

**Supporting Information**  
**For**  
**Rhodium-Catalyzed Transformation of Heteroaryl Aryl**  
**Ethers to Heteroaryl Fluorides**

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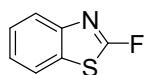
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## Supplementary Materials

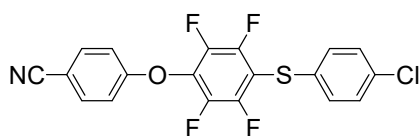
$^1\text{H}$ -,  $^{13}\text{C}$ -,  $^{19}\text{F}$ -,  $^{31}\text{P}$ -NMR spectra were recorded on a Varian Mercury (400 MHz) and tetramethylsilane, trifluoroacetic acid, triphenylphosphine were used as standard. IR spectra were measured on a JASCO FT/IR-410 spectrophotometer. Melting points were determined with a Yanagimoto micro melting point apparatus without correction. High- and low-resolution mass spectra were measured on a JEOL JMS-DX-303, a JEOL JMS-700, or a JMS-T100GC spectrometer. Silica gel 60 (40-50  $\mu\text{m}$ , Kanto Chemical CO., INC.) was employed for flash column chromatography.

**Typical experimental procedures for the synthesis of 2-Fluorobenzothiazole (3a):** In a two-necked flask equipped with a magnetic stirrer bar and a reflux condenser were placed  $\text{RhH}(\text{dppBz})_2$  (10 mol%, 24.9 mg), 4-[(2-benzothiazolyl)oxy]benzonitrile (**1a**) (0.25 mmol, 63.1 mg), and [(4-chlorophenyl)thio]pentafluorobenzene (**2a**) (1.00 mmol, 310.6 mg) in chlorobenzene (0.25 mL) under an argon atmosphere, and the solution was stirred and heated at reflux for 3 h. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel giving 2-fluorobenzothiazole (**3a**) (67%, 25.7 mg) and 1-[(4-Chlorophenyl)thio]-4-[(4-cyanophenyl)oxy]-2,3,5,6-tetrafluorobenzene (**4a**) (75%, 76.7 mg).

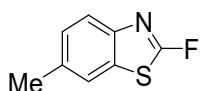
**2-Fluorobenzothiazole<sup>1</sup> (3a):** Colorless oil.  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38 (t,  $J = 8.0$  Hz), 7.48 (t,  $J = 8.0$  Hz), 7.73 (d,  $J = 8.0$  Hz), 7.84 (dt,  $J = 0.4, 8.0$  Hz).  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  121.8, 122.8 (d,  $J = 2.9$  Hz), 125.4 (d,  $J = 4.5$  Hz), 126.9, 132.6 (d,  $J = 4.5$  Hz), 146.2 (d,  $J = 18.6$  Hz), 168.7 (d,  $J = 285.2$  Hz).  $^{19}\text{F}$ -NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -75.8 (s). IR (neat) 3067, 1678, 1559, 1223, 755  $\text{cm}^{-1}$ . MS (EI)  $m/z$  153 ( $\text{M}^+$ , 100%). HRMS Calcd for  $\text{C}_7\text{H}_4\text{FN}$ S: 153.0048. Found: 153.0047.



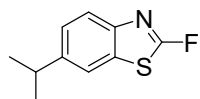
**1-[(4-Chlorophenyl)thio]-4-[(4-cyanophenyl)oxy]-2,3,5,6-tetrafluorobenzene (4a):** Colorless solid. Mp. 114.0-115.0  $^\circ\text{C}$  (Hexane/AcOEt = 4).  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.06 (2H, d,  $J = 8.8$  Hz), 7.30 (2H, d,  $J = 8.4$  Hz), 7.38 (2H, d,  $J = 8.8$  Hz), 7.67 (2H, d,  $J = 9.2$  Hz).  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  107.9, 111.0 (t,  $J = 20.9$  Hz), 116.3, 118.1, 129.6, 130.9, 132.6, 133.2 (t,  $J = 13.4$  Hz), 134.4, 134.6, 141.1 (dddd,  $J = 253.2, 17.1, 5.2, 3.0$  Hz), 147.6 (dddd,  $J = 248.0, 12.0, 3.7, 3.7$  Hz), 159.5.  $^{19}\text{F}$ -NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -155.5 (2F, dd,  $J = 8.1, 22.8$  Hz), -135.0 (2F, dd,  $J = 8.0, 22.7$  Hz). IR (KBr) 3079, 1603, 1222, 1167, 1089, 1082, 822  $\text{cm}^{-1}$ . MS (EI)  $m/z$  409 ( $\text{M}^+$ , 100%), 389 ( $\text{M}^+ - \text{Cl}$ , 3%), 307 ( $\text{M}^+ - \text{C}_7\text{H}_4\text{N}$ , 5%), 291 ( $\text{M}^+ - \text{C}_7\text{H}_4\text{NO}$ , 7%). HRMS Calcd for  $\text{C}_{19}\text{H}_8\text{F}_4\text{NOS}$ : 408.9951. Found: 408.9967.



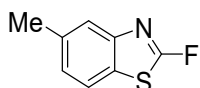
**2-Fluoro-6-methylbenzothiazole<sup>2</sup> (3b):** Colorless solid. Mp. 54.0-55.0 °C (Hexane). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 2.47 (3H, s), 7.28 (1H, dd, *J* = 1.6, 8.4 Hz), 7.52 (1H, s), 7.71 (1H, d, *J* = 8.4 Hz). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 21.5, 121.6, 122.4 (d, *J* = 3.0 Hz), 128.3, 132.6 (d, *J* = 4.5 Hz), 135.6 (d, *J* = 4.4 Hz), 144.0 (d, *J* = 17.8 Hz), 166.6 (d, *J* = 284.5 Hz). <sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) δ -76.5 (s). IR (KBr) 2918, 1560, 1228, 814 cm<sup>-1</sup>. MS (EI) *m/z* 167 (M<sup>+</sup>, 100%). HRMS Calcd for C<sub>8</sub>H<sub>6</sub>FNS: 167.0205. Found: 167.0182.



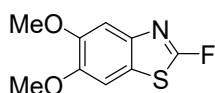
**2-Fluoro-6-(2-methylethyl)benzothiazole (3c):** Colorless oil. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 1.30 (6H, d, *J* = 7.2 Hz), 3.02 (1H, sep, *J* = 7.2 Hz), 7.34 (1H, dd, *J* = 2.0, 8.4 Hz), 7.57 (1H, m), 7.74 (1H, d, *J* = 8.4 Hz). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 24.8, 34.9, 35.0, 119.7 (d, *J* = 9.0 Hz), 123.2 (d, *J* = 21.6 Hz), 126.6 (d, *J* = 3.7 Hz), 133.4 (d, *J* = 3.7 Hz), 145.0 (d, *J* = 17.9 Hz), 147.4 (d, *J* = 3.7 Hz), 168.8 (d, *J* = 284.4 Hz). <sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) δ -76.2 (s). IR (neat) 2962, 2928, 2871, 1610, 1227, 824 cm<sup>-1</sup>. MS (EI) *m/z* 195 (M<sup>+</sup>, 56%), 180 (M<sup>+</sup>-C<sub>2</sub>H<sub>5</sub>, 100%). HRMS Calcd for C<sub>10</sub>H<sub>10</sub>FNS: 195.0518. Found: 195.0518.



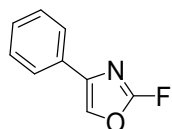
**2-Fluoro-5-methylbenzothiazole (3d):** Colorless oil. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 2.48 (3H, s), 7.21 (1H, d, *J* = 8.4 Hz), 7.60 (1H, dd, *J* = 0.8, 8.4 Hz), 7.64 (1H, s). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 21.5, 121.3, 123.1 (d, *J* = 2.9 Hz), 126.9 (d, *J* = 4.5 Hz), 129.4 (d, *J* = 4.5 Hz), 137.1, 146.4 (d, *J* = 17.8 Hz), 166.0 (d, *J* = 285.3 Hz). <sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) δ -75.3 (s). IR (neat) 2923, 1613, 1459, 1229, 799 cm<sup>-1</sup>. MS (EI) *m/z* 167 (M<sup>+</sup>, 100%). HRMS Calcd for C<sub>8</sub>H<sub>6</sub>FNS: 167.0205. Found: 167.0181.



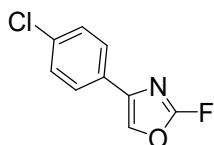
**2-Fluoro-5,6-dimethoxybenzothiazole (3e):** Colorless solid. Mp. 109.5-110.5 °C (Hexane). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 3.94 (6H, s), 7.15 (1H, s), 7.32 (1H, s). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 56.2, 56.4, 103.1, 105.1 (d, *J* = 2.3 Hz), 123.7 (d, *J* = 3.8 Hz), 140.0 (d, *J* = 17.9 Hz), 148.4 (d, *J* = 3.7 Hz), 149.6, 167.5 (d, *J* = 283.7 Hz). <sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) δ -78.3 (s). IR (KBr) 3058, 1606, 1564, 1226, 1204, 1058 cm<sup>-1</sup>. MS (EI) 213 (M<sup>+</sup>, 100%), 198 (M<sup>+</sup>-CH<sub>3</sub>, 38%). HRMS Calcd for C<sub>9</sub>H<sub>8</sub>FNO<sub>2</sub>S: 213.0260. Found: 213.0268.



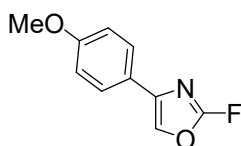
**2-Fluoro-4-(3,4-dimethoxyphenyl)oxazole<sup>3</sup> (3f):** Colorless oil. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 7.35 (1H, t, *J* = 7.2 Hz), 7.41 (2H, t, *J* = 7.2 Hz), 7.59 (1H, d, *J* = 1.2 Hz), 7.66 (2H, td, *J* = 1.2, 7.2 Hz). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 125.2, 128.7, 128.8, 129.5 (d, *J* = 6.7 Hz), 129.9, 140.4 (d, *J* = 4.5 Hz), 156.6 (d, *J* = 254.6 Hz). <sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) δ -99.4 (s). IR (neat) 1599, 1485, 1092, 713 cm<sup>-1</sup>. MS (EI) *m/z* 163 (M<sup>+</sup>, 100%), 135 (M<sup>+</sup>-CO, 23%). HRMS Calcd for C<sub>9</sub>H<sub>6</sub>FNO: 163.0433. Found: 163.0479.



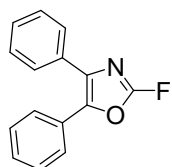
**2-Fluoro-4-(4-chlorophenyl)oxazole (3g):** Colorless solid. Mp. 91.5-92.5 °C (Hexane). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 7.38 (2H, d, *J* = 8.8 Hz), 7.57-7.61 (3H, m). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 126.5, 128.4, 129.0, 129.7 (d, *J* = 6.7 Hz), 134.5, 139.4 (d, *J* = 4.5 Hz), 156.7 (d, *J* = 255.4 Hz). <sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) δ -96.2 (s). IR (KBr) 3117, 1636, 1237, 1011, 833 cm<sup>-1</sup>. MS (EI) *m/z* 197 (M<sup>+</sup>, 100%), 169 (M<sup>+</sup>-CO, 32%). HRMS Calcd for C<sub>9</sub>H<sub>5</sub>ClFNO: 197.0044. Found: 197.0067.



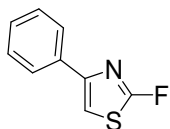
**2-Fluoro-4-(4-methoxyphenyl)oxazole (3h):** Colorless solid. Mp. 72.3-73.0 °C (Hexane). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 3.84 (3H, s), 6.93 (2H, d, *J* = 9.2 Hz), 7.49 (1H, d, *J* = 0.8 Hz), 7.58 (2H, d, *J* = 8.8 Hz). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 55.3, 114.2, 122.6, 126.6, 128.5 (d, *J* = 6.7 Hz), 140.1 (d, *J* = 4.4 Hz), 156.5 (d, *J* = 254.0 Hz), 160.0. <sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) δ -99.7 (s). IR (KBr) 3143, 1649, 1257, 1174, 841 cm<sup>-1</sup>. MS (EI) *m/z* 193 (M<sup>+</sup>, 100%), 178 (M<sup>+</sup>-CH<sub>3</sub>, 24%), 165 (M<sup>+</sup>-CO, 15%). HRMS Calcd for C<sub>10</sub>H<sub>8</sub>FNO<sub>2</sub>: 193.0539. Found: 193.0546.



**2-Fluoro-4,5-diphenyloxazole<sup>3</sup> (3i):** Colorless oil. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 7.33-7.40 (6H, m), 7.55 (2H, m), 7.63 (2H, m). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 126.5, 127.6, 127.8, 128.6, 128.7, 128.8, 129.0, 131.2, 134.2 (d, *J* = 3.7 Hz), 142.3 (d, *J* = 6.7 Hz), 155.5 (d, *J* = 255.5 Hz). <sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) δ -100.6 (s). IR (neat) 1639, 1223, 764, 692 cm<sup>-1</sup>. MS (EI) *m/z* 239 (M<sup>+</sup>, 100%), 211 (M<sup>+</sup>-CO, 15%). HRMS Calcd for C<sub>15</sub>H<sub>10</sub>FNO: 239.0746. Found: 239.0783.

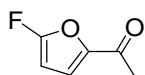


**2-Fluoro-4-phenylthiazole<sup>4</sup> (3j)**: Colorless oil. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 7.07 (1H, d, *J* = 1.2 Hz), 7.34 (1H, t, *J* = 7.2 Hz), 7.41 (2H, t, *J* = 7.6 Hz), 7.80 (2H, d, *J* = 7.2 Hz). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 107.8 (d, *J* = 4.5 Hz), 125.8, 128.5, 128.8, 133.5, 148.3 (d, *J* = 14.1 Hz), 169.8 (d, *J* = 281.5 Hz). <sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) δ -82.8 (s). IR (KBr) 3096, 3061, 3029, 1543, 1237, 1199, 745, 689 cm<sup>-1</sup>. MS (EI) *m/z* 179 (M<sup>+</sup>, 100%), 134 (M<sup>+</sup>-CHS, 17%). HRMS Calcd for C<sub>9</sub>H<sub>5</sub>FNS: 179.0205. Found: 179.0205.

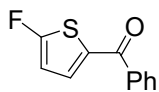


**1-(5-Fluoro-2-furyl)ethanone (3k)**: Colorless oil. <sup>1</sup>H-NMR (400 MHz, Chlorobenzene-*d*<sub>5</sub>) δ 2.04, 5.16 (dd, *J* = 3.6, 7.2 Hz), 6.63 (dd, *J* = 3.2, 3.6 Hz). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 25.2, 85.7 (d, *J* = 13.4 Hz), 119.6, 143.4, 159.1 (d, *J* = 285.3 Hz), 185.1. <sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) δ -109.4 (d, *J* = 3.8 Hz). IR (neat) 3026, 1683, 1619, 1122 cm<sup>-1</sup>. MS (EI) *m/z* 128 (M<sup>+</sup>, 50%), 113 (M<sup>+</sup>-CH<sub>3</sub>, 100%). HRMS Calcd for C<sub>6</sub>H<sub>5</sub>FO<sub>2</sub>: 128.0724. Found: 128.0306.

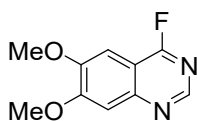
<sup>13</sup>C-NMR was observed before removal of chlorobenzene, because **3k** was volatile.



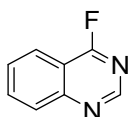
**(5-Fluoro-2-thienyl)phenylmethanone (3l)**: Yellow solid. Mp. 66.5-67.5 °C (Hexane). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 6.58 (1H, dd, *J* = 1.2, 4.4 Hz), 7.34 (1H, dd, *J* = 3.6, 4.4 Hz), 7.50 (2H, t, *J* = 8.0 Hz), 7.60 (1H, tt, *J* = 1.6, 7.6 Hz), 7.80 (2H, d, *J* = 7.2 Hz). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 109.6 (d, *J* = 11.9 Hz), 128.5, 129.0, 132.3, 133.0, 133.3 (d, *J* = 4.4 Hz), 137.1, 172.3 (d, *J* = 298.6 Hz), 188.0. <sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) δ -120.2 (d, *J* = 2.6 Hz). IR (KBr) 3053, 1623, 1207, 708 cm<sup>-1</sup>. MS (EI) *m/z* 206 (M<sup>+</sup>, 100%), 129 (M<sup>+</sup>-C<sub>6</sub>H<sub>5</sub>, 85%), 105 (M<sup>+</sup>-C<sub>7</sub>H<sub>5</sub>O, 93%). HRMS Calcd for C<sub>11</sub>H<sub>7</sub>FOS: 206.0202. Found: 206.0170.



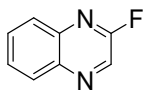
**4-Fluoro-6,7-dimethoxyquinazoline (3m)**: Colorless solid. Mp. 165.2-166.0 °C (Hexane/AcOEt = 4). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 4.06 (3H, s), 4.08 (3H, s), 7.29 (1H, s), 7.38 (1H, d, *J* = 1.6 Hz), 8.77 (1H, d, *J* = 1.6 Hz). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 56.4, 56.5, 99.5, 106.8 (d, *J* = 5.2 Hz), 109.0 (d, *J* = 25.3 Hz), 151.0, 151.6 (d, *J* = 6.7 Hz), 152.5 (d, *J* = 14.9 Hz), 156.8, 165.6 (d, *J* = 255.4 Hz). <sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) δ -71.3 (s). IR (KBr) 2952, 2925, 1617, 1601, 1237, 1127 cm<sup>-1</sup>. MS (EI) *m/z* 208 (M<sup>+</sup>, 100%), 193 (M<sup>+</sup>-CH<sub>3</sub>, 20%), 165 (M<sup>+</sup>-C<sub>2</sub>H<sub>3</sub>O, 23%). HRMS Calcd for C<sub>10</sub>H<sub>9</sub>FN<sub>2</sub>O<sub>2</sub>: 208.0648. Found: 208.0651.



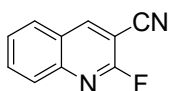
**4-Fluoroquinazoline<sup>5</sup> (3n):** Colorless solid. Mp. 81.5-82.5 °C (sublimation). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 7.74 (1H, t, *J* = 7.6 Hz), 8.00 (1H, td, *J* = 0.8, 8.0 Hz), 8.12 (1H, d, *J* = 8.8 Hz), 8.17 (1H, dd, *J* = 0.8, 8.4 Hz), 8.96 (1H, d, *J* = 1.2 Hz). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 114.6 (d, *J* = 26.1 Hz), 122.7, 128.1 (d, *J* = 4.5 Hz), 128.6, 135.2, 153.6 (d, *J* = 5.2 Hz), 153.9 (d, *J* = 14.9 Hz), 167.1 (d, *J* = 261.4 Hz). <sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) δ -67.5 (s). IR (KBr) 3059, 1674, 1596, 1561, 1112, 778 cm<sup>-1</sup>. MS (EI) *m/z* 148 (M<sup>+</sup>, 100%), 129 (M<sup>+</sup>-F, 28%). HRMS Calcd for C<sub>8</sub>H<sub>5</sub>FN<sub>2</sub>: 148.0437. Found: 148.0456.



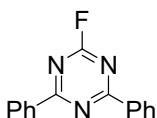
**2-Fluoroquinoxaline<sup>5</sup> (3o):** Brown oil. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 7.76-7.85 (2H, m), 7.98 (1H, dd, *J* = 1.6, 7.6 Hz), 8.17 (1H, dd, *J* = 1.6, 8.0 Hz), 8.72 (1H, d, *J* = 8.0 Hz). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 128.2 (d, *J* = 1.5 Hz), 129.2, 129.2 (d, *J* = 3.0 Hz), 131.4, 136.1 (d, *J* = 42.5 Hz), 139.5 (d, *J* = 10.4 Hz), 141.3 (d, *J* = 1.4 Hz), 156.4 (d, *J* = 256.9 Hz). <sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) δ -77.9 (d, *J* = 7.5 Hz). IR (neat) 3067, 1586, 1216, 764 cm<sup>-1</sup>. MS (EI) *m/z* 148 (M<sup>+</sup>, 100%), 129 (M<sup>+</sup>-F, 12%). HRMS Calcd for C<sub>8</sub>H<sub>5</sub>FN<sub>2</sub>: 148.0437. Found: 148.0429.



**3-Cyano-2-fluoroquinoline (3p):** Brown solid. Mp. 148.5-149.5 °C (Hexane/AcOEt = 4). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 7.70 (1H, t, *J* = 7.6 Hz), 7.94 (2H, m), 8.01 (1H, d, *J* = 8.4 Hz), 8.66 (1H, d, *J* = 8.8 Hz). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 96.5 (d, *J* = 38.0 Hz), 113.0 (d, *J* = 5.2 Hz), 125.3 (d, *J* = 2.2 Hz), 127.9 (d, *J* = 3.0 Hz), 128.2, 128.4 (d, *J* = 1.5 Hz), 134.1, 146.5 (d, *J* = 15.6 Hz), 147.3 (d, *J* = 3.0 Hz), 157.5 (d, *J* = 245.8 Hz). <sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) δ -63.0 (d, *J* = 8.3 Hz). IR (KBr) 3069, 2235, 1620, 1155, 763 cm<sup>-1</sup>. MS (EI) *m/z* 172 (M<sup>+</sup>, 100%), 145 (M<sup>+</sup>-CHN, 11%). HRMS Calcd for C<sub>10</sub>H<sub>5</sub>FN<sub>2</sub>: 172.0437. Found: 172.0439.

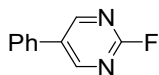


**2-Fluoro-4,6-diphenyltriazine<sup>6</sup> (3q):** Colorless solid. Mp. 111.5-112.0 °C (Hexane). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 7.56 (4H, t, *J* = 7.2 Hz), 7.65 (2H, t, *J* = 7.2 Hz), 8.65 (4H, d, *J* = 7.2 Hz). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 128.8, 129.4, 133.7, 134.4 (d, *J* = 1.5 Hz), 170.8 (d, *J* = 227.2 Hz), 176.2 (d, *J* = 10.4 Hz). <sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) δ -42.7 (s). IR (KBr) 3067, 1513, 1117, 766 cm<sup>-1</sup>. MS (EI) *m/z* 251 (M<sup>+</sup>, 100%). HRMS Calcd for C<sub>15</sub>H<sub>10</sub>FN<sub>3</sub>: 251.0859. Found: 251.0855.

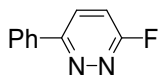


**2-Fluoro-5-phenylpyrimidine<sup>7</sup> (3r):** Colorless solid. Mp. 96.0-96.3 °C (Hexane/AcOEt = 4).

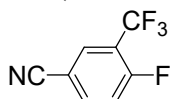
$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46-7.57 (5H, m), 8.82 (2H, d,  $J = 1.6$  Hz).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  126.9, 129.1, 129.5, 133.0 (d,  $J = 6.7$  Hz, two carbon overlapped), 158.8 (d,  $J = 12.0$  Hz), 162.4 (d,  $J = 218.9$  Hz).  $^{19}\text{F-NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -51.3 (s). IR (KBr) 3059, 1571, 1425, 1287, 771, 699  $\text{cm}^{-1}$ . MS (EI)  $m/z$  174 ( $\text{M}^+$ , 100%). HRMS Calcd for  $\text{C}_{10}\text{H}_7\text{FN}_2$ : 174.0593. Found: 174.0560.



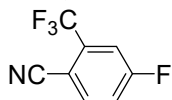
**3-Fluoro-6-phenylpyridazine<sup>8</sup> (3s):** Colorless solid. Mp. 129.6-130.5  $^\circ\text{C}$  (Hexane/AcOEt = 4).  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29 (1H, dd,  $J = 2.0, 9.2$  Hz), 7.51-7.56 (3H, m), 8.00-8.04 (3H, m).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  116.0 (d,  $J = 32.8$  Hz), 127.0, 129.1, 129.5 (d,  $J = 7.4$  Hz), 130.2, 135.1 (d,  $J = 1.5$  Hz), 159.2 (d,  $J = 3.0$  Hz), 166.0 (d,  $J = 243.5$  Hz).  $^{19}\text{F-NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -85.7 (d,  $J = 6.4$  Hz). IR (KBr) 3070, 1557, 1108, 844  $\text{cm}^{-1}$ . MS (EI)  $m/z$  174 ( $\text{M}^+$ , 100%), 146 ( $\text{M}^+ - \text{N}_2$ , 42%). HRMS Calcd for  $\text{C}_{10}\text{H}_7\text{FN}_2$ : 174.0593. Found: 174.0594.



**4-Fluoro-3-(trifluoromethyl)benzonitrile<sup>9</sup> (3t):** Colorless solid. Mp. 66.0-65.5  $^\circ\text{C}$  (Hexane).  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38 (1H, t,  $J = 9.2$  Hz), 7.90 (1H, m), 7.96 (1H, dd,  $J = 2.0, 6.4$  Hz).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  109.1 (d,  $J = 4.5$  Hz), 116.6, 118.6 (d,  $J = 21.6$  Hz), 120.0, 122.6, 131.7 (m), 138.1 (d,  $J = 10.5$  Hz), 162.0 (d,  $J = 265.9$  Hz).  $^{19}\text{F-NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -107.3 (1F, m), -65.5 (3F, d,  $J = 12.4$  Hz). IR (KBr) 3075, 2236, 1624, 1505, 1333, 1172, 847  $\text{cm}^{-1}$ . MS (EI)  $m/z$  189 ( $\text{M}^+$ , 100%), 170 ( $\text{M}^+ - \text{F}$ , 51%). HRMS Calcd for  $\text{C}_8\text{H}_3\text{F}_4\text{N}$ : 189.0202. Found: 189.0176.



