

# Supporting Information

## Transition-Metal-Free *N*-Difluoromethylation of Hydrazones with TMSCF<sub>2</sub>Br as Difluoromethylation Reagent

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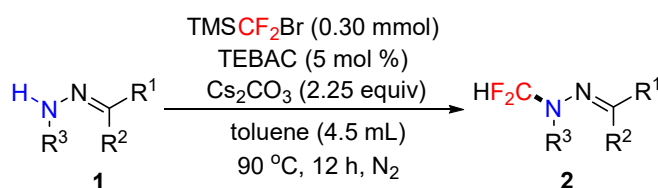
## A. General Methods

All the commercial reagents were used without further purification.  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR spectra were recorded on a Bruker DRX-400 spectrometer using  $\text{CDCl}_3$  as solvent. The chemical shifts of  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra are referenced to signals at 7.26 and 77.0 ppm, respectively. Mass spectra were recorded on a Thermo Scientific ISQ gas chromatograph-mass spectrometer. The data of HRMS was carried out on a high-resolution mass spectrometer (LCMS-IT-TOF). IR spectra were obtained either as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Bruker TENSOR 27 spectrometer. Melting points were determined with a Büchi Melting Point B-545 instrument. TLC was performed using commercially available 100-400 mesh silica gel plates ( $\text{GF}_{254}$ ). X-ray structural analyses were conducted on an x-ray analysis instrument.

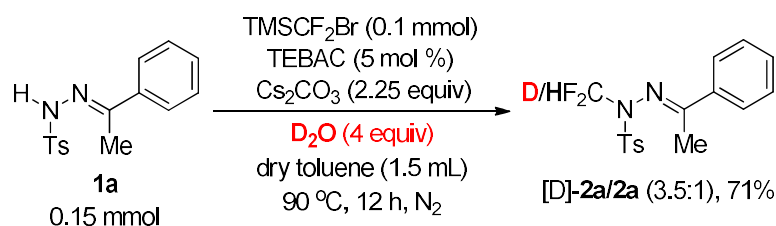
## B. General Procedures

**General procedure for preparation of *N*-tosylhydrazones:** a mixture of ketone or aldehyde compounds (5.0 mmol) and *p*-toluenesulfonylhydrazide (5.0 mmol) in 7.5 mL MeOH was stirred at 70 °C for 0.5-3 h to afford the corresponding *N*-tosylhydrazone **1**. After that, the precipitate was washed and filtered with petroleum ether twice and dried under vacuum to provide the pure compounds.

**General procedure for preparation of desired products **2a-2o**'**: a 25 mL Schlenk tube was charged with *N*-Tosylhydrazones **1** (0.45 mmol),  $\text{TMSCF}_2\text{Br}$  (0.30 mmol), TEBAC (5 mol %),  $\text{Cs}_2\text{CO}_3$  (2.25 equiv) and 4.5 mL toluene. The flask was evacuated and filled with nitrogen for three cycles. The reaction was allowed to stir at 90 °C for 12 h. Then water was added and the mixture was extracted with ethyl acetate twice. The combined organic phase was dried over  $\text{Na}_2\text{SO}_4$  and concentrated. The residue was purified by flash column chromatography on silica gel to afford the desired product. None of the  $^{19}\text{F}$  NMR spectra of the products are added the internal standard as a reference.



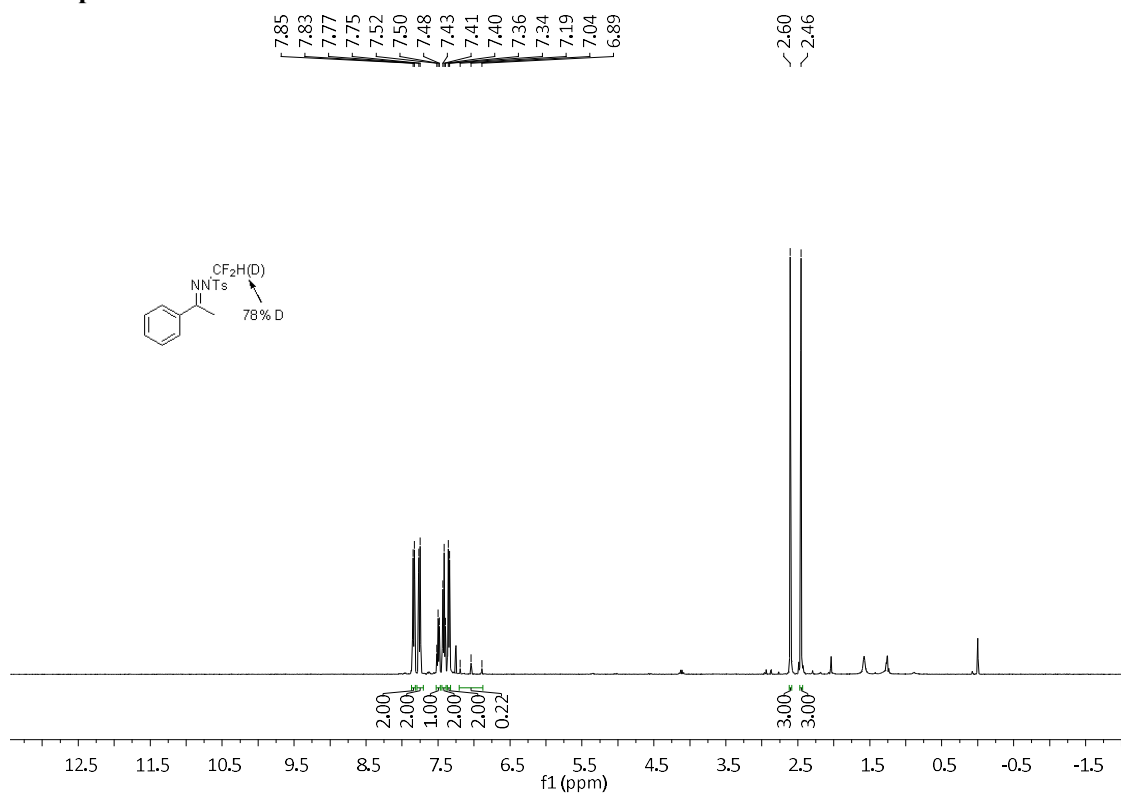
## C. Deuterium-Labeling Experiments



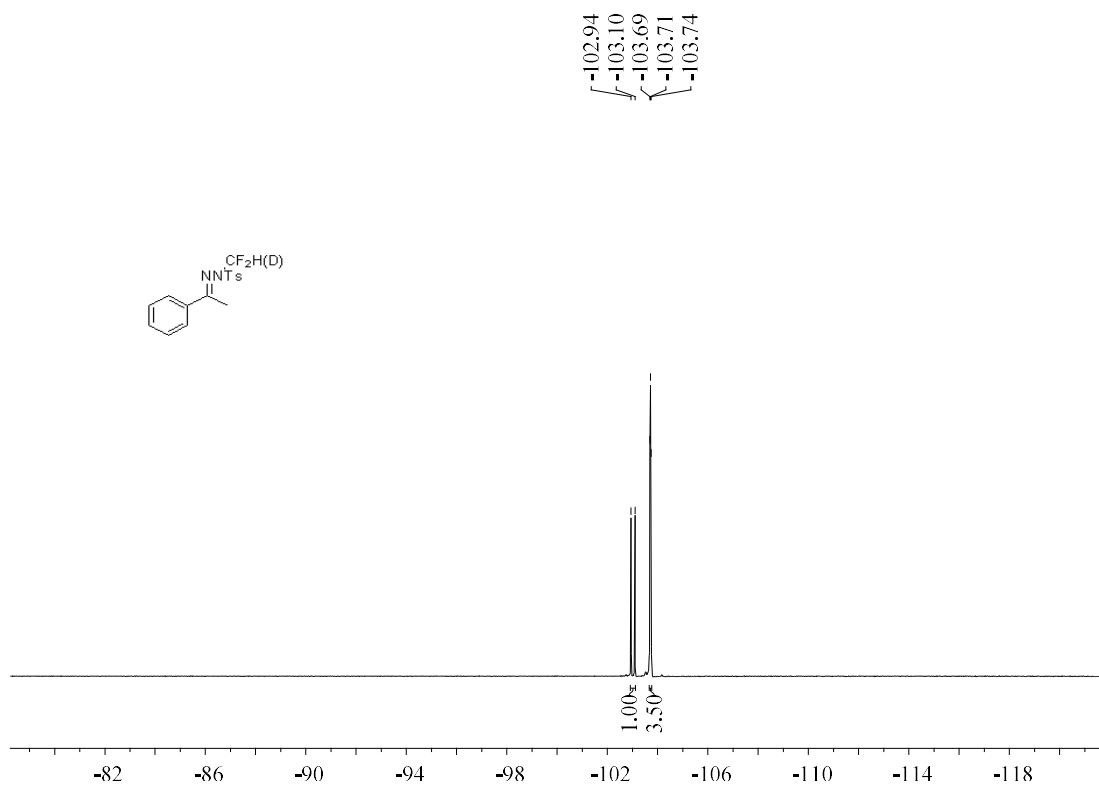
**Scheme S1.** Reaction conditions: **1a** (0.15 mmol),  $\text{TMSCF}_2\text{Br}$  (0.10 mmol),  $\text{Cs}_2\text{CO}_3$  (2.25 equiv), toluene (1.5 mL) in 90 °C under  $\text{N}_2$  for 12 h. The yield of product **[D]-2a** was determined by  $^1\text{H}$  NMR and  $^{19}\text{F}$  NMR.

[D]-2a was further confirmed by HRMS analysis: HRMS (ESI-TOF) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>15</sub>DF<sub>2</sub>N<sub>2</sub>NaO<sub>2</sub>S 362.0856; found 362.0861.

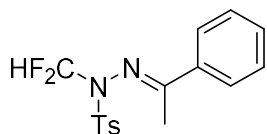
**<sup>1</sup>H NMR spectrum:**



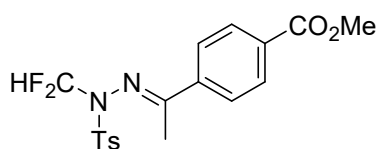
**<sup>19</sup>F NMR spectrum:**



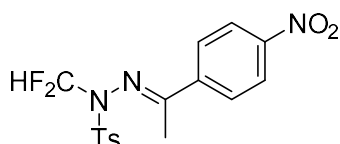
## D. Analytical Data



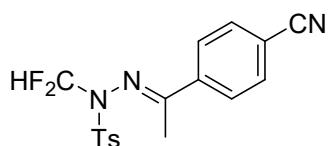
**(E)-N-(Difluoromethyl)-4-methyl-N'-(1-phenylethylidene)benzenesulfonohydrazide (2a):** White solid (91 mg, 90% yield), m.p. = 112.7-113.4 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ 7.84 (d, *J* = 7.7 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.50 (t, *J* = 7.3 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.04 (t, *J* = 59.7 Hz, 1H), 2.61 (s, 3H), 2.46 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm) δ 183.2, 145.2, 136.5, 133.5, 131.7, 129.6, 129.0, 128.5, 127.7, 112.0 (t, *J* = 250.5 Hz), 21.7, 17.9; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, ppm) δ -103.05 (d, *J* = 60.2 Hz, 2F). *v*<sub>max</sub>(KBr)/cm<sup>-1</sup> 3368, 2918, 2853, 1763, 1644, 1377, 1242, 1057, 568, 494. HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub>F<sub>2</sub>S 339.0973; found 339.0969.



**Methyl (E)-4-(1-(2-(Difluoromethyl)-2-tosylhydrazono)ethyl)benzoate (2b):** White solid (66 mg, 56% yield), m.p. = 177.8-179.0 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ 8.08 (d, *J* = 8.6 Hz, 2H), 7.89 (d, *J* = 8.6 Hz, 2H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.05 (t, *J* = 59.6 Hz, 1H), 3.94 (s, 3H), 2.63 (s, 3H), 2.46 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm) δ 182.5, 166.3, 145.4, 140.3, 133.2, 132.8, 129.7, 129.6, 128.9, 127.6, 112.0 (t, *J* = 255.9 Hz), 52.3, 21.7, 18.0; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, ppm) δ -102.96 (d, *J* = 56.4 Hz, 2F). *v*<sub>max</sub>(KBr)/cm<sup>-1</sup> 2947, 2853, 1724, 1606, 1374, 1284, 1176, 1111, 1038, 666. HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>19</sub>N<sub>2</sub>O<sub>4</sub>F<sub>2</sub>S 397.1028; found 397.1026.

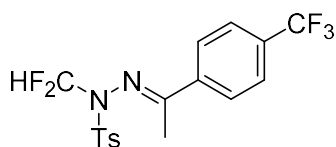


**(E)-N-(Difluoromethyl)-4-methyl-N'-(1-(4-nitrophenyl)ethylidene)benzenesulfonohydrazide (2c):** White solid (58 mg, 50% yield), m.p. = 136.8-138.6 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ 8.26 (d, *J* = 9.0 Hz, 2H), 8.00 (d, *J* = 9.0 Hz, 2H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.05 (t, *J* = 59.5 Hz, 1H), 2.65 (s, 3H), 2.47 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm) δ 181.5, 149.7, 145.6, 141.9, 133.1, 129.7, 128.8, 128.7, 123.6, 111.9 (t, *J* = 253.1 Hz), 21.7, 18.2; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, ppm) δ -102.86 (d, *J* = 56.4 Hz, 2F). *v*<sub>max</sub>(KBr)/cm<sup>-1</sup> 2928, 2859, 1692, 1594, 1526, 1359, 1301, 1110, 836, 669. HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>16</sub>N<sub>3</sub>O<sub>4</sub>F<sub>2</sub>S 384.0824; found 384.0820.

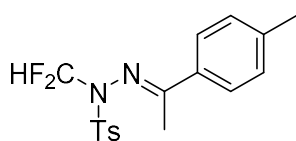


**(E)-N'-(1-(4-Cyanophenyl)ethylidene)-N-(difluoromethyl)-4-methylbenzenesulfonohydrazide (2d):** White solid (73 mg, 67% yield), m.p. = 184.6-186.1 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ 7.93 (d, *J* = 8.4

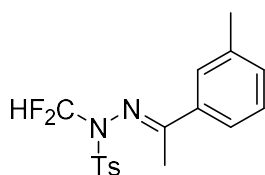
Hz, 2H), 7.71 (dd,  $J = 8.3, 2.4$  Hz, 4H), 7.36 (d,  $J = 8.2$  Hz, 2H), 7.04 (t,  $J = 60.0$  Hz, 1H), 2.62 (d,  $J = 7.7$  Hz, 3H), 2.46 (d,  $J = 5.9$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  181.8, 145.6, 140.3, 133.2, 132.3, 129.7, 128.9, 128.6, 118.1, 115.2, 112.0 (t,  $J = 253.0$  Hz), 21.7, 18.0;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  -102.87 (d,  $J = 60.16$  Hz, 2F).  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  2927, 2859, 2232, 1692, 1605, 1368, 1171, 1111, 836, 669. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{17}\text{H}_{16}\text{N}_3\text{O}_2\text{F}_2\text{S}$  364.0926; found 364.0924.



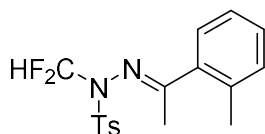
**(E)-N-(Difluoromethyl)-4-methyl-N'-(1-(4-(trifluoromethyl)phenyl)ethylidene)benzenesulfonohydrazide (2e):** Light yellow oil (78 mg, 64% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.95 (d,  $J = 8.3$  Hz, 2H), 7.75 (d,  $J = 8.2$  Hz, 2H), 7.68 (d,  $J = 8.3$  Hz, 2H), 7.36 (d,  $J = 8.2$  Hz, 2H), 7.06 (t,  $J = 59.6$  Hz, 1H), 2.63 (s, 3H), 2.46 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  182.1, 145.4, 139.6, 133.2 (p,  $J = 32.7$  Hz), 129.6, 128.9, 128.0, 125.5 (q,  $J = 3.8$  Hz), 123.7 (q,  $J = 272.6$  Hz), 111.9 (t,  $J = 252.6$  Hz), 21.6, 18.0;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  -63.04 (3F), -102.97 (d,  $J = 60.16$  Hz, 2F).  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  3065, 2929, 1739, 1602, 1317, 1171, 1120, 841, 671, 557. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2\text{F}_5\text{S}$  407.0847; found 407.0842.



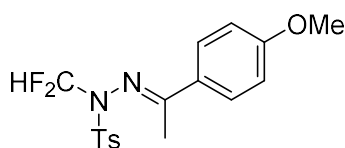
**(E)-N-(Difluoromethyl)-4-methyl-N'-(1-(p-tolyl)ethylidene)benzenesulfonohydrazide (2f):** White solid (88 mg, 83% yield), m.p. = 147.3-149.1  $^\circ\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.79 (d,  $J = 7.8$  Hz, 4H), 7.38 (d,  $J = 7.9$  Hz, 2H), 7.13 (m, 3H), 2.62 (s, 3H), 2.48 (s, 3H), 2.43 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  182.9, 145.1, 142.2, 133.6, 133.4, 129.5, 129.4, 128.9, 127.6, 112.0 (t,  $J = 252.3$  Hz), 21.6, 21.4, 17.6;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  -103.07 (d,  $J = 60.16$  Hz, 2F).  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  3058, 2923, 1676, 1595, 1353, 1170, 1098, 1033, 814, 665. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{17}\text{H}_{19}\text{N}_2\text{O}_2\text{F}_2\text{S}$  353.1130; found 353.1133.



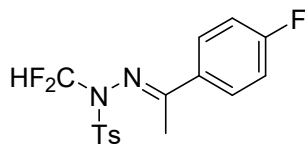
**(E)-N-(Difluoromethyl)-4-methyl-N'-(1-(m-tolyl)ethylidene)benzenesulfonohydrazide (2g):** White solid (86 mg, 81% yield), m.p. = 95.0-96.3  $^\circ\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.79 (d,  $J = 8.3$  Hz, 2H), 7.68-7.62 (m, 2H), 7.36 (d,  $J = 8.1$  Hz, 2H), 7.32 (d,  $J = 5.1$  Hz, 2H), 7.07 (t,  $J = 59.7$  Hz, 1H), 2.61 (s, 3H), 2.46 (s, 3H), 2.40 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  183.5, 145.1, 138.1, 136.4, 133.4, 132.4, 129.5, 128.9, 128.3, 128.2, 124.8, 112.0 (t,  $J = 252.0$  Hz), 21.6, 21.4, 18.0;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  -102.95 (d,  $J = 67.7$  Hz, 2F).  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  2925, 1591, 1371, 1306, 1173, 1108, 1040, 807, 671, 567. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{17}\text{H}_{19}\text{N}_2\text{O}_2\text{F}_2\text{S}$  353.1130; found 353.1129.



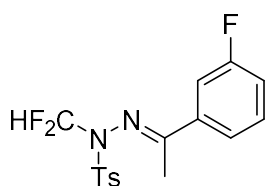
**(E)-N-(Difluoromethyl)-4-methyl-N'-(1-(*o*-tolyl)ethylidene)benzenesulfonohydrazide (2h):** White solid (85 mg, 80% yield), m.p. = 70.1-71.6 °C, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ 7.75 (d, *J* = 8.1 Hz, 2H), 7.31-7.20 (m, 6H), 7.03 (t, *J* = 59.6 Hz, 1H), 2.53 (s, 3H), 2.39 (s, 3H), 2.36 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm) δ 188.7, 145.1, 138.2, 134.8, 133.4, 130.7, 129.6, 129.3, 128.7, 127.0, 125.7, 111.8 (t, *J* = 251.8 Hz), 22.1, 21.5, 19.7; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, ppm) δ -102.53 (d, *J* = 60.2 Hz, 2F). *v*<sub>max</sub>(KBr)/cm<sup>-1</sup> 2925, 1602, 1368, 1302, 1171, 1107, 1040, 814, 668, 565. HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>19</sub>N<sub>2</sub>O<sub>2</sub>F<sub>2</sub>S 353.1130; found 353.1133.



**(E)-N-(Difluoromethyl)-N'-(1-(4-methoxyphenyl)ethylidene)-4-methylbenzenesulfonohydrazide (2i):** White solid (62 mg, 56% yield), m.p. = 142.2-143.9 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ 7.83 (d, *J* = 8.8 Hz, 2H), 7.75 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.19-6.89 (m, 3H), 3.86 (s, 3H), 2.57 (s, 3H), 2.47 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm) δ 182.1, 162.5, 145.2, 133.4, 129.5, 128.9, 113.8, 112.0 (t, *J* = 250.3 Hz), 55.4, 21.7, 17.4; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, ppm) δ -103.18 (d, *J* = 60.2 Hz, 2F). *v*<sub>max</sub>(KBr)/cm<sup>-1</sup> 3690, 1759, 1592, 1368, 1248, 1170, 1102, 820, 663, 559. HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>19</sub>N<sub>2</sub>O<sub>3</sub>F<sub>2</sub>S 369.1079; found 369.1078.

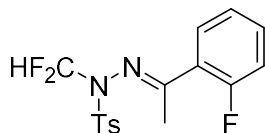


**(E)-N-(Difluoromethyl)-N'-(1-(4-fluorophenyl)ethylidene)-4-methylbenzenesulfonohydrazide (2j):** White solid (85 mg, 80% yield), m.p. = 128.2-129.2 °C, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ 7.90-7.83 (m, 2H), 7.75 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.21-6.91 (m, 3H), 2.59 (s, 3H), 2.46 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm) δ 181.8, 165.0 (d, *J* = 252.9 Hz), 145.2, 133.3, 132.5 (d, *J* = 3.3 Hz), 129.9 (d, *J* = 8.8 Hz), 129.5, 128.8, 115.5 (d, *J* = 21.8 Hz), 112.0 (t, *J* = 252.8 Hz), 21.6, 17.6; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, ppm) δ -103.02 (d, *J* = 56.4 Hz, 2F), -107.77 (1F). *v*<sub>max</sub>(KBr)/cm<sup>-1</sup> 3681, 1592, 1510, 1368, 1299, 1168, 1034, 833, 664, 561. HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>F<sub>3</sub>S 357.0879; found 357.0878.

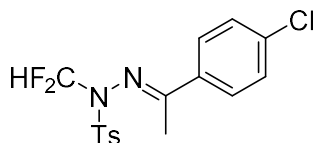


**(E)-N-(Difluoromethyl)-N'-(1-(3-fluorophenyl)ethylidene)-4-methylbenzenesulfonohydrazide (2k):** White solid (75 mg, 70% yield), m.p. = 75.1-75.9 °C, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ 7.77 (d, *J* = 8.1 Hz,

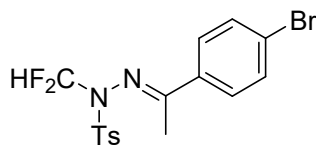
2H), 7.64 (d,  $J = 7.8$  Hz, 1H), 7.59 (d,  $J = 10.0$  Hz, 1H), 7.47-7.37 (m, 3H), 7.18 (ddd,  $J = 124.0, 66.2, 35.4$  Hz, 2H), 2.63 (s, 3H), 2.50 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  182.1, 162.6 (d,  $J = 246.6$  Hz), 145.4, 138.5 (d,  $J = 7.4$  Hz), 133.2, 130.1 (d,  $J = 8.0$  Hz), 129.6, 128.9, 123.5 (d,  $J = 3.0$  Hz), 111.9 (t,  $J = 252.4$  Hz), 118.7 (d,  $J = 21.4$  Hz), 114.5 (d,  $J = 23.2$  Hz), 21.7, 17.9;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  -103.46 (d,  $J = 56.4$  Hz, 2F), -112.74 (1F).  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  3688, 3311, 3082, 1721, 1576, 1366, 1171, 1104, 668, 563. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_2\text{F}_3\text{S}$  357.0879; found 357.0882.



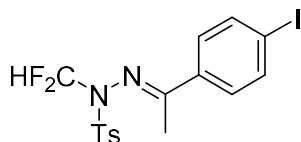
**(E)-N-(Difluoromethyl)-N'-(1-(2-fluorophenyl)ethylidene)-4-methylbenzenesulfonohydrazide (2l):** Light yellow oil (53 mg, 50% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.80 (d,  $J = 8.3$  Hz, 2H), 7.60 (td,  $J = 7.6, 1.7$  Hz, 1H), 7.47-7.42 (m, 1H), 7.35 (d,  $J = 8.1$  Hz, 2H), 7.20-6.90 (m, 3H), 2.63 (d,  $J = 2.9$  Hz, 3H), 2.43 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  183.3, 160.7 (d,  $J = 252.9$  Hz), 145.4, 133.3, 132.7 (d,  $J = 8.7$  Hz), 129.9 (d,  $J = 2.7$  Hz), 129.7, 129.0, 125.7 (d,  $J = 11.9$  Hz), 124.3 (d,  $J = 3.5$  Hz), 116.5 (d,  $J = 22.2$  Hz), 112.0 (t,  $J = 252.7$  Hz), 21.7, 21.0;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  -102.78 (d,  $J = 60.2$  Hz, 2F), -111.94 (1F).  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  1636, 1491, 1449, 1372, 1173, 1110, 1041, 761, 669, 562. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_2\text{F}_3\text{S}$  357.0879; found 357.0878.



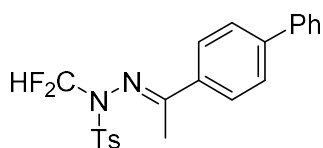
**(E)-N'-(1-(4-Chlorophenyl)ethylidene)-N-(difluoromethyl)-4-methylbenzenesulfonohydrazide (2m):** White solid (104 mg, 93% yield); m.p. = 65.1-65.9  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.79 (d,  $J = 8.4$  Hz, 2H), 7.74 (d,  $J = 8.0$  Hz, 2H), 7.37 (dd,  $J = 14.2, 8.2$  Hz, 4H), 7.05 (t,  $J = 59.6$  Hz, 1H), 2.59 (s, 3H), 2.46 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  182.0, 145.3, 138.0, 134.7, 133.2, 130.0, 129.0, 128.8, 129.0, 111.9 (t,  $J = 252.3$  Hz), 21.7, 17.7;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  -103.02 (d,  $J = 60.2$  Hz, 2F).  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  3049, 2927, 1688, 1596, 1371, 1298, 1171, 1103, 828, 558. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_2\text{F}_2\text{ClS}$  373.0584; found 373.0588.



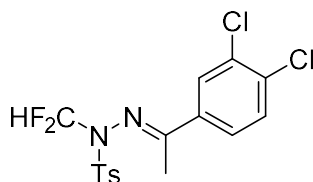
**(E)-N'-(1-(4-Bromophenyl)ethylidene)-N-(difluoromethyl)-4-methylbenzenesulfonohydrazide (2n):** Light yellow oil (106 mg, 85% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.72 (t,  $J = 7.5$  Hz, 4H), 7.56 (d,  $J = 8.5$  Hz, 2H), 7.35 (d,  $J = 8.0$  Hz, 2H), 7.04 (t,  $J = 59.6$  Hz, 1H), 2.58 (s, 3H), 2.46 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  182.1, 145.3, 135.1, 133.2, 131.7, 129.5, 129.1, 128.8, 126.6, 111.9 (t,  $J = 252.8$  Hz), 21.6, 17.6;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  -103.04 (d,  $J = 60.2$  Hz, 2F).  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  2927, 1596, 1375, 1301, 1173, 1109, 1040, 826, 667, 562. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_2\text{F}_2\text{BrS}$  417.0078; found 417.0081.



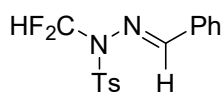
**(E)-N-(Difluoromethyl)-N'-(1-(4-iodophenyl)ethylidene)-4-methylbenzenesulfonohydrazide (2o):** White solid (83 mg, 60% yield), m.p. = 99.9-100.1 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ 7.75 (dd, *J* = 13.7, 8.4 Hz, 4H), 7.58-7.53 (m, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.04 (t, *J* = 59.6 Hz, 1H), 2.57 (s, 3H), 2.46 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm) δ 182.3, 145.6, 137.7, 135.7, 133.2, 129.5, 129.1, 128.8, 111.9 (t, *J* = 252.1 Hz), 98.9, 21.7, 17.5; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, ppm) δ -102.97 (d, *J* = 60.2 Hz, 2F). *v*<sub>max</sub>(KBr)/cm<sup>-1</sup> 2927, 1594, 1374, 1301, 1172, 1109, 1041, 824, 672, 563. HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>F<sub>2</sub>IS 464.9940; found 464.9938.



**(E)-N'-(1-([1,1'-Biphenyl]-4-yl)ethylidene)-N-(difluoromethyl)-4-methylbenzenesulfonohydrazide (2p):** Light yellow oil (50 mg, 40% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ 7.94 (d, *J* = 8.3 Hz, 2H), 7.79 (d, *J* = 8.1 Hz, 2H), 7.69-7.61 (m, 4H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.39 (m, 3H), 7.07 (t, *J* = 59.7 Hz, 1H), 2.65 (s, 3H), 2.48 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm) δ 182.7, 145.2, 144.5, 139.9, 135.1, 133.4, 129.5, 128.9, 128.9, 128.2, 128.0, 127.1, 112.0 (t, *J* = 252.1 Hz), 21.7, 17.7; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, ppm) δ -103.03 (d, *J* = 60.2 Hz, 2F). *v*<sub>max</sub>(KBr)/cm<sup>-1</sup> 2993, 1764, 1596, 1373, 1243, 1173, 1107, 913, 744, 565. HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>22</sub>H<sub>21</sub>N<sub>2</sub>O<sub>2</sub>F<sub>2</sub>S 415.1286; found 415.1285.



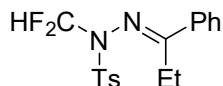
**(E)-N'-(1-(3,4-Dichlorophenyl)ethylidene)-N-(difluoromethyl)-4-methylbenzenesulfonohydrazide (2q):** White solid (108 mg, 89% yield), m.p. = 99.2-100.1 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ 7.93 (d, *J* = 1.9 Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.67 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.04 (t, *J* = 59.5 Hz, 1H), 2.58 (s, 3H), 2.47 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm) δ 181.2, 145.6, 136.2, 136.2, 133.1, 133.1, 130.6, 129.7, 129.6, 128.9, 126.8, 112.0 (t, *J* = 252.8 Hz), 21.8, 17.8; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, ppm) δ -102.98 (d, *J* = 60.2 Hz, 2F). *v*<sub>max</sub>(KBr)/cm<sup>-1</sup> 3686, 1721, 1596, 1376, 1174, 1108, 1037, 815, 666, 560. HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>15</sub>N<sub>2</sub>O<sub>2</sub>F<sub>2</sub>Cl<sub>2</sub>S 407.0194; found 407.0197.



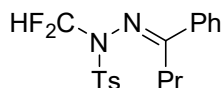
**(E)-N'-Benzylidene-N-(difluoromethyl)-4-methylbenzenesulfonohydrazide (2r):** White solid (85 mg, 87% yield), m.p. = 48.3-49.5 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ 8.56 (s, 1H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.70-7.67 (m, 2H), 7.46 (m, 1H), 7.40 (t, *J* = 7.3 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.20 (t, *J* = 58.7 Hz, 1H),



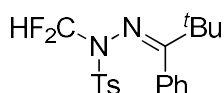
2.41 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  161.7, 145.4, 133.7, 132.9, 131.9, 129.7, 128.7, 128.5, 128.4, 111.7 (t,  $J = 253.1$  Hz), 21.6;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  -101.08 (d,  $J = 56.4$  Hz, 2F).  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  2453, 2919, 2852, 1640, 1370, 1170, 1107, 1033, 665, 559. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{15}\text{H}_{15}\text{N}_2\text{O}_2\text{F}_2\text{S}$  325.0817; found 325.0815.



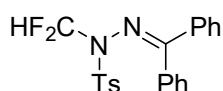
**(E)-N-(Difluoromethyl)-4-methyl-N'-(1-phenylpropylidene)benzenesulfonohydrazide (2s):** Light yellow oil (85 mg, 80% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.79 (d,  $J = 7.9$  Hz, 4H), 7.52-7.47 (m, 1H), 7.45-7.41 (m, 2H), 7.35 (d,  $J = 8.0$  Hz, 2H), 7.07 (t,  $J = 59.8$  Hz, 1H), 3.14 (q,  $J = 7.6$  Hz, 2H), 2.45 (s, 3H), 1.18 (t,  $J = 7.7$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  188.1, 145.1, 135.2, 133.3, 131.6, 129.5, 129.0, 128.5, 127.9, 111.9 (t,  $J = 252.2$  Hz), 23.7, 21.6, 11.6;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  -102.98 (d,  $J = 60.2$  Hz, 2F).  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  1597, 1452, 1311, 1172, 1108, 1037, 811, 669, 559. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{17}\text{H}_{19}\text{N}_2\text{O}_2\text{F}_2\text{S}$  353.1130; found 353.1132.



**(E)-N-(Difluoromethyl)-4-methyl-N'-(1-phenylbutylidene)benzenesulfonohydrazide (2t):** White solid (89 mg, 81% yield), m.p. = 123.8-124.5  $^\circ\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.77 (dd,  $J = 12.4, 5.3$  Hz, 4H), 7.49 (t,  $J = 7.0$  Hz, 1H), 7.44-7.41 (m, 2H), 7.37-7.33 (m, 2H), 7.05 (t,  $J = 59.8$  Hz, 1H), 3.14-3.05 (m, 2H), 2.45 (d,  $J = 3.1$  Hz, 3H), 1.68-1.46 (m, 2H), 1.17 (t,  $J = 7.7$  Hz, 1H), 1.01 (t,  $J = 7.3$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  187.2, 145.2, 135.8, 133.4, 131.3, 129.6, 129.1, 128.6, 127.9, 112.0 (t,  $J = 249.4$  Hz), 32.7, 21.7, 20.8, 14.4;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  -102.93 (d,  $J = 60.2$  Hz, 2F).  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  2965, 2875, 1600, 1452, 1373, 1173, 1111, 1041, 680, 567. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{18}\text{H}_{21}\text{N}_2\text{O}_2\text{F}_2\text{S}$  367.1286; found 367.1288.

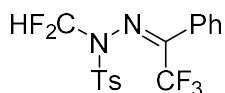


**(Z)-N-(Difluoromethyl)-N'-(2,2-dimethyl-1-phenylpropylidene)-4-methylbenzenesulfonohydrazide (2u):** White solid (57 mg, 50% yield), m.p. = 118.9-119.3  $^\circ\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.77 (d,  $J = 8.2$  Hz, 2H), 7.39-7.32 (m, 5H), 7.21-7.14 (m, 2H), 6.59 (t,  $J = 60.0$  Hz, 1H), 2.46 (s, 3H), 1.24 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  195.6, 144.9, 134.9, 133.8, 129.3, 129.2, 128.0, 127.5, 127.1, 111.51 (t,  $J = 251.5$  Hz), 40.7, 28.3, 21.7;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  -102.77 (d,  $J = 60.2$  Hz, 2F).  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  3687, 2972, 1595, 1370, 1175, 1113, 1037, 808, 668, 562. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{19}\text{H}_{23}\text{N}_2\text{O}_2\text{F}_2\text{S}$  381.1443; found 381.1442.



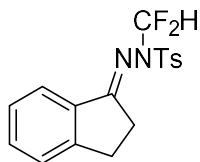
**N-(Difluoromethyl)-N'-(diphenylmethylene)-4-methylbenzenesulfonohydrazide (2v):** White solid (96 mg, 80% yield), m.p. = 148.2-150.1  $^\circ\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.81 (d,  $J = 8.1$  Hz, 2H), 7.63 (d,  $J =$

7.9 Hz, 2H), 7.53-7.44 (m, 6H), 7.38 (t,  $J = 7.4$  Hz, 4H), 6.80 (t,  $J = 59.8$  Hz, 1H), 2.50 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  183.1, 145.1, 136.8, 134.6, 133.6, 132.0, 129.9, 129.5, 129.3, 129.2, 129.1, 128.3, 127.7, 112.0 (t,  $J = 253.7$  Hz), 21.7;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  -102.64 (d,  $J = 60.2$  Hz, 2F).  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  3061, 2928, 1737, 1593, 1374, 1173, 1110, 1041, 685, 601. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{21}\text{H}_{19}\text{N}_2\text{O}_2\text{F}_2\text{S}$  401.1130; found 401.1132.



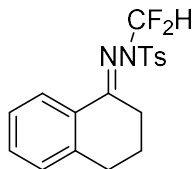
**(Z)-N-(Difluoromethyl)-4-methyl-N'-(2,2,2-trifluoro-1-phenylethylidene)benzenesulfonylhydrazide (2w):**

White solid (93 mg, 79% yield), m.p. = 89.9-91.8 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.78 (d,  $J = 8.0$  Hz, 2H), 7.51 (dt,  $J = 20.7, 7.2$  Hz, 5H), 7.38 (d,  $J = 8.1$  Hz, 2H), 6.74 (t,  $J = 59.0$  Hz, 1H), 2.47 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  170.76 (q,  $J = 32.9$  Hz), 146.0, 132.5, 131.2, 129.7, 129.2, 128.4, 128.3, 119.6 (q,  $J = 279.2$  Hz), 111.4 (t,  $J = 256.9$  Hz), 21.7;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  -68.59 (3F), -101.82 (d,  $J = 60.2$  Hz, 2F).  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  3066, 2928, 1598, 1450, 1381, 1194, 1118, 708, 670, 568. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_2\text{F}_5\text{S}$  393.0691; found 393.0693.



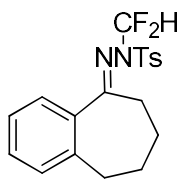
**N-(Difluoromethyl)-N'-(2,3-dihydro-1H-inden-1-ylidene)-4-methylbenzenesulfonylhydrazide (2x):**

White solid (53 mg, 50% yield), m.p. = 113.3-114.1 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.87 (d,  $J = 7.7$  Hz, 1H), 7.79 (d,  $J = 8.3$  Hz, 2H), 7.52 (t,  $J = 7.5$  Hz, 1H), 7.42 (d,  $J = 7.7$  Hz, 1H), 7.35 (m, 3H), 7.04 (t,  $J = 59.9$  Hz, 1H), 3.28-3.23 (m, 2H), 3.14-3.10 (m, 2H), 2.47 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  191.7, 152.4, 145.0, 136.2, 133.4, 133.3, 129.5, 128.9, 127.1, 125.9, 123.7, 112.1 (t,  $J = 251.7$  Hz), 30.8, 28.2, 21.6;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  -103.01 (d,  $J = 60.2$  Hz, 2F).  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  2929, 1602, 1454, 1367, 1172, 1101, 1039, 762, 664, 562. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{17}\text{H}_{17}\text{N}_2\text{O}_2\text{F}_2\text{S}$  351.0973; found 351.0975.

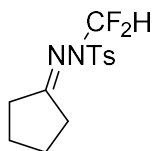


**N-(Difluoromethyl)-N'-(3,4-dihydronaphthalen-1(2H)-ylidene)-4-methylbenzenesulfonylhydrazide (2y):**

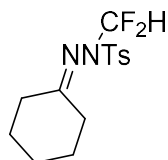
White solid (93 mg, 85% yield), m.p. = 126.1-126.9 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  8.10 (d,  $J = 8.3$  Hz, 1H), 7.74 (d,  $J = 8.2$  Hz, 2H), 7.41-7.32 (m, 3H), 7.21 (m, 2H), 7.02 (t,  $J = 59.8$  Hz, 1H), 3.10-3.03 (m, 2H), 2.89 (t,  $J = 6.1$  Hz, 2H), 2.45 (s, 3H), 1.99-1.91 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  182.3, 145.0, 142.3, 133.4, 132.0, 131.0, 129.4, 128.9, 126.4, 126.4, 112.0 (t,  $J = 251.5$  Hz), 29.7, 29.2, 22.3, 21.6;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  -103.26 (d,  $J = 56.4$  Hz, 2F).  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  2938, 1763, 1590, 1367, 1243, 1171, 1103, 1037, 666, 559. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{18}\text{H}_{19}\text{N}_2\text{O}_2\text{F}_2\text{S}$  365.1130; found 365.1132.



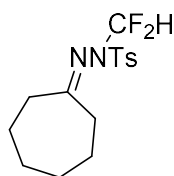
***N*-(Difluoromethyl)-4-methyl-*N'*-(6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-ylidene)benzenesulfonylhydrazide (2z)**: Light yellow oil (91 mg, 80% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.84 (d,  $J = 8.3$  Hz, 2H), 7.54 (dd,  $J = 7.5, 1.0$  Hz, 1H), 7.42-7.36 (m, 3H), 7.31-7.27 (m, 1H), 7.23-6.92 (m, 2H), 3.14-3.05 (m, 2H), 2.88-2.80 (m, 2H), 2.45 (s, 3H), 1.87-1.81 (m, 2H), 1.80-1.70 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  192.6, 145.2, 139.8, 137.1, 133.3, 130.7, 129.6, 128.9, 128.8, 128.0, 126.4, 111.92 (t,  $J = 252.3$  Hz), 32.1, 31.2, 25.6, 22.5, 21.6;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  -102.67 (d,  $J = 60.2$  Hz, 2F).  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  2938, 2864, 1595, 1452, 1370, 1172, 1108, 1039, 666, 562. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{19}\text{H}_{21}\text{N}_2\text{O}_2\text{F}_2\text{S}$  379.1286; found 379.1289.



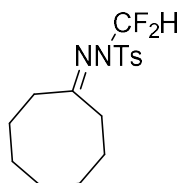
***N'*-Cyclopentylidene-*N*-(difluoromethyl)-4-methylbenzenesulfonylhydrazide (2a')**: Light yellow oil (22 mg, 24% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.73 (d,  $J = 8.0$  Hz, 2H), 7.33 (d,  $J = 8.1$  Hz, 2H), 6.92 (t,  $J = 59.7$  Hz, 1H), 2.75 (t,  $J = 7.1$  Hz, 2H), 2.59 (t,  $J = 7.0$  Hz, 2H), 2.43 (s, 3H), 1.87 (td,  $J = 12.4, 7.9$  Hz, 4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  201.2, 145.2, 133.2, 129.7, 128.8, 111.9 (t,  $J = 251.3$  Hz), 34.5, 32.7, 24.7, 24.4, 21.7;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  -103.00 (d,  $J = 56.4$  Hz, 2F).  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  3686, 2967, 1651, 1591, 1364, 1170, 1108, 1039, 668, 555. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{13}\text{H}_{17}\text{N}_2\text{O}_2\text{F}_2\text{S}$  303.0973; found 303.0974.



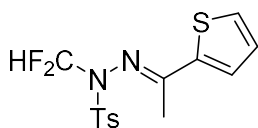
***N'*-Cyclohexylidene-*N*-(difluoromethyl)-4-methylbenzenesulfonylhydrazide (2b')**: Light yellow oil (48 mg, 51% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.72 (d,  $J = 8.1$  Hz, 2H), 7.33 (d,  $J = 8.1$  Hz, 2H), 6.95 (t,  $J = 59.9$  Hz, 1H), 2.67 (t,  $J = 6.3$  Hz, 2H), 2.48-2.44 (m, 2H), 2.43 (s, 3H), 1.83-1.73 (m, 4H), 1.67 (d,  $J = 4.8$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  192.4, 145.0, 133.3, 129.6, 128.7, 111.6 (t,  $J = 251.1$  Hz), 36.1, 31.2, 27.6, 26.7, 25.5, 21.6;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  -103.08 (d,  $J = 60.2$  Hz, 2F).  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  2939, 2863, 1619, 1367, 1169, 1108, 1038, 815, 670, 568. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{14}\text{H}_{19}\text{N}_2\text{O}_2\text{F}_2\text{S}$  317.1130; found 317.1132.



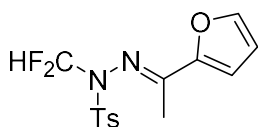
***N'*-Cycloheptylidene-*N*-(difluoromethyl)-4-methylbenzenesulfonylhydrazide (2c')**: Light yellow oil (46 mg, 46% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ 7.72 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 6.93 (t, *J* = 59.9 Hz, 1H), 2.92-2.84 (m, 2H), 2.67-2.59 (m, 2H), 2.43 (s, 3H), 1.77-1.70 (m, 4H), 1.67-1.56 (m, 4H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm) δ 196.6, 145.7, 133.2, 129.6, 128.8, 111.8 (t, *J* = 251.6 Hz), 37.1, 33.3, 30.2, 29.2, 26.9, 24.3, 21.69; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, ppm) δ -103.24 (d, *J* = 60.2 Hz, 2F).  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  2929, 2860, 1697, 1606, 1364, 1171, 1109, 815, 668, 559. HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>21</sub>N<sub>2</sub>O<sub>2</sub>F<sub>2</sub>S 331.1286; found 331.1284.



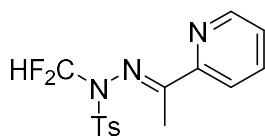
***N'*-Cyclooctylidene-*N*-(difluoromethyl)-4-methylbenzenesulfonylhydrazide (2d')**: Light yellow oil (32 mg, 31% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ 7.71 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 6.96 (t, *J* = 60.0 Hz, 1H), 2.82-2.71 (m, 2H), 2.60-2.52 (m, 2H), 2.43 (s, 3H), 1.90-1.80 (m, 4H), 1.58-1.47 (m, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm) δ 197.8, 145.1, 133.2, 129.6, 128.8, 112.2 (t, *J* = 252.0 Hz), 35.0, 32.2, 28.8, 27.9, 26.0, 24.3, 22.9, 21.7; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, ppm) δ -102.83 (d, *J* = 60.2 Hz, 2F).  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  2928, 1603, 1457, 1368, 1170, 1110, 1039, 970, 670, 559. HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>23</sub>N<sub>2</sub>O<sub>2</sub>F<sub>2</sub>S 345.1443; found 345.1445.



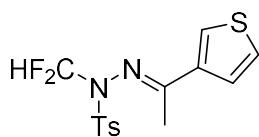
**(*E*)-*N*-(Difluoromethyl)-4-methyl-*N'*-(1-(thiophen-2-yl)ethylidene)benzenesulfonylhydrazide (2e')**: White solid (54 mg, 52% yield), m.p. = 97.6-98.1 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.59 (dd, *J* = 3.7, 0.9 Hz, 1H), 7.49 (dd, *J* = 5.0, 0.8 Hz, 1H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.16-6.86 (m, 2H), 2.61 (s, 3H), 2.46 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm) δ 177.3, 145.1, 140.9, 133.1, 131.6, 131.2, 129.4, 128.9, 127.6, 111.9 (t, *J* = 252.5 Hz), 21.6, 17.5; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, ppm) δ -103.24 (d, *J* = 60.2 Hz, 2F).  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  3103, 2929, 1584, 1369, 1296, 1111, 1040, 831, 665, 584. HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>14</sub>H<sub>15</sub>N<sub>2</sub>O<sub>2</sub>F<sub>2</sub>S<sub>2</sub> 345.0538; found 345.0540.



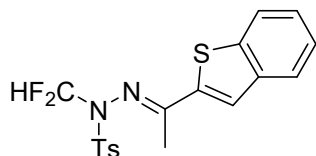
**(*E*)-*N*-(Difluoromethyl)-*N'*-(1-(furan-2-yl)ethylidene)-4-methylbenzenesulfonylhydrazide (2f')**: White solid (49 mg, 50% yield), m.p. = 127.2-128.9 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ 7.75 (d, *J* = 8.1 Hz, 2H), 7.60 (s, 1H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.17-6.86 (m, 2H), 6.54 (s, 1H), 2.53 (s, 3H), 2.45 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm) δ 173.4, 150.5, 146.2, 145.2, 133.1, 129.6, 128.8, 115.9, 112.1, 111.9 (t, *J* = 252.2 Hz), 21.7, 16.6; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, ppm) δ -103.04 (d, *J* = 60.2 Hz, 2F).  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  3043, 2927, 1687, 1592, 1373, 1171, 1108, 756, 666, 556. HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>14</sub>H<sub>15</sub>N<sub>2</sub>O<sub>3</sub>F<sub>2</sub>S 329.0766; found 329.0764.



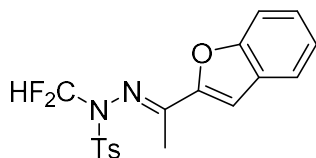
**(E)-N-(Difluoromethyl)-4-methyl-N'-(1-(pyridin-2-yl)ethylidene)benzenesulfonohydrazide (2g')**: White solid (36 mg, 35% yield), m.p. = 92.3-93.6 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ 8.68 (dd, *J* = 4.7, 0.7 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.78 - 7.70 (m, 3H), 7.41-7.37 (m, 1H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.06 (t, *J* = 59.6 Hz, 1H), 2.72 (s, 3H), 2.46 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm) δ 184.5, 153.9, 149.0, 145.2, 136.5, 133.3, 129.6, 128.9, 125.8, 122.2, 112.0 (t, *J* = 252.7 Hz), 21.7, 16.9; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, ppm) δ -102.91 (d, *J* = 60.2 Hz, 2F). *v*<sub>max</sub>(KBr)/cm<sup>-1</sup> 3071, 2931, 1601, 1373, 1173, 1111, 1039, 789, 671, 568. HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>16</sub>N<sub>3</sub>O<sub>2</sub>F<sub>2</sub>S 340.0926; found 340.0925.



**(E)-N-(Difluoromethyl)-4-methyl-N'-(1-(thiophen-3-yl)ethylidene)benzenesulfonohydrazide (2h')**: White solid (66 mg, 64% yield), m.p. = 136.6-137.3 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ 7.86 (d, *J* = 1.8 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.54 (d, *J* = 5.1 Hz, 1H), 7.38-7.30 (m, 3H), 7.03 (t, *J* = 59.8 Hz, 1H), 2.57 (s, 3H), 2.46 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm) δ 178.0, 145.1, 139.5, 133.3, 129.4, 129.4, 128.9, 126.3, 126.3, 112.0 (t, *J* = 252.4 Hz), 21.6, 18.0; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, ppm) δ -103.14 (d, *J* = 56.4 Hz, 2F). *v*<sub>max</sub>(KBr)/cm<sup>-1</sup> 3110, 2924, 1590, 1366, 1278, 1172, 1107, 1040, 665, 567. HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>14</sub>H<sub>15</sub>N<sub>2</sub>O<sub>2</sub>F<sub>2</sub>S<sub>2</sub> 345.0538; found 345.0539.

