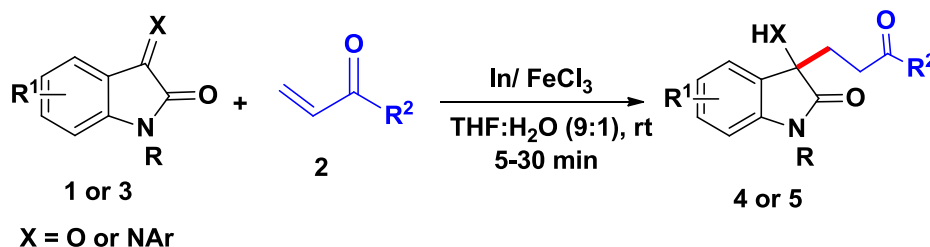


## Supporting Information file

### Indium/Fe(III) - mediated regioselective $\beta$ -cross-coupling aldol type addition reaction of activated alkenes to isatins/isatinimines in aqueous media

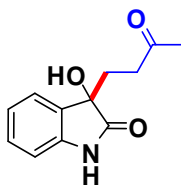
A. Sanjeeva Kumar<sup>a</sup>, Palakuri Ramesh<sup>a</sup>, G. Santosh Kumar<sup>a</sup>, Jagadeesh Babu Nanubolu<sup>b</sup>, T. Prabhakar Rao<sup>c</sup> and H. M. Meshram<sup>a,\*</sup>

**General procedure for the synthesis of compounds 4 or 5:** A mixture of isatin/isatinimine **1/2** (1 mmol),  $\alpha,\beta$ -unsaturated carbonyl compound **2** (1.5 mmol) in 5 mL THF:H<sub>2</sub>O (9:1) was added the Indium metal (2 mmol), FeCl<sub>3</sub> (5 mol%) and was stirred at rt for 5-30 min. The progress of the reaction was monitored by TLC. After the completion of the reaction, the reaction mixture was filtered off and the solvent was removed under vacuum. The residue obtained was then purified by silica gel column chromatography (60–120 mesh) using ethyl acetate/hexane as eluent to get corresponding products. All the obtained products **4** or **5** were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, Mass and IR spectral data.



## Characterization Data of All Compounds

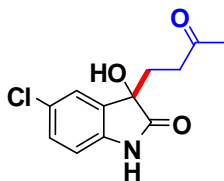
### 3-hydroxy-3-(3-oxobutyl)indolin-2-one (4a, Table 2)



**4a, 88%**

Pale yellow solid; Mp 99-101 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub> + DMSO-d<sub>6</sub>): δ 2.07 (s, 3H), 2.11-2.20 (m, 2H), 2.46-2.53 (m, 2H), 5.67 (s, 1H), 6.87 (d, *J* = 7.7 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 7.20 (t, *J* = 7.7 Hz, 1H), 7.29 (d, *J* = 7.1 Hz, 1H), 9.85 (s, 1H) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub> + DMSO-d<sub>6</sub>): δ 28.9, 31.1, 36.2, 74.3, 109.2, 121.1, 122.9, 128.2, 130.7, 140.4, 178.9, 207.0 ppm; IR (KBr) ν = 3383, 3198, 1697, 1616, 1446, 1192, 1093, 825 cm<sup>-1</sup>; MS-ESI: *m/z* = 242 [M+Na]<sup>+</sup>; HRMS (ESI) found: 242.0781, calcd. for C<sub>12</sub>H<sub>13</sub>NNaO<sub>3</sub>: 242.0793.

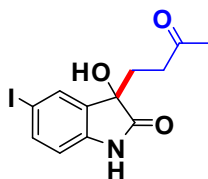
### 5-chloro-3-hydroxy-3-(3-oxobutyl)indolin-2-one (4b, Table 2)



**4b, 74%**

White solid; Mp 112-114 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub> + DMSO-d<sub>6</sub>): δ 1.97-2.09 (m, 5H), 2.45 (t, *J* = 7.3 Hz, 2H), 5.88 (s, 1H), 6.72-6.82 (m, 1H), 7.12-7.22 (m, 2H), 10.18 (s, 1H) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub> + DMSO-d<sub>6</sub>): δ 28.7, 30.8, 35.8, 74.1, 110.2, 123.0, 125.8, 127.7, 132.7, 139.0, 178.2, 206.1 ppm; IR (KBr) ν = 3333, 2927, 1729, 1654, 1476, 1171, 819 cm<sup>-1</sup>; MS -ESI: *m/z* = 276 [M+Na]<sup>+</sup>; HRMS (ESI) found: 276.0395, calcd. for C<sub>12</sub>H<sub>12</sub>ClNNaO<sub>3</sub>: 276.0403.

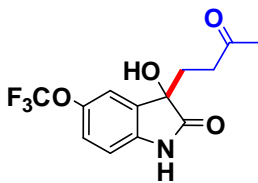
### 3-hydroxy-5-iodo-3-(3-oxobutyl)indolin-2-one (4c, Table 2)



4c, 79%

Pale brown solid; Mp 125-127 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub> + DMSO-d<sub>6</sub>): δ 2.07-2.19 (m, 5H), 2.51-2.58 (m, 2H), 5.79 (s, 1H), 6.67 (d, *J* = 7.9 Hz, 1H), 7.46-7.56 (m, 2H), 9.97 (s, 1H) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub> + DMSO-d<sub>6</sub>): δ 29.5, 31.6, 36.6, 74.7, 84.0, 111.9, 132.2, 133.9, 137.3, 140.6, 178.7, 207.4 ppm; IR (KBr) ν = 3277, 3180, 2928, 1700, 1614, 1475, 1186, 826 cm<sup>-1</sup>; MS-ESI: *m/z* = 368 [M+Na]<sup>+</sup>; HRMS (ESI) found: 367.9769, calcd. for C<sub>12</sub>H<sub>12</sub>INNaO<sub>3</sub>: 367.9759.

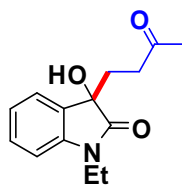
### 3-hydroxy-3-(3-oxobutyl)-5-(trifluoromethoxy)indolin-2-one (4d, Table 2)



4d, 77%

White solid; Mp 29-131 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub> + DMSO-d<sub>6</sub>): δ 1.86-1.93 (m, 2H), 2.01 (s, 3H), 2.33-2.37 (m, 2H), 6.11 (s, 1H), 6.89 (d, *J* = 8.3 Hz, 1H), 7.22 (d, *J* = 8.3 Hz, 1H), 7.26 (s, 1H), 10.45 (s, 1H) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub> + DMSO-d<sub>6</sub>): δ 29.5, 31.2, 36.3, 74.7, 110.4, 117.6, 121.1, 122.1, 133.5, 140.5, 143.0, 178.8, 207.1 ppm; IR (KBr) ν = 3369, 3279, 2925, 1729, 1630, 1488, 1277, 1162 cm<sup>-1</sup>; MS-ESI: *m/z* = 326 [M+Na]<sup>+</sup>; HRMS (ESI) found: 303.0621, calcd. for C<sub>13</sub>H<sub>12</sub>F<sub>3</sub>NNaO<sub>4</sub>: 326.0616.

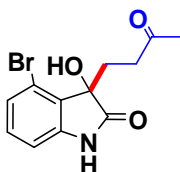
### 1-ethyl-3-hydroxy-3-(3-oxobutyl)indolin-2-one (4e, Table 2)



**4e, 80%**

White solid; Mp 103-105 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub> + DMSO-d<sub>6</sub>): δ 1.26 (t, *J* = 7.1 Hz, 3H), 2.08 (s, 3H), 2.13 (t, *J* = 7.3 Hz, 2H), 2.49 (t, *J* = 7.3 Hz, 2H), 3.62-3.83 (m, 2H), 5.75 (s, 1H), 6.86 (d, *J* = 7.7 Hz, 1H), 7.05 (t, *J* = 7.7 Hz, 1H), 7.27-7.36 (m, 2H) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub> + DMSO-d<sub>6</sub>): δ 11.9, 29.2, 31.4, 33.7, 36.5, 74.2, 107.6, 121.8, 123.1, 128.5, 130.7, 141.3, 176.7, 207.1 ppm; IR (KBr) ν = 3326, 2948, 177, 1691, 1615, 1470, 1372, 1114 cm<sup>-1</sup>; MS-ESI: *m/z* = 270 [M+Na]<sup>+</sup>; HRMS (ESI) found: 270.1098, calcd. for C<sub>14</sub>H<sub>17</sub>NNaO<sub>3</sub>: 270.1106.

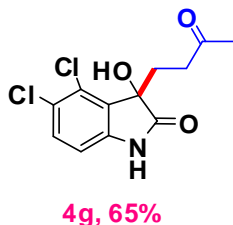
### 4-bromo-3-hydroxy-3-(3-oxobutyl)indolin-2-one (4f, Table 2)



**4f, 70%**

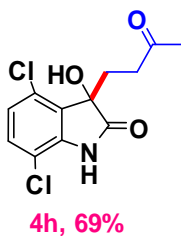
White solid; Mp 130-132 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub> + DMSO-d<sub>6</sub>): δ 2.06 (s, 3H), 2.35-2.41 (m, 4H), 5.81 (s, 1H), 6.80-6.86 (m, 1H), 7.07-7.10 (m, 2H), 10.19 (s, 1H) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub> + DMSO-d<sub>6</sub>): δ 29.1, 31.4, 36.5, 74.6, 109.5, 121.4, 123.2, 128.4, 130.9, 140.6, 179.2, 207.2 ppm; IR (KBr) ν = 3383, 3198, 1697, 1616, 1446, 1192, 1093, 825 cm<sup>-1</sup>; MS-ESI: *m/z* = 320 [M+Na]<sup>+</sup>; HRMS (ESI) found: 319.9890, calcd. for C<sub>12</sub>H<sub>12</sub>BrNNaO<sub>3</sub>: 319.9898.

#### 4,5-dichloro-3-hydroxy-3-(3-oxobutyl)indolin-2-one (4g, Table 2)



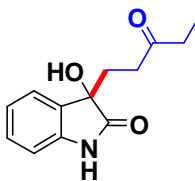
White solid; Mp 140-142 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3 + \text{DMSO-d}_6$ ):  $\delta$  2.03 (s, 3H), 2.23-2.29 (m, 4H), 6.02 (s, 1H), 6.76 (d,  $J = 8.3$  Hz, 1H), 7.33 (d,  $J = 8.3$  Hz, 1H), 10.44 (s, 1H) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3 + \text{DMSO-d}_6$ ): 27.7, 28.6, 35.8, 75.7, 108.5, 124.3, 128.0, 128.4, 129.4, 140.8, 177.2, 205.7 ppm; IR (KBr)  $\nu = 3375, 2938, 1727, 1615, 1513, 1468, 951$   $\text{cm}^{-1}$ ; MS-ESI:  $m/z = 310$   $[\text{M}+\text{Na}]^+$ ; HRMS (ESI) found: 310.0004, calcd. for  $\text{C}_{12}\text{H}_{11}\text{Cl}_2\text{NNaO}_3$ : 310.0014.

#### 4,7-dichloro-3-hydroxy-3-(3-oxobutyl)indolin-2-one (4h, Table 2)



White solid; Mp 143-145 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3 + \text{DMSO-d}_6$ ):  $\delta$  2.07 (s, 3H), 2.22-2.42 (m, 4H), 5.93 (s, 1H), 6.86 (d,  $J = 8.6$  Hz, 1H), 7.13 (d,  $J = 8.6$  Hz, 1H), 10.50 (s, 1H) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3 + \text{DMSO-d}_6$ ):  $\delta$  28.2, 28.9, 36.1, 76.2, 112.9, 123.1, 128.3, 128.6, 129.3, 140.1, 177.5, 206.1 ppm; IR (KBr)  $\nu = 3372, 3220, 2928, 1725, 1617, 1469, 1161$   $\text{cm}^{-1}$ ; MS-ESI:  $m/z = 310$   $[\text{M}+\text{Na}]^+$ ; HRMS (ESI) found: 310.0004, calcd. for  $\text{C}_{12}\text{H}_{11}\text{Cl}_2\text{NNaO}_3$ : 310.0014.

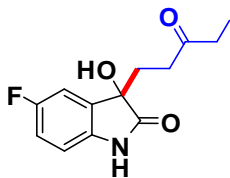
### 3-hydroxy-3-(3-oxopentyl)indolin-2-one (4i, Table 2)



**4i, 90%**

Pale yellow solid; Mp 89-91 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3 + \text{DMSO-d}_6$ ):  $\delta$  0.95 (t,  $J = 7.3$  Hz, 3H), 2.06-2.12 (m, 2H), 2.30-2.48 (m, 4H), 5.82 (s, 1H), 6.84 (d,  $J = 7.5$  Hz, 1H), 6.97 (t,  $J = 7.5$  Hz, 1H), 7.18 (t,  $J = 7.5$  Hz, 1H), 7.27 (d,  $J = 7.3$  Hz, 1H), 10.01 (s, 1H) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3 + \text{DMSO-d}_6$ ):  $\delta$  6.4, 30.6, 34.2, 34.4, 73.8, 108.7, 120.6, 122.5, 127.7, 130.4, 140.1, 178.4, 208.9 ppm; IR (KBr)  $\nu = 3224, 2929, 1715, 1621, 1473, 1114, 868$   $\text{cm}^{-1}$ ; MS-ESI:  $m/z = 256$   $[\text{M}+\text{Na}]^+$ ; HRMS (ESI) found: 256.09423, calcd. for  $\text{C}_{13}\text{H}_{15}\text{NNaO}_3$ : 256.0950.

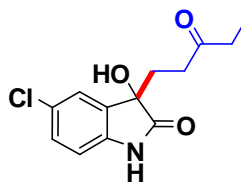
### 5-fluoro-3-hydroxy-3-(3-oxopentyl)indolin-2-one (4j, Table 2)



**4j, 75%**

Pale brown solid; Mp 94-96 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3 + \text{DMSO-d}_6$ ):  $\delta$  0.95 (t,  $J = 7.3$  Hz, 3H), 2.07 (t,  $J = 8.1$  Hz, 2H), 2.32-2.46 (m, 4H), 6.02 (s, 1H), 6.78-6.82 (m, 1H), 6.87-6.94 (m, 1H), 7.02 (d,  $J = 7.9$  Hz, 1H), 10.12 (s, 1H) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3 + \text{DMSO-d}_6$ ):  $\delta$  6.6, 30.8, 34.5, 34.5, 74.4, 110.7, 113.9, 114.2, 132.4, 136.2, 155.9, 178.5, 209.0 ppm; IR (KBr)  $\nu = 3348, 2976, 2933, 1719, 1671, 1487, 1191$   $\text{cm}^{-1}$ ; MS-ESI:  $m/z = 274$   $[\text{M}+\text{Na}]^+$ ; HRMS (ESI) found: 274.0843, calcd. for  $\text{C}_{13}\text{H}_{14}\text{FNNaO}_3$ : 274.0855.

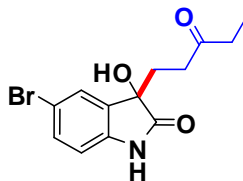
### 5-Chloro-3-hydroxy-3-(3-oxopentyl)indolin-2-one (4k, Table 2)



**4k, 82%**

White solid; Mp 162-164 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3 + \text{DMSO-d}_6$ ):  $\delta$  0.99 (t,  $J = 7.3$  Hz, 3H), 2.12 (t,  $J = 8.1$  Hz, 2H), 2.34-2.43 (m, 2H), 2.48 (q,  $J = 8.1$  Hz, 1H), 5.90 (s, 1H), 6.81 (d,  $J = 2.0$  Hz, 1H), 7.25 (d,  $J = 2.0$  Hz, 1H), 7.56 (s, 1H), 10.05 (s, 1H) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3 + \text{DMSO-d}_6$ ):  $\delta$  6.9, 31.1, 34.8, 34.9, 74.5, 110.4, 123.4, 126.2, 128.0, 132.8, 139.3, 178.6, 209.4 ppm; IR (KBr)  $\nu = 3340, 2970, 2930, 1721, 1619, 1178, 818 \text{ cm}^{-1}$ ; MS-ESI:  $m/z = 290$   $[\text{M}+\text{Na}]^+$ ; HRMS (ESI) found: 290.0562, calcd. for  $\text{C}_{13}\text{H}_{14}\text{ClO}_3\text{NNa}$ : 290.0559.

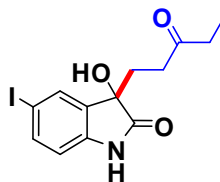
### 5-Bromo-3-hydroxy-3-(3-oxopentyl)indolin-2-one (4l, Table 2)



**4l, 78%**

Pale yellow solid; Mp 116-118 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3 + \text{DMSO-d}_6$ ):  $\delta$  0.98 (t,  $J = 7.1$  Hz, 3H), 2.11 (t,  $J = 7.7$  Hz, 2H), 2.23-2.59 (m, 4H), 5.91 (s, 1H), 6.77 (d,  $J = 8.3$  Hz, 1H), 7.31 (d,  $J = 8.3$  Hz, 1H), 7.38 (s, 1H), 10.07 (s, 1H) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3 + \text{DMSO-d}_6$ ):  $\delta$  6.4, 30.6, 34.3, 34.6, 73.9, 110.5, 112.8, 125.6, 130.4, 132.9, 139.4, 177.8, 208.7 ppm; IR (KBr)  $\nu = 3347, 3183, 2974, 2933, 1721, 1671, 1621, 1178 \text{ cm}^{-1}$ ; MS-ESI:  $m/z = 312$   $[\text{M}+\text{H}]^+$ ; HRMS (ESI) found: 334.0041, calcd. for  $\text{C}_{13}\text{H}_{14}\text{BrNNaO}_3$ : 334.0055.

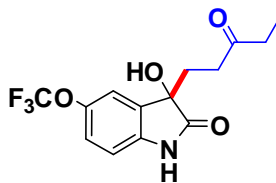
### 3-Hydroxy-5-iodo-3-(3-oxopentyl)indolin-2-one (4m, Table 2)



**4m, 80%**

White solid; Mp 123-125 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3 + \text{DMSO-d}_6$ ):  $\delta$  0.99 (t,  $J = 7.3$  Hz, 3H), 2.11 (t,  $J = 7.7$  Hz, 2H), 2.34-2.52 (m, 4H), 5.84 (s, 1H), 6.67 (d,  $J = 8.1$  Hz, 1H), 7.48-7.55 (m, 2H), 10.00 (s, 1H) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3 + \text{DMSO-d}_6$ ):  $\delta$  7.5, 31.5, 35.0, 35.2, 74.5, 112.0, 132.1, 133.2, 134.5, 137.2, 141.1, 178.3, 209.1 ppm; IR (KBr)  $\nu = 3343, 3178, 2969, 2932, 1719, 1672, 1445, 1175, 814$   $\text{cm}^{-1}$ ; MS-ESI:  $m/z = 360$   $[\text{M}+\text{H}]^+$ ; HRMS (ESI) found: 381.9917, calcd. for  $\text{C}_{13}\text{H}_{14}\text{INNaO}_3$ : 381.9916.

### 3-hydroxy-3-(3-oxopentyl)-5-(trifluoromethoxy)indolin-2-one (4n, Table 2)

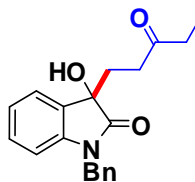


**4n, 83%**

Pale yellow solid; Mp 132-134 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3 + \text{DMSO-d}_6$ ):  $\delta$  1.00 (t,  $J = 7.3$  Hz, 3H), 2.16 (t,  $J = 7.3$  Hz, 2H), 2.32-2.44 (m, 4H), 5.45 (s, 1H), 6.86 (d,  $J = 8.4$  Hz, 1H), 7.07 (d,  $J = 8.4$  Hz, 1H), 7.20 (s, 1H), 9.67 (s, 1H) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3 + \text{DMSO-d}_6$ ):  $\delta$  7.0, 31.3, 34.9, 35.0, 74.7, 109.7, 109.9, 117.0, 121.4, 132.8, 139.5, 143.4, 179.0, 209.6 ppm; IR (KBr)  $\nu = 3374, 3275, 2972, 1726, 1625, 1145, 1175$   $\text{cm}^{-1}$ ; MS-ESI:  $m/z = 318$   $[\text{M}+\text{H}]^+$ ; HRMS (ESI) found: 340.0758, calcd. for  $\text{C}_{14}\text{H}_{14}\text{F}_3\text{NNaO}_4$ : 340.0773.



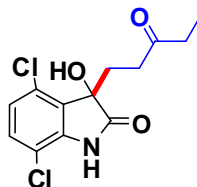
### 1-Benzyl-3-hydroxy-3-(3-oxopentyl)indolin-2-one (4o, Table 2)



**4o, 82%**

White solid; Mp 102-104 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3 + \text{DMSO-d}_6$ ):  $\delta$  0.97 (t,  $J = 7.3$  Hz, 3H), 2.16-2.22 (m, 2H), 2.31-2.40 (m, 2H), 2.45-2.53 (m, 2H), 4.87 (dd,  $J = 9.6, 15.6$  Hz, 2H), 5.97 (s, 1H), 6.73 (d,  $J = 7.7$  Hz, 1H), 7.03 (t,  $J = 7.7$  Hz, 1H), 7.16-7.21 (m, 1H), 7.23-7.36 (m, 6H) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3 + \text{DMSO-d}_6$ ):  $\delta$  6.6, 31.2, 34.4, 34.5, 42.1, 73.6, 121.4, 122.6, 126.0, 126.2, 126.3, 127.5, 127.8, 130.5, 134.8, 140.9, 176.6, 208.1 ppm; IR (KBr)  $\nu = 3363, 3060, 2971, 2931, 2898, 1707, 1464, 1365, 1104, 752$   $\text{cm}^{-1}$ ; MS-ESI:  $m/z = 346$   $[\text{M}+\text{Na}]^+$ ; HRMS (ESI) found: 346.1423, calcd. for  $\text{C}_{20}\text{H}_{21}\text{O}_3\text{NNa}$ : 346.1419.

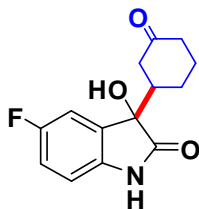
### 4,7-dichloro-3-hydroxy-3-(3-oxopentyl)indolin-2-one (4p, Table 2)



**4p, 72%**

White solid; Mp 150-152 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3 + \text{DMSO-d}_6$ ):  $\delta$  0.95 (t,  $J = 7.3$  Hz, 3H), 2.31-2.40 (m, 6H), 6.24 (s, 1H), 6.91 (d,  $J = 8.6$  Hz, 1H), 7.19 (d,  $J = 8.6$  Hz, 1H), 10.68 (s, 1H) ppm;  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3 + \text{DMSO-d}_6$ ):  $\delta$  6.7, 28.0, 34.6, 34.7, 76.1, 112.7, 122.9, 128.0, 128.4, 129.2, 140.0, 177.4, 208.8 ppm; IR (KBr)  $\nu = 3374, 3224, 2930, 1722, 1617, 1159, 1053$   $\text{cm}^{-1}$ ; MS-ESI:  $m/z = 324$   $[\text{M}+\text{Na}]^+$ ; HRMS (ESI) found: 324.0166, calcd. for:  $\text{C}_{13}\text{H}_{13}\text{Cl}_2\text{O}_3\text{NNa}$  324.0170.

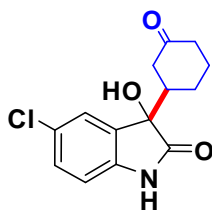
**5-fluoro-3-hydroxy-3-(3-oxocyclohexyl)indolin-2-one (4q, Table 3)**



**4q, 85%**

White solid; Mp 248-250 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$  +  $\text{DMSO-d}_6$ ):  $\delta$  1.23-1.34 (m, 1H), 1.46-1.62 (m, 2H), 1.87-2.32 (m, 2H), 2.11-2.31 (m, 4H), 5.88 (s, 1H), 6.78-6.84 (m, 1H), 6.90-6.97 (m, 1H), 6.99-7.07 (m, 1H), 10.00 (s, 1H) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$  +  $\text{DMSO-d}_6$ ): 23.8, 24.0, 40.4, 40.6, 45.0, 77.2, 110.0, 111.5, 114.5, 131.0, 137.1, 159.4, 178.8, 209.9 ppm; IR (KBr)  $\nu$  = 3268, 2949, 1705, 1483, 1188  $\text{cm}^{-1}$ ; MS-ESI:  $m/z$  = 286  $[\text{M}+\text{Na}]^+$ ; HRMS (ESI) found: 286.0846, calcd. for  $\text{C}_{14}\text{H}_{14}\text{FNNaO}_3$ : 286.0855.

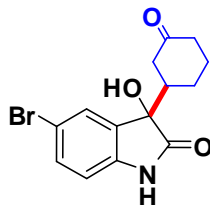
**5-chloro-3-hydroxy-3-(3-oxocyclohexyl)indolin-2-one (4r, Table 3)**



**4r, 87%**

White solid; Mp 176-178 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$  +  $\text{DMSO-d}_6$ ):  $\delta$  1.46-1.61 (m, 2H), 1.95-2.11 (m, 2H), 2.15-2.41 (m, 5H), 5.77 (s, 1H), 7.31- 7.37 (m, 2H), 7.43-7.46 (m, 1H), 9.99 (s, 1H) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$  +  $\text{DMSO-d}_6$ ): 23.8, 24.1, 40.6, 40.7, 45.1, 77.3, 111.0, 113.7, 126.9, 131.3, 131.8, 140.5, 178.2, 209.8 ppm; IR (KBr)  $\nu$  = 3261, 3018, 2865, 1730, 1615, 1449, 1215  $\text{cm}^{-1}$ ; MS-ESI:  $m/z$  = 302  $[\text{M}+\text{Na}]^+$ ; HRMS (ESI) found: 302.0552, calcd. for  $\text{C}_{14}\text{H}_{14}\text{ClNNaO}_3$ : 302.0560.

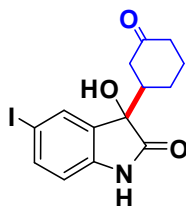
### 5-bromo-3-hydroxy-3-(3-oxocyclohexyl)indolin-2-one (4s, Table 3)



4s, 89%

White solid; Mp 188-190 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$  +  $\text{DMSO-d}_6$ ):  $\delta$  1.50-1.61 (m, 2H), 1.98-2.07 (m, 2H), 2.20-2.35 (m, 5H), 5.82 (s, 1H), 6.78 (d,  $J = 2.7$  Hz, 1H), 7.44 (d,  $J = 1.6$  Hz, 1H), 7.49 (s, 1H), 10.03 (s, 1H) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$  +  $\text{DMSO-d}_6$ ): 23.4, 23.8, 40.3, 40.4, 44.9, 76.7, 110.8, 113.3, 126.6, 131.0, 131.6, 140.3, 178.1, 209.5 ppm; IR (KBr)  $\nu = 3263$ , 2945, 1703, 1484, 1189  $\text{cm}^{-1}$ ; MS-ESI:  $m/z = 346$   $[\text{M}+\text{Na}]^+$ ; HRMS (ESI) found: 346.004, calcd. for  $\text{C}_{14}\text{H}_{14}\text{BrNNaO}_3$ : 346.0055.

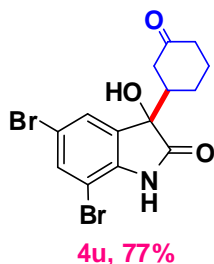
### 3-hydroxy-5-iodo-3-(3-oxocyclohexyl)indolin-2-one (4t, Table 3)



4t, 92%

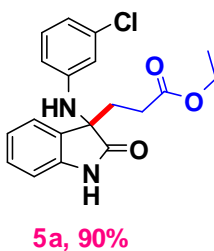
White solid; Mp 175-177 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$  +  $\text{DMSO-d}_6$ ):  $\delta$  1.50-1.61 (m, 2H), 1.99-2.07 (m, 2H), 2.27-2.34 (m, 5H), 5.60 (s, 1H), 7.52-7.54 (m, 2H), 7.61 (d,  $J = 1.1$  Hz, 1H), 9.86 (s, 1H) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$  +  $\text{DMSO-d}_6$ ): 23.4, 23.6, 40.1, 40.2, 44.6, 76.3, 94.9, 111.3, 131.9, 132.1, 136.6, 140.8, 177.4, 209.0 ppm; IR (KBr)  $\nu = 3297$ , 2923, 1704, 1620, 1468, 1179  $\text{cm}^{-1}$ ; MS-ESI:  $m/z = 394$   $[\text{M}+\text{Na}]^+$ ; HRMS (ESI) found: 393.9906, calcd. for  $\text{C}_{14}\text{H}_{14}\text{INNaO}_3$ : 393.9916.

**5,7-dibromo-3-hydroxy-3-(3-oxocyclohexyl)indolin-2-one (4u, Table 3)**



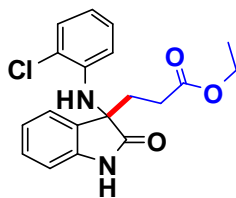
White solid; Mp 201-203 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$  +  $\text{DMSO-d}_6$ ):  $\delta$  1.26-1.58 (m, 4H), 2.22-2.33 (m, 4H), 2.49 (t,  $J = 11.1$  Hz, 1H), 6.19 (s, 1H), 7.52 (s, 1H), 7.66 (s, 1H), 10.36 (s, 1H) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$  +  $\text{DMSO-d}_6$ ): 23.5, 23.8, 40.3, 40.4, 44.9, 77.9, 102.6, 113.8, 125.6, 125.7, 133.2, 139.8, 177.5, 209.4 ppm; IR (KBr)  $\nu = 3264, 3014, 2937, 2868, 1729, 1613, 1455, 1158$   $\text{cm}^{-1}$ ; MS-ESI:  $m/z = 426$   $[\text{M}+\text{Na}]^+$ ; HRMS (ESI) found 425.9135, calcd. for  $\text{C}_{14}\text{H}_{13}\text{Br}_2\text{NNaO}_3$ : 425.9139.

