

## Electronic Supplementary Information

# A directly catalytic ring expansion approach to *o*-fluoronaphthols and *o/p*-fluorophenols from indanones and 2-cyclopentenones

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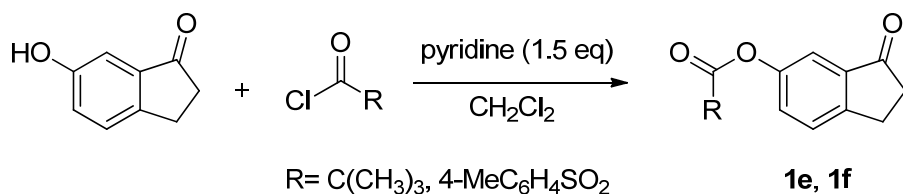
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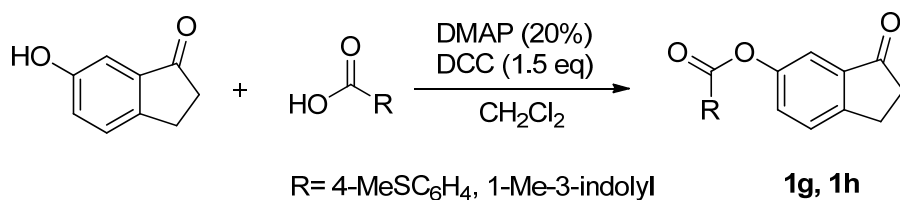
## I. General Information

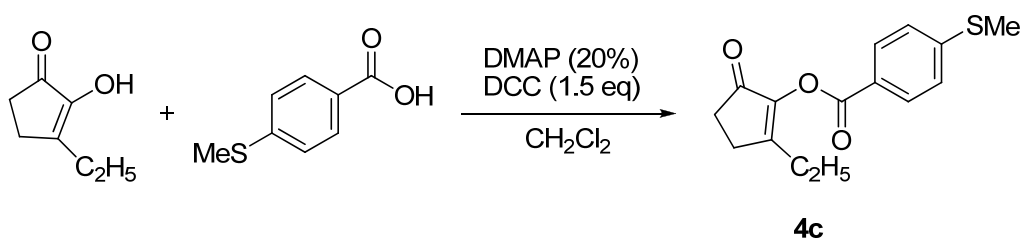
Most of reagents were purchased from commercial suppliers and used as received. TMSCF<sub>2</sub>Br was purchased from Shanghai iGreen Chemical Co. Ltd. Toluene was distilled over sodium/benzophenone before use. The products were purified by column chromatography over silica gel. <sup>1</sup>H NMR, and <sup>13</sup>C NMR were recorded at 25 °C on a Varian 500 MHz, 400 MHz, and 125 MHz spectrometer, respectively by using TMS as internal standard. <sup>19</sup>F NMR were recorded at 25 °C on a Varian 470 MHz spectrometer by using (trifluoromethyl)benzene (δ -63.2) as external standard. Data for <sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F were recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, ddd = doublet of doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, td = triplet of doublets). High-resolution mass spectra (HRMS) were obtained using a Bruker microTOF II focus spectrometer (ESI). Melting points were uncorrected. Substrates **1e**<sup>1</sup>, **1f**<sup>1</sup>, **1g**<sup>2</sup>, **1h**<sup>2</sup>, **4b**<sup>3</sup> and **4c**<sup>2</sup> were synthesized according to the corresponding methods reported in literature. Products **2a**<sup>4</sup> and **2p**<sup>4</sup> are known compounds.

## II. Synthetic procedures and analytical data of compounds 1 and 4

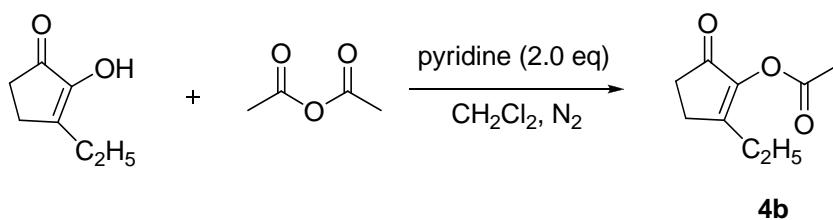


**General procedures for the synthesis of compounds 1e and 1f.** (taking **1e** as an example): To a solution of 6-hydroxy-2,3-dihydro-1H-inden-1-one (296 mg, 2.0 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was added pyridine (237 mg, 3.0 mmol) and pivaloyl chloride (253 mg, 2.1 mmol) at 0 °C. The reaction mixture was stirred for 16 h at room temperature. Saturated aqueous NH<sub>4</sub>Cl solution (30 mL) was then added. The aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 10 mL) and the combined organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After concentrated in vacuo, the crude product was purified by column chromatography (silica gel; petroleum ether/ethyl acetate: 30/1, v/v) to afford **1e** as a white solid (348 mg, 75%).



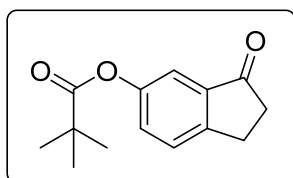


**General procedures for the synthesis of compounds **1g**, **1h** and **4c**.** (taking **1g** as an example): To a stirred solution of 4-(methylthio)benzoic acid (336 mg, 2.0 mmol) in 10 ml anhydrous  $\text{CH}_2\text{Cl}_2$  was added DMAP (24 mg, 0.4 mmol) and 6-hydroxy-2,3-dihydro-1H-inden-1-one (444 mg, 3.0 mmol). Then, DCC (619 mg, 3.0 mmol) was added to the reaction mixture and stirred for 5 min at 0 °C. The reaction mixture was warmed to room temperature and stirred until 4-(methylthio)benzoic acid was consumed (monitored by TLC). The precipitated urea was filtered off and the filtrate was evaporated down in vacuo. The residue was taken up in  $\text{CH}_2\text{Cl}_2$ , and, if necessary, filtered free of any further precipitated urea. The organic phase was then washed twice with dilute HCl, saturated aqueous  $\text{NaHCO}_3$  solution, and dried over anhydrous  $\text{MgSO}_4$ . After the solvent was removed by evaporation, the crude product was purified by column chromatography (silica gel; petroleum ether/ethyl acetate: 20/1, v/v) to afford **1g** as a white solid (477 mg, 80%).



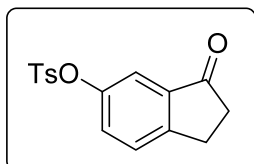
**General procedure for the synthesis of compound **4b**.** To a stirred solution of 3-ethyl-2-hydroxycyclopent-2-en-1-one (252 mg, 2.0 mmol) in  $\text{CH}_2\text{Cl}_2$  (6 mL) was added pyridine (408 mg, 4.0 mmol) and  $\text{Ac}_2\text{O}$  (316 mg, 4.0 mmol) at 0 °C under  $\text{N}_2$  atmosphere. The mixture was stirred for 4 h at room temperature until 3-ethyl-2-hydroxycyclopent-2-en-1-one was consumed (TLC monitoring). After diluted by additional  $\text{CH}_2\text{Cl}_2$  (10 mL), the resulting reaction mixture was washed with aqueous HCl solution (2 M, 3 × 5 mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated in vacuo. The crude product was purified by column chromatography (silica gel; petroleum ether/ethyl acetate: 30/1, v/v) to afford **4b** as a yellow oil. (306 mg, 91% yield).

### 3-oxo-2,3-dihydro-1H-inden-5-yl pivalate (**1e**)



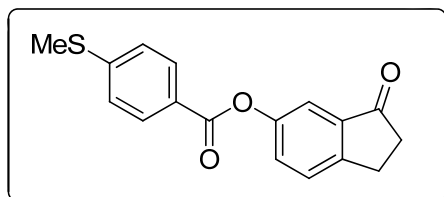
White solid, m.p. 121-123 °C. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 1.36 (s, 9H), 2.73-2.75 (m, 2H), 3.14 (t, *J* = 6.0 Hz, 2H) 7.28 (dd, *J* = 7.5 Hz, 2.5 Hz, 1H), 7.42 (d, *J* = 2.0 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 25.4, 27.1 (3C), 36.8, 39.1, 116.3, 127.4, 128.4, 138.3, 150.5, 152.1, 177.0, 206.0. **HRMS** (ESI-TOF) calcd for C<sub>14</sub>H<sub>17</sub>O<sub>3</sub><sup>+</sup> ([M+H]<sup>+</sup>) 233.1172, found 233.1170.

### 3-oxo-2,3-dihydro-1H-inden-5-yl 4-methylbenzenesulfonate (1f)



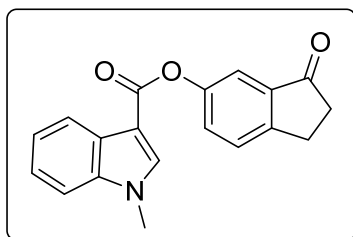
White solid, m.p. 193-195 °C. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 2.45 (s, 3H), 2.70-2.72 (m, 2H), 3.12 (t, *J* = 6.0 Hz, 2H), 7.23 (d, *J* = 2.5 Hz, 1H), 7.31-7.35 (m, 3H), 7.44 (d, *J* = 8.5 Hz, 1H), 7.71 (d, *J* = 8.5 Hz, 2H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 21.7, 25.4, 36.8, 117.0, 127.9, 128.4 (2C), 129.1, 129.9 (2C), 132.1, 138.3, 145.7, 149.1, 153.5, 205.5. **HRMS** (ESI-TOF) calcd for C<sub>16</sub>H<sub>14</sub>NaO<sub>4</sub>S<sup>+</sup> ([M+Na]<sup>+</sup>) 325.0505, found 325.0495.

### 3-oxo-2,3-dihydro-1H-inden-5-yl 4-(methylthio)benzoate (1g)



White solid, m.p. 180-182 °C. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 2.55 (s, 3H), 2.75-2.77 (m, 2H), 3.17 (t, *J* = 6.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.43-7.45 (m, 1H), 7.53 (d, *J* = 8.5 Hz, 1H), 7.57 (d, *J* = 2.0 Hz, 1H), 8.09 (d, *J* = 9.0 Hz, 2H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 14.8, 25.5, 36.9, 116.5 (2C), 125.0 (2C), 127.5, 128.5, 130.5 (2C), 138.4, 146.9, 150.4, 152.3, 164.8, 205.9. **HRMS** (ESI-TOF) calcd for C<sub>17</sub>H<sub>14</sub>NaO<sub>3</sub>S<sup>+</sup> ([M+Na]<sup>+</sup>) 321.0556, found 321.0551.

### 3-oxo-2,3-dihydro-1H-inden-5-yl 1-methyl-1H-indole-3-carboxylate (1h)

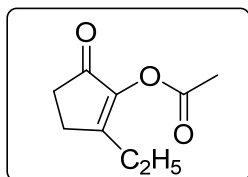


White solid, m.p. 232-234 °C. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 2.74-2.77 (m, 2H), 3.15-3.17 (m, 2H), 3.90 (s, 3H), 7.31-7.36 (m, 2H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.49-7.54 (m, 2H), 7.61 (d, *J* = 1.5 Hz, 1H), 7.97 (s, 1H), 8.22 (d, *J* = 7.5 Hz, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 25.4, 33.6, 36.9, 105.6,



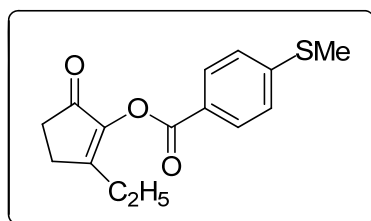
110.0, 116.7, 121.6, 122.4, 123.2, 126.7, 127.3, 129.0, 136.3, 137.3, 138.3, 150.4, 152.0, 162.9, 206.1. **HRMS** (ESI-TOF) calcd for  $C_{19}H_{16}NO_3^+$  ( $[M+H]^+$ ) 306.1125, found 306.1120.

### 2-ethyl-5-oxocyclopent-1-en-1-yl acetate (4b)



Yellow oil.  **$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  1.15 (t,  $J = 7.6$  Hz, 3H), 2.27 (s, 3H), 2.39 (q,  $J = 7.6$  Hz, 2H), 2.46-2.48 (m, 2H), 2.59-2.61 (m, 2H).  **$^{13}C$  NMR** (125 MHz,  $CDCl_3$ )  $\delta$  11.0, 20.3, 22.4, 25.3, 32.3, 145.3, 165.5, 167.6, 200.3. **HRMS** (ESI-TOF) calcd for  $C_9H_{12}NaO_3^+$  ( $[M+Na]^+$ ) 191.0679, found 191.0670.

### 2-ethyl-5-oxocyclopent-1-en-1-yl 4-(methylthio)benzoate (4c)



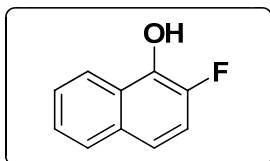
White solid, m.p. 101-103 °C.  **$^1H$  NMR** (500 MHz,  $CDCl_3$ )  $\delta$  1.17 (t,  $J = 7.5$  Hz, 3H), 2.44 (q,  $J = 7.5$  Hz, 2H), 2.52-2.54 (m, 5H), 2.64-2.66 (m, 2H), 7.27 (d,  $J = 9.0$  Hz, 2H), 8.02 (d,  $J = 9.0$  Hz, 2H).  **$^{13}C$  NMR** (125 MHz,  $CDCl_3$ )  $\delta$  11.0, 14.7, 22.5, 25.5, 32.4, 124.4, 124.8 (2C), 130.6 (2C), 145.5, 146.8, 163.1, 165.7, 200.3. **HRMS** (ESI-TOF) calcd for  $C_{15}H_{16}NaO_3S^+$  ( $[M+Na]^+$ ) 299.0712, found 299.0707.

## III. Synthetic procedures and analytical data of compounds 2, 3a, 5 and 6

**General procedures for the synthesis of compounds 2, 3a, 5 and 6** (taking 2a as an example): To a 15 mL oven-dried pressure tube were added 1a (66 mg, 0.5 mmol),  $nBu_4NBr$  (16 mg, 0.05 mmol),  $TMSCF_2Br$  (152 mg, 0.75 mmol), and 2 mL of toluene in sequence at room temperature. The tube was sealed by a rubber septum tightly and the reaction mixture was stirred at 110 °C for 3 h. Then, an additional  $TMSCF_2Br$  (152 mg, 0.75 mmol) was injected by a syringe to the reaction mixture followed by reacting another 4 h. After the reaction mixture was cooled to room temperature, a solution of  $nBu_4NF$  in THF (0.1 mL,  $M = 1$  mol/L, 0.1 mmol) was injected and the reaction continued to be stirred at room temperature for 2 h. The resulting mixture was then poured into diluted aqueous hydrochloric acid (20 mL), extracted with  $CH_2Cl_2$  ( $3 \times 15$  mL). The organic layers were combined and dried over anhydrous  $MgSO_4$ . After removal of the solvents in *vacuo*, the

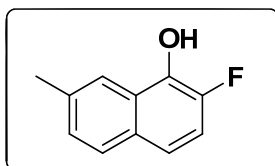
residue was subjected to column chromatography (silica gel; petroleum ether/ethyl acetate: 100/1, v/v) to give **2a** (73 mg, 90%) as a white solid.

#### 2-fluoronaphthalen-1-ol (**2a**)<sup>4</sup>



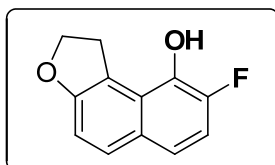
White solid, m.p. 77-79 °C (lit 72-74 °C).<sup>4</sup> **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 5.58 (d, *J* = 4.0 Hz, 1H), 7.26 (t, *J* = 9.5 Hz, 1H), 7.35 (dd, *J* = 9.0 Hz, 5.5 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 8.5 Hz, 1H), δ 8.19 (d, *J* = 8.5 Hz, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 115.4 (d, *J* = 21.8 Hz, 1C), 120.4 (d, *J* = 7.4 Hz, 1C), 121.5 (d, *J* = 6.7 Hz, 1C), 125.2 (d, *J* = 2.9 Hz, 1C), 125.5 (d, *J* = 2.4 Hz, 1C), 125.8, 127.6 (d, *J* = 1.5 Hz, 1C), 131.0, 137.3 (d, *J* = 13.9 Hz, 1C), 146.5 (d, *J* = 232.7 Hz, 1C). **<sup>19</sup>F NMR** (470 MHz, CDCl<sub>3</sub>) δ -147.3 (d, *J* = 4.2 Hz, 1F). **HRMS** (ESI-TOF) calcd for C<sub>10</sub>H<sub>8</sub>FO<sup>+</sup> ([M+H]<sup>+</sup>) 163.0554, found 163.0549.

#### 2-fluoro-7-methylnaphthalen-1-ol (**2b**)



White solid, m.p. 88-90 °C. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 2.57 (s, 3H), 5.63 (d, *J* = 4.5 Hz, 1H), 7.24 (t, *J* = 9.0 Hz, 1H), 7.31 (dd, *J* = 1.0 Hz, *J* = 8.5 Hz, 1H), 7.35 (dd, *J* = 5.5 Hz, *J* = 9.0 Hz, 1H), 7.72 (d, *J* = 8.5 Hz, 1H), 8.02 (s, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 21.8, 114.4 (d, *J* = 22.0 Hz, 1C), 120.1 (d, *J* = 28.5 Hz, 1C), 120.4 (d, *J* = 6.6 Hz, 1C), 125.3 (d, *J* = 3.4 Hz, 1C), 127.4 (d, *J* = 1.5 Hz, 1C), 127.8 (d, *J* = 2.4 Hz, 1C), 129.3, 135.7, 136.8 (d, *J* = 13.9 Hz, 1C), 146.7 (d, *J* = 230.7 Hz, 1C). **<sup>19</sup>F NMR** (470 MHz, CDCl<sub>3</sub>) δ -147.3 (t, *J* = 4.7 Hz, 1F). **HRMS** (ESI-TOF) calcd for C<sub>11</sub>H<sub>10</sub>FO<sup>+</sup> ([M]<sup>+</sup>) 177.0710, found 177.0711.

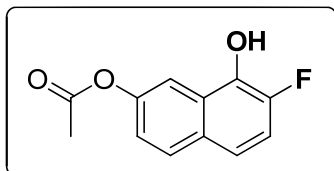
#### 8-fluoro-1,2-dihydronaphtho[2,1-b]furan-9-ol (**2c**)



Light yellow crystal, m.p. 157-159 °C. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 3.83 (t, *J* = 9.0 Hz, 2H), 4.71 (t, *J* = 9.0 Hz, 2H), 5.35 (d, *J* = 5.5 Hz, 1H), 7.03-7.07 (m, 2H), 7.28 (dd, *J* = 5.0 Hz, *J* = 9.0 Hz,

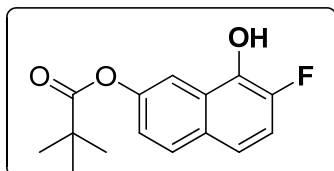
1H), 7.55 (d,  $J = 8.5$  Hz, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  31.3, 72.0, 111.7 (d,  $J = 2.5$  Hz, 1C), 112.3 (d,  $J = 21.9$  Hz, 1C), 117.3, 121.1, 123.5, 127.5, 128.7 (d,  $J = 1.6$  Hz, 1C), 137.1 (d,  $J = 15.0$  Hz, 1C), 147.7 (d,  $J = 230.6$  Hz, 1C), 158.1.  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -147.9 (dd,  $J = 5.2$  Hz,  $J = 9.4$  Hz, 1F). HRMS (ESI-TOF) calcd for  $\text{C}_{12}\text{H}_{10}\text{FO}_2^+$  ( $[\text{M}+\text{H}]^+$ ) 205.0659, found 205.0661.

#### 7-fluoro-8-hydroxynaphthalen-2-yl acetate (2d)



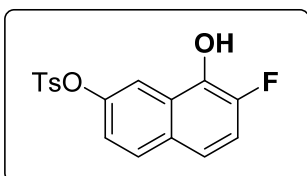
White crystal, m.p. 132-134 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  2.37 (s, 1H), 5.68 (s, 1H), 7.17-7.24 (m, 2H), 7.33 (dd,  $J = 5.0$  Hz,  $J = 9.0$  Hz, 1H), 7.77 (d,  $J = 9.0$  Hz, 2H), 7.86 (d,  $J = 2.0$  Hz, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  21.2, 113.0 (d,  $J = 6.9$  Hz, 1C), 115.3 (d,  $J = 21.9$  Hz, 1C), 120.2 (d,  $J = 7.6$  Hz, 1C), 120.8, 125.8 (d,  $J = 3.4$  Hz, 1C), 129.0, 129.2, 137.2 (d,  $J = 14.5$  Hz, 1C), 147.0 (d,  $J = 232.3$  Hz, 1C), 148.4, 169.9.  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  (-146.20) - (-146.16) (m, 1F). HRMS (ESI-TOF) calcd for  $\text{C}_{12}\text{H}_{10}\text{FO}_3^+$  ( $[\text{M}+\text{H}]^+$ ) 221.0608, found 221.0602.

#### 7-fluoro-8-hydroxynaphthalen-2-yl pivalate (2e)



White crystal, m.p. 131-133 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  1.41 (s, 9H), 5.95 (s, 1H), 7.12 (t,  $J = 7.5$  Hz, 2H), 7.24 (dd,  $J = 5.0$  Hz,  $J = 9.0$  Hz, 1H), 7.70 (d,  $J = 9.0$  Hz, 1H), 7.80 (s, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  27.1 (s, 3C), 39.2, 112.8 (d,  $J = 6.7$  Hz, 1C), 115.1 (d,  $J = 21.9$  Hz, 1C), 120.0 (d,  $J = 7.6$  Hz, 1C), 120.7 (d,  $J = 2.5$  Hz, 1C), 125.9 (d,  $J = 3.6$  Hz, 1C), 128.9, 129.0, 137.2 (d,  $J = 16.5$  Hz, 1C), 147.0 (d,  $J = 232.9$  Hz, 1C), 148.8, 177.6.  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  (-146.4) - (-146.3) (m, 1F). HRMS (ESI-TOF) calcd for  $\text{C}_{15}\text{H}_{15}\text{FNaO}_3^+$  ( $[\text{M}+\text{Na}]^+$ ) 285.0897, found 285.0896.

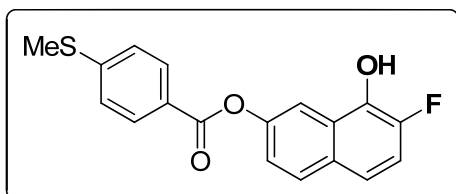
#### 7-fluoro-8-hydroxynaphthalen-2-yl 4-methylbenzenesulfonate (2f)



White solid, m.p. 191-193 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  2.44 (s, 3H), 5.65 (s, 1H), 7.10 (dd,  $J$

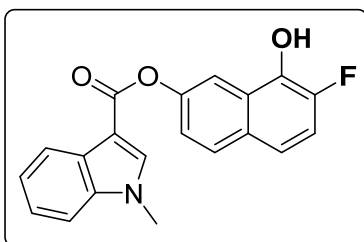
= 2.5 Hz,  $J = 9.0$  Hz, 1H), 7.26 (t,  $J = 9.5$  Hz, 1H), 7.30-7.35 (m, 3H), 7.69 (d,  $J = 9.0$  Hz, 1H), 7.75 (d,  $J = 8.0$  Hz, 2H), 7.78 (d,  $J = 2.5$  Hz, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  21.7, 114.3 (d,  $J = 6.9$  Hz, 1C), 116.0 (d,  $J = 9.4$  Hz, 1C), 120.2 (d,  $J = 7.6$  Hz, 1C), 120.9 (d,  $J = 2.6$  Hz, 1C), 125.6, 128.5 (2C), 129.4, 129.6, 129.8 (2C), 132.4, 137.4 (d,  $J = 14.5$  Hz, 1C), 145.4, 147.1 (d,  $J = 233.0$  Hz, 1C), 147.4.  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -145.6 (s, 1F). HRMS (ESI-TOF) calcd for  $\text{C}_{17}\text{H}_{13}\text{FNaO}_4\text{S}^+$  ( $[\text{M}+\text{Na}]^+$ ) 355.0411, found 355.0397.

### 7-fluoro-8-hydroxynaphthalen-2-yl 4-(methylthio)benzoate (2g)



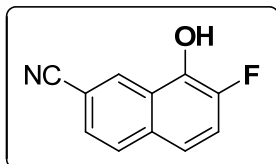
White solid, m.p. 178-180 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  2.56 (s, 3H), 5.70 (d,  $J = 3.5$  Hz, 1H), 7.24 (t,  $J = 9.5$  Hz, 1H), 7.30-7.34 (m, 3H), 7.37 (dd,  $J = 5.0$  Hz,  $J = 9.0$  Hz, 1H), 7.82 (d,  $J = 8.5$  Hz, 1H), 8.00 (d,  $J = 2.5$  Hz, 1H), 8.14 (d,  $J = 8.5$  Hz, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  14.8, 113.1 (d,  $J = 6.9$  Hz, 1C), 115.3 (d,  $J = 21.9$  Hz, 1C), 120.3 (d,  $J = 7.6$  Hz, 1C), 121.0 (d,  $J = 2.5$  Hz, 1C), 125.0 (2C), 125.4, 125.9, 129.1, 129.2, 130.5 (2C), 137.3 (d,  $J = 14.1$  Hz, 1C), 146.7, 147.1 (d,  $J = 232.5$  Hz, 1C), 148.8, 165.1.  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -146.1 (t,  $J = 4.7$  Hz, 1F). HRMS (ESI-TOF) calcd for  $\text{C}_{18}\text{H}_{14}\text{FO}_3\text{S}^+$  ( $[\text{M}+\text{H}]^+$ ) 329.0642, found 329.0640.

### 7-fluoro-8-hydroxynaphthalen-2-yl 1-methyl-1H-indole-3-carboxylate (2h)



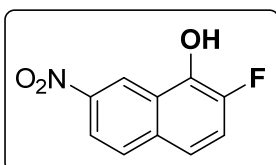
White solid, m.p. 251-253 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO}-d_6$ )  $\delta$  3.94 (s, 3H), 7.29-7.36 (m, 2H), 7.39-7.43 (m, 2H), 7.49 (dd,  $J = 5.0$  Hz,  $J = 8.0$  Hz, 1H), 7.63 (d,  $J = 8.0$  Hz, 1H), 7.95 (d,  $J = 2.0$  Hz, 1H), 7.97 (d,  $J = 9.0$  Hz, 1H), 8.08 (d,  $J = 7.5$  Hz, 1H), 8.45 (s, 1H), 10.3 (s, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO}-d_6$ )  $\delta$  33.7, 104.5, 111.5, 113.5 (d,  $J = 6.7$  Hz, 1C), 116.5 (d,  $J = 22.0$  Hz, 1C), 119.8 (d,  $J = 7.6$  Hz, 1C), 120.9, 121.8, 122.5, 123.2, 126.7, 127.4, 129.2, 129.8, 137.7, 138.1, 138.2 (d,  $J = 13.7$  Hz, 1C), 147.7 (d,  $J = 235.0$  Hz, 1C), 148.9, 162.9.  $^{19}\text{F}$  NMR (470 MHz,  $\text{DMSO}-d_6$ )  $\delta$  -135.9 (dd,  $J = 3.8$  Hz,  $J = 10.8$  Hz, 1F). HRMS (ESI-TOF) calcd for  $\text{C}_{20}\text{H}_{15}\text{FNO}_3^+$  ( $[\text{M}+\text{H}]^+$ ) 336.1030, found 336.1033.

### 7-fluoro-8-hydroxy-2-naphthonitrile (2i)



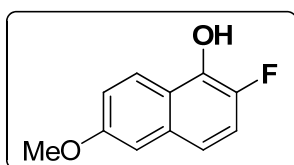
White solid, m.p. 219-221 °C. **<sup>1</sup>H NMR** (500 MHz, DMSO-*d*<sub>6</sub>) δ 7.55 (dd, *J* = 5.0 Hz, *J* = 9.0 Hz, 1H), 7.64 (dd, *J* = 9.0 Hz, *J* = 10.0 Hz, 1H), 7.73 (dd, *J* = 1.5 Hz, *J* = 8.5 Hz, 1H), 8.07 (d, *J* = 8.5 Hz, 1H), 8.61 (d, *J* = 1.0 Hz, 1H), 10.83 (s, 1H). **<sup>13</sup>C NMR** (125 MHz, DMSO-*d*<sub>6</sub>) δ 108.5, 119.7, 120.0 (d, *J* = 7.3 Hz, 1C), 120.4 (d, *J* = 22.0 Hz, 1C), 125.9 (d, *J* = 5.0 Hz, 1C), 126.1, 128.7 (d, *J* = 6.7 Hz, 1C), 129.8, 132.5, 139.3 (d, *J* = 13.4 Hz, 1C), 148.0 (d, *J* = 236.6 Hz, 1C). **<sup>19</sup>F NMR** (470 MHz, DMSO-*d*<sub>6</sub>) δ -133.9 (dd, *J* = 4.7 Hz, *J* = 10.3 Hz, 1F). **HRMS** (ESI-TOF) calcd for C<sub>11</sub>H<sub>7</sub>FNO<sup>+</sup> ([M+H]<sup>+</sup>) 188.0506, found 188.0507.

### 2-fluoro-7-nitronaphthalen-1-ol (2j)



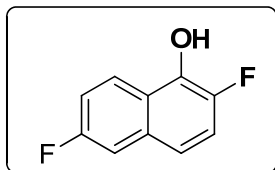
Yellow oil. **<sup>1</sup>H NMR** (500 MHz, DMSO-*d*<sub>6</sub>) δ 7.61 (dd, *J* = 5.0 Hz, *J* = 9.0 Hz, 1H), 7.67-7.71 (m, 1H), 8.12 (d, *J* = 9.0 Hz, 1H), 8.16 (dd, *J* = 2.0 Hz, *J* = 9.0 Hz, 1H), 9.02 (s, 1H), 11.09 (s, 1H). **<sup>13</sup>C NMR** (125 MHz, DMSO-*d*<sub>6</sub>) δ 118.9, 119.3 (d, *J* = 7.0 Hz, 1C), 119.9 (d, *J* = 7.3 Hz, 1C), 121.3 (d, *J* = 22.1 Hz, 1C), 125.5 (d, *J* = 5.5 Hz, 1C), 130.4, 133.7, 140.7 (d, *J* = 14.2 Hz, 1C), 145.3, 148.2 (d, *J* = 237.0 Hz, 1C), **<sup>19</sup>F NMR** (470 MHz, DMSO-*d*<sub>6</sub>) δ -133.7 (dd, *J* = 4.7 Hz, *J* = 11.3 Hz, 1F). **HRMS** (ESI-TOF) calcd for C<sub>10</sub>H<sub>7</sub>FNO<sub>3</sub><sup>+</sup> ([M+H]<sup>+</sup>) 208.0404, found 207.0405.

### 2-fluoro-6-methoxynaphthalen-1-ol (2k)



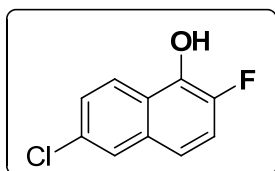
Brown oil. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 3.89 (s, 3H), 5.69 (d, *J* = 11.5 Hz, 1H), 7.06 (d, *J* = 2.5 Hz, 1H), 7.17 (dd, *J* = 2.0 Hz, *J* = 9.0 Hz, 1H), 7.22 (d, *J* = 7.5 Hz, 2H), 8.09 (d, *J* = 9.0 Hz, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 55.3, 105.6, 115.8 (d, *J* = 21.4 Hz, 1C), 118.6, 118.8 (d, *J* = 7.0 Hz, 1C), 120.4 (d, *J* = 2.4 Hz, 1C), 123.1 (d, *J* = 6.5 Hz, 1C), 132.2, 137.6 (d, *J* = 14.1 Hz, 1C), 145.5 (d, *J* = 229.0 Hz, 1C), 157.3 (d, *J* = 2.2 Hz, 1C). **<sup>19</sup>F NMR** (470 MHz, CDCl<sub>3</sub>) δ -150.4 (t, *J* = 6.8 Hz, 1F). **HRMS** (ESI-TOF) calcd for C<sub>11</sub>H<sub>10</sub>FO<sub>2</sub><sup>+</sup> ([M+H]<sup>+</sup>) 193.0659, found 192.0664.

### 2,6-difluoronaphthalen-1-ol (2l)



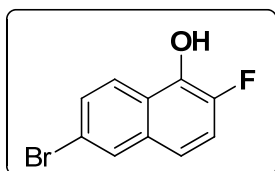
White solid, m.p. 118-120 °C. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 5.58 (d, *J* = 4.0 Hz, 1H), 7.25-7.30 (m, 3H), 7.38 (dd, *J* = 2.5 Hz, *J* = 10.0 Hz, 1H), 8.18 (dd, *J* = 6.5 Hz, *J* = 9.0 Hz, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 110.7 (d, *J* = 20.7 Hz, 1C), 116.2 (d, *J* = 25.4 Hz, 1C), 116.7 (d, *J* = 21.7 Hz, 1C), 119.4 (dd, *J* = 5.4 Hz, *J* = 7.2 Hz, 1C), 122.1, 124.2 (dd, *J* = 7.0 Hz, *J* = 8.9 Hz, 1C), 131.8 (d, *J* = 9.2 Hz, 1C), 137.7 (d, *J* = 14.3 Hz, 1C), 146.0 (d, *J* = 230.0 Hz, 1C), 160.5 (d, *J* = 245.4 Hz, 1C). **<sup>19</sup>F NMR** (470 MHz, CDCl<sub>3</sub>) δ -148.6 (dd, *J* = 4.7 Hz, *J* = 8.0 Hz, 1F), (-117.7) - (-117.6) (m, 1F). **HRMS** (ESI-TOF) calcd for C<sub>10</sub>H<sub>7</sub>F<sub>2</sub>O<sup>+</sup> ([M+H]<sup>+</sup>) 181.0459, found 181.0455.

### 6-chloro-2-fluoronaphthalen-1-ol (2m)



White solid, m.p. 101-103 °C. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 5.60 (d, *J* = 4.0 Hz, 1H), 7.24-7.30 (m, 2H), 7.42 (dd, *J* = 1.5 Hz, *J* = 9.0 Hz, 1H), 7.74 (d, *J* = 1.5 Hz, 1H), 8.12 (d, *J* = 9.0 Hz, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 116.6 (d, *J* = 21.7 Hz, 1C), 119.5 (d, *J* = 7.4 Hz, 1C), 123.4 (d, *J* = 6.7 Hz, 1C), 123.5 (d, *J* = 3.1 Hz, 1C), 126.2 (d, *J* = 1.6 Hz, 1C), 126.7, 131.5 (d, *J* = 2.9 Hz, 1C), 131.5, 137.6 (d, *J* = 14.2 Hz, 1C), 146.6 (d, *J* = 232.2 Hz, 1C). **<sup>19</sup>F NMR** (470 MHz, CDCl<sub>3</sub>) δ -146.7 (t, *J* = 4.7 Hz, 1F). **HRMS** (ESI-TOF) calcd for C<sub>10</sub>H<sub>7</sub>ClFO<sup>+</sup> ([M+H]<sup>+</sup>) 197.0164, found 197.0160.

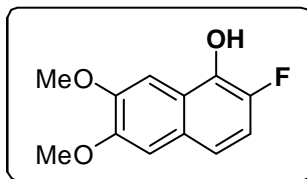
### 6-bromo-2-fluoronaphthalen-1-ol (2n)



White solid, m.p. 125-127 °C. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 5.55 (s, 1H), 7.27-7.32 (m, 2H), 7.56 (dd, *J* = 1.5 Hz, *J* = 9.0 Hz, 1H), 7.94 (d, *J* = 1.5 Hz, 1H), 8.06 (d, *J* = 9.0 Hz, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 116.3 (d, *J* = 21.7 Hz, 1C), 119.5 (d, *J* = 7.2 Hz, 1C), 123.5 (d, *J* = 6.7 Hz, 1C), 119.7 (d, *J* = 2.7 Hz, 1C), 129.1, 129.5 (d, *J* = 6.7 Hz, 1C), 123.0, 123.7, 137.6 (d, *J* = 14.2 Hz, 1C), 146.6 (d, *J* = 232.5 Hz, 1C). **<sup>19</sup>F NMR** (470 MHz, CDCl<sub>3</sub>) δ -146.3 (d, *J* = 3.4 Hz, 1F). **HRMS**

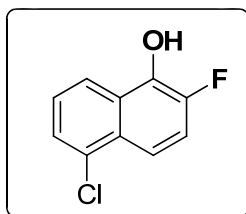
(ESI-TOF) calcd for  $C_{10}H_7BrFO^+$  ( $[M+H]^+$ ) 240.9659, found 240.9670.

### 2-fluoro-6,7-dimethoxynaphthalen-1-ol (2o)



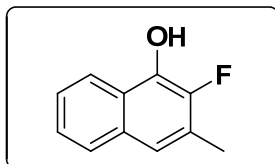
White solid, m.p. 141-143 °C.  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  3.98 (s, 3H), 4.02 (s, 3H), 5.59 (s, 1H), 7.05 (s, 1H), 7.12 (t,  $J = 9.0$  Hz, 1H), 7.19 (dd,  $J = 5.0$  Hz,  $J = 8.5$  Hz, 1H) 7.43 (s, 1H).  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  55.8, 55.9, 100.2 (d,  $J = 6.4$  Hz, 1C), 106.1, 113.2 (d,  $J = 21.2$  Hz, 1C), 118.4 (d,  $J = 7.6$  Hz, 1C), 120.4, 126.7, 136.6 (d,  $J = 14.4$  Hz, 1C), 146.1 (d,  $J = 228.9$  Hz, 1C), 149.1, 149.6.  $^{19}F$  NMR (470 MHz,  $CDCl_3$ )  $\delta$  -149.5 (dd,  $J = 9.4$  Hz,  $J = 4.7$  Hz, 1F). HRMS (ESI-TOF) calcd for  $C_{12}H_{12}FO_3^+$  ( $[M+H]^+$ ) 223.0765, found 223.0766.

### 5-chloro-2-fluoronaphthalen-1-ol (2p)<sup>4</sup>



White solid, m.p. 105-107 °C (lit 96-98 °C).<sup>4</sup>  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  5.60 (d,  $J = 4.0$  Hz, 1H), 7.35-7.40 (m, 2H), 7.53 (d,  $J = 7.5$  Hz, 1H), 7.80 (dd,  $J = 5.0$  Hz,  $J = 9.5$  Hz, 1H), 8.13 (d,  $J = 8.5$  Hz, 1H).  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  116.3 (d,  $J = 21.5$  Hz, 1C), 117.2 (d,  $J = 7.2$  Hz, 1C), 120.8 (d,  $J = 6.5$  Hz, 1C), 125.8, 125.9 (d,  $J = 2.1$  Hz, 1C), 126.5 (d,  $J = 3.1$  Hz, 1C), 128.3, 131.8, 137.5 (d,  $J = 14.2$  Hz, 1C), 146.9 (d,  $J = 233.4$  Hz, 1C).  $^{19}F$  NMR (470 MHz,  $CDCl_3$ )  $\delta$  -145.8 (t,  $J = 4.7$  Hz, 1F). HRMS (ESI-TOF) calcd for  $C_{10}H_7ClFO^+$  ( $[M+H]^+$ ) 197.0164, found 197.0162.

