EI) Calcd. for $C_{13}H_{15}N_3O_3$ $[M]^+$ 261.1113; Found 261.1107.

2-Benzoyloxy-3-methoxybenzoyl azide (precursor to 4h)

Yield: 87%. mp = 77-79ºC (dec.); R_F= 0.5 (CH_2Cl_2); ν_{max} (NaCl/ film)/cm^{-1} 2142, 1743, 1695, 1583, 1486, 1268, 1209, 1090, 894; ^{1}H NMR ($CDCl_3$) δ 3.85 (3H, s), 7.25 (1H, dd, *J*= 8.3, 1.7), 7.32 (1H, t, *J*= 7.9), 7.54 (2H, t, *J*= 7.5), 7.60-7.67 (2H, m), 8.26 (2H, dd, *J*= 7.2, 1.3); ^{13}C NMR ($CDCl_3$) δ 56.8, 118.0, 123.0, 125.2, 126.9, 129.0, 129.1, 130.9, 134.0, 140.9, 152.9, 165.0, 170.8; HRMS (EI) Calcd. for $C_{15}H_{11}NO_4$ $[M–N_2]^+$ 269.0688; Found 269.0689.

2-(4-Fluorobenzoyloxy)-3-methoxybenzoyl azide (precursor to 4i)

Yield: 88%. R_F= 0.5 (CH_2Cl_2); ν_{max} (NaCl/ film)/cm^{-1} 2142, 1743, 1698, 1603, 1477, 1271, 1209, 1090, 911, 758; ^{1}H NMR ($CDCl_3$) δ 3.85 (3H, s), 7.15-7.24 (3H, m, inc. 2H, t, *J*= 8.7), 7.32 (1H, t, *J*= 7.9), 7.61 (1H, dd, *J*= 7.7, 1.5), 8.25-8.29 (2H, dd, *J*= 8.8, 5.5); ^{13}C NMR ($CDCl_3$) δ 56.4, 115.8 (d, *J*= 21.9), 117.6, 122.6, 124.8, 125.6, 126.5, 133.1 (d, *J*= 10.5), 140.3, 152.5, 163.6, 166.2 (d, *J*= 255.3), 170.4; HRMS (EI) Calcd. for $C_{15}H_{10}FNO_4$ $[M–N_2]^+$ 287.0594; Found 287.0597.

2-(4-Methoxybenzoyloxy)-3-methoxybenzoyl azide (precursor to 4j)

Yield: 89%. R_F= 0.5 (CH_2Cl_2); ν_{max} (NaCl/ film)/cm^{-1} 2141, 1736, 1698, 1605, 1508, 1477, 1259, 1090, 893; ^{1}H NMR ($CDCl_3$) δ 3.84 (3H, s), 3.90 (3H, s), 7.02 (2H, d, *J*= 9.3). 7.24 (1H, dd, *J*= 8.2, 1.5), 7.31 (1H, t, *J*= 8.1), 7.60 (1H, dd, *J*= 7.8, 1.7), 8.21 (2H, d. *J*= 8.9); ^{13}C NMR ($CDCl_3$) δ 55.9, 56.8, 114.3, 118.0, 122.0, 123.0, 125.4, 126.7, 133.0, 141.1, 153.1, 164.4, 164.6, 170.8; HRMS (EI) Calcd. for $C_{16}H_{13}NO_5$ $[M–N_2]^+$ 299.0794; Found 299.0786.

2-Benzoyloxy-4-methoxybenzoyl azide (precursor to 4k)

Yield: 76%. mp = 85-88ºC (dec.); R_F= 0.6 (CH_2Cl_2); ν_{max} (NaCl/ film)/cm^{-1} 2137, 1740, 1690, 1611, 1490, 1263, 1094, 911; ^{1}H NMR ($CDCl_3$) δ 3.88 (3H, s), 6.77 (1H, d, *J*= 2.6), 6.87 (1H, dd, *J*= 9.0, 2.6), 7.54 (2H, t, *J*= 7.5), 7.66 (1H, tt, *J*= 7.4, 1.5), 8.03 (1H, d, *J*= 8.9), 8.24 (2H, dd, *J*= 7.1, 1.3); ^{13}C NMR ($CDCl_3$) δ 56.3, 110.2, 112.5, 116.3, 129.1, 129.7, 130.8, 134.0, 134.1, 153.6, 165.6, 169.8 (12 of 13 expected signals observed); HRMS (EI) Calcd. for $C_{15}H_{11}NO_4$ $[M–N_2]^+$ 269.0688; Found 269.0695.

2-(2'-Furoyloxy)-4-methoxybenzoyl azide (precursor to 4l)

Yield: 72%. R_F= 0.4 (CH_2Cl_2); ν_{max} (NaCl/ film)/cm^{-1} 2137, 1745, 1689, 1611, 1489, 1237, 1093, 911; ^{1}H NMR ($CDCl_3$) δ 3.89 (3H, s), 6.63 (1H, dd, *J*= 3.6, 1.8), 6.77 (1H, d, *J*= 2.6), 6.88 (1H, dd, *J*= 8.8, 2.4), 7.45 (1H, d, *J*= 3.3), 7.70 (1H, d, *J*= 1.5), 8.02 (1H, d, *J*= 9.0); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 55.9, 109.8, 112.3, 112.3, 115.9, 120.0, 133.5, 143.9, 147.3, 152.2, 156.6, 165.2, 169.4; HRMS (EI) Calcd. for $C_{13}H_9N_3O_5$ $[M]^+$ 287.0542; Found 287. 0553.

2-Benzoyloxy-5-fluorobenzoyl azide (precursor to 4m)

Yield: 69%. R_F= 0.5 (CH_2Cl_2); ν_{max} (NaCl/ film)/cm^{-1} 2147, 1743, 1698, 1593, 1267, 1212, 1093, 911; ^{1}H NMR ($CDCl_3$) δ 7.24 (1H, dd, *J*= 8.7, 4.6), 7.37 (1H, ddd, *J*= 8.8, 7.3, 3.2), 7.53 (2H, t, *J*= 7.7), 7.67 (1H, t, *J*= 7.4), 7.76 (1H, dd, *J*= 8.7, 3.1), 8.22 (2H, dd, *J*= 7.4, 1.3); ^{13}C NMR ($CDCl_3$) δ 118.2 (d, *J*= 25.3), 122.0 (d, *J*= 24.1), 124.9, 126.0 (d, *J*= 8.0), 128.7, 129.0, 130.4, 133.9, 143.1, 159.7 (d, *J*= 247.2), 165.2, 169.3; HRMS (EI) Calcd. for $C_{14}H_8FN_3O_3$ $[M]^+$ 285.0550; Found 285.0539.

2-(4-Fluorobenzoyloxy)-5-fluorobenzoyl azide (precursor to 4n)

Yield: 76%. mp = 86-88ºC (dec.); ν_{max} (NaCl/ film)/cm^{-1} 2147, 1744, 1698, 1604, 1508, 1268, 1212, 1058, 754; ^{1}H NMR ($CDCl_3$) δ 7.19-7.25 (3H, m, inc. 2H, t, *J*= 8.7), 7.38 (1H, ddd, *J*= 8.9, 7.2, 3.0), 7.77 (1H, dd, *J*= 8.4, 3.1), 8.22-8.28 (2H, dd, *J*= 8.8, 5.5); ^{13}C NMR ($CDCl_3$) δ 116.0 (d, *J*= 22.1), 118.3 (d, *J*= 25.5), 122.1 (d, *J*= 23.2), 124.9, 125.4, 125.9 (d, *J*= 8.0), 133.1 (d, *J*= 9.5), 146.9, 159.7 (d, *J*= 247.8), 164.3, 166.3 (d, *J*= 255.4), 169.3; HRMS (EI) Calcd. for $C_{14}H_7F_2N_3O_3$ $[M]^+$ 303.0455; Found 303.0456.

General procedure for catalytic aza-Wittig cyclisation:

6-Methoxyphenanthridine 2a

A solution of 2'-azidocarbonylbiphenyl-2-carboxylic acid methyl ester (344 mg, 1.2 mmol) in anhydrous PhMe (5 ml) was heated to reflux in order to form the isocyanate. The reaction was followed by disappearance of azide (2133 cm^{-1}) and formation of isocyanate (2269 cm^{-1}). After 1h, the solution of isocyanate was allowed to cool to room temperature, then diluted with PhMe (7 ml) and added *via* cannula to a clean, dry flask containing 3-methyl-1-phenyl phospholene-1-oxide (11.8 mg, 0.06 mmol). The resulting mixture was stirred at reflux under nitrogen and monitored by IR to follow disappearance of isocyanate. After 22h the reaction mixture was cooled and concentrated and purified by flash column chromatography, eluting with 1: 4 EtOAc: Petrol to afford the title compound (206 mg, 80 %) as a colourless solid; mp (Petrol/ EtOAc; colourless needles)= 55-56ºC (Lit.[1] 54.5ºC); R_F= 0.4 (1: 4 EtOAc: Petrol); ν_{max} (NaCl/ film)/cm^{-1} 3065, 2947, 2939, 1621, 1589, 1473, 1355, 1323, 1226, 1107, 727; ^{1}H NMR ($CDCl_3$) δ 4.25 (3H, s), 7.50 (1H, ddd, *J*= 8.2, 7.2, 1.2), 7.62-7.68 (2H, m), 7.82 (1H, ddd, *J*= 8.2, 7.2, 1.3), 7.92 (1H, dd, *J*= 8.1, 0.9), 8.37 (1H, dd, *J*= 8.2, 0.8), 8.44 (1H, dd, *J*= 8.2, 1.3), 8.52 (1H, d, *J*= 8.5); ^{13}C NMR ($CDCl_3$) δ 54.0, 120.5, 122.3, 122.5, 122.9, 124.8, 125.4, 127.6, 128.2, 129.2, 131.2, 135.2, 143.7, 159.6; m/z (ES) 209.9 $[M+H]^+$ 100%; Anal. Calcd. for $C_{14}H_{11}NO$: C, 80.36; H, 5.30; N, 6.69; Found C, 80.20; H, 5.20; N, 6.50%.

6-Ethoxyphenanthridine 2b

Yield: 82%. mp (Petrol/ EtOAc; colourless needles) = 56-58ºC (Lit.[2] 54.5-55.5ºC); R_F= 0.5 (1: 4 EtOAc: Petrol); ν_{max} (NaCl/ film)/cm^{-1} 3065, 2978, 2923, 1615, 1590, 1489, 1371, 1318, 1226, 1086, 888, 724; ^{1}H NMR ($CDCl_3$) δ 1.57 (3H, t, *J*= 7.0), 4.72 (2H, q, *J*= 7.1), 7.49 (1H, td, *J*= 8.2, 7.2, 1.3), 7.61-7.68 (2H, m), 7.82 (1H, ddd, *J*= 8.2, 7.1, 1.3), 7.89 (1H, dd, *J*= 8.0, 0.9), 8.42 (2H, td, *J*=8.2, 0.9), 8.51 (1H, d, *J*= 8.2); ^{13}C NMR ($CDCl_3$) δ 15.1, 62.4, 120.6, 122.2, 122.5, 122.8, 124.7, 125.5, 127.8, 128.2, 129.1, 131.2, 135.2, 143.9, 159.3; m/z (ES) 224.1 $[M+H]^+$ 100%; Anal. Calcd. for $C_{15}H_{13}NO$: C, 80.69; H, 5.87; N, 6.27; Found C, 80.45; H, 5.86; N, 6.15%.

6-Isopropoxyphenanthridine 2c

Yield: 72%. mp (Et_2O; colourless needles)= 73-74ºC; R_F= 0.6 (CH_2Cl_2); ν_{max} (NaCl/ film)/cm^{-1} 3065, 2977, 2923, 1618, 1589, 1376, 1313, 1109, 925, 726; ^1H NMR ($CDCl_3$) δ 1.52 (6H, d, *J*= 6.1), 5.79 (1H, septet, *J*= 6.2), 7.48 (1H, ddd, *J*= 8.2, 6.9, 1.0), 7.60-7.67 (2H, m), 7.81 (1H, ddd, *J*= 8.2, 7.2, 1.0), 7.88 (1H, d, *J*= 8.2), 8.42 (2H, t, *J*= 8.7), 8.51 (1H, d, *J*= 8.2); ^{13}C NMR ($CDCl_3$) δ 22.6, 68.7, 121.0, 122.2, 122.5, 122.7, 124.5, 125.6, 127.5, 128.2, 129.1, 131.1, 135.2, 144.0, 158.7; HRMS (ES) Calcd. for $C_{16}H_{16}NO$ $[M+H]^+$ 238.1226; Found 238.1236; Anal. Calcd. for $C_{16}H_{15}NO$: C, 80.98; H, 6.37; N, 5.90; Found C, 81.05; H, 6.35; N, 6.20%.

