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Chlorination and *ortho*-acetoxylation of 2-arylbenzoxazoles *via* C-H activation

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General

^{1}H NMR, ^{13}C NMR, ^{1}H-^{1}H COSY NMR, ^{1}H-^{13}C HSQC NMR, ^{1}H-^{13}C HBMC NMR spectra were recorded on a Bruker DPX-400 spectrometer with $CDCl_3$ as the solvent and TMS as an internal standard. Melting points were measured using a WC-1 microscopic apparatus and are uncorrected. GC analysis was performed on Agilent 4890D gas chromatograph. Mass spectra were measured on an LC-MSD-Trap-XCT instrument. High-resolution mass spectra were measured on a MALDI-FTMS. Elemental analyses were determined with a Carlo Erba elemental analyzer. IR spectra were recorded on a Bruker VECTOR 22 spectrophotometer. Dichloromethane, ethyl acetate and hexane (analytical grade) were used for column chromatography without further purification. Other solvents were purified according to the standard methods. Other chemicals were obtained from commercial sources and used as-received unless otherwise noted.

General procedure for synthesis of 2-arylbenzoxazoles

To a solution of 2-aminophenol (3.274 g, 30.0 mmol) in polyphosphoric acid (PPA, 30 mL), arylcarboxylic acid (30 mmol) was added. The resulting mixture was heated at 150 °C for 5 h. After the reaction was complete, the mixture was added into cold water and then the pH value was adjusted to 14 with an aqueous solution of sodium hydroxide. The mixture was extracted with ethyl acetate three times. The combined organic layer was dried over anhydrous Na_2SO_4 and filtered. After removal of the solvent *in vacuum*, the residue was purified by flash column chromatography (ethyl acetate/hexane) to afford the pure product.

General procedure for direct chlorination of 2-arylbenzoxazoles

Substrate **1** (0.5 mmol), chlorinating reagent (0.6 mmol) and $PdCl_2$ (5 mol%) were dissolved in AcOH (2 mL) in a 10 mL vial under air and heated at a specific temperature for 10 h. After the reaction was complete, the solvent was evaporated under reduced pressure. The residual was purified by flash chromatography on silica gel (ethyl acetate/hexane) to give the desired product.

General procedure for direct acetoxylation of 2-arylbenzoxazoles

Substrate **1** (0.5 mmol), $PhI(OAc)_2$ (0.55 mmol), $Pd(OAc)_2$ (5 mol%) were dissolved in AcOH (2 mL) and Ac_2O (2 mL) in a 10 ml vial under air and heated at a specific temperature for 48 h. Upon completion, the solvent was evaporated to dryness *in vacuo*. The residual was purified by flash chromatography on silica gel (ethyl acetate/hexane) to give the desired product.

Characterization data of products 1a-1m, 2a-2k and 3a-3f

2-(3-Methylphenyl)benzoxazole (1a)[1]:

White solid, mp 79–80 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.45 (s, 3H), 7.24–7.79 (m, 3H), 7.37–7.42 (m, 1H), 7.56–7.60 (m, 1H), 7.75–7.80 (m, 1H), 8.05 (d, J = 7.80 Hz, 1H), 8.08 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.4, 110.6, 119.9, 124.6, 124.8, 125.1, 126.9, 128.2, 128.8, 132.4, 138.8, 142.0, 150.7, 163.2.

2-(2-Methylphenyl)benzoxazole (1b)[2]:

White solid, mp 64–66 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.80(s, 3H), 7.31–7.40 (m, 5H), 7.56–7.58 (m, 1H), 7.79–7.81 (m, 1H), 8.16-8.18 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.2, 110.5, 120.1, 124.3, 125.0, 126.0, 126.2, 129.9, 130.9, 131.8, 138.8, 142.1, 150.2, 163.3.

2-(4-Methylphenyl)benzoxazole(1c)[3]:

White solid, mp 117–118 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.42 (s, 3H), 7.30–7.34 (m, 4H), 7.55–7.57 (m, 1H), 7.75–7.77 (m, 1H), 8.13 (d, J = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.6, 110.5, 119.8, 124.4, 124.5, 124.8, 127.6, 129.6, 142.0, 142.1, 150.6, 163.3.

2-Phenylbenzoxazole (1d)[4]:

White solid, mp 79–80 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30–7.40 (m, 2H), 7.40–7.60 (m, 4H), 7.72–7.80 (m, 1H), 8.26 (t, J = 2.40 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 110.6, 120.0, 124.6, 125.1, 127.2, 127.6, 128.9, 131.5, 142.1, 150.8, 163.1.

2-(3-Fluorophenyl)benzoxazole (1e)[5]:

White solid, mp 92–94 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20–7.21 (m, 1H), 7.25–7.36 (m, 2H), 7.47–7.56 (m, 2H), 7.75–7.78 (m, 1H), 7.94–8.03 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 110.7, 114.6 (d, J = 23.9 Hz), 118.5 (d, J = 21.2 Hz), 120.2, 123.3 (d, J = 3.1 Hz), 124.8, 125.5, 129.2 (d, J = 8.5 Hz), 130.6 (d, J = 8.1 Hz), 141.9, 150.7, 161.7 (d, J = 3.1 Hz), 162.9 (d, J = 245.4 Hz).

2-(3-Chlorophenyl)benzoxazole (1f)[5]:

White solid, mp 124–125 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35–7.40 (m, 2H), 7.44–7.53 (m, 2H), 7.58–7.62 (m, 1H), 7.77–7.79 (m, 1H), 8.15 (dt, J = 7.60, 1.40 Hz, 1H), 8.27 (d, J = 1.60 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 110.7, 120.2, 124.9, 125.6, 125.7, 127.6, 128.8, 130.3, 131.6, 135.1, 141.7, 150.7, 161.6.

2-(3-Bromophenyl)benzoxazole (1g)[5]:

White solid, mp 128–130 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25–7.44 (m, 3H), 7.56–7.65 (m, 1H), 7.65–7.69 (m, 1H), 7.76–7.81 (m, 1H), 8.20 (d, J = 8.02 Hz, 1H), 8.43 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 110.7, 120.2, 123.0, 124.9, 125.6, 126.1, 129.0, 130.5, 130.5, 134.5, 141.8, 150.8, 161.5.

2-(4-Fluorophenyl)benzoxazole (1h)[6]:

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White solid, mp 94–96 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16–7.20 (m, 2H), 7.32–7.35 (m, 2H), 7.54–7.55 (m, 1H), 7.74–7.76 (m, 1H), 8.21–8.25 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 110.3, 115.6 (d, J = 22.1 Hz), 119.7, 123.2 (d, J = 2.9 Hz), 124.4, 124.8, 129.5 (d, J = 8.8 Hz), 141.7, 150.4, 161.8, 165.5 (d, J = 251.2 Hz).

2-(4-Chlorophenyl)benzoxazole (1i)[7]:

white solid, mp 148–150 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36–7.39 (m, 2H), 7.51–7.57 (m, 2H), 7.57–7.59 (m, 1H), 7.76–7.78 (m, 1H), 8.18–8.20 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 110.6, 120.0, 124.7, 125.5, 125.6, 128.8, 129.2, 137.7, 141.9, 150.7, 162.0.

2-(4-Bromophenyl)benzoxazole (1j)[8]:

White solid, mp 157–158 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35–7.38 (m, 2H), 7.57–7.58 (m, 1H), 7.66 (d, J =8.4 Hz, 2H), 7.76–7.78 (m, 1H), 8.11 (d, J = 8.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 110.6, 120.1, 124.8, 125.4, 126.1, 126.2, 129.0, 132.2, 142.0, 150.7, 162.1.

2-(2,4-Dichlorophenyl)benzoxazole (1k)[9]:

White solid, mp 123–124 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38–7.44 (m, 3H), 7.58–7.65 (m, 2H), 7.83–7.87 (m, 1H), 8.13 (d, J = 8.40 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 110.8, 120.6, 124.7, 124.8, 125.8, 127.4, 131.3, 132.5, 134.2, 137.5, 141.6, 150.5, 160.1.

2-(3-Methoxyphenyl)benzoxazole (1l)[5]:

White solid, mp 71.3–73.8 °C; ^{1}H NMR (400 MHz, CDCl3): δ 3.92 (s, 3H), 7.07–7.09 (m, 1H), 7.35–7.37 (m, 2H), 7.40–7.45 (m, 1H), 7.57–7.59 (m, 1H), 7.77–7.79 (m, 2H), 7.85 (d, J = 7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.2, 110.3, 111.5, 118.07, 119.7, 119.8, 124.3, 124.9, 128.0, 129.7, 141.7, 150.4, 159.2, 162.7.

2-(3,4-Dimethoxylphenyl)benzoxazole (1m)[5]:

White solid, mp 109–111 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.97 (s, 3H), 4.02 (s, 3H), 6.98 (d, J = 0.88 Hz, 1H), 7.25–7.36 (m, 2H), 7.54–7.58 (m, 1H), 7.73–7.78 (m, 2H), 7.86 (d, J = 8.40 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 56.1, 56.1, 110.0, 110.4, 111.0, 119.6, 119.7, 121.2, 124.5, 124.7, 142.1, 149.2, 150.7, 152.0, 163.1.

6-Chloro-2-(3-methylphenyl)benzoxazole (2a):

Purification by flash chromatography over silica gel, eluting with ethyl acetate-hexane (1 : 30), provided the desired compound as a white solid; R_f = 0.40; mp 99–100 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.45 (s, 3H), 7.26–7.43 (m, 3H), 7.57 (s, 1H), 7.66 (d, J = 8.5 Hz, 1H), 8.02 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.4, 111.2, 120.4, 124.8, 125.2, 126.5, 128.2, 128.9, 130.6, 132.7, 138.8, 140.9, 150.9, 163.9; IR (KBr): 3057, 1615, 1554, 1453, 1423, 1329,1261, 1052, 920, 864, 803, 714, 681, 593, 434 cm^{-1}; HRMS-ESI (m/z): calcd for $C_{14}H_{11}ClNO$ (M+H): 244.0529, found 244.0530.

6-Chloro-2-(2-methylphenyl)benzoxazole (2b):

Purification by flash chromatography over silica gel, eluting with ethyl acetate-hexane (1 : 30), provided the desired compound as a white solid; R_f = 0.42; mp 85–86 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.79 (s, 3H), 7.30–7.42 (m, 4H), 7.57 (s, 1H), 7.68 (d, J = 8.4 Hz, 1H), 8.13 (d, J = 8.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.2, 111.0, 120.5, 125.0, 125.60, 126.0, 129.8, 130.50, 131.1, 131.8, 138.9, 140.7, 150.3, 163.9; IR (KBr): 3065, 1606, 1542, 1485, 1432, 1389, 1245, 1208, 1084, 1027, 961, 913, 844, 774, 723, 673, 598, 456 cm^{-1}; HRMS-ESI (m/z): calcd for $C_{14}H_{11}ClNO$ (M+H): 244.0529, found 244.0525.

6-Chloro-2-(4-methylphenyl)benzoxazole (2c):

Purification by flash chromatography over silica gel, eluting with ethyl acetate-hexane (1 : 30), provided the desired compound as a white solid; R_f = 0.41; mp 126–128 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.42 (s, 3H), 7.26–7.30 (m, 3H), 7.53 (s, 1H), 7.62 (d, J = 8.5 Hz, 1H), 8.12–8.14 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.6, 111.1, 120.2, 123.9, 125.1, 127.6, 129.6, 130.3, 140.9, 142.3, 150.8, 163.9; IR (KBr): 3035, 2921, 1617, 1555, 1496, 1457, 1418, 1326, 1281, 1254, 1173, 1117, 1047, 1011, 917, 834, 807, 725, 699, 635, 595, 501 cm^{-1}; HRMS-ESI (m/z): calcd for $C_{14}H_{11}ClNO$ (M+H): 244.0529, found 244.0526.

6-Chloro-2-phenylbenzoxazole (2d)[10]:

Purification by flash chromatography over silica gel, eluting with ethyl acetate-hexane (1 : 30), provided the desired compound as a white solid; R_f = 0.36; mp 59–61 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25–7.32 (m, 1H), 7.48–7.56 (m, 4H), 7.64 (d, J = 8.5 Hz, 1H), 8.18–8.21 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 111.2, 120.4, 125.2, 126.6, 127.6, 128.9, 130.6, 131.7, 140.8, 150.8, 163.6; IR (KBr): 3057, 2924, 2854, 1618, 1552, 1483, 1451, 1426, 1331, 1263, 1121, 1052, 1022, 919, 876, 809, 693, 595, 487 cm^{-1}; Anal. Calcd for $C_{13}H_8ClNO$ (229.03): C 67.99, H 3.51, N 6.10, found: C 68.37, H 3.61, N 5.94.

6-Chloro-2-(3-fluorophenyl)benzoxazole (2e):

Purification by flash chromatography over silica gel, eluting with ethyl acetate-hexane (1 : 30), provided the desired compound as a white solid; R_f = 0.38; mp 128–129 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18–7.24 (m, 1H), 7.24–7.26 (m, 1H),7.32-7.35 (m, 1H) 7.48–7.50 (m, 1H), 7.58 (s, 1H), 7.65–7.68 (m, 1H), 8.00 (d, J = 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 111.3, 114.5 (d, J = 24.4 Hz), 118.8 (d, J = 21.2 Hz), 120.7, 123.3 (d, J = 3.1 Hz), 125.5, 129.9 (d, J = 8.9 Hz), 130.7 (d, J = 8.1 Hz), 130.7, 140.7, 150.9, 162.4 (d, J = 3.4 Hz), 162.9 (d, J = 245.8 Hz); IR (KBr): 3069, 1592, 1556, 1481, 1452, 1328, 1295, 1265, 1210, 1176, 1051, 881, 811, 787, 722, 673, 596, 516 cm^{-1}; Anal. Calcd for $C_{13}H_7ClFNO$ (247.02): C 63.05, H 2.85, N 5.66, found: C 63.16, H 2.98, N 5.46.

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6-Chloro-2-(3-chlorophenyl)benzoxazole (2f)

Purification by flash chromatography over silica gel, eluting with ethyl acetate-hexane (1 : 30), provided the desired compound as a white solid; R_f = 0.35; mp 148–150 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26–7.33 (m, 1H), 7.43–7.48 (m, 2H), 7.55 (s, 1H), 7.64 (d, J = 8.5 Hz, 1H), 8.06 (d, J = 7.7 Hz, 1H), 8.17 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 111.3, 120.6, 125.5, 125.6, 127.6, 128.3, 130.21, 131.1, 131.7, 135.1, 140.6, 150.8, 162.2; IR (KBr): 3065, 1611, 1550, 1472, 1428, 1330, 1259, 1102, 1051, 921, 862, 839, 805, 756, 718, 675, 595, 433 cm^{-1}; Anal. Calcd for $C_{13}H_7Cl_2NO$ (262.99): C 59.12, H 2.67, N 5.30, found: C 59.23, H 2.64, N 5.22.

6-Chloro-2-(3-bromophenyl)benzoxazole (2g):

Purification by flash chromatography over silica gel, eluting with ethyl acetate-hexane (1 : 30), provided the desired compound as a white solid; R_f = 0.37; mp 141–143 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 – 7.39 (m, 2H), 7.56 (s, 1H), 7.63–7.66 (m, 2H), 8.11 (d, J = 7.7 Hz, 1H), 8.34 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 111.3, 120.6, 123.0, 125.5, 126.0, 128.5, 130.4, 131.1, 134.6, 140.6, 150.8, 162.0; IR (KBr): 3064, 1614, 1546, 1468, 1427, 1330, 1259, 1049, 860, 804, 715, 673, 594 cm^{-1}; Anal. Calcd for $C_{13}H_7BrClNO$ (306.94): C, 50.60; H, 2.29; N, 4.54, found: C, 50.76; H, 2.30; N, 4.24.

6-Chloro-2-(4-fluorophenyl)benzoxazole (2h):

Purification by flash chromatography over silica gel, eluting with ethyl acetate-hexane (1 : 30), provided the desired compound as a white solid; R_f = 0.33; mp 132–133 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17–7.21 (m, 2H), 7.30–7.32 (m, 1H), 7.54 (s, 1H), 7.63 (d, J = 8.5 Hz, 1H), 8.17–8.21 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 111.2, 116.2 (d, J = 22.1 Hz), 120.4, 123.0 (d, J = 3.3 Hz), 125.3, 130.0 (d, J = 8.9 Hz), 130.7, 140.8, 150.9, 162.7, 164.9 (d, J = 251.8 Hz); Anal. Calcd for $C_{13}H_7ClFNO$ (247.02): C 63.05, H 2.85, N 5.66, found: C 63.22, H 2.87, N 5.59.

6-Chloro-2-(4-chlorophenyl)benzoxazole (2i)[11]:

Purification by flash chromatography over silica gel, eluting with ethyl acetate-hexane (1 : 30), provided the desired compound as a white solid; R_f = 0.35; mp 148–150 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32–7.35 (m, 1H), 7.48–7.51 (m, 2H), 7.57 (d, J = 1.8 Hz, 1H), 7.66 (d, J = 8.5 Hz, 1H), 8.13–8.15 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 111.3, 120.5, 125.2, 125.5, 128.9, 129.3, 130.9, 138.1, 140.8, 150.9, 162.7.

6-Chloro-2-(4-bromophenyl)benzoxazole (2j):

Purification by flash chromatography over silica gel, eluting with ethyl acetate-hexane (1 : 30), provided the desired compound as a white solid; R_f = 0.38; mp 168–170 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31–7.33 (m, 1H), 7.55 (s, 1H), 7.63–7.65 (m, 3H), 8.04–8.06 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 111.2, 120.5, 125.4, 125.6, 126.5, 129.0, 131.0, 132.3, 140.7, 150.8, 162.7; IR (KBr): 3078, 2924, 1612, 1584, 1457, 1427, 1394, 1327, 1256, 1233, 1066, 1046, 1003, 918, 837, 814, 723, 559, 499 cm^{-1}; Anal. Calcd for $C_{13}H_7BrClNO$ (306.94): C 50.60, H 2.29, N 4.54, found: C 50.78, H 2.24, N 4.34.

6-Chloro-2-(2,4-dichlorophenyl)benzoxazole (2k):

Purification by flash chromatography over silica gel, eluting with ethyl acetate-hexane (1 : 30), provided the desired compound as a white solid; R_f = 0.39; mp 140–141 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37–7.40 (m, 2H), 7.57–7.61 (m, 2H), 7.73 (d, J = 8.5 Hz, 1H), 8.08 (d, J = 8.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 111.4, 121.0, 124.2, 125.6, 127.5, 131.4, 131.5, 132.4, 134.3, 137.8, 140.3, 150.6, 160.6; IR (KBr): 3075, 1609, 1584, 1554, 1467, 1426, 1370, 1108, 1080, 1020, 919, 844, 805, 596 cm^{-1}; HRMS-ESI (m/z): calcd for $C_{13}H_6Cl_3NO$ (M+H): 297.9593, found 297.9602.

2-(Benzoxazol-2-yl)-4-methylphenyl acetate (3a):

Purification by flash chromatography over silica gel, eluting with ethyl acetate-hexane (1 : 10), provided the desired compound as a white solid; R_f = 0.32; White solid; mp 113–114 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.45–2.47 (s, 3H), 2.48 (s, 3H), 7.11 (d, J = 8.2 Hz, 1H), 7.34–7.38 (m, 3H), 7.54–7.55 (m, 1 H), 7.74–7.76 (m, 1H), 8.10–8.11 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.8, 21.4, 110.4, 119.8, 120.2, 123.8, 124.5, 125.3, 130.5, 133.2, 136.3, 141.8, 147.0 150.1, 160.0, 170.2; IR (KBr): 2919, 1752, 1612, 1548, 1479, 1448, 1222, 1191, 1007, 908, 841, 739, 637, 547 cm^{-1}; HRMS-ESI (m/z): calcd for $C_{16}H_{14}NO_3$ (M+H): 268.0973, found 268.0968.

2-(Benzoxazol-2-yl)-5-methylphenyl acetate (3b):

Purification by flash chromatography over silica gel, eluting with ethyl acetate-hexane (1 : 10), provided the desired compound as a white solid; R_f = 0.35; mp 79–80 °C; ^{1}H NMR (400 MHz, CDCl3): δ 2.45 (s, 3H), 2.49 (s, 3H), 7.04 (s, 1H), 7.21–7.35 (m, 3H), 7.53–7.55 (m, 1H), 7.72–7.74 (m, 1H), 8.17 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.4, 21.4, 110.3, 117.5, 120.1, 124.4, 124.6, 125.2, 127.4, 130.0, 142.0, 143.6, 149.1, 150.0, 160.0, 170.0; IR (KBr): 2928, 1758, 1618, 1557, 1497, 1459, 1245, 1196, 1017, 910, 844, 740 cm^{-1}; HRMS-ESI (m/z): calcd for $C_{16}H_{14}NO_3$ (M+H): 268.0973, found 268.0967.

2-(Benzoxazol-2-yl)-3-methylphenyl acetate (3c):

Purification by flash chromatography over silica gel, eluting with ethyl acetate-hexane (1 : 10), provided the desired compound as a white solid; R_f = 0.35; mp 124–125 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.21 (s, 3H), 2.53 (s, 3H), 7.07–7.09 (m, 1H), 7.24–7.26 (m, 1H), 7.38–7.46 (m, 3H), 7.57–7.60 (m, 1H), 7.81–7.83 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.9, 21.4, 110.5, 120.3, 120.80, 121.0, 124.4, 125.3, 128.6, 131.3, 140.6, 141.40, 150.0, 150.4, 159.6, 169.6; IR (KBr): 2932, 2847, 1765, 1616, 1510, 1453, 1365, 1247, 1190, 1148, 1011, 896, 846, 753 cm^{-1}; HRMS-ESI (m/z): calcd for $C_{16}H_{14}NO_3$ (M+H): 268.0973, found 268.0977.

2-(Benzoxazol-2-yl)-phenyl acetate(3d)[12]:

Purification by flash chromatography over silica gel, eluting with ethyl acetate-hexane (1 : 10), provided the desired compound as a white solid; R_f = 0.33; mp 75–76 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.49 (s, 3H), 7.23–7.24 (m, 1 H), 7.35–7.37 (m, 3 H), 7.42 (m, 2 H), 7.55–7.56 (m, 1H), 8.30 (dd, J = 7.9 Hz, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.4, 110.4, 120.3, 120.4, 124.1, 124.6, 125.4, 126.5, 130.2, 132.4, 141.9, 149.2, 150.1, 159.8, 170.0; IR (KBr): 3070, 2920, 1754, 1612, 1547, 1480, 1446, 1367, 1185, 1032, 913, 737, 473 cm^{-1}.

2-(Benzoxazol-2-yl)-4-methoxyphenyl acetate (3e) :

Purification by flash chromatography over silica gel, eluting with ethyl acetate-hexane (1 : 6), provided the desired compound as a white solid; R_f = 0.32; mp 106–108 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.46 (s, 3 H), 3.89 (s, 3H), 7.05–7.14 (m, 2H), 7.34–7.36 (m, 2H), 7.53–7.54 (m, 1H), 7.74–7.77 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.2, 55.9, 110.4, 114.0, 118.7, 120.3, 120.7, 124.6, 125.0, 125.5, 141.8, 142.8, 150.2, 157.5, 159.8, 170.4; IR (KBr): 2937, 2838, 1763, 1597, 1552, 1499, 1453, 1365, 1326, 1242, 1180, 1033, 1006, 936, 876, 827, 755, 578, 516 cm^{-1}; HRMS-ESI (m/z): calcd for $C_{16}H_{14}NO_4$ (M+H): 284.0932, found 284.0931.

2-(Benzoxazol-2-yl)-4,5-dimethoxyphenyl acetate (3f):

Purification by flash chromatography over silica gel, eluting with ethyl acetate-hexane (1 : 4), provided the desired compound as a white solid; R_f = 0.35; mp 149–151 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.47 (s, 3 H), 3.95 (s, 3H), 4.01 (s, 3H), 6.71–6.72 (s, 1H), 7.27–7.35 (m, 2 H), 7.52–7.54 (m, 1H), 7.72–7.74 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.3, 56.2, 56.4, 107.1, 110.2, 111.1, 111.8, 119.9, 124.5, 125.0, 141.9, 143.7, 147.0, 150.0, 152.1, 160.0, 170.3; IR (KBr): 2936, 2838, 1765, 1615, 1560, 1503, 1453, 1245, 1175, 1134, 1025, 939, 877, 744 cm^{-1}; HRMS-ESI (m/z): calcd for $C_{17}H_{16}NO_5$ (M+H): 314.1028, found 314.1038.

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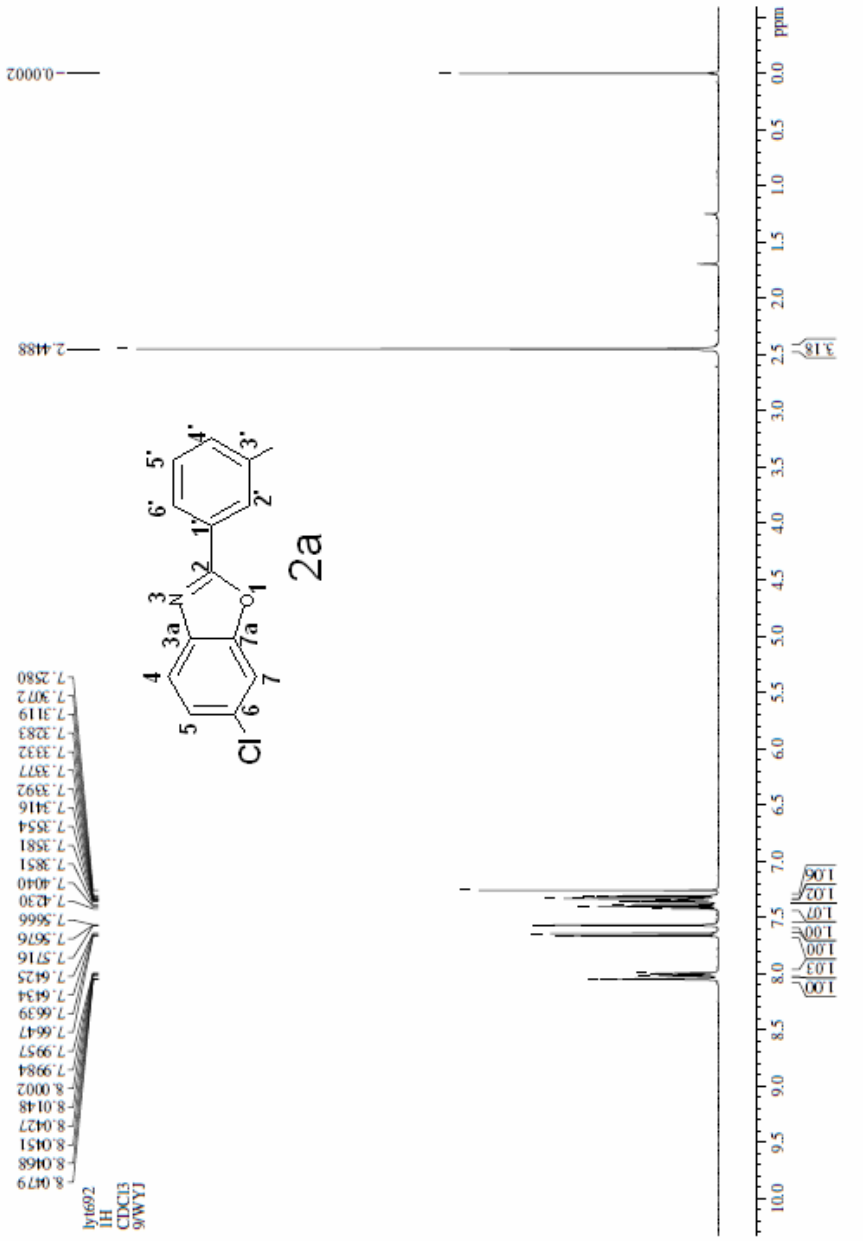
The ^{1}H and ^{13}C NMR spectra and 2D NMR spectra for Compounds 2a, 2g and 3a, 3c



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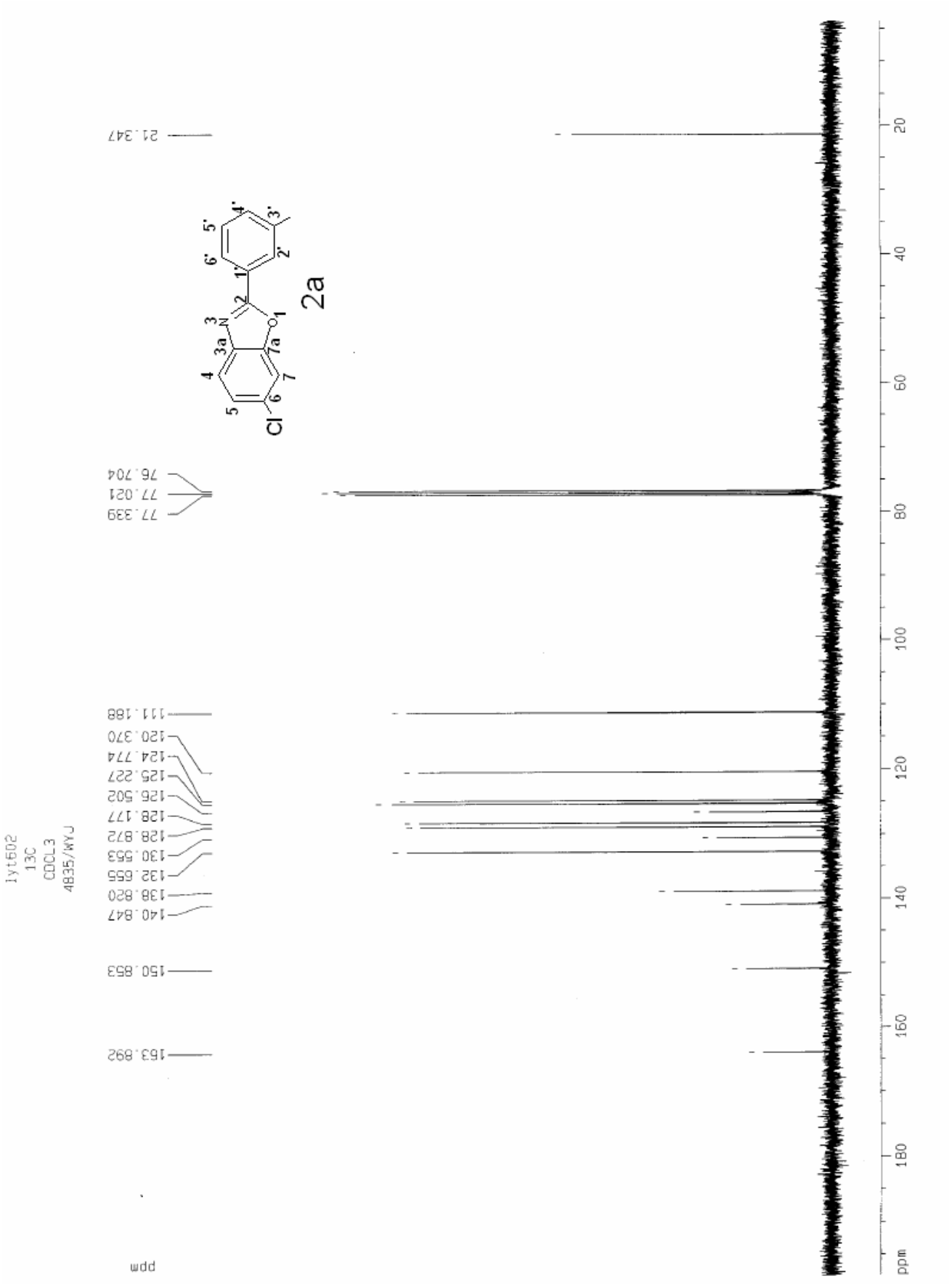

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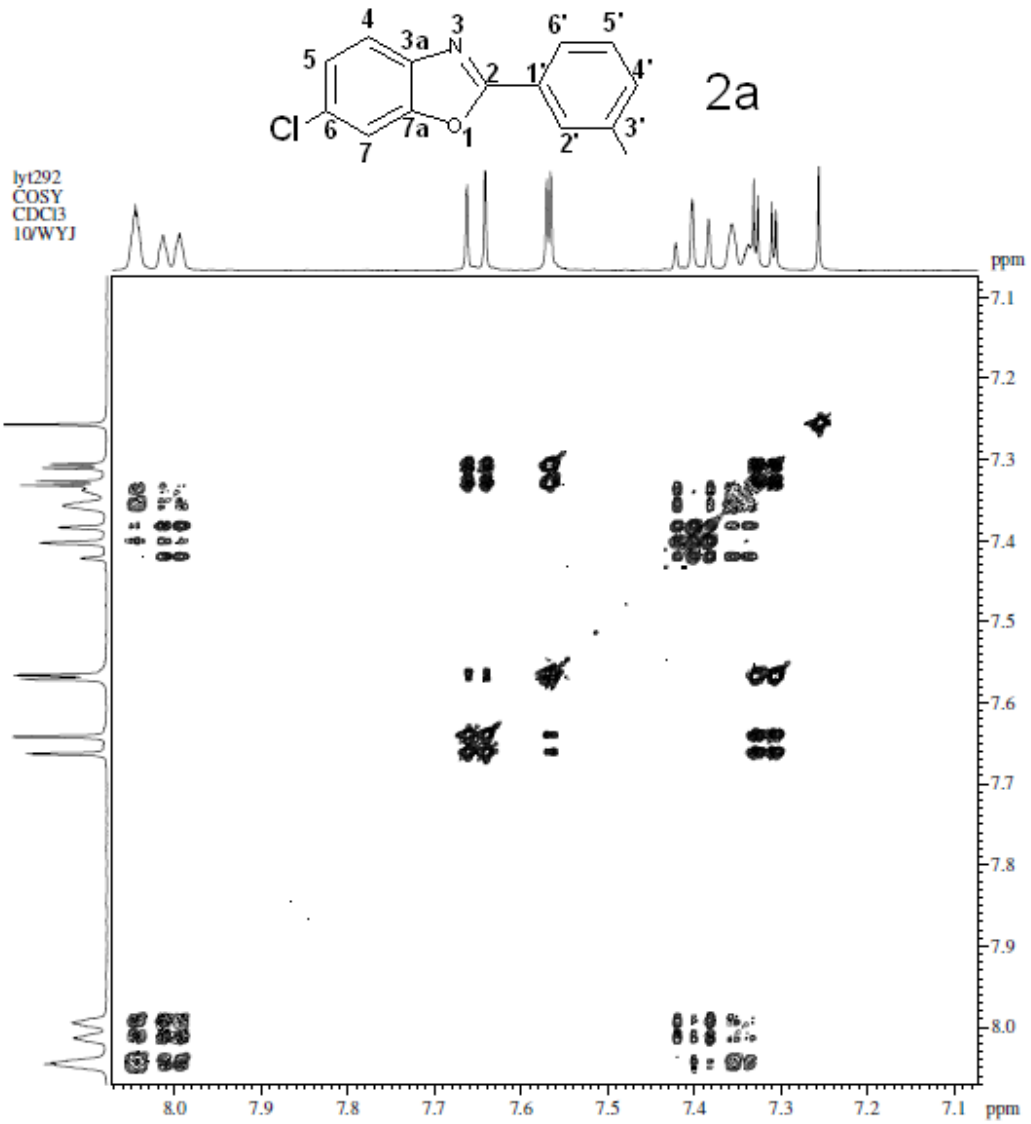

