

## Supporting Information

# Copper-Catalyzed C-H [3+2] Annulation of *N*-Substituted Anilines with $\alpha$ -Carbonyl Alkyl Bromides *via* C(sp<sup>3</sup>)-Br/C(sp<sup>2</sup>)-H Functionalization

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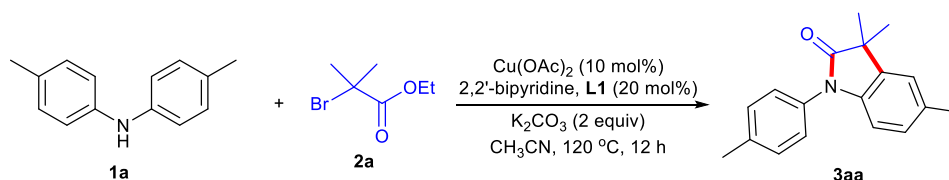
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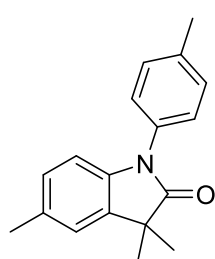
## (A) Typical experimental procedure

To a Schlenk tube were added substrates *N*-substituted anilines **1a** (0.3 mmol),  $\alpha$ -arbyl alkyl bromides **2a** (2 equiv), Cu(OAc)<sub>2</sub> (10 mol%), 2,2'-bipyridine (20 mol%), and CH<sub>3</sub>CN (2 mL), the tube was then charged with argon. The mixture was stirred at 120 °C until complete consumption of starting material as monitored by TLC and/or GC-MS analysis (about 12 h). After the reaction was finished, the reaction mixture was concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate) to afford the desired product **3aa**.



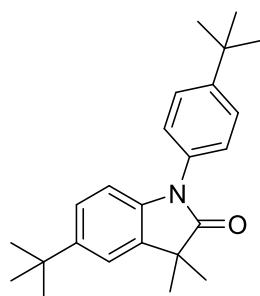
## (B) Analytical data

### 3,3,5-Trimethyl-1-(*p*-tolyl)indolin-2-one (**3aa**):



62.0 mg, 79%; White solid; 125.3-127.1 °C (uncorrected); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.31-7.27 (m, 4H), 7.08 (d,  $J$  = 2.0 Hz, 1H), 6.97 (dd,  $J$  = 8.0, 2.0 Hz, 1H), 6.71 (d,  $J$  = 8.0 Hz, 1H), 2.40 (s, 3H), 2.35 (s, 3H), 1.47 (s, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$ : 180.7, 140.3, 137.6, 135.7, 132.3, 132.1, 130.0, 127.7, 126.2, 123.3, 109.0, 44.3, 24.7, 21.2, 21.0; LRMS (EI, 70 eV)  $m/z$  (%): 265 (M<sup>+</sup>, 100), 250 (44), 222 (37); HRMS  $m/z$  (ESI) calcd for C<sub>18</sub>H<sub>20</sub>NO ([M+H]<sup>+</sup>) 266.1539, found: 266.1545.

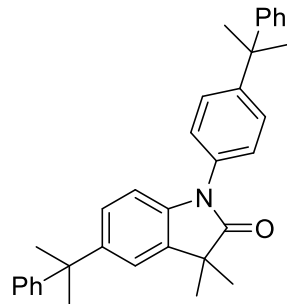
### 5-(*Tert*-butyl)-1-(4-(*tert*-butyl)phenyl)-3,3-dimethylindolin-2-one (**3ba**):



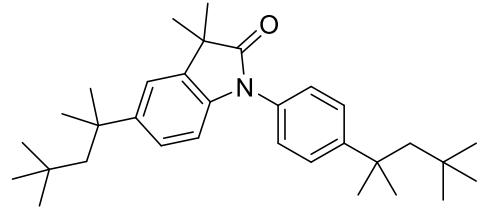
75.5 mg, 74%; White solid; mp 176.6-178.4 °C (uncorrected); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.51 (d,  $J$  = 8.5 Hz, 2H), 7.34 (d,  $J$  = 8.5 Hz, 2H), 7.29 (d,  $J$  = 2.0 Hz, 1H), 7.21 (dd,  $J$  = 8.5, 2.0 Hz, 1H), 6.81 (d,  $J$  = 8.0 Hz, 1H), 1.49 (s, 6H), 1.36 (s, 9H), 1.34 (s, 9H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$ : 180.9, 150.6,

146.1, 140.2, 135.3, 132.0, 126.4, 125.7, 124.1, 119.5, 108.9, 44.5, 34.7, 34.6, 31.6, 31.3, 24.8; LRMS (EI, 70 eV)  $m/z$  (%): 349 ( $M^+$ , 43), 334 (100); HRMS  $m/z$  (ESI) calcd for  $C_{24}H_{32}NO$  ( $[M+H]^+$ ) 350.2478, found: 350.2486.

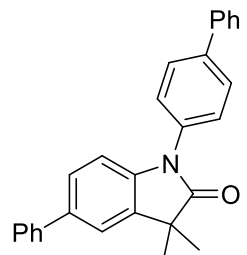
**3,3-Dimethyl-5-(2-phenylpropan-2-yl)-1-(4-(2-phenylpropan-2-yl)phenyl)indolin-2-one (3ca):**

 114.4 mg, 80%; White solid; mp 114.9-116.9 °C (uncorrected);  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$ : 7.35-7.23 (m, 12H), 7.19-7.15 (m, 2H), 7.13 (d,  $J = 1.5$  Hz, 1H), 7.02 (dd,  $J = 8.0, 2.0$  Hz, 1H), 6.77 (d,  $J = 8.5$  Hz, 1H), 1.71 (s, 6H), 1.69 (s, 6H), 1.43 (s, 6H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$ : 180.9, 150.5, 150.1 (2C), 145.7, 140.2, 135.2, 132.1, 128.0 (2C), 127.8, 126.8, 126.6, 125.9, 125.7, 125.6 (2C), 120.9, 108.8, 44.4, 42.9, 42.8, 31.0, 30.7, 24.7; HRMS  $m/z$  (ESI) calcd for  $C_{34}H_{36}NO$  ( $[M+H]^+$ ) 474.2791, found: 474.2803.

**3,3-Dimethyl-5-(2,4,4-trimethylpentan-2-yl)-1-(4-(2,4,4-trimethylpentan-2-yl)phenyl)indolin-2-one (3da):**

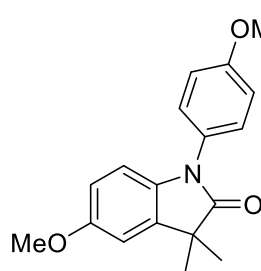
 71.3 mg, 59%; Colorless oil;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$ : 7.50 (d,  $J = 8.5$  Hz, 2H), 7.34 (d,  $J = 8.5$  Hz, 2H), 7.27 (d,  $J = 2.0$  Hz, 1H), 7.17 (dd,  $J = 8.5, 2.0$  Hz, 1H), 6.75 (d,  $J = 8.0$  Hz, 1H), 1.78 (s, 2H), 1.73 (s, 2H), 1.48 (s, 6H), 1.41 (s, 6H), 1.38 (s, 6H), 0.76 (s, 9H), 0.72 (s, 9H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$ : 180.8, 149.6, 144.7, 140.0, 135.1, 131.9, 127.1, 125.5, 124.8, 120.6, 108.5, 57.1, 57.0, 44.4, 38.6, 38.4, 32.4, 32.3, 31.8 (3C), 31.5, 24.8; LRMS (EI, 70 eV)  $m/z$  (%): 461 ( $M^+$ , 14), 390 (100); HRMS  $m/z$  (ESI) calcd for  $C_{32}H_{48}NO$  ( $[M+H]^+$ ) 462.3730, found: 462.3743.

**1-([1,1'-Biphenyl]-4-yl)-3,3-dimethyl-5-phenylindolin-2-one (3ea):**

 86.1 mg, 76%; White solid; mp 183.8-185.3 °C (uncorrected),  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$ : 7.75 (d,  $J = 8.5$  Hz, 2H), 7.64 (d,  $J = 7.0$  Hz, 2H), 7.59 (d,  $J = 7.0$  Hz, 2H), 7.54 (d,  $J = 8.5$  Hz, 2H), 7.52 (d,  $J = 1.5$  Hz, 1H), 7.50-7.44 (m, 5H), 7.41-7.34 (m, 2H),

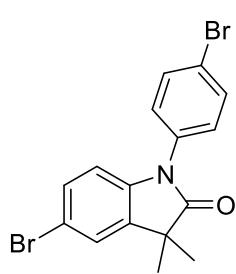
7.02 (d,  $J = 8.5$  Hz, 1H), 1.56 (s, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 180.8, 141.7, 140.9, 140.8, 140.3, 136.5, 136.2, 133.7, 128.9, 128.8, 128.3, 127.6, 127.2, 127.0, 126.9, 126.6, 126.5, 121.6, 109.7, 44.5, 24.8; HRMS  $m/z$  (ESI) calcd for  $\text{C}_{28}\text{H}_{24}\text{NO}$  ( $[\text{M}+\text{H}]^+$ ) 390.1852, found: 390.1856.

**5-Methoxy-1-(4-methoxyphenyl)-3,3-dimethylindolin-2-one (3fa):**



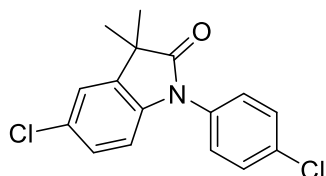
60.5 mg, 66%; Purple solid; mp 144.6-146.7 °C (uncorrected);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.32 (d,  $J = 8.5$  Hz, 2H), 7.02 (d,  $J = 8.0$  Hz, 2H), 6.87 (t,  $J = 1.5$  Hz, 1H), 6.71-6.70 (m, 2H), 3.85 (s, 3H), 3.80 (s, 3H), 1.47 (s, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 180.5, 158.8, 156.2, 136.9, 136.4, 127.7, 127.5, 114.7, 111.7, 109.8, 109.6, 55.8, 55.5, 44.6, 24.7; LRMS (EI, 70 eV)  $m/z$  (%): 297 ( $\text{M}^+$ , 100), 282 (41), 254 (32); HRMS  $m/z$  (ESI) calcd for  $\text{C}_{18}\text{H}_{20}\text{NO}_3$  ( $[\text{M}+\text{H}]^+$ ) 298.1438, found: 298.1455.

**5-Bromo-1-(4-bromophenyl)-3,3-dimethylindolin-2-one (3ga):**



78.3 mg, 66%; White solid; mp 102.5-103.9 °C (uncorrected);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.64 (d,  $J = 9.0$  Hz, 2H), 7.38 (d,  $J = 2.0$  Hz, 1H), 7.32 (dd,  $J = 8.5, 2.0$  Hz, 1H), 7.29 (d,  $J = 9.0$  Hz, 2H), 6.72 (d,  $J = 8.5$  Hz, 1H), 1.47 (s, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 179.8, 140.9, 137.6, 133.2, 132.8, 130.5, 127.9, 126.1, 121.6, 115.9, 110.7, 44.5, 24.6; LRMS (EI, 70 eV)  $m/z$  (%): 397 ( $\text{M}^++4$ , 50), 395 ( $\text{M}^++2$ , 100), 393 ( $\text{M}^+$ , 53), 334 (44), 131 (29); HRMS  $m/z$  (ESI) calcd for  $\text{C}_{16}\text{H}_{14}^{79}\text{Br}_2\text{NO}$  ( $[\text{M}+\text{H}]^+$ ) 393.9437, found: 393.9446.

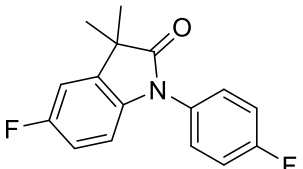
**5-Chloro-1-(4-chlorophenyl)-3,3-dimethylindolin-2-one (3ha):**



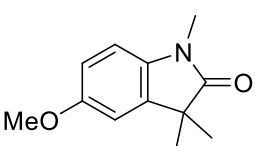
61.8 mg, 67%; White solid; mp 115.2-116.4 °C (uncorrected);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.49 (d,  $J = 9.0$  Hz, 2H), 7.35 (d,  $J = 8.5$  Hz, 2H), 7.25 (d,  $J = 2.5$  Hz, 1H), 7.17 (dd,  $J = 8.5, 2.0$  Hz, 1H), 6.76 (d,  $J = 8.5$  Hz, 1H), 1.48 (s, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 180.0, 140.5, 137.1, 133.6, 132.7, 129.8, 128.5, 127.6 (2C), 123.3, 110.2, 44.5, 24.6; LRMS (EI, 70 eV)  $m/z$  (%): 307 ( $\text{M}^++2$ , 68), 305 ( $\text{M}^+$ , 100),

291 (24), 227 (26); HRMS  $m/z$  (ESI) calcd for  $C_{16}H_{14}^{35}Cl_2NO$  ( $[M+H]^+$ ) 306.0447, found: 306.0449.

