

## Supporting Information

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## 1. General remarks

<sup>1</sup>H NMR spectra were recorded on commercial instruments (400 MHz). Chemical shifts were recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard (CDCl<sub>3</sub>, δ = 7.262). Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration. <sup>13</sup>C NMR data were collected on commercial instruments (100 MHz) with complete proton decoupling. Chemical shifts were reported in ppm from the tetramethylsilane with the solvent resonance as internal standard (CDCl<sub>3</sub>, δ = 77.160). Enantiomeric excesses were determined by chiral HPLC analysis on Daicel Chiralcel IA, IC, IE, and Phenomenex Chiralcel Lux 5u Cellulose-1, Lux 5u Cellulose-3 at 23 °C with UV detector at 254 nm in comparison with the authentic racemates. Optical rotations were determined after flash column chromatography purification and reported as follows: [α]<sub>D</sub><sup>T</sup> (c: g/100 mL, in CH<sub>2</sub>Cl<sub>2</sub>). HRMS were recorded on a commercial apparatus (ESI source). All the reactions were carried out under an atmosphere of nitrogen in over-dried apparatus. All the solvents were purified by usual methods before use. Chromatography: Qingdao Haiyang silica gel, HG/T2354-92, H CP.

## 2. General procedure for preparation 2-naphthols derivatives

The 2-naphthols derivatives **1a**, **1c**, **1r**, **1s**, **1x** **1ab** were prepared by previously reported methods from 2-naphthols.<sup>[1]</sup>

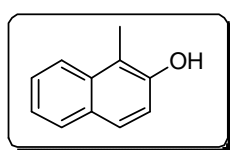
Compound **1b** is prepared according to the literature.<sup>[2]</sup>

Compounds **1d-1q**, **1t-1w** are prepared from compound **1b** according to the literature.

<sup>[3]</sup>

**1aa**<sup>[3]</sup>, **1ac**<sup>[3]</sup> and **1ad**<sup>[4]</sup> are known compounds.

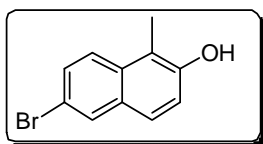
### 1-methylnaphthalen-2-ol (**1a**)



White solid; m.p. 78-80 °C, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 7.94 (d, *J* = 9.2 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.56 - 7.48 (m, 1H), 7.42 - 7.32 (m, 1H), 7.08 (d, *J* = 8.8 Hz,

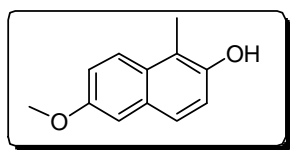
1H), 5.00 (s, 1H), 2.56 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 150.9, 132.5, 130.5, 130.4, 129.6, 126.6, 125.2, 118.8, 117.1, 115.8, 10.62. HRMS (ESI-TOF) calcd for  $\text{C}_{11}\text{H}_{10}\text{ONa}^+$  ( $[\text{M}+\text{Na}^+]$ ) = 181.0624, Found 181.0631.

### 6-bromo-1-methylnaphthalen-2-ol (1b)



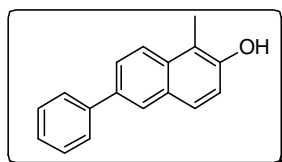
Purple solid; m.p. 94-96 °C,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.91 (d,  $J$  = 2.0 Hz, 1H), 7.78 (d,  $J$  = 8.8 Hz, 1H), 7.60 - 7.49 (m, 2H), 7.07 (d,  $J$  = 8.8 Hz, 1H), 4.91 (s, 1H), 2.51 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 150.9, 132.5, 130.5, 130.4, 129.6, 126.6, 125.2, 118.78, 117.1, 115.8, 10.6. HRMS (ESI-TOF) calcd for  $\text{C}_{11}\text{H}_9^{79}\text{BrO Na}^+$  ( $[\text{M}+\text{Na}^+]$ ) = 258.9729, Found 258.9723. HRMS (ESI-TOF) calcd for  $\text{C}_{11}\text{H}_9^{81}\text{BrONa}^+$  ( $[\text{M}+\text{Na}^+]$ ) = 260.9709, Found 260.9716.

### 6-methoxy-1-methylnaphthalen-2-ol (1c)



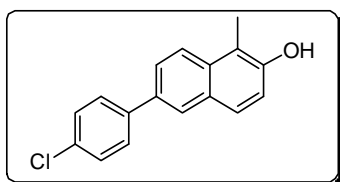
White solid; m.p. 116-119 °C,  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ )  $\delta$  = 9.23 (s, 1H), 7.77 (d,  $J$  = 8.8 Hz, 1H), 7.52 (d,  $J$  = 8.8 Hz, 1H), 7.24 - 7.18 (m, 1H), 7.16 - 7.07 (m, 2H), 3.82 (s, 3H), 2.39 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{DMSO-d}_6$ )  $\delta$  = 154.6, 150.4, 129.0, 128.8, 125.4, 124.3, 118.4, 118.1, 114.9, 106.6, 55.0, 10.5. HRMS (ESI-TOF) calcd for  $\text{C}_{12}\text{H}_{12}\text{O}_2\text{Na}^+$  ( $[\text{M}+\text{Na}^+]$ ) = 211.0730, Found 221.0739.

### 1-methyl-6-phenylnaphthalen-2-ol (1d)



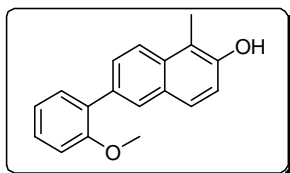
White solid; m.p. 149-152 °C,  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ )  $\delta$  = 9.59 (s, 1H), 8.09 (d,  $J$  = 1.2 Hz, 1H), 7.94 (d,  $J$  = 8.8 Hz, 1H), 7.84 - 7.75 (m, 3H), 7.72 (d,  $J$  = 8.8 Hz, 1H), 7.49 (t,  $J$  = 8.0 Hz, 2H), 7.37 (t,  $J$  = 7.6 Hz, 1H), 7.21 (d,  $J$  = 8.8 Hz, 1H), 2.45 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{DMSO-d}_6$ )  $\delta$  = 152.4, 140.1, 133.7, 133.0, 128.9, 128.2, 127.2, 127.0, 126.5, 125.6, 124.9, 123.6, 118.4, 114.5, 10.4. HRMS (ESI-TOF) calcd for  $\text{C}_{17}\text{H}_{14}\text{ONa}^+$  ( $[\text{M}+\text{Na}^+]$ ) = 257.0937, Found 257.0937.

### 6-(4-chlorophenyl)-1-methylnaphthalen-2-ol (1e)



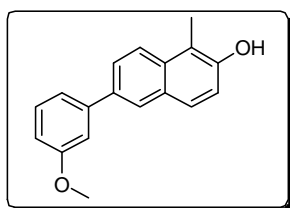
White solid; m.p. 164-167 °C,  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  = 9.64 (s, 1H), 8.10 (s, 1H), 7.94 (d,  $J$  = 8.8 Hz, 1H), 7.87 - 7.68 (m, 4H), 7.53 (d,  $J$  = 8.4 Hz, 2H), 7.21 (d,  $J$  = 8.8 Hz, 1H), 2.44 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz, DMSO- $d_6$ )  $\delta$  = 152.6, 138.9, 133.1, 132.3, 131.8, 128.8, 128.2, 128.2, 127.3, 125.7, 124.6, 123.7, 118.5, 114.6, 10.4. HRMS (ESI-TOF) calcd for  $\text{C}_{17}\text{H}_{13}^{35}\text{ClONa}^+$  ( $[\text{M}+\text{Na}^+]$ ) = 291.0547, Found 291.0543. HRMS (ESI-TOF) calcd for  $\text{C}_{17}\text{H}_{13}^{37}\text{ClONa}^+$  ( $[\text{M}+\text{Na}^+]$ ) = 293.0518, Found 293.0518.

### 6-(2-methoxyphenyl)-1-methylnaphthalen-2-ol (1f)



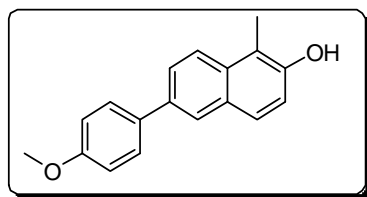
White solid; m.p. 92-94 °C,  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  = 9.53 (s, 1H), 7.94 - 7.78 (m, 2H), 7.65 (d,  $J$  = 8.8 Hz, 1H), 7.60 (dd,  $J$  = 8.8, 1.6 Hz, 1H), 7.44 - 7.30 (m, 2H), 7.15 (dd,  $J$  = 23.6, 8.8 Hz, 2H), 7.05 (t,  $J$  = 7.6 Hz, 1H), 3.77 (s, 3H), 2.45 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz, DMSO- $d_6$ )  $\delta$  = 156.3, 152.2, 132.6, 132.1, 130.5, 129.9, 128.6, 128.1, 127.8, 127.8, 127.0, 122.2, 120.8, 118.1, 114.4, 111.7, 55.4, 10.4. HRMS (ESI-TOF) calcd for  $\text{C}_{18}\text{H}_{16}\text{O}_2\text{Na}^+$  ( $[\text{M}+\text{Na}^+]$ ) = 287.1043, Found 287.1046.

### 6-(3-methoxyphenyl)-1-methylnaphthalen-2-ol (1g)



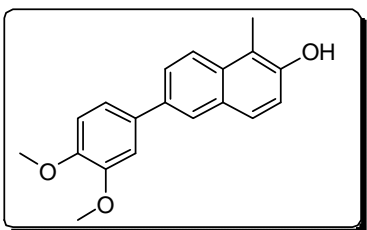
White solid; m.p. 114-118 °C,  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  = 9.59 (s, 1H), 8.10 (d,  $J$  = 2.0 Hz, 1H), 7.93 (d,  $J$  = 8.8 Hz, 1H), 7.78 (dd,  $J$  = 8.8, 2.0 Hz, 1H), 7.72 (d,  $J$  = 8.8 Hz, 1H), 7.43 - 7.28 (m, 3H), 7.21 (d,  $J$  = 8.8 Hz, 1H), 7.01 - 6.90 (m, 1H), 3.85 (s, 3H), 2.45 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz, DMSO- $d_6$ )  $\delta$  = 159.8, 152.4, 141.6, 133.6, 133.1, 129.9, 128.2, 127.2, 125.8, 125.0, 123.5, 118.9, 118.4, 114.5, 112.6, 112.0, 55.1, 10.4. HRMS (ESI-TOF) calcd for  $\text{C}_{18}\text{H}_{16}\text{O}_2\text{Na}^+$  ( $[\text{M}+\text{Na}^+]$ ) = 287.1043, Found 287.1045.

### 6-(4-methoxyphenyl)-1-methylnaphthalen-2-ol (1h)



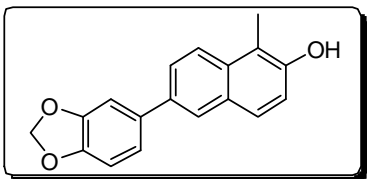
White solid; m.p. 180-186 °C,  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  = 9.54 (s, 1H), 8.01 (s, 1H), 7.90 (d,  $J$  = 8.8 Hz, 1H), 7.81 - 7.61 (m, 4H), 7.19 (d,  $J$  = 8.8 Hz, 1H), 7.04 (d,  $J$  = 8.4 Hz, 2H), 3.81 (s, 3H), 2.44 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz, DMSO- $d_6$ )  $\delta$  = 158.6, 152.1, 133.4, 132.6, 132.5, 128.3, 127.6, 127.0, 124.8, 123.5, 118.4, 114.5, 114.4, 55.1, 10.4. HRMS (ESI-TOF) calcd for  $\text{C}_{18}\text{H}_{16}\text{O}_2\text{Na}^+$  ( $[\text{M}+\text{Na}^+]$ ) = 287.1043, Found 287.1043.

### 6-(3,4-dimethoxyphenyl)-1-methylnaphthalen-2-ol (1i)



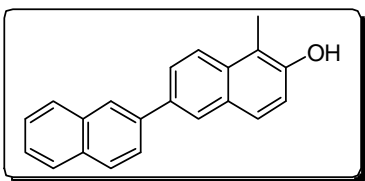
White solid; m.p. 184-186 °C,  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  = 9.53 (s, 1H), 8.04 (s, 1H), 7.90 (d,  $J$  = 8.8 Hz, 1H), 7.77 (d,  $J$  = 8.4 Hz, 1H), 7.69 (d,  $J$  = 8.8 Hz, 1H), 7.34 (s, 1H), 7.29 (d,  $J$  = 8.0 Hz, 1H), 7.19 (d,  $J$  = 8.4 Hz, 1H), 7.04 (d,  $J$  = 8.0 Hz, 1H), 3.88 (s, 3H), 3.80 (s, 3H), 2.44 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz, DMSO- $d_6$ )  $\delta$  = 152.2, 149.1, 148.2, 133.7, 132.9, 132.6, 128.3, 127.0, 125.0, 123.4, 118.7, 118.4, 114.5, 112.2, 110.3, 55.6, 10.4. HRMS (ESI-TOF) calcd for  $\text{C}_{19}\text{H}_{18}\text{O}_3\text{Na}^+$  ( $[\text{M}+\text{Na}^+]$ ) = 317.1148, Found 317.1149.

### 6-(benzo[d][1,3]dioxol-5-yl)-1-methylnaphthalen-2-ol (1j)



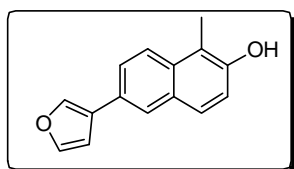
White solid; m.p. 127-129 °C,  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  = 9.53 (s, 1H), 8.01 (d,  $J$  = 1.6 Hz, 1H), 7.89 (d,  $J$  = 8.8 Hz, 1H), 7.72 (dd,  $J$  = 8.8, 2.0 Hz, 1H), 7.67 (d,  $J$  = 8.8 Hz, 1H), 7.36 (d,  $J$  = 1.6 Hz, 1H), 7.25 (dd,  $J$  = 8.4, 2.0 Hz, 1H), 7.18 (d,  $J$  = 8.8 Hz, 1H), 7.02 (d,  $J$  = 8.0 Hz, 1H), 6.08 (s, 2H), 2.43 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz, DMSO- $d_6$ )  $\delta$  = 152.2, 148.0, 146.5, 134.5, 133.5, 132.7, 128.2, 127.0, 125.2, 124.9, 123.4, 120.0, 118.4, 114.5, 108.7, 107.0, 101.0, 10.4. HRMS (ESI-TOF) calcd for  $\text{C}_{18}\text{H}_{14}\text{O}_3\text{Na}^+$  ( $[\text{M}+\text{Na}^+]$ ) = 301.0835, Found 301.0831.

### 5-methyl-[2,2'-binaphthalen]-6-ol (1k)



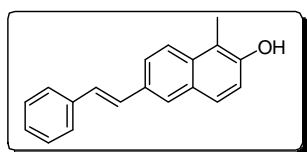
White solid; m.p. 170-174 °C, <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ = 9.63 (s, 1H), 8.33 (s, 1H), 8.26 (s, 1H), 8.07 - 7.88 (m, 6H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.60 - 7.48 (m, 2H), 7.24 (dd, *J* = 8.8, 2.0 Hz, 1H), 2.47 (s, 3H); <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>) δ = 152.6, 137.4, 133.4, 133.4, 133.1, 132.1, 128.4, 128.3, 128.1, 127.5, 127.3, 126.4, 126.0, 125.9, 125.1, 125.1, 124.8, 123.7, 118.5, 114.6, 10.5. HRMS (ESI-TOF) calcd for C<sub>21</sub>H<sub>16</sub>ONa<sup>+</sup> ([M+Na<sup>+</sup>]) = 307.1093, Found 307.1104.

### 6-(furan-3-yl)-1-methylnaphthalen-2-ol (1l)



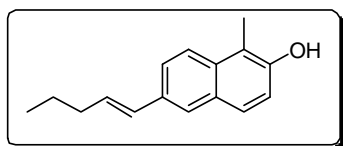
White solid; m.p. 163-165 °C, <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ = 9.53 (s, 1H), 8.24 (s, 1H), 7.99 (s, 1H), 7.85 (d, *J* = 8.8 Hz, 1H), 7.77 (d, *J* = 1.2 Hz, 1H), 7.71 (d, *J* = 8.8 Hz, 1H), 7.62 (d, *J* = 8.8 Hz, 1H), 7.19 (d, *J* = 8.8 Hz, 1H), 7.06 (s, 1H), 2.43 (s, 3H); <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>) δ = 152.6, 144.7, 139.5, 133.2, 128.7, 127.1, 126.4, 126.2, 124.8, 124.6, 123.8, 118.9, 115.2, 109.2, 10.9. HRMS (ESI-TOF) calcd for C<sub>15</sub>H<sub>12</sub>O<sub>2</sub>K<sup>+</sup> ([M+K<sup>+</sup>]) = 263.0469, Found 263.0471.

### (*E*)-1-methyl-6-styrylnaphthalen-2-ol (1m)



White solid; m.p. 146-150 °C, <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ = 9.58 (s, 1H), 7.92 - 7.77 (m, 3H), 7.70 - 7.59 (m, 3H), 7.43 - 7.23 (m, 5H), 7.18 (d, *J* = 8.8 Hz, 1H), 2.43 (s, 3H); <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>) δ = 152.6, 137.3, 133.3, 131.0, 128.7, 128.6, 128.0, 127.4, 127.2, 127.0, 126.9, 126.3, 123.6, 123.3, 118.3, 115.0, 10.4. HRMS (ESI-TOF) calcd for C<sub>19</sub>H<sub>16</sub>OK<sup>+</sup> ([M+K<sup>+</sup>]) = 299.0833, Found 299.0833.

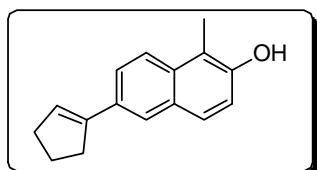
### (*E*)-1-methyl-6-(pent-1-en-1-yl)naphthalen-2-ol (1n)



White solid; m.p. 106-110 °C, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 7.84 (d, *J* = 8.8 Hz, 1H), 7.68 - 7.50 (m, 3H),

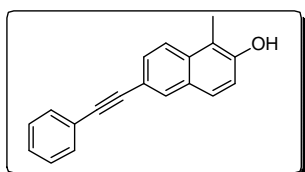
7.03 (d,  $J = 8.8$  Hz, 1H), 6.52 (d,  $J = 15.6$  Hz, 1H), 6.41 - 6.25 (m, 1H), 4.83 (s, 1H), 2.52 (s, 3H), 2.24 (q,  $J = 7.2$  Hz, 3H), 1.62 - 1.48 (m, 2H), 1.06 - 0.91 (m, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta = 150.4, 133.1, 132.9, 130.6, 129.9, 129.5, 127.4, 126.0, 124.2, 123.5, 117.8, 115.5, 35.4, 22.8, 13.9, 10.6$ . HRMS (ESI-TOF) calcd for  $\text{C}_{16}\text{H}_{18}\text{ONa}^+$  ( $[\text{M}+\text{Na}^+]$ ) = 227.1436, Found 227.1435.

#### 6-(cyclopent-1-en-1-yl)-1-methylnaphthalen-2-ol (1o)



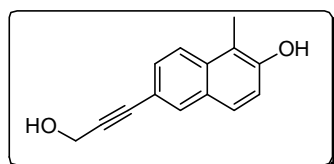
White solid; m.p. 158-161 °C,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.84$  (d,  $J = 8.8$  Hz, 1H), 7.76 - 7.68 (m, 1H), 7.66 (s, 1H), 7.59 (d,  $J = 8.8$  Hz, 1H), 7.04 (d,  $J = 8.4$  Hz, 1H), 6.29 (s, 1H), 4.85 (s, 1H), 2.90 - 2.75 (m, 2H), 2.64 - 2.55 (m, 2H), 2.53 (s, 3H), 2.15 - 2.00 (m, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta = 150.5, 142.4, 133.0, 131.7, 129.4, 127.6, 126.0, 124.9, 124.8, 123.2, 117.8, 115.5, 33.6, 33.3, 23.5, 10.6$ . HRMS (ESI-TOF) calcd for  $\text{C}_{16}\text{H}_{16}\text{ONa}^+$  ( $[\text{M}+\text{Na}^+]$ ) = 247.1093, Found 247.1098.

#### 1-methyl-6-(phenylethynyl)naphthalen-2-ol (1p)



Brown solid; m.p. 110-112 °C,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.99$  (s, 1H), 7.89 (d,  $J = 8.8$  Hz, 1H), 7.67 - 7.50 (m, 4H), 7.41 - 7.30 (m, 3H), 7.09 (d,  $J = 8.8$  Hz, 1H), 5.05 (s, 1H), 2.53 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta = 151.5, 133.5, 132.2, 131.7, 129.0, 128.9, 128.5, 128.3, 127.5, 123.6, 123.5, 118.4, 117.8, 115.6, 90.0, 89.3, 10.6$ . HRMS (ESI-TOF) calcd for  $\text{C}_{19}\text{H}_{14}\text{OK}^+$  ( $[\text{M}+\text{K}^+]$ ) = 297.0682, Found 297.0681.

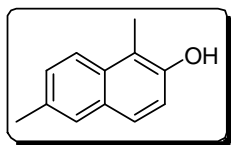
#### 6-(3-hydroxyprop-1-yn-1-yl)-1-methylnaphthalen-2-ol (1q)



Light yellow solid; m.p. 130-132 °C,  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ )  $\delta = 9.70$  (s, 1H), 7.89 (d,  $J = 1.6$  Hz, 1H), 7.84 (d,  $J = 8.8$  Hz, 1H), 7.63 (d,  $J = 8.8$  Hz, 1H), 7.42 (dd,  $J = 8.4, 2.0$  Hz, 1H), 7.20 (d,  $J = 9.2$  Hz, 1H), 5.33 (t,  $J = 6.0$  Hz, 1H), 4.34 (d,  $J = 6.0$  Hz, 2H), 2.40 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{DMSO-d}_6$ )  $\delta = 153.2, 133.1, 131.4,$

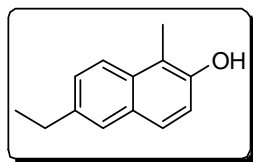
128.1, 127.5, 126.7, 123.3, 118.7, 115.8, 114.9, 89.2, 84.2, 49.5, 10.3. HRMS (ESI-TOF) calcd for  $C_{14}H_{12}O_2Na^+$  ( $[M+Na^+]$ ) = 235.0730, Found 235.0740.

### 1,6-dimethylnaphthalen-2-ol (1r)



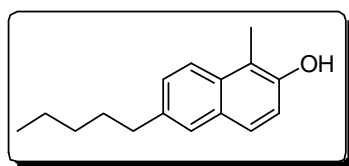
White solid; m.p. 53-56 °C,  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  = 7.82 (d,  $J$  = 8.8 Hz, 1H), 7.58 - 7.48 (m, 2H), 7.37 - 7.31 (m, 1H), 7.03 (d,  $J$  = 8.8 Hz, 1H), 4.84 (s, 1H), 2.52 (s, 3H), 2.48 (s, 3H);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  = 145.0, 132.6, 132.1, 129.5, 128.7, 127.6, 126.8, 123.2, 117.7, 115.2, 21.4, 10.6. HRMS (ESI-TOF) calcd for  $C_{12}H_{12}ONa^+$  ( $[M+Na^+]$ ) = 195.0780, Found 195.0785.

### 6-ethyl-1-methylnaphthalen-2-ol (1s)



White solid; m.p. 68-70 °C,  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  = 7.81 (d,  $J$  = 8.8 Hz, 1H), 7.61 - 7.47 (m, 2H), 7.34 (d,  $J$  = 8.8 Hz, 1H), 6.98 (d,  $J$  = 8.8 Hz, 1H), 5.11 (s, 1H), 2.76 (q,  $J$  = 7.6 Hz, 2H), 2.48 (s, 3H), 1.29 (t,  $J$  = 7.6 Hz, 3H);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  = 149.9, 139.0, 132.3, 129.5, 127.6, 126.9, 126.3, 123.3, 117.7, 115.4, 28.75, 15.7, 10.6. HRMS (ESI-TOF) calcd for  $C_{13}H_{15}O^+$  ( $[M+H^+]$ ) = 187.1117, Found 187.1117.

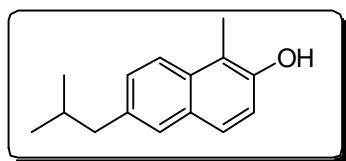
### 1-methyl-6-pentyl-naphthalen-2-ol (1t)



White solid; m.p. 75-78 °C,  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  = 7.85 (d,  $J$  = 8.8 Hz, 1H), 7.63 - 7.52 (m, 2H), 7.37 (d,  $J$  = 8.0 Hz, 1H), 7.04 (d,  $J$  = 8.8 Hz, 1H), 4.88 - 4.81 (m, 1H), 2.75 (t,  $J$  = 7.6 Hz, 2H), 2.54 (s, 3H), 1.76 - 1.65 (m, 2H), 1.46 - 1.29 (m, 4H), 0.96 - 0.86 (m, 3H);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  = 150.0, 137.7, 132.3, 129.5, 128.0, 127.1, 126.9, 123.2, 117.6, 115.2, 35.8, 31.7, 31.3, 22.7, 14.2, 10.6. HRMS (ESI-TOF) calcd for  $C_{16}H_{20}ONa^+$  ( $[M+Na^+]$ ) = 251.1406, Found 251.1403.

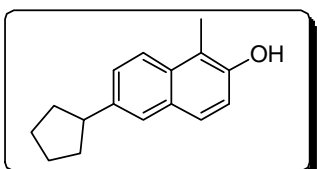


### 6-isobutyl-1-methylnaphthalen-2-ol (1u)



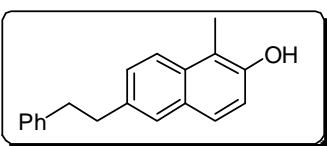
White solid; m.p. 102-104 °C,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.84 (d,  $J$  = 8.8 Hz, 1H), 7.57 (d,  $J$  = 8.8 Hz, 1H), 7.52 (d,  $J$  = 0.8 Hz, 1H), 7.33 (dd,  $J$  = 8.8, 2.0 Hz, 1H), 7.04 (d,  $J$  = 8.8 Hz, 1H), 4.82 (s, 1H), 2.62 (d,  $J$  = 7.2 Hz, 2H), 2.53 (s, 3H), 2.03 - 1.90 (m, 1H), 0.95 (d,  $J$  = 6.9 Hz, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 150.0, 136.5, 132.3, 129.4, 128.5, 128.0, 127.0, 123.0, 117.6, 115.2, 45.4, 30.4, 22.6, 10.6. HRMS (ESI-TOF) calcd for  $\text{C}_{15}\text{H}_{18}\text{ONa}^+$  ( $[\text{M}+\text{Na}^+]$ ) = 237.1250, Found 237.1254.

### 6-cyclopentyl-1-methylnaphthalen-2-ol (1v)



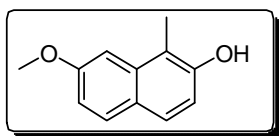
White solid; m.p. 80-83 °C,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.86 (d,  $J$  = 8.8 Hz, 1H), 7.62 - 7.53 (m, 2H), 7.43 (dd,  $J$  = 8.8, 2.0 Hz, 1H), 7.04 (d,  $J$  = 8.8 Hz, 1H), 4.80 (d,  $J$  = 2.0 Hz, 1H), 3.20 - 3.07 (m, 1H), 2.53 (s, 3H), 2.23 - 2.08 (m, 2H), 1.91 - 1.63 (m, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 150.0, 141.2, 132.4, 129.4, 127.0, 126.8, 125.6, 123.2, 117.7, 115.2, 45.8, 34.7, 25.7, 10.6. HRMS (ESI-TOF) calcd for  $\text{C}_{16}\text{H}_{19}\text{O}^+$  ( $[\text{M}+\text{H}^+]$ ) = 227.1430, Found 227.1444.

### 1-methyl-6-phenethylnaphthalen-2-ol (1w)



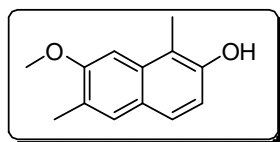
White solid; m.p. 88-92 °C,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.85 (d,  $J$  = 8.8 Hz, 1H), 7.62 - 7.52 (m, 2H), 7.38 - 7.28 (m, 3H), 7.24 - 7.16 (m, 3H), 7.05 (d,  $J$  = 8.8 Hz, 1H), 4.91 (s, 1H), 3.11 - 2.97 (m, 4H), 2.54 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 150.2, 142.0, 136.5, 132.5, 129.4, 128.6, 128.5, 127.9, 127.2, 127.0, 126.0, 123.3, 117.7, 115.3, 38.0, 37.8, 10.6. HRMS (ESI-TOF) calcd for  $\text{C}_{19}\text{H}_{18}\text{ONa}^+$  ( $[\text{M}+\text{Na}^+]$ ) = 285.1250, Found 285.1244.

### 7-methoxy-1-methylnaphthalen-2-ol (**1x**)



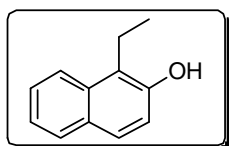
White solid; m.p. 106-108 °C,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.68 (d,  $J$  = 8.8 Hz, 1H), 7.55 (d,  $J$  = 8.8 Hz, 1H), 7.17 (d,  $J$  = 2.4 Hz, 1H), 7.03 (dd,  $J$  = 8.8, 2.4 Hz, 1H), 6.92 (d,  $J$  = 8.8 Hz, 1H), 5.00 (s, 1H), 3.96 (s, 3H), 2.50 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 158.3, 151.2, 135.3, 130.1, 127.2, 124.7, 115.4, 115.2, 114.4, 102.4, 55.4, 10.8. HRMS (ESI-TOF) calcd for  $\text{C}_{12}\text{H}_{12}\text{O}_2\text{Na}^+$  ( $[\text{M}+\text{Na}^+]$ ) = 221.0730, Found 221.0738.

### 7-methoxy-1,6-dimethylnaphthalen-2-ol (**1y**)



White solid; m.p. 169-170 °C,  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ )  $\delta$  = 9.29 (s, 1H), 7.49 (s, 1H), 7.43 (d,  $J$  = 8.4 Hz, 1H), 7.06 (s, 1H), 6.96 (d,  $J$  = 8.8 Hz, 1H), 3.91 (s, 3H), 2.38 (s, 3H), 2.25 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{DMSO-d}_6$ )  $\delta$  = 156.5, 151.9, 133.7, 129.0, 125.5, 123.2, 123.0, 115.2, 113.5, 100.3, 55.0, 16.2, 10.6. HRMS (ESI-TOF) calcd for  $\text{C}_{13}\text{H}_{14}\text{O}_2^+$  ( $[\text{M}+\text{H}^+]$ ) = 203.1072, Found 203.1275.

### 1-ethylnaphthalen-2-ol (**1ab**)

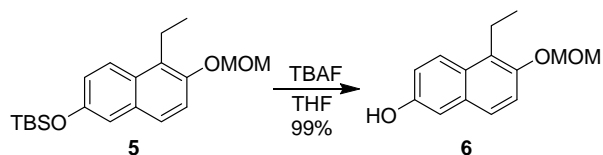


White solid; m.p. 92-95 °C,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.96 (d,  $J$  = 8.4 Hz, 1H), 7.79 (d,  $J$  = 8.0 Hz, 1H), 7.64 (d,  $J$  = 8.8 Hz, 1H), 7.53 - 7.47 (m, 1H), 7.38 - 7.32 (m, 1H), 7.07 (d,  $J$  = 8.8 Hz, 1H), 4.92 (s, 1H), 3.08 (q,  $J$  = 7.6 Hz, 2H), 1.30 (t,  $J$  = 7.6 Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 150.1, 133.0, 129.6, 128.8, 127.7, 126.5, 123.2, 123.0, 121.8, 117.8, 18.4, 14.3. HRMS (ESI-TOF) calcd for  $\text{C}_{12}\text{H}_{12}\text{ONa}^+$  ( $[\text{M}+\text{Na}^+]$ ) = 195.0780, Found 195.0780.

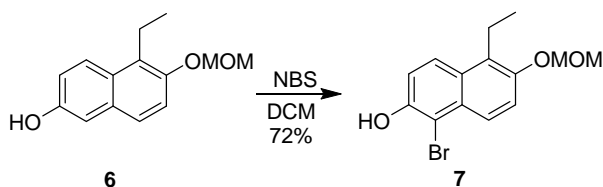
## 3. General procedure for the preparation **1y**, **1z**, **1ae** and **1af**

### 3.1. General procedure for the preparation **1z**, and **1ae**

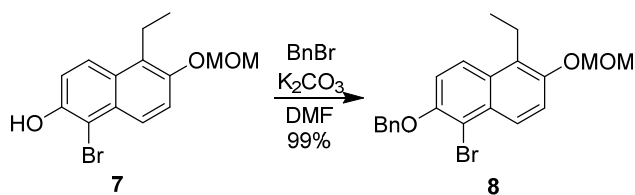
The compounds **5** were prepared by previously reported methods from 6-((tert-butyldimethylsilyl)oxy)naphthalen-2-ol.<sup>[1]</sup>



**5-ethyl-6-(methoxymethoxy)naphthalen-2-ol (6):** TBAF (12 mmol) was added to solution of **5** (10 mmol) in tetrahydrofuran (50.0 mL) at 0 °C and stirred for 10 min. After the reaction completion, the reaction was quenched by saturated NH<sub>4</sub>Cl, the organic layer was extracted with ethyl acetate, washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and then concentrated. The residue was purified by column chromatography (ethyl acetate/petroleum ether = 1/10, v/v) to afford the product **6**.

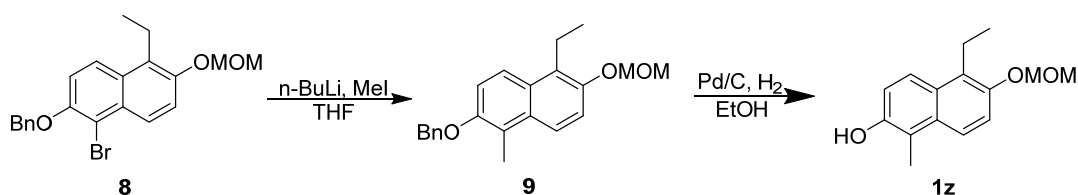


**1-bromo-5-ethyl-6-(methoxymethoxy)naphthalen-2-ol (7):** NBS (3.9 mmol) was added to solution of **6** (3.9 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20.0 mL) and stirred for 5 min. After the reaction completion, the reaction was quenched by H<sub>2</sub>O. The organic layer was extracted with CH<sub>2</sub>Cl<sub>2</sub>, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and then concentrated. The residue was purified by column chromatography (ethyl acetate/petroleum ether = 1/20, v/v) to afford the product **7**.

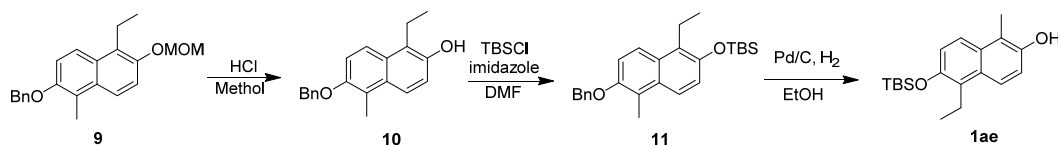


**2-(benzyloxy)-1-bromo-5-ethyl-6-(methoxymethoxy)naphthalene (8):** To a solution of **7** (8.0 mmol) in DMF (10 mL) were added K<sub>2</sub>CO<sub>3</sub> (12 mmol), BnBr (12 mmol) at room temperature. The mixture was continuously stirred for 3 h. After reaction completion, the resulting solution was quenched by water, extracted with ethyl acetate, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and then concentrated. The residue was

purified by column chromatography (ethyl acetate/petroleum ether = 1/30, v/v) to afford the product **8**.



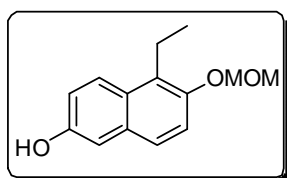
**2-(benzyloxy)-5-ethyl-6-(methoxymethoxy)-1-methylnaphthalene (1z):** To a solution of **8** (4.0 mmol) in THF (20.0 mL) under N<sub>2</sub> atmosphere was added n-BuLi (4.4 mmol), at -78 °C. The mixture was continuously stirred at the same temperature for 1 h, then MeI (10 mmol) was added. The mixture was warming up to room temperature and continuously stirred for 1 h. Then, the resulting solution was quenched by saturated NH<sub>4</sub>Cl solution and extracted with ethyl acetate. The combined organic layer was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and then concentrated. *This material was directly used in the next stage without further purification.* 10 % Pd/C (100 mg) and **9** was added EtOH (6 mL) under H<sub>2</sub> atmosphere. The mixture was stirred at room temperature for 7 h, filtered and then concentrated. The residue was purified by column chromatography (ethyl acetate/petroleum ether = 1/10, v/v) to afford the **1z** (590 mg, 60% yield for two steps).



**6-((tert-butyldimethylsilyloxy)-5-ethyl-1-methylnaphthalen-2-yl)benzyl ether (1ae):** To a solution of **9** (3 mmol) in CH<sub>3</sub>OH (6 mL) was warmed to 50 °C and conc. HCl aq. (35%, 4 drops) was added. After stirring for 1 h, 10 mL of water was added and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure to give a crude product of **10**. *This material was directly used in the next stage without further purification.* To a solution of **10** in DMF (10 mL) was added imidazole (4.5 mmol)

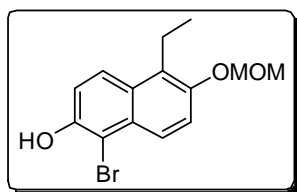
and TBSCl (4.5 mmol). The mixture was warming up to 60 °C and continuously stirred for 1 h. Then, the resulting solution was extracted with ethyl acetate. The combined organic layer was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and then concentrated. *This material was directly used in the next stage without further purification.* 10 % Pd/C (100 mg) and **11** was added EtOH (6 mL) under H<sub>2</sub> atmosphere. The mixture was stirred at room temperature for 7 h, filtered and then concentrated. The residue was purified by column chromatography (ethyl acetate/petroleum ether = 1/20, v/v) to afford the **1ae** (626 mg, 66% yield for three steps).

#### 5-ethyl-6-(methoxymethoxy)naphthalen-2-ol (**6**)



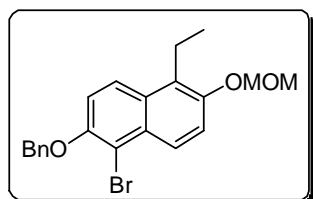
White solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 7.89 (d, *J* = 8.8 Hz, 1H), 7.48 - 7.40 (m, 1H), 7.37 - 7.29 (m, 1H), 7.18 - 7.03 (m, 2H), 5.89 (s, 1H), 5.30 (s, 2H), 3.59 (s, 3H), 3.12 (q, *J* = 7.2 Hz, 2H), 1.28 (t, *J* = 7.6 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 152.0, 150.1, 131.3, 128.0, 127.6, 125.8, 125.5, 118.2, 117.6, 110.3, 95.7, 56.3, 18.7, 14.9.

#### 1-bromo-5-ethyl-6-(methoxymethoxy)naphthalen-2-ol (**7**)



White solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 7.88 (d, *J* = 9.2 Hz, 2H), 7.46 (d, *J* = 9.2 Hz, 1H), 7.25 (d, *J* = 8.8 Hz, 1H), 5.87 (s, 1H), 5.27 (s, 2H), 3.53 (s, 3H), 3.09 (q, *J* = 7.6 Hz, 2H), 1.23 (t, *J* = 7.6 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 150.8, 149.1, 128.9, 128.7, 127.7, 124.8, 124.8, 118.2, 117.4, 106.9, 95.4, 56.3, 18.9, 14.9.

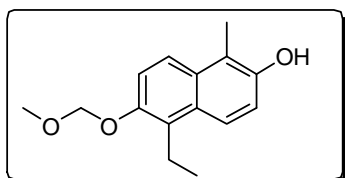
#### 2-(benzyloxy)-1-bromo-5-ethyl-6-(methoxymethoxy)naphthalene (**8**)



White solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 8.13 (d, *J* = 9.6 Hz, 1H), 7.91 (d, *J* = 9.2 Hz, 1H), 7.56 - 7.50 (m, 2H), 7.48 (d, *J* = 9.6 Hz, 1H), 7.42 - 7.37 (m, 2H), 7.35 - 7.31

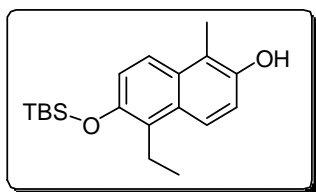
(m, 1H), 7.28 - 7.24 (m, 1H), 5.28 (s, 4H), 3.53 (s, 3H), 3.09 (q,  $J = 7.6$  Hz, 2H), 1.23 (t,  $J = 7.6$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta = 151.5, 151.0, 137.0, 129.7, 129.5, 128.7, 128.1, 127.4, 127.1, 125.9, 124.3, 118.3, 116.2, 111.0, 95.4, 72.1, 56.3, 18.8, 14.9$ .

#### 5-ethyl-6-(methoxymethoxy)-1-methylnaphthalen-2-ol (**1z**)



White solid; m.p. 110-112 °C,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.78$  (t,  $J = 8.8$  Hz, 2H), 7.41 (d,  $J = 9.6$  Hz, 1H), 7.08 (d,  $J = 9.2$  Hz, 1H), 5.28 (s, 2H), 4.82 (s, 1H), 3.55 (s, 3H), 3.11 (q,  $J = 7.6$  Hz, 2H), 2.52 (s, 3H), 1.26 (t,  $J = 7.6$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta = 150.0, 149.1, 130.5, 128.4, 127.8, 122.8, 122.5, 118.1, 117.1, 116.0, 95.6, 56.2, 18.8, 15.0, 10.9$ . HRMS (ESI-TOF) calcd for  $\text{C}_{15}\text{H}_{18}\text{O}_3\text{Na}^+$  ( $[\text{M}+\text{Na}^+]$ ) = 269.1154, Found 269.1149.

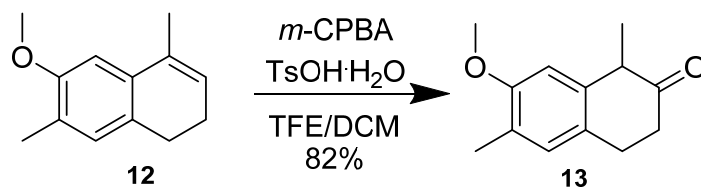
#### 6-((tert-butyldimethylsilyloxy)-5-ethyl-1-methylnaphthalen-2-ol (**1ae**)



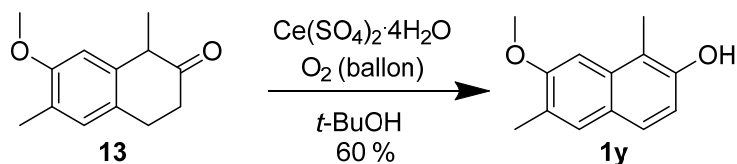
White solid; m.p. 70-74 °C,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.78$  (d,  $J = 8.8$  Hz, 1H), 7.71 (d,  $J = 8.8$  Hz, 1H), 7.14 (d,  $J = 9.2$  Hz, 1H), 7.08 (d,  $J = 9.2$  Hz, 1H), 4.96 - 4.85 (m, 1H), 3.09 (q,  $J = 7.2$  Hz, 2H), 2.54 (s, 3H), 1.26 (t,  $J = 7.6$  Hz, 3H), 1.10 (s, 9H), 0.30 (s, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta = 148.7, 148.3, 129.9, 128.9, 128.1, 122.8, 122.1, 120.8, 117.8, 116.0, 26.0, 19.0, 18.5, 14.7, 10.9, -3.8$ . HRMS (ESI-TOF) calcd for  $\text{C}_{19}\text{H}_{28}\text{O}_2\text{Si Na}^+$  ( $[\text{M}+\text{Na}^+]$ ) = 339.1756, Found 339.1747.

### 3.2. General procedure for the preparation **1y** and **1af**

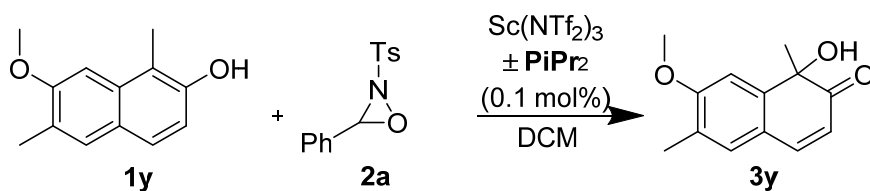
**6-methoxy-4,7-dimethyl-1,2-dihydronaphthalene (12)** was prepared by previously reported.<sup>[5]</sup>



**7-methoxy-1,6-dimethyl-3,4-dihydronaphthalen-2(1H)-one (13):** To a stirred solution of **12** (42 mmol) in TFE/CH<sub>2</sub>Cl<sub>2</sub> (1:4, 250 mL) at 0 °C was added *m*CPBA (52.5 mmol), and TsOH.H<sub>2</sub>O (52.5 mmol). After 20 min, the reaction was quenched with NaHCO<sub>3</sub>. Purification by column chromatography (ethyl acetate/petroleum ether = 1/10, v/v) to afford the **13** as colorless oil.

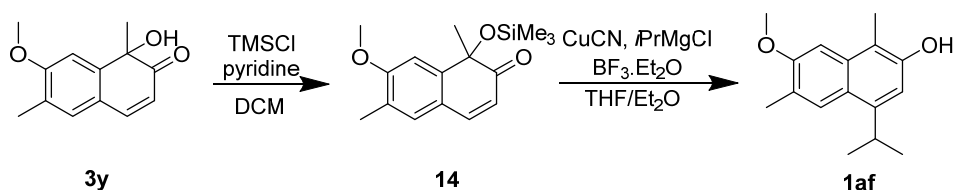


**7-methoxy-1,6-dimethylnaphthalen-2-ol (1y):** To a solution of **13** (20 mmol) and Ce(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O (20 mmol) in *t*-BuOH (30 mL) under O<sub>2</sub> atmosphere was heated to 80 °C. After stirring for 10 h, the resulting solution was filtered and then concentrated. Purification by column chromatography (ethyl acetate/petroleum ether = 1/10, v/v) to afford the **1y** as white solid.



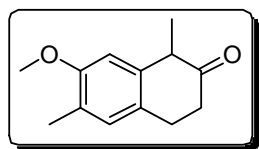
**hydroxy-7-methoxy-1,6-dimethylnaphthalen-2(1H)-one (3y):** To an oven-dried flask under nitrogen atmosphere was added Sc(NTf<sub>2</sub>)<sub>3</sub> (0.1 mol%), *rac*-L-PiPr<sub>2</sub> (0.1 mol%), compound **1y** (38.0 mmol) and CH<sub>2</sub>Cl<sub>2</sub> (80.0 mL). After stirring at 35 °C for 30 min. Then oxaziridine **2a** (45.0 mmol) was added. The reaction mixture was stirred for 15 h and directly purified by flash column chromatography (DCM / ethyl acetate =

1:0 - 10:1) to afford the desired product **3y** (7.4 g, 90% yield).



**4-isopropyl-7-methoxy-1,6-dimethylnaphthalen-2-ol (1af):** A solution of the **3y** (5.0 mmol) in dry dichloromethane (20 mL) and pyridine (5.5 mmol) was treated with TMSCl (6.3 mmol), and the mixture was stirred for 18 h at 20 °C. The resulting solution was extracted with DCM. The combined organic layer was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and then concentrated. *This material was directly used in the next stage without further purification.* A suspension of copper(I) cyanide (20 mmol) in THF (15 mL) and diethyl ether (15 mL) was treated under N<sub>2</sub> at -78 °C with a solution of the isopropyl magnesium chloride (40 mmol). Then, boron trifluoride etherate (10 mL) and the silyl ethers **14** (5.0 mmol) were added. The mixture was allowed to warm to 20 °C within 8 h and then hydrolyzed by addition of saturated aqueous ammonium chloride (200 mL). The organic phase was separated, the aqueous phase extracted twice with diethyl ether, dried (MgSO<sub>4</sub>), and then concentrated. Purification by column chromatography (ethyl acetate/petroleum ether = 1/10, v/v) to afford the **1af** (549 mg, 45% yield for two steps) as white solid.

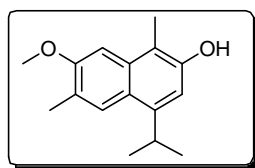
#### **7-methoxy-1,6-dimethyl-3,4-dihydronaphthalen-2(1H)-one (13)**



Colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 6.87 (s, 1H), 6.55 (s, 1H), 3.72 (s, 3H), 3.36 (q, *J* = 7.2 Hz, 1H), 2.91 - 2.82 (m, 2H), 2.53 - 2.33 (m, 2H), 2.10 (s, 3H), 1.36 (d, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 212.6, 156.8, 136.4, 129.8, 128.0, 124.8, 108.1, 55.4, 47.4, 37.6, 27.1, 15.7, 15.1.



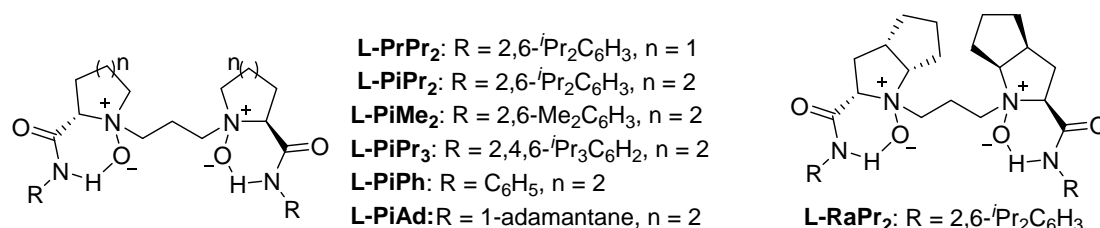
#### 4-isopropyl-7-methoxy-1,6-dimethylnaphthalen-2-ol (1af)



White solid; m.p. 162-164 °C,  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  = 7.77 (s, 1H), 7.09 (s, 1H), 6.83 (s, 1H), 4.82 (s, 1H), 3.95 (s, 3H), 3.70 - 3.58 (m, 1H), 2.46 (s, 3H), 2.37 (s, 3H), 1.34 (d,  $J$  = 6.8 Hz, 6H);  $^{13}\text{C}$  NMR (101 MHz, DMSO- $d_6$ )  $\delta$  = 156.9, 150.1, 143.6, 134.5, 125.0, 124.7, 122.1, 111.8, 111.3, 101.3, 55.2, 28.3, 23.6, 17.0, 10.7. HRMS (ESI-TOF) calcd for  $\text{C}_{16}\text{H}_{21}\text{O}_2^+$  ( $[\text{M}+\text{H}^+]$ ) = 245.1536, Found 245.1538.

#### 4. General procedure for the synthesis of chiral $N,N'$ -dioxides

The  $N,N'$ -dioxide ligands were prepared by the similar procedure in the literatures.<sup>[6]</sup>



#### 5. General procedure for the preparation of the racemic products

**3b**, **3d**, **3f**, **3r**, **3t**, **3ab** are Prepared by *Method A*, others are Prepared by *Method B*.

##### *Method A*

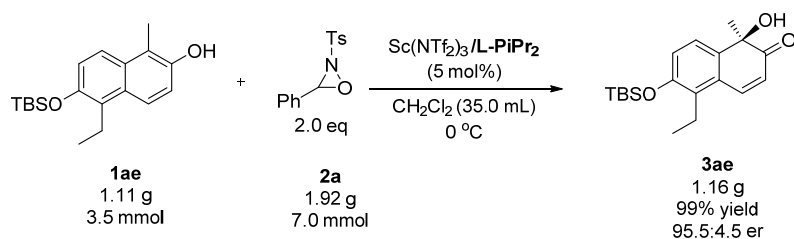
To a solution of Sc(OTf)<sub>3</sub> (10 mol%), 2-naphthols derivatives (0.1 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (1.0 mL), were added oxaziridine (0.2 mmol) and Et<sub>3</sub>N (0.1 mmol). After stirring at room temperature for 3 h. The reaction mixture was then directly purified by flash column chromatography (DCM / ethyl acetate = 1:0 - 10:1) to afford the desired product.

##### *Method B*

To an oven-dried flask under nitrogen atmosphere was added Sc(NTf<sub>2</sub>)<sub>3</sub> (5 mol%), *rac*-**L-PiPr<sub>2</sub>** (5 mol%), 2-naphthols derivatives (0.1 mmol) and CH<sub>2</sub>Cl<sub>2</sub> (1.0 mL). After stirring at 35 °C for 30 min, the reaction mixture was cool to 0 °C, oxaziridine **2a** (0.2 mmol) was then added. The reaction mixture was stirred at 0 °C for 3 h and directly purified by flash column chromatography (DCM / ethyl acetate = 1:0 - 10:1)

to afford the desired product.

## 6. Experimental procedure for the scale-up reaction

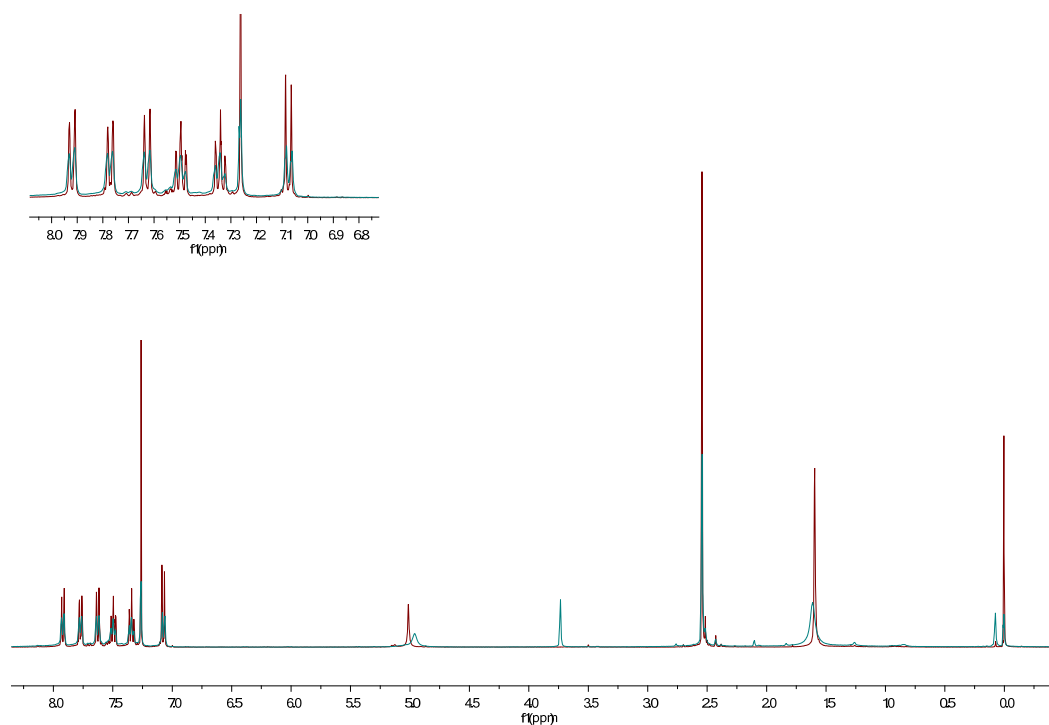


General Procedure: To an oven-dried flask under nitrogen atmosphere was added Sc(NTf<sub>2</sub>)<sub>3</sub> (5 mol%), **L-PiPr**<sub>2</sub> (5 mol%), compound **1ae** (1.11 g, 3.5 mmol) and CH<sub>2</sub>Cl<sub>2</sub> (35.0 mL). After stirring at 35 °C for 30 min, the reaction mixture was cool to 0 °C and stirring for another 5 min. Then oxaziridine **2a** (1.92 g, 7.0 mmol) was added. The reaction mixture was stirred at 0 °C for 3 h and directly purified by flash column chromatography (DCM / ethyl acetate = 1:0 - 10:1) to afford the desired product (1.16 g, 99% yield, 95.5:4.5 er).