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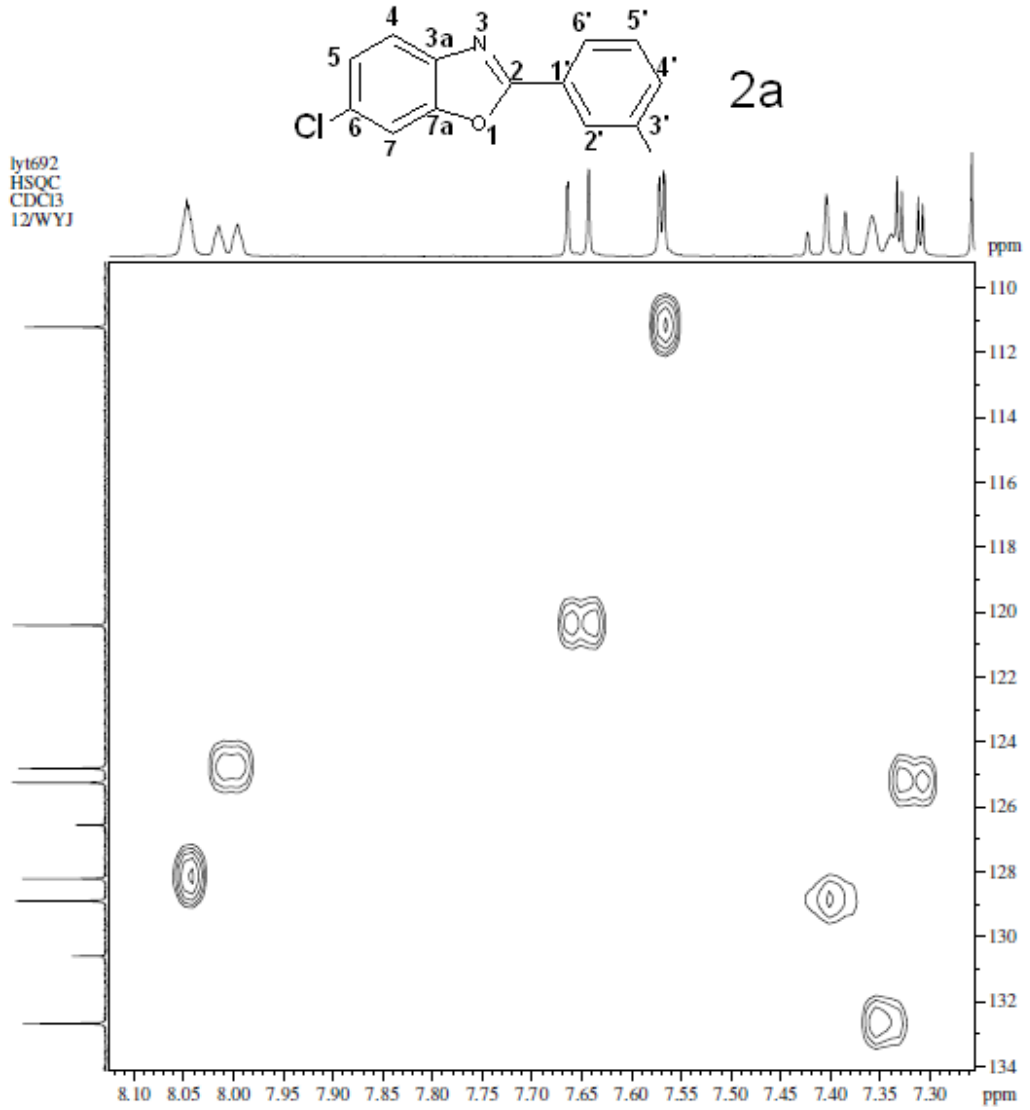

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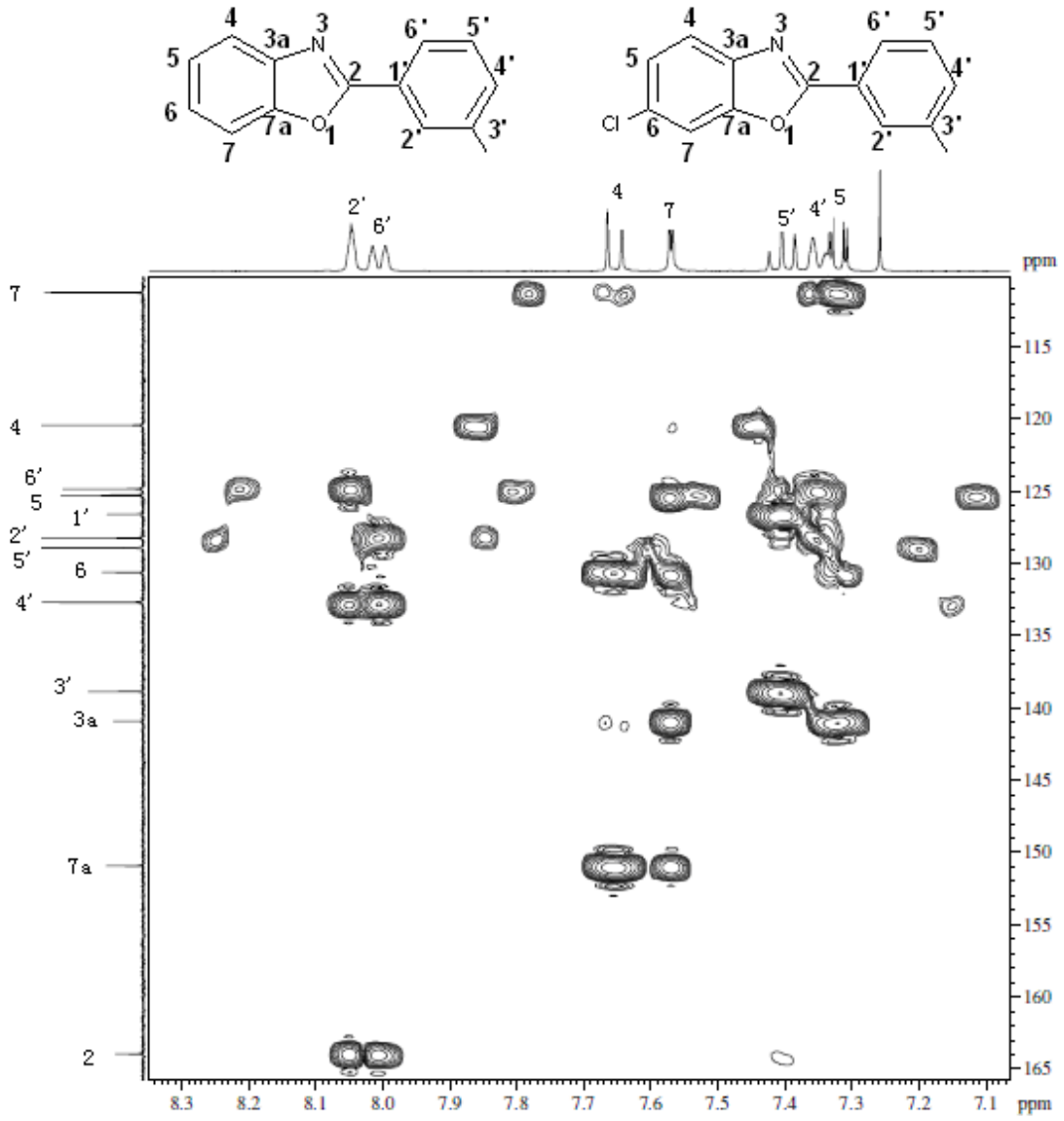

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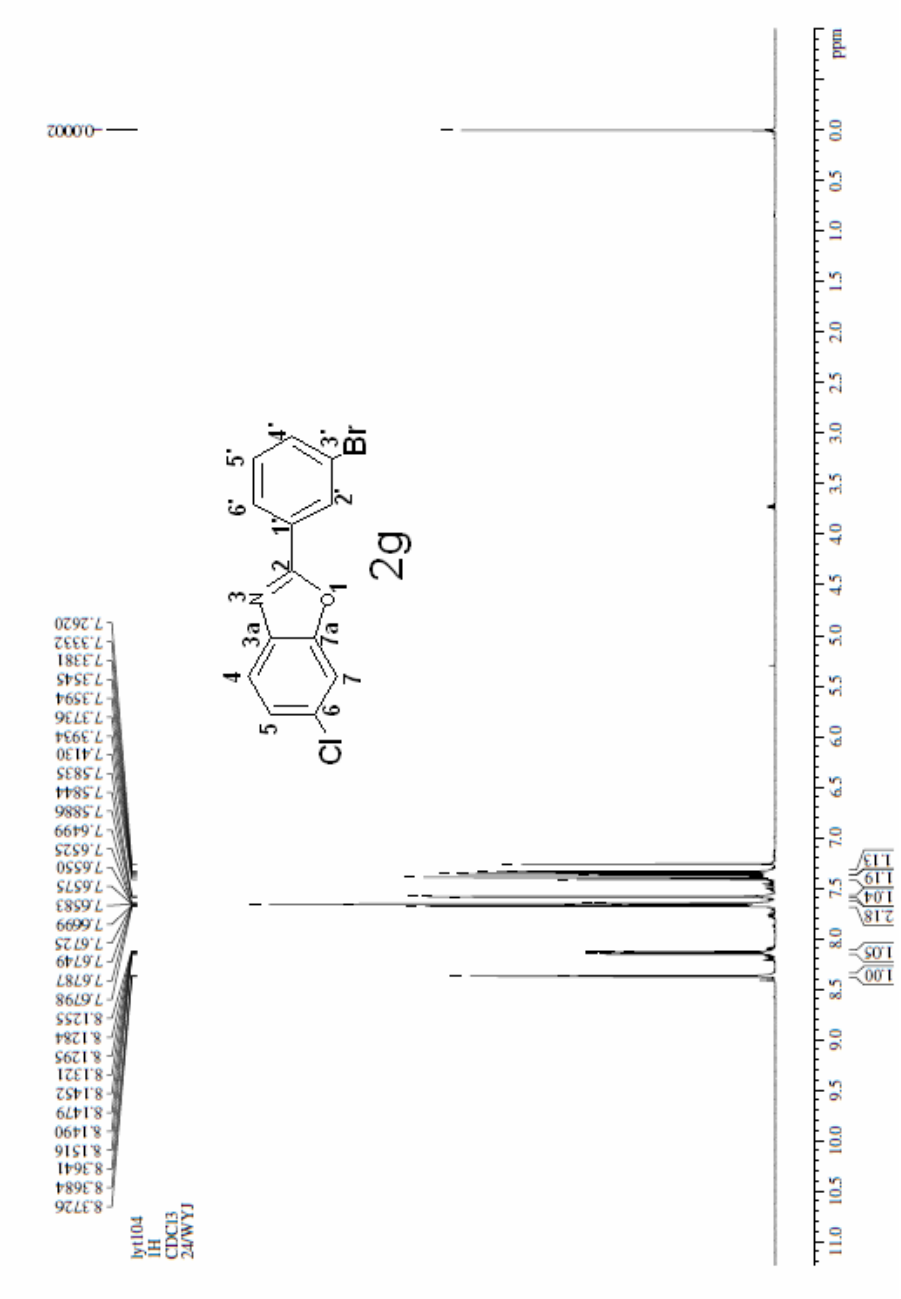

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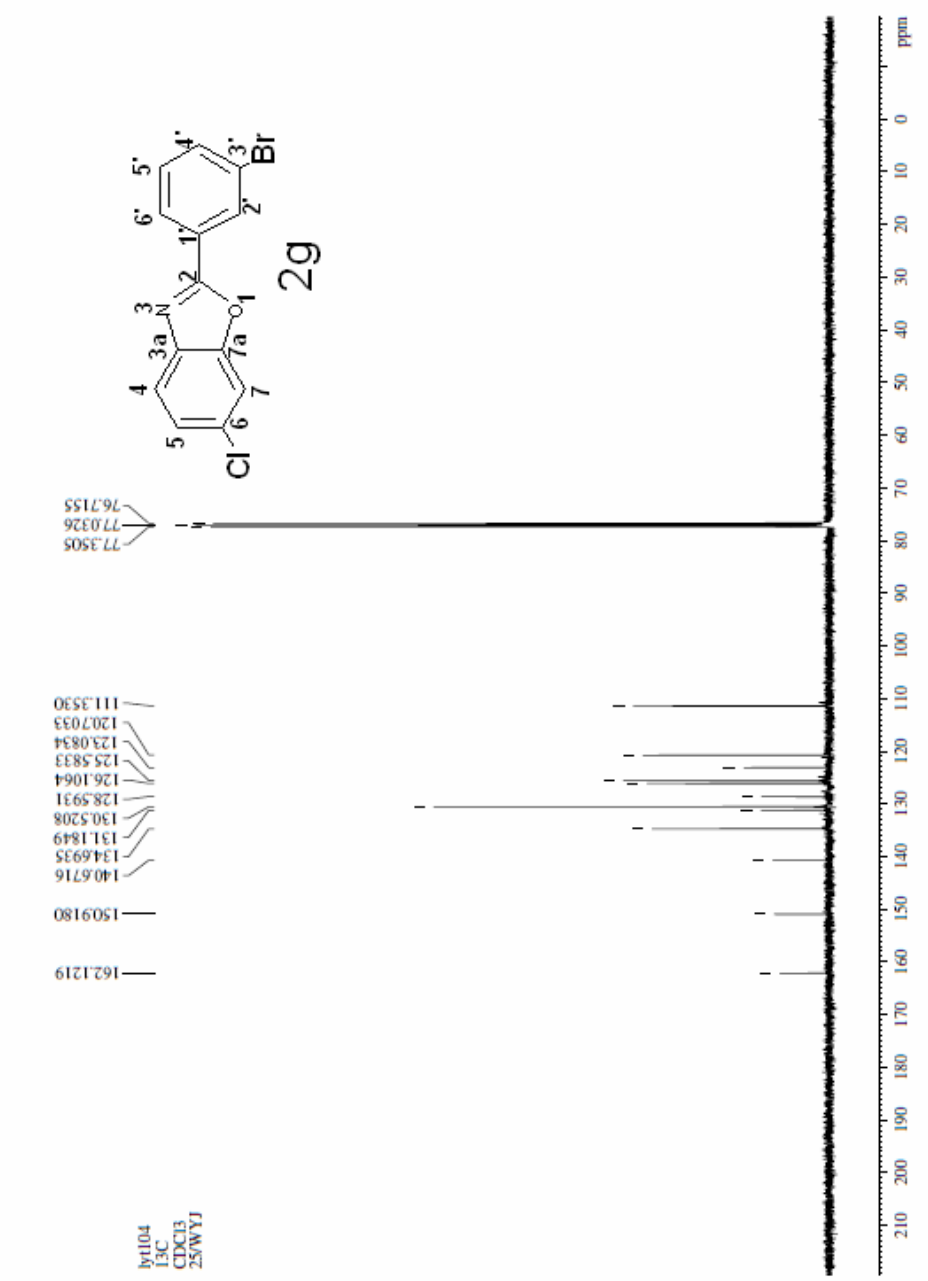

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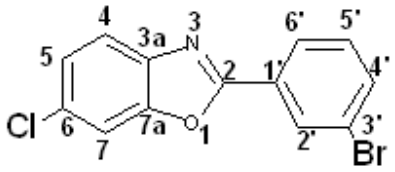

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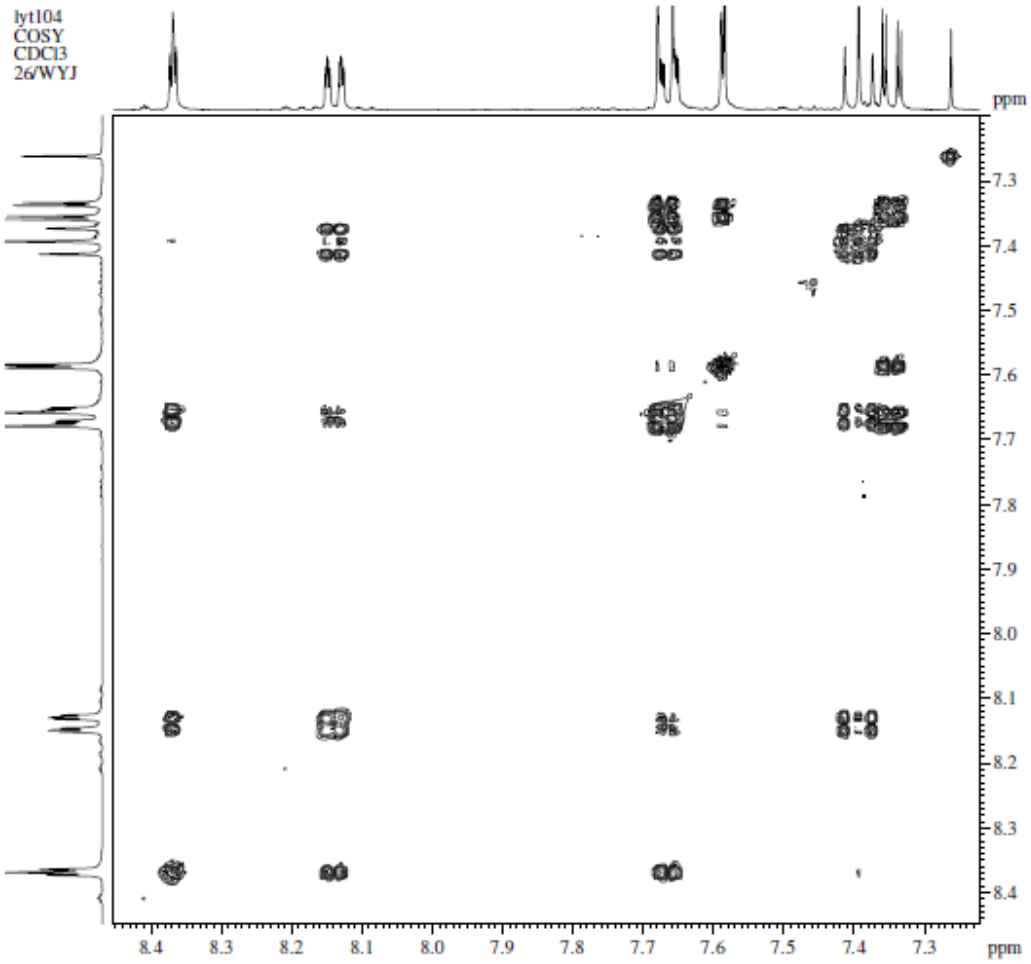

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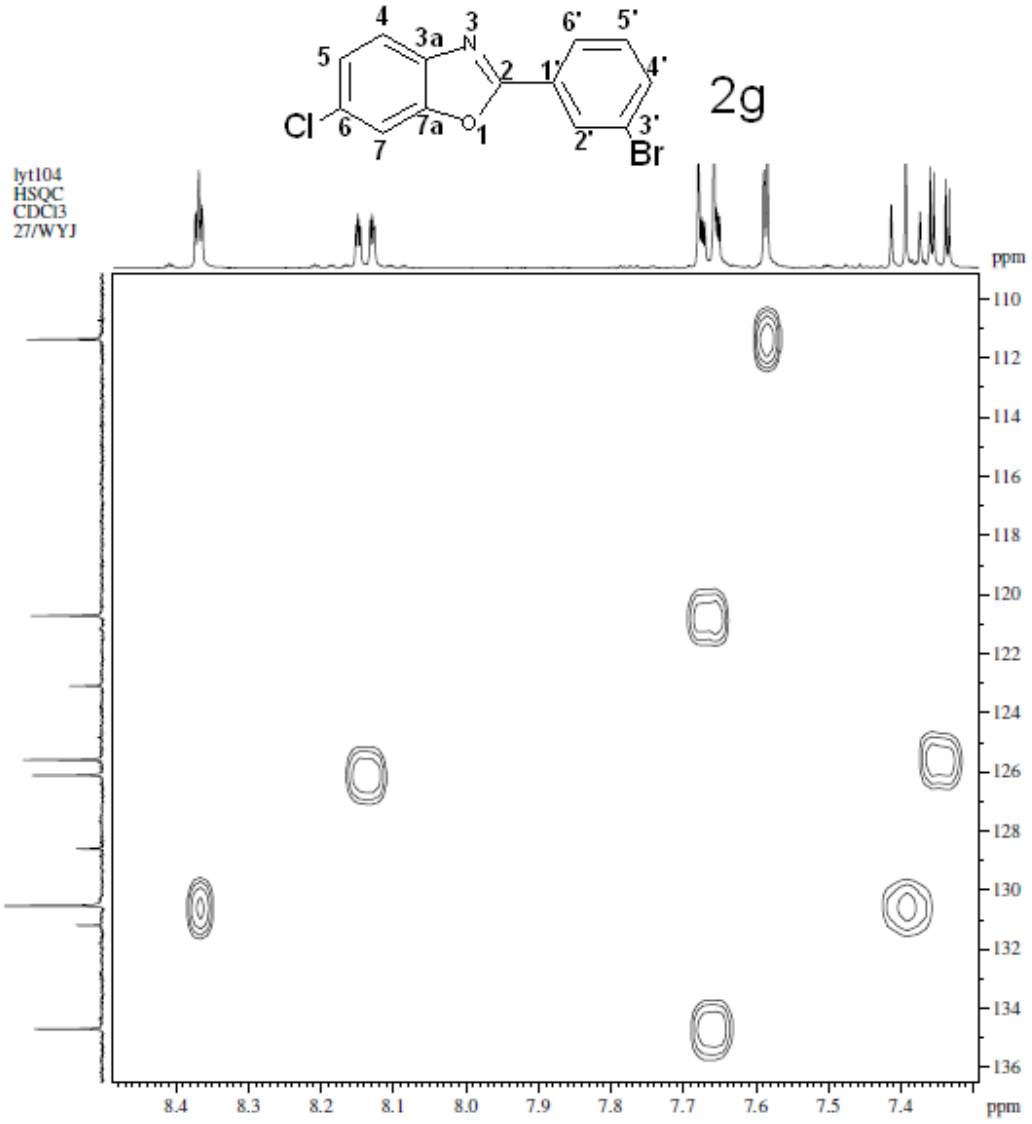

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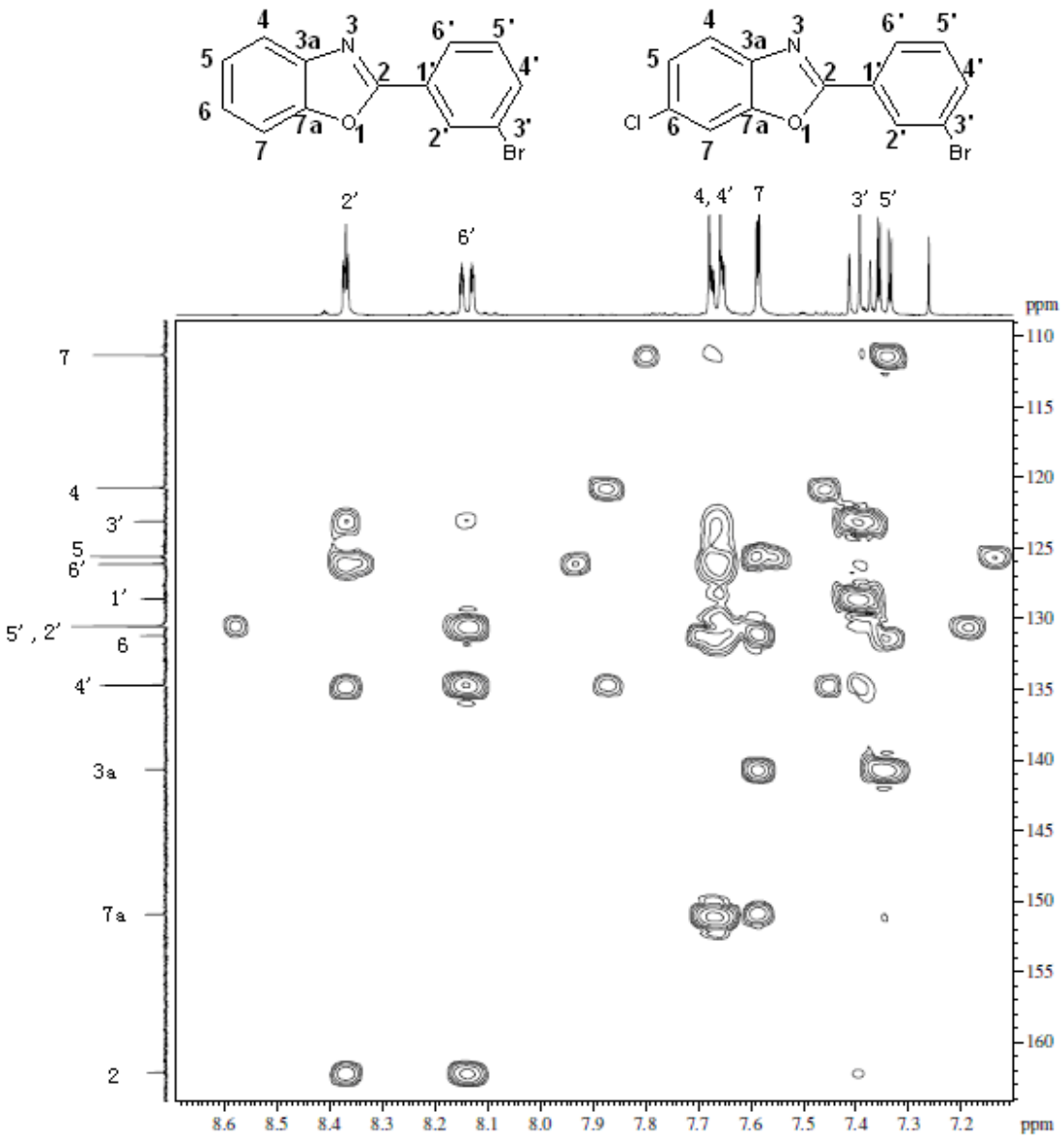

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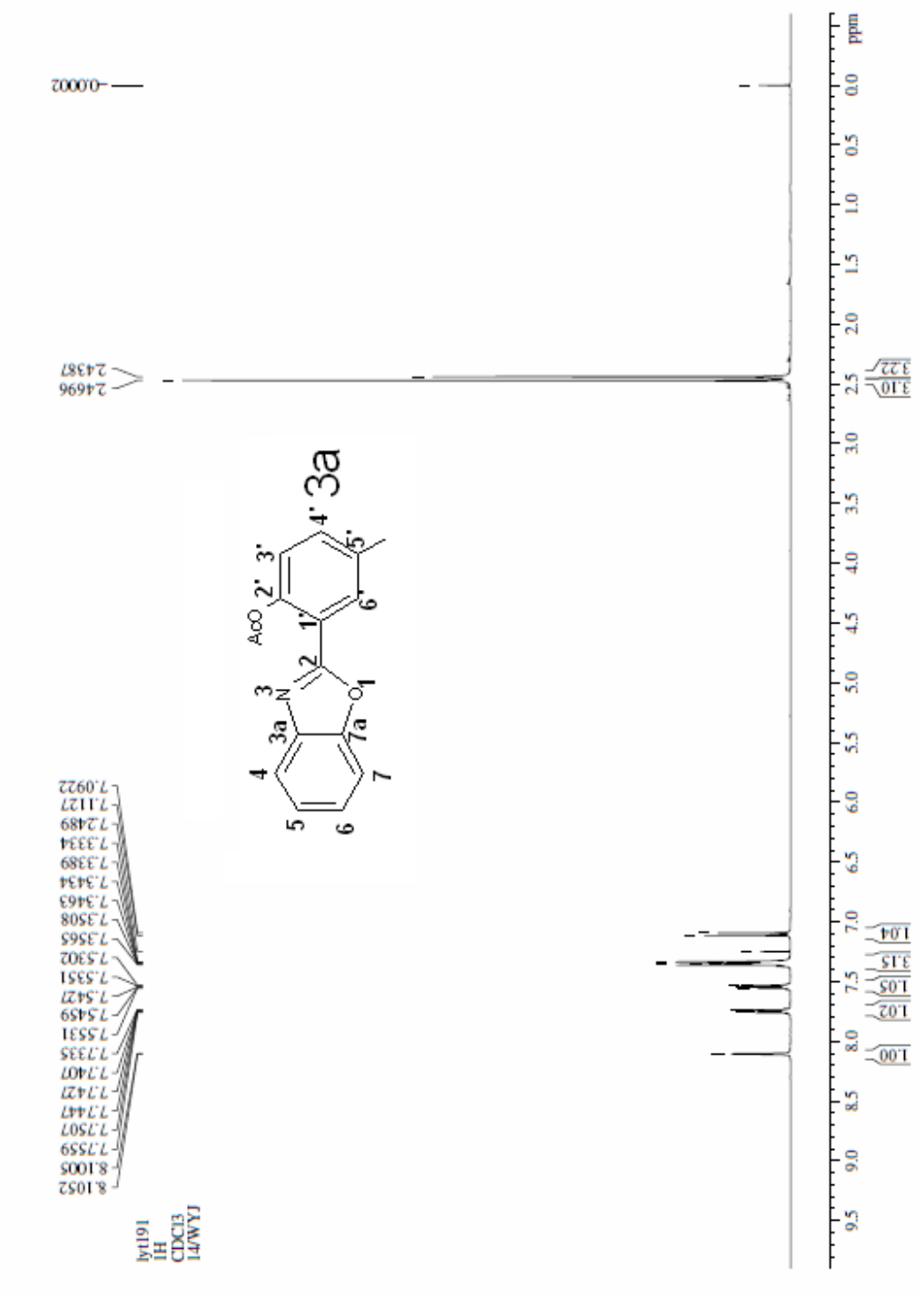

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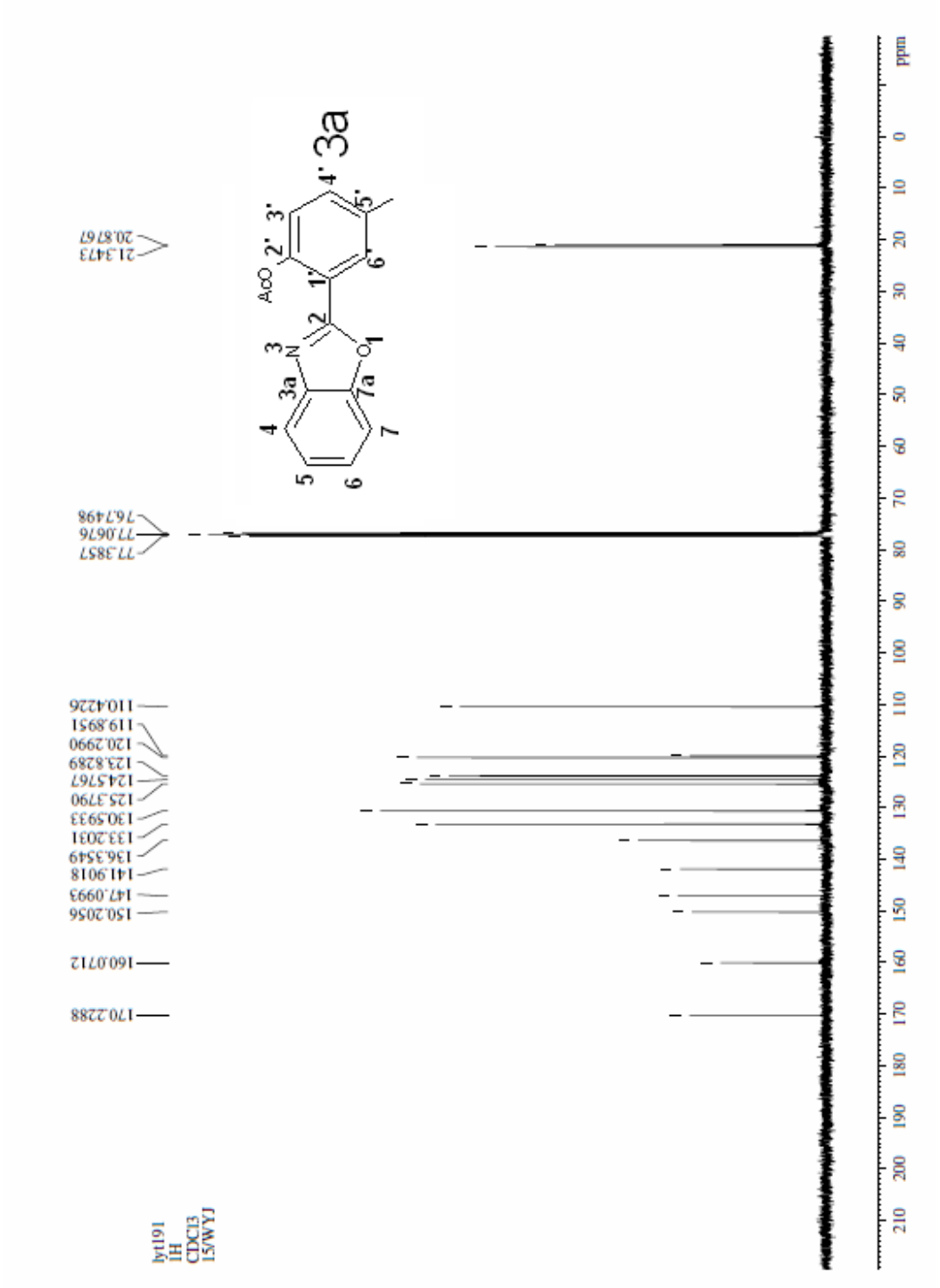

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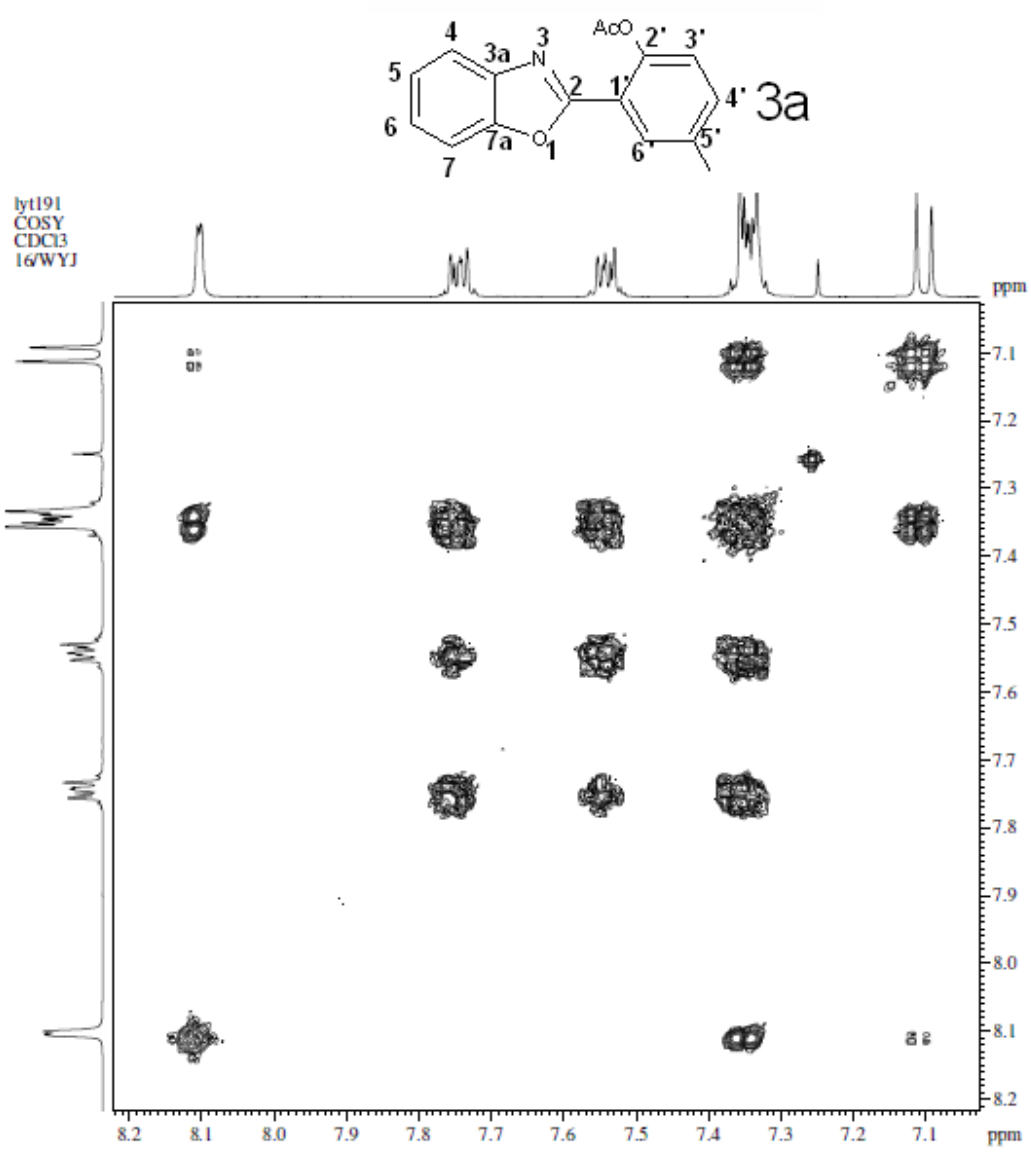