**ethyl 3-(3-(3-chlorophenylamino)-2-oxoindolin-3-yl)propanoate (5a, Table 4)**



Pale yellow semi solid;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.22 (t,  $J = 7.1$  Hz, 3H), 2.23-2.36 (m, 3H), 2.49-2.56 (m, 1H), 4.07-4.13 (m, 2H), 5.06 (s, 1H), 6.05 (dd,  $J = 1.8, 5.9$  Hz, 1H), 6.29 (t,  $J = 2.1$  Hz, 1H), 6.58-6.60 (m, 1H), 6.84 (t,  $J = 8.0$  Hz, 1H), 6.93 (d,  $J = 7.7$  Hz, 1H), 7.03-7.07 (m, 1H), 7.23 (d,  $J = 7.3$  Hz, 1H), 7.26-7.29 (m, 1H), 8.94 (s, 1H) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.0, 27.9, 34.6, 60.9, 64.0, 110.8, 112.1, 114.5, 118.7, 123.3, 124.0, 129.1, 129.4, 130.0, 134.5, 139.6, 146.3, 173.0, 179.6 ppm; IR (KBr)  $\nu = 3241, 2925, 1726, 1598, 1472, 1195, 756$   $\text{cm}^{-1}$ ; MS-ESI:  $m/z = 381$   $[\text{M}+\text{Na}]^+$ ; HRMS (ESI) found: 381.0973, calcd. for  $\text{C}_{19}\text{H}_{19}\text{ClN}_2\text{NaO}_3$ : 381.0982.

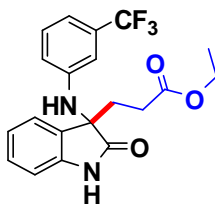
**ethyl 3-(3-(2-chlorophenylamino)-2-oxoindolin-3-yl)propanoate (5b, Table 4)**



**5b, 88%**

Pale yellow semi solid;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.23 (t,  $J = 7.1\text{Hz}$ , 3H), 2.27-2.45 (m, 3H), 2.49-2.55 (m, 1H), 4.07-4.13 (m, 2H), 5.19 (s, 1H), 5.85 (dd,  $J = 1.2, 6.8\text{ Hz}$ , 1H), 6.55-6.58 (m, 1H), 6.74-6.77 (m, 1H), 6.94 (d,  $J = 7.7\text{ Hz}$ , 1H), 7.02-7.06 (m, 1H), 7.20-7.23 (m, 2H), 7.25-7.29 (m, 1H), 8.85 (s, 1H) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.1, 27.9, 34.8, 60.9, 63.7, 110.7, 112.5, 118.8, 120.2, 123.3, 123.9, 127.5, 129.0, 129.2, 129.4, 139.5, 141.0, 172.5, 179.1 ppm; IR (KBr)  $\nu = 3243, 2981, 2927, 1728, 1620, 1597, 1470, 1194, 752\text{ cm}^{-1}$ ; MS-ESI:  $m/z = 381$   $[\text{M}+\text{Na}]^+$ ; HRMS (ESI) found: 381.0971, calcd. for  $\text{C}_{19}\text{H}_{19}\text{ClN}_2\text{NaO}_3$ : 381.0982.

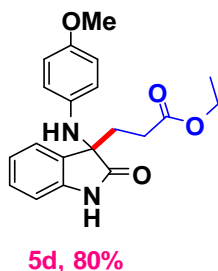
**ethyl 3-(2-oxo-3-(3-(trifluoromethyl)phenylamino)indolin-3-yl)propanoate (5c, Table 4)**



**5c, 95%**

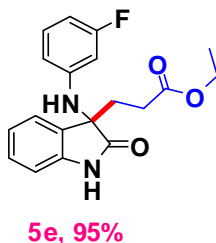
Pale yellow solid; Mp 120-122  $^\circ\text{C}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.22 (t,  $J = 7.1\text{ Hz}$ , 3H), 2.45 (t,  $J = 7.1\text{ Hz}$ , 2H), 2.78 (t,  $J = 7.1\text{ Hz}$ , 2H), 4.07-4.15 (m, 2H), 5.12 (s, 1H), 5.94 (d,  $J = 8.3\text{ Hz}$ , 1H), 6.67 (t,  $J = 7.4\text{ Hz}$ , 1H), 6.95-7.03 (m, 3H), 7.18 (d,  $J = 7.3\text{ Hz}$ , 1H), 7.23-7.27 (m, 1H), 7.42 (d,  $J = 7.7\text{ Hz}$ , 1H), 9.41 (s, 1H) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.1, 27.7, 34.9, 60.8, 63.6, 110.9, 113.6, 115.0, 115.2, 117.6, 123.3, 123.7, 126.5, 128.8, 129.4, 132.8, 139.6, 142.6, 172.4, 179.4 ppm; IR (KBr)  $\nu = 3417, 3165, 3081, 2977, 1729, 1614, 1472, 766\text{ cm}^{-1}$ ; MS-ESI:  $m/z = 415$   $[\text{M}+\text{Na}]^+$ ; HRMS (ESI) found: 415.1236, calcd. for  $\text{C}_{20}\text{H}_{19}\text{F}_3\text{N}_2\text{NaO}_3$ : 415.1245.

**ethyl 3-(3-(4-methoxyphenylamino)-2-oxoindolin-3-yl)propanoate (5d, Table 4)**



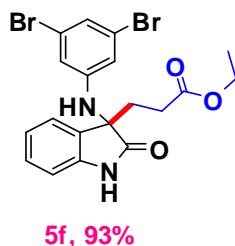
White solid; Mp 133-135 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.20 (t,  $J = 7.1$  Hz, 3H), 2.20-2.28 (m, 2H), 2.35-2.46 (m, 2H), 3.58 (s, 3H), 4.04-4.10 (m, 2H), 4.45 (s, 1H), 6.30 (d,  $J = 9.0$  Hz, 2H), 6.51 (d,  $J = 9.0$  Hz, 2H), 6.83 (d,  $J = 7.7$  Hz, 1H), 7.03-7.07 (m, 1H), 7.21-7.25 (m, 1H), 7.30 (d,  $J = 7.3$  Hz, 1H), 8.99 (s, 1H) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.0, 28.2, 34.4, 55.2, 60.7, 65.4, 110.7, 114.2, 117.9, 123.0, 12.3, 129.1, 129.6, 138.6, 140.1, 153.4, 172.7, 180.6 ppm; IR (KBr)  $\nu = 3319, 3084, 2920, 1732, 1709, 1623, 1243, 752$   $\text{cm}^{-1}$ ; MS-ESI:  $m/z = 377$   $[\text{M}+\text{Na}]^+$ ; HRMS (ESI) found: 377.1469, calcd. for  $\text{C}_{20}\text{H}_{22}\text{N}_2\text{NaO}_4$ : 377.1477.

**ethyl 3-(3-(3-fluorophenylamino)-2-oxoindolin-3-yl)propanoate (5e, Table 4)**



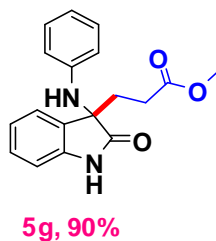
Pale yellow semi solid;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.25 (t,  $J = 7.1$  Hz, 3H), 2.27-2.43 (m, 3H), 2.47-2.59 (m, 1H), 4.10-4.17 (m, 2H), 5.21 (s, 1H), 5.93-5.97 (m, 1H), 6.07-6.10 (m, 1H), 6.32-6.36 (m, 1H), 6.90-6.96 (m, 2H), 7.06-7.09 (m, 1H), 7.27-7.31 (m, 2H), 9.31 (s, 1H) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.0, 27.9, 34.6, 60.8, 64.1, 105.2, 110.0, 111.0, 123.2, 123.9, 129.2, 129.3, 130.1, 139.6, 146.8, 146.9, 162.5, 173.0, 179.9 ppm; IR (KBr)  $\nu = 3339, 3091, 2982, 2931, 1723, 1620, 1182, 754$   $\text{cm}^{-1}$ ; MS-ESI:  $m/z = 365$   $[\text{M}+\text{Na}]^+$ ; HRMS (ESI) found: 365.1282, calcd. for  $\text{C}_{19}\text{H}_{19}\text{FN}_2\text{NaO}_3$ : 365.1277.

**ethyl 3-(3-(3,5-dibromophenylamino)-2-oxoindolin-3-yl)propanoate (5f, Table 4)**



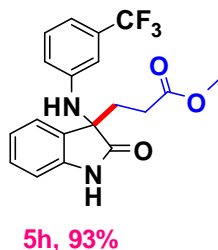
Brown semi solid;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.22 (t,  $J = 7.1$  Hz, 3H), 2.45 (t,  $J = 7.1$  Hz, 2H), 2.78 (t,  $J = 7.1$  Hz, 2H), 4.12 (q,  $J = 7.1$  Hz, 2H), 5.17 (s, 1H), 6.05-6.08 (m, 1H), 6.50 (t,  $J = 1.9$  Hz, 1H), 6.71-6.79 (m, 1H), 6.93 (d,  $J = 7.6$  Hz, 1H), 7.04 (t,  $J = 7.4$  Hz, 1H), 7.21-7.28 (m, 2H), 9.30 (s, 1H) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.1, 27.9, 32.7, 60.8, 63.9, 110.8, 112.3, 117.5, 121.4, 123.2, 123.9, 129.4, 130.3, 139.7, 146.5, 173.0, 179.7 ppm; IR (KBr)  $\nu = 3359, 2981, 2928, 1726, 1619, 1595, 1186, 755$   $\text{cm}^{-1}$ ; MS-ESI:  $m/z = 483$   $[\text{M}+\text{H}]^+$ ; HRMS (ESI) found: 502.9590, calcd. for  $\text{C}_{19}\text{H}_{18}\text{Br}_2\text{N}_2\text{NaO}_3$ : 502.9582.

**methyl 3-(2-oxo-3-(phenylamino)indolin-3-yl)propanoate (5g, Table 4)**



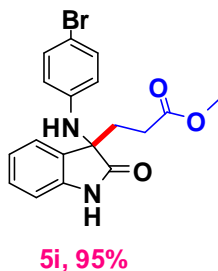
Yellow semi solid;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.23-2.41 (m, 3H), 2.46-2.53 (m, 1H), 3.62 (s, 3H), 6.26 (d,  $J = 7.7$  Hz, 2H), 6.63 (t,  $J = 7.3$  Hz, 1H), 6.89 (d,  $J = 7.9$  Hz, 1H), 6.95 (t,  $J = 7.4$  Hz, 2H), 7.02 (t,  $J = 7.3$  Hz, 1H), 7.23 (t,  $J = 7.7$  Hz, 2H), 9.38 (s, 1H) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  27.8, 34.7, 51.8, 64.3, 110.9, 114.5, 118.8, 123.1, 124.0, 128.9, 129.1, 129.5, 139.7, 145.0, 173.2, 180.6 ppm; IR (KBr)  $\nu = 3313, 3058, 3021, 2952, 1724, 1619, 1203, 751$   $\text{cm}^{-1}$ ; MS-ESI:  $m/z = 333$   $[\text{M}+\text{Na}]^+$ ; HRMS (ESI) found: 333.1223, calcd. for  $\text{C}_{18}\text{H}_{18}\text{N}_2\text{NaO}_3$ : 333.1215.

**methyl 3-(2-oxo-3-(3-(trifluoromethyl)phenylamino)indolin-3-yl)propanoate (5h, Table 4)**



Pale yellow solid; Mp 142-144 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.29-2.41 (m, 3H), 2.49-2.57 (m, 1H), 3.65 (s, 3H), 5.10 (s, 1H), 5.93 (d,  $J = 8.3$  Hz, 1H), 6.68 (t,  $J = 7.4$  Hz, 1H), 6.95-7.04 (m, 3H), 7.18 (d,  $J = 7.4$  Hz, 1H), 7.25-7.29 (m, 1H), 7.42 (d,  $J = 7.6$  Hz, 1H), 8.96 (s, 1H) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  27.5, 34.9, 51.9, 63.3, 110.9, 113.6, 115.3, 117.7, 123.4, 123.8, 125.9, 126.6, 128.8, 129.4, 132.8, 139.4, 142.6, 172.8, 179.2 ppm; IR (KBr)  $\nu = 3420, 3269, 2954, 1718, 1614, 1473, 1107, 750$   $\text{cm}^{-1}$ ; MS-ESI:  $m/z = 401$   $[\text{M}+\text{Na}]^+$ ; HRMS (ESI) found: 401.1078, calcd. for  $\text{C}_{19}\text{H}_{17}\text{F}_3\text{N}_2\text{NaO}_3$ : 401.1089.

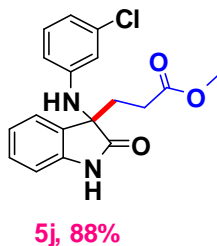
**methyl 3-(3-(4-bromophenylamino)-2-oxoindolin-3-yl)propanoate (5i, Table 4)**



Light pink semi solid;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.24-2.41 (m, 3H), 2.46-2.53 (m, 1H), 3.62 (s, 3H), 6.25-6.27 (m, 1H), 6.63 (t,  $J = 7.3$  Hz, 1H), 6.88 (d,  $J = 7.6$  Hz, 1H), 6.93-6.96 (m, 2H), 7.00-7.04 (m, 1H), 7.21-7.25 (m, 2H), 9.37 (s, 1H) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  27.8, 34.7, 51.8, 64.3, 110.9, 114.5, 118.8, 123.1, 124.6, 129.0, 129.1, 129.5, 139.8, 145.0, 173.2, 180.5 ppm; IR (KBr)  $\nu = 3305, 3092, 3025, 2950, 1721, 1620, 1470, 1181, 756$   $\text{cm}^{-1}$ ; MS-ESI:  $m/z = 389$   $[\text{M}+\text{H}]^+$ ; HRMS (ESI) found: 411.0315, calcd. for  $\text{C}_{18}\text{H}_{17}\text{BrN}_2\text{NaO}_3$ : 411.0320.

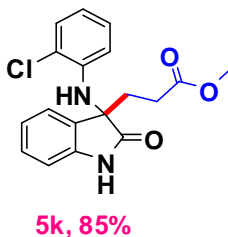


**methyl 3-(3-(3-chlorophenylamino)-2-oxoindolin-3-yl)propanoate (5j, Table 4)**



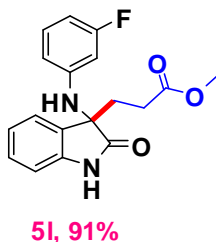
Yellow semi solid;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.25-2.37 (m, 3H), 2.49-2.55 (m, 1H), 3.63 (s, 3H), 5.14 (s, 1H), 6.05 (dd,  $J = 2.2, 8.2$  Hz, 1H), 6.31 (t,  $J = 1.9$  Hz, 1H), 6.58 (d,  $J = 7.9$  Hz, 1H), 6.81-6.85 (m, 1H), 6.91 (dd,  $J = 2.7, 7.7$  Hz, 1H), 7.02-7.06 (m, 1H), 7.21-7.27 (m, 2H), 9.24 (s, 1H) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  27.7, 34.6, 51.9, 64.0, 110.9, 112.0, 114.5, 118.6, 123.3, 123.9, 129.0, 129.4, 130.0, 134.5, 139.6, 146.3, 173.4, 179.8 ppm; IR (KBr)  $\nu = 3336, 3024, 2952, 1718, 1619, 1597, 1471, 1205, 754$   $\text{cm}^{-1}$ ; MS-ESI:  $m/z = 367$   $[\text{M}+\text{Na}]^+$ ; HRMS (ESI) found: 367.0834, calcd. for  $\text{C}_{18}\text{H}_{17}\text{ClN}_2\text{NaO}_3$ : 367.0825.

**methyl 3-(3-(2-chlorophenylamino)-2-oxoindolin-3-yl)propanoate (5k, Table 4)**



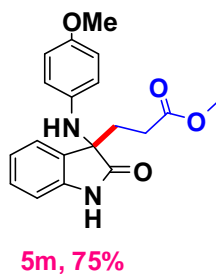
Yellow semi solid;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.29-2.45 (m, 3H), 2.51-2.58 (m, 1H), 3.65 (s, 3H), 5.17 (s, 1H), 5.86 (dd,  $J = 1.2, 7.0$  Hz, 1H), 6.56 (dt,  $J = 1.2, 7.6$  Hz, 1H), 6.73-6.77 (m, 1H), 6.93 (d,  $J = 7.7$  Hz, 1H), 7.03 (t,  $J = 7.4$  Hz, 1H), 7.21 (dd,  $J = 1.2, 7.7$  Hz, 2H), 7.26 (dt,  $J = 1.0, 7.7$  Hz, 1H), 8.93 (s, 1H) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  27.7, 34.8, 51.9, 63.7, 110.8, 112.6, 118.8, 120.2, 123.3, 123.9, 127.5, 129.0, 129.2, 129.4, 139.6, 141.0, 172.9, 179.2 ppm; IR (KBr)  $\nu = 3361, 3023, 2953, 1719, 1592, 1473, 1178, 753$   $\text{cm}^{-1}$ ; MS-ESI:  $m/z = 367$   $[\text{M}+\text{Na}]^+$ ; HRMS (ESI) found: 367.0836, calcd. for  $\text{C}_{18}\text{H}_{17}\text{ClN}_2\text{NaO}_3$ : 367.0825.

**methyl 3-(3-(3-fluorophenylamino)-2-oxoindolin-3-yl)propanoate (5l, Table 4)**



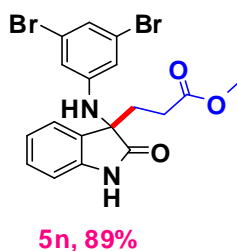
White semi solid;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.23-2.39 (m, 3H), 2.49-2.57 (m, 1H), 3.63 (s, 3H), 5.09 (s, 1H), 5.90-5.93 (m, 1H), 6.05 (dd,  $J = 2.1, 8.2$  Hz, 1H), 6.30-6.34 (m, 1H), 6.87-6.93 (m, 2H), 7.05 (t,  $J = 7.4$  Hz, 1H), 7.23-7.29 (m, 2H), 8.98 (s, 1H) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  27.7, 34.6, 51.9, 64.1, 101.3, 105.4, 110.1, 110.9, 123.3, 124.0, 129.1, 129.4, 130.1, 139.6, 146.9, 164.4, 173.4, 179.7 ppm; IR (KBr)  $\nu = 3310, 3091, 3027, 2953, 1724, 1619, 1471, 1179, 753$   $\text{cm}^{-1}$ ; MS-ESI:  $m/z = 351$   $[\text{M}+\text{Na}]^+$ ; HRMS (ESI) found: 351.1116, calcd. for  $\text{C}_{18}\text{H}_{17}\text{FN}_2\text{NaO}_3$ : 351.1120.

**methyl 3-(3-(4-methoxyphenylamino)-2-oxoindolin-3-yl)propanoate (5m, Table 4)**



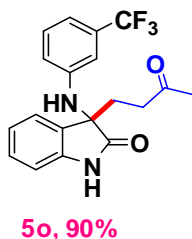
White solid; Mp 123-125  $^\circ\text{C}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.20-2.30 (m, 3H), 2.35-2.46 (m, 1H), 3.58 (s, 3H), 3.60 (s, 3H), 6.30 (d,  $J = 8.8$  Hz, 2H), 6.50 (d,  $J = 7.7$  Hz, 2H), 6.83 (d,  $J = 7.7$  Hz, 1H), 7.04 (t,  $J = 7.4$  Hz, 1H), 7.22 (t,  $J = 7.6$  Hz, 1H), 7.29 (d,  $J = 7.3$  Hz, 1H), 9.17 (s, 1H) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  27.1, 34.4, 51.7, 55.2, 65.4, 110.7, 114.2, 117.9, 122.9, 124.3, 129.1, 129.5, 138.6, 140.1, 153.4, 173.1, 180.6 ppm; IR (KBr)  $\nu = 3297, 3006, 2927, 1723, 1723, 1620, 1512, 1244, 1178, 756$   $\text{cm}^{-1}$ ; MS-ESI:  $m/z = 363$   $[\text{M}+\text{Na}]^+$ ; HRMS (ESI) found: 363.1334 calcd. for  $\text{C}_{19}\text{H}_{20}\text{N}_2\text{NaO}_4$ : 363.1321.

**methyl 3-(3-(3,5-dibromophenylamino)-2-oxoindolin-3-yl)propanoate (5n, Table 4)**



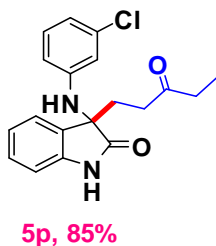
Brown semi solid;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.44 (t,  $J = 7.1$  Hz, 2H), 2.76 (t,  $J = 7.1$  Hz, 2H), 3.64 (s, 3H), 5.02 (s, 1H), 6.05-6.10 (m, 1H), 6.48 (t,  $J = 1.9$  Hz, 1H), 6.73-6.80 (m, 1H), 6.95 (d,  $J = 7.1$  Hz, 1H), 7.06 (t,  $J = 7.6$  Hz, 1H), 7.23 (d,  $J = 7.3$  Hz, 1H), 7.29-7.31 (m, 1H), 8.76 (s, 1H) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  27.7, 32.5, 51.5, 63.9, 110.7, 112.5, 117.6, 121.6, 123.3, 124.0, 129.4, 130.3, 139.6, 146.4, 172.8, 179.1 ppm; IR (KBr)  $\nu = 3356, 2985, 1723, 1593, 1472, 1183, 757$   $\text{cm}^{-1}$ ; MS-ESI:  $m/z = 465$   $[\text{M}+\text{H}]^+$ ; HRMS (ESI) found: 488.9432, calcd. for  $\text{C}_{18}\text{H}_{16}\text{Br}_2\text{N}_2\text{NaO}_3$ : 488.9425.

**3-(3-oxobutyl)-3-(3-(trifluoromethyl)phenylamino)indolin-2-one (5o, Table 4)**



Yellow solid; Mp 148-150  $^\circ\text{C}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.12 (s, 3H), 2.25-2.35 (m, 2H), 2.44-2.51 (m, 1H), 2.68-2.75 (m, 1H), 5.11 (s, 1H), 5.91 (d,  $J = 8.3$  Hz, 1H), 6.67 (t,  $J = 7.4$  Hz, 1H), 6.94-7.05 (m, 3H), 7.17 (d,  $J = 7.3$  Hz, 1H), 7.25-7.29 (m, 1H), 7.42 (d,  $J = 7.6$  Hz, 1H), 8.82 (s, 1H) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  29.9, 33.7, 36.4, 63.4, 110.7, 113.5, 117.6, 123.4, 123.6, 123.7, 125.9, 126.6, 129.3, 129.5, 132.8, 139.3, 142.6, 179.2, 207.0 ppm; IR (KBr)  $\nu = 3448, 3174, 1734, 1685, 1477, 1328, 1103, 751$   $\text{cm}^{-1}$ ; MS-ESI:  $m/z = 385$   $[\text{M}+\text{Na}]^+$ ; HRMS (ESI) found: 385.1133, calcd. for  $\text{C}_{19}\text{H}_{17}\text{N}_2\text{NaO}_2$ : 385.1140.

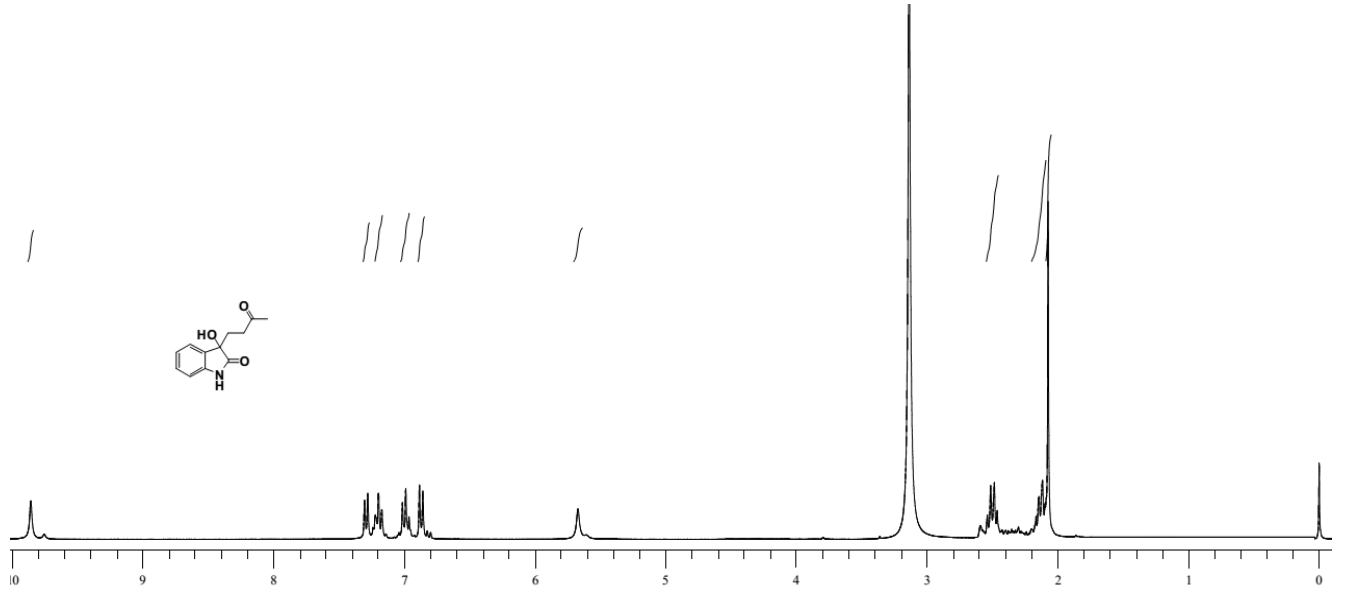
**3-(3-chlorophenylamino)-3-(3-oxopentyl)indolin-2-one (5p, Table 4)**



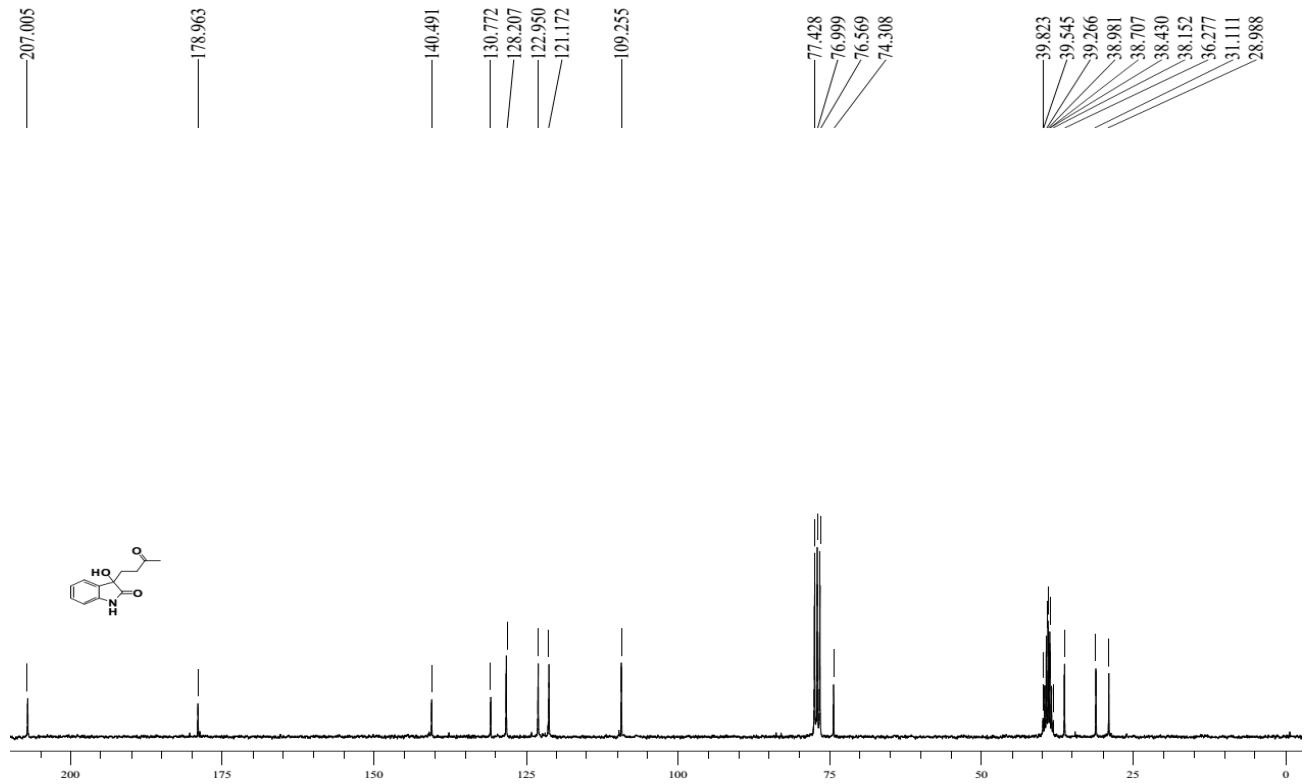
White solid; Mp 132-134 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.03 (t,  $J = 7.3$  Hz, 3H), 2.21-2.27 (m, 2H), 2.32-2.46 (m, 3H), 2.68-2.75 (m, 1H), 5.01 (s, 1H), 6.05-6.07 (m, 1H), 6.25 (t,  $J = 2.1$  Hz, 1H), 6.59-6.61 (m, 1H), 6.86 (t,  $J = 8.0$  Hz, 1H), 6.95 (d,  $J = 7.7$  Hz, 1H), 7.06 (t,  $J = 7.4$  Hz, 1H), 7.22 (d,  $J = 7.4$  Hz, 1H), 7.28-7.32 (m, 1H), 7.97 (s, 1H) ppm;  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.7, 33.5, 35.5, 36.0, 63.8, 110.7, 112.0, 114.3, 118.6, 123.4, 123.9, 129.3, 129.7, 130.0, 134.6, 139.4, 146.3, 179.5, 210.8 ppm; IR (KBr)  $\nu = 3303, 2929, 1711, 1598, 1471, 754$   $\text{cm}^{-1}$ ; MS-ESI:  $m/z = 365$   $[\text{M}+\text{Na}]^+$ ; HRMS (ESI) found: 365.1042, calcd. for  $\text{C}_{19}\text{H}_{19}\text{ClN}_2\text{NaO}_2$ : 364.1032.

