Supplementary Information (SI) for Organic & Biomolecular Chemistry.
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Supporting Information

One-pot Synthesis of Sulfonyl 3,6-Diarylpyridazines via Tandem Condensation of α-Sulfonyl Ketones with Methyl Ketones

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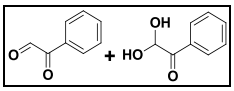
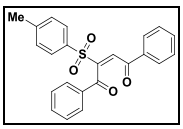
Experimental section

General. All reagents and solvents were obtained from commercial sources and used without further purification. Reactions were routinely carried out under an atmosphere of dry air with magnetic stirring. Products in organic solvents were dried with anhydrous magnesium sulfate before concentration in vacuo. Melting points were determined with a SMP3 melting apparatus. ^{1}H and ^{13}C NMR spectra were recorded on a Varian INOVA spectrometer operating at 400/600 and at 100/150 MHz, respectively. Chemical shifts (δ) are reported in parts per million (ppm) and the coupling constants (*J*) are given in Hertz. High resolution mass spectra (HRMS) were measured with a mass spectrometer Finnigan/Thermo Quest MAT 95XL. X-ray crystal structures were obtained with an Enraf-Nonius FR-590 diffractometer (CAD4, Kappa CCD).



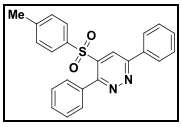
Phenylglyoxal (2a) and hydrate (2a'). SeO_2 (222 mg, 1.0 mmol) was added to a solution of acetophenone **1a** (60 mg, 0.5 mmol) in dioxane (10 mL) at 25 ^{o}C. The reaction mixture was stirred at reflux for 5 h. The reaction mixture was cooled to 25 ^{o}C and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 30/1~1/1) afforded a mixture of **2a** and **2a'** (ratio = 1:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.67 (s, 1/3H), 8.22-8.12 (m, 2H), 7.70-7.59 (m, 1H), 7.55-7.46 (m, 2H), 5.98 (s, 2/3H).



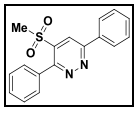
(*E*)-1,4-Diphenyl-2-tosylbut-2-ene-1,4-dione (4a). SeO_2 (222 mg, 1.0 mmol) was added to a solution of acetophenone **1a** (60 mg, 0.5 mmol) in dioxane (10 mL) at 25 ^{o}C. The reaction mixture was stirred at reflux for 5 h and then cooled to 25 ^{o}C. The process was monitored by TLC until **1a** was consumed and phenylglyoxal **2a** were generated. Then, piperidine (42 mg, 0.5 mmol), HOAc (30 mg, 0.5 mmol) and α-sulfonyl arylketone **3a** (137 mg, 0.5 mmol) in dioxane (10 mL) were added to the resulting reaction mixture at 25 ^{o}C. The reaction mixture was stirred at reflux for 20 h. The reaction mixture was cooled to 25 ^{o}C and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 30/1~1/1) afforded **4a**. Yield = 90% (176 mg); White solid; mp = 139-142

^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^{+}$ calcd for $C_{23}H_{19}O_4S$ 391.1004, found 391.1010; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.22 (s, 1H), 7.93-7.91 (m, 2H), 7.86-7.84 (m, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.64-7.61 (m, 1H), 7.55-7.52 (m, 1H), 7.50-7.47 (m, 2H), 7.41-7.38 (m, 2H), 7.33 (d, *J* = 7.6 Hz, 2H), 2.43 (s, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 190.0, 186.9, 154.4, 145.9, 135.9, 135.5, 134.6, 134.5, 134.0, 131.1, 130.0 (2x), 129.20 (2x), 129.16 (2x), 129.01 (2x), 128.90 (2x), 126.6 (2x), 21.7.

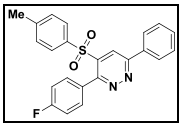
A representative synthetic procedure of skeletons 5 and 6 is as follows: SeO_2 (222 mg, 1.0 mmol) was added to a solution of acetophenones **1** (0.5 mmol) in dioxane (10 mL) at 25 ^{o}C. The reaction mixture was stirred at reflux for 5 h and then cooled to 25 ^{o}C. The process was monitored by TLC until **1** was consumed and arylglyoxals **2** were generated. Then, piperidine (42 mg, 0.5 mmol), HOAc (30 mg, 0.5 mmol) and α-sulfonyl arylketones or 1,3-dicarbonyls **3** (0.5 mmol) in dioxane (10 mL) were added to the resulting reaction mixture at 25 ^{o}C. The reaction mixture was stirred at reflux for 20 h. The reaction mixture was cooled to 25 ^{o}C. Without further purification, excess $N_2H_{4(aq)}$ solution (~80%, 0.3 mL) was added to the resulting sulfonyl butene-1,4-dione **4** at 25 ^{o}C. The reaction mixture was stirred at 25 ^{o}C for 10 h and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 30/1~1/1) afforded **5** and **6**.



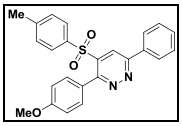
3,6-Diphenyl-4-tosylpyridazine (5a). Yield = 84% (162 mg); White solid; mp = 213-214 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^{+}$ calcd for $C_{23}H_{19}N_2O_2S$ 387.1167, found 387.1172; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73 (s, 1H), 8.27-8.23 (m, 2H), 7.63-7.57 (m, 3H), 7.49-7.45 (m, 1H), 7.37-7.33 (m, 4H), 7.13 (d, *J* = 8.4 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 2.34 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 159.3, 156.6, 145.2, 141.4, 135.0, 134.7, 134.5, 131.0, 130.2 (2x), 129.5, 129.4 (2x), 129.3 (2x), 128.4 (2x), 127.7 (2x), 127.3 (2x), 121.6, 21.6. Single-crystal X-Ray diagram: crystal of compound **5a** was grown by slow diffusion of EtOAc into a solution of compound **5a** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group Ia, *a* = 9.3268(5) Å, *b* = 15.1541(6) Å, *c* = 14.1675(7) Å, *V* = 1899.37(17) Å^3, *Z* = 4, d_{calcd} = 1.351 g/cm^3, *F*(000) = 808.0, 2*θ* range 4.05~54.162^{o}, R indices (all data) R1 = 0.0460, wR2 = 0.0984.



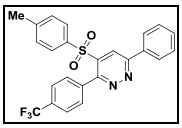
4-Methylsulfonyl-3,6-diphenylpyridazine (**5b**). Yield = 78% (121 mg); White solid; mp = 182-183 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{17}H_{15}N_2O_2S$ 311.0854, found 311.0856; ^1H NMR (600 MHz, $CDCl_3$): δ 8.55 (s, 1H), 8.21-8.20 (m, 2H), 7.83-7.81 (m, 2H), 7.60-7.54 (m, 6H), 2.69 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 159.3, 155.5, 140.2, 134.7, 134.5, 131.0, 130.34, 130.25 (2x), 129.3 (2x), 128.5 (2x), 127.2 (2x), 121.5, 42.1.



3-(4-Fluorophenyl)-6-phenyl-4-tosylpyridazine (5c). Yield = 81% (164 mg); White solid; mp =193-194 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{23}H_{18}FN_2O_2S$ 405.1073, found 405.1074; ^1H NMR (400 MHz, $CDCl_3$): δ 8.71 (s, 1H), 8.25-8.23 (m, 2H), 7.60-7.58 (m, 2H), 7.37-7.28 (m, 3H), 7.19-7.16 (m, 2H), 7.08-7.05 (m, 4H), 2.36 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 163.7 (d, *J* = 248.6 Hz), 159.3, 155.6, 145.4, 132.4 (d, *J* = 8.4 Hz, 2x), 131.1, 130.2, 129.5, 129.4 (2x), 129.3 (2x), 128.4, 128.3 (2x), 127.7, 127.3 (2x), 121.6, 114.8 (d, *J* = 21.9 Hz, 2x), 21.6; $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$): δ -110.74~-110.81 (m, 1F).

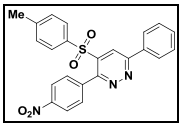


3-(4-Methoxyphenyl)-6-phenyl-4-tosylpyridazine (5d). Yield = 76% (158 mg); White solid; mp = 164-165 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{24}H_{21}N_2O_3S$ 417.1273, found 417.1280; ^1H NMR (400 MHz, $CDCl_3$): δ 8.69 (s, 1H), 8.25-8.22 (m, 2H), 7.62-7.56 (m, 3H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.89 (d, *J* = 8.4 Hz, 2H), 3.90 (s, 3H), 2.35 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 160.9, 158.8, 156.4, 145.2, 141.4, 135.1, 134.8, 131.9 (2x), 130.9, 129.32 (2x), 129.30 (2x), 128.4 (2x), 127.3 (2x), 127.0, 121.7, 113.2 (2x), 55.4, 21.6.

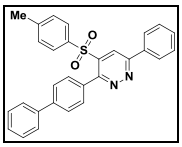


6-Phenyl-4-tosyl-3-(4-(trifluoromethyl)phenyl)pyridazine (5e). Yield = 78% (177 mg); White solid; mp = 177-178 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{24}H_{18}F_3N_2O_2S$ 455.1041, found 455.1038; ^1H NMR (400 MHz, $CDCl_3$): δ 8.73 (s, 1H), 8.26-8.23 (m, 2H), 7.60-7.58 (m, 5H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 2.34 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 159.8, 155.1, 145.6, 141.6, 138.1, 134.7, 134.4, 131.3 (q, *J* = 32.6 Hz), 131.2, 130.6 (2x), 129.5 (2x), 129.3 (2x), 128.2 (2x), 127.4 (2x), 124.6 (q, *J* = 3.8 Hz, 2x), 124.0 (q, *J* = 245.6 Hz), 121.5, 21.5;

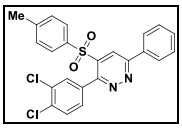
$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$): δ -62.65 (s, 3F).



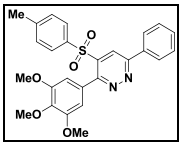
3-(4-Nitrophenyl)-6-phenyl-4-tosylpyridazine (5f). Yield = 74% (160 mg); White solid; mp = 176-177 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{23}H_{18}N_3O_4S$ 432.1018, found 432.1020; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.74 (s, 1H), 8.27-8.24 (m, 2H), 7.62-7.58 (m, 3H), 7.38-7.31 (m, 4H), 7.13 (d, *J* = 8.4 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 2.35 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 159.3, 156.6, 145.2, 141.6, 135.0, 134.6, 134.4, 131.1, 130.3 (2x), 129.6, 129.39 (2x), 129.35 (2x), 128.4 (2x), 127.7 (2x), 127.4 (2x), 121.8, 21.6.



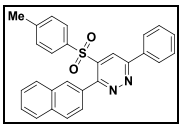
3-([1,1'-Biphenyl]-4-yl)-6-phenyl-4-tosylpyridazine (5g). Yield = 72% (166 mg); White solid; mp > 250 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{29}H_{23}N_2O_2S$ 463.1480, found 463.1485; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.78 (s, 1H), 8.35 (d, *J* = 8.4 Hz, 2H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.53-7.48 (m, 3H), 7.44-7.42 (m, 1H), 7.36-7.34 (m, 4H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 2.35 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 158.9, 156.5, 145.2, 143.8, 141.5, 139.9, 135.0, 134.6, 133.5, 130.3 (2x), 129.5, 129.4 (2x), 129.0 (2x), 128.4 (2x), 128.1, 128.0 (2x), 127.8 (2x), 127.7 (2x), 127.2 (2x), 121.4, 21.6.



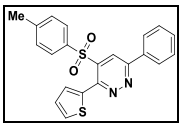
3-(3,4-Dichlorophenyl)-6-phenyl-4-tosylpyridazine (5h). Yield = 78% (177 mg); White solid; mp = 189-190 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{23}H_{17}Cl_2N_2O_2S$ 455.0388, found 455.0387; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.70 (s, 1H), 8.25-8.22 (m, 2H), 7.62-7.58 (m, 3H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.31 (dd, *J* = 2.4, 8.4 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 2.0 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 2.40 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 159.9, 154.2, 145.9, 141.7, 134.8, 134.4, 134.3, 134.1, 132.2, 131.6, 131.3, 129.74, 129.71, 129.6 (2x), 129.4 (2x), 128.3 (2x), 127.4 (2x), 121.5, 21.7.



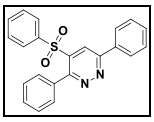
6-Phenyl-4-tosyl-3-(3,4,5-trimethoxyphenyl)pyridazine (5i). Yield = 76% (181 mg); White solid; mp = 194-196 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^{+}$ calcd for $C_{26}H_{25}N_2O_5S$ 477.1484, found 477.1486; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73 (s, 1H), 8.26-8.23 (m, 2H), 7.62-7.57 (m, 3H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.52 (s, 2H), 3.93 (s, 3H), 3.76 (s, 6H), 2.35 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 159.4, 156.2, 152.6 (2x), 145.0, 141.7, 139.1, 135.0, 134.6, 131.1, 129.4, 129.33 (2x), 129.26 (2x), 128.4 (2x), 127.3 (2x), 121.5, 107.6 (2x), 61.0, 55.9 (2x), 21.5.



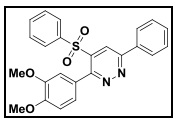
3-(Naphthalen-2-yl)-6-phenyl-4-tosylpyridazine (5j). Yield = 80% (174 mg); White solid; mp = 179-181 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^{+}$ calcd for $C_{27}H_{21}N_2O_2S$ 437.1324, found 437.1326; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.78 (s, 1H), 8.29-8.27 (m, 2H), 7.94 (d, *J* = 7.6 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.73 (s, 1H), 7.64-7.53 (m, 5H), 7.44 (d, *J* = 8.4 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.77 (d, *J* = 8.0 Hz, 2H), 2.21 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 159.3, 156.6, 145.1, 141.8, 134.9, 134.7, 133.4, 132.3, 131.9, 131.1, 130.3, 129.3 (2x), 129.2 (2x), 128.5, 128.3 (2x), 127.7, 127.40 (2x), 127.37, 127.2, 127.0, 126.5, 121.6, 21.5.



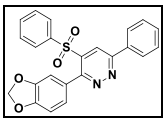
6-Phenyl-3-(thiophen-2-yl)-4-tosylpyridazine (5k). Yield = 74% (145 mg); White solid; mp = 169-170 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^{+}$ calcd for $C_{21}H_{17}N_2O_2S_2$ 393.0732, found 393.0729; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.65 (s, 1H), 8.23-8.21 (m, 2H), 7.97 (dd, *J* = 1.2, 4.0 Hz, 1H), 7.60-7.56 (m, 3H), 7.51 (dd, *J* = 1.2, 5.2 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.16 (dd, *J* = 4.0, 5.2 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 2.35 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 158.4, 150.4, 145.6, 140.2, 135.7, 134.5, 133.3, 131.0, 130.5 (2x), 129.5 (2x), 129.3 (2x), 128.4 (2x), 127.5, 127.2 (2x), 122.1, 21.6.



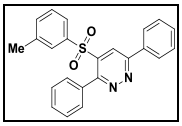
3,6-Diphenyl-4-(phenylsulfonyl)pyridazine (5l). Yield = 78% (145 mg); White solid; mp = 159-161 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^{+}$ calcd for $C_{22}H_{17}N_2O_2S$ 373.1011, found 373.1015; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76 (s, 1H), 8.27-8.24 (m, 2H), 7.63-7.58 (m, 3H), 7.49-7.44 (m, 2H), 7.36-7.20 (m, 8H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 159.3, 156.5, 141.2, 137.9, 134.7, 134.4, 133.8, 131.1, 130.2 (2x), 129.5, 129.3 (2x), 128.7 (2x), 128.3 (2x), 127.8 (2x), 127.3 (2x), 121.6.



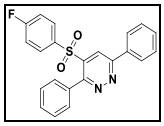
3-(3,4-Dimethoxyphenyl)-6-phenyl-4-(phenylsulfonyl)pyridazine (5m). Yield = 78% (168 mg); White solid; mp = 176-178 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^{+}$ calcd for $C_{24}H_{21}N_2O_4S$ 433.1222, found 433.1225; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73 (s, 1H), 8.25-8.23 (m, 2H), 7.62-7.58 (m, 3H), 7.49-7.45 (m, 1H), 7.31-7.24 (m, 4H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.81 (s, 1H), 3.96 (s, 3H), 3.76 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 159.0, 156.2, 150.3, 148.2, 141.4, 137.9, 134.6, 133.8, 131.0, 129.3 (2x), 128.6 (2x), 128.3 (2x), 127.3 (2x), 126.6, 123.7, 121.9, 113.1, 110.3, 56.1, 55.8.



3-(Benzo[*d*][1,3]dioxol-5-yl)-6-phenyl-4-(phenylsulfonyl)pyridazine (5n). Yield = 76% (158 mg); White solid; mp = 163-165 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^{+}$ calcd for $C_{23}H_{17}N_2O_4S$ 417.0909, found 417.0912; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (s, 1H), 8.25-8.23 (m, 2H), 7.62-7.58 (m, 3H), 7.55-7.51 (m, 1H), 7.40-7.37 (m, 2H), 7.24-7.30 (m, 2H), 6.88 (dd, *J* = 1.6, 8.0 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.74 (d, *J* = 1.6 Hz, 1H), 6.03 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 159.1, 155.9, 149.0, 147.2, 141.4, 138.1, 134.6, 134.0, 131.1, 129.3 (2x), 128.7 (2x), 128.4 (2x), 128.0, 127.3 (2x), 125.1, 121.8, 110.5, 107.8, 101.4.

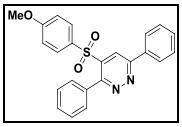


3,6-Diphenyl-4-(*m*-tolylsulfonyl)pyridazine (5o). Yield = 78% (151 mg); White solid; mp = 182-184 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^{+}$ calcd for $C_{23}H_{19}N_2O_2S$ 387.1167, found 387.1163; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (s, 1H), 8.27-8.25 (m, 2H), 7.62-7.56 (m, 3H), 7.49-7.44 (m, 1H), 7.37-7.30 (m, 4H), 7.27-7.25 (m, 1H), 7.12 (t, *J* = 8.0 Hz, 1H), 7.10-7.07 (m, 1H), 6.98 (br s, 1H), 2.18 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 159.2, 156.5, 141.3, 139.0, 137.6, 134.7, 134.6, 134.4, 131.0, 130.2 (2x), 129.4, 129.3 (2x), 128.9, 128.6, 127.6 (2x), 127.3 (2x), 125.3, 121.5, 20.9.

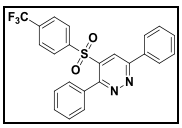


4-((4-Fluorophenyl)sulfonyl)-3,6-diphenylpyridazine (5p). Yield = 79% (154 mg); White solid; mp = 198-200 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M +

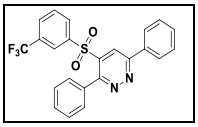
H]$^+$ calcd for $C_{22}H_{16}FN_2O_2S$ 391.0917, found 391.0915; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73 (s, 1H), 8.26-8.23 (m, 2H), 7.62-7.56 (m, 3H), 7.50-7.46 (m, 1H), 7.39-7.21 (m, 4H), 7.26-7.21 (m, 2H), 6.90-6.85 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.7 (d, *J* = 257.0 Hz), 159.3, 156.3, 141.0, 134.5, 134.4, 133.8 (d, *J* = 3.0 Hz), 131.2 (d, *J* = 9.8 Hz, 2x), 131.1, 130.2 (2x), 129.6, 129.3 (2x), 127.8 (2x), 127.3 (2x), 121.4, 116.0 (d, *J* = 22.8 Hz, 2x); ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ -110.72~-110.79 (m, 1F).



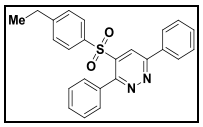
4-((4-Methoxyphenyl)sulfonyl)-3,6-diphenylpyridazine (5q). Yield = 82% (165 mg); White solid; mp = 186-187 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{23}H_{19}N_2O_3S$ 403.1116, found 403.1118; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (s, 1H), 8.25-8.23 (m, 2H), 7.61-7.56 (m, 3H), 7.49-7.44 (m, 1H), 7.39-7.35 (m, 4H), 7.15 (d, *J* = 9.2 Hz, 2H), 6.66 (d, *J* = 9.2 Hz, 2H), 3.78 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 163.8, 159.2, 156.5, 141.6, 134.7, 134.6, 130.9, 130.6 (2x), 130.2 (2x), 129.5, 129.2 (2x), 129.1, 127.7 (2x), 127.3 (2x), 121.4, 113.9 (2x), 55.6.



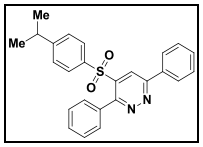
3,6-Diphenyl-4-((4-(trifluoromethyl)phenyl)sulfonyl)pyridazine (5r). Yield = 80% (176 mg); White solid; mp = 211-213 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{23}H_{16}F_3N_2O_2S$ 441.0885, found 441.0891; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76 (s, 1H), 8.27-8.25 (m, 2H), 7.61-7.59 (m, 3H), 7.47-7.44 (m, 3H), 7.37-7.25 (m, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 159.4, 156.1, 141.4, 140.5, 135.2 (q, *J* = 32.6 Hz), 134.4, 134.2, 131.2, 130.2 (2x), 129.7, 129.4 (2x), 128.8 (2x), 127.9 (2x), 127.3 (2x), 125.7 (q, *J* = 3.8 Hz, 2x), 125.5 (q, *J* = 272.2 Hz), 121.4; ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ -63.35 (s, 3F).



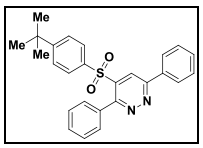
3,6-Diphenyl-4-((3-(trifluoromethyl)phenyl)sulfonyl)pyridazine (5s). Yield = 84% (185 mg); White solid; mp = 148-150 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{23}H_{16}F_3N_2O_2S$ 441.0885, found 441.0887; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.79 (s, 1H), 8.29-8.27 (m, 2H), 7.72 (d, *J* = 7.6 Hz, 1H), 7.65-7.60 (m, 3H), 7.49-7.28 (m, 8H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 159.5, 156.2, 140.5, 139.3, 134.5, 134.0, 131.7, 131.3, 131.2, 130.1 (2x), 130.7 (q, *J* = 3.5 Hz), 130.10 (2x), 130.05, 129.4, 128.0 (2x), 127.4 (2x), 125.5 (q, *J* = 3.8 Hz), 122.3 (q, *J* = 270.2 Hz), 121.6; ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ -63.35 (s, 3F).



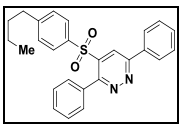
4-((4-Ethylphenyl)sulfonyl)-3,6-diphenylpyridazine (5t). Yield = 80% (160 mg); White solid; mp = 183-184 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^{+}$ calcd for $C_{24}H_{21}N_2O_2S$ 401.1324, found 401.1326; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.74 (s, 1H), 8.26-8.23 (m, 2H), 7.62-7.57 (m, 3H), 7.48-7.43 (m, 1H), 7.35-7.29 (m, 4H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 2.61 (q, *J* = 7.6 Hz, 2H), 1.18 (t, *J* = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 159.2, 156.5, 151.2, 141.4, 134.9, 134.7, 134.5, 131.0, 130.1 (2x), 129.4, 129.3 (2x), 128.4 (2x), 128.2 (2x), 127.7 (2x), 127.3 (2x), 121.5, 28.8, 15.1.



4-((4-Isopropylphenyl)sulfonyl)-3,6-diphenylpyridazine (5u). Yield = 82% (170 mg); White solid; mp = 152-153 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^{+}$ calcd for $C_{25}H_{23}N_2O_2S$ 415.1480, found 415.1484; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (s, 1H), 8.27-8.23 (m, 2H), 7.62-7.56 (m, 3H), 7.47-7.43 (m, 1H), 7.35-7.28 (m, 4H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 2.90-2.83 (m, 1H), 1.19 (d, *J* = 7.2 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 159.2, 156.5, 155.7, 141.4, 135.0, 134.7, 134.5, 131.0, 130.1 (2x), 129.4, 129.2 (2x), 129.4 (2x), 127.7 (2x), 127.3 (2x), 126.8 (2x), 121.4, 34.1, 23.4 (2x).

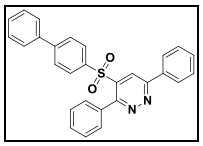


4-((4-(*t*-Butyl)phenyl)sulfonyl)-3,6-diphenylpyridazine (5v). Yield = 80% (171 mg); White solid; mp = 151-153 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^{+}$ calcd for $C_{26}H_{25}N_2O_2S$ 429.1637, found 429.1640; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (s, 1H), 8.26-8.24 (m, 2H), 7.62-7.56 (m, 3H), 7.46-7.42 (m, 1H), 7.33-7.28 (m, 4H), 7.21 (d, *J* = 8.8 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 1.26 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 159.2, 157.9, 156.5, 141.5, 134.7, 134.6, 134.5, 131.0, 130.1 (2x), 129.33, 129.25 (2x), 128.1 (2x), 127.7 (2x), 127.3 (2x), 125.7 (2x), 121.4, 35.1, 30.8 (3x).

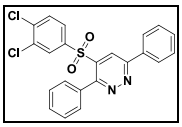


4-((4-(*n*-Butyl)phenyl)sulfonyl)-3,6-diphenylpyridazine (5w). Yield = 78% (167 mg); White solid; mp = 154-155 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^{+}$ calcd for $C_{26}H_{25}N_2O_2S$ 429.1637, found 429.1639; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.74 (s, 1H), 8.27-8.24 (m, 2H), 7.63-7.57 (m, 3H), 7.47-7.44 (m, 1H), 7.35-7.31 (m, 4H), 7.14 (d, *J* =

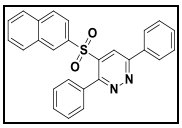
8.4 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 2.58 (t, *J* = 7.6 Hz, 2H), 1.57-1.49 (m, 2H), 1.32-1.27 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 159.2, 156.5, 150.0, 141.5, 135.0, 134.8, 134.6, 131.0, 130.2 (2x), 129.4, 129.3 (2x), 128.8 (2x), 128.4 (2x), 127.7 (2x), 127.3 (2x), 121.5, 35.5, 33.0, 22.0, 13.8.



4-([1,1'-Biphenyl]-4-ylsulfonyl)-3,6-diphenylpyridazine (5x). Yield = 76% (170 mg); White solid; mp = 195-197 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{28}H_{21}N_2O_2S$ 449.1324, found 449.1326; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.79 (s, 1H), 8.29-8.27 (m, 2H), 7.64-7.58 (m, 3H), 7.52-7.40 (m, 8H), 7.37-7.29 (m, 6H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 159.3, 156.4, 146.7, 141.3, 138.7, 136.2, 134.7, 134.5, 131.0, 130.2 (2x), 129.5, 129.3 (2x), 129.0 (2x), 128.80, 128.77 (2x), 127.7 (2x), 127.3 (2x), 127.24 (2x), 127.23 (2x), 121.5. Single-crystal X-Ray diagram: crystal of compound **5x** was grown by slow diffusion of EtOAc into a solution of compound **5x** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the triclinic crystal system, space group P-1, *a* = 9.3979(2) Å, *b* = 11.3031(3) Å, *c* = 12.3737(3) Å, *V* = 1097.50(5) $Å^3$, *Z* = 2, d_{calcd} = 1.363 g/cm^3, *F*(000) = 472.0, 2*θ* range 3.938~49.996°, R indices (all data) R1 = 0.0401, wR2 = 0.0898.

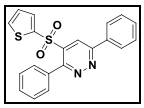


4-((3,4-Dichlorophenyl)sulfonyl)-3,6-diphenylpyridazine (5y). Yield = 75% (165 mg); White solid; mp = 163-164 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{22}H_{15}Cl_2N_2O_2S$ 441.0231, found 441.0238; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (s, 1H), 8.26-8.23 (m, 2H), 7.63-7.58 (m, 3H), 7.55-7.51 (m, 1H), 7.42-7.38 (m, 2H), 7.33-7.30 (m, 3H), 7.21 (d, *J* = 2.4 Hz, 1H), 7.07 (dd, *J* = 2.4, 8.4 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 159.4, 156.1, 140.6, 139.2, 137.5, 134.4, 133.9, 133.5, 131.2, 130.7, 130.5, 130.14 (2x), 130.09, 129.3 (2x), 127.9 (2x), 127.3 (2x), 127.0, 121.4.

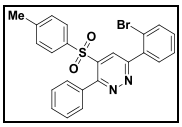


4-(Naphthalen-2-ylsulfonyl)-3,6-diphenylpyridazine (5z). Yield = 76% (160 mg); White solid; mp = 202-204 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{26}H_{19}N_2O_2S$ 423.1167, found 423.1171; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.82 (s, 1H), 8.29-8.27 (m, 2H), 7.81 (d, *J* = 8.8 Hz, 1H), 7.72-7.70 (m, 2H), 7.66-7.54 (m, 6H), 7.40-7.36 (m, 1H), 7.30-7.19 (m, 5H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 159.3, 156.6, 141.1, 135.1, 134.7, 134.32, 134.30, 131.5, 131.4, 131.0, 130.1 (2x), 129.7, 129.6, 129.5, 129.3 (2x),

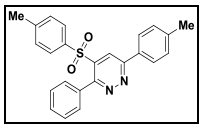
129.2, 127.8, 127.64 (2x), 127.61, 127.3 (2x), 122.1, 121.7.



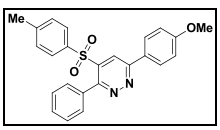
3,6-Diphenyl-4-(thiophen-2-ylsulfonyl)pyridazine (5aa). Yield = 80% (151 mg); White solid; mp = 222-224 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^{+}$ calcd for $C_{20}H_{15}N_2O_2S_2$ 379.0575, found 379.0580; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (s, 1H), 8.26-8.23 (m, 2H), 7.61-7.58 (m, 4H), 7.52-7.41 (m, 5H), 6.91 (dd, *J* = 1.2, 4.0 Hz, 1H), 6.83 (dd, *J* = 4.0, 5.2 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 159.4, 156.3, 141.7, 138.4, 136.3, 135.8, 134.7, 134.6, 131.1, 130.3 (2x), 129.8, 129.3 (2x), 127.9 (2x), 127.5, 127.3 (2x), 121.3.



6-(2-Bromophenyl)-3-phenyl-4-tosylpyridazine (5ab). Yield = 70% (162 mg); Colorless oil; HRMS (ESI-TOF) *m*/*z*: [M + H]$^{+}$ calcd for $C_{23}H_{18}BrN_2O_2S$ 465.0272, found 465.0278; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.71 (s, 1H), 7.81 (dd, *J* = 1.6, 7.6 Hz, 1H), 7.77-7.74 (m, 2H), 7.42-7.35 (m, 6H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 2.34 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 160.5, 156.7, 145.3, 140.1, 136.5, 134.4, 133.6, 131.9, 131.5, 130.2 (2x), 129.6, 129.4 (2x), 128.5, 128.4, 128.38 (2x), 128.0, 127.7 (2x), 126.2, 21.6.

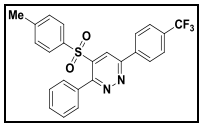


3-Phenyl-6-(*p*-tolyl)-4-tosylpyridazine (5ac). Yield = 76% (152 mg); White solid; mp = 178-179 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^{+}$ calcd for $C_{24}H_{21}N_2O_2S$ 401.1324, found 401.1326; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.70 (s, 1H), 8.15 (d, *J* = 8.0 Hz, 2H), 7.47-7.44 (m, 1H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.36-7.31 (m, 4H), 7.12 (d, *J* = 8.4 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 2.46 (s, 3H), 2.33 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 159.2, 156.2, 145.0, 141.4, 141.3, 135.0, 134.6, 131.9, 130.2 (2x), 130.0 (2x), 129.4, 129.3 (2x), 128.3 (2x), 127.6 (2x), 127.2 (2x), 121.2, 21.5, 21.4.

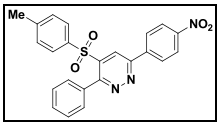


6-(4-Methoxyphenyl)-3-phenyl-4-tosylpyridazine (5ad). Yield = 78% (162 mg); White solid; mp = 178-180 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^{+}$ calcd for $C_{24}H_{21}N_2O_3S$ 417.1273, found 417.1278; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.66 (s, 1H), 8.23 (d, *J* = 8.8 Hz, 2H), 7.47-7.44 (m, 1H), 7.36-7.29 (m, 4H), 7.13-7.09 (m, 4H), 7.01 (d, *J* =

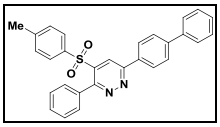
8.0 Hz, 2H), 3.92 (s, 3H), 2.34 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 162.1, 158.8, 155.8, 145.1, 141.3, 135.1, 134.7, 130.3 (2x), 129.4, 129.3 (2x), 128.8 (2x), 128.4 (2x), 127.7 (2x), 127.1, 120.7, 114.7 (2x), 55.5, 21.6.



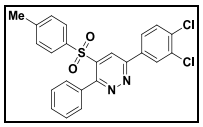
3-Phenyl-4-tosyl-6-(4-(trifluoromethyl)phenyl)pyridazine (5ae). Yield = 75% (170 mg); White solid; mp = 248-250 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{24}H_{18}F_3N_2O_2S$ 455.1041, found 455.1045; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.77 (s, 1H), 8.38 (dt, *J* = 0.8, 8.8 Hz, 2H), 7.87 (dt, *J* = 0.4, 8.4 Hz, 2H), 7.52-7.47 (m, 1H), 7.39-7.32 (m, 4H), 7.13 (d, *J* = 8.4 Hz, 2H), 7.02 (dd, *J* = 0.8, 8.8 Hz, 2H), 2.35 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 157.9, 157.3, 145.4, 141.7, 134.8, 134.3, 132.8 (q, *J* = 32.8 Hz), 130.2 (2x), 129.7, 129.4 (2x), 128.4 (2x), 127.8 (2x), 127.7 (2x), 127.2, 127.1, 126.3 (q, *J* = 3.8 Hz, 2x), 122.5 (q, *J* = 270.6 Hz), 21.6; $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$): δ -62.95 (s, 3F).



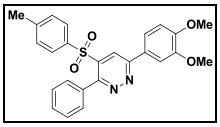
6-(4-Nitrophenyl)-3-phenyl-4-tosylpyridazine (5af). Yield = 75% (162 mg); White solid; mp > 250 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{23}H_{18}N_3O_4S$ 432.1018, found 432.1021; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (s, 1H), 8.46-8.41 (m, 4H), 7.51-7.47 (m, 1H), 7.38-7.31 (m, 4H), 7.12 (d, *J* = 8.4 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 2.34 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 157.6, 157.1, 149.3, 145.5, 141.8, 140.5, 134.6, 134.1, 130.1 (2x), 129.8, 129.4 (2x), 128.4 (2x), 128.3 (2x), 127.8 (2x), 124.4 (2x), 122.1, 21.6.



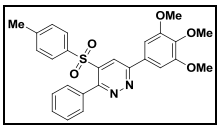
6-([1,1'-Biphenyl]-4-yl)-3-phenyl-4-tosylpyridazine (5ag). Yield = 72% (166 mg); White solid; mp = 218-220 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{29}H_{23}N_2O_2S$ 463.1480, found 463.1486; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.78 (s, 1H), 8.35 (d, *J* = 8.4 Hz, 2H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.72-7.69 (m, 2H), 7.52-7.42 (m, 5H), 7.36-7.35 (m, 3H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 2.35 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 158.9, 156.5, 145.1, 143.8, 141.4, 139.9, 135.0, 134.6, 130.3 (2x), 129.5, 129.4 (2x), 129.3, 128.9 (2x), 128.4 (2x), 128.0, 127.9 (2x), 127.73 (2x), 127.71 (2x), 127.1 (2x), 121.4, 21.6.



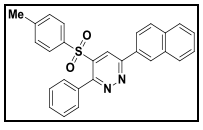
6-(3,4-Dichlorophenyl)-3-phenyl-4-tosylpyridazine (5ah). Yield = 76% (173 mg); White solid; mp = 198-200 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^{+}$ calcd for $C_{23}H_{17}Cl_2N_2O_2S$ 455.0388, found 455.0395; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.70 (s, 1H), 8.39 (d, *J* = 2.0 Hz, 1H), 8.09 (dd, *J* = 2.4, 8.4 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.50-7.46 (m, 1H), 7.37-7.30 (m, 4H), 7.11 (d, *J* = 8.4 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 2.34 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 157.2, 157.1, 145.3, 141.6, 135.5, 134.7, 134.6, 134.2, 133.9, 131.3, 130.2 (2x), 129.7, 129.4 (2x), 129.1, 128.4 (2x), 127.8 (2x), 126.3, 121.4, 21.6.



6-(3,4-Dimethoxyphenyl)-3-phenyl-4-tosylpyridazine (5ai). Yield = 71% (158 mg); White solid; mp = 197-199 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^{+}$ calcd for $C_{25}H_{23}N_2O_4S$ 447.1379, found 447.1382; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (s, 1H), 7.98 (d, *J* = 2.0 Hz, 1H), 7.73 (dd, *J* = 2.0, 8.4 Hz, 1H), 7.48-7.43 (m, 1H), 7.36-7.29 (m, 4H), 7.12 (d, *J* = 8.4 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 2H), 4.02 (s, 3H), 3.99 (s, 3H), 2.33 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 158.6, 155.9, 151.7, 149.7, 145.1, 141.3, 135.0, 134.6, 130.2 (2x), 129.4, 129.3 (2x), 128.3 (2x), 127.7 (2x), 127.3, 120.9, 120.4, 111.3, 109.7, 56.1, 56.0, 21.6.

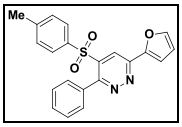


3-Phenyl-4-tosyl-6-(3,4,5-trimethoxyphenyl)pyridazine (5aj). Yield = 72% (171 mg); White solid; mp = 157-159 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^{+}$ calcd for $C_{26}H_{25}N_2O_5S$ 477.1484, found 477.1490; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.67 (s, 1H), 7.50 (s, 2H), 7.49-7.44 (m, 1H), 7.36-7.29 (m, 4H), 7.11 (d, *J* = 8.4 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 4.00 (s, 6H), 3.96 (s, 3H), 2.33 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 158.7, 156.3, 153.9 (2x), 145.2, 141.4, 140.8, 134.9, 134.5, 130.2 (2x), 129.9, 129.5, 129.3 (2x), 128.3 (2x), 127.7 (2x), 121.2, 104.5 (2x), 61.0, 56.4 (2x), 21.6.

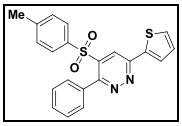


6-(Naphthalen-2-yl)-3-phenyl-4-tosylpyridazine (5ak). Yield = 78% (170 mg); White solid; mp = 183-185 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^{+}$

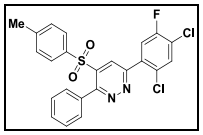
calcd for $C_{27}H_{21}N_2O_2S$ 437.1324, found 437.1320; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.90 (s, 1H), 8.73 (d, *J* = 1.2 Hz, 1H), 8.41 (dd, *J* = 2.0, 8.4 Hz, 1H), 8.05 (d, *J* = 9.2 Hz, 1H), 8.03-8.01 (m, 1H), 7.95-7.92 (m, 1H), 7.62-7.57 (m, 2H), 7.50-7.46 (m, 1H), 7.3-7.35 (m, 4H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 2.34 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 159.2, 156.5, 145.1, 141.4, 135.0, 134.6, 134.5, 133.3, 132.0, 130.3 (2x), 129.5, 129.3 (2x), 129.2, 129.0, 128.4 (2x), 127.8, 127.71 (2x), 127.68, 127.6, 126.9, 123.9, 121.7, 21.6.



6-(Furan-2-yl)-3-phenyl-4-tosylpyridazine (5al). Yield = 76% (143 mg); White solid; mp = 174-175 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{21}H_{17}N_2O_3S$ 377.0960, found 377.0966; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.66 (s, 1H), 7.72 (d, *J* = 1.6 Hz, 1H), 7.50 (d, *J* = 3.6 Hz, 1H), 7.48-7.44 (m, 1H), 7.36-7.28 (m, 4H), 7.13 (d, *J* = 8.4 Hz, 2H), 7.02 (d, *J* = 8.4 Hz, 2H), 6.67 (dd, *J* = 1.6, 3.6 Hz, 1H), 2.34 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.0, 152.1, 149.7, 145.6, 145.2, 141.4, 135.0, 134.6, 130.2 (2x), 129.5, 129.4 (2x), 128.4 (2x), 127.7 (2x), 119.8, 112.3, 112.2, 21.6.

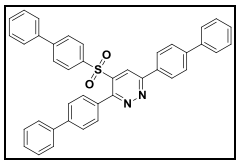


3-Phenyl-6-(thiophen-2-yl)-4-tosylpyridazine (5am). Yield = 78% (153 mg); White solid; mp = 231-232 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{21}H_{17}N_2O_2S_2$ 393.0732, found 393.0728; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.61 (s, 1H), 7.88 (dd, *J* = 1.2, 4.0 Hz, 1H), 7.59 (dd, *J* = 1.2, 5.2 Hz, 1H), 7.47-7.43 (m, 1H), 7.35-7.28 (m, 4H), 7.24 (dd, *J* = 4.0, 5.2 Hz, 1H), 7.11 (d, *J* = 8.4 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 2.33 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.2, 155.1, 145.2, 141.3, 139.2, 134.8, 134.5, 130.7, 130.2 (2x), 129.5, 129.3 (2x), 128.5, 128.3 (2x), 127.9, 127.7 (2x), 120.1, 21.6.

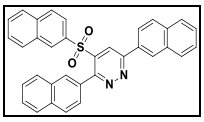


6-(2,4-Dichloro-5-fluorophenyl)-3-phenyl-4-tosylpyridazine (**5an**). Yield = 80% (189 mg); White solid; mp = 203-204 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{23}H_{16}Cl_2FN_2O_2S$ 473.0294, found 473.0301; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.77 (s, 1H), 7.77 (d, *J* = 9.2 Hz, 1H), 7.66 (d, *J* = 6.4 Hz, 1H), 7.52-7.48 (m, 1H), 7.41-7.36 (m, 4H), 7.16 (d, *J* = 8.4 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 2.35 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 157.4, 157.3, 157.2 (d, *J* = 249.4 Hz), 145.4, 140.5, 134.8, 134.5 (d, *J* = 6.8 Hz), 134.2, 132.1, 130.2 (2x), 129.8, 129.5 (2x), 128.5 (2x), 127.8 (2x), 125.8, 124.2 (d, *J* = 19.0 Hz), 119.6, 119.4, 21.6; ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ -115.50~-115.55

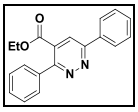
(m, 1F). Single-crystal X-Ray diagram: crystal of compound **5an** was grown by slow diffusion of EtOAc into a solution of compound **5an** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the triclinic crystal system, space group P-1, *a* = 9.7238(2) Å, *b* = 10.1366(2) Å, *c* = 11.2215(3) Å, *V* = 1033.14(4) Å^3, *Z* = 2, d_{calcd} = 1.522 g/cm^3, *F*(000) = 484.0, 2θ range 5.698~54.228^o, R indices (all data) R1 = 0.0346, wR2 = 0.0803.



3,6-Di([1,1'-biphenyl]-4-yl)-4-([1,1'-biphenyl]-4-ylsulfonyl)pyridazine (5ao). Yield = 70% (210 mg); White solid; mp > 250 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{40}H_{29}N_2O_2S$ 601.1950, found 601.1956; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.84 (s, 1H), 8.38 (d, *J* = 8.4 Hz, 2H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 7.2 Hz, 2H), 7.64-7.37 (m, 21H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 158.9, 156.1, 146.8, 143.8, 142.4, 141.5, 140.1, 139.9, 138.6, 136.2, 133.49, 133.46, 130.7, 129.1 (2x), 128.98 (2x), 128.96 (2x), 128.9 (2x), 128.8, 128.1, 128.0 (2x), 127.9, 127.8 (2x), 127.3 (2x), 127.18 (2x), 127.15 (4x), 127.1 (2x), 126.4, 121.3.

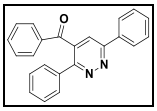


3,6-Di(naphthalen-2-yl)-4-(naphthalen-2-ylsulfonyl)pyridazine (5ap). Yield = 70% (183 mg); White solid; mp > 250 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{34}H_{23}N_2O_2S$ 523.1480, found 523.1488; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.03 (s, 1H), 8.79 (s, 1H), 8.46 (dd, *J* = 1.6, 8.4 Hz, 1H), 8.09 (d, *J* = 8.8 Hz, 1H), 8.07-8.05 (m, 1H), 7.97-7.94 (m, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.73 (s, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.64-7.53 (m, 6H), 7.48-7.43 (m, 3H), 7.34-7.27 (m, 3H), 6.95 (d, *J* = 8.4 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 159.3, 156.5, 141.5, 134.9, 134.6, 134.0, 133.44, 133.37, 132.2, 132.0, 131.6, 131.5, 131.3, 130.3, 129.5, 129.3, 129.12 (2x), 129.08, 128.4, 127.9, 127.8, 127.7, 127.6, 127.5, 127.39, 127.37, 127.2, 127.0, 126.8, 126.5, 123.9, 121.9, 121.8.

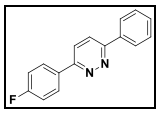


Ethyl 3,6-diphenylpyridazine-4-carboxylate (6a). Yield = 69% (105 mg); White solid; mp = 64-66 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{19}H_{17}N_2O_2$ 305.1290, found 305.1296; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19-8.16 (m, 2H), 8.14 (s, 1H), 7.71-7.68 (m, 2H), 7.57-7.45 (m, 6H), 4.24 (q, *J* = 7.2 Hz, 2H), 1.10 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 166.6, 157.9, 156.9, 136.4, 135.1, 130.4, 129.4, 129.1 (2x),

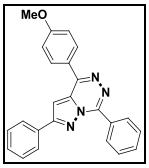
128.8 (2x), 128.6, 128.3 (2x), 127.0 (2x), 123.2, 62.3, 13.5.



(3,6-Diphenylpyridazin-4-yl)(phenyl)methanone (6b). Yield = 67% (113 mg); White solid; mp = 184-186 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{23}H_{17}N_2O$ 337.1341, found 337.1346; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20-8.18 (m, 2H), 7.92 (s, 1H), 7.70-7.68 (m, 4H), 7.58-7.50 (m, 4H), 7.38-7.31 (m, 5H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 195.0, 157.6, 156.2, 137.2, 135.7, 135.3, 135.2, 134.3, 130.5, 129.8 (2x), 129.7, 129.24 (2x), 129.16 (2x), 128.8 (2x), 128.6 (2x), 127.1 (2x), 122.6.

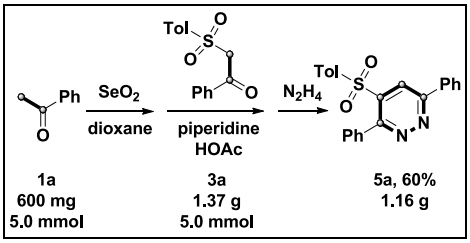


3-(4-Fluorophenyl)-6-phenylpyridazine (7). $NaBH_4$ (10 mg, 0.3 mmol) was added to a stirred solution of **5c** (202 mg, 0.5 mmol) in a cosolvent of THF and MeOH (10 mL, v/v = 1/1) at 25 ^{o}C. The reaction mixture was stirred at reflux for 10 h, and the solvent was concentrated. The residue was diluted with water (10 mL), and the mixture was extracted with CH_2Cl_2 (3 x 30 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 10/1~2/1) afforded **7**. Yield = 83% (104 mg); White solid; mp = 240-242 ^{o}C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{16}H_{12}FN_2$ 251.0985, found 251.0991; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19-8.15 (m, 4H), 7.97 (d, *J* = 8.8 Hz, 1H), 7.93 (d, *J* = 8.8 Hz, 1H), 7.58-7.50 (m, 3H), 7.26-7.21 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 164.3 (d, *J* = 248.7 Hz), 157.6, 156.6, 135.2, 131.6, 130.5, 129.2 (2x), 129.1 (d, *J* = 9.8 Hz, 2x), 127.1 (2x), 125.2, 124.8, 116.2 (d, *J* = 21.2 Hz, 2x); ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ -110.53 (s, 1F).



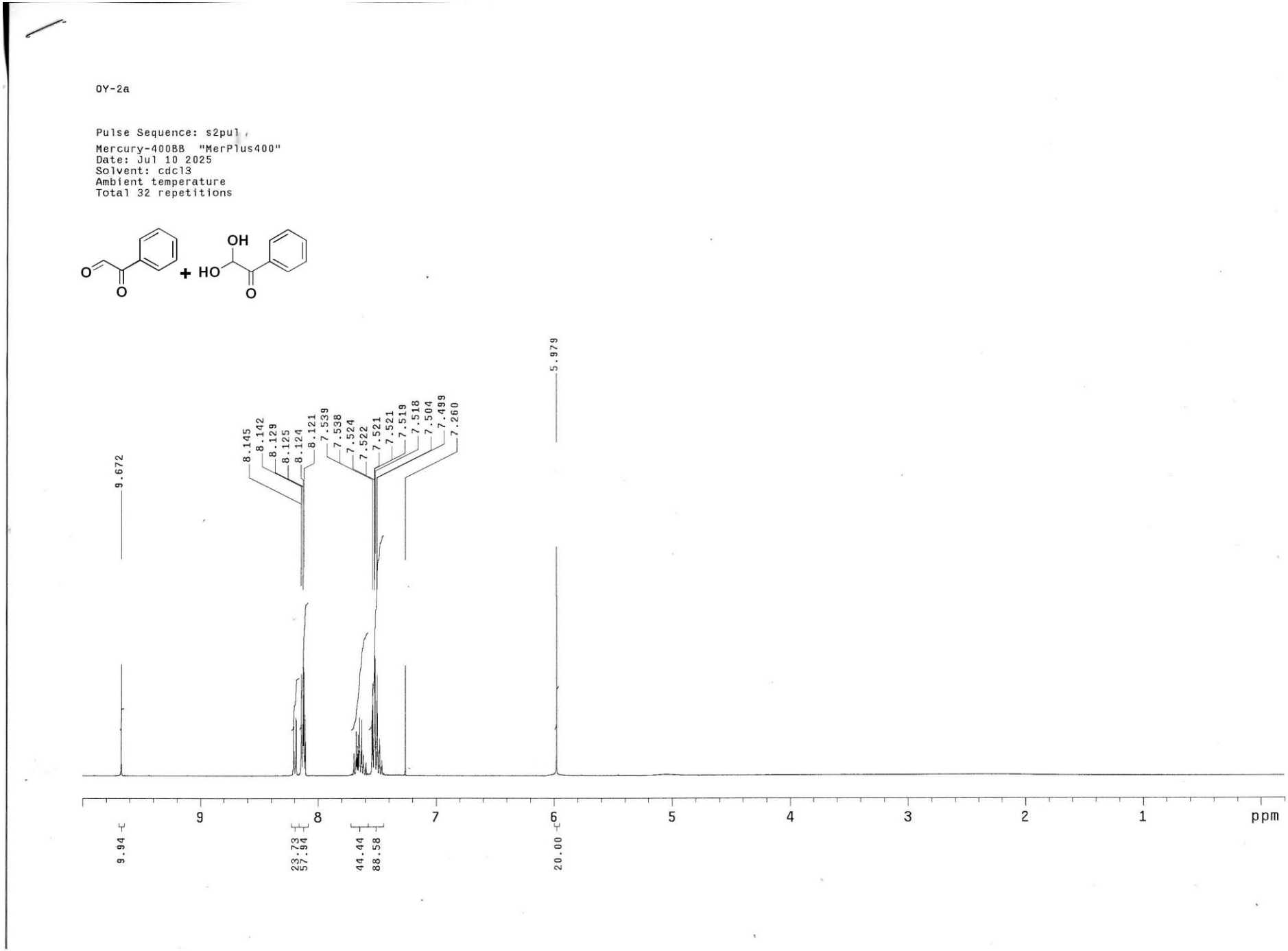
4-(4-Methoxyphenyl)-2,7-diphenylpyrazolo[1,5-*d*][1,2,4]triazine (8). Benzhydrazide (140 mg, 1.0 mmol) was added to a stirred solution of butene-1,4-dione **4a'** (133 mg, 0.5 mmol) in dioxane (10 mL) at 25 ^{o}C. The reaction mixture was stirred at reflux for 40 h and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 30/1~1/1) afforded **8**. Yield = 70% (132 mg); White solid; mp = 201-203 ^{o}C

(recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{24}H_{19}N_4O$ 379.1559, found 379.1567; ^1H NMR (600 MHz, $CDCl_3$): δ 8.68 (d, *J* = 7.2 Hz, 2H), 8.23 (br s, 2H), 8.05 (br d, *J* = 10.2 Hz, 2H), 7.67-7.63 (m, 3H), 7.52-7.47 (m, 4H), 7.17 (br s, 2H), 3.95 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 163.0, 157.2, 151.7, 147.2, 134.4, 132.3, 131.8, 130.9, 130.7 (2x), 130.6, 130.2 (2x), 129.9, 129.1 (2x), 128.5 (2x), 128.4, 127.3 (2x), 115.0 (2x), 55.8. Single-crystal X-Ray diagram: crystal of compound **8** was grown by slow diffusion of EtOAc into a solution of compound **8** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group $P2_1/c$, *a* = 11.1986(2) Å, *b* = 7.45530(10) Å, *c* = 21.8767(3) Å, *V* = 1824.14(5) $Å^3$, *Z* = 4, d_{calcd} = 1.378 g/cm^3, *F*(000) = 792.0, 2*θ* range 3.728~53.986°, R indices (all data) R1 = 0.0441, wR2 = 0.0997.

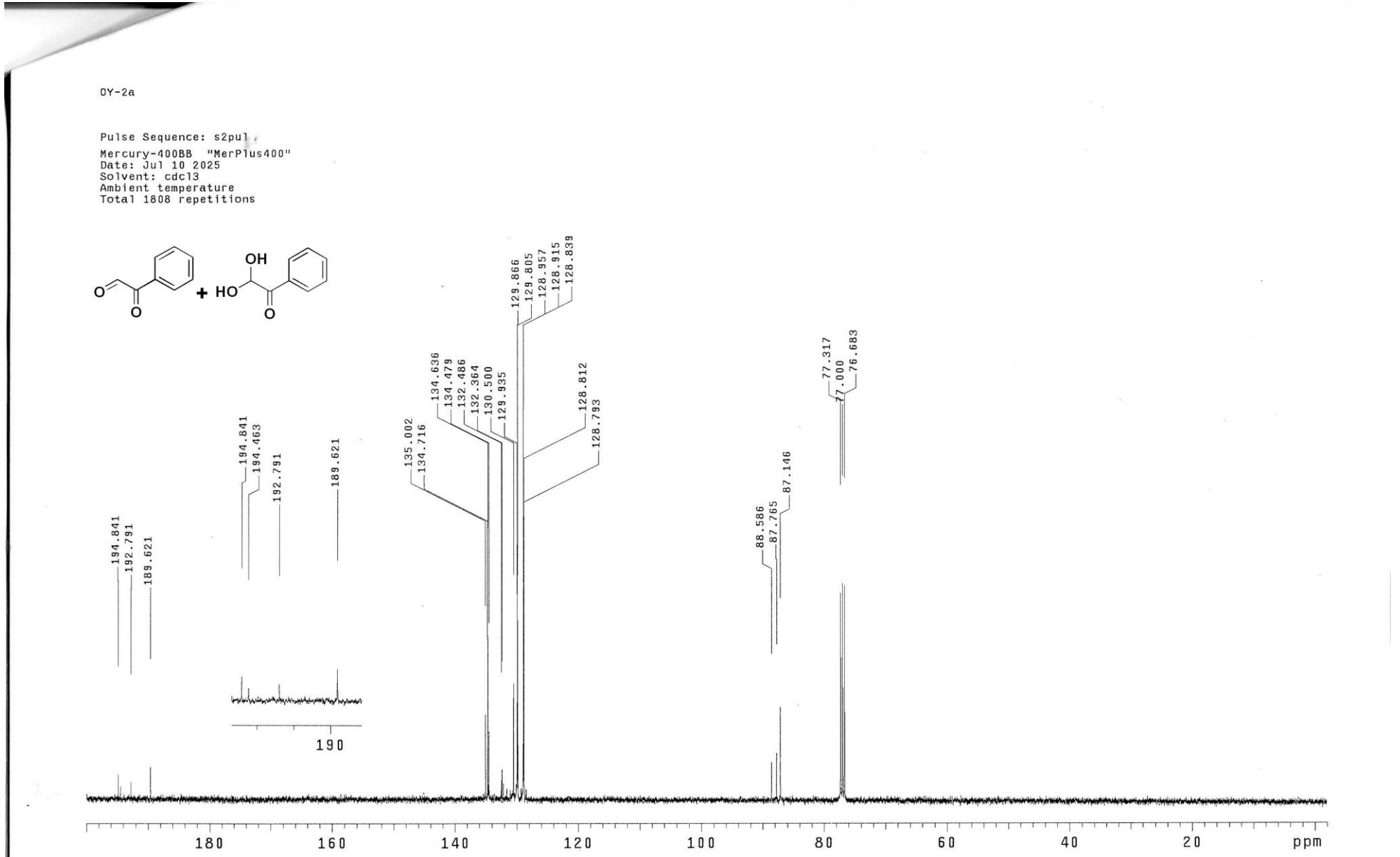


Gram-scale synthetic procedure of compound 5a is as follows: SeO_2 (2.22 g, 10.0 mmol) was added to a solution of acetophenone **1a** (600 mg, 5.0 mmol) in dioxane (50 mL) at 25 °C. The reaction mixture was stirred at reflux for 5 h and then cooled to 25 °C. The process was monitored by TLC until **1a** was consumed and phenylglyoxal **2a** were generated. Then, piperidine (420 mg, 5.0 mmol), HOAc (300 mg, 5.0 mmol) and **3a** (1.37 g, 5.0 mmol) in dioxane (50 mL) were added to the resulting reaction mixture at 25 °C. The reaction mixture was stirred at reflux for 20 h. The reaction mixture was cooled to 25 °C. Without further purification, excess $N_2H_{4(aq)}$ solution (~80%, 30 mL) was added to the resulting sulfonyl butene-1,4-dione **4a** at 25 °C. The reaction mixture was stirred at 25 °C for 10 h and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 30/1~2/1) afforded **5a** (1.16 g, 60%).