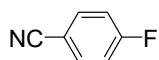
**4-Fluoro-2-(trifluoromethyl)benzonitrile<sup>10</sup> (3u):** Colorless solid. Mp. 43.0-43.8  $^\circ\text{C}$  (Hexane).  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41 (1H, dt,  $J = 2.8, 8.4$  Hz), 7.53 (1H, dd,  $J = 2.8, 8.0$  Hz), 7.90 (1H, dd,  $J = 5.2, 8.8$  Hz).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  106.3 (d,  $J = 2.3$  Hz), 114.6, 115.3 (ddd,  $J = 5.2, 9.6, 26.1$  Hz), 119.7 (d,  $J = 22.4$  Hz), 121.5 (qd,  $J = 2.3, 273.3$  Hz), 135.7 (qd,  $J = 8.2, 33.5$  Hz), 137.3 (d,  $J = 8.9$  Hz), 161.7 (d,  $J = 258.4$  Hz).  $^{19}\text{F-NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -103.3 (1F, m), -65.9 (3F, s). IR (KBr) 3064, 2238, 1615, 1499, 1320, 1130, 858  $\text{cm}^{-1}$ . MS (EI)  $m/z$  189 ( $\text{M}^+$ , 100%), 170 ( $\text{M}^+ - \text{F}$ , 40%). HRMS Calcd for  $\text{C}_8\text{H}_3\text{F}_4\text{N}$ : 189.0202. Found: 189.0182.



**Typical experimental procedures of Scheme 4:** In a two-necked flask equipped with a magnetic stirrer bar and a reflux condenser were placed  $\text{RhH}(\text{dppBz})_2$  (10 mol%, 24.9 mg), and

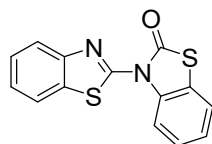
4-(4-phenyloxazolyloxy)benzonitrile (**1f**) (0.25 mmol, 65.6 mg), 2-fluorobenzothiazole (**3a**) (0.50 mmol, 76.6 mg) in chlorobenzene (1.0 mL) under argon atmosphere, and the solution was heated at reflux for 3 h. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel giving 2-fluoro-4-phenyloxazole (**3f**) (58%, 23.7 mg), 4-fluorobenzonitrile (**5a**) (67%, 20.3 mg), and [2,3'(2*H*)-bibenzothiazol]-2'-one (**6**) (56%, 39.8 mg).

**4-Fluorobenzonitrile<sup>8</sup>** (**5a**): Colorless solid. Mp. 33.0-33.5 °C (Hexane). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 7.19 (2H, dd, *J* = 0.8, 9.2 Hz), 7.69 (2H, dd, *J* = 4.0, 9.2 Hz). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 108.5 (d, *J* = 3.0 Hz), 116.8 (d, *J* = 22.3 Hz), 118.0, 134.7 (d, *J* = 8.9 Hz), 165.0 (d, *J* = 255.4 Hz). <sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) δ -105.9 (m). IR (KBr) 2232, 1508, 1238, 840 cm<sup>-1</sup>. MS (EI) *m/z* 121 (M<sup>+</sup>, 100%), 94 (M<sup>+</sup>-CHN, 30%). HRMS Calcd for C<sub>7</sub>H<sub>4</sub>FN: 121.0328. Found: 121.0321.



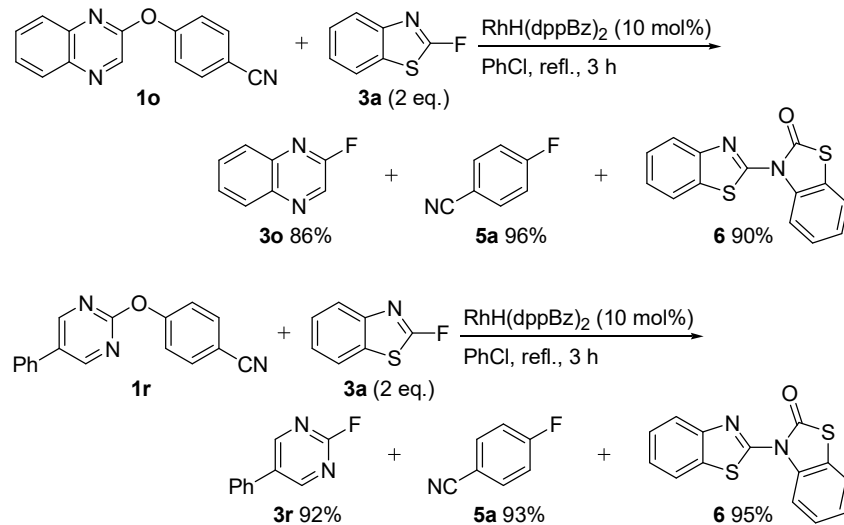
**[2,3'(2*H*)-Bibenzothiazol]-2'-one<sup>11</sup>** (**6**): Colorless solid. Mp. 157.0-158.0 °C (Hexane/AcOEt = 4).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 7.33 (1H, td, *J* = 1.2, 7.6 Hz), 7.41 (1H, td, *J* = 1.2, 7.6 Hz), 7.46-7.54 (3H, m), 7.90 (1H, d, *J* = 8.0 Hz), 8.02 (1H, d, *J* = 8.0 Hz), 9.16 (1H, dd, *J* = 1.2, 8.8 Hz). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 117.4, 121.1, 121.4, 122.1, 122.4, 125.1, 125.2, 126.4, 127.2, 132.4, 135.2, 148.2, 155.3, 169.8. IR (KBr) 3052, 1671, 1181, 746 cm<sup>-1</sup>. MS (EI) *m/z* 284 (M<sup>+</sup>, 100%), 256 (M<sup>+</sup>-CO, 86%). HRMS Calcd for C<sub>14</sub>H<sub>8</sub>N<sub>2</sub>OS<sub>2</sub>: 284.0078. Found: 284.0047.



4-[(2-Quinoxalinyloxy)] **1o** and 4-[(2-Pyrimidyl)oxy] **1r** benzonitrile were also fluorinated using **3a** (Scheme 1).

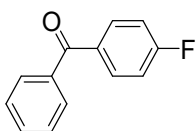
Scheme 1



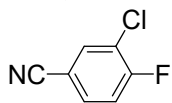


**Typical experimental procedures for Scheme 5:** In a two-necked flask equipped with a magnetic stirrer bar and a reflux condenser were placed RhH(dppBz)<sub>2</sub> (10 mol%, 24.9 mg), and 4-[(2-benzothiazolyl)oxy]benzotrile (1a) (0.25 mmol, 63.1 mg), 2-fluorobenzothiazole (3a) (0.25 mmol, 38.3 mg) in chlorobenzene (1.0 mL) under argon atmosphere, and the solution was heated at reflux for 3 h. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel giving 4-fluorobenzotrile (5a) (99%, 29.9 mg), and [2, 3'(2'H)-bibenzothiazol]-2'-one (6) (99%, 70.4 mg).

**(4-Fluorophenyl)phenylmethanone<sup>8)</sup> (5v):** Colorless solid. Mp. 46.1- 47.1 °C (Hexane). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 7.16 (2H, t, *J* = 8.8 Hz), 7.49 (2H, t, *J* = 7.6 Hz), 7.59 (1H, t, *J* = 7.6 Hz), 7.77 (2H, d, *J* = 6.8 Hz), 7.85 (2H, dd, *J* = 1.6, 8.8 Hz). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 155.4 (d, *J* = 21.6 Hz), 128.3, 129.8, 132.4, 132.6 (d, *J* = 9.7 Hz), 133.7 (d, *J* = 3.0 Hz), 137.4, 165.3 (d, *J* = 253.2 Hz), 195.2. <sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) δ -109.5 (m). IR (KBr) 3069, 1646, 1227, 816, 735, 700 cm<sup>-1</sup>. MS (EI) *m/z* 200 (M<sup>+</sup>, 97%), 123 (M<sup>+</sup>-C<sub>6</sub>H<sub>5</sub>, 100%), 105 (M<sup>+</sup>-C<sub>6</sub>H<sub>4</sub>F, 87%). HRMS Calcd for C<sub>13</sub>H<sub>8</sub>FO: 200.0637. Found: 200.0633.



**3-Chloro-4-fluorobenzotrile<sup>12)</sup> (5w):** Colorless solid. Mp. 67.0-67.8 °C (Hexane). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 7.28 (1H, t, *J* = 8.4 Hz), 7.60 (1H, m), 7.75 (1H, dd, *J* = 2.0, 6.8 Hz). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 109.5 (d, *J* = 4.5 Hz), 116.8, 117.9 (d, *J* = 22.3 Hz), 122.8 (d, *J* = 18.6 Hz), 132.6 (d, *J* = 8.2 Hz), 134.7, 160.8 (d, *J* = 257.7 Hz). <sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) δ -108.2 (m). IR (KBr) 3076, 3062, 3049, 2236, 1262, 1067, 835 cm<sup>-1</sup>. MS (EI) *m/z* 155 (M<sup>+</sup>, 100%), 128 (M<sup>+</sup>-CHN, 4%), 120 (M<sup>+</sup>-Cl, 30%). HRMS Calcd for C<sub>7</sub>H<sub>3</sub>ClFN: 154.9938. Found: 154.9920.



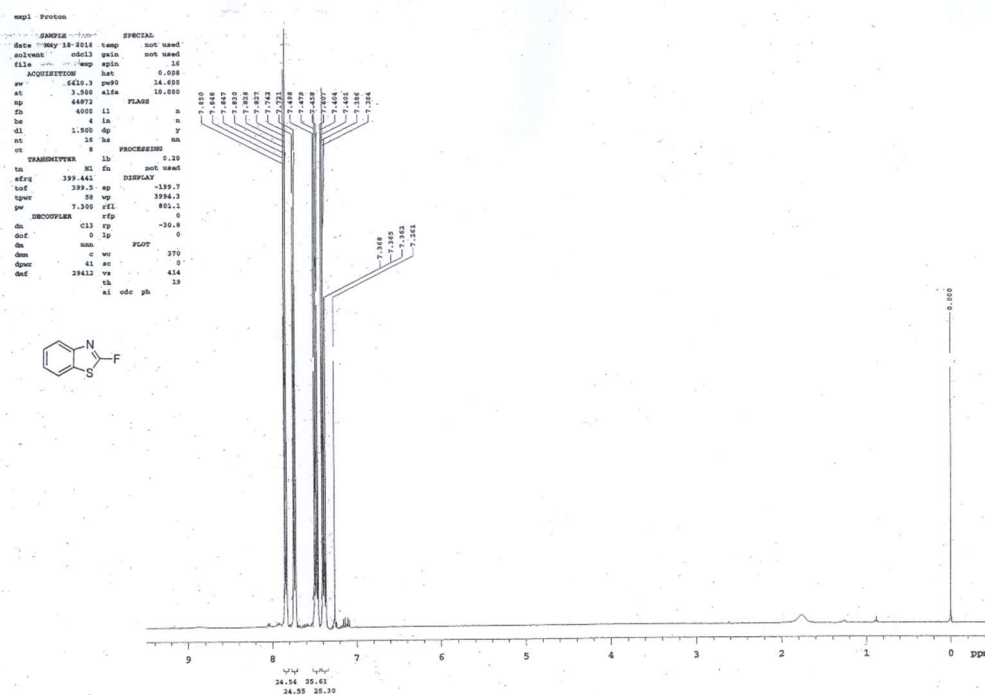
**Typical experimental procedures for synthesis of RhH(dppBz)<sub>2</sub>:** RhH(dppBz)<sub>2</sub> was synthesized by ligand exchange of RhH(PPh<sub>3</sub>)<sub>4</sub> and dppBz. In a two-necked flask equipped with a magnetic stirrer bar were placed RhH(PPh<sub>3</sub>)<sub>4</sub> (0.5 mmol, 576.5 mg), 1,2-bis(diphenylphosphino)benzene (0.84 mmol, 375.0 mg), and degassed acetone (6.0 mL) under an argon atmosphere, and the solution was stirred at room temperature for 1 h. The color of solution changed from yellow to orange. The reaction mixture was settled, and orange rhodium complex precipitated. Then supernatant layer was removed by syringe. The residue was washed with degassed acetone (4.0 mL) 5 times. Then, the residue was washed 5 times using degassed hexane. The residue was dried under vacuum for 1 h giving orange RhH(dppBz)<sub>2</sub>, which was stored under argon atmosphere.

**Bis[1,2-bis(diphenylphosphino)benzene]hydriderhodium( I )**: Orange solid. <sup>1</sup>H-NMR (400 MHz, Benzene-d<sub>6</sub>) δ -9.39 (1H, td, *J* = 18.4, 12.0 Hz), 6.83 (28H, m), 6.96 (8H, t, *J* = 7.2 Hz), 7.32 (8H, m), 7.52 (4H, m). <sup>31</sup>P-NMR (161 MHz, Benzene-d<sub>6</sub>) δ 57.6 (d, *J* = 141.4 Hz). MS (EI) *m/z* 996 (M<sup>+</sup>, 5%). HRMS Calcd for C<sub>60</sub>H<sub>49</sub>P<sub>4</sub>Rh: 996.1840. Found: 996.1825.

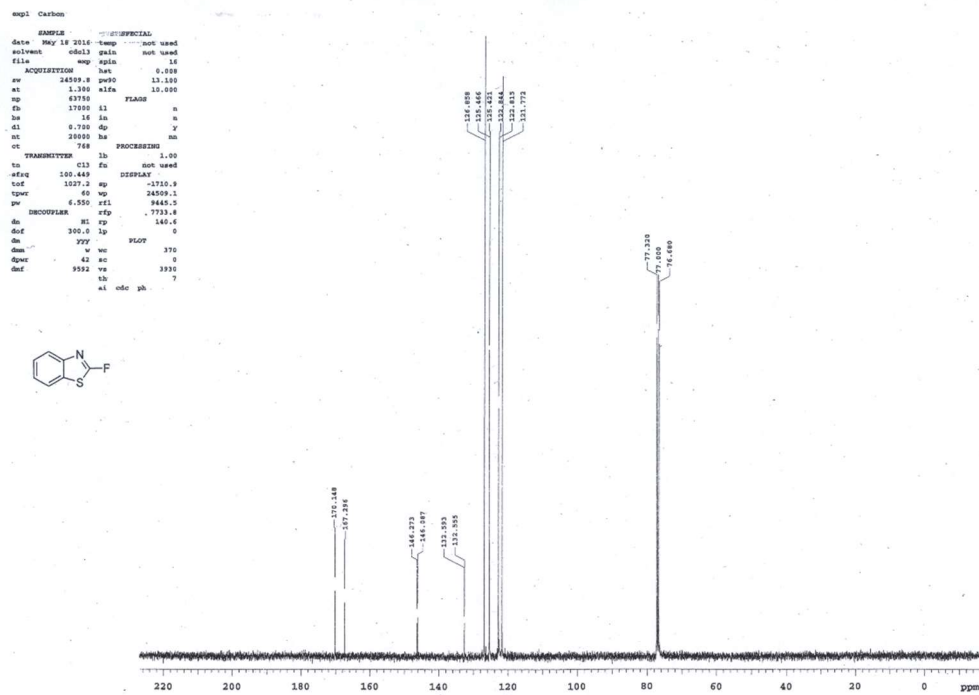
Ref.

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## 2-fluorobenzothiazole (3a) <sup>1</sup>H-NMR



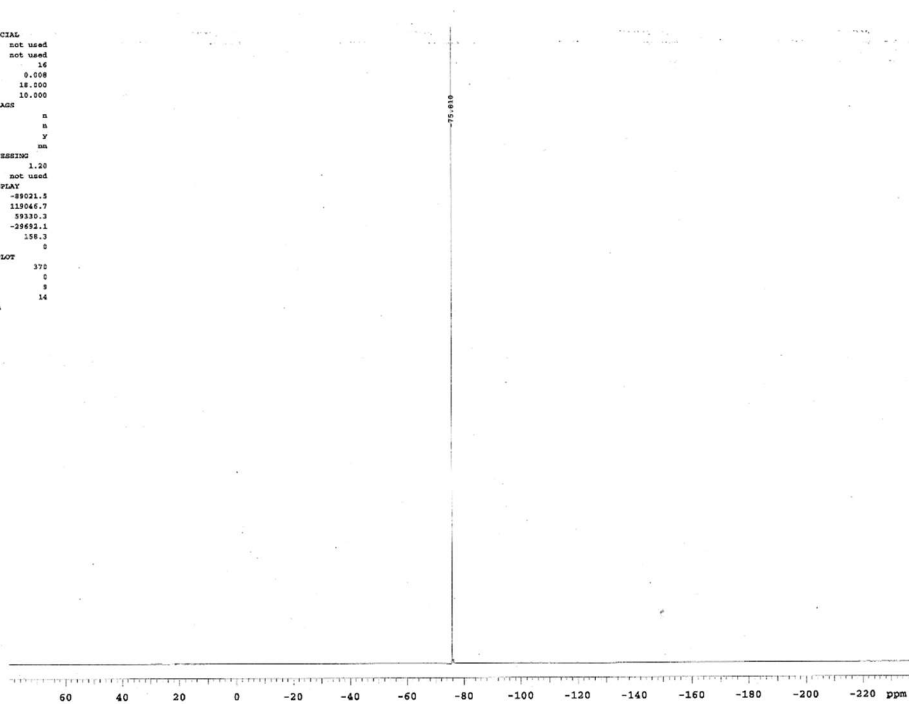
## 2-fluorobenzothiazole (3a) <sup>13</sup>C-NMR



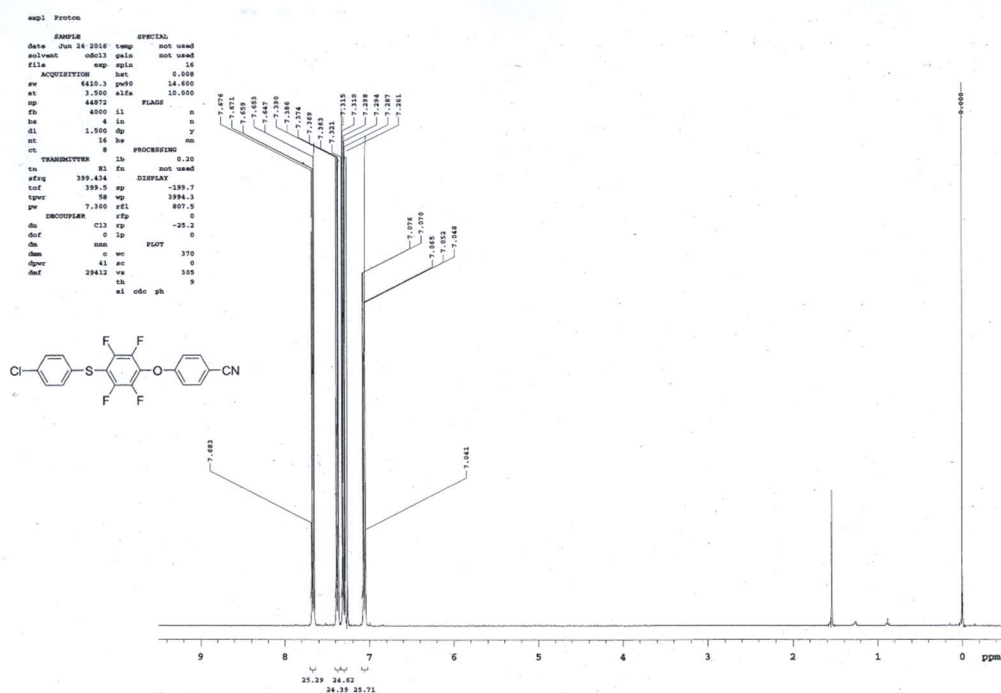
## 2-fluorobenzothiazole (3a) <sup>19</sup>F-NMR

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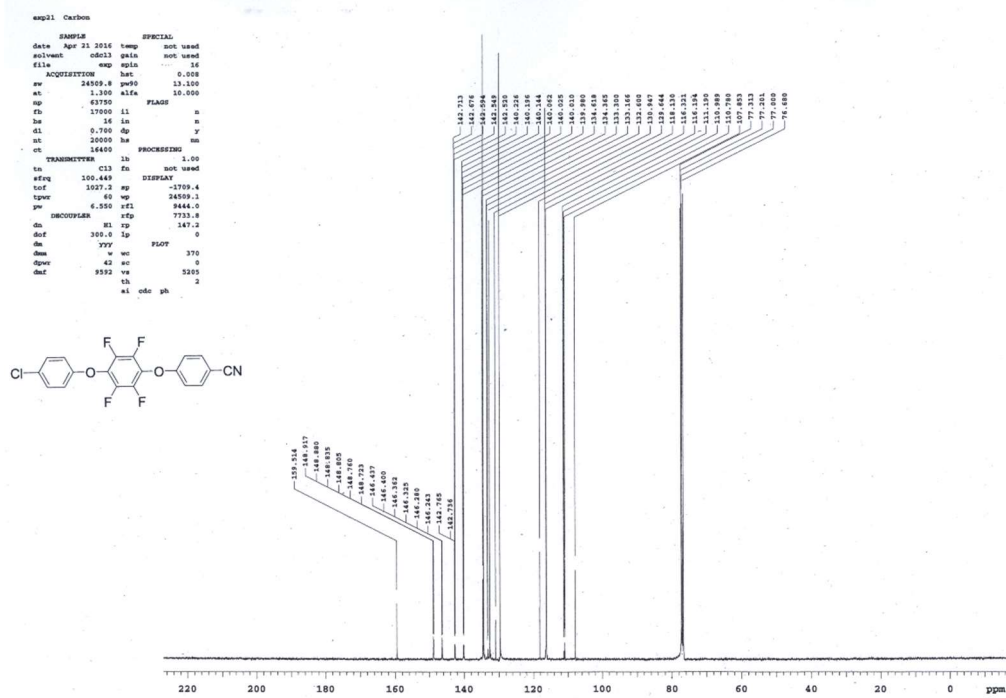
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solvent cdcl3  gain    not used
file          exp  spin    16
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sv      119047.6 pm90   18.000
st      0.000  n1fa    10.000
rg      142898
=====
f0      51800  i1      n
h0      4      in      n
d1      4.400  dp      y
nt      16    he      mn
c0      16    PROCESING
=====
TRANSMITTER  lb      1.20
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sfrq      375.820  DISPLAY
tof      13623.7  sp      -89021.9
tprf      81    vp      119046.7
prf      6.000  rfl    59330.3
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          sl  ph
    
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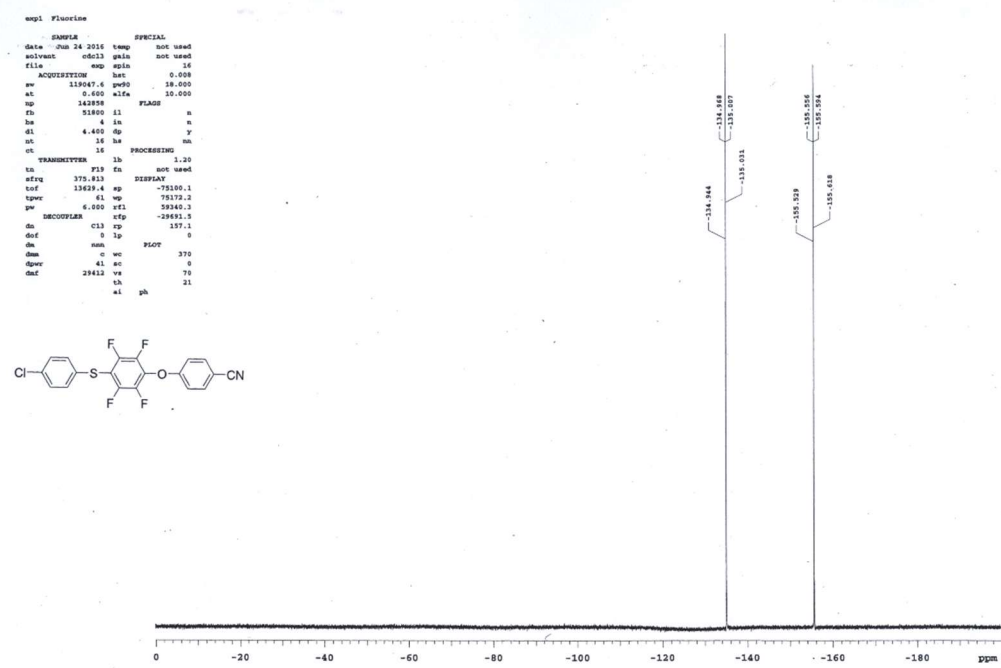
1-[(4-Chlorophenyl)thio]-4-[(4-cyanophenyl)oxy]-2,3,5,6-tetrafluorobenzene (4a) <sup>1</sup>H-NMR



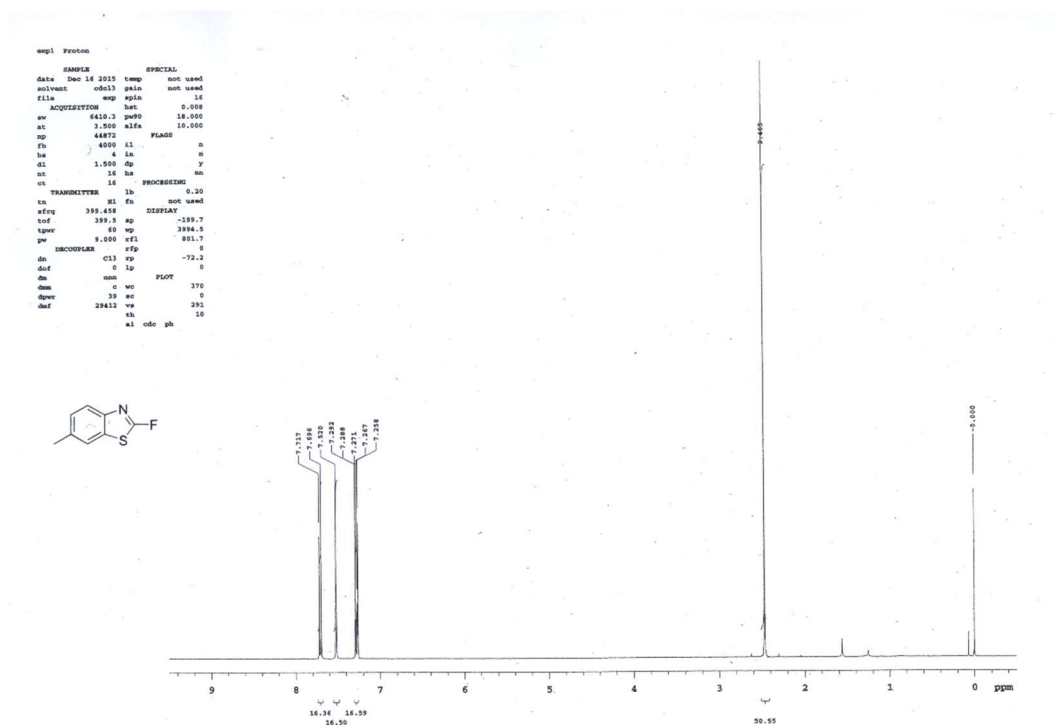
1-[(4-Chlorophenyl)thio]-4-[(4-cyanophenyl)oxy]-2,3,5,6-tetrafluorobenzene (4a) <sup>13</sup>C-NMR



