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Supporting Information
For

Rhodium-Catalyzed Synthesis of Unsymmetrical Di(aryl/heteroaryl)methanes Using Aryl/Heteroarylmethyl Ketones via CO-C Bond Cleavage

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Supplementary Materials

^{1}H, ^{13}C NMR spectra were recorded on a Varian Mercury (400 MHz) or a JNM-ECA 600 spectrometer. Tetramethylsilane (δ 0.00) was used as internal standard for ^{1}H NMR. ^{13}C NMR was referenced to the residual solvent ($CDCl_3$, δ 77.0). IR spectra were measured on a JASCO FT/IR-410 spectrophotometer. Melting points were determined with a Yanaco micro melting point apparatus without correction. High- and low-resolution mass spectra were measured on a JEOL JMS-DX 303 or a JEOL JMS-700 spectrometer. KANTO CHEMICAL Co., Inc. silica gel 60 (40-50 μm) was employed for flash column chromatography.

Benzylation of phenyl 2-benzoxazolyl ether 1a (Table 1, entry 1)

In a two-necked flask were placed phenyl 2-benzoxazolyl ether **1a** (52.8 mg, 0.25 mmol), 1,2-diphenyl-1-ethanone **2a** (147.2 mg, 0.75 mmol), $RhH(PPh_3)_4$ (28.8 mg, 10 mol%), and 1,2-bis(diphenylphosphino)benzene (dppBz, 22.3 mg, 20 mol%) in chlorobenzene (0.25 mL) under an argon atmosphere, and the solution was heated at reflux for 6 h. The reaction mixture was concentrated, and purified by flash column chromatography on silica gel giving 2-benzylbenzoxazole **3a** (40.3 mg, 77%) as colorless oil and phenyl benzoate **4a** (37.7 mg, 76%) as colorless solid. **3a**[1]**:** Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.27 (2H, s), 7.26-7.40 (7H, m), 7.44-7.47 (1H, m), 7.68-7.70 (1H, m). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 35.3, 110.4, 119.8, 124.2, 124.7, 127.3, 128.8, 129.0, 134.8, 141.3. IR (neat) 3062, 3032, 1614, 1570, 1496, 1454, 1242, 1140, 841, 746, 694 cm^{-1}. MS (EI) *m/z* 209 (M^+, 100%), 91 (M^+-C_7H_4ON, 16%). HRMS Calcd for $C_{14}H_{11}ON$: 209.0841. Found: 209.0844. **4a**[2]**:** Colorless solid. Mp. 69.5-70.0 °C (Hexane). Lit. [2] 69.5-70 °C (Hexane). 7.22 (2H, d, J = 8.0 Hz), 7.27 (1H, t, J = 8.0 Hz), 7.43 (2H, t, J = 8.0 Hz), 7.51 (2H, t, J = 8.0 Hz), 7.64 (1H, t, J = 8.0 Hz), 8.21 (2H, d, J = 8.0 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 121.7, 125.9, 128.5, 129.5, 129.6, 130.1, 133.6, 150.9, 165.2. IR (KBr) 3058, 1731, 1266, 1199, 1064 cm^{-1}. MS (EI) m/z 198 (M^+, 20%), 105 (M^+-C_6H_5O, 100%). HRMS Calcd for $C_{13}H_{10}O_2$: 198.0681. Found: 198.0677.

2-(*p*-Methoxybenzyl)benzoxazole (Table 1, entry 2) [3]

Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.78 (3H, s), 4.21 (2H, s), 6.88 (2H, d, J = 8.8 Hz), 7.21-7.31 (4H, m), 7.44-7.47 (1H, m), 7.67-7.70 (1H, m). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 34.4, 55.2, 110.4, 114.2, 119.8, 124.1, 124.6, 126.7, 130.0, 141.3, 151.0, 158.8, 165.6. IR (neat) 3034, 2933, 2834, 1614, 1568, 1511, 1243, 1034, 746 cm^{-1}. MS (EI) *m/z* 239 (M^+, 100%), 224 (M^+-Me, 32%), 121 (M^+-C_7H_4ON, 27%). HRMS Calcd for $C_{15}H_{13}O_2N$: 239.0946. Found: 239.0956.

2-(*p*-Methylbenzyl)benzoxazole (Table 1, entry 3) [3]

Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 3H), 4.24 (s, 2H), 7.15-7.17(m, 2H), 7.26-7.30 (m, 4H), 7.45-7.47 (m, 1H), 7.68-7.70 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 34.9, 110.5, 119.8, 124.2, 124.7, 128.9, 129.6, 131.7, 137.0, 141.4, 151.1, 165.5. IR (neat) 3036, 1614, 1570, 1242, 841, 746 cm^{-1}. MS (EI) (M^+, 100%). HRMS (ESI) calcd. for $C_{15}H_{14}ON$: 224.1070. found: 224.1076.

2-(*p*-Chlorobenzyl)benzoxazole (Table 1, entry 4) [4]

Colorless crystals. Mp. 78.0-80.0 °C (Hexane : Ether = 10 : 1). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.23 (2H, s), 7.28-7.33 (6H, m), 7.44-7.47 (1H, m), 7.67-7.69 (1H, m). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 34.5, 110.4, 119.8, 124.3, 124.8, 128.9, 130.3, 133.1, 133.3, 141.1, 150.9, 164.6. IR (KBr) 3030, 1613, 1567, 1489, 1454, 1242, 747 cm^{-1}. MS (EI) *m/z* 245 (M^++2, 37%), 244 (M^++1, 26%), 243 (M^+, 100%), 208 (M^+-Cl, 22%), 125 (M^+-C_7H_4ON, 20%). HRMS Calcd for $C_{14}H_{10}ONCl$: 243.0451. Found: 243.0443.

4-(2-Benzoxazolylmethyl)benzoic ethyl ester (Table 1, entry 5)

Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.38 (3H, t, J = 7.2 Hz), 4.36 (2H, q, J = 7.2 Hz), 7.29-7.32 (2H, m), 7.45 (2H, d, J = 8.4 Hz), 7.45-7.48 (1H, m), 7.68-7.71 (1H, m), 8.03 (2H, d, J = 8.4 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 14.3, 35.2, 60.9, 110.4, 119.9, 124.3, 124.9, 129.0, 129.6, 130.1, 139.7, 141.2, 151.0, 164.3, 166.2. IR (neat) 3059, 2981, 1718, 1455, 1277, 1105, 747 cm^{-1}. MS (EI) *m/z* 281 (M^+, 100%), 253 (M^+-C_2H_5, 13%), 236 (M^+-C_2H_5O, 25%). HRMS Calcd for $C_{17}H_{15}O_3N$: 281.1052. Found: 281.1052.

4-(2-Benzoxazolylmethyl)benzonitrile (Table 1, entry 6)

Colorless crystals. Mp. 82.0-83.5 °C (Ethyl acetate). Lit. [5] 82-83.5 °C (petroleum ether). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.35 (2H, s), 7.31-7.34 (2H, m), 7.47-7.48 (1H, m), 7.50 (2H, d, J = 8.4 Hz), 7.65 (2H, d, J = 8.4 Hz), 7.68-7.70 (1H, m). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 35.2, 110.5, 111.4, 118.5, 119.9, 124.4, 125.1, 129.8, 132.6,

140.0, 141.0, 151.0. IR (KBr) 3051, 2227, 1568, 1456, 1240, 1138, 820, 742 cm^{-1}. MS (EI) *m/z* 234 (M^+, 100%). HRMS Calcd for $C_{15}H_{10}O\ N_2$: 234.0793. Found: 234.0783.

4-(4-Methyl-2-benzoxazolylmethyl)benzonitrile (Table 1, entry 7)
Colorless crystals. Mp. 102.0-103.0 °C (Hexane : Ether = 10 : 1). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.61 (3H, s), 4.34 (2H, s), 7.11 (1H, d, J = 7.6 Hz), 7.20 (1H, t, J = 7.6 Hz), 7.28 (1H, t, J = 7.2 Hz), 7.49 (2H, d, J = 8.4 Hz), 7.63 (2H, d, J = 8.0 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 18.2, 35.2, 107.8, 111.3, 118.6, 124.7, 125.0, 129.7, 130.3, 132.5, 140.3, 150.8, 162.5. IR (KBr) 3037, 2918, 2226, 1422, 754 cm^{-1}. MS (EI) *m/z* 248 (M^+, 100%). HRMS Calcd for $C_{16}H_{12}O\ N_2$: 248.0950. Found: 248.0946.

4-(5-Methyl-2-benzoxazolylmethyl)benzonitrile (Table 1, entry 8)
Colorless crystals. Mp. 101.0-102.0 °C (Ethyl acetate). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.46 (3H, s), 4.31 (2H, s), 7.13 (1H, dd, J = 8.0, 1.2 Hz), 7.34 (1H, d, J = 8.0 Hz), 7.47 (1H, d, J = 1.2 Hz), 7.49 (2H, d, J = 8.4 Hz), 7.64 (2H, d, J = 8.4 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 21.4, 35.3, 109.9, 111.4, 118.6, 119.9, 126.2, 129.8, 132.6, 134.3, 140.2, 141.3, 149.2, 163.6. IR (KBr) 3067, 3037, 2918, 2223, 1572, 1259, 796 cm^{-1}. MS (EI) *m/z* 248 (M^+, 100%). HRMS Calcd for $C_{16}H_{12}ON_2$: 248.0950. Found: 248.0970.

4-(5-Chloro-2-benzoxazolylmethyl)benzonitrile (Table 1, entry 9)
Colorless crystals. Mp. 119.0-120.0 °C (Ethyl acetate). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.33 (2H, s), 7.30 (1H, dd, J = 9.2, 1.6 Hz), 7.40 (1H, d, J = 9.2 Hz), 7.49 (2H, d, J = 8.4 Hz), 7.65 (2H, d, J = 8.4 Hz), 7.67 (1H, d, J = 1.6 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 35.2, 111.3, 111.6, 118.5, 120.0, 125.4, 129.9, 130.0, 132.7, 139.6, 142.2, 149.5, 165.0. IR (KBr) 3099, 2923, 2223, 1562, 1450, 803 cm^{-1}. MS (EI) *m/z* 268 (M^+, 100%). HRMS Calcd for $C_{15}H_9ON_2Cl$: 268.0403. Found: 268.0393.

4-(5-Phenyl-2-benzoxazolylmethyl)benzonitrile (Table 1, entry 10)
Colorless crystals. Mp. 109.0-110.0 °C (Ethyl acetate). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.35 (2H, s), 7.36 (1H, tt, J = 7.2, 1.6 Hz), 7.46 (2H, dd, J = 8.0, 7.2 Hz), 7.52 (2H, d, J = 8.4 Hz), 7.52 (1H, d, J = 8.4 Hz), 7.55 (1H, dd, J = 8.4, 1.6 Hz), 7.59 (2H, dd, J = 8.0, 1.6 Hz), 7.66 (2H, d, J = 8.4 Hz), 7.88 (1H, d, 1.6 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 35.3, 110.5, 111.5, 118.4, 118.6, 127.3, 127.4, 127.4, 128.9, 129.9, 132.6, 138.4, 140.0, 140.9, 141.7, 150.5, 164.2. IR (KBr) 3061, 2229, 1571, 1469, 817, 763 cm^{-1}. MS (EI) *m/z* 310 (M^+, 100%). HRMS Calcd for $C_{21}H_{14}ON_2$: 310.1106. Found: 310.1104.

4-(6-Methyl-2-benzoxazolylmethyl)benzonitrile (Table 1, entry 11)
Colorless crystals. Mp. 117.0-118.0 °C (Ethyl acetate). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.46 (3H, s), 4.30 (2H, s), 7.13 (1H, dd, J = 8.0, 1.2 Hz), 7.27 (1H, d, J = 1.2 Hz), 7.48 (2H, d, J = 8.4 Hz), 7.55 (1H, d, J = 8.0 Hz), 7.63 (2H, d, J = 8.4 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 21.7, 35.2, 110.6, 111.3, 118.6, 119.2, 125.6, 129.8, 132.5, 135.5, 138.8, 140.2, 151.2, 162.9. IR (KBr) 3054, 2919, 2225, 1608, 1421, 1114, 818 cm^{-1}. MS (EI) *m/z* 248 (M^+, 100%). HRMS Calcd for $C_{16}H_{12}ON_2$: 248.0950. Found: 248.0958.

4-(6-Chloro-2-benzoxazolylmethyl)benzonitrile (Table 1, entry 12)
Colorless crystals. Mp. 101.5-102.5 °C (Ethyl acetate). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.32 (2H, s), 7.30 (1H, dd, J = 8.4, 1.6 Hz), 7.49 (2H, d, J = 7.6 Hz), 7.50 (1H, d, J = 1.6 Hz), 7.59 (1H, d, J = 8.4 Hz), 7.65 (2H, d, J = 7.6 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 35.1, 111.2, 111.6, 118.5, 120.4, 125.2, 129.8, 130.8, 132.6, 139.6, 139.8, 151.1, 164.2. IR (KBr) 3089, 2925, 2853, 2225, 1610, 1452, 1216, 1145, 917 cm^{-1}. MS (EI) *m/z* 268 (M^+, 100%). HRMS Calcd for $C_{15}H_9\ ON_2Cl$: 250.3183. Found: 250.3183.

4-Pyridylmethylation of phenyl 2-benzoxazolyl ether 1a (Table 1, entry 13)
In a two-necked flask were placed 1-phenyl-(4-pyridinyl)ethanone (147.9 mg, 0.75 mmol), phenyl 2-benzoxazolyl ether **1a** (52.8 mg, 0.25 mmol), $RhH(PPh_3)_4$ (28.8 mg, 10 mol%), and dppBz (22.3 mg, 20 mol%) in chlorobenzene (0.25 mL) under an argon atmosphere, and the solution was heated at reflux for 6 h. The reaction mixture was concentrated, and purified by flash column chromatography on silica gel giving 2-(4-pyridiylmethyl)benzoxazole (43.6 mg, 83%) and **4a** (41.1 mg, 83%). **2-(4-Pyridylmethyl)benzoxazole:** Colorless crystals. Mp. 87.0-88.0 °C (Ethyl acetate). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.28 (2H, s), 7.31-7.35 (4H, m), 7.48-7.50 (1H, m), 7.70-7.72 (1H, m), 8.59 (2H, d, J = 4.8 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 34.6, 110.5, 120.0, 124.2, 124.5,125.1, 141.1,143.6, 150.2, 151.0,163.3. IR (KBr) 3052, 2923, 1667, 1521, 746 cm^{-1}. MS (EI) *m/z* 210 (M^+, 100%). HRMS Calcd for $C_{13}H_{10}ON_2$: 210.0793. Found: 210.0793.

2-(2-Benzothiazoylmethyl)benzoxazole (Table 1, entry 14)
Colorless crystals. Mp. 56.0-57.0 °C (Ethyl acetate). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.81 (2H, s), 7.32-7.40 (3H, m), 7.46-7.52 (2H, m), 7.46-7.52 (1H, m), 7.73-7.75 (1H, m),7.85 (1H, d, J = 8.0 Hz), 8.03 (1H, d, J = 8.0 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 34.0, 110.6, 120.1, 121.5, 123.2, 124.5, 125.2, 125.3, 126.2, 135.7, 141.1, 151.1, 152.9, 161.4, 163.1. IR (KBr) 3056, 2936, 1508, 1456, 748 cm^{-1}. MS (EI) *m/z* 266 (M^+, 100%). HRMS Calcd for $C_{15}H_{10}ON_2S$: 266.0514. Found: 266.0520.

2-(2-Thienylmethyl)benzoxazole (Table 1, entry 15)
Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.48 (2H, s), 6.97-7.00 (1H, m), 7.50 (1H, d, J = 2.4. Hz), 7.23 (1H, dd, J = 4.8, 1.2 Hz). 7.29-7.33 (2H, m), 7.48-7.50 (1H, m), 7.69-7.71 (1H, m). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 44.9, 124.7, 128.6, 128.9, 132.7, 135.6, 145.8, 149.8, 171.6, 176.6. IR (Neat) 3073, 2920, 1614, 1455, 746 cm^{-1}. MS (EI) *m/z* 215 (M^+, 100%). HRMS Calcd for $C_{21}H_{16}ON_2$: 215.0405. Found: 215.0403.

2-(2-Furylmethyl)benzoxazole (Table 1, entry 16)
Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.33 (2H, s), 6.31 (1H, d, J = 3.2 Hz), 6.36 (1H, dd, J = 3.2, 1.6 Hz), 7.30-7.34 (2H, m), 7.40 (1H, d, J = 1.6. Hz), 7.49-7.51 (1H, m), 7.69-7.72 (1H, m). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 28.3, 108.0, 110.5, 110.7, 120.0, 124.3, 124.9, 141.2, 142.4, 147.9. IR (Neat) 3052, 2964, 2924, 1574, 1455, 1242, 744 cm^{-1}. MS (EI) *m/z* 199 (M^+, 100%). HRMS Calcd for $C_{12}H_9O_2N$: 199.0633. Found: 199.0640.

Reverse reaction of 2-benzylbenzoxazole and phenyl benzoate
In a two-necked flask were placed 2-benzylbenzoxazole **3a** (52.3 mg, 0.25 mmol), phenyl benzoate **4a** (49.6 mg, 0.25 mmol), $RhH(PPh_3)_4$ (28.8 mg, 10 moll%), and dppBz (22.3 mg, 20 mol%) in chlorobenzene (0.25 mL) under an argon atmosphere, and the solution was heated at reflux for 6 h. The mixture was concentrated, and ^{1}H-NMR analysis was conducted. **1a** and **2a** were not detected in the mixture, and **3a** (51.8 mg, 99%) and **4a** (47.6 mg, 96%) were recovered.

4-Cyanobenzylation of 2-(*p*-chlorophenoxy)benzothiazole 1b (Table 2)
In a two-necked flask were placed *p*-cyanobenzyl phenyl ketone **2b** (55.3 mg, 0.25 mmol), 2-(*p*-chlorophenoxy)benzothiazole **1b** (196.3 mg, 0.75 mmol), $RhH(PPh_3)_4$ (28.8 mg, 10 mol%), and 1,2-bis(diphenylphosphino)benzene (22.3 mg, 20 mol%) in chlorobenzene (0.25 mL) under an argon atmosphere, and the solution was heated at reflux for 12 h. The reaction mixture was concentrated, and purified by flash column chromatography on silica gel giving 4-(2-benzothiazolylmethyl)benzonitrile **3b** (46.9 mg, 75%) and 4-chlorophenyl benzoate **4b** (40.1 mg, 69%). **3b:** Colorless crystals. Mp. 93.5-94 °C (Ethyl acetate). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.50 (2H, s), 7.38 (1H, ddd, J = 8.0, 8.0, 1.2 Hz), 7.48 (1H, ddd, J = 8.0, 8.0, 1.2 Hz), 7.49 (2H, d, J = 8.4 Hz), 7.65 (2H, d, J = 8.4 Hz), 7.83 (1H, dd, J = 8.0, 1.2 Hz), 8.01 (1H, dd, J = 8.0, 1.2 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 40.2, 111.2, 118.4, 121.4, 122.8, 125.1, 126.1, 129.7, 132.5, 135.3, 142.2, 153.1, 168.2. IR (KBr) 3062, 2927, 2225, 1604, 1506, 1435, 1315, 858, 756 cm^{-1}. MS (EI) *m/z* 250 (M^+, 100%). HRMS Calcd for $C_{15}H_{10}N_2S$: 250.3183. Found: 250.3183. **4b** [6]**:** Colorless crystals. Mp. 89.5-90.0 °C (Hexane). Lit. [7] 89.5-90.0 °C (Hexane). ^{1}H-NMR (400MHz, $CDCl_3$) δ 7.17 (2H, d, J = 8.8 Hz), 7.40 (2H, d, J = 8.8 Hz), 7.52 (2H, d, J = 8.0 Hz), 7.65 (1H, t, J = 7.6 Hz), 8.19 (2H, d, J = 8.4 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 123.1, 128.6, 129.1, 129.5, 130.2, 131.2, 133.8, 149.4, 164.9. IR (KBr) 1734, 1489, 1450, 1269, 1218, 1161, 1082, 1061, 876, 808, 706, 685, 513 cm^{-1}. MS (EI) m/z 232 (M^+, 12%), 105 (M^+-C_6H_4OCl, 100%). HRMS Calcd for $C_{13}H_9O_2$: 232.0291. Found: 232.0290.

4-(5-Chloro-2-benzothiazolylmethyl)benzonitrile (3c)
Colorless crystals. Mp. 119.0-120.0 °C (Ethyl acetate). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.47 (2H, s), 7.43 (1H, dd, J = 8.4, 2.4 Hz), 7.48 (2H, d, J = 8.4 Hz), 7.65 (2H, d, J = 8.4 Hz), 7.79 (1H, d, J = 2.4 Hz), 7.90 (1H, d, J = 8.4 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 40.2, 111.4, 118.5, 121.2, 123.7, 127.0, 129.8, 1312., 132.6, 136.6, 142.0, 151.7, 168.9. IR (KBr) 3064, 2926, 2225, 1509, 1434, 808 cm^{-1}. MS (EI) *m/z* 286 (M^++2, 40%), 285 (M^++1, 36%), 284 (M^+, 100%). HRMS Calcd for $C_{15}H_9ClN_2S$: 286.0175. Found: 286.0157.

4-(5-Methoxy-2-benzothiazolylmethyl)benzonitrile (3d)
Colorless crystals. Mp. 78.0-79.0 °C (Hexane:Diethyl ether = 10 : 1). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.86 (3H, s), 4.45 (2H, s), 7.07 (1H, dd, J = 8.8, 2.4 Hz), 7.26 (1H, d, J = 2.4 Hz), 7.47 (2H, d, J = 8.4 Hz), 7.63 (2H, d, J = 8.4 Hz), 7.87 (1H, d, J = 8.8 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 40.2, 55.8, 104.1, 111.2, 115.5, 118.6, 123.4,

129.8, 132.6, 136.8, 142.6, 147.6, 157.7, 165.6. IR (KBr) 2927, 2228, 1604, 1462, 1054, 803 cm^{-1}. MS (EI) *m/z* 280 (M^+, 100%), 265 (M^+-CN, 19%). HRMS Calcd for $C_{16}H_{12}ON_2S$: 280.0670. Found: 280.0671.

4-(5-Phenyl-2-oxazolylmethyl)benzonitrile (3e)
Colorless crystals. Mp. 114.0-114.5 °C (Ethyl acetate). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.23 (2H, s), 7.26 (1H, s), 7.31 (1H, tt, *J* = 7.2, 1.2 Hz), 7.40 (2H, dd, *J* = 7.6, 7.2 Hz), 7.46 (2H, d, *J* = 8.4 Hz), 7.58 (2H, dd, *J* = 7.6, 1.2 Hz), 7.63 (2H, d, *J* = 8.4 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 34.7, 111.1, 118.6, 122.0, 124.0, 127.6, 128.5, 128.8, 129.6, 132.5, 140.7, 151.8, 160.9. IR (KBr) 3067, 2933, 2232, 1548, 754, 685 cm^{-1}. MS (EI) *m/z* 260 (M^+, 100%). HRMS Calcd for $C_{17}H_{12}ON_2$: 260.0950. Found: 260.0968.

4-(4,5-Diphenyl-2-oxazolylmethyl)benzonitrile (3f)
Colorless crystals. Mp. 85.0-86.0 °C (Ethyl acetate). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.26 (2H, s), 7.30-7.39 (6H, m), 7.51-7.58 (4H, m), 7.61-7.67 (4H, m). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 34.6, 111.1, 118.6, 126.4, 127.8, 128.2, 128.5, 128.5, 128.6, 128.6, 129.6, 132.0, 132.5, 135.3, 140.7, 146.0, 159.9. IR (KBr) 3059, 2228, 1566, 1502, 1444, 1057, 763, 693 cm^{-1}. MS (EI) *m/z* 336 (M^+, 100%). HRMS Calcd for $C_{23}H_{16}ON_2$: 336.1263. Found: 336.1251.

4-(4,5-Diphenyl-2-oxazolylmethyl)pyridine (3g)
Colorless crystals. Mp. 97.5-98.0 °C (Ethyl acetate). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.21 (2H, s), 7.34-7.39 (8H, m), 7.55 (2H, d, *J* = 6.8 Hz), 7.64 (2H, d, *J* = 6.8 Hz), 8.59 (2H, d, *J* = 5.2 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 34.1, 124.1, 126.5, 127.9, 128.2, 128.6, 128.7, 132.1, 135.4, 144.3, 146.1, 150.1, 159.7. IR (KBr) 3063, 2936, 1540, 1519, 1372, 1057, 703 cm^{-1}. MS (EI) *m/z* 312 (M^+, 100%). HRMS Calcd for $C_{21}H_{16}ON_2$: 312.1263. Found: 336.1285.

2-(4,5-Diphenyl-2-oxazolylmethyl)benzothiazole (3h)
Colorless crystals. Mp. 75.0-76.0 °C (Ethyl acetate). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.74 (2H, s), 7.32-7.41 (7H, m), 7.49 (1H, *t*, *J* = 7.2 Hz), 7.59 (2H, dd, *J* = 8.0, 2.0 Hz), 7.67 (2H, *d*, *J* = 8.4 Hz), 7.86 (1H, *d*, *J* = 8.0 Hz), 8.04 (1H, *d*, *J* = 8.0 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 33.7, 121.6, 123.1, 125.2, 126.2, 126.6, 127.9, 128.2, 128.6, 128.7, 132.1, 135.8, 146.5, 153.0, 158.0, 164.3. IR (KBr) 3053, 2926, 1698, 1558, 1507, 1057, 761 cm^{-1}. MS (EI) *m/z* 368 (M^+, 100%). HRMS Calcd for $C_{23}H_{10}ON_2S$: 368.0983 Found: 368.0984.

4-(2-Thiazolylmethyl)benzonitrile (3i)
Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.41 (2H, s), 7.25 (1H, d, *J* = 3.2 Hz), 7.43 (2H, d, *J* = 8.0 Hz), 7.63 (2H, d, *J* = 8.4 Hz), 7.73 (2H, d, *J* = 3.2 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 39.6, 126.6, 128.4, 129.1, 129.7, 131.1, 132.6, 138.1, 140.0, 143.0, 166.8. IR (Neat) 3076, 2926, 2228, 1607, 1500 cm^{-1}. MS (EI) *m/z* 200 (M^+, 100%). HRMS Calcd for $C_{11}H_8N_2S$: 200.0408. Found: 200.0387.

4-(5-Phenyl-2-thiazolylmethyl)benzonitrile (3j)
Colorless crystals. Mp. 78.0-79.0 °C (Ethyl acetate). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.39 (2H, s), 7.32 (1H, tt, *J* = 7.4 Hz), 7.38 (2H, t, *J* = 7.4 Hz), 7.46-7.51 (4H, m), 7.65 (2H, d, *J* = 8.4 Hz), 7.86 (1H, s). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 39.6, 126.6, 128.4, 129.1, 129.7, 131.1, 132.6, 138.1, 140.0, 143.0, 166.8. IR (KBr) 3063, 2919, 2229, 855, 754 cm^{-1}. MS (EI) *m/z* 276 (M^+, 100%). HRMS Calcd for $C_{17}H_{12}N_2S$: 276.0721. Found: 276.0707.

4-(1,3,4-Oxadiazol-2-yl-methyl)pyridine (3k)
Colorless crystals. Mp. 111.0-115.0 °C (Ethyl acetate). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.30 (2H, s), 7.30 (2H, d, *J* = 5.2 Hz), 7.48-7.56 (3H, m), 8.01 (2H, d, *J* = 7.2 Hz), 8.61 (2H, t, *J* = 5.2 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 31.2, 123.5, 123.9, 126.8, 129.0, 131.9, 142.7, 150.3, 163.6, 165.4. IR (KBr) 3053, 3035, 2926, 1653, 1558, 1507, 710 cm^{-1}. MS (EI) *m/z* 237 (M^+, 100%). HRMS Calcd for $C_{14}H_{11}ON_3$: 237.0902. Found: 237.0891.

4-(5-Acetyl-2-thienylmethyl)benzonitrile (3l)
Colorless crystals. Mp. 94.0-95.0 °C (Ethyl acetate). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.51 (3H, s), 4.22 (2H, s), 6.83 (1H, d, *J* = 3.6 Hz), 7.35 (2H, d, *J* = 8.0 Hz), 7.54 (1H, d, *J* = 3.6 Hz), 7.62 (2H, d, *J* = 8.0 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 26.5, 36.6, 110.9, 118.6, 127.0, 129.4, 132.5, 132.7, 143.6, 144.3, 151.2, 190.4. IR (KBr) 3067, 3002, 2223, 1653, 1447, 1279, 808 cm^{-1}. MS (EI) *m/z* 241 (M^+, 72%), 226 (M^+-Me, 100%). HRMS Calcd for $C_{14}H_{11}ONS$: 241.0561. Found: 241.0560.

5-(*p*-Cyanobenzyl)-2-thiophenecarbonitrile (3m)
Colorless crystals. Mp. 65.0-66.0 °C (Ethyl acetate).[1]H-NMR (400 MHz, $CDCl_3$) δ4.23 (2H, s), 6.83 (1H, d, J = 3.6 Hz), 7.34 (2H, d, J = 8.0 Hz), 7.48 (1H, d, J = 3.6 Hz), 7.64 (2H, d, J = 8.0 Hz). ^{13}C-NMR (150 MHz, $CDCl_3$) δ 36.0, 108.8, 111.4, 114.0, 118.4, 126.4, 129.3, 132.7, 137.8, 143.6, 150.1. IR (KBr) 3093, 2922, 2228, 2214, 1449 cm^{-1}. MS (EI) *m/z* 224 (M^+, 100%). HRMS Calcd for $C_{13}H_8N_2S$: 224.0408. Found: 224.0395.

4-(5-Acetyl-2-Furylmethyl)benzonitrile (3n)
Colorless crystals. Mp. 69.0-70.0 °C (Ethyl acetate). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.43 (3H, s), 4.11 (2H, s), 6.17 (1H, d, J = 3.2 Hz), 7.11 (1H, d, J = 3.6 Hz), 7.36 (2H, d, J = 8.0 Hz), 7.62 (2H, d, J = 8.4 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 25.8, 34.8, 109.9, 111.0, 118.6, 118.9, 129.6, 132.5, 142.0, 152.2, 157.8, 186.2. IR (KBr) 3125, 2920, 2224, 1667, 1515, 1300, 804 cm^{-1}. MS (EI) *m/z* 225 (M^+, 100%), 210 (M^+-Me, 99%). HRMS Calcd for $C_{14}H_{11}O_2N$: 225.0790. Found: 225.0789.

1-[5-(2-Benzothiazolylmethyl)-2-furanyl]ethanone (3o)
Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.4 6(3H, s), 4.57 (2H, s), 6.45 (1H, *t*, J = 3.6 Hz) 7.16 (1H, *t*, J = 3.6 Hz), 7.39 (1H, *t*, J = 8.0 Hz), 7.49 (1H, *t*, J = 8.0 Hz), 7.85 (1H, *t*, J = 8.0 Hz), 7.85 (1H, *d*, J = 8.0 Hz), 8.01 (1H, *d*, J = 8.0 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 33.7, 121.6, 123.1, 125.2, 126.2, 126.6, 127.9, 128.2, 128.6, 128.7, 132.1, 135.8, 146.5, 153.0, 158.0, 164.3. IR (Neat) 3117, 3056, 2920, 1673, 1516, 1300, 761 cm^{-1}. MS (EI) *m/z* 257 (M^+, 100%). HRMS Calcd for $C_{14}H_{11}ON_2S$: 257.0510 Found: 257.0514.

1-[5-(2-Thienylmethyl)-2-furanyl]ethanone (3p)
Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.44 (3H, s), 4.25 (2H, s), 6.22 (1H, d, J = 3.2 Hz), 6.92-6.97 (2H, m), 7.11 (1H, d, J = 3.6 Hz), 7.20 (2H, d, J = 3.2 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 26.5, 36.6, 110.9, 118.6, 127.0, 129.4, 132.5, 132.7, 143.6, 144.3, 151.2, 190.4. IR (Neat) 3111, 2924, 1673, 1512, 1297, 699 cm^{-1}. MS (EI) *m/z* 206 (M^+, 100%). HRMS Calcd for $C_{11}H_{10}O_2S$: 206.0402. Found: 206.0384.

2-(*p*-Cyanobenzyl)-4-pyridinecarbonitrile (3q)
Colorless crystals. Mp. 175.0-176.0 °C (Ethyl acetate). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.28 (2H, s), 7.29 (1H, d, J = 7.2 Hz), 7.38 (2H, d, J = 7.2 Hz), 7.61 (2H, d, J = 6.8 Hz). 7.90 (1H, d, J = 7.2 Hz), 8.82 (1H, s). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 44.6, 108.0, 110.9, 116.4, 118.6, 123.1, 129.9, 132.5, 139.8, 143.2, 152.3, 163.5. IR (KBr) 3049, 2933, 2226, 1684, 1557, 1507, 668 cm^{-1}. MS (EI) *m/z* 219 (M^+, 46%), 218 (M^+-H, 100%). HRMS Calcd for $C_{14}H_9N_3$: 219.0796. Found: 219.0770.

2-(4-Pyridiylmethyl)-4-pyridinecarbonitrile (3r)
Colorless crystals. Mp. 109.0-110.0 °C (Ethyl acetate). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.21 (2H, s), 7.18 (2H, d, J = 5.6 Hz), 7.28 (1H, d, J = 7.6 Hz), 7.90 (1H, dd, J = 7.6, 2.0 Hz), 8.55 (2H, d, J = 5.6 Hz), 8.84 (1H, t, J = 2.0 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 44.0, 108.1, 116.5, 123.2, 124.3, 139.9, 146.5, 150.2, 152.4, 163.2. IR (KBr) 3066, 3046, 2229, 1684, 1588, 1417, 806, 597 cm^{-1}. MS (EI) *m/z* 195 (M^+, 41%), 194 (M^+-H, 100%). HRMS Calcd for $C_{12}H_9N_3$: 195.0796. Found: 195.0766.

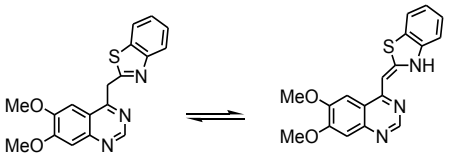
4-(*p*-Cyanobenzyl)quinazoline (3s)
Colorless crystals. Mp. 156.0-157.0 °C (Ethyl acetate). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.69 (2H, s), 7.43 (2H, d, J = 8.8 Hz), 7.60 (2H, d, J = 8.4 Hz), 7.65 (1H, t, J = 8 Hz), 7.91 (1H, t, J = 7.8 Hz),8.07-8.11 (2H, m), 9.27 (1H, s). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 40.8, 110.8, 118.6, 12.7, 124.4, 128.1, 129.4, 129.7, 132.4, 133.9, 142.8, 150.3, 154.6, 167.8. IR (KBr) 3035, 3002, 2224, 1494,1387, 754 cm^{-1}. MS (EI) *m/z* 245 (M^+, 48%), 244 (M^+-H, 100%). HRMS Calcd for $C_{16}H_{11}N_3$: 245.0953. Found: 245.0916.

4-(*p*-Cyanobenzyl)-6,7-dimethoxyquinolone (3t)
Colorless crystals. Mp. 222.0-223.0 °C (Ethyl acetate). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.96 (3H, s),4.06 (3H, s), 4.60 (2H, s), 7.15 (1H, s), 7.33 (1H, s), 7.41 (2H, d, J = 8.0 Hz), 7.60 (2H, d, J = 8.0 Hz), 9.09 (1H, s). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 41.1, 56.1, 56.4, 101.5, 107.3, 110.7, 118.6, 119.3, 129.6, 132.4, 143.2, 148.5, 150.5, 153.5, 155.8, 164.1. IR (KBr) 3002, 2960, 2224, 1557, 1507,1235, 838 cm^{-1}. MS (EI) *m/z* 305 (M^+, 70%), 290 (M^+-Me, 100%). HRMS Calcd for $C_{18}H_{15}O_2N_3$: 305.1164. Found: 305.1169.

6,7-Dimethoxy-4-(4-pyridiylmethyl)quinolone (3u)
Colorless crystals. Mp. 135.0-136.0 °C (Ethyl acetate). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.94 (3H, s),4.05 (3H, s), 4.54 (2H, s), 7.13 (1H, s), 7.20 (2H, d, J = 5.2 Hz), 7.34 (1H, s), 8.52 (2H, d, J = 5.2 Hz), 9.10 (1H, s). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 40.6,56.1, 56.4, 101.6, 107.3, 119.4, 124.0, 146.7, 148.6, 150.0, 150.5, 153.5, 155.9, 163.9. IR (KBr) 3026, 2984, 1602, 1558, 1506,1236, 1173 cm^{-1}. MS (EI) *m/z* 281 (M^+, 49%), 280 (M^+-H, 50%), 266 (M^+-Me, 100%). HRMS Calcd for $C_{16}H_{15}O_2N_3$: 281.1164. Found: 281.1172.

4-(2-Benzothiazoylmethyl)-6,7-dimethoxyquinolone (3v) (Scheme 3)
Yellow crystals. Mp.195.0-196.0 °C ($CHCl_3$). A mixture of tautomats **3v** and **3v'** (1:1.6) was formed in $CDCl_3$. ^{1}H-NMR (400 MHz, $CDCl_3$) of the **3v** form, δ 4.02 (3H, s), 4.03 (3H, s), 5.03 (2H, s), 7.32 (1H, s), 7.35 (1H, t, J = 7.6 Hz), 7.46 (1H, t, J = 7.6 Hz), 7.57 (1H, s), 7.80 (2H, d, J = 8.0 Hz), 7.99 (2H, d, J = 8.0 Hz). ^{1}H-NMR (400 MHz, $CDCl_3$) of the 3**v'** form, δ 3.98 (3H, s), 4.02 (3H, s), 6.00 (1H, s), 7.01 (1H, s), 7.10 (1H, s), 7.24 (1H, t, J = 7.6 Hz), 7.41 (1H, t, J = 7.6 Hz), 7.76 (1H, t, J = 7.6 Hz), 7.81 (2H, d, J = 8.0 Hz), 7.94 (1H, s), 13.6 (1H, br.s). ^{13}C-NMR (100 MHz, $CDCl_3$) of the **3v** form, δ 40.9, 56.3, 56.4, 102.2, 107.1, 120.0, 121.6, 122.8, 125.2, 126.1, 135.8, 148.7, 150.5, 152.8, 156.0, 162.1, 166.9, 167.1. ^{13}C-NMR (100 MHz, $CDCl_3$) of the 3**v'** form, δ 56.1, 56.2, 82.4, 103.0, 108.9 113.7, 119.6, 121.1, 123.2, 126.0, 132.0, 140.4, 141.5, 142.0, 149.0, 153.1, 153.4, 153.5. IR (KBr) 3022, 2960, 2931, 1619, 1507,1271, 1258, 752 cm^{-1}. MS (EI) *m/z* 281 (M^+, 49%), 280 (M^+-H, 50%), 266 (M^+-Me, 100%). MS (EI) *m/z* 337 (M^+, 100%). HRMS Calcd for $C_{18}H_{15}O_2N_3S$: 337.0885 Found: 337.0870.

A small amount of chloroform was added to a mixture of ttautomer **3v**/3**v'** (1:1.6, 67.5 mg), and the insoluble materials were filtered to gave solid 3**v'**. The filtrate was concentrated, a small amount of chloroform was added, and the insoluble materials were filtered to gave solid 3**v'**. The combined 3**v'** (59.0 mg, 70%) was obtained. Pure 3**v'** was dissolved in $CDCl_3$, and immediately analysed ^{1}H-NMR. The equilibrium was reached after 30 min. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.99 (3H, s), 4.03 (3H, s), 6.01 (1H, s), 7.03 (1H, s), 7.12 (1H, s), 7.24 (1H, t, J = 7.6 Hz), 7.42 (1H, t, J = 7.6 Hz), 7.77 (1H, t, J = 7.6 Hz), 7.82 (2H, d, J = 8.0 Hz), 7.96 (1H, s), 13.6 (1H, br.s).



3v **3v'**

6,7-Dimethoxy-4-(2-thienylmethyl)quinazoline (3w)
Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.98 (3H, s), 4.04 (3H, s), 4.71 (2H, s), 6.90-6.93 (2H, m), 7.16 (1H, dd, J = 5.2, 1.2 Hz), 7.31 (2H, d, J = 3,2 Hz), 9.10 (1H,s). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 36.0, 56.2, 54.1, 102.1, 107.2, 119.2, 124.5, 126.0, 127.0, 139.7, 148.6, 150.3, 153.6, 155.7, 164.8. IR (Neat) 2925, 1616, 1555, 1503, 1426, 1233 cm^{-1}. MS (EI) *m/z* 286 (M^+, 100%). HRMS Calcd for $C_{15}H_{14}O_2N_2S$: 286.0776 Found: 286.0779.

6,7-Dimethoxy-4-(2-furylmethyl)quinazoline (3x)
Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.00 (3H, s), 4.05 (3H, s), 4.55 (2H, s), 6.15 (1H, d, J = 3.2 Hz), 6.31 (1H, t, J = 2.4 Hz), 7.32-7.34 (3H, m), 9.08 (1H,s). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 34.8, 56.2, 56.4, 102.2, 107.1, 107.4, 110.7, 119.6, 141.8, 150.2, 151.2, 153.6, 155.7, 163.3. IR (Neat) 3002, 2940, 1505, 1233, 668 cm^{-1}. MS (EI) *m/z* 270 (M^+, 100%). HRMS Calcd for $C_{15}H_{14}O_3N_2$: 270.1004 Found: 270.0996.

4,6-Diphenyl-2-(4-prydiylmethyl)-1,3,5-triazine (3y)
Colorless crystals. Mp. 95.0-96.0 °C (Ethyl acetate). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.29 (2H, s), 7.41 (2H, d, J = 6.0 Hz),7.50-7.60 (6H, m), 8.57 (2H, d, J = 6.0 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 44.9, 124.7, 128.6, 128.9, 132.7, 135.6, 145.8, 149.8, 171.6, 176.6. IR (KBr) 3049, 3029, 1683, 1558, 1507, 765, 695 cm^{-1}. MS (EI) *m/z* 324 (M^+, 100%). HRMS Calcd for $C_{12}H_{16}N_4$: 324.1375. Found: 324.1362.

2-[(4,6-Diphenyl-1,3,5-triazin-2-yl)methyl]benzothiazole (3z)
Yellow crystals. Mp. 150.0-151.0 °C (Ethyl acetate). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.87 (2H, s), 7.37 (1H, t, J = 7.6 Hz), 7.47 (1H, t, J = 7.6 Hz), 7.52-7.61 (6H, m), 7.88 (1H, d, J = 8.0 Hz), 8.03 (1H, d, J = 8.0Hz), 8.67 (4H, d, J = 7.2 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 44.3,121.4, 122.9, 125.0, 126.0, 128.3, 128.7, 129.1, 132.8, 135.5, 136.0, 152,8, 165.8, 171.7, 174.9. IR (KBr) 3053, 2960, 1684, 1524, 1373, 686 cm^{-1}. MS (EI) *m/z* 380 (M^+, 100%). HRMS Calcd for $C_{23}H_{16}N_4S$: 380.1096. Found: 380.1107.

The reaction of phenyl 2-benzoxazolyl ether 1a with 2-(*p*-cyanophenyl)cyclopentanoe 8b (Scheme 4)
In a two-necked flask were placed phenyl 2-benzoxazolyl ether **1a** (52.8 mg, 0.25 mmol), 2-(*p*-cyanophenyl)cyclopentanoe **7b** (120.2 mg, 0.75 mmol), $RhH(PPh_3)_4$ (28.8 mg, 10 mol%), and dppBz (22.3 mg, 20 mol%) in chlorobenzene (0.25 mL) under an argon atmosphere, and the solution was heated at reflux for 12 h. The reaction mixture was concentrated, and purified by flash column chromatography on silica gel giving 1-(2-benzoxazole)-1-(*p*-cyanophenyl)pentanoic phenyl ester **8b** (59.5 mg, 60%). **8b:** Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.73-1.87 (2H, m), 2.20-2.30 (1H, m), 2.48-2.57 (1H, m), 2.64 (2H, t, J = 7.2), 4.34 (1H, t, J = 7.6), 7.04 (2H, d, J = 7.8 Hz), 7.20-7.26 (1H, m), 7.31-7.38 (4H, m), 7.44-7.46 (1H, m), 7.52 (2H, d, J = 8.0), 7.63 (2H, d, J = 8.4), 7.71-7.74 (1H, m). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 22.7, 33.4, 33.7, 45.9, 110.6, 111.5, 118.5, 120.0, 124.5, 125.1, 125.8, 128.8, 129.4, 132.7, 140.9, 144.6, 150.5, 150.7, 166.1, 171.4. IR (KBr) 3063, 2936, 2228, 1755, 1563, 1455, 747 cm^{-1}. MS (EI) *m/z* 396 (M^+, 6%), 303 (M^+-OPh, 100%). HRMS Calcd for $C_{25}H_{20}O_2N_3$: 396.1474. Found: 396.1480.

1-(2-Benzoxazole)-1-phenylpentanoic phenylester (8a)
Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.77-1.86 (2H, m), 2.22-2.31 (1H, m), 2.47-2.52 (1H, m), 2.62 (2H, t, J = 7.6), 4.28 (1H, t, J = 8.0), 7.05 (2H, d, J = 8.4 Hz), 7.21 (1H, t, J = 7.4 Hz), 7.25-7.41 (9H, m), 7.43-7.46 (1H, m), 7.70-7.72 (1H, m). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 22.9, 33.6, 34.0, 45.9, 110.5, 119.9, 121.5, 124.2, 124.7, 125.7, 127.5, 127.9, 128.9, 129.4, 139.3, 141.1, 150.6, 150.8, 167.6, 171.6. IR (KBr) 3021, 2928, 1757, 1492, 747 cm^{-1}. MS (EI) *m/z* 371 (M^+, 9%), 278 (M^+-OPh, 100%). HRMS Calcd for $C_{24}H_{21}ON_3$: 371.1521. Found: 371.1506.