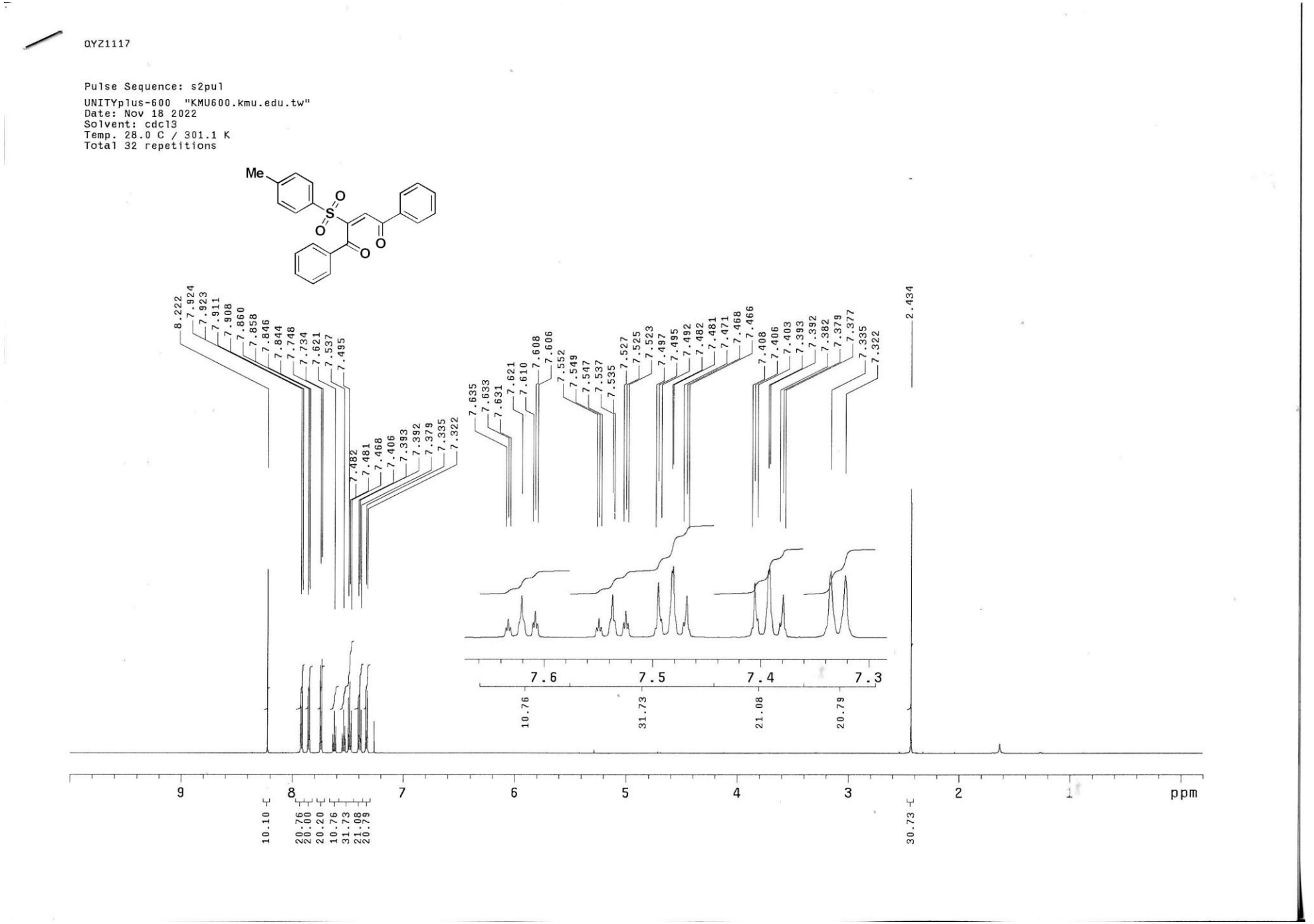
Compounds 2a/2a' (^{1}H-NMR spectral data)



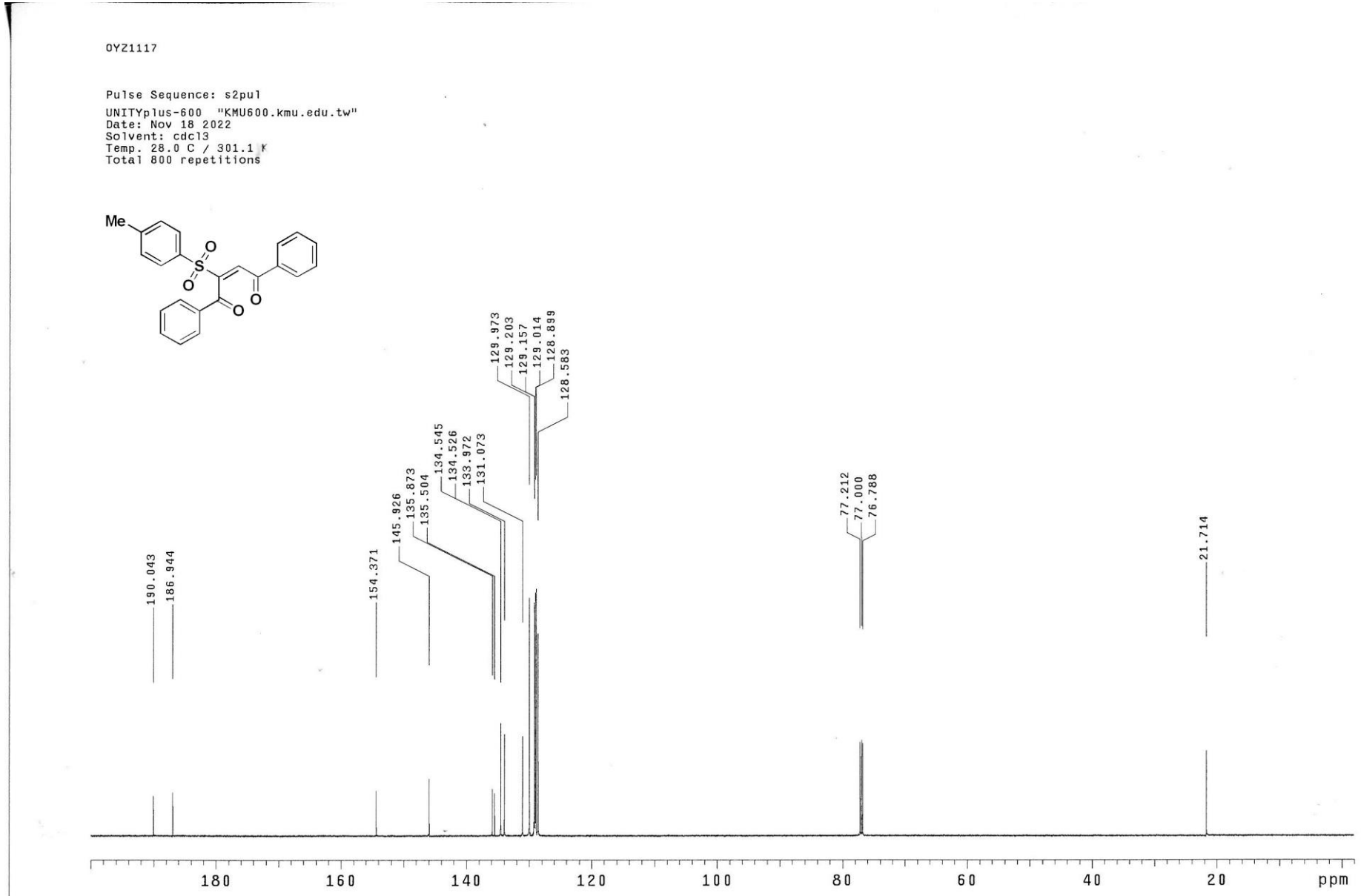
Compounds 2a/2a' (^{13}C-NMR spectral data)



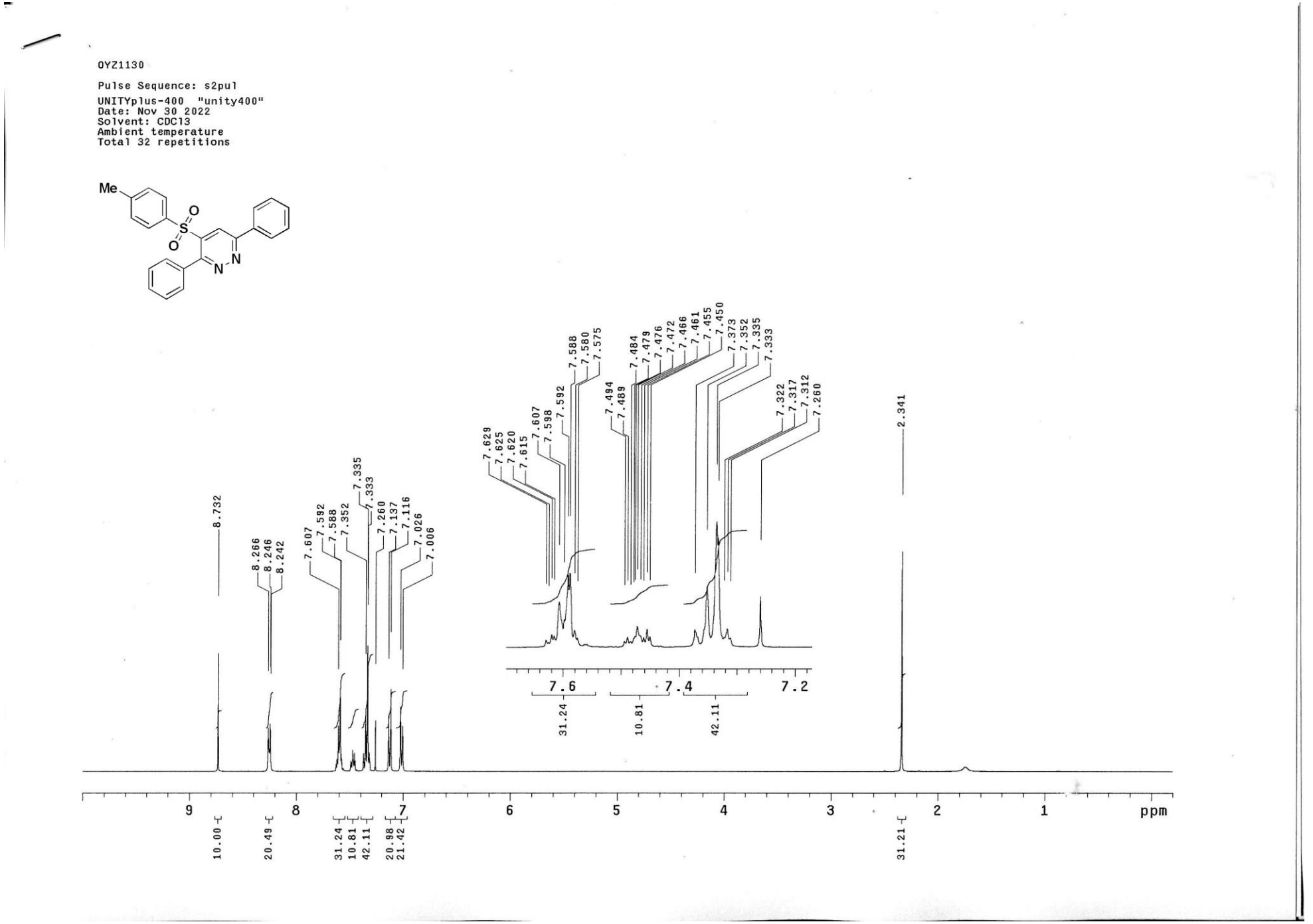
Compound 4a (^{1}H-NMR spectral data)



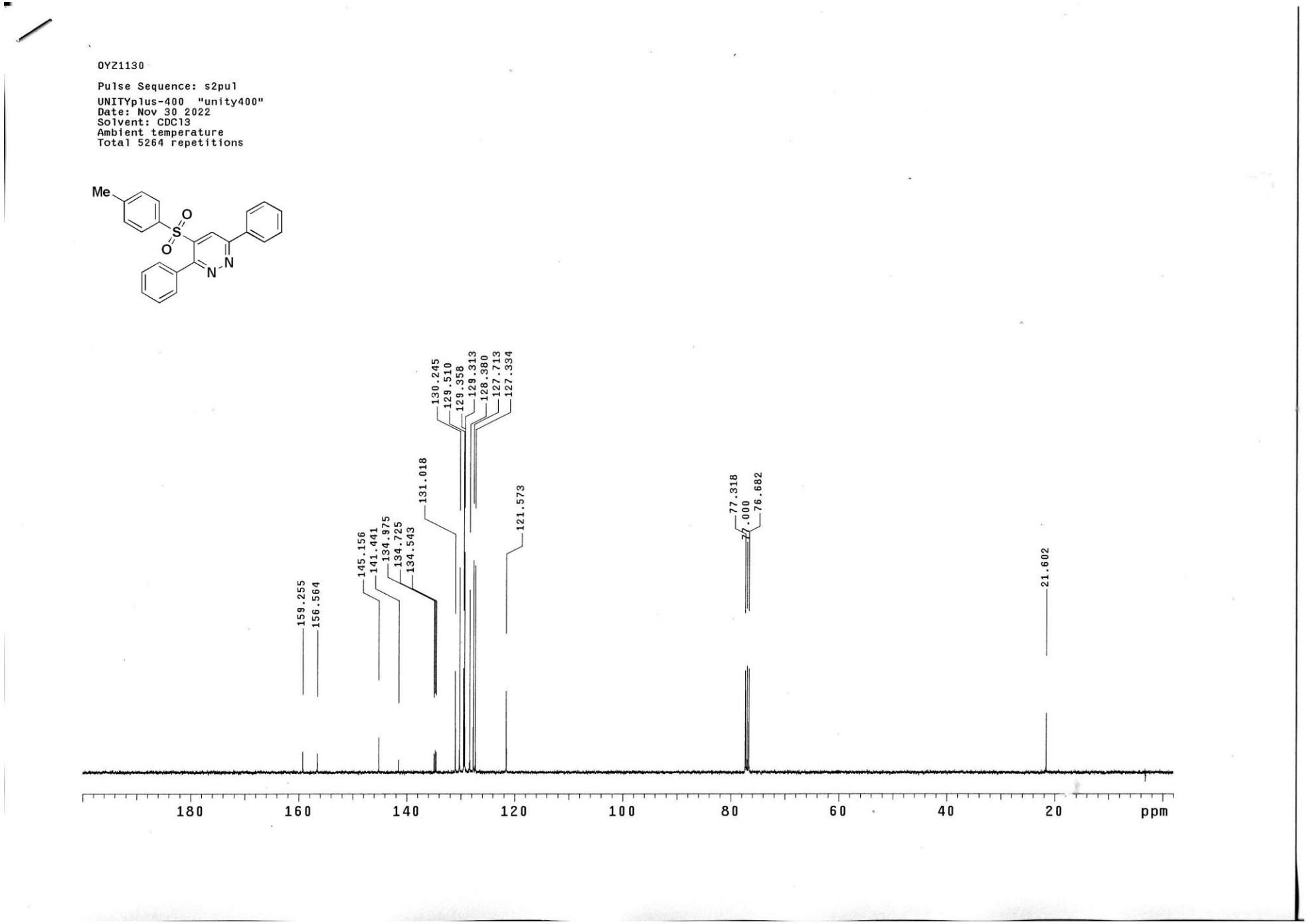
Compound 4a (^{13}C-NMR spectral data)



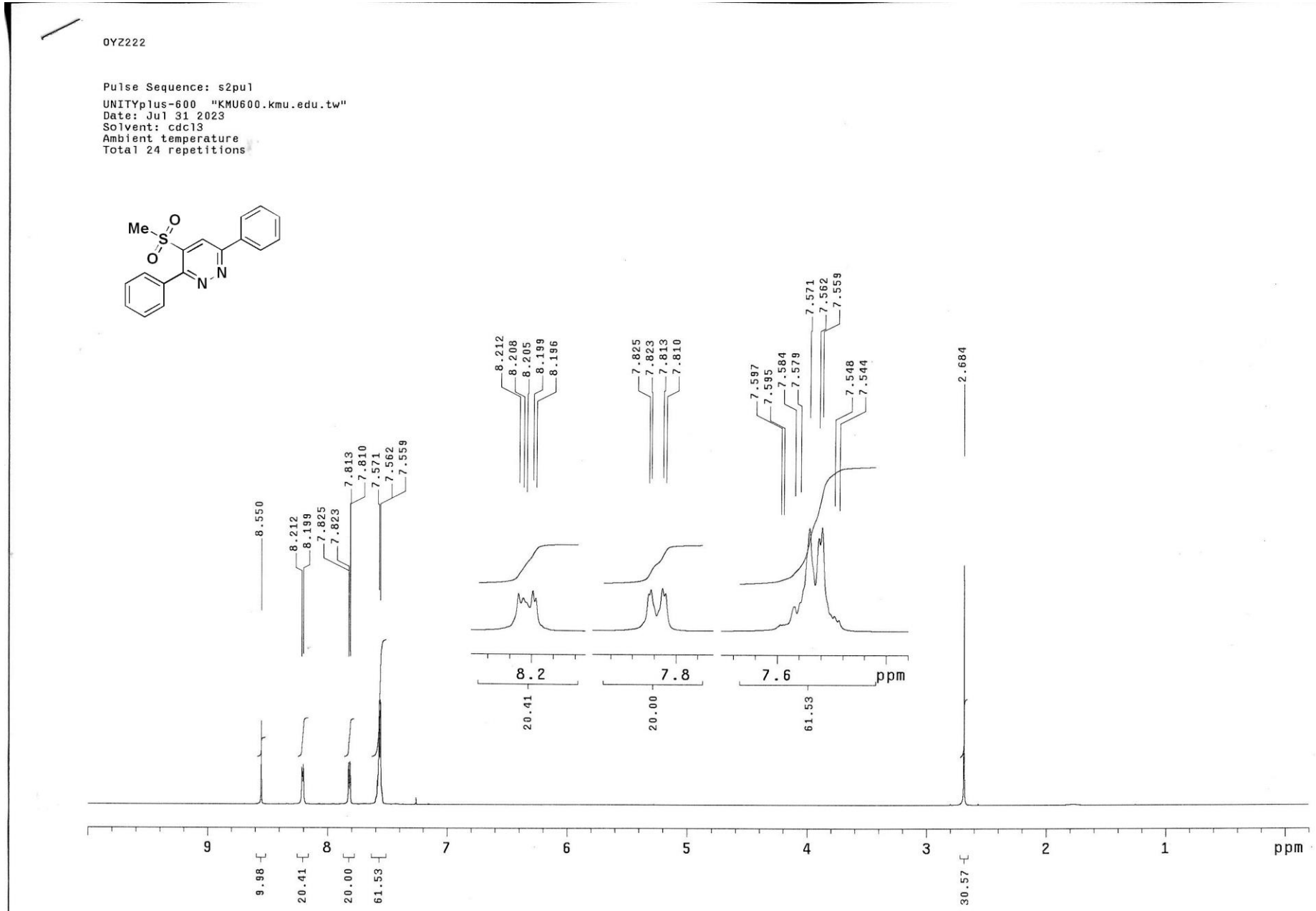
Compound 5a (^{1}H-NMR spectral data)



Compound 5a (^{13}C-NMR spectral data)



Compound 5b (^{1}H-NMR spectral data)

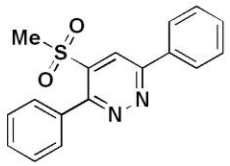


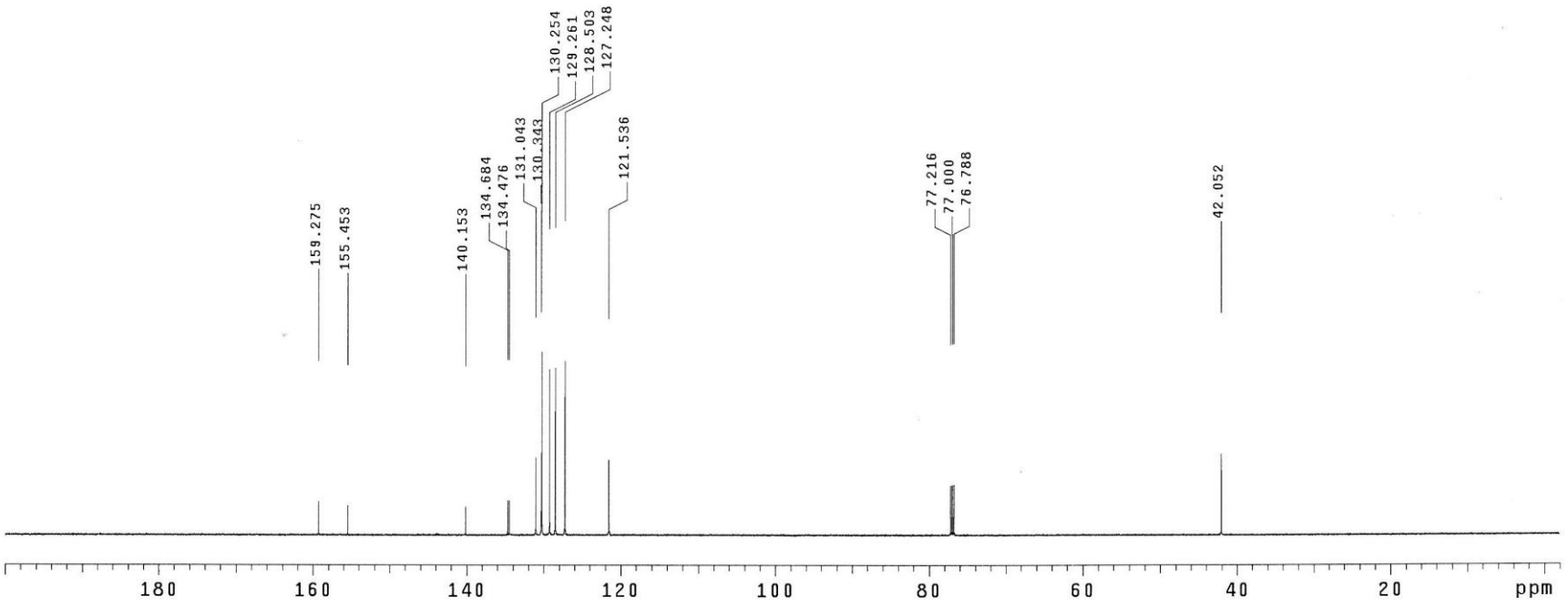
Compound 5b (^{13}C-NMR spectral data)

OYZ222

Pulse Sequence: s2pul

UNITYplus-600 "KMU600.kmu.edu.tw"
Date: Jul 31 2023
Solvent: cdcl3
Ambient temperature
Total 184 repetitions



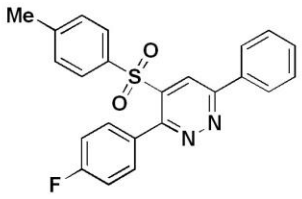


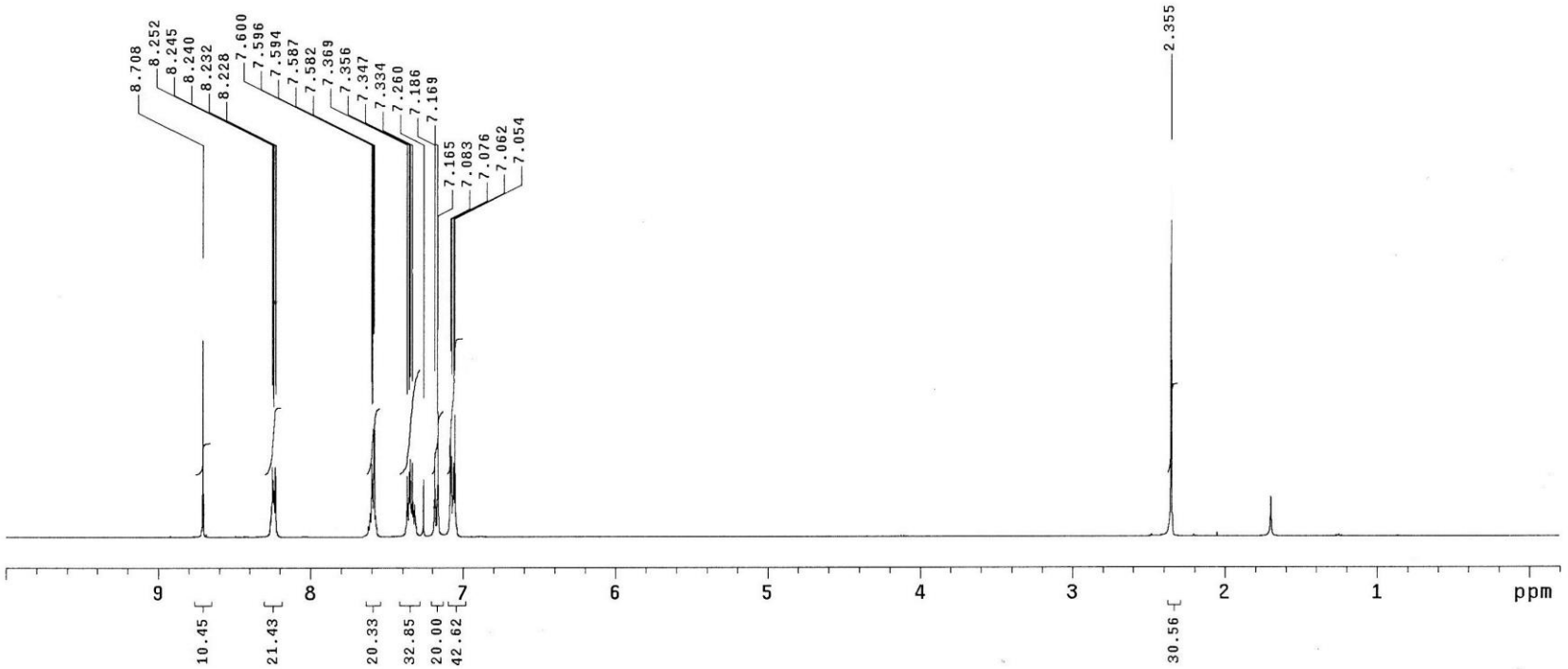
Compound 5c (^{1}H-NMR spectral data)

OYZ1201

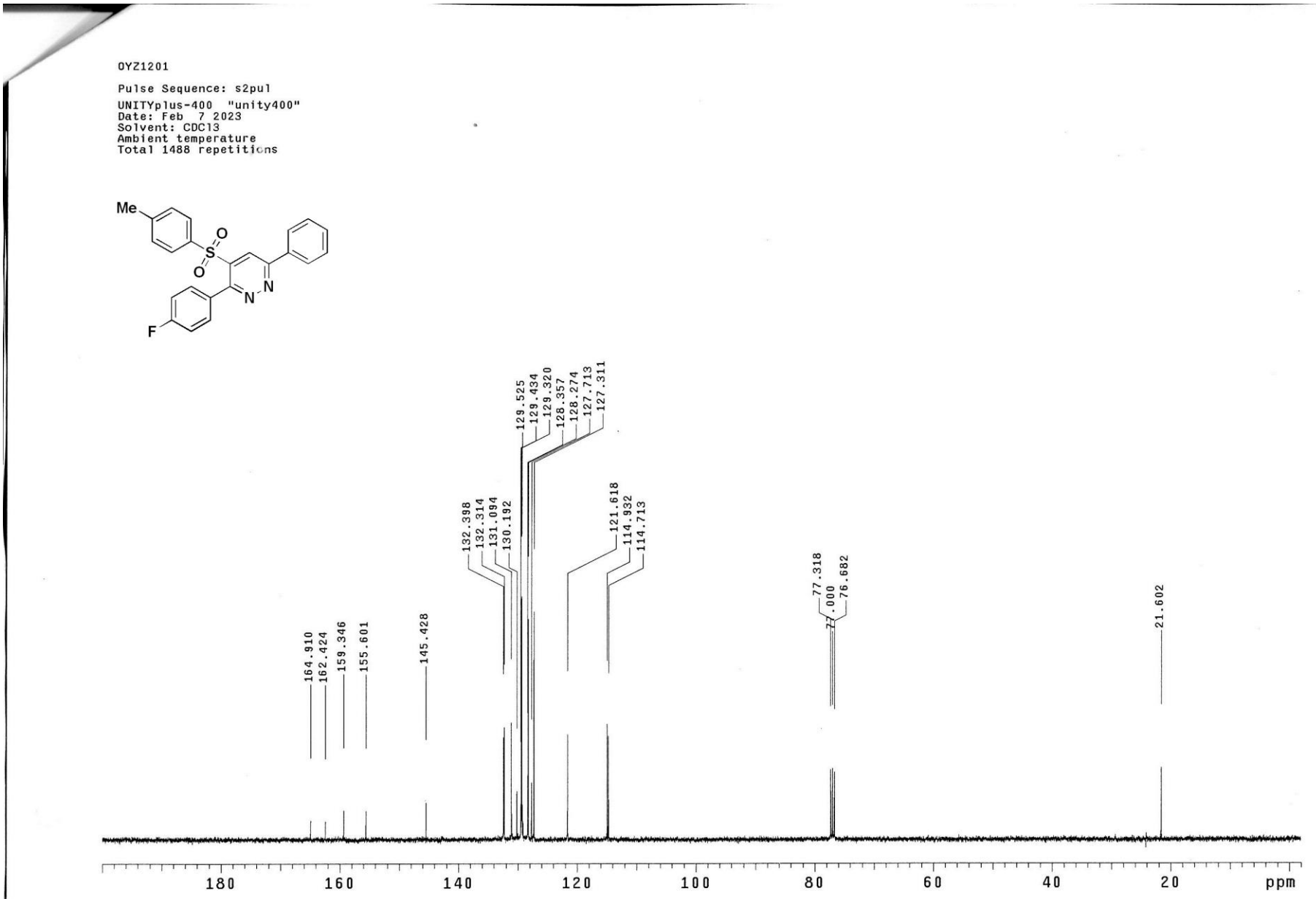
Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Feb 7 2023
Solvent: CDCl3
Ambient temperature
Total 32 repetitions

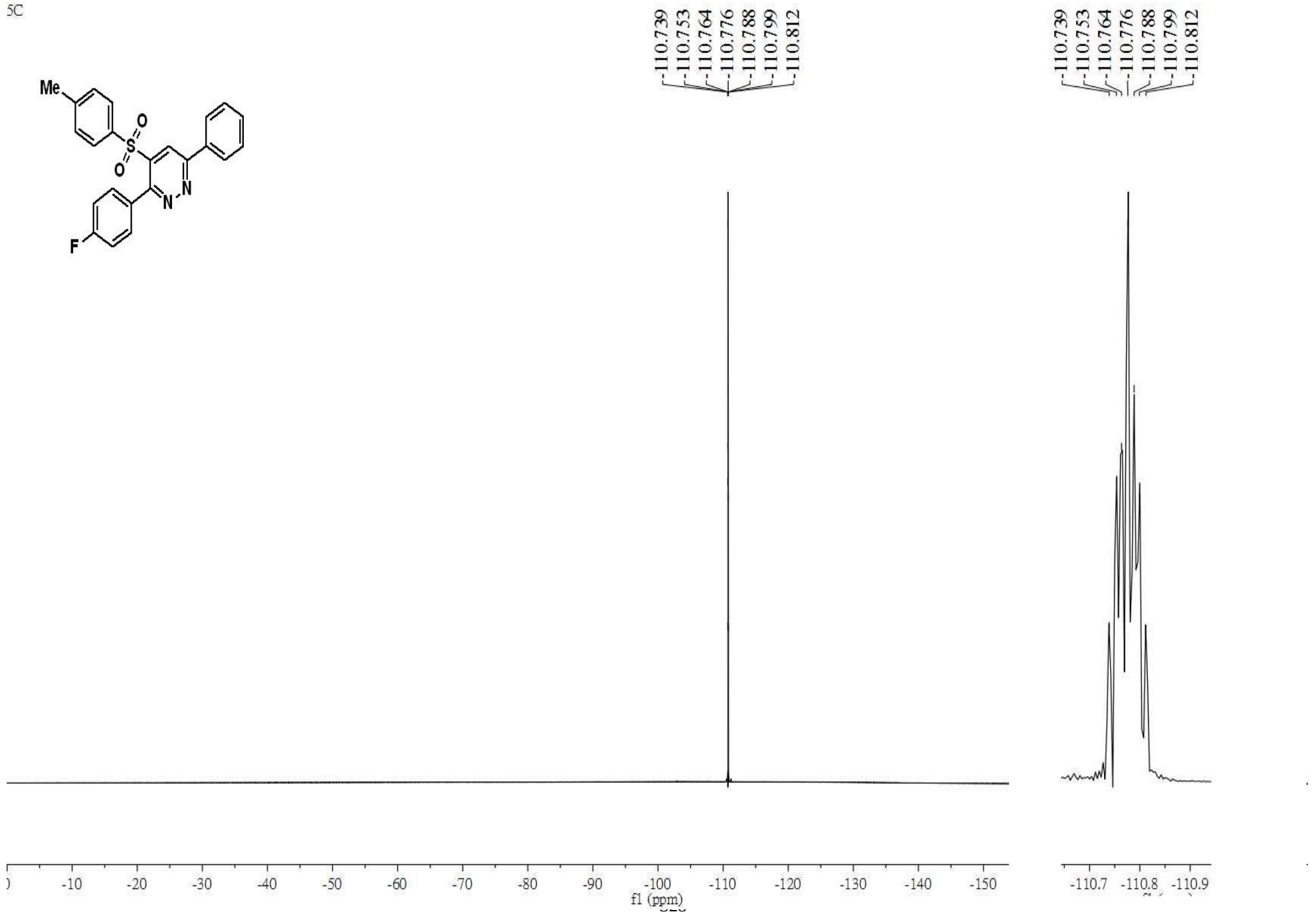




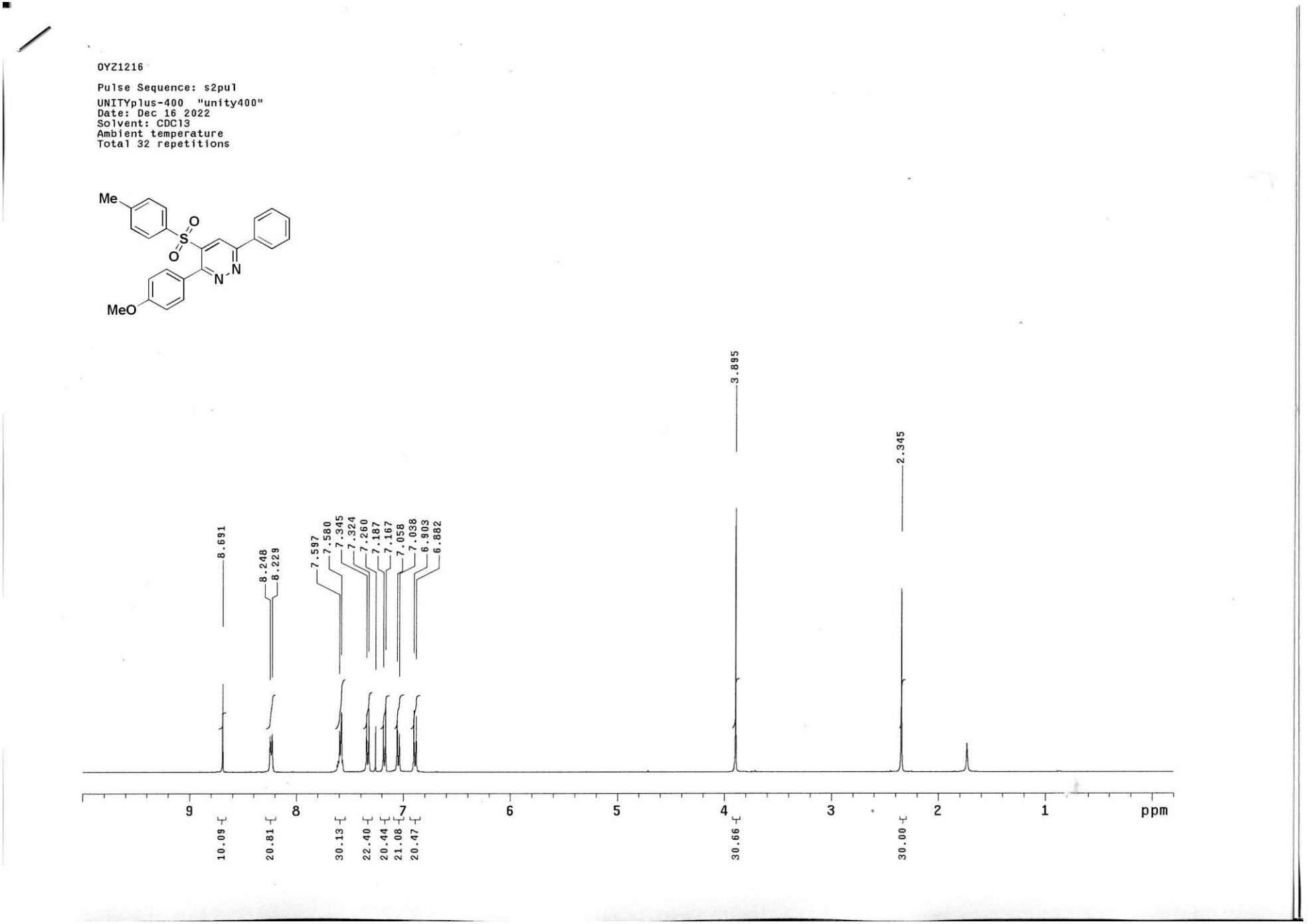
Compound 5c (^{13}C-NMR spectral data)



Compound 5c (^{19}F-NMR spectral data)



Compound 5d (^{1}H-NMR spectral data)

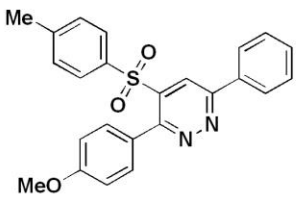


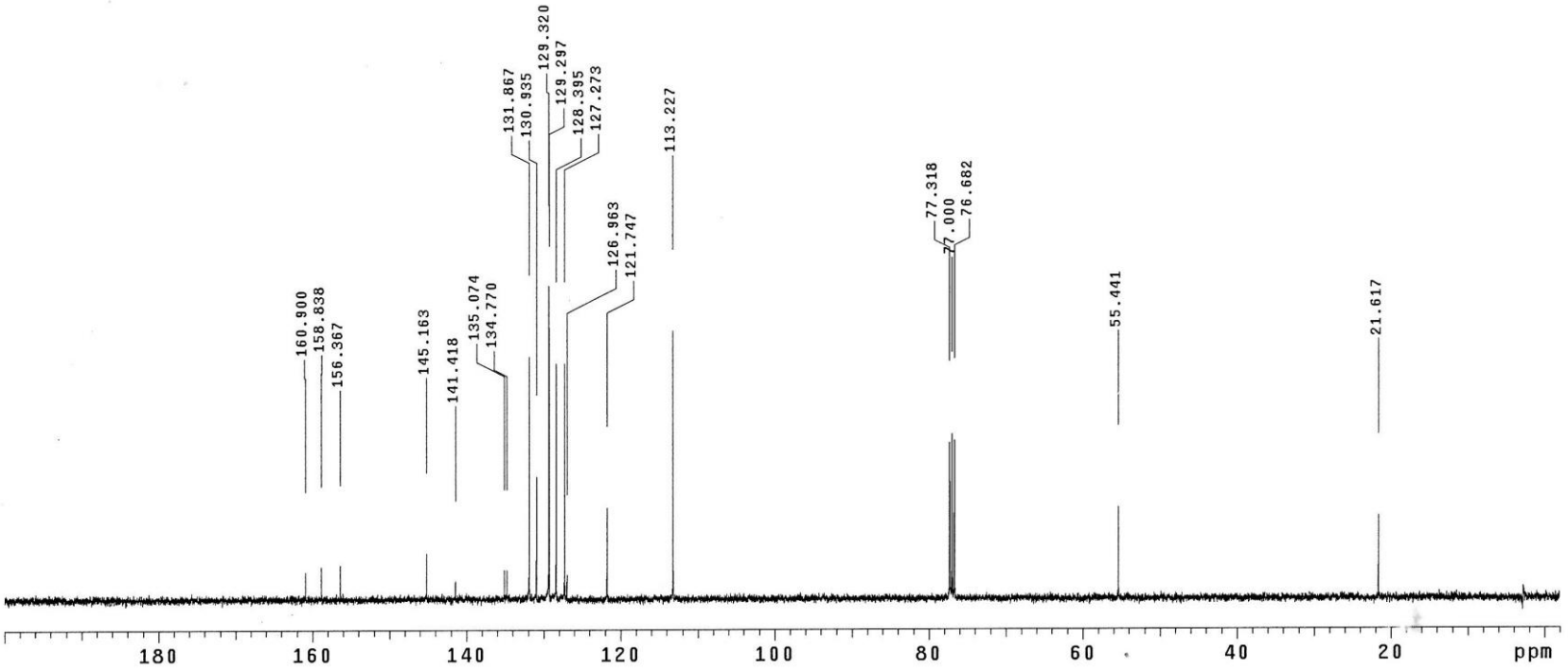
Compound 5d (^{13}C-NMR spectral data)

OYZ1216

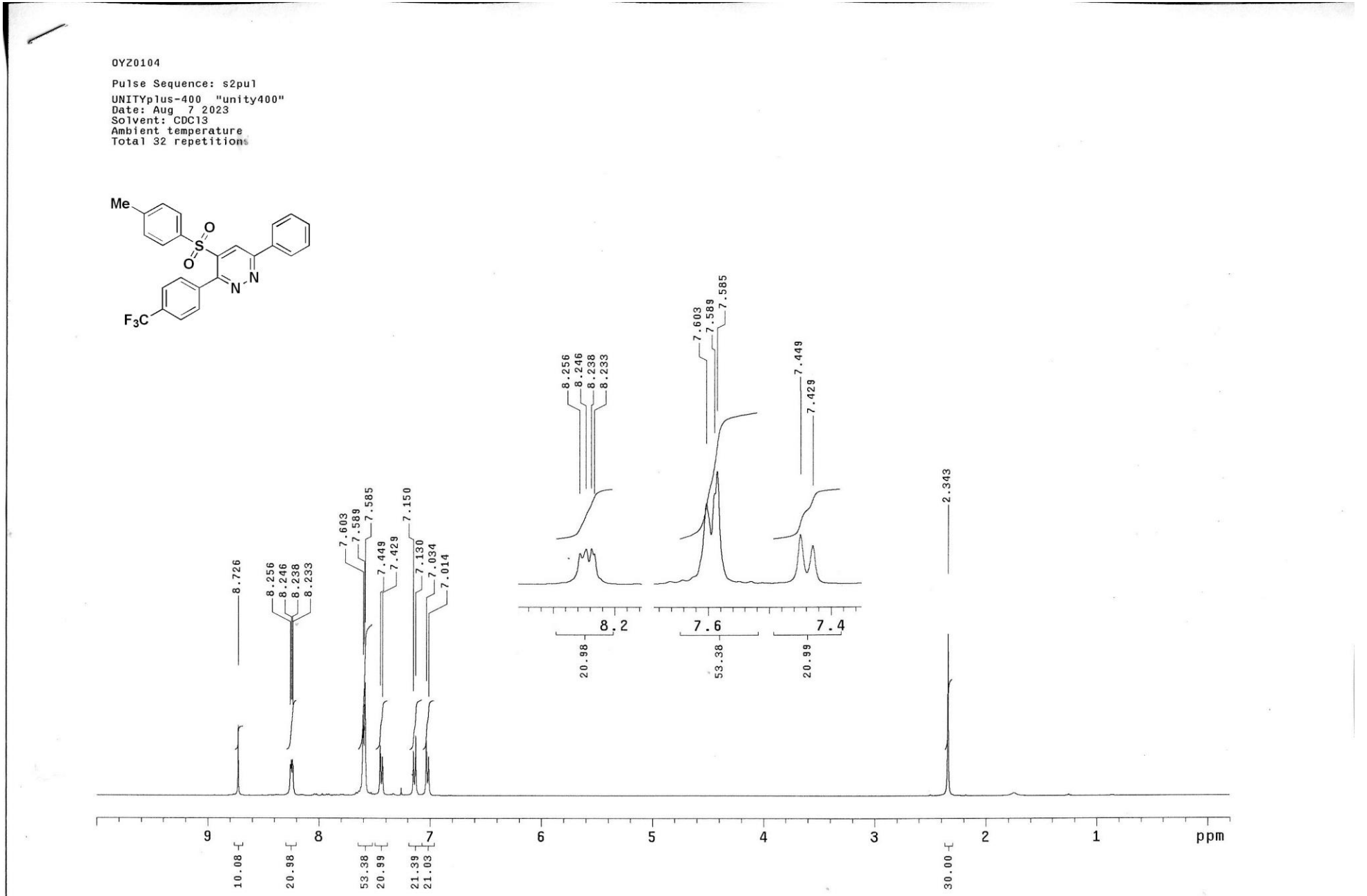
Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Dec 16 2022
Solvent: CDCl3
Ambient temperature
Total 2832 repetitions

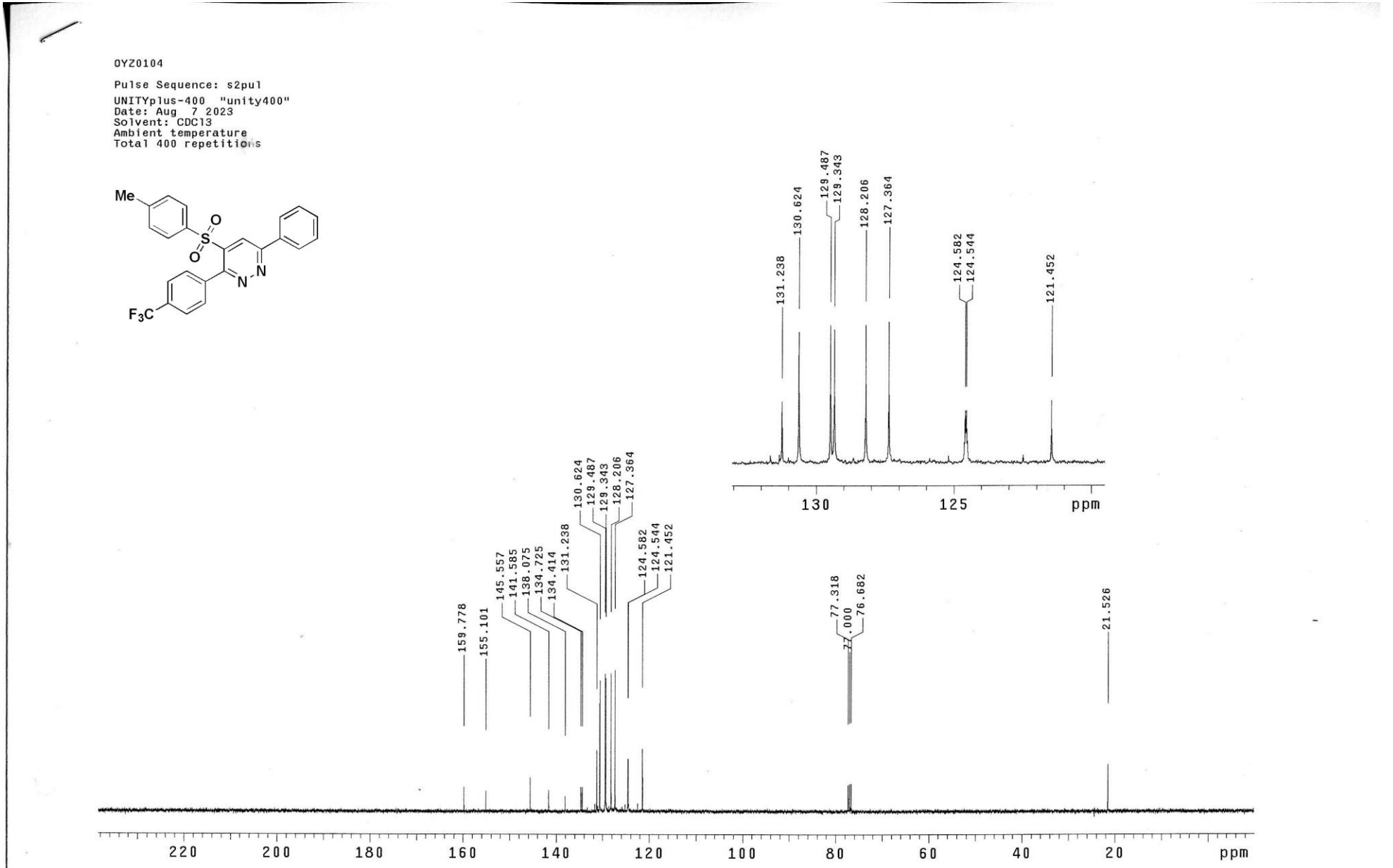




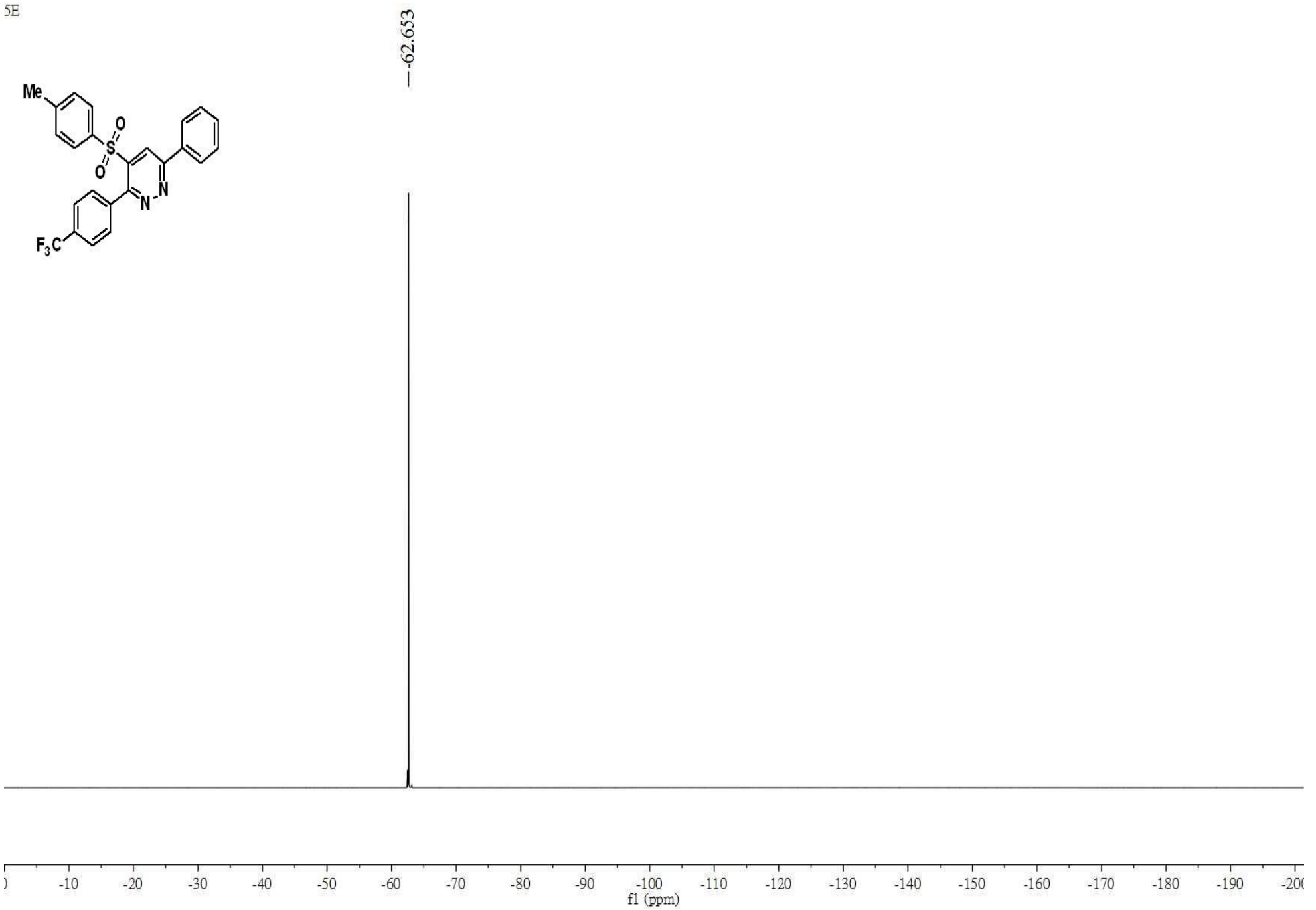
Compound 5e (^{1}H-NMR spectral data)



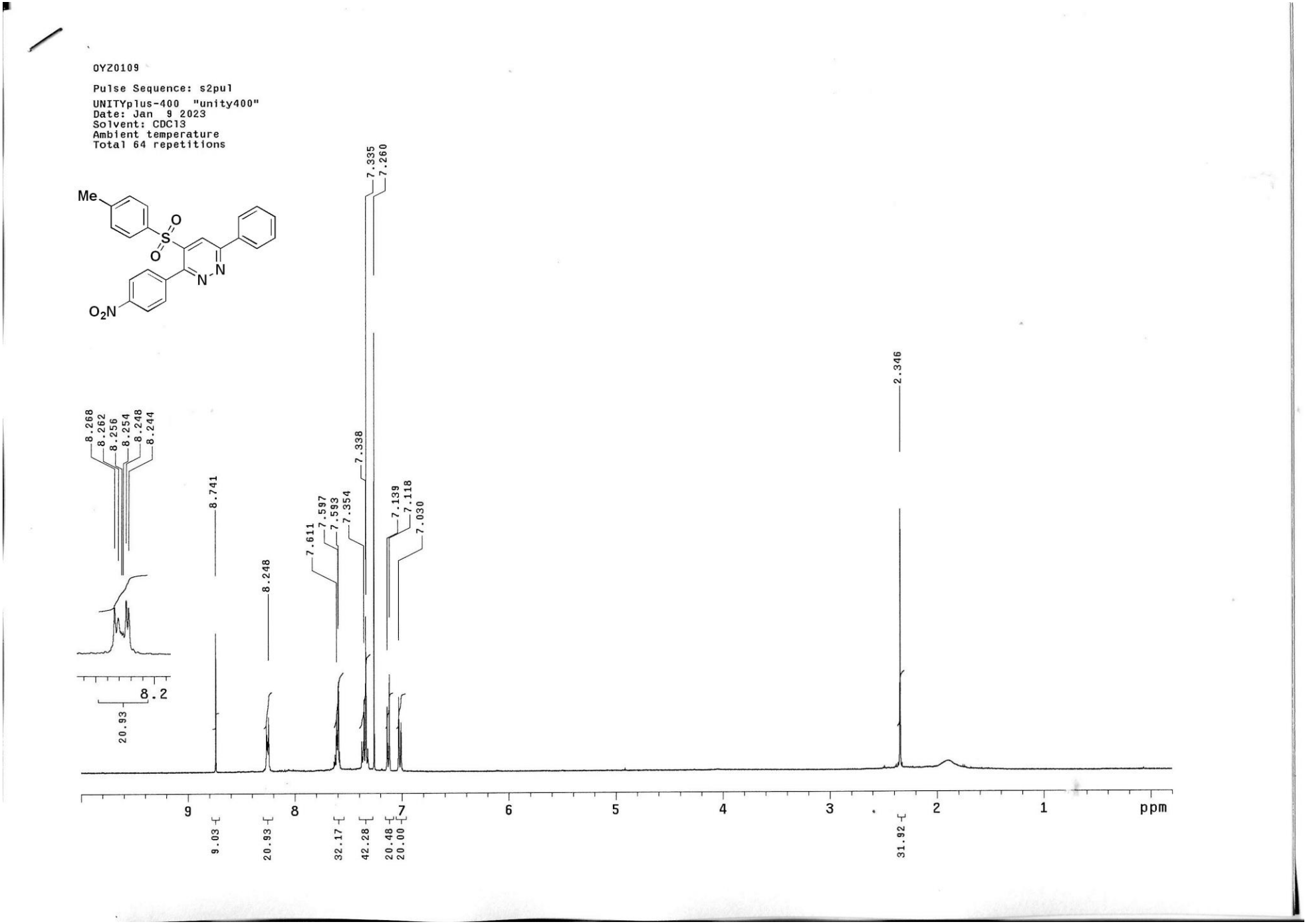
Compound 5e (^{13}C-NMR spectral data)