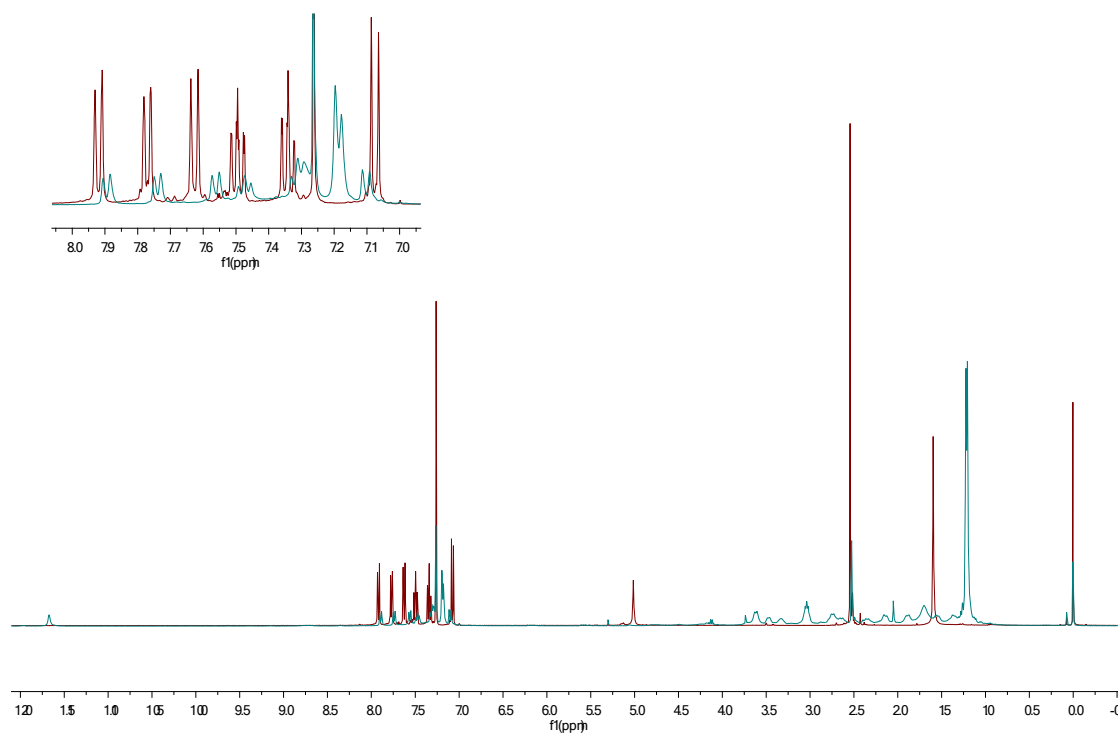
## 7. <sup>1</sup>H NMR and HRMS experiments

7.1 <sup>1</sup>H NMR spectra of **1a** in diverse conditions:

1. Red: **1a** in CDCl<sub>3</sub>; Blue: Sc(NTf<sub>2</sub>)<sub>3</sub>/**1a** in CDCl<sub>3</sub>

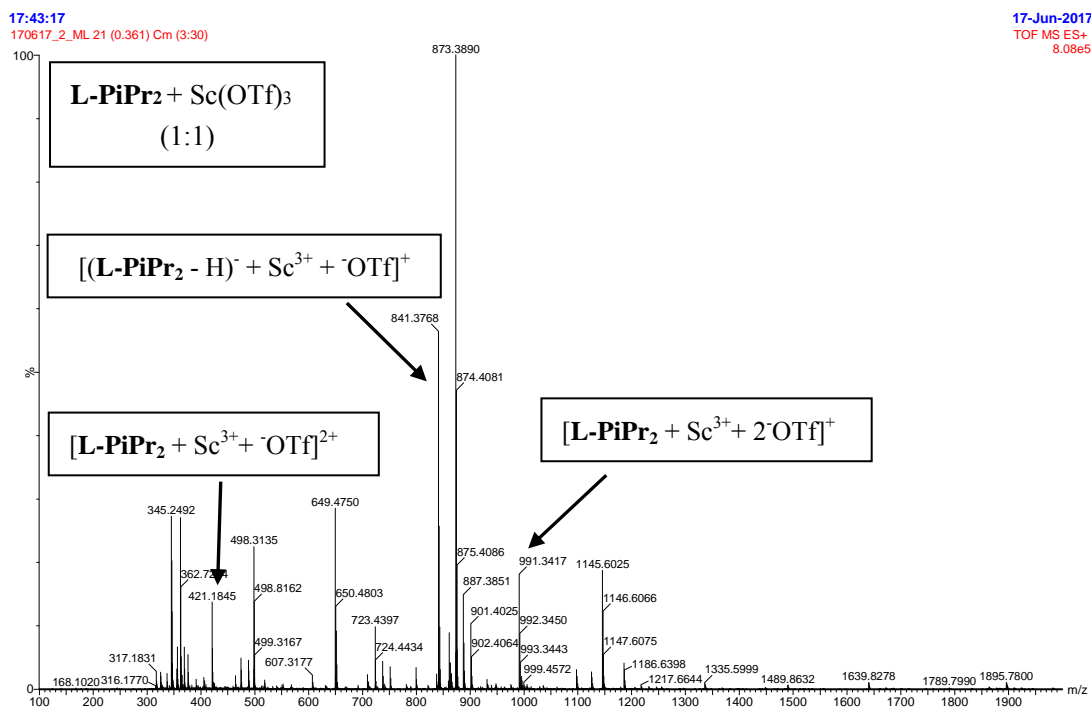


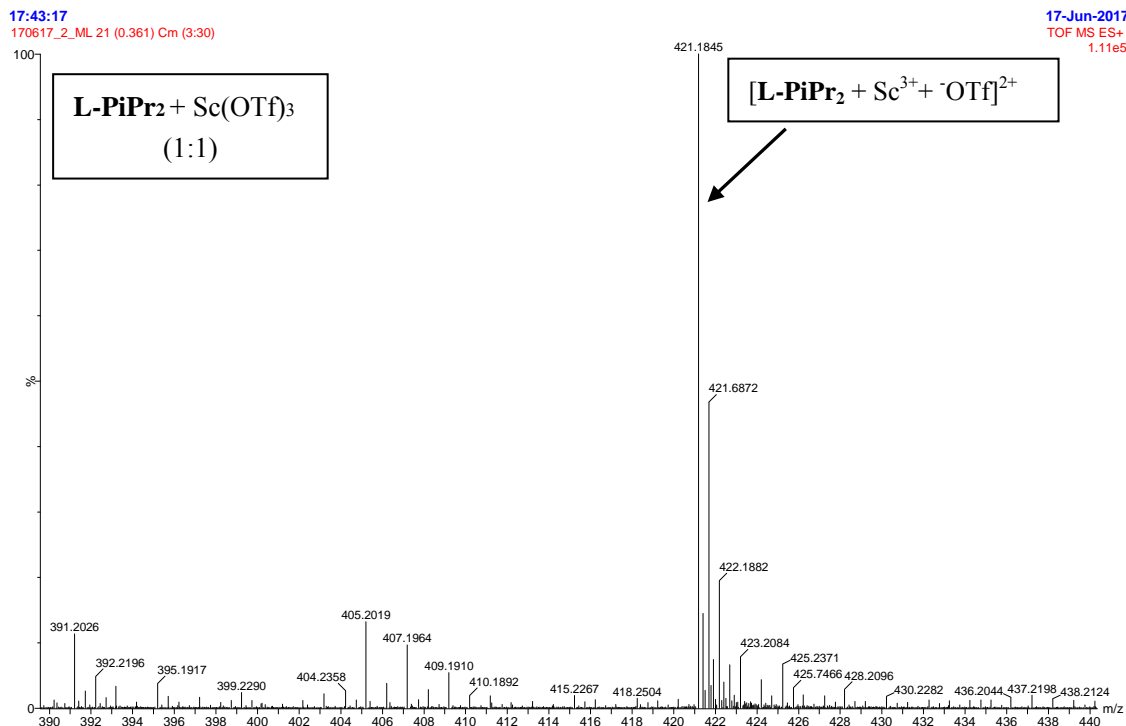
2. Red: **1a** in CDCl<sub>3</sub>; Blue: **L-PiPr<sub>2</sub>/Sc(NTf<sub>2</sub>)<sub>3</sub>/1a** in CDCl<sub>3</sub>



## 7.2 HRMS experiments

1. The mixture of Sc(OTf)<sub>3</sub> and **L-PiPr<sub>2</sub>**.



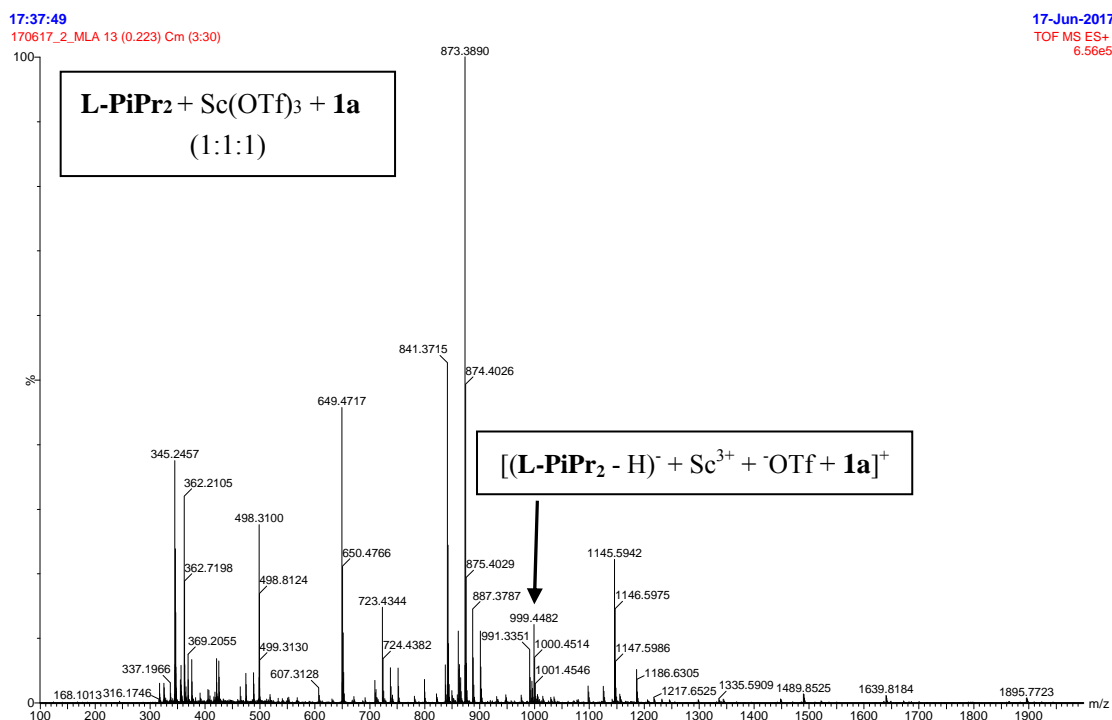


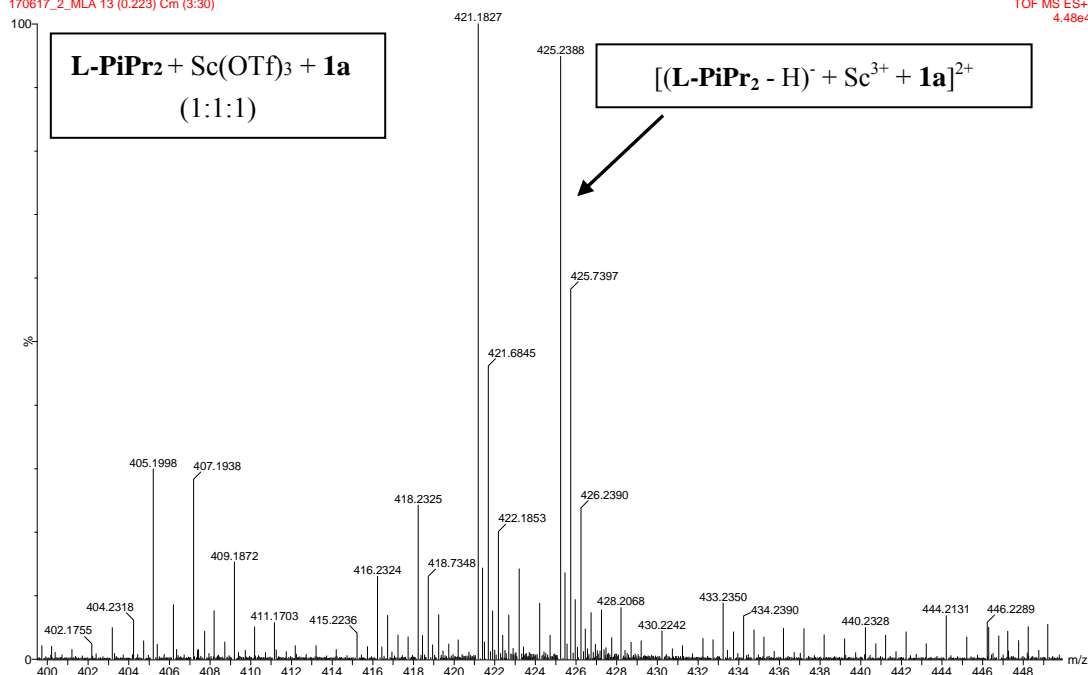
HRMS (ESI-TOF) calcd for  $[\text{L-PiPr}_2 + \text{Sc}^{3+} + ^-\text{OTf}]^{2+} = 421.1841$ , Found 421.1845.

HRMS (ESI-TOF) calcd for  $[(\text{L-PiPr}_2 - \text{H})^- + \text{Sc}^{3+} + ^-\text{OTf}]^+ = 841.3610$ , Found 841.3768.

HRMS (ESI-TOF) calcd for  $[\text{L-PiPr}_2 + \text{Sc}^{3+} + 2^-\text{OTf}]^+ = 991.3209$ , Found 991.3417.

## 2. The mixture of Sc(OTf)<sub>3</sub>, L-PiPr<sub>2</sub> and 1a.

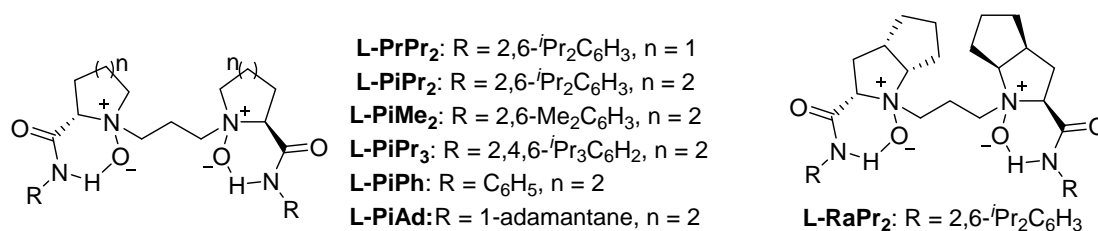
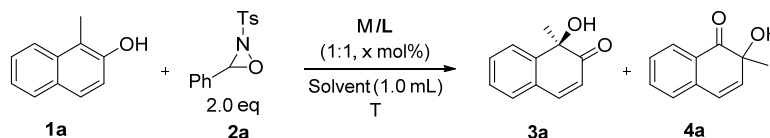




HRMS (ESI-TOF) calcd for  $[(\mathbf{L}\text{-PiPr}_2\text{-H})^- + \text{Sc}^{3+} + \mathbf{1a}]^{2+} = 425.2408$ , Found 425.2388.

HRMS (ESI-TOF) calcd for  $[(\mathbf{L}\text{-PiPr}_2\text{-H})^- + \text{Sc}^{3+} + \text{OTf} + \mathbf{1a}]^+ = 999.4342$ , Found 999.4482.

## 8. Optimization of reaction conditions

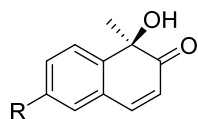
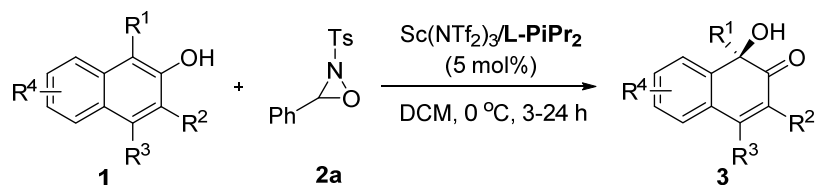


Entry <sup>a</sup>	Ligand	Metal salt	Oxidant	Solvent	x	T (°C)	Yield (%) <sup>b</sup>	ratio (3a:4a) <sup>c</sup>	Ee(3a/4a) (%) <sup>c</sup>
1	<b>L-PiPr<sub>2</sub></b>	Sc(OTf) <sub>3</sub>	oxaziridine	DCM	10	30	96	73:27	60/64
2	<b>L-PrPr<sub>2</sub></b>	Sc(OTf) <sub>3</sub>	oxaziridine	DCM	10	30	99	79:21	26/45
3	<b>L-RaPr<sub>2</sub></b>	Sc(OTf) <sub>3</sub>	oxaziridine	DCM	10	30	99	75:25	7/11
4	<b>L-PiMe<sub>2</sub></b>	Sc(OTf) <sub>3</sub>	oxaziridine	DCM	10	30	90	>95:5	20/n.d.

5	<b>L-PiPh</b>	Sc(OTf) <sub>3</sub>	oxaziridine	DCM	10	30	92	>95:5	24/n.d.
6	<b>L-PiPr<sub>3</sub></b>	Sc(OTf) <sub>3</sub>	oxaziridine	DCM	10	30	96	89:11	46/55
7	<b>L-PiAd</b>	Sc(OTf) <sub>3</sub>	oxaziridine	DCM	10	30	99	87:13	20/58
8	<b>L-PiPr<sub>2</sub></b>	Sc(acac) <sub>3</sub>	oxaziridine	DCM	10	30	99	>95:5	10/n.d.
9	<b>L-PiPr<sub>2</sub></b>	Sc(O <sup>i</sup> Pr) <sub>3</sub>	oxaziridine	DCM	10	30	99	>95:5	18/n.d.
10	<b>L-PiPr<sub>2</sub></b>	ScCl <sub>3</sub> ·6H <sub>2</sub> O	oxaziridine	DCM	10	30	99	>95:5	10/n.d.
11	<b>L-PiPr<sub>2</sub></b>	Sc(NTf <sub>2</sub> ) <sub>3</sub>	oxaziridine	DCM	10	30	99	>95:5	84/n.d.
12	<b>L-PiPr<sub>2</sub></b>	Sc(NTf <sub>2</sub> ) <sub>3</sub>	<i>m</i> CPBA	DCM	10	30	60	>95:5	0/n.d.
13	<b>L-PiPr<sub>2</sub></b>	Sc(NTf <sub>2</sub> ) <sub>3</sub>	H <sub>2</sub> O <sub>2</sub>	DCM	10	30	n.r.	--	--
14	<b>L-PiPr<sub>2</sub></b>	Sc(NTf <sub>2</sub> ) <sub>3</sub>	<sup>t</sup> BuOOH	DCM	10	30	n.r.	--	--
15	<b>L-PiPr<sub>2</sub></b>	Sc(NTf <sub>2</sub> ) <sub>3</sub>	oxaziridine	DCM	10	0	99	>95:5	90
16 <sup>d</sup>	<b>L-PiPr<sub>2</sub></b>	Sc(NTf <sub>2</sub> ) <sub>3</sub>	oxaziridine	DCM	10	-20	99	>95:5	89
17 <sup>e</sup>	<b>L-PiPr<sub>2</sub></b>	Sc(NTf <sub>2</sub> ) <sub>3</sub>	oxaziridine	DCM	10	-40	58	89:11	85
18	<b>L-PiPr<sub>2</sub></b>	Sc(NTf <sub>2</sub> ) <sub>3</sub>	oxaziridine	toluene	10	0	94	>95:5	86
19	<b>L-PiPr<sub>2</sub></b>	Sc(NTf <sub>2</sub> ) <sub>3</sub>	oxaziridine	DCE	10	0	97	>95:5	88
20	<b>L-PiPr<sub>2</sub></b>	Sc(NTf <sub>2</sub> ) <sub>3</sub>	oxaziridine	TCE	10	0	96	>95:5	74
21	<b>L-PiPr<sub>2</sub></b>	Sc(NTf <sub>2</sub> ) <sub>3</sub>	oxaziridine	CHCl <sub>3</sub>	10	0	92	>95:5	87
22 <sup>f</sup>	<b>L-PiPr<sub>2</sub></b>	Sc(NTf <sub>2</sub> ) <sub>3</sub>	oxaziridine	DCM	10	0	99	>95:5	89
23	<b>L-PiPr<sub>2</sub></b>	Sc(NTf <sub>2</sub> ) <sub>3</sub>	oxaziridine	DCM	5	0	99	>95:5	90
24	<b>L-PiPr<sub>2</sub></b>	Sc(NTf <sub>2</sub> ) <sub>3</sub>	oxaziridine	CHCl <sub>3</sub>	2.5	0	94	>95:5	88
25 <sup>d</sup>	<b>L-PiPr<sub>2</sub></b>	Sc(NTf <sub>2</sub> ) <sub>3</sub>	oxaziridine	CHCl <sub>3</sub>	1	0	86	>95:5	87

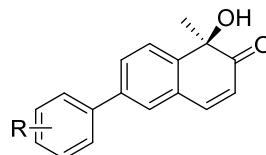
<sup>a</sup>Unless otherwise noted, the reactions were performed with x mol% metal, x mol% ligand, **1a** (0.1 mmol) and **2** (0.2 mmol) in solvent (1.0 mL) under N<sub>2</sub> at 30 °C for 3 h. <sup>b</sup>Isolated total yield of **3a** and **4a** by silica gel chromatography. <sup>c</sup>Determined by chiral HPLC analysis (Chiralcel IE) after flash column chromatography purification. <sup>d</sup>The reaction time was 4 h. <sup>e</sup>The reaction time was 22 h. <sup>f</sup>**2a** (0.15 mmol) was used.

## 9. Full list of the substrate scope



**3b**: R = Br, 3 h, 99% yield, 94:6 er

**3c**: R = OMe, 3 h, 99% yield, 94.5:5.5 er



**3d**: R = H, 3 h, 99% yield, 94:6 er

**3e**: R = 4-Cl, 3 h, 95% yield, 94:6 er

**3f**: R = 2-MeO, 3 h, 99% yield, 93.5:6.5 er

**3g**: R = 3-MeO, 3 h, 99% yield, 95:5 er

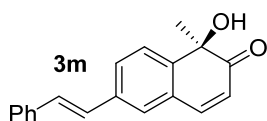
**3h**: R = 4-MeO, 3 h, 99% yield, 94.5:5.5 er

**3i**: R = 3,4-MeO<sub>2</sub>, 7 h, 99% yield, 93.5:6.5 er

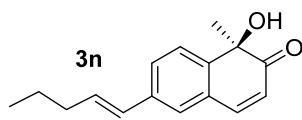
**3j**: R = Piperonyl, 4 h, 99% yield, 95:5 er

**3k**: R = 2-Naphthyl, 5 h, 96% yield, 94:6 er

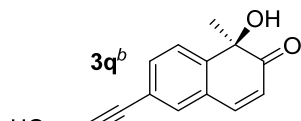
**3l**: R = 3-Furyl, 3 h, 99% yield, 95:5 er



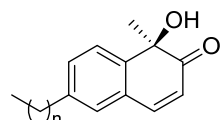
**3m**: 3.5 h, 99% yield, 94.5:5.5 er



**3n**: 3 h, 99% yield, 95:5 er



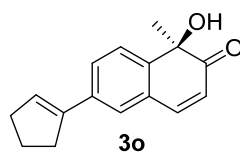
**3q<sup>b</sup>**: 24 h, 66% yield, 91:9 er



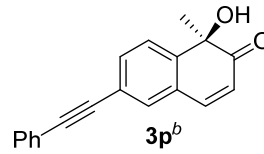
n = 0, **3r**: 3 h, 99% yield, 94:6 er

n = 1, **3s**: 3 h, 99% yield, 94:6 er

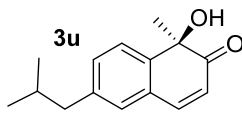
n = 4, **3t**: 3 h, 99% yield, 94:6 er



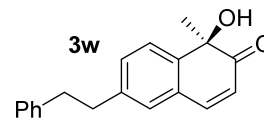
**3o**: 3 h, 95% yield, 95:5 er



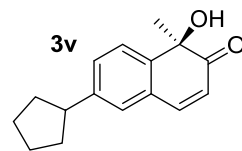
**3p<sup>b</sup>**: 5 h, 99% yield, 92:8 er



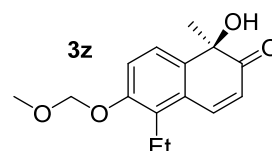
**3u**: 3h, 96% yield, 94.5:5.5 er



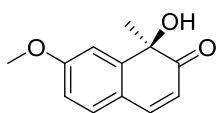
**3w**: 3 h, 95% yield, 95:5 er



**3v**: 3 h, 99% yield, 94.5:5.5 er



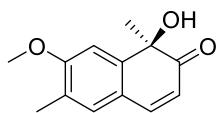
**3z**: 3 h, 99% yield, 95:5 er



**3x**

3 h

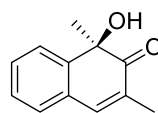
99% yield, 94.5:5.5 er



**3y**

3 h

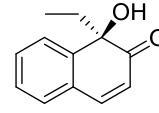
99% yield, 95:5 er



**3aa<sup>c</sup>**

3 h

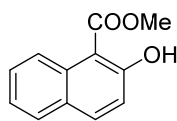
99% yield, 83.5:16.5 er



**3ab**

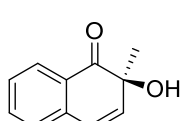
22 h

64% yield<sup>d</sup>, 75:25 er



**1ac**

no reaction



**3ad**

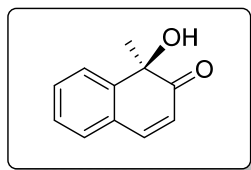
22h, 46% yield, 77:23 er

<sup>a</sup> Reaction conditions: The same as entry 7 in Table 1. <sup>b</sup> 10 mol% catalyst loading.

<sup>c</sup> L-PiEt<sub>2</sub>-Sc(OTf)<sub>3</sub> (1:1, 5 mol%). <sup>d</sup> Total yield of **3ab** and **4ab**, **3ab/4ab** = 87:13.

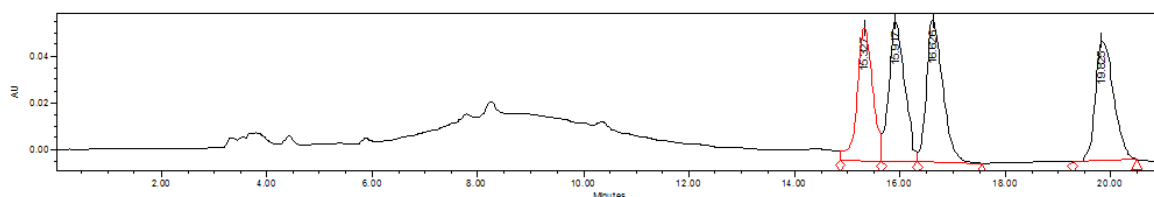
## 10. The analytical and spectral characterization data of the products

### (*R*)-1-hydroxy-1-methylnaphthalen-2(1H)-one (3a)

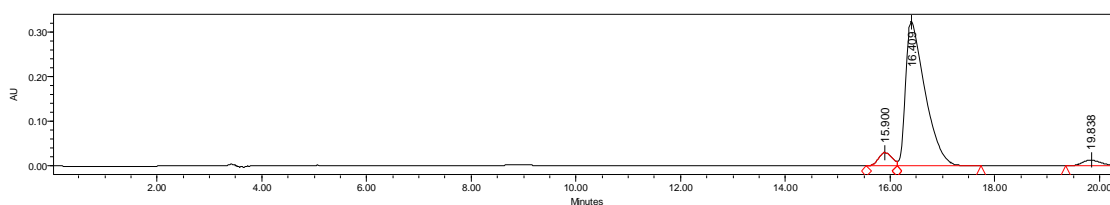


Colorless oil; 99% yield, 95:5 er;  $[\alpha]_D^{25} = 265.96$  ( $c = 0.28$  in  $\text{CH}_2\text{Cl}_2$ ).

HPLC DAICEL CHIRALCEL IE, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min,  $\lambda = 254$  nm,  $t_R$  (minor) = 15.90 min,  $t_R$  (major) = 16.42 min.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.72$  (d,  $J = 7.6$  Hz, 1H), 7.47 - 7.41 (m, 2H), 7.35 - 7.28 (m, 2H), 6.20 (d,  $J = 10.0$  Hz, 1H), 3.74 (s, 1H), 1.55 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta = 205.4, 146.1, 145.2, 130.8, 129.6, 128.4, 128.0, 125.7, 122.5, 77.3, 33.3$ . HRMS (ESI-TOF) calcd for  $\text{C}_{11}\text{H}_{10}\text{O}_2\text{Na}^+$  ( $[\text{M}+\text{Na}^+]$ ) = 197.0573, Found 197.0574.



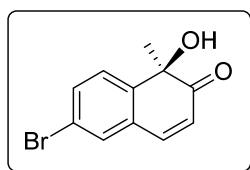
	Retention Time	Area	% Area
1	15.327	1171769	23.50
2	15.917	1270613	25.48
3	16.626	1316241	26.40
4	19.825	1227859	24.62



	Retention Time	Area	% Area
1	15.900	254413	4.77
2	16.419	4909175	92.03
3	19.838	170718	3.20

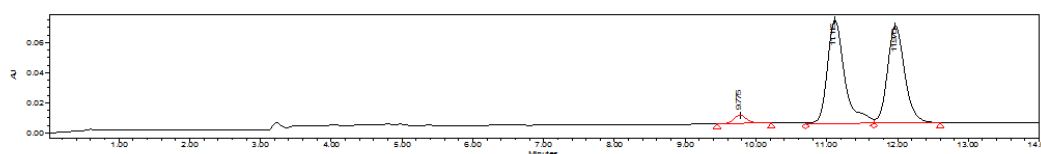


### (R)-6-bromo-1-hydroxy-1-methylnaphthalen-2(1H)-one (3b)

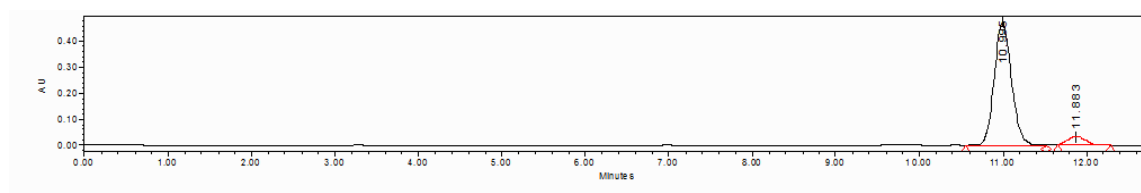


White solid; m.p. 54-56 °C; 99% yield, 94:6 er;  $[\alpha]_D^{16} = 115.26$  ( $c = 0.49$  in  $\text{CH}_2\text{Cl}_2$ ).

UPC<sup>2</sup> Phenomenex CHIRALCEL Lux 5u Cellulose-1,  $\text{scCO}_2/\text{Methol} = 97/3$ , flow rate = 1.0 mL/min,  $\lambda = 254$  nm,  $t_R$  (major) = 11.0 min,  $t_R$  (minor) = 11.88 min.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.61 - 7.57$  (m, 1H), 7.57 - 7.52 (m, 1H), 7.44 (d,  $J = 2.0$  Hz, 1H), 7.35 (d,  $J = 10.0$  Hz, 1H), 6.23 (d,  $J = 9.8$  Hz, 1H), 3.71 (s, 1H), 1.52 (s, 3H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta = 204.5, 144.4, 143.9, 133.4, 132.0, 130.3, 127.5, 123.8, 121.7, 77.1, 33.0$ . HRMS (ESI-TOF) calcd for  $\text{C}_{11}\text{H}_9^{79}\text{BrO}_2\text{Na}^+$  ( $[\text{M}+\text{Na}^+]$ ) = 274.9678, Found 274.9678. HRMS (ESI-TOF) calcd for  $\text{C}_{11}\text{H}_9^{81}\text{BrO}_2\text{Na}^+$  ( $[\text{M}+\text{Na}^+]$ ) = 276.9658, Found 276.9660.

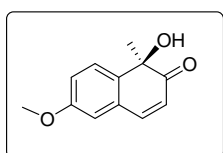


	Retention Time	Area	% Area
1	9.775	67163	2.89
2	11.115	1170495	50.32
3	11.970	1088509	46.79



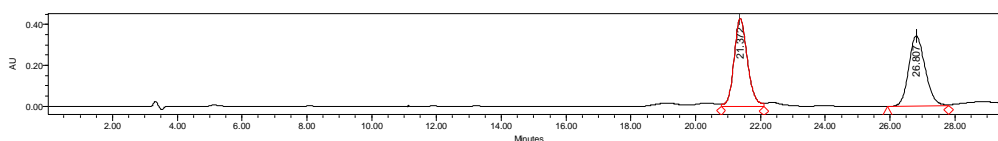
	Retention Time	Area	% Area
1	10.995	6817001	93.99
2	11.883	435620	6.01

### (R)-1-hydroxy-6-methoxy-1-methylnaphthalen-2(1H)-one (3c)

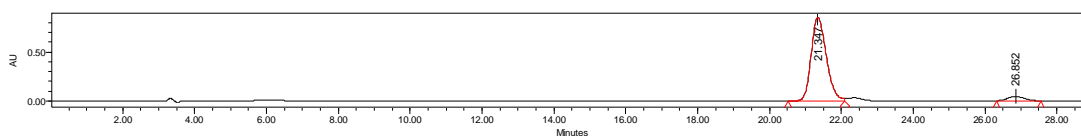


Colorless oil; m.p. 106-108 °C; 99% yield, 94.5:5.5 er;  $[\alpha]_D^{25} = 216.97$  ( $c = 0.33$  in  $\text{CH}_2\text{Cl}_2$ ).

HPLC DAICEL CHIRALCEL IC, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min,  $\lambda = 254$  nm,  $t_R$  (major) = 21.35 min,  $t_R$  (minor) = 26.86 min.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.61$  (d,  $J = 8.4$  Hz, 1H), 7.37 (d,  $J = 9.6$  Hz, 1H), 6.97 (dd,  $J = 8.4, 2.4$  Hz, 1H), 6.82 (d,  $J = 2.4$  Hz, 1H), 6.20 (d,  $J = 10.0$  Hz, 1H), 3.83 (s, 3H), 3.66 (s, 1H), 1.52 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta = 205.5, 159.2, 145.9, 137.1, 129.5, 127.0, 123.1, 116.0, 114.8, 77.2, 55.6, 33.2$ . HRMS (ESI-TOF) calcd for  $\text{C}_{12}\text{H}_{12}\text{O}_3$  ( $[\text{M}+\text{Na}^+]$ ) = 227.0679, Found 227.0671.

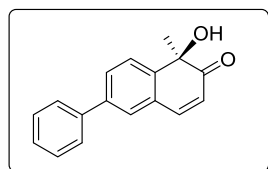


	Retention Time	Area	% Area
1	21.372	12393739	50.80
2	26.807	12001302	49.20



	Retention Time	Area	% Area
1	21.347	25145644	94.49
2	26.852	1466626	5.51

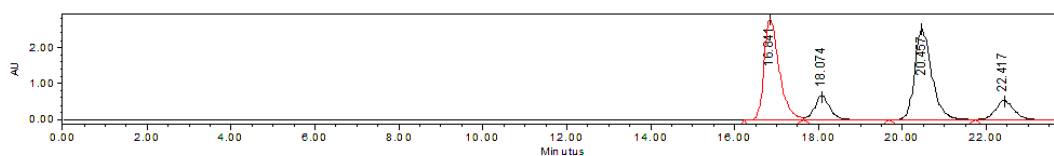
### **(R)-1-hydroxy-1-methyl-6-phenylnaphthalen-2(1H)-one (3d)**



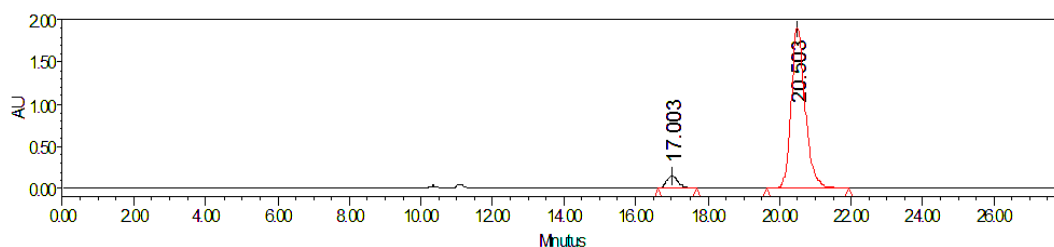
Colorless oil; 99% yield, 94:6 er;  $[\alpha]_{\text{D}}^{16} = 82.69$  ( $c = 0.34$  in  $\text{CH}_2\text{Cl}_2$ ).

HPLC DAICEL CHIRALCEL IA, n-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min,  $\lambda = 254$  nm,  $t_R$  (minor) = 17.00 min,  $t_R$  (major) = 20.50 min.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.79$  (d,  $J = 8.0$  Hz, 1H), 7.67 (dd,  $J = 8.0, 2.0$  Hz, 1H), 7.63 - 7.56 (m, 2H), 7.54 - 7.44 (m, 4H), 7.43 - 7.36 (m, 1H), 6.27 (d,  $J = 9.6$  Hz, 1H), 3.76 (s, 1H), 1.60 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta = 205.2, 146.0, 143.9, 141.1, 140.0, 129.4, 129.0, 128.8, 128.2, 127.9, 127.1, 126.2, 122.9, 77.2, 33.2$ .

HRMS (ESI-TOF) calcd for  $C_{17}H_{14}O_2Na^+$  ( $[M+Na^+]$ ) = 273.0886, Found 273.0890.

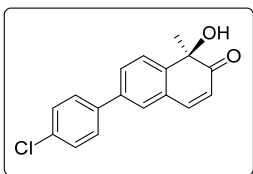


	Retention Time	Area	% Area
1	16.841	69088735	40.19
2	18.074	16437326	9.56
3	20.457	70564046	41.05
4	22.417	15815117	9.20



	Retention Time	Area	% Area
1	17.003	3235758	5.88
2	20.503	51822510	94.12

**(R)-6-(4-chlorophenyl)-1-hydroxy-1-methylnaphthalen-2(1H)-one (3e)**

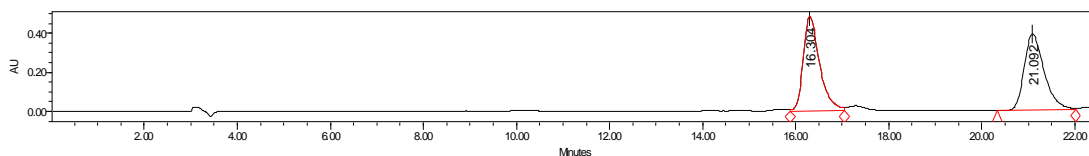


White solid; m.p. 60-61 °C; 95% yield, 94:6 er;  $[\alpha]_D^{25} = 46.67$  ( $c = 0.42$  in  $CH_2Cl_2$ ).

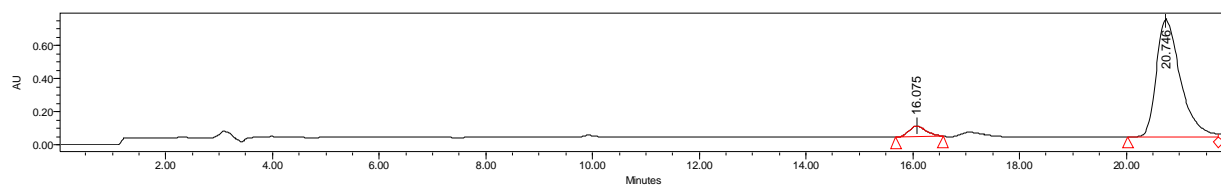
HPLC DAICEL CHIRALCEL IA, n-hexane/2-propanol = 90/10,

flow rate = 1.0 mL/min,  $\lambda = 254$  nm,  $t_R$  (major) = 20.75 min,  $t_R$  (minor) = 16.08 min.

$^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta = 7.83 - 7.74$  (m, 1H), 7.65 - 7.60 (m, 1H), 7.55 - 7.40 (m, 6H), 6.35 - 6.22 (m, 1H), 3.79 - 3.72 (m, 2H), 1.64 - 1.54 (m, 3H);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta = 205.1, 145.8, 144.2, 139.9, 138.4, 134.1, 129.2, 129.2, 129.0, 128.4, 128.0, 126.3, 123.1, 77.2, 33.2$ . HRMS (ESI-TOF) calcd for  $C_{17}H_{13}^{35}ClO_2Na^+$  ( $[M+Na^+]$ ) = 307.0496, Found 307.0501. HRMS (ESI-TOF) calcd for  $C_{17}H_{13}^{37}ClO_2Na^+$  ( $[M+Na^+]$ ) = 309.0467, Found 309.0481.

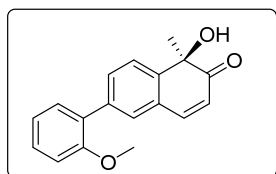


	Retention Time	Area	% Area
1	16.304	11815349	50.21
2	21.092	11716966	49.79



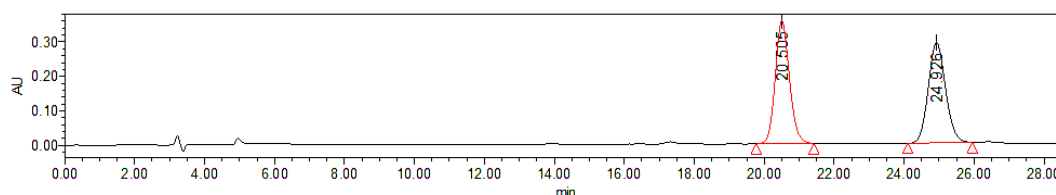
	Retention Time	Area	% Area
1	16.075	1420823	6.03
2	20.746	22148076	93.97

**(R)-1-hydroxy-6-(2-methoxyphenyl)-1-methylnaphthalen-2(1H)-one (3f)**

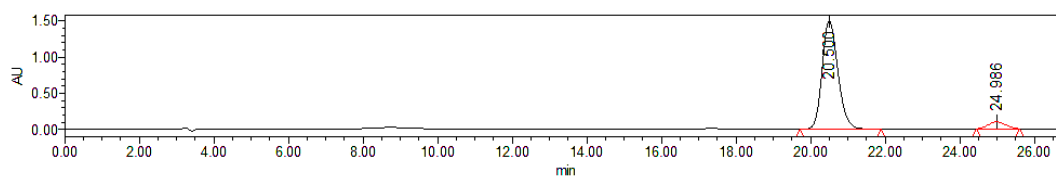


Colorless oil; 99% yield, 93.5:6.5 er;  $[\alpha]_D^{25} = 77.08$  ( $c = 0.48$  in  $\text{CH}_2\text{Cl}_2$ ).

HPLC DAICEL CHIRALCEL IC, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min,  $\lambda = 254$  nm,  $t_R$  (major) = 20.50 min,  $t_R$  (minor) = 24.99 min.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.75$  (d,  $J = 7.6$  Hz, 1H), 7.61 (d,  $J = 7.6$  Hz, 1H), 7.51 - 7.44 (m, 2H), 7.39 - 7.29 (m, 2H), 7.09 - 6.97 (m, 2H), 6.22 (d,  $J = 10.0$  Hz, 1H), 3.83 (s, 3H), 3.74 (s, 1H), 1.60 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta = 205.5, 156.5, 146.4, 143.5, 138.4, 131.9, 130.8, 130.7, 129.4, 129.3, 128.2, 125.5, 122.5, 121.1, 111.4, 77.2, 55.7, 33.2$ . HRMS (ESI-TOF) calcd for  $\text{C}_{18}\text{H}_{16}\text{O}_3\text{Na}^+$  ( $[\text{M}+\text{Na}^+]$ ) = 303.0992, Found 303.0995.

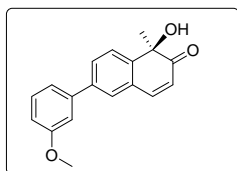


	Retention Time	Area	% Area
1	20.505	10062884	50.24
2	24.926	9968259	49.76



	Retention Time	Area	% Area
1	20.500	44063776	93.50
2	24.986	3062300	6.50

### **(R)-1-hydroxy-6-(3-methoxyphenyl)-1-methylnaphthalen-2(1H)-one (3g)**

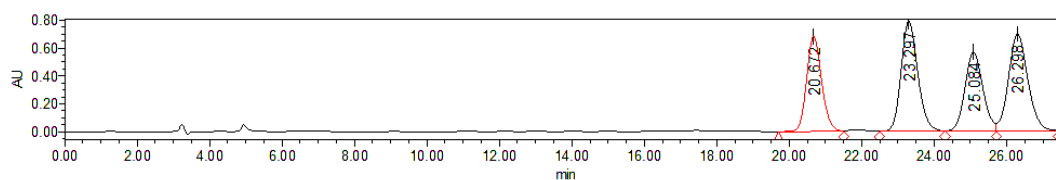


Colorless oil; 99% yield, 95:5 er;  $[\alpha]_D^{25} = 66.67$  ( $c = 0.49$  in  $\text{CH}_2\text{Cl}_2$ ).

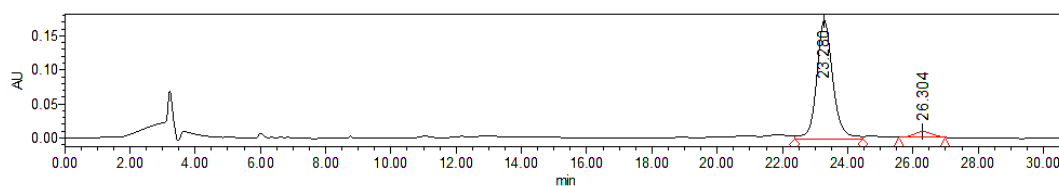
HPLC DAICEL CHIRALCEL IC, n-hexane/2-propanol = 90/10,

flow rate = 1.0 mL/min,  $\lambda = 254$  nm,  $t_R$  (major) = 23.28 min,  $t_R$  (minor) = 26.30 min.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.78$  (d,  $J = 8.0$  Hz, 1H), 7.68 - 7.63 (m, 1H), 7.53 - 7.46 (m, 2H), 7.41 - 7.35 (m, 1H), 7.21 - 7.15 (m, 1H), 7.14 - 7.08 (m, 1H), 6.93 (d,  $J = 8.4$  Hz, 1H) 6.25 (d,  $J = 10.0$  Hz, 1H), 3.88 (s, 3H), 3.76 (s, 1H), 1.59 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta = 205.2, 160.2, 146.0, 144.1, 141.5, 141.0, 130.1, 129.4, 128.8, 128.2, 126.2, 123.0, 119.6, 113.2, 113.0, 77.2, 55.5, 33.2$ . HRMS (ESI-TOF) calcd for  $\text{C}_{18}\text{H}_{16}\text{O}_3\text{Na}^+$  ( $[\text{M}+\text{Na}^+]$ ) = 303.0992, Found 303.0999.

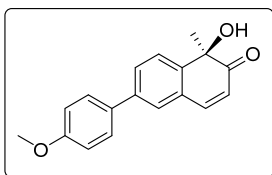


	Retention Time	Area	% Area
1	20.672	19684235	21.67
2	23.297	25374240	27.94
3	25.084	19703184	21.69
4	26.298	26065449	28.70



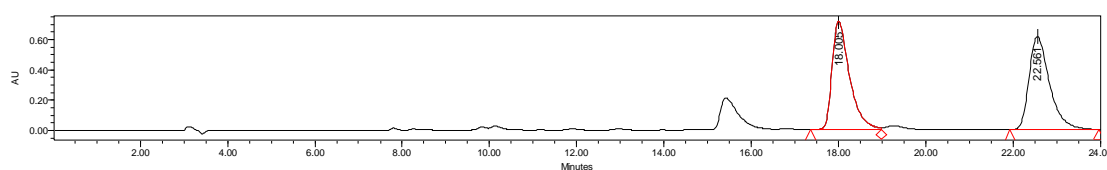
	Retention Time	Area	% Area
1	23.280	6046085	94.83
2	26.304	329482	5.17

**(R)-1-hydroxy-6-(4-methoxyphenyl)-1-methylnaphthalen-2(1H)-one (3h)**

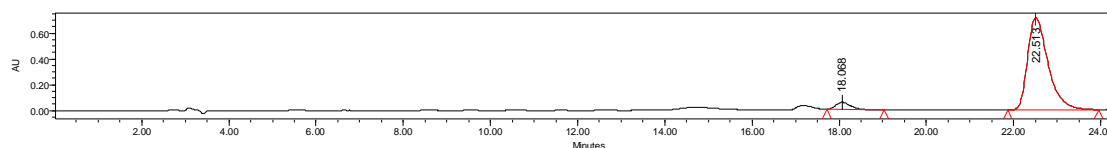


White solid; m.p. 106-108 °C; 99% yield, 94.5:5.5 er;  $[\alpha]_D^{25} = 56.40$  ( $c = 0.49$  in  $\text{CH}_2\text{Cl}_2$ ).

HPLC DAICEL CHIRALCEL IA, n-hexane/2-propanol = 90/10, flow rate = 1 mL/min,  $\lambda = 254$  nm,  $t_R$  (minor) = 18.07 min,  $t_R$  (major) = 22.51 min.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.76$  (d,  $J = 8.0$  Hz, 1H), 7.65 - 7.59 (m, 1H), 7.56 - 7.44 (m, 4H), 7.04 - 6.95 (m, 2H), 6.24 (d,  $J = 10.0$  Hz, 1H), 3.86 (s, 3H), 3.76 (s, 1H), 1.59 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta = 205.3, 159.6, 146.1, 143.2, 140.7, 132.5, 128.9, 128.8, 128.2, 127.8, 126.2, 122.8, 114.5, 77.1, 55.5, 33.2$ . HRMS (ESI-TOF) calcd for  $\text{C}_{18}\text{H}_{16}\text{O}_3\text{Na}^+$  ( $[\text{M}+\text{Na}^+]$ ) = 303.0992, Found 303.0998.

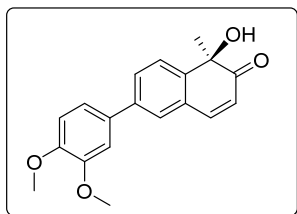


	Retention Time	Area	% Area
1	18.005	20033195	50.05
2	22.561	19992568	49.95



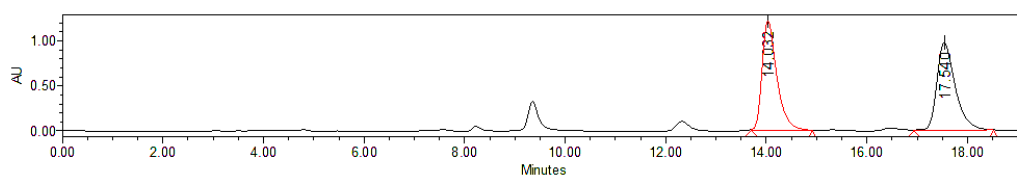
	Retention Time	Area	% Area
1	18.068	1375884	5.55
2	22.513	23435575	94.45

**(R)-6-(3,4-dimethoxyphenyl)-1-hydroxy-1-methylnaphthalen-2(1H)-one (3i)**

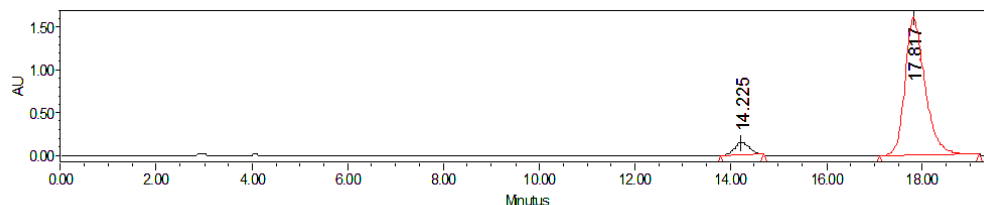


Yellow solid; m.p. 126-128 °C; 99% yield, 93.5:5.5 er;  $[\alpha]_D^{25} = 48.32$  ( $c = 0.24$  in  $\text{CH}_2\text{Cl}_2$ ).

HPLC DAICEL CHIRALCEL IA, n-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min,  $\lambda = 254$  nm,  $t_R$  (minor) = 14.22 min,  $t_R$  (major) = 17.81 min.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.76$  (d,  $J = 8.0$  Hz, 1H), 7.66 - 7.60 (m, 1H), 7.53 - 7.44 (m, 2H), 7.17 - 7.12 (m, 1H), 7.11 - 7.05 (m, 1H) 6.96 (d,  $J = 8.4$  Hz, 1H), 6.25 (d,  $J = 9.6$  Hz, 2H), 3.96 (s, 3H), 3.93 (s, 3H), 3.72 (s, 1H), 1.59 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta = 205.3, 149.4, 149.2, 146.1, 143.4, 141.0, 133.0, 129.1, 128.8, 127.9, 126.2, 122.9, 119.5, 111.7, 110.4, 77.2, 56.1, 33.2$ . HRMS (ESI-TOF) calcd for  $\text{C}_{19}\text{H}_{18}\text{O}_4$  ( $[\text{M}+\text{K}^+]$ ) = 333.1097, Found 333.1089.

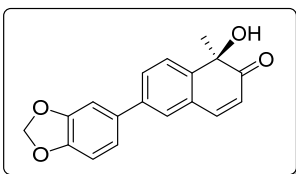


	Retention Time	Area	% Area
1	14.032	25022993	50.37
2	17.540	24659166	49.63



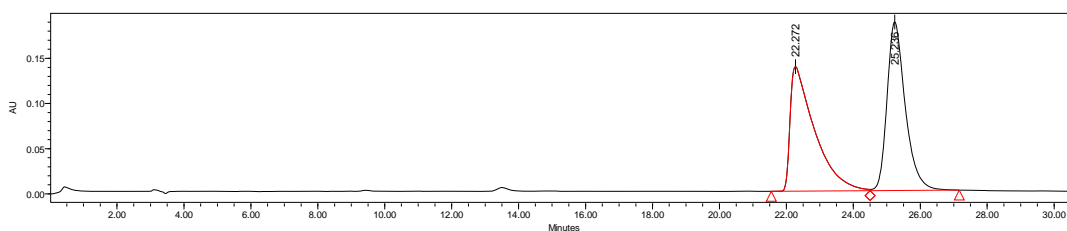
	Retention Time	Area	% Area
1	14.225	3182310	6.39
2	17.817	46586421	93.61

**(R)-6-(benzo[d][1,3]dioxol-5-yl)-1-hydroxy-1-methylnaphthalen-2(1H)-one (3j)**

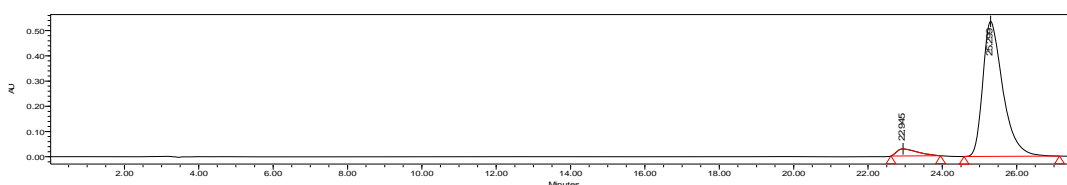


White solid; m.p. 79-83 °C 99% yield, 95:5 er;  $[\alpha]_D^{25} = 48.05$   
( $c = 0.31$  in  $\text{CH}_2\text{Cl}_2$ ).

HPLC DAICEL CHIRALCEL IA, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min,  $\lambda = 254$  nm,  $t_R$  (minor) = 22.94 min,  $t_R$  (major) = 25.30 min.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.74$  (d,  $J = 8.0$  Hz, 1H), 7.58 (dd,  $J = 8.0, 2.0$  Hz, 1H), 7.48 (d,  $J = 10.0$  Hz, 1H), 7.42 (d,  $J = 2.0$  Hz, 1H), 7.11 - 6.98 (m, 2H), 6.90 (d,  $J = 8.4$  Hz, 1H), 6.24 (d,  $J = 9.6$  Hz, 1H), 6.02 (s, 2H), 3.71 (s, 1H), 1.58 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta = 205.2, 148.4, 147.6, 146.0, 143.6, 140.8, 134.3, 129.1, 128.8, 127.9, 126.2, 123.0, 120.7, 108.8, 107.6, 101.4, 77.2, 33.2$ . HRMS (ESI-TOF) calcd for  $\text{C}_{18}\text{H}_{14}\text{O}_4\text{Na}^+$  ( $[\text{M}+\text{Na}^+]$ ) = 317.0784, Found 317.0782.

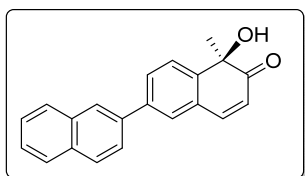


	Retention Time	Area	% Area
1	22.272	6984701	49.77
2	25.236	7050306	50.23



	Retention Time	Area	% Area
1	22.945	1074667	5.09
2	25.299	20022264	94.91

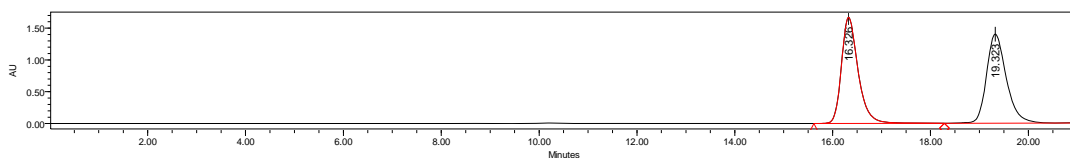
**(R)-5-hydroxy-5-methyl-[2,2'-binaphthalen]-6(5H)-one (3k)**



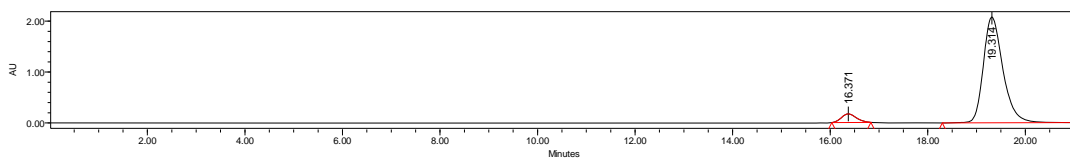
White solid; m.p. 84-87 °C 96% yield, 94:6 er;  $[\alpha]_D^{25} = 23.85$   
( $c = 0.52$  in  $\text{CH}_2\text{Cl}_2$ ).



HPLC DAICEL CHIRALCEL IA, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min,  $\lambda = 254$  nm,  $t_R$  (minor) = 16.37 min,  $t_R$  (major) = 19.31 min.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 8.04$  (s, 1H), 7.96 - 7.86 (m, 3H), 7.86 - 7.77 (m, 2H), 7.75 - 7.71 (m, 1H), 7.66 - 7.61 (m, 1H), 7.57 - 7.48 (m, 3H) 6.28 (d,  $J = 9.6$  Hz, 1H), 3.75 (s, 1H), 1.62 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta = 205.2, 146.0, 144.0, 141.0, 137.3, 133.7, 132.9, 129.6, 129.0, 128.8, 128.4, 128.3, 127.8, 126.6, 126.4, 126.3, 126.0, 125.3, 123.0, 77.2, 33.2$ . HRMS (ESI-TOF) calcd for  $\text{C}_{21}\text{H}_{16}\text{O}_2\text{Na}^+$  ( $[\text{M}+\text{Na}^+]$ ) = 323.1043, Found 323.1042.

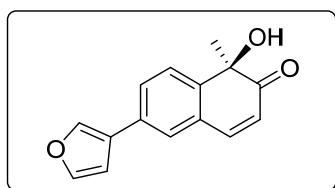


	Retention Time	Area	% Area
1	16.326	39385592	50.02
2	19.323	39357923	49.98



	Retention Time	Area	% Area
1	16.371	3592299	5.84
2	19.314	57955793	94.16

**(R)-6-(furan-3-yl)-1-hydroxy-1-methylnaphthalen-2(1H)-one (3l)**

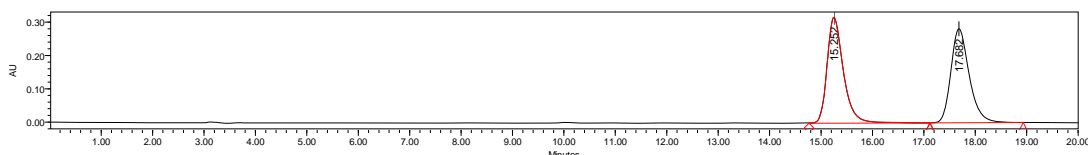


Yellow solid; m.p. 60-63 °C; 99% yield, 95:5 er;  $[\alpha]^{25}_{\text{D}} = 105.71$  ( $c = 0.42$  in  $\text{CH}_2\text{Cl}_2$ ).

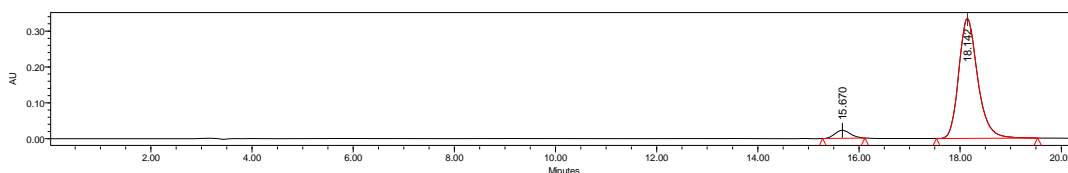
HPLC DAICEL CHIRALCEL IA, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min,  $\lambda = 254$  nm,  $t_R$  (major)

= 18.14 min,  $t_R$  (minor) = 15.67 min.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.78 - 7.67$  (m, 2H), 7.57 - 7.52 (m, 1H), 7.52 - 7.48 (m, 1H), 7.44 (d,  $J = 9.6$  Hz, 1H) 7.40 (s, 1H),

6.74 - 6.65 (m, 1H), 6.29 - 6.17 (m, 1H), 3.73 (s, 1H), 1.56 (d,  $J = 1.2$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta = 205.2, 145.8, 144.1, 143.6, 138.9, 132.4, 128.9, 128.0, 126.8, 126.2, 125.6, 123.0, 108.8, 77.2, 33.2$ . HRMS (ESI-TOF) calcd for  $\text{C}_{15}\text{H}_{12}\text{O}_3\text{Na}^+$  ( $[\text{M}+\text{Na}^+]$ ) = 263.0679, Found 263.0683.

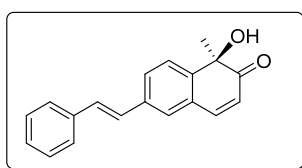


	Retention Time	Area	% Area
1	15.252	6964243	49.96
2	17.682	6975280	50.04



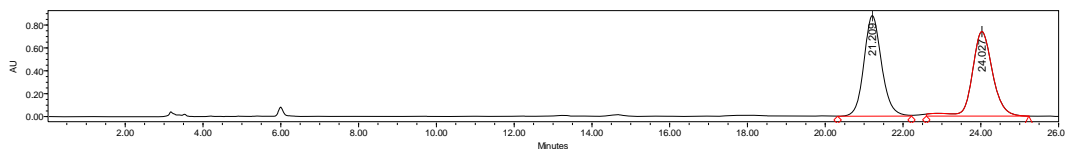
	Retention Time	Area	% Area
1	15.670	475066	5.20
2	18.142	8658167	94.80

### **(*R,E*)-1-hydroxy-1-methyl-6-styrylnaphthalen-2(1H)-one (3m)**

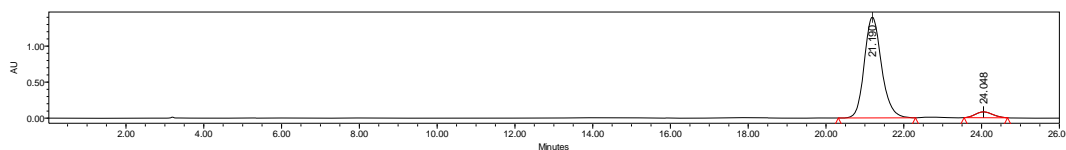


Yellow oil; 99% yield, 94.5:5.5 er;  $[\alpha]_D^{25} = 22.20$  ( $c = 0.54$  in  $\text{CH}_2\text{Cl}_2$ ).

HPLC DAICEL CHIRALCEL IC, n-hexane/2-propanol = 90/10, flow rate = 1 mL/min,  $\lambda = 254$  nm,  $t_R$  (major) = 21.19 min,  $t_R$  (minor) = 24.05 min.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.70$  (d,  $J = 8.0$  Hz, 1H), 7.60 - 7.55 (m, 1H), 7.54 - 7.48 (m, 2H), 7.47 - 7.33 (m, 4H), 7.32 - 7.27 (m, 1H), 7.18 - 7.05 (m, 2H), 6.23 (d,  $J = 10.0$  Hz, 1H), 3.73 (s, 1H), 1.56 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta = 205.2, 146.0, 144.1, 137.3, 137.0, 129.8, 128.9, 128.8, 128.6, 128.1, 127.5, 127.4, 126.7, 126.1, 123.0, 77.2, 33.2$ . HRMS (ESI-TOF) calcd for  $\text{C}_{19}\text{H}_{16}\text{O}_2\text{Na}^+$  ( $[\text{M}+\text{Na}^+]$ ) = 299.1043, Found 299.1042.