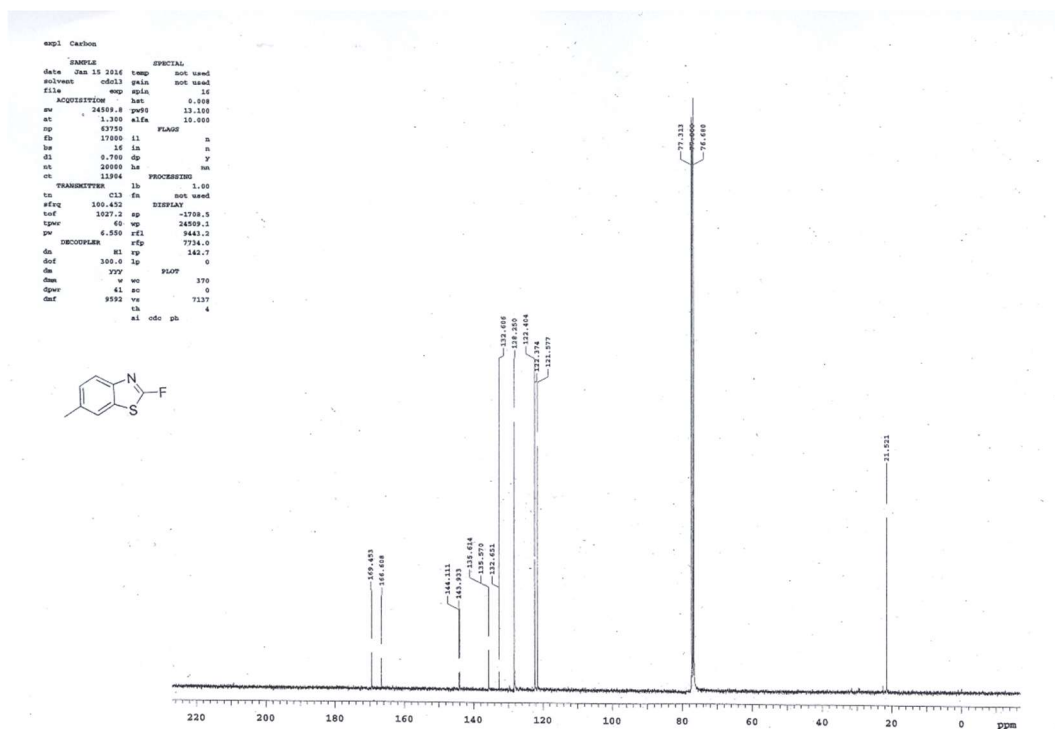
1-[(4-Chlorophenyl)thio]-4-[(4-cyanophenyl)oxy]-2,3,5,6-tetrafluorobenzene (4a) <sup>19</sup>F-NMR



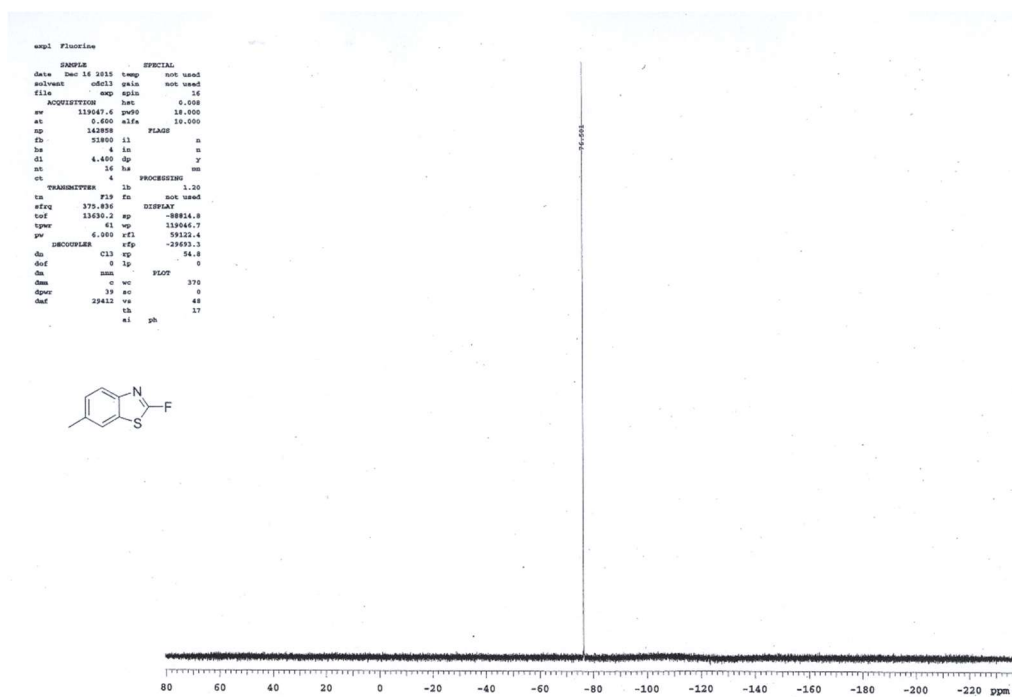
## 2-Fluoro-6-methylbenzothiazole (3b) <sup>1</sup>H-NMR



## 2-Fluoro-6-methylbenzothiazole (3b) <sup>13</sup>C-NMR

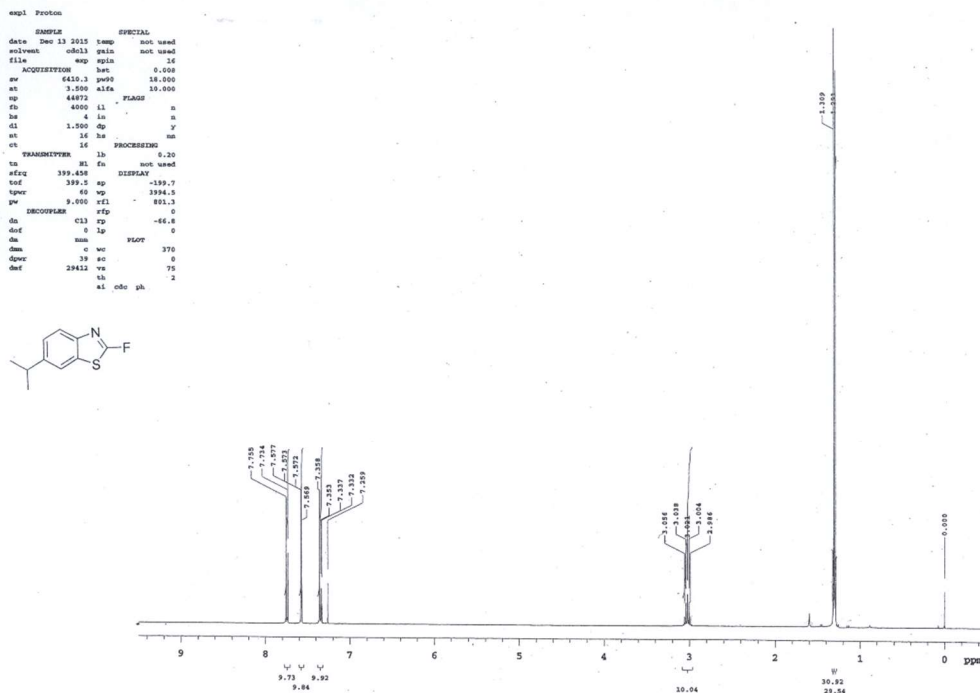


## 2-Fluoro-6-methylbenzothiazole (3b) <sup>19</sup>F-NMR

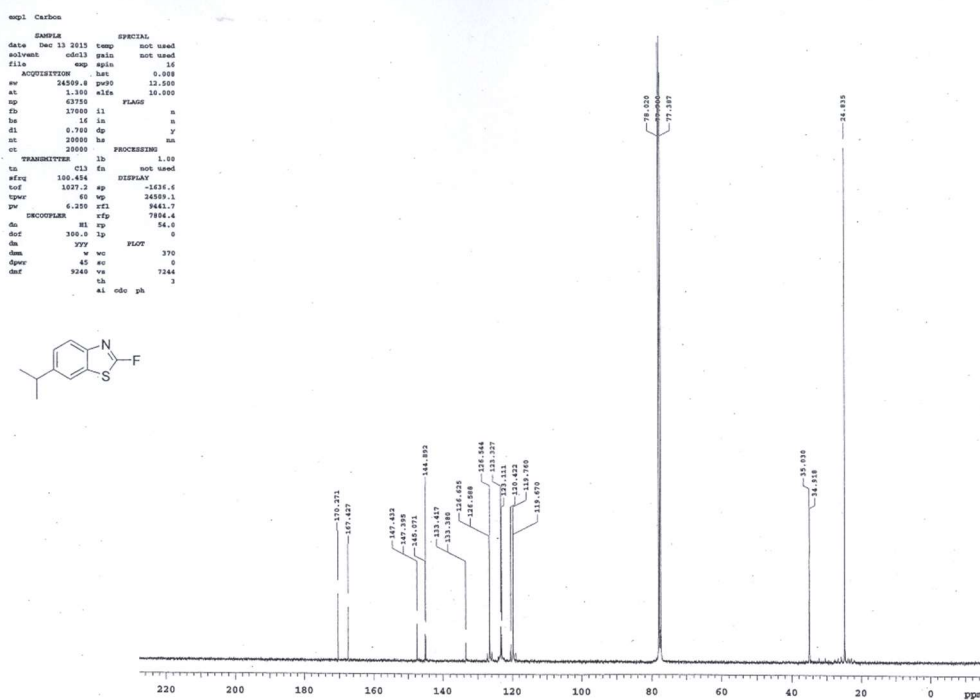




## 2-Fluoro-6-(2-methylethyl)benzothiazole (3c) <sup>1</sup>H-NMR

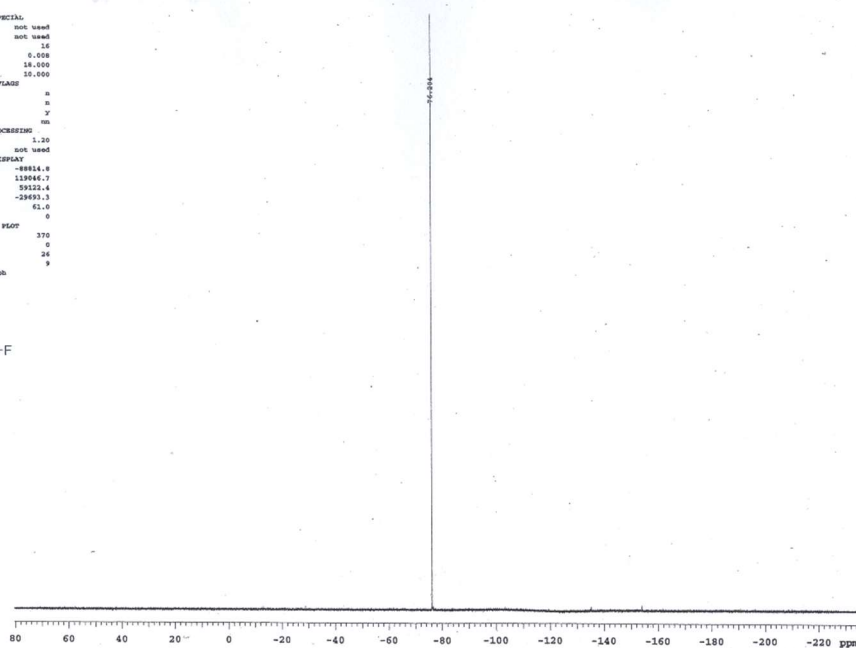
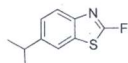


## 2-Fluoro-6-(2-methylethyl)benzothiazole (3c) <sup>13</sup>C-NMR

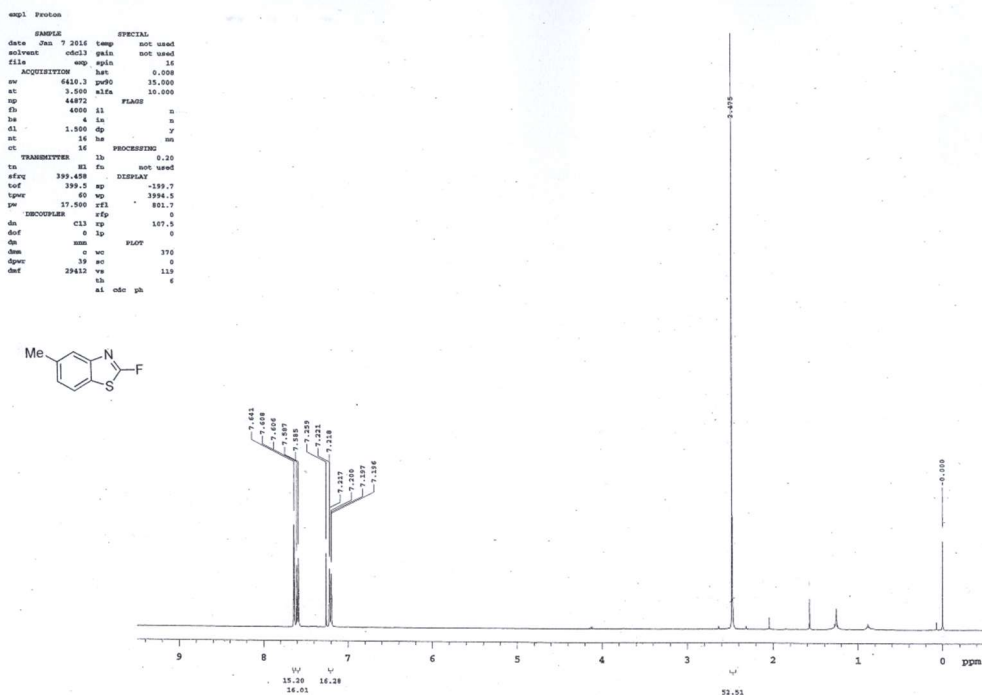


## 2-Fluoro-6-(2-methylethyl)benzothiazole (3c) <sup>19</sup>F-NMR

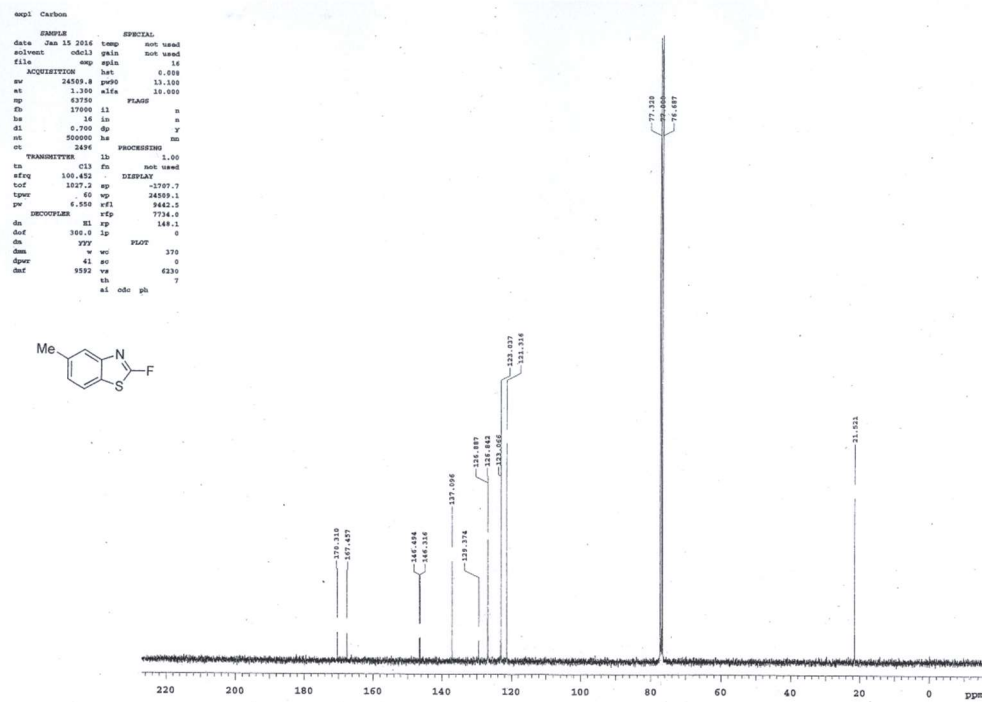
```
exp1 Fluorine
=====
SAMPLE          SPECIAL
date    Dec 11 2013 temp    not used
solvent  cdcl3 gain    not used
file
=====
ACQUISITION  exp  spin    IS
av      119047.6 pw90    18.000
sc      5.400  x12a    18.000
sp      142858  F1AGS
zb      51806  il
hs      4  in
dl      4.400  dp
sc      15  ds
ct
=====
PROCESSED
=====
TRANSMITTER  lb    not used
tn            F19  fu    not used
afreq        376.876  DISPLAY
tof          13630.1  sp    -48814.8
tpwr         61  wp    119044.7
pw           6.000  rfl    39223.4
=====
DECOUPLER    rfp    -29493.3
da          C13  rd    61.0
dof         0  rd    0
dm          0  no
dms         39  ac
dpr         29412  vs    26
dof         0  vs
=====
SI  PH
=====
```



## 2-Fluoro-5-methylbenzothiazole (3d) <sup>1</sup>H-NMR

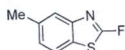


## 2-Fluoro-5-methylbenzothiazole (3d) <sup>13</sup>C-NMR



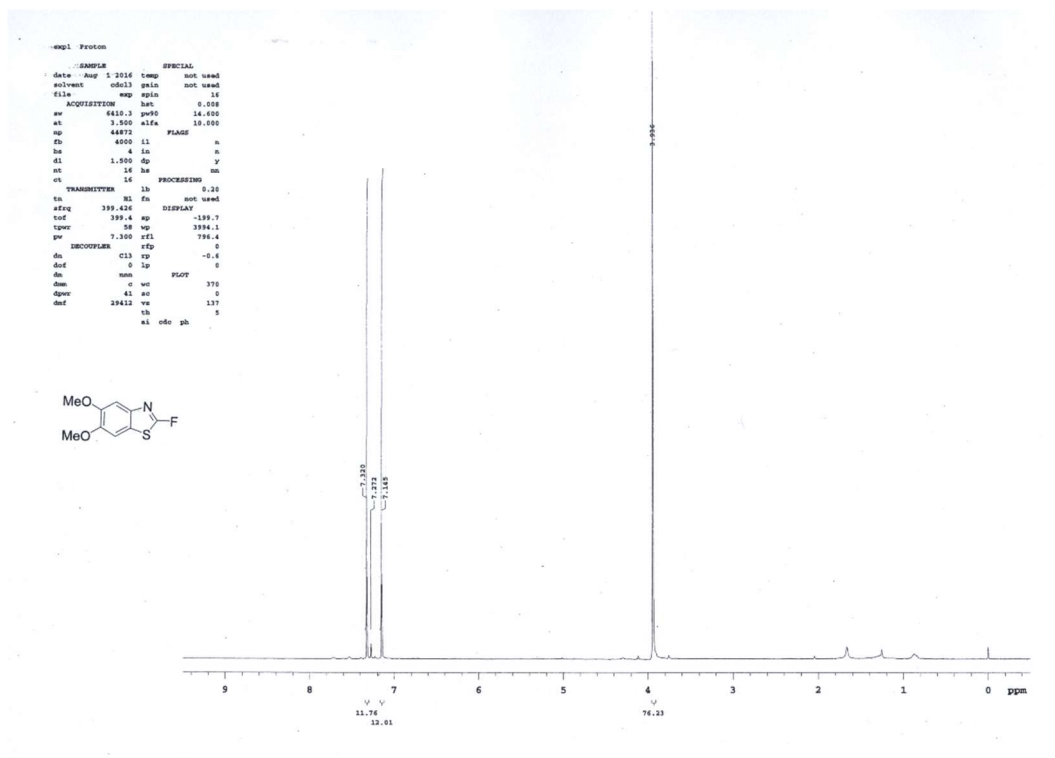
## 2-Fluoro-5-methylbenzothiazole (3d) <sup>19</sup>F-NMR

```
WD1 Fluorine
=====
SAMPLE
date   Jul 7 2016   temp   not used
solvent  cdcl3     gain   not used
file    exp 0116    IS
=====
ACQUISITION
sw      119049.6     pwr0    18.000
at      9.600      a1a     10.000
=====
sp      142858      F1A0    n
fn      51800      l1      n
ba      4          in      n
cl      4.400     dp      0
st      16       ha      na
ct
=====
TRANSMITTER  1b   PROCESSING  1.20
ts          F19   En   not used
=====
sfile  371.836      DEFLAY
tof    13638.2   sp   -88814.8
tprw   61        wp   119046.7
pw     6.600     rfg   39522.4
=====
DECOUPLER  c13   rfp   -39493.3
du      c13     rp   -81.0
duf     0       lp   0
=====
dm      mm      p107   370
dmw     0       vo
dprw   29      ac   0
daf    19412   ve   28
          th   14
          al   ph
```

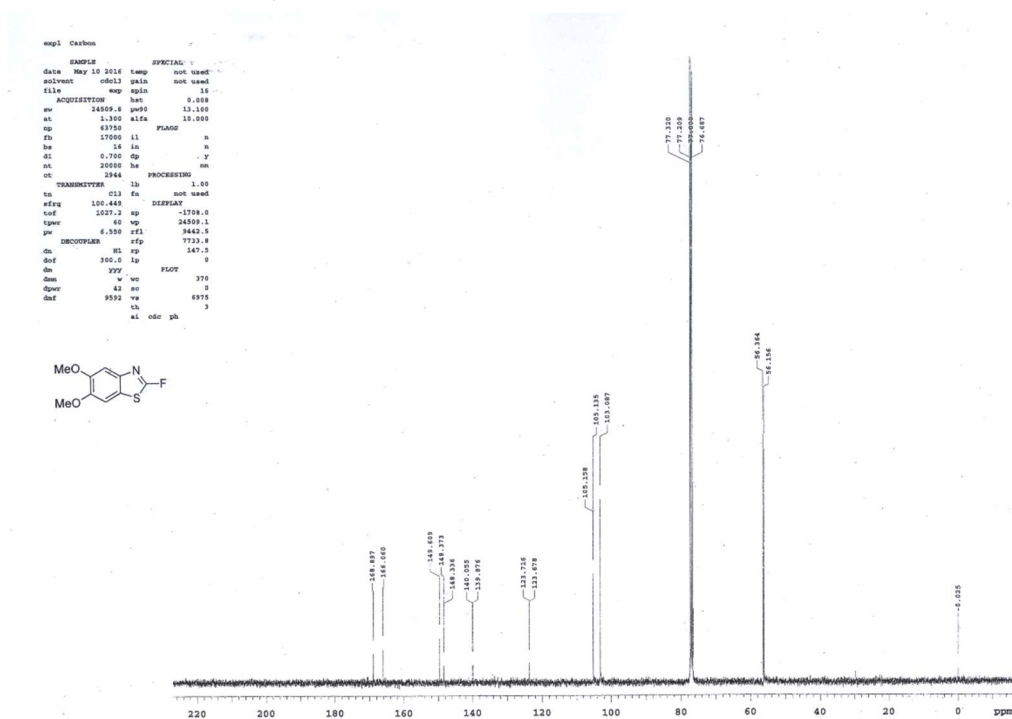


80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 ppm

## 2-fluoro-5,6-dimethoxybenzothiazole (3e) <sup>1</sup>H-NMR

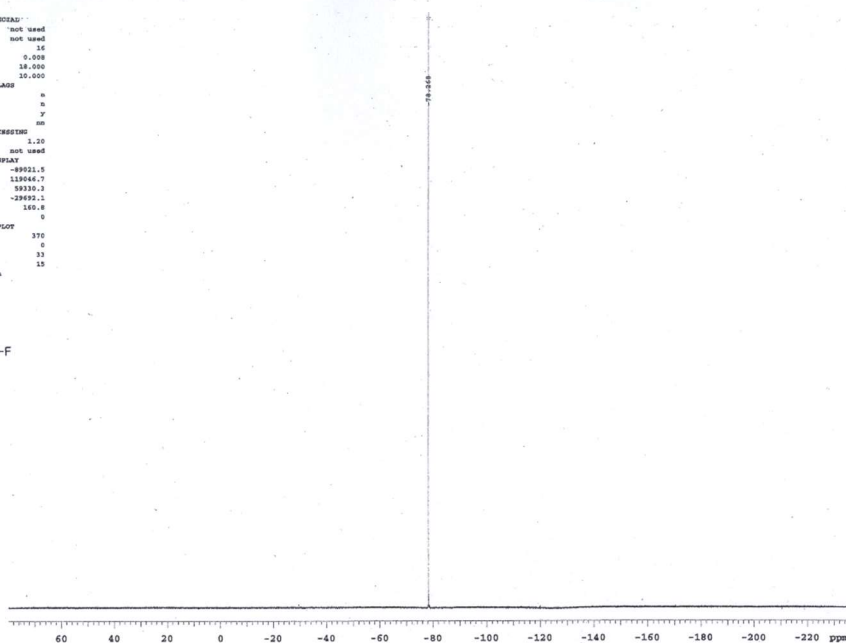
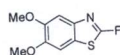