# Compound 4a

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

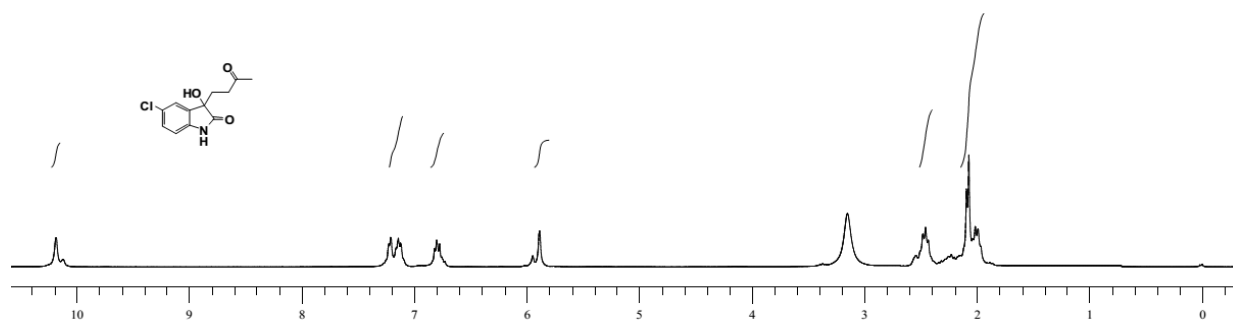


## <sup>13</sup>C NMR

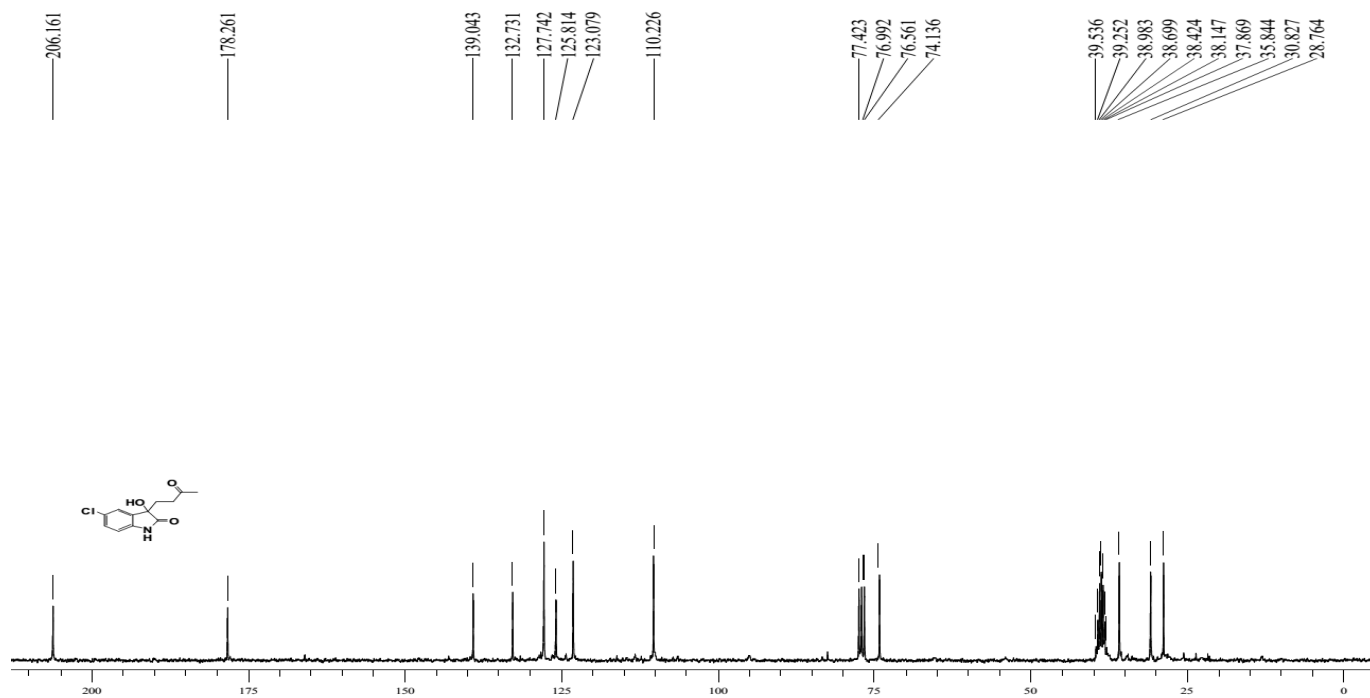


## Compound 4b

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

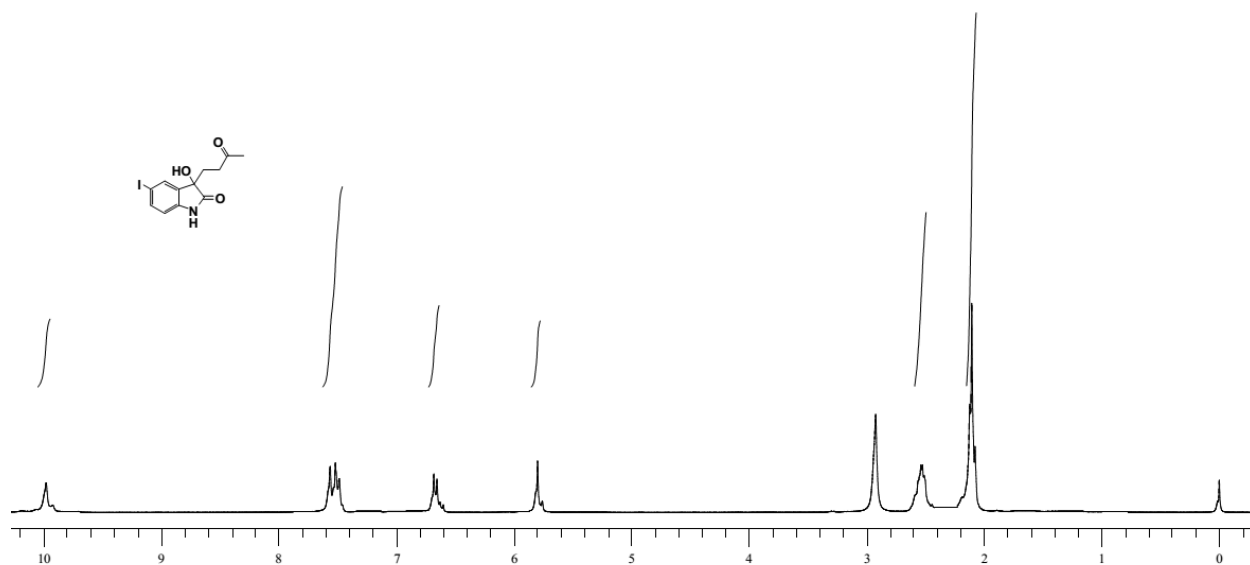


### <sup>13</sup>C NMR

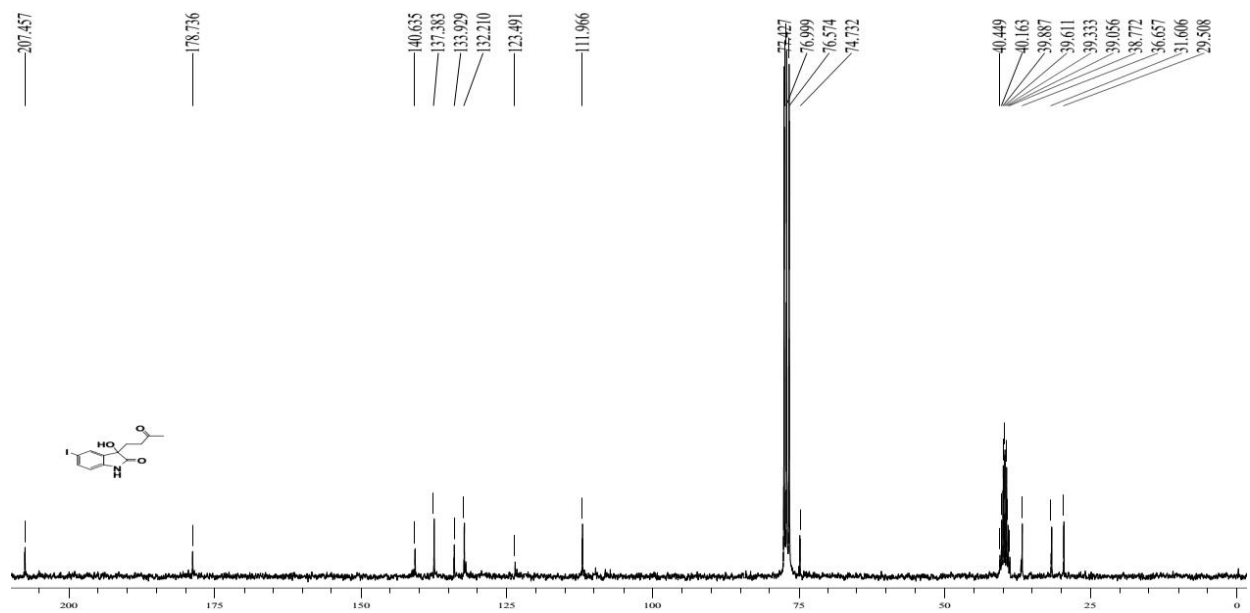


## Compound 4c

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

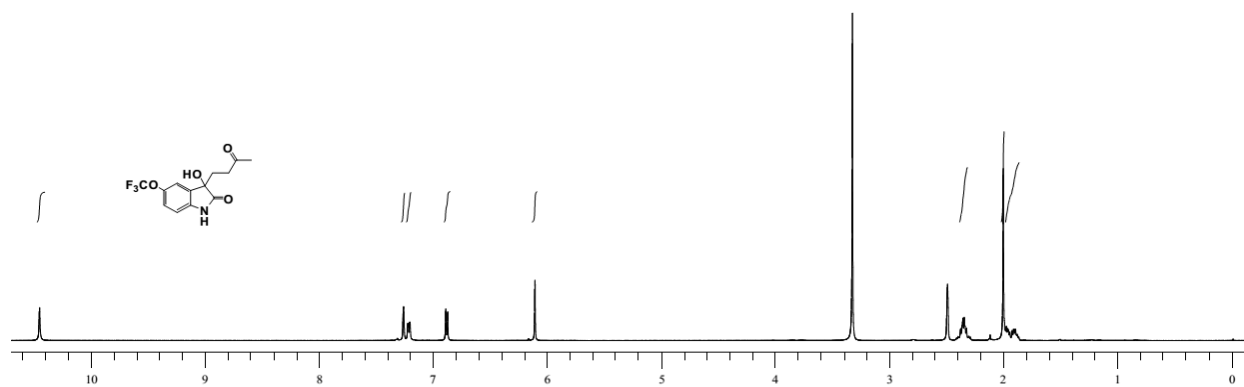


### <sup>13</sup>C NMR

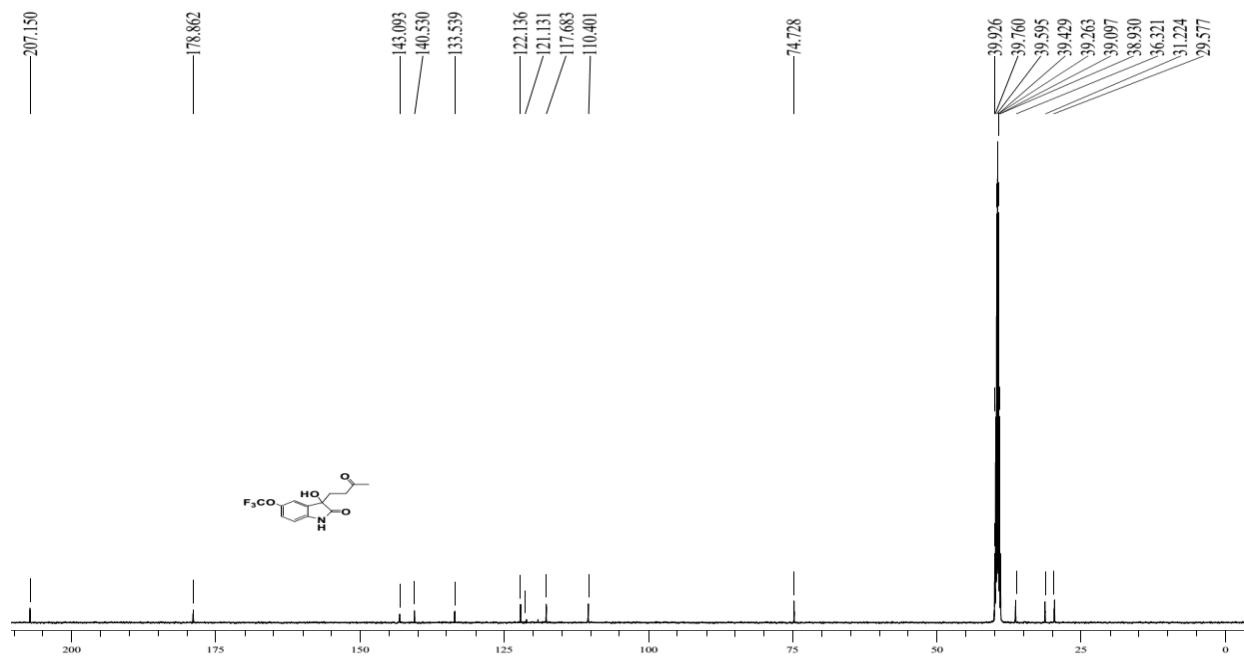


## Compound 4d

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



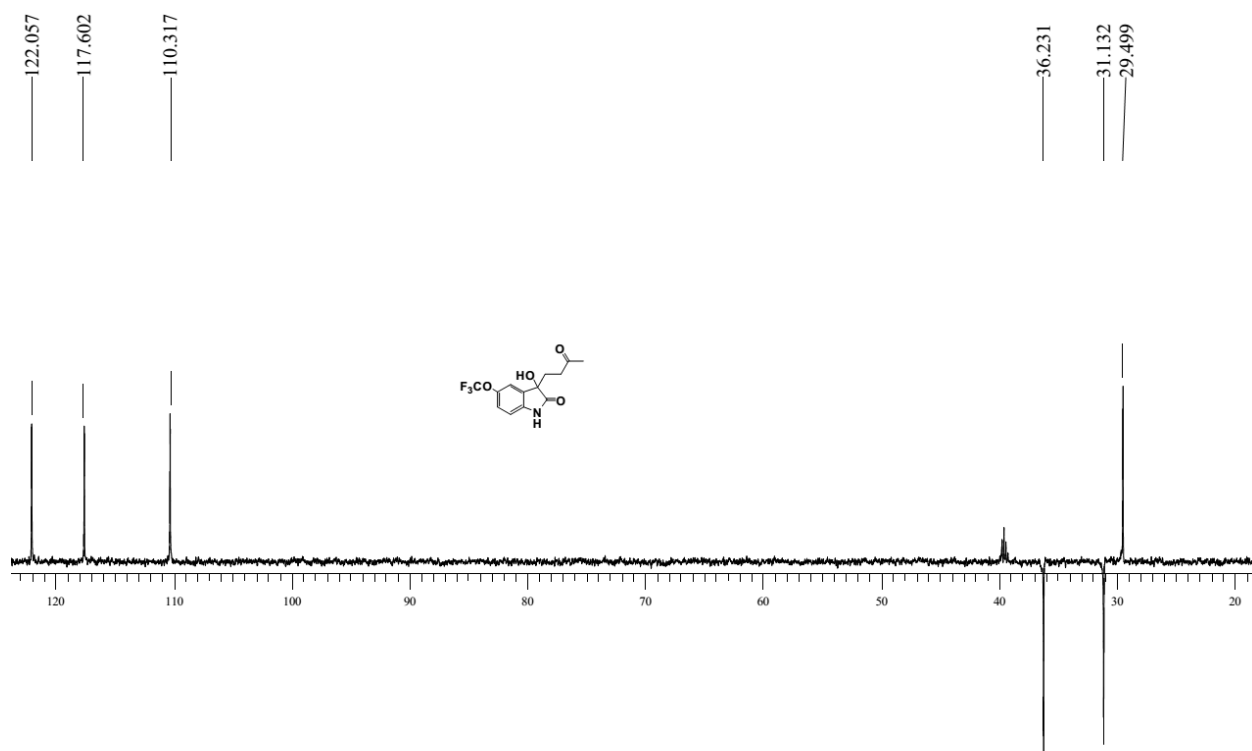
### <sup>13</sup>C NMR





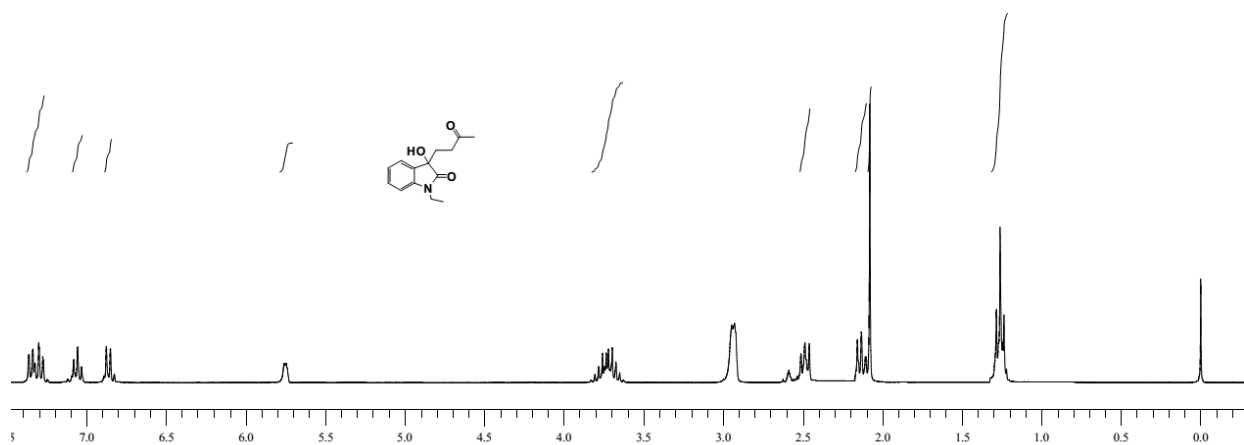
## Compound 4d

### DEPT $^{13}\text{C}$ NMR

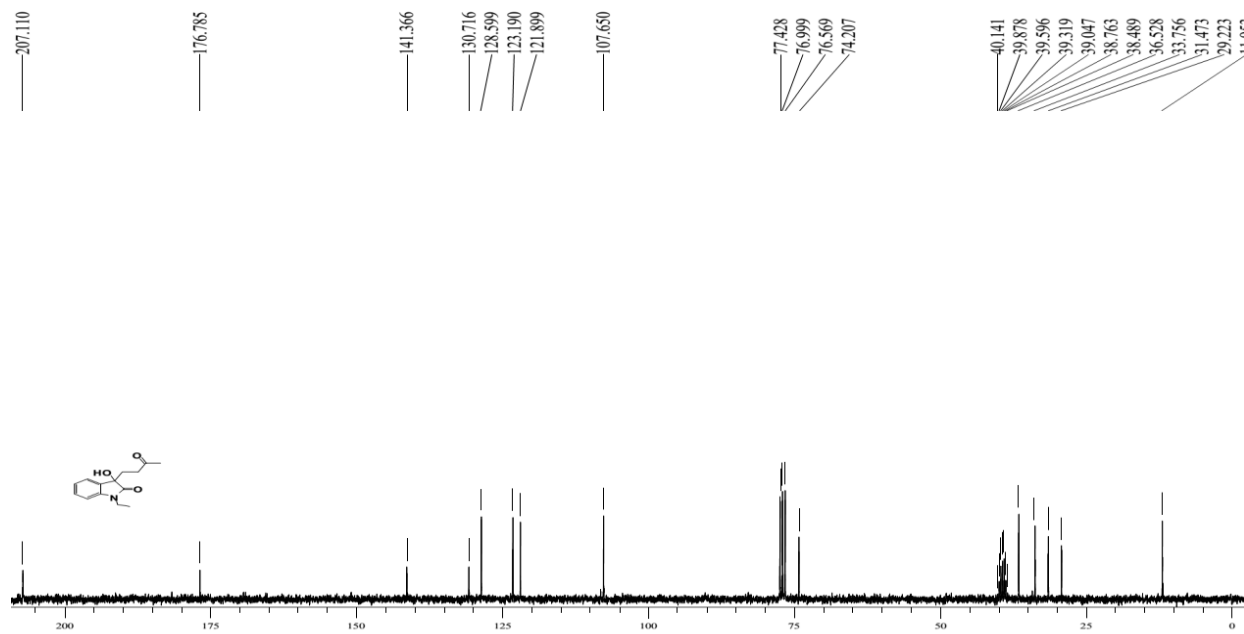


## Compound 4e

### $^1\text{H}$ NMR

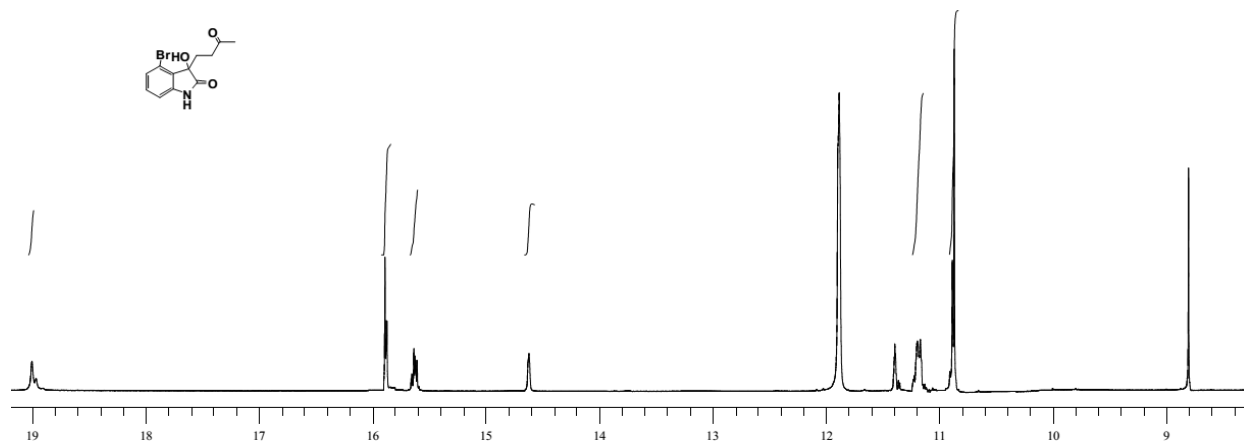


### $^{13}\text{C}$ NMR

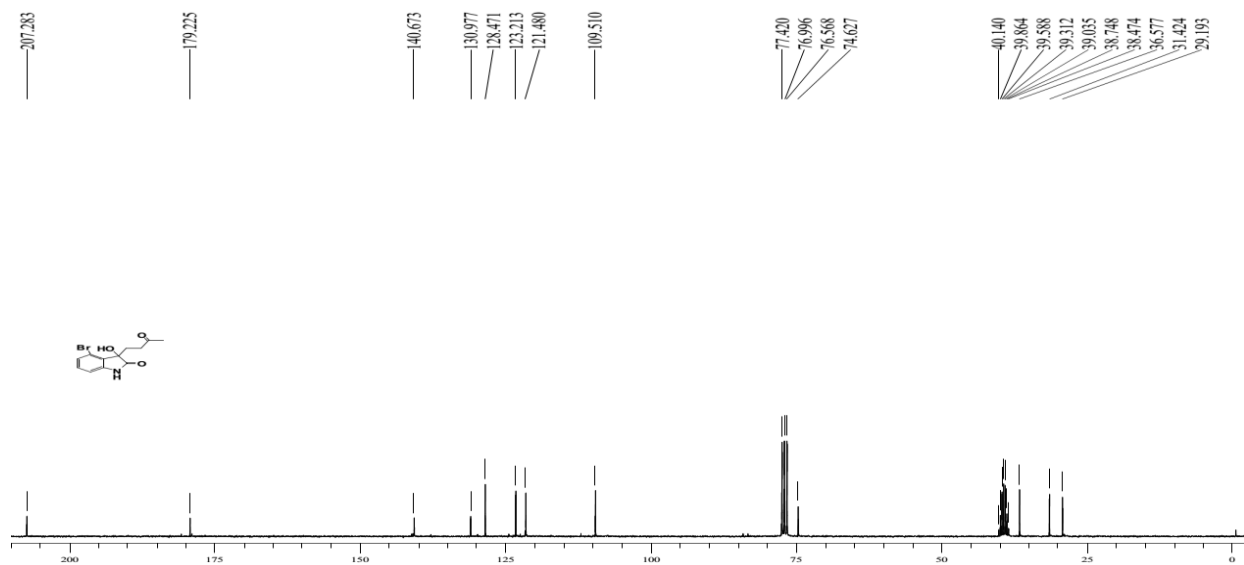


## Compound 4f

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

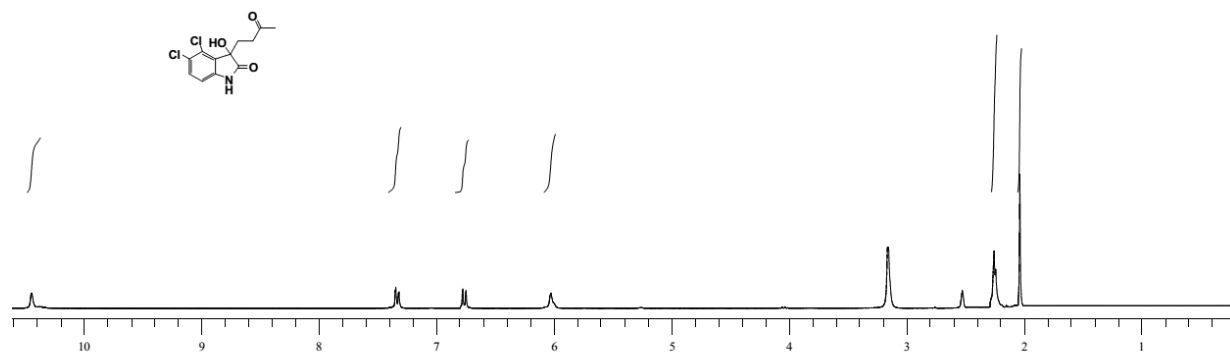


### <sup>13</sup>C NMR

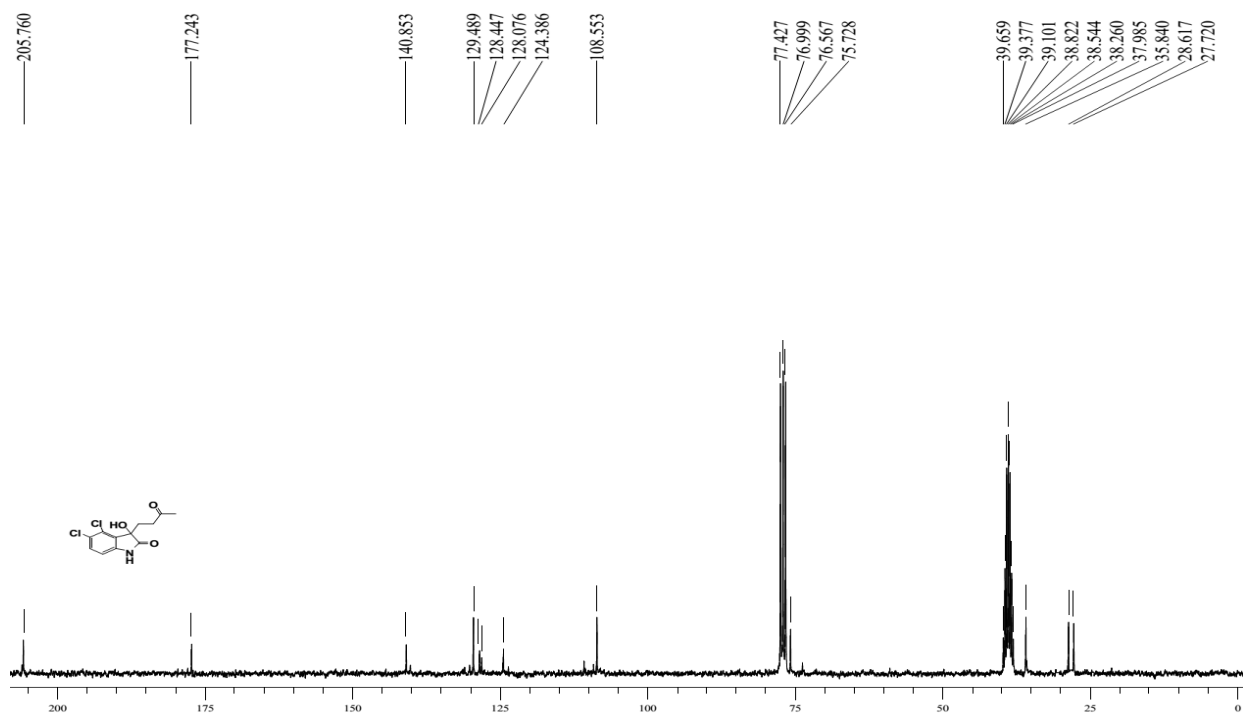


## Compound 4g

### $^1\text{H}$ NMR

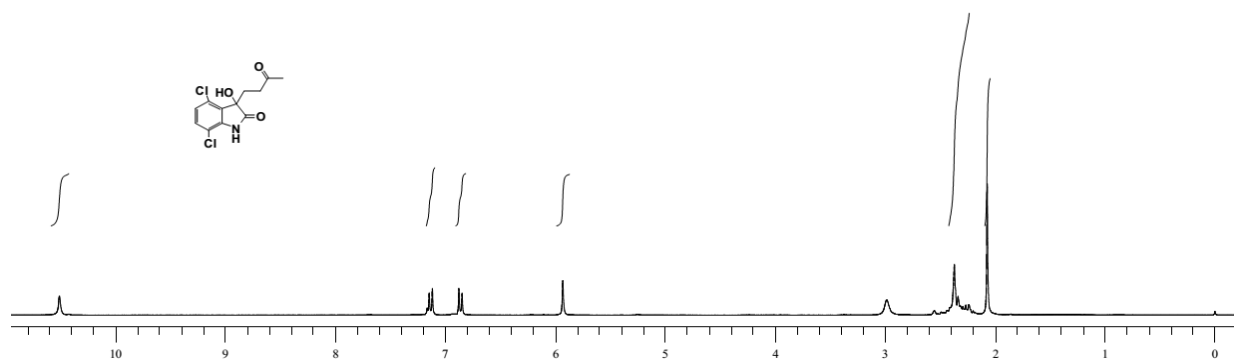


### $^{13}\text{C}$ NMR

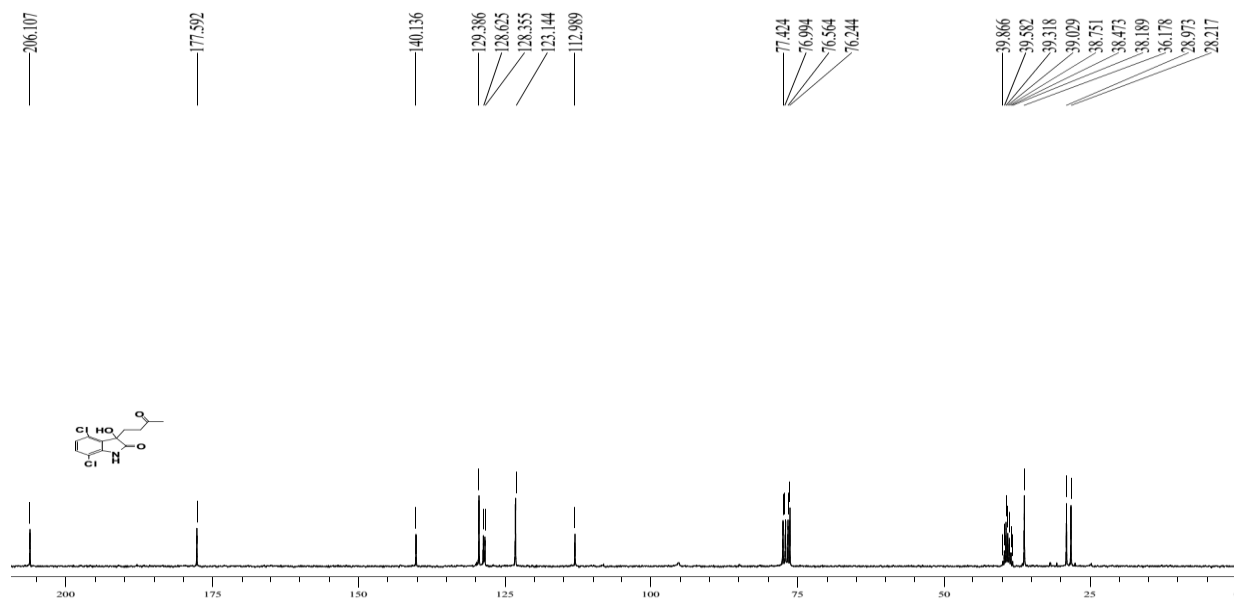


## Compound 4h

### $^1\text{H}$ NMR

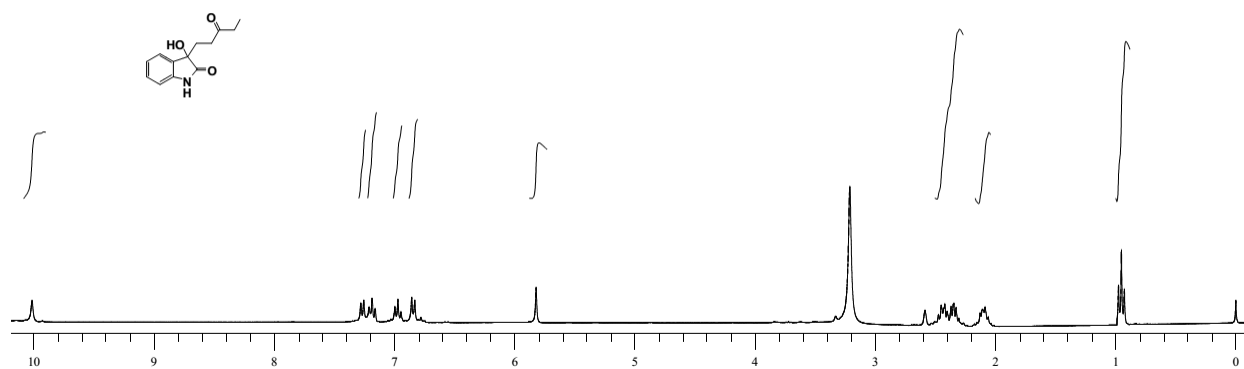


### $^{13}\text{C}$ NMR

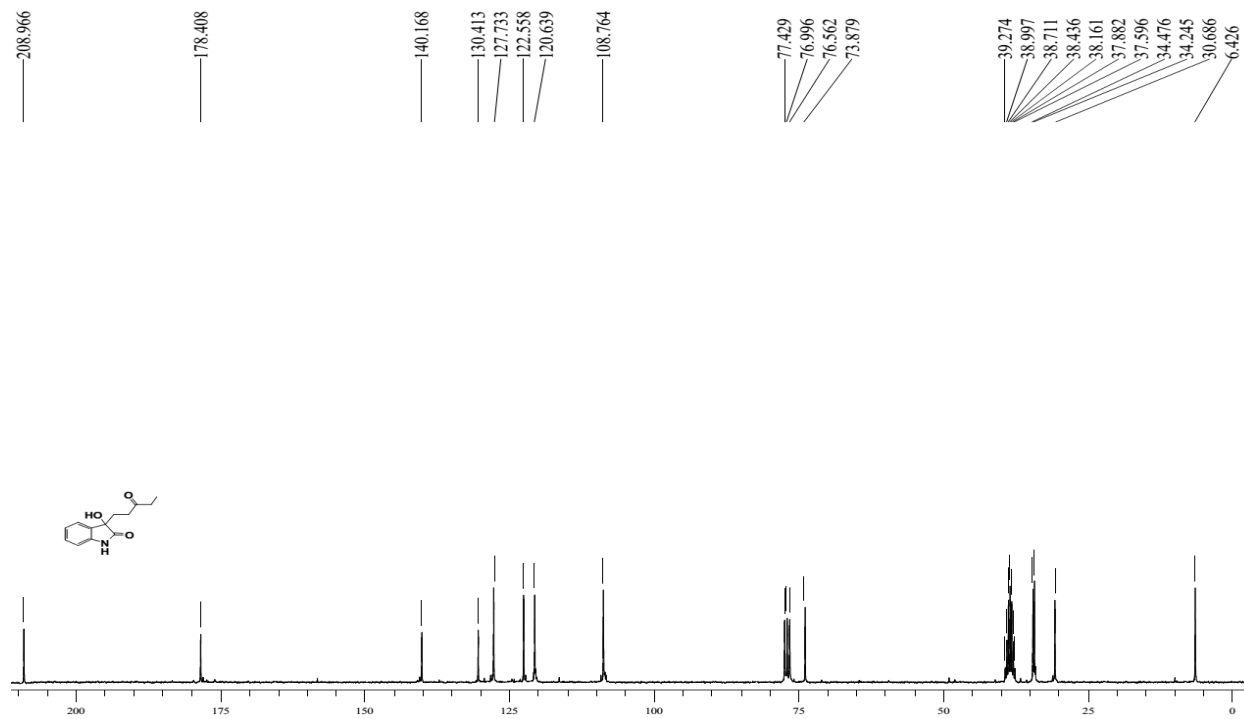