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6) Reddy, R. S.; Rosa, J. N.; Veiros, L. F.; Caddick, S.; Gois, P. M. P. *Org. Biomol. Chem.,* **2011**, *9*, 3126-3129.
7) Arisawa, M.; Kuwajima, M.; Toriyama, F.; Li, G.; Yamaguchi, M. *Org. Lett.*, **2012**, *14*, 3804-3807.
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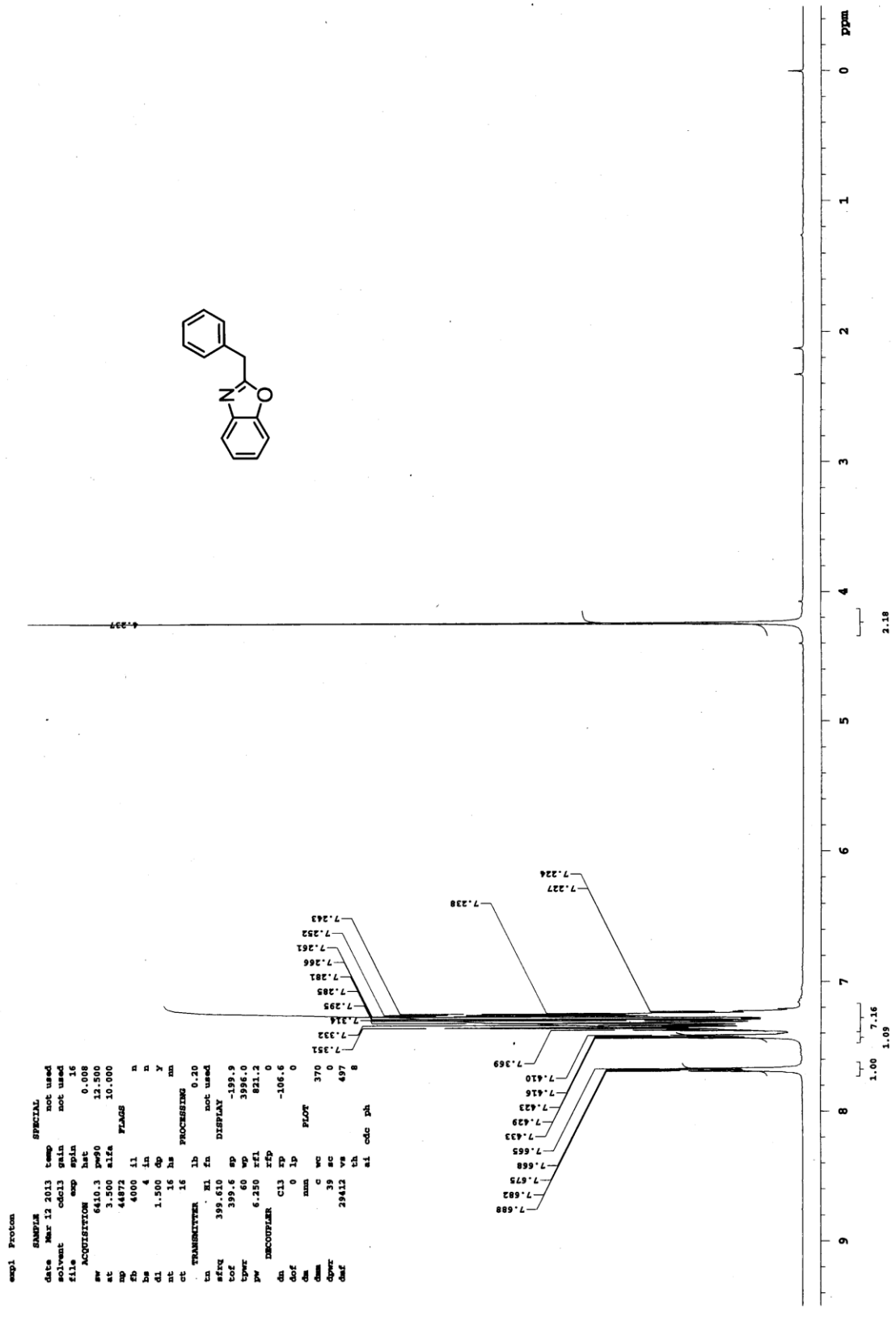
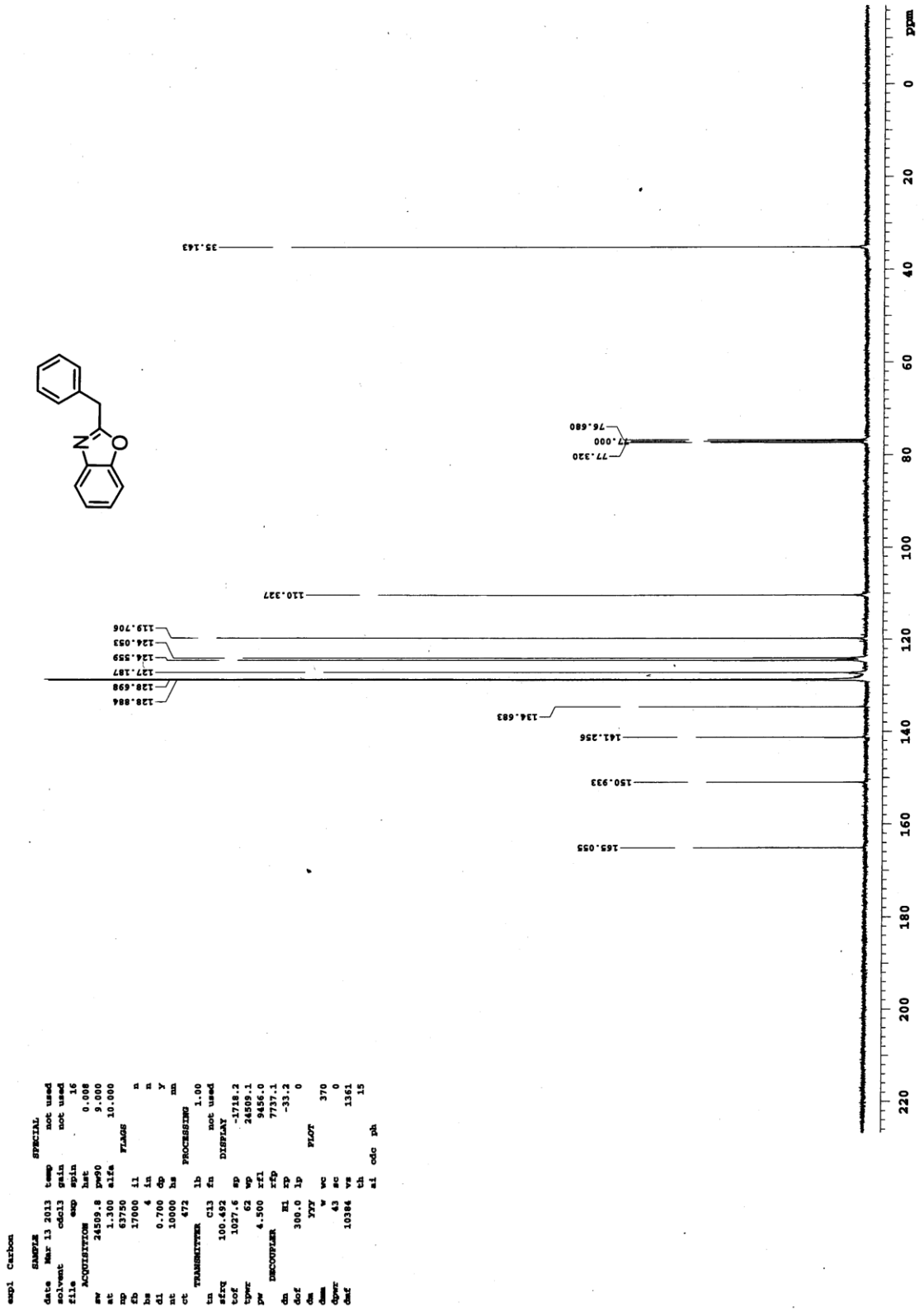
2-Benzylbenzoxazole (3a) (^{1}H-NMR)



2-Benzylbenzoxazole (3a) (^{13}C-NMR)



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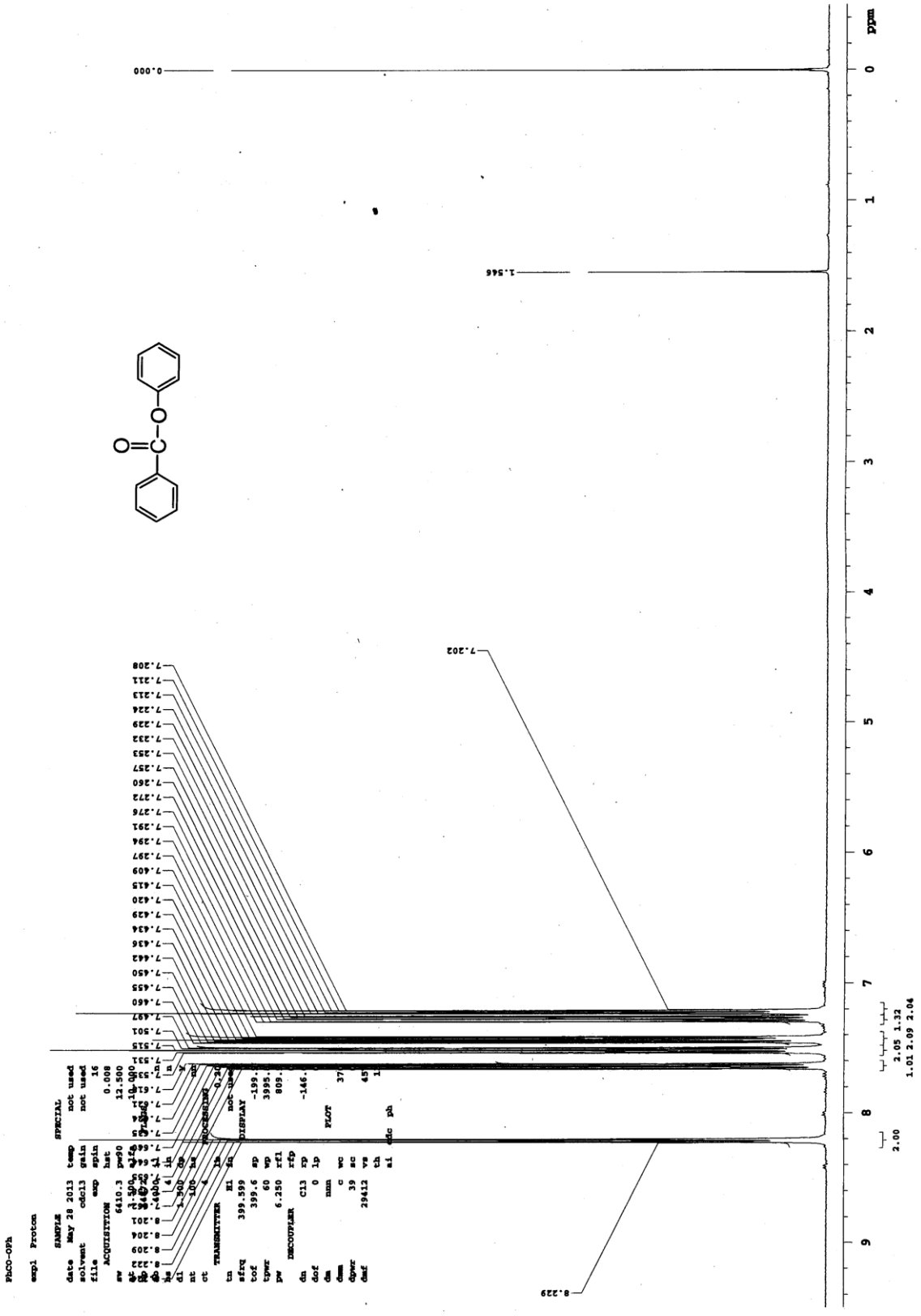
Phenyl benzoate (4a) (^{1}H-NMR)



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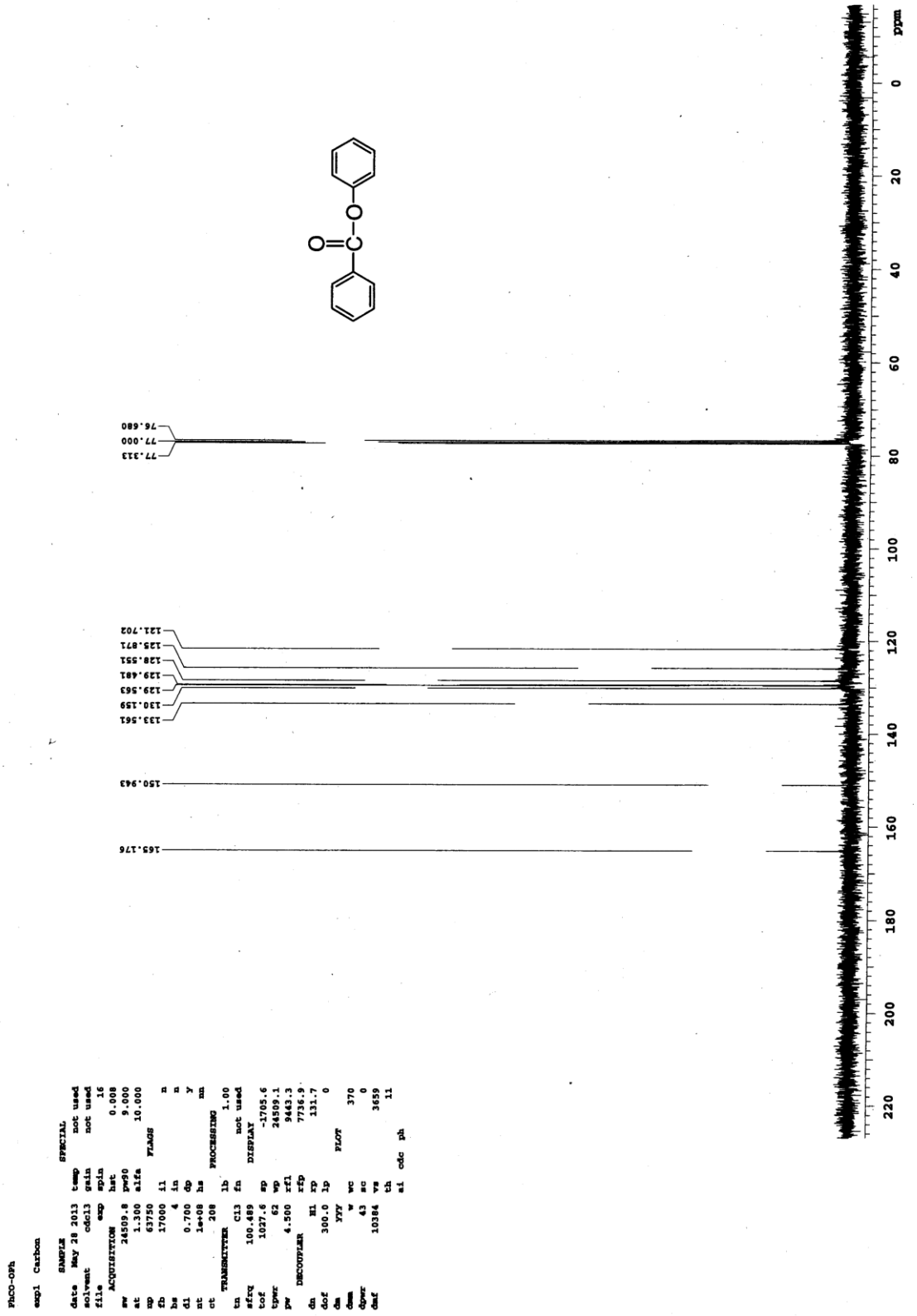
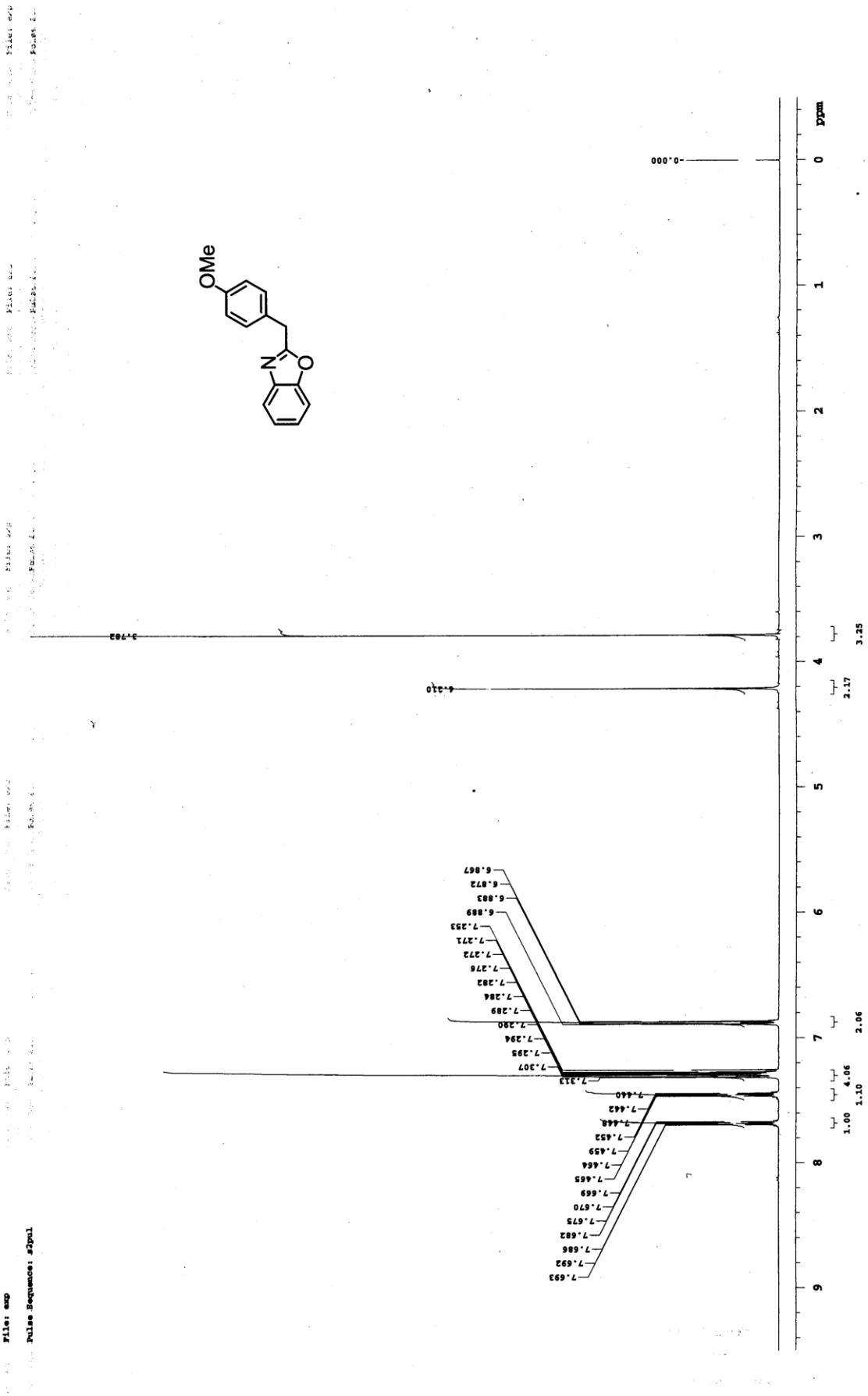
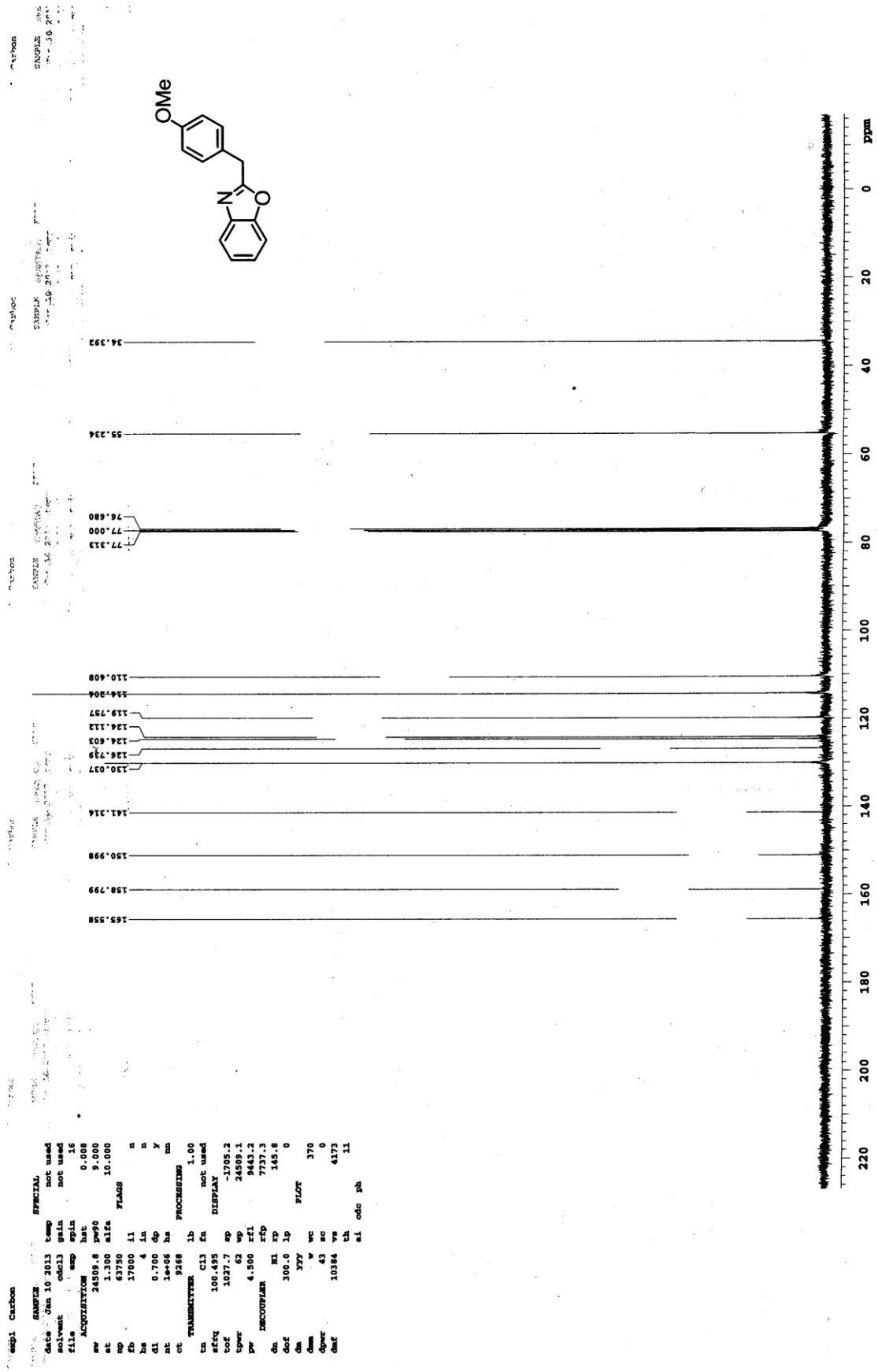


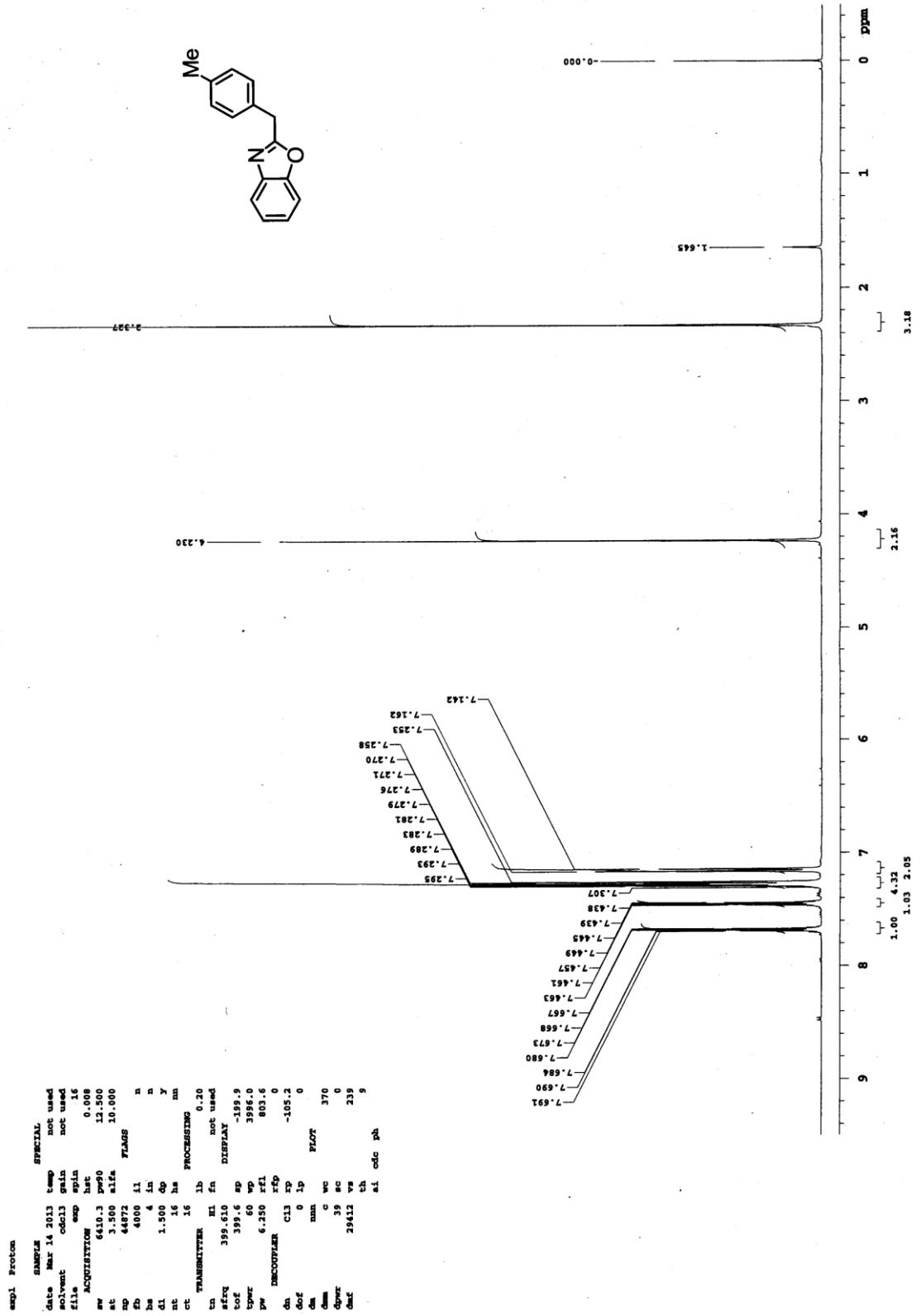
2-(*p*-Methoxybenzyl)benzoxazole (Table 1, entry 2) (^{1}H-NMR)



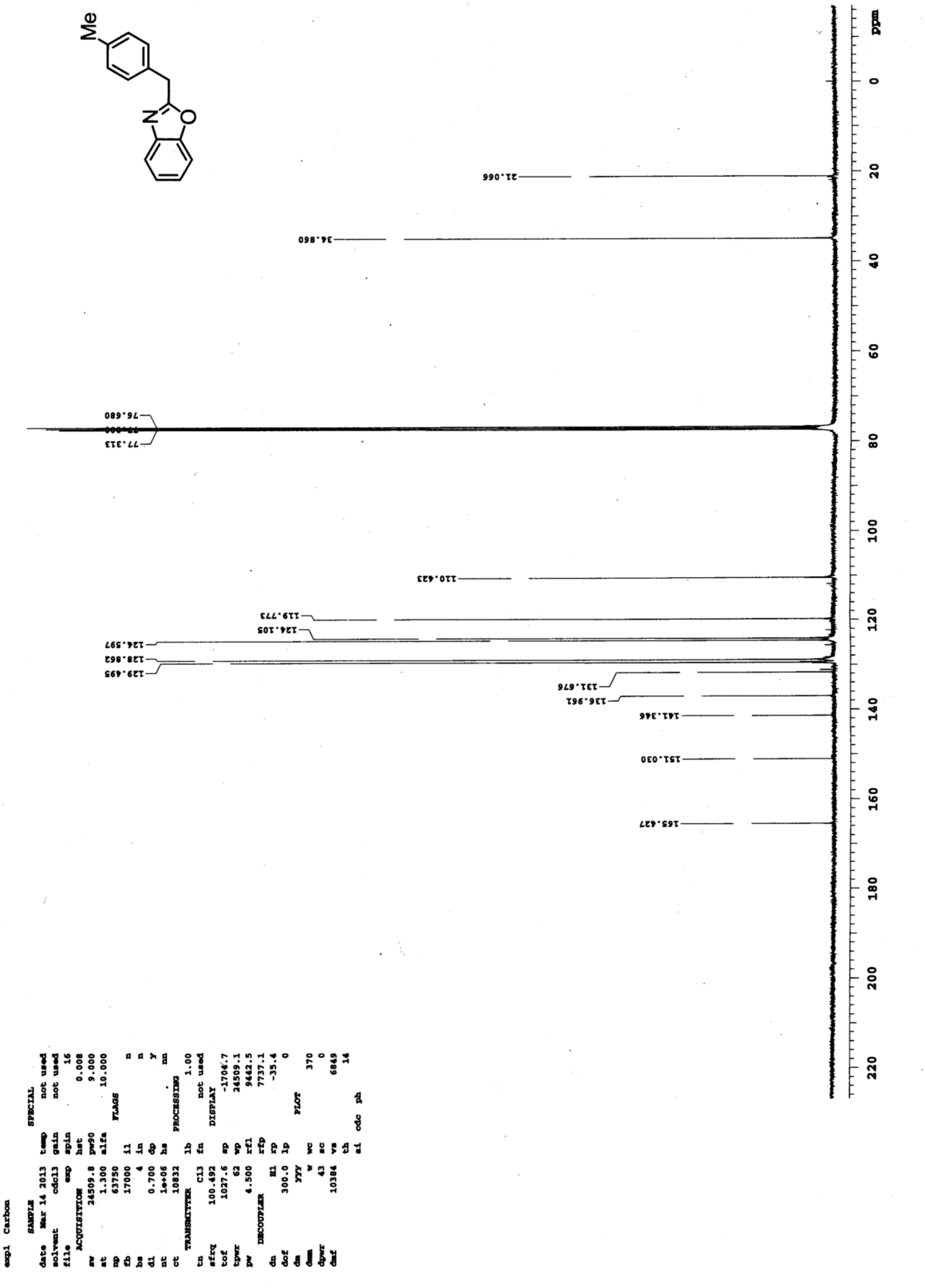
2-(*p*-Methoxybenzyl)benzoxazole (Table 1, entry 2) (^{13}C-NMR)



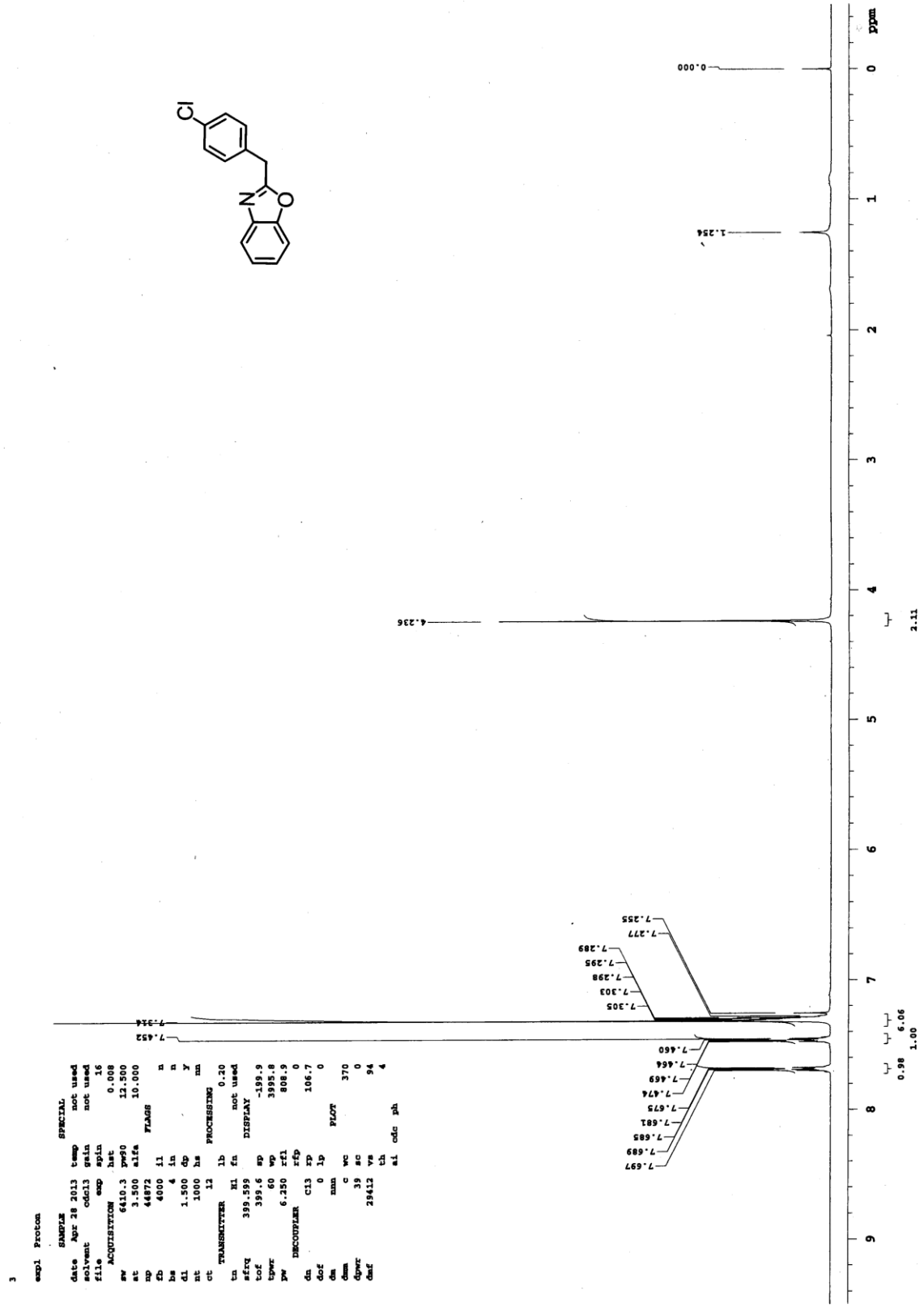
2-(*p*-Methylbenzyl)benzoxazole (Table 1, entry 3) (^{1}H-NMR)



2-(*p*-Methylbenzyl)benzoxazole (Table 1, entry 3)



2-(*p*-Chlorobenzyl)benzoxazole (Table 1, entry 4) (^{1}H-NMR)



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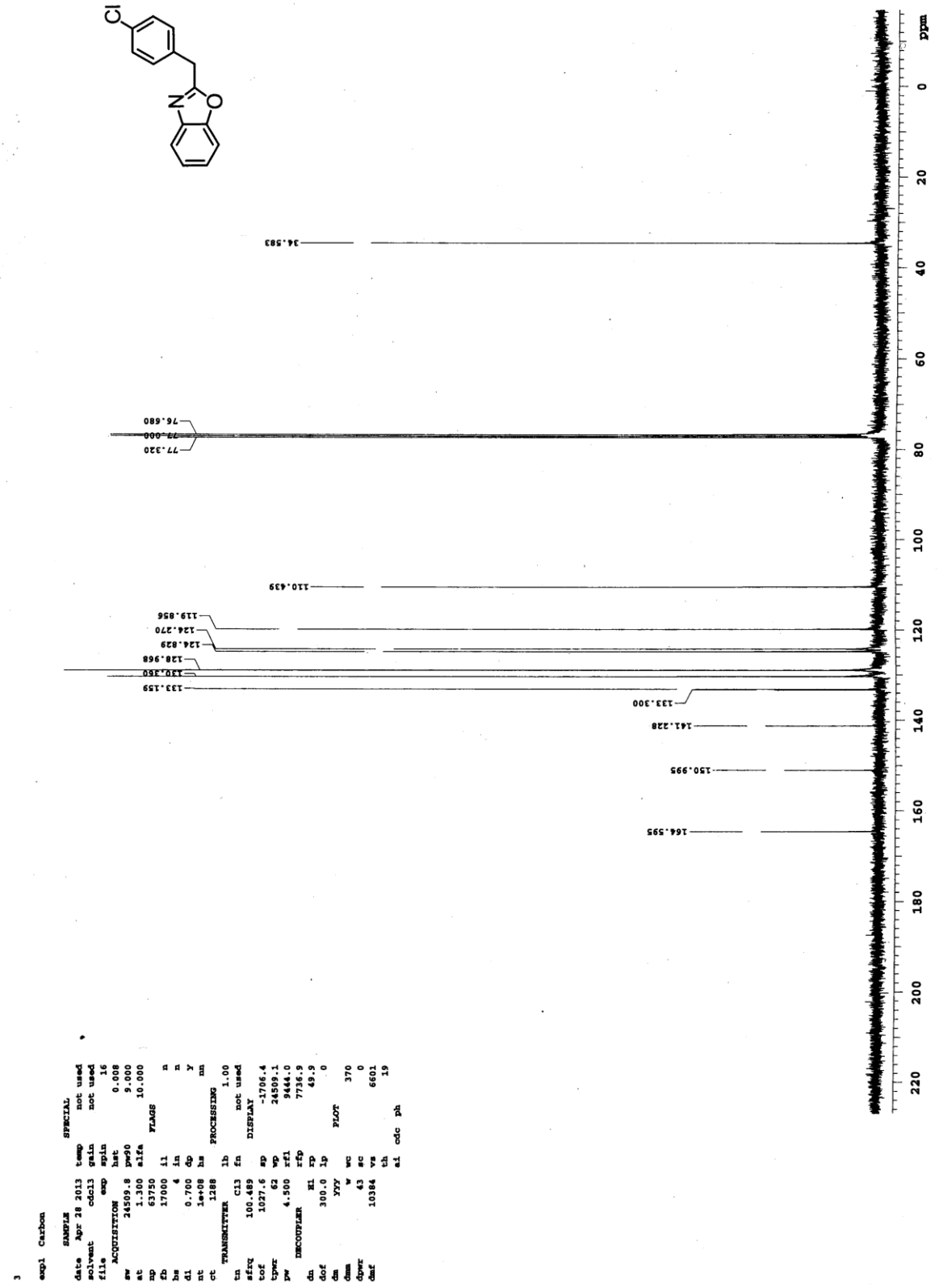

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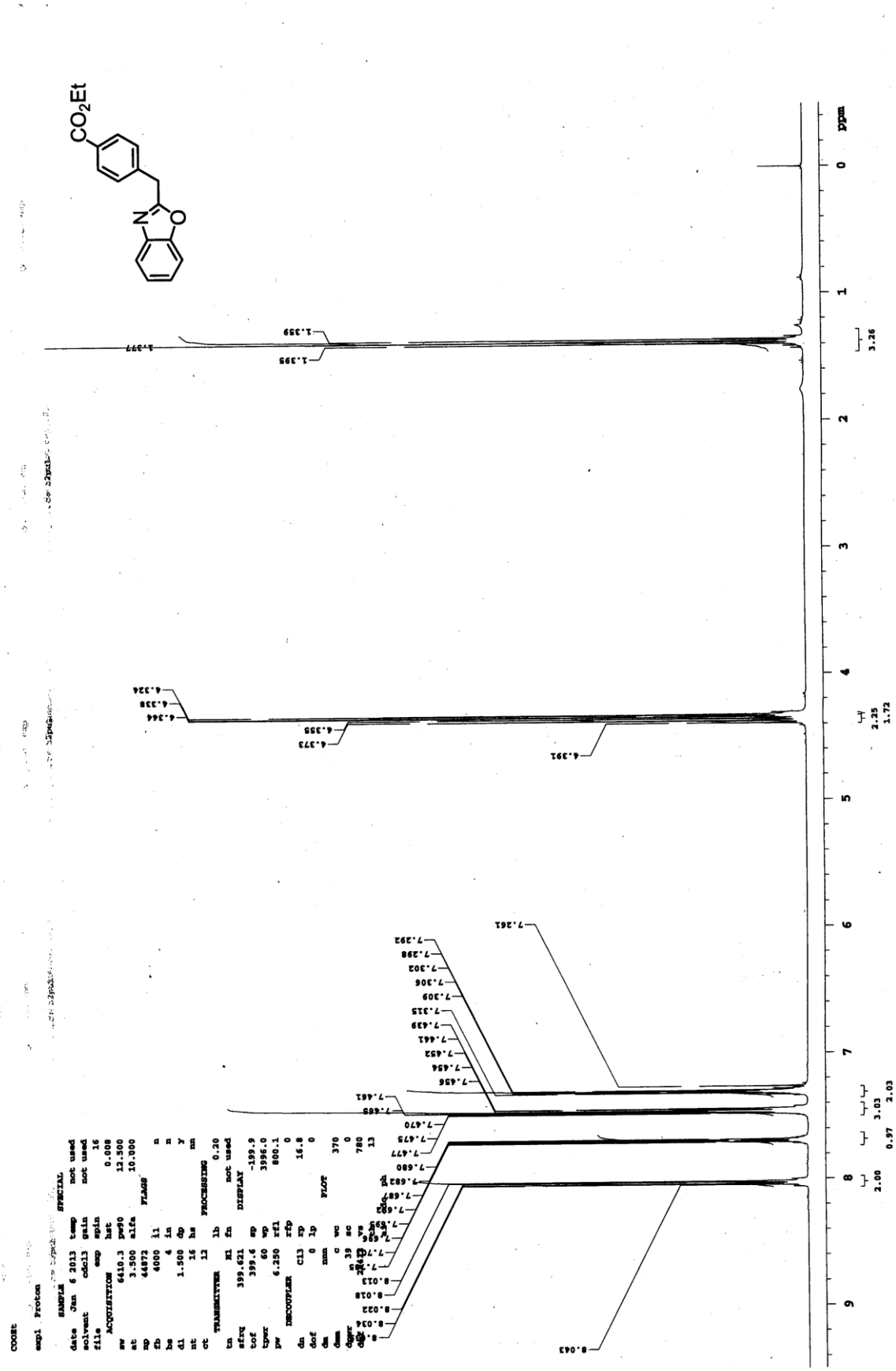
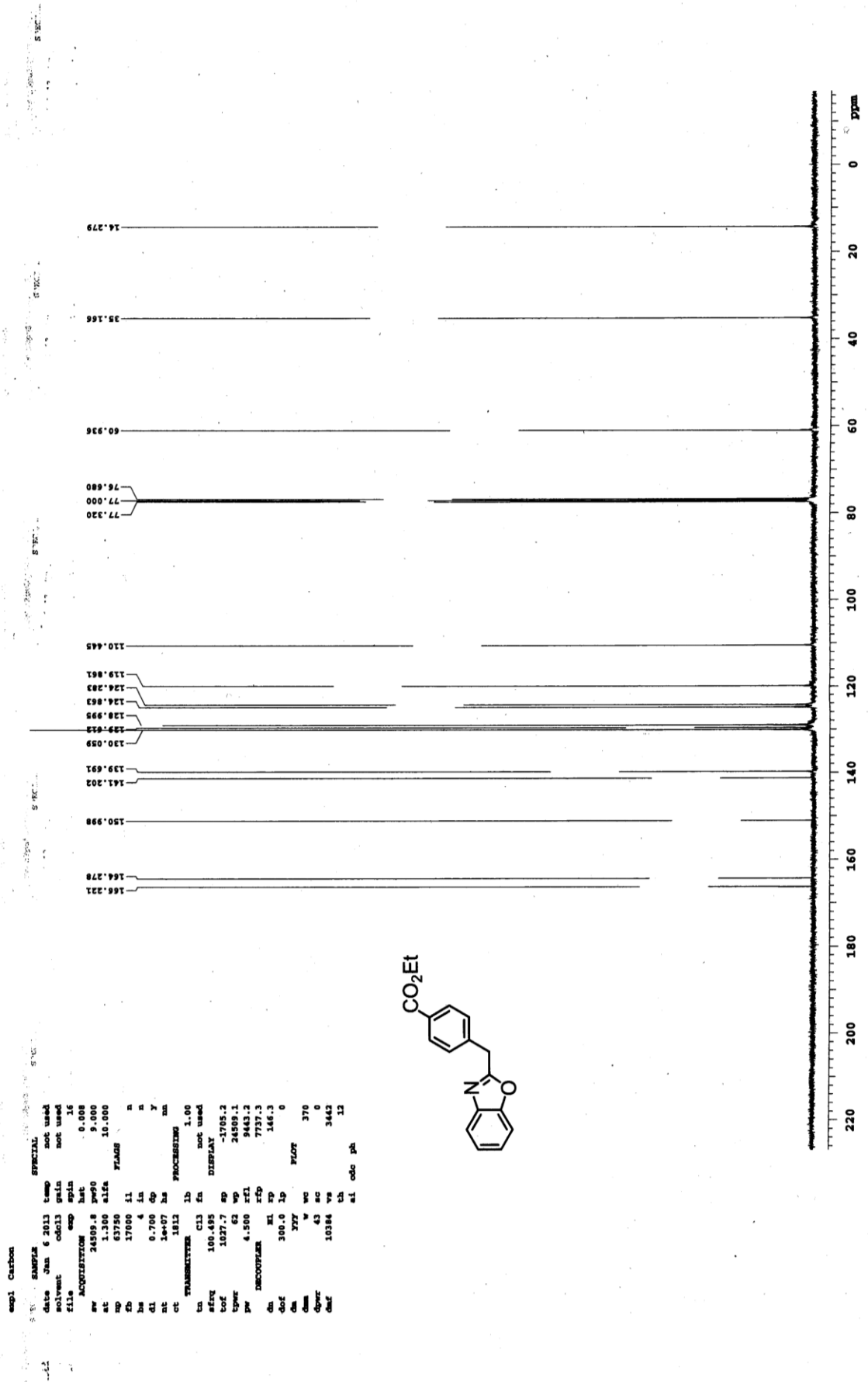
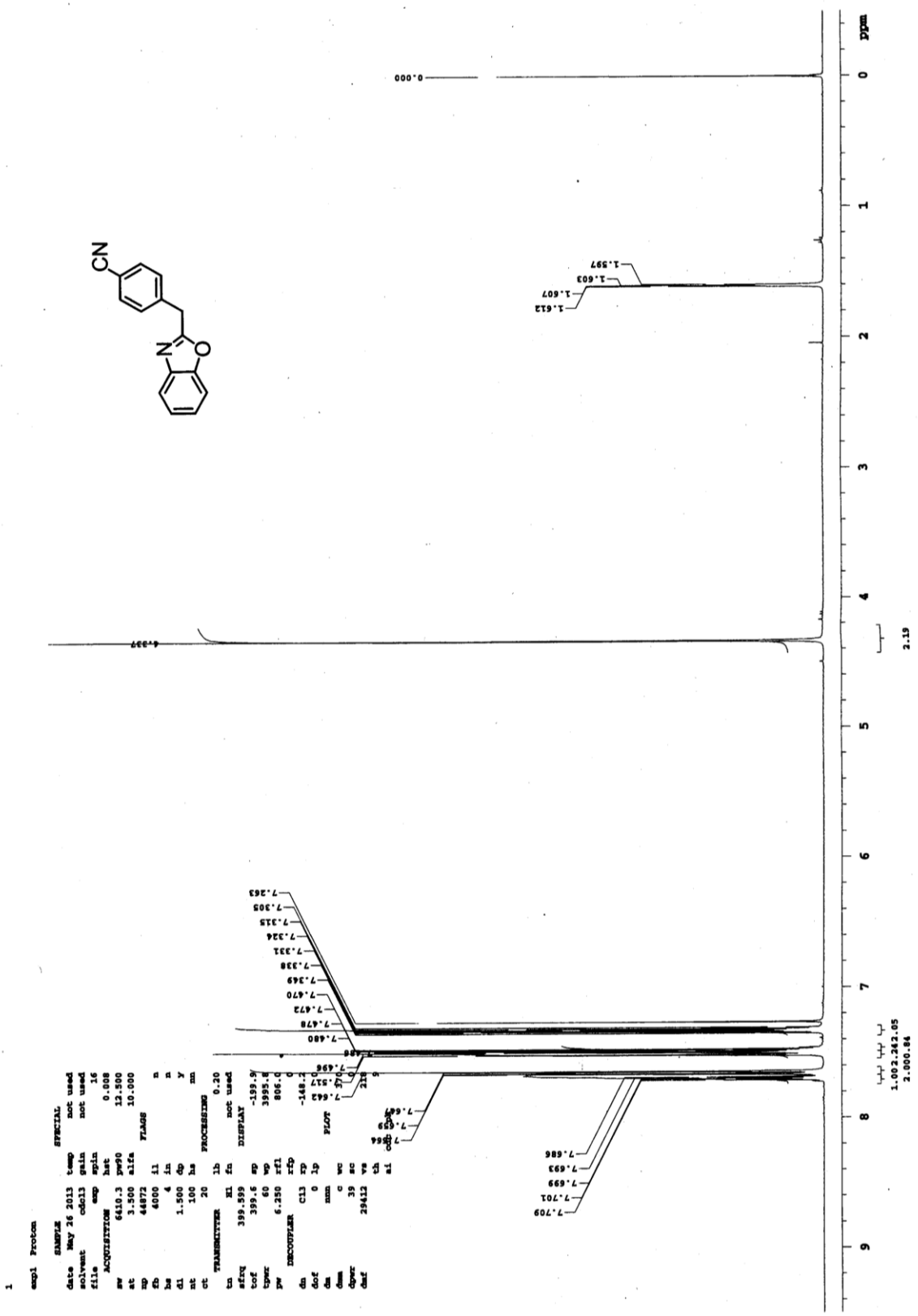


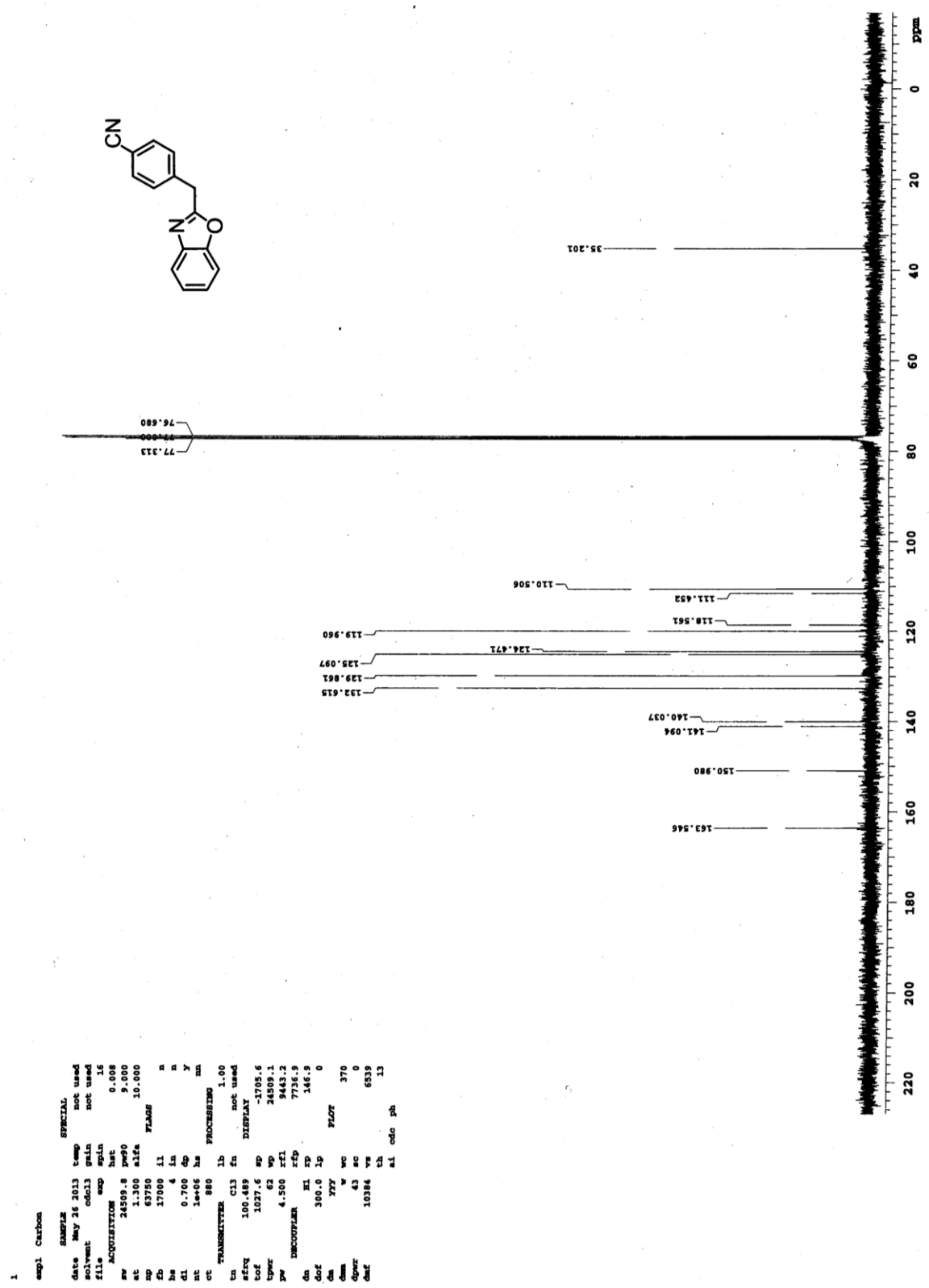
4-(2-Benzoxazolylmethyl)benzoic ethyl ester (Table 1, entry 5) (^{13}C-NMR)