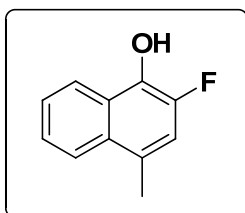
### 2-fluoro-3-methylnaphthalen-1-ol (2q)



White solid, m.p. 97-99 °C.  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  2.47 (d,  $J = 1.0$  Hz, 3H), 5.56 (d,  $J = 5.0$  Hz, 1H), 7.22 (d,  $J = 7.5$  Hz, 1H), 7.42-7.48 (m, 2H), 7.70-7.72 (m, 1H), 8.16-8.18 (m, 1H).  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  15.3 (d,  $J = 3.7$  Hz, 1C), 120.2 (d,  $J = 4.0$  Hz, 1C), 121.3 (d,  $J = 6.6$  Hz, 1C), 123.8 (d,  $J = 1.5$  Hz, 1C), 124.8, 125.2 (d,  $J = 19.2$  Hz, 1C), 125.4 (d,  $J = 1.0$  Hz, 1C), 126.8 (d,  $J = 1.7$  Hz, 1C), 130.5, 137.1 (d,  $J = 14.6$  Hz, 1C), 146.3 (d,  $J = 231.2$  Hz, 1C).  $^{19}F$  NMR (470 MHz,

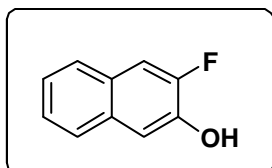
CDCl<sub>3</sub>)  $\delta$  -151.3 (s, 1F). **HRMS** (ESI-TOF) calcd for C<sub>11</sub>H<sub>10</sub>FO<sup>+</sup> ([M+H]<sup>+</sup>) 177.0710, found 177.0708.

### 2-fluoro-4-methylnaphthalen-1-ol (2r)



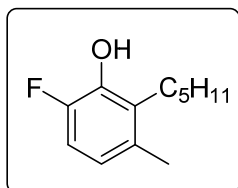
White solid, m.p. 115-117 °C. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  2.62 (s, 3H), 5.44 (d,  $J$  = 4.0 Hz, 1H), 7.14 (d,  $J$  = 11.0 Hz, 1H), 7.50-7.56 (m, 2H), 7.92 (d,  $J$  = 8.0 Hz, 1H), 8.25 (d,  $J$  = 8.0 Hz, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>)  $\delta$  18.7, 115.9 (d,  $J$  = 21.6 Hz, 1C), 122.0 (d,  $J$  = 6.9 Hz, 1C), 124.1 (d,  $J$  = 1.9 Hz, 1C), 125.2 (d,  $J$  = 2.4 Hz, 1C), 125.5, 125.6, 127.3 (d,  $J$  = 7.1 Hz, 1C), 129.9, 135.4 (d,  $J$  = 13.6 Hz, 1C), 145.9 (d,  $J$  = 231.0 Hz, 1C). **<sup>19</sup>F NMR** (470 MHz, CDCl<sub>3</sub>)  $\delta$  -147.8 (d,  $J$  = 10.8 Hz, 1F). **HRMS** (ESI-TOF) calcd for C<sub>11</sub>H<sub>10</sub>FO<sup>+</sup> ([M+H]<sup>+</sup>) 177.0710, found 177.0716.

### 1-fluoronaphthalen-2-ol (3a)



White solid, m.p. 94-96 °C. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  5.40 (s, 1H), 7.35-7.38 (m, 2H), 7.42 (t,  $J$  = 8.0 Hz, 1H), 7.25 (d,  $J$  = 11.5 Hz, 1H), 7.71 (d,  $J$  = 6.5 Hz, 2H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>)  $\delta$  111.6 (d,  $J$  = 17.6 Hz, 1C), 112.3 (d,  $J$  = 2.1 Hz, 1C), 124.5, 125.7 (d,  $J$  = 2.4 Hz, 1C), 126.5, 127.0 (d,  $J$  = 5.1 Hz, 1C), 128.4 (d,  $J$  = 8.0 Hz, 1C), 131.2, 143.2 (d,  $J$  = 17.4 Hz, 1C), 151.2 (d,  $J$  = 240.2 Hz, 1C). **<sup>19</sup>F NMR** (470 MHz, CDCl<sub>3</sub>)  $\delta$  -140.2 (t,  $J$  = 9.4 Hz, 1F). **HRMS** (ESI-TOF) calcd for C<sub>10</sub>H<sub>8</sub>FO<sup>+</sup> ([M+H]<sup>+</sup>) 163.0554, found 163.0538.

### 6-fluoro-3-methyl-2-pentylphenol (5a)

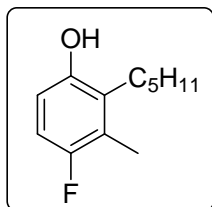


Yellow oil. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  0.90 (t,  $J$  = 7.0 Hz, 3H), 1.34-1.40 (m, 4H), 1.48-1.54 (m, 2H), 2.24 (s, 3H), 2.62-2.65 (m, 2H), 5.07 (d,  $J$  = 5.5 Hz, 1H), 6.61 (dd,  $J$  = 5.5 Hz,  $J$  = 8.5 Hz, 1H), 6.79 (dd,  $J$  = 8.5 Hz,  $J$  = 10.0 Hz, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>)  $\delta$  14.0, 19.0, 22.6, 26.5



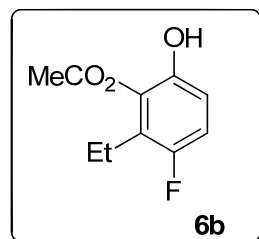
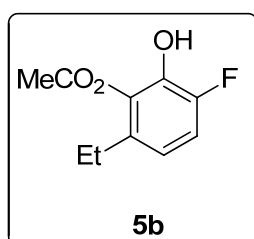
(d,  $J = 2.5$  Hz, 1C), 28.6, 32.1, 111.7 (d,  $J = 17.7$  Hz, 1C), 121.0 (d,  $J = 6.7$  Hz, 1C), 129.9, 132.6 (d,  $J = 3.4$  Hz, 1C), 141.3 (d,  $J = 13.9$  Hz, 1C), 149.5 (d,  $J = 231.7$  Hz, 1C).  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -146.4 (t,  $J = 4.7$  Hz, 1F). HRMS (ESI-TOF) calcd for  $\text{C}_{12}\text{H}_{18}\text{FO}^+$  ( $[\text{M}+\text{H}]^+$ ) 197.1336, found 197.1337.

#### 4-fluoro-3-methyl-2-pentylphenol (6a)



Yellow oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  0.90 (t,  $J = 7.0$  Hz, 3H), 1.26-1.40 (m, 4H), 1.46-1.52 (m, 2H), 2.19 (d,  $J = 2.0$  Hz, 3H), 2.61 (t,  $J = 8.0$  Hz, 2H), 4.75 (s, 1H), 6.54 (dd,  $J = 5.0$  Hz,  $J = 9.0$  Hz, 1H), 6.72 (d,  $J = 9.0$  Hz, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  10.8 (d,  $J = 5.2$  Hz, 1C), 14.0, 22.6, 26.6 (d,  $J = 1.7$  Hz, 1C), 28.8, 32.0, 112.2 (d,  $J = 25.0$  Hz, 1C), 112.8 (d,  $J = 8.6$  Hz, 1C), 124.0 (d,  $J = 16.9$  Hz, 1C), 129.2 (d,  $J = 3.2$  Hz, 1C), 149.2 (d,  $J = 1.9$  Hz, 1C), 155.8 (d,  $J = 234.0$  Hz, 1C).  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -127.5 (dd,  $J = 2.3$  Hz,  $J = 4.2$  Hz, 1F). HRMS (ESI-TOF) calcd for  $\text{C}_{12}\text{H}_{18}\text{FO}^+$  ( $[\text{M}+\text{H}]^+$ ) 197.1336, found 197.1339.

#### 6-ethyl-3-fluoro-2-hydroxyphenyl acetate (5b) and 2-ethyl-3-fluoro-6-hydroxyphenyl acetate (6b)

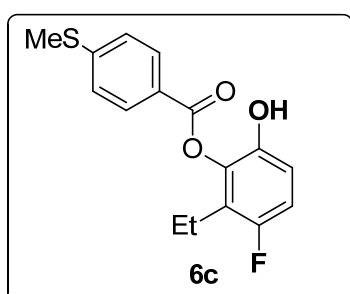
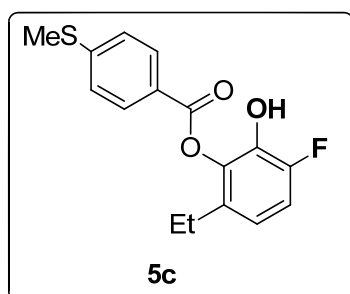


**5b : 6b = 6 : 4**

Two isomers could not be completely isolated from each other. Yellow oil. Compound **5b**:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  1.15 (t,  $J = 8.0$  Hz, 3H), 2.35 (s, 3H), 2.49 (q,  $J = 7.5$  Hz, 2H), 5.68 (s, 1H), 6.71 (dd,  $J = 6.0$  Hz,  $J = 8.5$  Hz, 1H), 6.90-6.95 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  14.0, 20.2, 22.8, 112.8 (d,  $J = 17.9$  Hz, 1C), 118.8 (d,  $J = 7.5$  Hz, 1C), 131.0, 132.6, 136.3 (d,  $J = 15.6$  Hz, 1C), 147.8 (d,  $J = 238.6$  Hz, 1C), 169.6.  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -141.6 (dd,  $J = 1.4$  Hz,  $J = 8.9$  Hz, 1F). HRMS (ESI-TOF) calcd for  $\text{C}_{10}\text{H}_{12}\text{FO}_3^+$  ( $[\text{M}+\text{H}]^+$ ) 199.0765, found 199.0762. Compound **6b**:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  1.19 (t,  $J = 8.0$  Hz, 3H), 2.34 (s, 3H), 2.60 (q,  $J = 7.5$  Hz, 2H), 5.68 (s, 1H), 6.66 (t,  $J = 8.5$  Hz, 1H), 6.90-6.95 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  13.4, 19.9, 22.5, 106.9 (d,  $J = 18.2$  Hz, 1C), 125.6 (d,  $J = 8.7$  Hz, 1H), 127.5, 128.8, 137.8, 152.3 (d,  $J = 255.4$  Hz, 1C), 169.0.  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -133.0 (dd,  $J = 6.6$  Hz,  $J = 8.9$  Hz, 1F). HRMS

(ESI-TOF) calcd for  $C_{10}H_{12}FO_3^+$  ( $[M+H]^+$ ) 199.0765, found 199.0762.

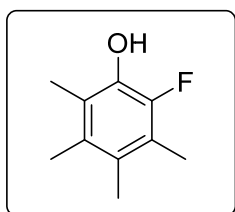
**6-ethyl-3-fluoro-2-hydroxyphenyl 4-(methylthio)benzoate (5c) and  
2-ethyl-3-fluoro-6-hydroxyphenyl 4-(methylthio)benzoate (6c)**



**5c : 6c = 7 : 3**

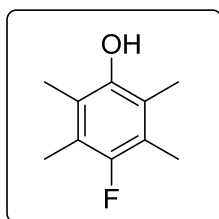
Two isomers could not be completely isolated from each other. White solid. Compound **5c**:  $^1H$  NMR (500 MHz,  $DMSO-d_6$ )  $\delta$  1.07 (t,  $J = 7.5$  Hz, 3H), 2.42 (q,  $J = 7.5$  Hz, 2H), 2.57 (s, 3H), 6.73-6.77 (m, 1H), 7.01-7.08 (m, 1H), 7.45 (d,  $J = 7.5$  Hz, 2H), 8.04 (d,  $J = 7.5$  Hz, 2H), 9.86 (s, 1H).  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  14.2, 14.6, 23.1, 112.8 (d,  $J = 17.9$  Hz, 1C), 119.1 (d,  $J = 7.9$  Hz, 1C), 124.5, 124.9 (2C), 130.2, 130.5 (2C), 132.9 (d,  $J = 3.1$  Hz, 1C), 136.4 (d,  $J = 15.6$  Hz, 1C), 146.9, 150.3 (d,  $J = 236.8$  Hz, 1C), 164.2.  $^{19}F$  NMR (470 MHz,  $CDCl_3$ )  $\delta$  (-142.3) - (-142.2) (m, 1F). HRMS (ESI-TOF) calcd for  $C_{16}H_{16}FO_3S^+$  ( $[M+H]^+$ ) 307.0799, found 307.0808. Compound **6c**:  $^1H$  NMR (500 MHz,  $DMSO-d_6$ )  $\delta$  1.14 (t,  $J = 7.5$  Hz, 3H), 2.54-2.59 (m, 5H), 6.73-6.77 (m, 1H), 7.01-7.08 (m, 1H), 7.44 (d,  $J = 7.5$  Hz, 2H), 8.04 (d,  $J = 7.5$  Hz, 2H), 9.61 (s, 1H).  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  13.9, 14.5, 22.6, 107.2 (d,  $J = 19.4$  Hz, 1C), 123.8, 124.9 (2C), 125.6 (d,  $J = 8.8$  Hz, 1C), 127.8 (d,  $J = 3.0$  Hz, 1C), 130.1, 130.6 (2C), 138.0, 147.4, 152.8 (d,  $J = 244.9$  Hz, 1C), 163.8.  $^{19}F$  NMR (470 MHz,  $CDCl_3$ )  $\delta$  -132.5 (dd,  $J = 6.1$  Hz,  $J = 8.9$  Hz, 1F). HRMS (ESI-TOF) calcd for  $C_{16}H_{16}FO_3S^+$  ( $[M+H]^+$ ) 307.0799, found 307.0808.

**2-fluoro-3,4,5,6-tetramethylphenol (5d)**



White crystal, m.p. 74 - 76 °C.  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  2.12 (s, 3H), 2.13 (s, 3H), 2.17 (d,  $J = 2.0$  Hz, 3H), 2.18 (s, 3H), 5.00 (d,  $J = 6.0$  Hz, 1H).  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  11.3 (d,  $J = 5.6$  Hz, 1C), 11.9 (d,  $J = 3.1$  Hz, 1C), 15.4 (d,  $J = 2.7$  Hz, 1C), 15.8, 119.9 (d,  $J = 13.1$  Hz, 1C), 121.4, 126.7 (d,  $J = 3.0$  Hz, 1C), 130.6 (d,  $J = 3.5$  Hz, 1C), 139.0 (d,  $J = 2.9$  Hz, 1C), 147.9 (d,  $J = 227.7$  Hz, 1C).  $^{19}F$  NMR (470 MHz,  $CDCl_3$ )  $\delta$  -149.3 (s, 1F). HRMS (ESI-TOF) calcd for  $C_{10}H_{14}FO^+$  ( $[M+H]^+$ ) 169.1023, found 169.1020.

#### 4-fluoro-2,3,5,6-tetramethylphenol (**6d**)



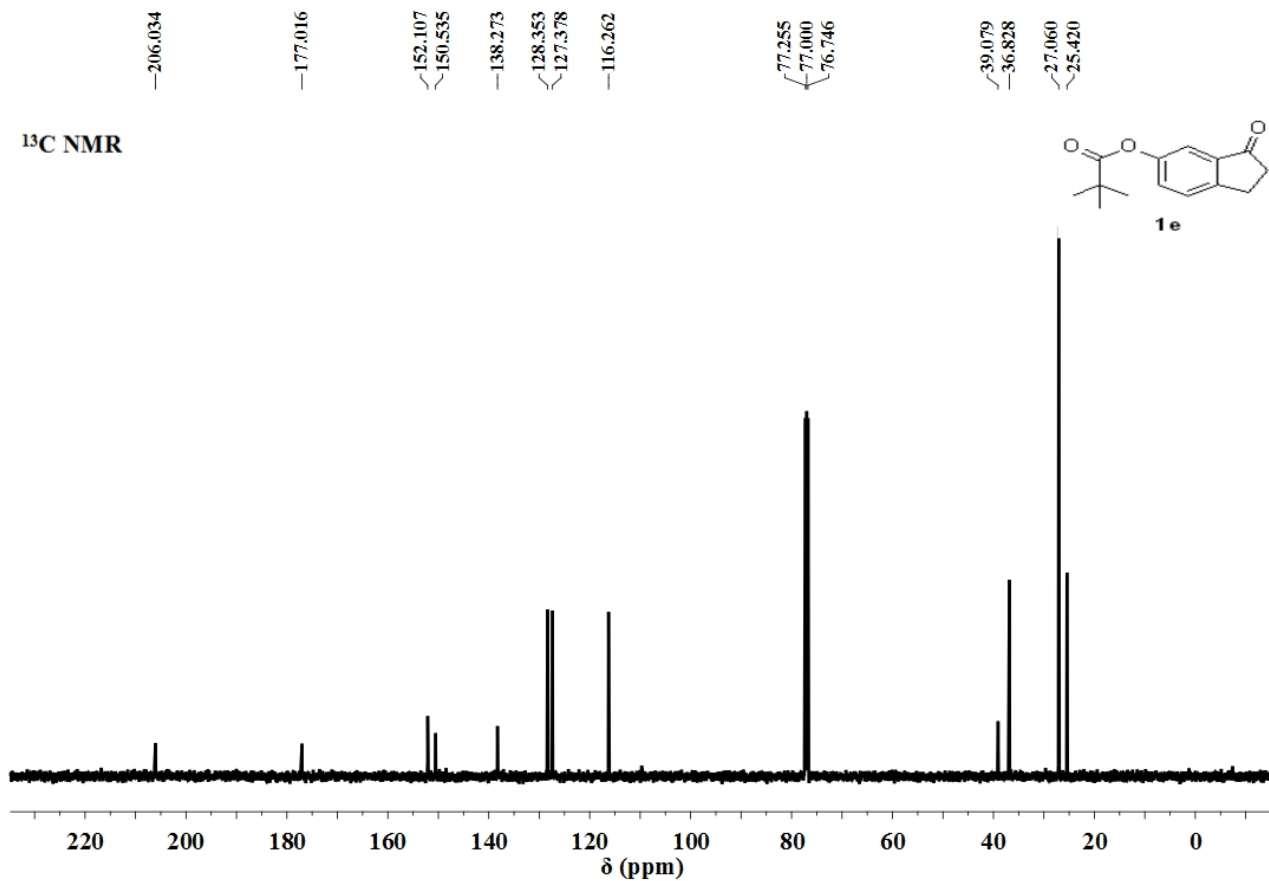
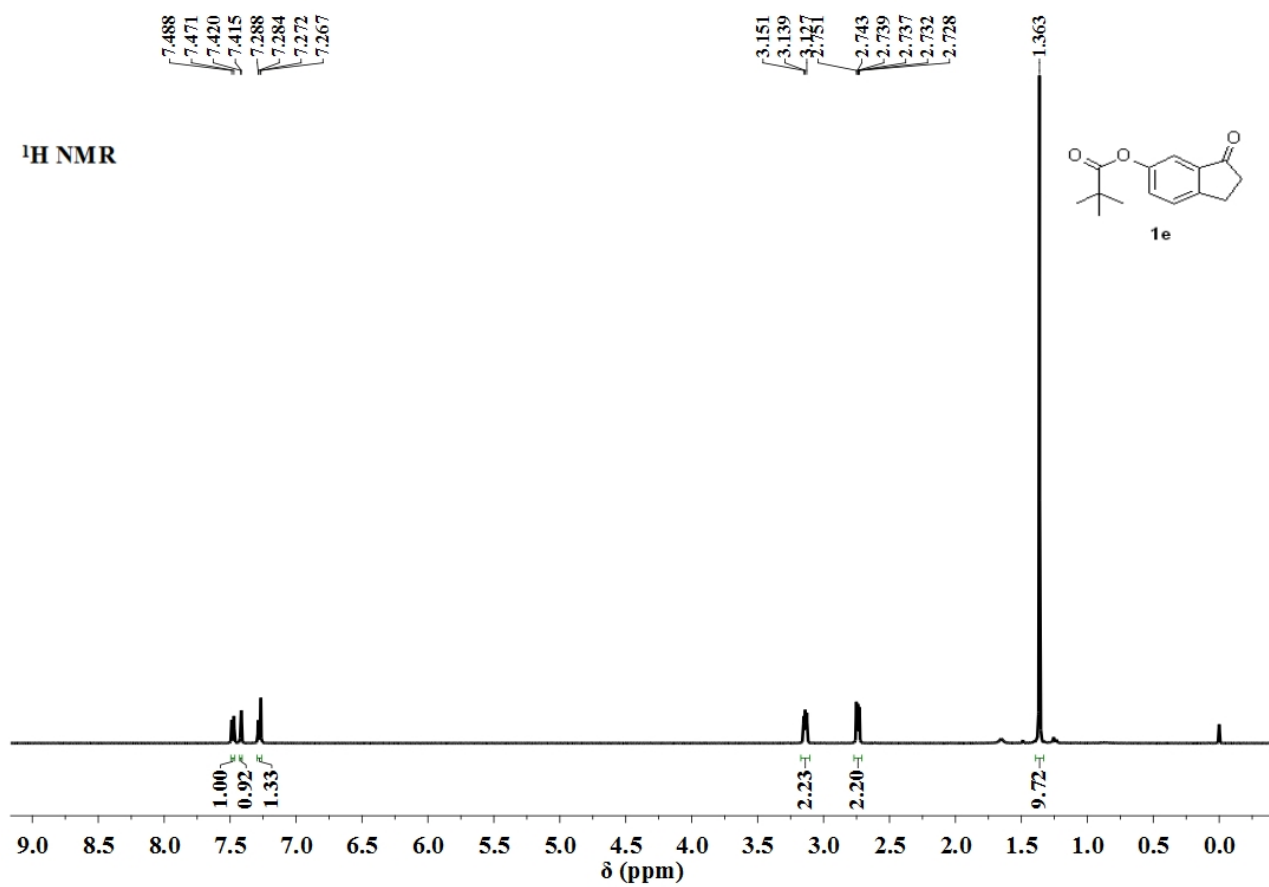
Light yellow crystal, m.p. 119 - 121 °C. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 2.15-2.16 (m, 12H), 4.38 (s, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 11.3, (d, *J* = 5.9 Hz, 2C), 11.9 (d, *J* = 2.5 Hz, 2C), 120.2 (d, *J* = 4.2 Hz, 2C), 120.6 (d, *J* = 18.7 Hz, 2C), 147.2, 154.0 (d, *J* = 231.9 Hz, 1C). **<sup>19</sup>F NMR** (470 MHz, CDCl<sub>3</sub>) δ -130.7 (s, 1F). **HRMS** (ESI-TOF) calcd for C<sub>10</sub>H<sub>14</sub>FO<sup>+</sup> ([M+H]<sup>+</sup>) 169.1023, found 169.1021.

#### IV. References

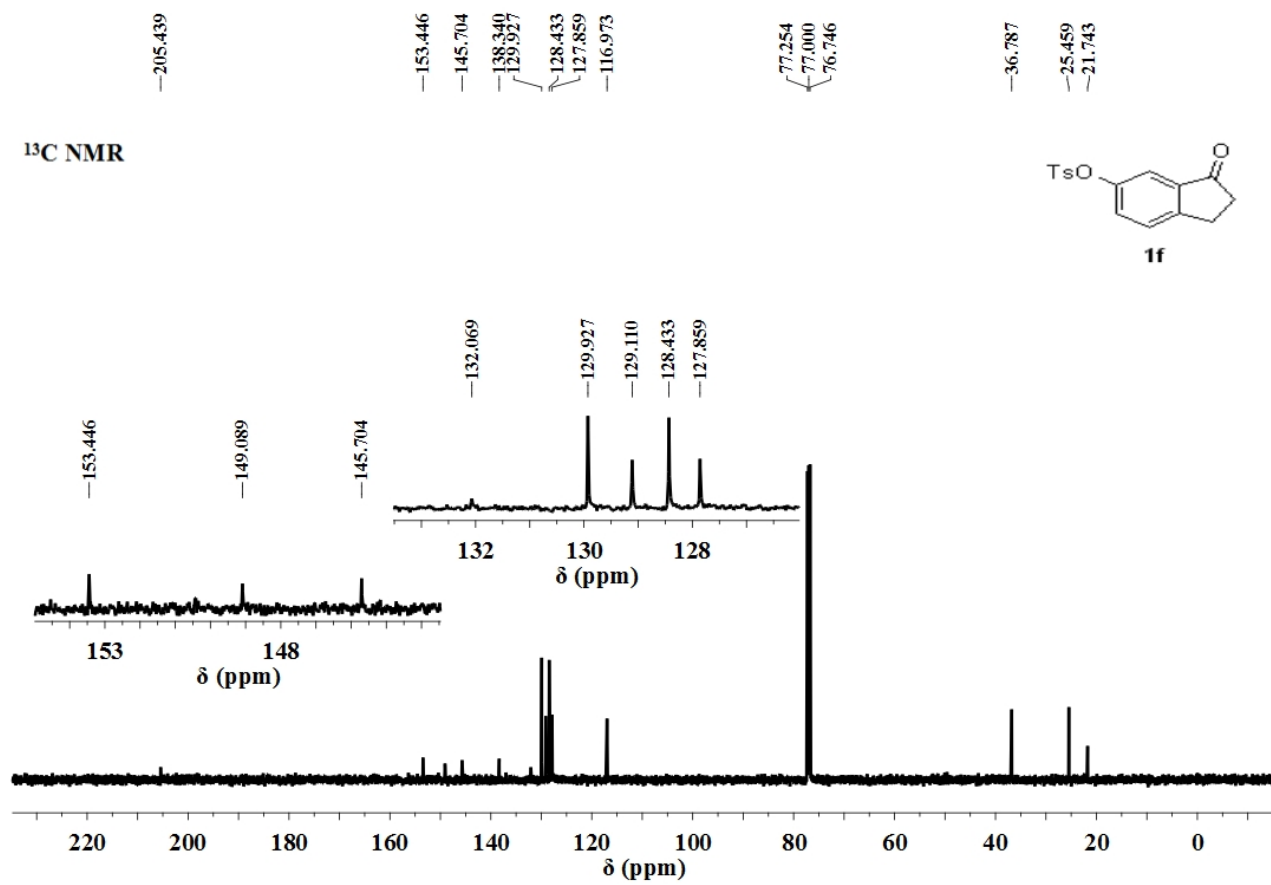
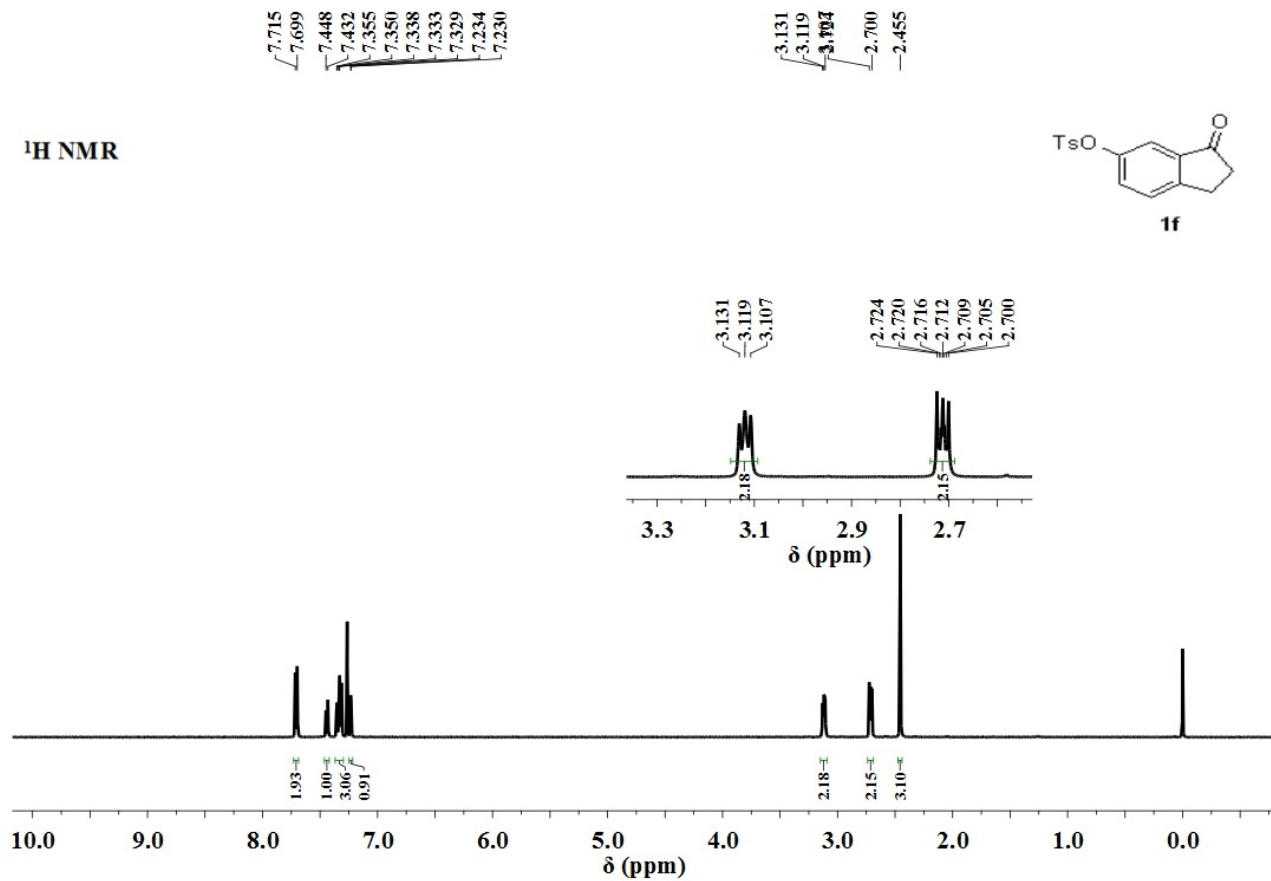
- 1 T. M. Neubauer, T. Leeuwen, D. Zhao, A. S. Lubbe, J. C. M. Kistemaker and B. L. Feringa, *Org. Lett.*, 2014, **16**, 4220-4223.
- 2 B. Neises and W. Steglich, *Angew. Chem. Int. Ed.*, 1987, **17**, 522-524.
- 3 A. Rioz-Martínez, G. de Gonzalo and V. Gotor, *Synthesis*, 2010, 110-114.
- 4 X. Cai, K. Wu, W. R. Dolbier Jr. *J. Fluorine Chem.*, 2005, **126**, 479-482.

## V. Copies of the NMR spectra of new compounds

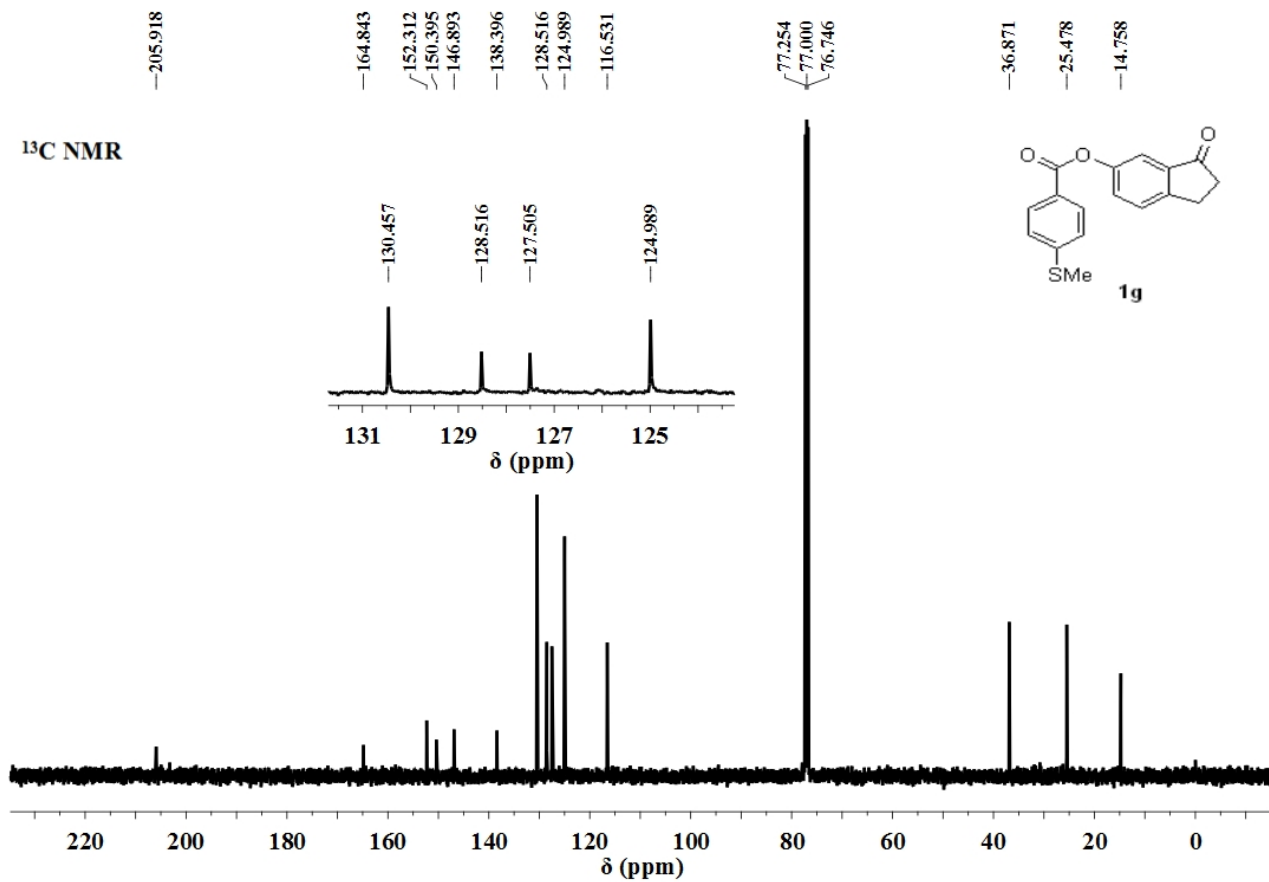
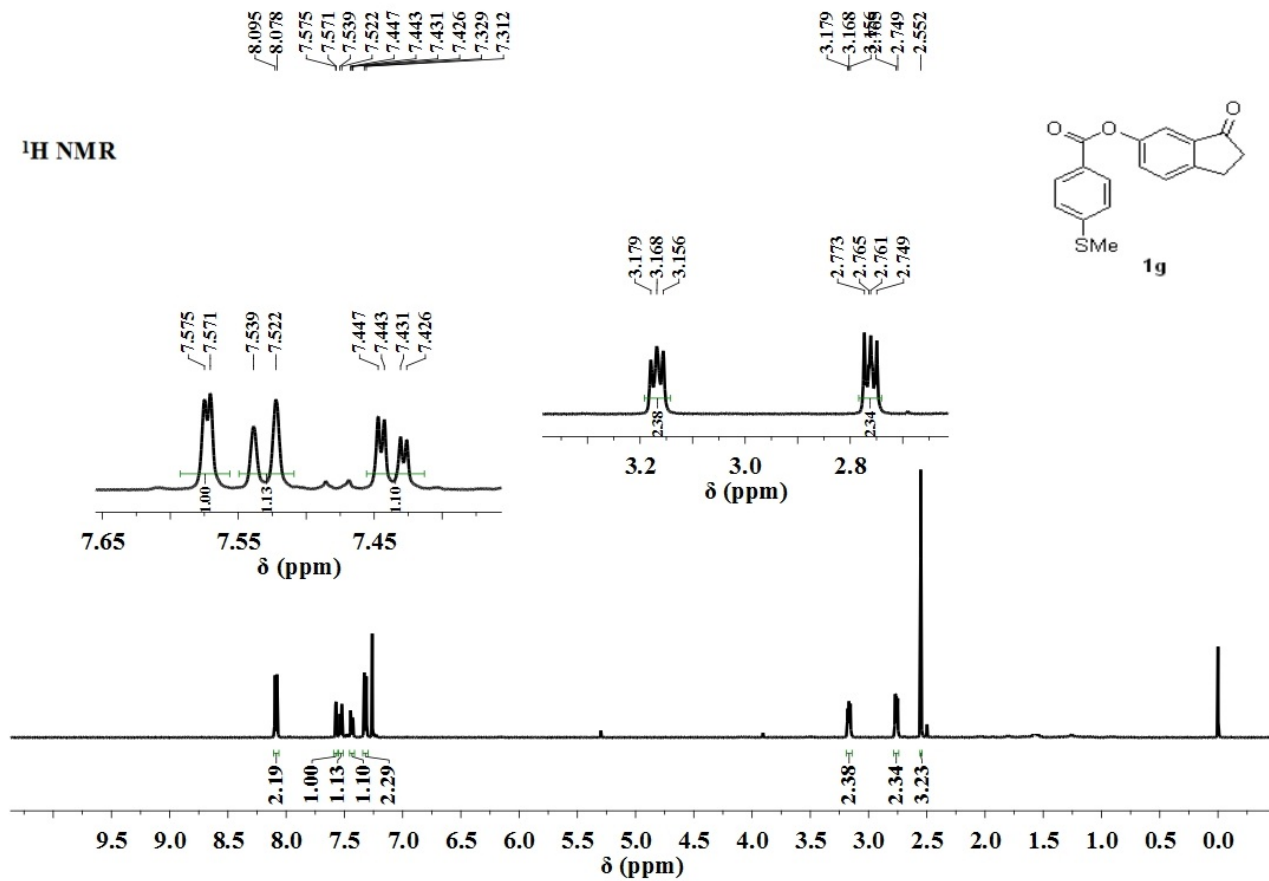
### Compound 1e