6-Diethylaminophenanthridine 2d

Yield: 30%. R_F= 0.4 (1: 4 EtOAc: Petrol); ν_{max} (NaCl/ film)/cm^{-1} 3065, 2967, 2928, 1610, 1581, 1459, 1349, 1286, 1229, 1070, 728; ^1H NMR ($CDCl_3$) δ 1.27 (6H, t, *J*= 7.0), 3.53 (4H, q, *J*= 7.0), 7.47 (1H, ddd, *J*= 8.2, 6.9, 1.0), 7.59-7.65 (2H, m), 7.76 (1H, ddd, *J*= 8.2, 6.9, 1.3), 7.91 (1H, d, *J*= 8.2), 8.23 (1H, d, *J*= 8.2), 8.43 (1H, d, *J*= 8.2), 8.56 (1H, d, *J*= 8.5); ^{13}C NMR ($CDCl_3$) δ 13.7, 46.2, 122.2, 122.7, 123.0, 123.2, 124.6, 126.9, 127.1, 128.8, 129.0, 130.2, 135.4, 144.4, 160.1; m/z (ES) 251.1 $[M+H]^+$ 100%. Data agrees with literature values.[3]

6-Piperidinylphenanthridine 2e

Yield: 52%. mp (MeOH)= 86-87ºC (Lit.[3] 86ºC); R_F= 0.5 (1: 4 EtOAc: Petrol); ν_{max} (NaCl/ film)/cm^{-1} 3060, 2928, 2840, 1604, 1558, 1459, 1368, 1223, 1009, 858, 757; ^1H NMR (300 MHz, $CDCl_3$) δ 1.70-1.78 (2H, m), 1.85-1.92 (4H, m), 3.44-3.48 (4H, m), 7.48 (1H, ddd, *J*= 8.2, 7.2, 1.1), 7.59-7.66 (2H, m), 7.77 (1H, ddd, *J*= 8.2, 7.2, 1.3), 7.93 (1H, dd, *J*= 8.2, 0.8), 8.21 (1H, dd, *J*= 8.2, 0.8), 8.43

(1H, dd, *J*= 8.2, 1.0), 8.55 (1H, d, *J*= 8.2); ^{13}C NMR ($CDCl_3$) δ 25.4, 26.6, 52.9, 122.2, 122.3, 122.9, 123.0, 124.8, 127.0, 127.2, 128.8, 129.0, 130.4, 135.3, 144.4, 161.6; m/z (ES) 263.2 $[M+H]^+$ 100%. Data agrees with literature values.[3]

2-Phenylbenzoxazole 5a

Yield: 87%. mp (hexane; colourless needles)= 102-103ºC (Lit.[4] 101-102ºC); R_F= 0.3 (1: 4 EtOAc: Petrol); ν_{max} (NaCl/ film)/cm^{-1} 3063, 1617, 1554, 1455, 1243, 1053, 925; ^{1}H NMR ($CDCl_3$) δ 7.34-7.40 (2H, m), 7.51-7.57 (3H, m), 7.57-7.64 (1H, m), 7.77-7.83 (1H, m), 8.26-8.29 (2H, m); ^{13}C NMR ($CDCl_3$) δ 110.6, 120.0, 124.6, 125.1, 127.2, 127.6, 128.9, 131.5, 142.1, 150.8, 163.0; m/z (ES+) 195.8 $[M+H]^+$ 100%. Data agrees with literature values.[4]

2-(4'-Fluorophenyl)benzoxazole 5b

Yield: 70%. mp (Petrol/Et_2O; colourless cubes)= 100-101ºC (Lit.[5] 97-98ºC); R_F= 0.4 (1: 4 EtOAc: Petrol); ν_{max} (NaCl/ film)/cm^{-1} 3065, 1615, 1596, 1451, 1410, 1289, 1146, 845; ^{1}H NMR ($CDCl_3$) δ 7.19-7.27 (2H, t, *J*= 8.7), 7.34-7.40 (2H, m), 7.56-7.62 (1H, m), 7.75-7.80 (1H, m), 8.27 (2H, dd, *J*= 8.9, 5.4); ^{13}C NMR ($CDCl_3$) δ 110.6, 116.2 (d, *J*= 22.4), 120.0, 123.5, 124.7, 125.2, 129.8 (d, *J*= 9.0), 142.1, 150.8, 162.2, 164.8 (d, *J*= 252.6); m/z (ES+) 213.9 $[M+H]^+$ 100%; Anal. Calcd. For $C_{13}H_8FNO$: C, 73.23; H, 3.78; F, 8.91; N, 6.57; Found C, 73.05; H, 3.90; F, 8.65; N, 6.40%.

2-(4'-Methoxyphenyl)benzoxazole 5c

Yield: 62%. mpt (aq. EtOH; colourless needles)= 97-99ºC (Lit.[6] 98ºC) R_F= 0.5 (1: 1 EtOAc: Petrol); ν_{max} (NaCl/ film)/cm^{-1} 2978, 2950, 2846, 1615, 1604, 1454, 1243, 1169, 828; ^{1}H NMR ($CDCl_3$) δ 3.90 (3H, s), 7.04 (2H, d, *J*= 9.5), 7.32-7.35 (2H, m), 7.53-7.58 (1H, m), 7.72-7.76 (1H, m), 8.21 (2H, d, *J*= 9.5); ^{13}C NMR ($CDCl_3$) δ 55.4, 110.4, 114.3, 119.6, 119.7, 124.4, 124.6, 129.4, 142.3, 150.7, 162.3, 163.2; m/z (ES+) 226.0 $[M+H]^+$ 100%. Data agrees with literature values.[6]

2-(2'-Furyl)benzoxazole 5d

Yield: 77%. mp (aq. EtOH; colourless needles)= 83-85ºC (Lit.[7] 83-85ºC); R_F= 0.4 (CH_2Cl_2); ν_{max} (NaCl/ film)/cm^{-1} 3142, 3115, 2961, 1648, 1635, 1591, 1536, 1525, 1448, 1240, 1155, 1080, 932, 740; ^{1}H NMR ($CDCl_3$) δ 6.62 (1H, dd, *J*= 3.5, 1.7), 7.28 (1H, d, *J*= 3.3), 7.33-7.39 (2H, m), 7.53-7.58 (1H, m), 7.67 (1H, d, *J*= 1.8), 7.73-7.79 (1H, m); ^{13}C NMR ($CDCl_3$) δ 109.5, 111.2, 113.2, 119.1, 123.8, 124.3, 140.6, 141.6, 144.7, 149.1, 154.2; HRMS (ES) Calcd. for $C_{11}H_8NO_2$ $[M+H]^+$ 186.0550; Found 186.0553. Data agrees with literature values.[8]

2-Methylbenzoxazole 5e

Yield: 82%. R_F= 0.3 (1: 1 Et_2O: Petrol); ν_{max} (NaCl/ film)/cm^{-1} 3054, 2928, 2857, 1617, 1577, 1456, 1242, 1167, 744; ^{1}H NMR ($CDCl_3$) δ 2.65 (3H, s), 7.19-7.34 (2H, m), 7.43-7.49 (1H, m), 7.64-7.69 (1H, m); ^{13}C NMR ($CDCl_3$) δ 14.9, 110.6, 119.8, 124.5, 124.8, 141.9, 151.4, 164.2; m/z (ES+) 134.0 $[M+H]^+$ 100%. Data agrees with literature values.[9]

2-Hexylbenzoxazole 5f

Yield: 69%. R_F= 0.3 (1: 1 CH_2Cl_2: Petrol); ν_{max} (NaCl/ film)/cm^{-1} 2956, 2930, 2858, 1615, 1572, 1455, 1242, 745; ^{1}H NMR ($CDCl_3$) δ 0.90 (3H, t, *J*= 6.9), 1.18-1.46 (6H, m), 1.89 (2H, quintet, *J*= 7.6), 2.94 (2H, t, *J*= 7.5), 7.29-7.33 (2H, m), 7.46-7.51 (1H, m), 7.65-7.71 (1H, m); ^{13}C NMR ($CDCl_3$) δ 14.0, 22.5, 26.8, 28.7, 28.9, 31.4, 110.3, 119.5, 124.0, 124.4, 141.4, 150.8, 167.4; m/z (ES+) 203.9 $[M+H]^+$ 100%. Data agrees with literature values.[9]

2-(2'-Methylbutyl)benzoxazole 5g

Yield: 65%. R_F= 0.3 (1: 1 CH_2Cl_2: Petrol); ν_{max} (NaCl/ film)/cm^{-1} 2961, 2928, 2868, 1610, 1566, 1454, 1240, 1130, 930, 749; ^{1}H NMR ($CDCl_3$) δ 0.93 (3H, t, *J*= 7.4), 1.26-1.47 (2H, m), 1.44 (3H, d, *J*=

7.2), 1.63-1.75 (1H, m) 1.83-1.93 (1H, m), 3.15 (1H, sextet, *J*= 7.0), 7.27-7.31 (2H, m), 7.46-7.52 (1H, m), 7.66-7.72 (1H, m); ^{13}C NMR ($CDCl_3$) δ 13.9, 18.4, 20.4, 34.0, 37.2, 110.3, 119.6, 124.0, 124.4, 141.2, 150.6, 170.9; m/z (ES+) 189.9 $[M+H]^+$ 100%; HRMS (ES) Calcd. for $C_{12}H_{16}NO$ $[M+H]^+$ 190.1226; Found 190.1223.

7-Methoxy-2-phenylbenzoxazole 5h

Yield: 70%. mp (Petrol/Et_2O; colourless plates)= 80-82ºC; R_F= 0.6 (1: 1 EtOAc: Petrol); ν_{max} (NaCl/ film)/cm^{-1} 3060, 2961, 2840, 1629, 1552, 1454, 1289, 1105, 968, 773; ^{1}H NMR ($CDCl_3$) δ 4.08 (3H, s), 6.89 (1H, d, *J*= 8.0), 7.29 (1H, t, *J*= 8.1), 7.40 (1H, dd, *J*= 8.0, 0.5), 7.51-7.55 (3H, m), 8.26-8.32 (2H, m); ^{13}C NMR ($CDCl_3$) δ 56.4, 107.9, 112.4, 125.1, 127.0, 127.7, 128.9, 131.5, 139.9, 143.8, 144.9, 162.9; HRMS (ES) Calcd. for $C_{14}H_{12}NO_2$ $[M+H]^+$ 226.0863; Found 226.0858.

2-(4'-Fluorophenyl)-7-methoxybenzoxazole 5i

Yield: 62%. mp (aq. EtOH; colourless needles)= 90-92ºC; R_F= 0.4 (CH_2Cl_2); ν_{max} (NaCl/ film)/cm^{-1} 3065, 2864, 1624, 1593, 1434, 1294, 1106, 973, 727; ^{1}H NMR ($CDCl_3$) δ 4.07 (3H, s), 6.89 (1H, d, *J*= 7.9), 7.19-7.32 (3H, m), 7.38 (1H, d, *J*= 7.4), 8.27-8.30 (2H, m); ^{13}C NMR ($CDCl_3$) δ 56.4, 107.9, 112.4, 116.2 (d, *J*= 22.1), 123.4, 125.2, 129.9 (d, *J*= 9.0), 139.9, 143.8, 144.9, 162.1, 164.1 (d, *J*= 252.6); m/z (ES+) 244.0 $[M+H]^+$ 100%; Anal. Calcd. For $C_{14}H_{10}FNO_2$: C, 69.13; H, 4.14; F, 7.81; N, 5.76; Found C, 68.85; H 4.10; F, 7.80; N, 5.65%.

7-Methoxy-2-(4'-methoxyphenyl)benzoxazole 5j

Yield: 59%. mp (EtOH; colourless needles)= 102-104ºC; R_F= 0.5 (1: 1 EtOAc: Petrol); ν_{max} (NaCl/ film)/cm^{-1} 3038, 2967, 2835, 1613, 1602, 1580, 1465, 1297, 1106, 973, 773; ^{1}H NMR ($CDCl_3$) δ 3.88 (3H, s), 4.06 (3H, s), 6.85 (1H, d, *J*= 7.9), 7.02 (2H, d, *J*= 9.5), 7.25 (1H, t, *J*= 8.0), 7.35 (1H, dd, *J*= 8.2, 0.8), 8.22 (2H, d, *J*= 9.4); ^{13}C NMR ($CDCl_3$) δ 55.9, 56.8, 107.9, 112.5, 114.7, 119.9, 125.3, 129.9, 140.1, 144.4, 145.2, 162.7, 163.5; HRMS (ES) Calcd. for $C_{15}H_{14}NO_3$ $[M+H]^+$ 256.0968; Found 256.0973; Anal. Calcd. for $C_{15}H_{13}NO_3$: C, 70.58; H, 5.13; N, 5.49; Found C, 70.30; H, 5.10; N, 5.45%.

6-Methoxy-2-phenylbenzoxazole 5k

Yield: 62%. mp (aq. EtOH; colourless cubes) = 75-76ºC (Lit.[10] 81-82ºC); R_F= 0.3 (1: 4 EtOAc: Petrol); ν_{max} (NaCl/ film)/cm^{-1} 3065, 2956, 2829, 1618, 1552, 1478, 1448, 1270, 1144, 1020, 919, 698; ^{1}H NMR ($CDCl_3$) δ 3.88 (3H, s), 6.97 (1H, dd, *J*= 8.7, 2.3), 7.12 (1H, d, *J*= 2.6), 7.50-7.60 (3H, m), 7.65 (1H, d, *J*= 8.7), 8.18-8.23 (2H, m); ^{13}C NMR ($CDCl_3$) δ 56.4, 95.8, 113.2, 120.4, 127.6, 127.8, 129.3, 131.5, 136.3, 152.1, 158.7, 162.7; HRMS (ES) Calcd. for $C_{14}H_{12}NO_2$ $[M+H]^+$ 226.0863; Found 226.0865.

2-Furyl-6-methoxybenzoxazole 5l

Yield: 38%. mp (aq. EtOH; colourless needles)= 93-95ºC; R_F= 0.2 (CH_2Cl_2); ν_{max} (NaCl/ film)/cm^{-1} 3104, 2961, 2835, 1640, 1621, 1451, 1270, 1135, 946, 795; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.86 (3H, s), 6.59 (1H, dd, *J*= 3.3, 1.8), 6.95 (1H, dd, *J*= 8.7, 2.3), 7.08 (1H, d, *J*= 2.3), 7.10 (1H, d, *J*= 3.3), 7.60-7.64 (2H, m); ^{13}C NMR ($CDCl_3$) δ 56.4, 95.8, 112.6, 113.4, 113.7, 120.5, 135.7, 143.1, 145.7, 151.5, 155.0, 158.8; HRMS (ES) Calcd. for $C_{12}H_{10}NO_3$ $[M+H]^+$ 216.0655; Found 216.0648.