## 2-fluoro-5,6-dimethoxybenzothiazole (3e) <sup>13</sup>C-NMR

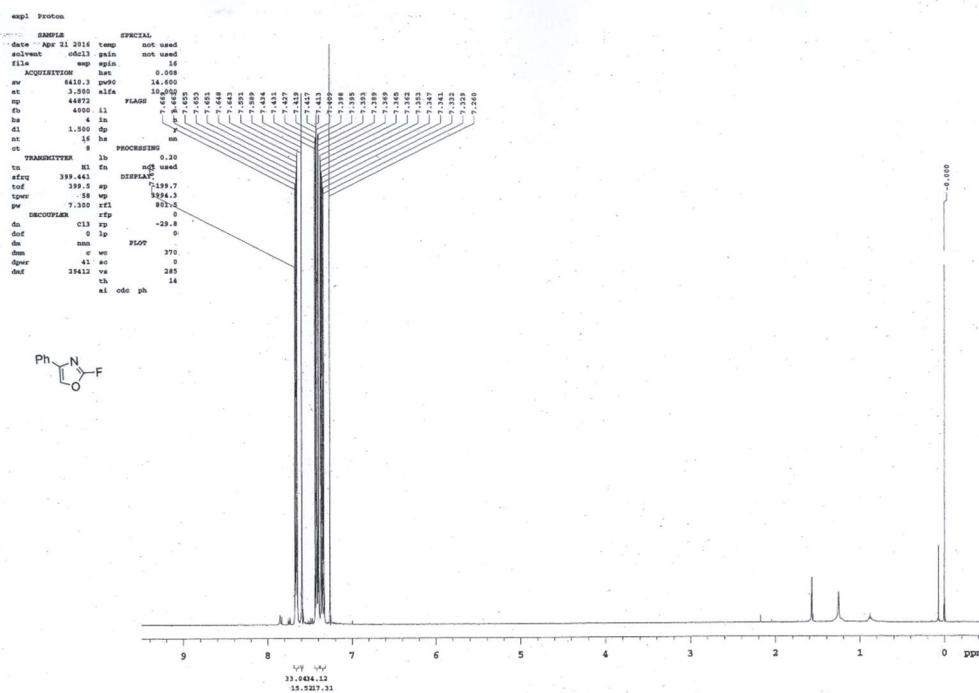


## 2-fluoro-5,6-dimethoxybenzothiazole (3e) <sup>19</sup>F-NMR

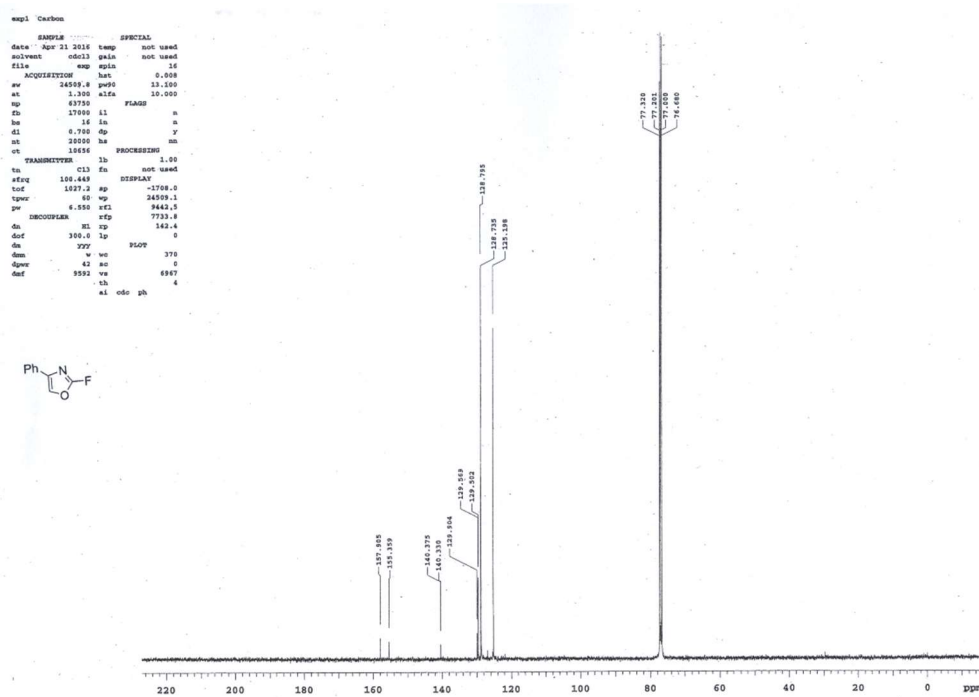
```
exp1 fluorine
=====
SAMPLE
Date MAY 10 2016 Temp not used
solvent dms-d6 dms not used
file exp #10 16
ACQUISITION
pr 11947.6 hz 9.008
at 0.400 nfa 10.000
tp 142858 FID
fb 51800 f1
hs 4 in
st 4.400 sp 7
xt 16 ha nm
cs 16 PROCESSED
=====
TRANSMITTER
ts F15 fb not used
rfreq 375.820 DISPLAY
tof 11629.7 sp -8921.0
tqwr 41 wv 119046.7
pc 6.000 rF1 59330.3
DECOUPLER
ds C13 sp 160.8
def 0 lp FID
ds nmw FID
dmn c wo 370
dpcw 41 wo 0
def 28432 ve 33
sh
sl ph 10
```



## 2-Fluoro-4-phenyloxazole (3f) <sup>1</sup>H-NMR

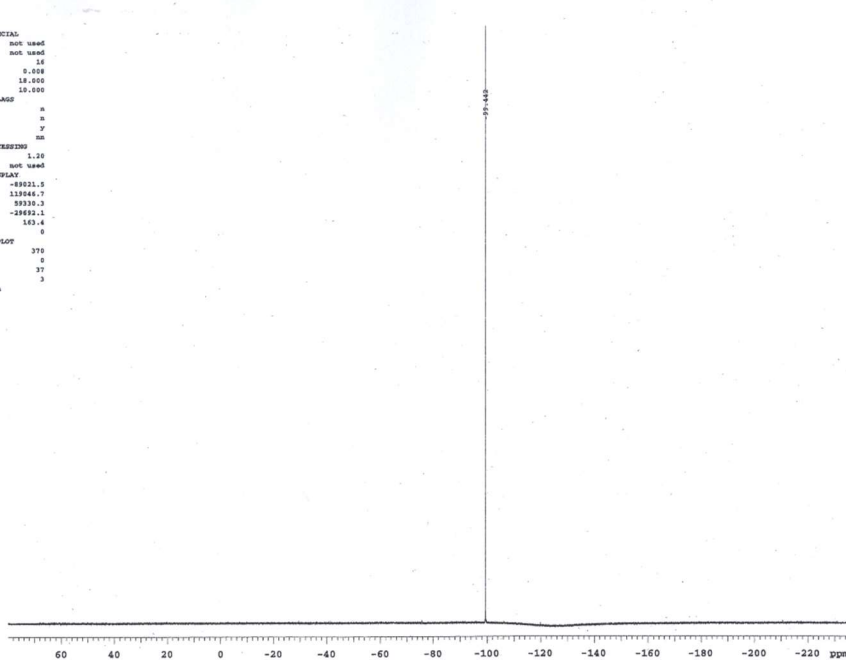


## 2-Fluoro-4-phenyloxazole (3f) <sup>13</sup>C-NMR



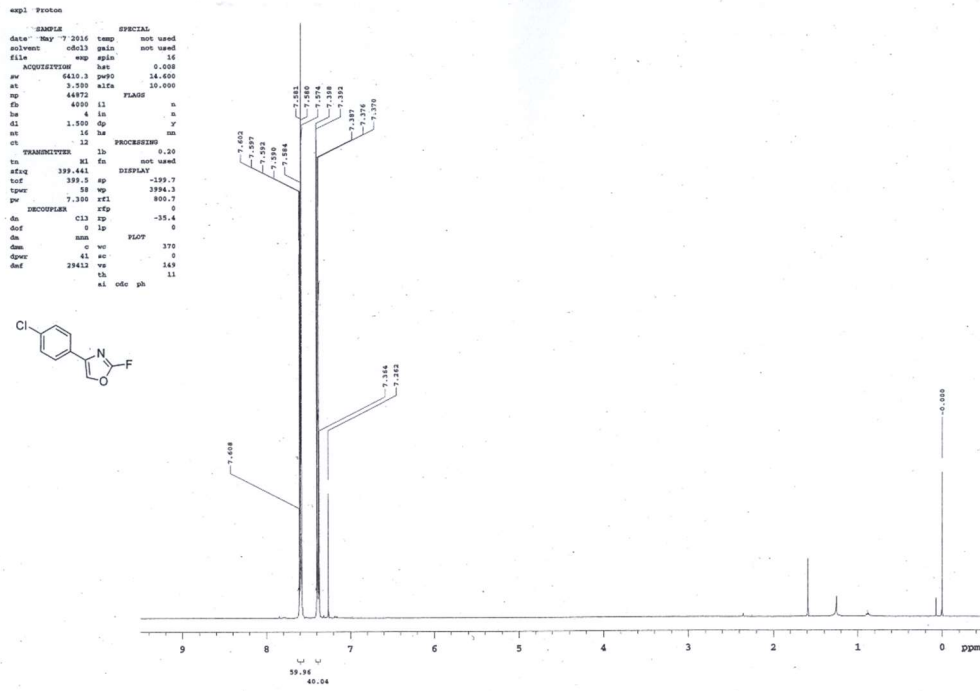
## 2-Fluoro-4-phenyloxazole (3f) <sup>19</sup>F-NMR

```
mp1 Fluorine
=====
SAMPLE
date Apr 21 2016 temp not used
solvent cdcl3 gain not used
file mp1.mri 16
=====
ACQUISITION
sc 119047.6 pps0 16.000
st 0.400 sfsa 12.000
sp 142858 FLAGS
fo 51800 il n
hs 4 in n
dl 4.400 qp y
st 16 ha m
ct
=====
TRANSMITTER 16 PROCESSING 1.20
=====
ts F19 fn not used
sfreq 375.820 DISPLAY
tolf 11625.7 sp -8921.5
tqwr 61 wp 119046.7
pw 6.000 rfi 39239.3
=====
DECOUPLER
ds c13 sp 163.4
ds 0 ip 0
ds msa msa PLOP 370
ds 0 wo
dspr 41 ac 0
dsf 29412 vv 37
ds ch 3
ds al ph
```

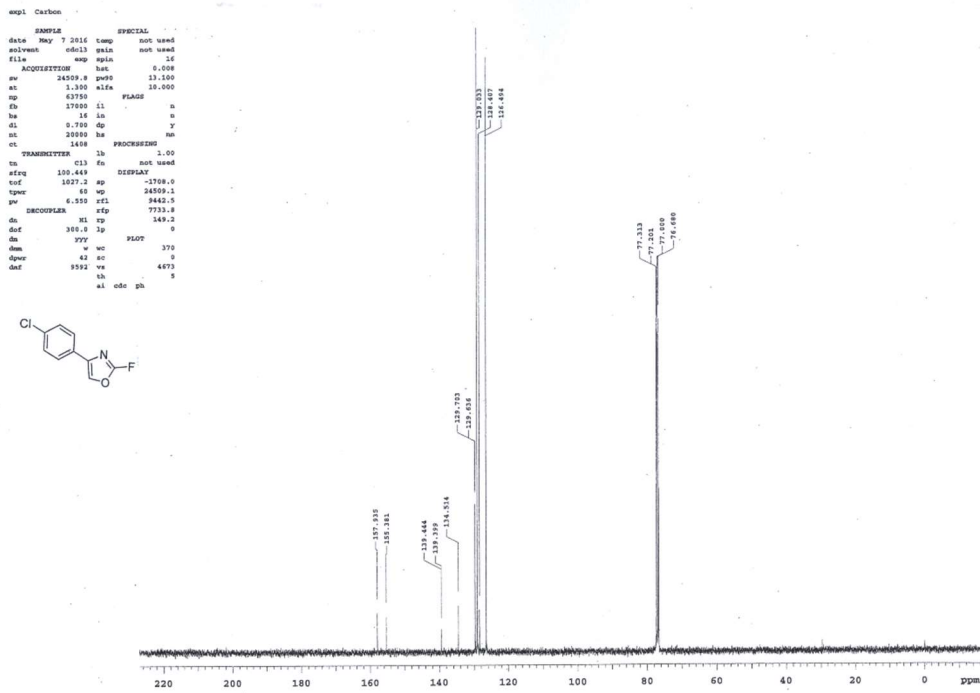




## 2-Fluoro-4-(4-chlorophenyl)oxazole (3g) <sup>1</sup>H-NMR



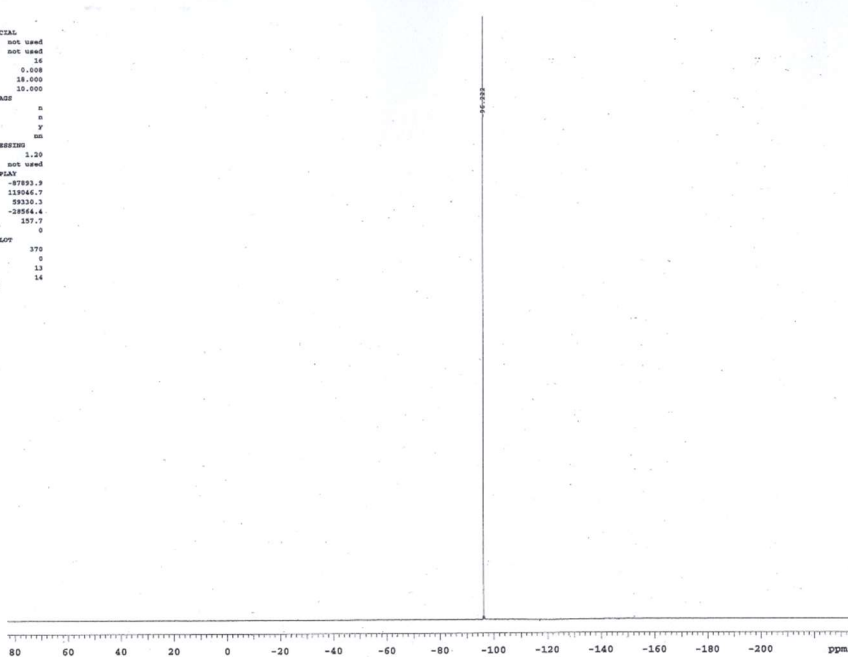
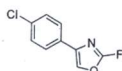
## 2-Fluoro-4-(4-chlorophenyl)oxazole (3g) <sup>13</sup>C-NMR



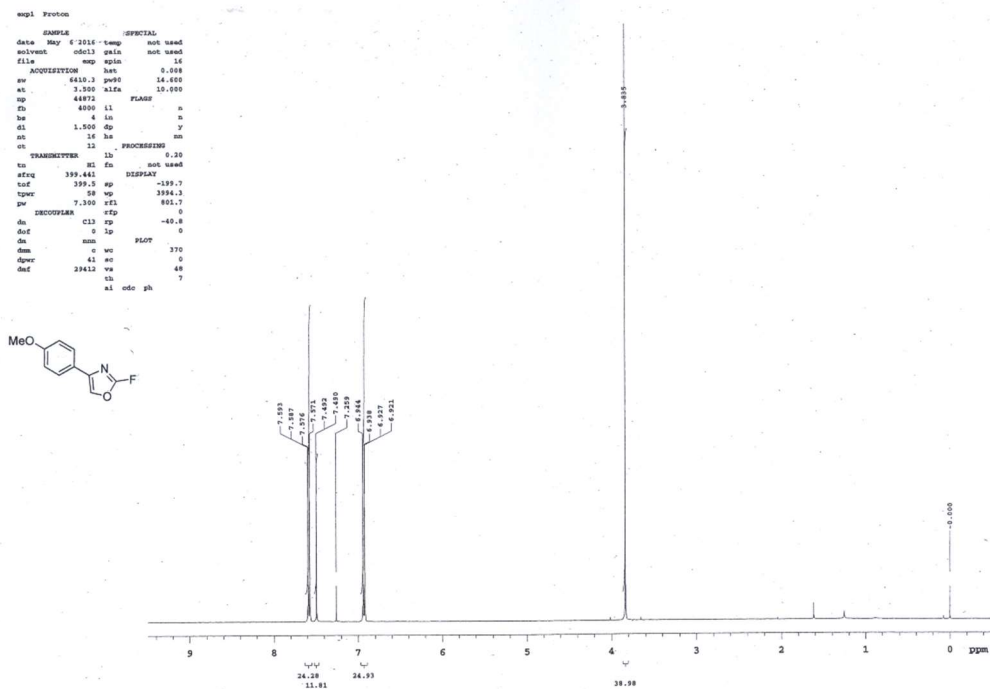
## 2-Fluoro-4-(4-chlorophenyl)oxazole (3g) <sup>19</sup>F-NMR

exp1 Fluorine

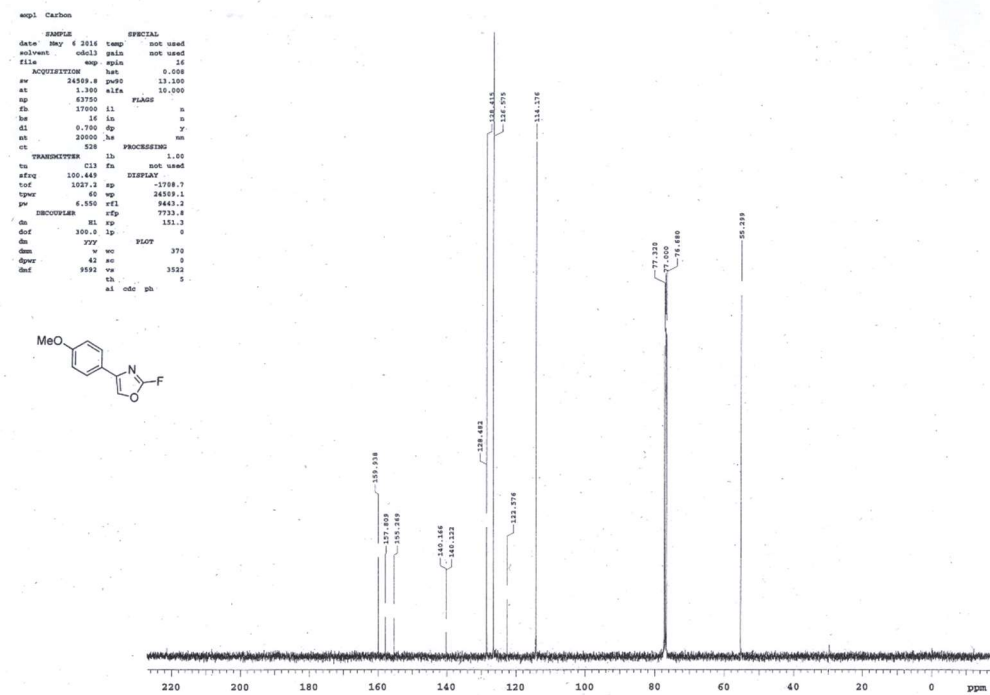
```
SAMPLE          SPECIAL
date 09y 7-2016 temp not used
solvent cde13 gain not used
file          exp gain not used
ACQUISITION    hist 0.008
av 139497.6 ppsf 18.000
sc 0.400 sfile 18.000
sp 143958
En 51900 il FLAGE n
ds 4 in n
dl 4.400 sp Y
sc 16 sa HQ
ct 16 PROCESSING
TRANSMITTER    th 1.20
ta F19 En not used
rfc9 370.820 DEPLAN
tact 13939.7 sp -87893.9
tpwr 41 wp 139046.7
sw 0.000 vst1 19320.3
DECOUPLER      rfp -28564.4
ds c13 sp 157.7
dnt 0 sp 0
ds n n n FLOW 370
dca n w 0
dpcw 41 sc 0
dnt 28413 va 13
th 14
si pn
```



## 2-Fluoro-4-(4-methoxyphenyl)oxazole (3h) <sup>1</sup>H-NMR

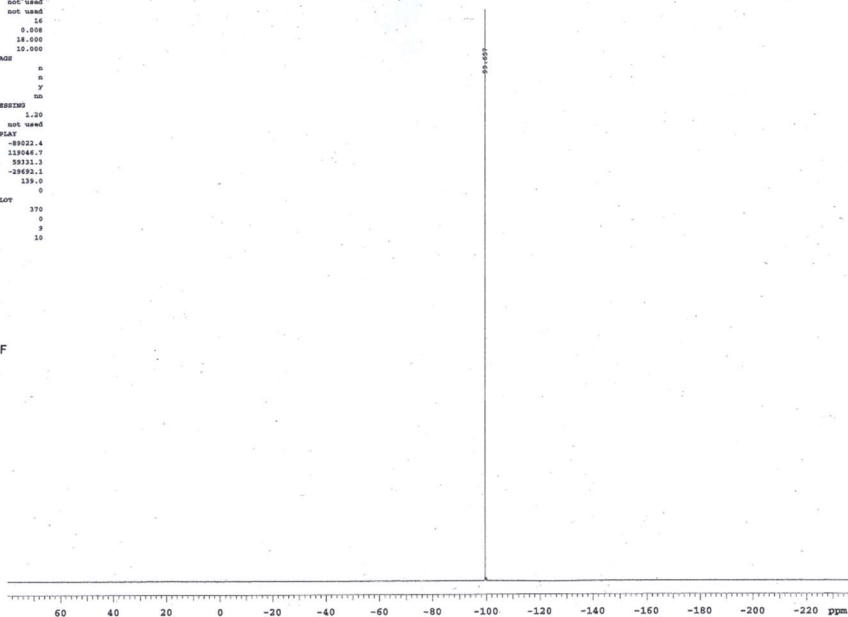
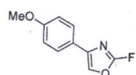


## 2-Fluoro-4-(4-methoxyphenyl)oxazole (3h) <sup>13</sup>C-NMR

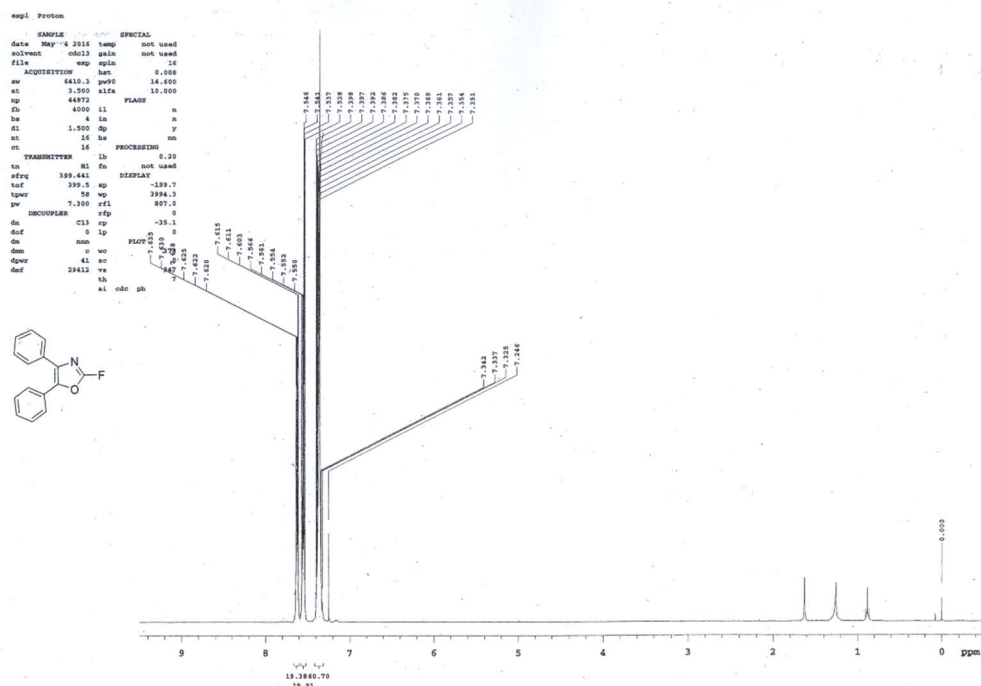


## 2-Fluoro-4-(4-methoxyphenyl)oxazole (3h) <sup>19</sup>F-NMR

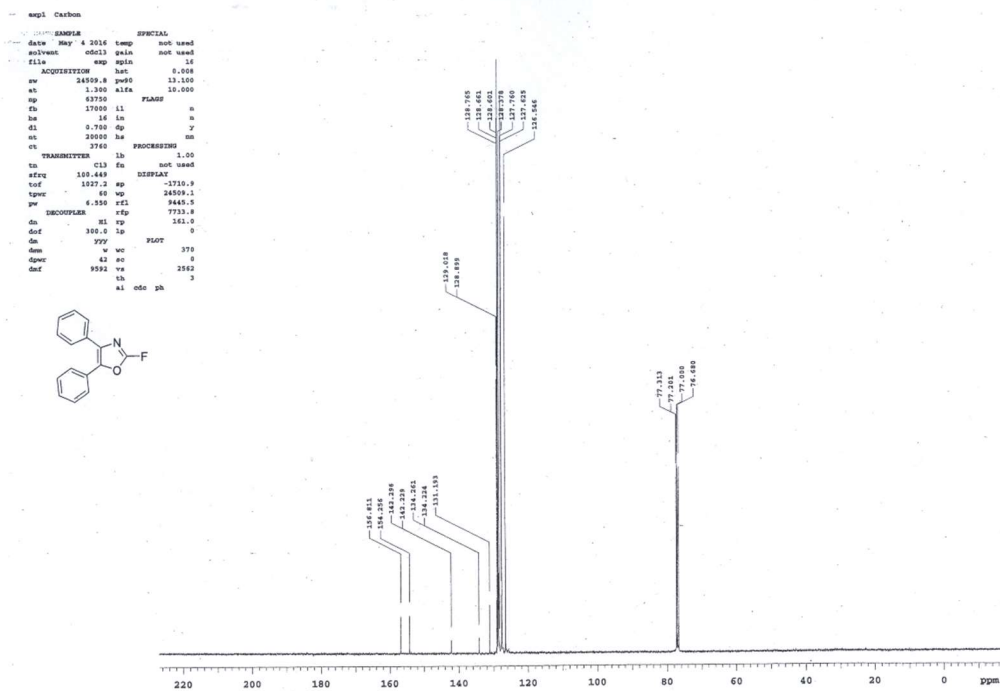
```
exp1_19toprim
=====
NAME          SAMPLE
Date          May 6 2016  temp      not used
solvent       cdcl3  gain      not used
file          cdcl3  gain      not used
file          cdcl3  gain      not used
ACQUISITION  exp      16
sv           113047.6  pps0    16.000
sc           0.400  rfa     10.000
sp           142838  FIDMS
fn           51400  ll      n
fs           4  ln      n
dl           4.490  dp      y
sc           16  ha     no
cs           8  PROCSIMP
=====
TRANSMITTER  f19  fn      not used
tn           f19  fn      not used
sfreq       376.320  DISPLAY
tot         11829.7  sp      -8922.4
tpwr        61  wp      139046.7
sv          4.000  rfa     39321.3
sv          4.000  rfa     39321.3
DECOUPLE    rfp      -24992.1
da          cl3  rp      139.0
daf         0  lp      0
da          mmn  wc      PLOT  170
dms         0  ac      0
dpr         41  ve      9
daf         29413  ve      9
da          tm      10
=====
at          ph
```