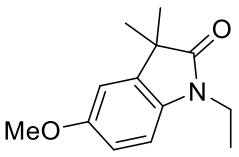
**5-Fluoro-1-(4-fluorophenyl)-3,3-dimethylindolin-2-one (3ia):**

 44.7 mg, 53%; Yellow solid; mp 117.2-118.3 °C (uncorrected);  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$ : 7.40-7.37 (m, 2H), 7.23-7.19 (m, 2H), 7.02-7.00 (m, 1H), 6.91-6.87 (m, 1H), 6.74-6.71 (m, 1H), 1.48 (s, 6H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$ : 180.4, 161.8 (d,  $J = 246.3$  Hz), 159.6 (d,  $J = 240.0$  Hz), 138.2 (d,  $J = 1.9$  Hz), 137.2 (d,  $J = 7.8$  Hz), 130.4 (d,  $J = 3.3$  Hz), 128.3 (d,  $J = 8.5$  Hz), 116.6 (d,  $J = 22.6$  Hz), 113.8 (d,  $J = 23.4$  Hz), 110.7 (d,  $J = 24.3$  Hz), 109.7 (d,  $J = 8.1$  Hz), 44.7 (d,  $J = 1.9$  Hz), 24.6;  $^{19}F$  NMR (471 MHz,  $CDCl_3$ )  $\delta$ : -112.96, -119.93; LRMS (EI, 70 eV)  $m/z$  (%): 273 ( $M^+$ , 100), 258 (33), 230 (52), 150 (27); HRMS  $m/z$  (ESI) calcd for  $C_{16}H_{14}F_2NO$  ( $[M+H]^+$ ) 274.1038, found: 274.1025.

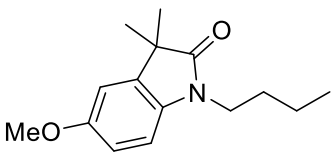
**5-Methoxy-1,3,3-trimethylindolin-2-one (3ka):**

 40.9 mg, 73%; Pale yellow oil;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$ : 6.83 (d,  $J = 2.0$  Hz, 1H), 6.78 (dd,  $J = 8.5, 2.5$  Hz, 1H), 6.74 (d,  $J = 8.5$  Hz, 1H), 3.81 (s, 3H), 3.19 (s, 3H), 1.36 (s, 6H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$ : 181.0, 156.0, 137.2, 136.2, 111.5, 110.1, 108.2, 55.8, 44.6, 26.3, 24.4; LRMS (EI, 70 eV)  $m/z$  (%): 205 ( $M^+$ , 86), 190 (100), 162 (38); HRMS  $m/z$  (ESI) calcd for  $C_{12}H_{16}NO_2$  ( $[M+H]^+$ ) 206.1176, found: 206.1183.

**1-Ethyl-5-methoxy-3,3-dimethylindolin-2-one (3la):**

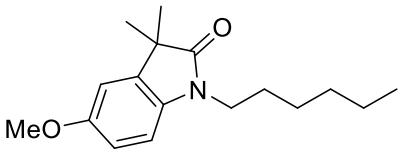
 35.1 mg, 53%; yellow oil;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$ : 6.84-6.83 (m, 1H), 6.77-6.76 (m, 2H), 3.81 (s, 3H), 3.76-3.72 (m, 2H), 1.35 (s, 6H), 1.25 (t,  $J = 7.5$  Hz, 3H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$ : 180.5, 155.8, 137.5, 135.1, 111.5, 110.2, 108.4, 55.8, 44.5, 34.6, 24.4, 12.7; LRMS (EI, 70 eV)  $m/z$  (%): 219 ( $M^+$ , 91), 204 (100), 176 (46); HRMS  $m/z$  (ESI) calcd for  $C_{13}H_{18}NO_2$  ( $[M+H]^+$ ) 220.1332, found: 220.1341.

**1-Butyl-5-methoxy-3,3-dimethylindolin-2-one (3ma):**

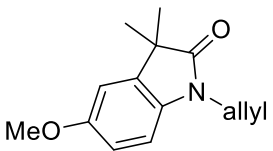
 56.5 mg, 70%; Pale yellow oil;  $^1H$  NMR (500 MHz,

CDCl<sub>3</sub>)  $\delta$ : 6.83-6.82 (m, 1H), 6.77-6.76 (m, 2H), 3.80 (s, 3H), 3.70-3.67 (m, 2H), 1.68-1.62 (m, 2H), 1.49-1.34 (m, 8H), 0.95 (t,  $J = 7.5$  Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$ : 180.9, 155.8, 137.4, 135.5, 111.5, 110.1, 108.5, 55.8, 44.4, 39.6, 29.4, 24.5, 20.0, 13.7; LRMS (EI, 70 eV)  $m/z$  (%): 247 (M<sup>+</sup>, 100), 204 (79), 176 (80); HRMS  $m/z$  (ESI) calcd for C<sub>15</sub>H<sub>22</sub>NO<sub>2</sub> ([M+H]<sup>+</sup>) 248.1645, found: 248.1650.

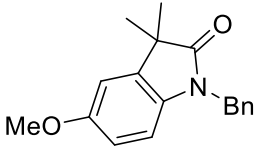
**1-Hexyl-5-methoxy-3,3-dimethylindolin-2-one (3na):**

 45.2 mg, 51%; Pale yellow oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ : 6.83-6.82 (m, 1H), 6.77-6.76 (m, 2H), 3.81 (s, 3H), 3.69-3.66 (m, 2H), 1.68-1.63 (m, 2H), 1.68-1.36 (s, 6H), 1.32-1.28 (m, 6H), 0.87 (t,  $J = 7.0$  Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$ : 180.8, 155.7, 137.4, 135.4, 111.4, 110.0, 108.5, 55.8, 44.4, 39.8, 31.4, 27.3, 26.4, 24.4, 22.5, 14.0; LRMS (EI, 70 eV)  $m/z$  (%): 275 (M<sup>+</sup>, 100), 204 (74), 176 (71); HRMS  $m/z$  (ESI) calcd for C<sub>17</sub>H<sub>26</sub>NO<sub>2</sub> ([M+H]<sup>+</sup>) 276.1958, found: 276.1960.

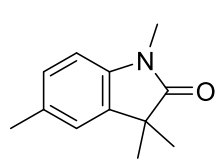
**1-Allyl-5-methoxy-3,3-dimethylindolin-2-one (3oa):**

 38.2 mg, 53%; Pale yellow oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ : 6.84-6.83 (m, 1H), 6.75-6.74 (m, 2H), 5.87-5.79 (m, 1H), 5.21-5.16 (m, 2H), 4.33-4.31 (m, 2H), 3.80 (s, 3H), 1.38 (s, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$ : 180.7, 156.0, 137.2, 135.2, 131.7, 117.1, 111.6, 110.0, 109.2, 55.8, 44.5, 42.2, 24.5; LRMS (EI, 70 eV)  $m/z$  (%): 231 (M<sup>+</sup>, 100), 216 (66); HRMS  $m/z$  (ESI) calcd for C<sub>14</sub>H<sub>18</sub>NO<sub>2</sub> ([M+H]<sup>+</sup>) 232.1332, found: 232.1339.

**1-Benzyl-5-methoxy-3,3-dimethylindolin-2-one (3pa):**

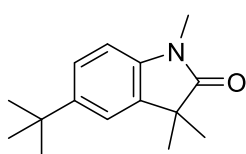
 51.1 mg, 62%; Pale yellow oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.32-7.28 (m, 2H), 7.26-7.22 (m, 3H), 6.83 (d,  $J = 2.5$  Hz, 1H), 6.65 (dd,  $J = 8.5, 2.5$  Hz, 1H), 6.60 (d,  $J = 8.5$  Hz, 1H), 4.90 (s, 2H), 3.75 (s, 3H), 1.43 (s, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$ : 181.1, 156.0, 137.2, 136.1, 135.0, 128.7, 127.4, 127.1, 111.5, 110.0, 109.3, 55.7, 44.6, 43.5, 24.5; LRMS (EI, 70 eV)  $m/z$  (%): 281 (M<sup>+</sup>, 71), 266 (20), 91 (100); HRMS  $m/z$  (ESI) calcd for C<sub>18</sub>H<sub>20</sub>NO<sub>2</sub> ([M+H]<sup>+</sup>) 282.1489, found: 282.1503.

### 1,3,3,5-Tetramethylindolin-2-one (3qa):



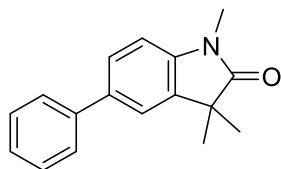
26.1 mg, 50%; Pale yellow oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.07-7.05 (m, 1H), 7.02 (d,  $J = 2.0$  Hz, 1H), 6.73 (d,  $J = 8.0$  Hz, 1H), 3.20 (s, 3H), 2.35 (s, 3H), 1.36 (s, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 181.3, 140.3, 135.9, 132.0, 127.8, 123.1, 107.7, 44.2, 26.2, 24.4, 21.1; LRMS (EI, 70 eV)  $m/z$  (%): 189 ( $\text{M}^+$ , 67), 174 (100), 146 (23); HRMS  $m/z$  (ESI) calcd for  $\text{C}_{12}\text{H}_{16}\text{NO}$  ( $[\text{M}+\text{H}]^+$ ) 190.1226, found: 190.1232.

### 5-(*Tert*-butyl)-1,3,3-trimethylindolin-2-one (3ra):



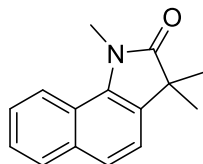
37.6 mg, 48%; Pale yellow oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.29 (dd,  $J = 8.0, 2.0$  Hz, 1H), 7.24 (d,  $J = 2.0$  Hz, 1H), 6.78 (d,  $J = 8.0$  Hz, 1H), 3.21 (s, 3H), 1.38 (s, 6H), 1.33 (s, 9H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 181.5, 145.7, 140.2, 135.5, 124.2, 119.3, 107.3, 44.4, 34.6, 31.6, 26.2, 24.4; LRMS (EI, 70 eV)  $m/z$  (%): 231 ( $\text{M}^+$ , 24), 219 (88), 216 (84), 204 (100), 176 (48); HRMS  $m/z$  (ESI) calcd for  $\text{C}_{15}\text{H}_{22}\text{NO}$  ( $[\text{M}+\text{H}]^+$ ) 232.1696, found: 232.1711.

### 1,3,3-Trimethyl-5-phenylindolin-2-one (3sa):



33.5 mg, 45%; Pale yellow oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.58-7.56 (m, 2H), 7.49 (dd,  $J = 8.0, 2.0$  Hz, 1H), 7.45-7.42 (m, 3H), 7.33 (t,  $J = 7.0$  Hz, 1H), 6.91 (d,  $J = 8.0$  Hz, 1H), 3.25 (s, 3H), 1.42 (s, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 181.4, 142.0, 141.1, 136.4, 136.0, 128.8, 126.9, 126.8, 126.5, 121.2, 108.2, 44.3, 26.3, 24.4; LRMS (EI, 70 eV)  $m/z$  (%): 251 ( $\text{M}^+$ , 100), 208 (14), 193 (18); HRMS  $m/z$  (ESI) calcd for  $\text{C}_{17}\text{H}_{18}\text{NO}$  ( $[\text{M}+\text{H}]^+$ ) 252.1383, found: 252.1386.