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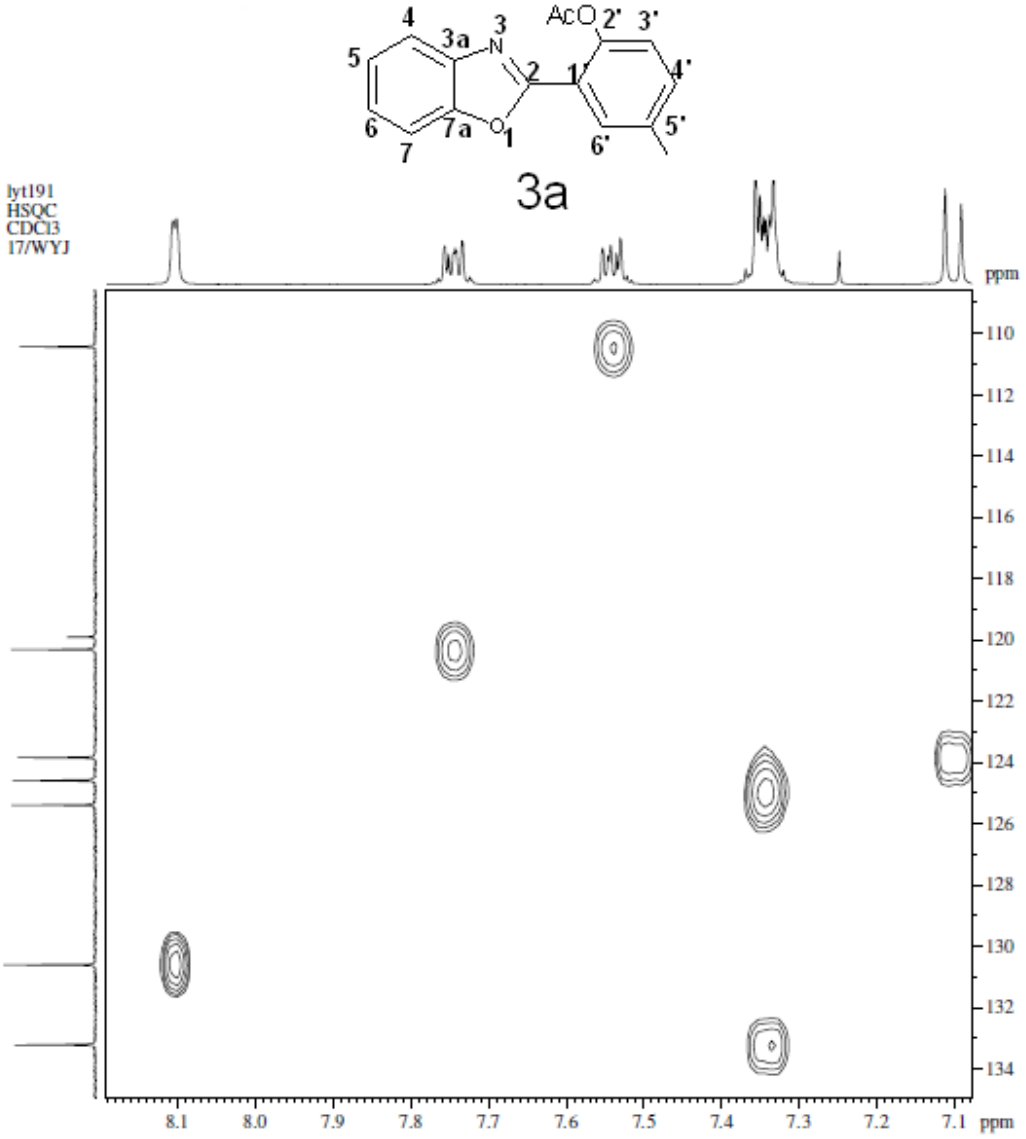

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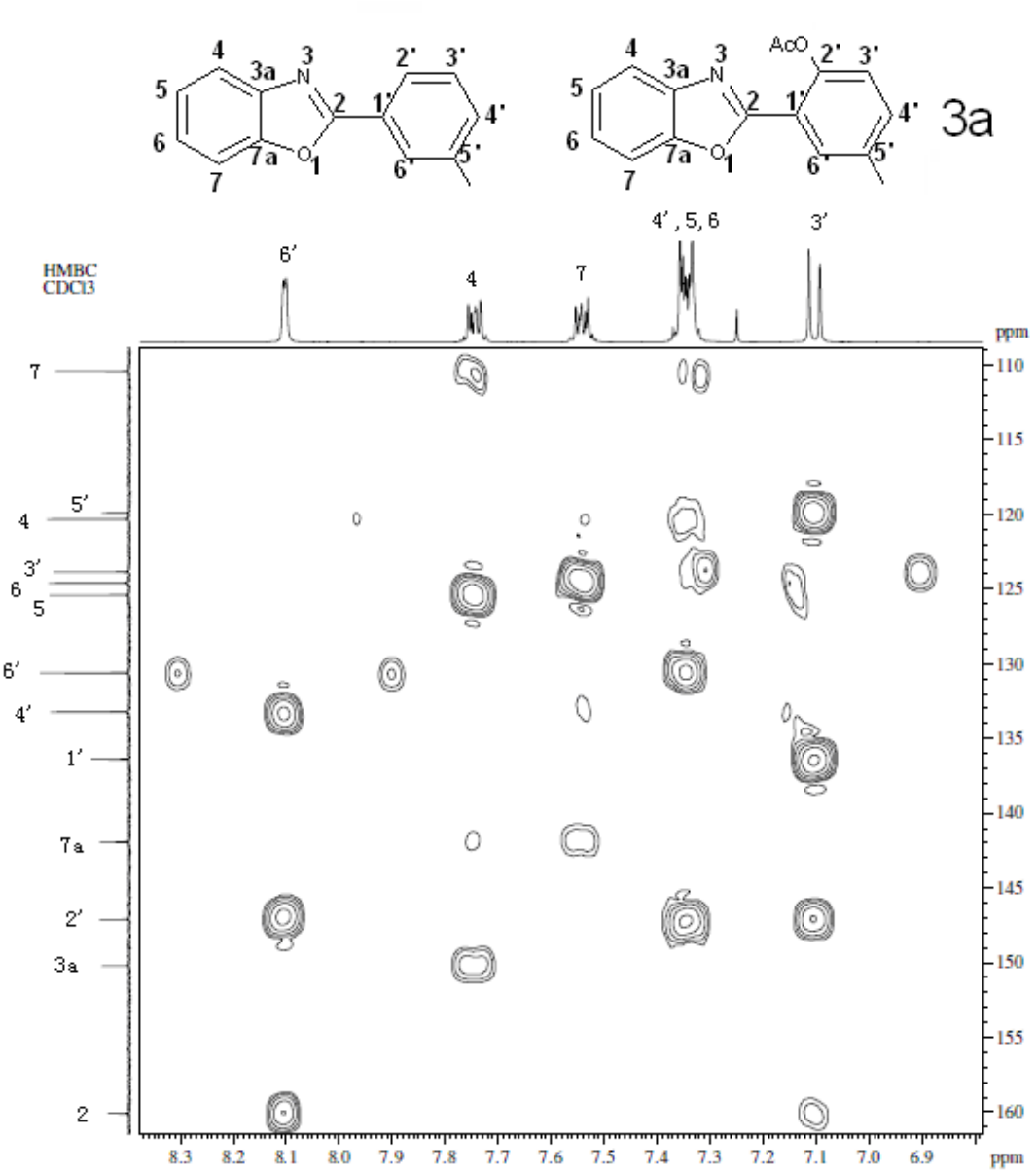

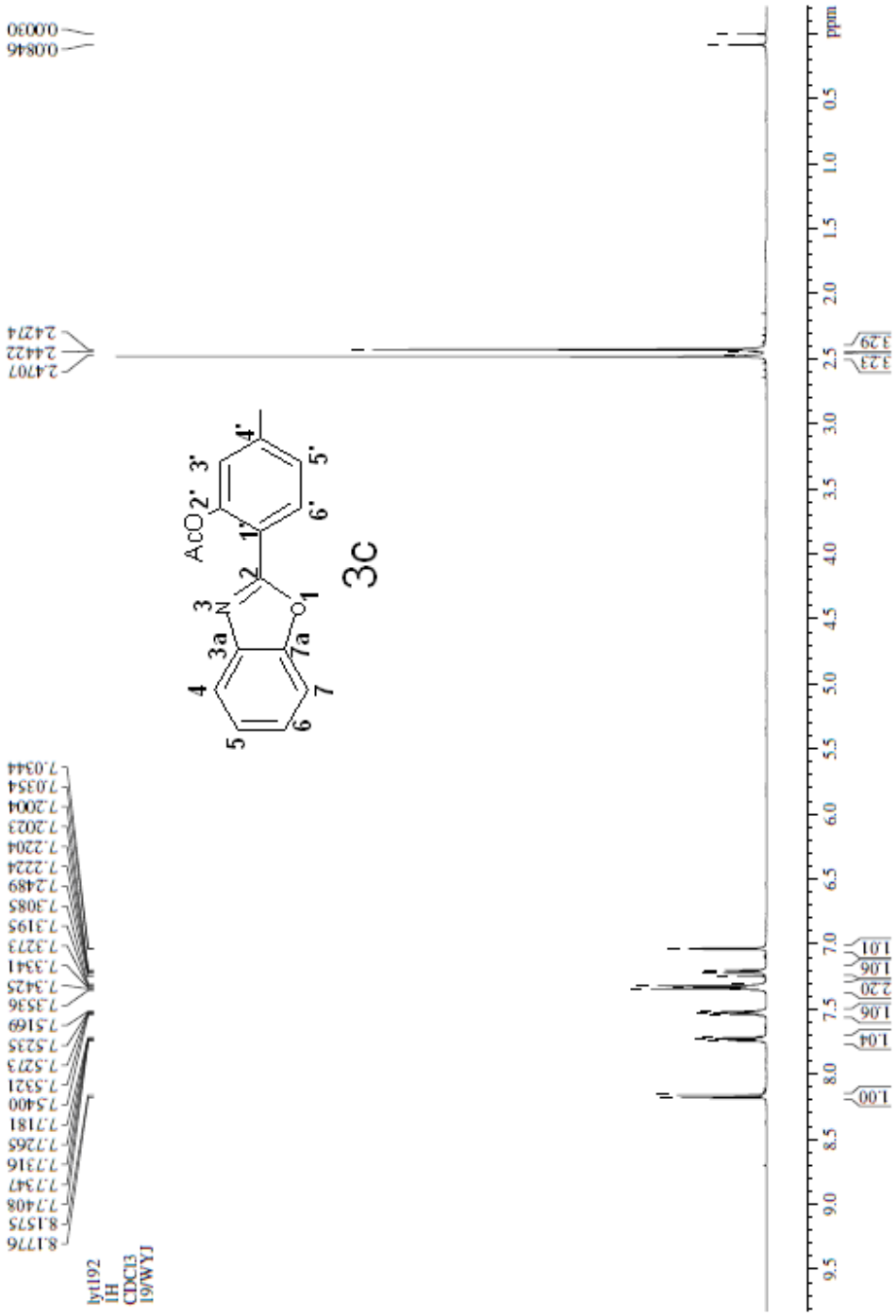
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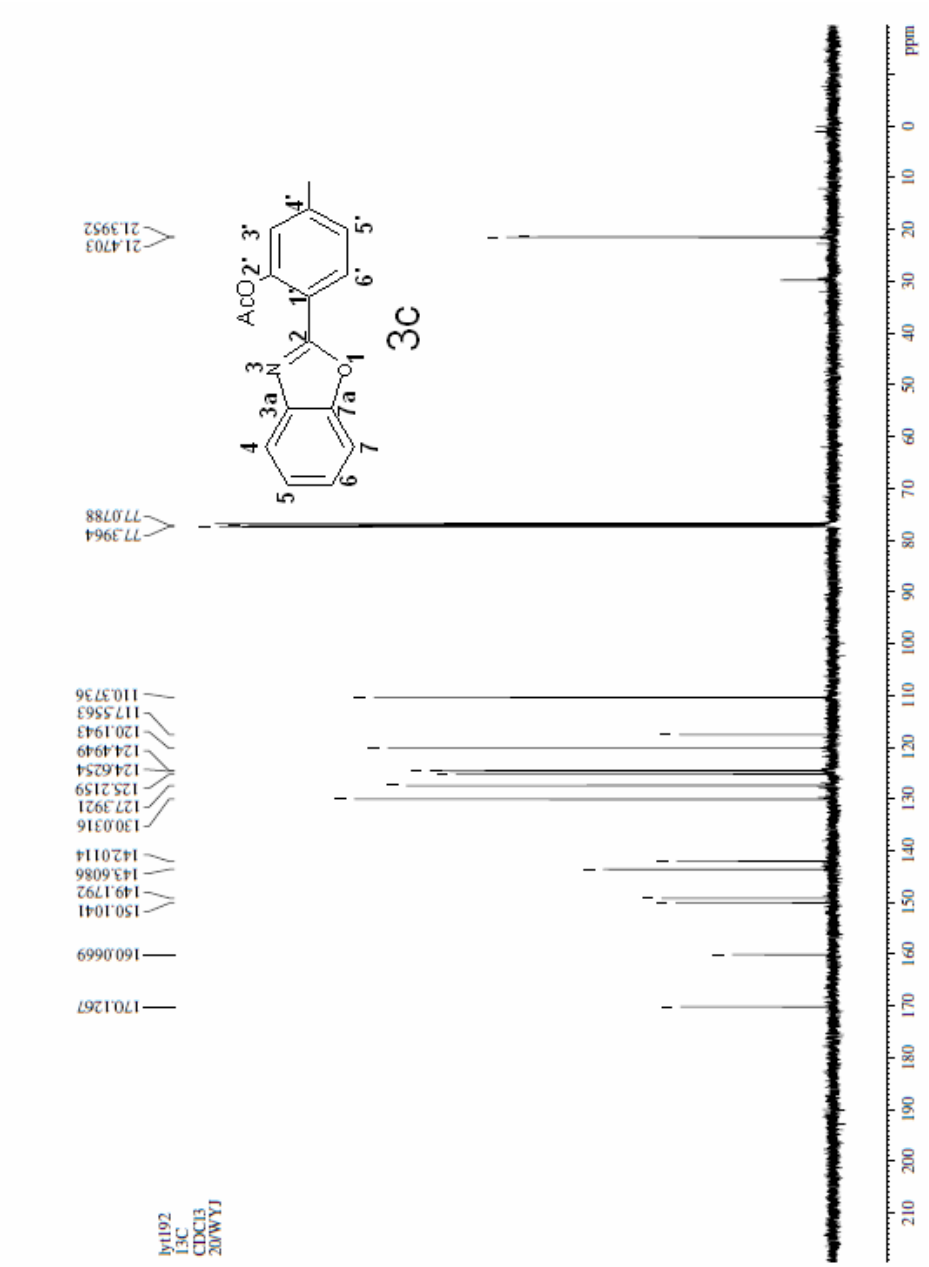

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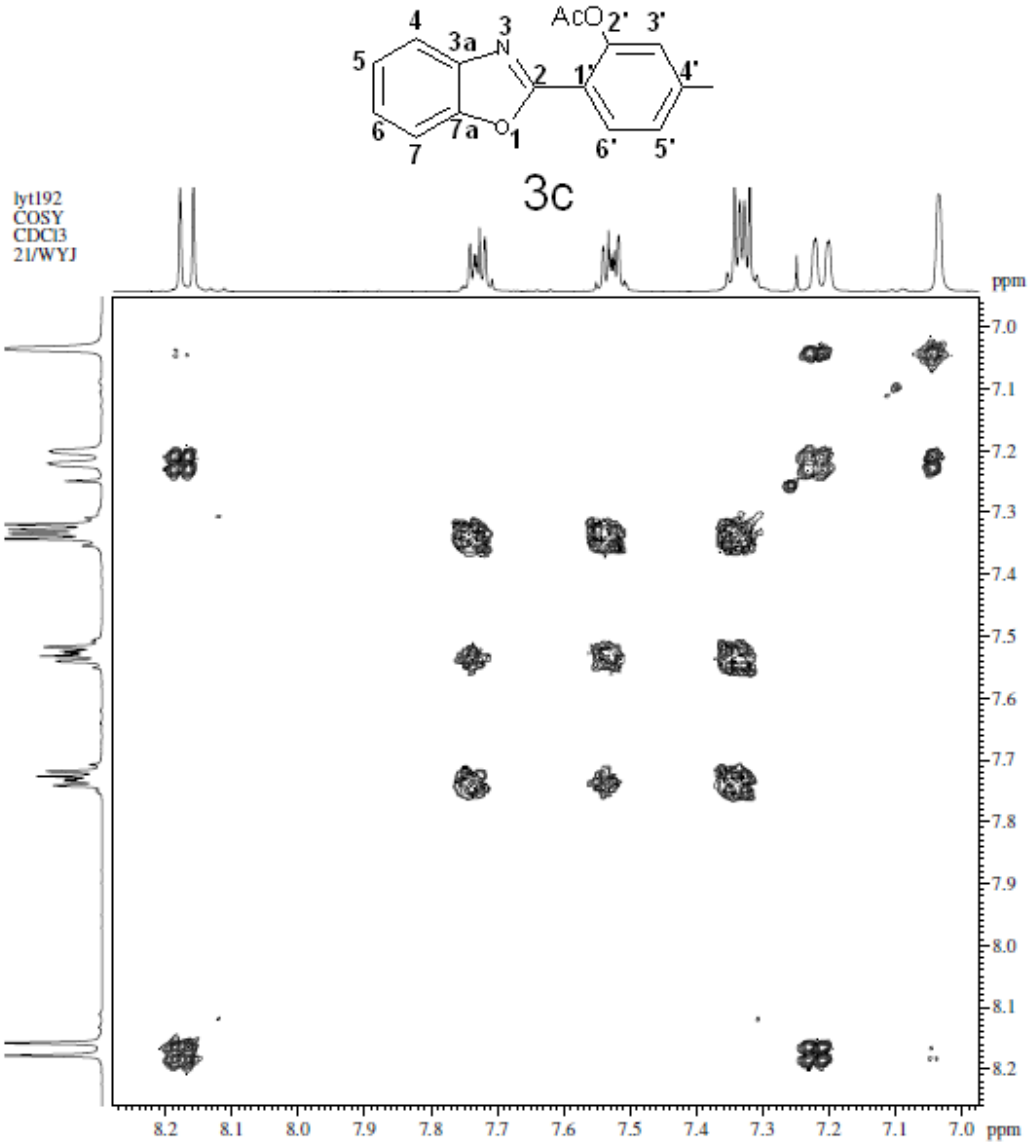

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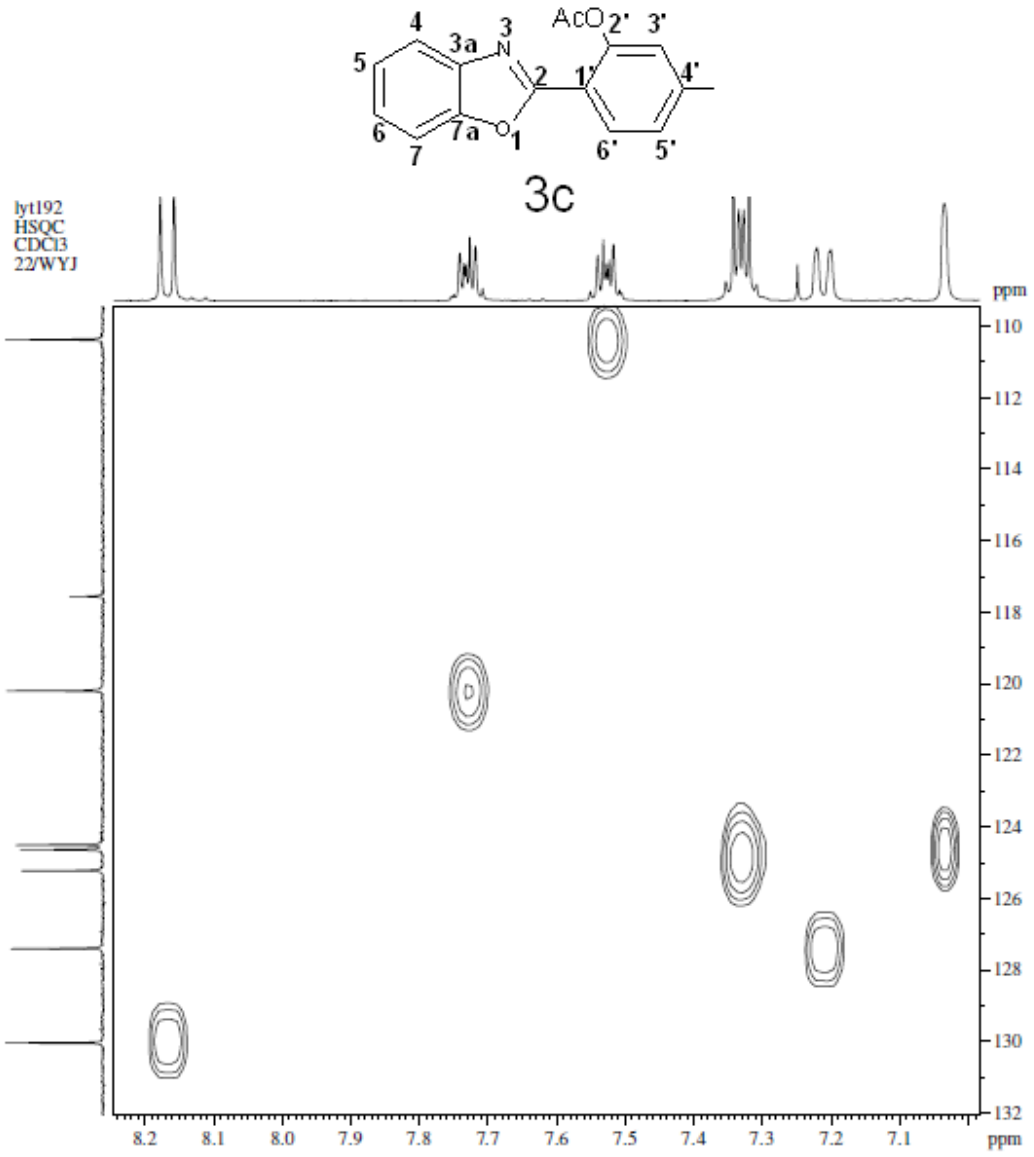

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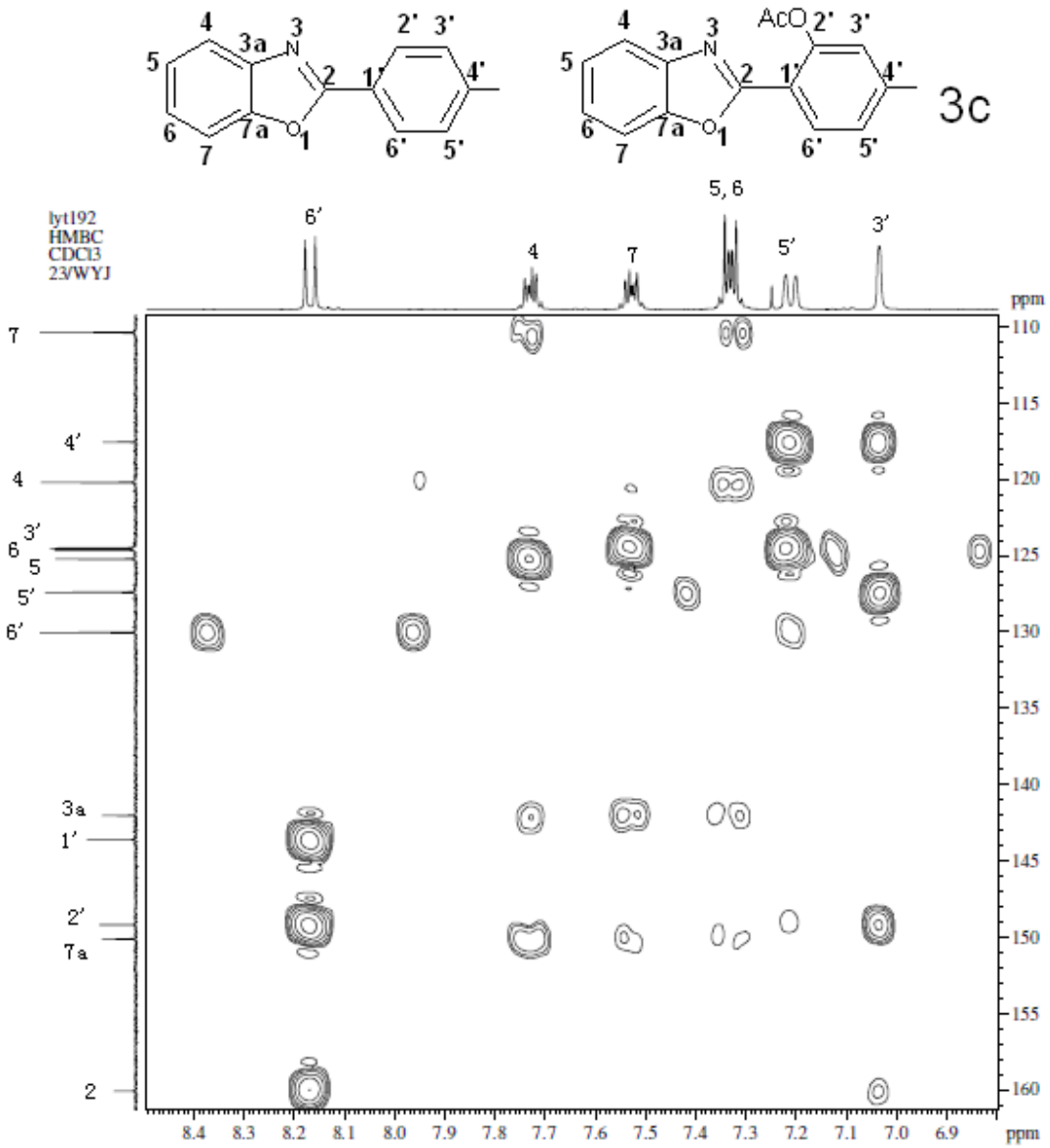

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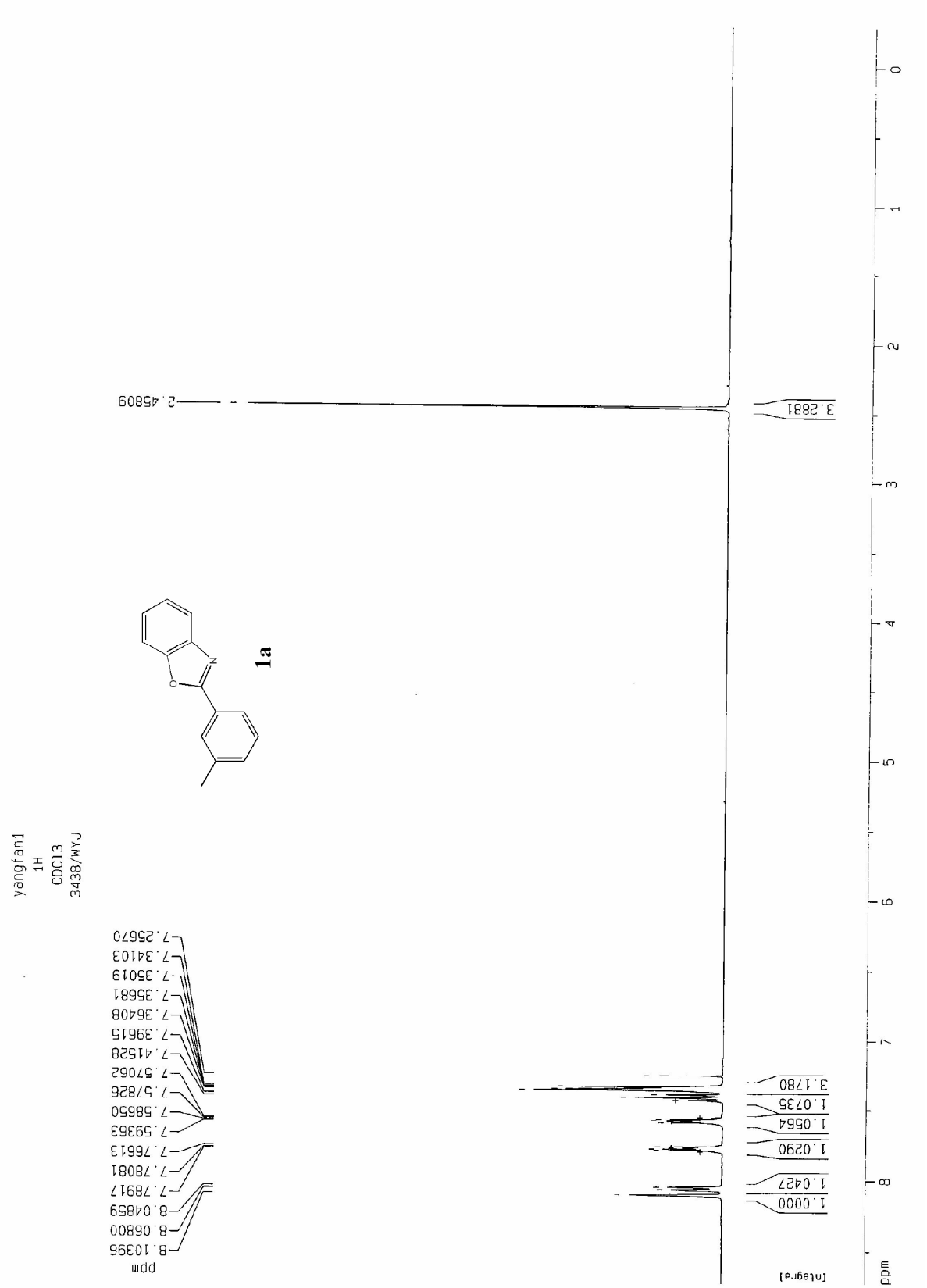
^{1}H and ^{13}C NMR spectra for compounds 1a-1m, 2b-2f, 2h-2k and 3b, 3d-3f



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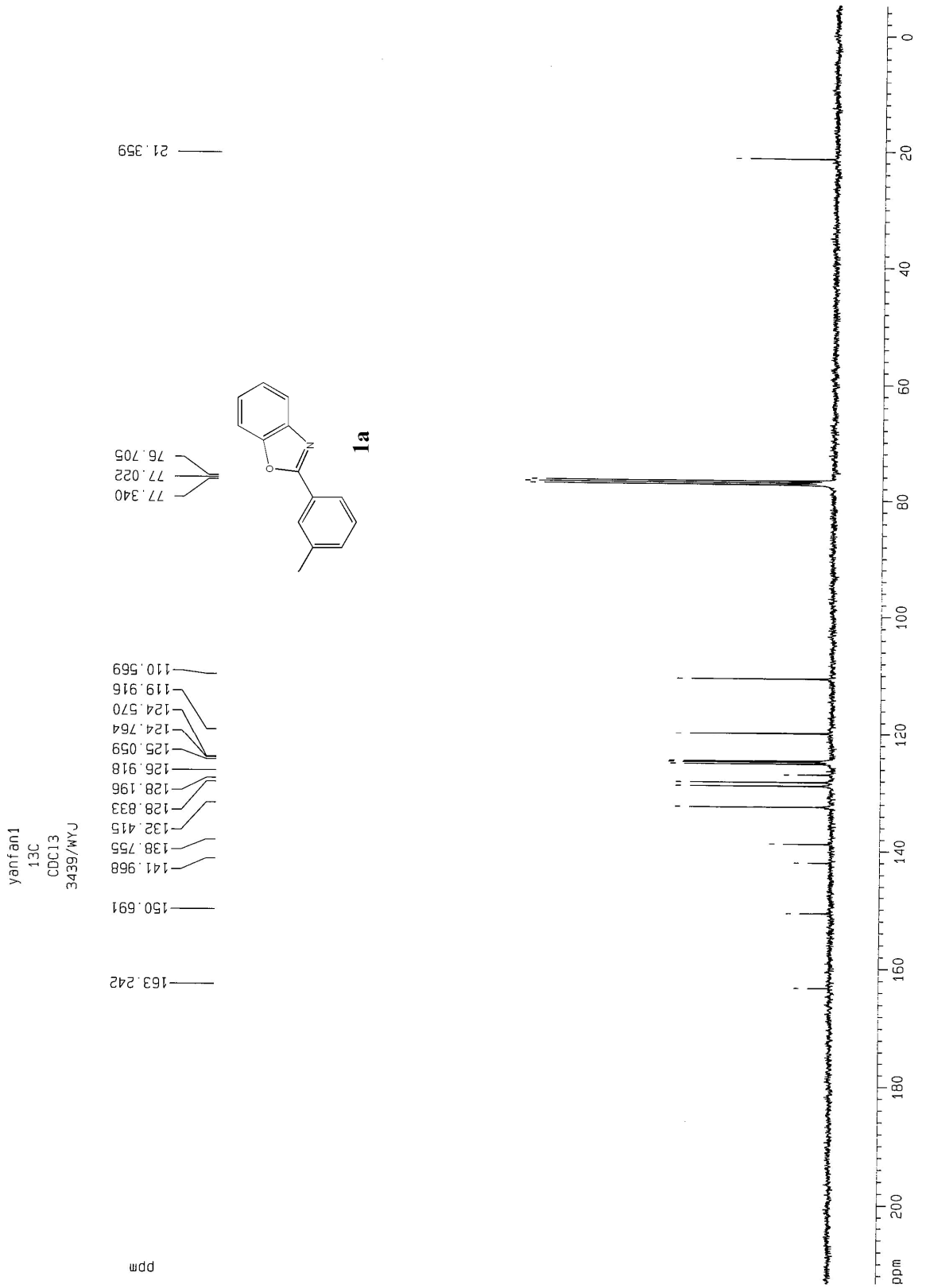

