

Supporting Information for:

Direct Access to 2-(Hetero)arylated Pyridines from 6-Substituted 2-Bromopyridines *via* Phosphine-Free Palladium-Catalyzed C–H Bond Arylations: The Importance of the C6 Substituent

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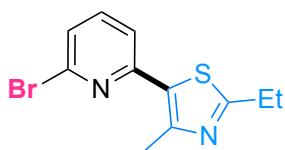
General information: All reactions were carried out under argon atmosphere with standard Schlenk techniques. DMA was purchased from Acros Organics and was not purified before use. ¹H NMR spectra were recorded on Bruker GPX (400 MHz) spectrometer. Chemical shifts (δ) were reported in parts per million relative to residual chloroform (7.26 ppm for ¹H; 77.0 ppm for ¹³C), constants were reported in Hertz. ¹H NMR assignment abbreviations were the following: singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), doublet of triplets (dt), and multiplet (m). ¹³C NMR spectra were recorded at 100 MHz on the same spectrometer and reported in ppm. All reagents were weighed and handled in air.

General Procedure A: As a typical experiment, the reaction of 2,6-dibromopyridine (355 mg, 1.5 mmol), (hetero)arene derivative (1 mmol), CF₃CO₂K (2 equiv. 304 mg) at 150 °C during 5 h in DMA (4 mL) in the presence of Pd(OAc)₂ (1 mol%) (see tables or schemes) under argon affords the desired product after evaporation of the solvent and purification by silica column chromatography.

General Procedure B: As a typical experiment, the reaction of 2,5-dibromopyridine (237 mg, 1 mmol), (hetero)arene derivative (2.5 mmol), KOAc (2 equiv., 196 mg) at 150 °C during 16 h in DMA (4 mL) in the presence of Pd(OAc)₂ (1 mol%) (see tables or schemes) under argon affords the desired product after evaporation of the solvent and purification by silica column chromatography.

General Procedure C: As a typical experiment, the reaction of the 6-substituted 2-bromopyridine (1 mmol), (hetero)arene derivative (1.5 mmol), KOAc (2 equiv., 196 mg) at 150 °C during 16 h in DMA (4 mL) in the

presence of Pd(OAc)₂ (1 mol%) (see tables or schemes) under argon affords the desired product after evaporation of the solvent and purification by silica column chromatography.

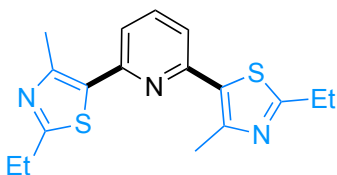


5-(6-Bromopyridin-2-yl)-2-ethyl-4-methylthiazole (2): Following the general procedure **A** using 2,6-dibromopyridine (355 mg, 1.5 mmol) and 2-ethyl-4-methylthiazole (127 mg, 1 mmol), the residue was purified by flash chromatography on silica gel to afford the desired compound **2** (249 mg, 88%).

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.51 (t, *J* = 7.8 Hz, 1H), 7.42 (dd, *J* = 1.0 and 7.8 Hz, 1H), 7.29 (dd, *J* = 1.0 and 7.8 Hz, 1H), 2.96 (q, *J* = 7.6 Hz, 2H), 2.61 (s, 3H), 1.36 (t, *J* = 7.6 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ (ppm) 172.6, 152.8, 150.2, 141.5, 138.7, 130.1, 125.6, 120.2, 27.0, 17.5, 14.1.

Elemental analysis: calcd (%) C₁₁H₁₁BrN₂S for (283.18): C 46.66, H 3.92; found: C 46.97, H 3.51.



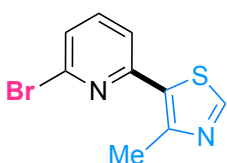
2,6-Bis(2-ethyl-4-methylthiazol-5-yl)pyridine (3): Following the general procedure **B** using 2,6-dibromopyridine (237 mg, 1 mmol) and 2-ethyl-4-methylthiazole (318 mg, 2.5 mmol), the residue was purified by flash chromatography on silica gel to afford the desired compound **3** (300 mg, 91%).

91%).

¹H NMR (300 MHz, CDCl₃) δ (ppm) 7.54 (t, *J* = 7.7 Hz, 1H), 7.43 (d, *J* = 7.7 Hz, 1H), 7.33 (d, *J* = 7.7 Hz, 1H), 2.98 (q, *J* = 7.6 Hz, 4H), 2.30 (s, 6H), 1.38 (t, *J* = 7.6 Hz, 6H).

¹³C NMR (75 MHz, CDCl₃) δ (ppm) 172.4, 150.8, 141.5, 138.7, 125.6, 120.2, 26.9, 15.8, 14.1

Elemental analysis: calcd (%) C₁₇H₁₉N₃S₂ for (329.48): C 61.97, H 5.81; found: C 62.08, H 5.46.

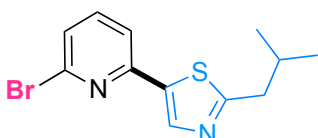


5-(6-Bromopyridin-2-yl)-4-methylthiazole (4): Following the general procedure **A** using 2,6-dibromopyridine (355 mg, 1.5 mmol) and 4-methylthiazole (99 mg, 1 mmol), the residue was purified by flash chromatography on silica gel to afford the desired compound **4** (117 mg, 46%).

¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.72 (s, 1H), 7.58 (t, *J* = 7.8 Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.37 (d, *J* = 7.7 Hz, 1H), 2.72 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ (ppm) 152.5, 151.4, 141.7, 138.9, 131.3, 126.2, 120.6, 17.6.

Elemental analysis: calcd (%) C₉H₇BrN₂S for (255.13): C 42.37, H 2.77; found: C 42.54, H 3.09.



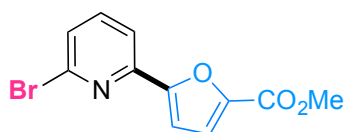
5-(6-Bromopyridin-2-yl)-2-isobutylthiazole (5): Following the general procedure **A** using 2,6-dibromopyridine (355 mg, 1.5 mmol) and 2-isobutylthiazole (141 mg, 1 mmol), the residue was purified by flash

chromatography on silica gel to afford the desired compound **5** (232 mg, 78%).

¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.11 (s, 1H), 7.55-7.72 (m, 2H), 7.34 (dd, *J* = 3.1 and 5.5 Hz, 1H), 2.89 (d, *J* = 7.2 Hz, 2H), 2.15-2.11 (m, 1H), 1.01 (d, *J* = 6.6 Hz, 6H).

¹³C NMR (100 MHz, CDCl₃) δ (ppm) 173.0, 151.8, 141.9, 140.3, 138.9, 137.6, 126.4, 118.2, 42.7, 29.9, 22.3.

Elemental analysis: calcd (%) C₁₂H₁₃BrN₂S for (297.21): C 48.49, H 4.41; found: C 48.62, H 4.76.



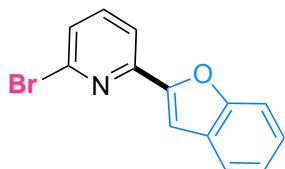
Methyl 5-(6-bromopyridin-2-yl)furan-2-carboxylate (6): Following the general procedure **A** using 2,6-dibromopyridine (355 mg, 1.5 mmol) and methyl furan-2-carboxylate (126 mg, 1 mmol), the residue was purified by flash chromatography on silica gel to afford the desired compound **6** (169 mg, 60%).

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.86 (d, *J* = 7.7 Hz, 1H), 7.62 (t, *J* = 7.7 Hz, 1H), 7.43 (d, *J* = 7.7 Hz, 1H), 7.29 (d, *J* = 3.6 Hz, 1H), 7.24 (d, *J* = 3.6 Hz, 1H), 3.94 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ (ppm) 154.2, 150.5, 144.3, 140.1, 137.4, 134.3, 122.8, 115.1, 113.4, 106.6, 47.3.

Elemental analysis: calcd (%) C₁₁H₈BrNO₃ for (282.09): C 46.84, H 2.86; found: C 46.98, H 3.02.

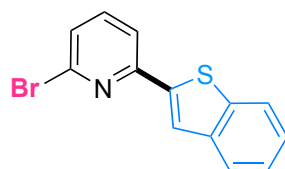
2-(Benzofuran-2-yl)-6-bromopyridine (7): Following the general procedure **A** using 2,6-dibromopyridine (355 mg, 1.5 mmol) and benzofuran (118 mg, 1 mmol), the residue was purified by flash chromatography on silica gel to afford the desired compound **7** (233 mg, 85%).



¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.90-7.84 (m, 1H), 7.70-7.61 (m, 2H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.54 (s, 1H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.37 (dt, *J* = 1.0 and 7.6 Hz, 1H), 7.32-7.26 (m, 1H).

¹³C NMR (100 MHz, CDCl₃) δ (ppm) 155.4, 153.6, 150.2, 142.2, 138.9, 128.3, 127.1, 125.6, 123.3, 121.9, 118.2, 111.5, 106.3.

Elemental analysis: calcd (%) C₁₃H₈BrNO for (274.12): C 56.96, H 2.94; found: C 57.18, H 3.06.

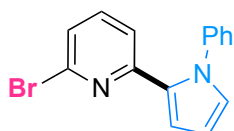


2-(Benzo[b]thiophen-2-yl)-6-bromopyridine (8): Following the general procedure **A** using 2,6-dibromopyridine (355 mg, 1.5 mmol) and benzo[b]thiophene (134 mg, 1 mmol), the residue was purified by flash chromatography on silica gel to afford the desired compound **8** (151 mg, 52%).

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.89 (s, 1H), 7.87-7.84 (m, 1H), 7.81 (dd, *J* = 3.5 and 5.6 Hz, 1H), 7.69 (d, *J* = 7.7 Hz, 1H), 7.56 (t, *J* = 7.7 Hz, 1H), 7.42-7.34 (m, 3H).

¹³C NMR (100 MHz, CDCl₃) δ (ppm) 153.6, 142.6, 142.0, 140.8, 140.2, 138.8, 126.7, 125.4, 124.7, 124.8, 122.6, 122.5, 118.4.

Elemental analysis: calcd (%) C₁₃H₈BrNS for (290.18): C 53.81, H 2.78; found: C 54.06, H 2.56.

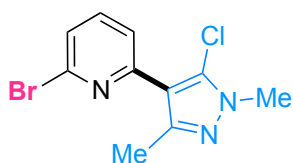


2-Bromo-6-(1-phenylpyrrol-2-yl)pyridine (9): Following the general procedure **A** using 2,6-dibromopyridine (355 mg, 1.5 mmol) and 1-phenylpyrrole (143 mg, 1 mmol), the residue was purified by flash chromatography on silica gel to afford the desired compound **9** (215 mg, 72%).

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.39-7.36 (m, 2H), 7.35 (t, *J* = 1.6 Hz, 1H), 7.28 (t, *J* = 6.7 Hz, 1H), 7.24-7.21 (m, 2H), 7.16 (d, *J* = 7.8 Hz, 1H), 6.96 (dd, *J* = 1.8 and 2.7 Hz, 1H), 6.90 (d, *J* = 7.7 Hz, 1H), 6.87 (dd, *J* = 1.8 and 3.7 Hz, 1H), 6.37 (dd, *J* = 2.8 and 3.7 Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 152.2, 141.2, 140.7, 137.9, 131.6, 129.0, 127.1, 127.0, 126.0, 124.5, 120.0, 113.9, 109.7.

Elemental analysis: calcd (%) $\text{C}_{15}\text{H}_{11}\text{BrN}_2$ for (299.17): C 60.22, H 3.71; found: C 60.53, H 2.74.

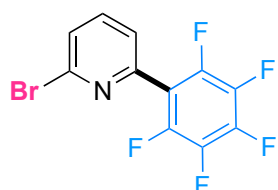


2-Bromo-6-(5-chloro-1,3-dimethylpyrazol-4-yl)pyridine (10): Following the general procedure **A** using 2,6-dibromopyridine (355 mg, 1.5 mmol) and 5-chloro-1,3-dimethylpyrazole (131 mg, 1 mmol), the residue was purified by flash chromatography on silica gel to afford the desired compound **10** (80 mg, 28%).

^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.55 (t, $J = 7.6$ Hz, 1H), 7.50 (dd, $J = 1.1$ and 7.6 Hz, 1H), 7.34 (dd, $J = 1.1$ and 7.6 Hz, 1H), 3.82 (s, 3H), 2.44 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 152.5, 148.0, 141.5, 138.4, 126.3, 125.3, 121.0, 115.2, 36.2, 14.1.

Elemental analysis: calcd (%) $\text{C}_{10}\text{H}_9\text{BrClN}_3$ for (286.56): C 41.91, H 3.17; found: C 42.05, H 3.35.

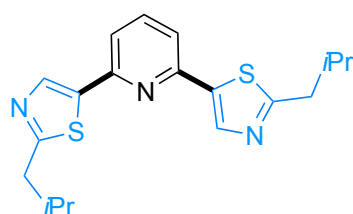


2-Bromo-6-(perfluorophenyl)pyridine (11): Following the general procedure **A** using 2,6-dibromopyridine (355 mg, 1.5 mmol) and 1,2,3,4,5-pentafluorobenzene (168 mg, 1 mmol), the residue was purified by flash chromatography on silica gel to afford the desired compound **11** (188 mg, 58%).

^1H NMR (400 MHz, d_6 -DMSO) δ (ppm) 7.91 (t, $J = 7.8$ Hz, 1H), 7.74 (d, $J = 7.8$ Hz, 1H), 7.67 (d, $J = 7.8$ Hz, 1H).

^{13}C NMR (100 MHz, d_6 -DMSO) δ (ppm) 147.9, 144.1 (md, $J = 246.0$ Hz), 141.0, 140.3, 138.6 (md, $J = 243.2$ Hz), 138.3 (md, $J = 243.2$ Hz), 128.1, 125.6, 107.3 (t, $J = 16.8$ Hz).

Elemental analysis: calcd (%) $\text{C}_{11}\text{H}_3\text{BrF}_5\text{N}$ for (324.05): C 40.77, H 0.93; found: C 41.02, H 1.07.

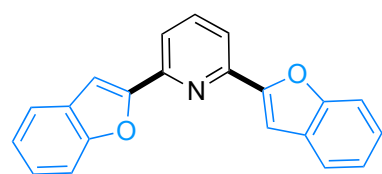


2,6-Bis(2-isobutylthiazol-5-yl)pyridine (12): Following the general procedure **B** using 2,6-dibromopyridine (237 mg, 1 mmol) and 2-isobutylthiazole (353 mg, 2.5 mmol), the residue was purified by flash chromatography on silica gel to afford the desired compound **12** (222 mg, 62%).

^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.09 (s, 2H), 7.65 (t, $J = 7.8$ Hz, 1H), 7.44 (d, $J = 7.8$ Hz, 2H), 2.87 (d, $J = 7.2$ Hz, 4H), 2.20-2.08 (m, 2H), 1.00 (d, $J = 6.7$ Hz, 12H).

^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 172.6, 150.8, 139.5, 139.1, 137.4, 117.6, 42.7, 29.9, 22.3.

Elemental analysis: calcd (%) $\text{C}_{19}\text{H}_{23}\text{N}_3\text{S}_2$ for (357.53): C 63.83, H 6.48; found: C 64.05, H 6.59.

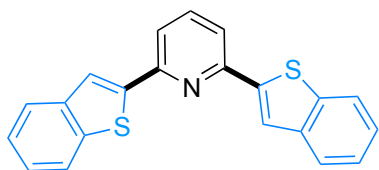


2,6-Di(benzofuran-2-yl)pyridine (13): Following the general procedure **B** using 2,6-dibromopyridine (237 mg, 1 mmol) and benzofuran (295 mg, 2.5 mmol), the residue was purified by flash chromatography on silica gel to afford the desired compound **13** (193 mg, 62%).

^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.89-7.86 (m, 4H), 7.69 (d, $J = 7.7$ Hz, 2H), 7.61 (s, 2H), 7.59 (d, $J = 8.4$ Hz, 2H), 7.36 (t, $J = 7.4$ Hz, 1H), 7.29 (d, $J = 7.5$ Hz, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 155.4, 155.1, 149.3, 137.5, 128.9, 125.2, 123.2, 121.8, 118.8, 111.5, 105.3.

Elemental analysis: calcd (%) $\text{C}_{21}\text{H}_{13}\text{NO}_2$ for (311.34): C 81.01, H 4.21; found: C 81.26, H 4.49.



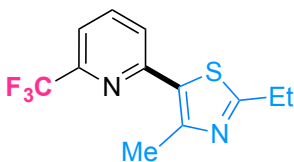
2,6-Bis(benzo[b]thiophen-2-yl)pyridine (14): Following the general procedure **B** using 2,6-dibromopyridine (237 mg, 1 mmol) and benzo[b]thiophene (336 mg, 2.5 mmol), the residue was purified by flash chromatography on silica gel to afford the desired compound **14** (192 mg,

56%).

^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.92 (s, 2H), 7.89 (d, $J = 3.7$ Hz, 1H), 7.86-7.82 (m, 2H), 7.81-7.75 (m, 2H), 7.70 (d, $J = 7.5$ Hz, 2H), 7.40-7.35 (m, 4H).

^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 152.3, 144.7, 141.0, 140.5, 137.3, 125.1, 124.5, 124.2, 122.6, 121.4, 118.1.

Elemental analysis: calcd (%) $\text{C}_{21}\text{H}_{13}\text{NS}_2$ for (343.46): C 73.44, H 3.82; found: C 73.59, H 4.06.



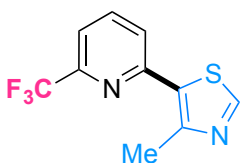
2-Ethyl-4-methyl-5-(6-(trifluoromethyl)pyridin-2-yl)thiazole (15): Following the general procedure **C** using 2-bromo-6-(trifluoromethyl)pyridine (272 mg, 1 mmol) and 2-ethyl-4-methylthiazole (191 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel to afford the desired compound **15** (250

mg, 92%).

^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.85 (t, $J = 7.9$ Hz, 1H), 7.64 (d, $J = 8.0$ Hz, 1H), 7.50 (d, $J = 7.7$ Hz, 1H), 2.99 (q, $J = 7.6$ Hz, 2H), 2.69 (s, 3H), 1.39 (t, $J = 7.6$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 172.7, 152.5, 151.0, 148.0 (q, $J = 34.8$ Hz), 137.9, 130.0, 124.1, 121.3 (q, $J = 276.5$ Hz), 117.6 (q, $J = 2.7$ Hz), 27.0, 17.6, 14.1.

Elemental analysis: calcd (%) $\text{C}_{12}\text{H}_{11}\text{F}_3\text{N}_2\text{S}$ for (272.29): C 52.93, H 4.07; found: C 53.12, H 4.29.

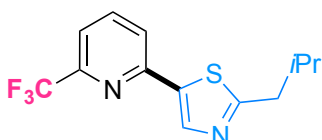


4-Methyl-5-(6-(trifluoromethyl)pyridin-2-yl)thiazole (16): Following the general procedure **C** using 2-bromo-6-(trifluoromethyl)pyridine (272 mg, 1 mmol) and 4-methylthiazole (150 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel to afford the desired compound **16** (220 mg, 90%).

^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.73 (s, 1H), 7.90 (t, $J = 7.9$ Hz, 1H), 7.71 (d, $J = 7.9$ Hz, 1H), 7.55 (d, $J = 7.9$ Hz, 1H), 2.76 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 152.5, 152.2, 152.1, 148.2 (q, $J = 35.0$ Hz), 138.2, 131.1, 124.4, 121.3 (q, $J = 276.5$ Hz), 118.2 (q, $J = 2.7$ Hz), 17.6.

Elemental analysis: calcd (%) $\text{C}_{10}\text{H}_7\text{F}_3\text{N}_2\text{S}$ for (244.24): C 49.18, H 2.89; found: C 49.35, H 3.12.



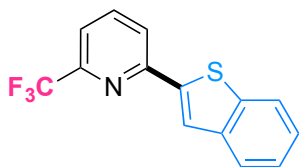
2-Isobutyl-5-(6-(trifluoromethyl)pyridin-2-yl)thiazole (17): Following the general procedure **C** using 2-bromo-6-(trifluoromethyl)pyridine (272 mg, 1 mmol) and 2-isobutylthiazole (212 mg, 1.5 mmol), the residue was purified by

flash chromatography on silica gel to afford the desired compound **17** (269 mg, 94%).

^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.14 (s, 1H), 7.82 (t, $J = 7.8$ Hz, 1H), 7.73 (d, $J = 7.8$ Hz, 1H), 7.49 (d, $J = 7.8$ Hz, 1H), 2.86 (d, $J = 7.2$ Hz, 2H), 2.15-2.08 (m, 1H), 0.98 (d, $J = 6.7$ Hz, 6H).

^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 173.4, 151.4, 148.2 (q, $J = 34.8$ Hz), 140.5, 138.1, 137.9, 121.9, 121.2 (q, $J = 276.2$ Hz), 118.5 (q, $J = 2.7$ Hz), 42.6, 30.3, 22.2.

Elemental analysis: calcd (%) $\text{C}_{13}\text{H}_{13}\text{F}_3\text{N}_2\text{S}$ for (286.32): C 54.54, H 4.58; found: C 54.76, H 4.86.

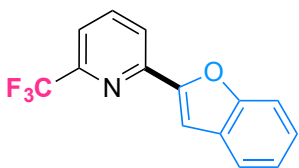


2-(Benzo[b]thiophen-2-yl)-6-(trifluoromethyl)pyridine (18): Following the general procedure **C** using 2-bromo-6-(trifluoromethyl)pyridine (272 mg, 1 mmol) and benzo[b]thiophene (201 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel to afford the desired compound **18** (190 mg, 68%).

^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.94 (s, 1H), 7.91-7.81 (m, 4H), 7.57 (dd, $J = 2.2$ and 6.4 Hz, 1H), 7.42-7.36 (m, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 153.1, 148.2 (q, $J = 34.8$ Hz), 143.0, 141.0, 140.2, 138.0, 125.8, 124.7, 124.5, 122.8, 122.6, 122.0, 121.3 (d, $J = 276.6$ Hz), 118.8 (q, $J = 2.8$ Hz).