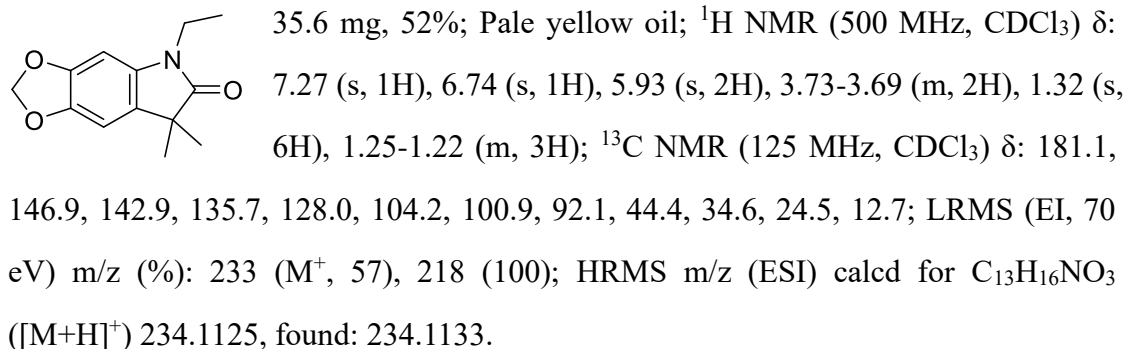
### 1,3,3-Trimethyl-1,3-dihydro-2H-benzo[*g*]indol-2-one (3ta):



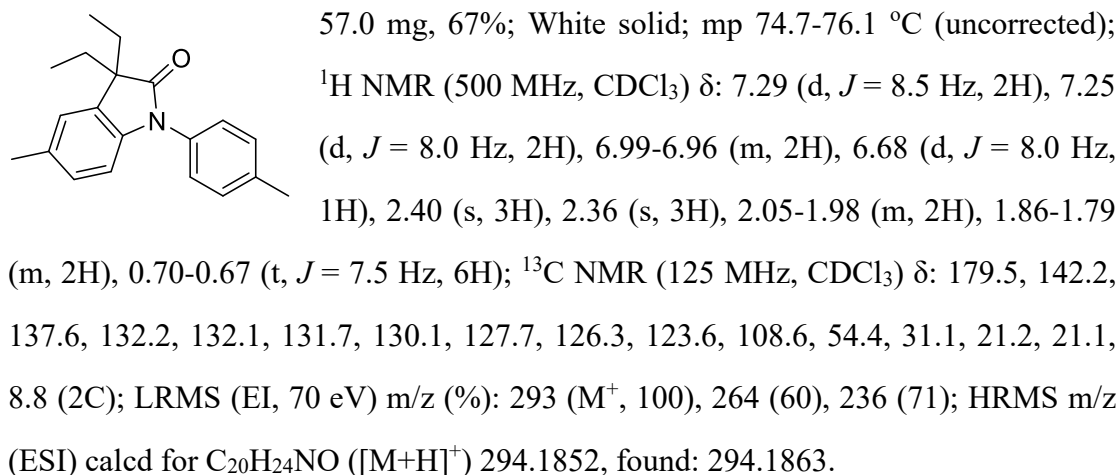
31.5 mg, 44%; Pale yellow oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.44 (d,  $J = 8.5$  Hz, 1H), 7.87-7.86 (m, 1H), 7.60 (d,  $J = 8.0$  Hz, 1H), 7.49-7.42 (m, 2H), 7.37 (d,  $J = 8.0$  Hz, 1H), 3.83 (s, 3H), 1.43 (s, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 182.9, 137.2, 134.3, 131.6, 129.4, 125.7, 125.2, 123.1, 121.5, 121.2, 120.0, 44.0, 30.6, 24.4; LRMS (EI, 70 eV)  $m/z$  (%): 225 ( $\text{M}^+$ , 58), 210 (100); HRMS  $m/z$  (ESI) calcd for  $\text{C}_{15}\text{H}_{16}\text{NO}$  ( $[\text{M}+\text{H}]^+$ ) 226.1226, found:

226.1236.

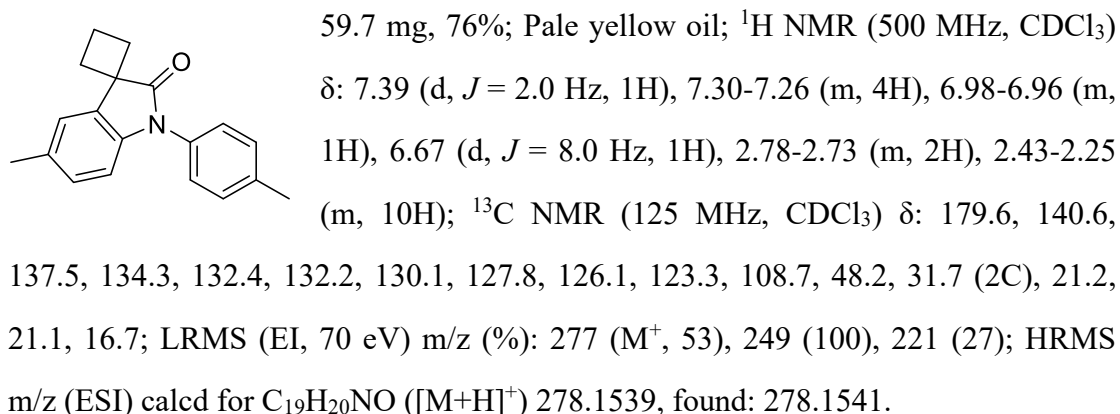
**5-Ethyl-7,7-dimethyl-5,7-dihydro-6H-[1,3]dioxolo[4,5-f]indol-6-one (3ua):**



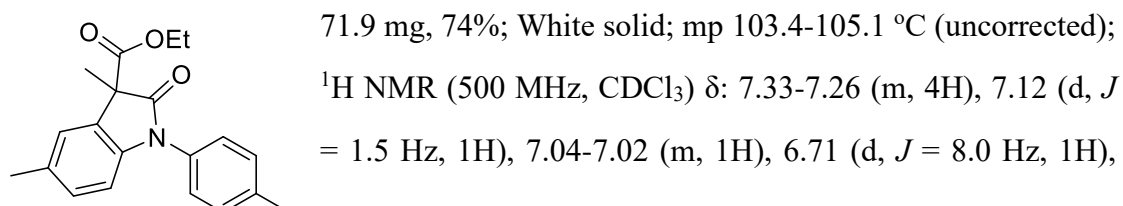
**3,3-Diethyl-5-methyl-1-(p-tolyl)indolin-2-one (3ab):**



**5'-Methyl-1'-(p-tolyl)spiro[cyclobutane-1,3'-indolin]-2'-one (3ac):**



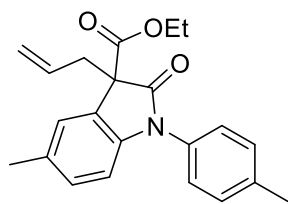
**Ethyl 3,5-dimethyl-2-oxo-1-(p-tolyl)indoline-3-carboxylate (3ad):**





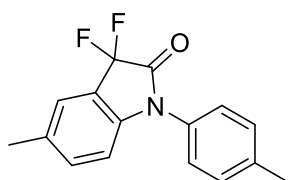
4.23-4.18 (m, 1H), 4.13-4.07 (m, 1H), 2.42 (s, 3H), 2.34 (s, 3H), 1.75 (s, 3H), 1.19 (t,  $J = 7.0$  Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 174.7, 169.9, 141.4, 138.0, 132.8, 131.8, 130.2, 130.0, 129.1, 126.2, 123.8, 109.4, 61.9, 55.2, 21.2, 21.0, 20.0, 13.9; LRMS (EI, 70 eV)  $m/z$  (%): 323 ( $\text{M}^+$ , 52), 250 (100); HRMS  $m/z$  (ESI) calcd for  $\text{C}_{20}\text{H}_{22}\text{NO}_3$  ( $[\text{M}+\text{H}]^+$ ) 324.1594, found: 324.1586.

**Ethyl 3-allyl-5-methyl-2-oxo-1-(*p*-tolyl)indoline-3-carboxylate (3ae):**



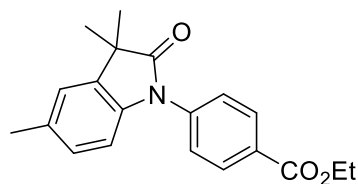
40.8 mg, 39%; Pale yellow oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.31 (d,  $J = 8.0$  Hz, 2H), 7.25 (d,  $J = 8.0$  Hz, 2H), 7.14 (d,  $J = 2.0$  Hz, 1H), 7.04-7.02 (m, 1H), 6.67 (d,  $J = 7.5$  Hz, 1H), 5.49-5.41 (m, 1H), 5.13-5.10 (m, 1H), 5.00-4.98 (m, 1H), 4.26-4.19 (m, 1H), 4.16-4.10 (m, 1H), 3.10-3.02 (m, 2H), 2.41 (s, 3H), 2.35 (s, 3H), 1.21 (t,  $J = 7.0$  Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 173.2, 169.2, 142.0, 138.1, 132.7, 131.7, 131.0, 130.2, 129.2, 127.3, 126.3, 124.3, 119.9, 109.2, 62.0, 59.3, 38.3, 21.2, 21.1, 13.9; LRMS (EI, 70 eV)  $m/z$  (%): 349 ( $\text{M}^+$ , 91), 308 (100), 276 (27), 236 (45); HRMS  $m/z$  (ESI) calcd for  $\text{C}_{22}\text{H}_{24}\text{NO}_3$  ( $[\text{M}+\text{H}]^+$ ) 350.1751, found: 350.1763.

**3,3-Difluoro-5-methyl-1-(*p*-tolyl)indolin-2-one (3af):**



29.2 mg, 38%; Colorless oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.43 (d,  $J = 2.0$  Hz, 1H), 7.33 (d,  $J = 8.0$  Hz, 2H), 7.27 (d,  $J = 8.5$  Hz, 2H), 7.22-7.20 (m, 1H), 6.74 (d,  $J = 8.0$  Hz, 1H), 2.41 (s, 3H), 2.37 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 164.6 (t,  $J = 30.3$  Hz), 141.8 (t,  $J = 6.8$  Hz), 138.8, 134.2 (t,  $J = 1.9$  Hz), 133.7 (t,  $J = 1.8$  Hz), 130.4, 130.0, 125.8, 125.3, 119.7 (t,  $J = 22.6$  Hz), 110.0 (t,  $J = 247.8$  Hz), 110.5, 21.2, 20.8;  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$ : -110.58; LRMS (EI, 70 eV)  $m/z$  (%): 273 ( $\text{M}^+$ , 96), 230 (70), 226 (86), 225 (100), 197 (58); HRMS  $m/z$  (ESI) calcd for  $\text{C}_{16}\text{H}_{14}\text{F}_2\text{NO}$  ( $[\text{M}+\text{H}]^+$ ) 274.1038, found: 274.1042.

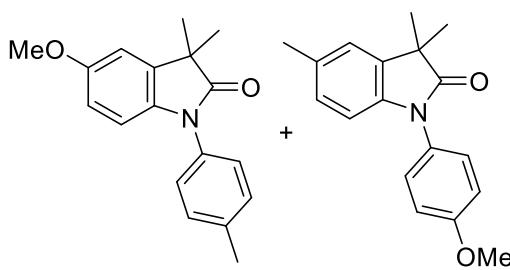
**Ethyl 4-(3,3,5-trimethyl-2-oxoindolin-1-yl)benzoate (3va):**



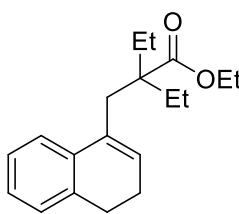
43.9 mg, 46%; White solid; mp 61.5-63.5 °C (uncorrected);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.19 (d,  $J = 8.5$  Hz, 2H), 7.55 (d,  $J = 8.5$  Hz, 2H), 7.11 (d,  $J = 1.5$

Hz, 1H), 7.01 (d,  $J = 8.0$  Hz, 1H), 6.83 (d,  $J = 8.0$  Hz, 1H), 4.43-4.39 (m, 2H), 2.37 (s, 3H), 1.48 (s, 6H), 1.42 (t,  $J = 7.0$  Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 180.4, 165.8, 139.1, 138.9, 135.6, 133.0, 130.7, 129.2, 127.8, 125.6, 123.6, 109.2, 61.1, 44.4, 24.8, 21.1, 14.3; LRMS (EI, 70 eV)  $m/z$  (%): 323 ( $\text{M}^+$ , 100), 308 (22), 280 (12), 255 (16), 207 (17); HRMS  $m/z$  (ESI) calcd for  $\text{C}_{20}\text{H}_{22}\text{NO}_3$  ( $[\text{M}+\text{H}]^+$ ) 324.1594, found: 324.1588.