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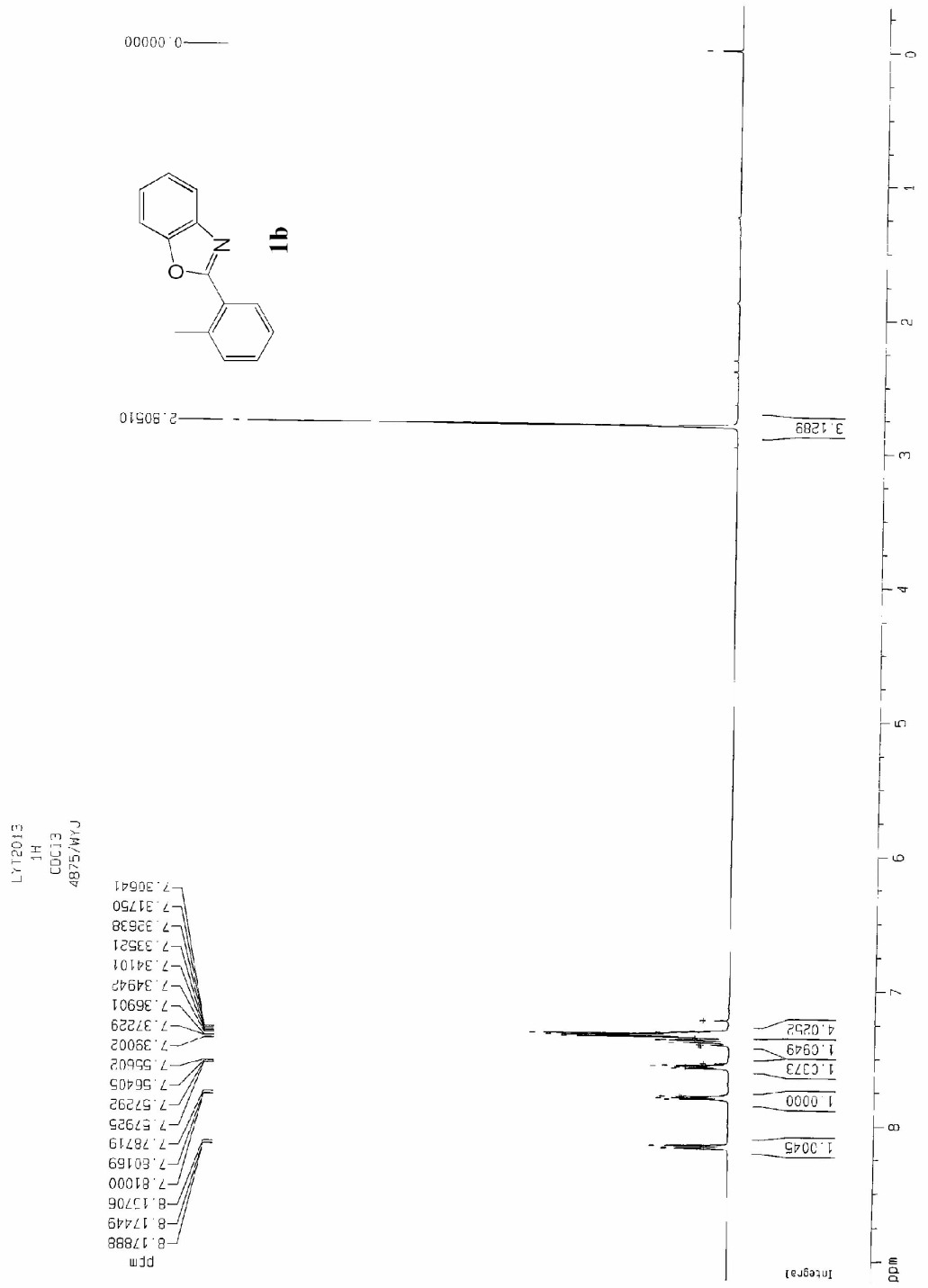

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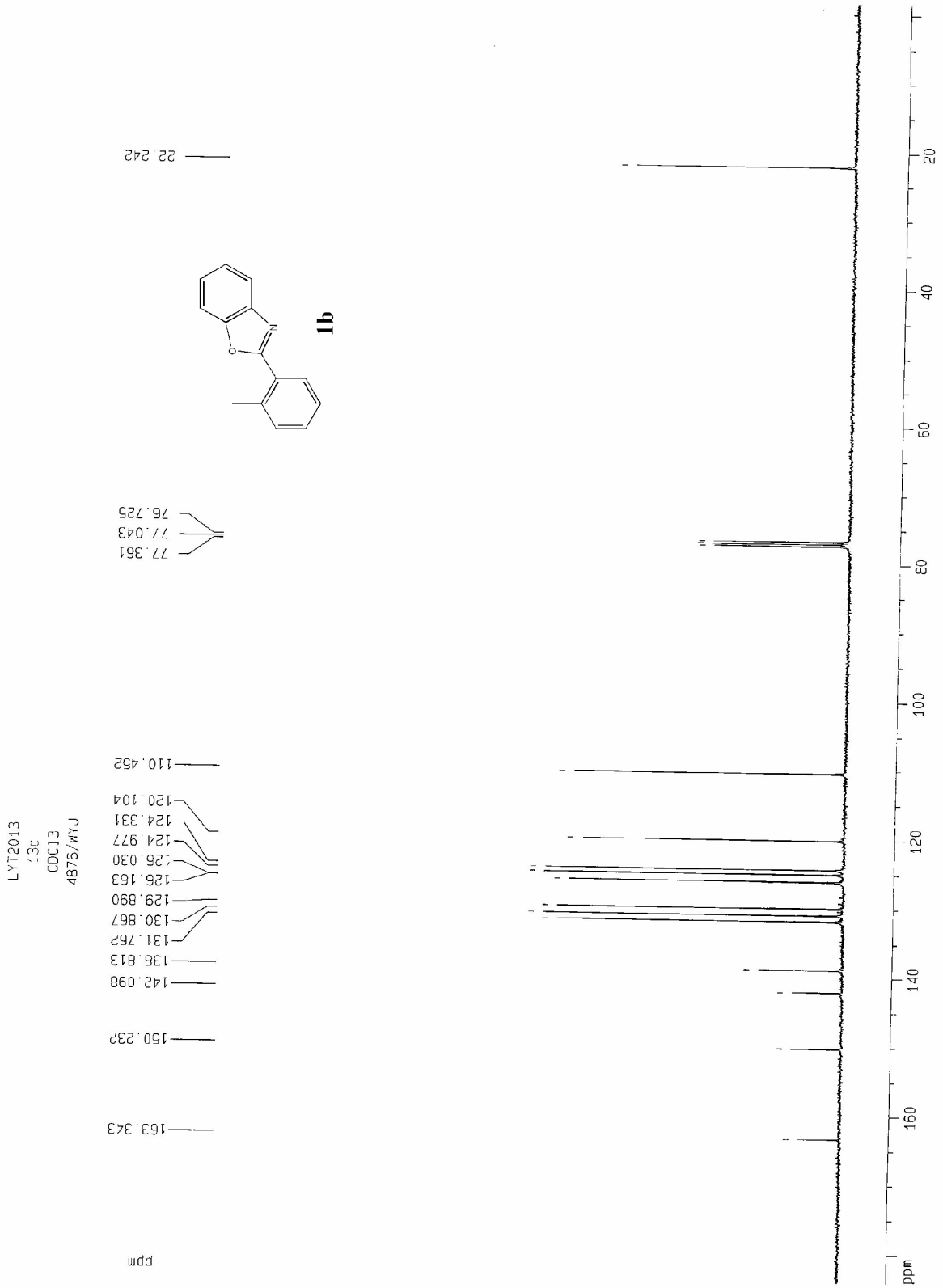

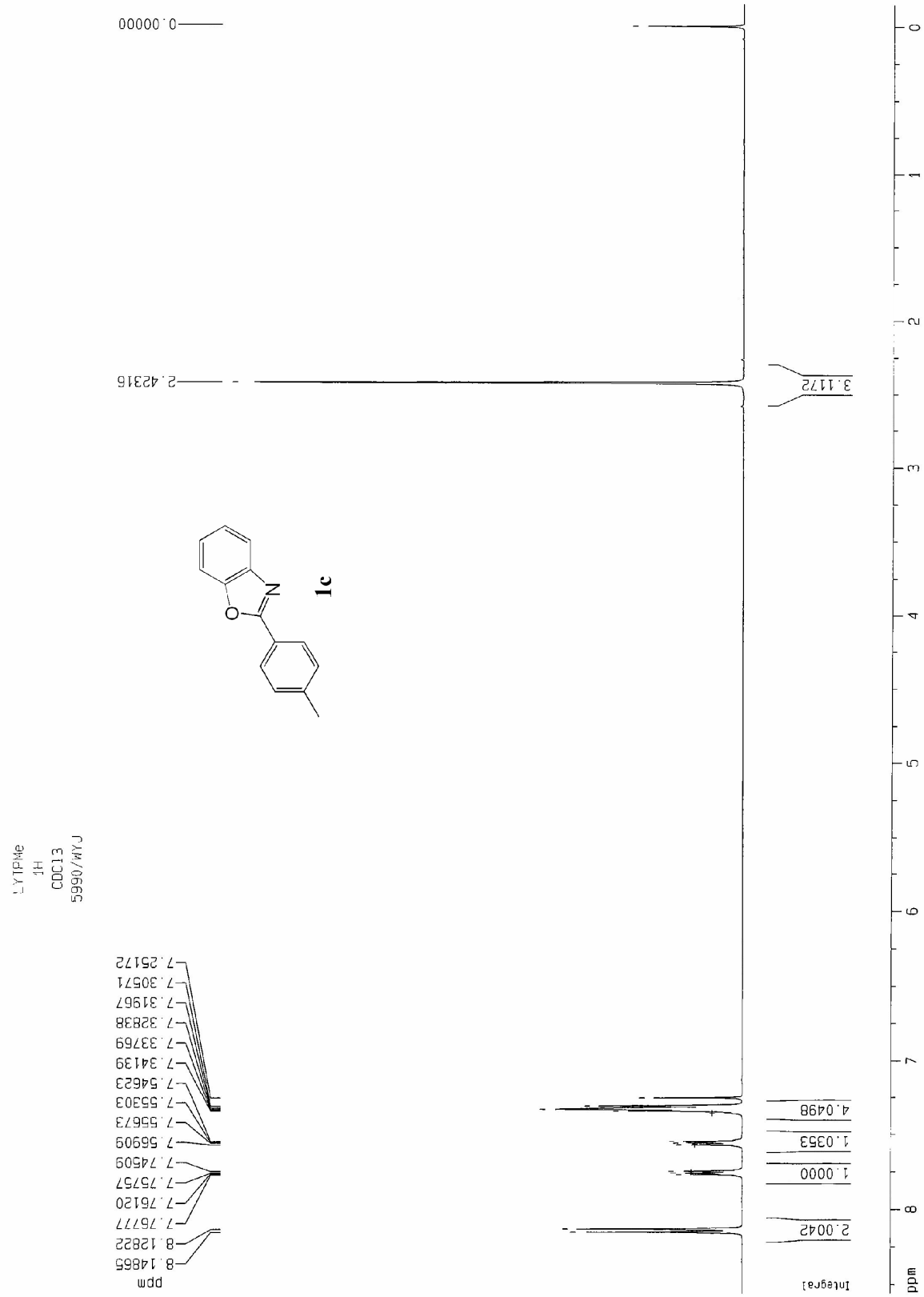
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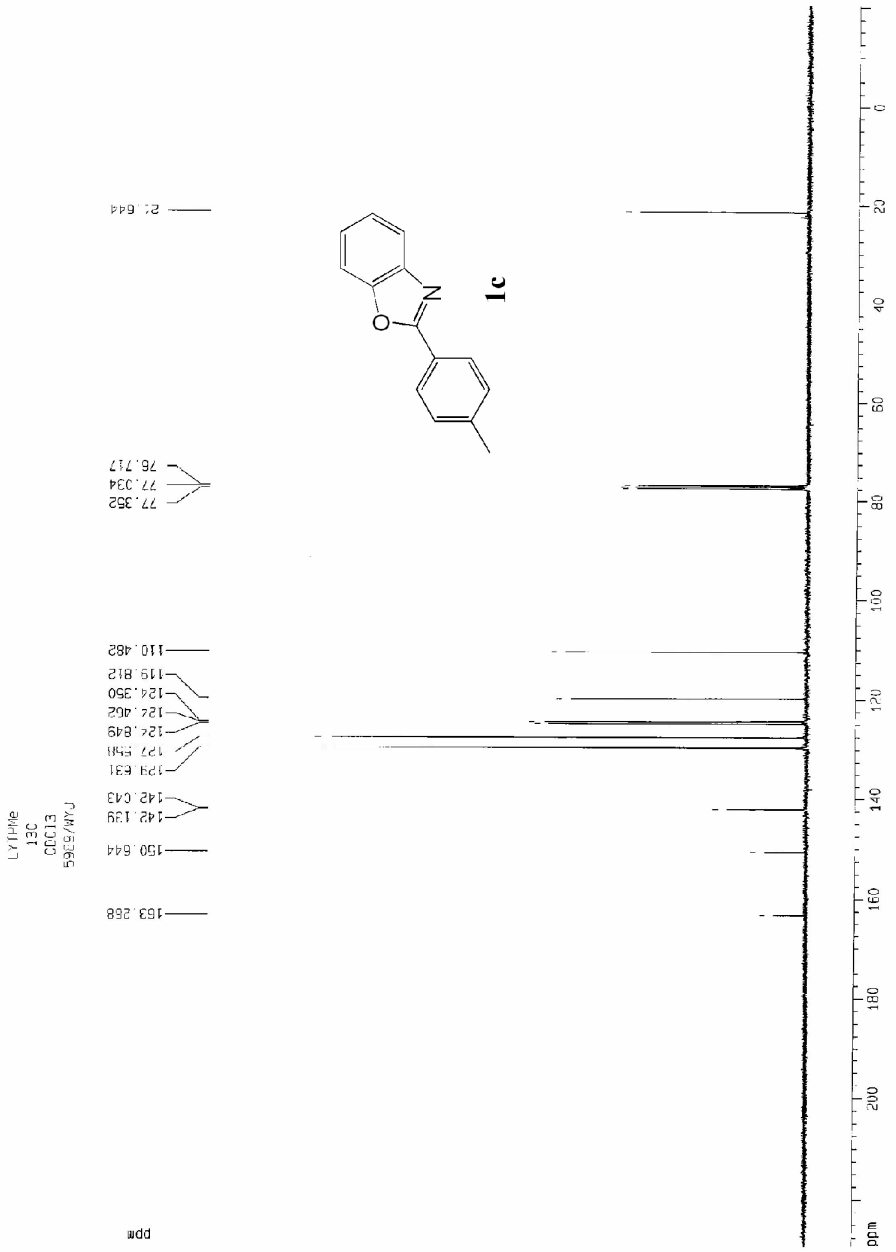

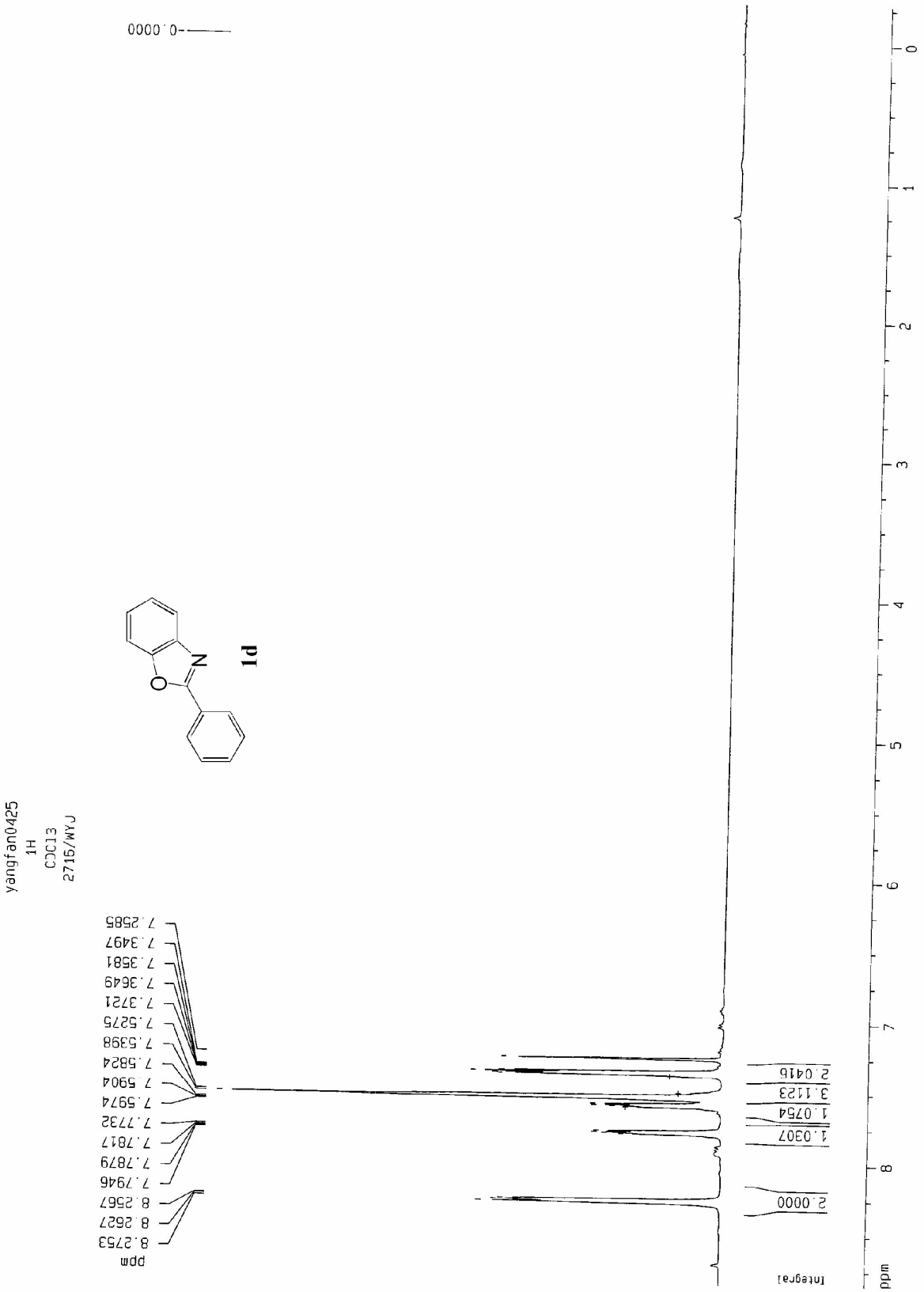
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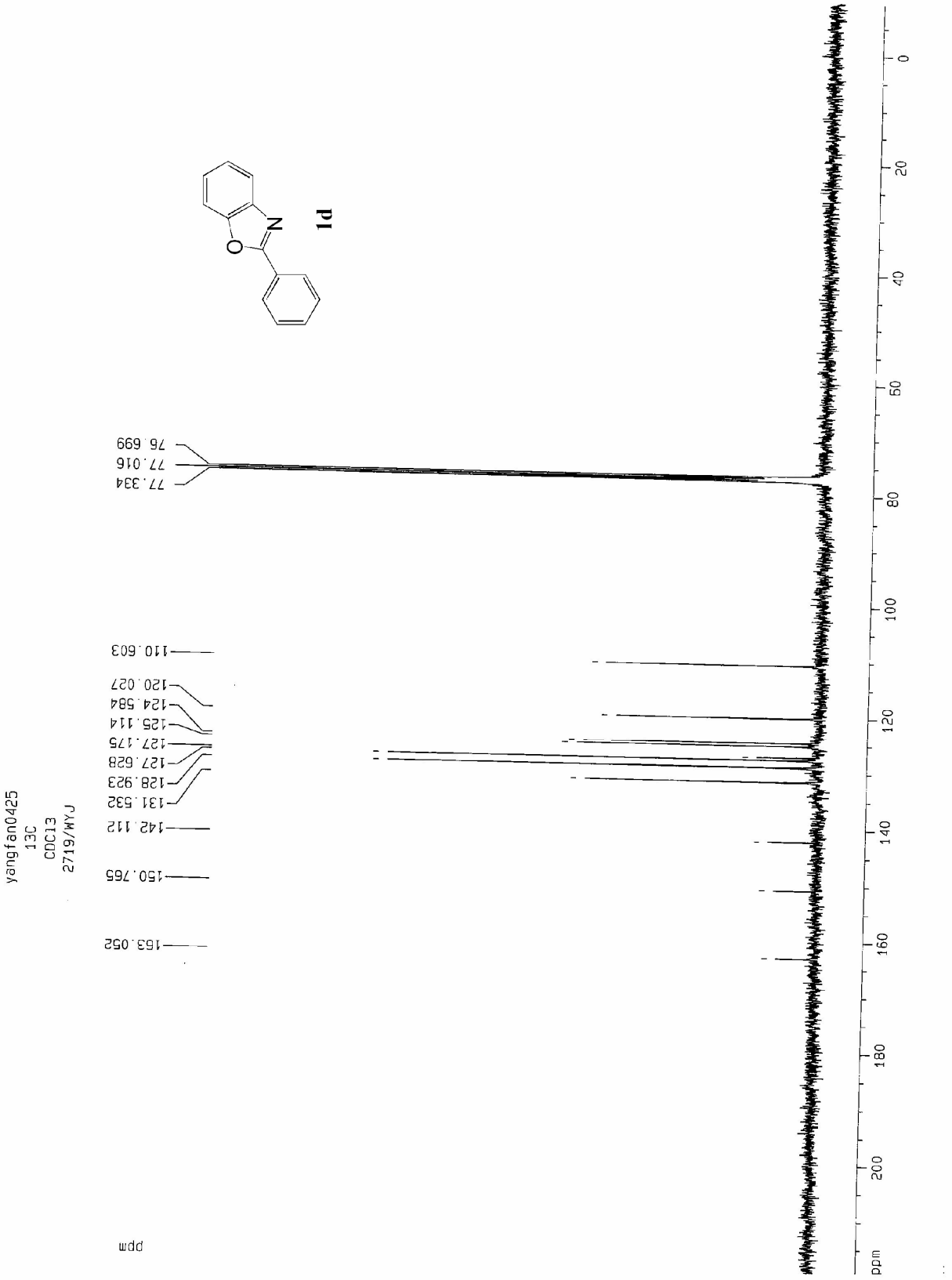


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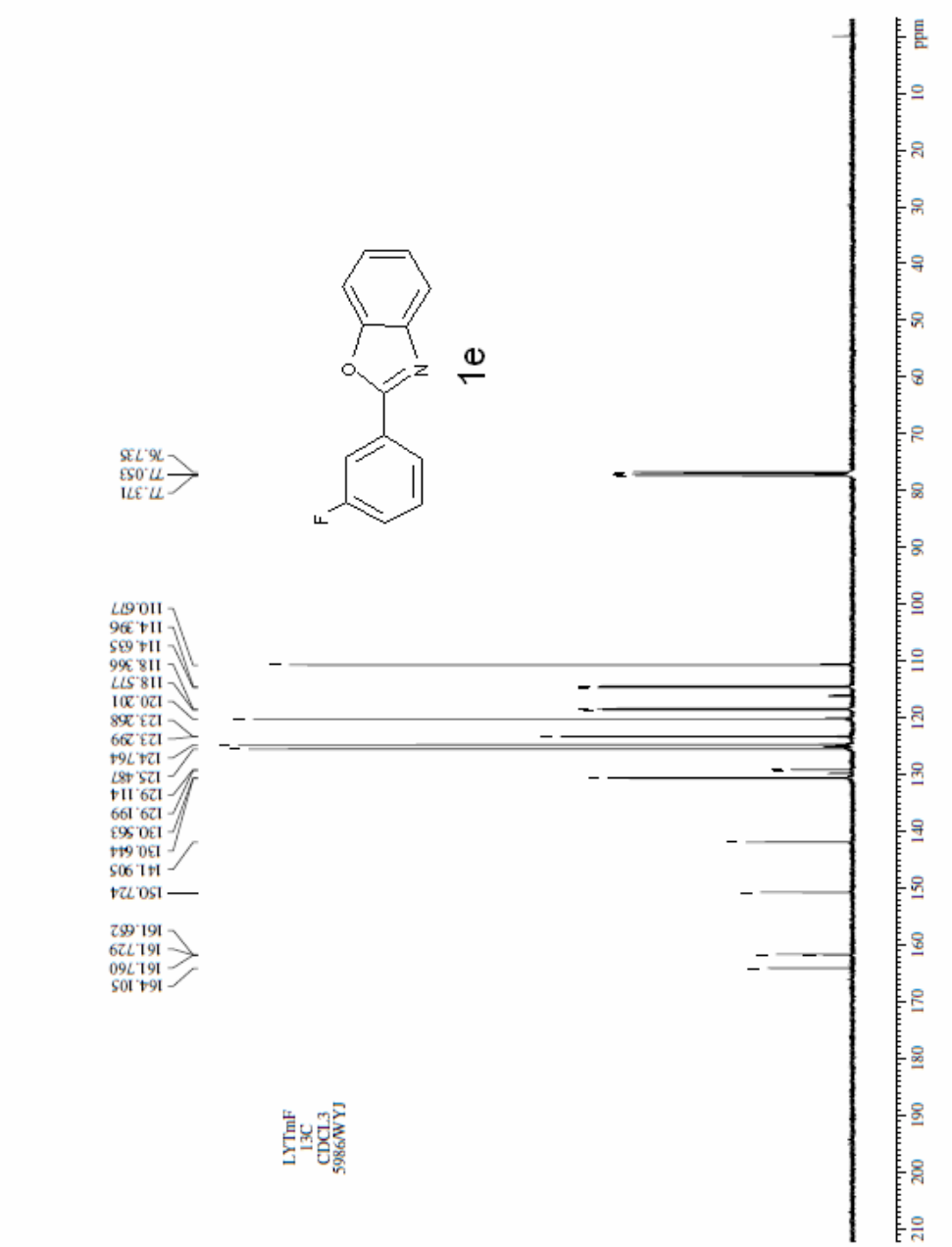

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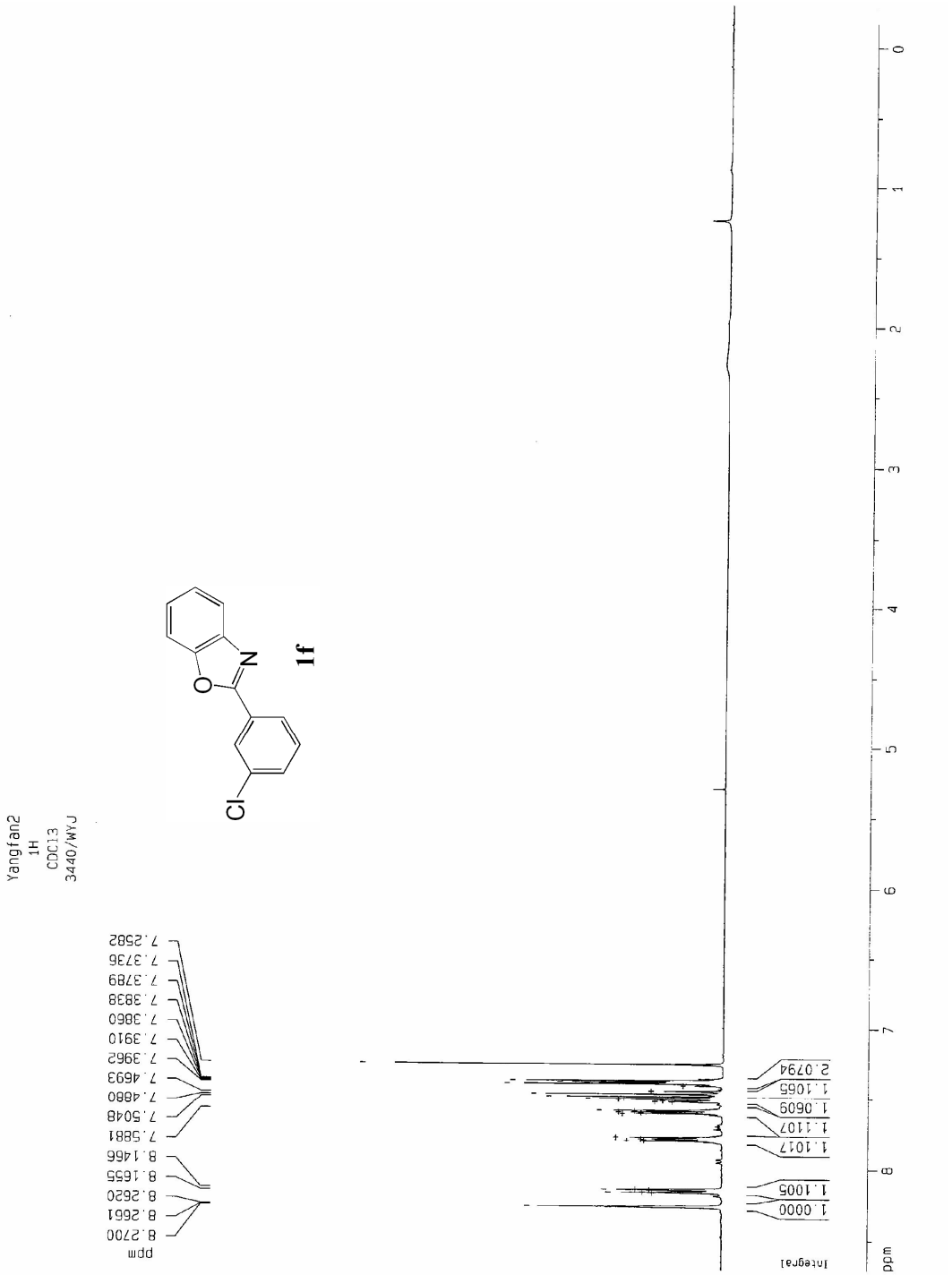

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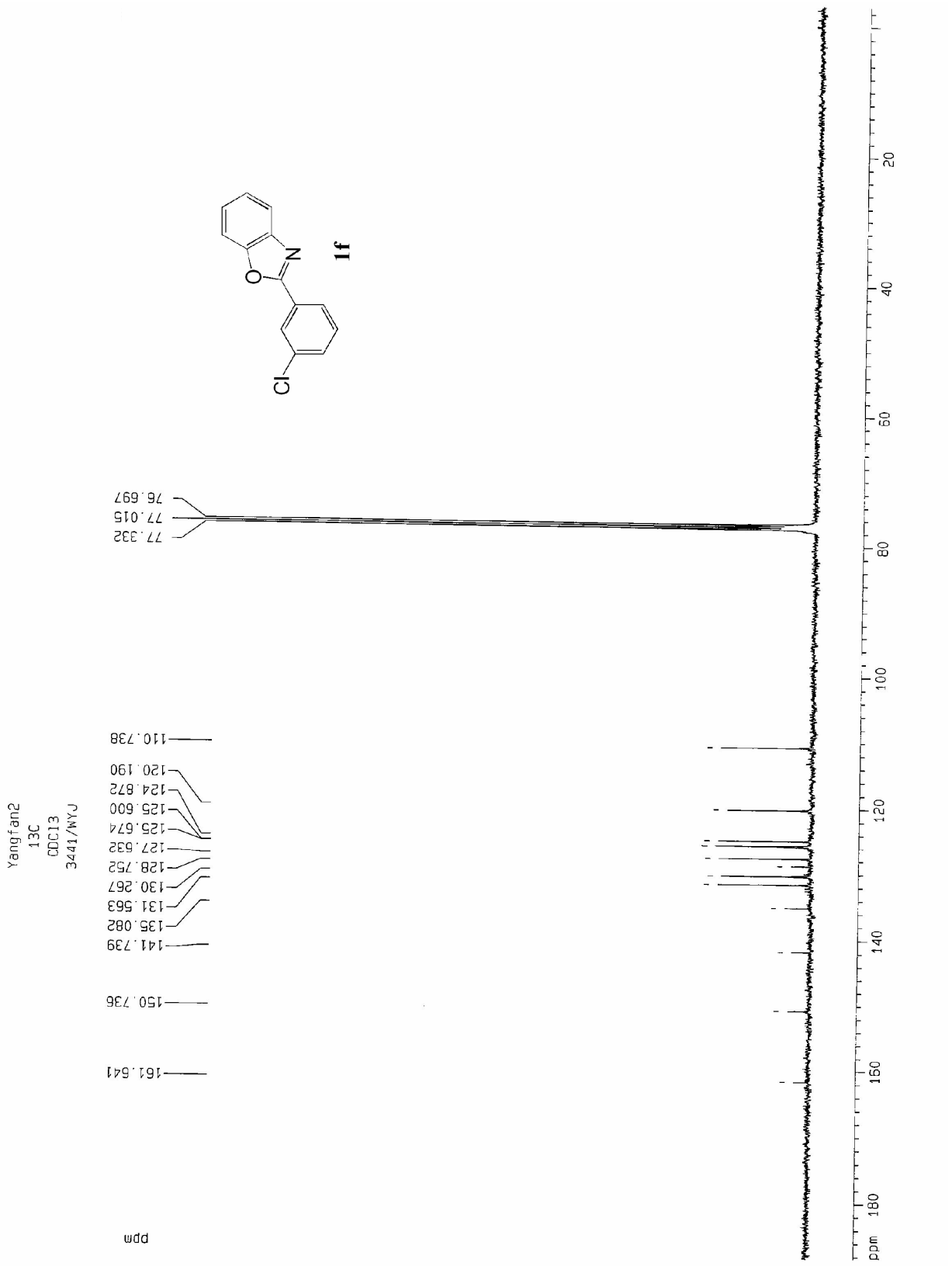