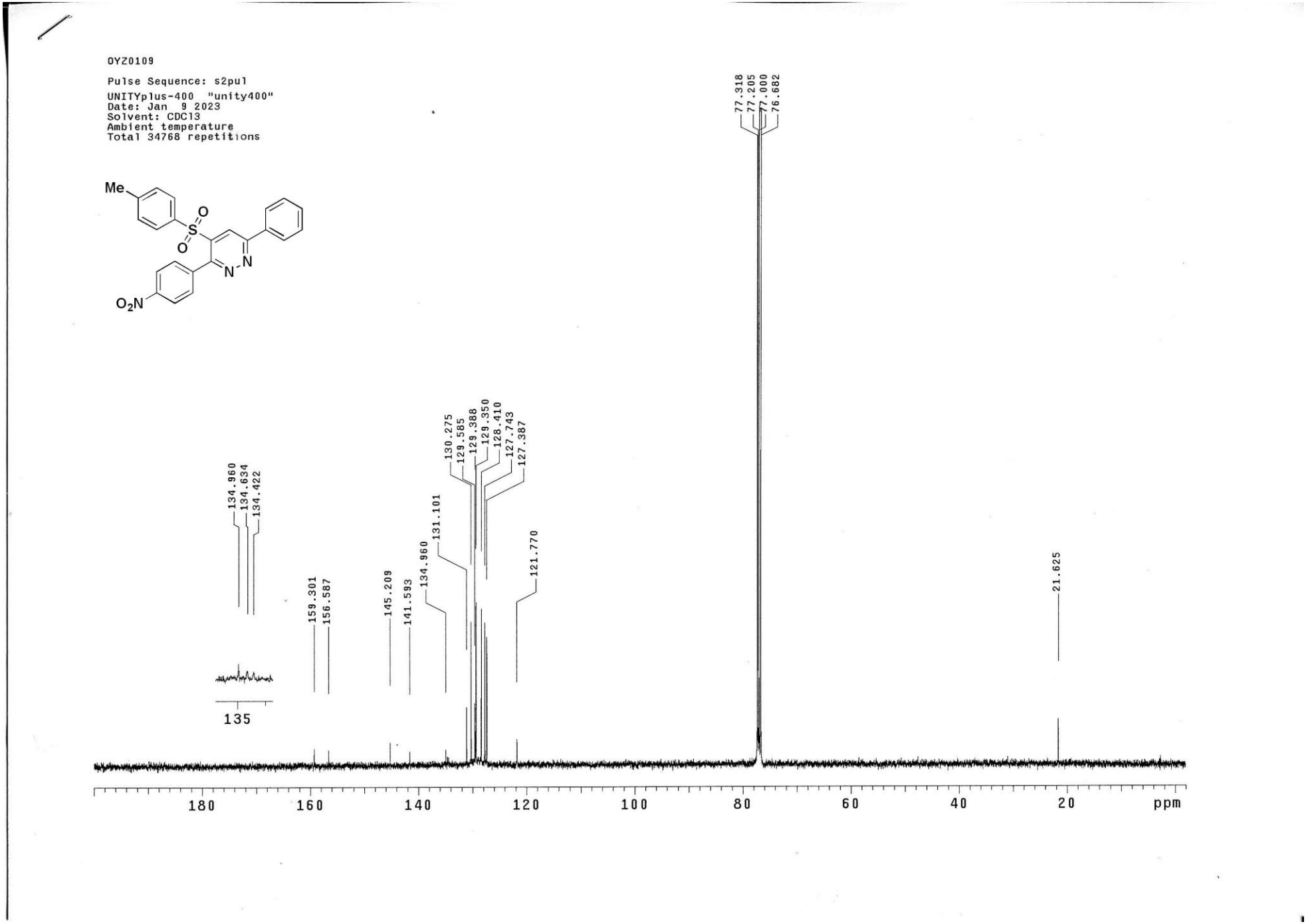
Compound 5e (^{19}F-NMR spectral data)



Compound 5f (^{1}H-NMR spectral data)



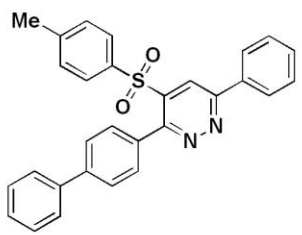
Compound 5f (^{13}C-NMR spectral data)

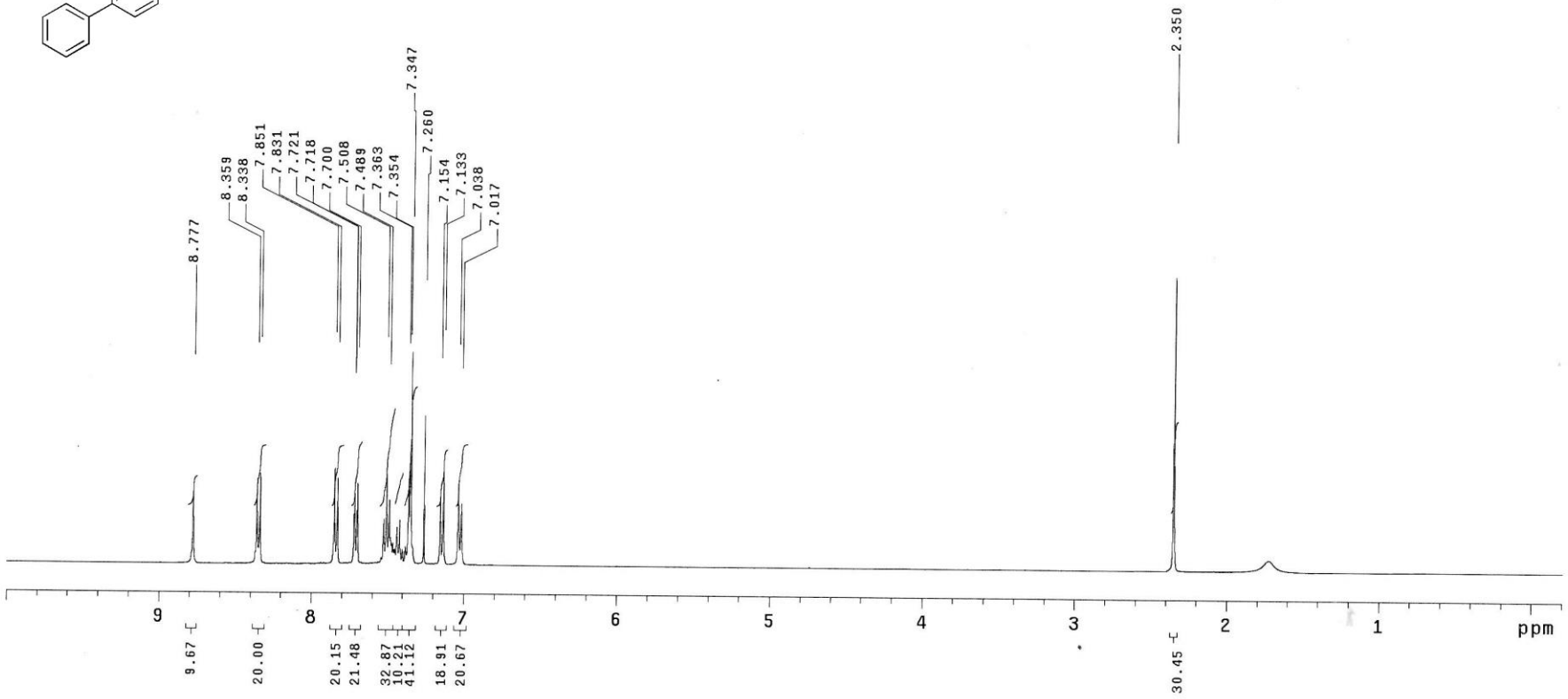


Compound 5g (^{1}H-NMR spectral data)

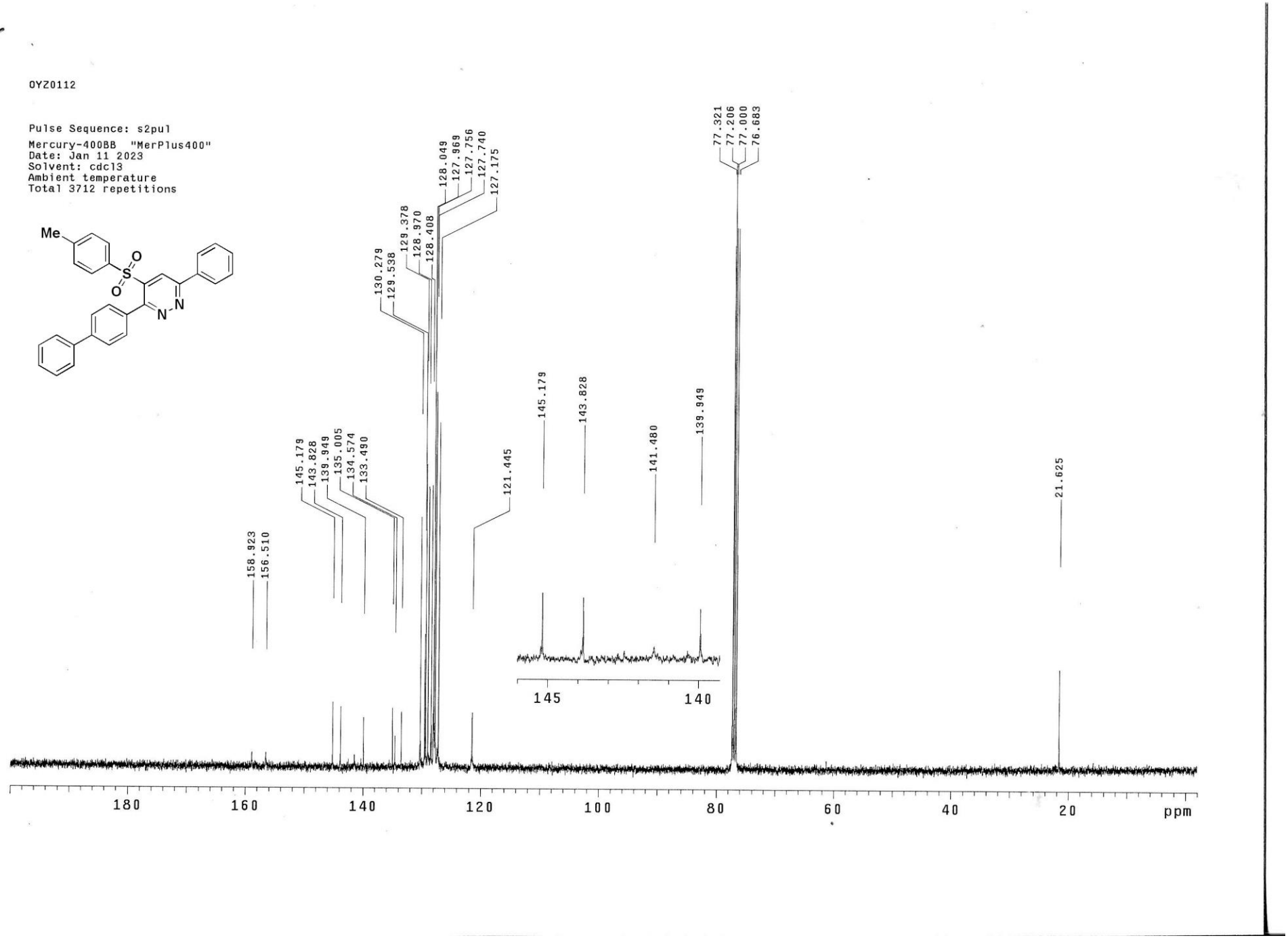
OYZ0112

Pulse Sequence: s2pul
Mercury-400BB "MerPlus400"
Date: Jan 11 2023
Solvent: cdcl3
Ambient temperature
Total 32 repetitions





Compound 5g (^{13}C-NMR spectral data)

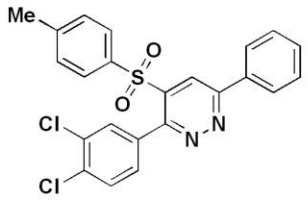


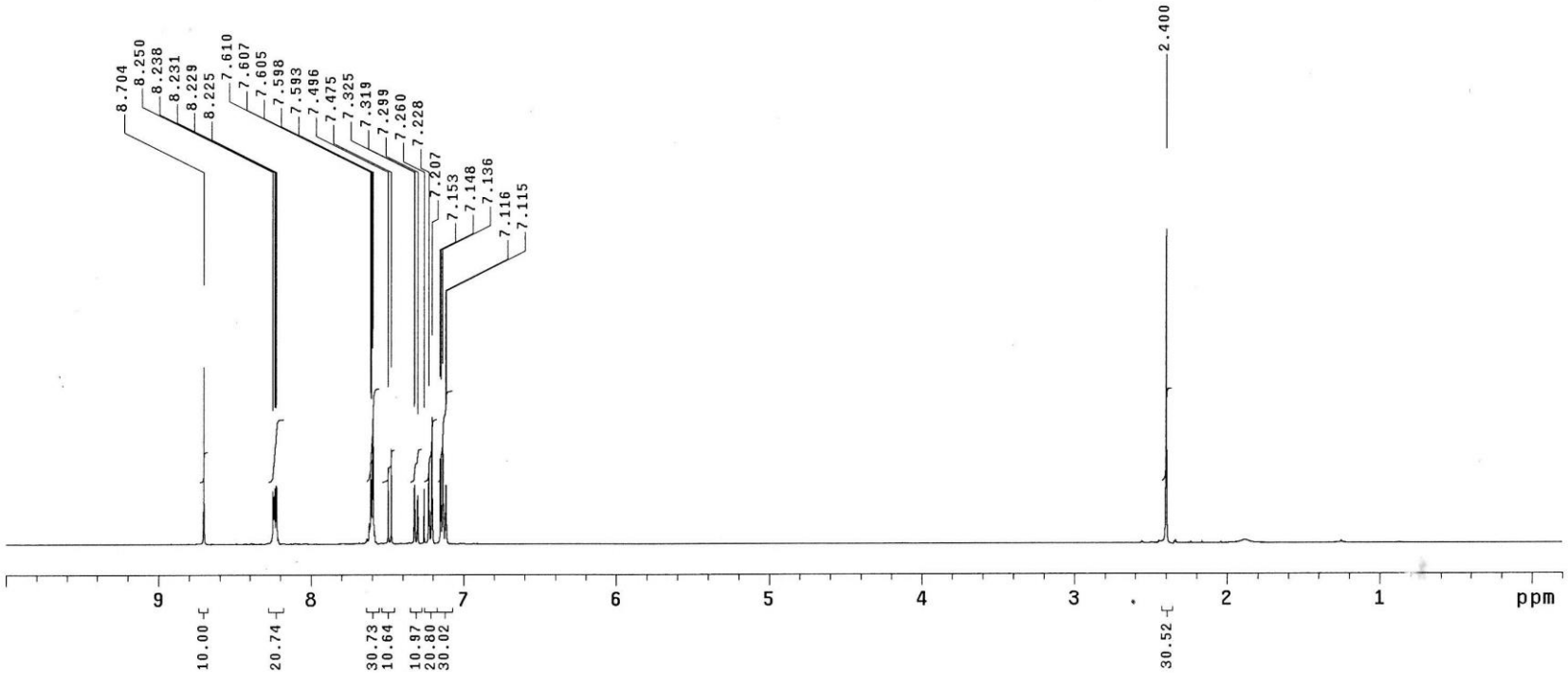
Compound 5h (^{1}H-NMR spectral data)

OYZ0110

Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Jan 10 2023
Solvent: CDCl3
Ambient temperature
Total 32 repetitions



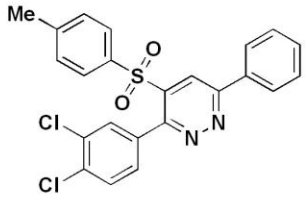


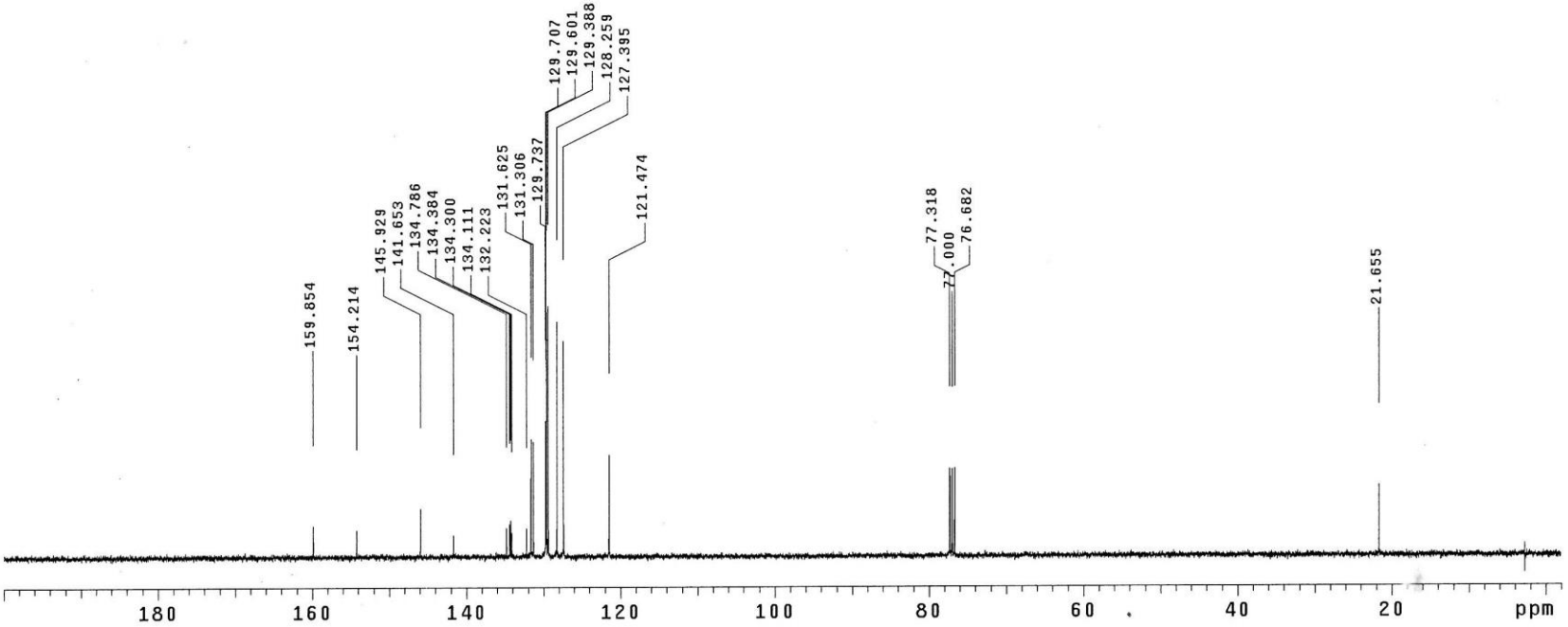
Compound 5h (^{13}C-NMR spectral data)

OYZ0110

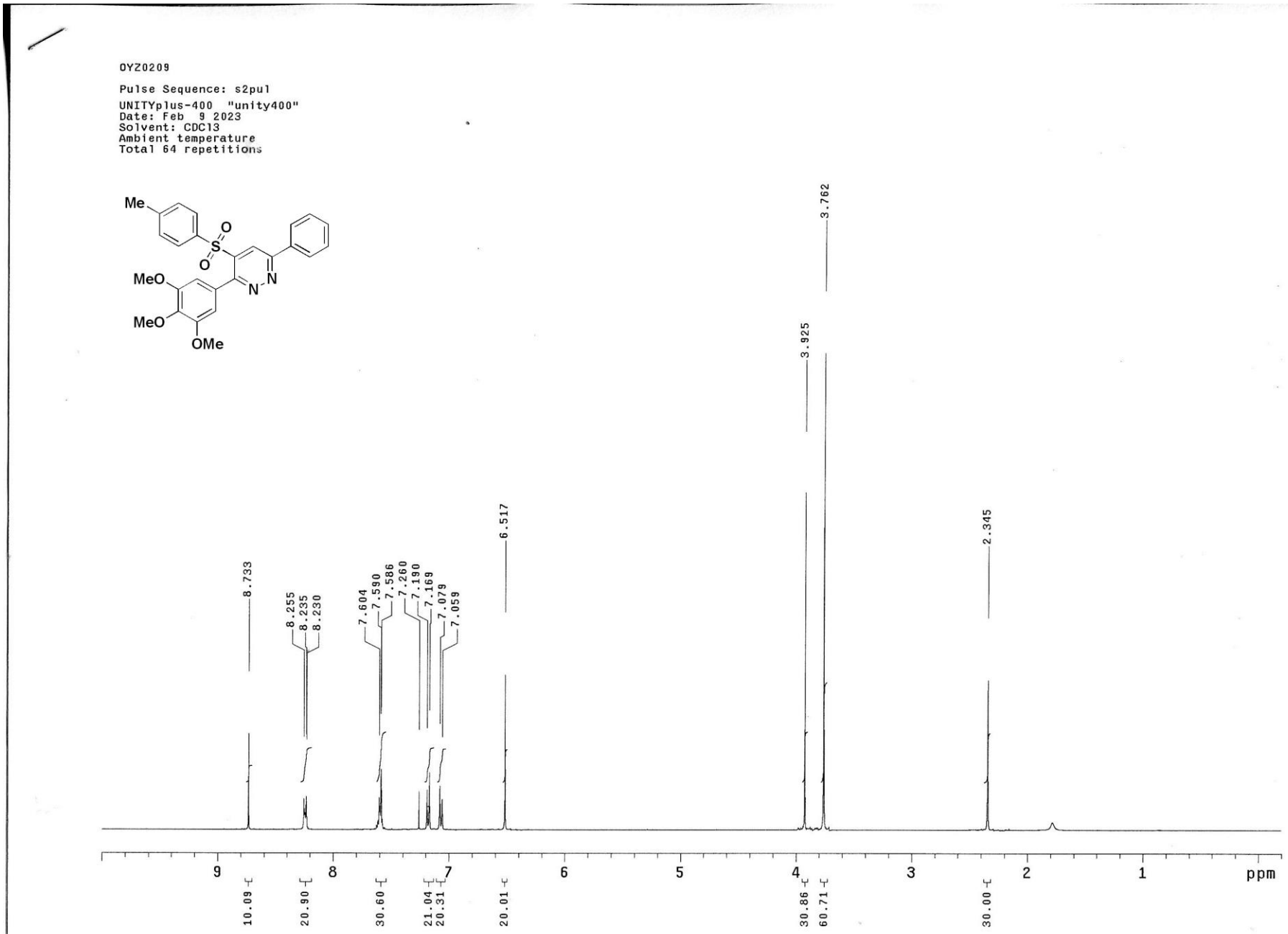
Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Jan 10 2023
Solvent: CDCl3
Ambient temperature
Total 1024 repetitions





Compound 5i (^{1}H-NMR spectral data)

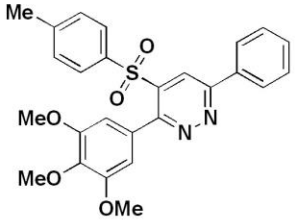


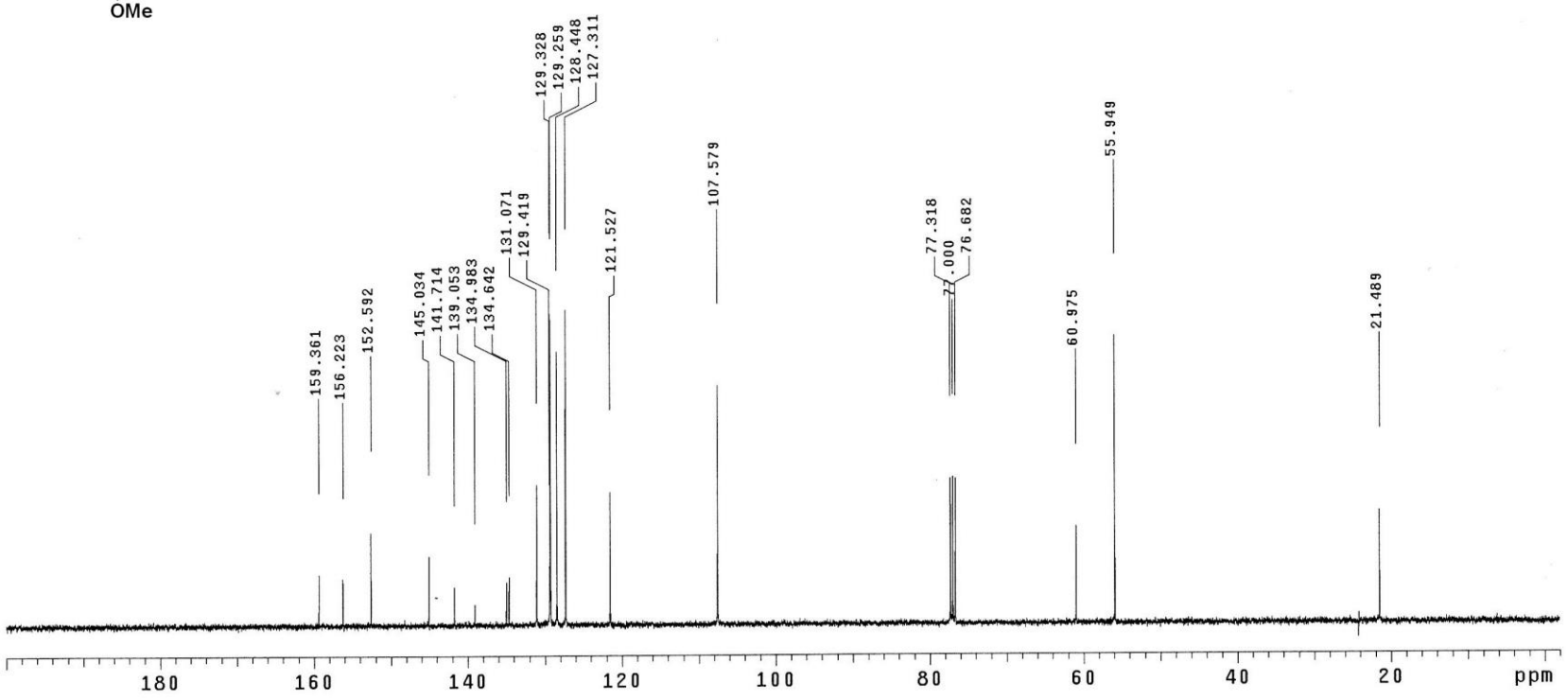
Compound 5i (^{13}C-NMR spectral data)

OYZ0209

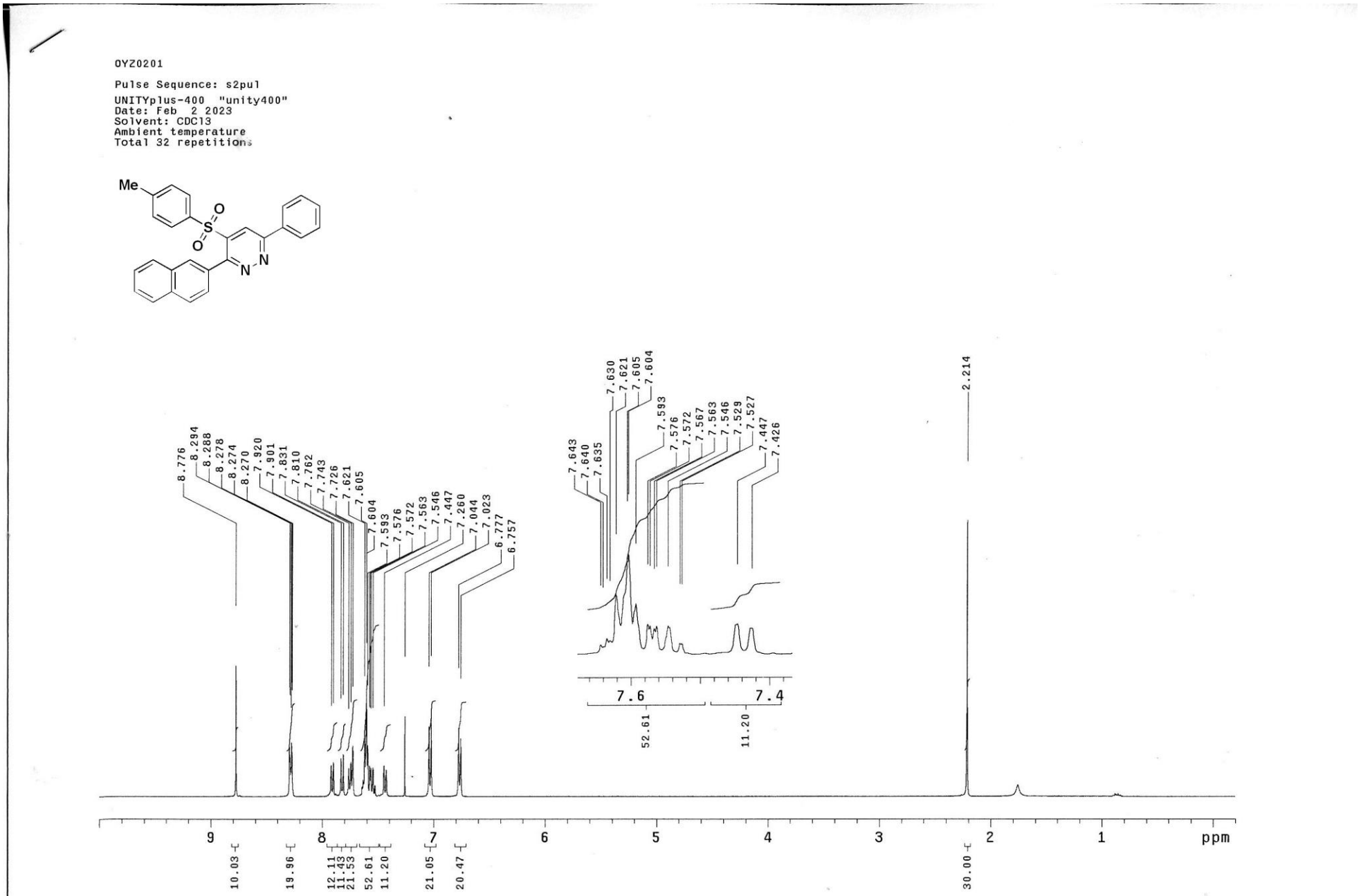
Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Feb 9 2023
Solvent: CDCl3
Ambient temperature
Total 3408 repetitions





Compound 5j (^{1}H-NMR spectral data)

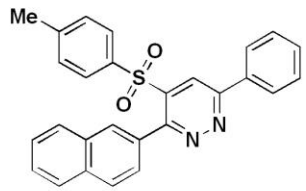


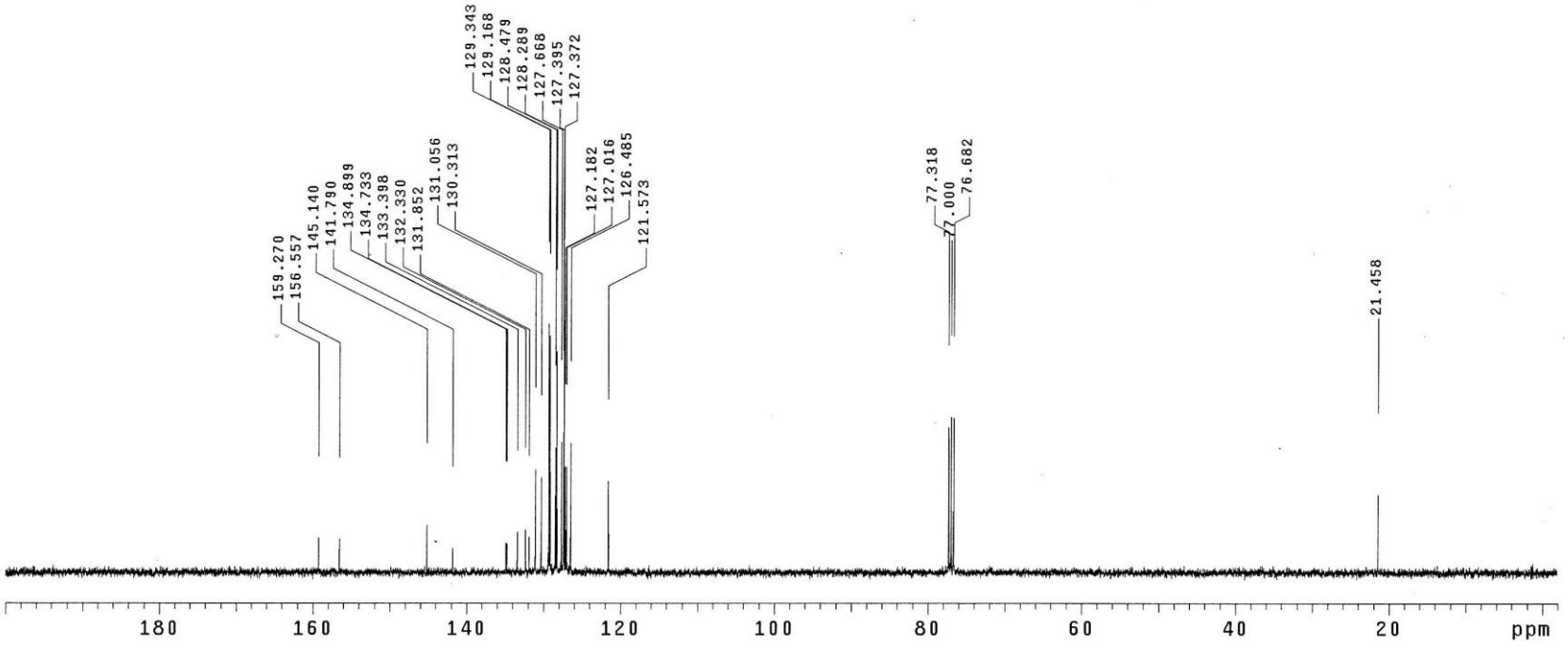
Compound 5j (^{13}C-NMR spectral data)

OYZ0201

Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Feb 2 2023
Solvent: CDCl3
Ambient temperature
Total 2080 repetitions



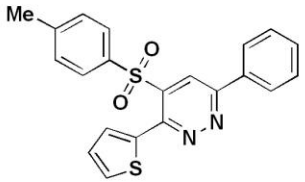


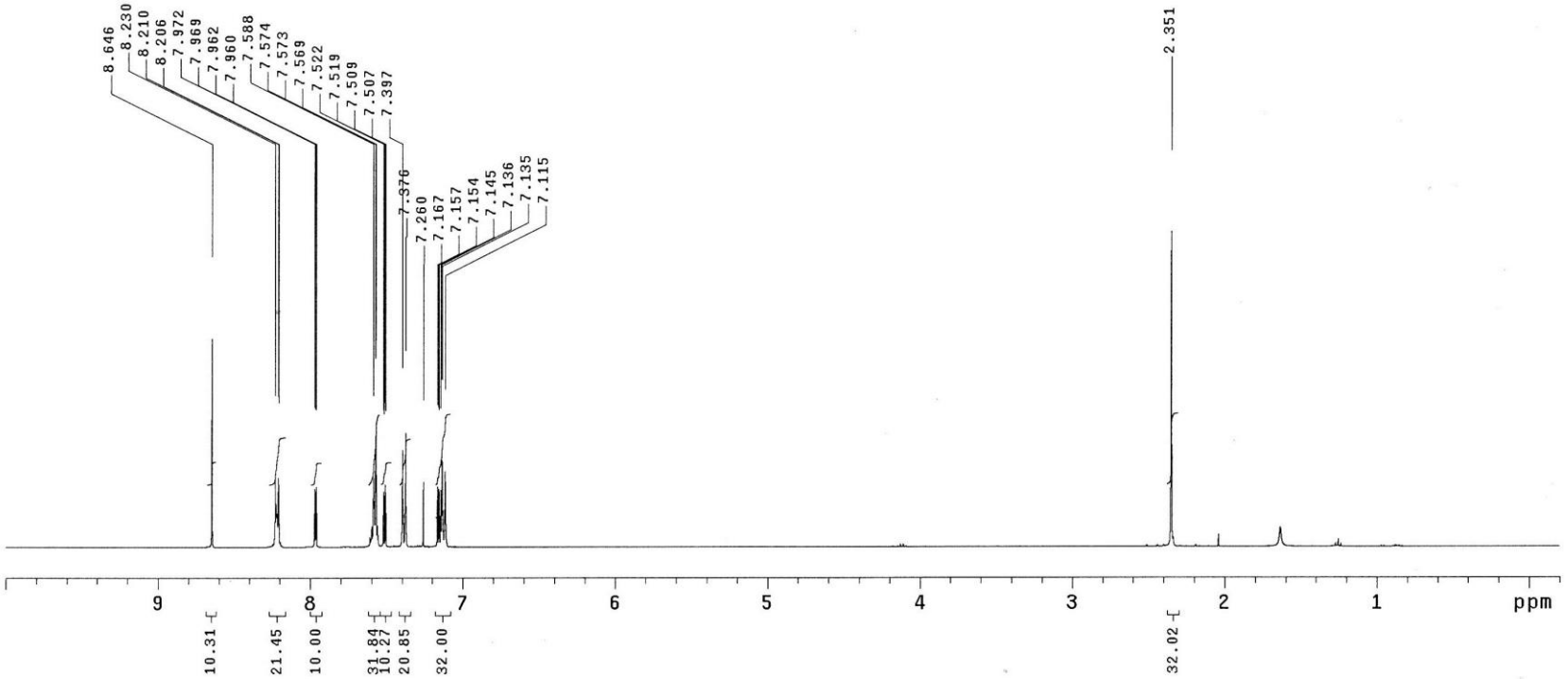
Compound 5k (^{1}H-NMR spectral data)

OYZ0208

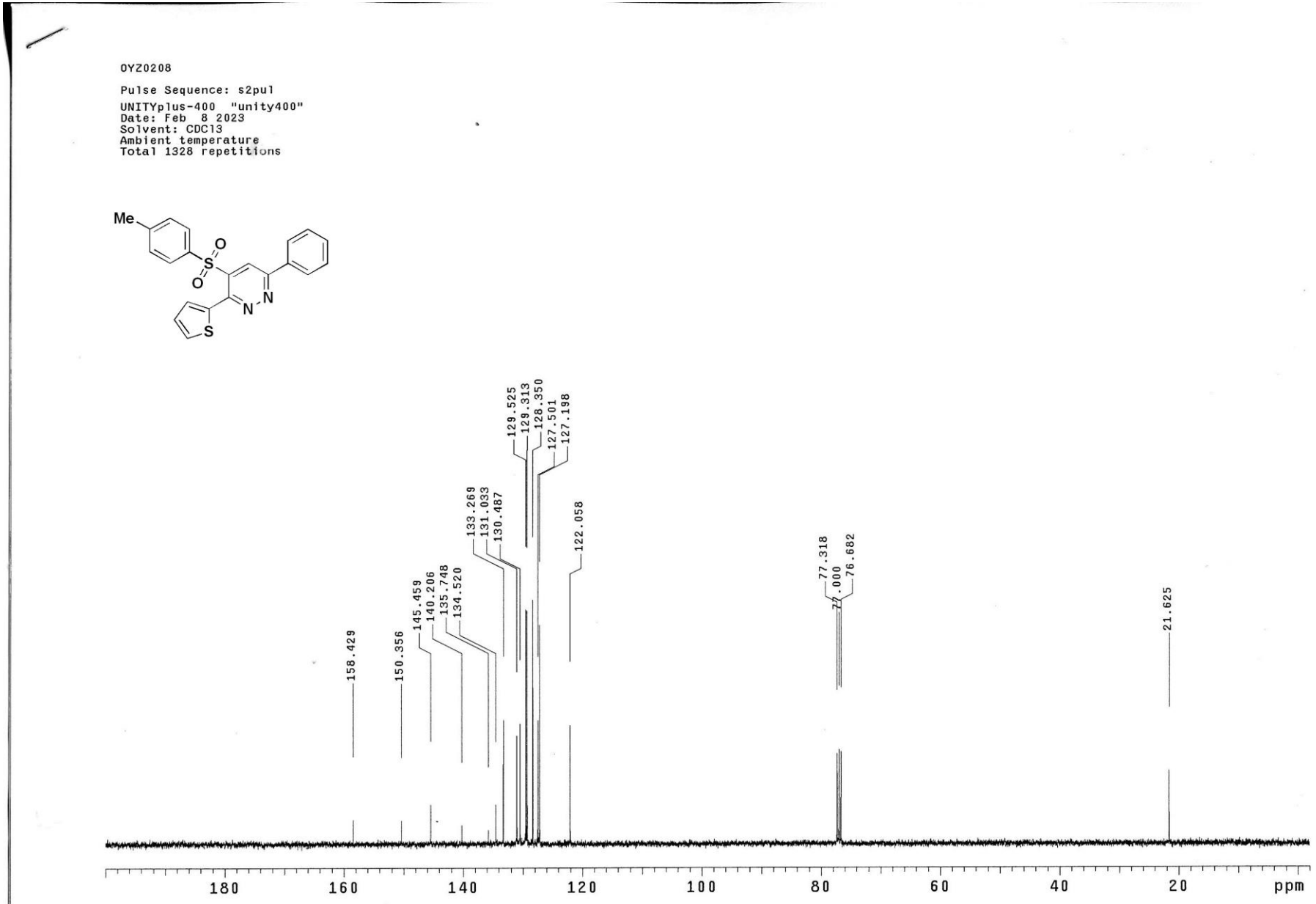
Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Feb 8 2023
Solvent: CDCl3
Ambient temperature
Total 32 repetitions

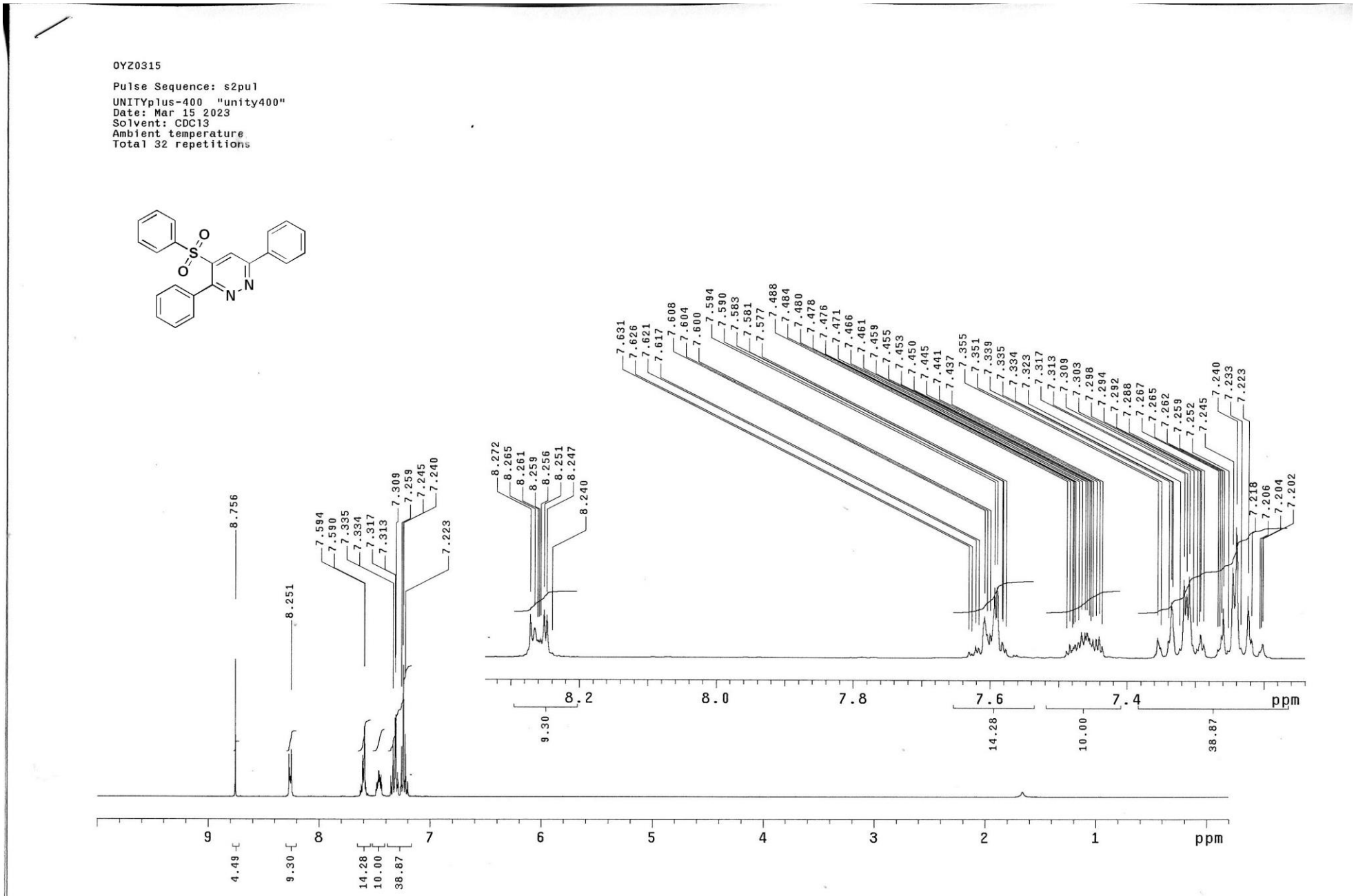




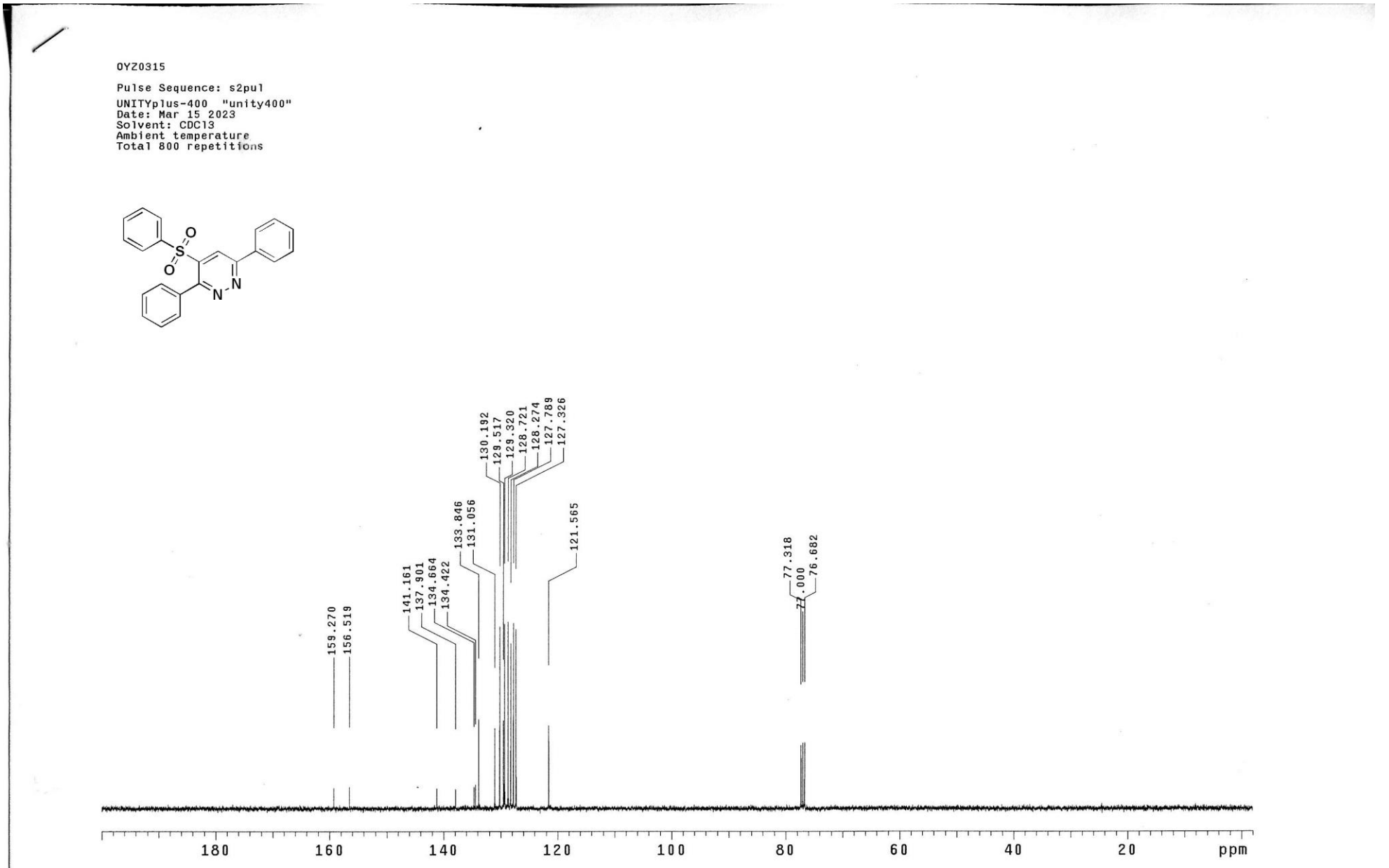
Compound 5k (^{13}C-NMR spectral data)



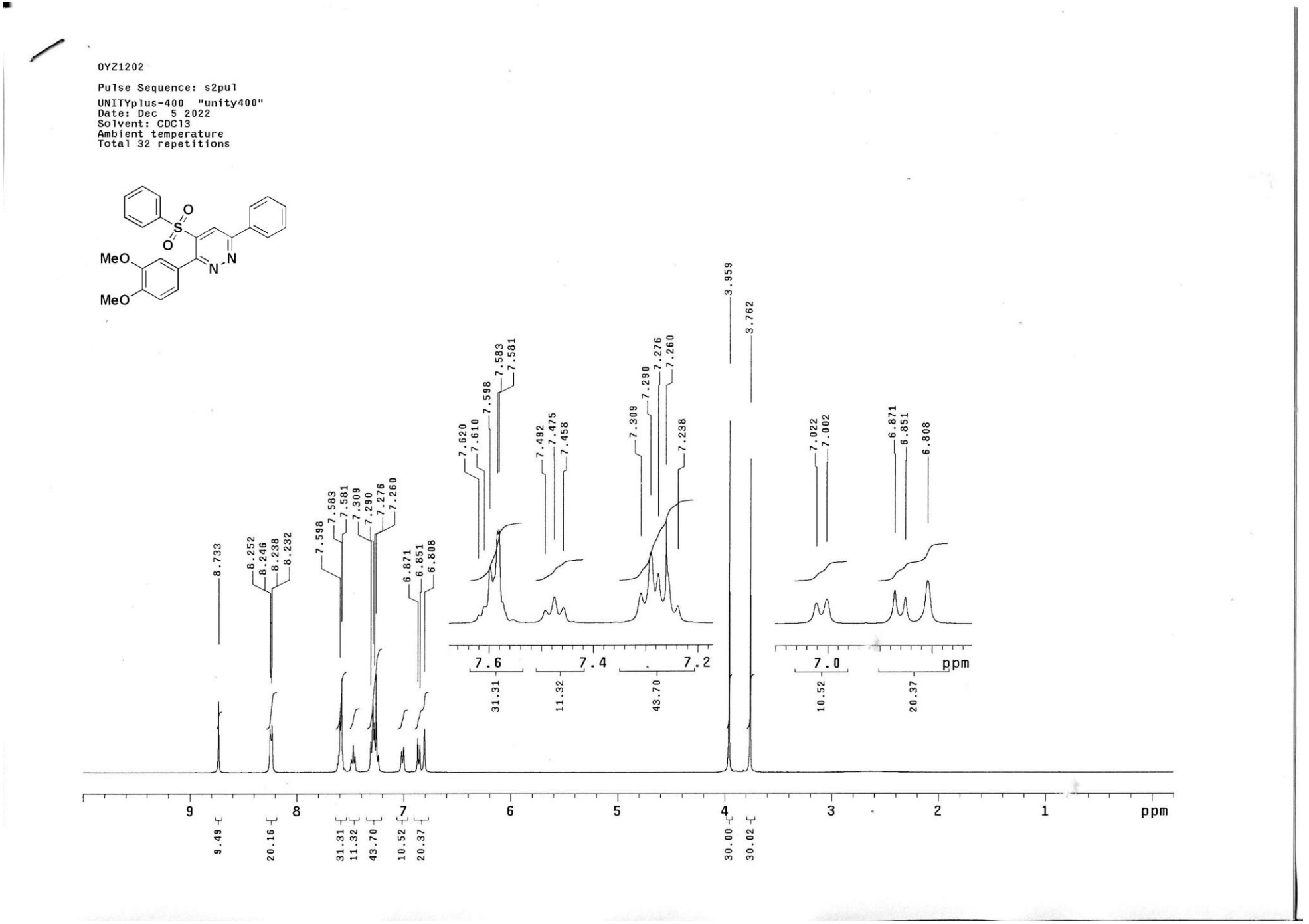
Compound 5l (^{1}H-NMR spectral data)



Compound 5l (^{13}C-NMR spectral data)



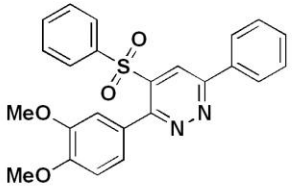
Compound 5m (^{1}H-NMR spectral data)

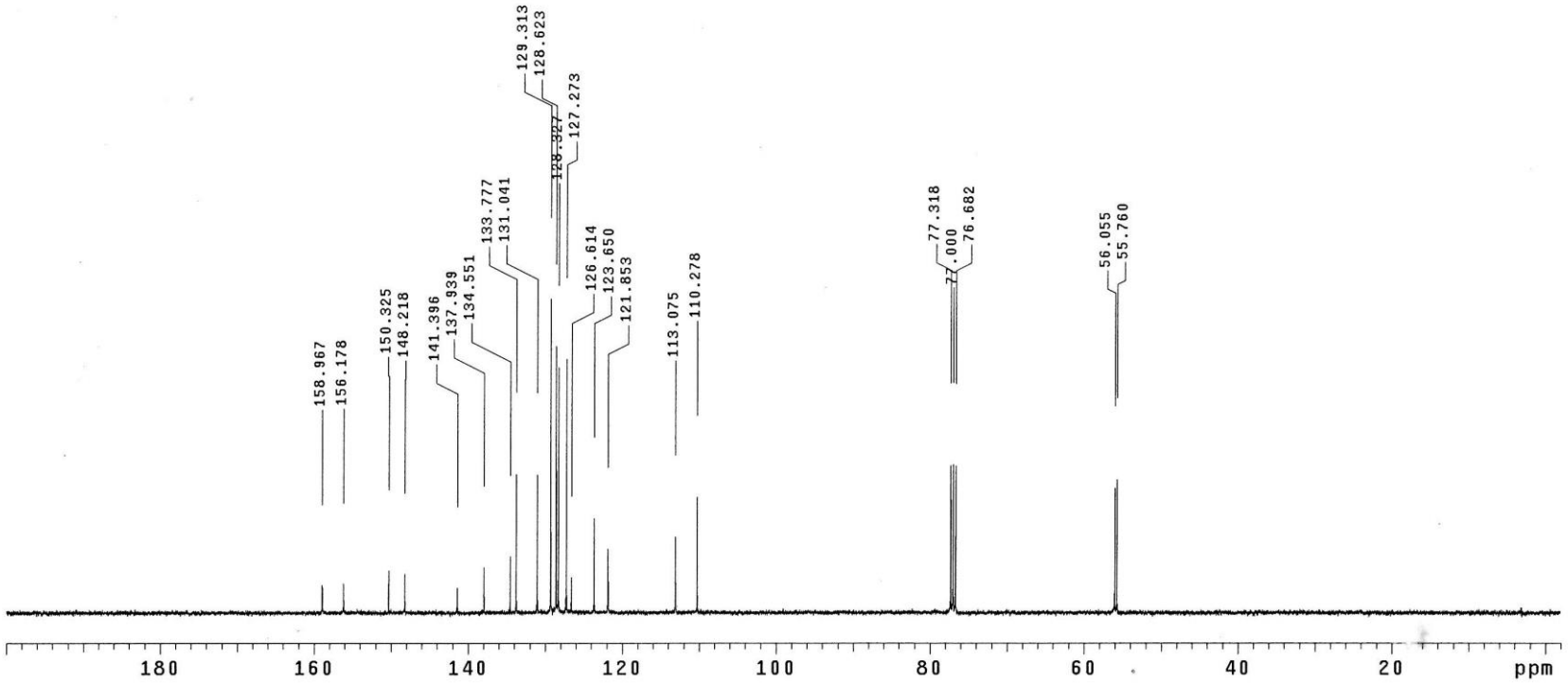


Compound 5m (^{13}C-NMR spectral data)

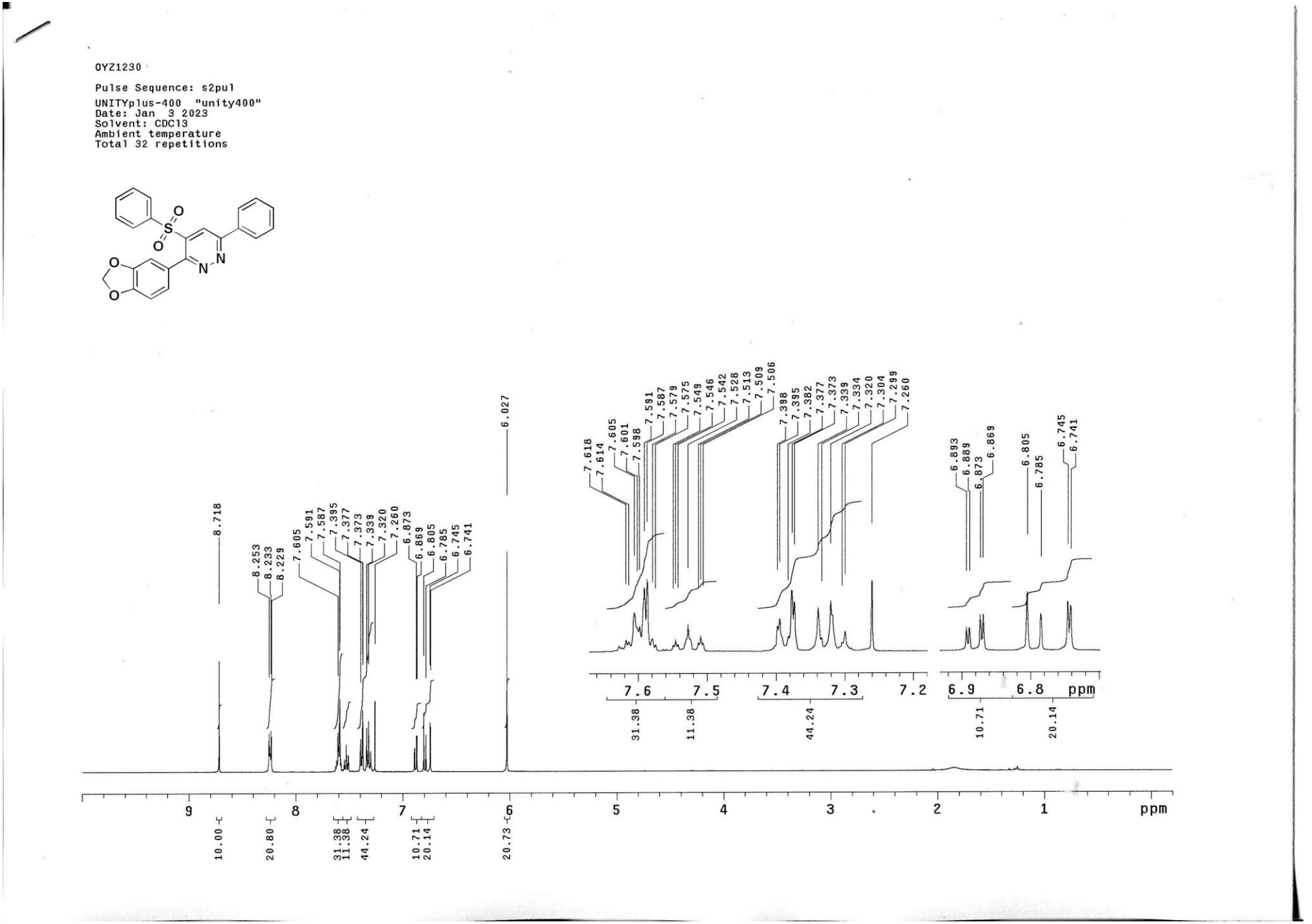
OYZ1202

Pulse Sequence: s2pul
UNITYplus-400 "unity400"
Date: Dec 5 2022
Solvent: CDCl3
Ambient temperature
Total 3360 repetitions