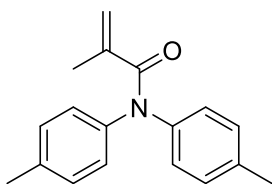
**5-Methoxy-3,3-dimethyl-1-(*p*-tolyl)indolin-2-one (3wa) and 1-(4-Methoxyphenyl)-3,3,5-trimethylindolin-2-one (3wa')**:


 Mixture, 54.6 mg, 63%; White solid; mp 124.8-126.0 °C (uncorrected);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.33-7.28 (m, 10H), 7.08 (d,  $J = 1.5$  Hz, 1H), 7.01 (d,  $J = 9.0$  Hz, 2H), 6.98 (dd,  $J = 8.0, 1.5$  Hz, 1H), 6.87 (d,  $J = 2.5$  Hz, 2H), 6.74 (d,  $J = 8.5$  Hz, 2H), 6.71-6.69 (m, 3H), 3.84 (s, 3H), 3.80 (s, 6H), 2.40 (s, 6H), 2.35 (s, 3H), 1.47 (s, 12H), 1.46 (s, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 180.8, 180.4, 158.9, 156.2, 140.5, 137.5, 137.0, 136.2, 135.6, 132.3, 132.2, 130.0, 127.8, 127.7, 127.5, 126.1, 123.3, 114.7, 111.7, 109.9, 109.7, 109.0, 55.8, 55.5, 44.6, 44.2, 24.8, 24.7, 21.2, 21.0.

**Ethyl 2-((3,4-dihydronaphthalen-1-yl)methyl)-2-ethylbutanoate (4):**


 8.2 mg, 13%; Colorless oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.18 (d,  $J = 7.5$  Hz, 1H), 7.09-7.00 (m, 3H), 5.77 (t,  $J = 5.0$  Hz, 1H), 3.69-3.65 (m, 2H), 2.62-2.59 (m, 4H), 2.13-2.09 (m, 2H), 1.68-1.61 (m, 2H), 1.55-1.47 (m, 2H), 1.00 (t,  $J = 7.5$  Hz, 3H), 0.73 (t,  $J = 7.5$  Hz, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ : 176.6, 136.6, 135.5, 133.3, 128.4, 127.3, 126.4, 125.9, 122.7, 59.9, 49.8, 37.2, 28.7, 25.8, 23.3, 13.9, 8.4; LRMS (EI, 70 eV)  $m/z$  (%): 286 ( $\text{M}^+$ , 7), 213 (10), 183 (10), 144 (100), 129 (44); HRMS  $m/z$  (ESI) calcd for  $\text{C}_{19}\text{H}_{27}\text{O}_2$  ( $[\text{M}+\text{H}]^+$ ) 287.2006, found: 287.2010.

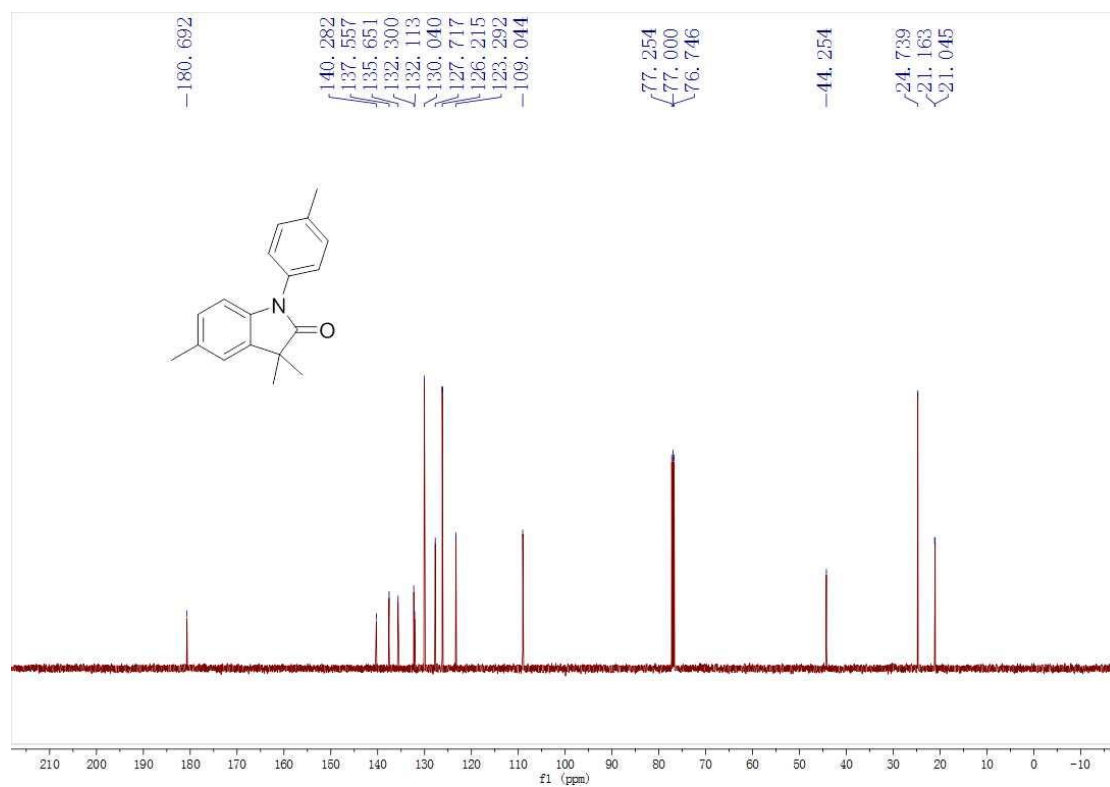
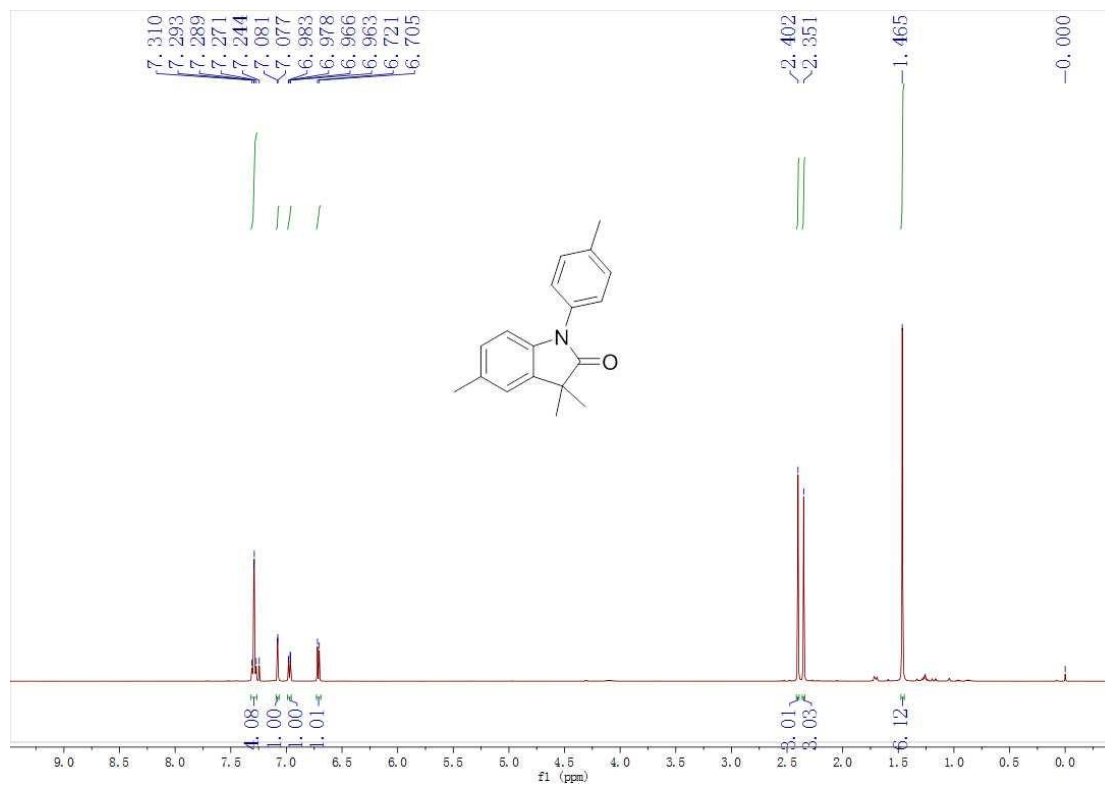
***N,N*-di-*p*-tolylmethacrylamide (6):**



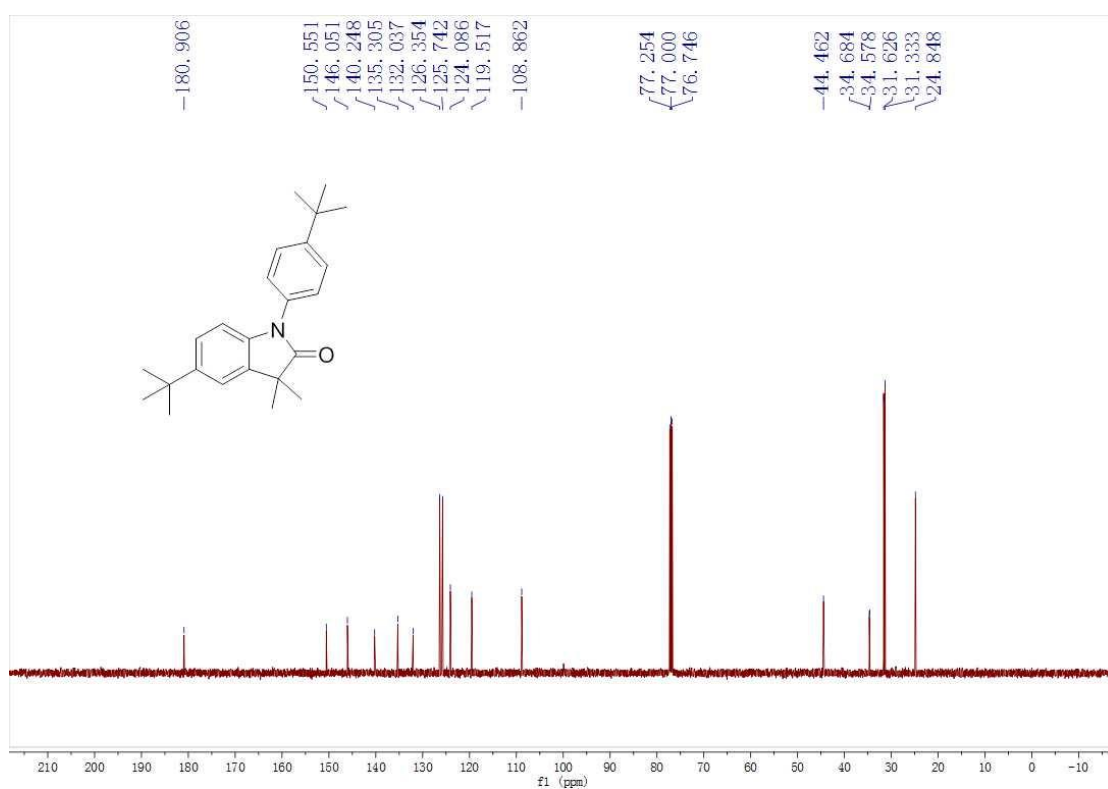
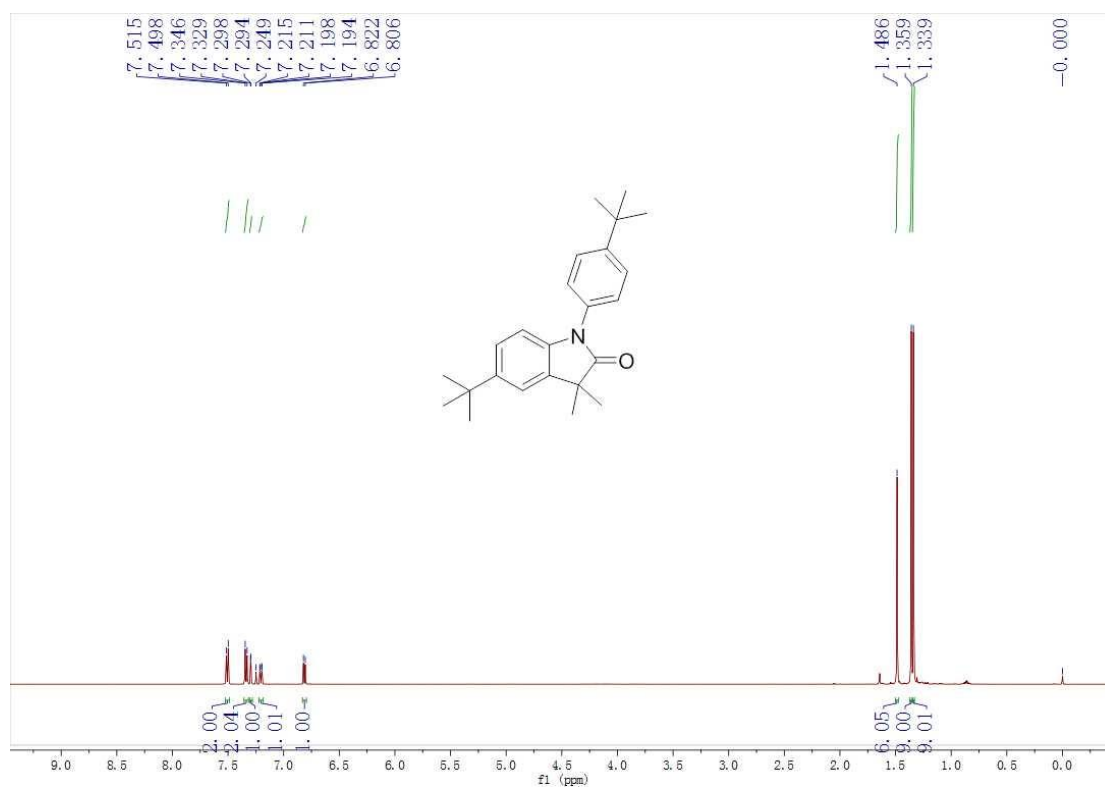
54.7 mg, 66%; White solid; mp 90.9-92.6 °C (uncorrected); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ: 7.12 (d, *J* = 8.0 Hz, 4H), 7.05 (d, *J* = 8.5 Hz, 4H), 5.22 (t, *J* = 1.0 Hz, 1H), 5.14 (t, *J* = 1.5 Hz, 1H), 2.32 (s, 6H), 1.83 (t, *J* = 1.5 Hz, 3H), <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ: 171.9, 141.3, 140.9, 136.2, 129.6, 126.8, 120.5, 21.0, 20.0; LRMS (EI, 70 eV) *m/z* (%): 265 (*M*<sup>+</sup>, 86), 236 (14), 222 (33), 196 (55), 181 (100), 158 (99); HRMS *m/z* (ESI) calcd for C<sub>18</sub>H<sub>20</sub>NO (*[M+H]*<sup>+</sup>) 266.1539, found: 266.1549.