4-(2-Benzoxazolylmethyl)benzonitrile (Table 1, entry 6) (^{1}H-NMR)



4-(2-Benzoxazolylmethyl)benzonitrile (Table 1, entry 6) (^{13}C-NMR)



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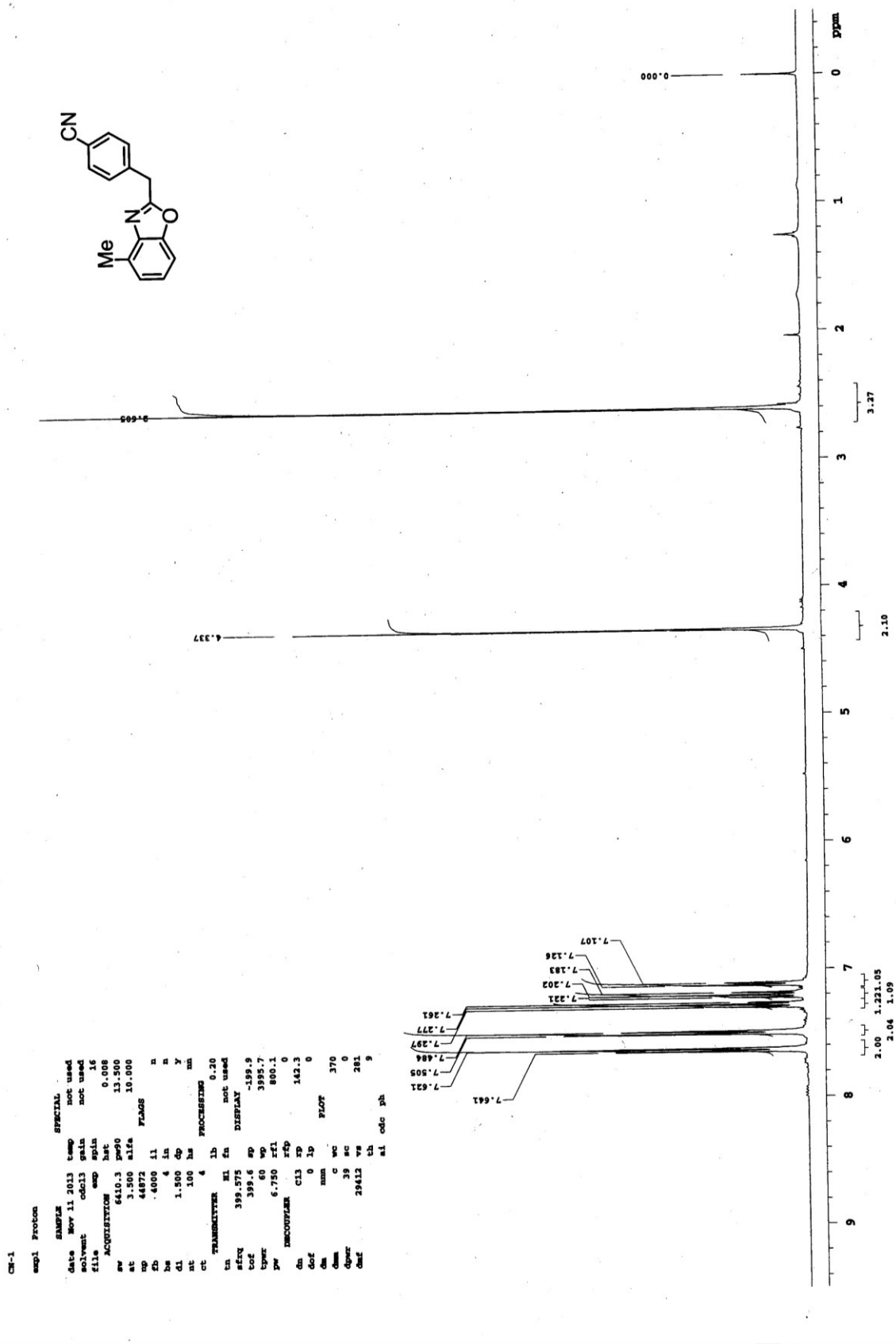
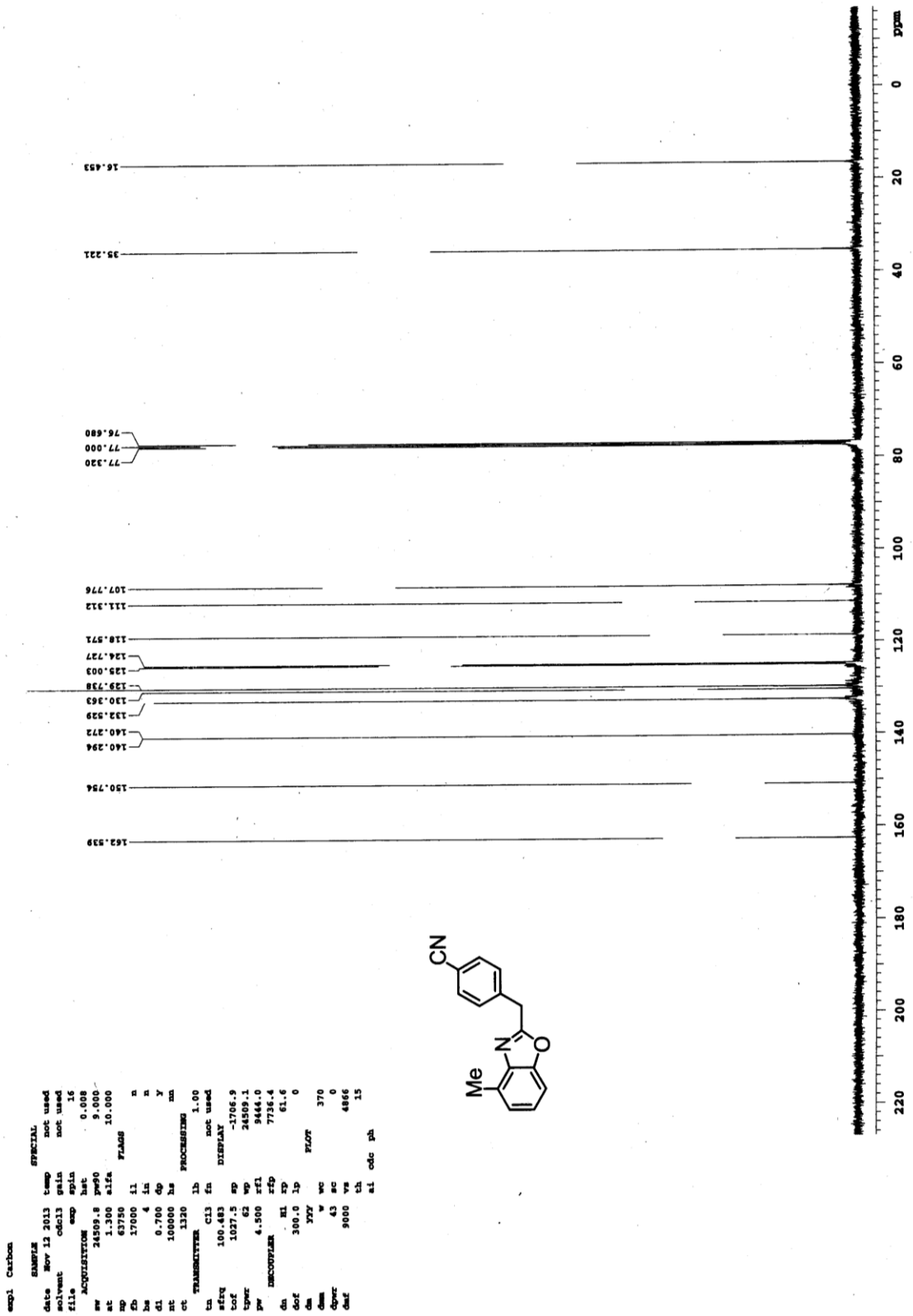
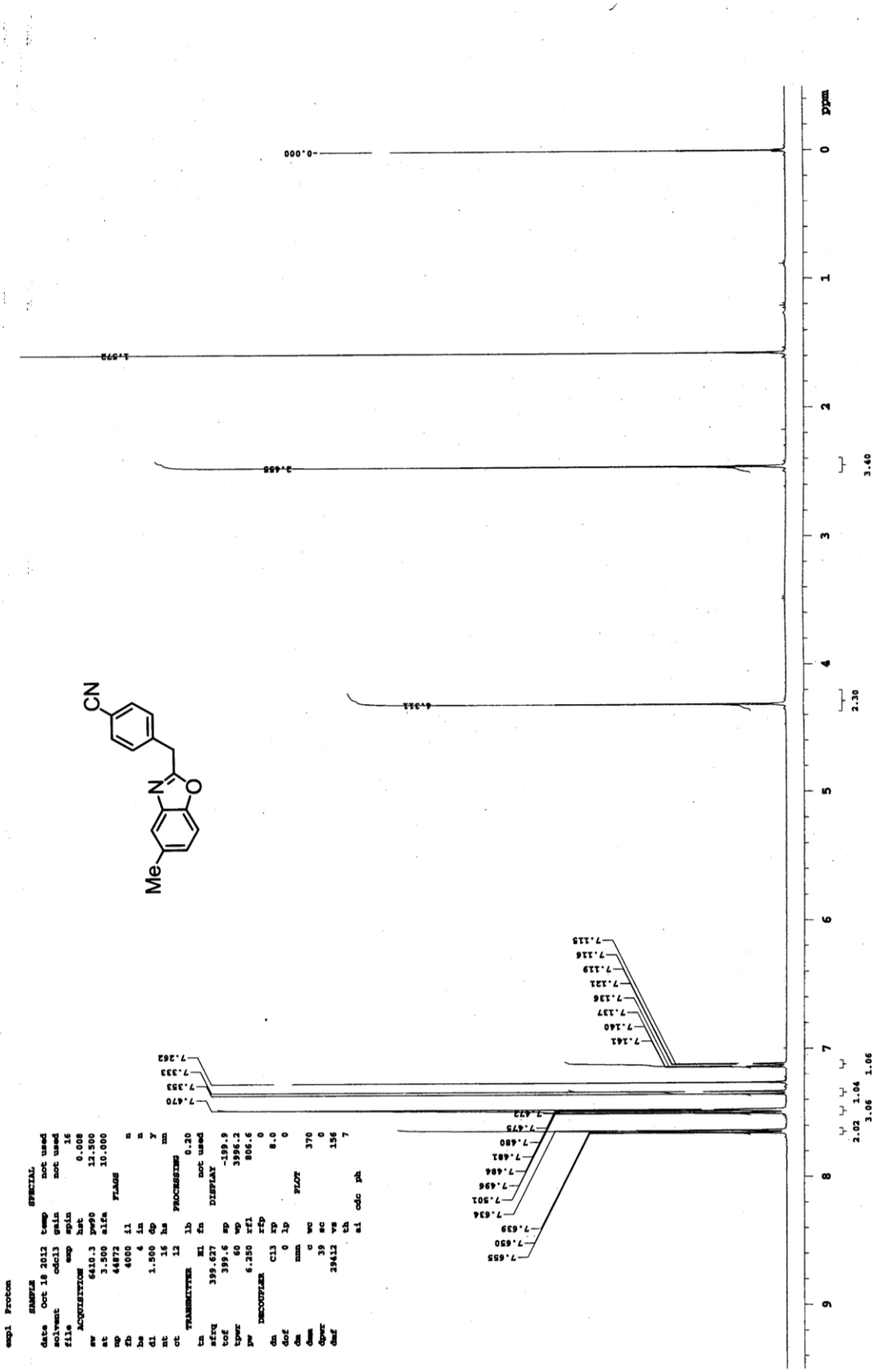


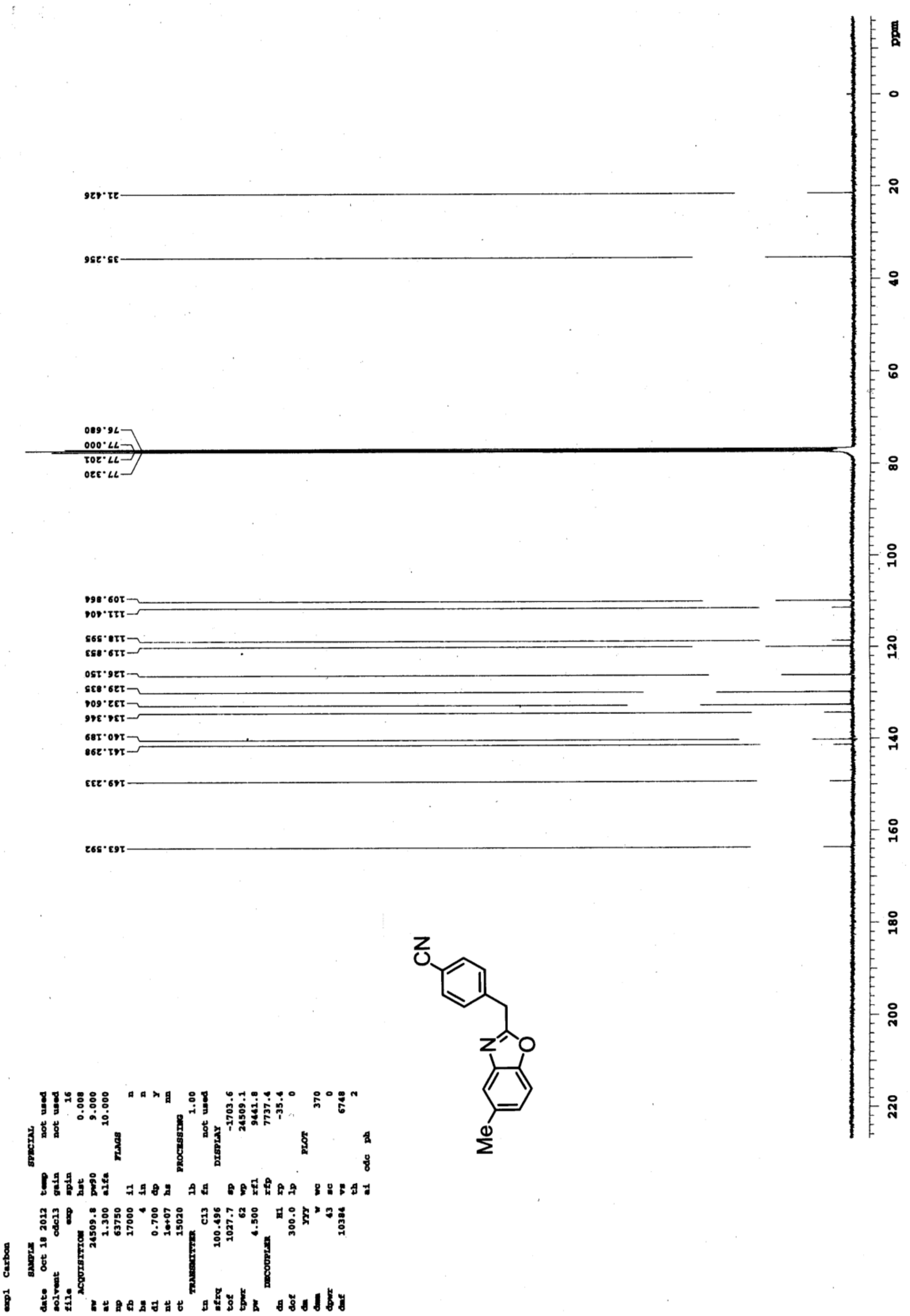
4-(4-Methyl-2-benzoxazolylmethyl)benzonitrile (Table 1, entry 7) (^{13}C-NMR)



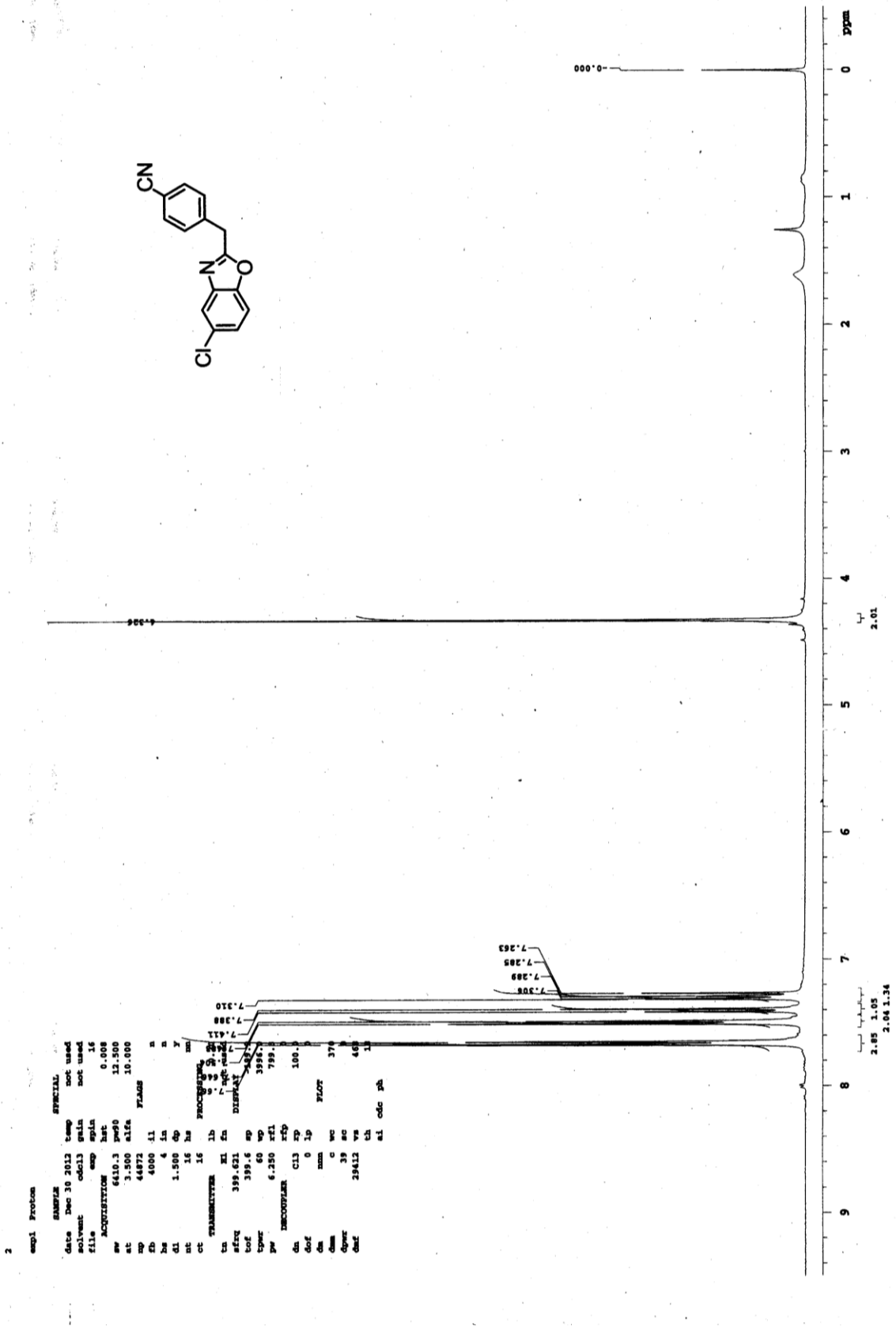
4-(5-Methyl-2-benzoxazolylmethyl)benzonitrile (Table 1, entry 8) (^{1}H-NMR)



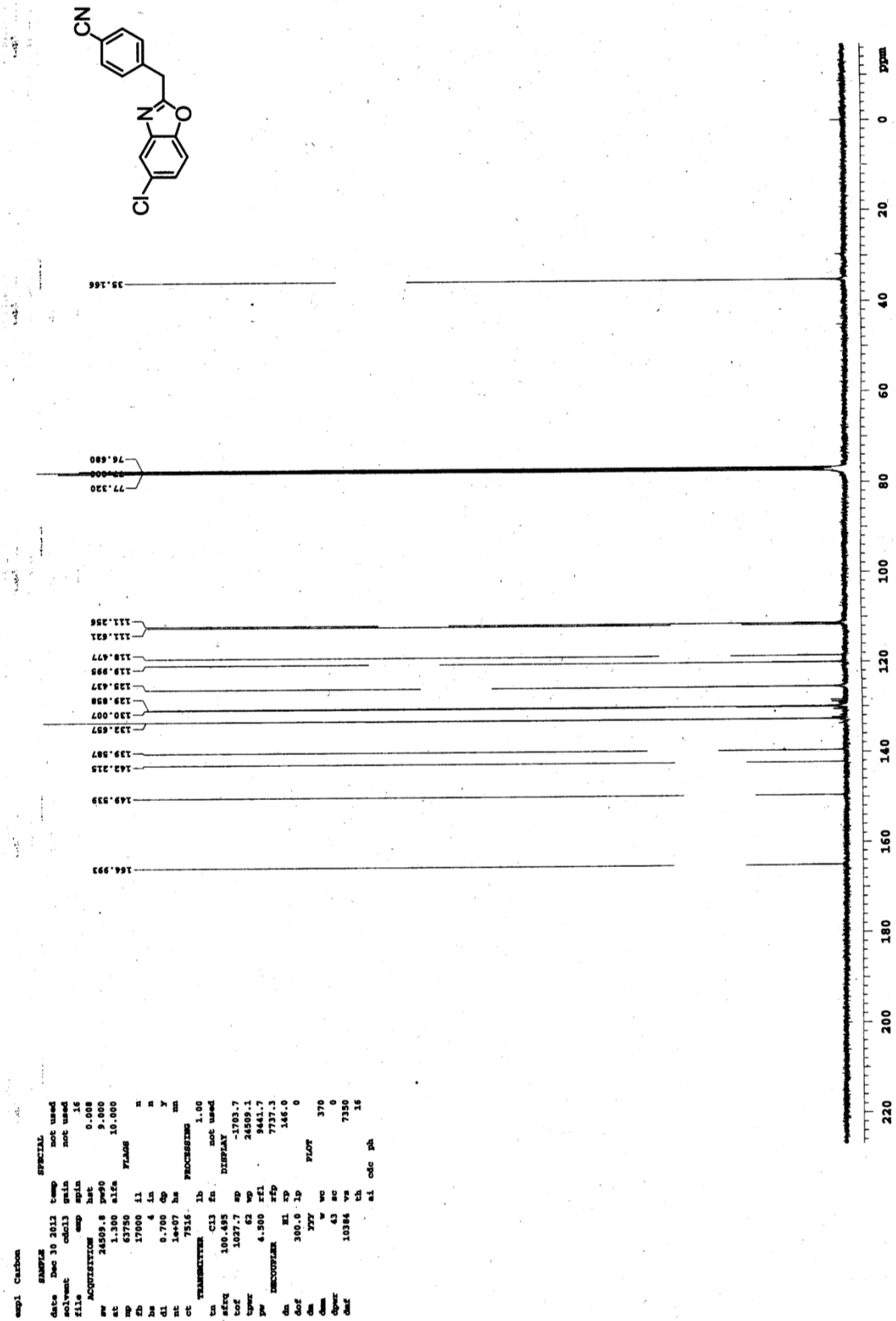
4-(5-Methyl-2-benzoxazolylmethyl)benzonitrile (Table 1, entry 8) ([13]C-NMR)



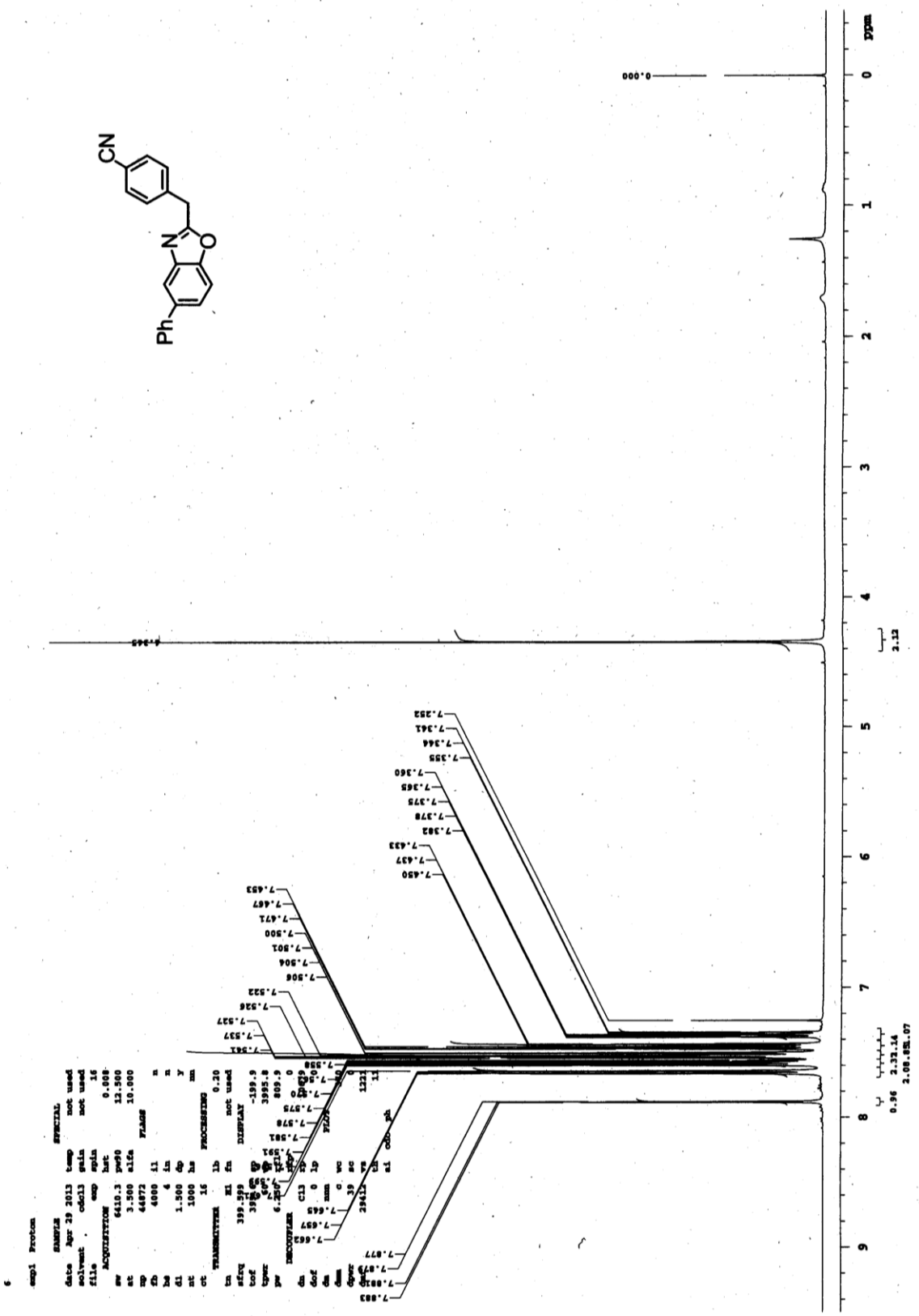
4-(5-Chloro-2-benzoxazolylmethyl)benzonitrile (Table 1, entry 9) (^{1}H-NMR)



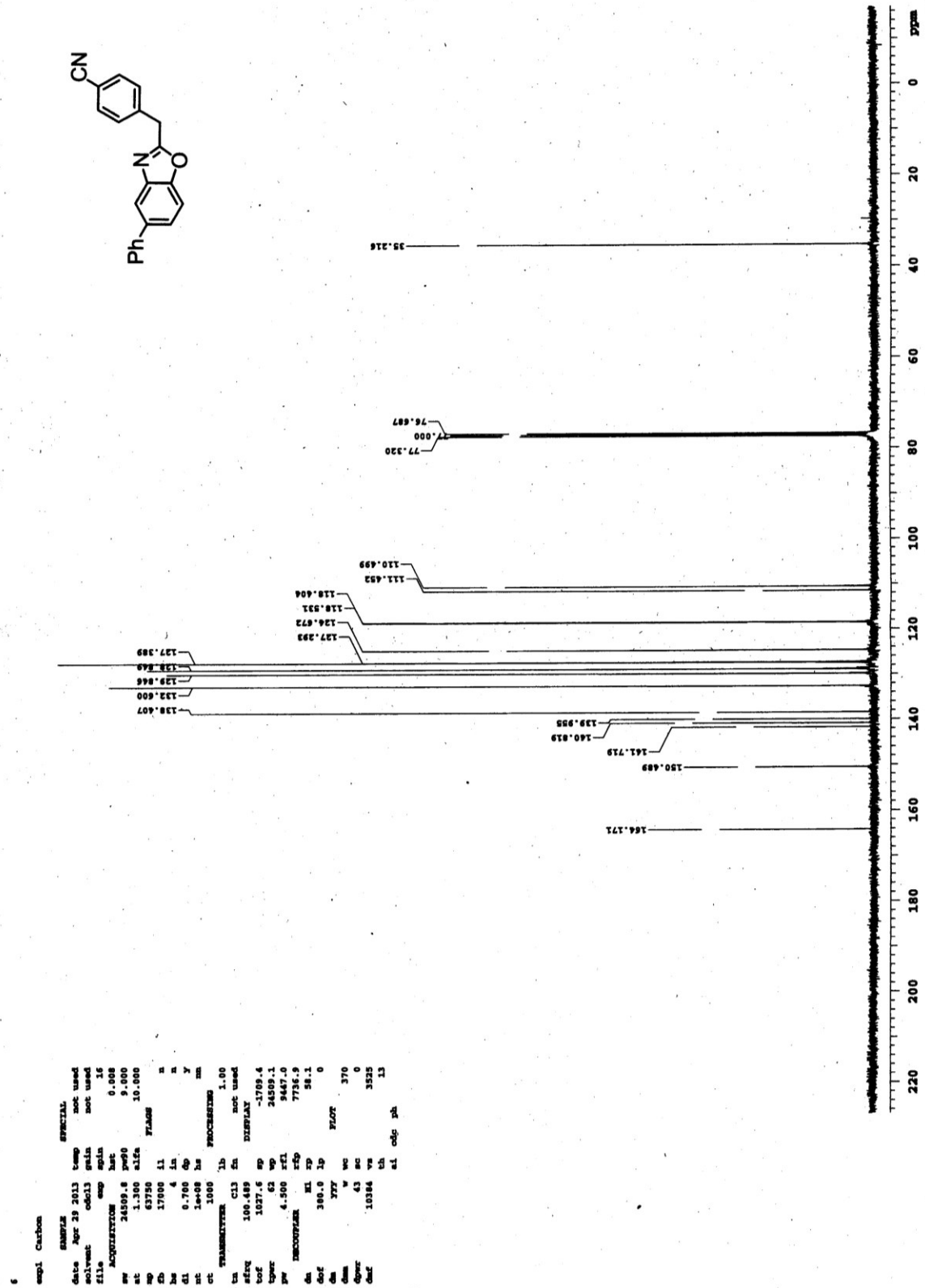
4-(5-Chloro-2-benzoxazolylmethyl)benzonitrile (Table 1, entry 9) (^{13}C-NMR)



4-(5-Phenyl-2-benzoxazolylmethyl)benzonitrile (Table 1, entry 10) (^{1}H-NMR)



4-(5-Phenyl-2-benzoxazolylmethyl)benzonitrile (Table 1, entry 10) (^{13}C-NMR)



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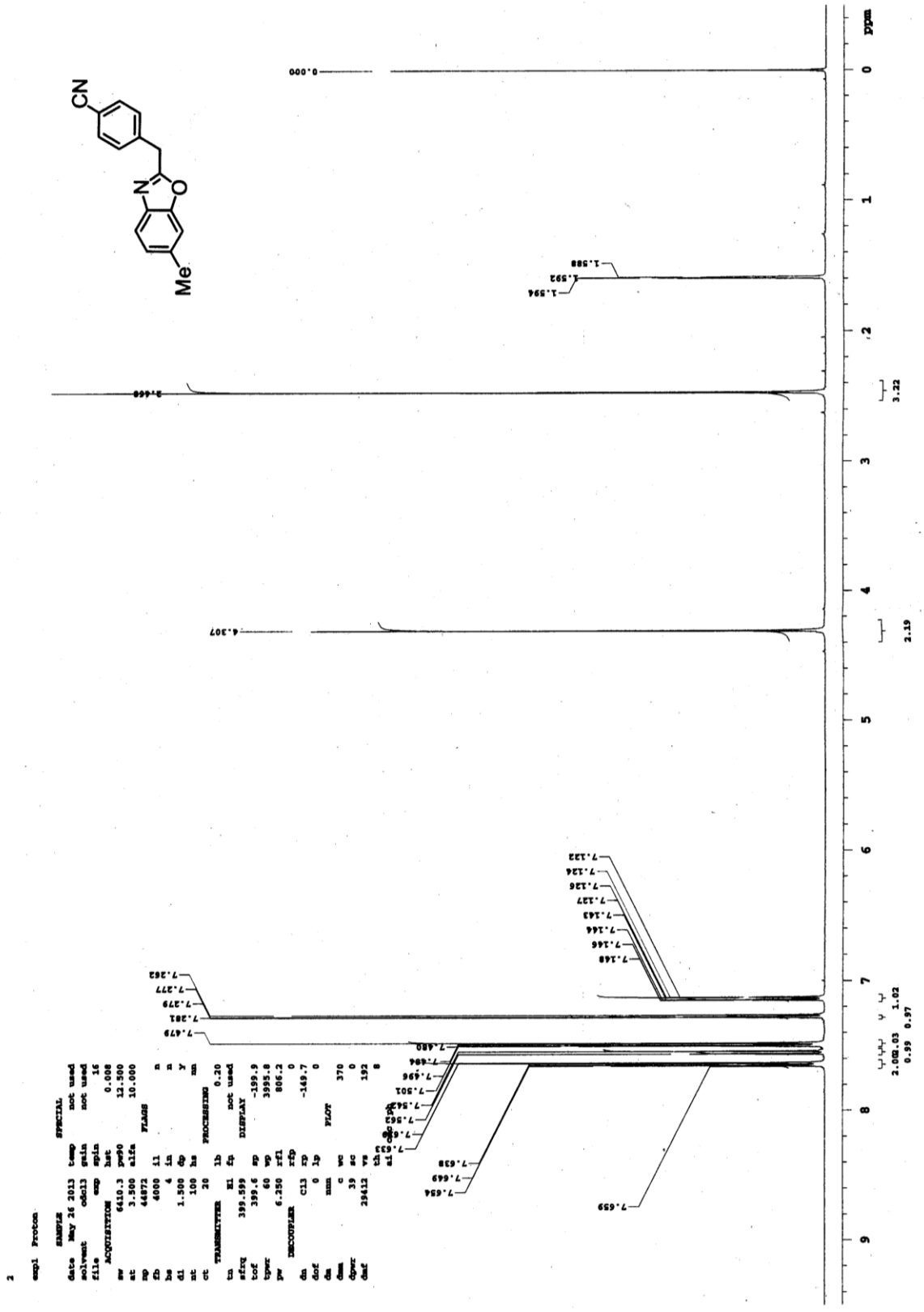
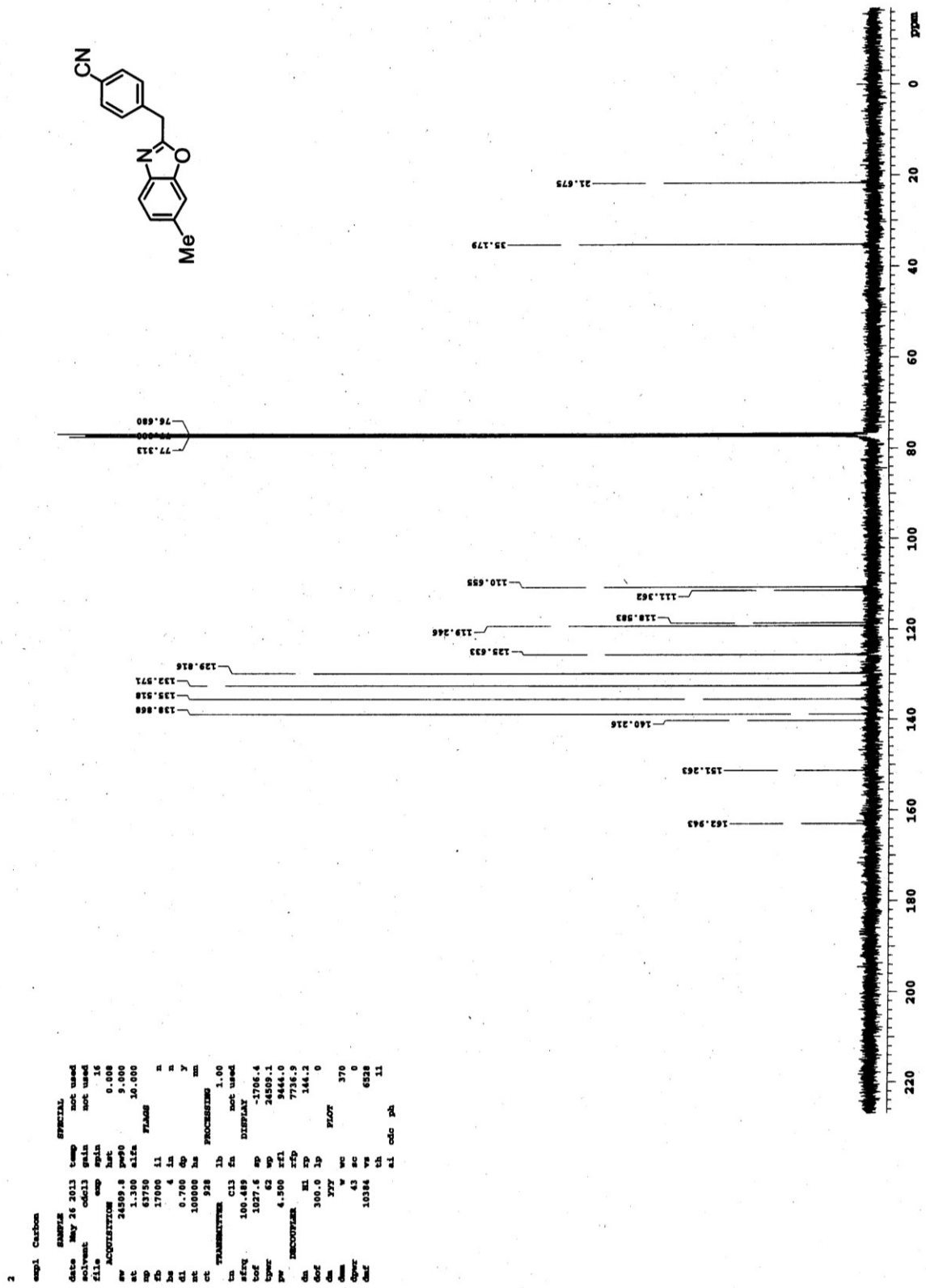
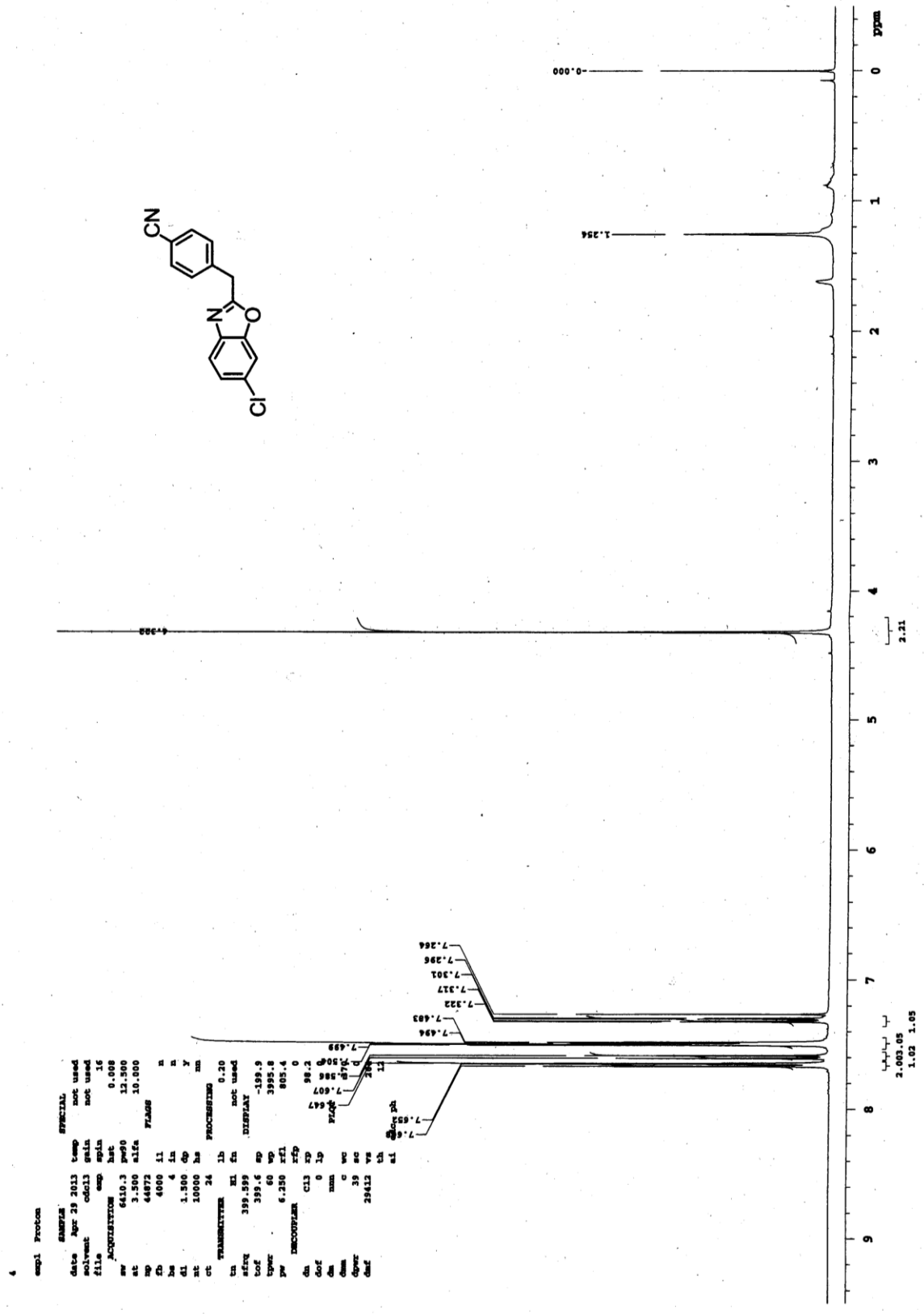
4-(6-Methyl-2-benzoxazolylmethyl)benzonitrile (Table 1, entry 11) (^{1}H-NMR)



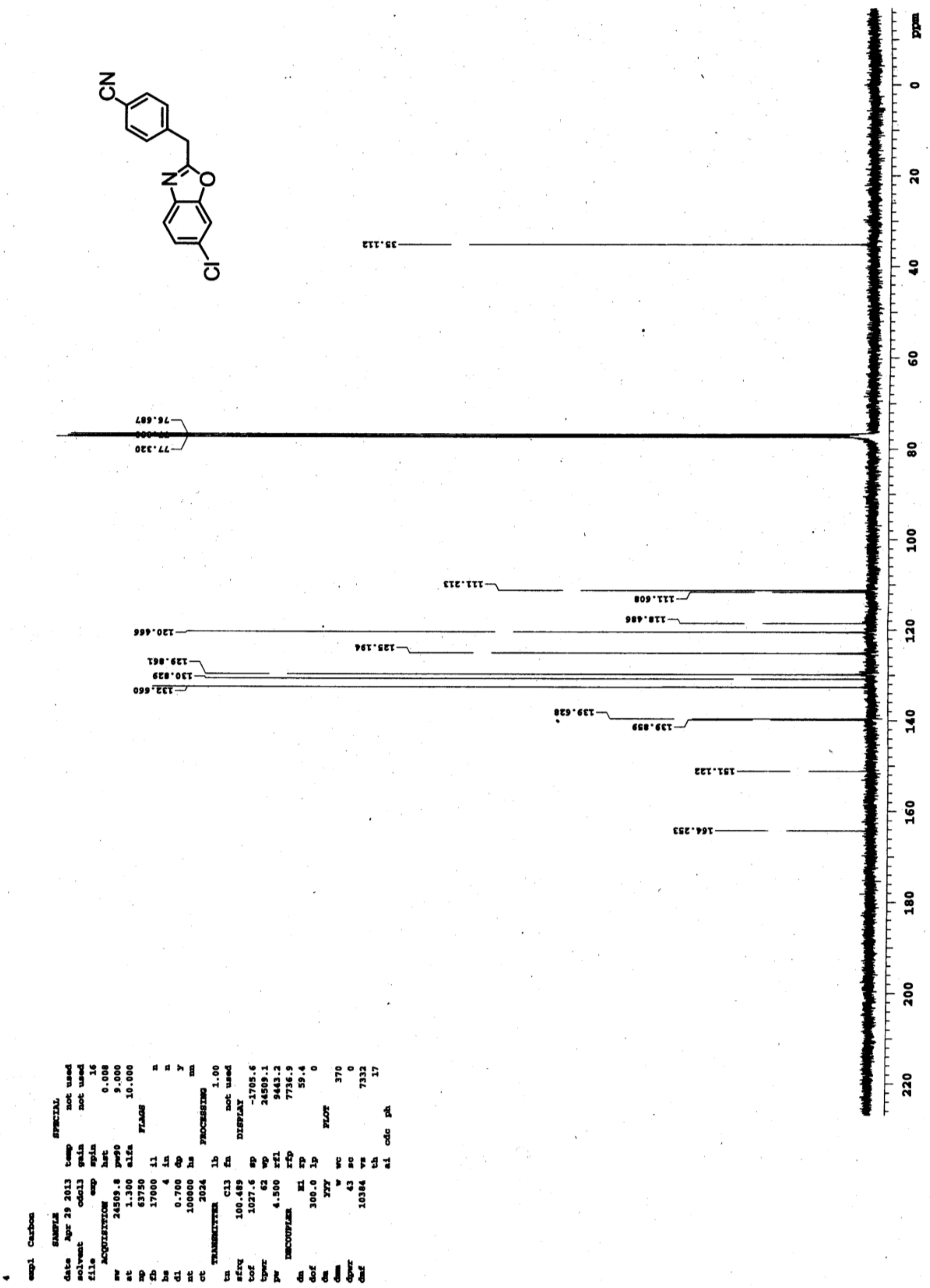
4-(6-Methyl-2-benzoxazolylmethyl)benzonitrile (Table 1, entry 11) (^{13}C-NMR)



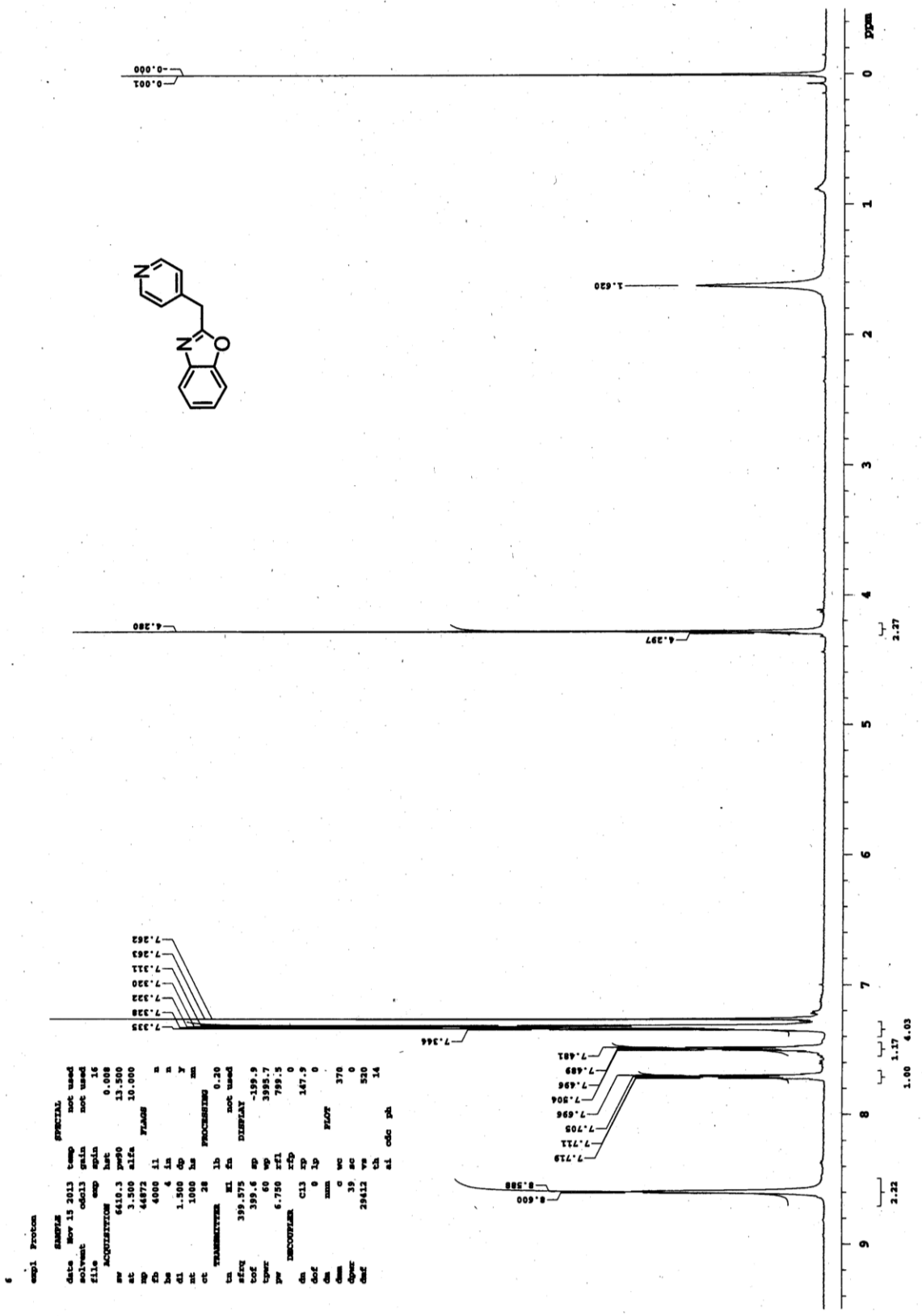
4-(6-Chloro-2-benzoxazolylmethyl)benzonitrile (Table 1, entry 12) (^{1}H-NMR)