Compound 5n (^{1}H-NMR spectral data)

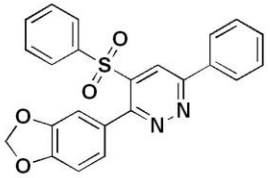


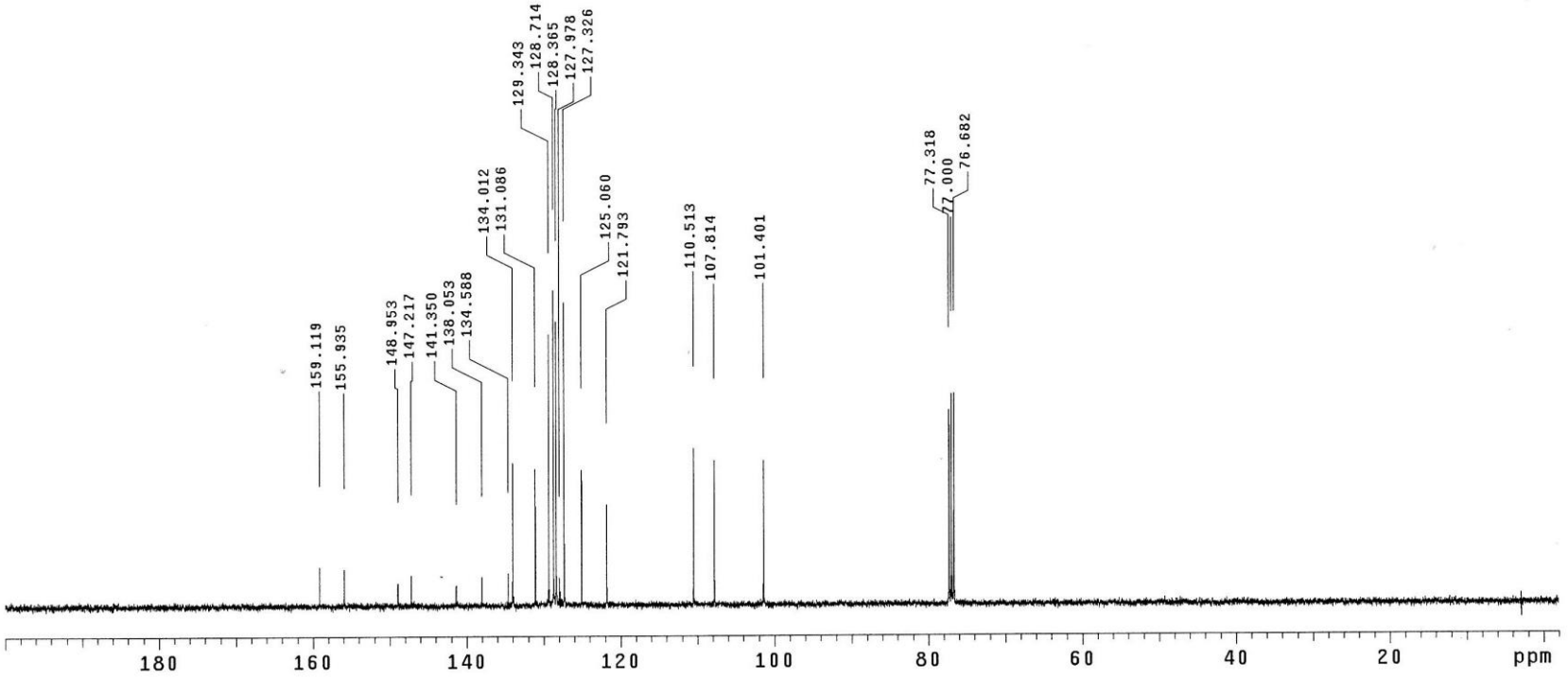
Compound 5n (^{13}C-NMR spectral data)

OYZ1230

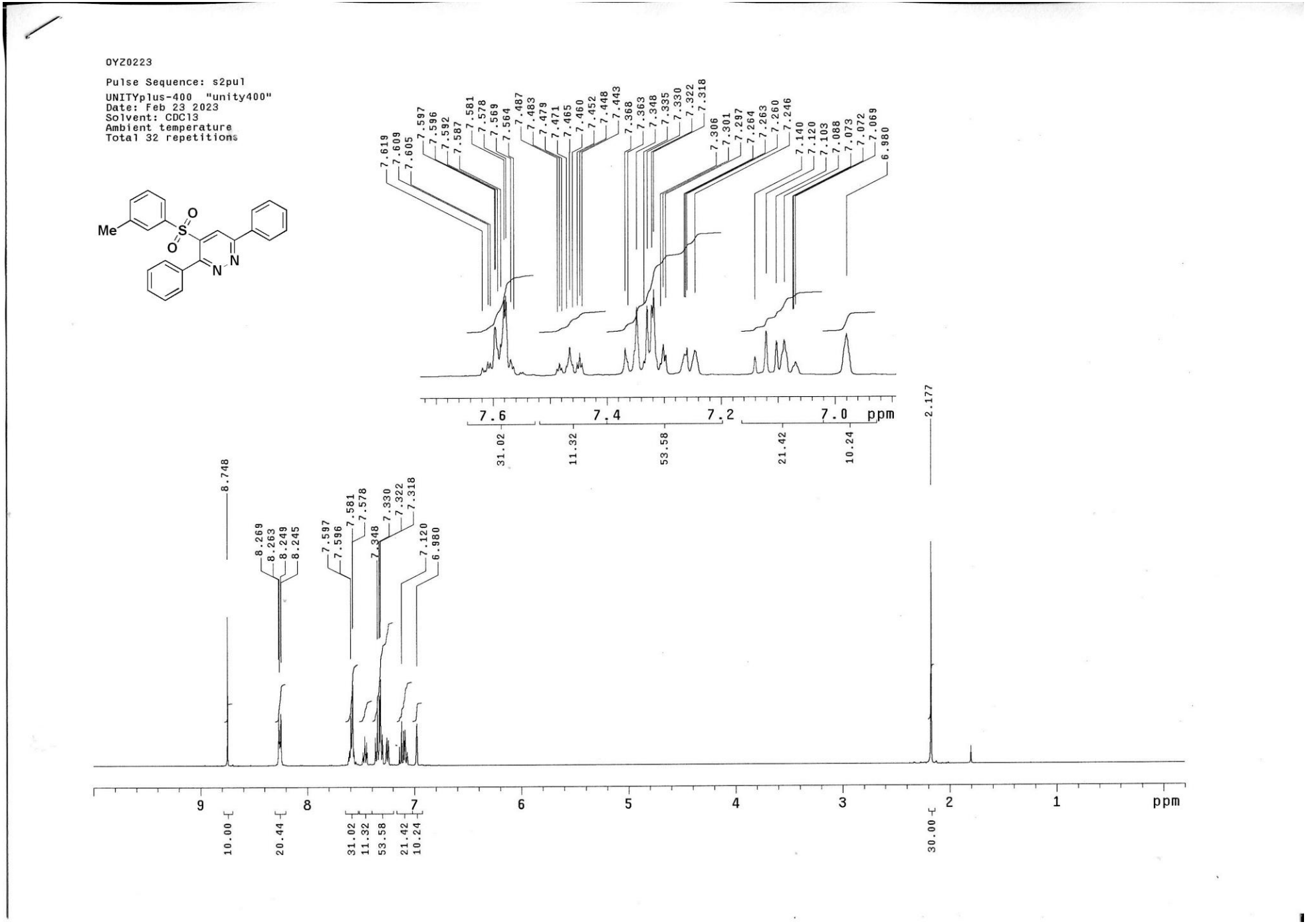
Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Jan 3 2023
Solvent: CDCl3
Ambient temperature
Total 6048 repetitions





Compound 5o (^{1}H-NMR spectral data)

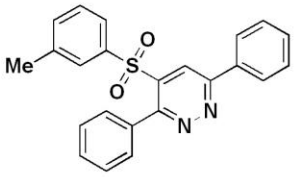


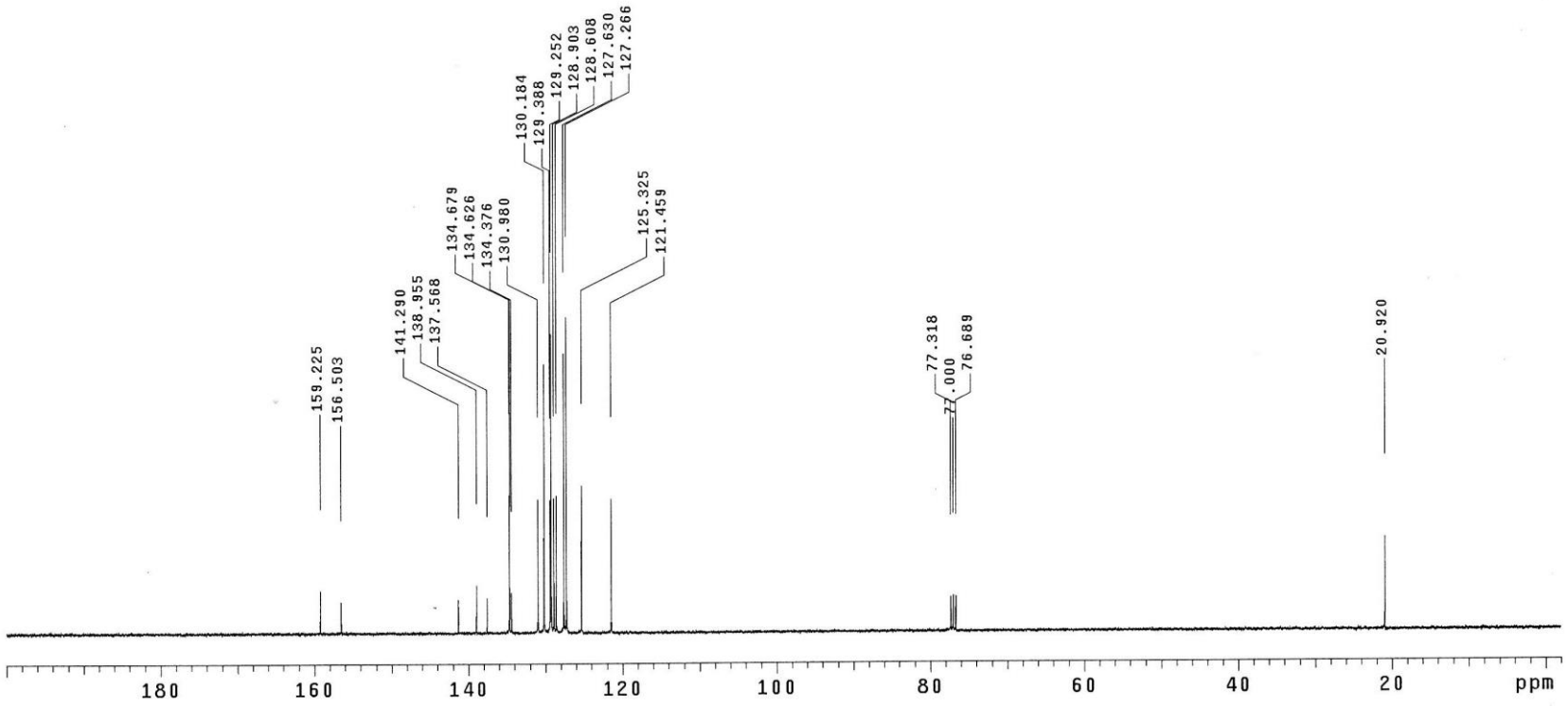
Compound 5o (^{13}C-NMR spectral data)

OYZ0223

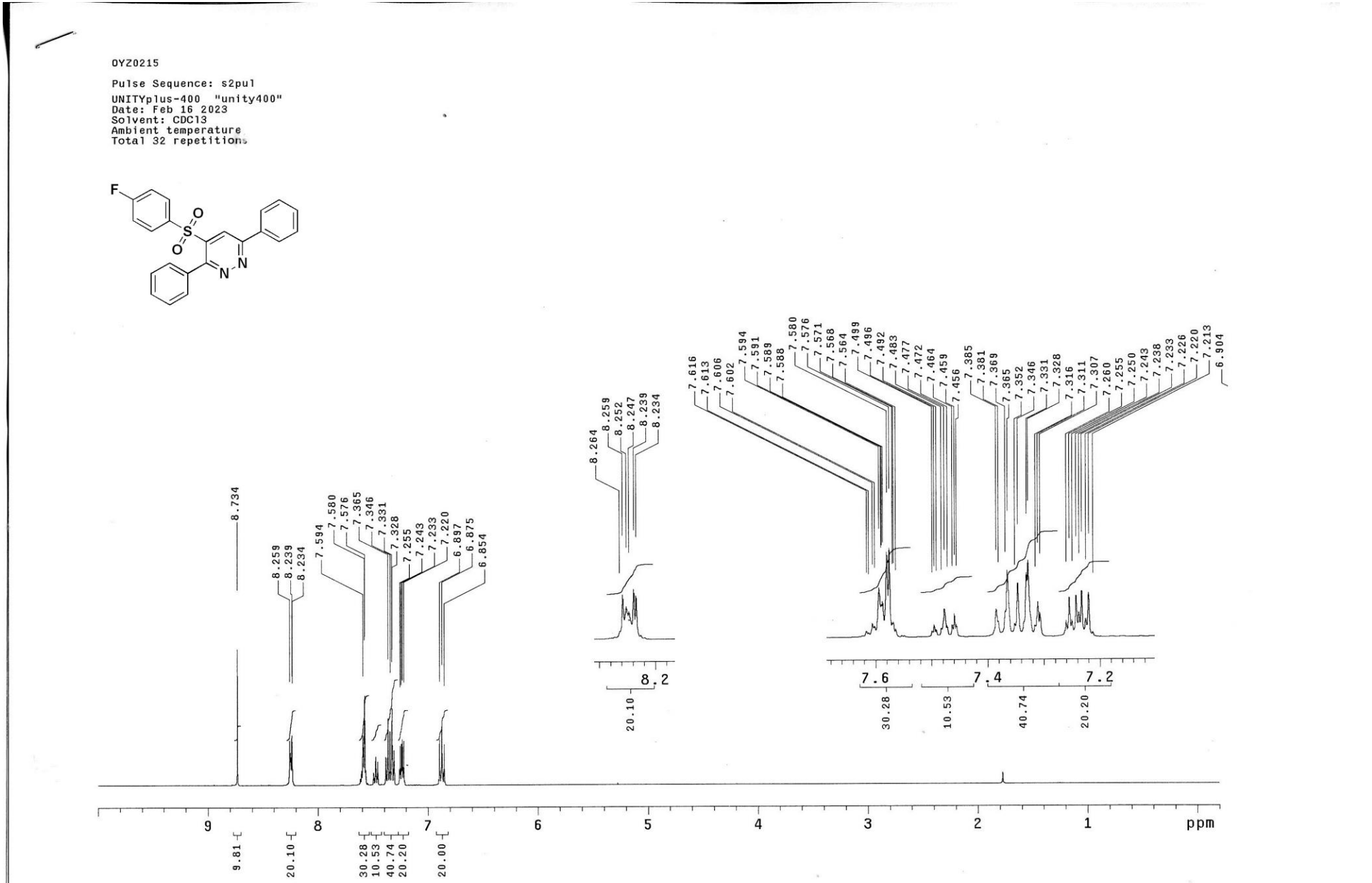
Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Feb 23 2023
Solvent: CDCl3
Ambient temperature
Total 1088 repetitions





Compound 5p (^{1}H-NMR spectral data)

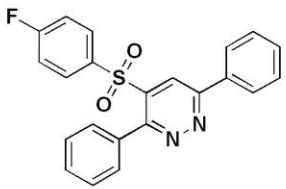


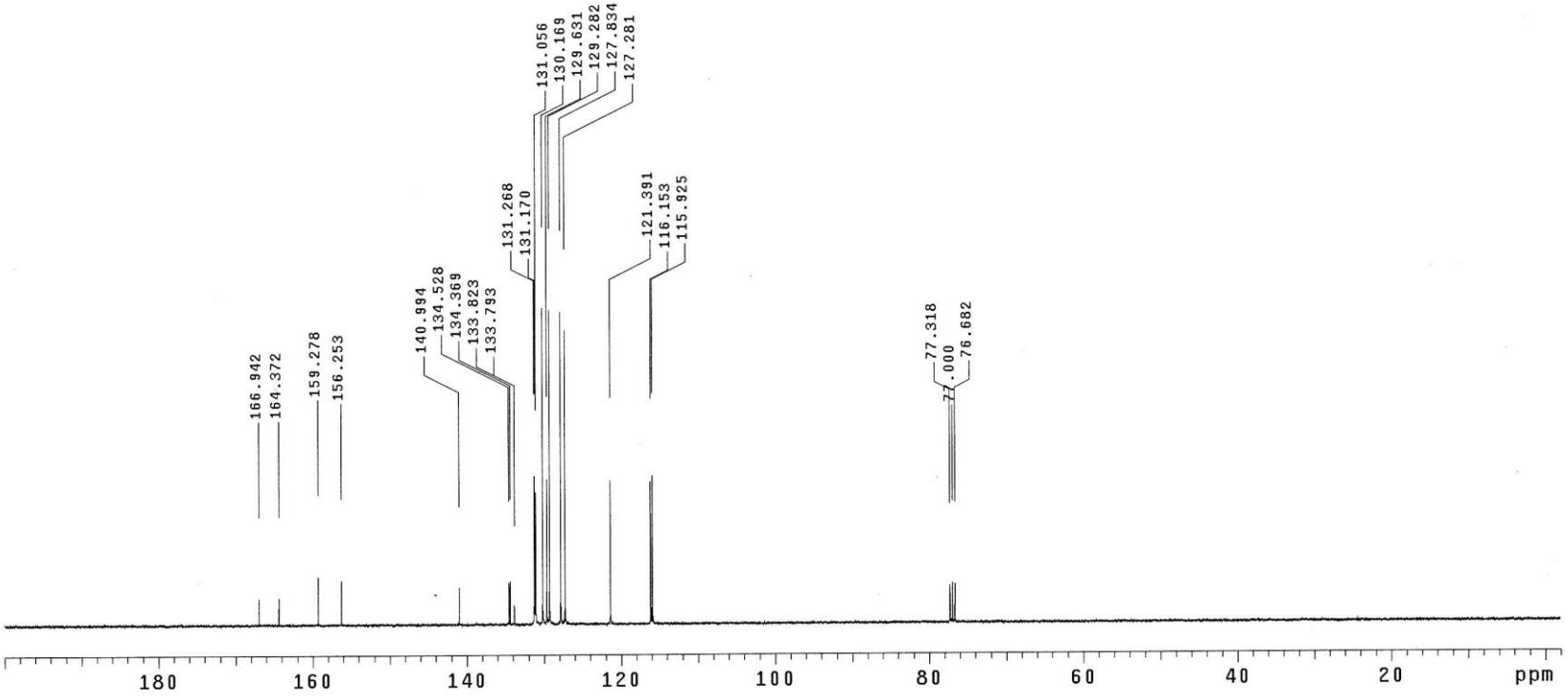
Compound 5p (^{13}C-NMR spectral data)

OYZ0215

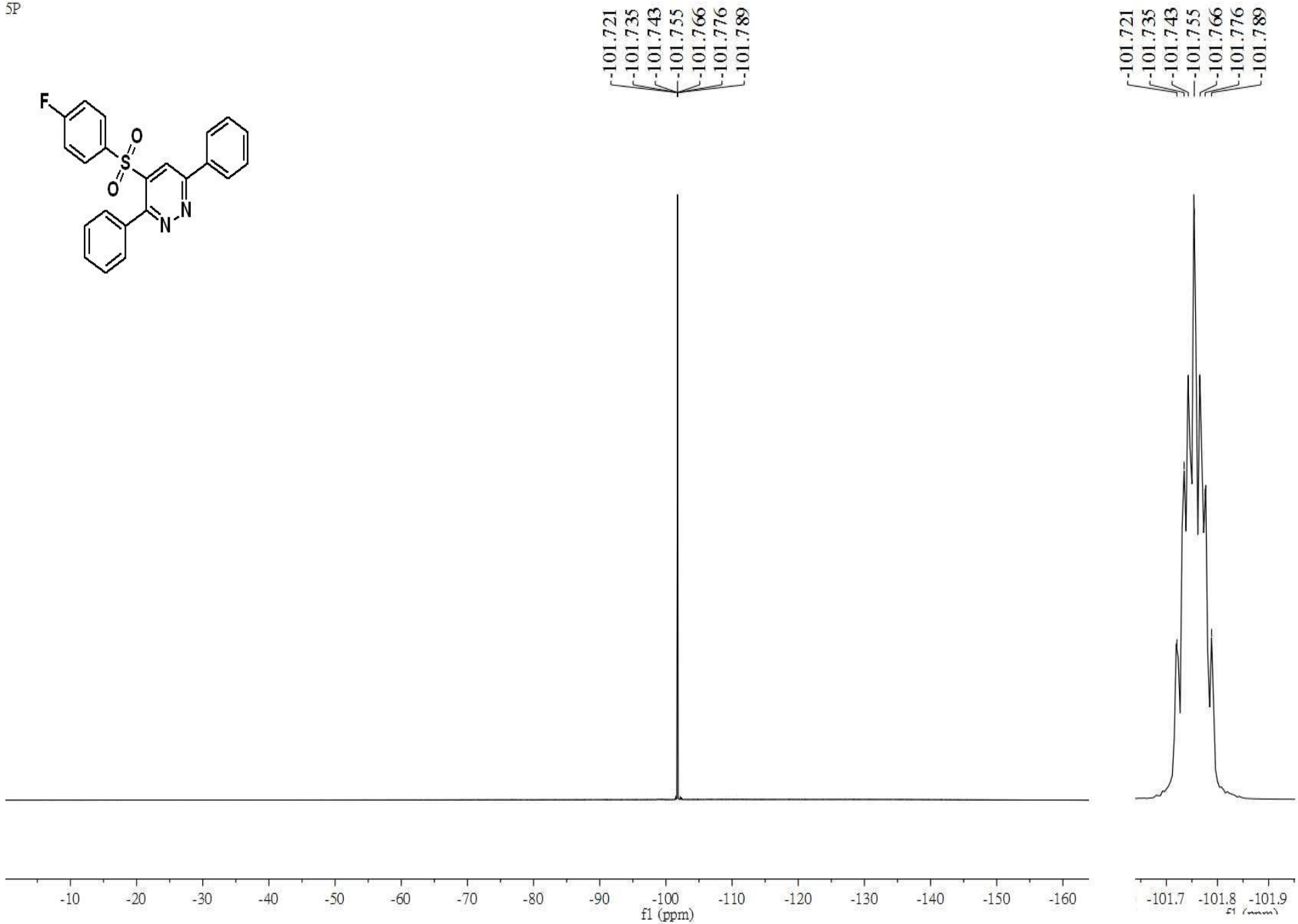
Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Feb 16 2023
Solvent: CDCl3
Ambient temperature
Total 1168 repetitions

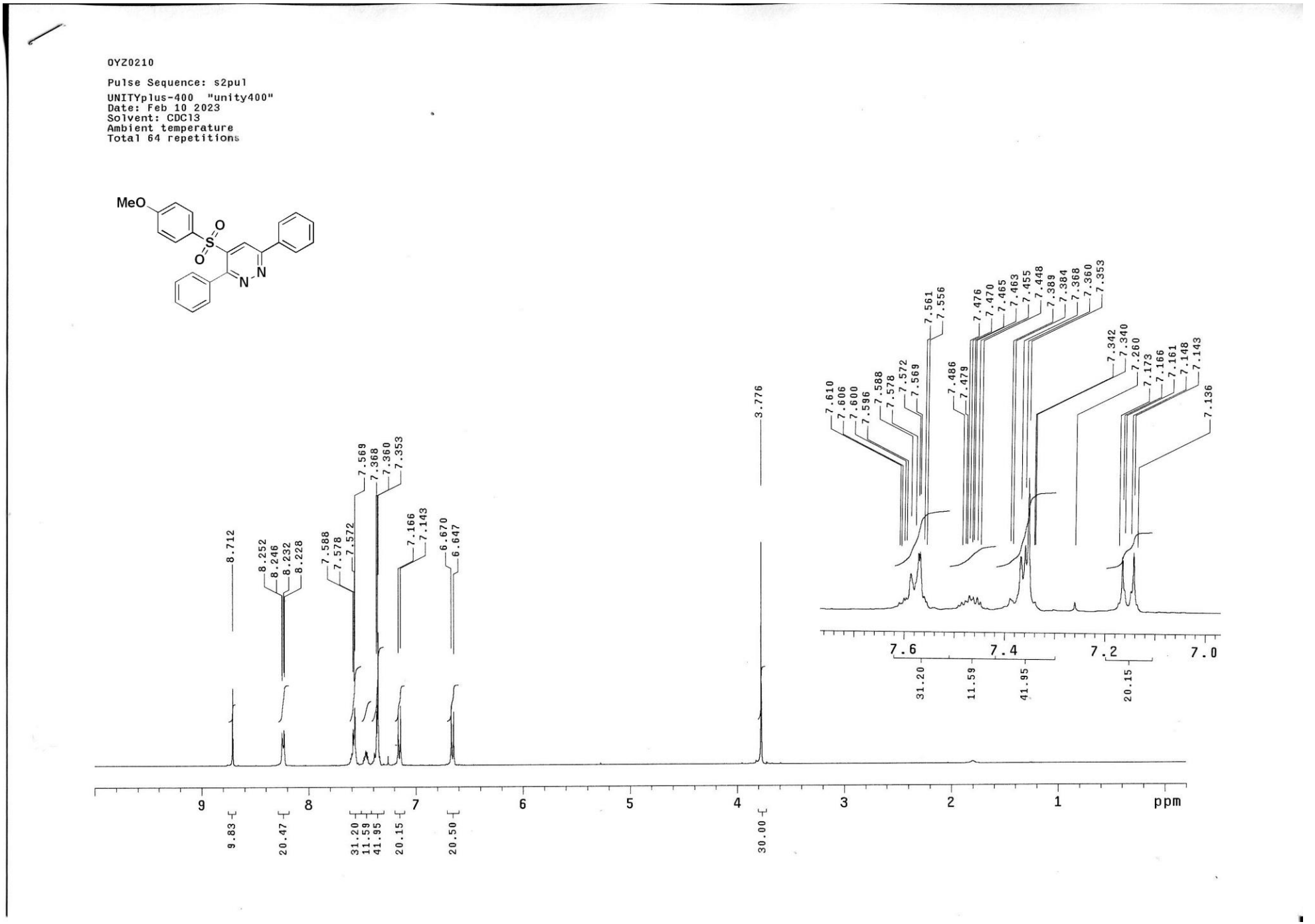




Compound 5p (^{19}F-NMR spectral data)



Compound 5q (^{1}H-NMR spectral data)

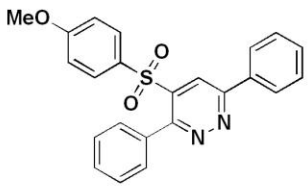


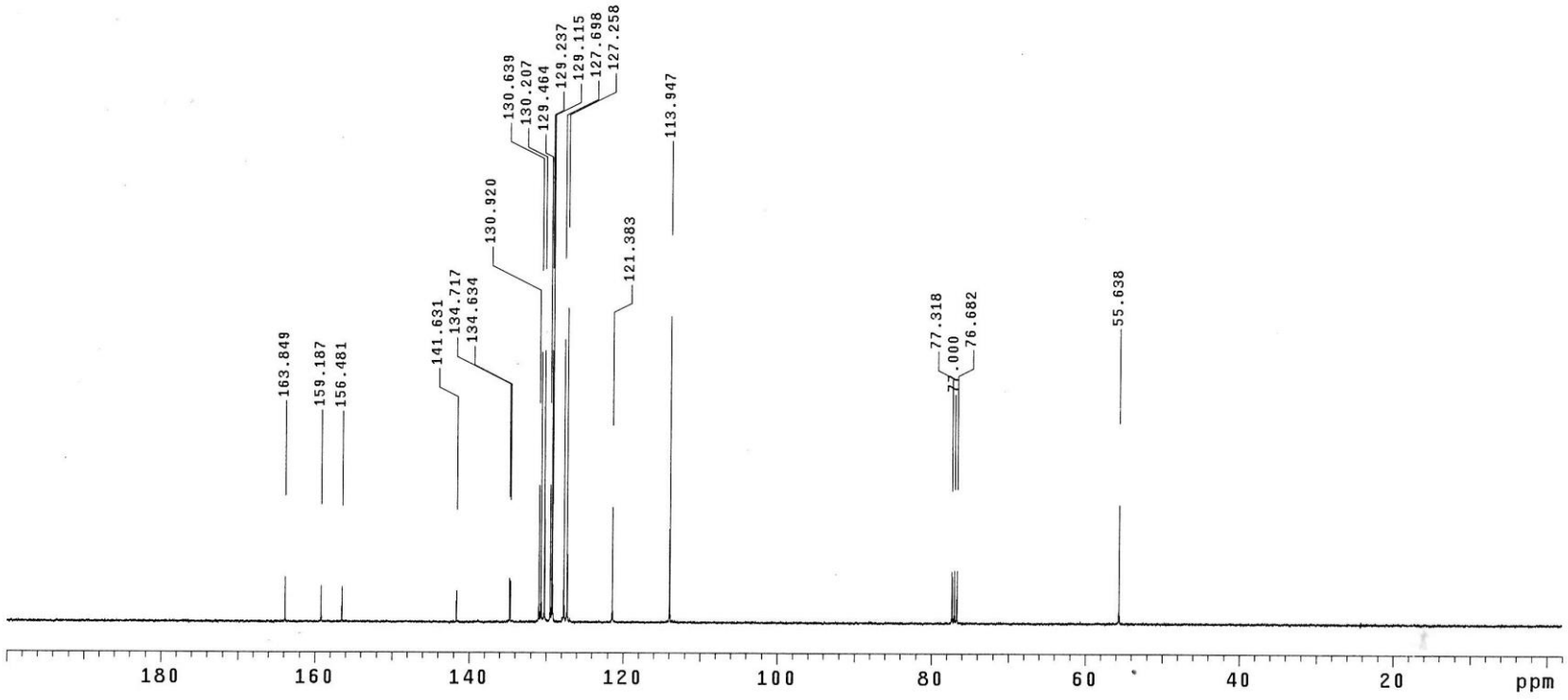
Compound 5q (^{13}C-NMR spectral data)

OYZ0210

Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Feb 10 2023
Solvent: CDCl3
Ambient temperature
Total 64000 repetitions



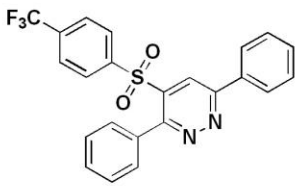


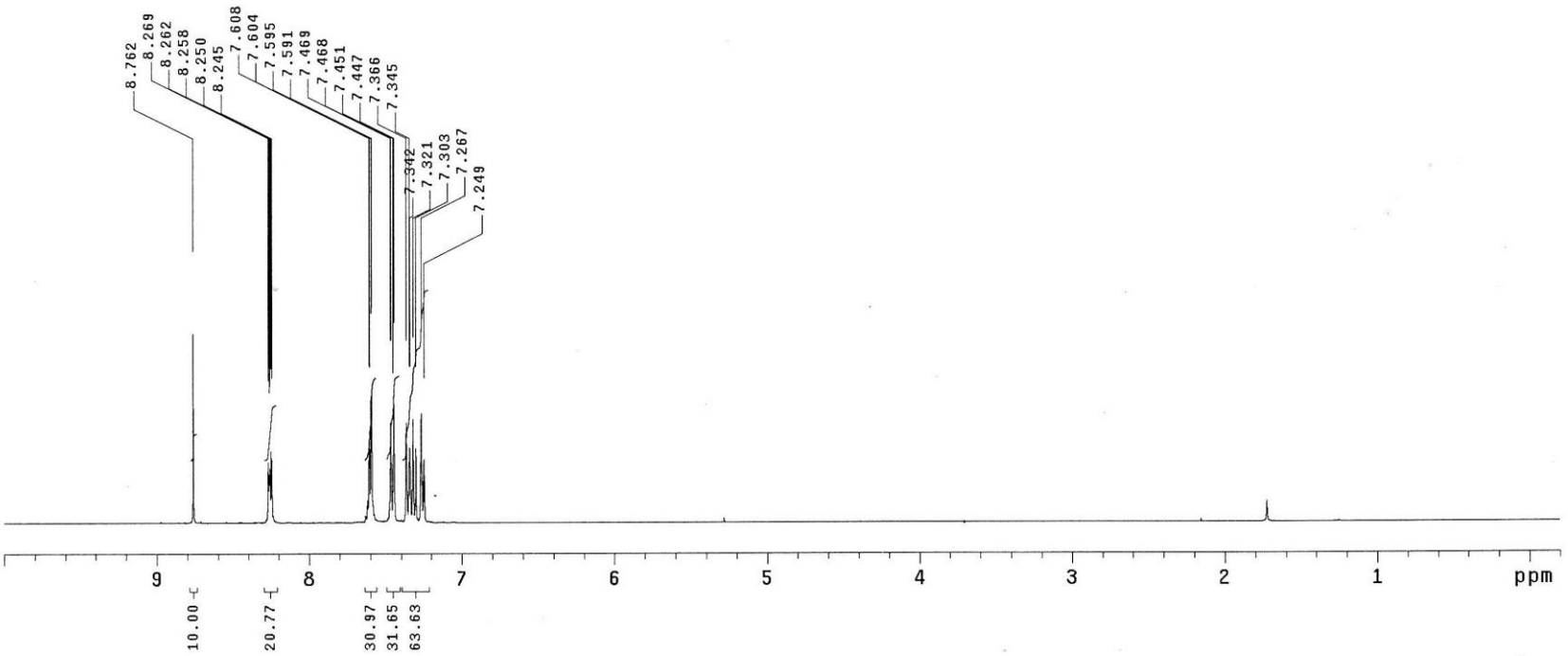
Compound 5r (^{1}H-NMR spectral data)

OYZ0314

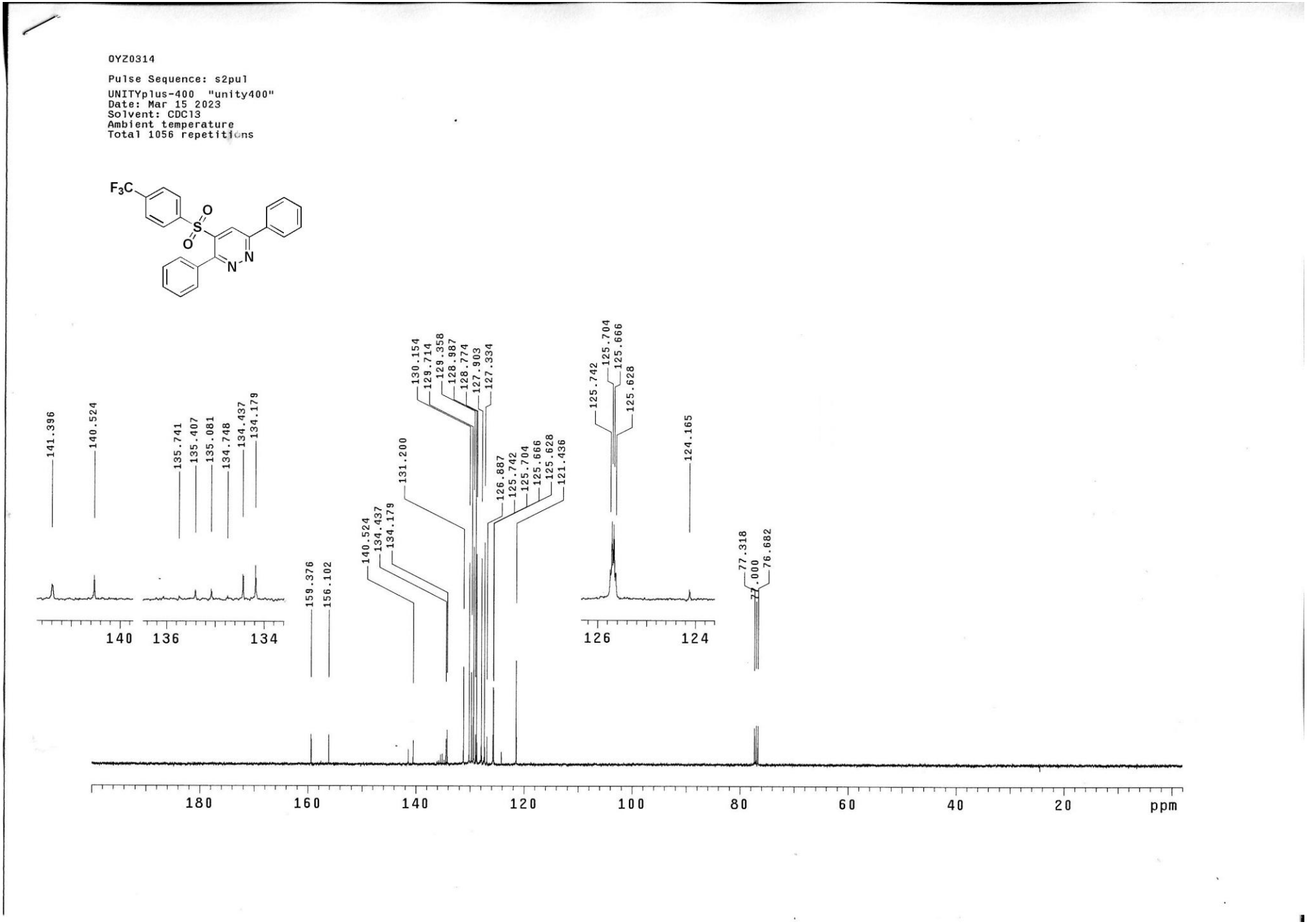
Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Mar 15 2023
Solvent: CDCl3
Ambient temperature
Total 32 repetitions

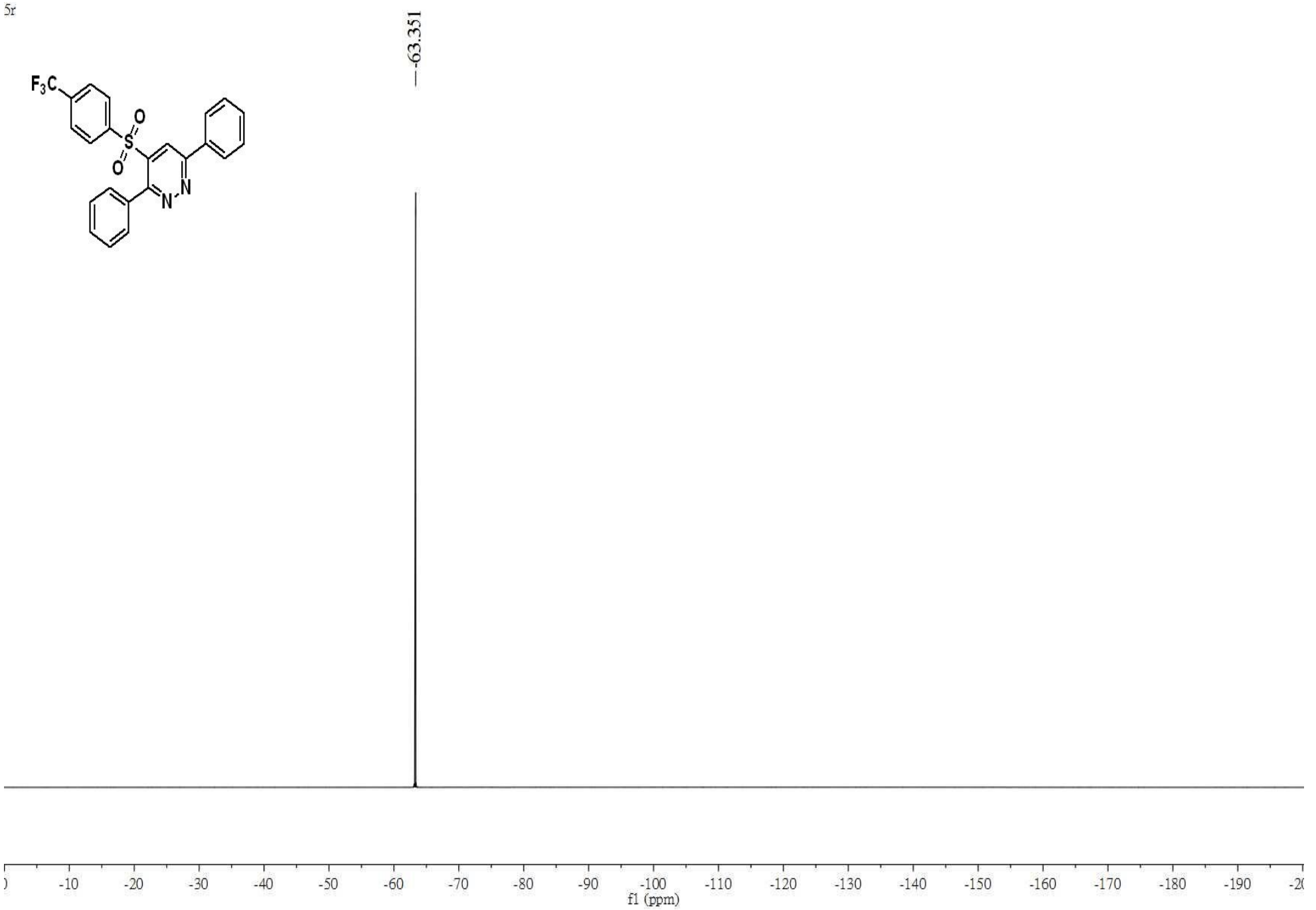




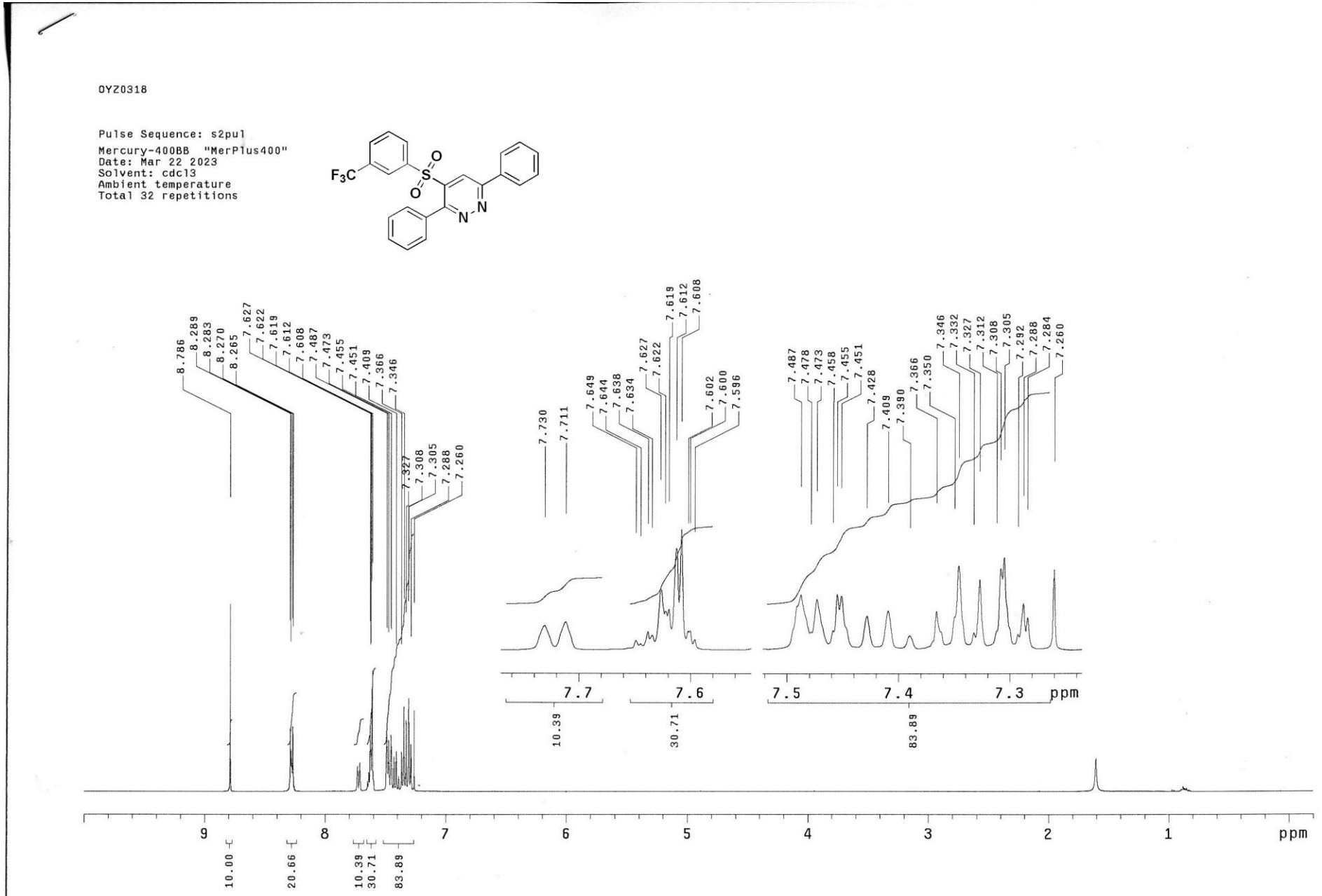
Compound 5r (^{13}C-NMR spectral data)



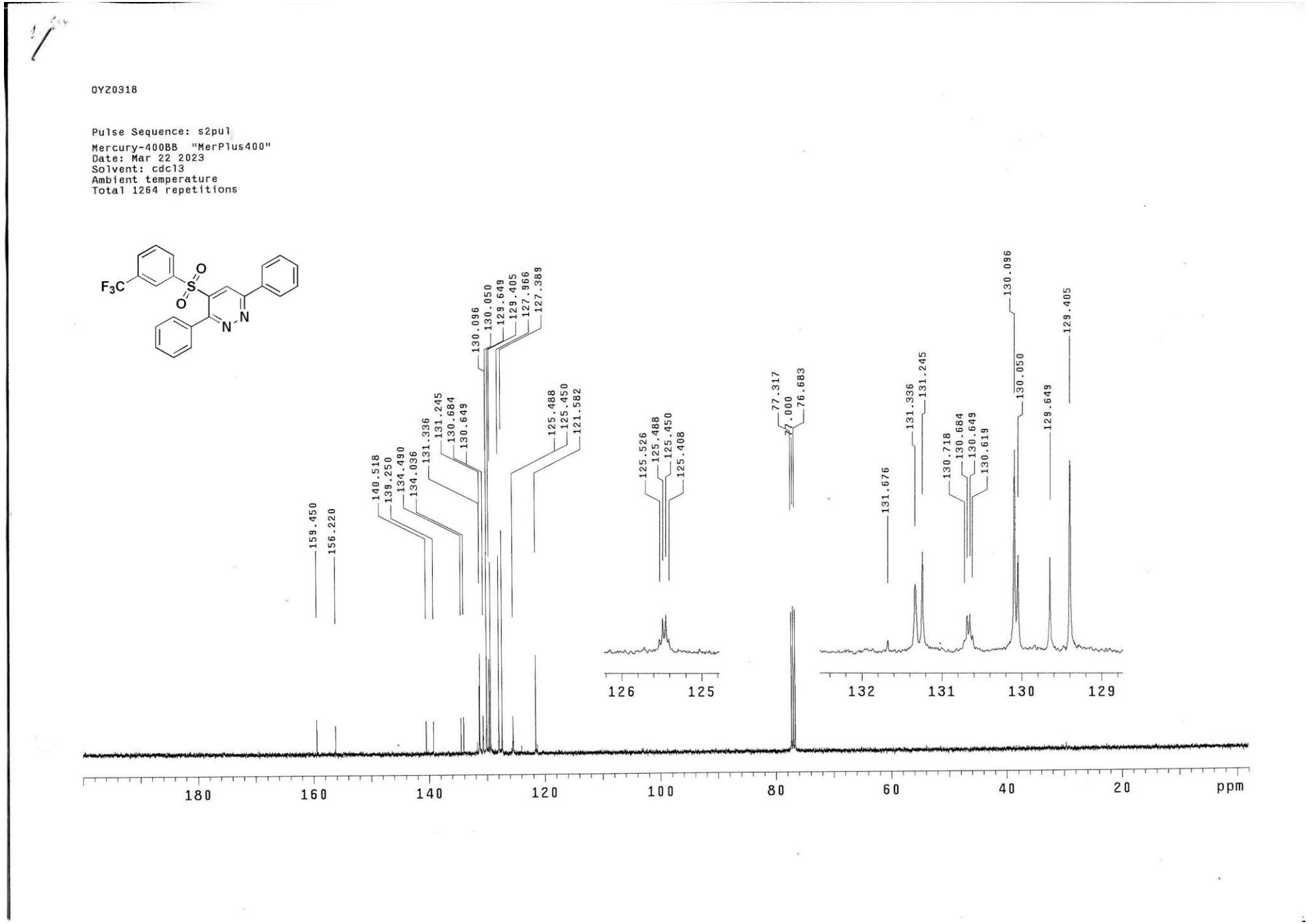
Compound 5r (^{19}F-NMR spectral data)



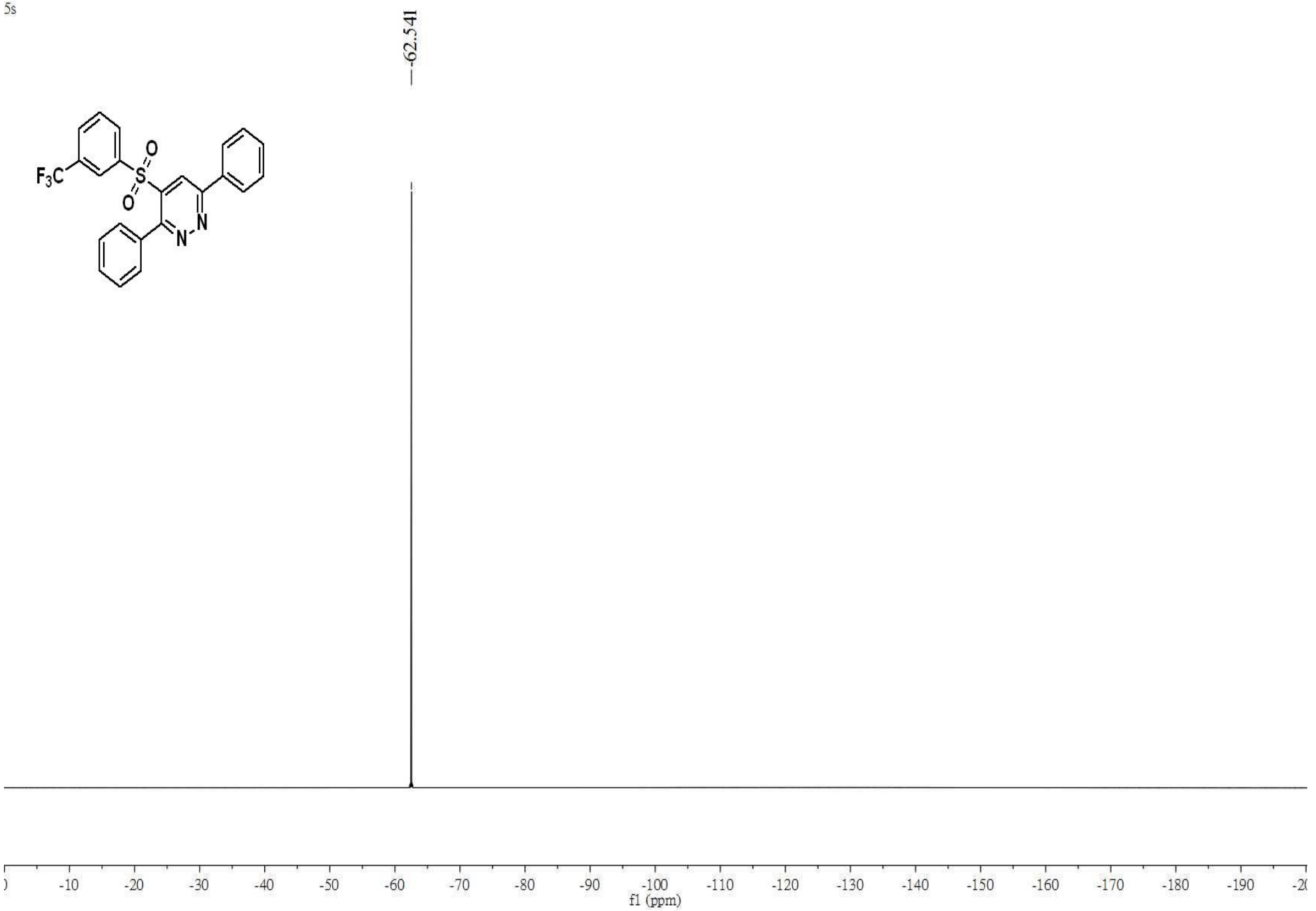
Compound 5s (^{1}H-NMR spectral data)



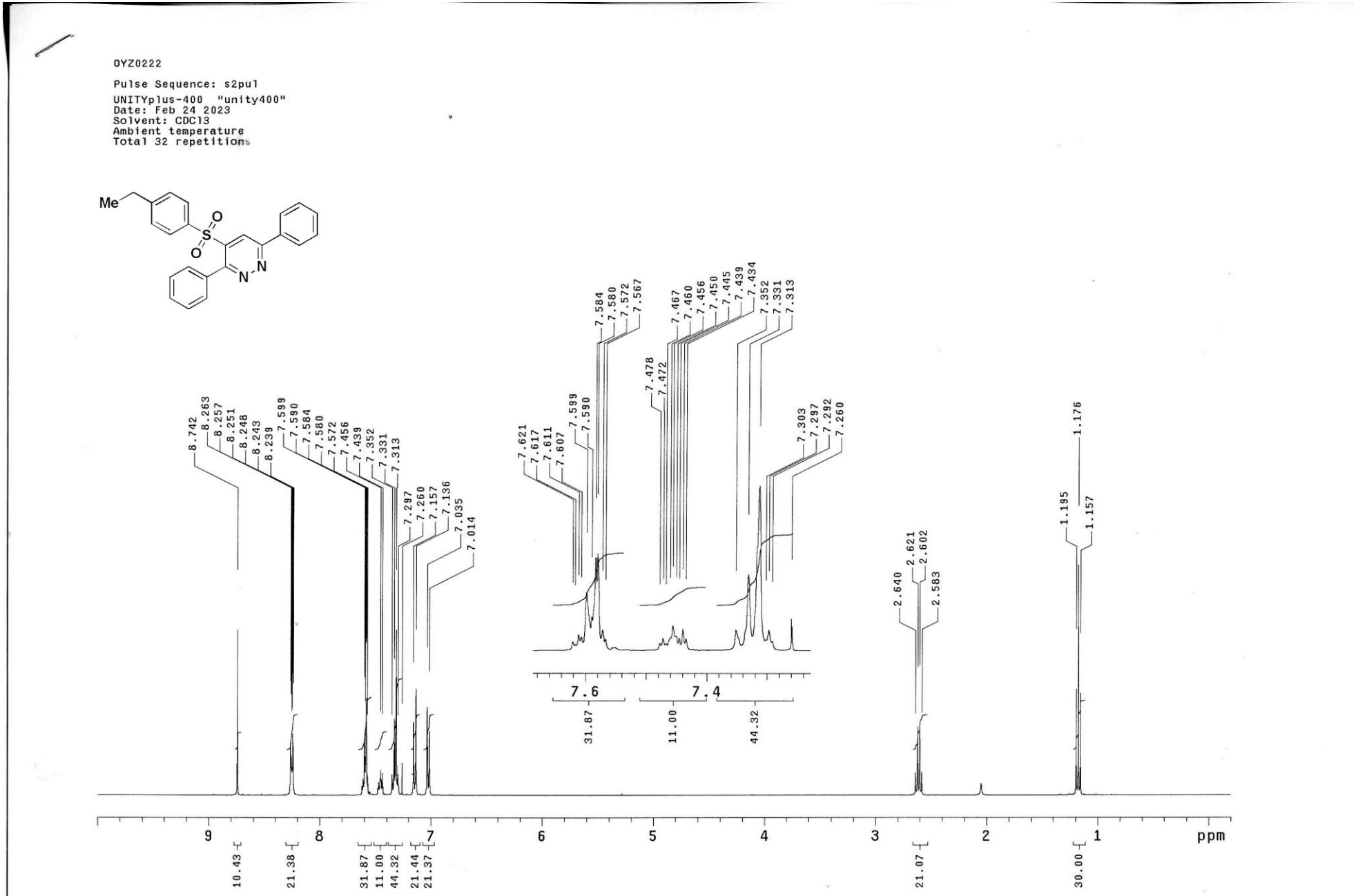
Compound 5s (^{13}C-NMR spectral data)



