Cobalt-Catalyzed Cross-Coupling of Lithium (Hetero)Aryl Zinates with Heteroaryl Chlorides and Bromides

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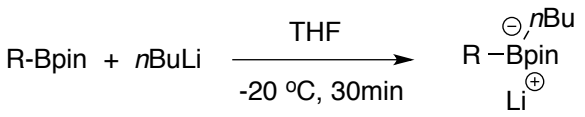
General Information

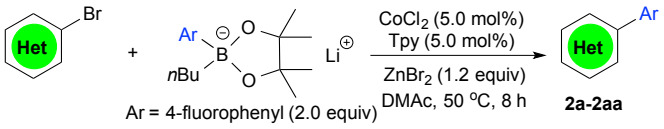
All glassware were oven or flame dried immediately prior to use. Solvents were freshly degassed according to the procedures in Purification of Laboratory Chemicals prior to use. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. and were degassed and stored over activated 4 Å molecular sieves. Unless otherwise noted, all other reagents and starting materials were purchased from commercial sources and used without further purification. The ^{1}H, ^{19}F, ^{31}P and ^{13}C NMR spectra were obtained at 293 K on a 400 MHz or 500 MHz spectrometer, and chemical shifts were recorded relative to the solvent resonance. ^{19}F shifts were determined relative to $CFCl_3$ as outside standard and low field is positive. Coupling constants are reported in hertz. The following abbreviations were used to explain the multiplicities: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; br = broad.

General procedure A for the preparation of lithium (hetero)aryl organoborate[1, 2]

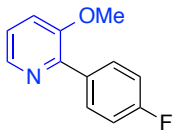


General procedure for the preparation of lithium (hetero)aryl organoboronate: boronic acid pinacol ester (RBpin, 2.50 mmol) and a stirring bar were placed into a 25 mL Shlenk tube. The system was evacuated and refilled three times with argon. Anhydrous THF (5.0 mL) was added into a Schlenk tube under argon atmosphere. The Schlenk tube was immersed into a cold bath of -20 °C and *n*BuLi (1.0 mL, 2.5 mmol/mL) was added drop by drop. The mixture was stirred for 30 min at -20 °C then was warmed slowly up to room temperature. After stirred for another 30 min, solvent was removed under vacuum and the residue was used directly without further purification.

General procedure for cobalt-catalyzed cross-coupling of heteroaryl bromides with lithium 4-fluorophenyl boronate.

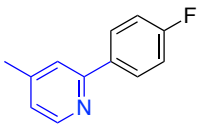


In an argon-filled glove box, (hetero)aryl bromide (0.50 mmol, 1.0 equiv), 2,2′:6′,2″-terpyridine (5.83 mg, 0.0250 mmol, 0.0500 equiv), $CoCl_2$ (3.25 mg, 0.0250 mmol, 0.0500 equiv), zinc bromide (135 mg, 0.600 mmol, 1.20 equiv) and lithium 4-fluorophenyl boronate (430 mg, 1.00 mmol, 2.00 equiv) were placed into a 25 mL Schlenk tube. Anhydrous *N,N*-dimethylacetamide (DMAc, 5.0 mL) was added and the mixture was stirred at 50 °C for 8 h. The mixture solution was diluted with Et_2O (100 mL) then filtered through a short plug of silica gel and washed with H_2O (100 mL × 3). The organic layer was combined, dried by Na_2SO_4, filtered and concentrated under vacuum. The crude was purified by column chromatography.



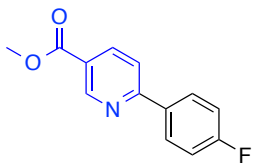
***2-(4-Fluorophenyl)-3-methoxypyridine (2a)*[3].** The product was obtained via the general procedure conducted with 2-bromo-3-methoxypyridine (94 mg, 0.50 mmol, 1.0 equiv), 2,2′:6′,2″-terpyridine (5.83 mg, 0.0250 mmol, 0.0500 equiv), $CoCl_2$ (3.25 mg, 0.0250 mmol, 0.0500 equiv), zinc bromide (135 mg, 0.600 mmol, 1.20 equiv), lithium 4-fluorophenyl boronate (430 mg, 1.00 mmol, 2.00 equiv) and purified by column chromatography (petroleum ether : EtOAc = 20:1) as a yellow oil (86 mg, 85%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (dd, *J* = 4.6, 1.4 Hz, 1 H), 7.91 (dd, *J* = 8.9, 5.5 Hz, 2 H), 7.25 (dd, *J* = 8.4, 1.5 Hz, 1 H), 7.19 (dd, *J* = 8.3, 4.5 Hz, 1 H), 7.14 – 7.07 (m, 2 H), 3.83 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.61 – -123.09 (m); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.78 (d, *J* = 247.6 Hz), 153.40, 146.93, 141.24, 133.71 (d, *J* = 3.1 Hz), 131.20 (d, *J* = 8.3 Hz), 122.94, 118.51, 114.77 (d, *J* = 21.4 Hz), 55.39 ppm. MS (EI): 202 (100), 203 (75.1). HRMS (EI) *m/z*: [M^+] Calcd for $C_{12}H_{10}FON$: 203.0746; Found: 203.0743. IR (KBr): ν_{max} = 3372, 3057, 2938, 2838 cm^{-1}.



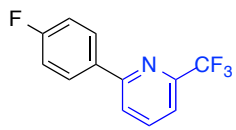
***2-(4-Fluorophenyl)-4-methylpyridine (2b)*[4].** The product was obtained via the general procedure conducted with 2-bromo-4-methylpyridine (86 mg, 0.50 mmol, 1.0 equiv), 2,2′:6′,2″-terpyridine (5.83 mg, 0.0250 mmol, 0.0500 equiv), t $CoCl_2$ (3.25 mg, 0.0250 mmol, 0.0500 equiv), zinc bromide (135 mg, 0.600 mmol, 1.20 equiv), lithium 4-fluorophenyl boronate (430 mg, 1.00 mmol, 2.00 equiv) and purified by column chromatography (petroleum ether : EtOAc = 20:1) as a colorless oil (67 mg, 72%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 5.0 Hz, 1 H), 7.92 (ddd, *J* = 8.9, 4.7, 2.1 Hz, 2 H), 7.44 (d, *J* = 3.0 Hz, 1 H), 7.10 (tt, *J* = 8.8, 2.1 Hz, 2 H), 7.00 (dt, *J* = 5.0, 2.1 Hz, 1 H), 2.35 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.40 – -113.47 (m); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.41 (d, *J* = 248.1 Hz), 156.30, 149.38, 147.83, 135.65, 128.69 (d, *J* = 8.6 Hz), 123.06, 121.16, 115.52 (d, *J* = 21.6 Hz), 21.16 ppm. MS (EI): 187 (100), 187 (100). HRMS (EI) *m/z*: [M^+] Calcd for $C_{12}H_{10}NF$: 187.0797; Found: 187.0793. IR (KBr): ν_{max} = 3384, 3052, 3005, 2923, 1901 cm^{-1}.



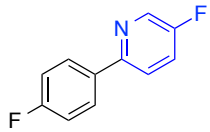
***6-(4-fluorophenyl)nicotinate (2c)*[5].** The product was obtained via the general procedure conducted with 6-bromonicontinic acid methyl ester (108 mg, 0.500 mmol, 1.00 equiv), 2,2′:6′,2″-terpyridine (5.83 mg, 0.0250 mmol, 0.0500 equiv), $CoCl_2$ (3.25 mg, 0.0250 mmol, 0.0500 equiv), zinc bromide (135 mg, 0.600 mmol, 1.20 equiv), lithium 4-fluorophenyl boronate (430 mg, 1.00 mmol, 2.00 equiv) and purified by column chromatography (petroleum ether : EtOAc = 20:1) as a white solid (92 mg, 79%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.26 – 9.20 (m, 1 H), 8.32 (dd, *J* = 8.3, 2.2 Hz, 1 H), 8.08 – 8.00 (m, 2 H), 7.74 (d, *J* = 8.3 Hz, 1 H), 7.21 – 7.12 (m, 2 H), 3.95 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -103.05 – -122.11 (m); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.78, 164.10 (d, *J* = 250.3 Hz), 159.80, 150.95, 137.94, 134.44, 129.28 (d, *J* = 8.5 Hz), 124.15, 119.45, 115.89 (d, *J* = 21.7 Hz), 52.35 ppm. MS (EI): 200 (100), 231 (99.82). HRMS (EI) *m/z*: [M^+] Calcd for $C_{13}H_{10}NO_2F$: 231.0696; Found: 231.0691. IR (KBr): ν_{max} = 3854, 3788, 3695, 3016, 2962, 1729 cm^{-1}.



2-(4-Fluorophenyl)-6-(trifluoromethyl)pyridine (2d). The product was obtained via the general procedure conducted with 2-bromo-6-(trifluoromethyl)pyridine (113 mg, 0.500 mmol, 1.00 equiv), 2,2′:6′,2″-terpyridine (5.83 mg, 0.0250 mmol, 0.0500 equiv), $CoCl_2$ (3.25 mg, 0.0250 mmol, 0.0500 equiv), zinc bromide (135 mg, 0.600 mmol, 1.20 equiv), lithium 4-fluorophenyl boronate (430 mg, 1.00 mmol, 2.00 equiv) and purified by column chromatography (petroleum ether : EtOAc = 20:1) as a yellow oil (98 mg, 81%).

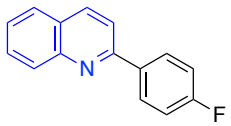
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.01 (m, 2 H), 7.92 – 7.82 (m, 2 H), 7.58 (dd, *J* = 7.5, 1.2 Hz, 1 H), 7.19 – 7.11 (m, 2 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.21, -111.61 – -111.71 (m); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.00 (d, *J* = 249.8 Hz), 156.73, 148.36 (q, *J* = 34.34 Hz), 138.15, 133.92 (d, *J* = 3.2 Hz), 129.02 (d, *J* = 8.5 Hz), 122.38, 121.52 (q, *J* = 275.7 Hz)118.41 (d, *J* = 3.1 Hz), 115.86 (d, *J* = 21.7 Hz) ppm. MS (EI): 241 (100), 240 (21.24). HRMS (EI) *m/z*: [M^+] Calcd for $C_{12}H_7NF_4$: 241.0515; Found: 241.0520. IR (KBr): ν_{max} = 3392, 2958, 2928, 2872 cm^{-1}.



2-(4-Fluorophenyl)-5-fluoropyridine (2e). The product was obtained via the general procedure conducted with 2-bromo-5-fluoropyridine (88 mg, 0.50 mmol, 1.0 equiv), 2,2′:6′,2″-terpyridine (5.83 mg, 0.0250 mmol, 0.0500 equiv), $CoCl_2$ (3.25 mg, 0.0250 mmol, 0.0500 equiv), zinc bromide (135 mg, 0.600 mmol, 1.20 equiv), lithium 4-fluorophenyl boronate (430 mg, 1.00 mmol, 2.00 equiv) and purified by column chromatography (petroleum ether : EtOAc = 20:1) as a white solid (58 mg, 61%).

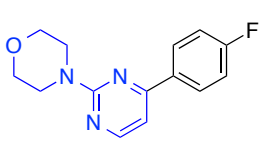
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 2.9 Hz, 1 H), 7.95 – 7.86 (m, 2 H), 7.65 (dd, *J* = 8.8, 4.2 Hz, 1 H), 7.44 (td, *J* = 8.4, 2.9 Hz, 1 H), 7.17 – 7.10 (m, 2 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.22 (ddd, *J* = 14.0, 8.8, 5.4 Hz), -129.86 (dd, *J* = 8.1, 4.2 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.44 (d, *J* = 248.6 Hz), 158.77 (d, *J* = 256.3 Hz), 152.75, 137.75 (d, *J* = 23.6 Hz), 134.60 (d, *J* = 3.2 Hz), 128.56 (d, *J* = 8.3 Hz), 123.57 (d, *J* = 18.7 Hz), 120.96 (d, *J* = 4.3 Hz), 115.71 (d, *J* = 21.7 Hz) ppm. MS (EI): 191

(100), 190 (58.23). HRMS (EI) *m/z*: [M^+] Calcd for $C_{11}H_7NF_2$: 191.0547; Found: 191.0548. Mp: 76.8~77.2 °C. IR (KBr): ν_{max} = 1599 cm^{-1}.



2-(4-Fluorophenyl)quinolone (2f)[6]. The product was obtained via the general procedure conducted with 2-bromoquinoline (104 mg, 0.500 mmol, 1.00 equiv), 2,2′:6′,2″-terpyridine (5.83 mg, 0.0250 mmol, 0.0500 equiv), $CoCl_2$ (3.25 mg, 0.0250 mmol, 0.0500 equiv), zinc bromide (135 mg, 0.600 mmol, 1.20 equiv), lithium 4-fluorophenyl boronate (430 mg, 1.00 mmol, 2.00 equiv) and purified by column chromatography (petroleum ether : EtOAc = 20:1) as a white solid (92 mg, 83%).

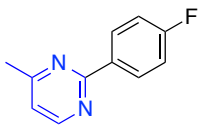
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.5 Hz, 1 H), 8.18 – 8.11 (m, 3 H), 7.81 (dd, *J* = 8.3, 1.7 Hz, 2 H), 7.72 (ddd, *J* = 8.5, 6.9, 1.5 Hz, 1 H), 7.52 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1 H), 7.23 – 7.15 (m, 2 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.87 – -137.68 (m); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.77 (d, *J* = 249.0 Hz), 156.20, 148.18, 136.89, 135.76, 131.24 – 128.98 (m), 127.44, 127.04, 126.32, 118.60, 115.74 (d, *J* = 21.6 Hz) ppm. MS (EI): 223 (100), 222 (87.78). HRMS (EI) *m/z*: [M^+] Calcd for $C_{15}H_{10}NF$: 223.0797; Found: 223.0798. IR (KBr): ν_{max} = 3062, 2924 cm^{-1}.



4-(4-(4-Fluorophenyl)pyrimidin-2-yl)morpholine (2g). The product was obtained via the general procedure conducted with 4-(4-bromopyrimidin-2-yl)morpholine (122 mg, 0.500 mmol, 1.00 equiv), 2,2′:6′,2″-terpyridine (5.83 mg, 0.0250 mmol, 0.0500 equiv), $CoCl_2$ (3.25 mg, 0.0250 mmol, 0.0500 equiv), zinc bromide (135 mg, 0.600 mmol, 1.20 equiv), lithium 4-fluorophenyl boronate (430 mg, 1.00 mmol, 2.00 equiv) and purified by column chromatography (petroleum ether : EtOAc = 20:1) as a white solid (108 mg, 83.0%).

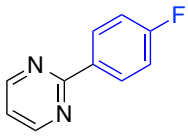
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 5.2 Hz, 1 H), 8.08 – 7.98 (m, 2 H), 7.13 (t, *J* = 8.6 Hz, 2 H), 6.91 (d, *J* = 5.2 Hz, 1 H), 3.91 – 3.85 (m, 4 H), 3.79 (t, *J* = 4.7 Hz, 4 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -102.07 – -127.97 (m); ^{13}C NMR (101 MHz, $CDCl_3$)

δ 164.41 (d, *J* = 251.5), 163.24, 161.94, 158.40, 133.67 (d, *J* = 3.2 Hz), 128.98 (d, *J* = 8.6 Hz), 115.66 (d, *J* = 21.8 Hz), 105.71, 66.90, 44.30 ppm. MS (EI): 228 (100), 259 (56.89). HRMS (EI) *m/z*: [M^+] Calcd for $C_{14}H_{14}N_3OF$: 259.1121; Found: 259.1113. Mp: 110.2~111.8 °C. IR (KBr): ν_{max} = 3704, 3636, 2988, 2864 cm^{-1}.



2-(4-Fluorophenyl)-4-methylpyrimidine (2h). The product was obtained via the general procedure conducted with 2-bromo-4-methylpyrimidine (87 mg, 0.50 mmol, 1.0 equiv), 2,2′:6′,2″-terpyridine (5.83 mg, 0.0250 mmol, 0.0500 equiv), $CoCl_2$ (3.25 mg, 0.0250 mmol, 0.0500 equiv), zinc bromide (135 mg, 0.600 mmol, 1.20 equiv), lithium 4-fluorophenyl boronate (430 mg, 1.00 mmol, 2.00 equiv) and purified by column chromatography (petroleum ether : EtOAc = 20:1) as a yellow oil (63 mg, 67%).

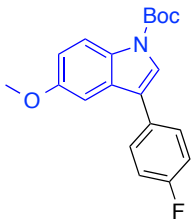
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 5.1 Hz, 1 H), 8.47 – 8.36 (m, 2 H), 7.17 – 7.08 (m, 2 H), 7.02 (d, *J* = 5.1 Hz, 1 H), 2.55 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.81 (ddd, *J* = 8.7, 5.6, 3.0 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.29, 164.6 (d, *J* = 250.5), 163.46, 156.78, 134.02 (d, *J* = 2.8 Hz), 130.27 (d, *J* = 8.6 Hz), 118.47, 115.41 (d, *J* = 21.6 Hz), 24.37 ppm. MS (EI): 188 (100), 188 (100). HRMS (EI) *m/z*: [M^+] Calcd for $C_{11}H_9N_2F$: 188.0750; Found: 188.0743. IR (KBr): ν_{max} = 3075, 3054, 2967, 2923, 2852, 2427, 2362 cm^{-1}.



2-(4-Fluorophenyl)pyrimidine (2i)[7]**.** The product was obtained via the general procedure conducted with 2-bromopyrimidine (80 mg, 0.50 mmol, 1.0 equiv), 2,2′:6′,2″-terpyridine (5.83 mg, 0.0250 mmol, 0.0500 equiv), $CoCl_2$ (3.25 mg, 0.0250 mmol, 0.0500 equiv), zinc bromide (135 mg, 0.600 mmol, 1.20 equiv), lithium 4-fluorophenyl boronate (430 mg, 1.00 mmol, 2.00 equiv) and purified by column chromatography (petroleum ether : EtOAc = 20:1) as a white solid (74 mg, 85%).

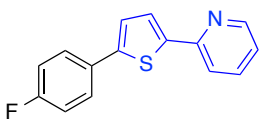
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, *J* = 4.8 Hz, 2 H), 8.45 (dd, *J* = 8.6, 5.6 Hz, 2 H), 7.22 – 7.11 (m, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.70 – -121.55 (m); ^{13}C NMR

(101 MHz, $CDCl_3$) δ 164.68 (d, J = 251.5 Hz), 157.17, 133.73 (d, J = 2.0 Hz), 130.22 (d, J = 8.6 Hz), 118.91, 115,58, 115.37 ppm. MS(EI): 174 (100). HRMS (EI) *m/z*: [M^+] Calcd for $C_{10}H_7N_2F$: 174.0593; Found: 174.0598. IR (KBr): ν_{max} = 3048, 2418, 1921, 1789 cm^{-1}.



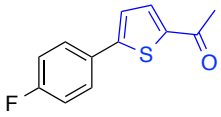
tert-Butyl 3-(4-fluorophenyl)-5-methoxy-1H-indole-1-carboxylate (2j). The product was obtained via the general procedure conducted with 3-bromo-5-methoxyindole (163 mg, 0.500 mmol, 1.00 equiv), 2,2′:6′,2″-terpyridine (5.83 mg, 0.0250 mmol, 0.0500 equiv), $CoCl_2$ (3.25 mg, 0.0250 mmol, 0.0500 equiv), zinc bromide (135 mg, 0.600 mmol, 1.20 equiv), lithium 4-fluorophenyl boronate (430 mg, 1.00 mmol, 2.00 equiv) and purified by column chromatography (petroleum ether : EtOAc = 20:1) as a white solid (131 mg, 77.0%).

^1H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1 H), 7.62 (s, 1 H), 7.58 – 7.53 (m, 2 H), 7.19 – 7.11 (m, 3 H), 6.97 (dd, J = 9.0, 2.6 Hz, 1 H), 3.84 (s, 3 H), 1.67 (s, 9 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.14 (m); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.11 (d, J = 246.2 Hz), 156.24, 149.65, 130.53, 129.93 (d, J = 3.3 Hz), 129.74, 129.41 (d, J = 7.9 Hz), 123.44, 121.04, 116.06 (d, J = 30.0 Hz), 115.70, 113.22, 102.51, 83.77, 55.80, 28.24 ppm. HRMS (ESI) $[M+H]^+$ Calcd for $C_{20}H_{21}NO_3F$: 342.1500; Found: 342.1496. Mp: 85.6~86.9 °C. IR (KBr): ν_{max} = 3158, 3063, 2983, 2935, 2840, 1904 cm^{-1}.



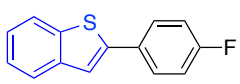
2-(5-(4-Fluorophenyl)thiophen-2-yl)pyridine (2k). The product was obtained via the general procedure conducted with 2-(5-bromothien-2-yl)pyridine (120 mg, 0.500 mmol, 1.00 equiv), 2,2′:6′,2″-terpyridine (5.83 mg, 0.0250 mmol, 0.0500 equiv), $CoCl_2$ (3.25 mg, 0.0250 mmol, 0.0500 equiv), zinc bromide (135 mg, 0.600 mmol, 1.20 equiv), lithium 4-fluorophenyl boronate (430 mg, 1.00 mmol, 2.00 equiv) and purified by column chromatography (petroleum ether : EtOAc = 20:1) as a yellow solid (86 mg, 67%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 4.9 Hz, 1 H), 7.69 – 7.58 (m, 4 H), 7.51 (d, *J* = 3.9 Hz, 1 H), 7.23 (d, *J* = 3.9 Hz, 1 H), 7.15 – 7.04 (m, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -101.38 – -124.41 (m); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.49 (d, *J* = 248.1 Hz), 152.40, 149.59, 145.04, 143.93, 136.61, 130.57 (d, *J* = 3.3 Hz), 127.42 (d, *J* = 8.1 Hz), 125.38, 123.94, 121.89, 118.47, 115.93 (d, *J* = 21.9 Hz) ppm. MS (EI): 255 (100), 255 (100). HRMS (EI) *m/z*: [M^+] Calcd for $C_{15}H_{10}NSF$: 255.0518; Found: 255.0512. Mp: 151.5~153.2 °C. IR (KBr): ν_{max} = 3051, 1764 cm^{-1}.



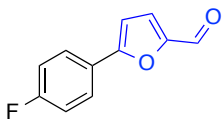
***1-(5-(4-Fluorophenyl)thiophen-2-yl)ethan-1-one (2l)*[8].** The product was obtained via the general procedure conducted with 2-acetyl-5-bromothiophene (103 mg, 0.500 mmol, 1.00 equiv), 2,2′:6′,2″-terpyridine (5.83 mg, 0.0250 mmol, 0.0500 equiv), $CoCl_2$ (3.25 mg, 0.0250 mmol, 0.0500 equiv), zinc bromide (135 mg, 0.600 mmol, 1.20 equiv), lithium 4-fluorophenyl boronate (430 mg, 1.00 mmol, 2.00 equiv) and purified by column chromatography (petroleum ether : EtOAc = 20:1) as a yellow solid (91 mg, 82%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.56 (m, 3 H), 7.25 – 7.23 (m, 1 H), 7.10 (t, *J* = 8.6 Hz, 2 H), 2.55 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.95 (ddd, *J* = 8.4, 5.3, 3.0 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.49, 163.18 (d, *J* = 249.7 Hz), 151.56, 143.21, 133.43, 129.67 (d, *J* = 3.6 Hz), 128.09 (d, *J* = 8.2 Hz), 123.87, 116.19 (d, *J* = 22.0 Hz), 26.53 ppm. MS (EI): 205 (100), 220 (555.58). HRMS (EI) *m/z*: [M^+] Calcd for $C_{12}H_9OSF$: 220.0358; Found: 220.0353. IR (KBr): ν_{max} = 3077, 1651 cm^{-1}.



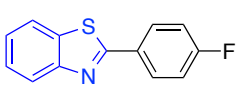
***2-(4-Fluorophenyl)benzo[b]thiophene (2m)*[9].** The product was obtained via the general procedure conducted with 2-bromobenzo[b]thiophene (107 mg, 0.500 mmol, 1.00 equiv), 2,2′:6′,2″-terpyridine (5.83 mg, 0.0250 mmol, 0.0500 equiv), $CoCl_2$ (3.25 mg, 0.0250 mmol, 0.0500 equiv), zinc bromide (135 mg, 0.600 mmol, 1.20 equiv), lithium 4-fluorophenyl boronate (430 mg, 1.00 mmol, 2.00 equiv) and purified by column chromatography (petroleum ether : EtOAc = 20:1) as a white solid (108 mg, 95.0%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.90 (m, 1 H), 7.87 – 7.83 (m, 1 H), 7.56 – 7.52 (m, 2 H), 7.42 – 7.38 (m, 2 H), 7.36 (s, 1 H), 7.18 (t, *J* = 8.7 Hz, 2 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.59 (m); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.39 (d, *J* = 246.7 Hz), 140.66, 137.87, 137.01, 132.04 (d, *J* = 3.5 Hz), 130.30 (d, *J* = 8.0 Hz), 124.48 (d, *J* = 7.4 Hz), 123.45, 122.99, 122.71, 115.68 (d, *J* = 21.4 Hz), 106.65 ppm. MS (EI): 228 (100), 228 (100). HRMS (EI) *m/z*: [M^+] Calcd for $C_{14}H_9SF$: 228.0409; Found: 228.0412. IR (KBr): ν_{max} = 3853, 3649, 3061, 2924, 2852, 1891 cm^{-1}.



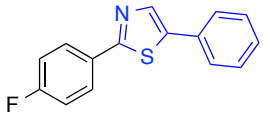
***5-(4-Fluorophenyl)furan-2-carbaldehyde (2n)*[10]**. The product was obtained via the general procedure conducted with 5-bromo-2-furaldehyde (88 mg, 0.50 mmol, 1.0 equiv), 2,2′:6′,2″-terpyridine (5.83 mg, 0.0250 mmol, 0.0500 equiv), \ $CoCl_2$ (3.25 mg, 0.0250 mmol, 0.0500 equiv), zinc bromide (135 mg, 0.600 mmol, 1.20 equiv), lithium 4-fluorophenyl boronate (430 mg, 1.00 mmol, 2.00 equiv) and purified by column chromatography (petroleum ether : EtOAc = 10:1) as a white solid (68 mg, 71%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.62 (s, 1 H), 7.83 – 7.74 (m, 2 H), 7.29 (d, *J* = 3.7 Hz, 1 H), 7.12 (t, *J* = 8.6 Hz, 2 H), 6.76 (d, *J* = 3.7 Hz, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.18 (td, *J* = 8.7, 4.4 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.12, 163.50 (d, *J* = 251.0 Hz), 158.49, 152.05, 127.32 (d, *J* = 8.3 Hz), 125.37 (d, *J* = 3.4 Hz), 123.62, 116.17 (d, *J* = 22.1 Hz), 107.37 ppm. MS (EI): 133 (100), 190 (95.28). HRMS (EI) *m/z*: [M^+] Calcd for $C_{11}H_7O_2F$: 190.0430; Found: 190.0426. IR (KBr): ν_{max} = 3302, 3115, 3051, 2852 cm^{-1}.



***2-(4-Fluorophenyl)benzo[d]thiazole (2o)*[11]**. The product was obtained via the general procedure conducted with 2-bromo-1,3-benzothiazole (107 mg, 0.500 mmol, 1.00 equiv), 2,2′:6′,2″-terpyridine (5.83 mg, 0.0250 mmol, 0.0500 equiv), $CoCl_2$ (3.25 mg, 0.0250 mmol, 0.0500 equiv), zinc bromide (135 mg, 0.600 mmol, 1.20 equiv), lithium 4-fluorophenyl boronate (430 mg, 1.00 mmol, 2.00 equiv) and purified by column chromatography (petroleum ether : EtOAc = 20:1) as a white solid (93 mg, 81%).

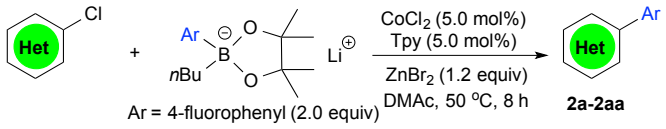
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.02 (m, 3 H), 7.89 – 7.85 (m, 1 H), 7.50 – 7.46 (m, 1 H), 7.40 – 7.34 (m, 1 H), 7.20 – 7.12 (m, 2 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -97.19 – -121.20 (m); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.73, 164.45 (d, J = 251.9 Hz), 154.10, 135.06, 129.98, 129.52 (d, J = 8.7 Hz), 126.42, 125.25, 123.20, 121.62, 116.16 (d, J = 22.1 Hz) ppm. MS (EI): 229 (100), 229 (100). HRMS (EI) *m/z*: [M^+] Calcd for $C_{13}H_8NSF$: 229.0361; Found: 229.0357. IR (KBr): ν_{max} = 3053, 1671 cm^{-1}.



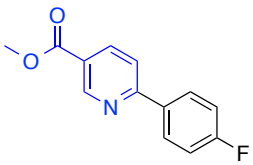
***2-(4-Fluorophenyl)-5-phenylthiazole (2p)*[12].** The product was obtained via the general procedure conducted with 2-bromo-5-phenylthiazole (120 mg, 0.500 mmol, 1.00 equiv), 2,2′:6′,2″-terpyridine (5.83 mg, 0.0250 mmol, 0.0500 equiv), $CoCl_2$ (3.25 mg, 0.0250 mmol, 0.0500 equiv), zinc bromide (135 mg, 0.600 mmol, 1.20 equiv), lithium 4-fluorophenyl boronate (430 mg, 1.00 mmol, 2.00 equiv) and purified by column chromatography (petroleum ether : EtOAc = 20:1) as a yellow solid (90 mg, 70%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1 H), 7.94 (dd, J = 8.5, 5.3 Hz, 2 H), 7.59 (d, J = 7.6 Hz, 2 H), 7.41 (t, J = 7.4 Hz, 2 H), 7.33 (t, J = 7.3 Hz, 1 H), 7.13 (t, J = 8.3 Hz, 2 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.43 (dt, J = 8.8, 3.5 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.90, 163.81 (d, J = 250.5 Hz), 139.33, 139.10, 131.24, 130.01 (d, J = 3.3 Hz), 129.11, 128.35, 128.22 (d, J = 8.5 Hz), 126.63, 116.04 (d, J = 22.1 Hz) ppm. MS (EI): 255 (100), 255 (100). HRMS (EI) *m/z*: [M^+] Calcd for $C_{15}H_{10}NSF$: 255.0518; Found: 255.0509. IR (KBr): ν_{max} = 3446, 3062, 1877 cm^{-1}.

General procedure for cobalt-catalyzed cross-coupling of heteroaryl chlorides with lithium 4-fluorophenyl boronate.

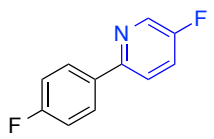


In an argon-filled glove box, (hetero)aryl chloride (0.50 mmol, 1.0 equiv), 2,2′:6′,2″-terpyridine (5.83 mg, 0.0250 mmol, 0.0500 equiv), $CoCl_2$ (3.25 mg, 0.0250 mmol, 0.0500 equiv), zinc bromide (135 mg, 0.600 mmol, 1.20 equiv) and lithium 4-fluorophenyl boronate (430 mg, 1.00 mmol, 2.00 equiv) were placed into a 25 mL Schlenk tube. Anhydrous *N,N*-dimethylacetamide (DMAc, 5.0 mL) was added into the tube and the mixture was stirred at 50 °C for 8 h. The mixture solution was diluted with Et_2O (100 mL) then filtered through a short plug of silica gel and washed with H_2O (100 mL × 3). The organic layer was combined, dried over Na_2SO_4, filtered and concentrated under vacuum. The crude was purified by column chromatography.



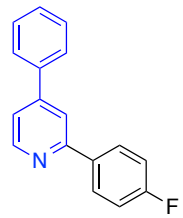
6-(4-fluorophenyl)nicotinate (2q). The product was obtained via the general procedure conducted with methyl 6-chloronicotinate (86 mg, 0.500 mmol, 1.00 equiv), 2,2′:6′,2″-terpyridine (5.83 mg, 0.0250 mmol, 0.0500 equiv), $CoCl_2$ (3.25 mg, 0.0250 mmol, 0.0500 equiv), zinc bromide (135 mg, 0.600 mmol, 1.20 equiv), lithium 4-fluorophenyl boronate (430 mg, 1.00 mmol, 2.00 equiv) and purified by column chromatography (petroleum ether : EtOAc = 20:1) as a white solid (84 mg, 73%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.26 – 9.20 (m, 1 H), 8.32 (dd, *J* = 8.3, 2.2 Hz, 1 H), 8.08 – 8.00 (m, 2 H), 7.74 (d, *J* = 8.3 Hz, 1 H), 7.21 – 7.12 (m, 2 H), 3.95 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -103.05 – -122.11 (m); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.78, 164.10 (d, *J* = 250.3 Hz), 159.80, 150.95, 137.94, 134.44, 129.28 (d, *J* = 8.5 Hz), 124.15, 119.45, 115.89 (d, *J* = 21.7 Hz), 52.35 ppm. MS (EI): 200 (100), 231 (99.82). HRMS (EI) *m/z*: [M^+] Calcd for $C_{13}H_{10}NO_2F$: 231.0696; Found: 231.0691. IR (KBr): ν_{max} = 3854, 3788, 3695, 3016, 2962, 1729 cm^{-1}.



2-(4-Fluorophenyl)-5-fluoropyridine (2r). The product was obtained via the general procedure conducted with 2-chloro-5-fluoropyridine (66 mg, 0.50 mmol, 1.0 equiv), 2,2′:6′,2″-terpyridine (5.83 mg, 0.0250 mmol, 0.0500 equiv), $CoCl_2$ (3.25 mg, 0.0250 mmol, 0.0500 equiv), zinc bromide (135 mg, 0.600 mmol, 1.20 equiv), lithium 4-fluorophenyl boronate (430 mg, 1.00 mmol, 2.00 equiv) and purified by column chromatography (petroleum ether : EtOAc = 20:1) as a white solid (67 mg, 70%).

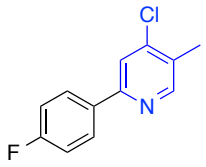
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 2.9 Hz, 1 H), 7.95 – 7.86 (m, 2 H), 7.65 (dd, *J* = 8.8, 4.2 Hz, 1 H), 7.44 (td, *J* = 8.4, 2.9 Hz, 1 H), 7.17 – 7.10 (m, 2 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.22 (ddd, *J* = 14.0, 8.8, 5.4 Hz), -129.86 (dd, *J* = 8.1, 4.2 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.44 (d, *J* = 248.6 Hz), 158.77 (d, *J* = 256.3 Hz), 152.75, 137.75 (d, *J* = 23.6 Hz), 134.60 (d, *J* = 3.2 Hz), 128.56 (d, *J* = 8.3 Hz), 123.57 (d, *J* = 18.7 Hz), 120.96 (d, *J* = 4.3 Hz), 115.71 (d, *J* = 21.7 Hz) ppm. MS (EI): 191 (100), 190 (58.23). HRMS (EI) *m/z*: [M^+] Calcd for $C_{11}H_7NF_2$: 191.0547; Found: 191.0548. Mp: 76.8~77.2 °C. IR (KBr): ν_{max} = 1599 cm^{-1}.



***2-(4-Fluorophenyl)-4-phenylpyridine (2s)*[13].** The product was obtained via the general procedure conducted with 2-chloro-4-phenylpyridine (95 mg, 0.50 mmol, 1.0 equiv), 2,2′:6′,2″-terpyridine (5.83 mg, 0.0250 mmol, 0.0500 equiv), $CoCl_2$ (3.25 mg, 0.0250 mmol, 0.0500 equiv), zinc bromide (135 mg, 0.600 mmol, 1.20 equiv), lithium 4-fluorophenyl boronate (430 mg, 1.00 mmol, 2.00 equiv) and purified by column chromatography (petroleum ether : EtOAc = 10:1) as a colorless oil (86 mg, 69%).

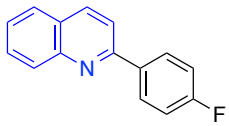
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (dd, *J* = 5.1, 0.9 Hz, 1 H), 8.07 – 7.99 (m, 2 H), 7.86 (dd, *J* = 1.8, 0.9 Hz, 1 H), 7.70 – 7.64 (m, 2 H), 7.53 – 7.40 (m, 4 H), 7.16 (t, *J* = 8.7 Hz, 2 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.03 (m); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.58 (d, *J* = 248.3 Hz), 157.07, 150.09, 149.42, 138.46, 135.67, 129.15, 129.11, 128.84 (d, *J* = 8.4 Hz), 127.08, 120.22, 118.42, 115.68 (d, *J* = 21.5 Hz) ppm. MS (EI):

249 (100), 249 (100). HRMS (EI) *m/z*: [M^+] Calcd for $C_{17}H_{12}NF$: 249.0954; Found: 249.0944. IR (KBr): ν_{max} = 3405, 3059, 2926, 1899 cm^{-1}.



4-Chloro-2-(4-fluorophenyl)-5-methylpyridine (2t). The product was obtained via the general procedure conducted with 2,4-dichloro-5-methylpyridine (81 mg, 0.50 mmol, 1.0 equiv), 2,2′:6′,2″-terpyridine (5.83 mg, 0.0250 mmol, 0.0500 equiv), $CoCl_2$ (3.25 mg, 0.0250 mmol, 0.0500 equiv), zinc bromide (135 mg, 0.600 mmol, 1.20 equiv), lithium 4-fluorophenyl boronate (430 mg, 1.00 mmol, 2.00 equiv) and purified by column chromatography (petroleum ether : EtOAc = 20:1) as a white solid (75 mg, 68%).

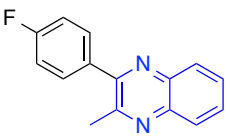
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1 H), 7.94 – 7.86 (m, 2 H), 7.63 (s, 1 H), 7.17 – 7.06 (m, 2 H), 2.36 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.64 (m); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.60 (d, *J* = 248.8 Hz), 155.50, 151.08, 144.75, 134.35 (d, *J* = 3.2 Hz), 130.13, 128.54 (d, *J* = 8.4 Hz), 120.36, 115.72 (d, *J* = 21.6 Hz), 16.43 ppm. MS (EI): 221 (100), 221 (100). HRMS (EI) *m/z*: [M^+] Calcd for $C_{12}H_9NClF$: 221.0408; Found: 221.0417. Mp: 65.7~66.8 °C. IR (KBr): ν_{max} = 2983, 2920, 2362, 1923 cm^{-1}.



2-(4-Fluorophenyl)quinolone (2u)[6]. The product was obtained via the general procedure conducted with 2-chloroquinoline (82 mg, 0.500 mmol, 1.00 equiv), 2,2′:6′,2″-terpyridine (5.83 mg, 0.0250 mmol, 0.0500 equiv), $CoCl_2$ (3.25 mg, 0.0250 mmol, 0.0500 equiv), zinc bromide (135 mg, 0.600 mmol, 1.20 equiv), lithium 4-fluorophenyl boronate (430 mg, 1.00 mmol, 2.00 equiv) and purified by column chromatography (petroleum ether : EtOAc = 20:1) as a white solid (91 mg, 81%).

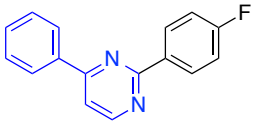
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.5 Hz, 1 H), 8.18 – 8.11 (m, 3 H), 7.81 (dd, *J* = 8.3, 1.7 Hz, 2 H), 7.72 (ddd, *J* = 8.5, 6.9, 1.5 Hz, 1 H), 7.52 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1 H), 7.23 – 7.15 (m, 2 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.87 – -137.68 (m); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.77 (d, *J* = 249.0 Hz), 156.20, 148.18, 136.89, 135.76, 131.24 – 128.98 (m), 127.44, 127.04, 126.32, 118.60, 115.74 (d, *J* = 21.6 Hz)

ppm. MS (EI): 223 (100), 222 (87.78). HRMS (EI) *m/z*: [M^+] Calcd for $C_{15}H_{10}NF$: 223.0797; Found: 223.0798. IR (KBr): ν_{max} = 3062, 2924 cm^{-1}.



***2-(4-Fluorophenyl)-3-methylquinoxaline (2v)*[14].** The product was obtained via the general procedure conducted with 2-chloro-3-methylquinoxaline (90 mg, 0.50 mmol, 1.0 equiv), 2,2′:6′,2″-terpyridine (5.83 mg, 0.0250 mmol, 0.0500 equiv), $CoCl_2$ (3.25 mg, 0.0250 mmol, 0.0500 equiv), zinc bromide (135 mg, 0.600 mmol, 1.20 equiv), lithium 4-fluorophenyl boronate (430 mg, 1.00 mmol, 2.00 equiv) and purified by column chromatography (petroleum ether : EtOAc = 10:1) as a yellow solid (92 mg, 77%).