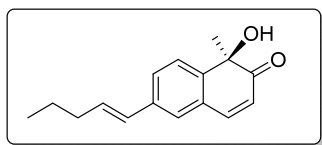


	Retention Time	Area	% Area
1	21.209	27722402	50.88
2	24.027	26758844	49.12



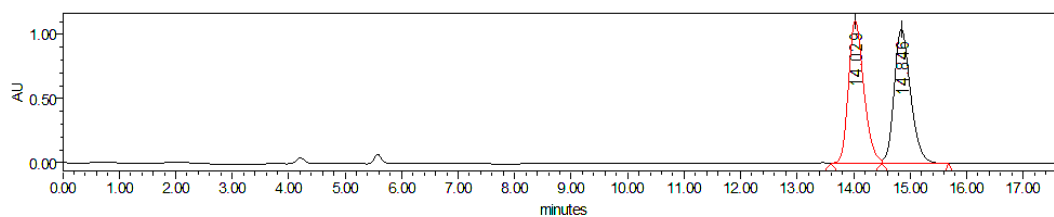
	Retention Time	Area	% Area
1	21.190	42856182	94.49
2	24.048	2498166	5.51

### **(*R,E*)-1-hydroxy-1-methyl-6-(pent-1-en-1-yl)naphthalen-2(1H)-one (3n)**

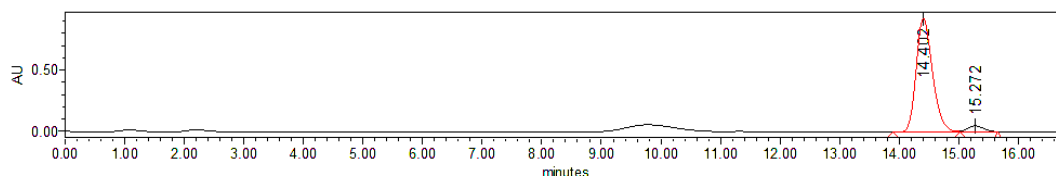


Colorless oil; 99% yield, 95:5 er;  $[\alpha]_D^{25} = 124.19$  ( $c = 0.43$  in  $\text{CH}_2\text{Cl}_2$ ).

HPLC DAICEL CHIRALCEL IE, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min,  $\lambda = 254$  nm,  $t_R$  (major) = 14.40 min,  $t_R$  (minor) = 15.27 min.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.63$  (d,  $J = 8.0$  Hz, 1H), 7.46 - 7.34 (m, 2H), 7.28 - 7.23 (m, 1H), 6.42 - 6.33 (m, 1H), 6.33 - 6.22 (m, 1H), 6.20 (d,  $J = 10.0$  Hz, 1H), 3.70 (s, 1H), 2.35 - 2.11 (m, 2H), 1.63 - 1.42 (m, 5H), 0.96 (t,  $J = 7.6$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta = 205.3, 146.2, 143.3, 137.8, 132.3, 128.8, 128.5, 128.1, 127.0, 125.8, 122.7, 77.1, 35.2, 33.2, 22.6, 13.9$ . HRMS (ESI-TOF) calcd for  $\text{C}_{16}\text{H}_{18}\text{O}_2\text{Na}^+$  ( $[\text{M}+\text{Na}^+]$ ) = 265.1199, Found 265.1197.

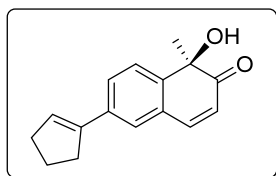


	Retention Time	Area	% Area
1	14.029	21080415	49.91
2	14.846	21157140	50.09



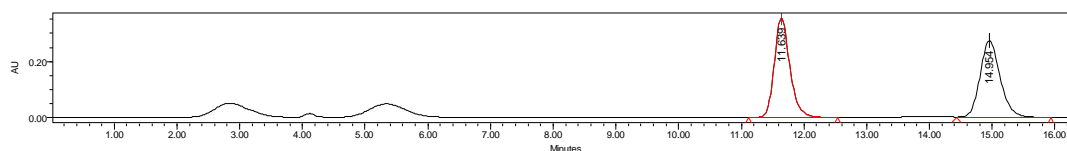
	Retention Time	Area	% Area
1	14.402	17594228	95.14
2	15.272	898529	4.86

**(R)-6-(cyclopent-1-en-1-yl)-1-hydroxy-1-methylnaphthalen-2(1H)-one (3o)**

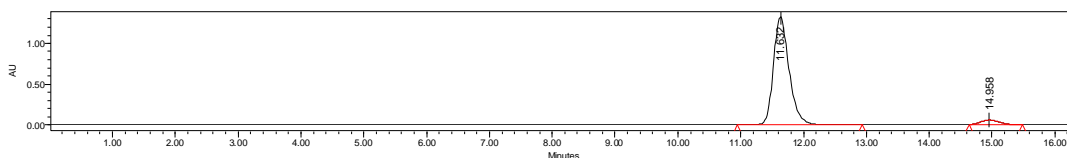


Yellow solid; m.p. 48-52 °C; 95% yield, 95:5 er;  $[\alpha]_D^{25} = 114.11$  ( $c = 0.33$  in  $\text{CH}_2\text{Cl}_2$ ).

HPLC DAICEL CHIRALCEL IC, n-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min,  $\lambda = 254$  nm,  $t_R$  (major) = 11.63 min,  $t_R$  (minor) = 14.96 min.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.64$  (d,  $J = 8.0$  Hz, 1H), 7.52 - 7.48 (m, 1H), 7.43 (d,  $J = 9.6$  Hz, 1H), 7.34 (d,  $J = 1.6$  Hz, 1H), 6.25 - 6.22 (m, 1H), 6.20 (d,  $J = 10.0$  Hz, 1H), 3.69 (s, 1H), 2.75 - 2.67 (m, 2H), 2.58 - 2.51 (m, 2H), 2.09 - 1.99 (m, 2H), 1.54 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta = 205.3, 146.3, 143.3, 141.4, 136.7, 128.3, 127.8, 127.4, 126.7, 125.6, 122.7, 77.2, 33.5, 33.3, 33.2, 23.4$ . HRMS (ESI-TOF) calcd for  $\text{C}_{16}\text{H}_{16}\text{O}_2\text{Na}^+$  ( $[\text{M}+\text{Na}^+]$ ) = 263.1043, Found 263.1039.

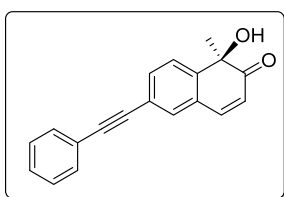


	Retention Time	Area	% Area
1	11.639	6085407	50.11
2	14.954	6059655	49.89



	Retention Time	Area	% Area
1	11.632	23003935	94.85
2	14.958	1249869	5.15

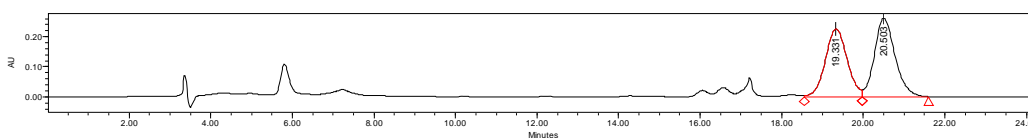
**(R)-1-hydroxy-1-methyl-6-(phenylethynyl)naphthalen-2(1H)-one (3p)**



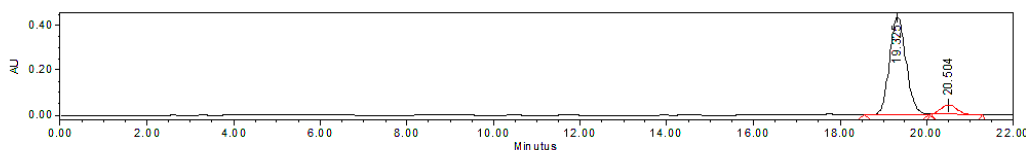
Brown oil; 99% yield, 92:8 er;  $[\alpha]_D^{16} = 23.84$  ( $c = 0.34$  in  $\text{CH}_2\text{Cl}_2$ ).

HPLC DAICEL CHIRALCEL IC, n-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min,  $\lambda = 254$  nm,  $t_R$  (major) = 19.32

min,  $t_R$  (minor) = 20.50 min.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.71$  (d,  $J = 8.0$  Hz, 1H), 7.63 - 7.53 (m, 3H), 7.50 - 7.45 (m, 1H), 7.45 - 7.31 (m, 4H), 6.25 (d,  $J = 10.0$  Hz, 1H), 3.73 (s, 1H), 1.56 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta = 204.8, 145.3, 144.8, 133.6, 132.4, 131.8, 128.7, 128.6, 128.6, 125.8, 123.3, 123.2, 122.9, 90.4, 88.3, 77.2, 33.2$ . HRMS (ESI-TOF) calcd for  $\text{C}_{19}\text{H}_{14}\text{O}_2\text{Na}^+$  ( $[\text{M}+\text{Na}^+]$ ) = 297.0886, Found 297.0887.

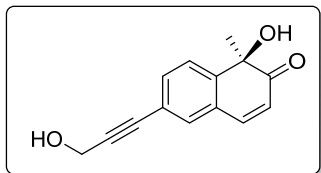


	Retention Time	Area	% Area
1	19.331	8350795	47.68
2	20.503	9162875	52.32



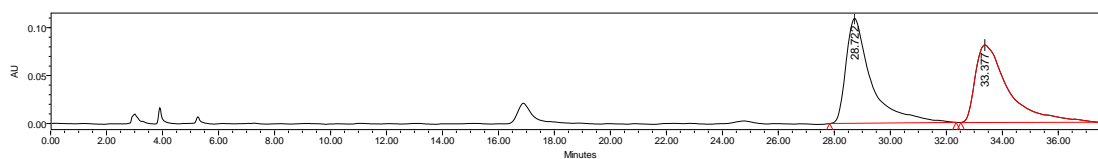
	Retention Time	Area	% Area
1	19.325	11536519	91.90
2	20.504	1016463	8.10

**(R)-1-hydroxy-6-(3-hydroxyprop-1-yn-1-yl)-1-methylnaphthalen-2(1H)-one (3q)**

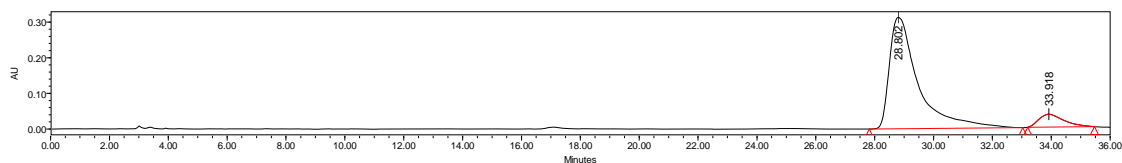


White solid; m.p. 62-64 °C; 66% yield, 91:9 er;  $[\alpha]_D^{16} = 90.94$  ( $c = 0.27$  in  $\text{CH}_2\text{Cl}_2$ ).

HPLC DAICEL CHIRALCEL IA, n-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min,  $\lambda = 254$  nm,  $t_R$  (major) = 28.80 min,  $t_R$  (minor) = 33.92 min.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.66$  (d,  $J = 8.0$  Hz, 1H), 7.48 (d,  $J = 8.0$  Hz, 1H), 7.40 - 7.33 (m, 2H), 6.23 (d,  $J = 10.0$  Hz, 1H), 4.50 (s, 2H), 3.73 (s, 1H), 1.53 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta = 204.7, 145.1, 133.7, 132.4, 128.6, 125.8, 123.3, 122.5, 88.3, 84.6, 77.2, 51.7, 33.1$ . HRMS (ESI-TOF) calcd for  $\text{C}_{14}\text{H}_{12}\text{O}_3\text{Na}^+$  ( $[\text{M}+\text{Na}^+]$ ) = 251.0679, Found 251.0679.

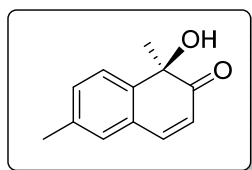


	Retention Time	Area	% Area
1	28.722	6847239	50.76
2	33.377	6643174	49.24



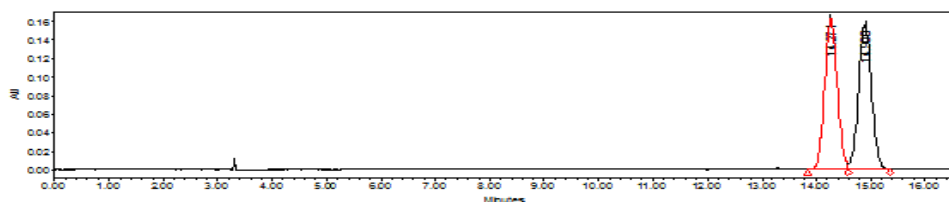
	Retention Time	Area	% Area
1	28.802	21249718	90.89
2	33.918	2130104	9.11

### (*R*)-1-hydroxy-1,6-dimethylnaphthalen-2(1H)-one (3r)

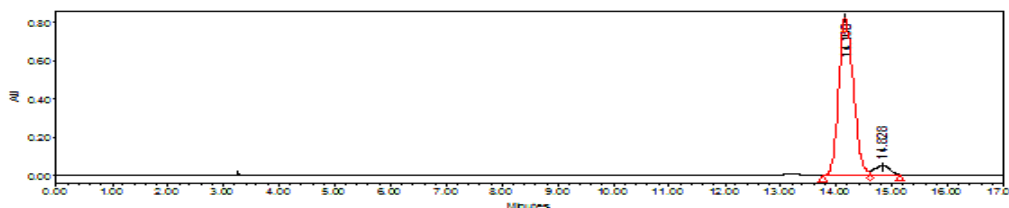


White solid; m.p. 54-56 °C; 99% yield, 94:6 er;  $[\alpha]_D^{25} = 245.14$  ( $c = 0.21$  in  $\text{CH}_2\text{Cl}_2$ ).

SFC Phenomenex CHIRALCEL Lux 5u Cellulose-1,  $\text{CO}_2/\text{Methol} = 97/3$ , flow rate = 1.0 mL/min,  $\lambda = 254$  nm,  $t_R$  (minor) = 10.92 min,  $t_R$  (major) = 11.81 min.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.59$  (d,  $J = 7.6$  Hz 1H), 7.39 (d,  $J = 10.0$  Hz 1H), 7.28 - 7.23 (m, 1H), 7.11 (s, 1H), 6.18 (d,  $J = 10.0$  Hz, 1H), 3.68 (s, 1H), 2.37 (s, 3H), 1.53 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta = 205.6, 146.3, 142.2, 137.7, 131.5, 130.2, 128.3, 125.6, 122.5, 77.1, 33.3, 21.1$ . HRMS (ESI-TOF) calcd for  $\text{C}_{12}\text{H}_{12}\text{O}_2\text{Na}^+$  ( $[\text{M}+\text{Na}^+]$ ) = 211.0730, Found 211.0730.

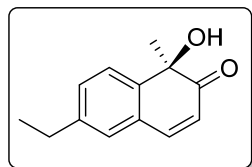


	Retention Time	Area	% Area
1	14.271	2601128	49.92
2	14.900	2609500	50.08



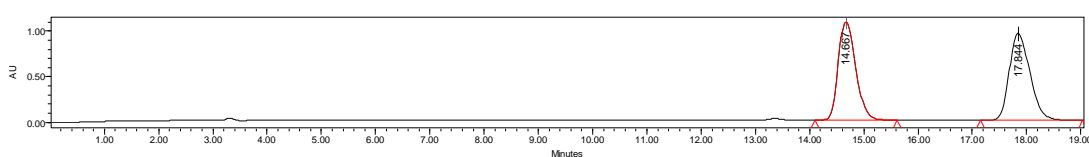
	Retention Time	Area	% Area
1	14.160	15018997	94.07
2	14.828	947460	5.93

### (*R*)-6-ethyl-1-hydroxy-1-methylnaphthalen-2(1H)-one (3s)

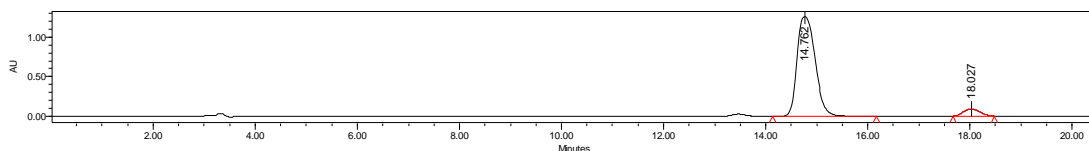


Colorless oil; 99% yield, 94:6 er;  $[\alpha]_D^{25} = 226.64$  ( $c = 0.27$  in  $\text{CH}_2\text{Cl}_2$ ).

HPLC DAICEL CHIRALCEL IC, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min,  $\lambda = 254$  nm,  $t_R$  (major) = 14.76 min,  $t_R$  (minor) = 18.02 min.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.62$  (d,  $J = 7.6$  Hz, 1H), 7.41 (d,  $J = 10.0$  Hz, 1H), 7.31 - 7.26 (m, 1H), 7.13 (s, 1H), 6.18 (d,  $J = 10.0$  Hz, 1H), 3.69 (s, 1H), 2.67 (q,  $J = 7.6$  Hz, 2H), 1.54 (s, 3H), 1.25 (t,  $J = 7.6$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta = 205.6$ , 146.4, 144.1, 142.5, 130.4, 129.0, 128.4, 125.7, 122.4, 77.2, 33.3, 28.5, 15.6. HRMS (ESI-TOF) calcd for  $\text{C}_{13}\text{H}_{14}\text{O}_2\text{Na}^+$  ( $[\text{M}+\text{Na}^+]$ ) = 225.0886, Found 225.0891.

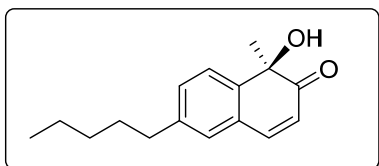


	Retention Time	Area	% Area
1	14.667	24147643	48.98
2	17.844	25150812	51.02



	Retention Time	Area	% Area
1	14.762	30630052	94.04
2	18.027	1942747	5.96

**(R)-1-hydroxy-1-methyl-6-pentyl-naphthalen-2(1H)-one (3t)**



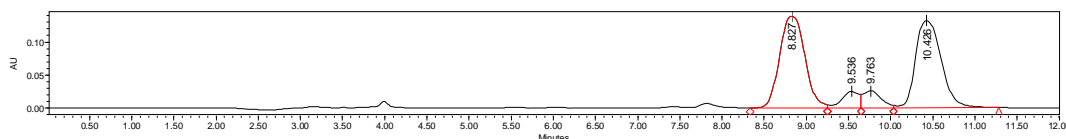
Colorless oil; 99% yield, 94:6 er;  $[\alpha]_D^{25} = 168.94$  ( $c = 0.45$  in  $\text{CH}_2\text{Cl}_2$ ).

HPLC DAICEL CHIRALCEL IC,

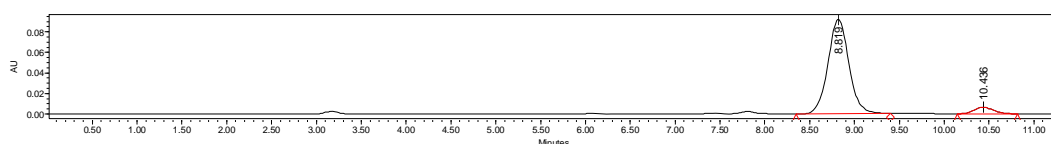
n-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min,  $\lambda = 254$  nm,  $t_R$  (major) = 8.82 min,  $t_R$  (minor) = 10.44 min.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.64 - 7.56$  (m, 1H), 7.44 - 7.38 (m, 1H), 7.28 - 7.24 (m, 1H), 7.13 - 7.08 (m, 1H), 6.18 (m, d,  $J = 10.0$  Hz, 2H), 3.68 (s, 1H), 2.61 (t,  $J = 7.6$  Hz, 2H), 1.68 - 1.56 (m, 2H), 1.55 - 1.52 (m, 3H),



1.39 - 1.26 (m, 4H), 0.92 - 0.85 (m, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 205.6, 146.4, 142.8, 142.4, 130.9, 129.6, 128.3, 125.6, 122.4, 77.1, 35.5, 33.2, 31.5, 31.1, 22.6, 14.1. HRMS (ESI-TOF) calcd for  $\text{C}_{16}\text{H}_{20}\text{O}_2\text{Na}^+$  ( $[\text{M}+\text{Na}^+]$ ) = 267.1356, Found 267.1354.

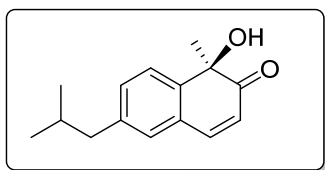


	Retention Time	Area	% Area
1	8.827	2871356	44.86
2	9.536	353367	5.52
3	9.763	377053	5.89
4	10.426	2799469	43.73



	Retention Time	Area	% Area
1	8.819	1492708	93.82
2	10.436	98368	6.18

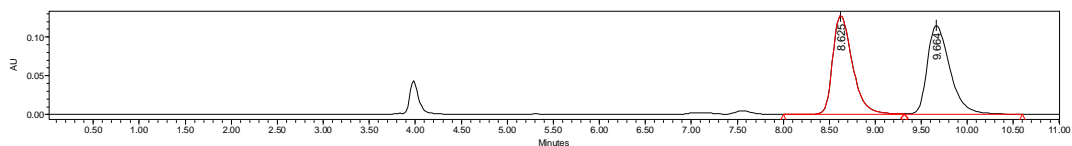
### (*R*)-1-hydroxy-6-isobutyl-1-methylnaphthalen-2(1H)-one (**3u**)



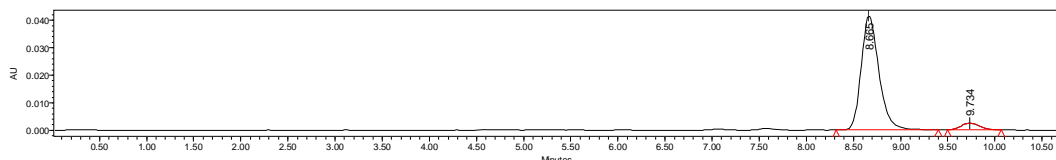
Colorless oil; 96% yield, 94.5:5.5 er;  $[\alpha]_D^{25} = 180.57$  ( $c = 0.39$  in  $\text{CH}_2\text{Cl}_2$ ).

HPLC DAICEL CHIRALCEL IB, n-hexane/2-propanol =

80/20, flow rate = 1.0 mL/min,  $\lambda = 254$  nm,  $t_R$  (major) = 8.66 min,  $t_R$  (minor) = 9.73 min.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.61 (d,  $J = 8.0$  Hz, 1H), 7.40 (d,  $J = 9.6$  Hz, 1H), 7.25 - 7.18 (m, 1H), 7.12 - 7.04 (m, 1H), 6.18 (d,  $J = 10.0$  Hz, 1H), 3.68 (s, 1H), 2.48 (d,  $J = 7.2$  Hz, 2H), 1.93 - 1.81 (m, 1H), 1.54 (s, 3H), 0.91 (d,  $J = 6.8$  Hz, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 205.6, 146.5, 142.5, 141.6, 131.6, 130.2, 128.2, 125.5, 122.4, 77.2, 45.0, 33.3, 30.3, 22.4. HRMS (ESI-TOF) calcd for  $\text{C}_{15}\text{H}_{18}\text{O}_2\text{Na}^+$  ( $[\text{M}+\text{Na}^+]$ ) = 253.1199, Found 253.1198.

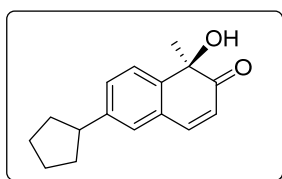


	Retention Time	Area	% Area
1	8.625	1899547	49.35
2	9.664	1949880	50.65



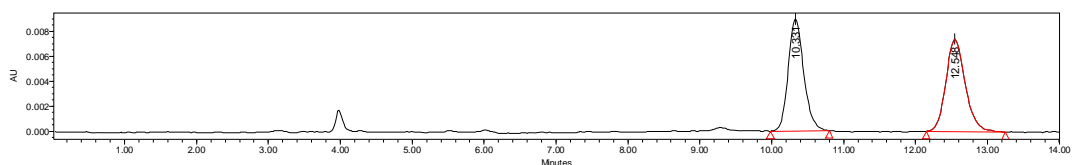
	Retention Time	Area	% Area
1	8.665	544106	94.32
2	9.734	32762	5.68

### **(R)-6-cyclopentyl-1-hydroxy-1-methylnaphthalen-2(1H)-one (3v)**

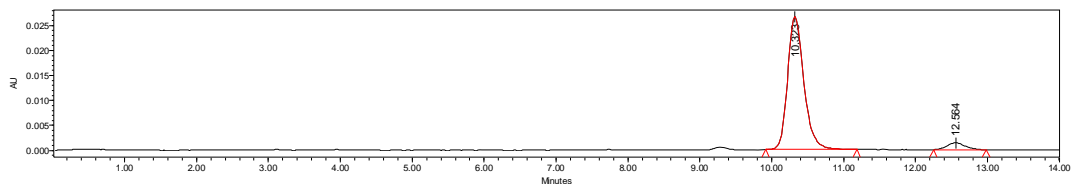


Colorless oil; 96% yield, 94.5:5.5 er;  $[\alpha]_D^{25} = 146.82$  ( $c = 0.44$  in  $\text{CH}_2\text{Cl}_2$ ).

HPLC DAICEL CHIRALCEL IC, n-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min,  $\lambda = 210$  nm,  $t_R$  (major) = 10.32 min,  $t_R$  (minor) = 12.56 min.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.62$  (d,  $J = 8.0$  Hz, 1H), 7.41 (d,  $J = 10.0$  Hz, 1H), 7.34 - 7.30 (m, 1H), 7.18 - 7.13 (m, 1H), 6.18 (d,  $J = 10.0$  Hz, 1H), 3.67 (s, 1H), 3.06 - 2.95 (m, 1H), 2.14 - 2.03 (m, 2H), 1.88 - 1.77 (m, 2H), 1.76 - 1.65 (m, 2H), 1.64 - 1.52 (m, 5H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta = 205.6, 146.5, 146.5, 142.5, 129.6, 128.3, 128.3, 125.6, 122.4, 77.1, 45.5, 34.6, 33.2, 25.6$ . HRMS (ESI-TOF) calcd for  $\text{C}_{16}\text{H}_{18}\text{O}_2\text{Na}^+$  ( $[\text{M}+\text{Na}^+]$ ) = 265.1199, Found 265.1205.

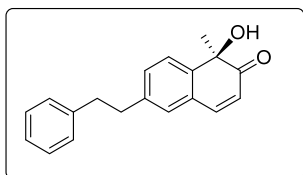


	Retention Time	Area	% Area
1	10.331	134646	49.42
2	12.548	137832	50.58



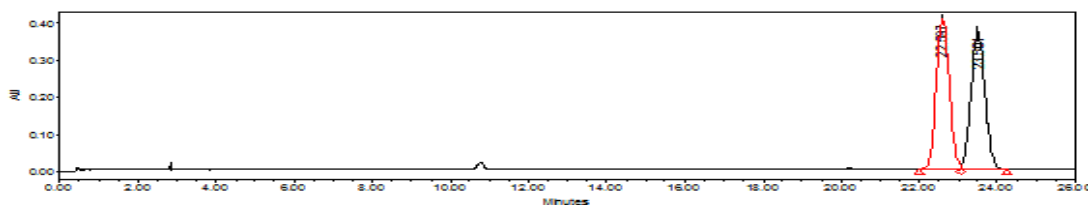
	Retention Time	Area	% Area
1	10.323	417283	94.41
2	12.564	24718	5.59

**(R)-1-hydroxy-1-methyl-6-phenethylnaphthalen-2(1H)-one (3w)**

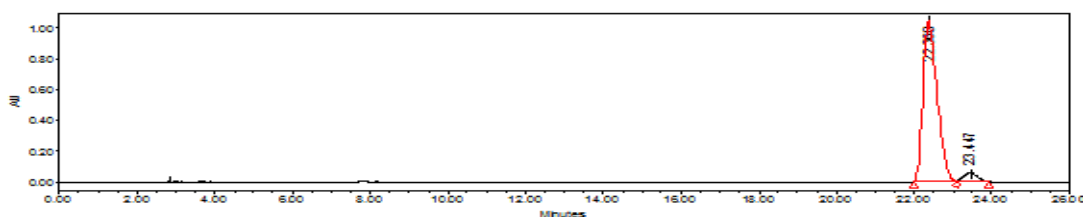


White solid; m.p. 56-58 °C; 95% yield, 95:5 er;  $[\alpha]_D^{25} = 125.34$  ( $c = 0.44$  in  $\text{CH}_2\text{Cl}_2$ ).

UPC<sup>2</sup> Phenomenex CHIRALCEL Lux 5u Cellulose-1,  $\text{scCO}_2/\text{Methol} = 90/10$ , flow rate = 1.0 mL/min,  $\lambda = 254$  nm,  $t_R$  (major) = 22.37 min,  $t_R$  (minor) = 23.45 min. <sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.62$  (d,  $J = 6.0$  Hz, 1H), 7.38 (d,  $J = 10.0$  Hz, 1H), 7.32 - 7.24 (m, 3H), 7.23 - 7.15 (m, 3H), 7.08 (s, 1H), 6.18 (d,  $J = 10.0$  Hz, 1H), 3.69 (s, 1H), 2.93 (s, 4H), 1.54 (s, 3H); <sup>13</sup>C NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta = 205.5, 146.3, 142.8, 141.6, 141.4, 131.0, 129.6, 128.6, 128.6, 128.4, 126.3, 125.7, 122.5, 77.1, 37.8, 37.5, 33.3$ . HRMS (ESI-TOF) calcd for  $\text{C}_{19}\text{H}_{18}\text{O}_2\text{Na}^+$  ( $[\text{M}+\text{Na}^+]$ ) = 301.1199, Found 301.1205.

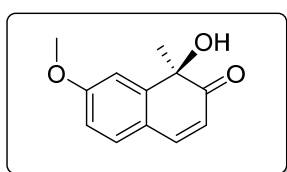


	Retention Time	Area	% Area
1	22.597	9332521	50.23
2	23.501	9247022	49.77



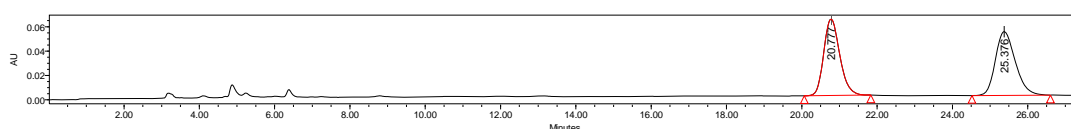
	Retention Time	Area	% Area
1	22.368	26257261	94.78
2	23.447	1446971	5.22

**(R)-1-hydroxy-7-methoxy-1-methylnaphthalen-2(1H)-one (3x)**

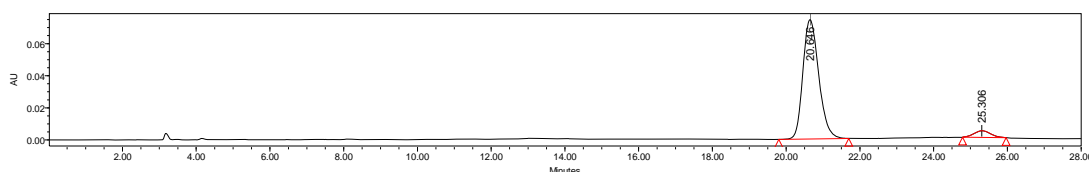


White solid; m.p. 42-43 °C; 99% yield, 94.5:5.5 er;  $[\alpha]_D^{25} = 319.50$  ( $c = 0.40$  in  $\text{CH}_2\text{Cl}_2$ ).

HPLC DAICEL CHIRALCEL IC, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min,  $\lambda = 254$  nm,  $t_R$  (major) = 20.65 min  $t_R$  (minor) = 25.31 min.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.39$  (d,  $J = 10.0$  Hz, 1H), 7.28 - 7.25 (m, 1H), 7.23 (d,  $J = 8.4$  Hz, 1H), 6.82 (dd,  $J = 8.8$  Hz, 2.4 Hz, 1H), 6.07 (d,  $J = 9.6$  Hz, 1H), 3.88 (s, 3H), 3.84 - 3.79 (m, 1H), 1.54 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta = 205.4, 162.0, 147.8, 146.1, 131.3, 121.6, 119.7, 113.6, 111.2, 77.4, 55.7, 33.7$ . HRMS (ESI-TOF) calcd for  $\text{C}_{12}\text{H}_{12}\text{O}_3\text{Na}^+$  ( $[\text{M}+\text{Na}^+]$ ) = 227.0679, Found 227.0678.

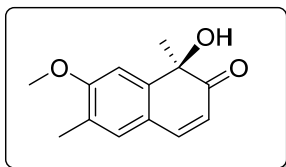


	Retention Time	Area	% Area
1	20.777	1856593	49.14
2	25.376	1921465	50.86



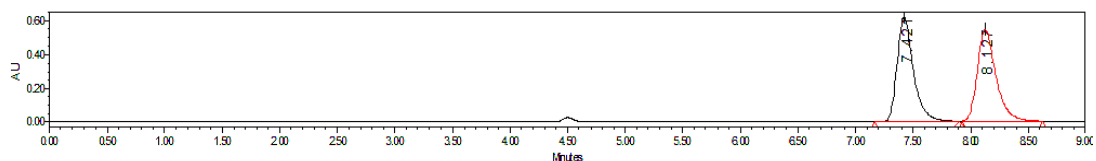
	Retention Time	Area	% Area
1	20.646	2219533	94.46
2	25.306	130079	5.54

**(R)-1-hydroxy-7-methoxy-1,6-dimethylnaphthalen-2(1H)-one (3y)**

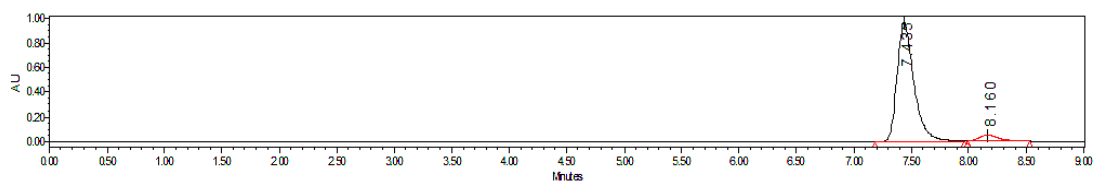


Yellow oil; 99% yield, 95:5 er;  $[\alpha]_D^{16} = 348.98$  ( $c = 0.40$  in  $\text{CH}_2\text{Cl}_2$ ).

HPLC DAICEL CHIRALCEL IA, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min,  $\lambda = 254$  nm,  $t_R$  (major) = 7.44 min,  $t_R$  (minor) = 8.16 min.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.35$  (d,  $J = 10.0$  Hz, 1H), 7.18 (s, 1H), 7.06 (s, 1H), 6.05 (d,  $J = 9.6$  Hz, 1H), 3.92 (s, 3H), 3.83 - 3.73 (m, 1H), 2.20 (s, 3H), 1.54 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta = 205.8, 160.2, 146.4, 145.4, 132.0, 126.0, 120.9, 119.5, 107.4, 77.4, 55.8, 55.8, 33.8, 15.9$ . HRMS (ESI-TOF) calcd for  $\text{C}_{13}\text{H}_{14}\text{O}_3\text{Na}^+$  ( $[\text{M}+\text{Na}^+]$ ) = 241.0835, Found 241.0838.

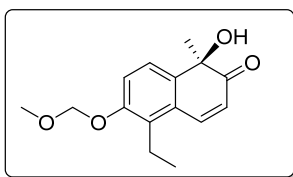


	Retention Time	Area	% Area
1	7.421	6202438	50.52
2	8.127	6075532	49.48



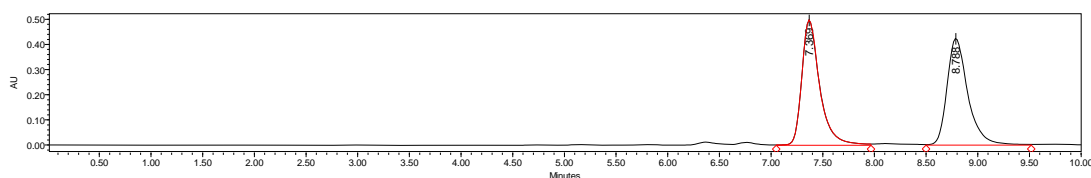
	Retention Time	Area	% Area
1	7.435	9925051	94.75
2	8.160	550175	5.25

**(R)-5-ethyl-1-hydroxy-6-(methoxymethoxy)-1-methylnaphthalen-2(1H)-one (3z)**

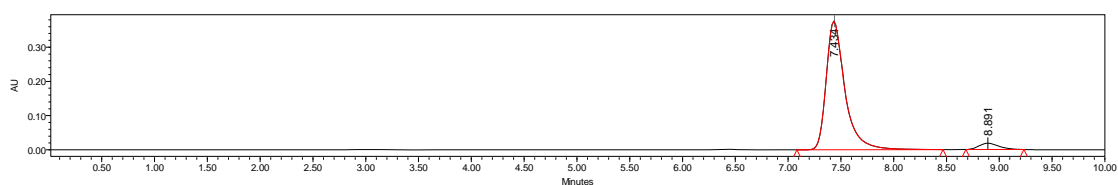


Yellow solid; m.p. 82-84 °C; 99% yield, 95:5 er;  $[\alpha]_D^{16} = 126.92$  ( $c = 0.66$  in  $\text{CH}_2\text{Cl}_2$ ).

HPLC DAICEL CHIRALCEL IA, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min,  $\lambda = 254$  nm,  $t_R$  (major) = 7.43 min,  $t_R$  (minor) = 8.89 min.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.75$  (d,  $J = 10.4$  Hz, 1H), 7.49 (d,  $J = 8.4$  Hz, 1H), 7.16 (d,  $J = 8.4$  Hz, 1H), 6.22 (d,  $J = 10.0$  Hz, 4H), 5.27 - 5.17 (m, 2H), 3.66 (s, 1H), 3.49 (s, 3H), 2.94 - 2.78 (m, 2H), 1.53 (s, 3H), 1.16 (t,  $J = 7.6$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta = 205.5, 154.4, 142.0, 132.8, 124.0, 122.6, 116.0, 94.6, 77.1, 56.2, 33.5, 18.7, 15.6$ . HRMS (ESI-TOF) calcd for  $\text{C}_{15}\text{H}_{18}\text{O}_4\text{Na}^+$  ( $[\text{M}+\text{Na}^+]$ ) = 285.1097, Found 285.1107.

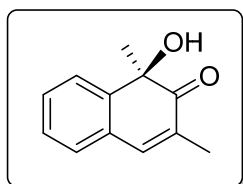


	Retention Time	Area	% Area
1	7.369	6012927	50.27
2	8.788	5948623	49.73



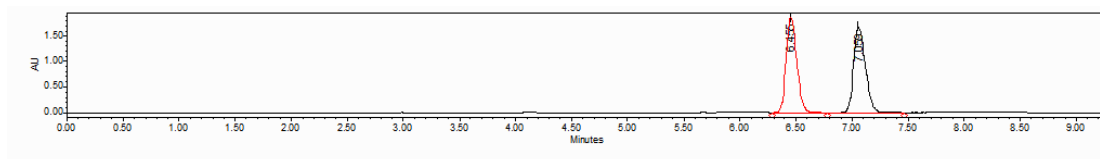
	Retention Time	Area	% Area
1	7.434	4632099	95.03
2	8.891	242466	4.97

**(R)-1-hydroxy-1,3-dimethylnaphthalen-2(1H)-one (3aa)**

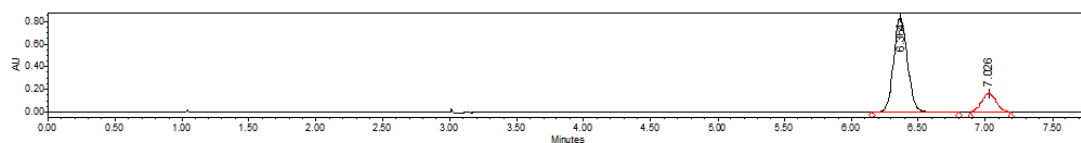


Colorless oil; 99% yield, 83.5:16.5 er;  $[\alpha]_D^{19} = 289.62$  ( $c = 0.21$  in  $\text{CH}_2\text{Cl}_2$ ).

UPC<sup>2</sup> Phenomenex CHIRALCEL Lux 5u Cellulose-3, scCO<sub>2</sub>/Methol = 95/5, flow rate = 1.0 mL/min,  $\lambda$  = 254 nm,  $t_R$  (major) = 6.36 min,  $t_R$  (minor) = 7.03 min. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.66 (d,  $J$  = 7.6 Hz, 1H), 7.40 - 7.34 (m, 1H), 7.32 - 7.26 (m, 1H), 7.24 - 7.17 (m, 2H), 3.73 (s, 1H), 2.04 (d,  $J$  = 1.6 Hz, 3H), 1.52 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 206.0, 144.2, 142.2, 130.5, 129.6, 128.7, 128.6, 127.9, 125.4, 77.1, 33.4, 15.5. HRMS (ESI-TOF) calcd for C<sub>12</sub>H<sub>12</sub>O<sub>2</sub>Na<sup>+</sup> ([M+Na<sup>+</sup>]) = 211.0730, Found 211.0733.

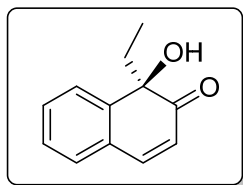


	Retention Time	Area	% Area
1	6.455	12197643	50.14
2	7.059	12130866	49.86



	Retention Time	Area	% Area
1	6.364	5965937	83.60
2	7.026	1170699	16.40

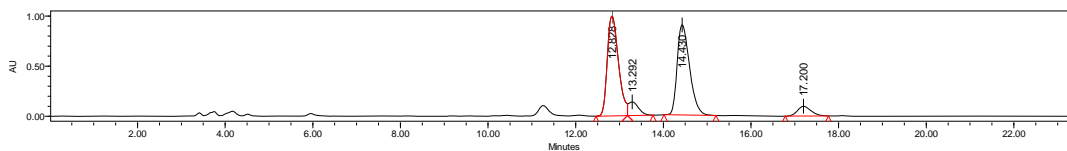
### (*R*)-1-ethyl-1-hydroxynaphthalen-2(1H)-one (**3ab**)



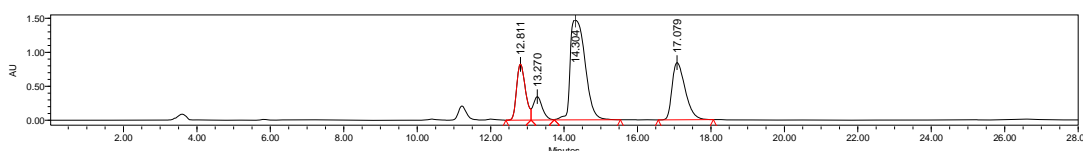
Colorless oil; 64% for total yield of **3ab** and **4ab**, **3ab/4ab** = 85:15 by <sup>1</sup>H NMR. 75:25 er/78:22 er.

HPLC DAICEL CHIRALCEL IE, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min,  $\lambda$  = 254 nm,  $t_R$  (minor) = 12.81 min,  $t_R$  (major) = 14.30 min. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.65 (d,  $J$  = 7.6 Hz, 1H), 7.46 - 7.37 (m, 2H), 7.34 - 7.24 (m, 2H), 6.17 (d,  $J$  = 9.6 Hz, 1H), 3.74 (s, 1H), 1.92 - 1.70 (m, 2H), 0.82 (t,  $J$  = 7.6 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 205.6, 146.0,

144.5 130.3, 129.4, 129.1 127.9, 126.2, 122.9, 80.3, 38.7, 8.2. HRMS (ESI-TOF)  
 calcd for C<sub>12</sub>H<sub>12</sub>O<sub>2</sub>Na<sup>+</sup> ([M+Na<sup>+</sup>]) = 211.0730, Found 211.0735.

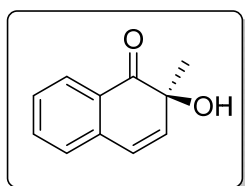


	Retention Time	Area	% Area
1	12.828	17644988	44.52
2	13.292	2195792	5.54
3	14.430	17700654	44.66
4	17.200	2092157	5.28



	Retention Time	Area	% Area
1	12.811	13769071	16.75
2	13.270	5985305	7.28
3	14.304	41585000	50.58
4	17.079	20869517	25.39

### (S)-2-hydroxy-2-methylnaphthalen-1(2H)-one (3ad)



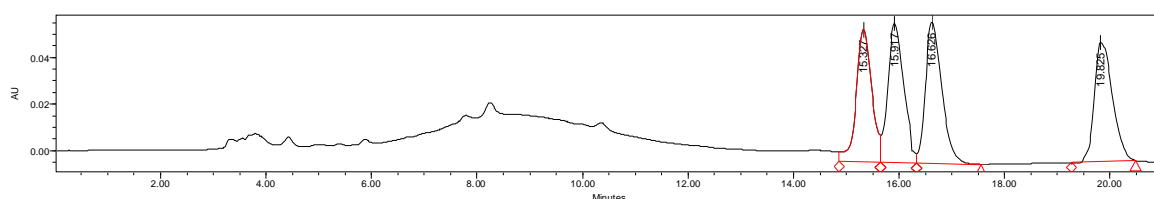
Colorless oil; 46% yield, 77:23 er.  $[\alpha]_D^{19} = 142.27$  ( $c = 0.19$  in CH<sub>2</sub>Cl<sub>2</sub>).

HPLC DAICEL CHIRALCEL IE, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min,  $\lambda = 254$  nm,  $t_R$  (major) = 15.53 min,  $t_R$

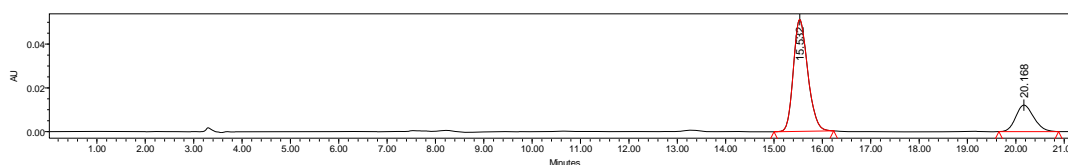
(minor) = 20.17 min. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta = 7.98$  (d,  $J = 8.0$  Hz, 1H), 7.59 (t,  $J = 7.6$  Hz, 1H), 7.36 (t,  $J = 7.6$  Hz, 1H), 7.22 (d,  $J = 7.6$  Hz, 1H), 6.51 - 6.44 (m, 1H), 6.37 - 6.29 (m, 1H), 3.40 (s, 1H), 1.45 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta = 204.4, 138.0, 137.1, 135.3, 128.3, 128.3, 127.6, 127.4, 124.4, 75.5, 28.7$ . HRMS



(ESI-TOF) calcd for  $C_{11}H_{10}O_2Na^+$  ( $[M+Na^+]$ ) = 197.0573, Found 197.0574.

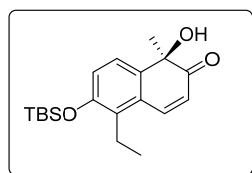


	Retention Time	Area	% Area
1	15.327	1171769	23.50
2	15.917	1270613	25.48
3	16.626	1316241	26.40
4	19.825	1227859	24.62



	Retention Time	Area	% Area
1	15.532	1058324	77.12
2	20.168	313993	22.88

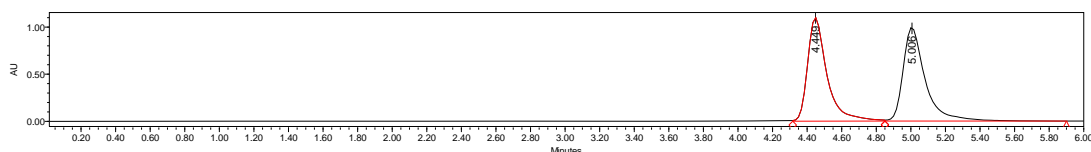
**(R)-6-((tert-butyldimethylsilyl)oxy)-5-ethyl-1-hydroxy-1-methylnaphthalen-2(1H)-one (3ae)**



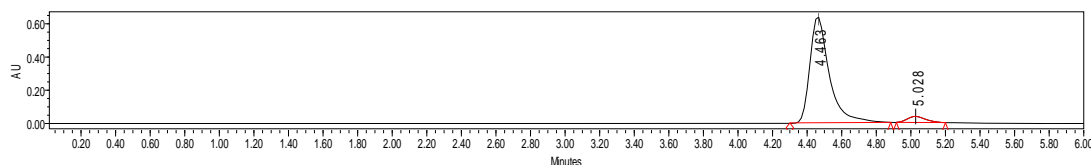
White solid; m.p. 70-72 °C; 99% yield, 95:5 er;  $[\alpha]_D^{19} = 86.56$  ( $c = 0.45$  in  $CH_2Cl_2$ ).

HPLC DAICEL CHIRALCEL IA, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min,  $\lambda = 254$  nm,  $t_R$  (major) = 4.46 min,  $t_R$  (minor) = 5.03 min.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta = 7.73$  (d,  $J = 10.0$  Hz, 1H), 7.41 (d,  $J = 8.4$  Hz, 1H), 6.86 (d,  $J = 8.4$  Hz, 1H), 6.20 (d,  $J = 10.4$  Hz, 1H), 3.65 (s, 1H), 2.89 - 2.75 (m, 2H), 1.53 (s, 3H), 1.13 (t,  $J = 7.6$  Hz, 3H), 1.03 (s, 9H), 0.27 (s, 3H), 0.24 (s, 3H);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta = 205.6, 153.0, 142.4, 138.3, 134.3, 127.2, 123.8, 122.4, 120.2, 77.1, 33.5, 25.8, 19.0, 18.4, 15.6, -3.9, -4.2$ . HRMS (ESI-TOF) calcd for  $C_{19}H_{28}O_3Si$

$\text{Na}^+$  ( $[\text{M}+\text{Na}^+]$ ) = 355.1705, Found 355.1707.

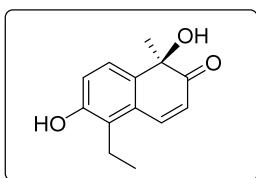


	Retention Time	Area	% Area
1	4.449	8561111	49.28
2	5.006	8812535	50.72



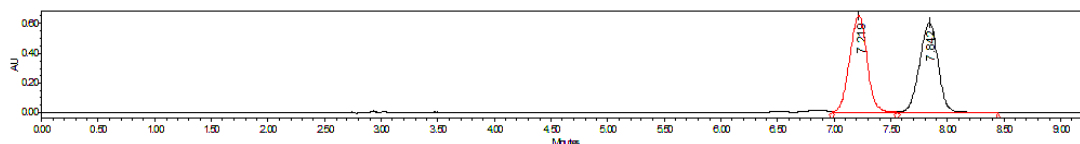
	Retention Time	Area	% Area
1	4.463	4940562	94.91
2	5.028	264748	5.09

**(R)-5-ethyl-1,6-dihydroxy-1-methylnaphthalen-2(1H)-one (lacinilene D)**

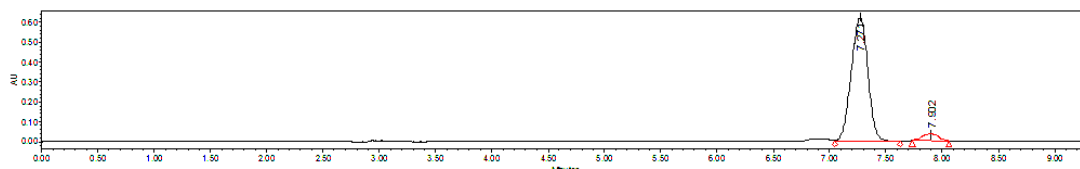


Yellow solid; m.p. 134-136 °C; 99% yield, 95:5 er;  $[\alpha]_D^{19} = 162.11$  ( $c = 0.45$  in  $\text{CH}_2\text{Cl}_2$ ).

UPC<sup>2</sup> Phenomenex CHIRALCEL Lux 5u Cellulose-1,  $\text{scCO}_2/\text{Methol} = 80/20$ , flow rate = 1.0 mL/min,  $\lambda = 254$  nm,  $t_R$  (major) = 7.27 min,  $t_R$  (minor) = 7.90 min.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.75$  (d,  $J = 10.4$  Hz, 1H), 7.41 (d,  $J = 8.4$  Hz, 1H), 6.84 (d,  $J = 8.4$  Hz, 1H), 6.23 (d,  $J = 10.4$  Hz, 1H), 5.33 (s, 1H), 3.67 (s, 1H), 2.91 - 2.71 (m, 2H), 1.53 (s, 3H), 1.18 (t,  $J = 7.6$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta = 205.8, 153.0, 142.2, 138.1, 129.9, 127.1, 124.0, 122.6, 117.4, 77.2, 33.5, 18.6, 15.4$ . HRMS (ESI-TOF) calcd for  $\text{C}_{13}\text{H}_{14}\text{O}_3\text{Na}^+$  ( $[\text{M}+\text{Na}^+]$ ) = 241.0841, Found 241.0841.

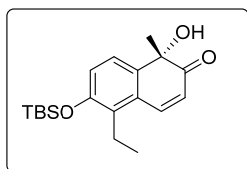


	Retention Time	Area	% Area
1	7.219	6889209	50.37
2	7.842	6787522	49.63



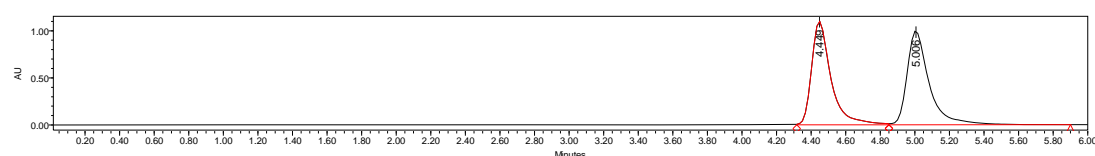
	Retention Time	Area	% Area
1	7.271	6421072	94.92
2	7.902	343676	5.08

**(S)-6-((tert-butyldimethylsilyl)oxy)-5-ethyl-1-hydroxy-1-methylnaphthalen-2(1H)-one (3ae)**

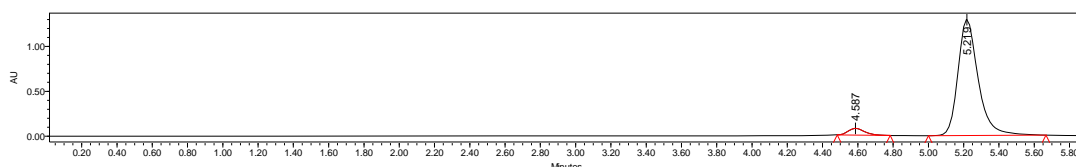


White solid; m.p. 68-70 °C; 99% yield, 95.5:4.5 er;  $[\alpha]_D^{19} = -91.25$  ( $c = 0.56$  in  $\text{CH}_2\text{Cl}_2$ ).

HPLC DAICEL CHIRALCEL IA, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min,  $\lambda = 254$  nm,  $t_R$  (minor) = 4.59 min,  $t_R$  (major) = 5.22 min.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.73$  (d,  $J = 10.0$  Hz, 1H), 7.41 (d,  $J = 8.4$  Hz, 1H), 6.86 (d,  $J = 8.4$  Hz, 1H), 6.20 (d,  $J = 10.4$  Hz, 1H), 3.65 (s, 1H), 2.89 - 2.75 (m, 2H), 1.53 (s, 3H), 1.13 (t,  $J = 7.6$  Hz, 3H), 1.03 (s, 9H), 0.27 (s, 3H), 0.24 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta = 205.6, 153.0, 142.4, 138.3, 134.3, 127.2, 123.8, 122.4, 120.2, 77.1, 33.5, 25.8, 19.0, 18.4, 15.6, -3.9, -4.2$ . HRMS (ESI-TOF) calcd for  $\text{C}_{19}\text{H}_{28}\text{O}_3\text{Si Na}^+$  ( $[\text{M}+\text{Na}^+]$ ) = 355.1705, Found 355.1707.

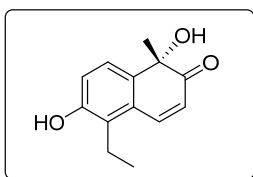


	Retention Time	Area	% Area
1	4.449	8561111	49.28
2	5.006	8812535	50.72



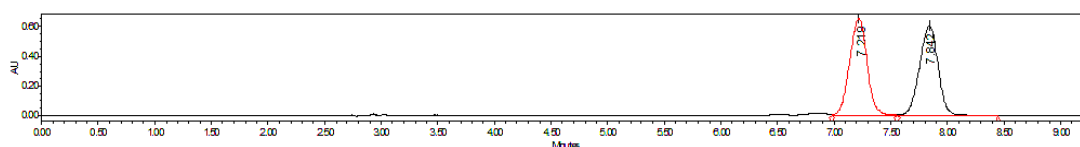
	Retention Time	Area	% Area
1	4.587	487245	4.52
2	5.219	10302329	95.48

**(S)-5-ethyl-1,6-dihydroxy-1-methylnaphthalen-2(1H)-one (lacinilene D)**

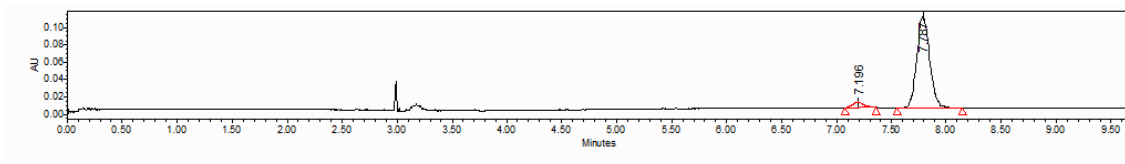


Yellow solid; m.p. 134-136 °C; 99% yield, 95:5 er;  $[\alpha]_D^{19} = -177.58$  ( $c = 0.33$  in  $\text{CH}_2\text{Cl}_2$ ).

UPC<sup>2</sup> Phenomenex CHIRALCEL Lux 5u Cellulose-1,  $\text{scCO}_2/\text{Methol} = 80/20$ , flow rate = 1.0 mL/min,  $\lambda = 254$  nm,  $t_R$  (minor) = 7.20 min,  $t_R$  (major) = 7.79 min.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.75$  (d,  $J = 10.4$  Hz, 1H), 7.41 (d,  $J = 8.4$  Hz, 1H), 6.84 (d,  $J = 8.4$  Hz, 1H), 6.23 (d,  $J = 10.4$  Hz, 1H), 5.33 (s, 1H), 3.67 (s, 1H), 2.91 - 2.71 (m, 2H), 1.53 (s, 3H), 1.18 (t,  $J = 7.6$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta = 205.8, 153.0, 142.2, 138.1, 129.9, 127.1, 124.0, 122.6, 117.4, 77.2, 33.5, 18.6, 15.4$ . HRMS (ESI-TOF) calcd for  $\text{C}_{13}\text{H}_{14}\text{O}_3\text{Na}^+$  ( $[\text{M}+\text{Na}^+]$ ) = 241.0841, Found 241.0841.

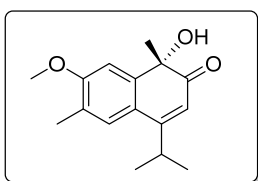


	Retention Time	Area	% Area
1	7.219	6889209	50.37
2	7.842	6787522	49.63



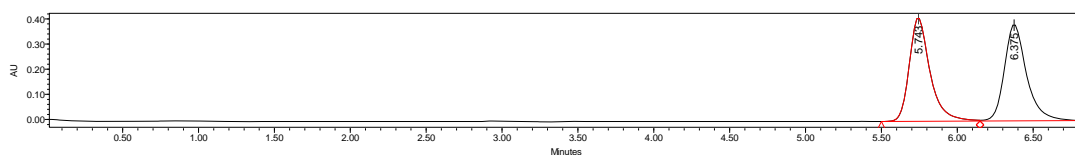
	Retention Time	Area	% Area
1	7.196	48556	5.27
2	7.787	872067	94.73

**(S)-1-hydroxy-4-isopropyl-7-methoxy-1,6-dimethylnaphthalen-2(1H)-one  
(lacinilene C methyl ether)**

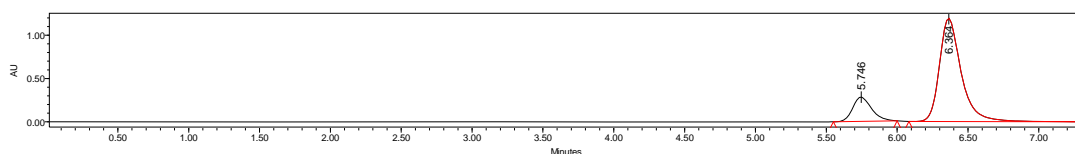


White solid; m.p. 98-100 °C; 99% yield, 83:17 er;  $[\alpha]_D^{19} = -237.29$  ( $c = 0.24$  in  $\text{CH}_2\text{Cl}_2$ ).

HPLC DAICEL CHIRALCEL IA, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min,  $\lambda = 254$  nm,  $t_R$  (minor) = 5.75 min,  $t_R$  (major) = 6.36 min.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.35$  (s, 1H), 7.21 (s, 1H), 6.02 (s, 1H), 3.92 (s, 3H), 3.87 (s, 1H), 3.28 - 3.15 (m, 1H), 2.24 (s, 3H), 1.53 (s, 3H), 1.27 (t,  $J = 6.4$  Hz, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta = 205.7, 164.4, 159.6, 145.7, 127.8, 125.5, 121.0, 114.9, 107.4, 77.0, 55.8, 34.1, 29.3, 22.4, 22.1, 16.4$ . HRMS (ESI-TOF) calcd for  $\text{C}_{16}\text{H}_{20}\text{O}_3\text{Na}^+$  ( $[\text{M}+\text{Na}^+]$ ) = 283.1305, Found 283.1315.



	Retention Time	Area	% Area
1	5.743	3907821	50.08
2	6.375	3894746	49.92



	Retention Time	Area	% Area
1	5.746	2596264	16.99
2	6.364	12682637	83.01

## 11. The X-ray data for 3ae

The **3ae** was recrystallized from Pet.