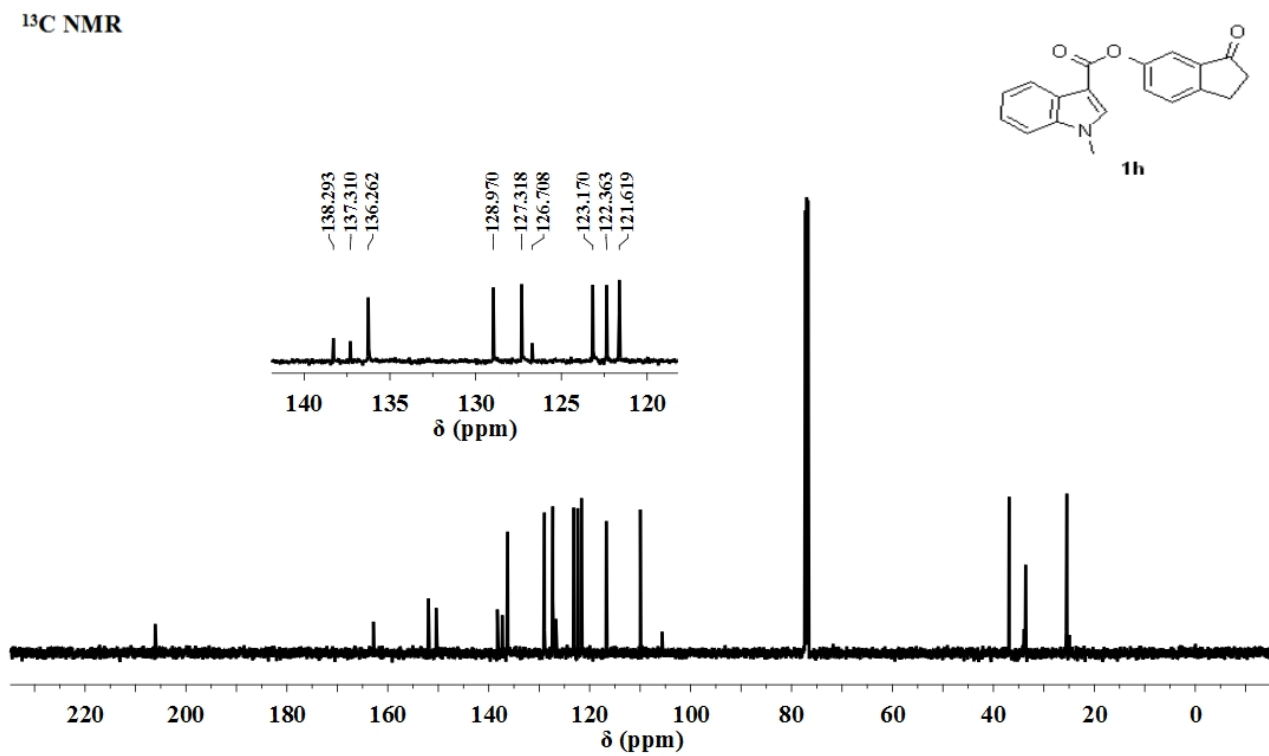
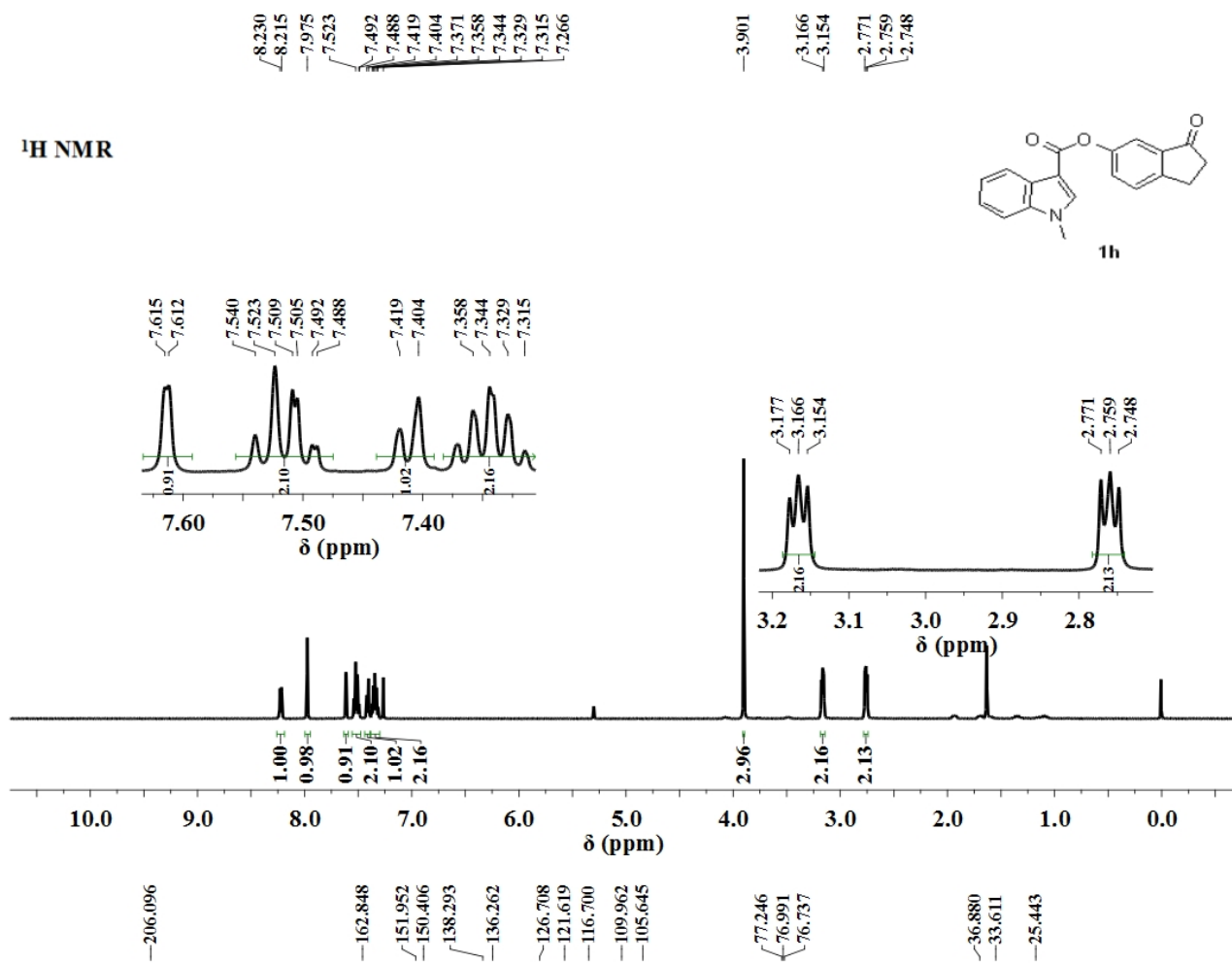
Compound 1f



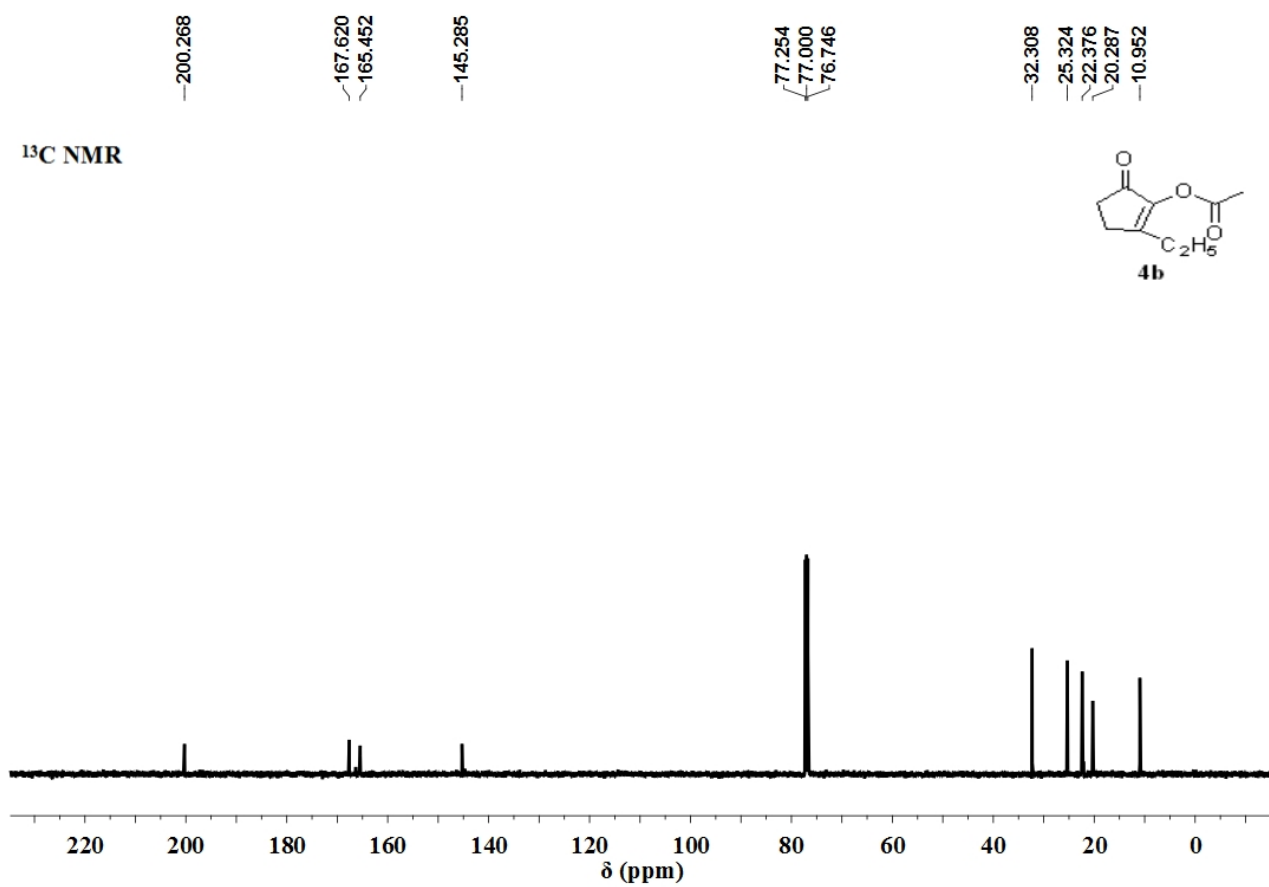
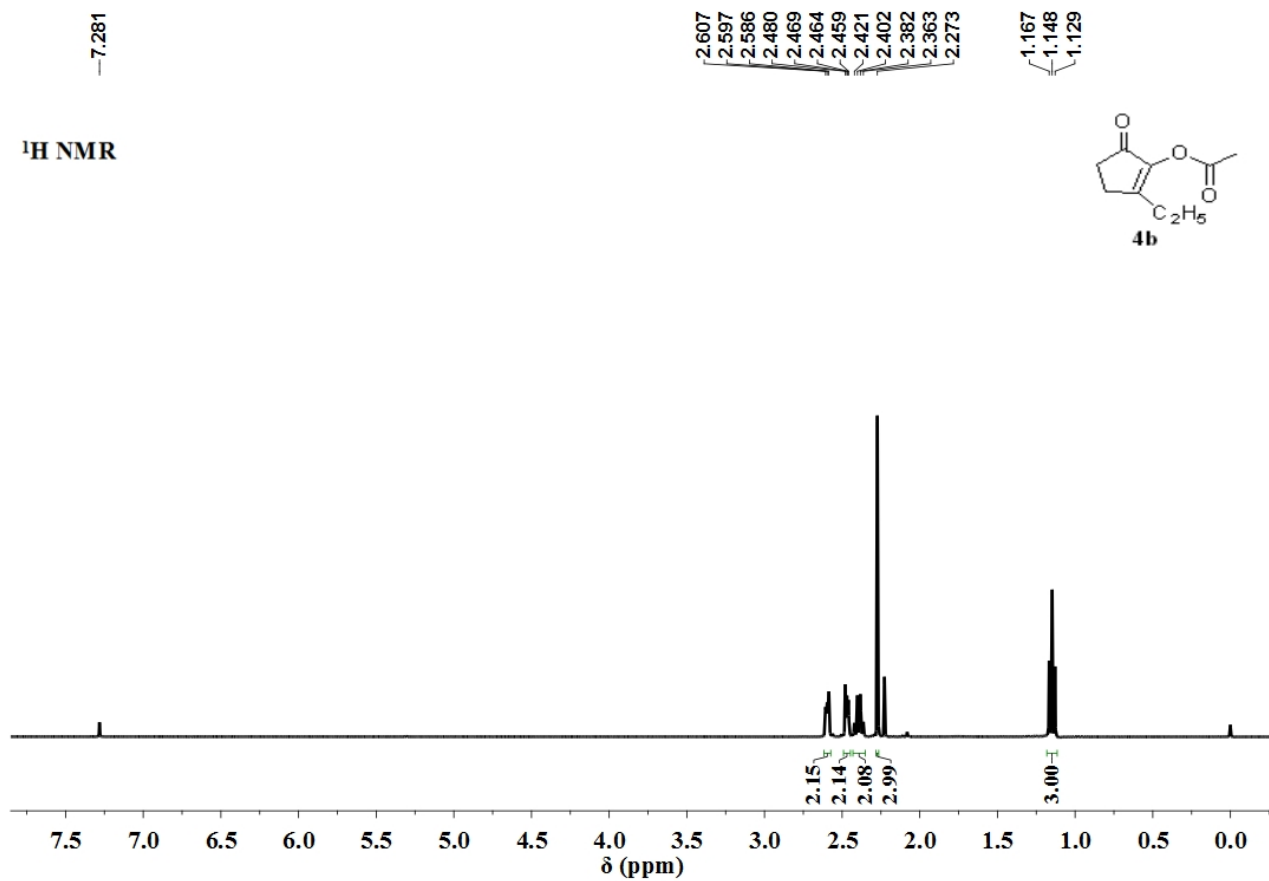
Compound 1g



# Compound 1h



# Compound 4b



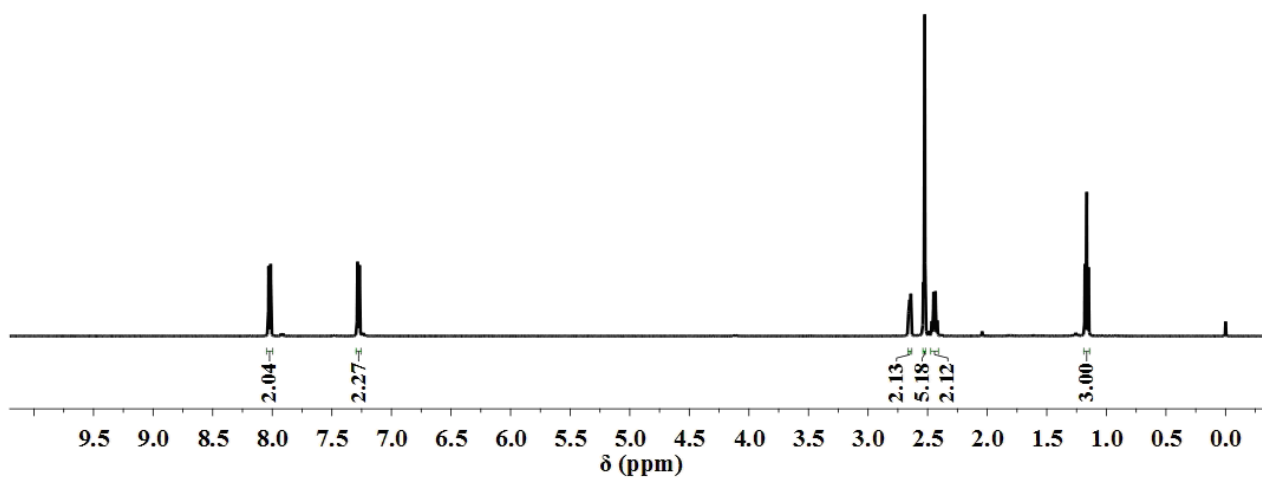
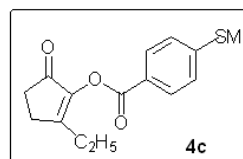


# Compound 4c

8.030  
8.013  
7.284  
7.271  
7.267

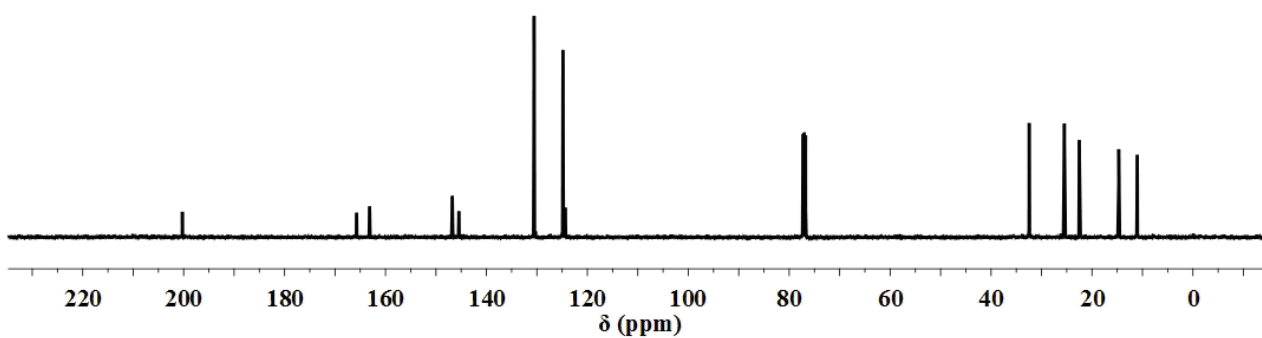
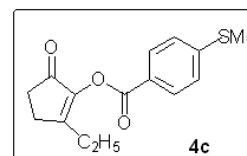
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2.650  
2.641  
2.537  
2.524  
2.465  
2.450  
2.434  
2.419  
1.180  
1.165  
1.149

## <sup>1</sup>H NMR



200.259  
165.705  
163.131  
146.748  
145.463  
130.552  
124.843  
124.377  
77.254  
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76.746  
32.448  
25.472  
22.521  
14.700  
11.009

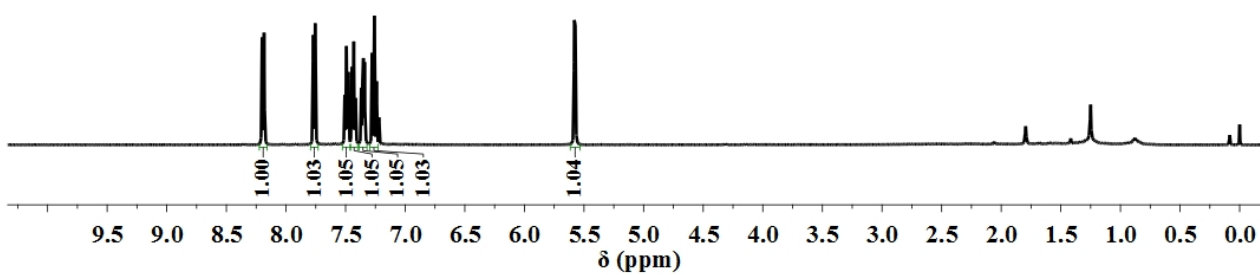
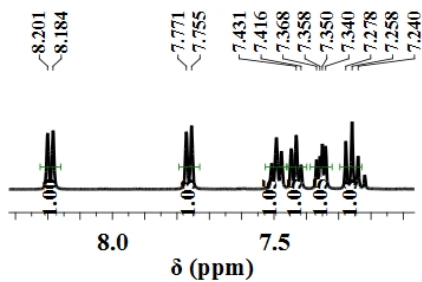
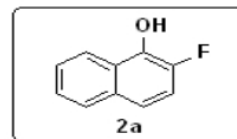
## <sup>13</sup>C NMR



# Compound 2a

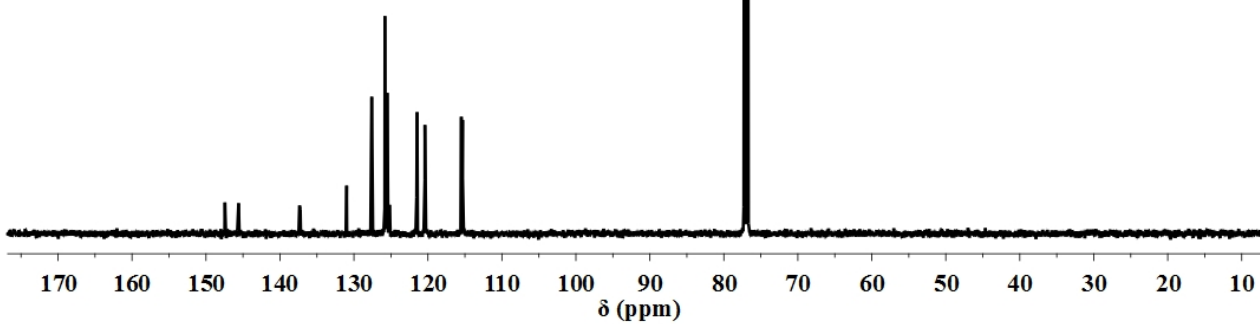
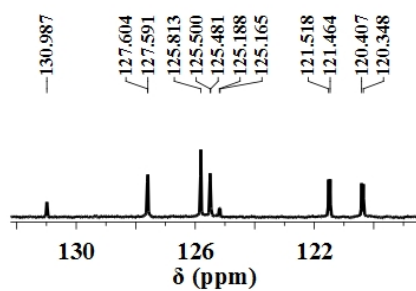
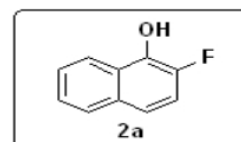
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5.581  
5.573

## <sup>1</sup>H NMR



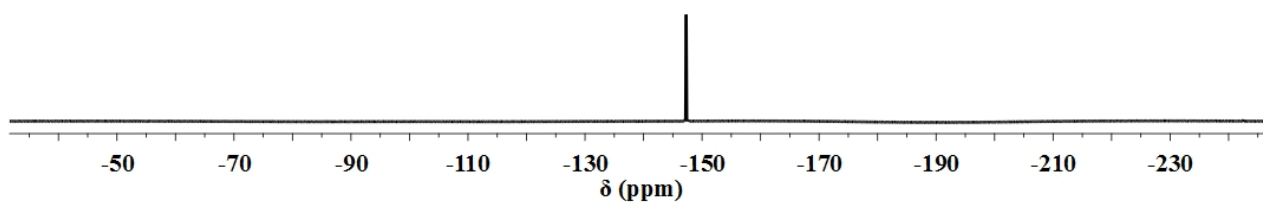
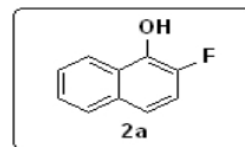
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137.247  
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125.165  
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77.000  
76.746

## <sup>13</sup>C NMR



<sup>19</sup>F NMR

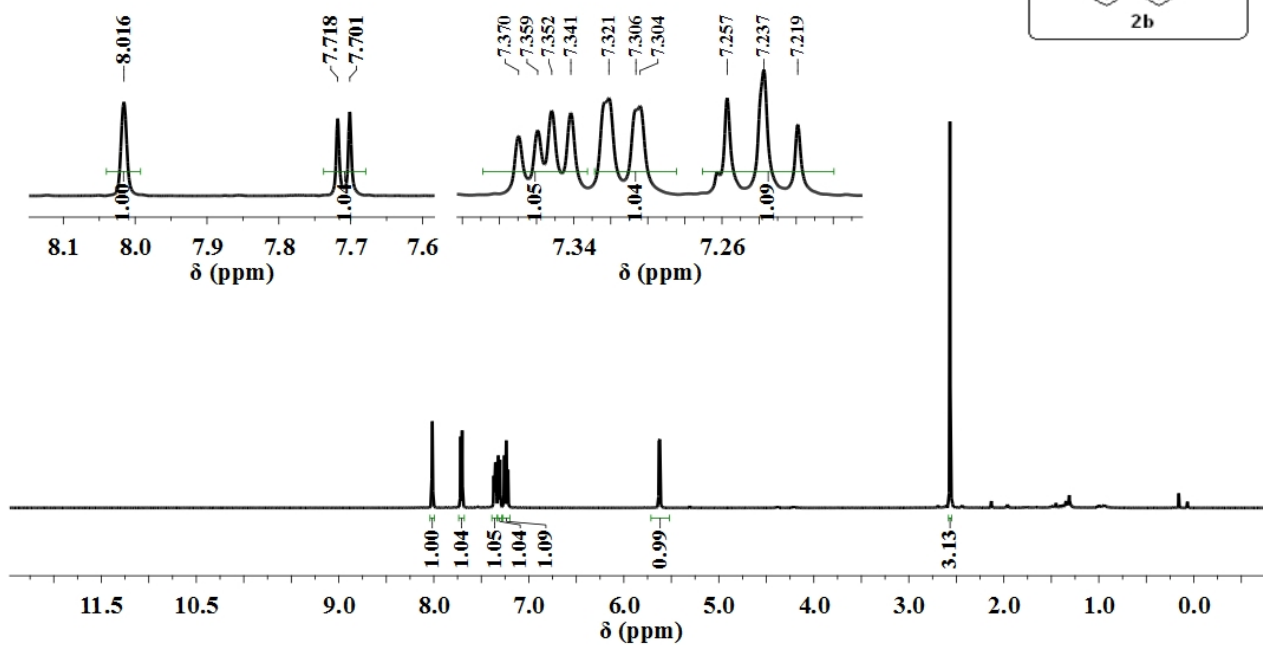
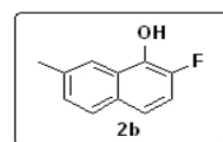
-147.290  
-147.299



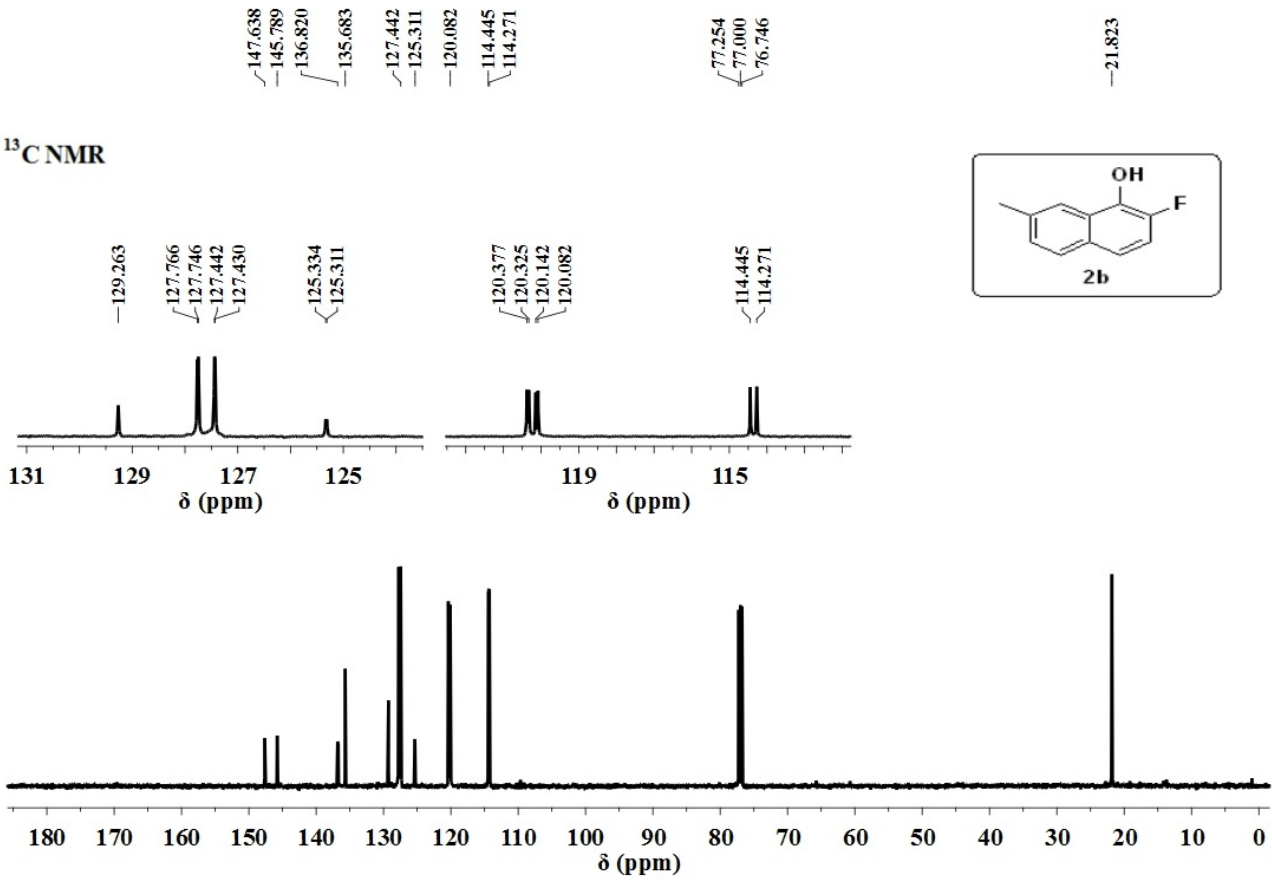
Compound 2b

-8.016  
-7.701  
-7.323  
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-7.219  
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-2.567

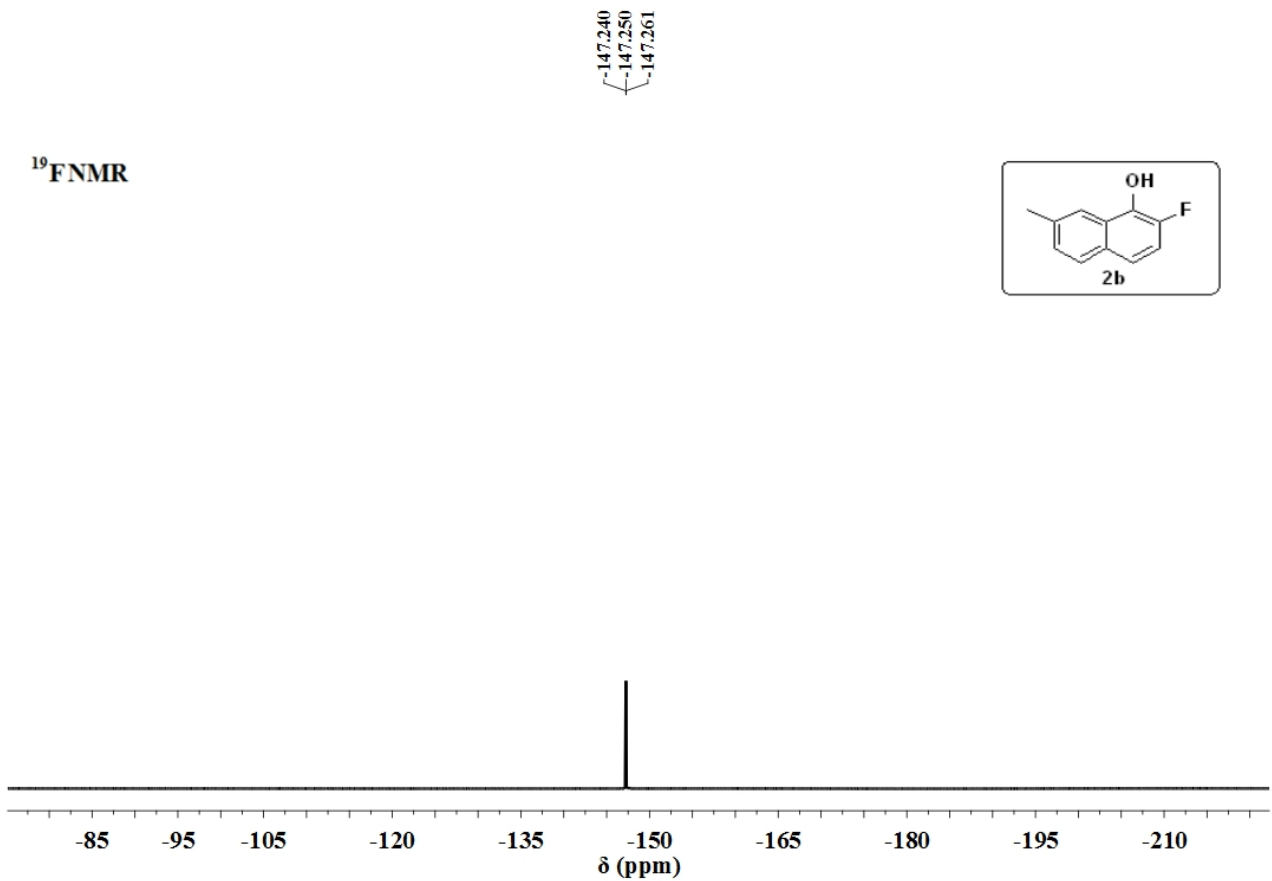
<sup>1</sup>H NMR



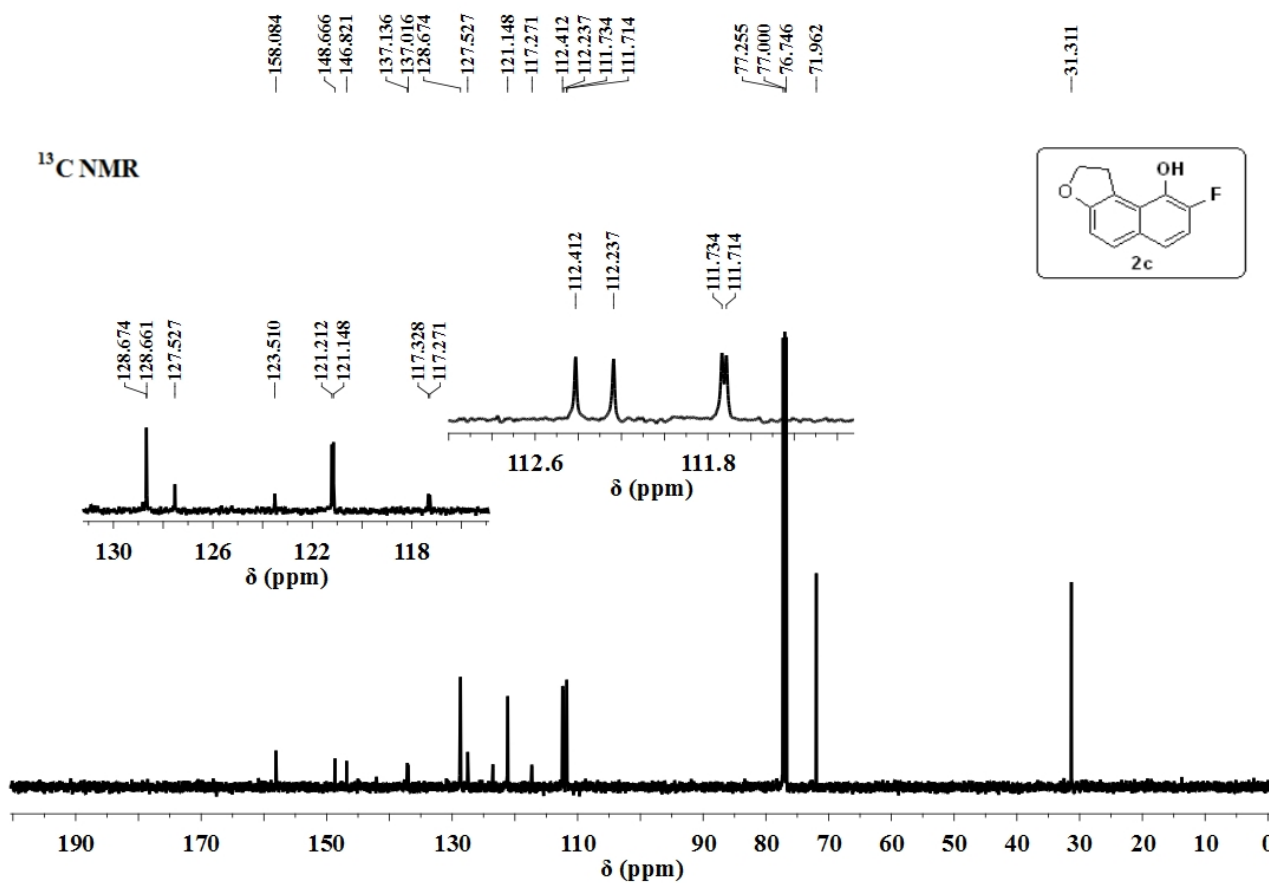
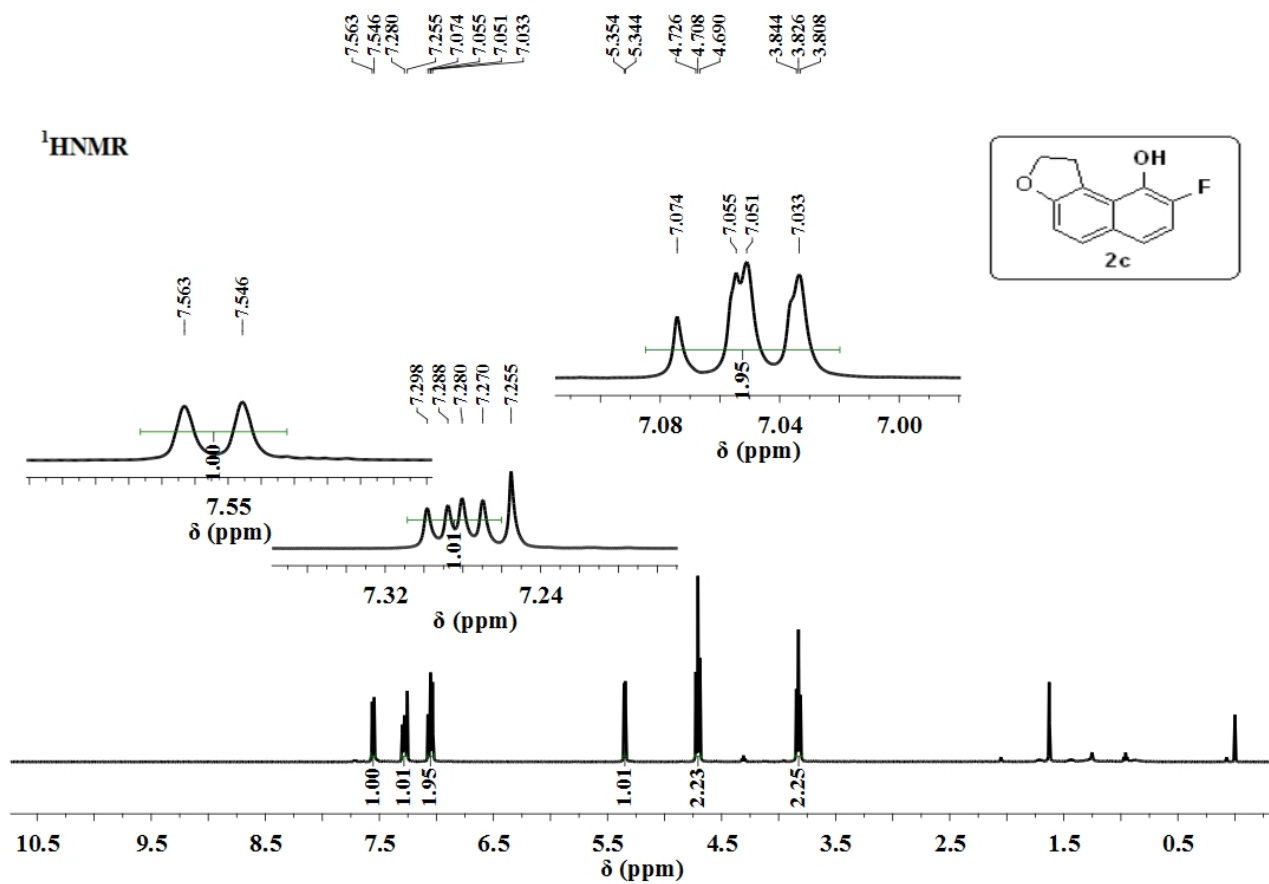
<sup>13</sup>C NMR



<sup>19</sup>F NMR

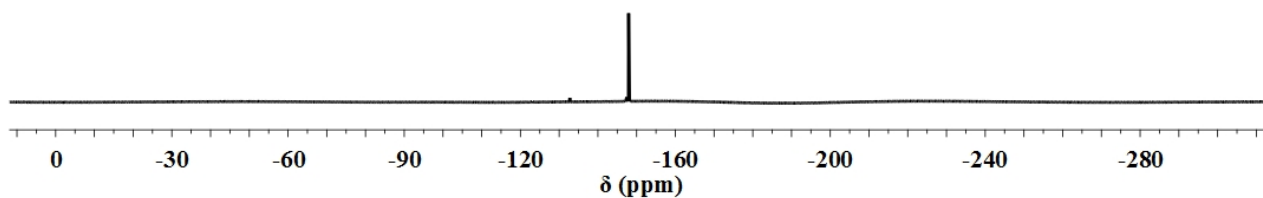
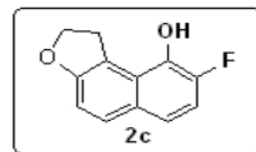