## 2-Fluoro-4,5-diphenyloxazole (3i) <sup>1</sup>H-NMR

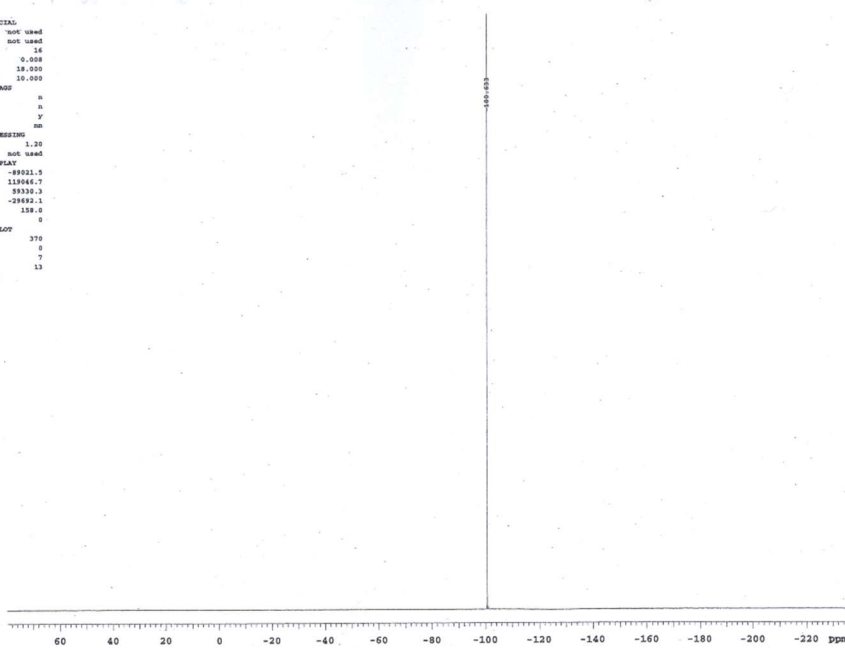
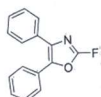


## 2-Fluoro-4,5-diphenyloxazole (3i) <sup>13</sup>C-NMR

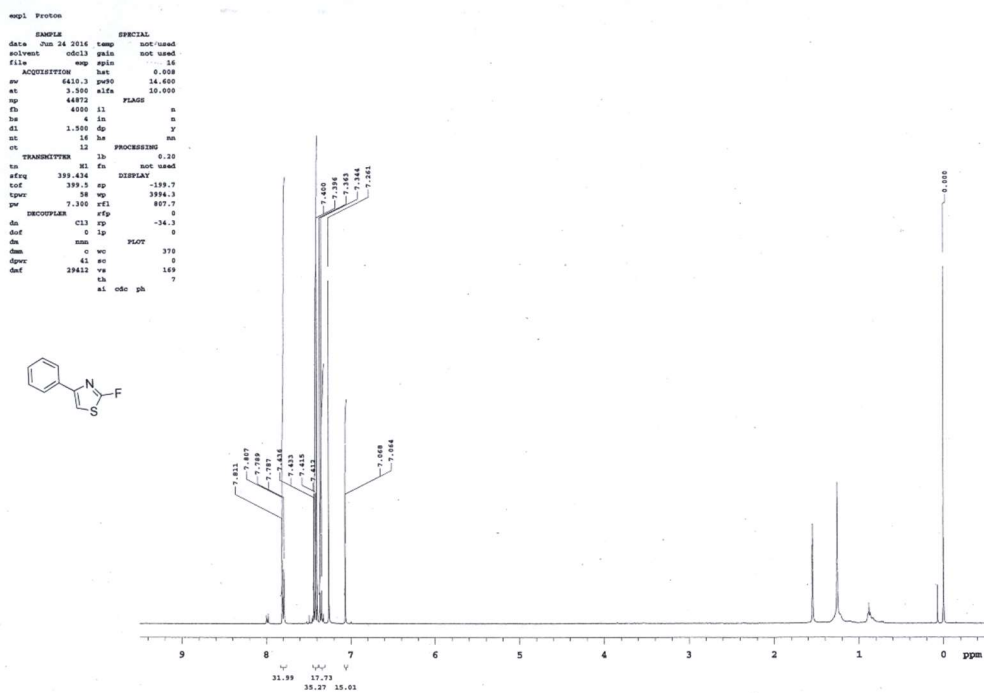


## 2-Fluoro-4,5-diphenyloxazole (3i) <sup>19</sup>F-NMR

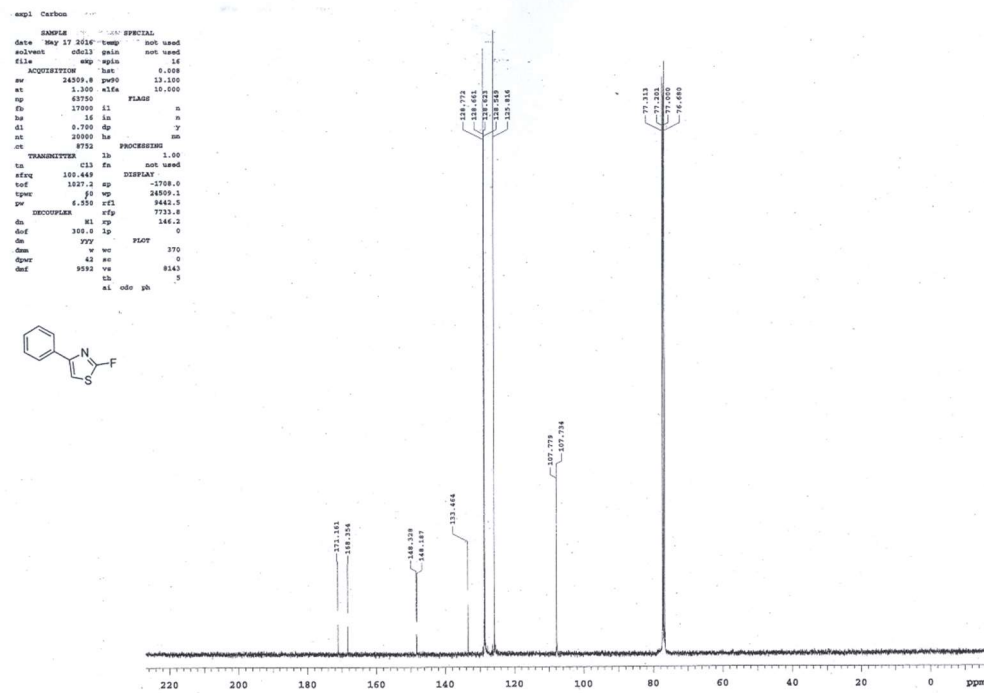
```
expt Fluorine
-----
SAMPLE
Date May 4 2016 temp not used
solvent cdcl3 gain not used
file exp-31a 16
ACQUISITION
aw 119047.6 ppsf 18.000
at 0.400 wfa 16.000
ap 143958 FLAG
cp 16800 ll n
hs 4 in n
ql 4.400 sp F
rt 16 hs nm
ct 8 PROCESSING 1.20
TRANSMITTER 1b
tu P19 En not used
wfreq 375.010 DISPLAY
tof 11429.7 ap -89211.5
tpwr 81 sp 119046.7
aw 6.000 rfp 59350.3
ENCODER
du C13 rp 128.0
dof 0 sp 0
du mm
dm c wo 370
dpr 43 ec 0
dof 29413 ve 7
th 13
sl ph
```



## 2-Fluoro-4-phenylthiazole (3j) <sup>1</sup>H-NMR

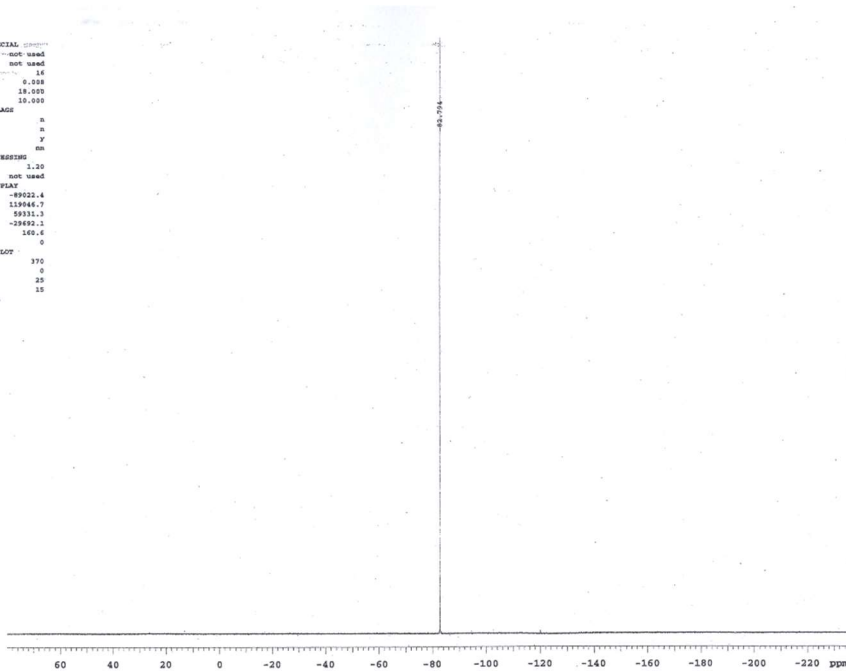
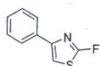


## 2-Fluoro-4-phenylthiazole (3j) <sup>13</sup>C-NMR



## 2-Fluoro-4-phenylthiazole (3j) <sup>19</sup>F-NMR

```
NAME: 3j
EXPNO: 1
PROCNO: 1
PROCNAME: 3j
DATE_UTC: May 17 2016
TIME: 12:00:00
INSTRUM: spect
PROBHD: 5mm
PULPROG: zgpg30
TD: 65536
SFO: 470.413
AQ: 0.10000000
RG: 327.68000000
AQ2: 0.10000000
RG2: 327.68000000
RG3: 327.68000000
RG4: 327.68000000
RG5: 327.68000000
RG6: 327.68000000
RG7: 327.68000000
RG8: 327.68000000
RG9: 327.68000000
RG10: 327.68000000
RG11: 327.68000000
RG12: 327.68000000
RG13: 327.68000000
RG14: 327.68000000
RG15: 327.68000000
RG16: 327.68000000
RG17: 327.68000000
RG18: 327.68000000
RG19: 327.68000000
RG20: 327.68000000
RG21: 327.68000000
RG22: 327.68000000
RG23: 327.68000000
RG24: 327.68000000
RG25: 327.68000000
RG26: 327.68000000
RG27: 327.68000000
RG28: 327.68000000
RG29: 327.68000000
RG30: 327.68000000
RG31: 327.68000000
RG32: 327.68000000
RG33: 327.68000000
RG34: 327.68000000
RG35: 327.68000000
RG36: 327.68000000
RG37: 327.68000000
RG38: 327.68000000
RG39: 327.68000000
RG40: 327.68000000
RG41: 327.68000000
RG42: 327.68000000
RG43: 327.68000000
RG44: 327.68000000
RG45: 327.68000000
RG46: 327.68000000
RG47: 327.68000000
RG48: 327.68000000
RG49: 327.68000000
RG50: 327.68000000
RG51: 327.68000000
RG52: 327.68000000
RG53: 327.68000000
RG54: 327.68000000
RG55: 327.68000000
RG56: 327.68000000
RG57: 327.68000000
RG58: 327.68000000
RG59: 327.68000000
RG60: 327.68000000
RG61: 327.68000000
RG62: 327.68000000
RG63: 327.68000000
RG64: 327.68000000
RG65: 327.68000000
RG66: 327.68000000
RG67: 327.68000000
RG68: 327.68000000
RG69: 327.68000000
RG70: 327.68000000
RG71: 327.68000000
RG72: 327.68000000
RG73: 327.68000000
RG74: 327.68000000
RG75: 327.68000000
RG76: 327.68000000
RG77: 327.68000000
RG78: 327.68000000
RG79: 327.68000000
RG80: 327.68000000
RG81: 327.68000000
RG82: 327.68000000
RG83: 327.68000000
RG84: 327.68000000
RG85: 327.68000000
RG86: 327.68000000
RG87: 327.68000000
RG88: 327.68000000
RG89: 327.68000000
RG90: 327.68000000
RG91: 327.68000000
RG92: 327.68000000
RG93: 327.68000000
RG94: 327.68000000
RG95: 327.68000000
RG96: 327.68000000
RG97: 327.68000000
RG98: 327.68000000
RG99: 327.68000000
RG100: 327.68000000
SPECIAL:
date May 17 2016 temp not used
solvent cdcl3 gate not used
file exp name 16
ACQUISITION
acq bat 0.000
aw 118047.6 pps0 18.000
at 0.400 a1ex 10.000
ap 142858 FLAG
fb 51800 ll n
ha 4 in n
cl 4.400 qp Y
ct 16 ha nm
ct TRANSMITTER lb PROCESSING 1.20
ta F19 fa not used
sfreq 375.830 DISPLAY
tolf 11823.7 ap -8922.4
tprw 41 wp 11946.7
pw 6.000 rfd 59311.1
DECOUPLER rfp -29492.1
ds c13 rp 140.4
ds 0 lp 0
dm 0 wa FLOW 370
dum 0
dprw 41 eo 0
dof 29412 re 25
al ph 15
```



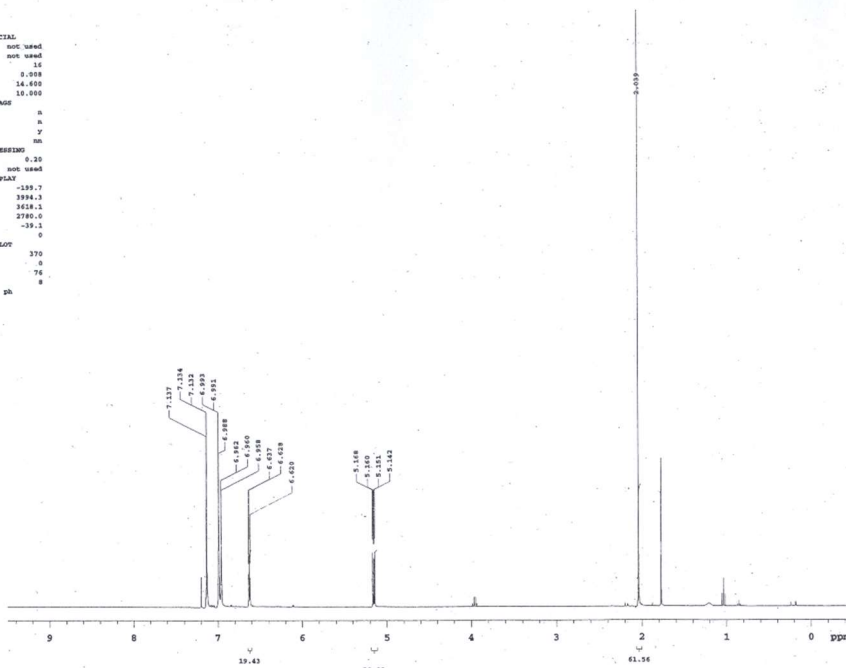


# 1-(5-fluoro-2-furyl)ethanone (3k) <sup>1</sup>H-NMR

2-fluoroacetyl furans  
1H-NMR in Chlorobenzene-d5

```

SAMPLE          SPECIAL
date May 21 2016 temp not used
solvent cdcl3 gain not used
file exp spin 16
ACQUISITION    het 0.008
sv 4410.3 ppsd 14.800
at 1.300 a1fa 10.000
sp 44872
cb 4000 il FLAGG n
hs 4 in n
sl 1.000 sp y
st 16 ha nm
nt
TRANSMITTER lb 1b PROCESSING 0.20
ts kl en not used
sfreq 399.424 DISPLAY
tof 399.5 sp 199.7
tproc 58 wp 3994.3
pw 7.300 rfl 2828.1
DECOUPLER cl3 rp 2780.0
ds 0 ip 0
dm mm PLOT 370
dmc 41 no 0
dnd 28422 vs 76
sh
sl odc ph 8
  
```

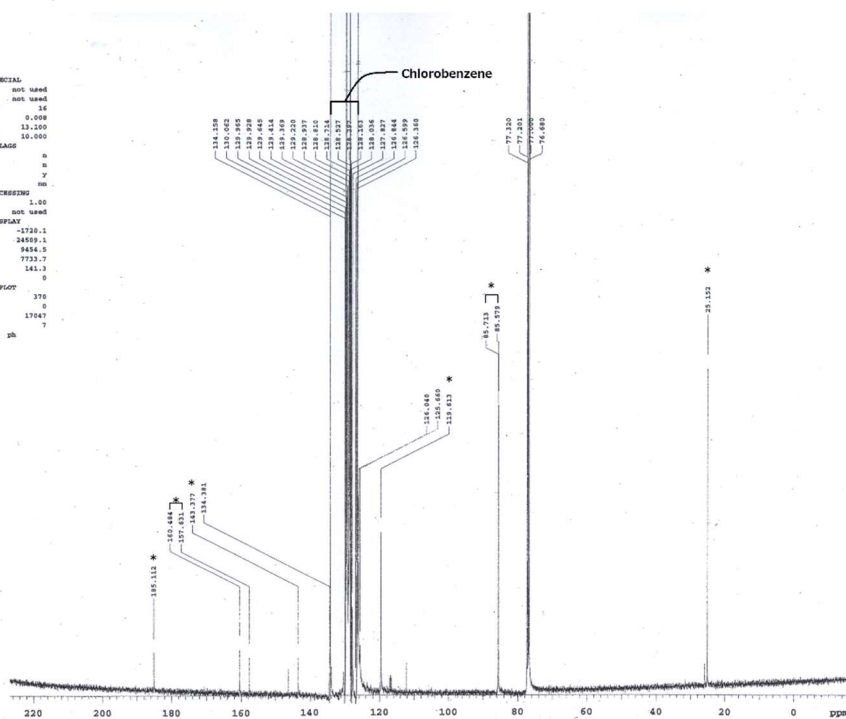


# 1-(5-fluoro-2-furyl)ethanone (3k) <sup>13</sup>C-NMR

2-fluoroacetyl furans  
13C-NMR in CDCl3

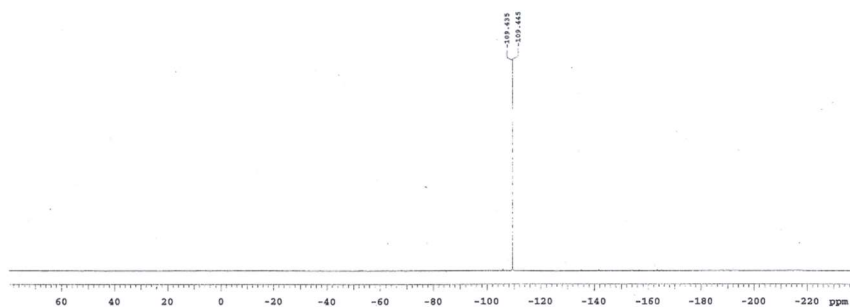
```

SAMPLE          SPECIAL
date May 22 2016 temp not used
solvent cdcl3 gain not used
file exp spin 16
ACQUISITION    het 0.008
sv 2459.4 ppsd 13.200
at 1.300 a1fa 10.000
sp 42750
cb 17000 il FLAGG n
hs 16 in n
sl 0.700 sp y
st 200000 ha nm
nt
TRANSMITTER lb 1b PROCESSING 1.00
ts kl en not used
sfreq 100.644 DISPLAY
tof 1027.1 sp -1720.1
tproc 60 wp 24500.1
pw 6.550 rfl 8484.5
DECOUPLER kl rp 7723.7
ds 389.0 ip 141.3
dm mm PLOT 370
dmc 42 no 0
dnd 9592 vs 17047
sh
sl odc ph 7
  
```

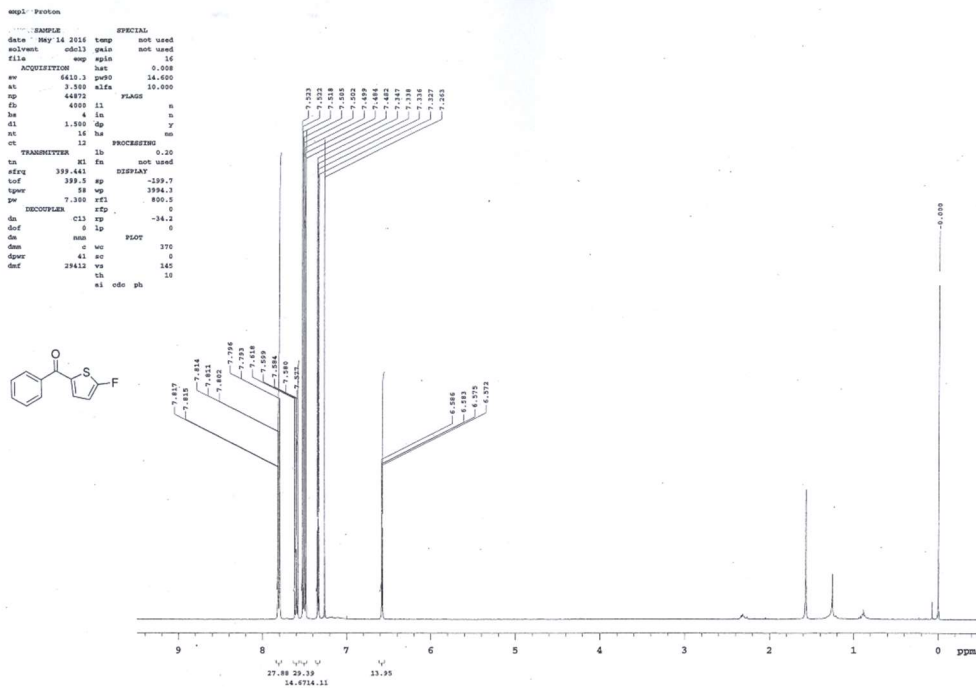


# 1-(5-fluoro-2-furyl)ethanone (3k) <sup>19</sup>F-NMR

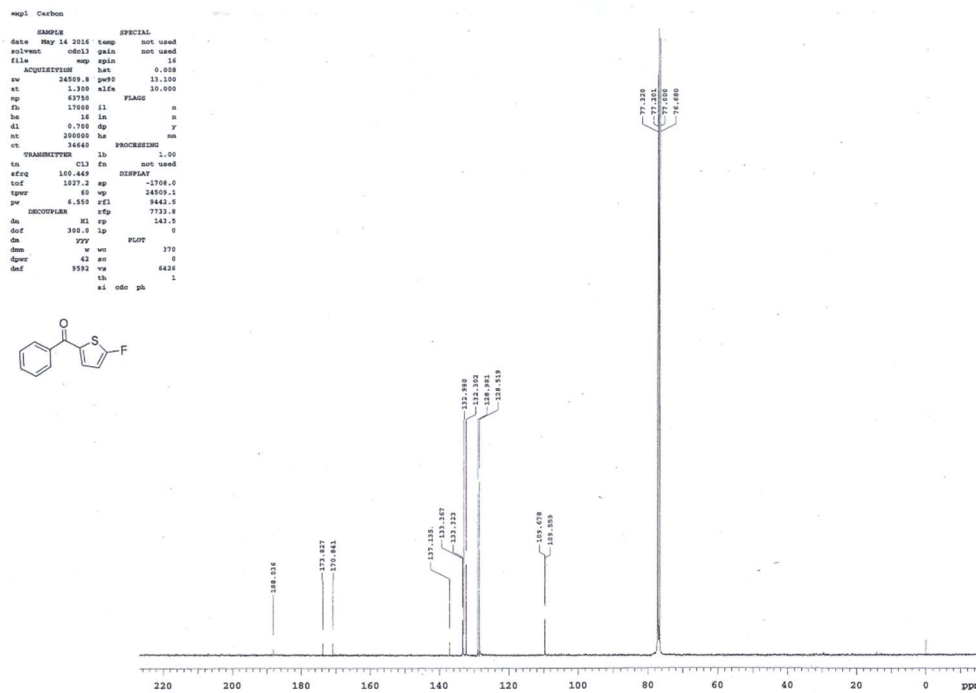
```
expt Fluorine
-----
NAME          SPECIAL
date          May 21 2016 temp      not used
solvent       cdcl3 gain          not used
file          exp spin           16
ACQUISITION  hsc          0.058
av           119047.6 pwrF        18.000
sc           0.000 sfile        16.000
sp           142858 P1AS2
fn           51890 f1
hs           4 in
dl           4.400 dp          Y
sc           16 hsc
ut           14 PROCESSING
-----
TRANSMITTER  f1          1.20
fn           f1          not used
freq         376.813
hsc          11639.4 sp          -89237.5
pwr          41 wF          119044.7
sc           0.000 rF1          47899.3
DECOUPLER    rFp          -41132.2
ds          c13 xp          156.9
ds          5 lp          0
ds          nnn
ds          w wF          370
ds          41 sc          0
ds          21413 vs          16
ds          11
ds          ai ph          17
```