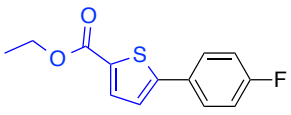
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 17.3, 7.7 Hz, 2 H), 7.73 (m, 2 H), 7.64 (m, 2 H), 7.20 (t, *J* = 8.4 Hz, 2 H), 2.75 (s, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.14 (m); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.24 (d, *J* = 249.2 Hz), 153.79, 152.29, 141.26, 140.94, 135.09 (d, *J* = 3.4 Hz), 130.95 (d, *J* = 8.5 Hz), 129.83, 129.33, 129.15, 128.34, 115.62 (d, *J* = 21.8 Hz), 24.39 ppm. MS (EI): 237 (100), 238 (92.38). HRMS (EI) *m/z*: [M^+] Calcd for $C_{15}H_{11}N_2F$: 238.0906; Found: 238.0908. IR (KBr): ν_{max} = 3058, 2996, 2970, 2926, 1601 cm^{-1}.



***2-(4-Fluorophenyl)-4-phenylpyrimidine (2w)*[15].** The product was obtained via the general procedure conducted with 2-chloro-4-phenylpyrimidine (96 mg, 0.50 mmol, 1.0 equiv), 2,2′:6′,2″-terpyridine (5.83 mg, 0.0250 mmol, 0.0500 equiv), $CoCl_2$ (3.25 mg, 0.0250 mmol, 0.0500 equiv), zinc bromide (135 mg, 0.600 mmol, 1.20 equiv), lithium 4-fluorophenyl boronate (430 mg, 1.00 mmol, 2.00 equiv) and purified by column chromatography (petroleum ether : EtOAc = 20:1) as a white solid (90 mg, 72%).

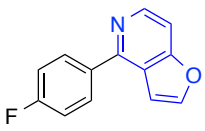
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (d, *J* = 5.3 Hz, 1 H), 8.62 – 8.49 (m, 2 H), 8.19 (dd, *J* = 6.7, 3.0 Hz, 2 H), 7.57 (d, *J* = 5.3 Hz, 1 H), 7.52 (p, *J* = 3.5 Hz, 3 H), 7.17 (t, *J* = 8.7 Hz, 2 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.49 (ddd, *J* = 13.9, 8.7, 5.5 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.7 (d, *J* = 250.5), 163.81 (d, *J* = 22.9 Hz), 157.84, 136.87,

134.06 (d, J = 3.2 Hz), 131.03, 130.40 (d, J = 8.6 Hz), 128.96, 127.18, 115.56, 115.34, 114.41 ppm. MS (EI): 250 (100), 249 (11.65). HRMS (EI) *m/z*: [M^+] Calcd for $C_{16}H_{11}N_2F$: 250.0906; Found: 250.0899. IR (KBr): ν_{max} = 3031, 1915 cm^{-1}.



***5-(4-Fluorophenyl)thiophene-2-carboxylate (2x)*[16].** The product was obtained via the general procedure conducted with Ethyl 5-chlorothiophene-2-carboxylate (96 mg, 0.50 mmol, 1.0 equiv), 2,2′:6′,2″-terpyridine (5.83 mg, 0.0250 mmol, 0.0500 equiv), $CoCl_2$ (3.25 mg, 0.0250 mmol, 0.0500 equiv), zinc bromide (135 mg, 0.600 mmol, 1.20 equiv), lithium 4-fluorophenyl boronate (430 mg, 1.00 mmol, 2.00 equiv) and purified by column chromatography (petroleum ether : EtOAc = 30:1) as a white solid (88 mg, 71%).

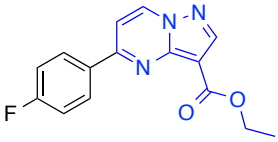
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 3.9 Hz, 1 H), 7.61 – 7.55 (m, 2 H), 7.19 (d, J = 3.9 Hz, 1 H), 7.12 – 7.05 (m, 2 H), 4.35 (q, J = 7.1 Hz, 2 H), 1.37 (t, J = 7.1 Hz, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.13 – -112.76 (m); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.01 (d, J = 250.5 Hz), 162.17, 149.87, 134.20, 132.63, 129.80 (d, J = 3.7 Hz), 127.98 (d, J = 8.4 Hz), 123.55, 116.12 (d, J = 21.8 Hz), 61.21, 14.36 ppm. MS (EI): 205 (100), 250 (70.57). HRMS (EI) *m/z*: [M^+] Calcd for $C_{13}H_{11}O_2SF$: 250.0464; Found: 250.0468. IR (KBr): ν_{max} = 3081, 2984, 2940, 1685 cm^{-1}.



4-(4-Fluorophenyl)furo[3,2-c]pyridine (2y). The product was obtained via the general procedure conducted with 4-chloro-furo[3,2-c]pyridine (77 mg, 0.50 mmol, 1.0 equiv), 2,2′:6′,2″-terpyridine (5.83 mg, 0.0250 mmol, 0.0500 equiv), $CoCl_2$ (3.25 mg, 0.0250 mmol, 0.0500 equiv), zinc bromide (135 mg, 0.600 mmol, 1.20 equiv), lithium 4-fluorophenyl boronate (430 mg, 1.00 mmol, 2.00 equiv) and purified by column chromatography (petroleum ether : EtOAc = 10:1) as a white solid (80 mg, 75%).

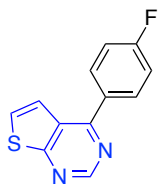
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, J = 5.7 Hz, 1 H), 7.97 – 7.88 (m, 2 H), 7.68 (d, J = 2.3 Hz, 1 H), 7.40 (dd, J = 5.7, 1.1 Hz, 1 H), 7.23 – 7.15 (m, 2 H), 7.01 (dd, J = 2.3,

1.1 Hz, 1 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.57 (ddd, *J* = 8.8, 5.5, 3.2 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.36 (d, *J* = 248.8 Hz), 160.31, 152.26, 145.69, 144.33, 135.37, 130.23 (d, *J* = 8.2 Hz), 121.97, 115.70 (d, *J* = 21.7 Hz), 105.96, 105.61 ppm. MS (EI): 185 (100), 213 (95.42). HRMS (EI) *m/z*: [M^+] Calcd for $C_{13}H_8NOF$: 213.0590; Found: 213.0591. Mp: 101.2~102.4 °C. IR (KBr): ν_{max} = 3138, 3088, 3038, 2886, 1915 cm^{-1}.



5-(4-Fluorophenyl)pyrazolo[1,5-a]pyrimidine-3-carboxylate (2z). The product was obtained via the general procedure conducted with Ethyl 5-chloropyrazolo[1,5-a]pyrimidine-3-carboxylate (113 mg, 0.500 mmol, 1.00 equiv), 2,2′:6′,2″-terpyridine (5.83 mg, 0.0250 mmol, 0.0500 equiv), $CoCl_2$ (3.25 mg, 0.0250 mmol, 0.0500 equiv), zinc bromide (135 mg, 0.600 mmol, 1.20 equiv), lithium 4-fluorophenyl boronate (430 mg, 1.00 mmol, 2.00 equiv) and purified by column chromatography (petroleum ether : EtOAc = 3:1 to 1:1) as a yellow solid (92 mg, 65%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 7.4 Hz, 1 H), 8.54 (s, 1 H), 8.25 – 8.17 (m, 2 H), 7.40 (d, *J* = 7.4 Hz, 1 H), 7.19 (t, *J* = 8.6 Hz, 2 H), 4.42 (d, *J* = 7.1 Hz, 2 H), 1.43 (t, *J* = 7.1 Hz, 3 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.60 – -108.64 (m); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.91 (d, *J* = 252.7 Hz), 162.55, 157.99, 148.28, 147.62, 136.05, 132.48 (d, *J* = 3.2 Hz), 129.85 (d, *J* = 9.0 Hz), 116.16 (d, *J* = 22.0 Hz), 106.30, 103.15, 60.28, 14.51 ppm. MS (EI): 240 (100), 285 (42.10). HRMS (EI) *m/z*: [M^+] Calcd for $C_{15}H_{12}N_3O_2F$: 285.0914; Found: 285.0913. Mp: 137.4~137.9 °C. IR (KBr): ν_{max} = 3399, 3118, 3085, 2982, 2953, 2902 cm^{-1}.

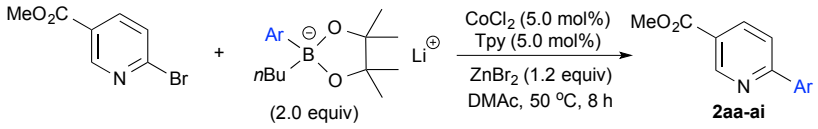


4-(4-Fluorophenyl)thieno[2,3-d]pyrimidine (2aa). The product was obtained via the general procedure conducted with 4-chlorothieno[2,3-d]pyrimidine (86 mg, 0.50 mmol, 1.0 equiv), 2,2′:6′,2″-terpyridine (5.83 mg, 0.0250 mmol, 0.0500 equiv), $CoCl_2$ (3.25 mg, 0.0250 mmol, 0.0500 equiv), zinc bromide (135 mg, 0.600 mmol, 1.20 equiv), lithium 4-fluorophenyl

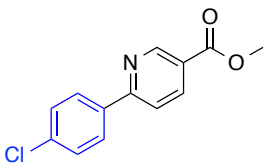
boronate (430 mg, 1.00 mmol, 2.00 equiv) and purified by column chromatography (petroleum ether : EtOAc = 3:1 to 1:1) as a white solid (103 mg, 89.0%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.12 (s, 1 H), 7.99 – 7.90 (m, 2 H), 7.62 – 7.49 (m, 2 H), 7.27 – 7.20 (m, 2 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.68 – -109.83 (m); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.86, 164.18 (d, J = 251.4 Hz), 159.72, 153.27, 133.82, 131.20 (d, J = 8.6 Hz), 127.66, 127.36, 120.67, 116.04 (d, J = 21.9 Hz) ppm. MS (EI): 229 (100), 230 (95.63). HRMS (EI) *m/z*: [M^+] Calcd for $C_{12}H_7N_2SF$: 230.0314; Found: 230.0319. Mp: 138.3~139.4 °C. IR (KBr): ν_{max} = 3106, 3084, 3045, 1919 cm^{-1}.

General procedure for cobalt-catalyzed cross-coupling of methyl 6-bromonicotinate with lithium (hetero)aryl boronate

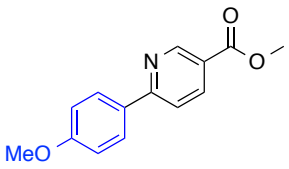


In an argon-filled glovebox, 6-bromonicontinic acid methyl ester (108 mg, 0.500 mmol, 1.00 equiv), 2,2′:6′,2″-terpyridine (5.83 mg, 0.0250 mmol, 0.0500 equiv), $CoCl_2$ (3.25 mg, 0.0250 mmol, 0.0500 equiv), zinc bromide (135 mg, 0.600 mmol, 1.20 equiv) and lithium (hetero)aryl boronate (1.0 mmol, 2.0 equiv) were placed into a 25 mL Schlenk tube. Anhydrous *N,N*-dimethylacetamide (DMAc, 5.0 mL) was added into the tube and the mixture was stirred at 50 °C for 8 h. The mixture solution was diluted with Et_2O (100 mL) then filtered through a short plug of silica gel and washed with H_2O (100 mL × 3). The organic layer was combined, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The crude was purified by column chromatography.



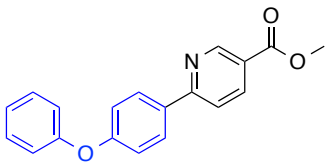
***6-(4-Chlorophenyl)nicotinate (2ab)*[17].** The product was obtained via the general procedure conducted with 6-bromonicontinic acid methyl ester (108 mg, 0.500 mmol, 1.00 equiv), 2,2′:6′,2″-terpyridine (5.83 mg, 0.0250 mmol, 0.0500 equiv), $CoCl_2$ (3.25 mg, 0.0250 mmol, 0.0500 equiv), zinc bromide (135 mg, 0.600 mmol, 1.20 equiv), lithium 4-chlorophenyl boronate (444 mg, 1.00 mmol, 2.00 equiv) and purified by column chromatography (petroleum ether : EtOAc = 20:1) as a white solid (85 mg, 69%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 (d, J = 2.2 Hz, 1 H), 8.31 (dd, J = 8.4, 2.2 Hz, 1 H), 7.98 (d, J = 8.5 Hz, 2 H), 7.75 (d, J = 8.3 Hz, 1 H), 7.44 (d, J = 8.6 Hz, 2 H), 3.95 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.70, 159.59, 150.98, 137.97, 136.65, 136.23, 129.09, 128.59, 124.43, 119.56, 52.37 ppm. MS (EI): 247 (100), 247 (100). HRMS (EI) *m/z*: [M^+] Calcd for $C_{13}H_{10}NO_2Cl$: 247.0400; Found: 247.0401. IR (KBr): ν_{max} = 3070, 3001, 2951, 2850 cm^{-1}.



***Methyl 6-(4-methoxyphenyl)nicotinate (2ac)*[17].** The product was obtained via the general procedure conducted with 6-bromonicontinic acid methyl ester (108 mg, 0.500 mmol, 1.00 equiv), 2,2′:6′,2″-terpyridine (5.83 mg, 0.0250 mmol, 0.0500 equiv), $CoCl_2$ (3.25 mg, 0.0250 mmol, 0.0500 equiv), zinc bromide (135 mg, 0.600 mmol, 1.20 equiv), lithium 4-methoxyphenyl boronate (440 mg, 1.00 mmol, 2.00 equiv) and purified by column chromatography (petroleum ether : EtOAc = 20:1 to 10:1) as a white solid (71 mg, 59%).

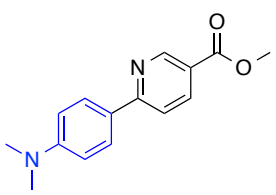
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (dd, *J* = 2.2, 0.9 Hz, 1 H), 8.26 (dd, *J* = 8.4, 2.3 Hz, 1 H), 8.04 – 7.97 (m, 2 H), 7.71 (dd, *J* = 8.4, 0.9 Hz, 1 H), 7.03 – 6.95 (m, 2 H), 3.93 (s, 3 H), 3.85 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.97, 161.29, 160.50, 150.90, 137.74, 130.80, 128.77, 123.42, 118.90, 114.28, 55.39, 52.25 ppm. MS (EI): 243 (100), 243 (100). HRMS (EI) *m/z*: [M^+] Calcd for $C_{14}H_{13}NO_3$: 243.0895; Found: 243.0892. IR (KBr): ν_{max} = 3066, 3005, 2950, 2843 cm^{-1}.



Methyl 6-(4-phenoxyphenyl)nicotinate (2ad). The product was obtained via the general procedure conducted with 6-bromonicontinic acid methyl ester (108 mg, 0.500 mmol, 1.00 equiv), 2,2′:6′,2″-terpyridine (5.83 mg, 0.0250 mmol, 0.0500 equiv), $CoCl_2$ (3.25 mg, 0.0250 mmol, 0.0500 equiv), zinc bromide (135 mg, 0.600 mmol, 1.20 equiv), lithium 4-phenoxyphenyl boronate (504 mg, 1.00 mmol, 2.00 equiv) and purified by column chromatography (petroleum ether : EtOAc = 10:1) as a yellow solid (77 mg, 51%).

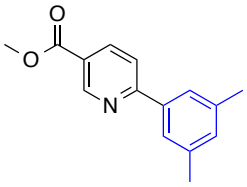
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 (d, *J* = 2.1 Hz, 1 H), 8.30 (dd, *J* = 8.4, 2.2 Hz, 1 H), 8.07 – 7.99 (m, 2 H), 7.74 (d, *J* = 8.4 Hz, 1 H), 7.41 – 7.30 (m, 2 H), 7.14 (t, *J* = 7.4 Hz, 1 H), 7.08 (d, *J* = 8.9 Hz, 2 H), 7.07 – 7.04 (m, 2 H), 3.95 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.89, 160.24, 159.30, 156.47, 150.95, 137.86, 133.04, 129.89, 128.97, 123.88, 123.81, 119.48, 119.26, 118.64, 52.32 ppm. MS (EI): 305 (100),304 (6.61).

HRMS (EI) *m/z*: [M^+] Calcd for $C_{19}H_{15}NO_3$: 305.1052; Found: 305.1047. Mp: 153.8~155.6 °C. IR (KBr): ν_{max} = 3067, 2996, 2947, 1718 cm^{-1}.



Methyl 6-(4-(dimethylamino)phenyl)nicotinate (2ae). The product was obtained via the general procedure conducted with 6-bromonicontinic acid methyl ester (108 mg, 0.500 mmol, 1.00 equiv), 2,2′:6′,2″-terpyridine (5.83 mg, 0.0250 mmol, 0.0500 equiv), $CoCl_2$ (3.25 mg, 0.0250 mmol, 0.0500 equiv), zinc bromide (135 mg, 0.600 mmol, 1.20 equiv), lithium *N*,*N*-dimethylphenyl boronate (455 mg ,1.00 mmol, 2.00 equiv) and purified by column chromatography (petroleum ether : EtOAc = 10:1) as a yellow solid (76 mg, 59%).

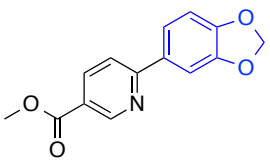
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.17 (dd, *J* = 2.3, 0.9 Hz, 1 H), 8.21 (dd, *J* = 8.4, 2.3 Hz, 1 H), 8.00 – 7.94 (m, 2 H), 7.67 (dd, *J* = 8.4, 0.9 Hz, 1 H), 6.78 – 6.73 (m, 2 H), 3.92 (s, 3 H), 3.02 (s, 6 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.20, 160.98, 151.68, 150.91, 137.46, 128.40, 125.68, 122.38, 117.99, 112.01, 52.12, 40.22 ppm. MS (EI): 256 (100), 255 (77.07). HRMS (EI) *m/z*: [M^+] Calcd for $C_{15}H_{16}N_2O_2$: 256.1212; Found: 256.1205. Mp: 178.1~178.9 °C. IR (KBr): ν_{max} = 3853, 3735, 3649, 2945, 2890, 2810, 1712 cm^{-1}.



Methyl 6-(3,5-dimethylphenyl)nicotinate (2af). The product was obtained via the general procedure conducted with 6-bromonicontinic acid methyl ester (108 mg, 0.500 mmol, 1.00 equiv), 2,2′:6′,2″-terpyridine (5.83 mg, 0.0250 mmol, 0.0500 equiv), $CoCl_2$ (3.25 mg, 0.0250 mmol, 0.0500 equiv), zinc bromide (135 mg, 0.600 mmol, 1.20 equiv), lithium 2-(3,5-dimethylphenyl) boronate (438 mg ,1.00 mmol, 2.00 equiv) and purified by column chromatography (petroleum ether : EtOAc = 30:1) as a white solid (78 mg, 65%).

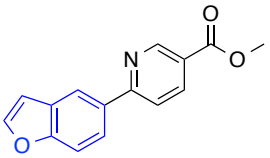
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 (d, *J* = 2.2 Hz, 1 H), 8.28 (dd, *J* = 8.3, 2.2 Hz, 1 H), 7.75 (d, *J* = 8.3 Hz, 1 H), 7.63 (s, 2 H), 7.08 (s, 1 H), 3.94 (s, 3 H), 2.38 (s, 6 H); ^{13}C

NMR (101 MHz, $CDCl_3$) δ 165.88, 161.26, 150.83, 138.46, 138.22, 137.73, 131.64, 125.19, 124.01, 119.92, 52.27, 21.36 ppm. MS (EI): 241 (100), 241 (100). HRMS (EI) *m/z*: [M^+] Calcd for $C_{15}H_{15}NO_2$: 241.1103; Found: 241.1095. Mp: 65.2~66.7 °C. IR (KBr): ν_{max} = 3414, 3012, 2957, 2919 cm^{-1}.



Methyl 6-(benzo[d][1,3]dioxol-5-yl)nicotinate (2ag). The product was obtained via the general procedure conducted with 6-bromonicontinic acid methyl ester (108 mg, 0.500 mmol, 1.00 equiv), 2,2′:6′,2″-terpyridine (5.83 mg, 0.0250 mmol, 0.0500 equiv), $CoCl_2$ (3.25 mg, 0.0250 mmol, 0.0500 equiv), zinc bromide (135 mg, 0.600 mmol, 1.20 equiv), lithium 3,4-methylenedioxyphenyl boronate (454 mg, 1.00 mmol, 2.00 equiv) and purified by column chromatography (petroleum ether : EtOAc = 20:1) as a white solid (93 mg, 73%).

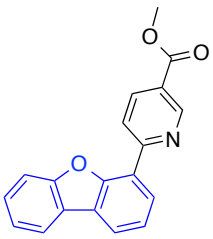
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 – 9.15 (m, 1 H), 8.27 (dd, *J* = 8.4, 2.2 Hz, 1 H), 7.73 – 7.64 (m, 1 H), 7.61 – 7.53 (m, 2 H), 6.94 – 6.86 (m, 1 H), 6.01 (s, 2 H), 3.94 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.88, 160.28, 150.84, 149.35, 148.46, 137.77, 132.67, 123.68, 121.79, 119.10, 108.55, 107.62, 101.50, 52.27 ppm. MS (EI): 257 (100), 257 (100). HRMS (EI) *m/z*: [M^+] Calcd for $C_{14}H_{11}NO_4$: 257.0688; Found: 257.0684. Mp: 146.9~147.6 °C. IR (KBr): ν_{max} = 3011, 2958, 2906, 2788, 1726 cm^{-1}.



Methyl 6-(benzofuran-5-yl)nicotinate (2ah). The product was obtained via the general procedure conducted with 6-bromonicontinic acid methyl ester (108 mg, 0.500 mmol, 1.00 equiv), 2,2′:6′,2″-terpyridine (5.83 mg, 0.0250 mmol, 0.0500 equiv), $CoCl_2$ (3.25 mg, 0.0250 mmol, 0.0500 equiv), zinc bromide (135 mg, 0.600 mmol, 1.20 equiv), lithium 2-benzofuran-6-yl boronate (452mg, 1.00 mmol, 2.00 equiv) and purified by column chromatography (petroleum ether : EtOAc = 10:1) as a yellow solid (43 mg, 34%).

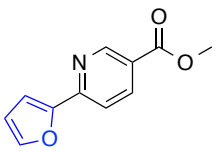
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.26 (dd, *J* = 2.3, 0.9 Hz, 1 H), 8.39 – 8.29 (m, 2 H), 7.99 (dd, *J* = 8.7, 1.9 Hz, 1 H), 7.82 (dd, *J* = 8.3, 0.9 Hz, 1 H), 7.66 (d, *J* = 2.2 Hz, 1

H), 7.58 (dt, *J* = 8.7, 0.8 Hz, 1 H), 6.83 (dd, *J* = 2.3, 1.0 Hz, 1 H), 3.95 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.95, 161.26, 156.07, 150.92, 145.96, 137.88, 133.47, 128.11, 123.98, 123.80, 120.65, 119.80, 111.75, 107.07, 52.32 ppm. MS (EI): 253 (100), 253 (100). HRMS (EI) *m/z*: [M^+] Calcd for $C_{15}H_{11}NO_3$: 253.0739; Found: 253.0744. Mp: 132.8~134.5 °C. IR (KBr): ν_{max} = 3147, 3118, 3006, 2956, 1722 cm^{-1}.



Methyl 6-(dibenzo[b,d]furan-4-yl)nicotinate (2ai). The product was obtained via the general procedure conducted with 6-bromonicontinic acid methyl ester (108 mg, 0.500 mmol, 1.00 equiv), 2,2′:6′,2″-terpyridine (5.83 mg, 0.0250 mmol, 0.0500 equiv), $CoCl_2$ (3.25 mg, 0.0250 mmol, 0.0500 equiv), zinc bromide (135 mg, 0.600 mmol, 1.20 equiv), lithium 2-(dibenzo[b,d]furan-4-yl) boronate (520 mg, 1.00 mmol, 2.00 equiv) and purified by column chromatography (petroleum ether : EtOAc = 10:1) as a white solid (93 mg, 62%).

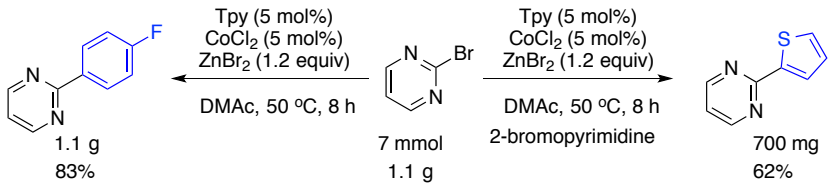
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.33 (dd, *J* = 2.2, 0.9 Hz, 1 H), 8.51 (dd, *J* = 8.3, 0.9 Hz, 1 H), 8.42 (dd, *J* = 8.3, 2.2 Hz, 1 H), 8.36 (dd, *J* = 7.7, 1.3 Hz, 1 H), 8.00 (dd, *J* = 7.6, 1.3 Hz, 1 H), 7.98 – 7.92 (m, 1 H), 7.62 (dt, *J* = 8.3, 0.9 Hz, 1 H), 7.50 – 7.44 (m, 2 H), 7.36 (td, *J* = 7.5, 1.0 Hz, 1 H), 3.97 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.86, 157.24, 156.00, 153.85, 150.80, 137.76, 127.64, 127.46, 125.34, 124.28, 123.76, 123.52, 123.33, 123.14, 123.08, 122.27, 120.70, 111.80, 52.37 ppm. MS (EI): 303 (100), 303 (100). HRMS (EI) *m/z*: [M^+] Calcd for $C_{19}H_{13}NO_3$: 303.0895; Found: 303.0890. Mp: 158.9~159.6 °C. IR (KBr): ν_{max} = 2956, 1904 cm^{-1}.



Methyl 6-(furan-2-yl)nicotinate (2aj). The product was obtained via the general procedure conducted with 6-bromonicontinic acid methyl ester (108 mg, 0.500 mmol, 1.00 equiv), 2,2′:6′,2″-terpyridine (5.83 mg, 0.0250 mmol, 0.0500 equiv), $CoCl_2$ (3.25 mg, 0.0250 mmol, 0.0500 equiv), zinc bromide (135 mg, 0.600 mmol, 1.20 equiv), lithium 2-furanyl boronate (402 mg, 1.00 mmol, 2.00 equiv) and purified by column chromatography (petroleum ether : EtOAc = 20:1 to 10:1) as a white solid (57 mg, 56%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.14 (dd, *J* = 2.2, 0.9 Hz, 1 H), 8.27 (dd, *J* = 8.3, 2.2 Hz, 1 H), 7.71 (dd, *J* = 8.4, 0.9 Hz, 1 H), 7.56 (dd, *J* = 1.8, 0.8 Hz, 1 H), 7.17 (dd, *J* = 3.4, 0.9 Hz, 1 H), 6.54 (dd, *J* = 3.4, 1.8 Hz, 1 H), 3.92 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.64, 152.91, 152.33, 151.04, 144.48, 137.80, 123.71, 117.74, 112.51, 111.13, 52.30 ppm. MS (EI): 203 (100), 203 (100). HRMS (EI) *m/z*: [M^+] Calcd for $C_{11}H_9NO_3$: 203.0582; Found: 203.0585. Mp: 102.5~102.9 °C. IR (KBr): ν_{max} = 3142, 3121, 2953, 1716 cm^{-1}.

Gram scale reactions



A. In an argon-filled glove box, 2-bromopyrimidine (1.1 g, 7.0 mmol, 1.0 equiv), 2,2′:6′,2″-terpyridine (81.5 mg, 0.350 mmol, 0.0500 equiv), $CoCl_2$ (45.5 mg, 0.350 mmol, 0.0500 equiv), zinc bromide (1.9 g, 8.4 mmol, 1.2 equiv) and lithium 4-fluorophenyl boronate (6.0 g, 14 mmol, 2.0 equiv) were placed into a 50 mL Schlenk tube. Anhydrous *N,N*-dimethylacetamide (DMAc, 25 mL) was added into the tube and the mixture was stirred at 50 °C for 8 h. The mixture solution was diluted with Et_2O (500 mL). The mixture solution was diluted with Et_2O (100 mL) then filtered through a short plug of silica gel and washed with H_2O (200 mL × 3). The organic layer was combined, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The crude was purified by column chromatography on silica gel with ethyl acetate/ petroleum ether = 1/20 to give compound **2i** as a white solid (1.1 g, 83%).

B. In an argon-filled glove box, 2-bromopyrimidine (1.1 g, 7.0 mmol, 1.0 equiv), 2,2′:6′,2″-terpyridine (81.5 mg, 0.350 mmol, 0.0500 equiv), $CoCl_2$ (45.5 mg, 0.350 mmol, 0.0500 equiv), zinc bromide (1.9 g, 8.4 mmol, 1.2 equiv) and lithium thiophene-2-yl boronate (5.9 g, 14 mmol, 2.0 equiv) were placed into a 50 mL Schlenk tube. Anhydrous *N,N*-dimethylacetamide (DMAc, 25 mL) was added into the tube and the mixture was stirred at 50 °C for 8 h. The mixture solution was diluted with Et_2O (200 mL) then filtered through a short plug of silica gel and washed with H_2O (100 mL × 3). The organic layer was combined, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The crude was purified by column chromatography on silica gel with ethyl acetate/ petroleum ether = 1/20 to give compound **2ak** as a white solid (700 mg, 62%).[7]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 4.9 Hz, 2 H), 8.00 (dd, *J* = 3.7, 1.2 Hz, 1 H), 7.48 (dd, *J* = 5.1, 1.2 Hz, 1 H), 7.15 (dd, *J* = 5.0, 3.7 Hz, 1 H), 7.09 (t, *J* = 4.9 Hz, 1 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.53, 157.18, 143.15, 129.87, 128.96, 128.28, 118.45 ppm. MS(EI): 162 (100). HRMS (EI) *m/z*: [M^+] Calcd for $C_8H_6N_2S$: 162.0252; Found: 162.0256. IR (KBr): ν_{max} = 3070, 1995 cm^{-1}.

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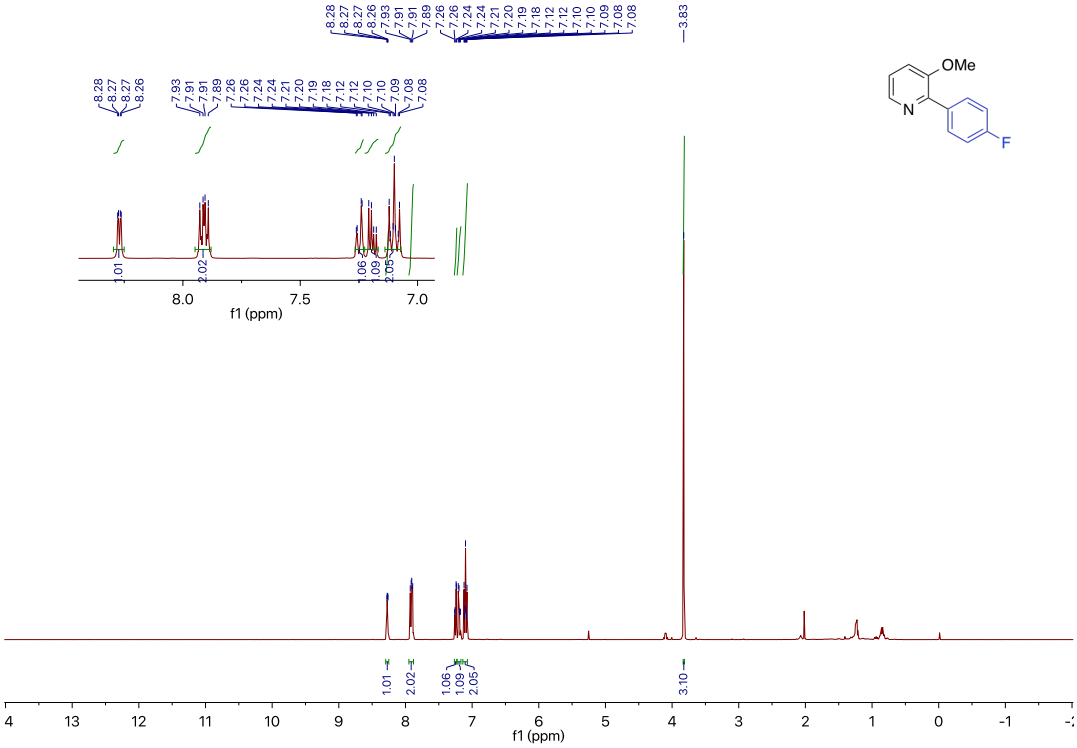
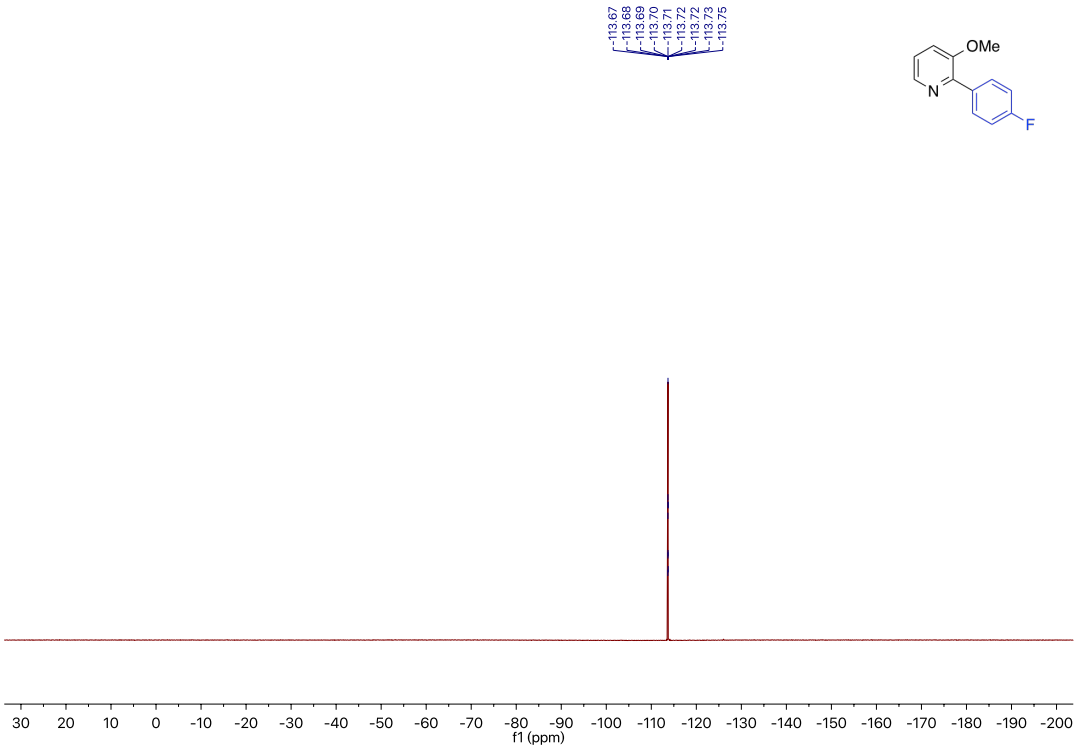
Copies of ^{1}H, ^{19}F and ^{13}C NMR spectra of 2a~2ak

^{1}H spectrum of 2-(4-Fluorophenyl)-3-methoxypyridine **2a** (400 MHz, $CDCl_3$)



^{19}F spectrum of 2-(4-Fluorophenyl)-3-methoxypyridine **2a** (376 MHz, $CDCl_3$)



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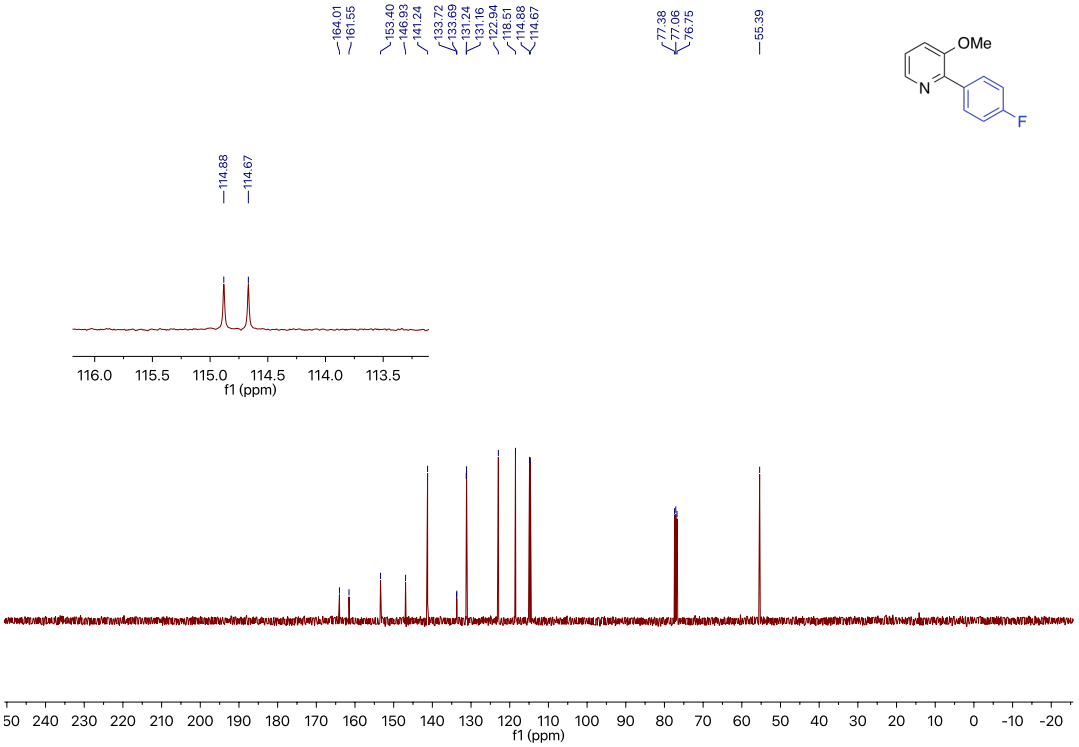
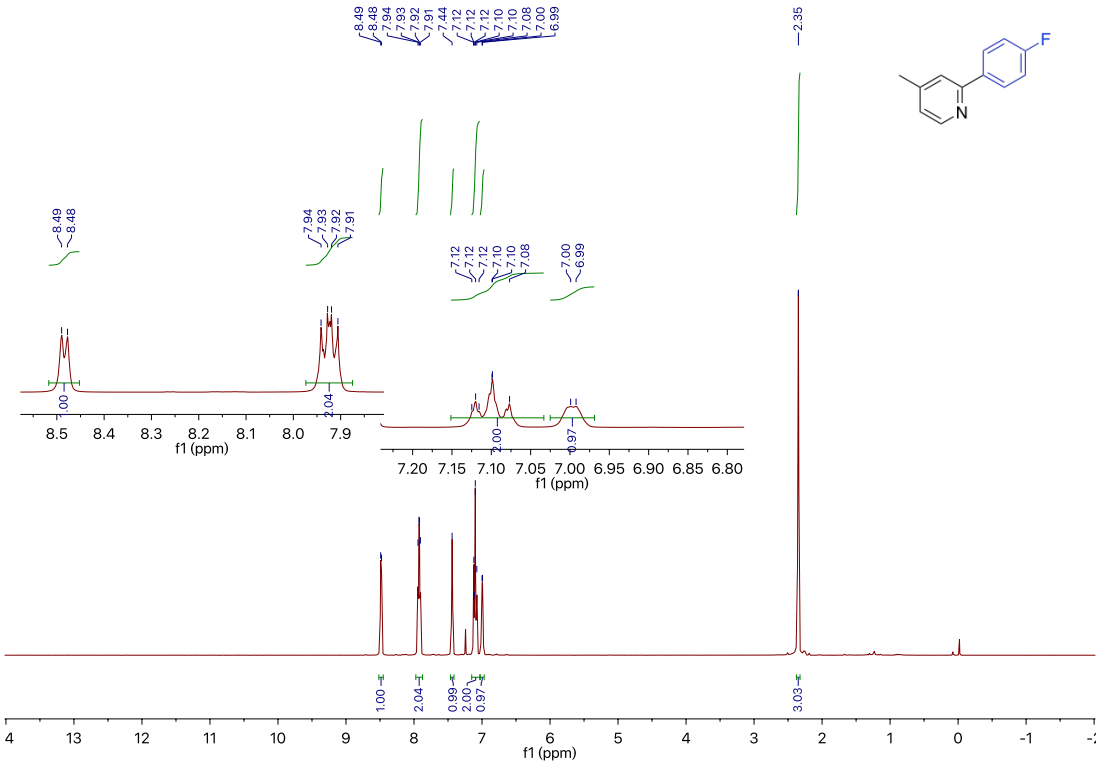


^{1}H spectrum of 2-(4-fluorophenyl)-4-methylpyridine **2b** (400 MHz, $CDCl_3$)