### (C) Spectra

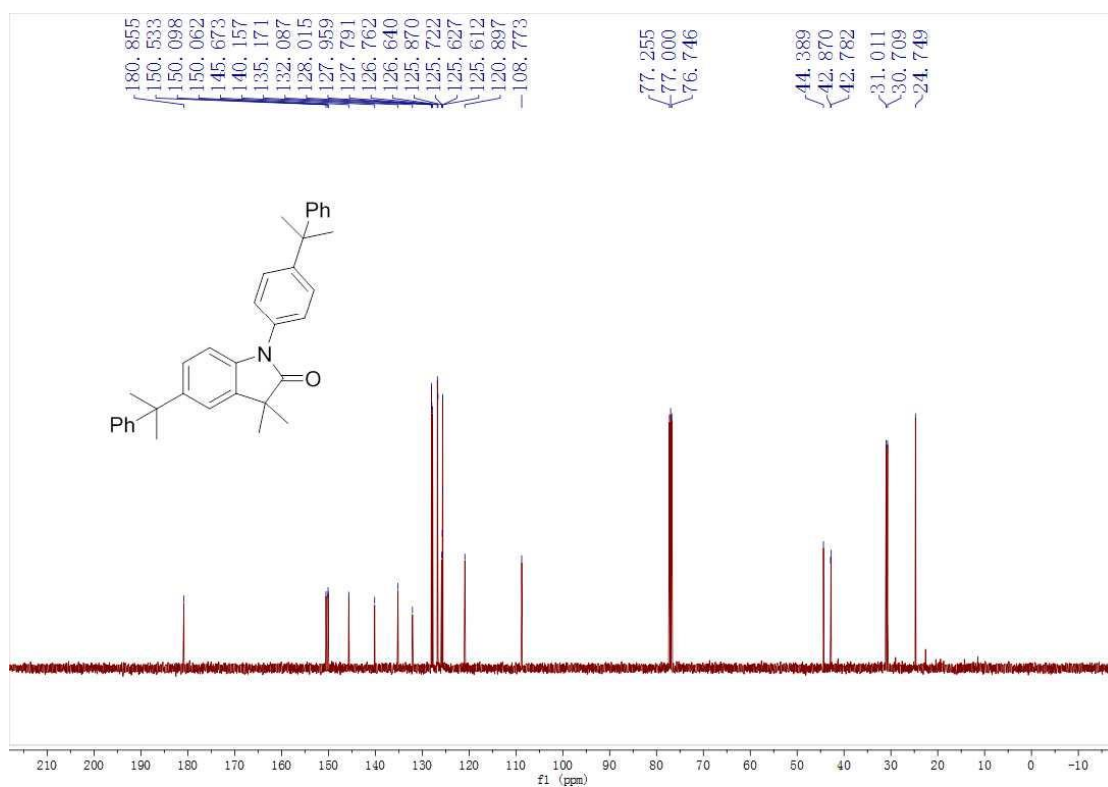
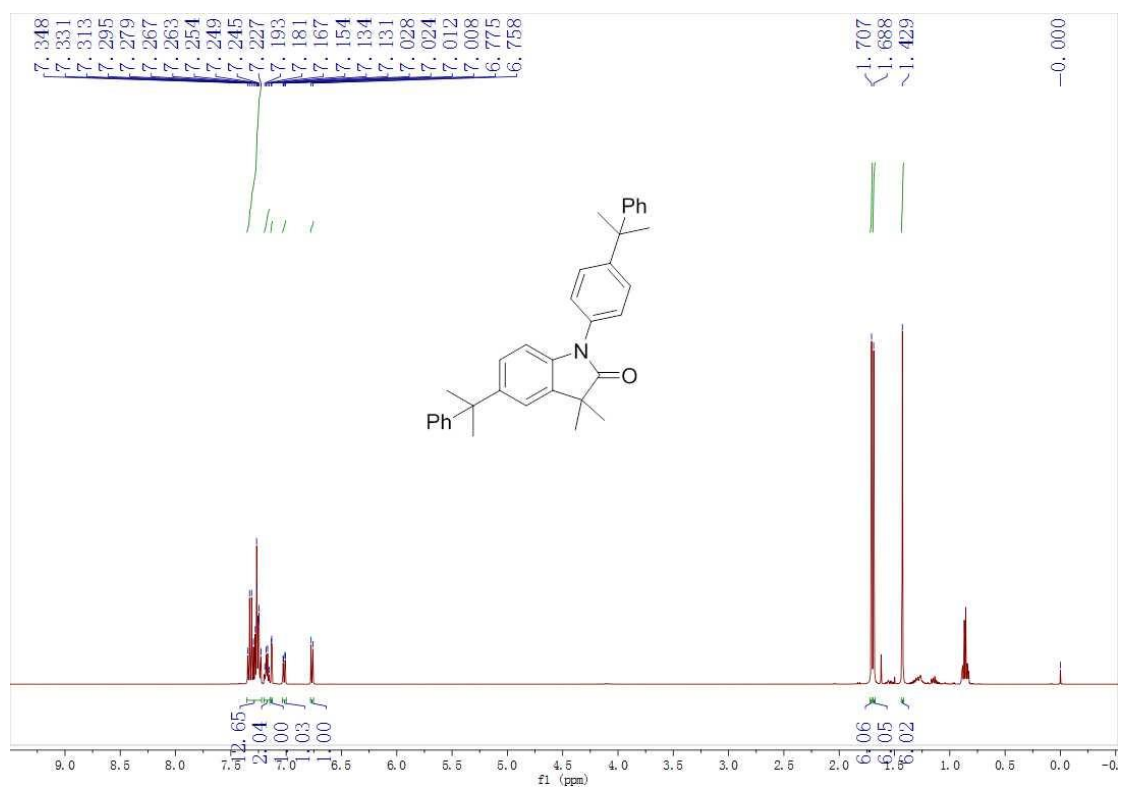
**3,3,5-Trimethyl-1-(*p*-tolyl)indolin-2-one (3aa)**



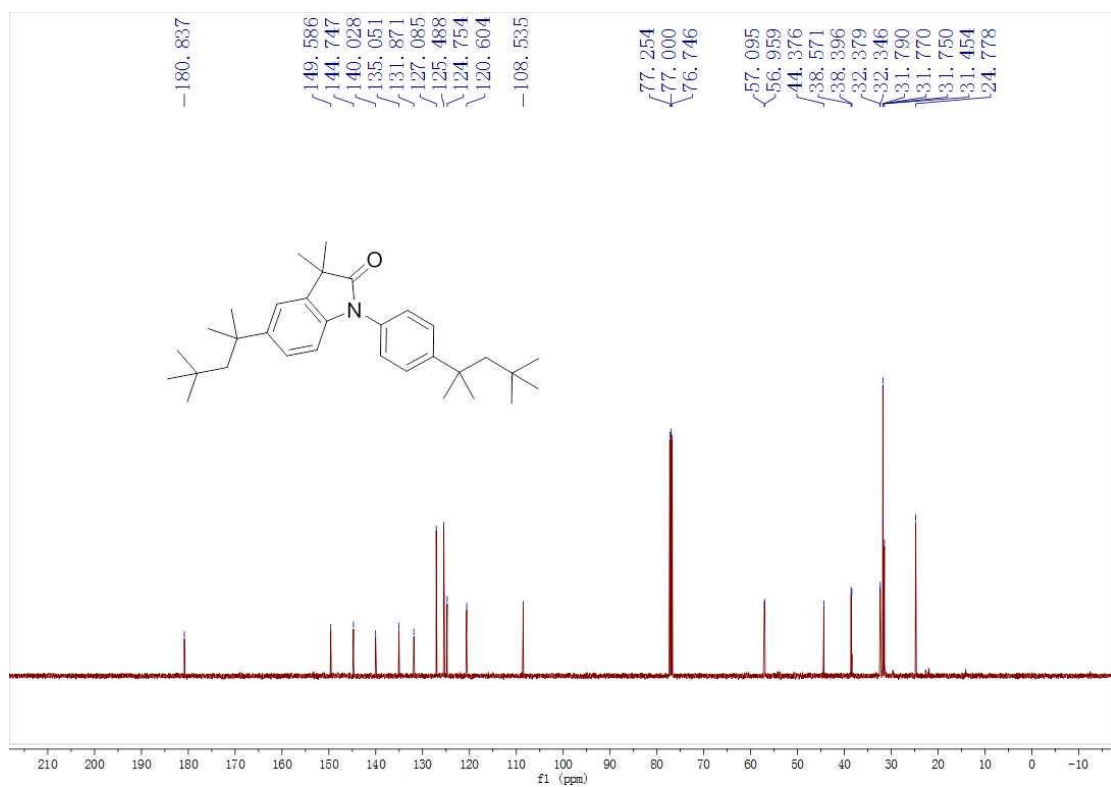
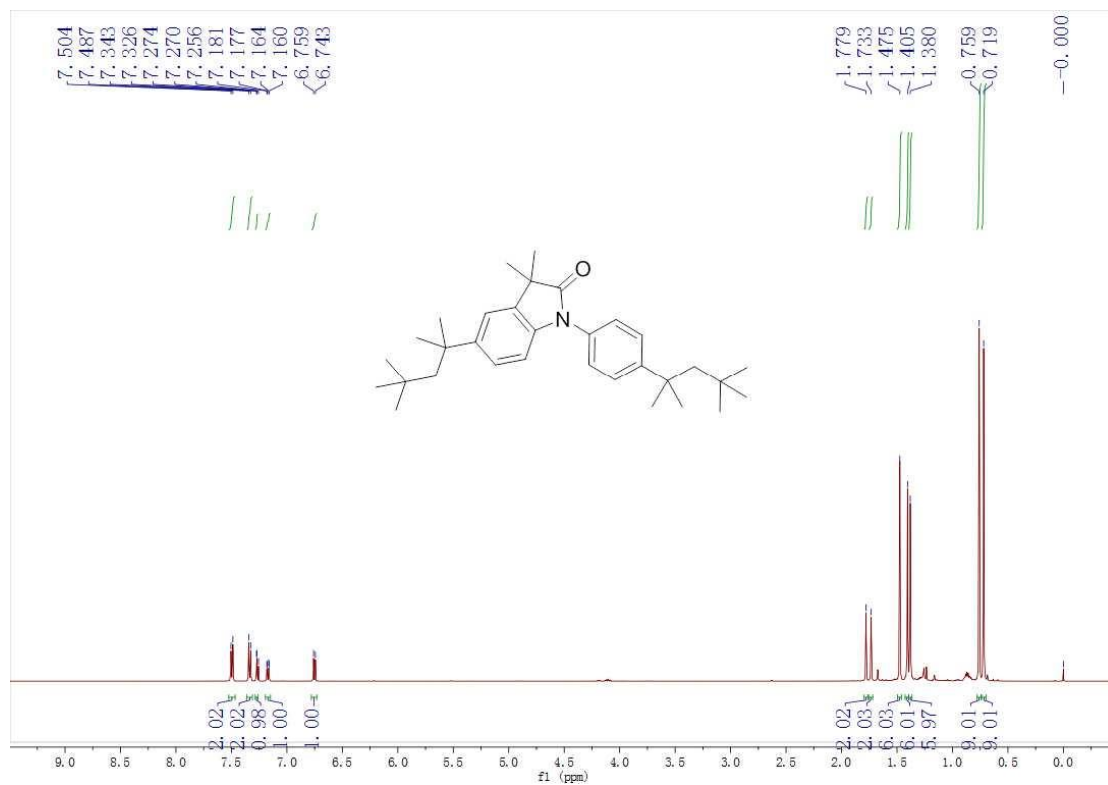
5-(*Tert*-butyl)-1-(4-(*tert*-butyl)phenyl)-3,3-dimethylindolin-2-one (3ba)