5-Fluoro-2-phenylbenzoxazole 5m

Yield: 51%. mp (aq. EtOH; colourless cubes)= 109-111ºC (Lit.[6] 114ºC); R_F= 0.4 (CH_2Cl_2); ν_{max} (NaCl/ film)/cm^{-1} 3065, 1621, 1583, 1451, 1273, 1053, 924, 770; ^{1}H NMR ($CDCl_3$) δ 7.11 (1H, td, *J*= 9.1, 2.6), 7.46 (1H, dd, *J*= 8.3, 2.4), 7.49-7.57 (4H, m), 8.23-8.26 (2H, m); ^{13}C NMR ($CDCl_3$) δ 107.2 (d, *J*= 25.5), 111.6 (d, *J*= 10.2), 113.5 (d, *J*= 26.2), 127.6, 128.5, 129.8, 132.6, 143.7 (d, *J*= 12.9), 147.9, 160.9 (d, *J*= 240.6), 165.6; HRMS (ES) Calcd. for $C_{13}H_9FNO$ $[M+H]^+$ 214.0663; Found 214.0654. Data agrees with literature values.[6]

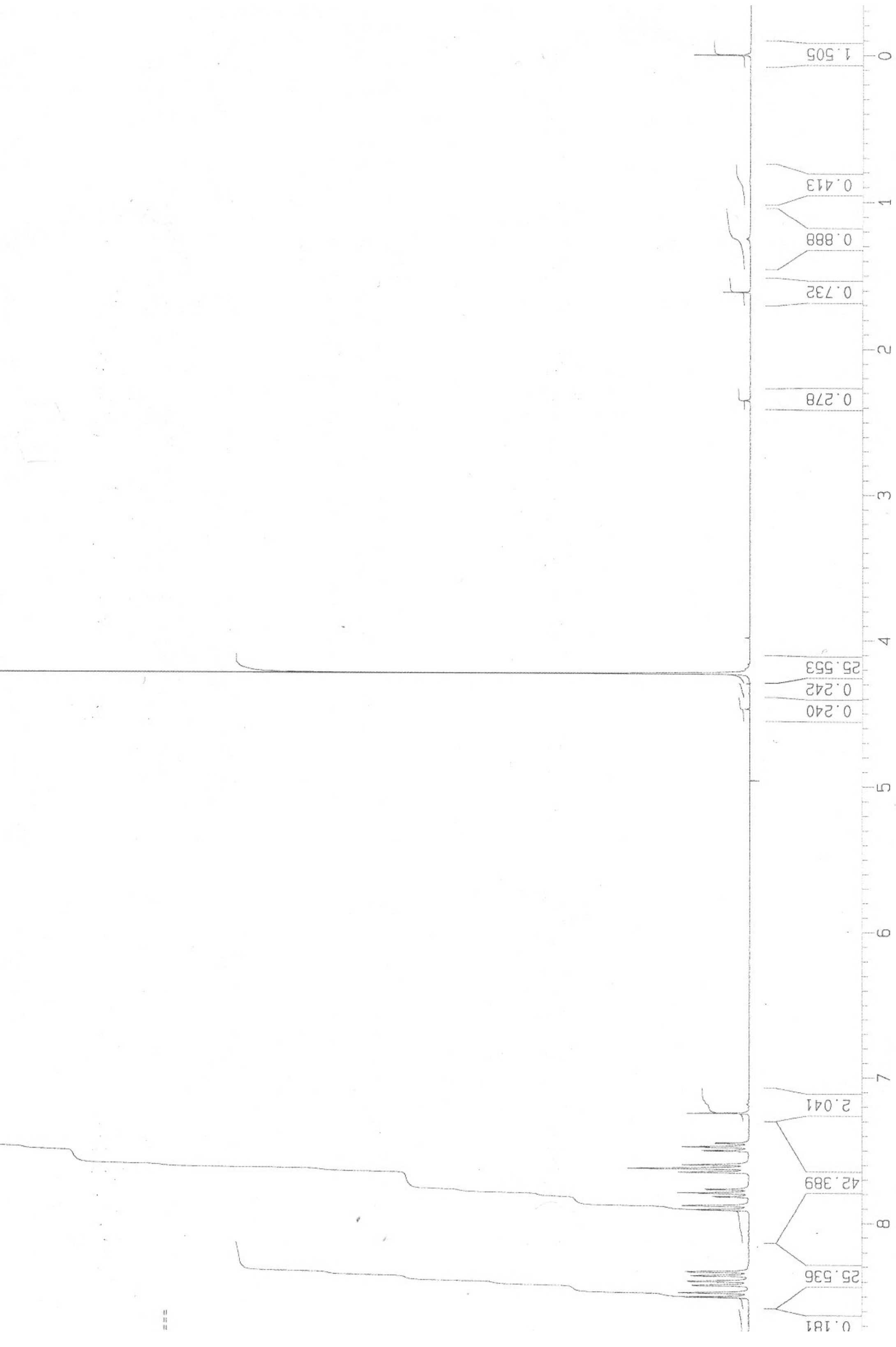
5-Fluoro-2-(4'-fluorophenyl)benzoxazole 5n

Yield: 48%. mp (EtOH; fine colourless needles)= 121-123ºC; R_F= 0.4 (1: 1 CH_2Cl_2: Petrol); ν_{max} (NaCl/ film)/cm^{-1} 3065, 1599, 1552, 1470, 1267, 1133, 838, 732; ^1H NMR ($CDCl_3$) δ 7.09 (1H, td, *J*= 9.1, 2.6), 7.23 (2H, t, *J*= 8.6), 7.44 (1H, dd, *J*= 8.3, 2.4), 7.51 (1H, dd, *J*= 9.0, 4.4), 8.23-8.29 (2H, m); ^{13}C NMR ($CDCl_3$) δ 106.4 (d, *J*= 25.6), 110.8 (d, *J*= 10.1), 112.7 (d, *J*= 26.4), 116.3 (d, *J*= 22.3), 123.2 (d, *J*= 3.2), 129.9 (d, *J*= 8.9), 142.9 (d, *J*= 13.2), 147.1, 160.2 (d, *J*= 240.7), 163.9, 165.0 (d, *J*= 253.3); HRMS (ES) Calcd. for $C_{13}H_8F_2NO$ $[M+H]^+$ 232.0568; Found 232.0560.

References

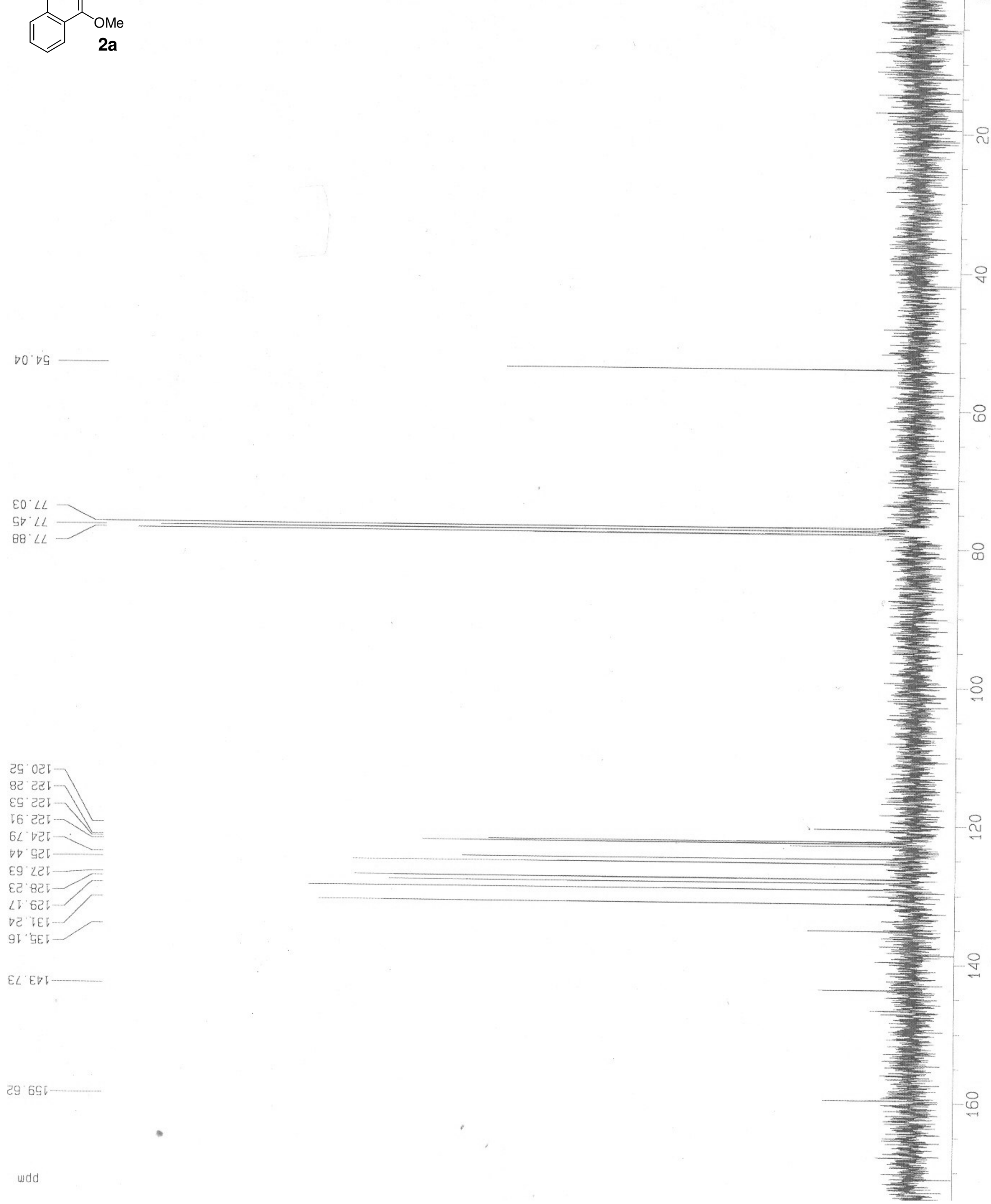
[1] C. L. Arcus, M. M. Coombs, J. V. Evans, *J. Chem. Soc., Trans.* **1956**, 1498.
[2] S. Harusawa, Y. Hamada, T. Shioiri, *Heterocycles* **1981,** *15*, 981.
[3] M. Lysen, J. L. Kristensen, P. Vedso, M. Begtrup, *Org. Lett.* **2002,** *4*, 257.
[4] N. A. Al-Awadi, B. J. George, H. H. Dib, M. R. Ibrahim, Y. A. Ibrahim, O. M. E. El-Dusouqui, *Tetrahedron* **2005,** *61*, 8257.
[5] I. Y. Postovskii, S. A. Mazalov, L. N. Pushkina, *J. Gen. Chem. USSR* **1962,** *32*, 2578.
[6] G. Evindar, R. A. Batey, *J. Org. Chem.* **2006,** *71*, 1802.
[7] L. C. Raiford, W. G. Huey, *J. Org. Chem.* **1941,** *6*, 858.
[8] C. S. Cho, D. T. Kim, J. Q. Zhang, S. L. Ho, T. J. Kim, S. C. Shim, *J. Heterocycl. Chem.* **2002,** *39*, 421.
[9] T. Shimada, Y. Yamamoto, *J. Am. Chem. Soc.* **2003,** *125*, 6646.
[10] H. Sato, T. Dan, E. Onuma, H. Tanaka, B. Aoki, H. Koga, *Chem. Pharm. Bull.* **1991,** *39*, 1760.

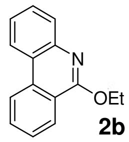
2a




N
OMe

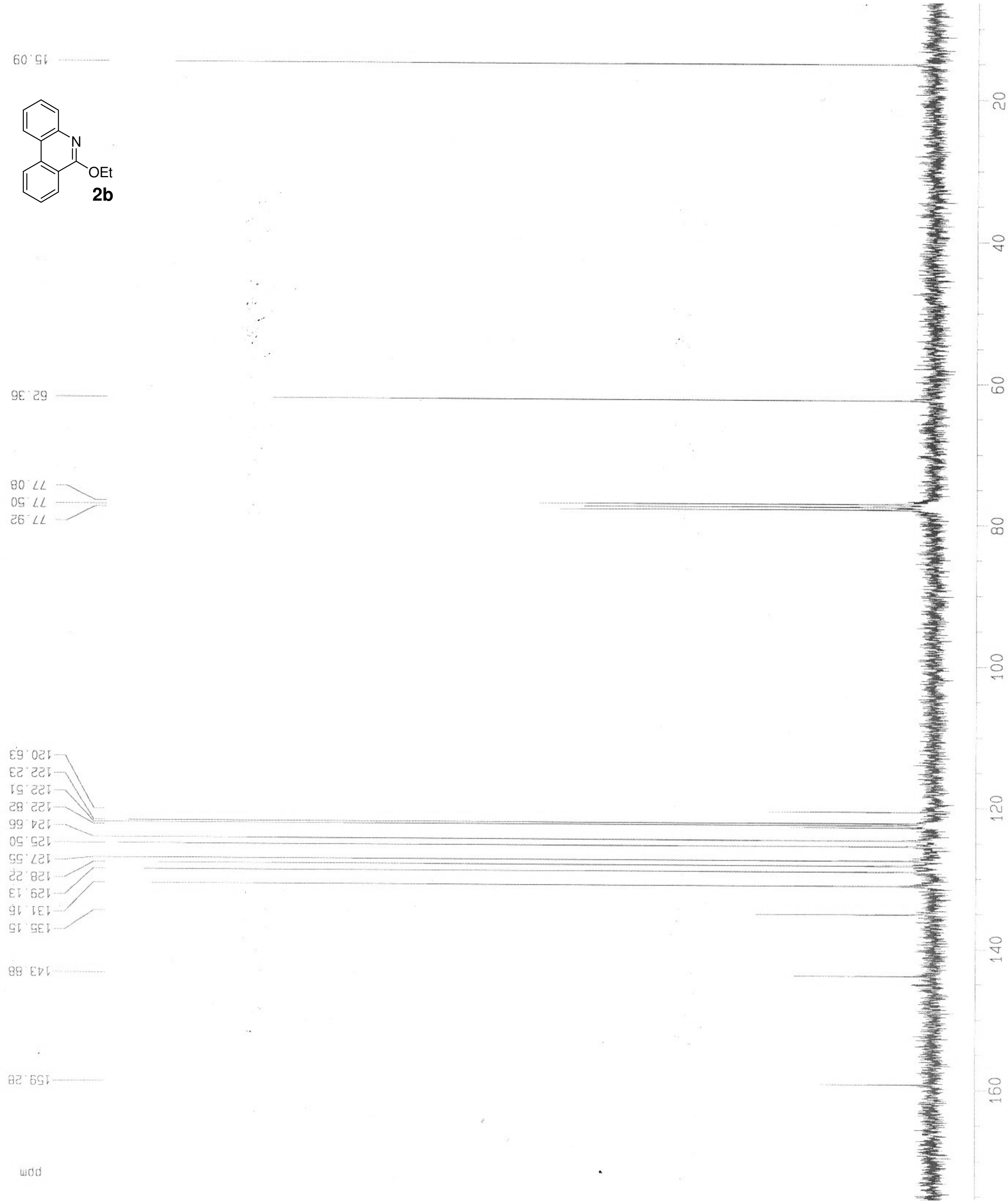
2a

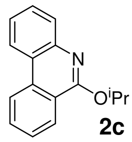

54.04
77.03
77.45
77.88
120.52
122.28
122.53
122.91
124.79
125.44
127.63
128.23
129.17
131.24
135.16
143.73
159.62
ppm
0
20
40
60
80
100
120
140
160