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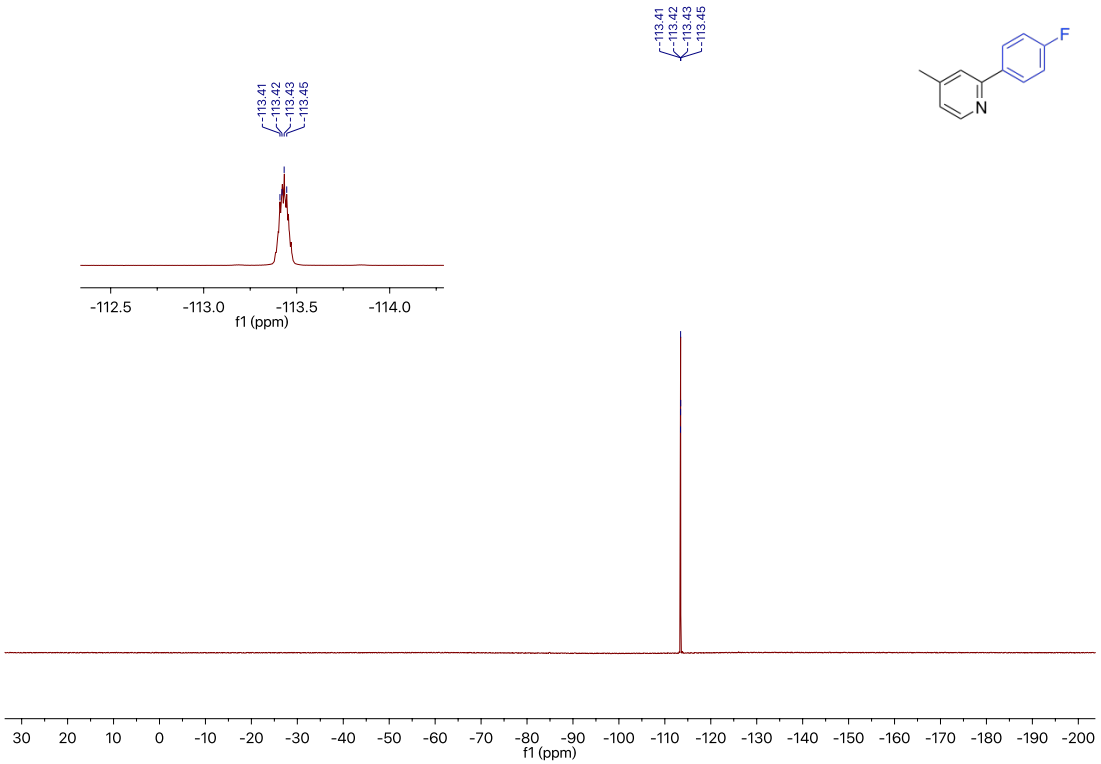

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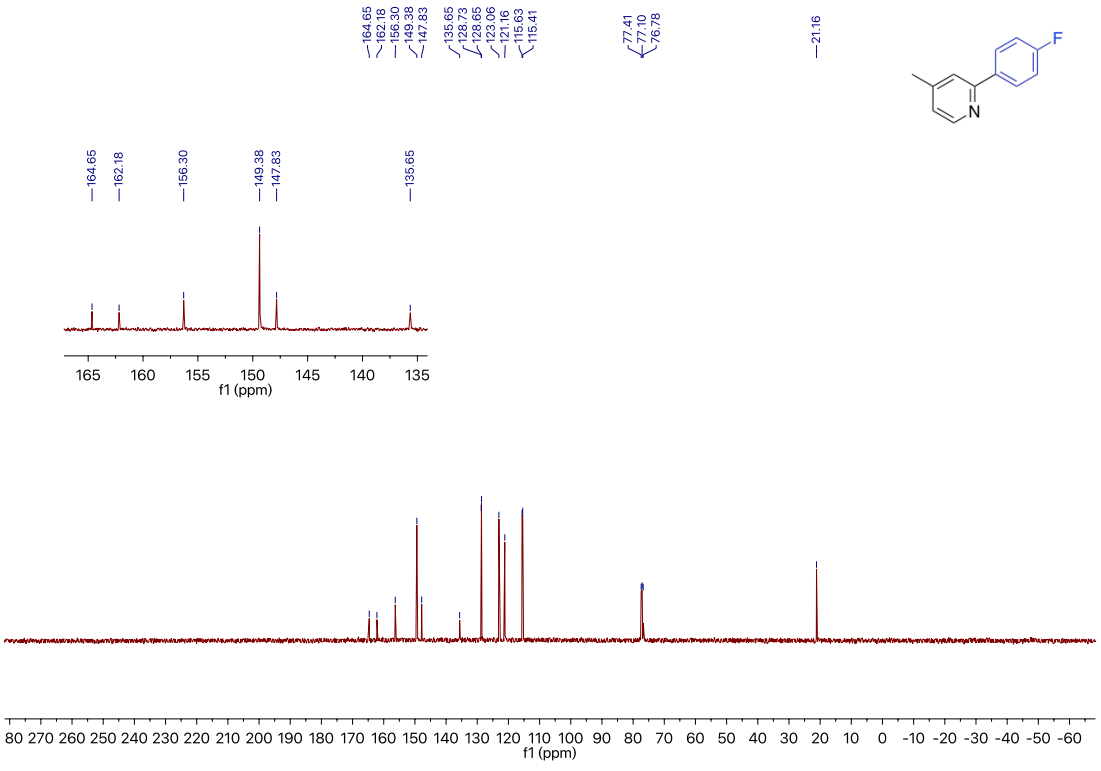
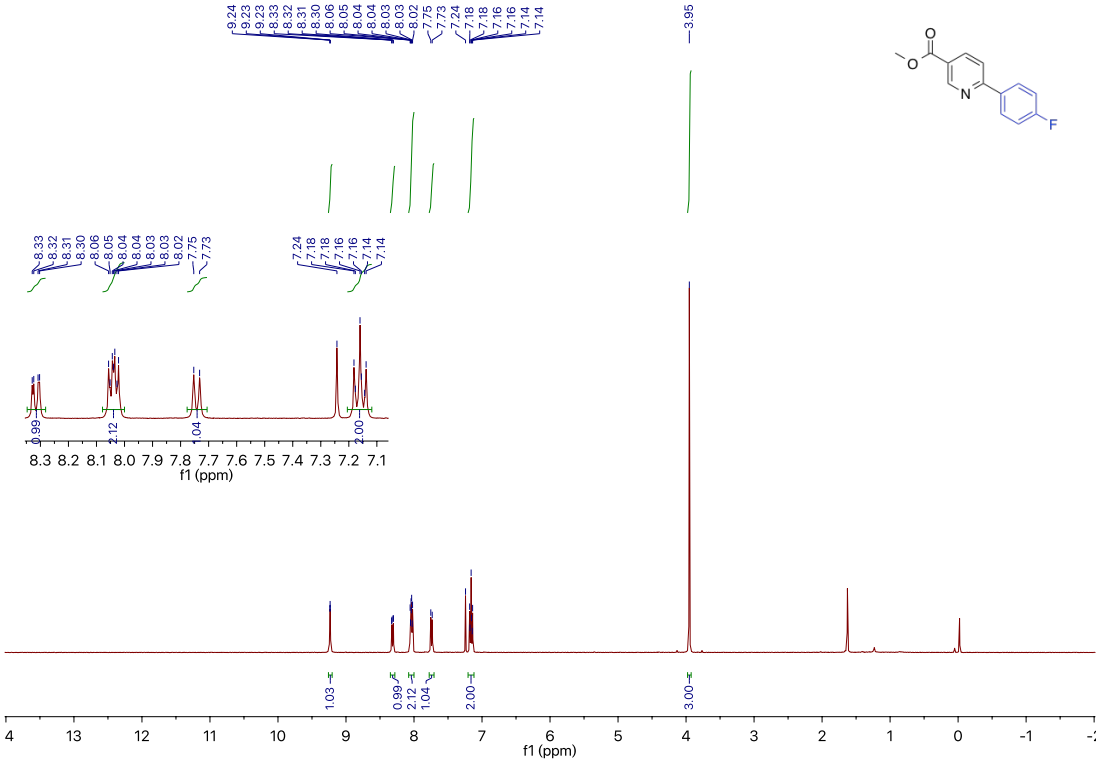


^{1}H spectrum of Methyl 6-(4-fluorophenyl)nicotinate **2c, 2q** (400 MHz, $CDCl_3$)



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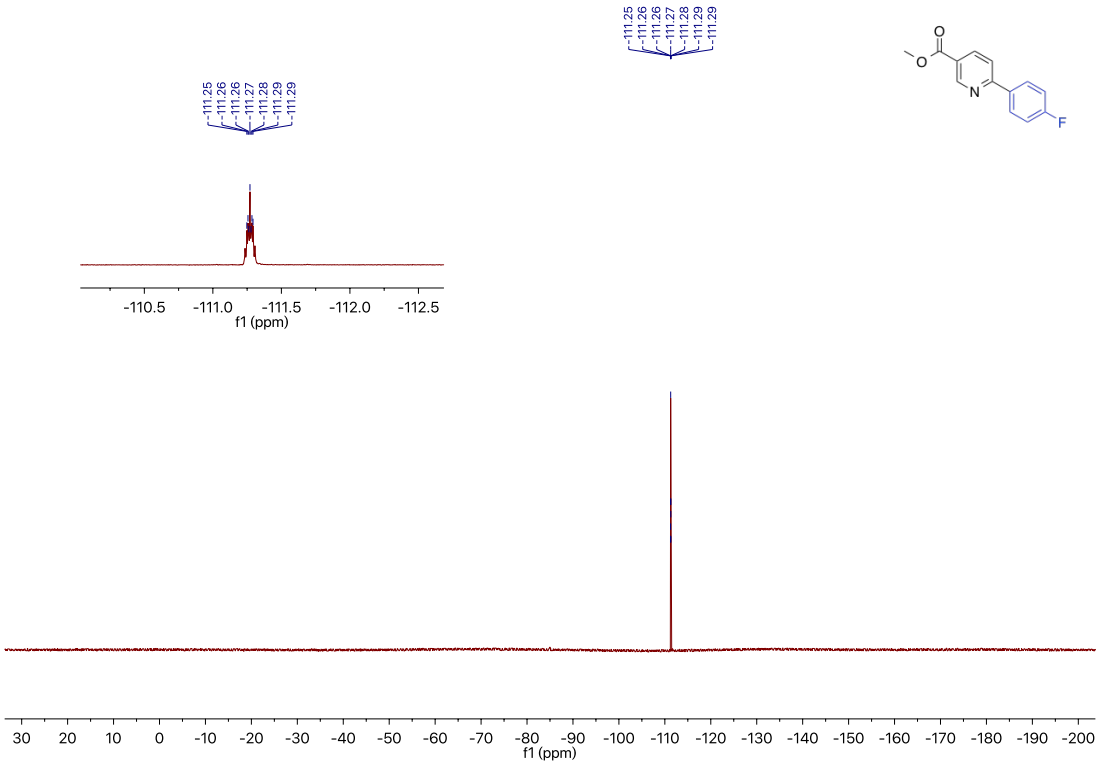

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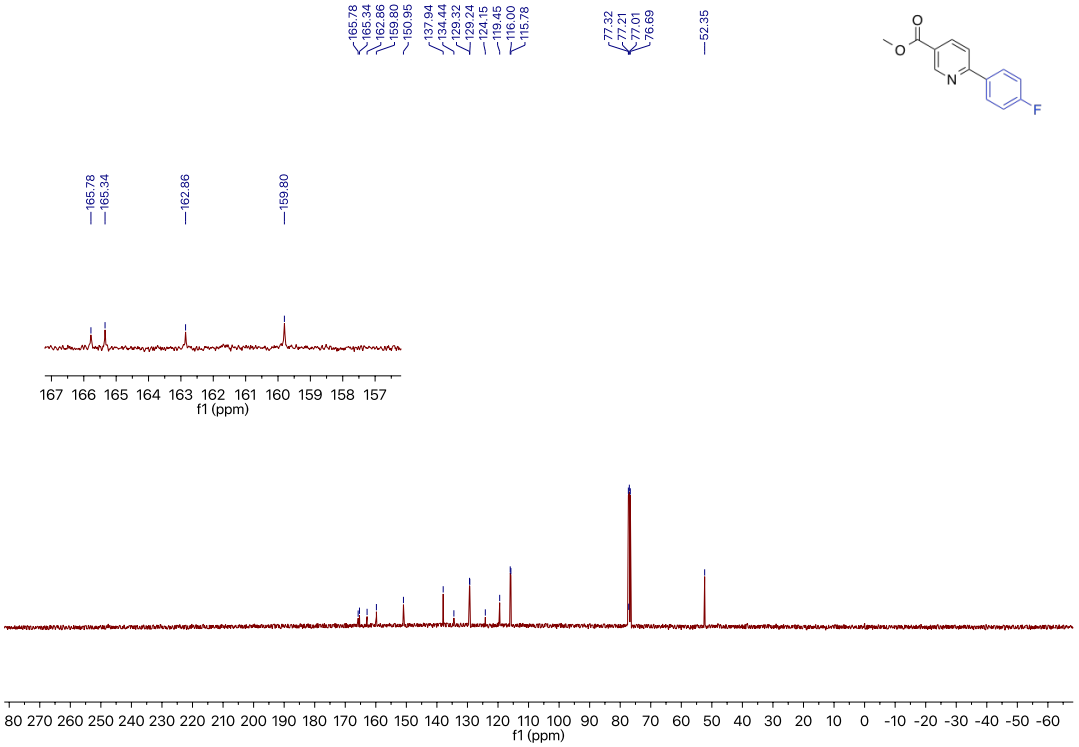
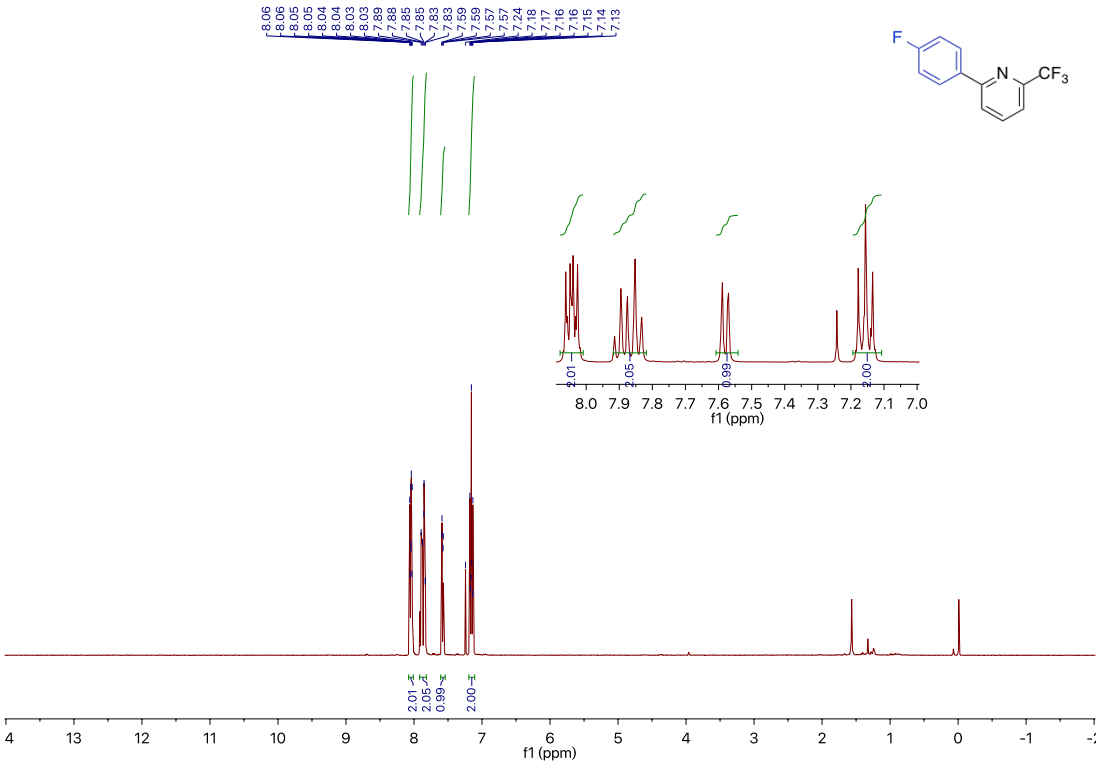


^{1}H spectrum of 2-(4-fluorophenyl)-6-(trifluoromethyl)pyridine **2d** (400 MHz, $CDCl_3$)



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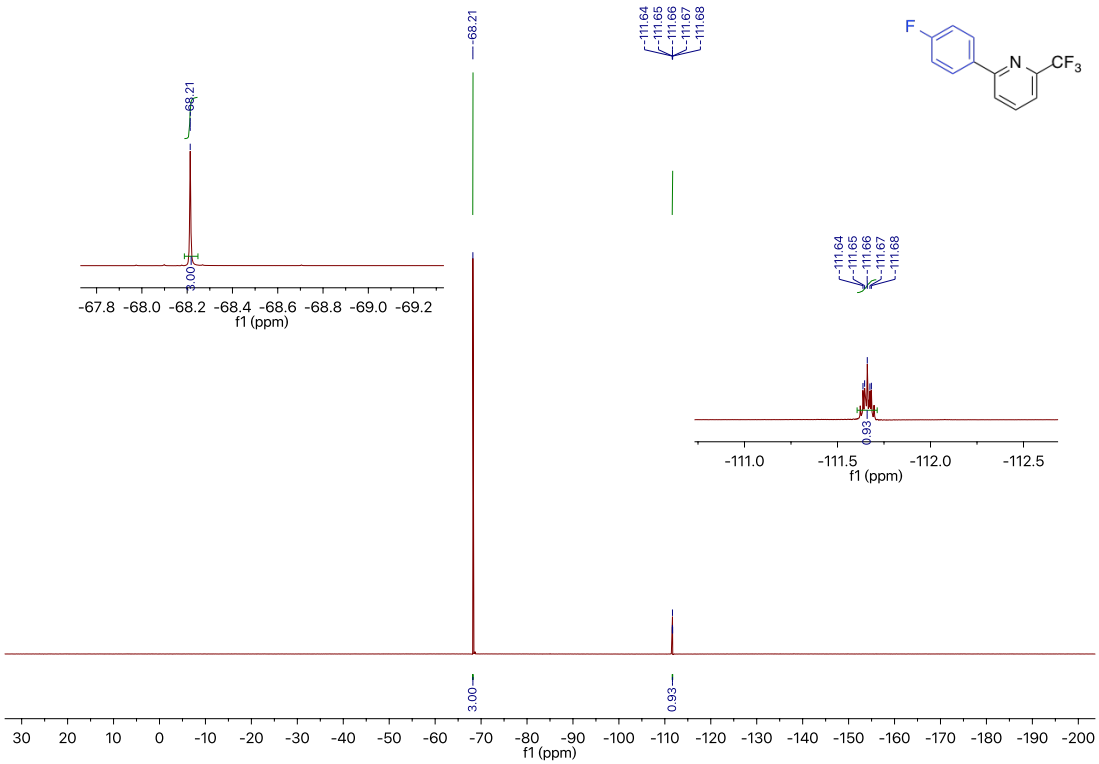

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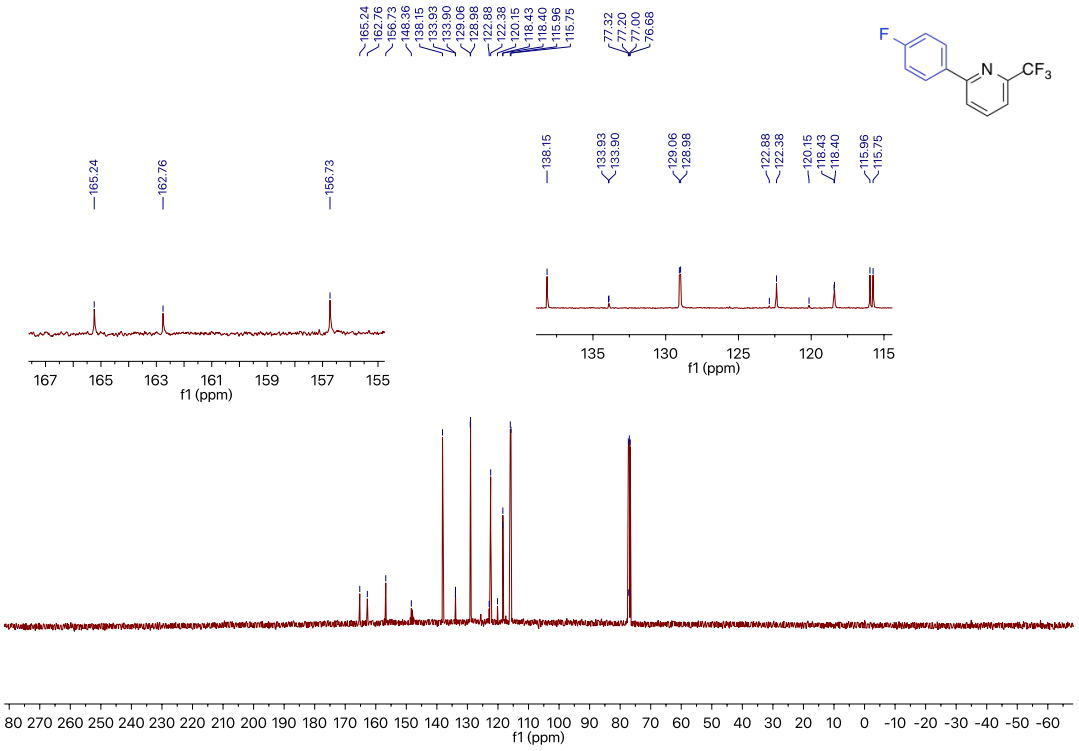
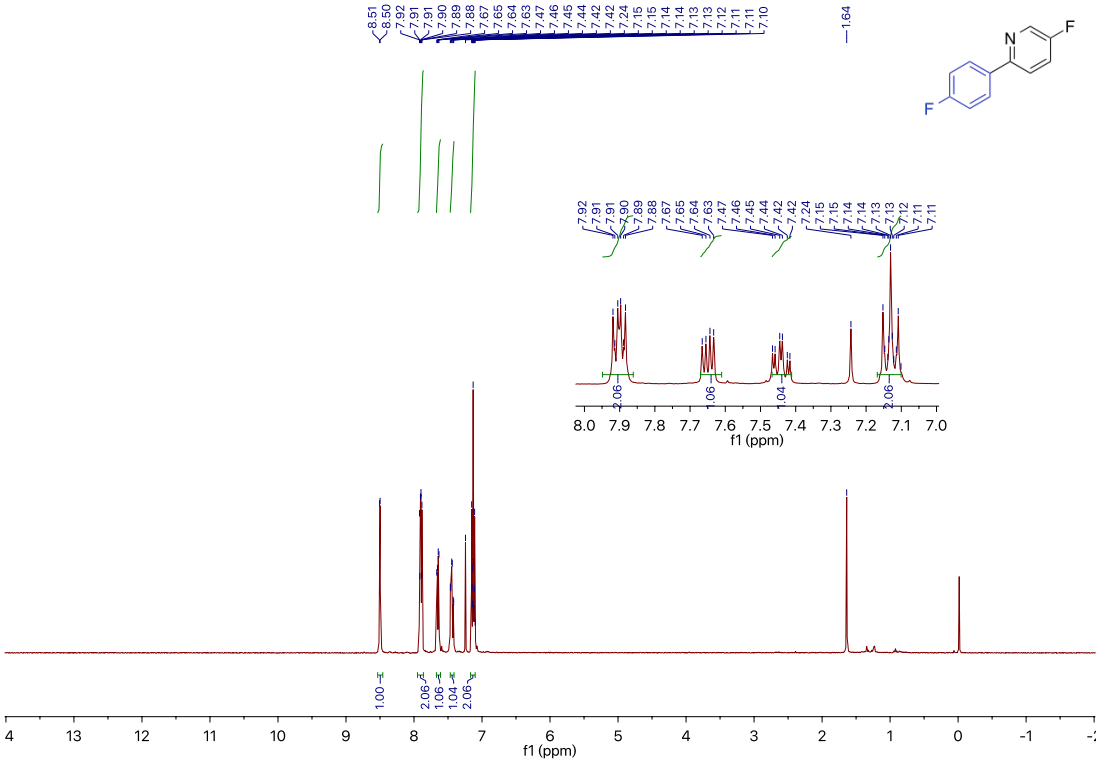


^{1}H spectrum of 2-(4-fluorophenyl)-5-fluoropyridine **2e, 2r** (400 MHz, $CDCl_3$)



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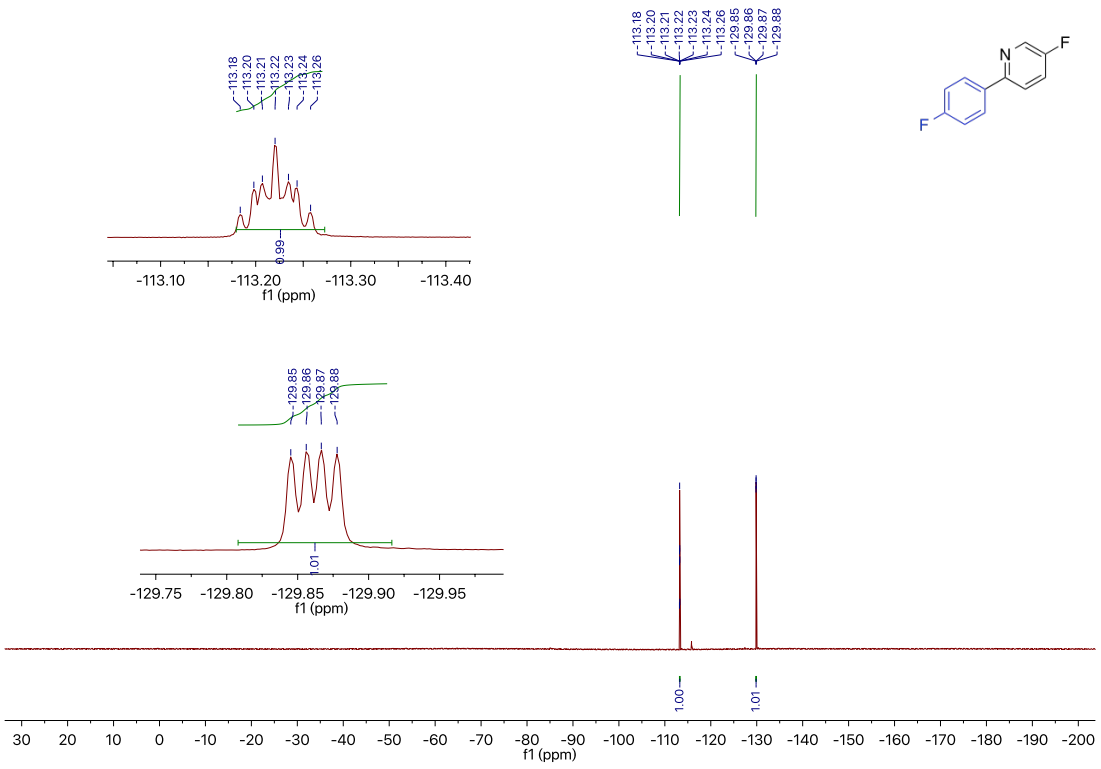

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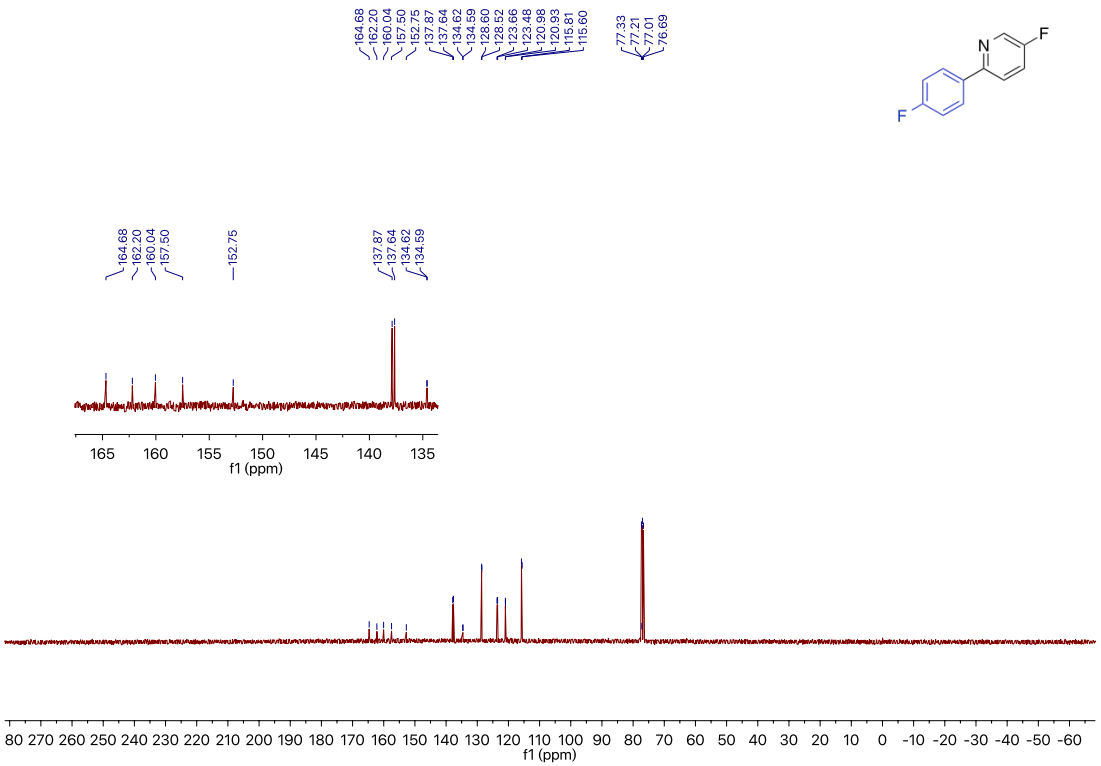
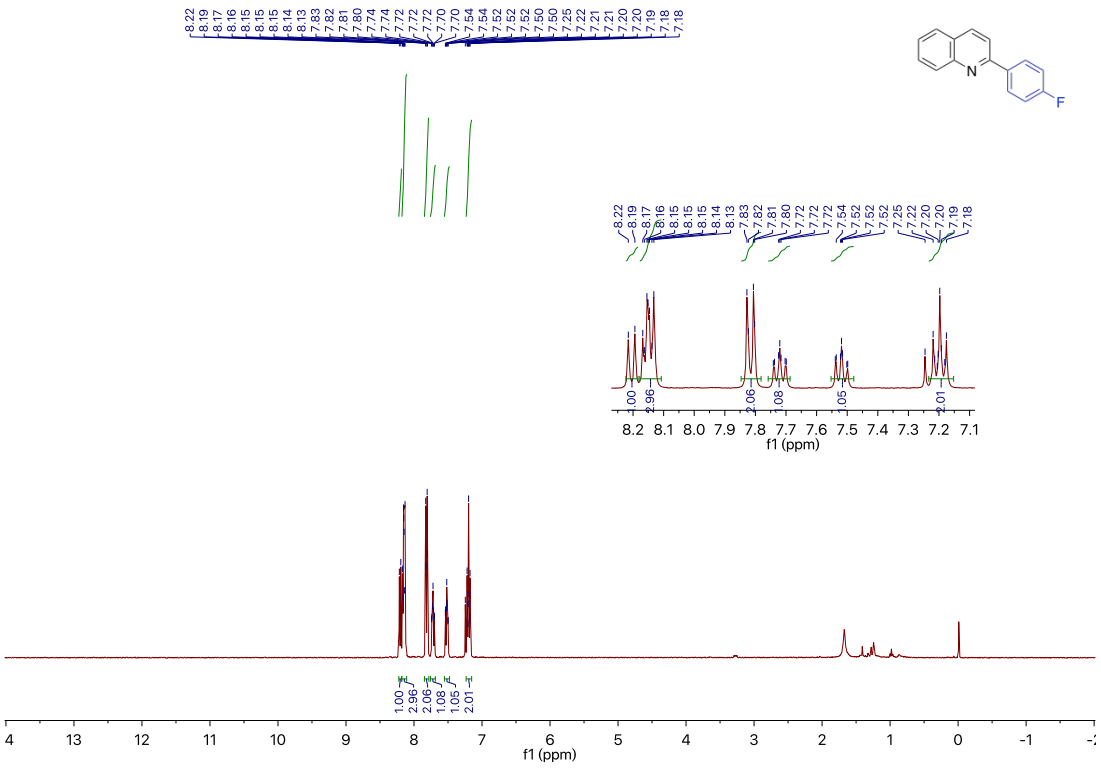


^{1}H spectrum of 2-(4-fluorophenyl)quinolone **2f, 2u** (400 MHz, $CDCl_3$)



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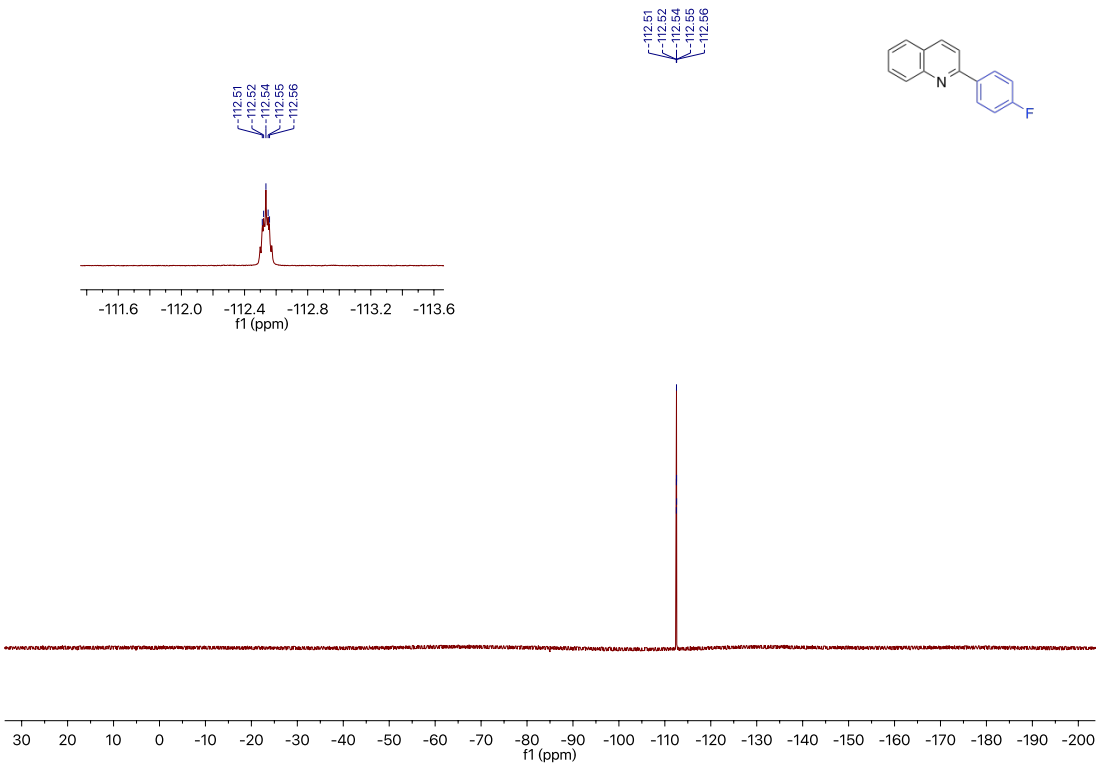

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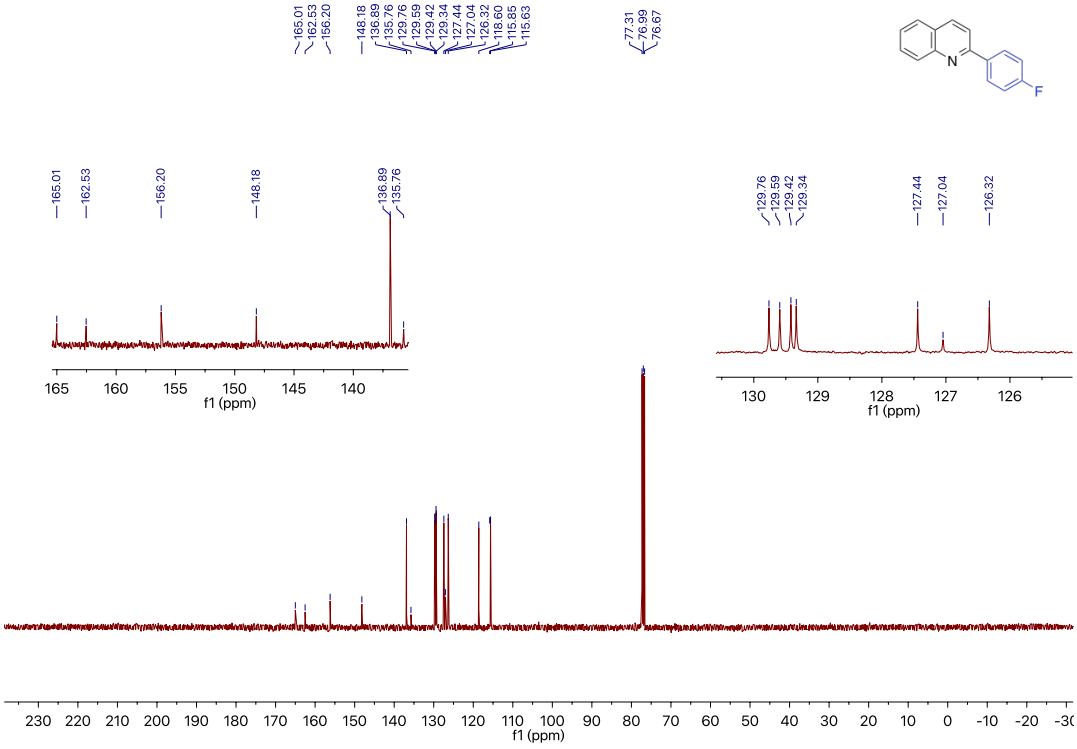
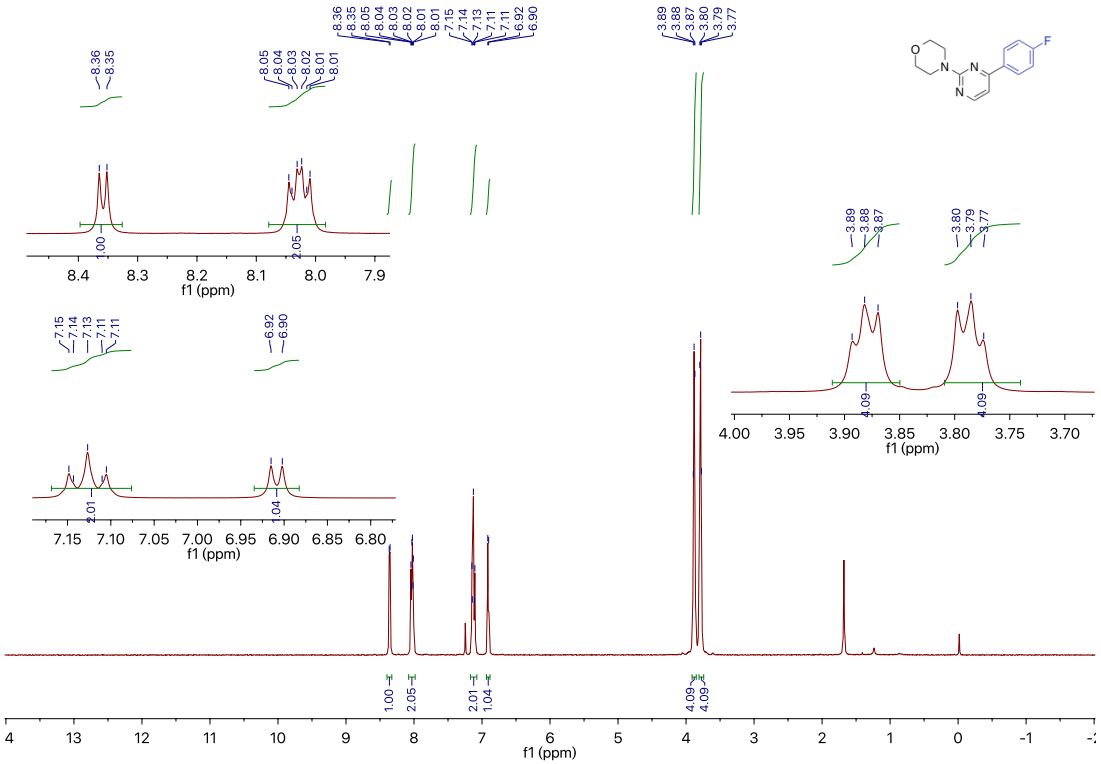
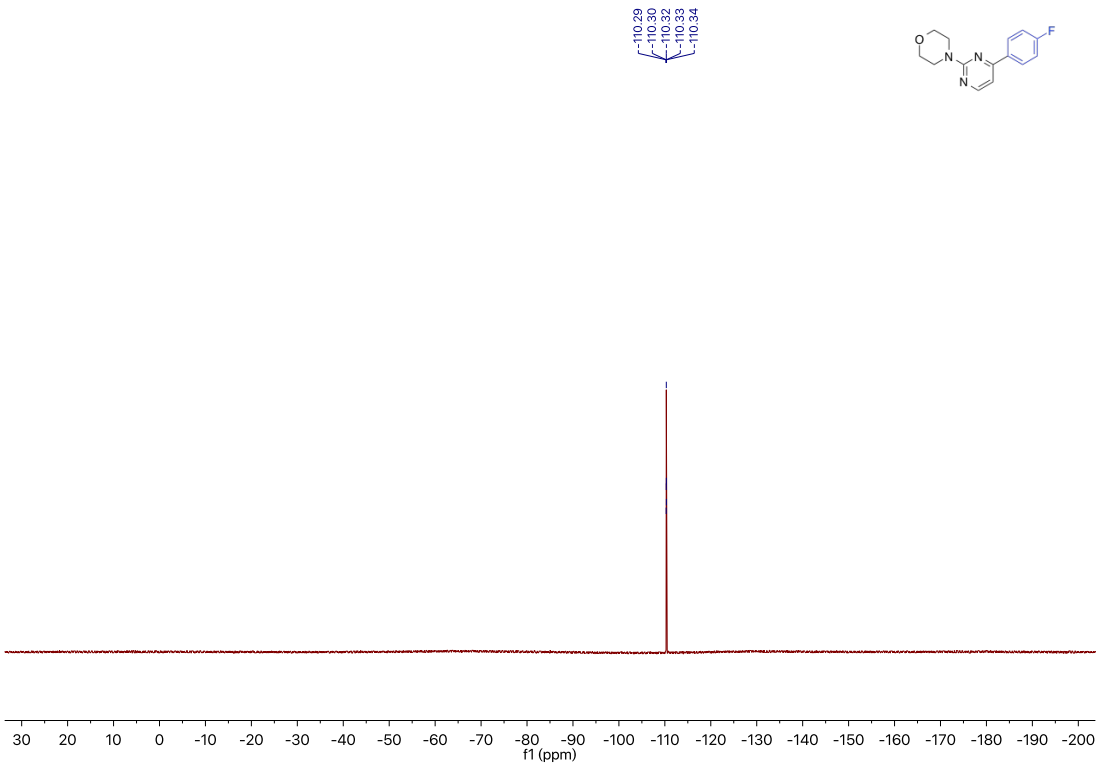