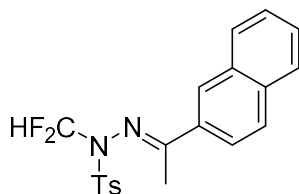


**(E)-N'-(1-(Benzo[b]thiophen-2-yl)ethylidene)-N-(difluoromethyl)-4-methylbenzenesulfonohydrazide (2i')**: White solid (21 mg, 18% yield), m.p. = 174.8-175.6 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ 7.86-7.75 (m, 5H), 7.45-7.36 (m, 4H), 7.01 (t, *J* = 59.6 Hz, 1H), 2.69 (s, 3H), 2.49 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm) δ 178.0, 145.3, 141.8, 141.2, 139.0, 133.1, 129.6, 129.1, 128.7, 127.0, 125.1, 124.8, 122.5, 112.0 (t, *J* = 252.7 Hz), 21.8, 17.38; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, ppm) δ -103.18 (d, *J* = 60.2 Hz, 2F). *v*<sub>max</sub>(KBr)/cm<sup>-1</sup> 1698, 1581, 1372, 1293, 1173, 1106, 1046, 911, 751, 665. HRMS (ESI-TOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub>F<sub>2</sub>S<sub>2</sub> 395.0694; found 395.0693.



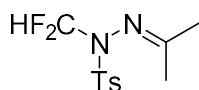
**(E)-N'-(1-(Benzofuran-2-yl)ethylidene)-N-(difluoromethyl)-4-methylbenzenesulfonohydrazide (2j')**: White solid (28 mg, 25% yield), m.p. = 116.1-117.0 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ 7.78 (d, *J* = 8.1 Hz, 2H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.46-7.40 (m, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.30

(t,  $J = 7.5$  Hz, 1H), 7.05 (t,  $J = 59.6$  Hz, 1H), 2.65 (s, 3H), 2.47 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  174.6, 155.9, 151.7, 145.3, 133.2, 129.7, 128.9, 127.3 (d,  $J = 10.4$  Hz), 123.6, 122.3, 112.2, 112.0, 111.9 (t,  $J = 252.5$  Hz), 21.7, 17.1;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  -102.75 (d,  $J = 60.2$  Hz, 2F).  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  3694, 3311, 3083, 1727, 1585, 1372, 1174, 1106, 665, 563. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{18}\text{H}_{17}\text{N}_2\text{O}_3\text{F}_2\text{S}$  379.0922; found 379.0924.

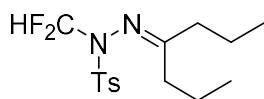


**(E)-N-(Difluoromethyl)-4-methyl-N'-(1-(naphthalen-2-yl)ethylidene)benzenesulfonohydrazide (2k')**:

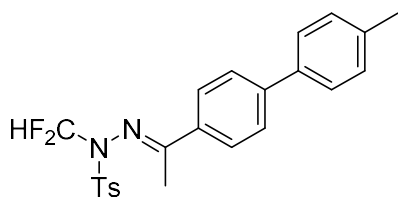
White solid (82 mg, 70% yield), m.p. = 142.3-144.2 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  8.30 (s, 1H), 8.00 (dd,  $J = 8.7, 1.8$  Hz, 1H), 7.92 (d,  $J = 7.5$  Hz, 1H), 7.85 (t,  $J = 8.2$  Hz, 2H), 7.79 (d,  $J = 8.3$  Hz, 2H), 7.56 (pd,  $J = 6.9, 1.5$  Hz, 2H), 7.37 (d,  $J = 8.1$  Hz, 2H), 7.09 (t,  $J = 59.7$  Hz, 1H), 2.73 (s, 3H), 2.48 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  182.9, 145.2, 134.9, 133.8, 133.4, 132.7, 129.6, 129.1, 129.0, 128.9, 128.2, 127.8, 127.7, 126.6, 123.9, 112.0 (t,  $J = 252.1$  Hz), 21.7, 17.8;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  -103.01 (d,  $J = 60.2$  Hz, 2F).  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  3061, 2924, 1591, 1370, 1170, 1104, 1029, 817, 659, 560. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{20}\text{H}_{19}\text{N}_2\text{O}_2\text{F}_2\text{S}$  389.1130; found 389.1133.



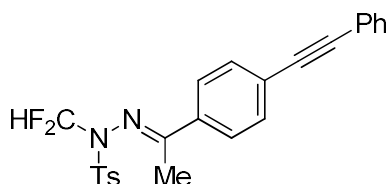
**N-(Difluoromethyl)-4-methyl-N'-(propan-2-ylidene)benzenesulfonohydrazide (2l')**: White solid (41 mg, 50% yield), m.p. = 61.7-62.3 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.72 (d,  $J = 8.0$  Hz, 2H), 7.33 (d,  $J = 8.1$  Hz, 2H), 6.94 (t,  $J = 59.8$  Hz, 1H), 2.43 (s, 3H), 2.20 (d,  $J = 8.2$  Hz, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  187.6, 145.1, 133.3, 129.6, 128.7, 111.8 (t,  $J = 251.5$  Hz), 25.5, 21.6, 20.9;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  -103.13 (d,  $J = 60.2$  Hz, 2F).  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  3385, 2925, 1597, 1355, 1167, 1111, 1032, 812, 671, 557. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{11}\text{H}_{15}\text{N}_2\text{O}_2\text{F}_2\text{S}$  277.0817; found 277.0819.



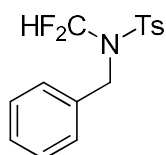
**N-(Difluoromethyl)-N'-(heptan-4-ylidene)-4-methylbenzenesulfonohydrazide (2m')**: White solid (63 mg, 63% yield), m.p. = 74.1-74.9 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.72 (d,  $J = 8.1$  Hz, 2H), 7.32 (d,  $J = 8.0$  Hz, 2H), 6.93 (t,  $J = 59.9$  Hz, 1H), 2.64-2.54 (m, 2H), 2.46-2.39 (m, 5H), 1.61 (ddd,  $J = 23.4, 15.3, 7.6$  Hz, 4H), 0.98 (t,  $J = 7.3$  Hz, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  193.0, 145.0, 133.4, 129.5, 128.8, 111.7 (t,  $J = 251.8$  Hz), 38.2, 34.3, 21.6, 20.0, 19.6, 14.3, 13.7;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  -103.03 (d,  $J = 60.2$  Hz, 2F).  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  3385, 2928, 1708, 1601, 1354, 1167, 1111, 811, 670, 556. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{15}\text{H}_{23}\text{N}_2\text{O}_2\text{F}_2\text{S}$  333.1443; found 333.1445.



**(E)-N-(Difluoromethyl)-4-methyl-N'-(1-(4'-methyl-[1,1'-biphenyl]-4-yl)ethylidene)benzenesulfonohydrazide (3):** Light yellow oil (114 mg, 89% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.93 (d,  $J = 8.2$  Hz, 2H), 7.80 (d,  $J = 8.0$  Hz, 2H), 7.65 (d,  $J = 8.1$  Hz, 2H), 7.54 (d,  $J = 7.8$  Hz, 2H), 7.38 (d,  $J = 8.0$  Hz, 2H), 7.29 (d,  $J = 7.7$  Hz, 2H), 7.08 (t,  $J = 59.7$  Hz, 1H), 2.65 (s, 3H), 2.48 (s, 3H), 2.43 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  182.8, 145.2, 144.5, 138.1, 137.1, 134.9, 133.5, 129.7, 129.6, 129.0, 128.2, 127.0, 126.9, 112.1 (t,  $J = 252.1$  Hz), 21.7, 21.2, 17.8;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  -102.98 (d,  $J = 56.4$  Hz, 2F).  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  3045, 2927, 1751, 1677, 1602, 1380, 1266, 808, 736, 592. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{23}\text{H}_{23}\text{N}_2\text{O}_2\text{F}_2\text{S}$  429.1443; found 429.1442.



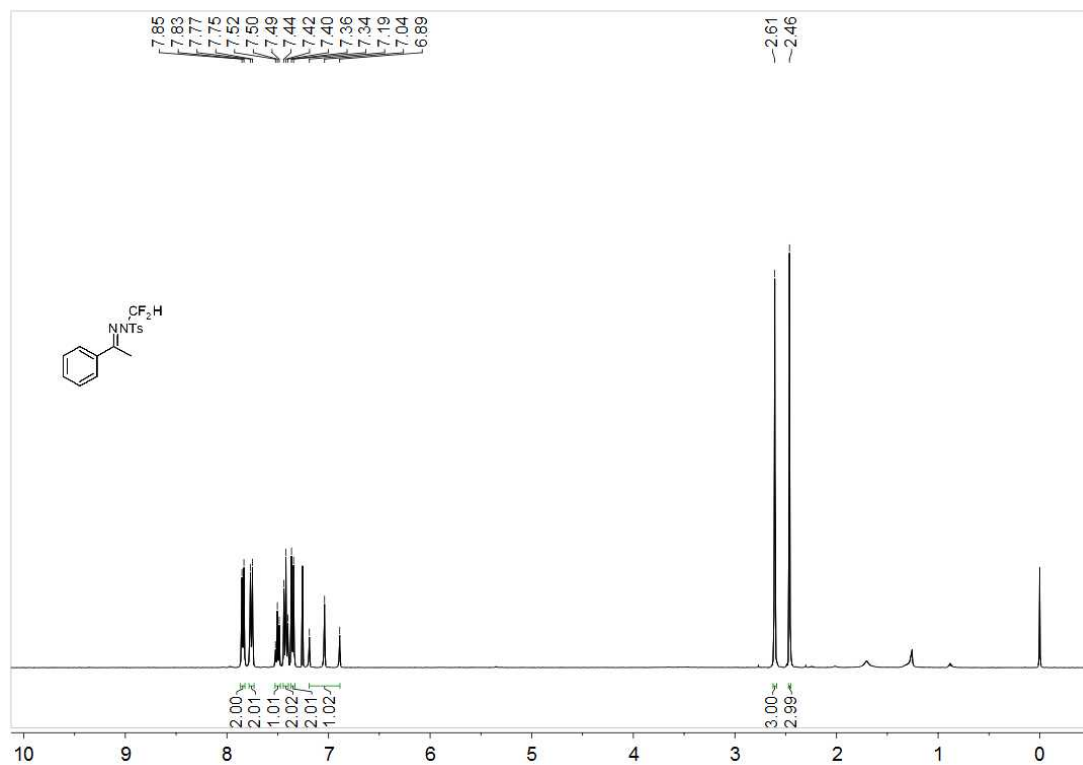
**(E)-N-(Difluoromethyl)-4-methyl-N'-(1-(4-(phenylethynyl)phenyl)ethylidene)benzenesulfonohydrazide (4):** Light yellow oil (112 mg, 85% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.85 (d,  $J = 8.5$  Hz, 2H), 7.77 (d,  $J = 8.3$  Hz, 2H), 7.60-7.55 (m, 4H), 7.39-7.34 (m, 5H), 7.08 (t,  $J = 59.7$  Hz, 1H), 2.62 (s, 3H), 2.46 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  182.4, 145.2, 135.7, 133.3, 131.7, 131.6, 129.5, 128.9, 128.7, 128.4, 127.6, 126.8, 122.7, 112.1 (t,  $J = 252.2$  Hz), 92.1, 88.7, 21.7, 17.8;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  -102.94 (d,  $J = 60.2$  Hz, 2F).  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  3638, 1597, 1517, 1373, 1283, 1111, 1036, 755, 672, 571. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{24}\text{H}_{21}\text{N}_2\text{O}_2\text{F}_2\text{S}$  439.1286; found 439.1286.



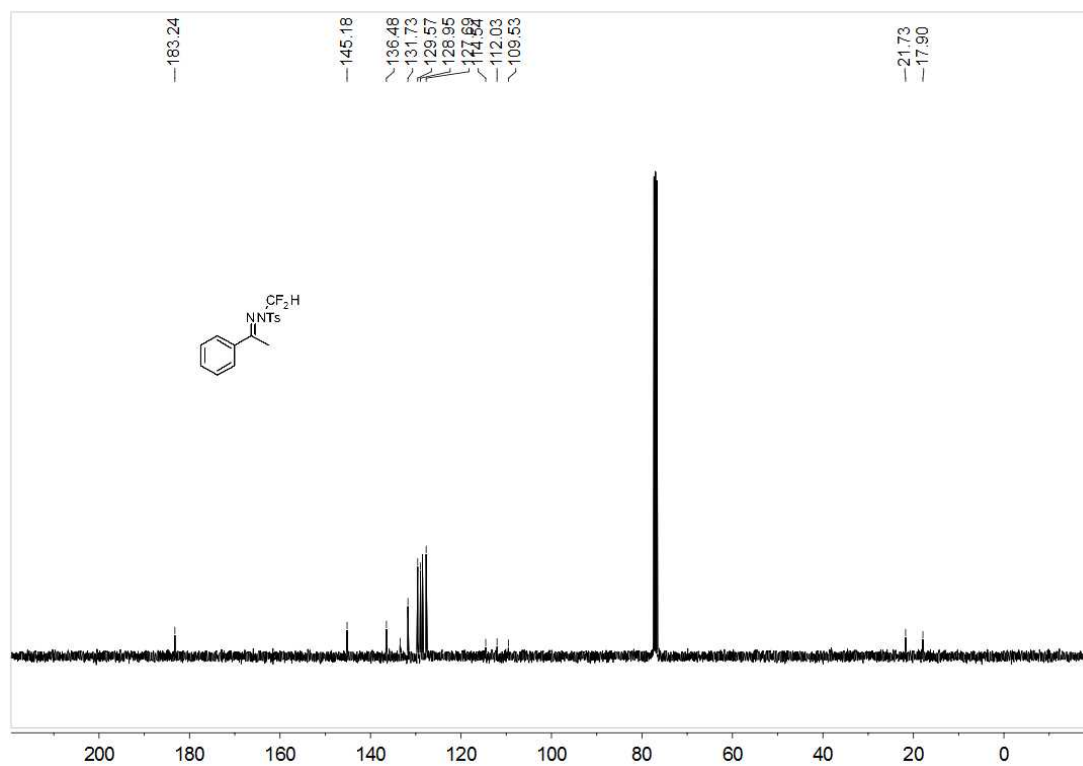
**N-Benzyl-N-(difluoromethyl)-4-methylbenzenesulfonamide (6):** Yellow solid (27 mg, 42% yield), m.p. = 185.8-186.3  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.57 (d,  $J = 7.9$  Hz, 2H), 7.32-7.20 (m, 7H), 4.41 (s, 2H), 2.40 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  144.6, 135.7, 135.5, 129.9, 128.4, 128.3, 127.7, 127.3, 112.3 (t,  $J = 245.0$  Hz), 45.5, 21.6;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  -95.46 (d,  $J = 56.4$  Hz, 2F).  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  = 3667, 3380, 2939, 1700, 1597, 917, 822, 578  $\text{cm}^{-1}$ ; HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{Na}]^+$  Calcd for  $\text{C}_{15}\text{H}_{15}\text{F}_2\text{NNaO}_2\text{S}$  334.0689; found 334.0683.

## E. NMR Spectra

$^1\text{H}$  NMR spectrum of 3a:

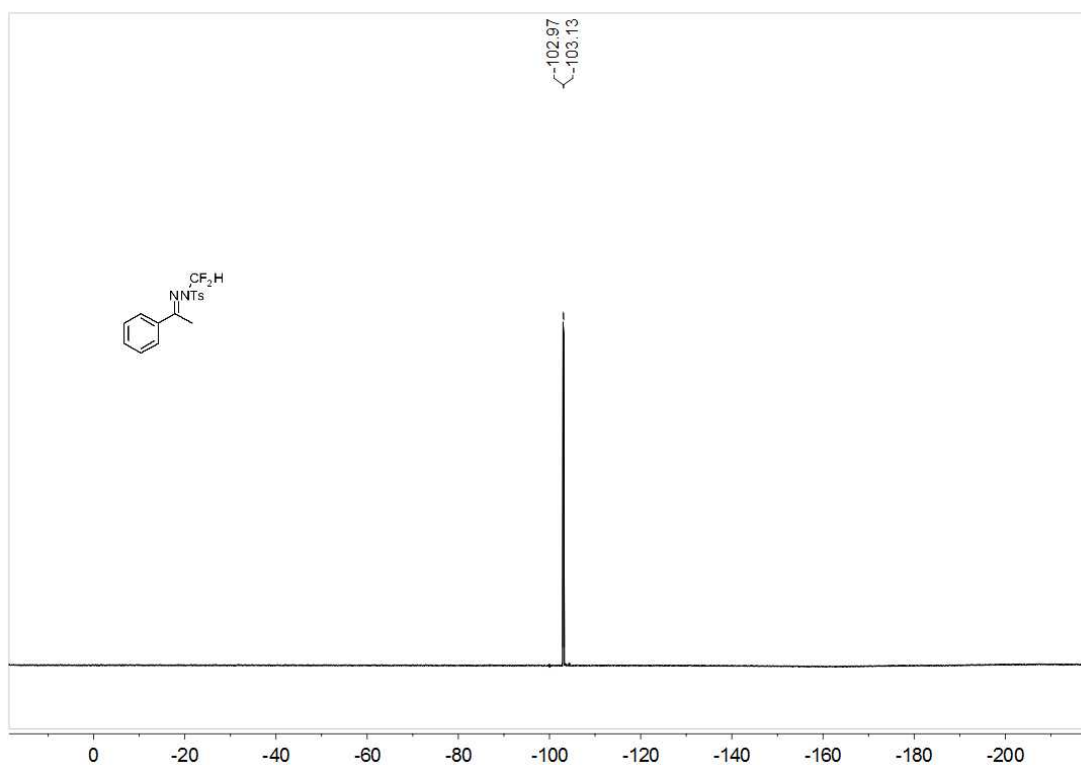


$^{13}\text{C}$  NMR spectrum of 3a:

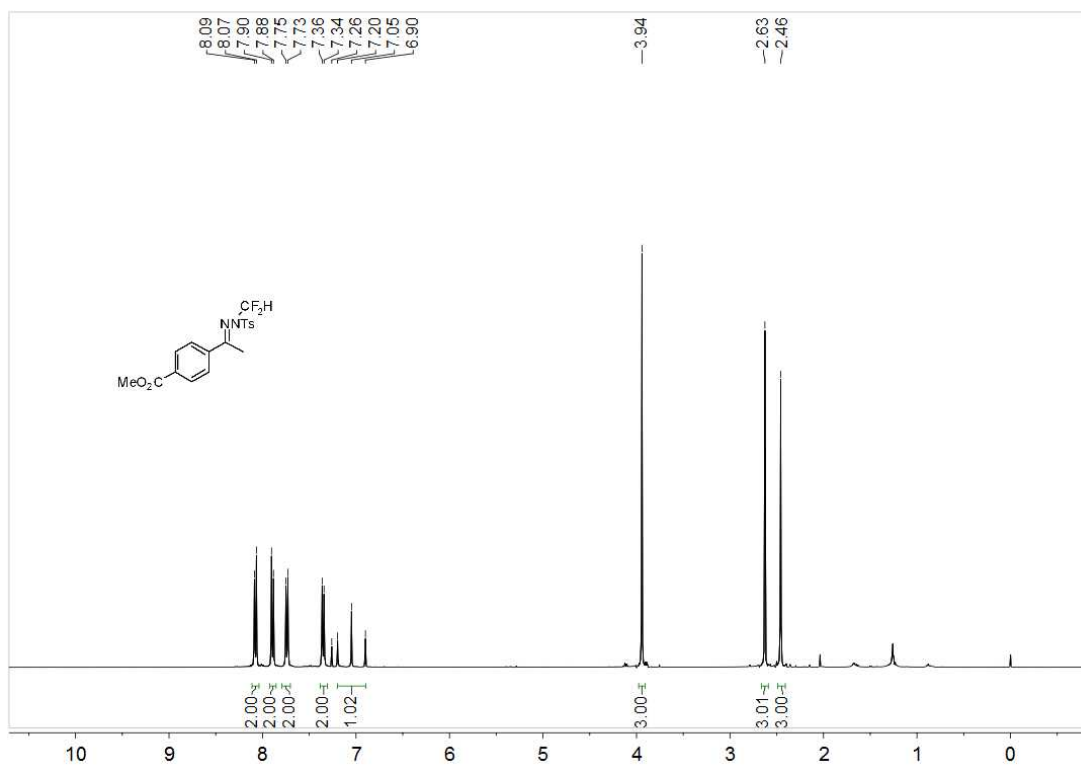




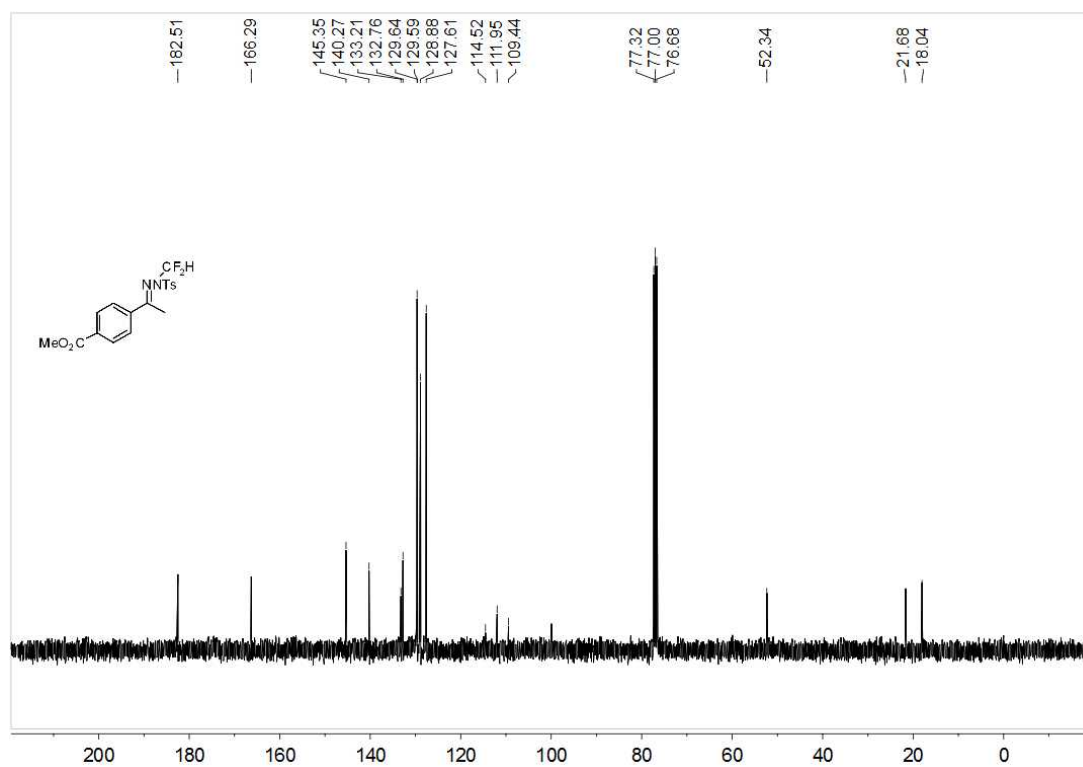
**<sup>19</sup>F NMR spectrum of 3a:**



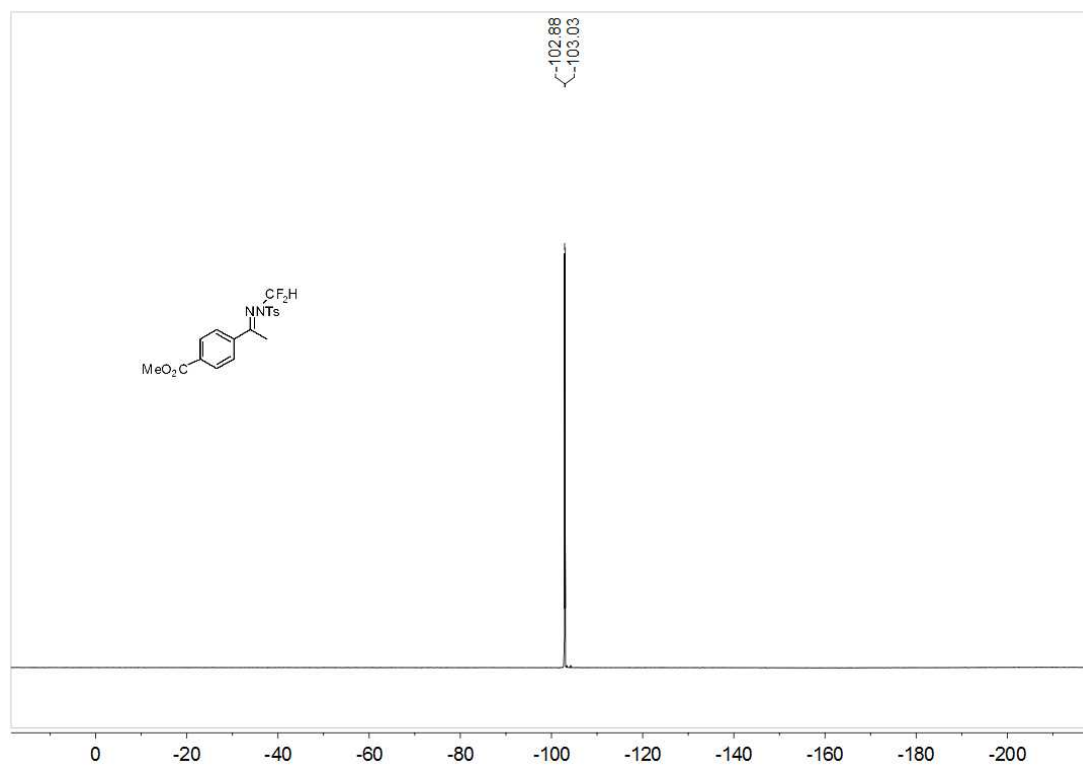
**<sup>1</sup>H NMR spectrum of 2b:**



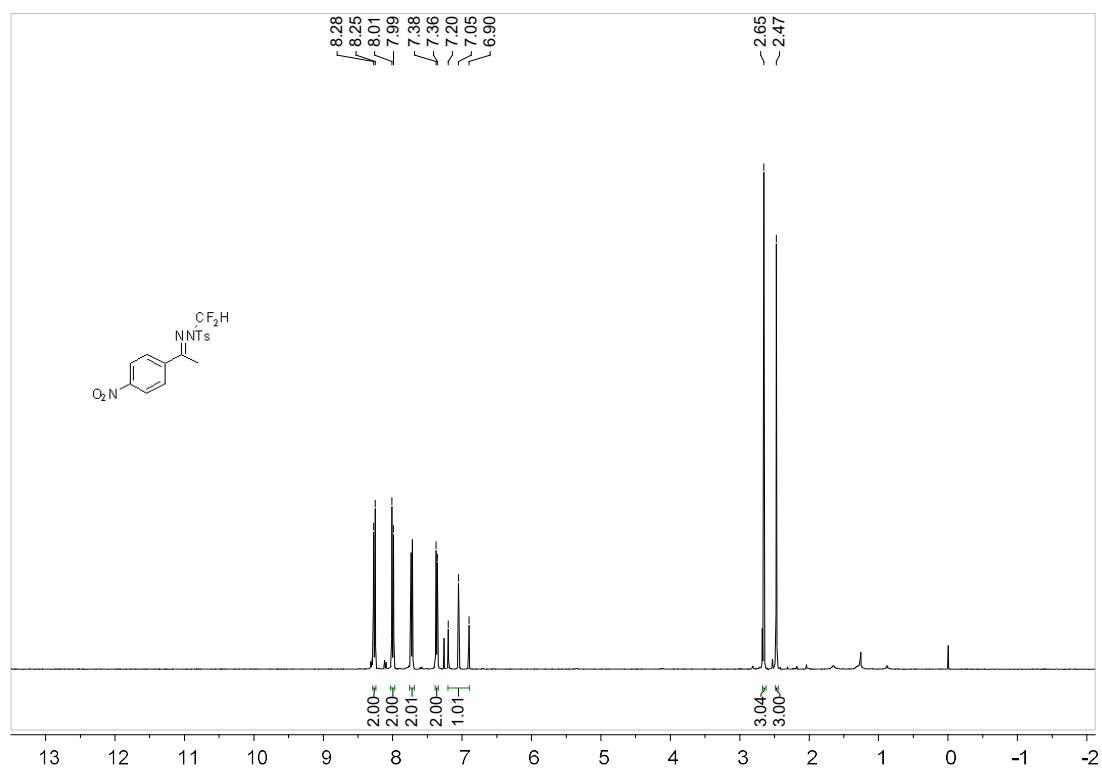
**<sup>13</sup>C NMR spectrum of 2b:**



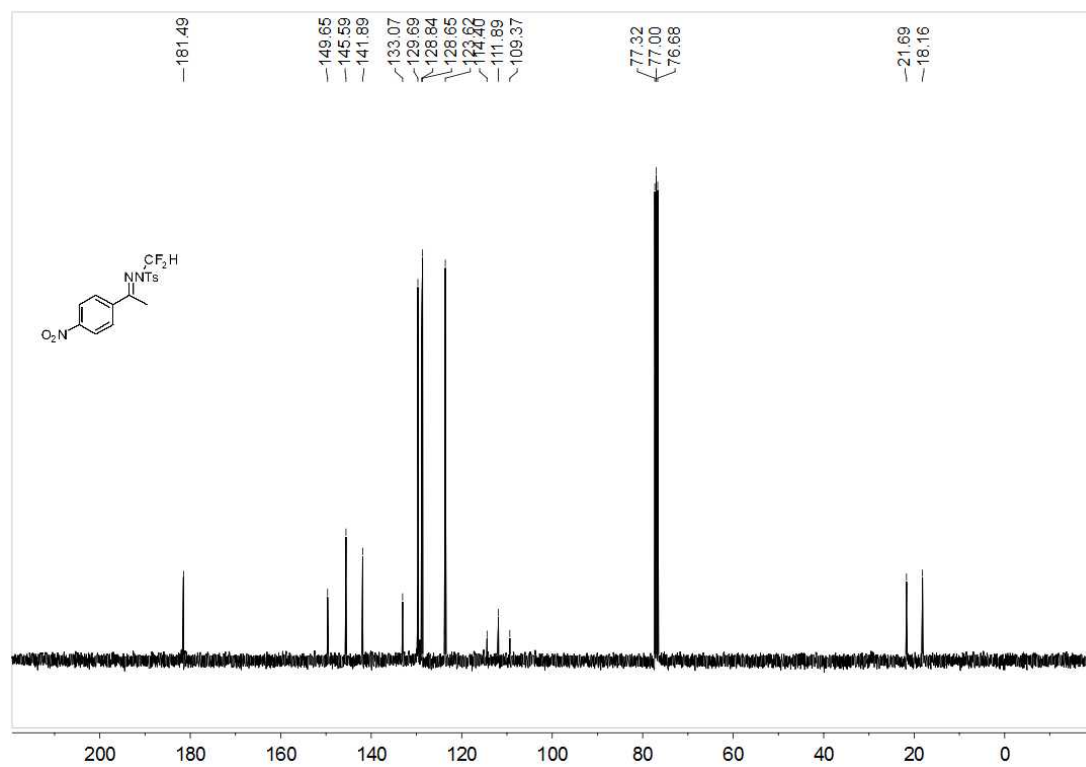
**<sup>19</sup>F NMR spectrum of 2b:**



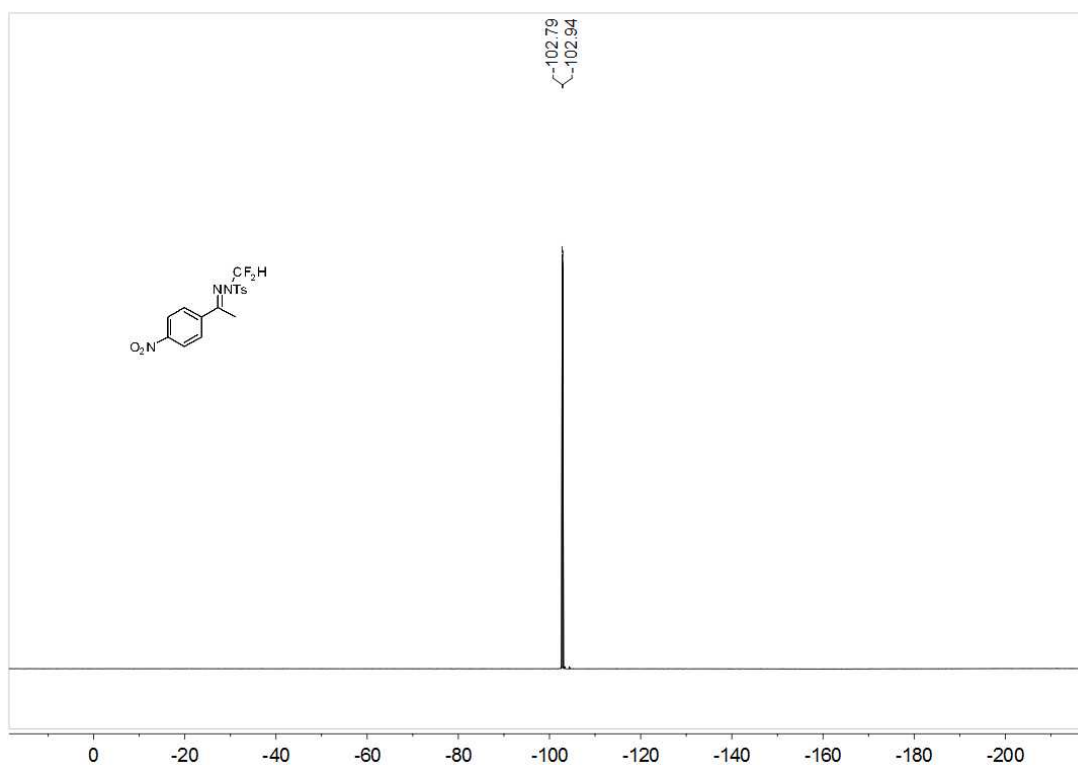
**<sup>1</sup>H NMR spectrum of 2c:**



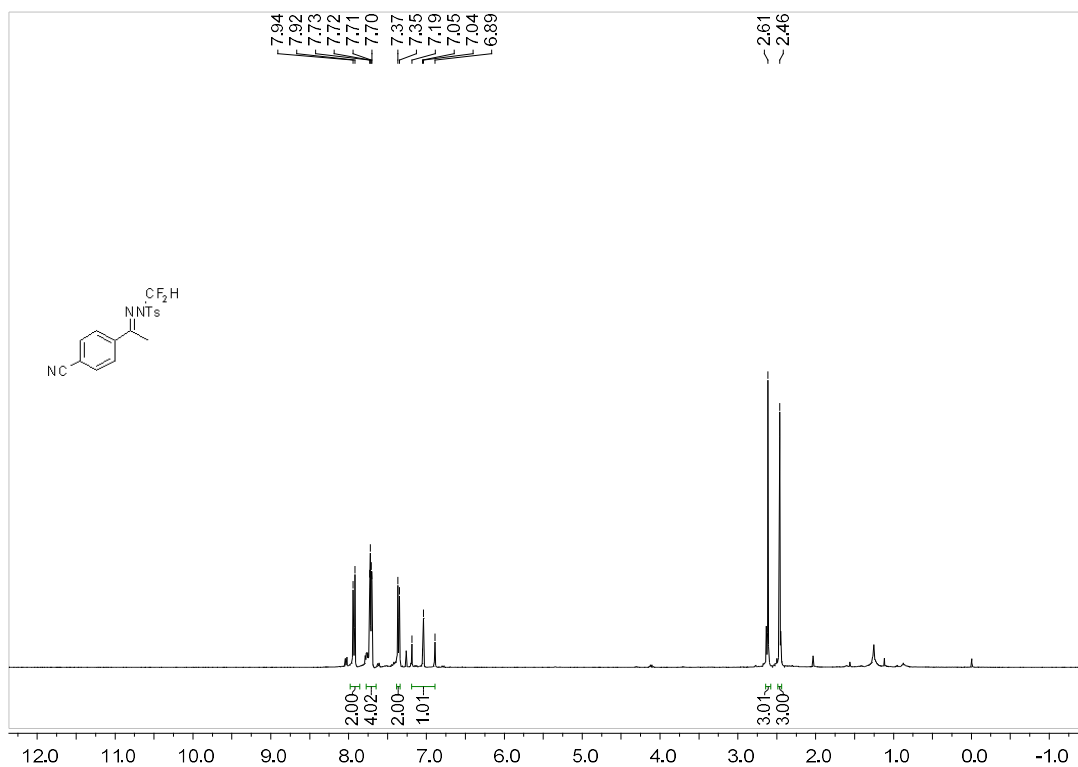
**<sup>13</sup>C NMR spectrum of 2c:**



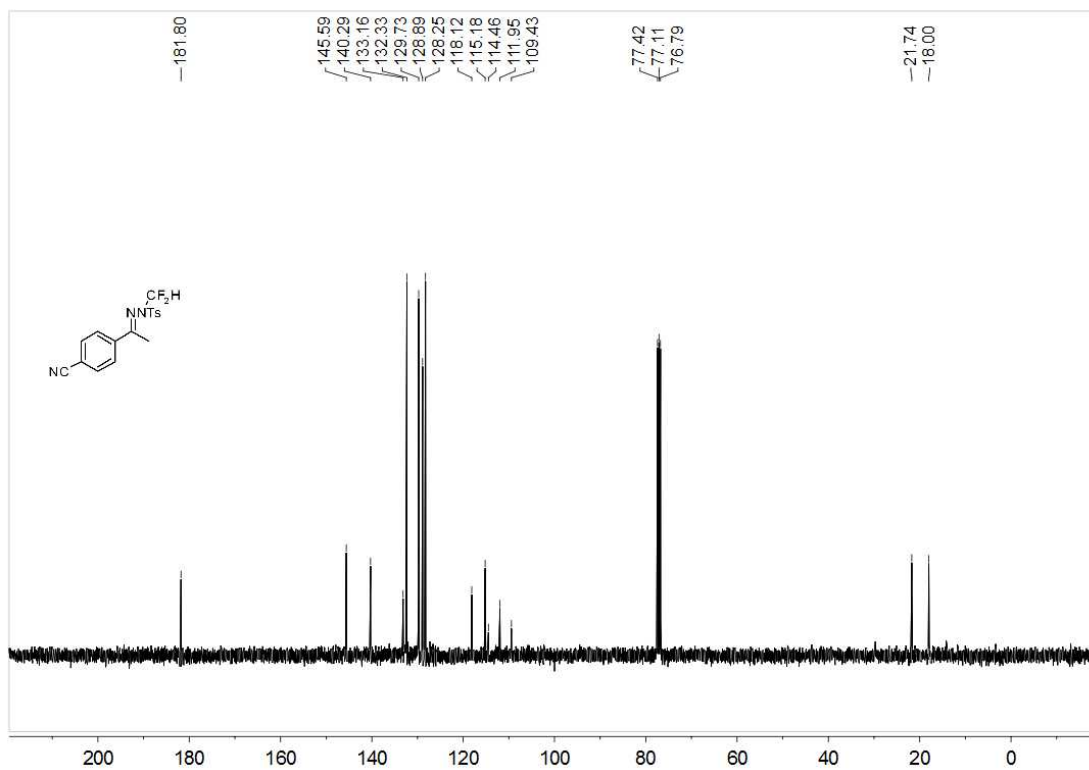
**$^{19}\text{F}$  NMR spectrum of 2c:**