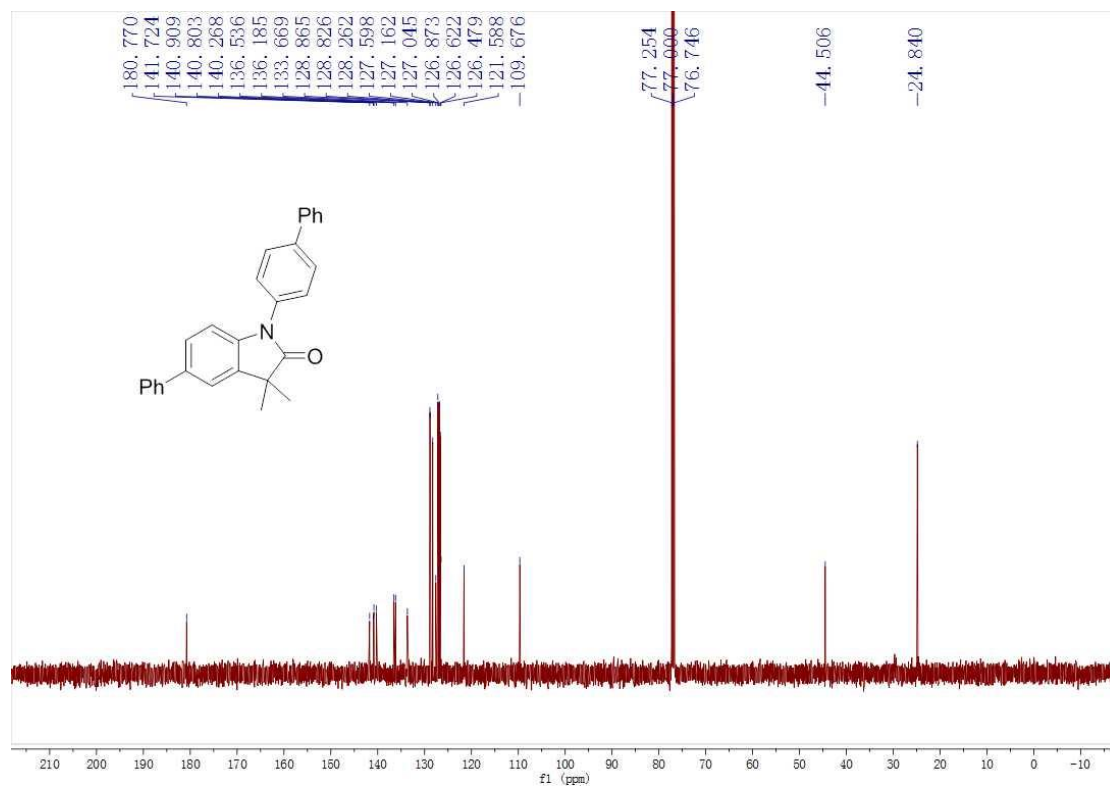
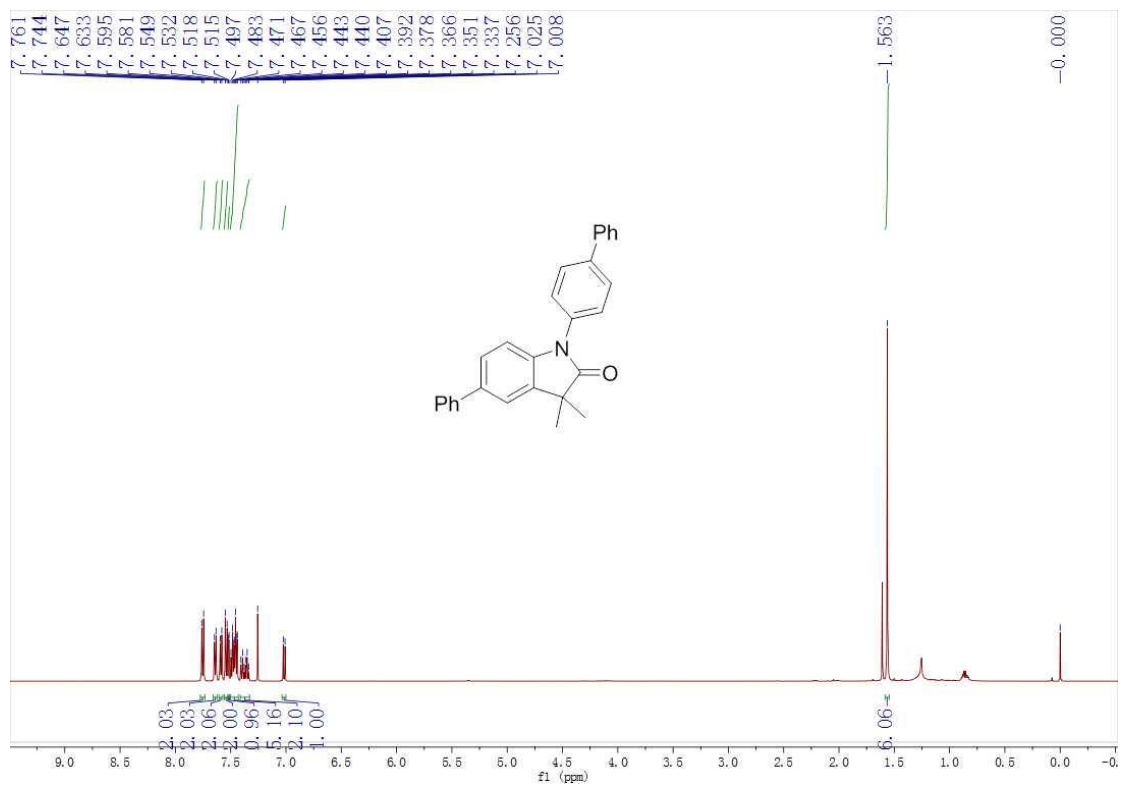
**1-([1,1'-Biphenyl]-4-yl)-3,3-dimethyl-5-phenylindolin-2-one (3ca)**



**3,3-Bimethyl-5-(2,4,4-trimethylpentan-2-yl)-1-(4-(2,4,4-trimethylpentan-2-yl)phenyl)indolin-2-one (3da)**

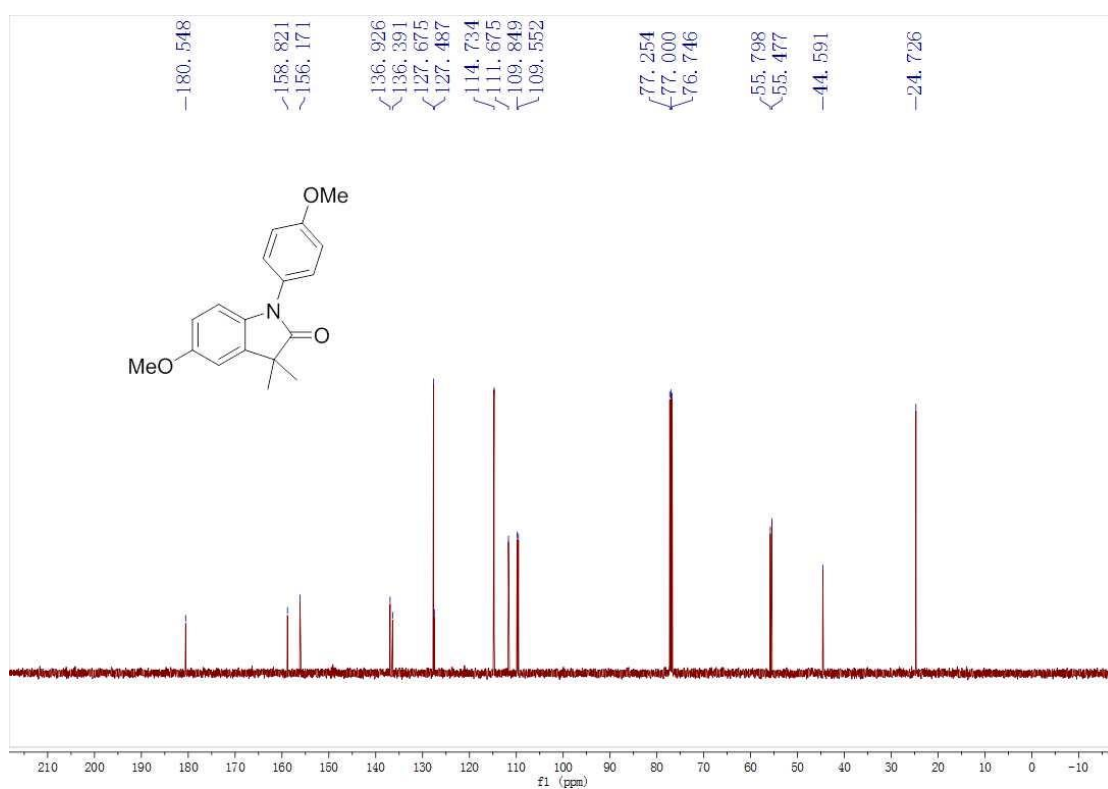
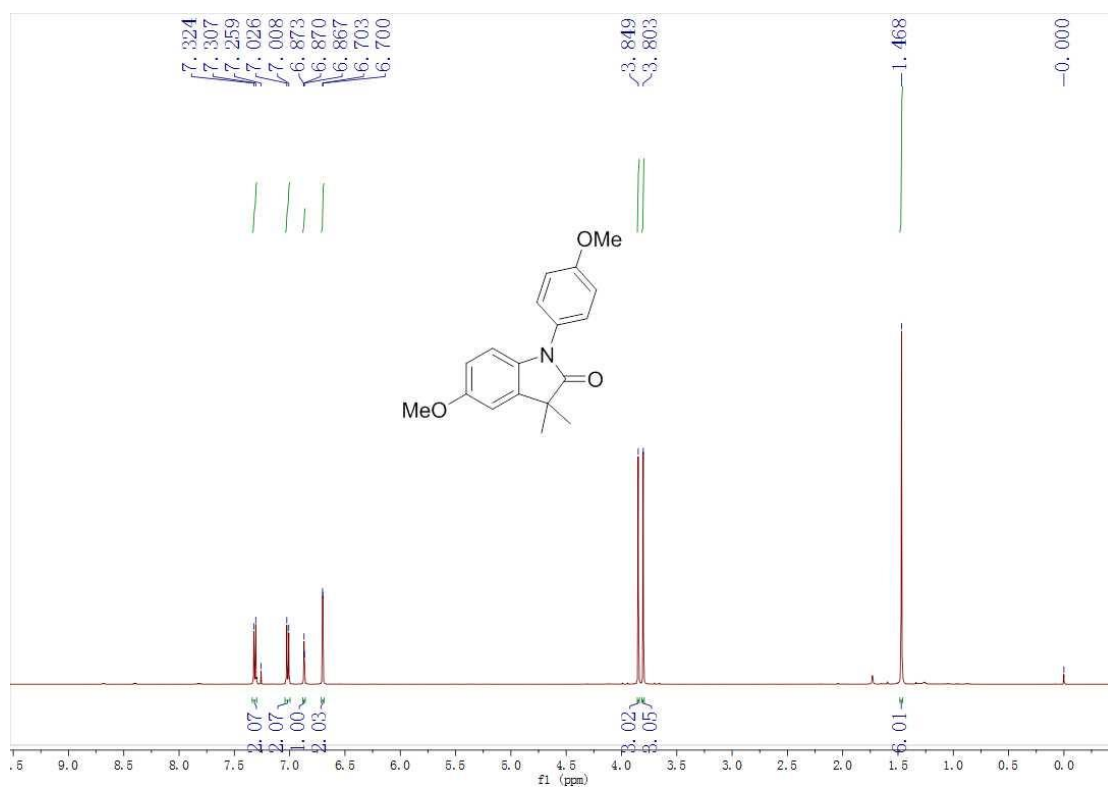