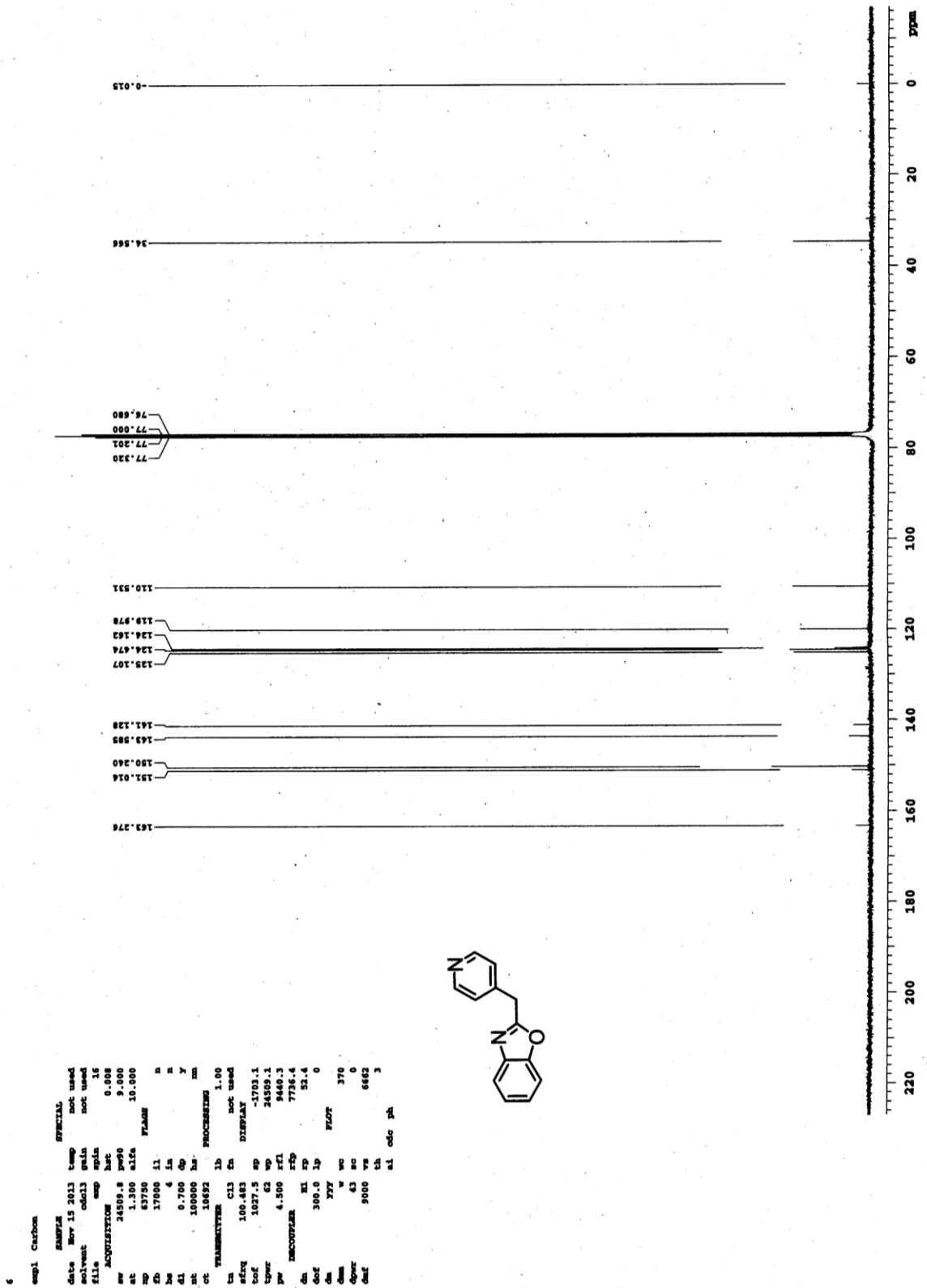
4-(6-Chloro-2-benzoxazolylmethyl)benzonitrile (Table 1, entry 12) (^{13}C-NMR)



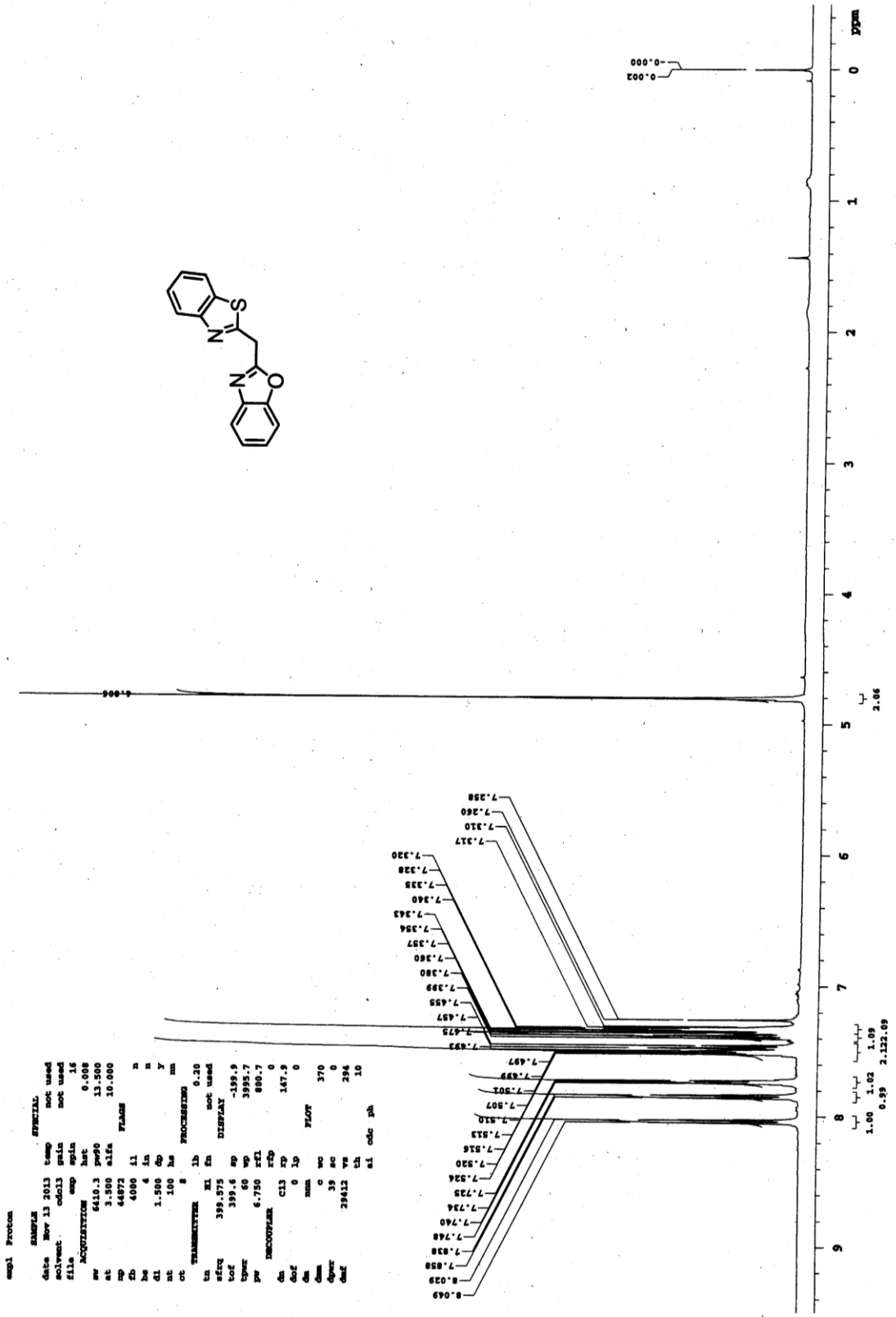
2-(4-Pyridylmethyl)benzoxazole (Table 1, entry 13) (^{1}H-NMR)



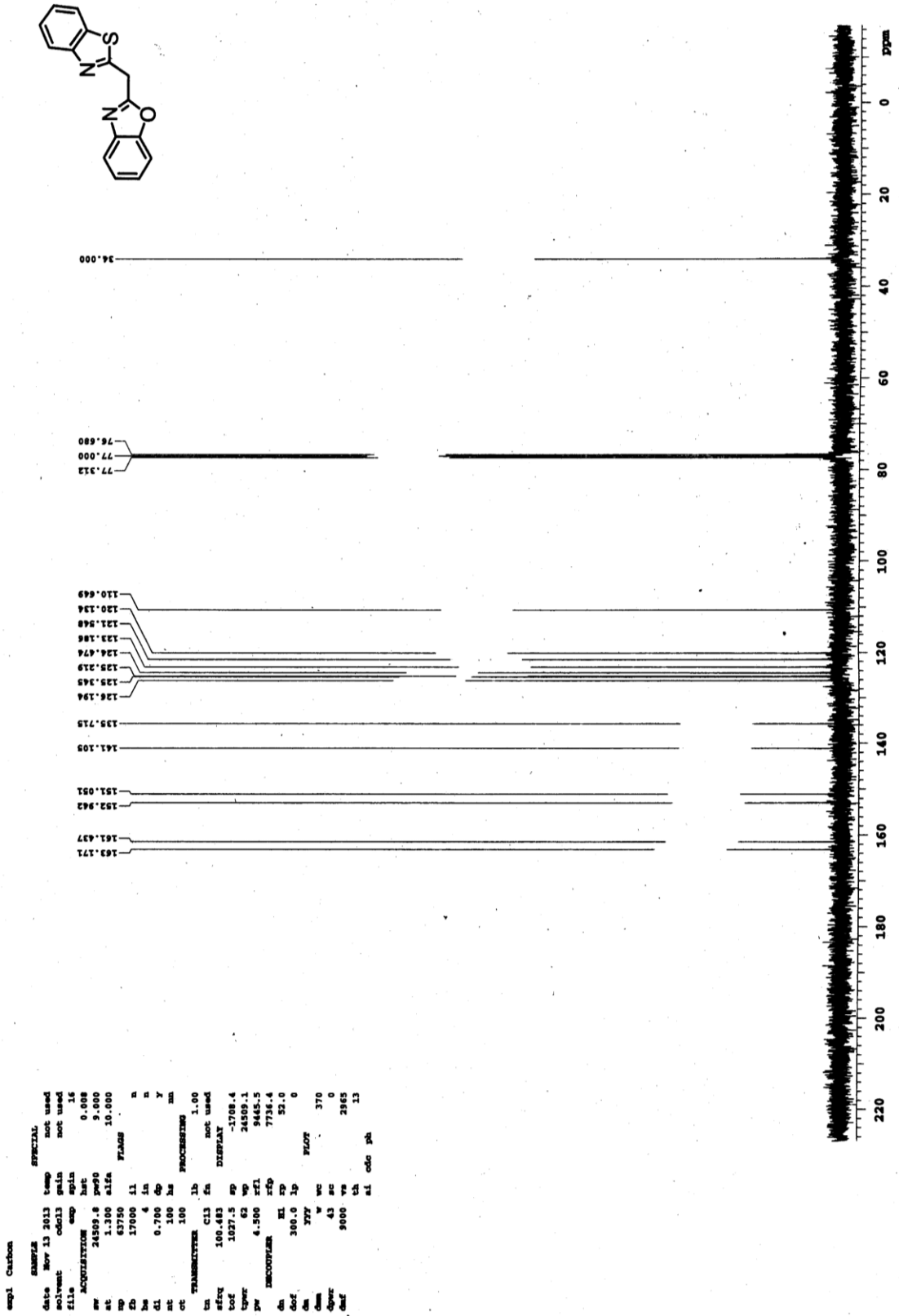
2-(4-Pyridylmethyl)benzoxazole (Table 1, entry 13) (^{13}C-NMR)



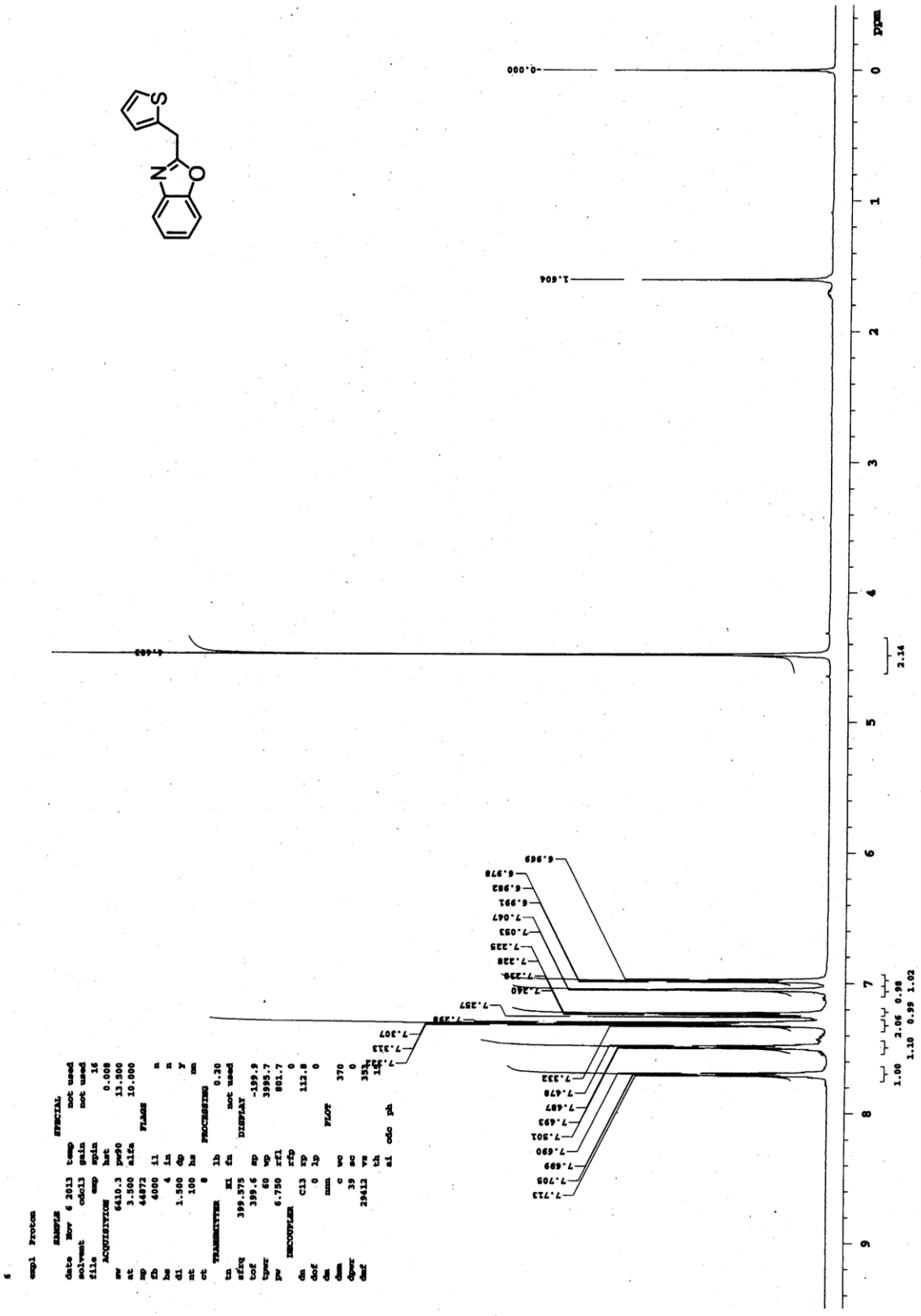
2-(2-Benzothiazoylmethyl)benzoxazole (Table 1, entry 14) (^{1}H-NMR)



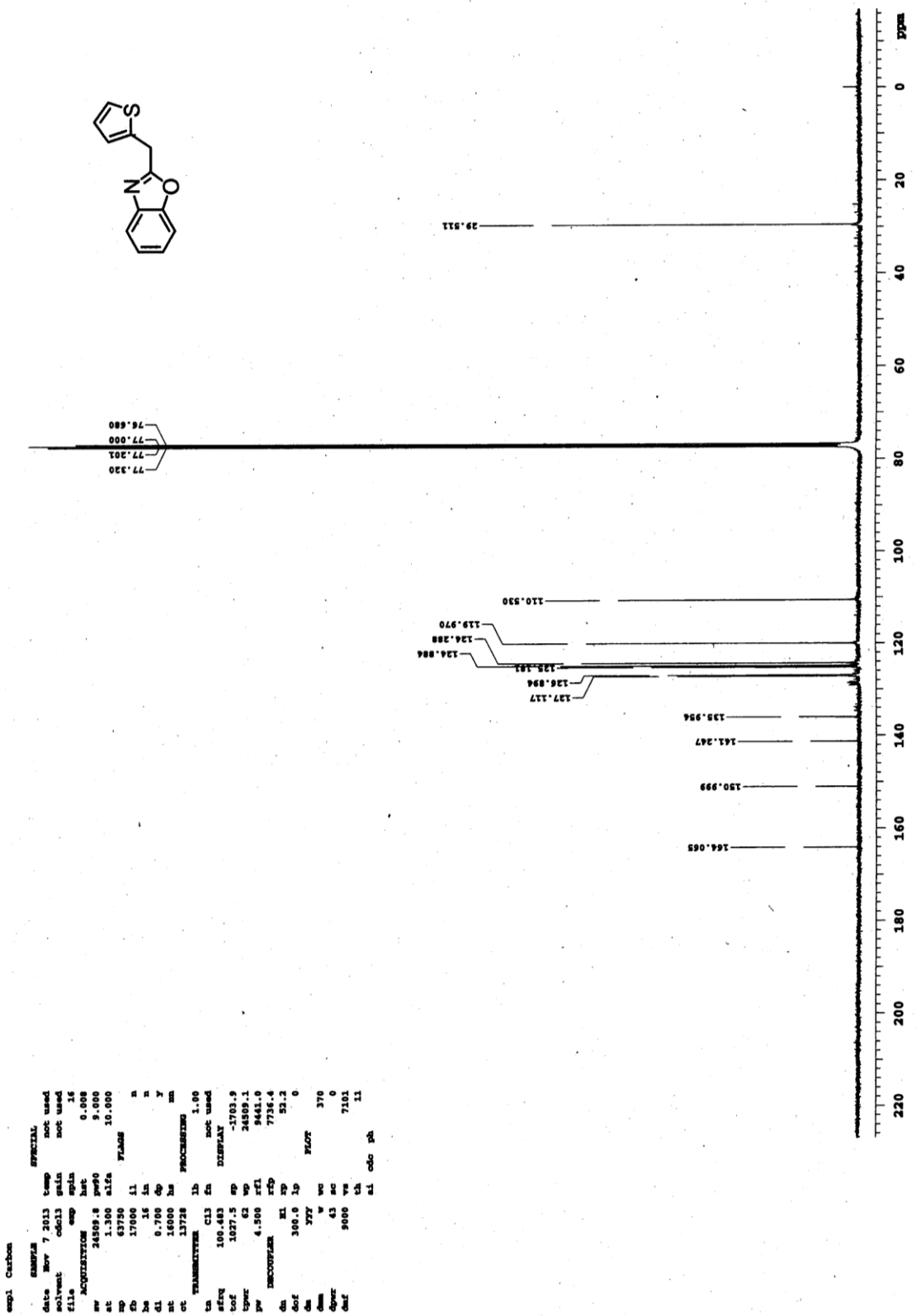
2-(2-Benzothiazoylmethyl)benzoxazole(Table 1, entry 14) (^{13}C-NMR)



2-(2-Thienylmethyl)benzoxazole (Table 1, entry 15) (^{1}H-NMR)



2-(2-Thienylmethyl)benzoxazole (Table 1, entry 15) (^{13}C-NMR)



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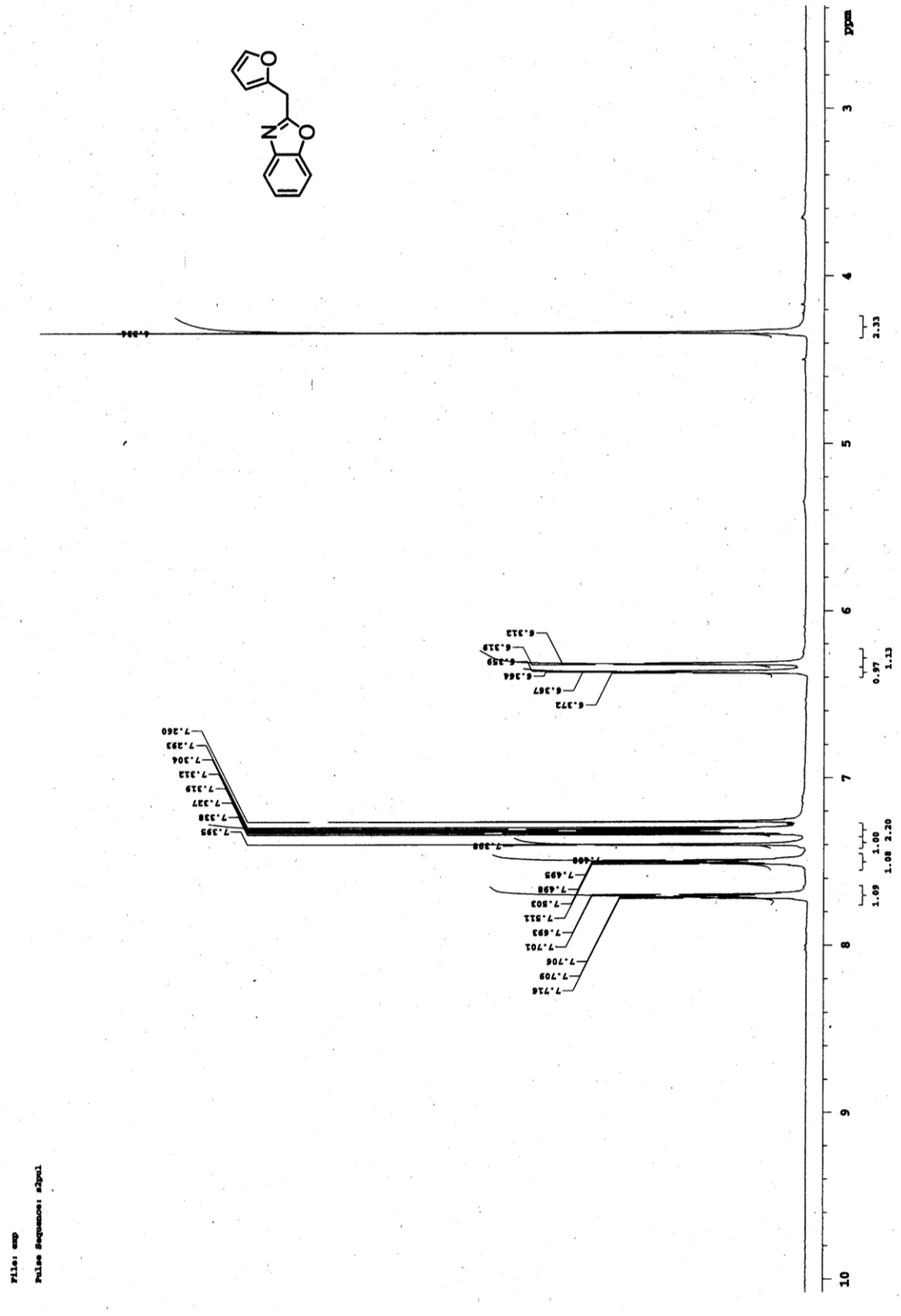
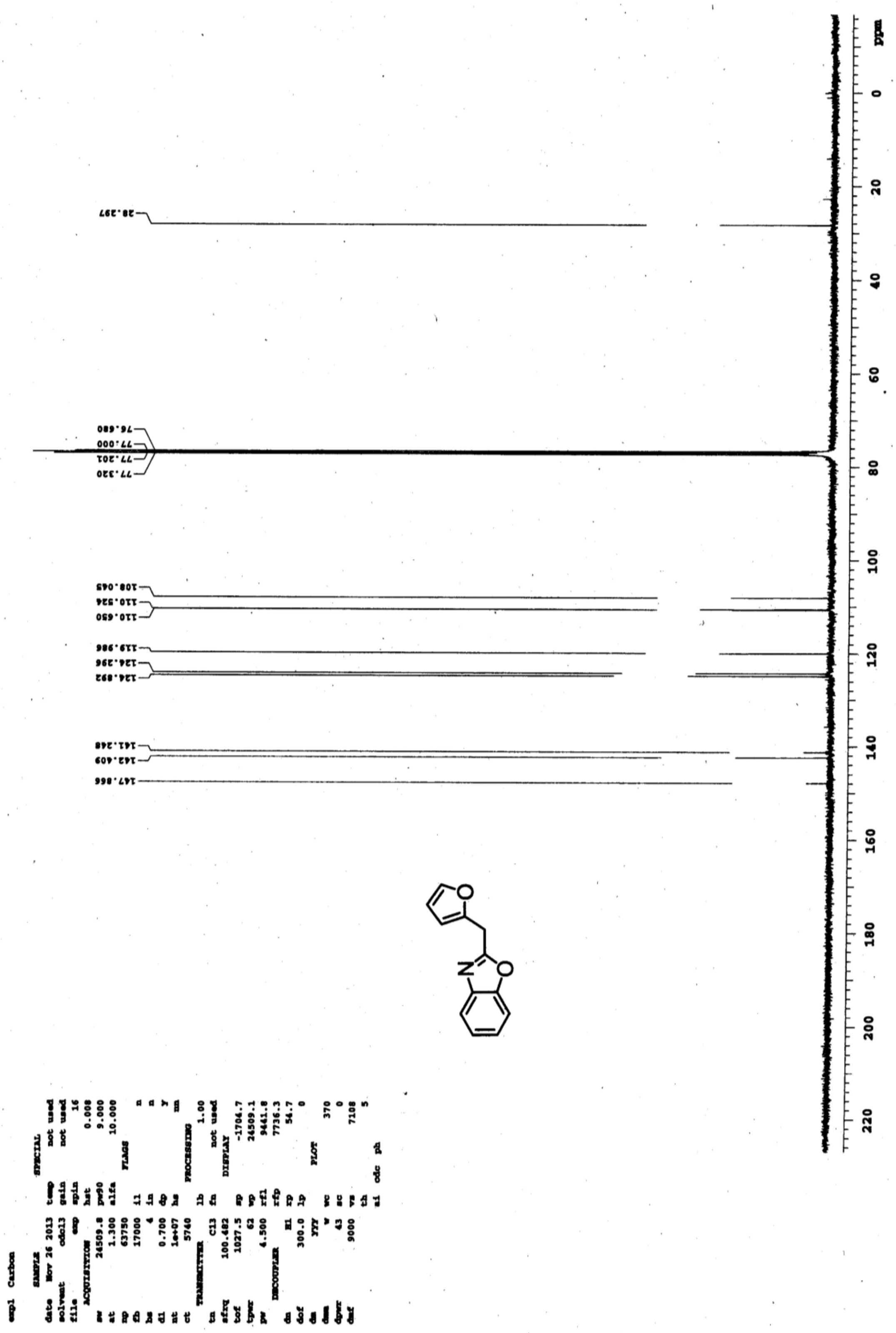
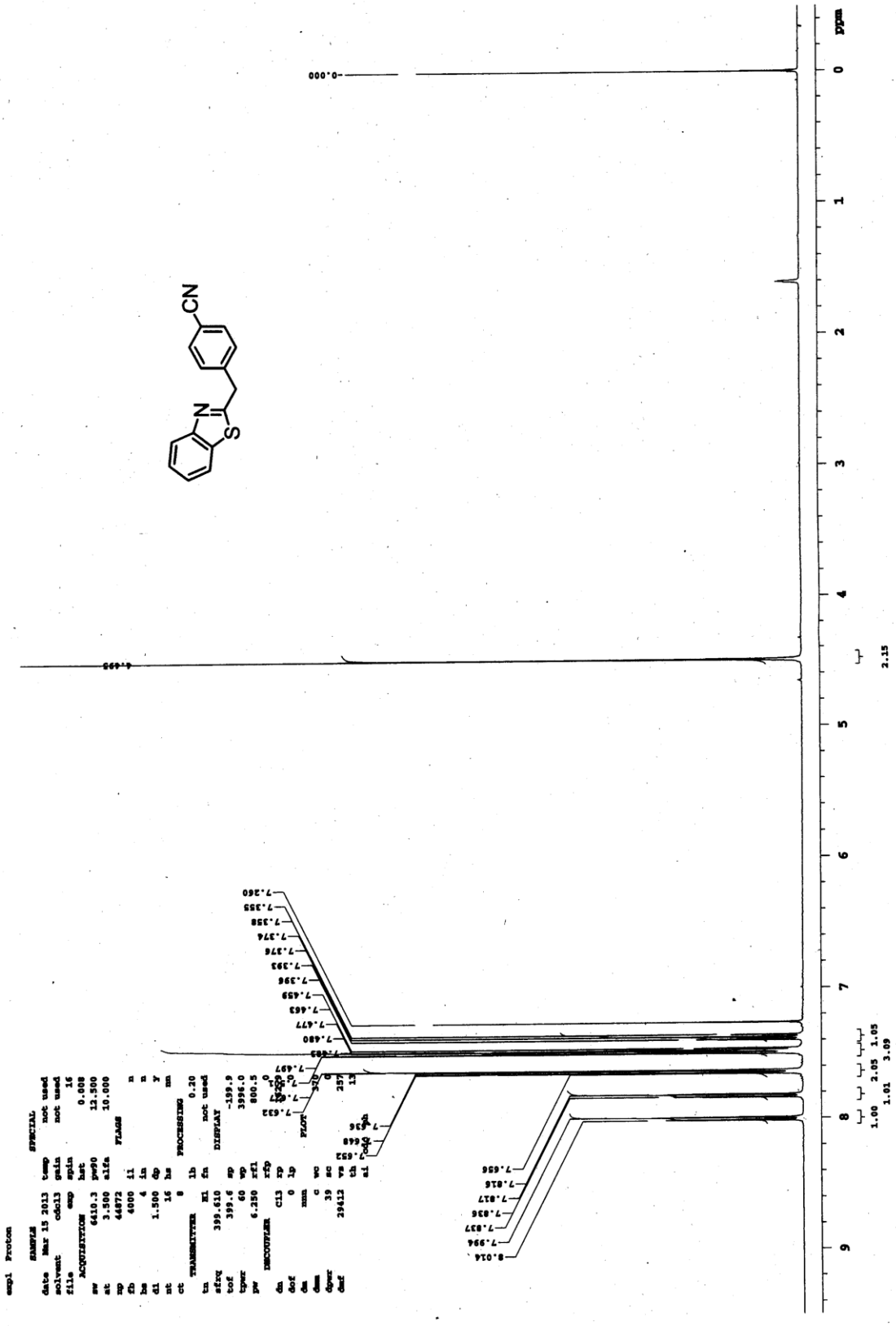
2-(2-Furylmethyl)benzoxazole (Table 1, entry 16) (^{1}H-NMR)



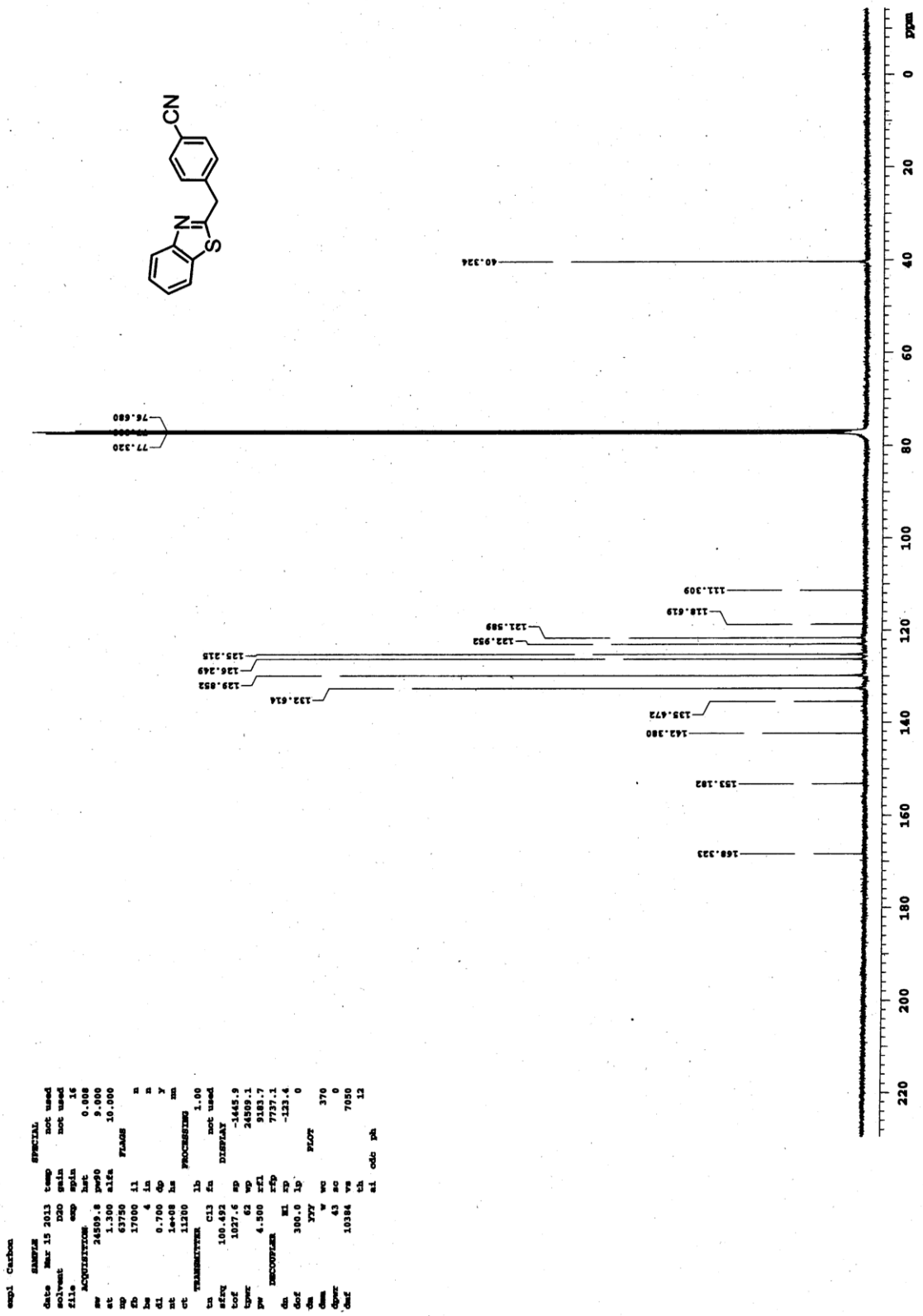
2-(2-Furylmethyl)benzoxazole (Table 1, entry 16) ([13]C-NMR)



4-(2-Benzothiazolylmethyl)benzonitrile (3b) (^{1}H-NMR)



4-(2-benzothiazolylmethyl)benzonitrile (3b) (^{13}C-NMR)



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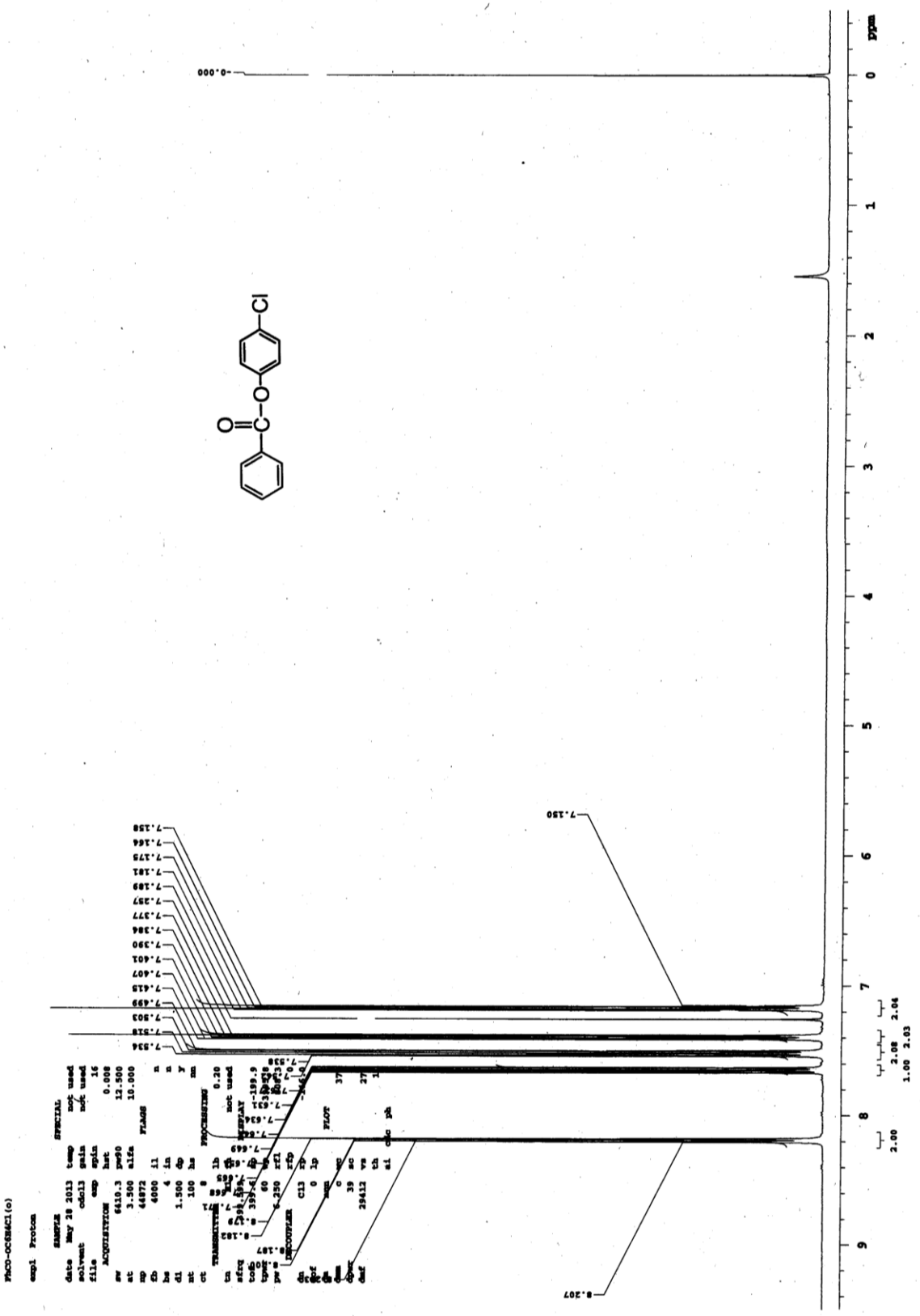
4-Chlorophenyl benzoate (4b) (^{1}H-NMR)



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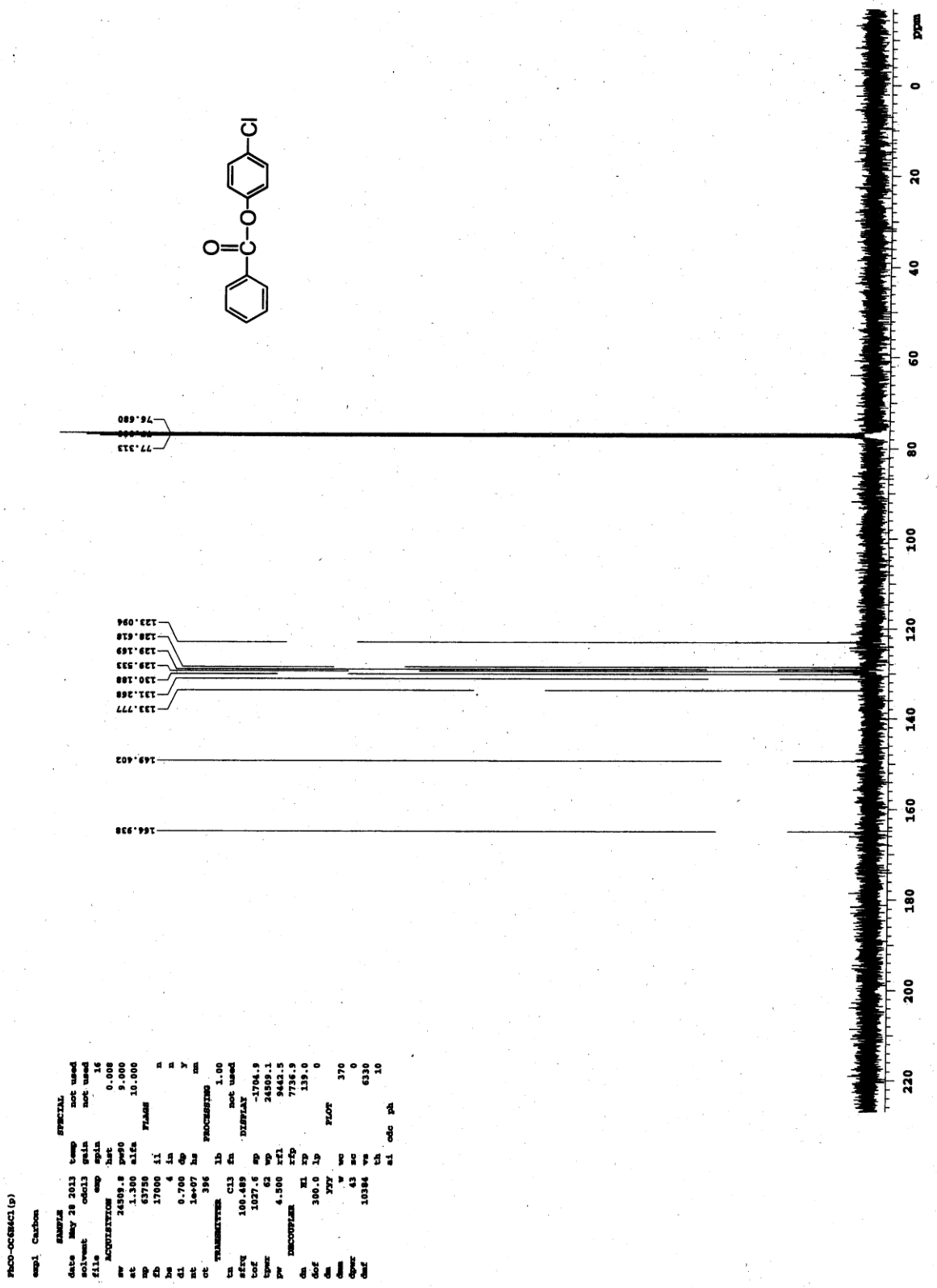
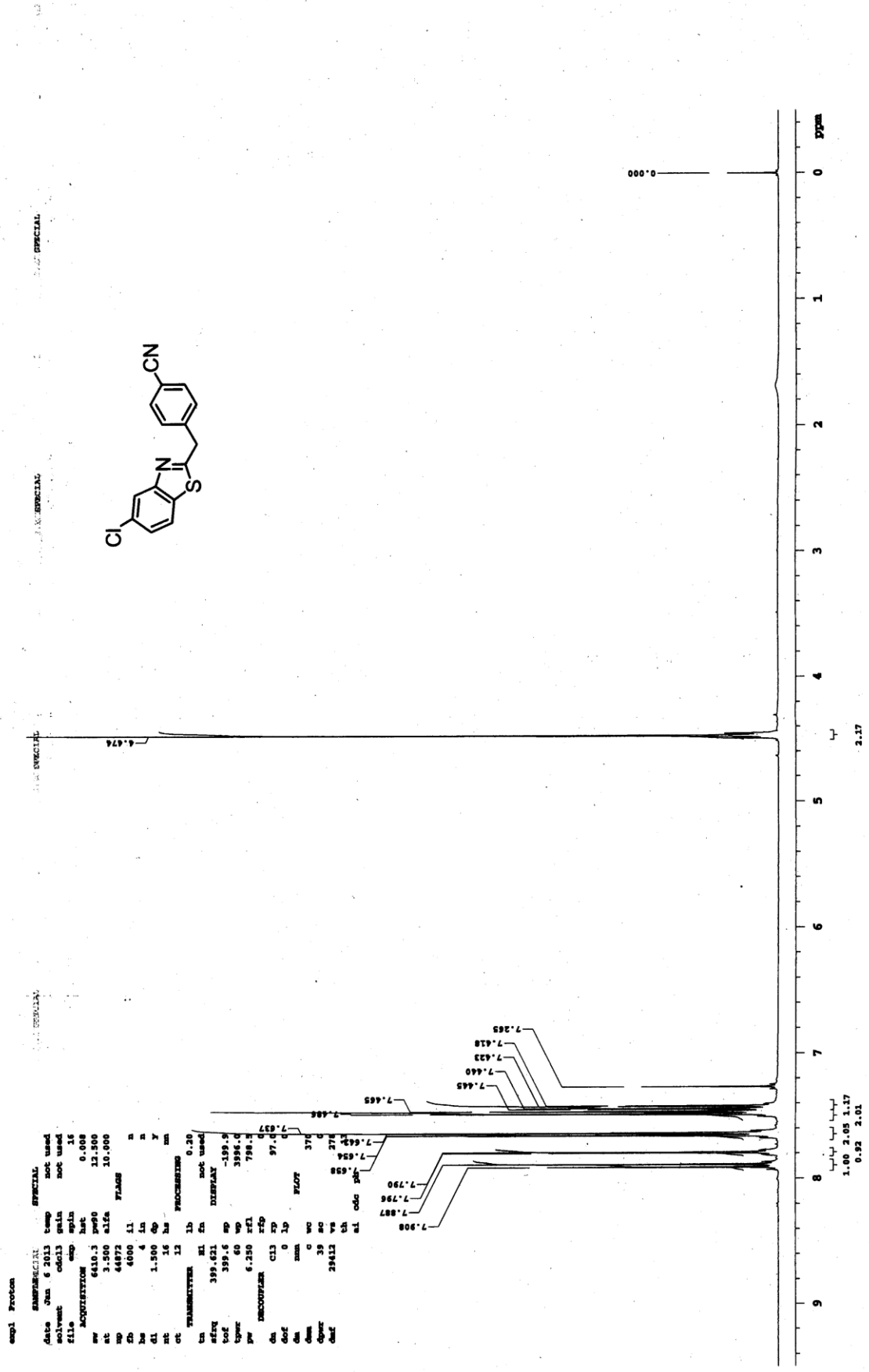


4-(5-Chloro-2-benzothiazolylmethyl)benzonitrile (3c) (^{1}H-NMR)