Compound 5s (^{19}F-NMR spectral data)



Compound 5t (^{1}H-NMR spectral data)

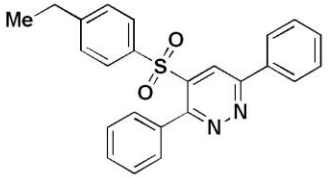


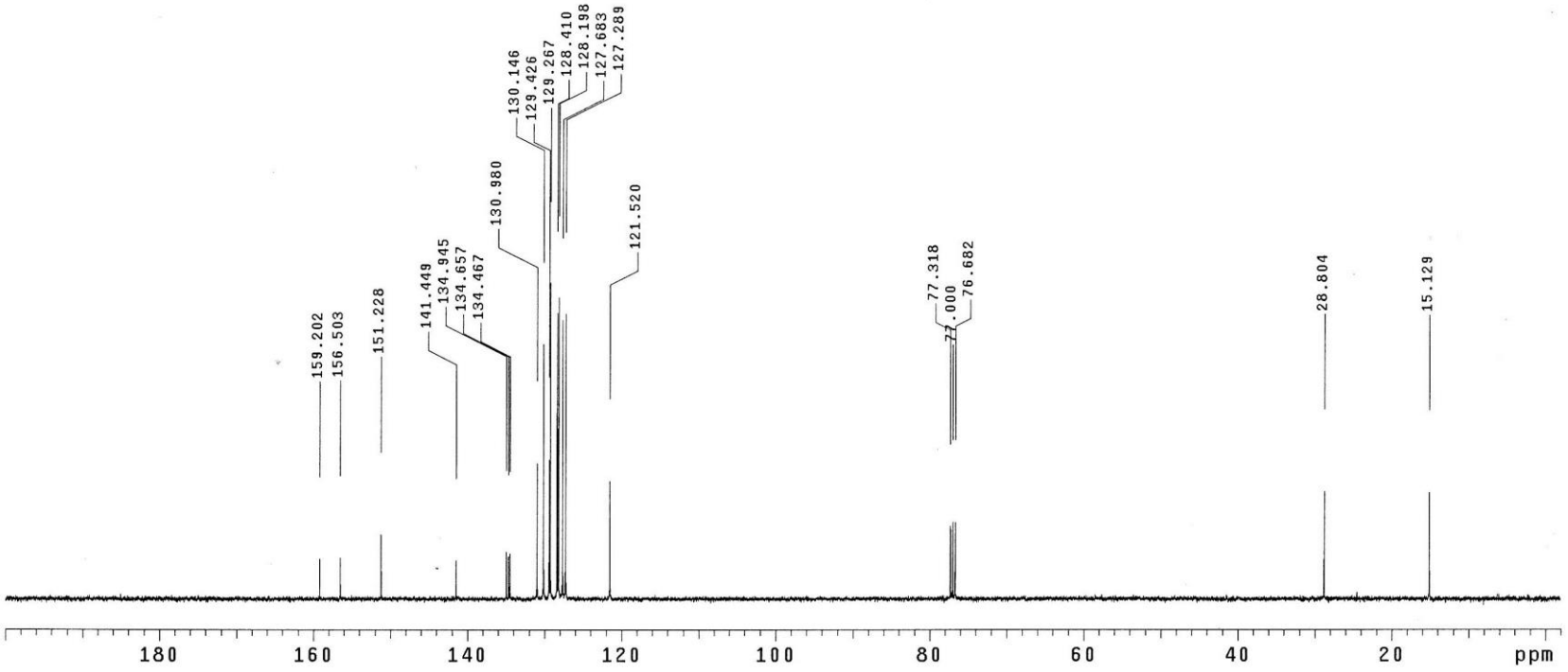
Compound 5t (^{13}C-NMR spectral data)

OYZ0222

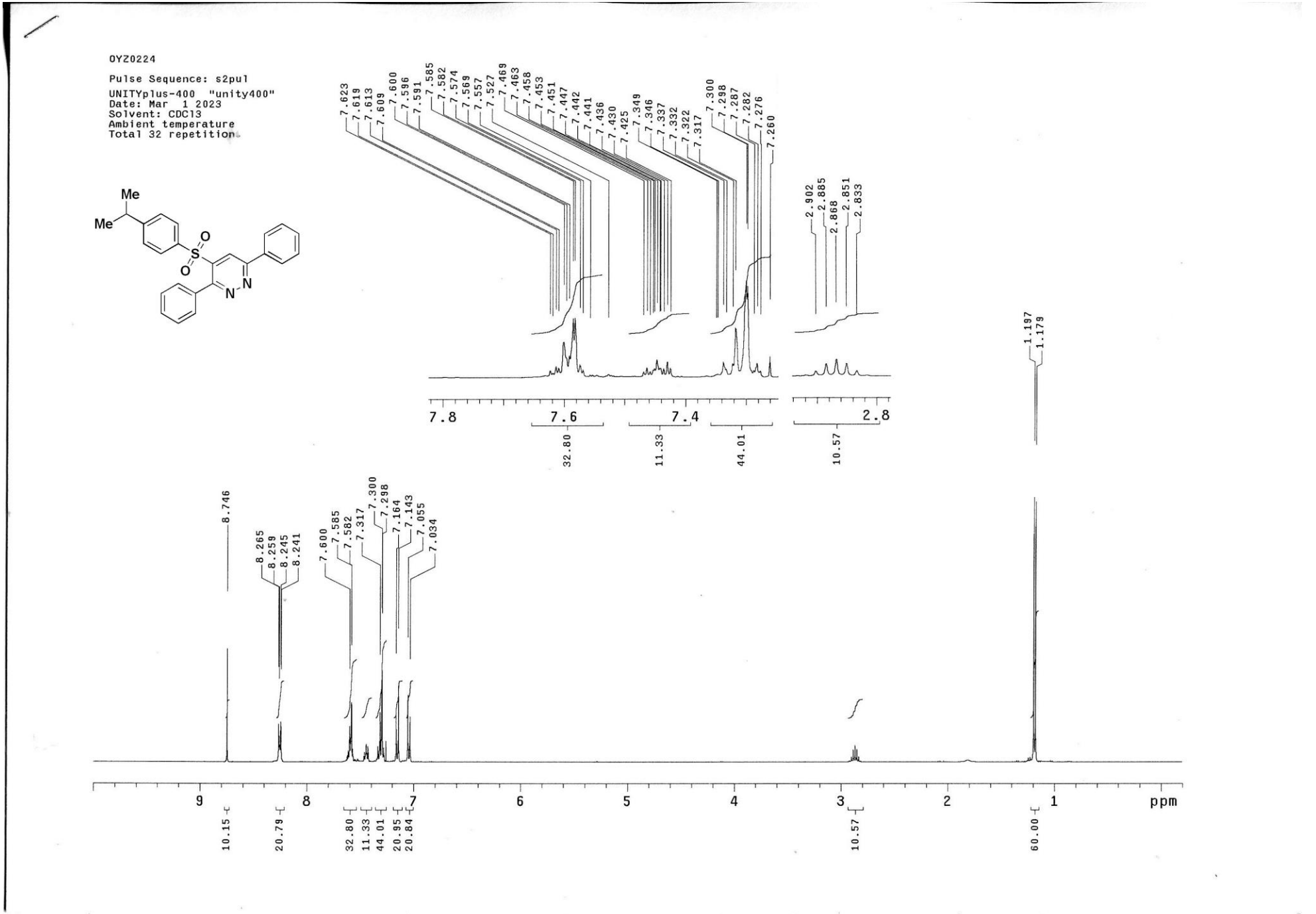
Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Feb 24 2023
Solvent: CDCl3
Ambient temperature
Total 384 repetitions





Compound 5u (^{1}H-NMR spectral data)

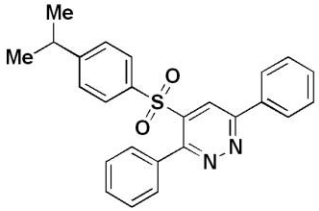


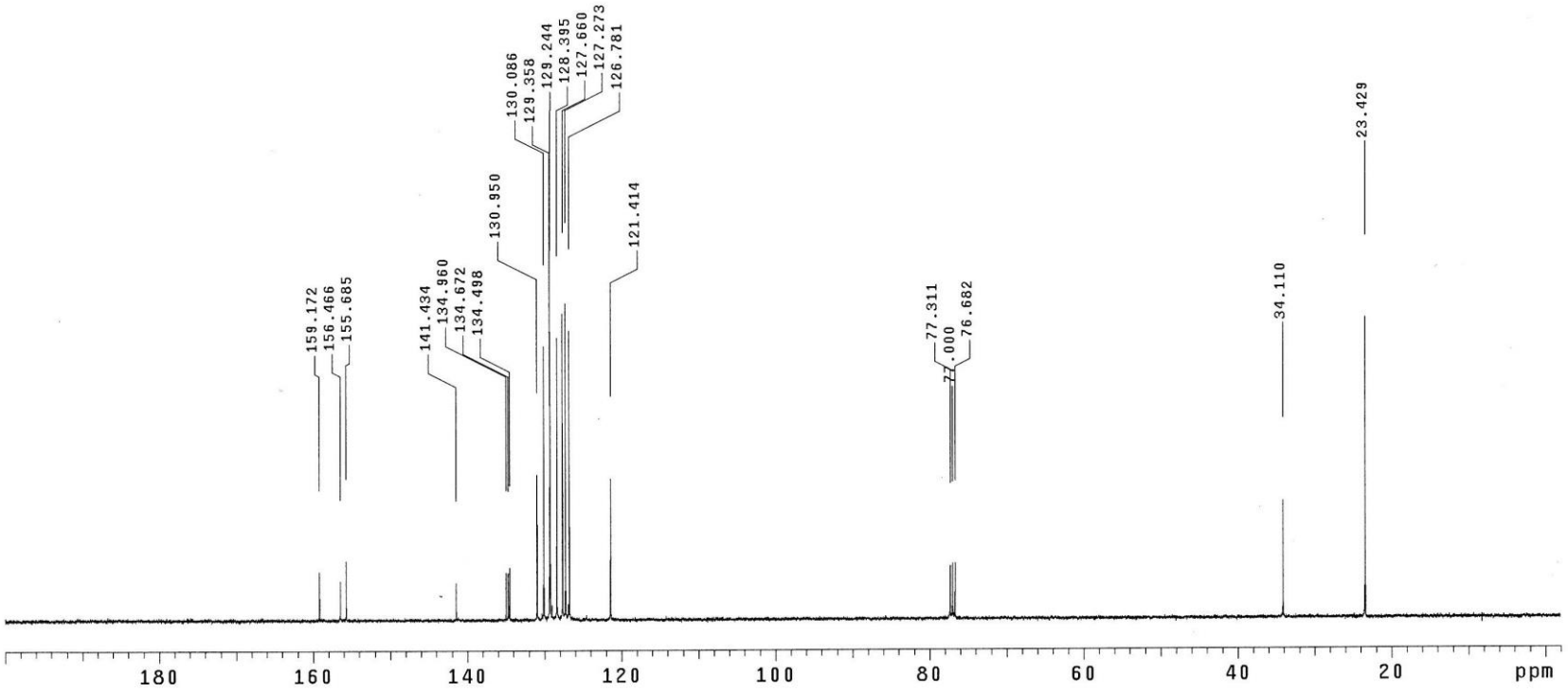
Compound 5u (^{13}C-NMR spectral data)

OYZ0224

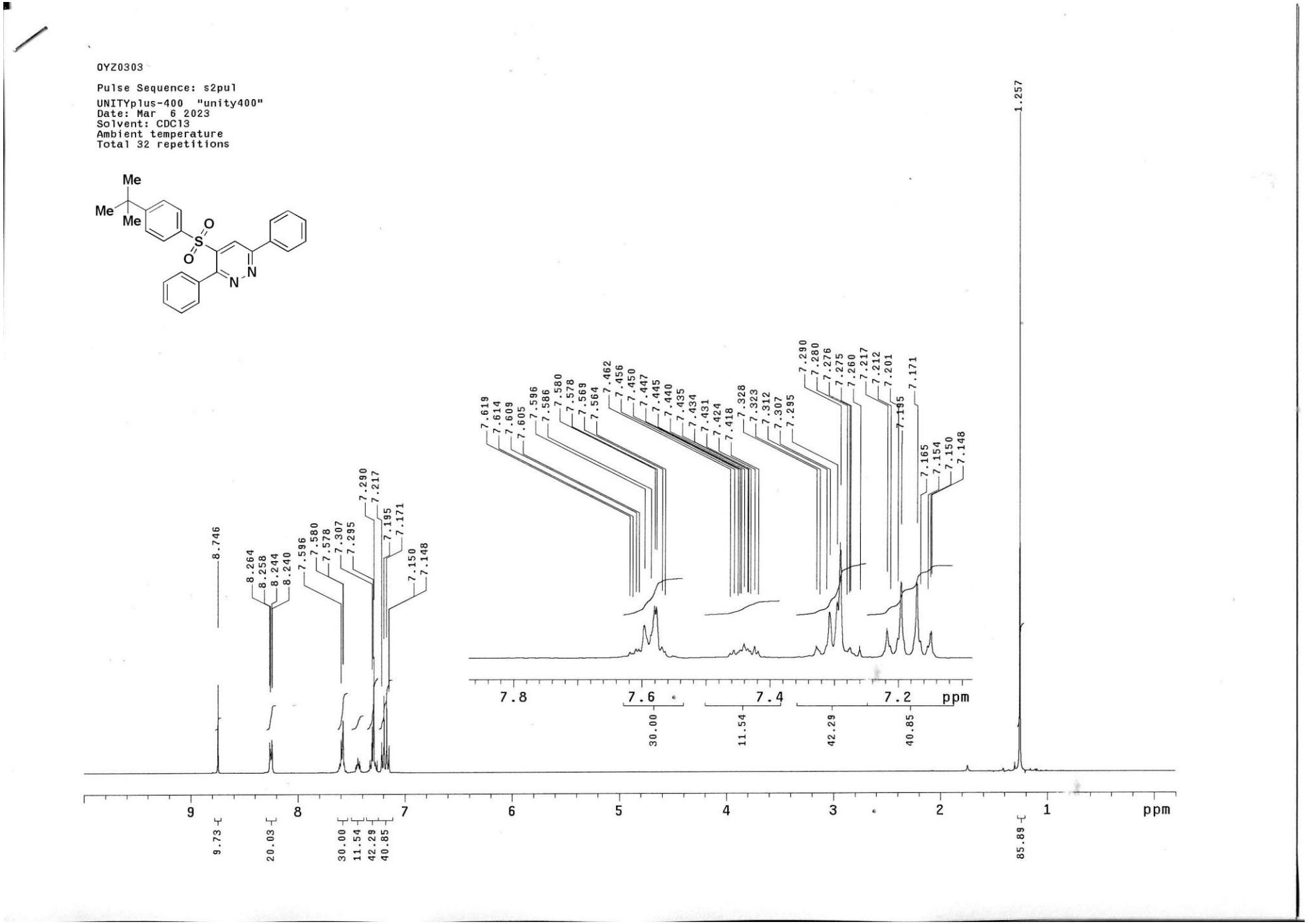
Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Mar 1 2023
Solvent: CDCl3
Ambient temperature
Total 1648 repetitions

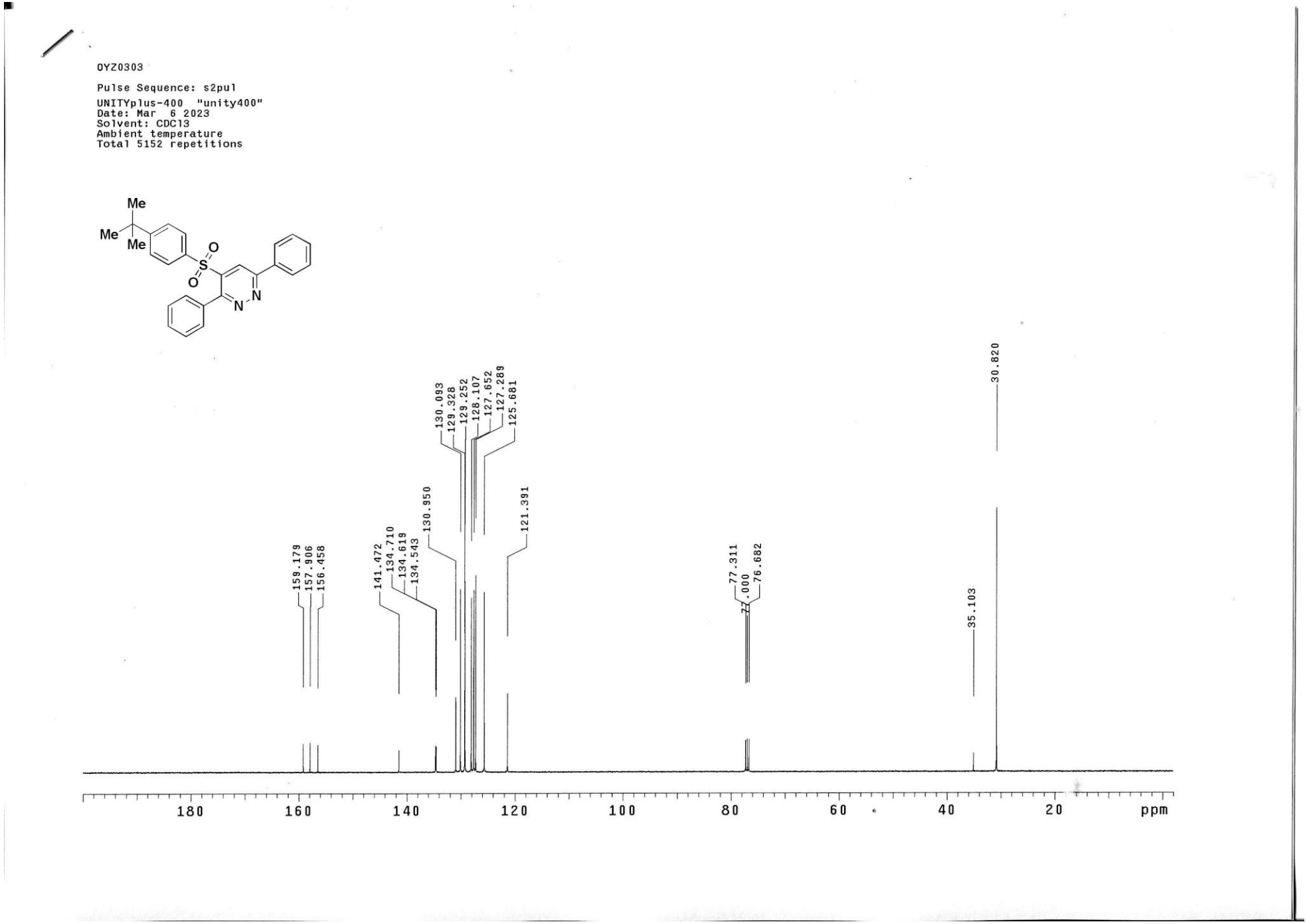




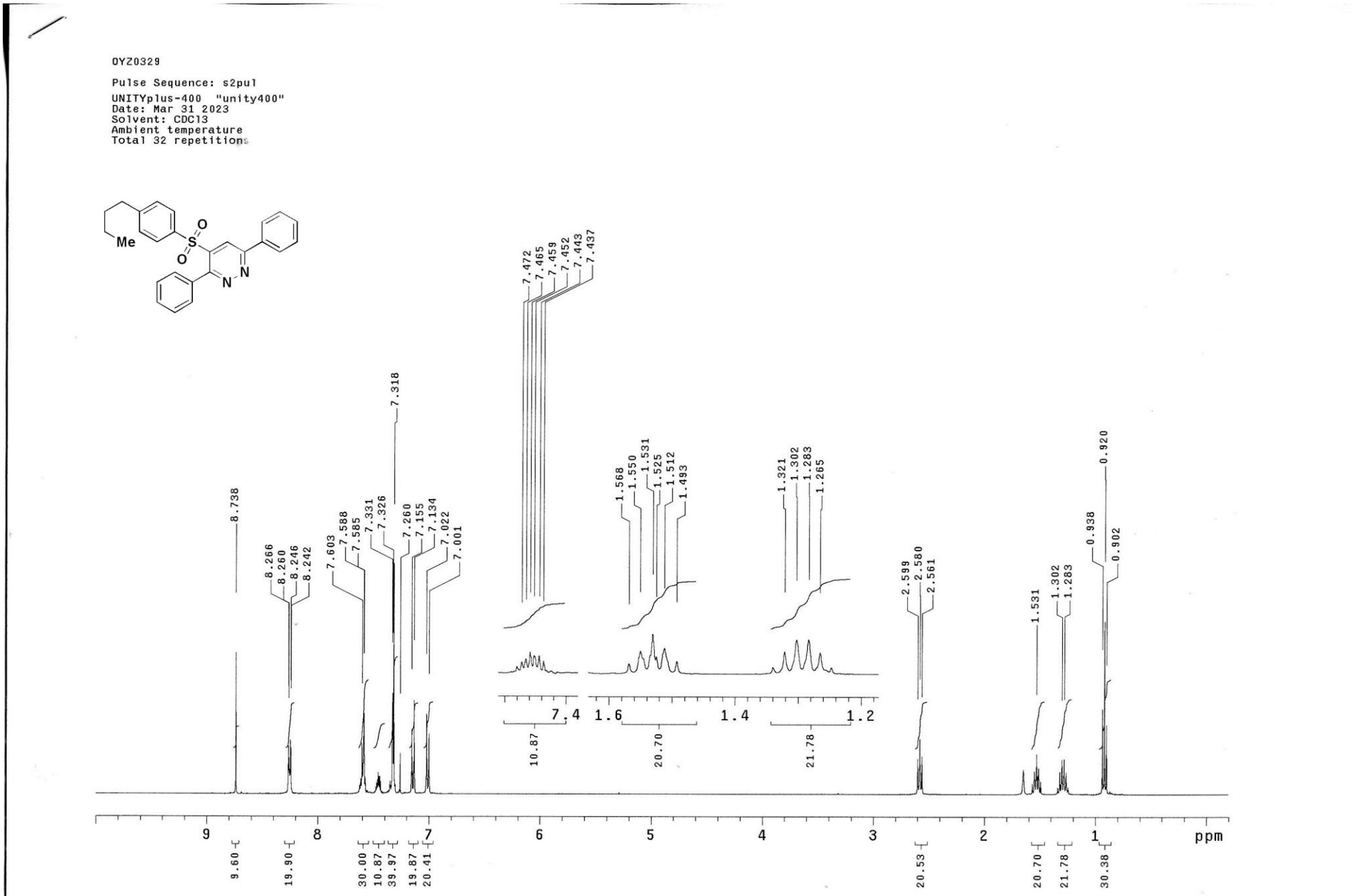
Compound 5v (^{1}H-NMR spectral data)



Compound 5v (^{13}C-NMR spectral data)



Compound 5w (^{1}H-NMR spectral data)

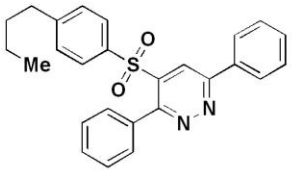


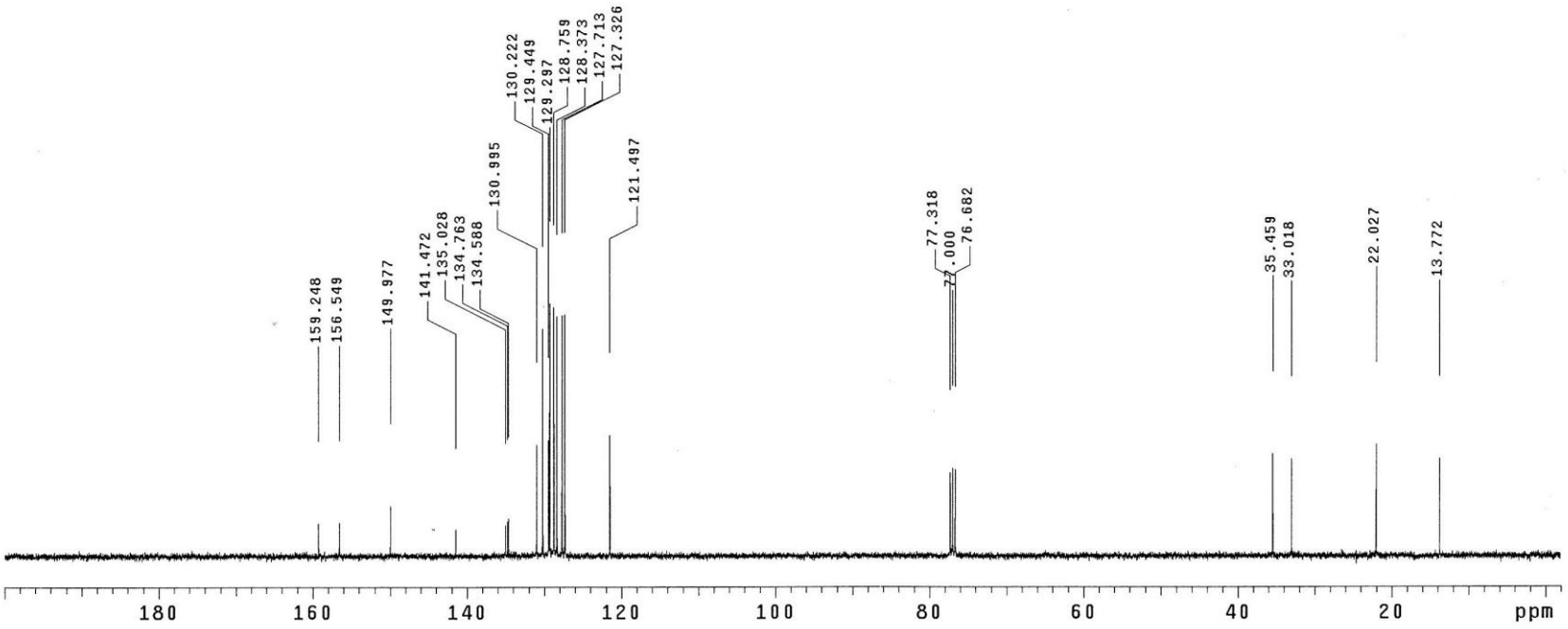
Compound 5w (^{13}C-NMR spectral data)

OYZ0329

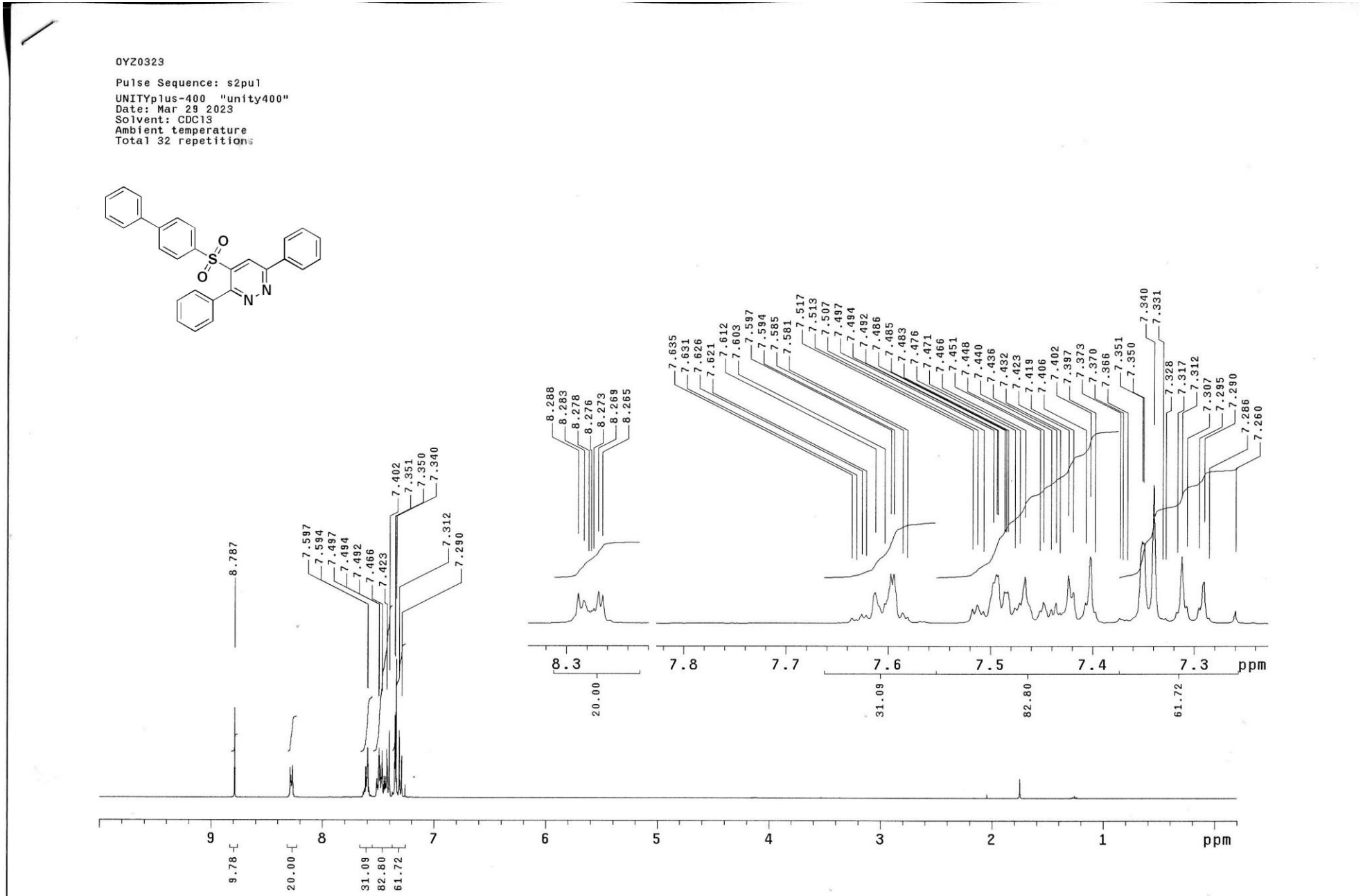
Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Mar 31 2023
Solvent: CDCl3
Ambient temperature
Total 1184 repetitions





Compound 5x (^{1}H-NMR spectral data)

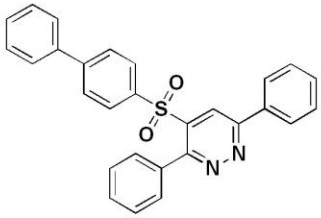


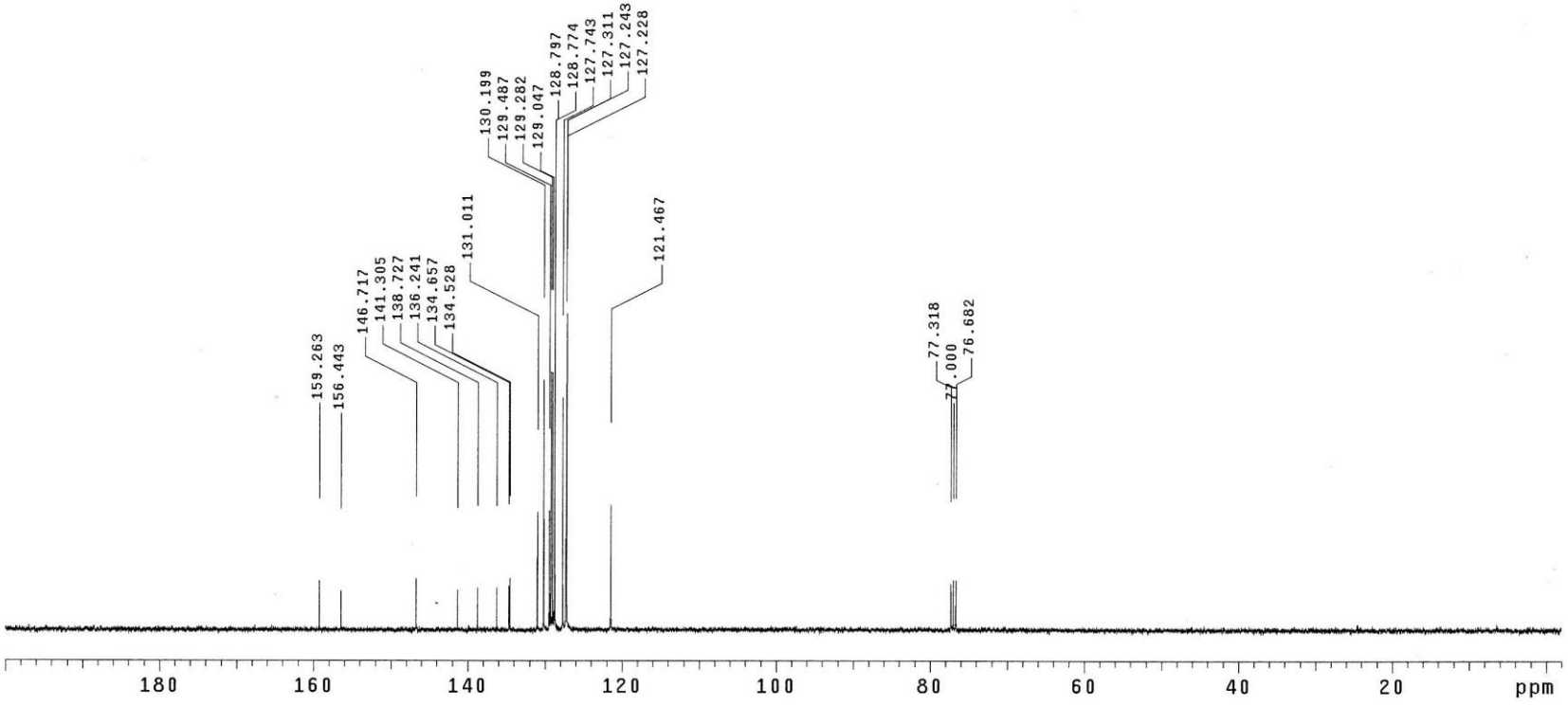
Compound 5x (^{13}C-NMR spectral data)

OYZ0323

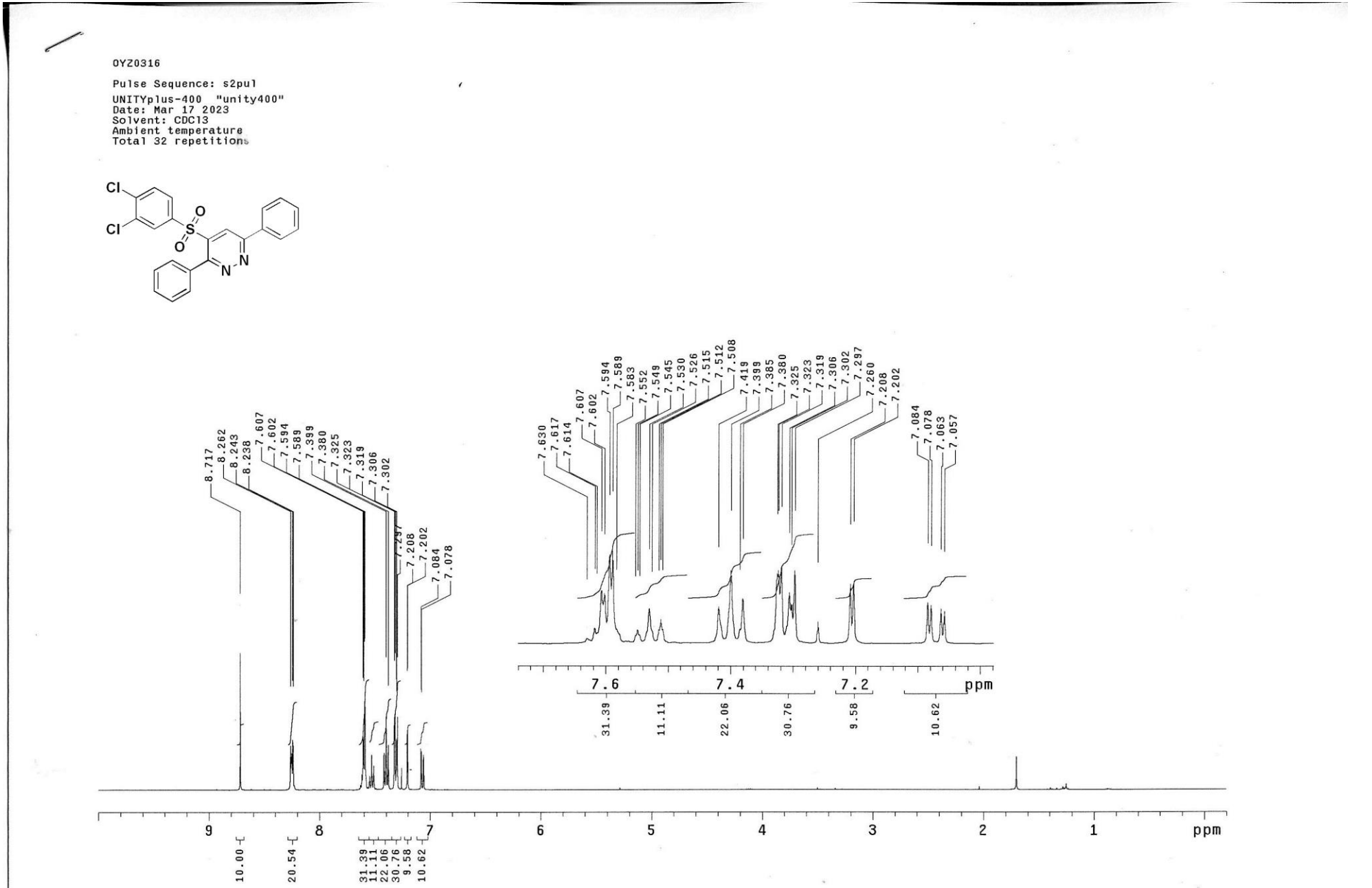
Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Mar 29 2023
Solvent: CDCl3
Ambient temperature
Total 512 repetitions





Compound 5y (^{1}H-NMR spectral data)

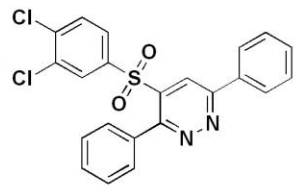


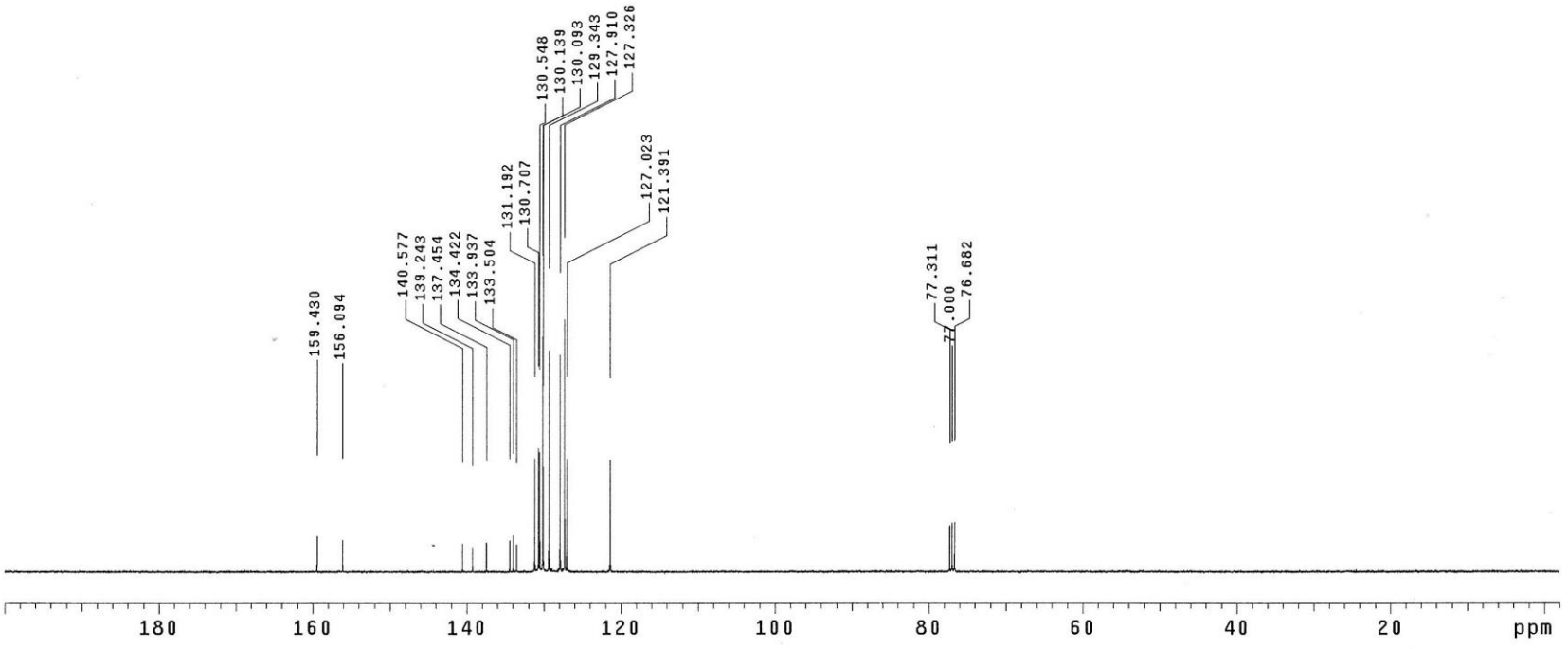
Compound 5y (^{13}C-NMR spectral data)

OYZ0316

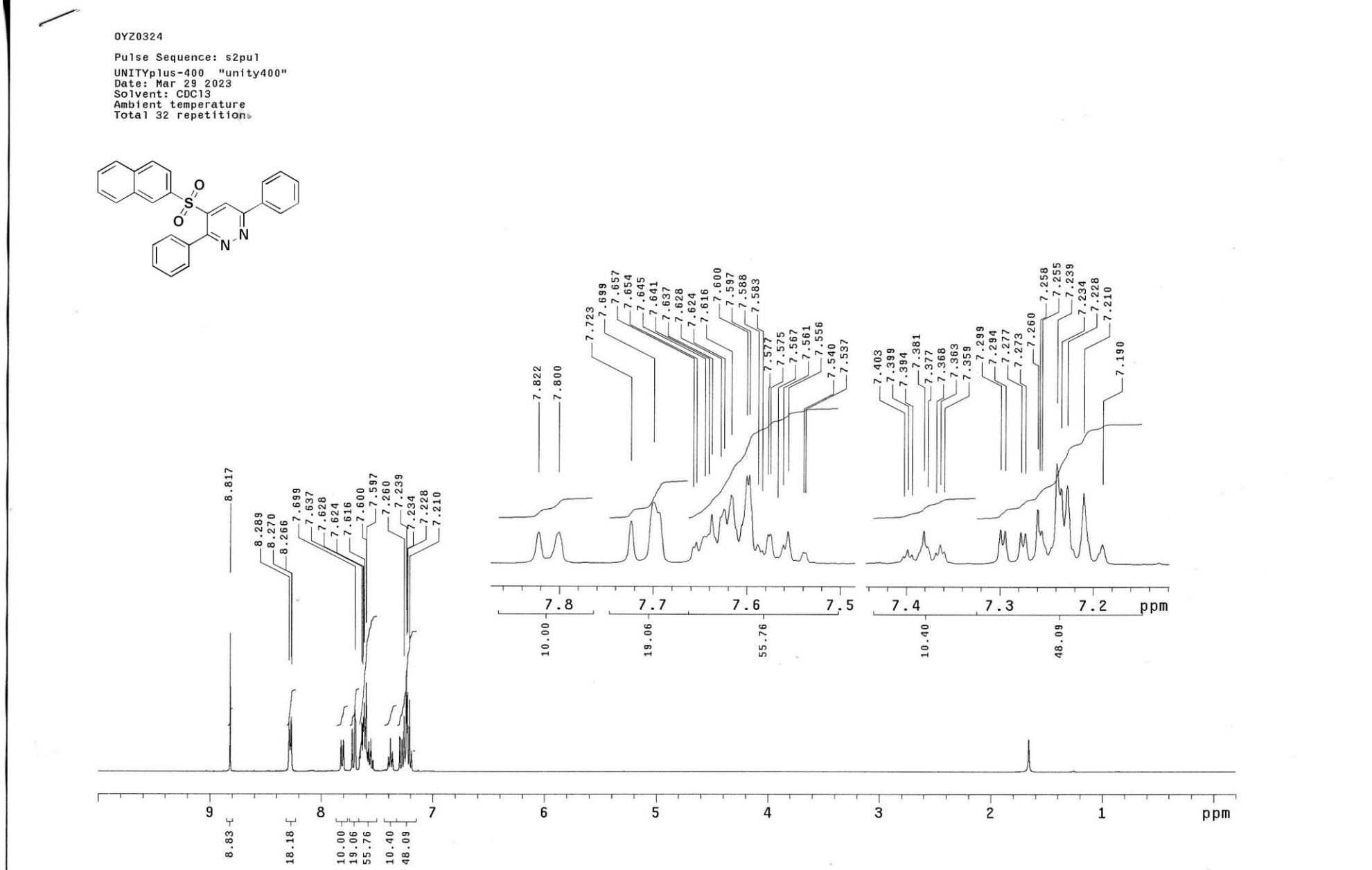
Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Mar 17 2023
Solvent: CDCl3
Ambient temperature
Total 3712 repetitions





Compound 5z (^{1}H-NMR spectral data)

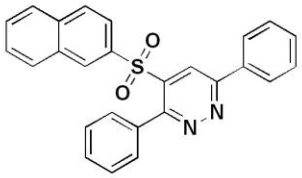


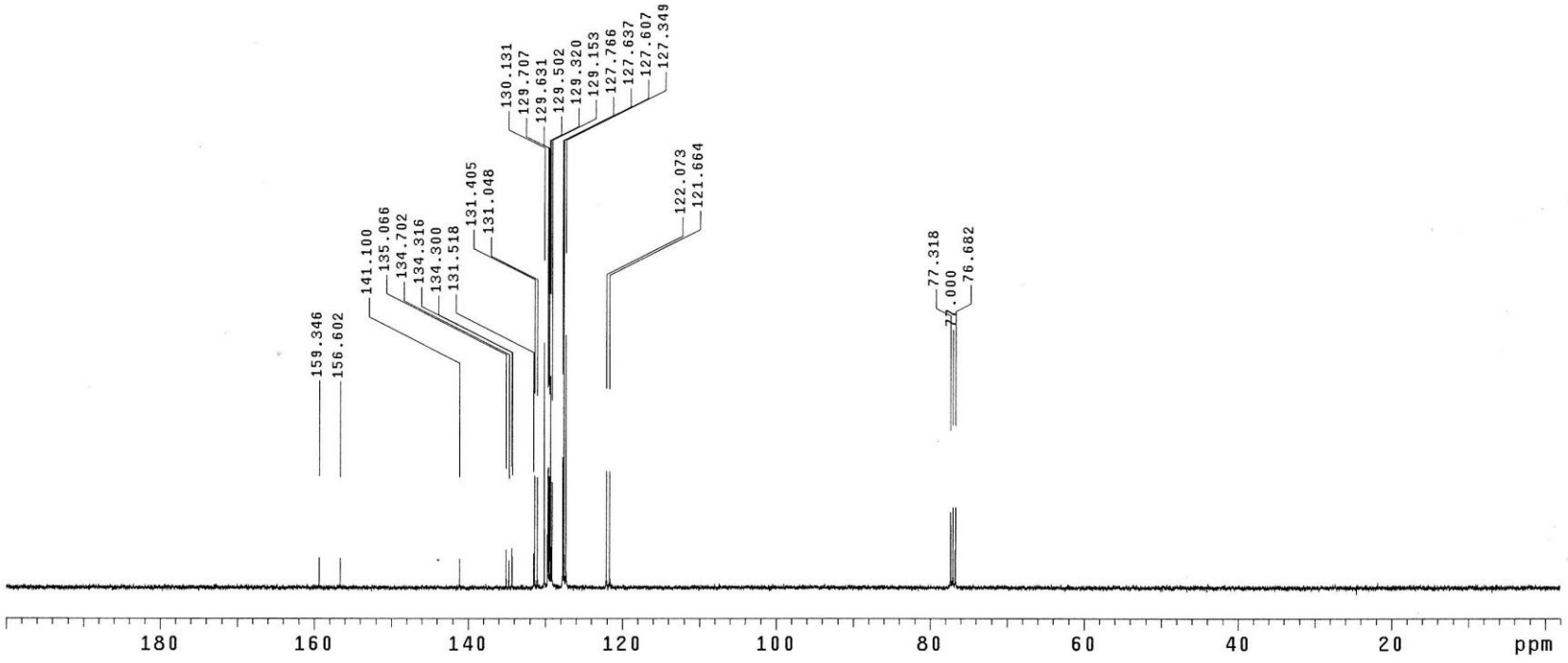
Compound 5z (^{13}C-NMR spectral data)

OYZ0324

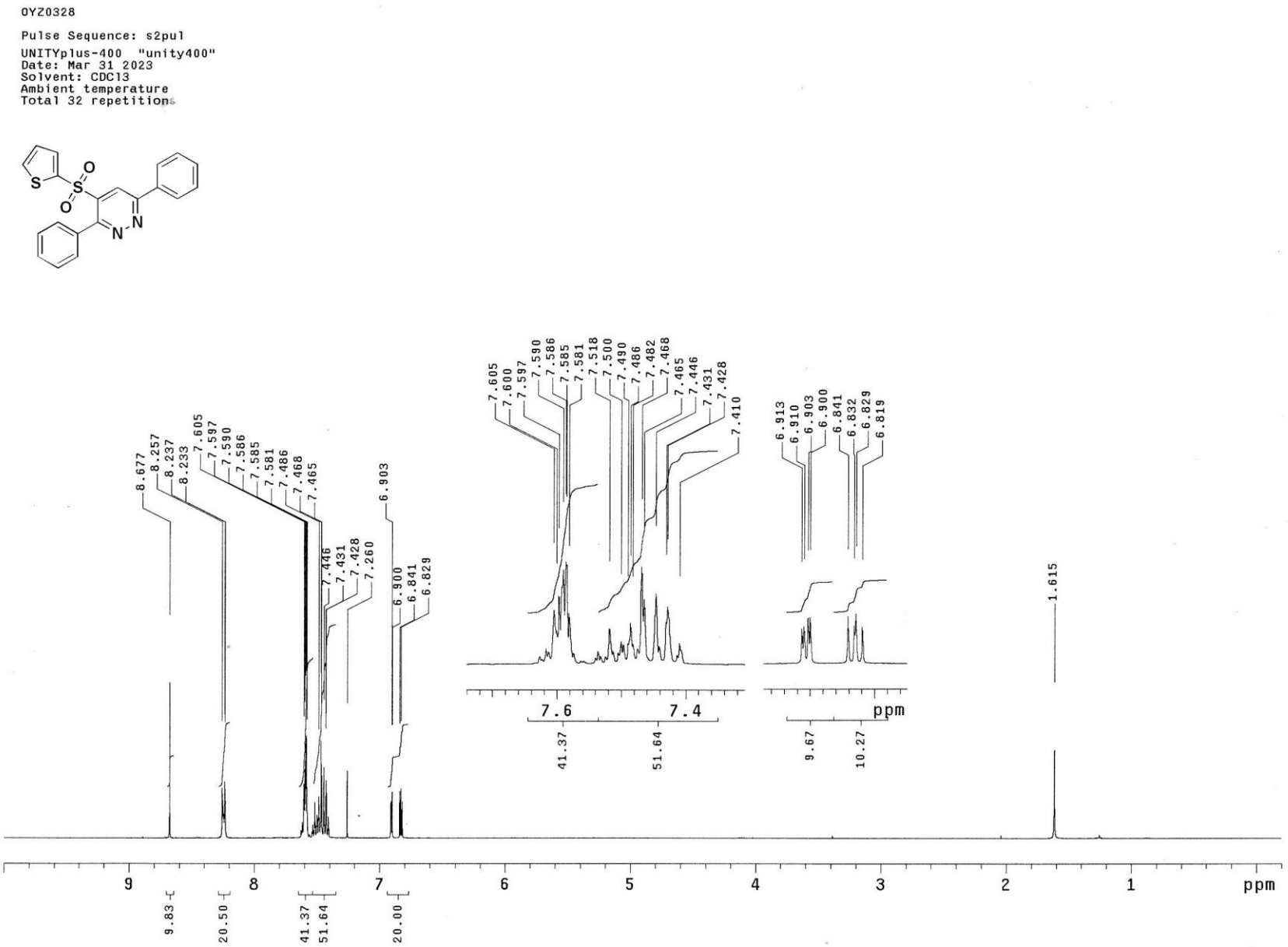
Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Mar 29 2023
Solvent: CDCl3
Ambient temperature
Total 2016 repetitions





Compound 5aa (^{1}H-NMR spectral data)

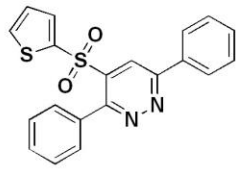


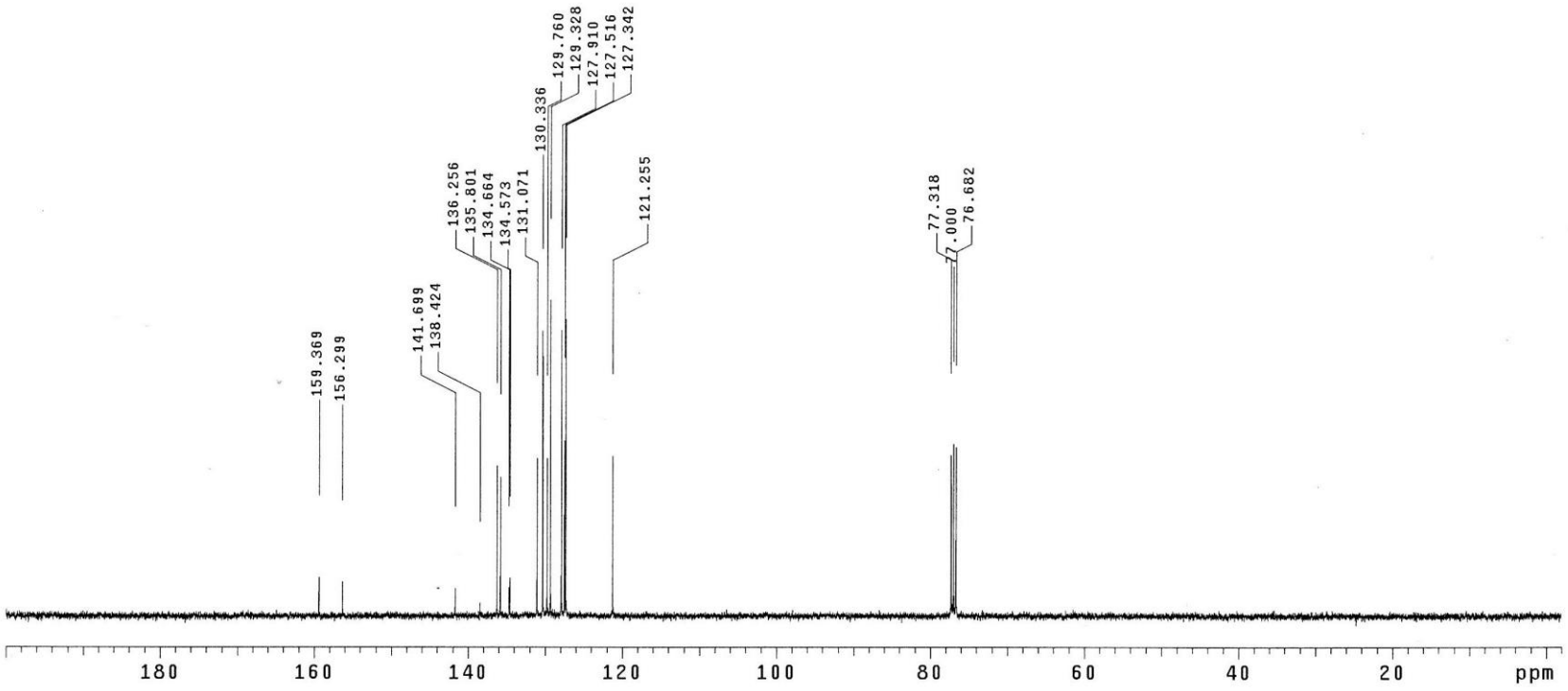
Compound 5aa (^{13}C-NMR spectral data)