## Compound 4i

### $^1\text{H NMR}$

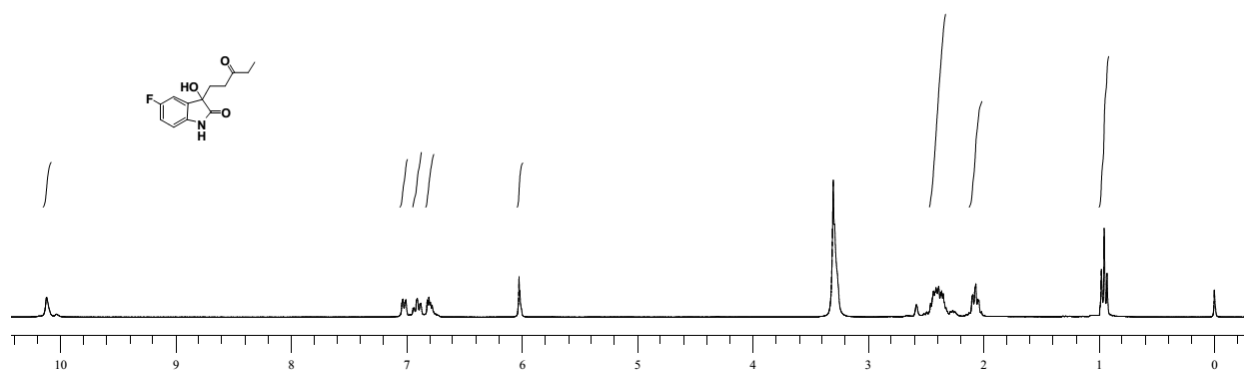


### $^{13}\text{C NMR}$

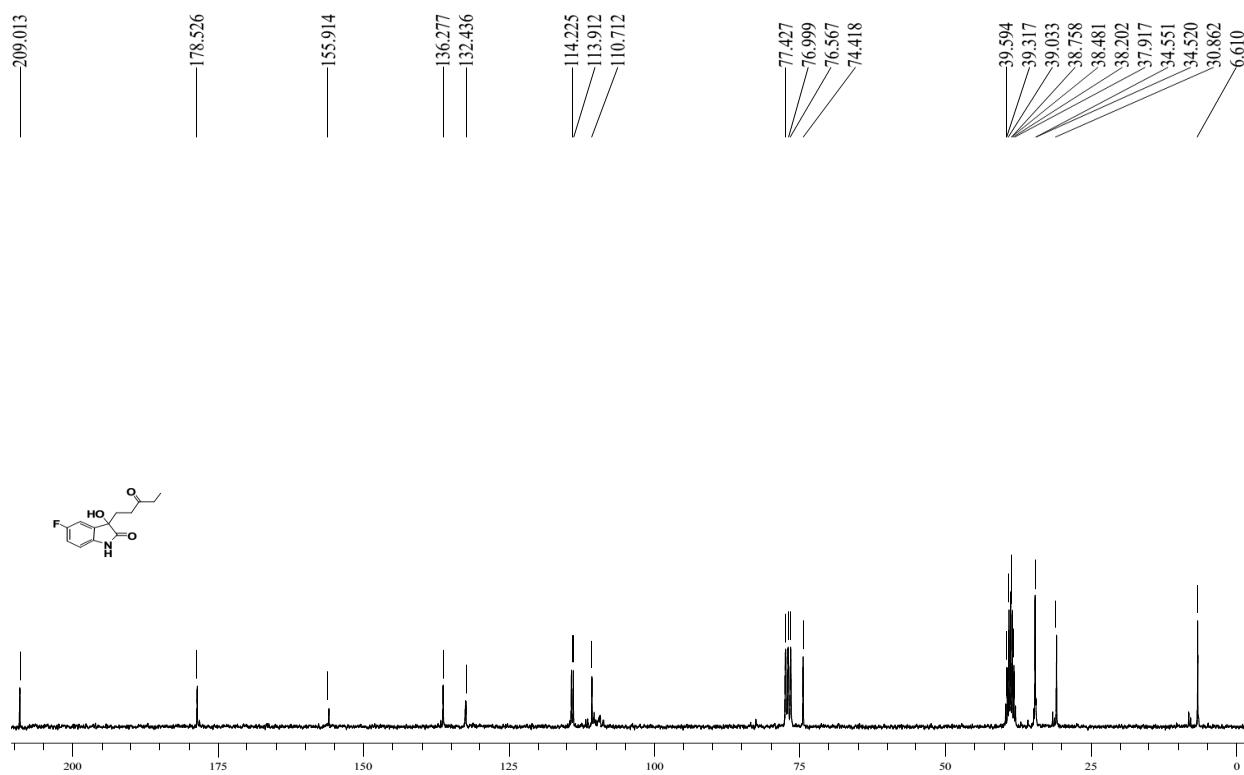


## Compound 4j

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

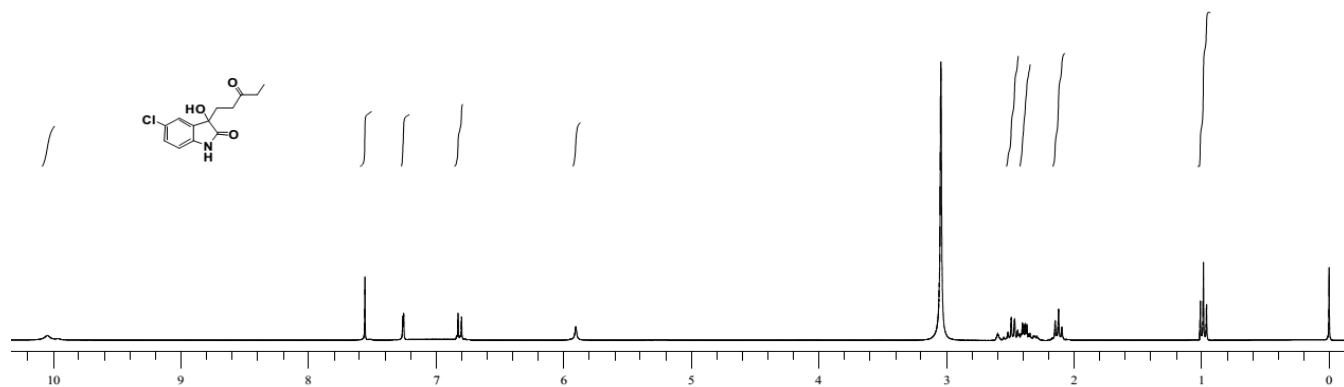


### <sup>13</sup>C NMR

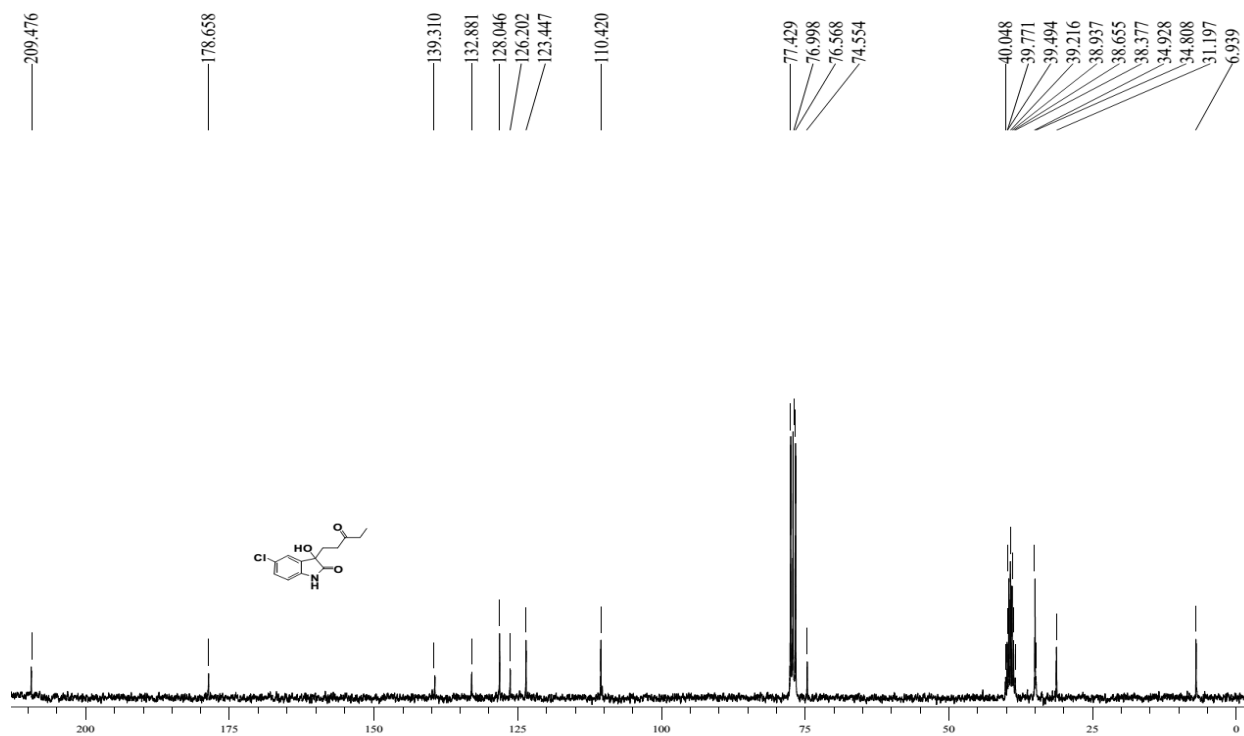


## Compound 4k

### $^1\text{H}$ NMR



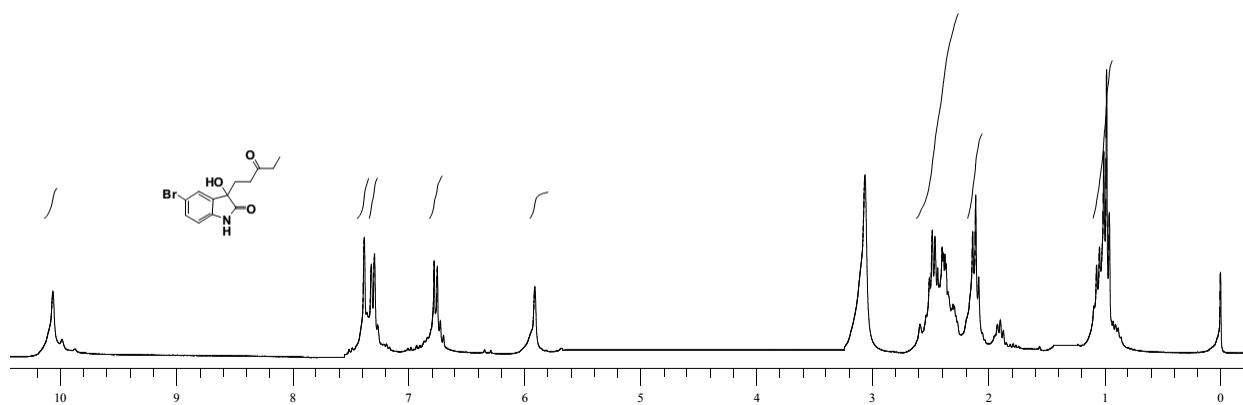
### $^{13}\text{C}$ NMR



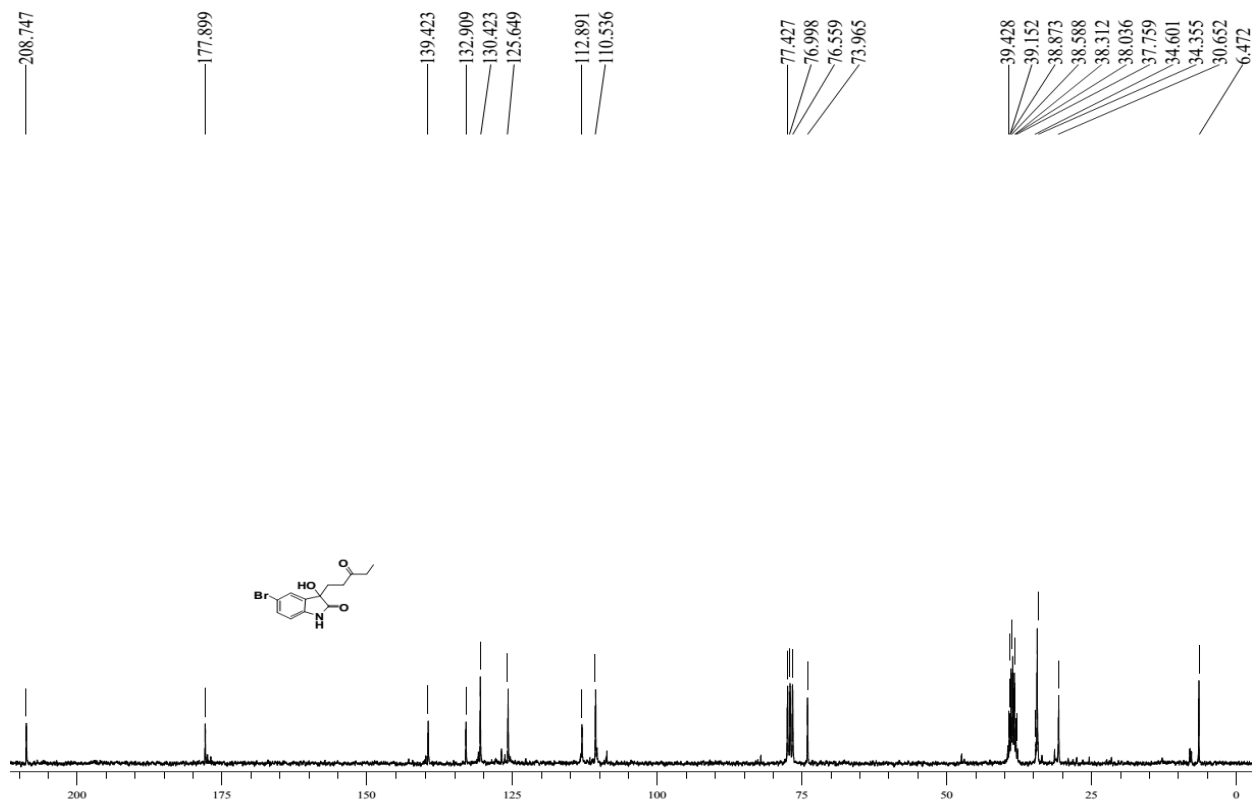


## Compound 4l

### $^1\text{H NMR}$

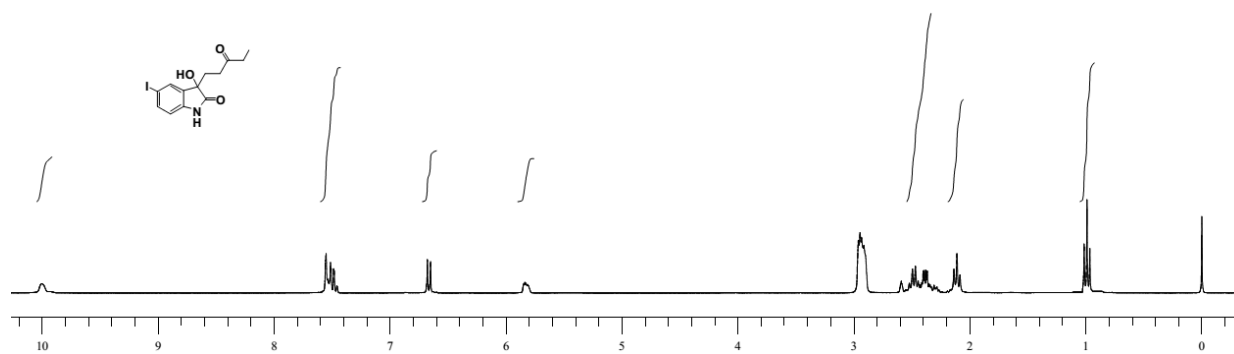


### $^{13}\text{C NMR}$

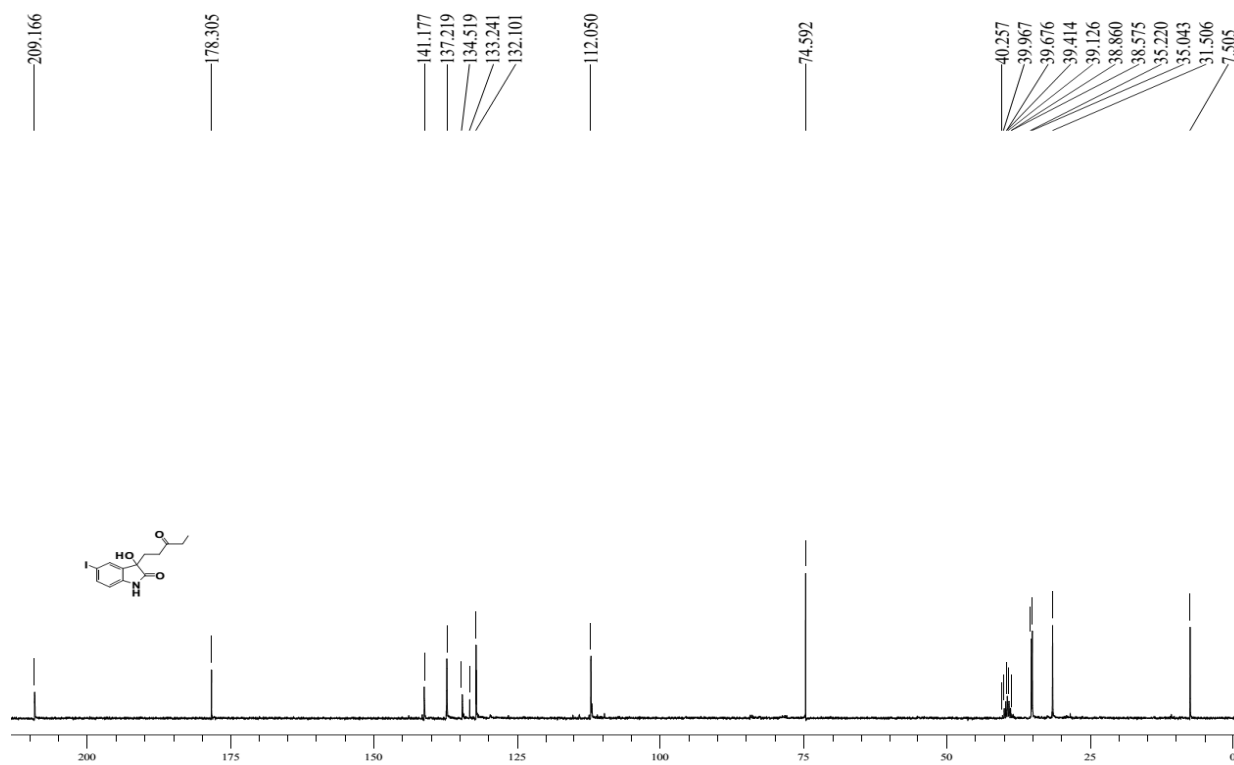


## Compound 4m

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

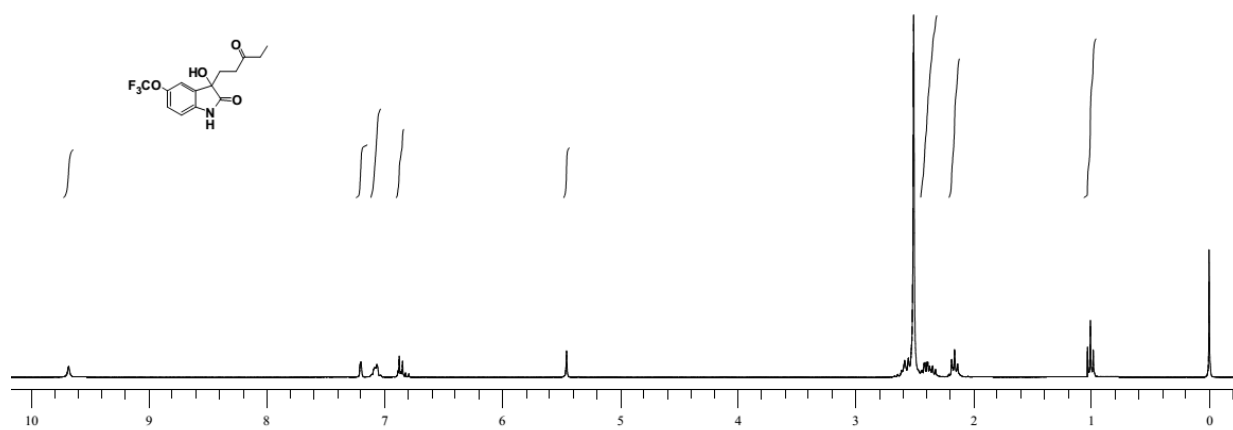


### <sup>13</sup>C NMR

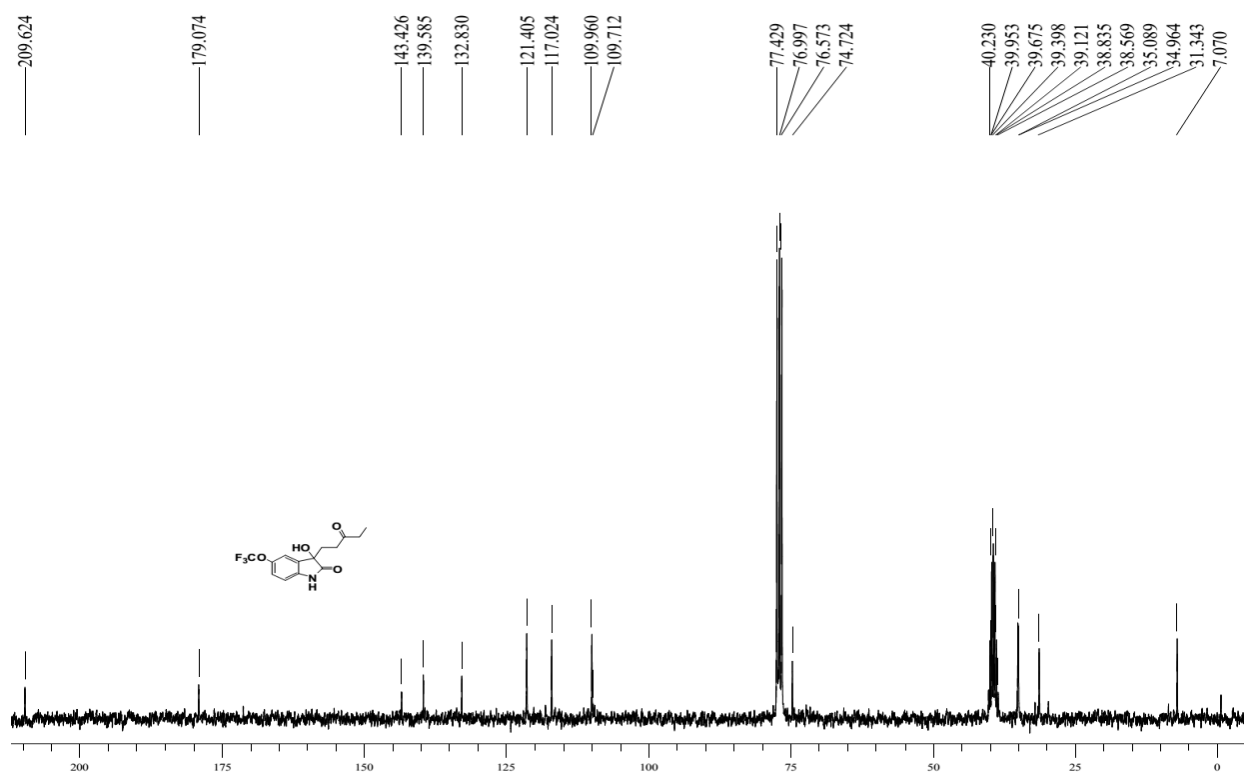


## Compound 4n

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

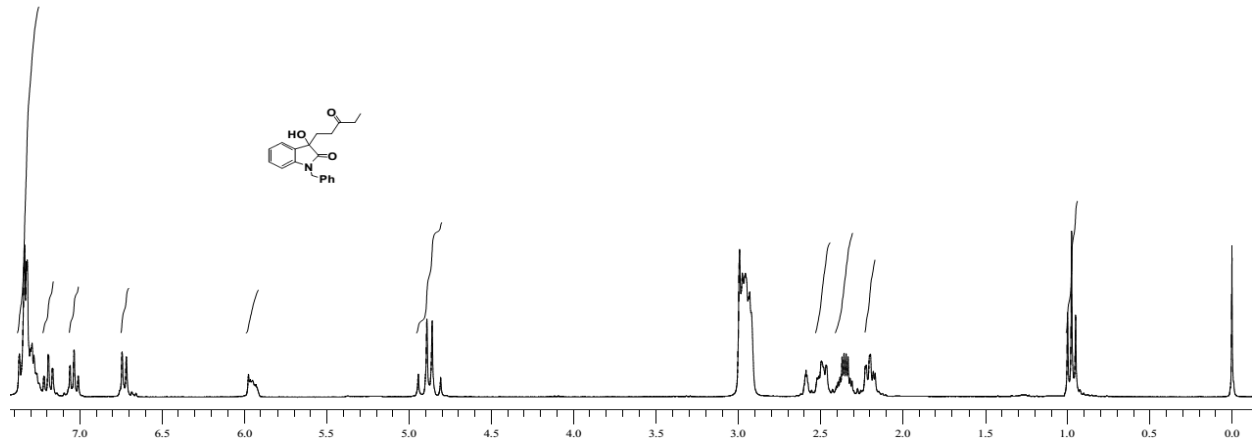


### <sup>13</sup>C NMR

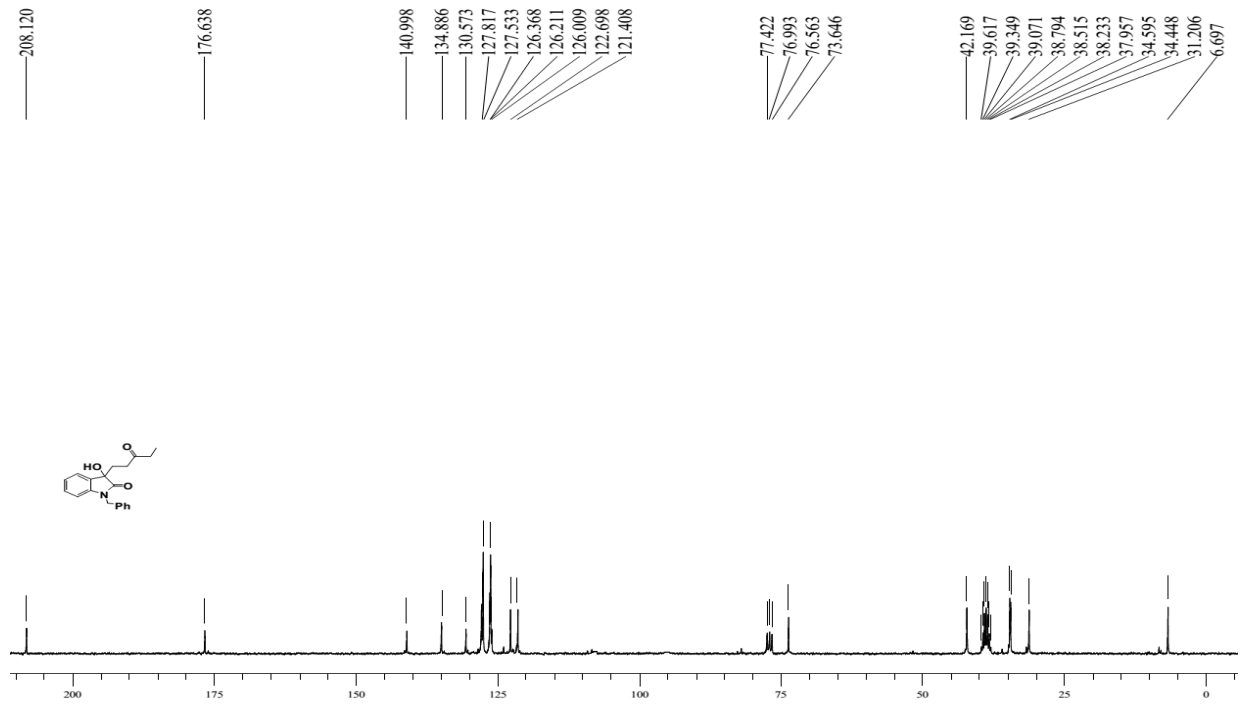


## Compound 4o

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

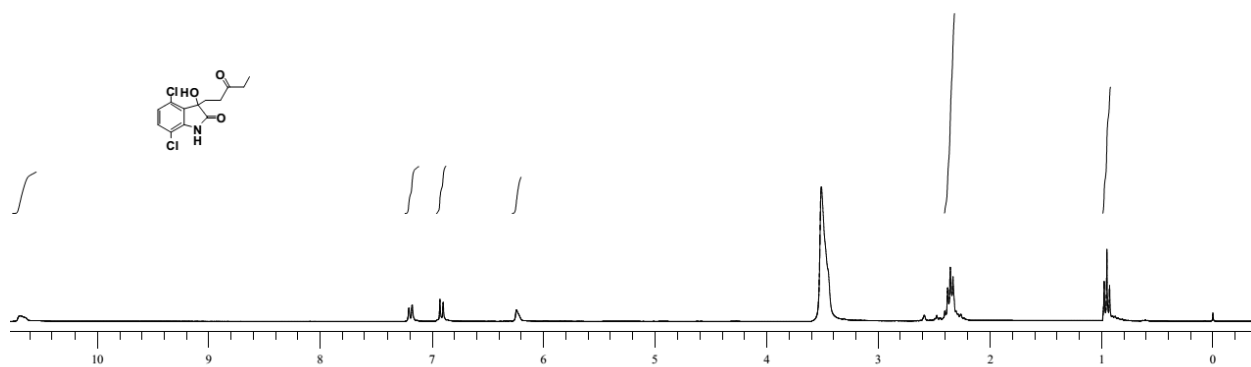


### <sup>13</sup>C NMR

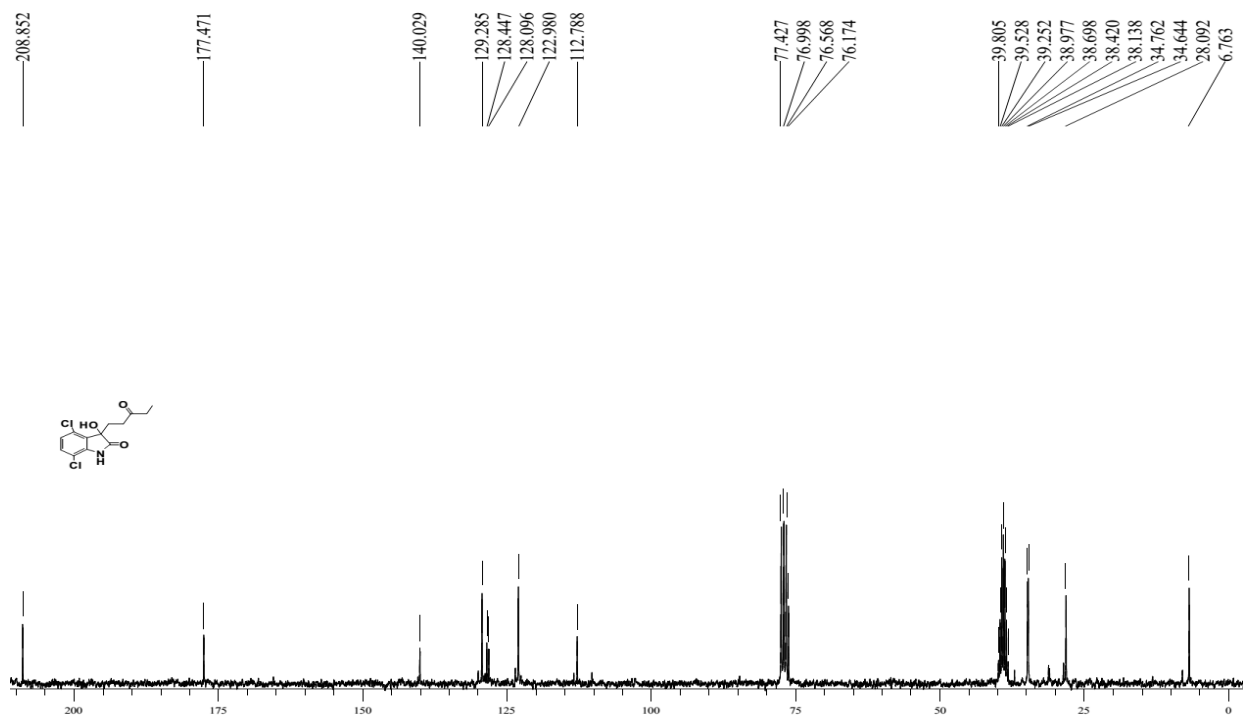


## Compound 4p

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

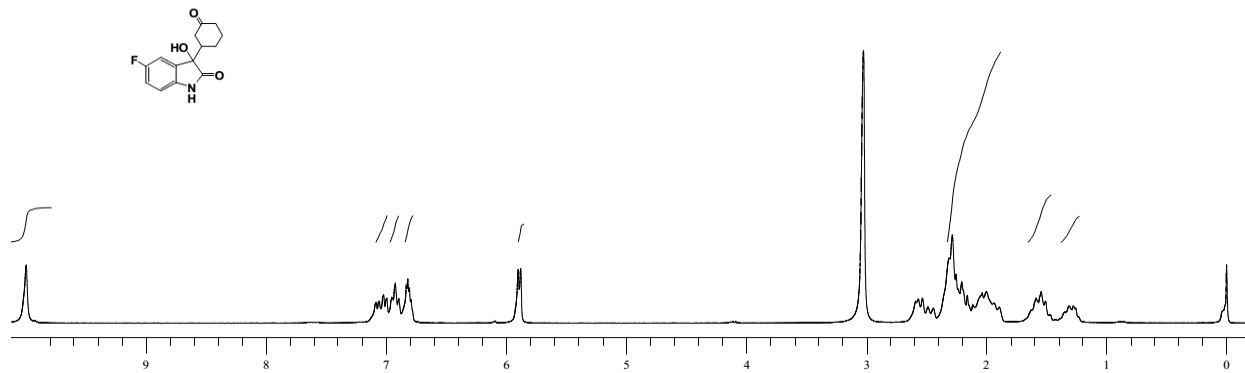


### <sup>13</sup>C NMR

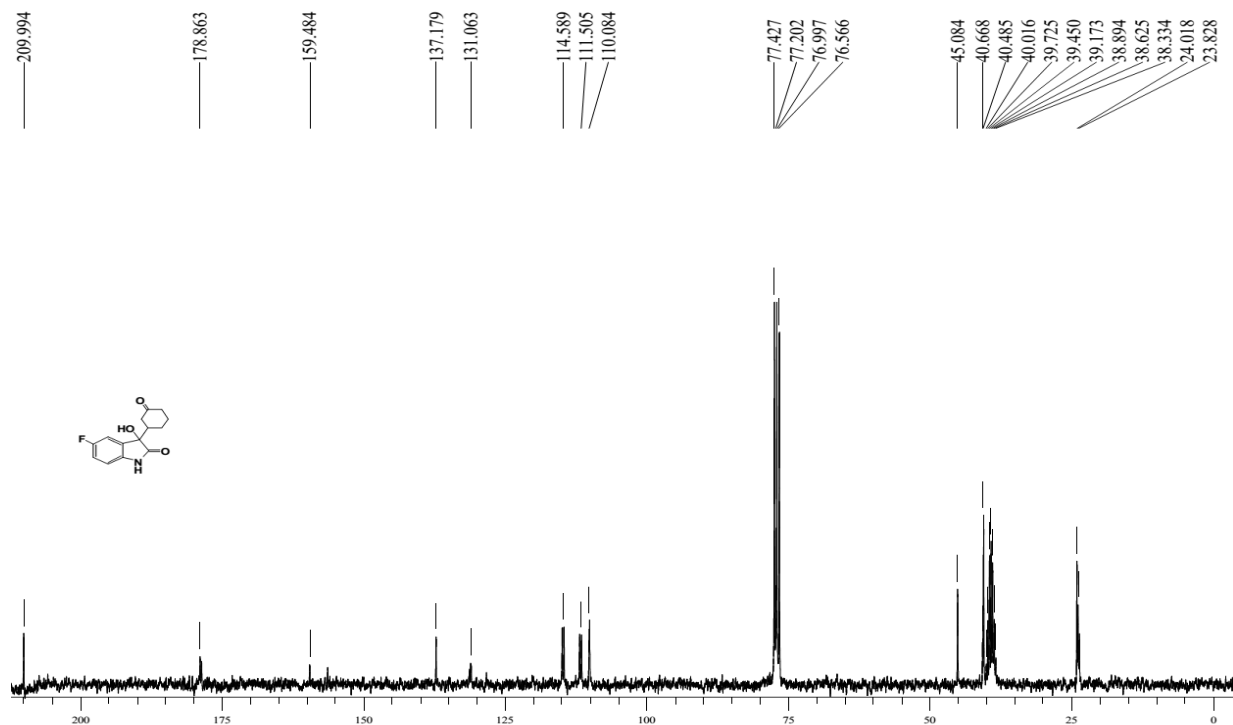


## Compound 4q

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

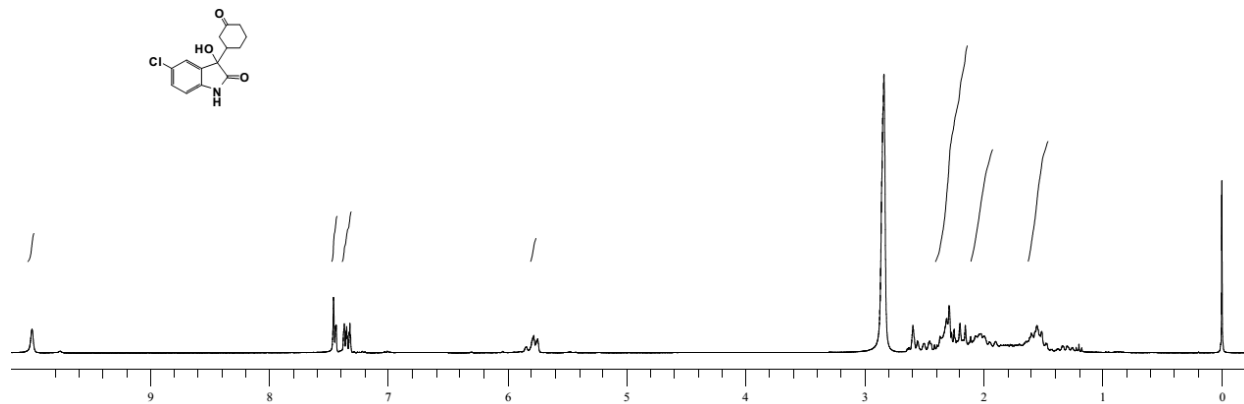


### <sup>13</sup>C NMR

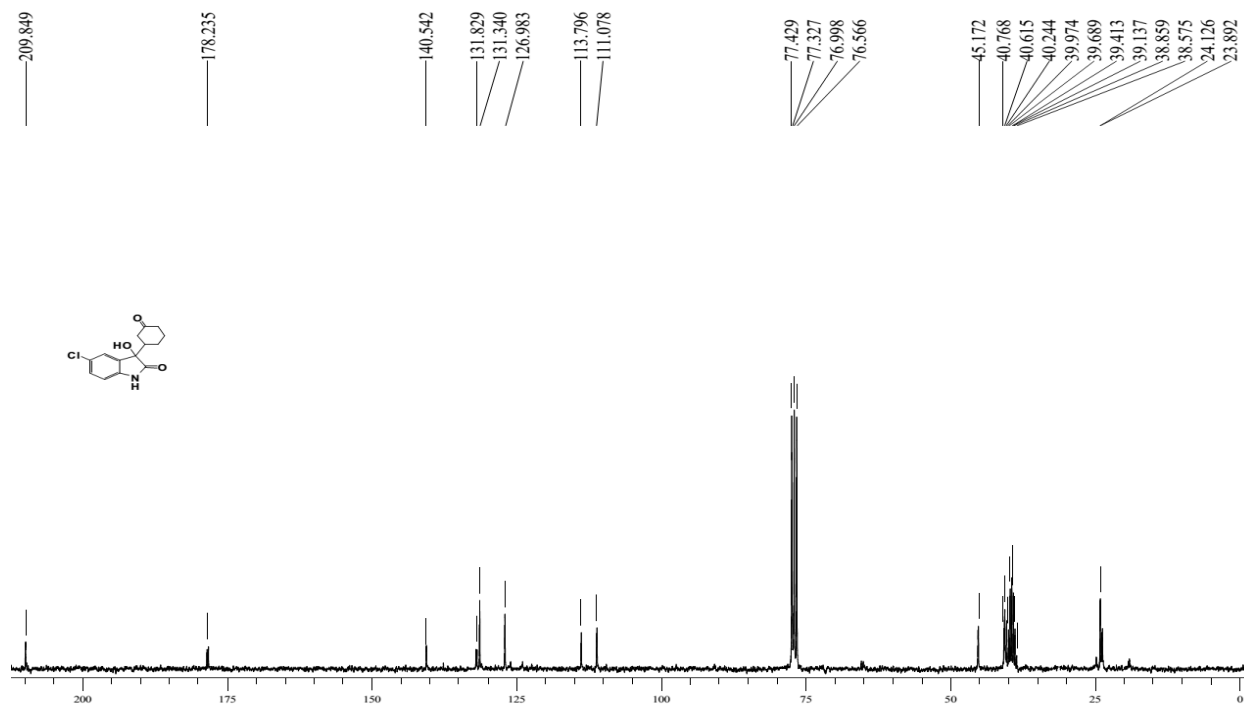