Elemental analysis: calcd (%) $\text{C}_{14}\text{H}_8\text{F}_3\text{NS}$ for (279.28): C 60.21, H 2.89; found: C 60.47, H 3.09.

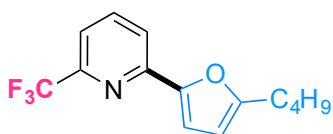


2-(Benzofuran-2-yl)-6-(trifluoromethyl)pyridine (19): Following the general procedure **C** using 2-bromo-6-(trifluoromethyl)pyridine (272 mg, 1 mmol) and benzofuran (177 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel to afford the desired compound **19** (155 mg, 59%).

^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.08 (d, $J = 8.0$ Hz, 1H), 7.96 (t, $J = 8.0$ Hz, 1H), 7.72-7.66 (m, 1H), 7.63 (s, 1H), 7.59 (dd, $J = 0.8$ and 9.2 Hz, 2H), 7.39 (ddd, $J = 1.4$, 7.3 and 8.3 Hz, 1H), 7.33-7.27 (m, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 155.5, 153.8, 149.7, 148.5 (q, $J = 34.9$ Hz), 138.2, 128.7, 125.7, 123.42, 122.0, 121.8, 121.4 (q, $J = 270.8$ Hz), 119.1 (q, $J = 2.7$ Hz), 111.5, 106.6.

Elemental analysis: calcd (%) $\text{C}_{14}\text{H}_8\text{F}_3\text{NO}$ for (263.22): C 63.88, H 3.06; found: C 64.03, H 3.21.



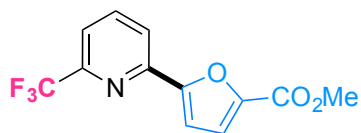
2-(5-Butylfuran-2-yl)-6-(trifluoromethyl)pyridine (20): Following the general procedure **C** using 2-bromo-6-(trifluoromethyl)pyridine (272 mg, 1 mmol) and 2-butylfuran (186 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel to afford the desired compound **20** (240 mg,

89%).

^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.84-7.78 (m, 2H), 7.44 (dd, $J = 1.2$ and 7.3 Hz, 1H), 7.11 (d, $J = 3.3$ Hz, 1H), 6.15 (d, $J = 3.3$ Hz, 1H), 2.72 (t, $J = 7.6$ Hz, 2H), 1.73-1.66 (m, 2H), 1.43 (quint., $J = 7.4$ Hz, 2H), 0.95 (t, $J = 7.4$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 158.8, 150.8, 150.1, 148.0 (q, $J = 34.5$ Hz), 137.7, 122.9, 121.5 (q, $J = 275.1$ Hz), 117.4 (q, $J = 2.9$ Hz), 111.5, 107.9, 30.1, 28.0, 22.3, 13.8.

Elemental analysis: calcd (%) $\text{C}_{14}\text{H}_{14}\text{F}_3\text{NO}$ for (269.26): C 62.45, H 5.24; found: C 62.58, H 5.37.



Methyl 5-(6-(trifluoromethyl)pyridin-2-yl)furan-2-carboxylate (21):

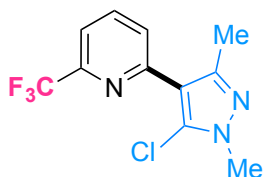
Following the general procedure **C** using 2-bromo-6-(trifluoromethyl)pyridine (272 mg, 1 mmol) and 2-butylfuran (189 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel to afford the desired

compound **21** (192 mg, 71%).

¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.06 (d, *J* = 8.0 Hz, 1H), 7.94 (t, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.28-7.26 (m, 2H), 3.93 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ (ppm) 158.9, 155.4, 148.6, 148.6 (q, *J* = 34.5 Hz), 145.0, 138.3, 121.8, 121.3 (q, *J* = 269.4 Hz), 119.9, 119.5 (q, *J* = 2.7 Hz), 111.8, 52.1.

Elemental analysis: calcd (%) C₁₂H₈F₃NO₃ for (271.20): C 53.15, H 2.97; found: C 53.32, H 3.19.



2-(5-Chloro-1,3-dimethyl-1H-pyrazol-4-yl)-6-(trifluoromethyl)pyridine (22):

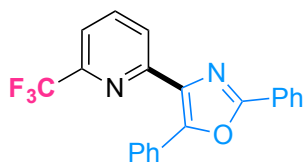
Following the general procedure **C** using 2-bromo-6-(trifluoromethyl)pyridine (272 mg, 1 mmol) and 5-chloro-1,3-dimethylpyrazole (196 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel to afford the desired compound

22 (234 mg, 85%).

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.88 (t, *J* = 7.9 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 7.1 Hz, 1H), 3.85 (s, 3H), 2.49 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ (ppm) 152.2, 148.5, 147.9 (q, *J* = 34.6 Hz), 137.5, 126.4, 124.6, 121.6 (q, *J* = 276.3 Hz), 117.4 (q, *J* = 2.7 Hz), 115.3, 36.2, 14.3.

Elemental analysis: calcd (%) C₁₁H₉ClF₃N₃ for (275.66): C 47.93, H 3.29; found: C 47.81, H 3.08.

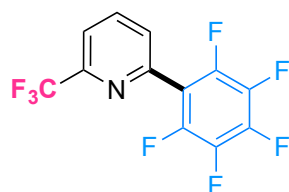


2,5-Diphenyl-4-(6-(trifluoromethyl)pyridin-2-yl)oxazole (23): Following the general procedure **C** using 2-bromo-6-(trifluoromethyl)pyridine (272 mg, 1 mmol) and 2,5-diphenyloxazole (332 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel to afford the desired compound **23** (311 mg, 85%).

¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.36 (d, *J* = 8.2 Hz, 1H), 8.32 (dd, *J* = 1.8 and 7.8 Hz, 2H), 8.23-8.19 (m, 2H), 7.98 (t, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 7.3 Hz, 1H), 7.57-7.43 (m, 6H).

¹³C NMR (100 MHz, CDCl₃) δ (ppm) 159.8, 152.5, 149.6, 147.2 (q, *J* = 34.9 Hz), 137.9, 134.9, 130.6, 129.4, 128.9, 128.4, 128.2, 128.1, 127.0, 126.6, 125.3, 121.6 (q, *J* = 273.5 Hz), 118.9 (q, *J* = 2.7 Hz).

Elemental analysis: calcd (%) C₂₁H₁₃F₃N₂O for (366.34): C 68.85, H 3.58; found: C 68.65, H 3.91.

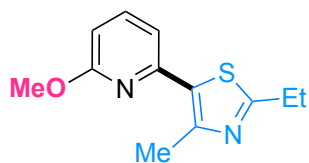


2-(Perfluorophenyl)-6-(trifluoromethyl)pyridine (24): Following the general procedure **C** using 2-bromo-6-(trifluoromethyl)pyridine (272 mg, 1 mmol) and 1,2,3,4,5-pentafluorobenzene (252 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel to afford the desired compound **24** (266 mg, 85%).

¹H NMR (400 MHz, *d*₆-DMSO) δ (ppm) 7.98 (t, *J* = 7.9 Hz, 1H), 7.70 (d, *J* = 7.9 Hz, 1H), 7.65 (d, *J* = 7.9 Hz, 1H).

^{13}C NMR (100 MHz, d_6 -DMSO) δ (ppm) 148.5, 147.2 (q, $J = 34.5$ Hz), 144.7 (dm, $J = 245.8$ Hz), 140.1, 138.6 (tdd, $J = 5.3, 12.7$ and 238.9 Hz), 138.1 (tt, $J = 4.8$ and 13.8 Hz), 129.9, 121.8 (q, $J = 270.0$ Hz), 121.0, 107.9 (t, $J = 16.3$ Hz).

Elemental analysis: calcd (%) $\text{C}_{12}\text{H}_3\text{F}_8\text{N}$ for (313.15): C 46.03, H 0.97; found: C 46.29, H 0.58.

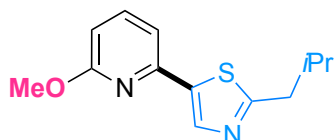


2-Ethyl-5-(6-methoxypyridin-2-yl)-4-methylthiazole (25): Following the general procedure **C** using 2-bromo-6-methoxypyridine (188 mg, 1 mmol) and 2-ethyl-4-methylthiazole (191 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel to afford the desired compound **25** (124 mg, 53%).

^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.56 (t, $J = 7.8$ Hz, 1H), 7.06 (d, $J = 7.4$ Hz, 1H), 6.61 (d, $J = 8.2$ Hz, 1H), 3.96 (s, 3H), 2.99 (q, $J = 7.6$ Hz, 2H), 2.69 (s, 3H), 1.40 (t, $J = 7.6$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 171.4, 163.4, 149.2, 149.1, 139.0, 131.7, 114.2, 108.7, 53.4, 27.0, 17.7, 14.2.

Elemental analysis: calcd (%) $\text{C}_{12}\text{H}_{14}\text{N}_2\text{OS}$ for (234.32): C 61.51, H 6.02; found: C 62.84, H 6.29.



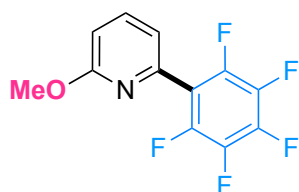
2-Isobutyl-5-(6-methoxypyridin-2-yl)thiazole (26): Following the general procedure **C** using 2-bromo-6-methoxypyridine (188 mg, 1 mmol) and 2-isobutylthiazole (212 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel to afford the desired compound **26** (154 mg,

62%).

^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.10 (s, 1H), 7.56 (t, $J = 7.8$ Hz, 1H), 7.18 (d, $J = 7.4$ Hz, 1H), 6.62 (d, $J = 8.2$ Hz, 1H), 3.97 (s, 3H), 2.89 (d, $J = 7.2$ Hz, 2H), 2.17-2.10 (m, 1H), 1.03 (d, $J = 6.6$ Hz, 6H).

^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 171.7, 163.7, 148.2, 139.4, 139.1, 112.1, 109.5, 53.4, 42.7, 29.9, 22.3.

Elemental analysis: calcd (%) $\text{C}_{13}\text{H}_{16}\text{N}_2\text{OS}$ for (248.34): C 62.87, H 6.49; found: C 62.91, H 6.59.

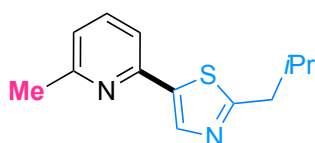


2-Methoxy-6-(perfluorophenyl)pyridine (27): Following the general procedure **C** using 2-bromo-6-methoxypyridine (188 mg, 1 mmol) and 1,2,3,4,5-pentafluorobenzene (252 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel to afford the desired compound **27** (88 mg, 32%).

^1H NMR (400 MHz, d_6 -DMSO) δ (ppm) 7.84 (t, $J = 7.8$ Hz, 1H), 7.18 (d, $J = 7.3$ Hz, 1H), 6.89 (d, $J = 8.3$ Hz, 1H), 3.85 (s, 3H).

^{13}C NMR (100 MHz, d_6 -DMSO) δ (ppm) 163.3, 144.5, 144.2 (md, $J = 241.5$ Hz), 139.7, 138.2 (md, $J = 239.7$ Hz), 138.0 (md, $J = 239.7$ Hz), 119.1, 110.6, 108.6 (t, $J = 18.7$ Hz), 53.2.

Elemental analysis: calcd (%) $\text{C}_{12}\text{H}_6\text{F}_5\text{NO}$ for (275.18): C 52.38, H 2.20; found: C 52.49, H 2.49.

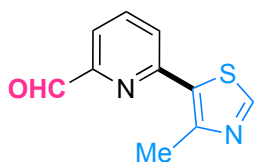


2-Isobutyl-5-(6-methylpyridin-2-yl)thiazole (28): Following the general procedure **C** using 2-bromo-6-methylpyridine (172 mg, 1 mmol) and 2-isobutylthiazole (212 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel to afford the desired compound **28** (84 mg, 36%).

^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.09 (s, 1H), 7.6 (t, $J = 7.7$ Hz, 1H), 7.45 (d, $J = 7.8$ Hz, 1H), 7.05 (d, $J = 7.5$ Hz, 1H), 2.91 (d, $J = 7.3$ Hz, 2H), 2.58 (s, 3H), 2.24-2.10 (m, 1H), 1.04 (d, $J = 6.7$ Hz, 6H).

^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 171.9, 158.8, 150.2, 139.7, 139.0, 136.9, 121.9, 116.6, 42.7, 29.9, 24.5, 22.4.

Elemental analysis: calcd (%) $\text{C}_{13}\text{H}_{16}\text{N}_2\text{S}$ for (232.34): C 67.20, H 6.94; found: C 67.49, H 7.18.

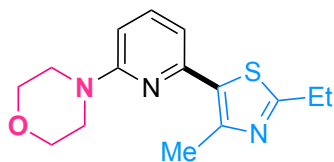


6-(4-Methylthiazol-5-yl)picolinaldehyde (29): Following the general procedure **C** using 6-bromopicolinaldehyde (186 mg, 1 mmol) and 4-methylthiazole (150 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel to afford the desired compound **29** (86 mg, 42%).

^1H NMR (400 MHz, CDCl_3) δ (ppm) 10.11 (s, 1H), 8.80 (s, 1H), 7.97 (t, $J = 7.6$ Hz, 1H), 7.90 (d, $J = 7.7$ Hz, 1H), 7.82 (d, $J = 7.7$ Hz, 1H), 2.80 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 193.2, 152.8, 152.7, 152.6, 152.3, 151.4, 137.9, 125.8, 119.4, 17.7.

Elemental analysis: calcd (%) $\text{C}_{10}\text{H}_8\text{N}_2\text{OS}$ for (204.25): C 58.81, H 3.95; found: C 58.54, H 4.24.



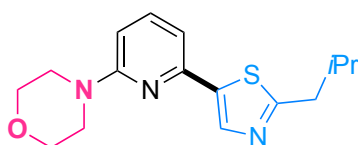
4-(6-(2-Ethyl-4-methylthiazol-5-yl)pyridin-2-yl)morpholine (30): Following the general procedure **C** using 4-(6-bromopyridin-2-yl)morpholine (243 mg, 1 mmol) and 2-ethyl-4-methylthiazole (191 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel to afford the desired compound

30 (255 mg, 88%).

^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.50 (dd, $J = 7.5$ and 8.5 Hz, 1H), 6.89 (d, $J = 7.5$ Hz, 1H), 6.49 (d, $J = 8.5$ Hz, 1H), 3.82 (dd, $J = 4.6$ and 5.5 Hz, 4H), 3.53 (dd, $J = 4.1$ and 5.6 Hz, 4H), 2.97 (q, $J = 7.6$ Hz, 2H), 2.65 (s, 3H), 1.38 (t, $J = 7.6$ Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ (ppm) 171.4, 158.9, 149.9, 148.6, 138.2, 132.9, 111.4, 104.8, 66.8, 45.5, 27.1, 17.9, 14.4.

Elemental analysis: calcd (%) $\text{C}_{15}\text{H}_{19}\text{N}_3\text{OS}$ for (289.40): C 62.26, H 6.62; found: C 62.37, H 6.20.



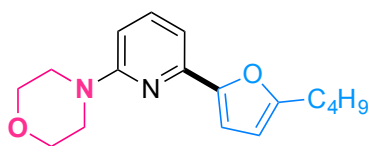
4-(6-(2-Isobutylthiazol-5-yl)pyridin-2-yl)morpholine (31): Following the general procedure **C** using 4-(6-bromopyridin-2-yl)morpholine (243 mg, 1 mmol) and 2-isobutylthiazole (212 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel to afford the desired compound **31**

(264 mg, 87%).

^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.04 (s, 1H), 7.49 (dd, $J = 7.5$ and 8.6 Hz, 1H), 7.00 (d, $J = 7.5$ Hz, 1H), 6.50 (d, $J = 8.6$ Hz, 1H), 3.83 (dd, $J = 4.0$ and 5.3 Hz, 4H), 3.54 (dd, $J = 4.0$ and 5.3 Hz, 4H), 2.86 (d, $J = 7.2$ Hz, 2H), 2.23-2.05 (m, 1H), 1.01 (d, $J = 6.7$ Hz, 6H).

^{13}C NMR (75 MHz, CDCl_3) δ (ppm) 171.7, 159.1, 148.9, 140.5, 138.8, 138.3, 109.2, 105.4, 66.9, 45.4, 42.8, 30.0, 22.4.

Elemental analysis: calcd (%) $\text{C}_{16}\text{H}_{21}\text{N}_3\text{OS}$ for (303.42): C 63.34, H 6.98; found: C 63.54, H 7.18.

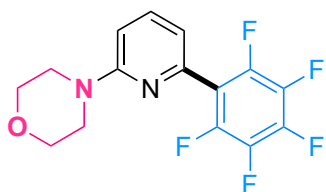


4-(6-(5-Butylfuran-2-yl)pyridin-2-yl)morpholine (32): Following the general procedure **C** using 4-(6-bromopyridin-2-yl)morpholine (243 mg, 1 mmol) and 2-butylfuran (186 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel to afford the desired compound **32** (218 mg, 76%).

^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.53 (dd, $J = 7.6$ and 8.4 Hz, 1H), 7.07 (d, $J = 7.6$ Hz, 1H), 6.90 (d, $J = 3.3$ Hz, 1H), 6.50 (d, $J = 8.4$ Hz, 1H), 6.11 (d, $J = 3.3$ Hz, 1H), 3.87 (dd, $J = 4.3$ and 5.6 Hz, 4H), 3.57 (dd, $J = 4.3$ and 5.6 Hz, 4H), 2.71 (t, $J = 7.5$ Hz, 2H), 1.69 (quint., $J = 7.5$ Hz, 2H), 1.49-1.41 (m, 2H), 0.96 (t, $J = 7.3$ Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ (ppm) 170.9, 159.2, 152.8, 148.0, 138.2, 125.8, 115.8, 108.4, 105.0, 67.0, 45.8, 30.4, 28.2, 22.5, 14.0.

Elemental analysis: calcd (%) $\text{C}_{17}\text{H}_{22}\text{N}_2\text{O}_2$ for (286.38): C 71.30, H 7.74; found: C 71.56, H 7.58.

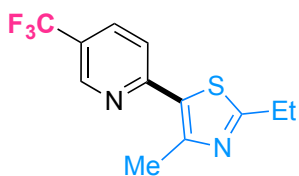


4-(6-(Perfluorophenyl)pyridin-2-yl)morpholine (33): Following the general procedure **C** using 4-(6-bromopyridin-2-yl)morpholine (243 mg, 1 mmol) and 1,2,3,4,5-pentafluorobenzene (252 mg, 1.5 mmol), the residue was purified by flash chromatography on silica gel to afford the desired compound **33** (211 mg, 64%).

^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.32 (t, $J = 7.9$ Hz, 1H), 6.80 (d, $J = 7.6$ Hz, 1H), 6.52 (d, $J = 8.6$ Hz, 1H), 3.83 (dd, $J = 4.3$ and 5.6 Hz, 4H), 3.52 (dd, $J = 4.3$ and 5.6 Hz, 4H),

^{13}C NMR (75 MHz, CDCl_3) δ (ppm) 171.6, 159.3, 144.9 (dm, $J = 250.1$ Hz), 138.2 (dm, $J = 249.8$ Hz), 127.8 (dm, $J = 248.9$ Hz), 138.0, 115.6, 107.1, 102.0 (t, $J = 25.0$ Hz), 66.6, 45.3.

Elemental analysis: calcd (%) $\text{C}_{15}\text{H}_{11}\text{F}_5\text{N}_2\text{O}$ for (330.25): C 54.55, H 3.36; found: C 54.20, H 3.43.



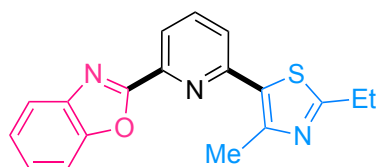
2-Ethyl-4-methyl-5-(5-(trifluoromethyl)pyridin-2-yl)thiazole (34): The reaction of 2-bromo-5-(trifluoromethyl)pyridine (226 mg, 1 mmol), 2-ethyl-4-methylthiazole (191 mg, 1.5 mmol), KOAc (196 mg, 2 equiv.) at 150°C during 16 h in DMA (4 mL) in the presence of $\text{PdCl}(\text{C}_3\text{H}_5)(\text{dppb})$ (12 mg, 2 mol%) under argon affords after evaporation of the solvent and purification by silica column

chromatography the desired product **34** (142 mg, 52%).

^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.78 (s, 1H), 7.87 (dd, $J = 2.4$ and 8.4 Hz, 1H), 7.57 (d, $J = 8.4$ Hz, 1H), 2.95 (q, $J = 7.6$ Hz, 2H), 2.63 (s, 3H), 1.35 (t, $J = 7.6$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 173.7, 155.5, 151.1, 146.7 (q, $J = 4.1$ Hz), 134.0 (q, $J = 3.5$ Hz), 131.0, 124.2 (q, $J = 28.6$ Hz), 123.7 (q, $J = 273.5$ Hz), 120.9, 27.3, 18.0, 14.3.

Elemental analysis: calcd (%) $\text{C}_{12}\text{H}_{11}\text{F}_3\text{N}_2\text{S}$ for (272.28): C 52.93, H 4.07; found: C 53.17, H 4.01.



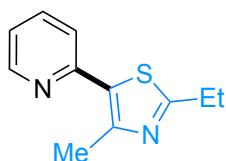
2-(6-(2-Ethyl-4-methylthiazol-5-yl)pyridin-2-yl)benzoxazole (38): The reaction of 5-(6-bromopyridin-2-yl)-2-ethyl-4-methylthiazole (**2**) (283 mg, 1 mmol), benzoxazole (179 mg, 1.5 mmol), Cs_2CO_3 (650 mg, 2 equiv.) at

150 °C during 16 h in DMF (4 mL) in the presence of PdCl(C₃H₅)(dppb)¹ (12 mg, 2 mol%) under argon affords after evaporation of the solvent and purification by silica column chromatography the desired product **38** (238 mg, 74%).

¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.25 (d, *J* = 7.8 Hz, 1H), 7.92 (t, *J* = 7.8 Hz, 1H), 7.86 (dd, *J* = 2.1 and 7.3 Hz, 1H), 7.71-7.68 (m, 1H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.47-7.36 (m, 2H), 3.06 (q, *J* = 7.6 Hz, 2H), 2.76 (s, 3H), 1.44 (t, *J* = 7.6 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ (ppm) 172.7, 161.3, 152.6, 151.2, 150.1, 146.1, 141.8, 137.7, 131.0, 126.1, 124.9, 123.6, 121.3, 120.7, 111.4, 27.1, 17.4, 14.3.

Elemental analysis: calcd (%) C₁₈H₁₅N₃OS for (321.39): C 67.27, H 4.70; found: C 67.39, H 4.55.



2-Ethyl-4-methyl-5-(pyridin-2-yl)thiazole (1): Autoclave was charged with 5-(6-bromopyridin-2-yl)-2-ethyl-4-methylthiazole (**2**) (283 mg, 1 mmol), Et₃N (270 μL; 2 mmol), Pd/C (29 mg, 10% of the weight of the 2-bromopyridine derivative) and MeOH (5 mL) and pressurized with hydrogen (3-5 bar). The crude mixture was stirred at 20

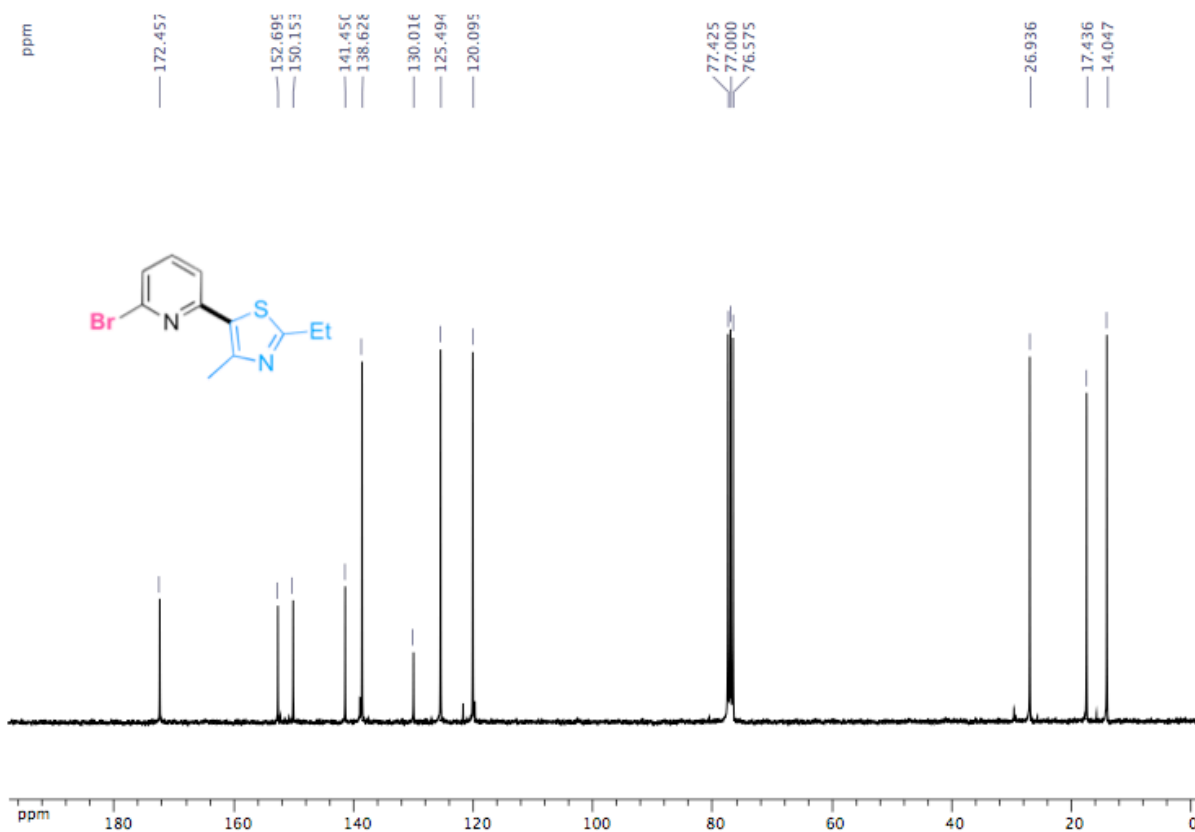
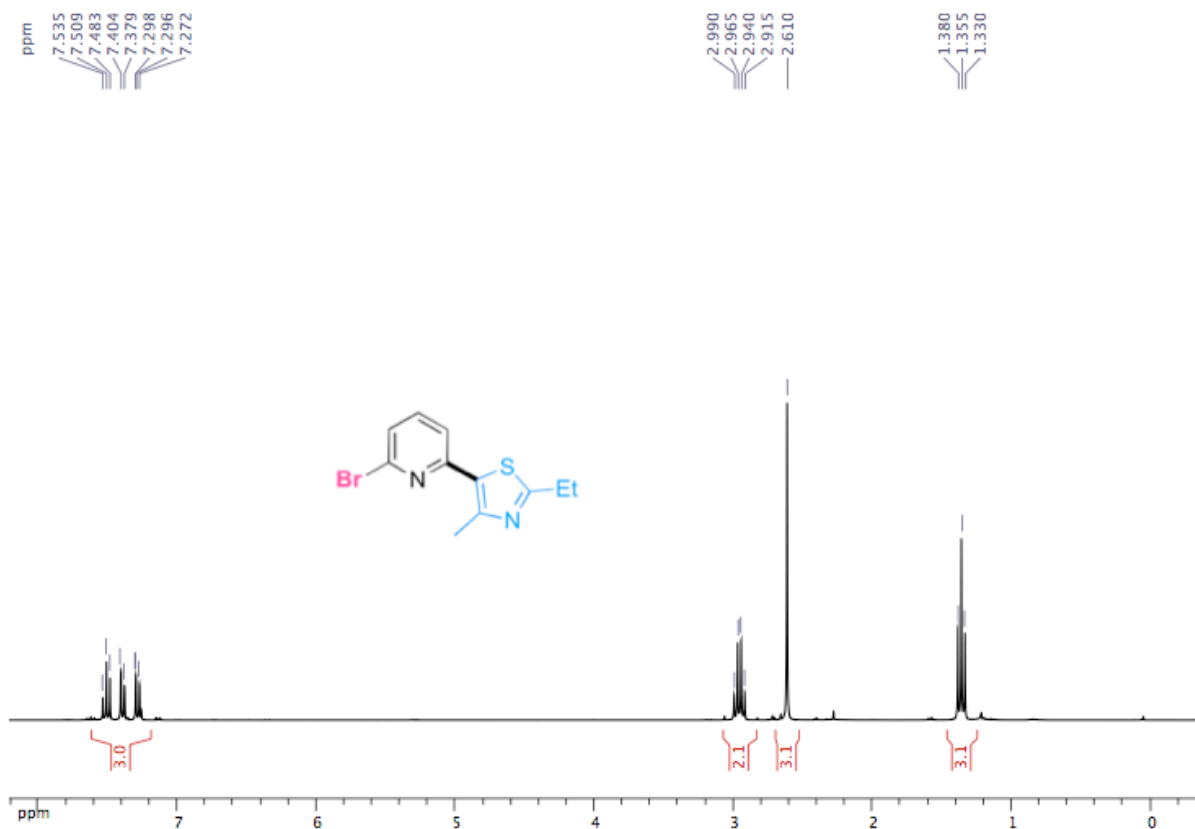
°C during 16 h, and then the reaction was cooled down and filtered in the pad of Celite. After evaporation of the solvent and purification on silica gel **1** was isolated in 96% (0.196 g) yield.

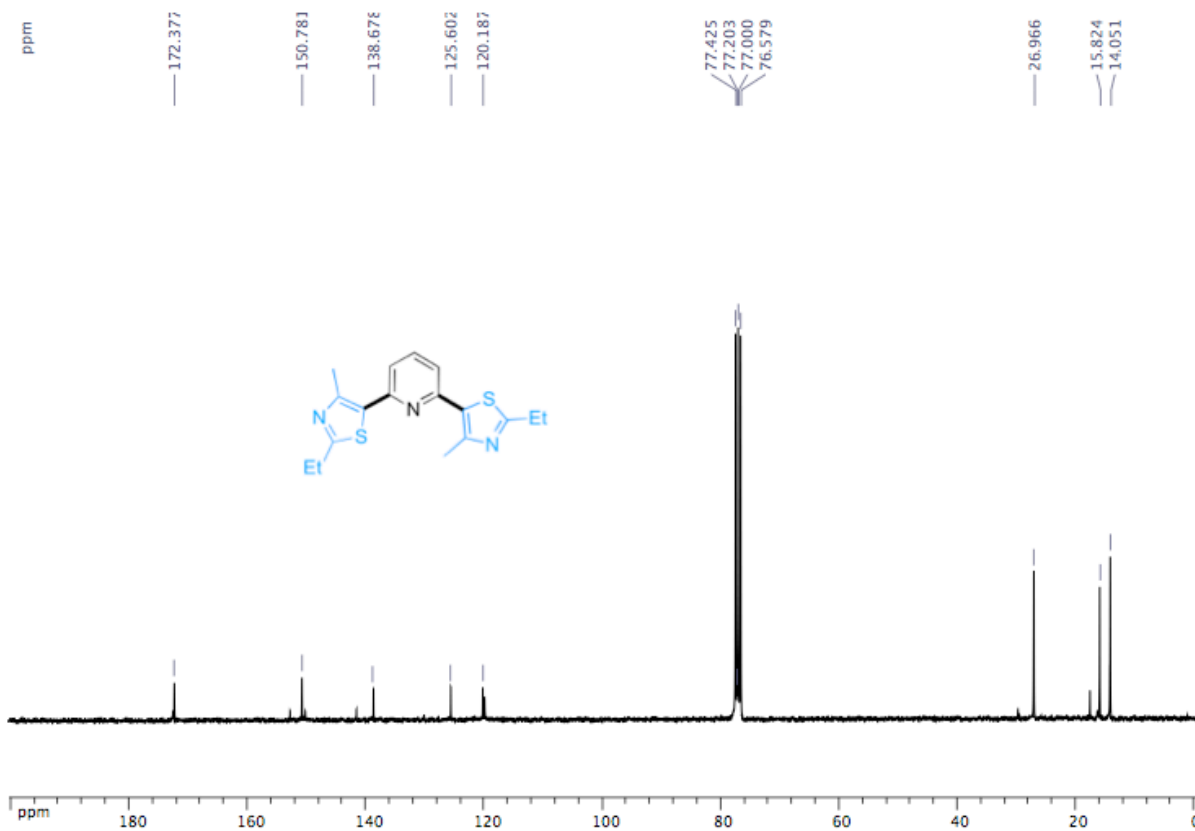
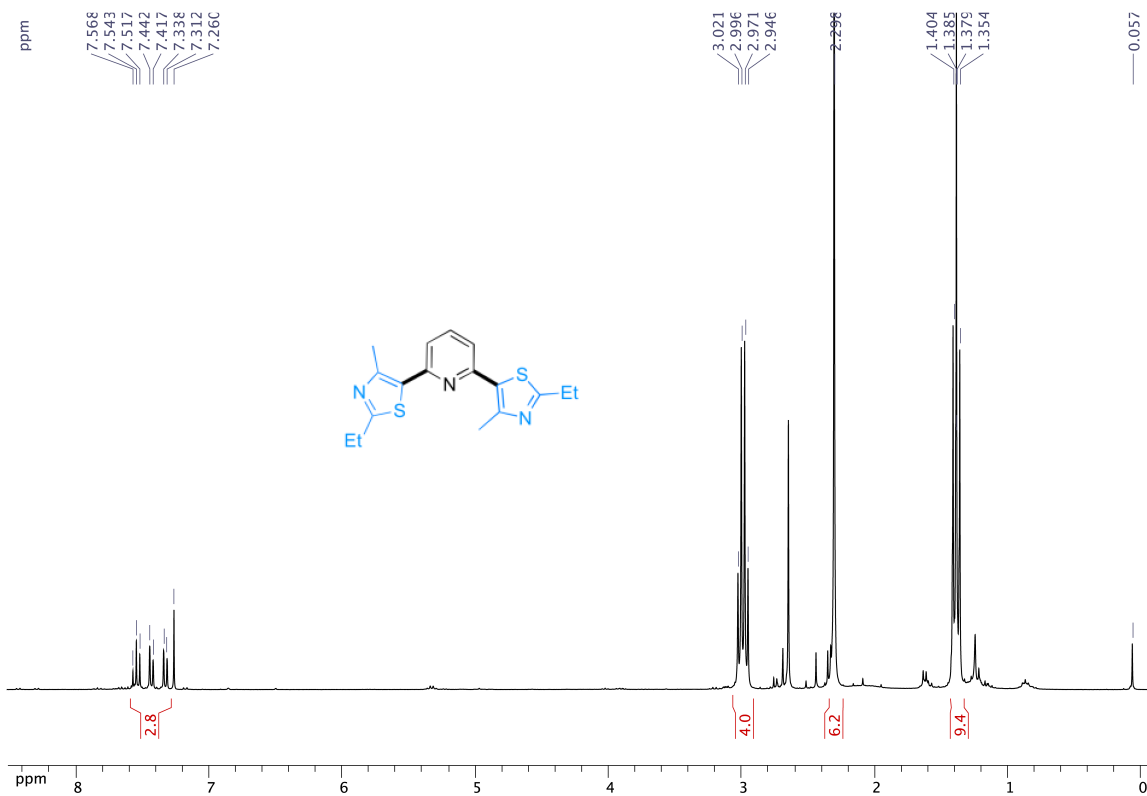
¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.51 (d, *J* = 4.9 Hz, 1H), 7.62 (ddd, *J* = 1.9, 7.5 and 8.0 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.06 (dd, *J* = 4.9 and 7.5 Hz, 1H), 2.91 (q, *J* = 7.6 Hz, 2H), 2.56 (s, 3H), 1.31 (t, *J* = 7.6 Hz, 3H).

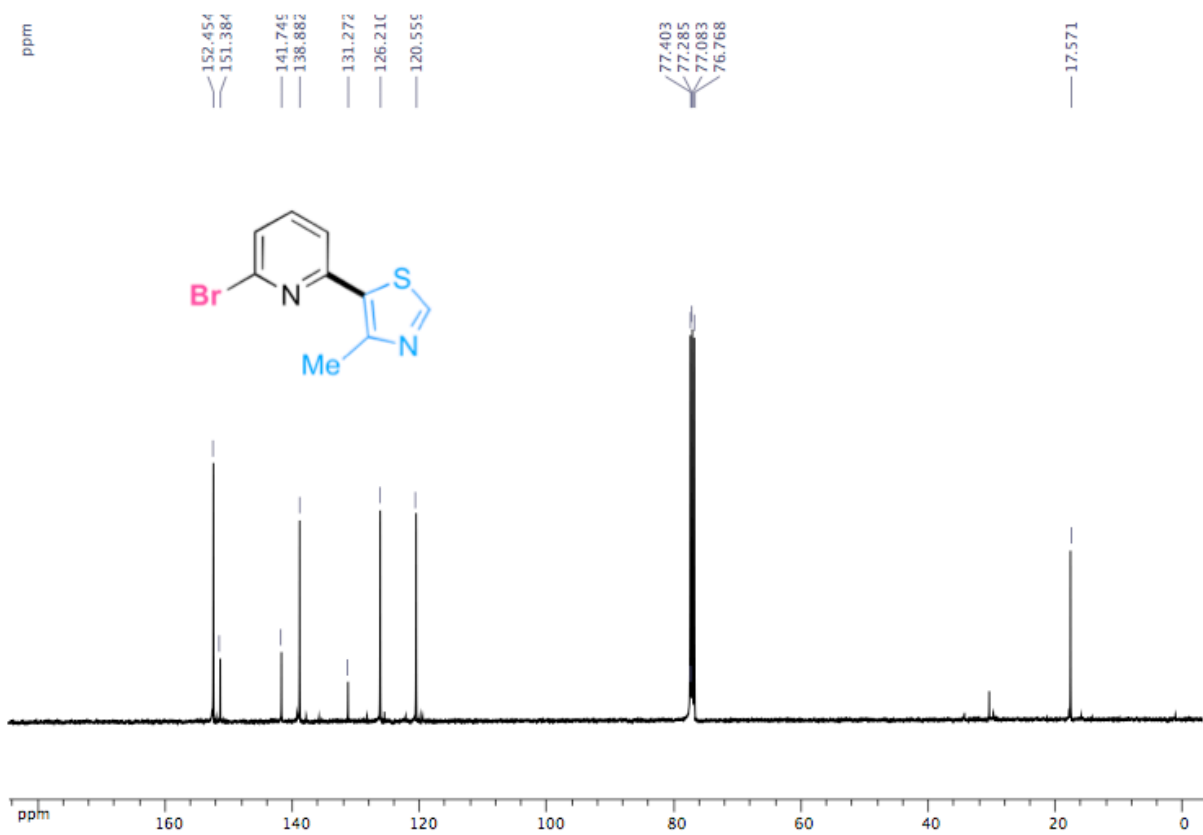
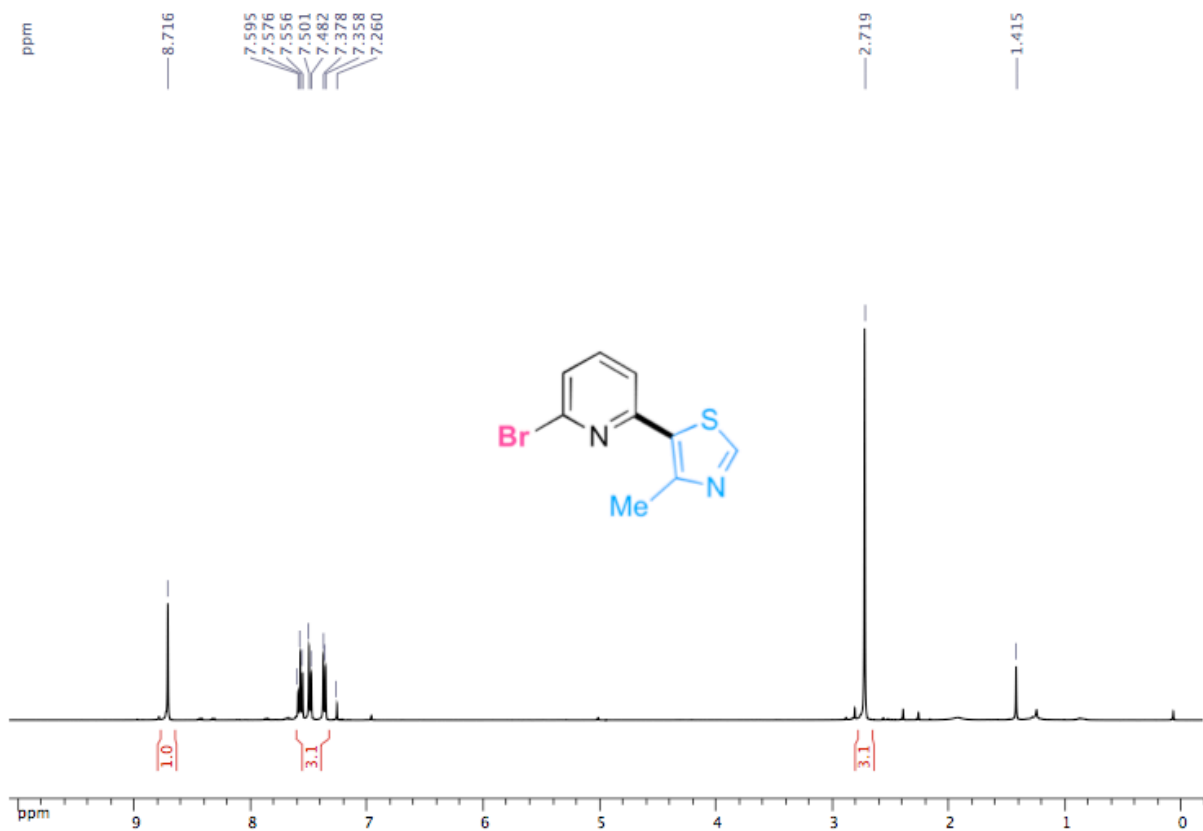
¹³C NMR (100 MHz, CDCl₃) δ (ppm) 172.1, 152.0, 149.8, 148.9, 136.6, 132.1, 121.6, 121.6, 27.1, 17.5, 14.3.