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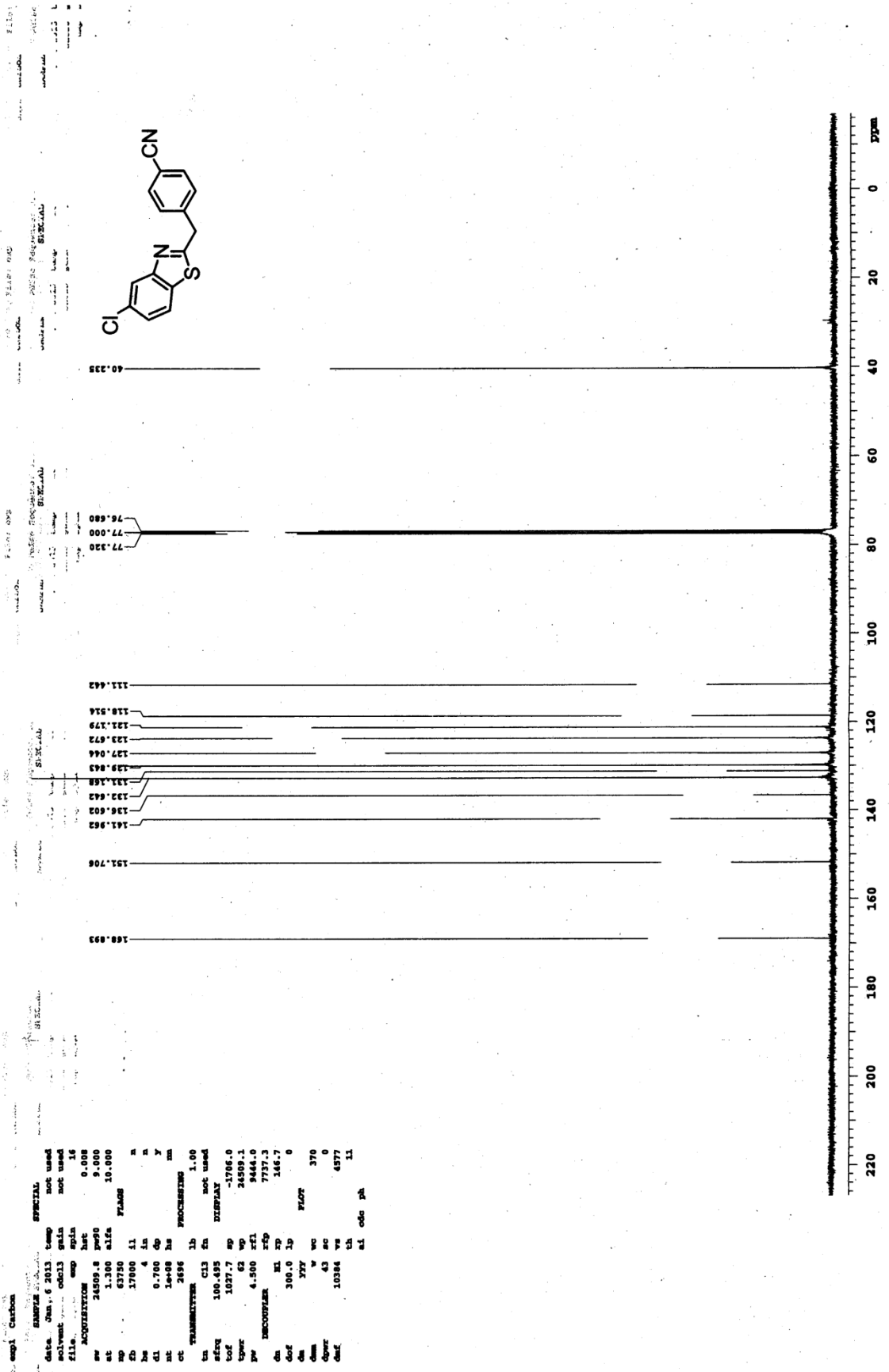
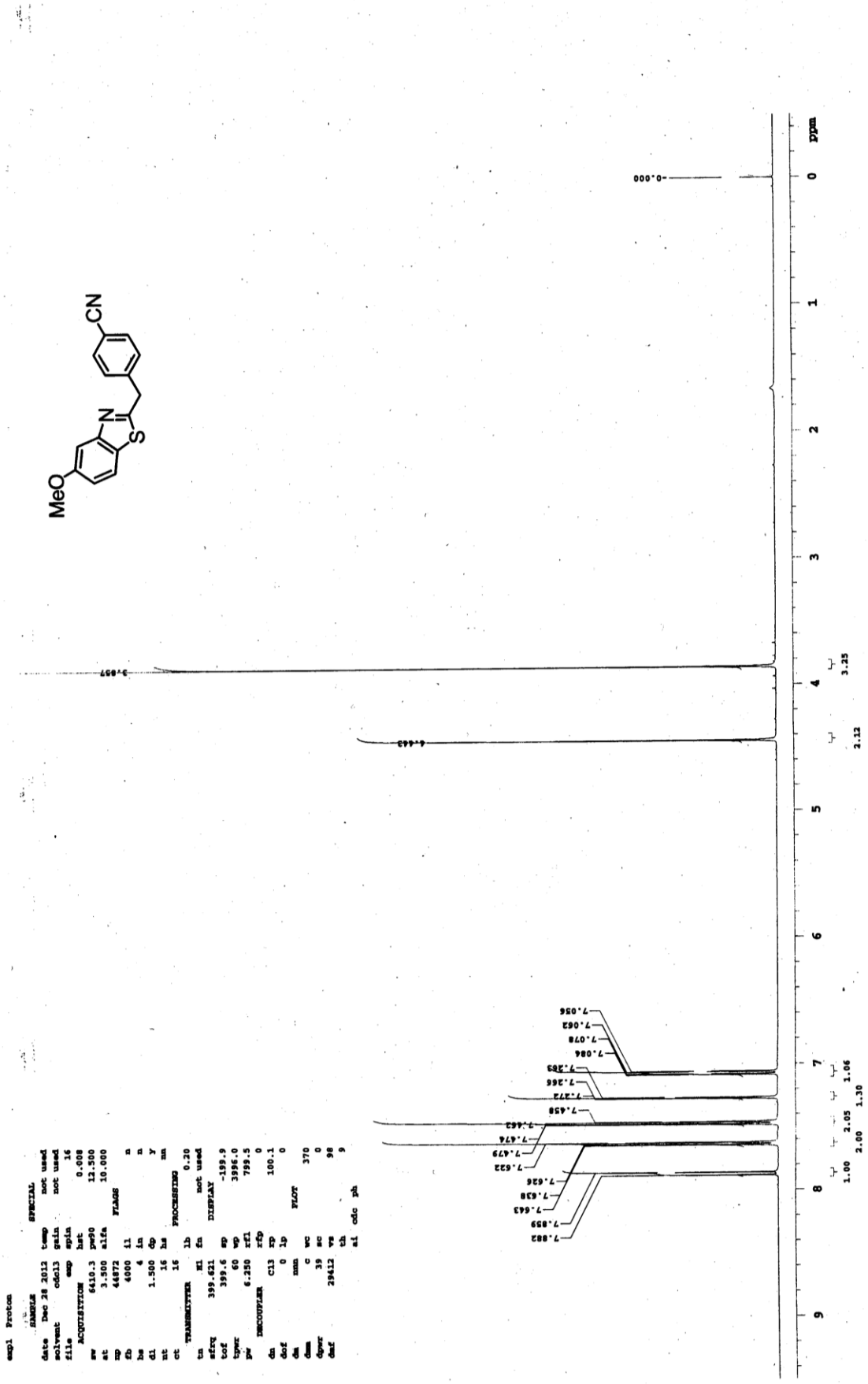


4-(5-Methoxy-2-benzothiazolylmethyl)benzonitrile (3d) (^{1}H-NMR)



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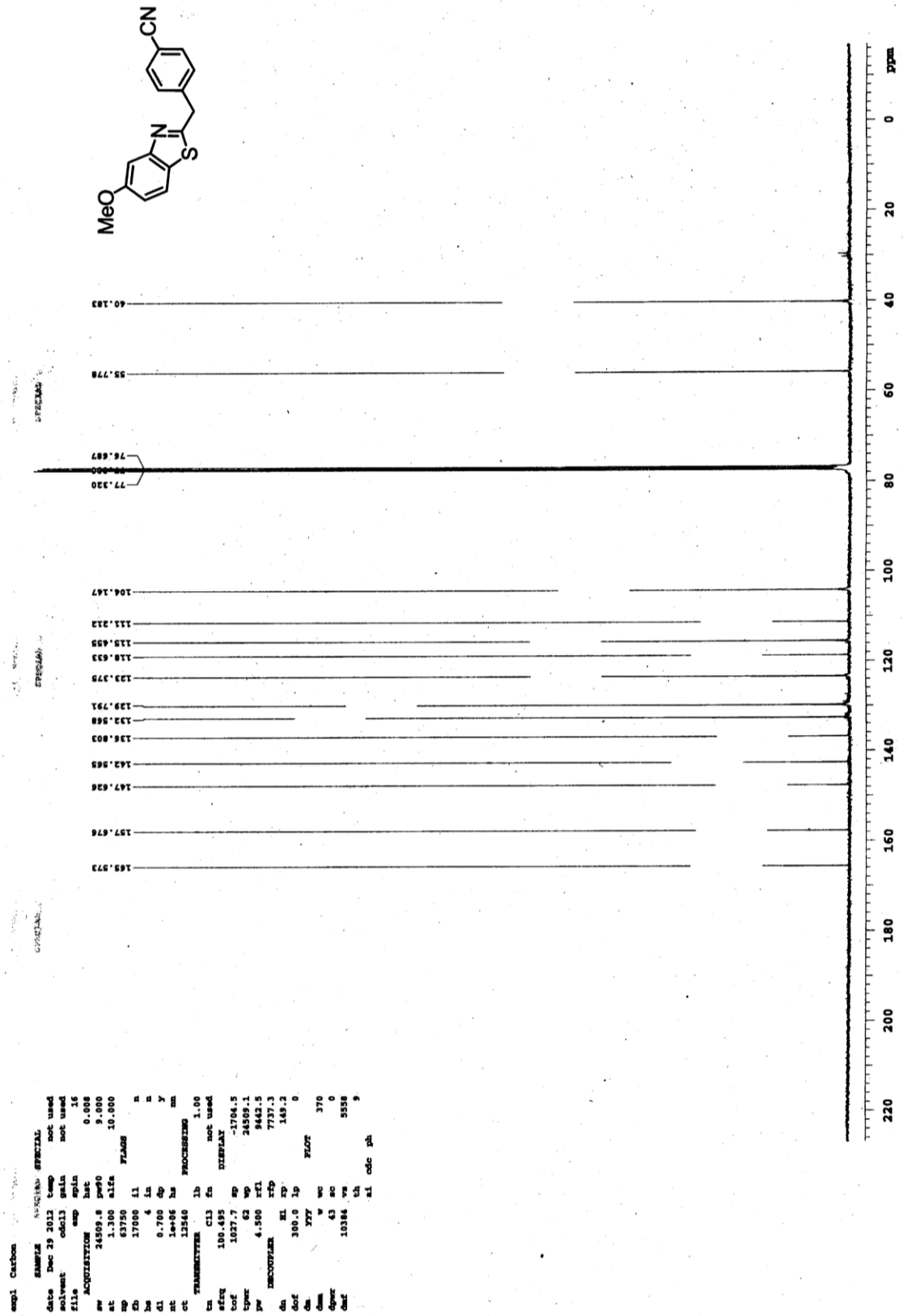

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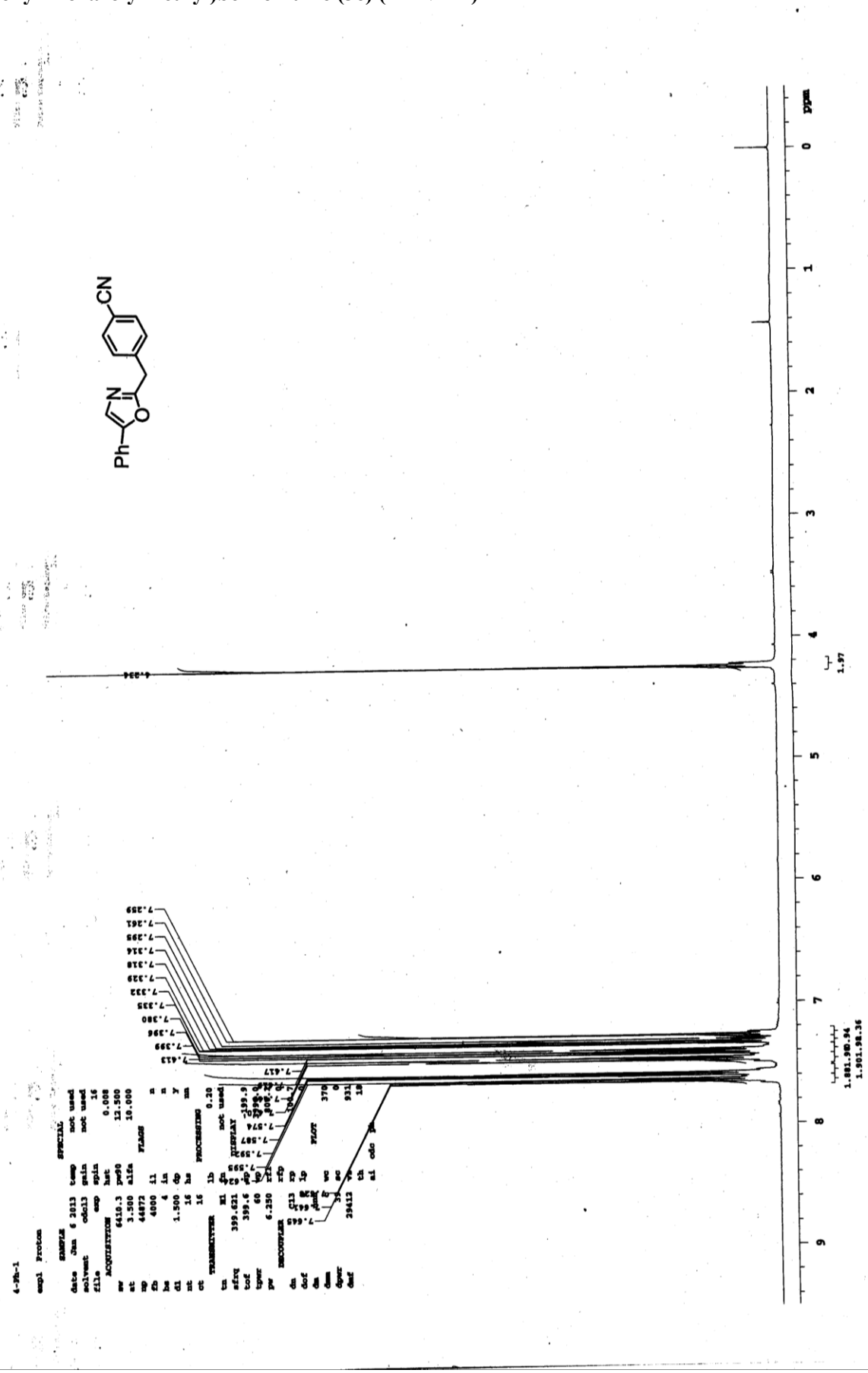

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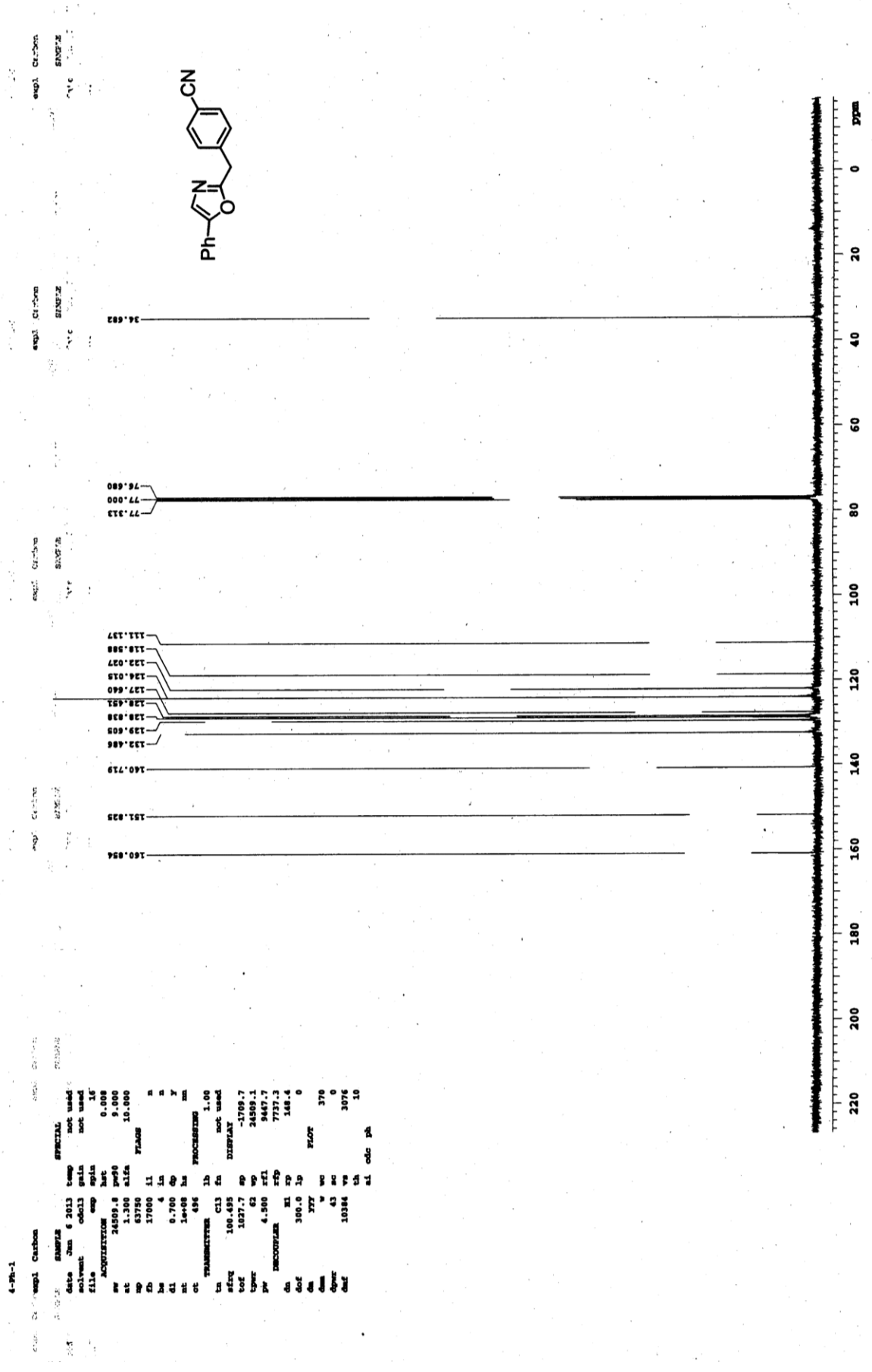

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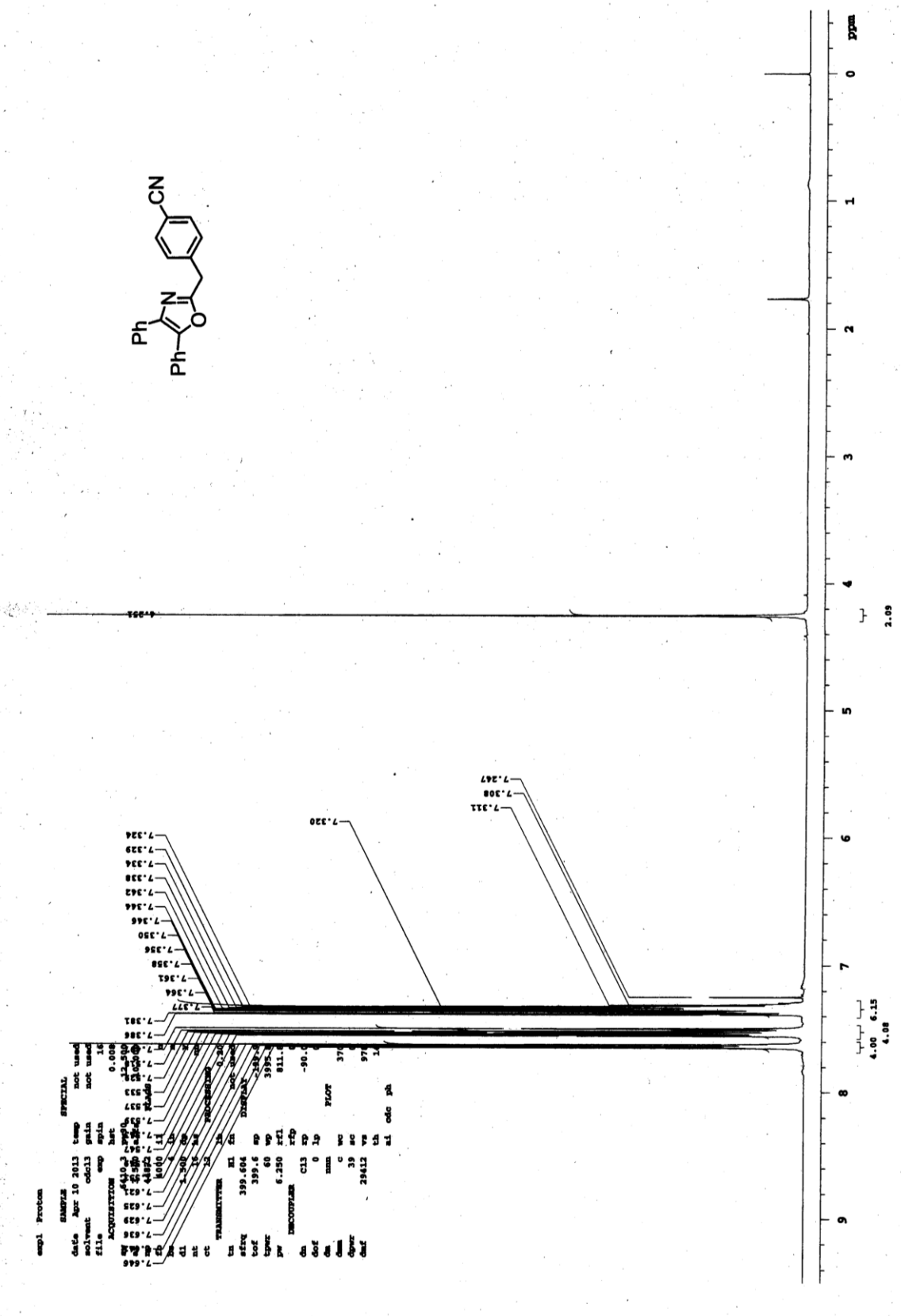

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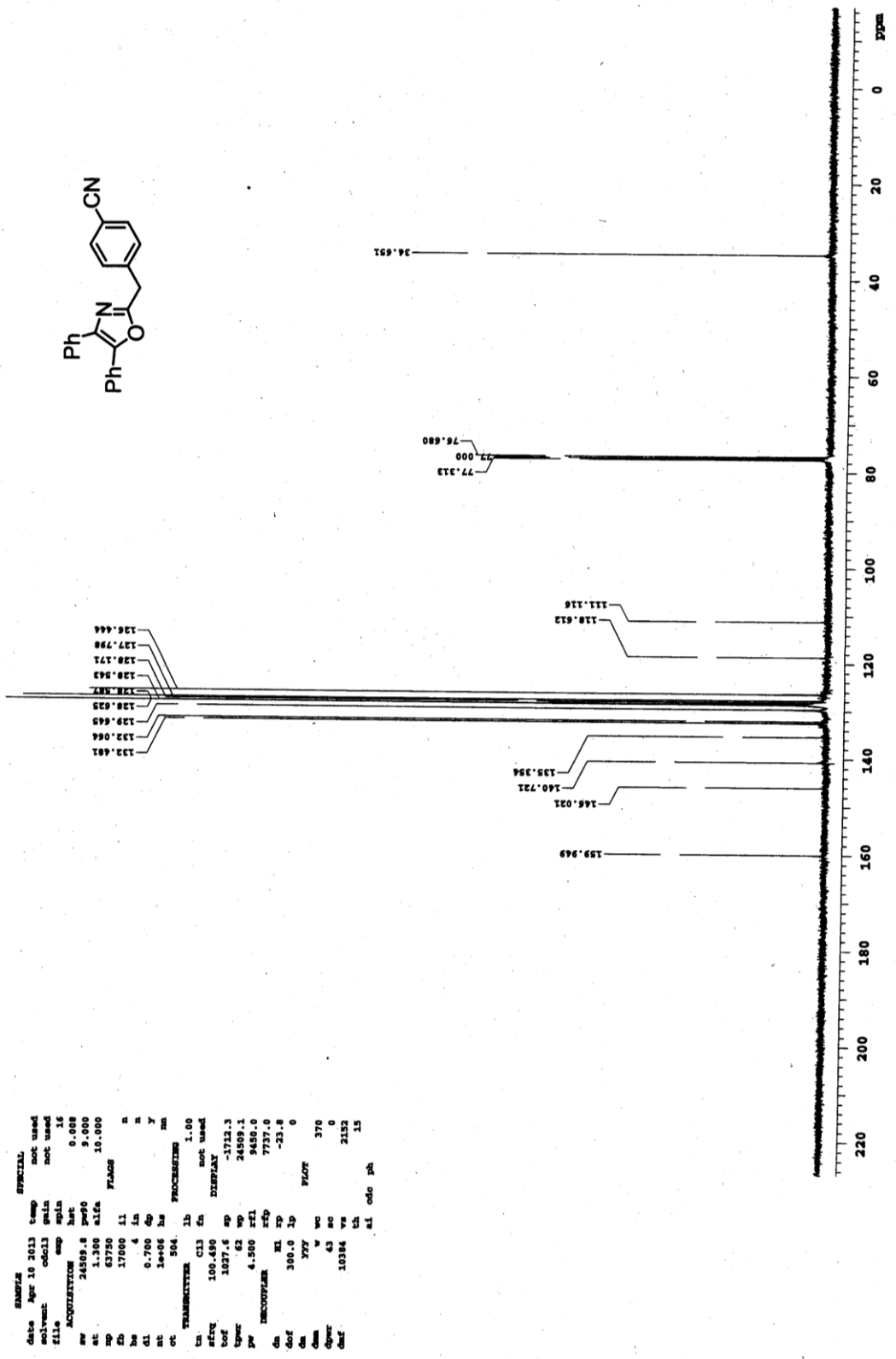

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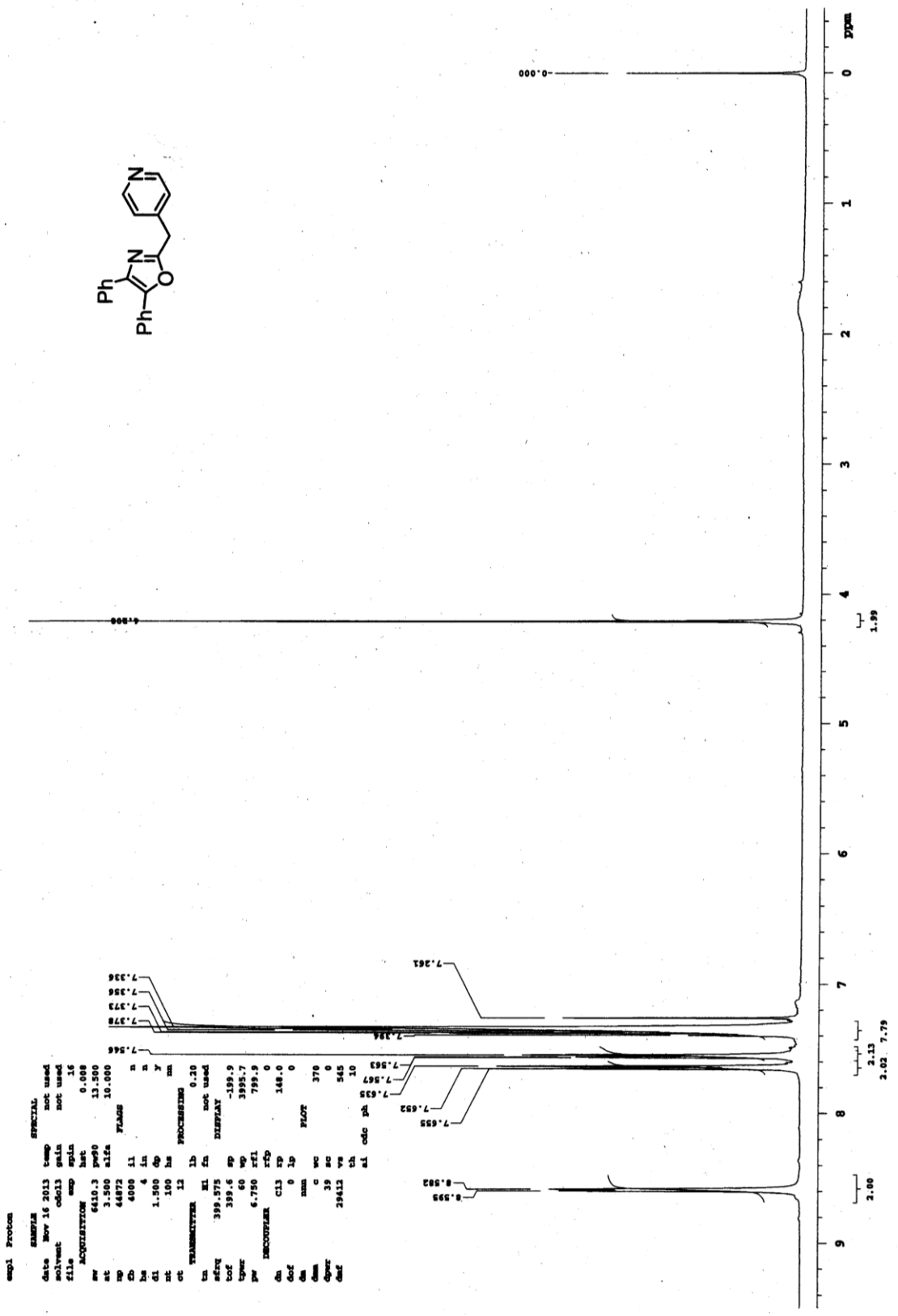
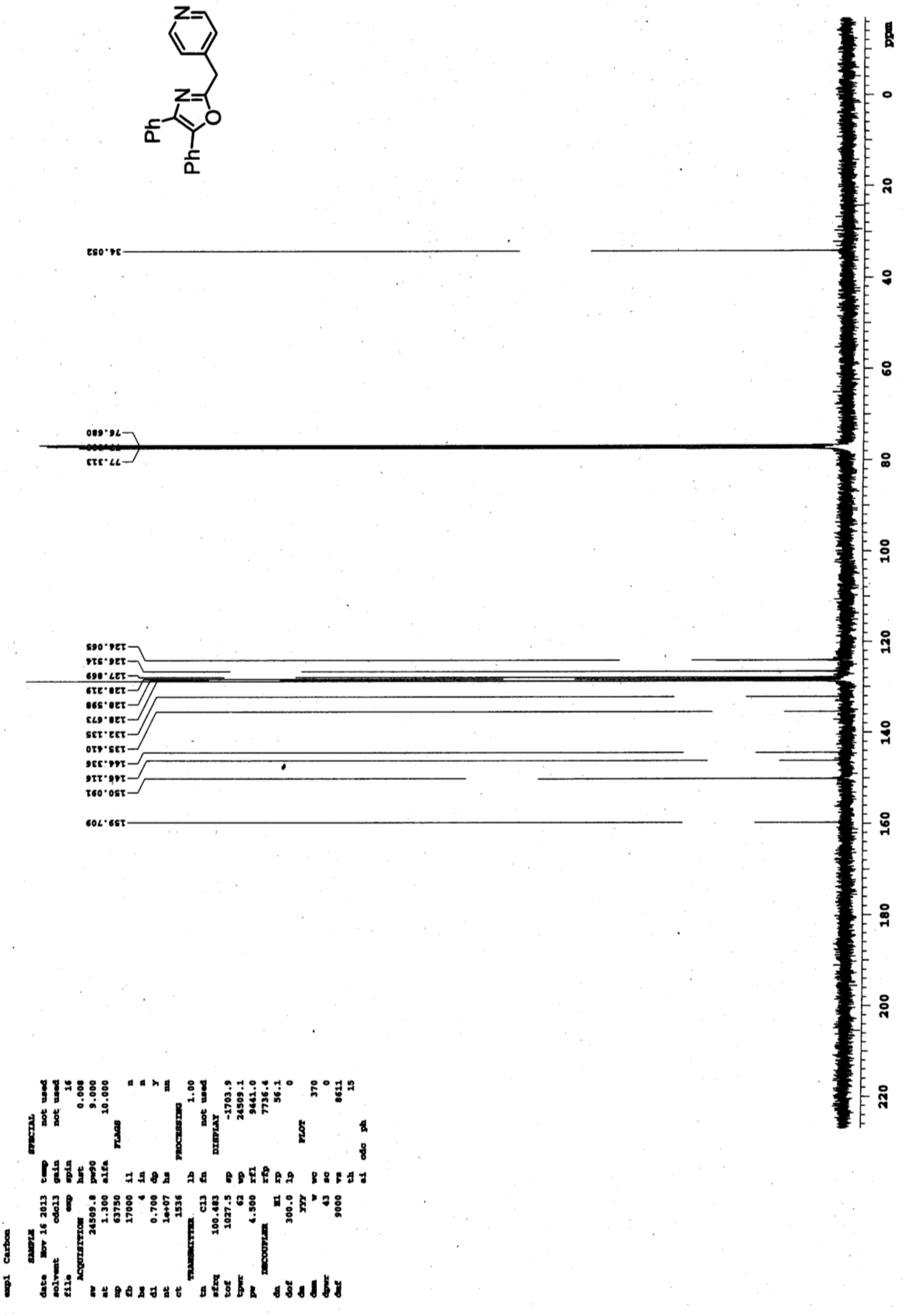
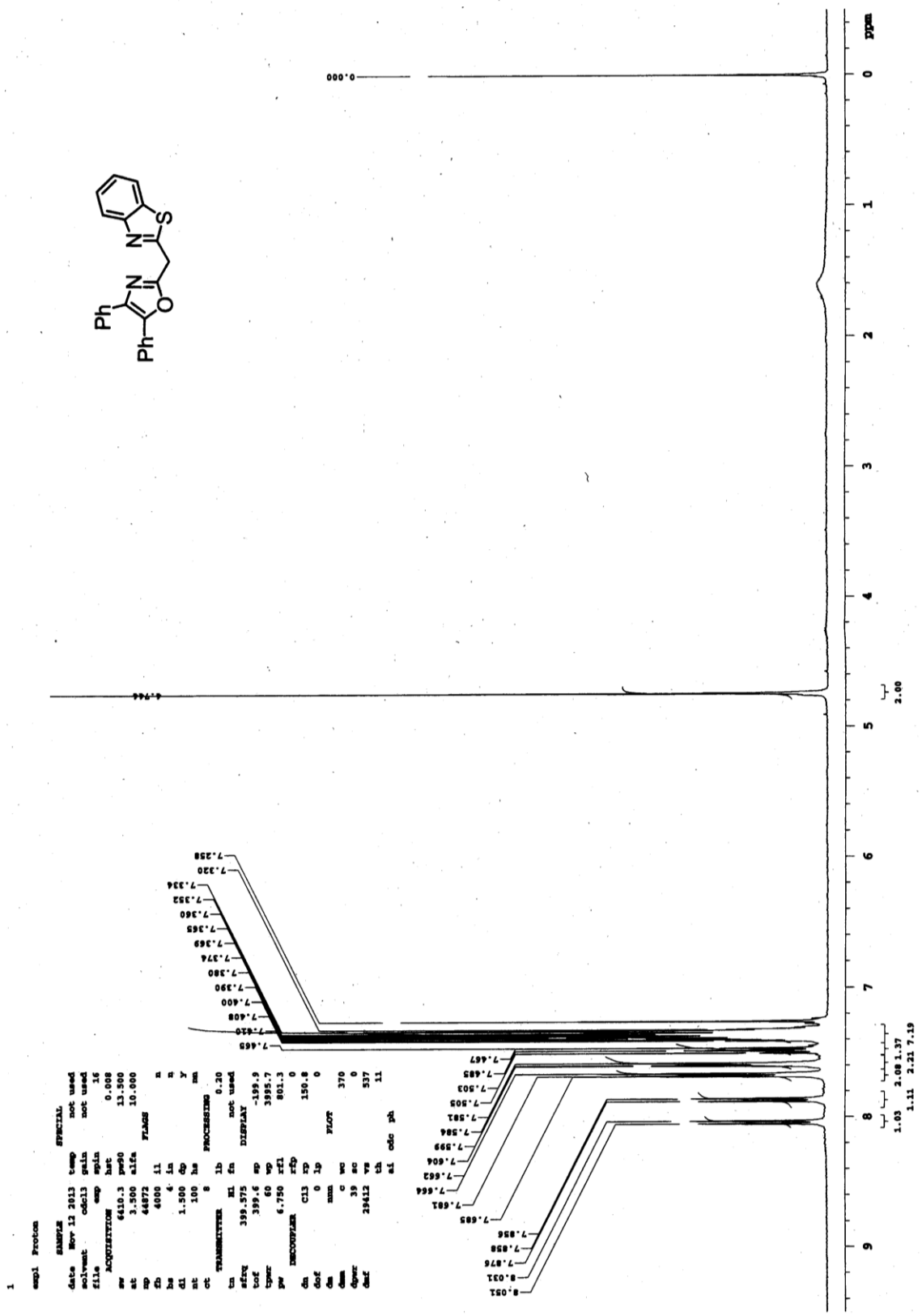


4-(4,5-Diphenyl-2-oxazolylmethyl)pyridine (3g) (^{13}C-NMR)



2-(4,5-Diphenyl-2-oxazolylmethyl)benzothiazole (3h) (^{1}H-NMR)



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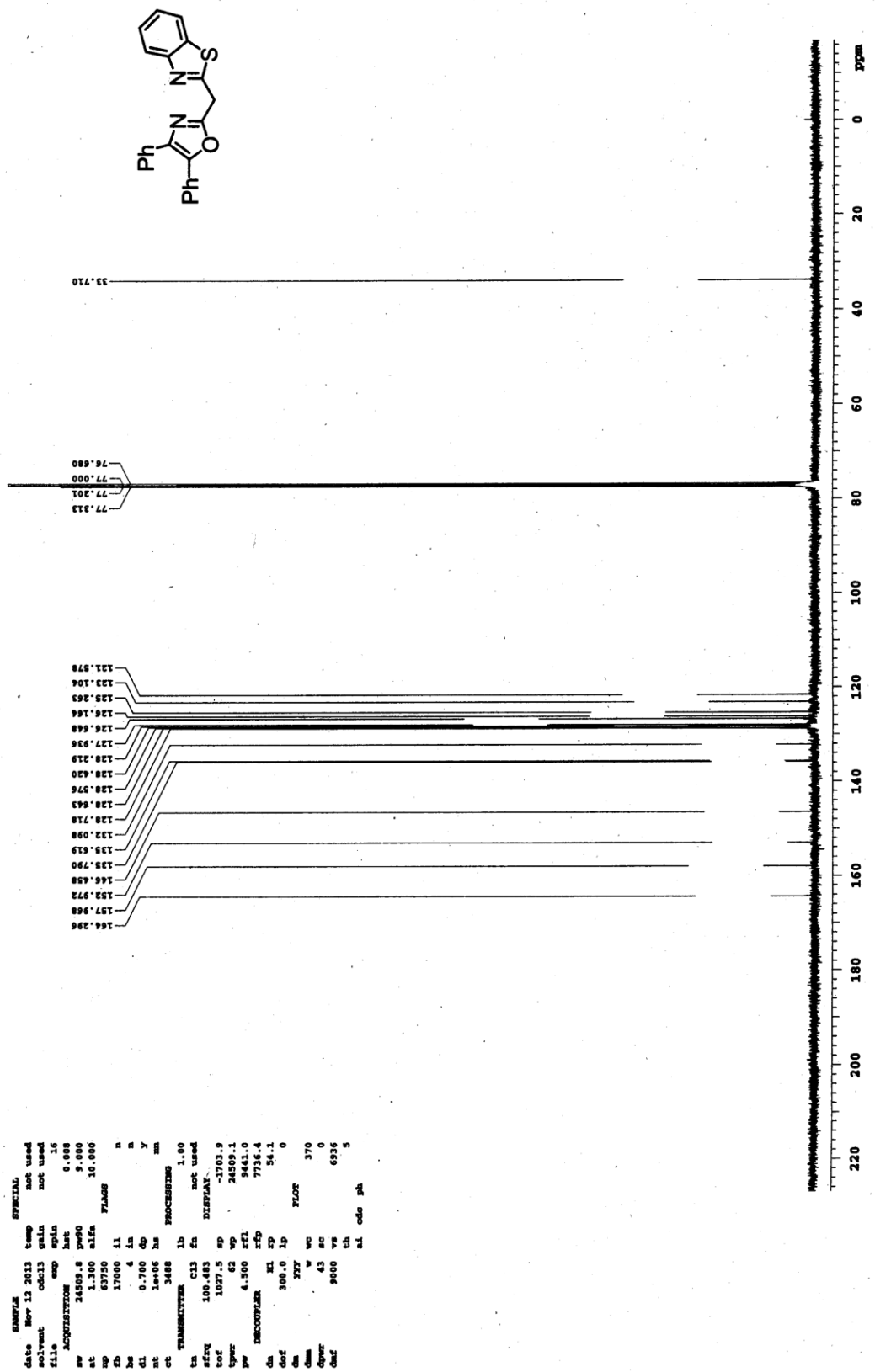

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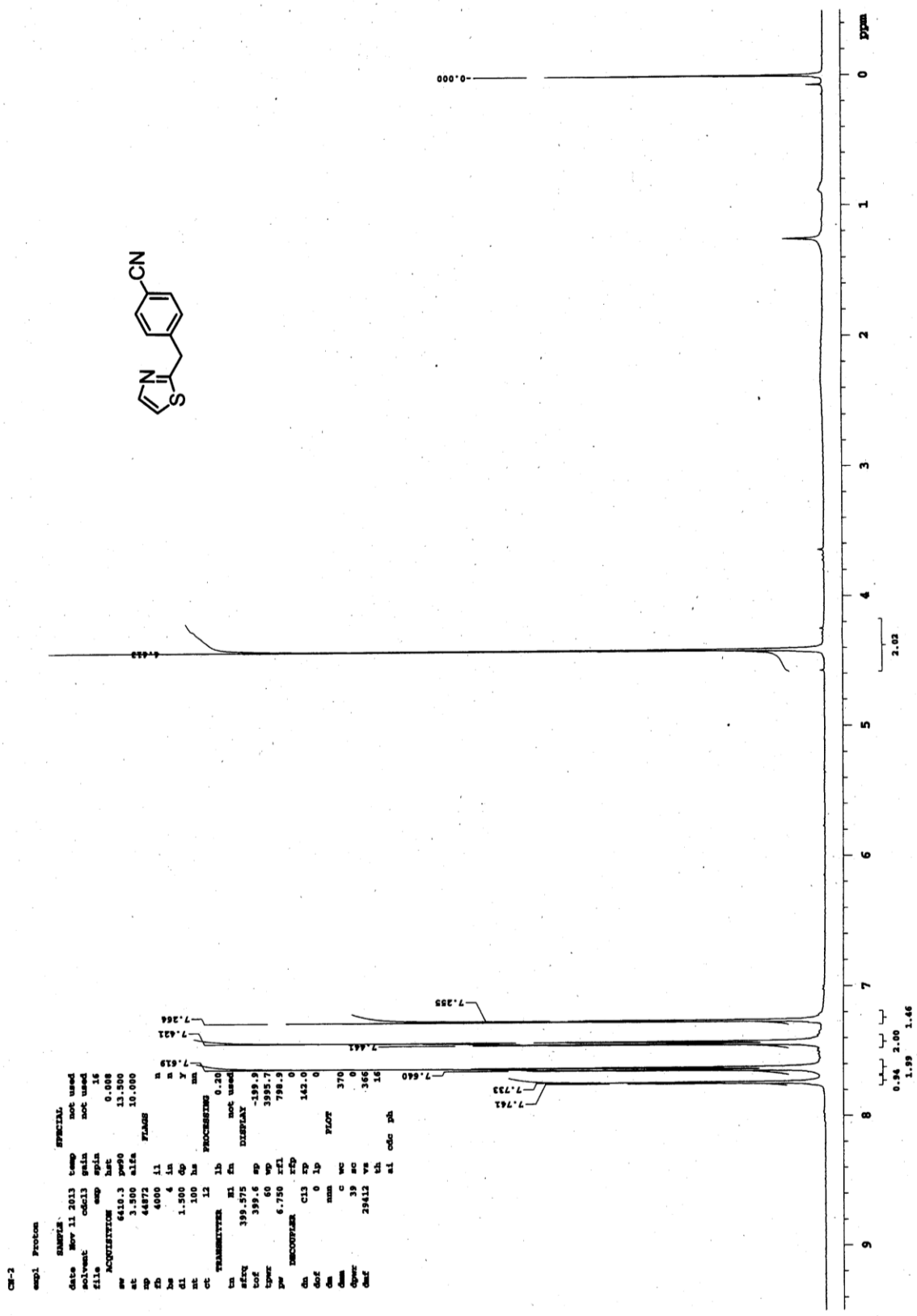

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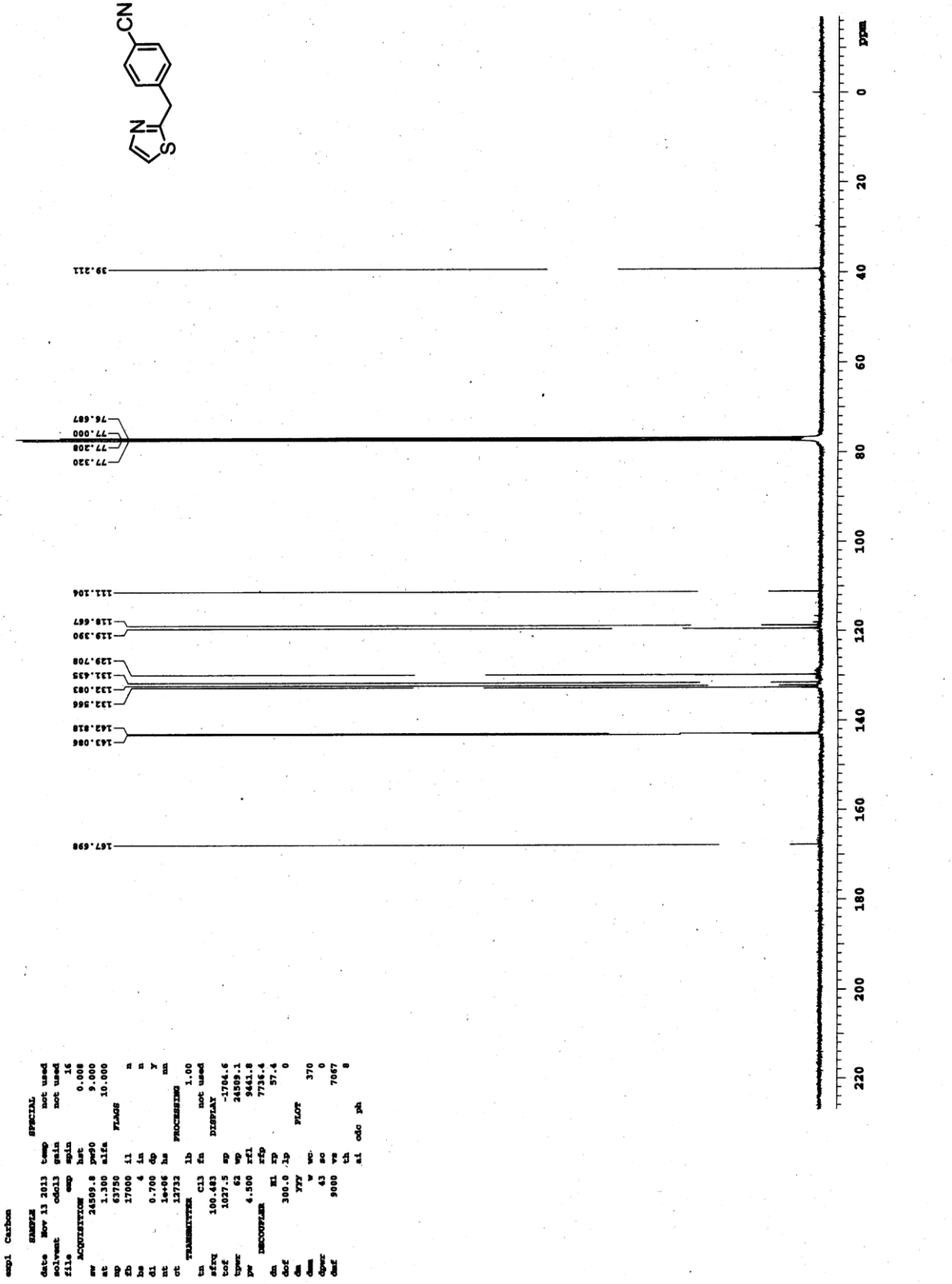