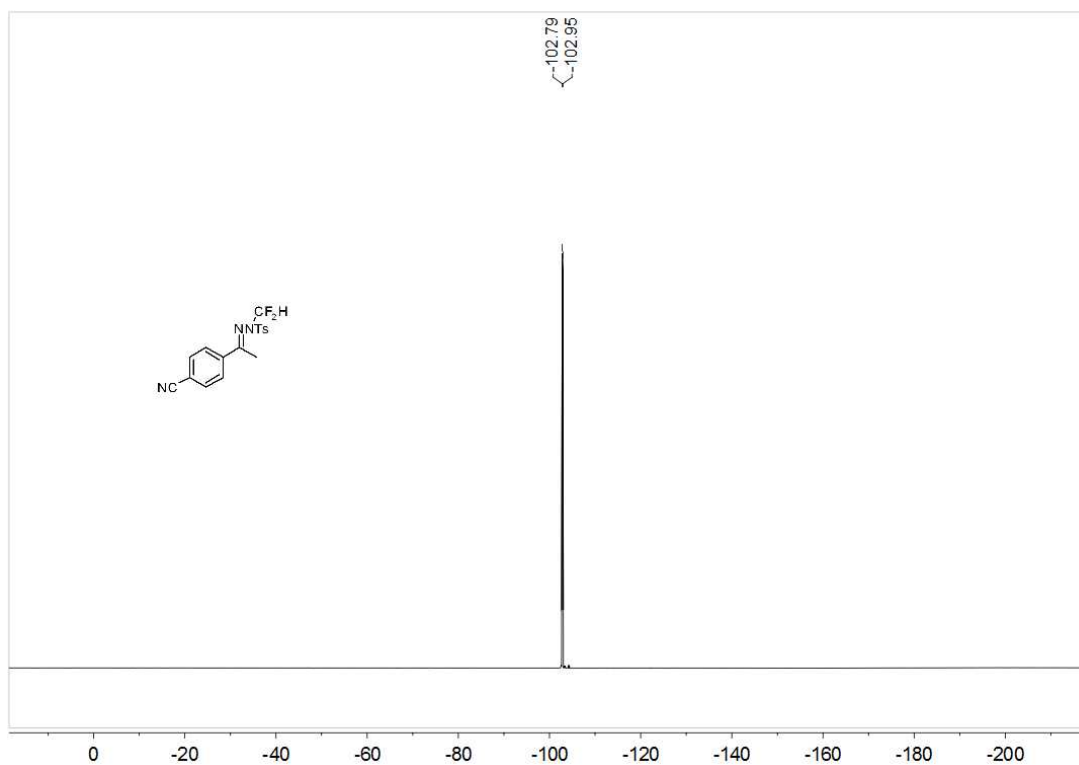
**$^1\text{H}$  NMR spectrum of 2d:**



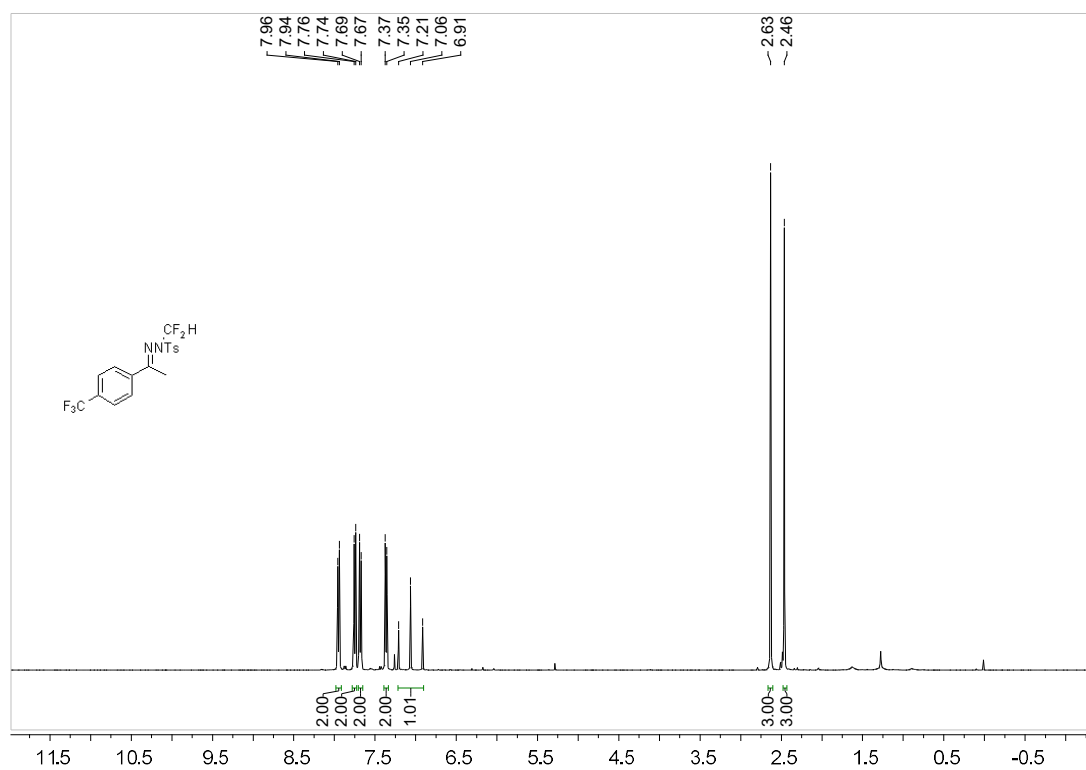
**<sup>13</sup>C NMR spectrum of 2d:**



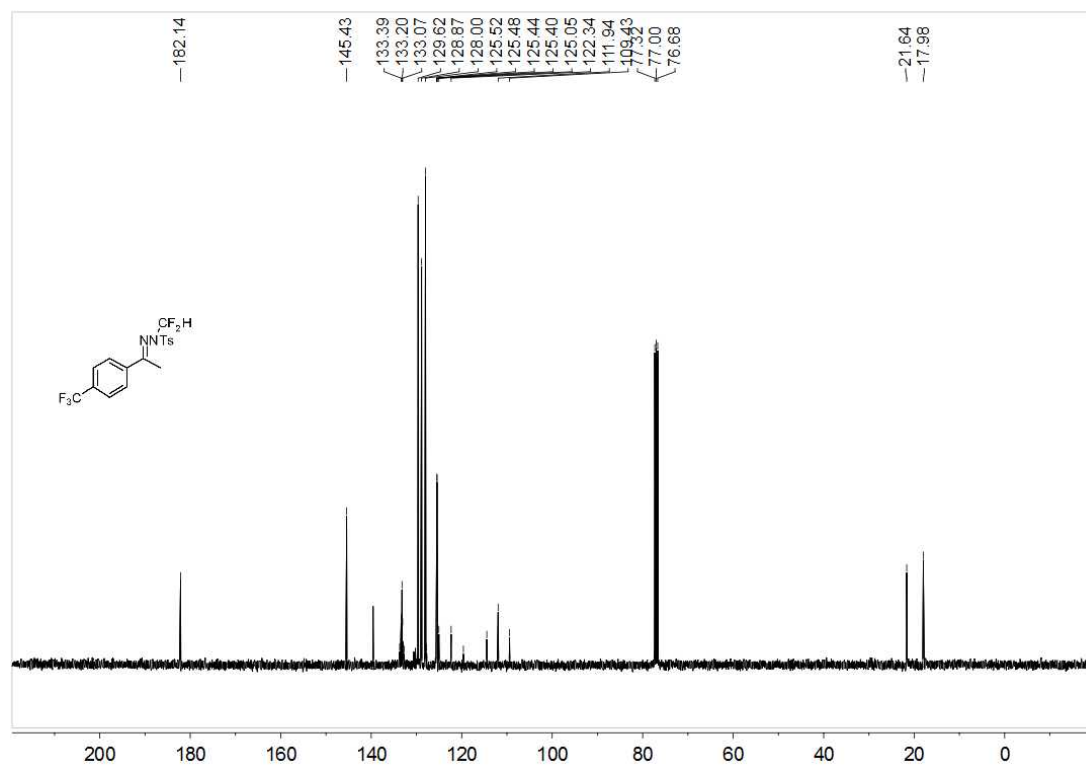
**<sup>19</sup>F NMR spectrum of 2d:**



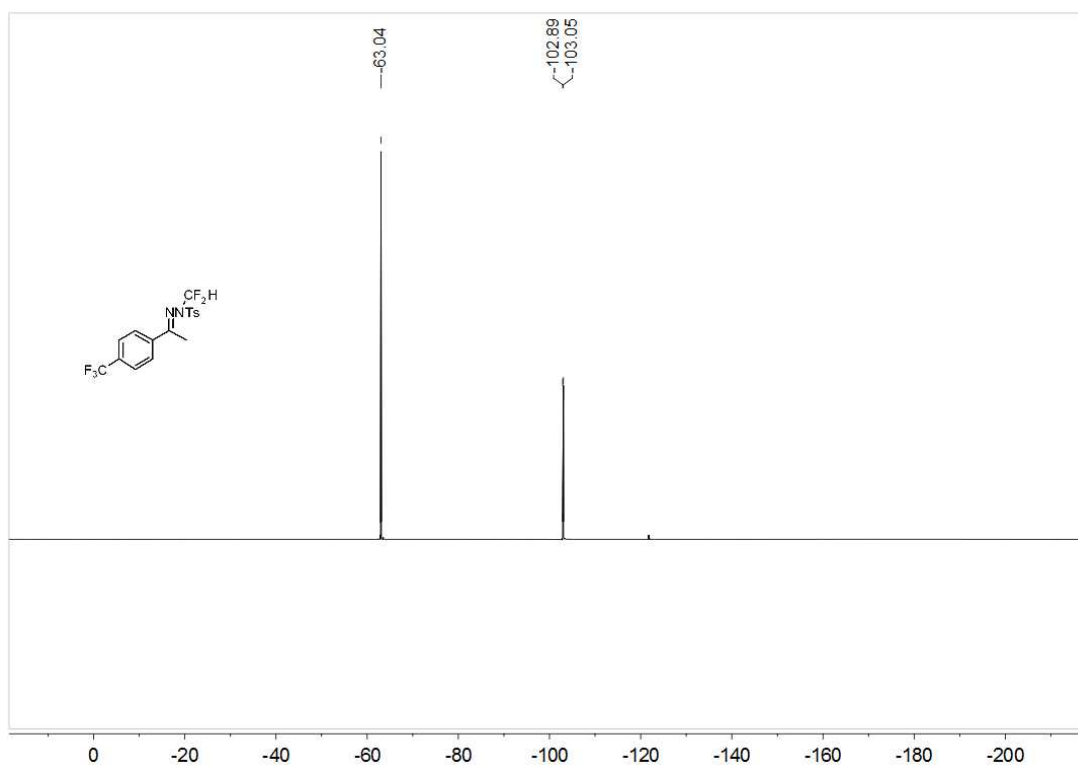
**<sup>1</sup>H NMR spectrum of 2e:**



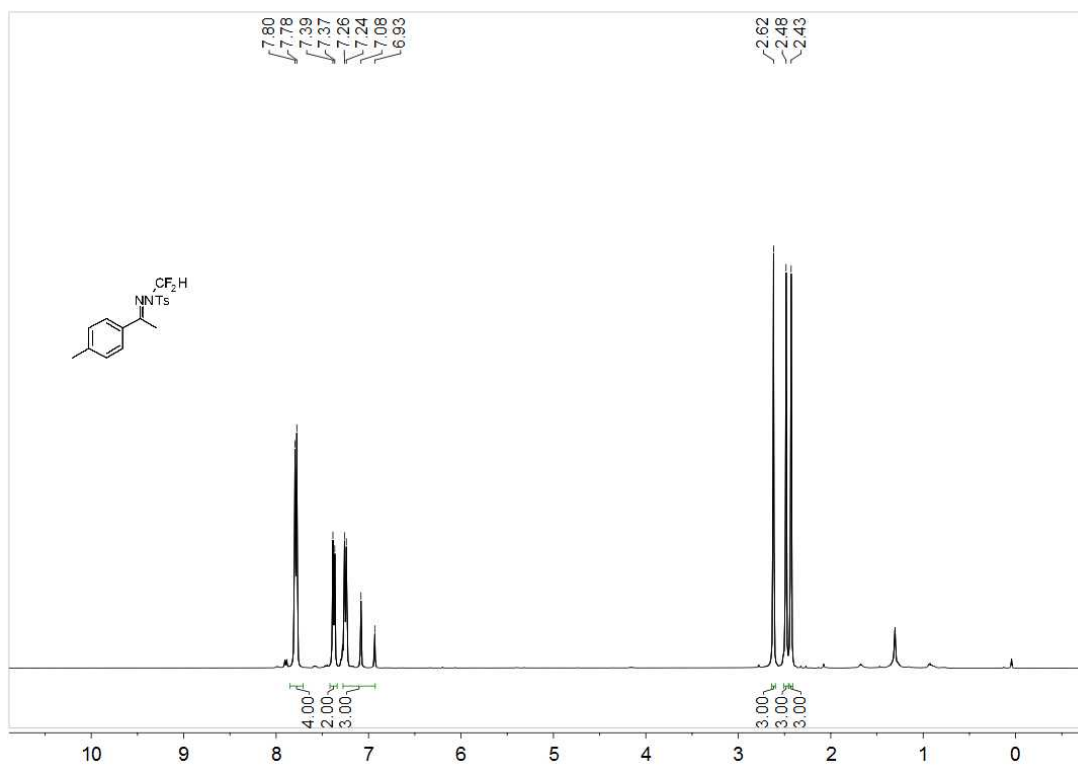
**<sup>13</sup>C NMR spectrum of 2e:**



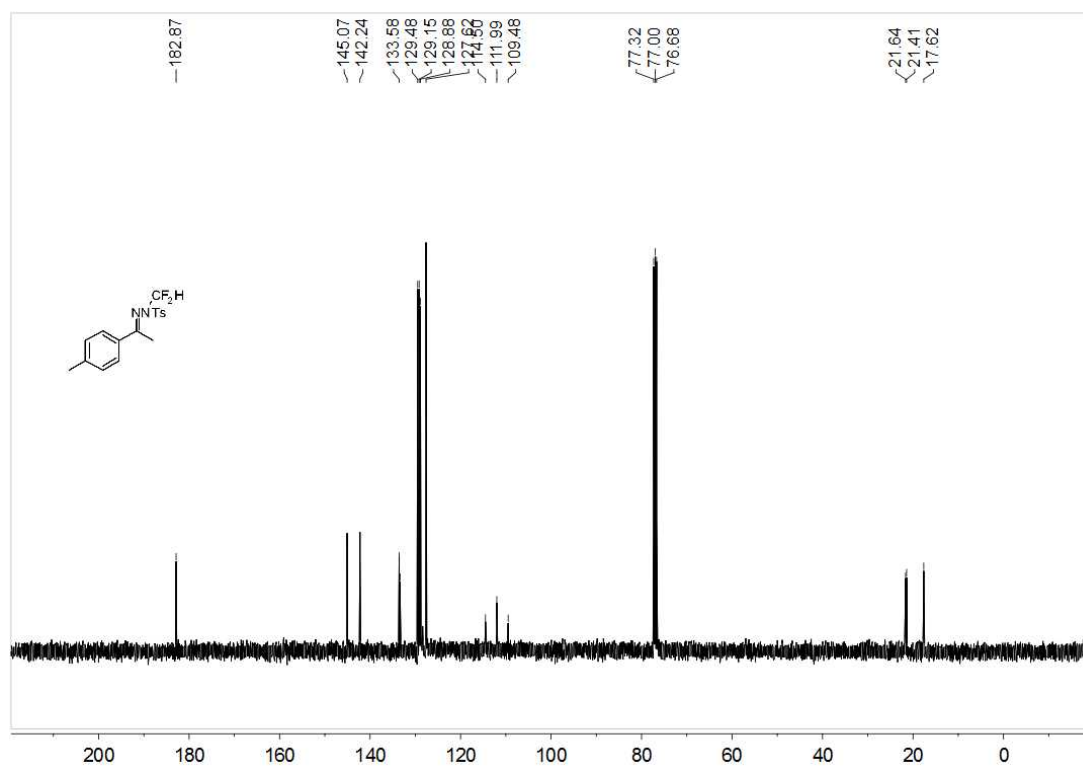
**<sup>19</sup>F NMR spectrum of 2e:**



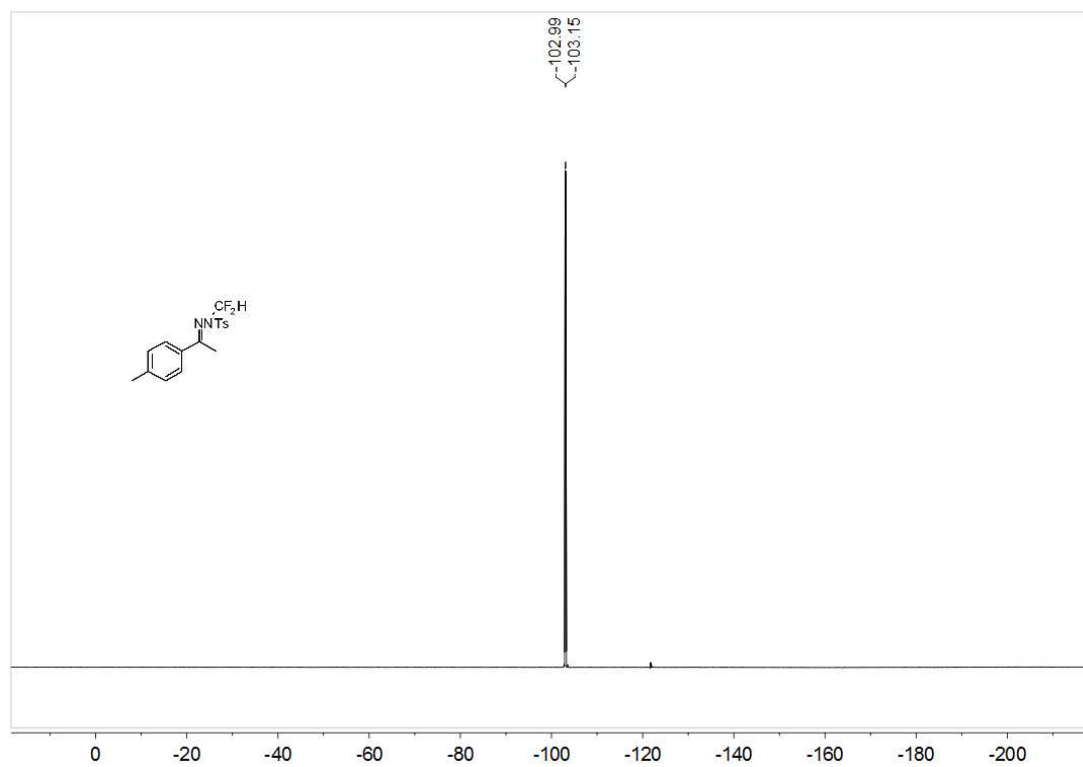
**<sup>1</sup>H NMR spectrum of 2f:**



**<sup>13</sup>C NMR spectrum of 2f:**

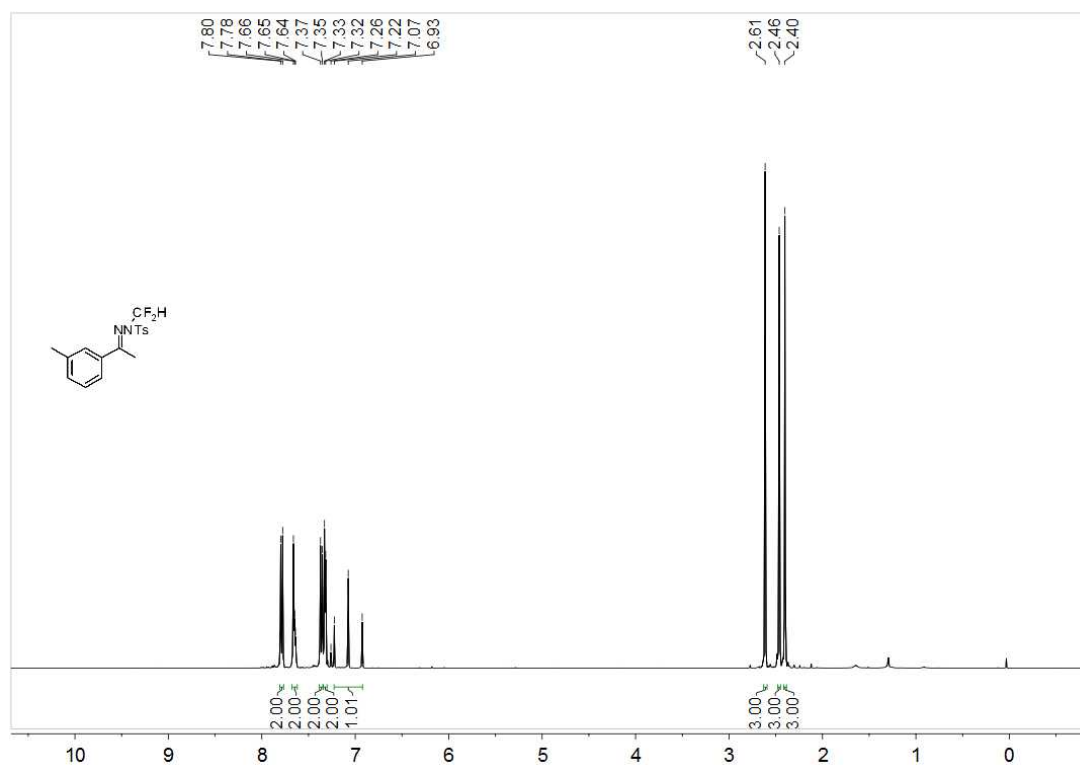


**<sup>19</sup>F NMR spectrum of 2f:**

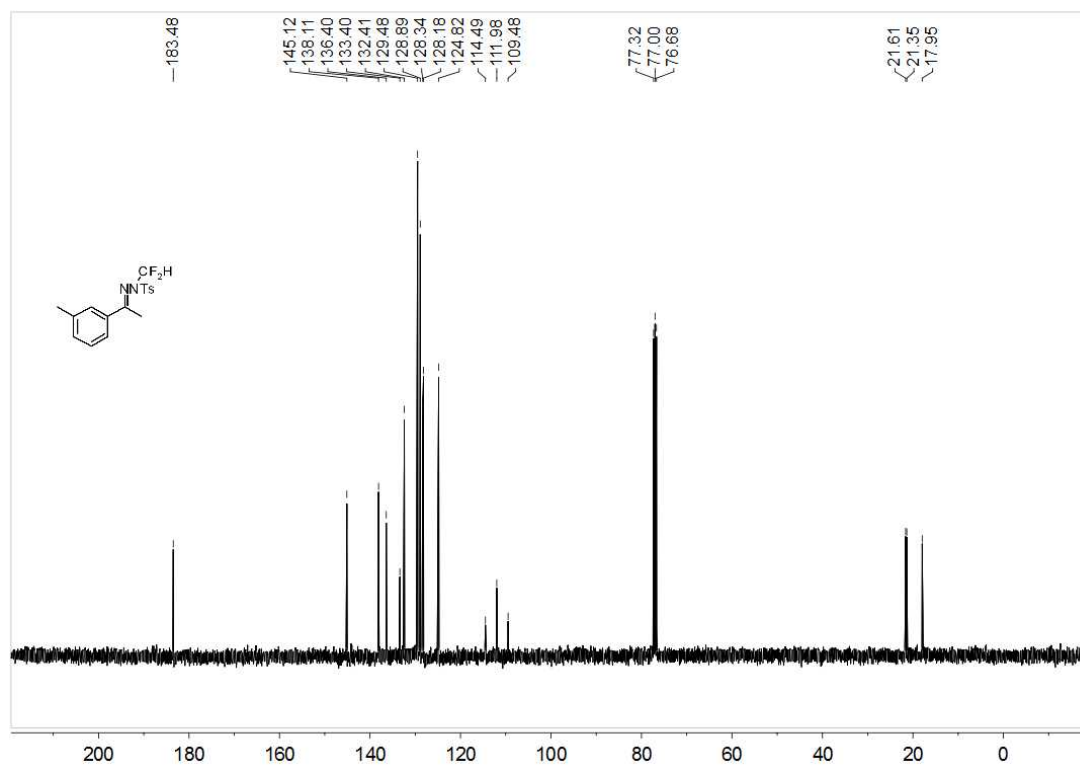




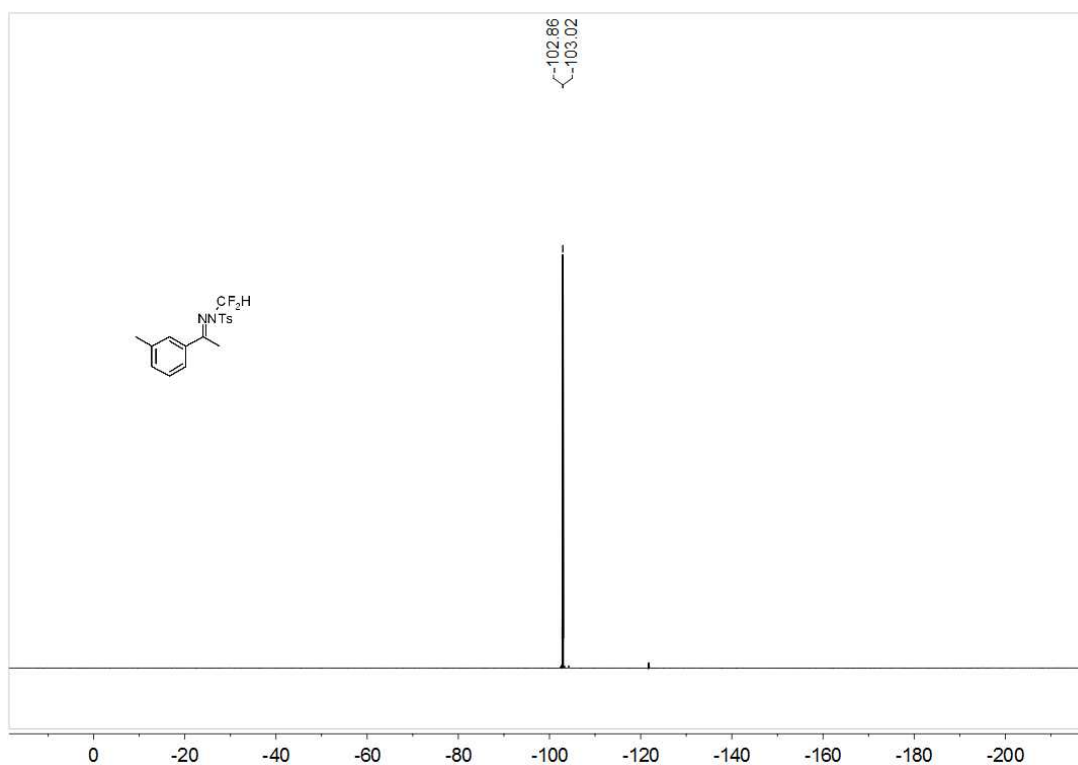
**<sup>1</sup>H NMR spectrum of 2g:**



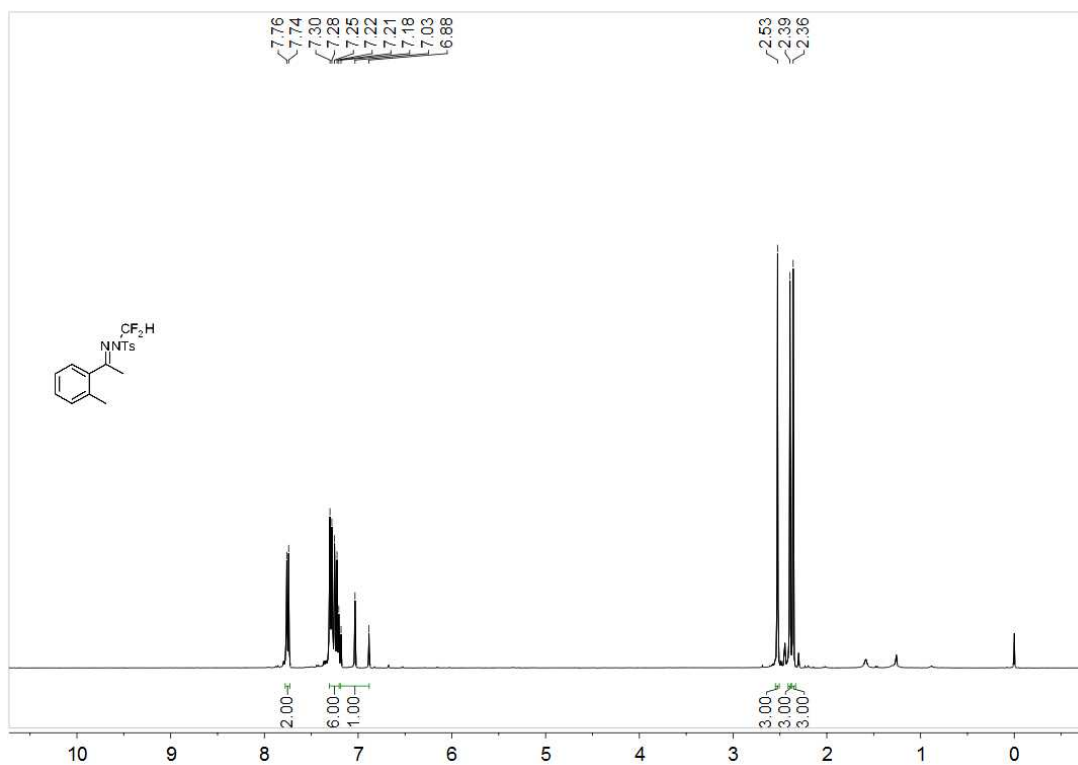
**<sup>13</sup>C NMR spectrum of 2g:**



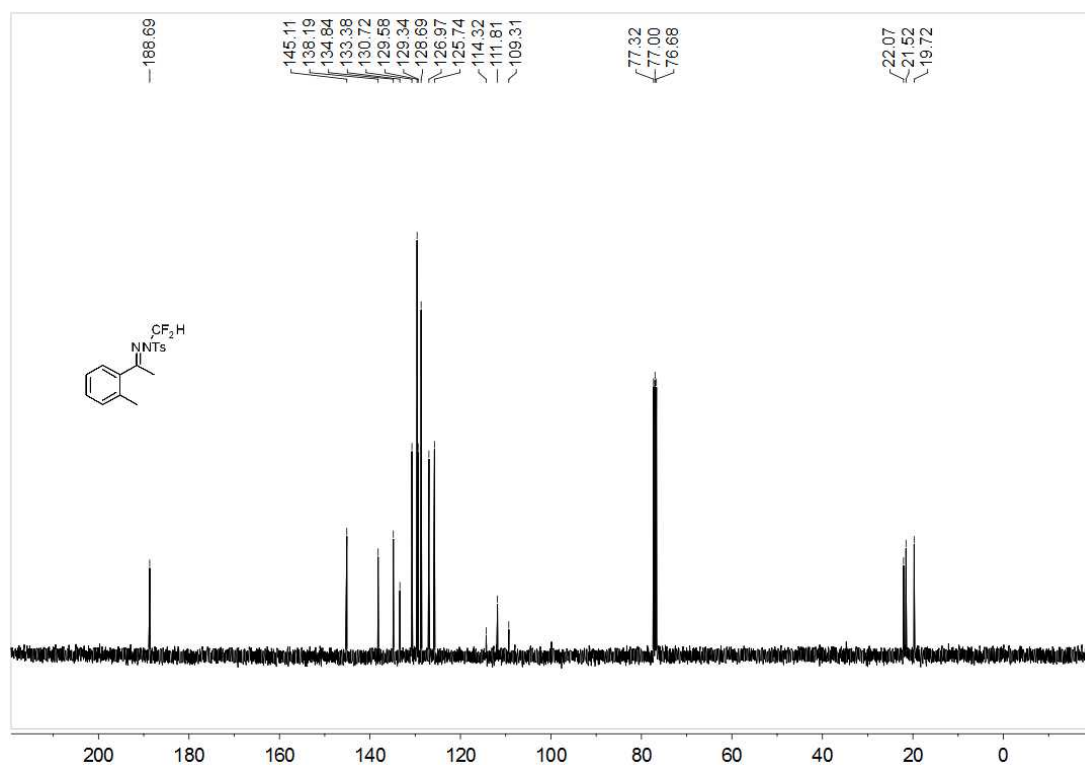
**<sup>19</sup>F NMR spectrum of 2g:**



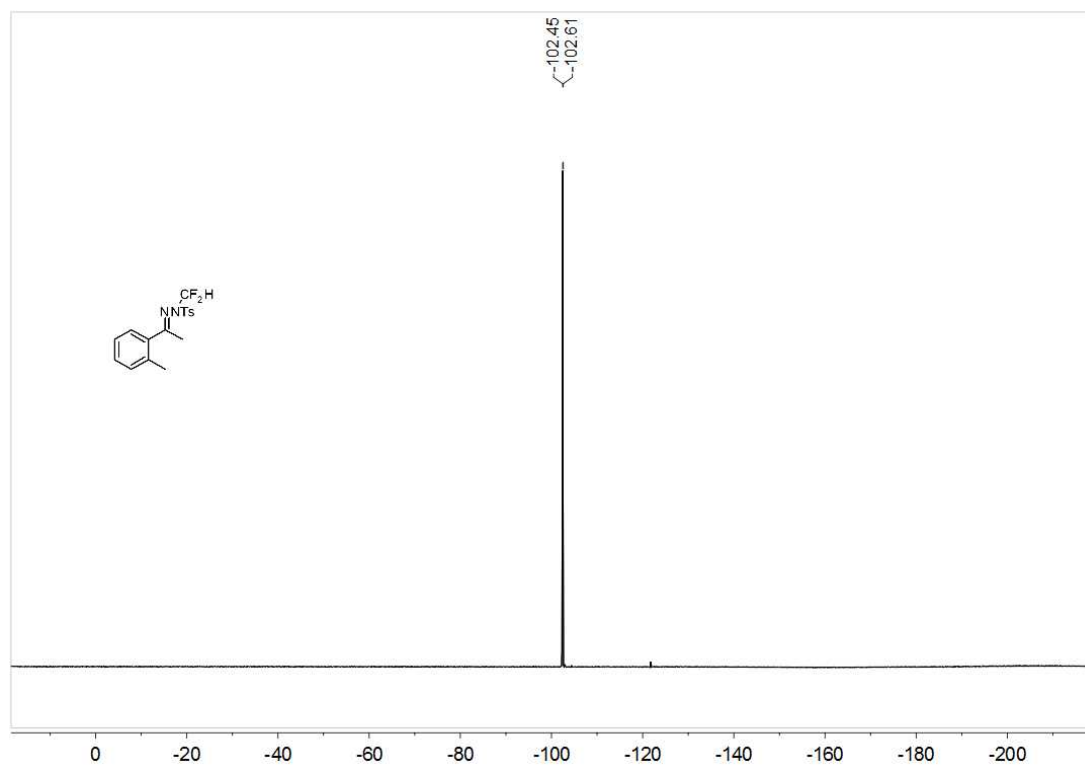
**<sup>1</sup>H NMR spectrum of 2h:**



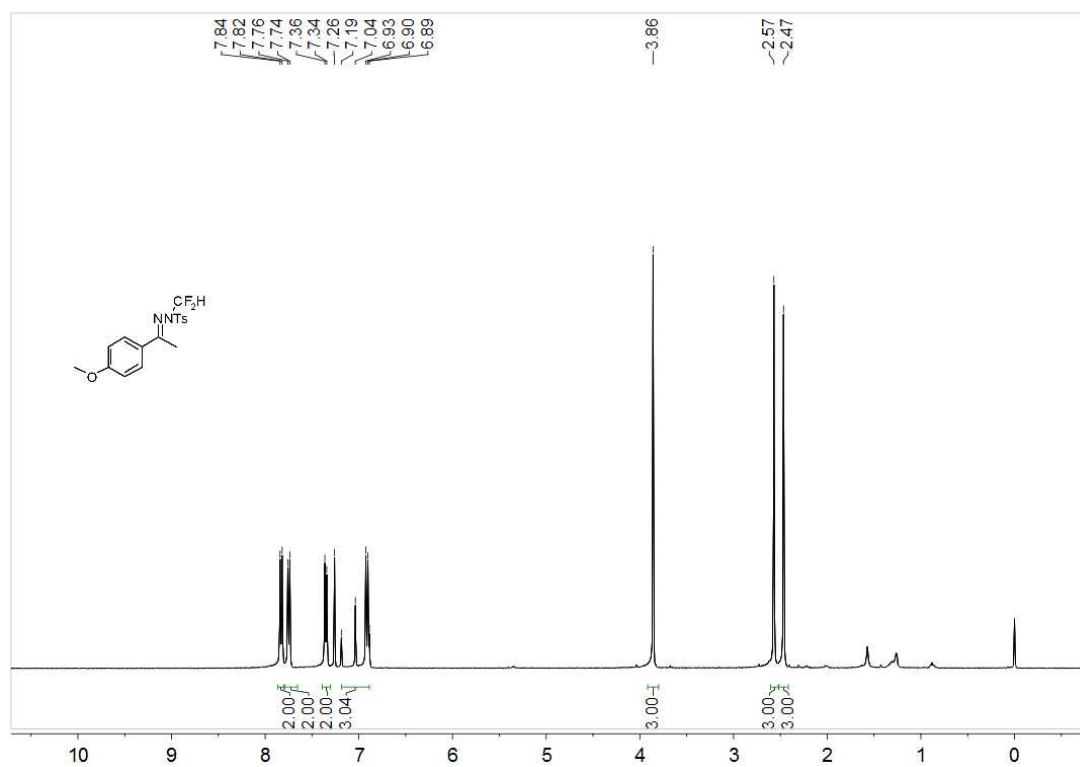
**<sup>13</sup>C NMR spectrum of 2h:**



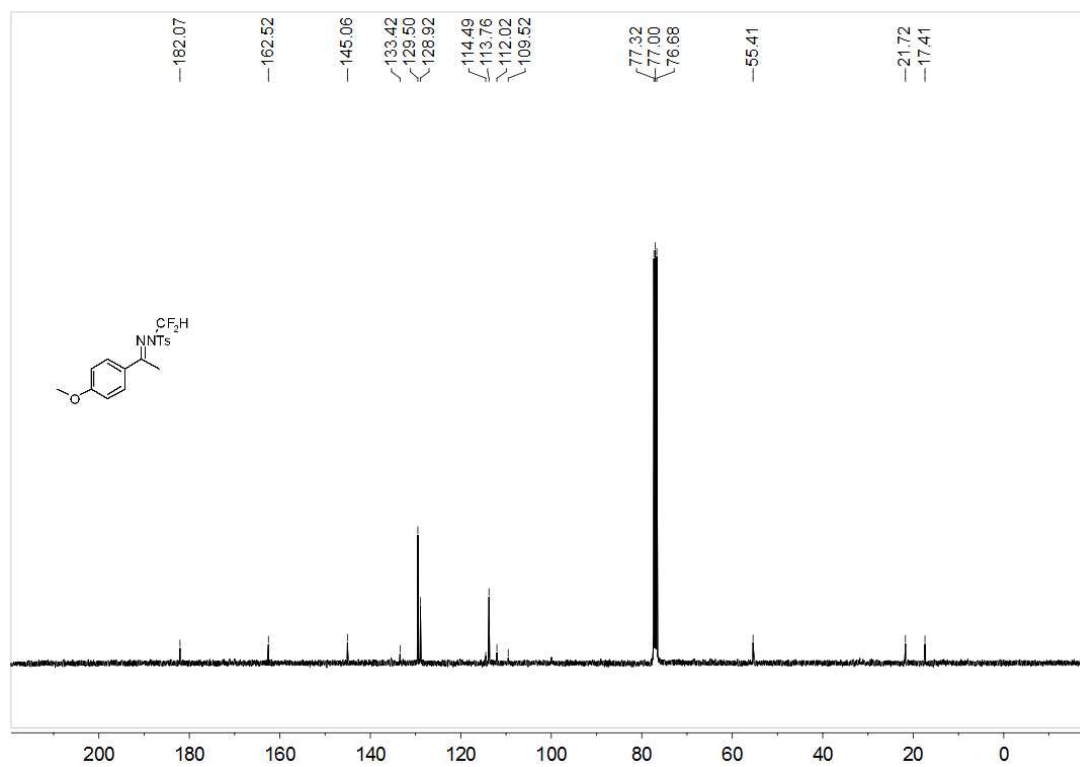
**<sup>19</sup>F NMR spectrum of 2h:**



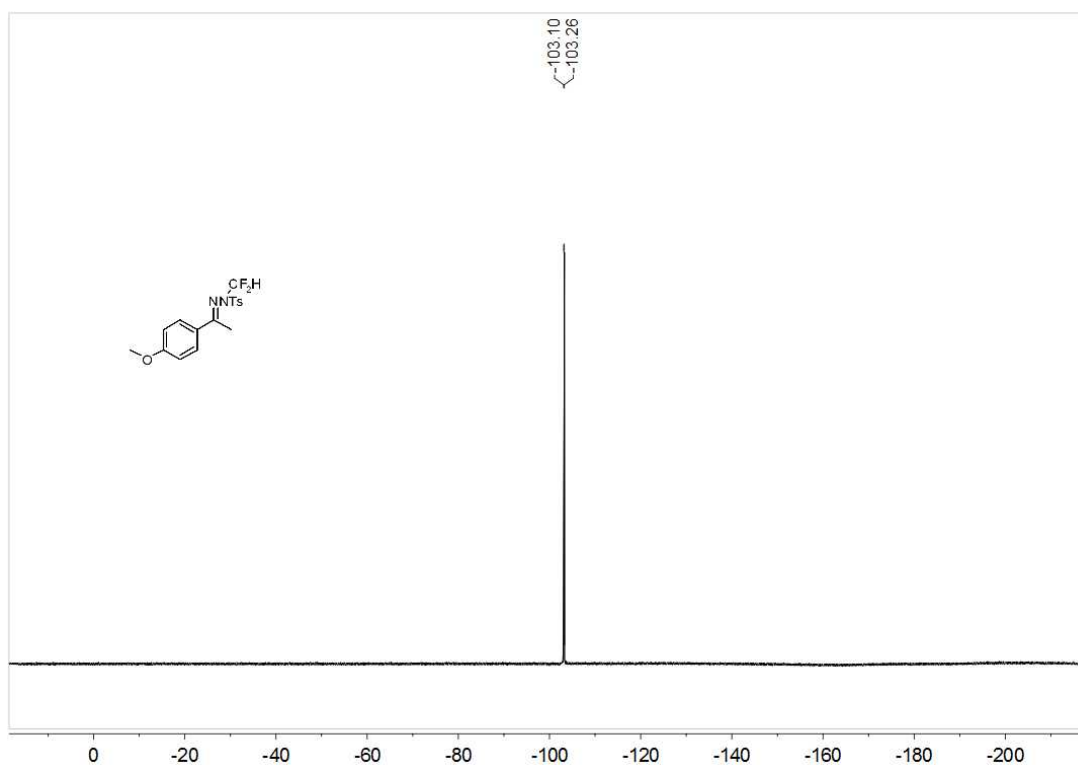
**<sup>1</sup>H NMR spectrum of 2i:**



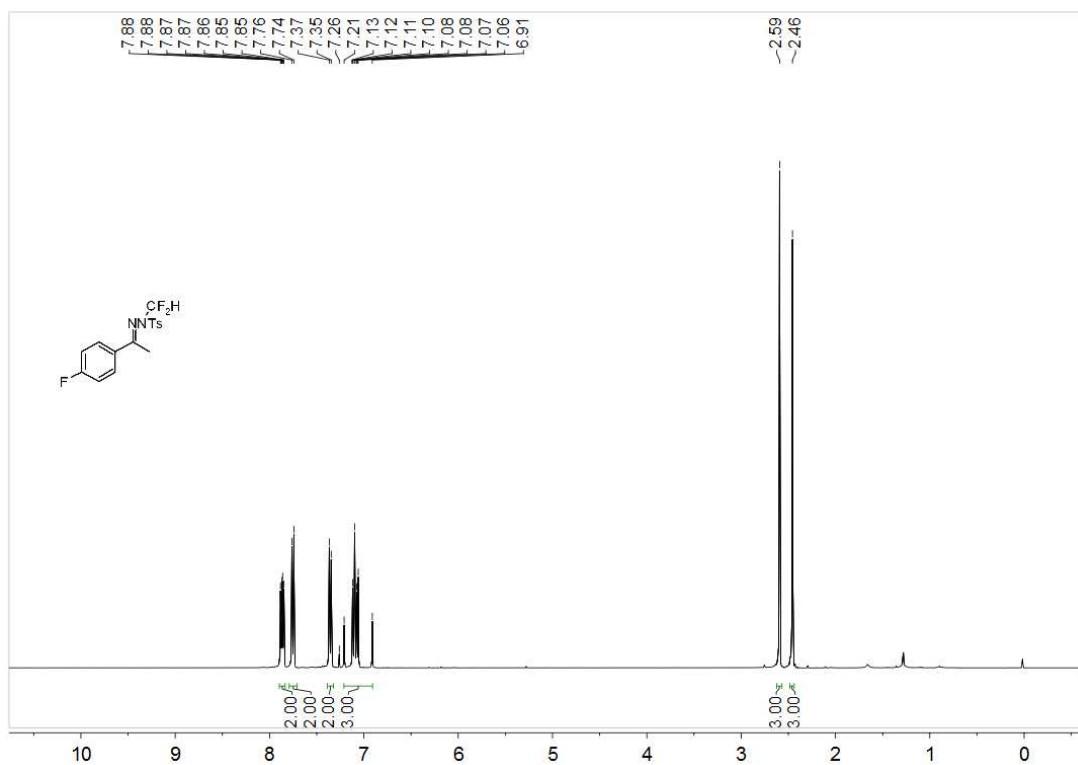
**<sup>13</sup>C NMR spectrum of 2i:**



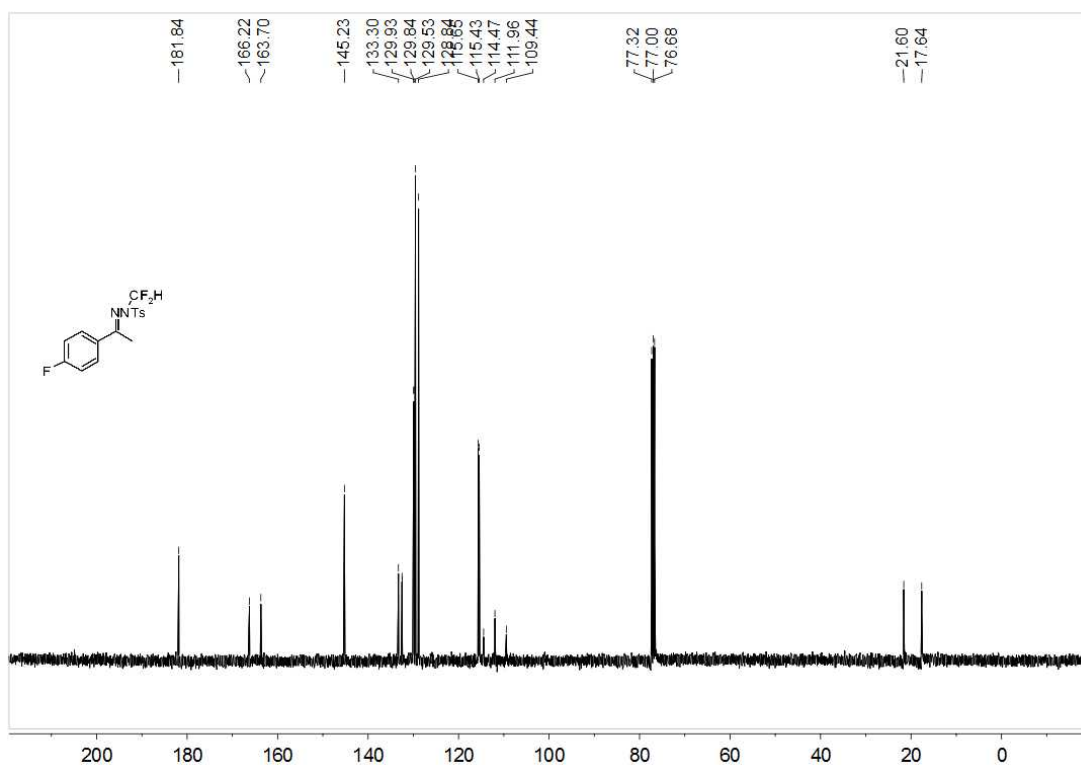
**<sup>19</sup>F NMR spectrum of 2i:**



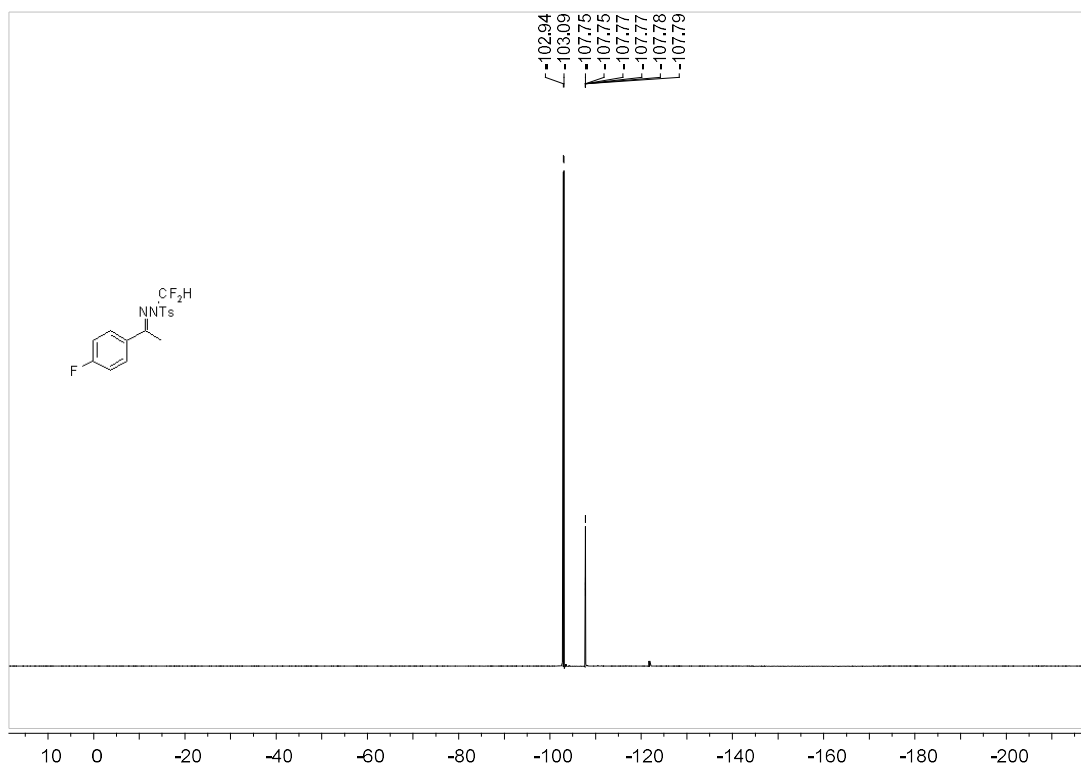
**<sup>1</sup>H NMR spectrum of 2j:**



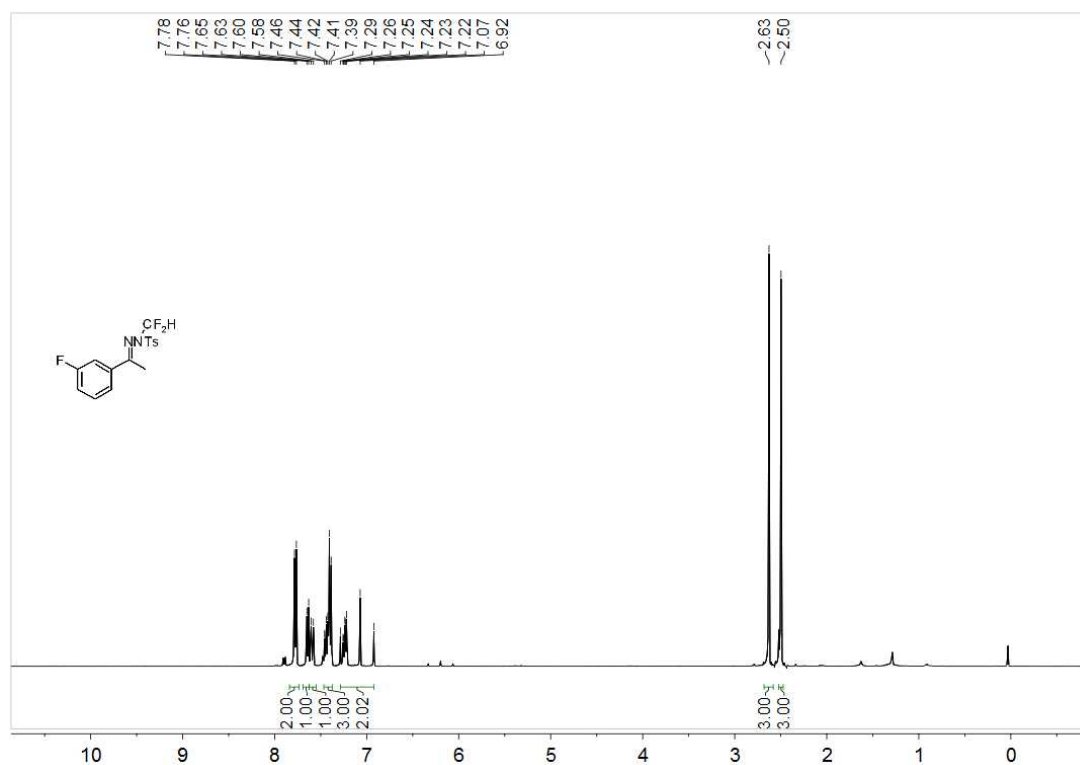
**<sup>13</sup>C NMR spectrum of 2j:**



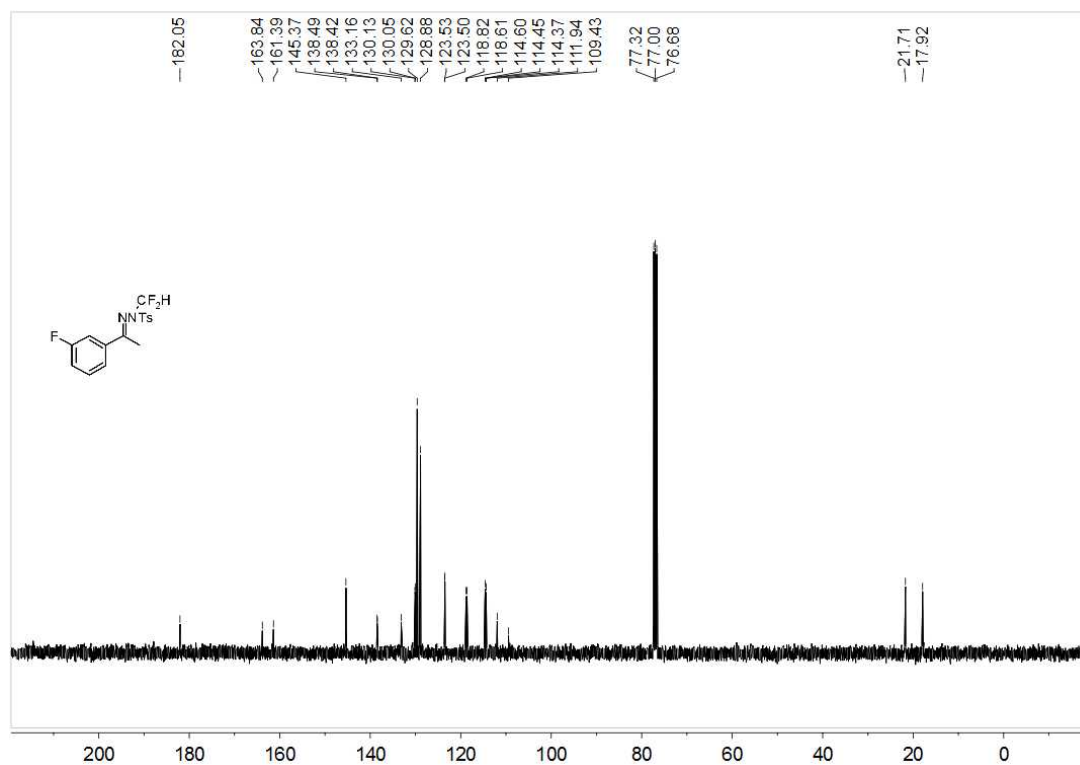
**<sup>19</sup>F NMR spectrum of 2j:**



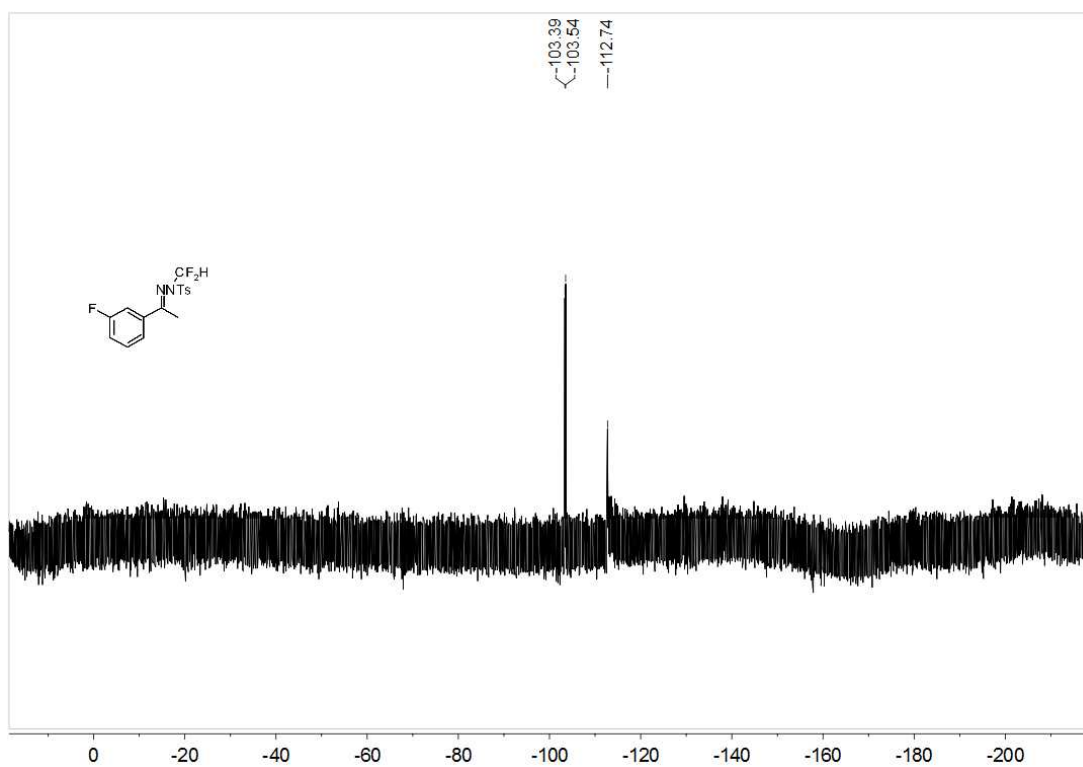
**<sup>1</sup>H NMR spectrum of 2k:**



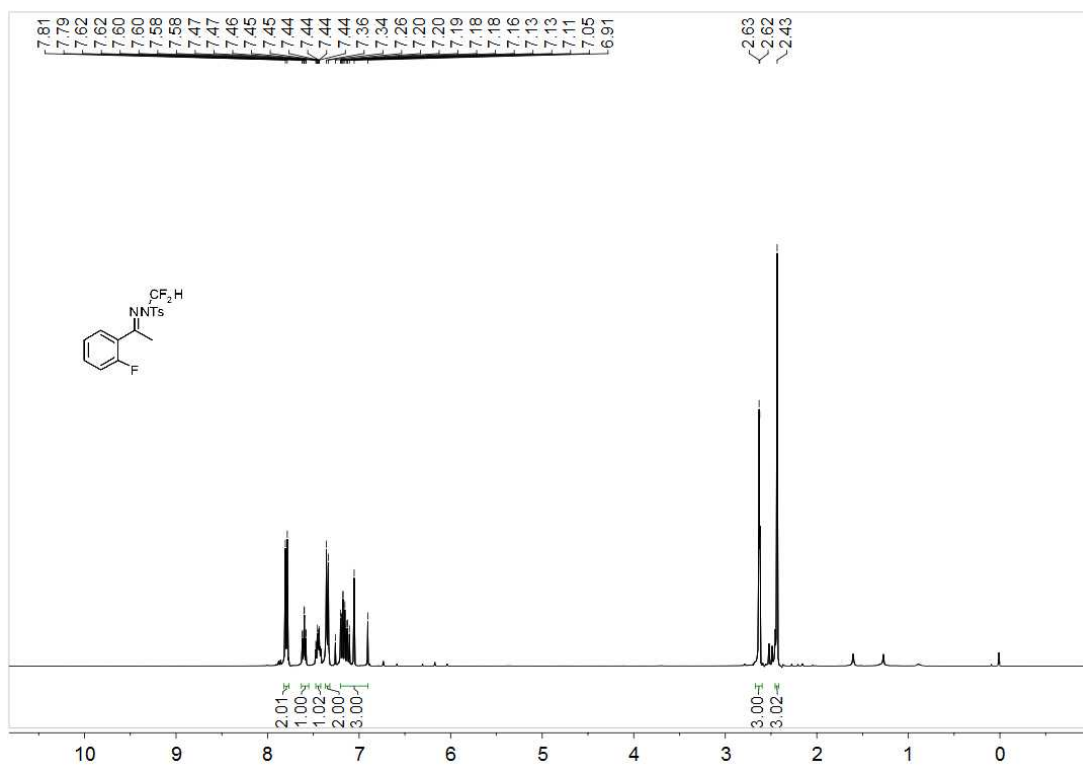
**<sup>13</sup>C NMR spectrum of 2k:**



**<sup>19</sup>F NMR spectrum of 2k:**

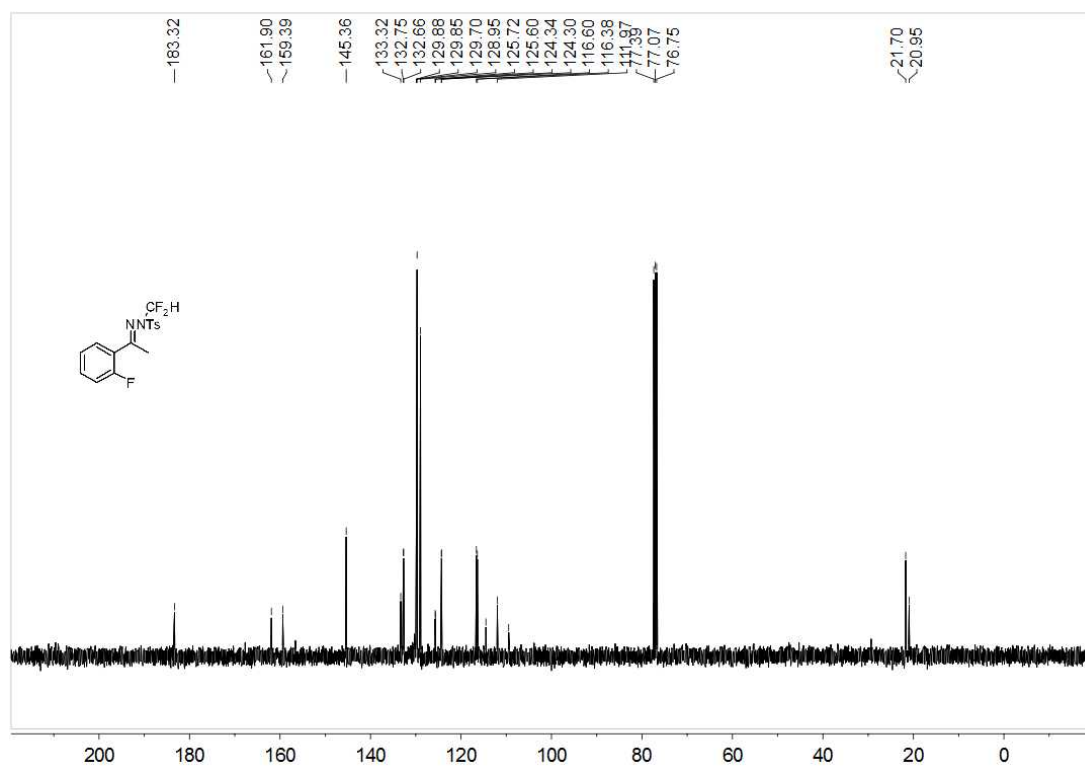


**<sup>1</sup>H NMR spectrum of 2l:**

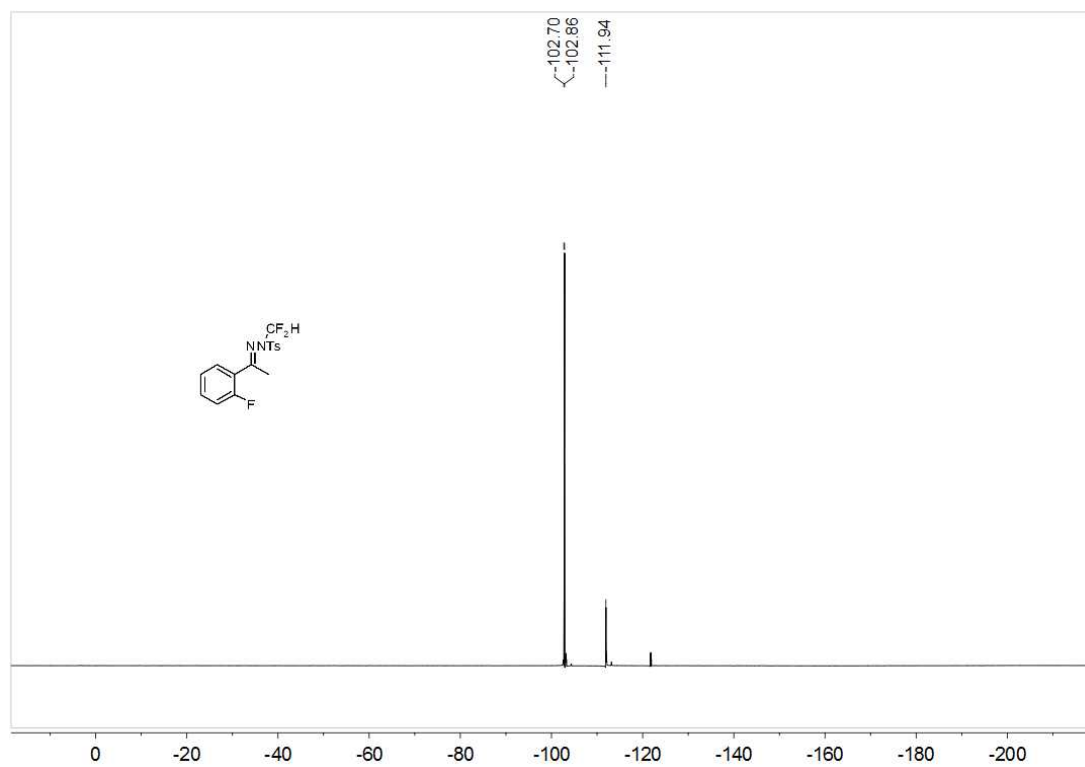




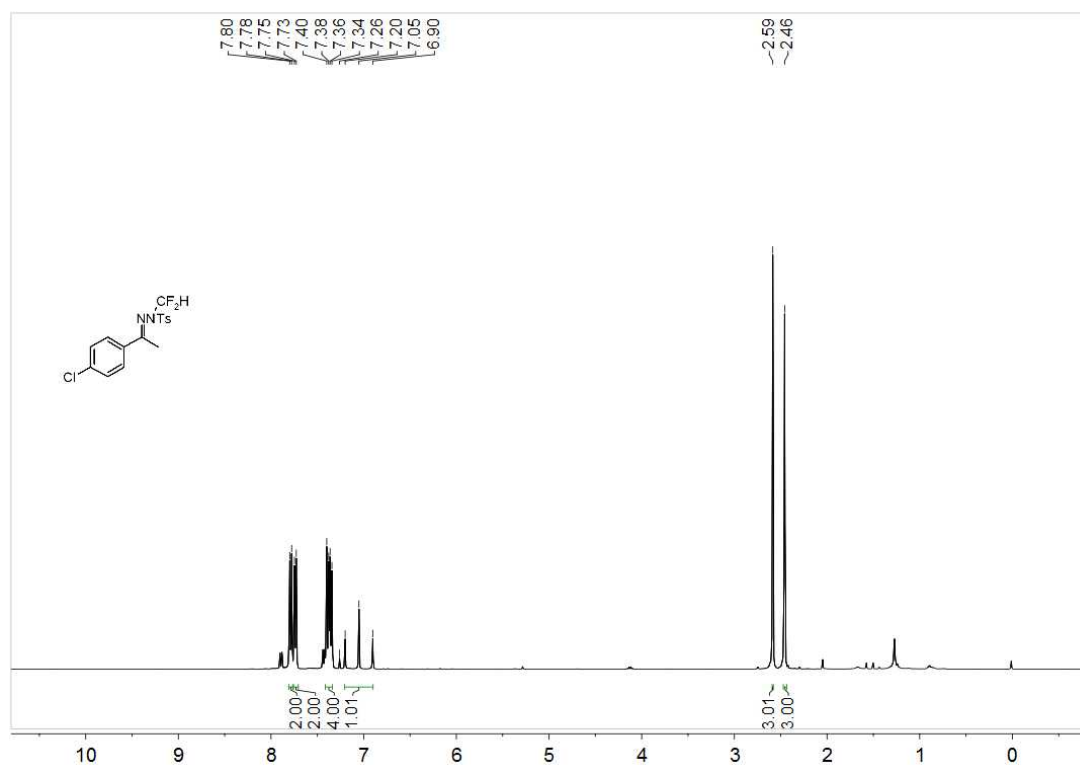
**<sup>13</sup>C NMR spectrum of 2l:**



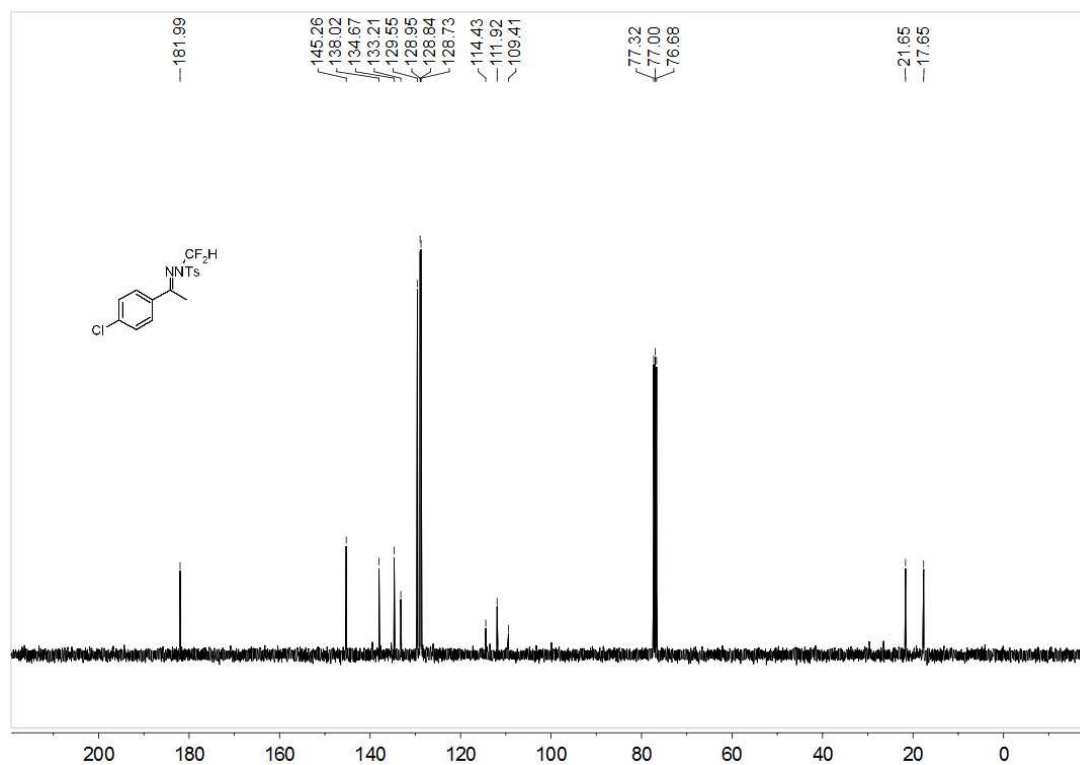
**<sup>19</sup>F NMR spectrum of 2l:**



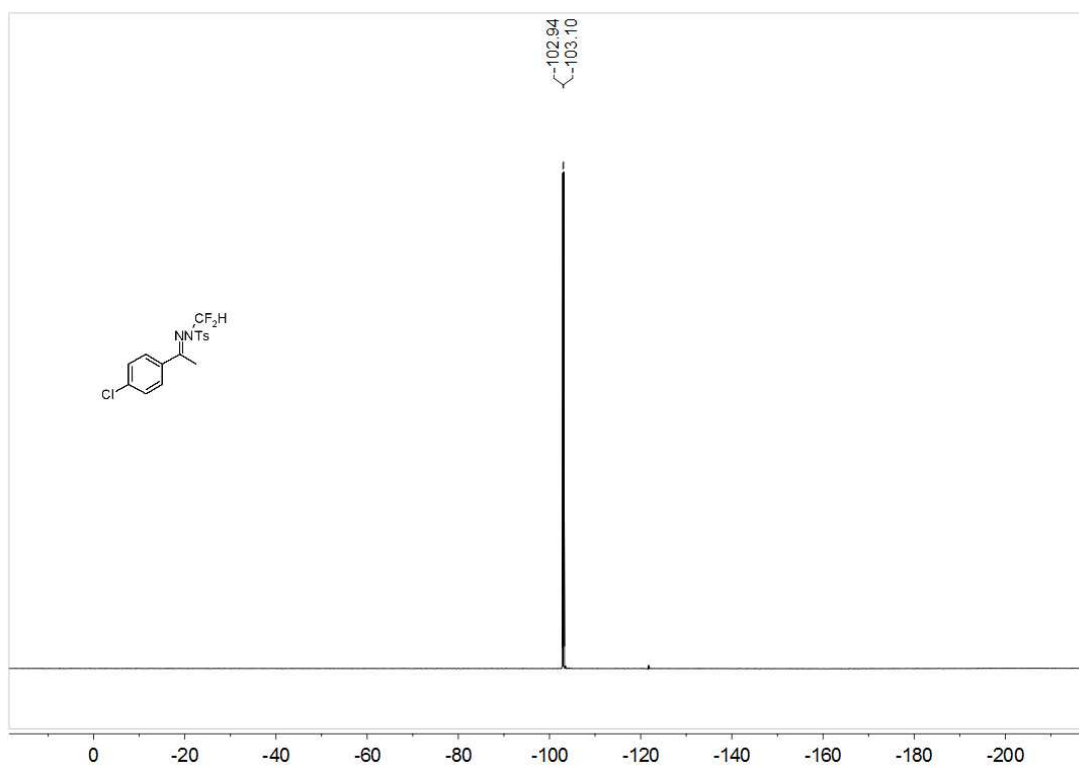
**<sup>1</sup>H NMR spectrum of 2m:**



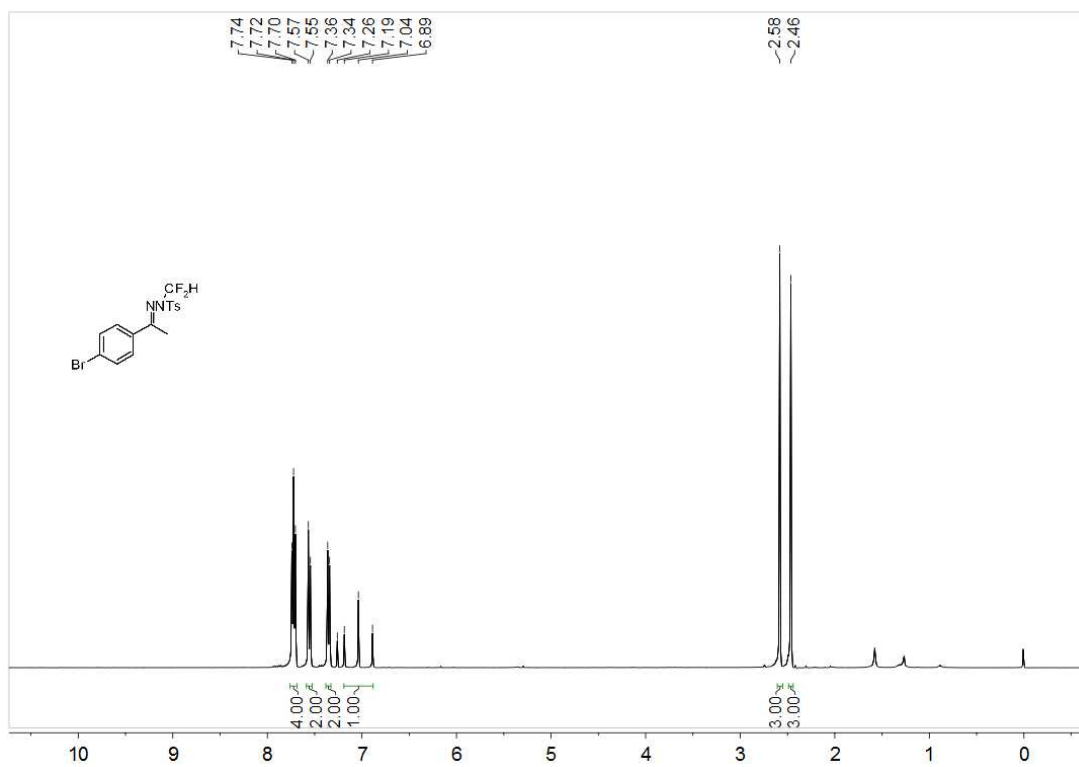
**<sup>13</sup>C NMR spectrum of 2m:**



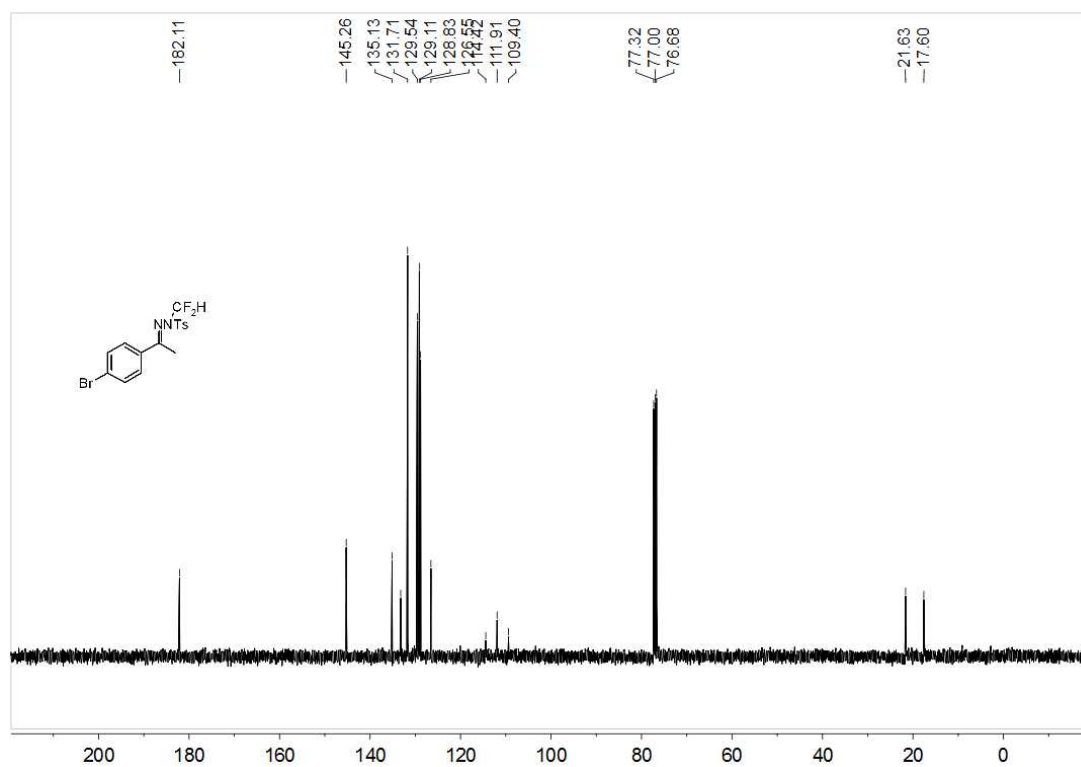
**$^{19}\text{F}$  NMR spectrum of 2m:**