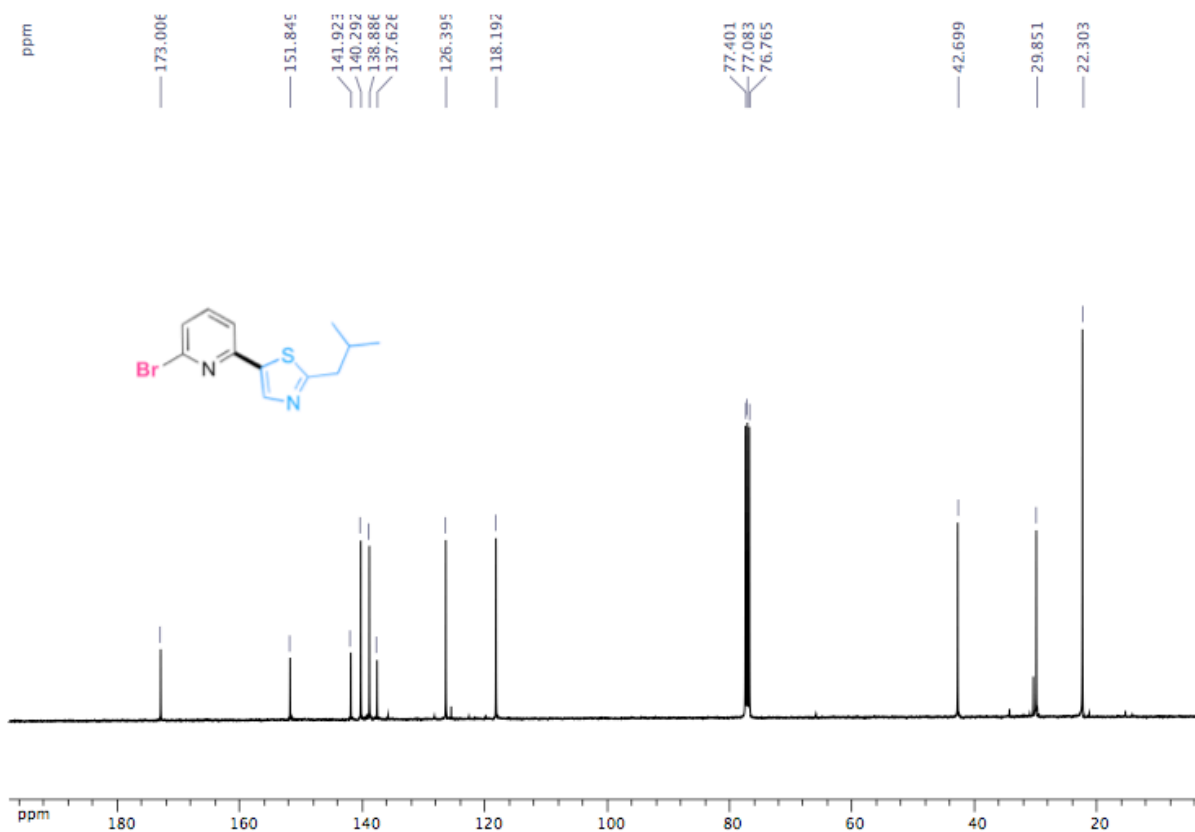
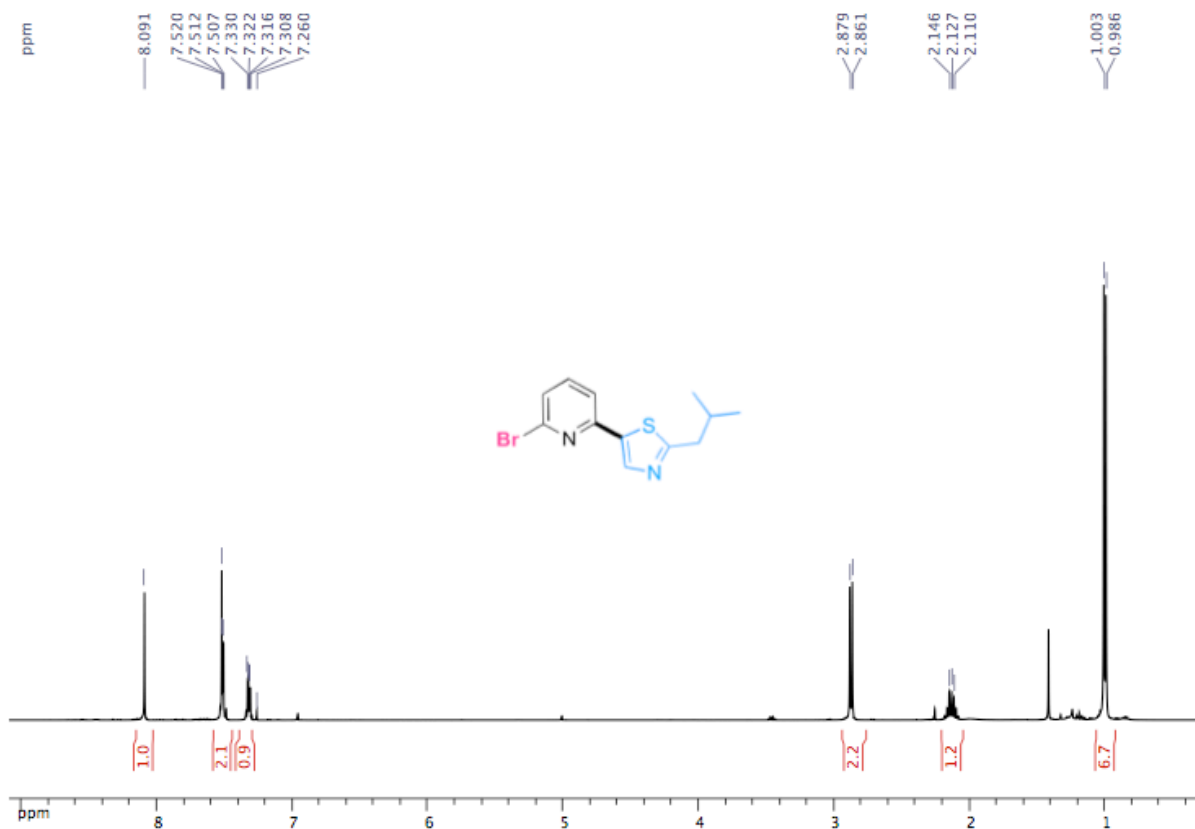
Elemental analysis: calcd (%) C₁₁H₁₂N₂S for (204.29): C 64.67, H 5.92; found: C 64.98, H 6.27.

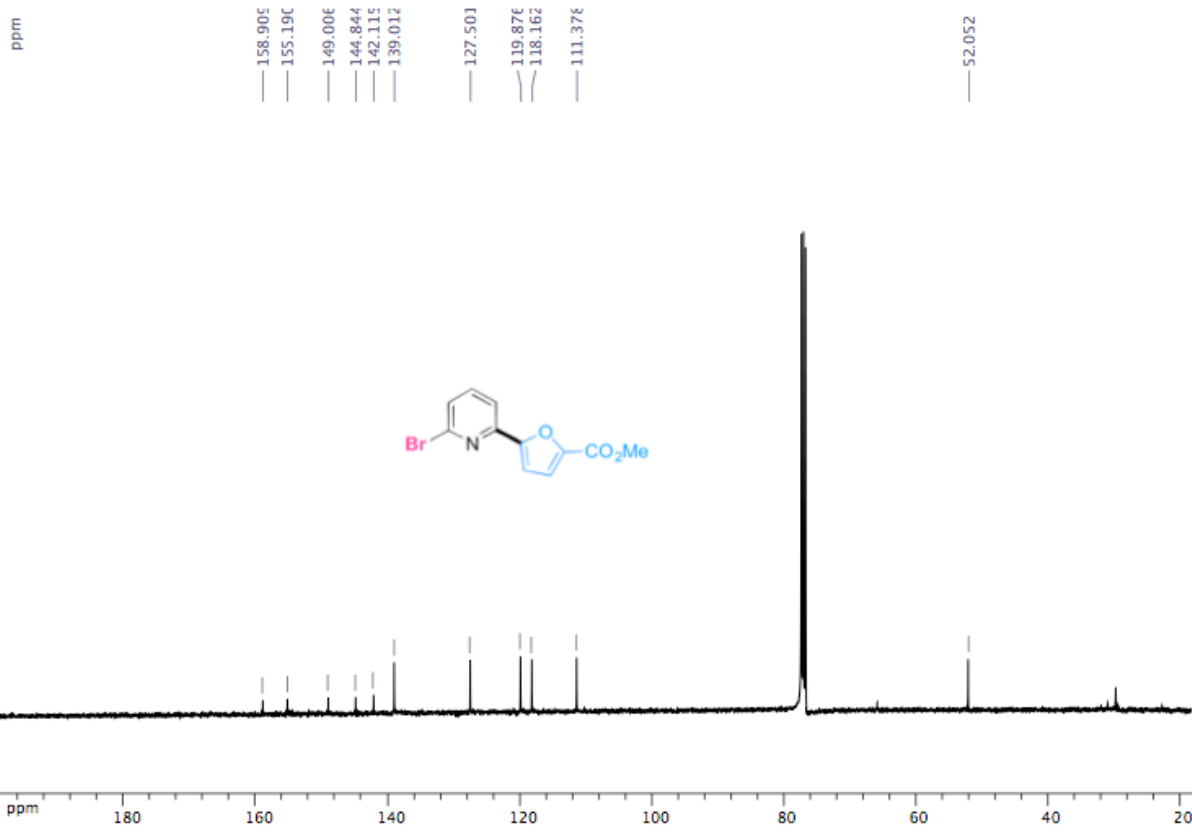
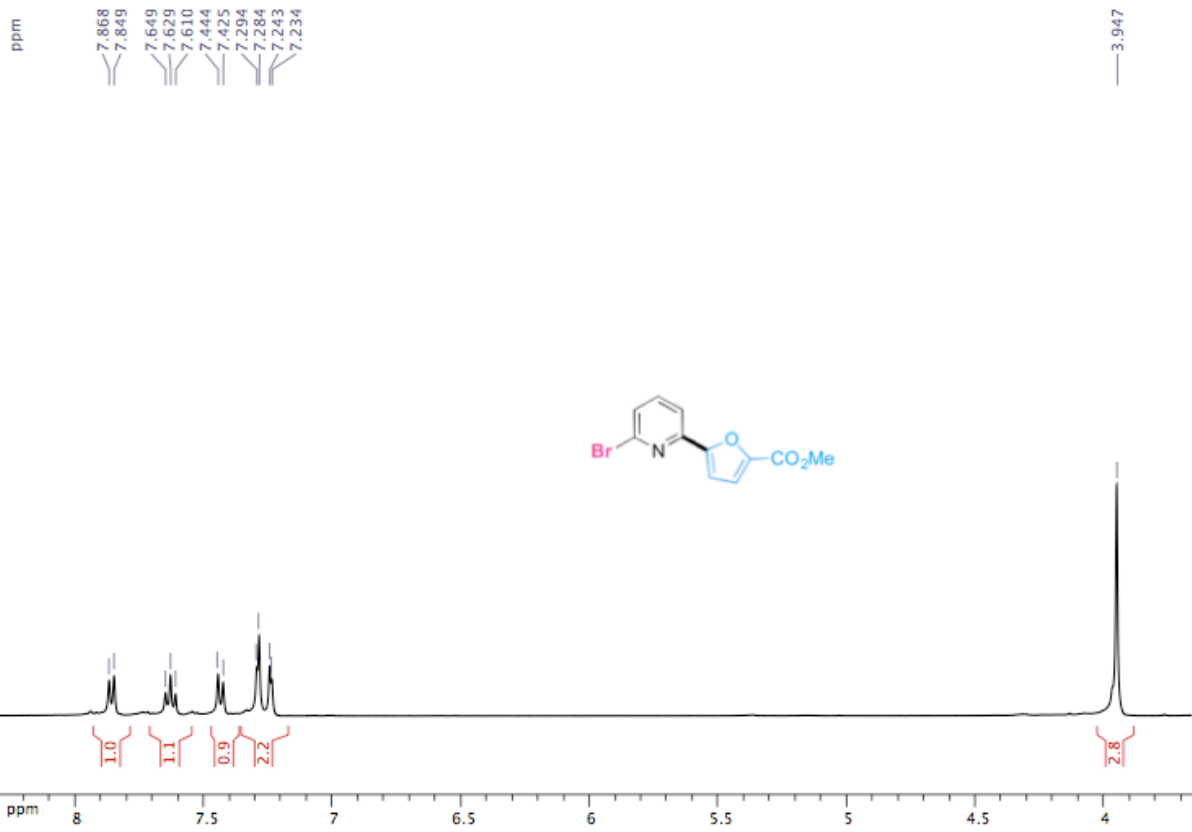
¹ Cantat, T.; Génin, E.; Giroud, C.; Meyer, G.; Jutand, A. *J. Organomet. Chem.* **2003**, 687, 365-376.

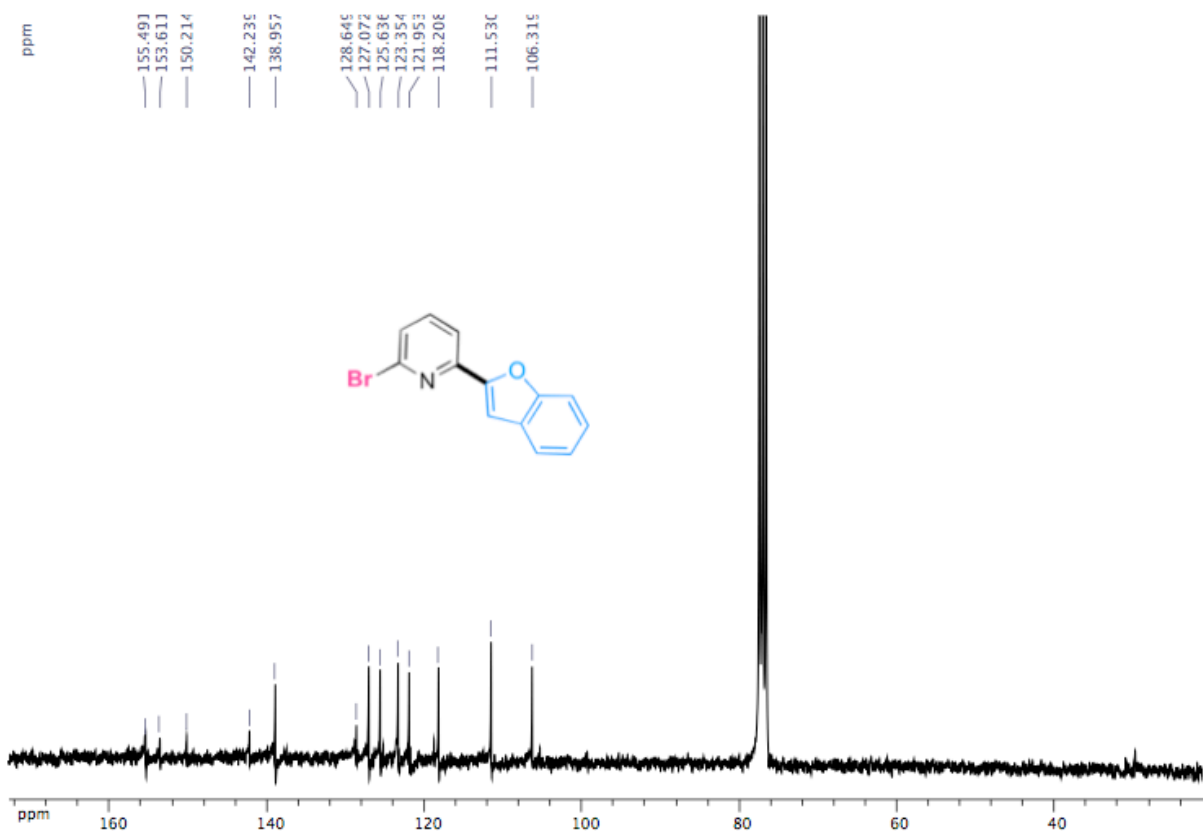
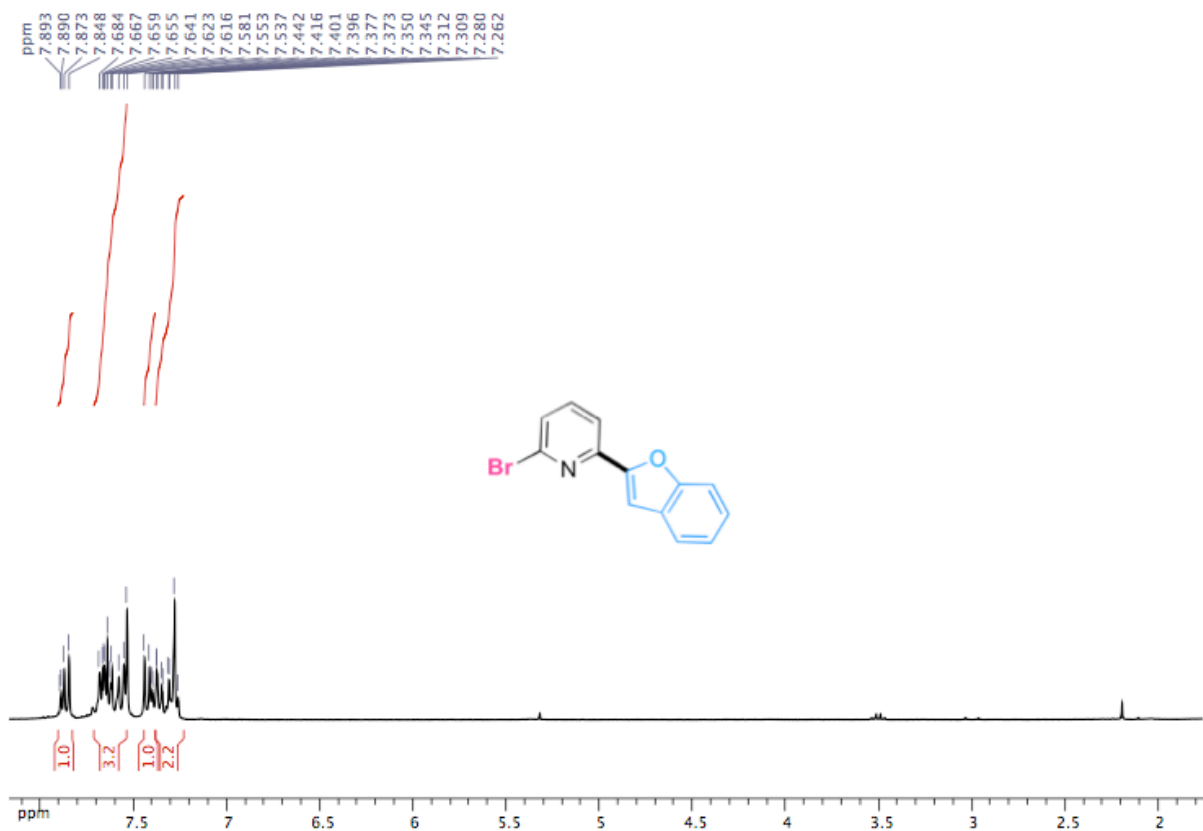


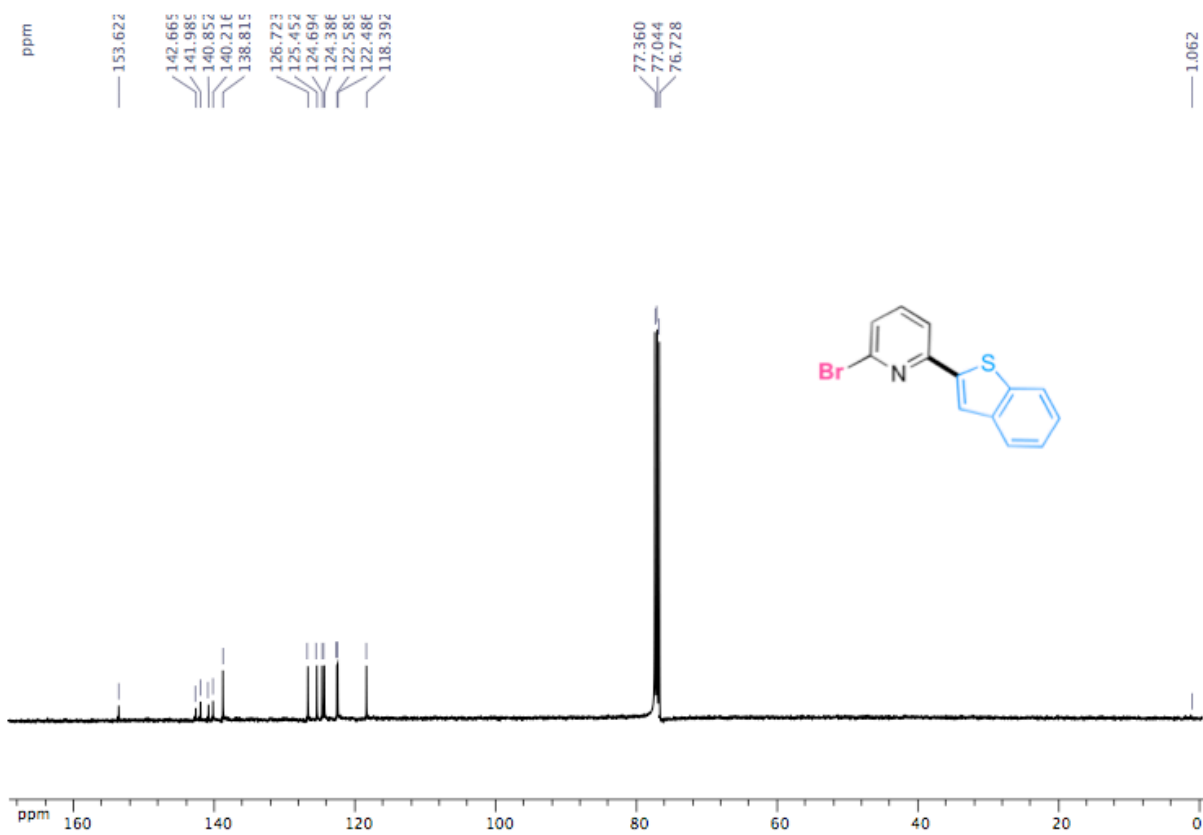
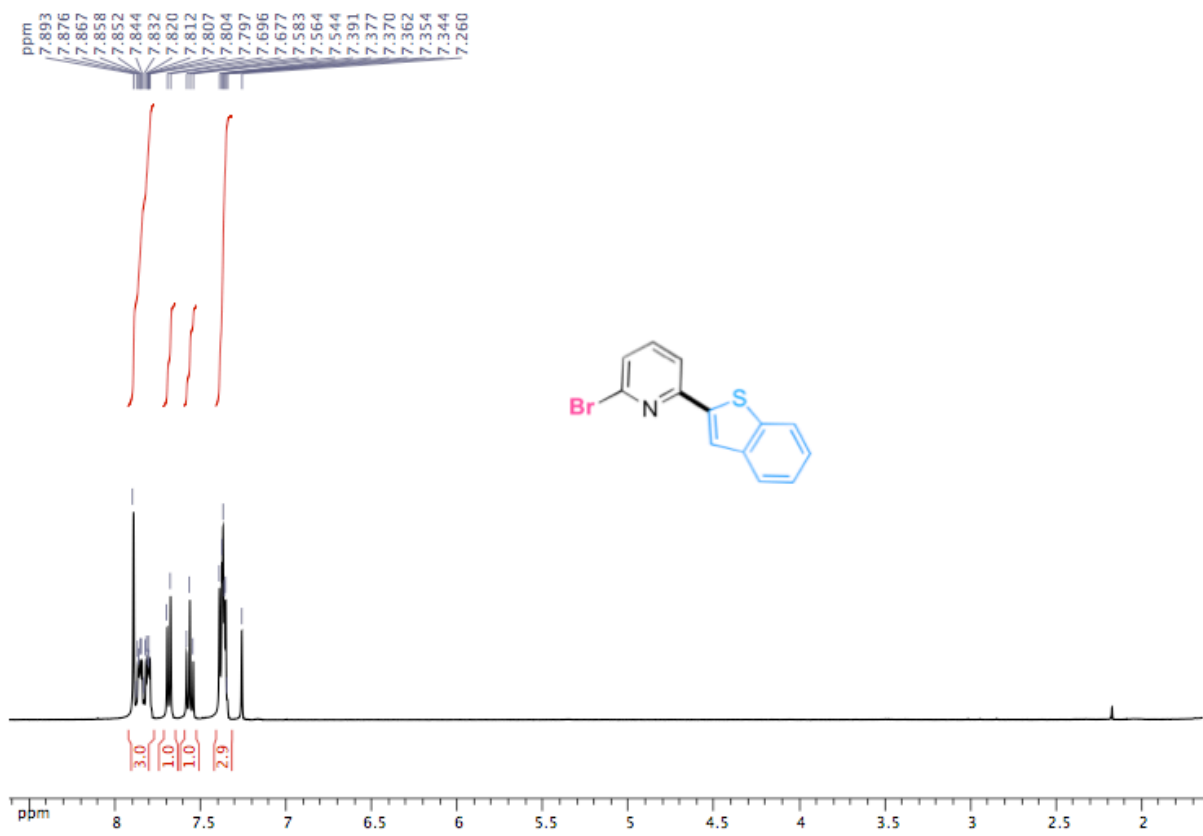