**3,3-Dimethyl-5-(2-phenylpropan-2-yl)-1-(4-(2-phenylpropan-2-yl)phenyl)indolin-2-one (3ea)**

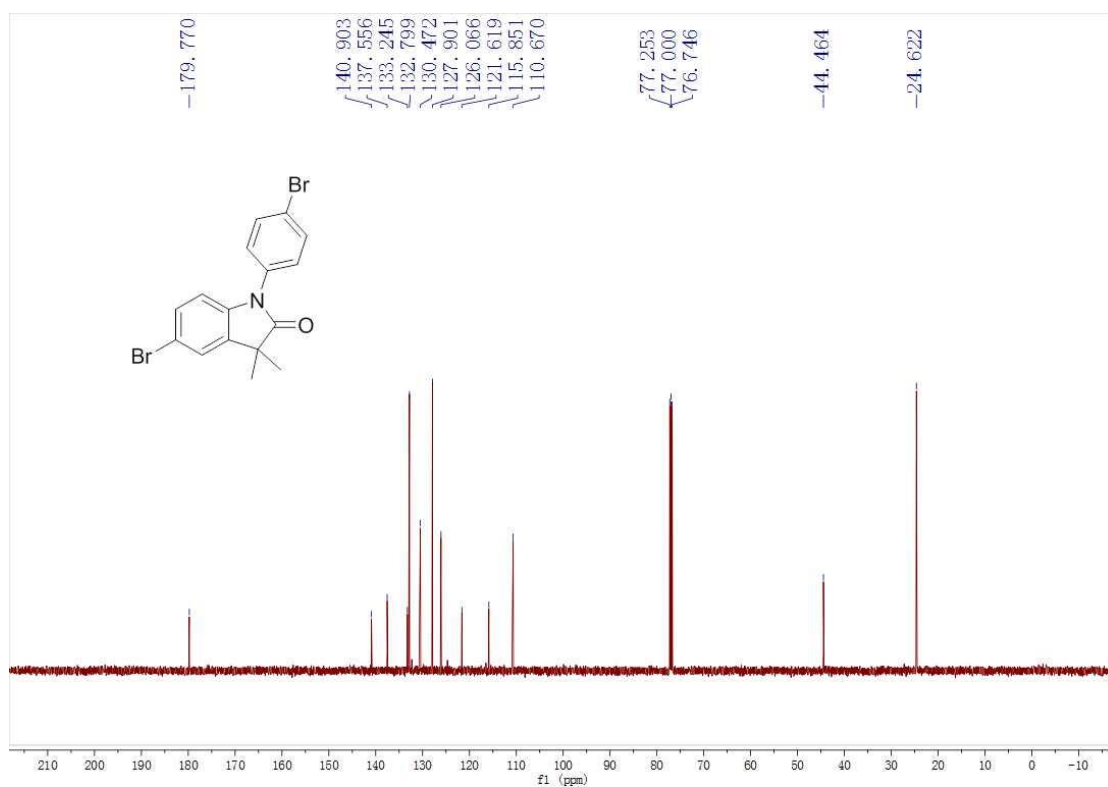
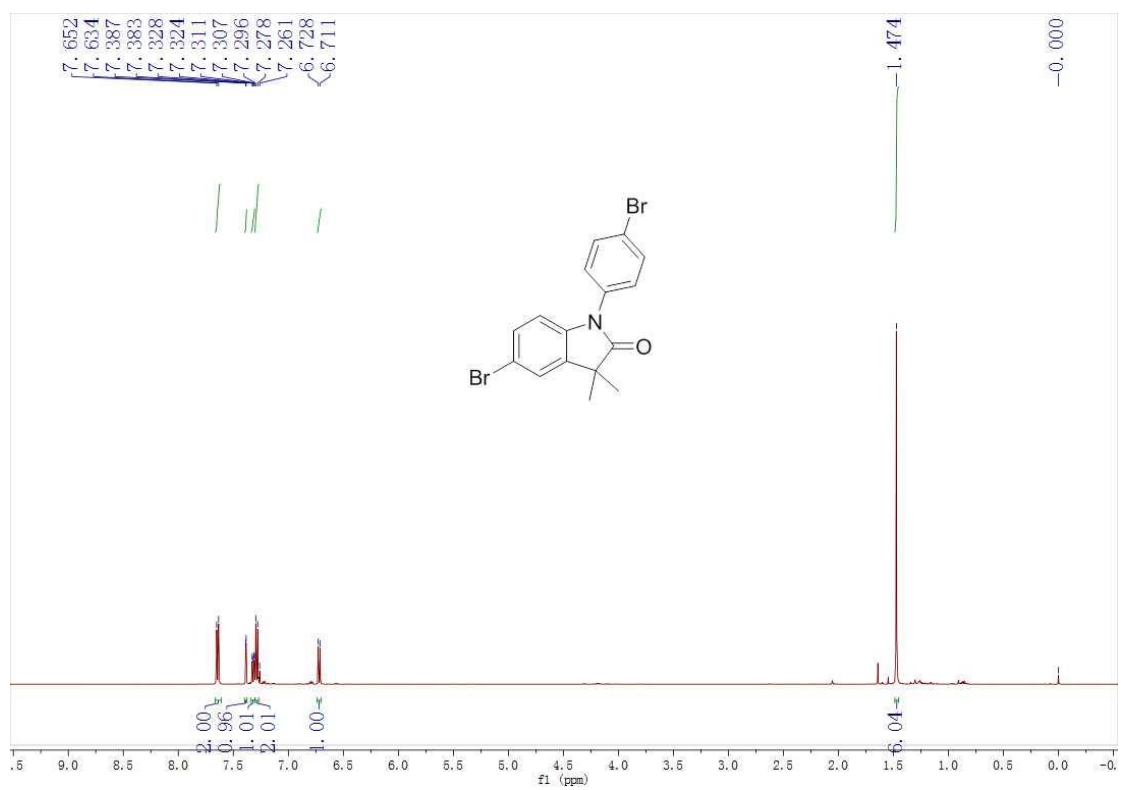




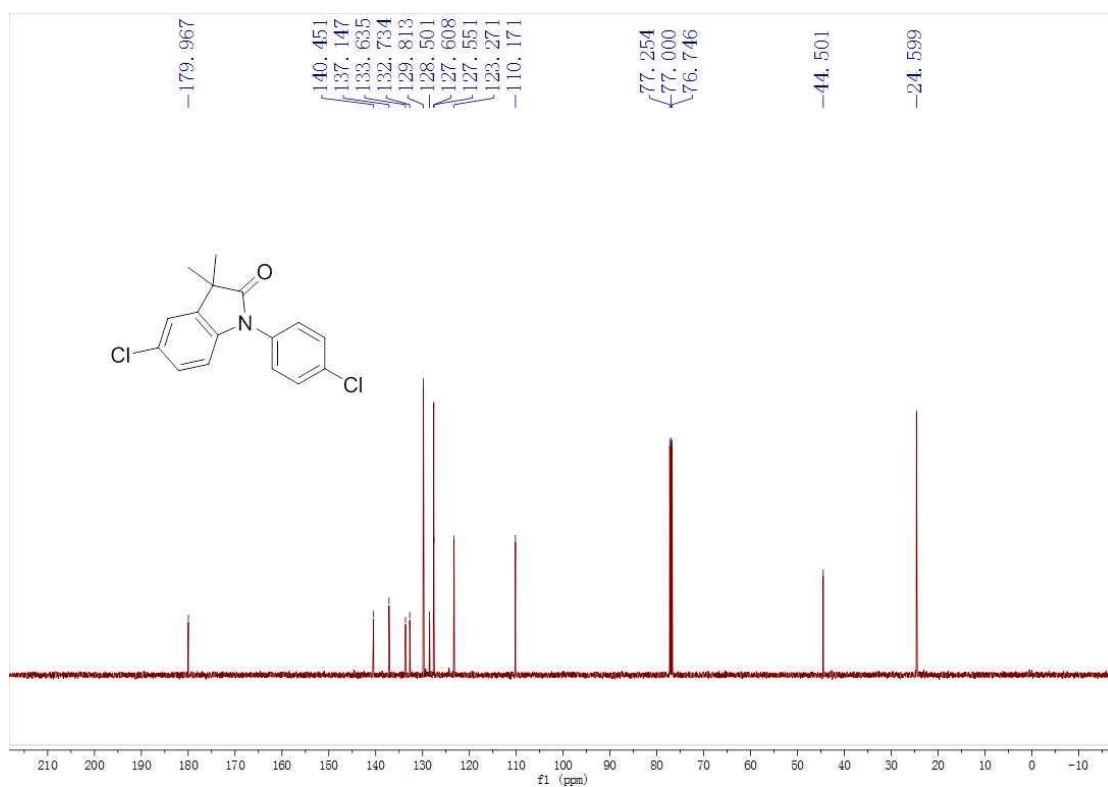
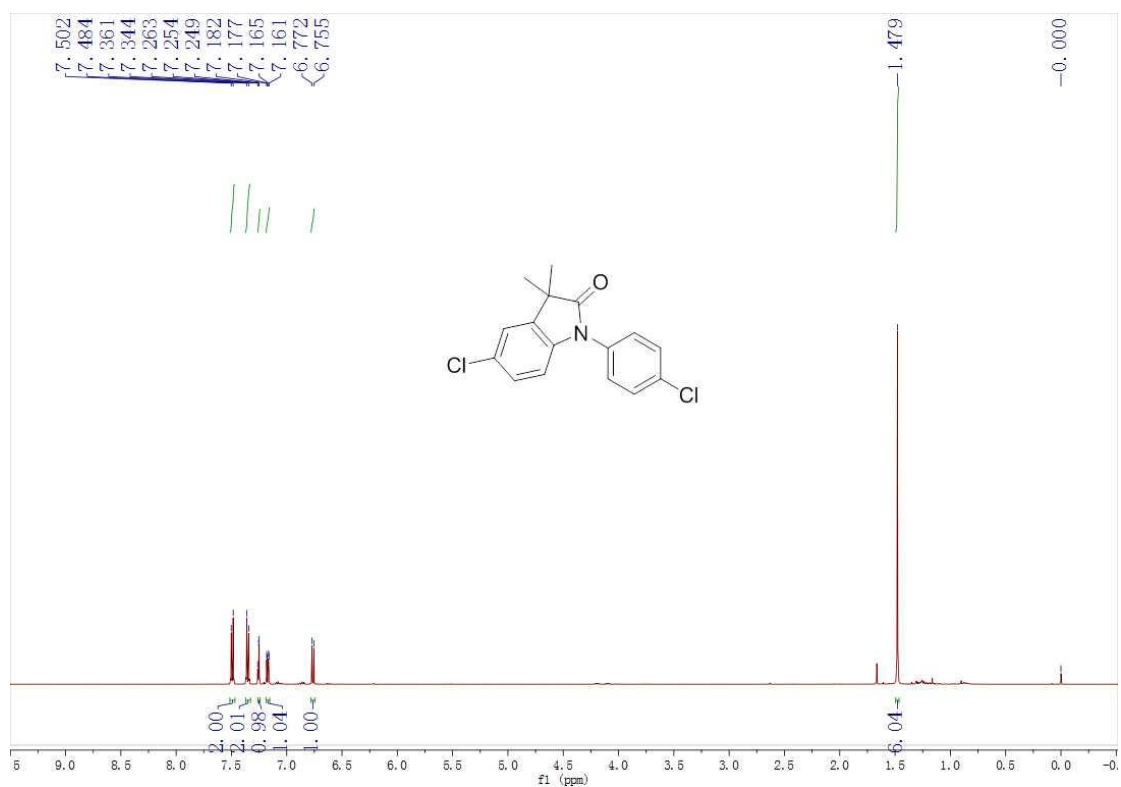
### 5-Methoxy-1-(4-methoxyphenyl)-3,3-dimethylindolin-2-one (3fa)