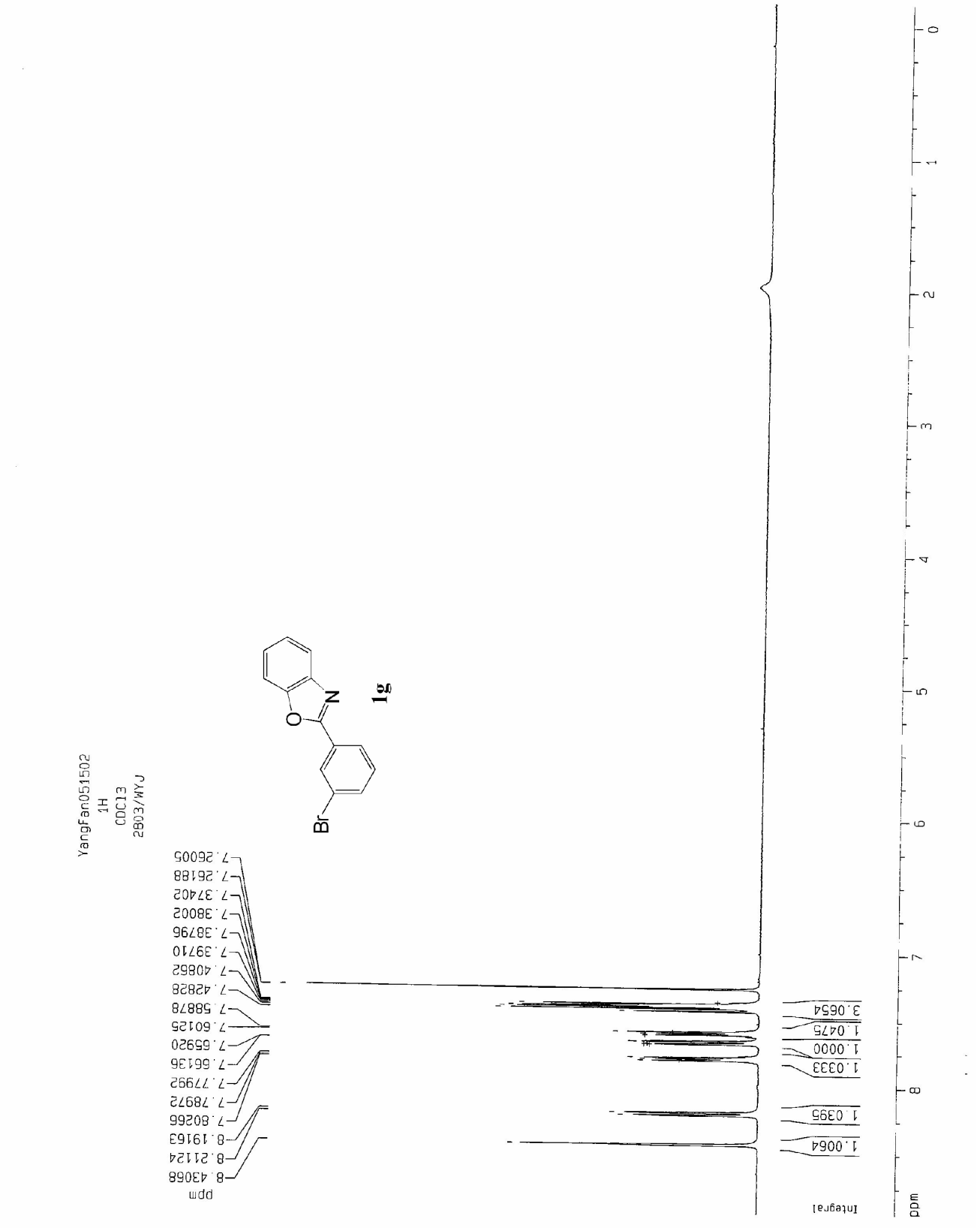
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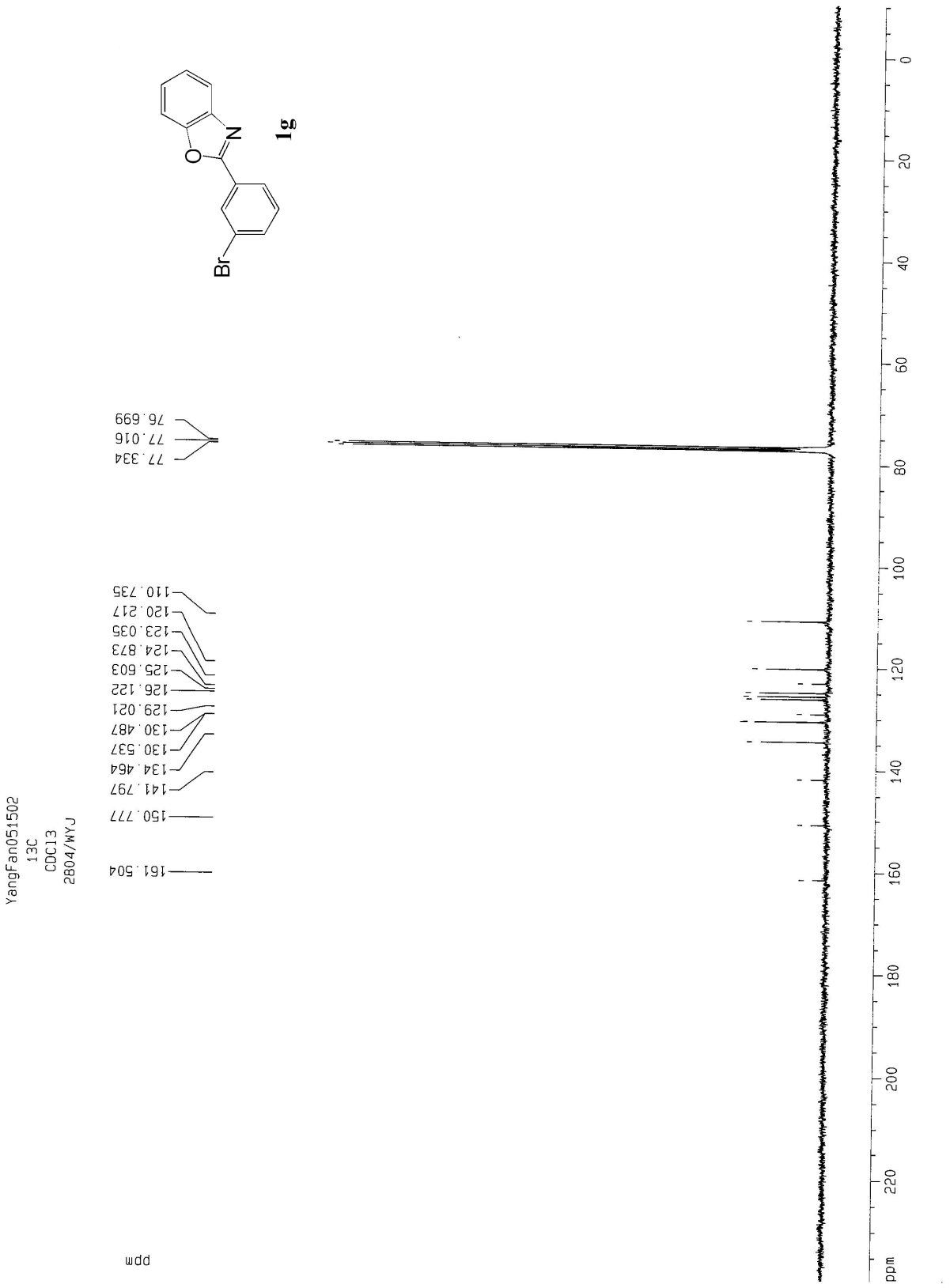

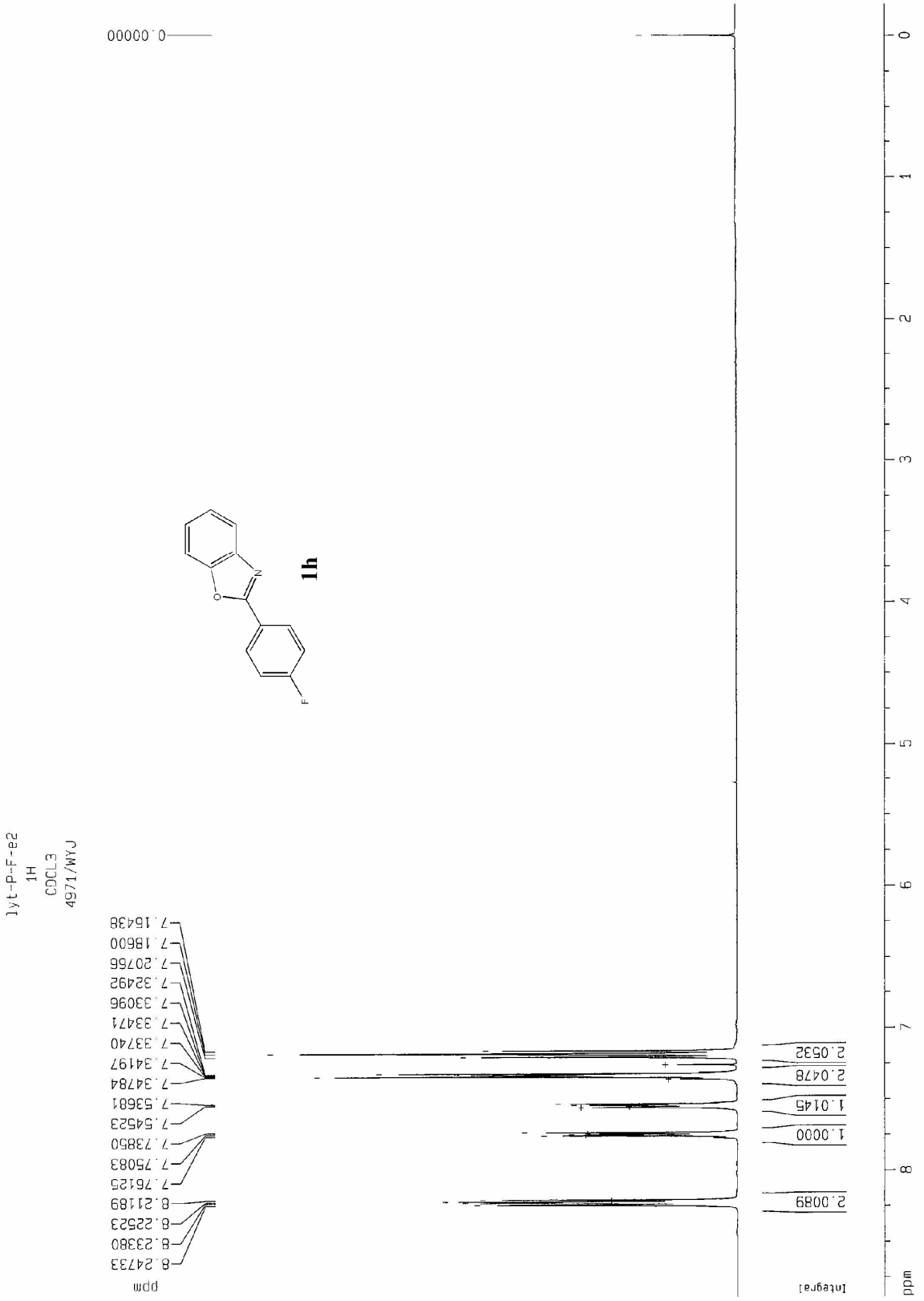
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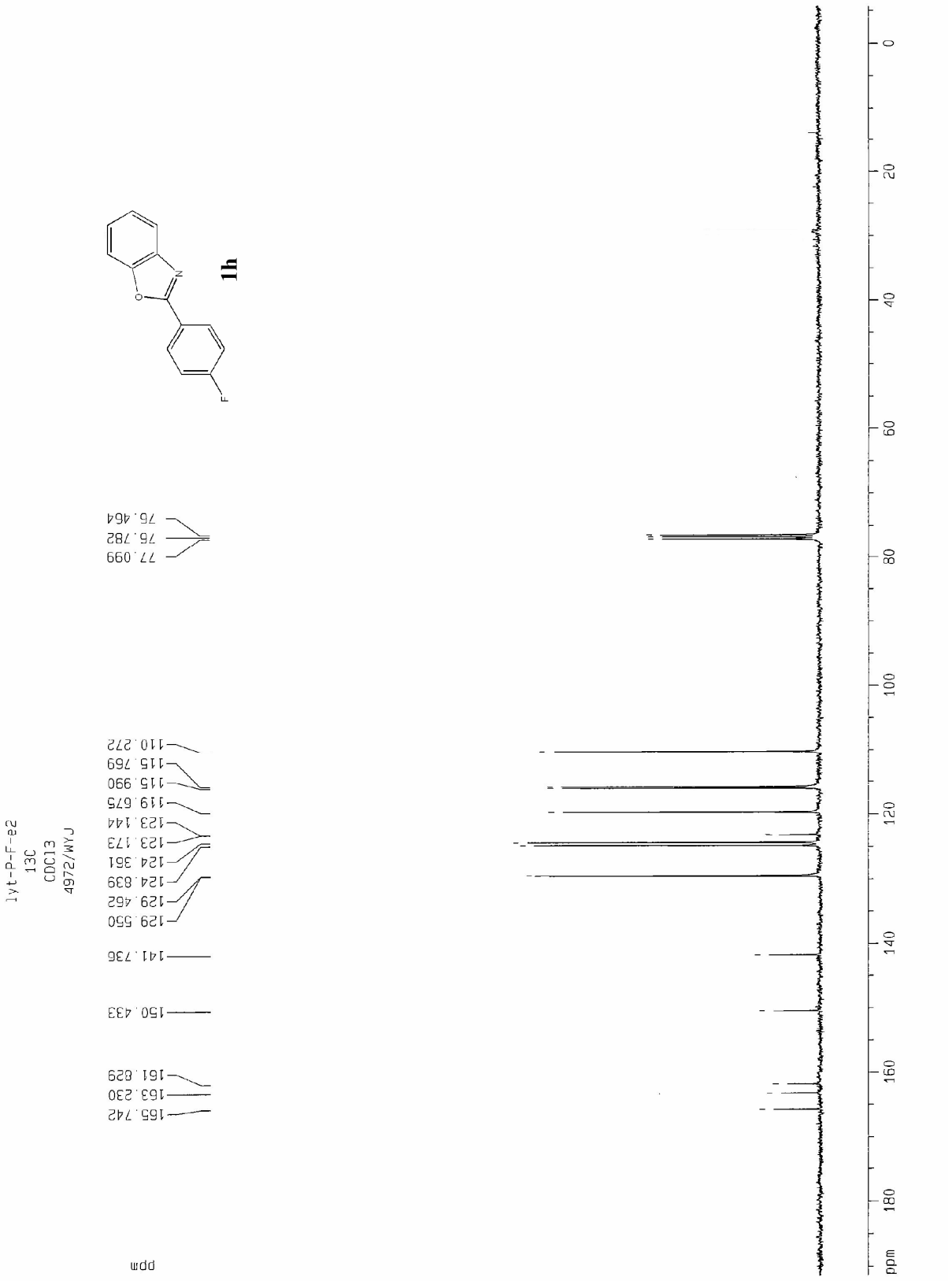

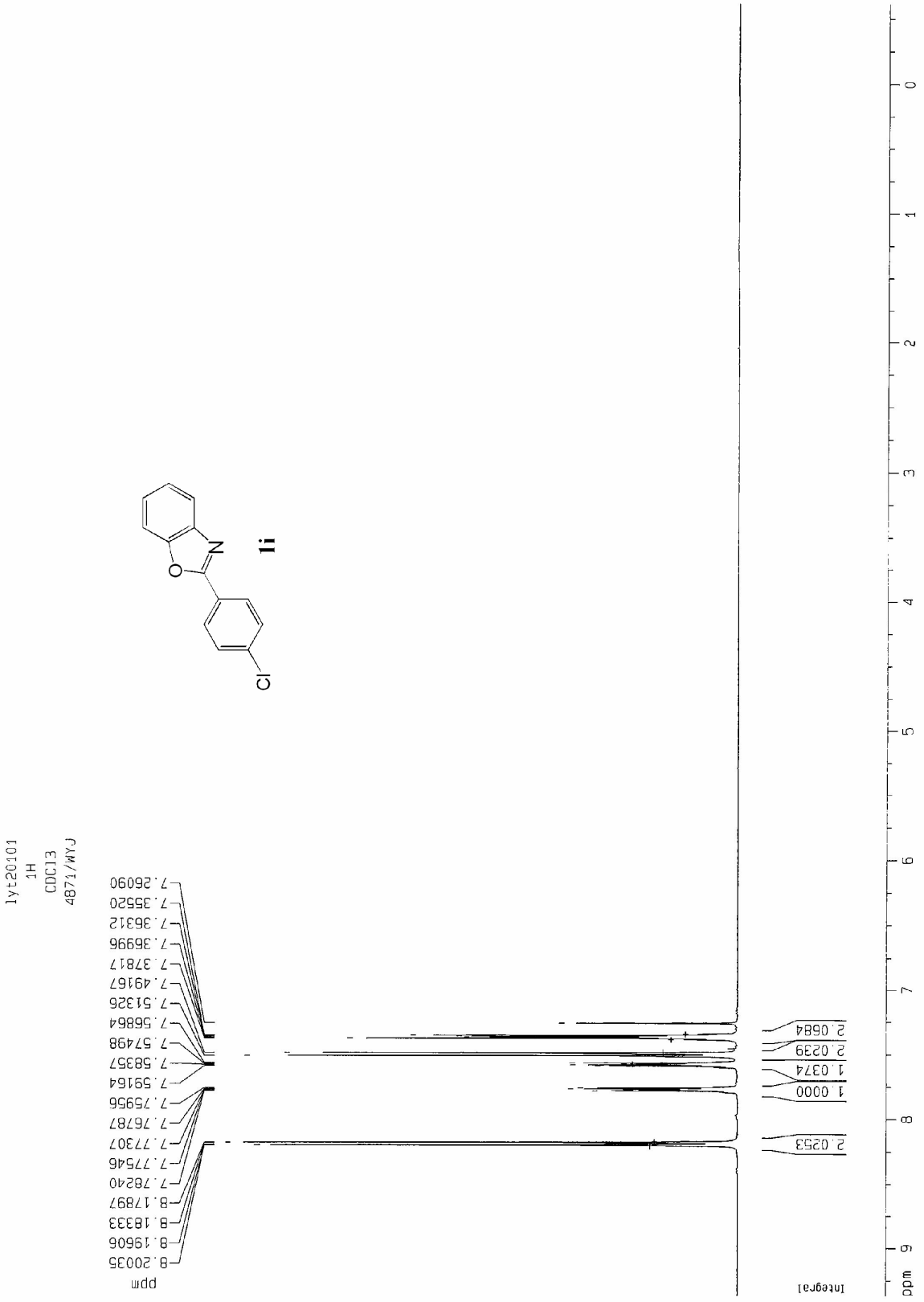
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O
ppm
Integral
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8.17897
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7.49167
7.37817
7.36996
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2.0239
2.0684

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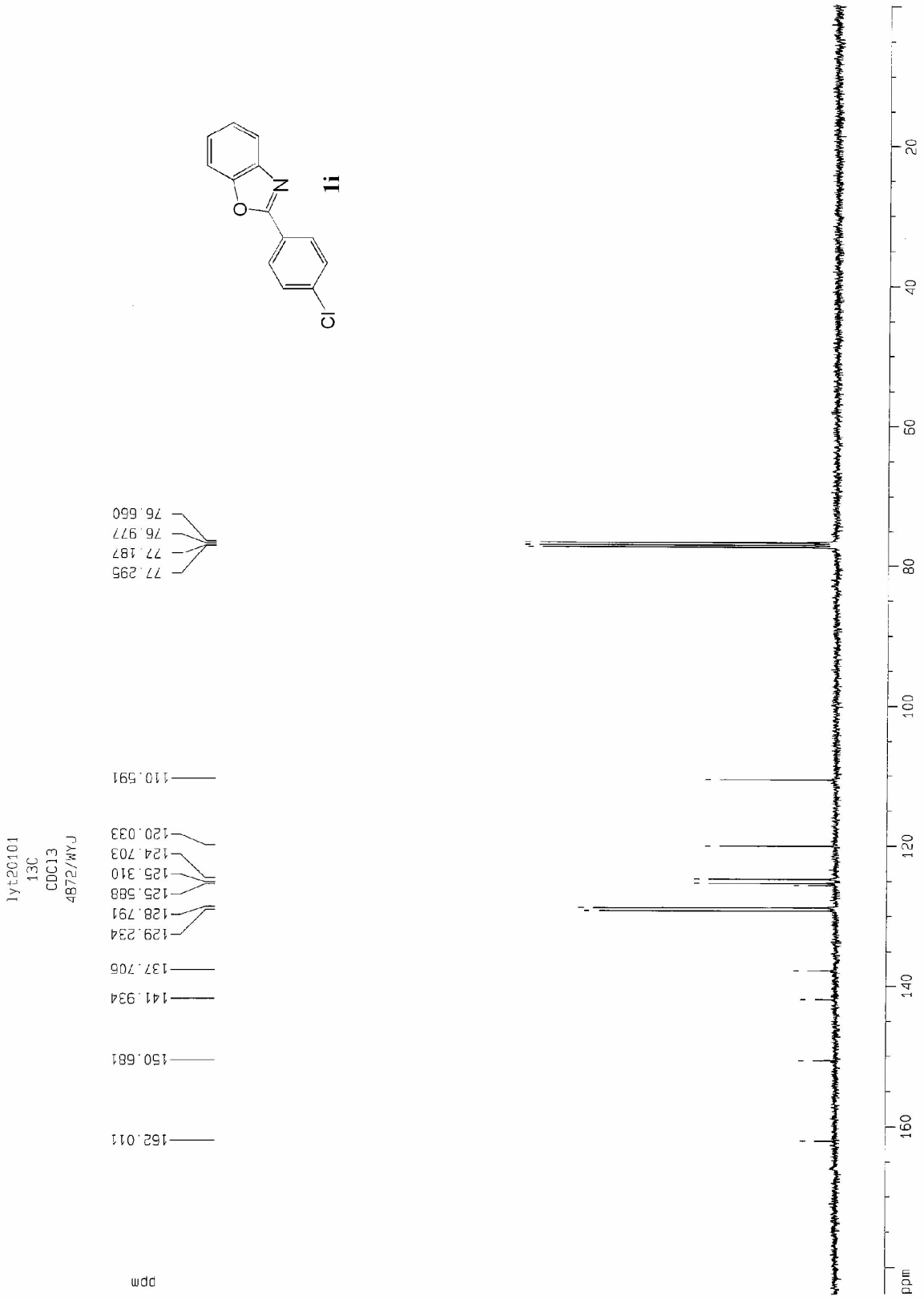

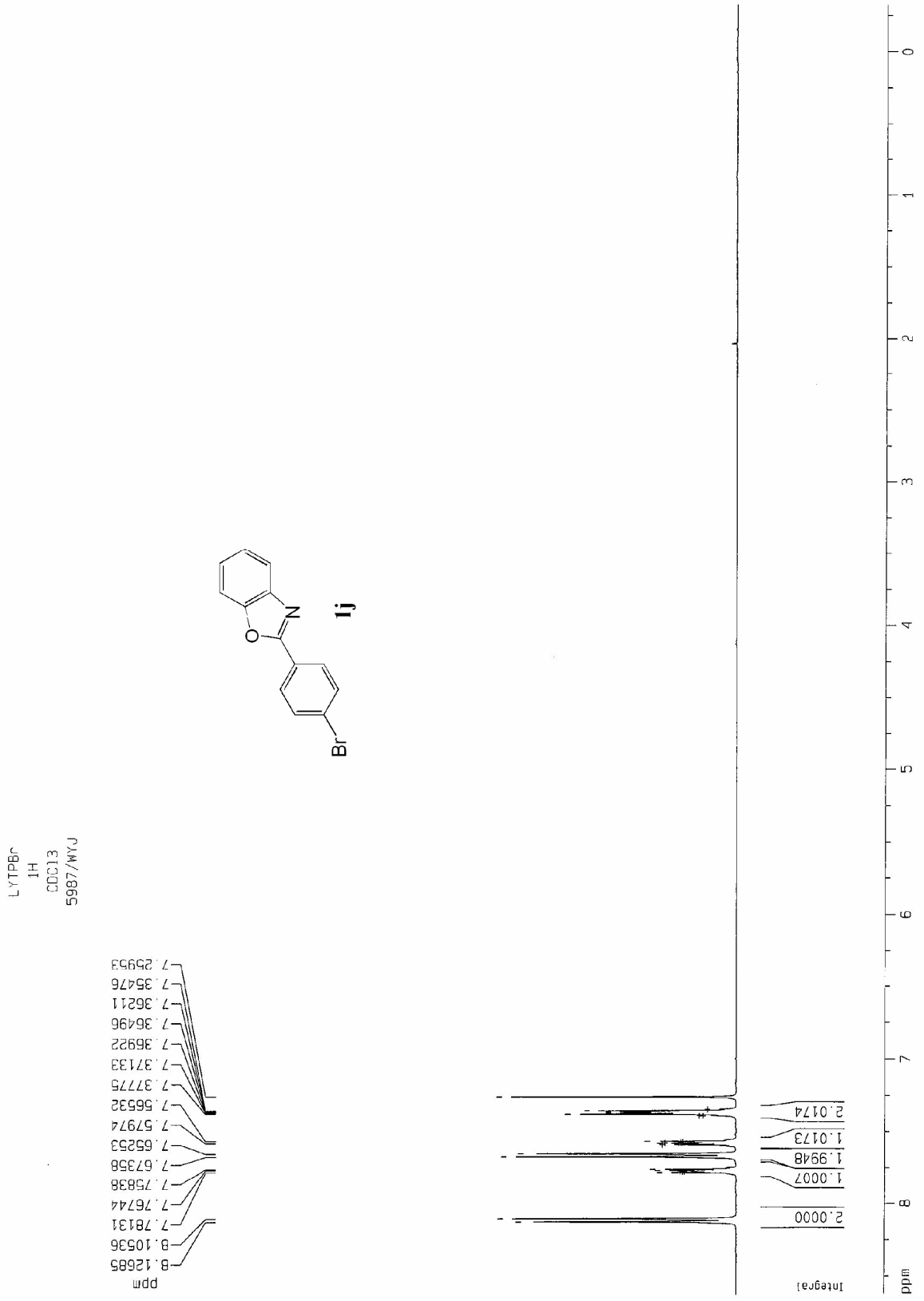
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7.36922
7.36496
7.36211
7.35476
7.25953
Br
N
O
1j
Integral
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ppm
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3
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5
6
7
8

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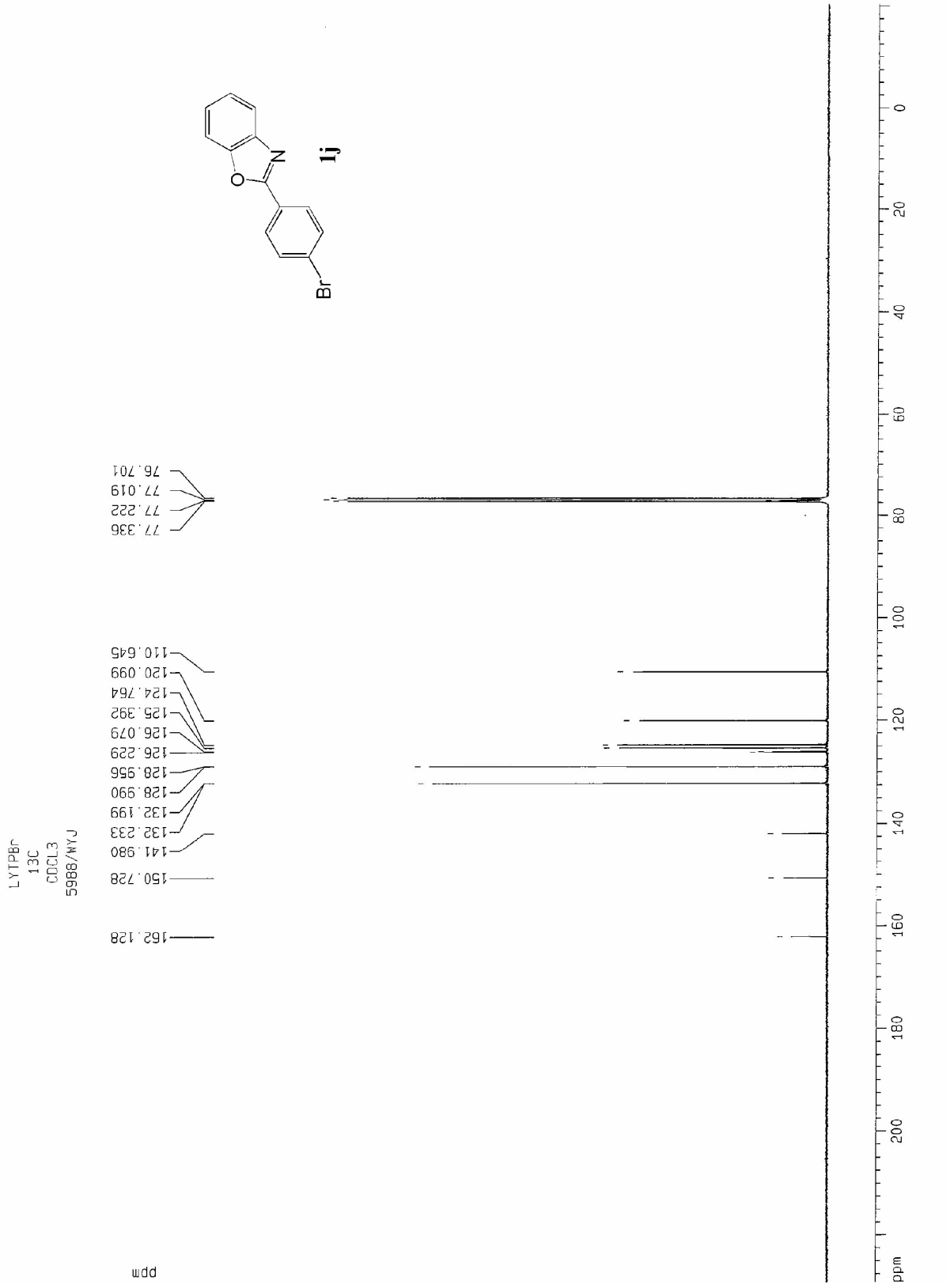

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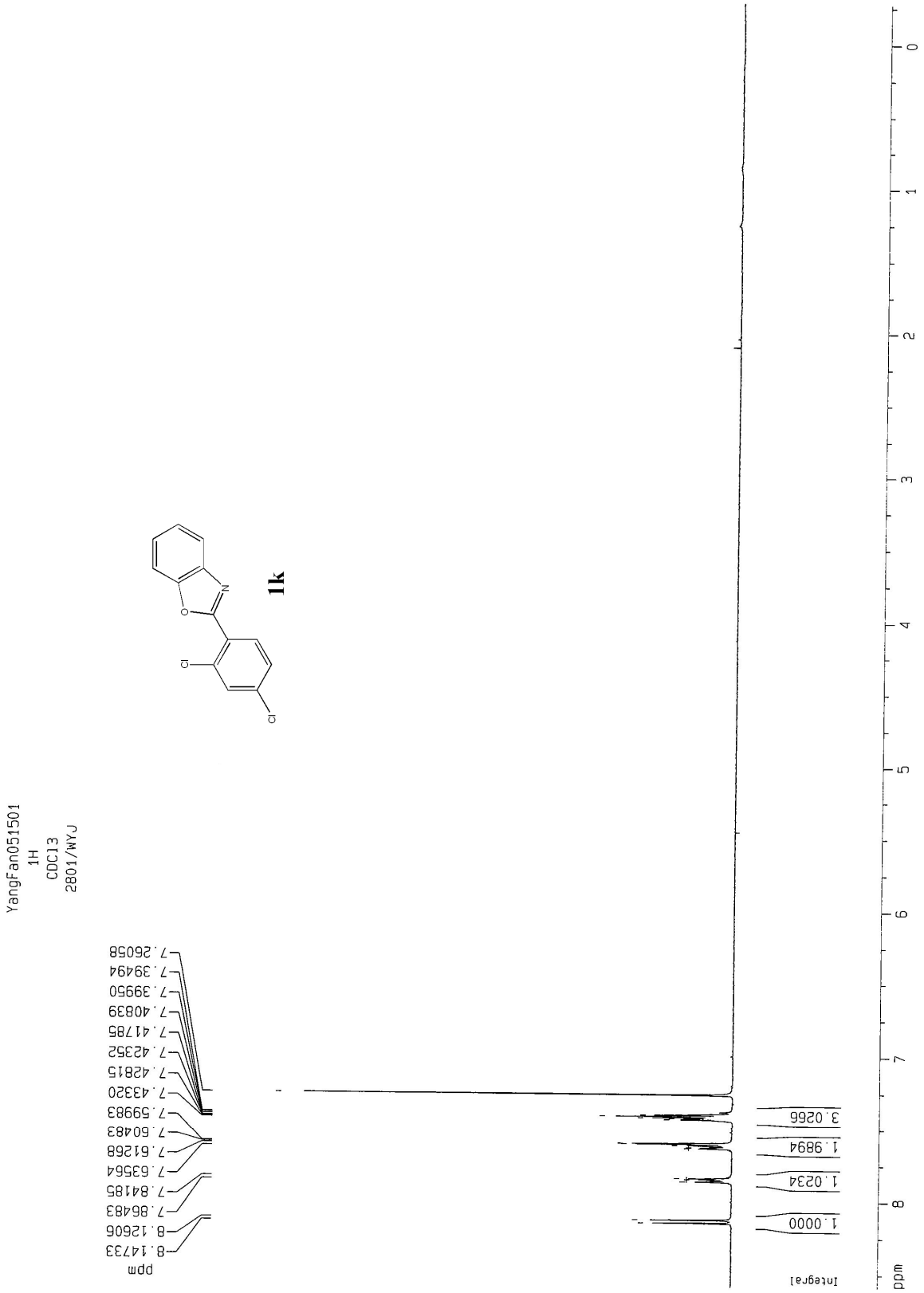

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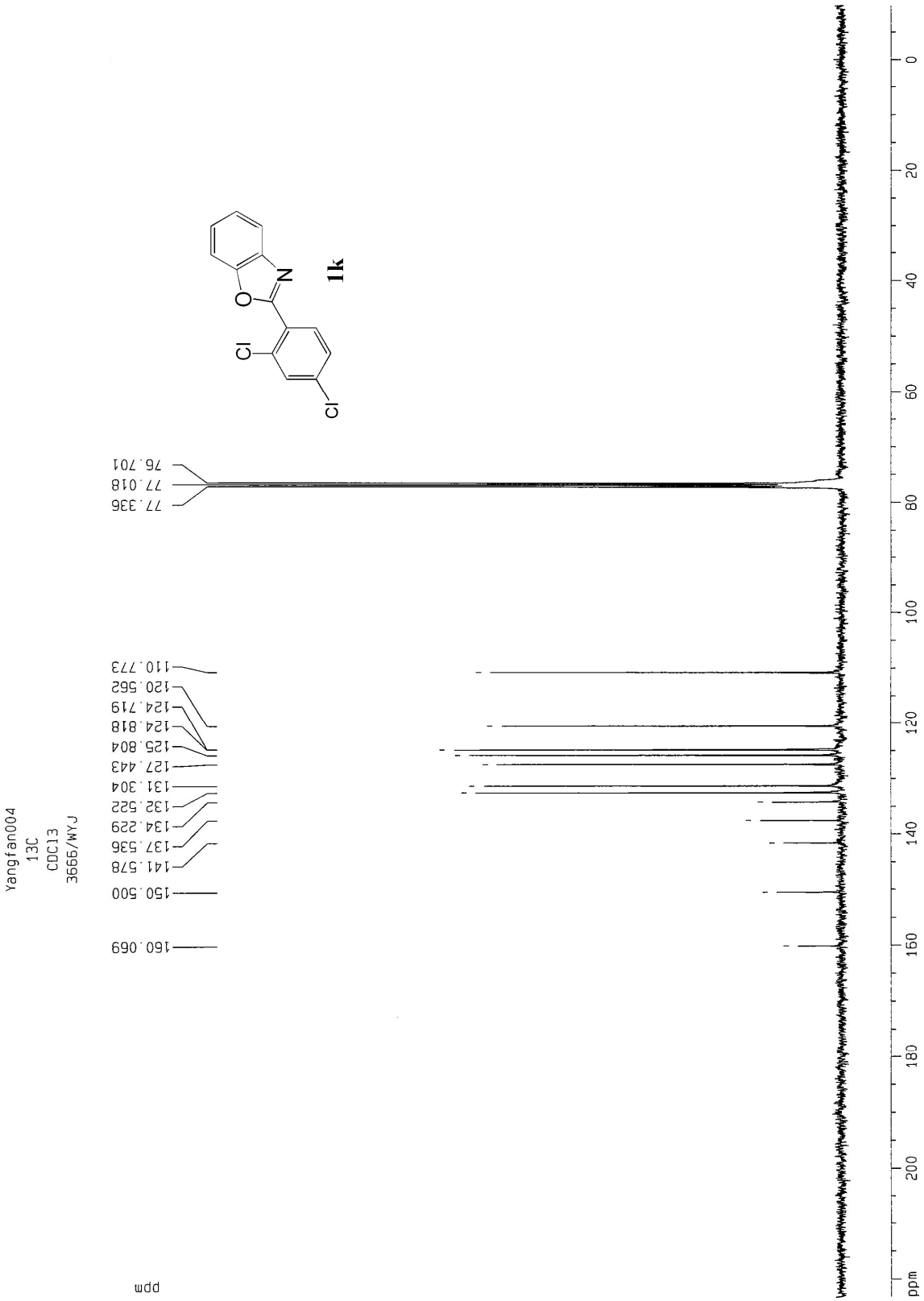