N
OEt

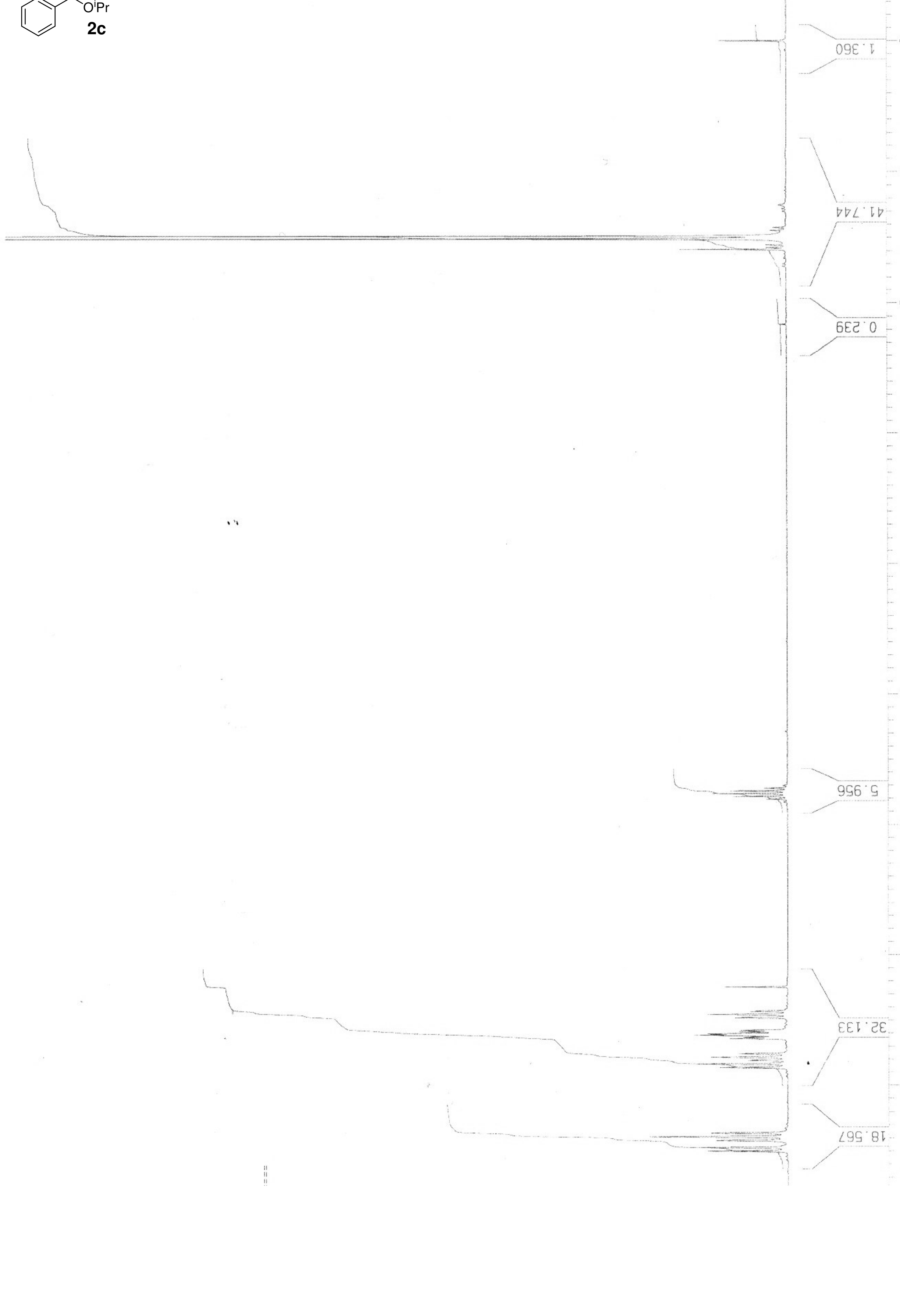
2b

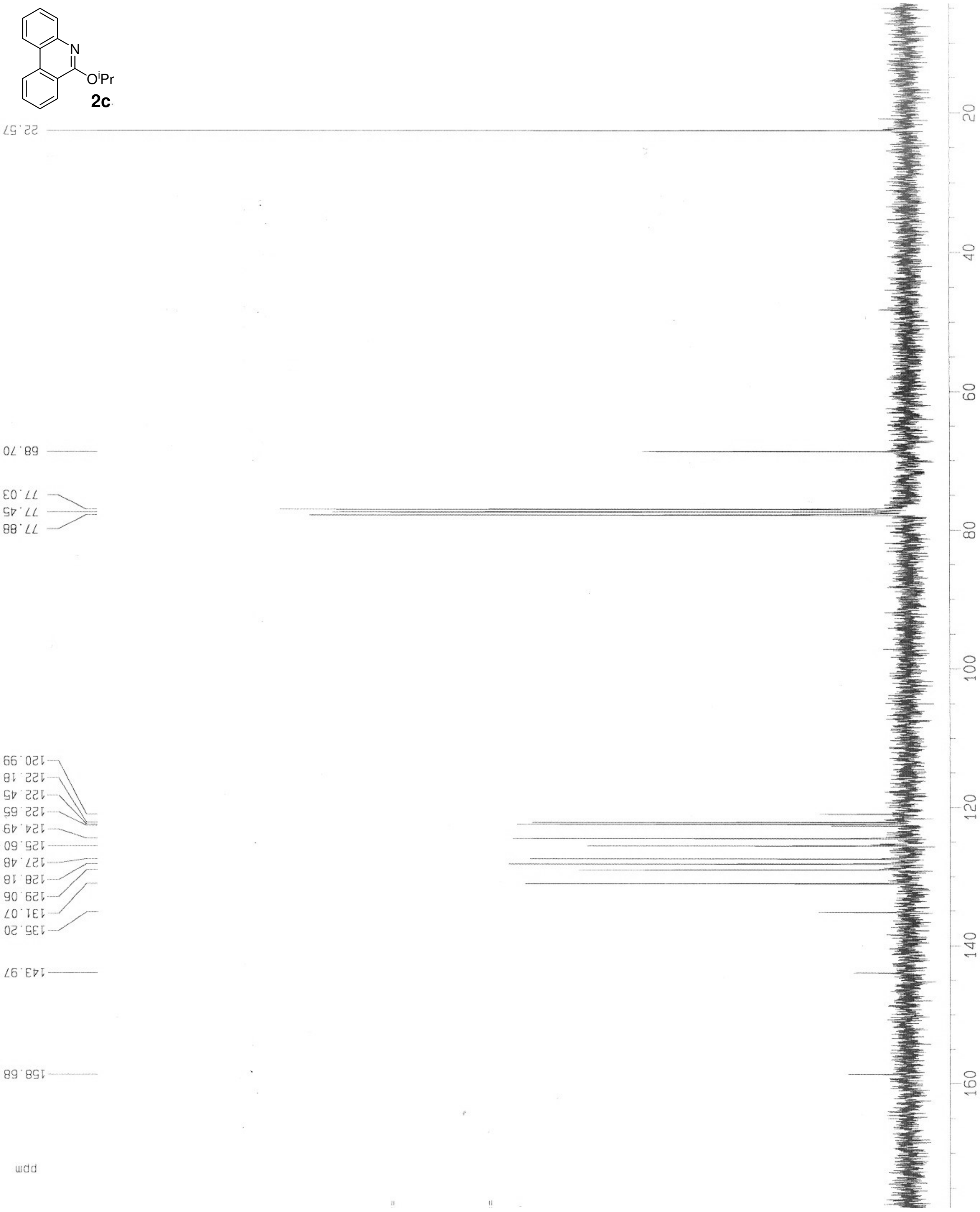

1.956
0.325
0.593
1.039
22.840
0.190
14.253
37.325
0.252
21.227
0
1
2
3
4
5
6
7
8

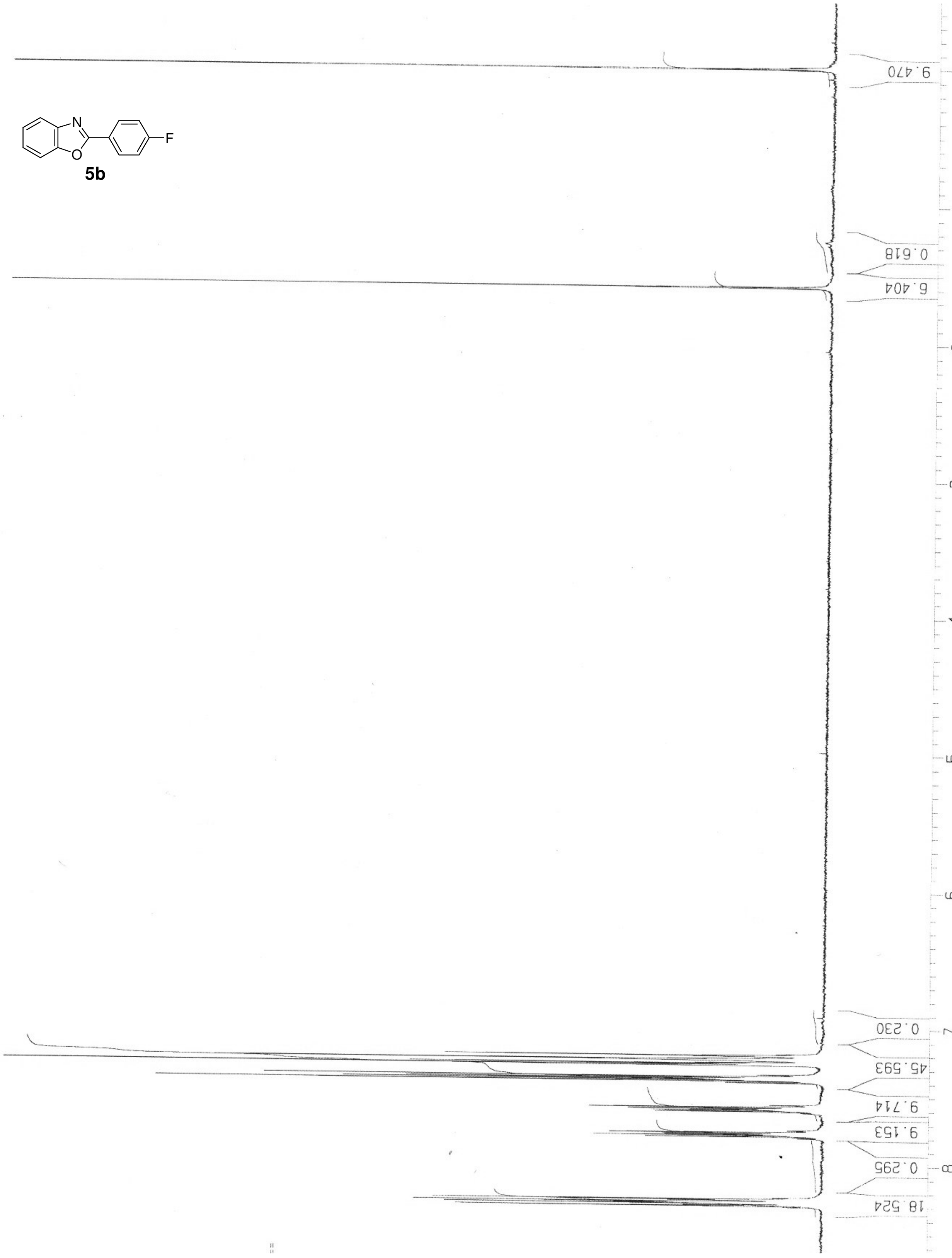

N
OEt
2b
15.09
62.36
77.08
77.50
77.92
120.63
122.23
122.51
122.82
124.66
125.50
127.55
128.22
129.13
131.16
135.15
143.88
159.28
ppm
20
40
60
80
100
120
140
160



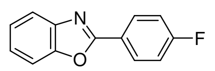
2c



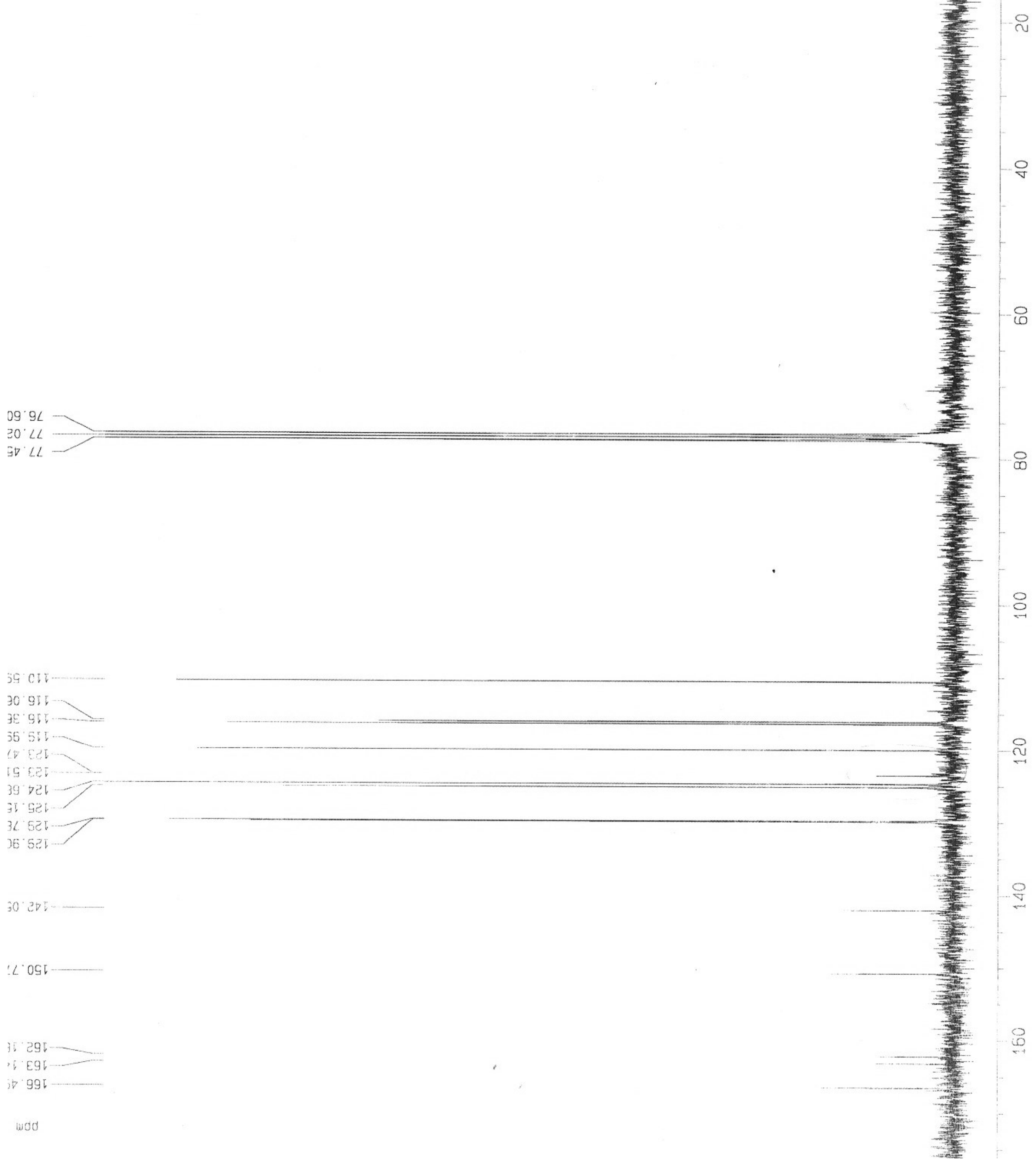

O^{i}Pr
N
2c
22.57
68.70
77.03
77.45
77.88
120.99
122.18
122.45
122.65
124.49
125.60
127.48
128.18
129.06
131.07
135.20
143.97
158.68
ppm
20
40
60
80
100
120
140
160