OYZ0328

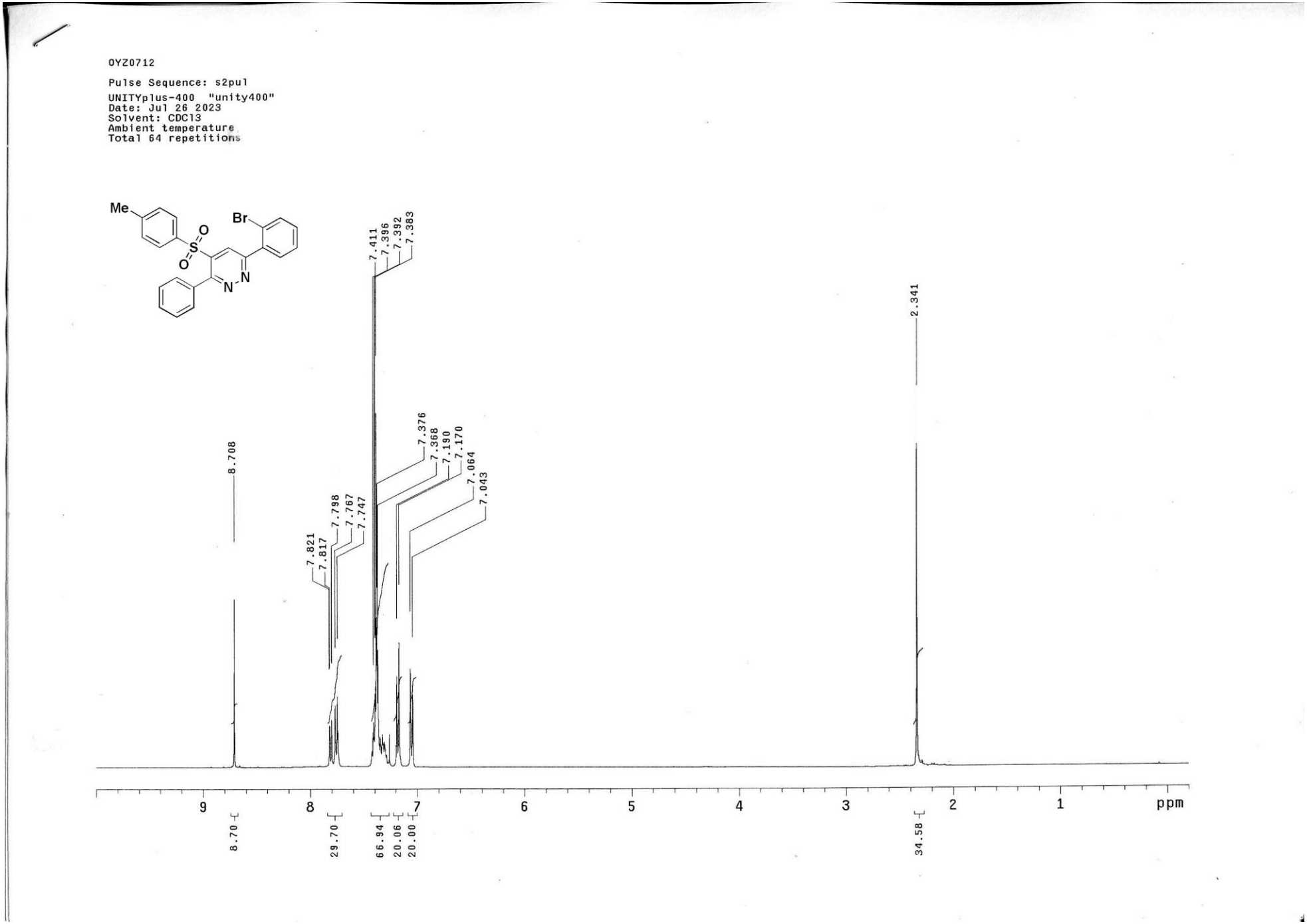
Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Mar 31 2023
Solvent: CDCl3
Ambient temperature
Total 3648 repetitions

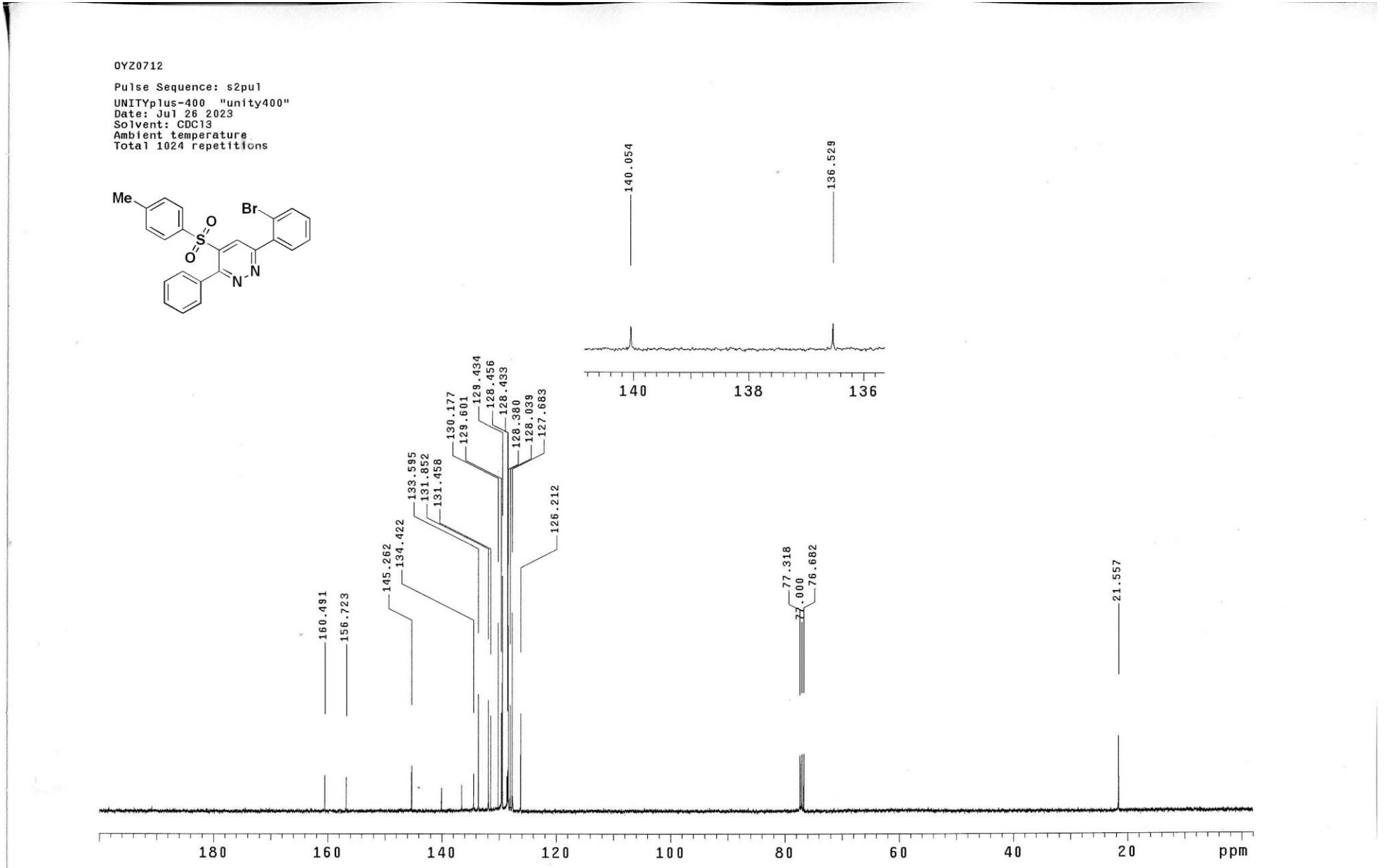




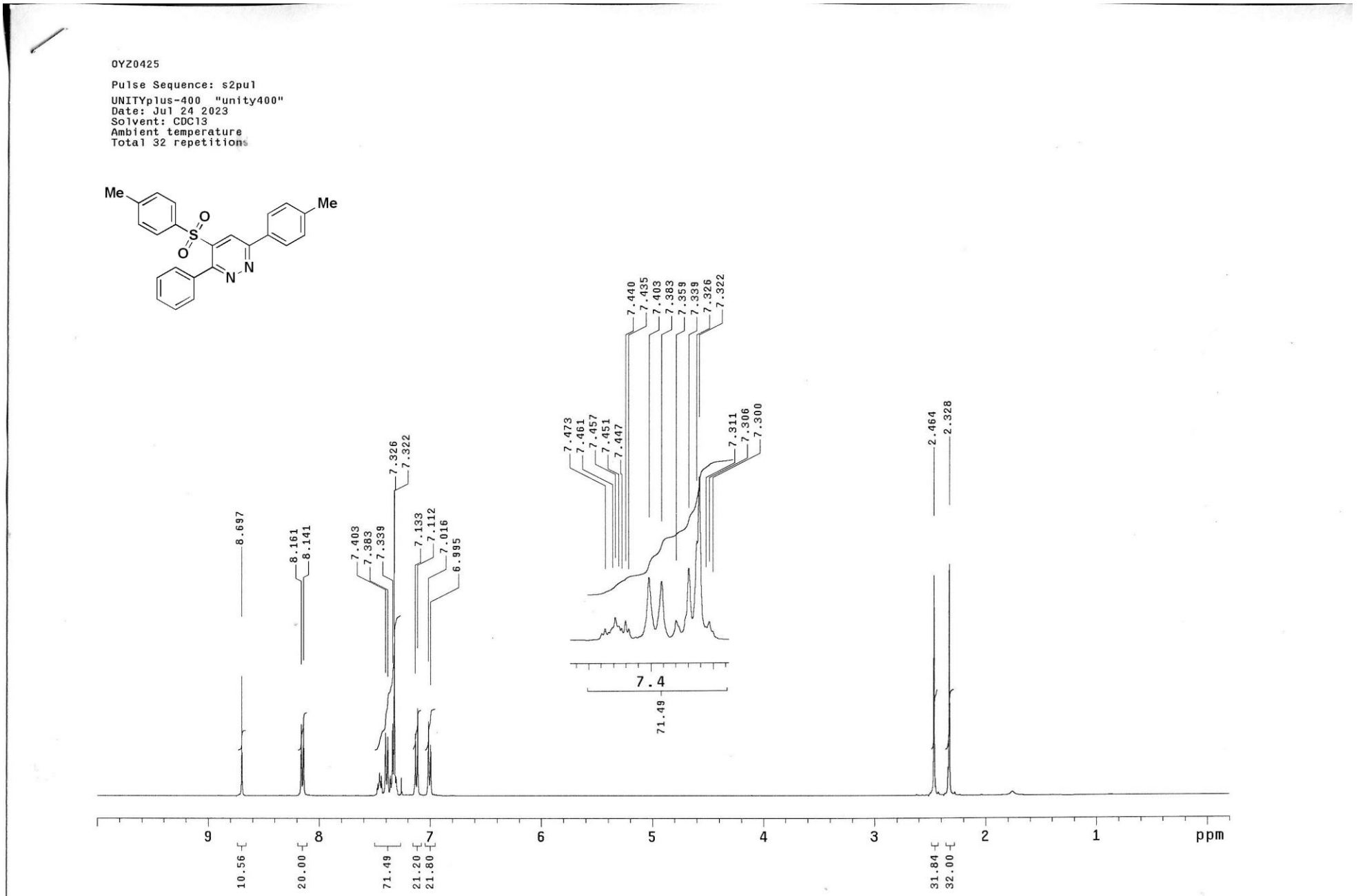
Compound 5ab (^{1}H-NMR spectral data)



Compound 5ab (^{13}C-NMR spectral data)



Compound 5ac (^{1}H-NMR spectral data)

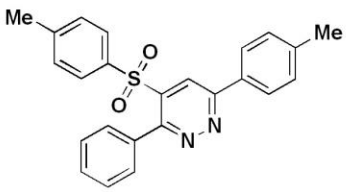


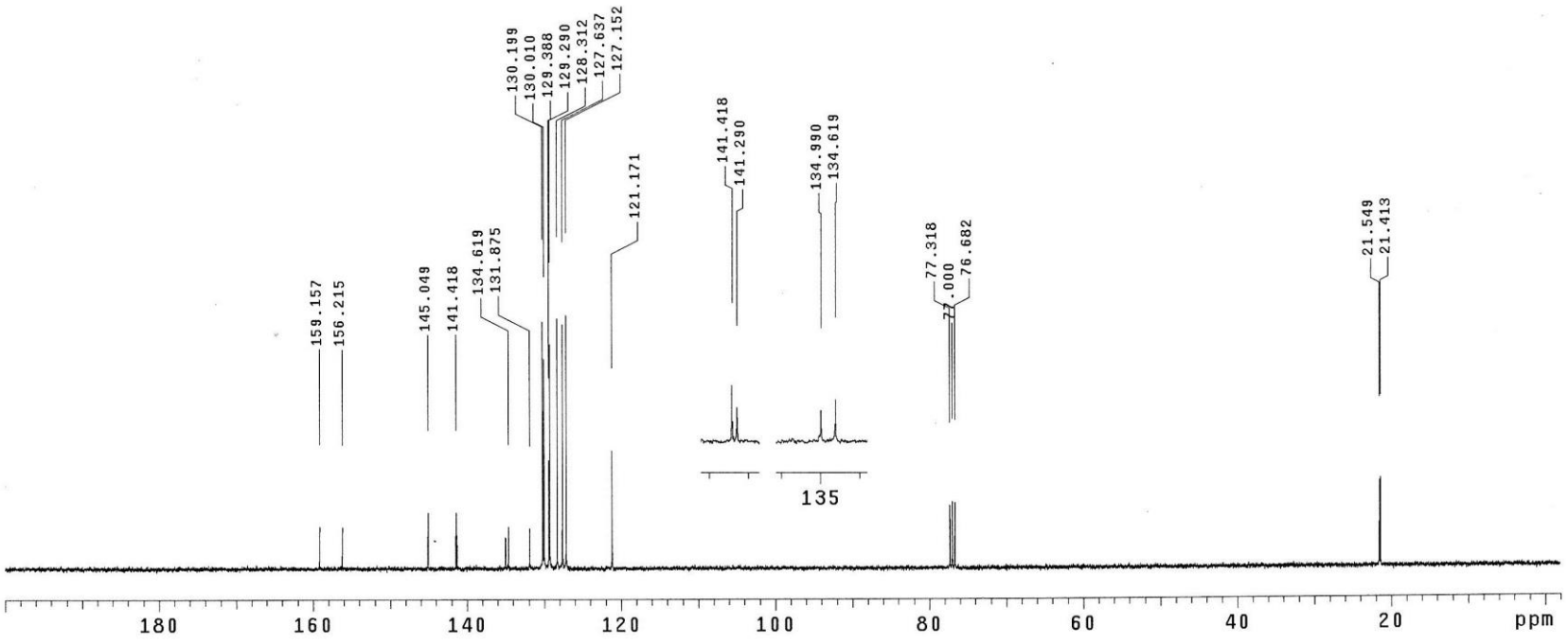
Compound 5ac (^{13}C-NMR spectral data)

OYZ0425

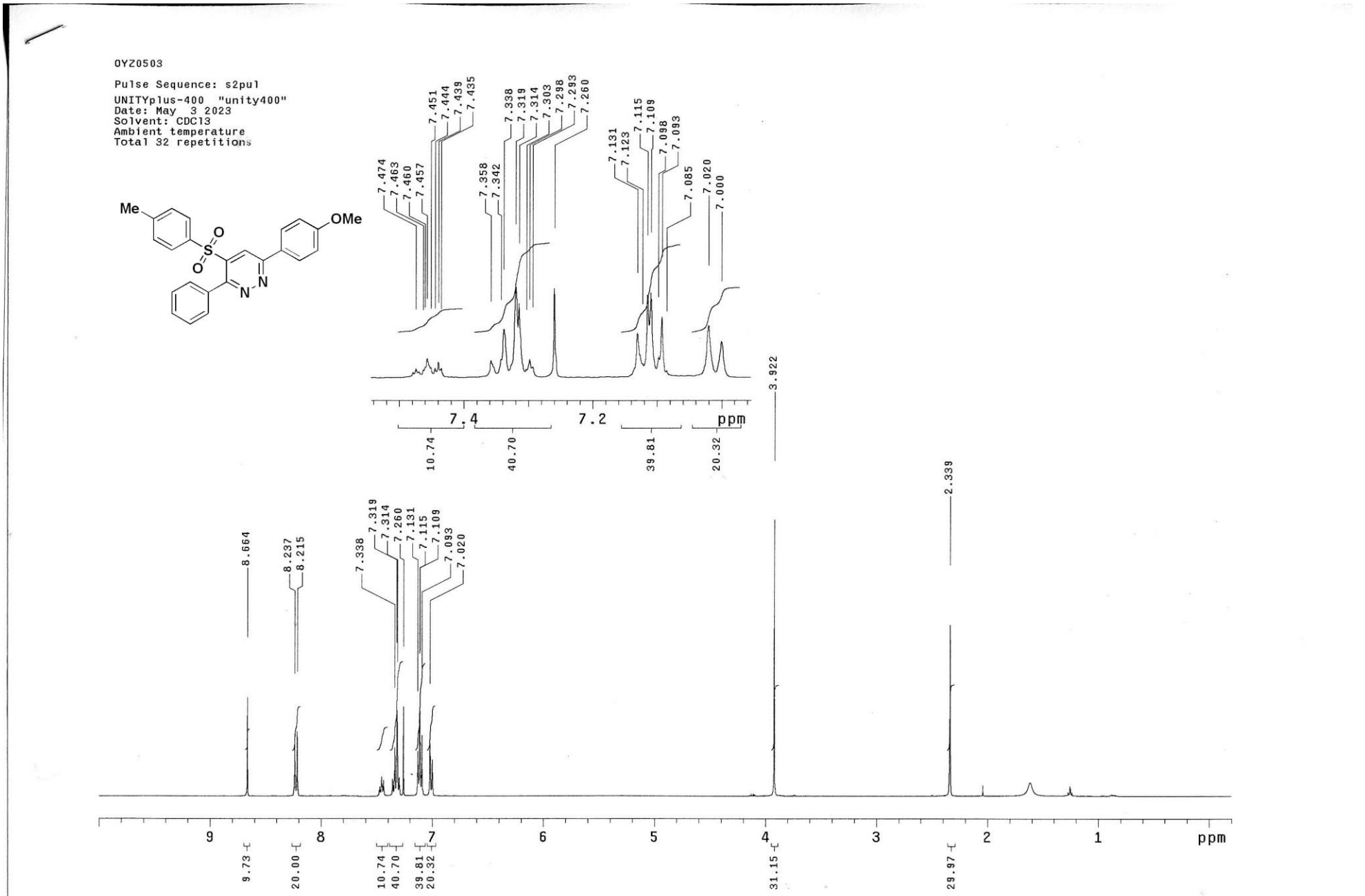
Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Jul 24 2023
Solvent: CDCl3
Ambient temperature
Total 880 repetitions





Compound 5ad (^{1}H-NMR spectral data)

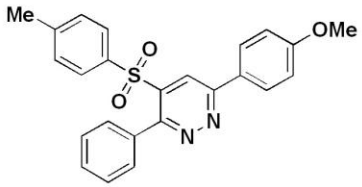


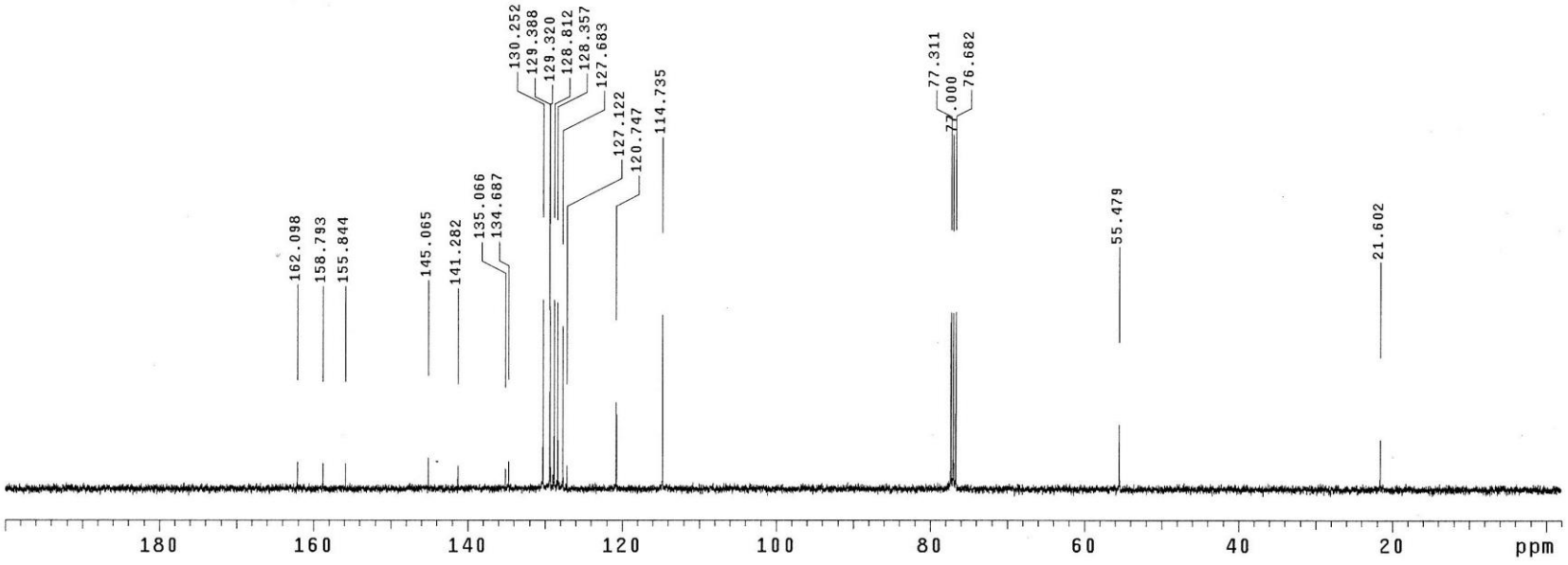
Compound 5ad (^{13}C-NMR spectral data)

OYZ0503

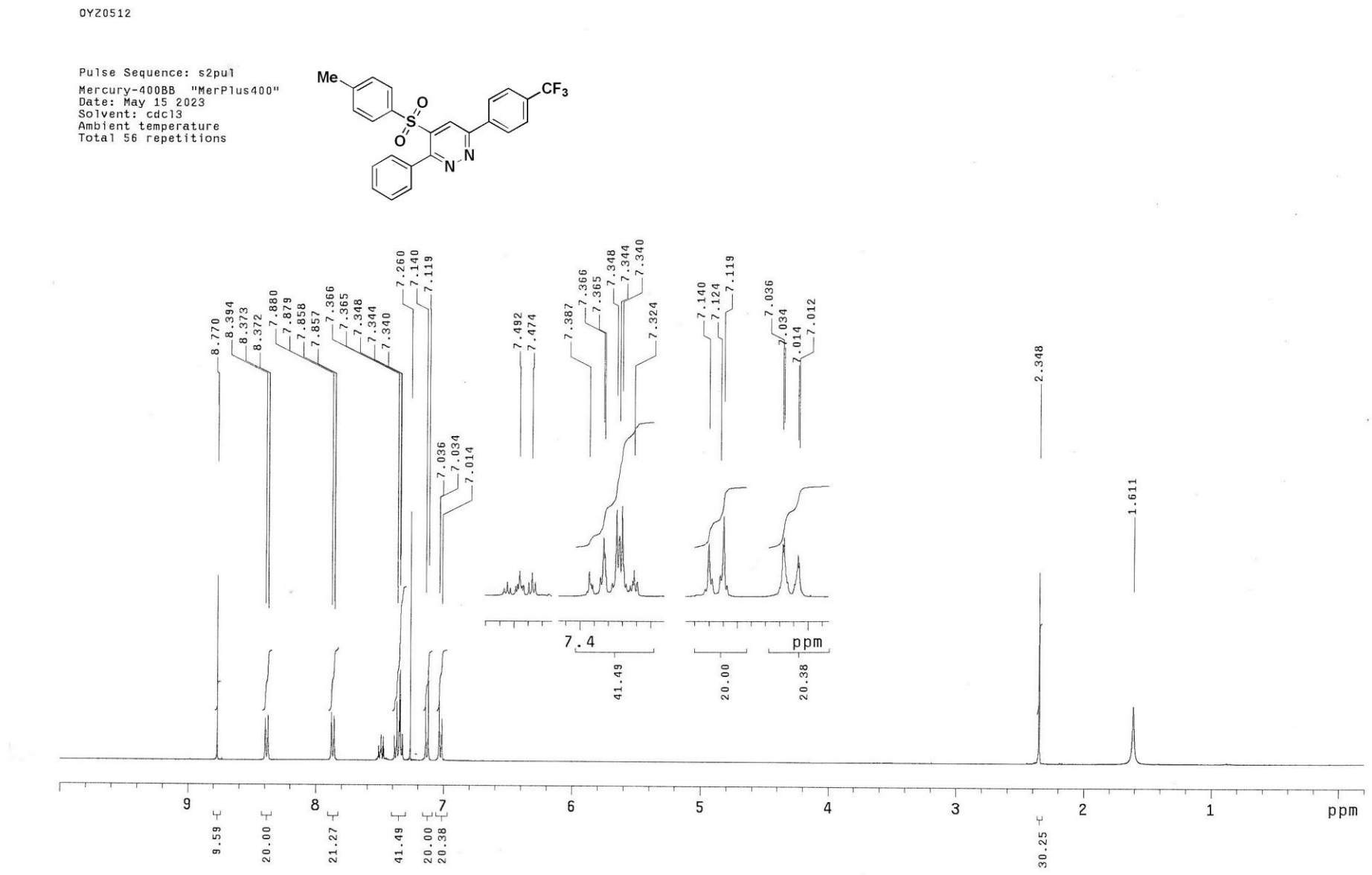
Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: May 3 2023
Solvent: CDCl3
Ambient temperature
Total 3808 repetitions

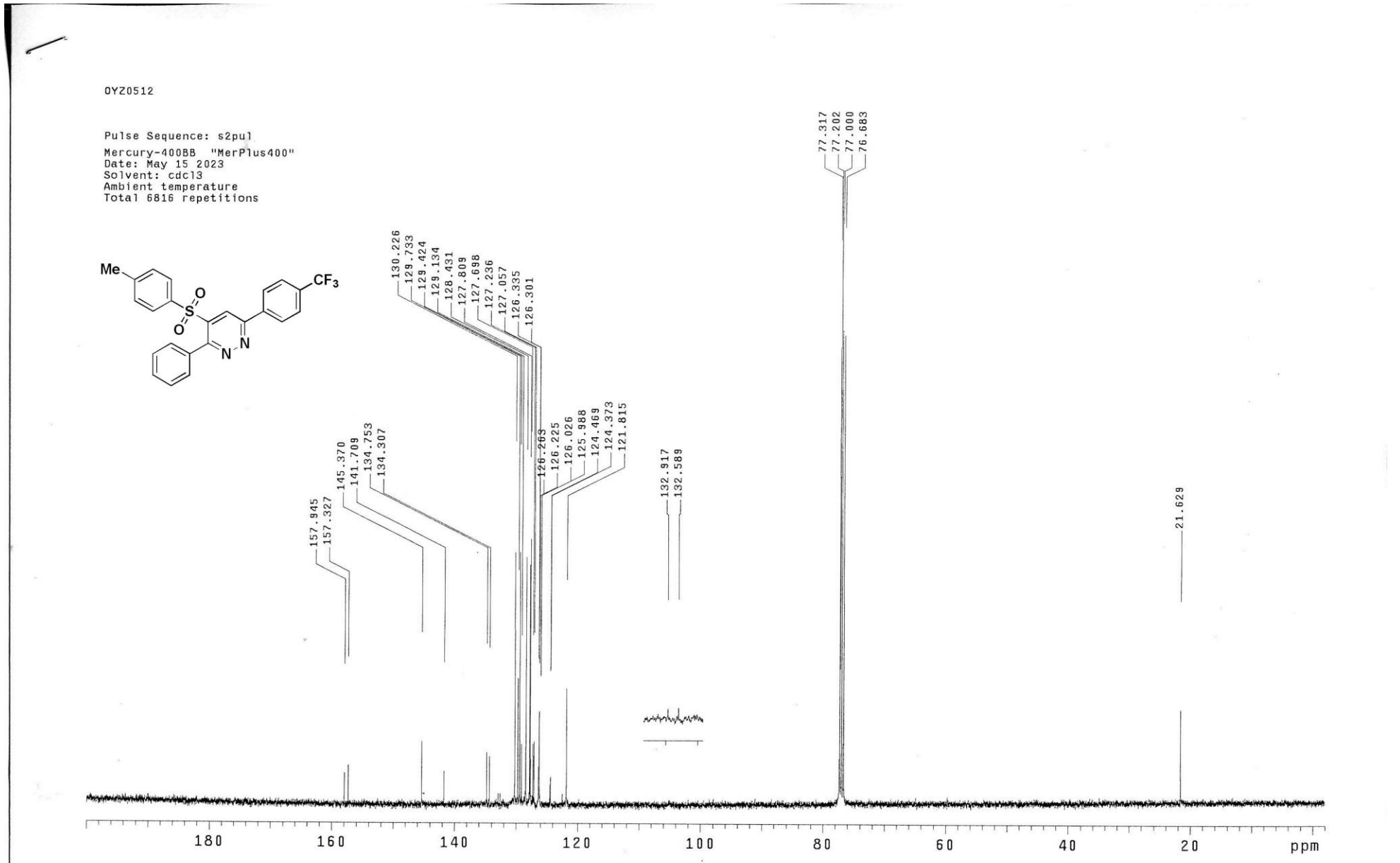




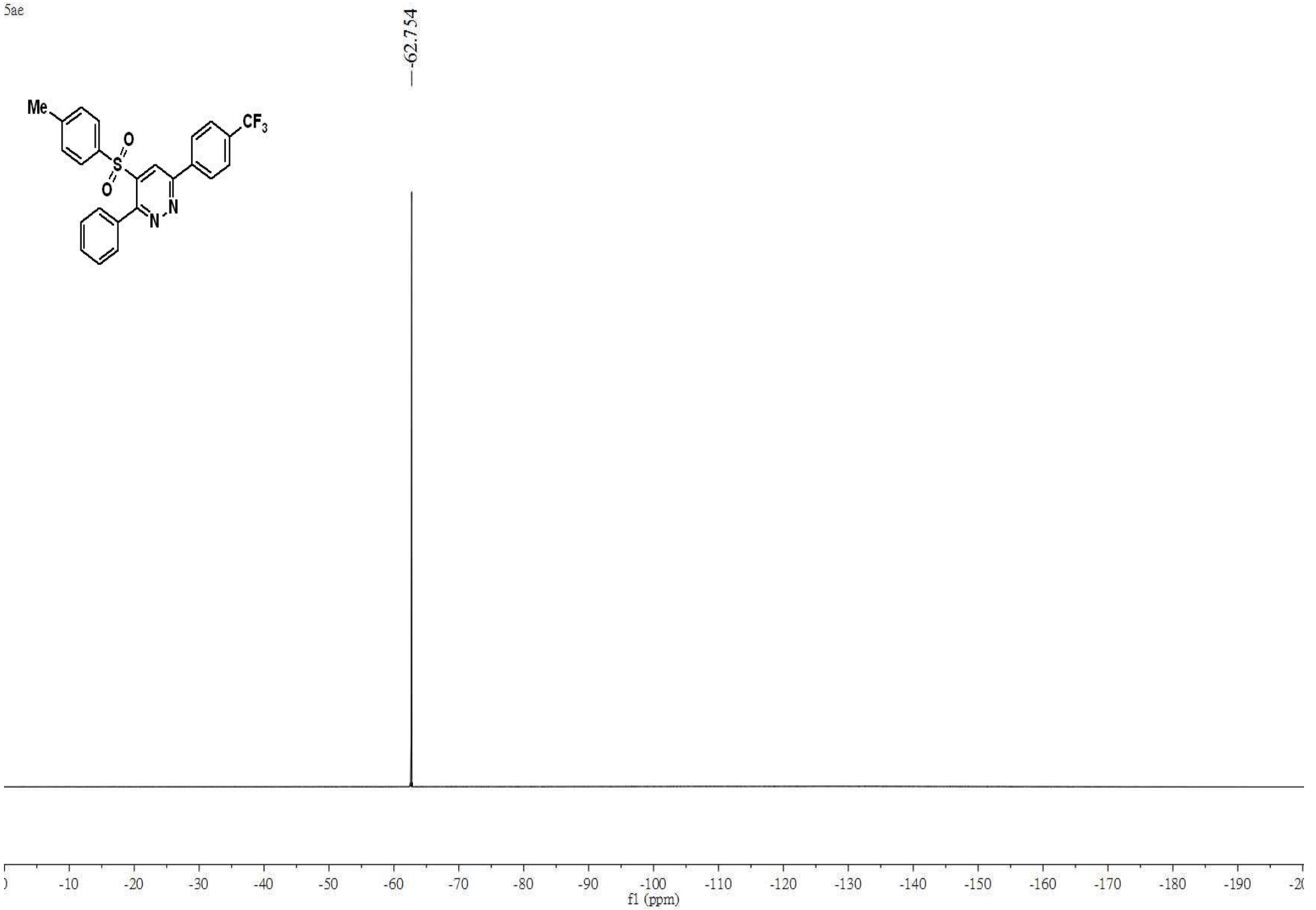
Compound 5ae (^{1}H-NMR spectral data)



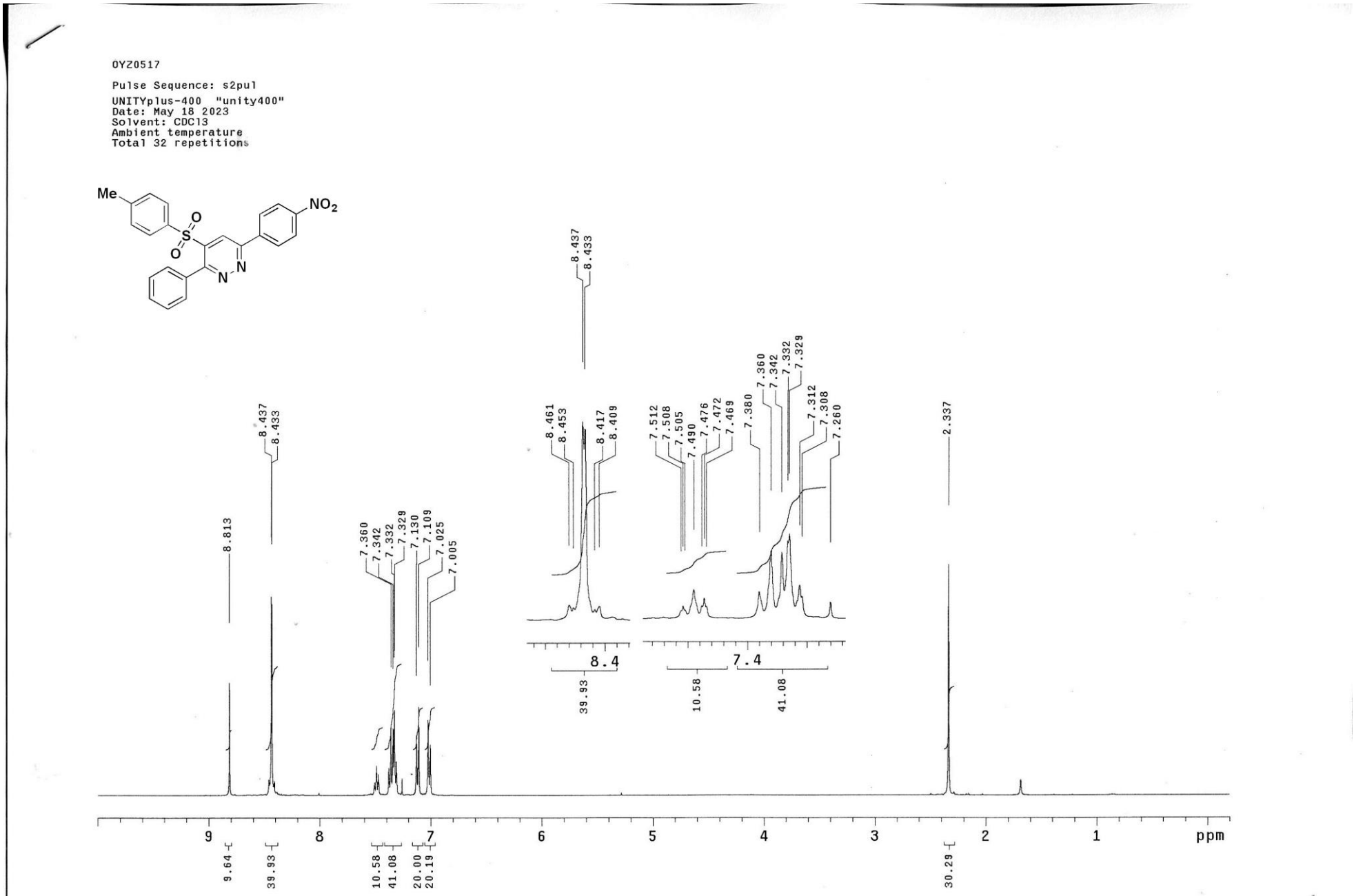
Compound 5ae (^{13}C-NMR spectral data)



Compound 5ae (^{19}F-NMR spectral data)



Compound 5af (^{1}H-NMR spectral data)

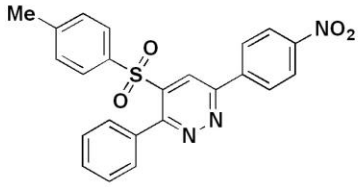


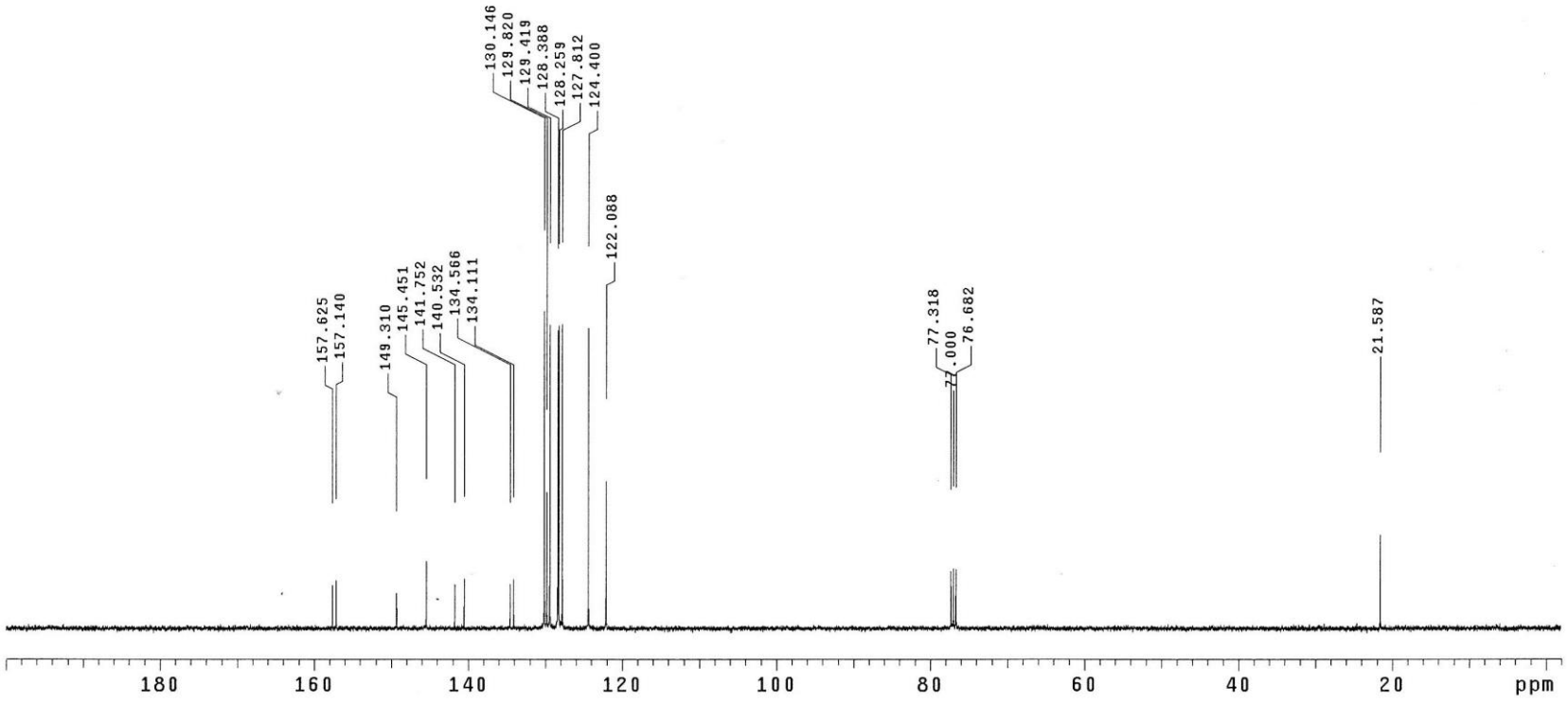
Compound 5af (^{13}C-NMR spectral data)

OYZ0517

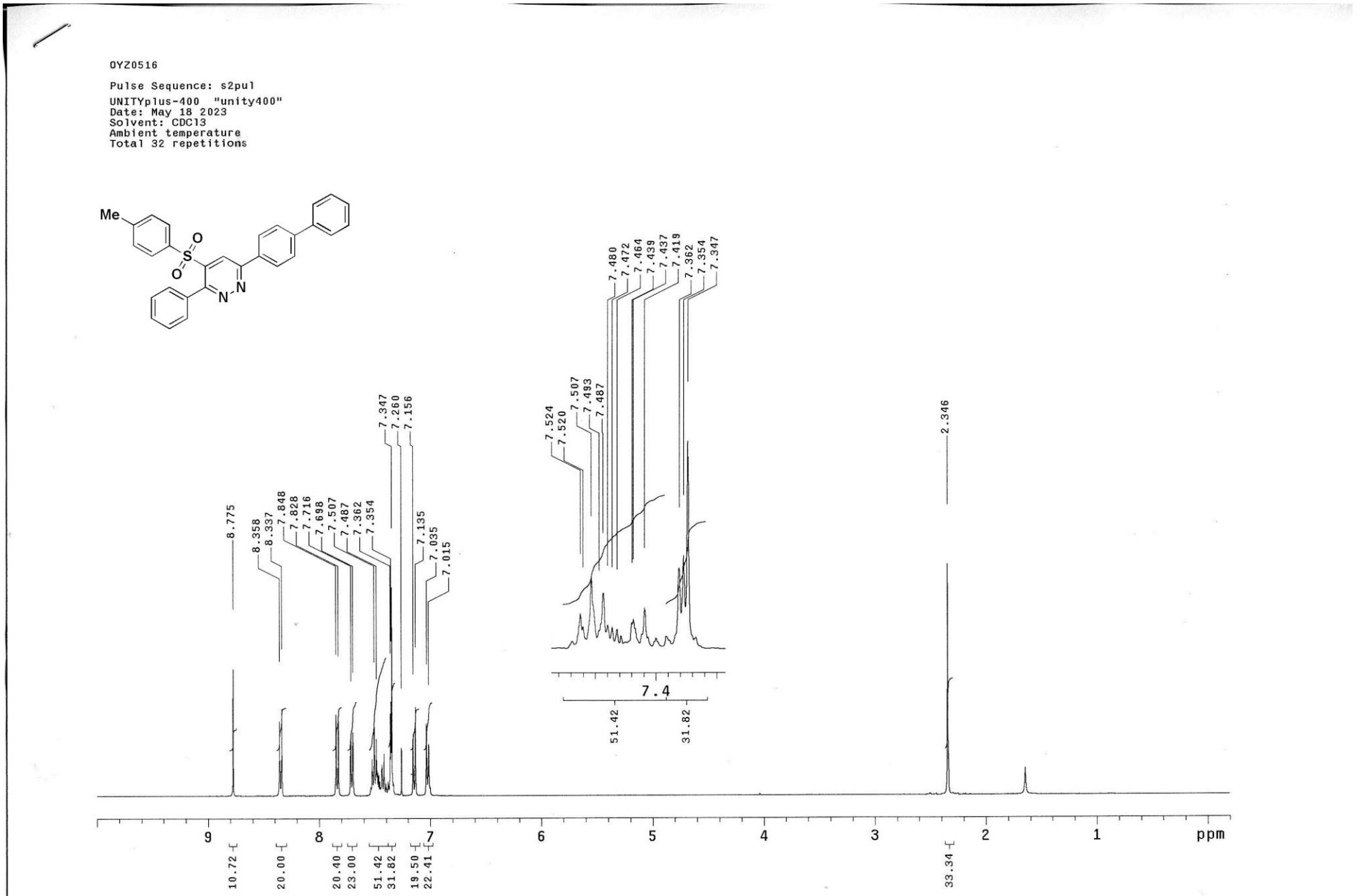
Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: May 18 2023
Solvent: CDCl3
Ambient temperature
Total 1504 repetitions





Compound 5ag (^{1}H-NMR spectral data)

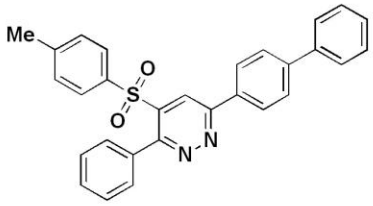


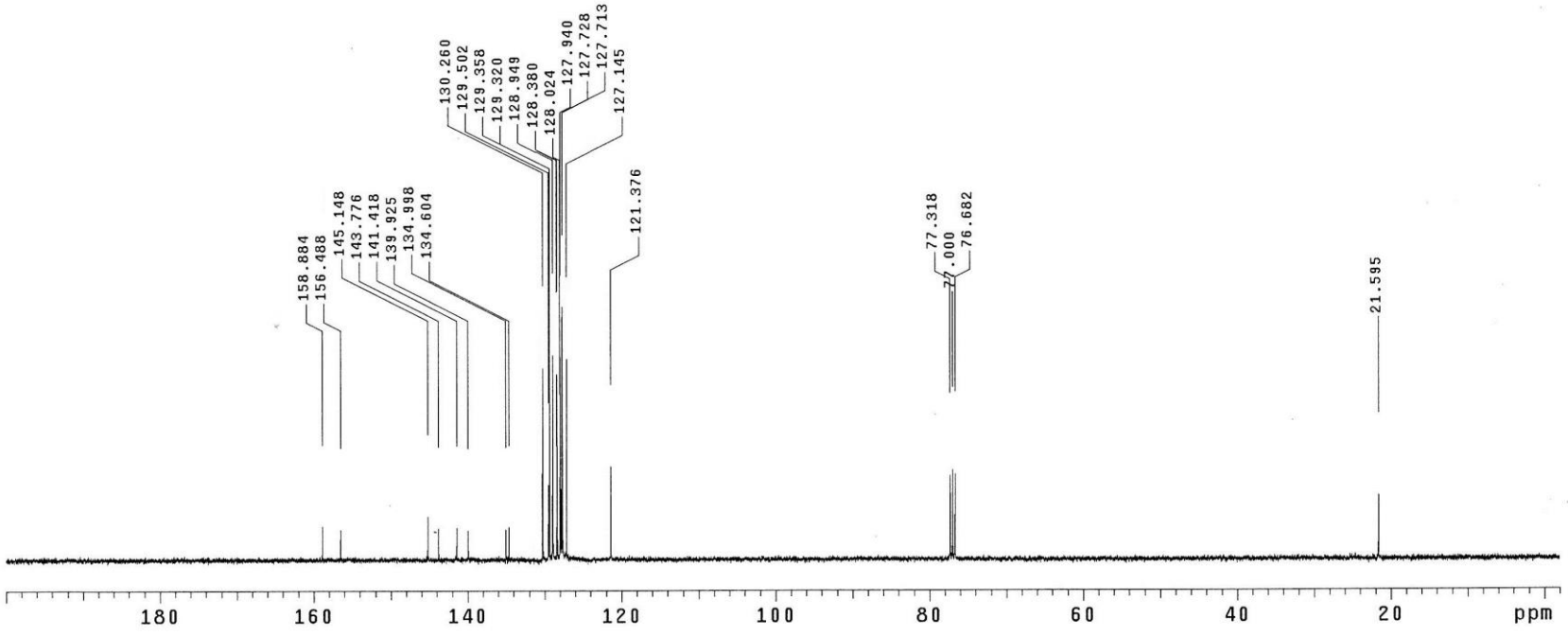
Compound 5ag (^{13}C-NMR spectral data)

OYZ0516

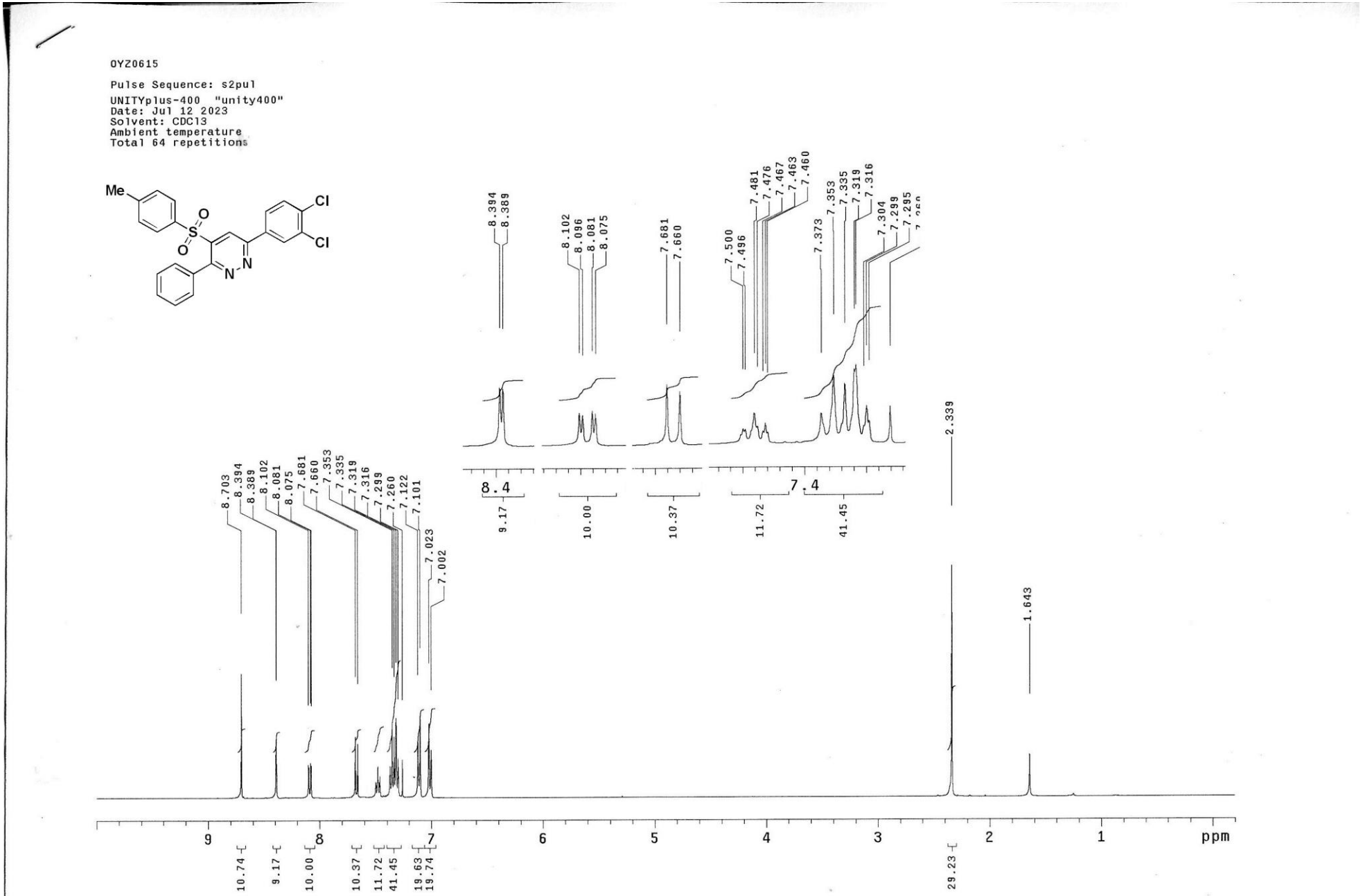
Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: May 18 2023
Solvent: CDCl3
Ambient temperature
Total 2208 repetitions

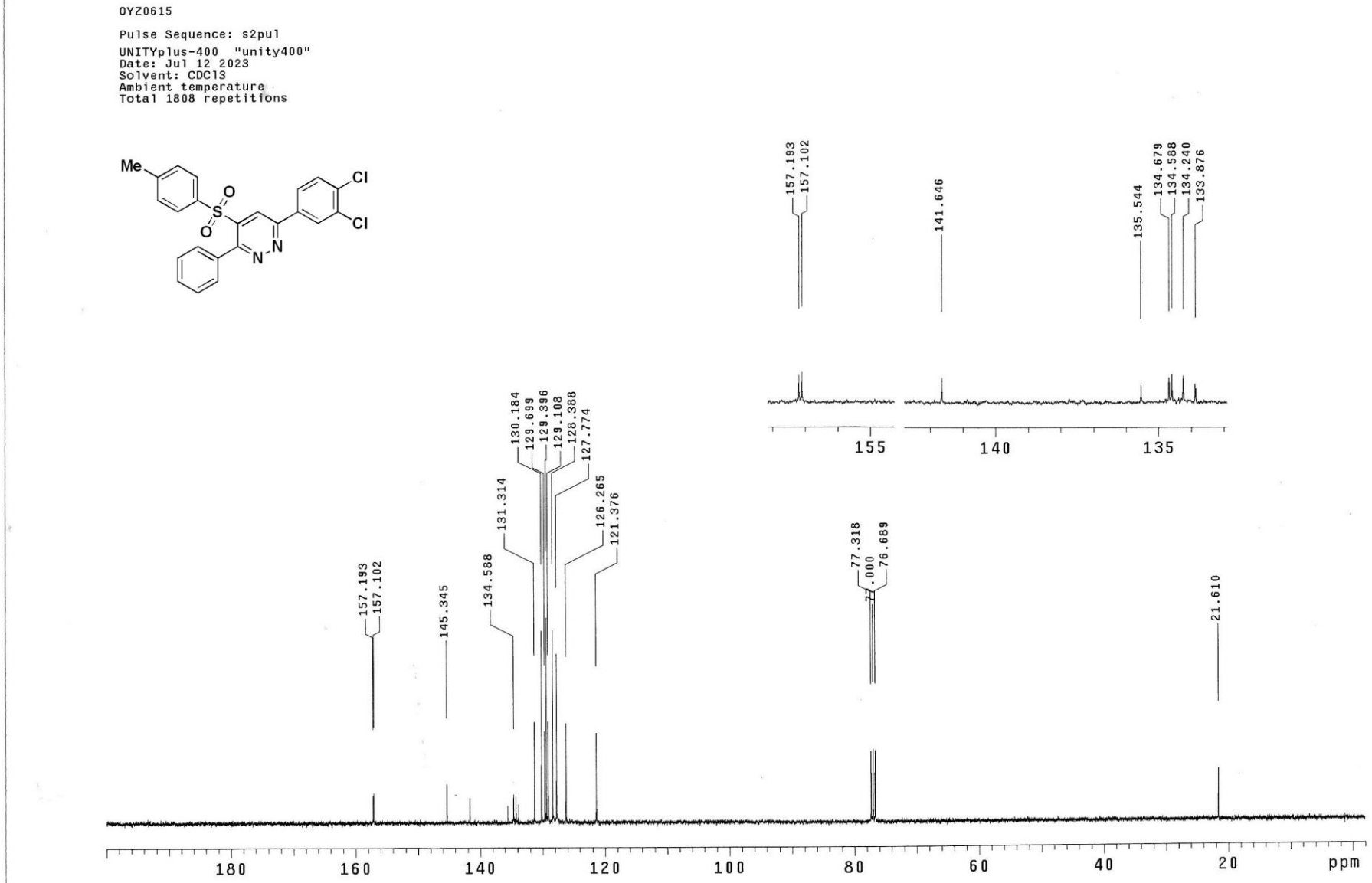




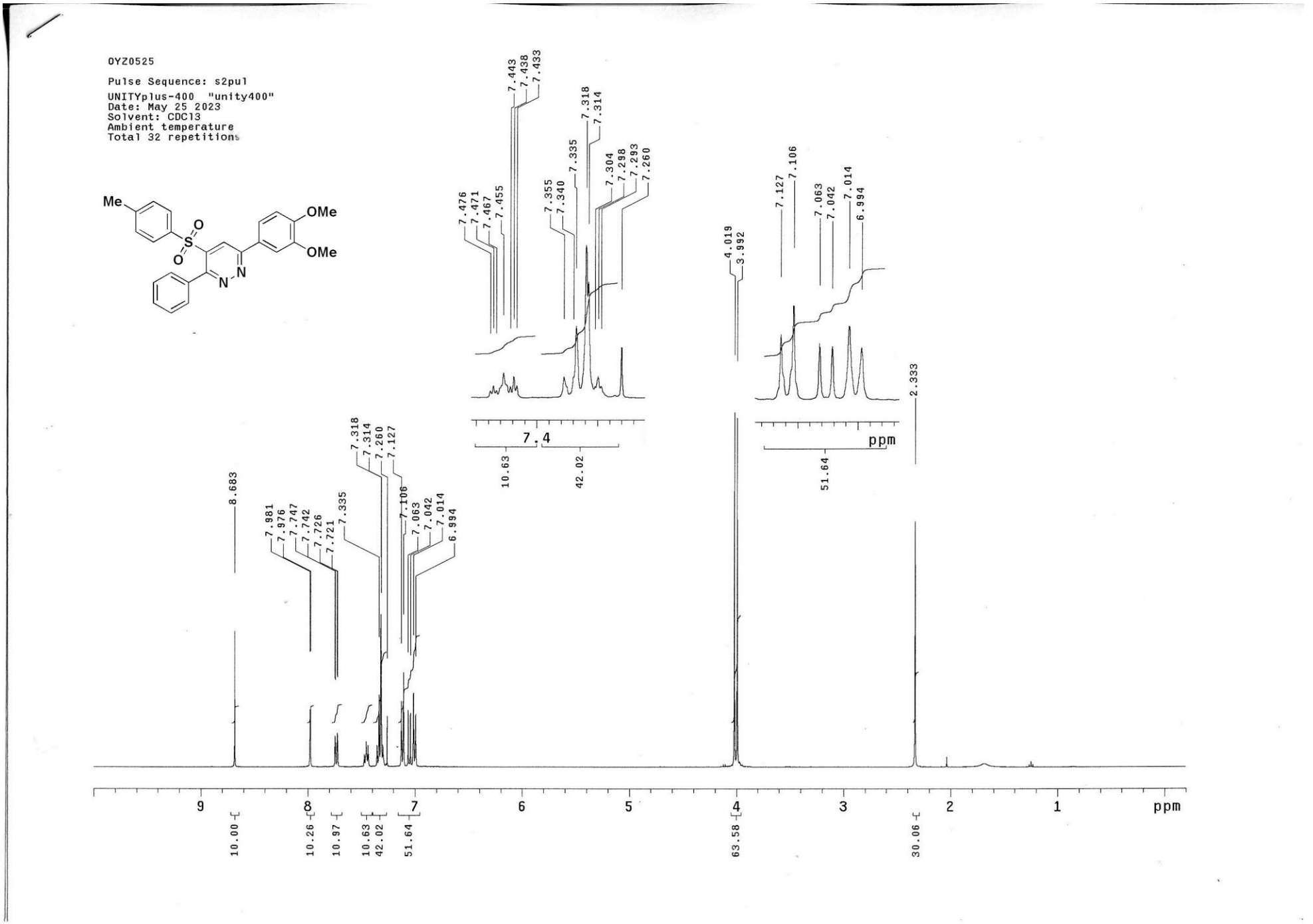
Compound 5ah (^{1}H-NMR spectral data)