Compound 2c



$^{19}\text{F}$ NMR

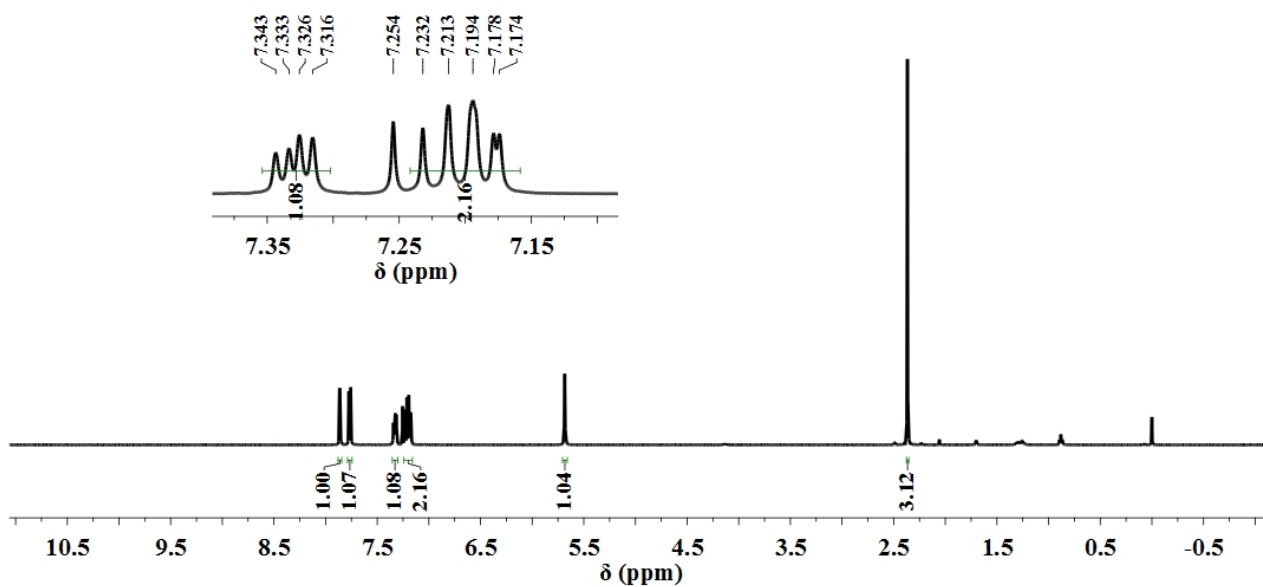
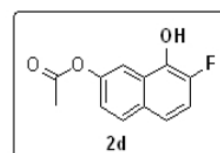
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-147,927  
-147,936  
-147,947



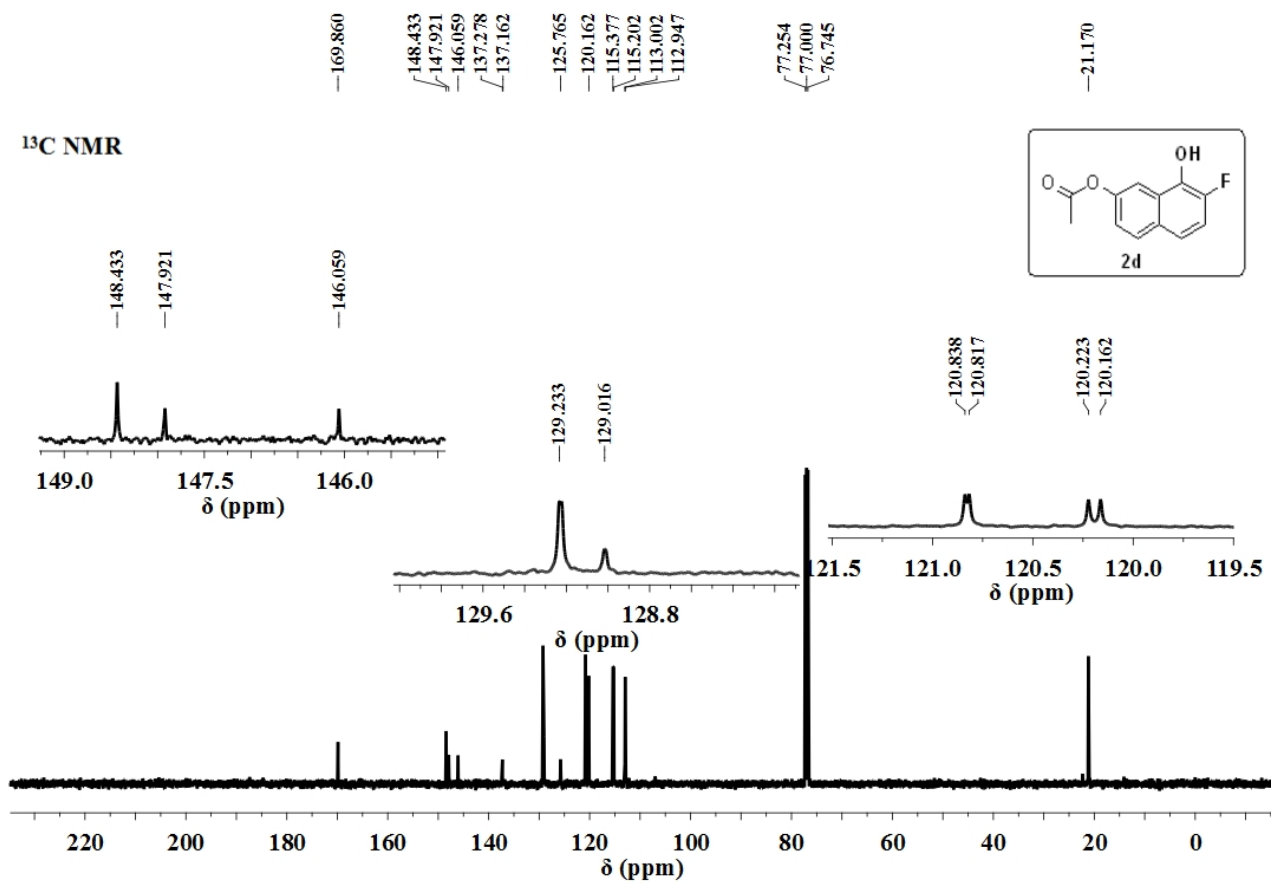
Compound 2d

7.865  
7.861  
7.775  
7.757  
7.333  
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7.232  
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-5.685  
-2.367

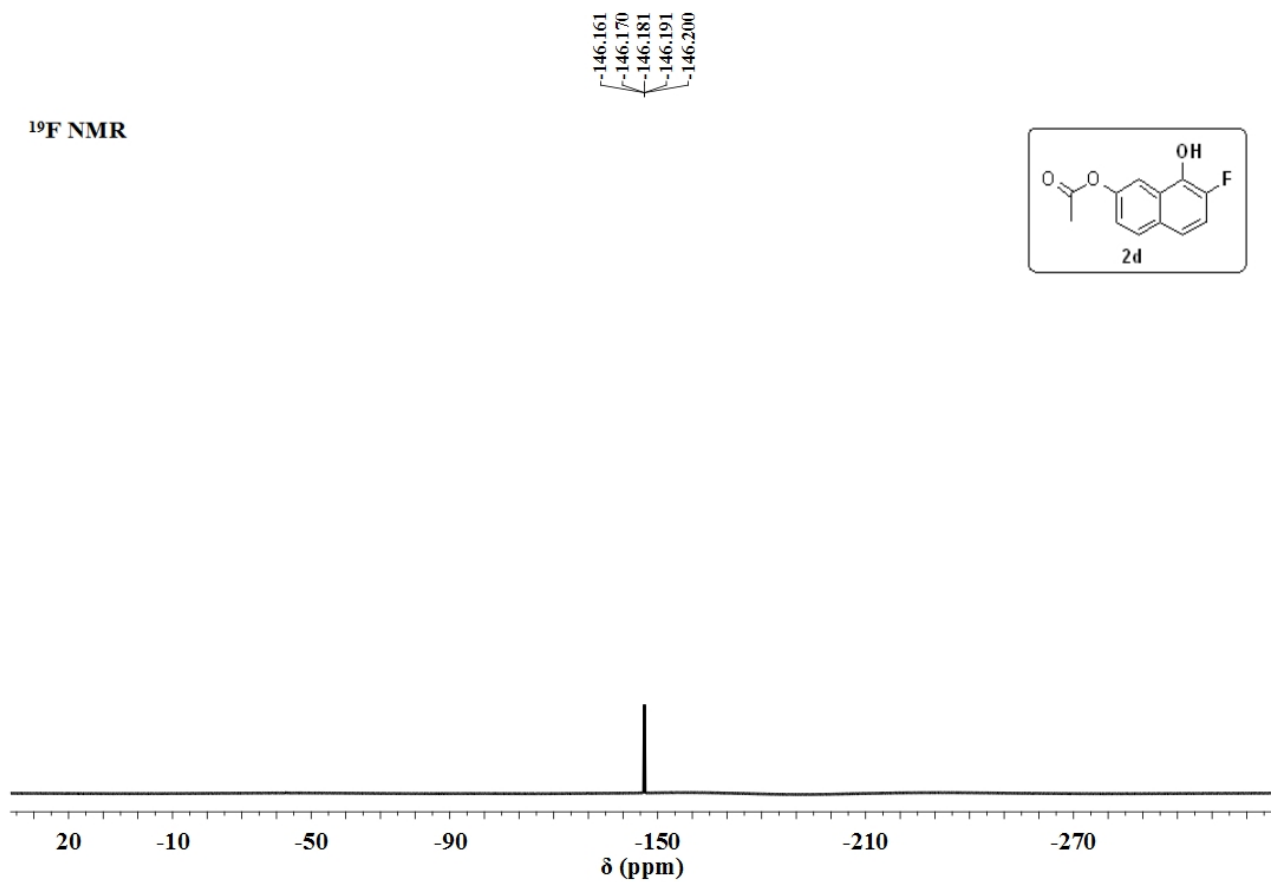
$^1\text{H}$  NMR



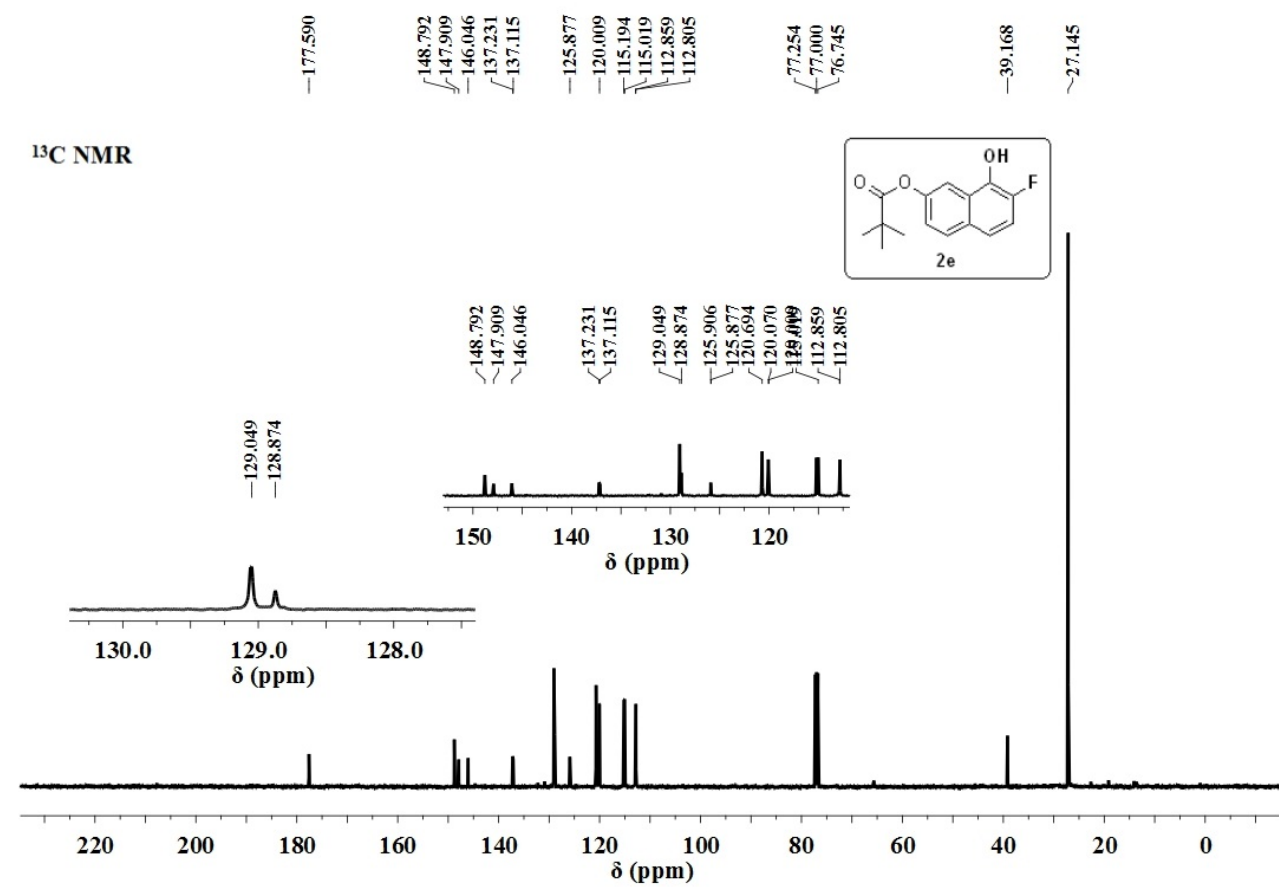
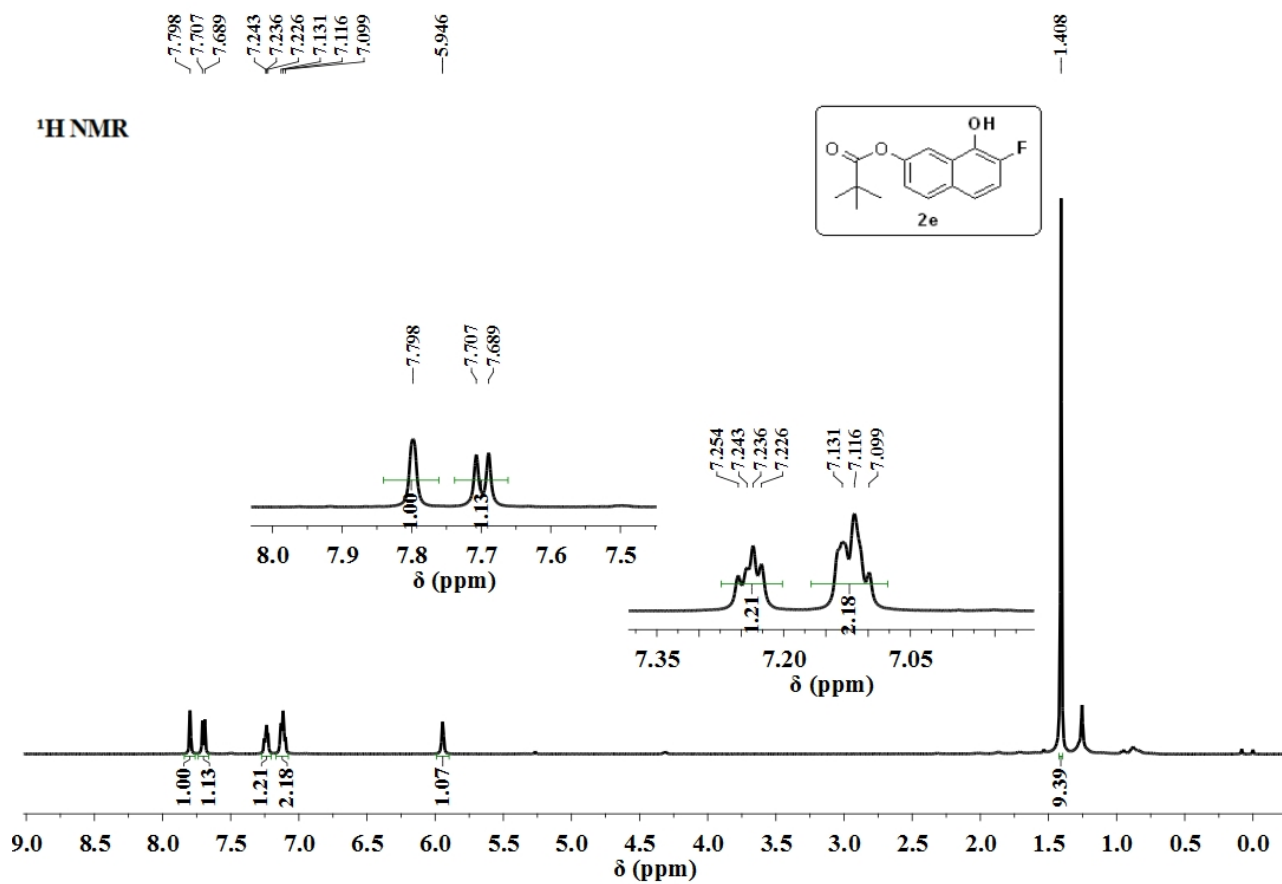
<sup>13</sup>C NMR



<sup>19</sup>F NMR



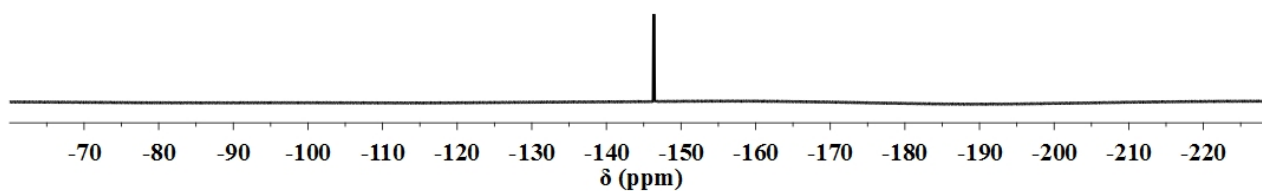
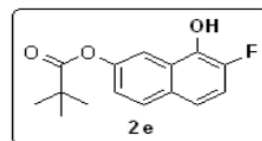
Compound 2e





-146.332  
-146.341  
-146.352  
-146.362  
-146.371

<sup>19</sup>F NMR



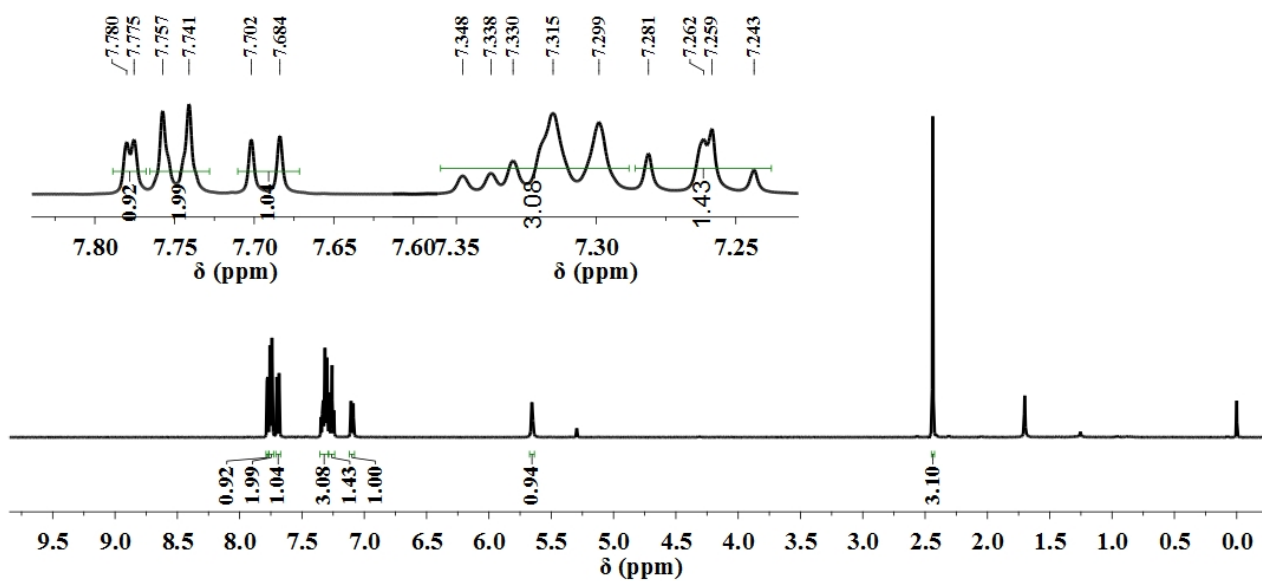
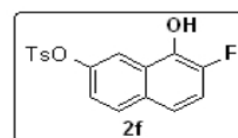
Compound 2f

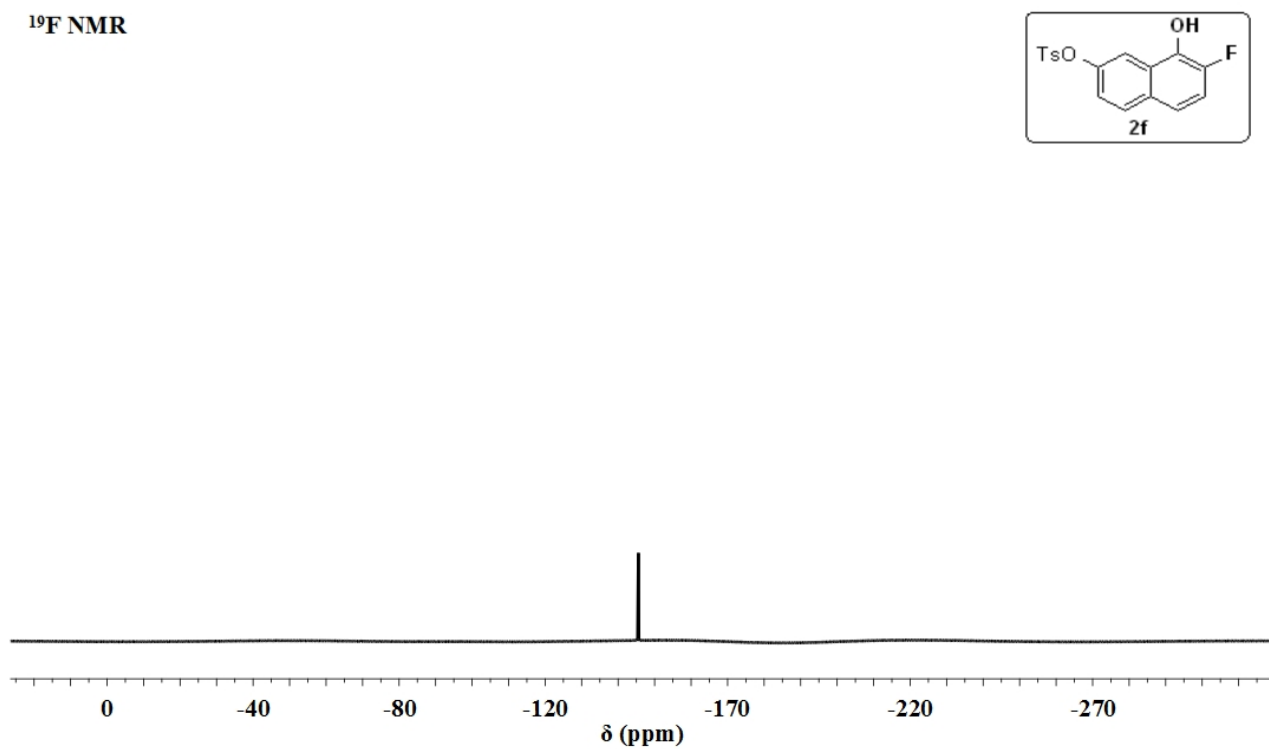
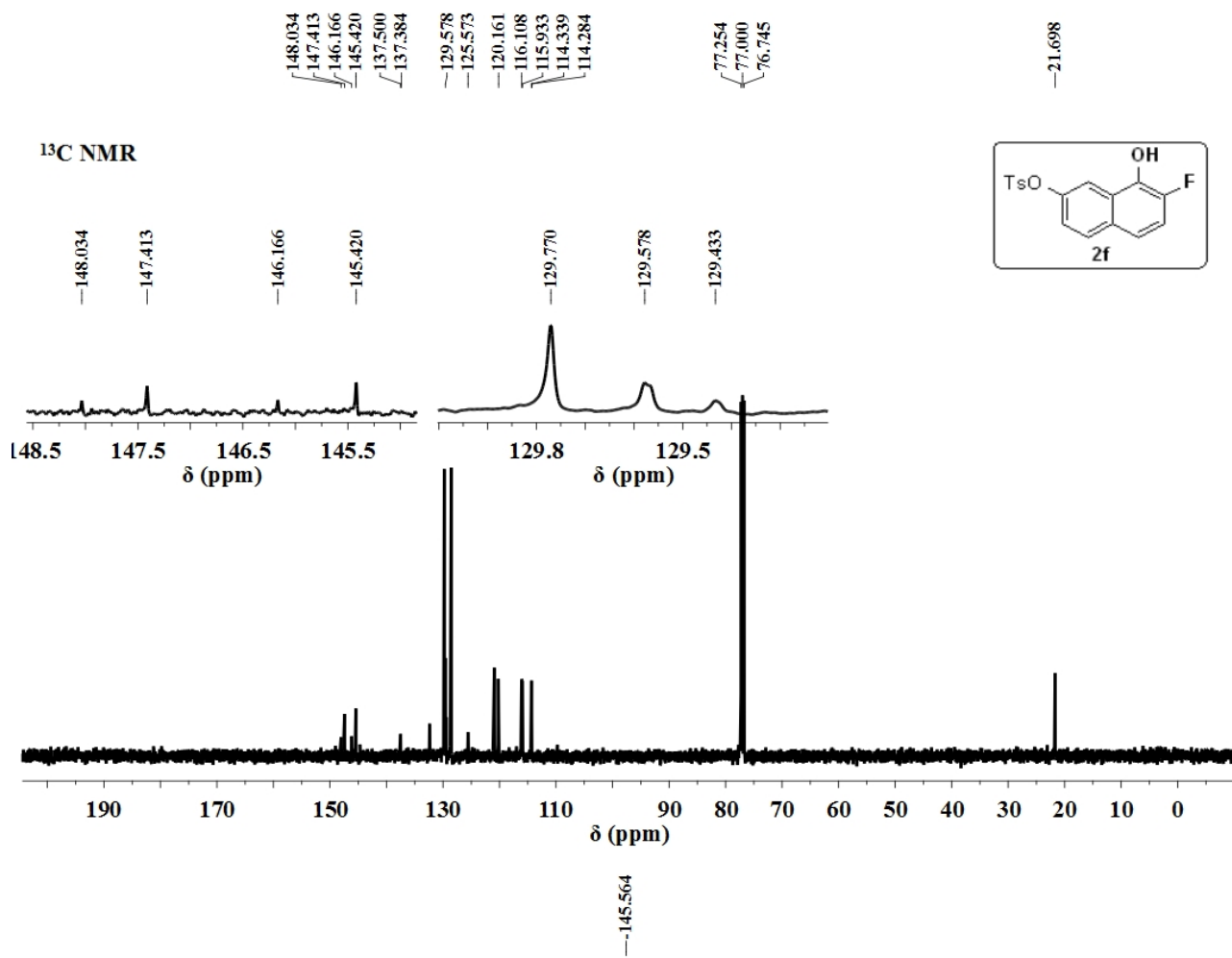
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-5.655

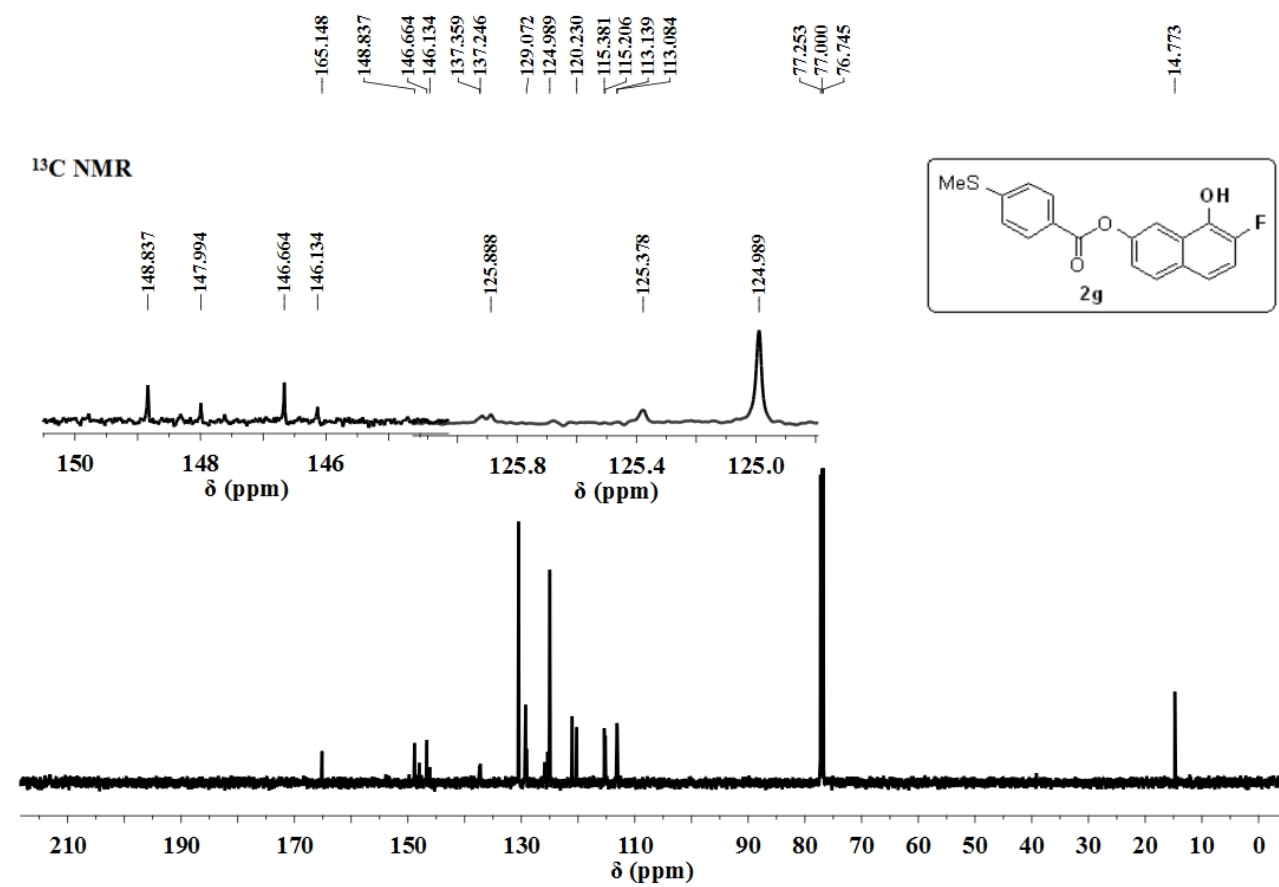
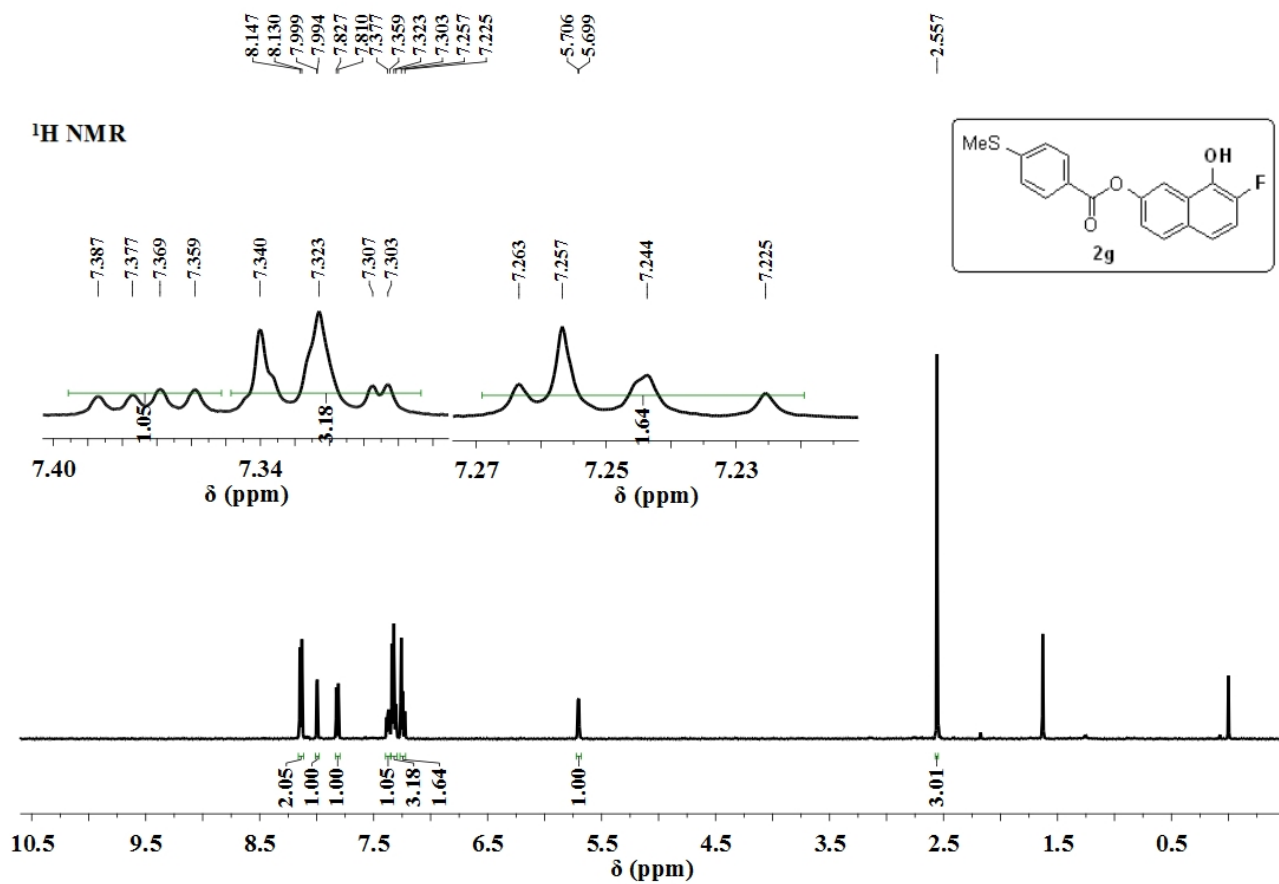
-2.439

<sup>1</sup>H NMR



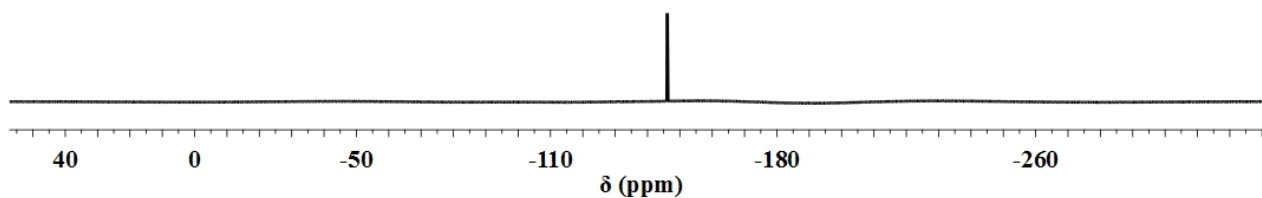
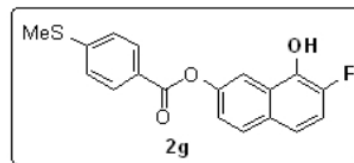


Compound 2g



-146.133  
-146.143  
-146.153

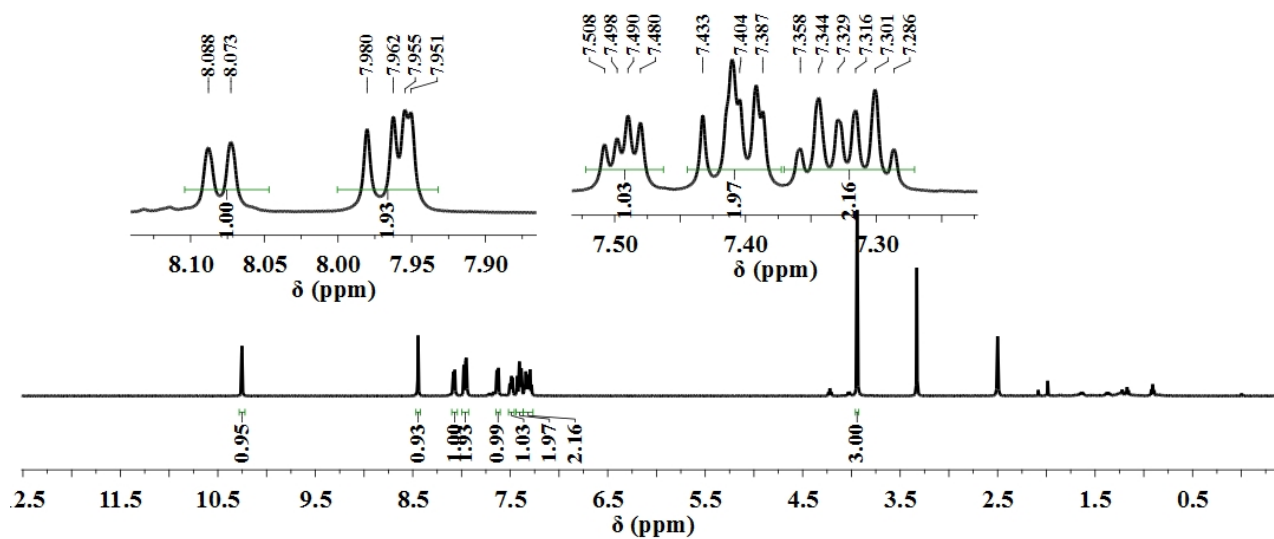
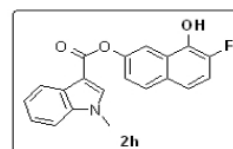
### <sup>19</sup>F NMR