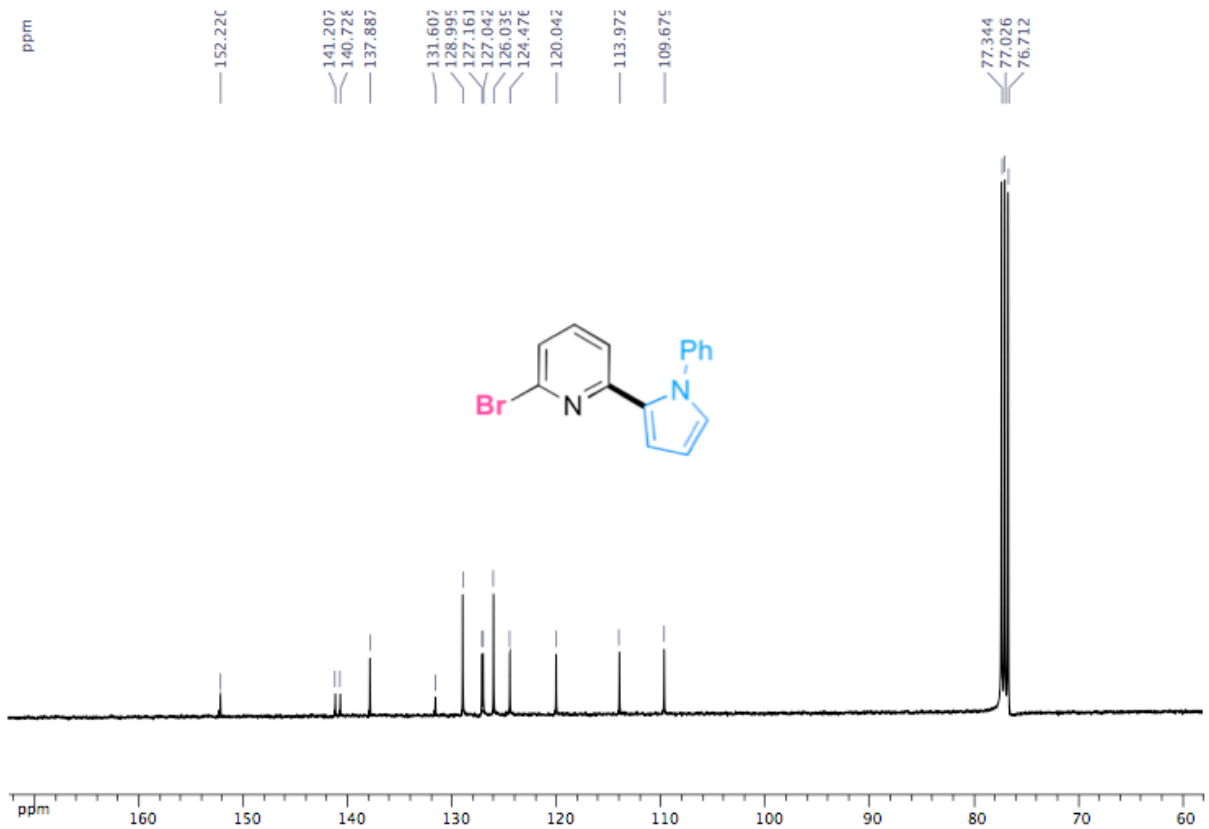
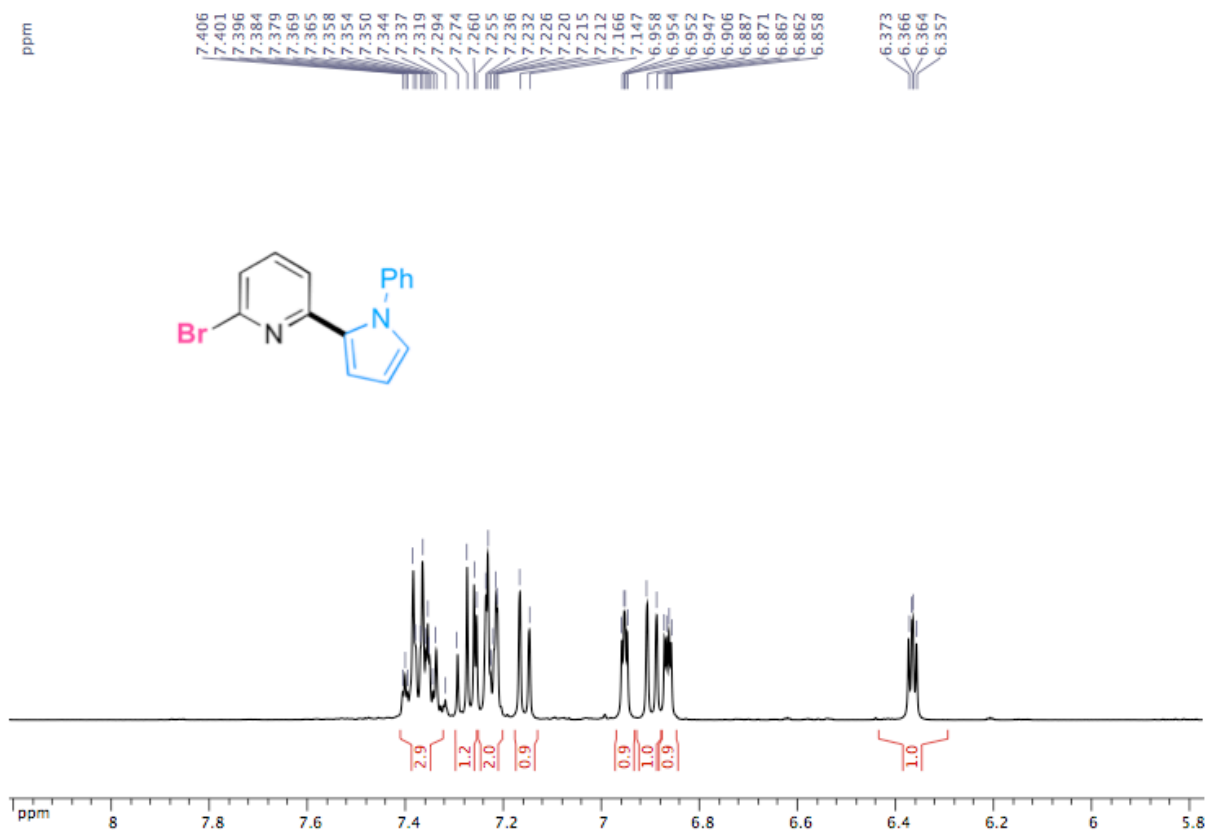


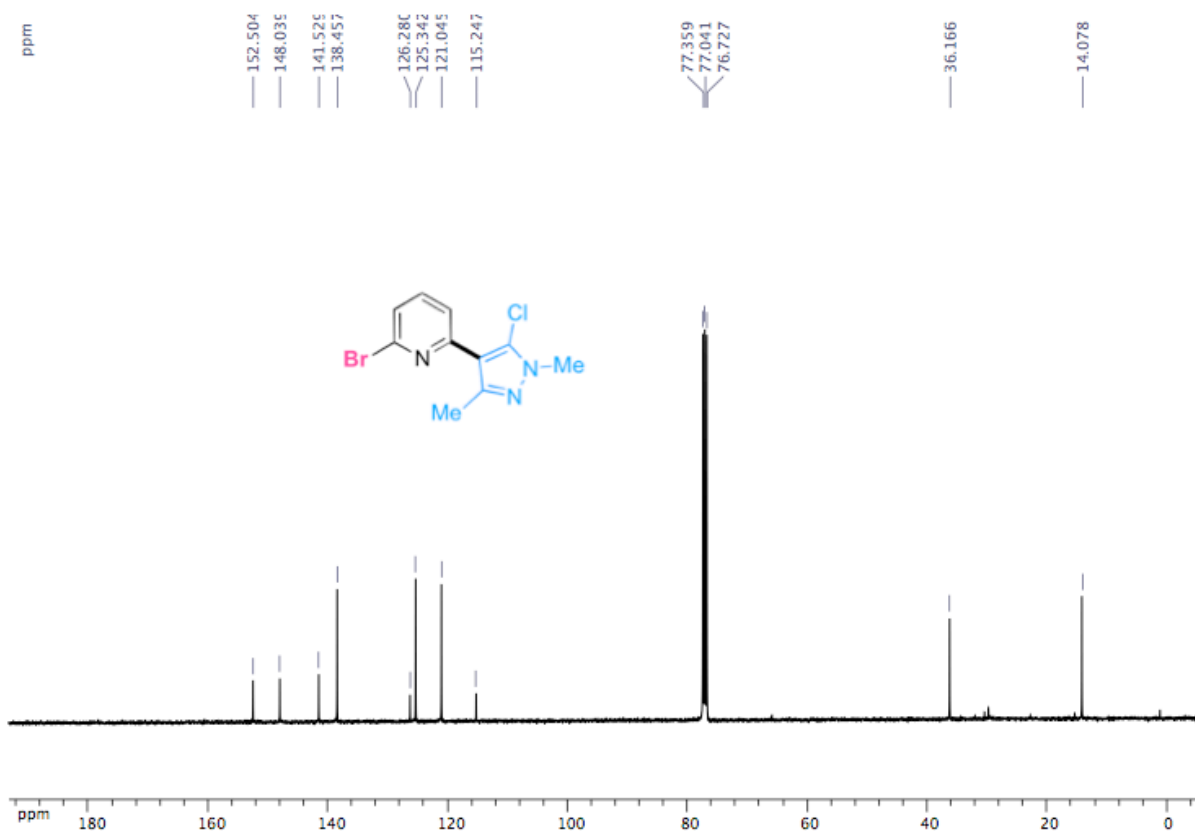
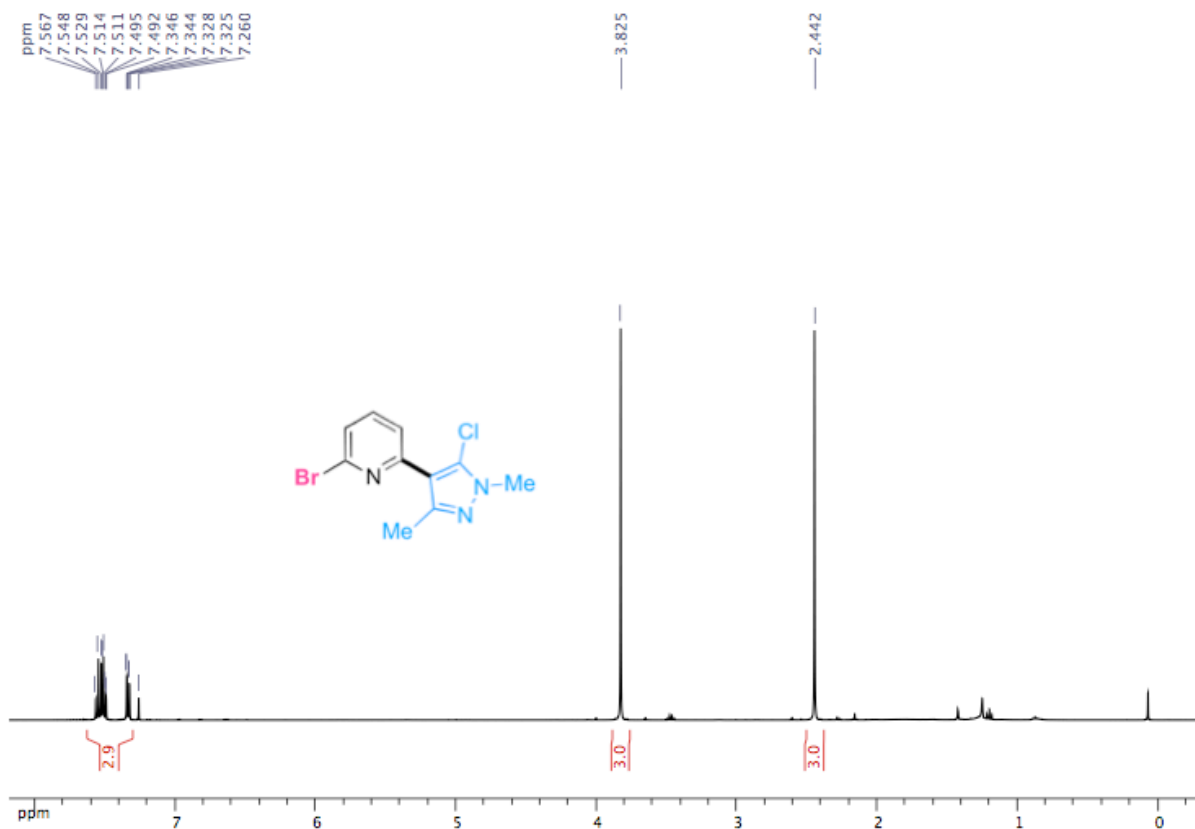






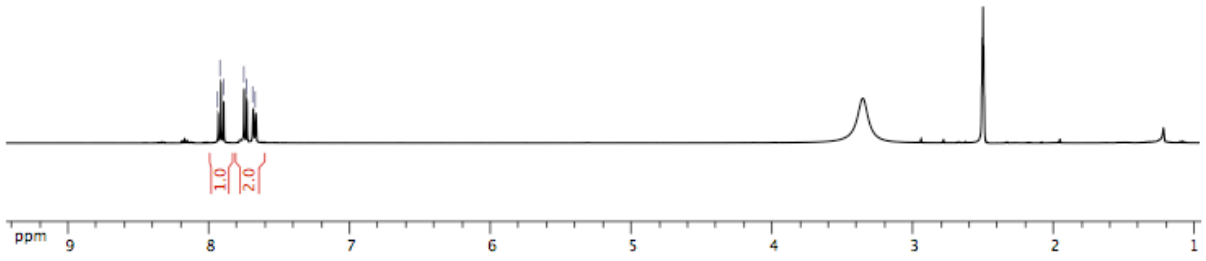
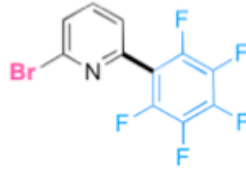






ppm

7.935
7.916
7.896
7.751
7.732
7.687
7.669



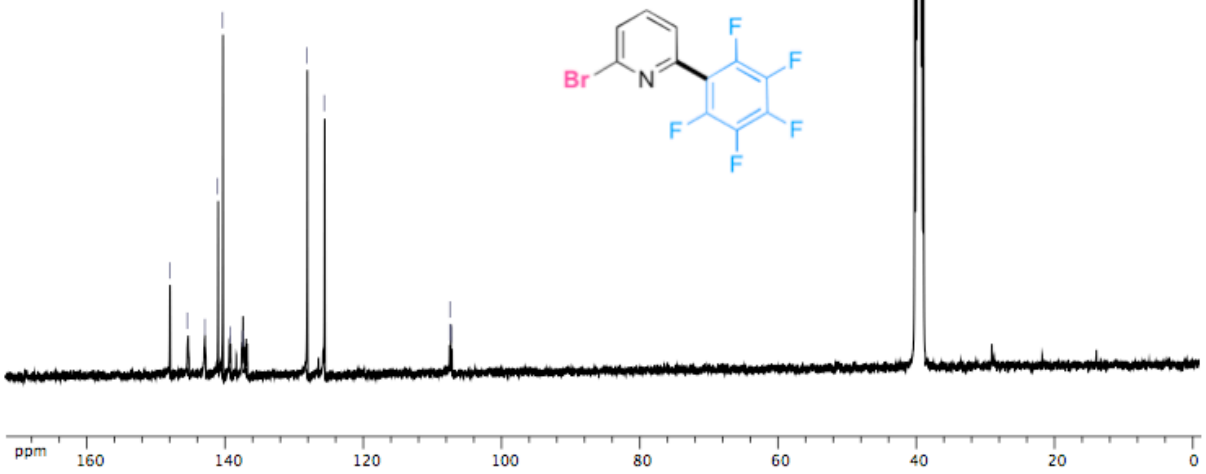
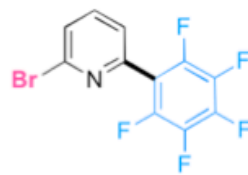
ppm

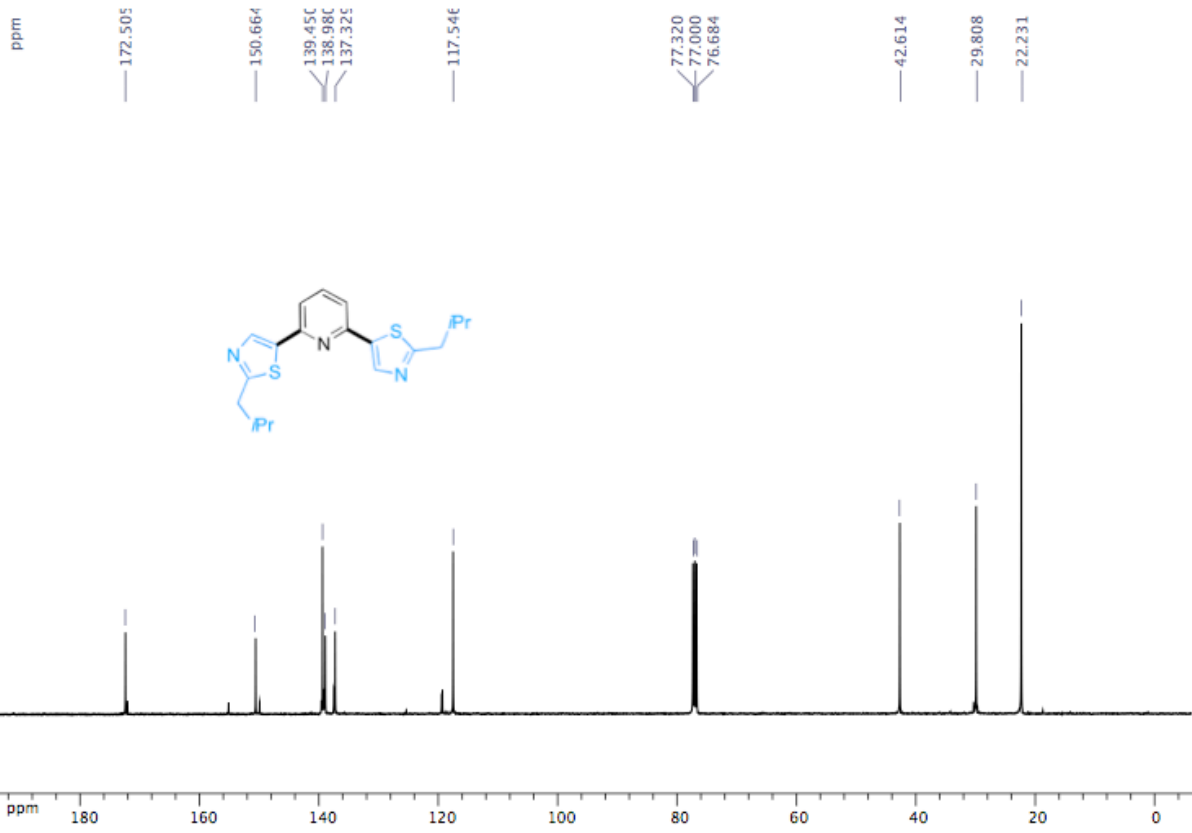
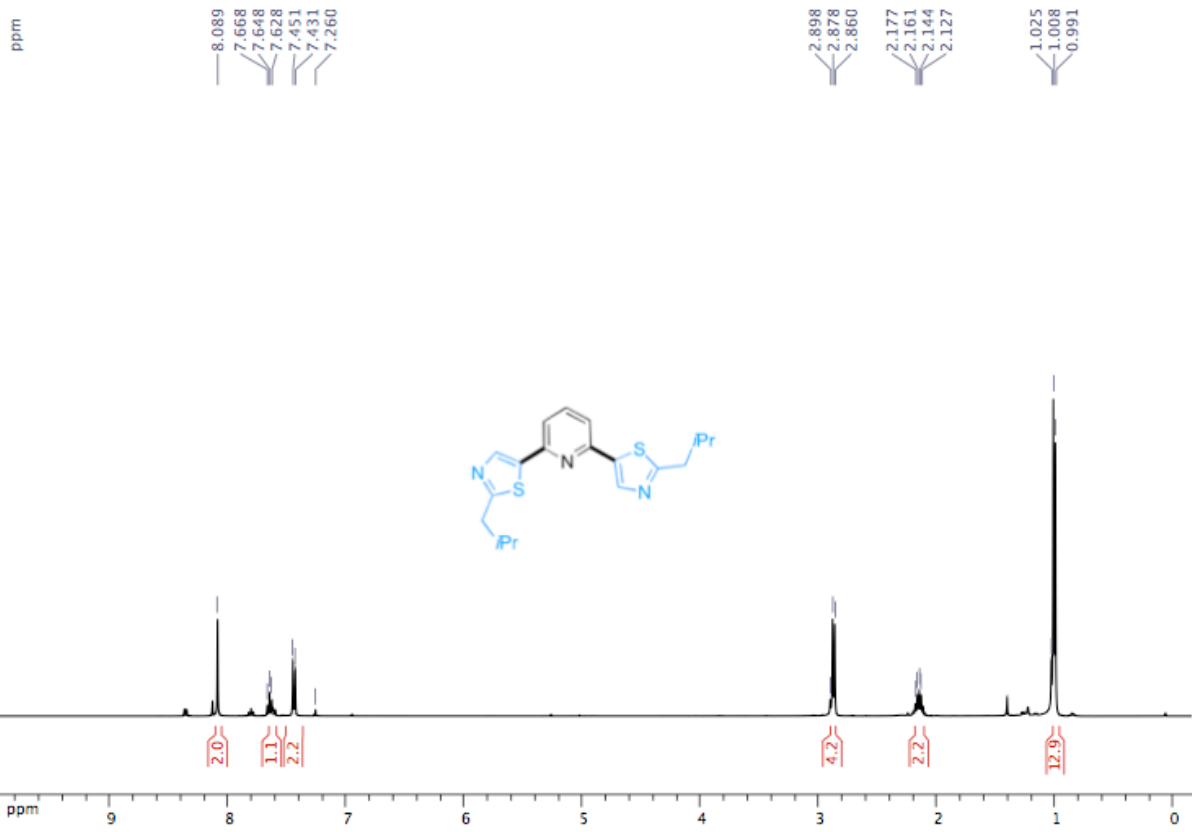
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145.313
142.910
140.982
140.281
139.205
137.455