(5-Fluoro-2-thienyl)phenylmethanone (3) <sup>1</sup>H-NMR

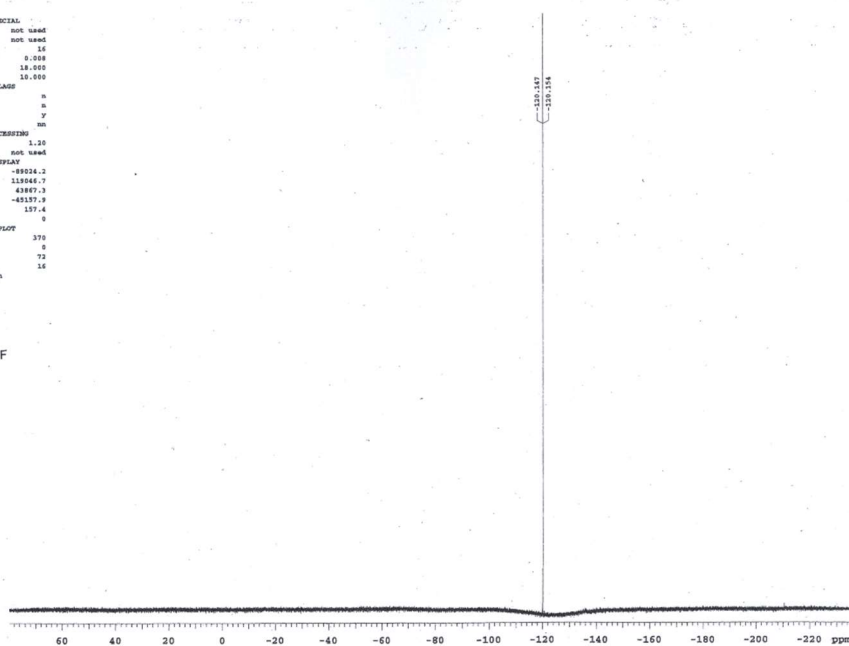
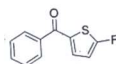


(5-Fluoro-2-thienyl)phenylmethanone (3) <sup>13</sup>C-NMR

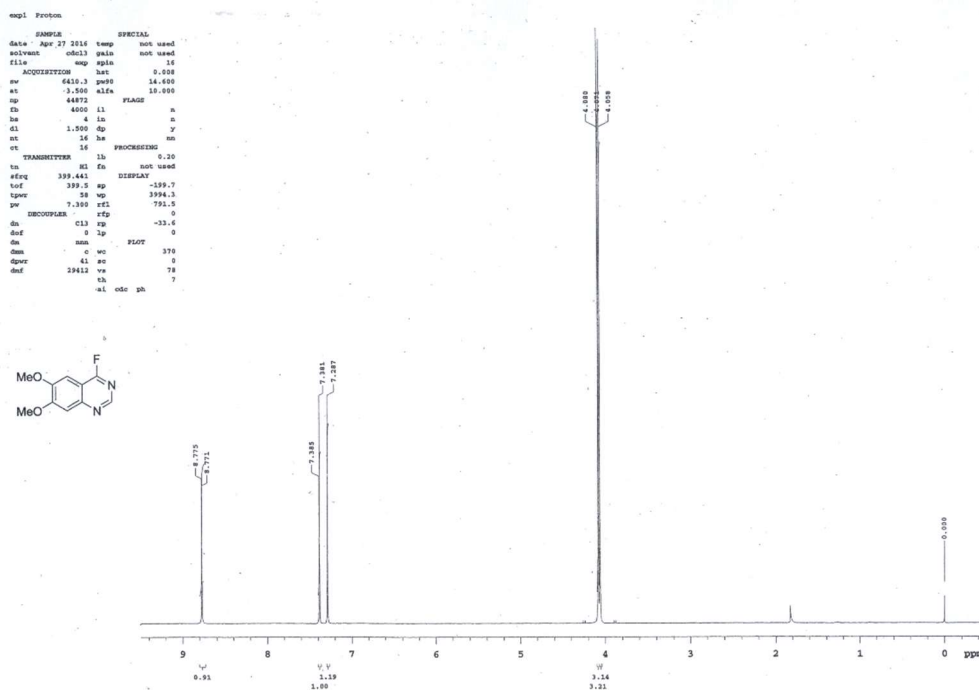


# (5-Fluoro-2-thienyl)phenylmethanone (3) <sup>19</sup>F-NMR

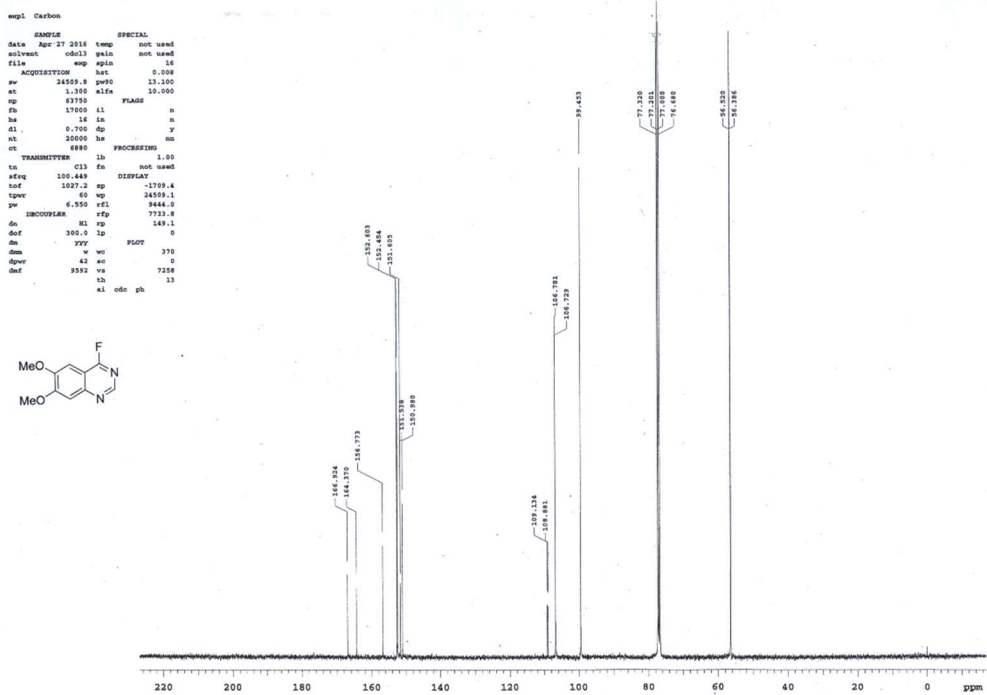
```
exp1 Fluor1m  
===== SPECIAL =====  
date May 14 2010 temp not used  
solvent CDCl3 spin not used  
file exp spin 16  
===== ACQUISITION =====  
acq 119047.6 pw90 10.000  
at 0.000 alfa 10.000  
ap 142800 n1 PLANS  
cb 51800 n1 n  
ca 4 n1 n  
cl 4.400 sp y  
ct 14 n1 m  
===== TRANSMITTER =====  
tr 1b 1.20  
===== PROCESSING =====  
in p19 fa not used  
sfreq 375.820 DEPRAN  
h1 21623.7 sp -49024.2  
tproc 61 wv 119046.7  
pw 6.000 rfl 43987.3  
===== DECOUPLER =====  
dc C13 rp 157.4  
dof 0 lp 0  
===== PLOT =====  
dm 0 wv 370  
sm 41 ac 0  
dof 23412 va 73  
in 1b 14  
al ph
```



### 4-Fluoro-6,7-dimethoxyquinazoline (3m) <sup>1</sup>H-NMR

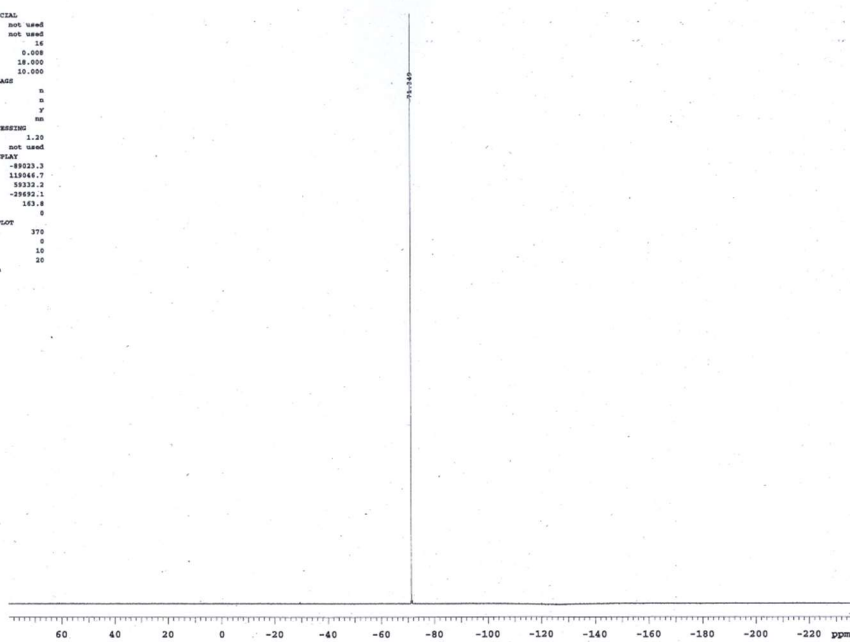
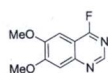


### 4-Fluoro-6,7-dimethoxyquinazoline (3m) <sup>13</sup>C-NMR



# 4-Fluoro-6,7-dimethoxyquinazoline (3m) <sup>19</sup>F-NMR

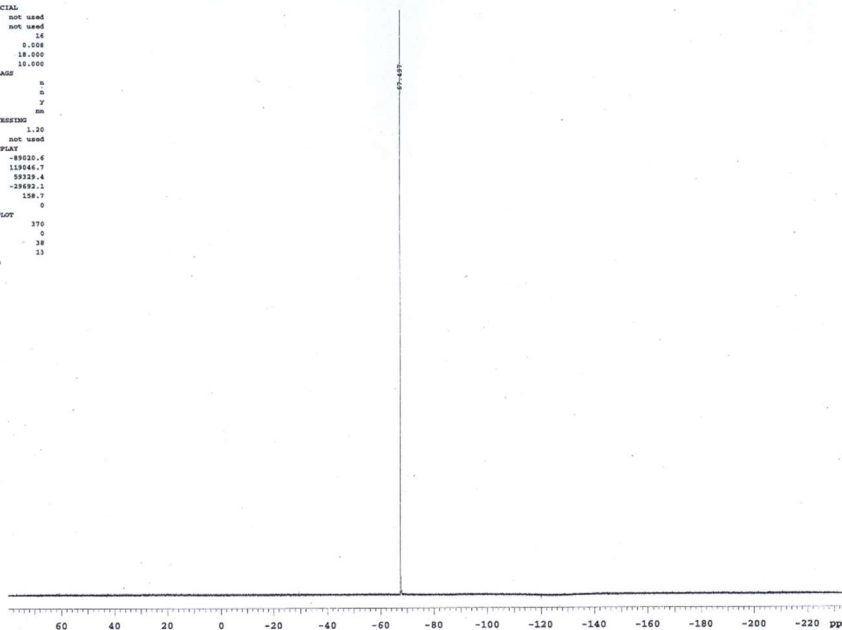
```
exp1 Fluorine
=====
SMPX4          SPECIAL
Date   Apr 21 2016   temp   not used
solvent cdcl3   gain   not used
f1in   emp   spin   16
ACQUISITION emp   hat   0.008
sw     119047.4   pwr9   10.000
st     8.800   a1a    10.000
sp     142858          FLAGS
ch     51800   l1      n
hs     4       in      n
dl     4.400   sp      y
st     16     ha      no
ct
=====
TRANSMITTER 8   IN   PROCESSING 1.20
ta     F19   fn   not used
sfrq   375.820   DIRPACT
conf   18429.7   sp   -89023.3
tqwr   61   vp   119046.7
pw     6.000   rfl   9832.2
=====
DECOUPLER  C13   rp   -28452.1
ch     0       ip   193.8
ds     mmn          PLOT
dms     c   wc   370
spwr   41   sc   0
dnc    28412   va   10
st     20     th   20
at     ph
```





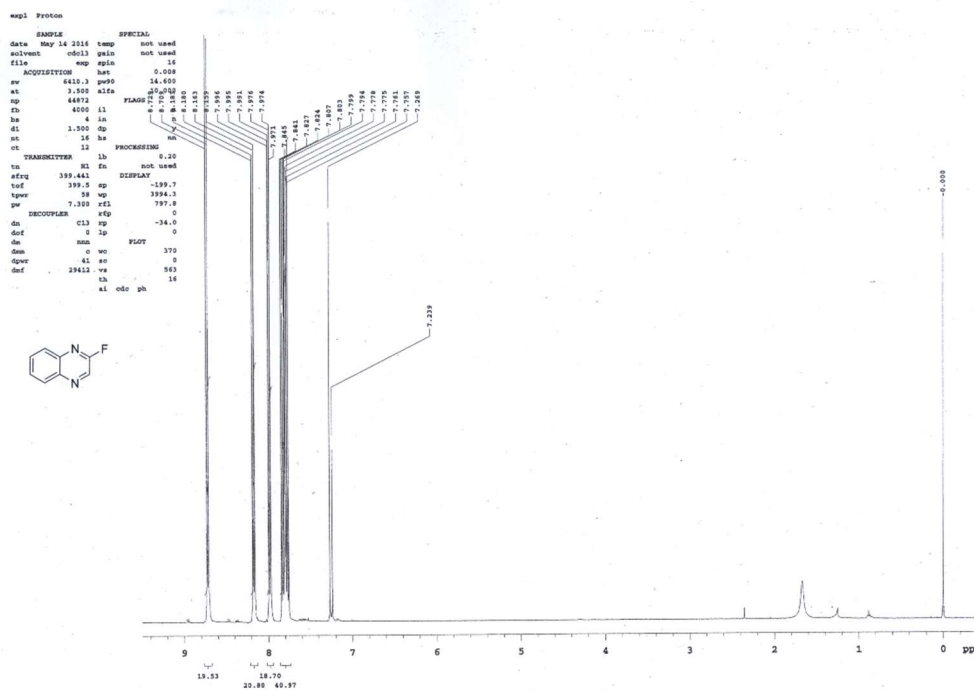
# 4-Fluoroquinazoline (3n) <sup>19</sup>F-NMR

```
exp1 Fluorine
-----
SAMPLE:
date   May 18 2016   temp   not used
solvent  cdcl3   gain   not used
file    exp   spin   16
ACQUISITION:
av      119047.4   pu90   18.000
at      0.000   n1fa   10.000
ap      102818
-----
PROBHD:
fb      51800   l1
hs      4   in   n
dl      4.400   sp   y
nt      16   hs
ct      16
-----
TRANSMITTER:
ts      F13   sh   1.20
rfreq   375.820   DISPLAY
cpl     13429.7   sp   -89226.6
tpwr    41   wp   119046.7
pw      6.000   rfi   99329.4
-----
RECOUPLER:
dn      c13   fp   150.7
dnt     0   fp
dm      non
dmn     c   wo   370
dprw    41   wo   0
dnt     29413   va   38
al      sh   13
al      ph
```

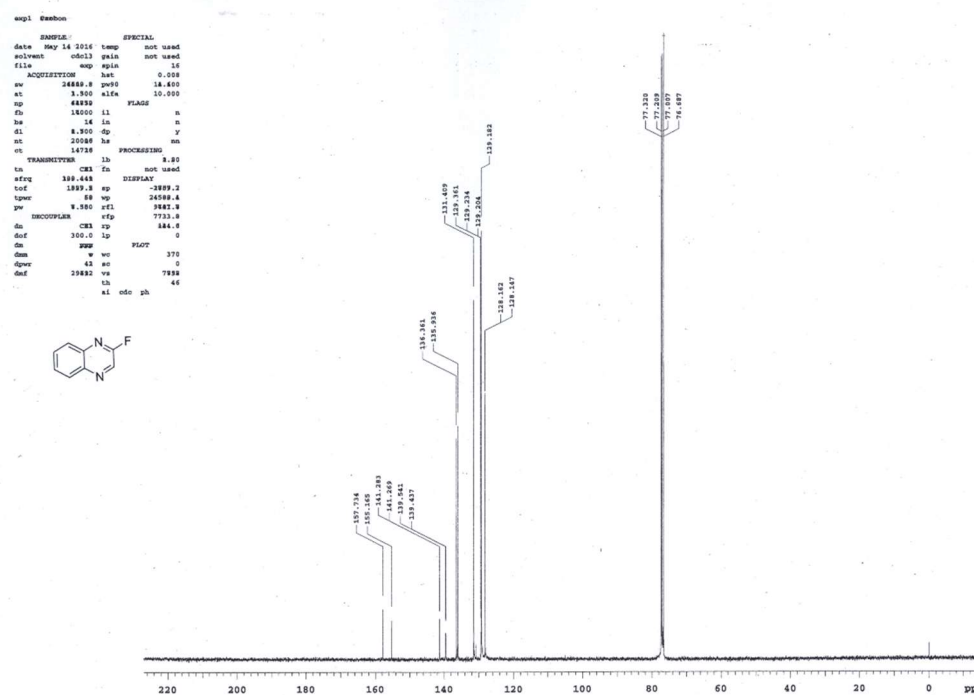




## 2-Fluoroquinoxaline (3o) <sup>1</sup>H-NMR

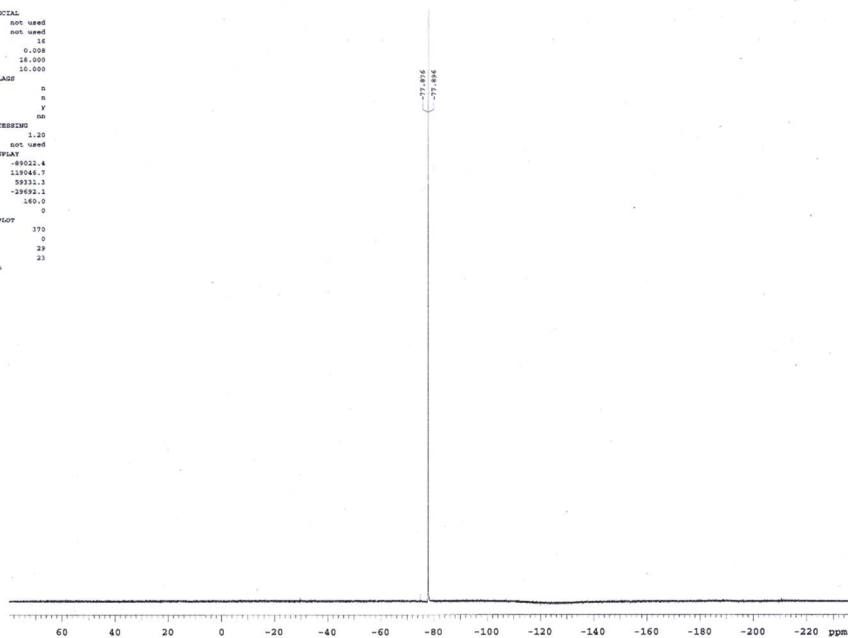


## 2-Fluoroquinoxaline (3o) <sup>13</sup>C-NMR

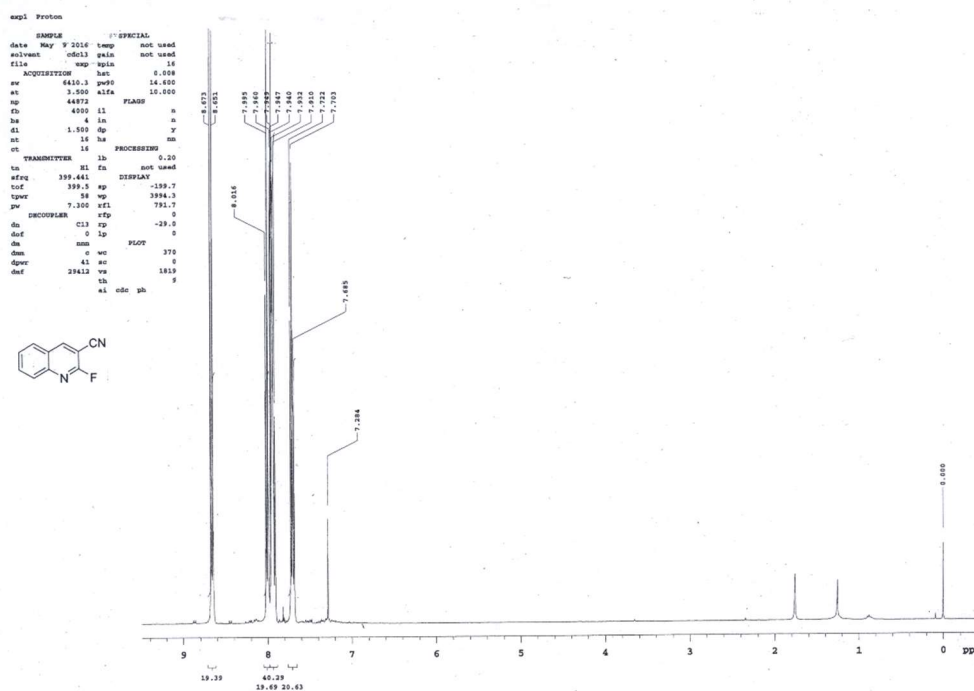


## 2-Fluoroquinoxaline (3o) <sup>19</sup>F-NMR

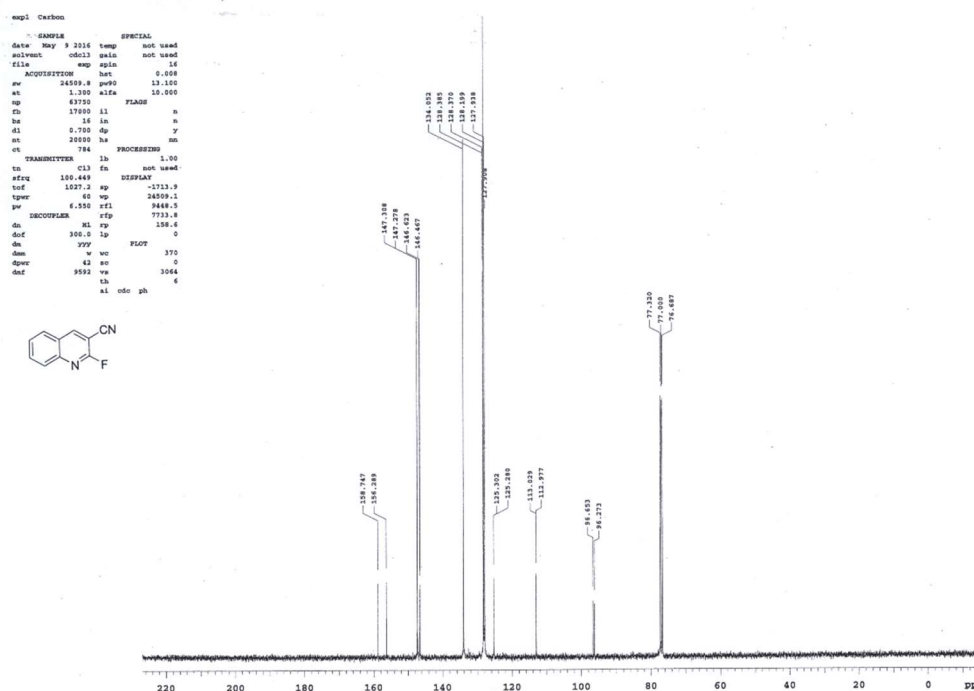
```
exp3 Fluorine
=====
SAMPLE          SPECIAL
date   May 14 2016   temp   not used
solvent  cdcl3      gain   not used
file    exp         gain   16
=====
ACQUISITION
pw      119047.6     ppsf   10.000
at      0.600       aifa   10.000
np      142808
fu      51800       li     FLAGS  n
ds      4          in     n
dl      4.400      sp     y
st      16        ha     nn
ec      8          PROCESSED
=====
TRANSMITTER
td      F3P      fd     1.20   not used
rfc1    375.820  DISPAN
tof     13429.7  sp     -85022.4
tproc   51      sp     119046.7
pw      6.000   rfl    59331.3
ds      DECOUPLER  rfp    -29692.1
dl      C13      tp     1600.0
dof     0       ip     0
ds      none    plot  0
dm      c       w0    370
-dm     41      w1    0
-ql     28412  v2    29
ch      ch     23
al     ph
=====
```



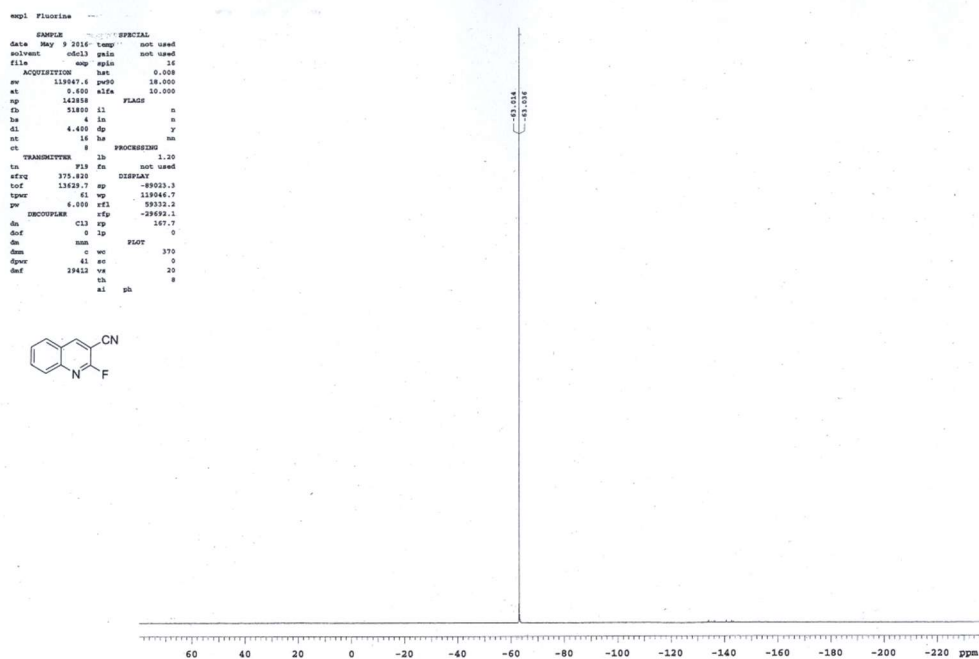
### 3-Cyano-2-fluoroquinoline (3p) <sup>1</sup>H-NMR