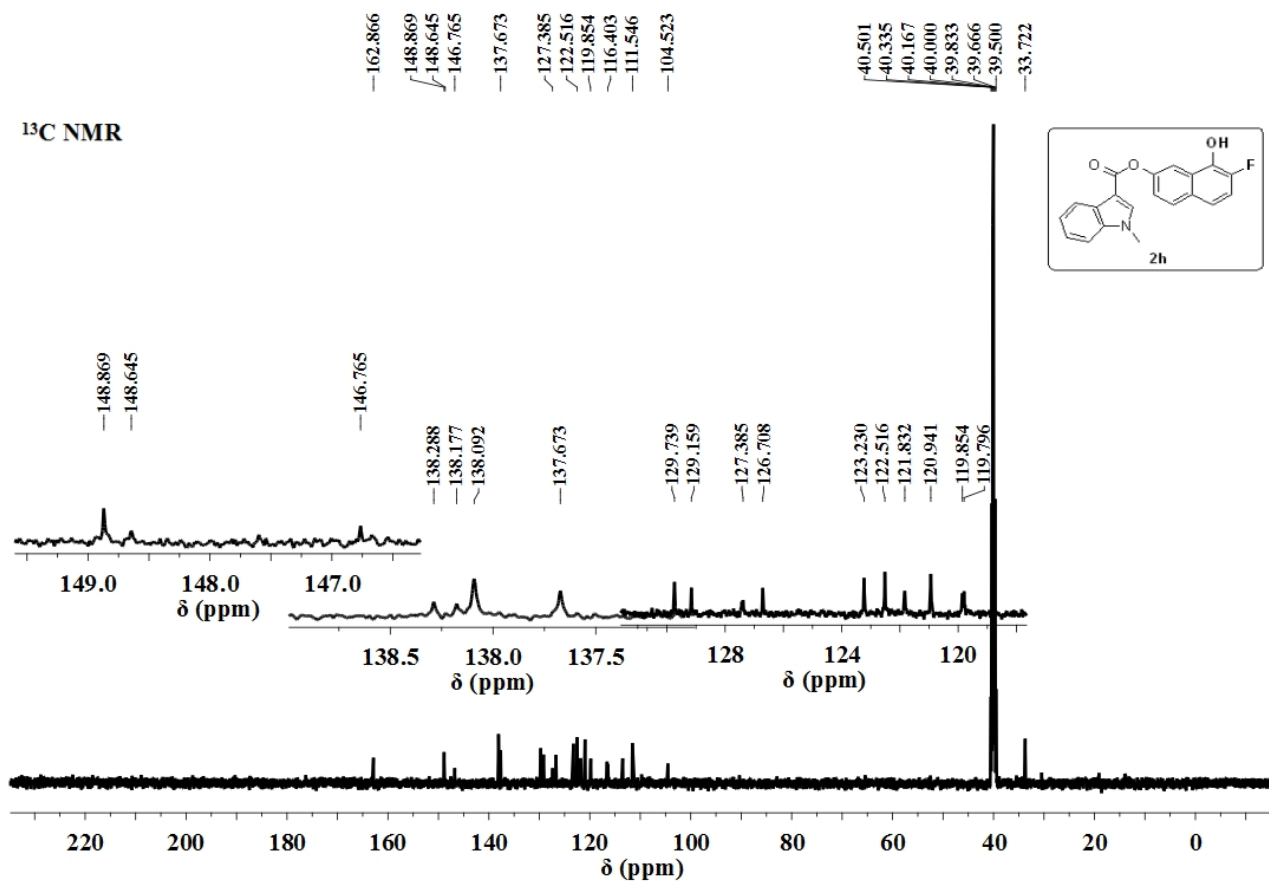
### Compound 2h

-10.253  
-8.446  
-7.947  
-7.406  
-7.400  
-7.388  
-7.383  
-7.354  
-7.340  
-7.325  
-7.312  
-7.297  
-7.282  
-3.942  
-3.329  
-2.500

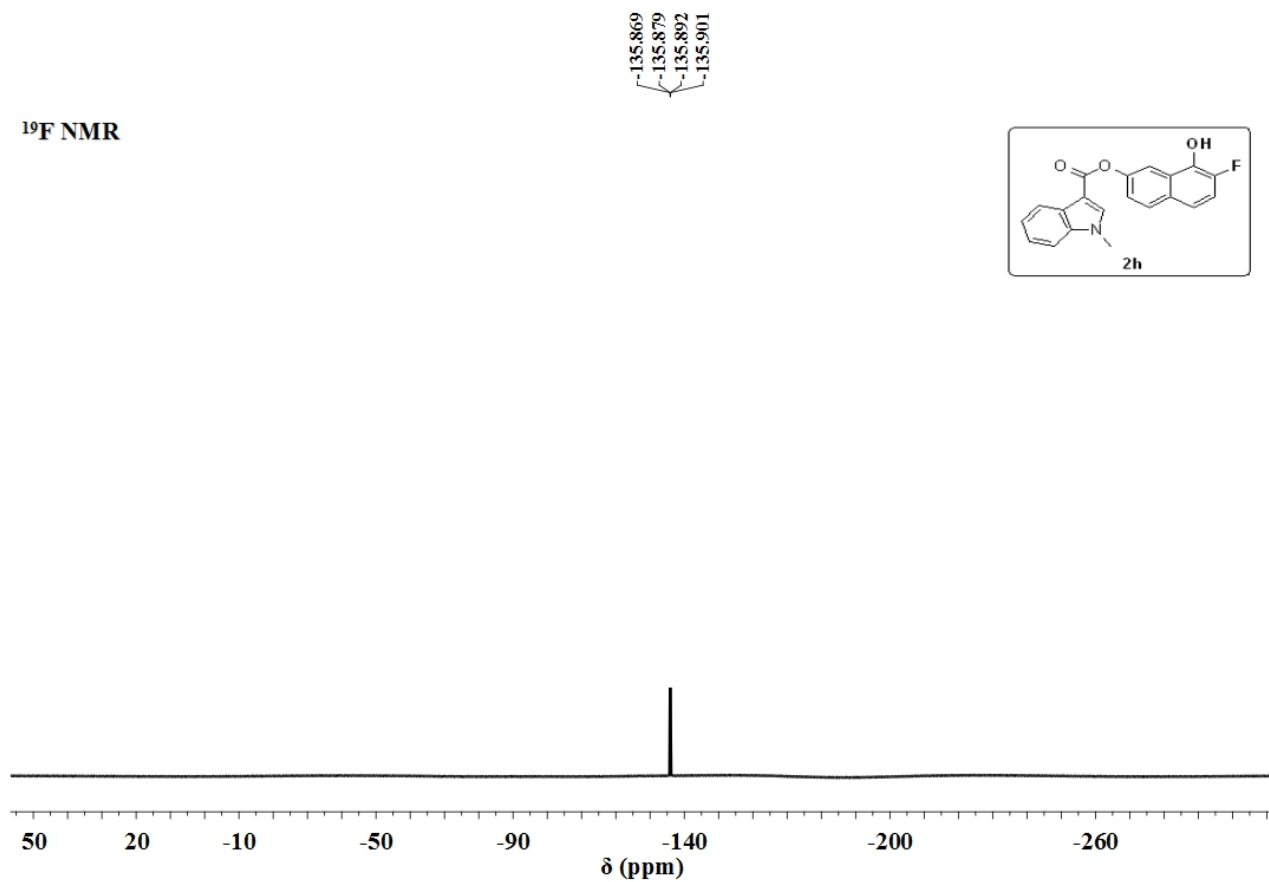
### <sup>1</sup>H NMR



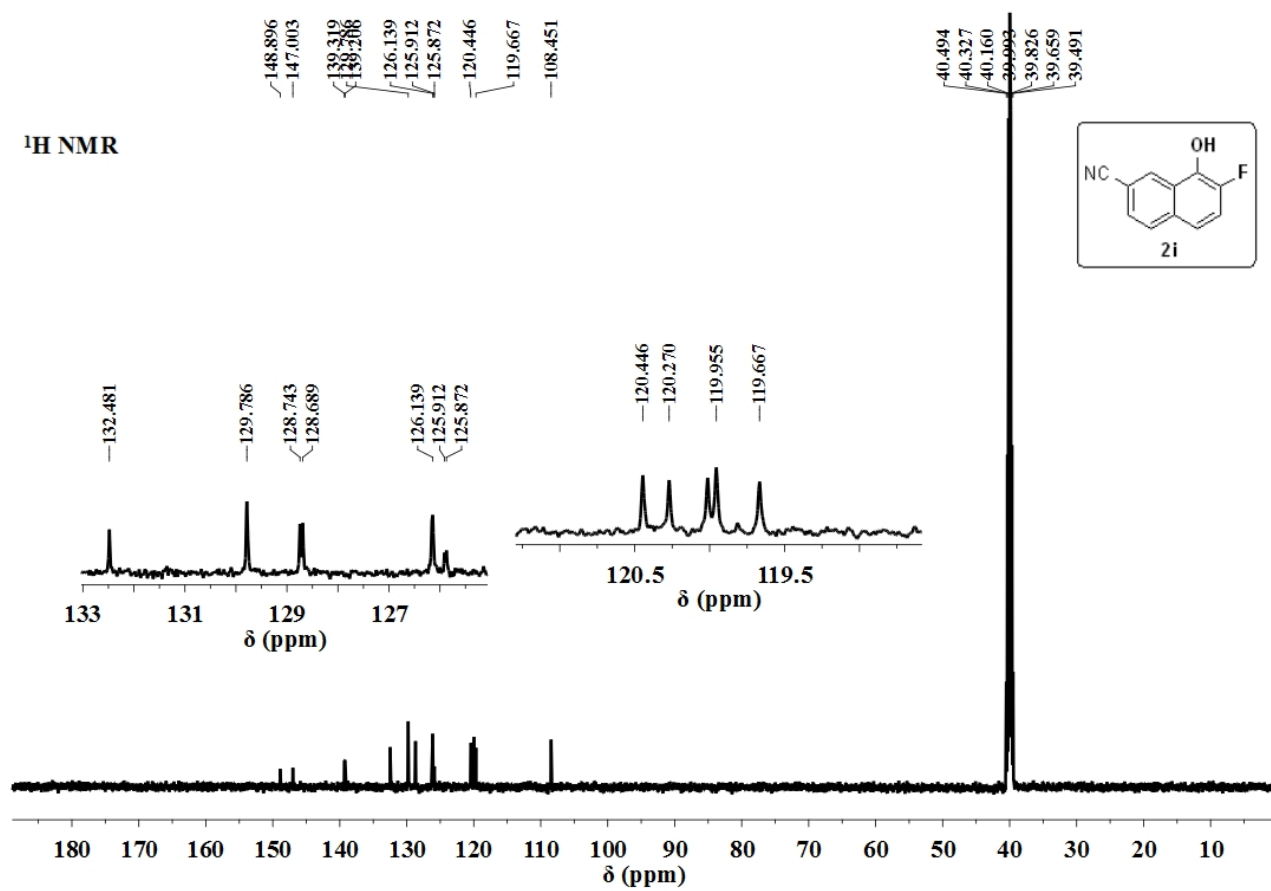
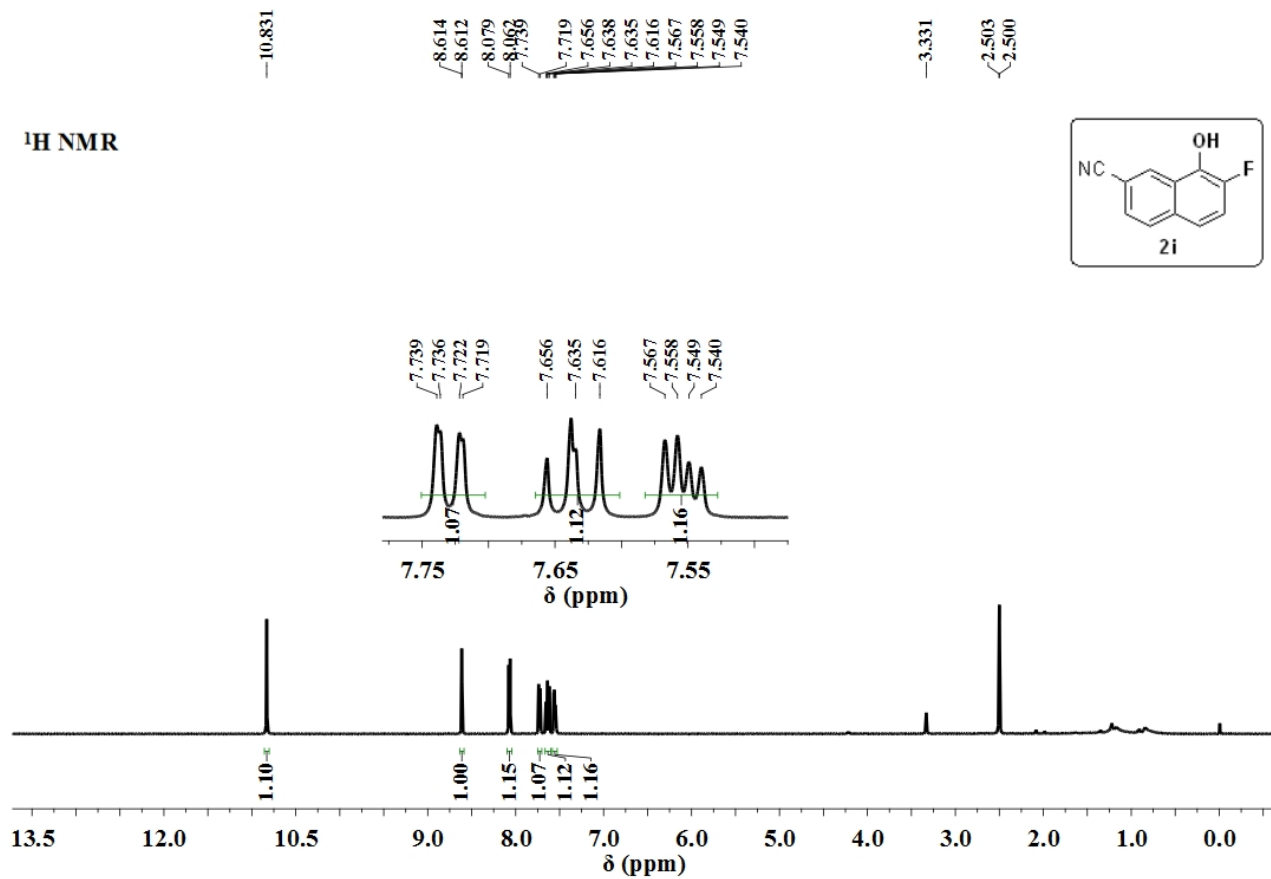
<sup>13</sup>C NMR



<sup>19</sup>F NMR

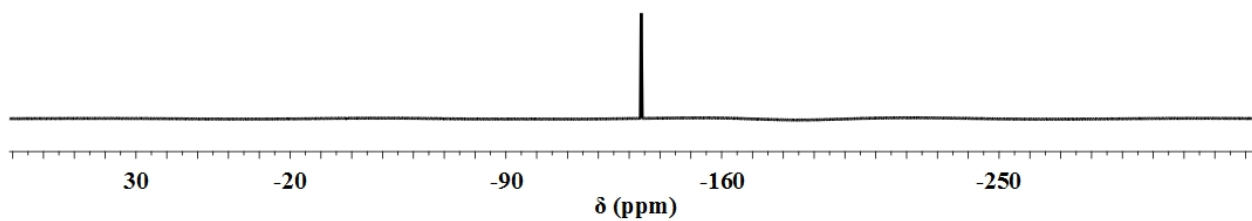
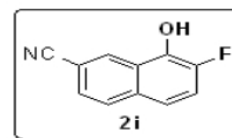


Compound 2i



<sup>19</sup>F NMR

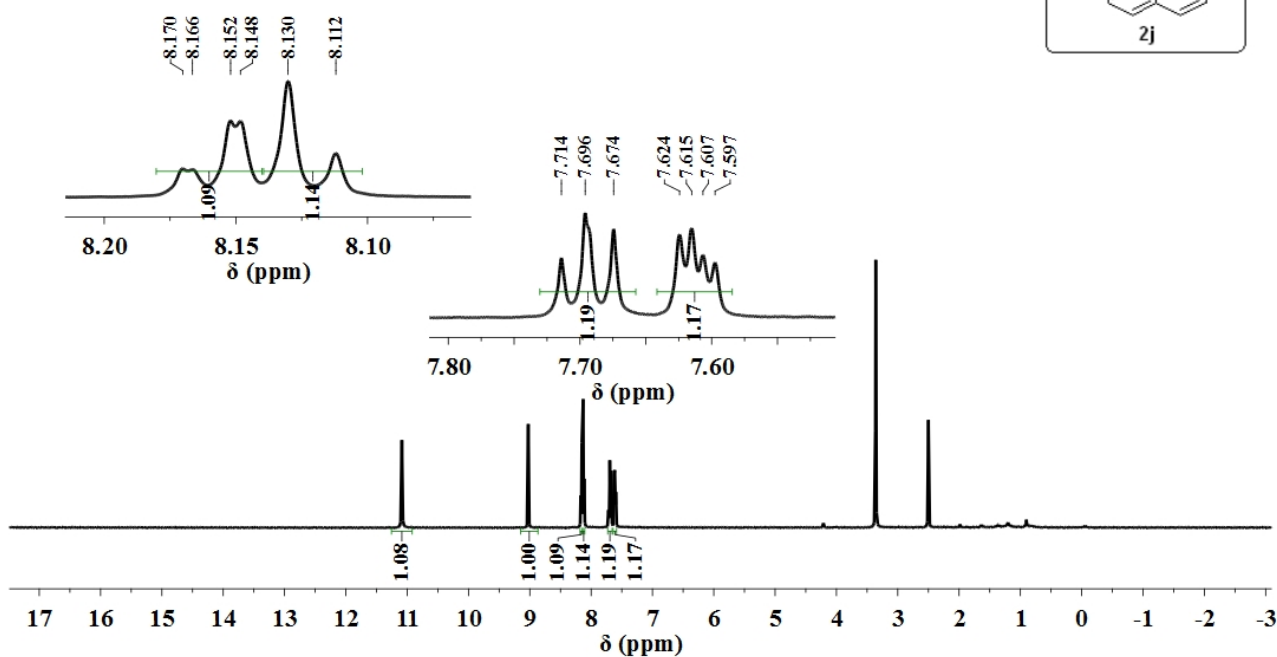
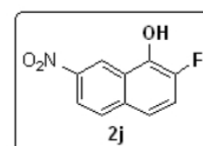
-133.892  
-133.902  
-133.915  
-133.924



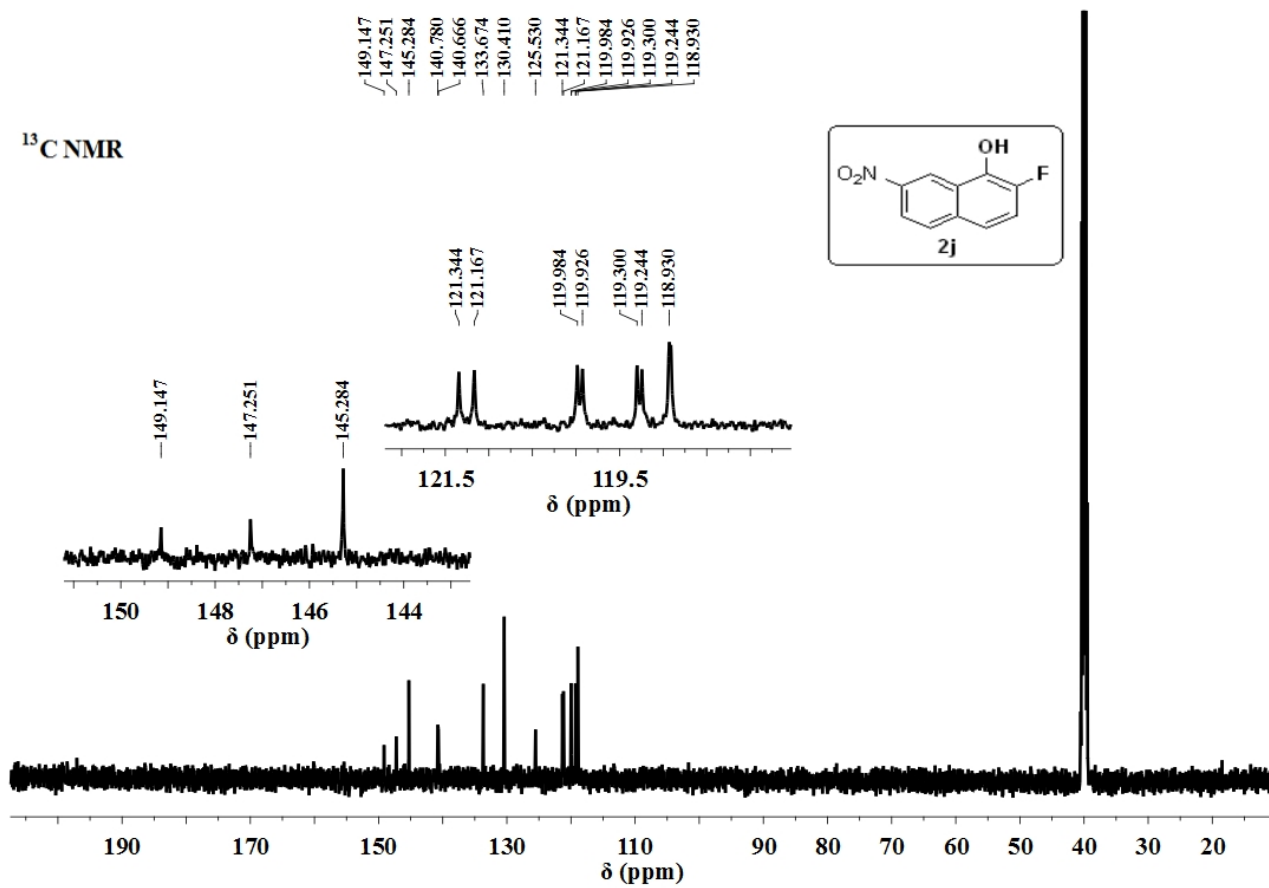
Compound 2j

-11.086  
-9.024  
-8.152  
-8.112  
-7.714  
-7.696  
-7.674  
-7.624  
-7.615  
-7.607  
-7.597  
-3.359  
-2.500

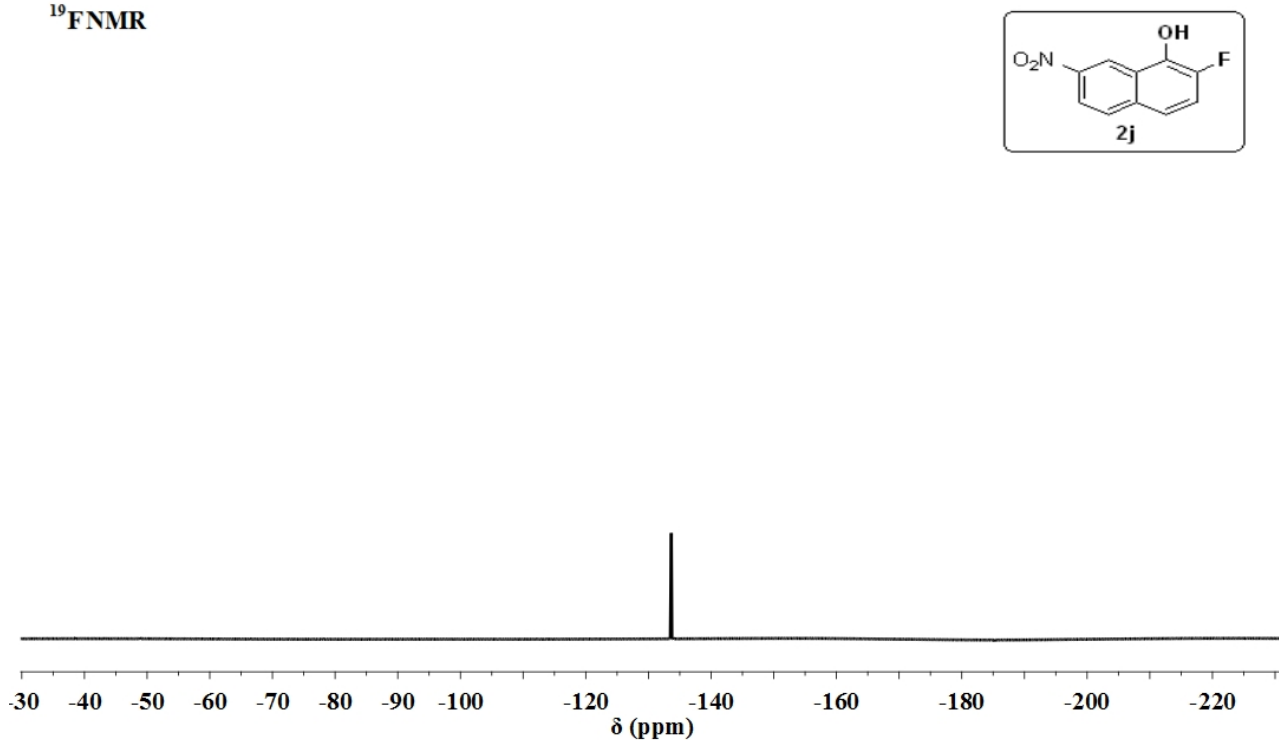
<sup>1</sup>H NMR



<sup>13</sup>C NMR

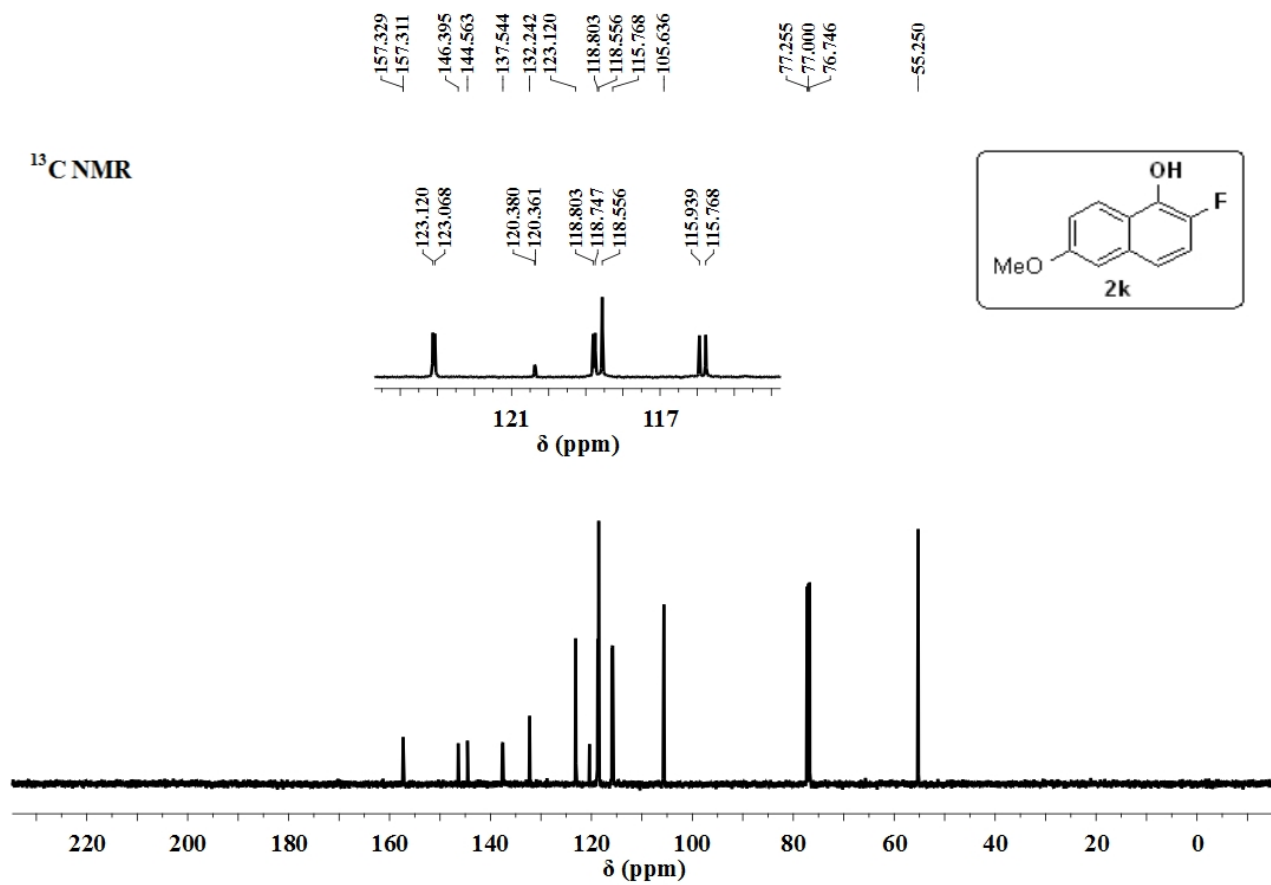
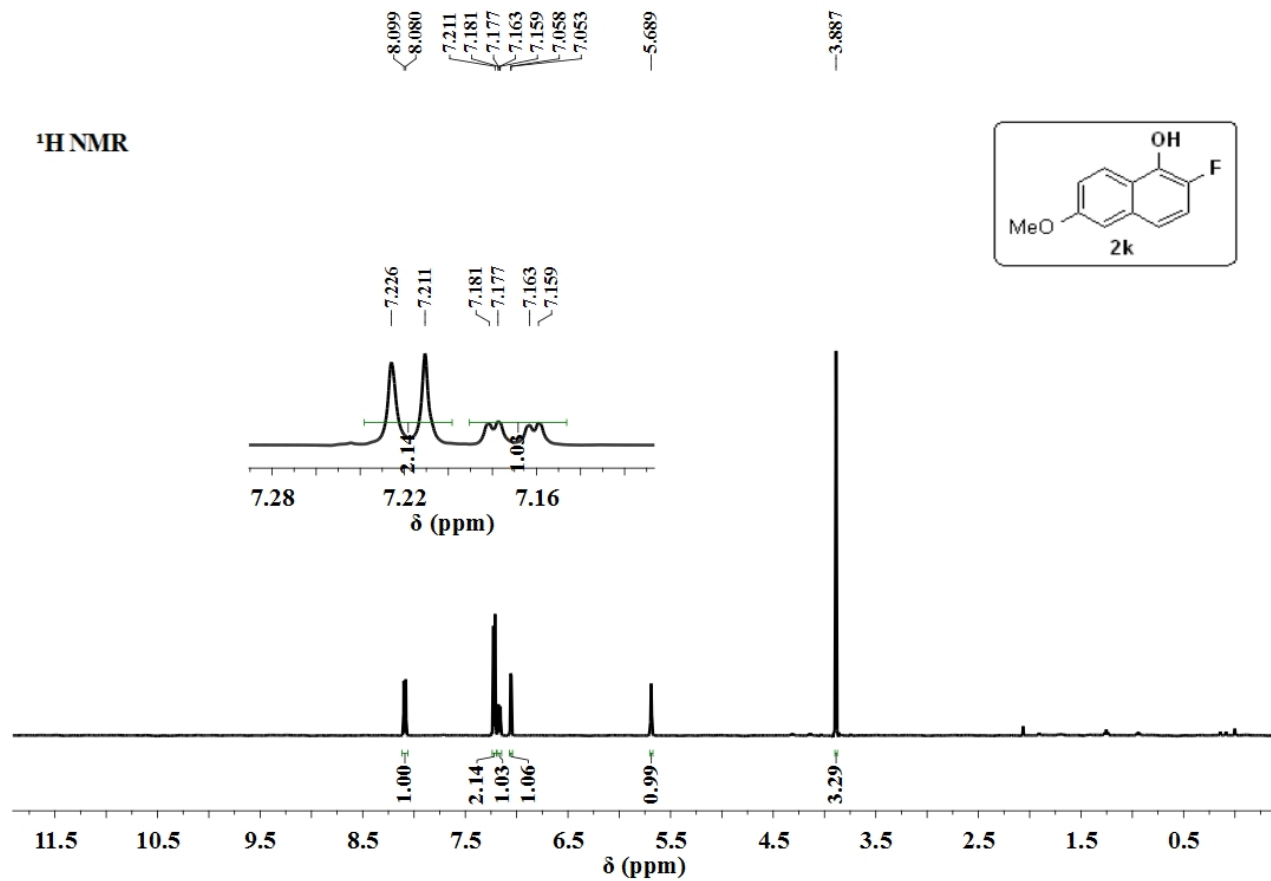


<sup>19</sup>F NMR

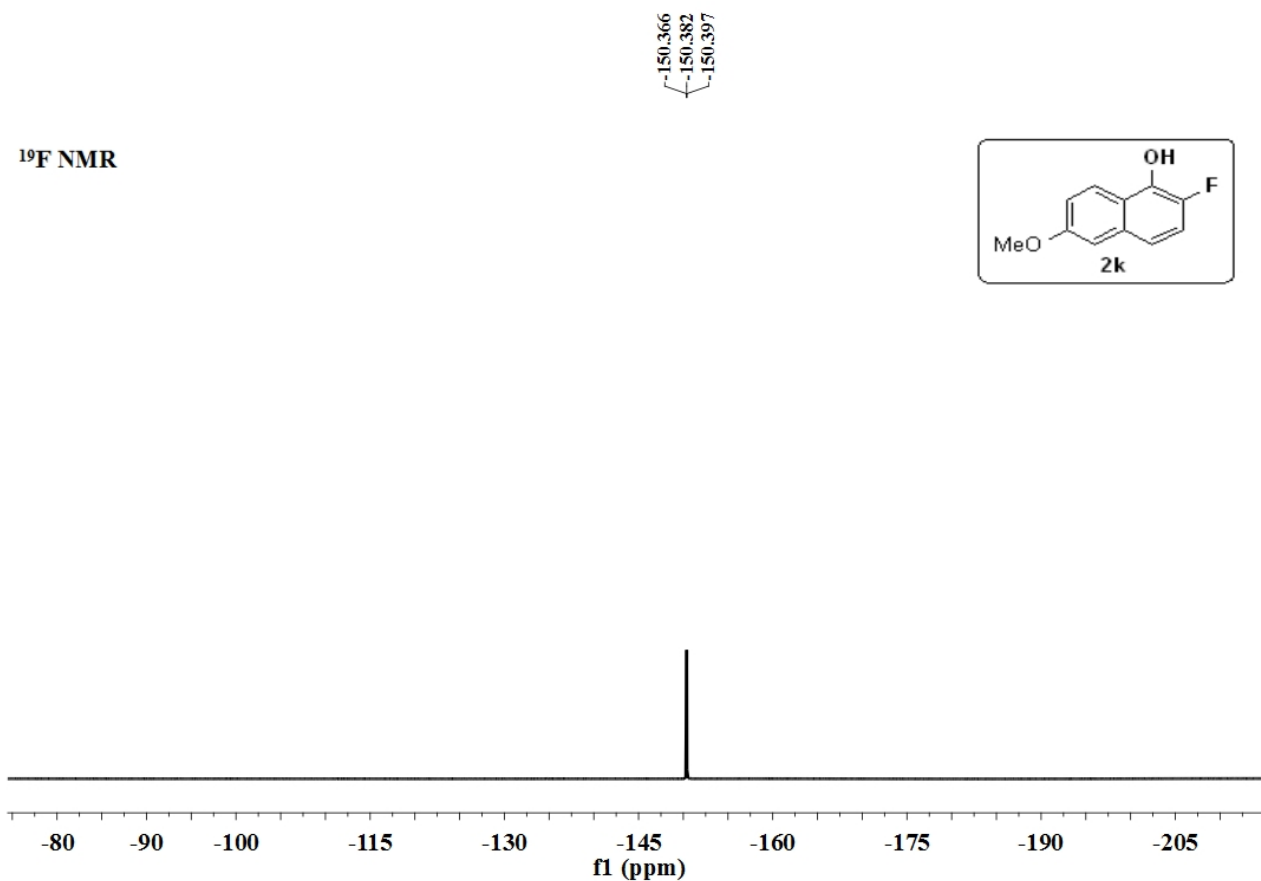
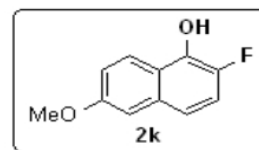