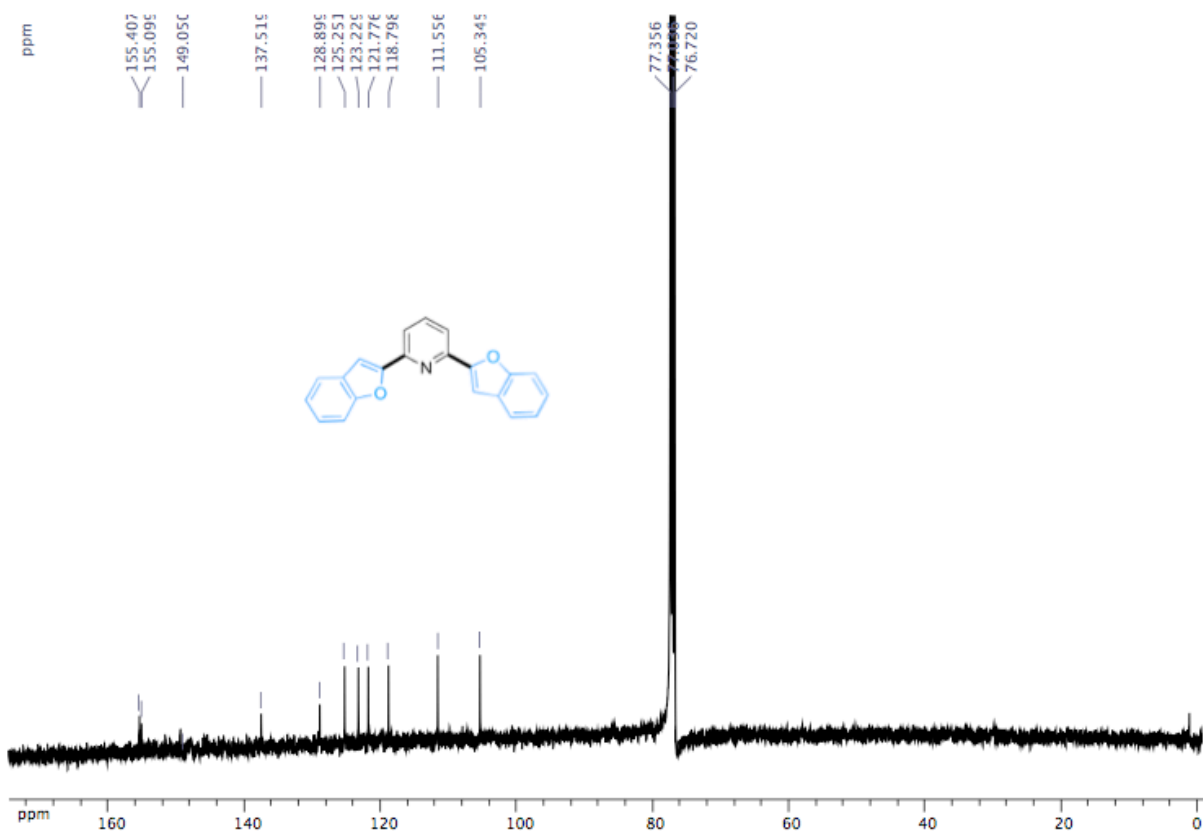
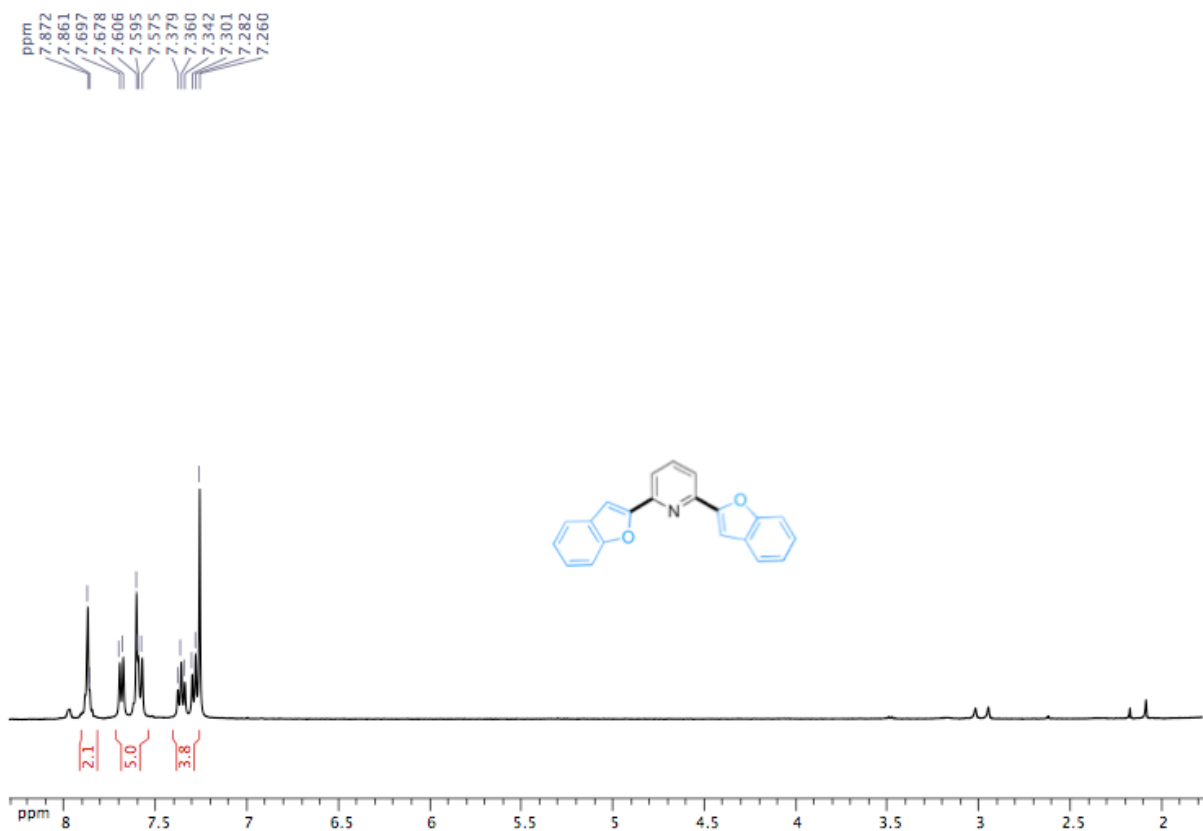
128.065
125.545

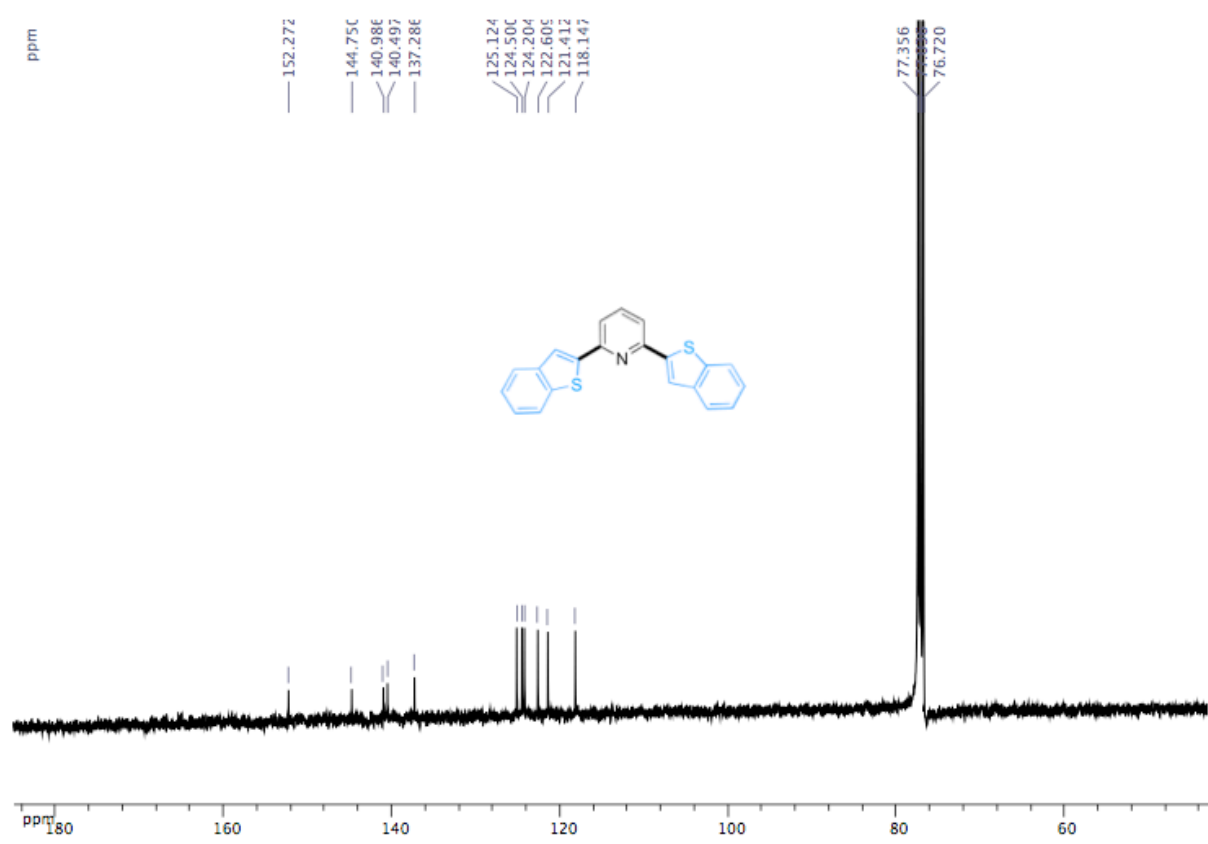
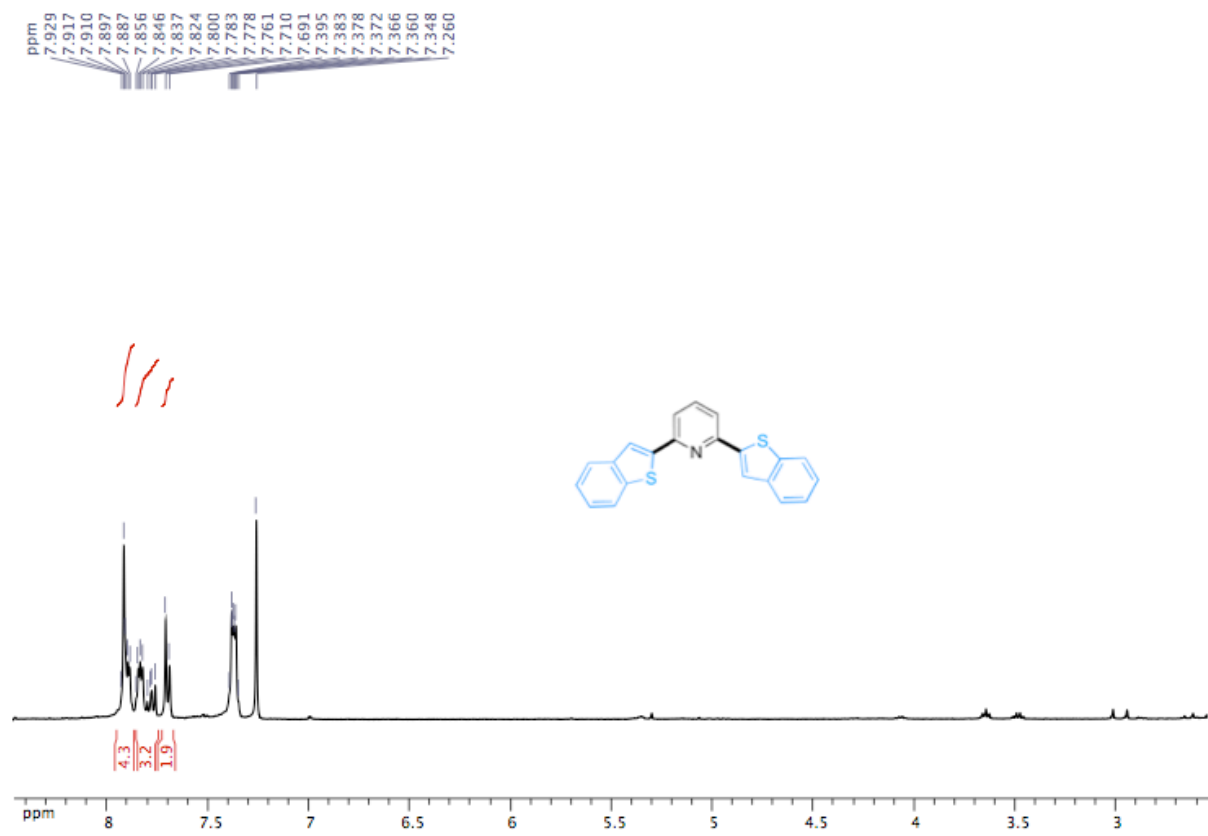
107.463
107.295
107.130

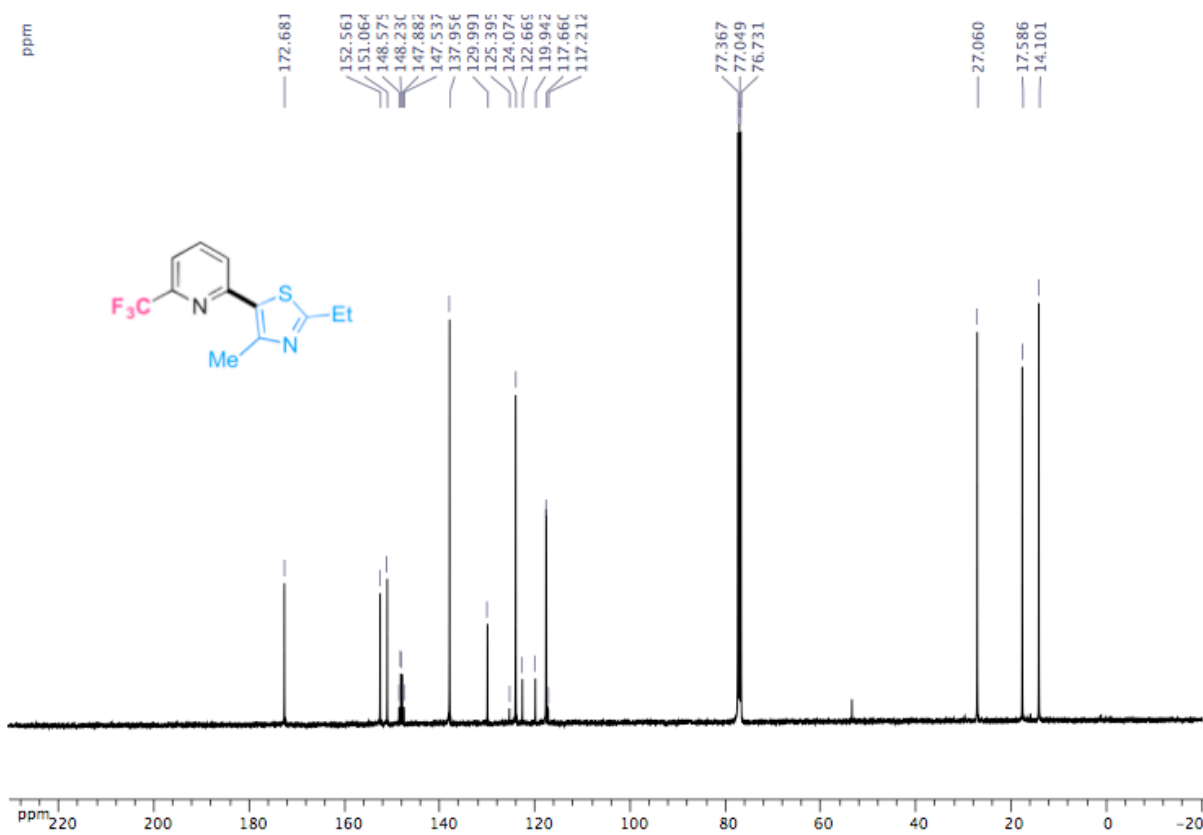
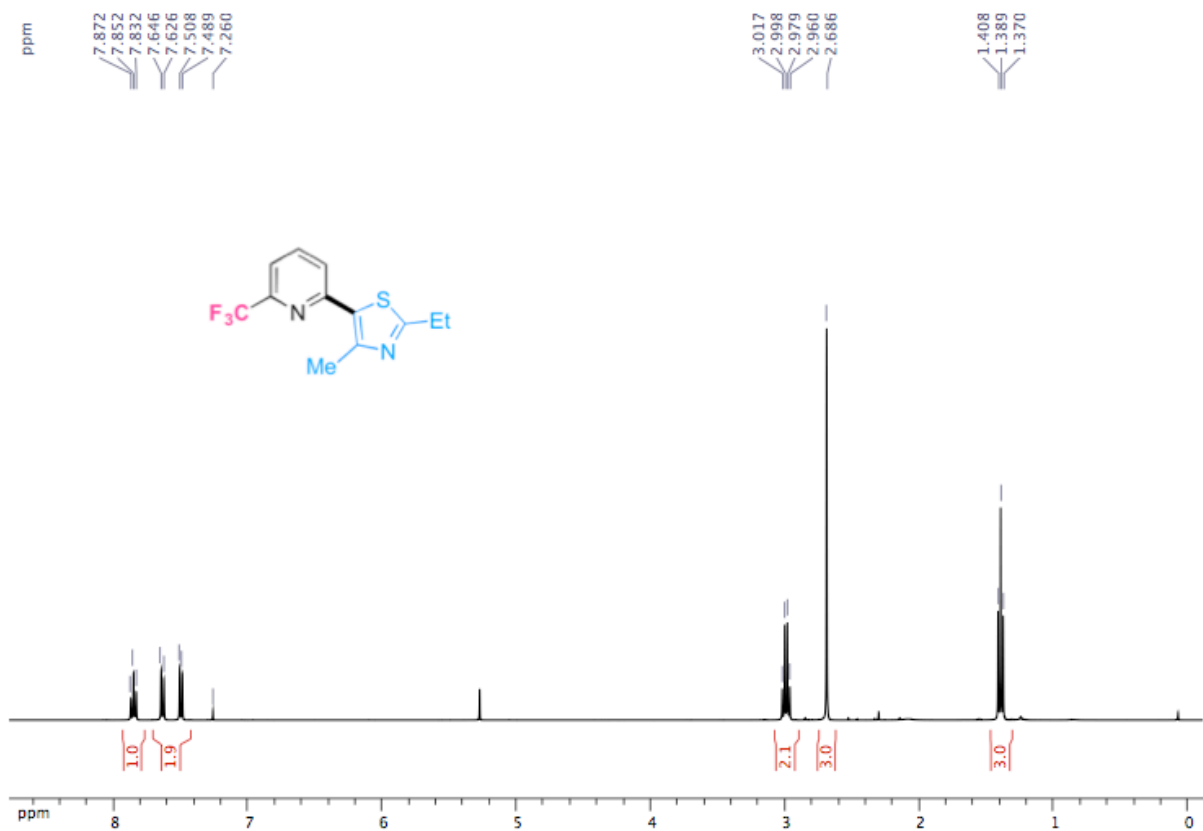
40.138
39.927
39.721
39.303
39.093
38.886