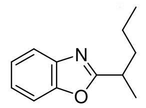


5b

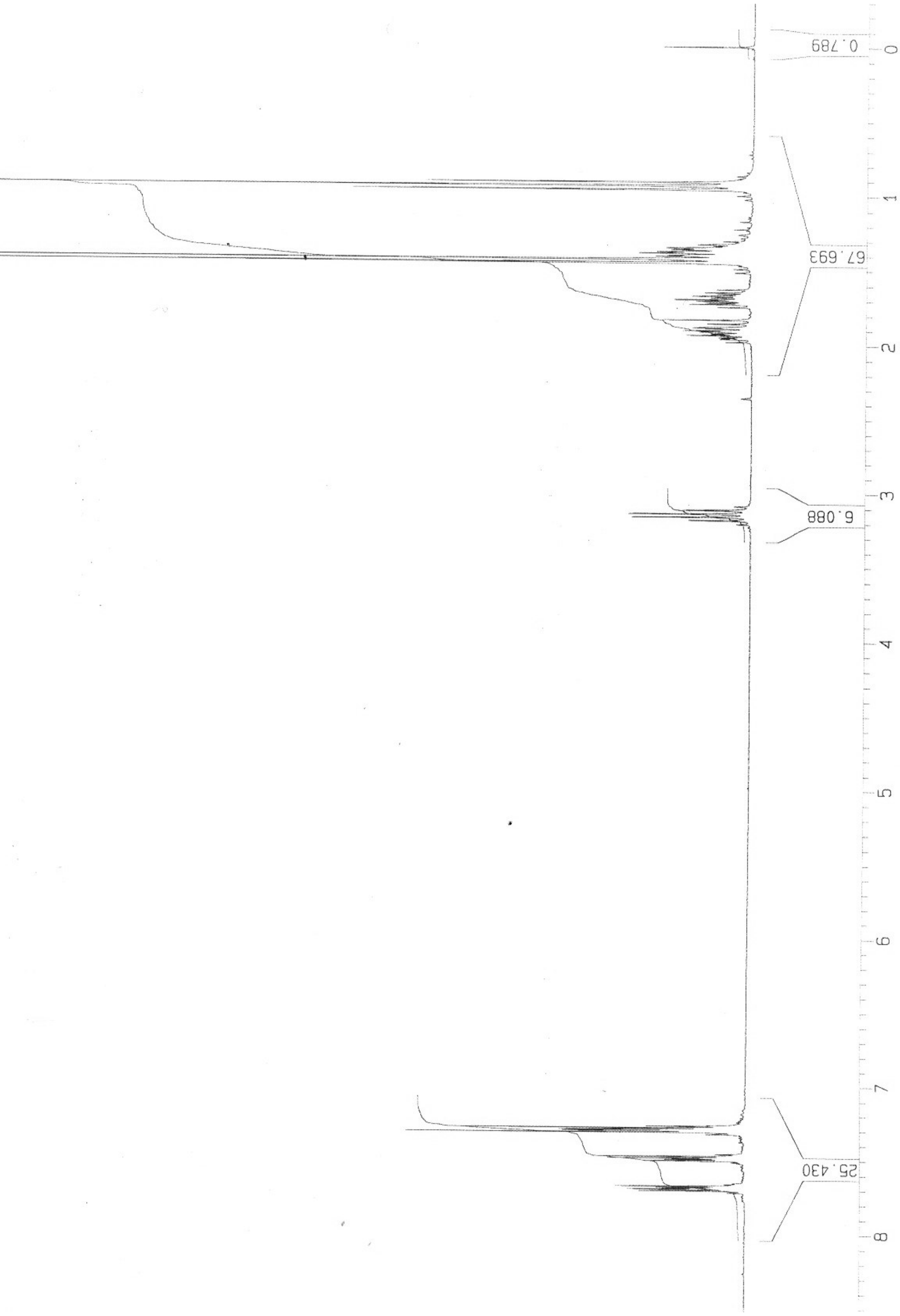


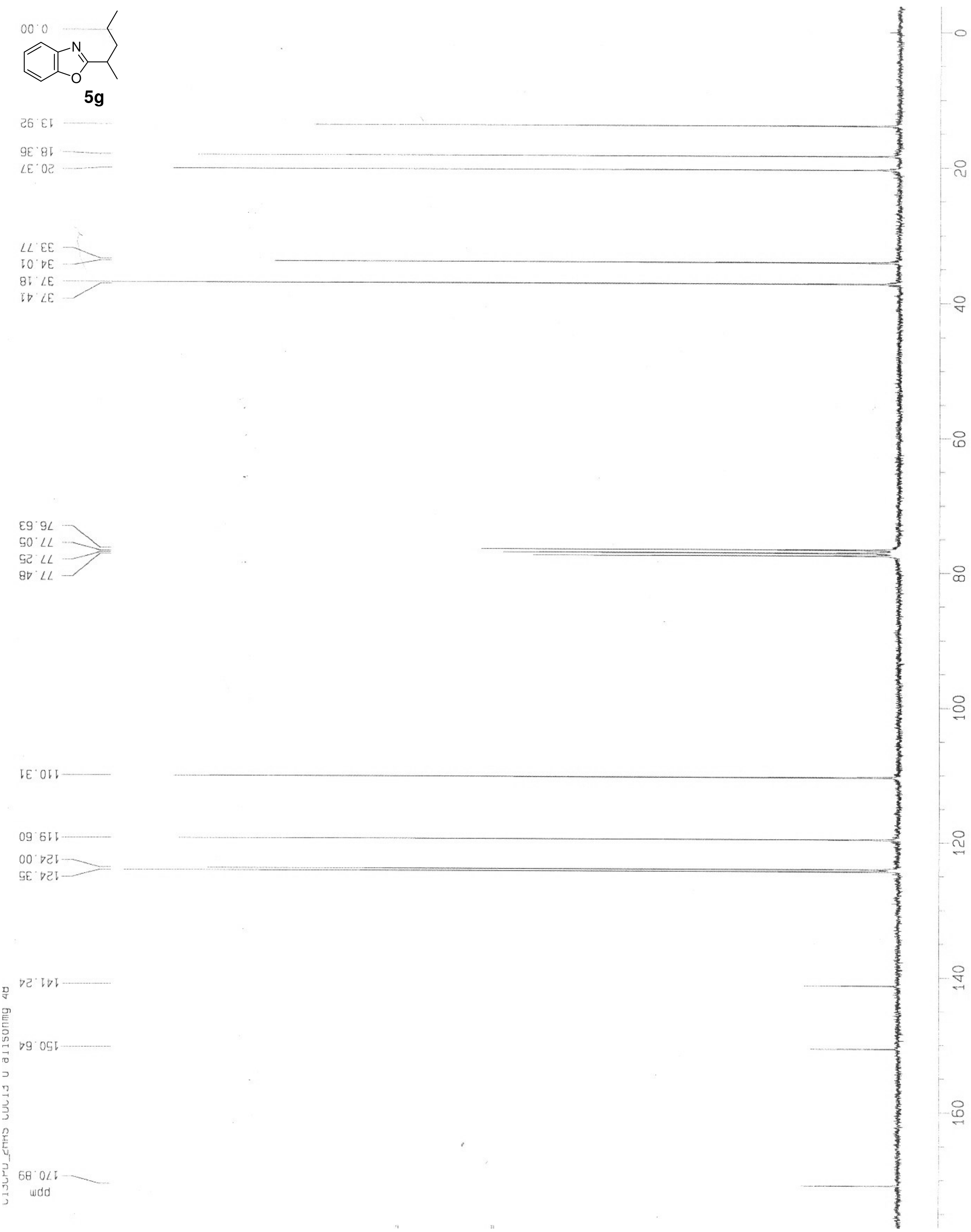
5b

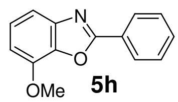




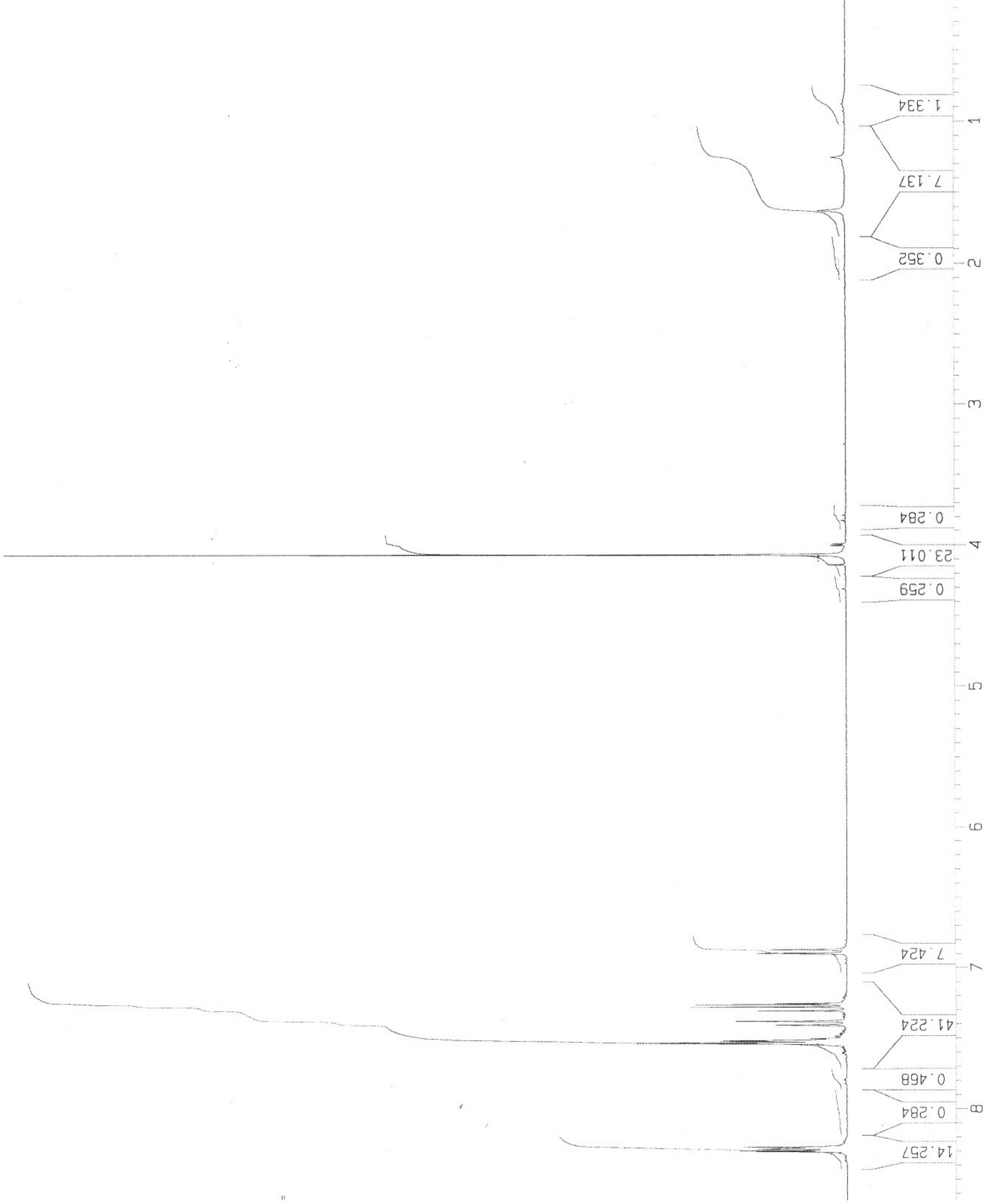
5g

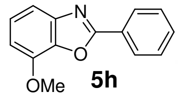



5g
0.00
13.92
18.36
20.37
33.77
34.01
37.18
37.41
76.63
77.05
77.25
77.48
110.31
119.60
124.00
124.35
141.24
150.64
170.89
ppm
0
20
40
60
80
100
120
140
160