## Compound 4r

### $^1\text{H NMR}$

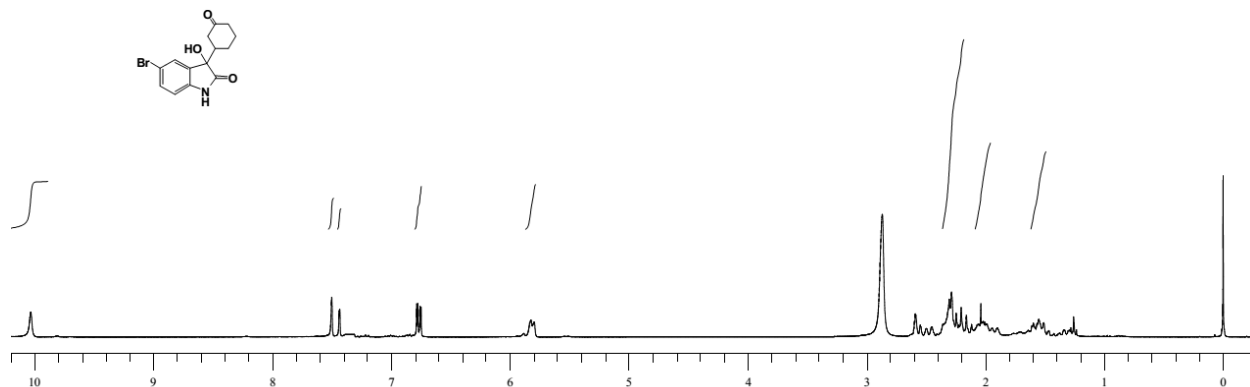


### $^{13}\text{C NMR}$

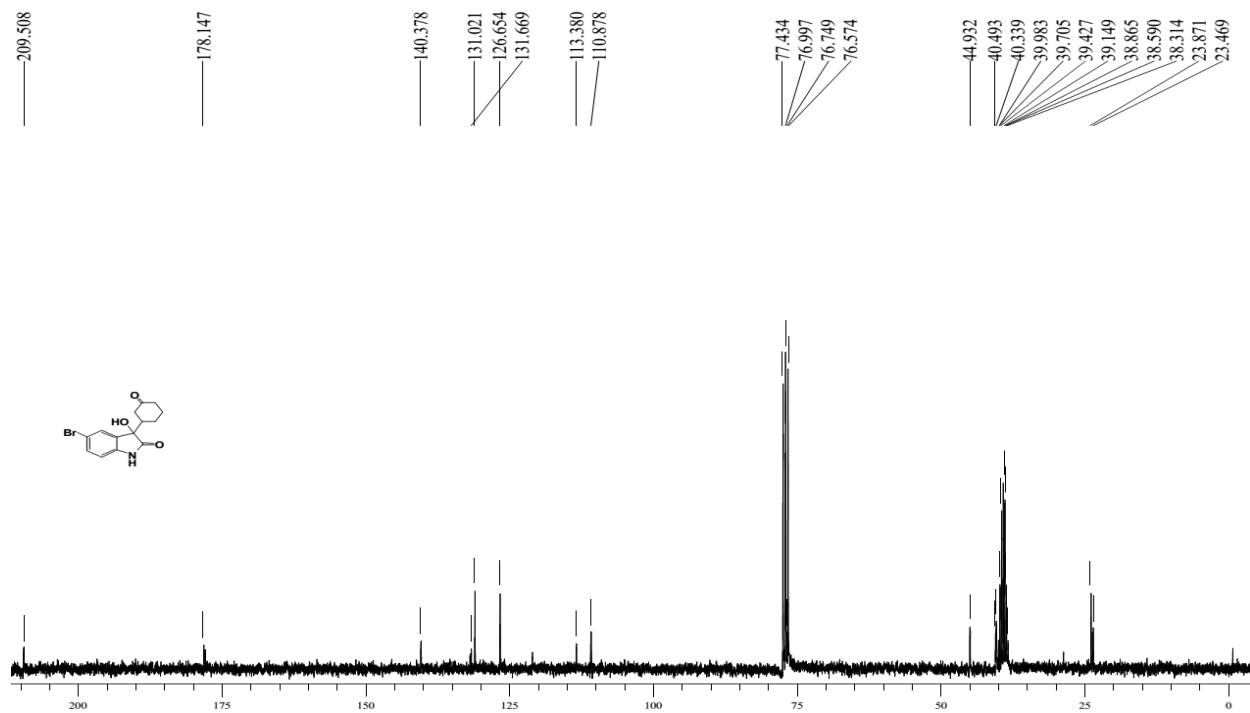


## Compound 4s

### $^1\text{H NMR}$



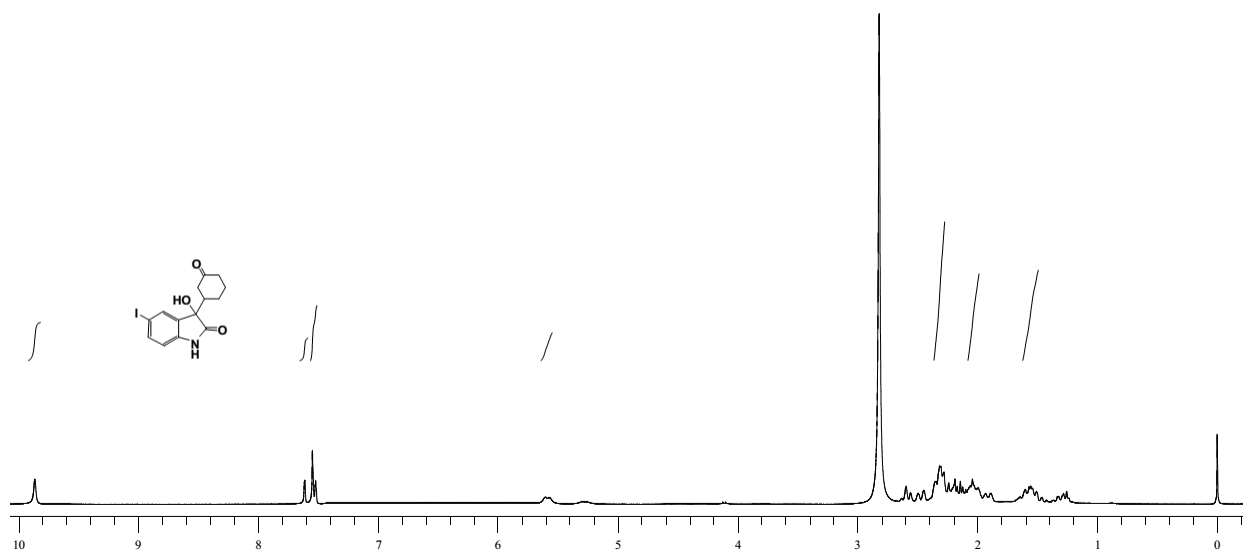
### $^{13}\text{C NMR}$



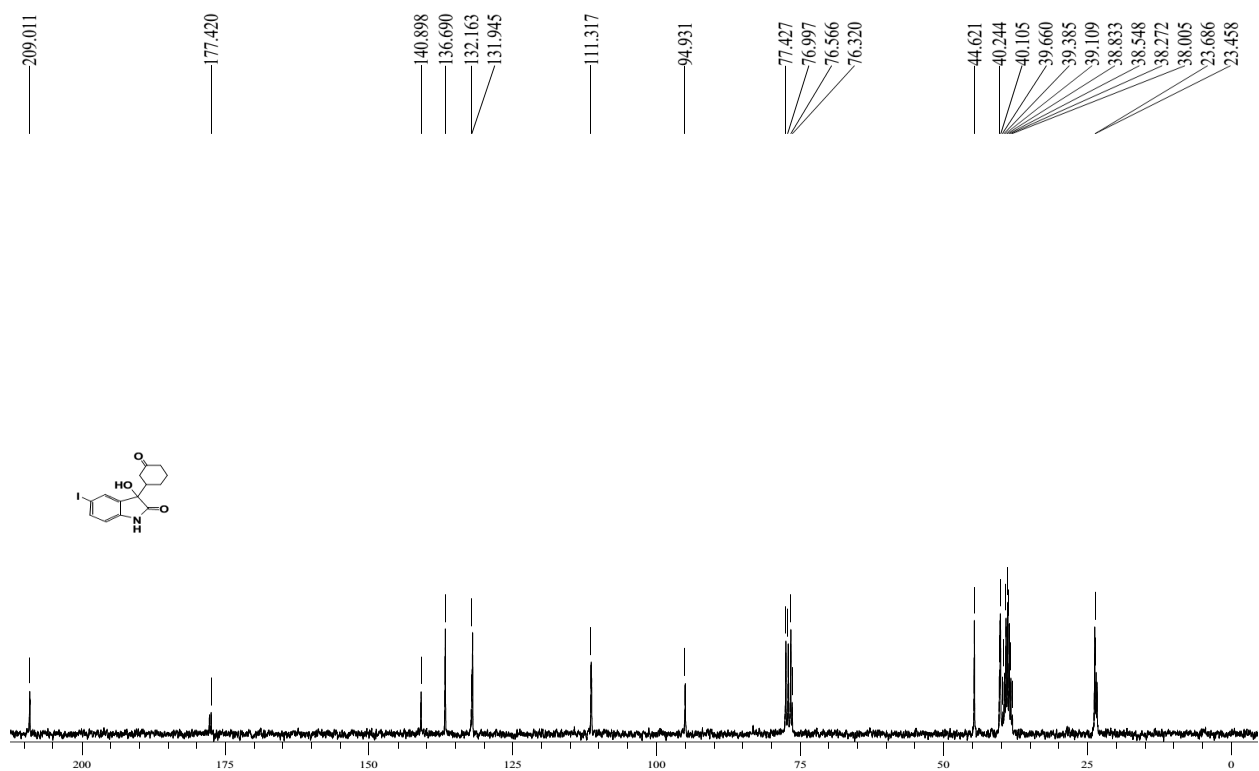


## Compound 4t

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

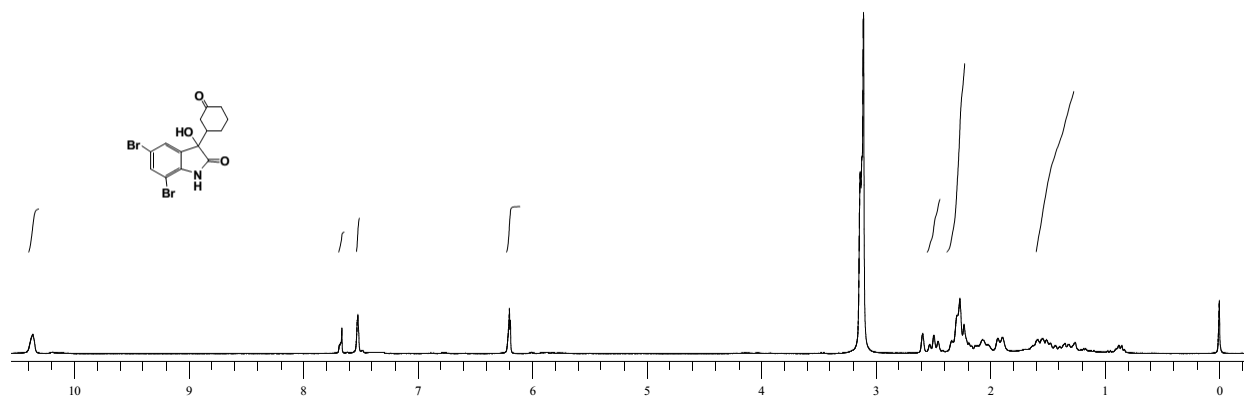


### <sup>13</sup>C NMR

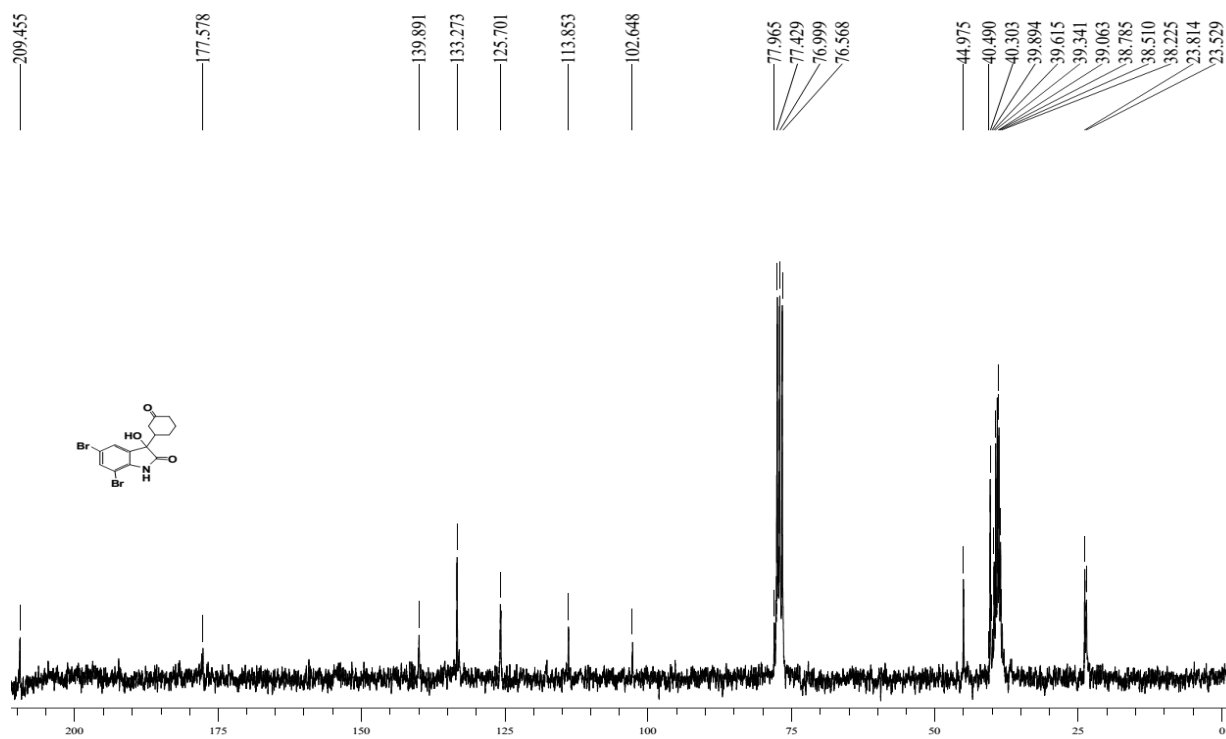


## Compound 4u

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

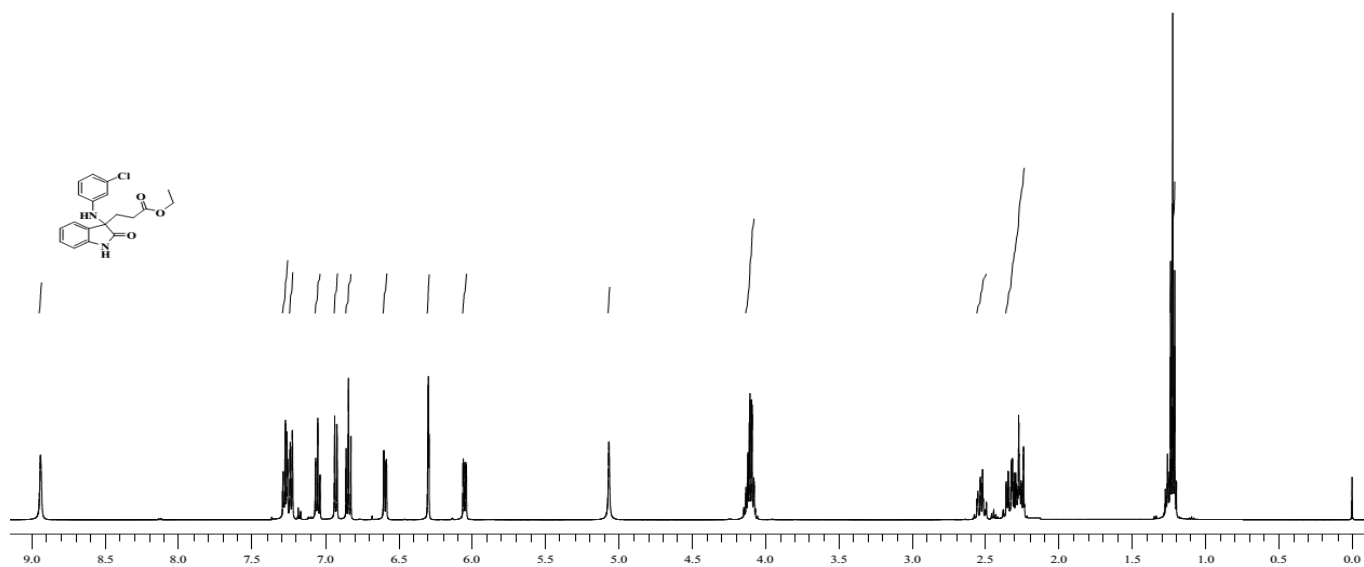


### <sup>13</sup>C NMR

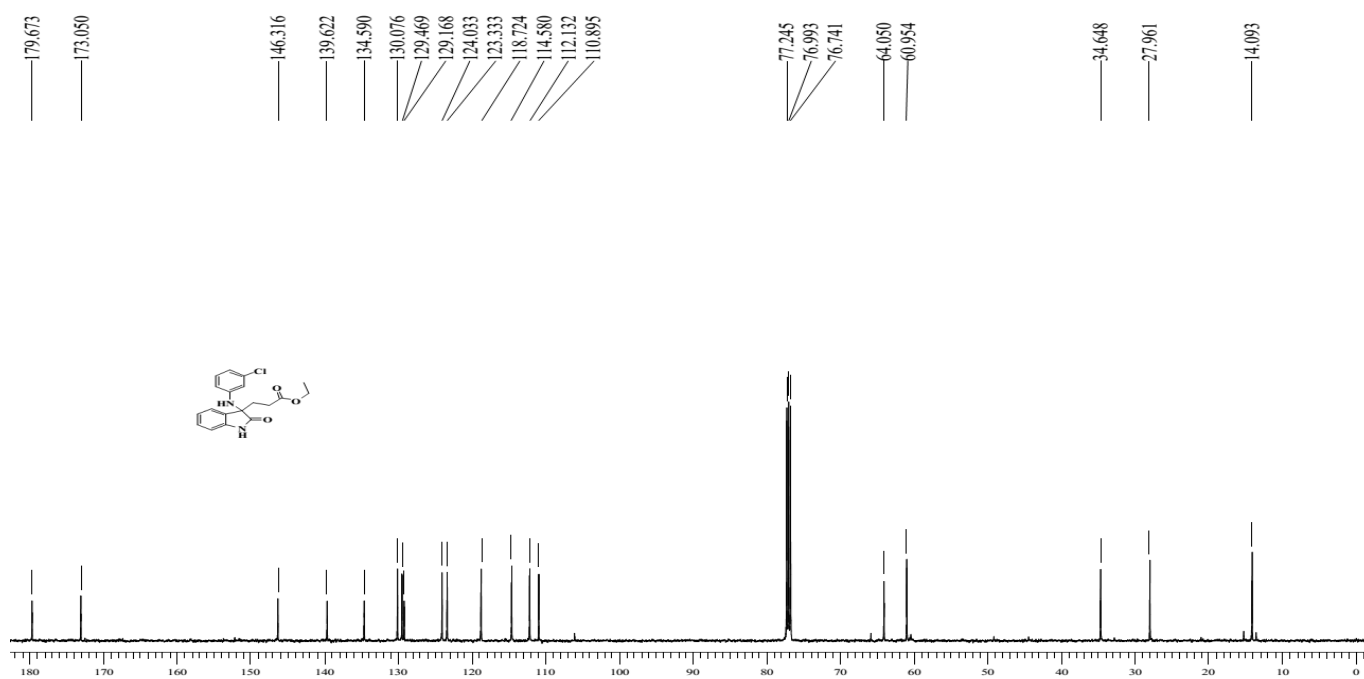


## Compound 5a

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

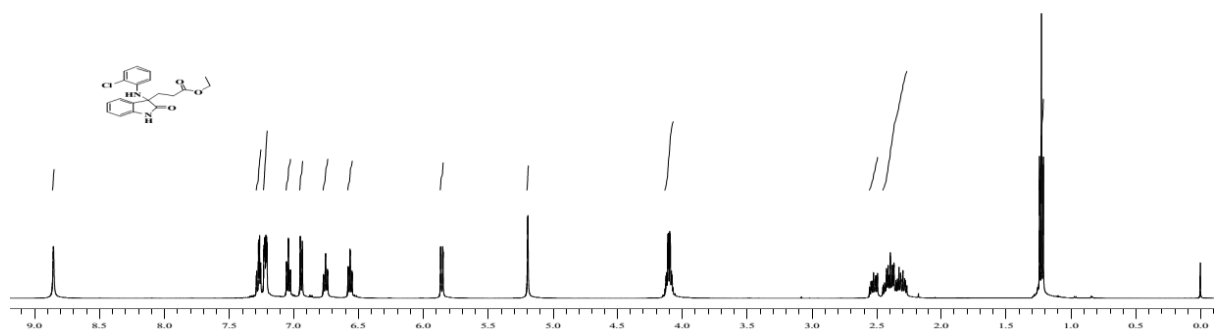


### <sup>13</sup>C NMR

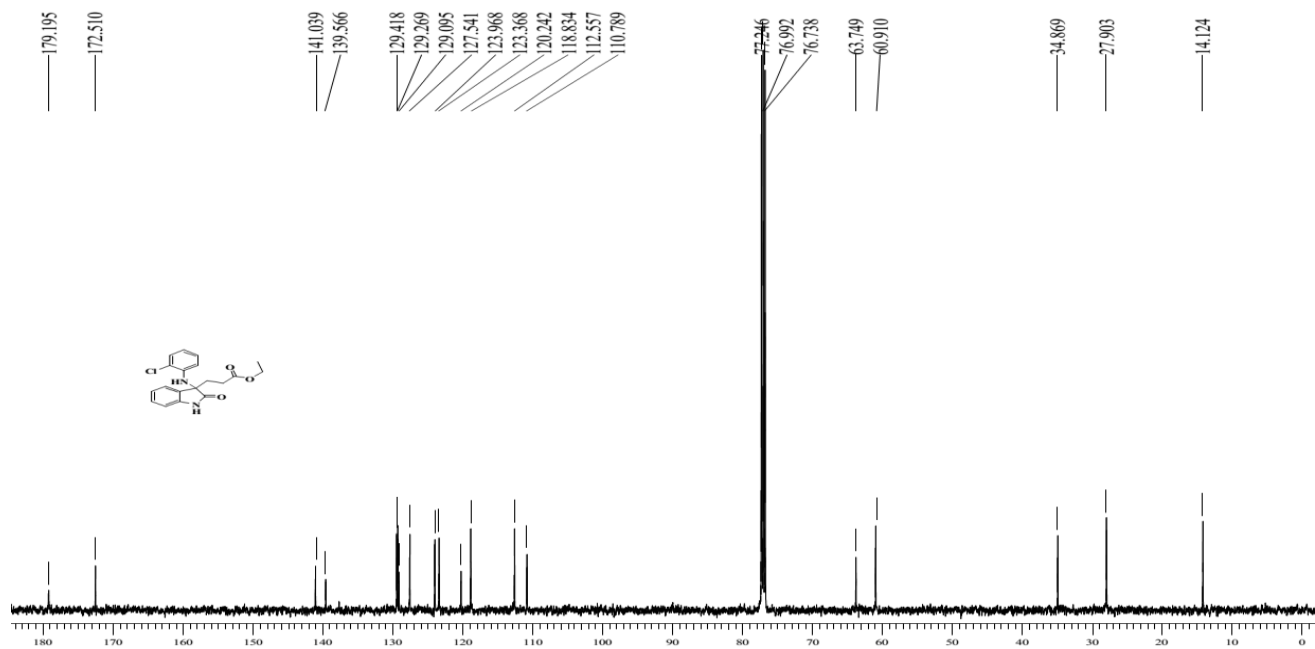


## Compound 5b

### $^1\text{H NMR}$

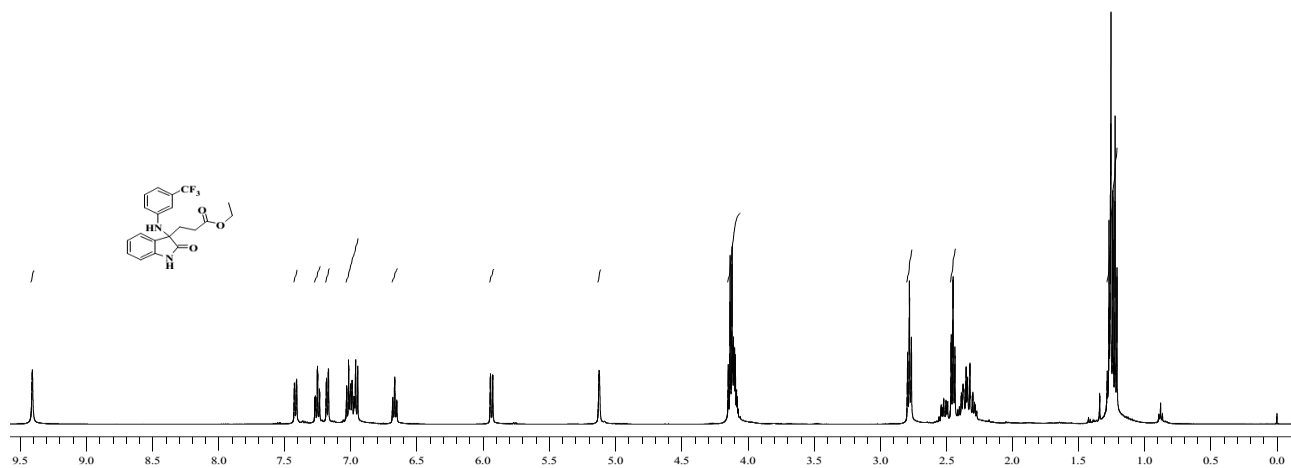


### $^{13}\text{C NMR}$

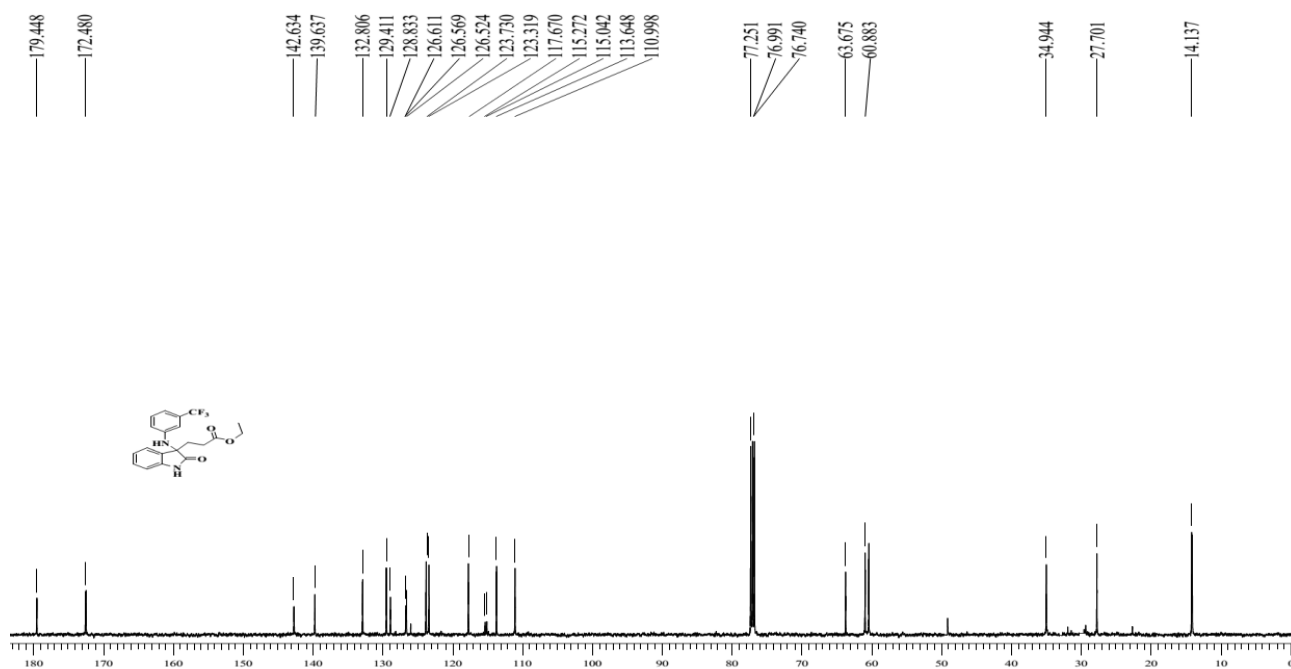


## Compound 5c

### $^1\text{H NMR}$

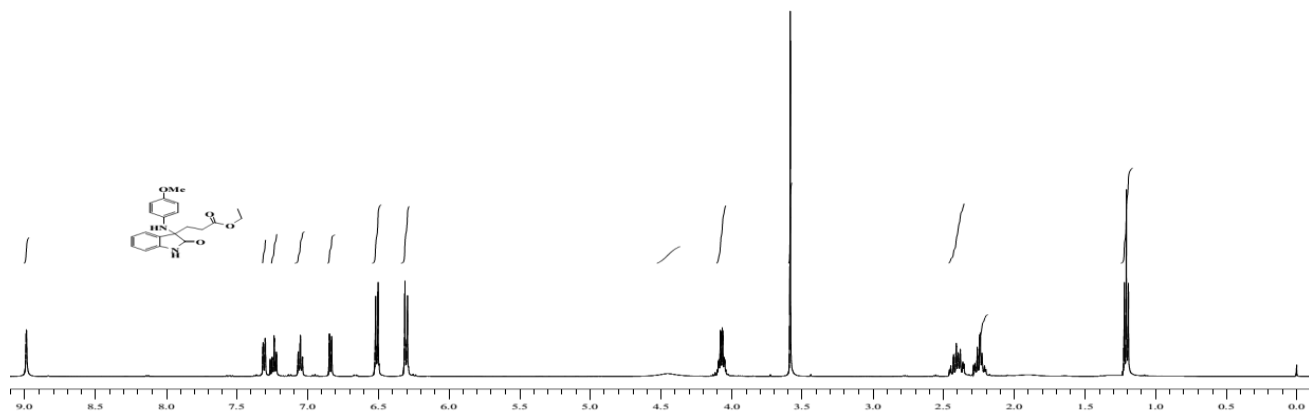


### $^{13}\text{C NMR}$

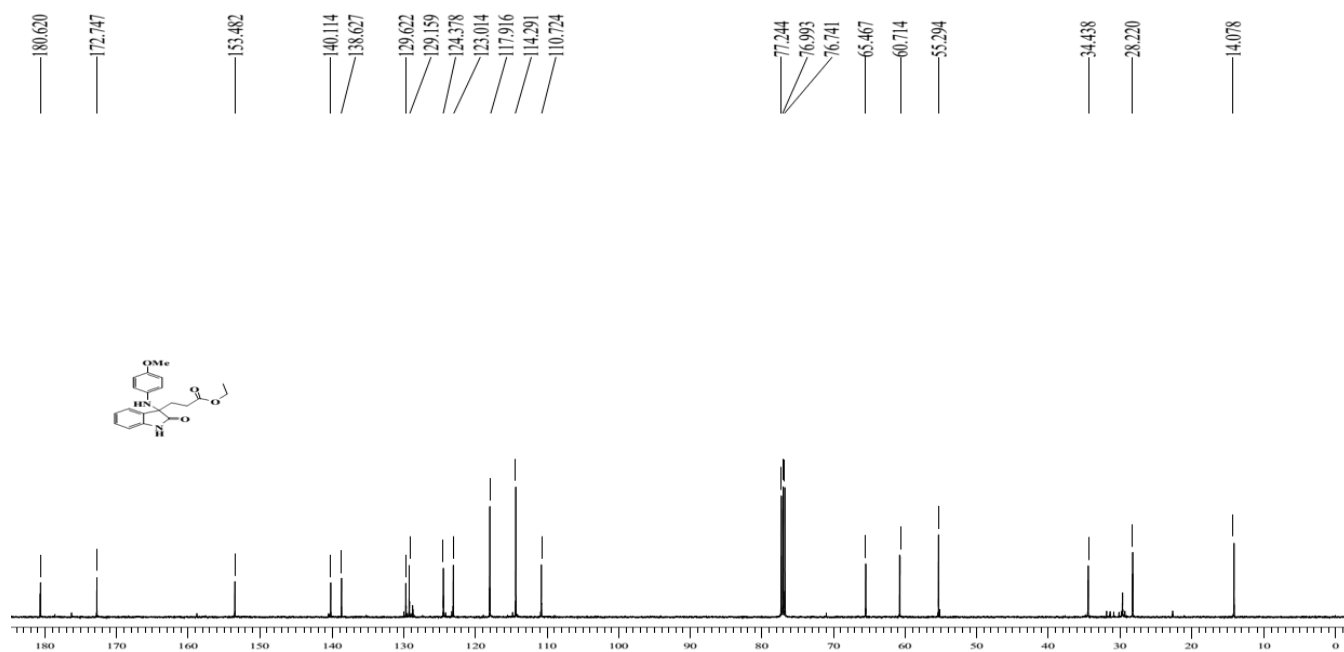


## Compound 5d

### $^1\text{H}$ NMR

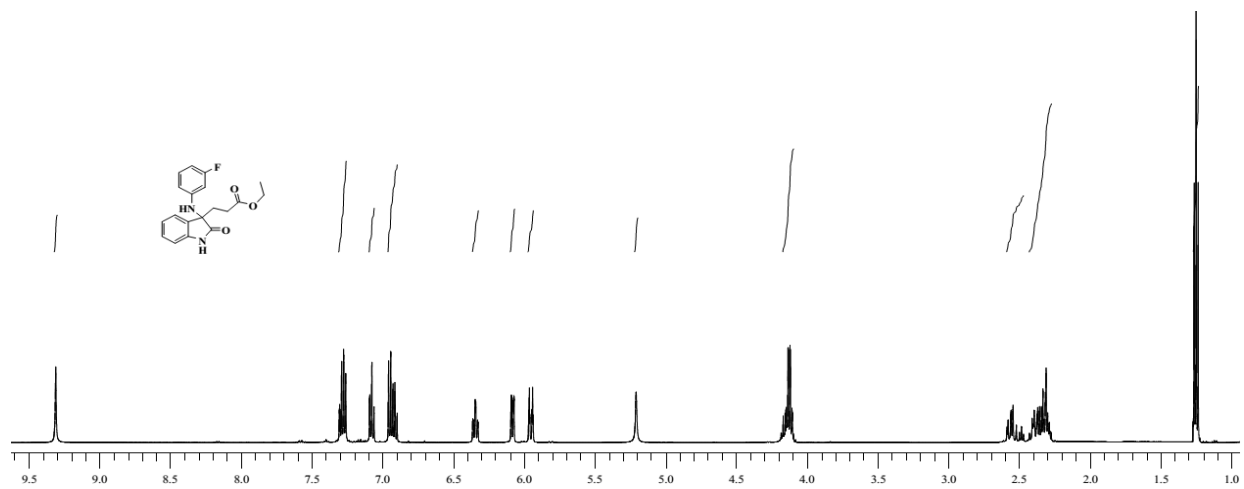


### $^{13}\text{C}$ NMR

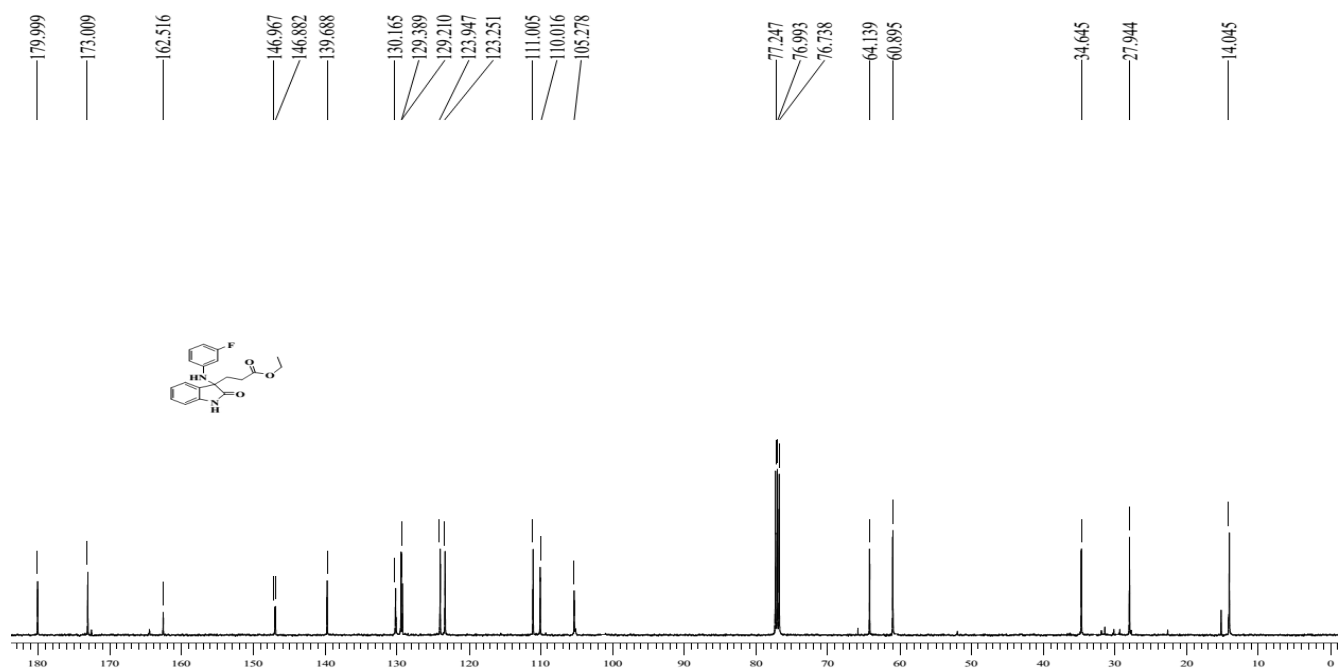


## Compound 5e

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

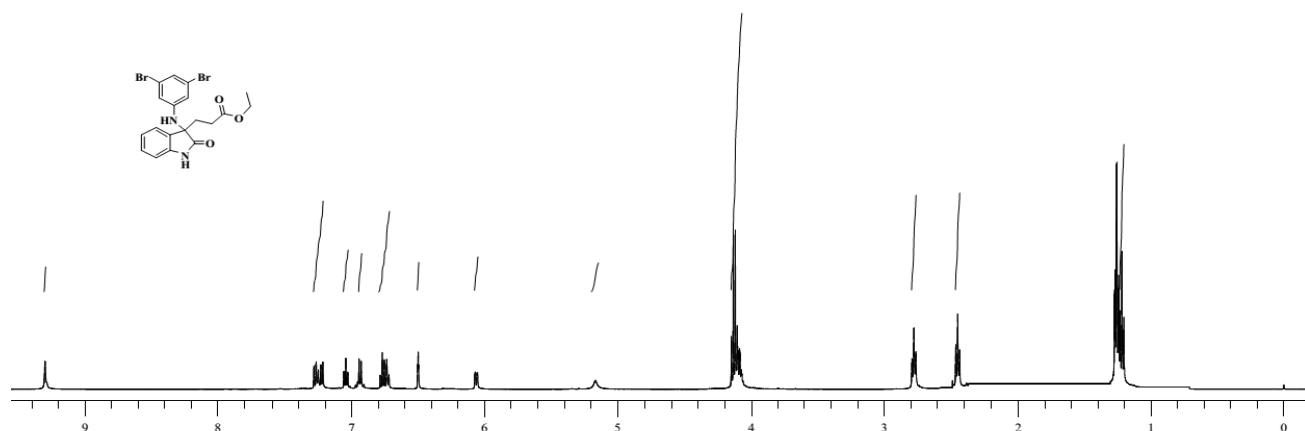


### <sup>13</sup>C NMR

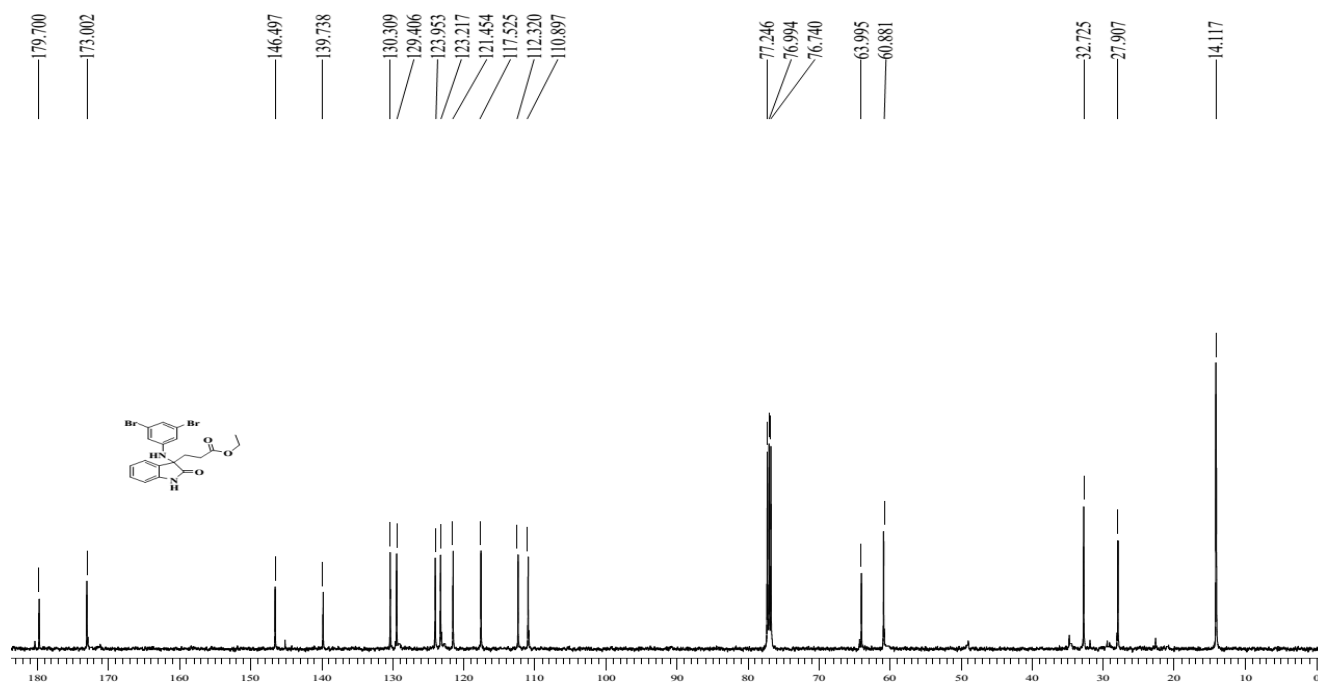