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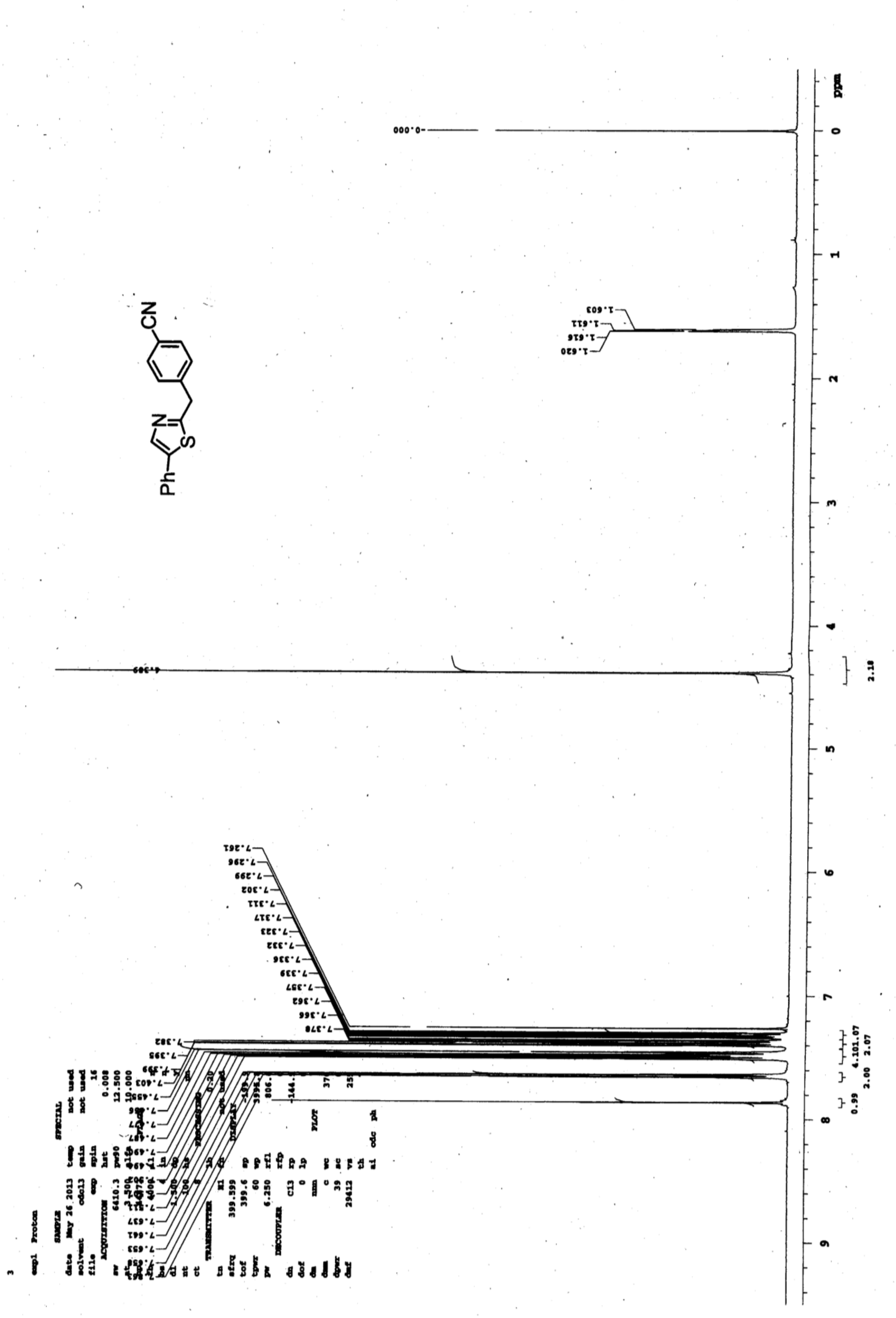
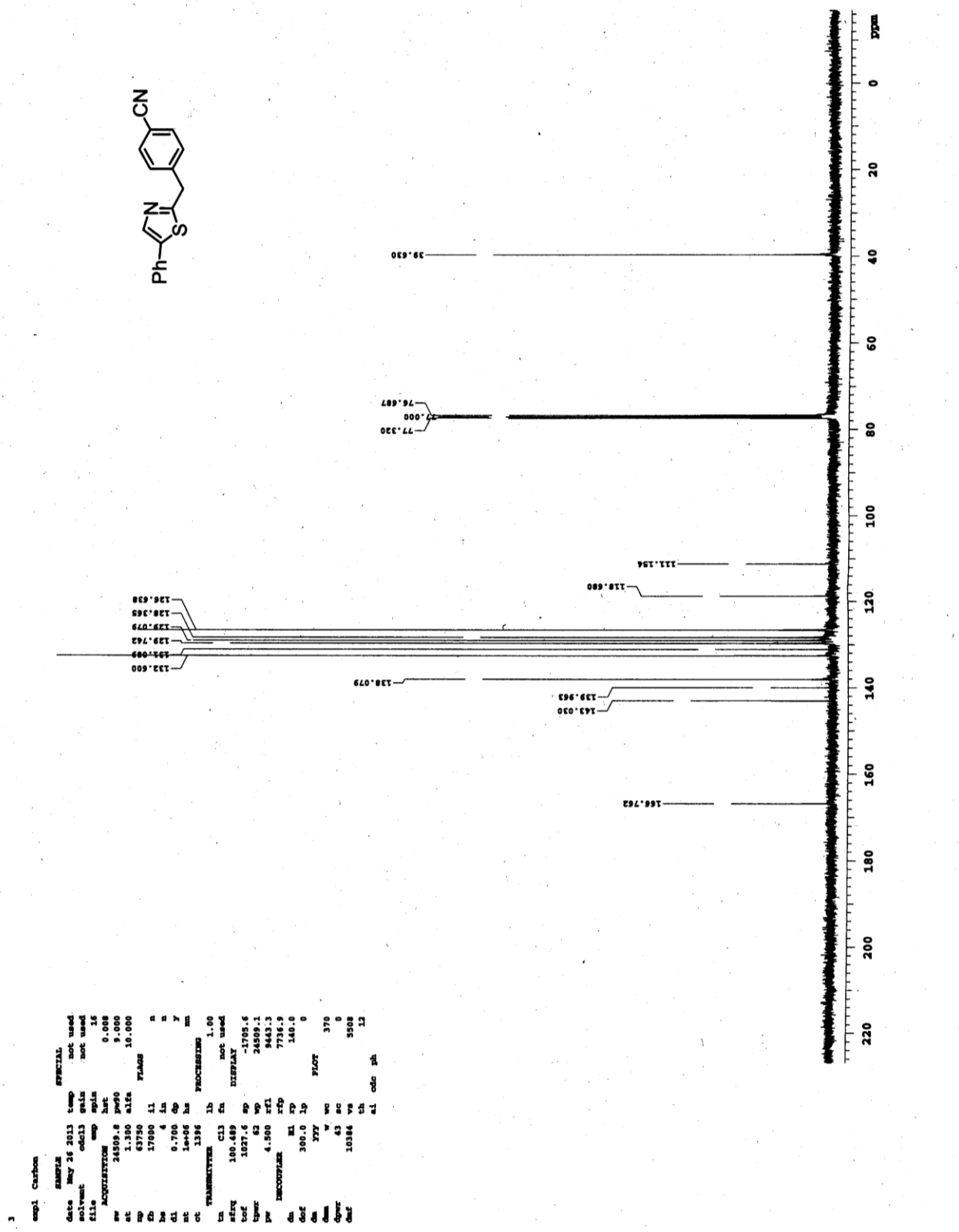
4-(5-Phenyl-2-thiazolylmethyl)benzonitrile (3j) ([1]H-NMR)



4-(5-Phenyl-2-thiazolylmethyl)benzonitrile (3j) (^{13}C-NMR)



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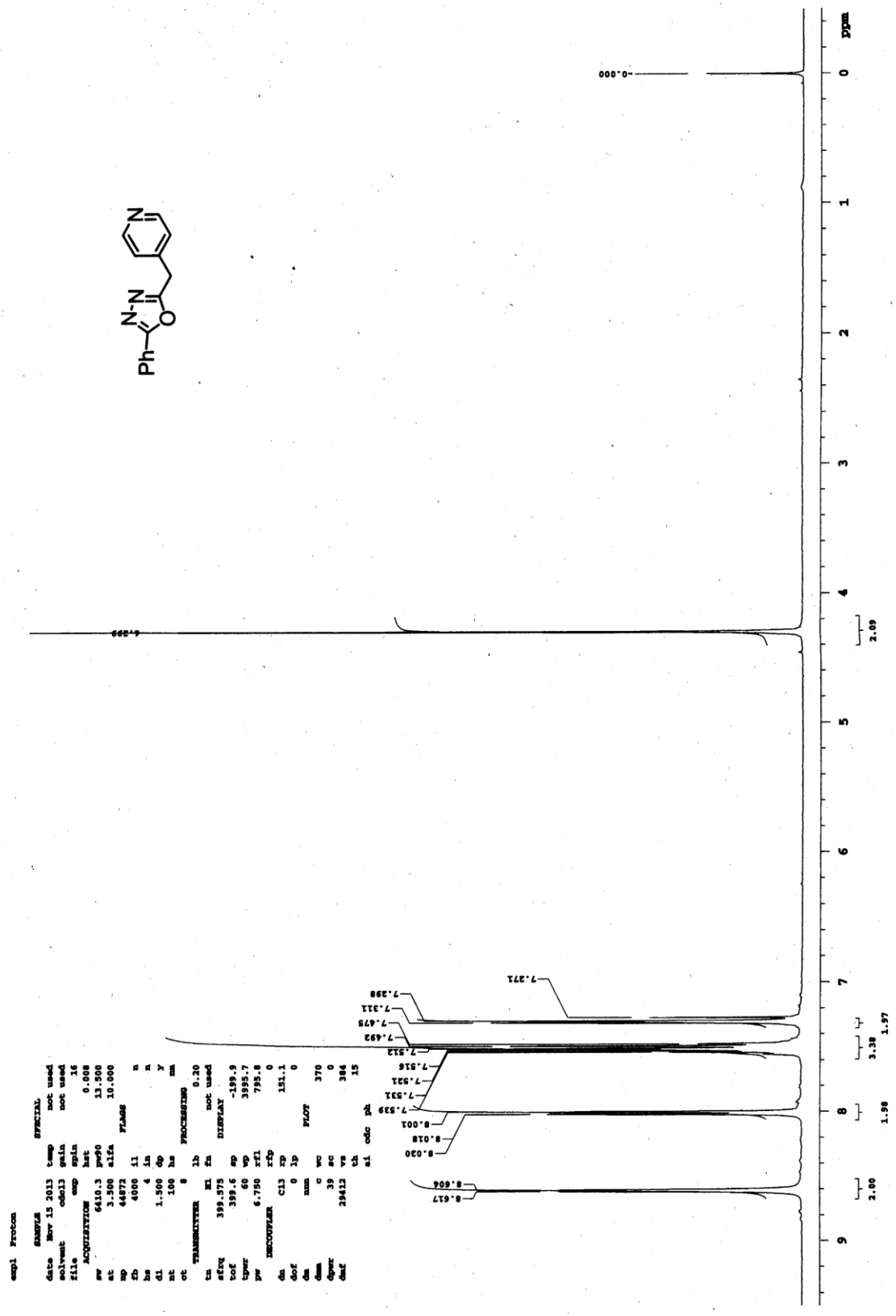

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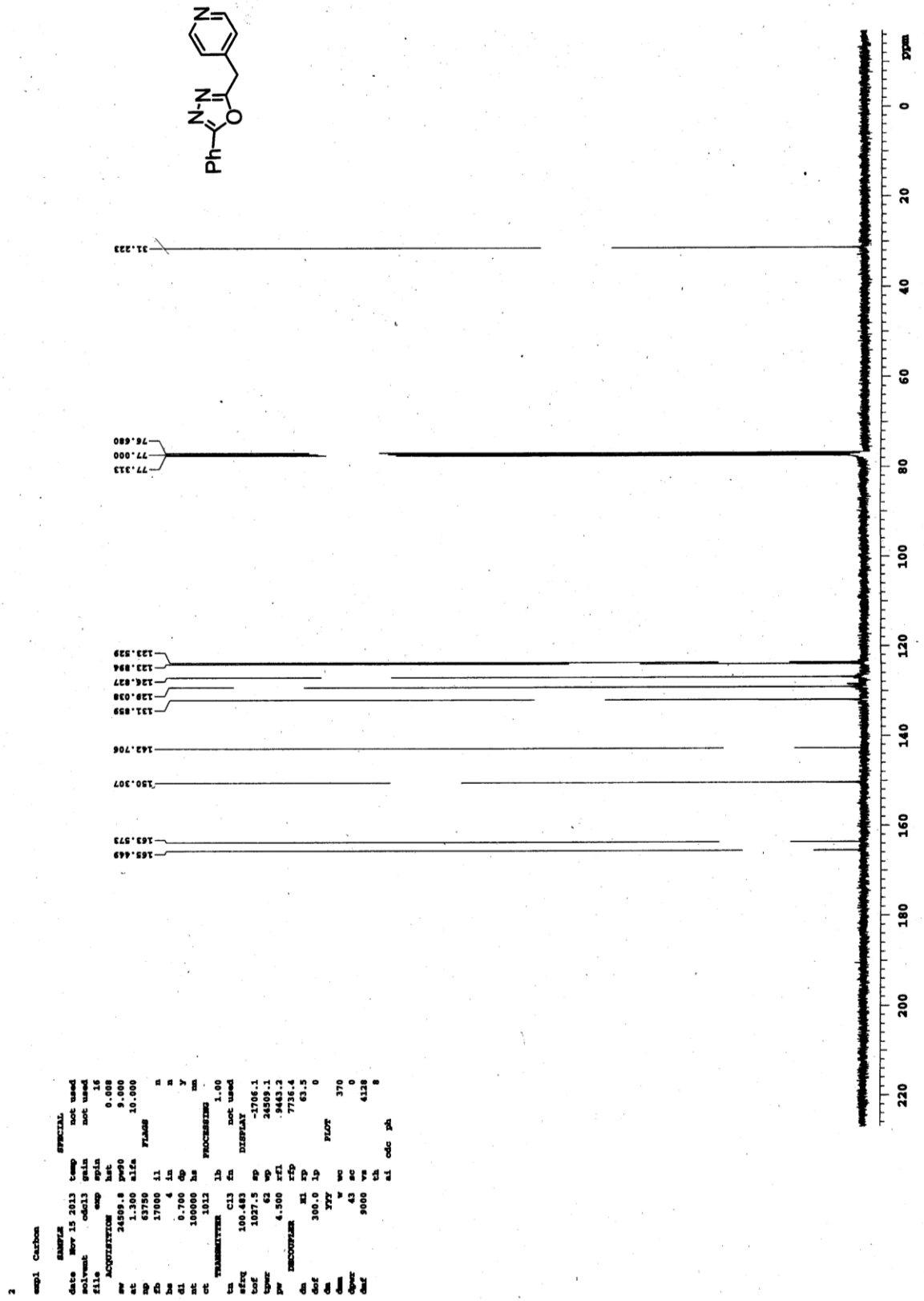

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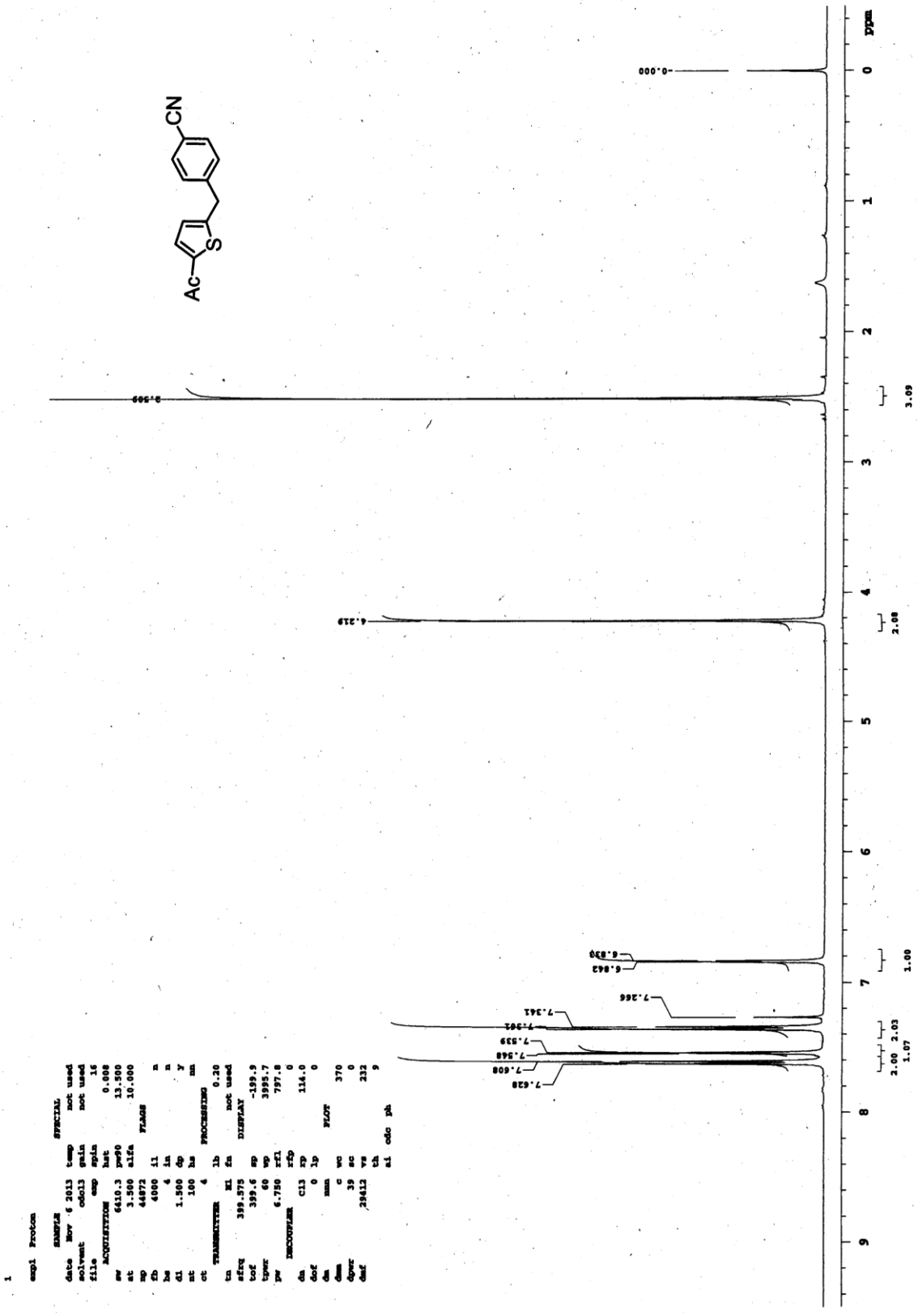
4-(5-Acetyl-2-thienylmethyl)benzonitrile (3l) (^{1}H-NMR)



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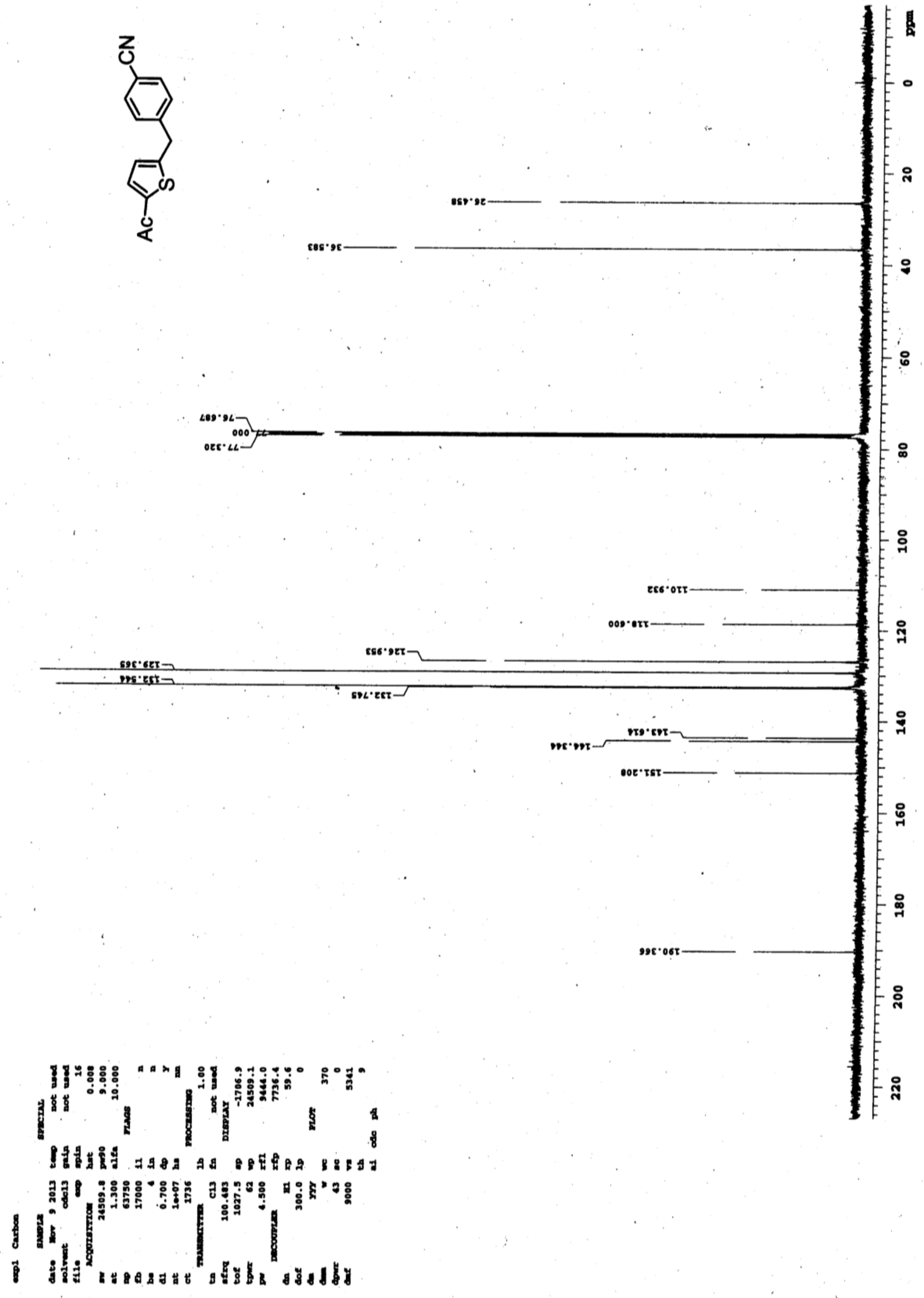
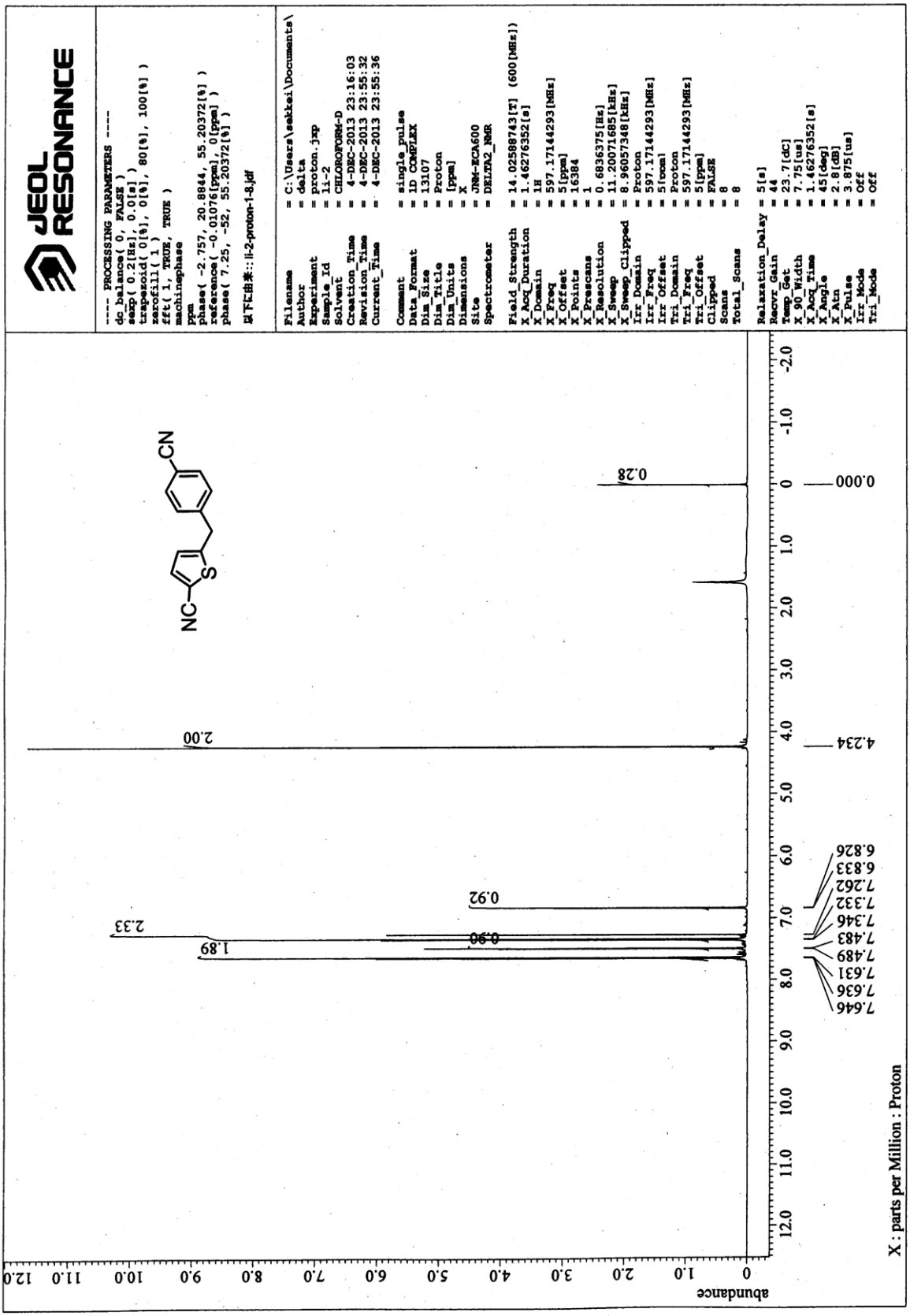
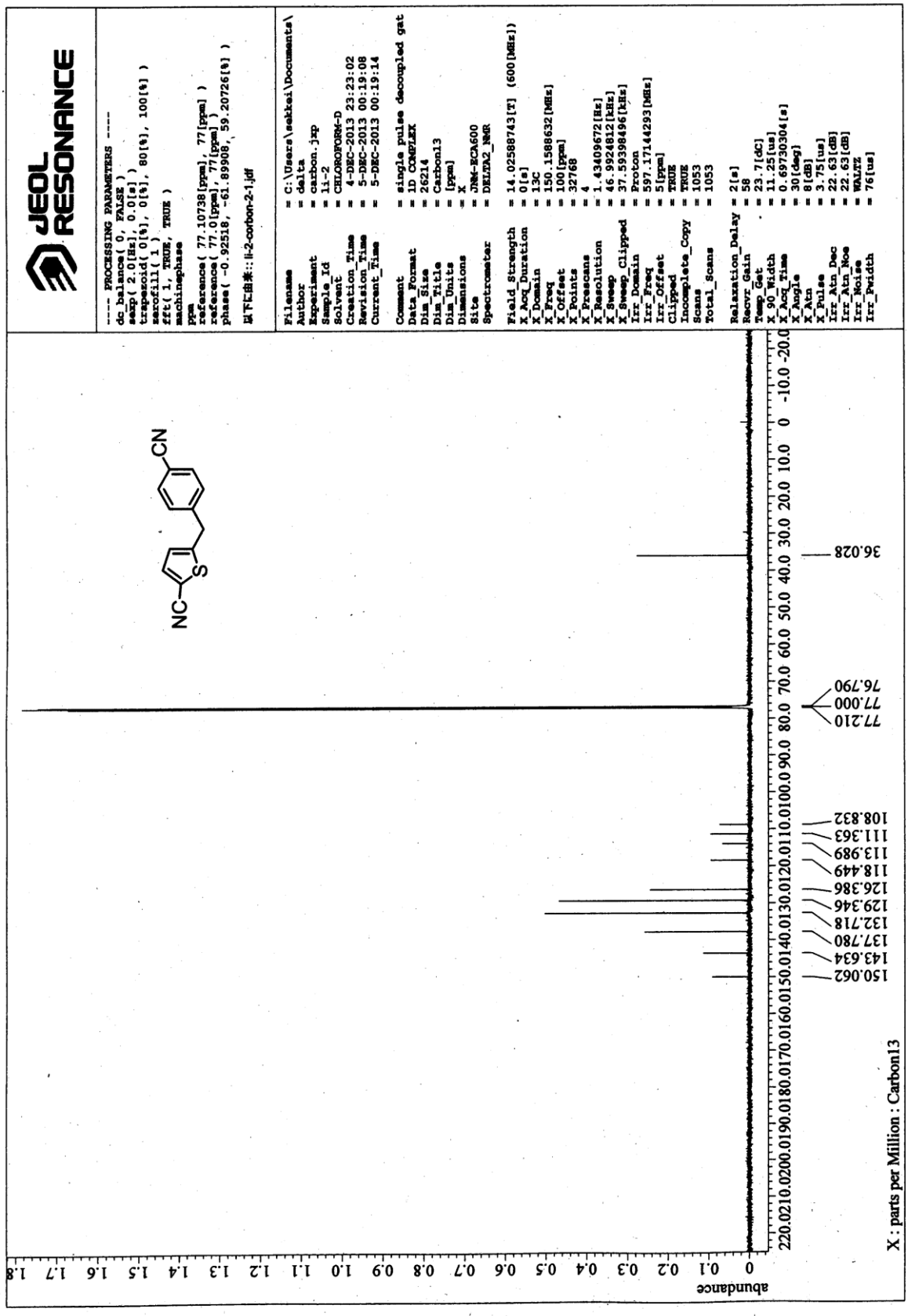


5-(*p*-Cyanobenzyl)-2-thiophenecarbonitrile (3m) (^{1}H-NMR)



5-(*p*-Cyanobenzyl)-2-thiophenecarbonitrile (3m) (^{13}C-NMR)



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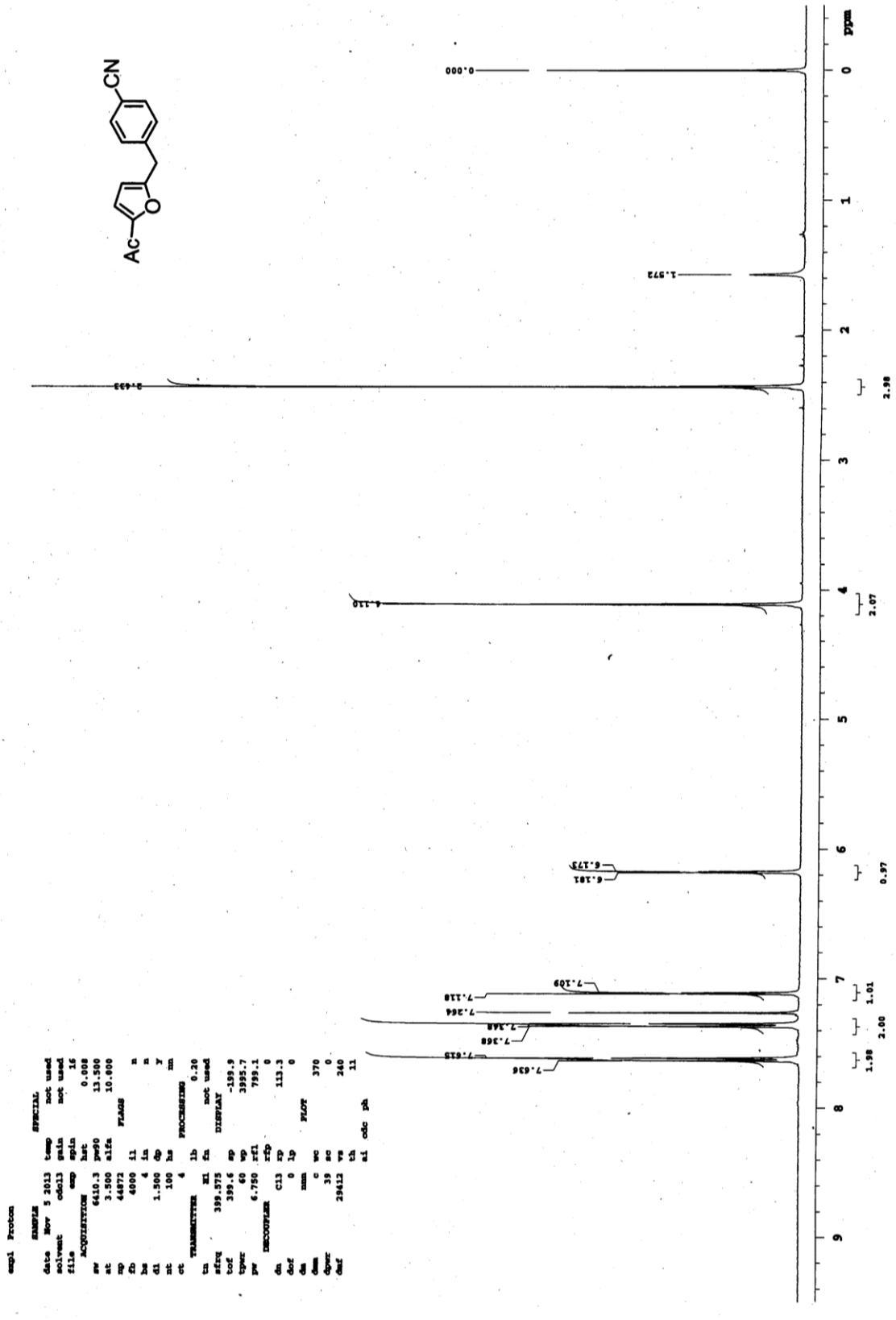
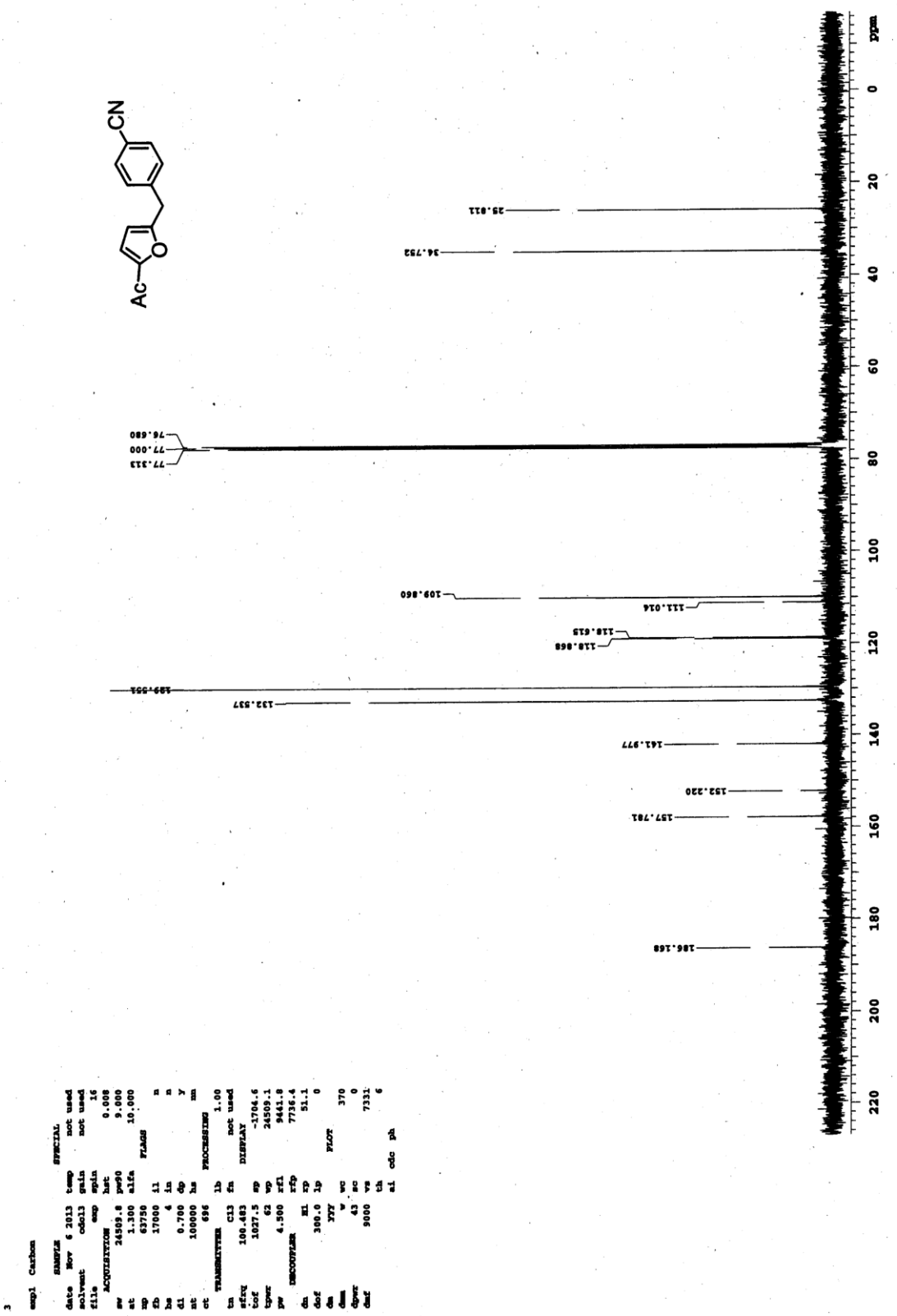


4-(5-Acetyl-2-Furylmethyl)benzonitrile (3n) (^{13}C-NMR)



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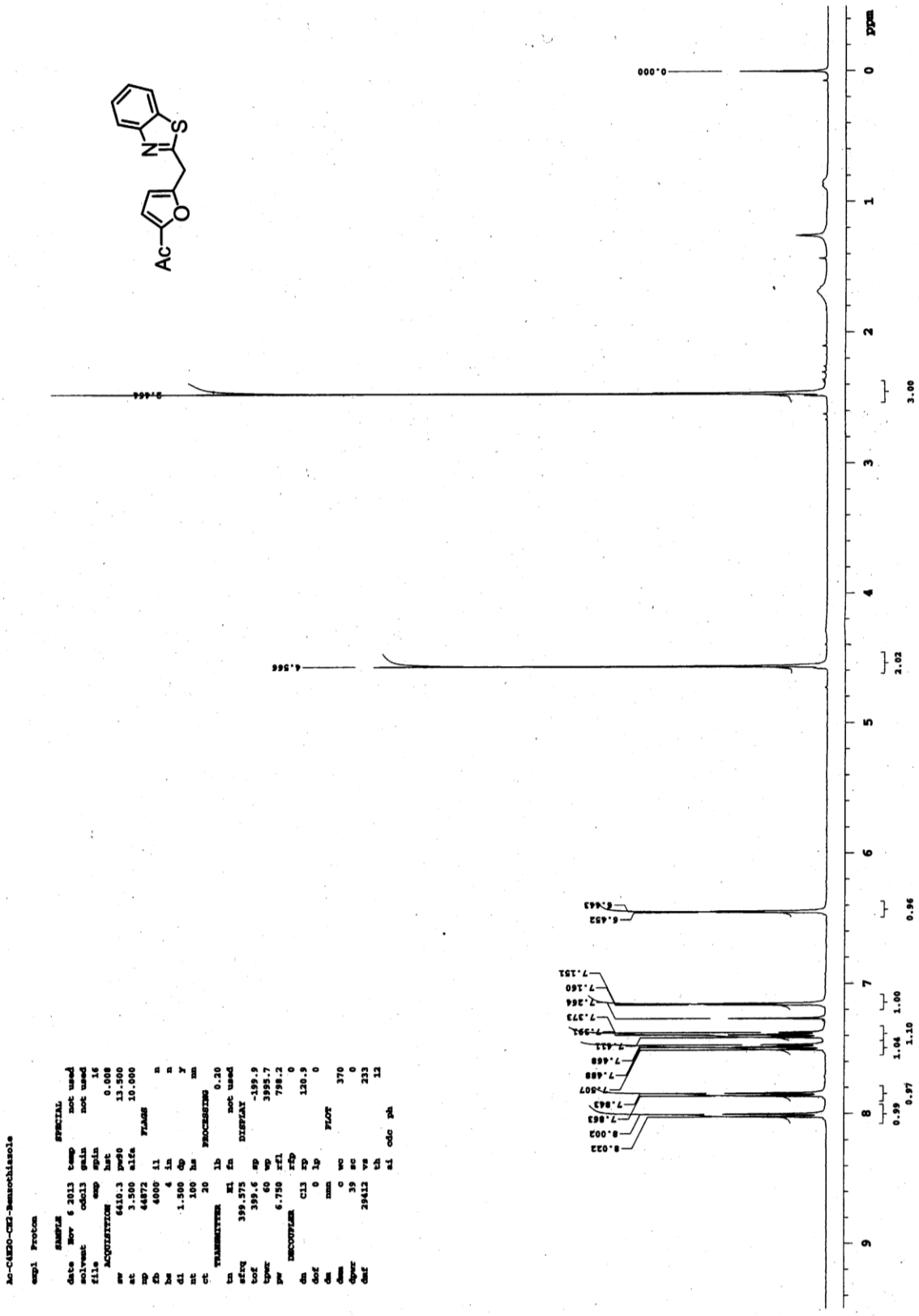
1-[5-(2-Benzothiazolylmethyl)-2-furanyl]ethanone (3o) (^{1}H-NMR)



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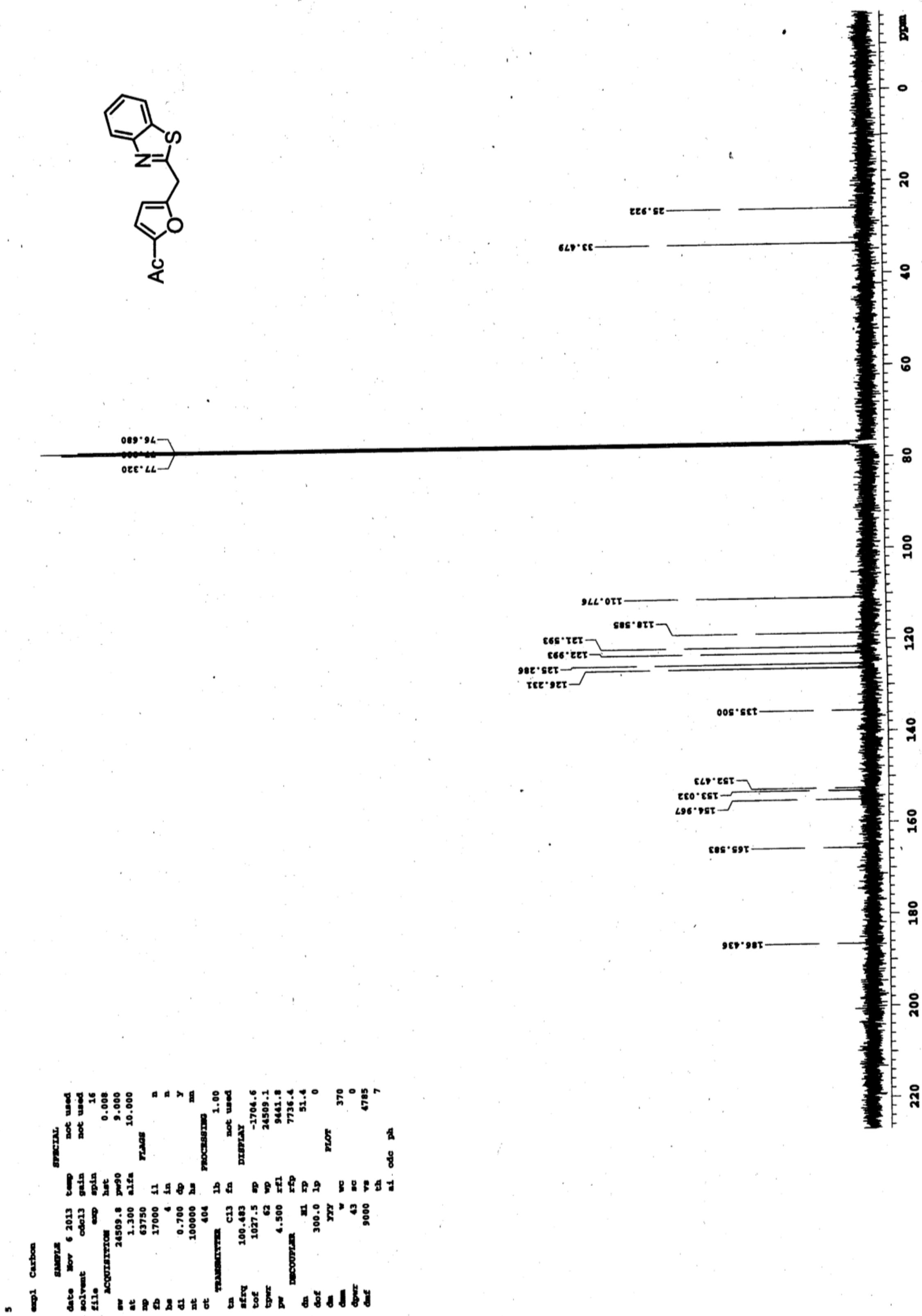

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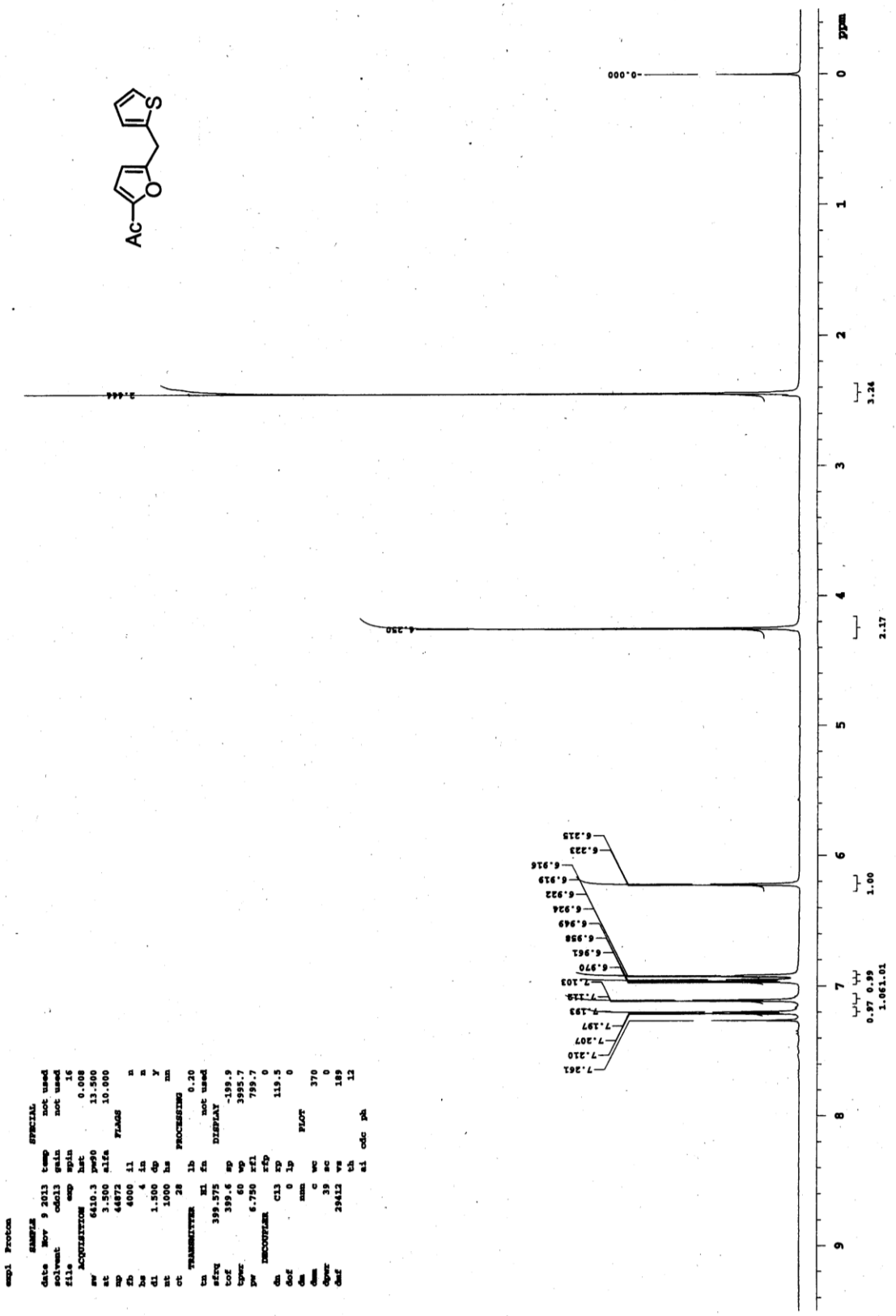

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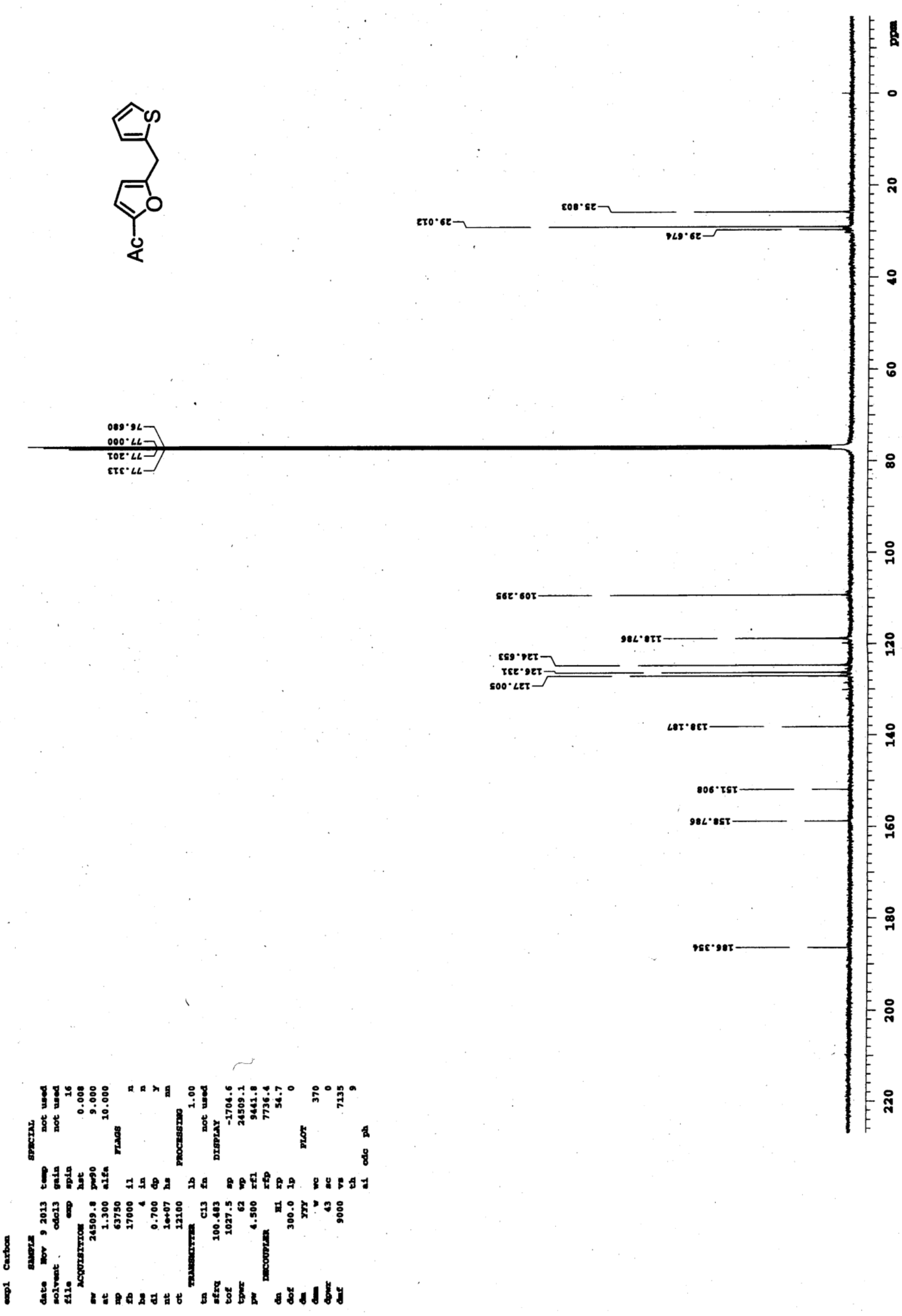
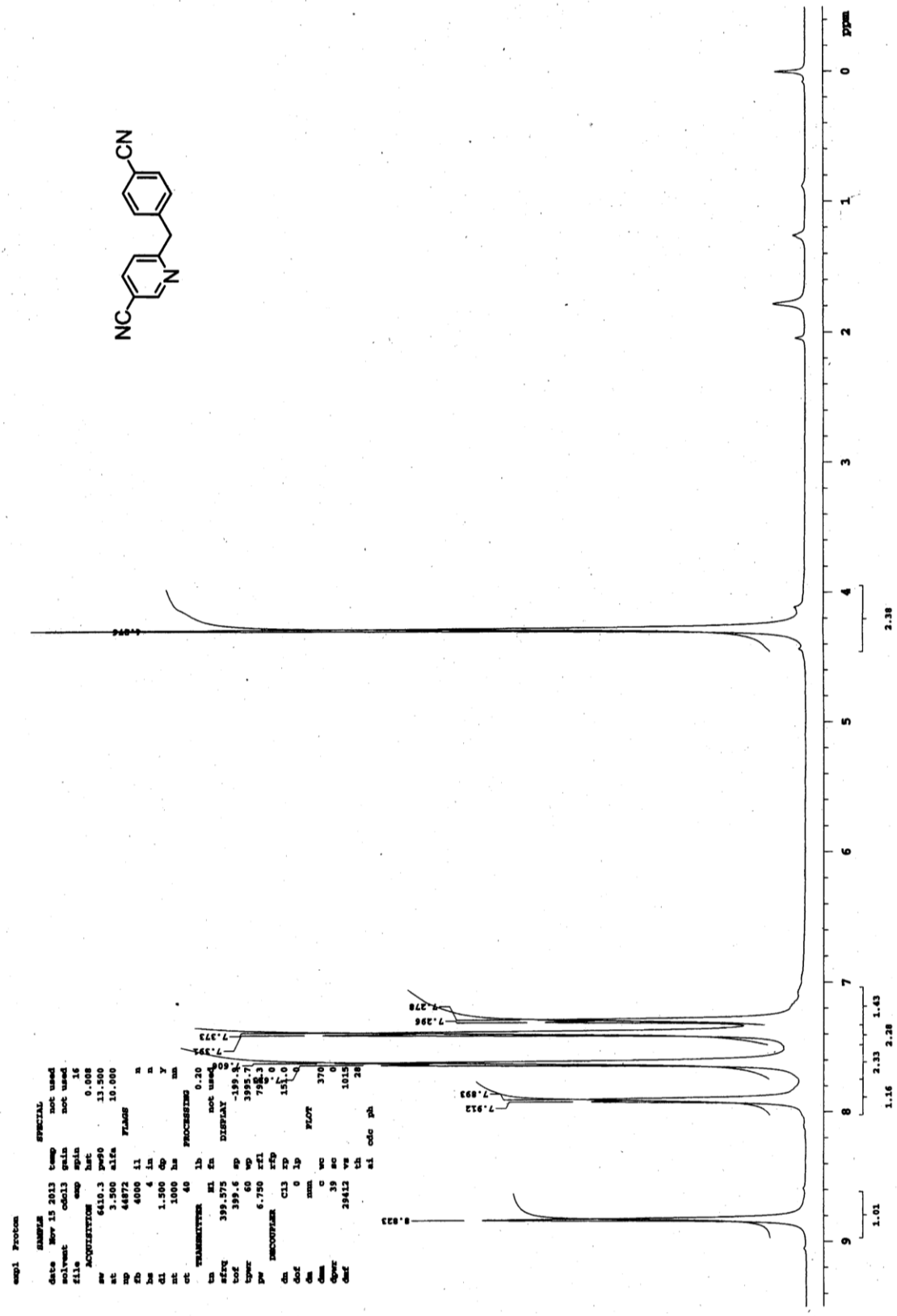