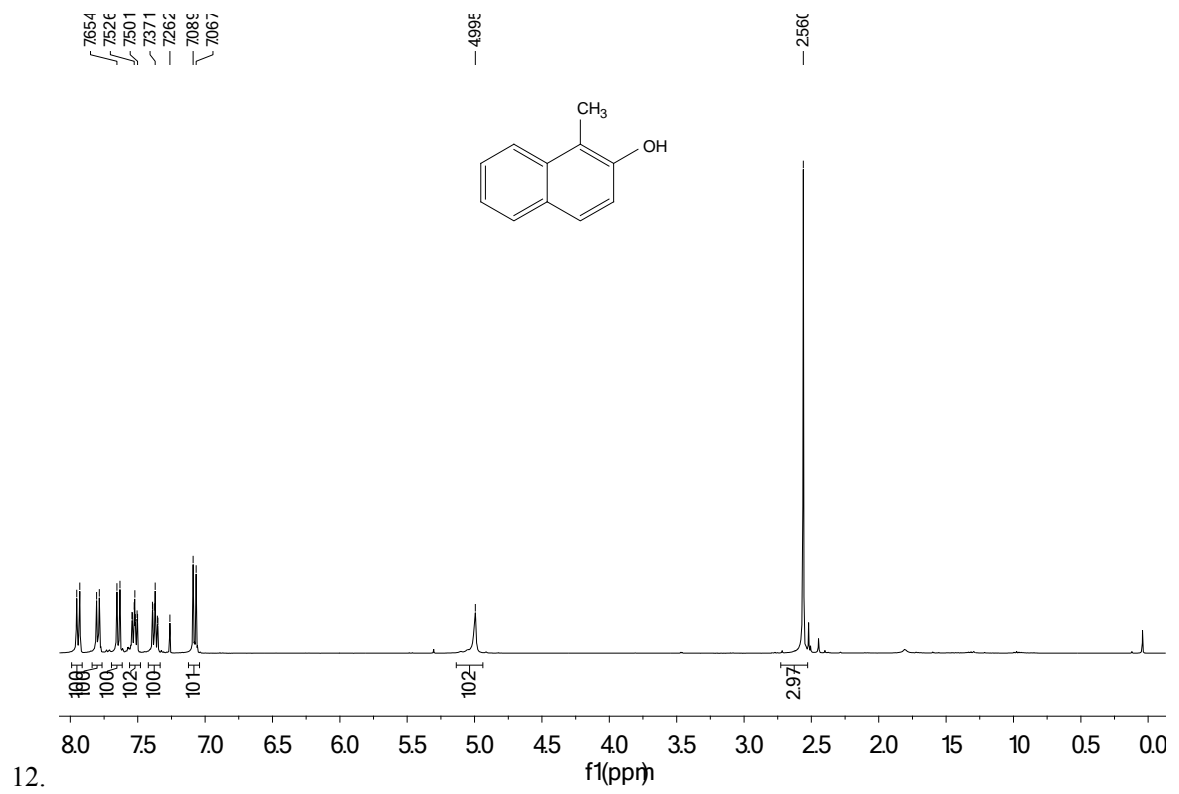
CCDC-1536822 (**3ae**) contain the supplementary crystallographic data for this paper.

These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/ data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

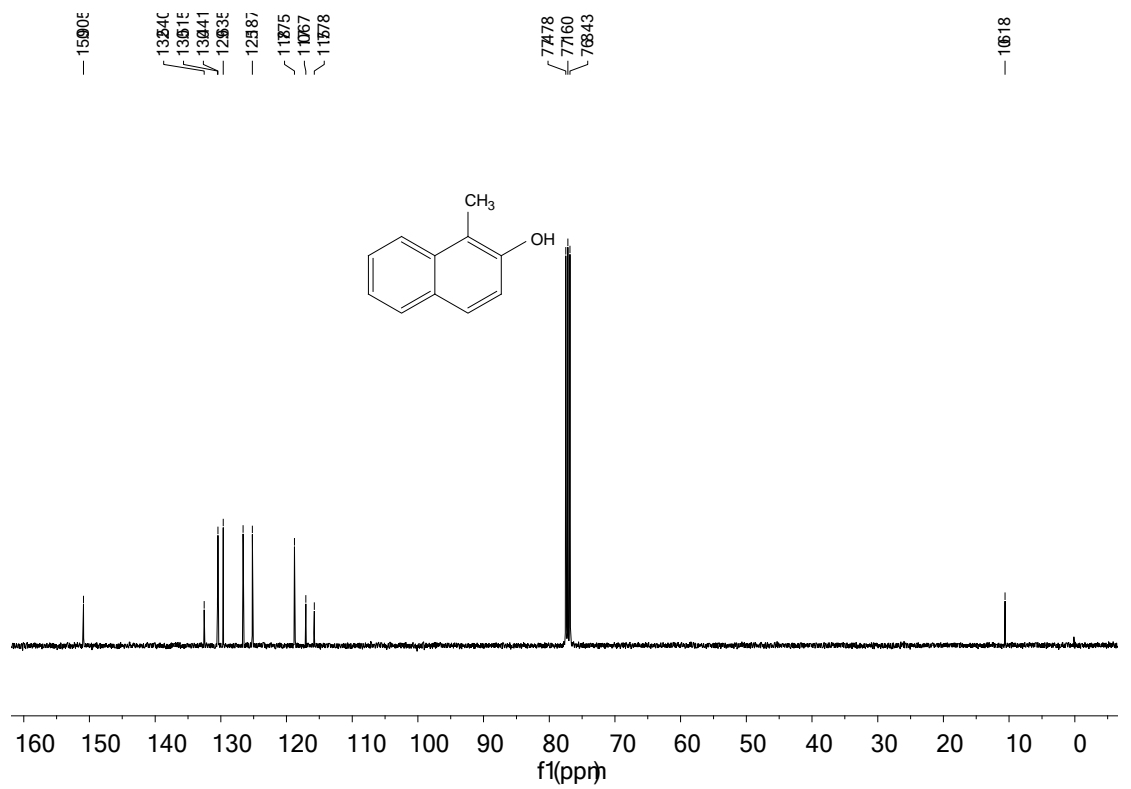
## 12. References

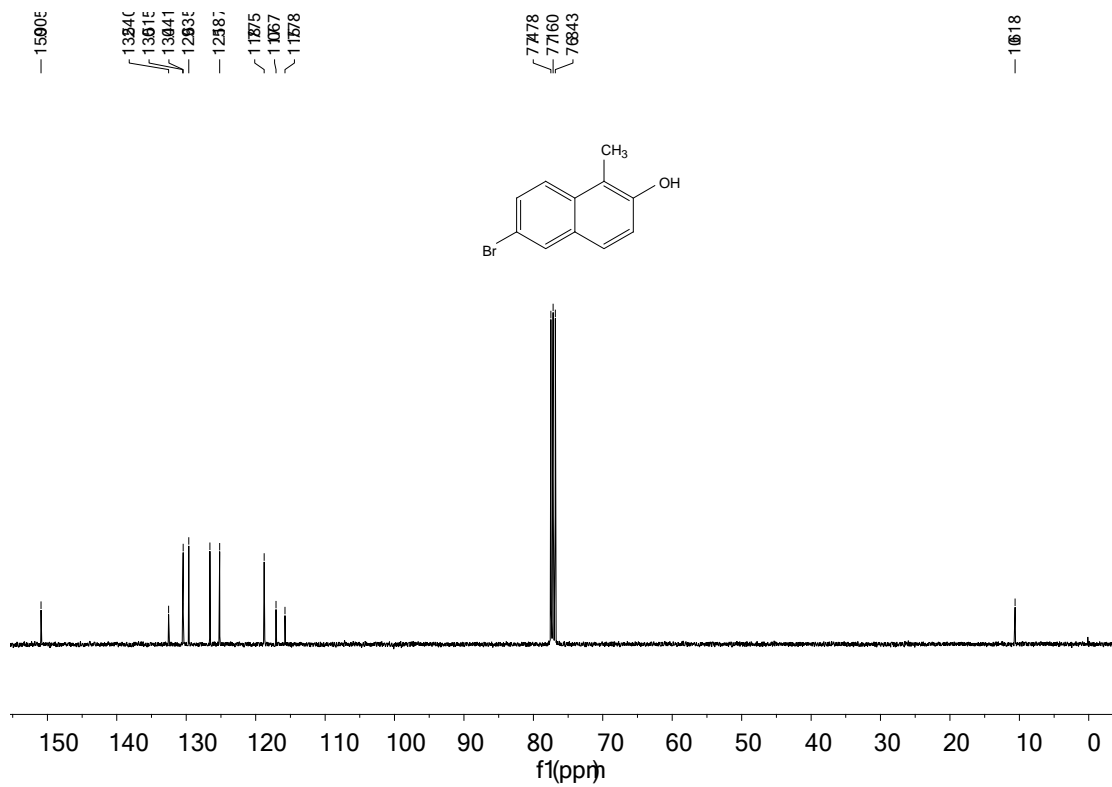
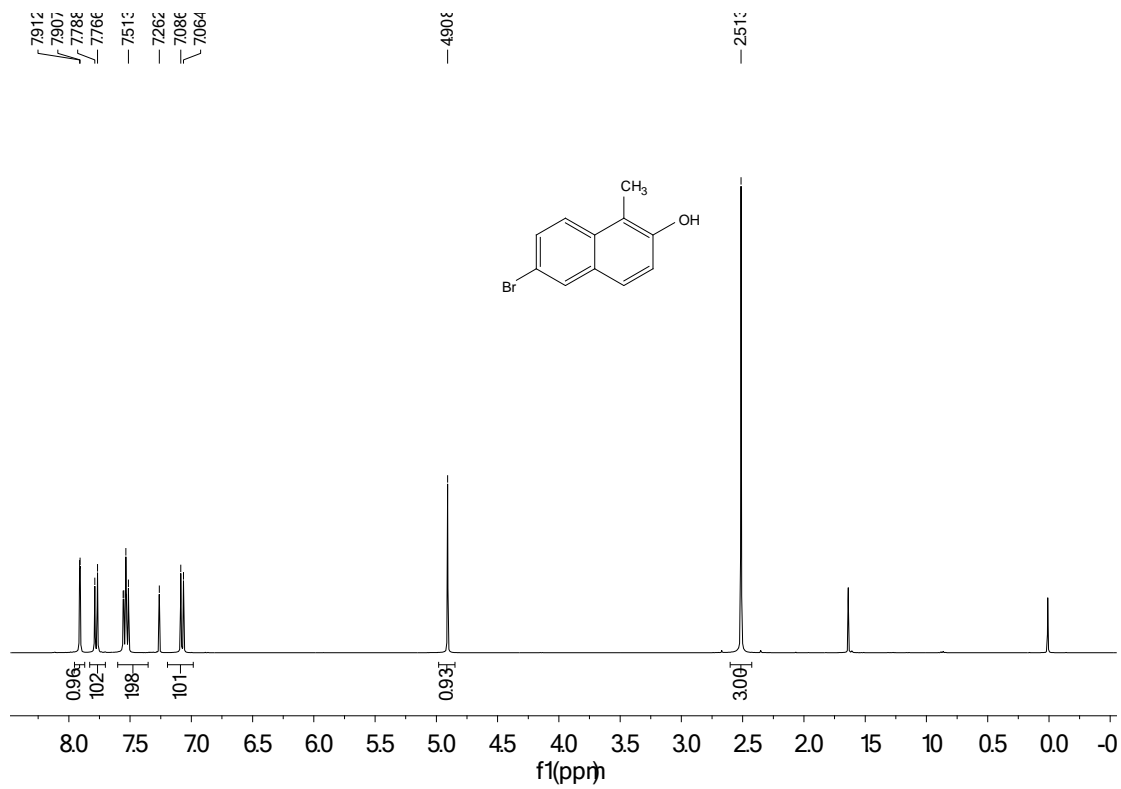
- [1]. T. Oguma, T. Katsuki, *J. Am. Chem. Soc.* **2012**, *134*, 20017-20020.
- [2]. T. Kaku, N. Matsunaga, A. Ojida, T. Tanaka, T. Hara, M. Yamaoka, M. Kusaka, A. Tasaka, *Bioorganic & Medicinal Chemistry*. **2011**, *19*, 1751-1770.
- [3]. Q. Yin, S.-G. Wang, X.-W. Liang, D.-W. Gao, J. Zheng S.-L. You, *Chem. Sci.* **2015**, *6*, 4179-4183.
- [3]. C. Bosset, R. Coffinier, P. A. Peixoto, M. El Assal, K. Miqueu, J.-M. Sotiropoulos, L. Pouységu, S. Quideau, *Angew. Chem.* **2014**, *126*, 10018-10022; *Angew. Chem., Int. Ed.* **2014**, *53*, 9860-9864.
- [5]. K. Krohn, G. Zimmermann, *J. Org. Chem.* **1998**, *63*, 4140-4142.
- [6]. a) X. H. Liu, L. L. Lin, X. M. Feng, *Acc. Chem. Res.* **2011**, *44*, 574-587; b) X. H. Liu, L. L. Lin, X. M. Feng, *Org. Chem. Front.* **2014**, *1*, 298-302.

### 13. Copies of NMR spectra

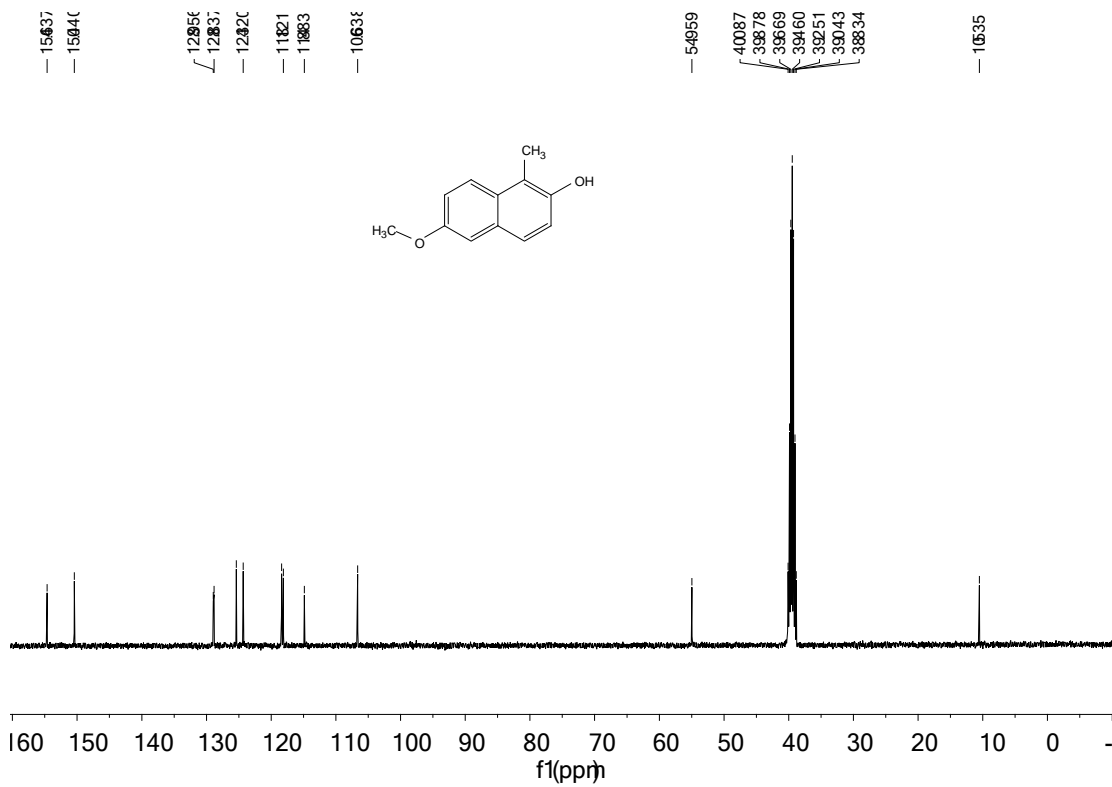
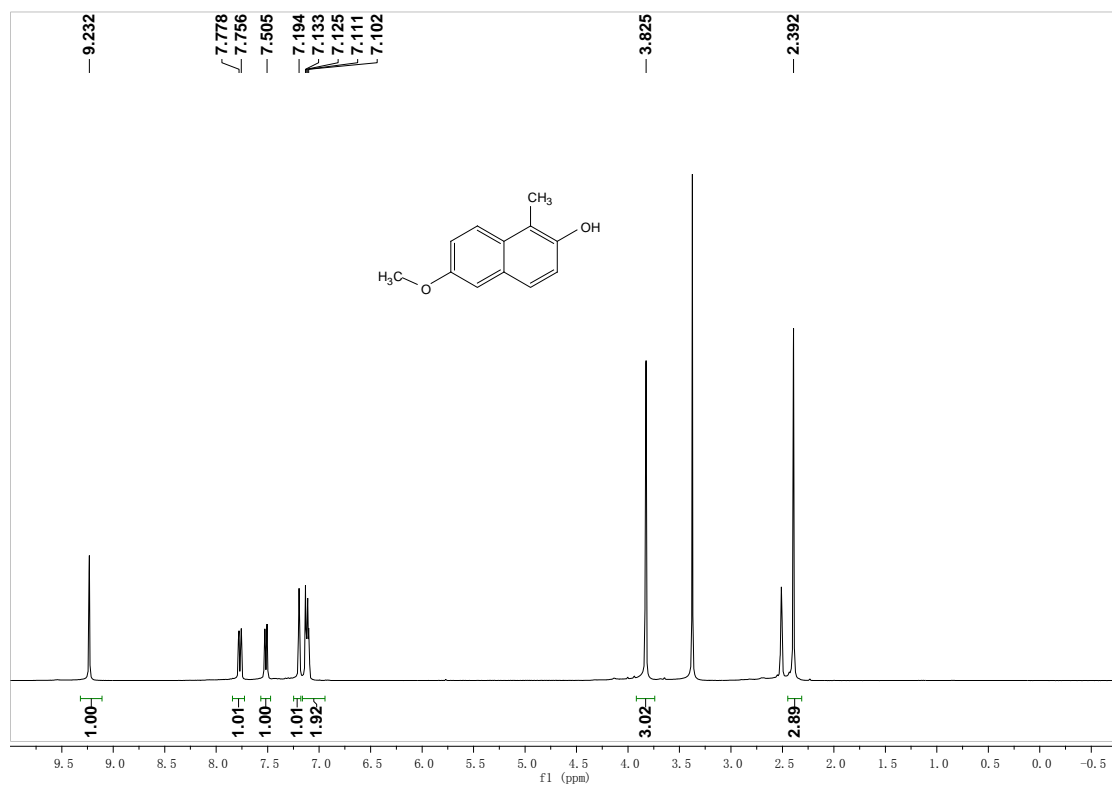


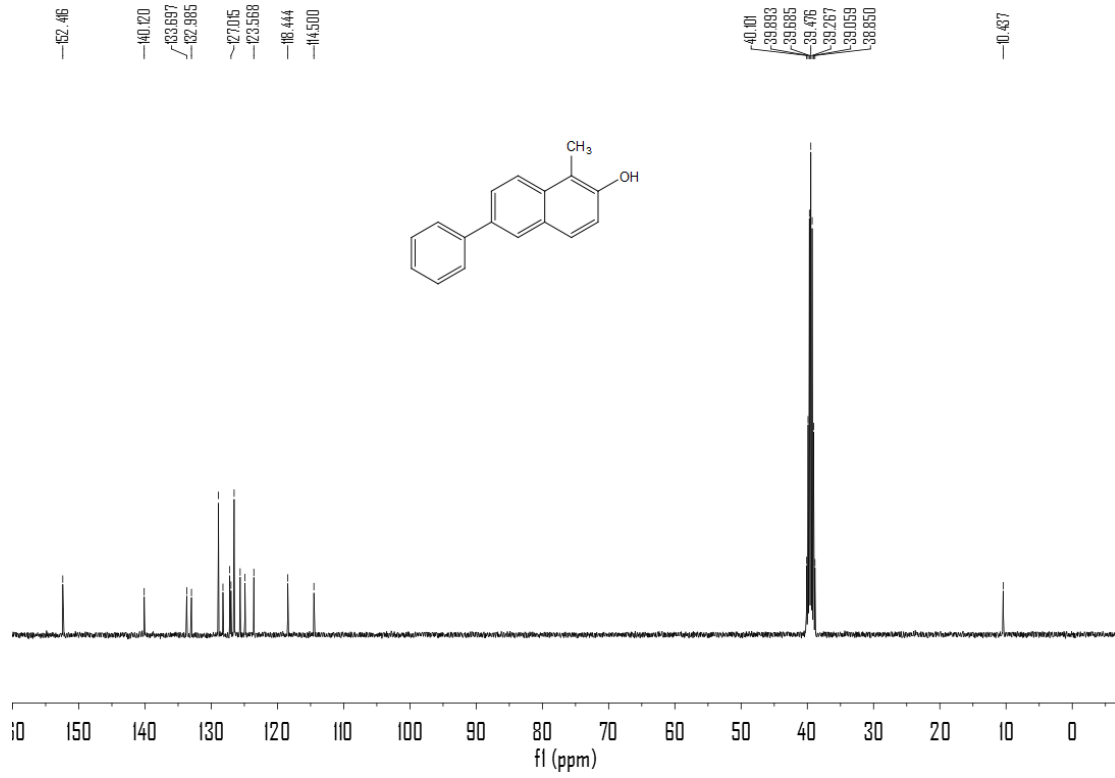
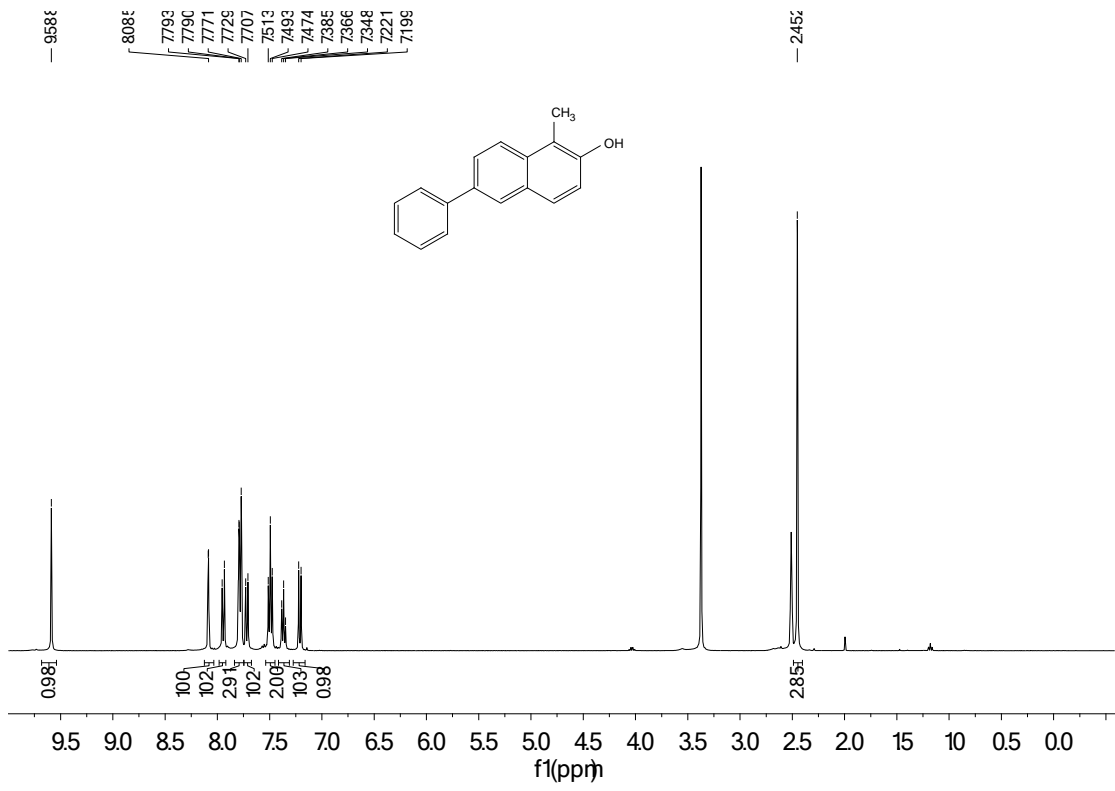
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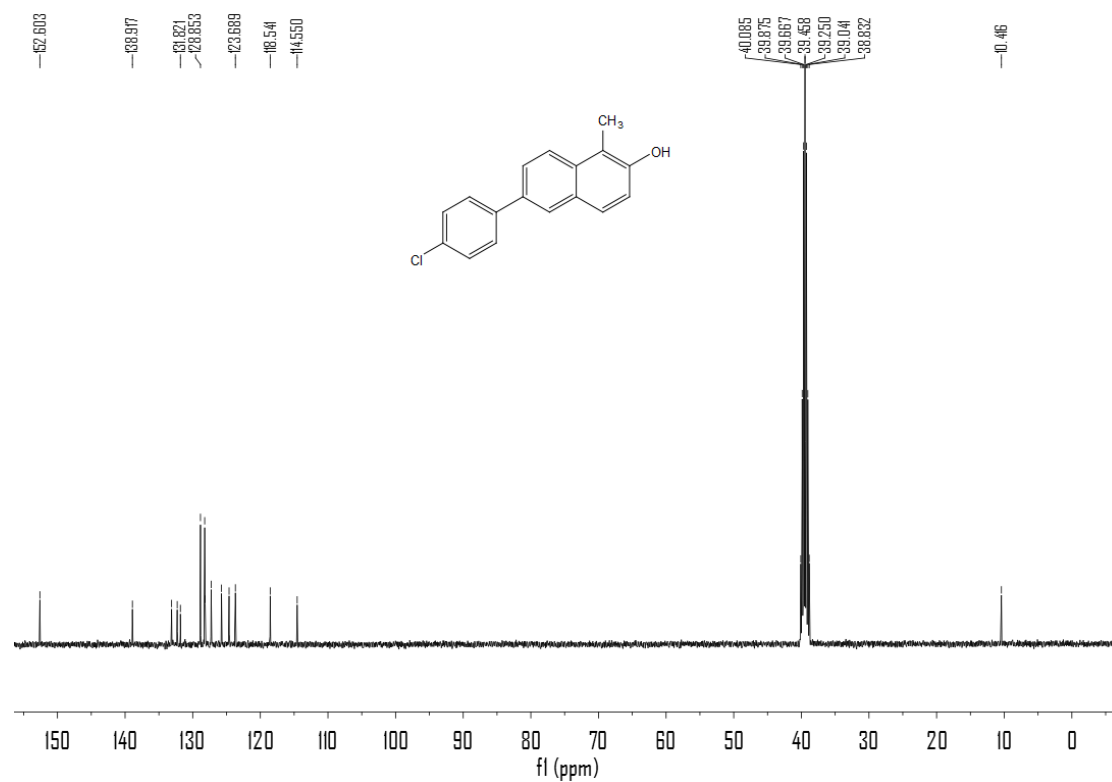
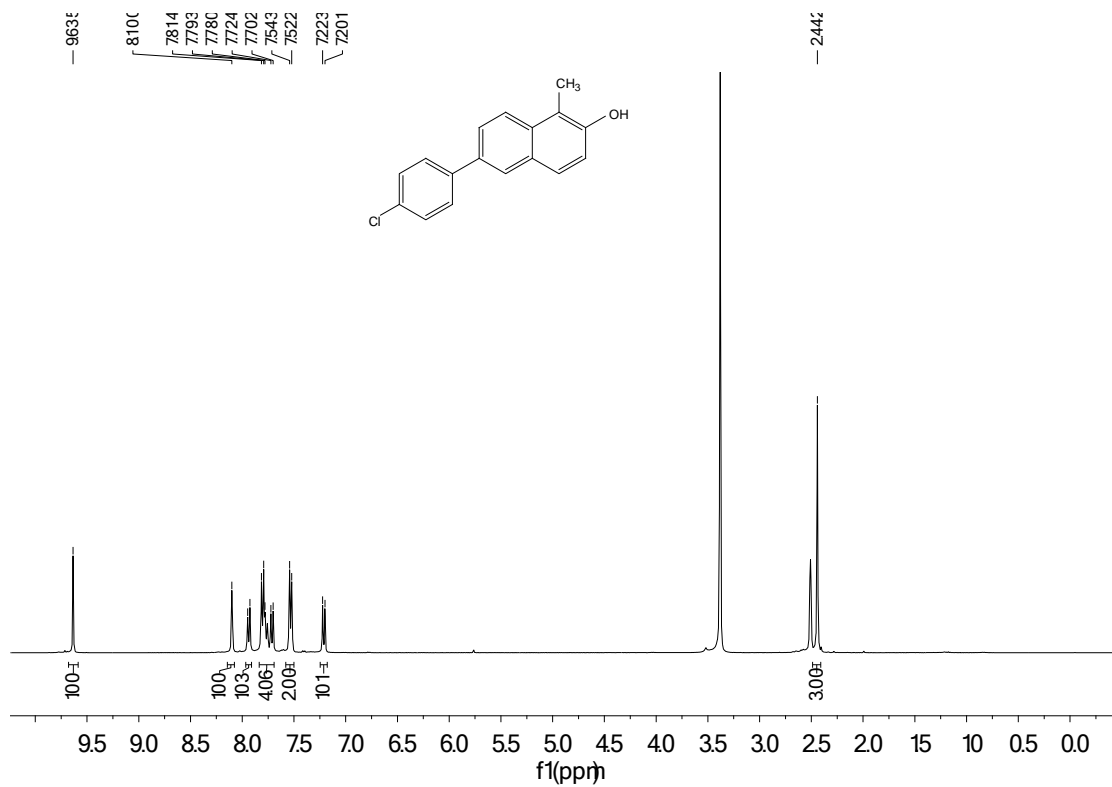


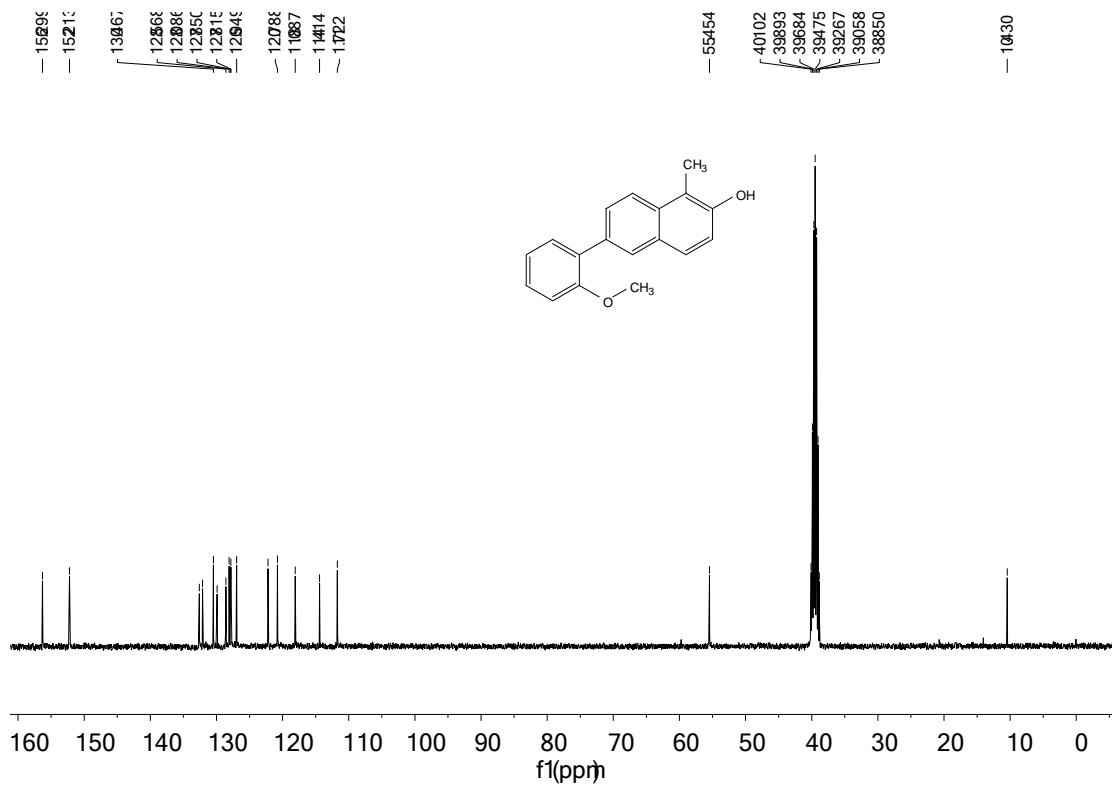
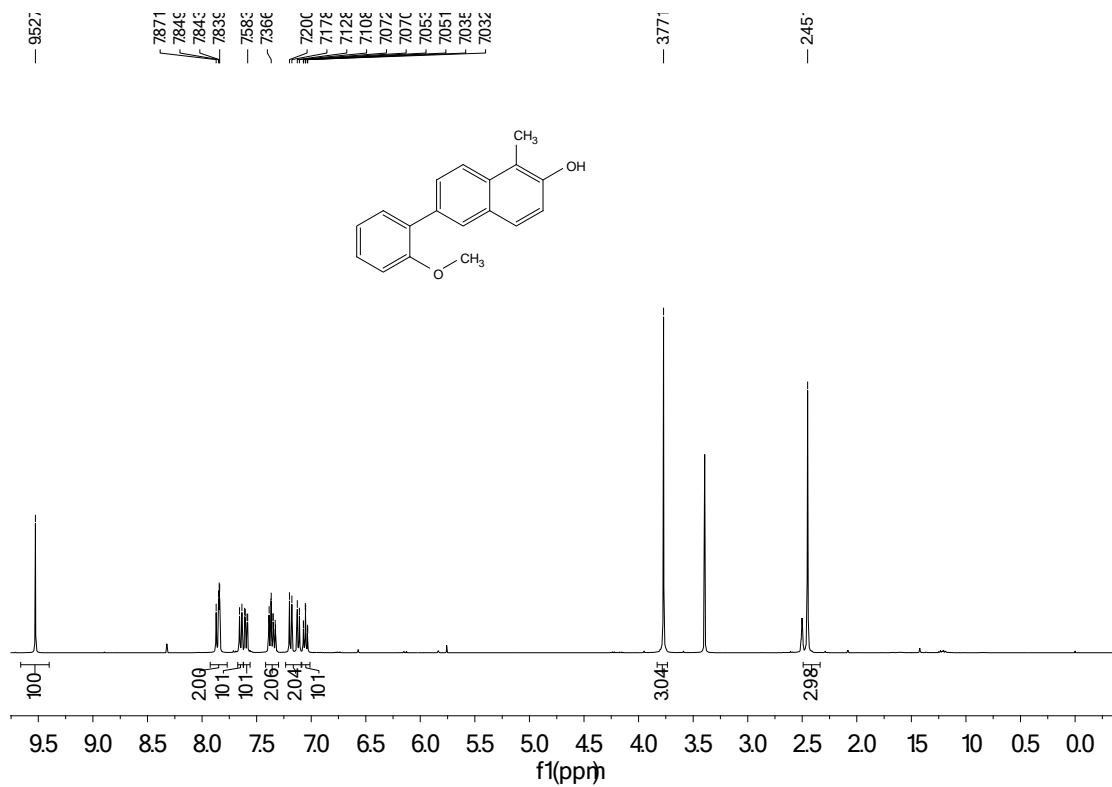


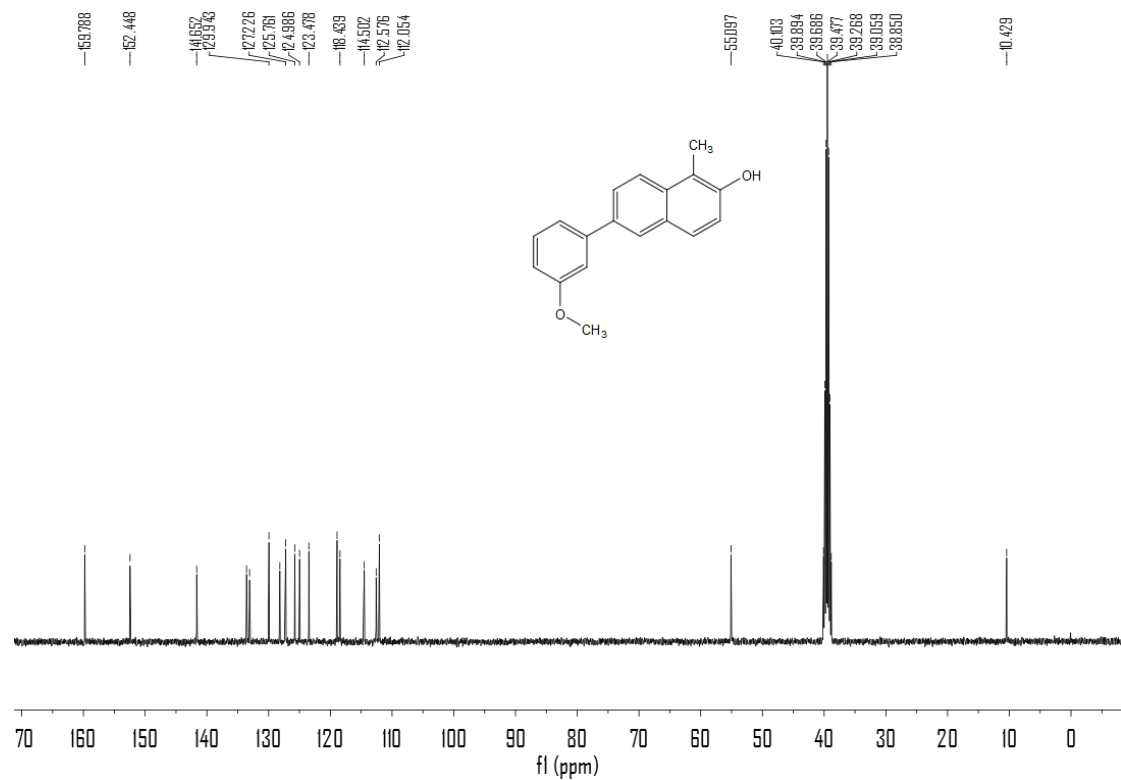
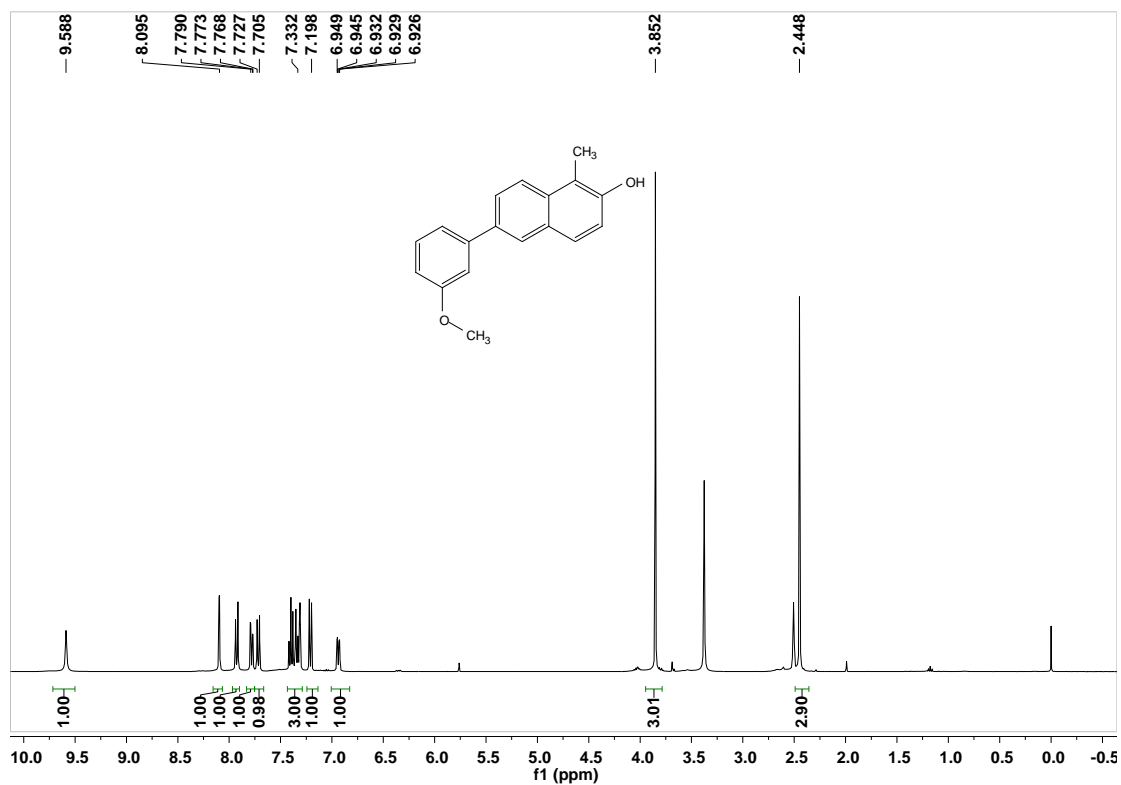


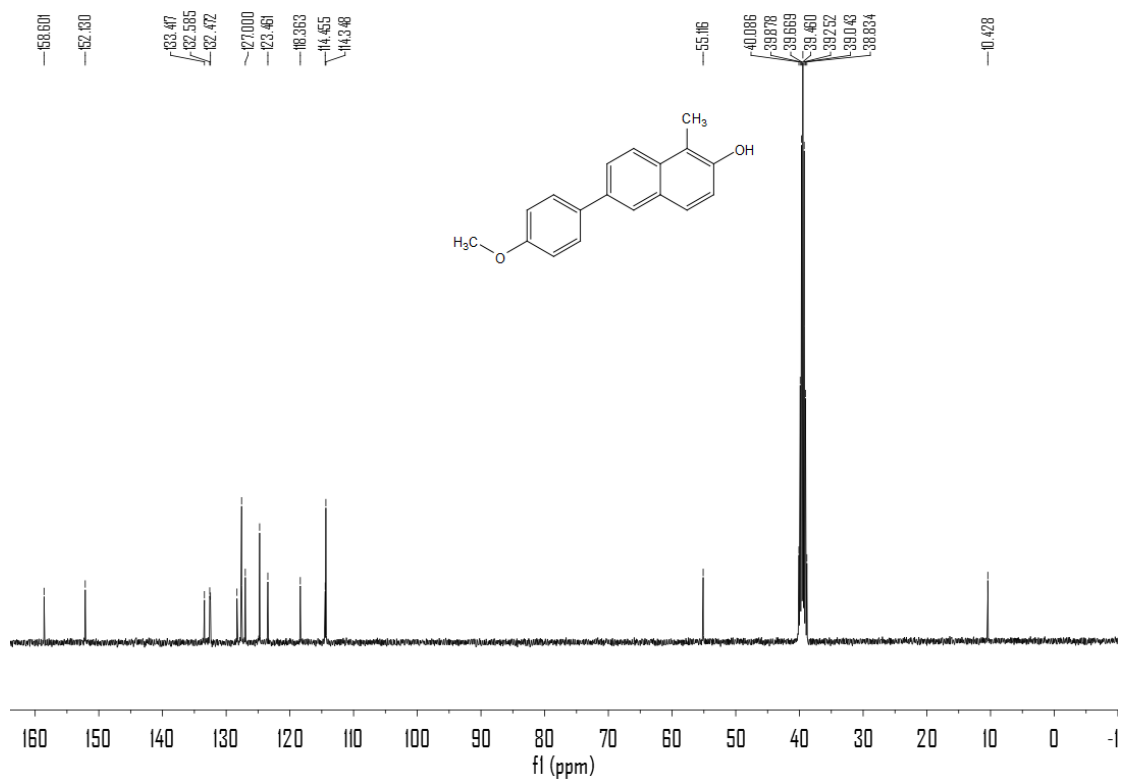
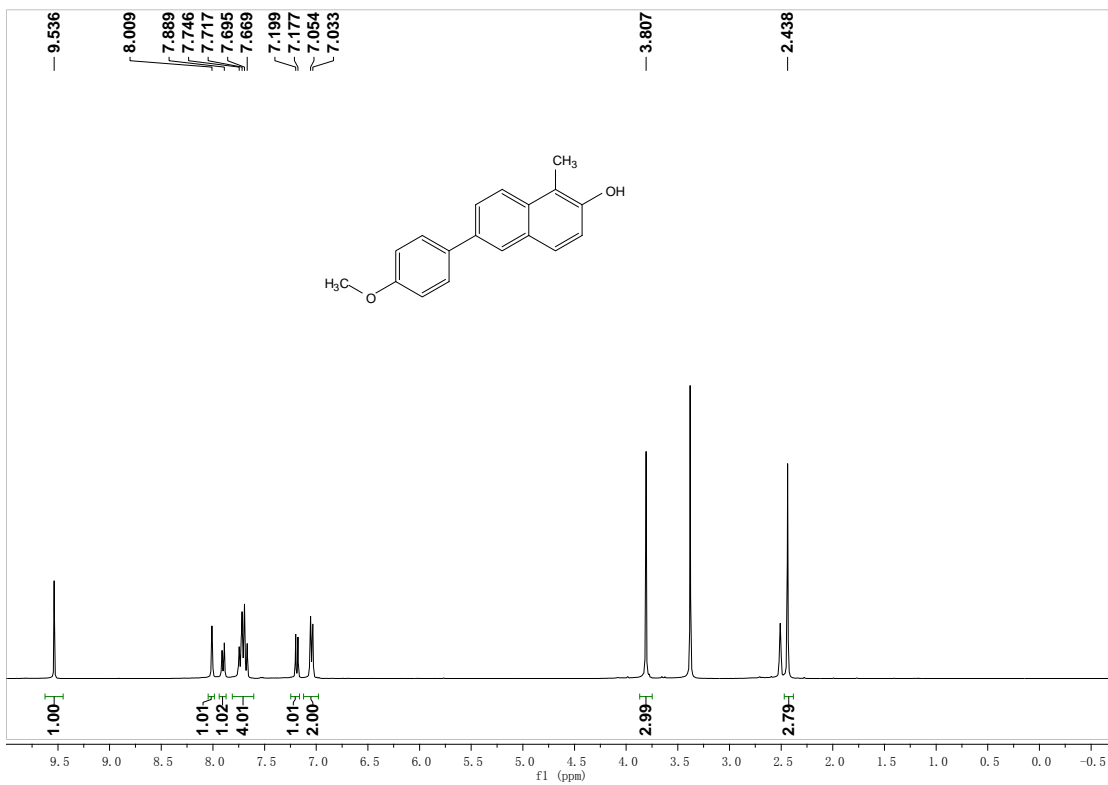


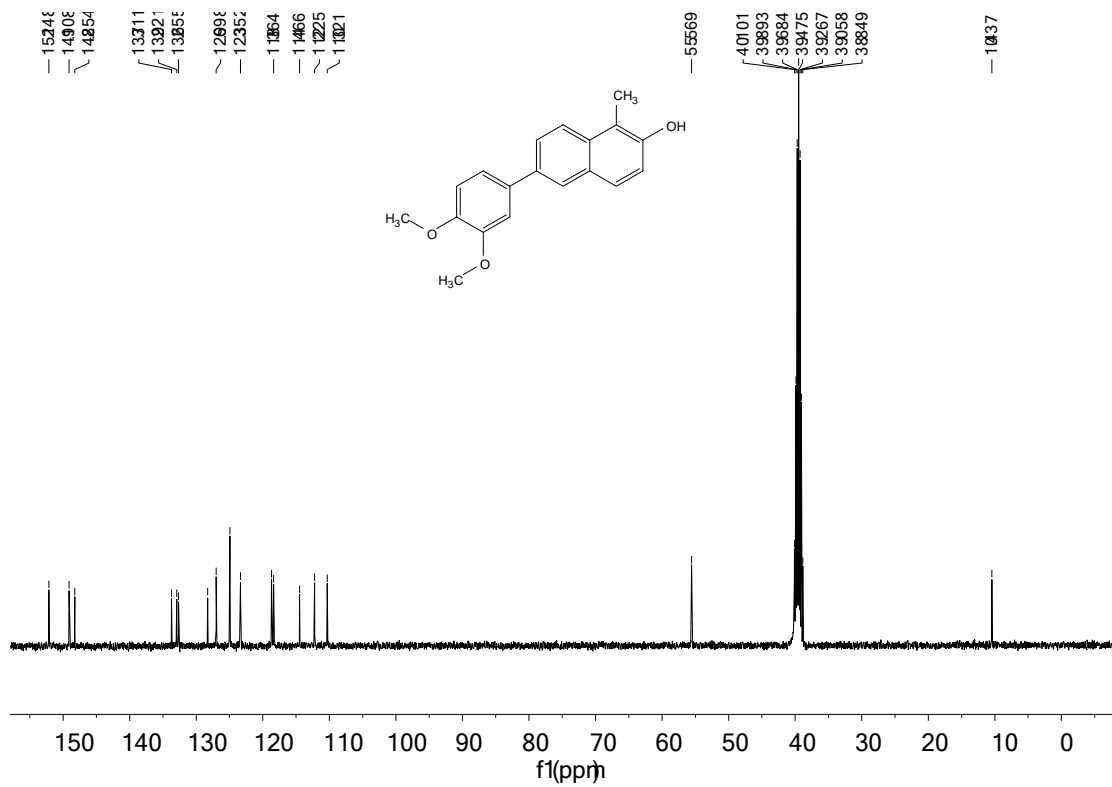
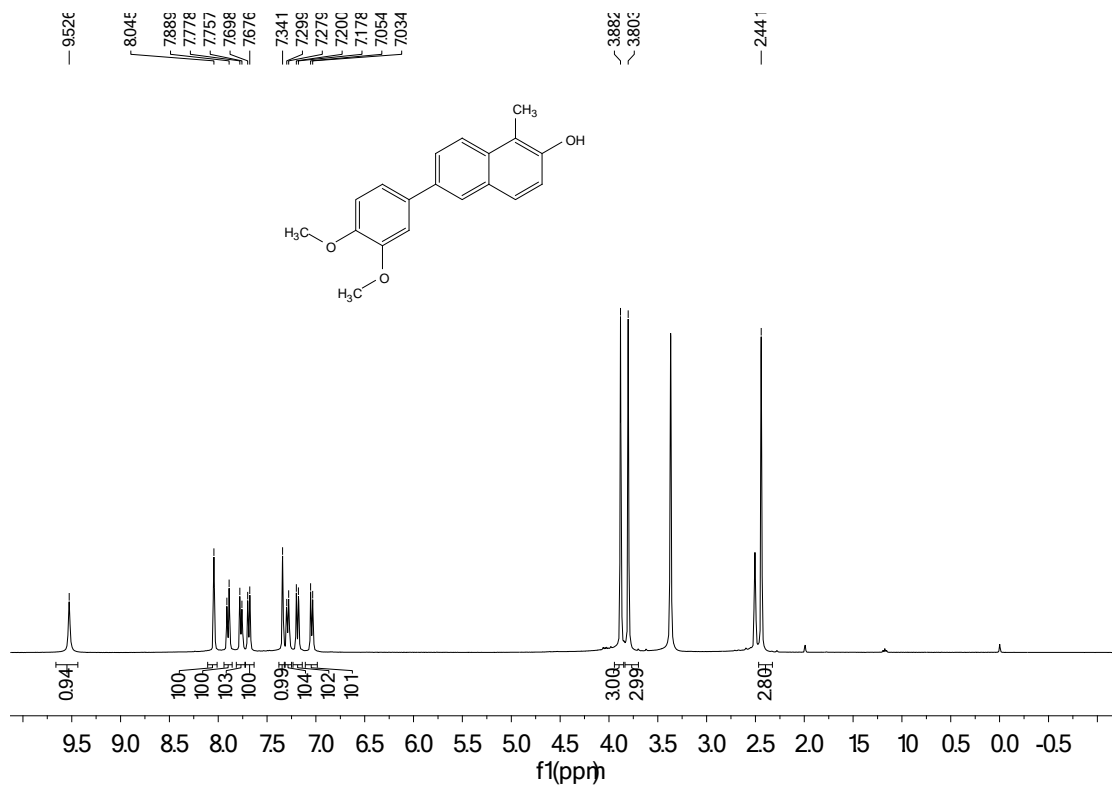


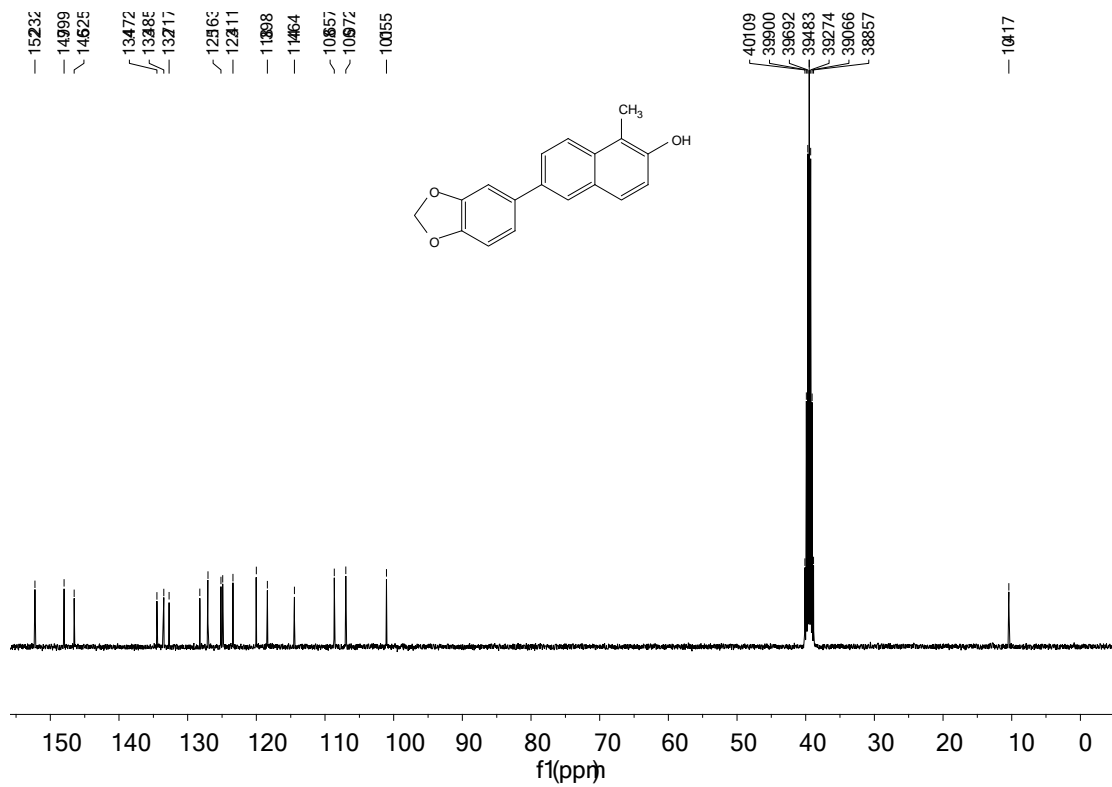
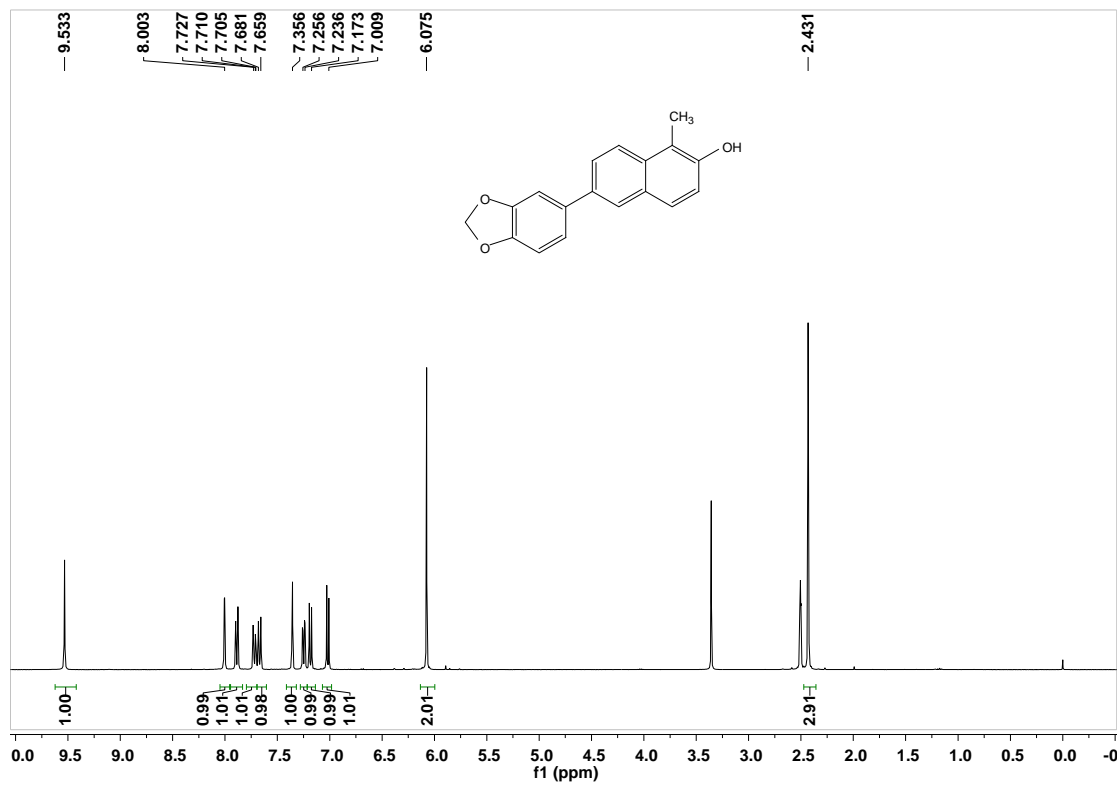




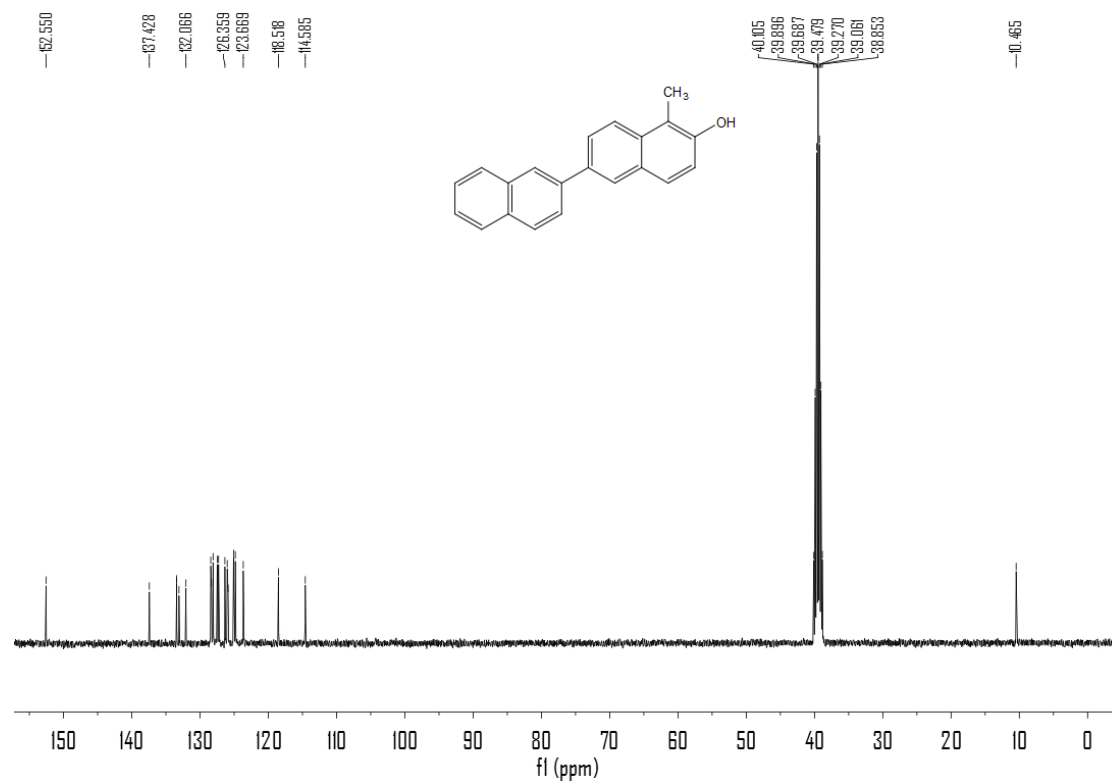
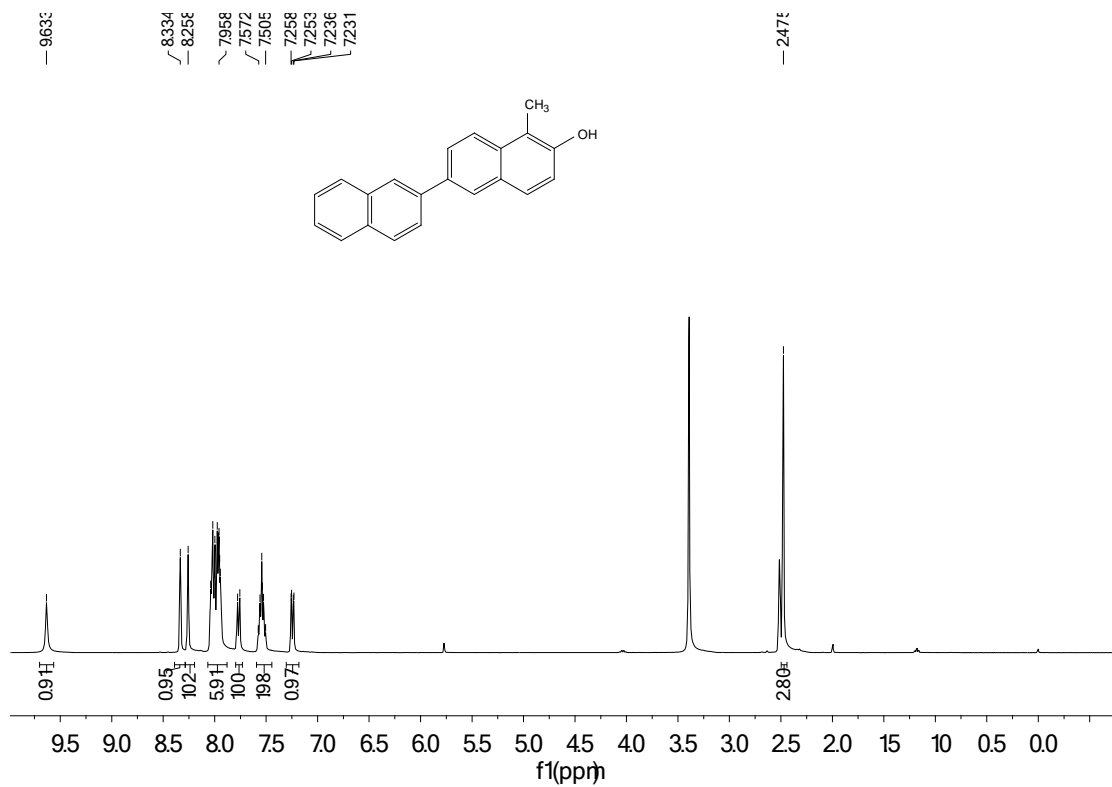