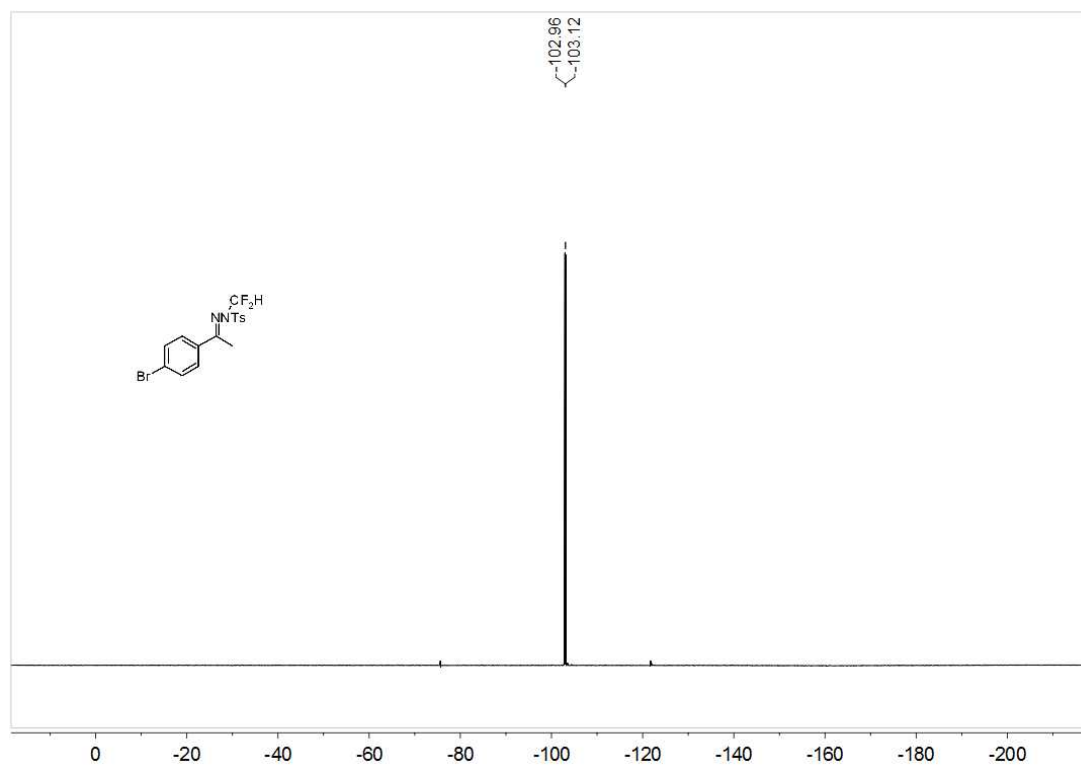
**$^1\text{H}$  NMR spectrum of 2n:**



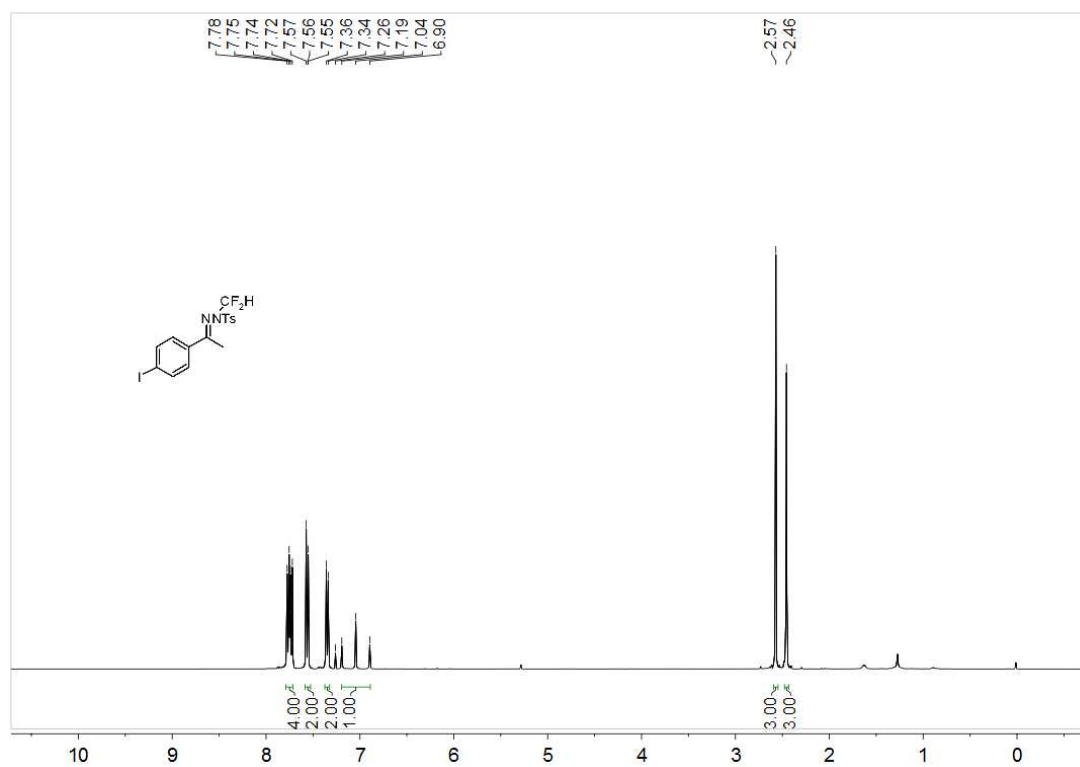
**<sup>13</sup>C NMR spectrum of 2n:**



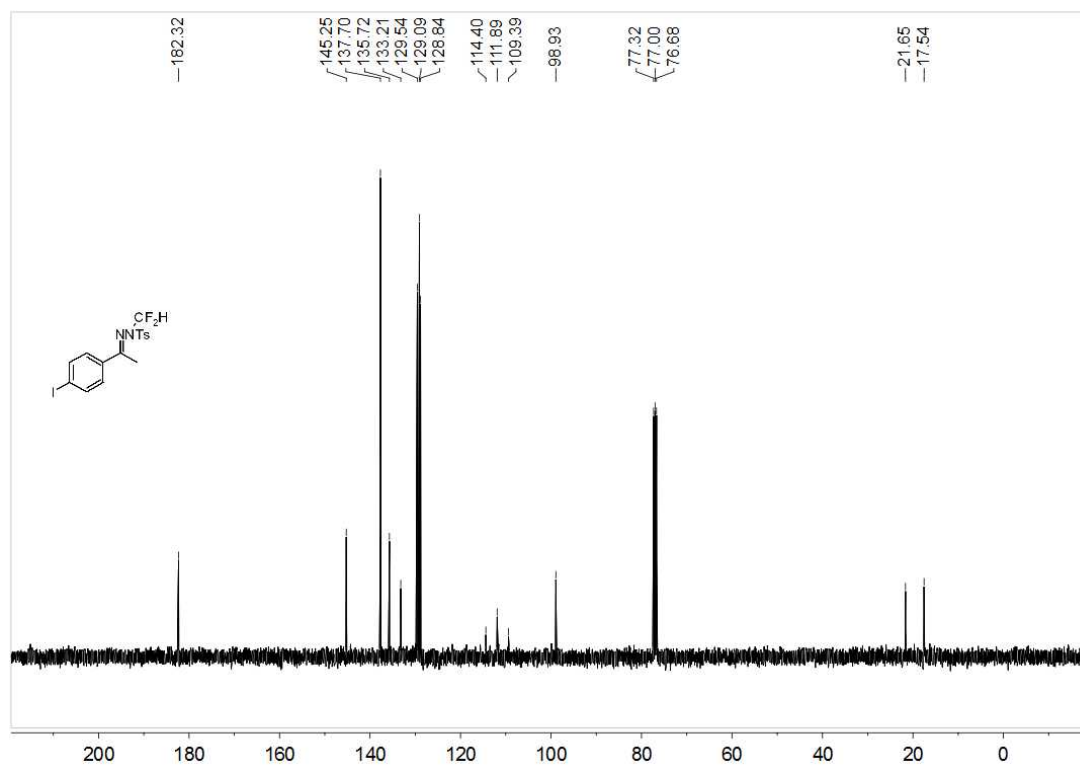
**<sup>19</sup>F NMR spectrum of 2n:**



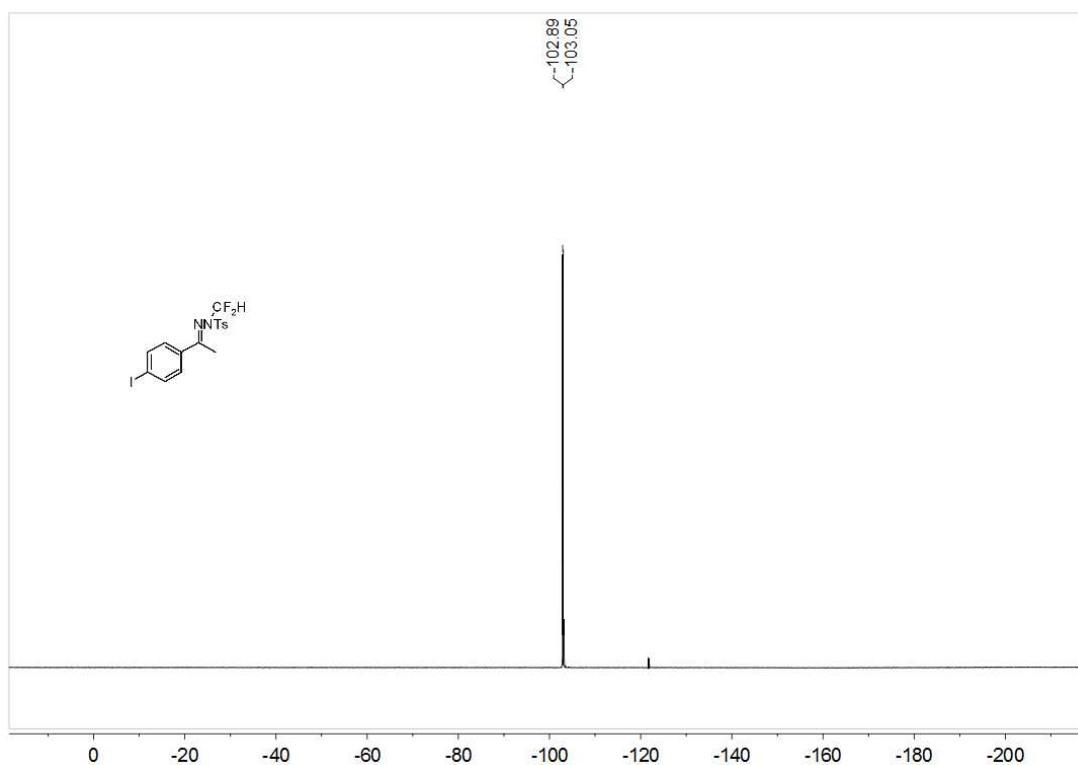
**<sup>1</sup>H NMR spectrum of 2o:**



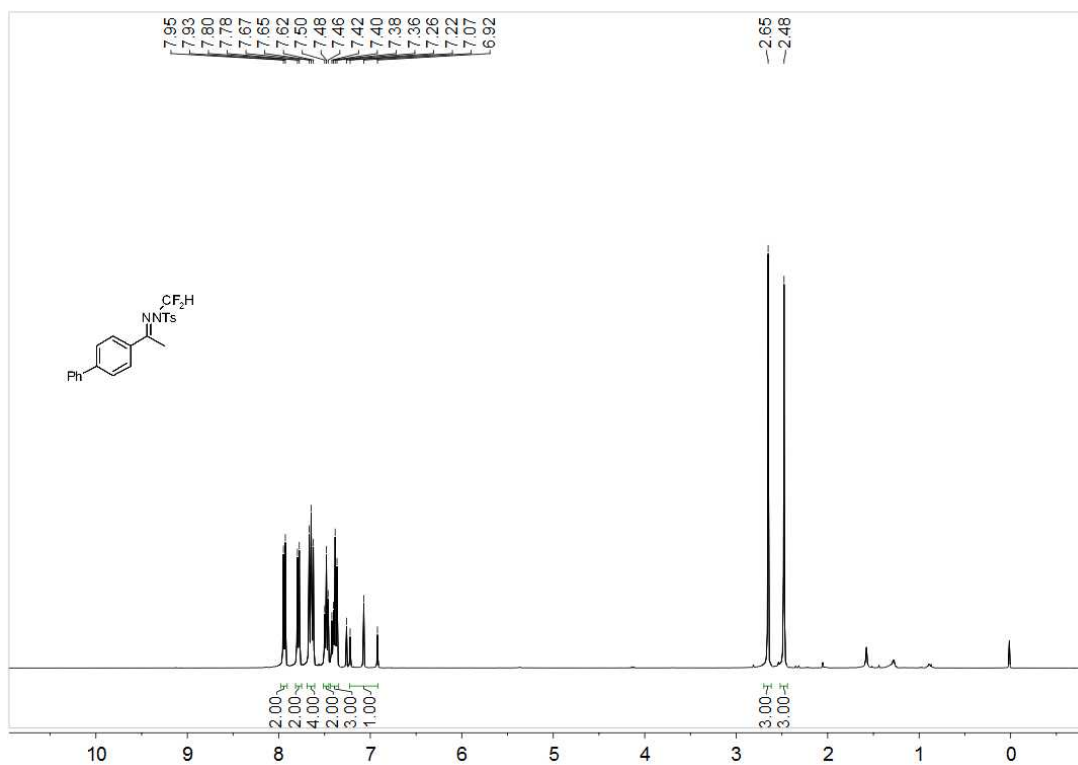
**<sup>13</sup>C NMR spectrum of 2o:**



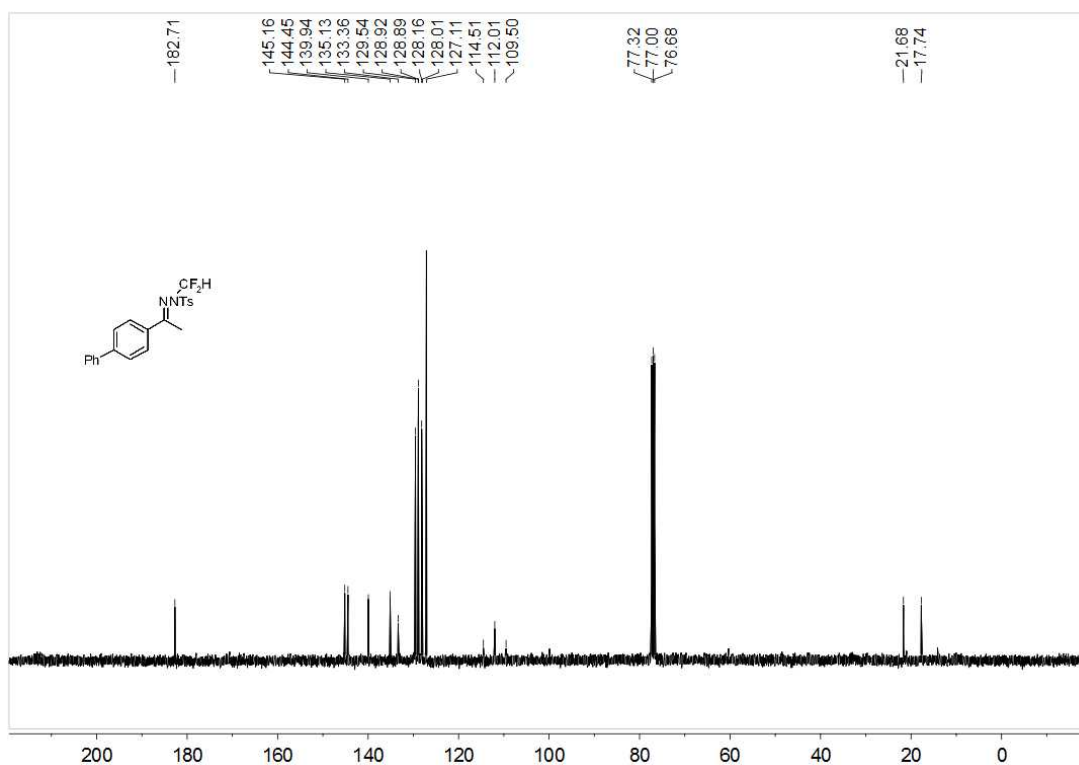
**<sup>19</sup>F NMR spectrum of 2o:**



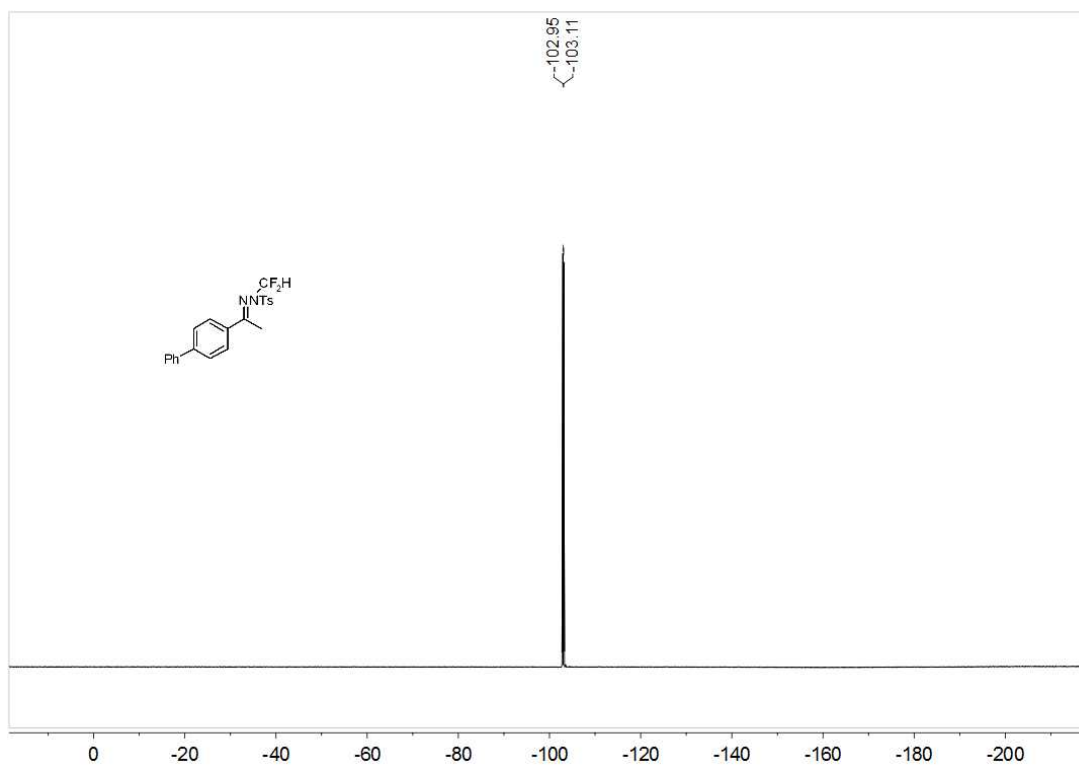
**<sup>1</sup>H NMR spectrum of 2p:**



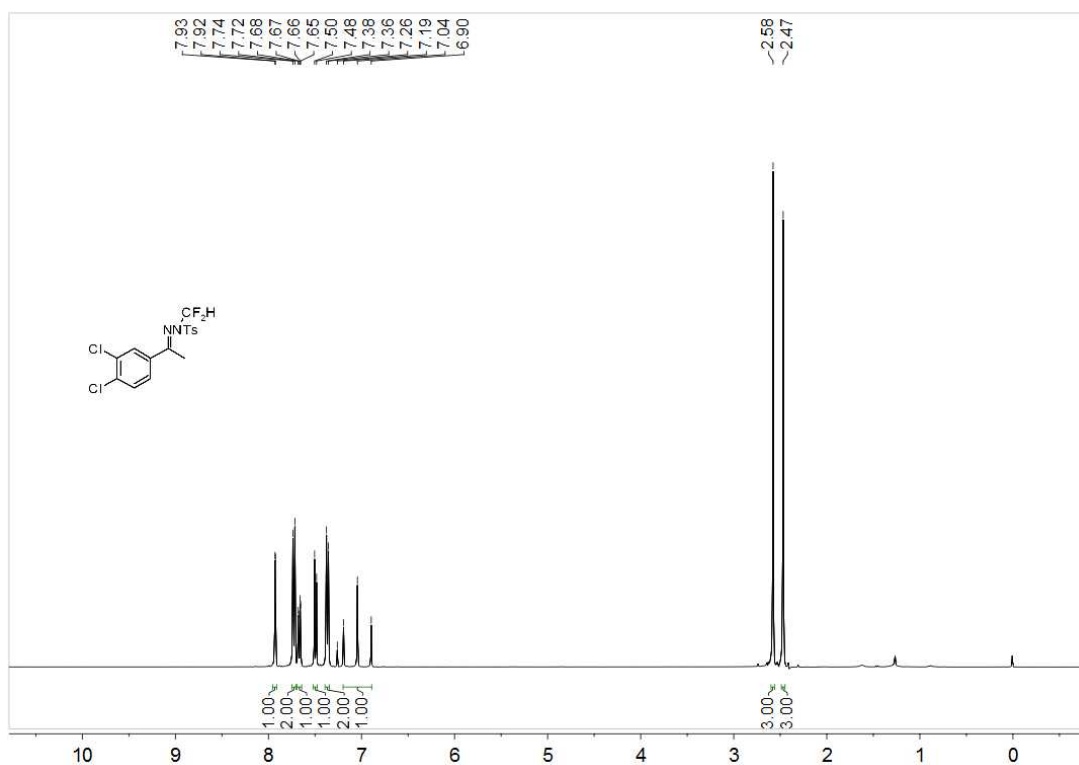
**<sup>13</sup>C NMR spectrum of 2p:**



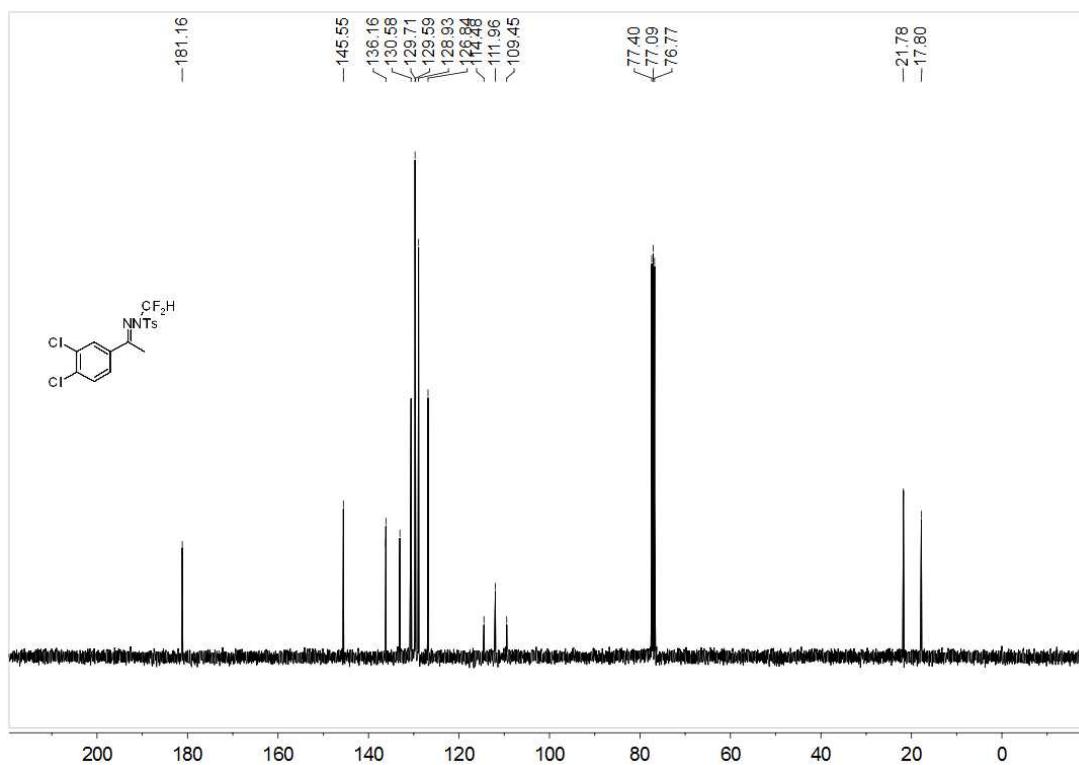
**<sup>19</sup>F NMR spectrum of 2p:**



**<sup>1</sup>H NMR spectrum of 2q:**

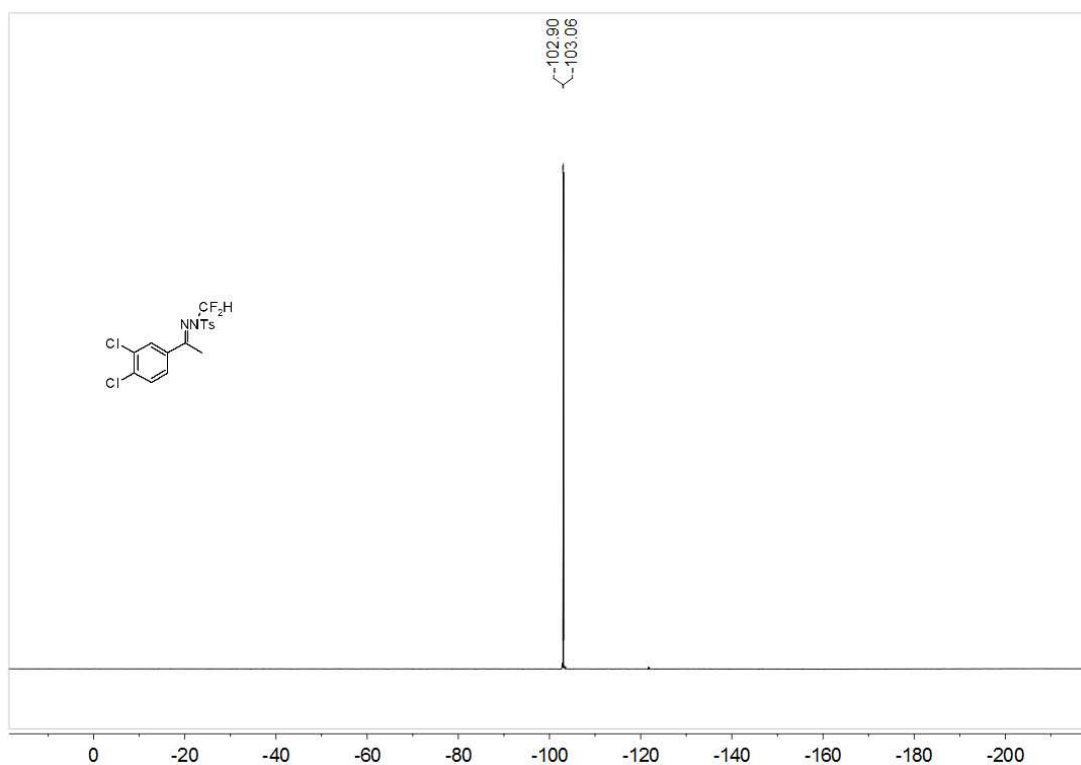


**<sup>13</sup>C NMR spectrum of 2q:**

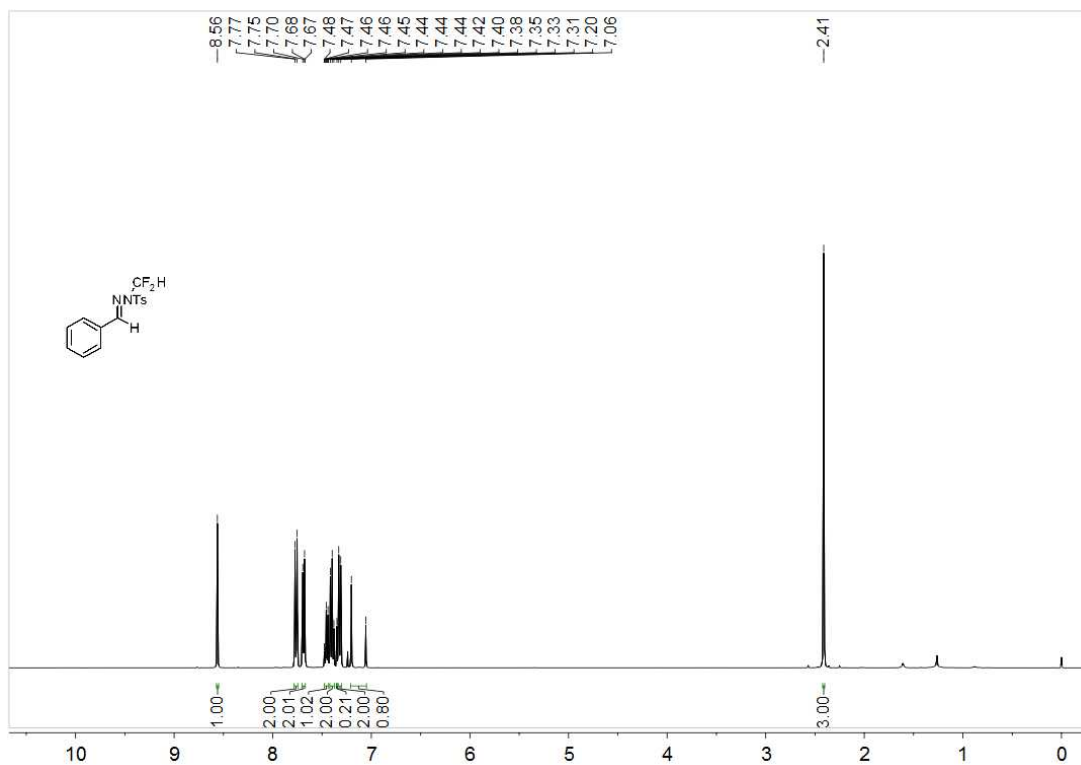




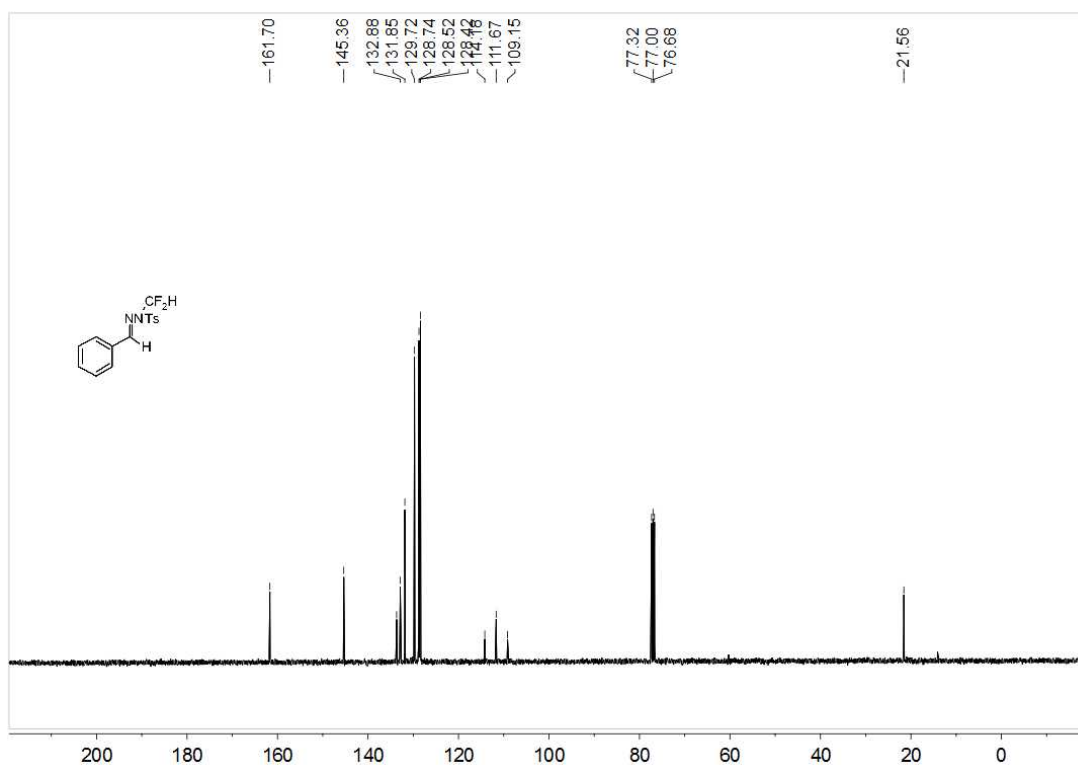
**<sup>19</sup>F NMR spectrum of 2q:**



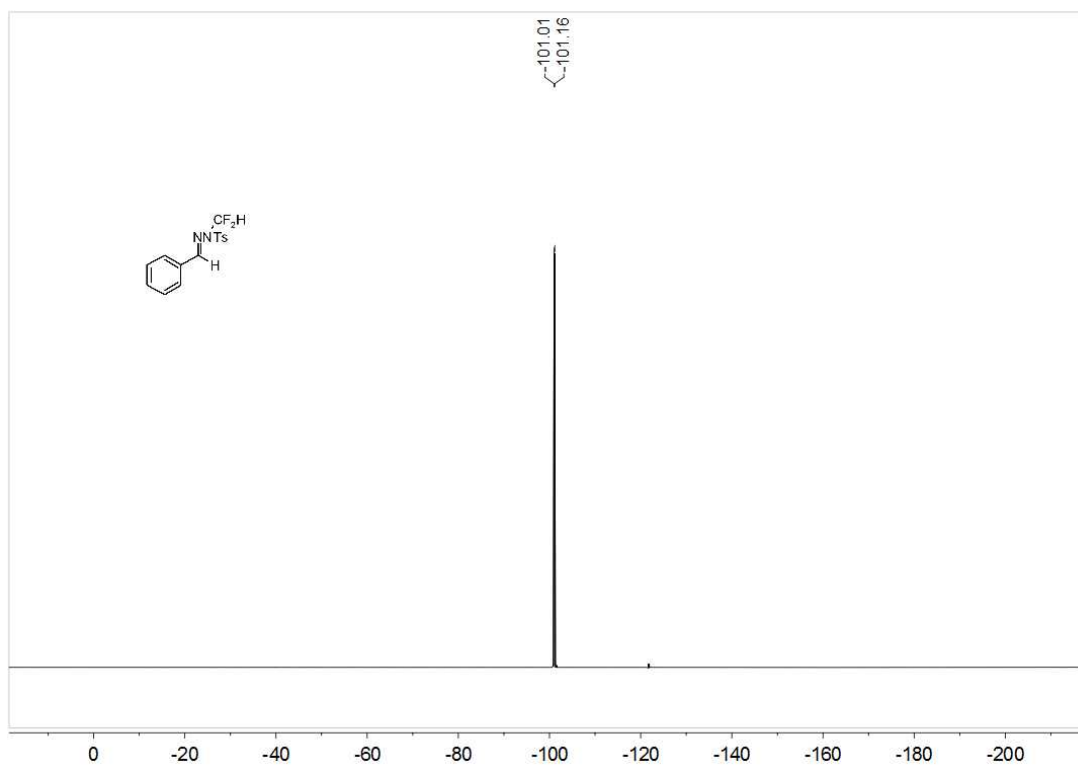
**<sup>1</sup>H NMR spectrum of 2r:**



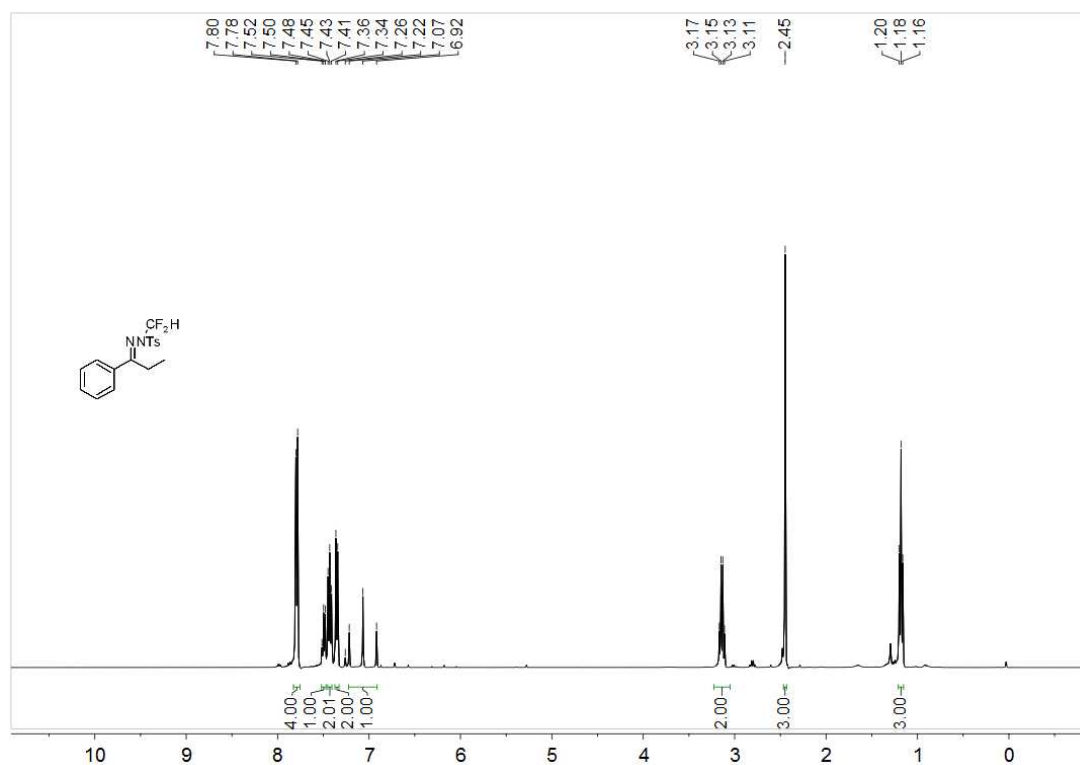
**<sup>13</sup>C NMR spectrum of 2r:**



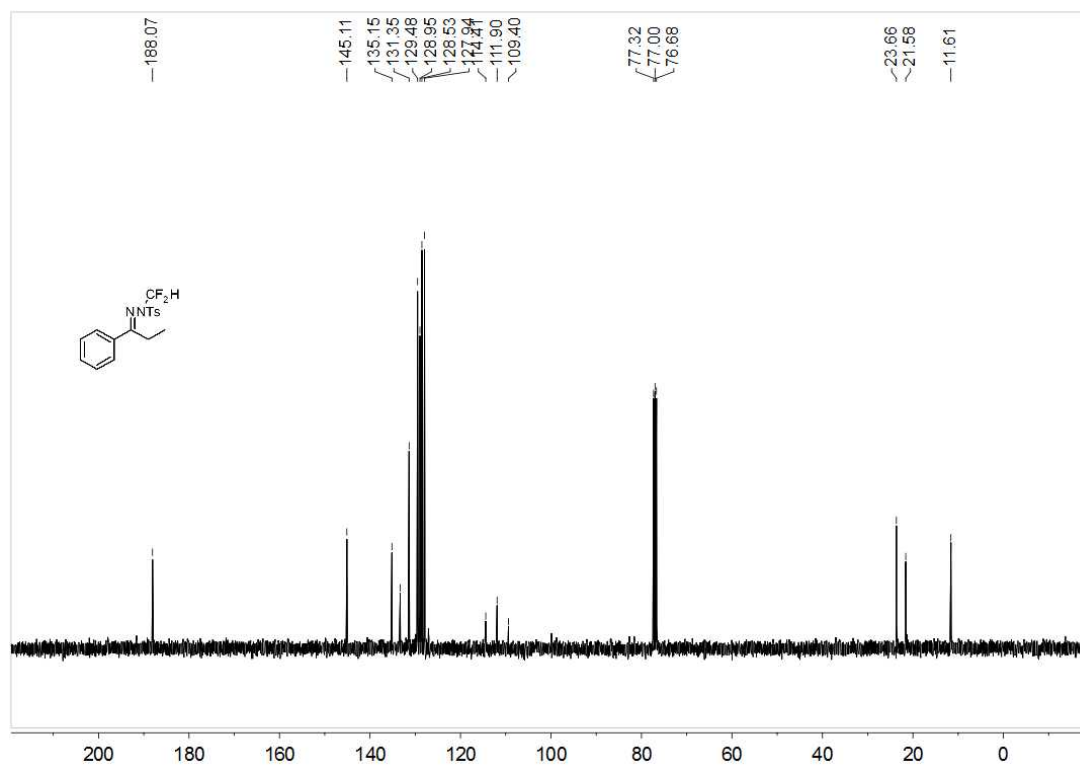
**<sup>19</sup>F NMR spectrum of 2r:**



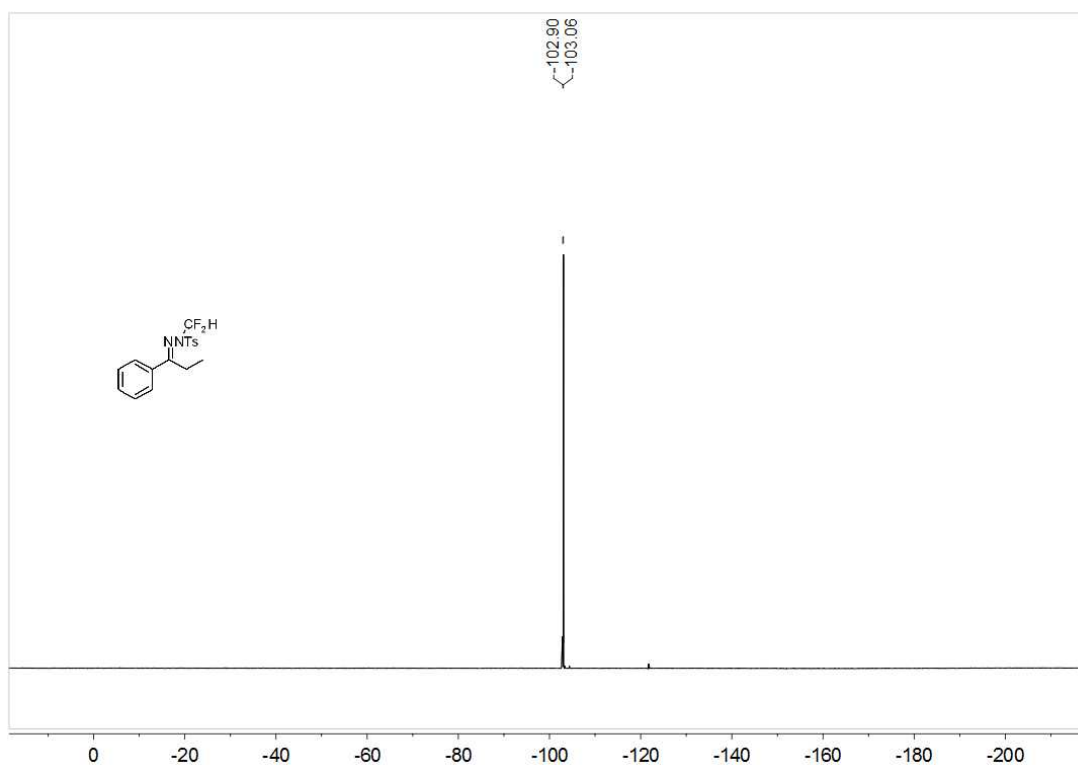