2-(*p*-Cyanobenzyl)-4-pyridinecarbonitrile (3q) (^{1}H-NMR)



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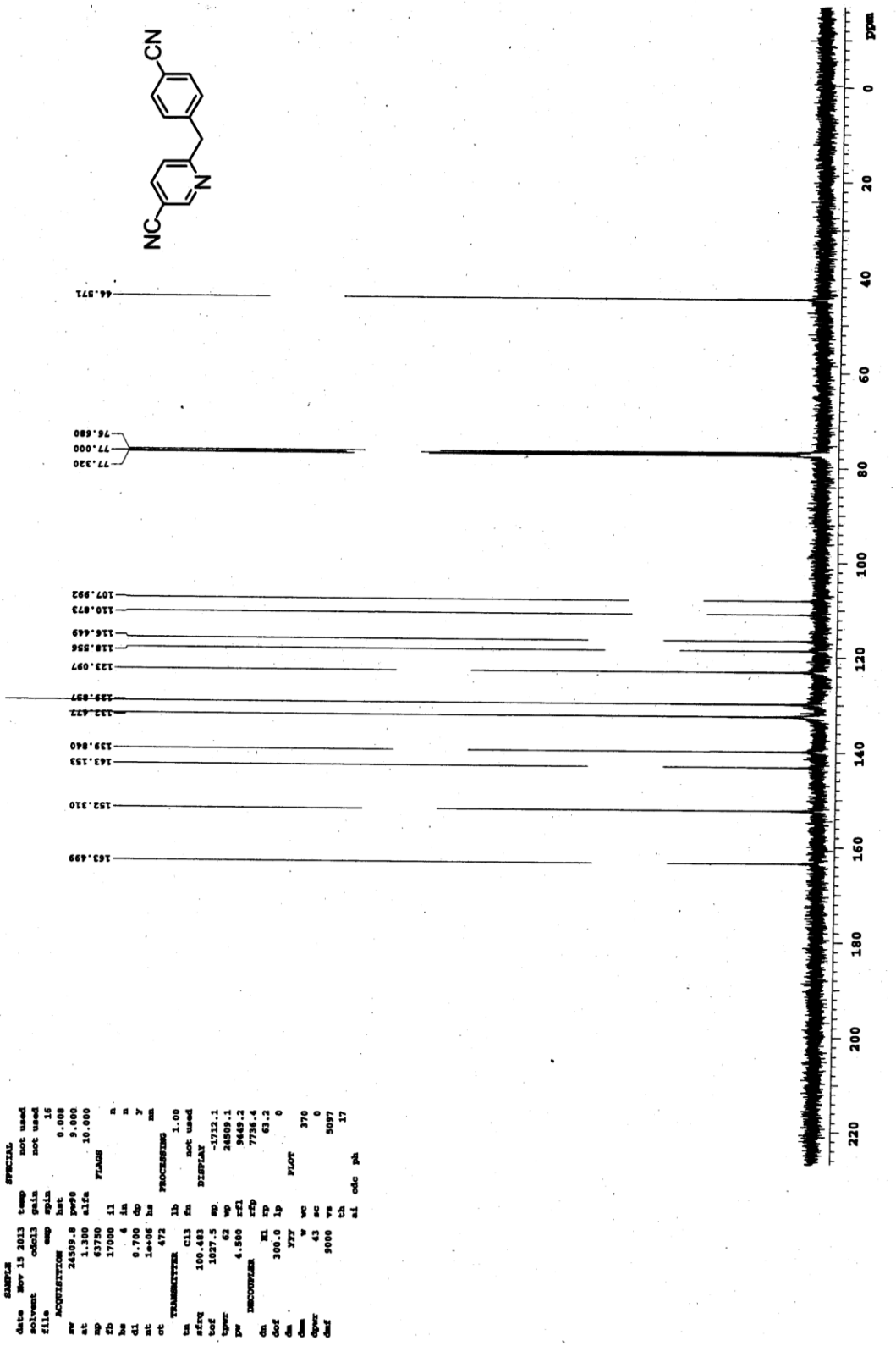

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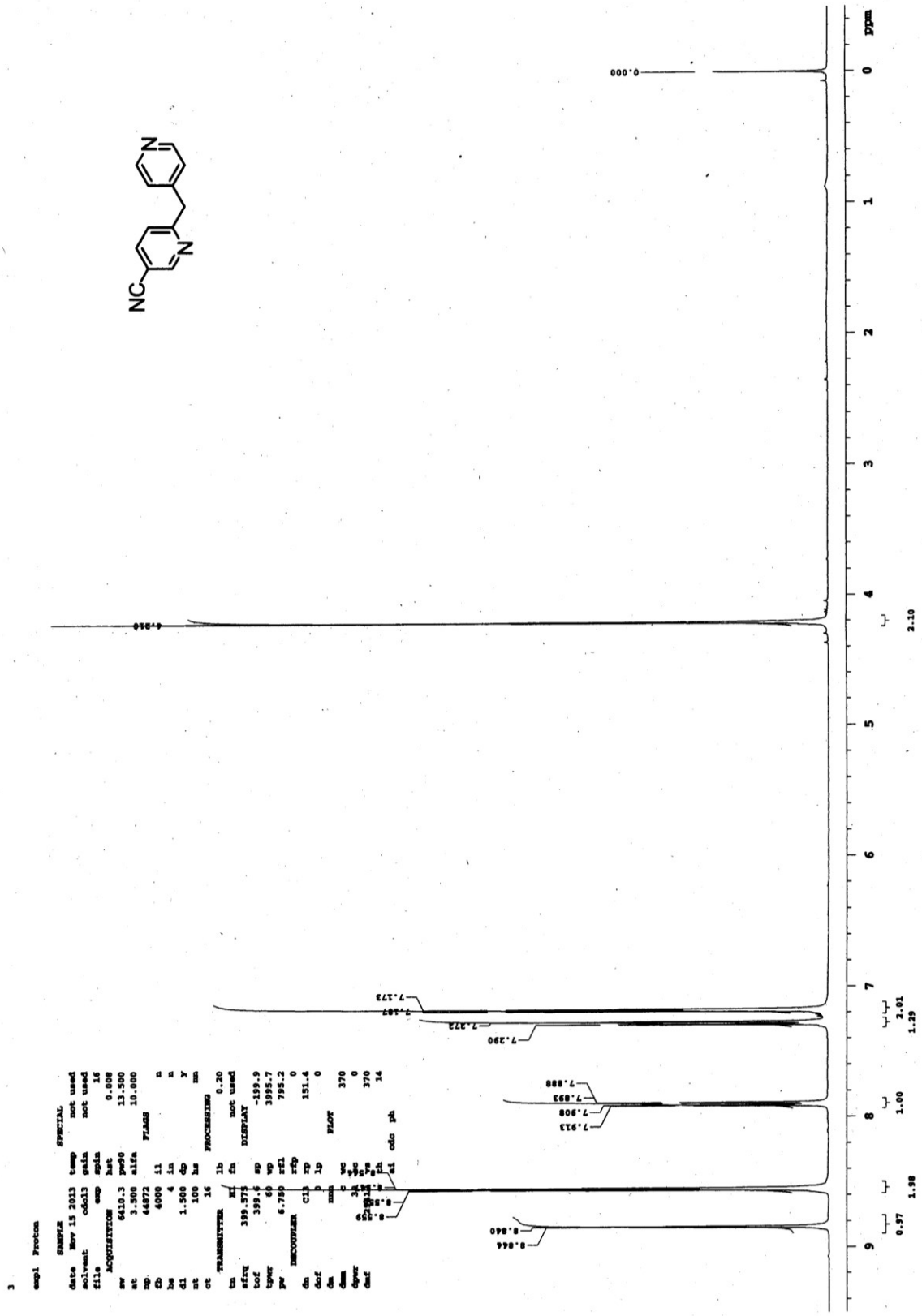
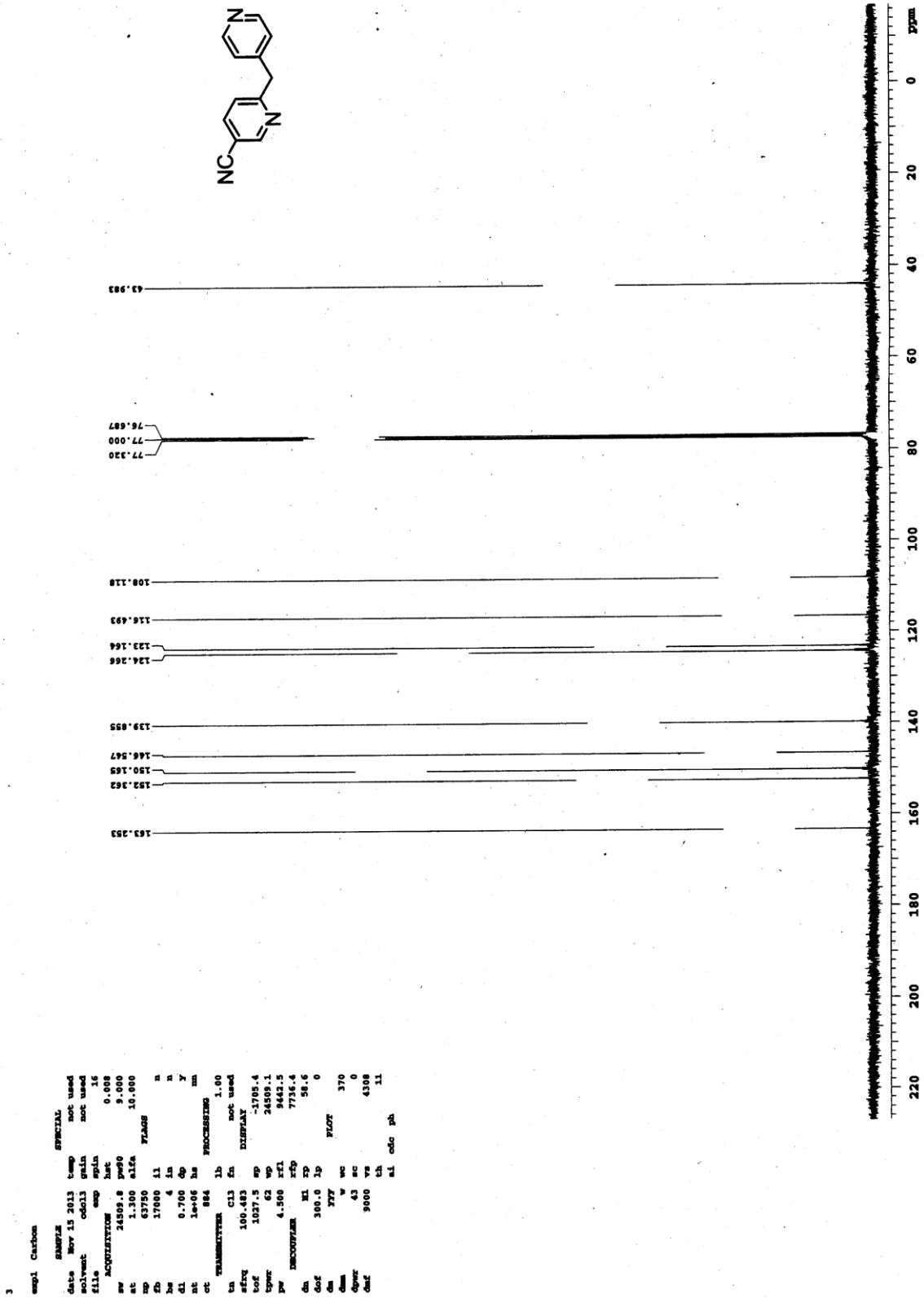


2-(4-Pyridiylmethyl)-4-pyridinecarbonitrile (3r) (^{13}C-NMR)



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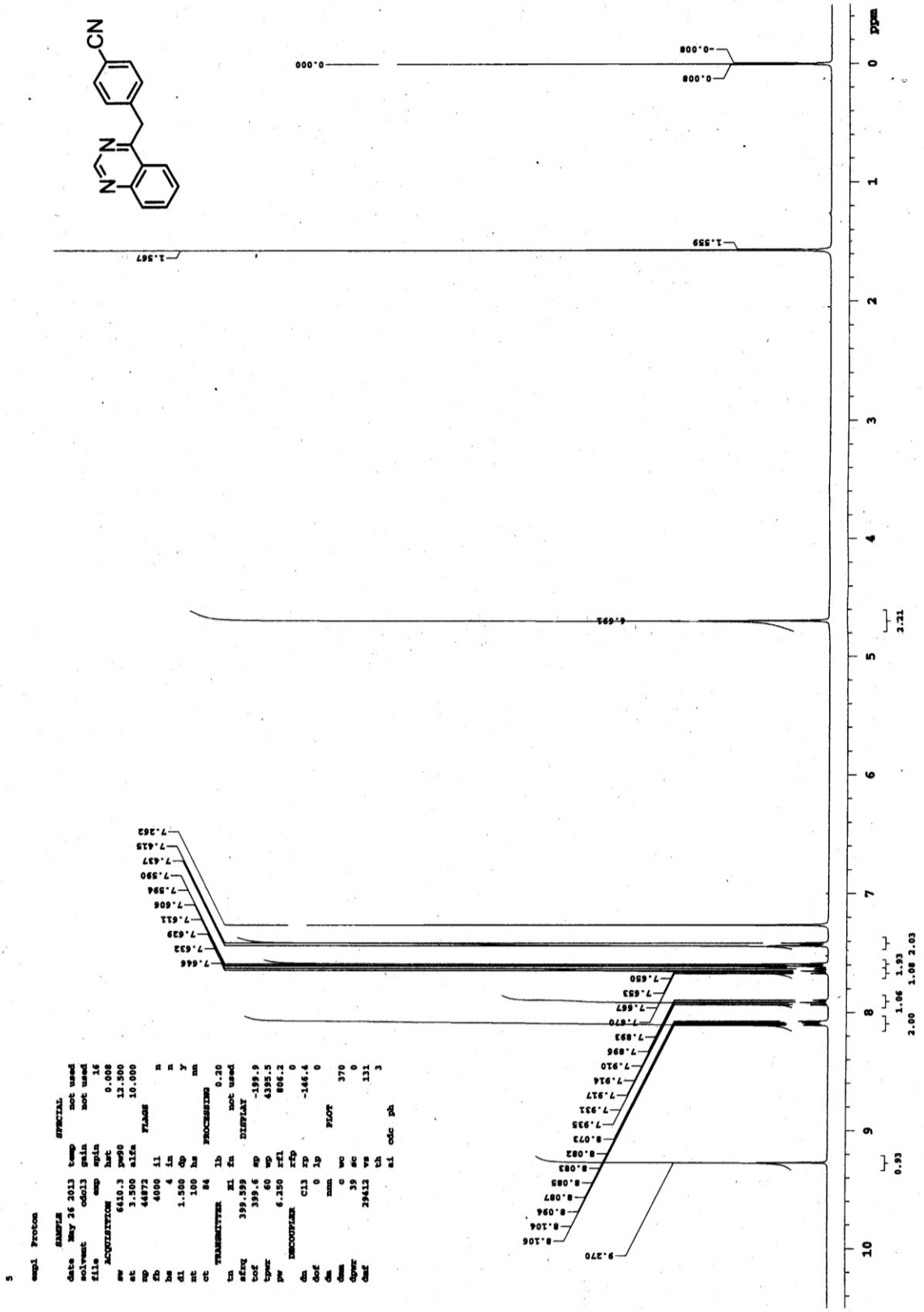
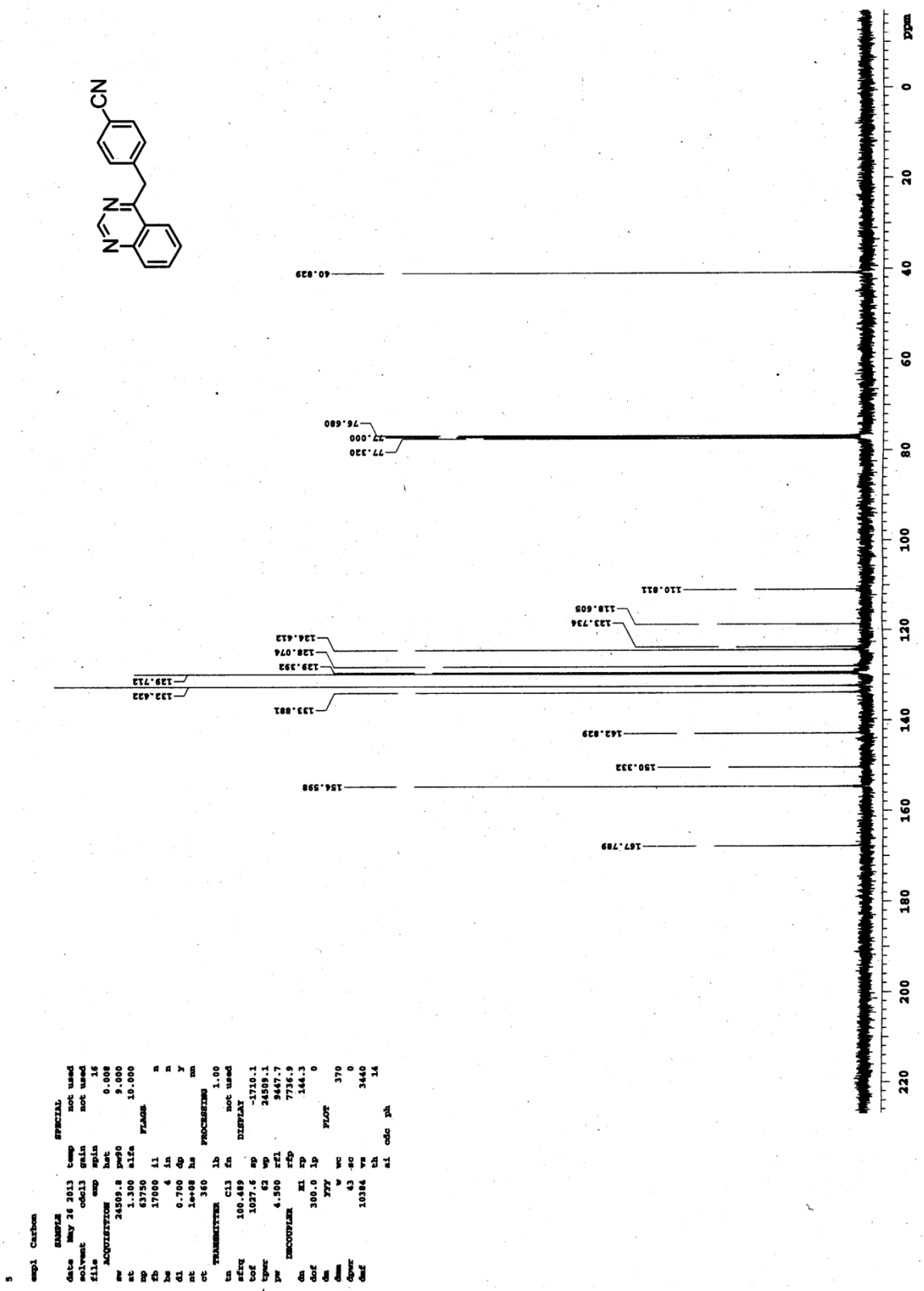
4-(*p*-Cyanobenzyl)quinazoline (3s) (^{1}H-NMR)



4-(*p*-Cyanobenzyl)quinazoline (3s) (^{13}C-NMR)



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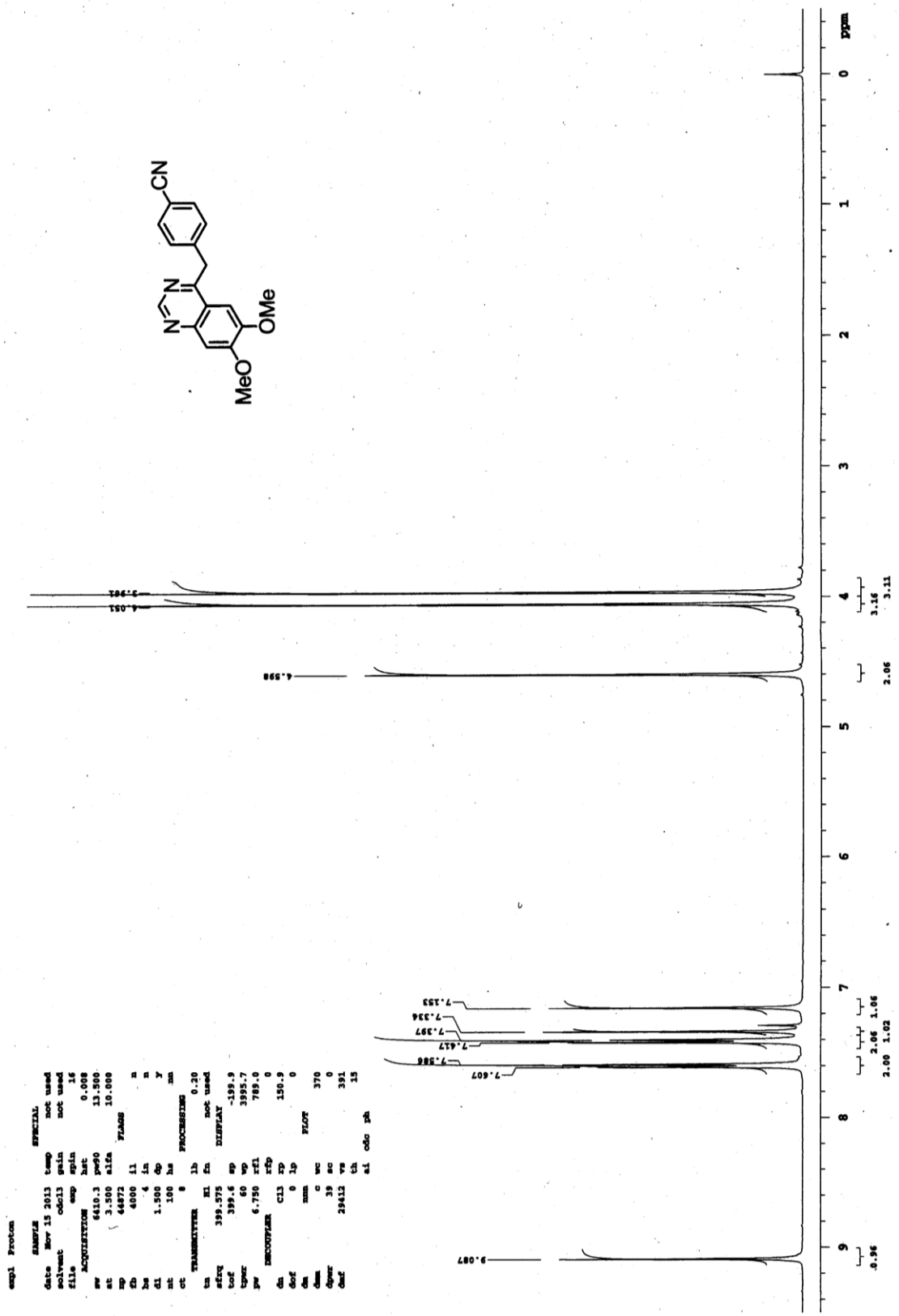

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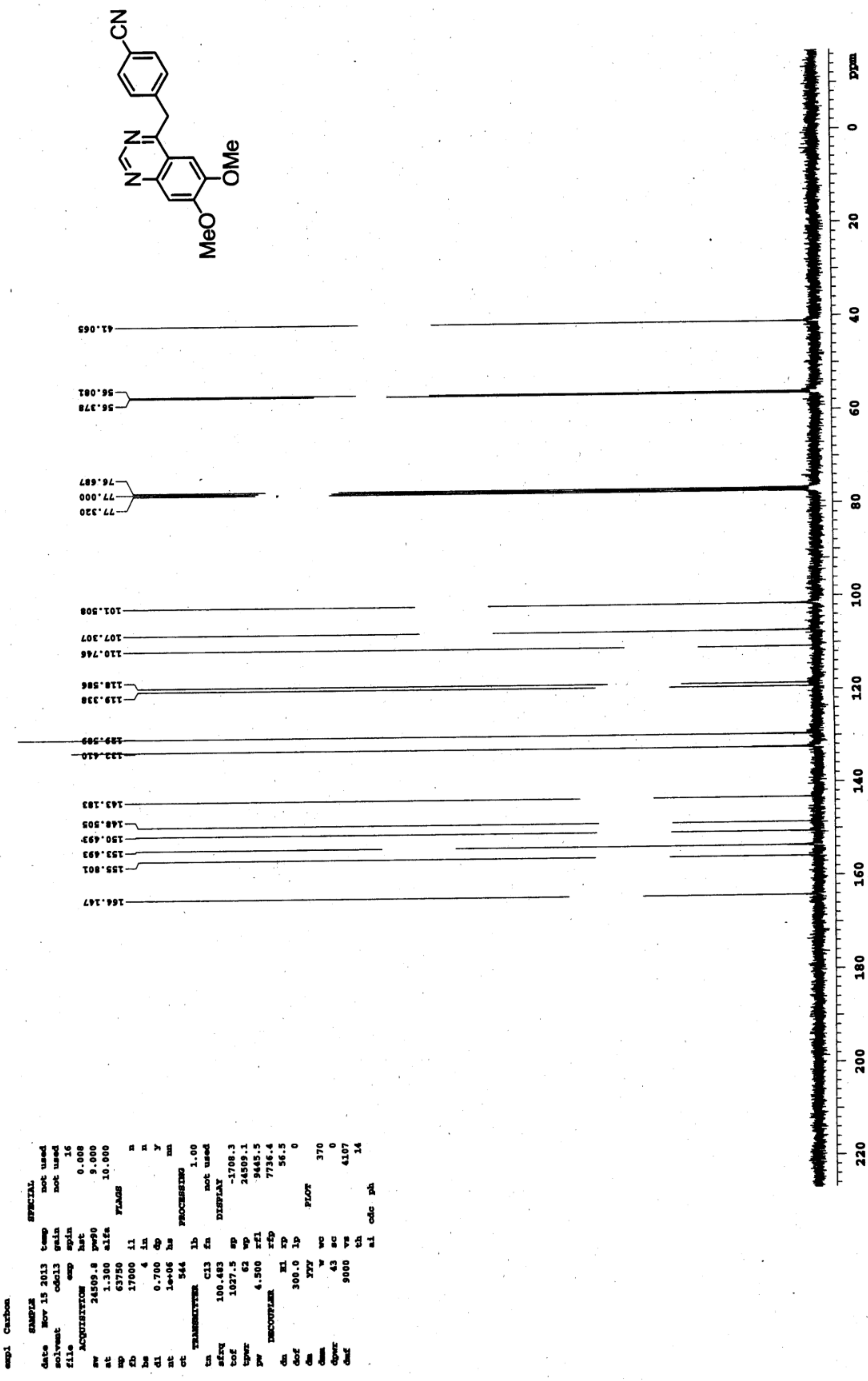
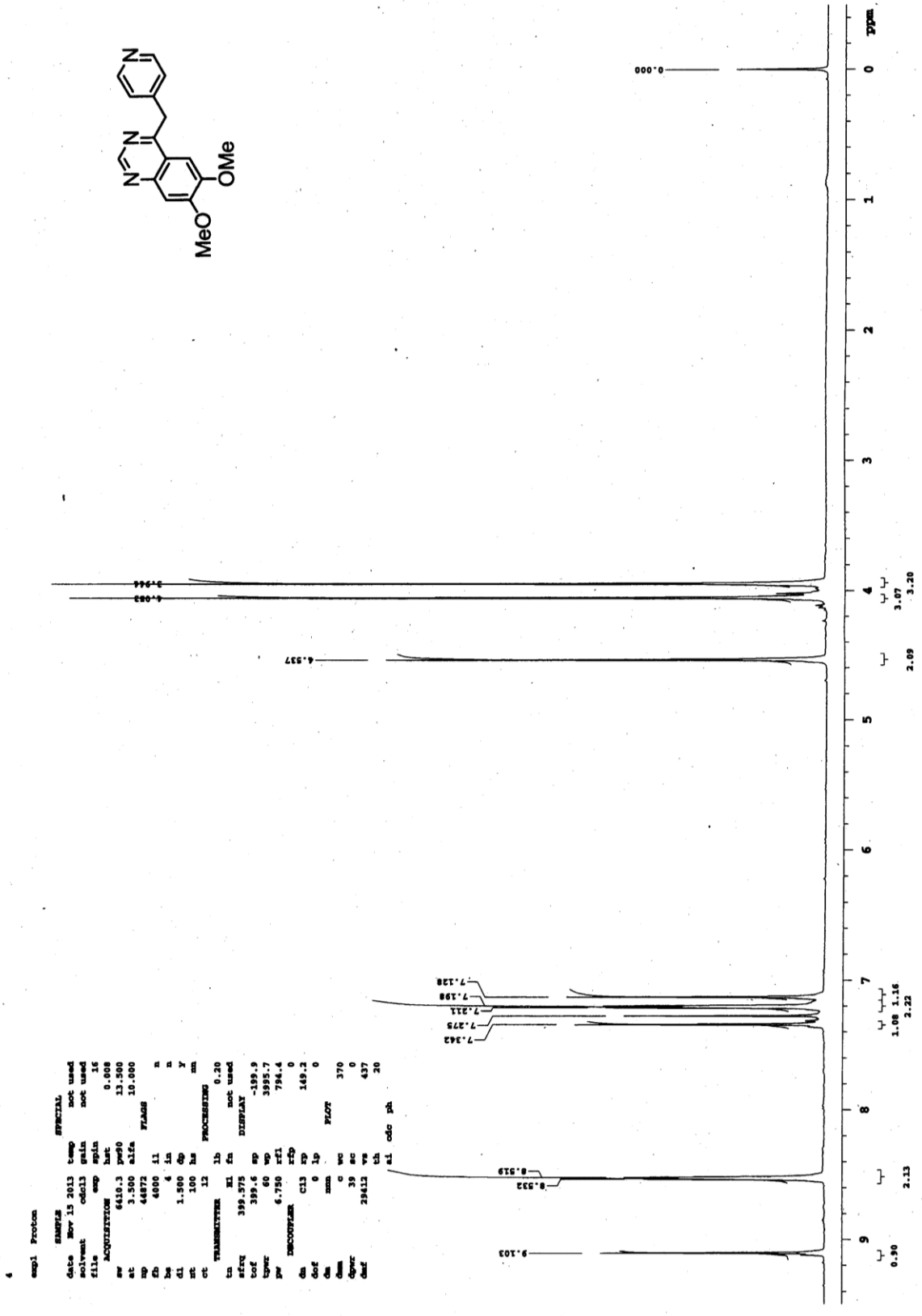
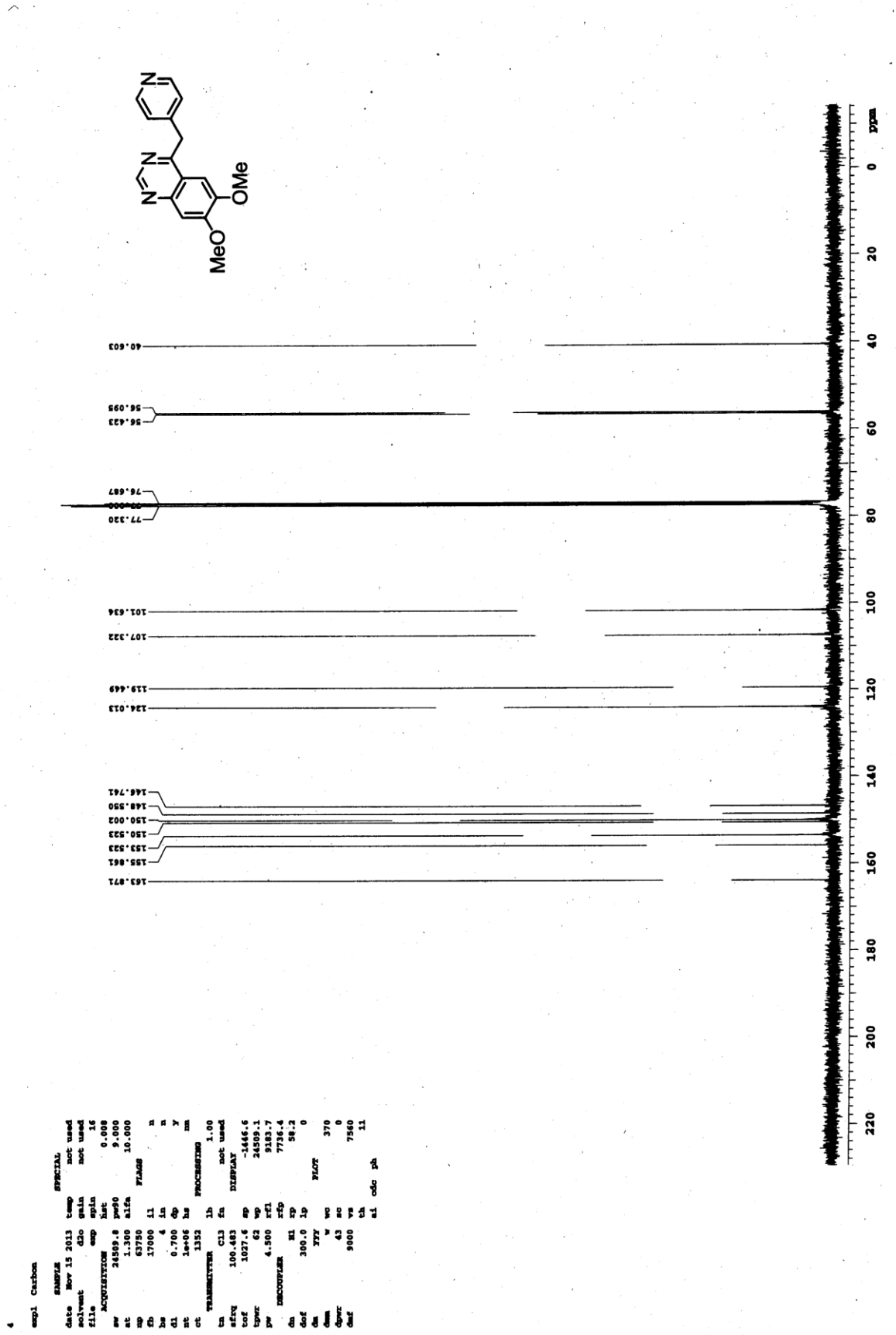


6,7-Dimethoxy-4-(4-pyridiylmethyl)quinolone (3u) (^{1}H-NMR)



6,7-Dimethoxy-4-(4-pyridiylmethyl)quinolone (3u) (^{13}C-NMR)



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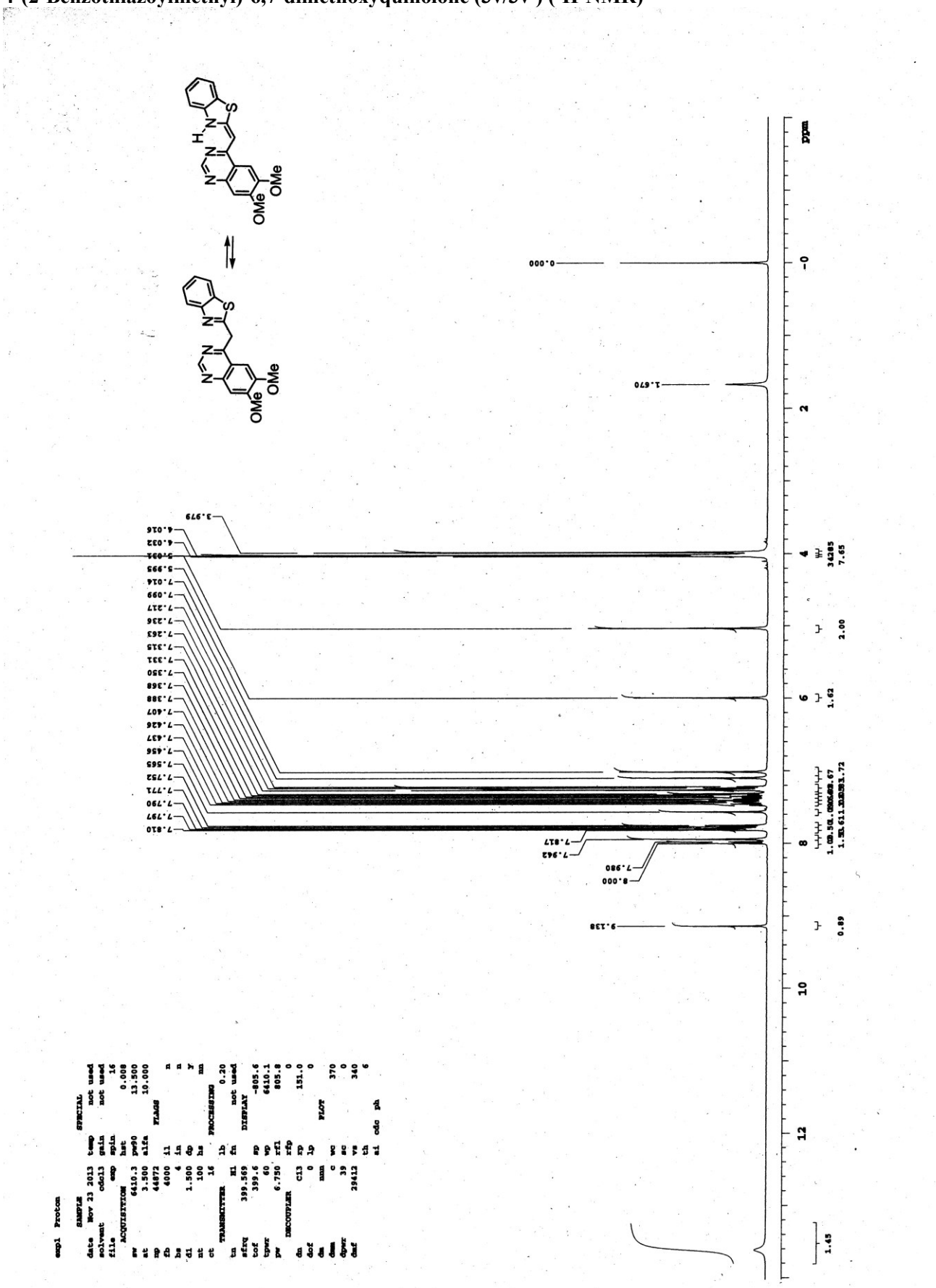
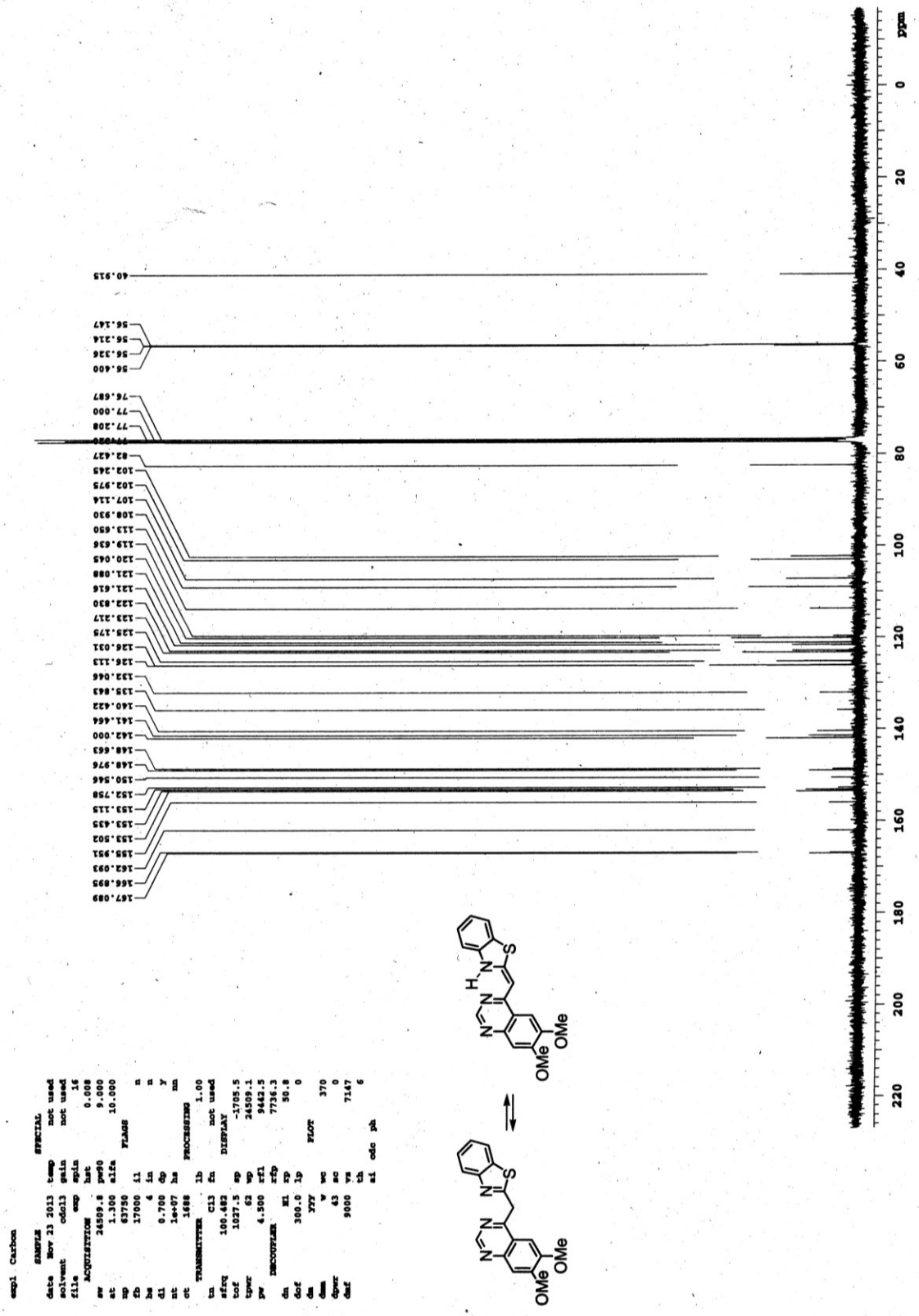
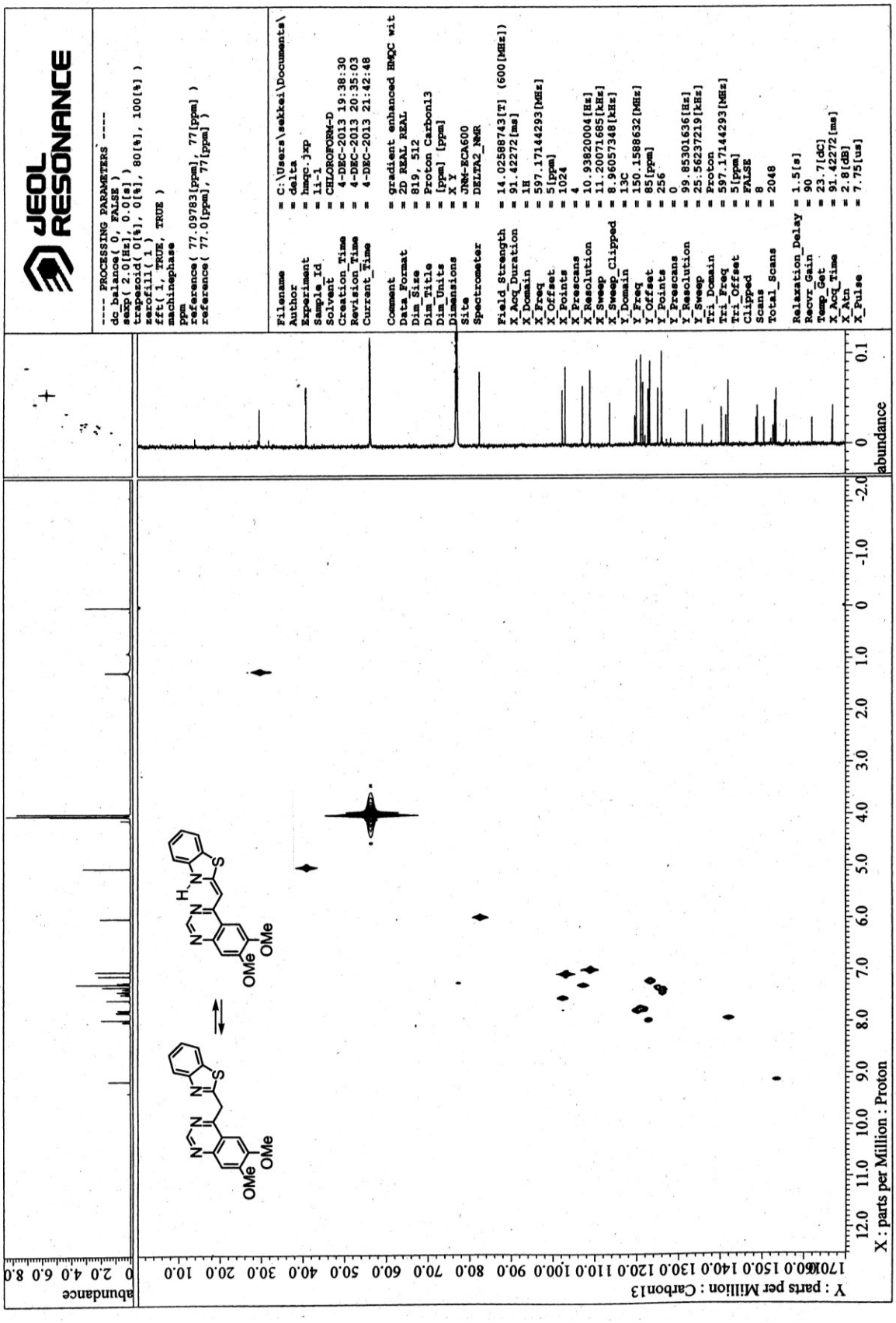