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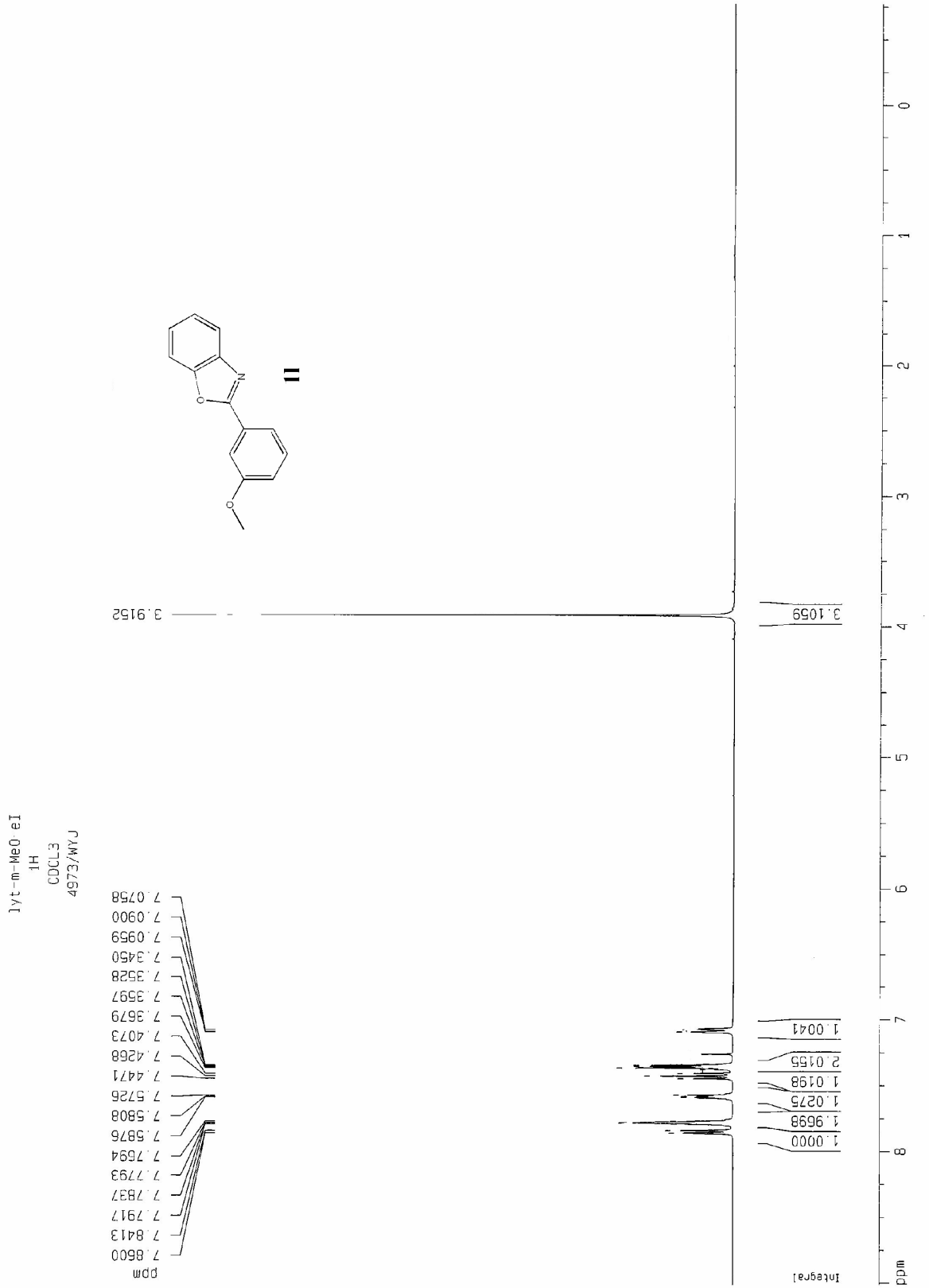

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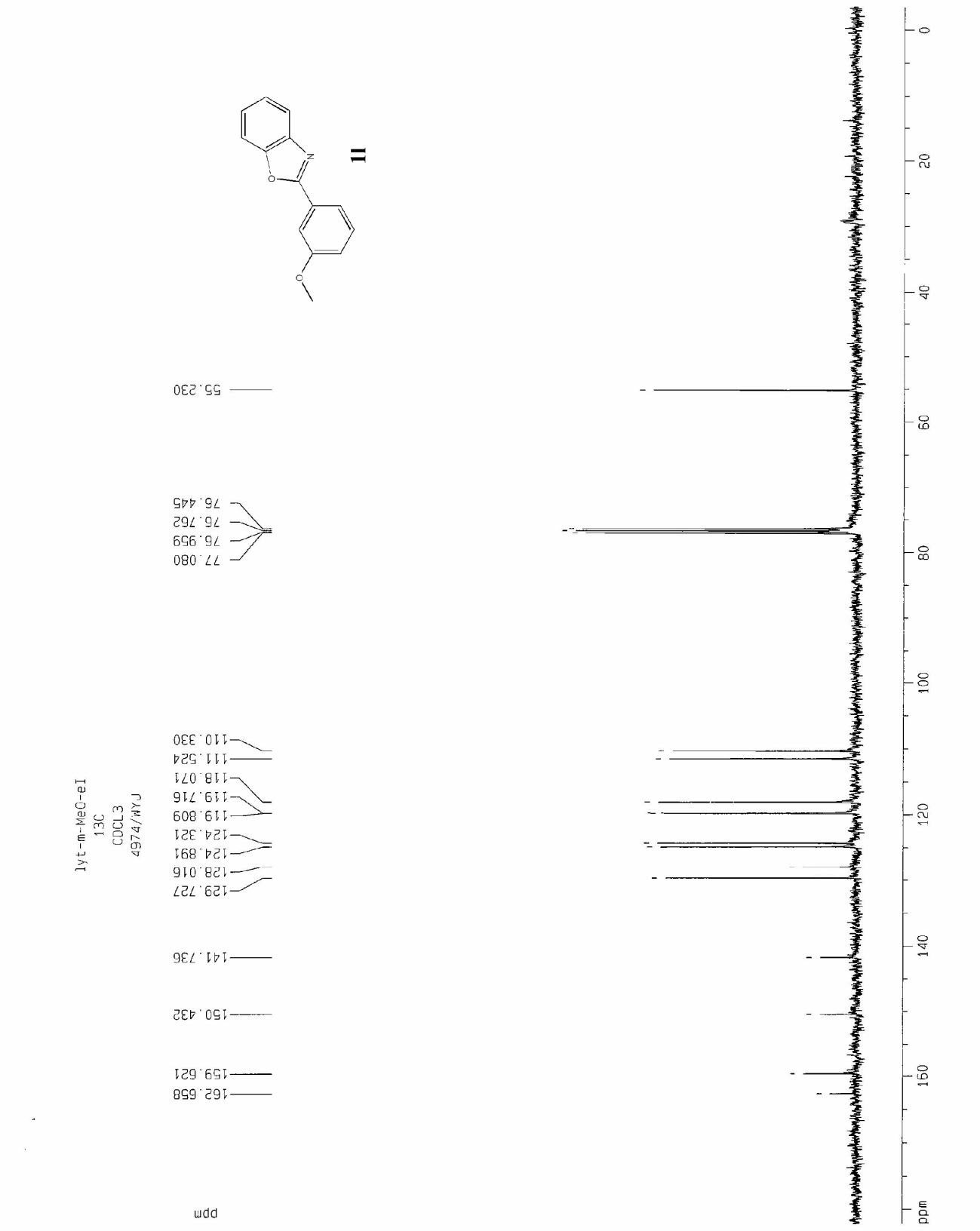

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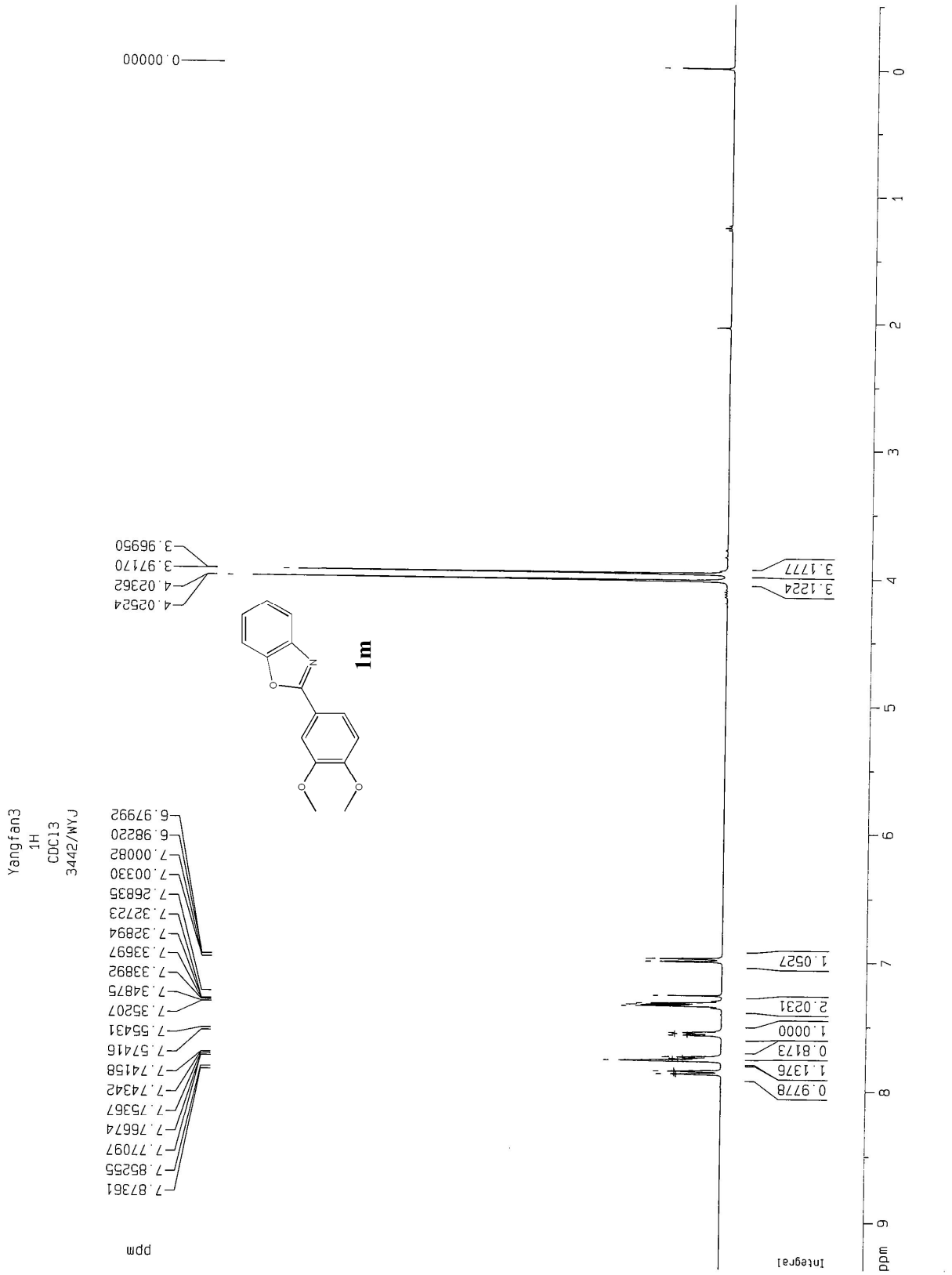

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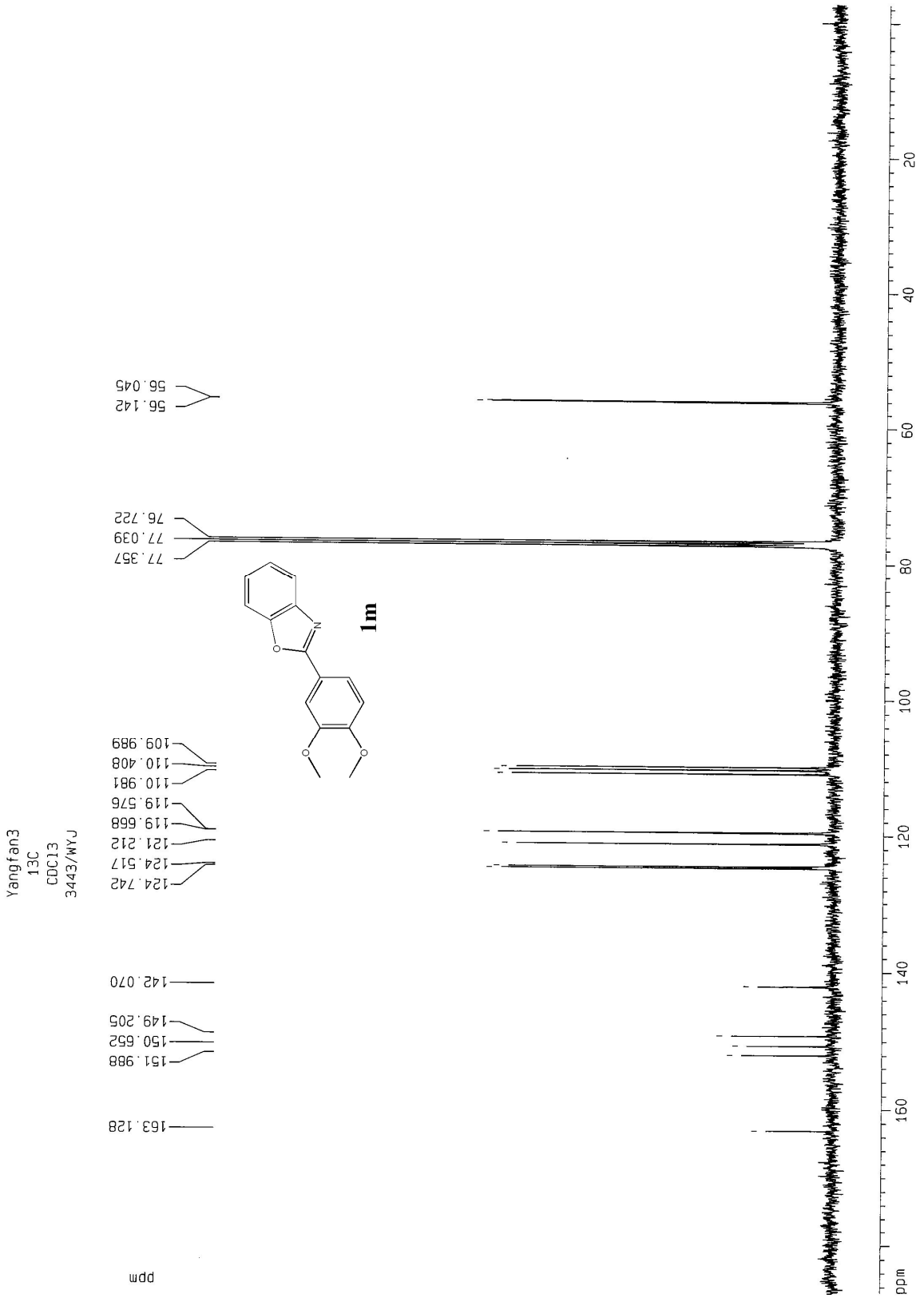

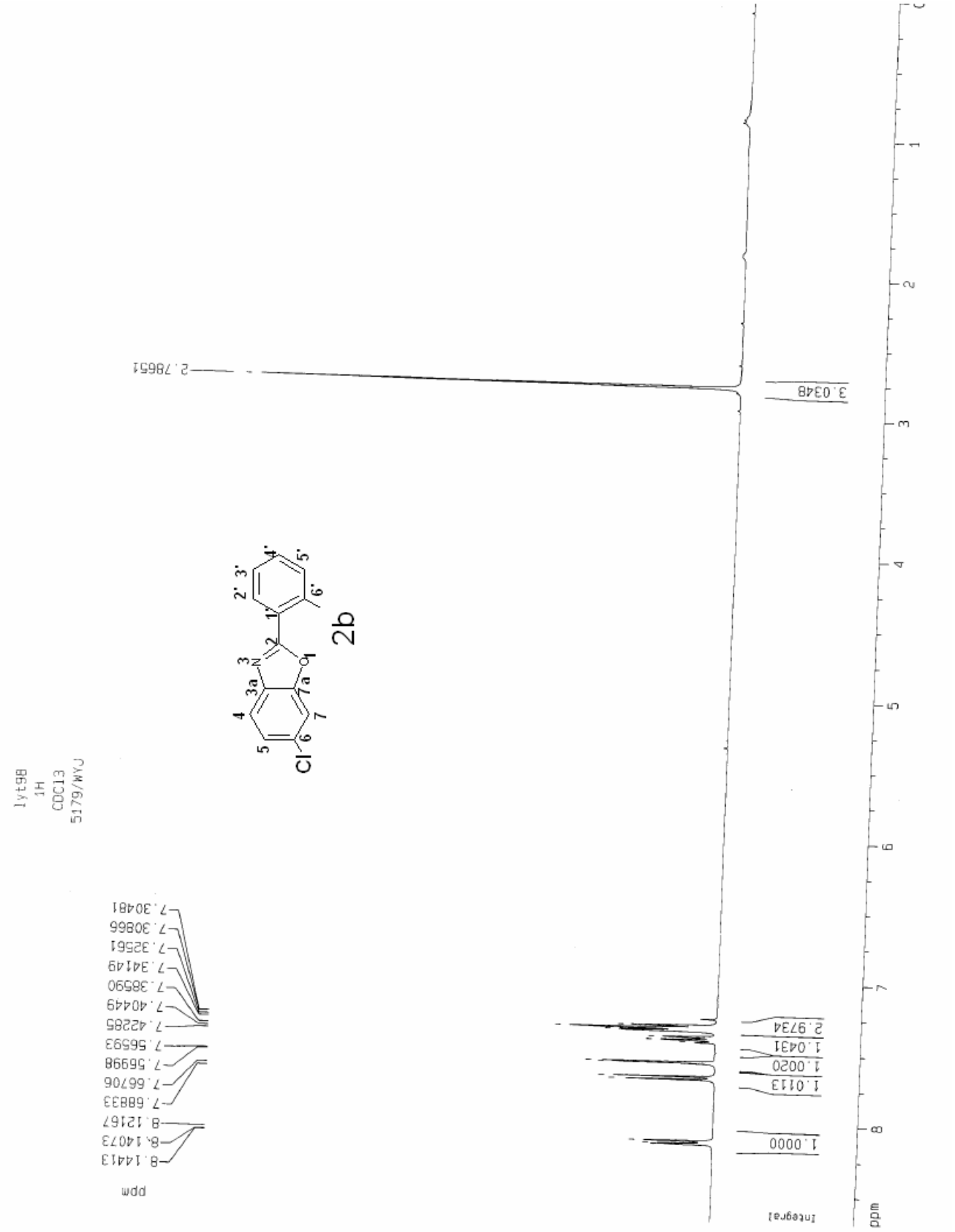
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2b
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1.0113
1.0000
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8.14073
8.12167
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ppm
Integral

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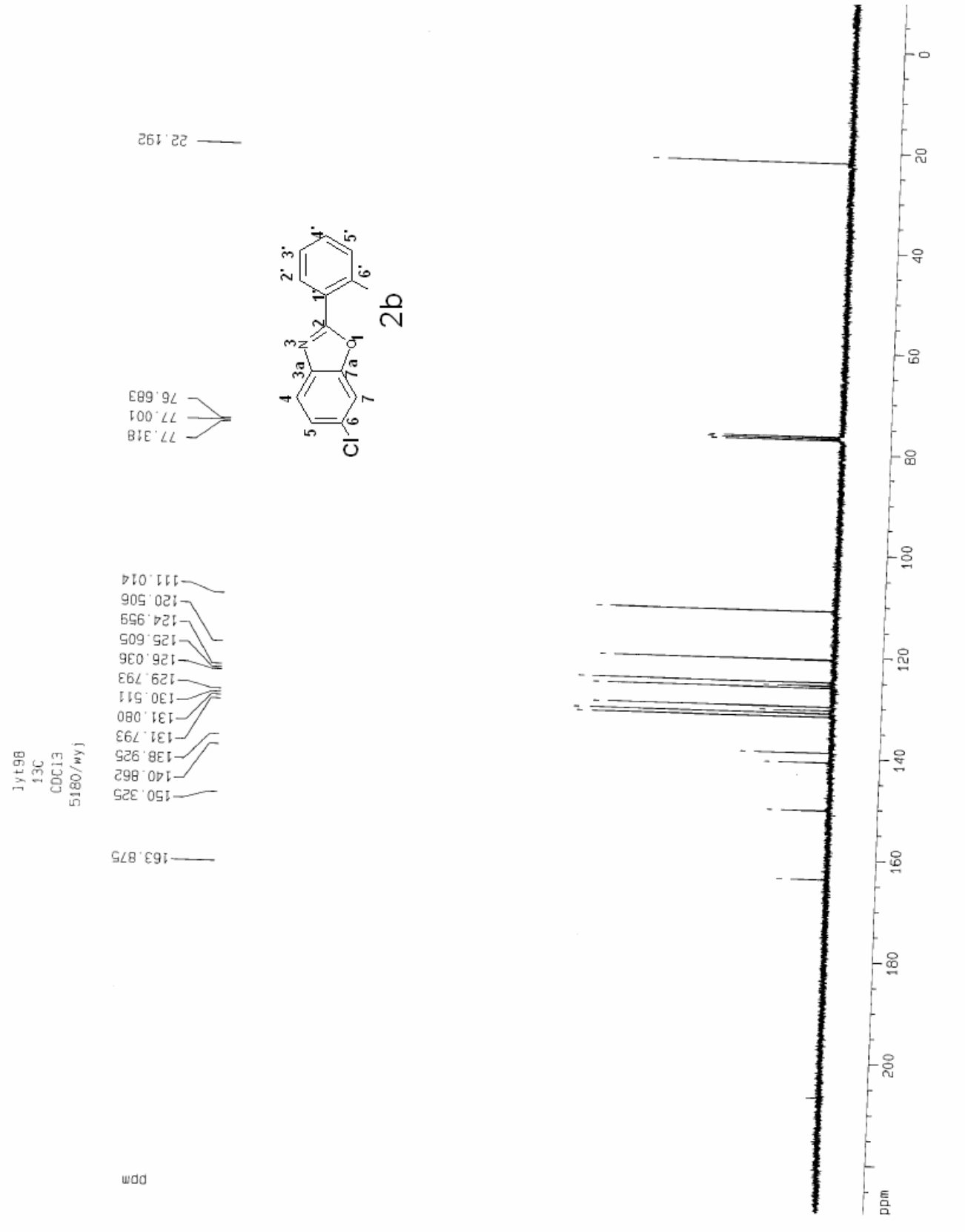

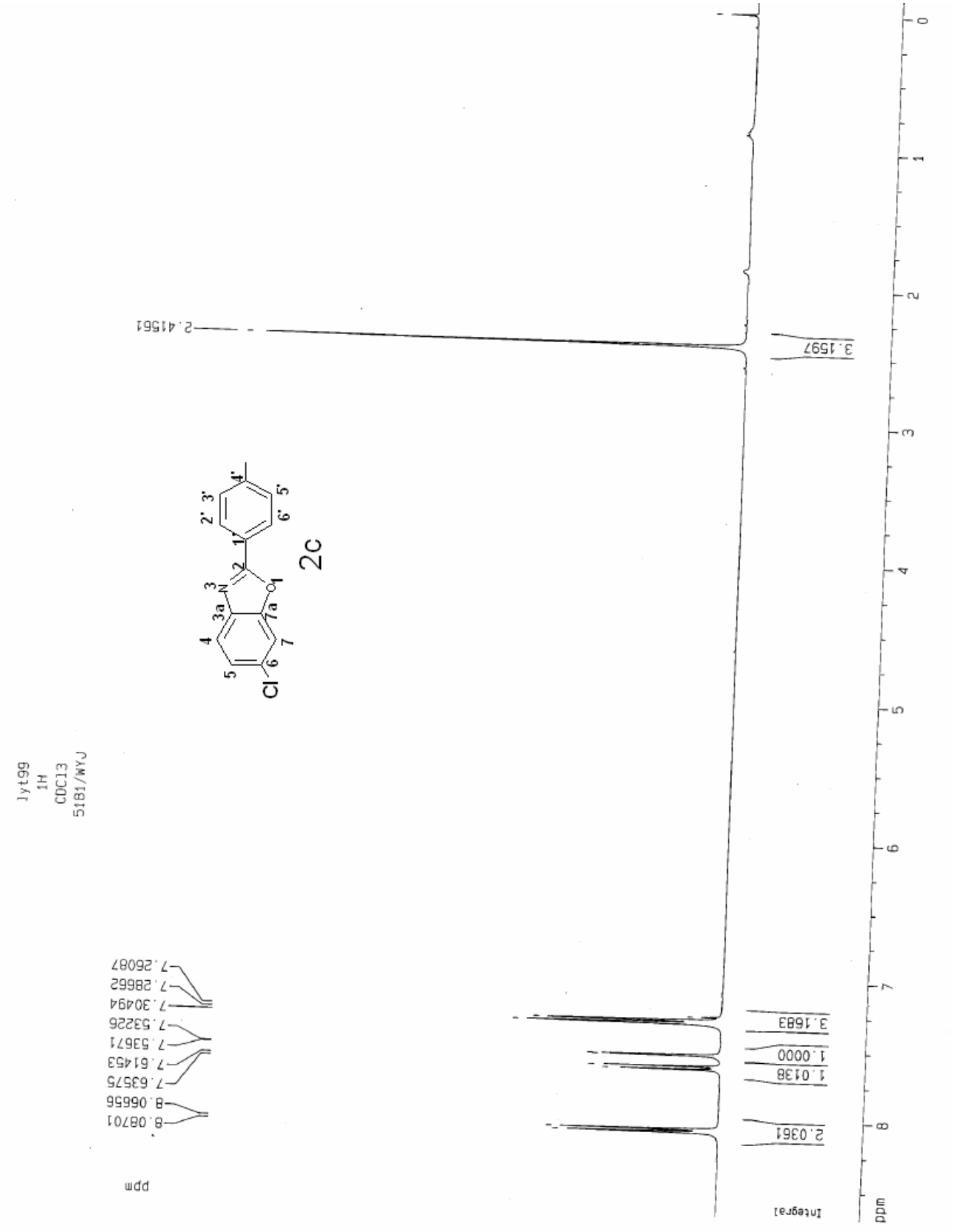
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5181/WYJ
2c
Cl
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3.1683
1.0000
1.0138
2.0361
8.08701
8.06656
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7.26087
ppm
Integral

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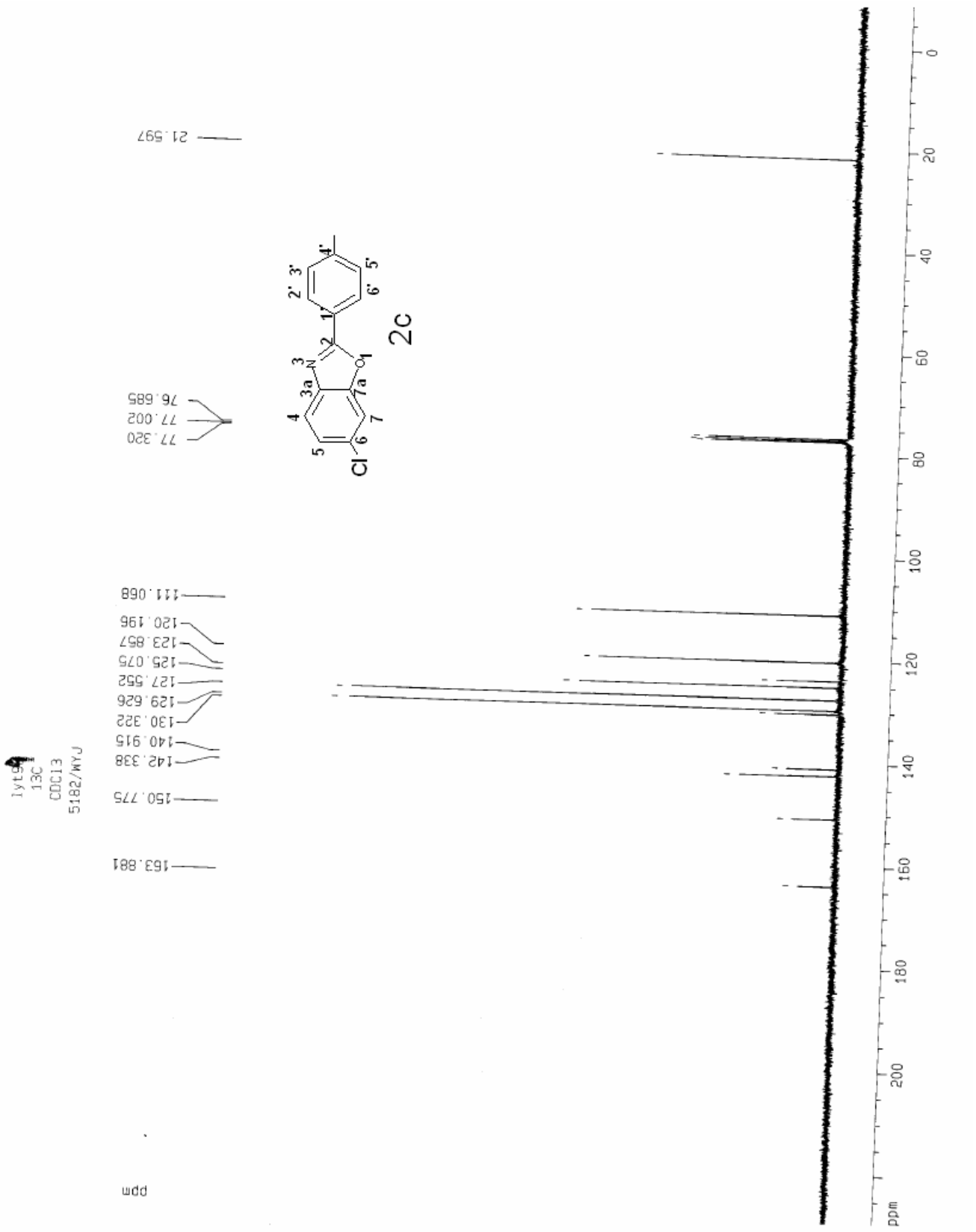

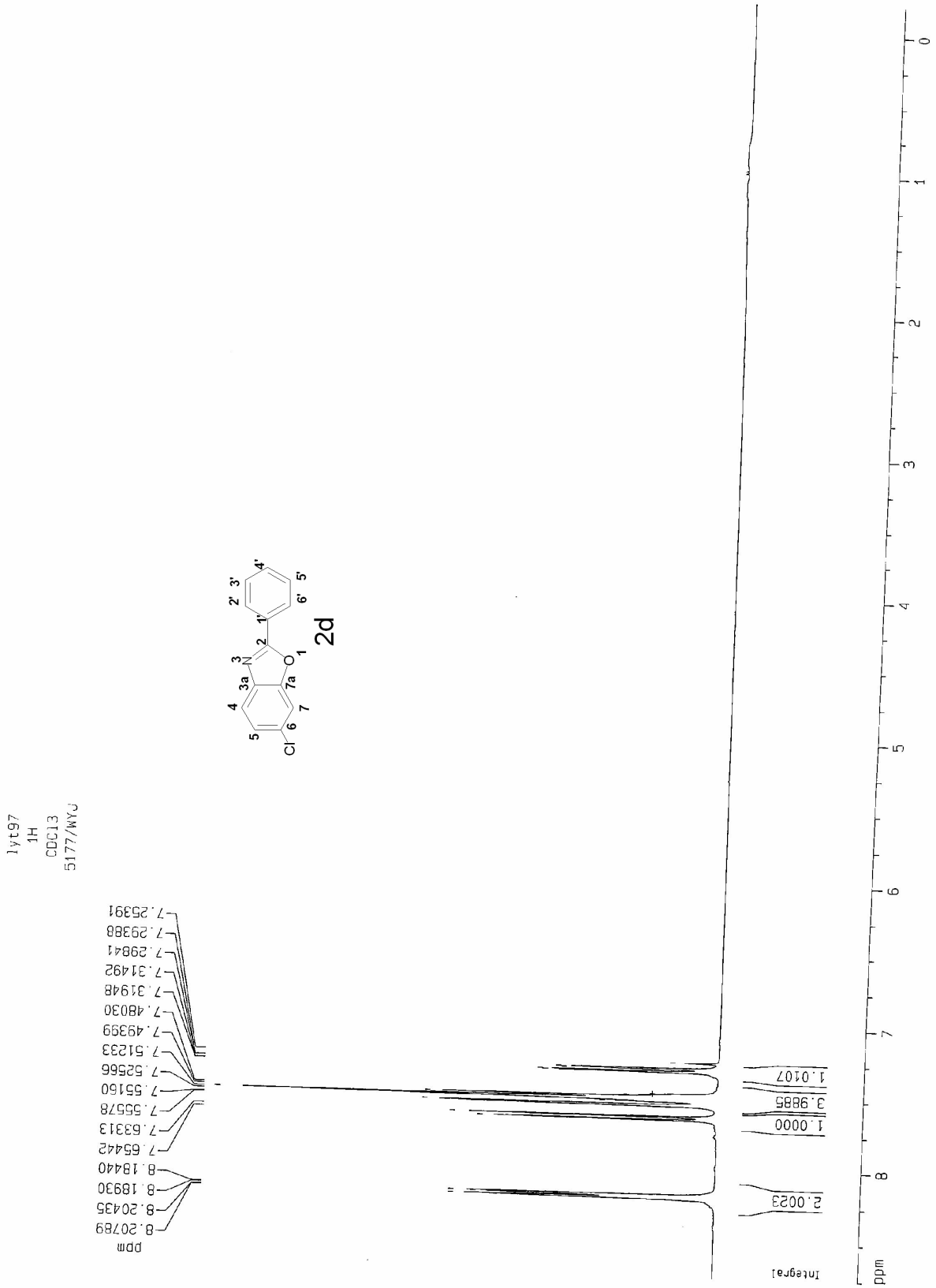
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2d
Cl
O
N
ppm
Integral
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7.63313
7.55578
7.55160
7.52566
7.51233
7.49359
7.48030
7.31948
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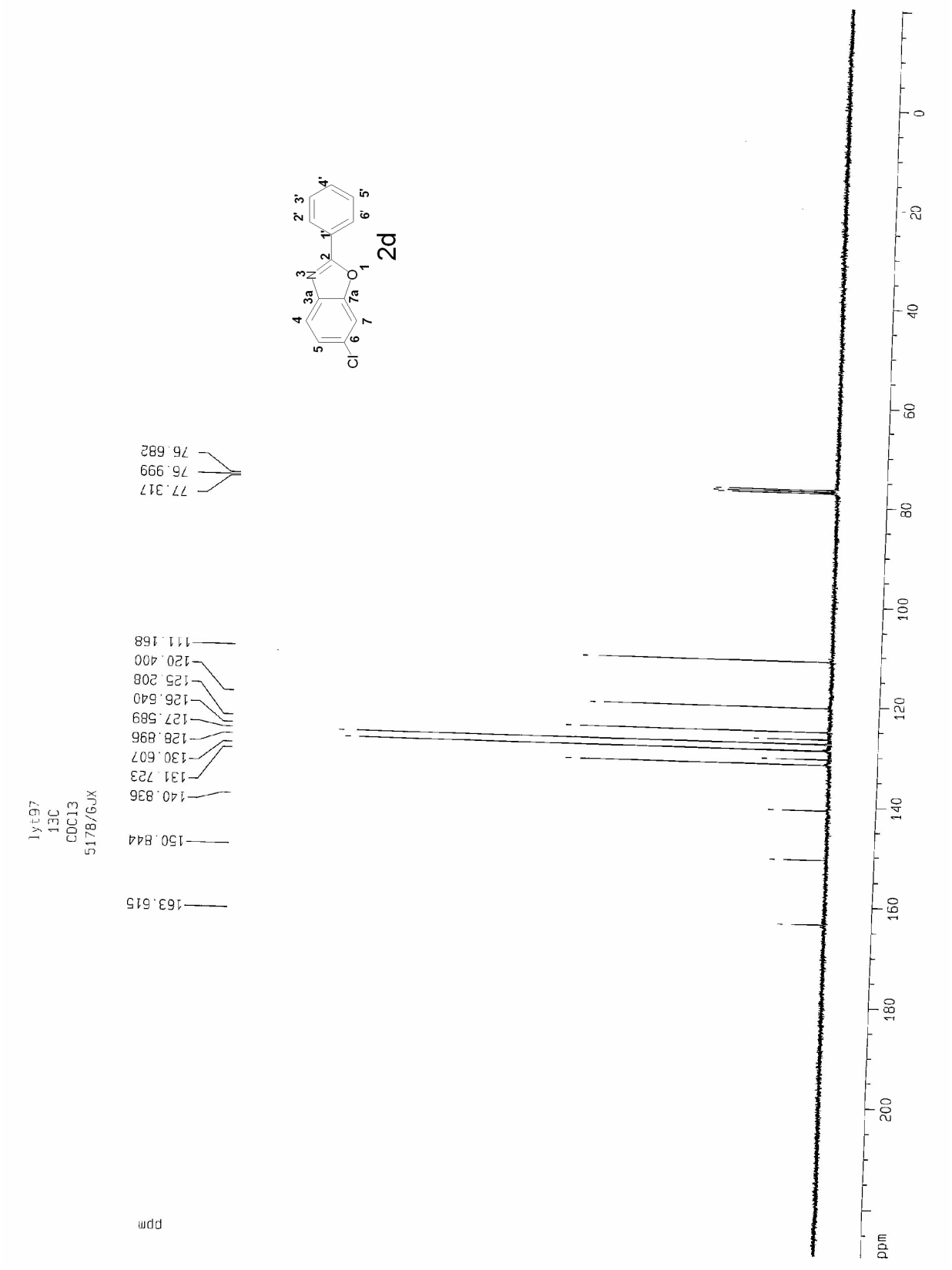