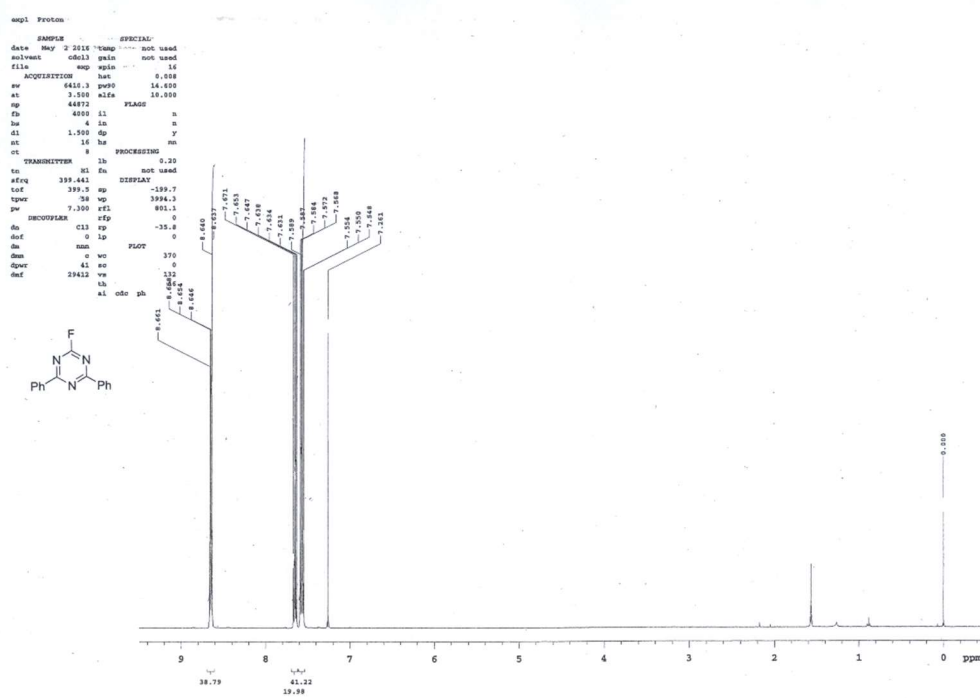
### 3-Cyano-2-fluoroquinoline (3p) <sup>13</sup>C-NMR



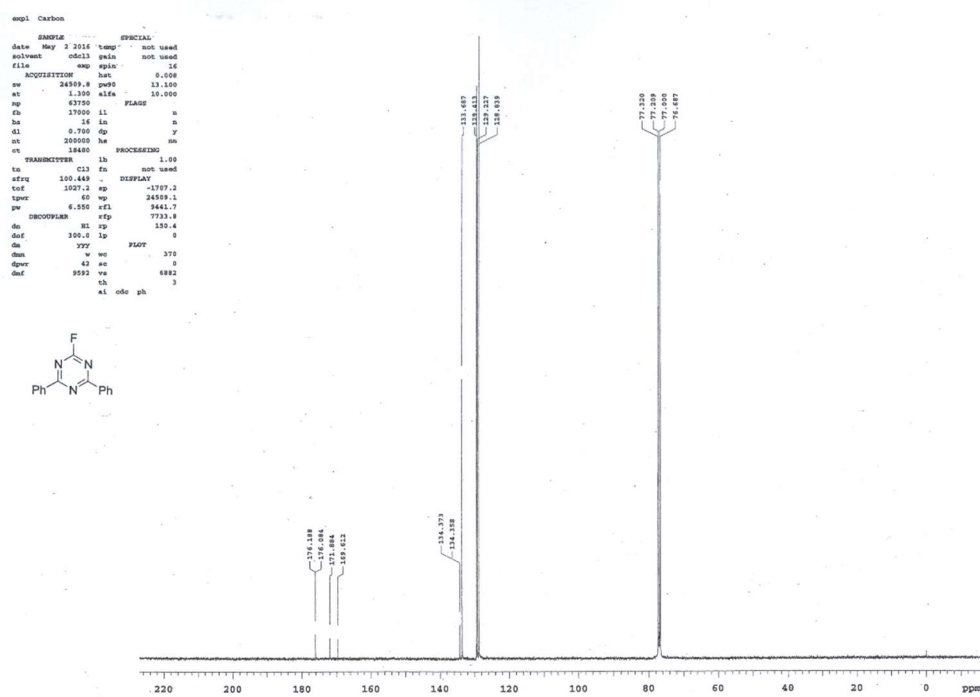
### 3-Cyano-2-fluoroquinoline (3p) <sup>19</sup>F-NMR



## 2-Fluoro-4,6-diphenyltriazine (3q) <sup>1</sup>H-NMR

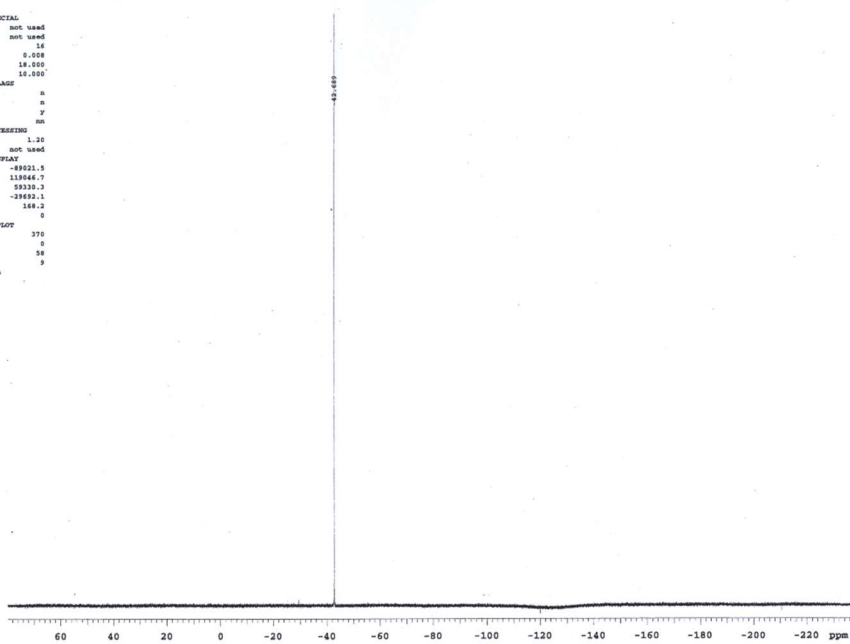


## 2-Fluoro-4,6-diphenyltriazine (3q) <sup>13</sup>C-NMR

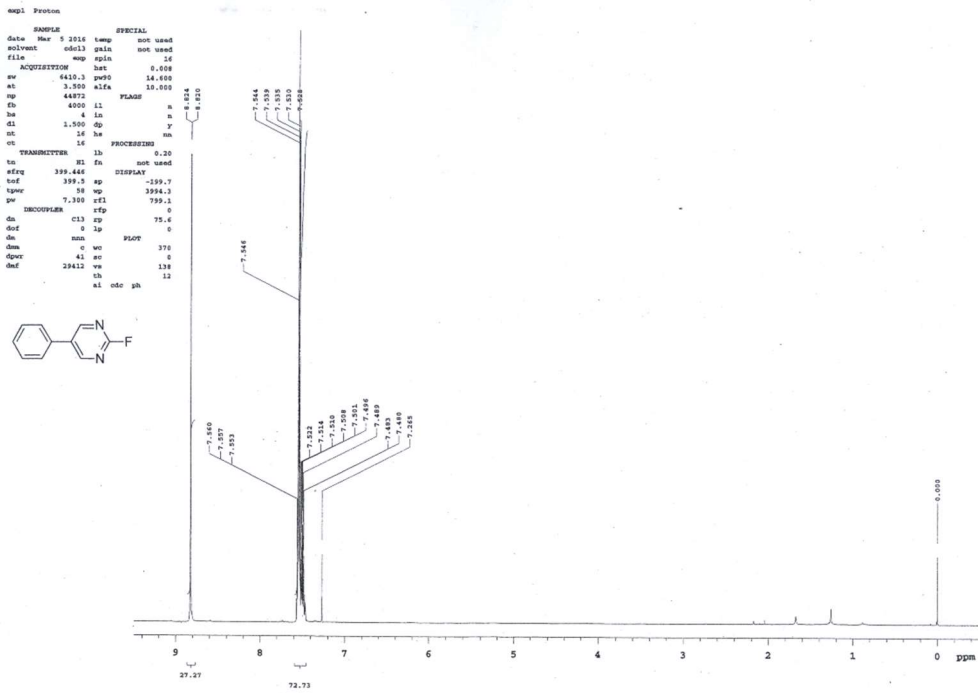


## 2-Fluoro-4,6-diphenyltriazine (3q) <sup>19</sup>F-NMR

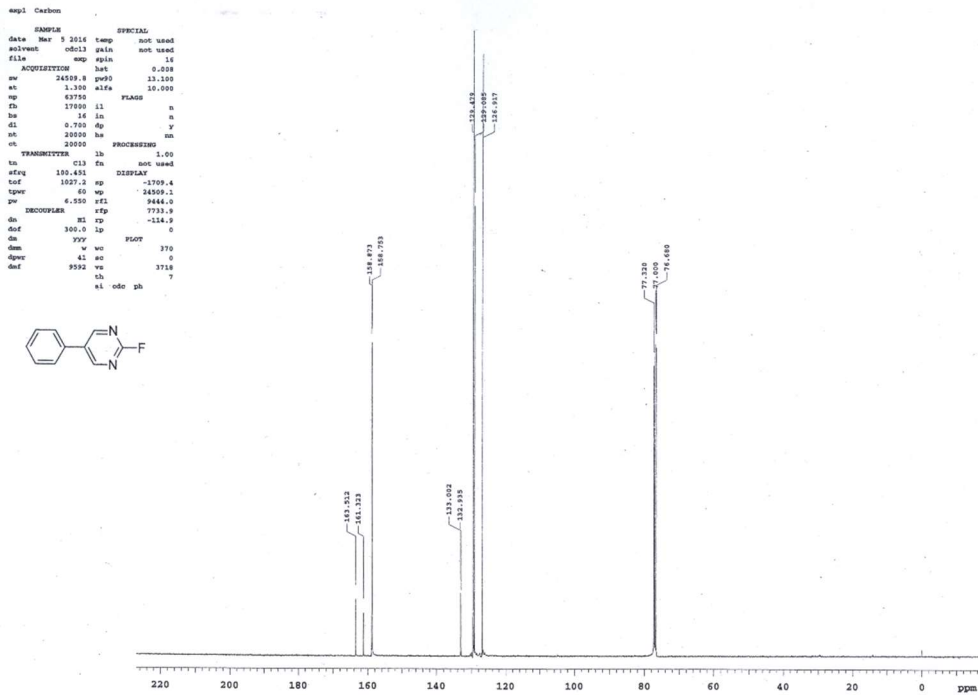
```
exp1 Fluorine
-----
SAMPLE
date May 3 2016 temp not used
solvent cdcl3 glna not used
filn exp spia 16
ACQUISITION
pr 110247.6 pps0 16.000
at 0.600 alfa 16.000
sp 142858
rb 51800 l1 FLAG n
hs 4 in n
dl 4.400 qp x
nt 16 hs nn
vt 16 PROCESSING
TRANSMITTER lb 1.20
sa F19 fn not used
rfreq 375.800 DISPLAY
tof 11629.7 sp -89021.5
tqwe 61 sp 113066.7
pr 6.000 rfi 59330.2
DECOUPLER rfp -29492.1
dc C13 vp 169.2
dof 0 lp 0
ds nmn FLOC
dms c wv 370
dpcw 41 wv 0
dof 29413 vq 59
ch ch 9
al ph 9
```



2-fluoro-5-phenylpyrimidine (3r) <sup>1</sup>H-NMR

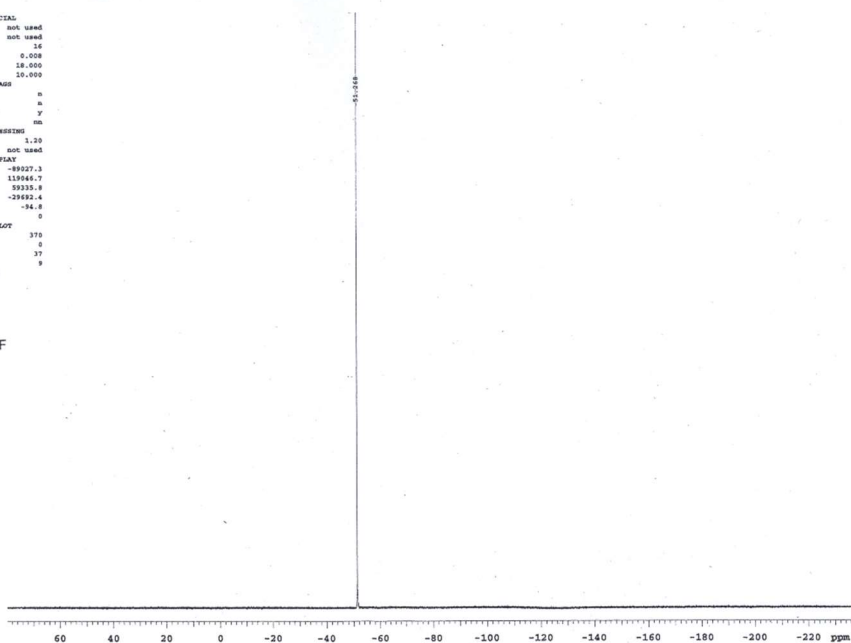
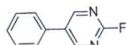


2-fluoro-5-phenylpyrimidine (3r) <sup>13</sup>C-NMR



## 2-fluoro-5-phenylpyrimidine (3r) <sup>19</sup>F-NMR

```
exp1 Fluorine  
-----  
SAMPLE  
date Mar 7 2016 temp not used  
solvent CDCl3 gain not used  
file exp spin 16  
ACQUISITION  
sw 119047.6 dat 0.008  
st 0.400 alfa 10.000  
sp 142850 FLAME  
fo 51800 il n  
ba 4 in n  
dl 4.400 dp y  
st 16 ha mn  
ct 4 PROCESSING  
-----  
TRANSMITTER lb 1.20  
ts 910 zn not used  
wfreq 375.824 DISPLAY  
totf 11628.8 ap -89227.3  
tqwr 61 119046.7  
pw 6.000 pfl 59335.8  
DECOUPLER rfp -29652.4  
ds C13 xp -34.8  
dnt 0 ip 0  
dm hnm PLOT 0  
dmn c wo 370  
dpar 41 ec 0  
dnt 29413 va 37  
lb 0b 8  
sl ph
```

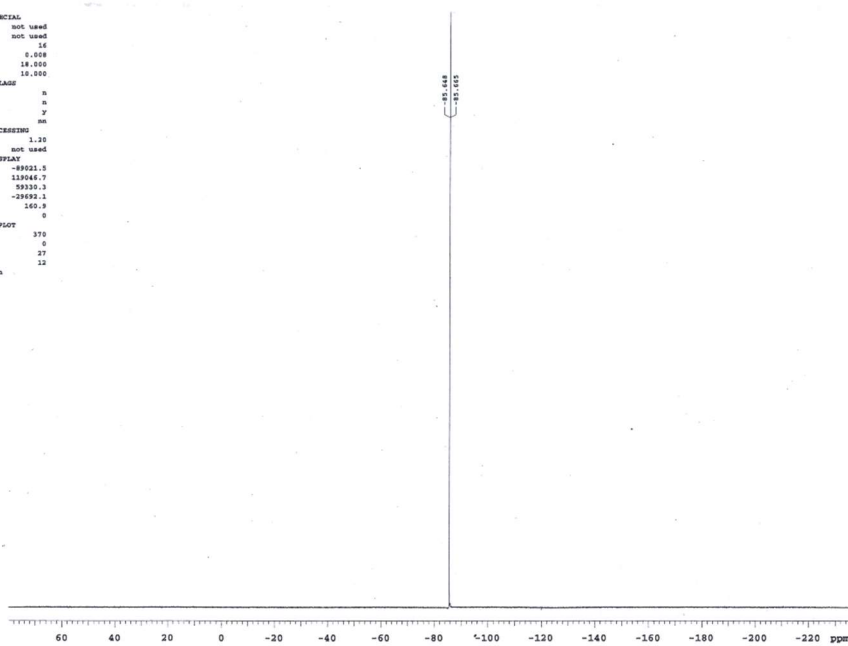




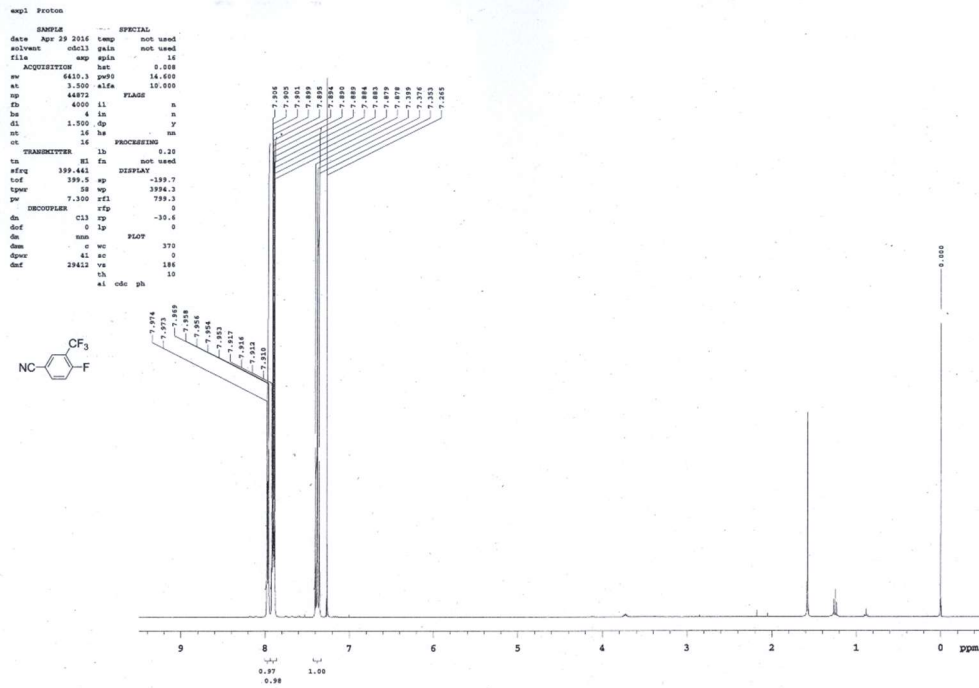


### 3-fluoro-6-phenylpyridazine (3s) <sup>19</sup>F-NMR

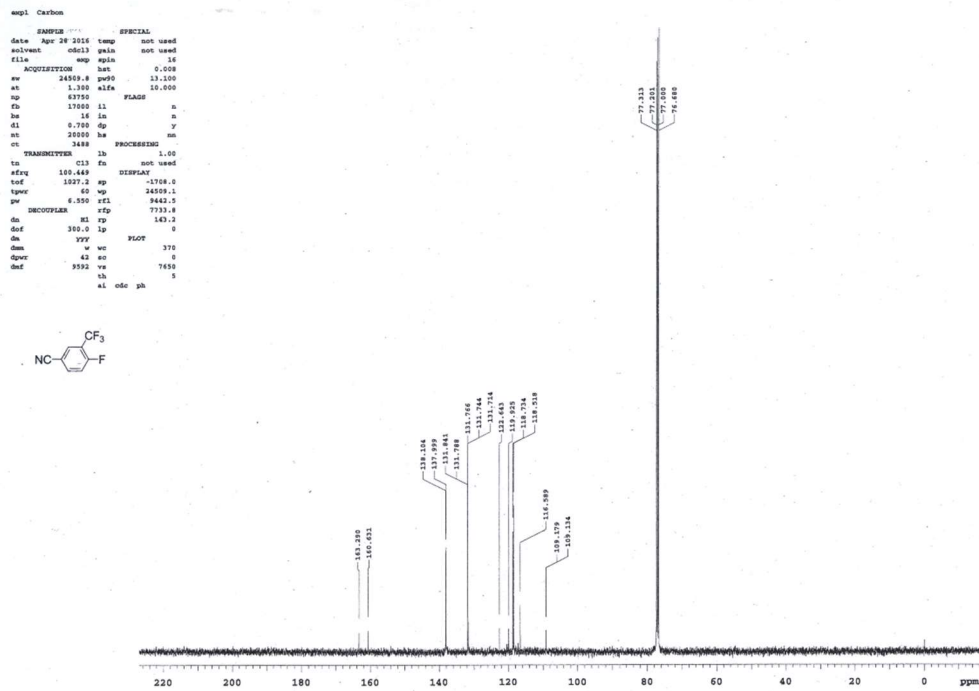
```
exp1 Fluorine
-----
SAMPLE
date Apr 21 2016 temp not used
solvent cdcl3 gain not used
file exp 0310 16
ACQUISITION
ac 119041.4 ppsf 18.000
at 0.400 alfa 18.000
ap 142808 f1
cb 31800 f1
ha 4 in n
hl 4.400 sp f
nt 16 ha nm
ot
TRANSMITTER 1b PROCESSING 1.20
ta F19 fn not used
rfq 375.810 DISPLAY
tof 116429.7 sp -89231.3
tqvr f1 sp 119040.7
wv 0.000 rfi 39200.0
DECOUPLER c13 sp -29592.1
ds c13 sp 160.9
dof 0 ip 0
ds nm
dm u wc 370
dprv 41 ac 0
dat 29412 ve 27
th 12
al ph
```



### 4-fluoro-3-(trifluoromethyl)benzonitrile (3t) <sup>1</sup>H-NMR



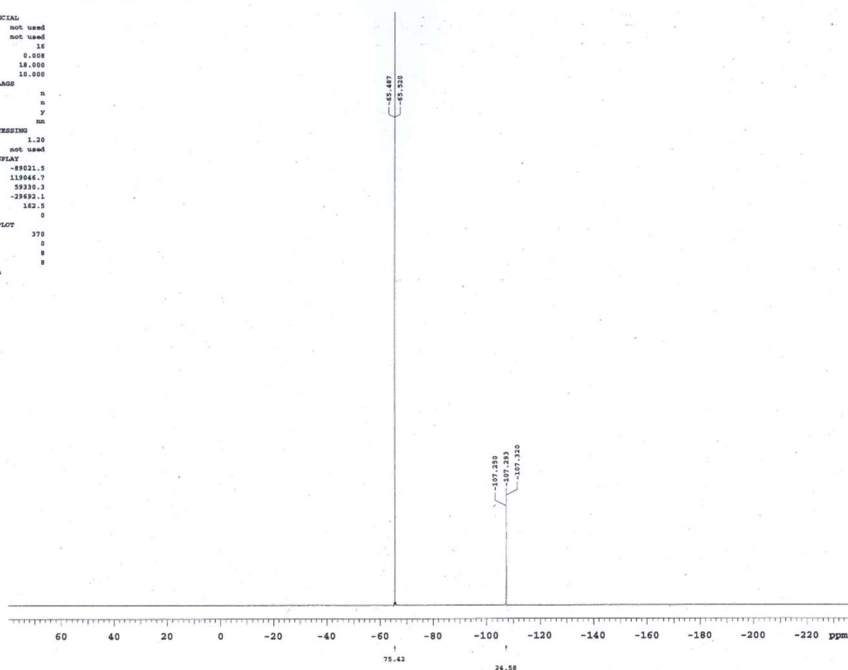
### 4-fluoro-3-(trifluoromethyl)benzonitrile (3t) <sup>13</sup>C-NMR



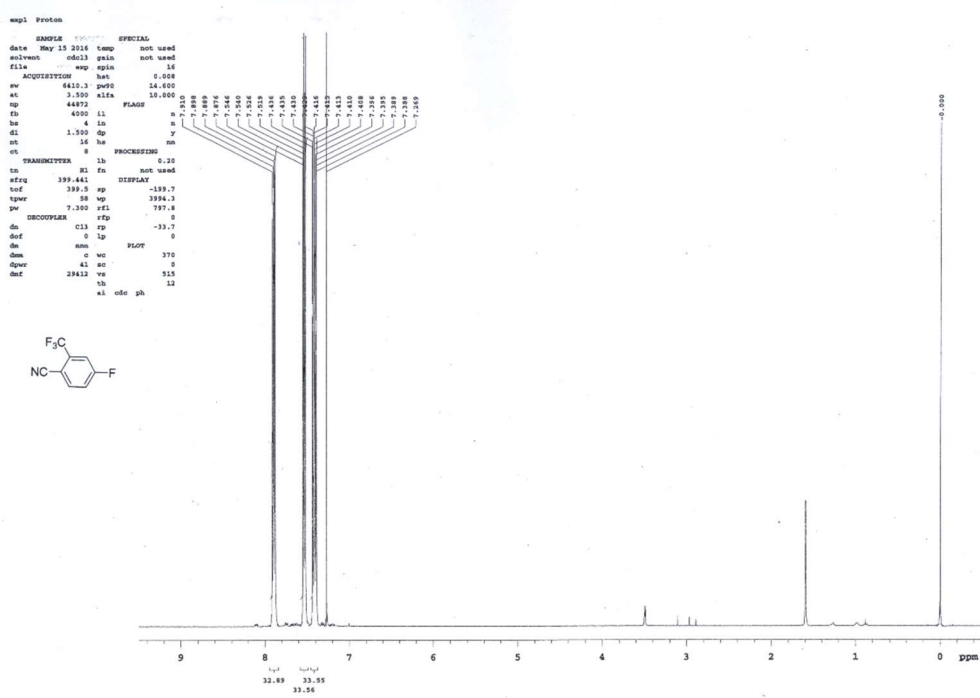
# 4-fluoro-3-(trifluoromethyl)benzonitrile (3t) <sup>19</sup>F-NMR

```

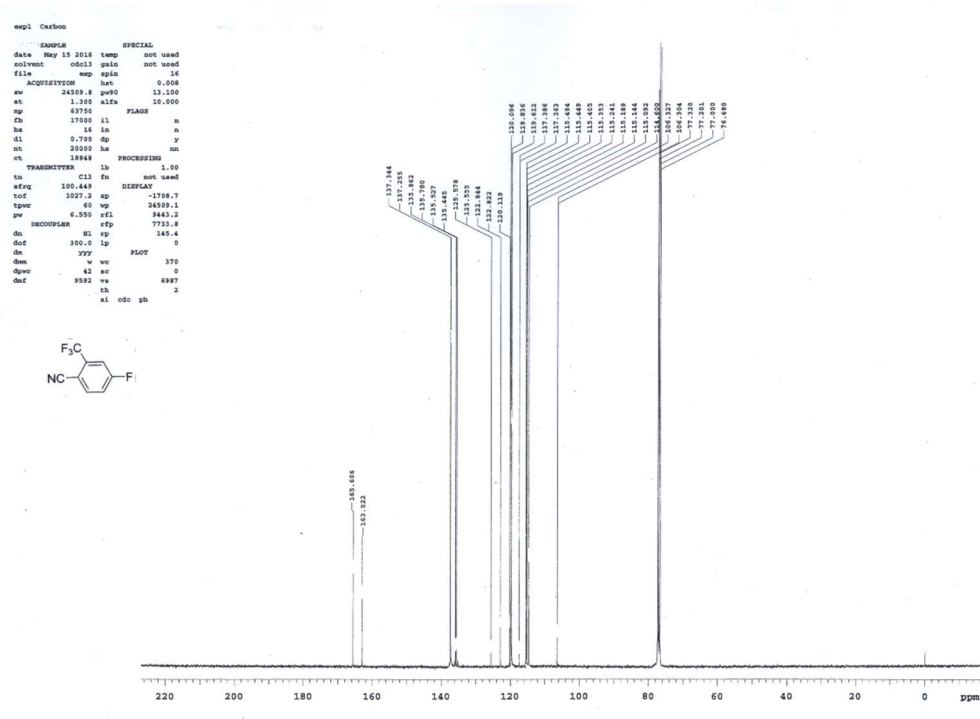
expt Fluorine
SAMPLE
-----
Data Apr 29 2016 temp not used
solvent cdc13 main not used
file exp spin 16
ACQUISITION 0.008
av 115047.6 hz 18.000
at 0.400 alfa 18.000
rg 142898
f2 51800 il n
hs 4 ls m
dl 4.400 sp y
nt 16 hs mn
ct 16 PROCESSING
TRANSMITTER lb 1.20
ts f19 fa not used
efrq 375.820
tod 13429.7 sp -8921.0
tper 41 sp 119646.7
pw 6.000 rfi 59330.3
CIRCULARS fcp -23652.1
da c13 sp 162.5
dof 0
dm 0
dms 0 wo 370
Spar 41 so 0
dof 29413 va 8
al ph 8
  