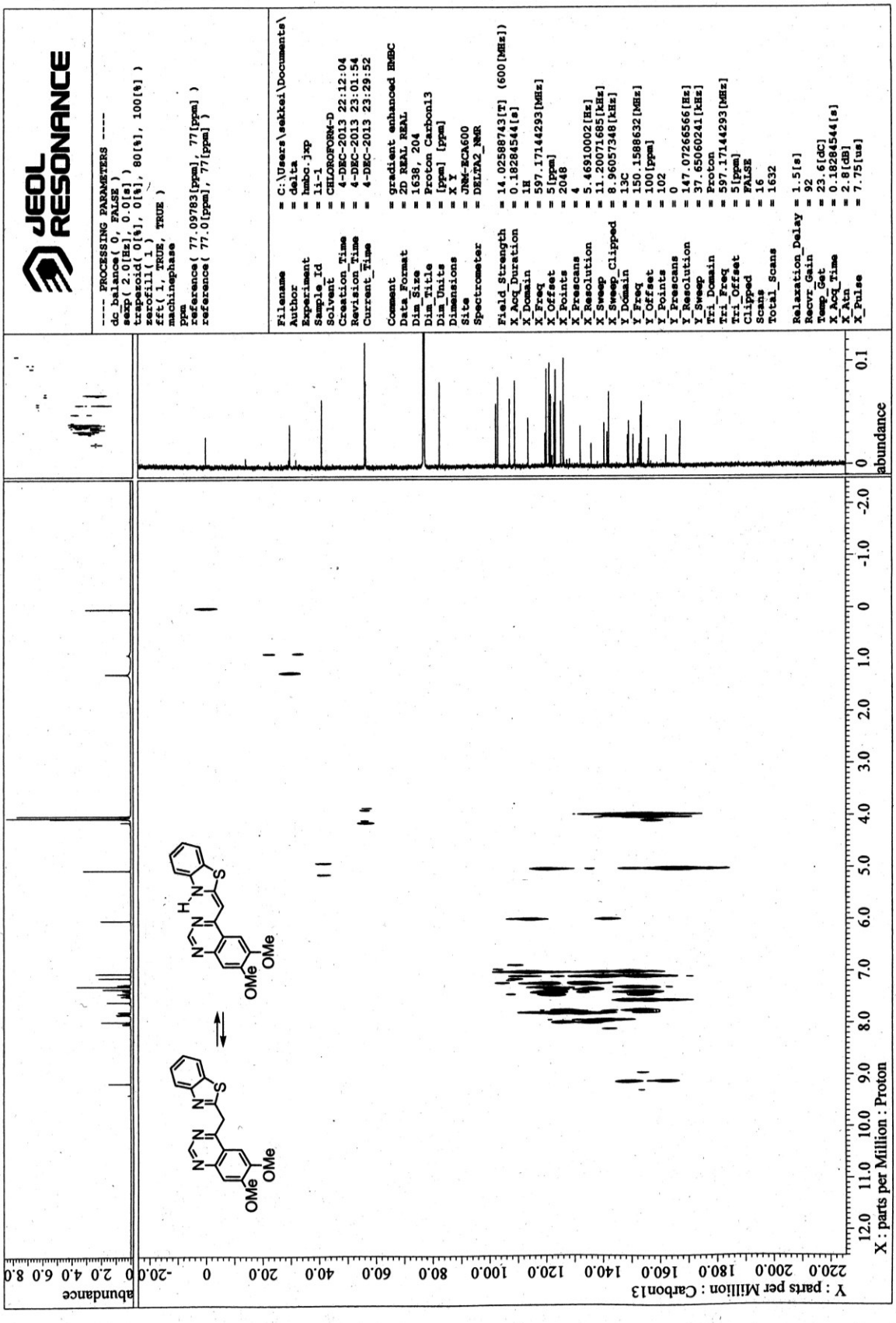
4-(2-Benzothiazoylmethyl)-6,7-dimethoxyquinolone (3v/3v') (^{13}C-NMR)



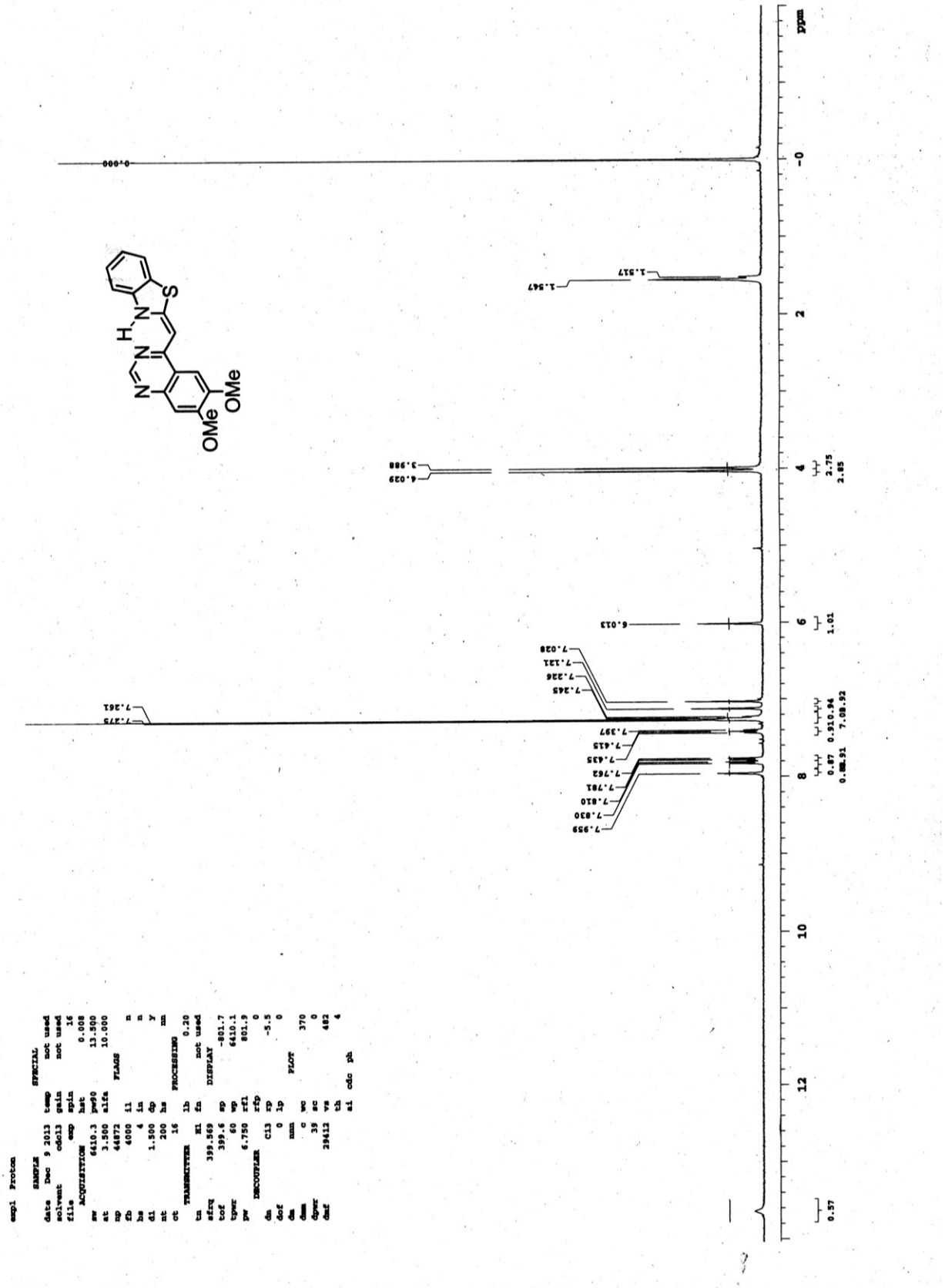
4-(2-Benzothiazoylmethyl)-6,7-dimethoxyquinolone (3v/3v') (HMQC)



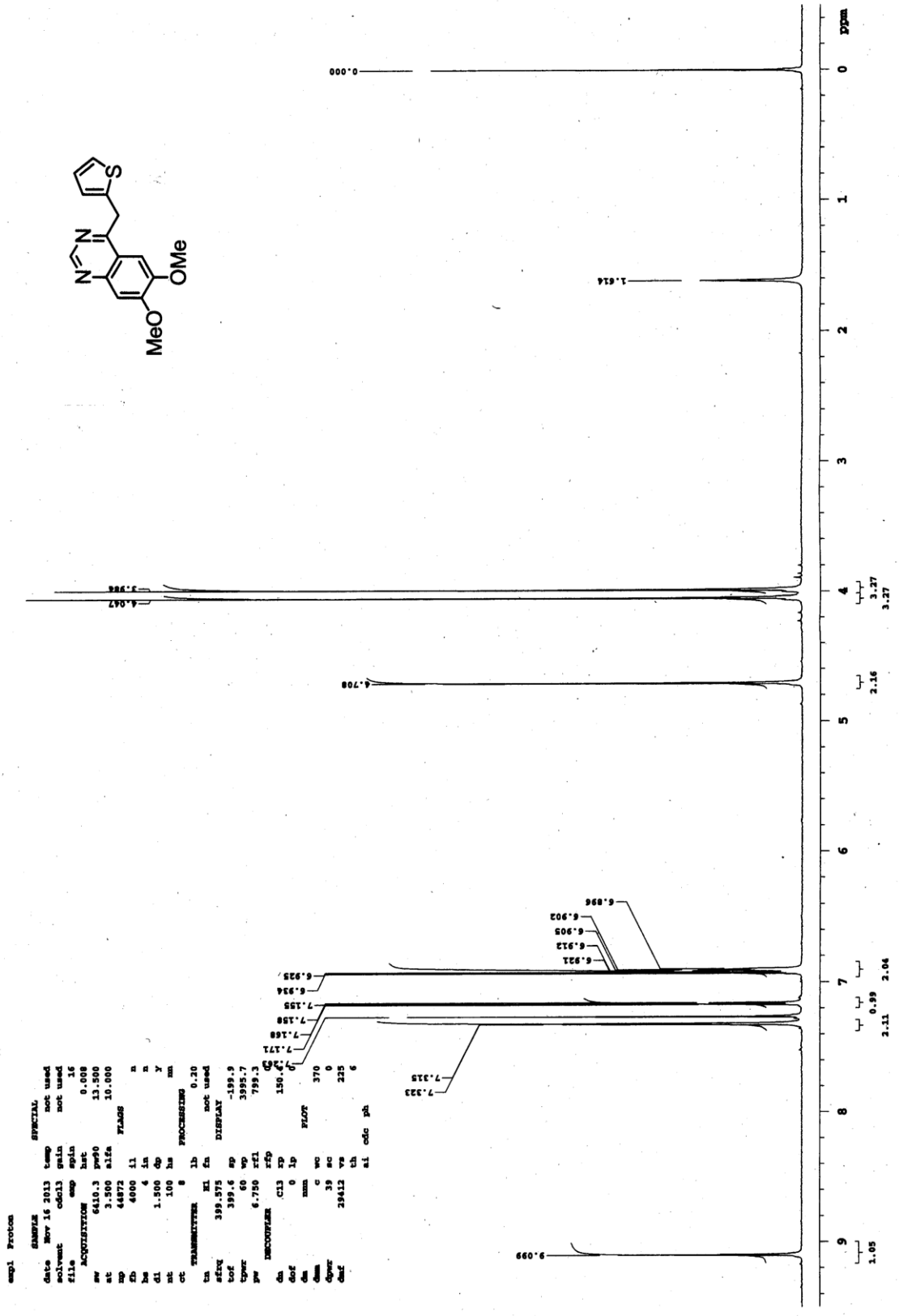
4-(2-Benzothiazoylmethyl)-6,7-dimethoxyquinolone (3v/3v') (HMBC)



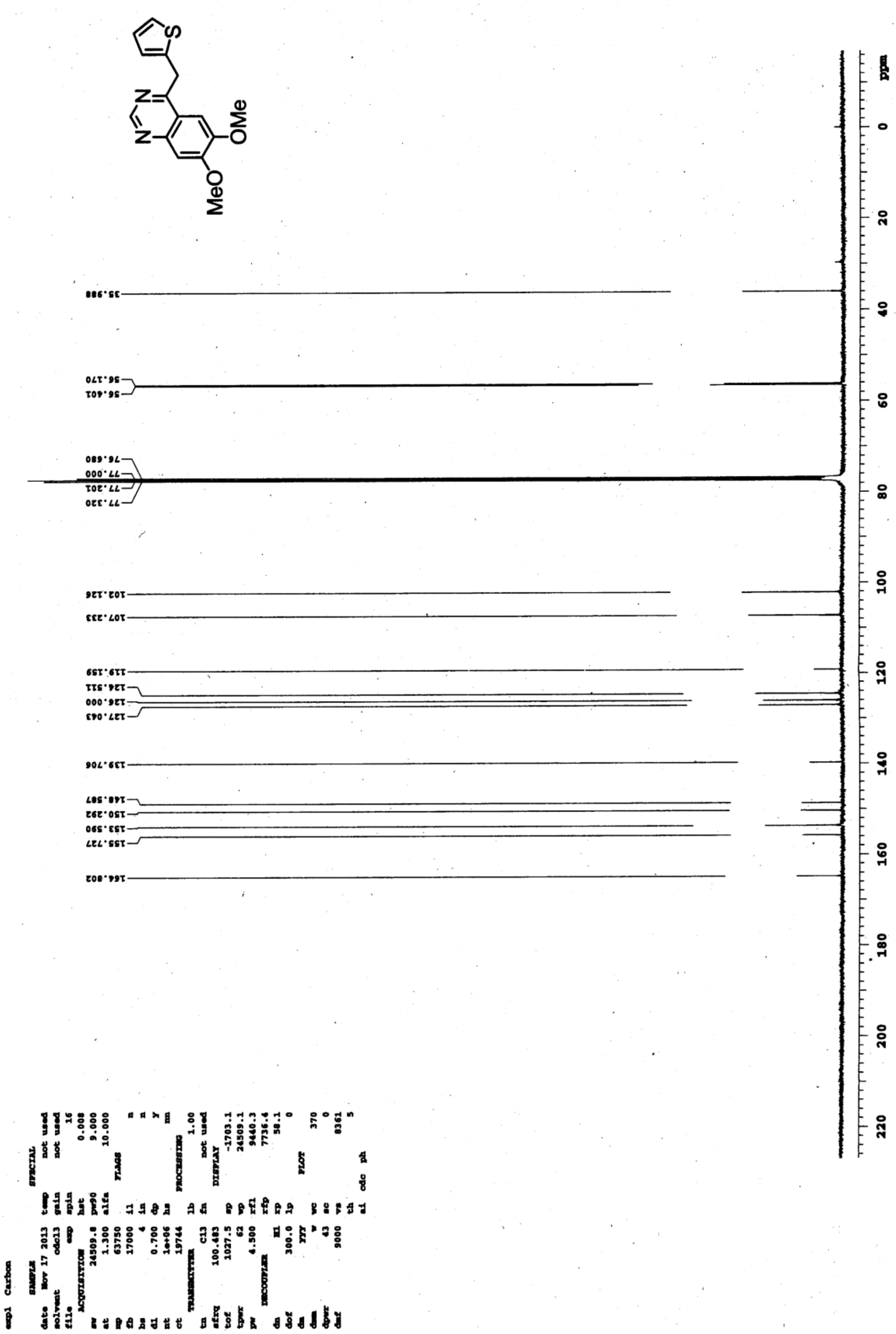
4-(2-Benzothiazoylmethyl)-6,7-dimethoxyquinolone (3v') (^{1}H-NMR)



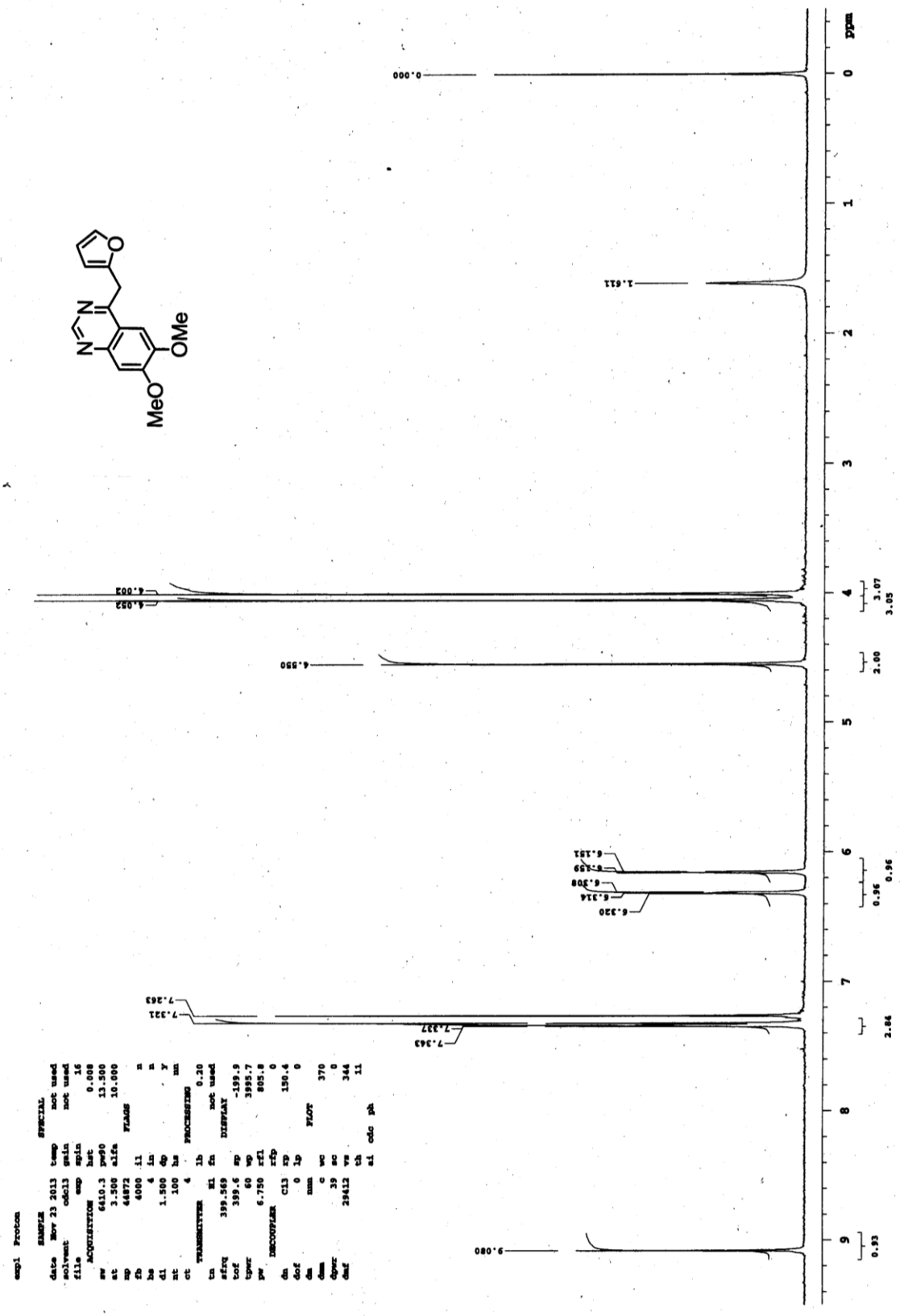
6,7-Dimethoxy-4-(2-thienylmethyl)quinazoline (3w) (^{1}H-NMR)



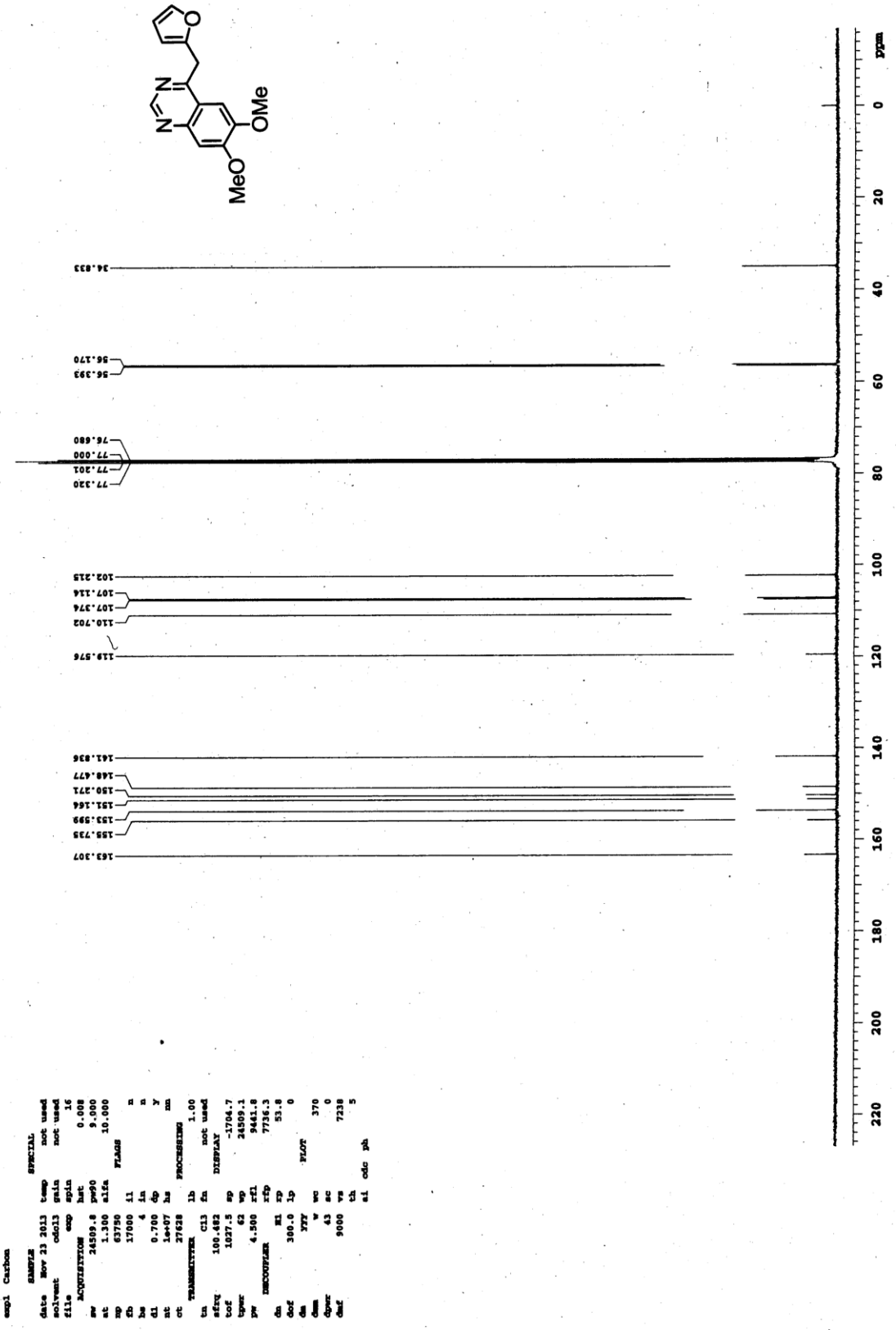
6,7-Dimethoxy-4-(2-thienylmethyl)quinazoline (3w) (^{13}C-NMR)



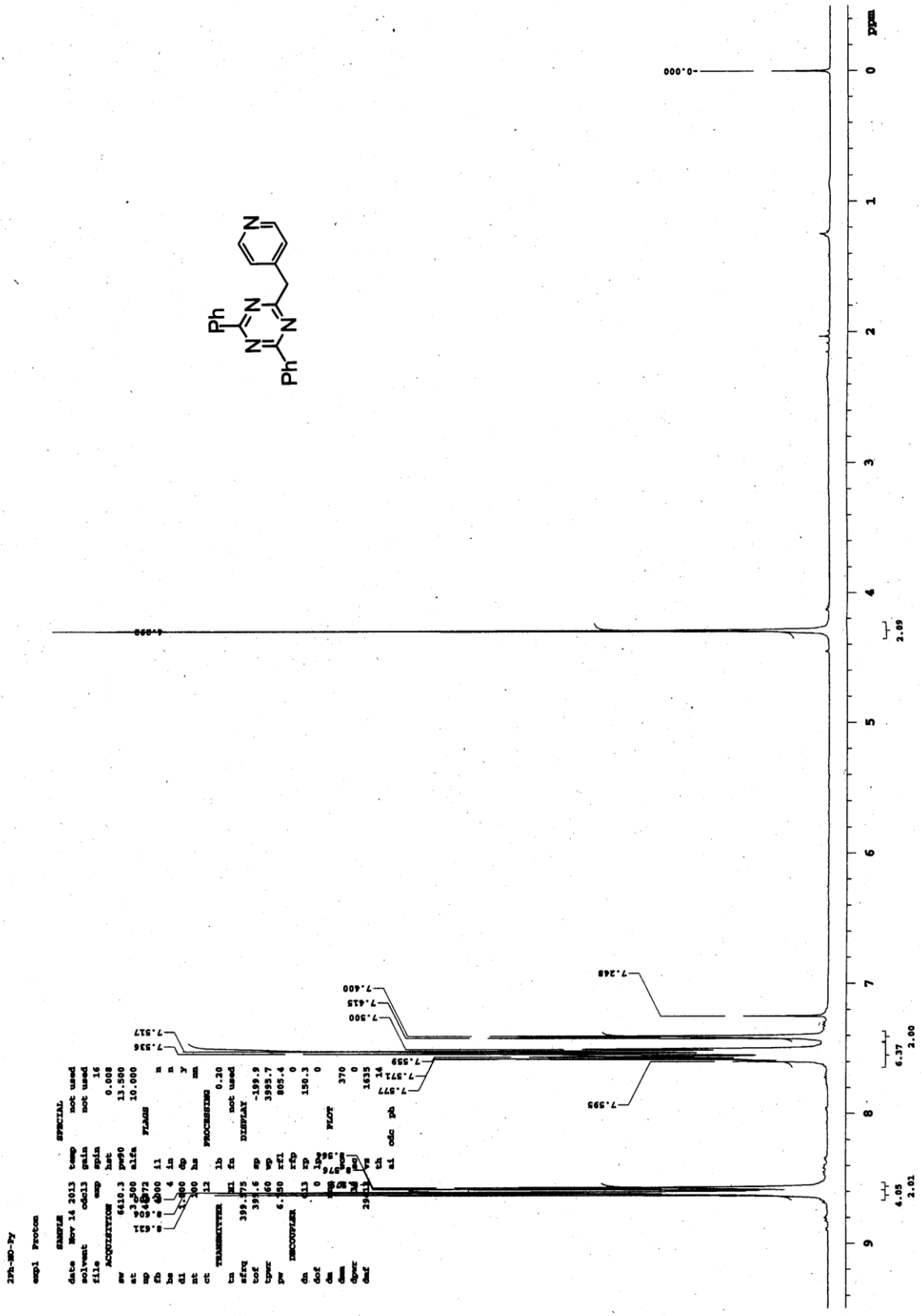
6,7-Dimethoxy-4-(2-furylmethyl)quinazoline (3x) (^{1}H-NMR)



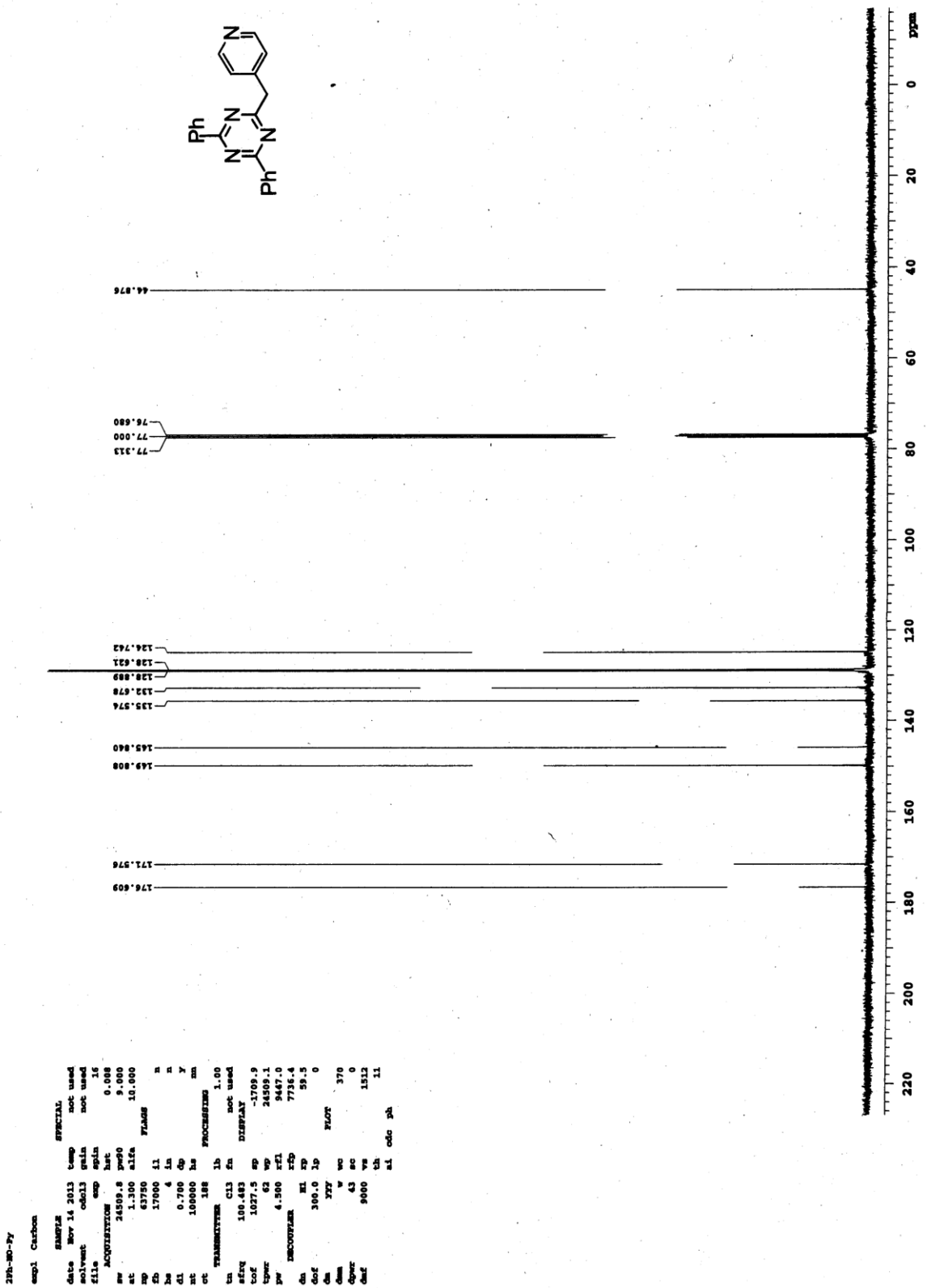
6,7-Dimethoxy-4-(2-furylmethyl)quinazoline (3x) (^{13}C-NMR)



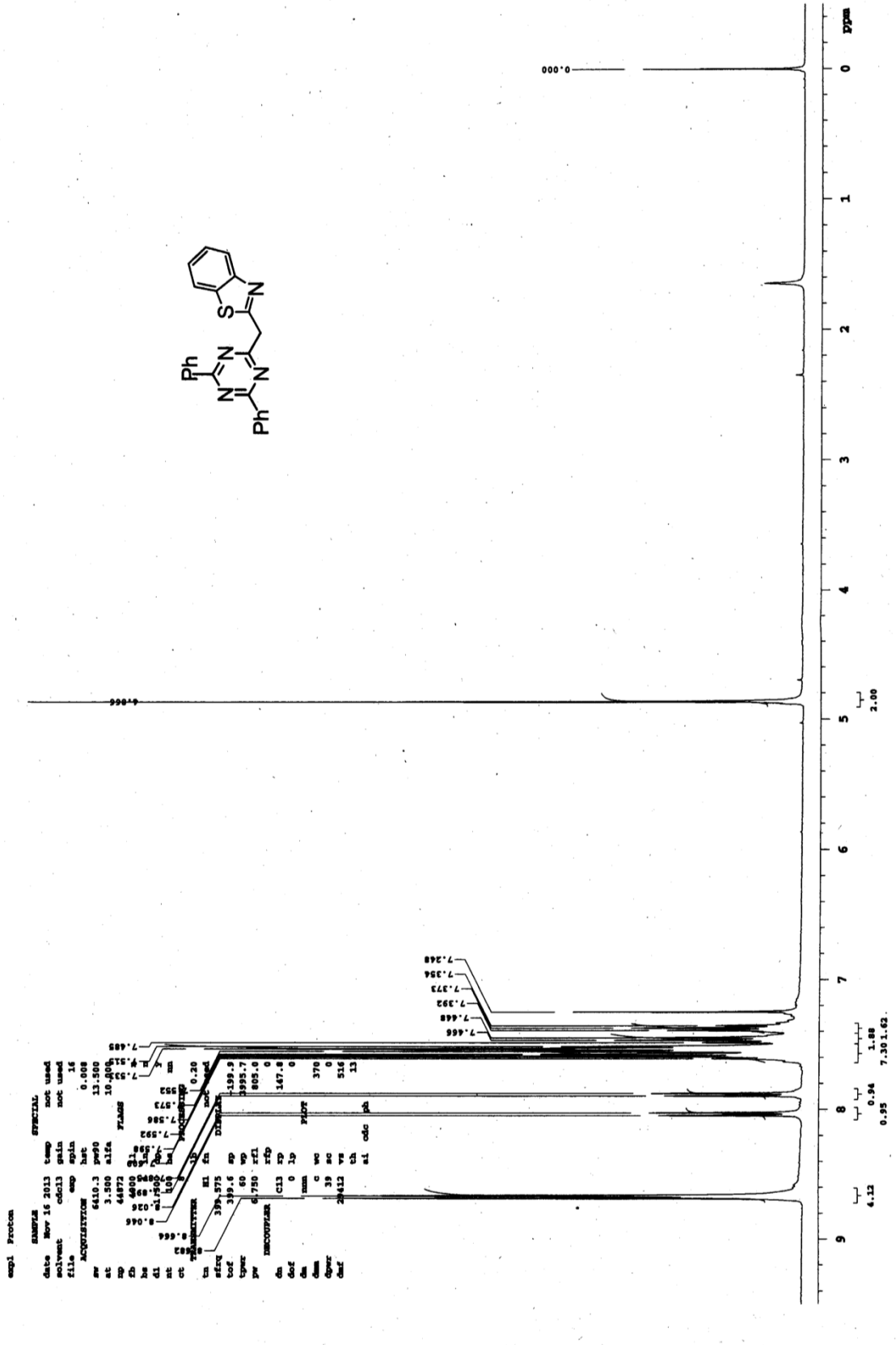
4,6-Diphenyl-2-(4-prydiylmethyl)-1,3,5-triazine (3y) (^{1}H-NMR)



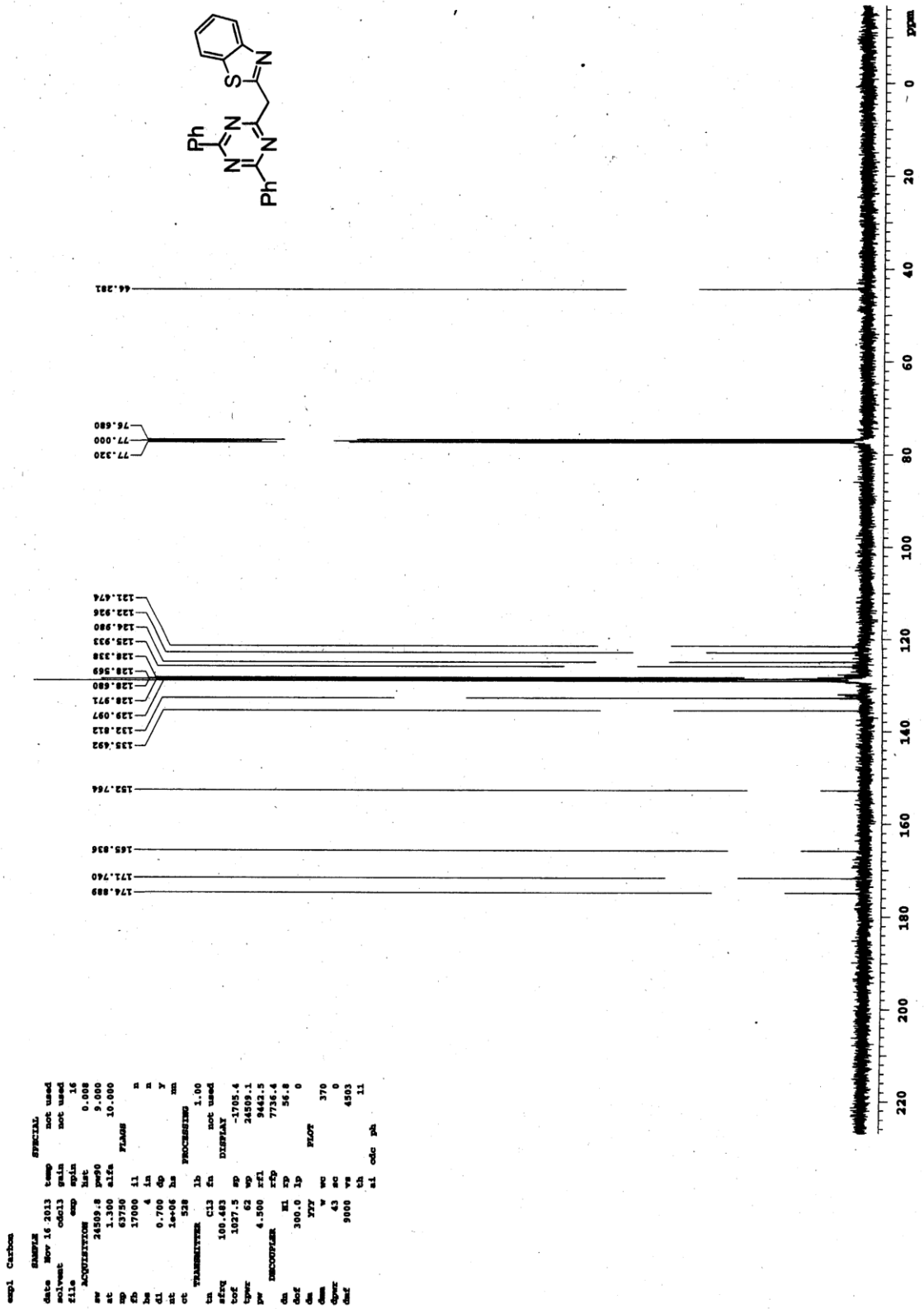
4,6-Diphenyl-2-(4-prydiylmethyl)-1,3,5-triazine (3y) (^{13}C-NMR)



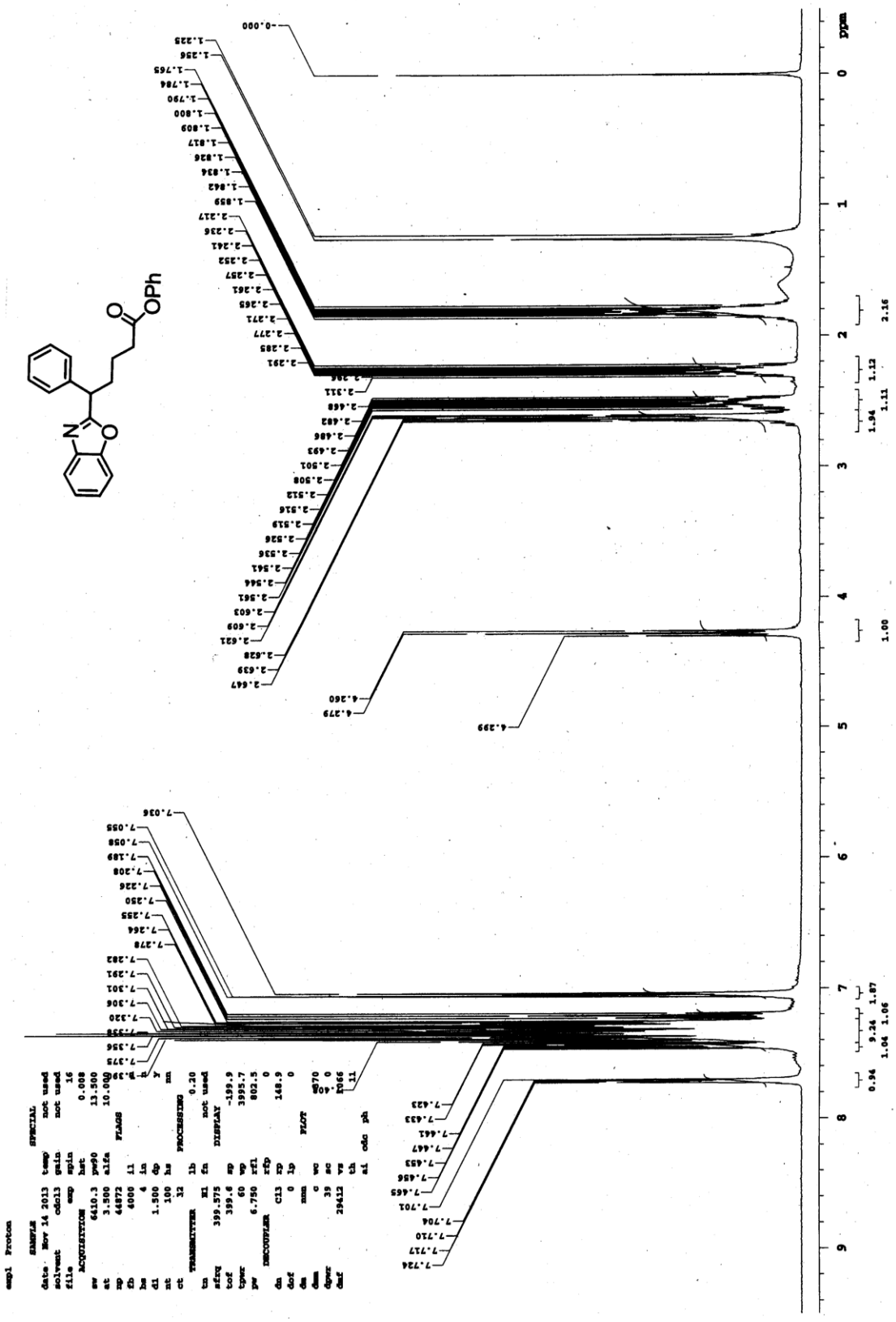
2-[(4,6-Diphenyl-1,3,5-triazin-2-yl)methyl]benzothiazole (3z) (^{1}H-NMR)



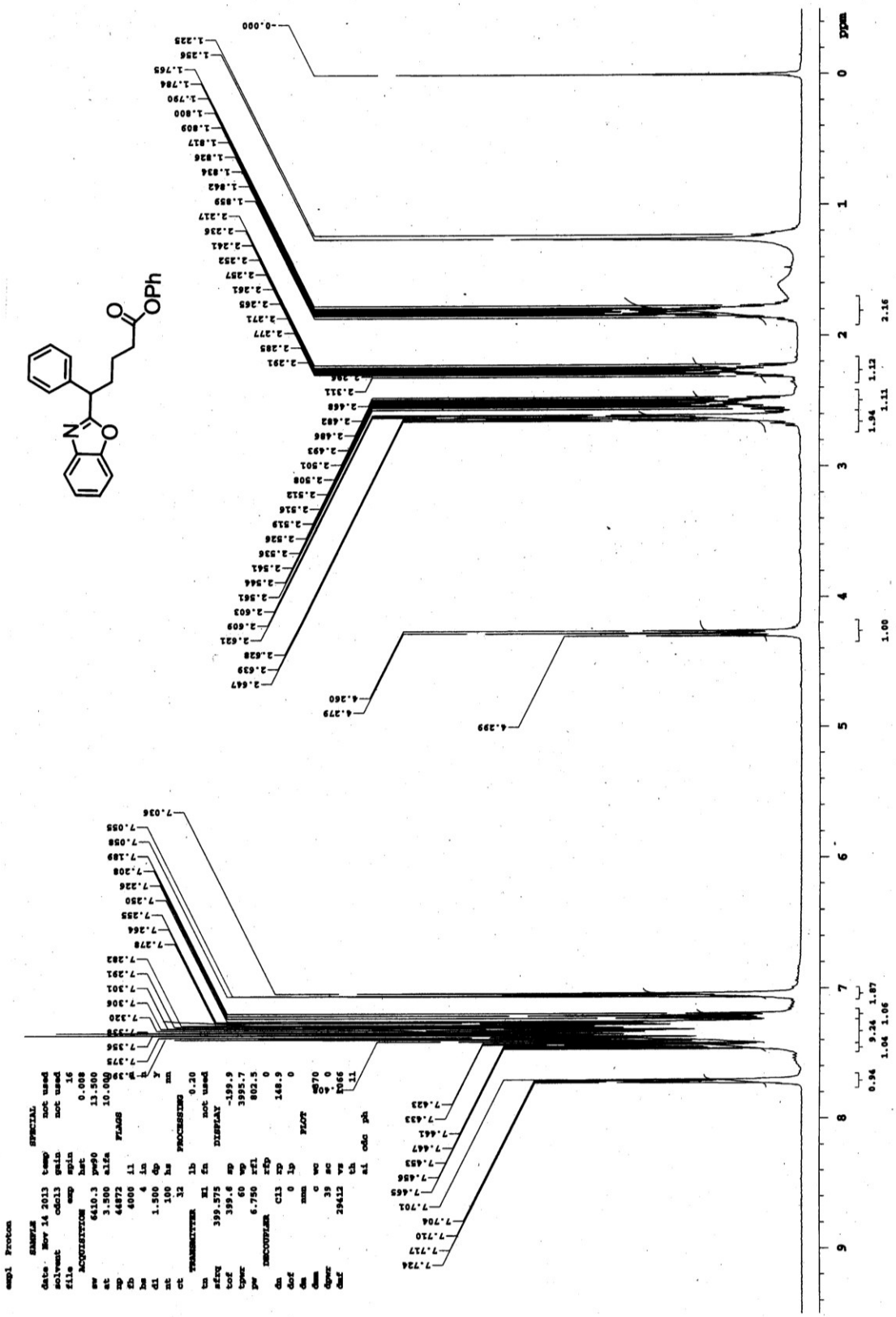
2-[(4,6-Diphenyl-1,3,5-triazin-2-yl)methyl]benzothiazole (3z) (^{13}C-NMR)



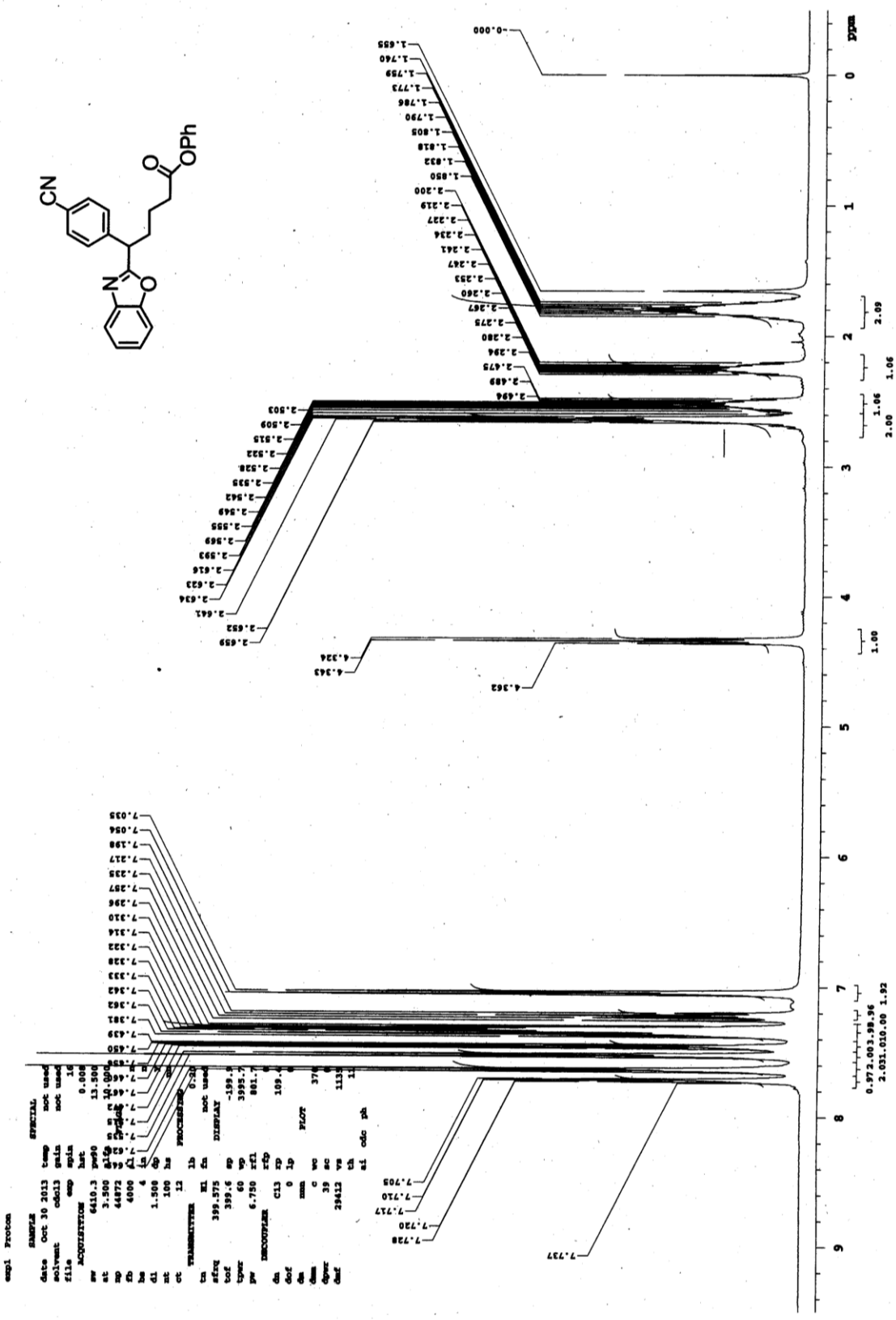
1-(2-Benzoxazole)-1-phenylpentanoic phenylester (8a) (^{1}H-NMR)



1-(2-Benzoxazole)-1-phenylpentanoic phenylester (8a) (^{13}C-NMR)



1-(2-Benzoxazole)-1-(*p*-cyanophenyl)pentanoic phenyl ester (8b) (^{1}H-NMR)



1-(2-Benzoxazole)-1-(*p*-cyanophenyl)pentanoic phenyl ester (8b) (^{13}C-NMR)