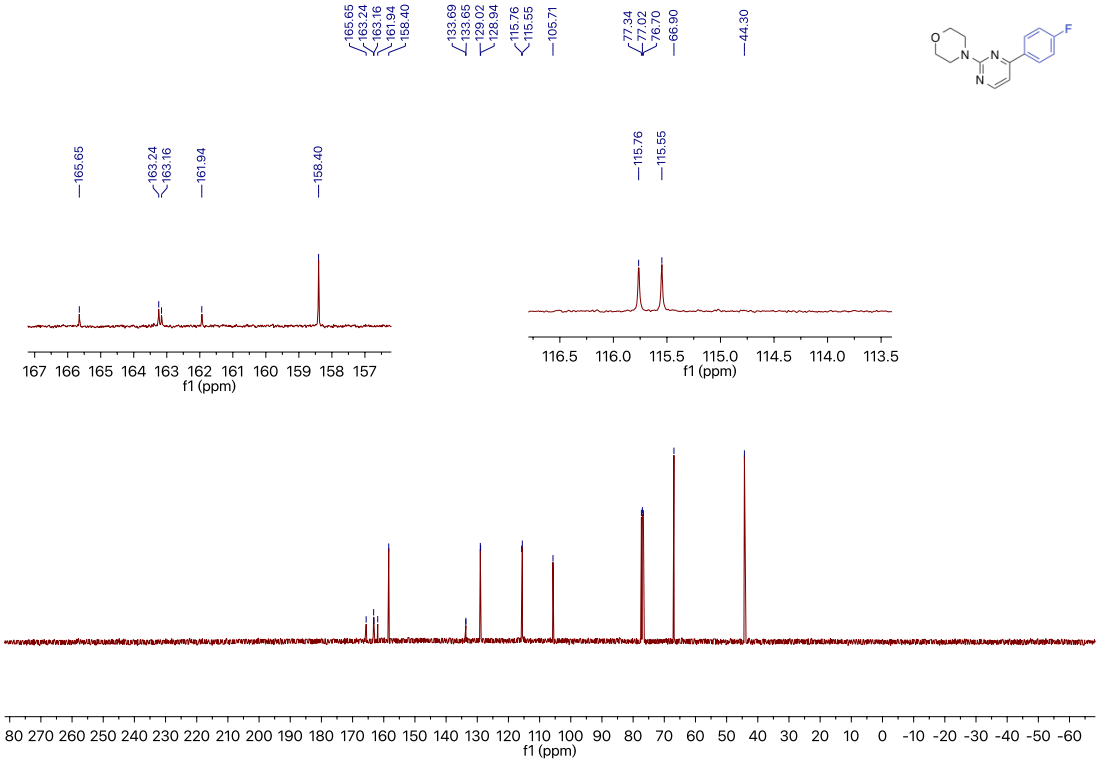
^{1}H spectrum of 4-(4-(4-fluorophenyl)pyrimidin-2-yl)morpholine **2g** (400 MHz, $CDCl_3$)



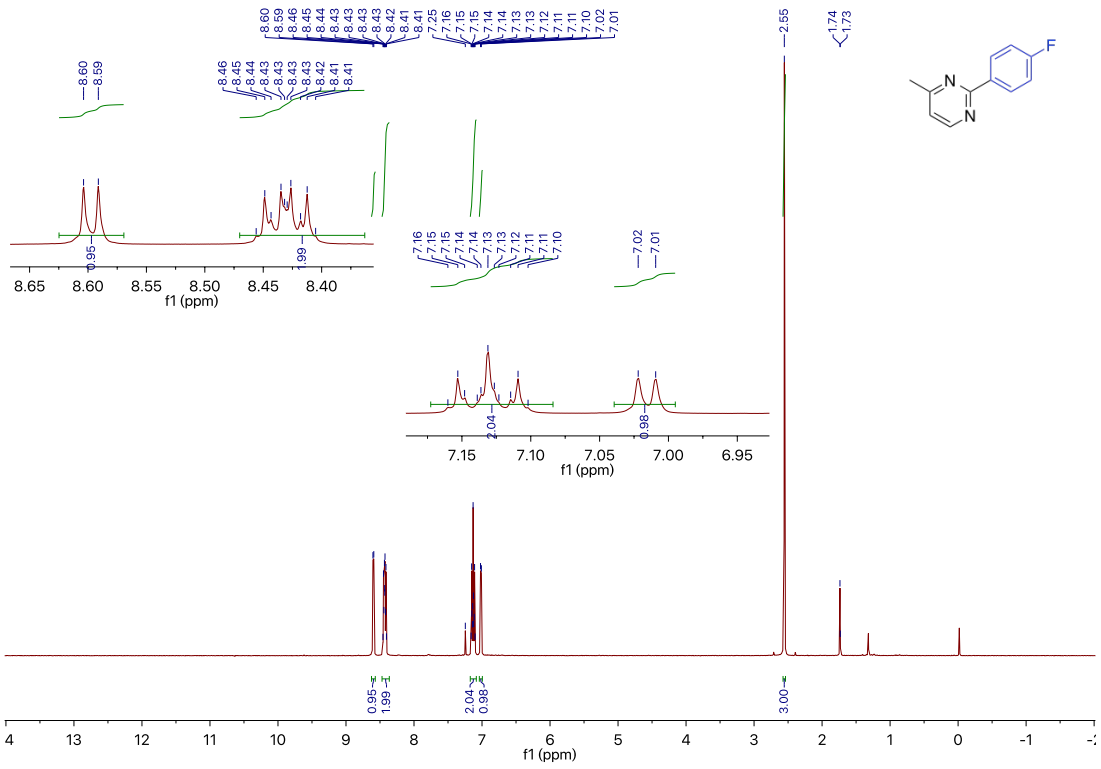
^{19}F spectrum of 4-(4-(4-fluorophenyl)pyrimidin-2-yl)morpholine **2g** (376 MHz, $CDCl_3$)



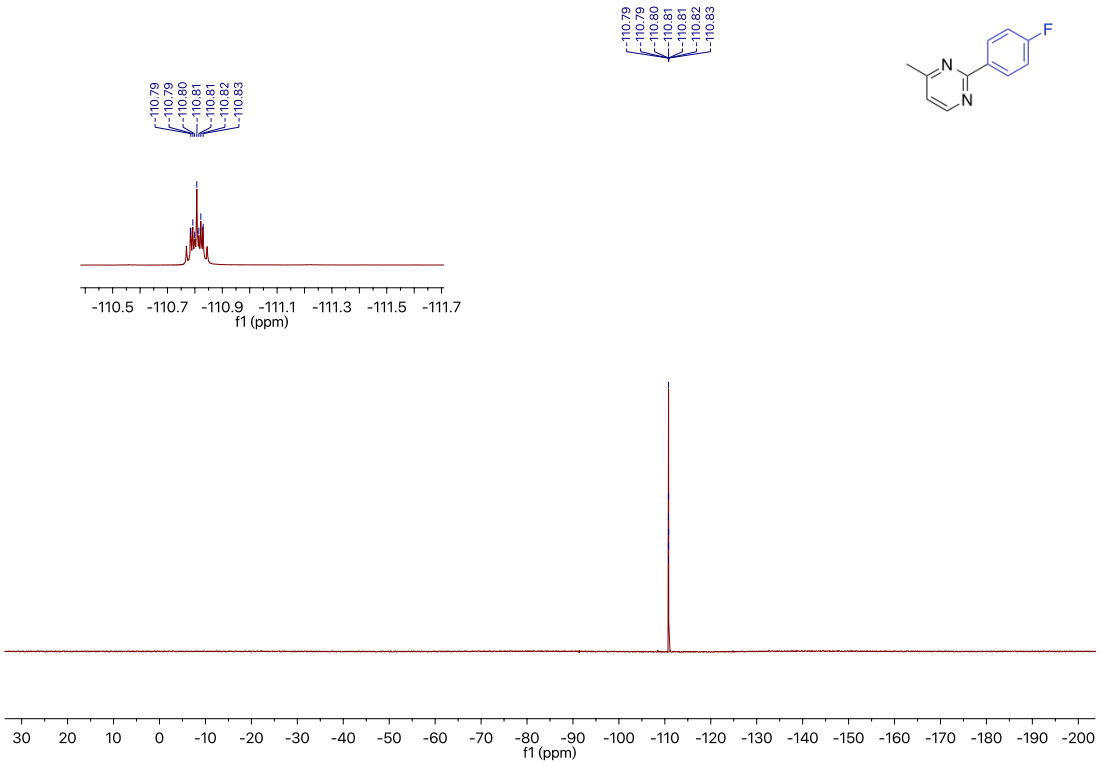
^{13}C spectrum of 4-(4-(4-fluorophenyl)pyrimidin-2-yl)morpholine **2g** (101 MHz, $CDCl_3$)



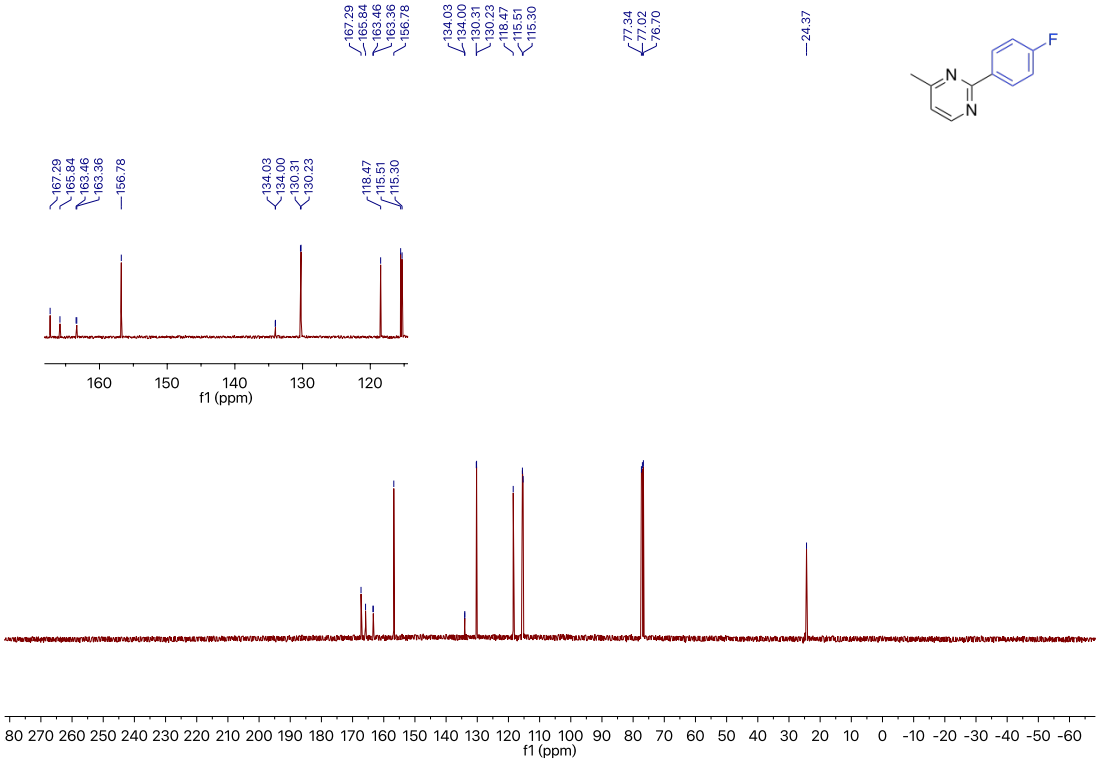
^{1}H spectrum of 2-(4-fluorophenyl)-4-methylpyrimidine **2h** (400 MHz, $CDCl_3$)



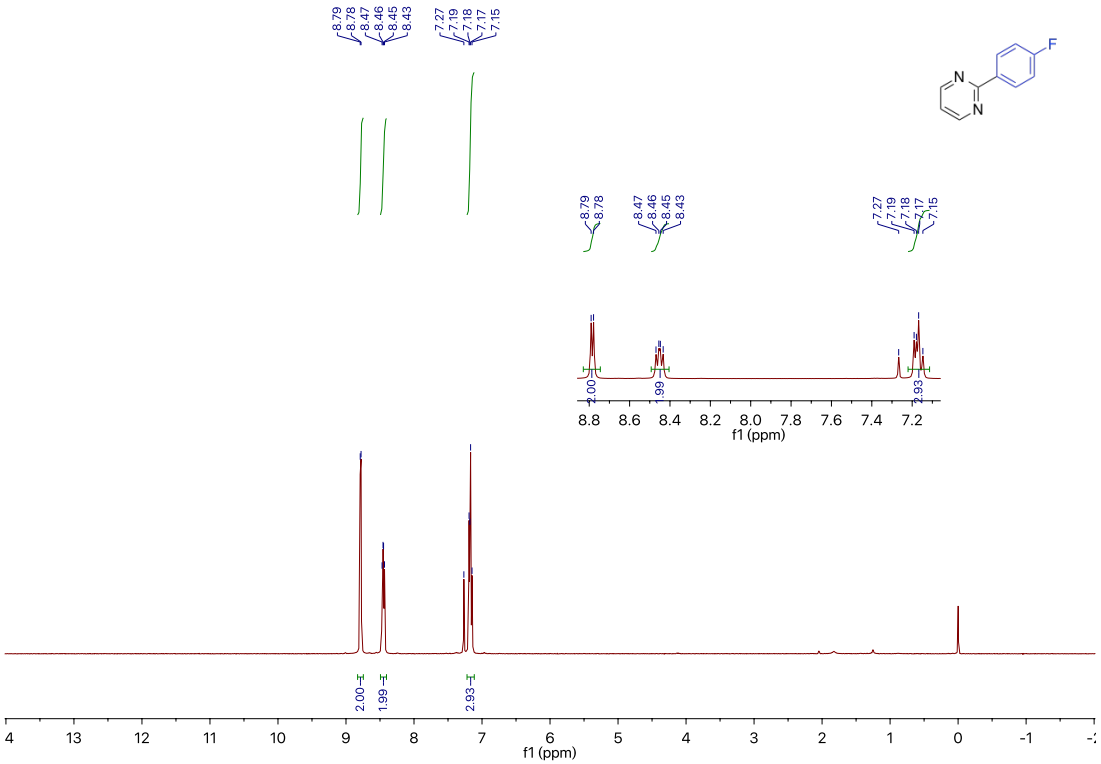
^{19}F spectrum of 2-(4-fluorophenyl)-4-methylpyrimidine **2h** (376 MHz, $CDCl_3$)



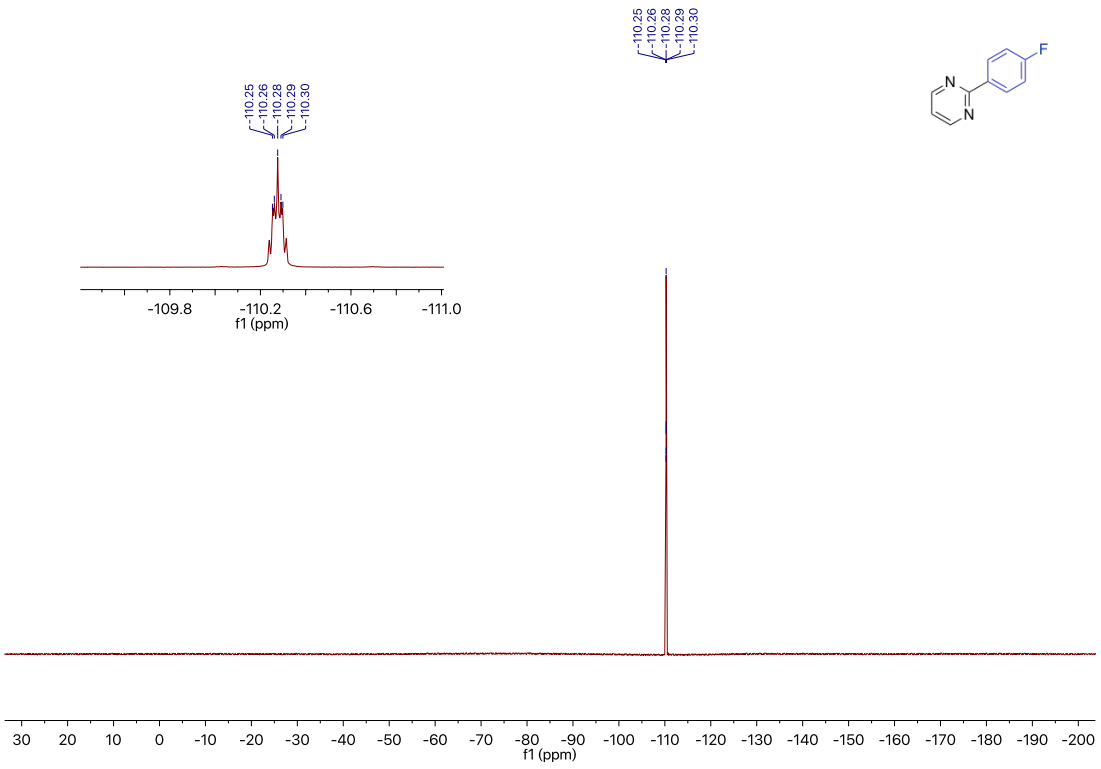
^{13}C spectrum of 2-(4-fluorophenyl)-4-methylpyrimidine **2h** (101 MHz, $CDCl_3$)



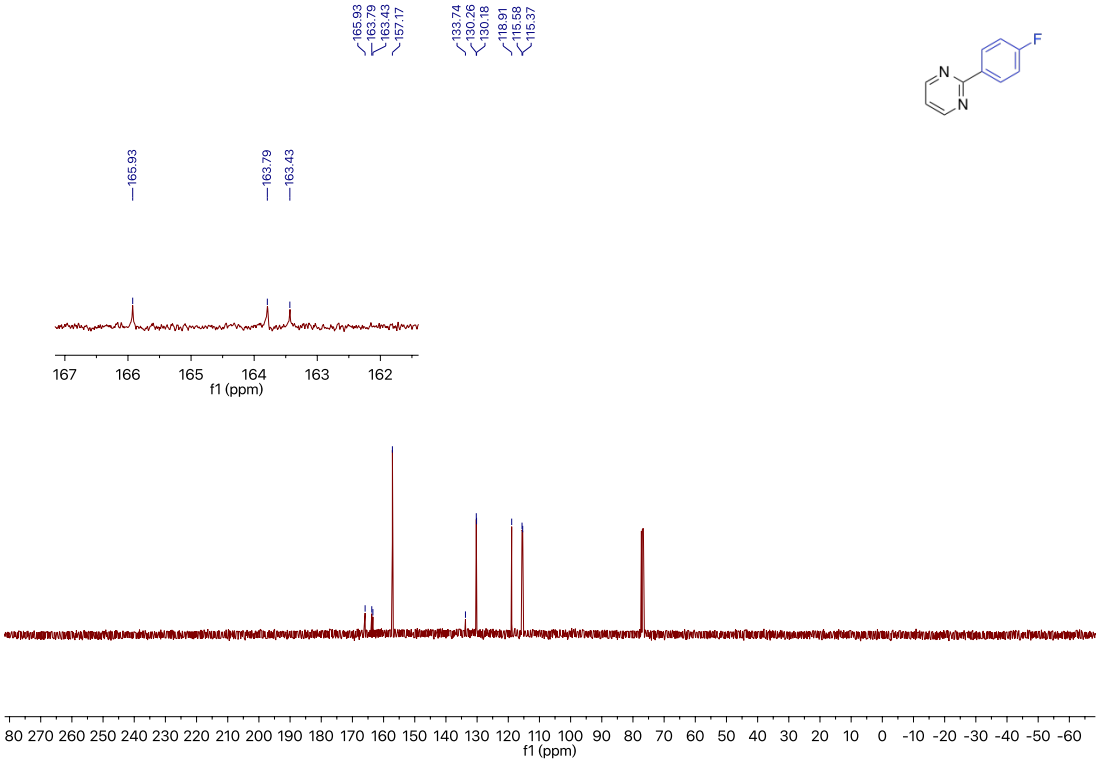
^{1}H spectrum of 2-(4-fluorophenyl)pyrimidine **2i** (400 MHz, $CDCl_3$)



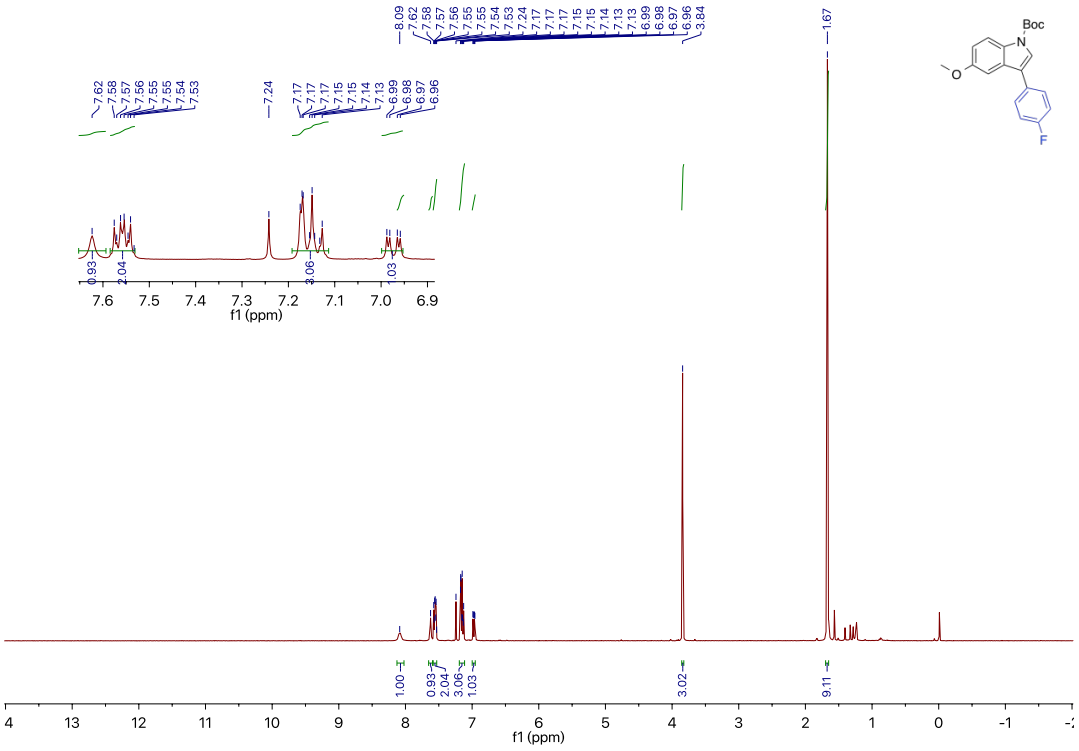
^{19}F spectrum of 2-(4-fluorophenyl)pyrimidine **2i** (376 MHz, $CDCl_3$)



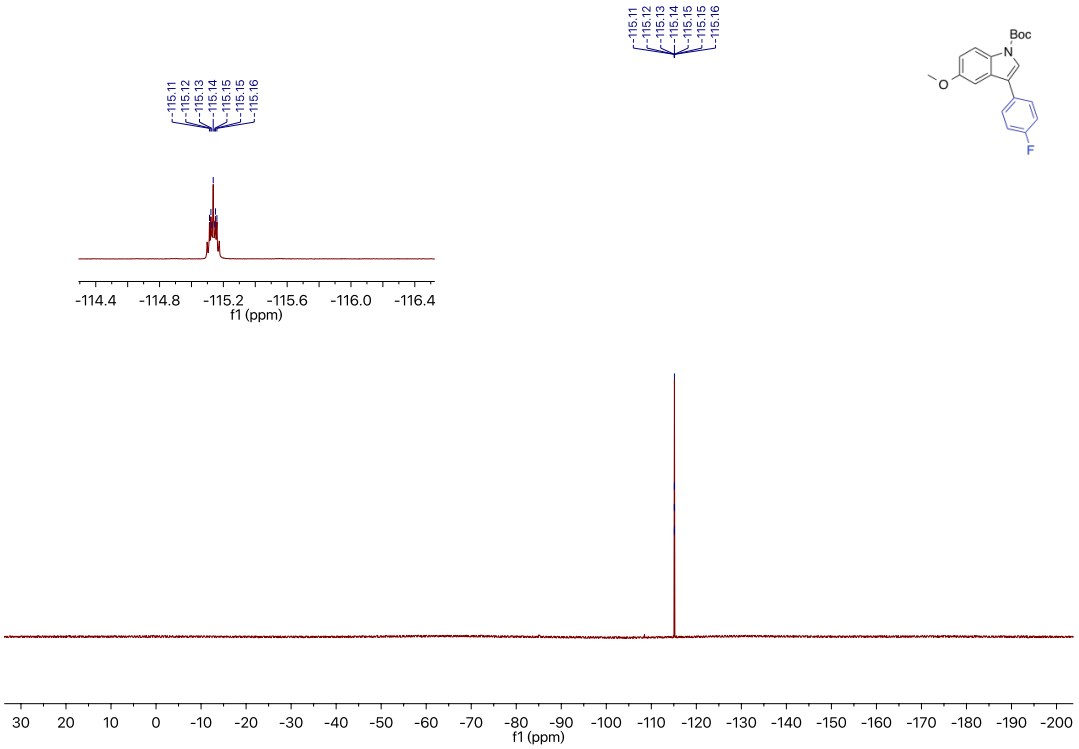
^{13}C spectrum of 2-(4-fluorophenyl)pyrimidine **2i** (101 MHz, $CDCl_3$)



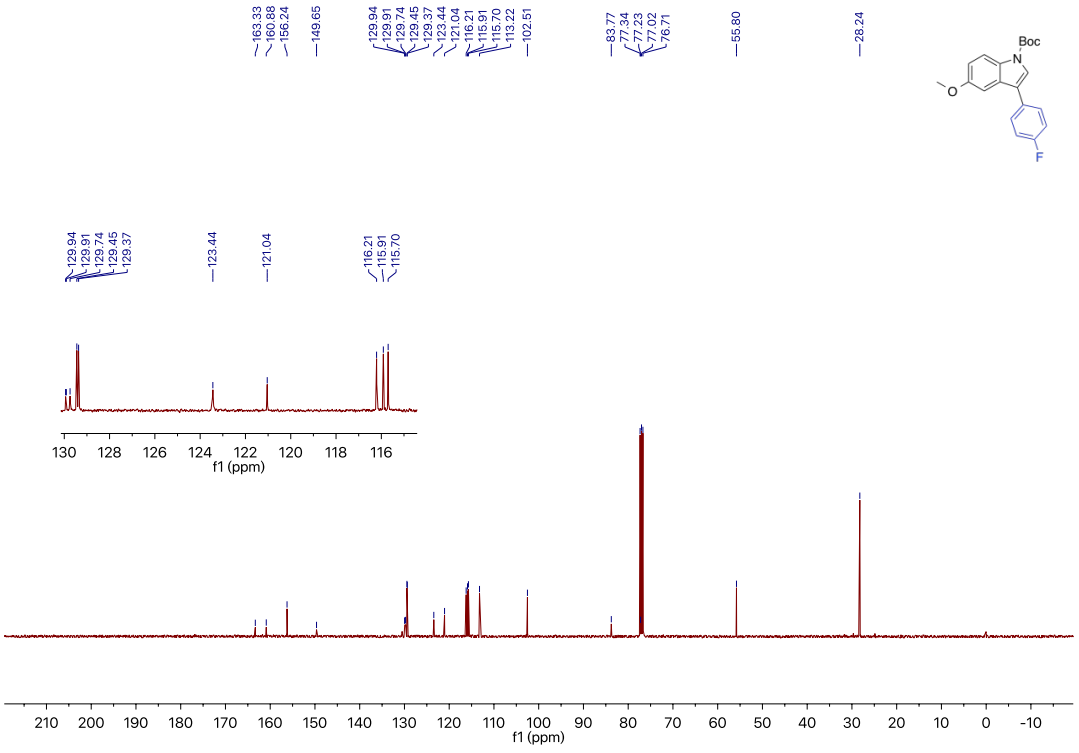
^{1}H spectrum of tert-butyl 3-(4-fluorophenyl)-5-methoxy-1*H*-indole -1-carboxylate **2j** (400 MHz, $CDCl_3$)



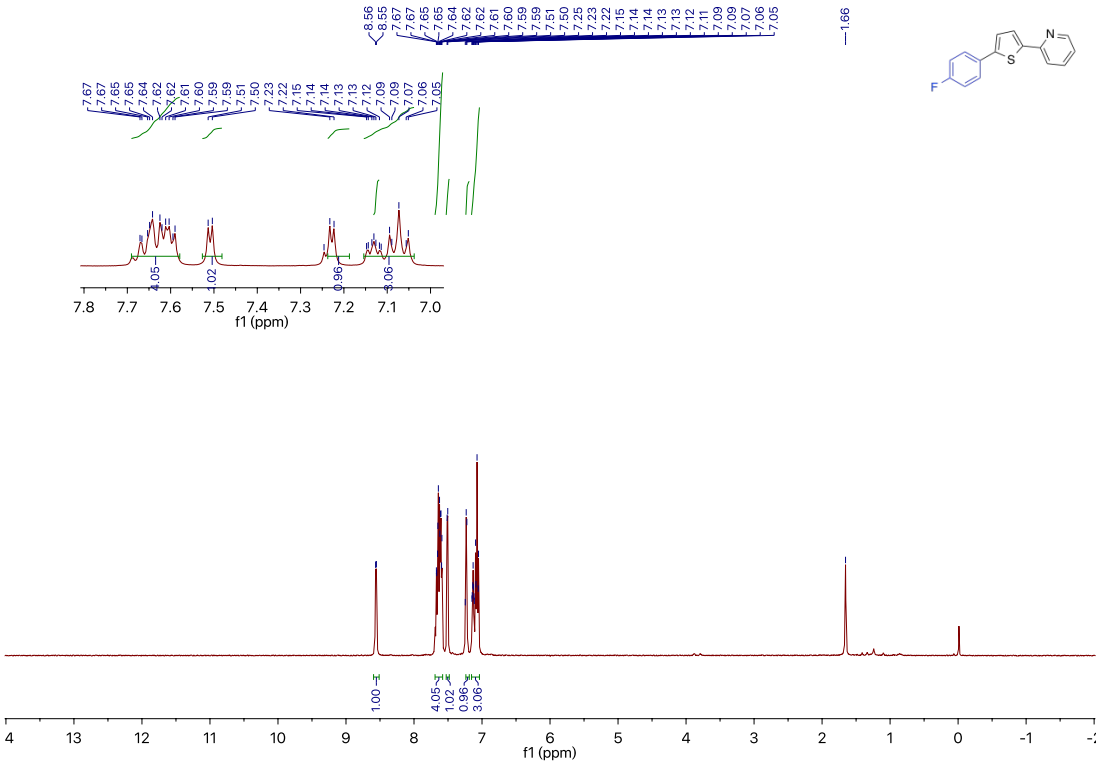
^{19}F spectrum of tert-butyl 3-(4-fluorophenyl)-5-methoxy-1*H*-indole-1-carboxylate **2j** (376 MHz, $CDCl_3$)



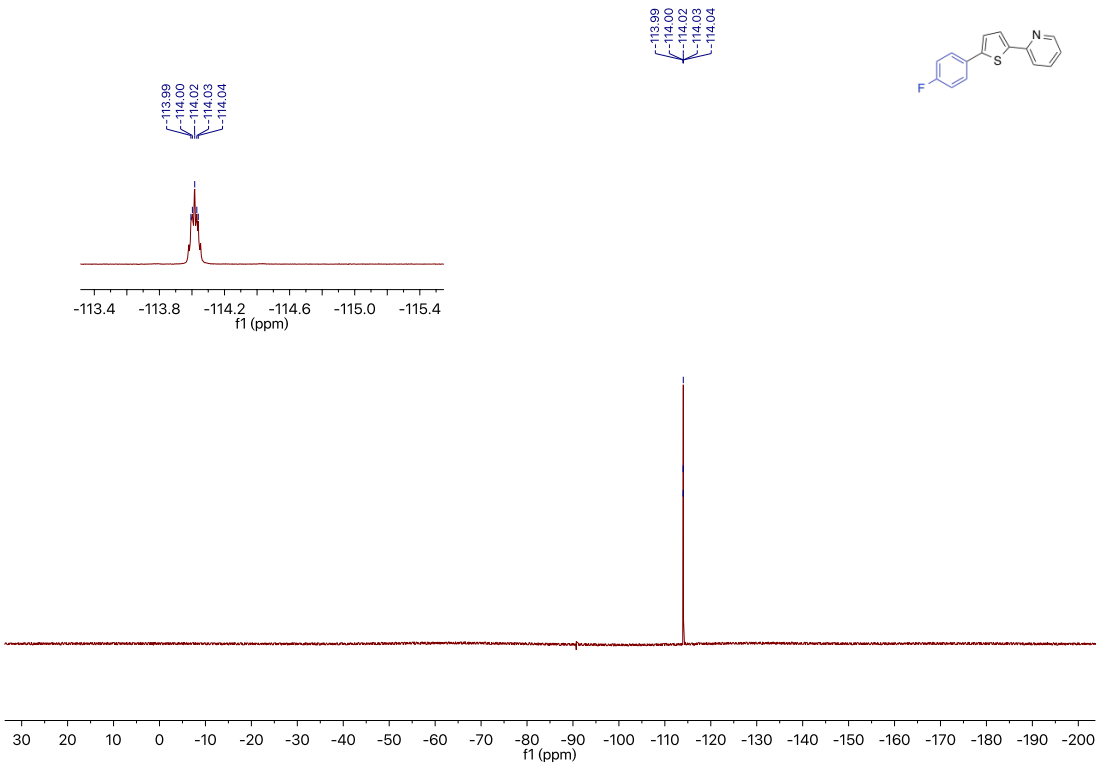
^{13}C spectrum of tert-butyl 3-(4-fluorophenyl)-5-methoxy-1*H*-indole-1-carboxylate **2j** (101 MHz, $CDCl_3$)



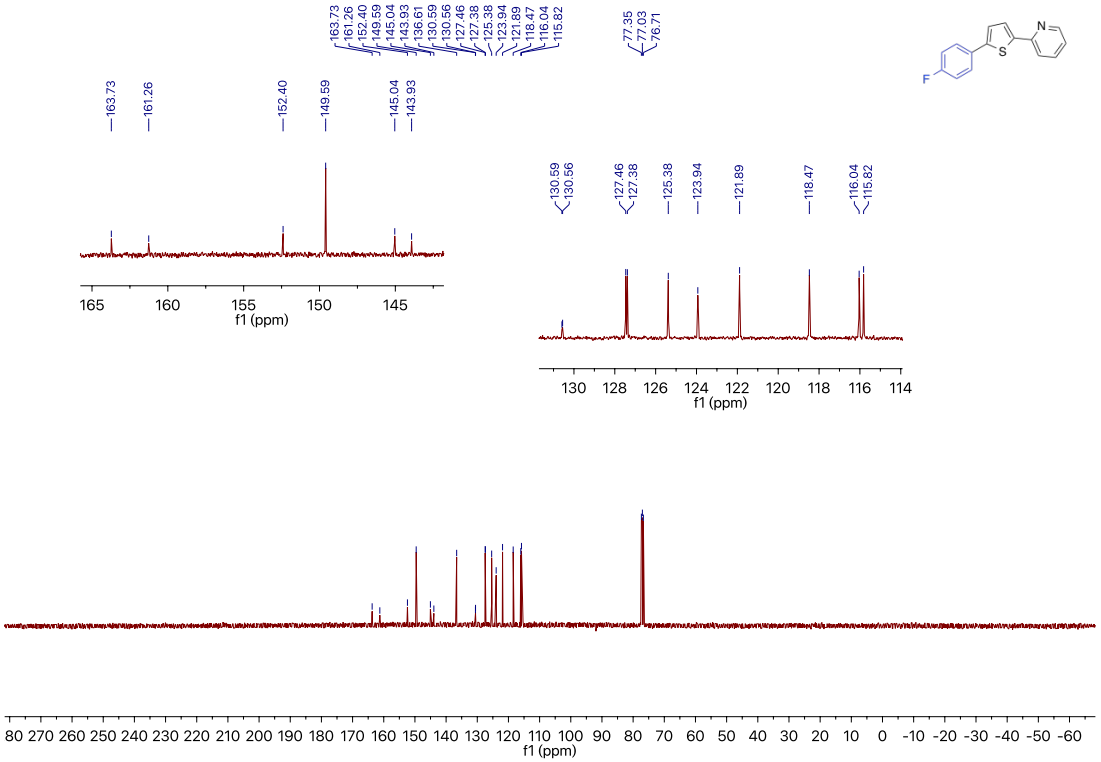
^{1}H spectrum of 2-(5-(4-fluorophenyl)thiophen-2-yl)pyridine **2k** (400 MHz, $CDCl_3$)



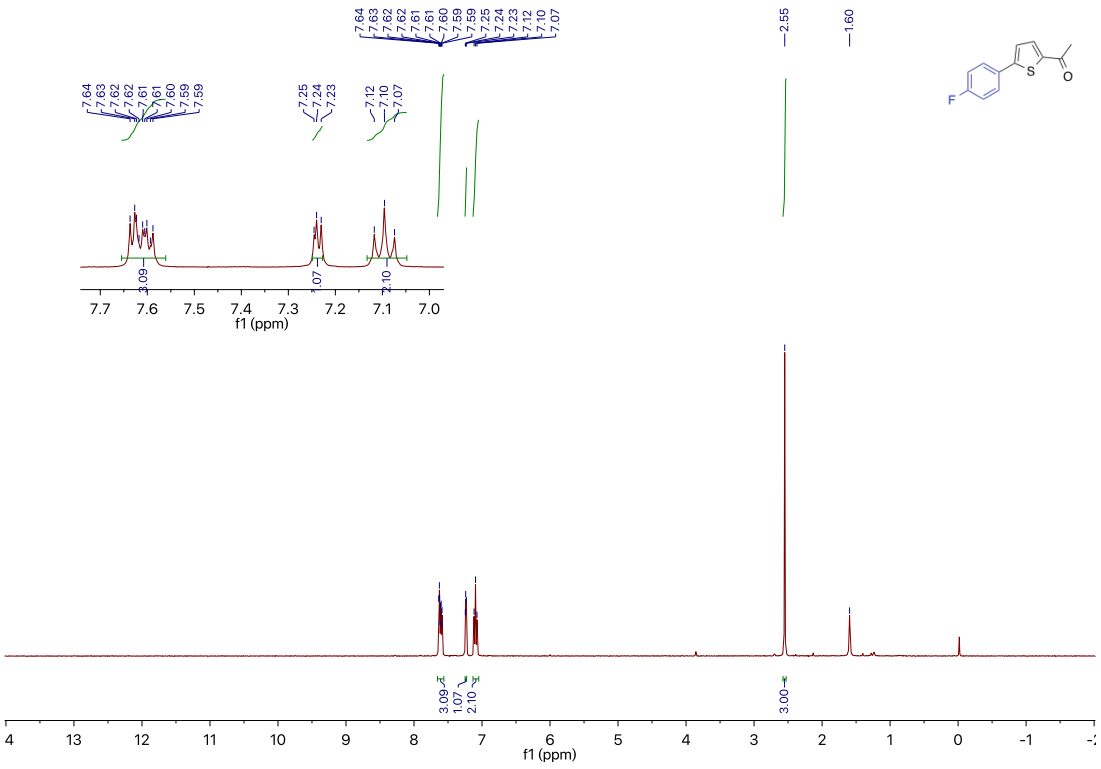
^{19}F spectrum of 2-(5-(4-fluorophenyl)thiophen-2-yl)pyridine **2k** (376 MHz, $CDCl_3$)