```



### 4-fluoro-2-(trifluoromethyl)benzonitrile (3u) <sup>1</sup>H-NMR

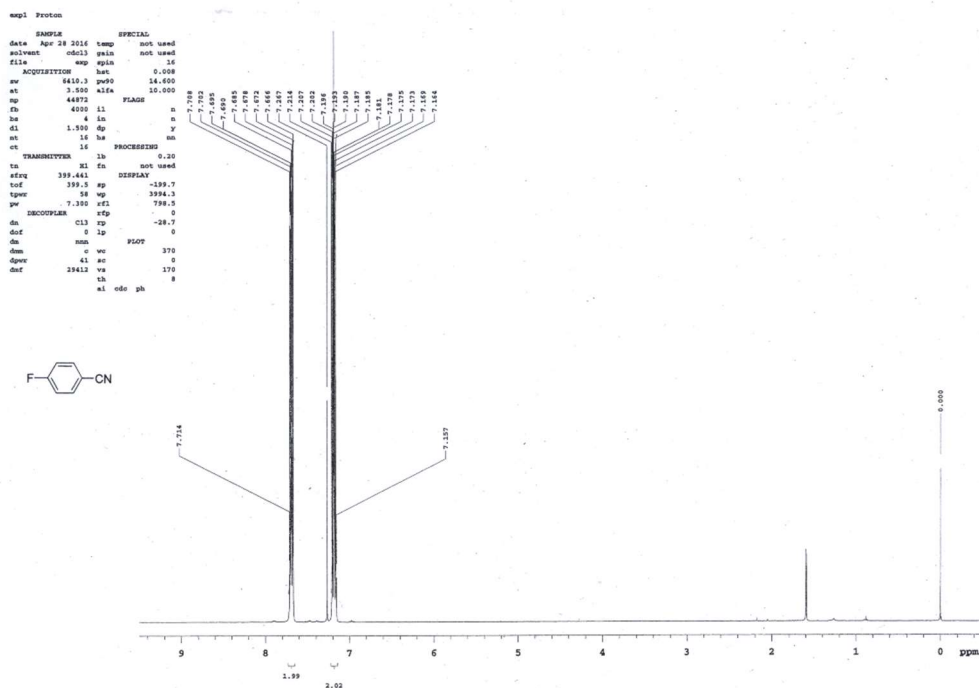


### 4-fluoro-2-(trifluoromethyl)benzonitrile (3u) <sup>13</sup>C-NMR





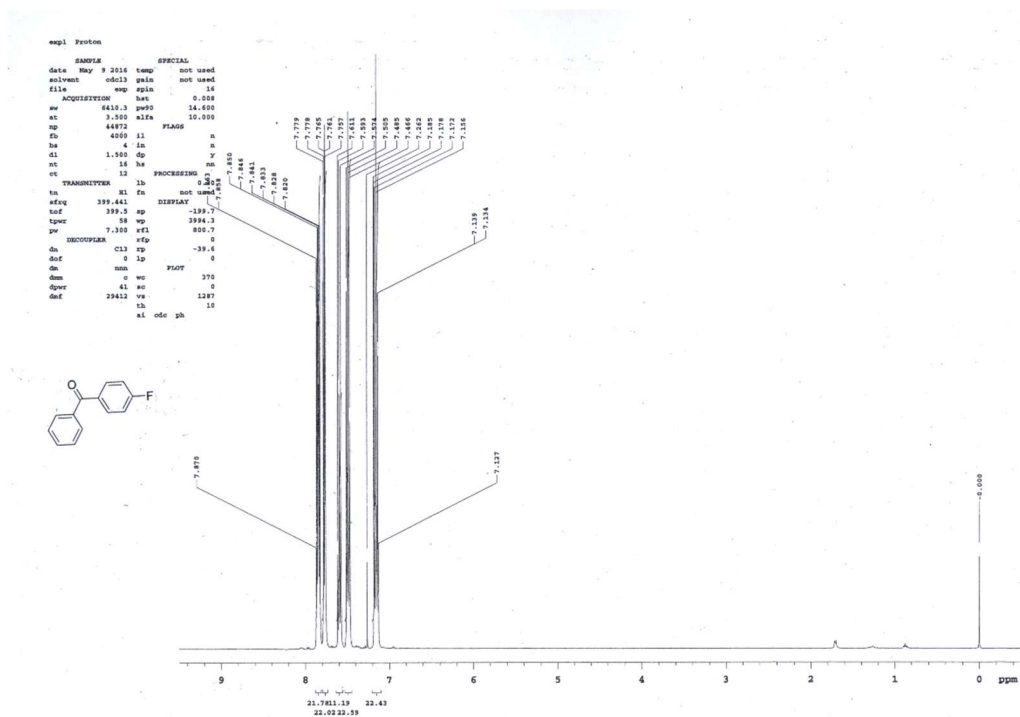
### 4-fluorobenzonitrile (5a) <sup>1</sup>H-NMR



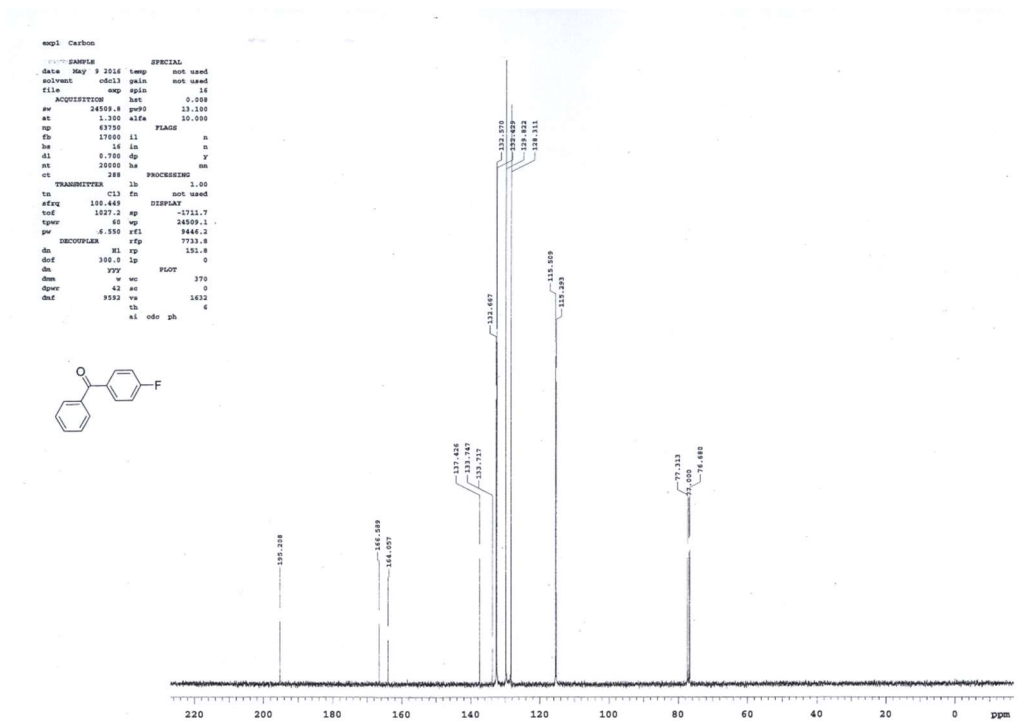




(4-Fluorophenyl)phenylmethanone (5v) <sup>1</sup>H-NMR

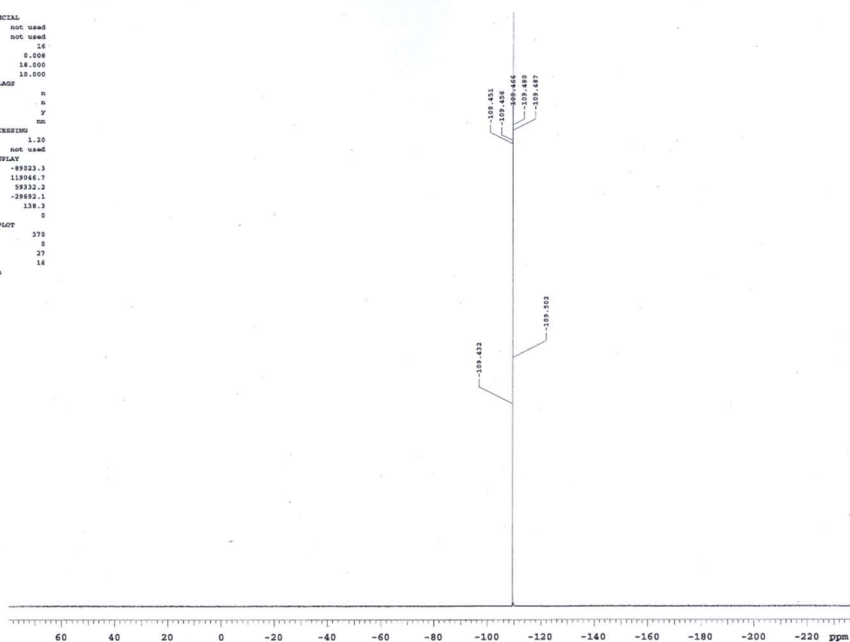
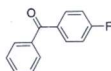


(4-Fluorophenyl)phenylmethanone (5v) <sup>13</sup>C-NMR

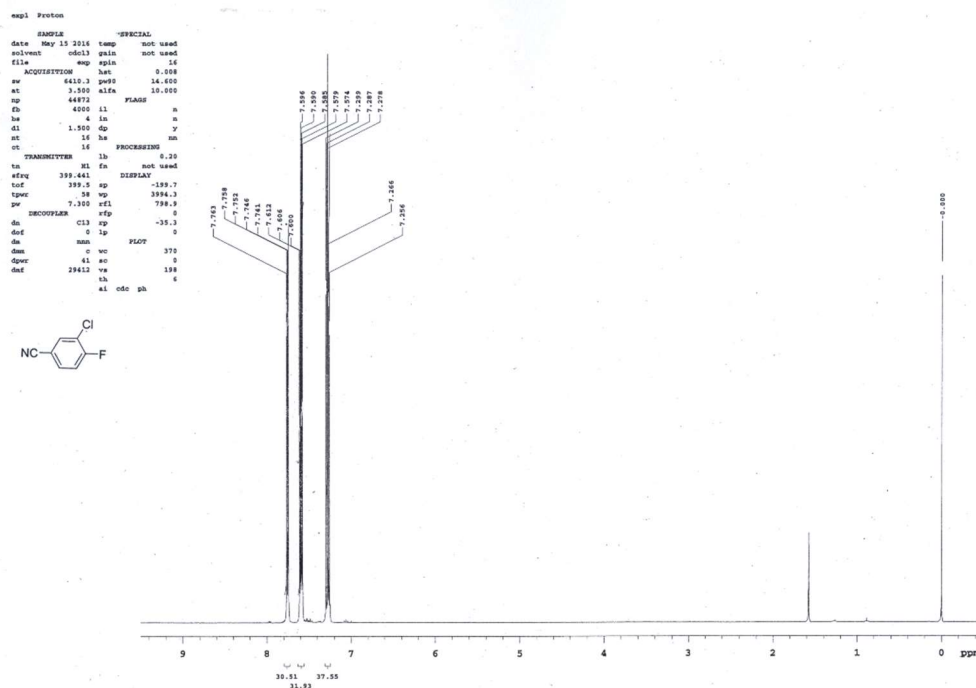


# (4-Fluorophenyl)phenylmethanone (5v) $^{19}\text{F}$ -NMR

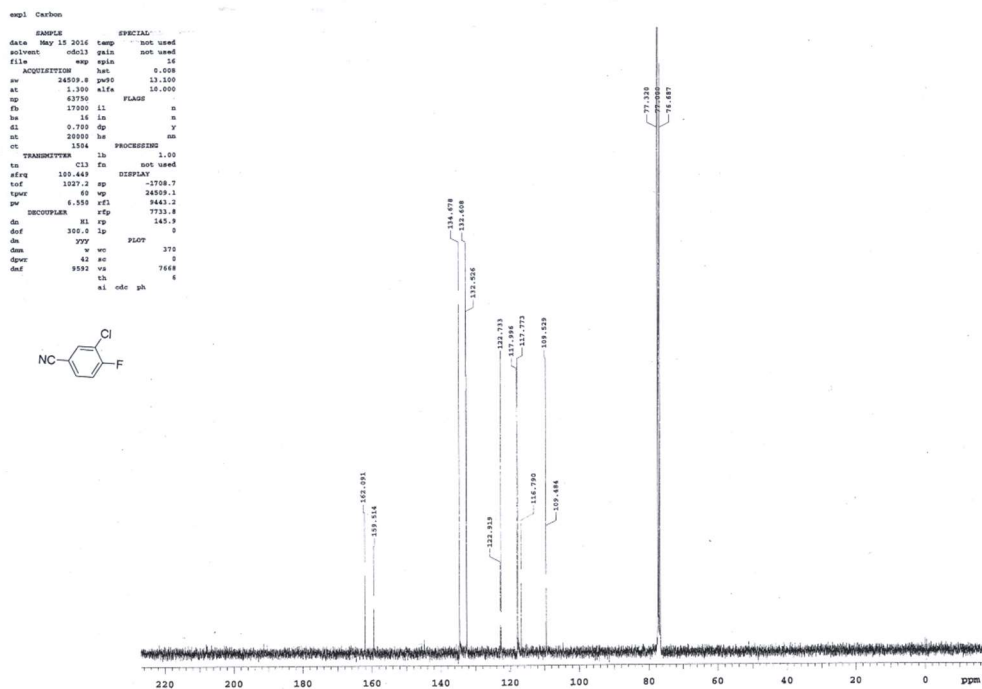
```
expt Fluorine
===== SPECIAL
date May 9 2016 temp not used
solvent cdc13 gain not used
file exp gain 16
=====
ACQUISITION bat 0.008
sw 119.047.6 pps0 18.000
at 0.600 aifa 10.000
=====
rg 162858
fn 51800 il FLAG n
ba 4 in n
dl 4.450 dd Y
at 16 hs nm
=====
PROGRAM
=====
TRANSMITTER lb 1.20
tn #19 fu not used
=====
REQD 370.020 DISPLAY
tof 13629.7 sp -89023.3
=====
cpwr 61 wp 119046.7
pw 6.000 rfl 59332.2
=====
DECOUPLE c13 sp -29492.1
ds 0 ip 139.3
=====
da nm PLGT 0
=====
dms 0 wo 370
=====
dpcw 41 so 0
=====
dnd 13621 ve 37
=====
th 16
=====
sl ph
```



### 3-Chloro-4-fluorobenzonitrile (5w) <sup>1</sup>H-NMR



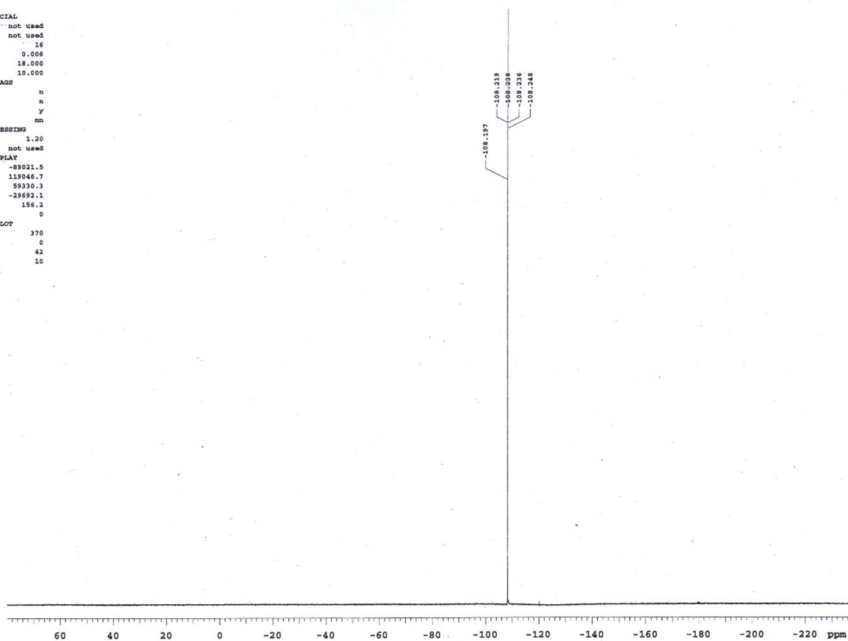
### 3-Chloro-4-fluorobenzonitrile (5w) <sup>13</sup>C-NMR



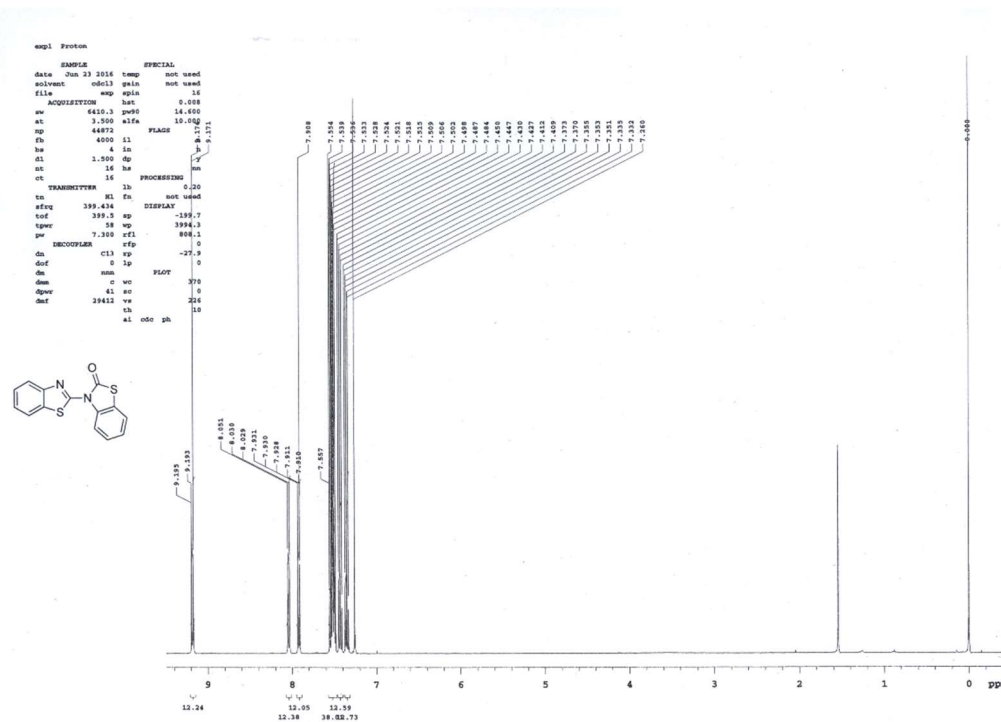
### 3-Chloro-4-fluorobenzonitrile (5w) <sup>19</sup>F-NMR

mp1 Fluorine

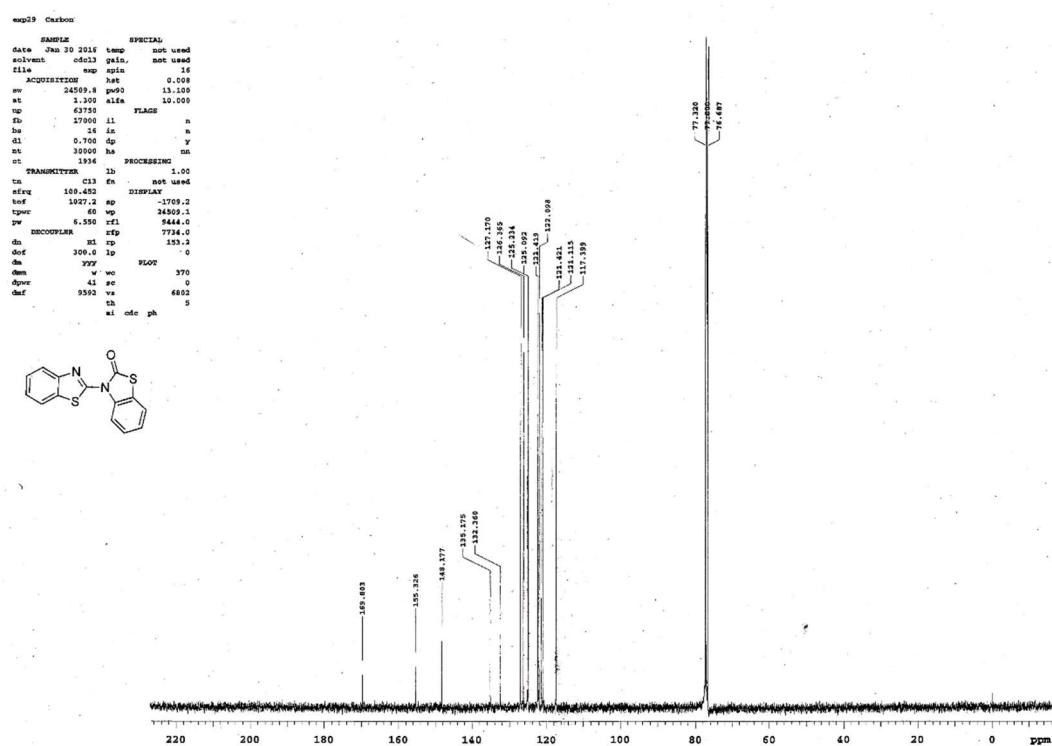
```
-----SPECIAL-----
date May 15 2016 temp not used
solvent c6d13 gain not used
file exp spin 16
ACQUISITION het 0.008
av 119047.6 nu90 18.000
at 0.600 aiaa 10.000
sp 142858
En 11000 il FLAG n
hs 4 ln n
hl 4.400 du Y
nt 16 ha no
ct 16 PROCESSING
ts 1b 1.20
tu F19 En not used
freq 376.820 DISPLAN
tof 119029.7 sp -89021.5
tpwr 61 wp 119046.7
sw 6.000 rfi 93309.1
DECOUPLER rfp -28492.1
ds c13 1p 150.2
dsf 0 1p 0
dm nno PLOP
dmn 0 wo 370
dprw 41 so 0
dsf 28412 ve 42
sh 10
al ph
```



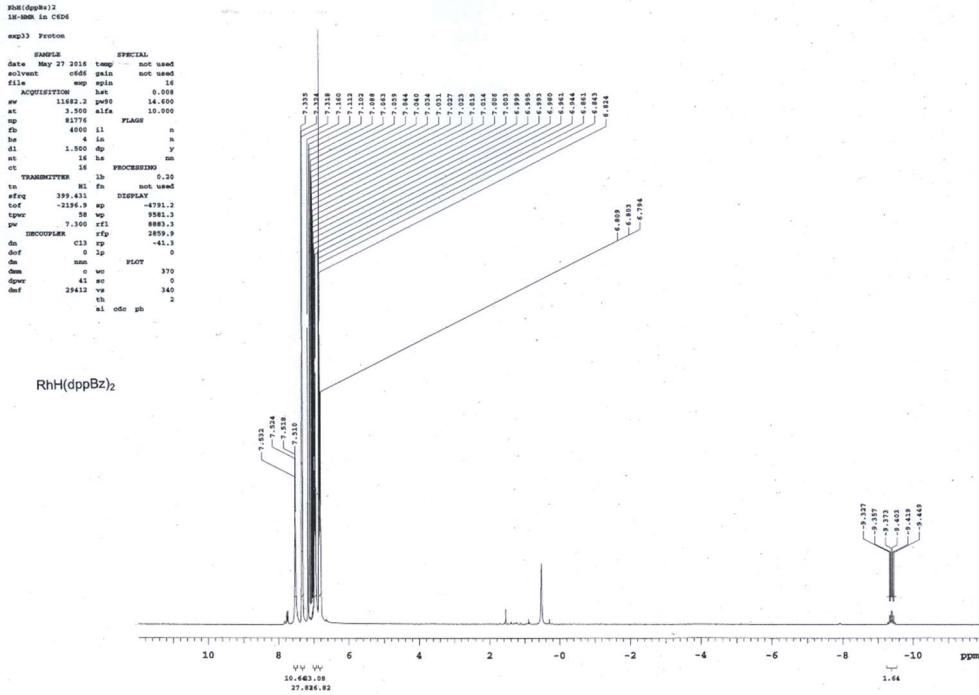
[2,3'(2'H)-bibenzothiazol]-2'-one (6) <sup>1</sup>H-NMR



[2,3'(2'H)-bibenzothiazol]-2'-one (6) <sup>13</sup>C-NMR



### RhH(dppBz)<sub>2</sub> <sup>1</sup>H-NMR



### RhH(dppBz)<sub>2</sub> <sup>31</sup>P-NMR