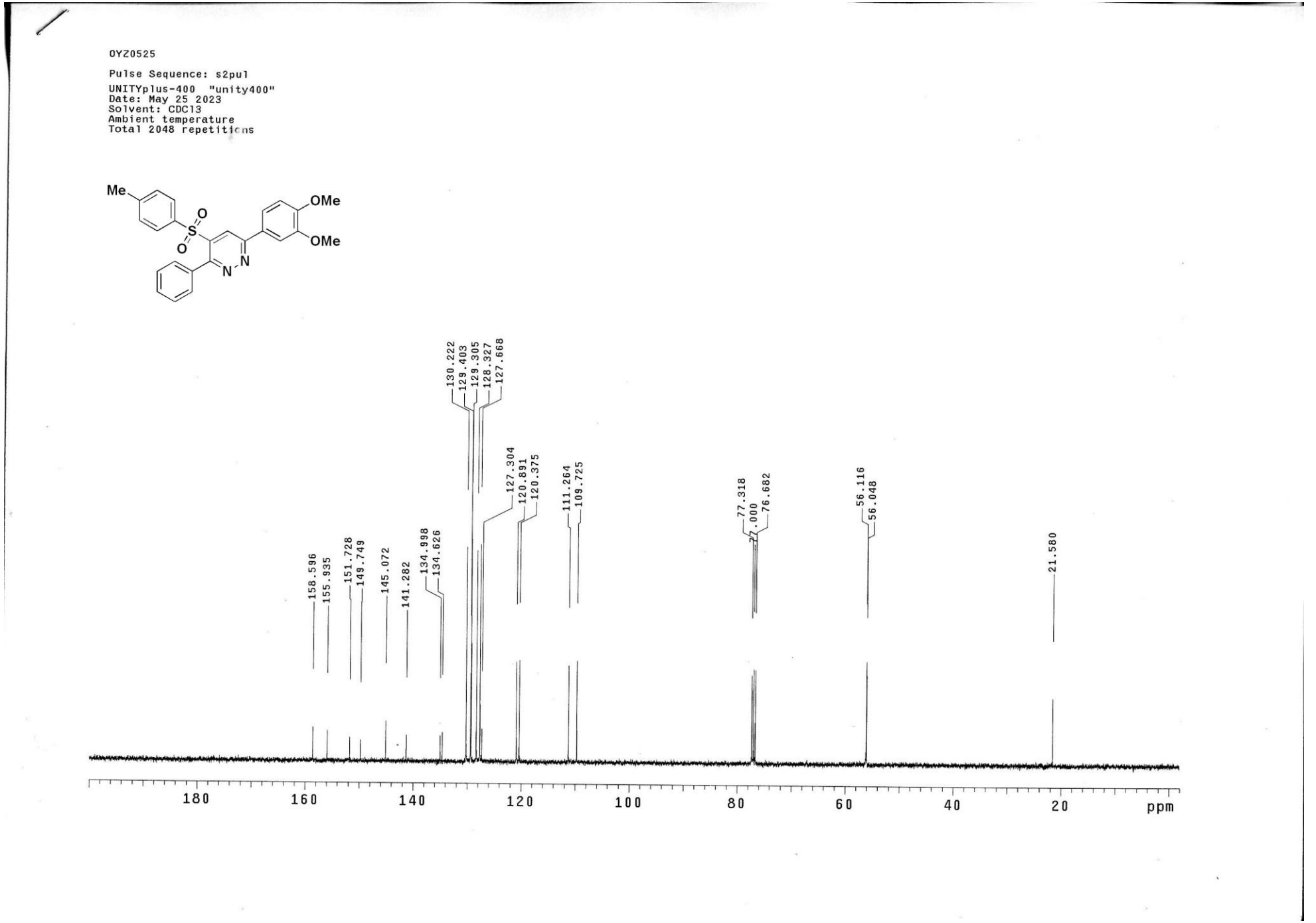
Compound 5ah (^{13}C-NMR spectral data)



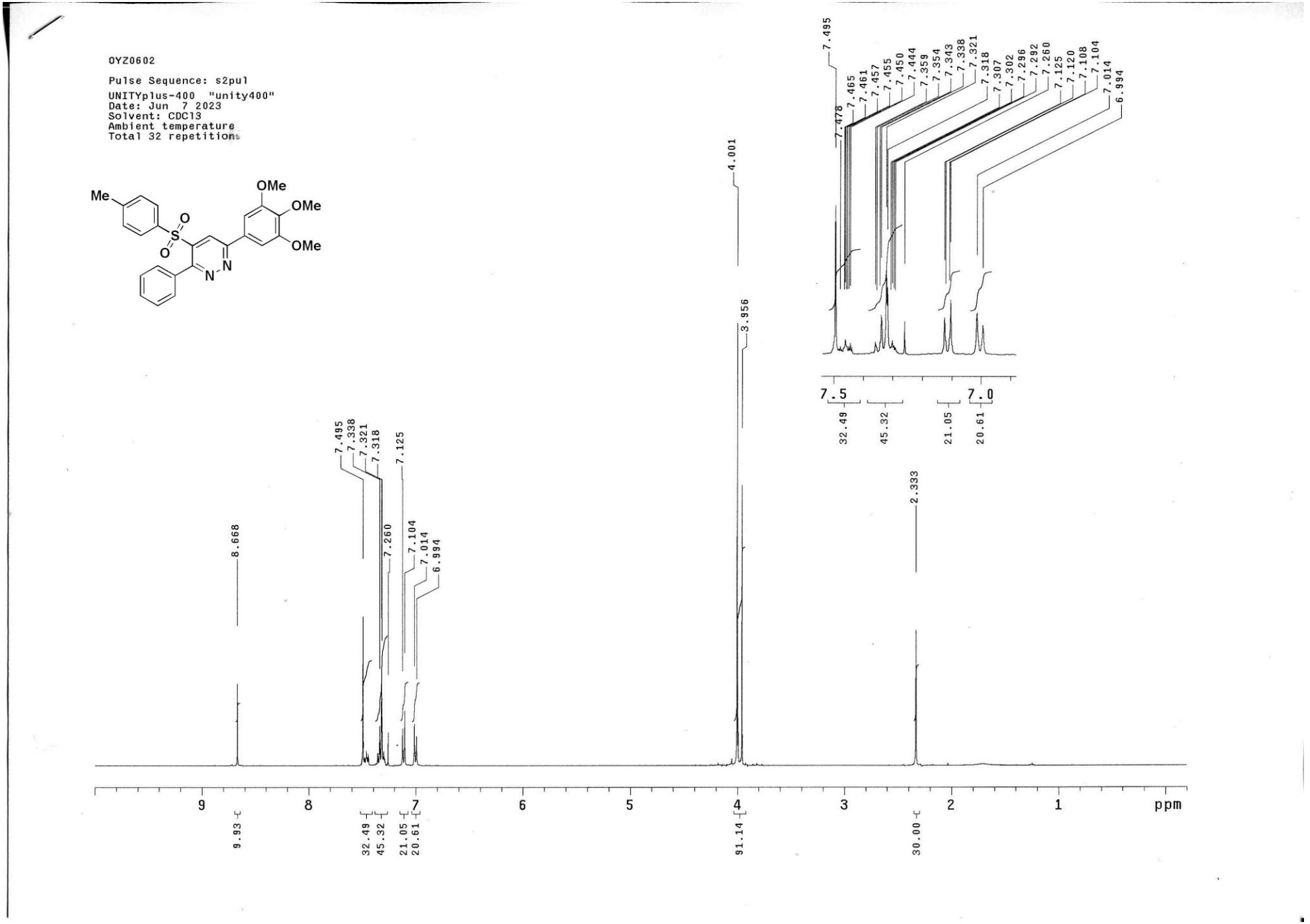
Compound 5ai (^{1}H-NMR spectral data)



Compound 5ai (^{13}C-NMR spectral data)



Compound 5aj (^{1}H-NMR spectral data)

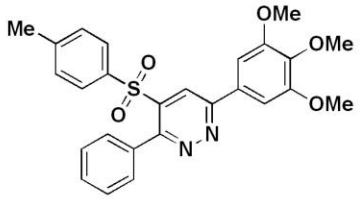


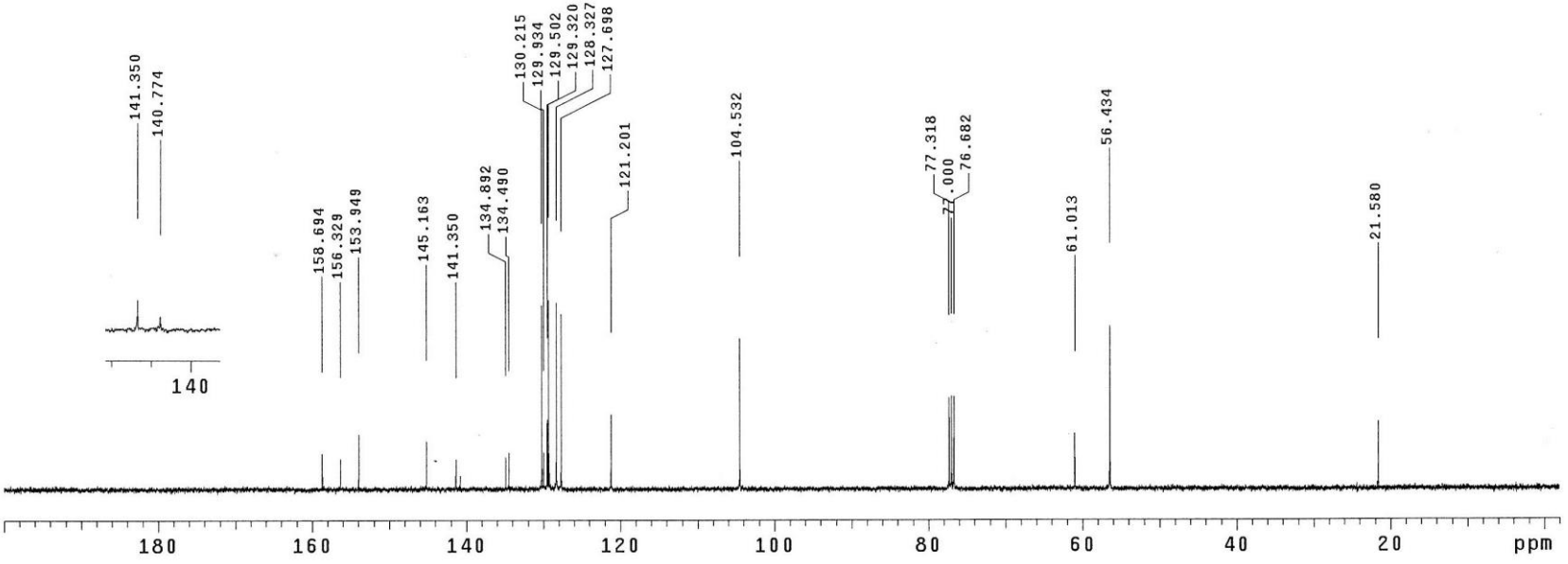
Compound 5aj (^{13}C-NMR spectral data)

OYZ0602

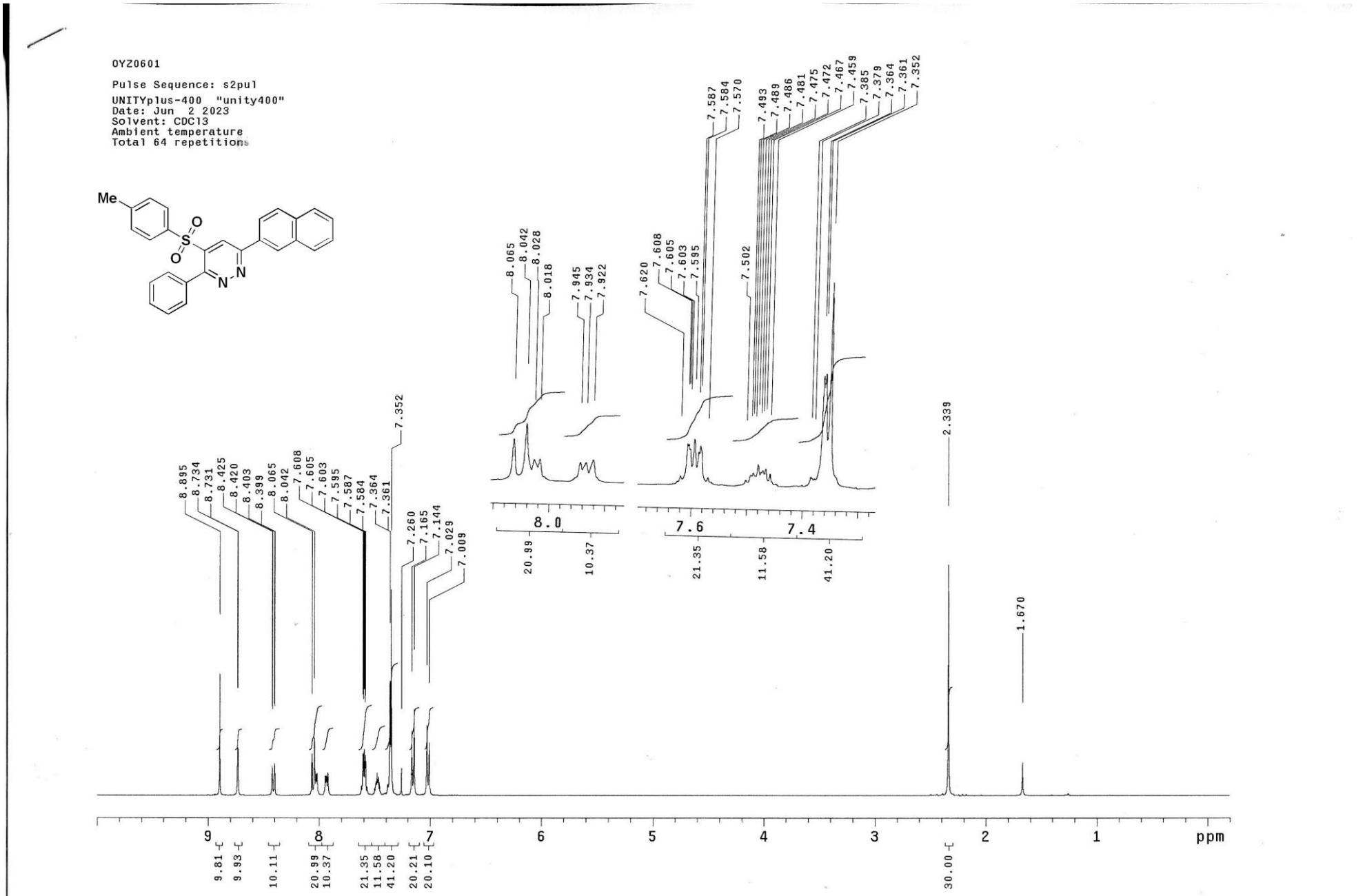
Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Jun 7 2023
Solvent: CDCl3
Ambient temperature
Total 1776 repetitions





Compound 5ak (^{1}H-NMR spectral data)

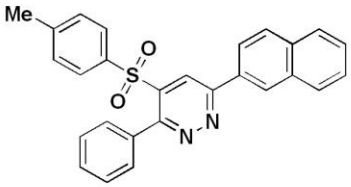


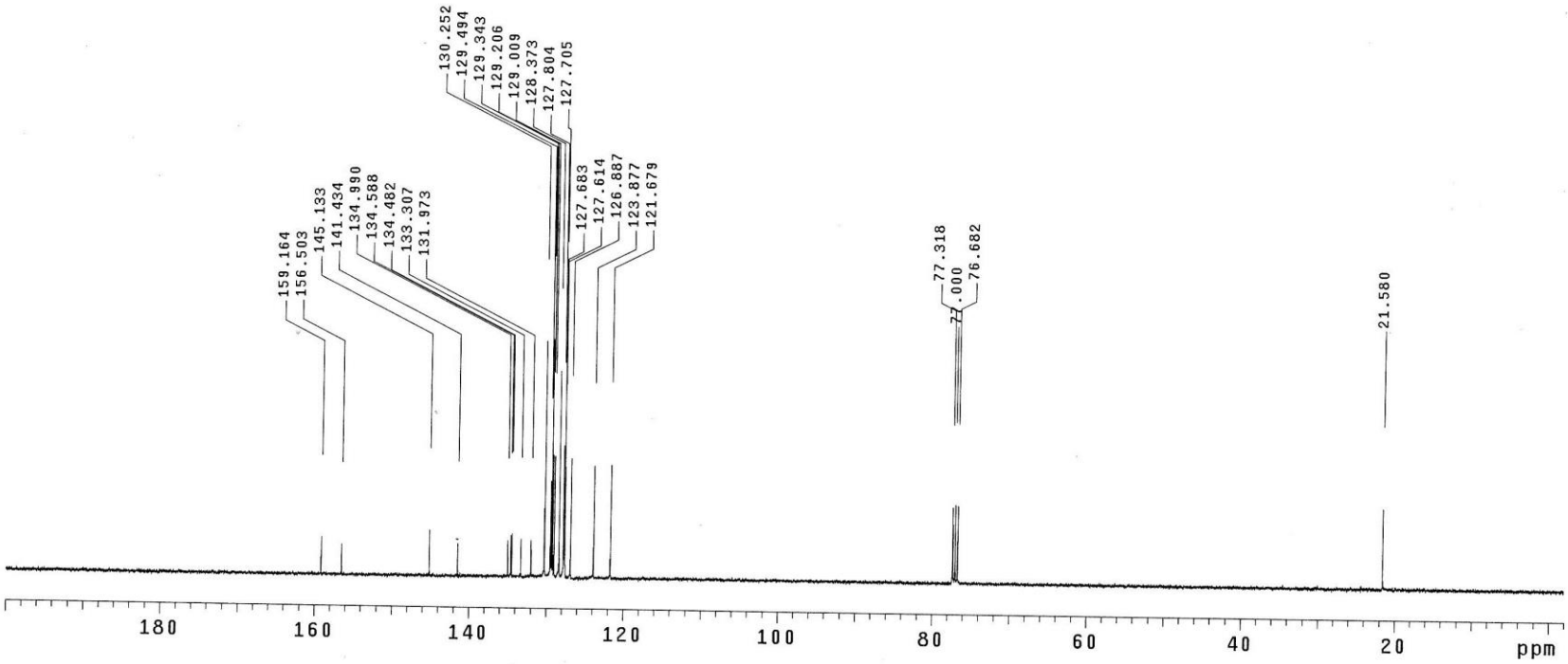
Compound 5ak (^{13}C-NMR spectral data)

OYZ0601

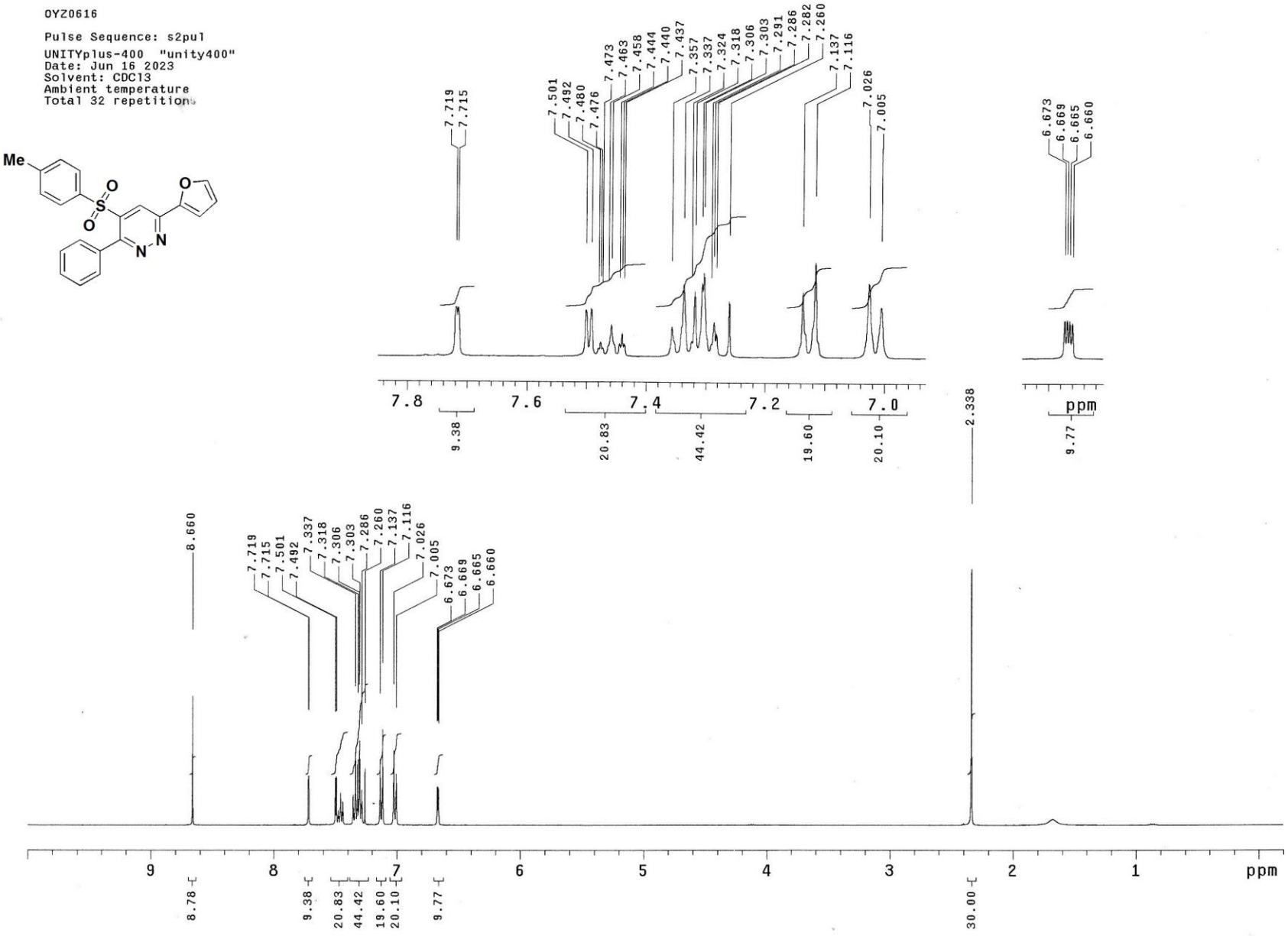
Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Jun 2 2023
Solvent: CDCl3
Ambient temperature
Total 2624 repetitions





Compound 5al (^{1}H-NMR spectral data)

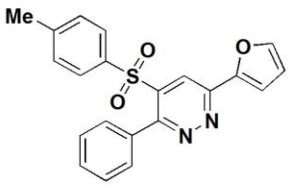


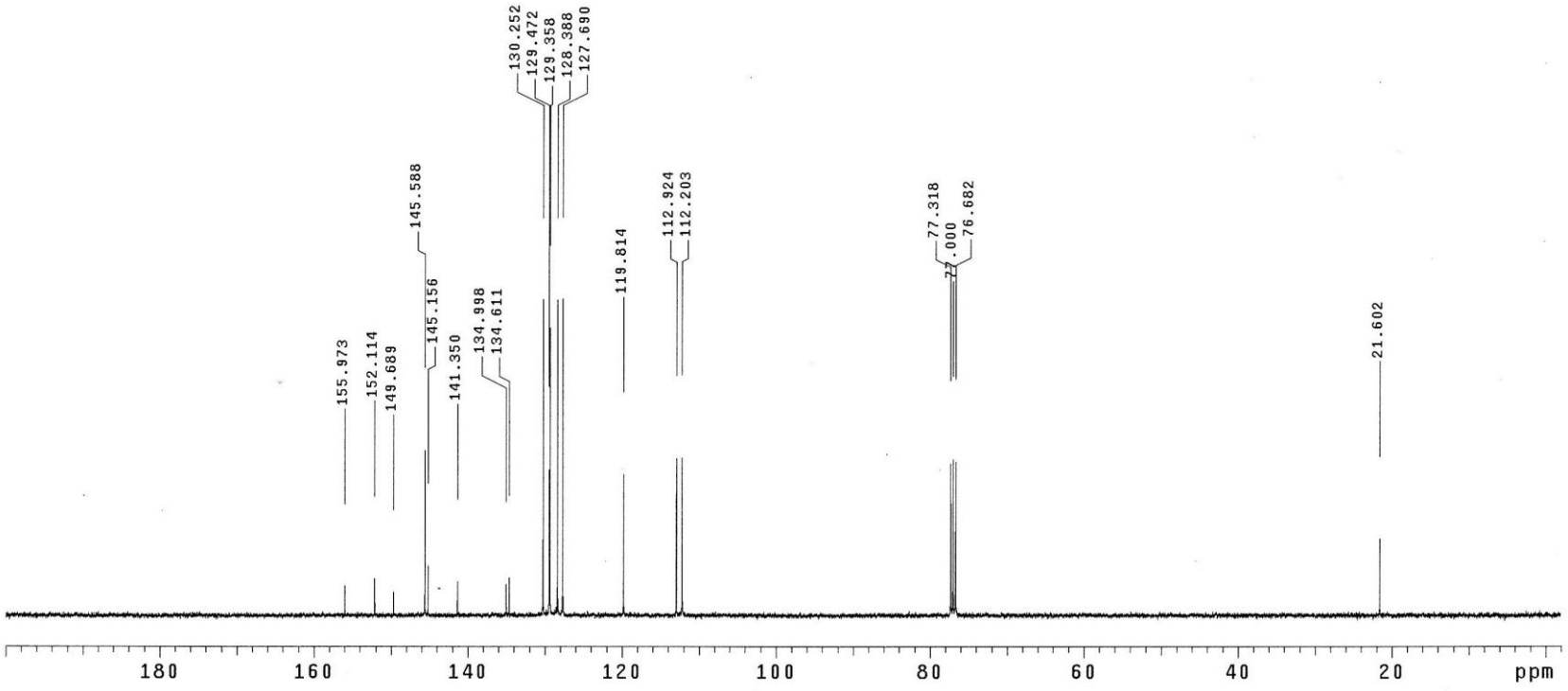
Compound 5al (^{13}C-NMR spectral data)

OYZ0616

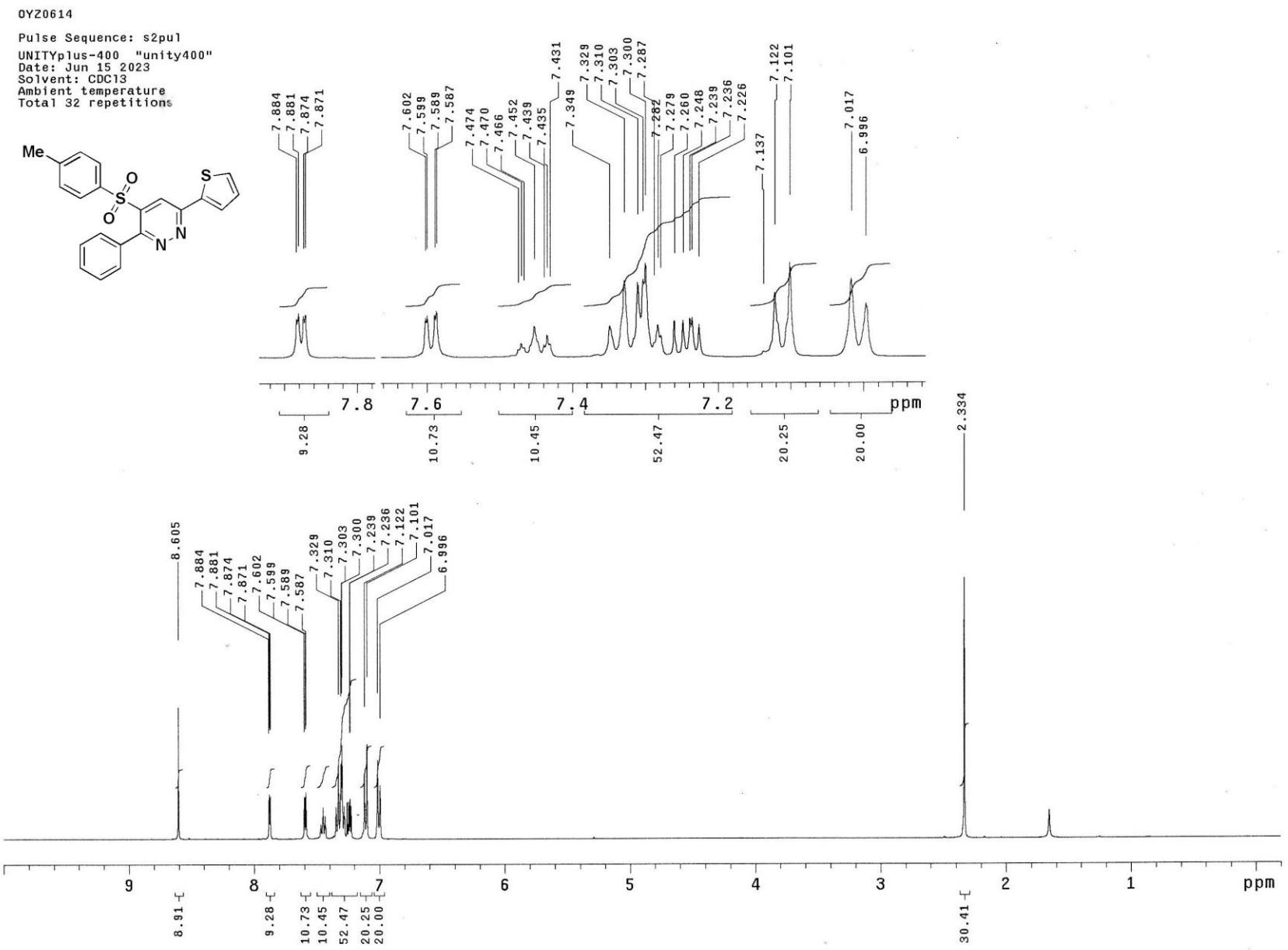
Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Jun 16 2023
Solvent: CDCl3
Ambient temperature
Total 5872 repetitions





Compound 5am (^{1}H-NMR spectral data)

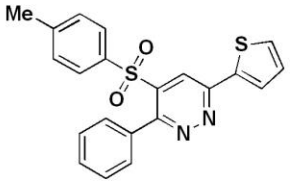


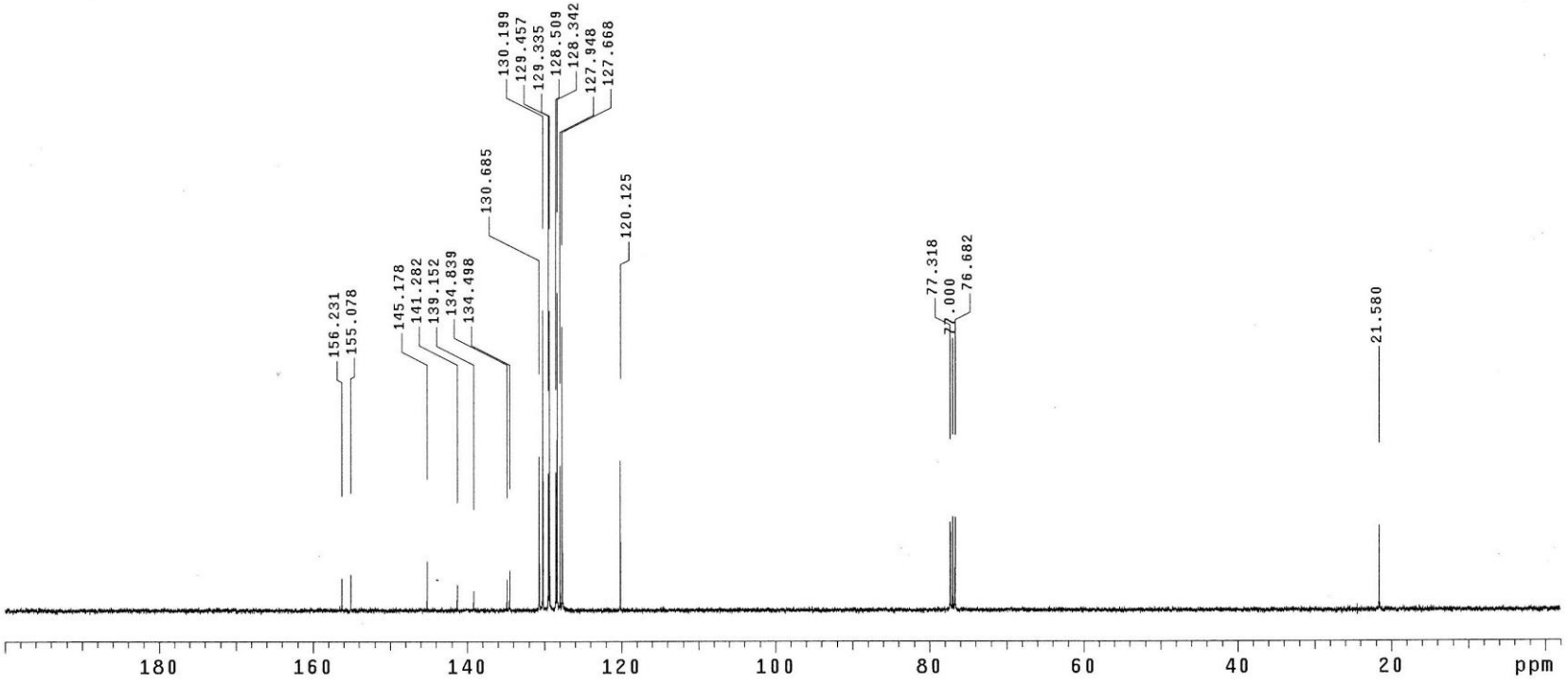
Compound 5am (^{13}C-NMR spectral data)

OYZ0614

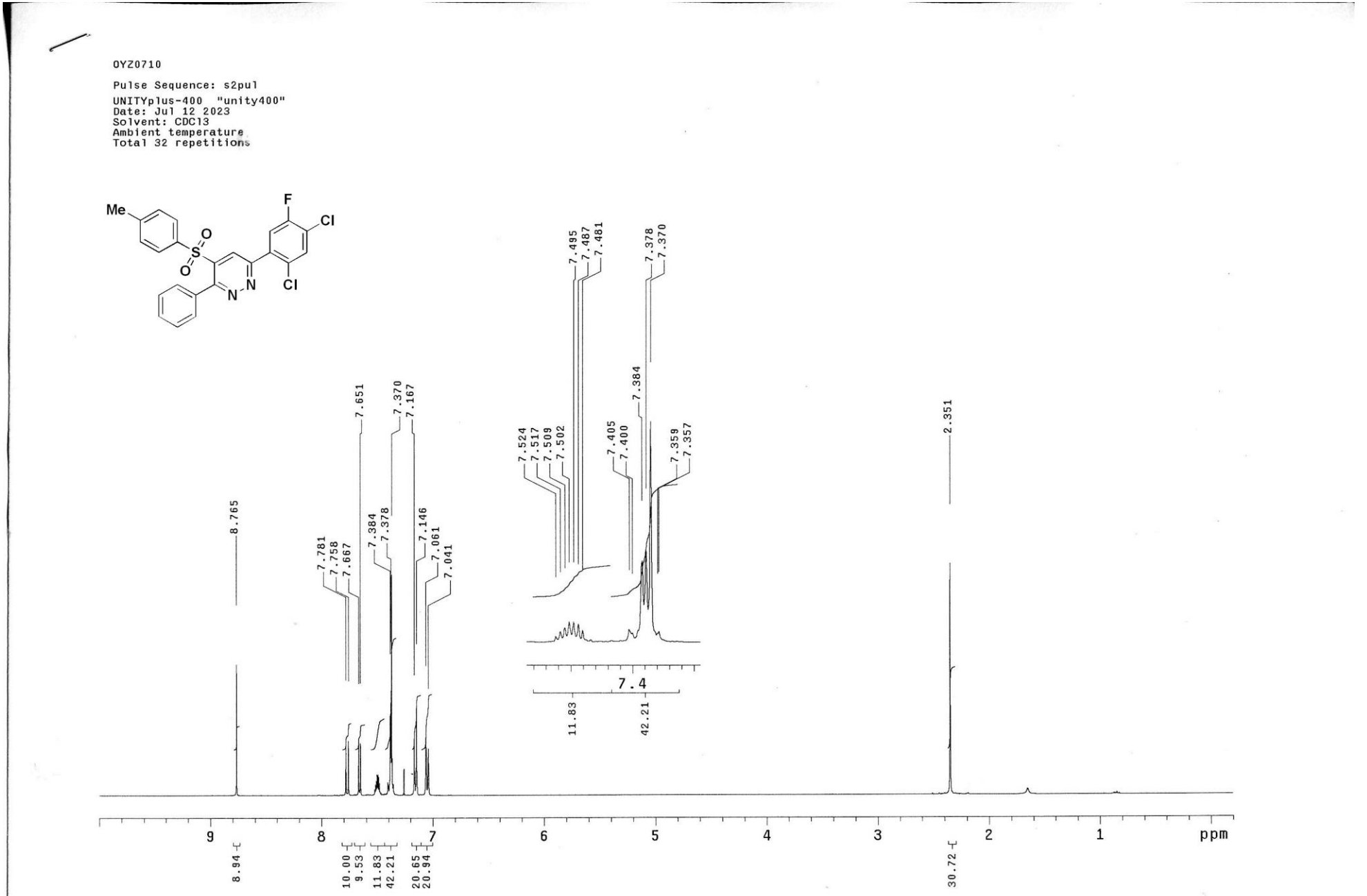
Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Jun 15 2023
Solvent: CDCl3
Ambient temperature
Total 2576 repetitions

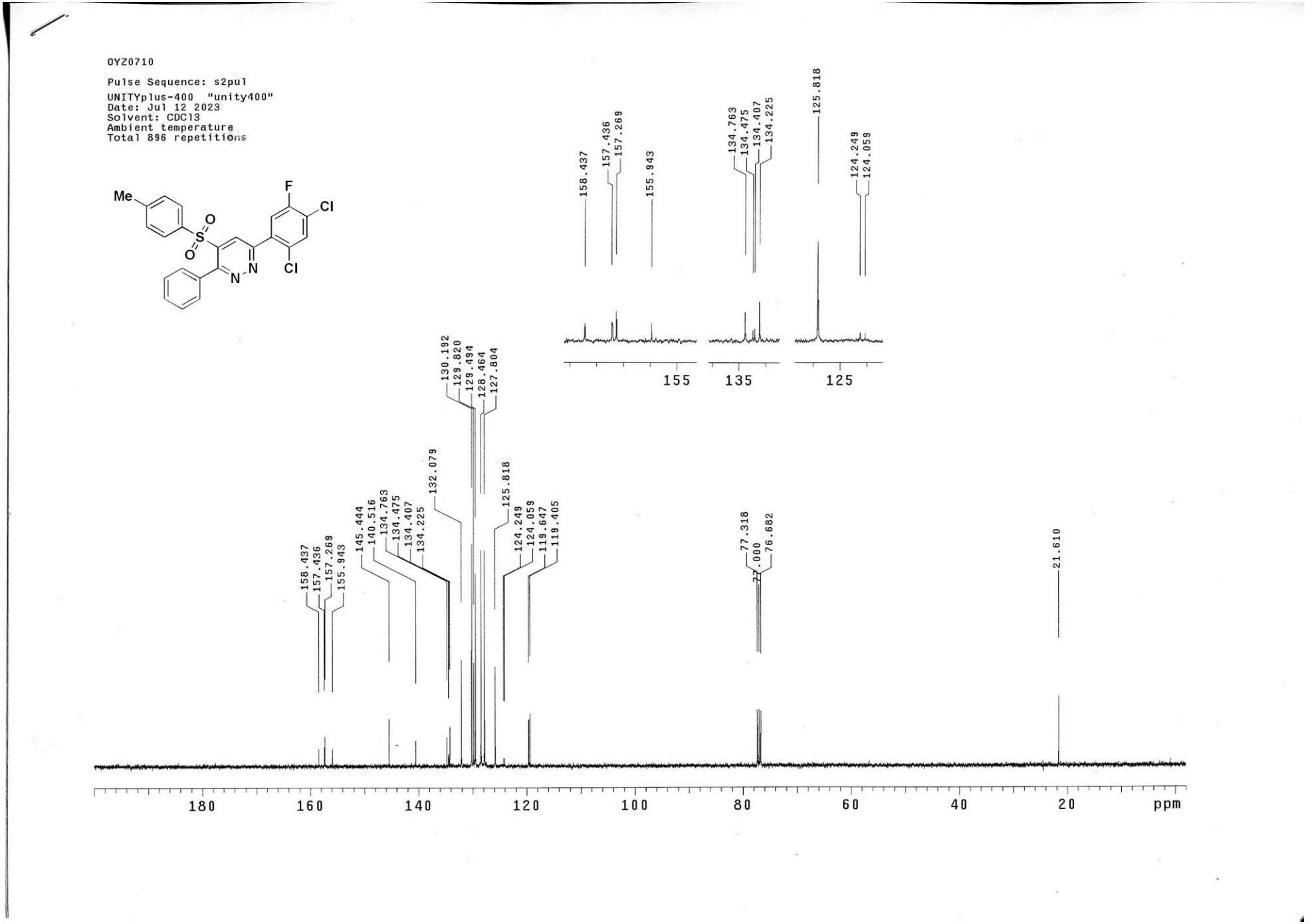




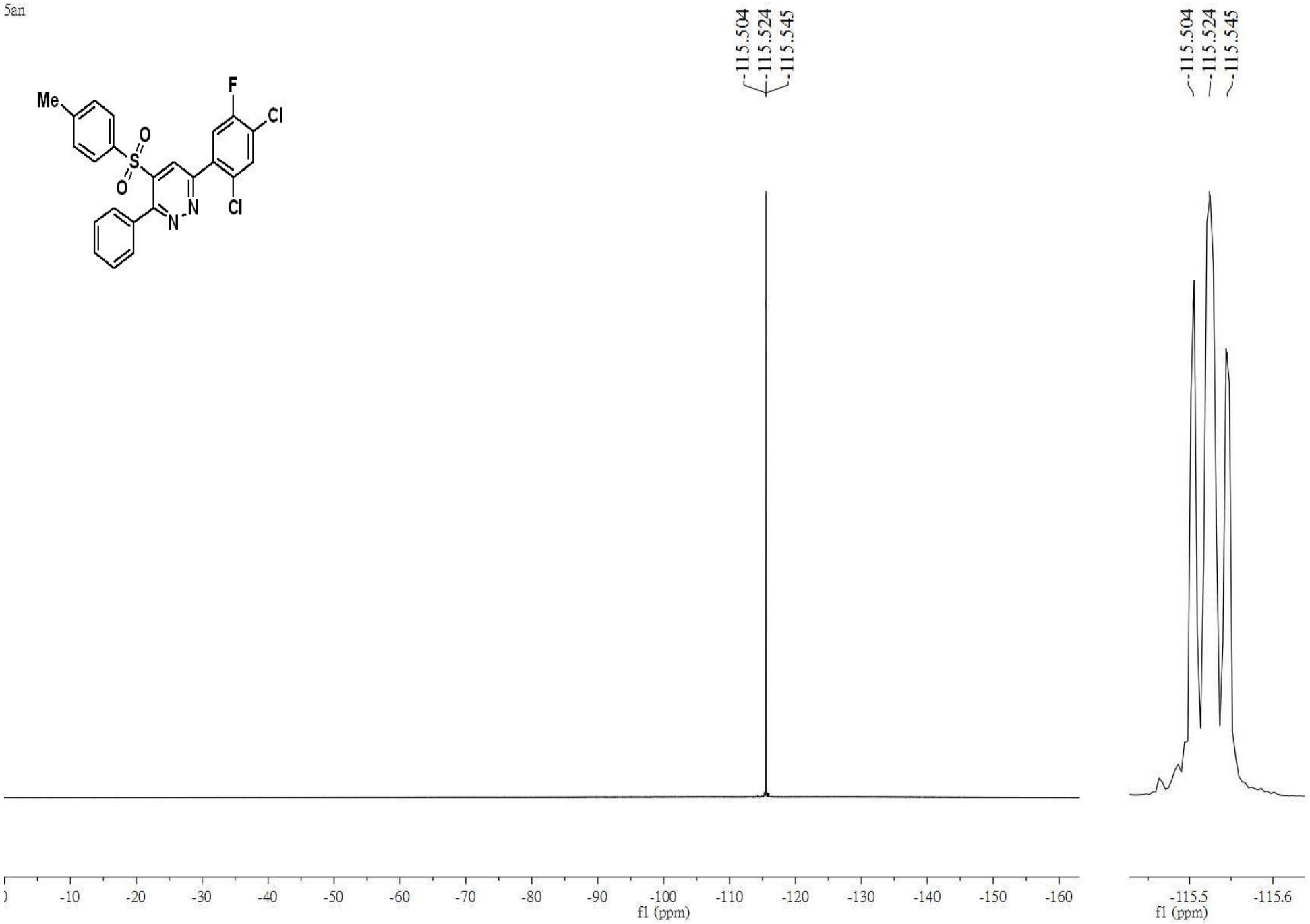
Compound 5an (^{1}H-NMR spectral data)



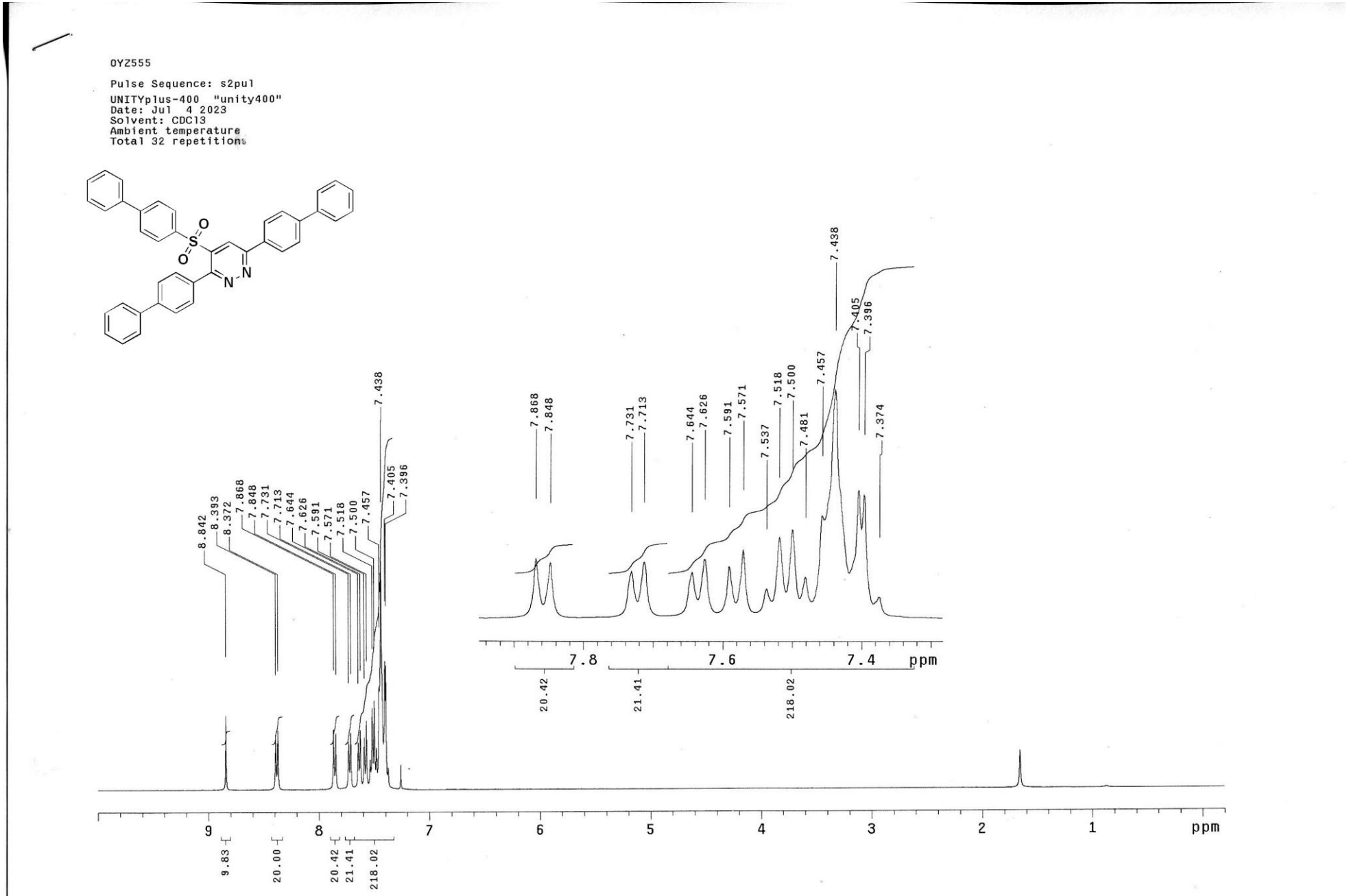
Compound 5an (^{13}C-NMR spectral data)



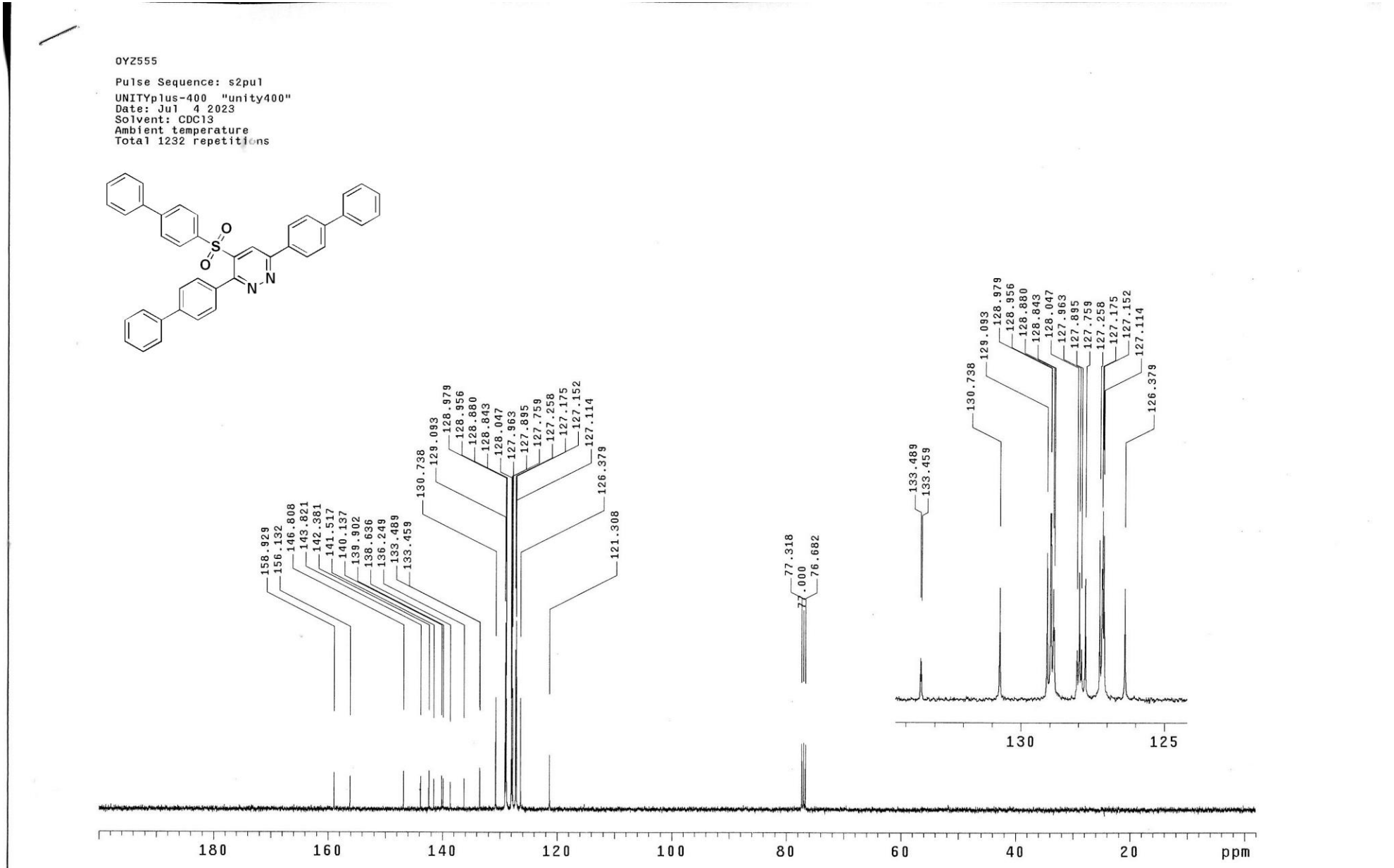
Compound 5an (^{19}F-NMR spectral data)



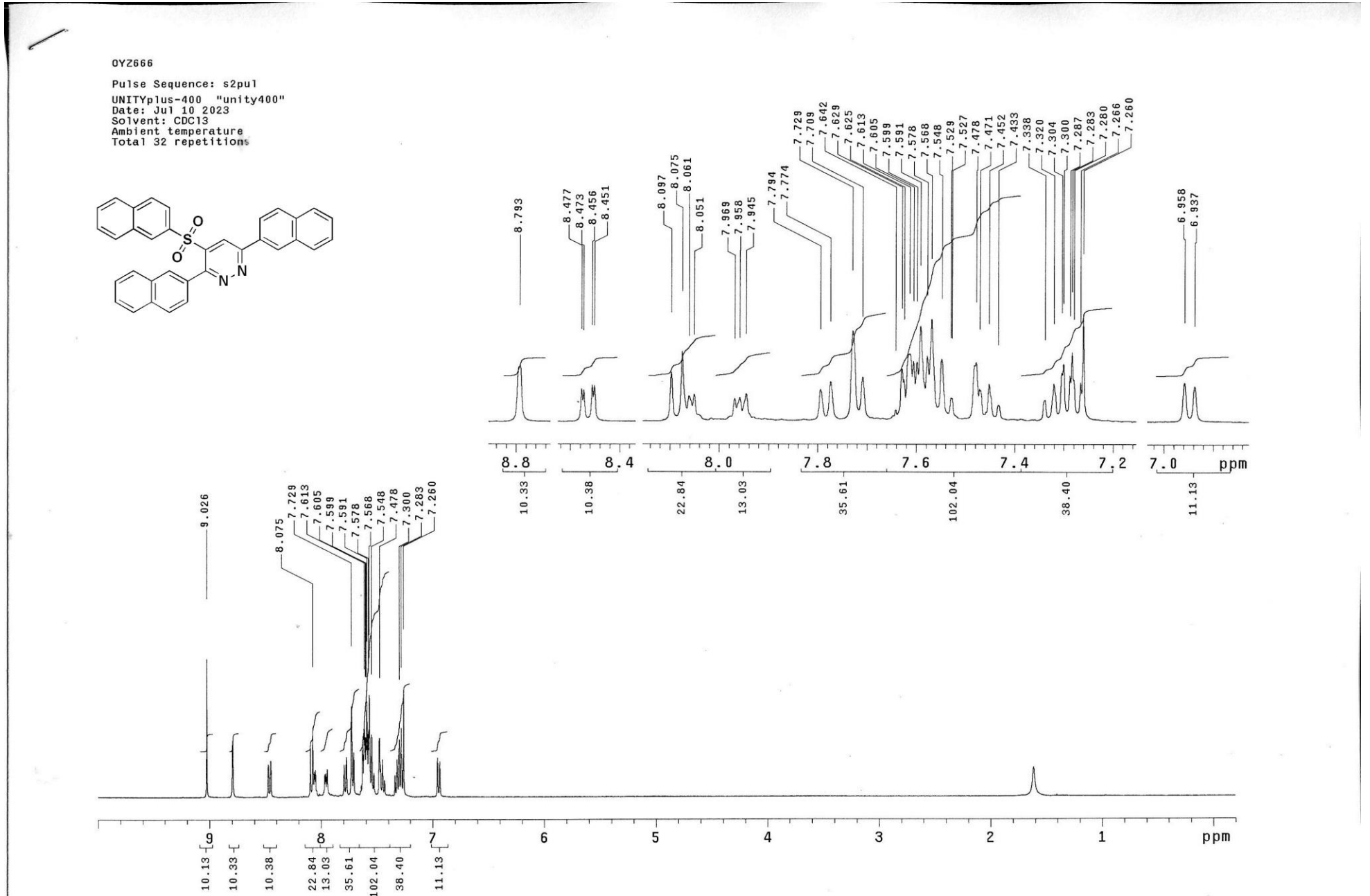
Compound 5ao (^{1}H-NMR spectral data)