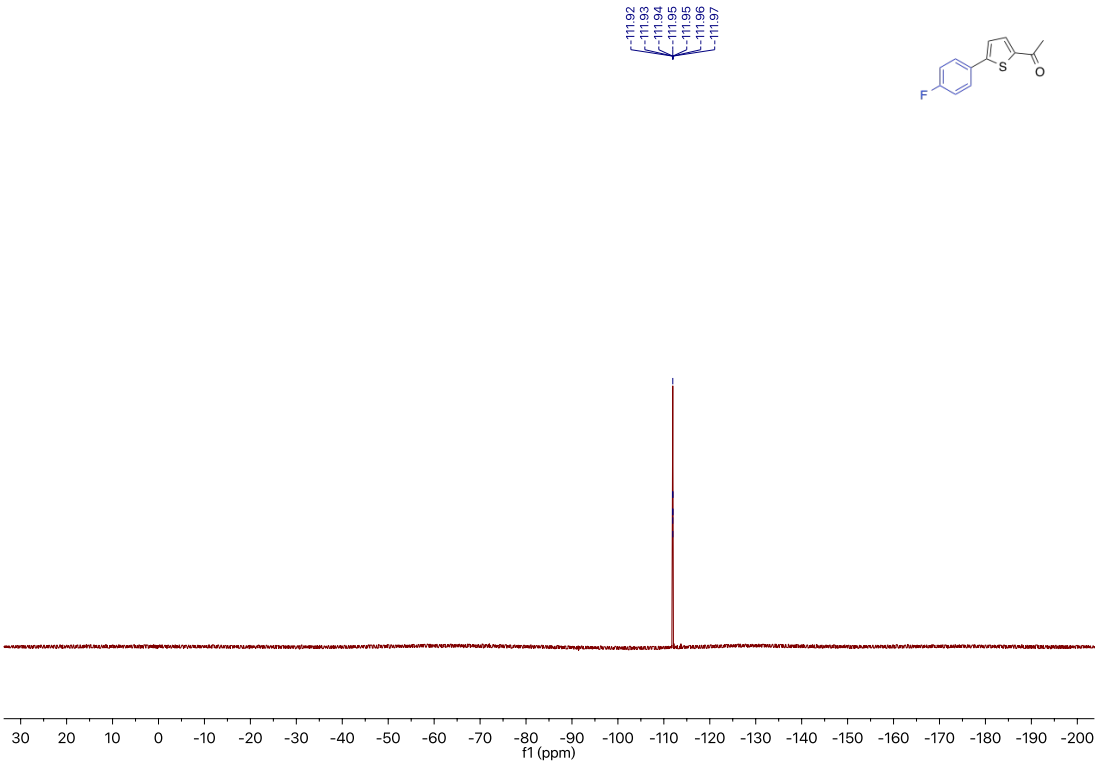
^{13}C spectrum of 2-(5-(4-fluorophenyl)thiophen-2-yl)pyridine **2k** (101 MHz, $CDCl_3$)



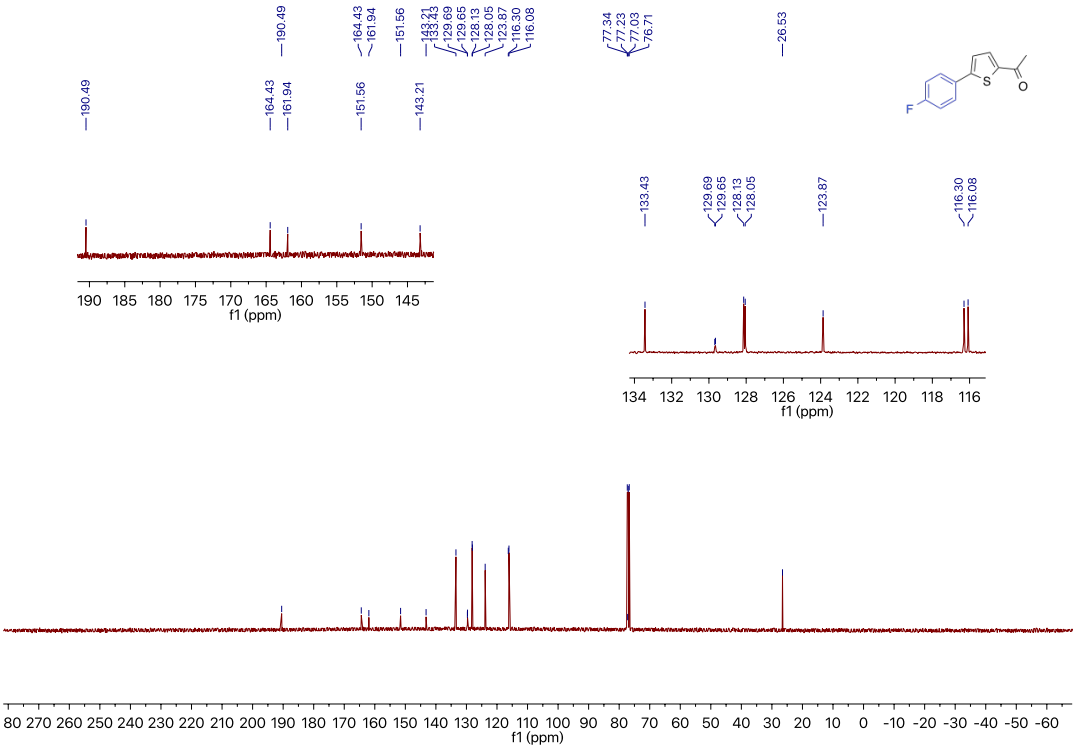
^{1}H spectrum of 1-(5-(4-fluorophenyl)thiophen-2-yl)ethan-1-one **2l** (400 MHz, $CDCl_3$)



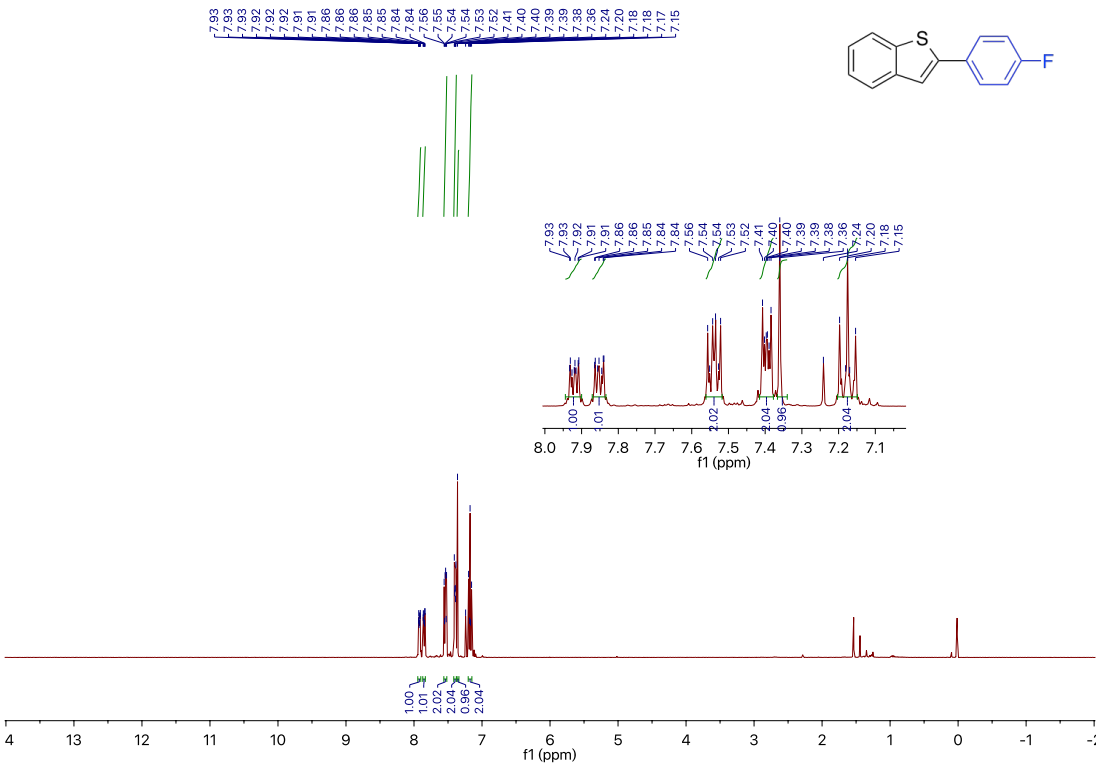
^{19}F spectrum of 1-(5-(4-fluorophenyl)thiophen-2-yl)ethan-1-one **2l** (376 MHz, $CDCl_3$)



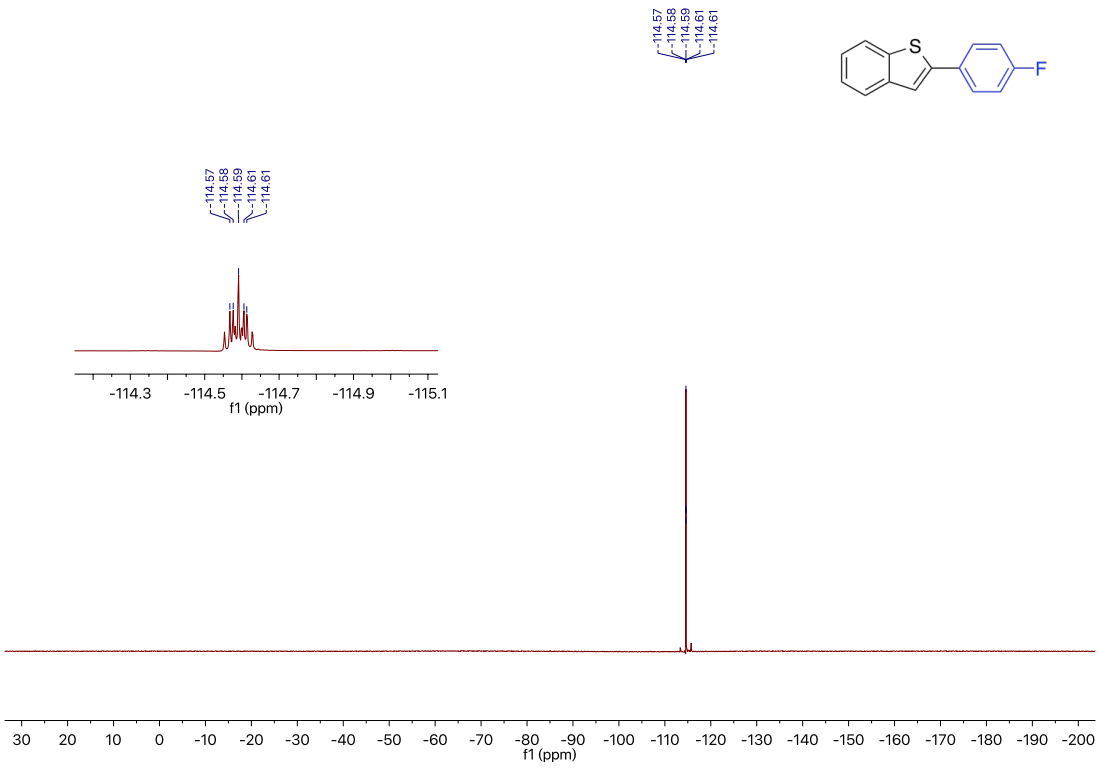
^{13}C spectrum of 1-(5-(4-fluorophenyl)thiophen-2-yl)ethan-1-one **2l**(101 MHz, $CDCl_3$)



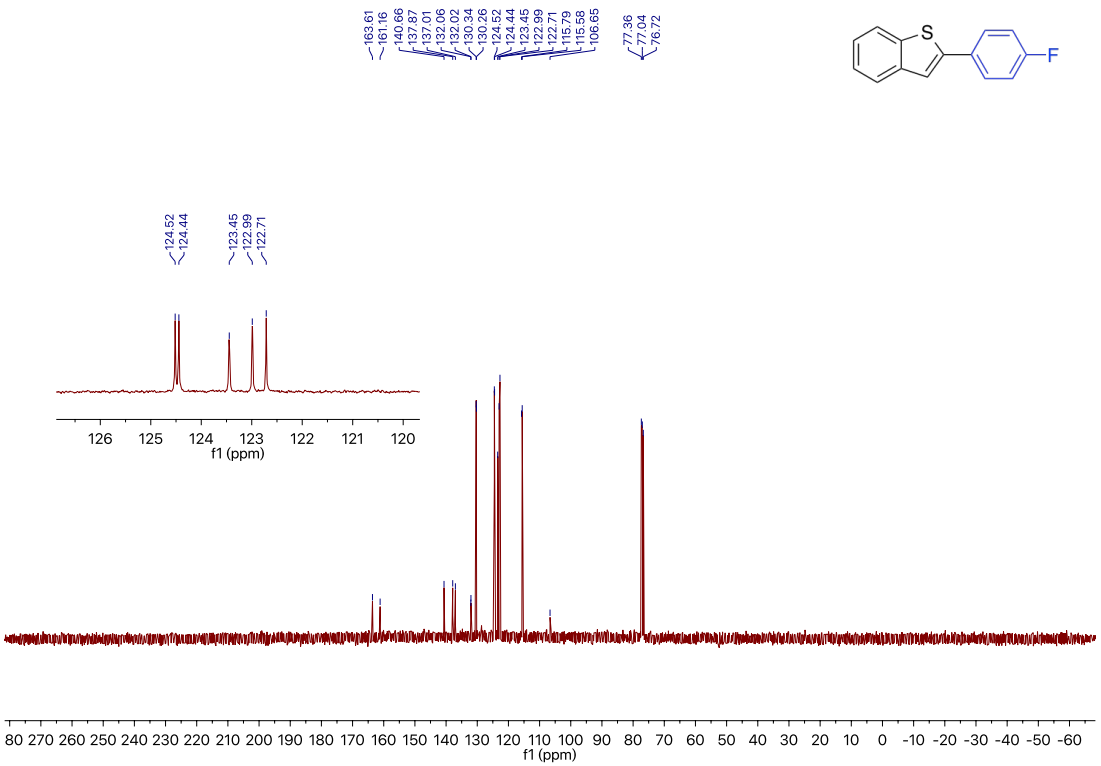
^{1}H spectrum of 2-(4-fluorophenyl)benzo[b]thiophene **2m** (400 MHz, $CDCl_3$)



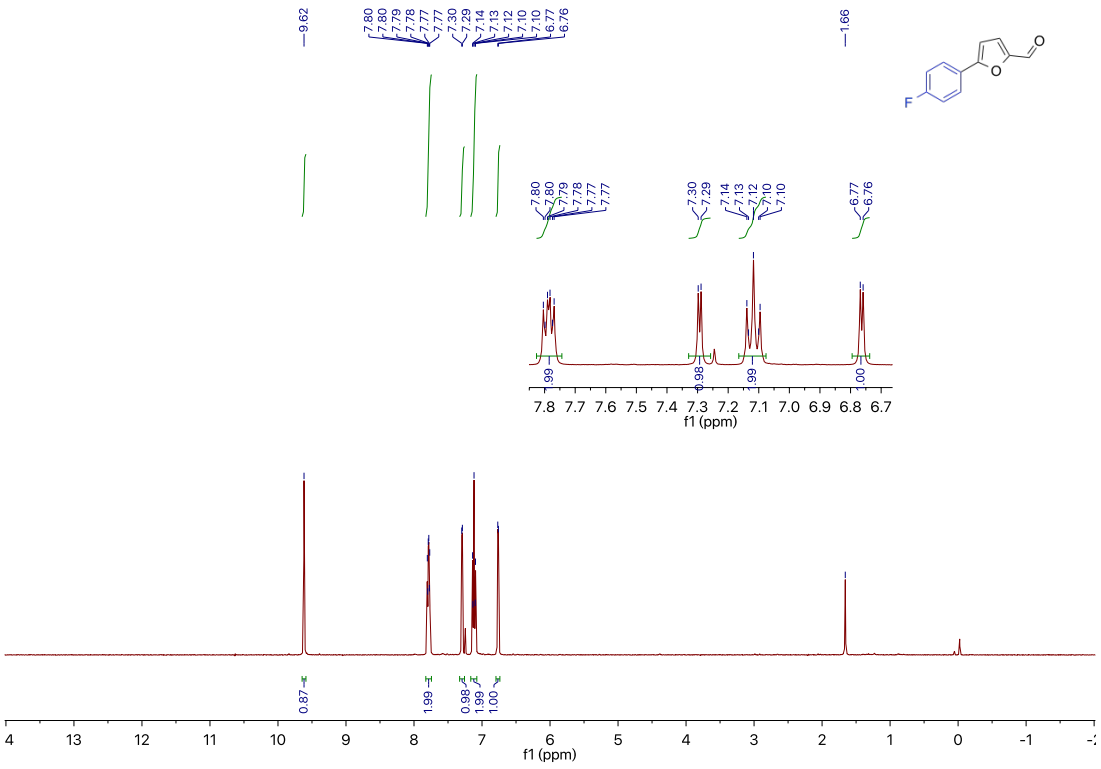
^{19}F spectrum of 2-(4-fluorophenyl)benzo[b]thiophene **2m** (376 MHz, $CDCl_3$)



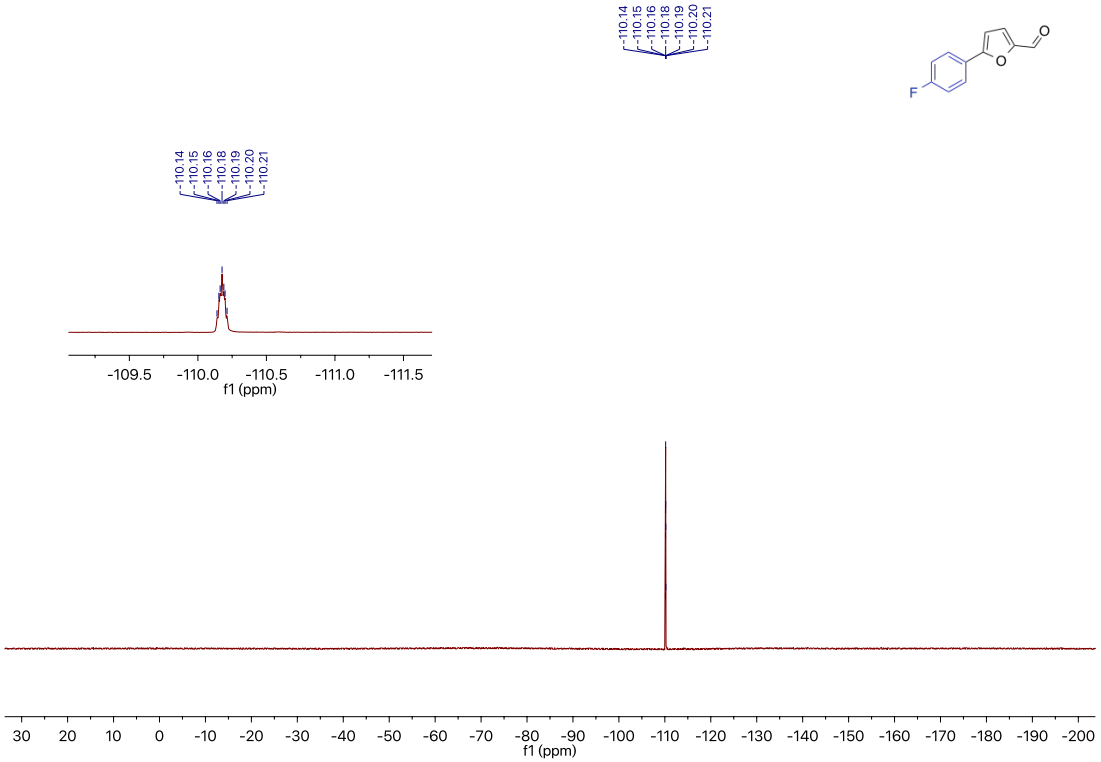
^{13}C spectrum of 2-(4-fluorophenyl)benzo[b]thiophene **2m** (101 MHz, $CDCl_3$)



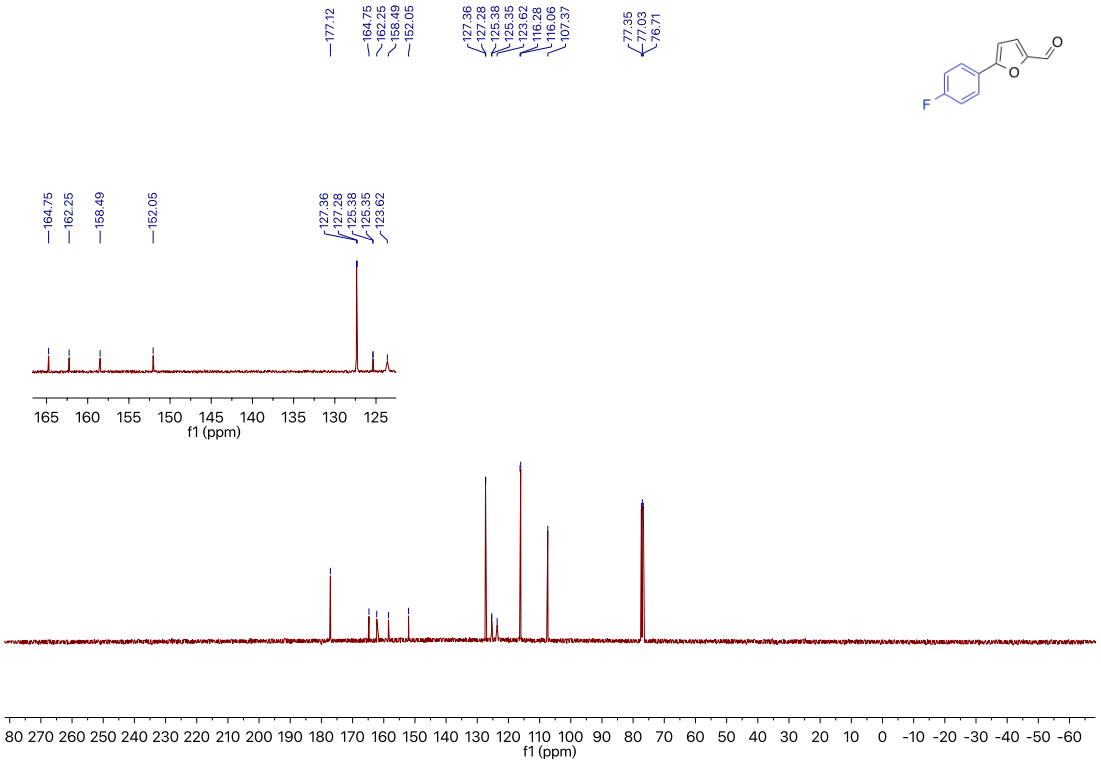
^{1}H spectrum of 5-(4-fluorophenyl)furan-2-carbaldehyde **2n** (400 MHz, $CDCl_3$)



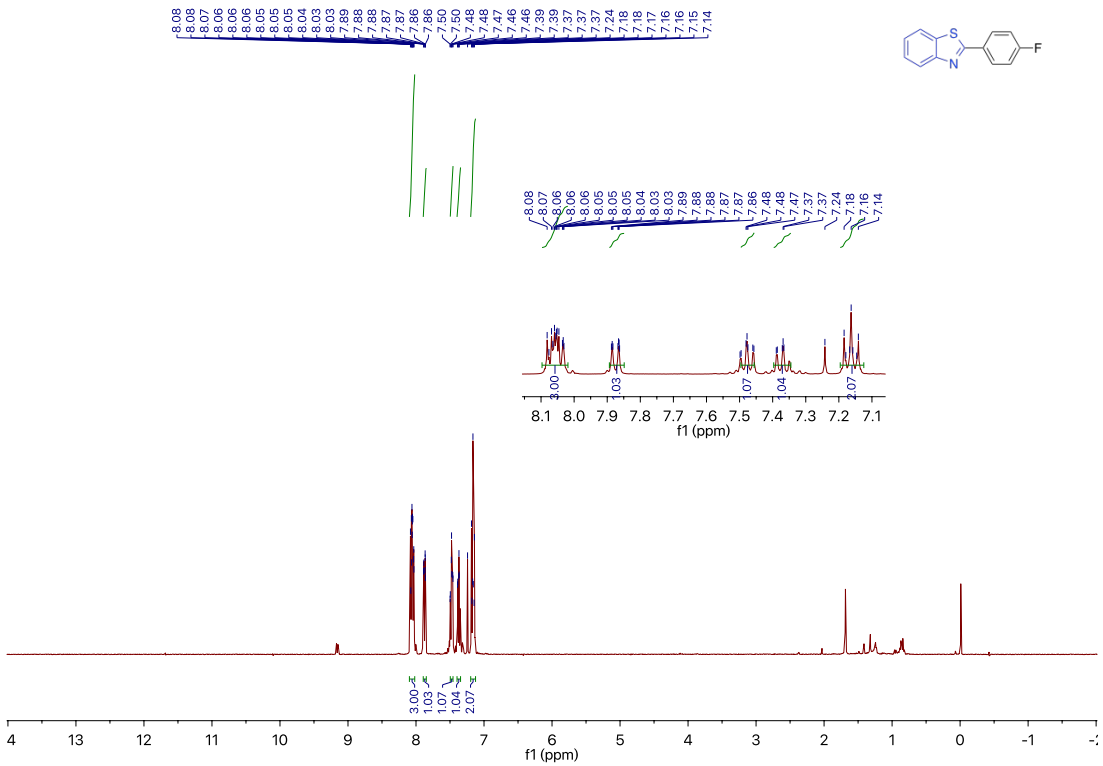
^{19}F spectrum of 5-(4-fluorophenyl)furan-2-carbaldehyde **2n** (376 MHz, $CDCl_3$)



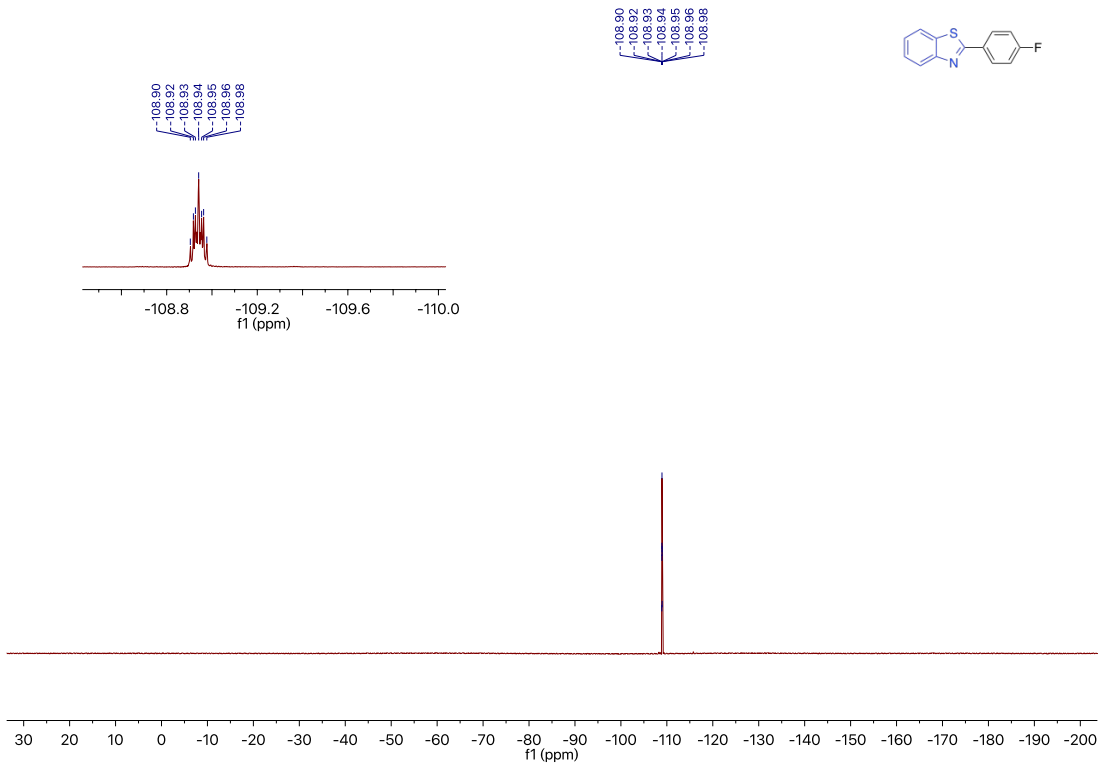
^{13}C spectrum of 5-(4-fluorophenyl)furan-2-carbaldehyde **2n** (101 MHz, $CDCl_3$)



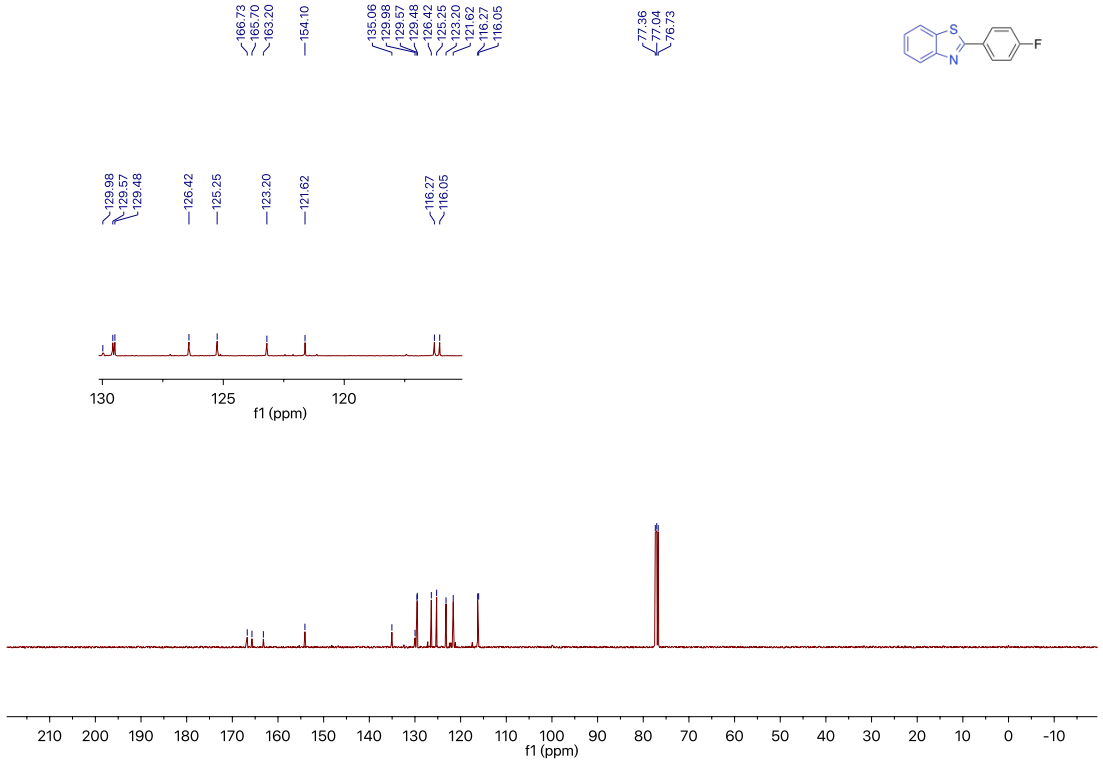
^{1}H spectrum of 2-(4-Fluorophenyl)benzo[d]thiazole **2o** (400 MHz, $CDCl_3$)



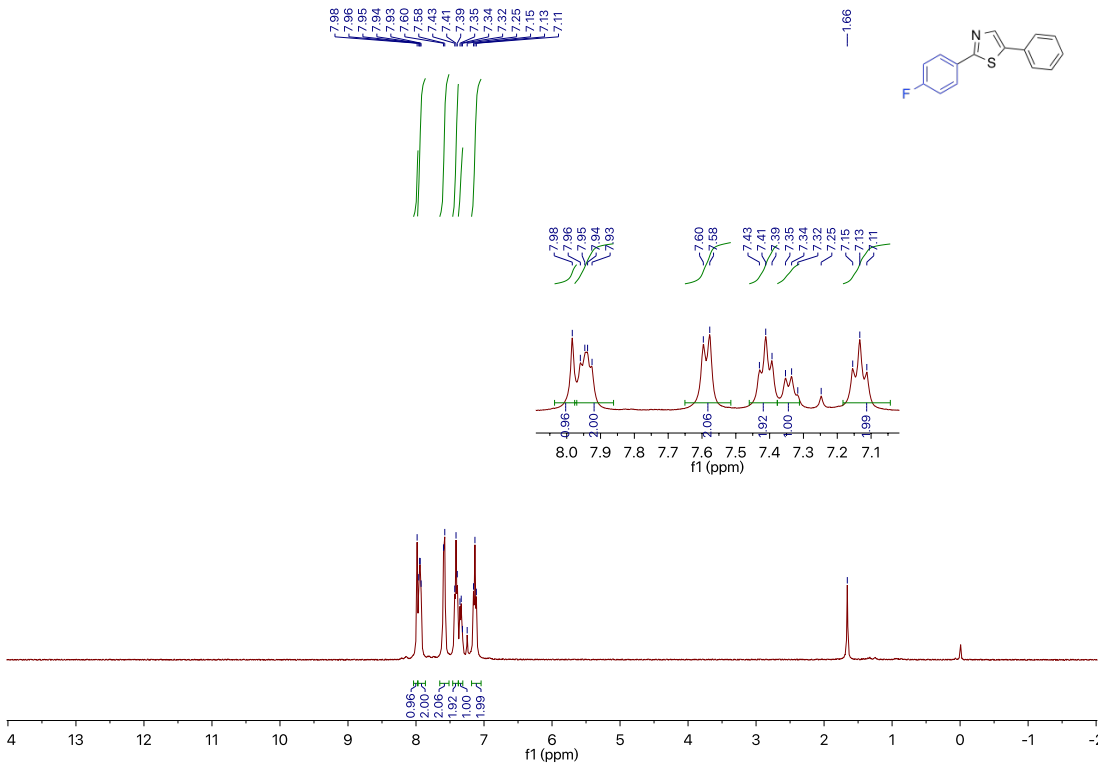
^{19}F spectrum of 2-(4-Fluorophenyl)benzo[d]thiazole **2o** (376 MHz, $CDCl_3$)



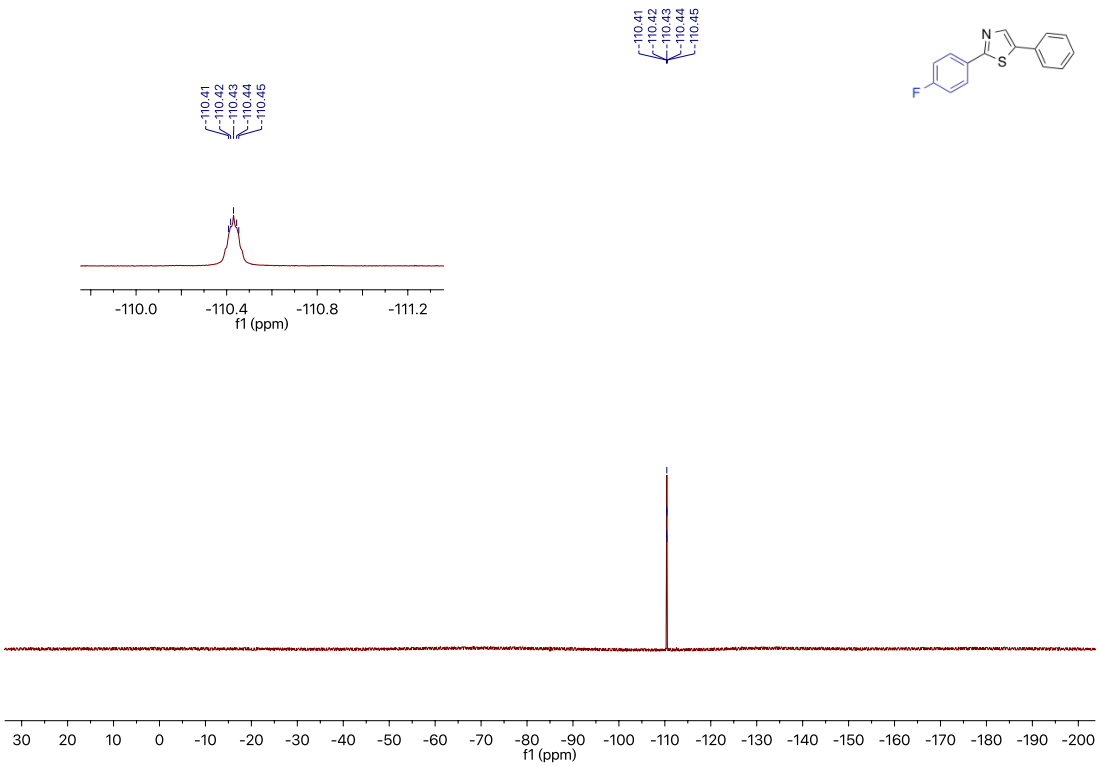
^{13}C spectrum of 2-(4-Fluorophenyl)benzo[d]thiazole **2o** (101 MHz, $CDCl_3$)



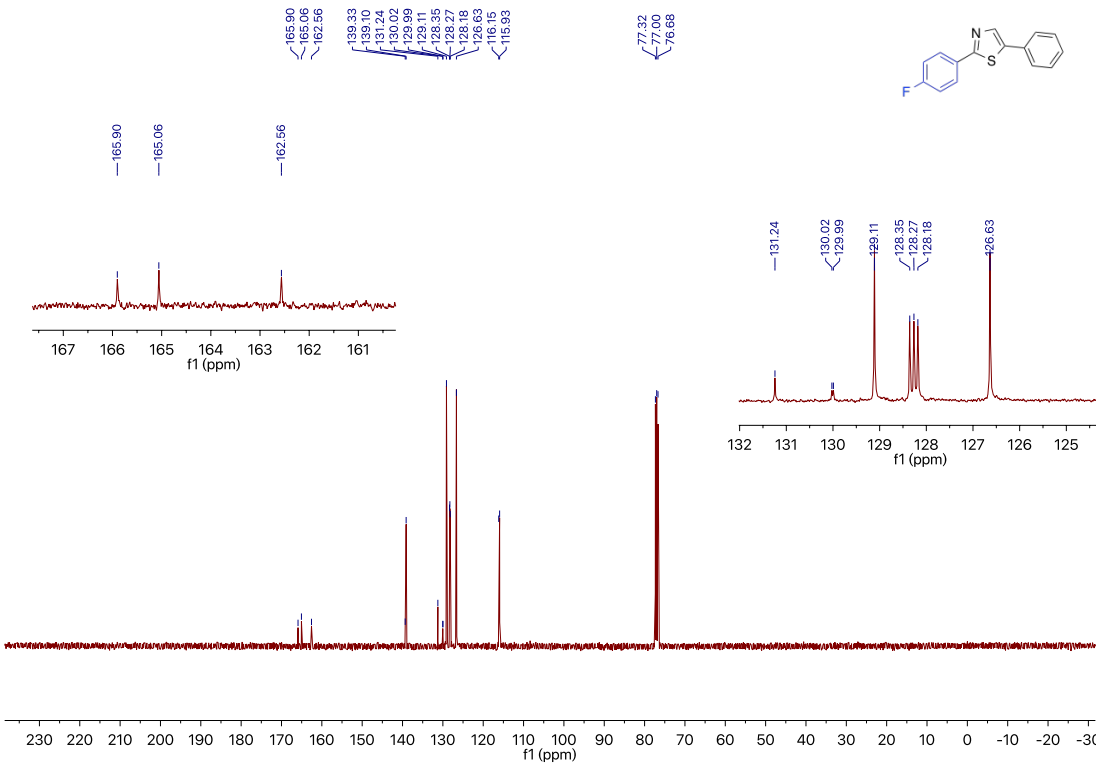
^{1}H spectrum of 2-(4-Fluorophenyl)-5-phenylthiazole **2p** (400 MHz, $CDCl_3$)