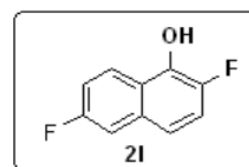
Compound 2k



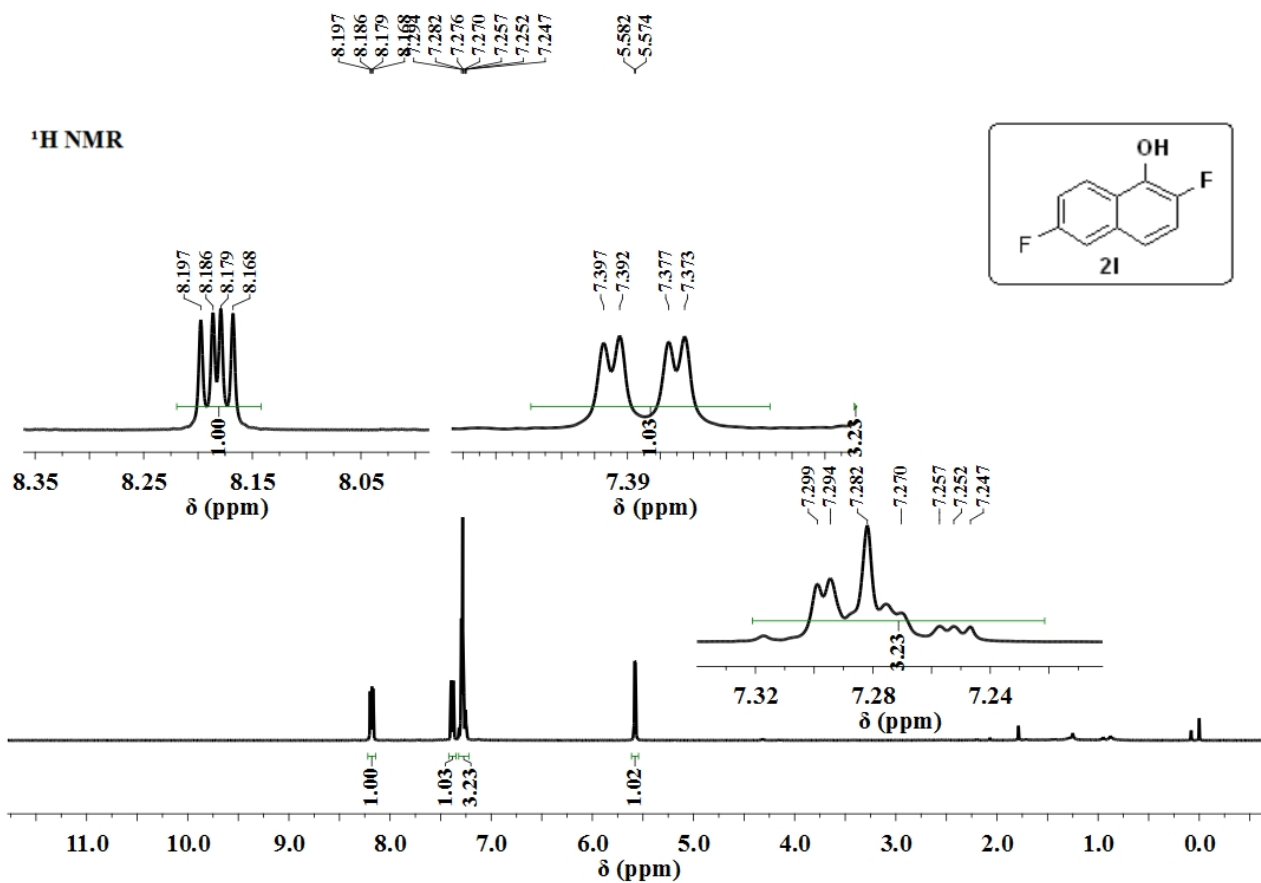
<sup>19</sup>F NMR



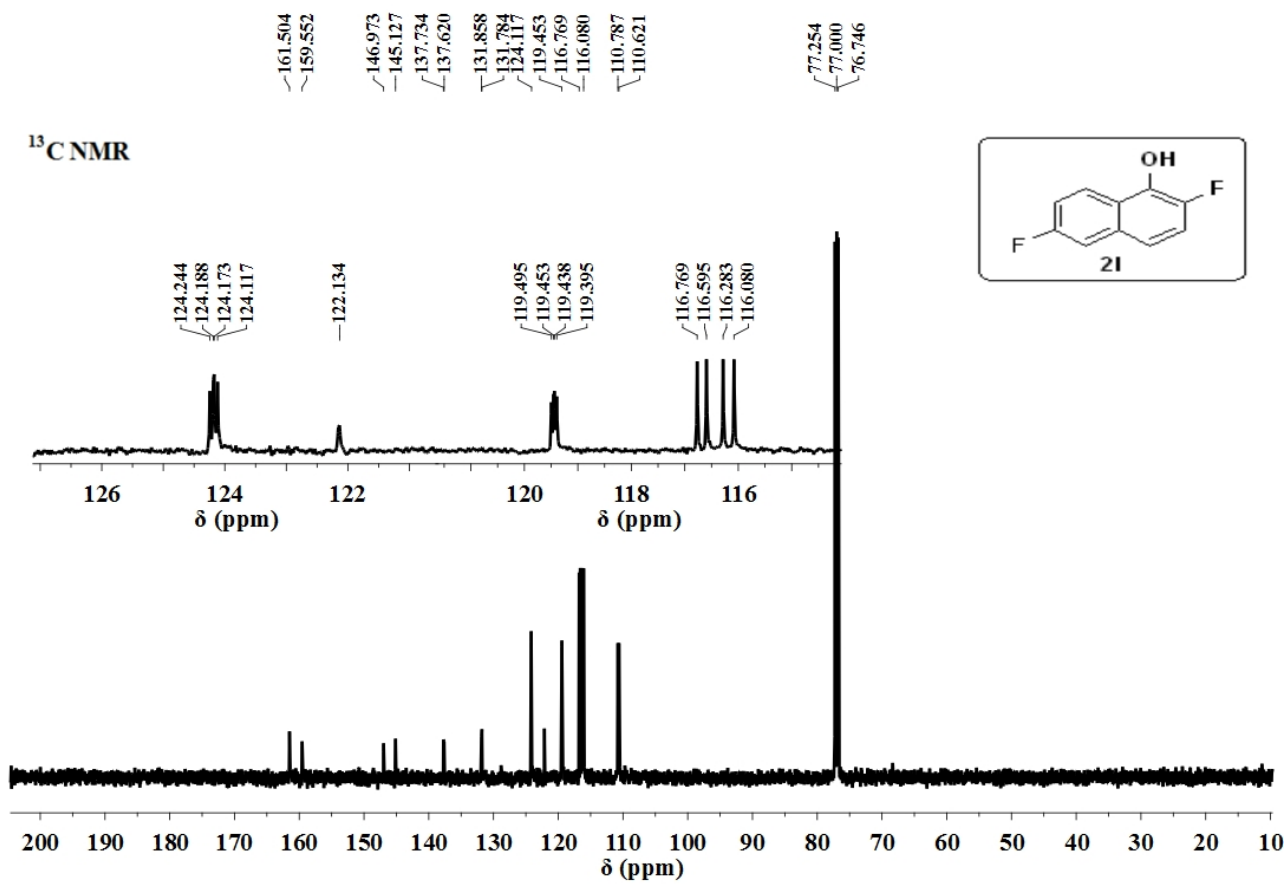
Compound 2l



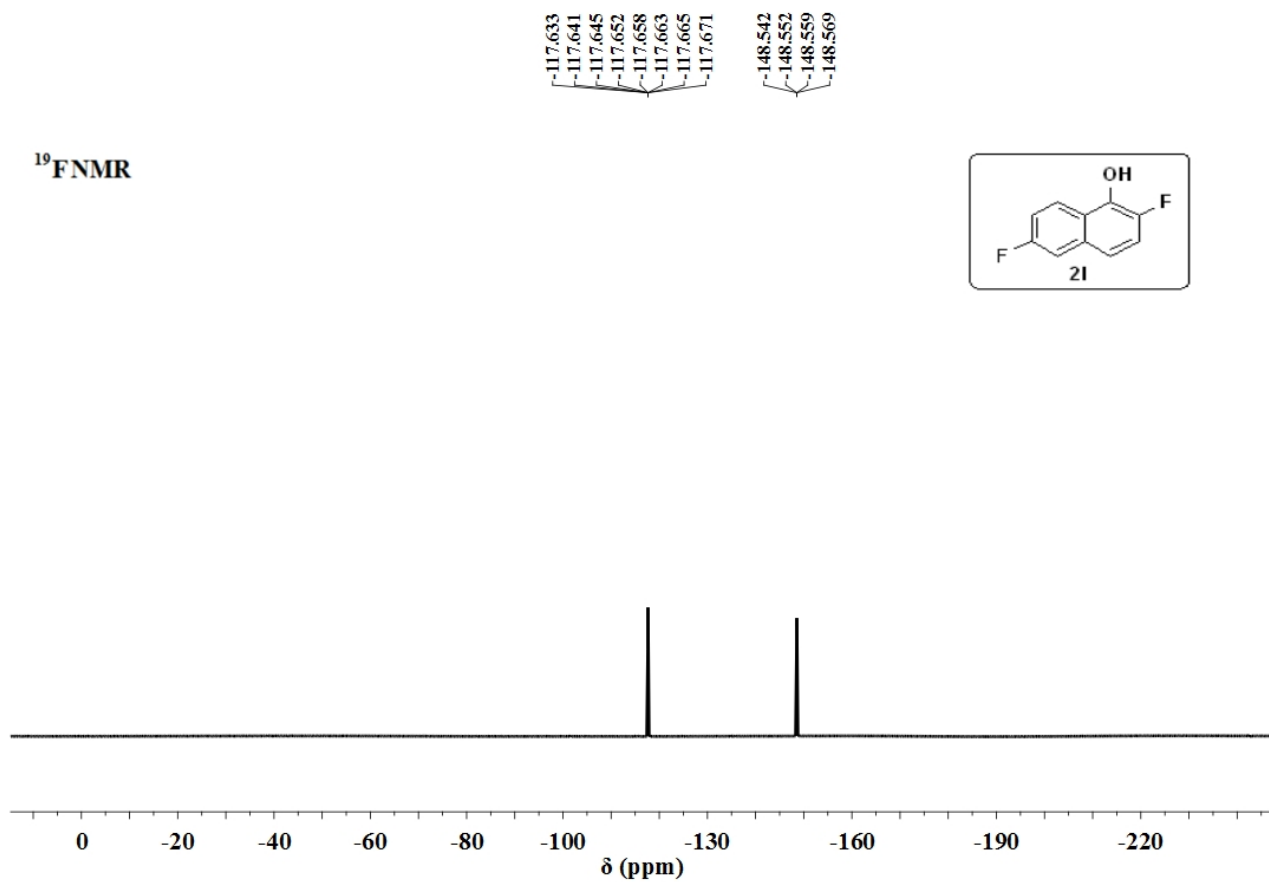
<sup>1</sup>H NMR



<sup>13</sup>C NMR



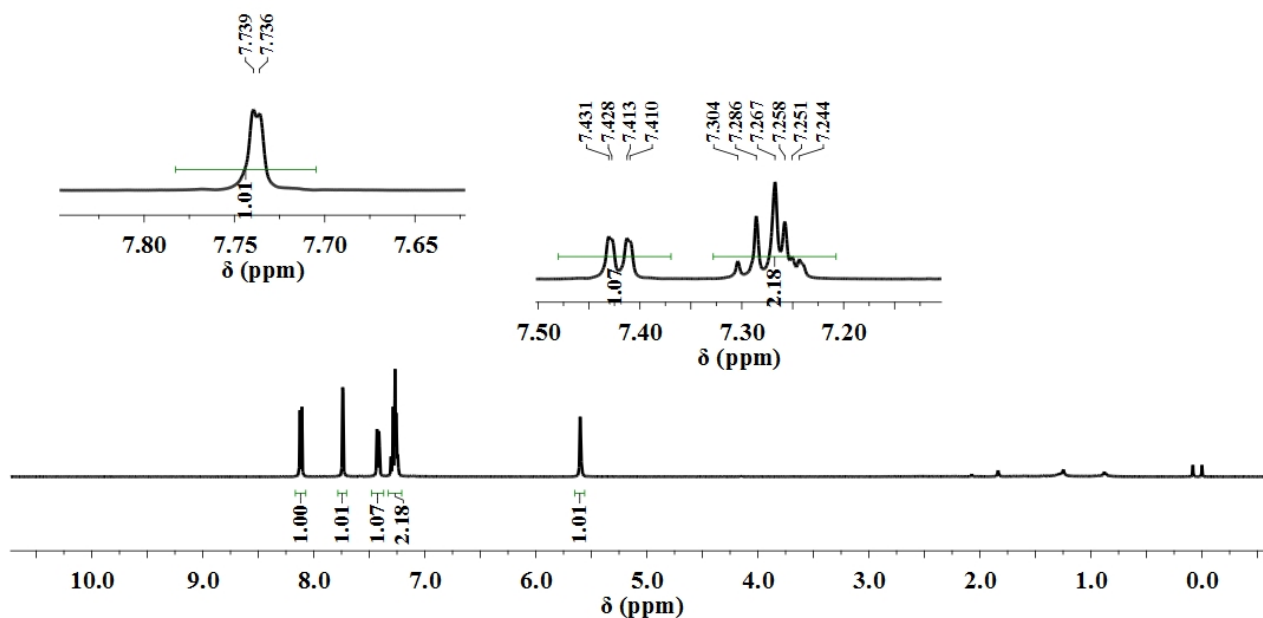
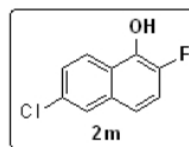
<sup>19</sup>F NMR



# Compound 2m

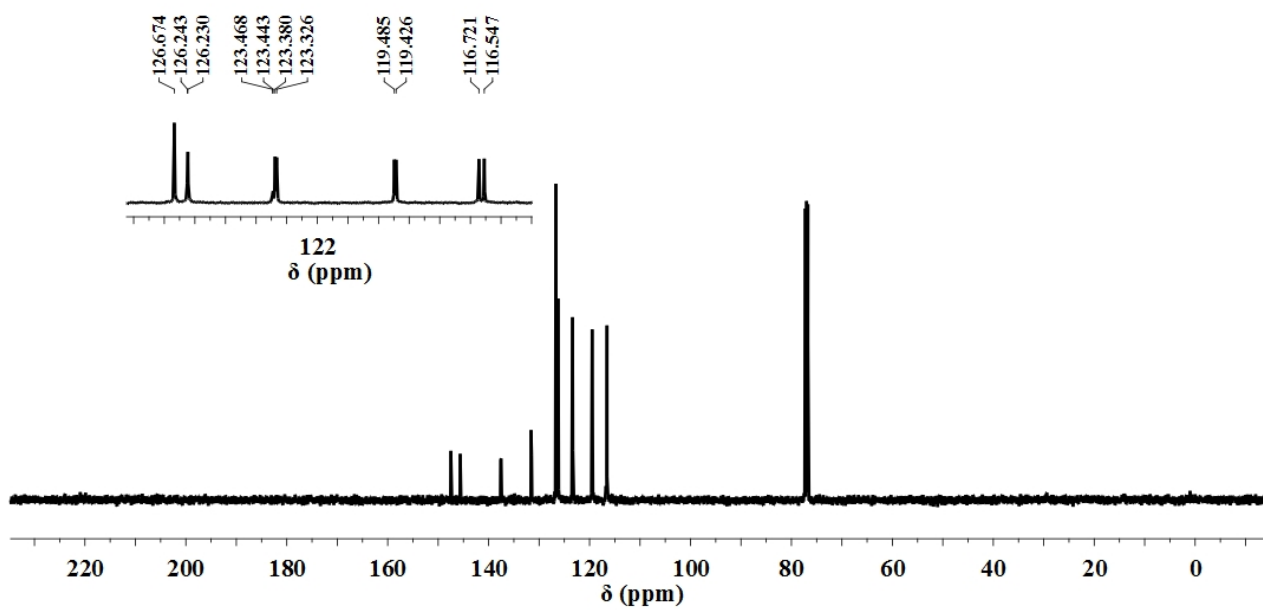
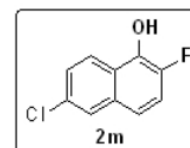
8.124  
8.106  
7.736  
7.428  
7.410  
7.286  
7.258  
7.244  
5.601  
5.595

## <sup>1</sup>H NMR



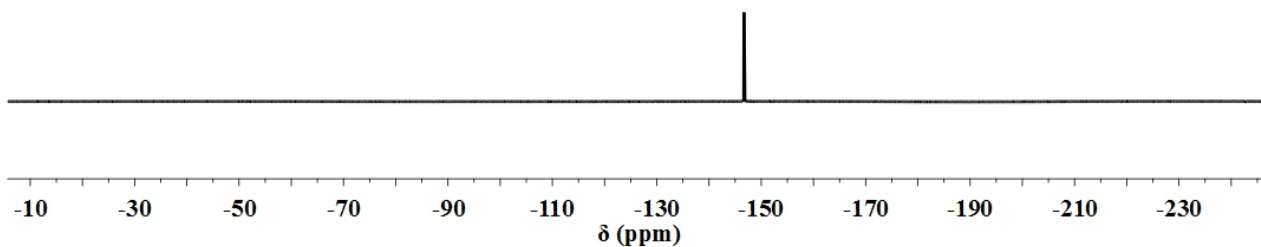
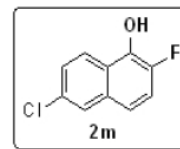
147.490  
145.632  
137.520  
136.884  
123.380  
123.326  
119.485  
119.426  
116.721  
116.547  
77.254  
77.000  
76.746

## <sup>13</sup>C NMR



<sup>19</sup>F NMR

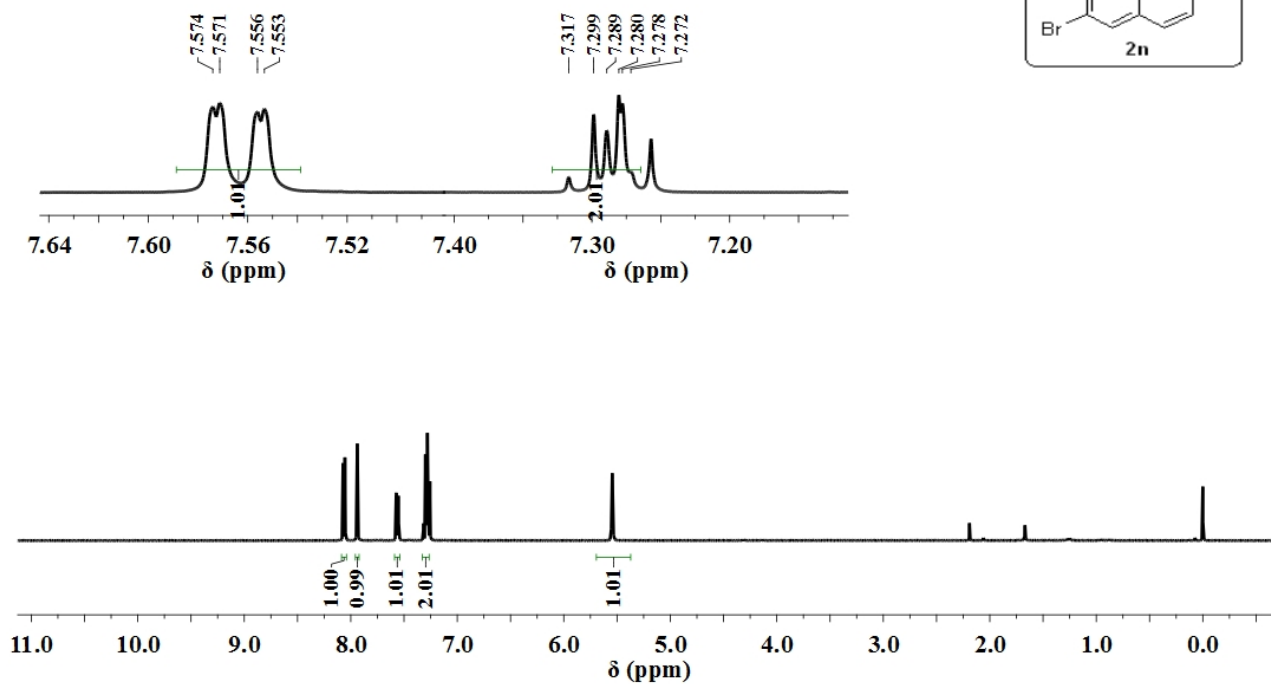
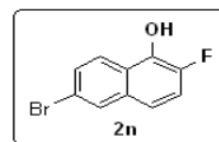
-146.692  
-146.702  
-146.711



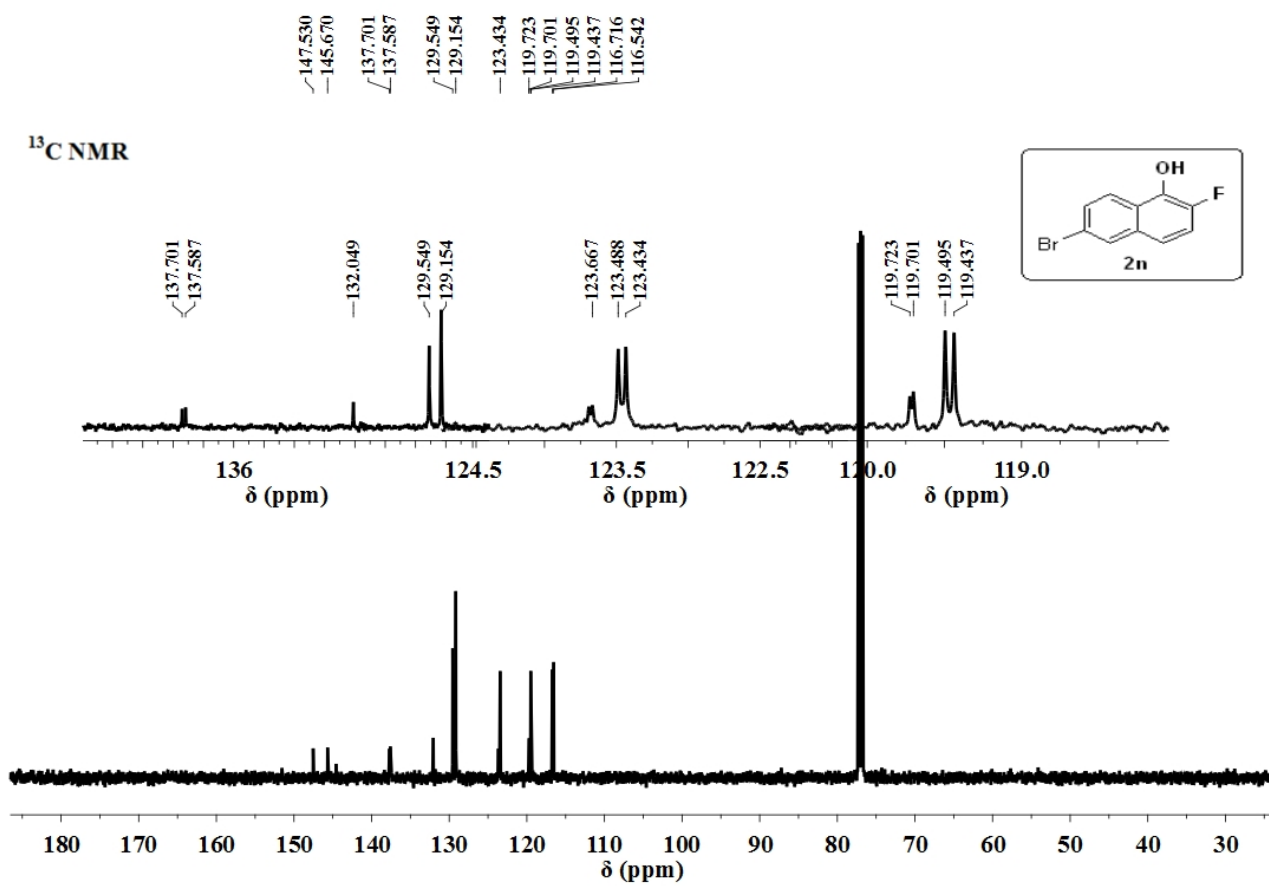
Compound 2n

8.073  
8.055  
7.942  
7.939  
7.553  
7.299  
7.289  
7.280  
7.278  
7.272  
5.545

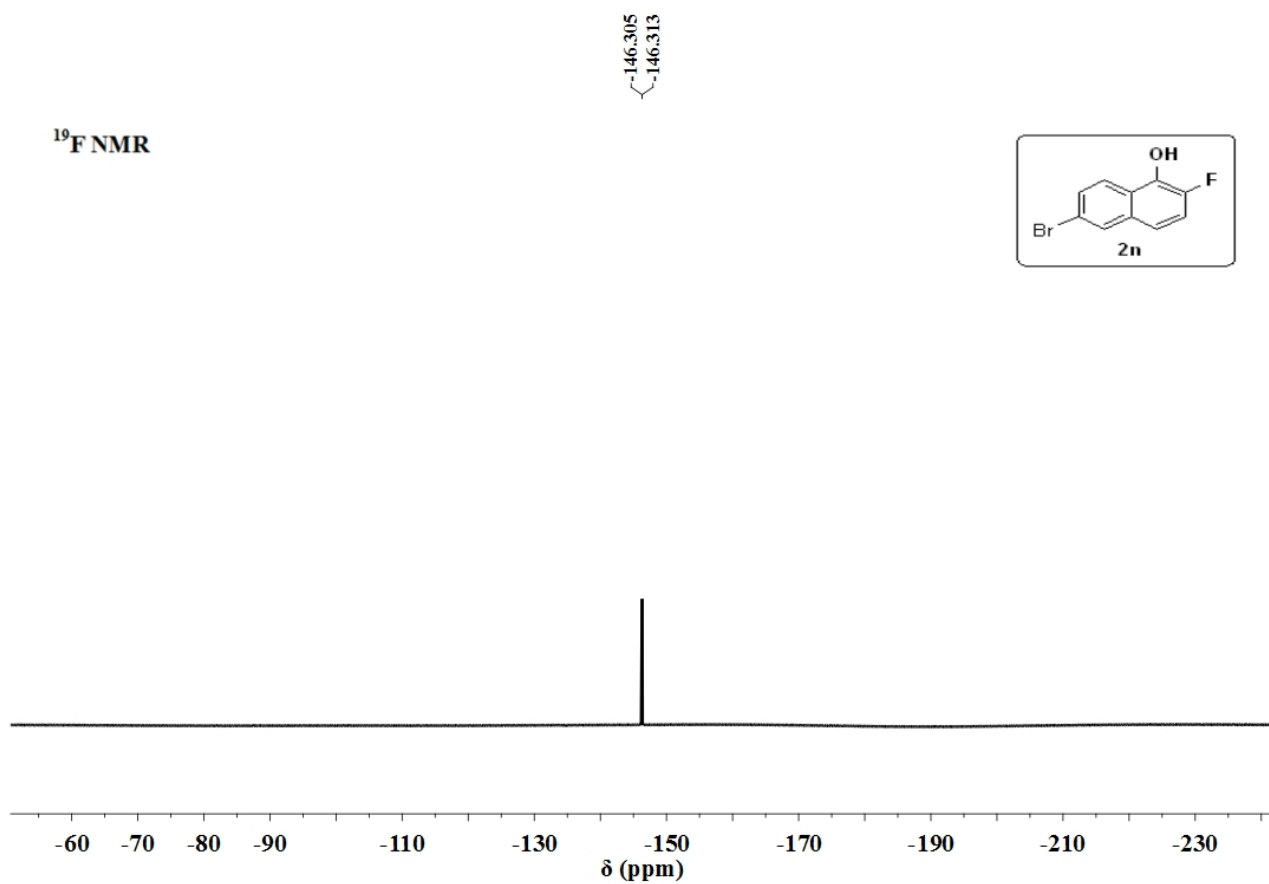
<sup>1</sup>H NMR



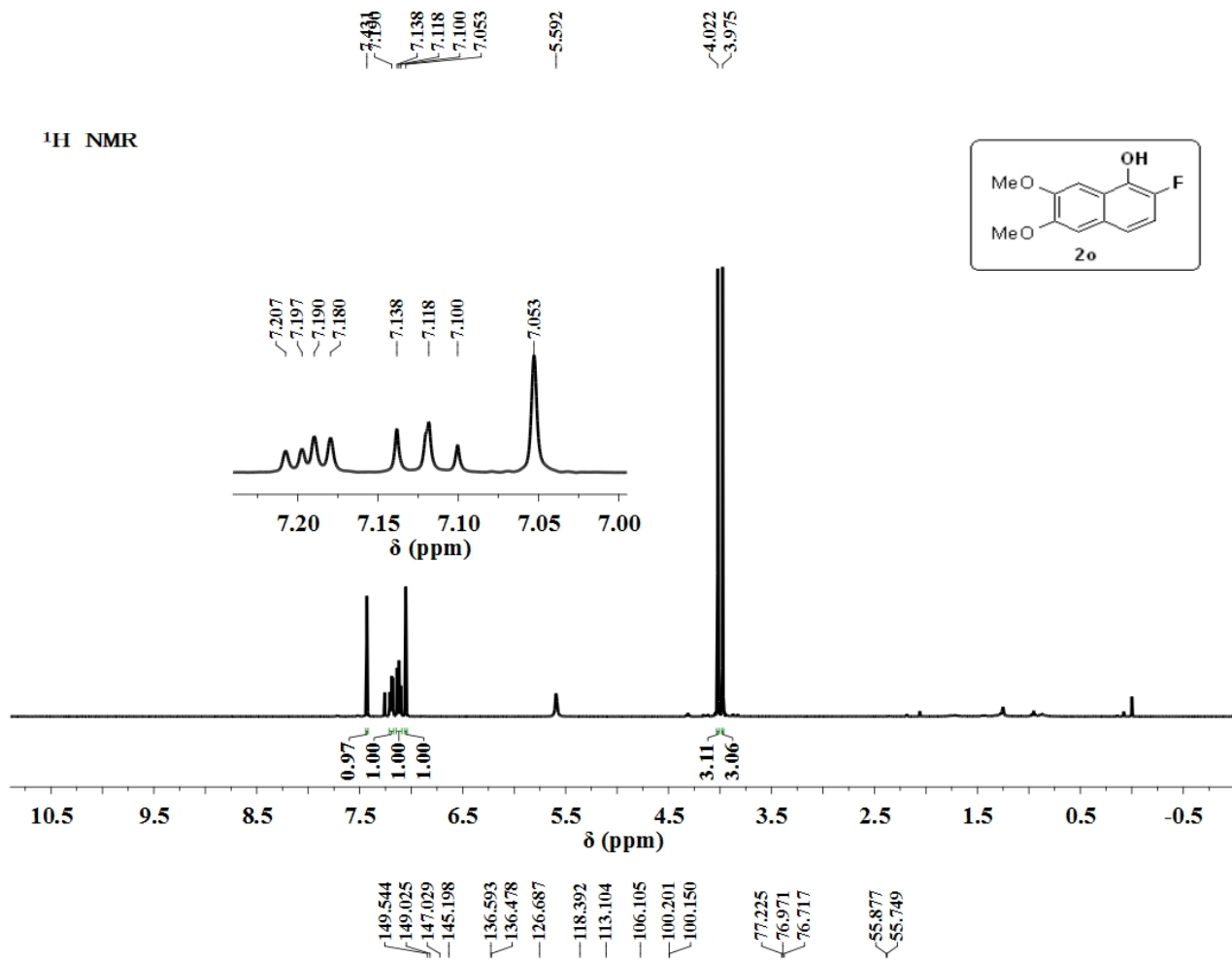
<sup>13</sup>C NMR



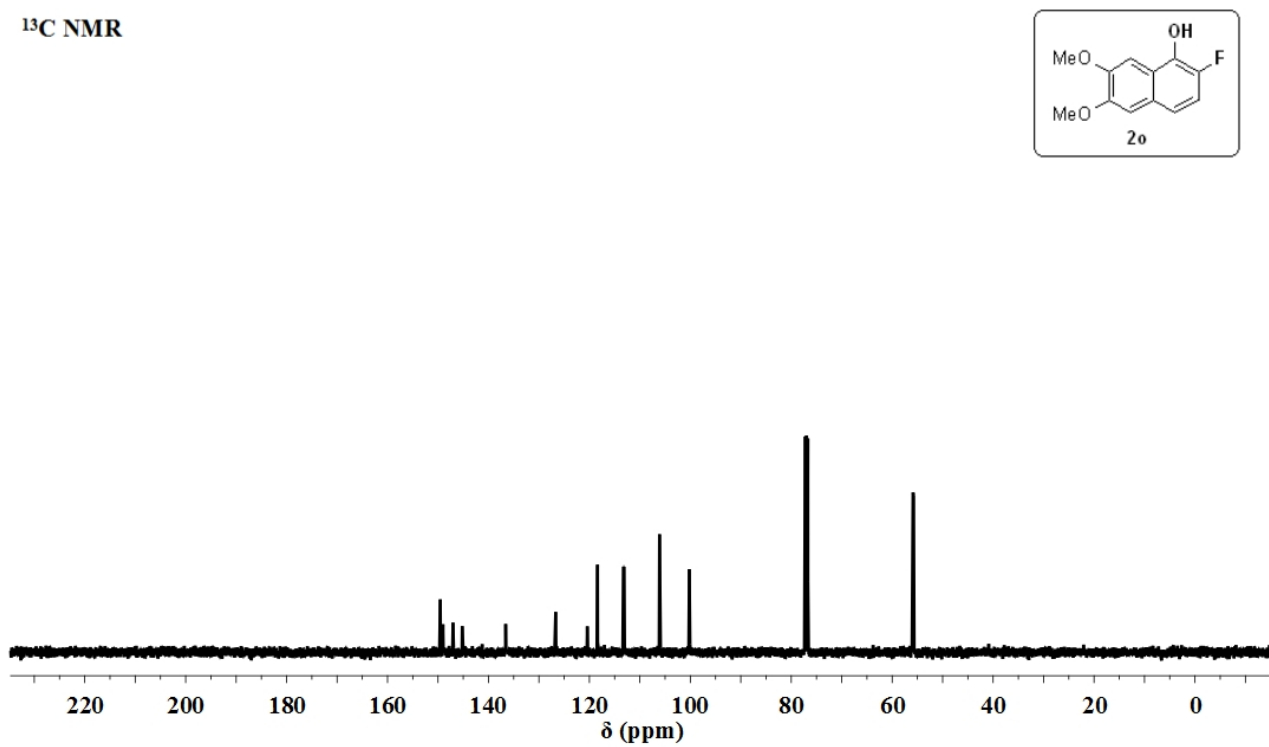
<sup>19</sup>F NMR



# Compound 2o

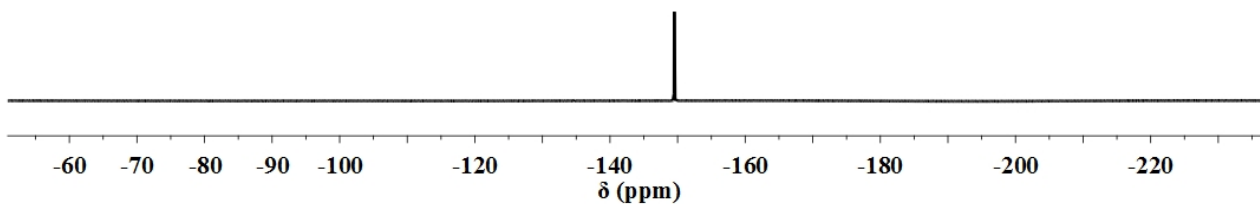
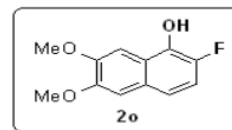


# <sup>13</sup>C NMR



<sup>19</sup>F NMR

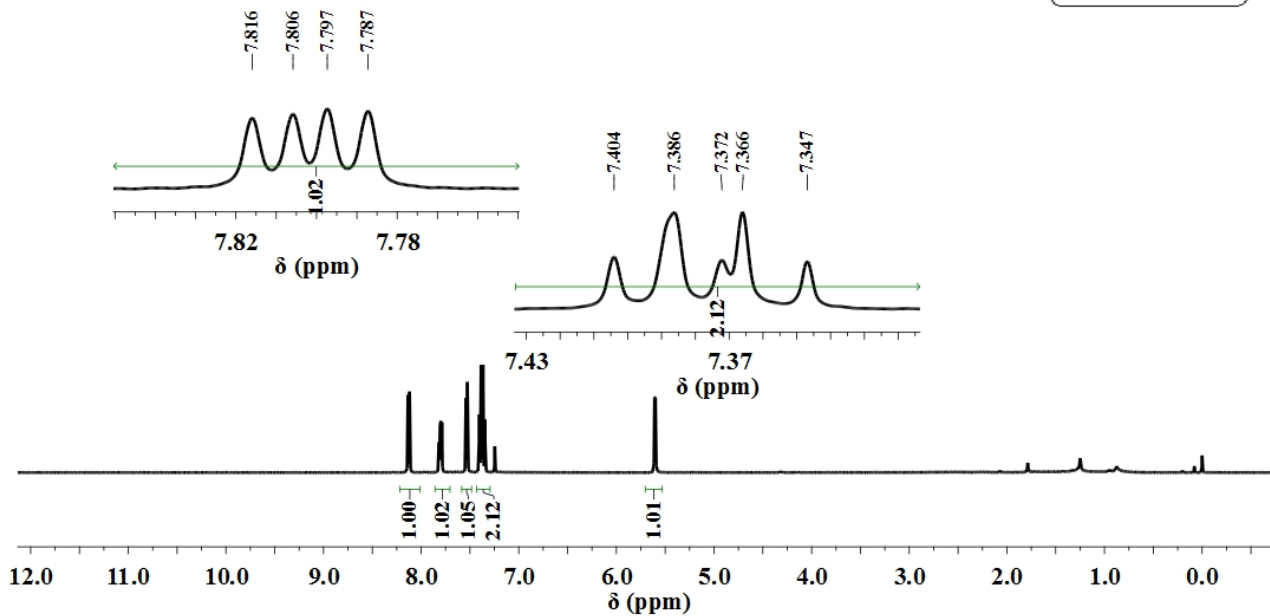
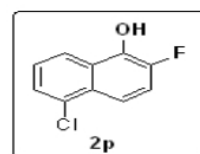
-149.504  
-149.515  
-149.525  
-149.535



Compound 2p

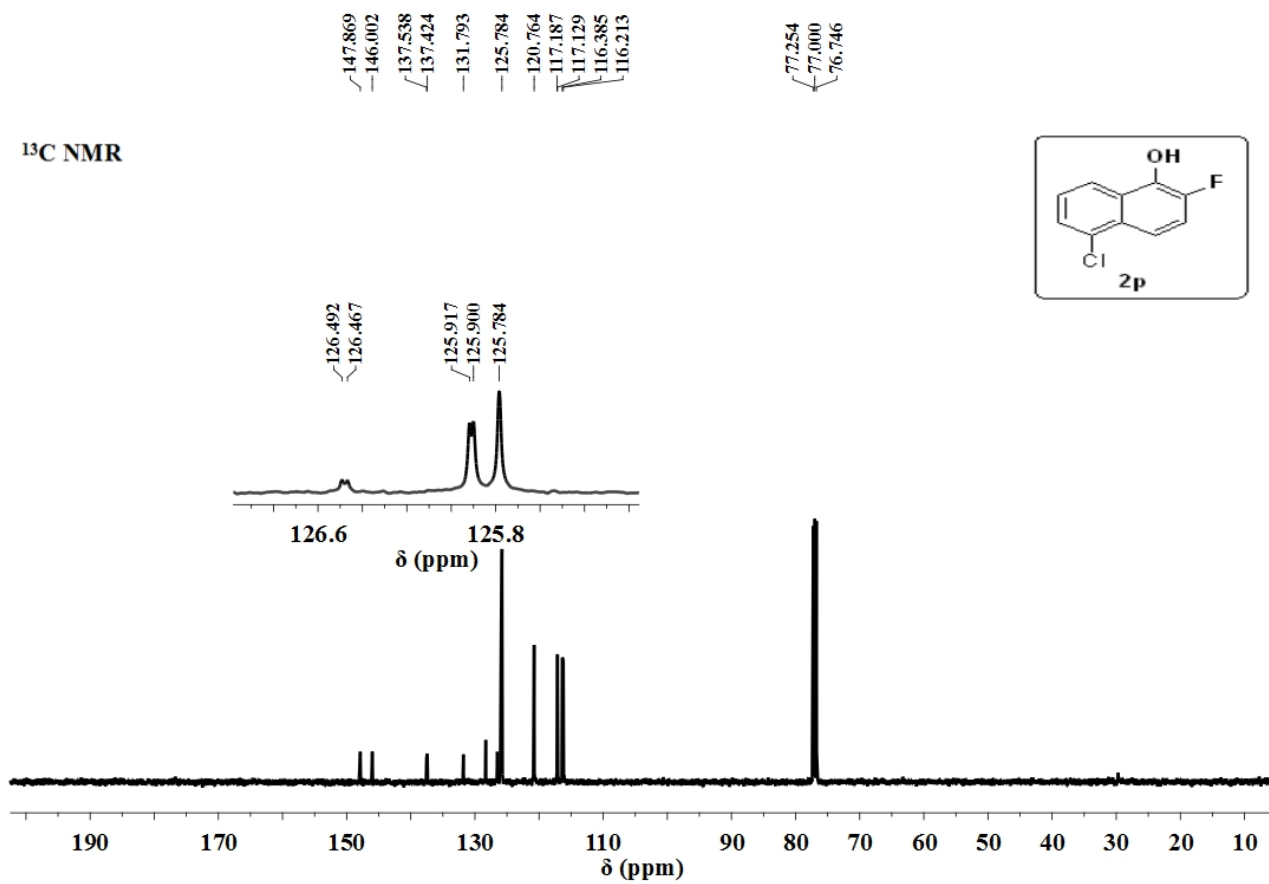
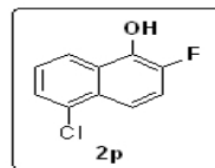
8.136  
8.119  
8.089  
7.787  
7.536  
7.386  
7.372  
7.366  
7.347  
5.608  
5.600

<sup>1</sup>H NMR

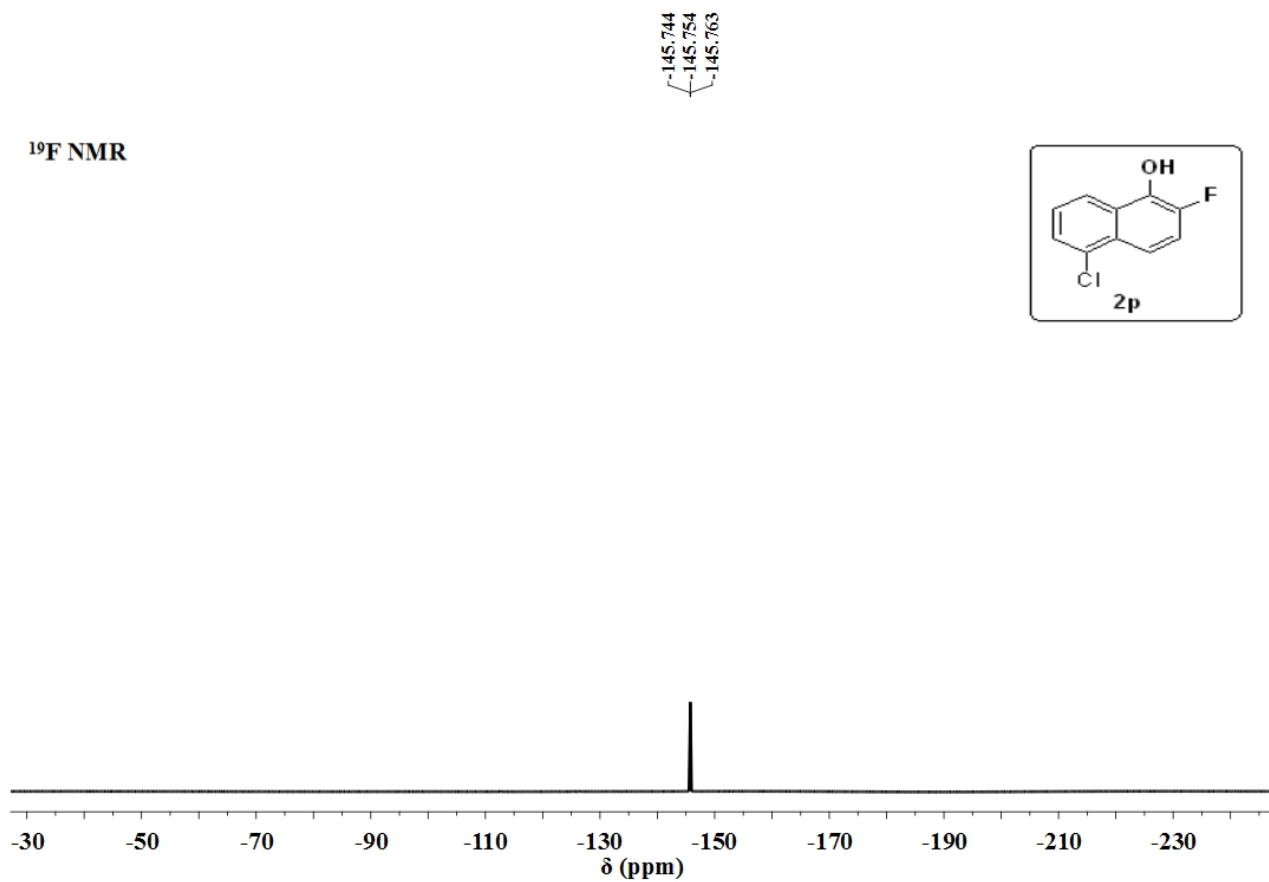
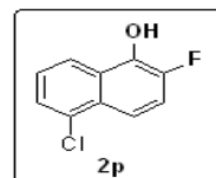