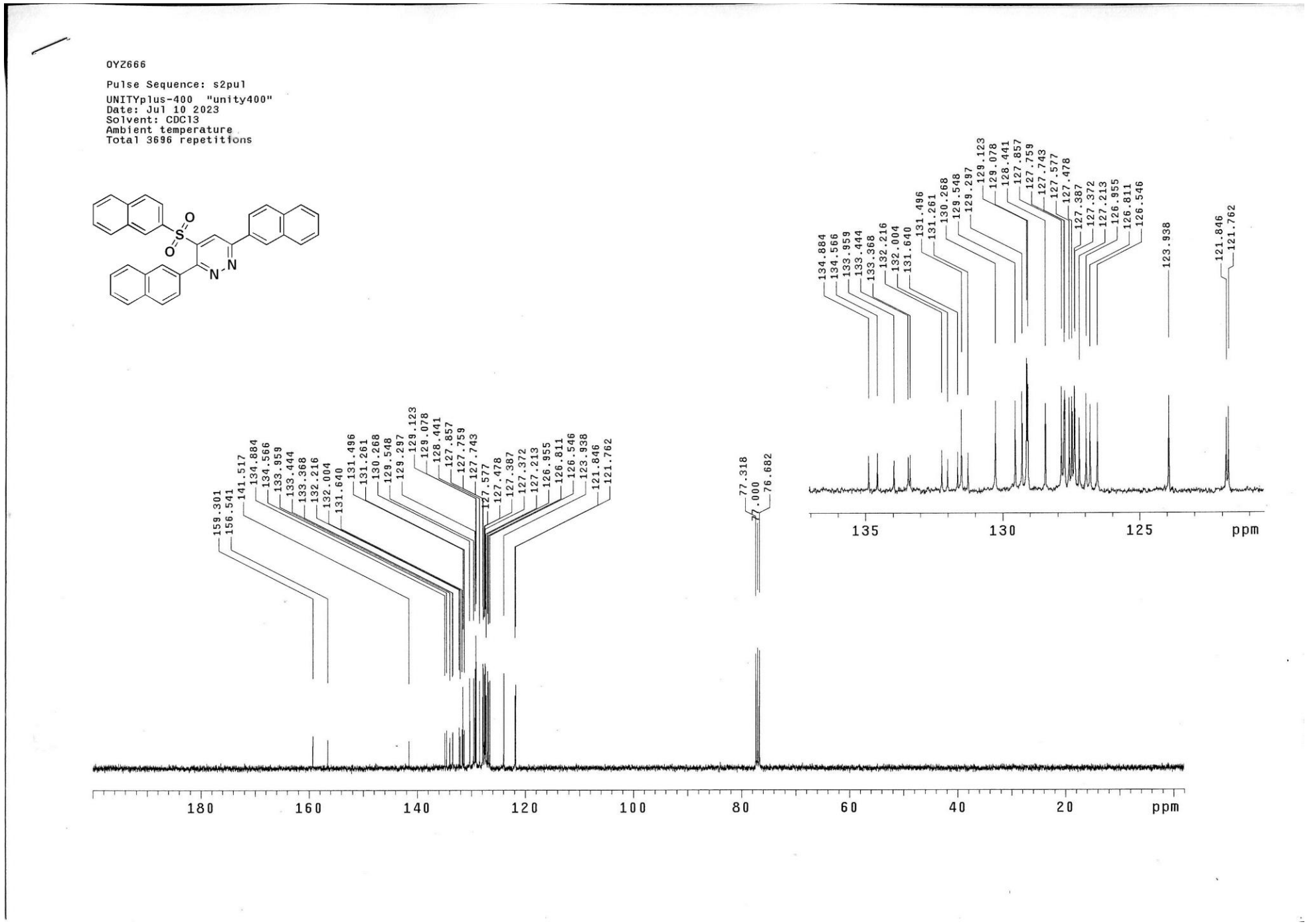
Compound 5ao (^{13}C-NMR spectral data)



Compound 5ap (^{1}H-NMR spectral data)



Compound 5ap (^{13}C-NMR spectral data)

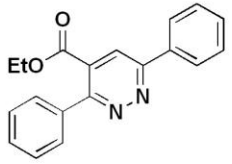


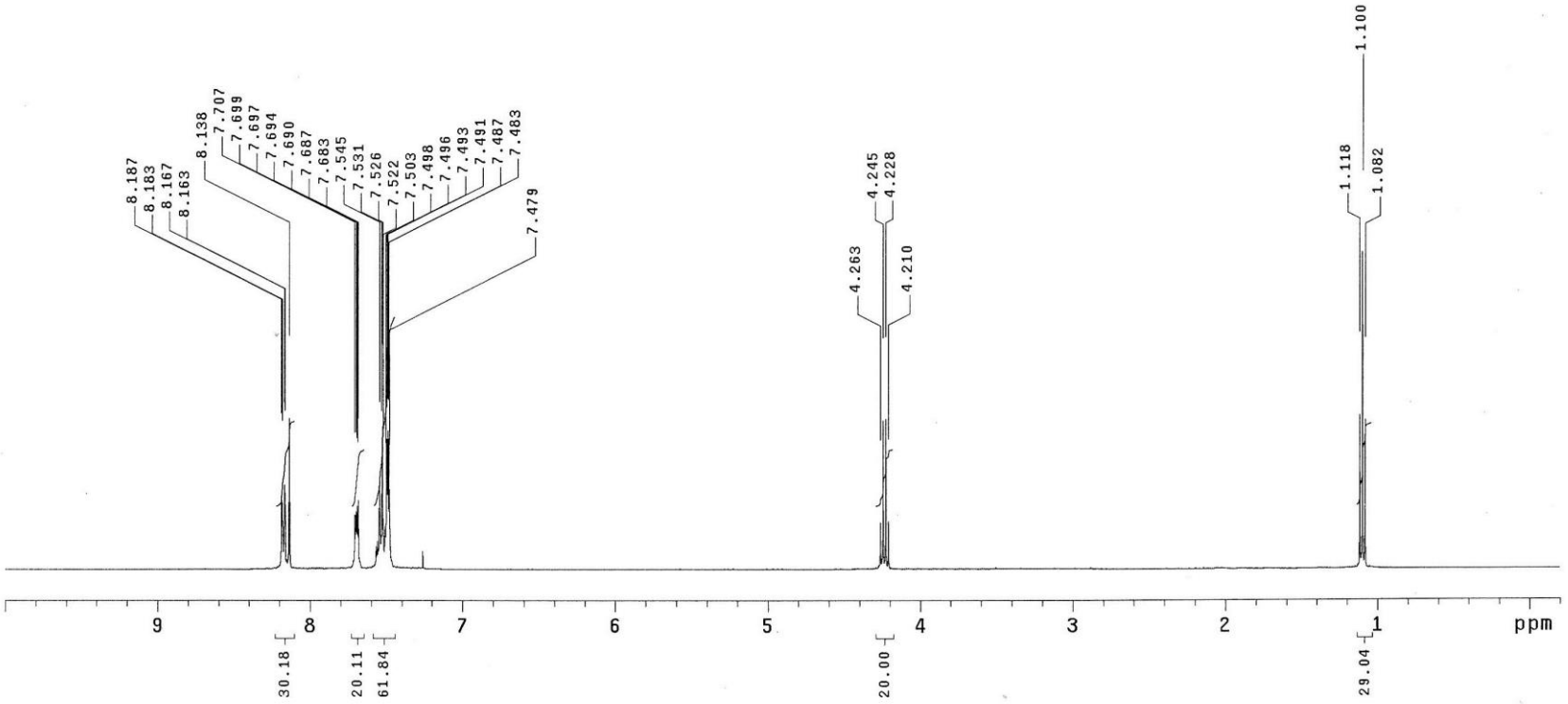
Compound 6a (^{1}H-NMR spectral data)

OYZ ester

Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Aug 10 2023
Solvent: CDCl3
Ambient temperature
Total 104 repetitions



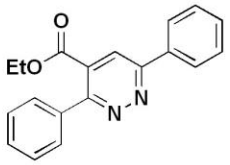


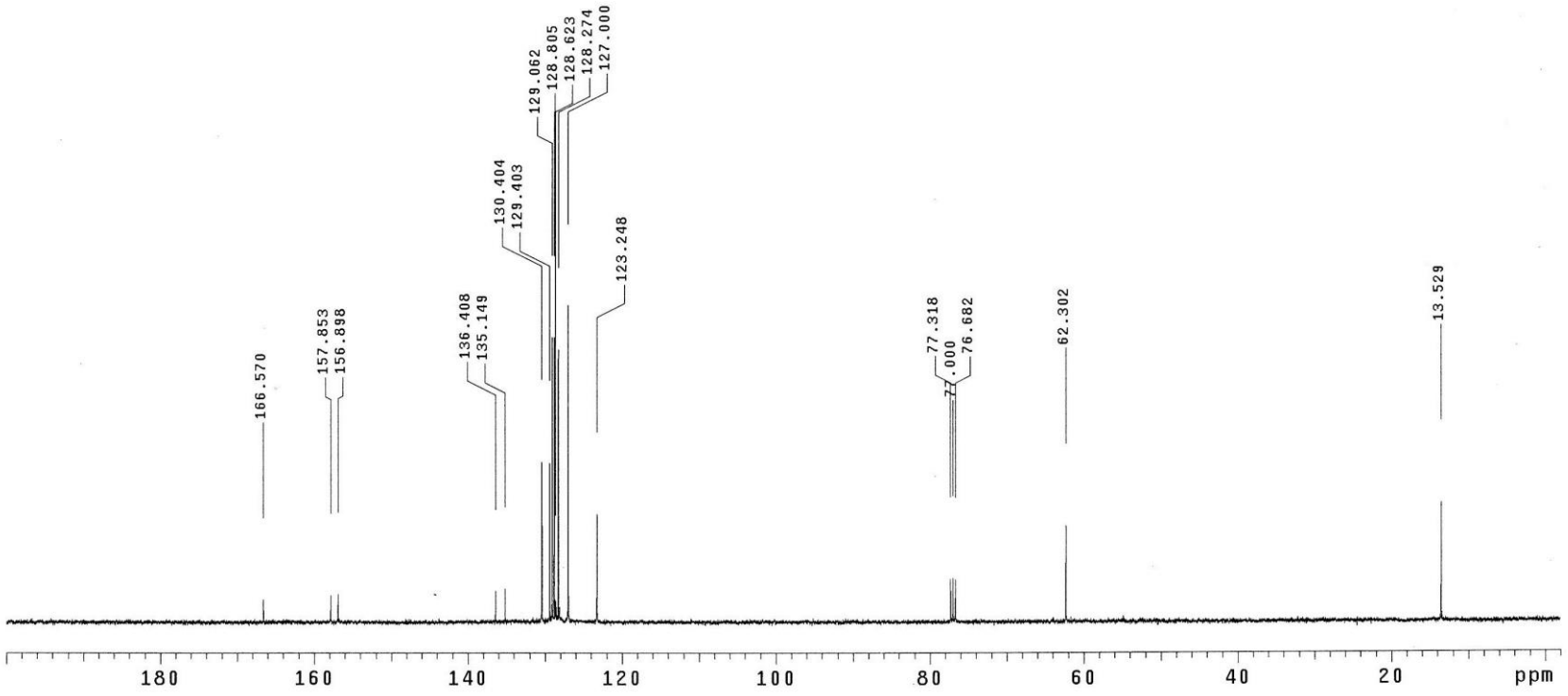
Compound 6a (^{13}C-NMR spectral data)

OYZ ester

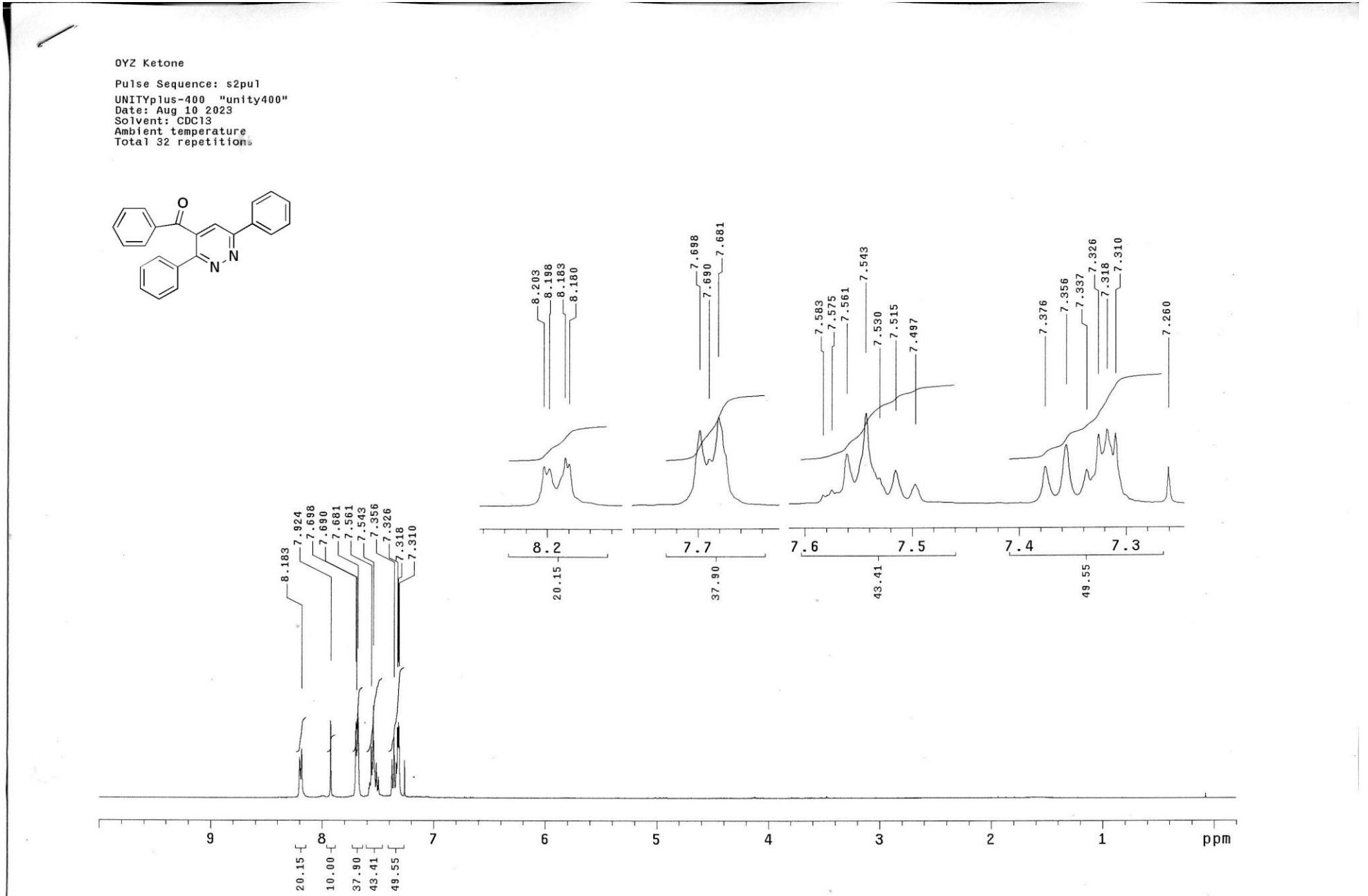
Pulse Sequence: s2pul

UNITYplus-400 "unity400"
Date: Aug 10 2023
Solvent: CDCl3
Ambient temperature
Total 512 repetitions

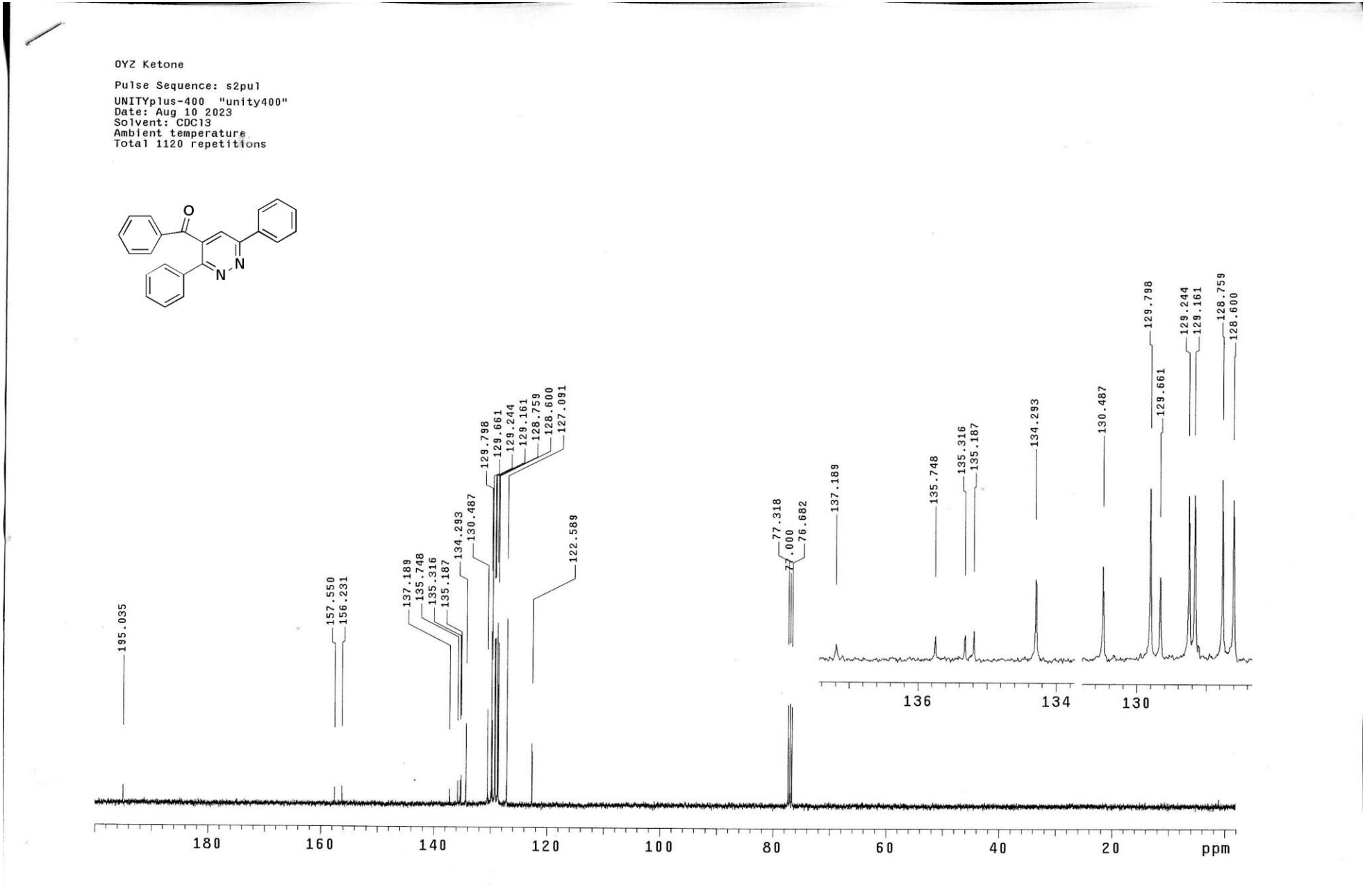




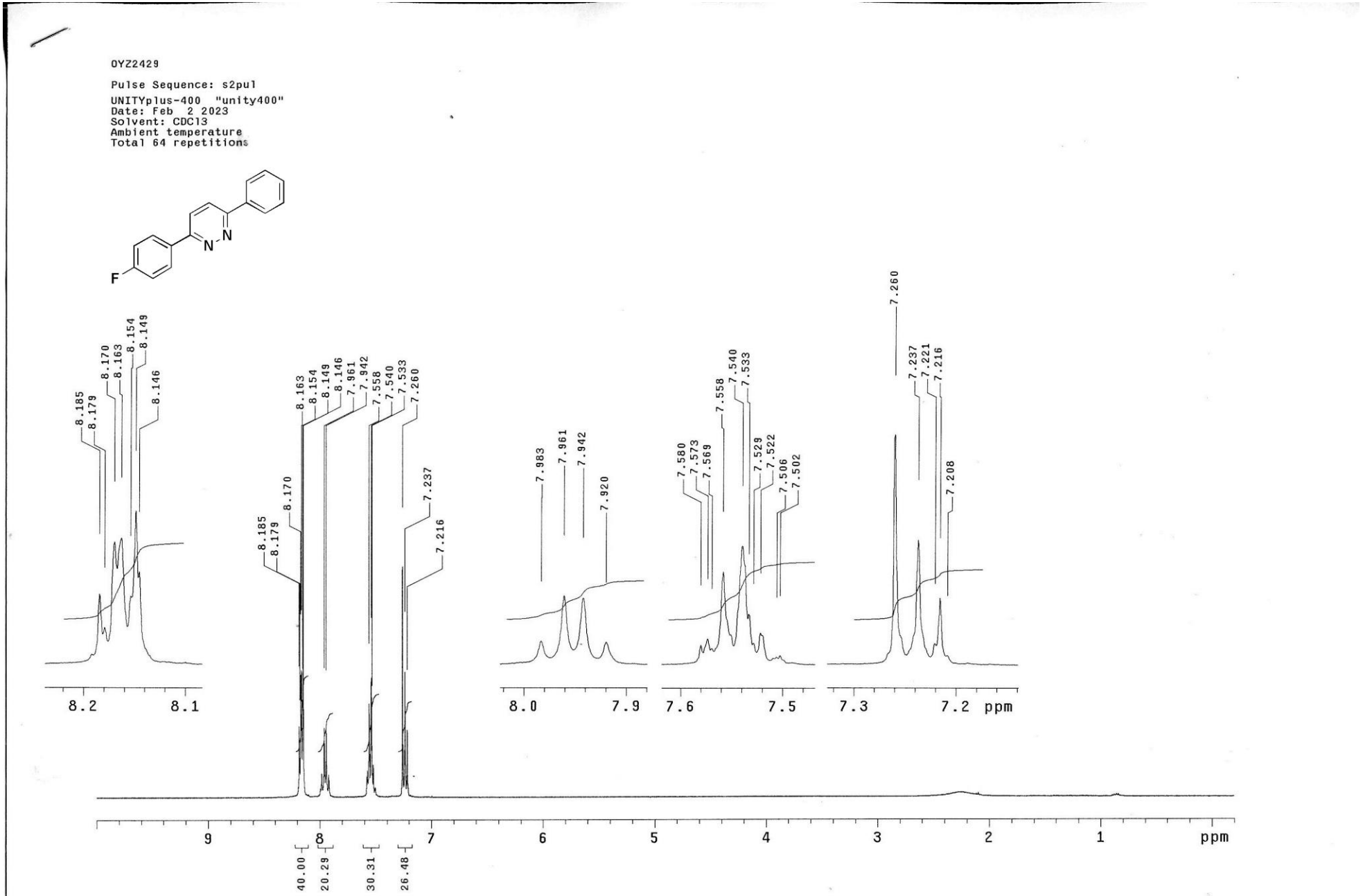
Compound 6b (^{1}H-NMR spectral data)



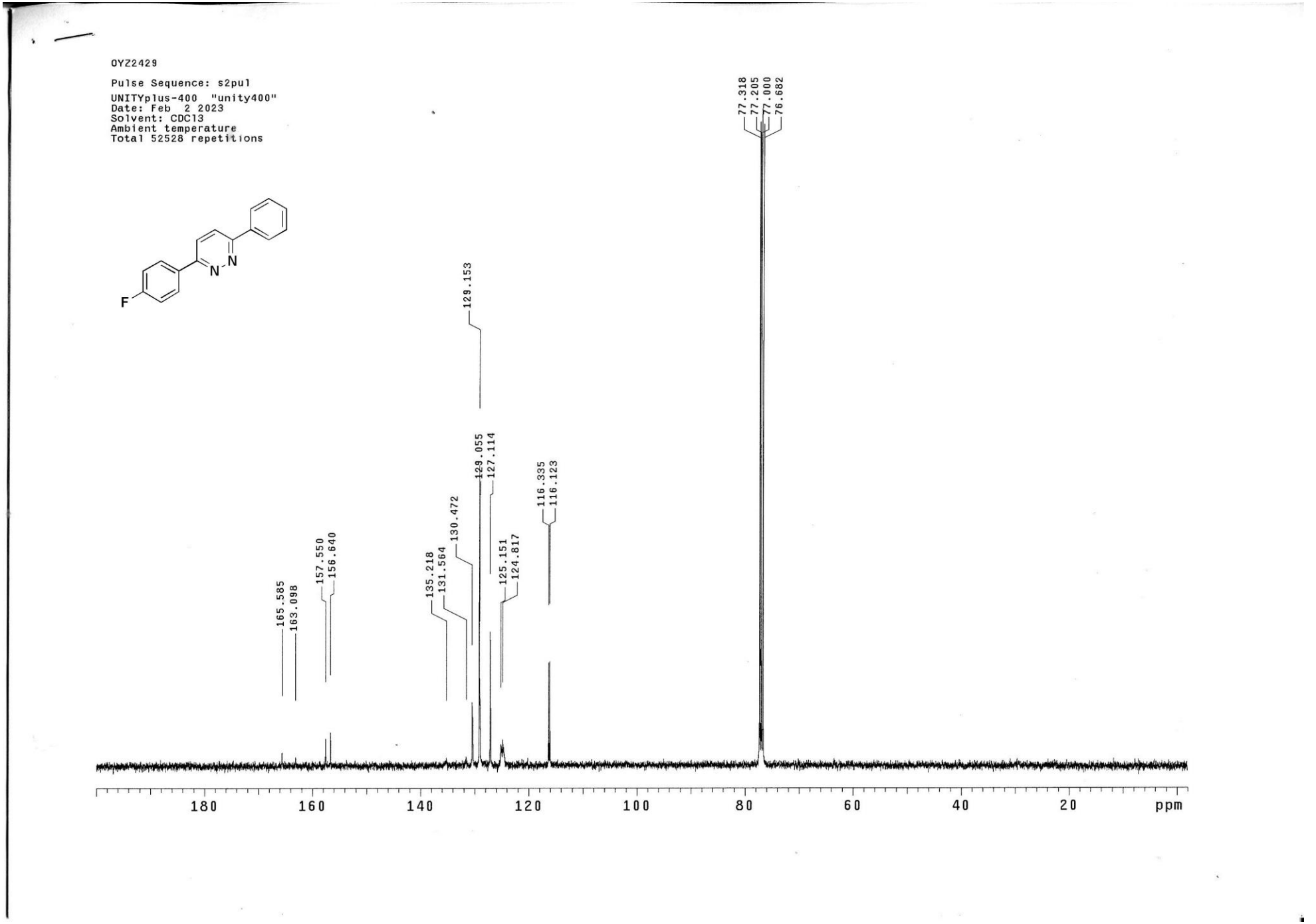
Compound 6b (^{13}C-NMR spectral data)



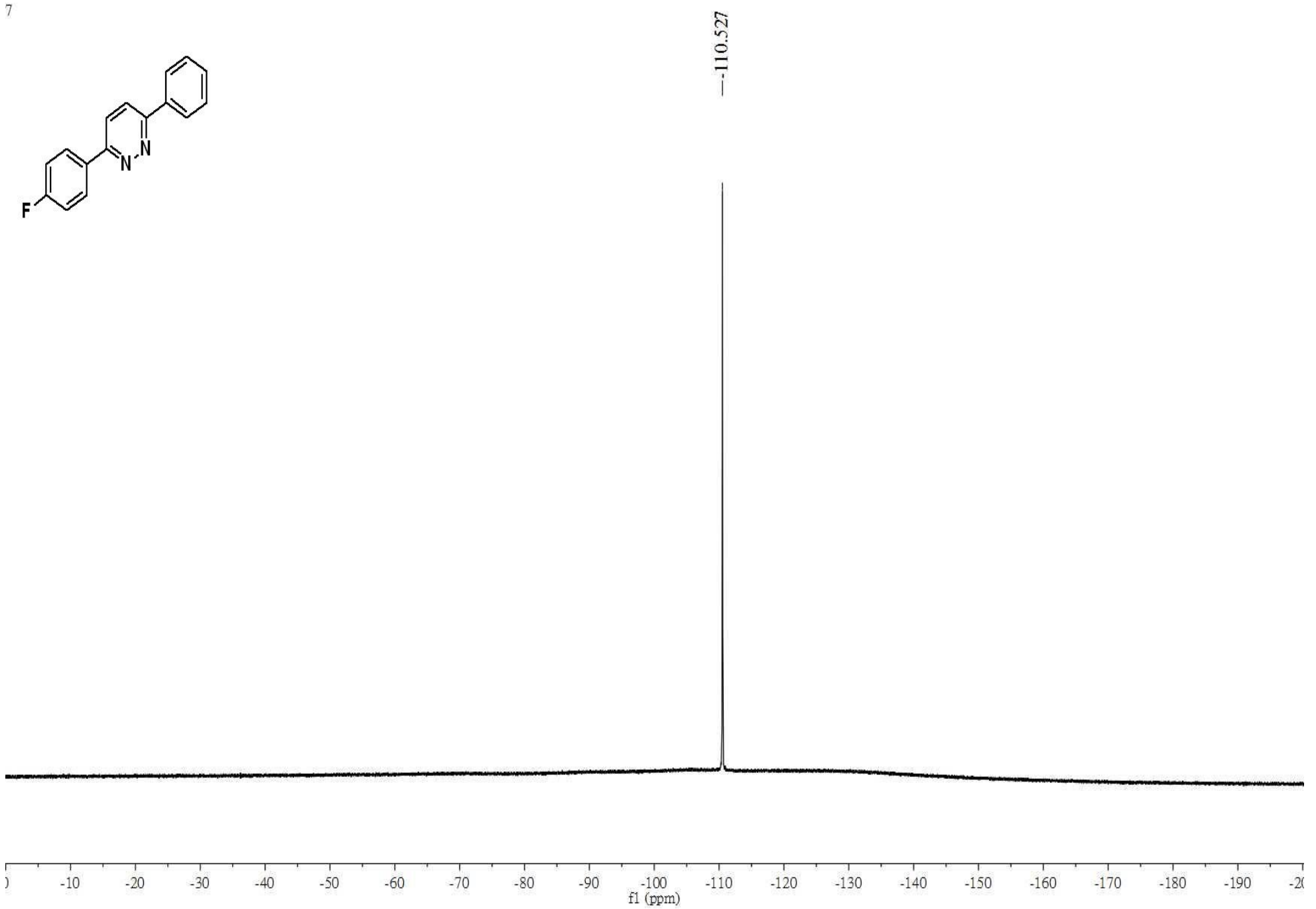
Compound 7 (^{1}H-NMR spectral data)



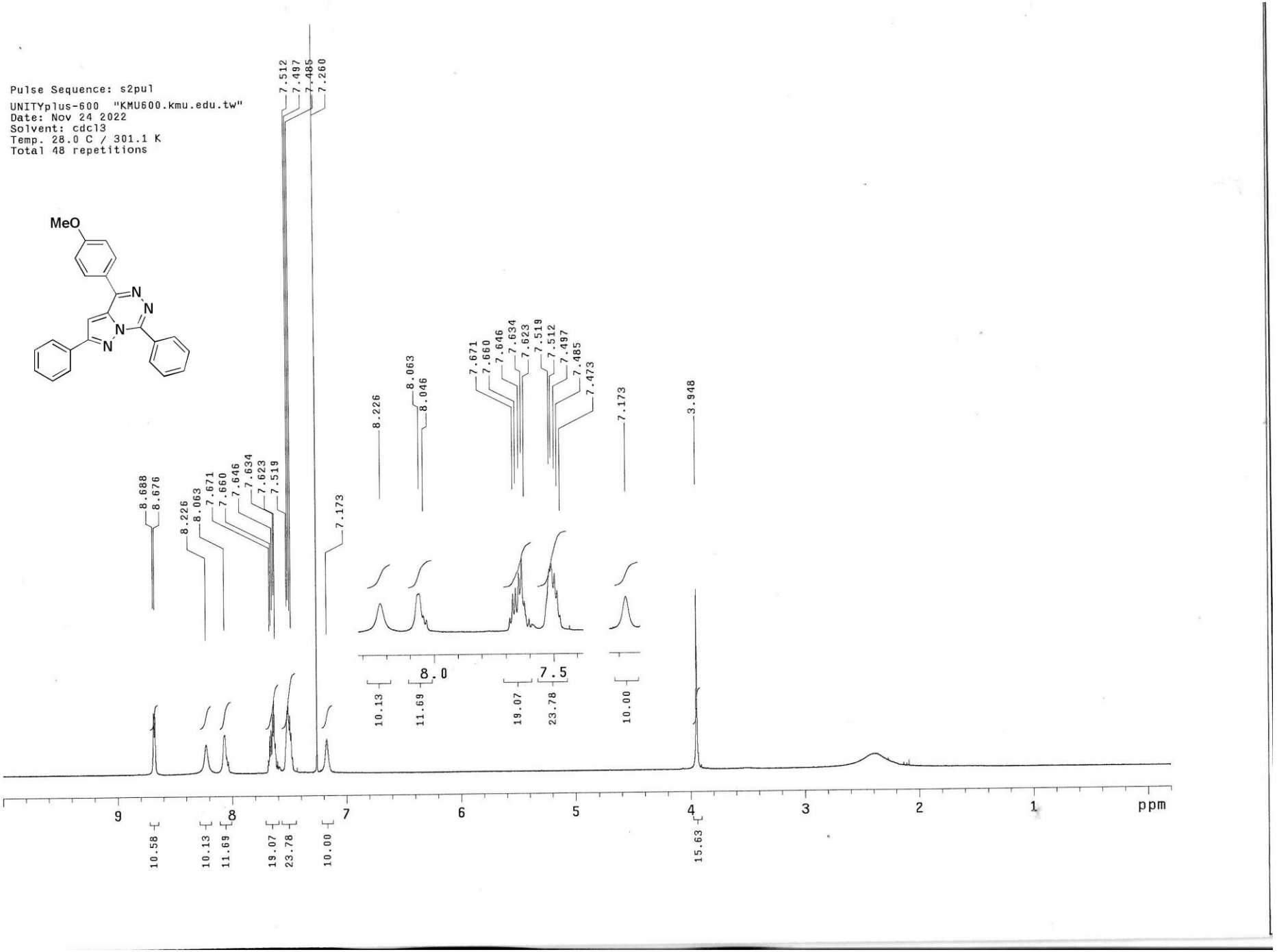
Compound 7 (^{13}C-NMR spectral data)



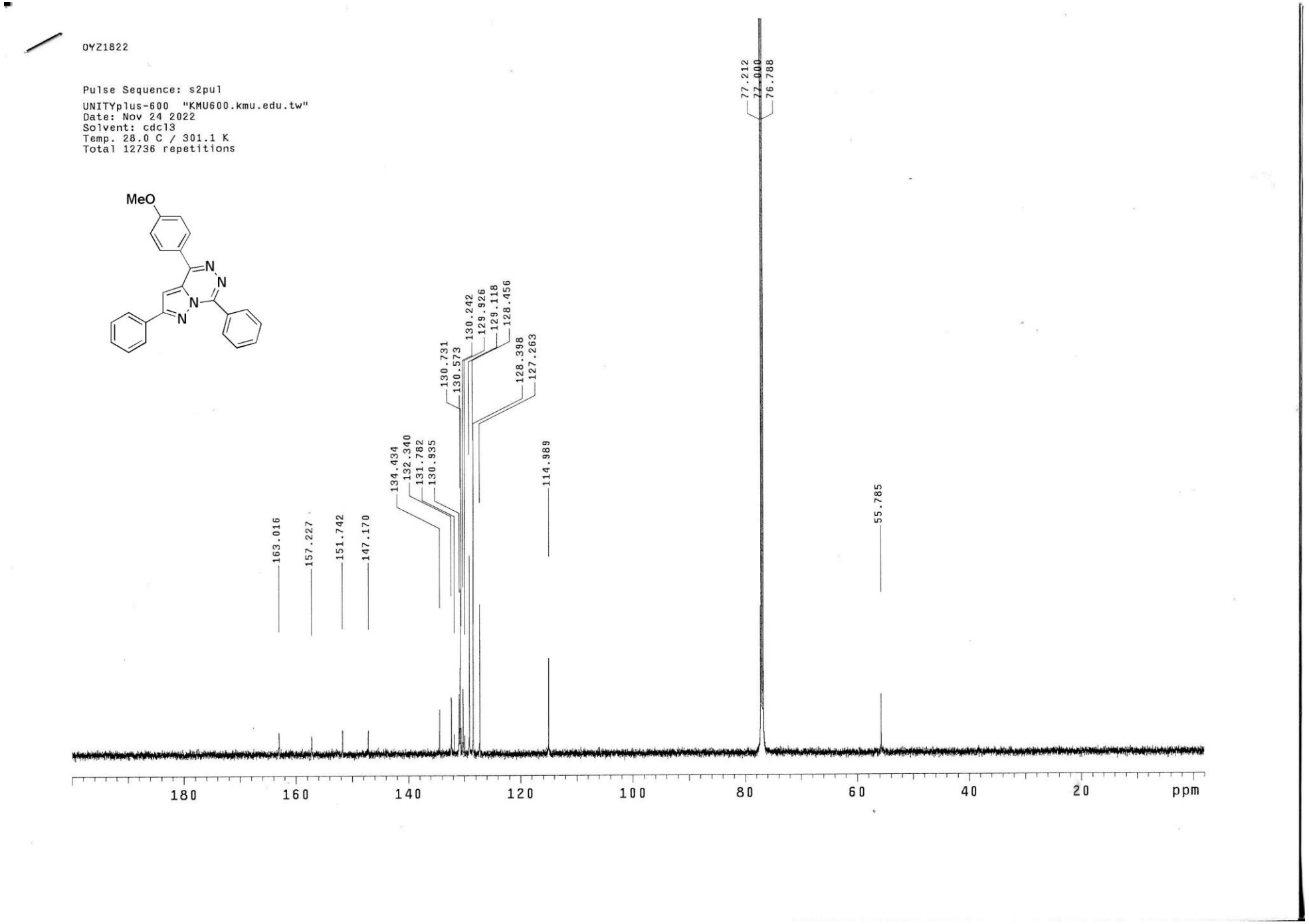
Compound 7 (^{19}F-NMR spectral data)



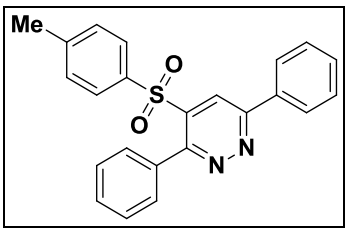
Compound 8 (^{1}H-NMR spectral data)



Compound 8 (^{13}C-NMR spectral data)

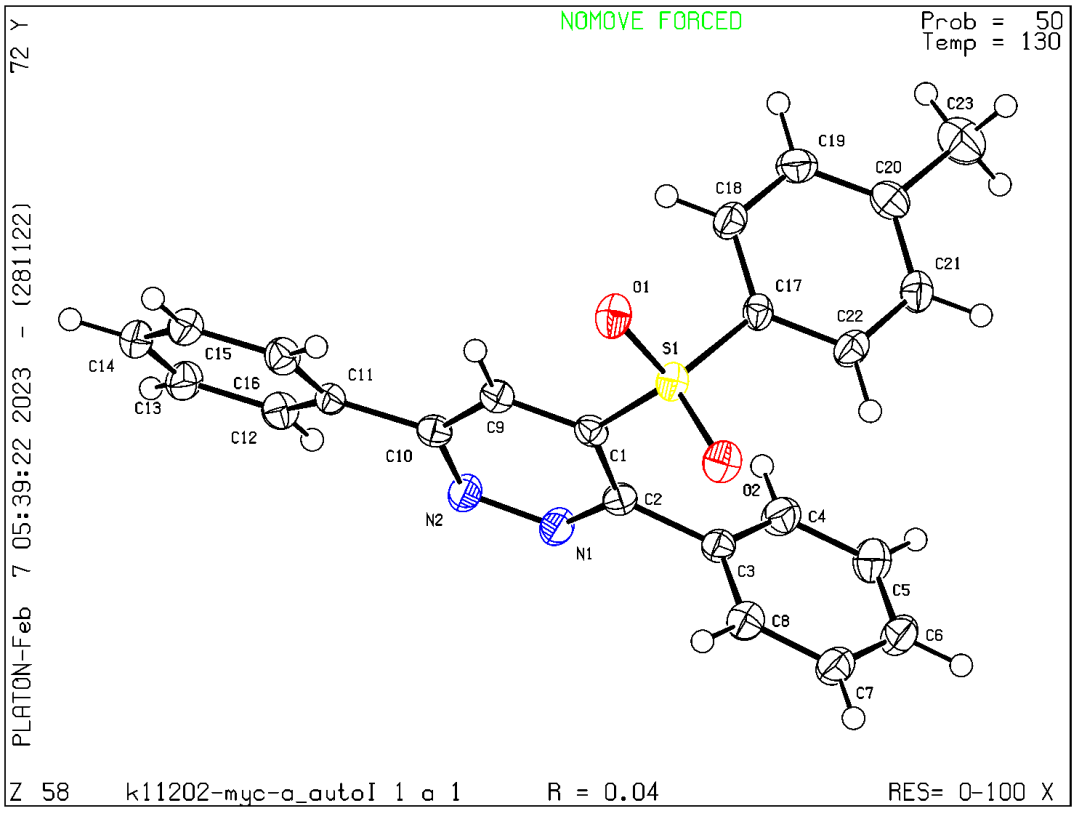


X-ray crystal data of compound 5a



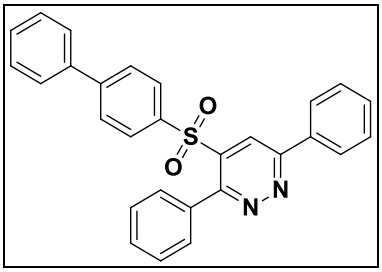
Sample preparation : A solution of compound **5a** (30 mg) in CH_2Cl_2 (10 mL) was placed in a tube (10 mL). EtOAc (2 mL) was added slowly to the vial with a dropper. The vial was closed with little cotton and kept at room temperature for 2 days. Then, colorless prisms were observed.

Crystal measurement : X-ray crystal structures were determined with a Bruker Enraf-Nonius single-crystal diffractometer (CAD4, Kappa CCD). Thermal ellipsoids are drawn at 50% probability level.



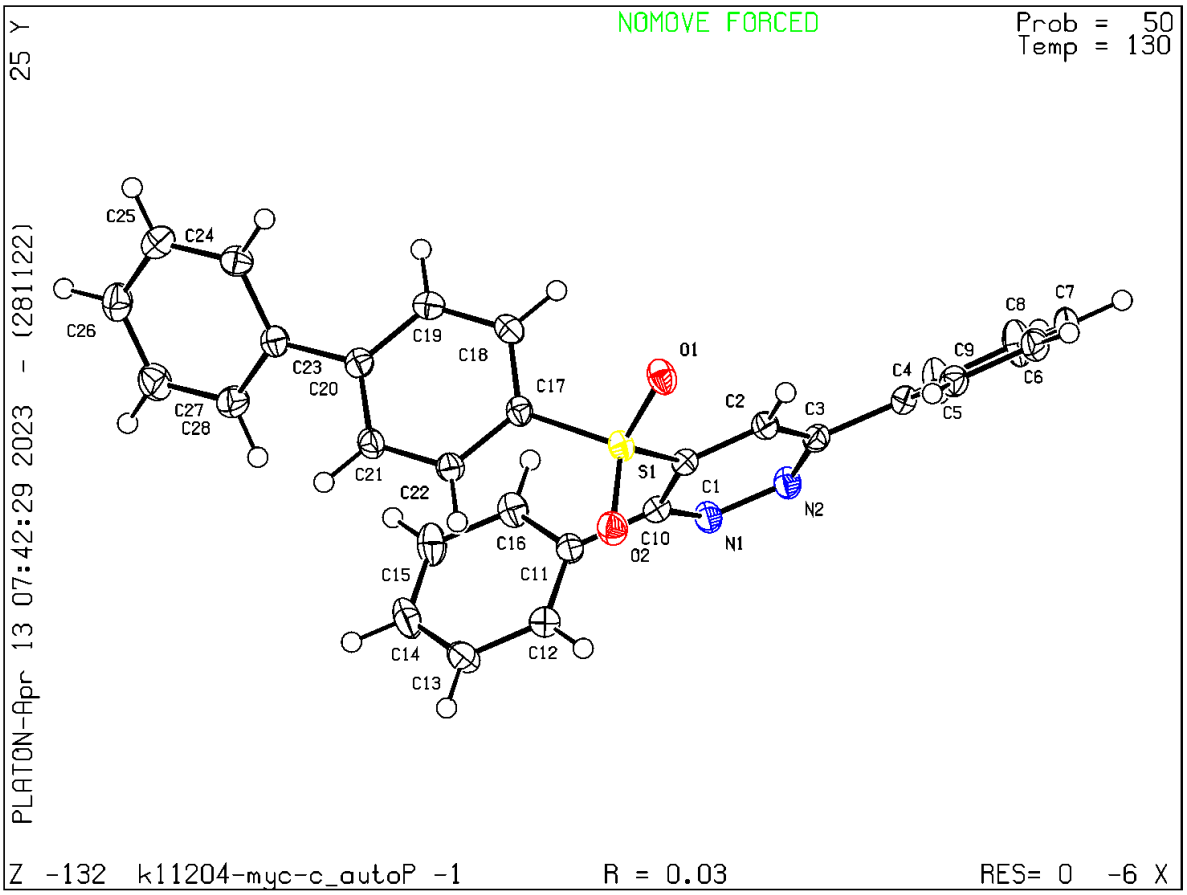
Empirical formula	$C_{23}H_{18}N_2O_2S$
Formula weight	386.45
Temperature/K	130(2)
Crystal system	monoclinic
Space group	Ia
a/Å	9.3268(5)
b/Å	15.1541(6)
c/Å	14.1675(7)
α/°	90
β/°	108.462(6)
γ/°	90
Volume/Å ^{3}	1899.37(17)
Z	4
ρ_{calc}g/cm^3	1.351
μ/mm^{-1}	0.192
F(000)	808.0
Crystal size/mm^3	0.5 × 0.4 × 0.3
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.05 to 54.162
Index ranges	$-11 \leq h \leq 11$, $-19 \leq k \leq 19$, $-17 \leq l \leq 18$
Reflections collected	12473
Independent reflections	3723 [R_{int} = 0.0777, R_{sigma} = 0.0627]
Data/restraints/parameters	3723/2/254
Goodness-of-fit on F^2	1.012
Final R indexes [I>=2σ (I)]	R_1 = 0.0418, wR_2 = 0.0965
Final R indexes [all data]	R_1 = 0.0460, wR_2 = 0.0984
Largest diff. peak/hole / e Å $^{-3}$	0.21/-0.36
Flack parameter	-0.06(6)

X-ray crystal data of compound 5x



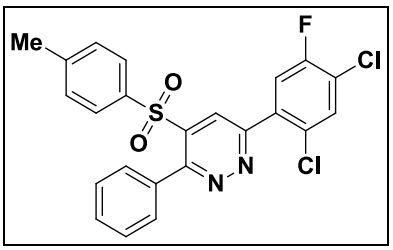
Sample preparation : A solution of compound **5x** (30 mg) in CH_2Cl_2 (10 mL) was placed in a tube (10 mL). EtOAc (2 mL) was added slowly to the vial with a dropper. The vial was closed with little cotton and kept at room temperature for 2 days. Then, colorless prisms were observed.

Crystal measurement : X-ray crystal structures were determined with a Bruker Enraf-Nonius single-crystal diffractometer (CAD4, Kappa CCD). Thermal ellipsoids are drawn at 50% probability level.



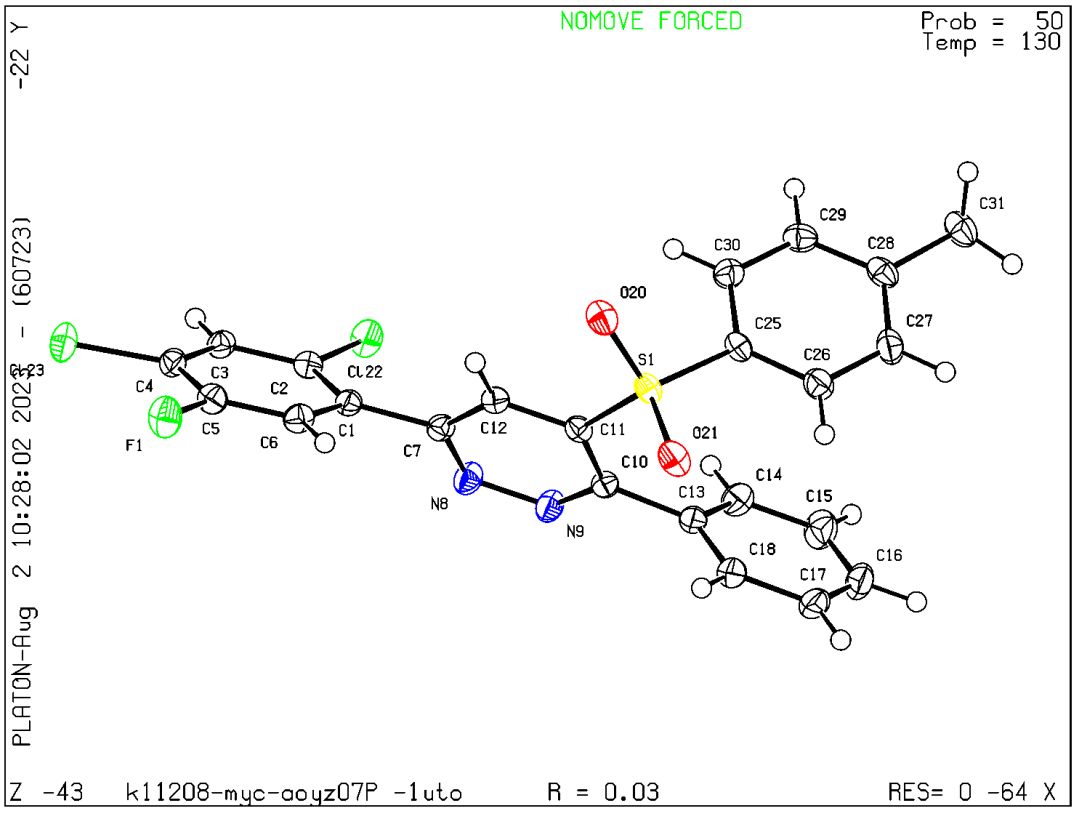
Empirical formula	$C_{28}H_{20}N_2O_2S$
Formula weight	450.53
Temperature/K	130(2)
Crystal system	triclinic
Space group	P-1
a/Å	9.3979(2)
b/Å	11.3031(3)
c/Å	12.3737(3)
α/°	114.887(3)
β/°	109.317(2)
γ/°	92.845(2)
Volume/Å ^{3}	1097.50(5)
Z	2
ρ_{calc}g/cm^3	1.363
μ/mm^{-1}	0.177
F(000)	472.0
Crystal size/mm^3	0.4 × 0.4 × 0.3
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.938 to 49.996
Index ranges	-11 ≤ h ≤ 11, -13 ≤ k ≤ 13, -14 ≤ l ≤ 14
Reflections collected	27690
Independent reflections	3861 [R_{int} = 0.0348, R_{sigma} = 0.0267]
Data/restraints/parameters	3861/0/298
Goodness-of-fit on F^2	1.081
Final R indexes [I>=2σ (I)]	R_1 = 0.0343, wR_2 = 0.0871
Final R indexes [all data]	R_1 = 0.0401, wR_2 = 0.0898
Largest diff. peak/hole / e Å $^{-3}$	0.34/-0.44

X-ray crystal data of compound 5ao



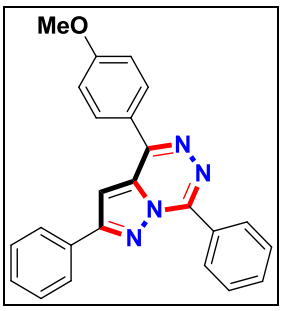
Sample preparation : A solution of compound **5ao** (30 mg) in CH_2Cl_2 (10 mL) was placed in a tube (10 mL). EtOAc (2 mL) was added slowly to the vial with a dropper. The vial was closed with little cotton and kept at room temperature for 2 days. Then, colorless prisms were observed.

Crystal measurement : X-ray crystal structures were determined with a Bruker Enraf-Nonius single-crystal diffractometer (CAD4, Kappa CCD). Thermal ellipsoids are drawn at 50% probability level.



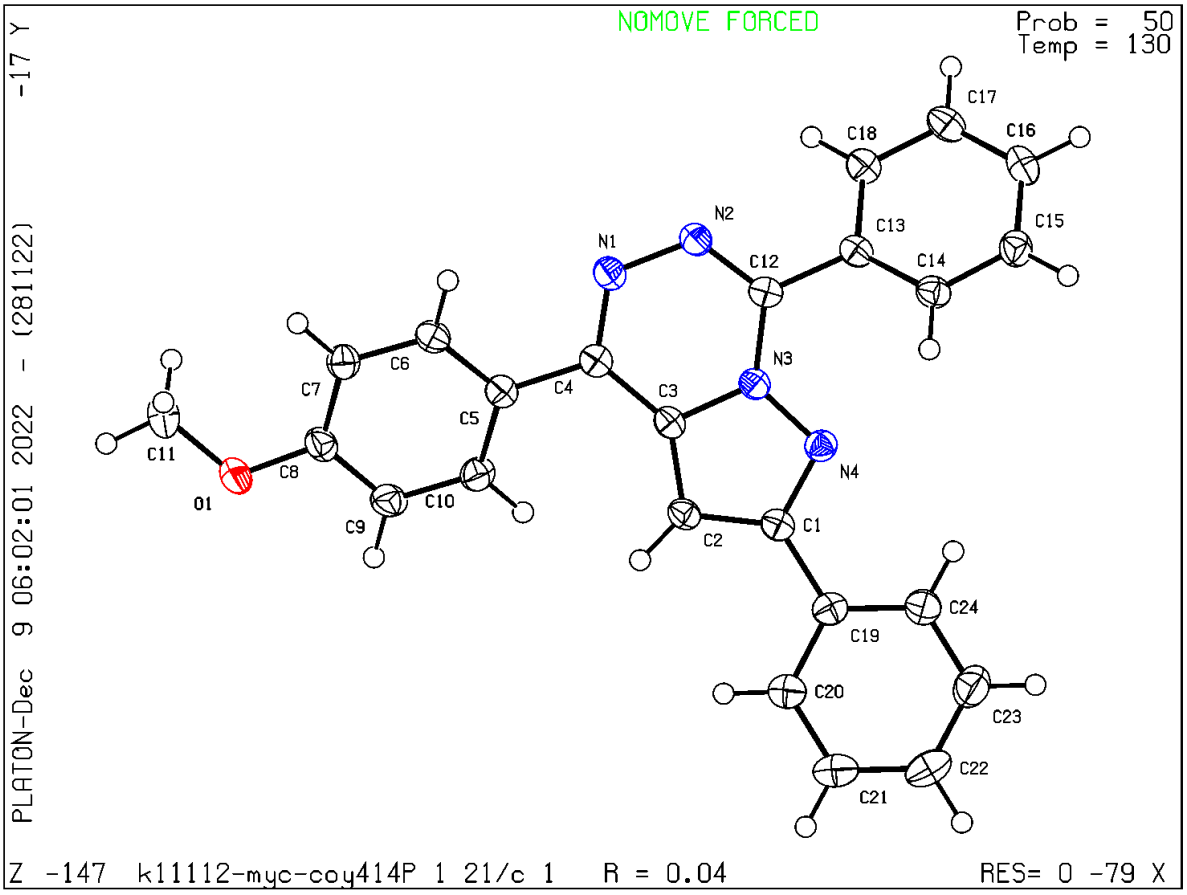
Empirical formula	$C_{23}H_{15}Cl_2FN_2O_2S$
Formula weight	473.33
Temperature/K	130(2)
Crystal system	triclinic
Space group	P-1
a/Å	9.7238(2)
b/Å	10.1366(2)
c/Å	11.2215(3)
α/°	71.447(2)
β/°	86.430(2)
γ/°	80.166(2)
Volume/Å ^{3}	1033.14(4)
Z	2
ρ_{calc}g/cm^3	1.522
μ/mm^{-1}	0.449
F(000)	484.0
Crystal size/mm^3	0.4 × 0.4 × 0.2
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.698 to 54.228
Index ranges	$-12 \leq h \leq 12$, $-12 \leq k \leq 12$, $-14 \leq l \leq 14$
Reflections collected	69896
Independent reflections	4400 [R_{int} = 0.0503, R_{sigma} = 0.0224]
Data/restraints/parameters	4400/0/281
Goodness-of-fit on F^2	1.060
Final R indexes [I>=2σ (I)]	R_1 = 0.0303, wR_2 = 0.0783
Final R indexes [all data]	R_1 = 0.0346, wR_2 = 0.0803
Largest diff. peak/hole / e Å $^{-3}$	0.41/-0.47

X-ray crystal data of compound 8



Sample preparation : A solution of compound **8** (30 mg) in CH_2Cl_2 (10 mL) was placed in a tube (10 mL). EtOAc (2 mL) was added slowly to the vial with a dropper. The vial was closed with little cotton and kept at room temperature for 2 days. Then, colorless prisms were observed.

Crystal measurement : X-ray crystal structures were determined with a Bruker Enraf-Nonius single-crystal diffractometer (CAD4, Kappa CCD). Thermal ellipsoids are drawn at 50% probability level.



Empirical formula	$C_{24}H_{18}N_4O$
Formula weight	378.42
Temperature/K	130(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.1986(2)
b/Å	7.45530(10)
c/Å	21.8767(3)
α/°	90
β/°	92.888(2)
γ/°	90
Volume/Å ^{3}	1824.14(5)
Z	4
ρ_{calc}g/cm^3	1.378
μ/mm^{-1}	0.087
F(000)	792.0
Crystal size/mm^3	0.4 × 0.4 × 0.3
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.728 to 53.986
Index ranges	$-14 \leq h \leq 14$, $-9 \leq k \leq 9$, $-27 \leq l \leq 27$
Reflections collected	33305
Independent reflections	3873 [R_{int} = 0.0610, R_{sigma} = 0.0299]
Data/restraints/parameters	3873/0/264
Goodness-of-fit on F^2	1.097
Final R indexes [I>=2σ (I)]	R_1 = 0.0384, wR_2 = 0.0964
Final R indexes [all data]	R_1 = 0.0441, wR_2 = 0.0997
Largest diff. peak/hole / e Å $^{-3}$	0.29/-0.21