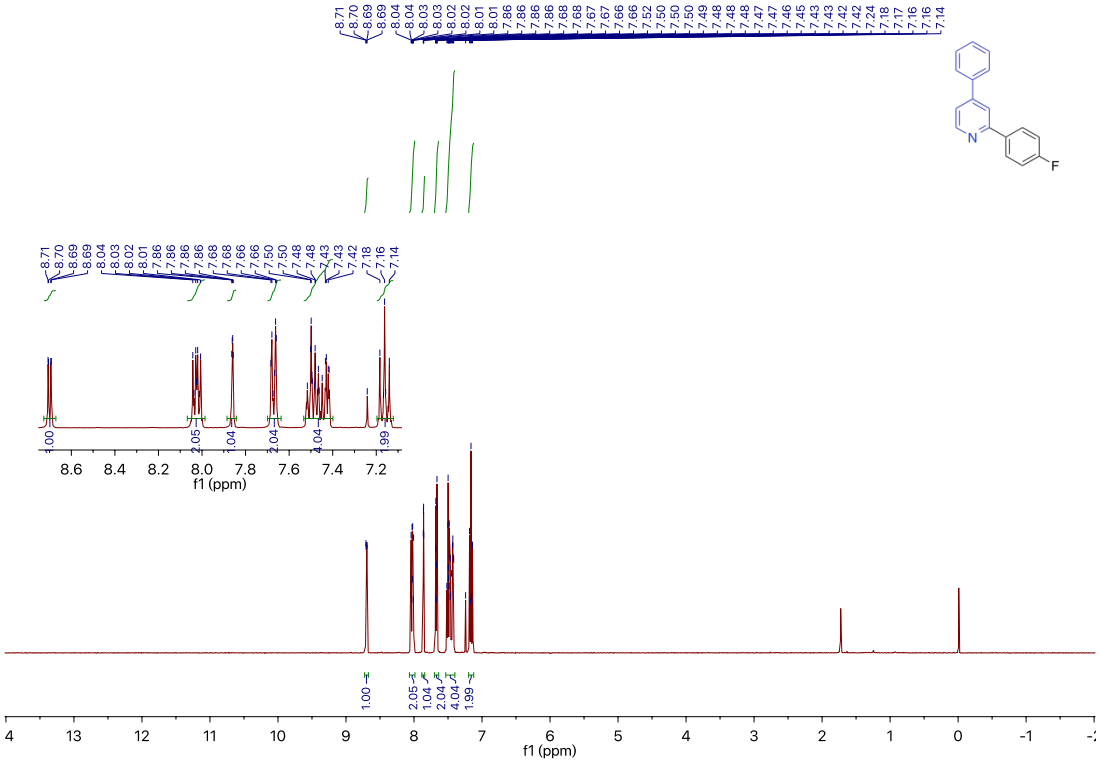
^{19}F spectrum of 2-(4-Fluorophenyl)-5-phenylthiazole **2p** (376 MHz, $CDCl_3$)



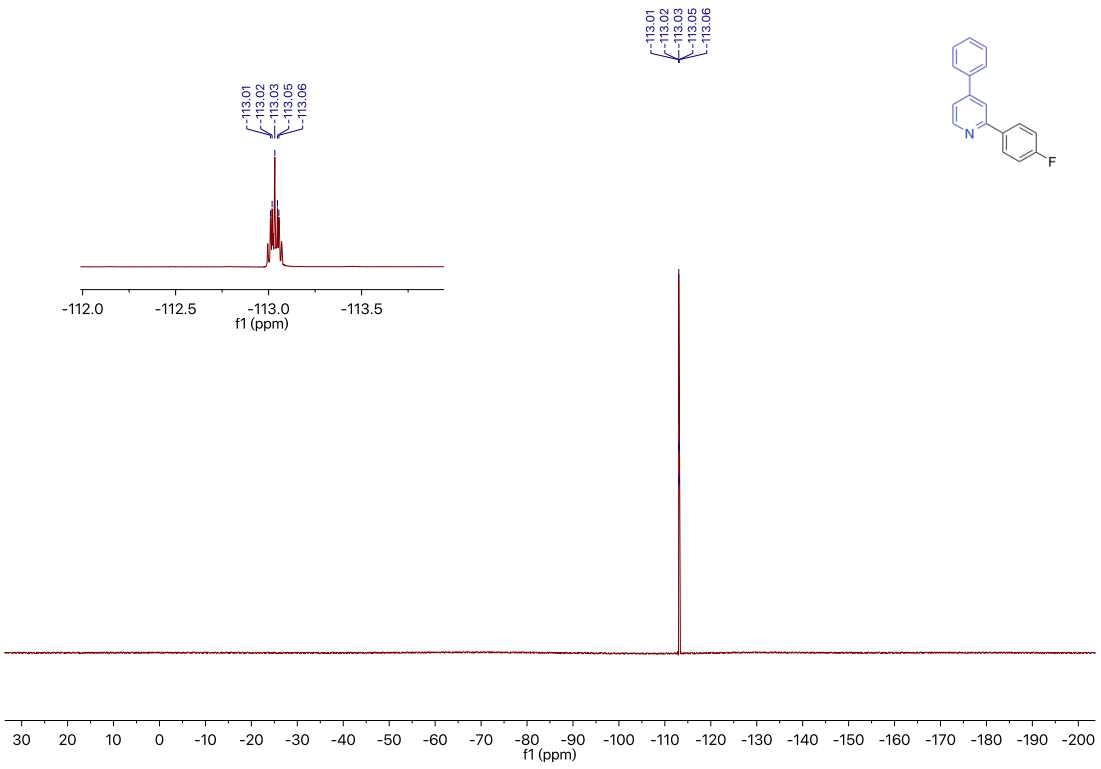
^{13}C spectrum of 2-(4-Fluorophenyl)-5-phenylthiazole **2p** (101 MHz, $CDCl_3$)



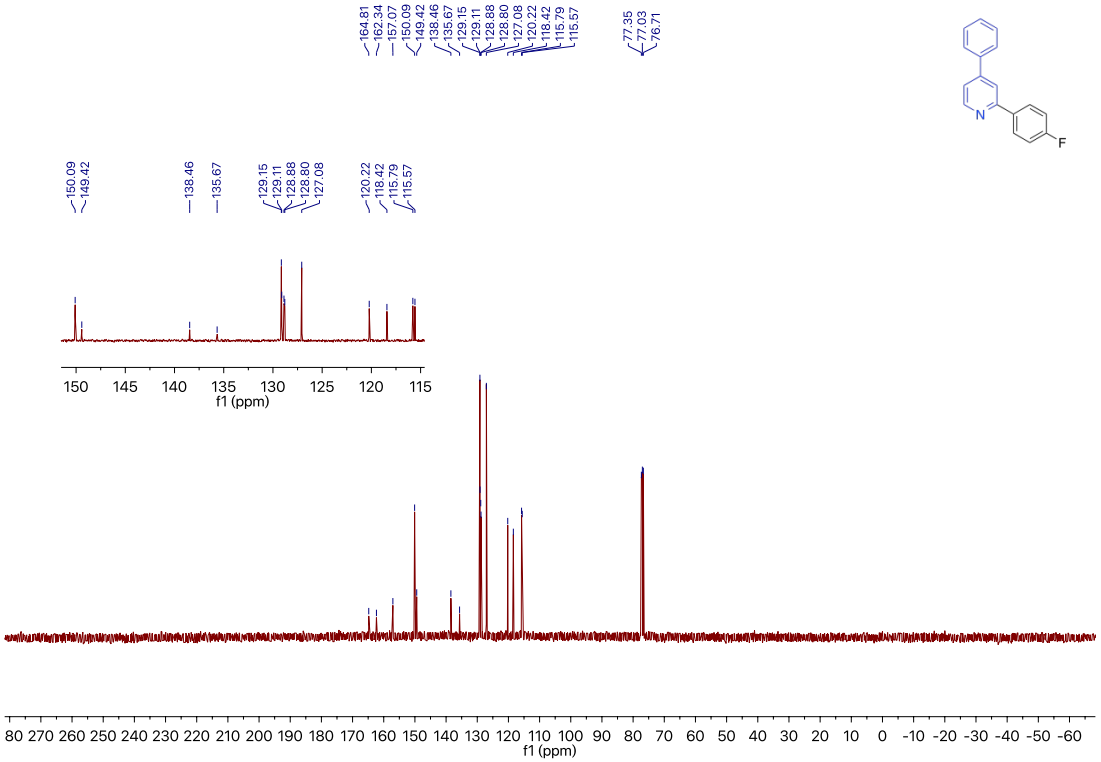
^{1}H spectrum of 2-(4-fluorophenyl)-4-phenylpyridine **2s** (400 MHz, $CDCl_3$)



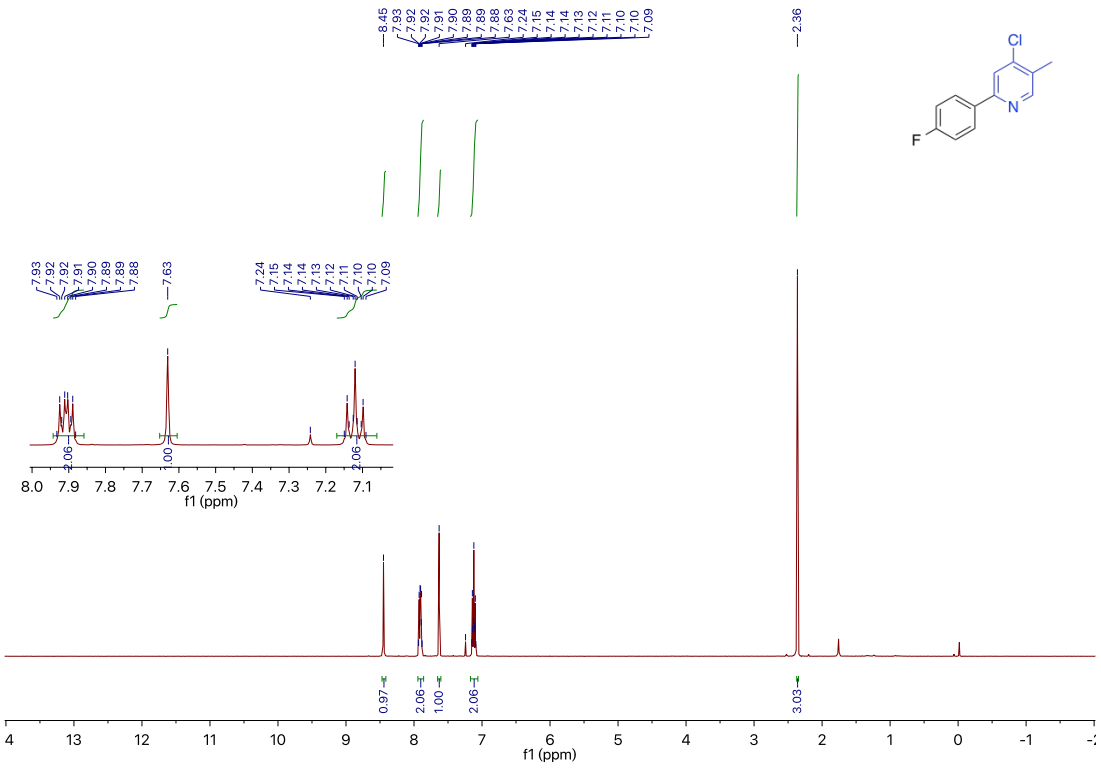
^{19}F spectrum of 2-(4-fluorophenyl)-4-phenylpyridine **2s** (376 MHz, $CDCl_3$)



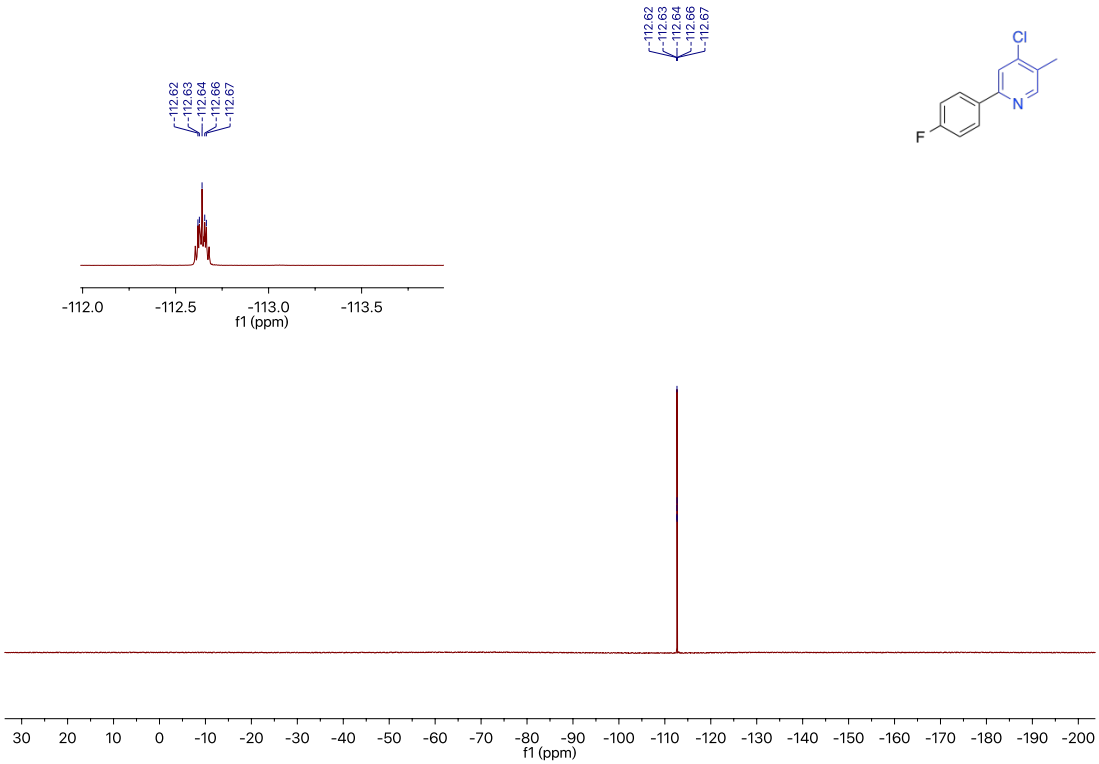
^{13}C spectrum of 2-(4-fluorophenyl)-4-phenylpyridine **2s** (101 MHz, $CDCl_3$)



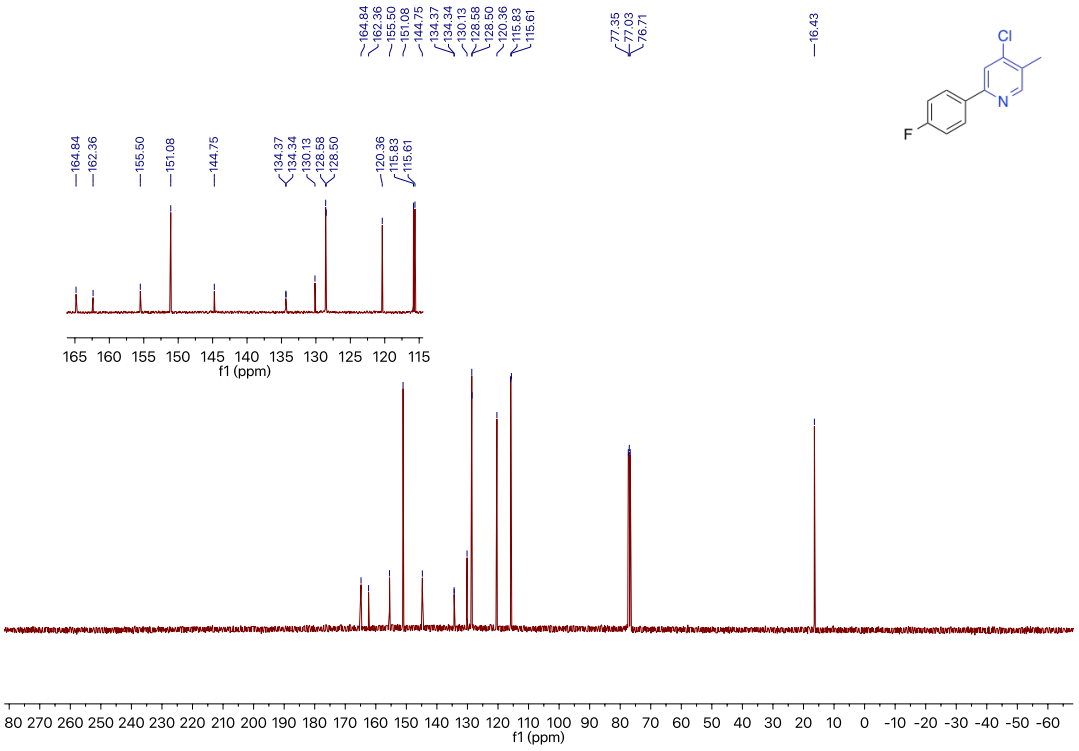
^{1}H spectrum of 4-chloro-2-(4-fluorophenyl)-5-methylpyridine **2t** (400 MHz, $CDCl_3$)



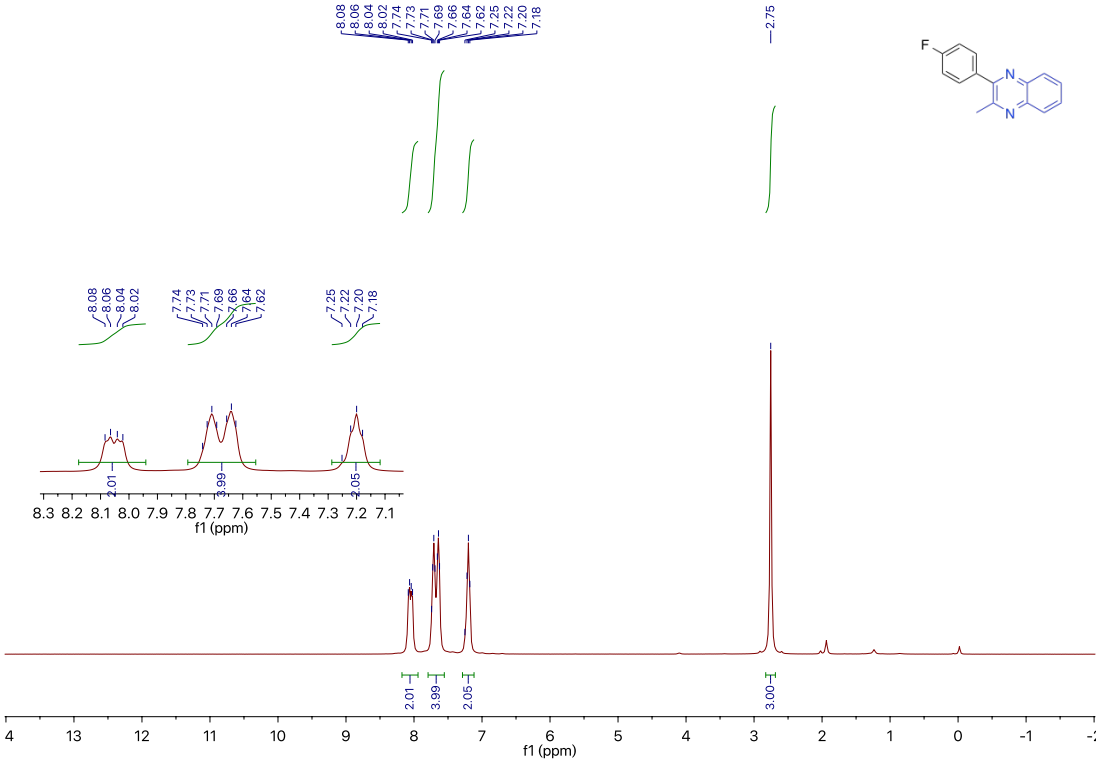
^{19}F spectrum of 4-chloro-2-(4-fluorophenyl)-5-methylpyridine **2t** (376 MHz, $CDCl_3$)



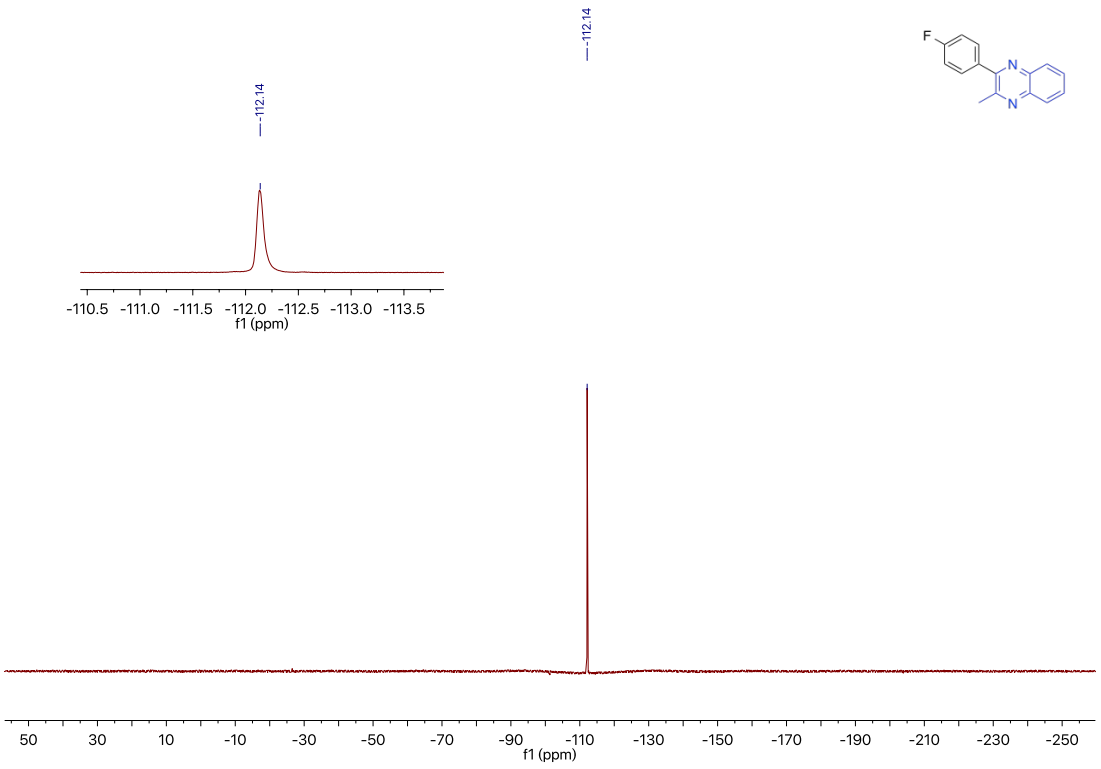
^{13}C spectrum of 4-chloro-2-(4-fluorophenyl)-5-methylpyridine **2t** (101 MHz, $CDCl_3$)



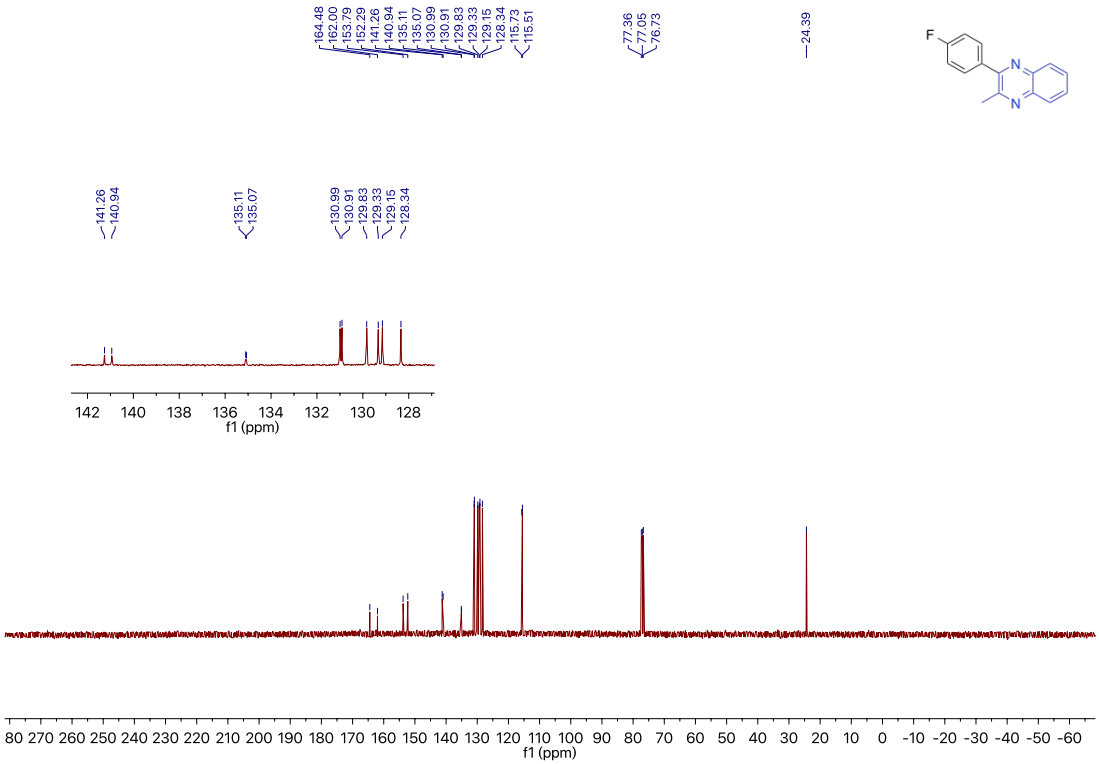
^{1}H spectrum of 2-(4-fluorophenyl)-3-methylquinoxaline **2v** (400 MHz, $CDCl_3$)



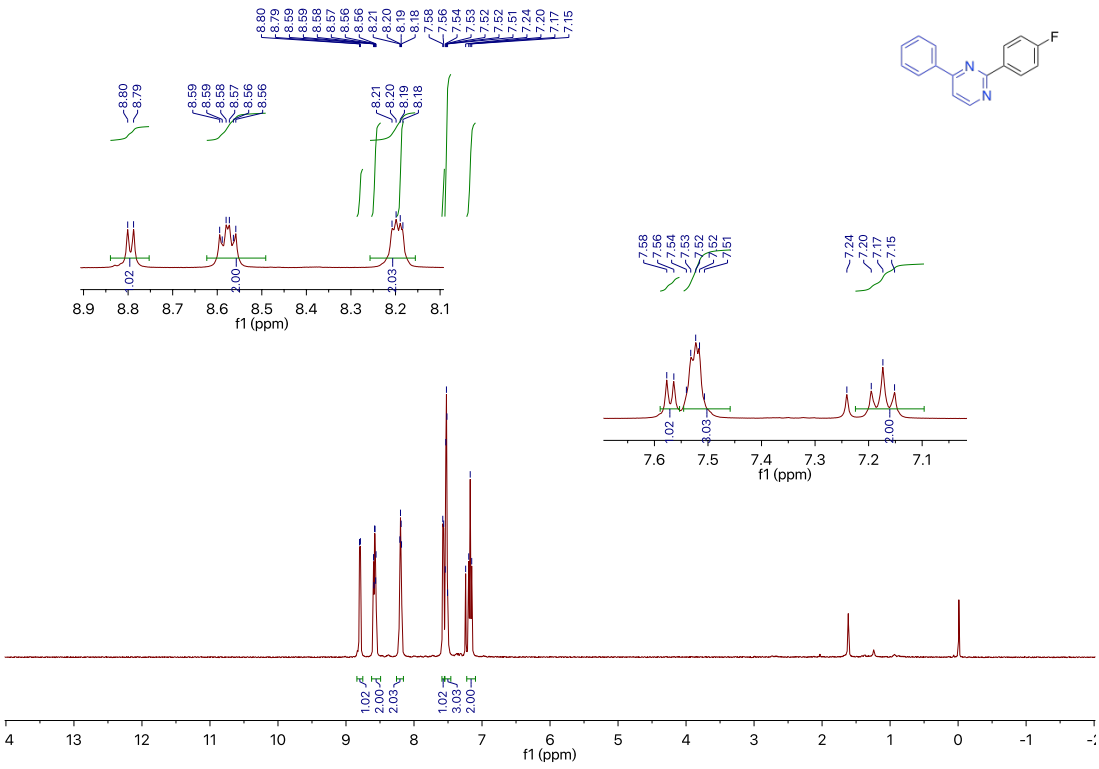
^{19}F spectrum of 2-(4-fluorophenyl)-3-methylquinoxaline **2v** (376 MHz, $CDCl_3$)



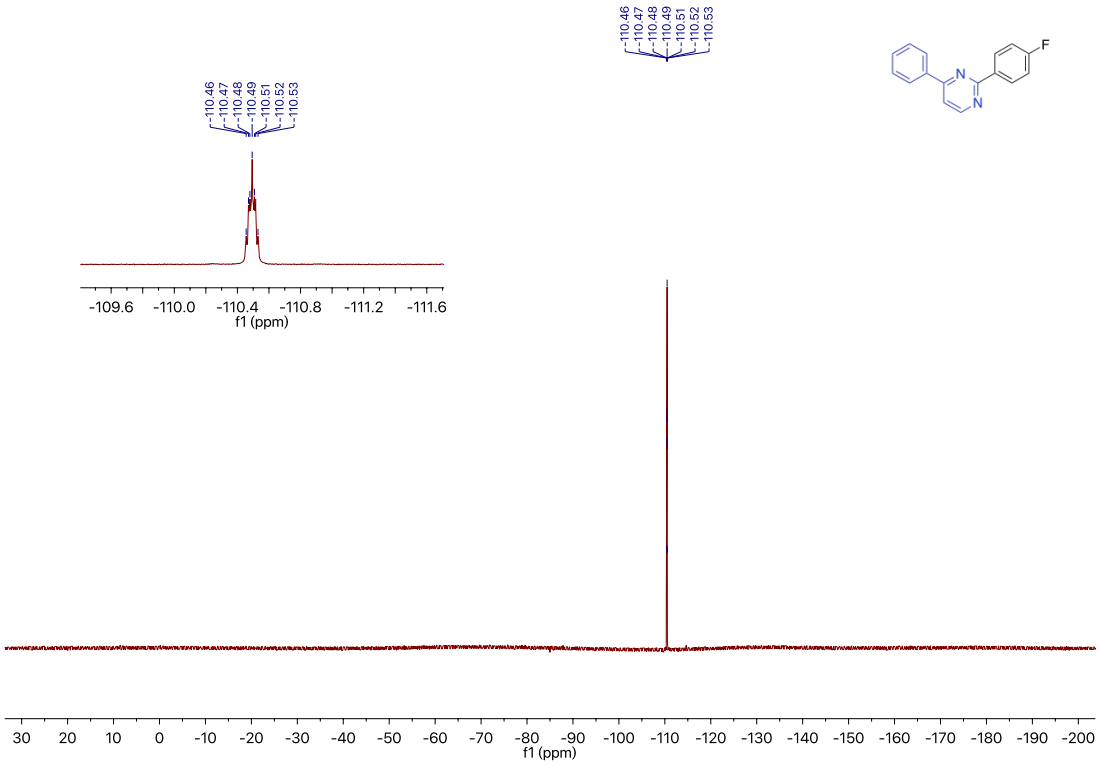
^{13}C spectrum of 2-(4-fluorophenyl)-3-methylquinoxaline **2v** (101 MHz, $CDCl_3$)



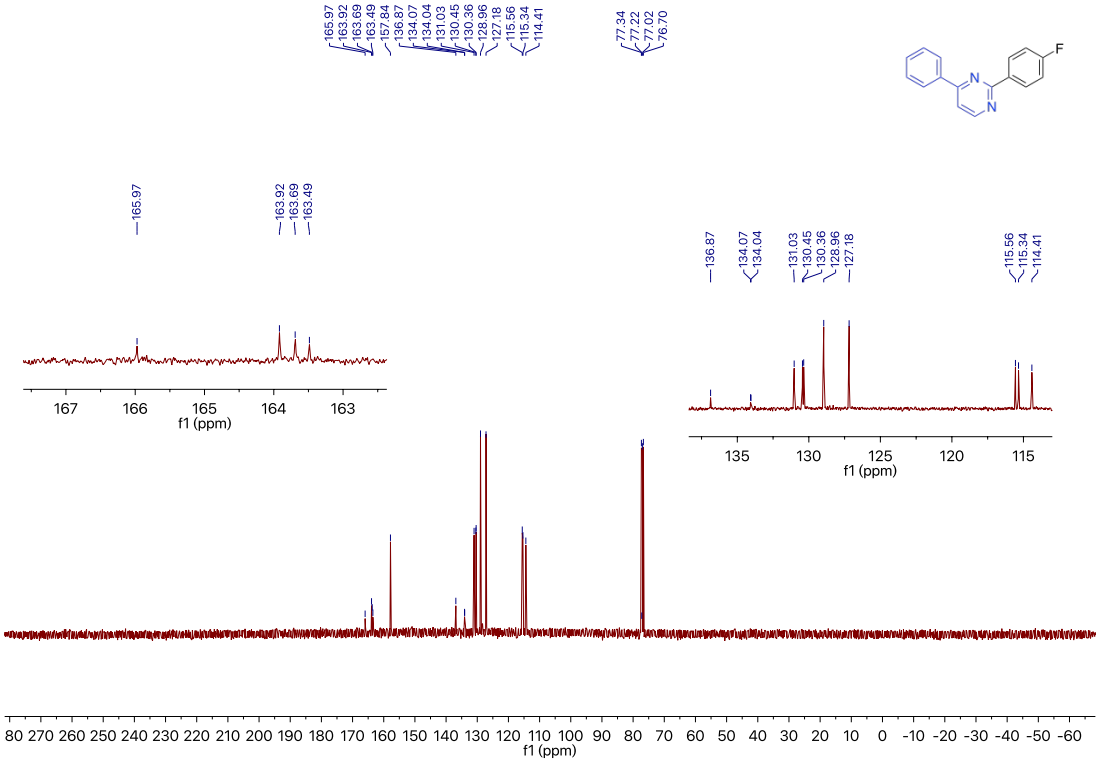
^{1}H spectrum of 2-(4-fluorophenyl)-4-phenylpyrimidine **2w** (400 MHz, $CDCl_3$)



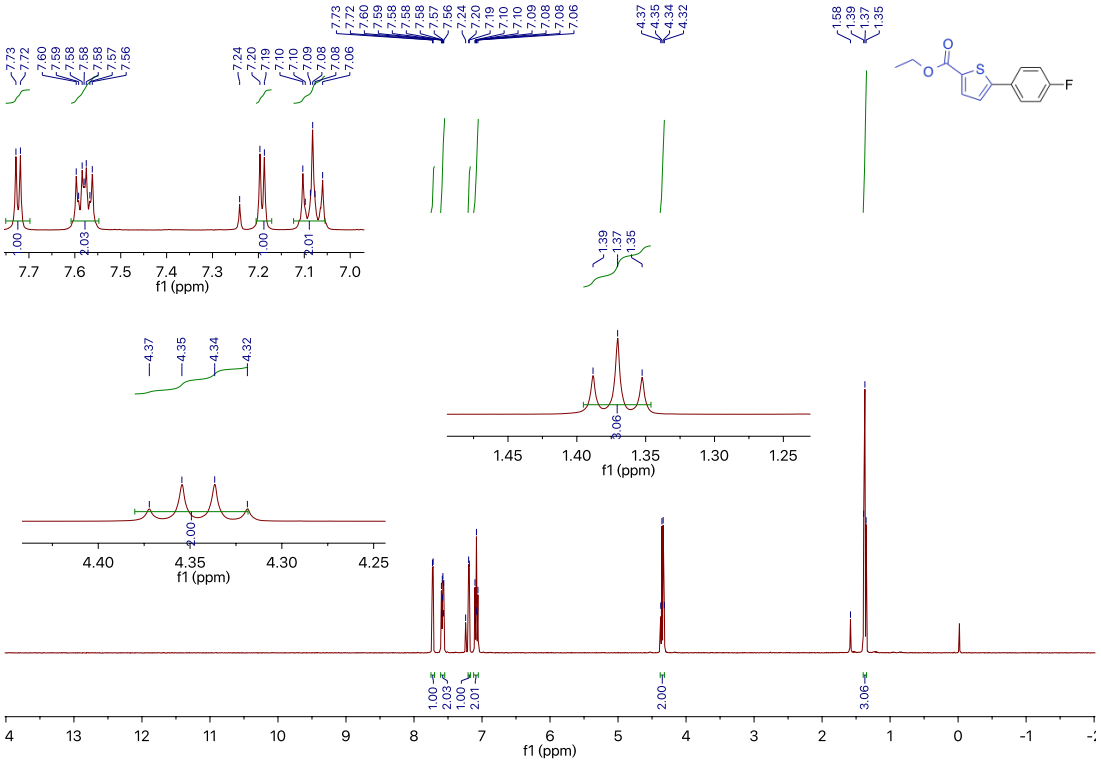
^{19}F spectrum of 2-(4-fluorophenyl)-4-phenylpyrimidine **2w** (376 MHz, $CDCl_3$)



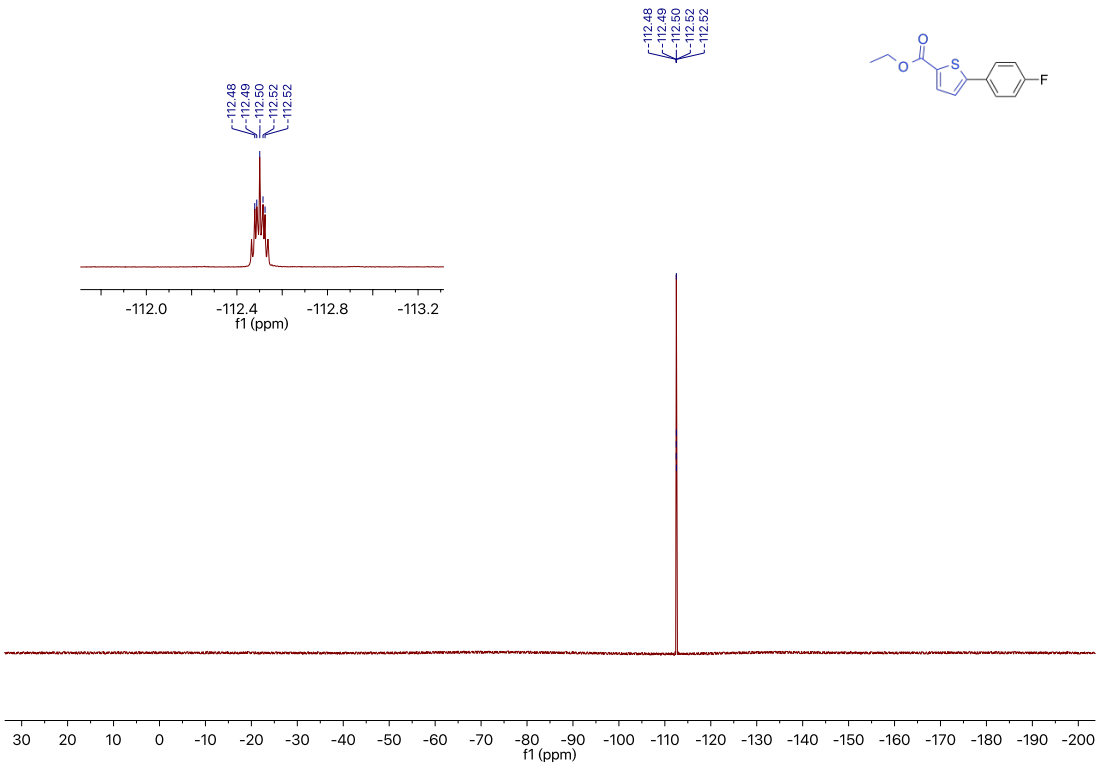
^{13}C spectrum of 2-(4-fluorophenyl)-4-phenylpyrimidine **2w** (101 MHz, $CDCl_3$)