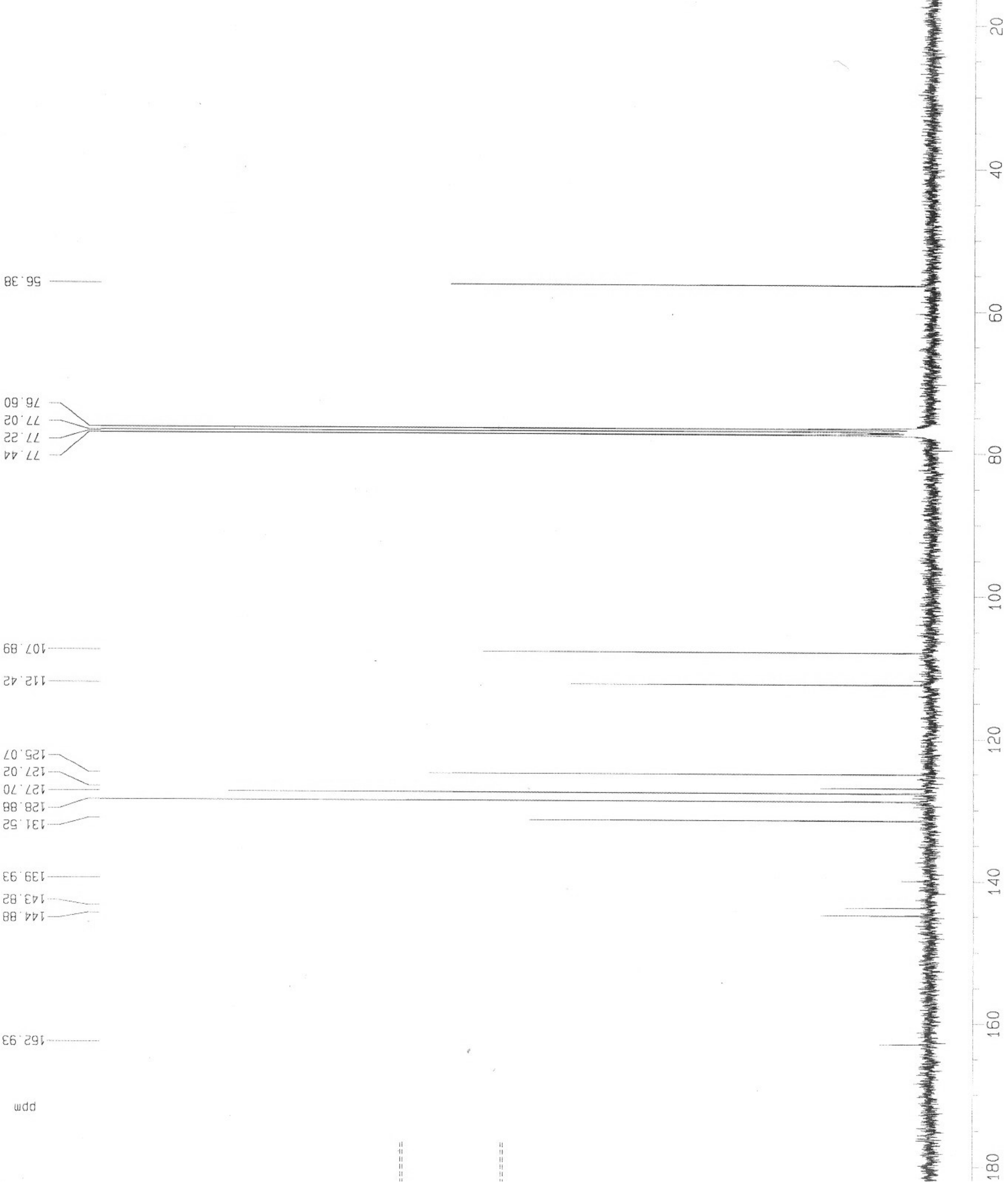


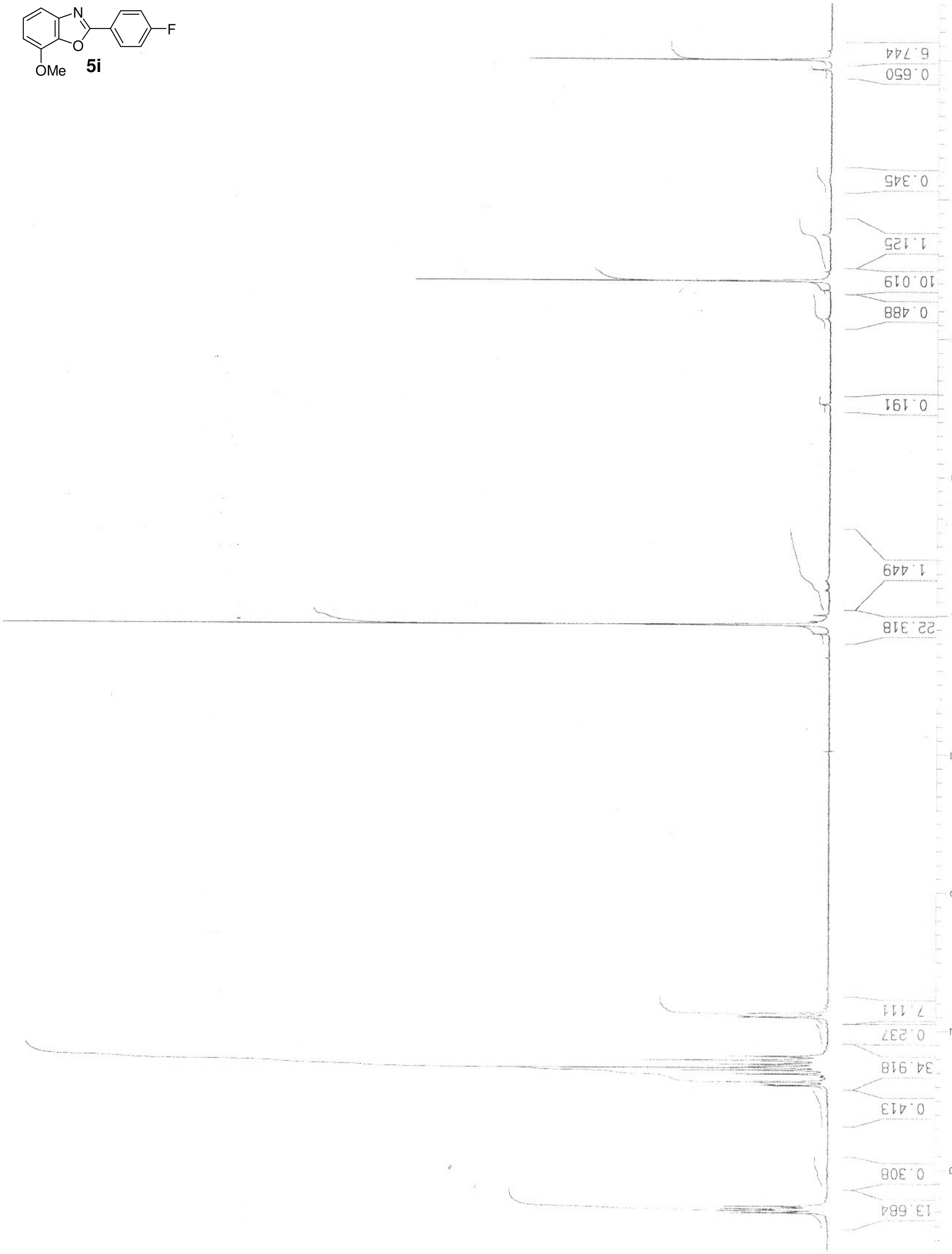
5h


3.669
1.334
7.137
0.352
0.284
23.011
0.259
7.424
41.224
0.468
0.284
14.257
0
1
2
3
4
5
6
7
8

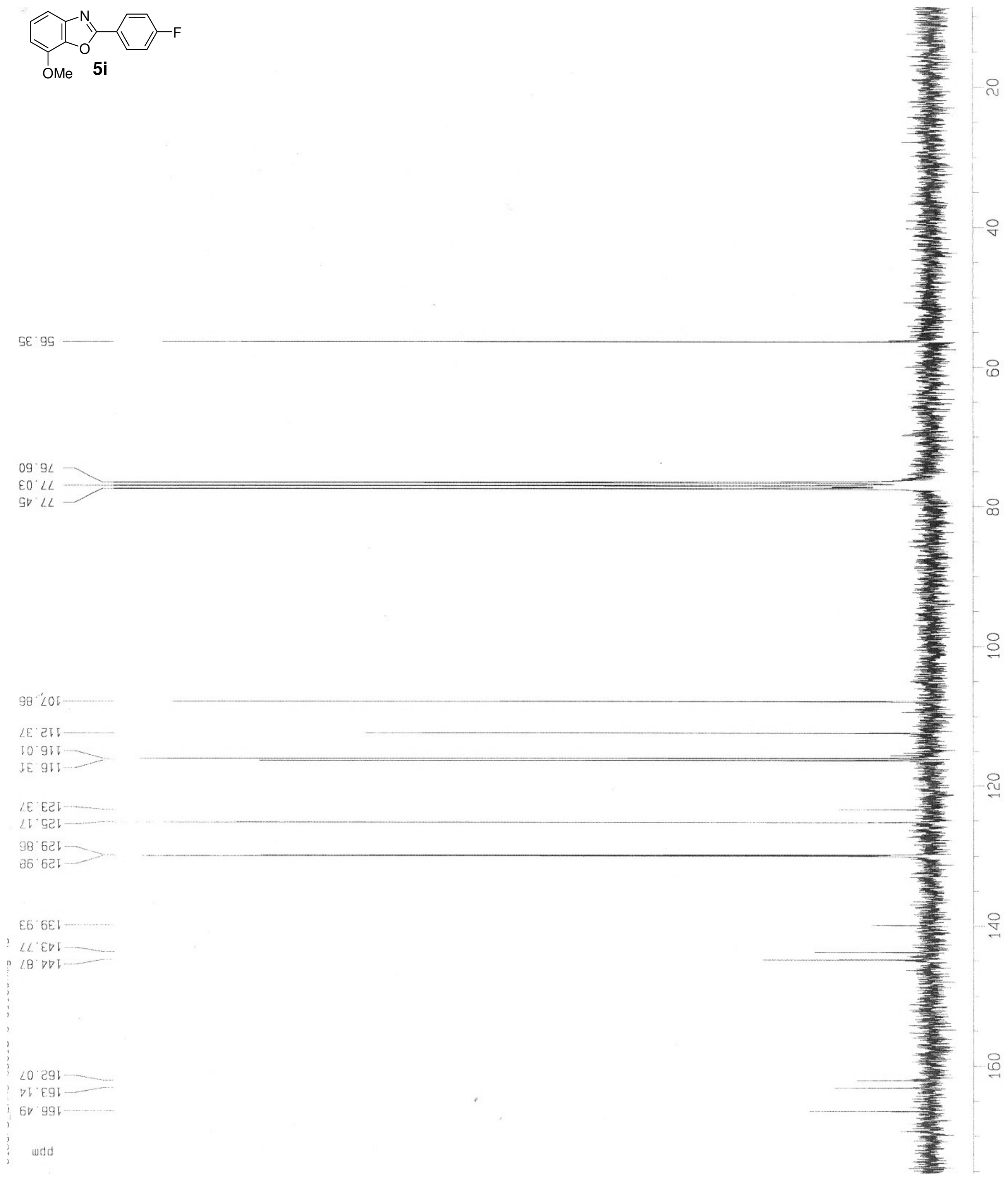

N
O
OMe

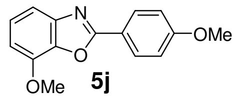
5h


56.38
76.60
77.02
77.22
77.44
107.89
112.42
125.07
127.02
127.70
128.88
131.52
139.93
143.82
144.88
162.93
ppm
20
40
60
80
100
120
140
160
180

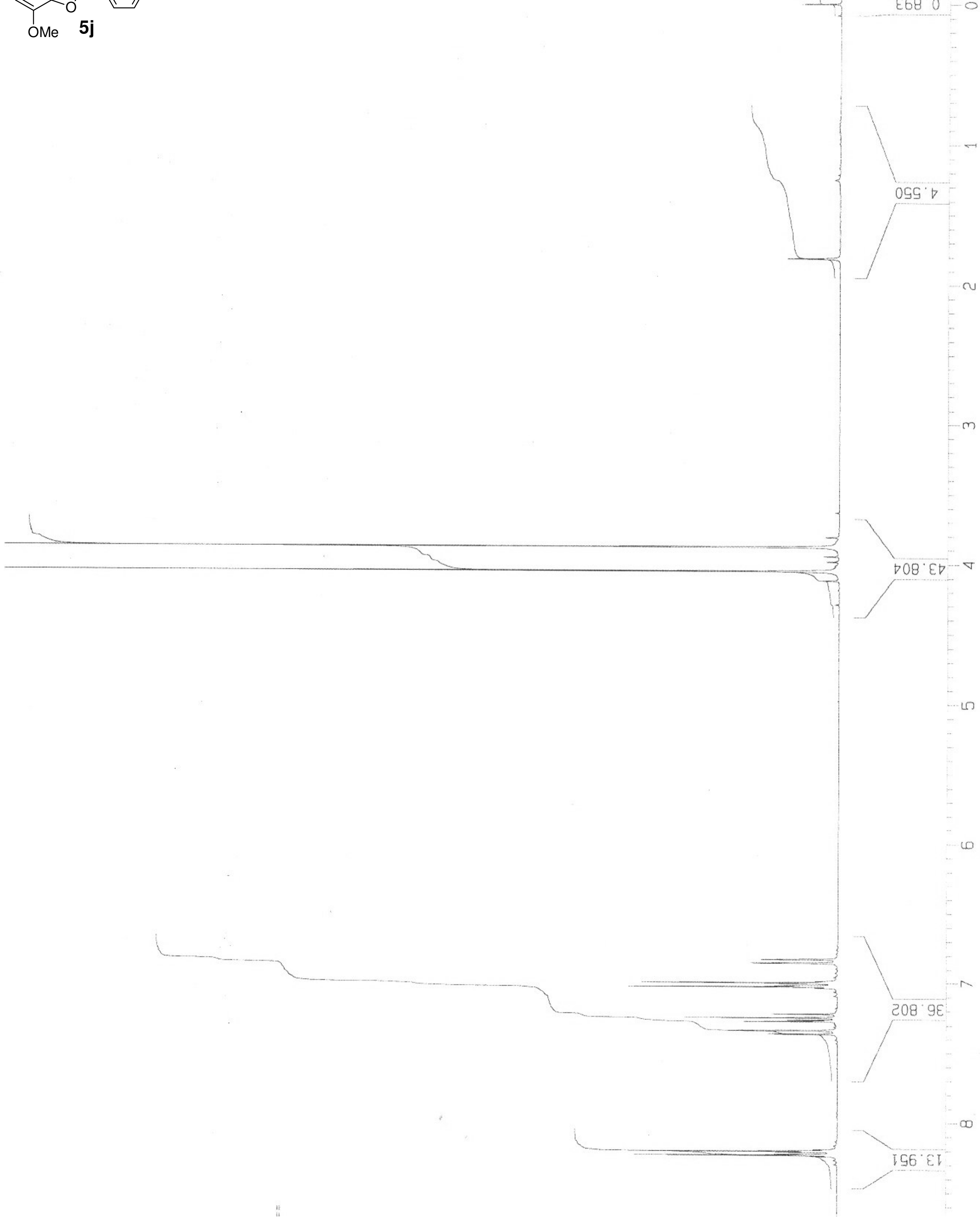


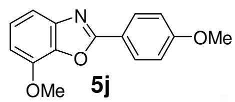
5i


F
OMe
N
O
5i
56.35
76.60
77.03
77.45
107.86
112.37
116.01
116.31
123.37
125.17
129.86
129.96
139.93
143.77
144.87
162.07
163.14
166.49
ppm
20
40
60
80
100
120
140
160