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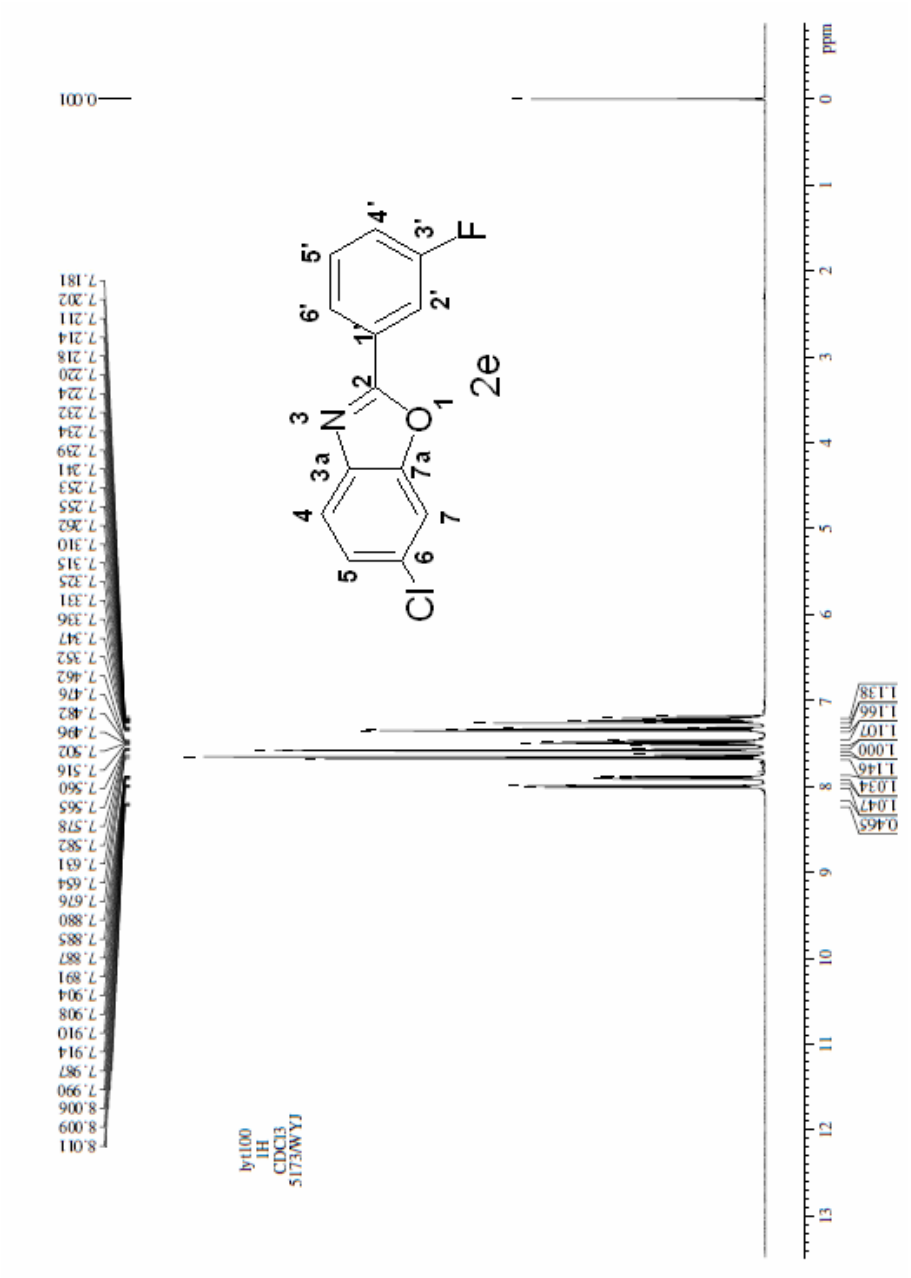

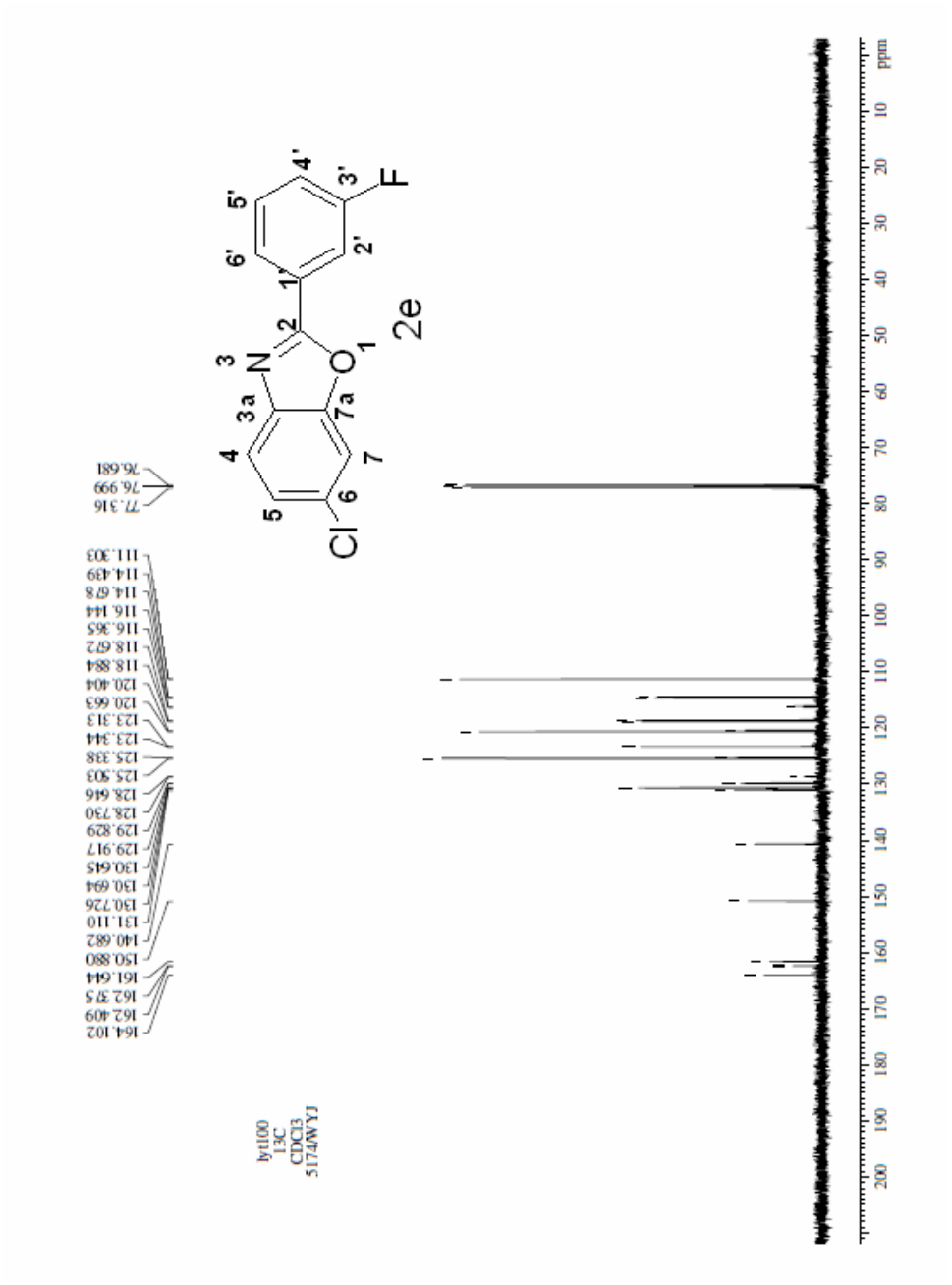
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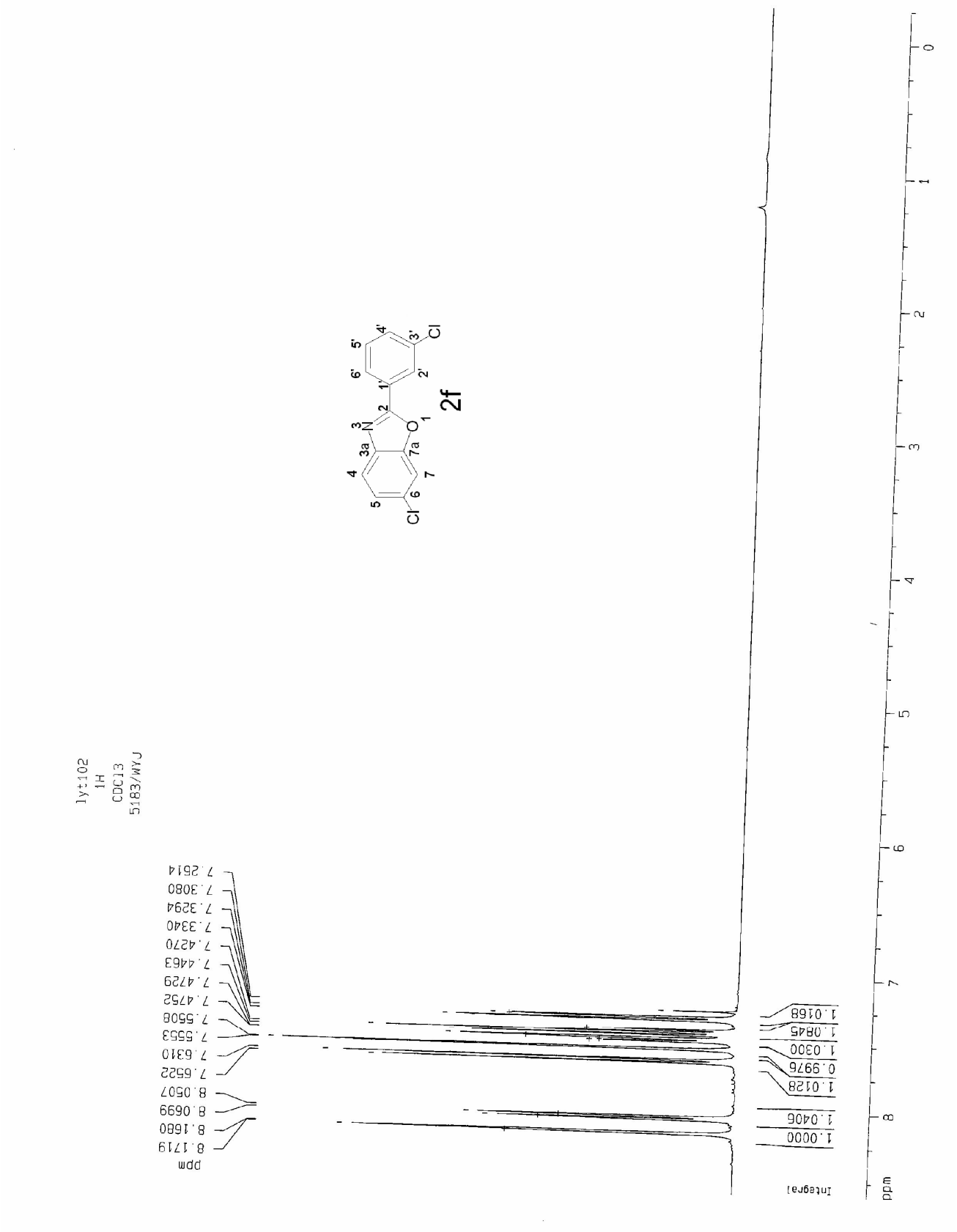
5174AWYJ
ppm


2f
Cl
Cl
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CDCl3
5183/WYJ
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7.5508
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7.4729
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7.4270
7.3340
7.3294
7.3080
7.2614
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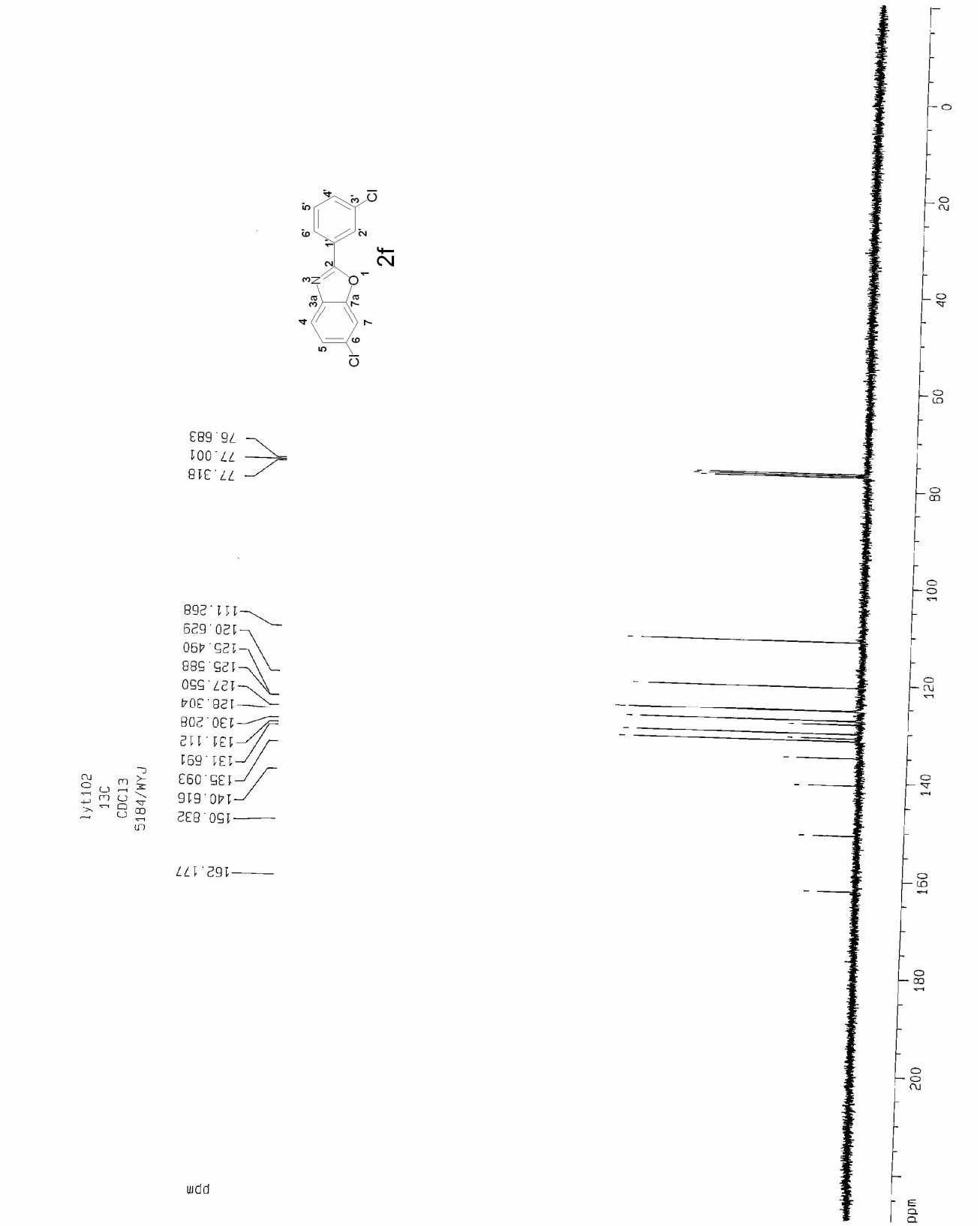

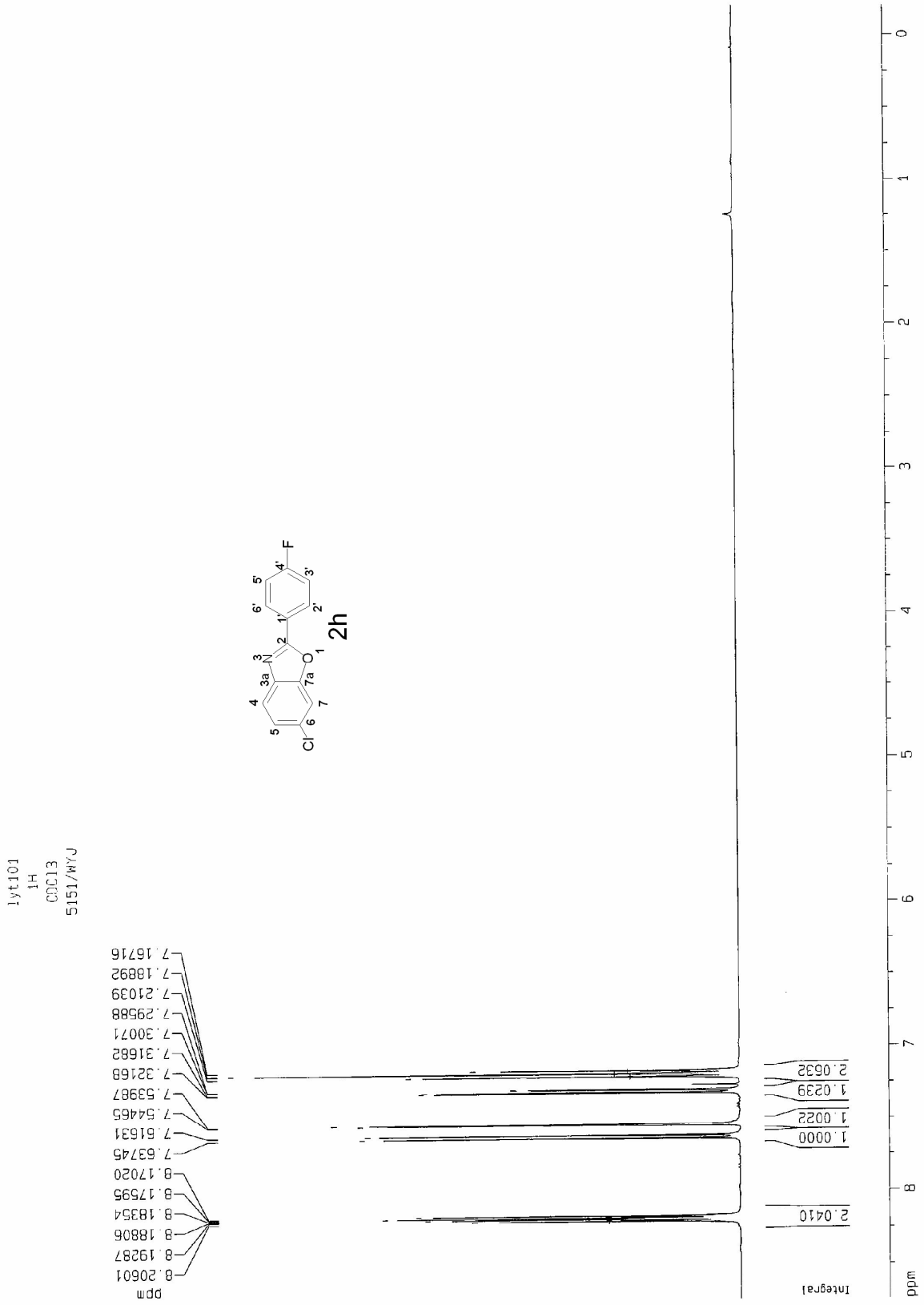
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Cl
ppm
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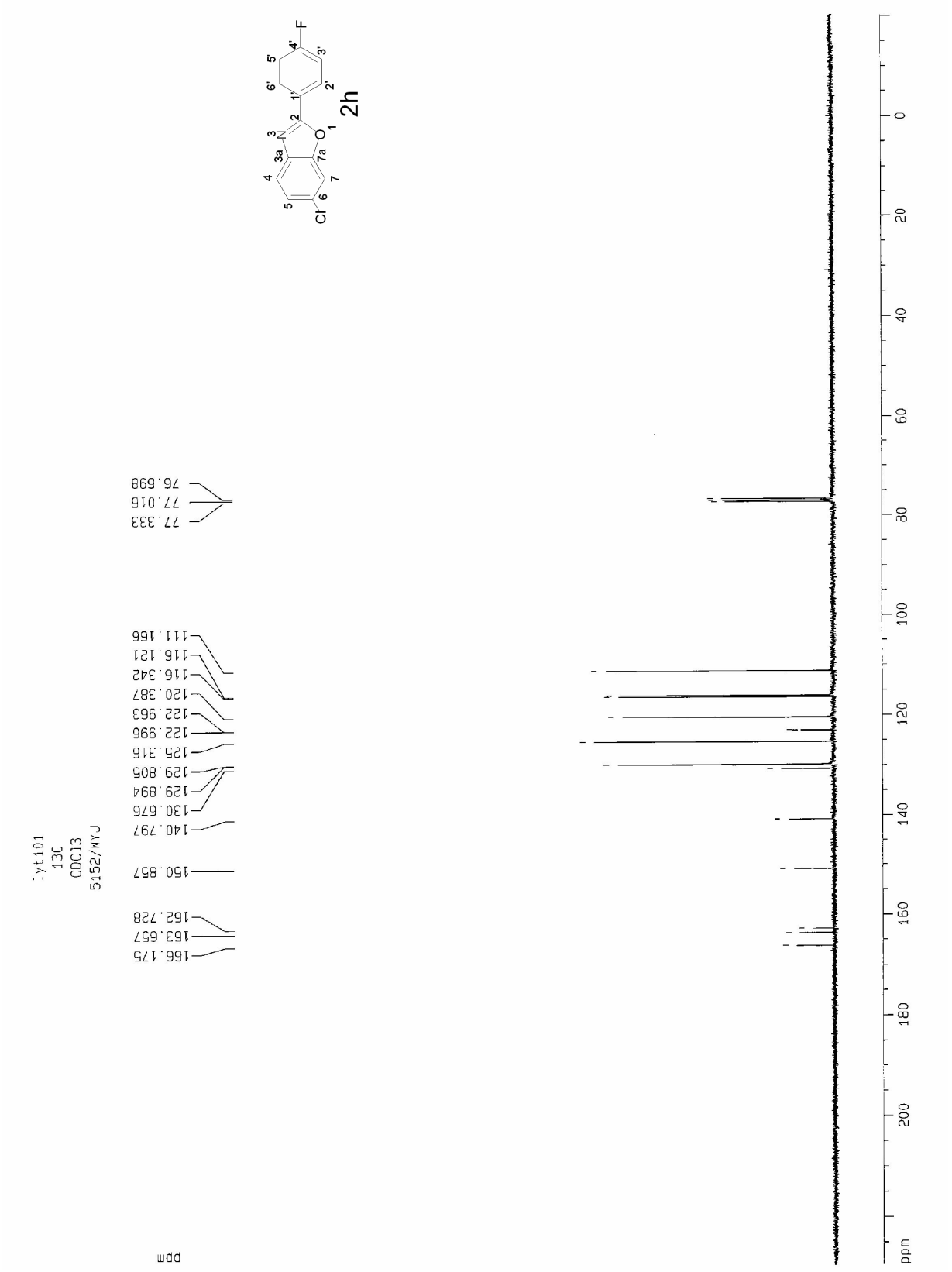
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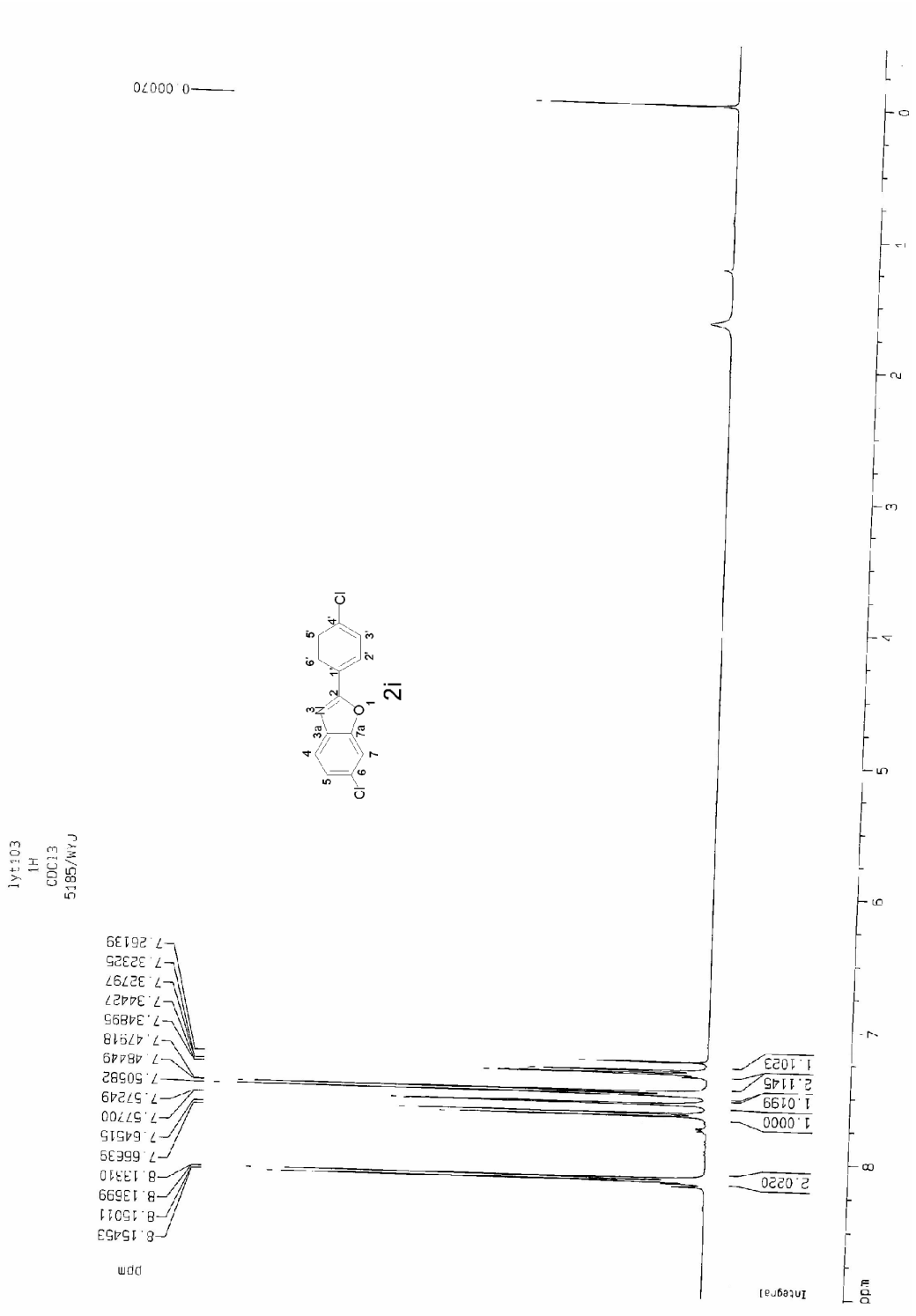

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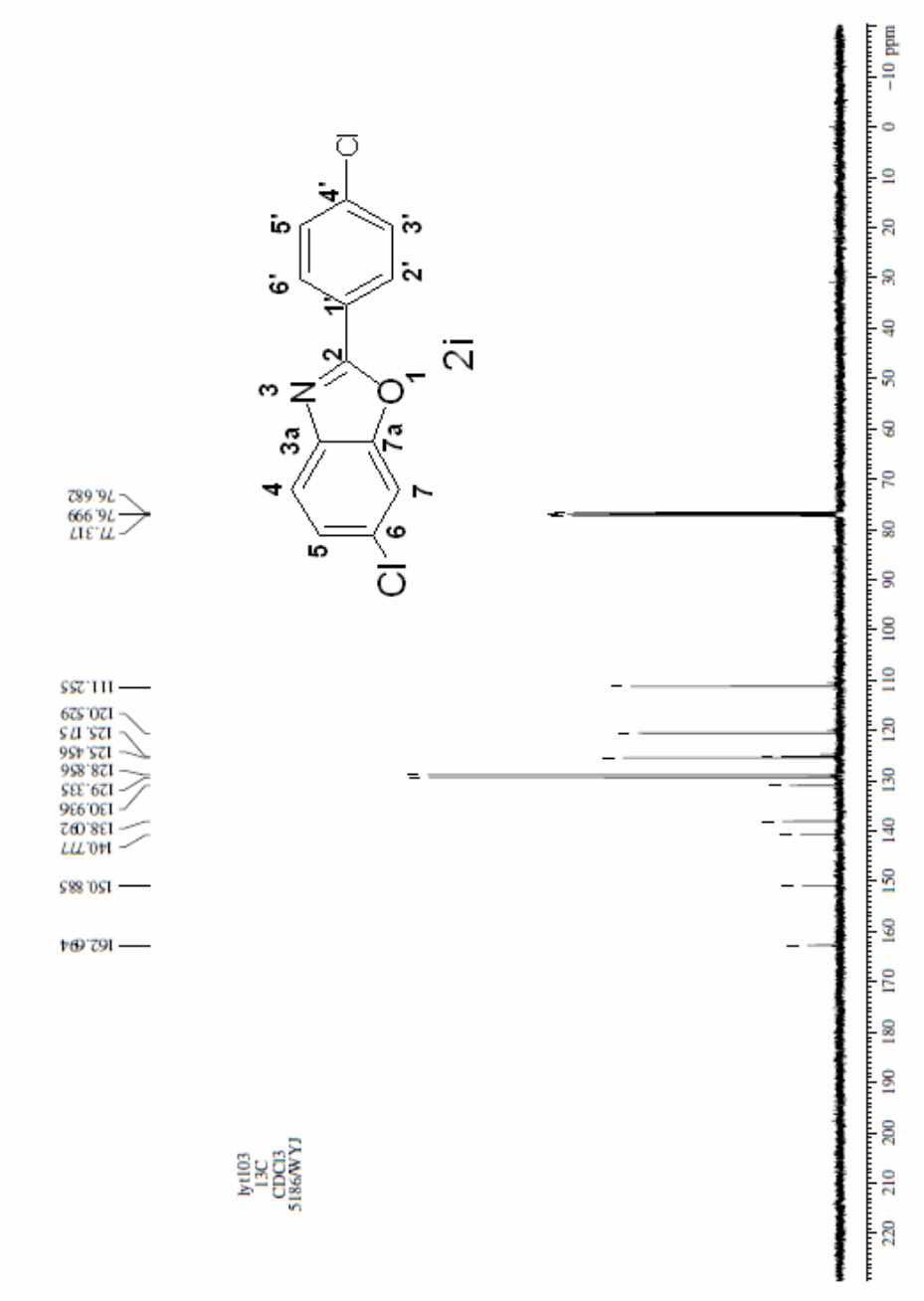

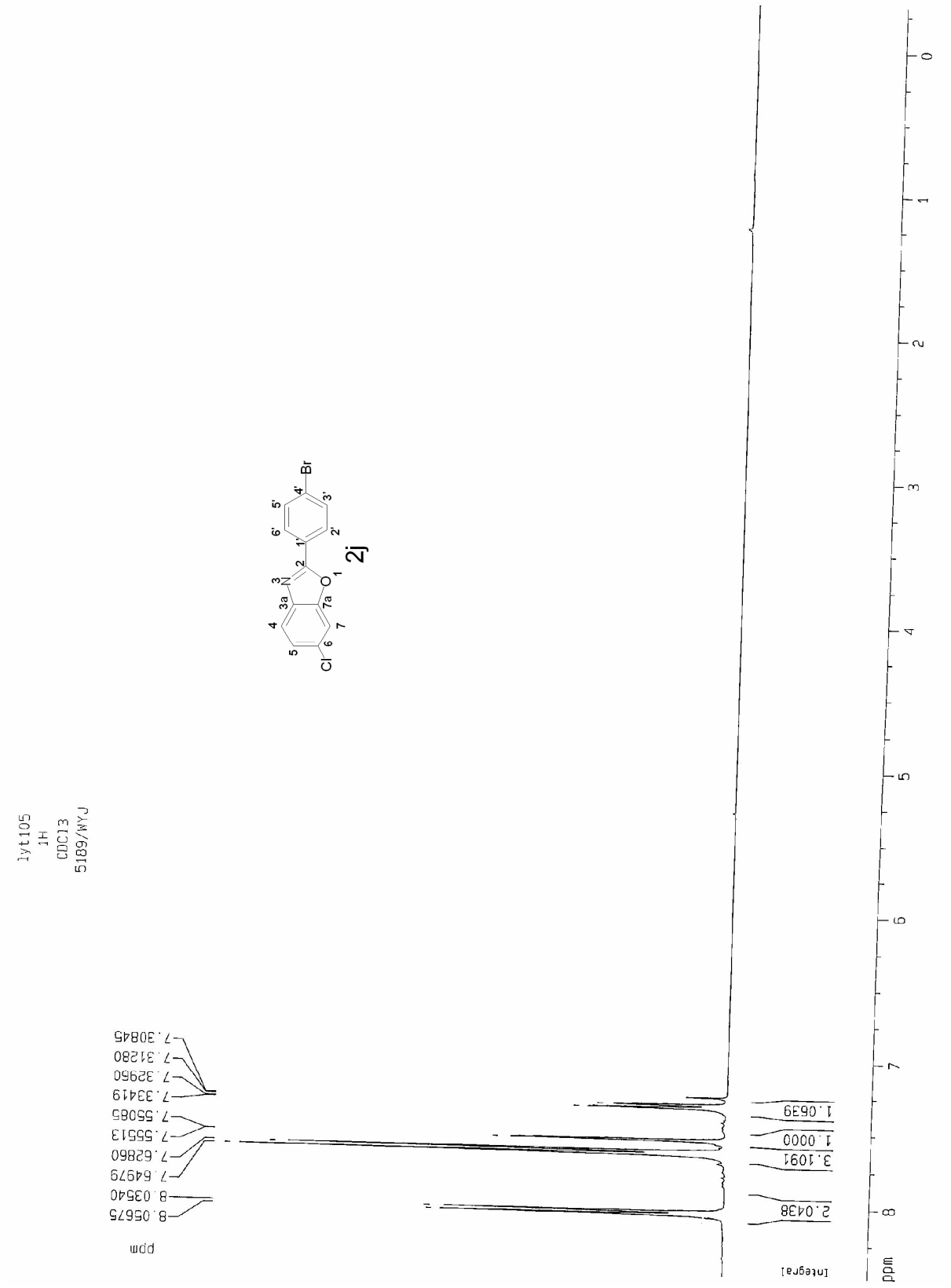
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Integral
ppm