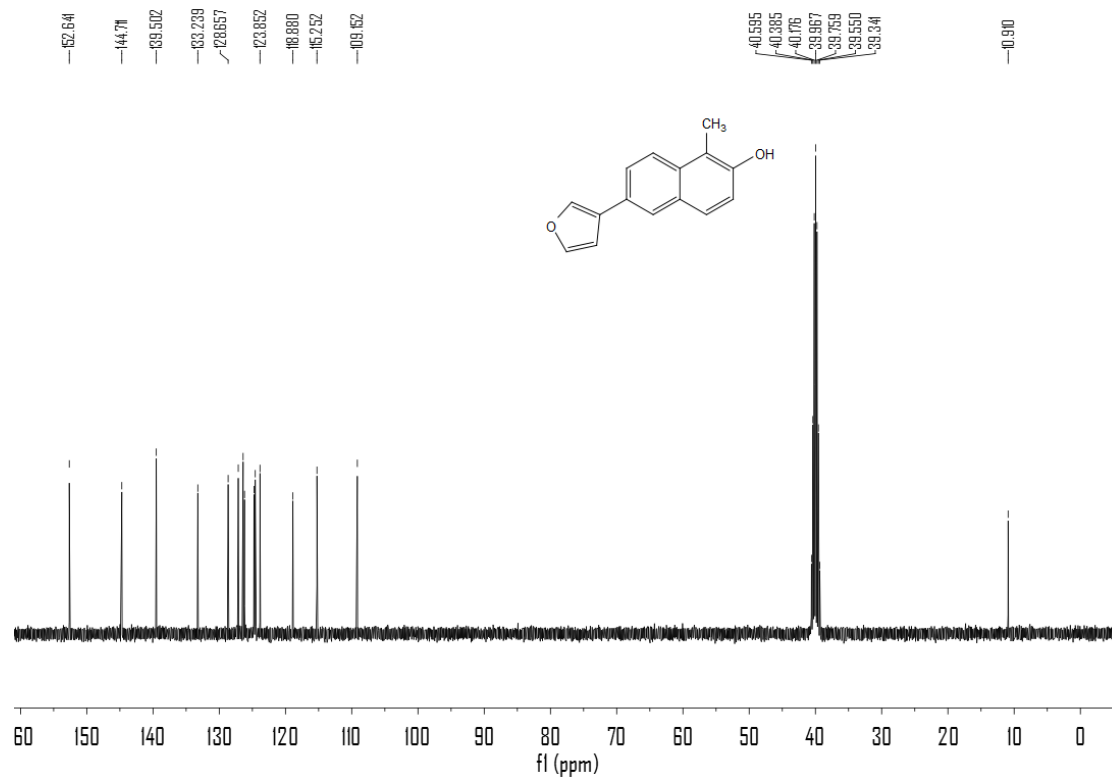
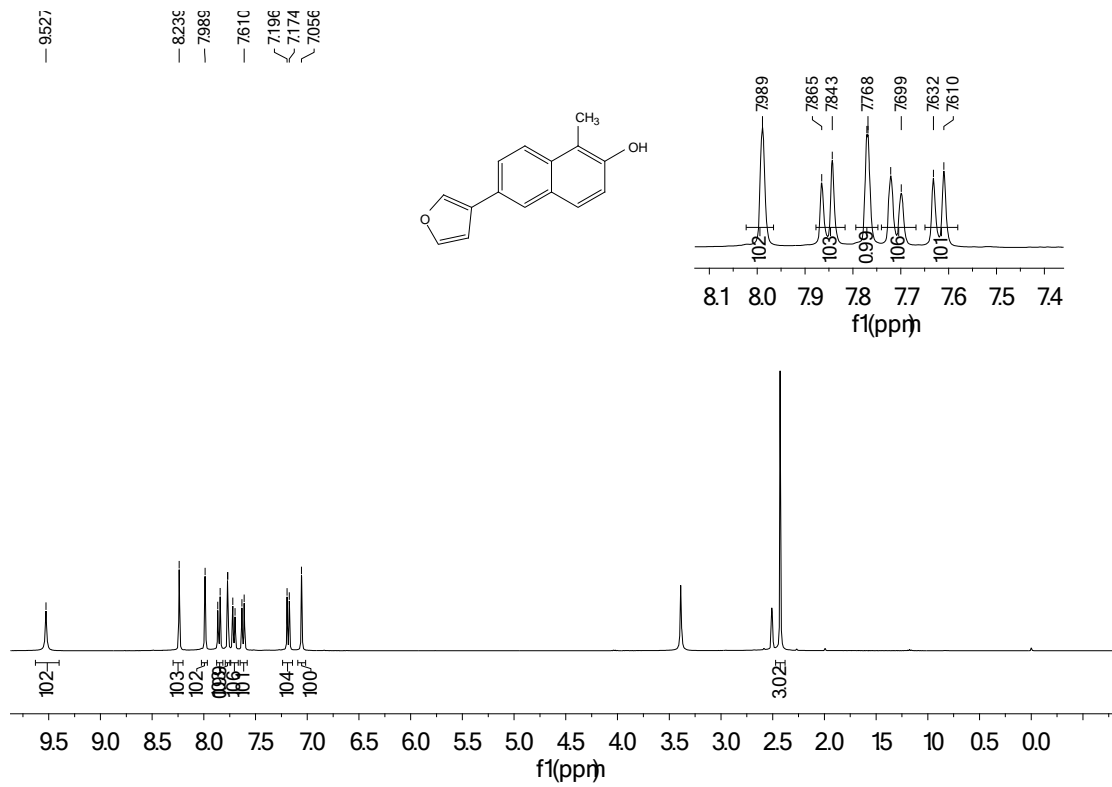


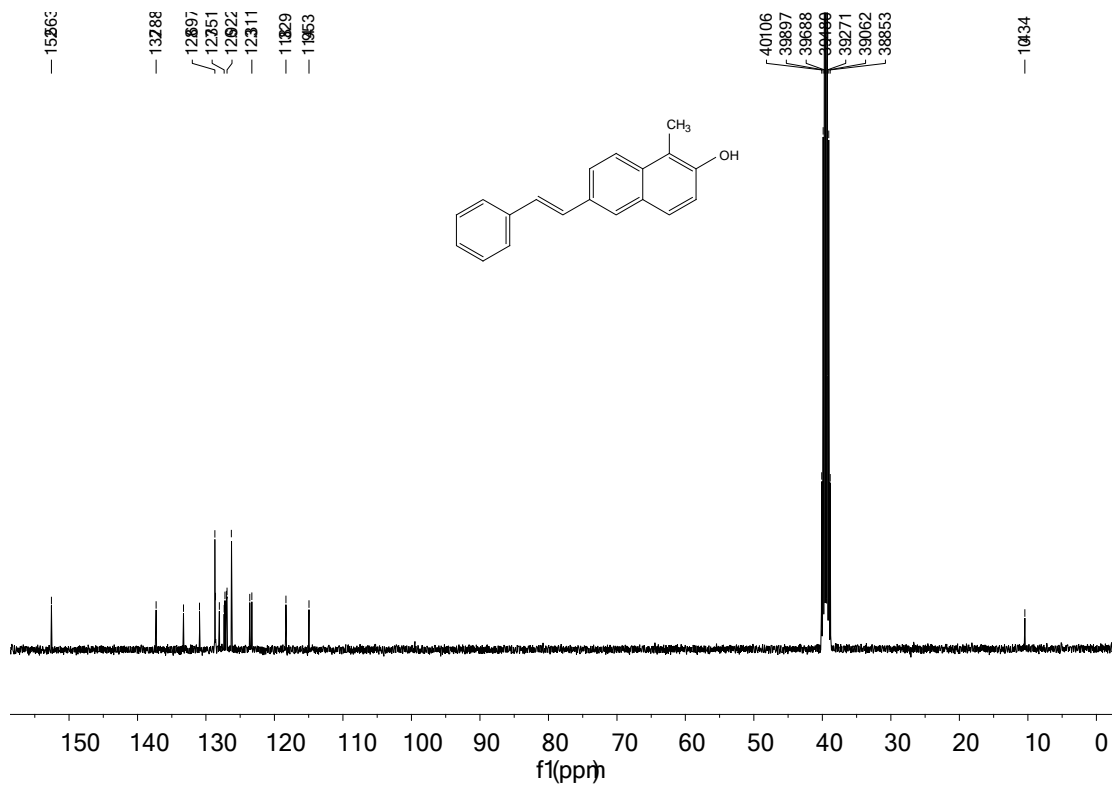
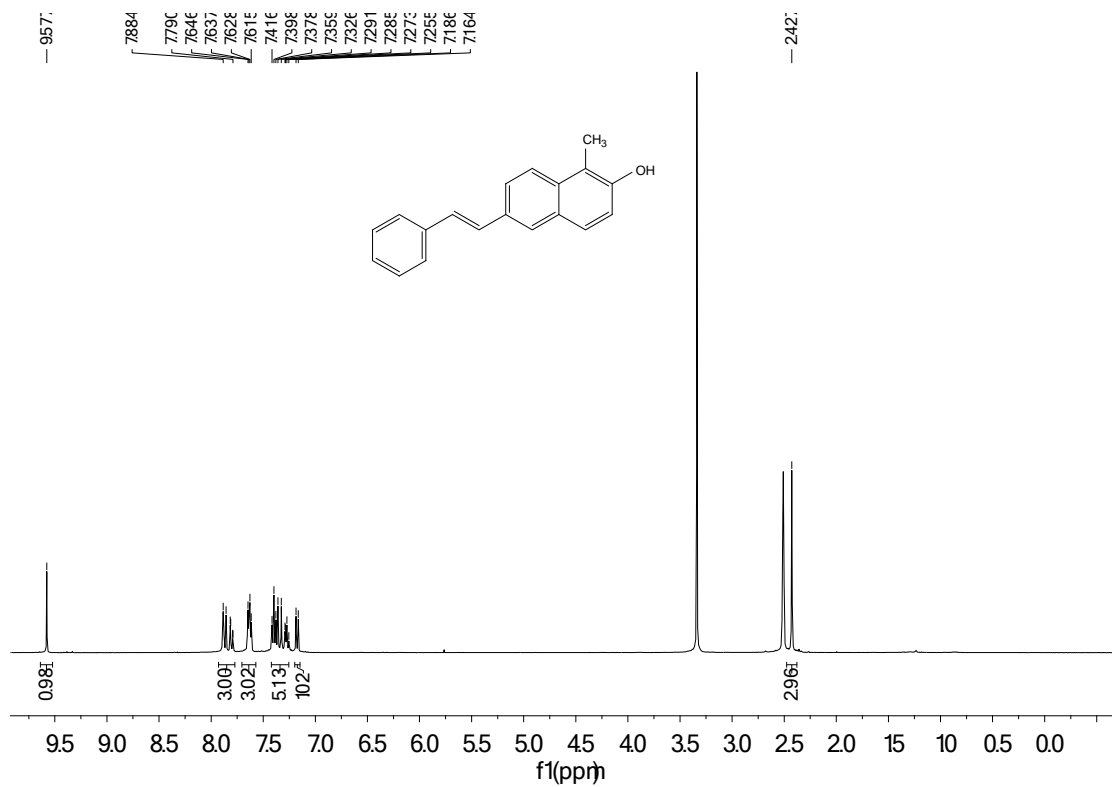


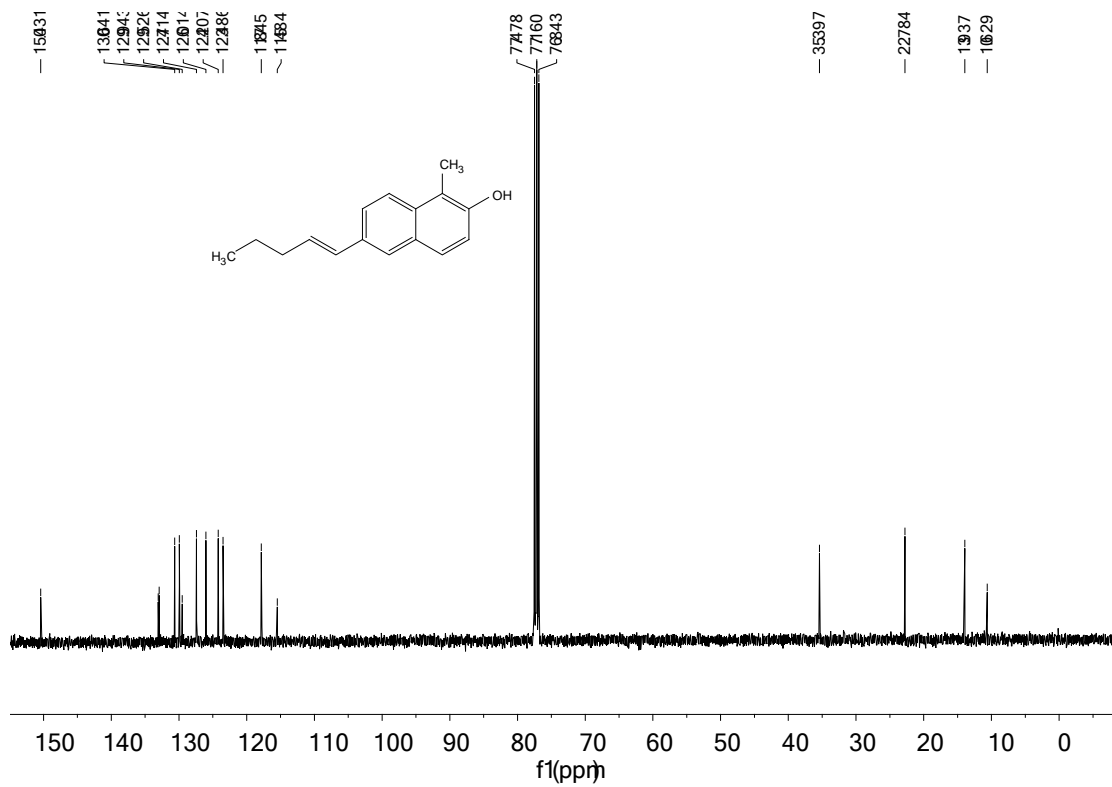
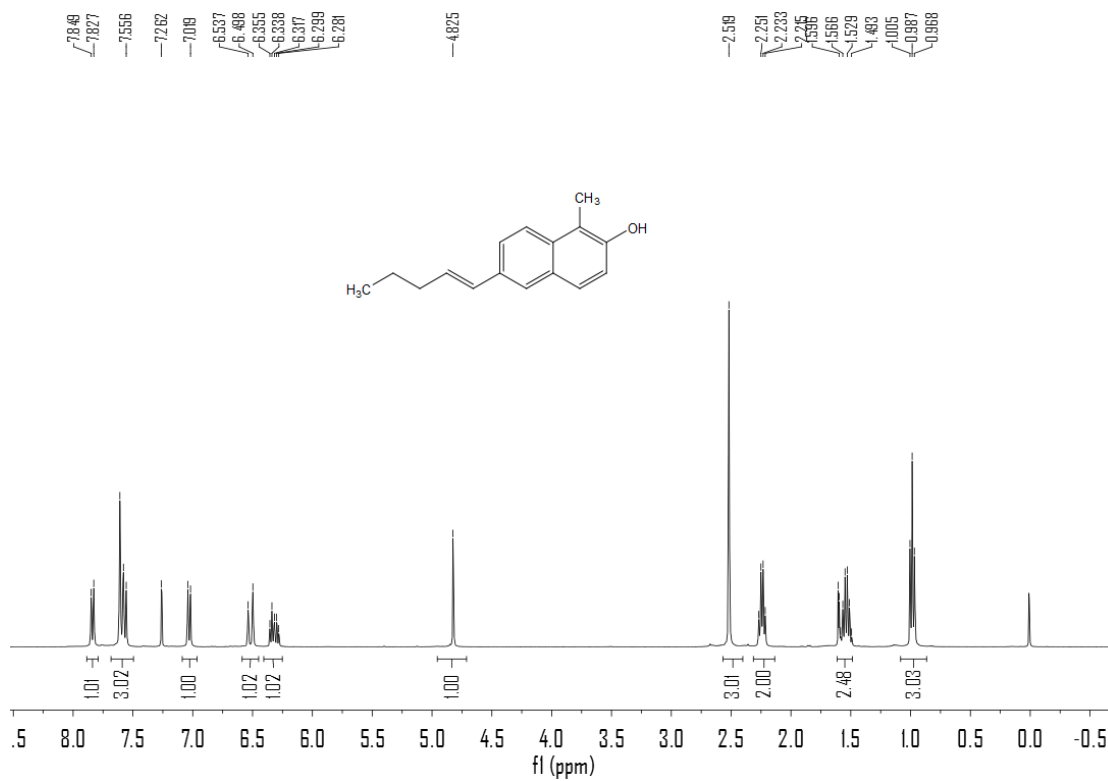


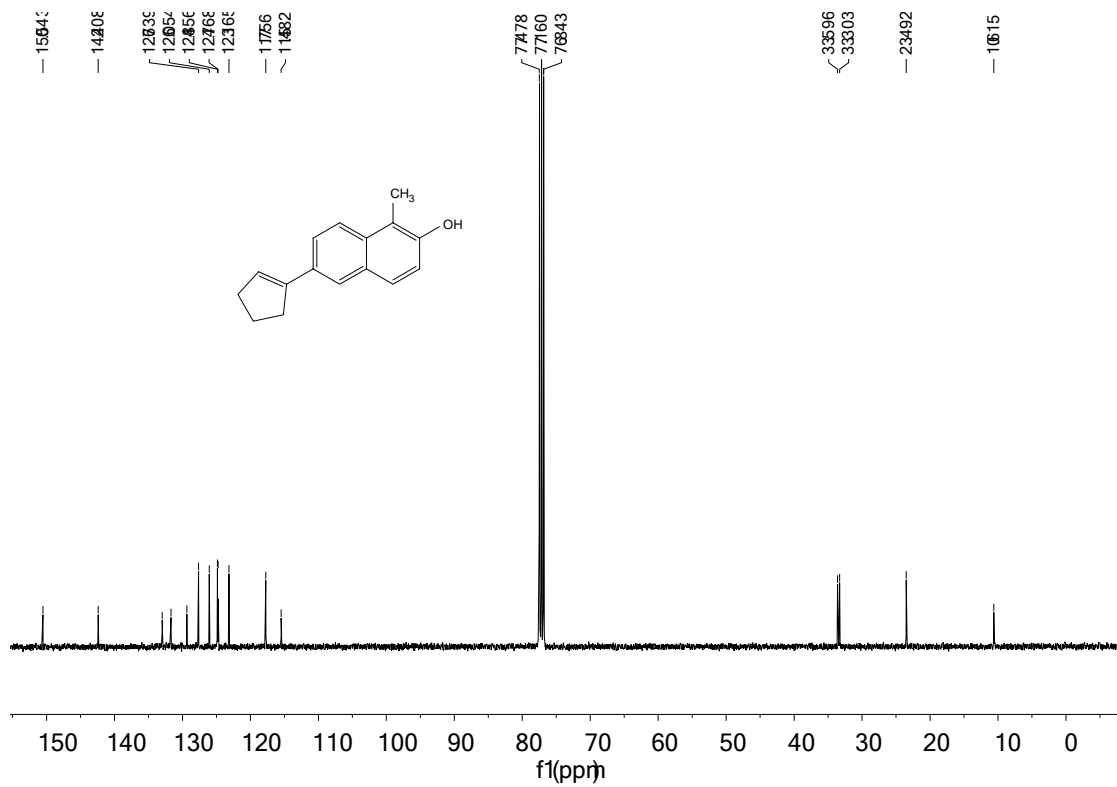
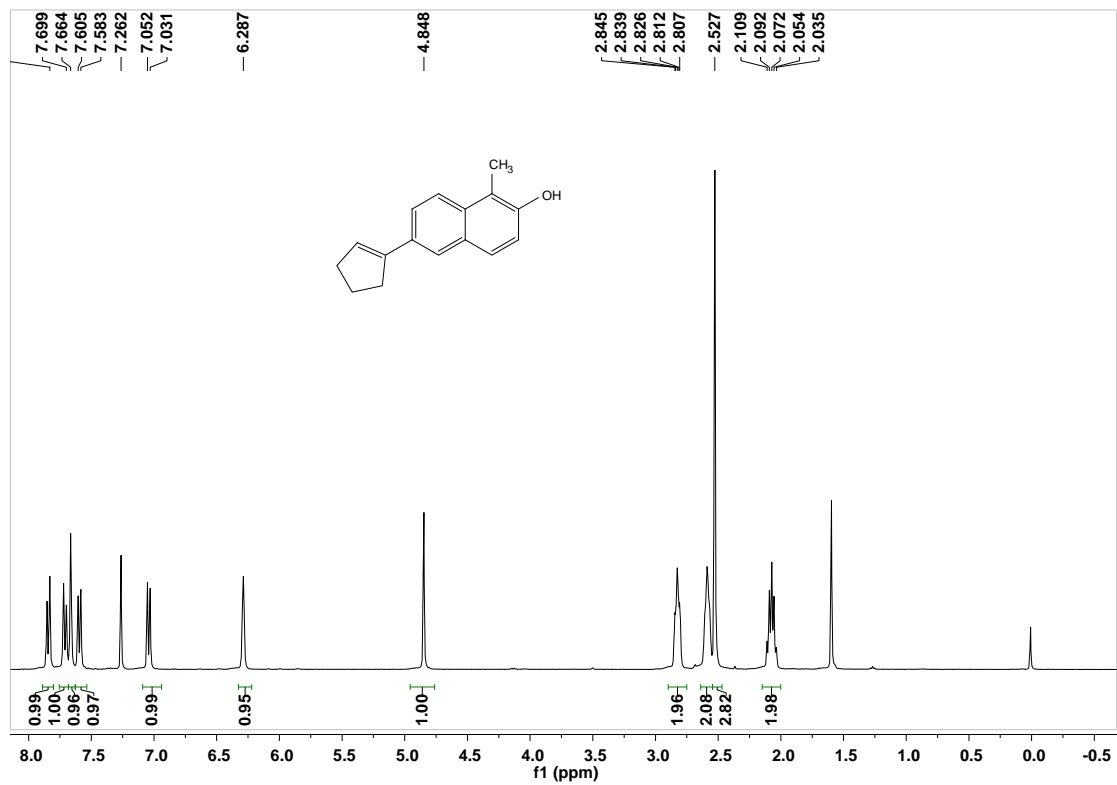


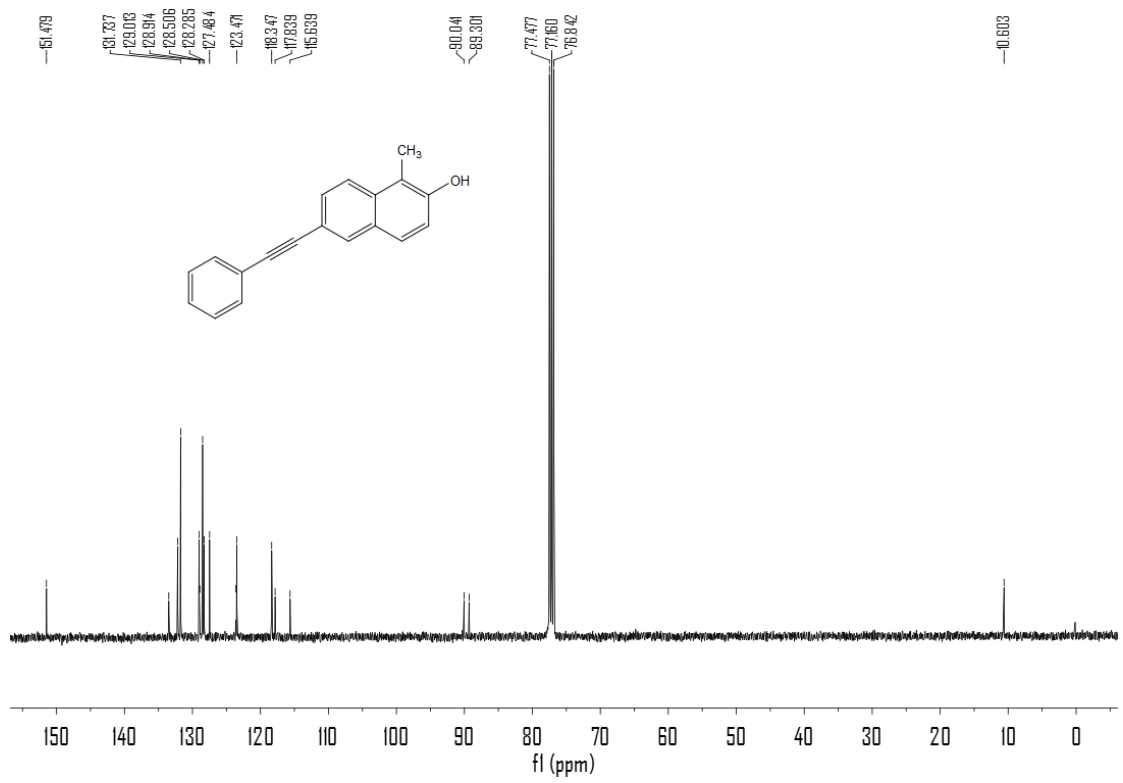
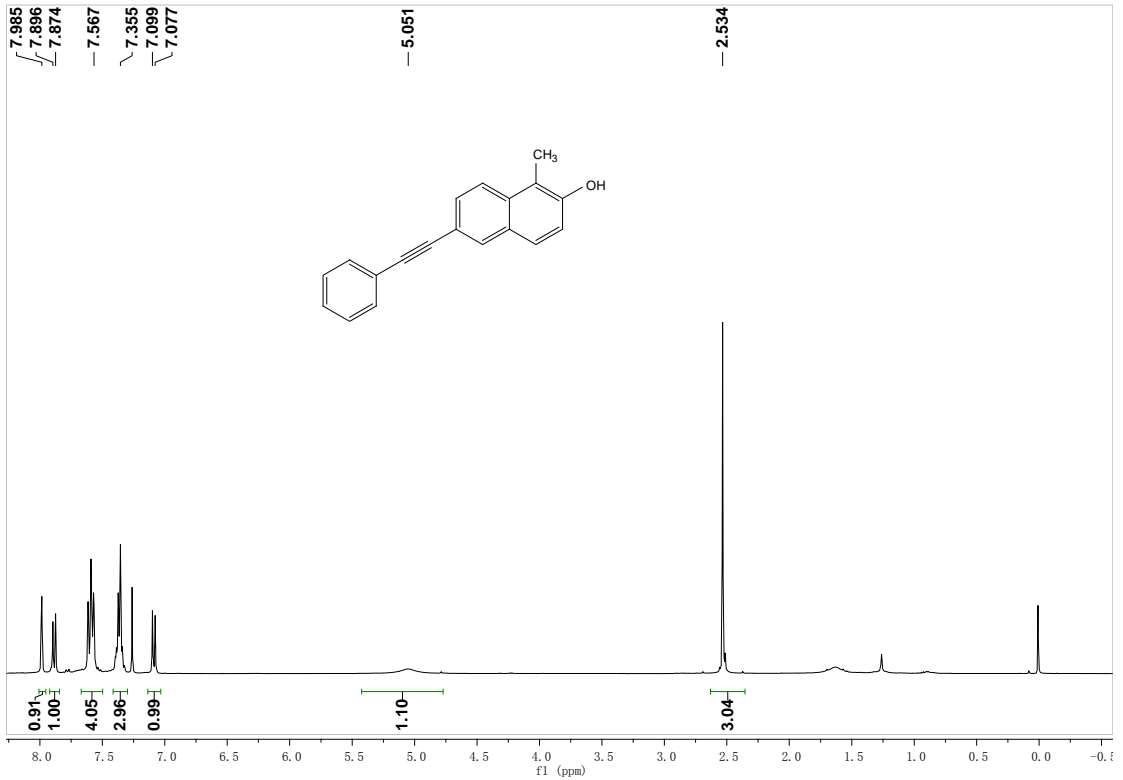


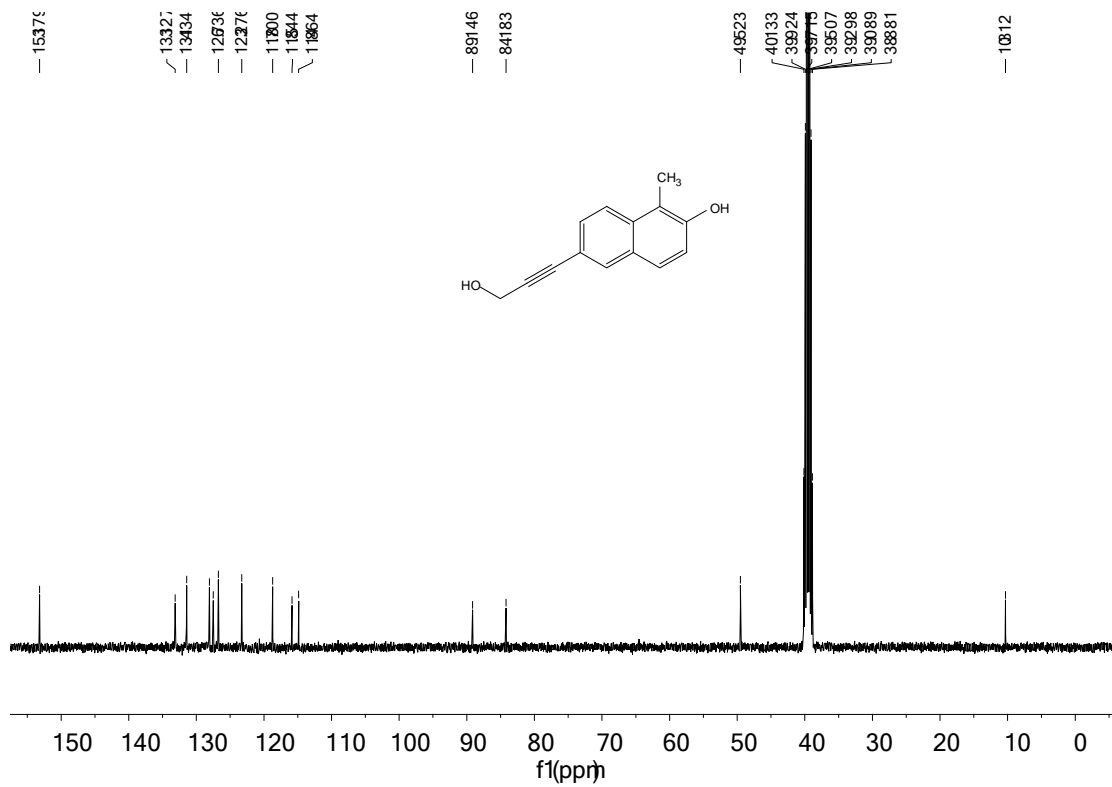
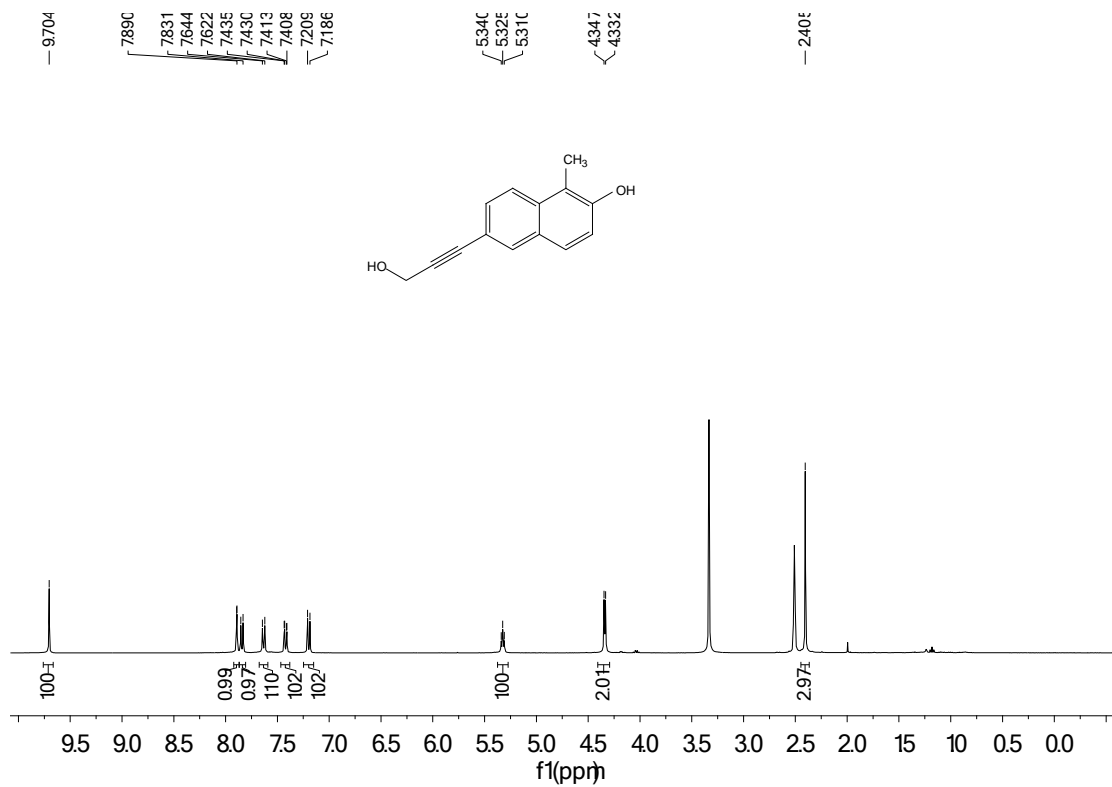


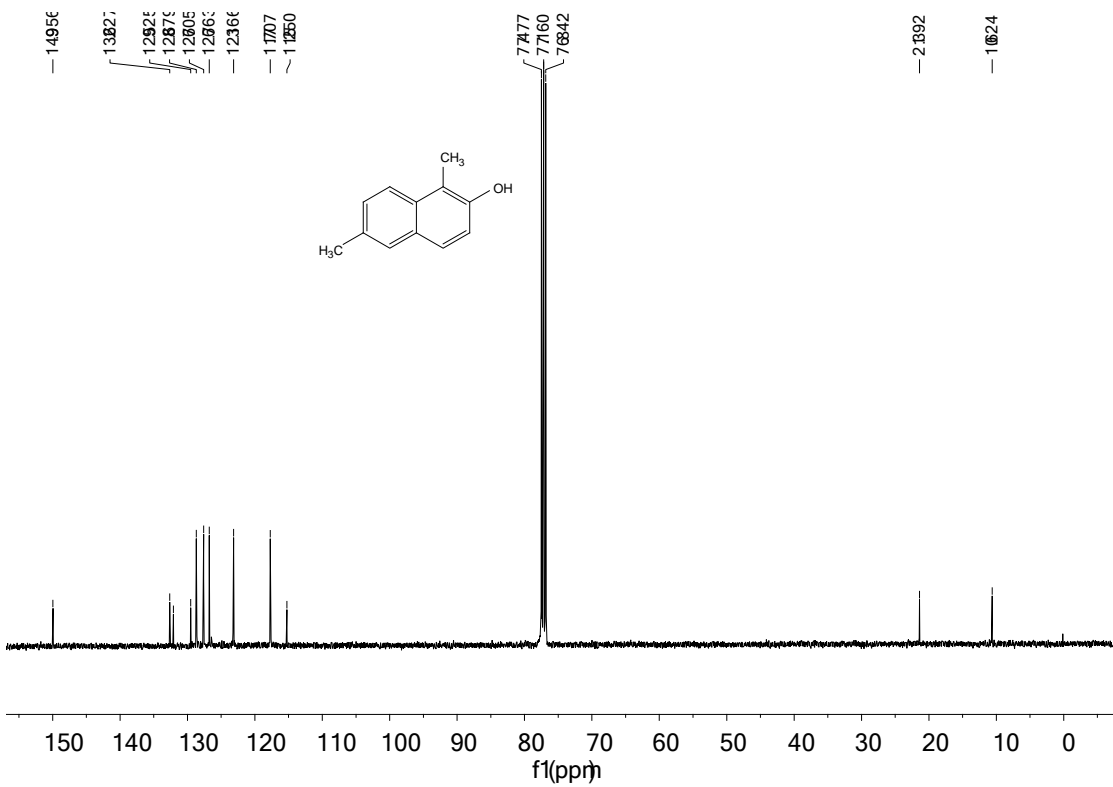
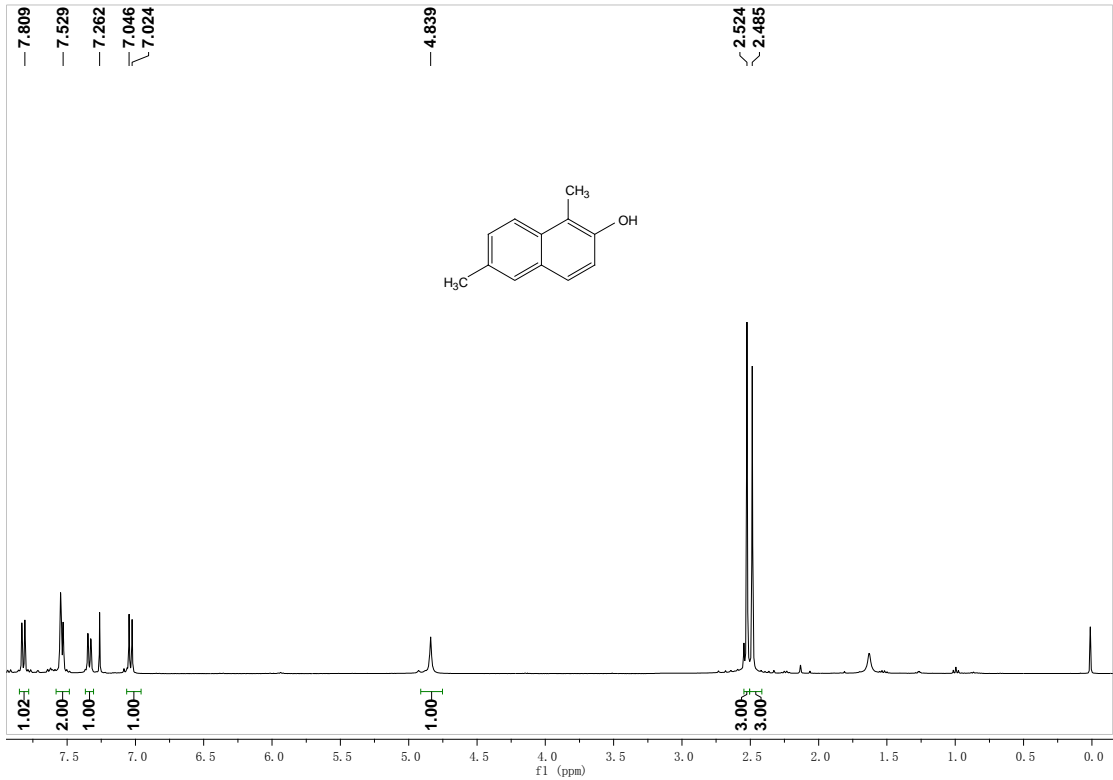




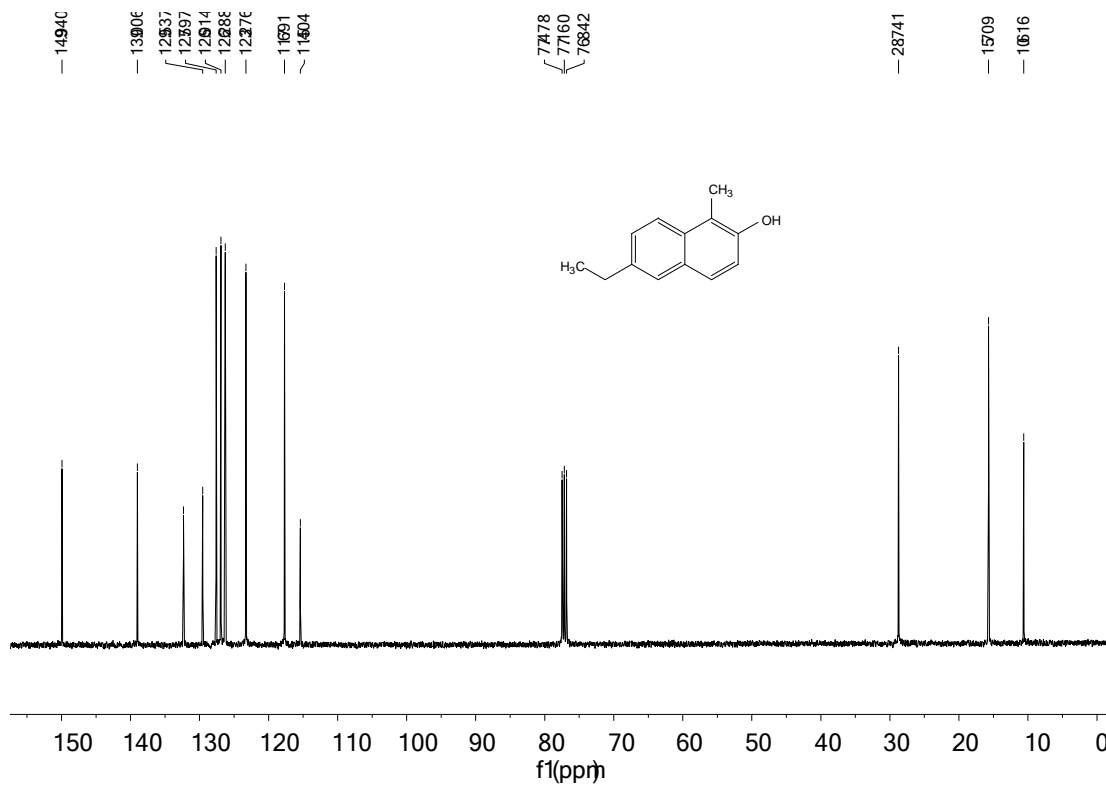
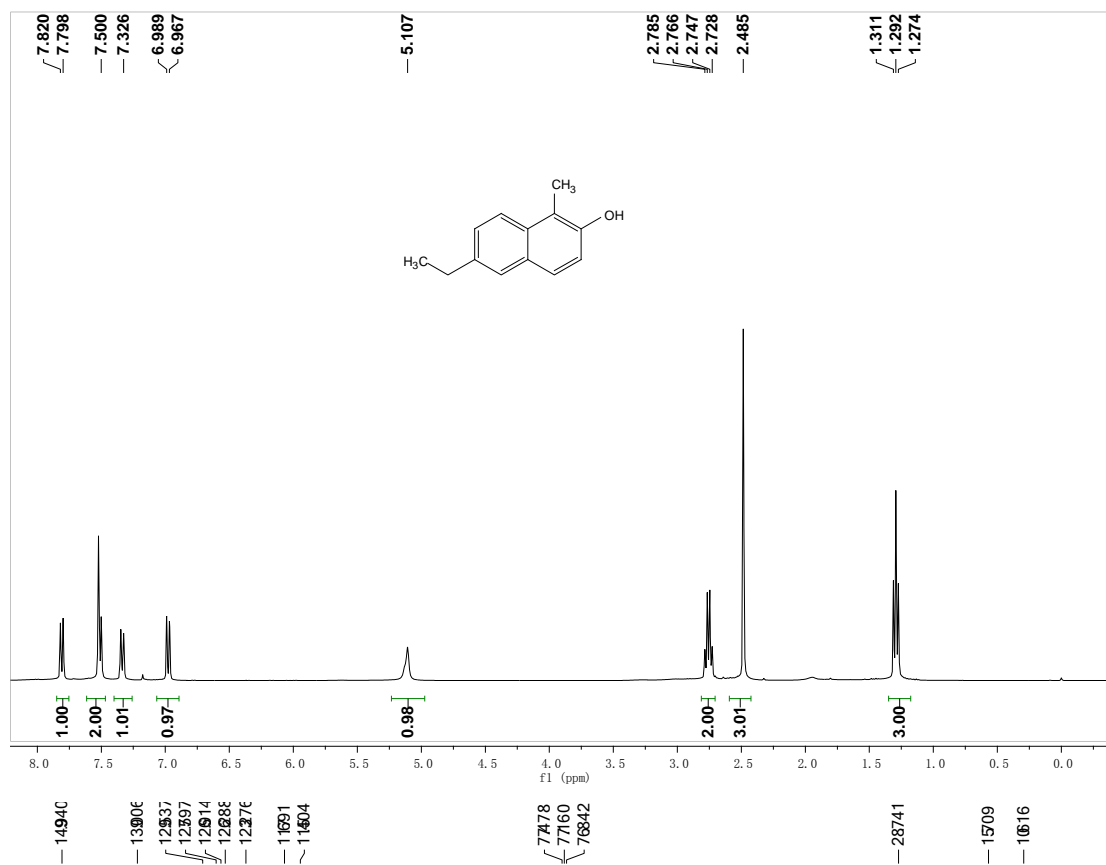


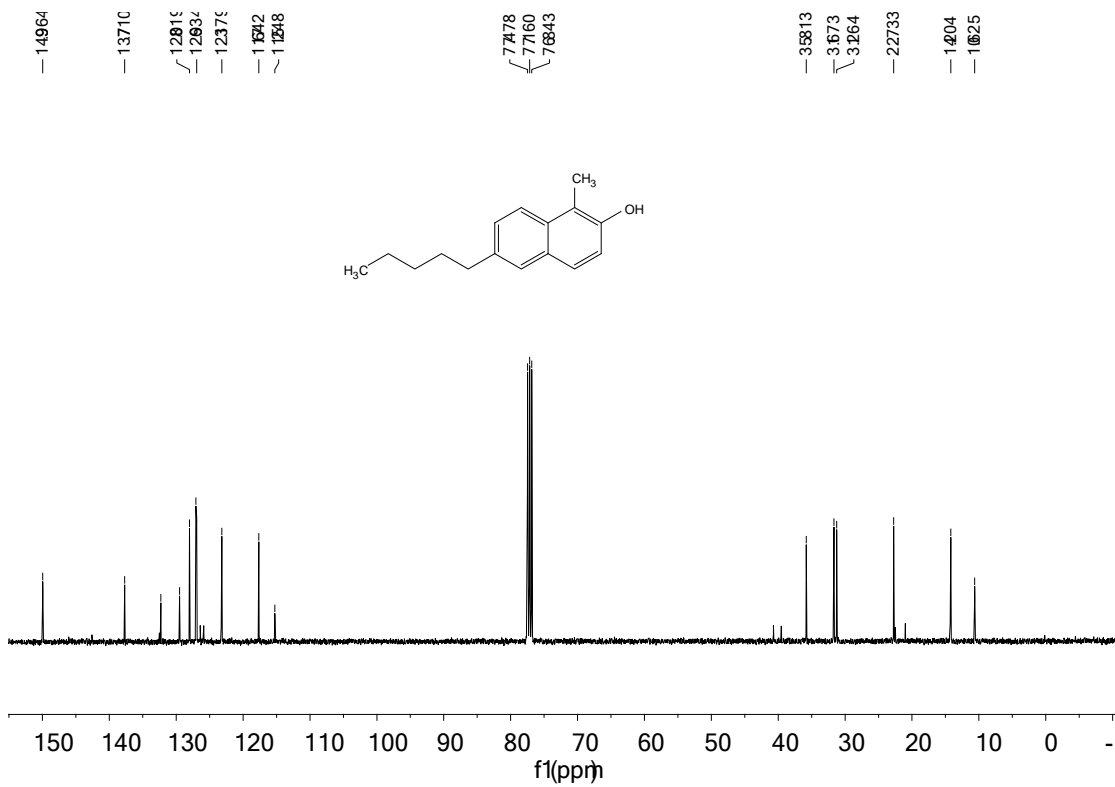
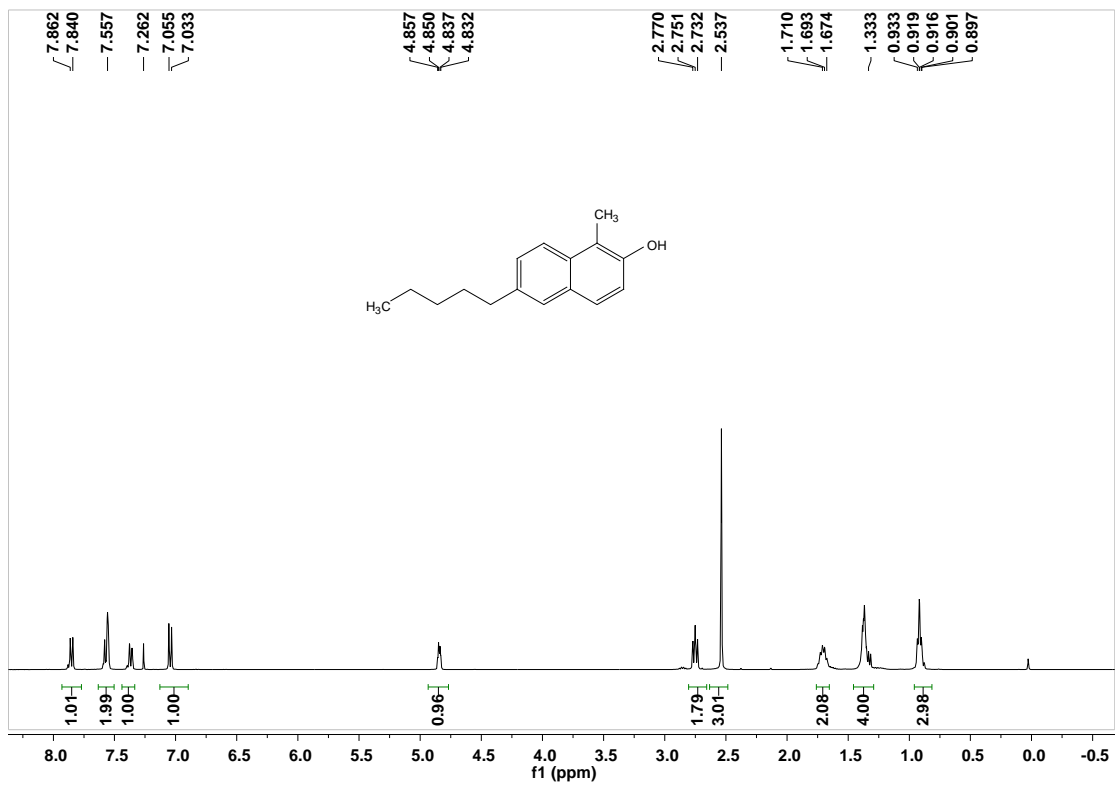


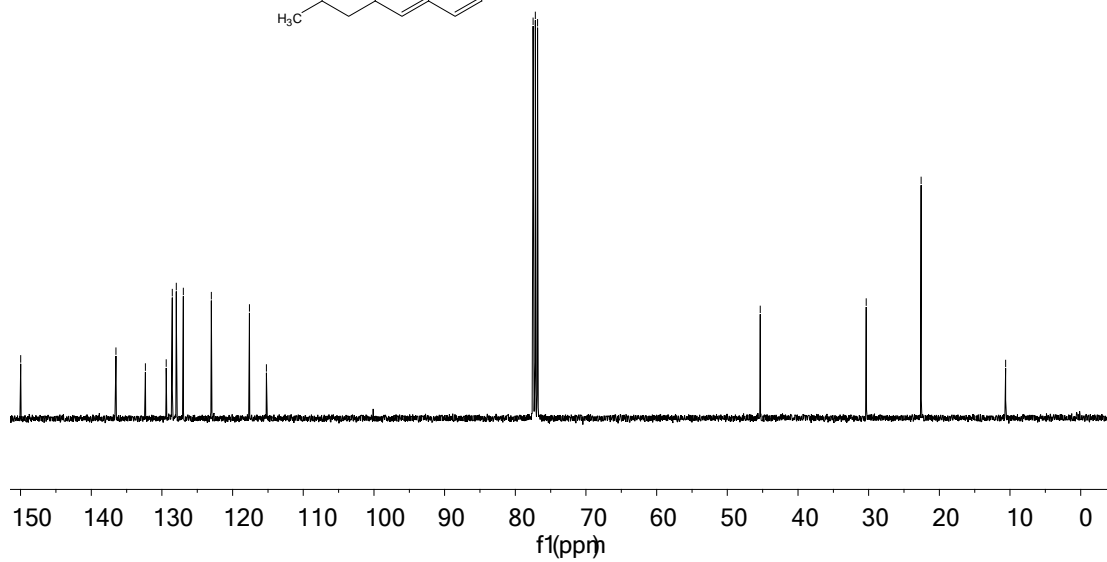
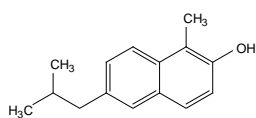
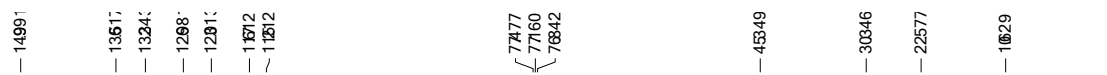
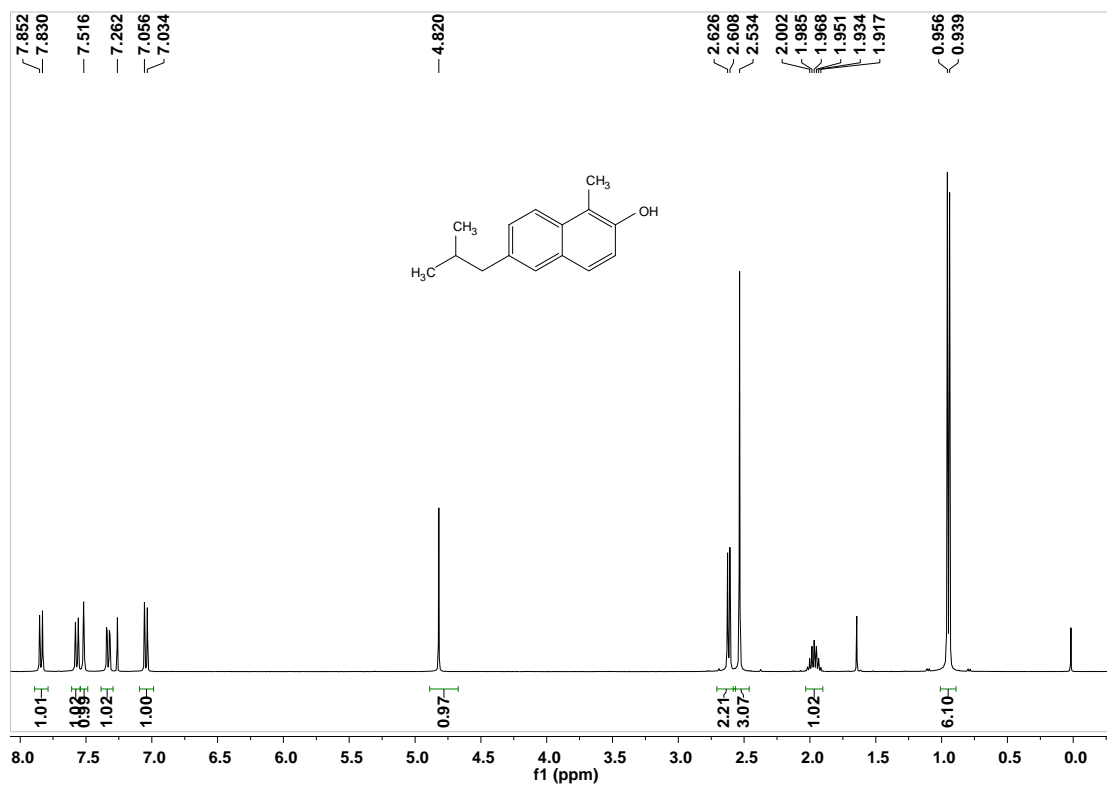


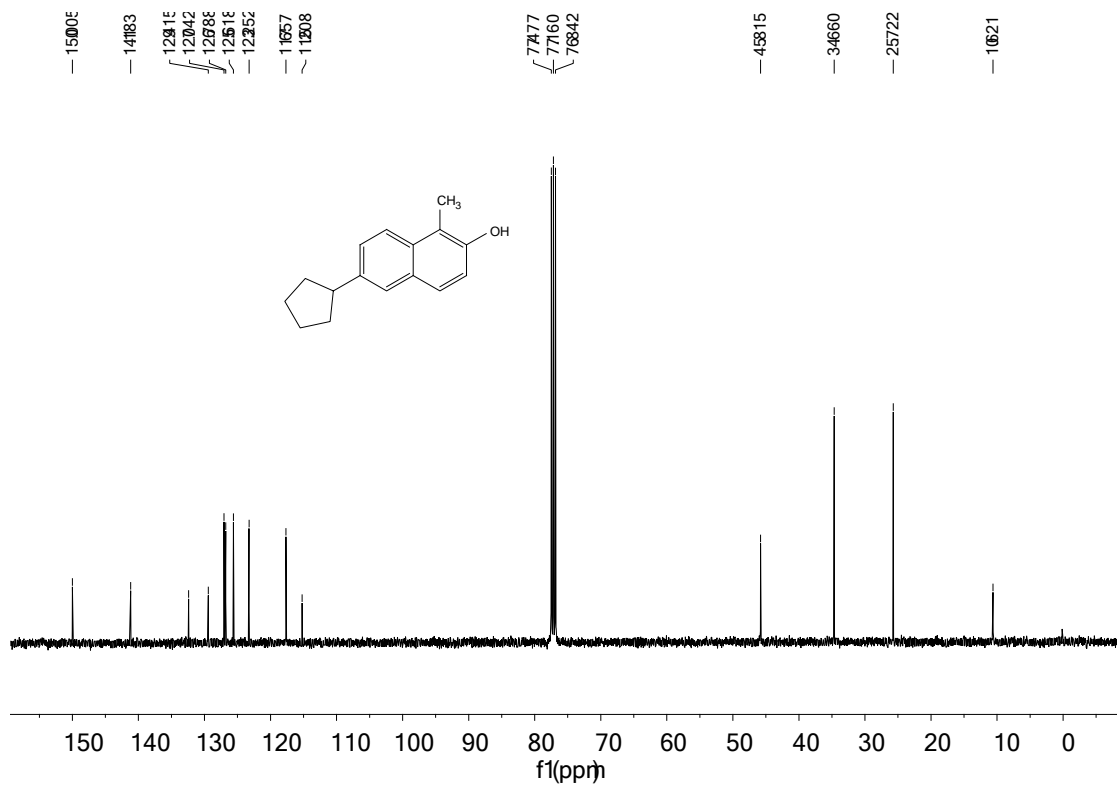
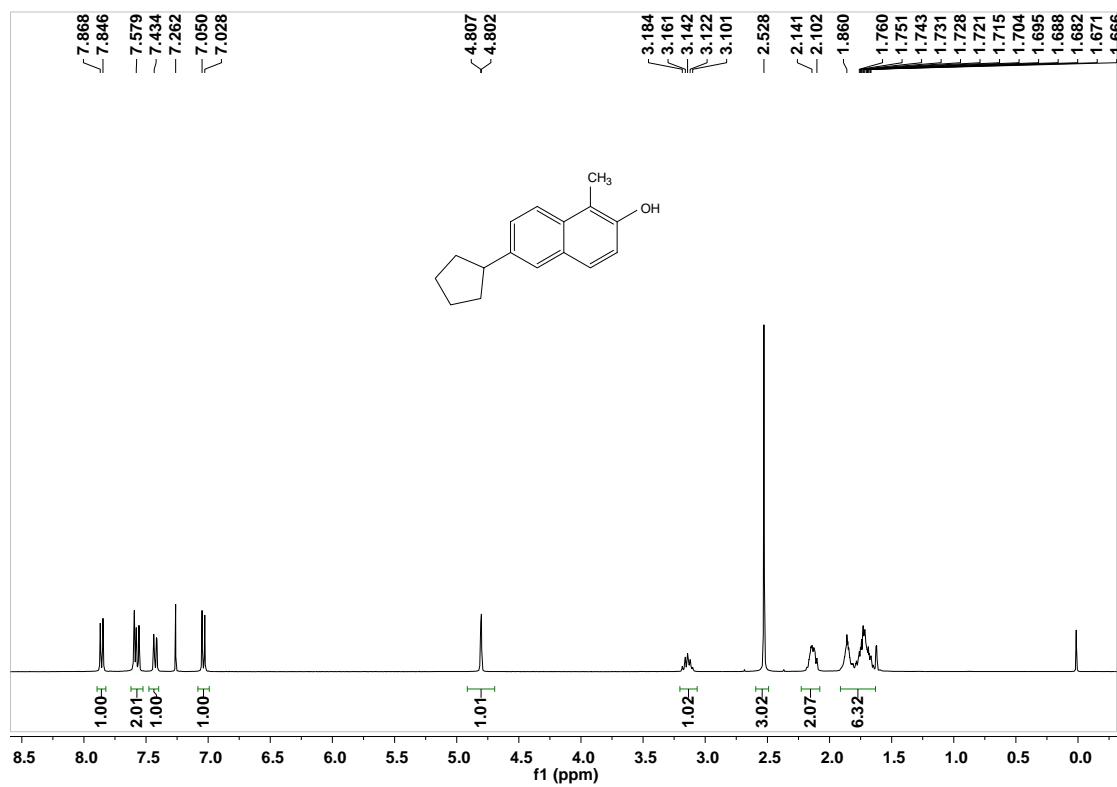