**<sup>1</sup>H NMR spectrum of 2s:**



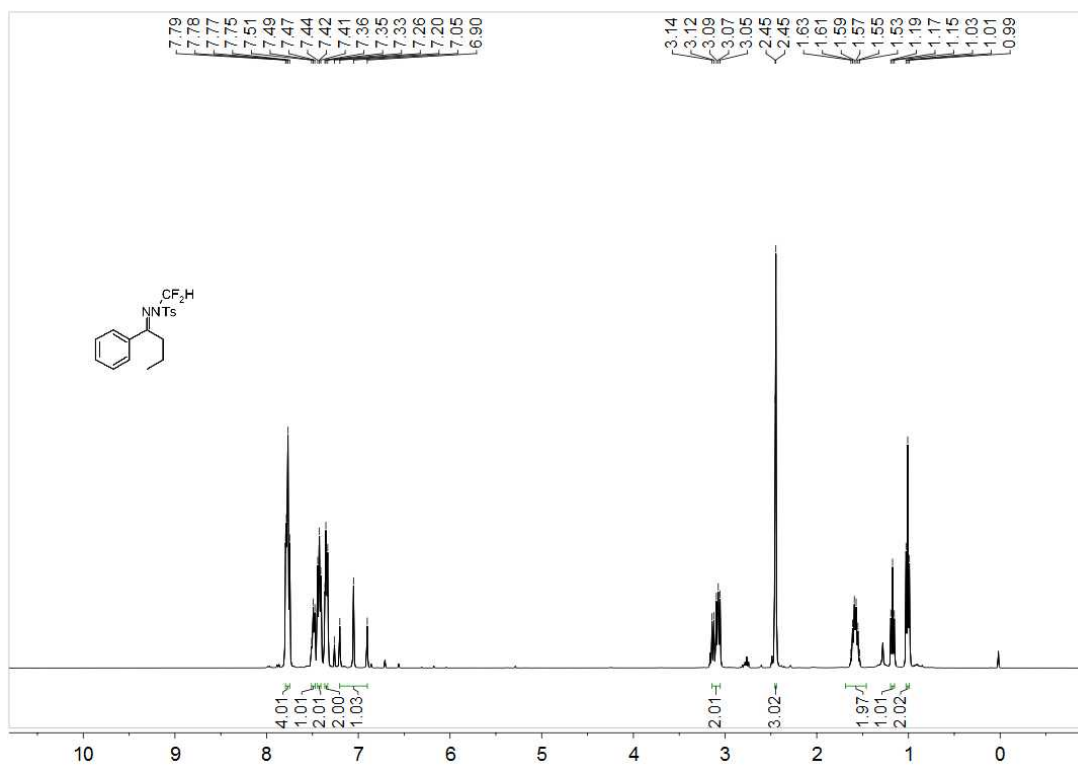
**<sup>13</sup>C NMR spectrum of 2s:**



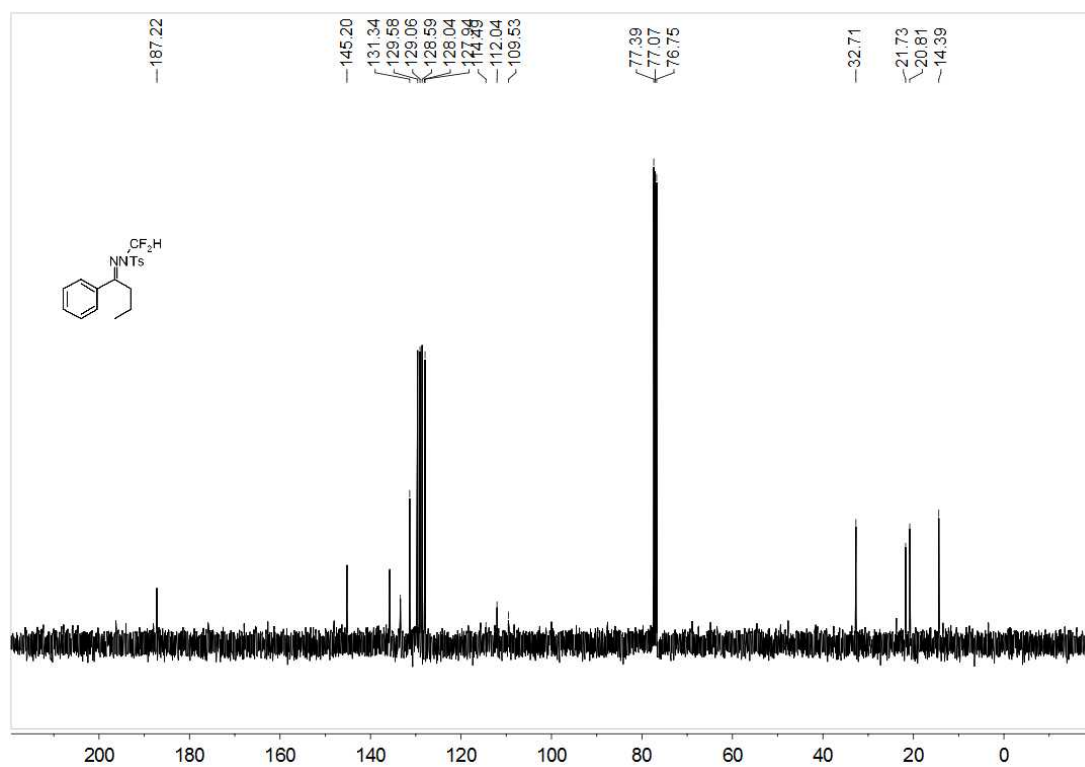
**<sup>19</sup>F NMR spectrum of 2s:**



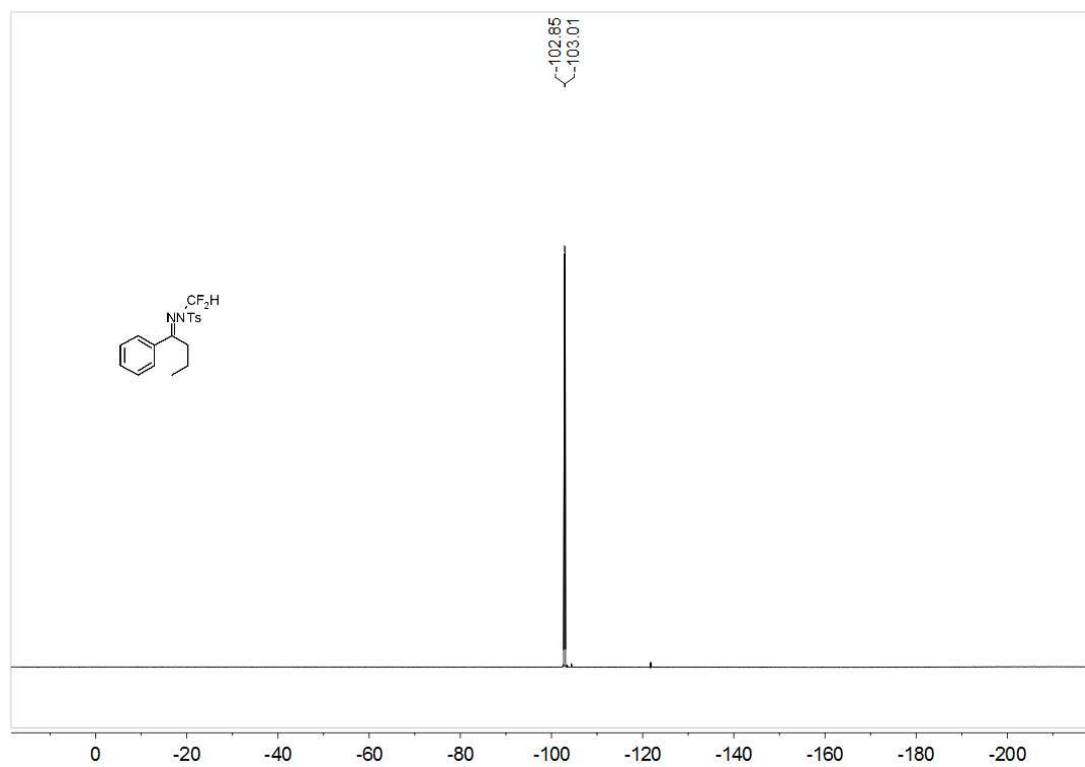
**<sup>1</sup>H NMR spectrum of 2t:**



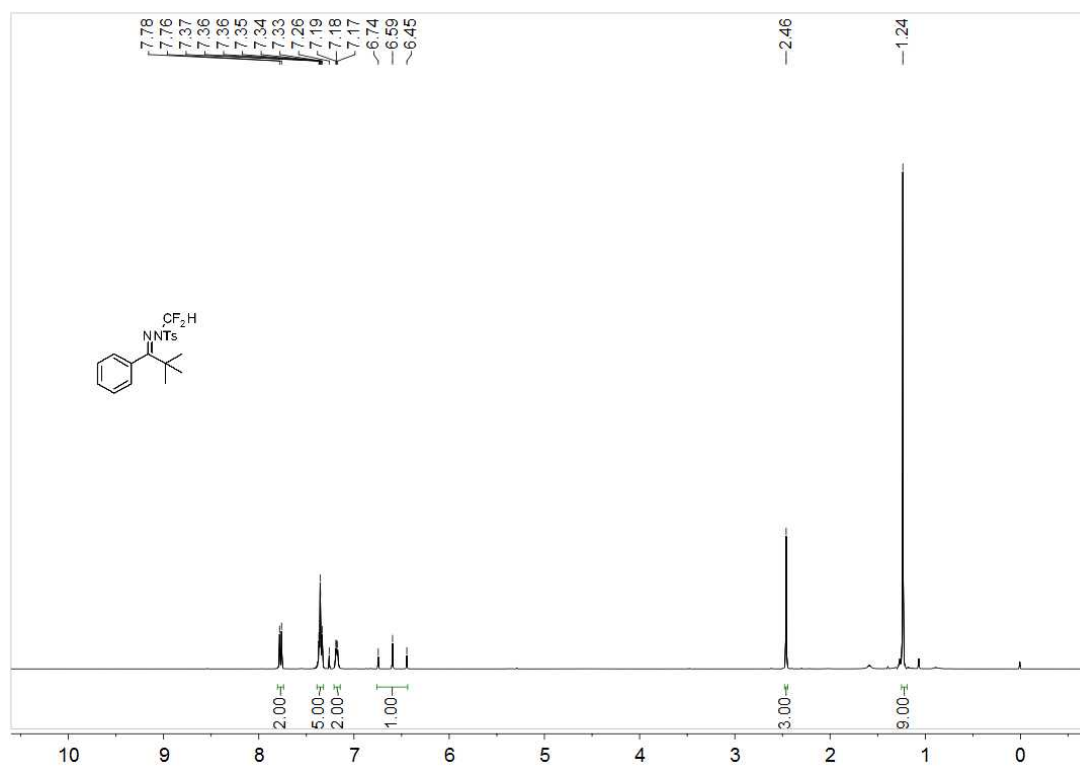
**<sup>13</sup>C NMR spectrum of 2t:**



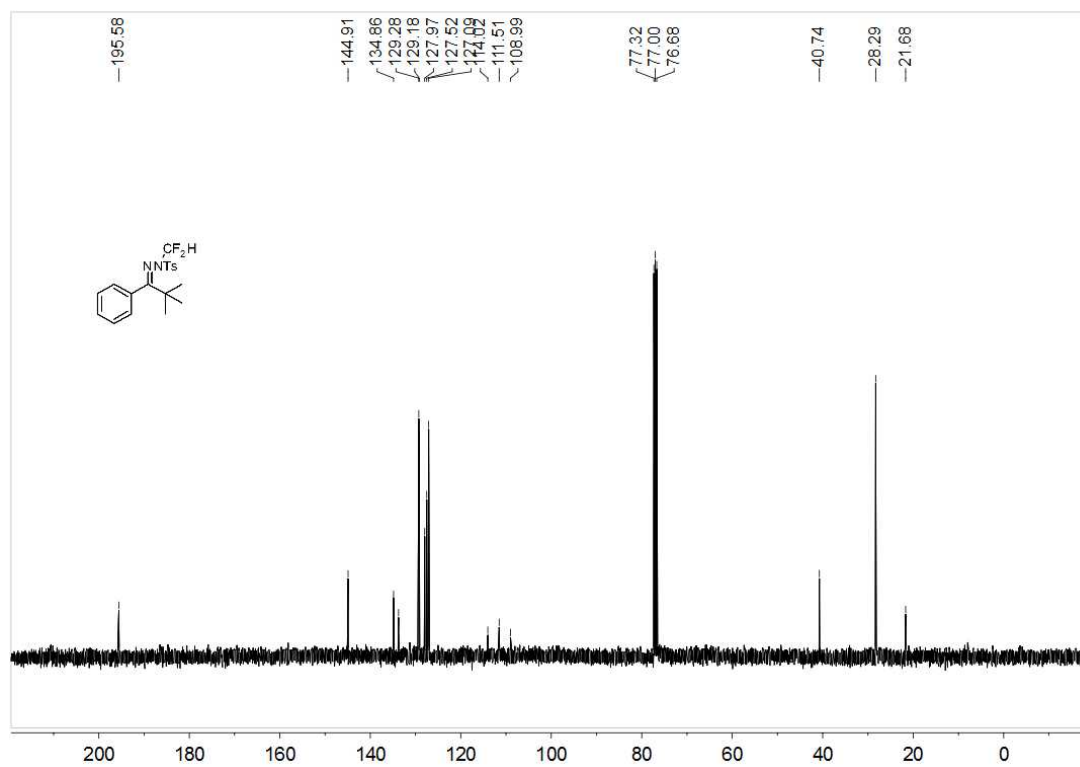
**<sup>19</sup>F NMR spectrum of 2t:**



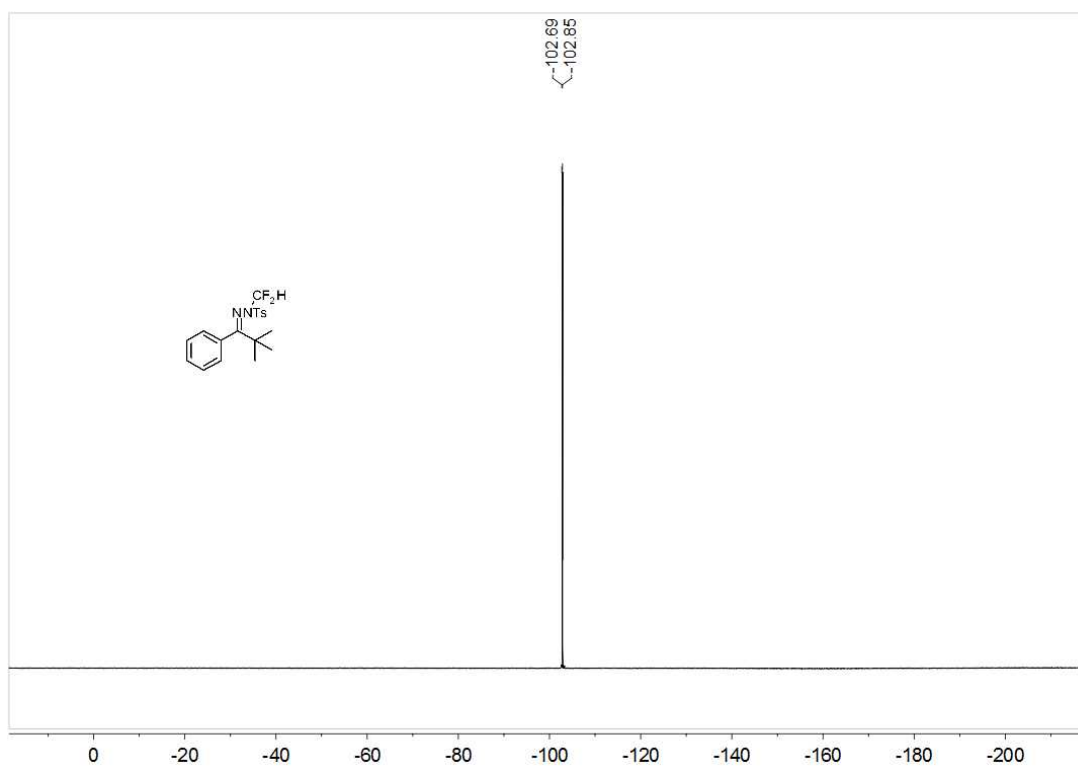
**<sup>1</sup>H NMR spectrum of 2u:**



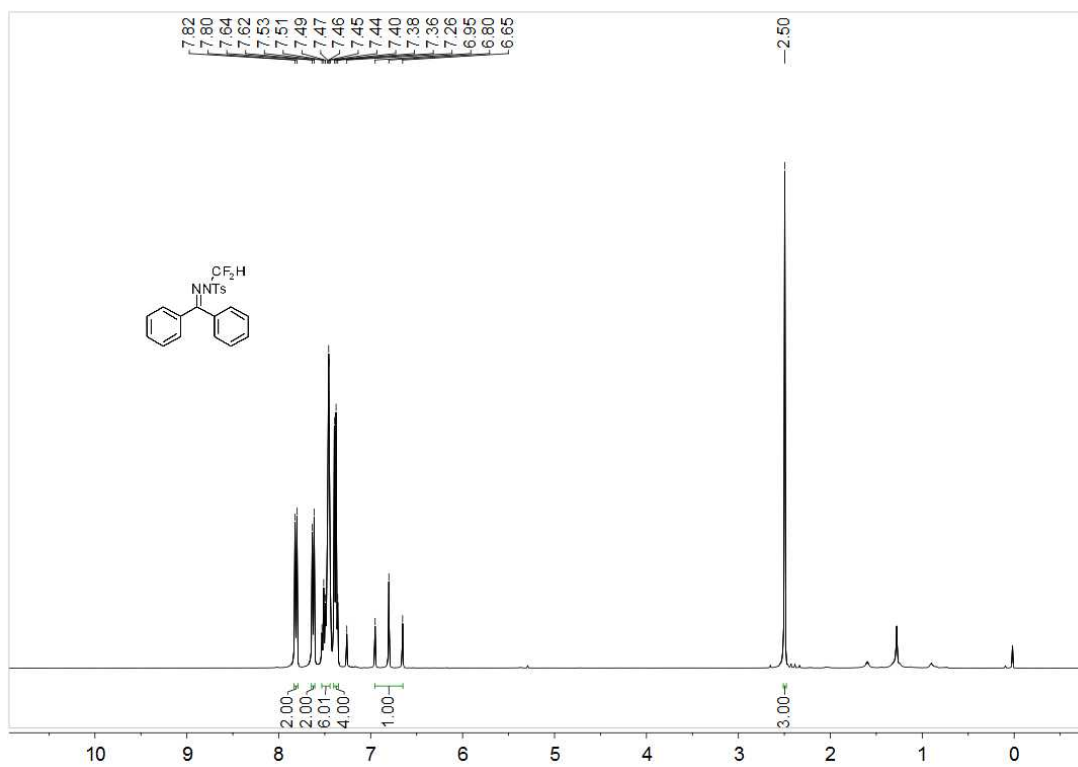
**<sup>13</sup>C NMR spectrum of 2u:**



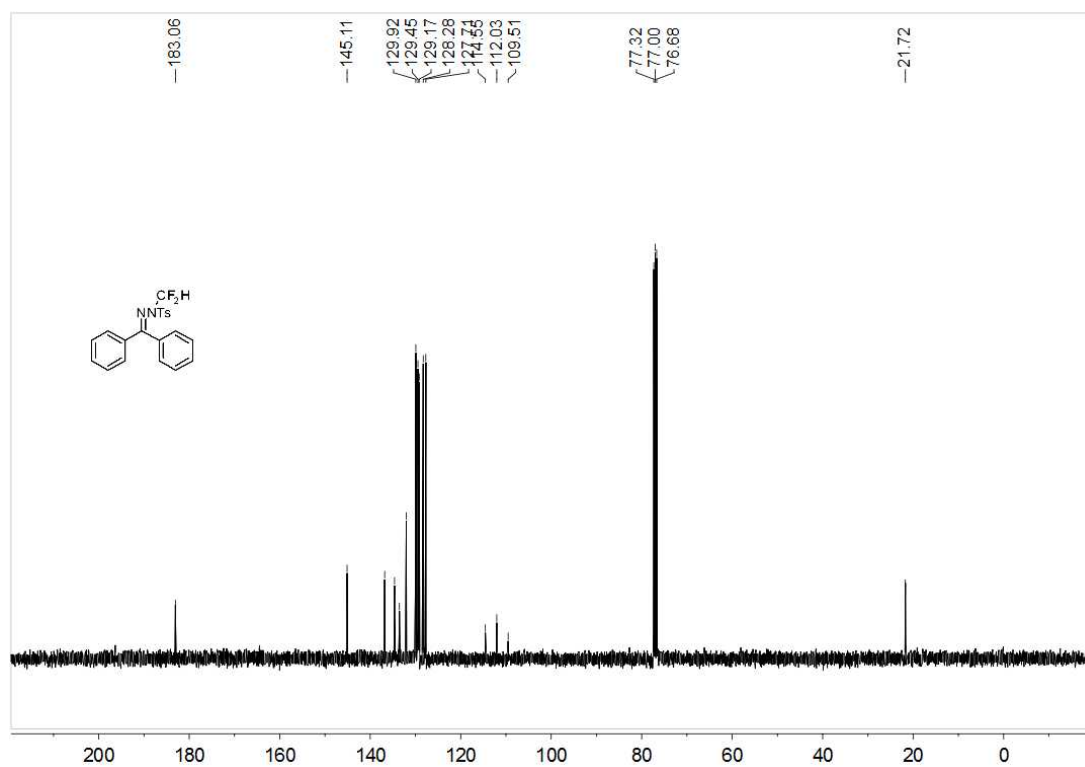
**$^{19}\text{F}$  NMR spectrum of 2u:**



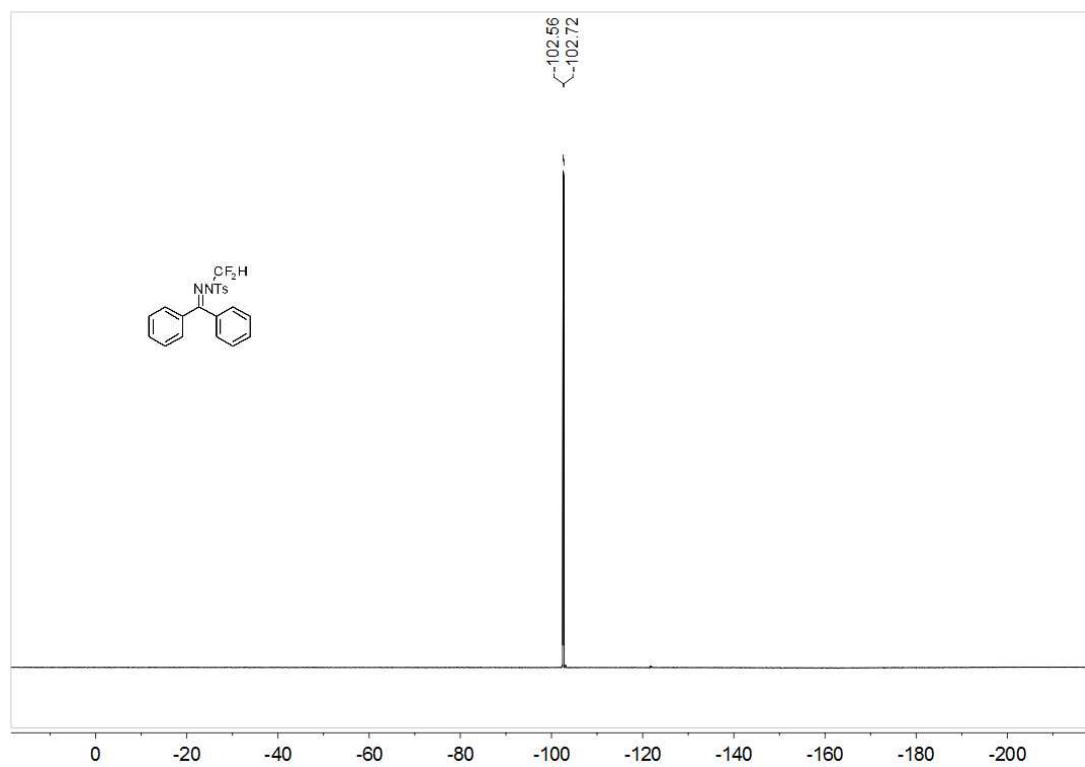
**$^1\text{H}$  NMR spectrum of 2v:**



**<sup>13</sup>C NMR spectrum of 2v:**

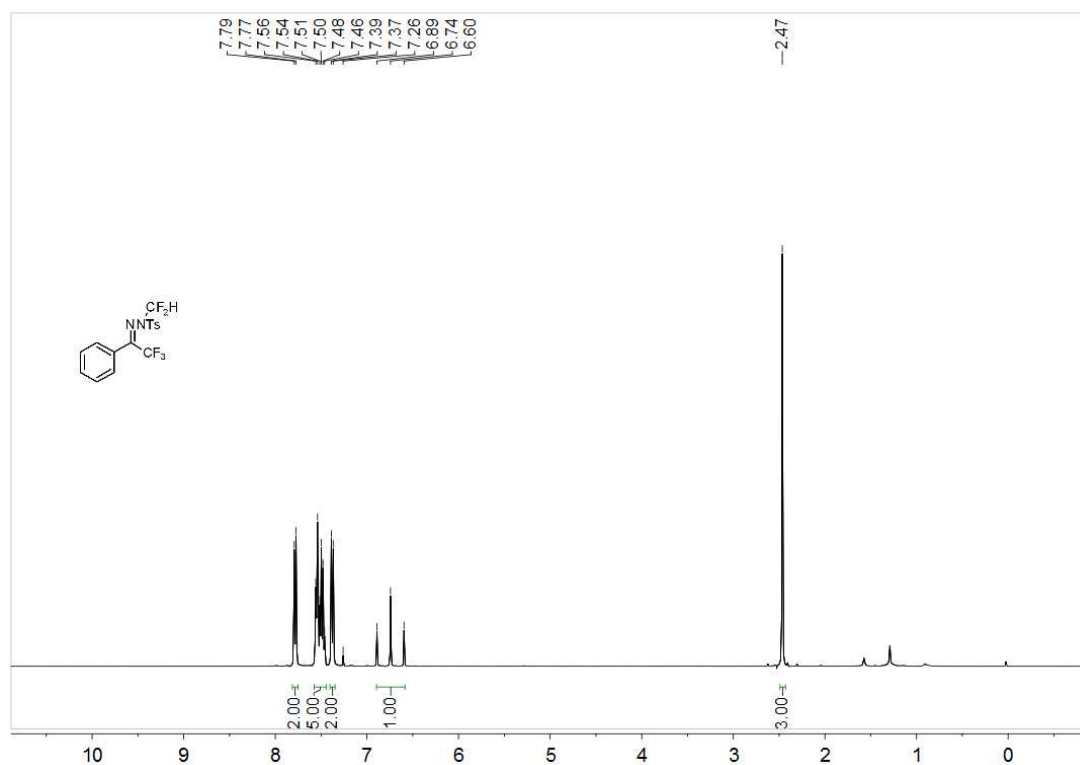


**<sup>19</sup>F NMR spectrum of 2v:**

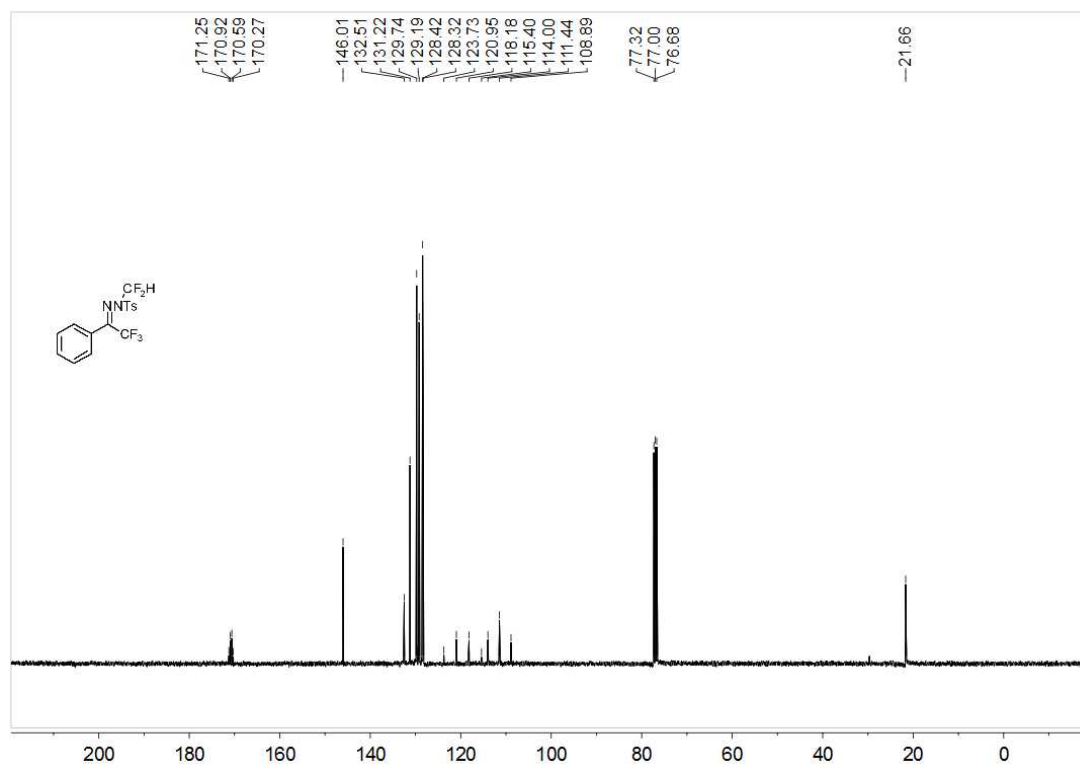




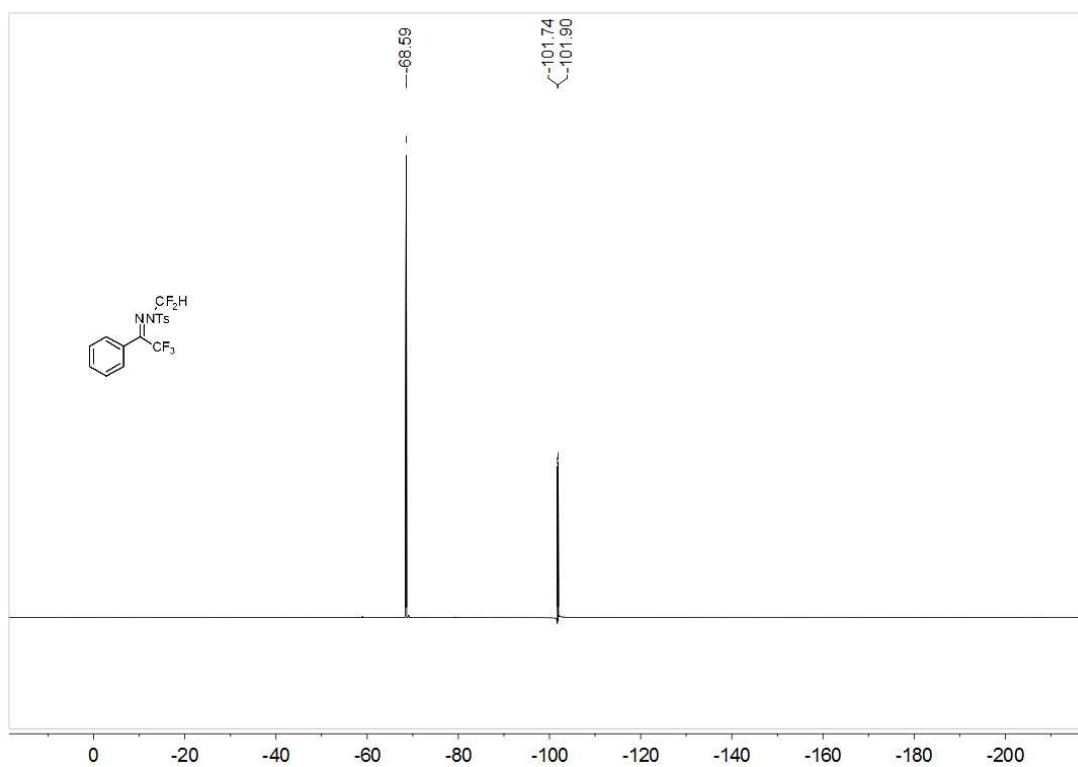
**<sup>1</sup>H NMR spectrum of 2w:**



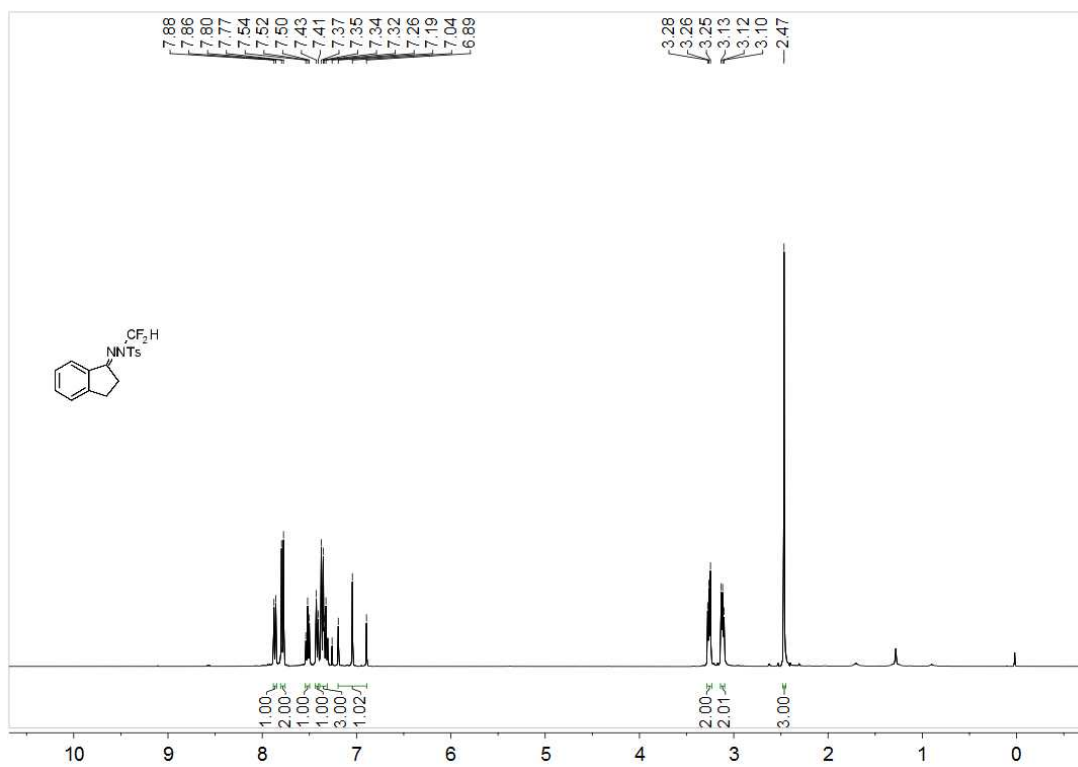
**<sup>13</sup>C NMR spectrum of 2w:**



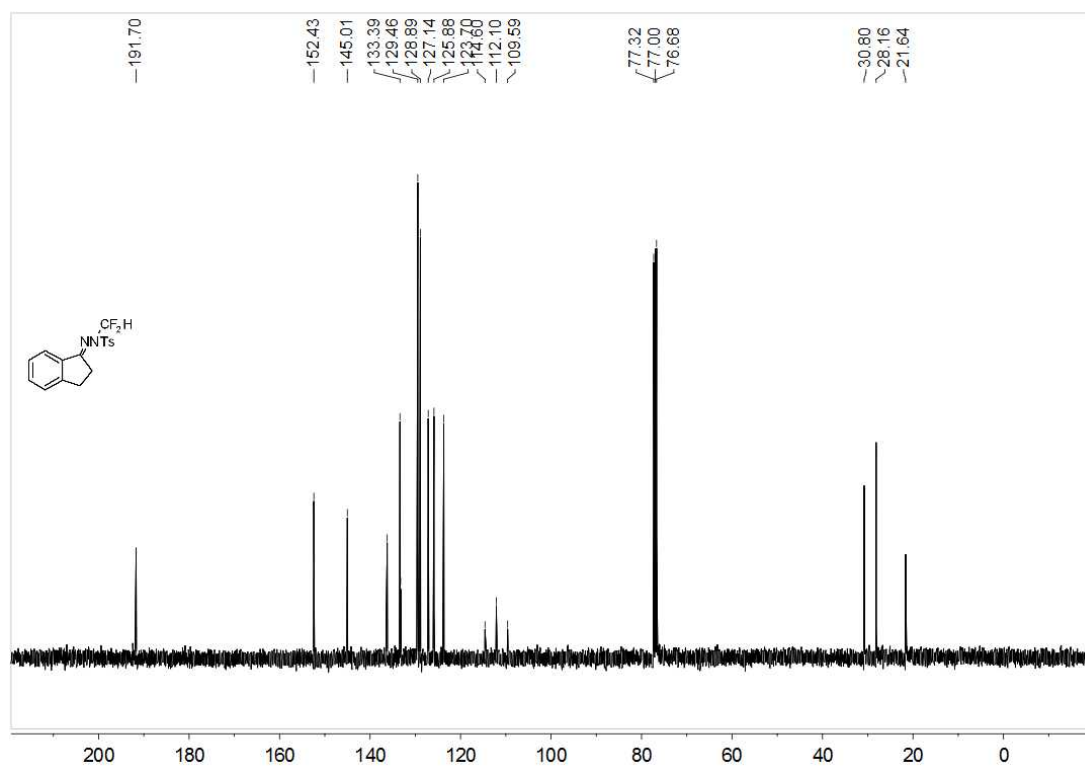
**$^{19}\text{F}$  NMR spectrum of 2w:**