<sup>13</sup>C NMR



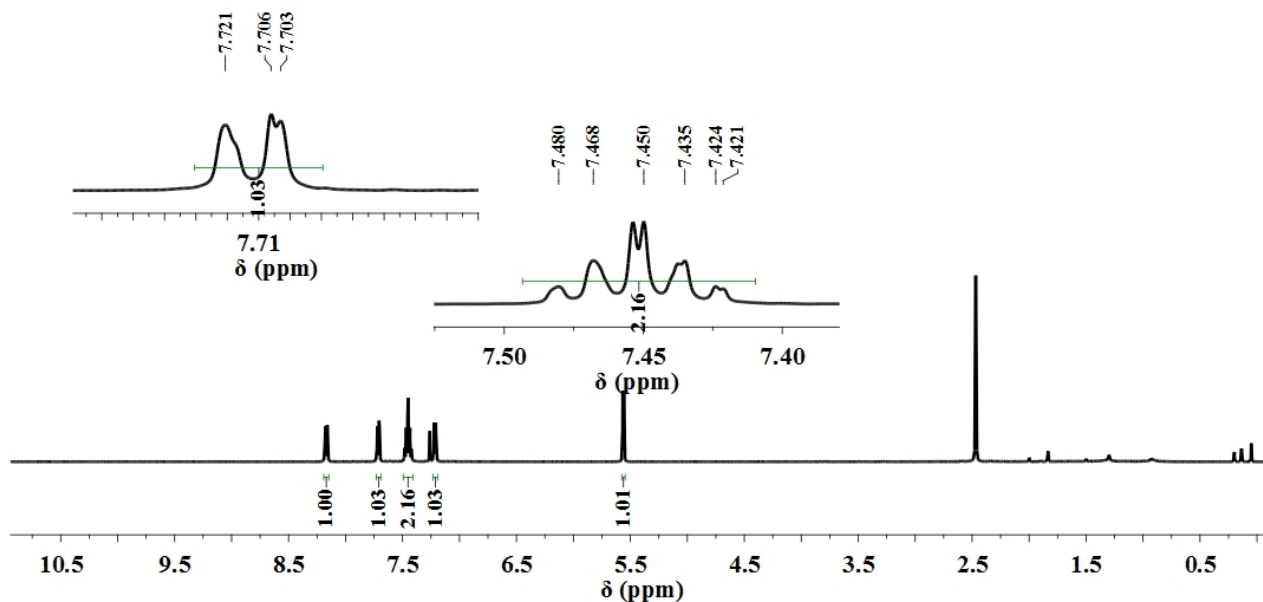
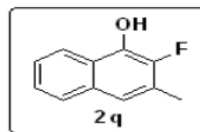
<sup>19</sup>F NMR



Compound 2q

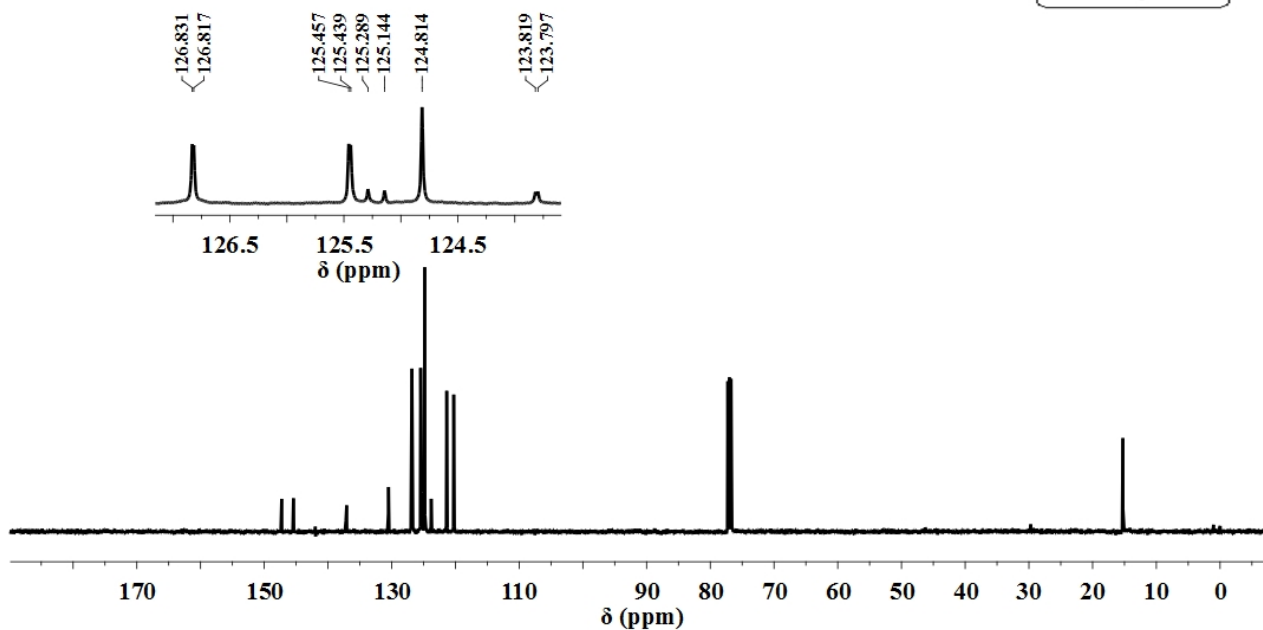
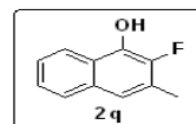
8.178, 8.176, 8.168, 7.703, 7.424, 7.223, 7.208, 5.566, 5.556, 2.469, 2.467

<sup>1</sup>H NMR

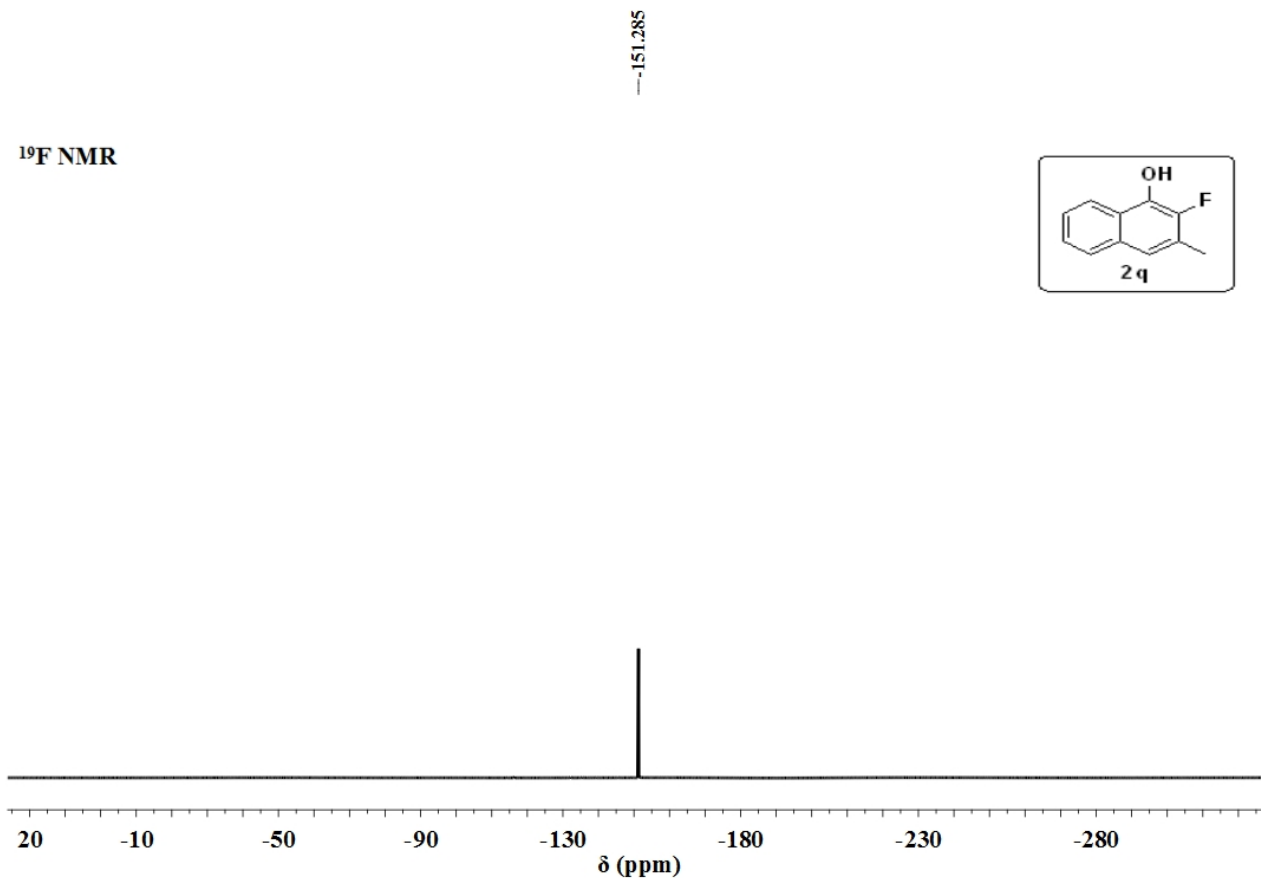
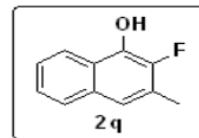


147.272, 145.422, 137.186, 137.069, 130.500, 125.457, 124.814, 123.819, 123.797, 121.365, 121.312, 120.263, 120.231, 77.254, 77.000, 76.746, 15.283, 15.253

<sup>13</sup>C NMR



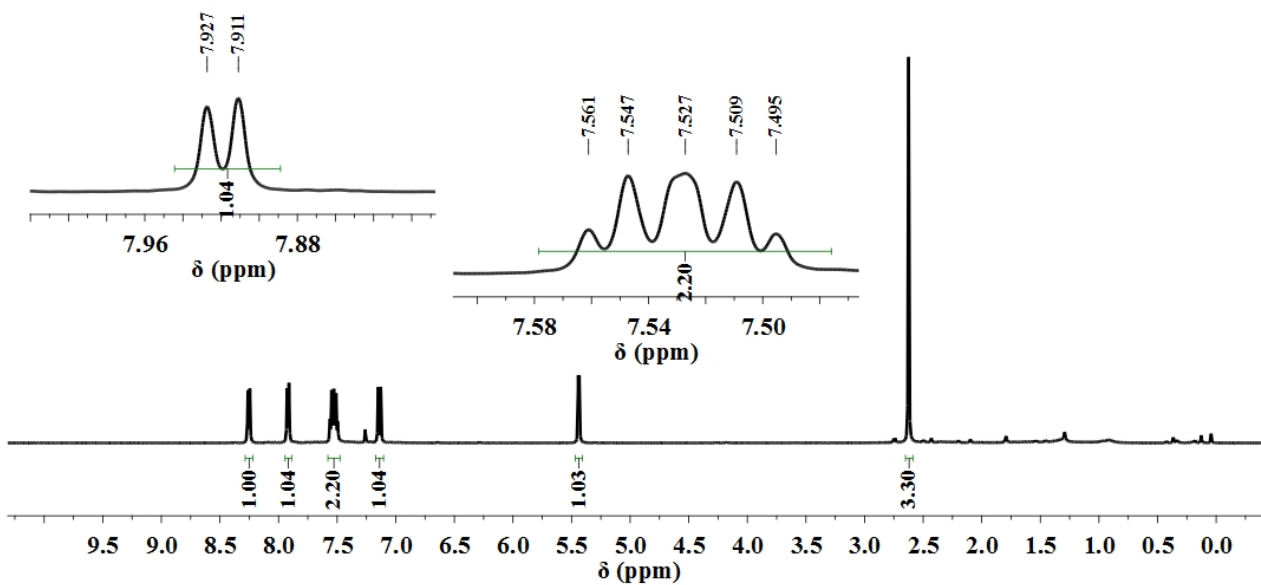
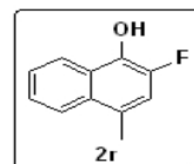
<sup>19</sup>F NMR



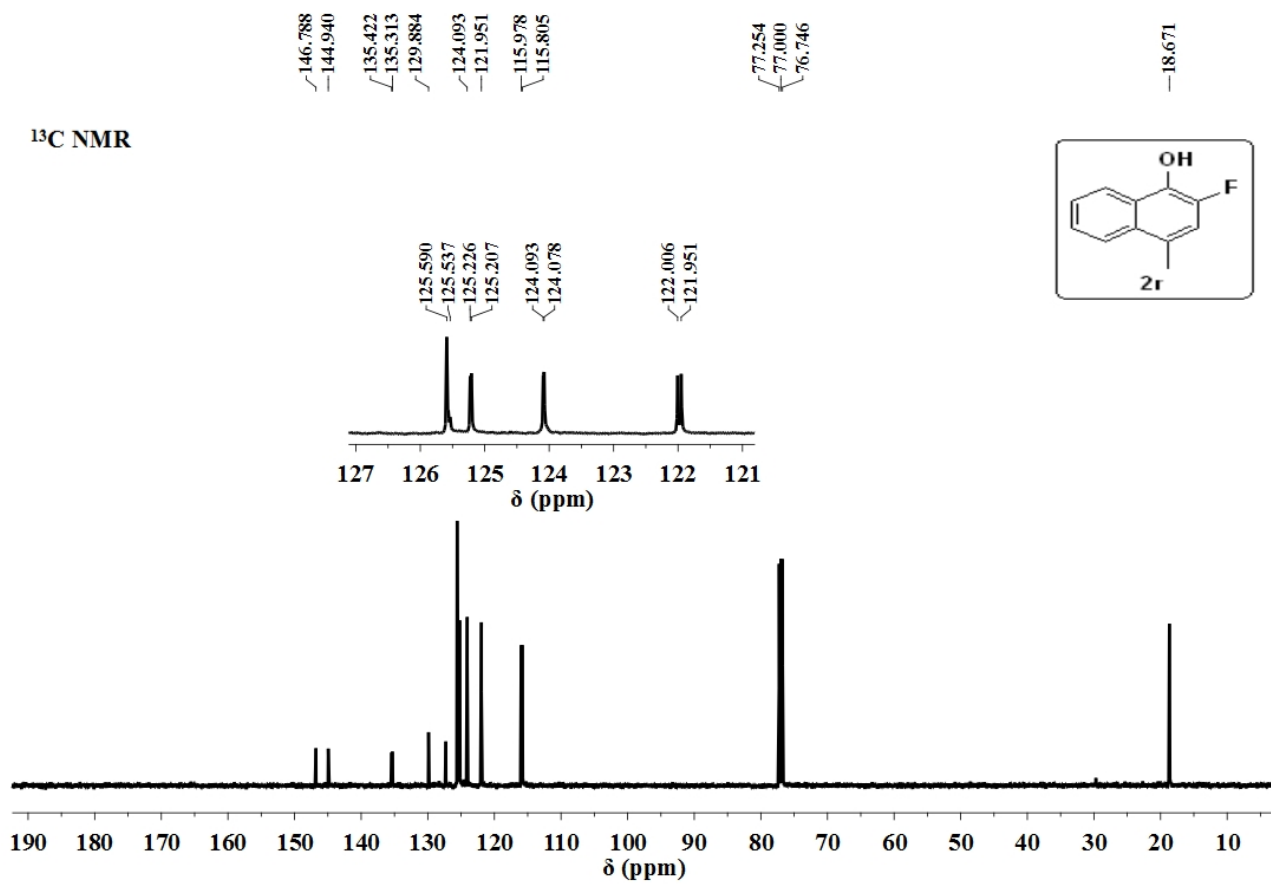
Compound 2r

8.261  
8.245  
7.911  
7.495  
7.150  
7.128  
5.442  
5.434  
2.624

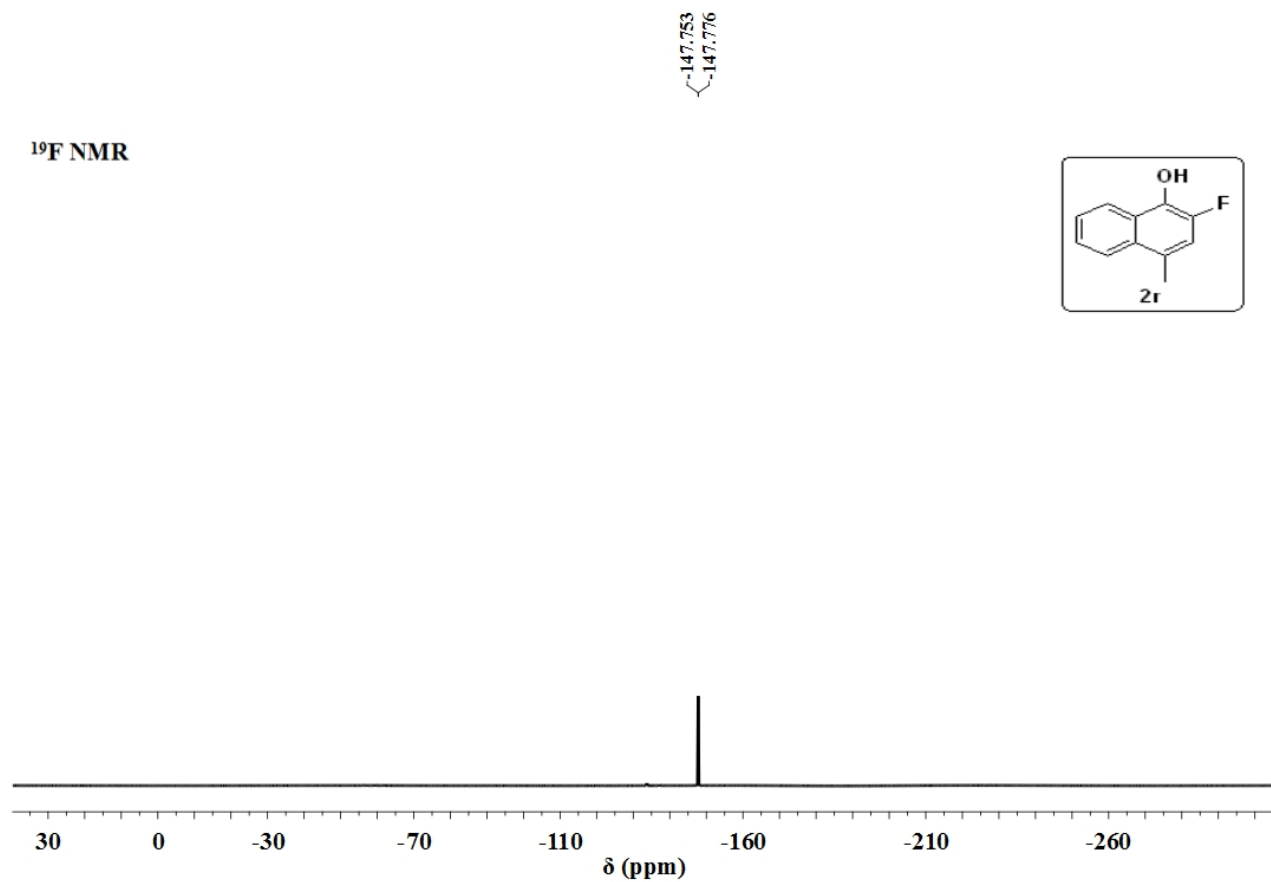
<sup>1</sup>H NMR



<sup>13</sup>C NMR



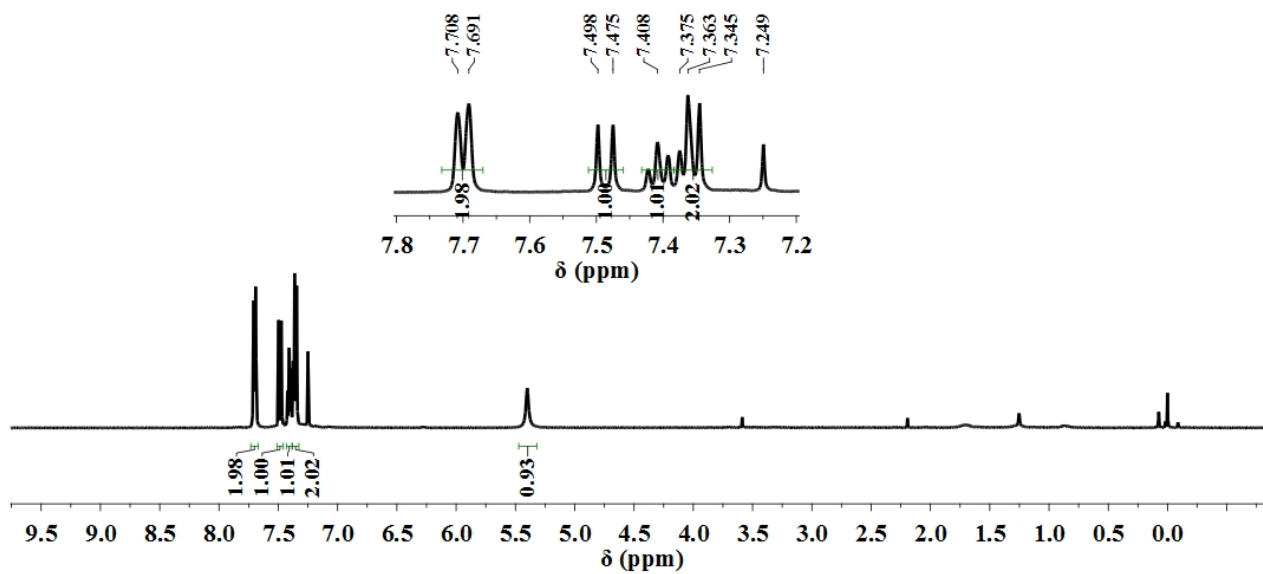
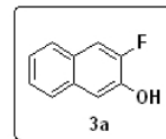
<sup>19</sup>F NMR



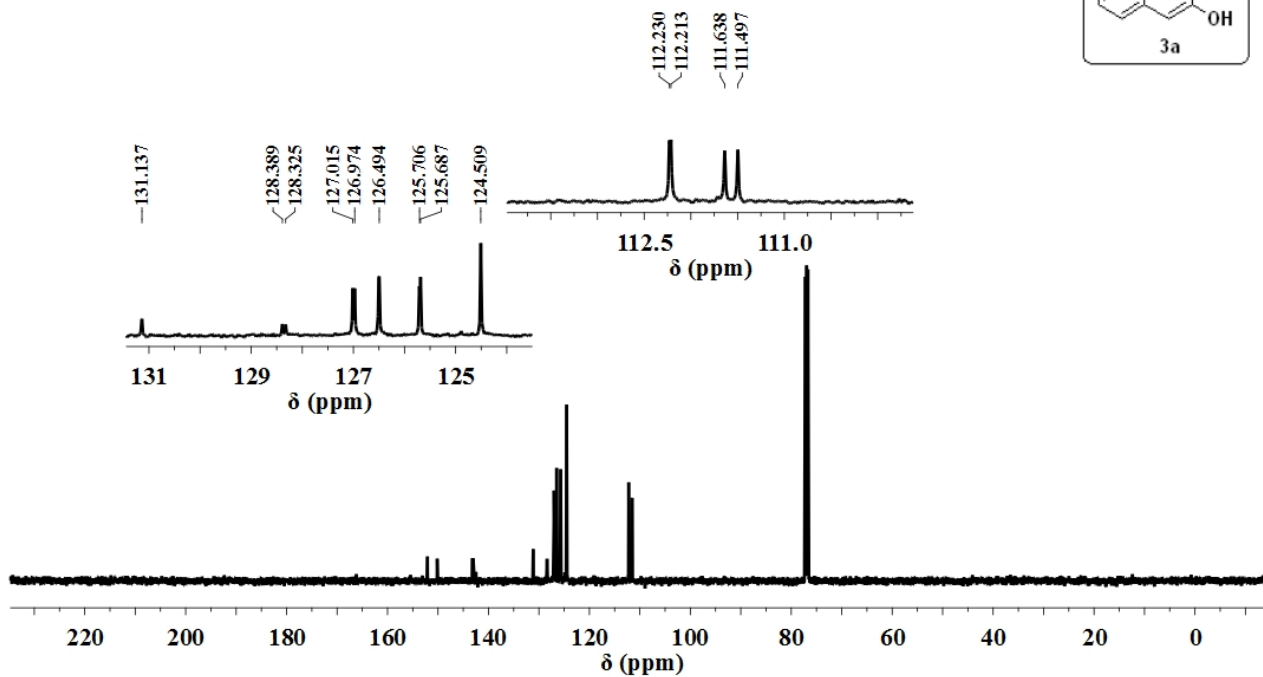
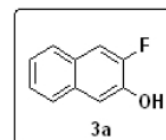
### Compound 3a

7.708  
7.691  
7.408  
7.392  
7.375  
7.363  
7.345  
7.249  
-5.400

### <sup>1</sup>H NMR

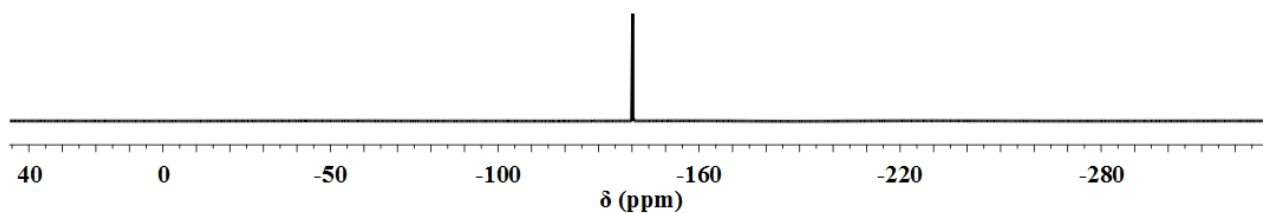
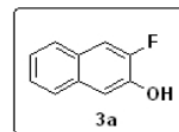


### <sup>13</sup>C NMR



<sup>19</sup>F NMR

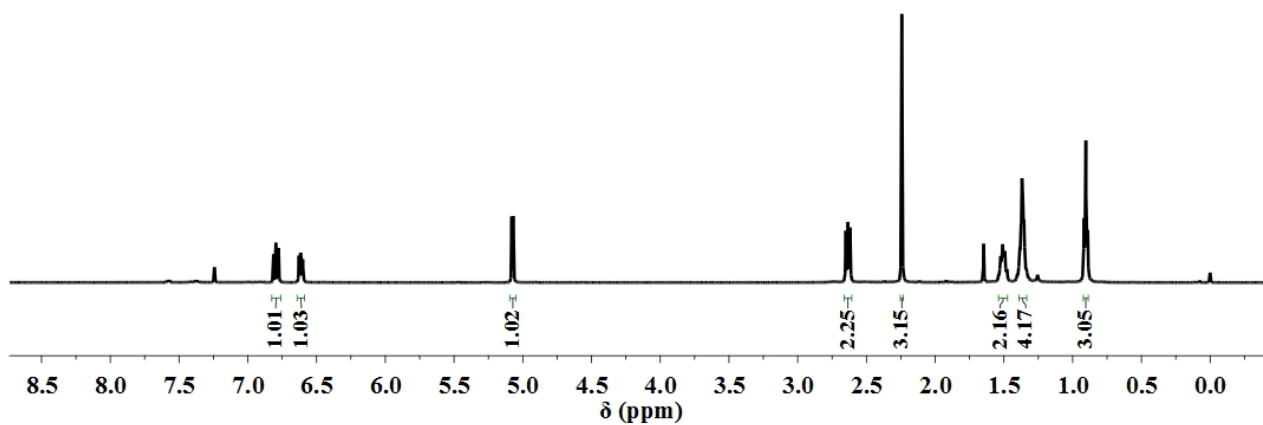
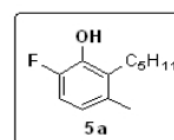
-140.179  
-140.200  
-140.220



Compound 5a

6.813 6.796 6.793 6.776 6.628 6.617 6.611 6.600  
5.080 5.069  
2.650 2.635 2.619 2.243  
1.493 1.391 1.368 1.337  
0.918 0.904 0.890

<sup>1</sup>H NMR

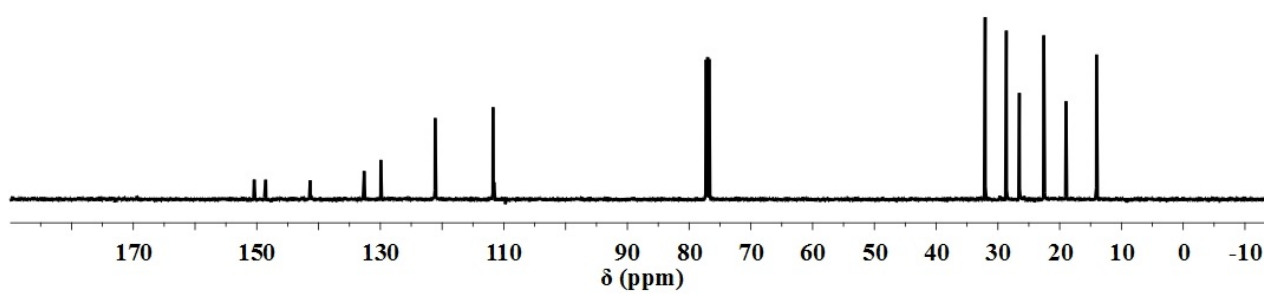
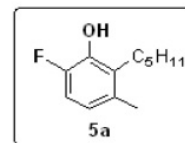


<sup>13</sup>C NMR

150.416  
148.561  
141.358  
141.249  
132.624  
129.919  
121.123  
121.069  
111.750  
111.608

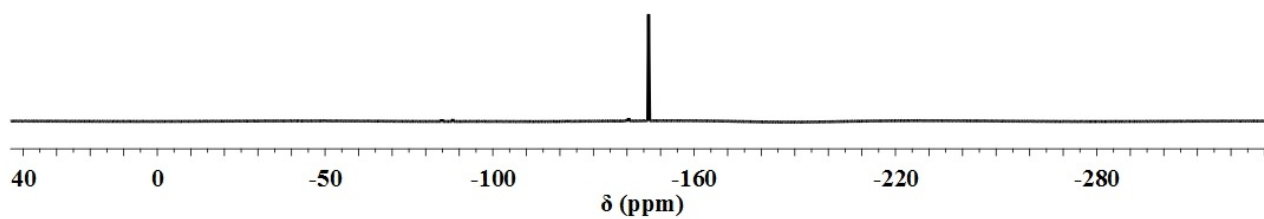
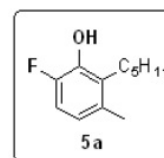
77.254  
77.000  
76.745

32.064  
28.637  
26.544  
26.524  
22.570  
18.967  
14.034

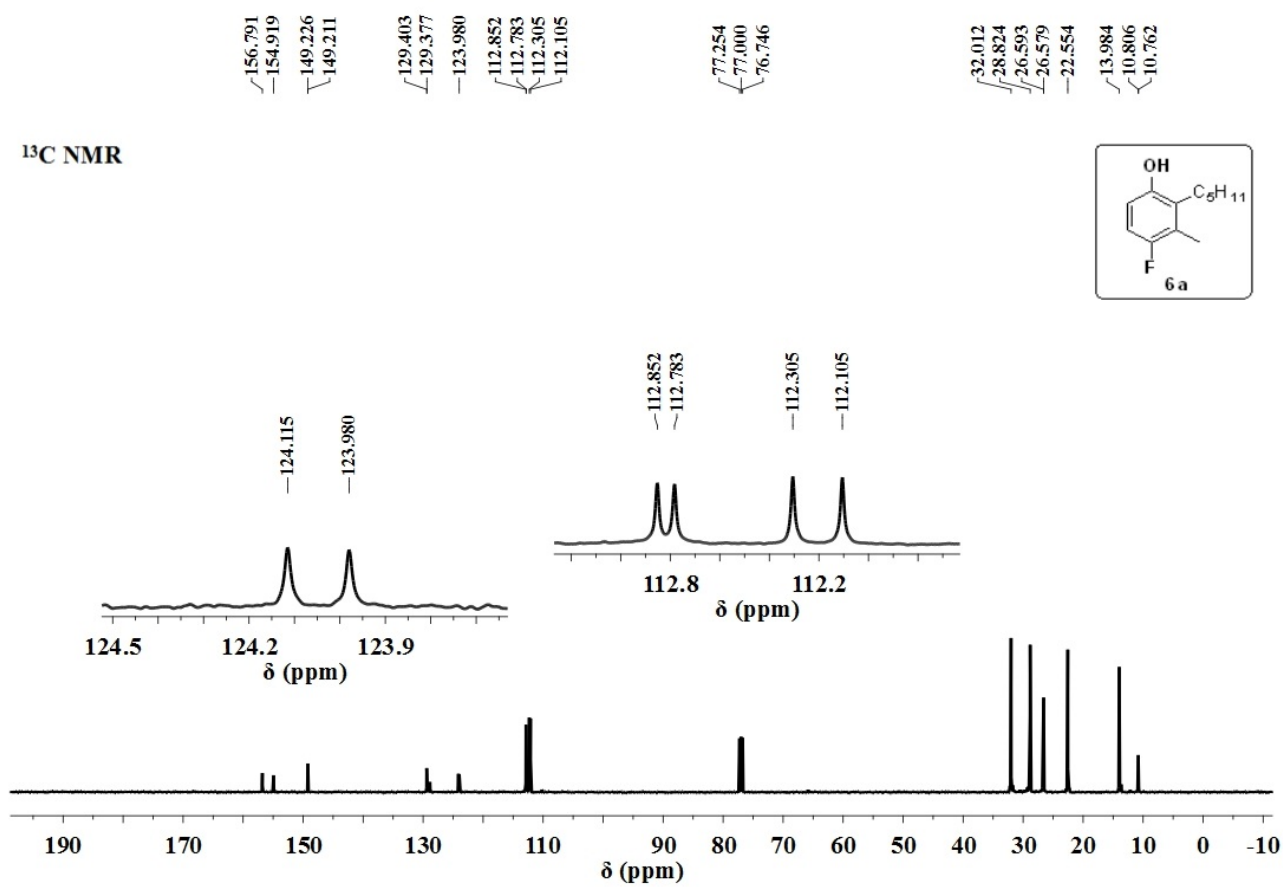
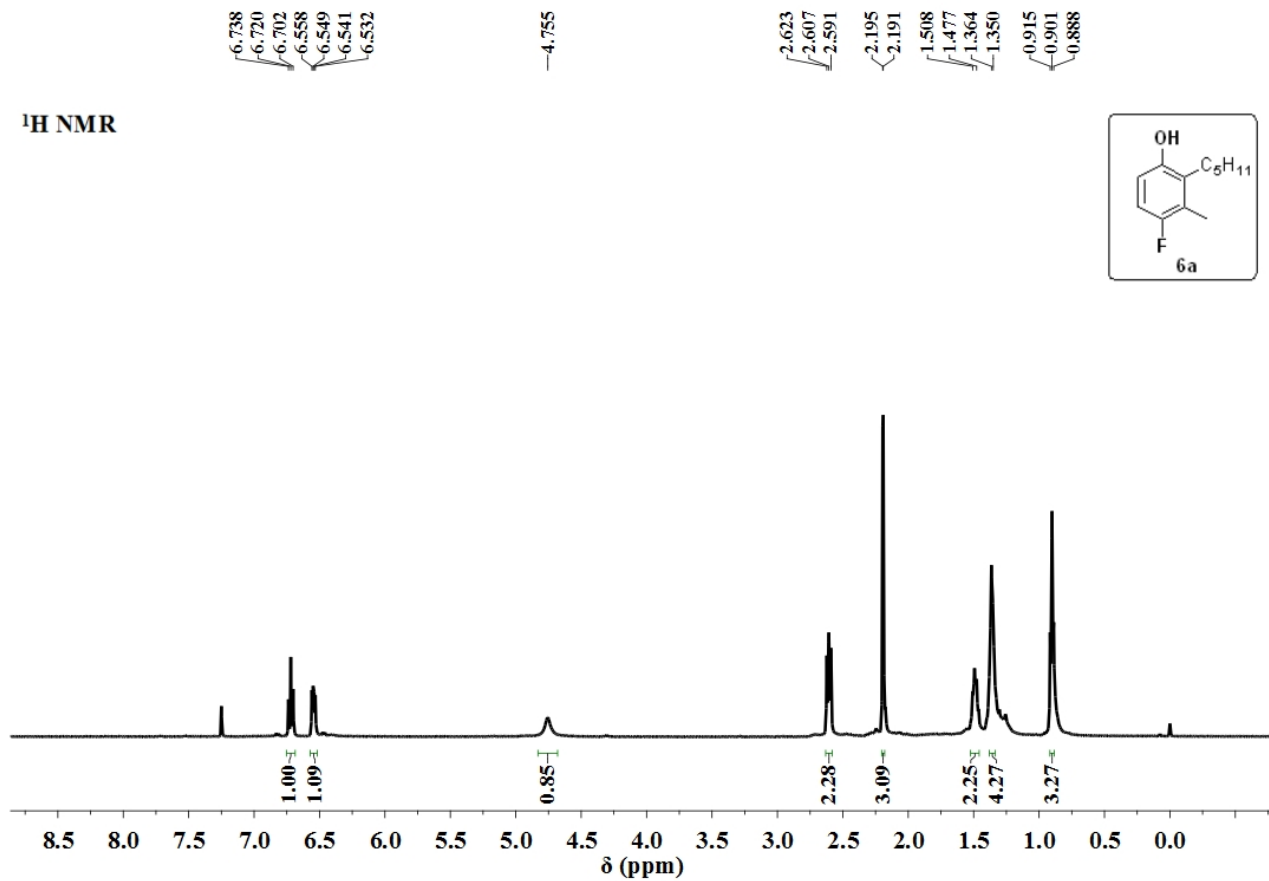