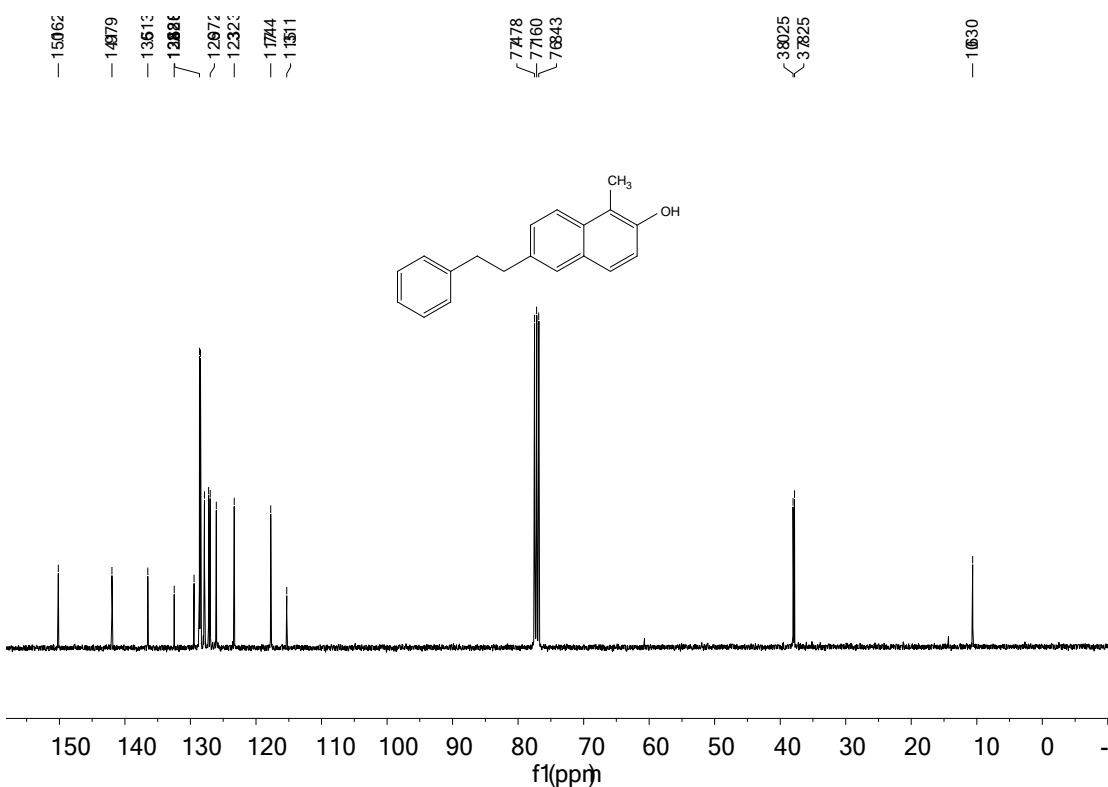
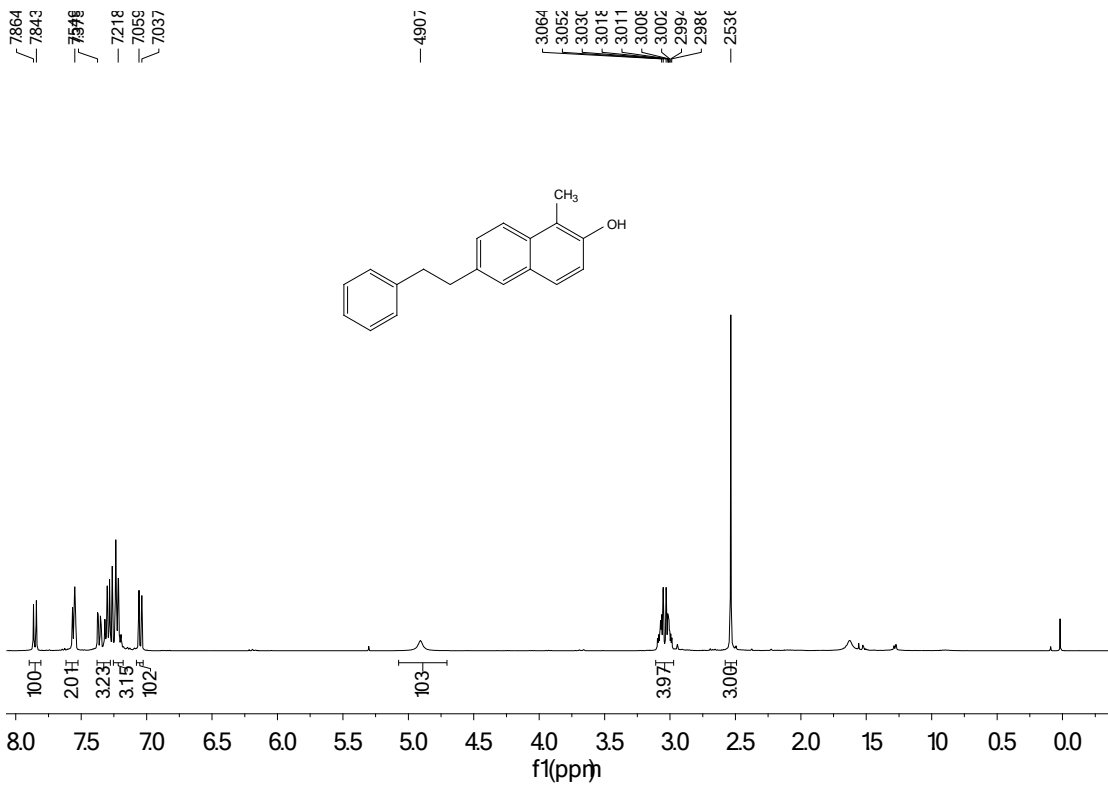


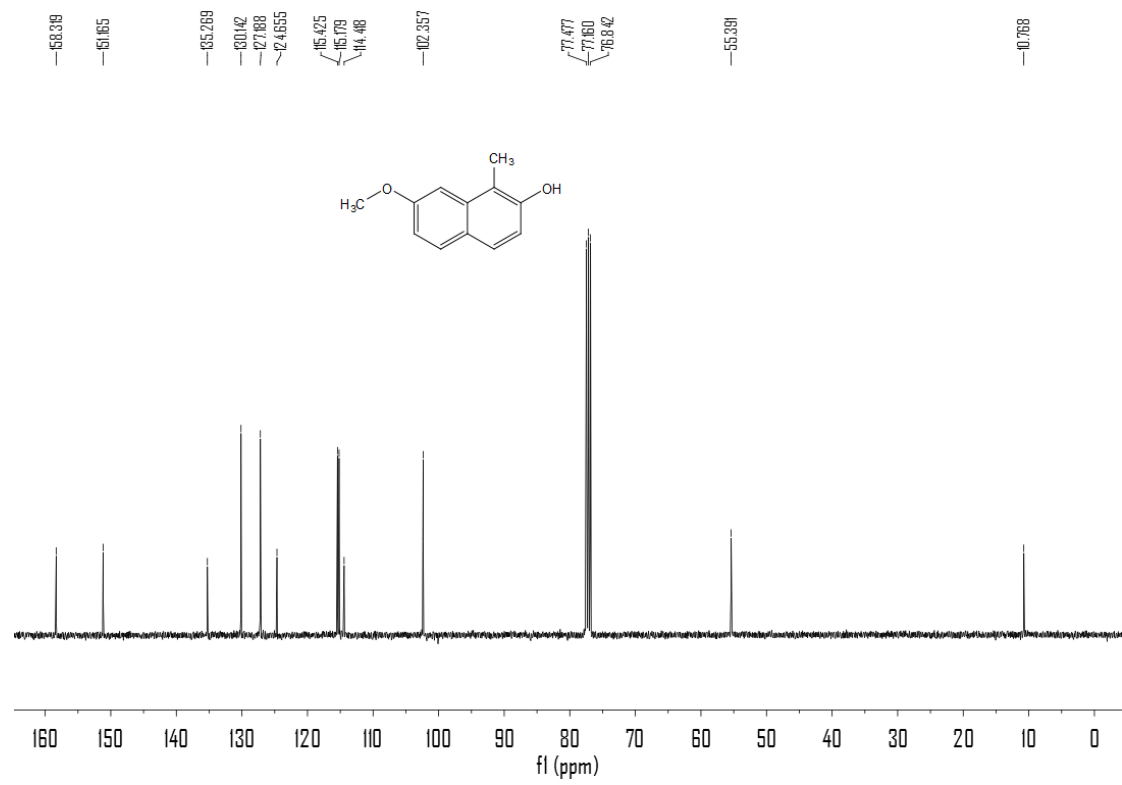
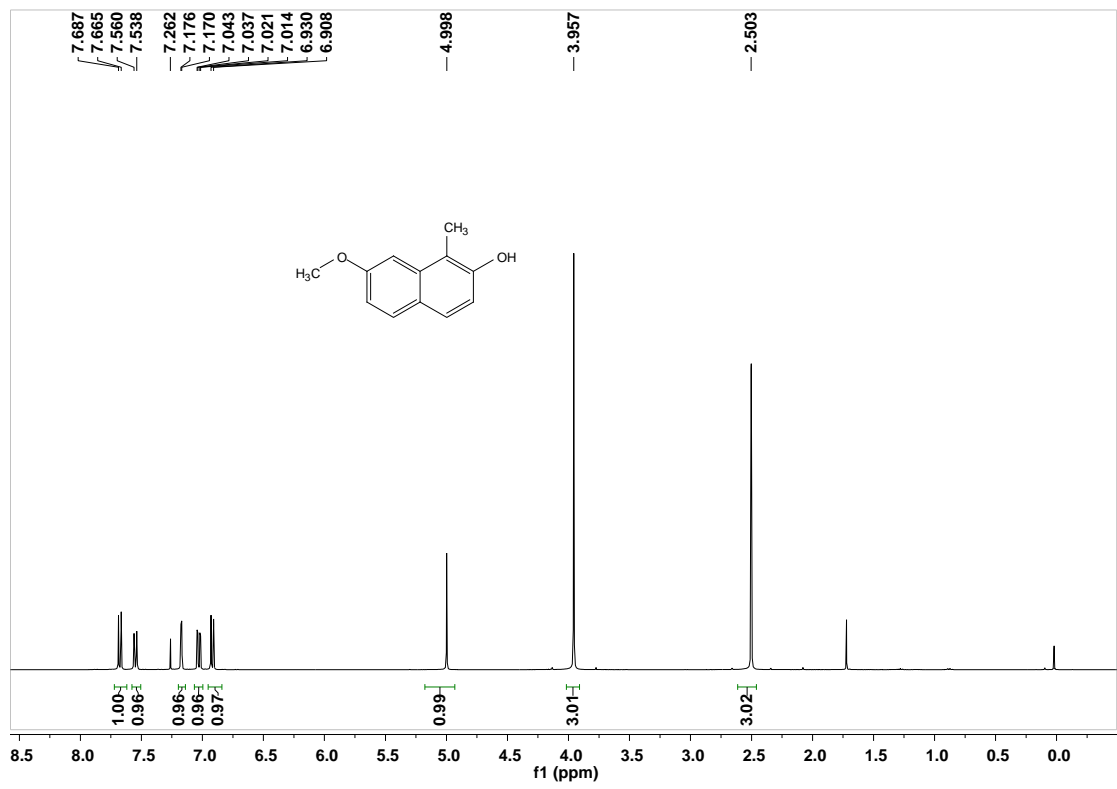


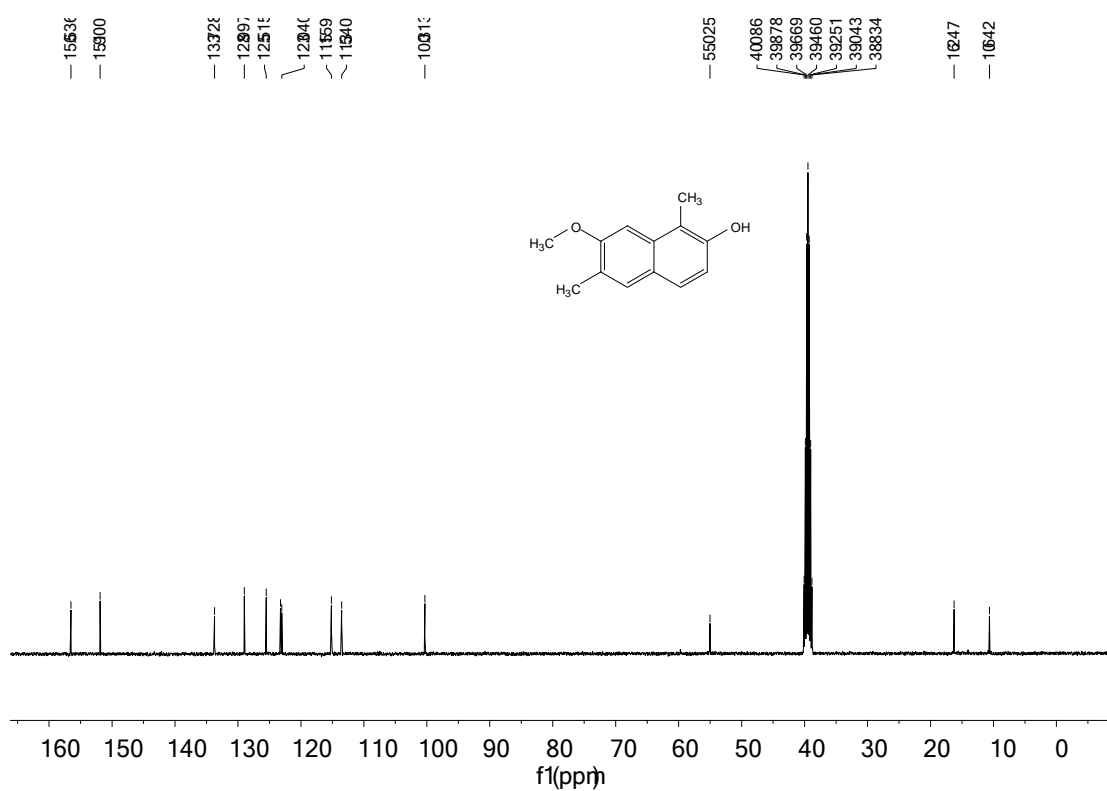
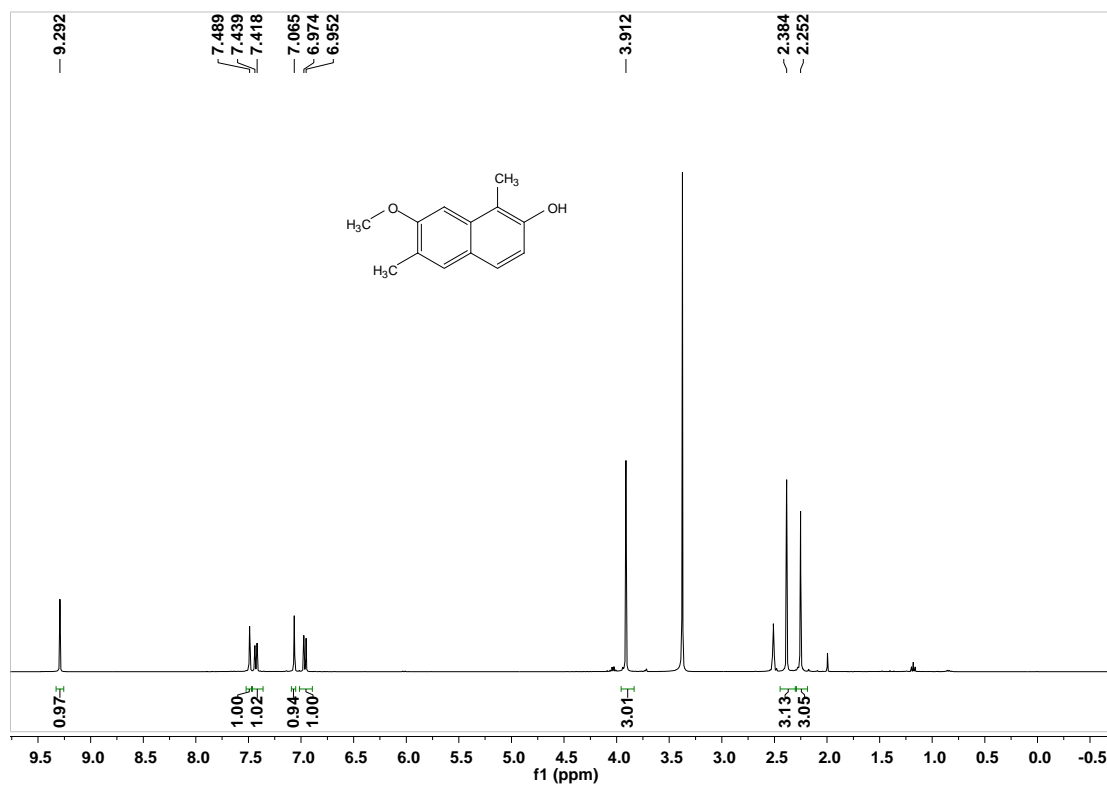


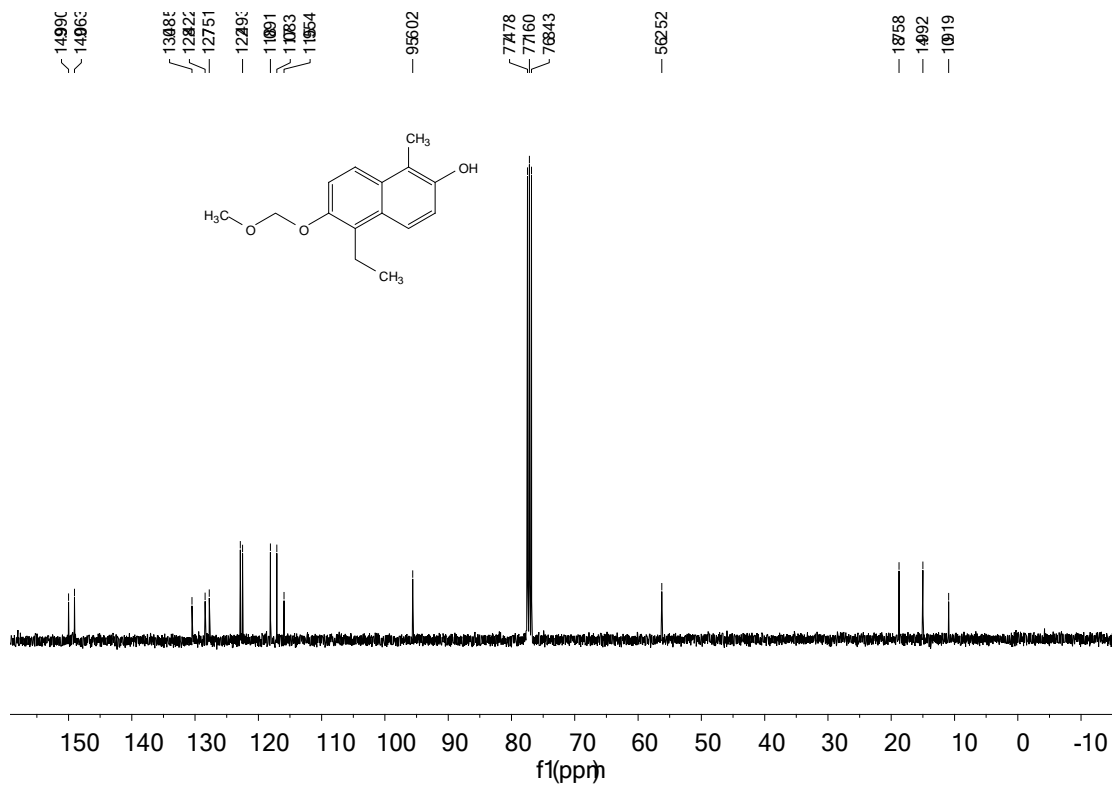
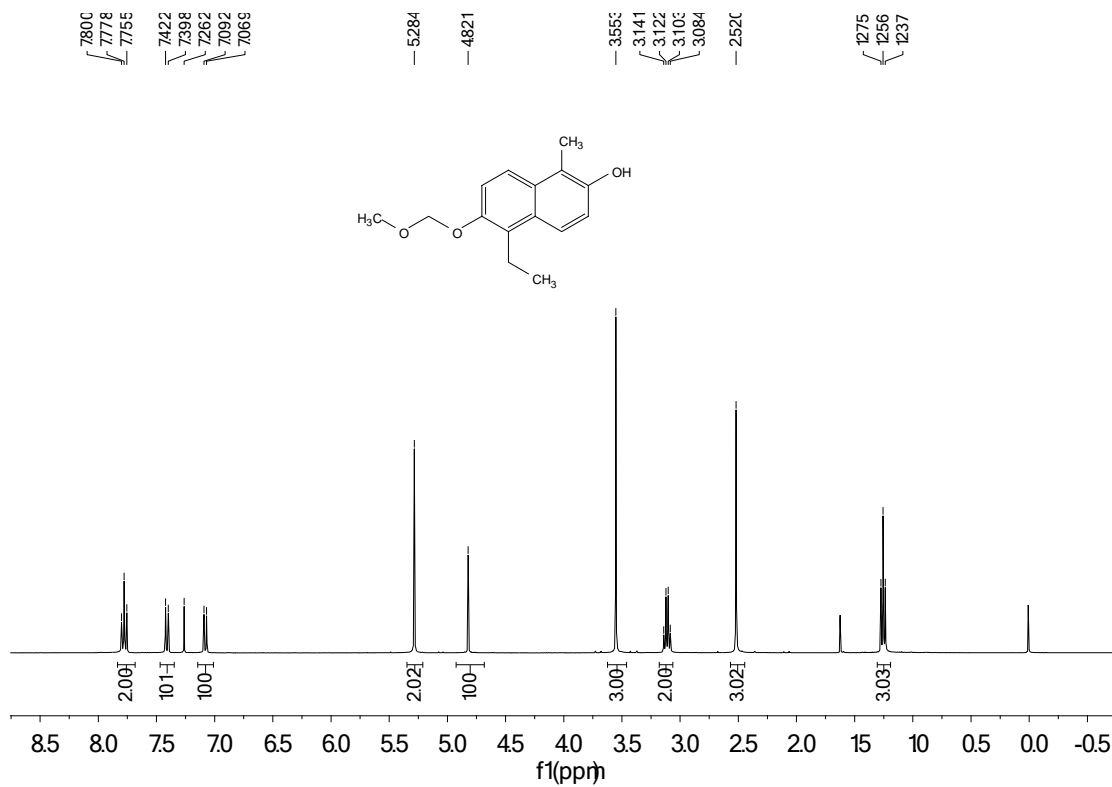




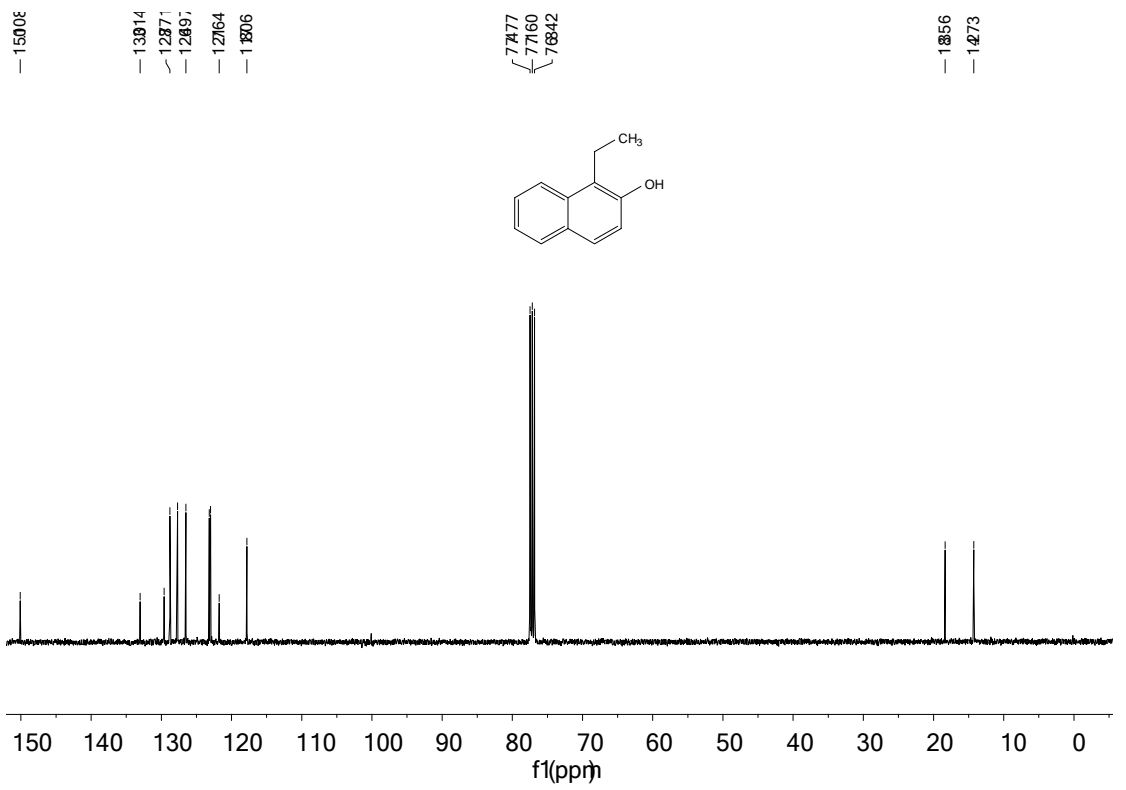
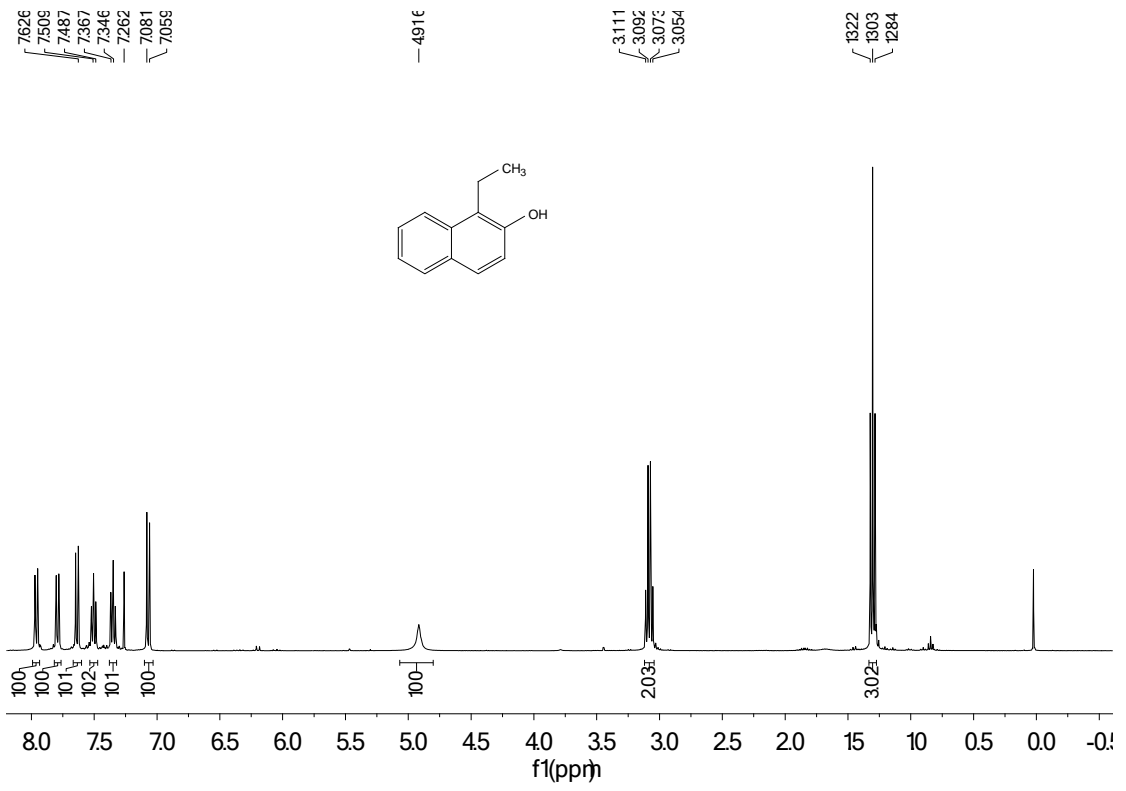


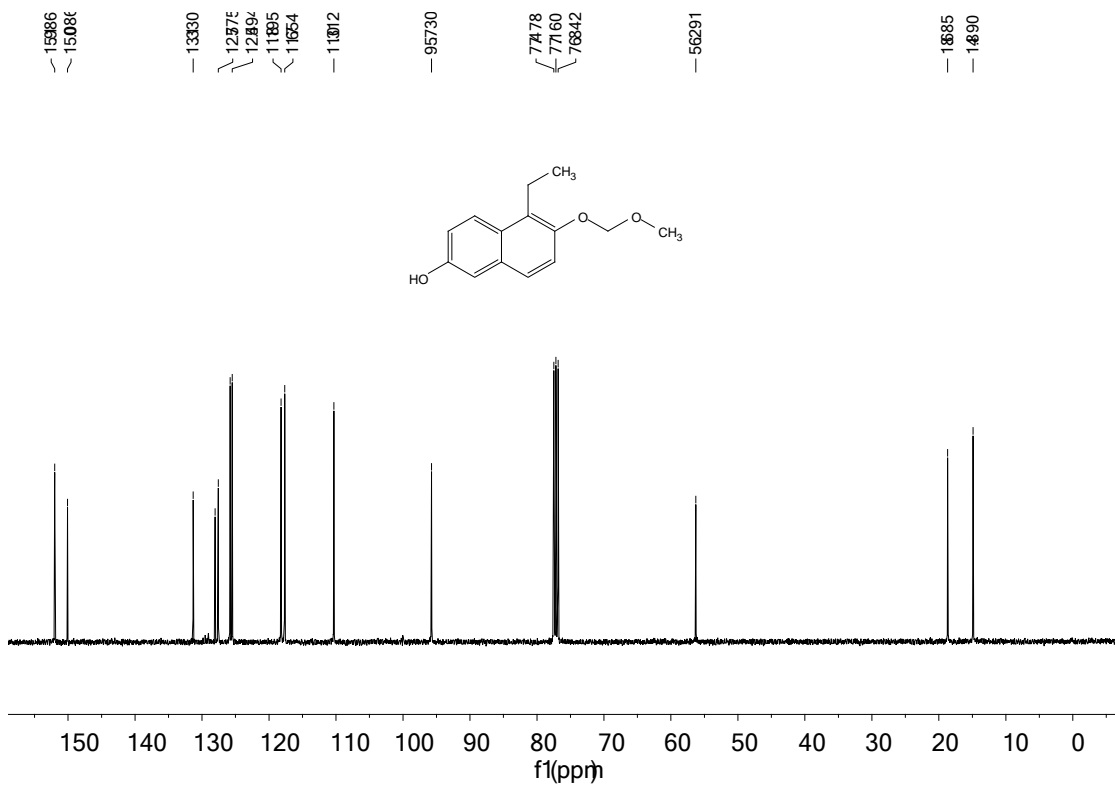
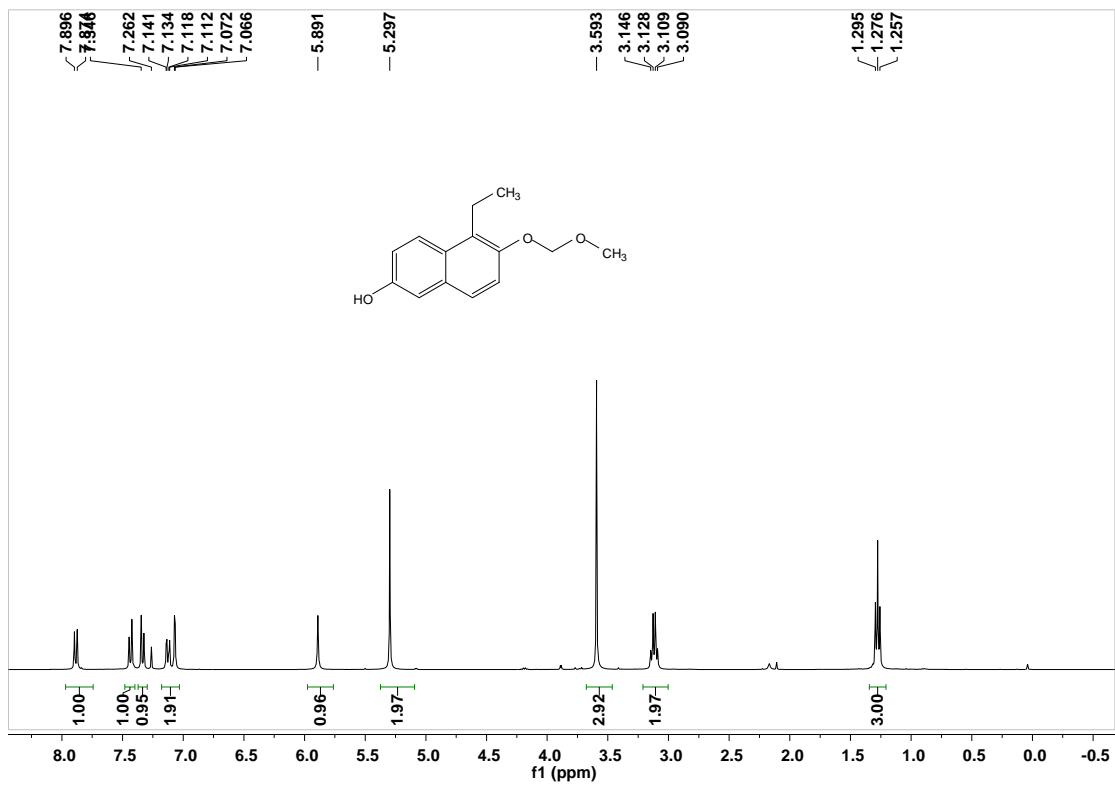


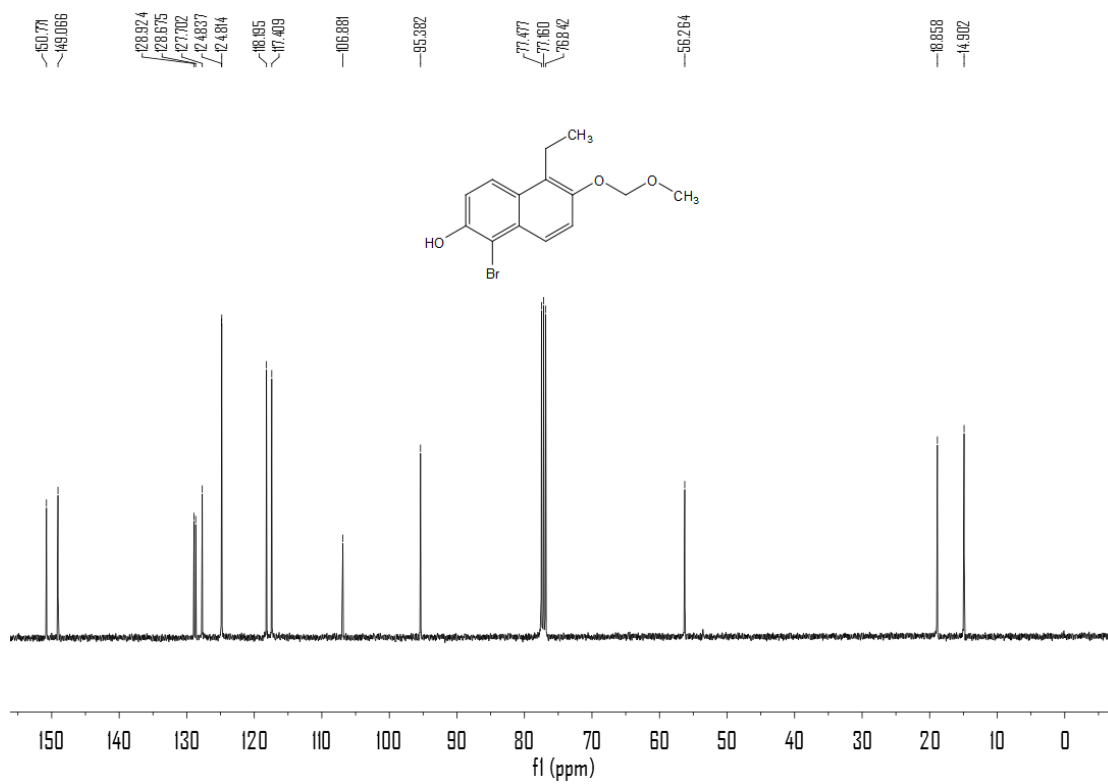
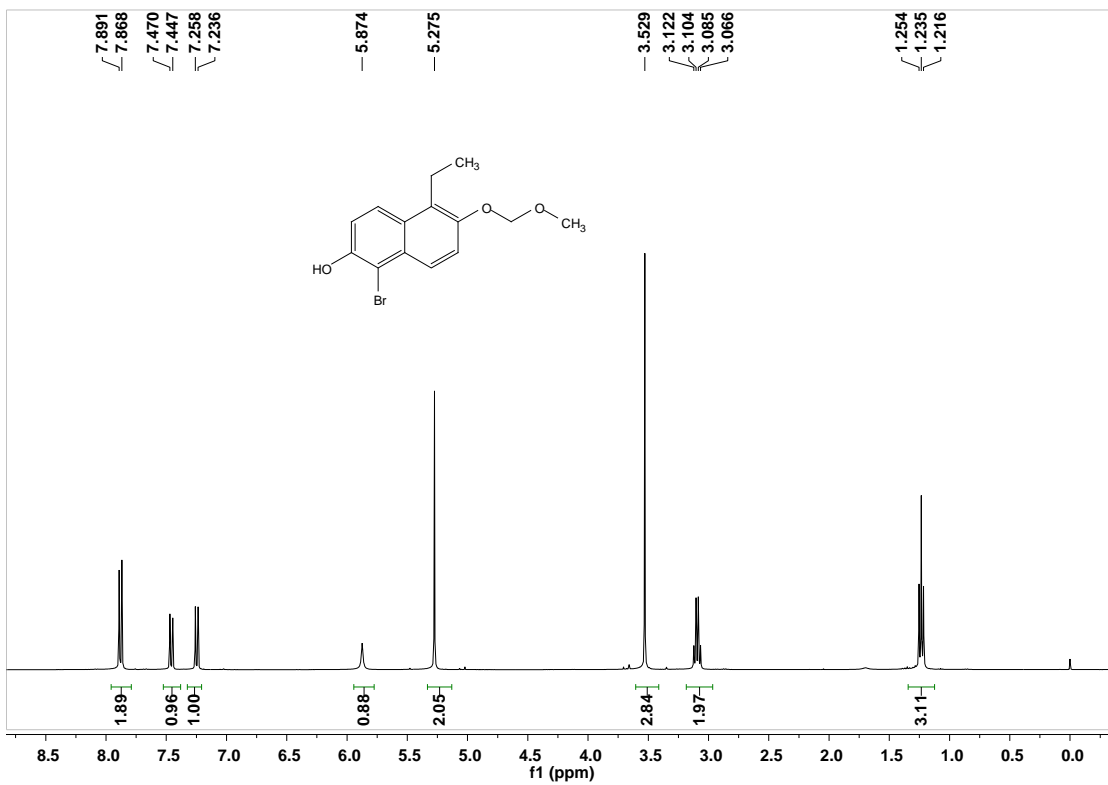


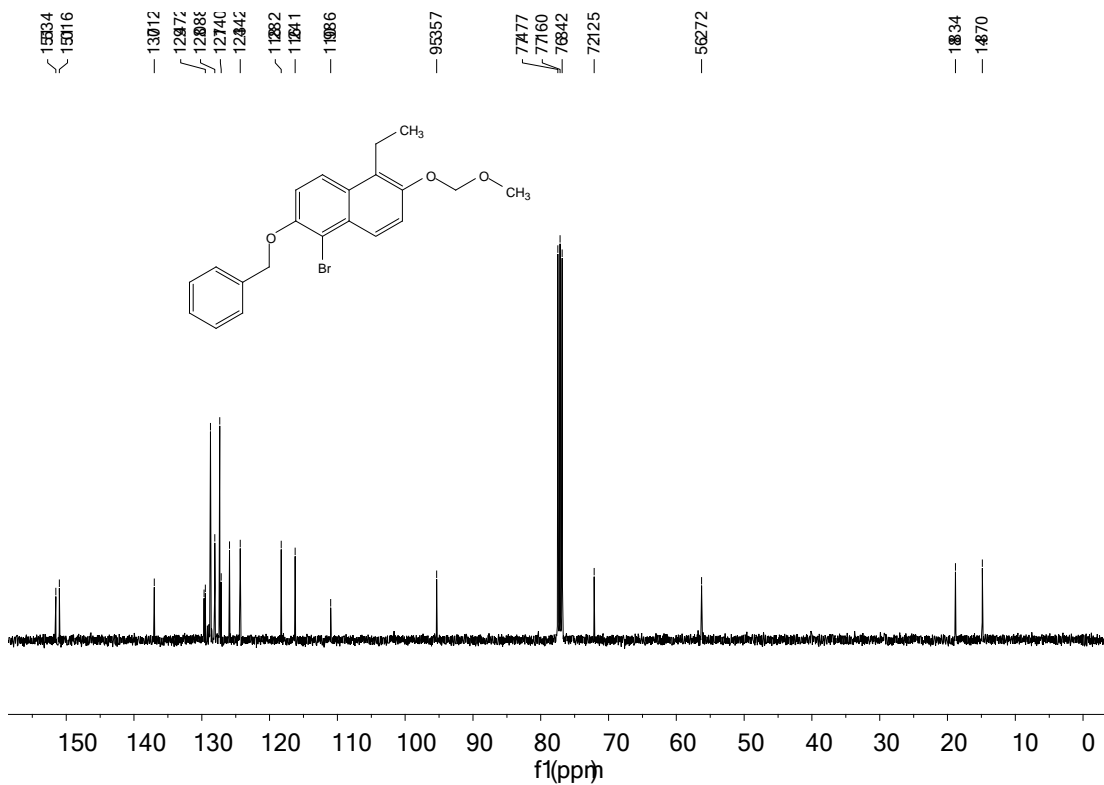
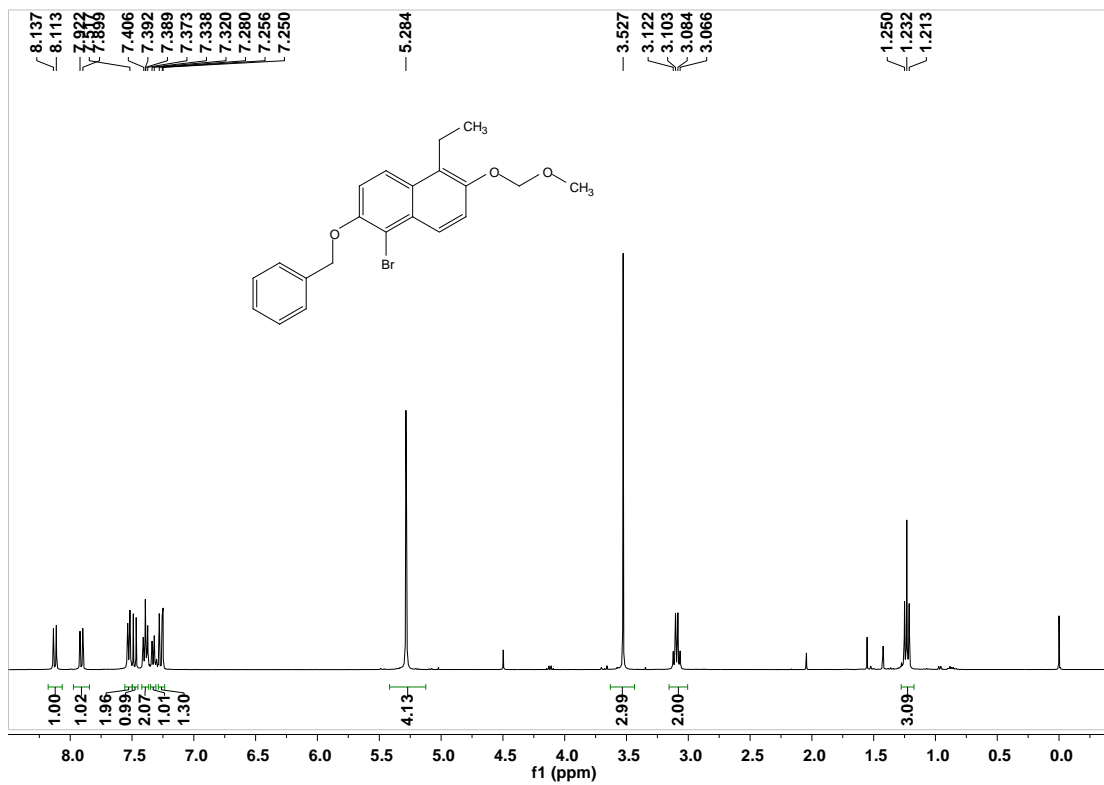


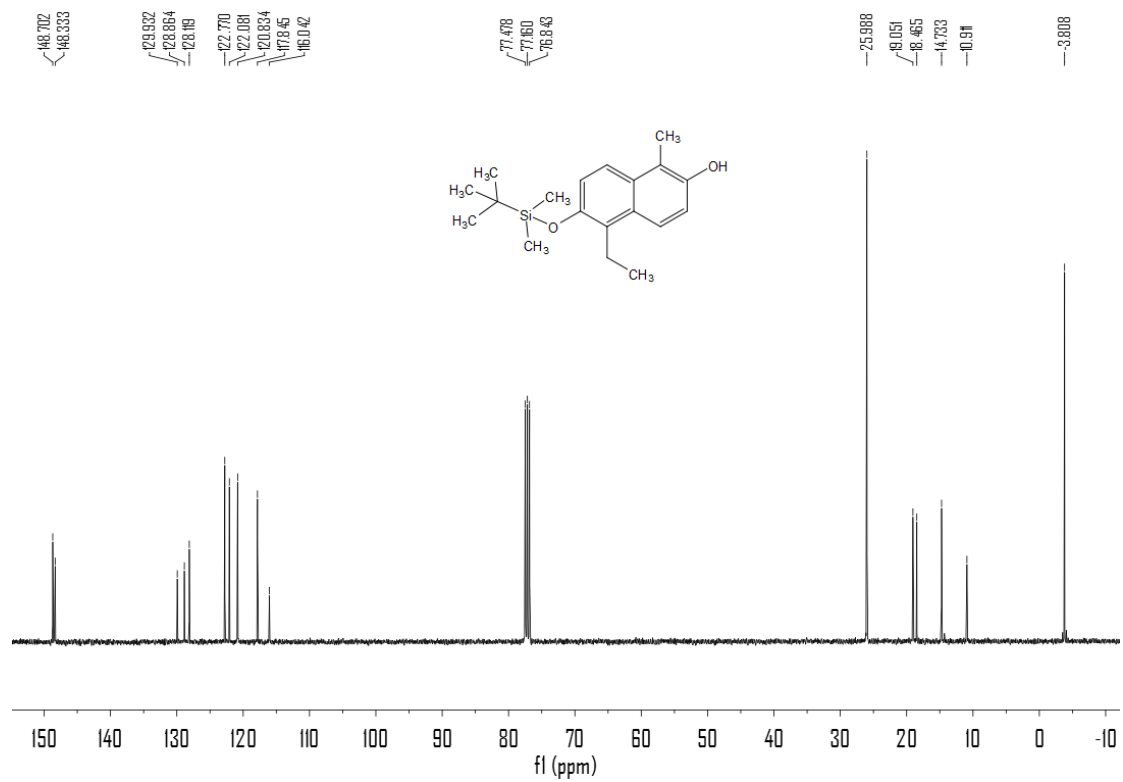
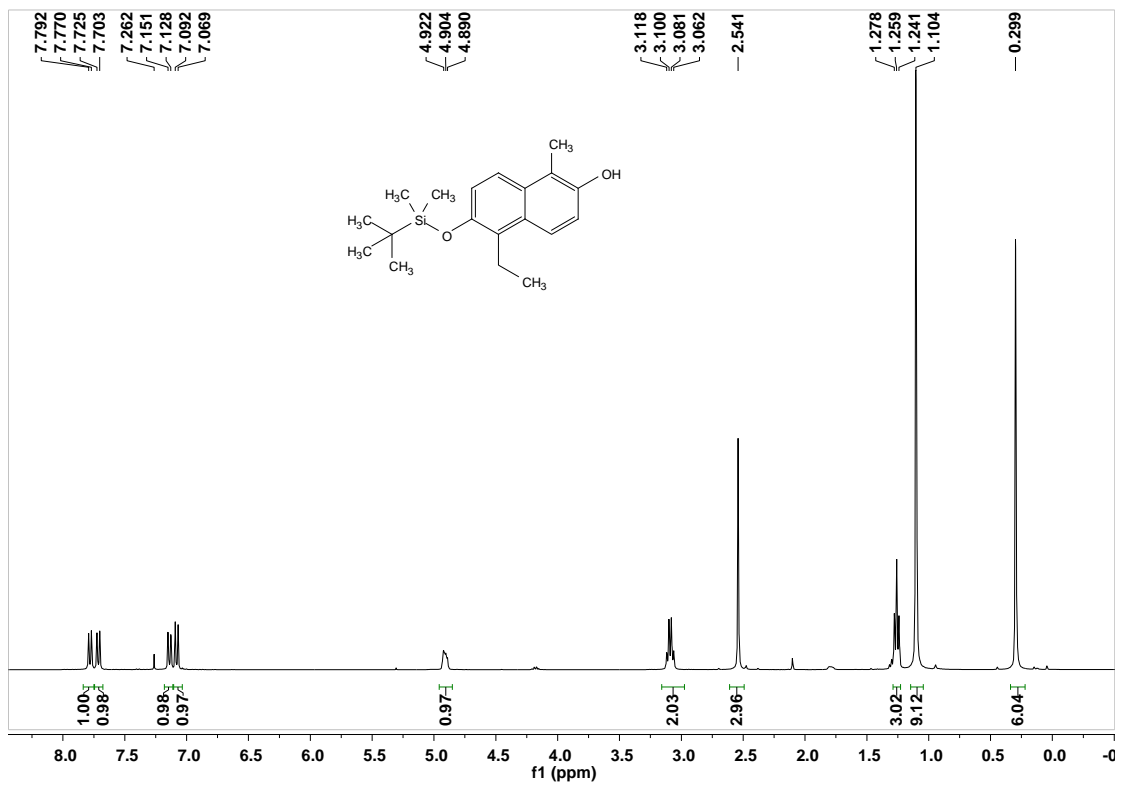


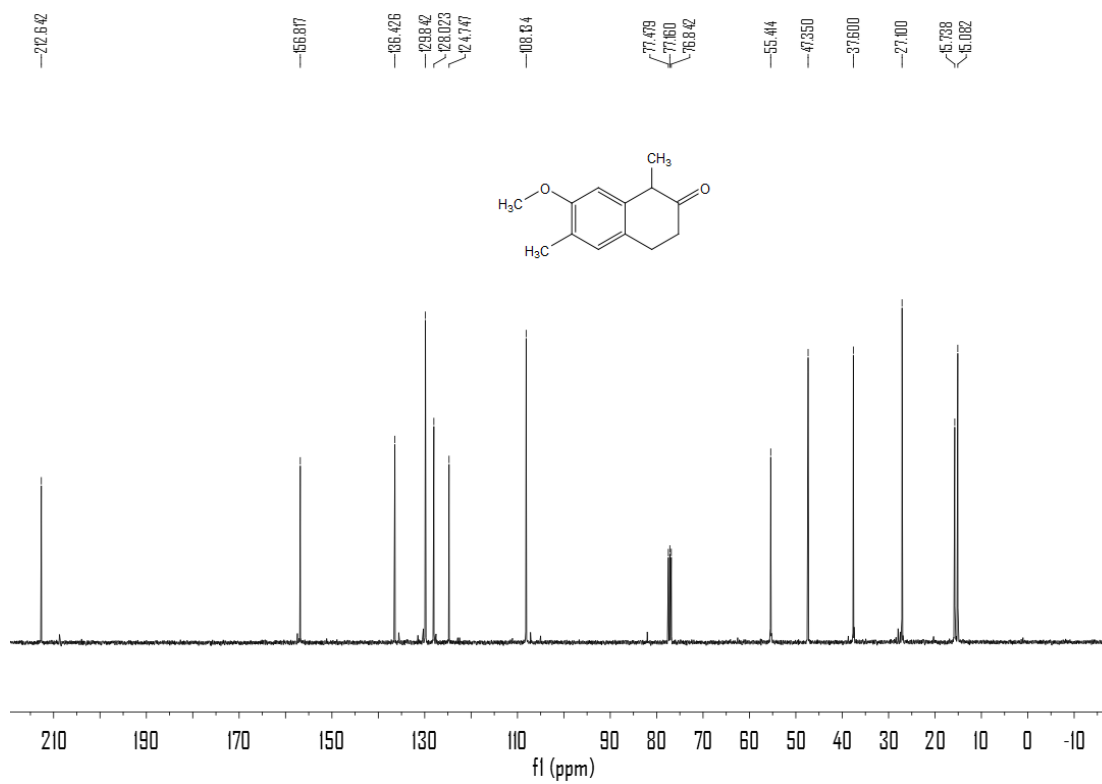
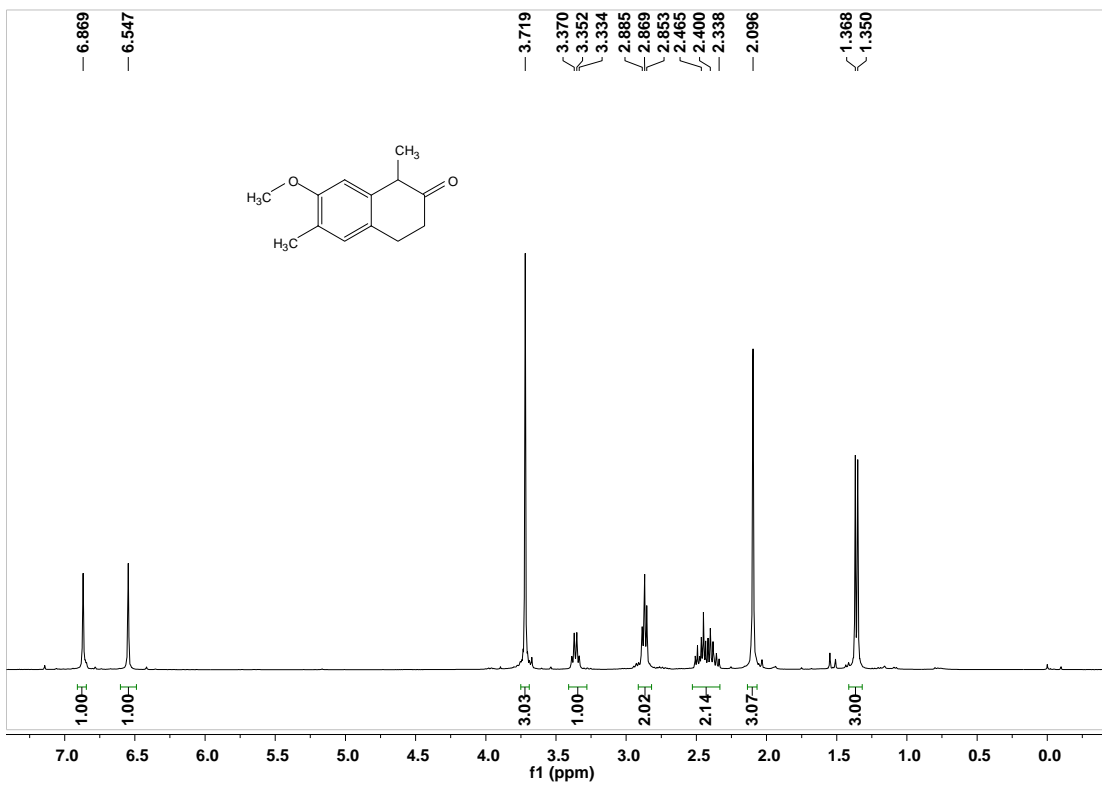


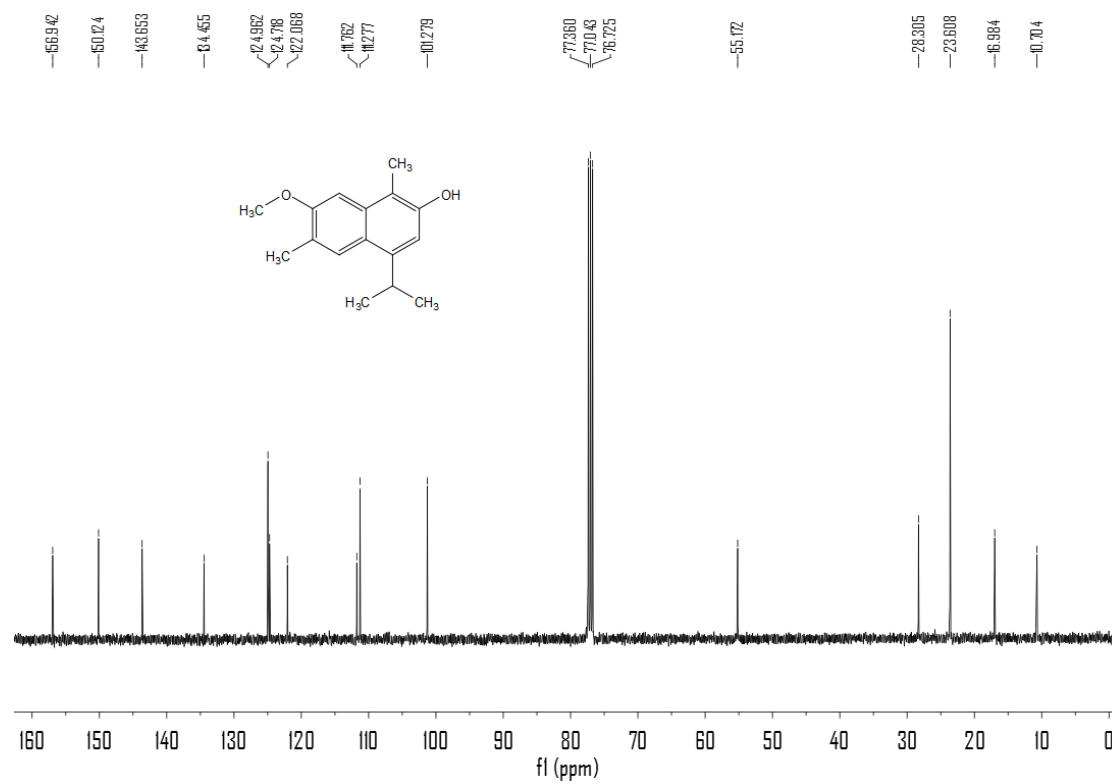
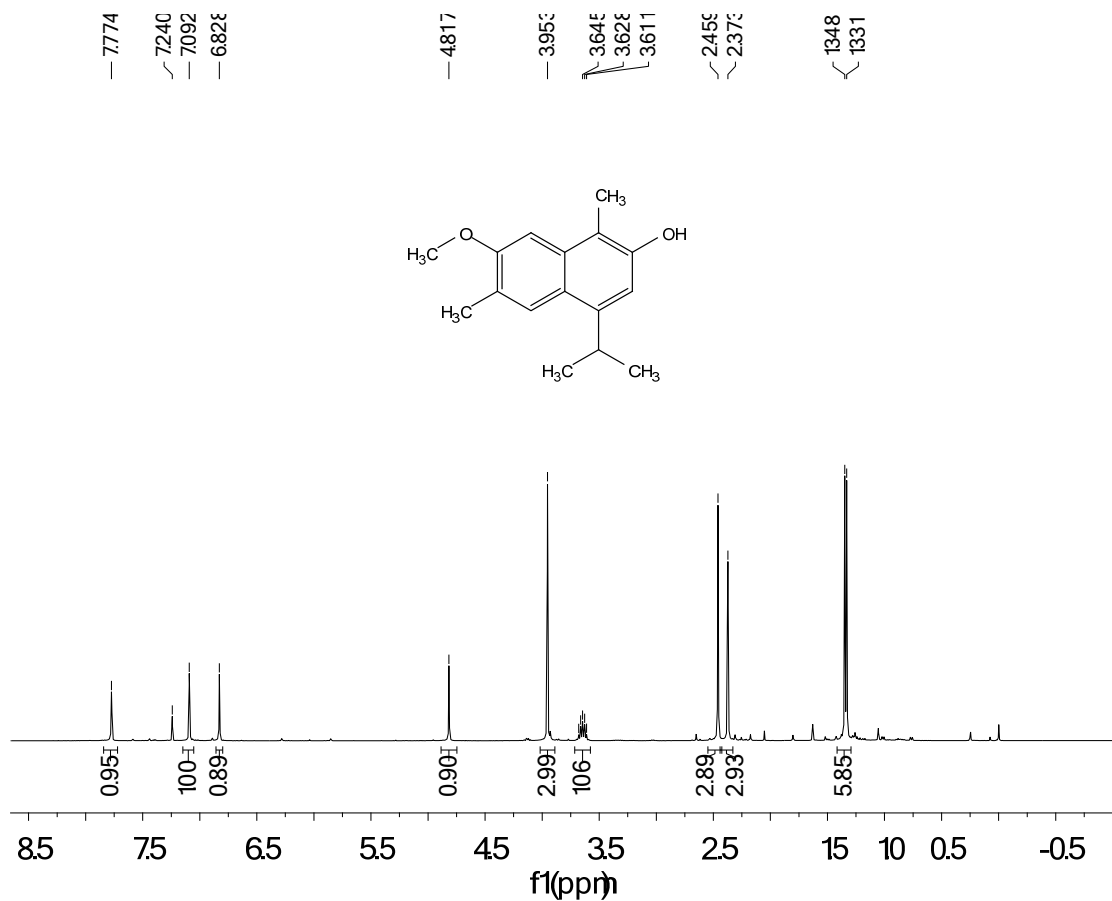