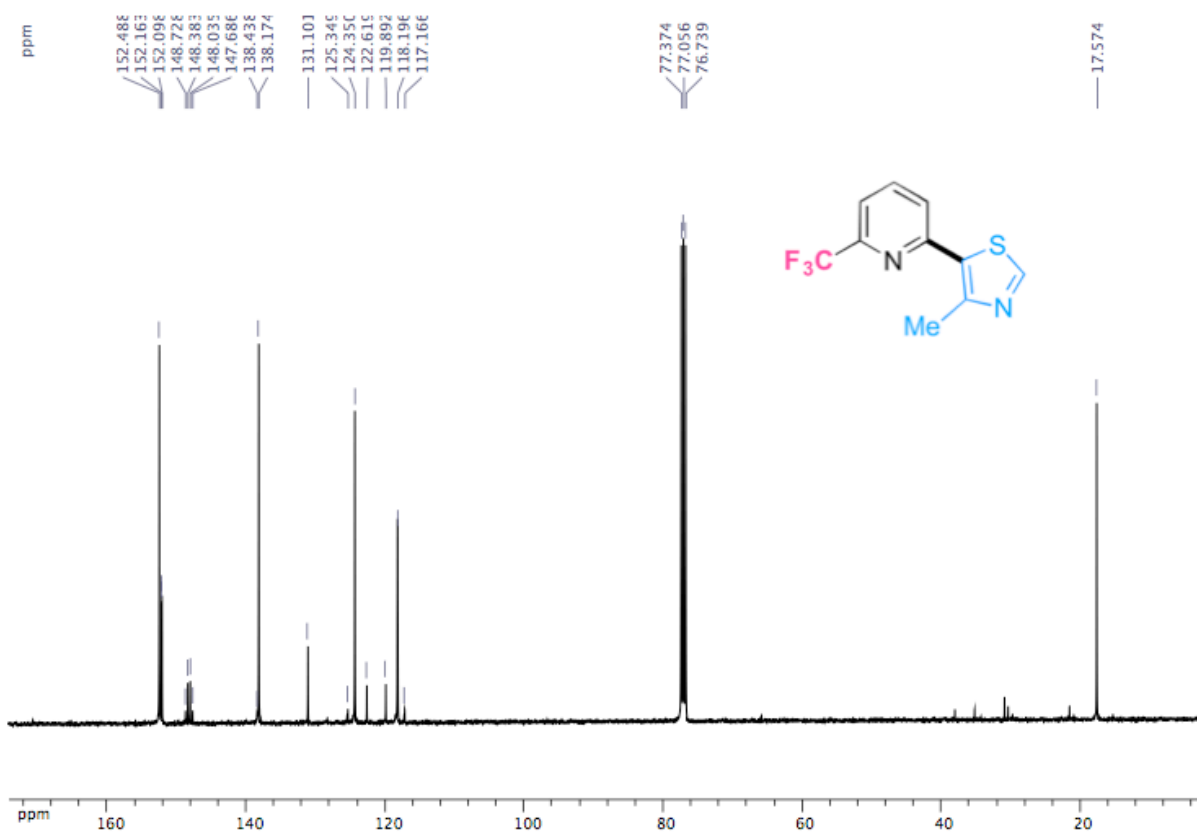
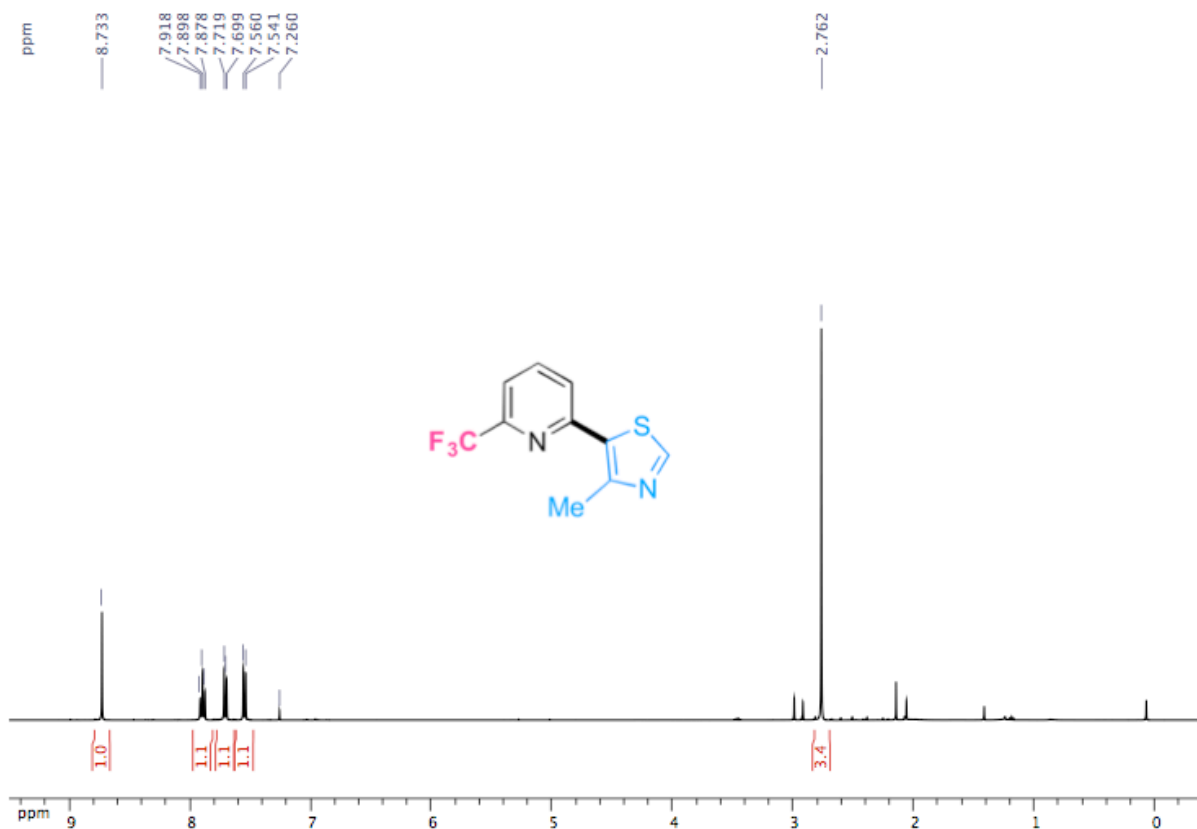


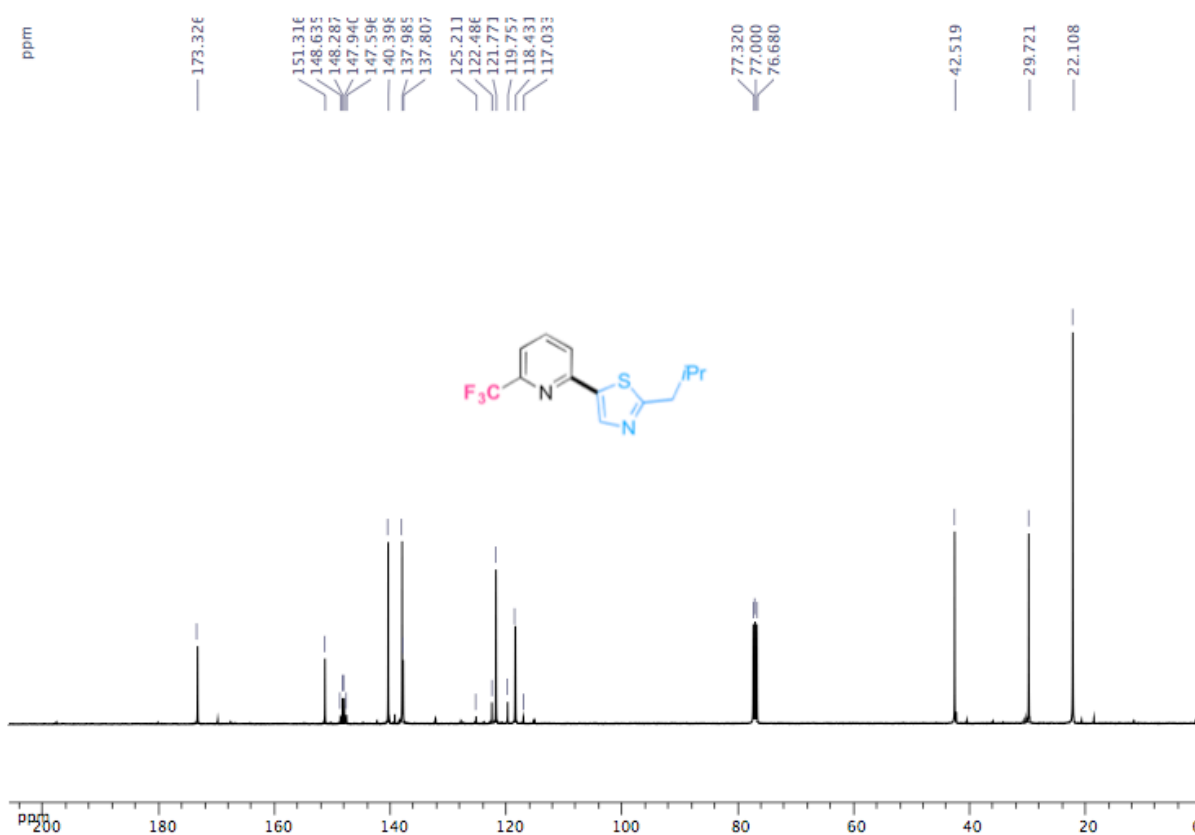
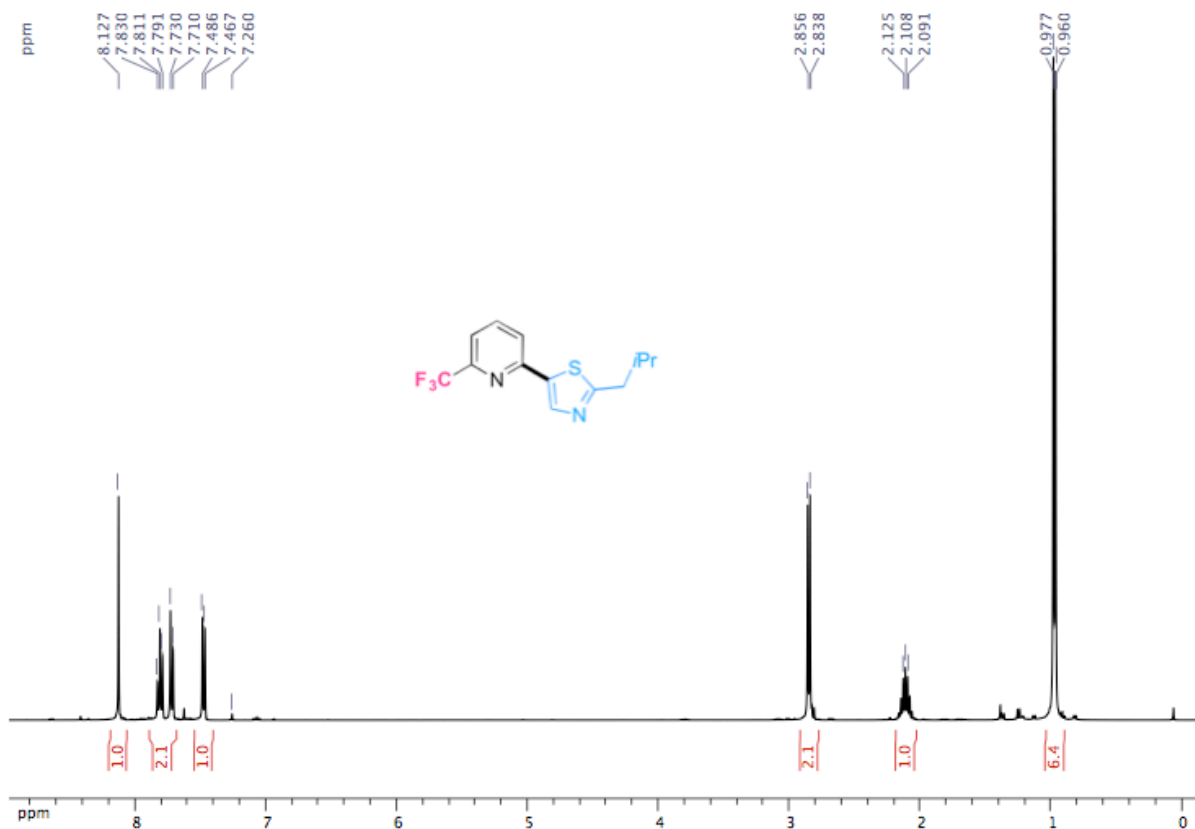


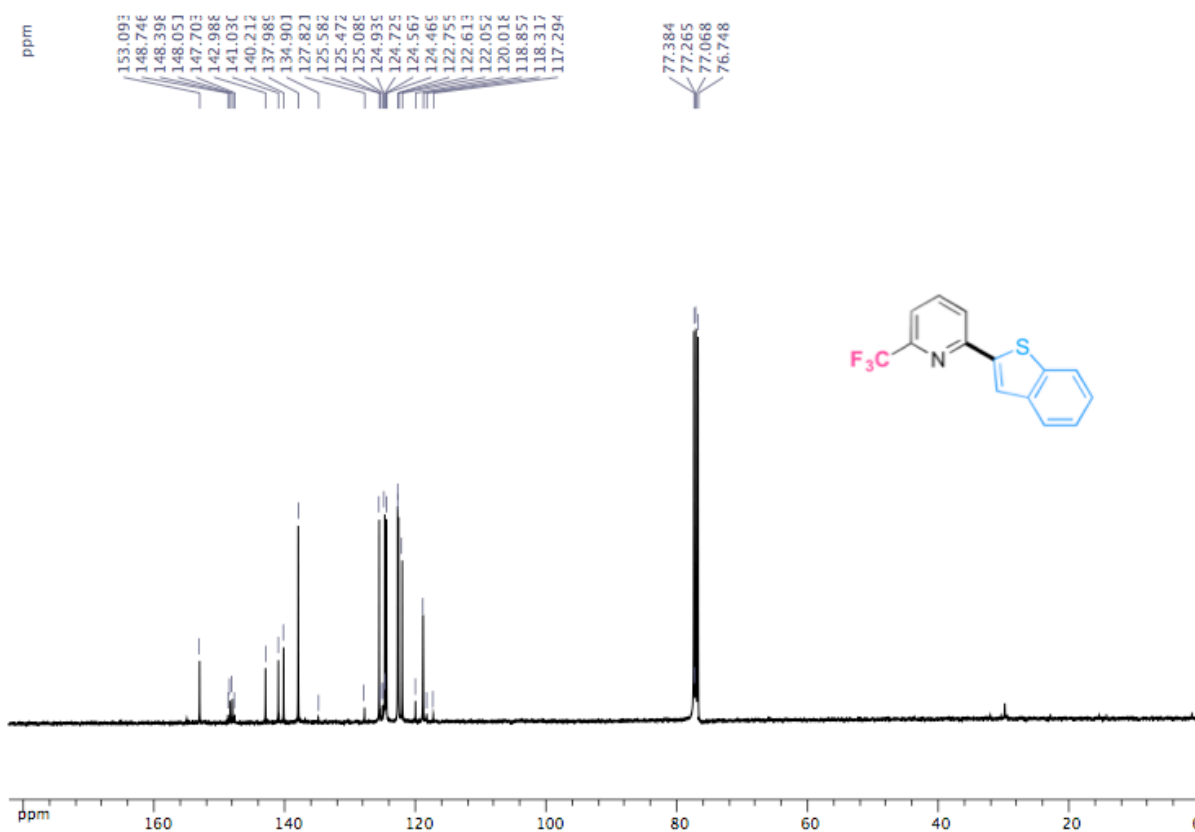
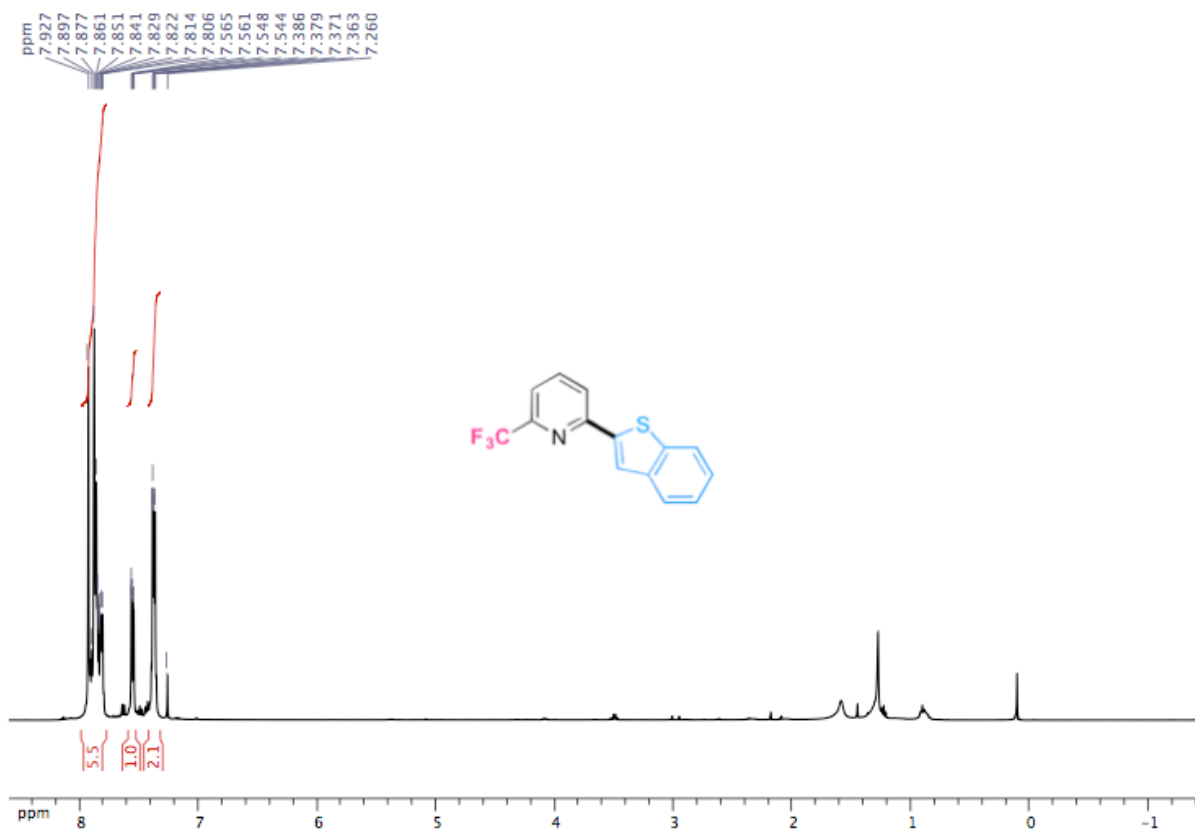