## Compound 5f

### $^1\text{H NMR}$



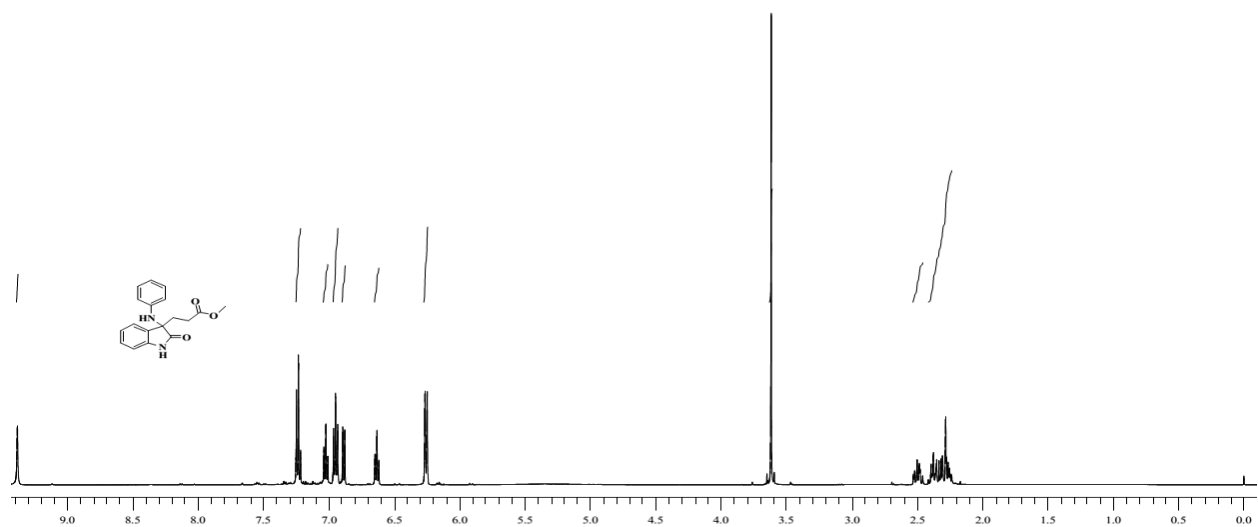
### $^{13}\text{C NMR}$



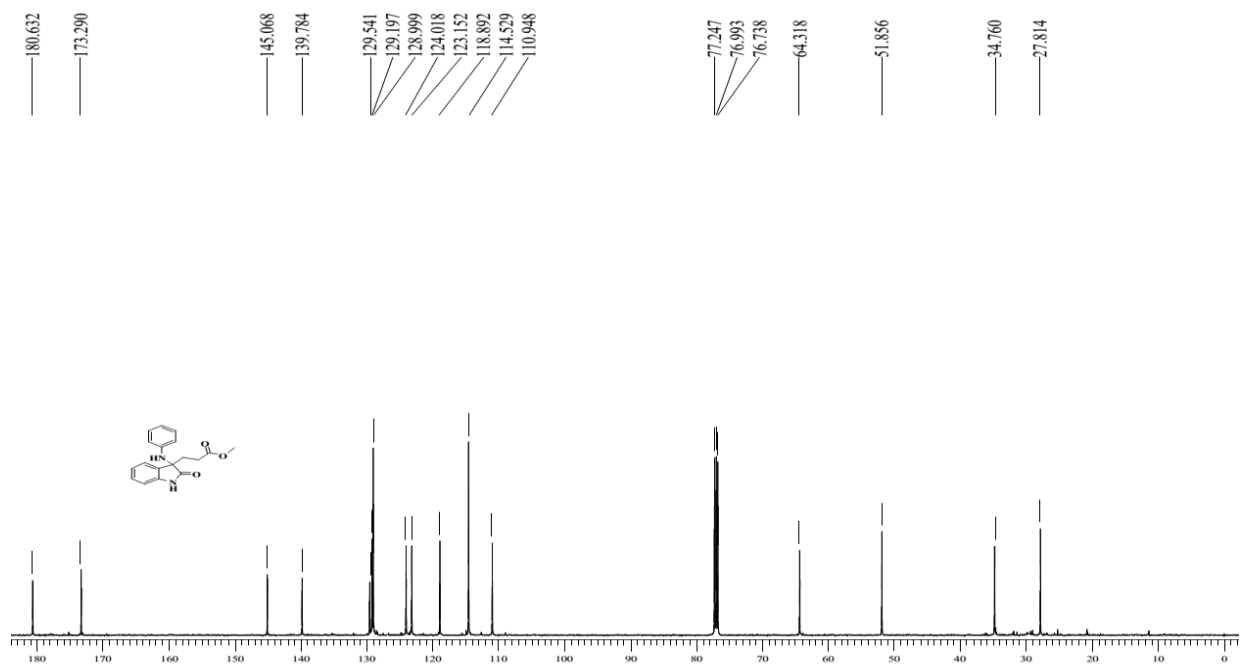


## Compound 5g

### $^1\text{H}$ NMR

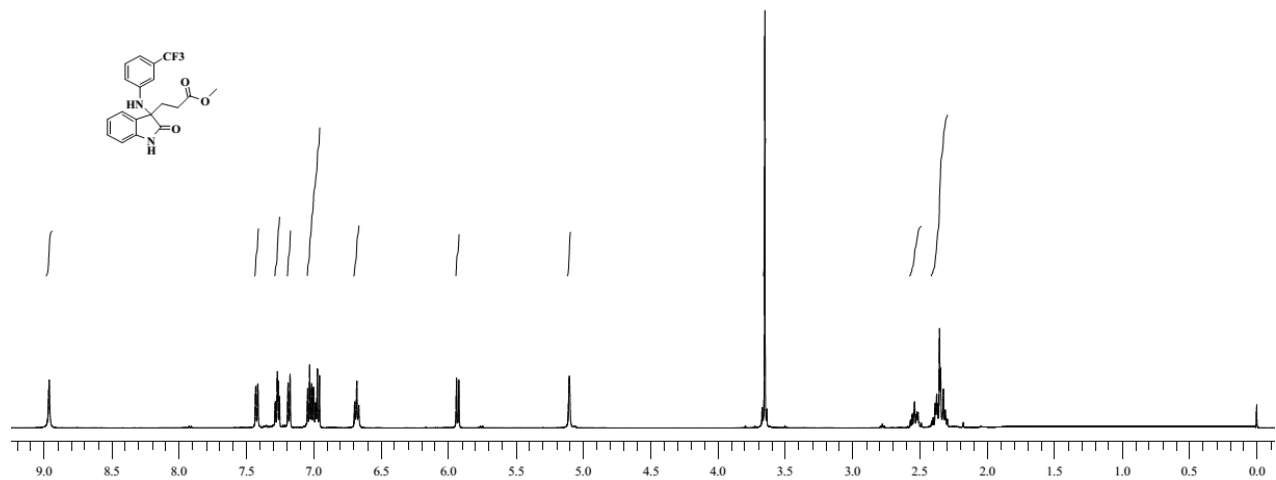


### $^{13}\text{C}$ NMR

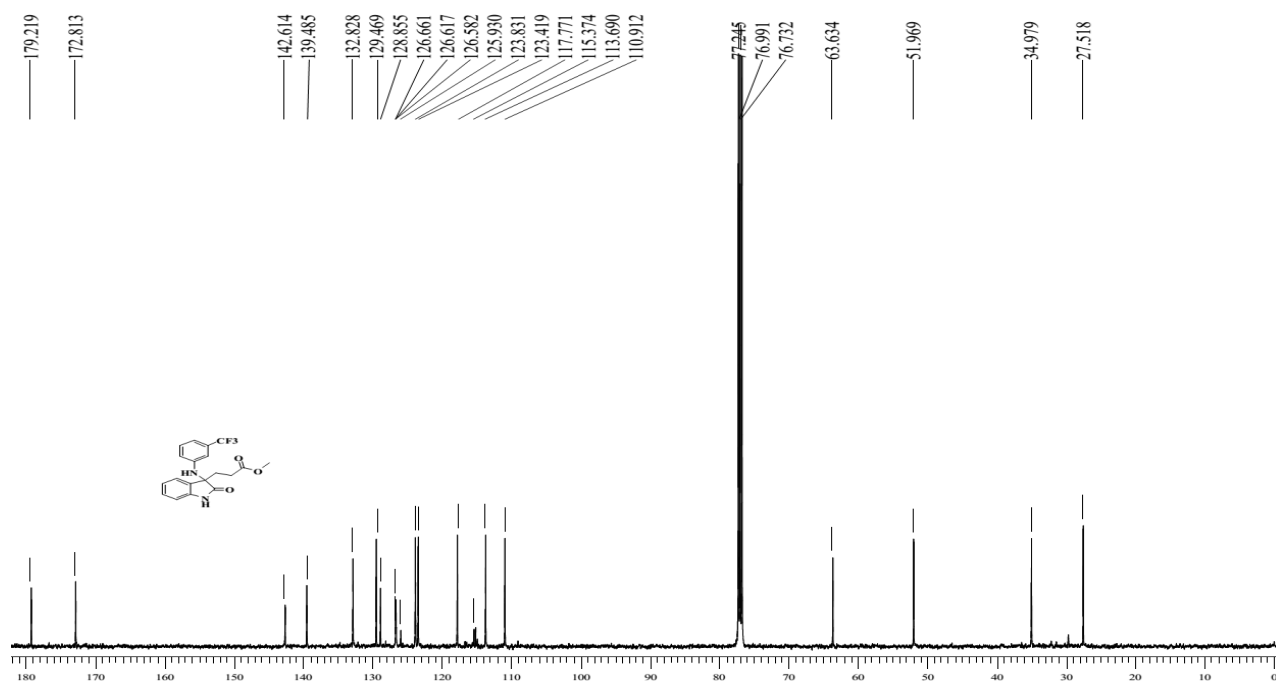


## Compound 5h

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

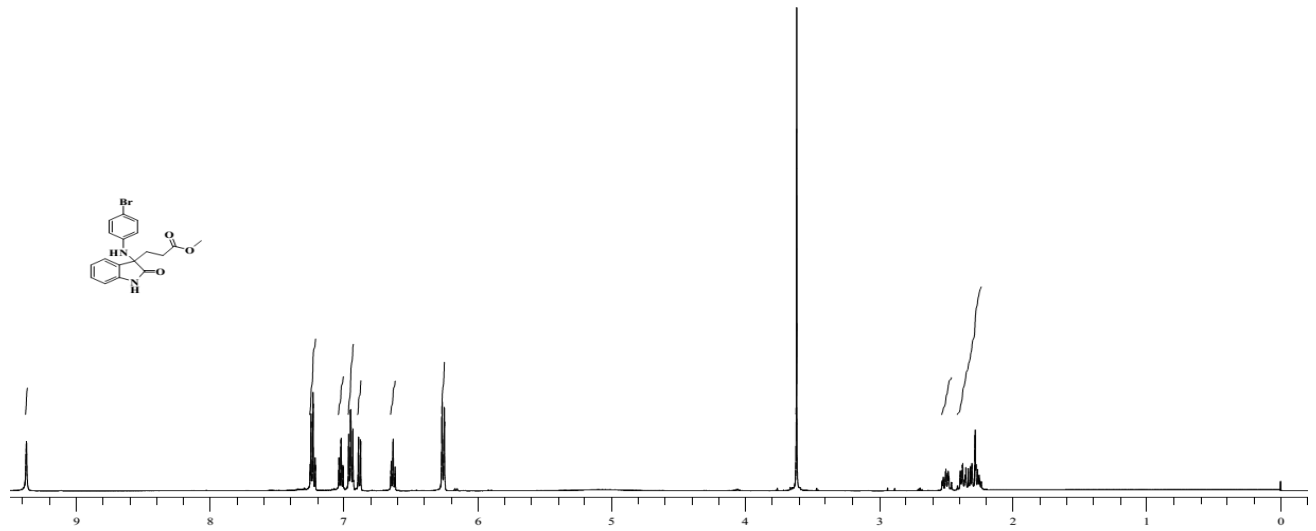


### <sup>13</sup>C NMR

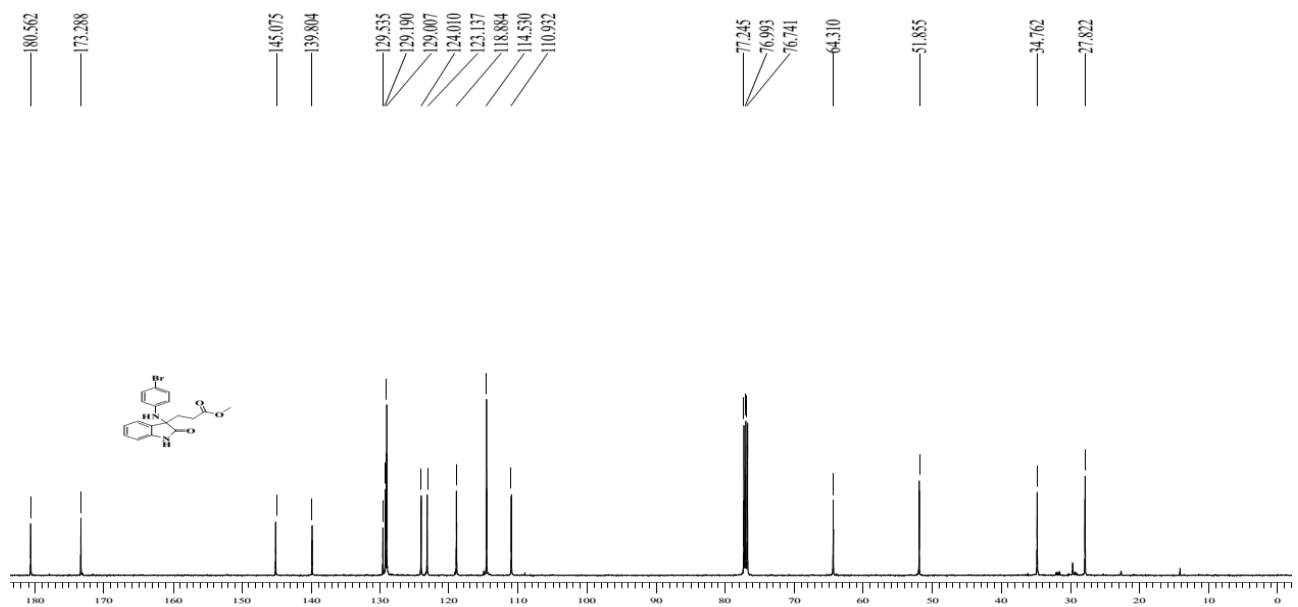


## Compound 5i

### $^1\text{H NMR}$

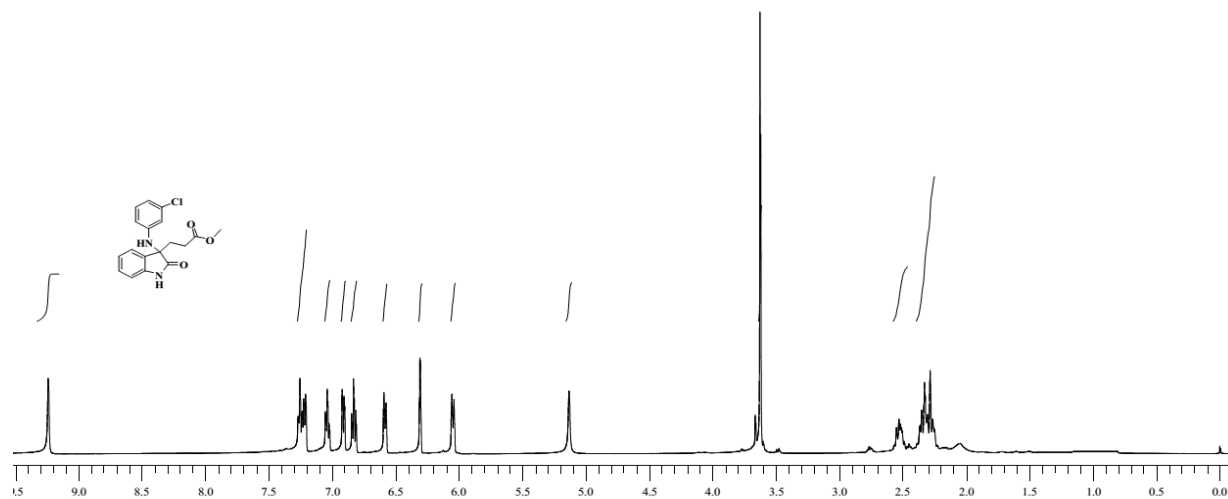


### $^{13}\text{C NMR}$

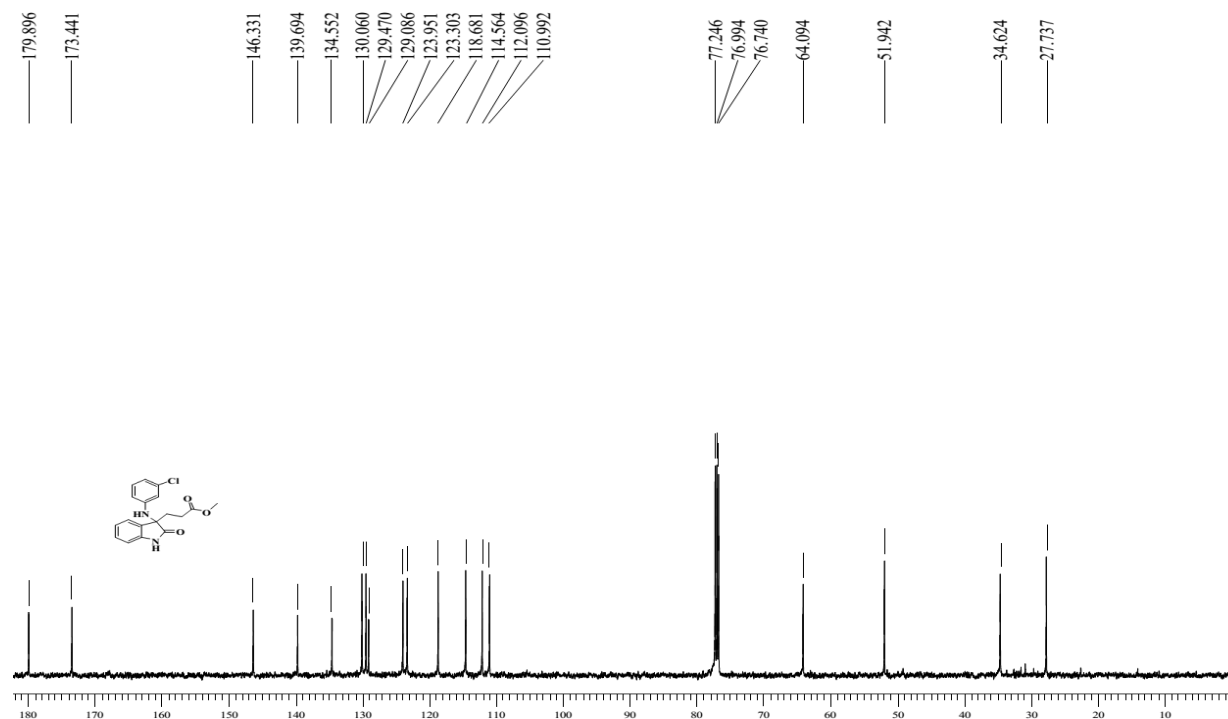


## Compound 5j

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

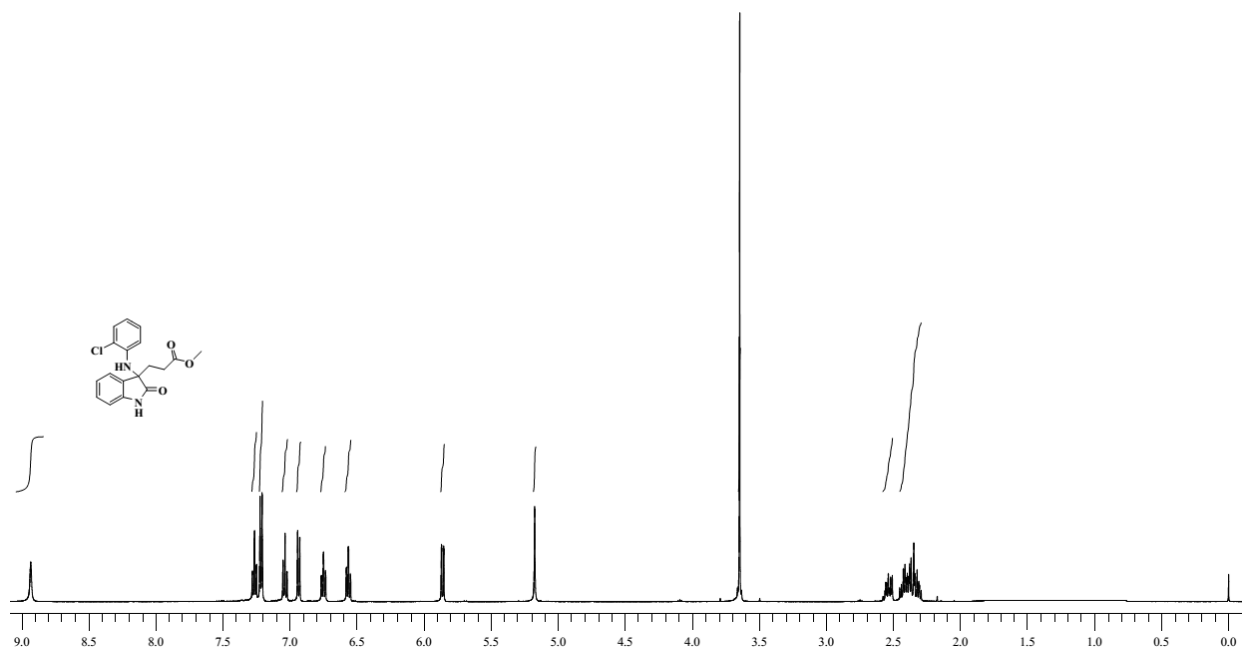


### <sup>13</sup>C NMR

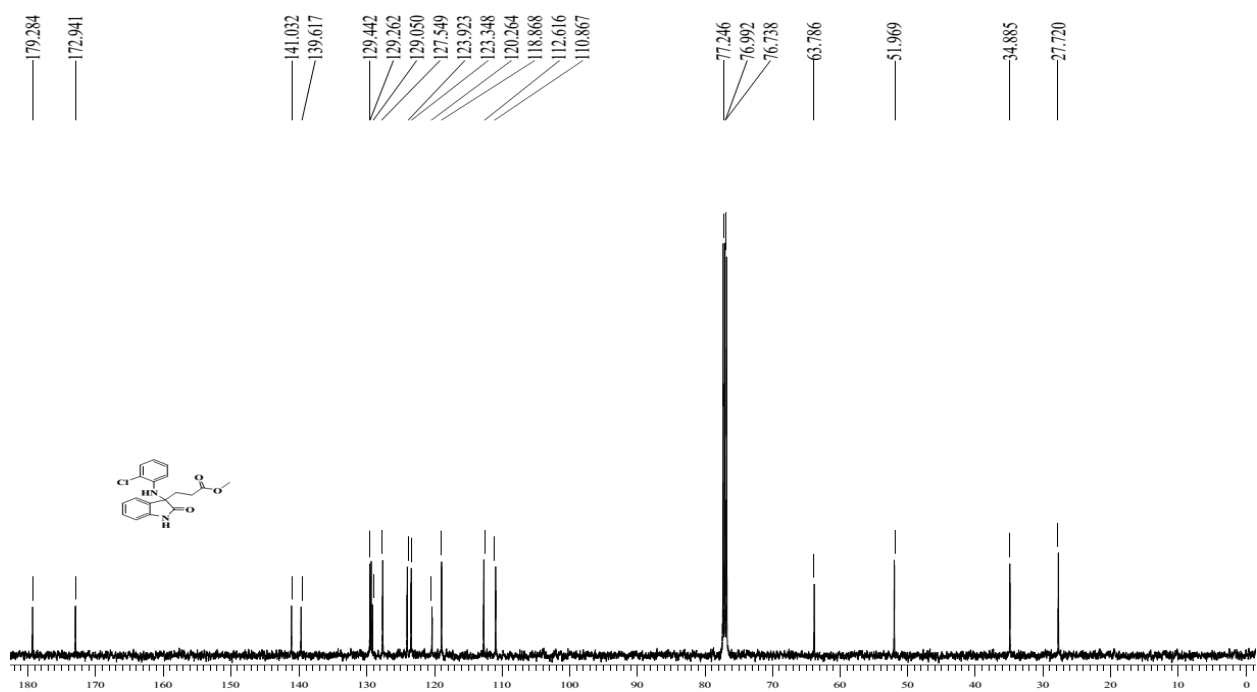


## Compound 5k

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

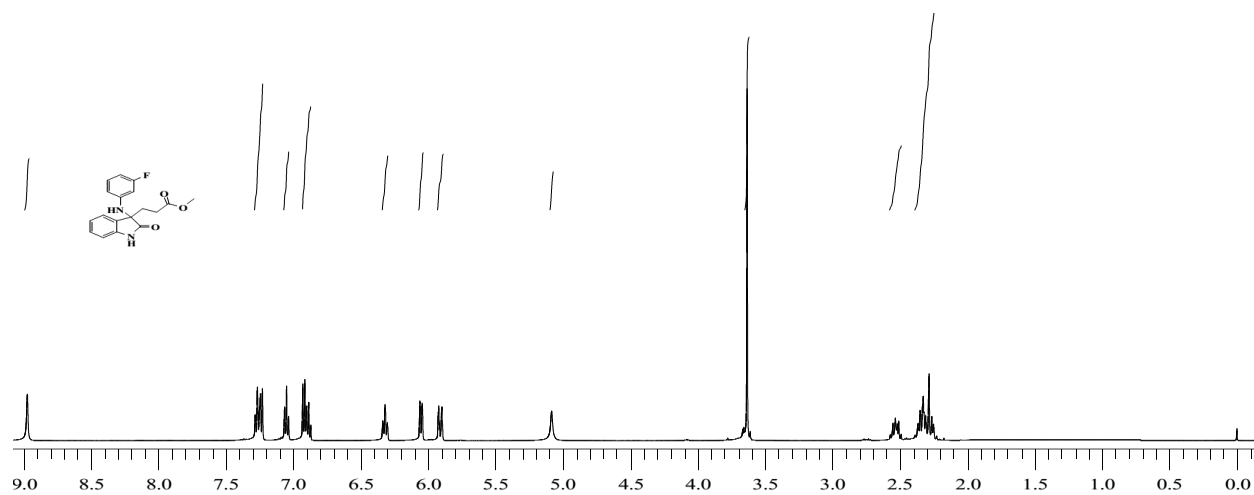


### <sup>13</sup>C NMR

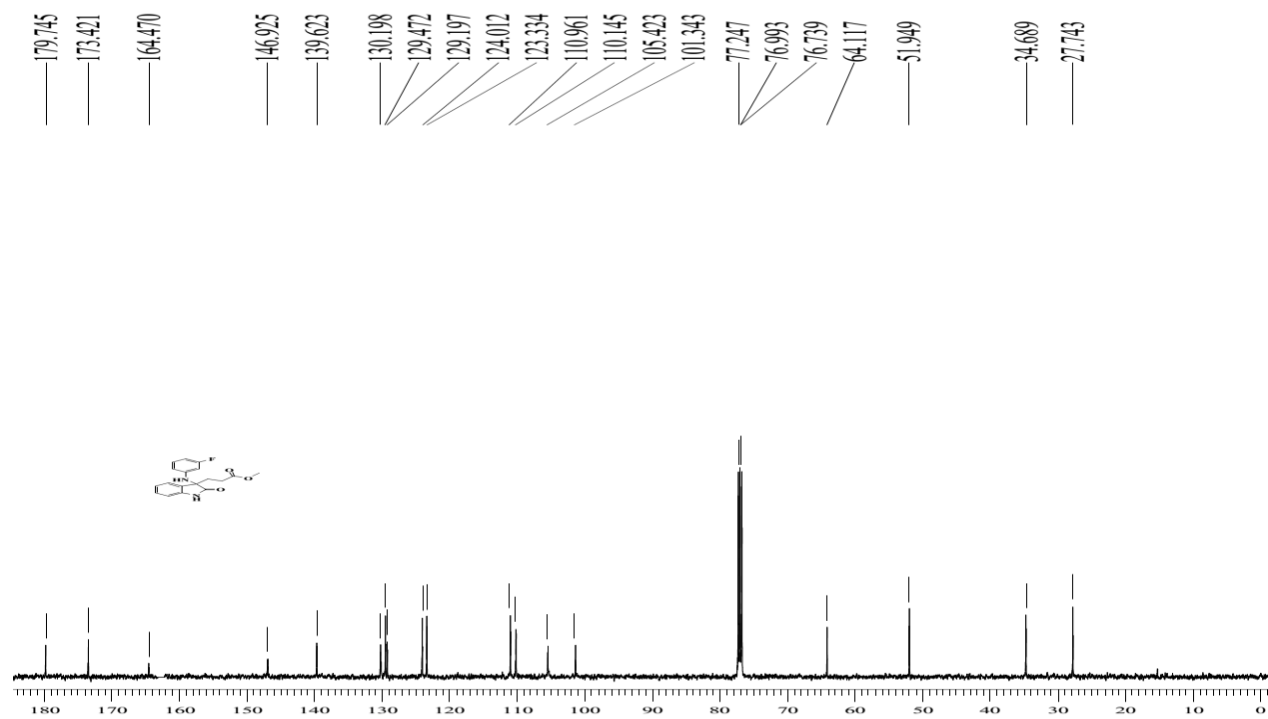


## Compound 5l

### $^1\text{H NMR}$

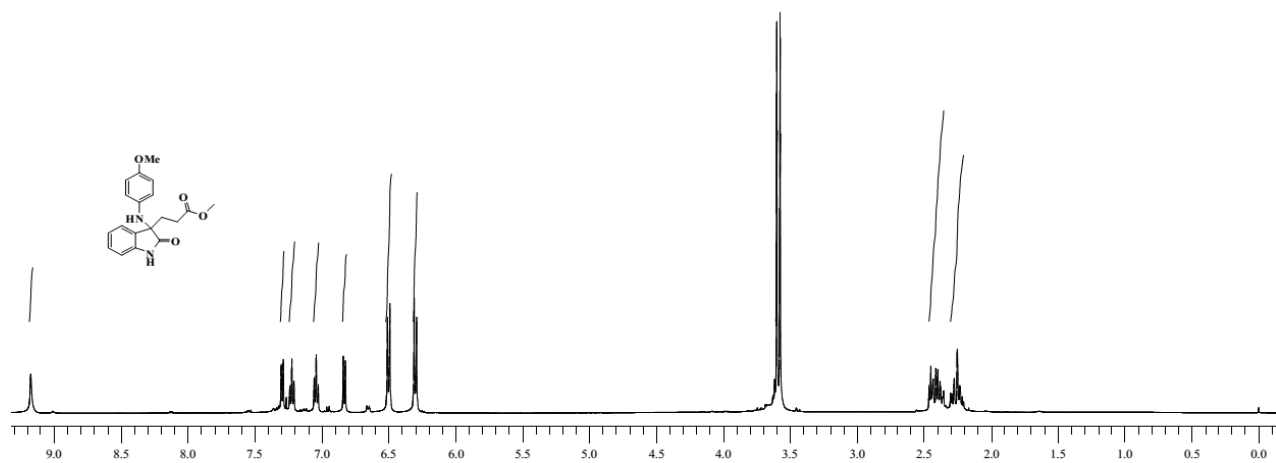


### $^{13}\text{C NMR}$

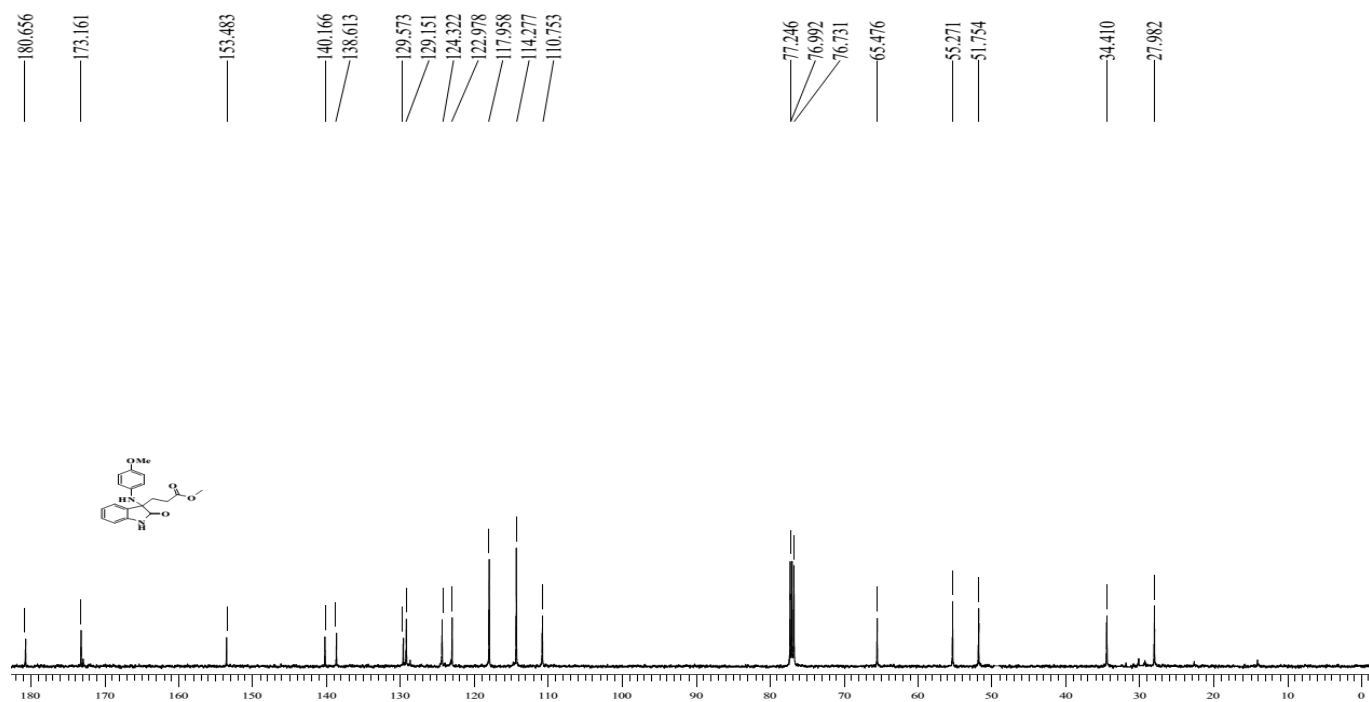


## Compound 5m

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

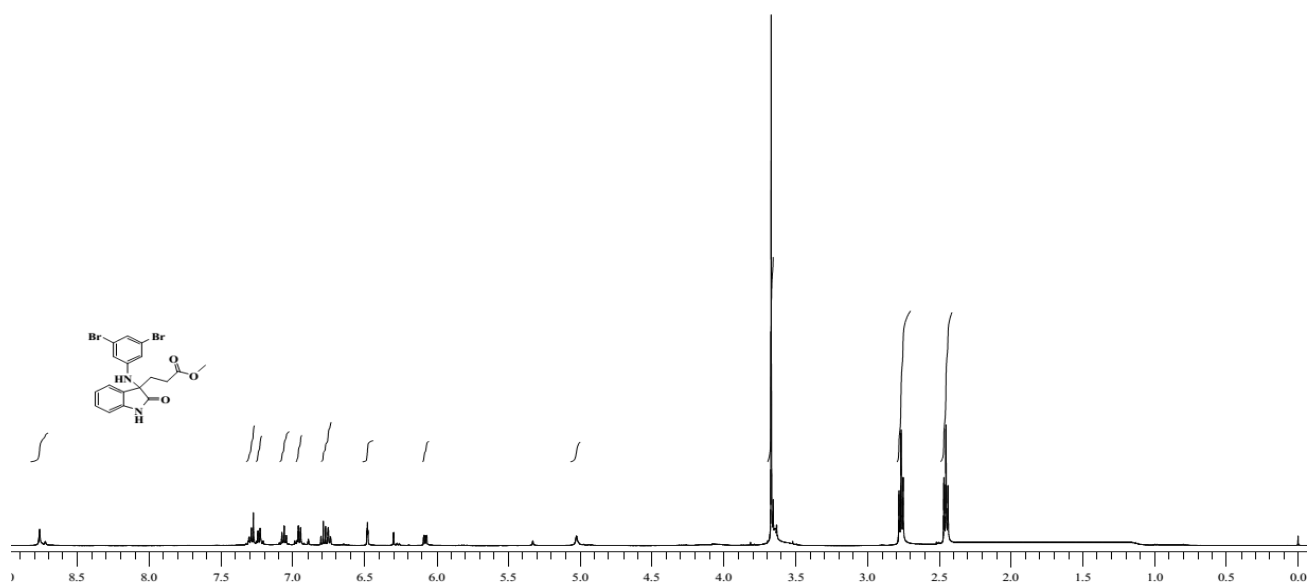


### <sup>13</sup>C NMR

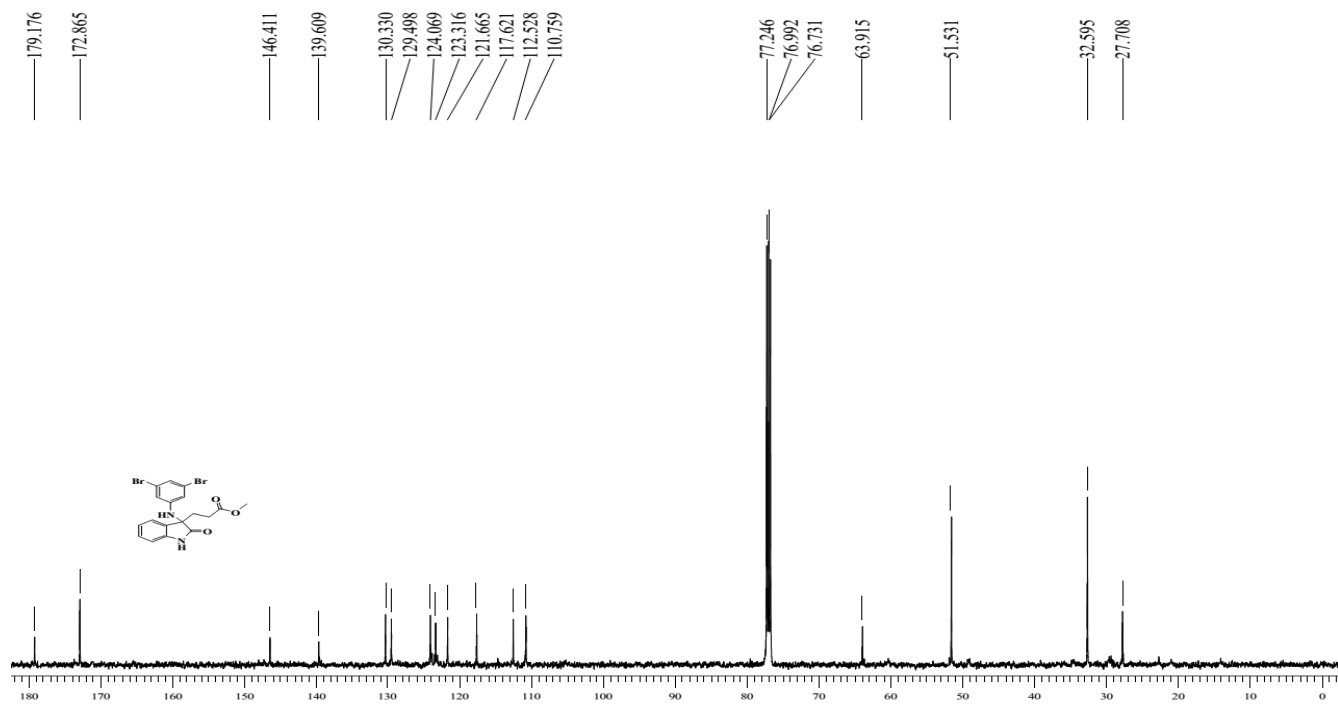


## Compound 5n

### $^1\text{H NMR}$



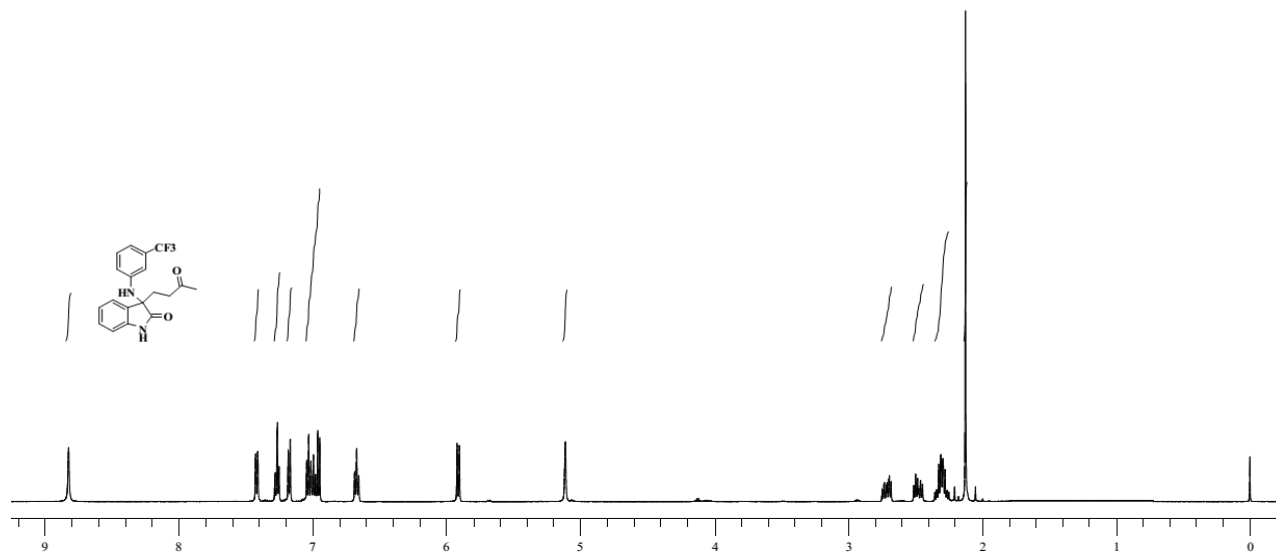
### $^{13}\text{C NMR}$



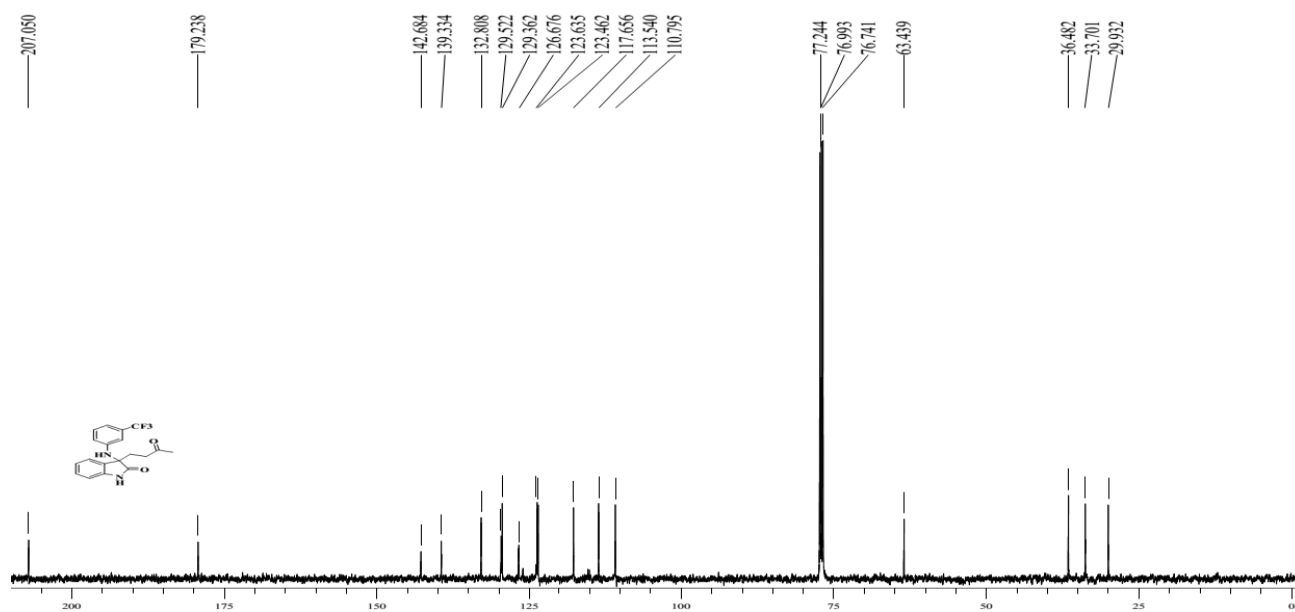