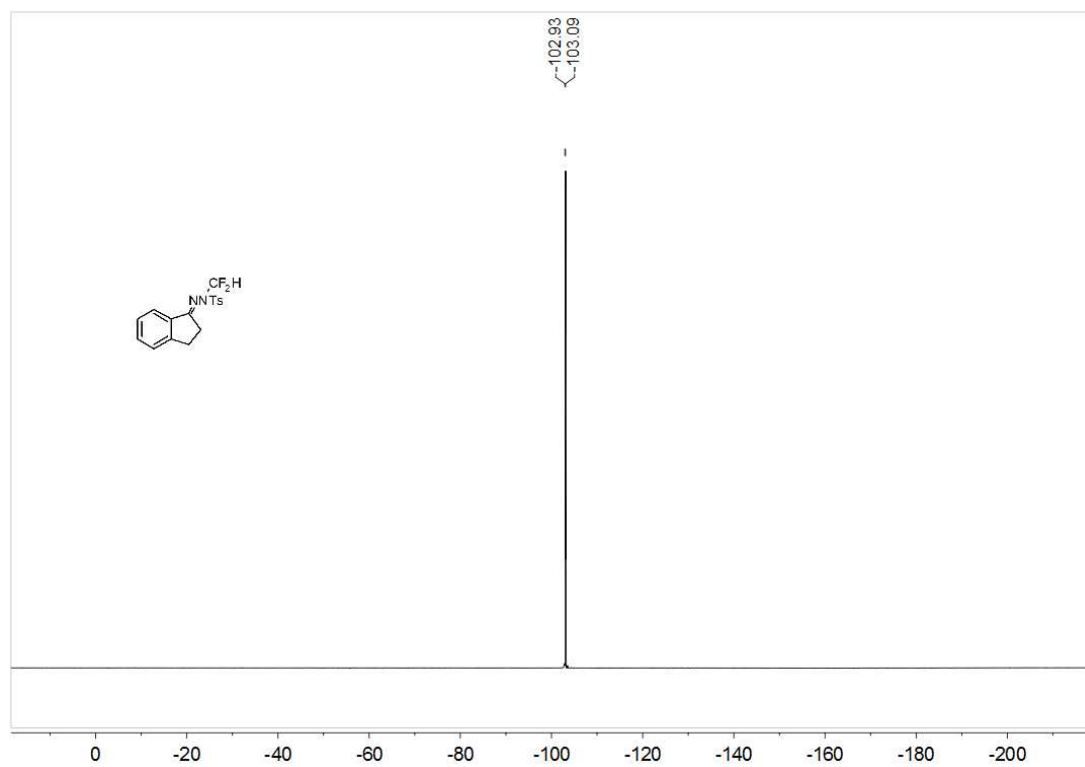
**$^1\text{H}$  NMR spectrum of 2x:**



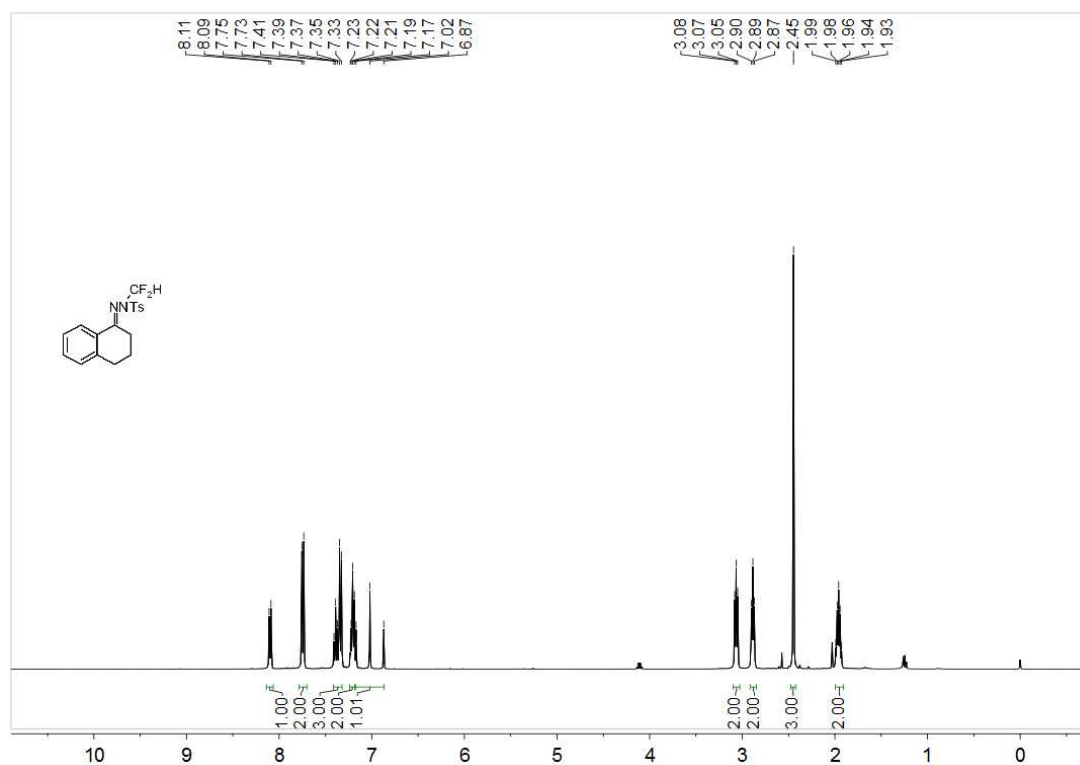
**<sup>13</sup>C NMR spectrum of 2x:**



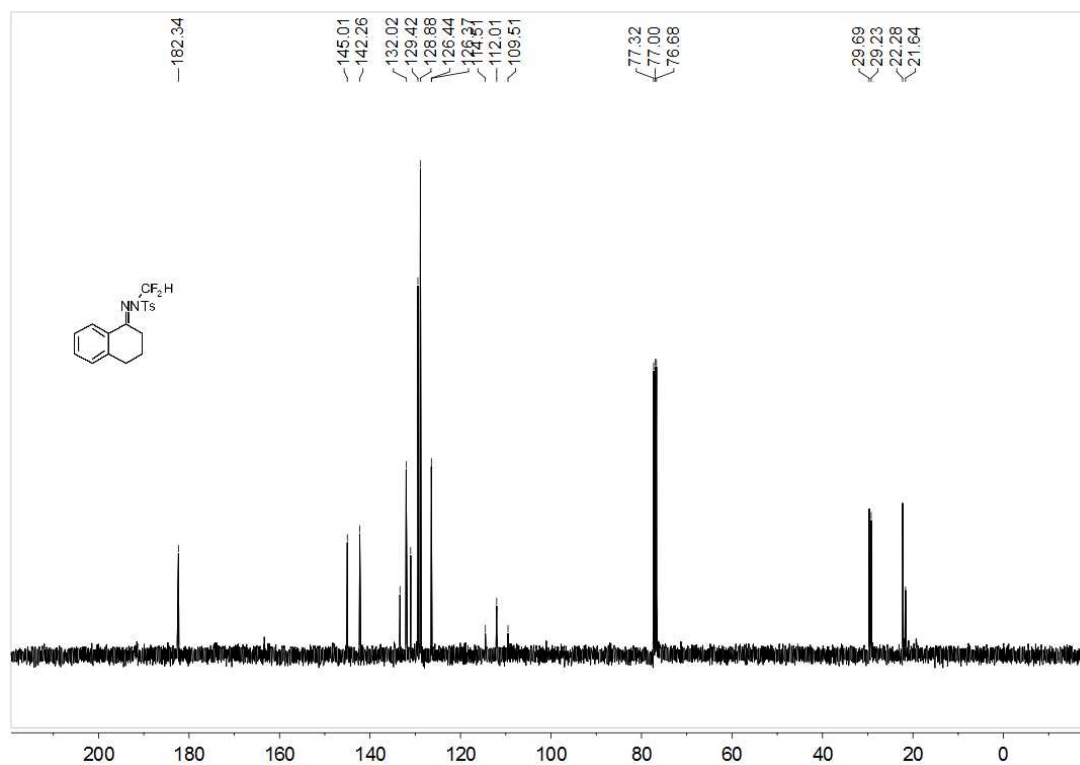
**<sup>19</sup>F NMR spectrum of 2x:**



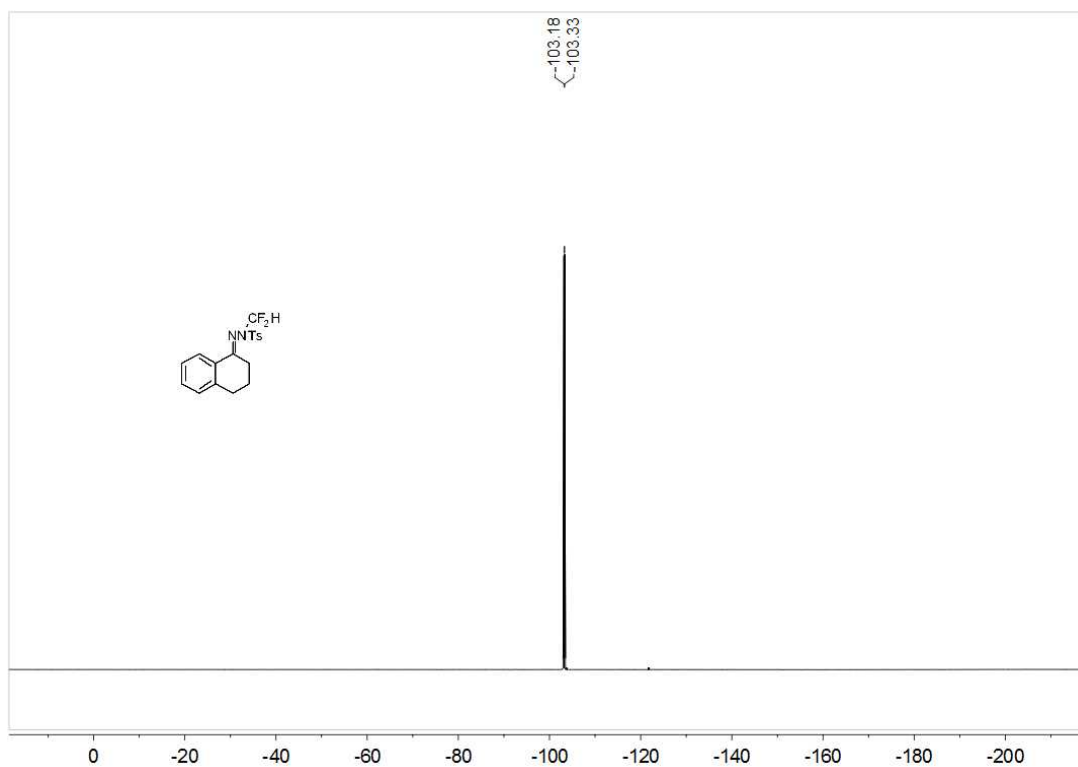
**<sup>1</sup>H NMR spectrum of 2y:**



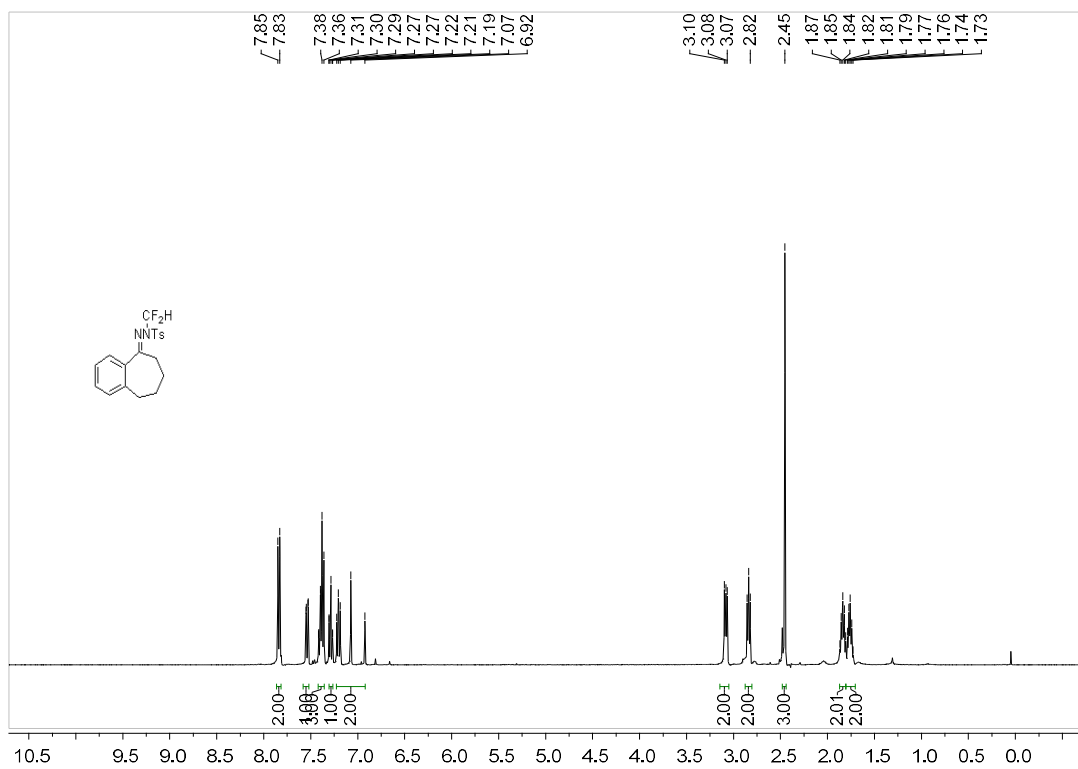
**<sup>13</sup>C NMR spectrum of 2y:**



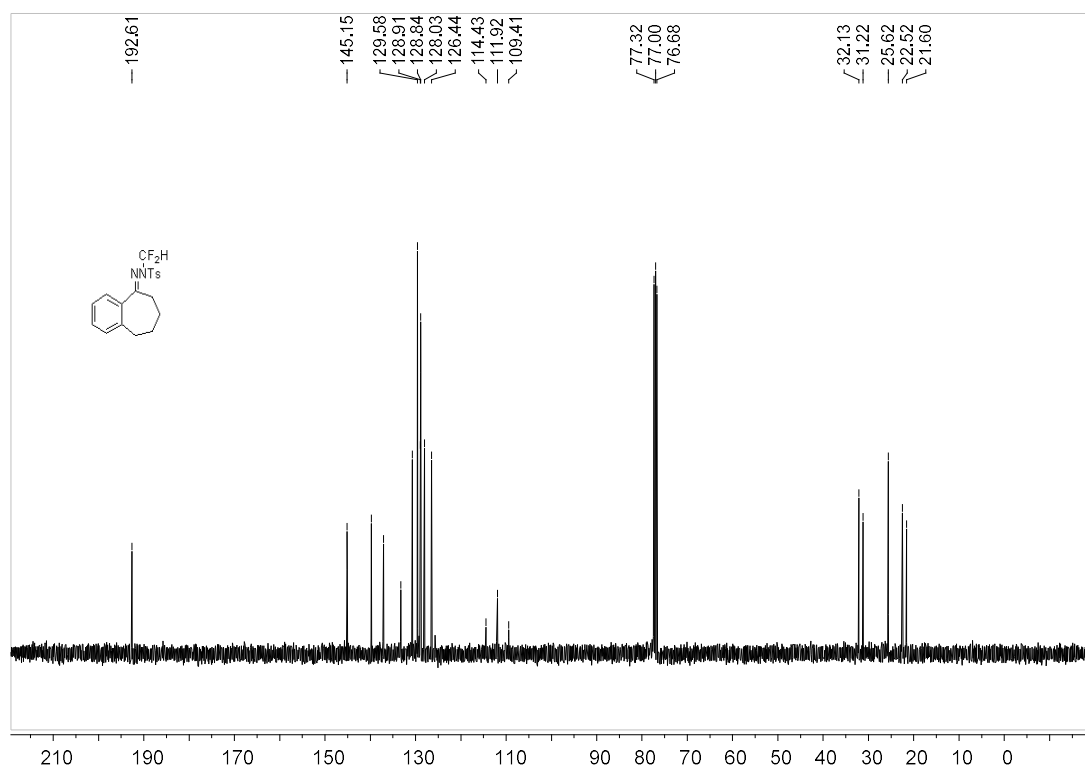
**<sup>19</sup>F NMR spectrum of 2y:**



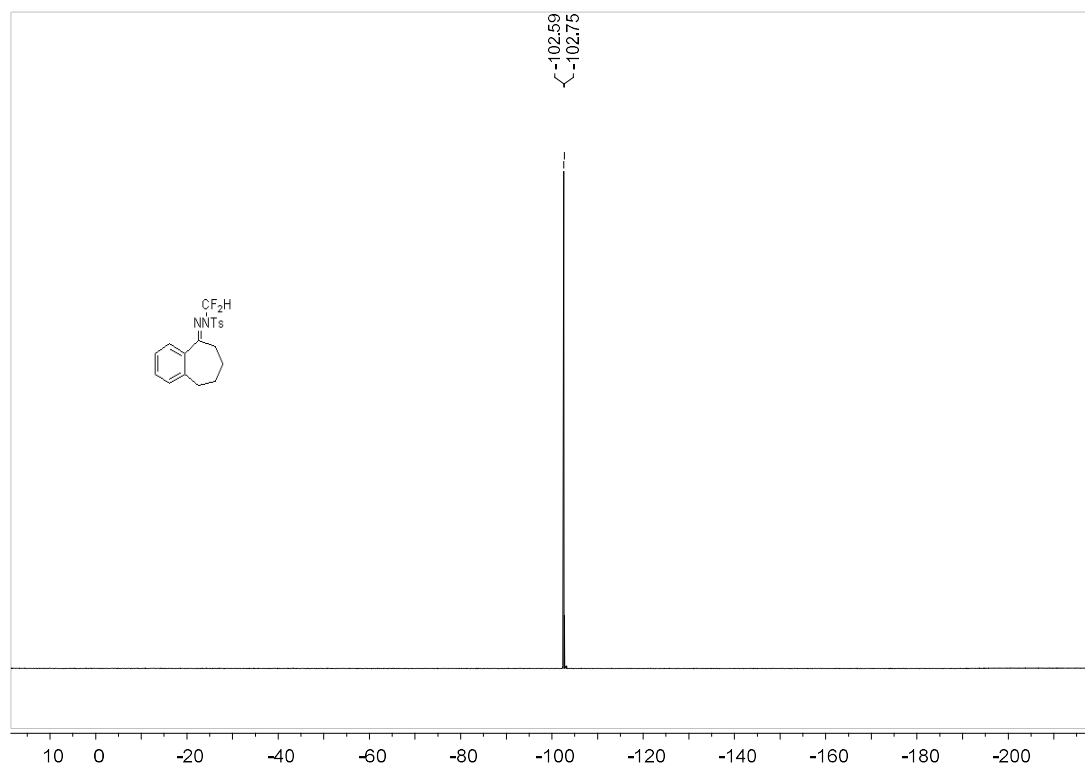
**<sup>1</sup>H NMR spectrum of 2z:**



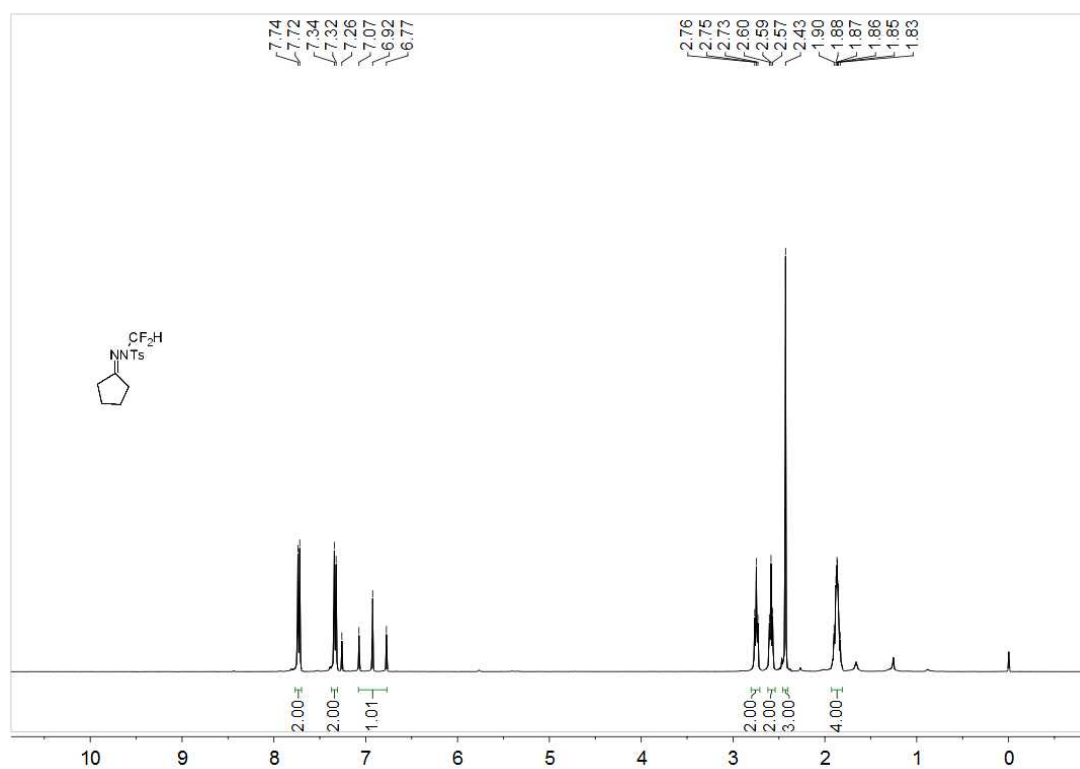
**<sup>13</sup>C NMR spectrum of 2z:**



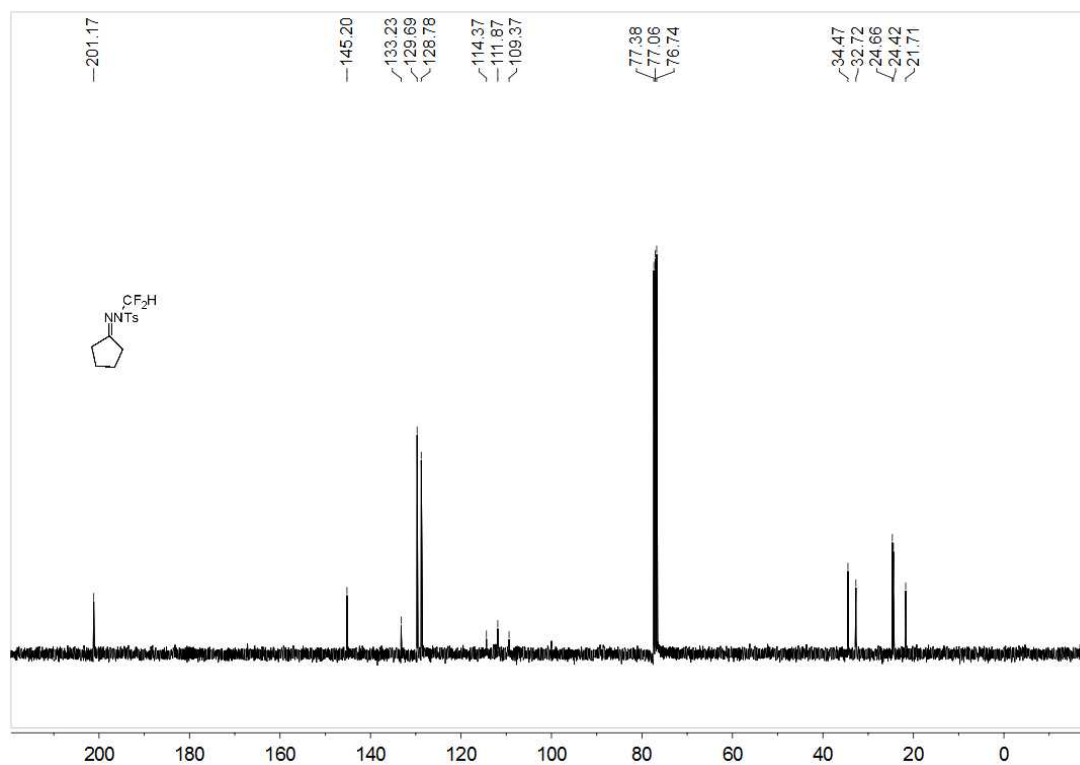
**<sup>19</sup>F NMR spectrum of 2z:**



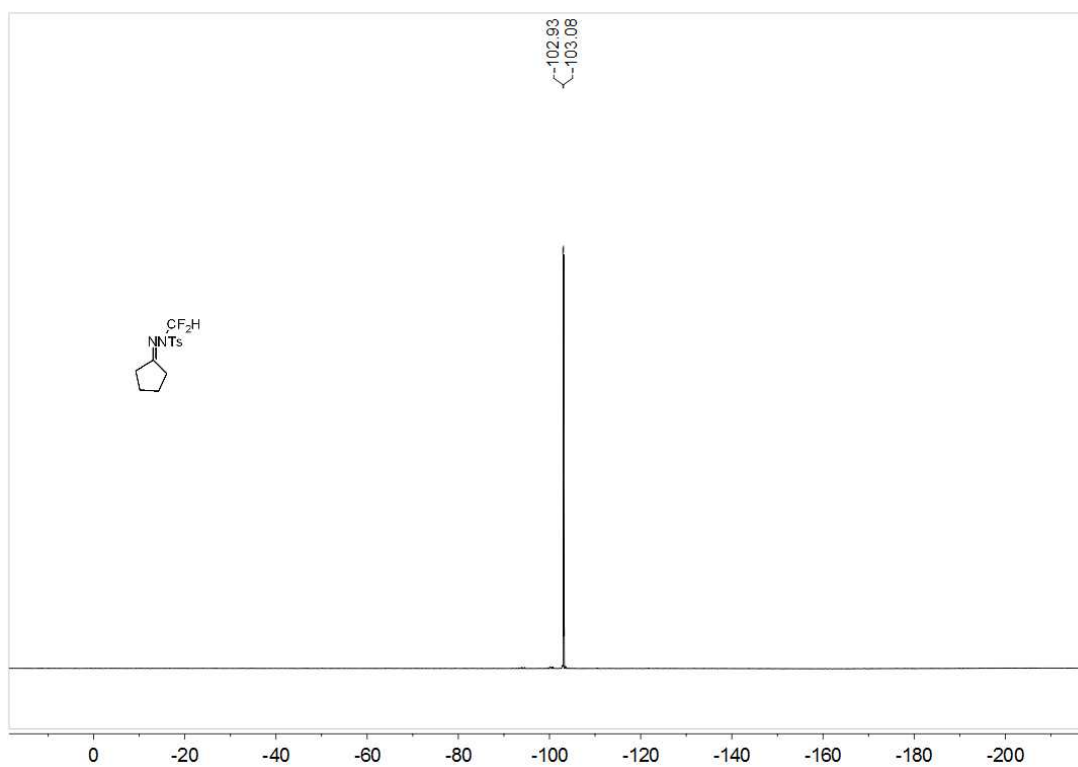
**<sup>1</sup>H NMR spectrum of 2a':**



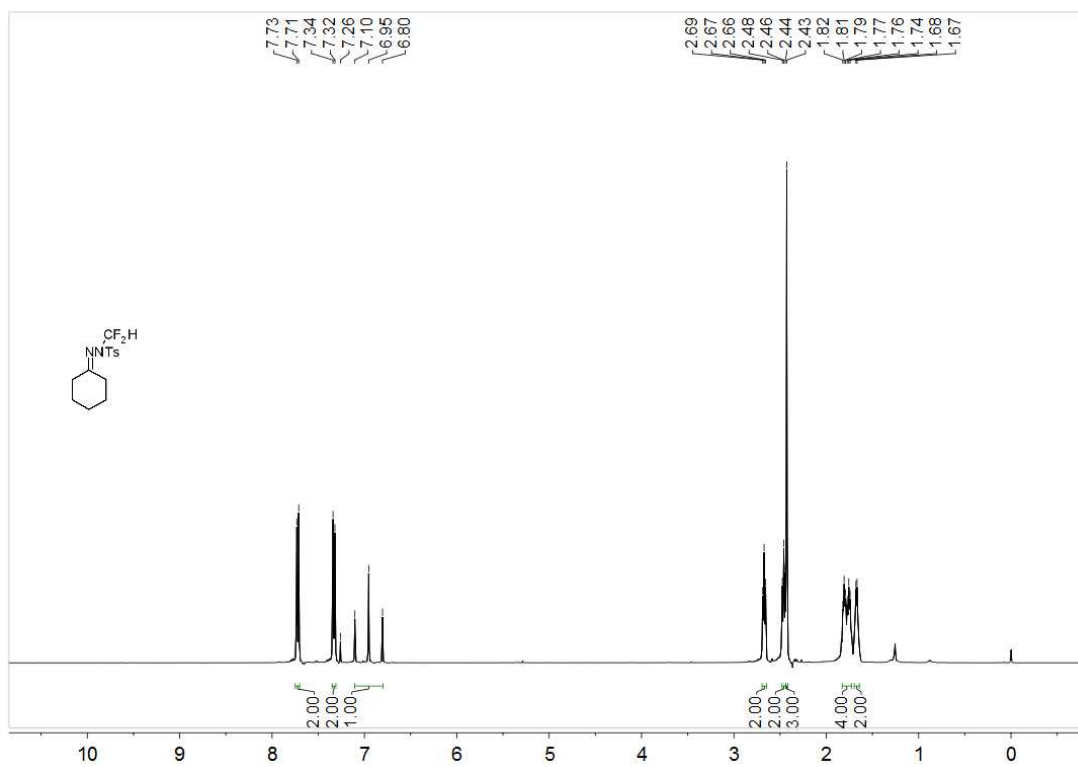
**<sup>13</sup>C NMR spectrum of 2a':**



**<sup>19</sup>F NMR spectrum of 2a':**

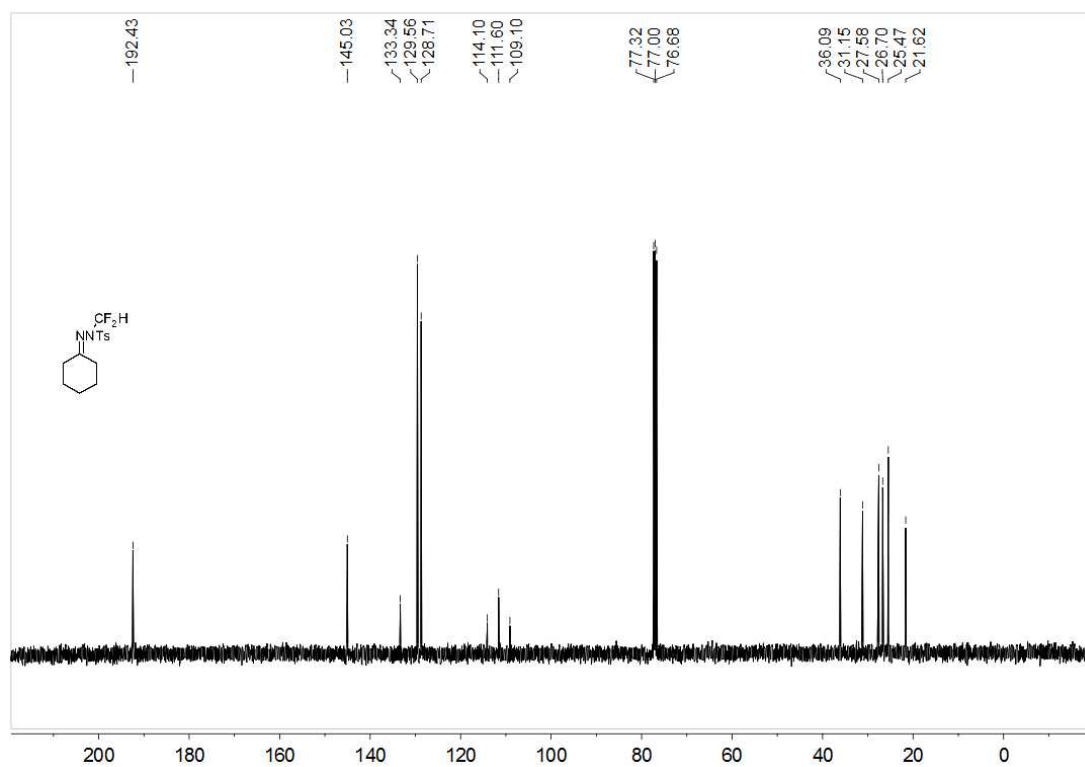


**<sup>1</sup>H NMR spectrum of 2b':**

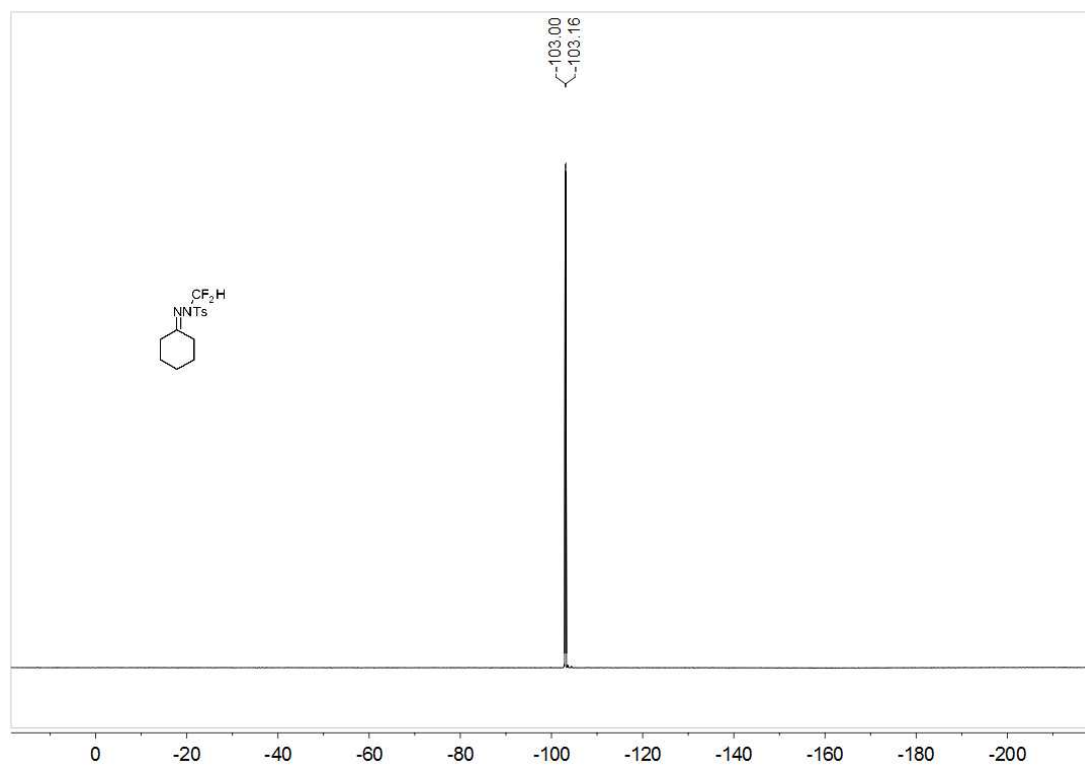




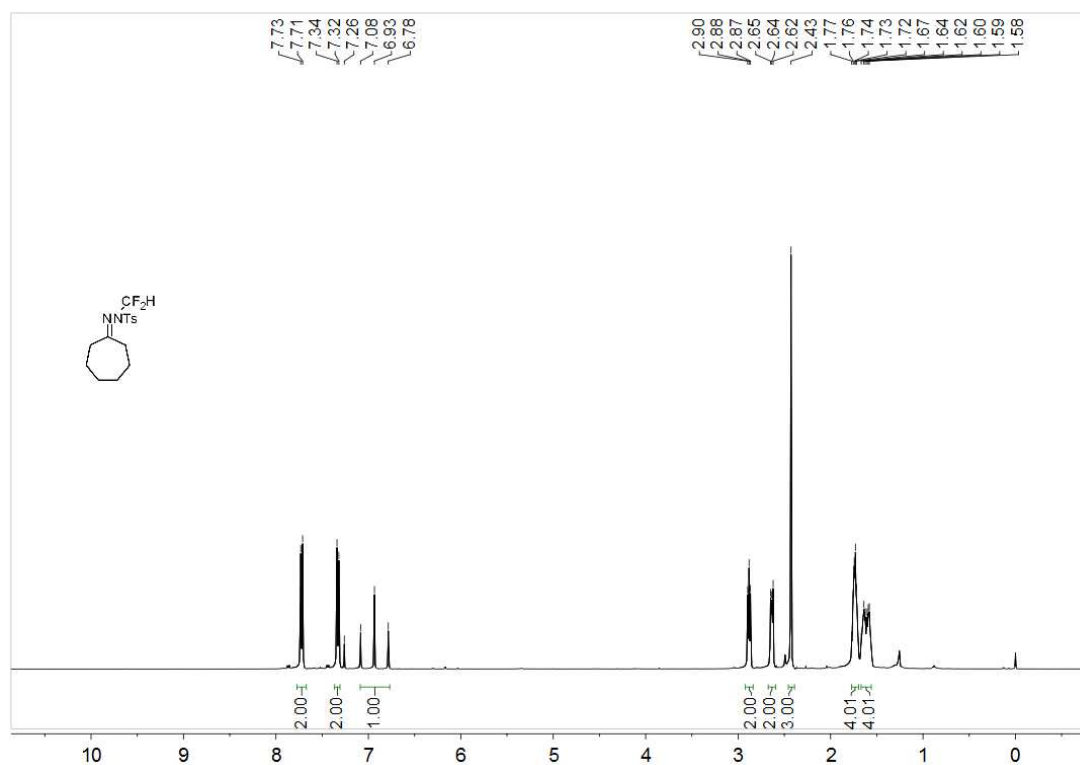
**<sup>13</sup>C NMR spectrum of 2b':**



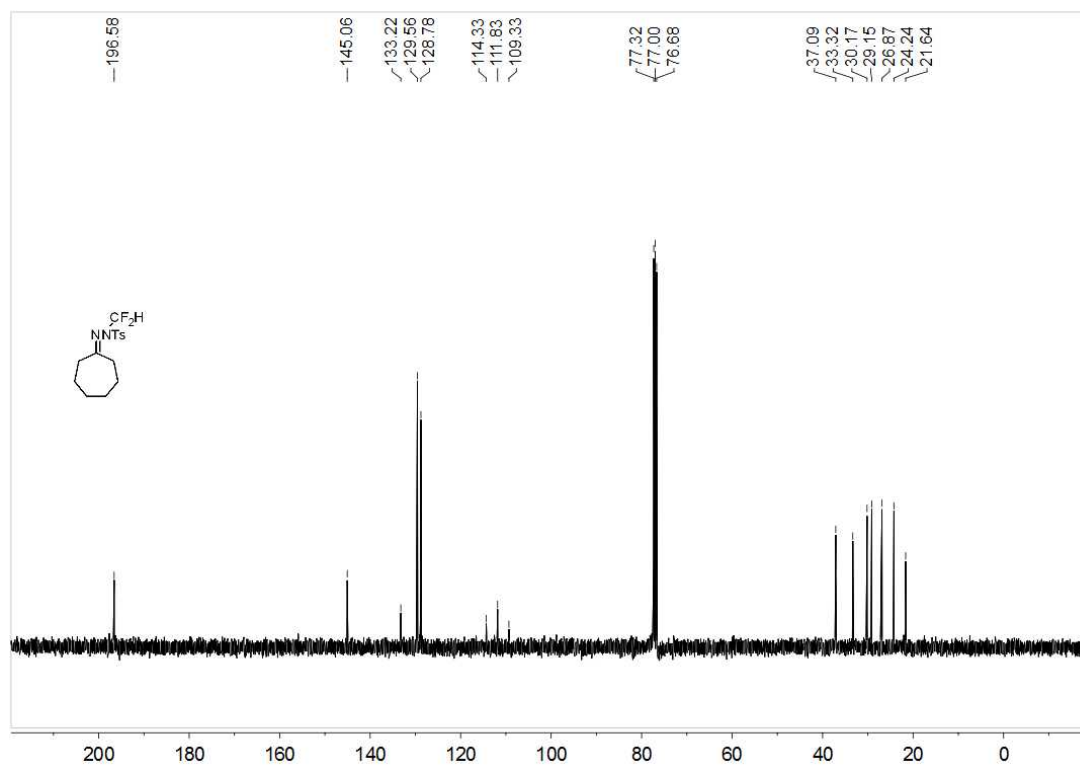
**<sup>19</sup>F NMR spectrum of 2b':**



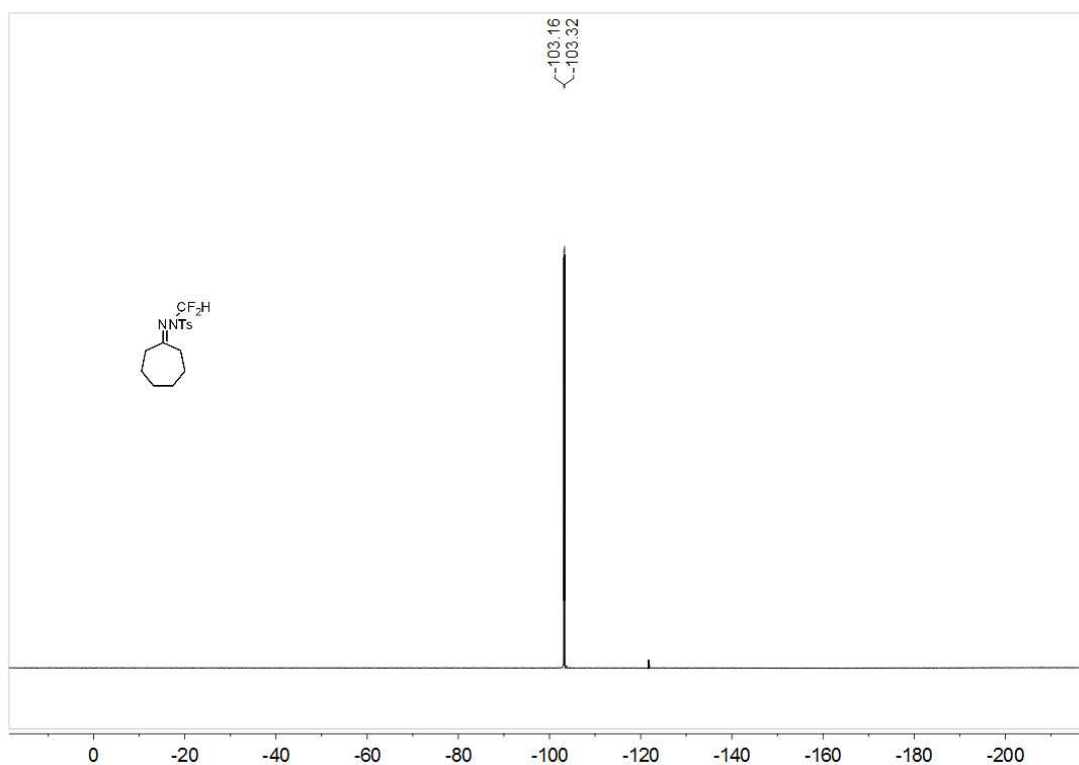
**<sup>1</sup>H NMR spectrum of 2c':**



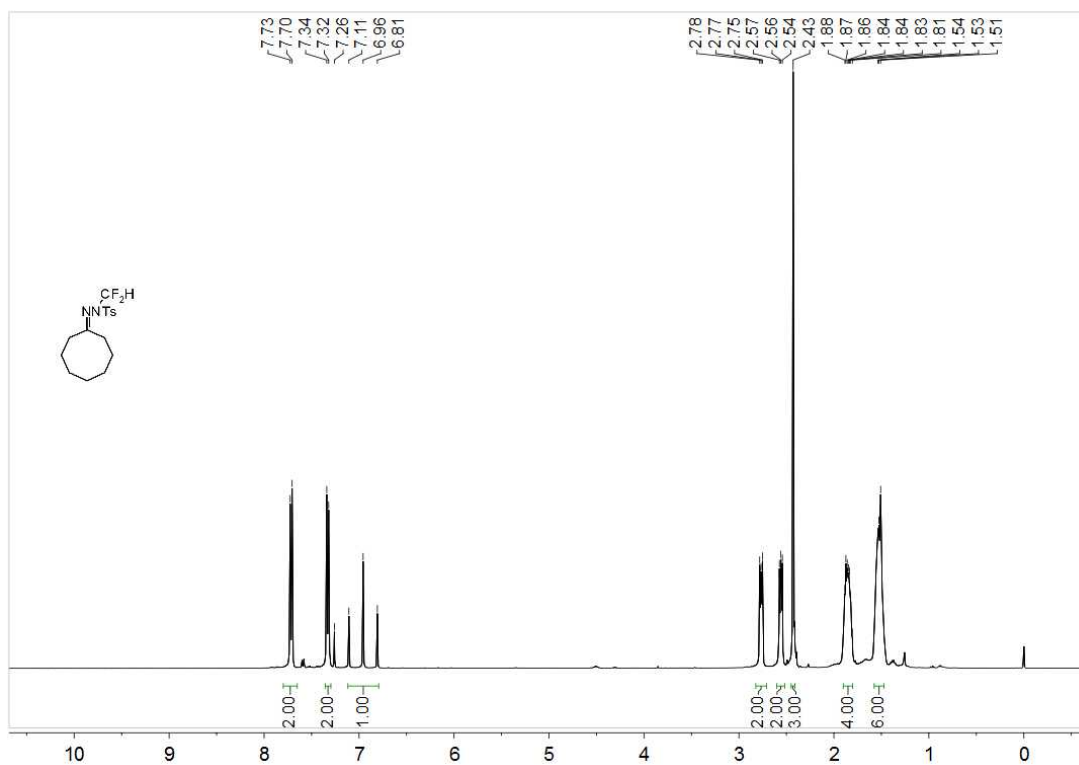
**<sup>13</sup>C NMR spectrum of 2c':**



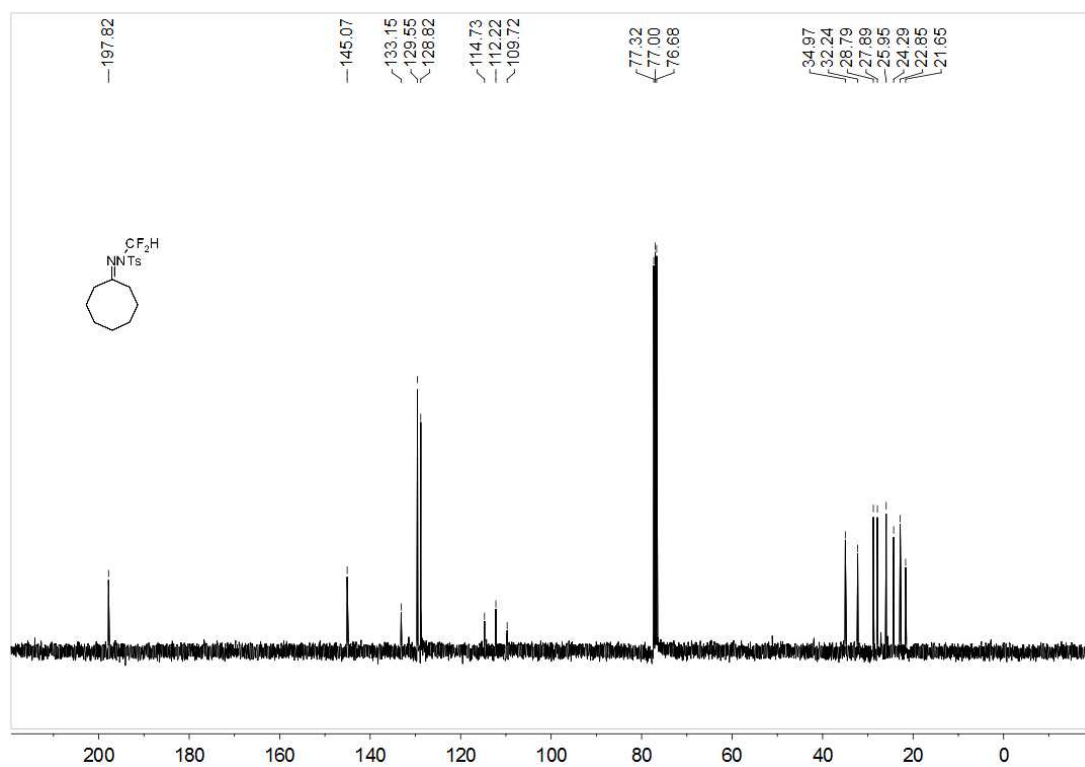
**$^{19}\text{F}$  NMR spectrum of 2c':**