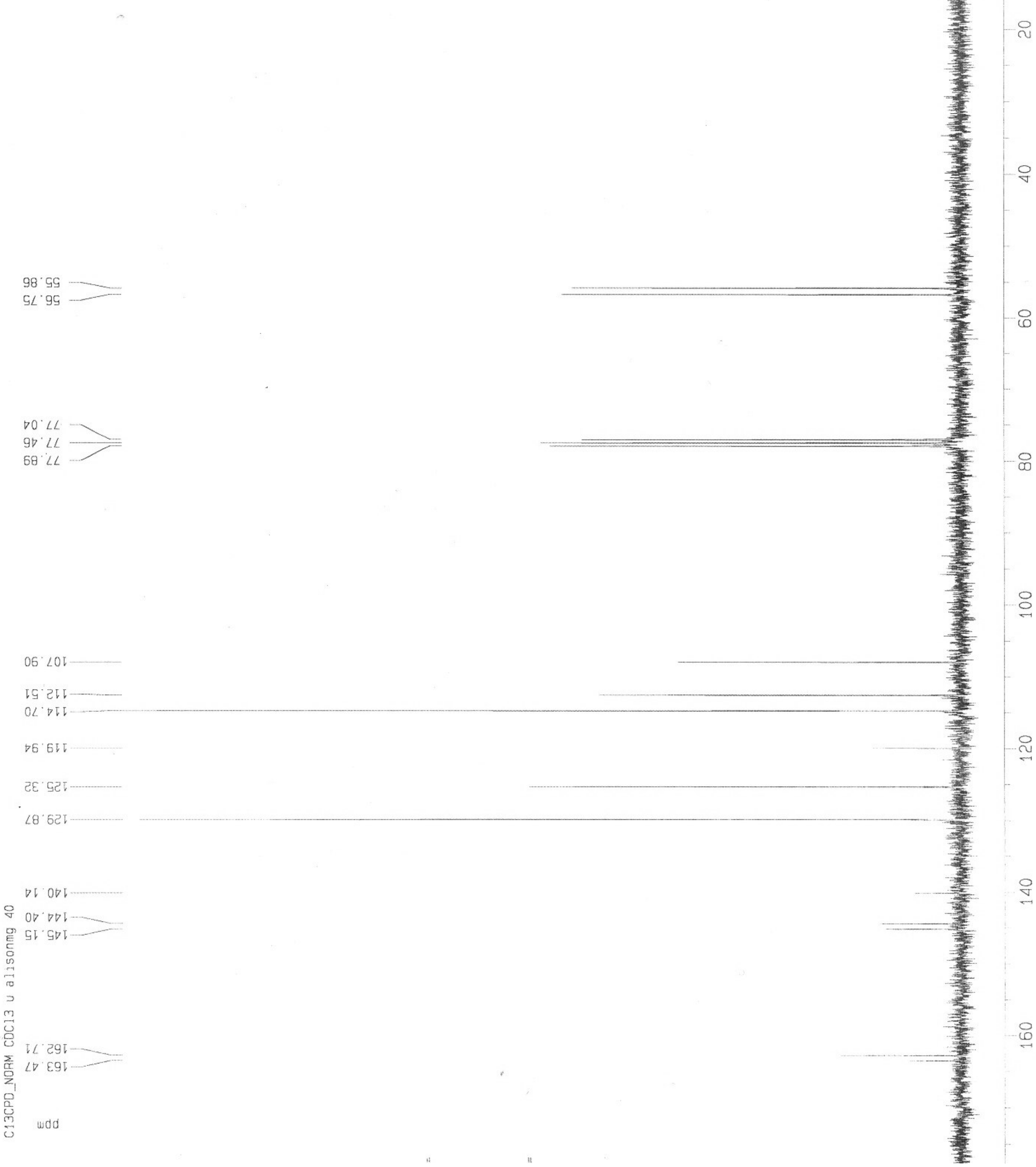


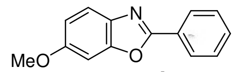
5j



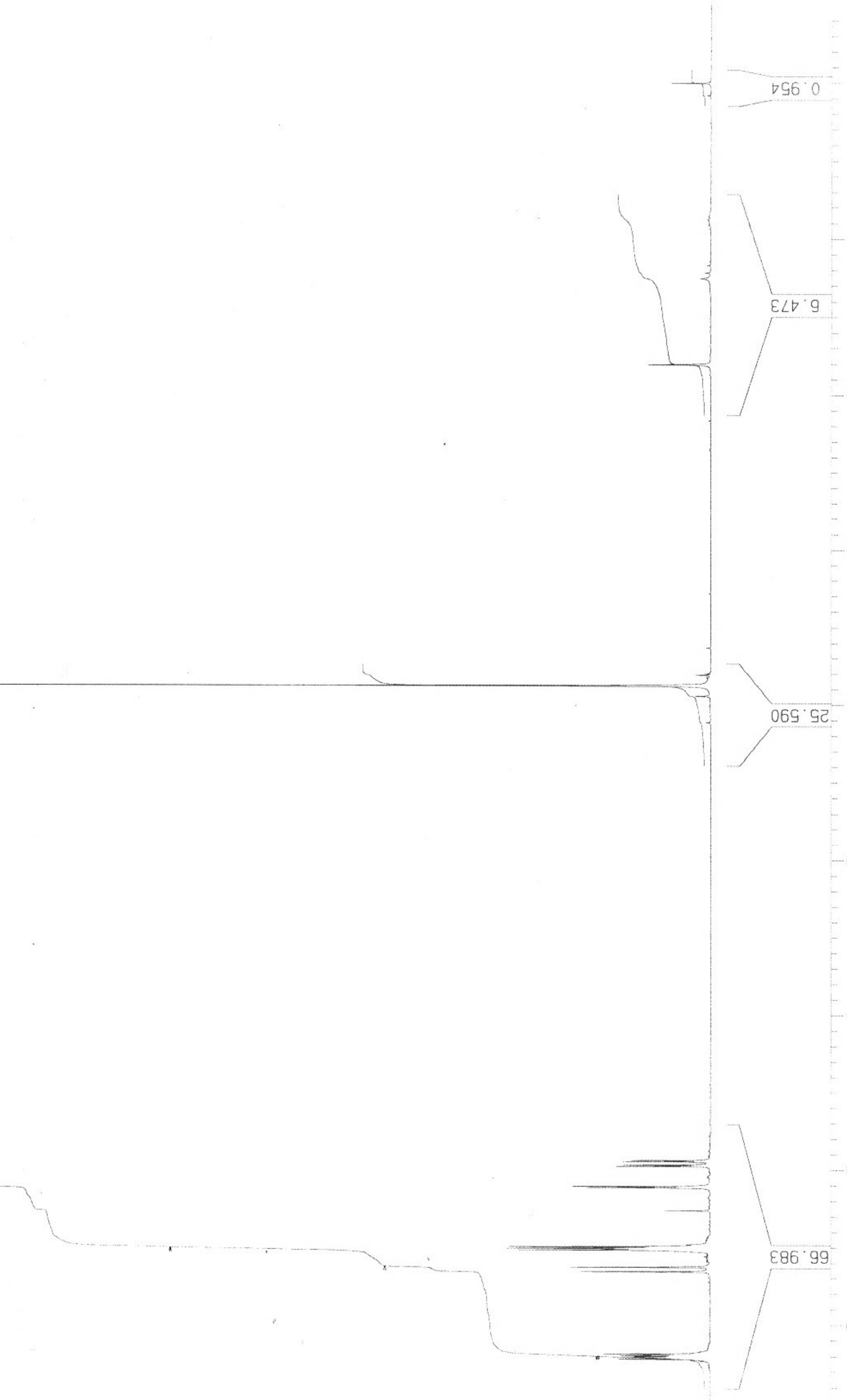


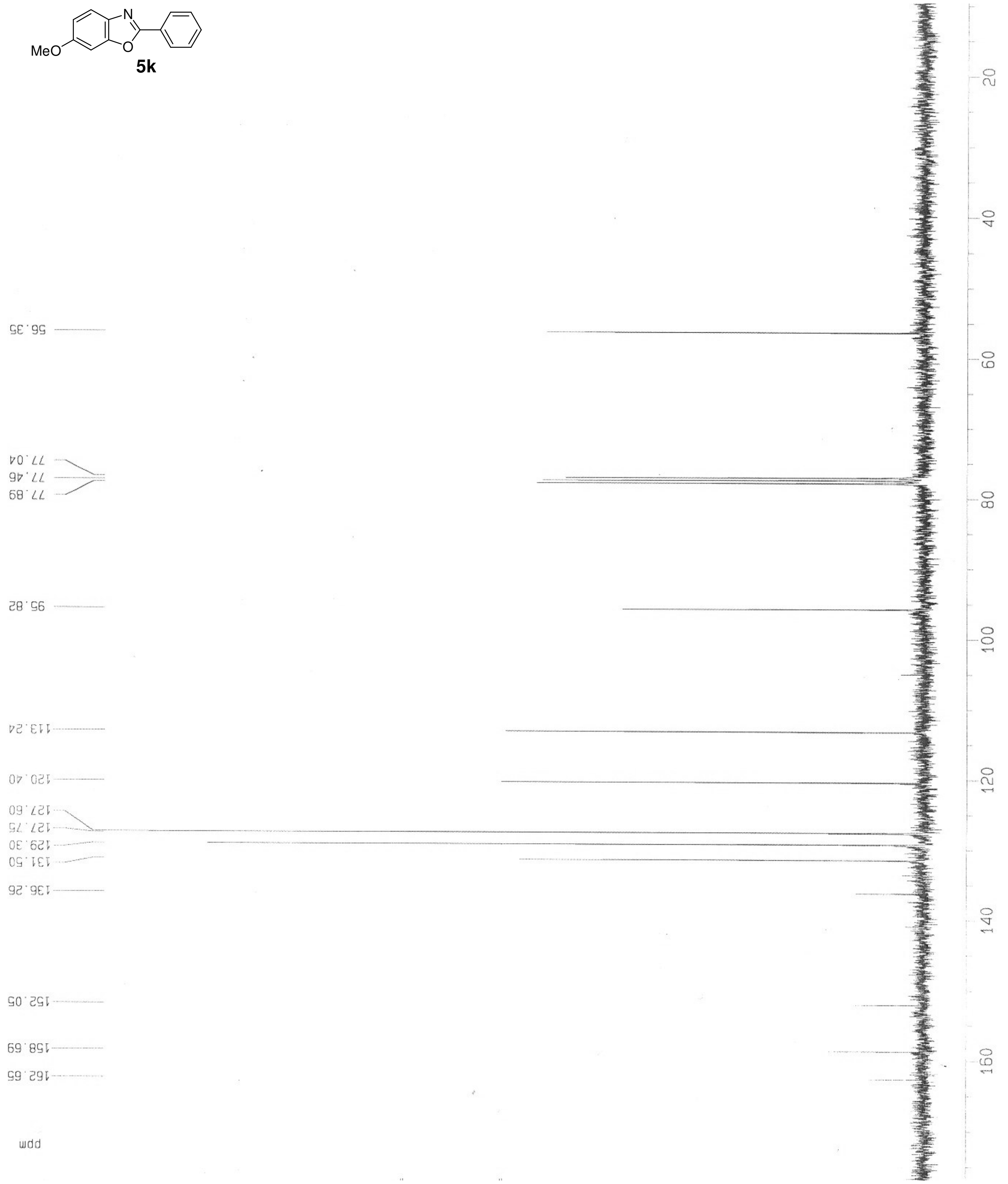
5j


55.86
56.75
77.04
77.46
77.89
107.90
112.51
114.70
119.94
125.32
129.87
140.14
144.40
145.15
162.71
163.47
C13CPD_NORM CDCl3 u alisonmg 40
ppm
20
40
60
80
100
120
140
160