## Compound 5o

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

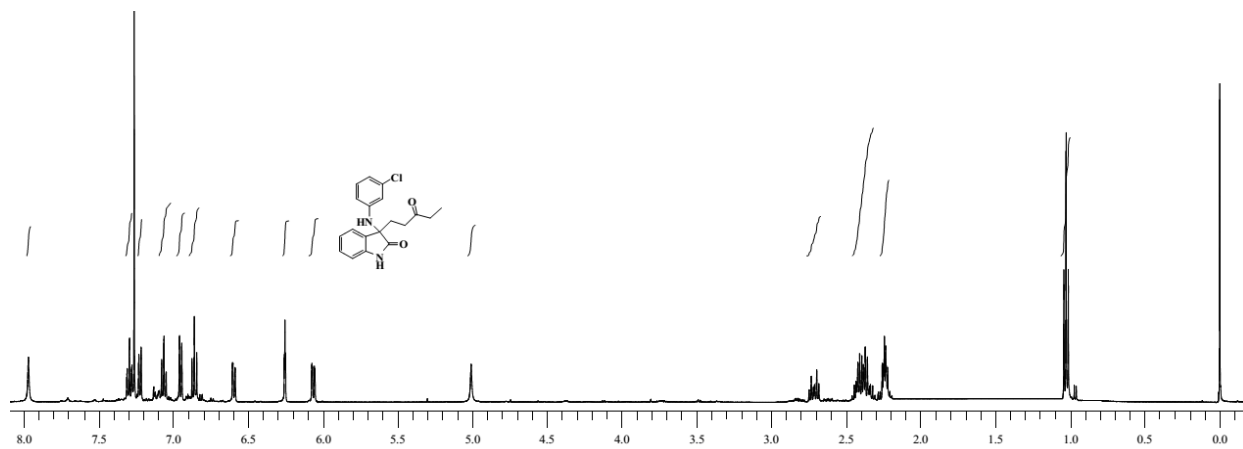


### <sup>13</sup>C NMR

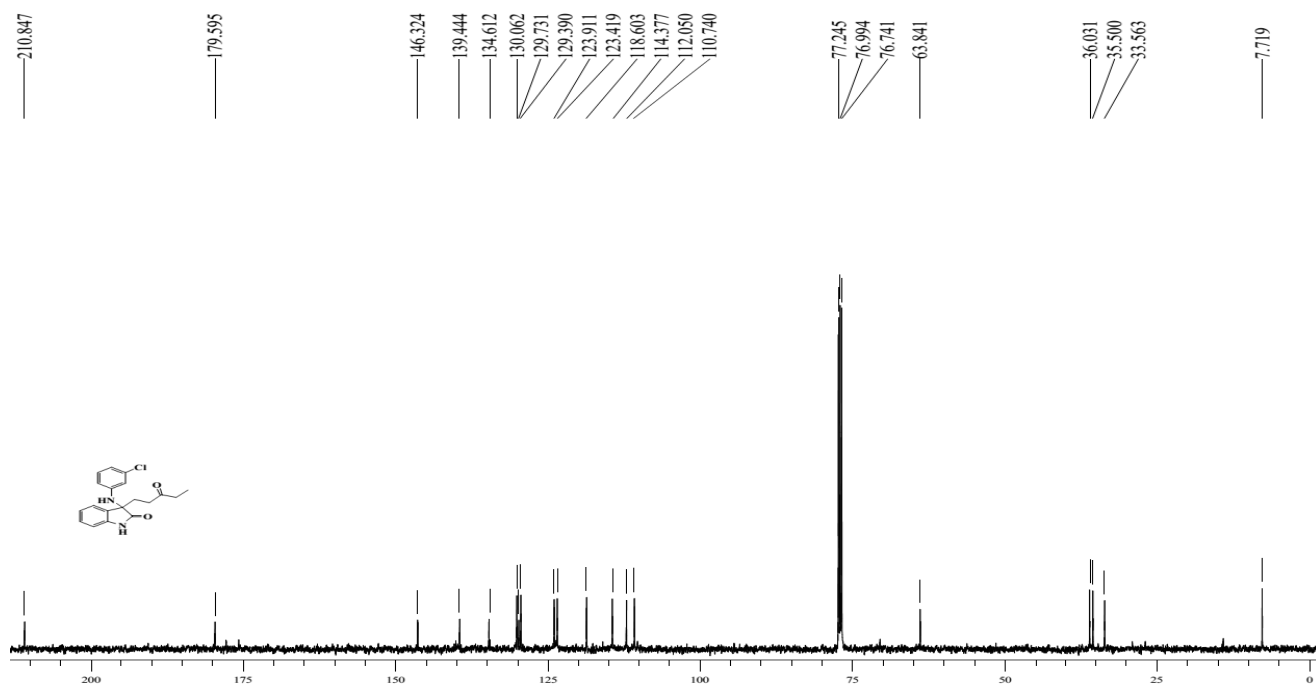


## Compound 5p

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



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

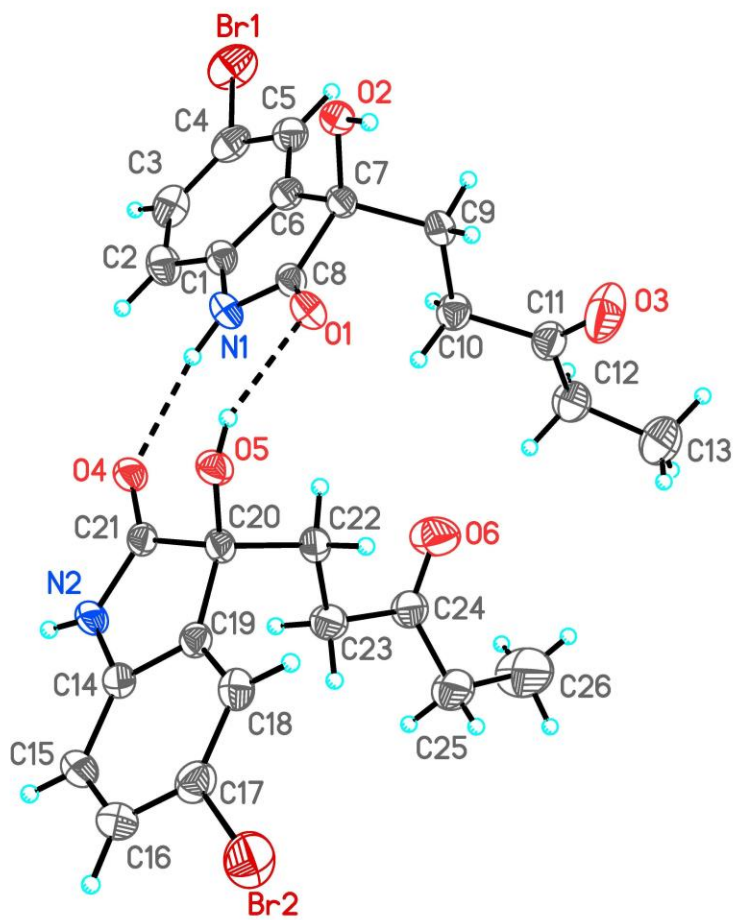


### Crystallographic data for 4I

X-ray data for the compound were collected at room temperature using a Bruker Smart Apex CCD diffractometer with graphite monochromated MoK $\alpha$  radiation ( $\lambda=0.71073\text{\AA}$ ) with  $\omega$ -scan method.<sup>1</sup> Preliminary lattice parameters and orientation matrices were obtained from four sets of frames. Unit cell dimensions were determined using 3385 reflections. Integration and scaling of intensity data were accomplished using SAINT program.<sup>1</sup> The structures were solved by Direct Methods using SHELXS97<sup>2</sup> and refinement was carried out by full-matrix least-squares technique using SHELXL97.<sup>2</sup> Anisotropic displacement parameters were included for all non-hydrogen atoms. All H atoms were positioned geometrically and treated as riding on their parent C atoms, with C-H distances of 0.93--0.97  $\text{\AA}$ , and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  or  $1.5U_{\text{eq}}$  for methyl atoms.