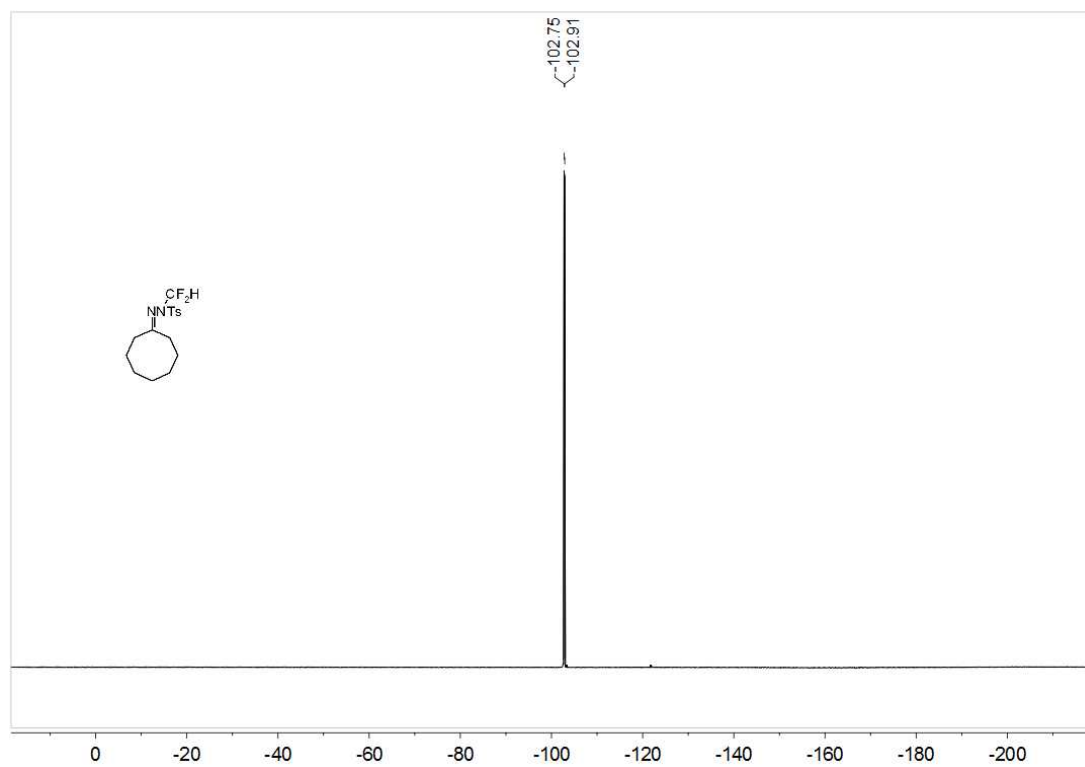
**$^1\text{H}$  NMR spectrum of 2d':**



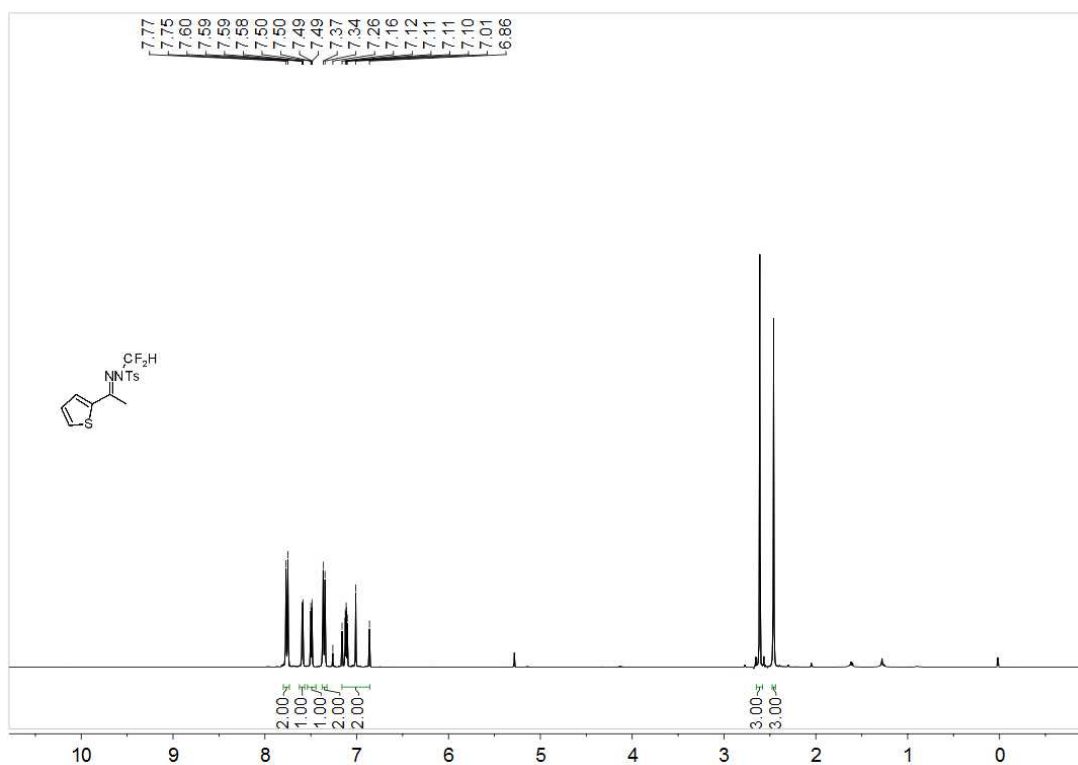
**<sup>13</sup>C NMR spectrum of 2d':**



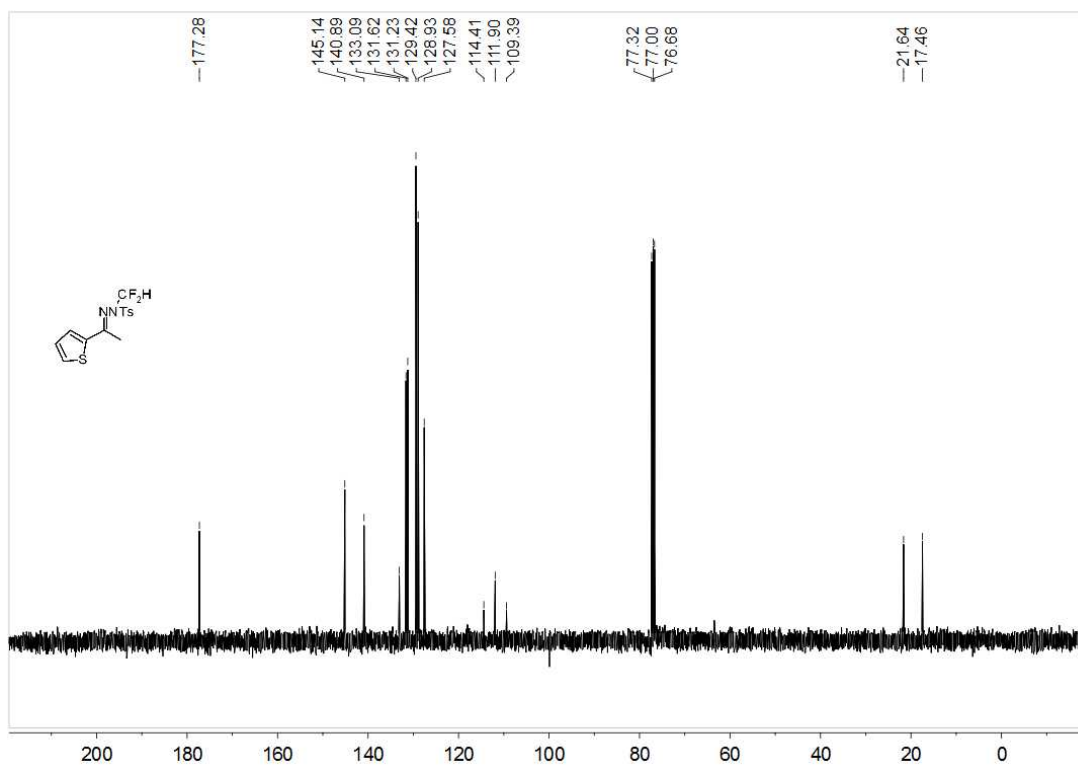
**<sup>19</sup>F NMR spectrum of 2d':**



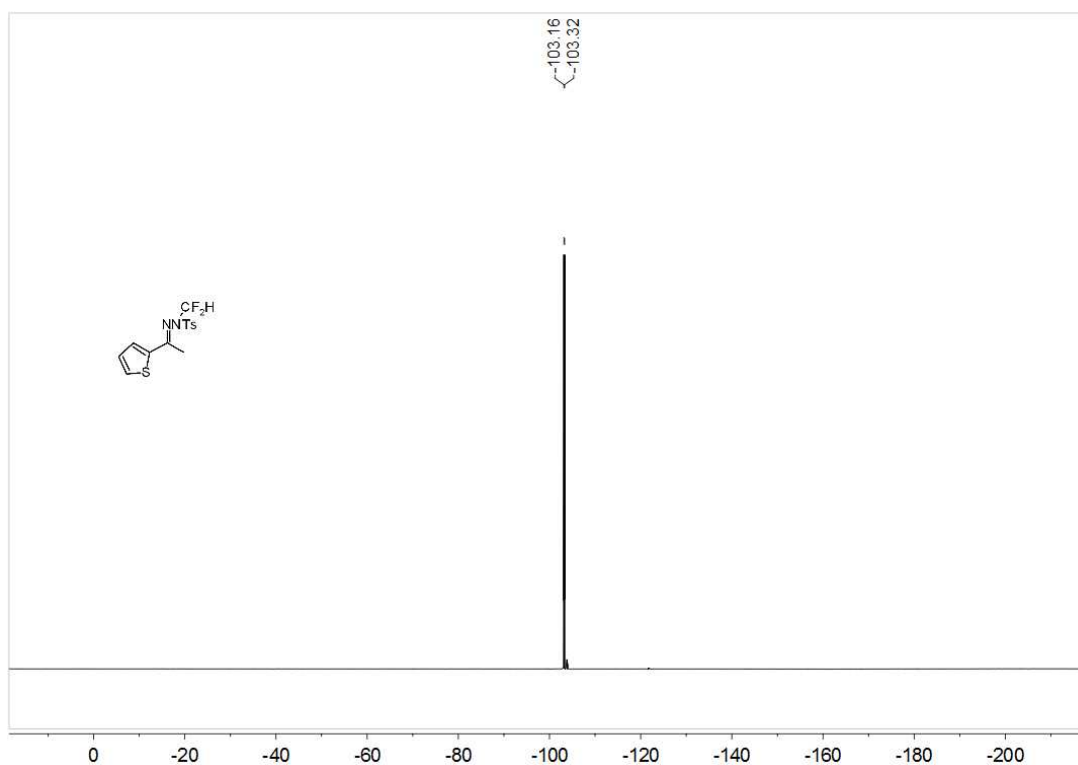
**<sup>1</sup>H NMR spectrum of 2e':**



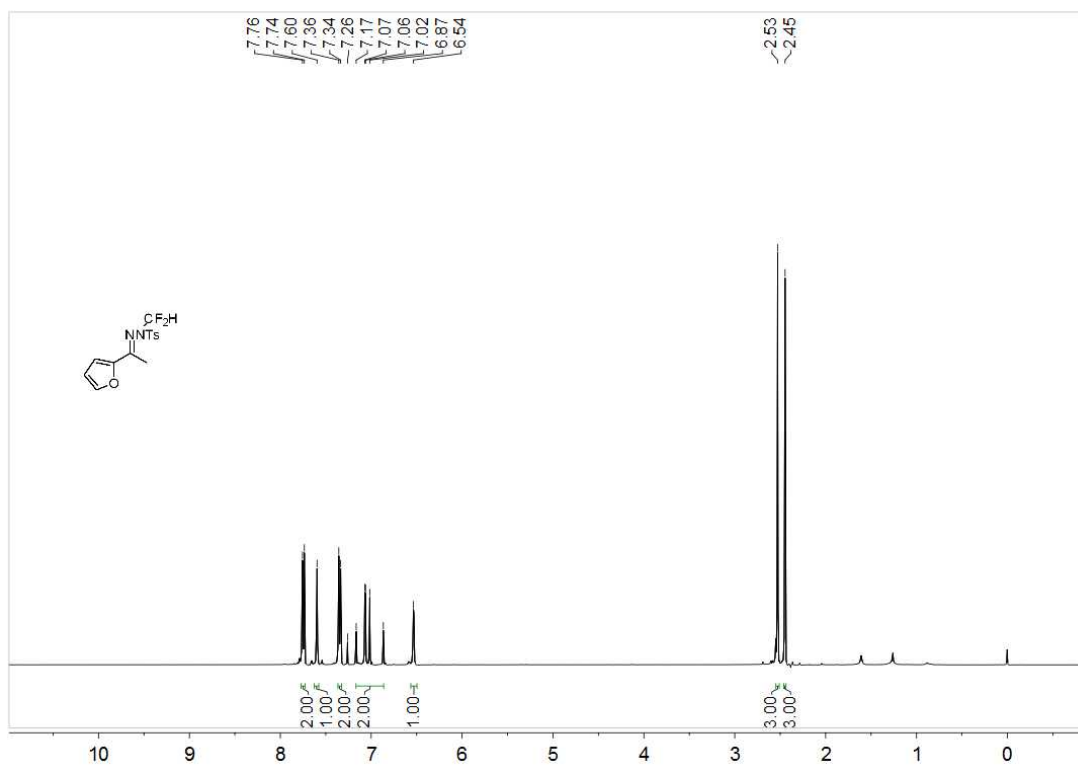
**<sup>13</sup>C NMR spectrum of 2e':**



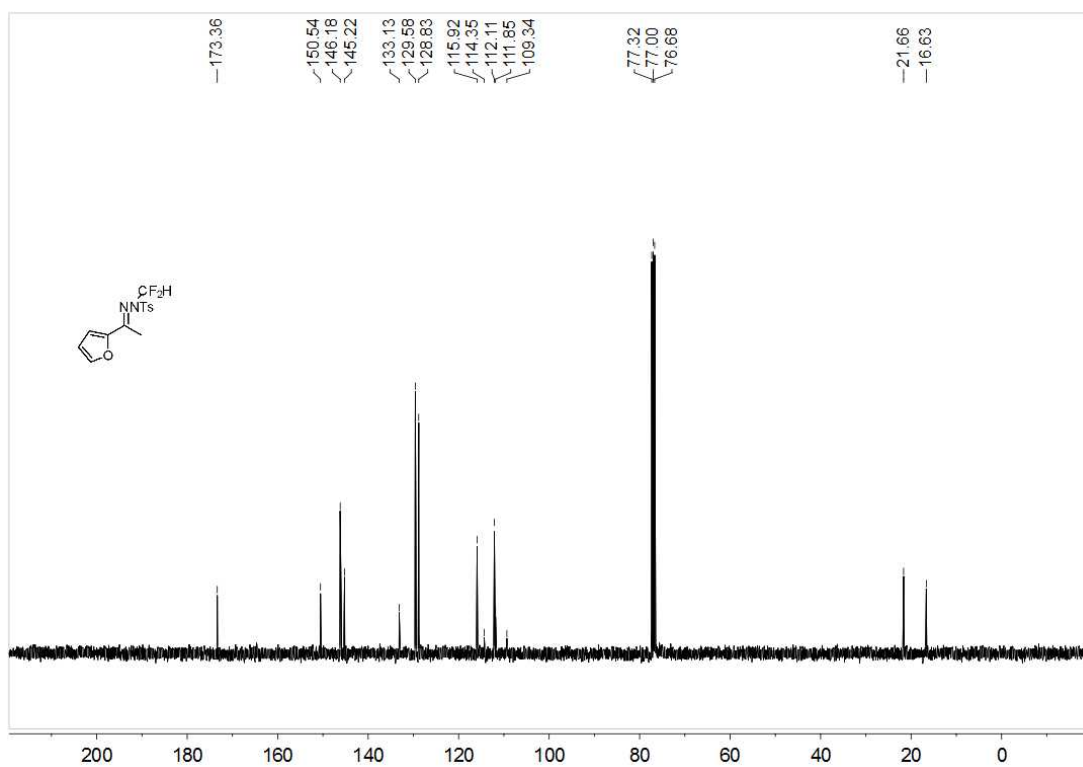
**$^{19}\text{F}$  NMR spectrum of 2e':**



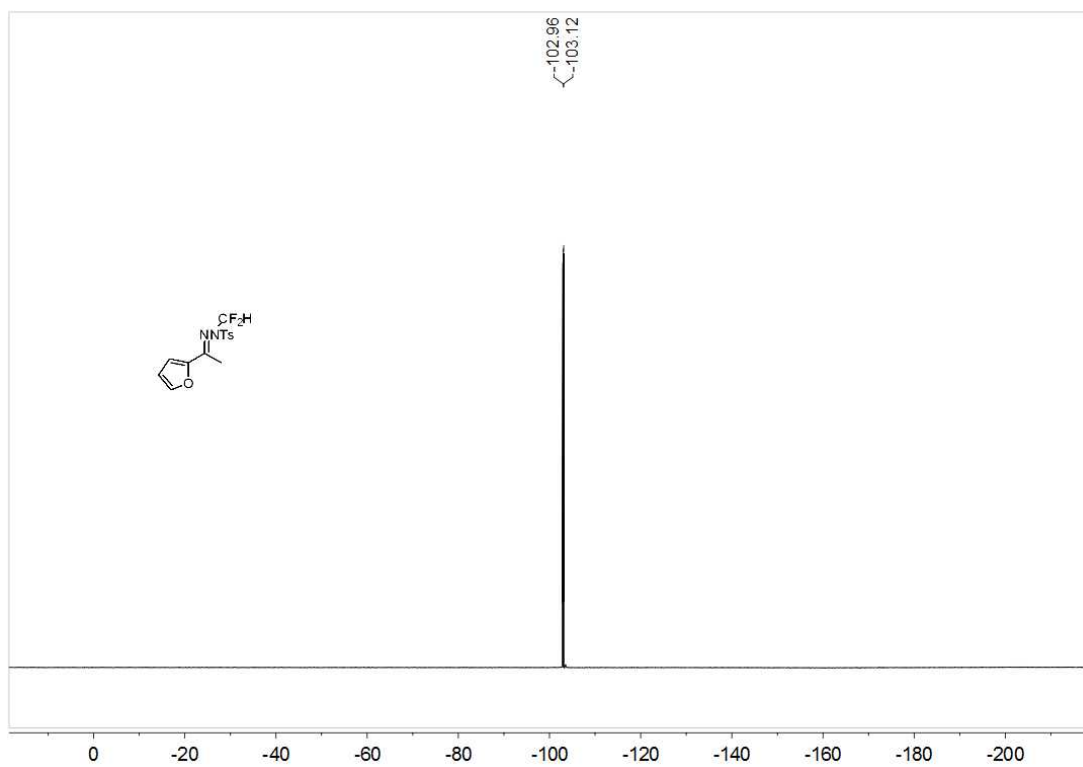
**$^1\text{H}$  NMR spectrum of 2f':**



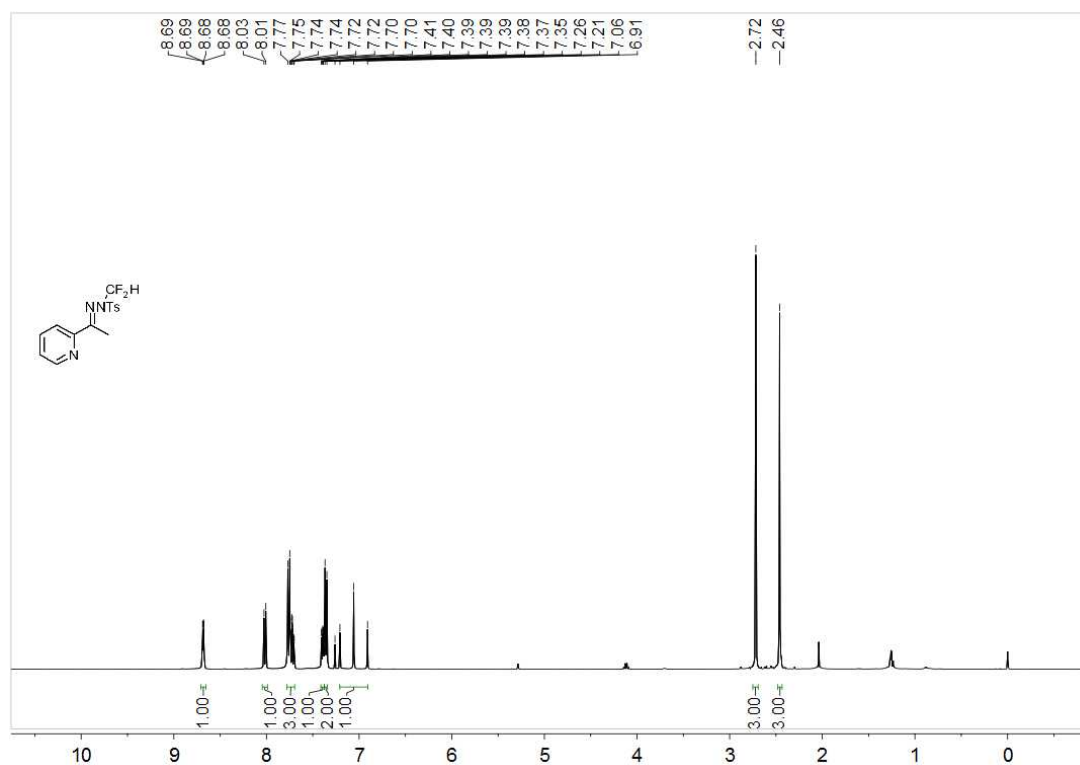
**<sup>13</sup>C NMR spectrum of 2f':**



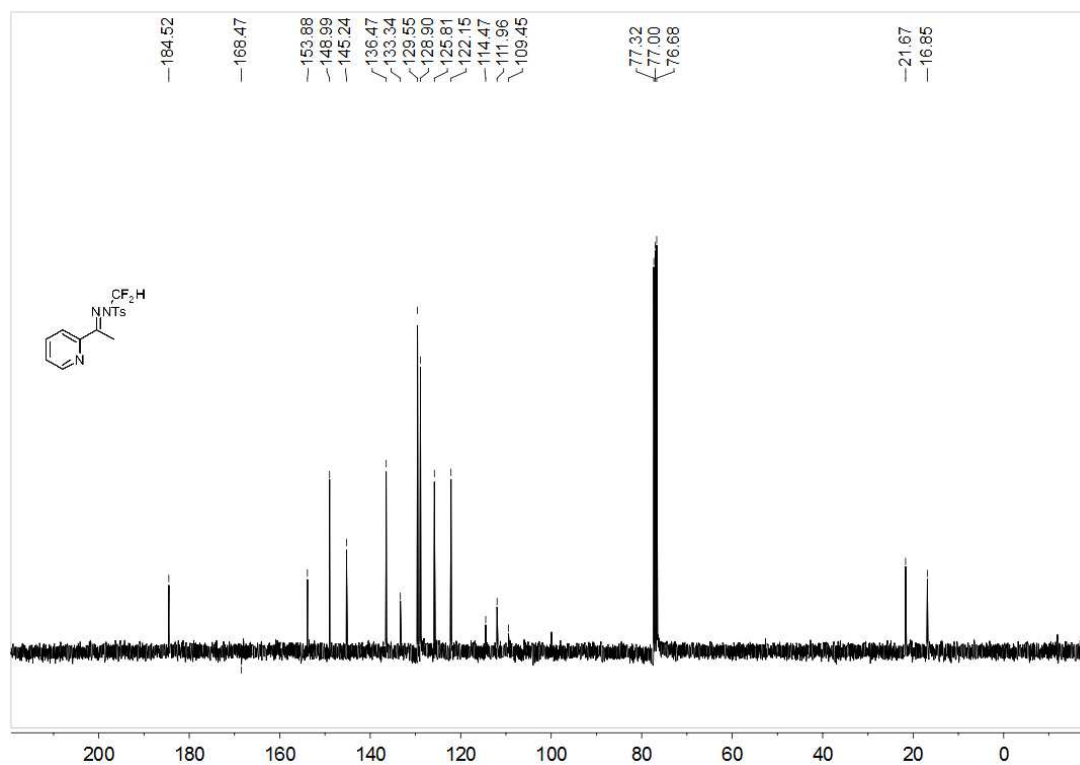
**<sup>19</sup>F NMR spectrum of 2f':**



**<sup>1</sup>H NMR spectrum of 2g':**

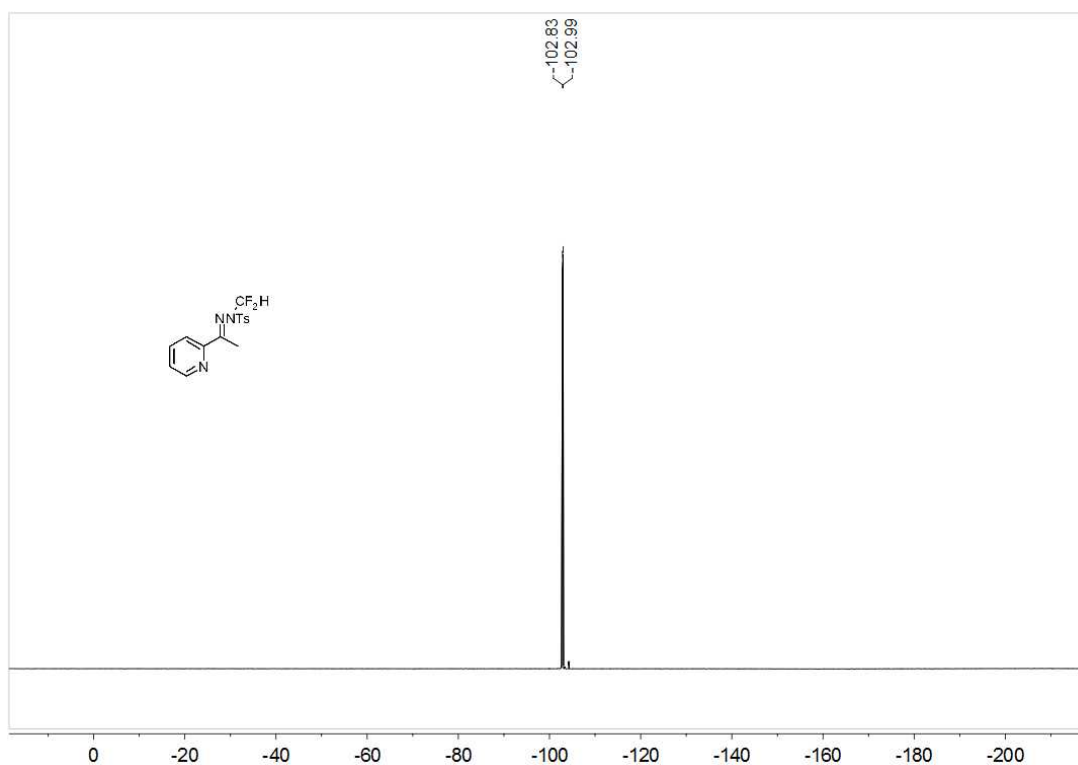


**<sup>13</sup>C NMR spectrum of 2g':**

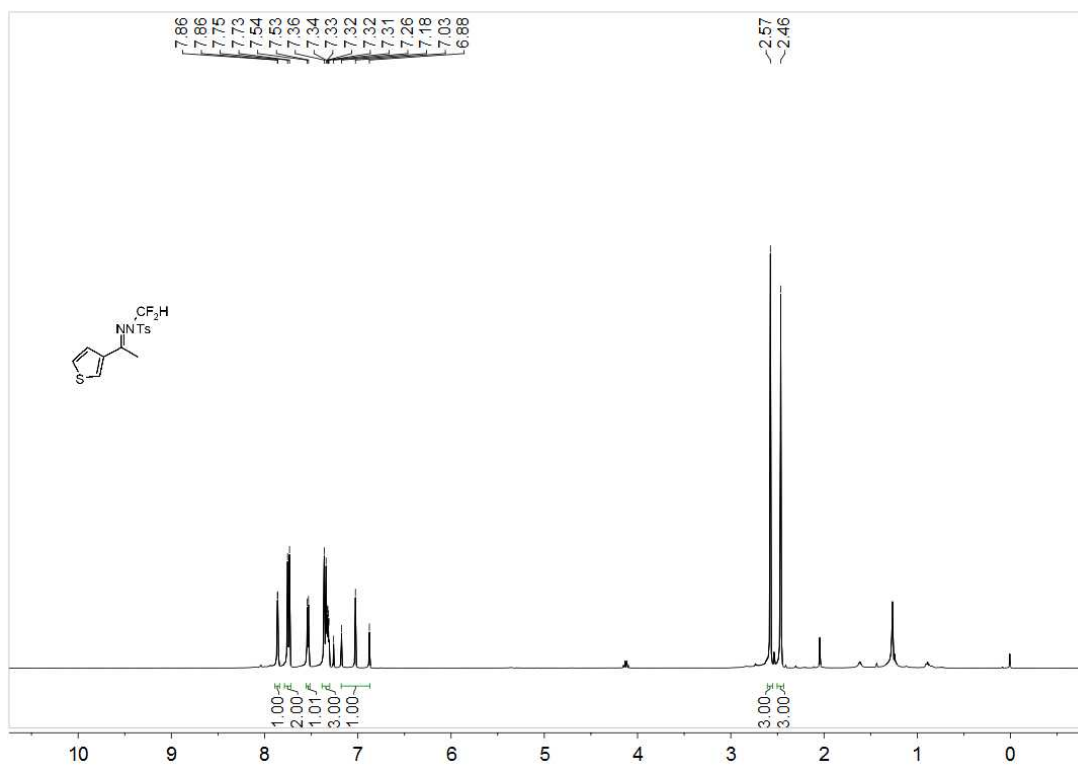




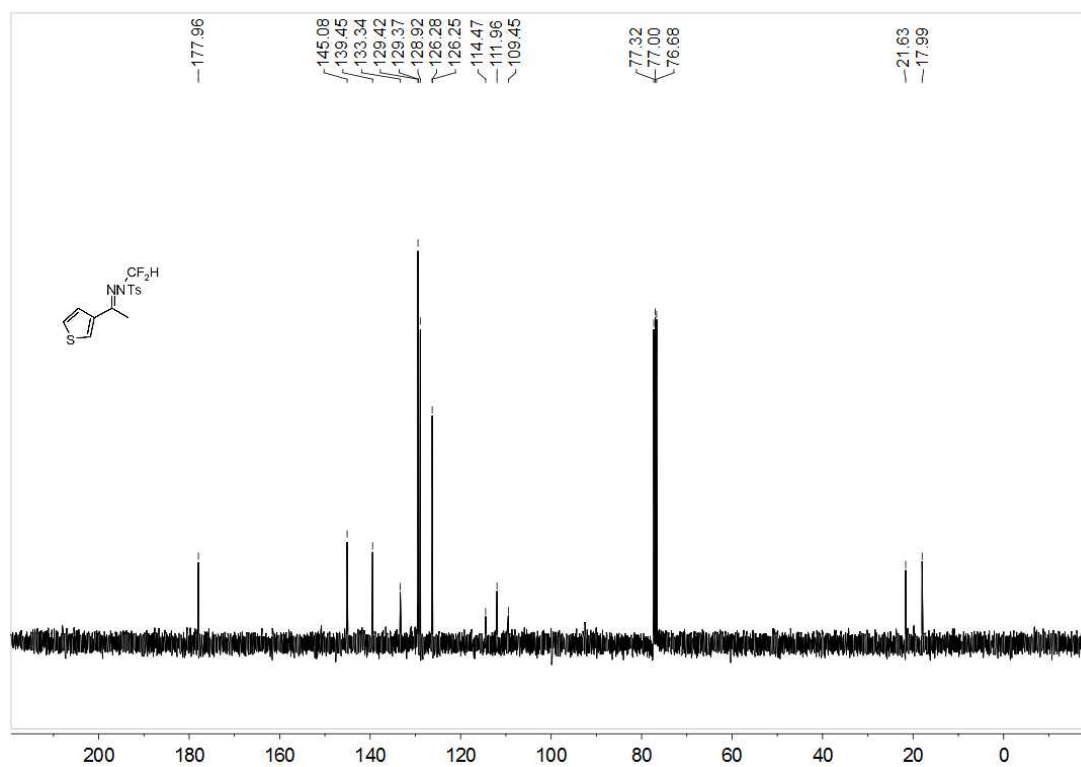
**<sup>19</sup>F NMR spectrum of 2g':**



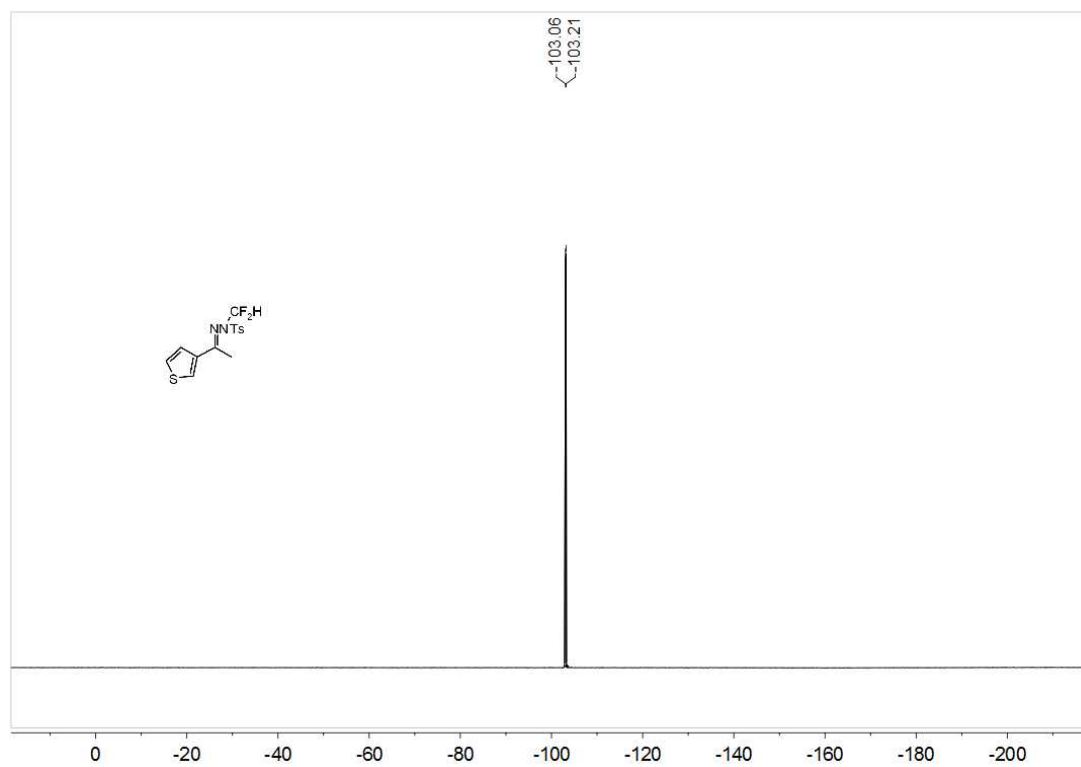
**<sup>1</sup>H NMR spectrum of 2h':**



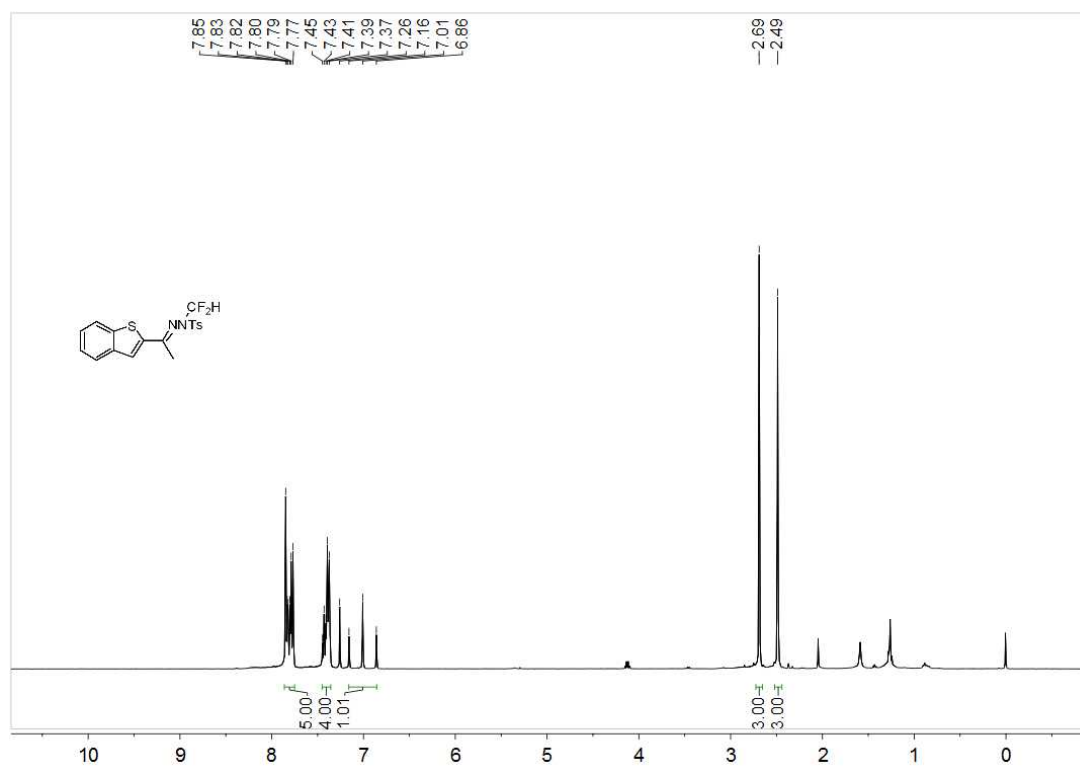
**<sup>13</sup>C NMR spectrum of 2h':**



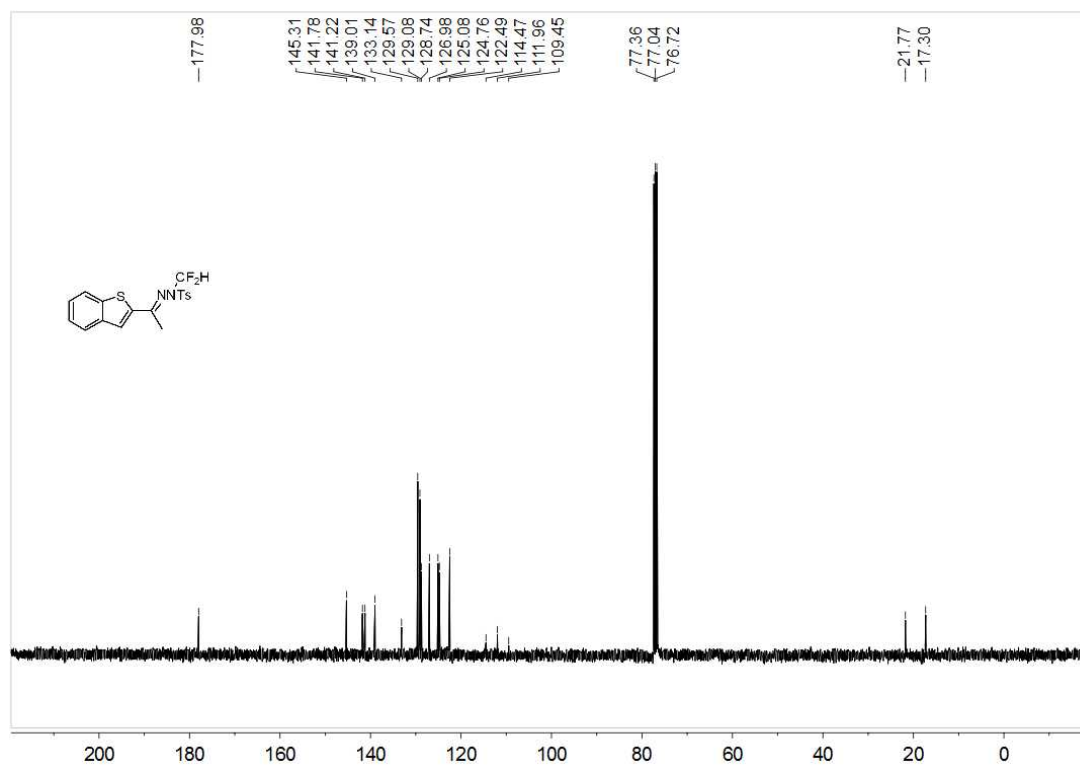
**<sup>19</sup>F NMR spectrum of 2h':**



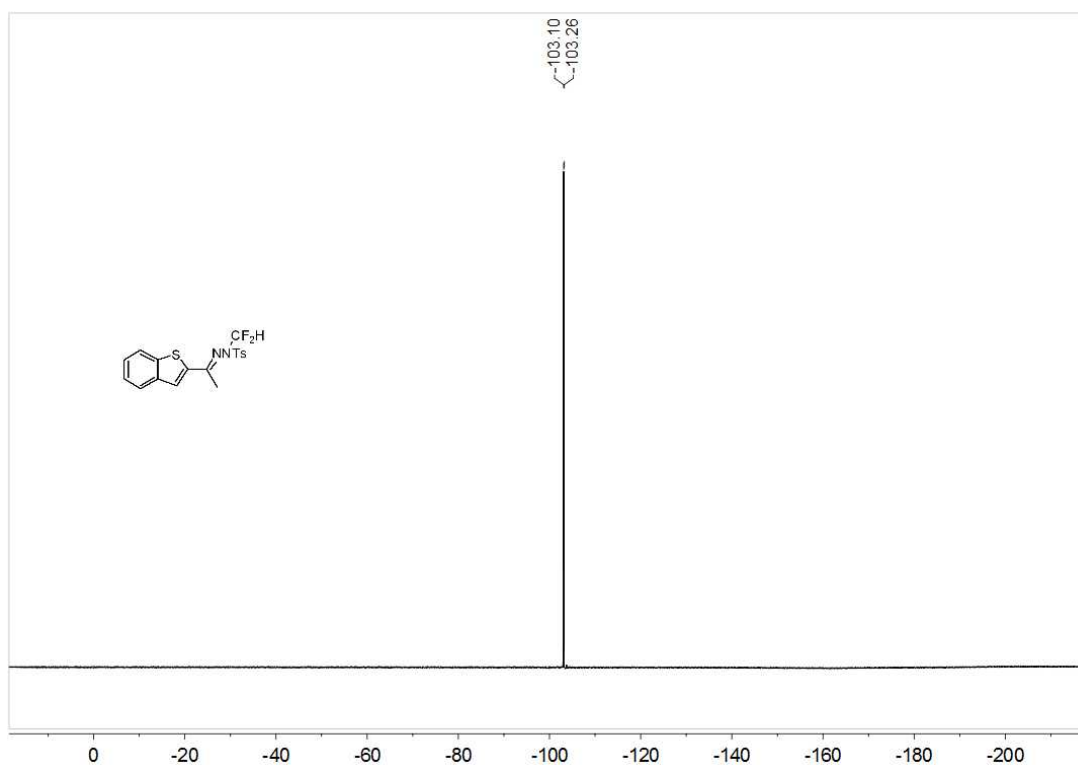
**<sup>1</sup>H NMR spectrum of 2i':**



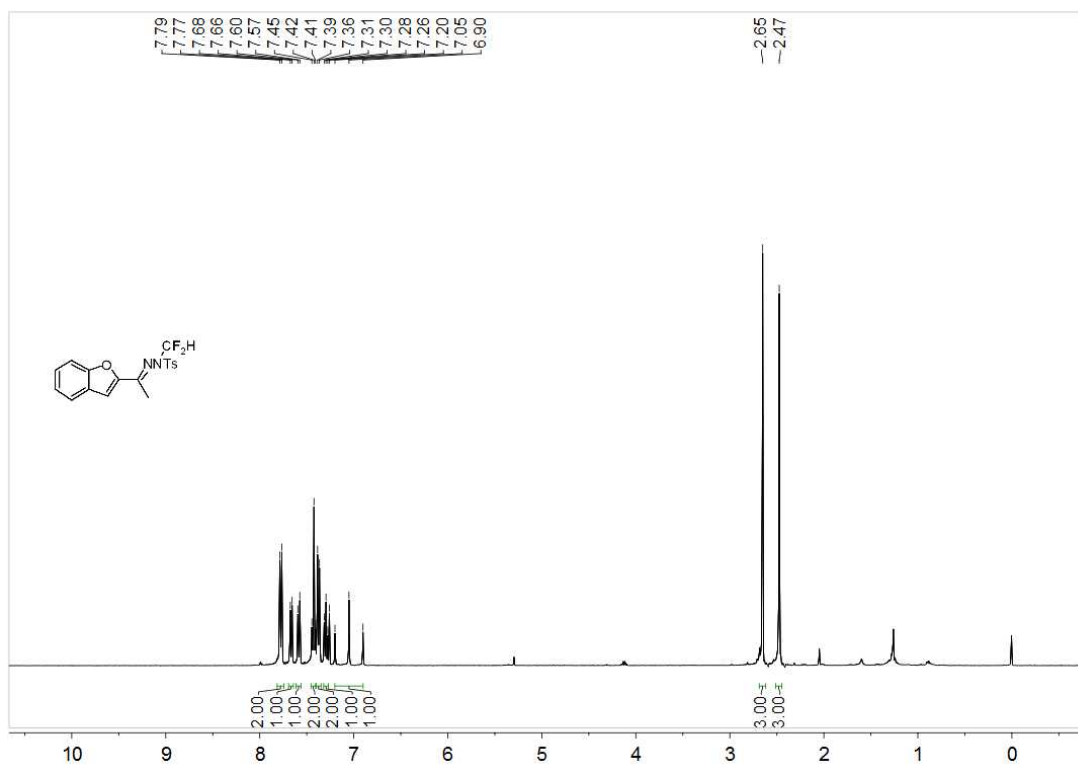
**<sup>13</sup>C NMR spectrum of 2i':**



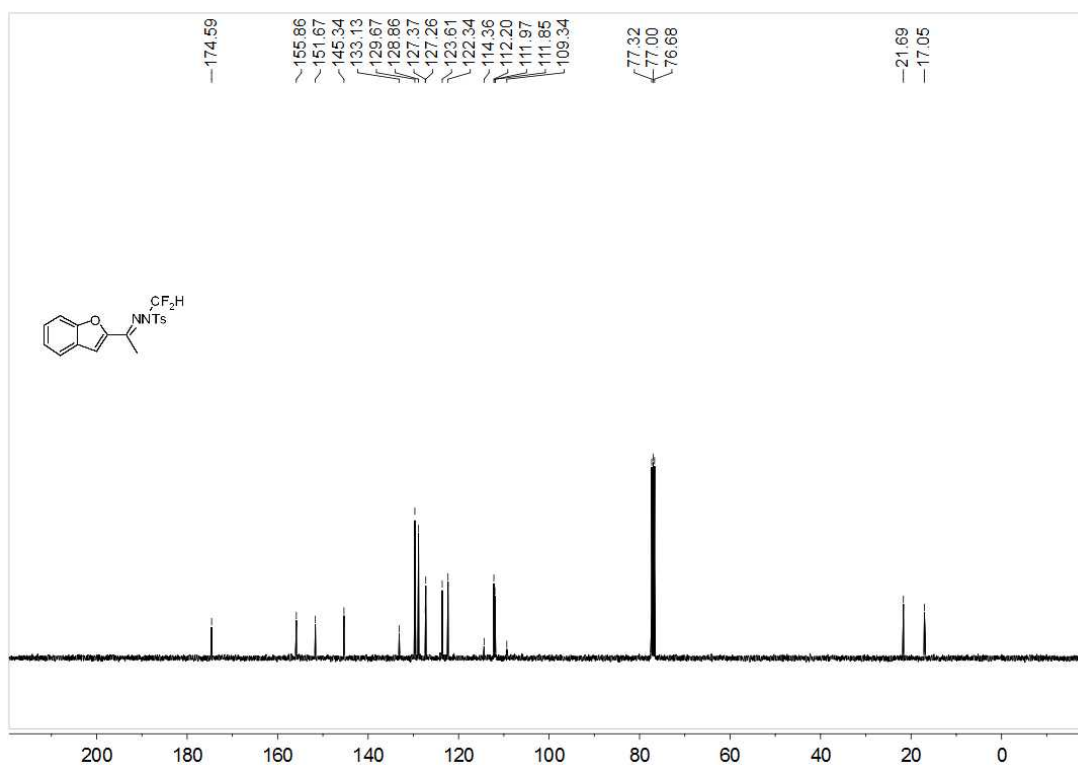
**$^{19}\text{F}$  NMR spectrum of 2i:**