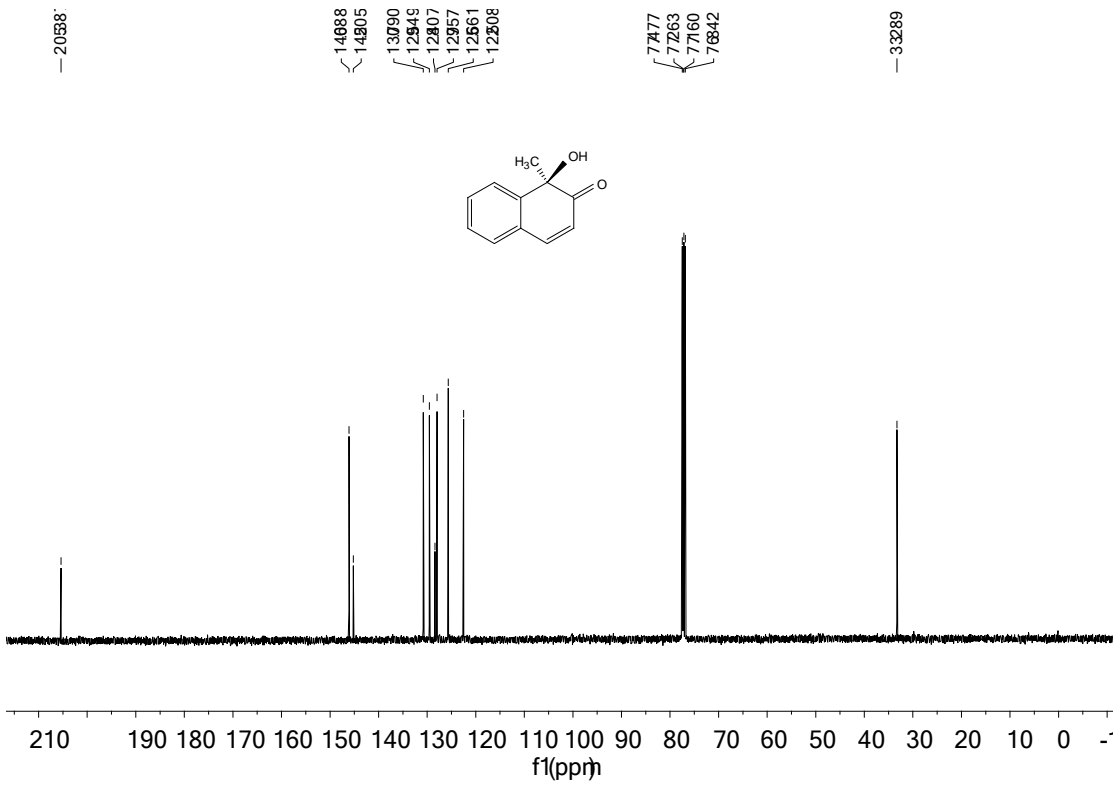
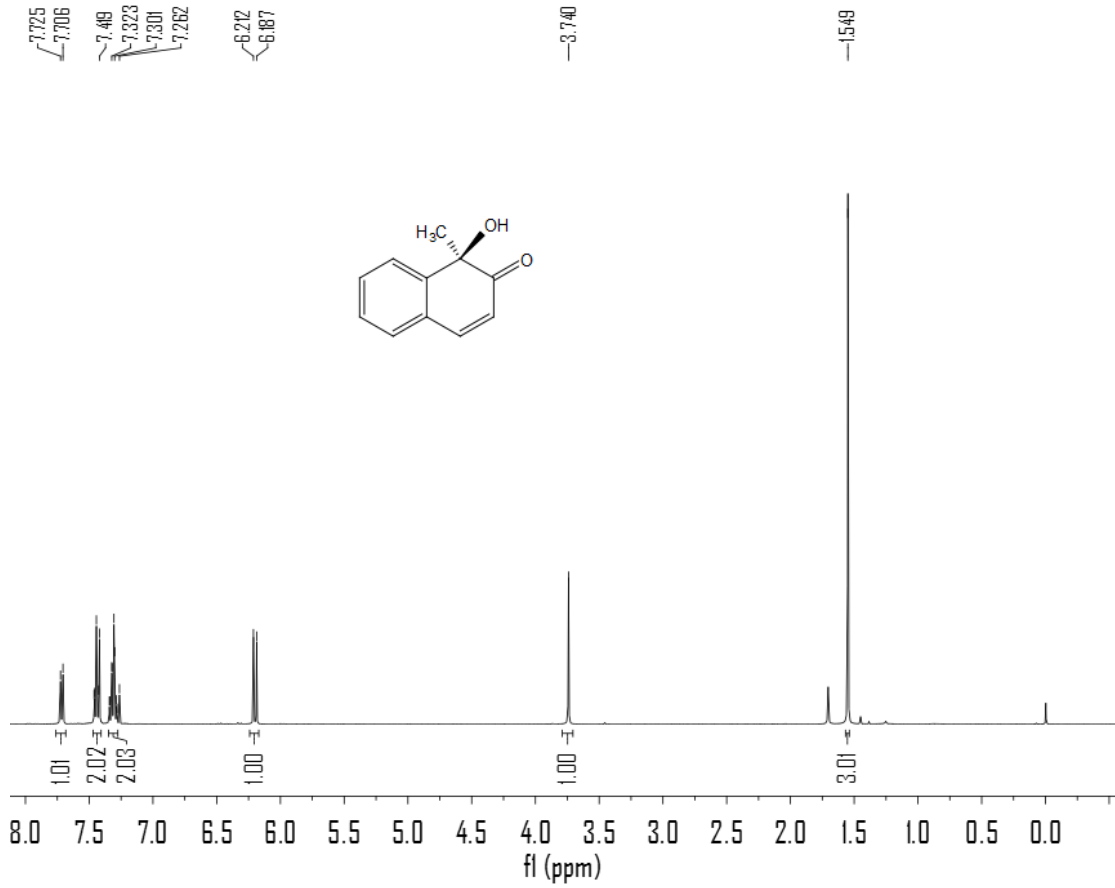




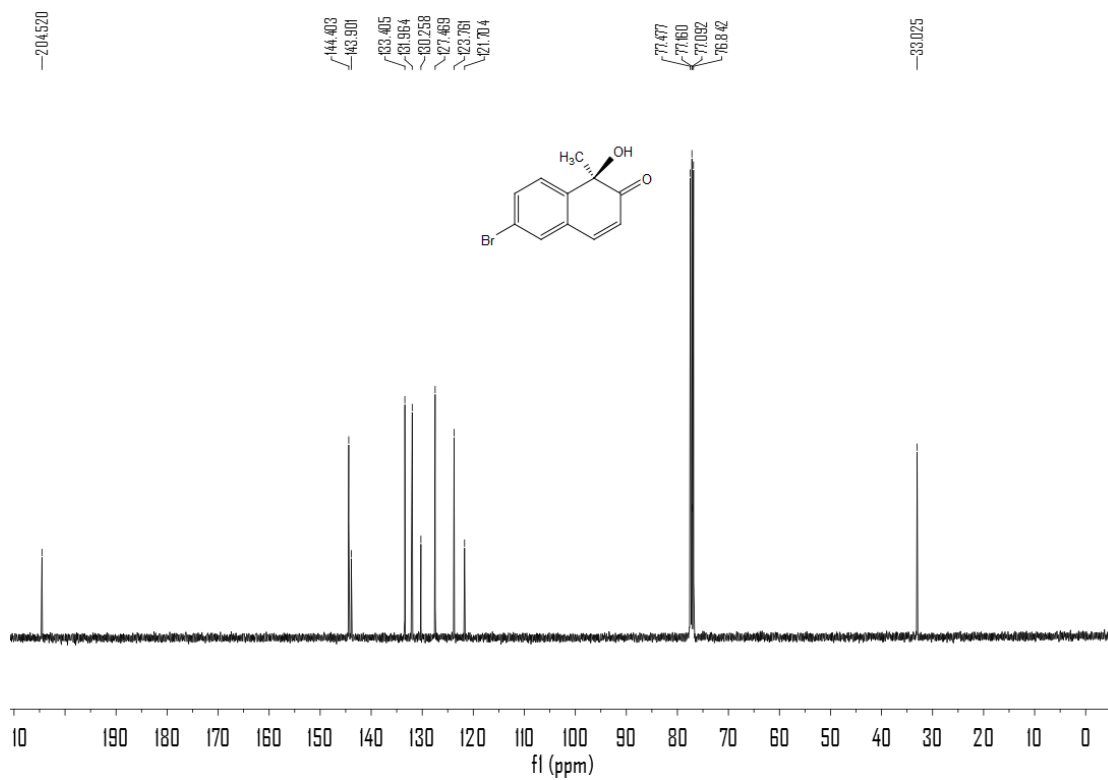
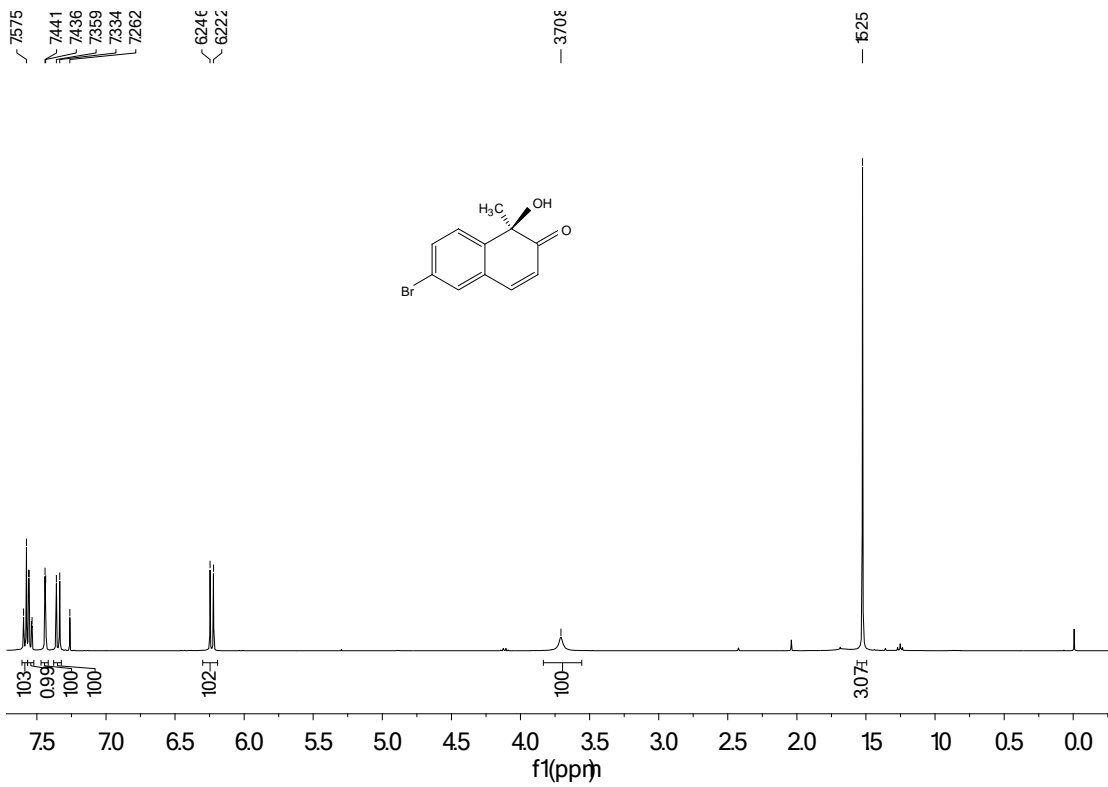


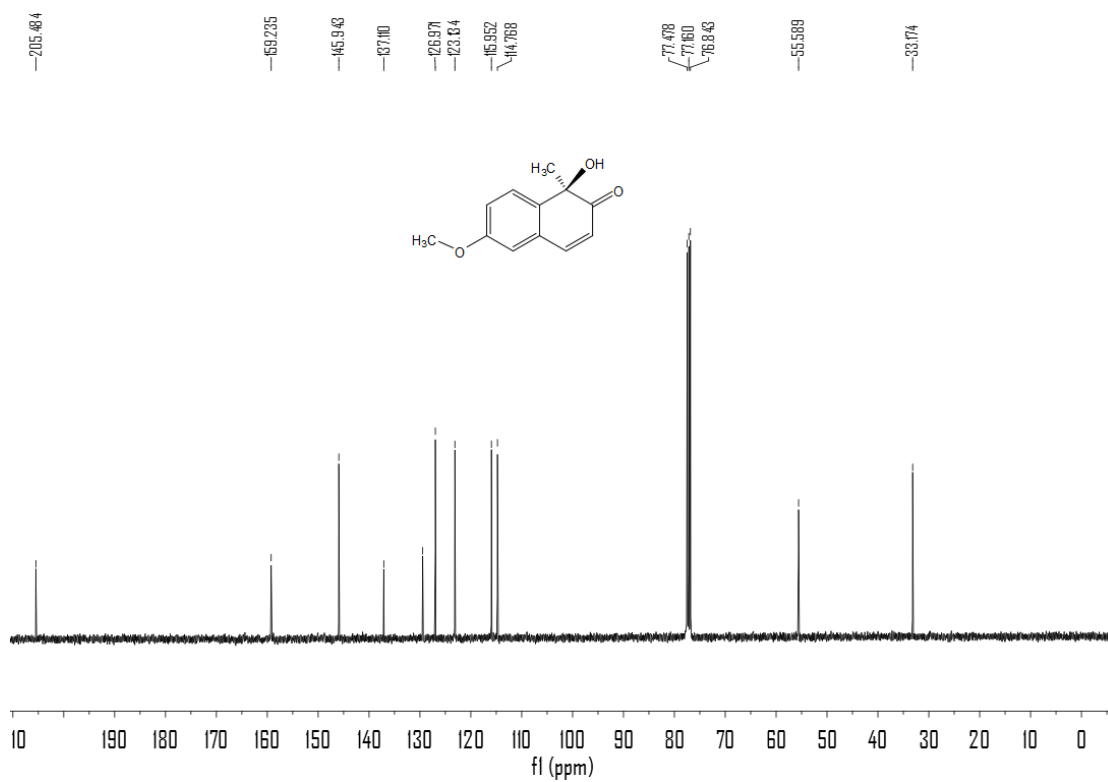


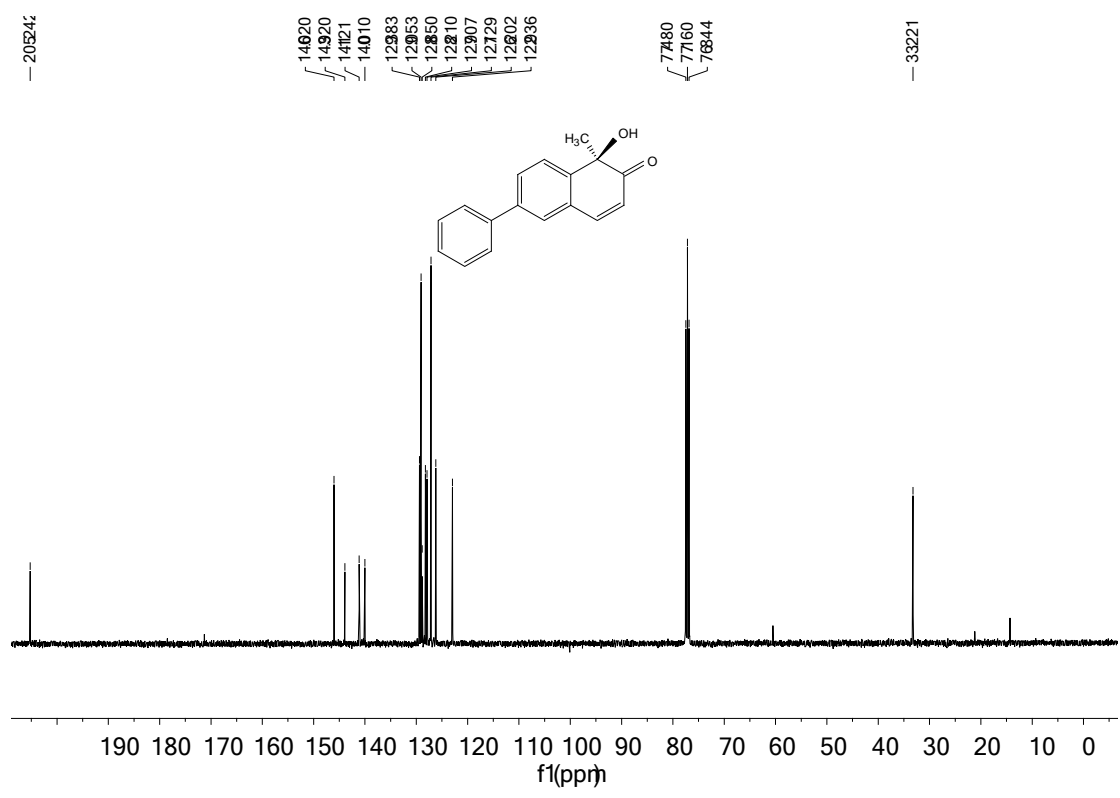
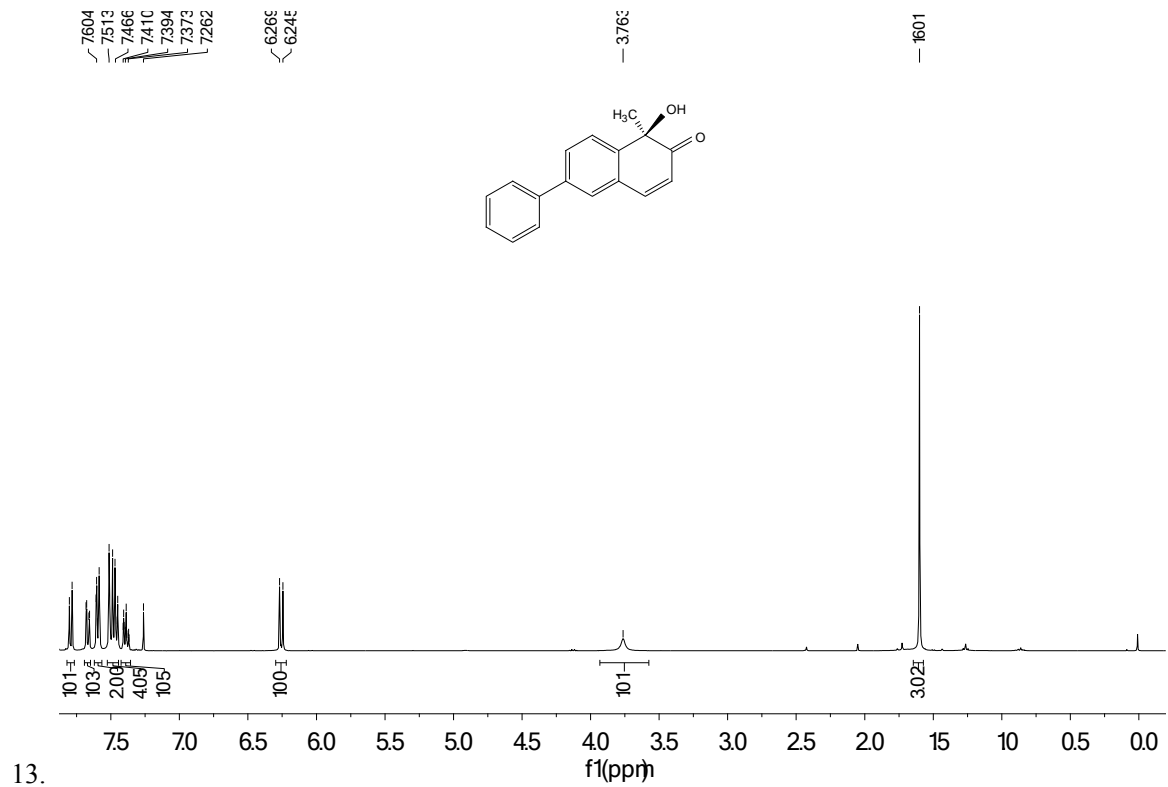


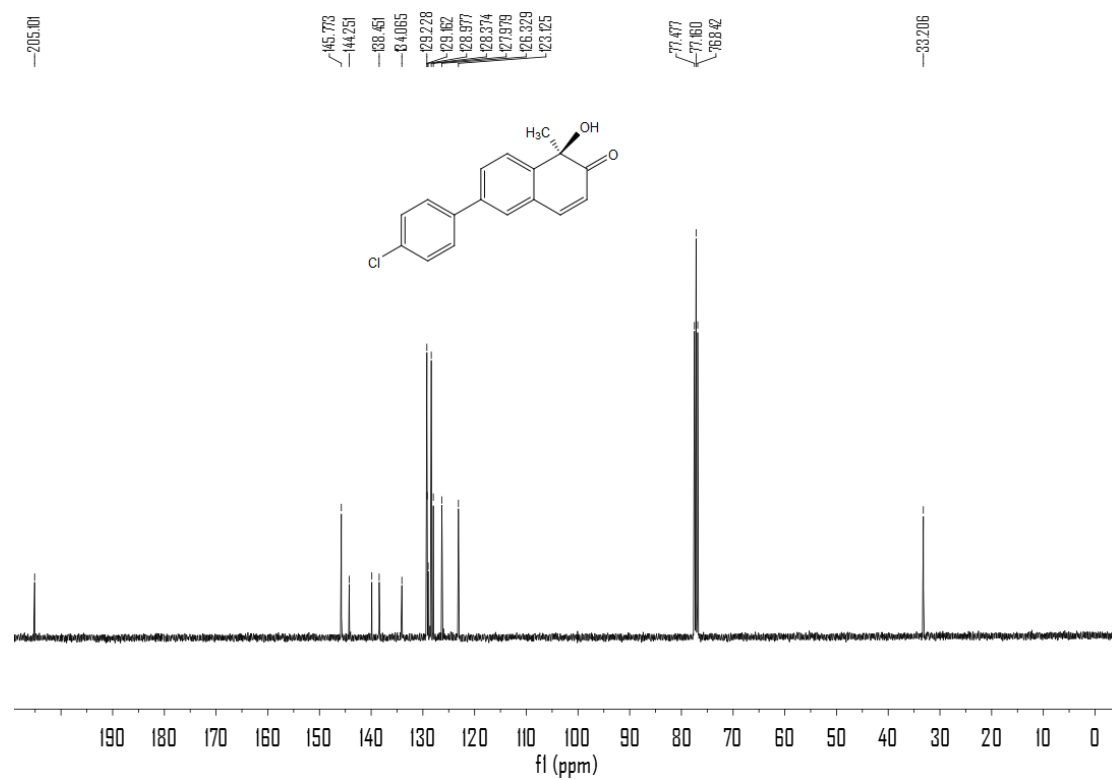
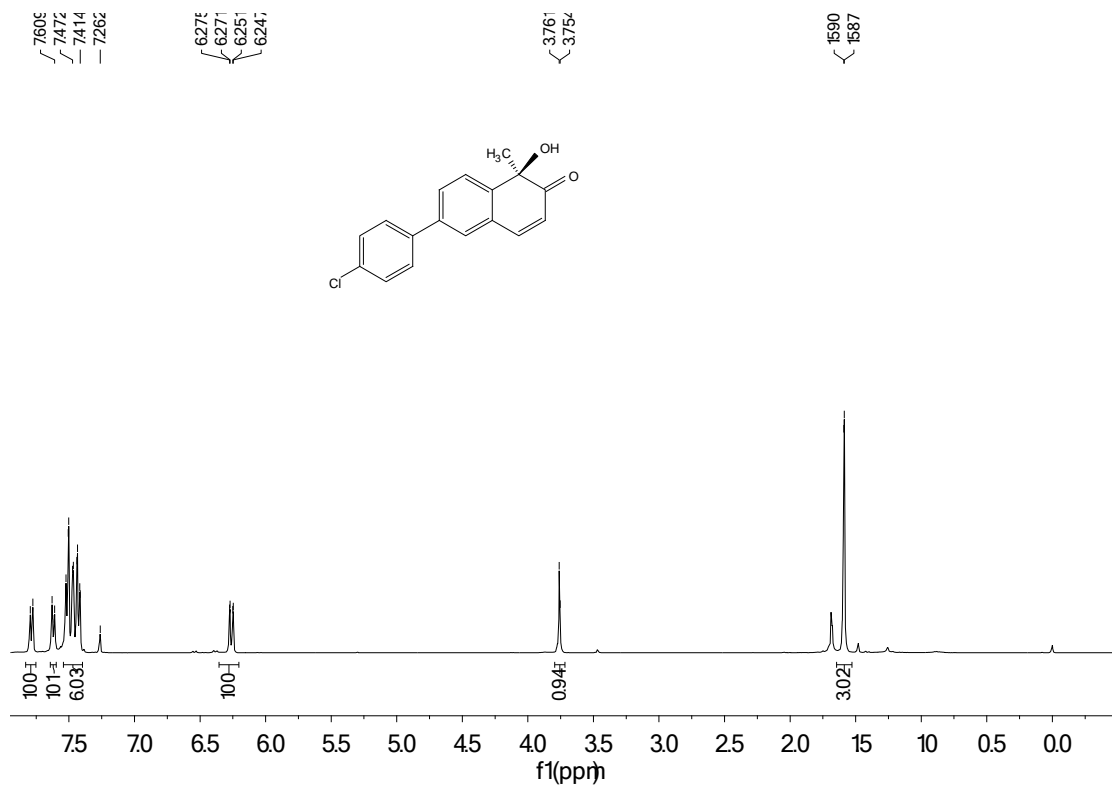


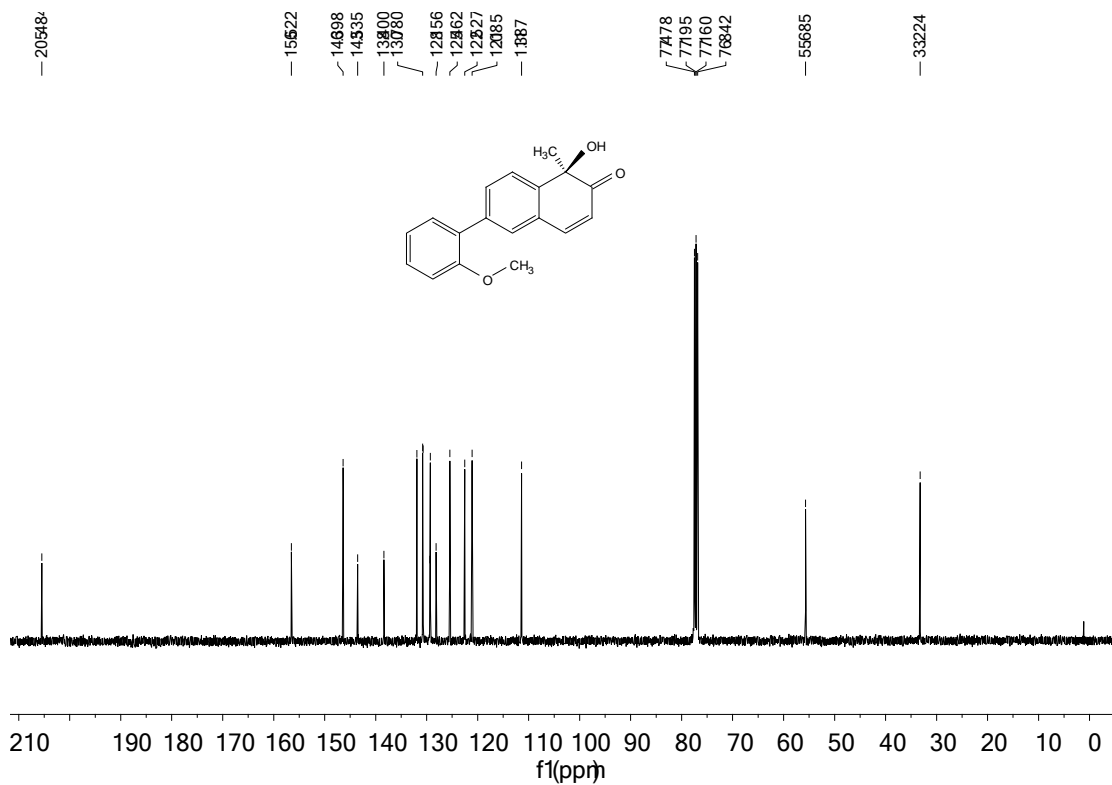
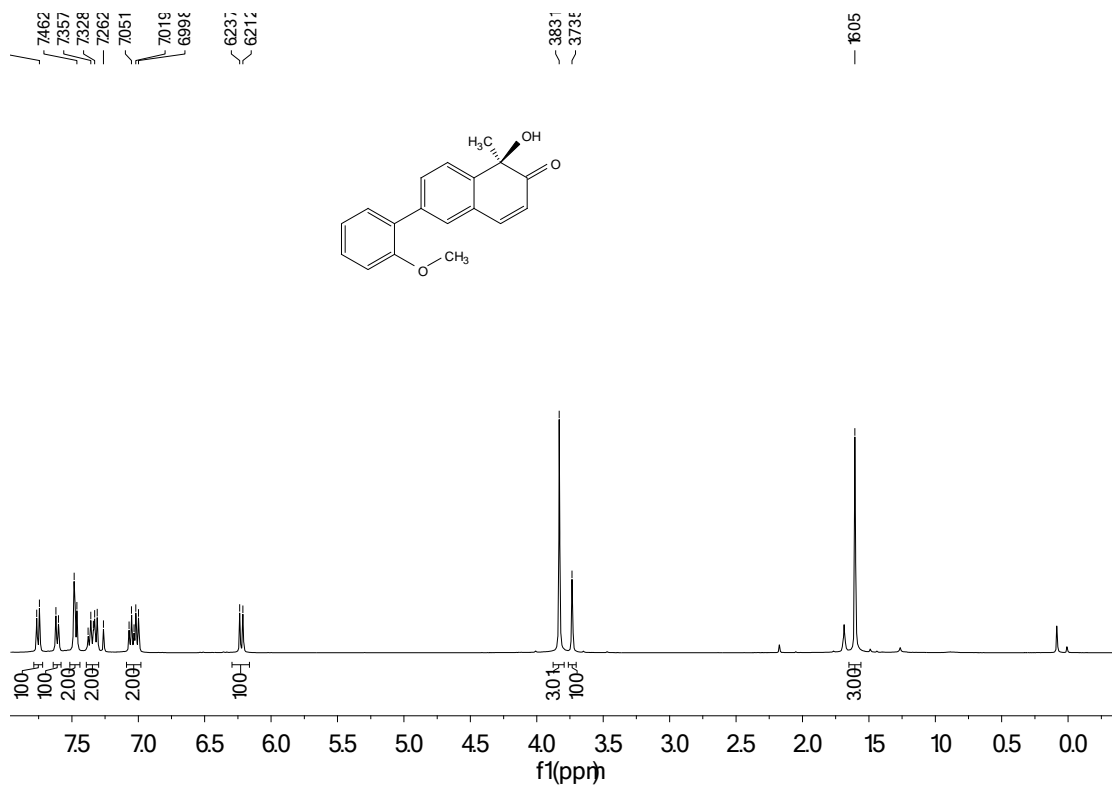


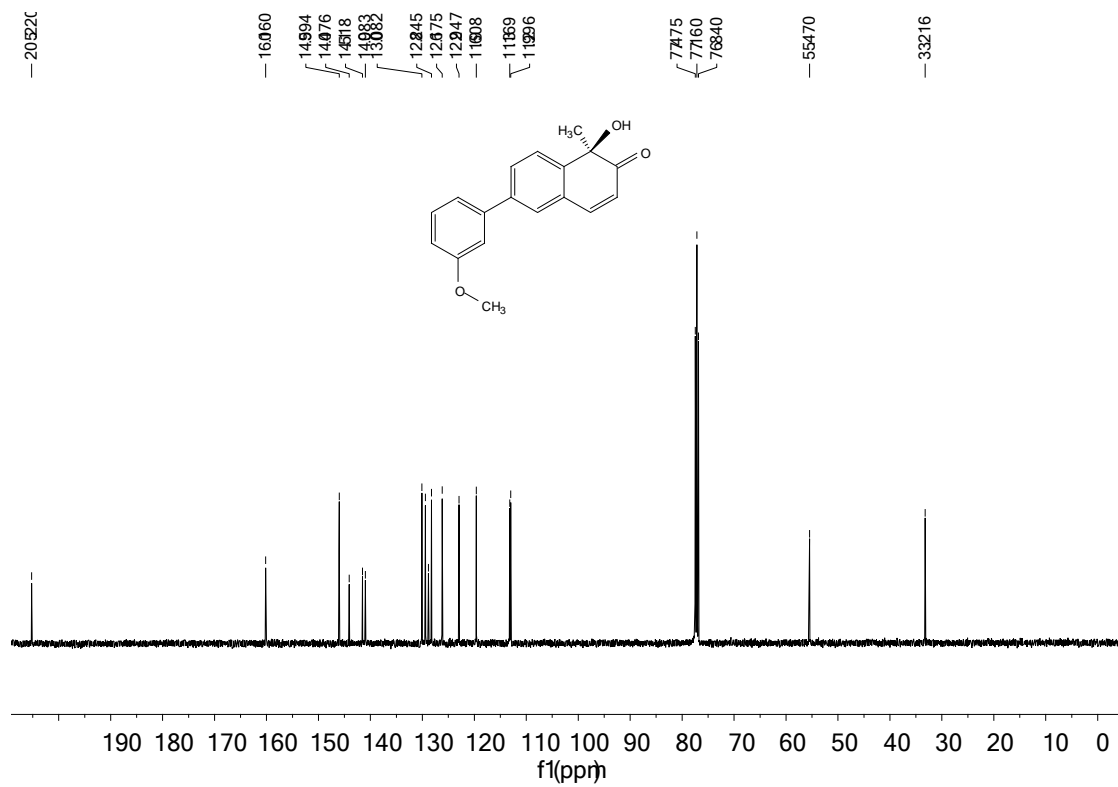
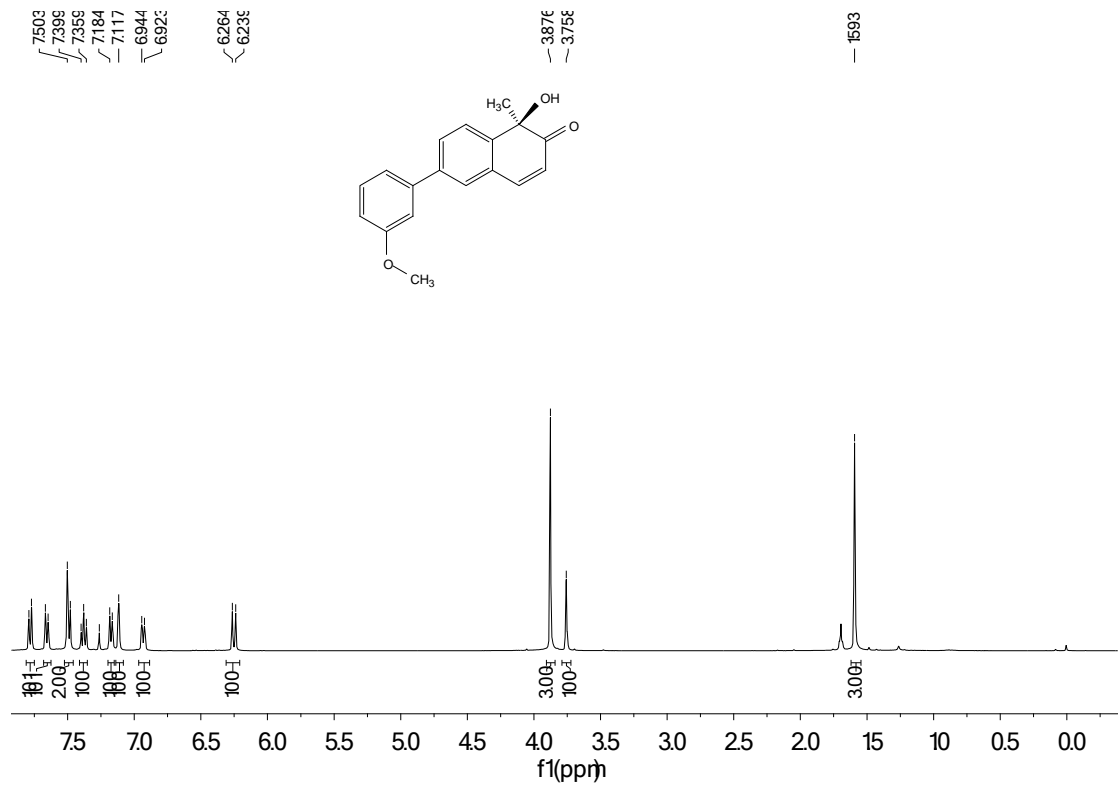


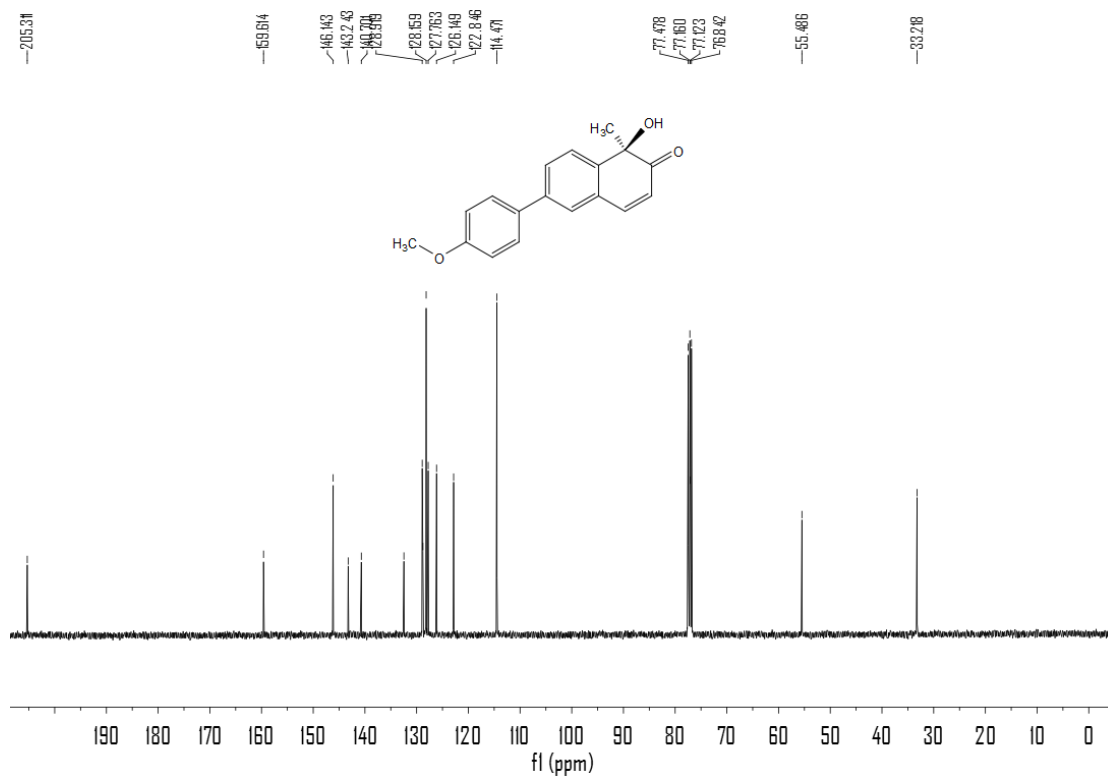
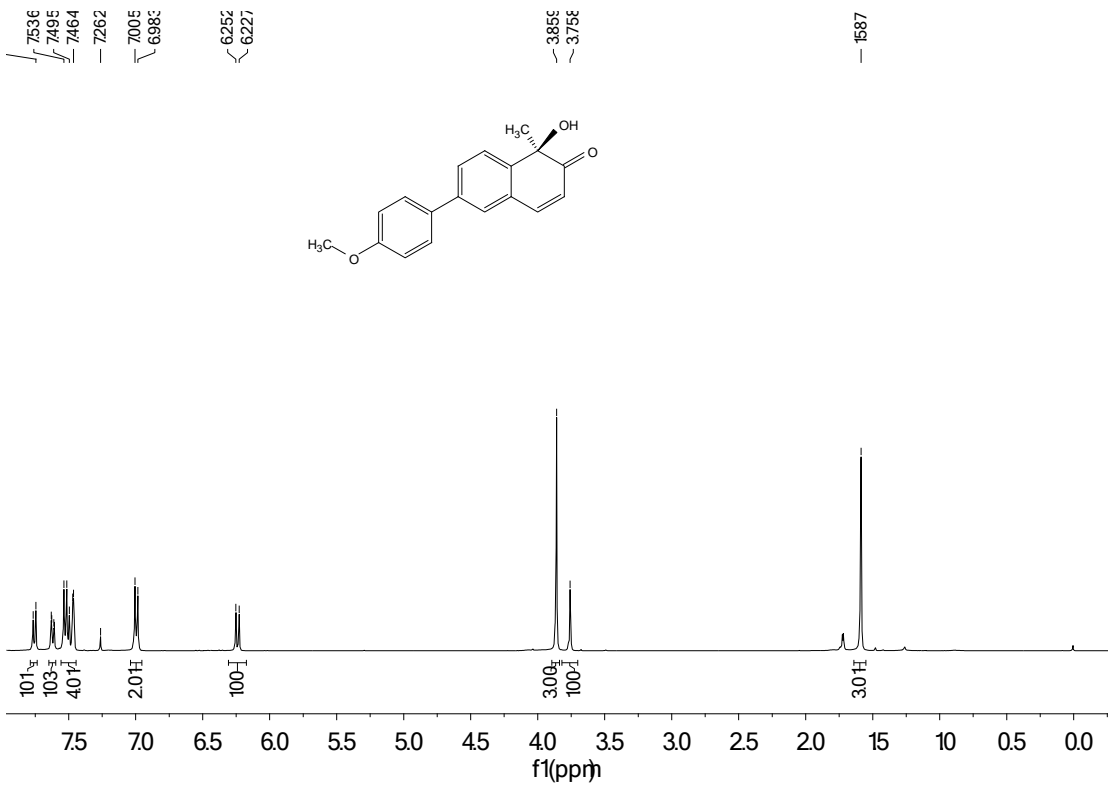


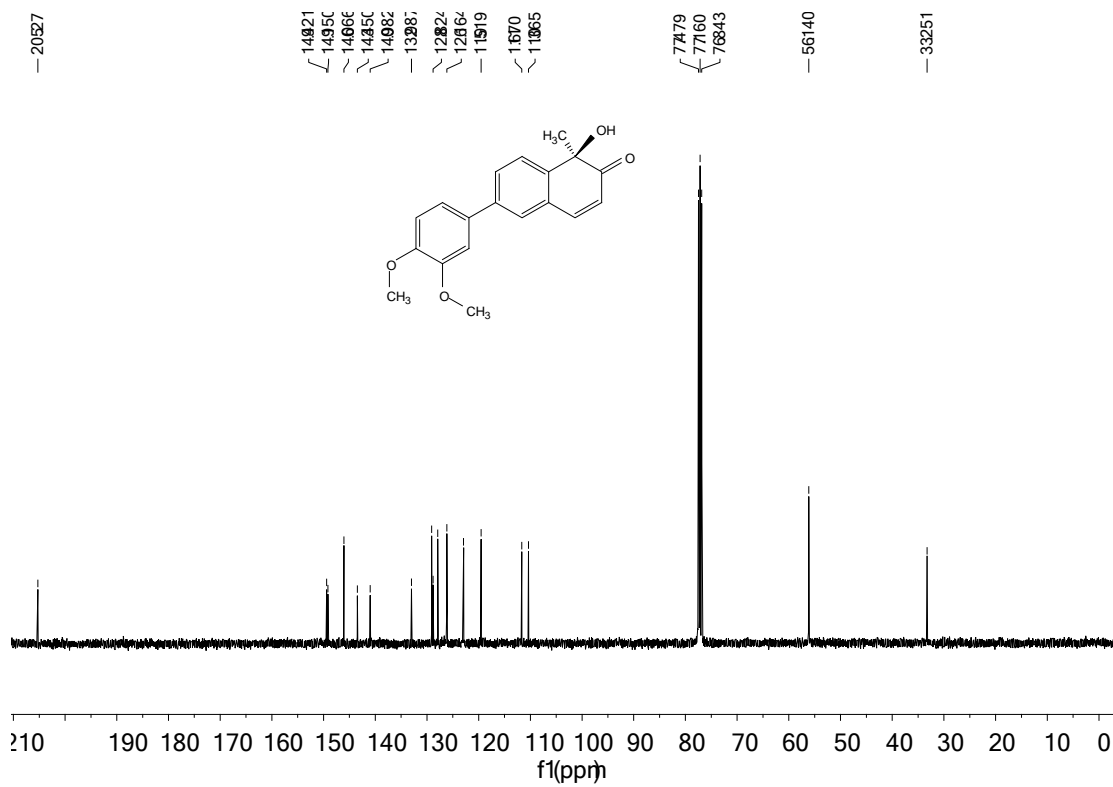
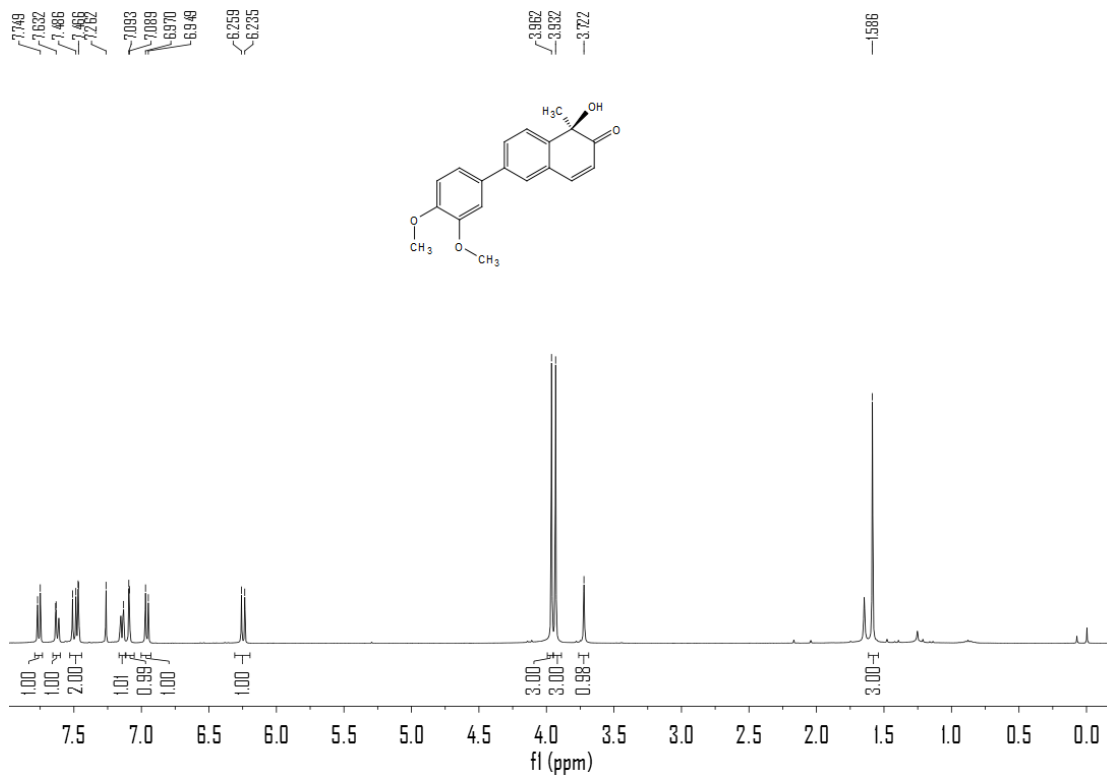




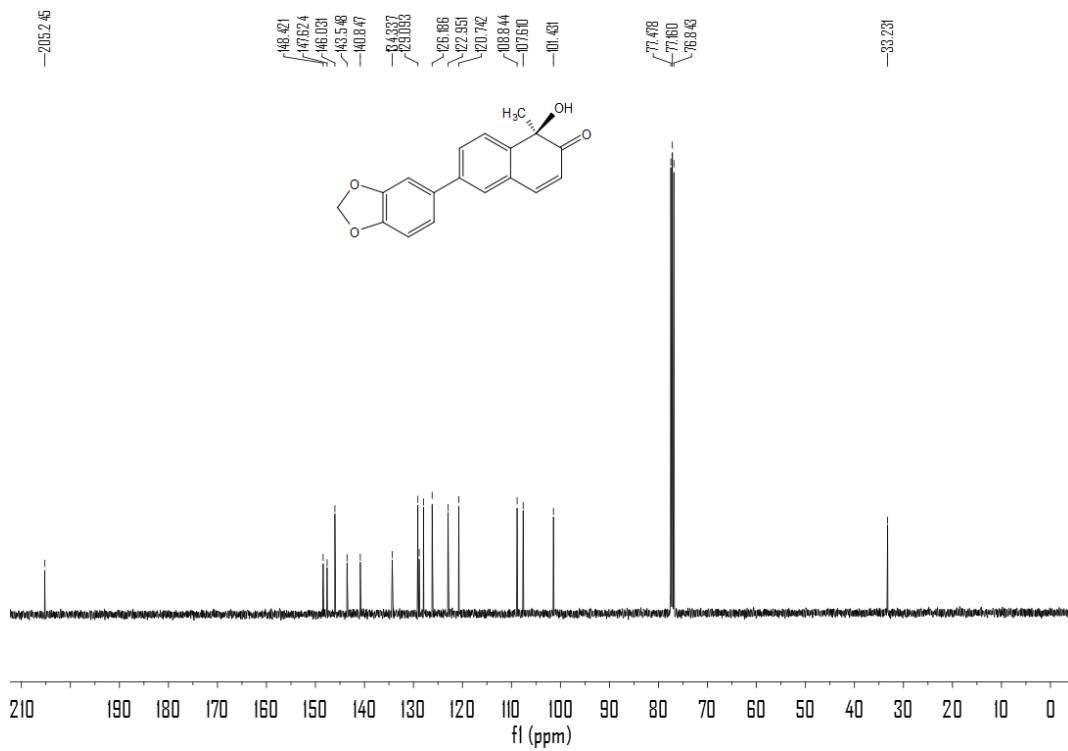
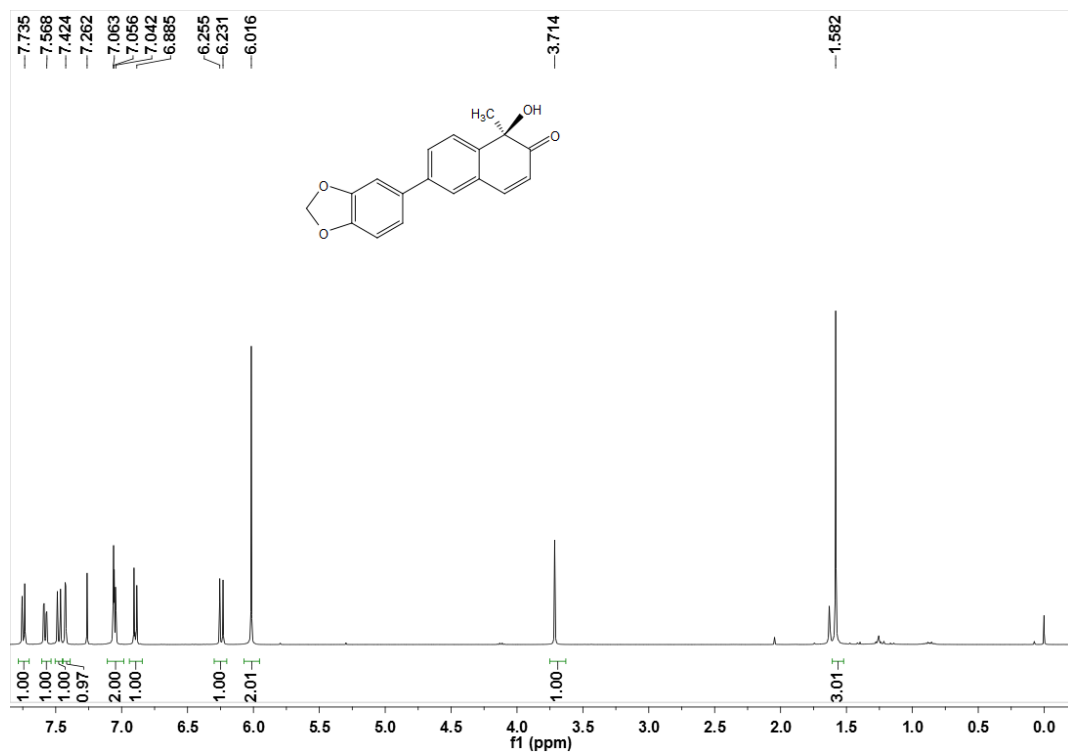


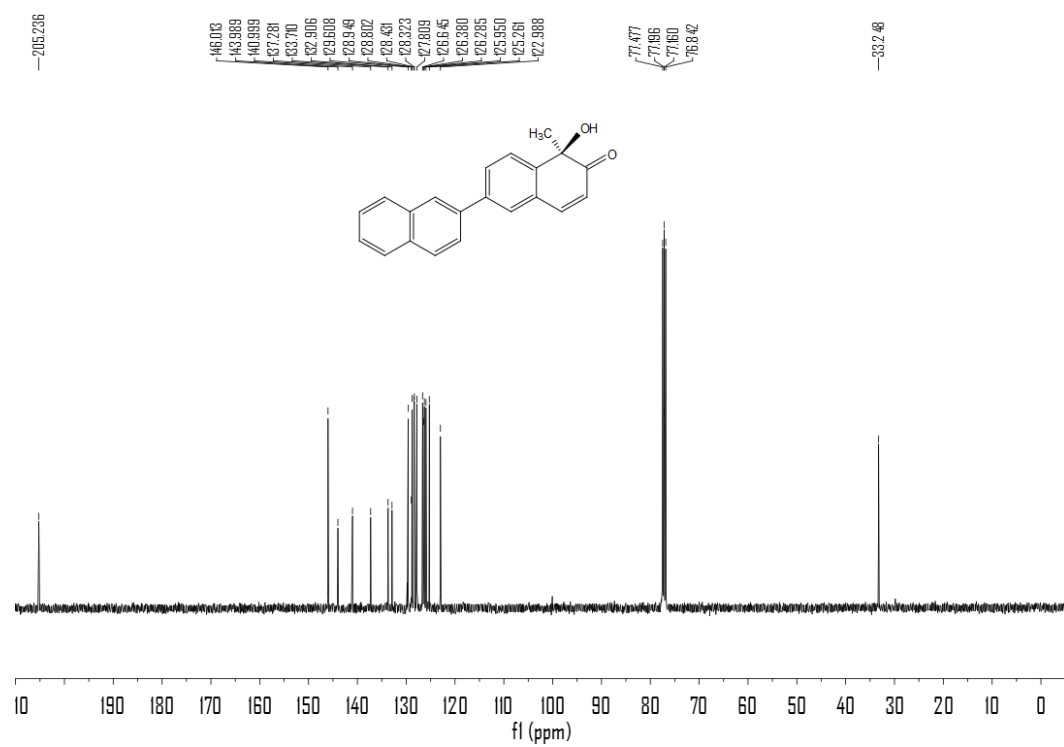
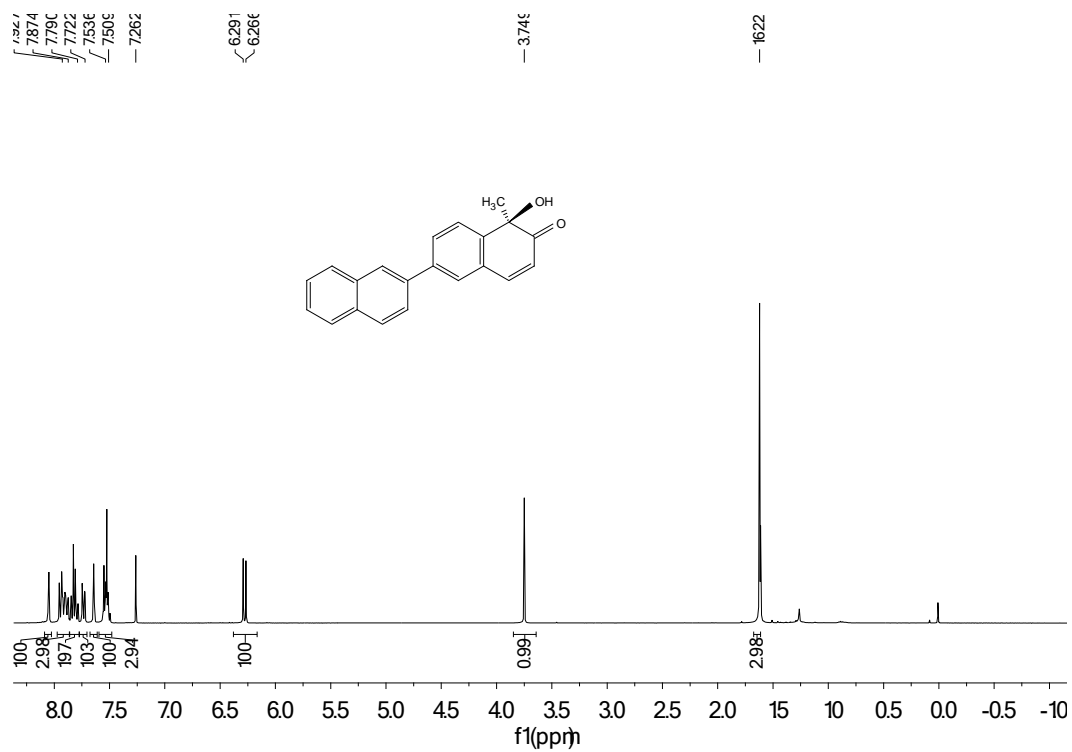