Crystal data for AO69 (**4I**, Table 3):  $\text{C}_{13}\text{H}_{14}\text{Br}_1\text{N}_1\text{O}_3$ ,  $M = 312.16$ , colourless plate,  $0.16 \times 0.10 \times 0.06 \text{ mm}^3$ , triclinic, space group  $P\bar{1}$  (No. 2),  $a = 7.5781(13)$ ,  $b = 13.148(2)$ ,  $c = 14.903(3) \text{\AA}$ ,  $\alpha = 71.939(3)$ ,  $\beta = 78.573(4)$ ,  $\gamma = 82.292(4)^\circ$ ,  $V = 1379.5(4) \text{\AA}^3$ ,  $Z = 4$ ,  $D_c = 1.503 \text{ g/cm}^3$ ,  $F_{000} = 632$ , CCD area detector, MoK $\alpha$  radiation,  $\lambda = 0.71073 \text{\AA}$ ,  $T = 293(2)\text{K}$ ,  $2\theta_{\text{max}} = 50.0^\circ$ , 13331 reflections collected, 4833 unique ( $R_{\text{int}} = 0.0295$ ), Final  $Goof = 1.023$ ,  $R1 = 0.0443$ ,  $wR2 = 0.1100$ ,  $R$  indices based on 3481 reflections with  $I > 2\sigma(I)$  (refinement on  $F^2$ ), 327 parameters,  $\mu = 2.979 \text{ mm}^{-1}$ . **CCDC 950572** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0) 1223 336 033; email: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)].

1. SMART & SAINT. Software Reference manuals. Versions 6.28a & 5.625, Bruker Analytical X-ray Systems Inc., Madison, Wisconsin, U.S.A., 2001.
2. Sheldrick, G. M. SHELXS97 and SHELXL97, Programs for crystal structure solution and refinement; University of Gottingen: Germany, 1997.



**Figure 1:** ORTEP diagram of the single crystal X-ray structure of the compound **4I** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius. There are two molecules in the asymmetric unit which are connected by N-H $\cdots$ O and O-H $\cdots$ O hydrogen bonds (shown as dotted lines).