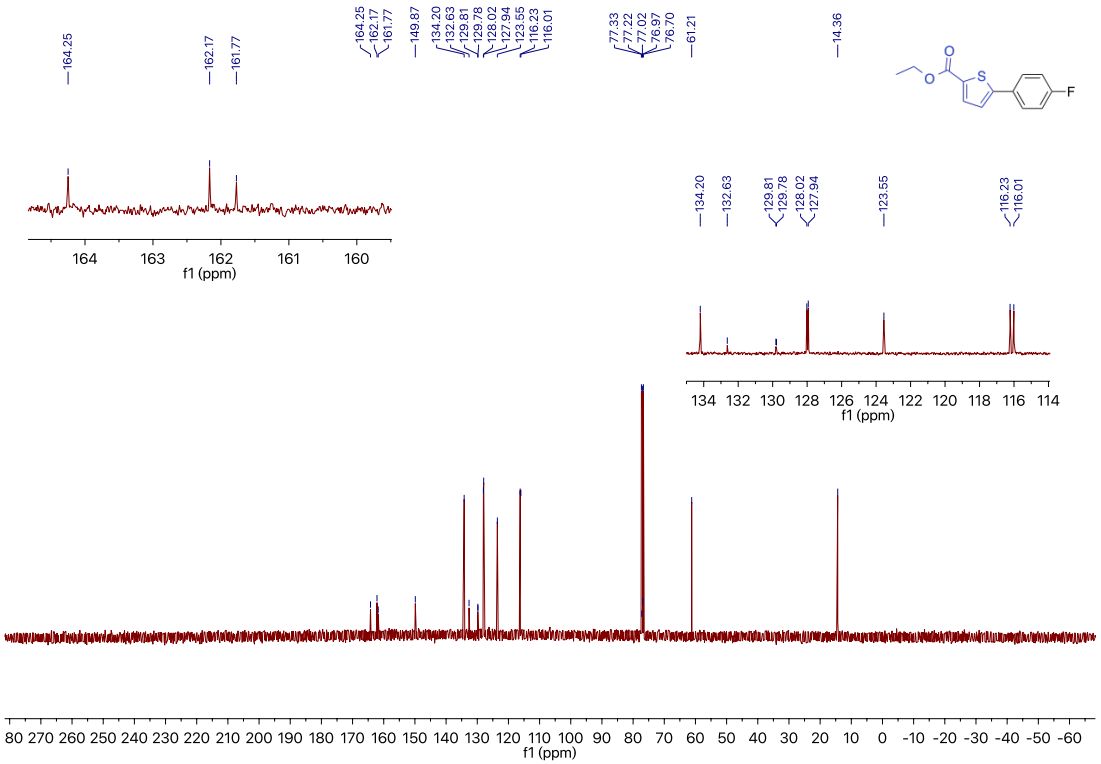
^{1}H spectrum of ethyl 5-(4-fluorophenyl)thiophene-2-carboxylate **2x** (400 MHz, $CDCl_3$)



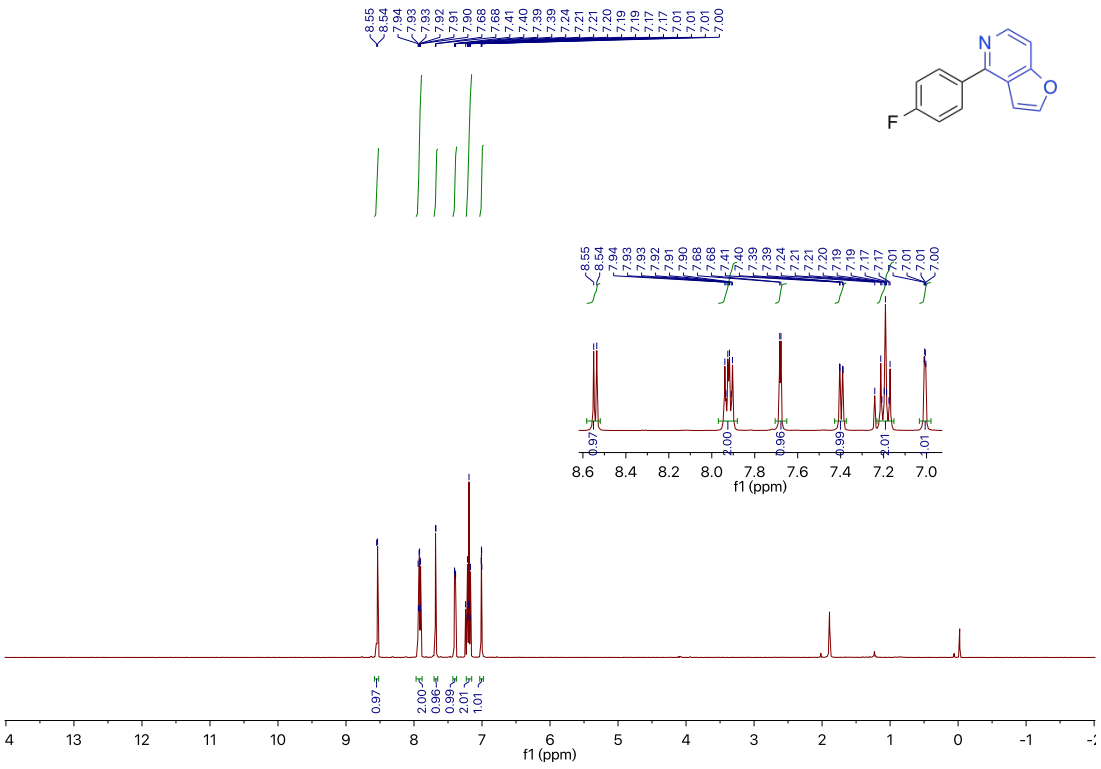
^{19}F spectrum of ethyl 5-(4-fluorophenyl)thiophene-2-carboxylate **2x** (376 MHz, $CDCl_3$)



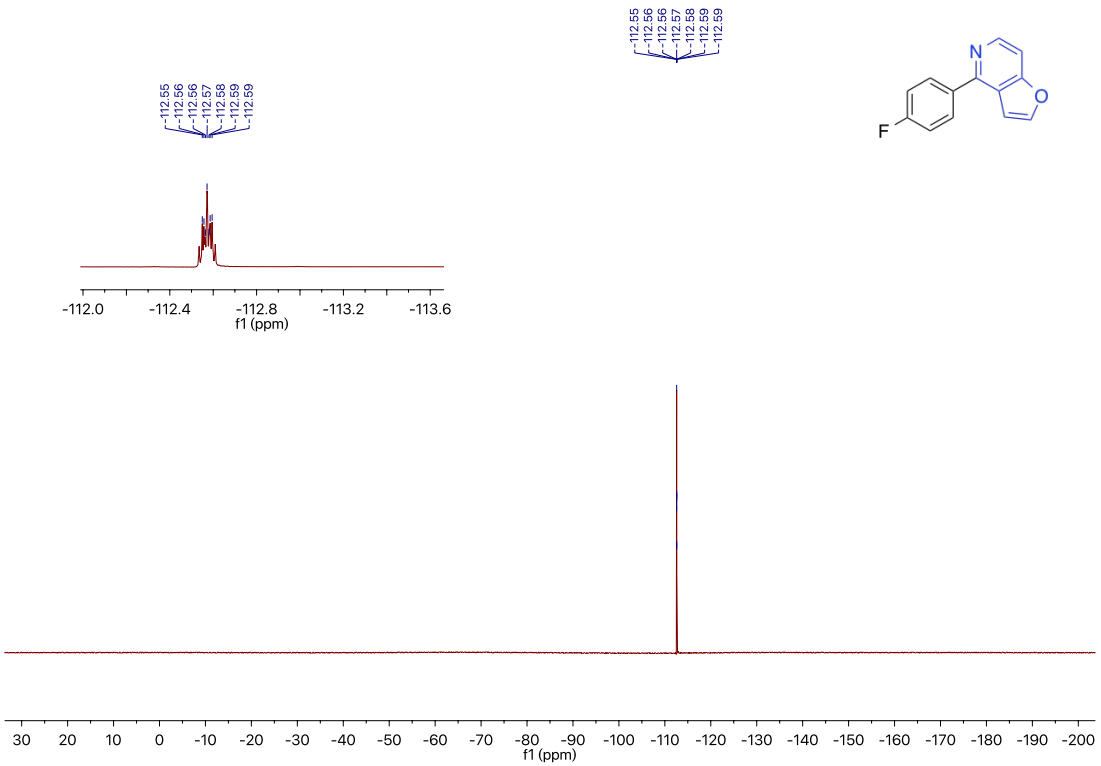
^{13}C spectrum of ethyl 5-(4-fluorophenyl)thiophene-2-carboxylate **2x** (101MHz, $CDCl_3$)



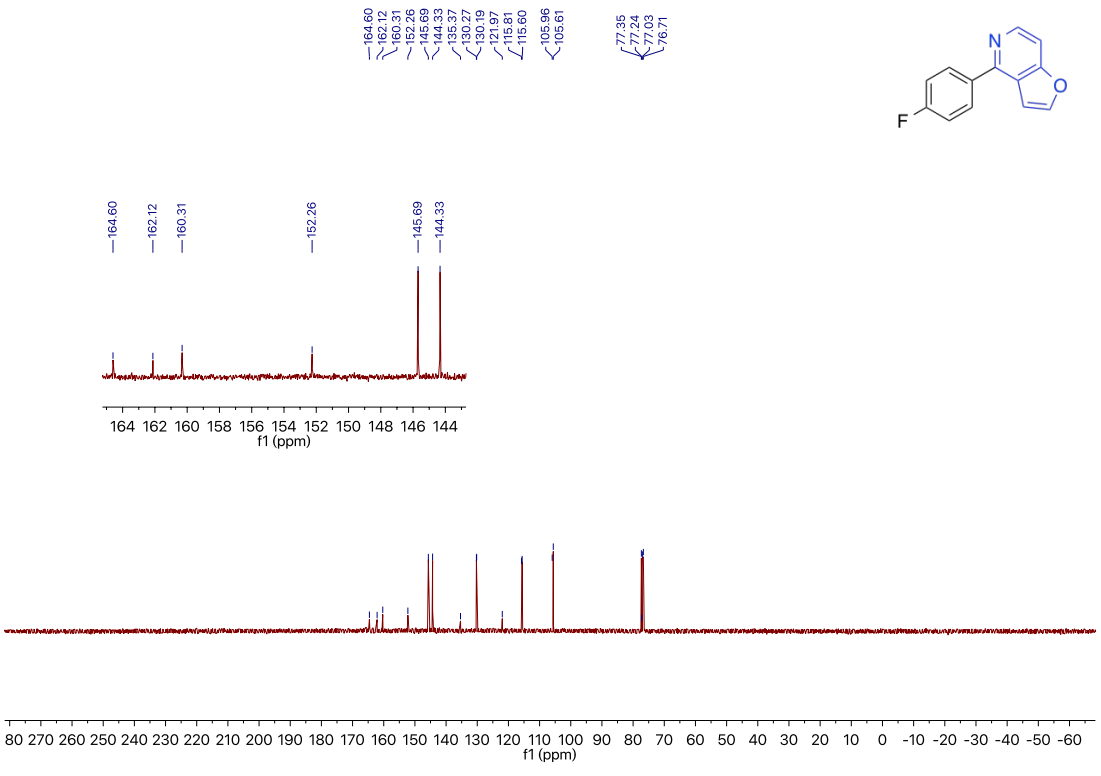
^{1}H spectrum of 4-(4-fluorophenyl)furo[3,2-c]pyridine **2y** (400 MHz, $CDCl_3$)



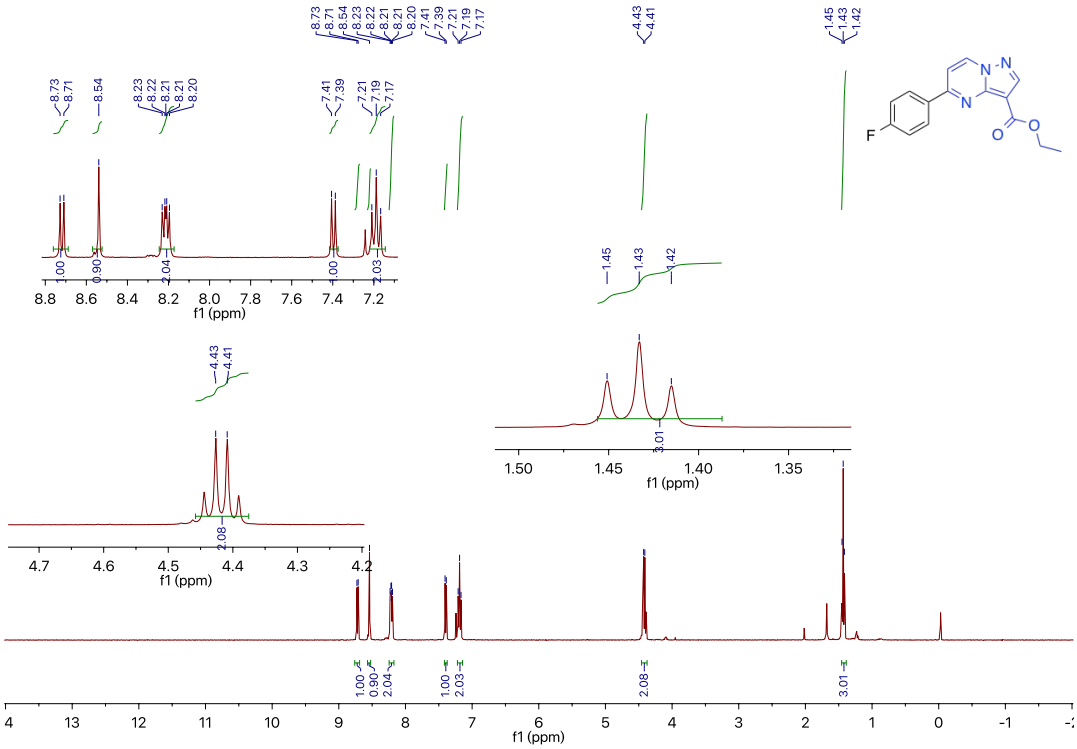
^{19}F spectrum of 4-(4-fluorophenyl)furo[3,2-c]pyridine **2y** (376 MHz, $CDCl_3$)



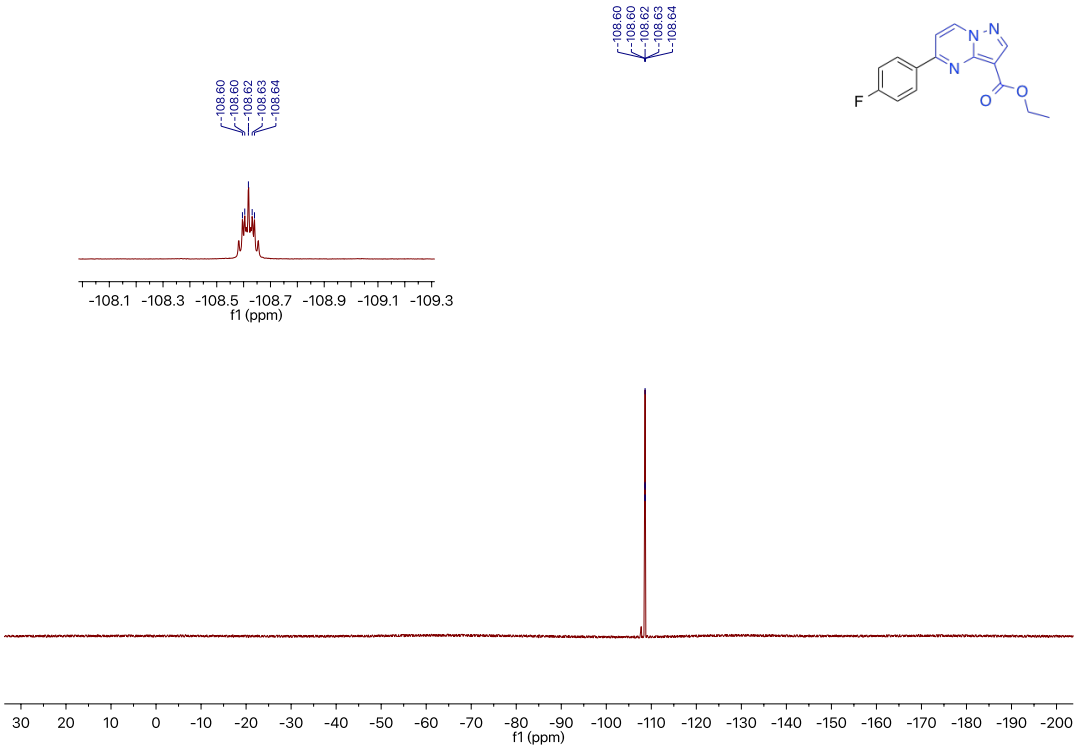
^{13}C spectrum of 4-(4-fluorophenyl)furo[3,2-c]pyridine **2y** (101 MHz, $CDCl_3$)



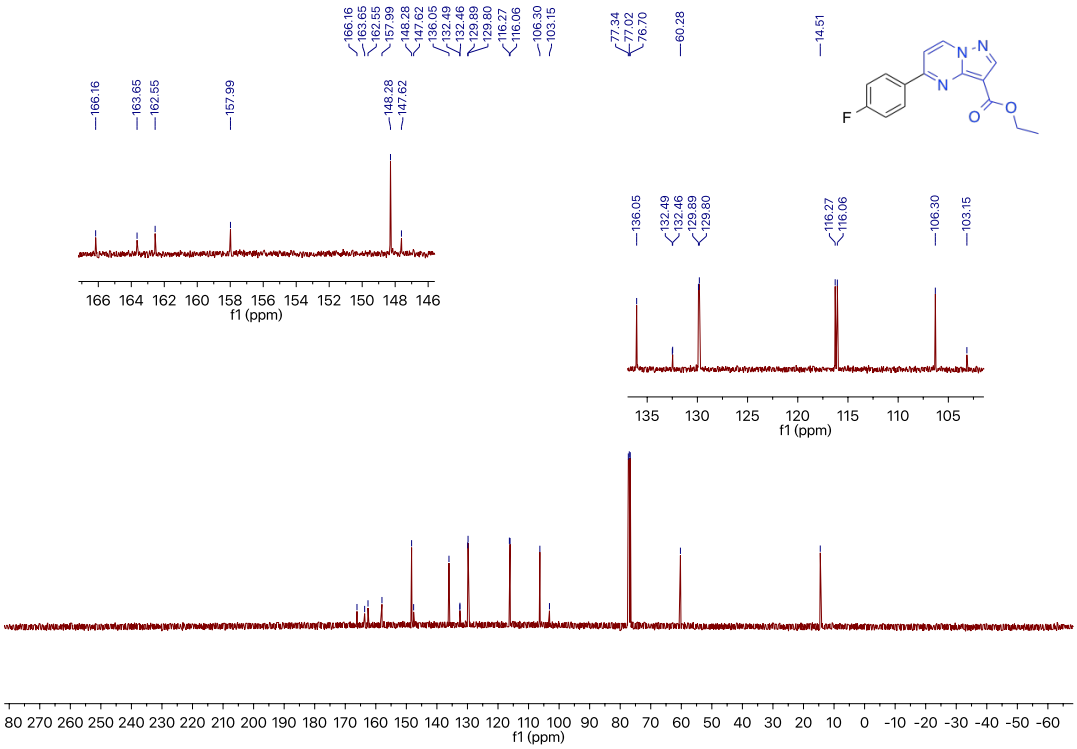
^{1}H spectrum of ethyl 5-(4-fluorophenyl)pyrazolo[1,5-a]pyrimidine-3-carboxylate **2z** (400 MHz, $CDCl_3$)



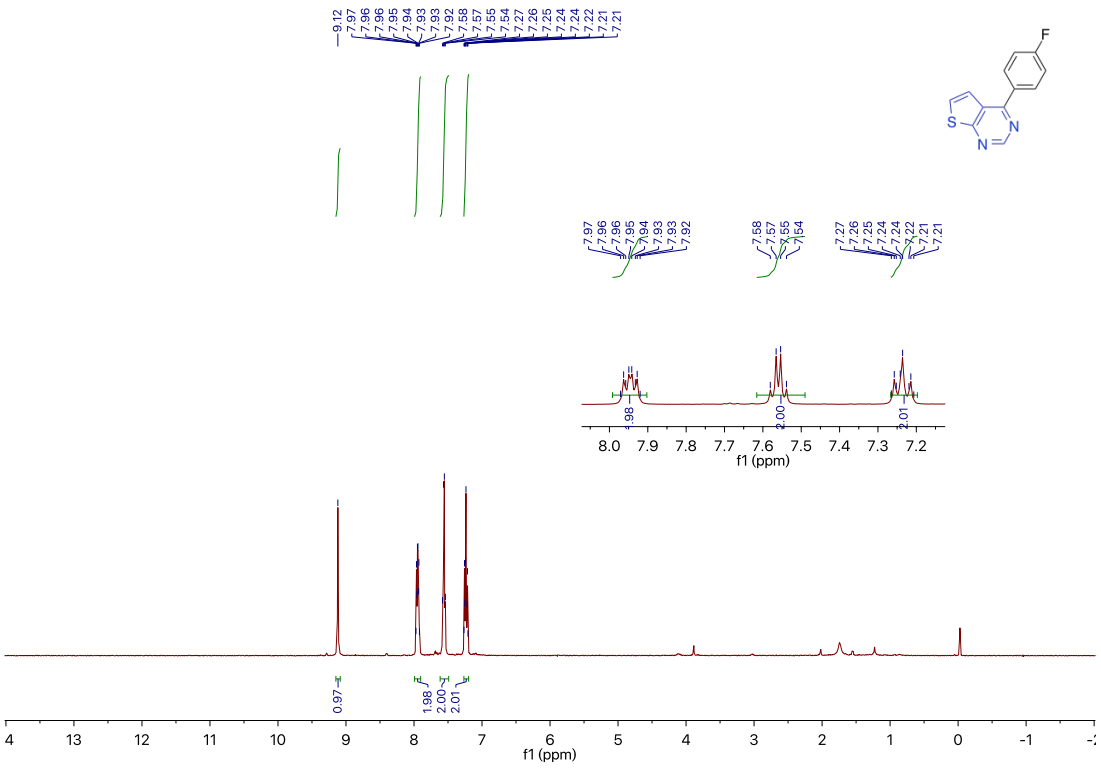
^{19}F spectrum of ethyl 5-(4-fluorophenyl)pyrazolo[1,5-a]pyrimidine-3-carboxylate **2z** (376 MHz, $CDCl_3$)



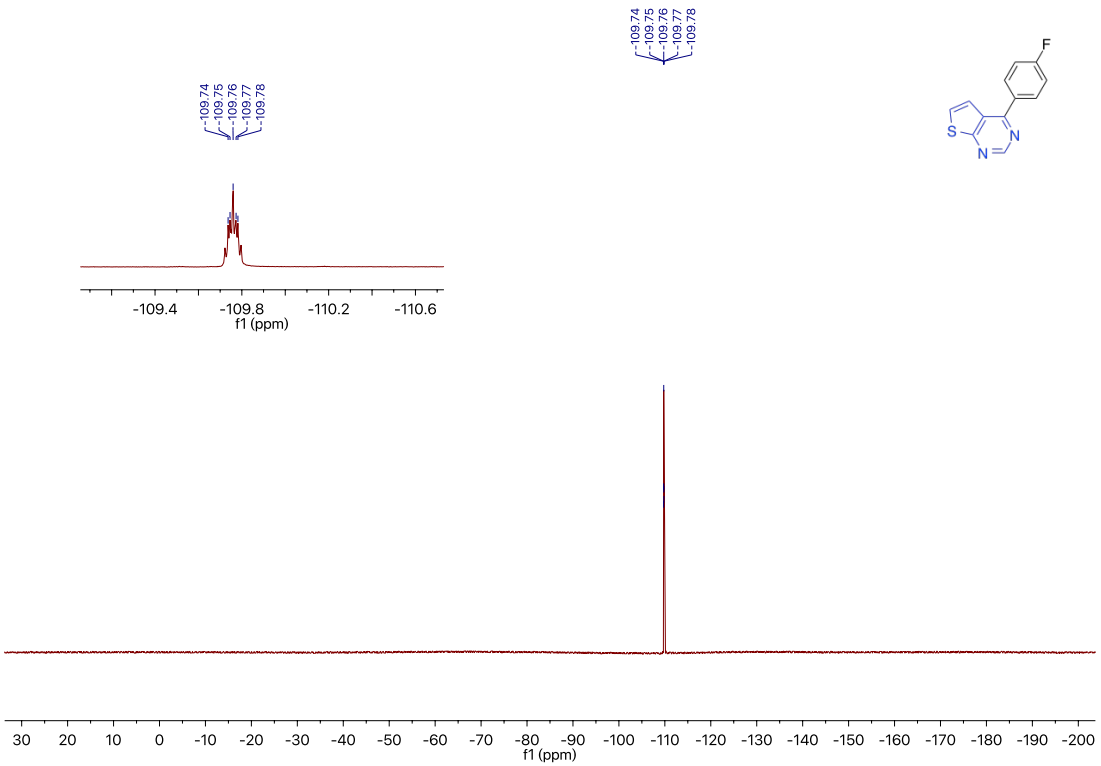
^{13}C spectrum of ethyl 5-(4-fluorophenyl)pyrazolo[1,5-a]pyrimidine-3-carboxylate **2z** (101 MHz, $CDCl_3$)



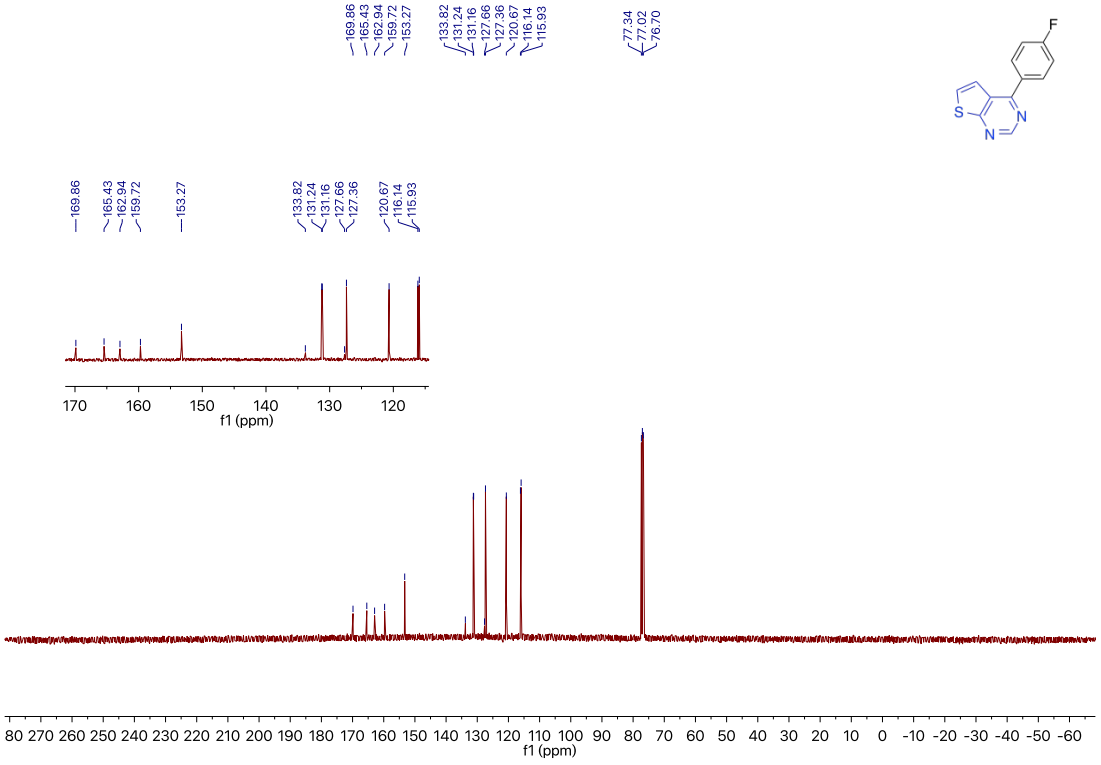
^{1}H spectrum of 4-(4-fluorophenyl)thieno[2,3-d]pyrimidine **2aa** (400 MHz, $CDCl_3$)



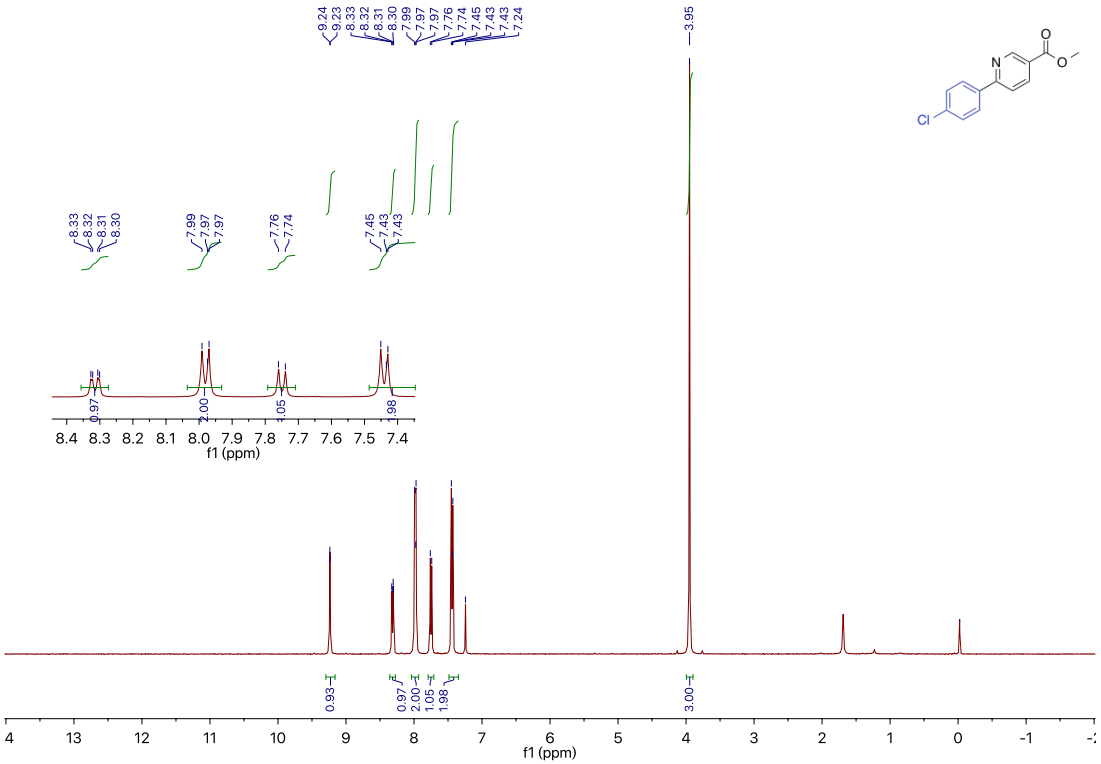
^{19}F spectrum of 4-(4-fluorophenyl)thieno[2,3-d]pyrimidine **2aa** (376 MHz, $CDCl_3$)



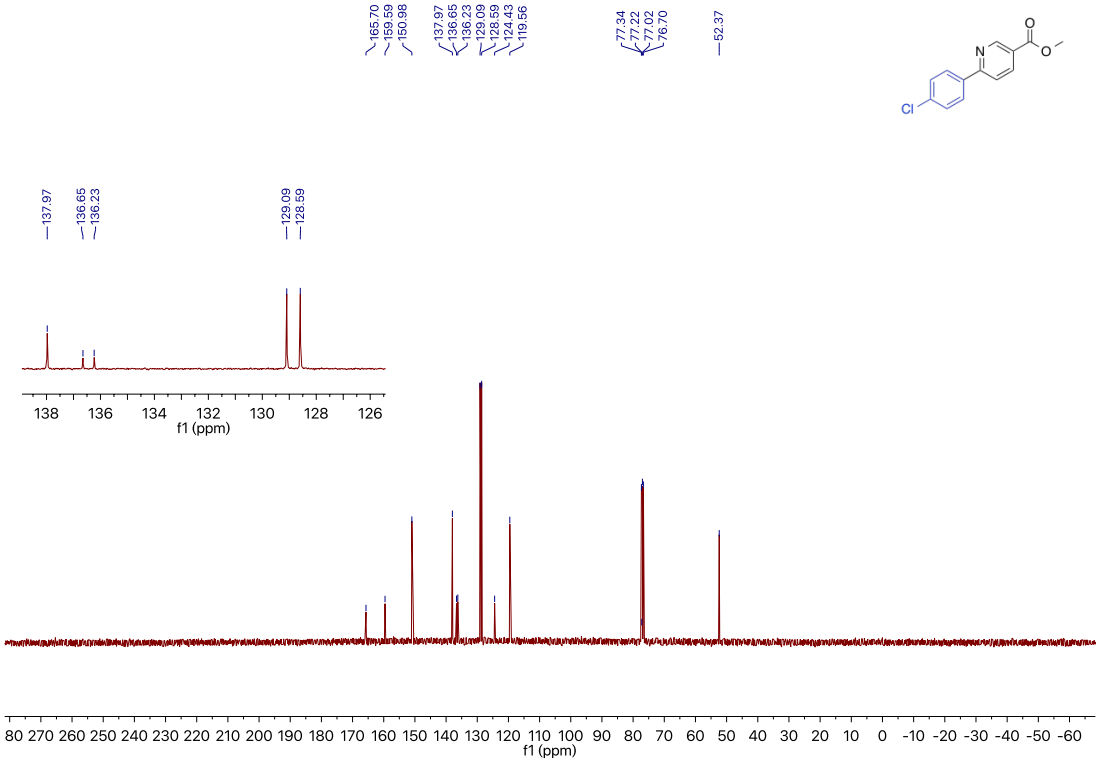
^{13}C spectrum of 4-(4-fluorophenyl)thieno[2,3-d]pyrimidine **2aa** (101 MHz, $CDCl_3$)



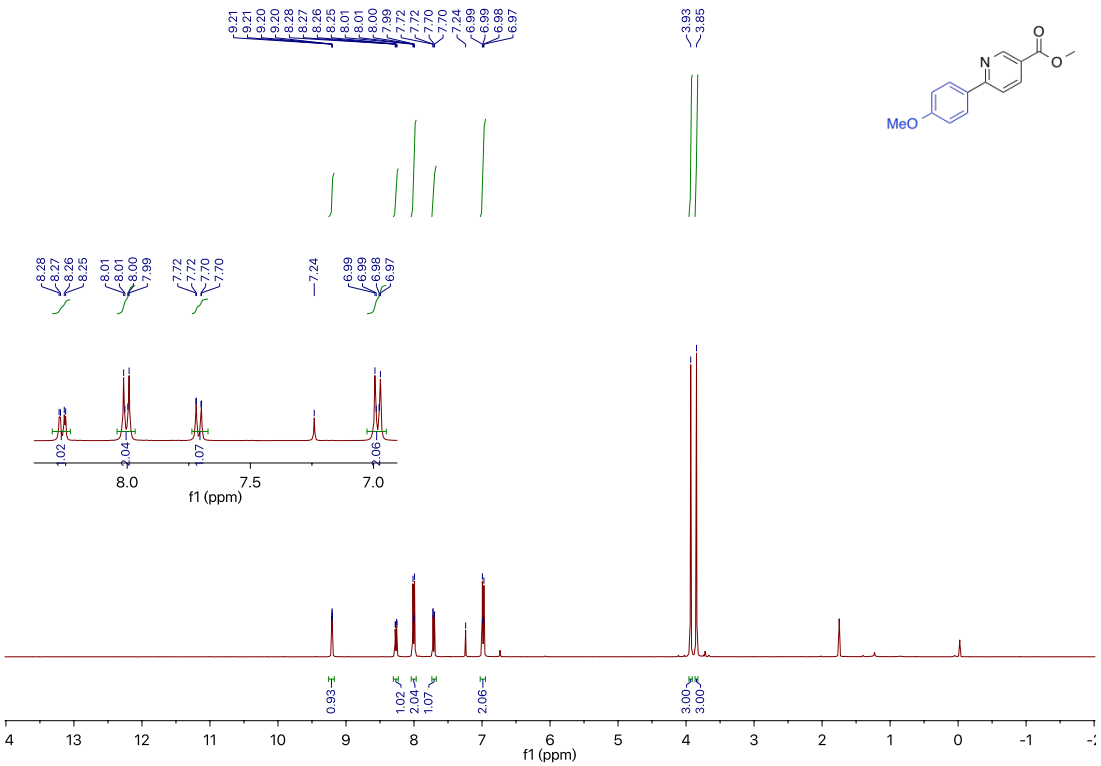
^{1}H spectrum of methyl 6-(4-chlorophenyl)nicotinate **2ab** (400 MHz, $CDCl_3$)



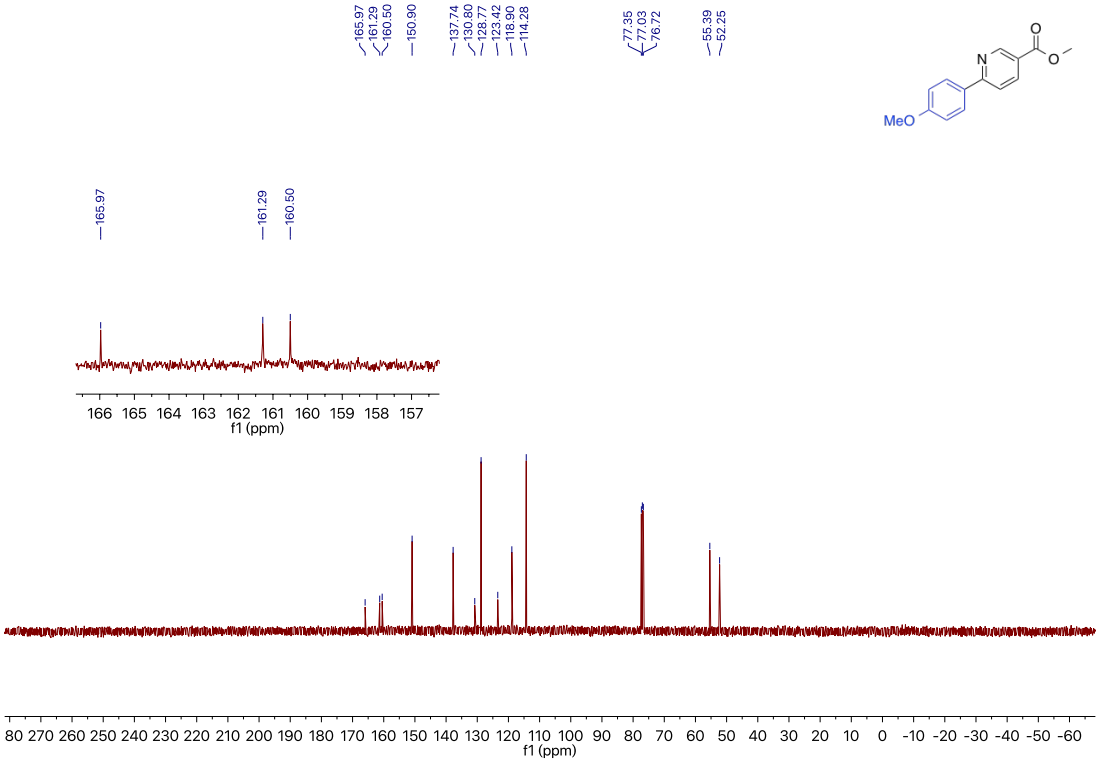
^{13}C spectrum of methyl 6-(4-chlorophenyl)nicotinate **2ab** (101 MHz, $CDCl_3$)



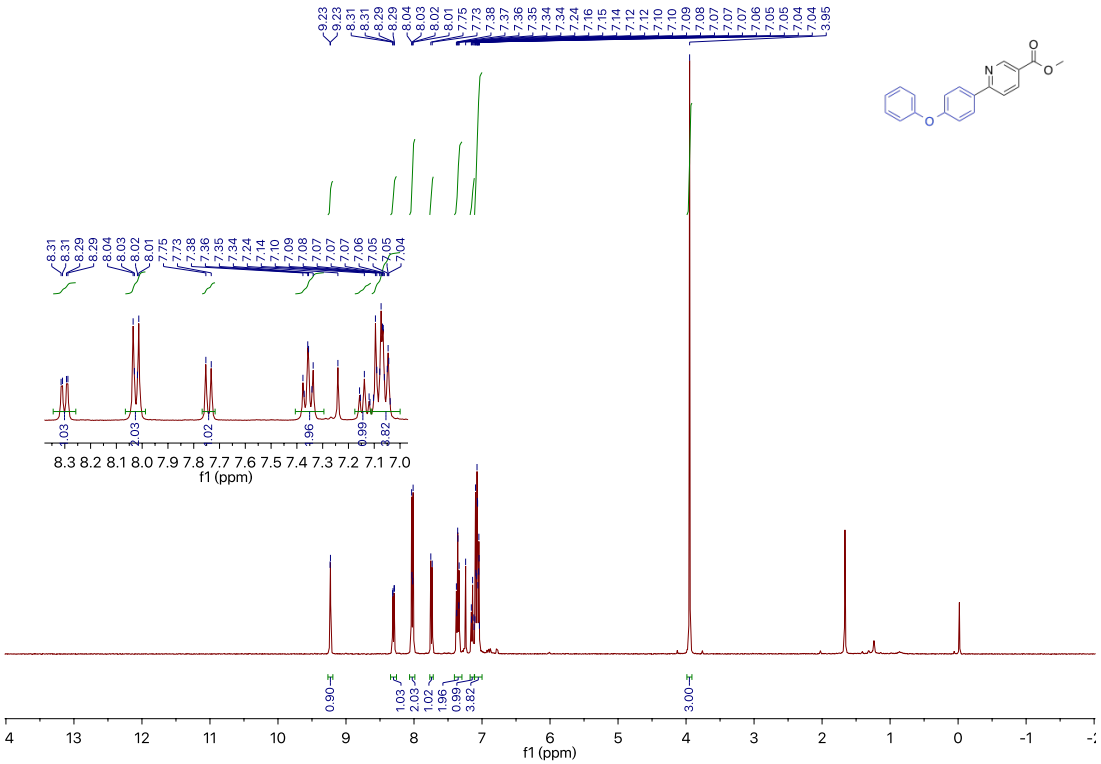
^{1}H spectrum of methyl 6-(4-methoxyphenyl)nicotinate **2ac** (400 MHz, $CDCl_3$)