146.409  
146.418  
146.428

<sup>19</sup>F NMR



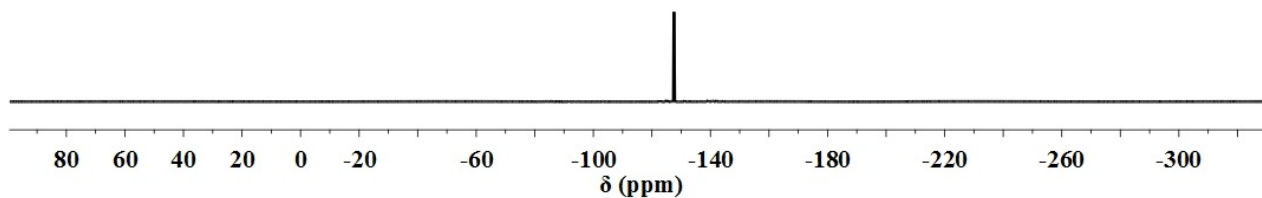
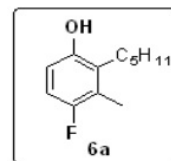
Compound 6a





$^{19}\text{F}$  NMR

-127.533  
-127.538  
-127.542  
-127.547

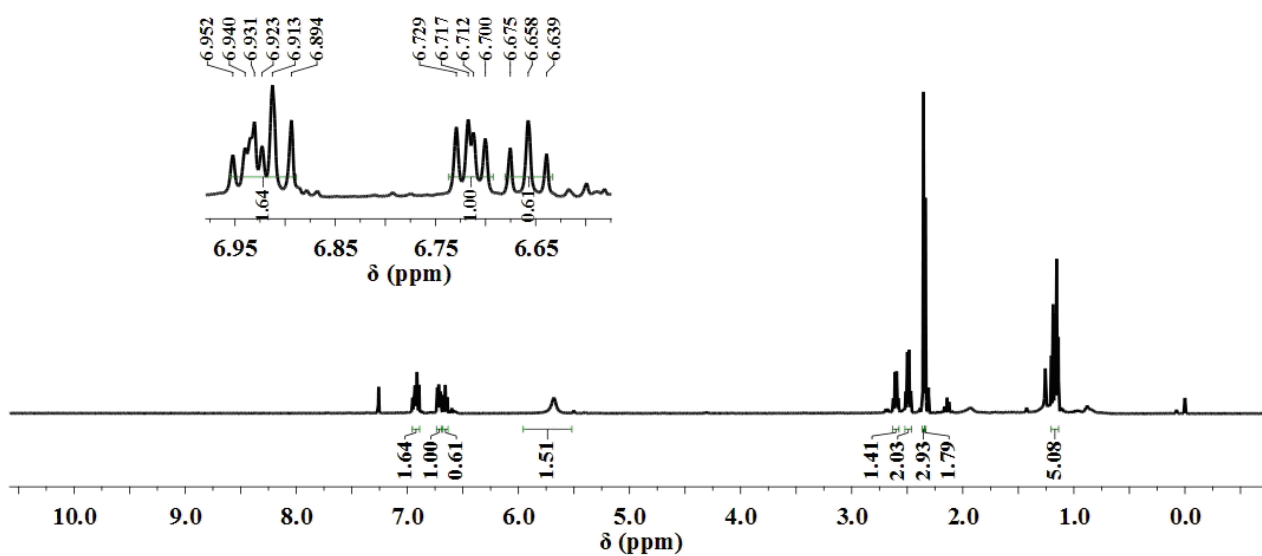
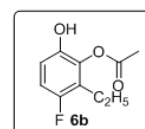
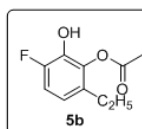


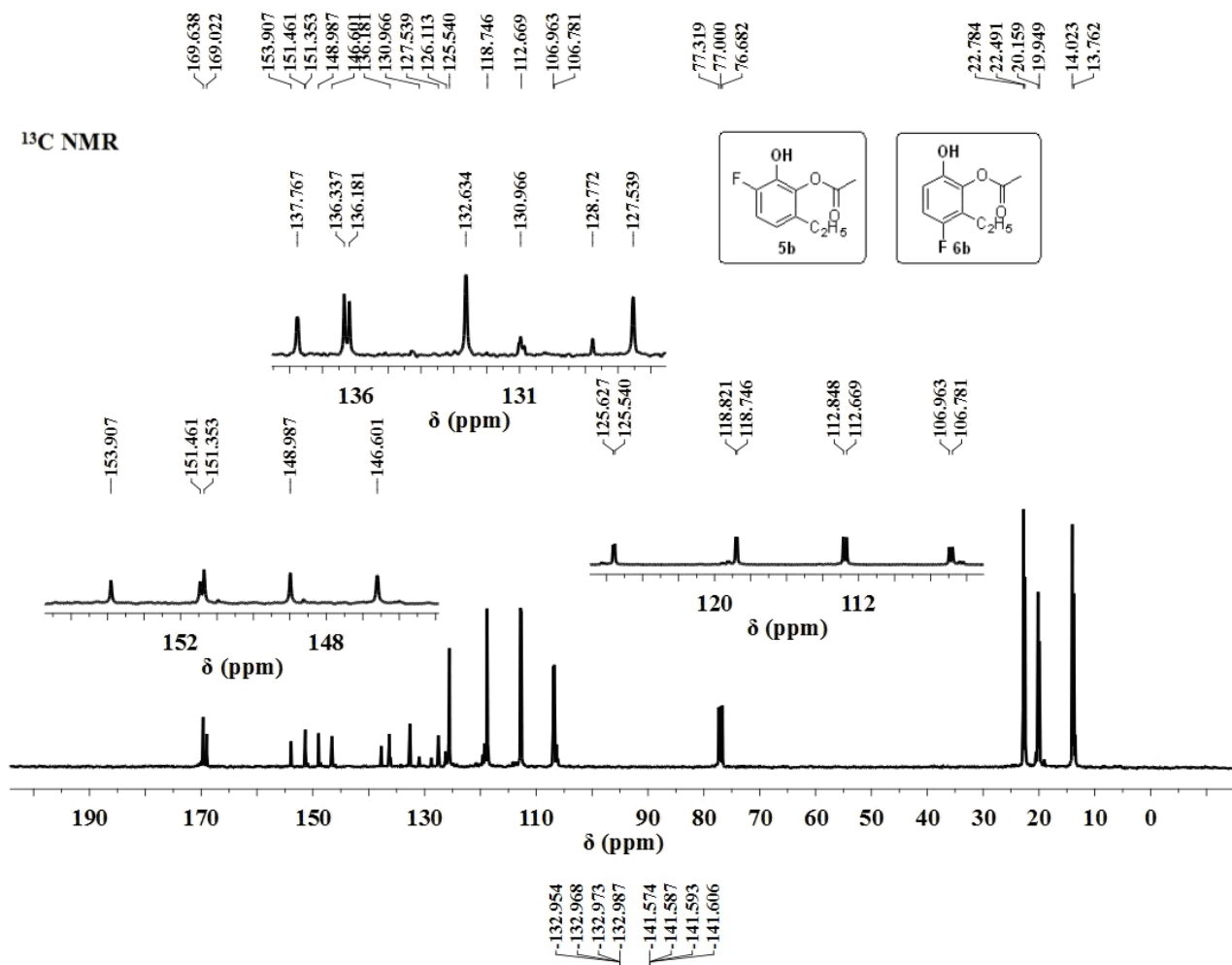
Compound 5b + 6b

6.952  
6.940  
6.931  
6.923  
6.913  
6.894  
6.729  
6.717  
6.712  
6.700  
6.675  
6.658  
6.639  
-5.681

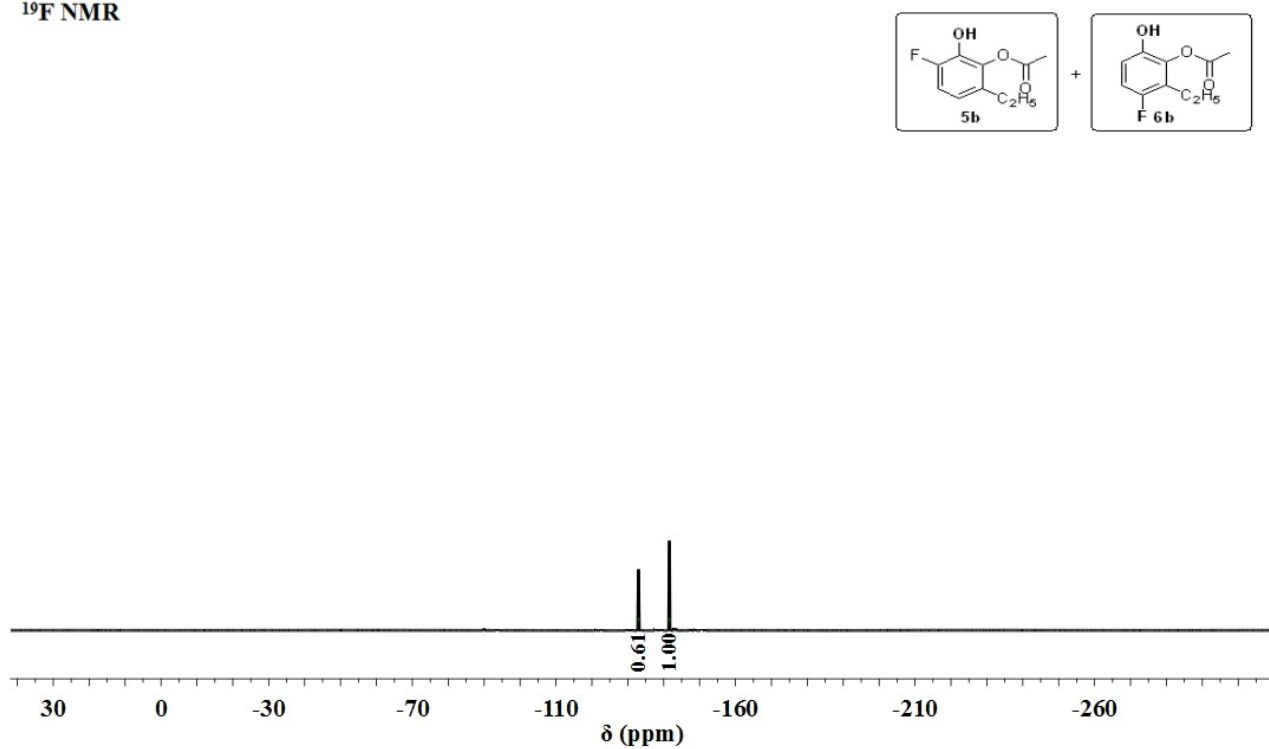
2.625  
2.610  
2.595  
2.580  
2.513  
2.498  
2.483  
2.468  
2.354  
2.337  
1.202  
1.187  
1.171  
1.155  
1.139

$^1\text{H}$  NMR

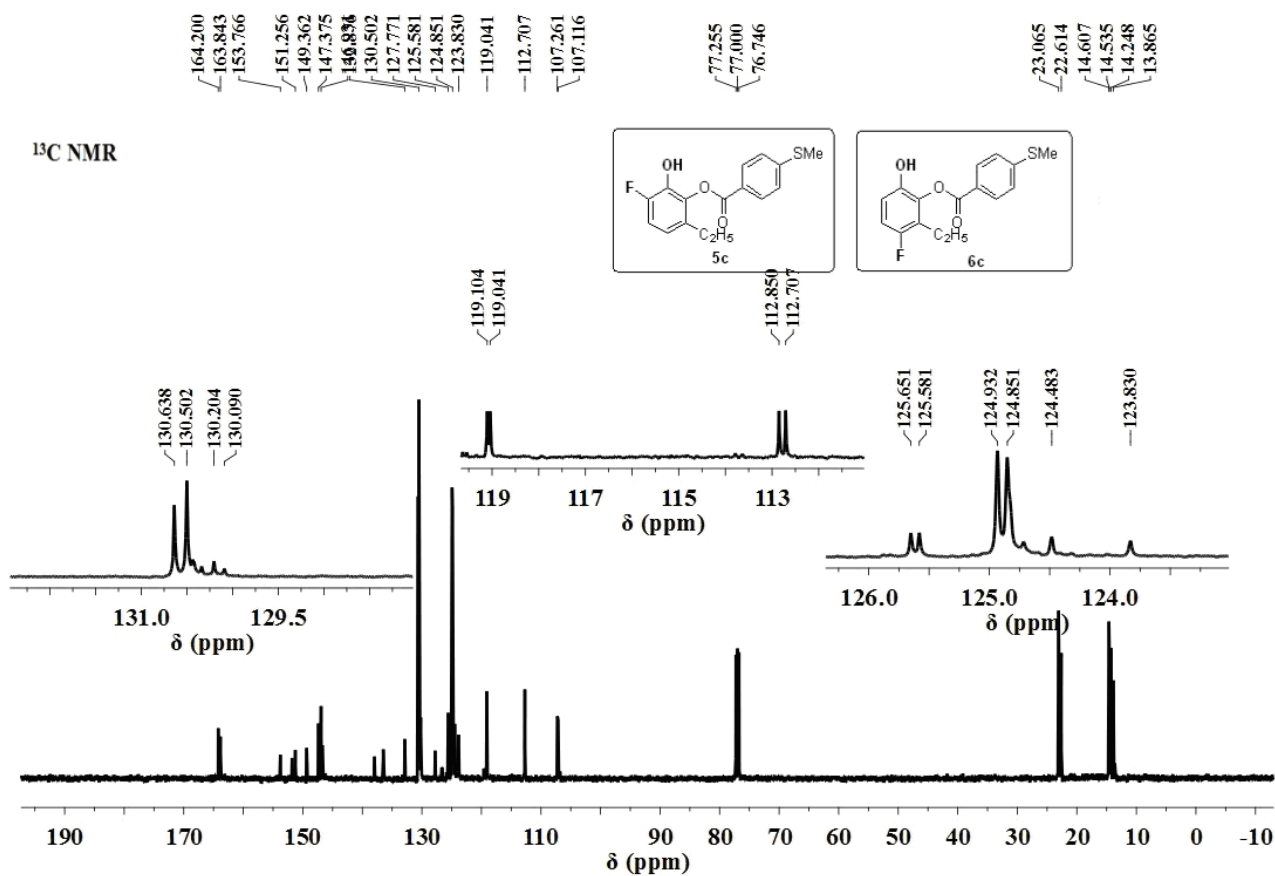
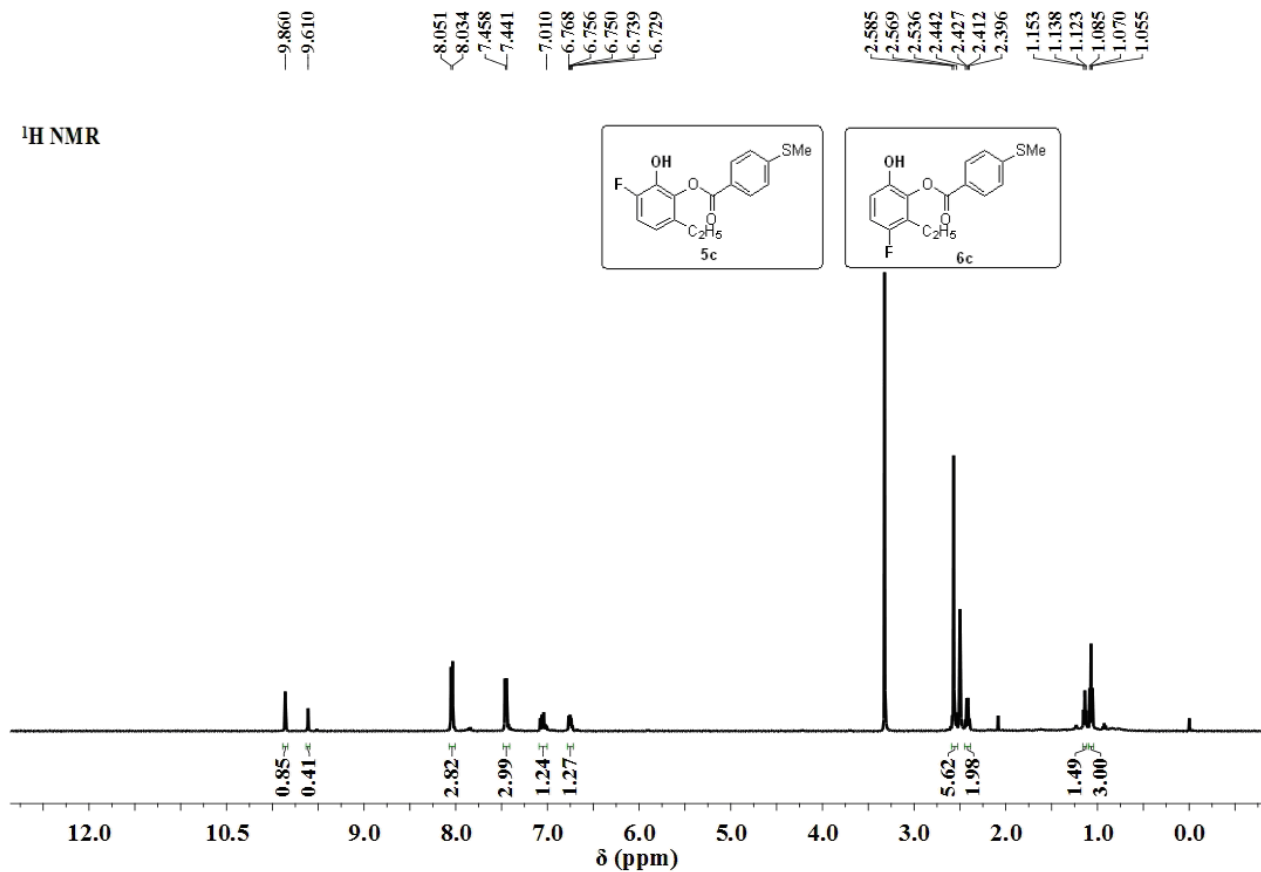




**<sup>19</sup>F NMR**

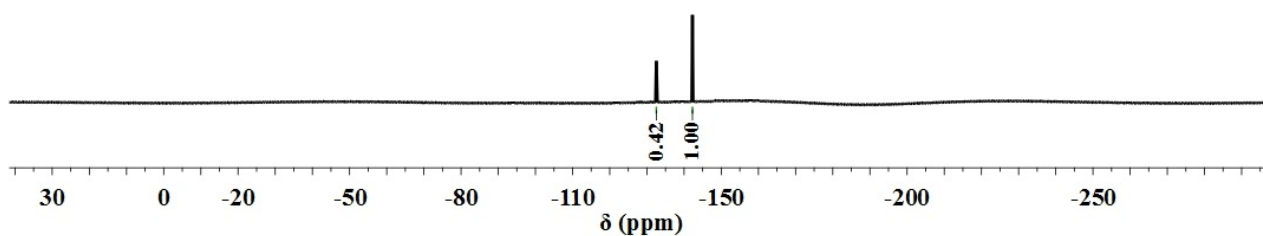
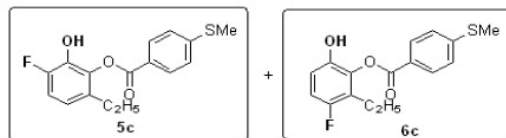


Compound 5c + 6c



<sup>19</sup>F NMR

-132.514  
-132.527  
-132.533  
-132.546  
-142.235  
-142.252  
-142.266

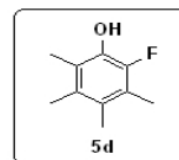


Compound 5d

5.008  
4.996

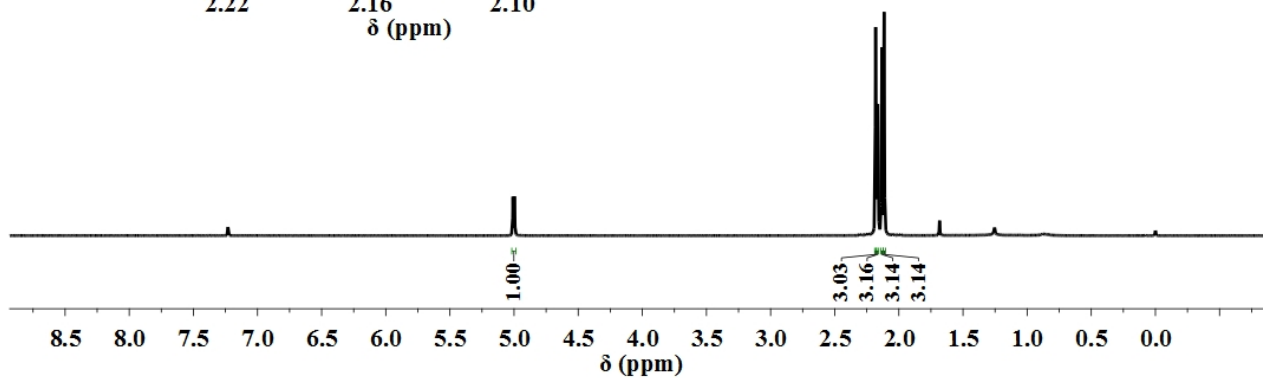
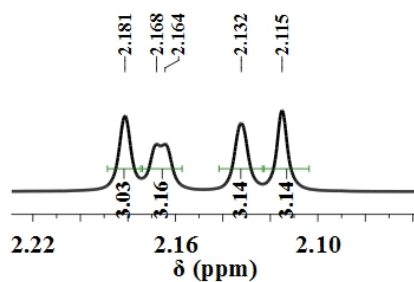
2.181  
2.168  
2.164  
2.132  
2.115

<sup>1</sup>H NMR

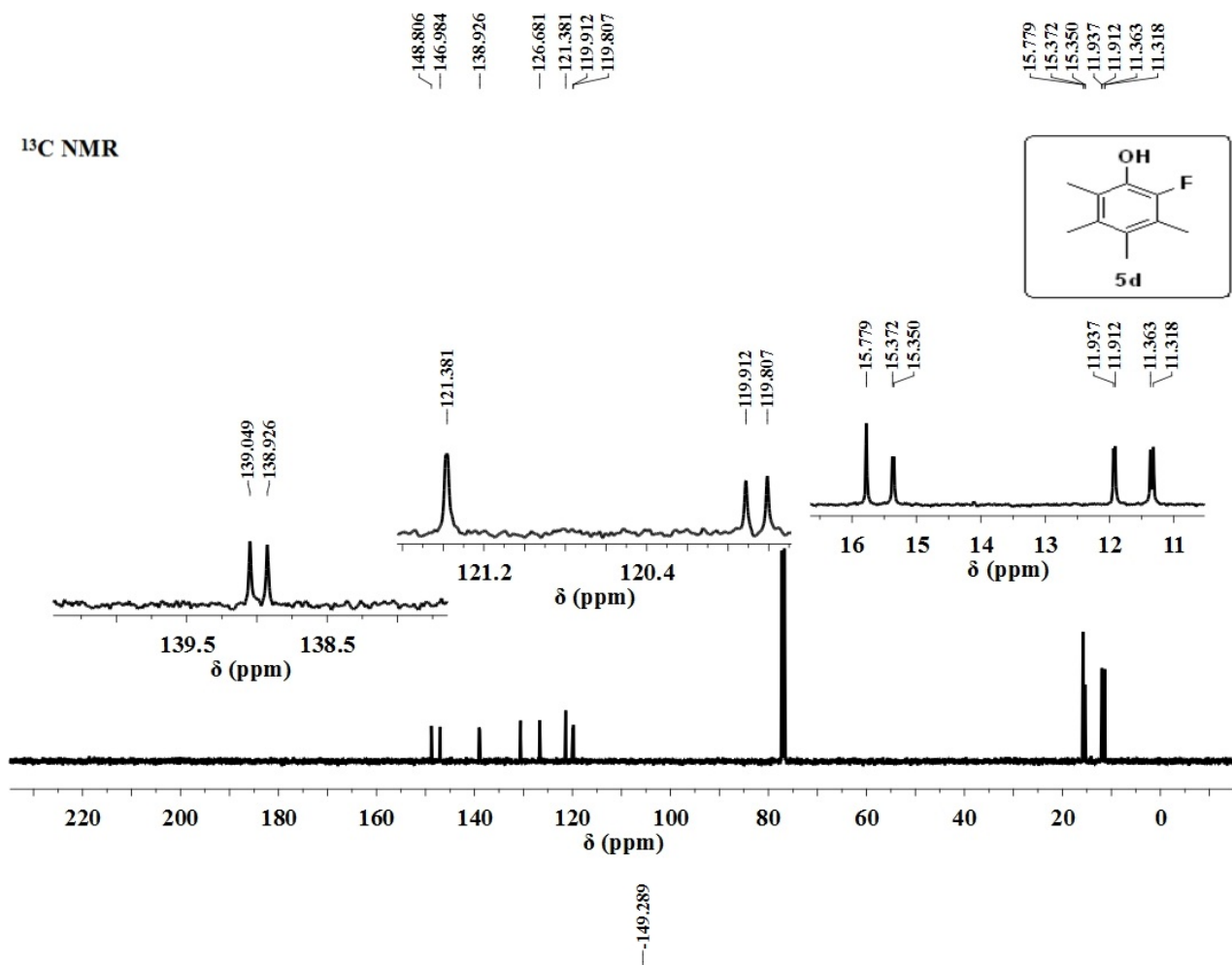


2.181  
2.168  
2.164

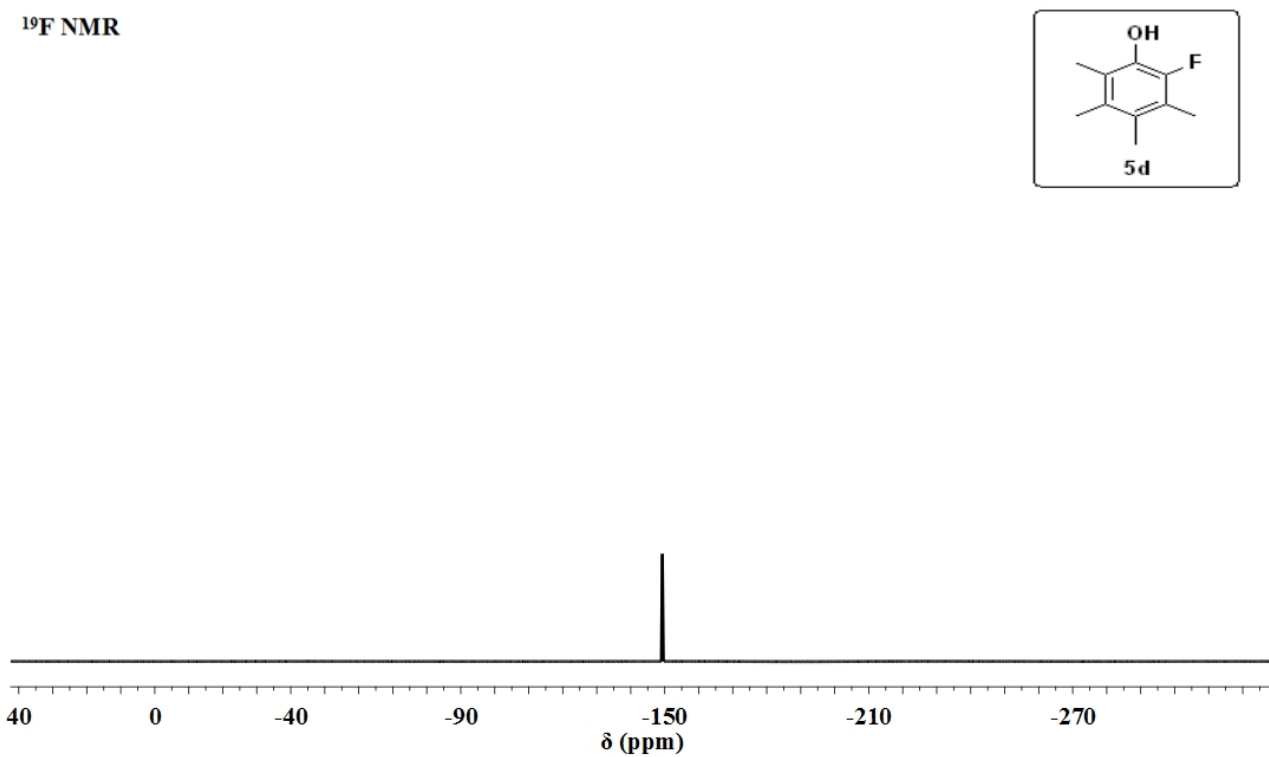
2.132  
2.115



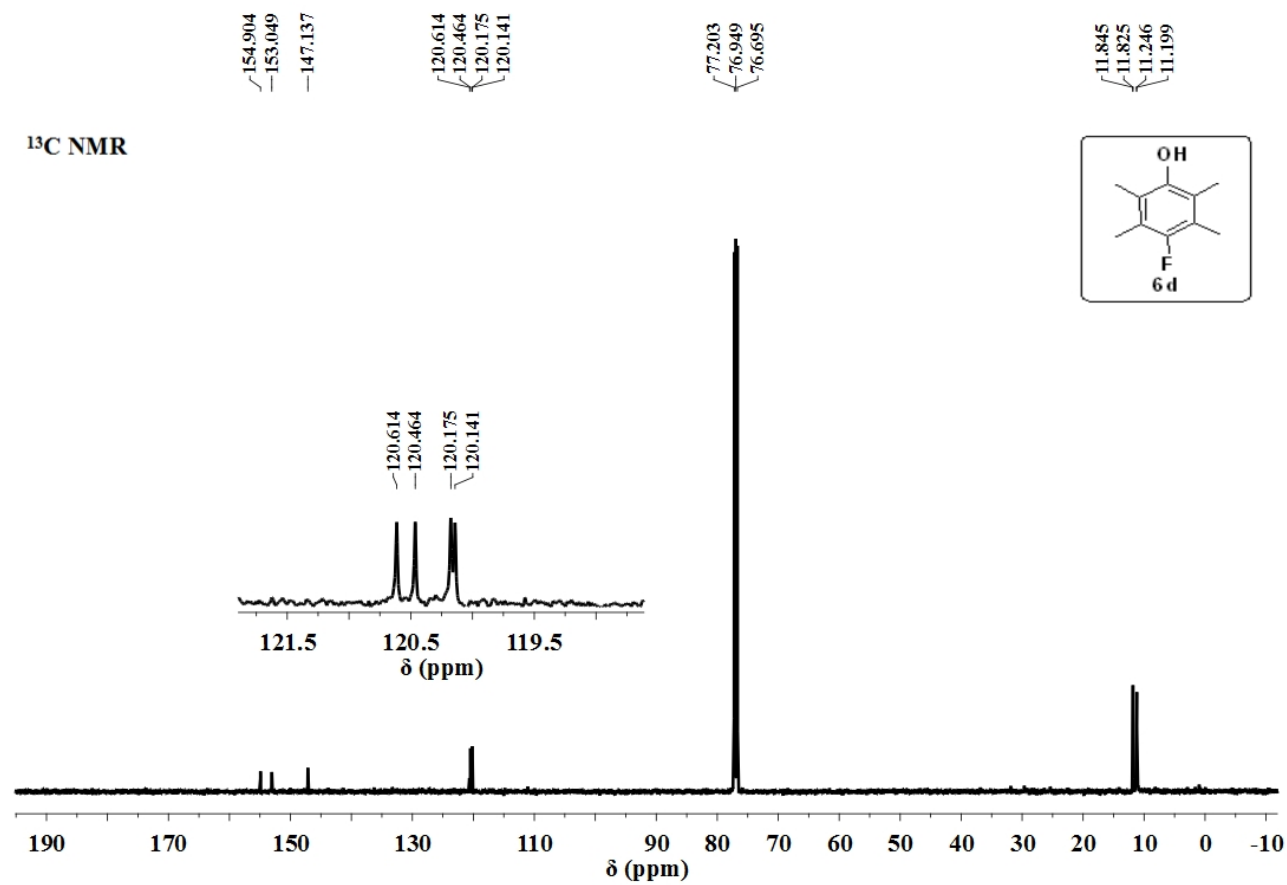
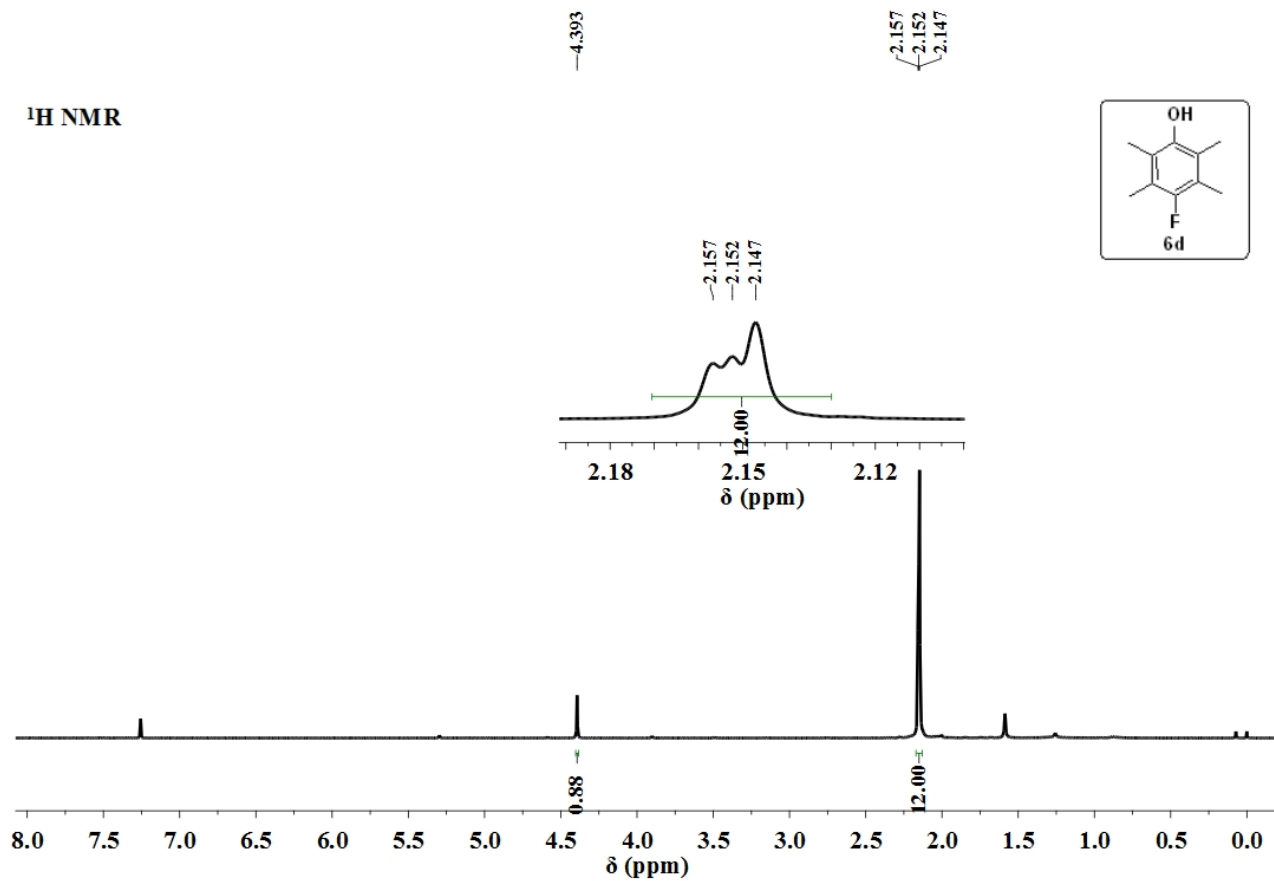
<sup>13</sup>C NMR



<sup>19</sup>F NMR

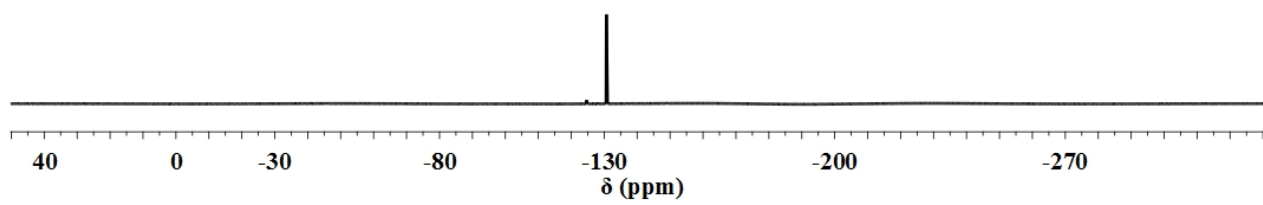
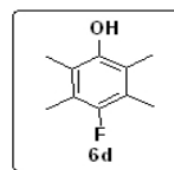


Compound 6d

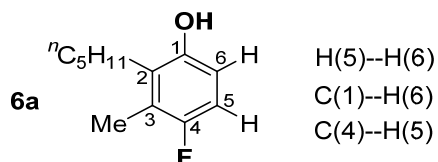


<sup>19</sup>F NMR

—130.677



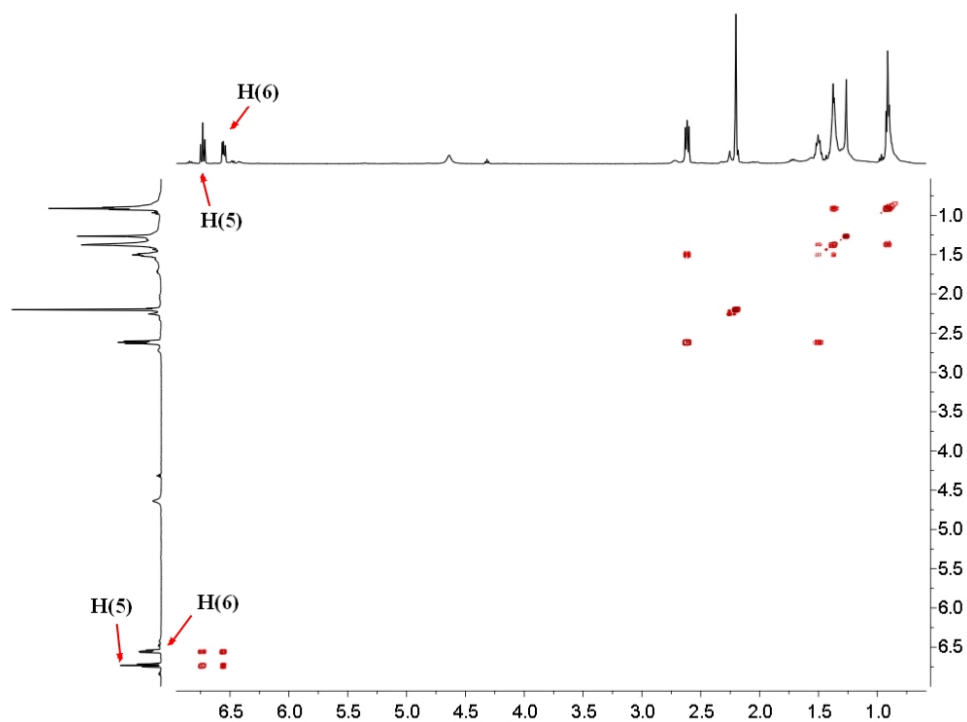
## VI. Copies of the $^1\text{H}$ -- $^1\text{H}$ and $^{13}\text{C}$ -- $^1\text{H}$ cosy spectra of **6a**



$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.54 (dd,  $J = 5.0$  Hz,  $J = 9.0$  Hz, H(6)) , 6.72 (d,  $J = 9.0$  Hz, H(5)).

$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  149.2 (d,  $J = 1.9$  Hz, C(1)), 155.8 (d,  $J = 234.0$  Hz, C(4)).

$^1\text{H}$ -- $^1\text{H}$  cosy spectrum of the **6a**



$^{13}\text{C}$ -- $^1\text{H}$  HMBC spectrum of the **6a**