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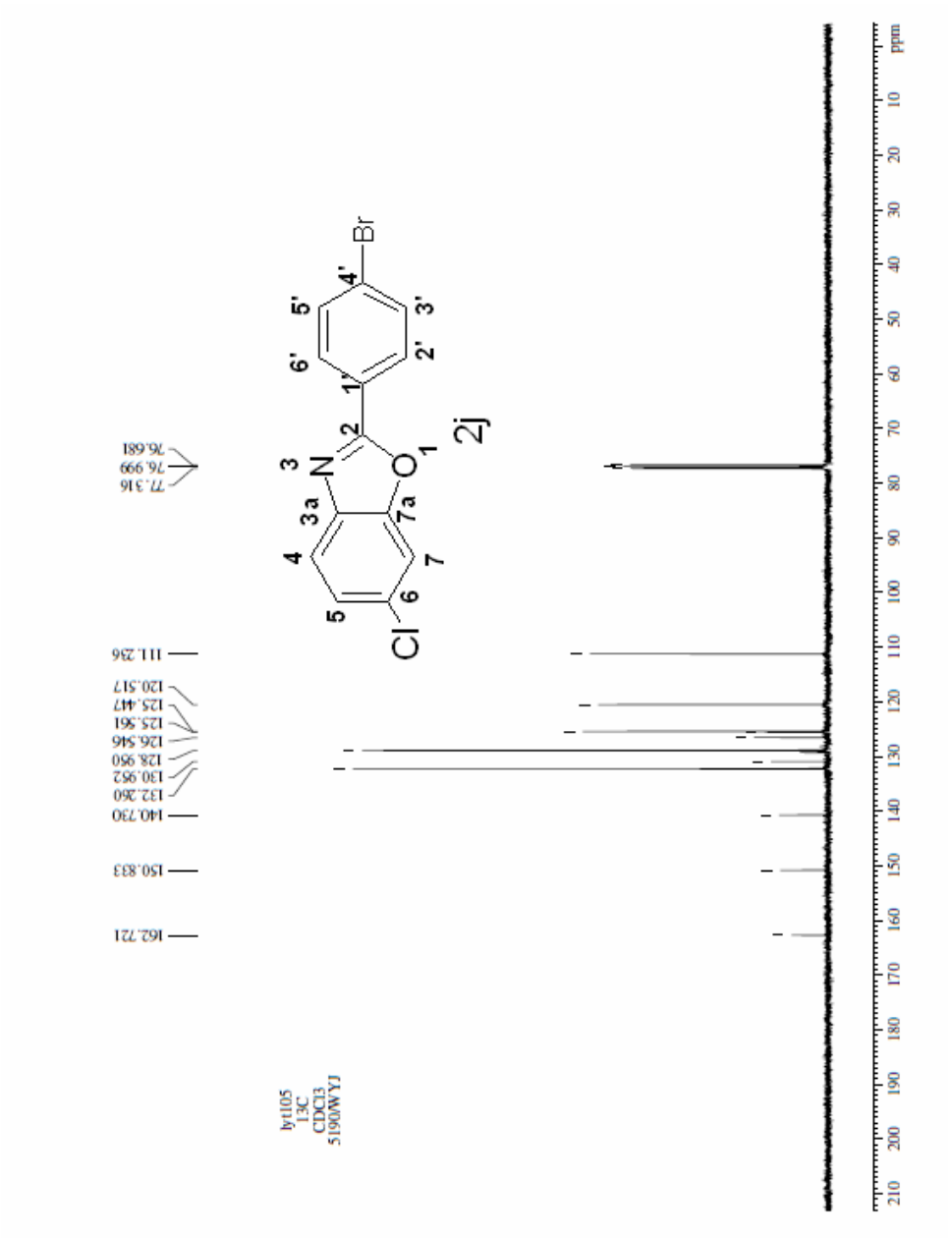

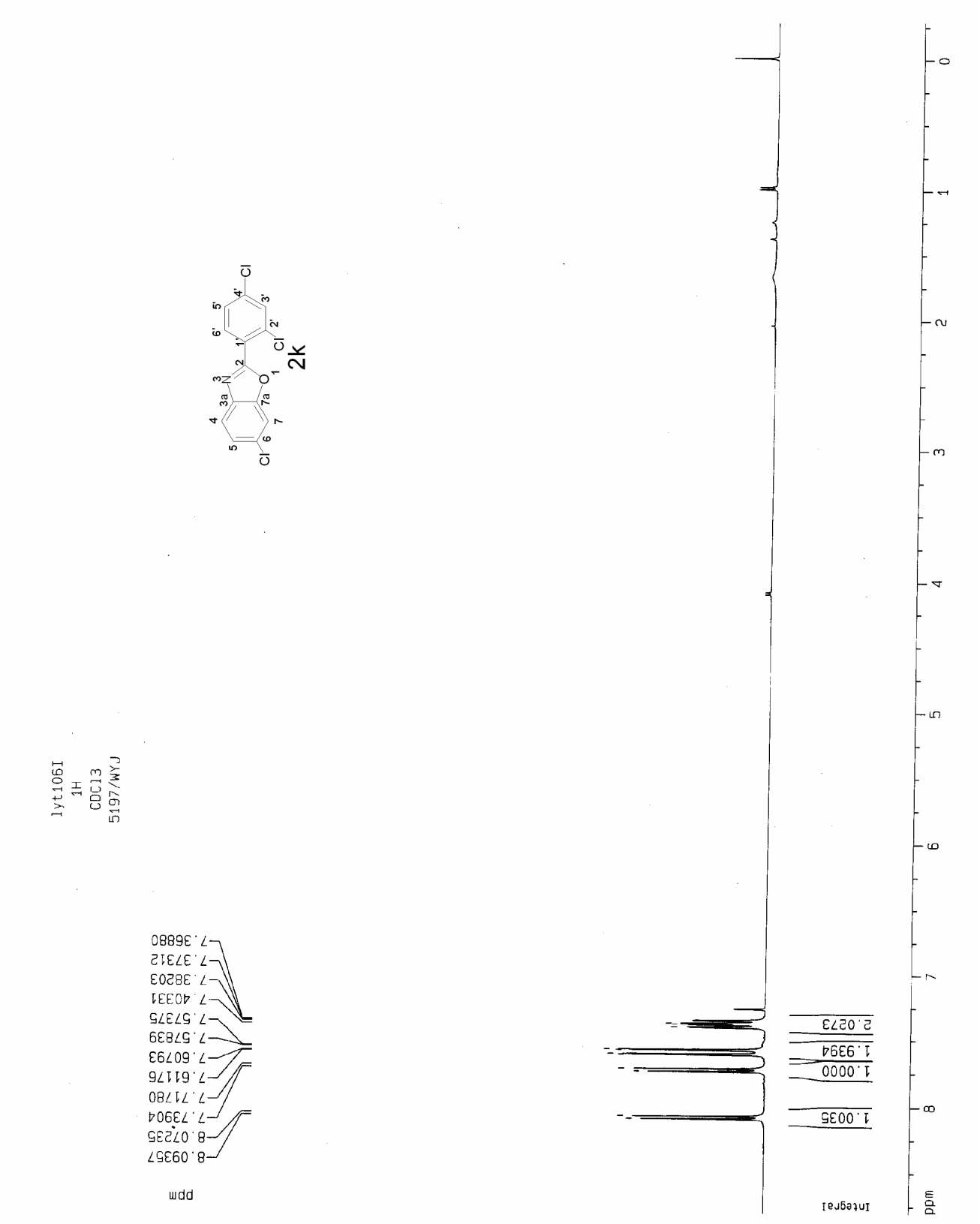
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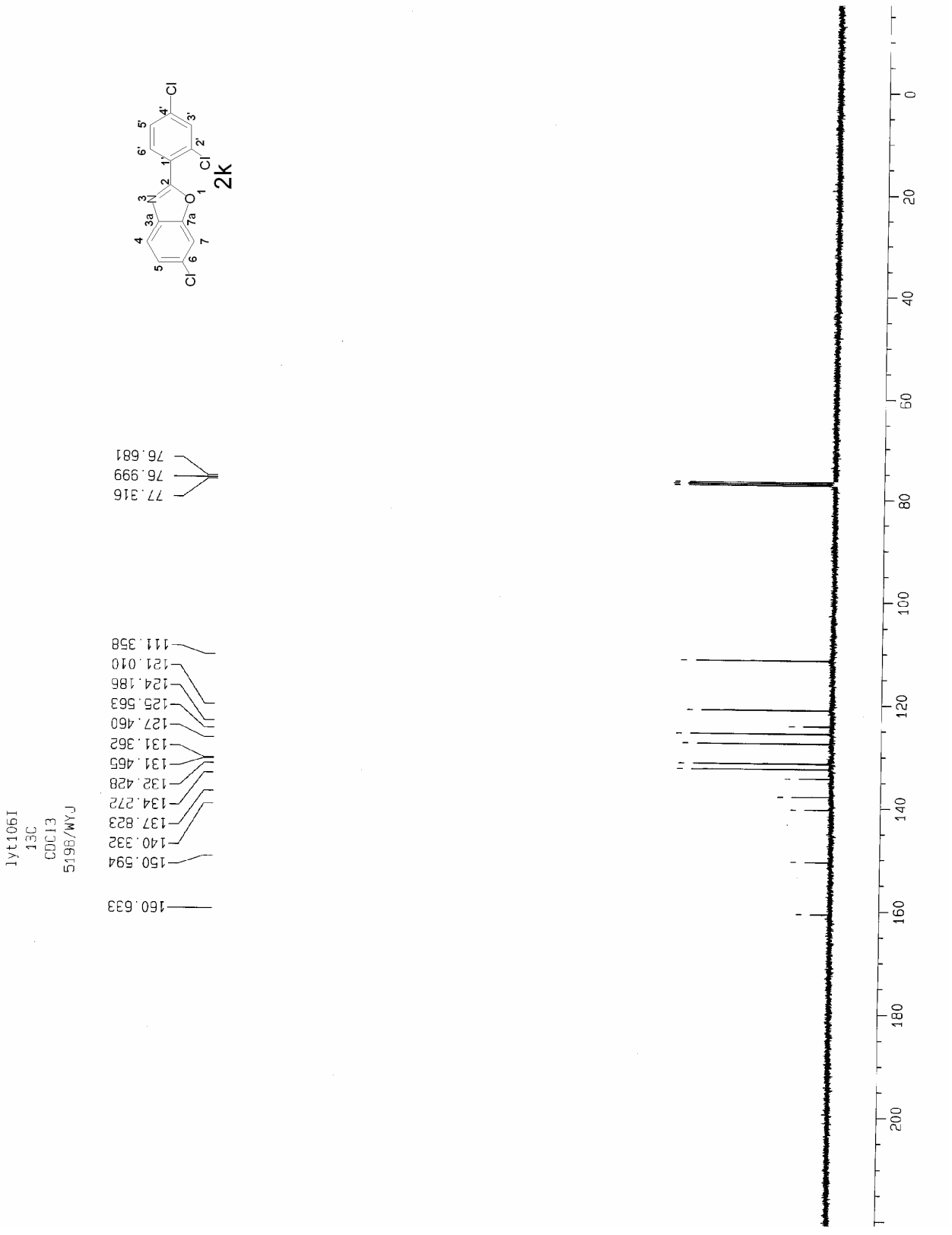

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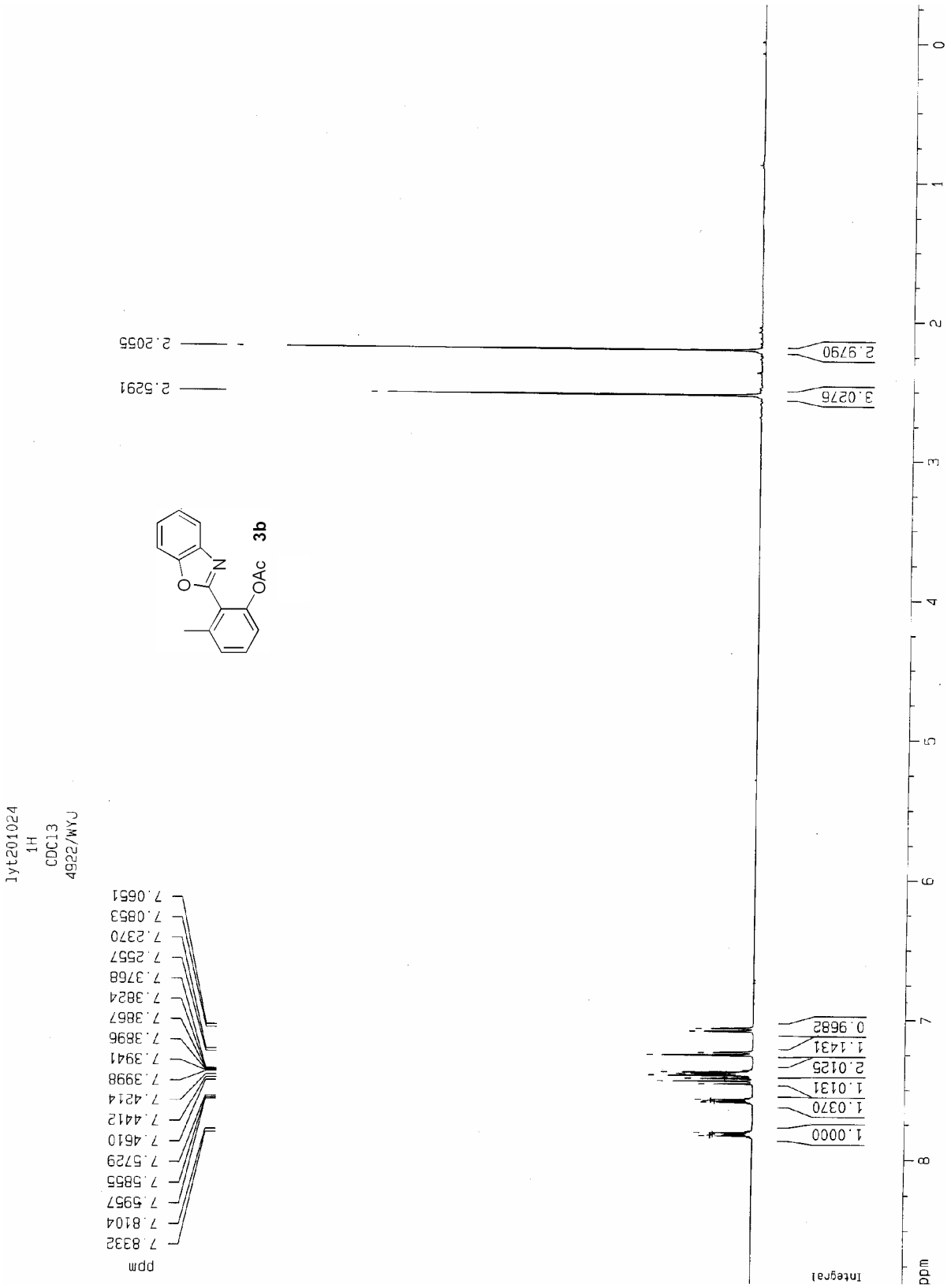

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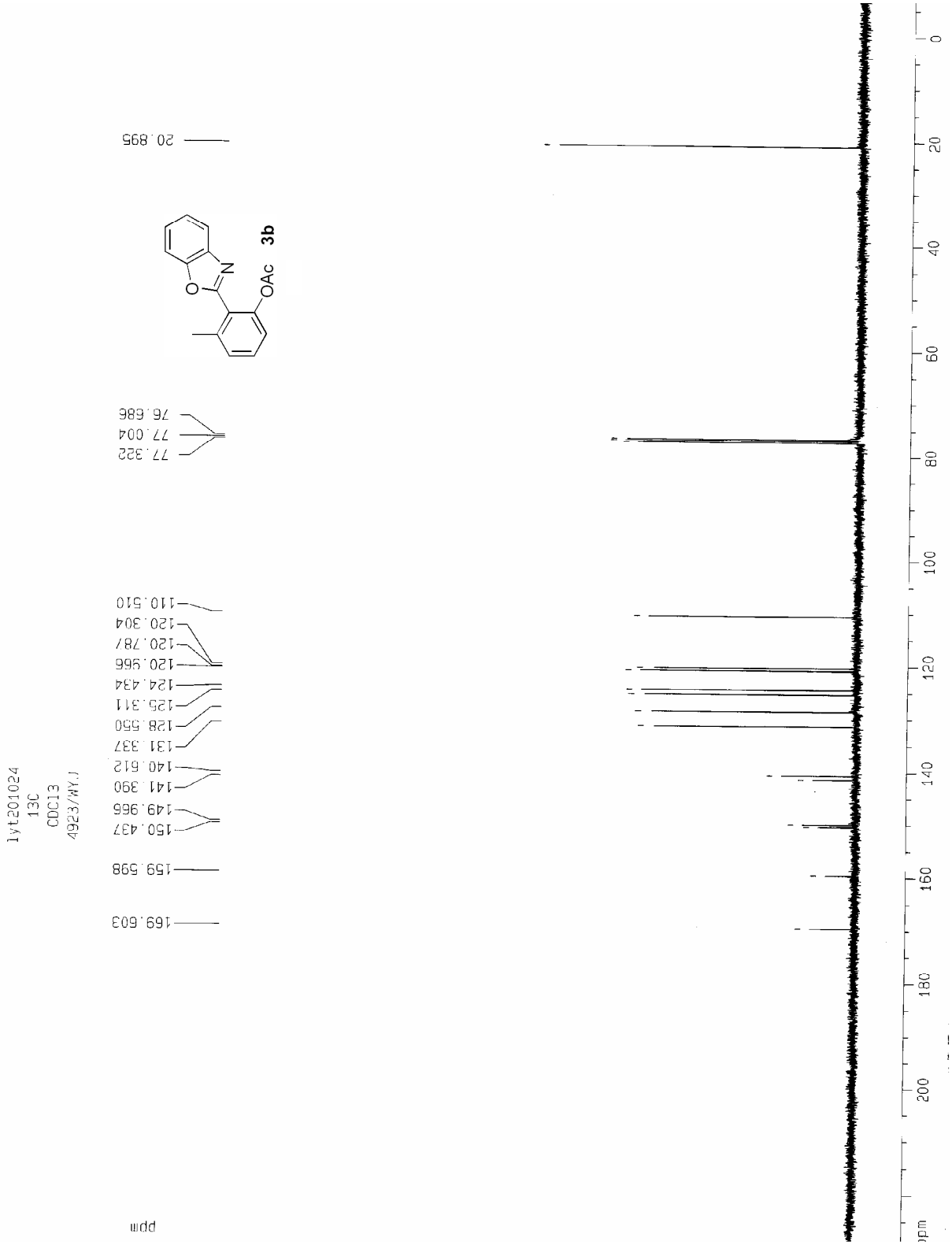

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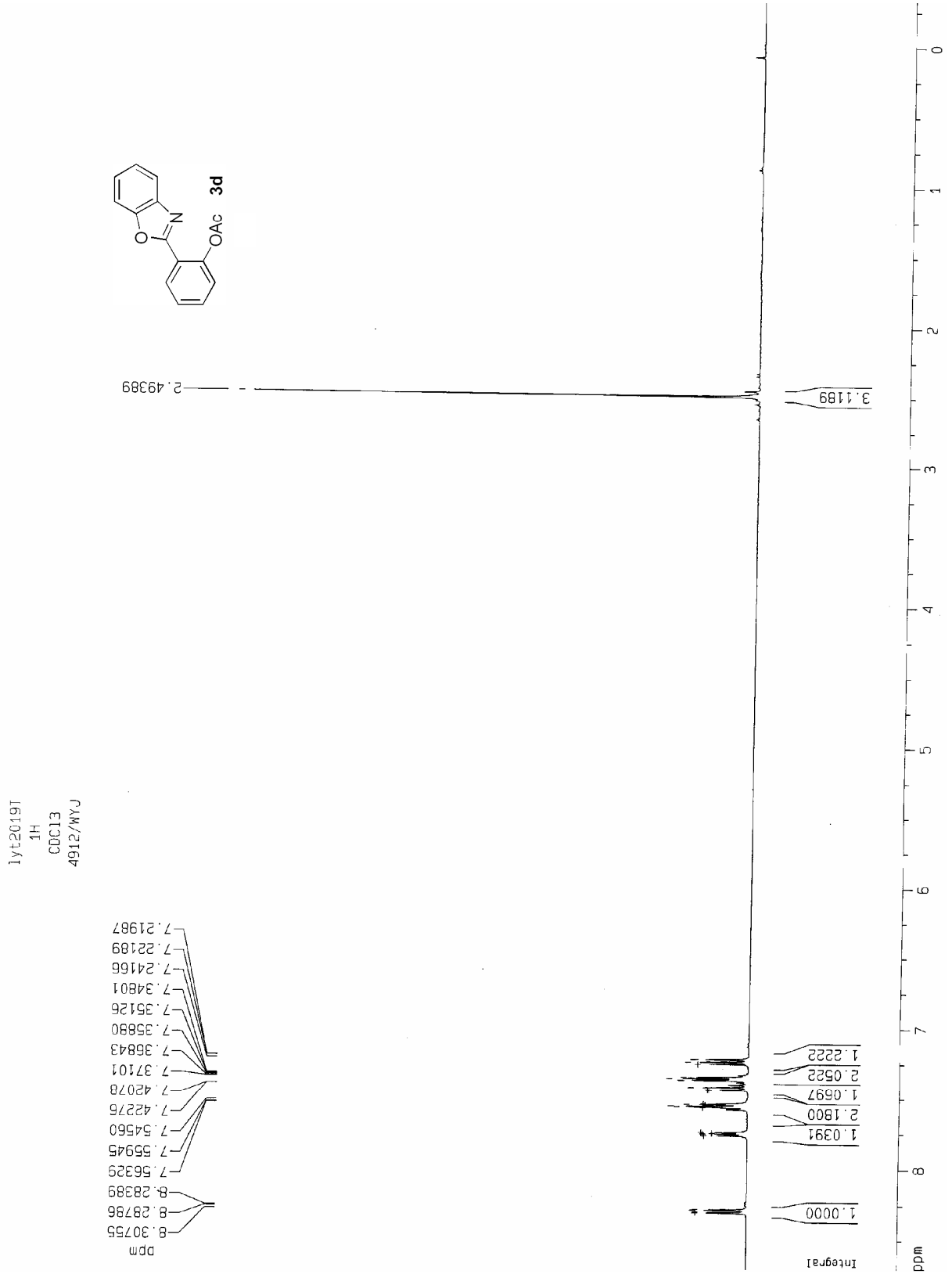

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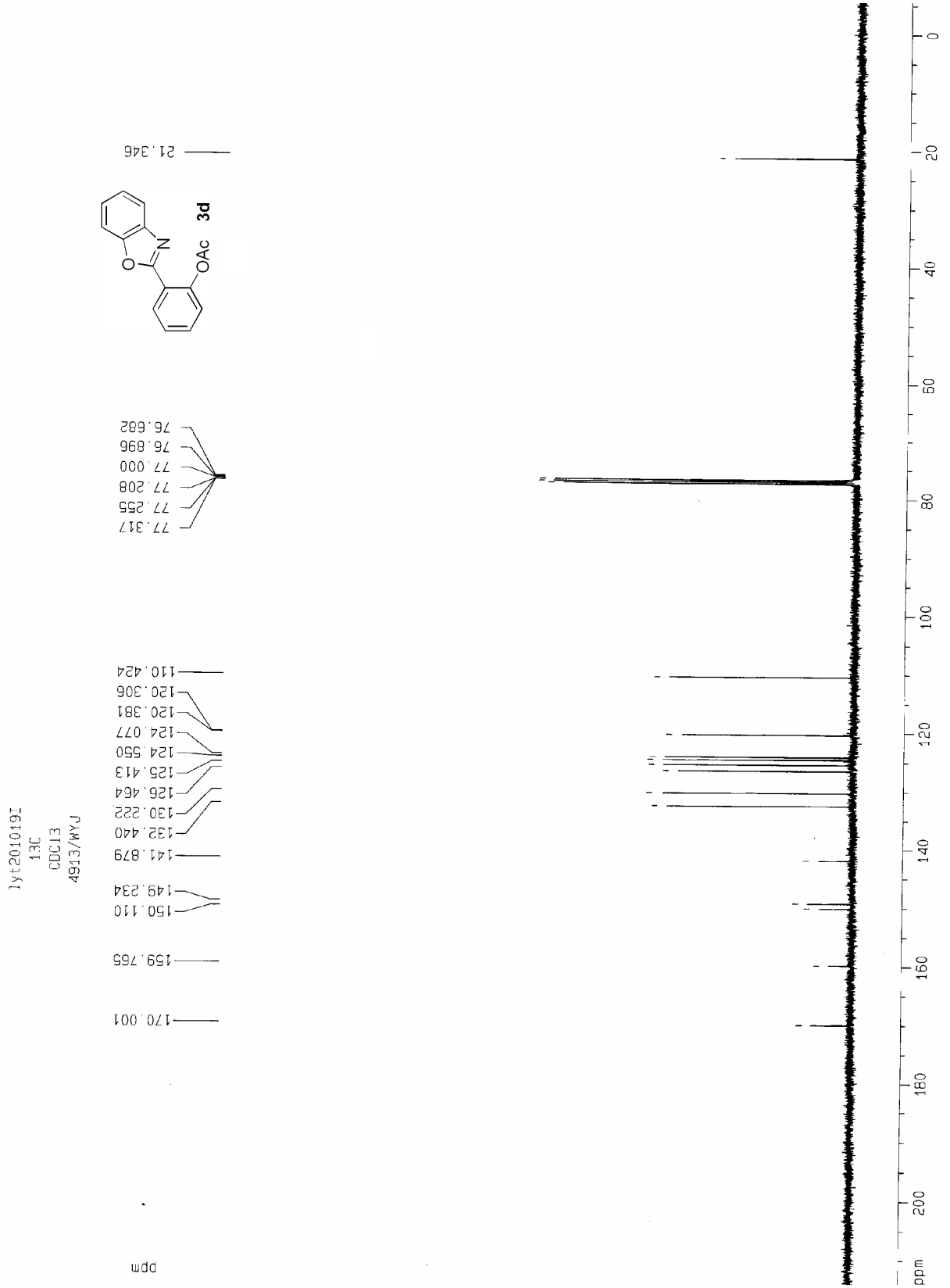

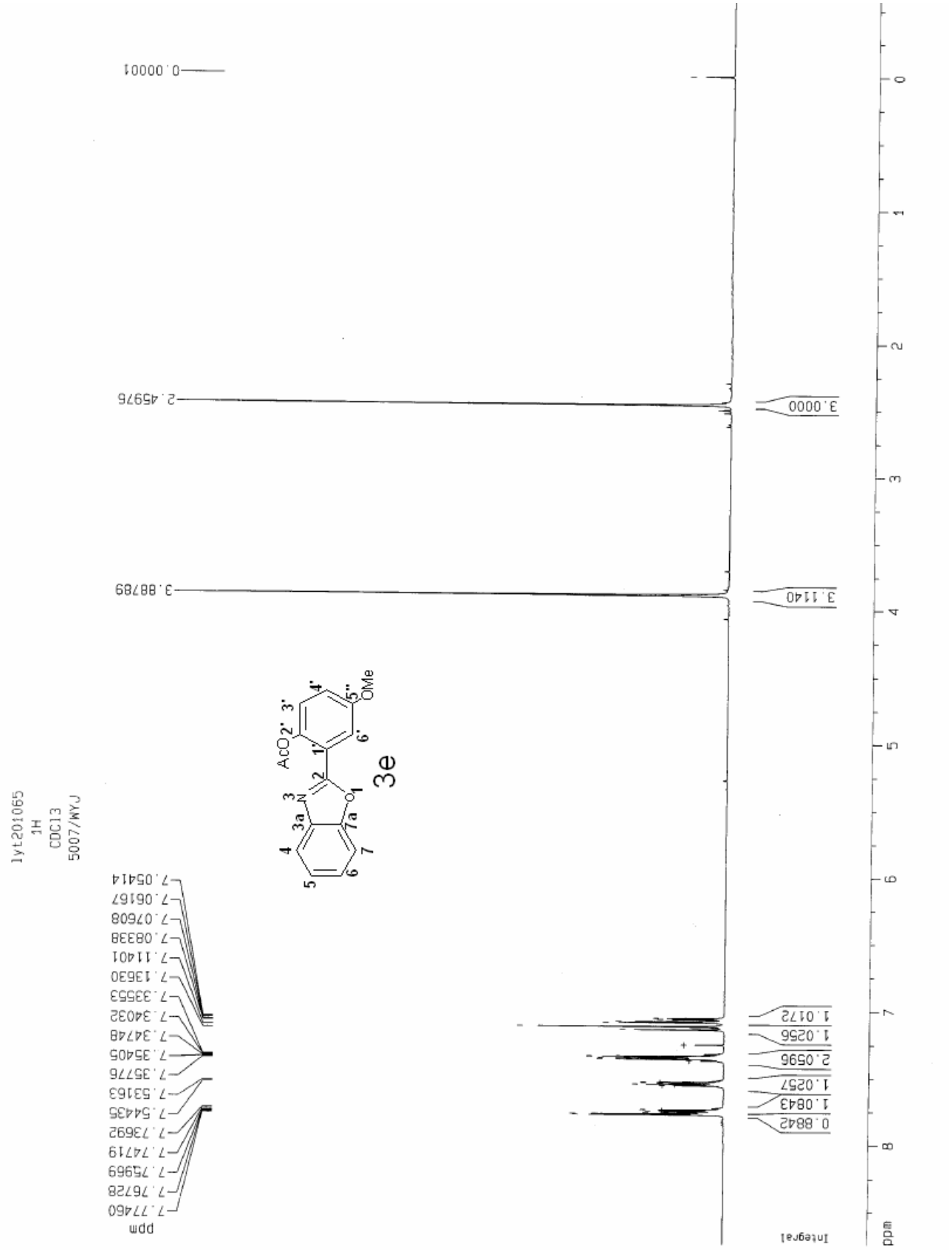
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AcO
OMe
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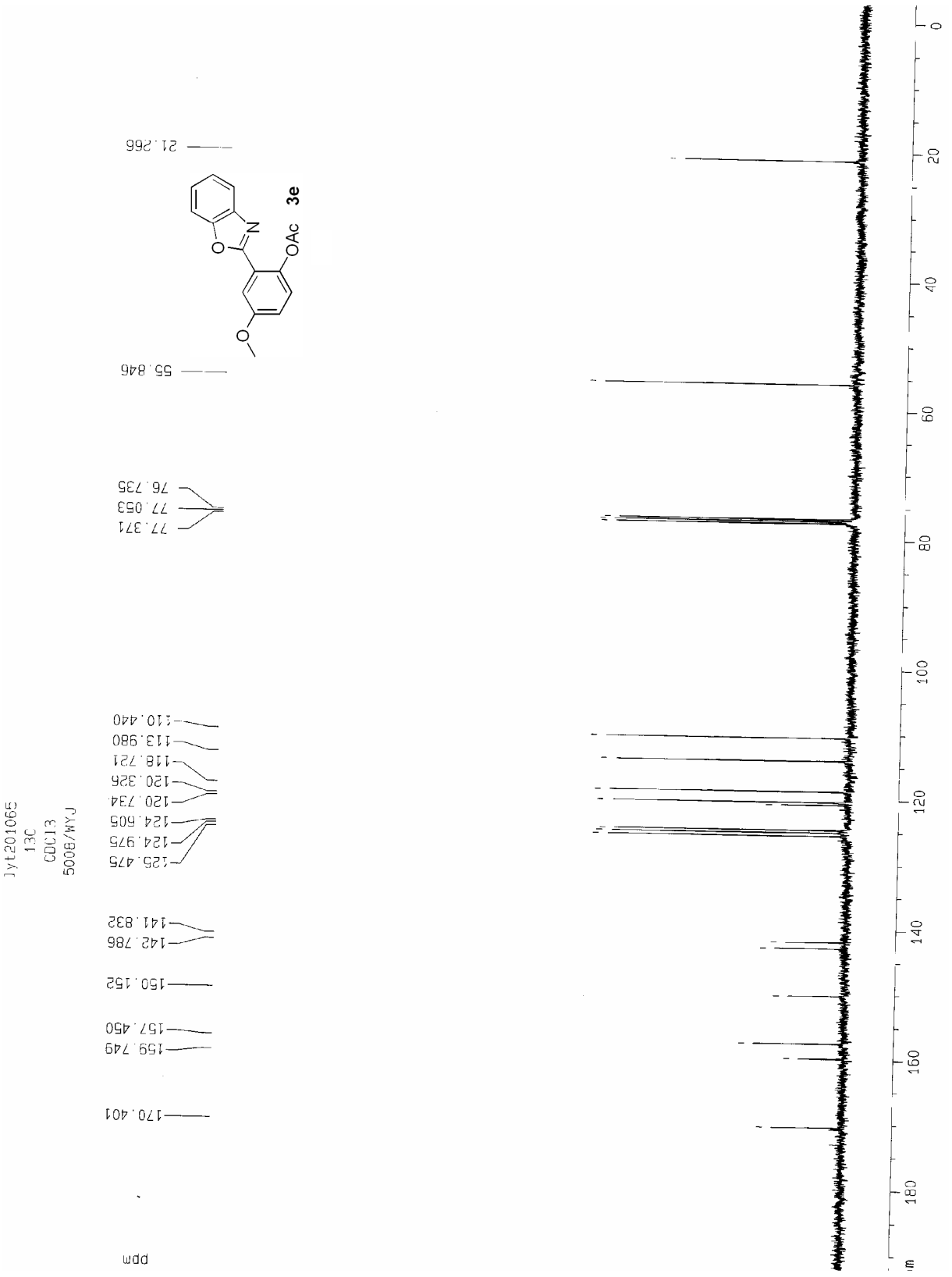

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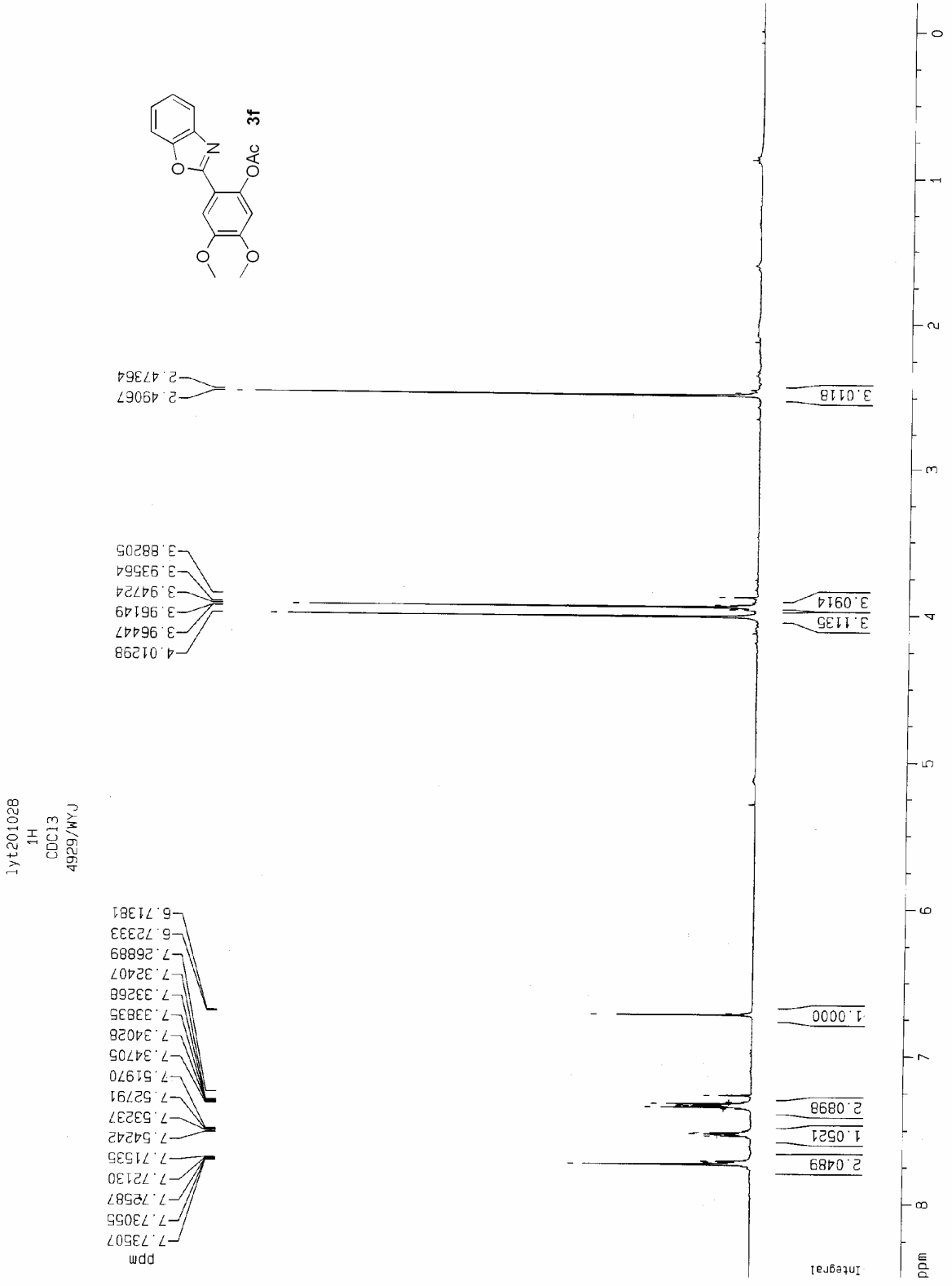

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