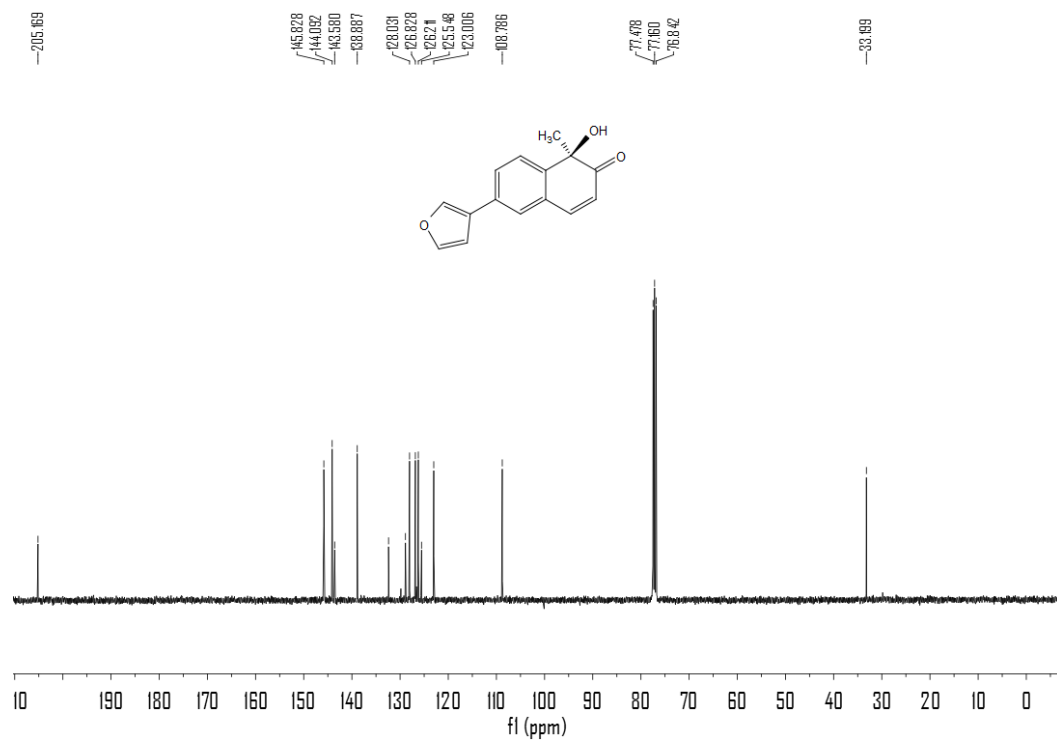
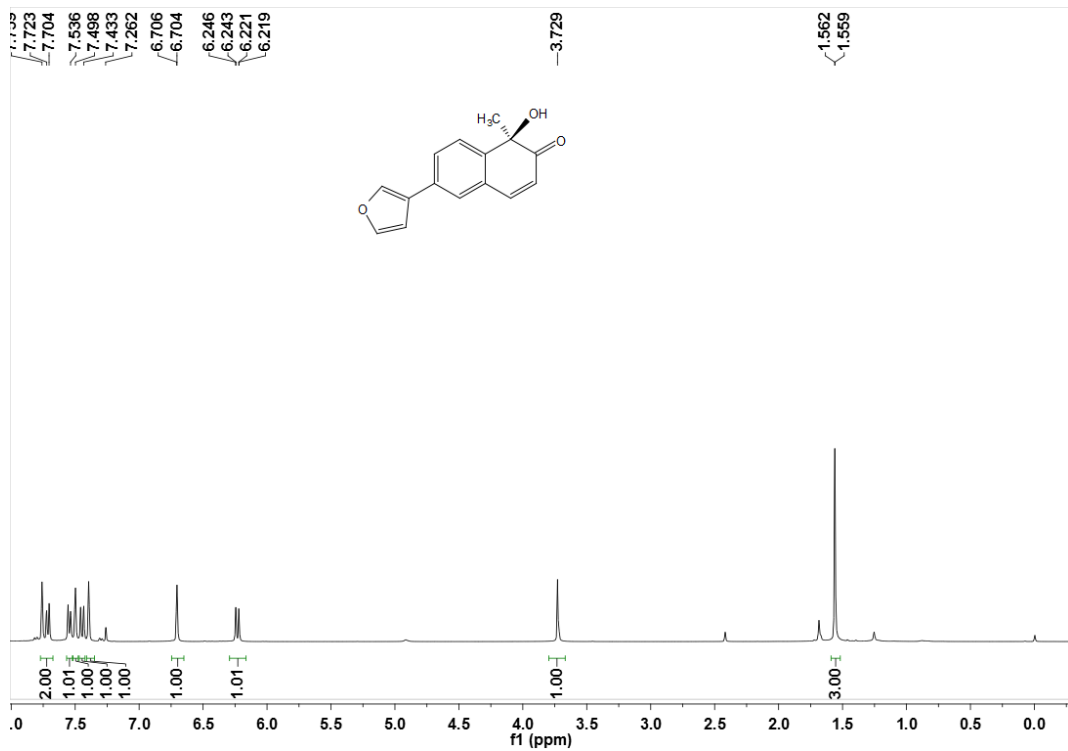


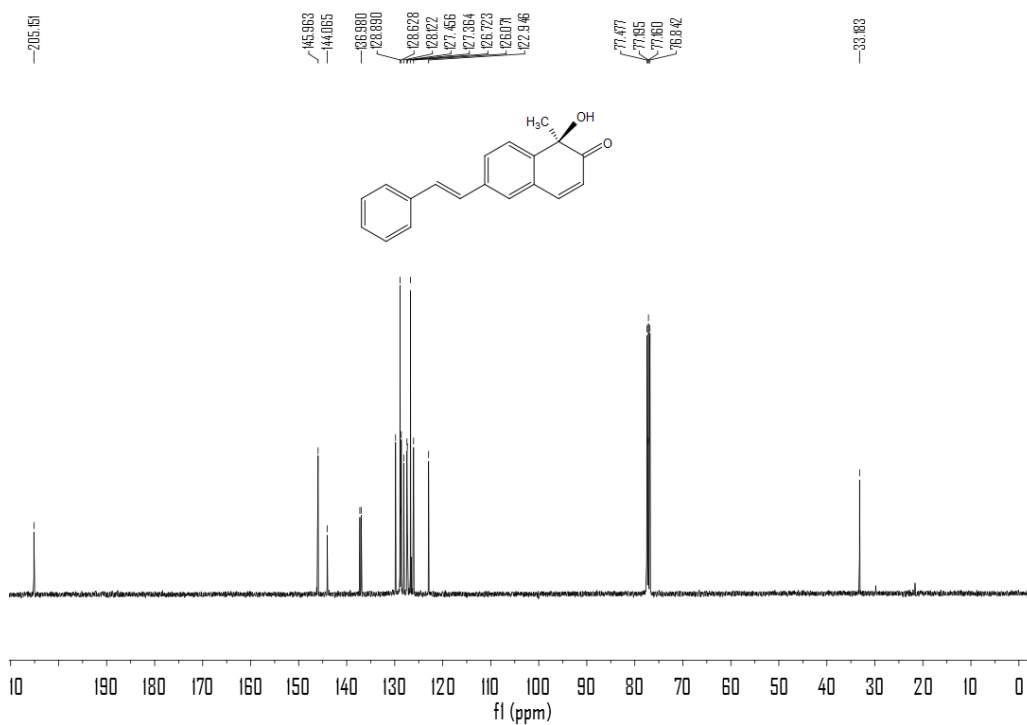
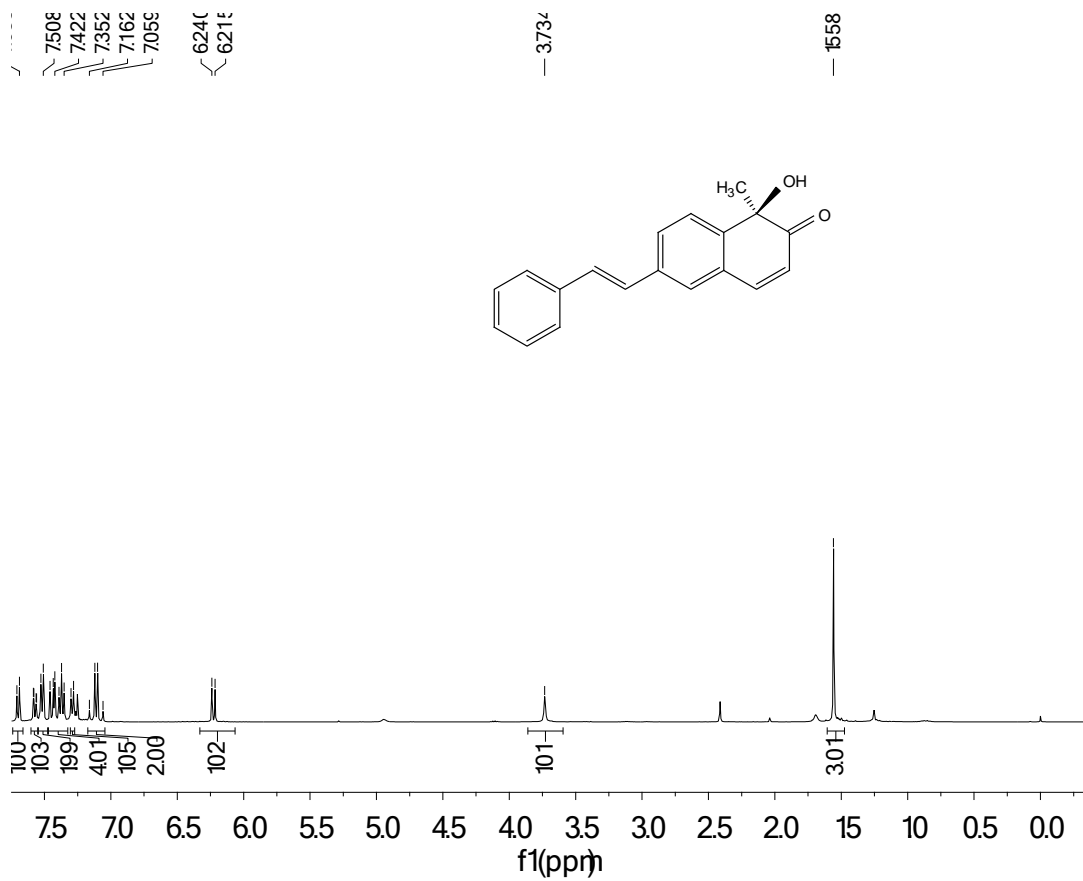


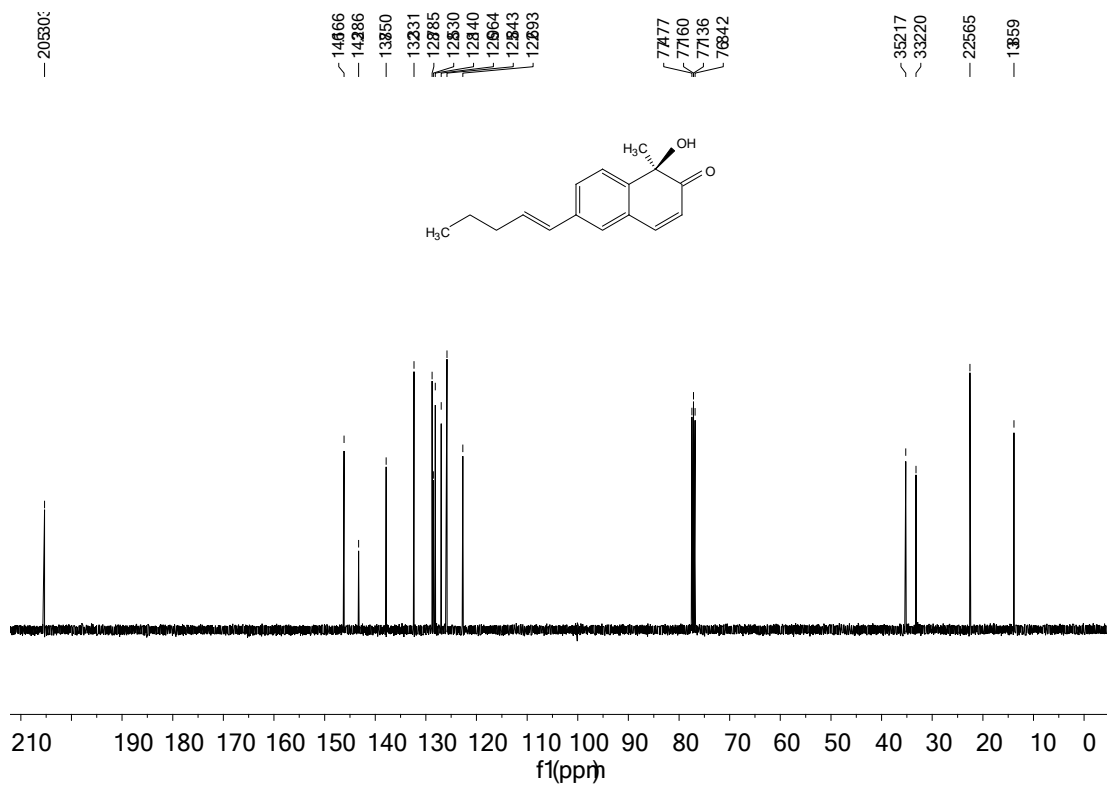
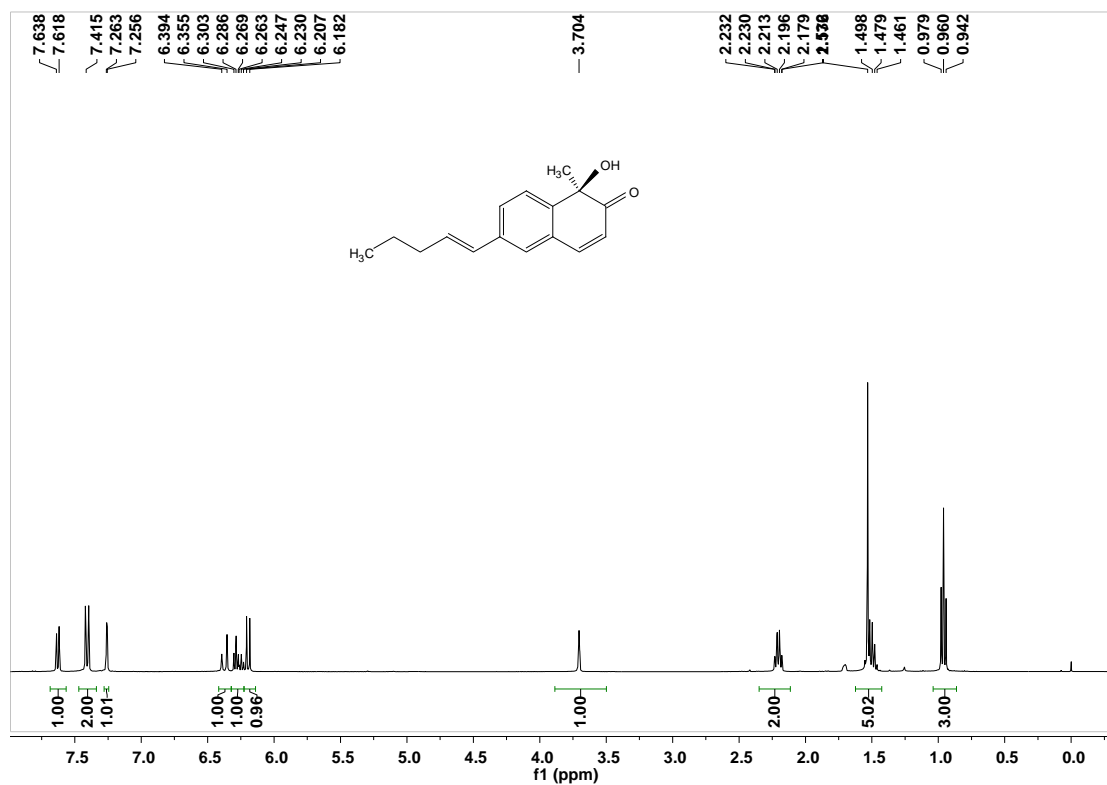


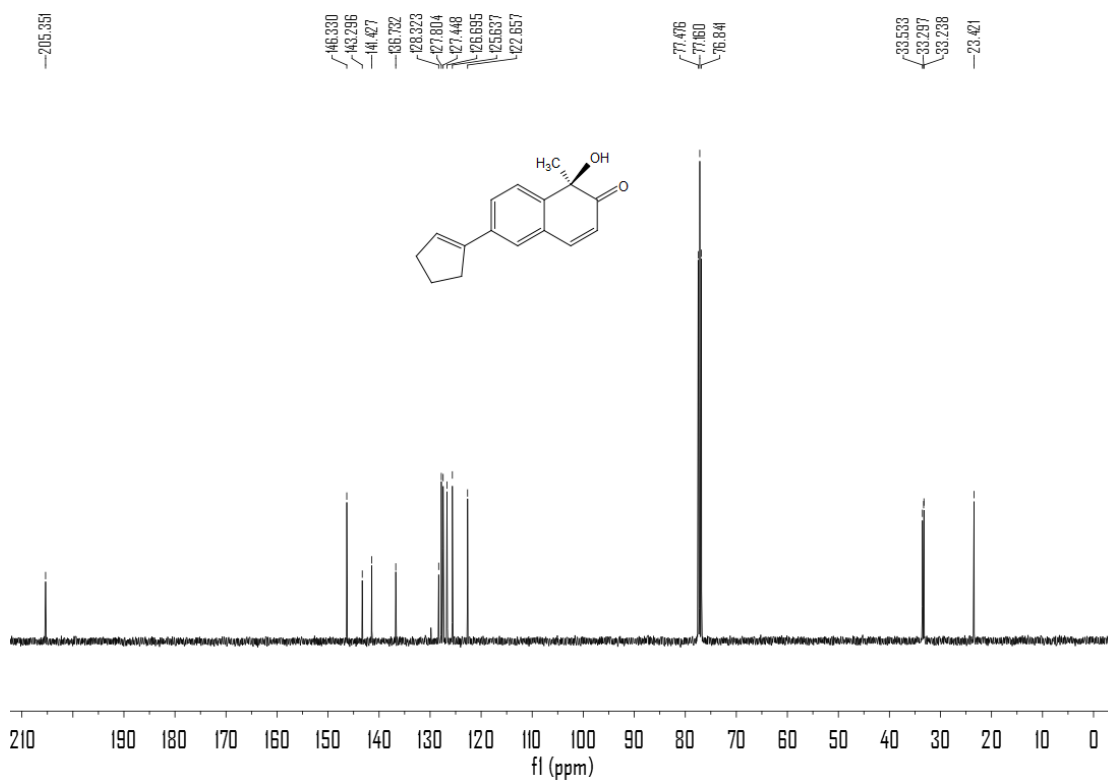
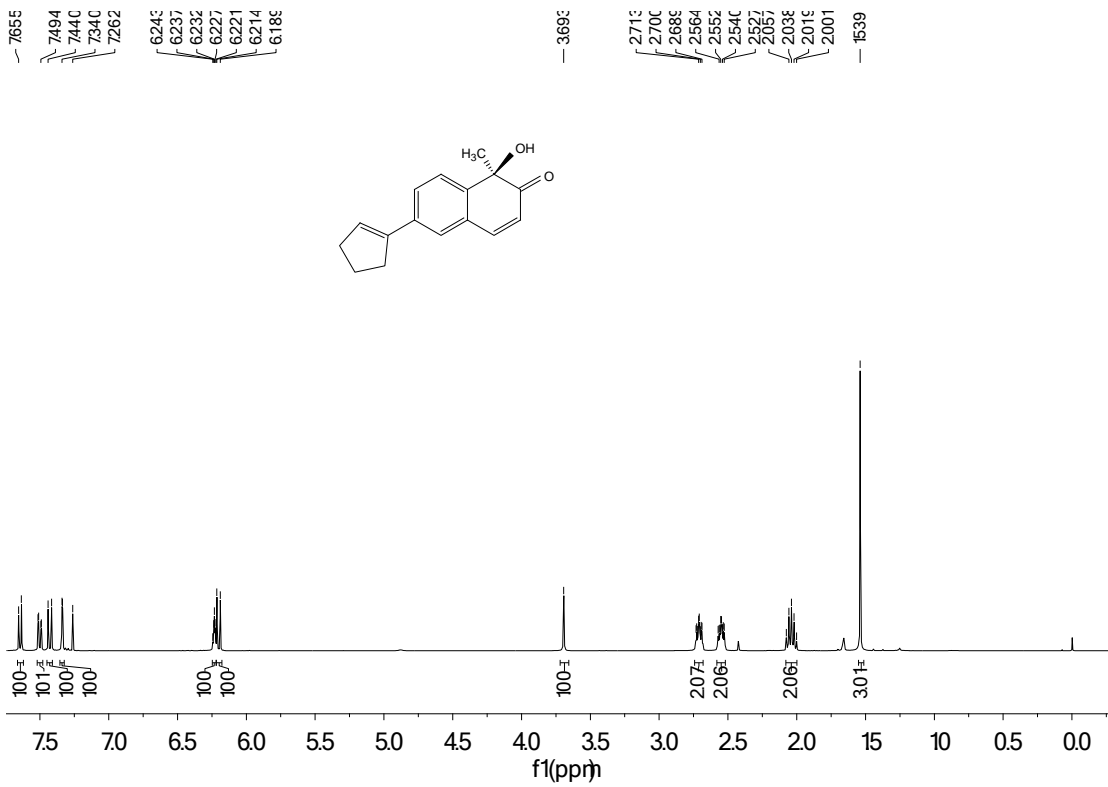


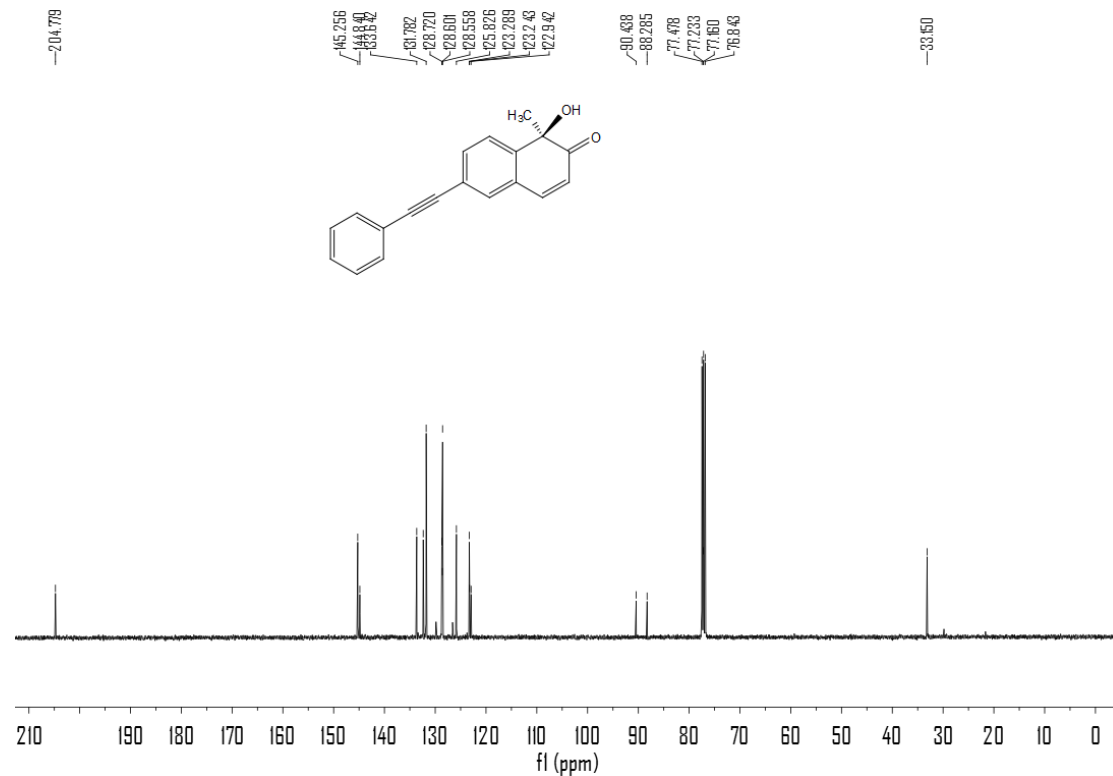
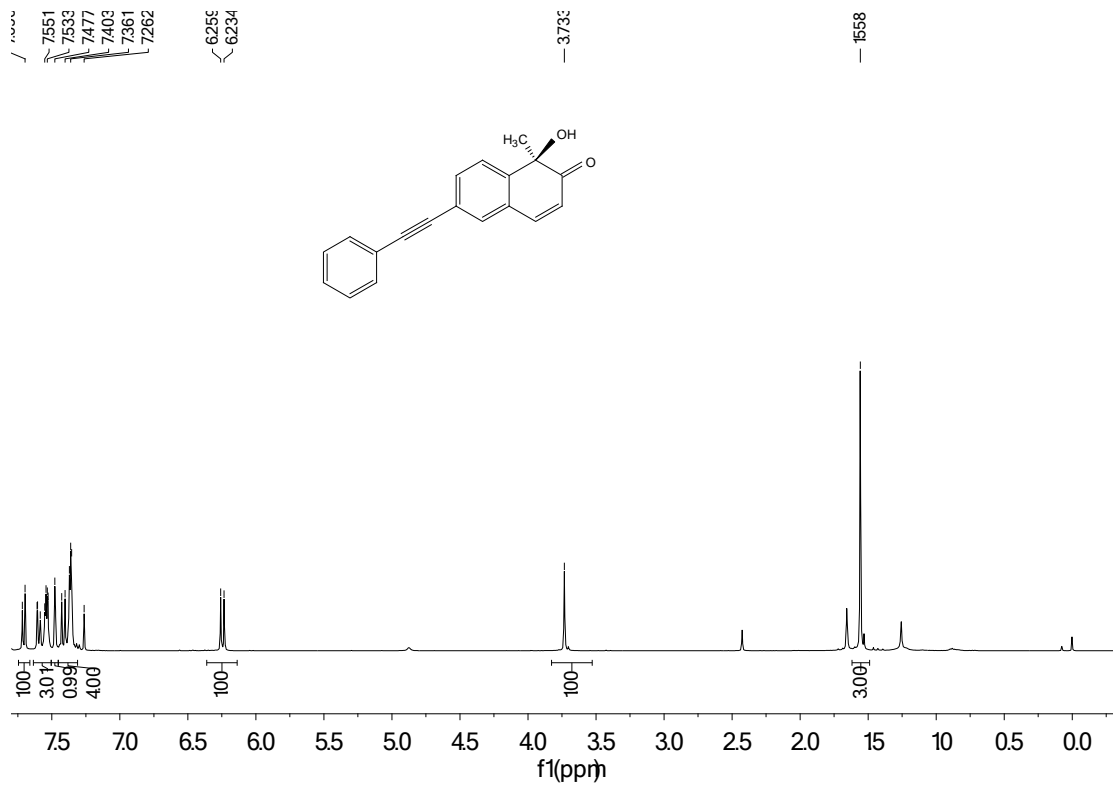


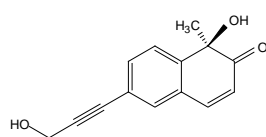
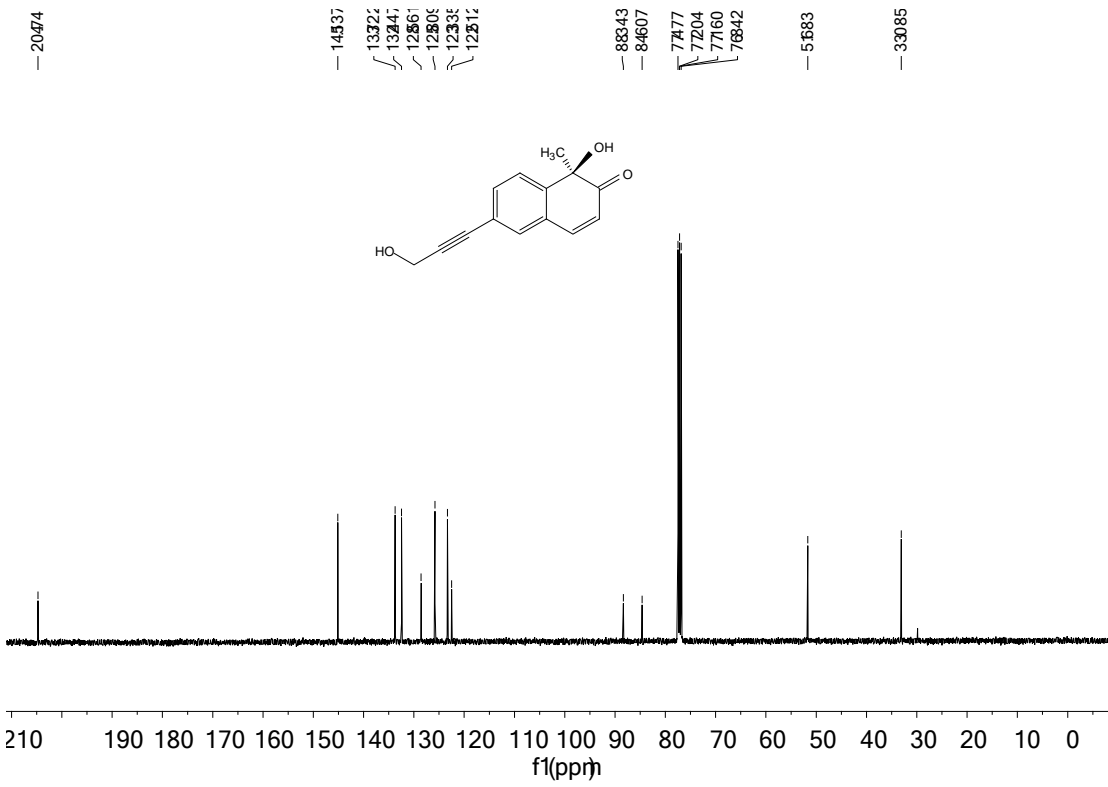
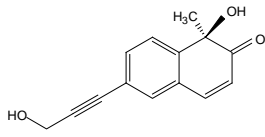
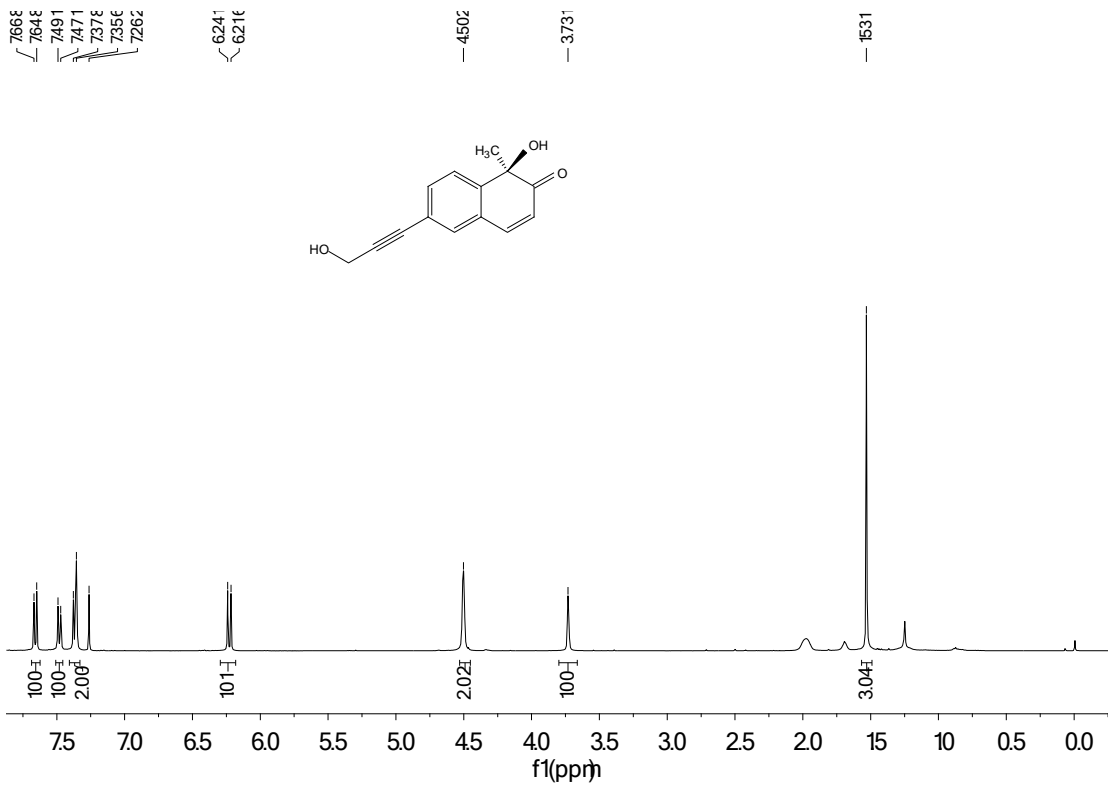




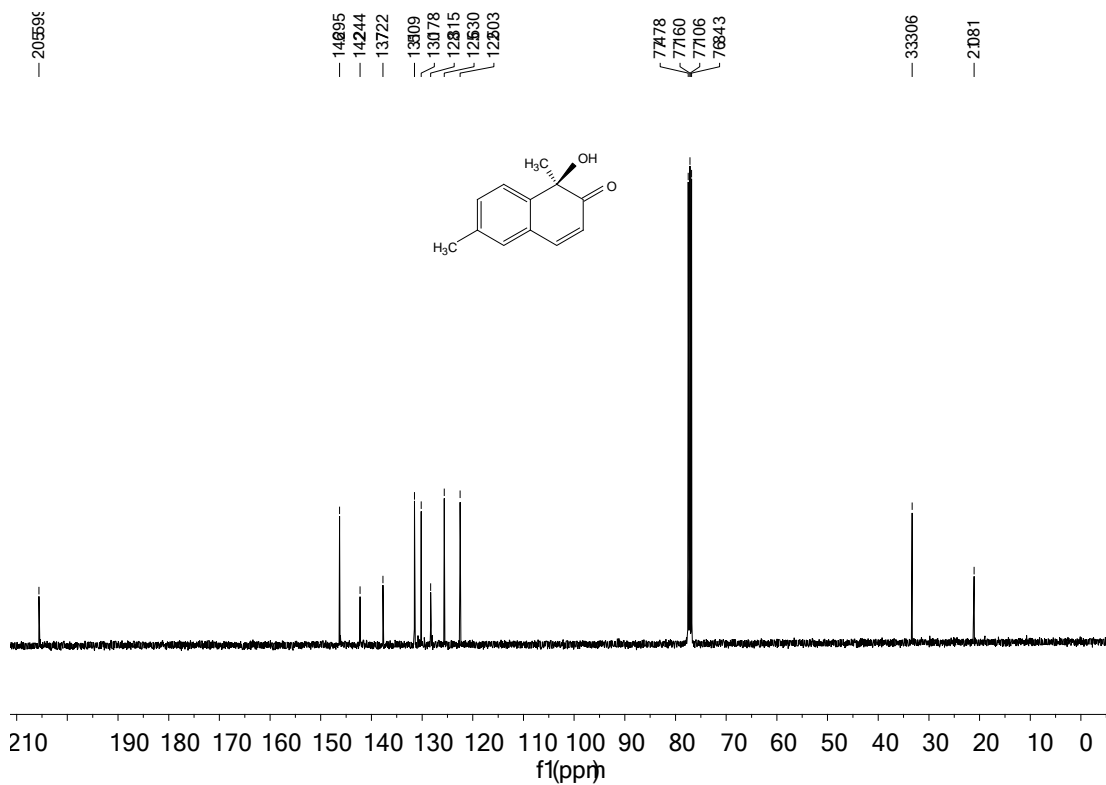
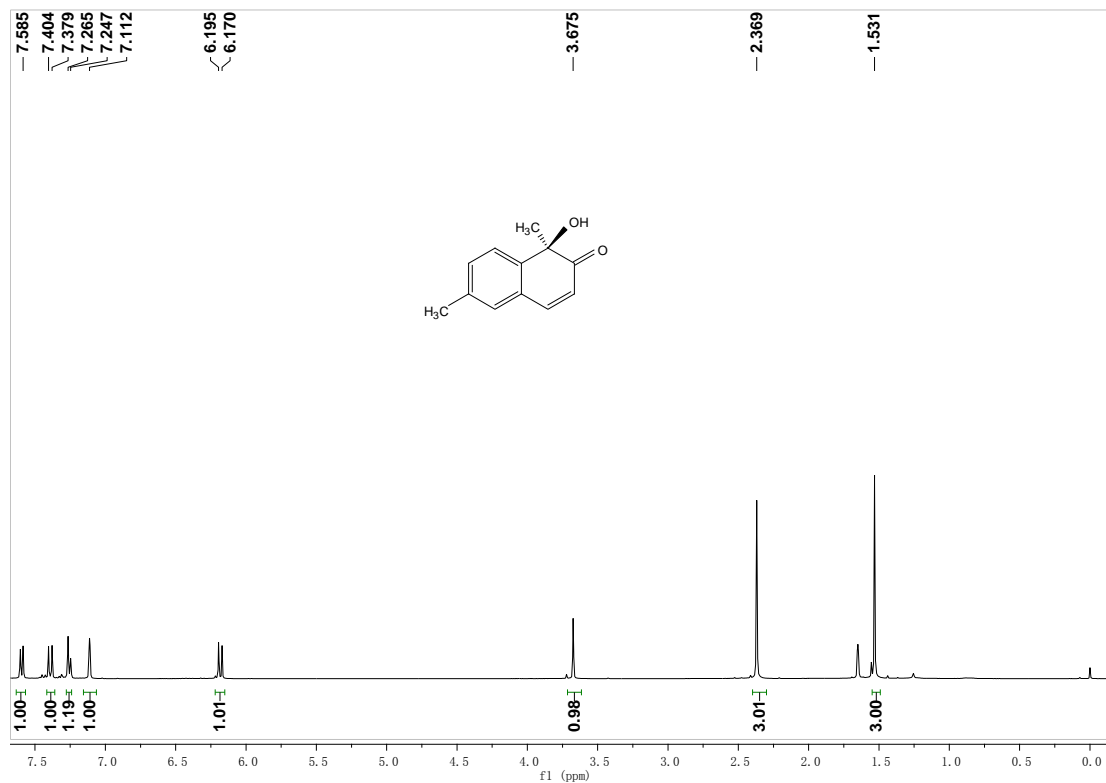


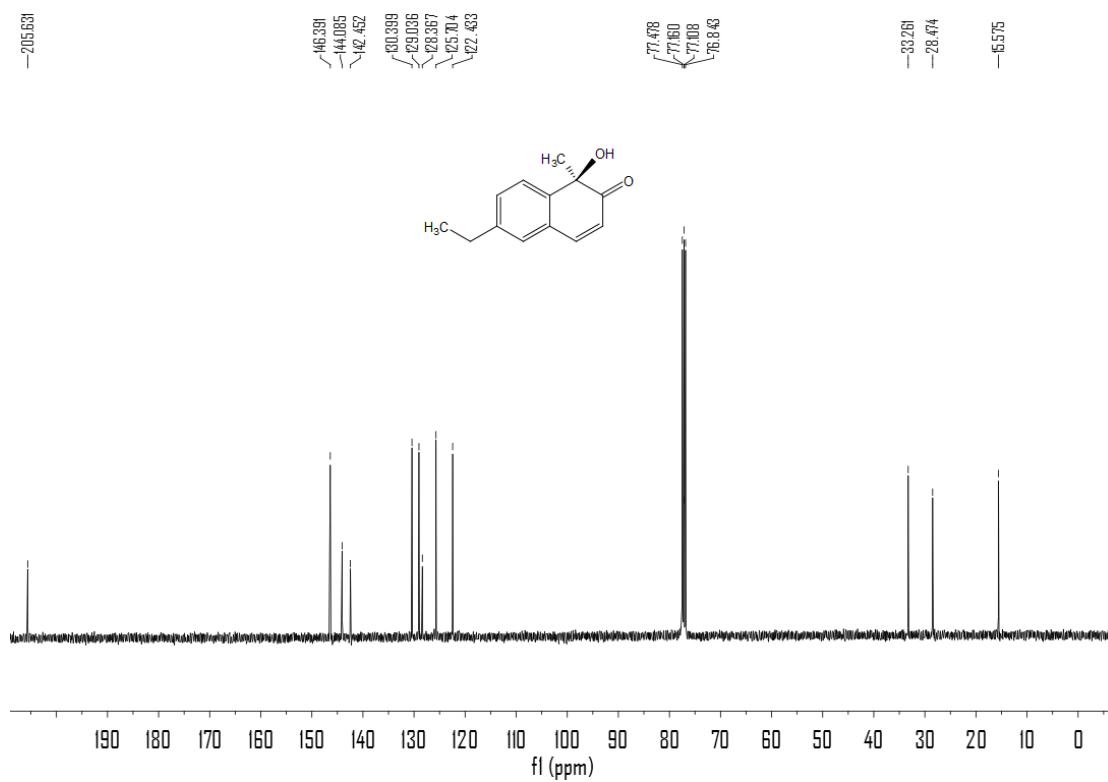
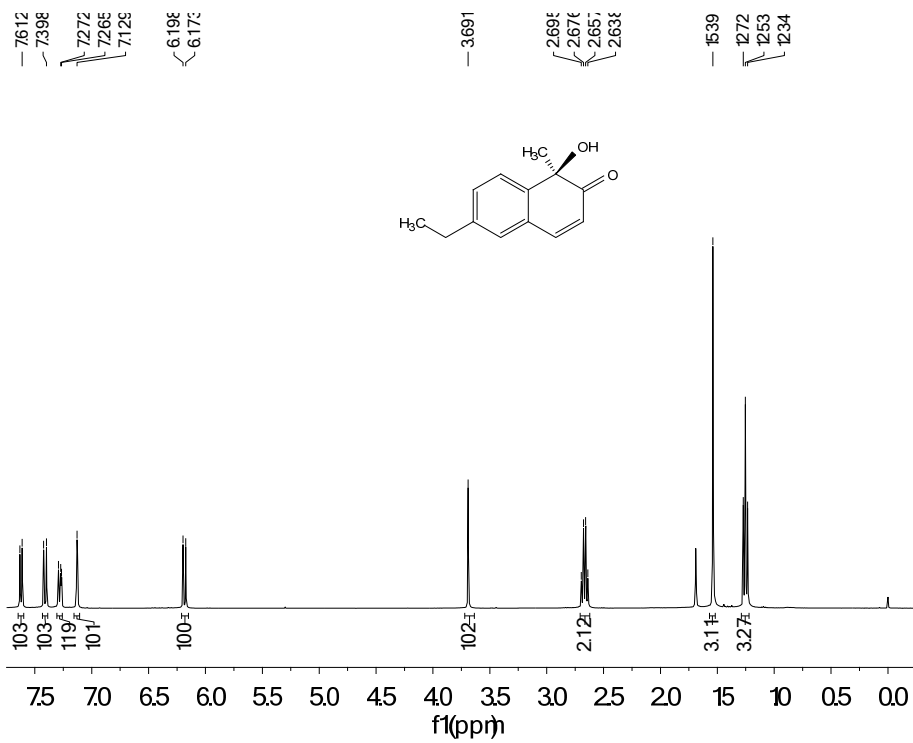


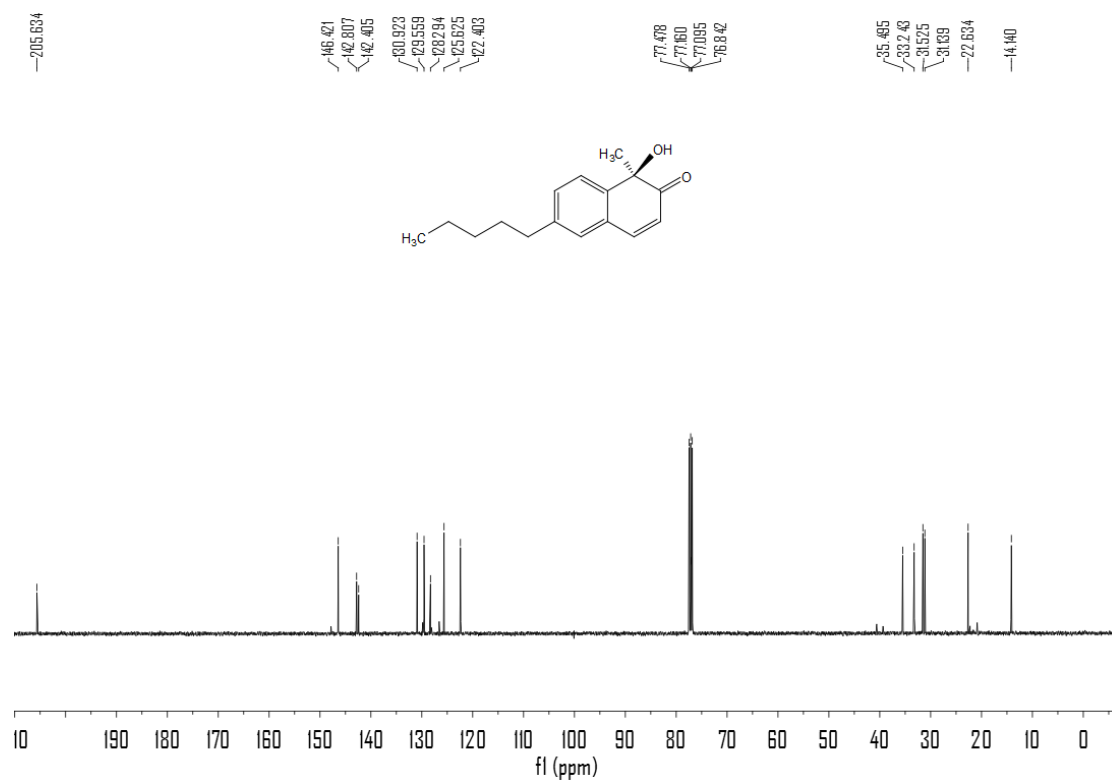
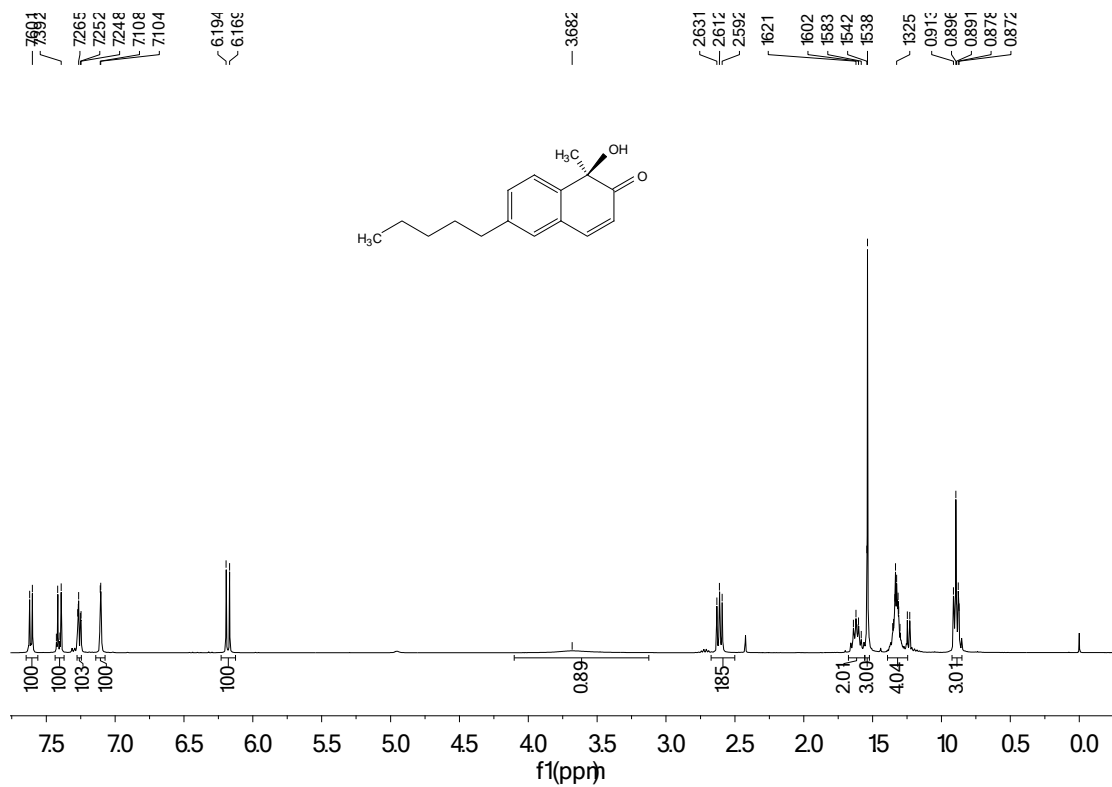


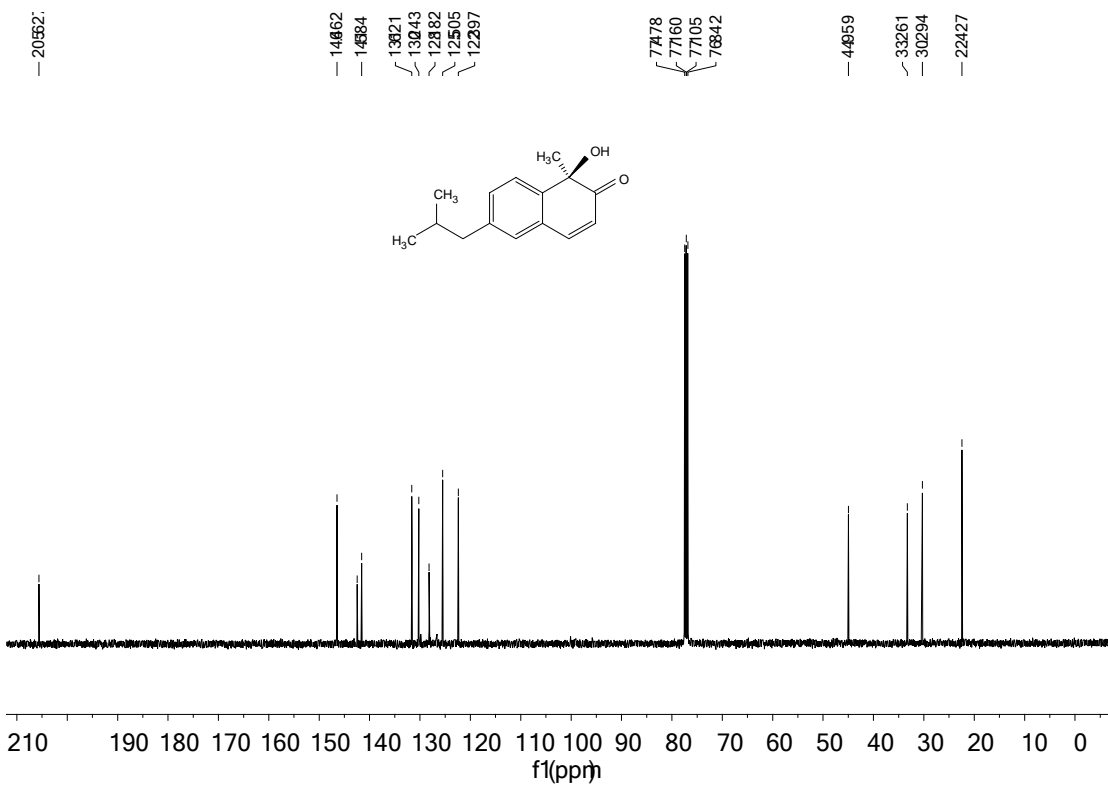
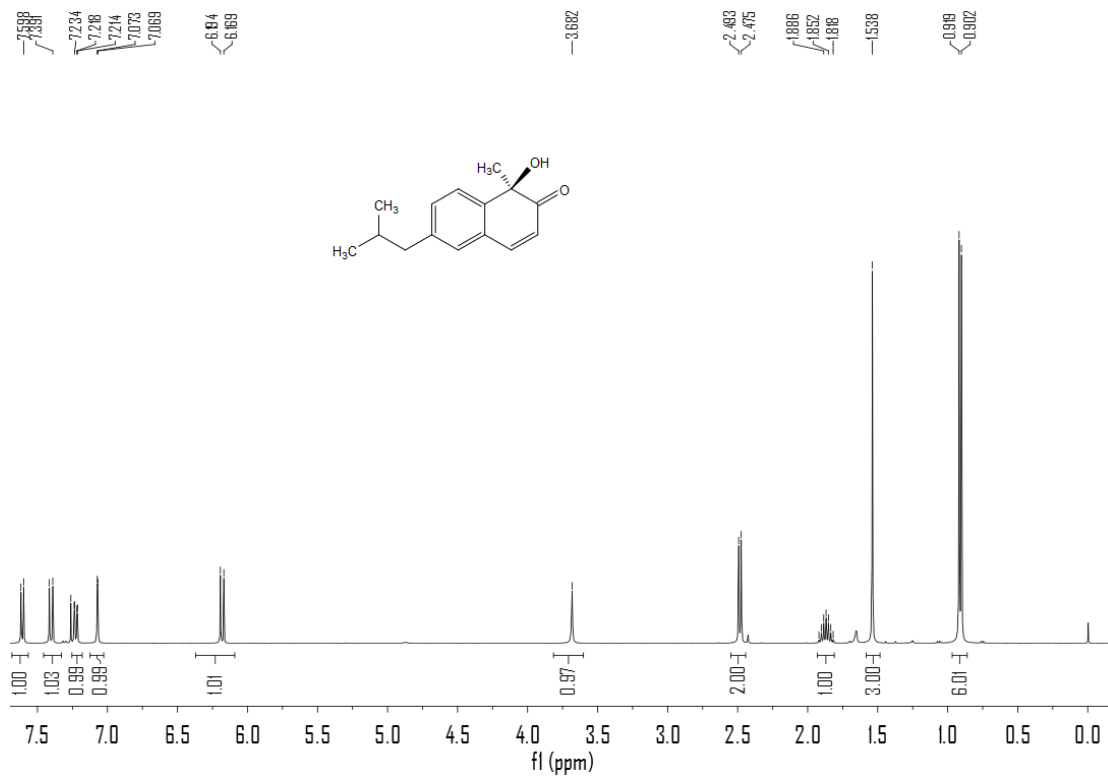


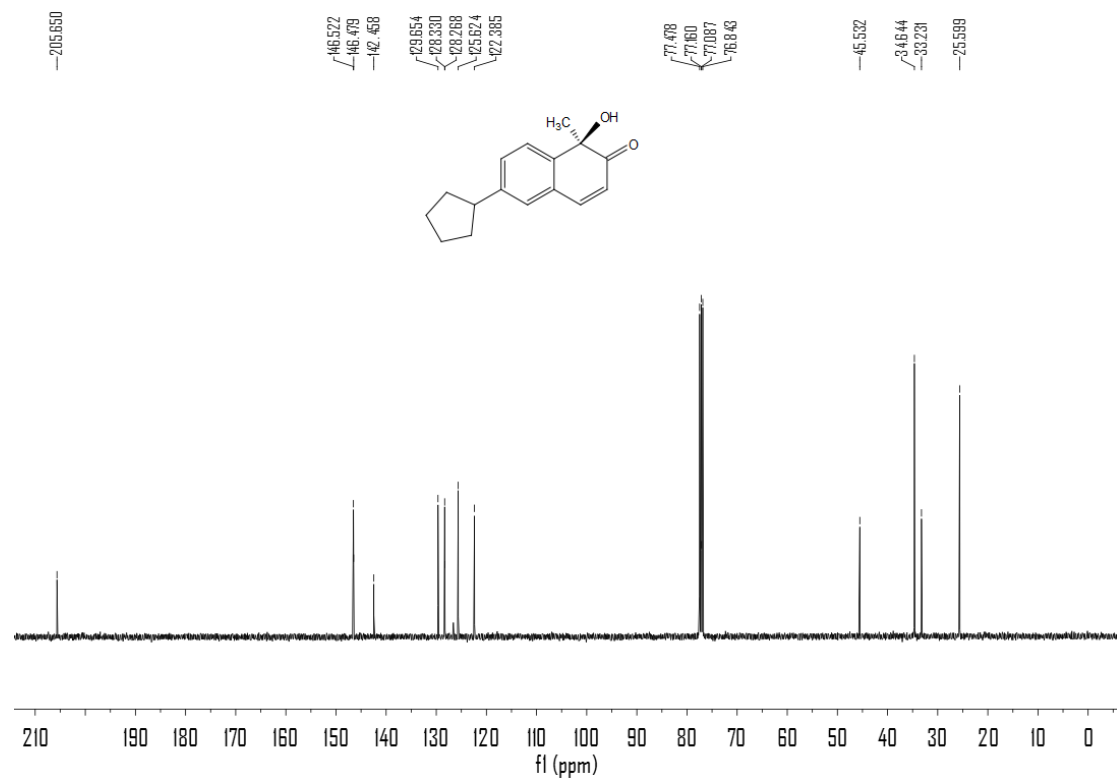
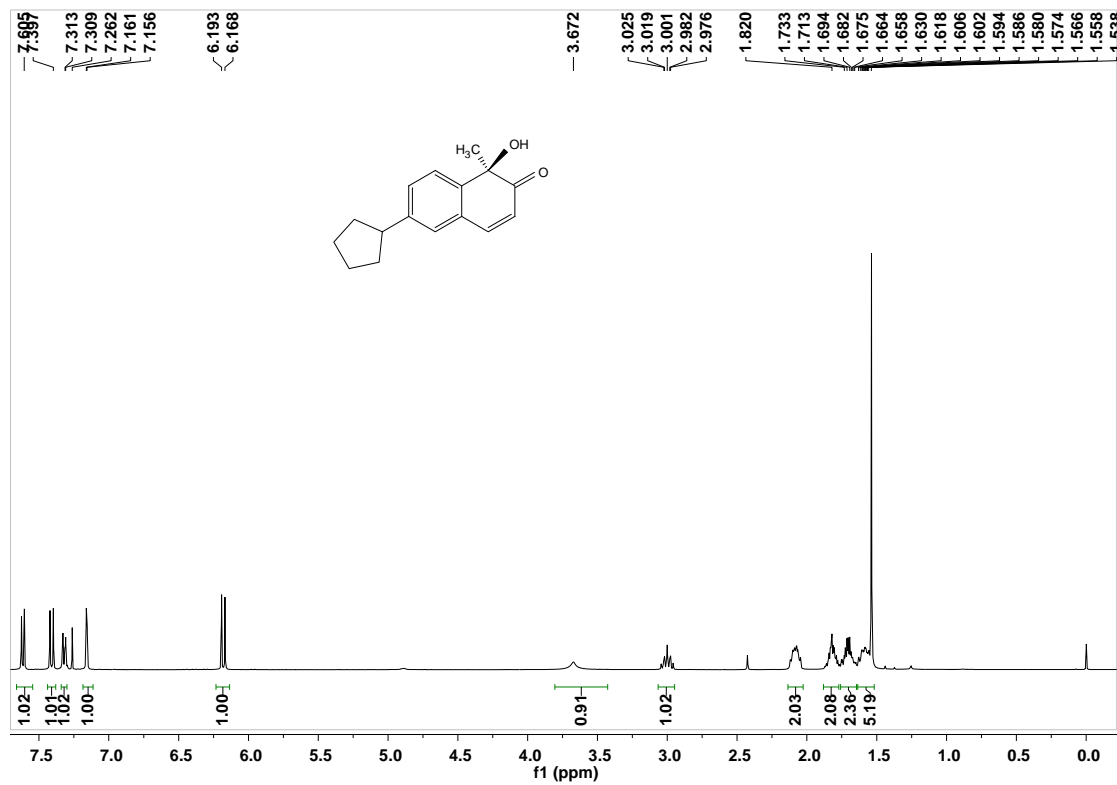




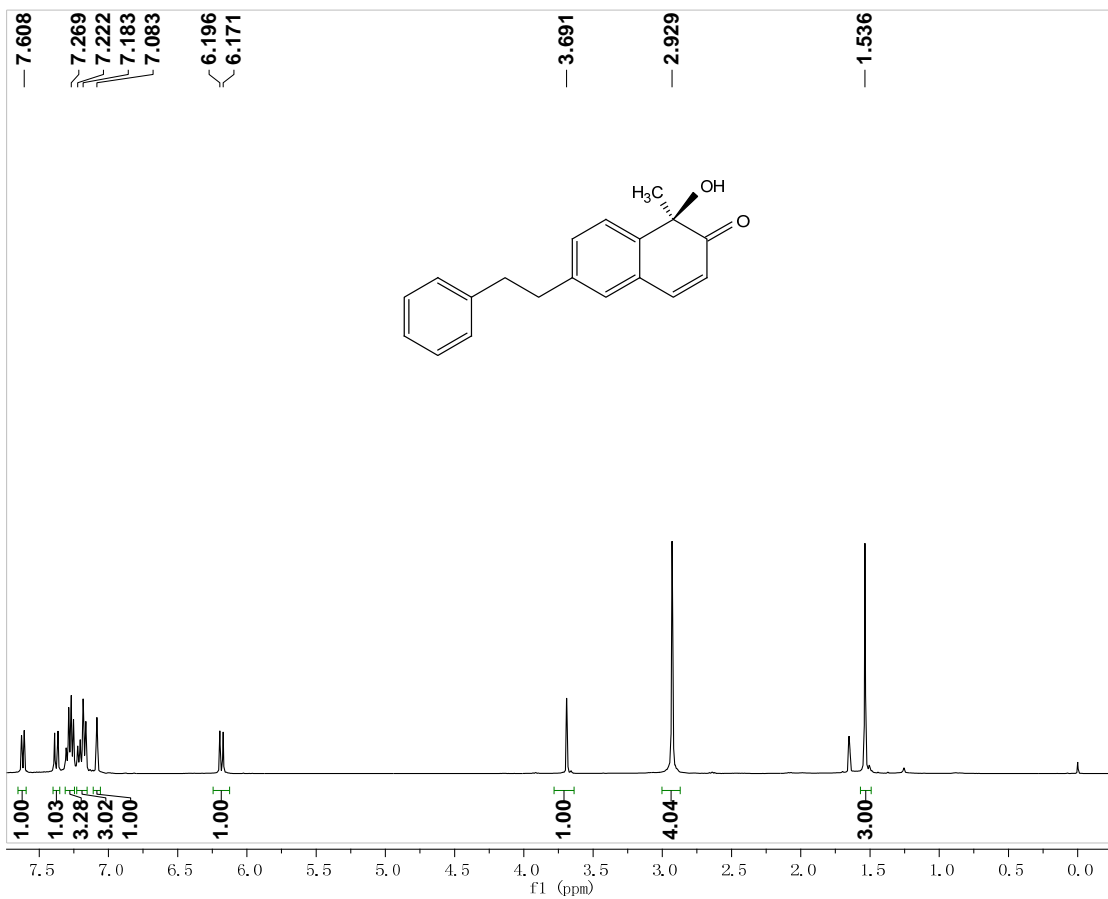








14.



15.