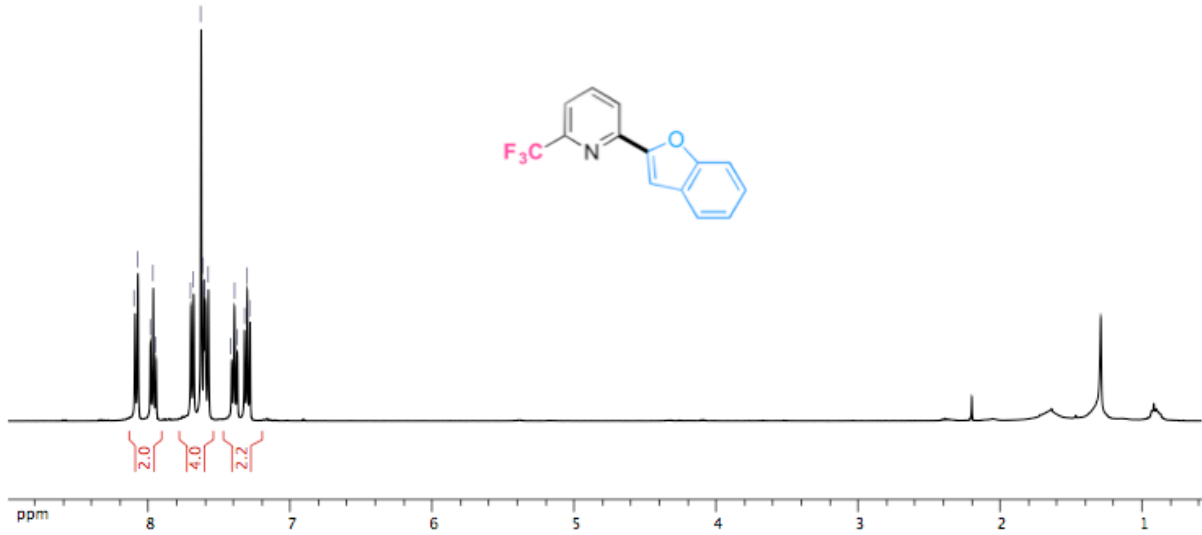






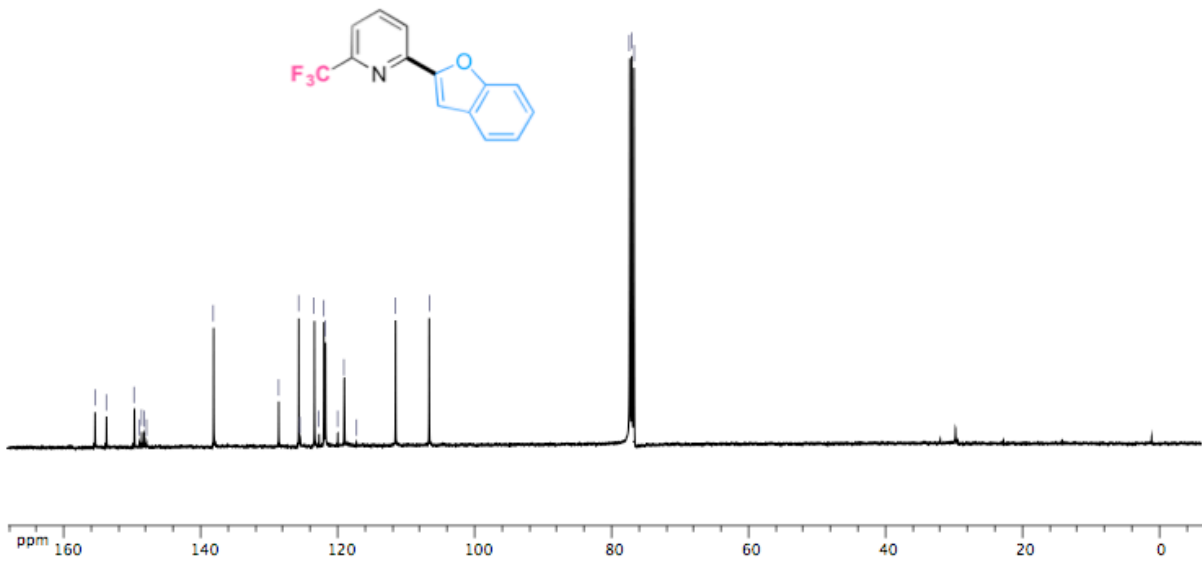


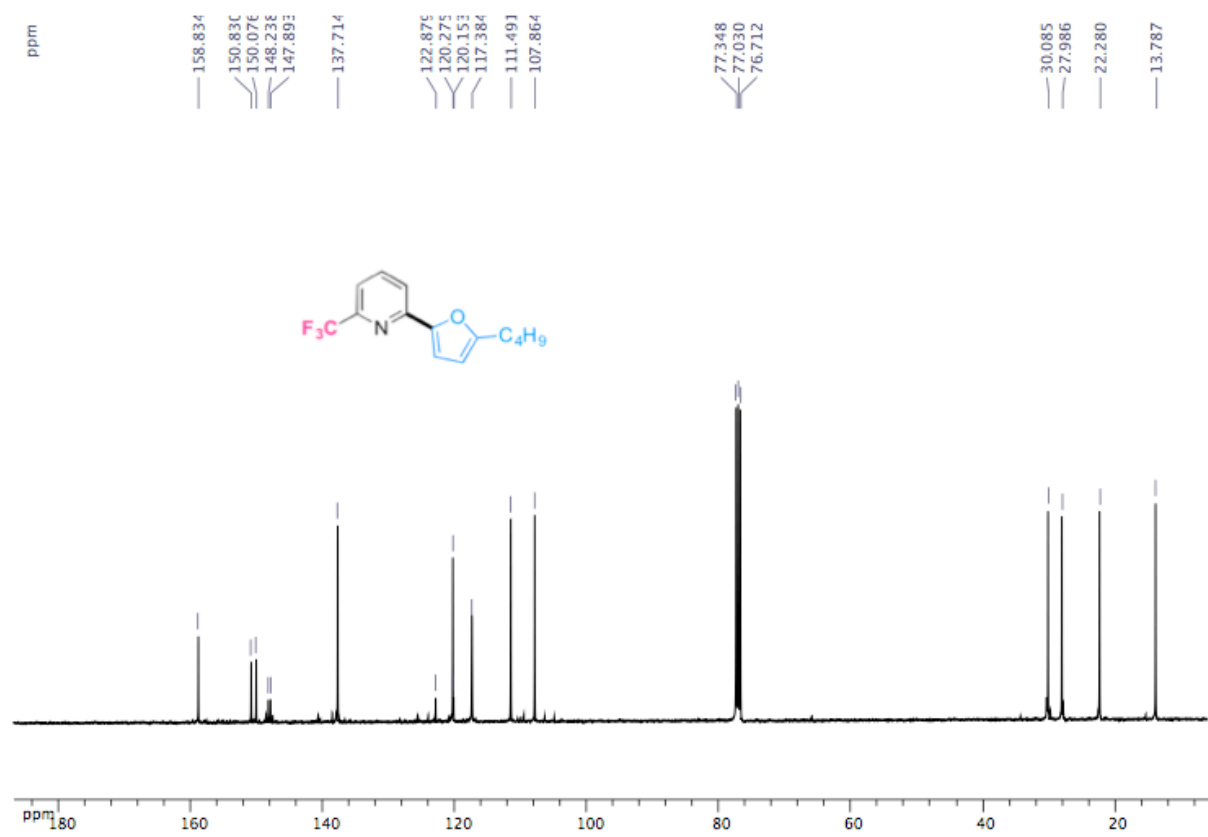
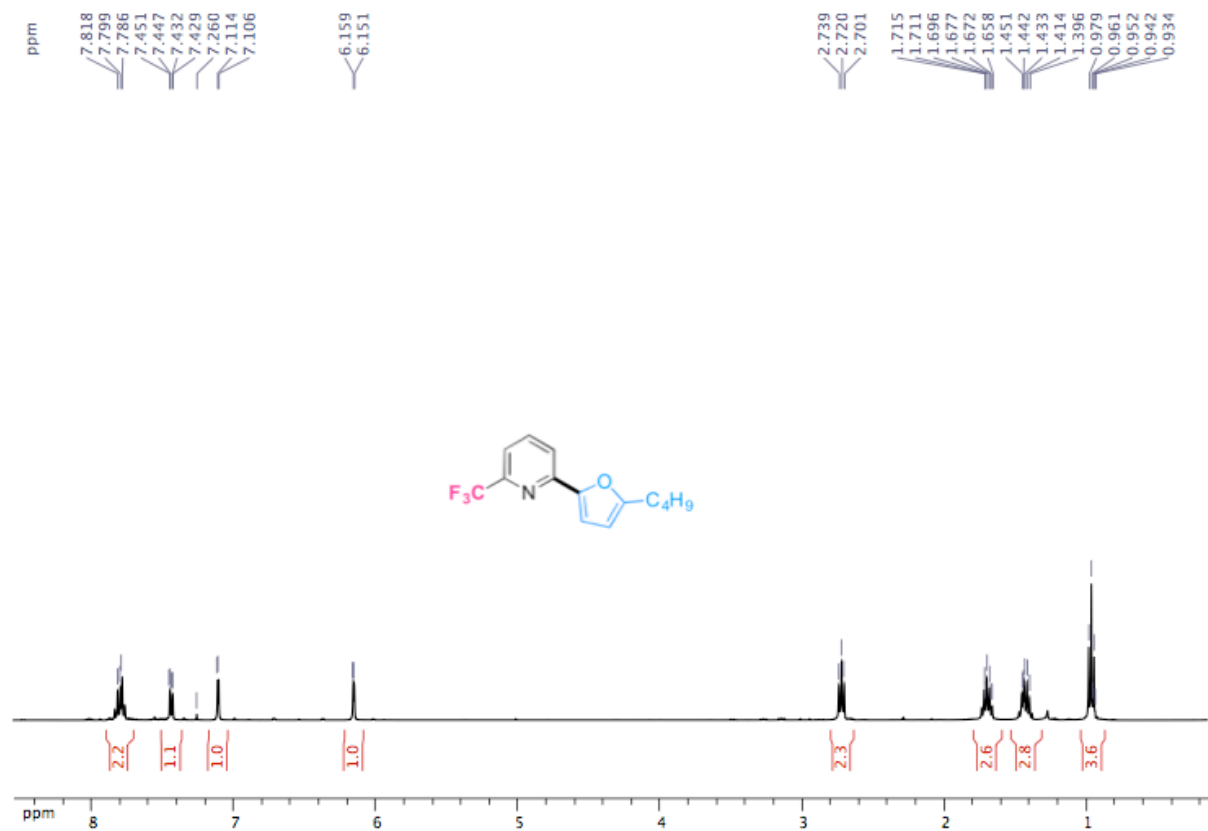
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 7.968
 7.948
 7.703
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 7.580
 7.415
 7.396
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 7.325
 7.306
 7.286

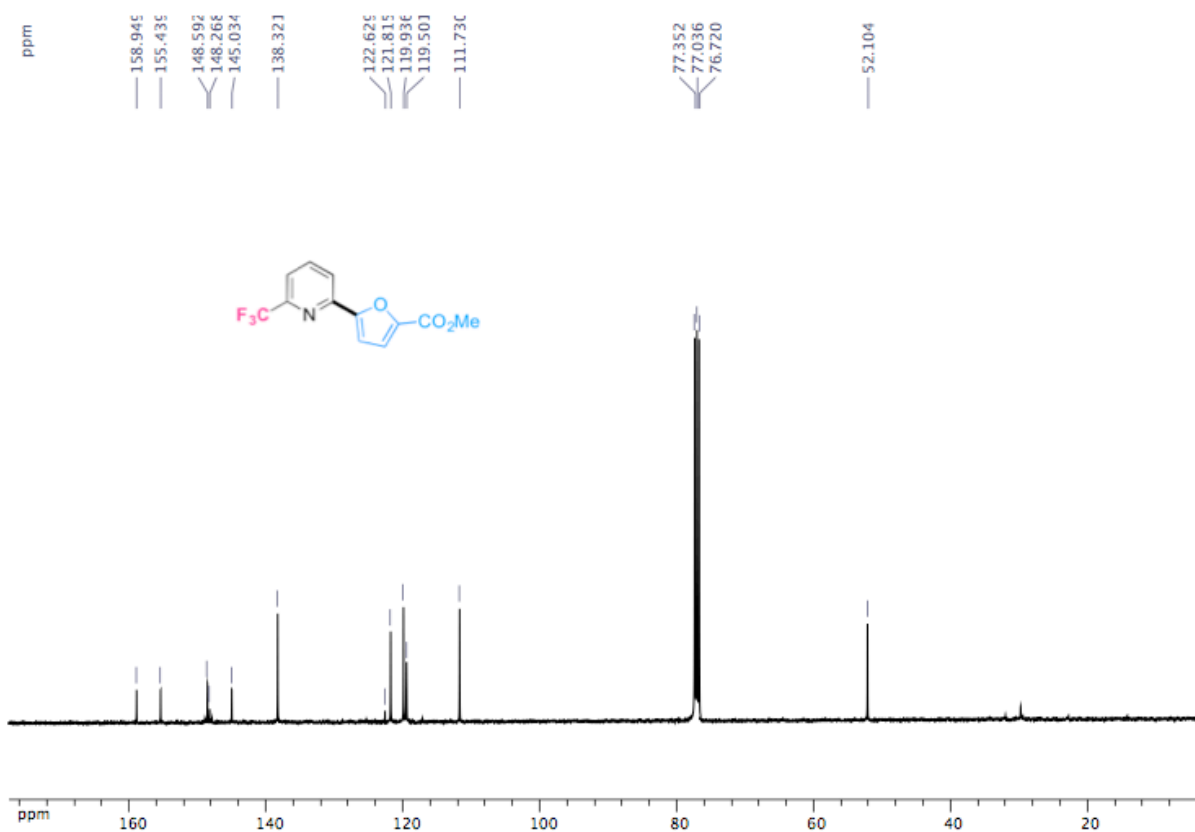
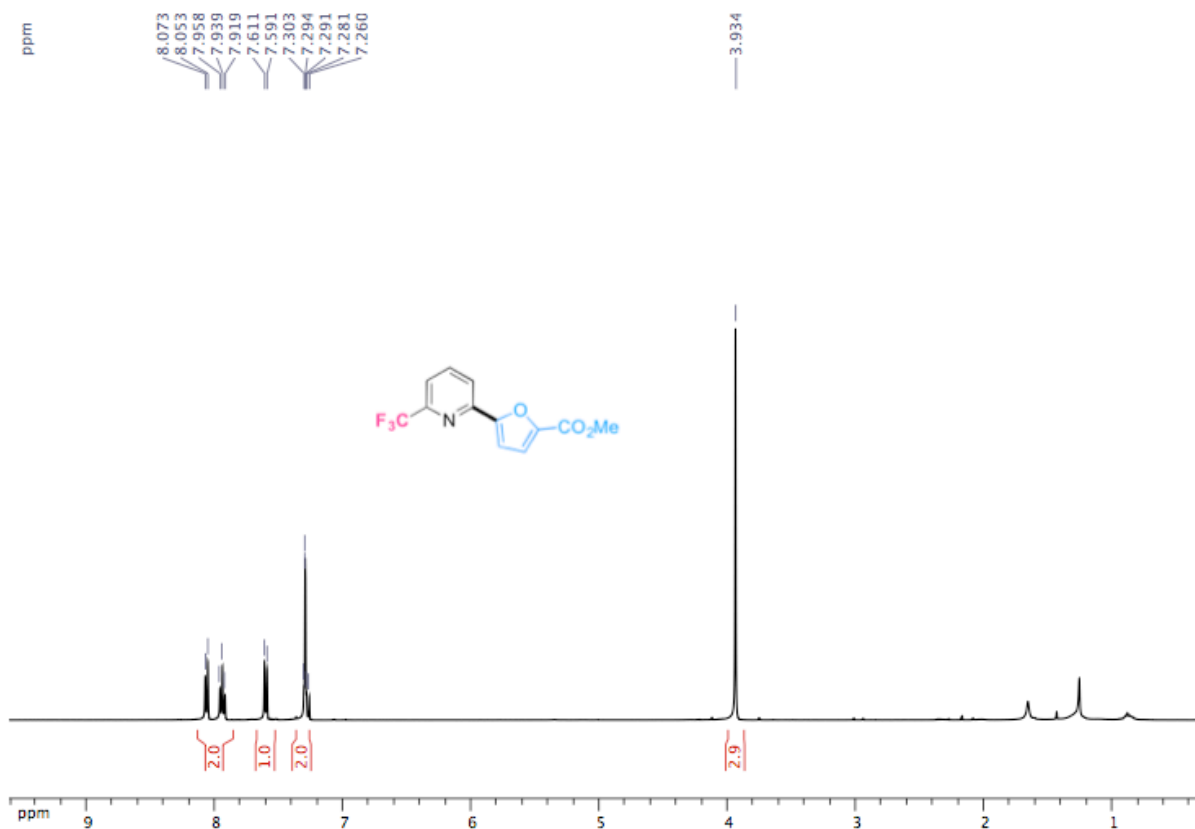


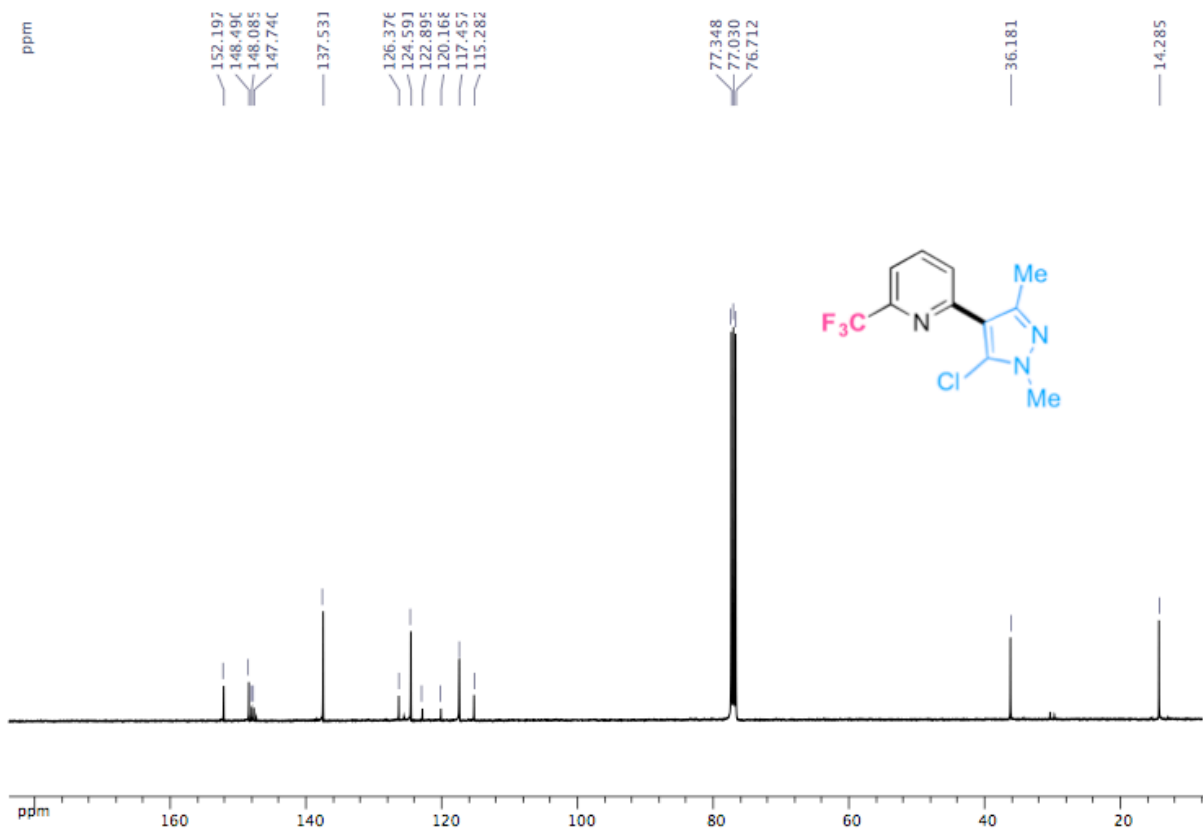
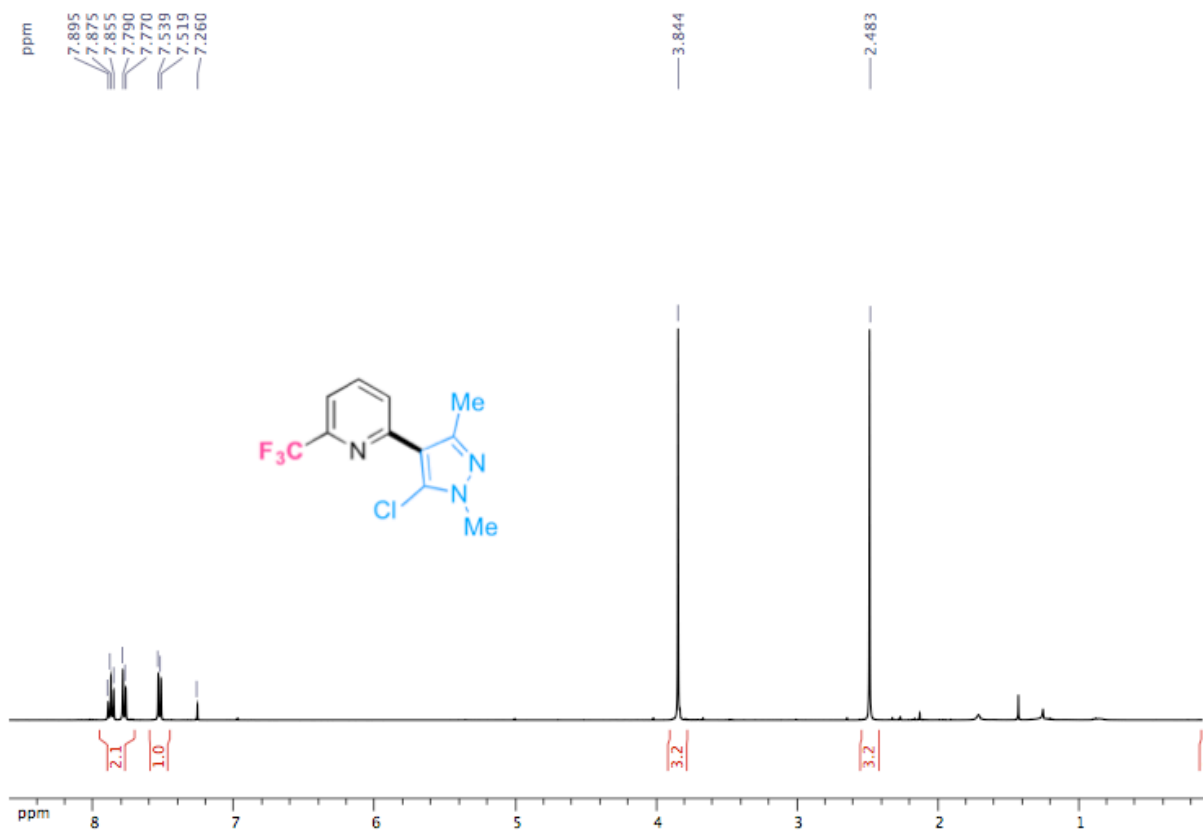
ppm
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 149.022
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 148.327
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 138.181
 128.674
 125.740
 125.491
 123.440
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 121.843
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 119.075
 117.306
 111.584
 106.672

ppm
 77.360
 77.044
 76.724

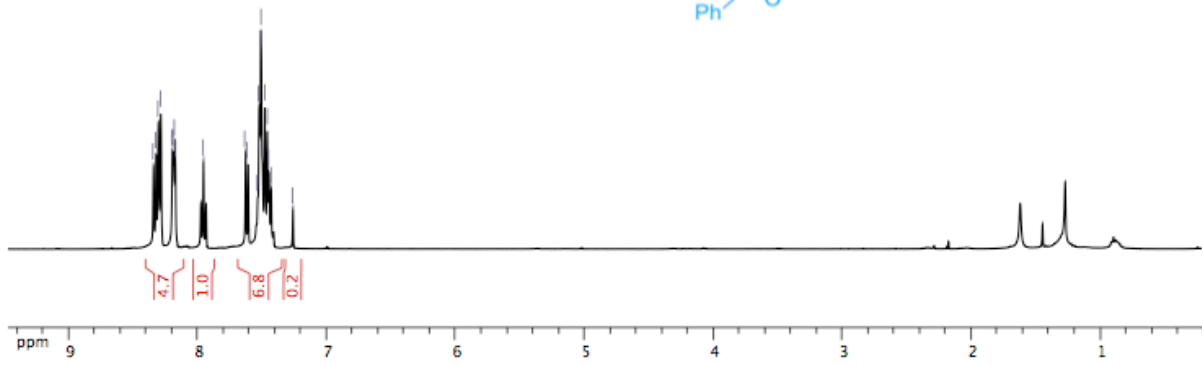
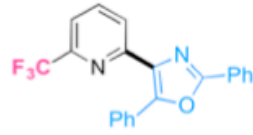








ppm
 8.343
 8.323
 8.304
 8.286
 8.196
 8.188
 8.177
 8.173
 7.955
 7.628
 7.608
 7.534
 7.523
 7.510
 7.506
 7.497
 7.479
 7.460
 7.446
 7.429
 7.260



ppm
 159.803
 152.481
 149.647
 147.422
 147.074
 137.914
 134.904
 130.684
 129.397
 128.880
 128.355
 128.283
 128.076
 127.053
 126.582
 125.265
 122.990
 120.260
 118.946
 117.533
 77.359
 77.041
 76.723