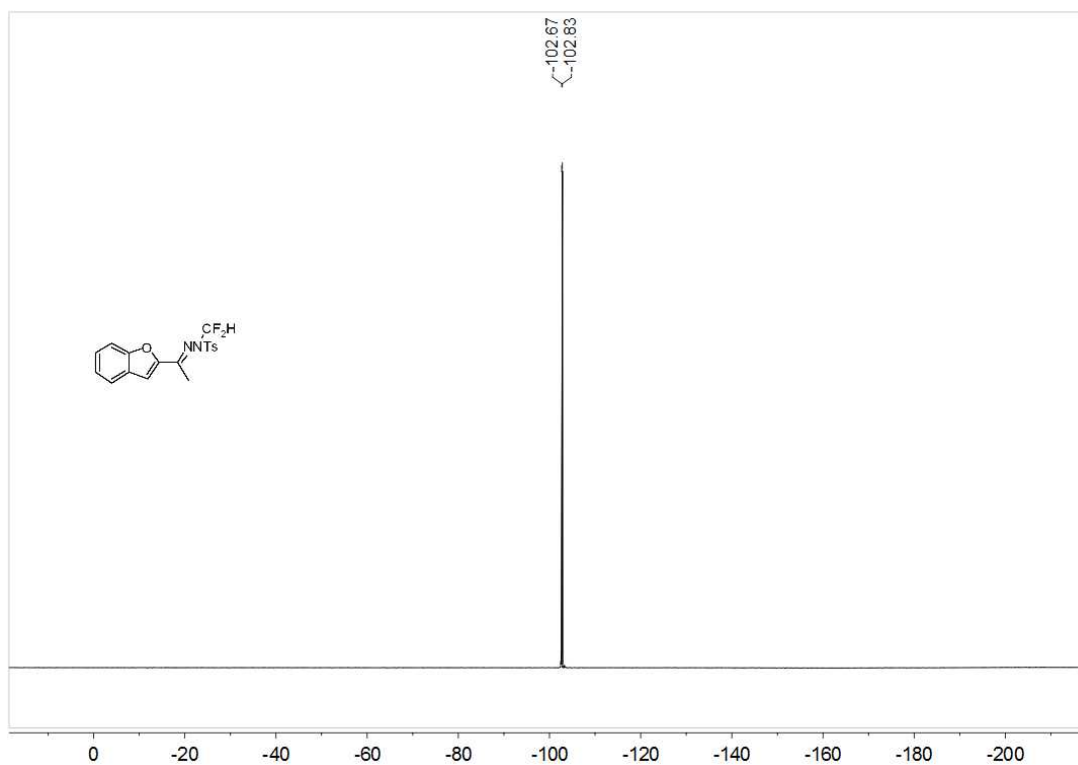
**$^1\text{H}$  NMR spectrum of 2j:**



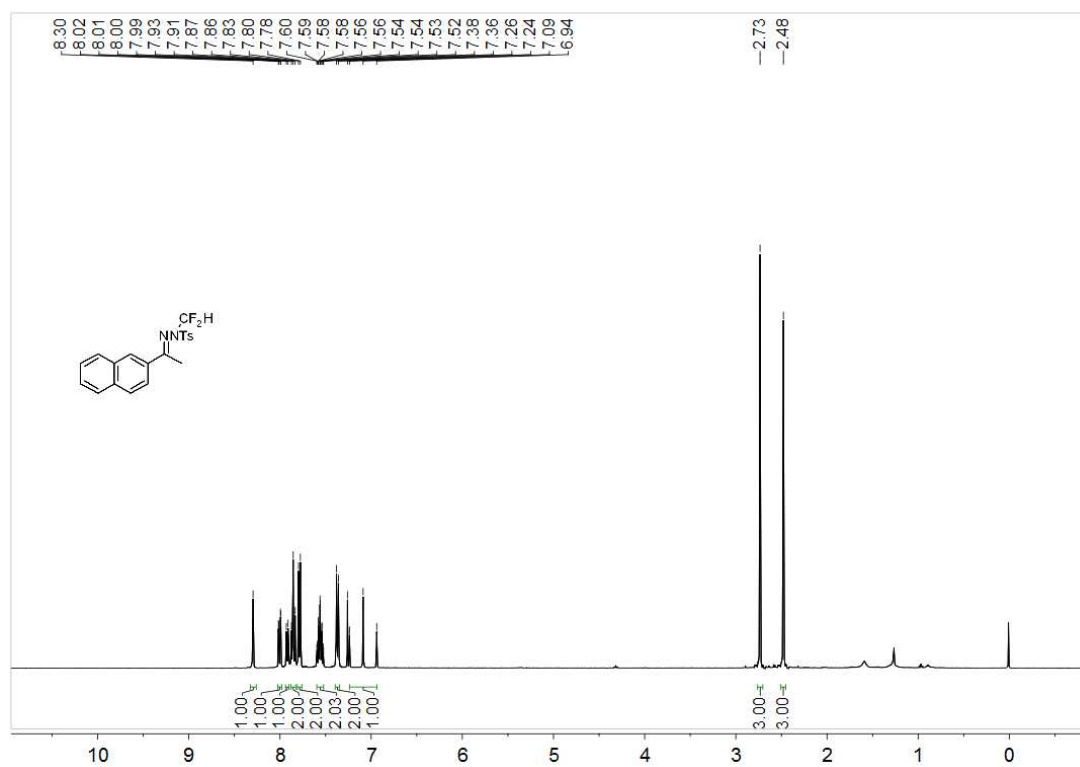
**<sup>13</sup>C NMR spectrum of 2j':**



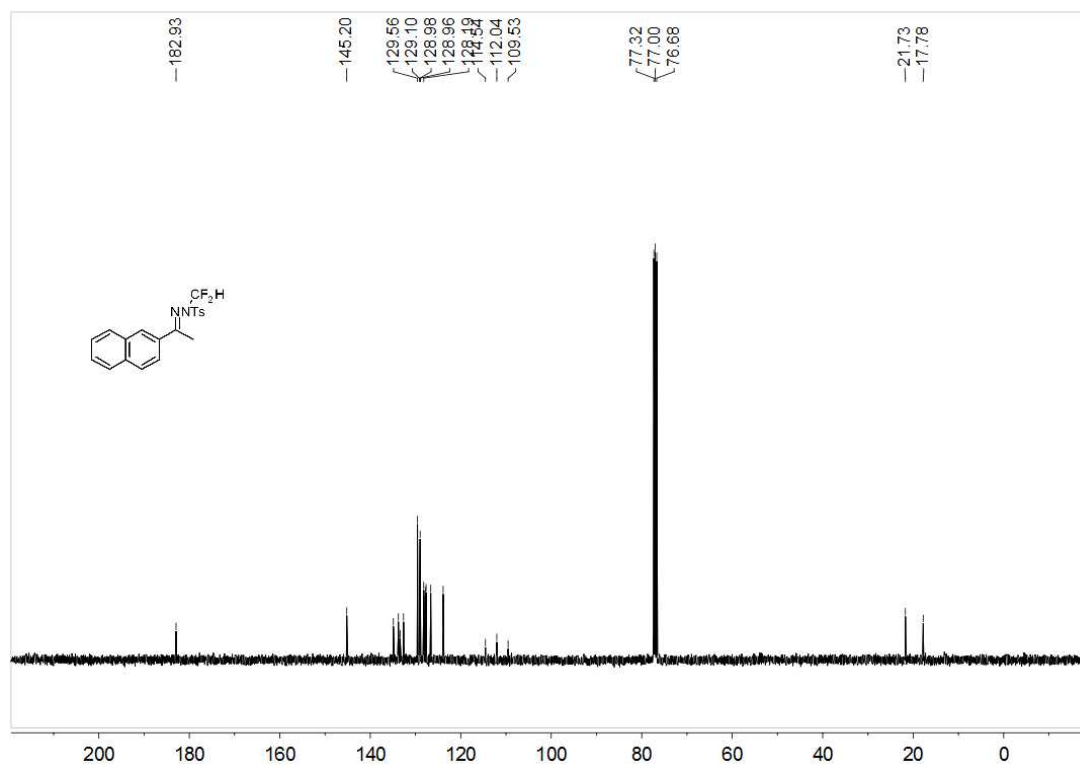
**<sup>19</sup>F NMR spectrum of 2j':**



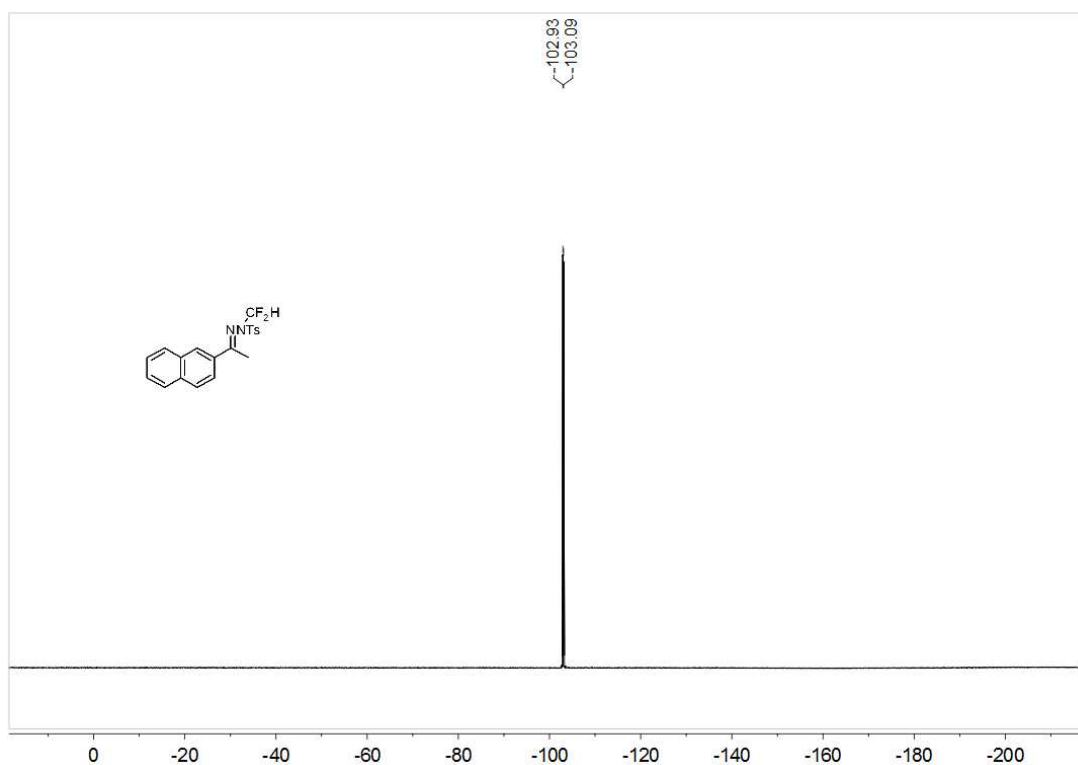
**<sup>1</sup>H NMR spectrum of 2k':**



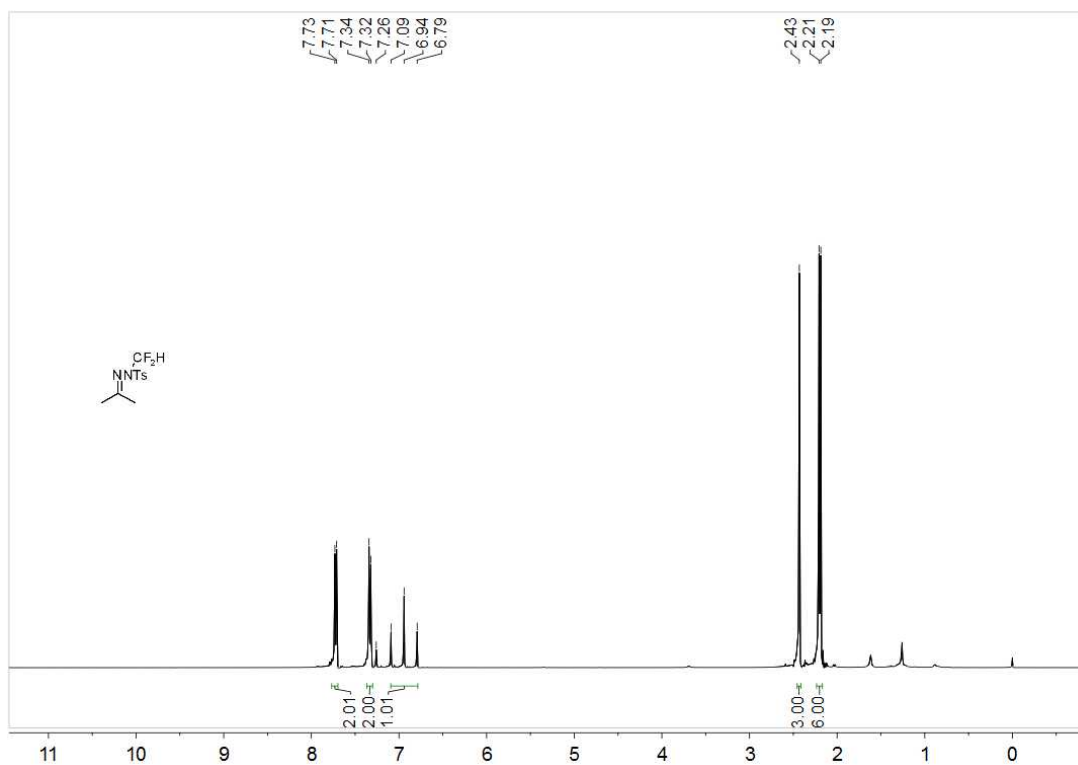
**<sup>13</sup>C NMR spectrum of 2k':**



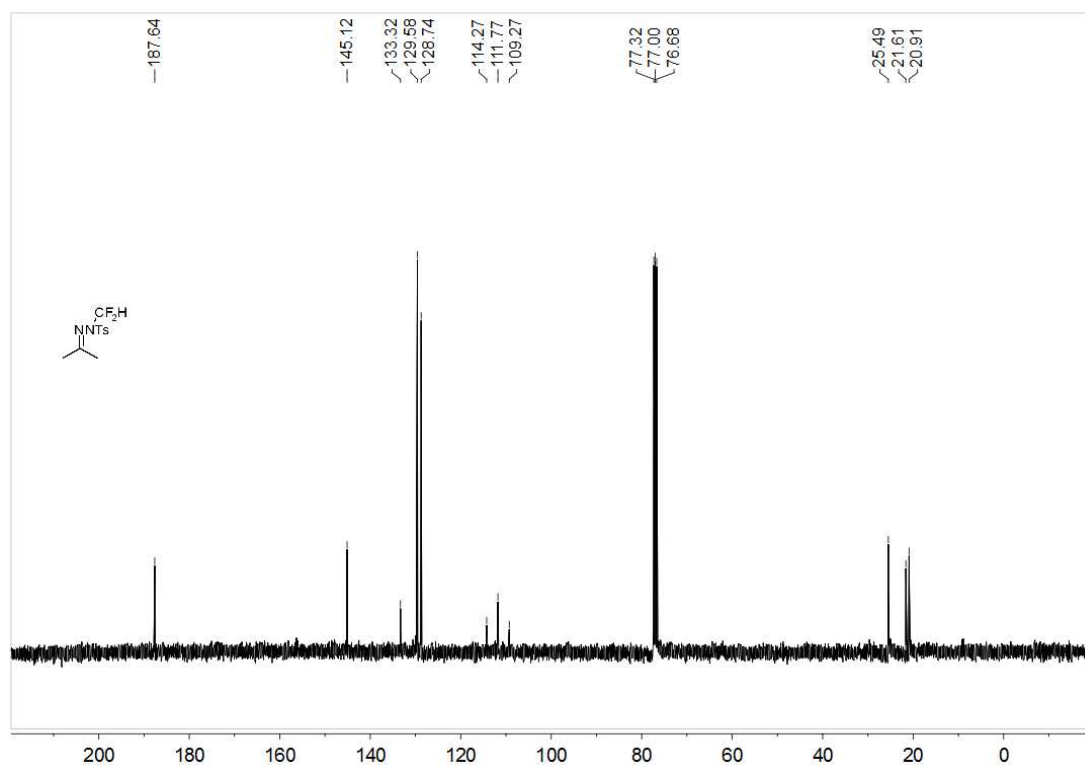
**<sup>19</sup>F NMR spectrum of 2k':**



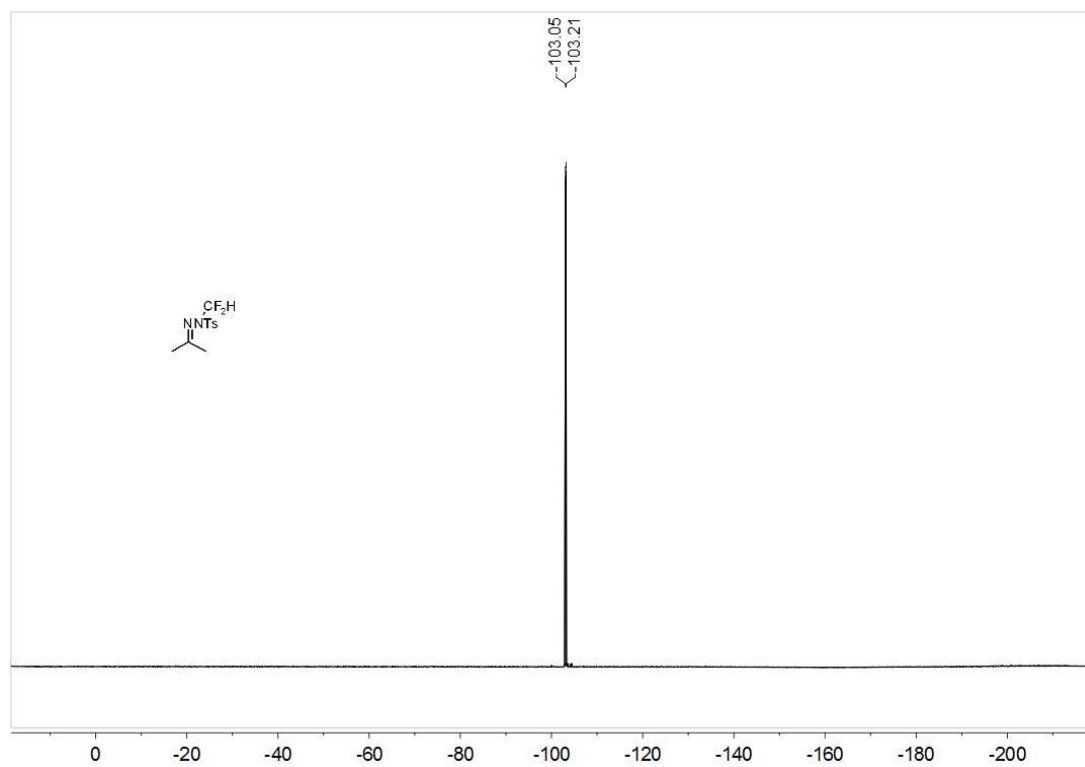
**<sup>1</sup>H NMR spectrum of 2l':**



**$^{13}\text{C}$  NMR spectrum of 2l':**

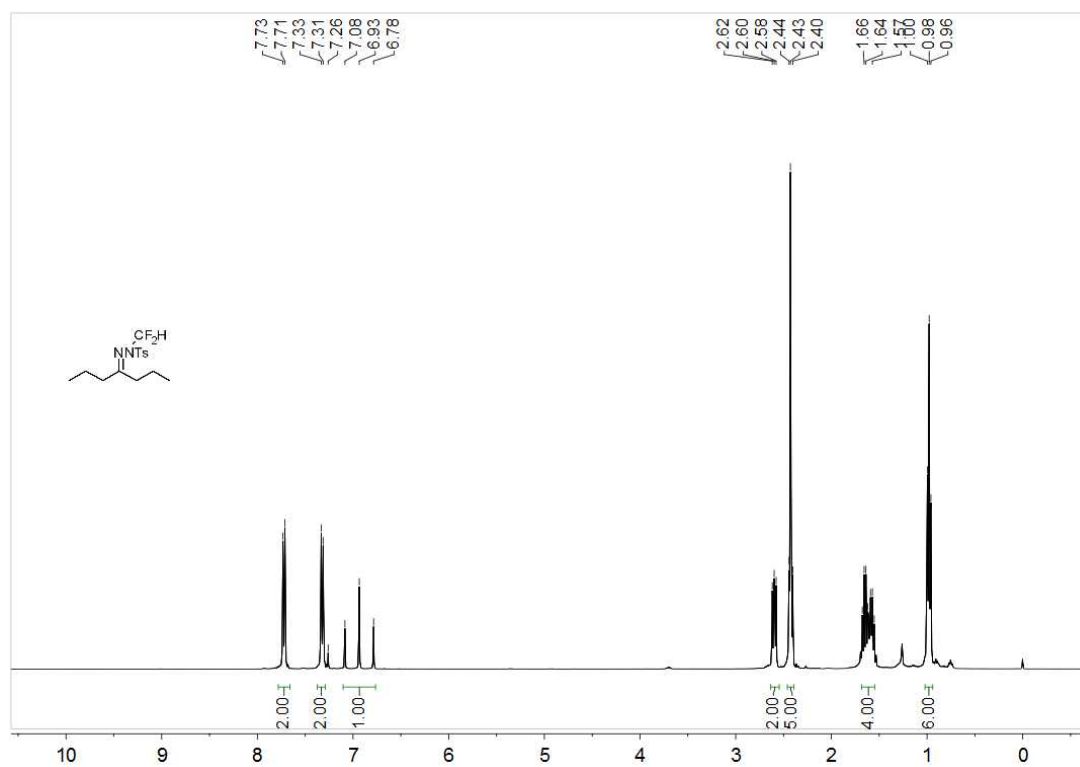


**$^{19}\text{F}$  NMR spectrum of 2l':**

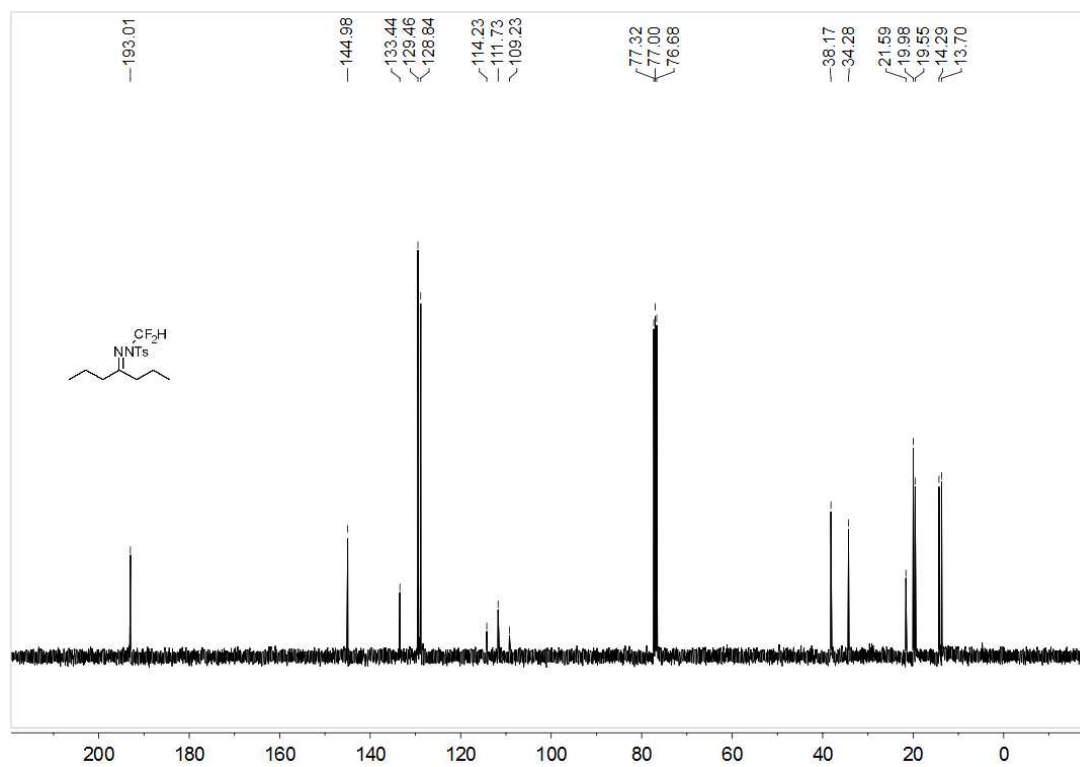




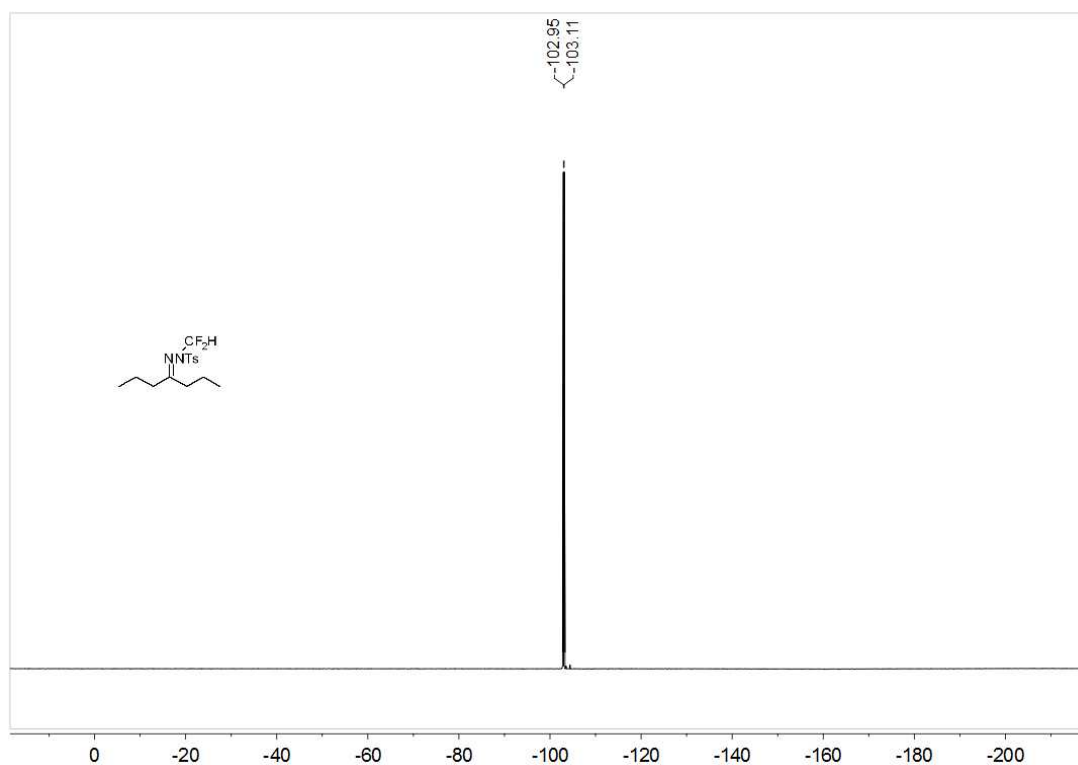
**<sup>1</sup>H NMR spectrum of 2m':**



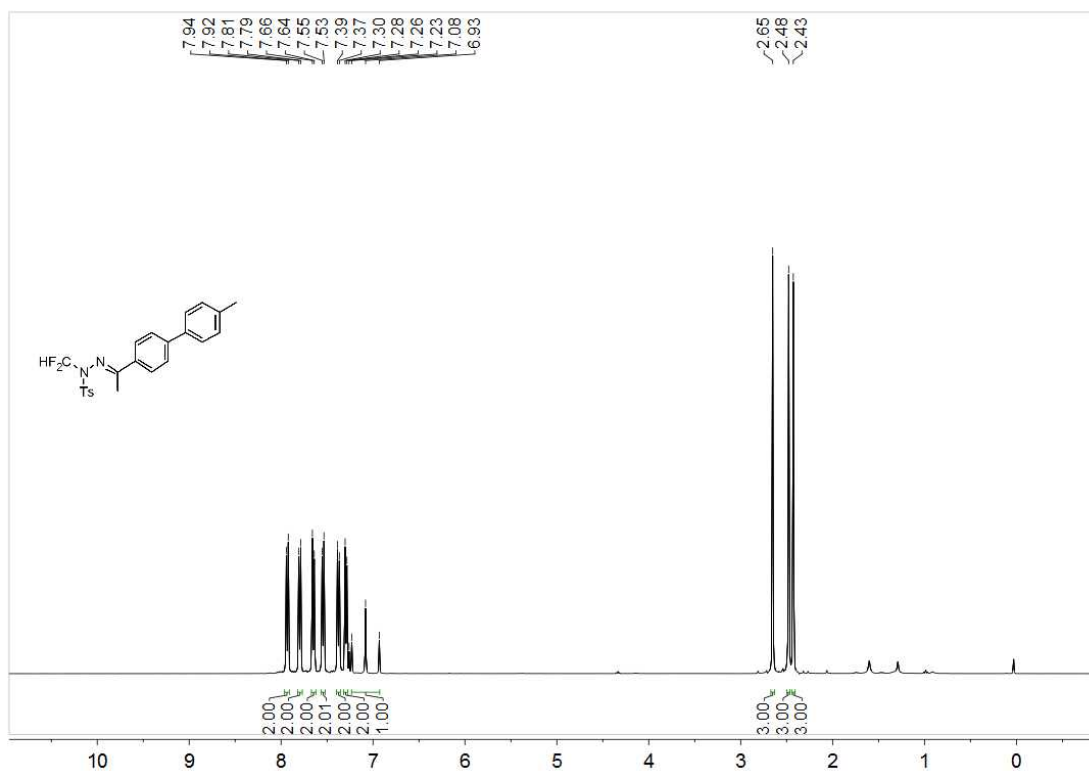
**<sup>13</sup>C NMR spectrum of 2m':**



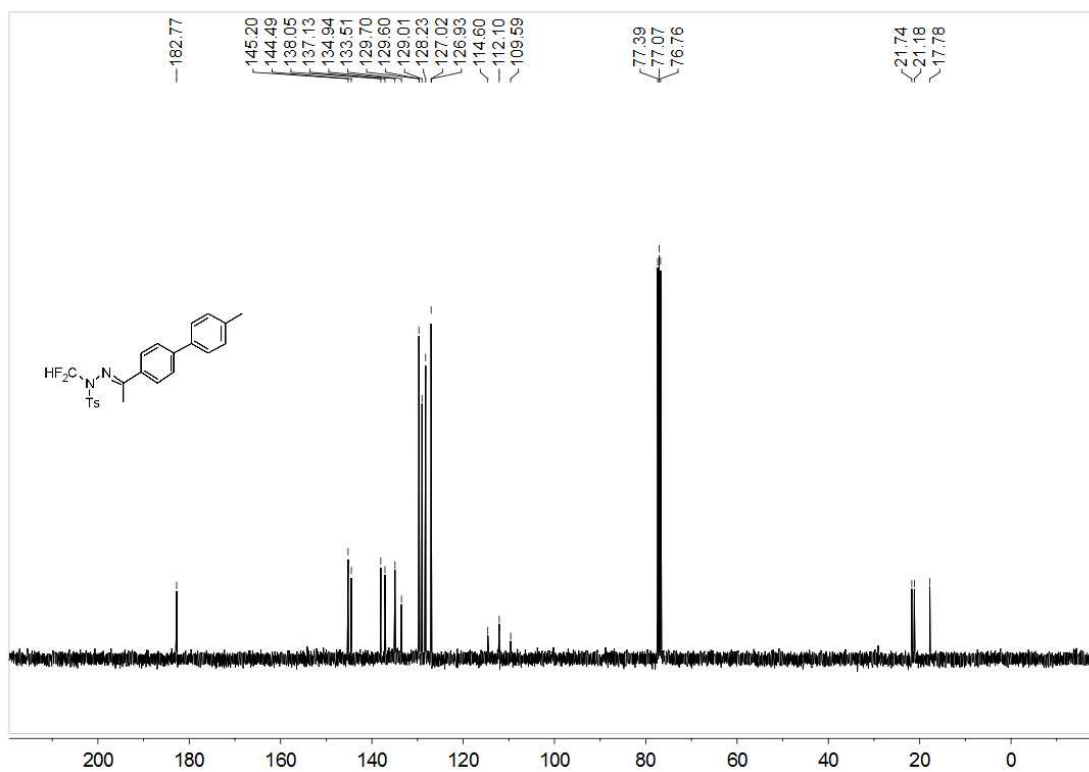
**$^{19}\text{F}$  NMR spectrum of 2m':**



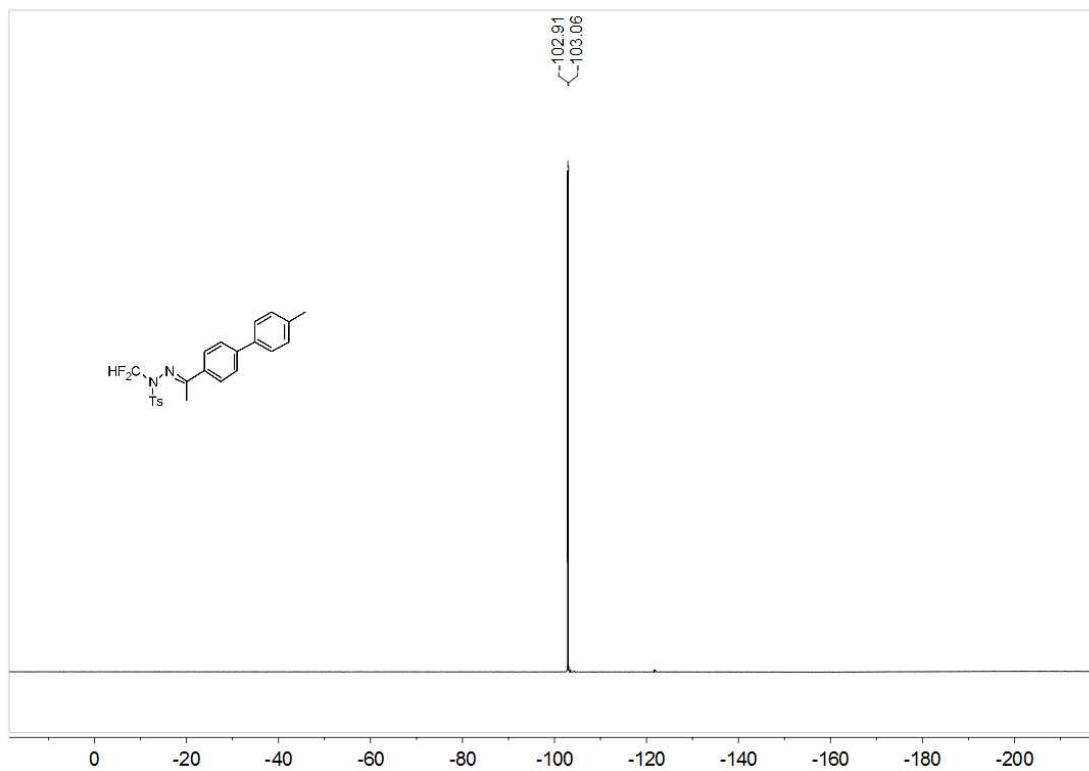
**$^1\text{H}$  NMR spectrum of 3:**



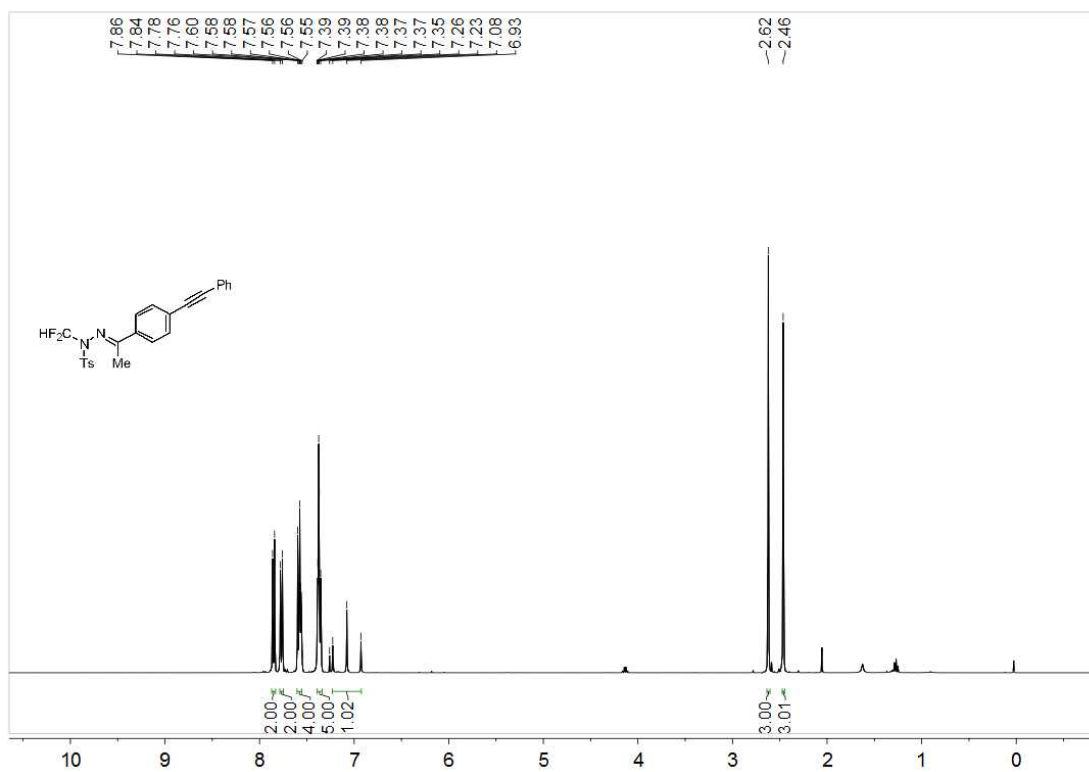
**<sup>13</sup>C NMR spectrum of 3:**



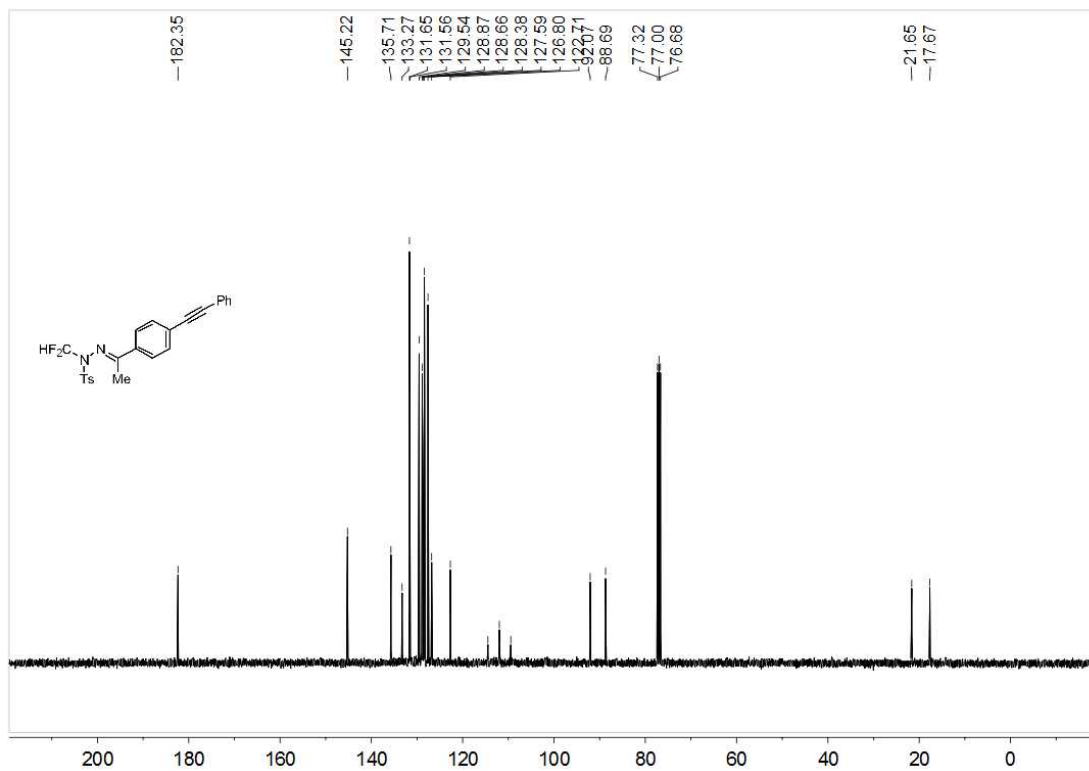
**<sup>19</sup>F NMR spectrum of 3:**



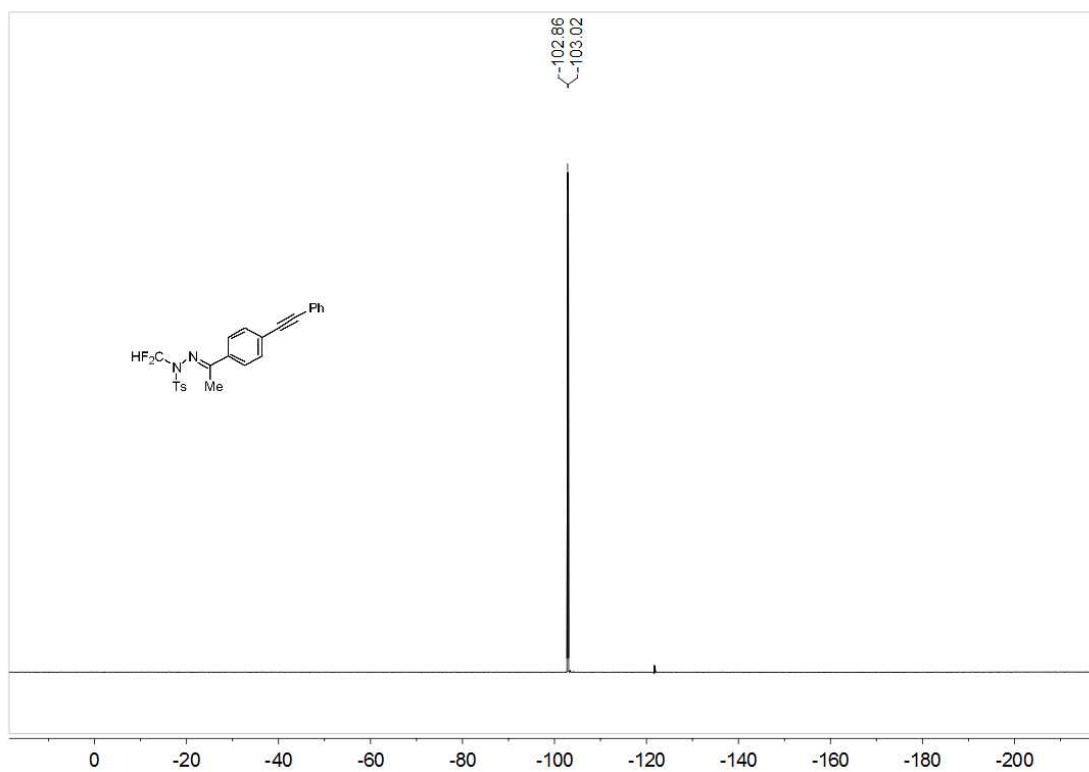
**<sup>1</sup>H NMR spectrum of 4:**



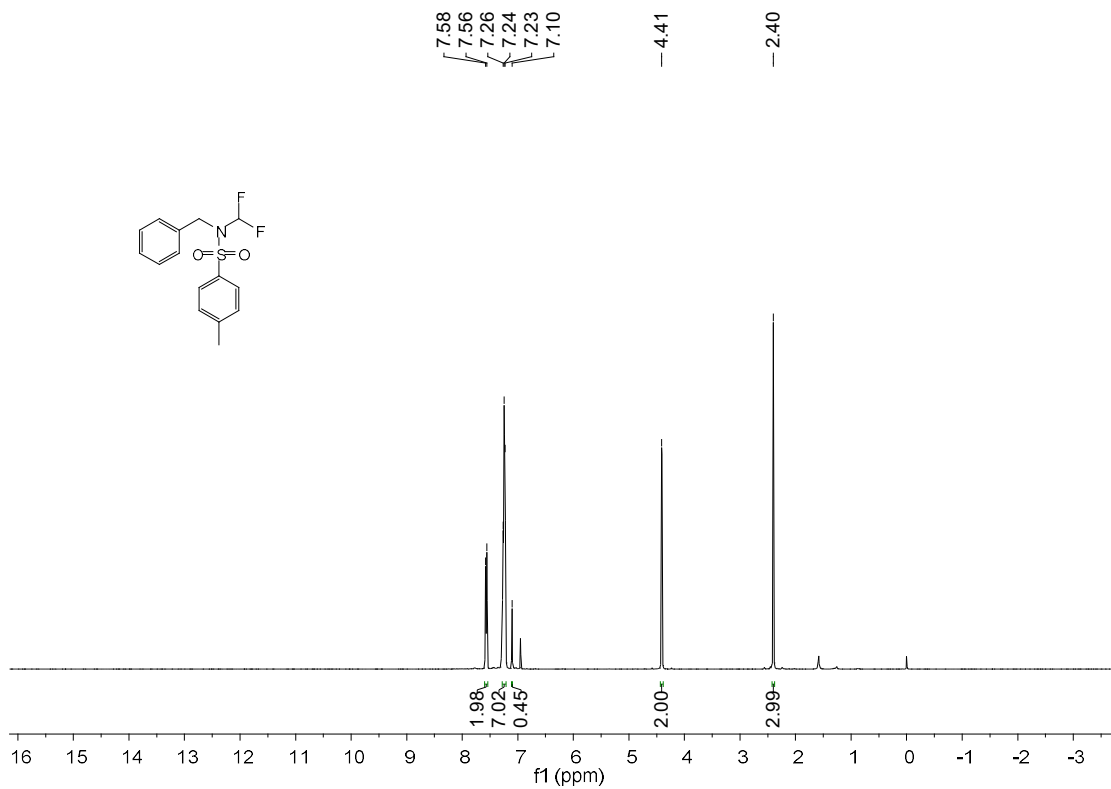
**<sup>13</sup>C NMR spectrum of 4:**



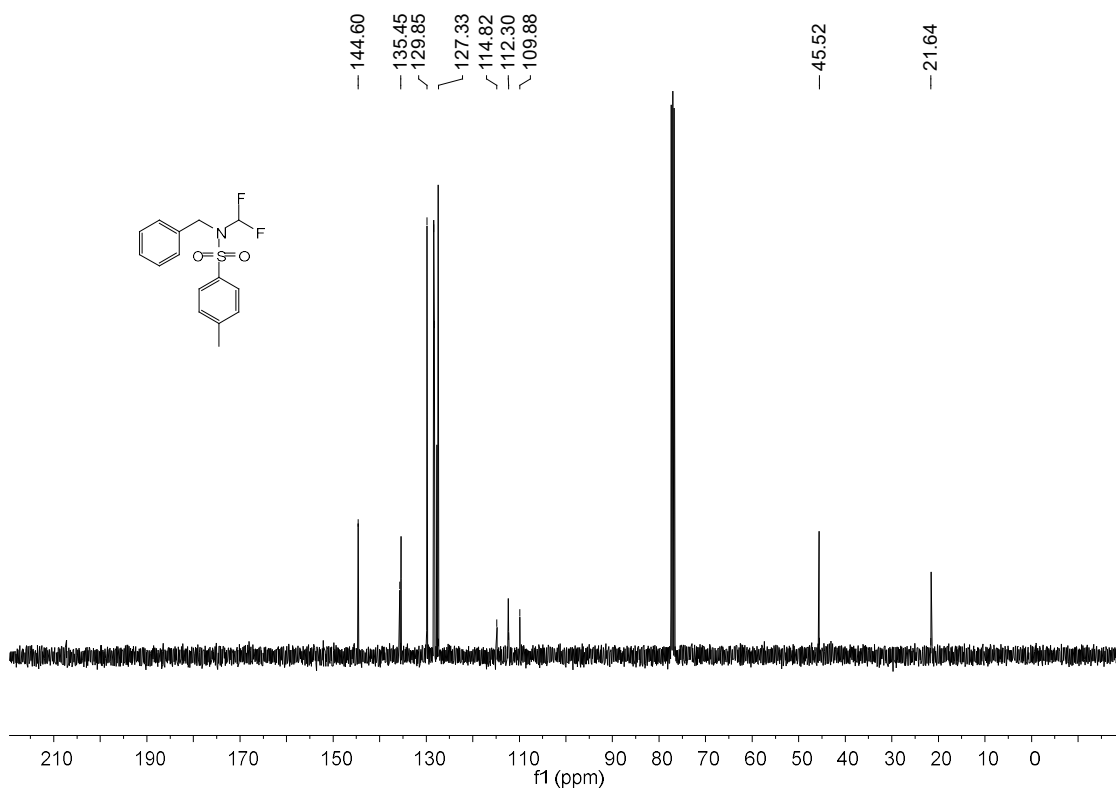
**<sup>19</sup>F NMR spectrum of 4:**



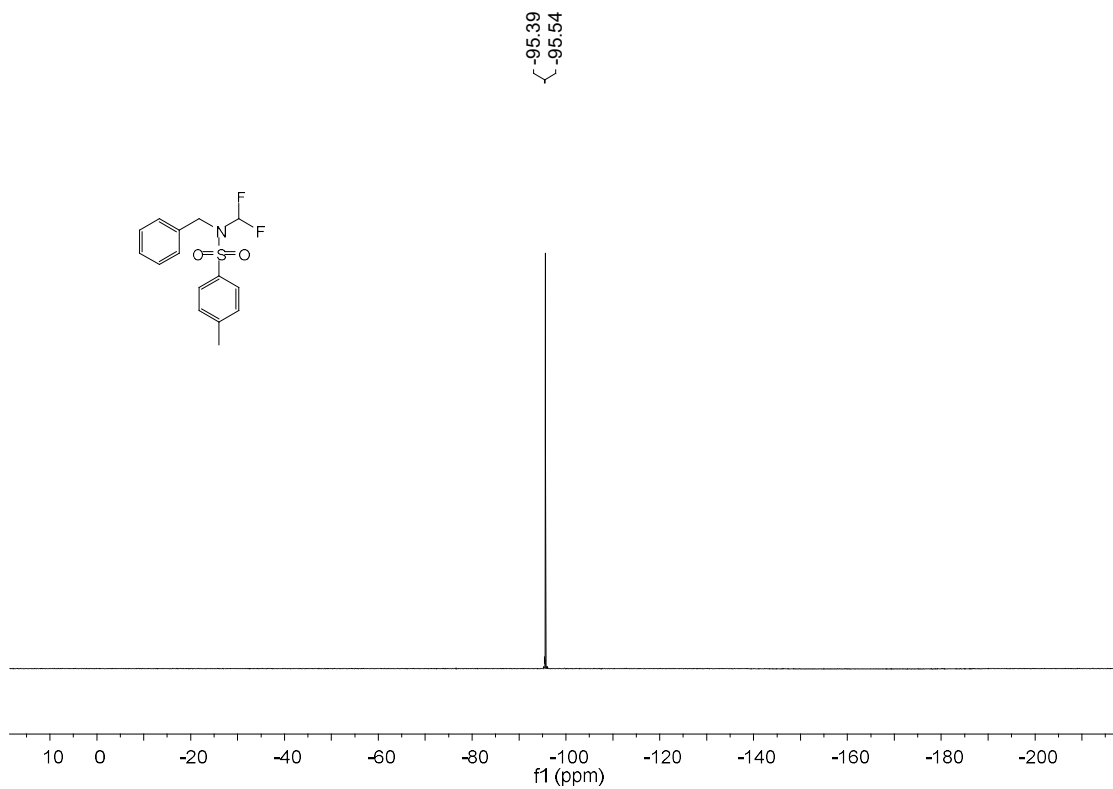
**<sup>1</sup>H NMR spectrum of 6:**



**<sup>13</sup>C NMR spectrum of 6:**

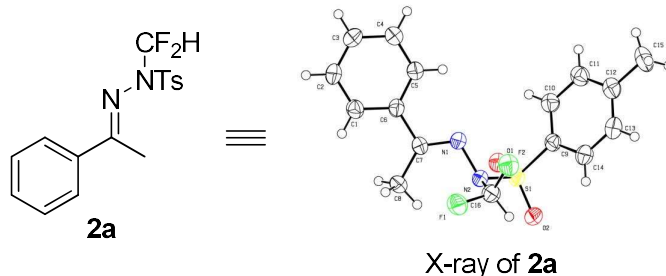


**<sup>19</sup>F NMR spectrum of 6:**



## F. X-ray Crystallographic Data

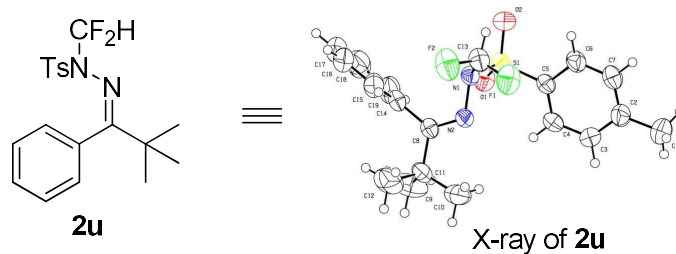
The X-ray crystallographic structures for **2a**. ORTEP representation with 50% probability thermal ellipsoids. Solvent and hydrogen are omitted for clarity. Solvent and hydrogen are omitted for clarity. Crystal data have been deposited to CCDC, number 1834414.



Empirical formula	$\text{C}_{16}\text{H}_{16}\text{F}_2\text{N}_2\text{O}_2\text{S}$
Formula weight	338.37
Temperature	149.5 (10) K
Wavelength	1.54184 Å
Crystal system, space group	monoclinic, $P12_1/c1$
Unit cell dimensions	$a = 8.8310(10)$ Å $\alpha = 89.975$ deg. $b = 16.990(3)$ Å $\beta = 99.969$ deg. $c = 10.851(2)$ Å $\gamma = 90.035$ deg.
Volume	$1603.4(4)$ Å <sup>3</sup>
Z, Calculated density	4, 1.402 Mg/m <sup>3</sup>
Absorption coefficient	$2.088$ mm <sup>-1</sup>
F(000)	704
Crystal size	$0.15 \times 0.12 \times 0.1$ mm
Theta range for data collection	4.890 to 73.965 deg.
Limiting indices	$-10 \leq h \leq 5$ , $-16 \leq k \leq 21$ , $-13 \leq l \leq 13$
Reflections collected / unique	7440 / 3066, [R(int) = 0.0778]
Completeness to theta = 67.684	99.99%

Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	3066 / 0 / 210
Goodness-of-fit on F <sup>2</sup>	1.005
Final R indices [I>2sigma(I)]	R1 = 0.0629, wR2 = 0.1695
R indices (all data)	R1 = 0.1028, wR2 = 0.2175

The X-ray crystallographic structures for **2u**. ORTEP representation with 50% probability thermal ellipsoids. Solvent and hydrogen are omitted for clarity. Solvent and hydrogen are omitted for clarity. Crystal data have been deposited to CCDC, number 1888355.



Empirical formula	C <sub>19</sub> H <sub>22</sub> F <sub>2</sub> N <sub>2</sub> O <sub>2</sub> S
Formula weight	380.14
Temperature	296 K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, C1c1
Unit cell dimensions	a = 13.066(3) Å    alpha = 90 deg. b = 12.853(3) Å    beta = 92.841(6) deg. c = 11.974(3) Å    gamma = 90 deg.
Volume	2008.4(9) Å <sup>3</sup>
Z, Calculated density	4, 1.258 Mg/m <sup>3</sup>
Absorption coefficient	0.193 mm <sup>-1</sup>
F(000)	800
Crystal size	0.28×0.19×0.12 mm
Theta range for data collection	2.22 to 25.27 deg.



Limiting indices	$-16 \leq h \leq 14, -16 \leq k \leq 16, -14 \leq l \leq 15$
Reflections collected / unique	6388 / 3463, [R(int) = 0.0269]
Completeness to theta = 25.242	98.3%
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	3463 / 203 / 239
Goodness-of-fit on F <sup>2</sup>	1.031
Final R indices [I > 2sigma(I)]	R1 = 0.0411, wR2 = 0.1145
R indices (all data)	R1 = 0.0479, wR2 = 0.1200