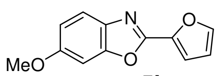


5k

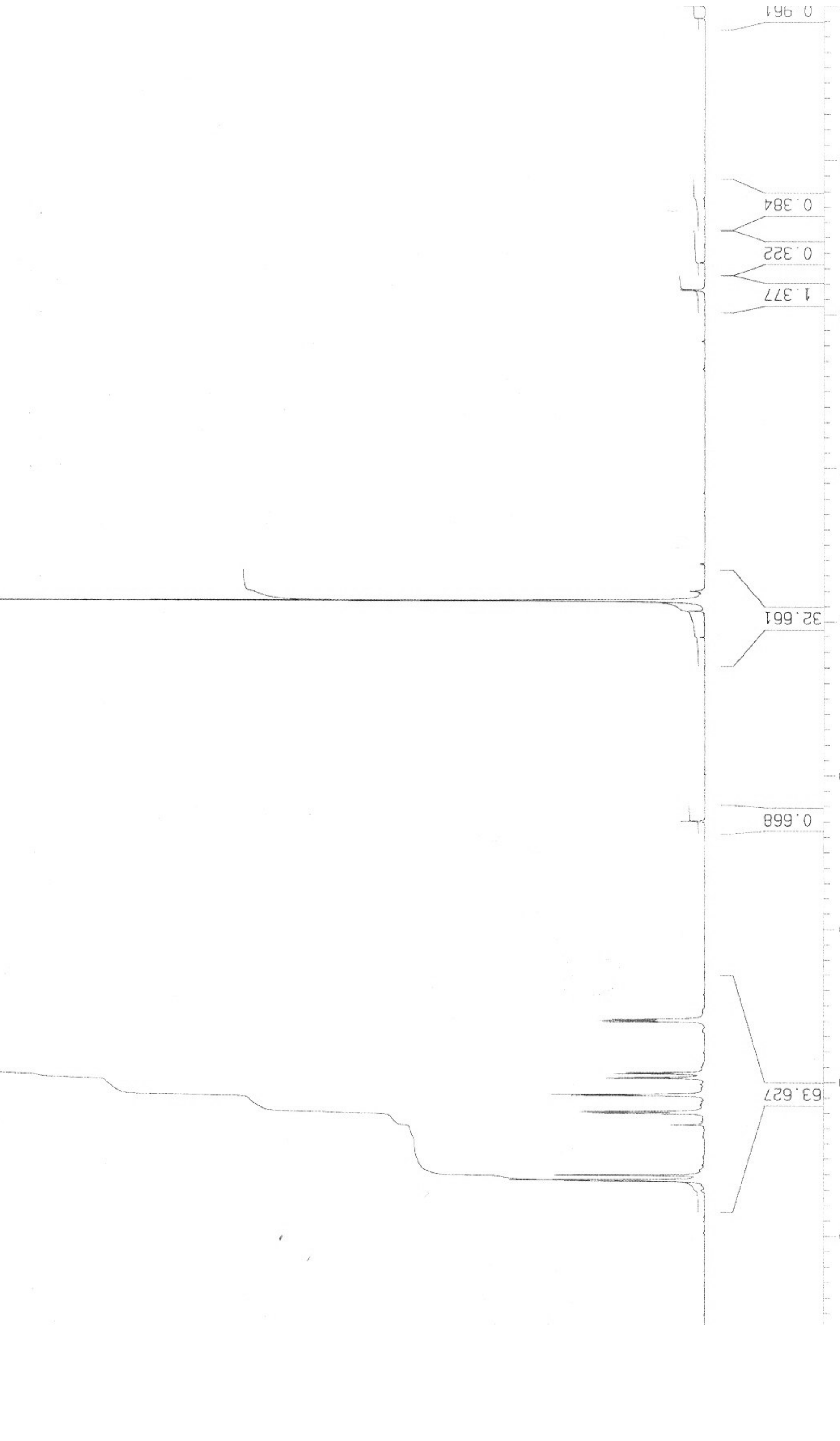


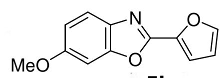


MeO
N
O
5k
56.35
77.04
77.46
77.89
95.82
113.24
120.40
127.60
127.75
129.30
131.50
136.26
152.05
158.69
162.65
ppm
20
40
60
80
100
120
140
160

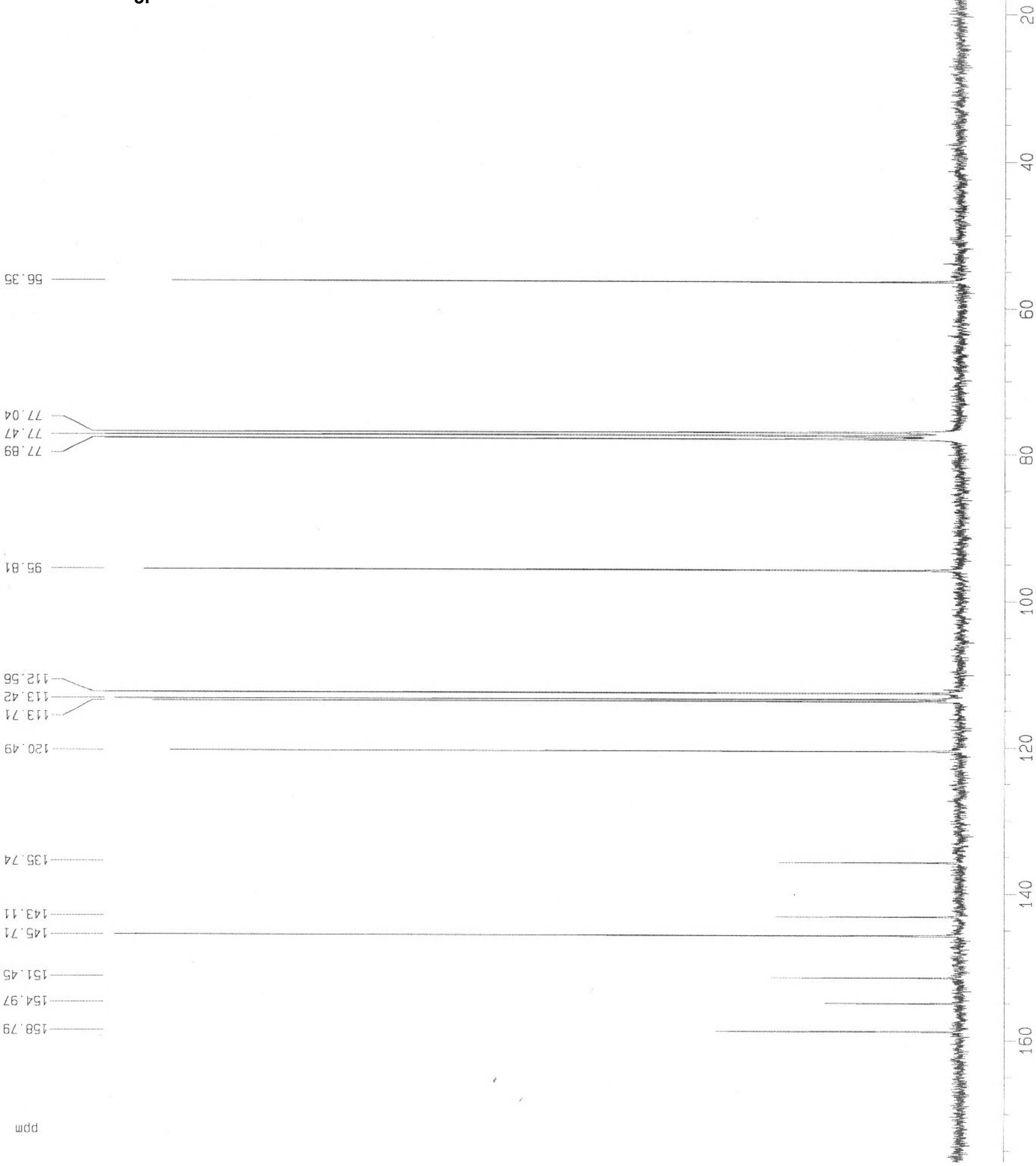


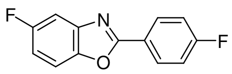
5l



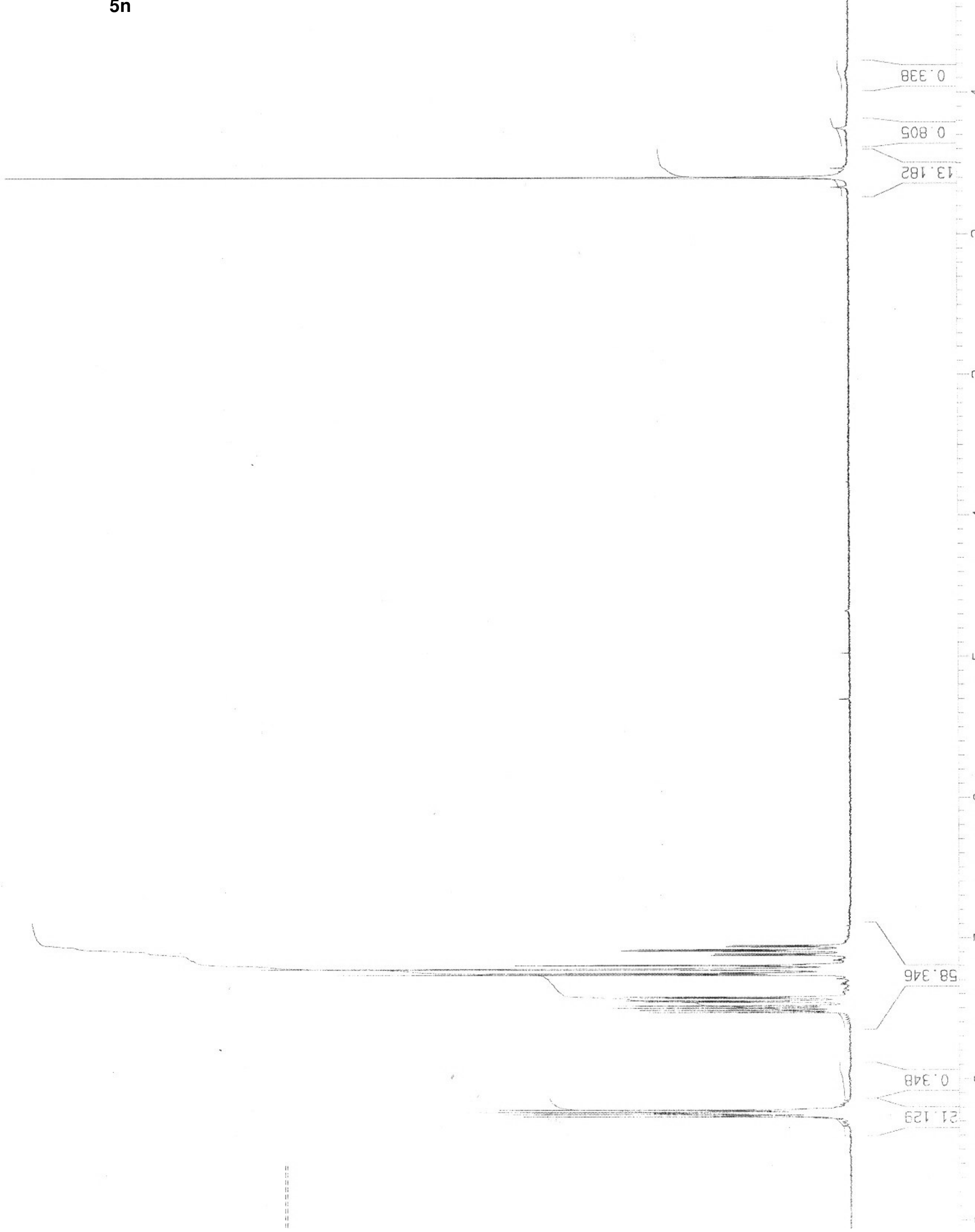

MeO
N
O
O

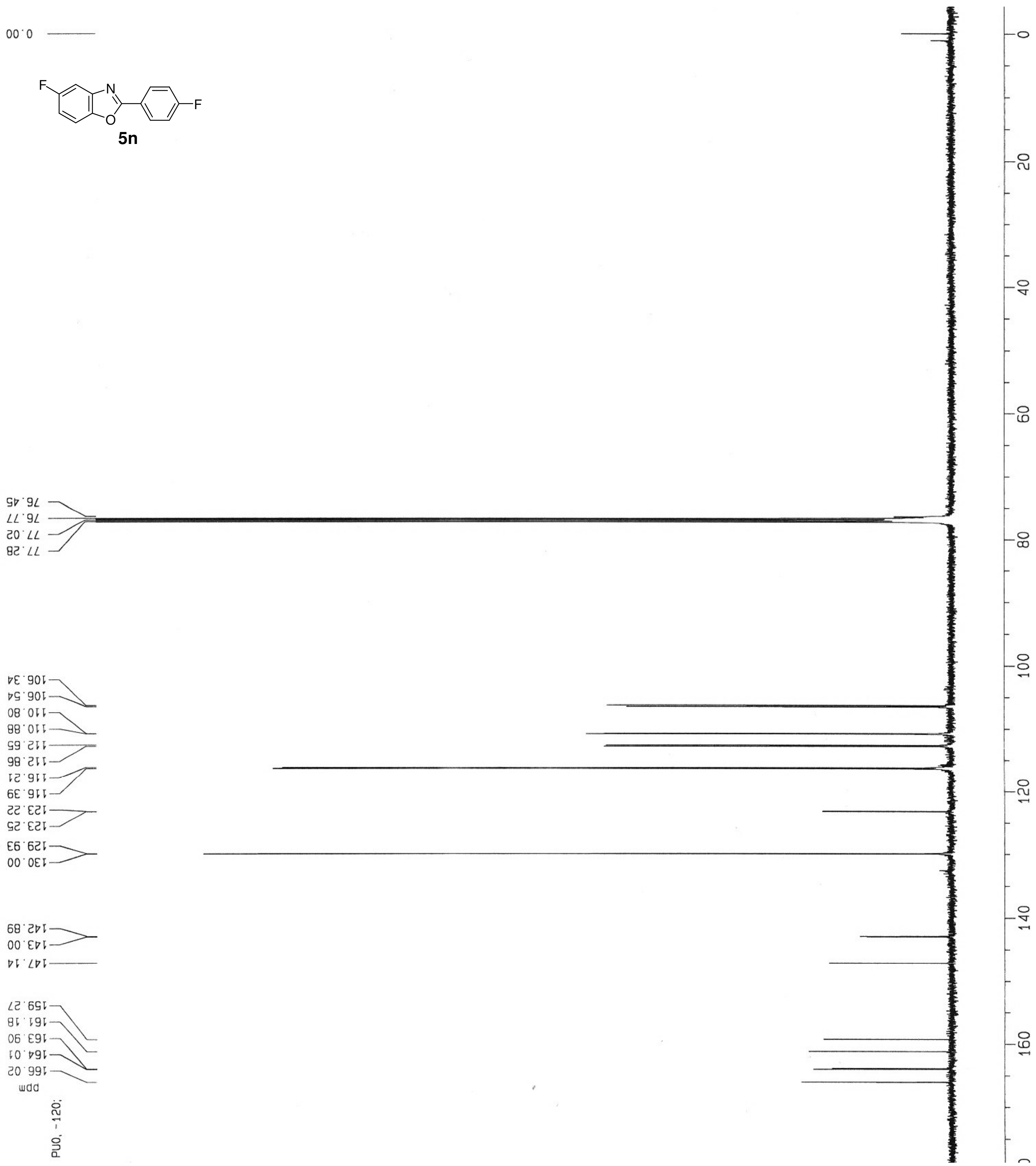
5l


56.35
77.04
77.47
77.89
95.81
112.56
113.42
113.71
120.49
135.74
143.11
145.71
151.45
154.97
158.79
ppm
20
40
60
80
100
120
140
160



5n




5n
0.00
76.45
76.77
77.02
77.28
106.34
106.54
110.80
110.88
112.65
112.86
116.21
116.39
123.22
123.25
129.93
130.00
142.89
143.00
147.14
159.27
161.18
163.90
164.01
166.02
ppm
PU0, -120;
0
20
40
60
80
100
120
140
160