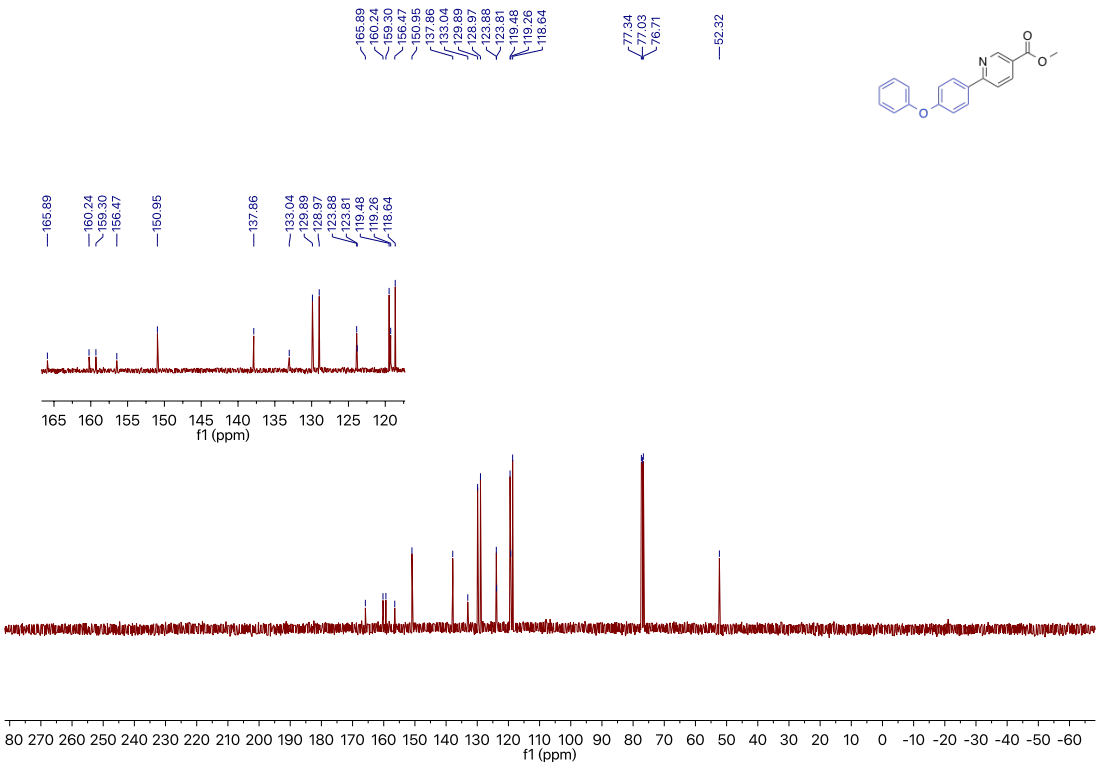
^{13}C spectrum of methyl 6-(4-methoxyphenyl)nicotinate **2ac** (101 MHz, $CDCl_3$)



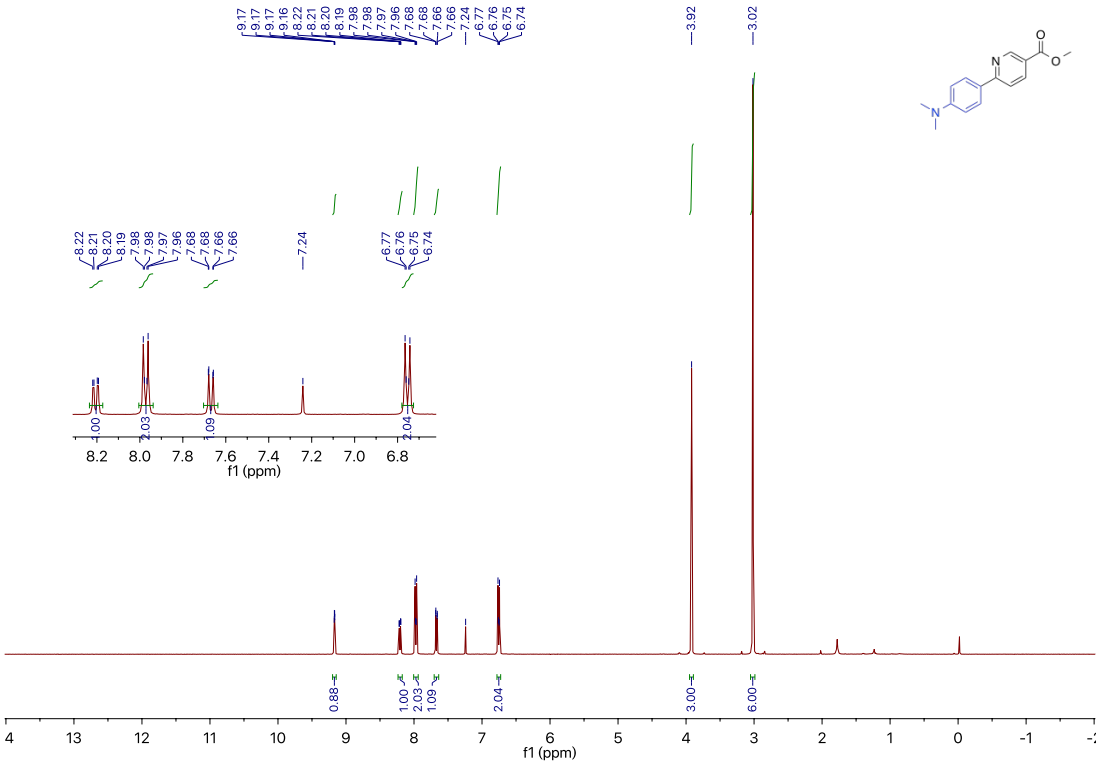
^{1}H spectrum of methyl 6-(4-phenoxyphenyl)nicotinate **2ad** (400 MHz, $CDCl_3$)



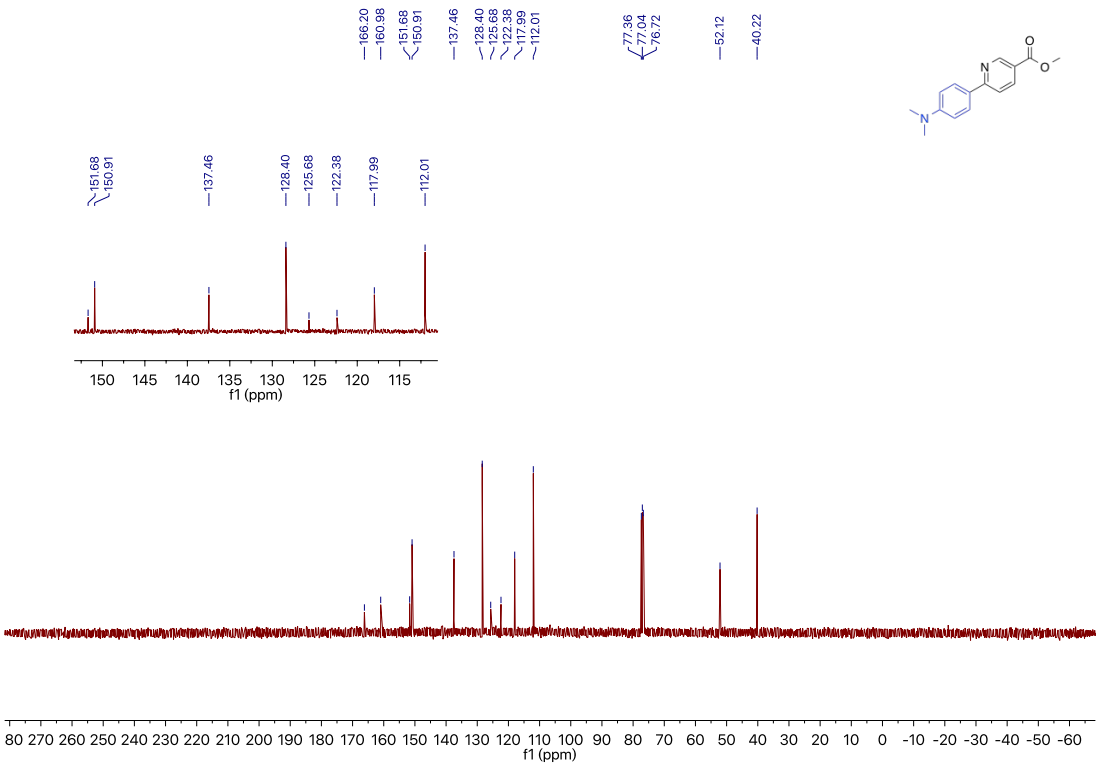
^{13}C spectrum of methyl 6-(4-phenoxyphenyl)nicotinate **2ad** (101 MHz, $CDCl_3$)



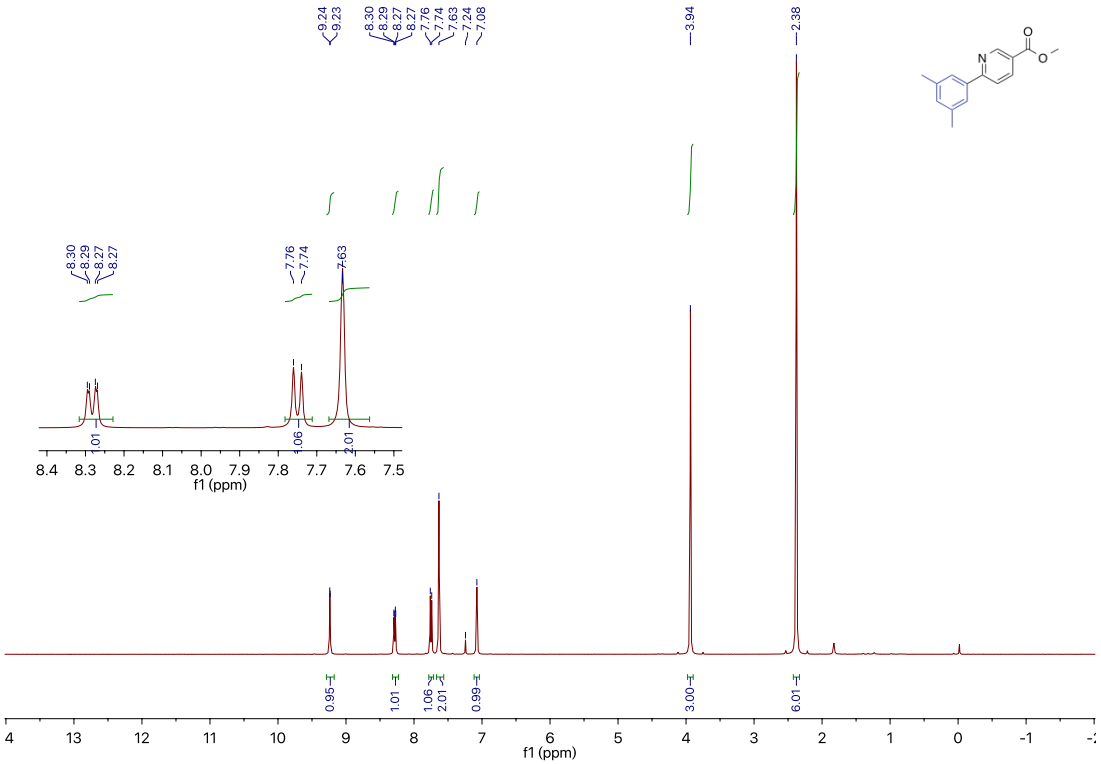
^{1}H spectrum of methyl 6-(4-(dimethylamino)phenyl)nicotinate **2ae** (400 MHz, $CDCl_3$)



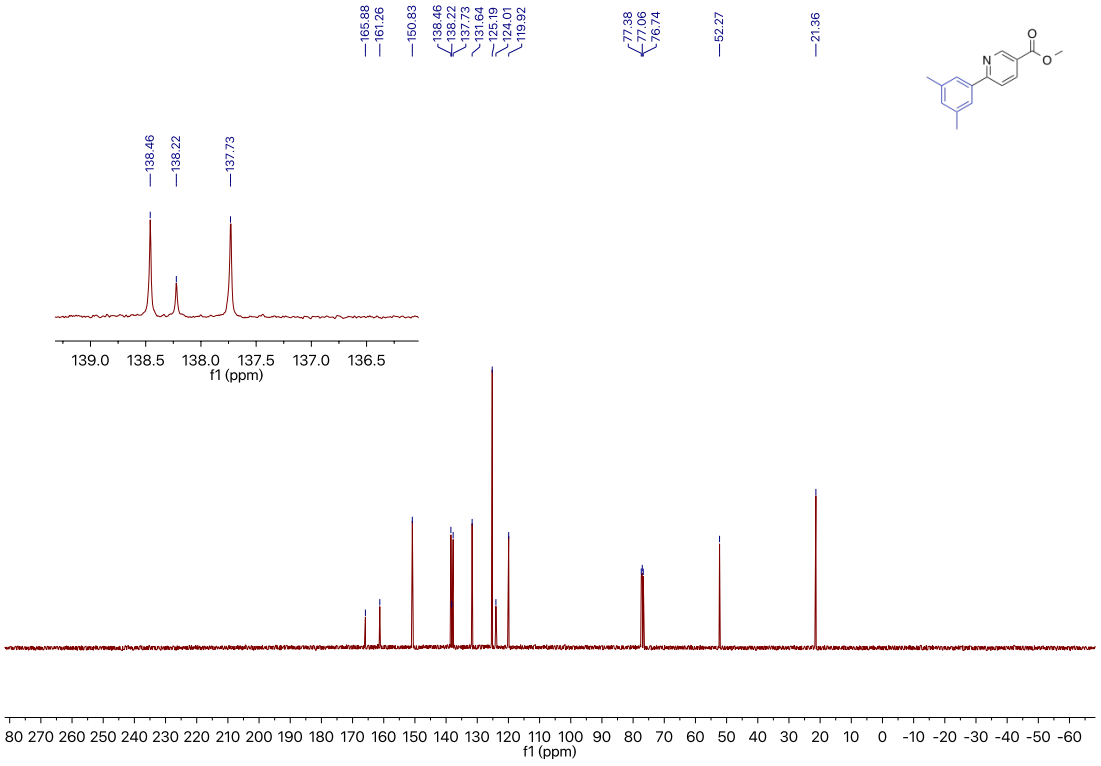
^{13}C spectrum of methyl 6-(4-(dimethylamino)phenyl)nicotinate **2ae** (101 MHz, $CDCl_3$)



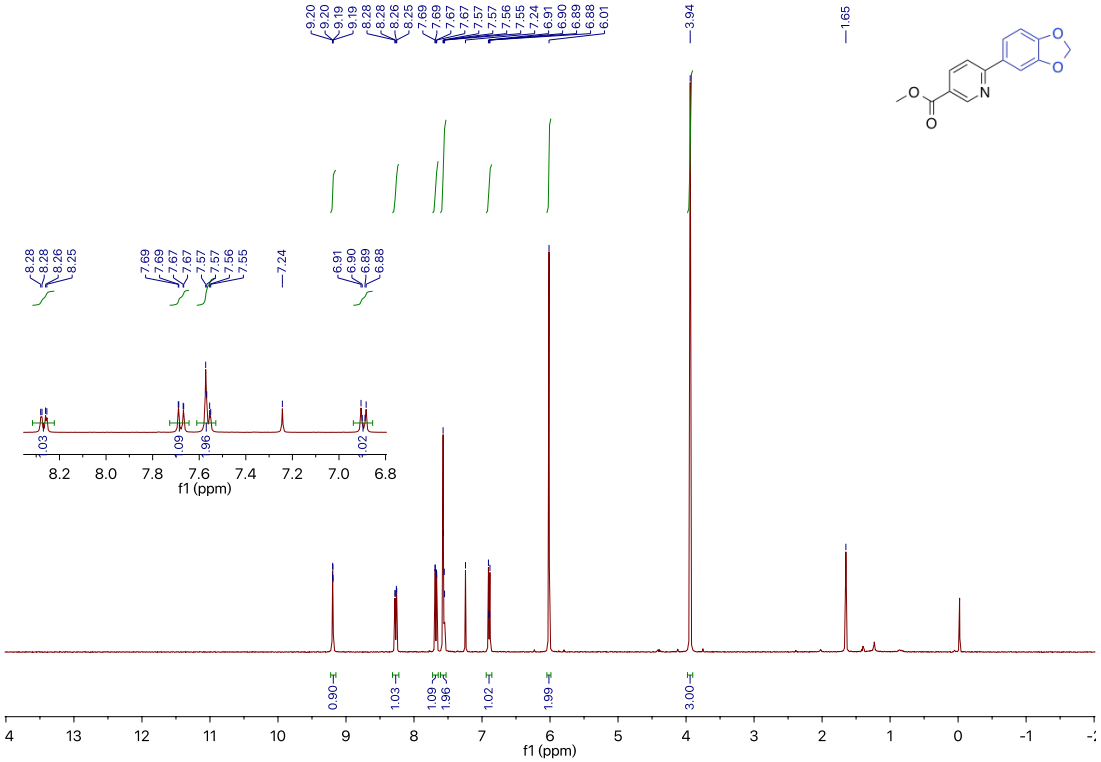
^{1}H spectrum of methyl 6-(3,5-dimethylphenyl)nicotinate **2af** (400 MHz, $CDCl_3$)



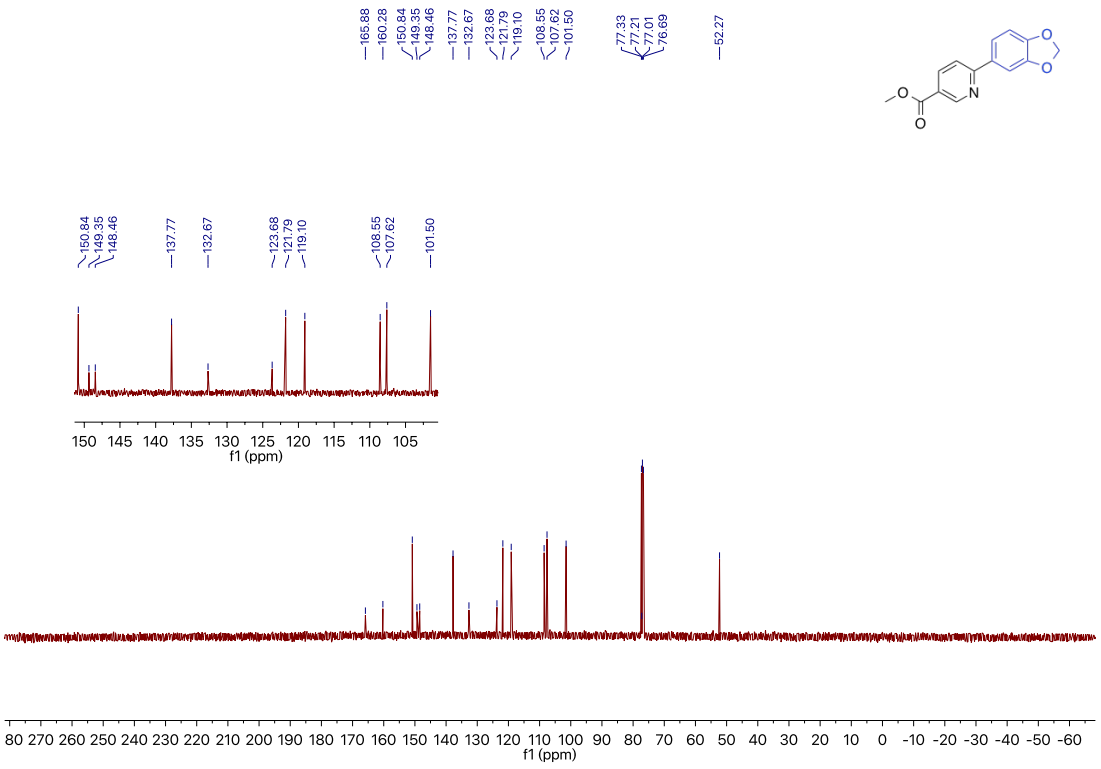
^{13}C spectrum of methyl 6-(3,5-dimethylphenyl)nicotinate **2af** (101 MHz, $CDCl_3$)



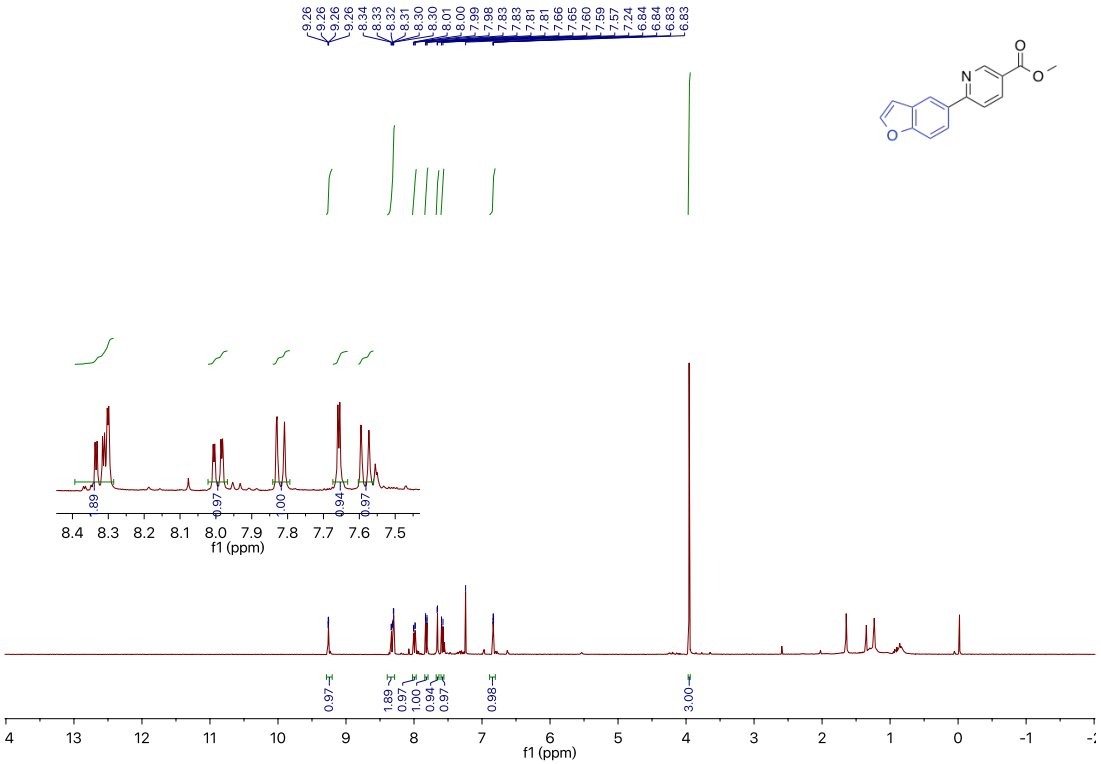
^{1}H spectrum of methyl 6-(benzo[d][1,3]dioxol-5-yl)nicotinate **2ag** (400 MHz, $CDCl_3$)



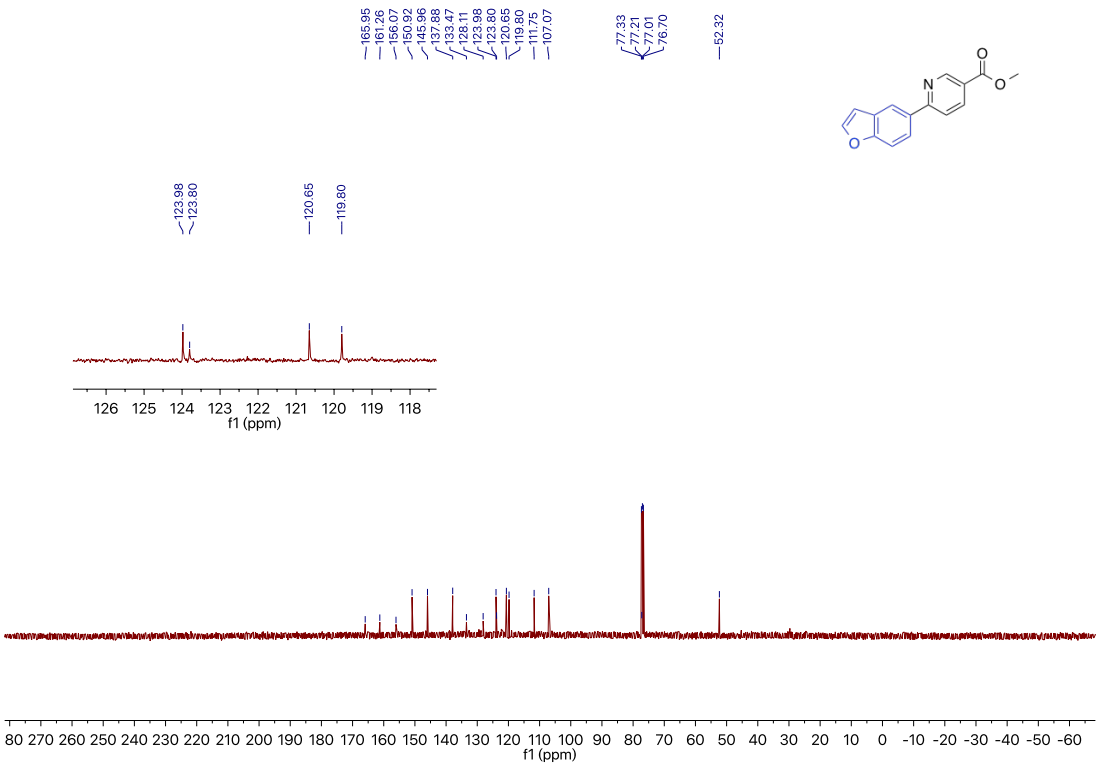
^{13}C spectrum of methyl 6-(benzo[d][1,3]dioxol-5-yl)nicotinate **2ag** (101 MHz, $CDCl_3$)



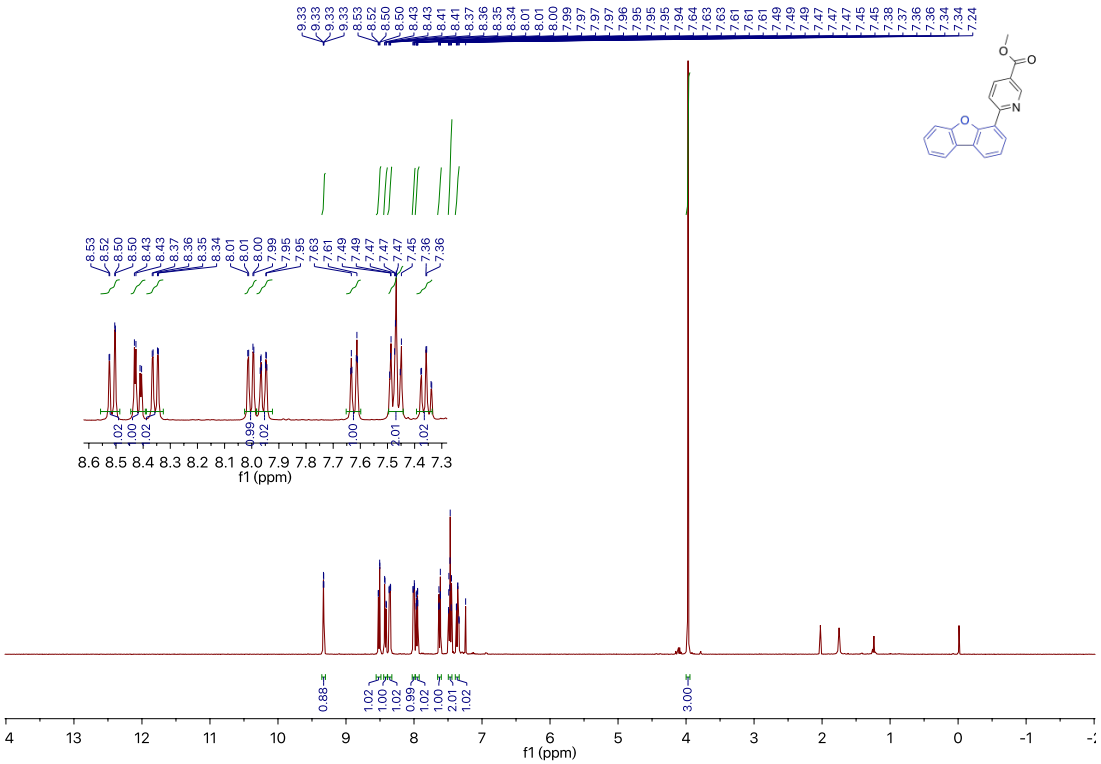
^{1}H spectrum of methyl 6-(benzofuran-5-yl)nicotinate **2ah** (400 MHz, $CDCl_3$)



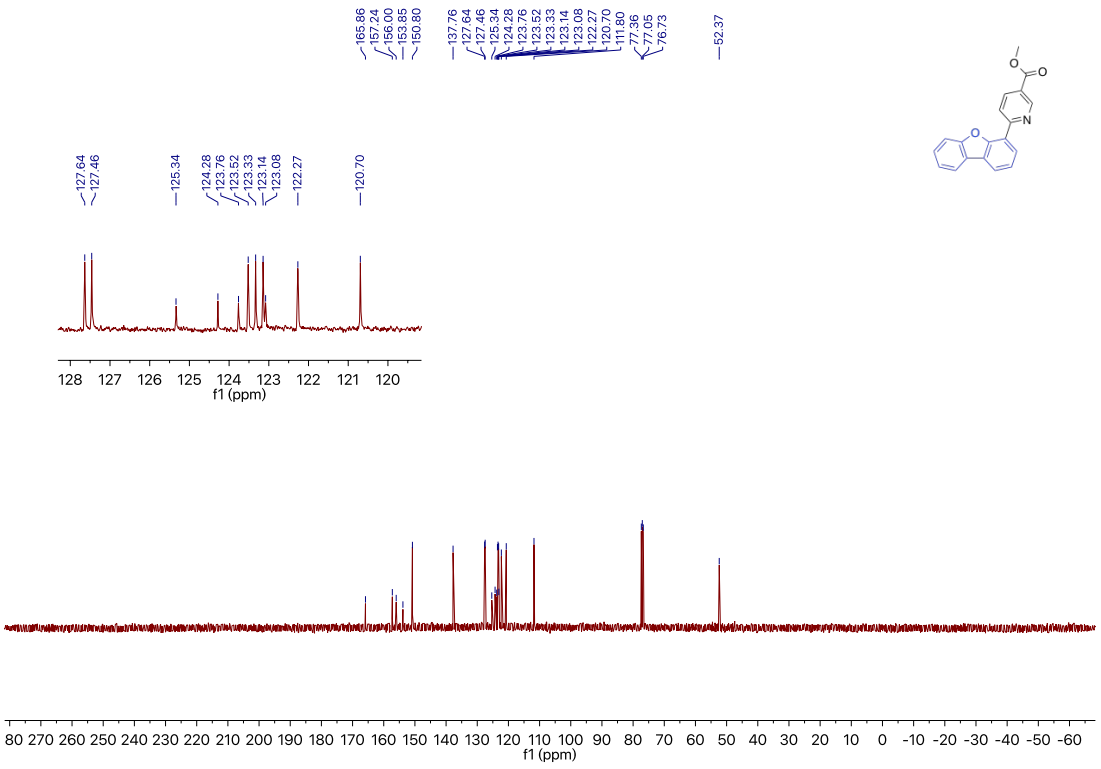
^{13}C spectrum of methyl 6-(benzofuran-5-yl)nicotinate **2ah** (101 MHz, $CDCl_3$)



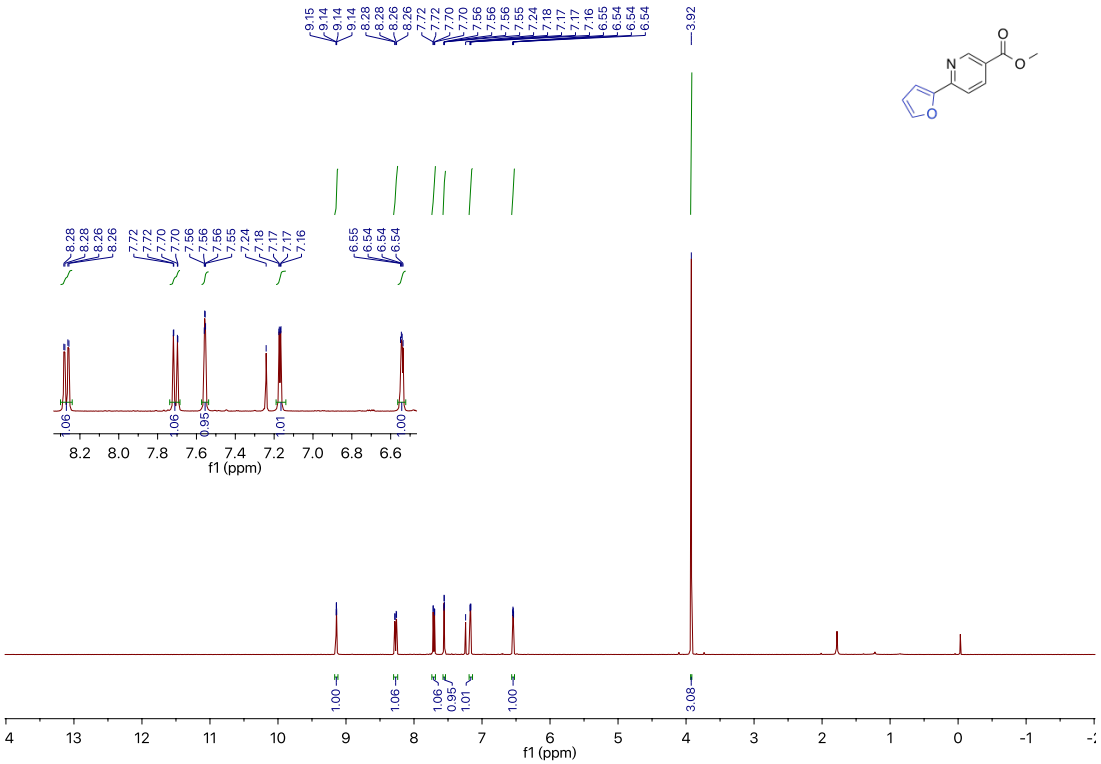
^{1}H spectrum of methyl 6-(dibenzo[b,d]furan-4-yl)nicotinate **2ai** (400 MHz, $CDCl_3$)



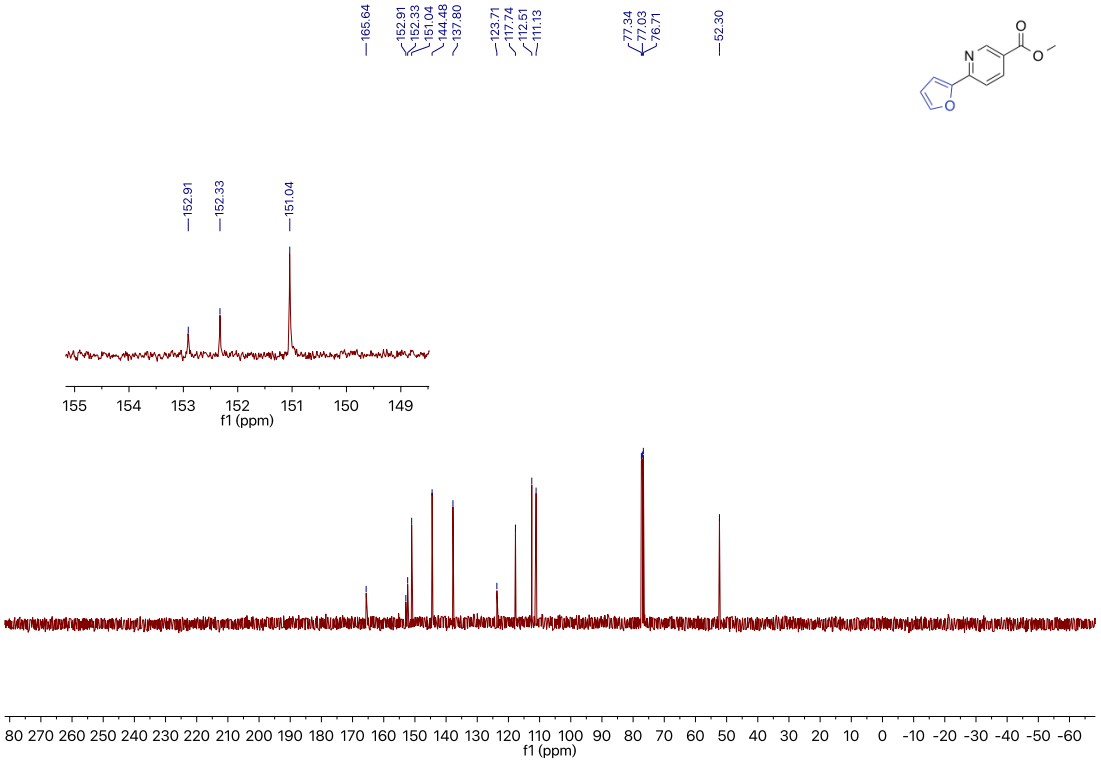
^{13}C spectrum of methyl 6-(dibenzo[b,d]furan-4-yl)nicotinate **2ai** (101 MHz, $CDCl_3$)



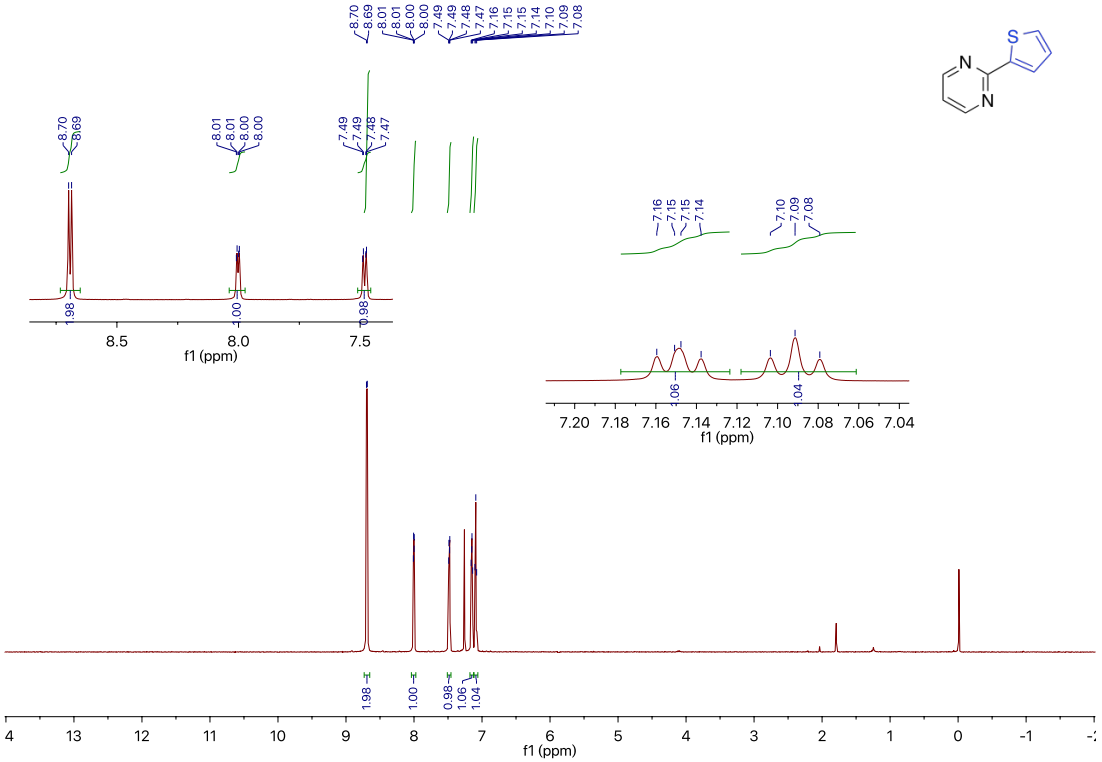
^{1}H spectrum of methyl 6-(furan-2-yl)nicotinate **2aj** (400 MHz, $CDCl_3$)



^{13}C spectrum of methyl 6-(furan-2-yl)nicotinate **2aj** (101 MHz, $CDCl_3$)



^{1}H spectrum of 2-(thiophen-2-yl)pyrimidine **2ak** (400 MHz, $CDCl_3$)



^{13}C spectrum of 2-(thiophen-2-yl)pyrimidine **2ak** (101 MHz, $CDCl_3$)