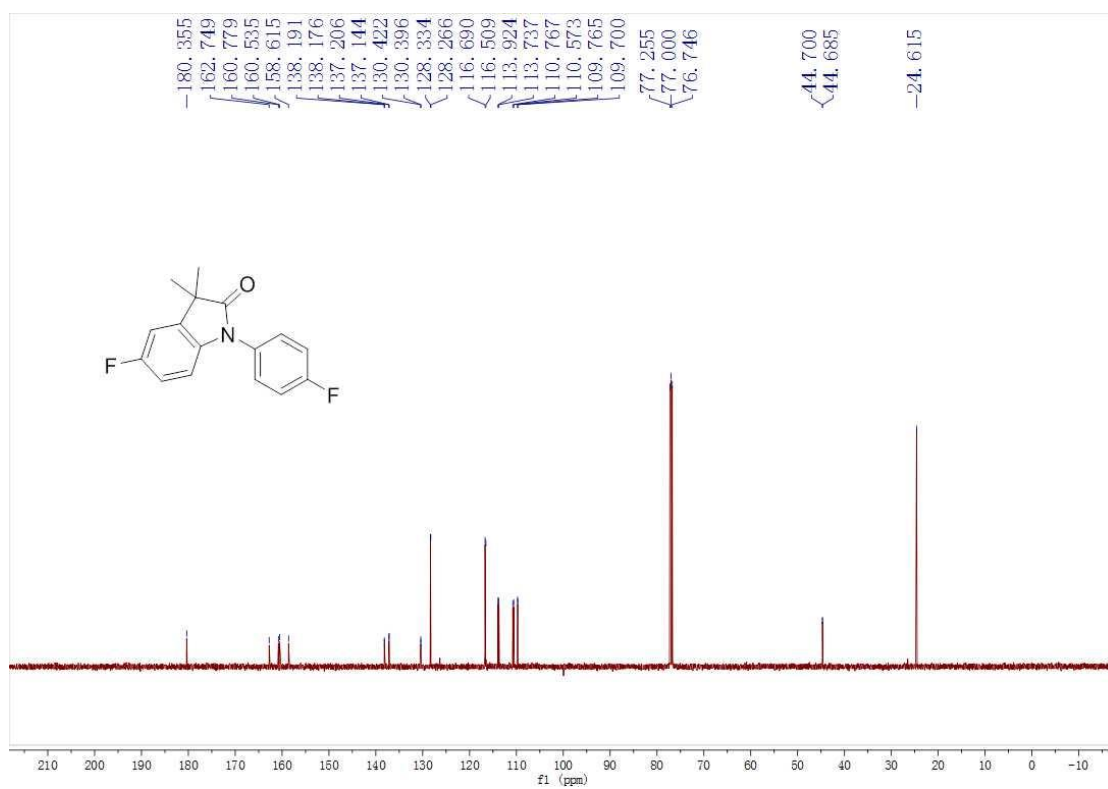
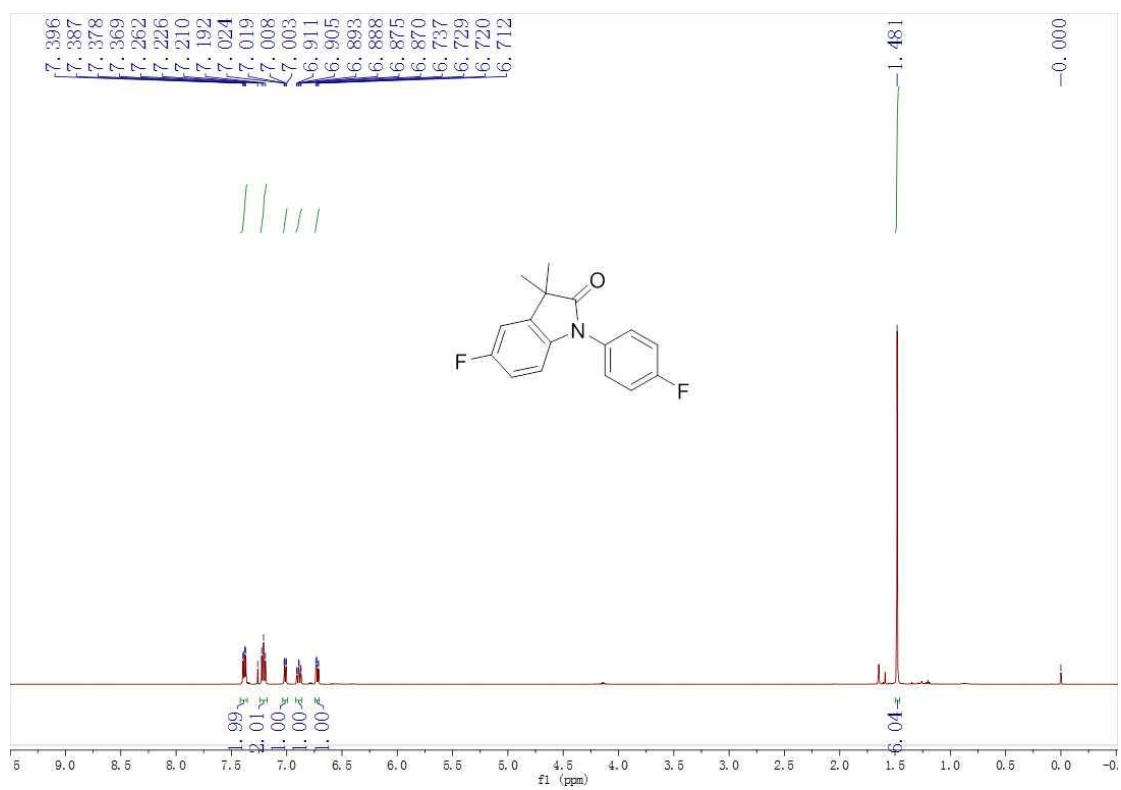
### 5-Bromo-1-(4-bromophenyl)-3,3-dimethylindolin-2-one (3ga)

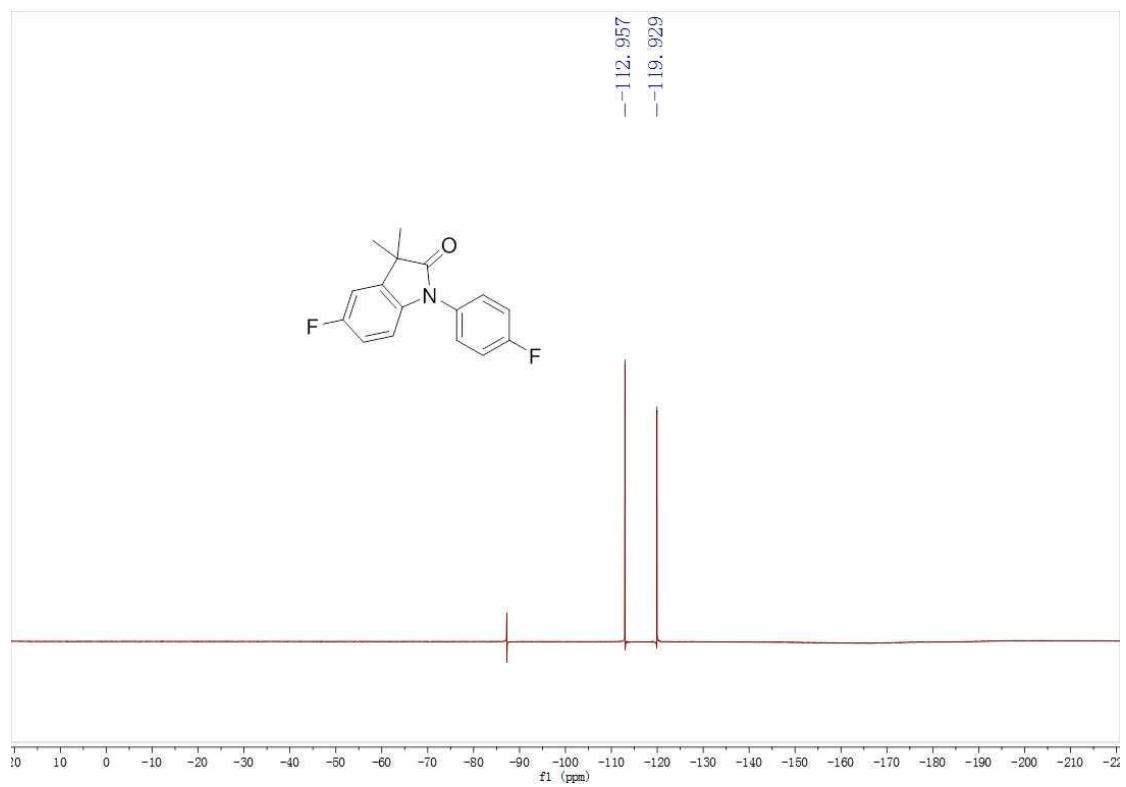


### 5-Chloro-1-(4-chlorophenyl)-3,3-dimethylindolin-2-one (3ha)

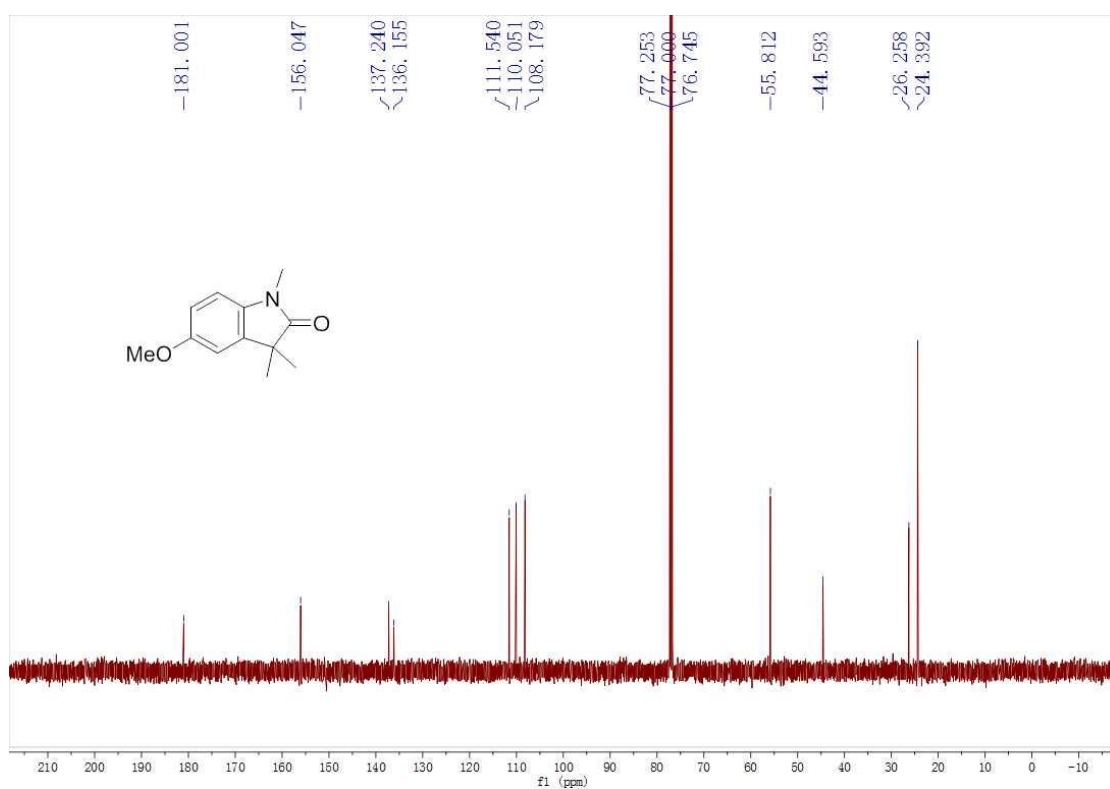
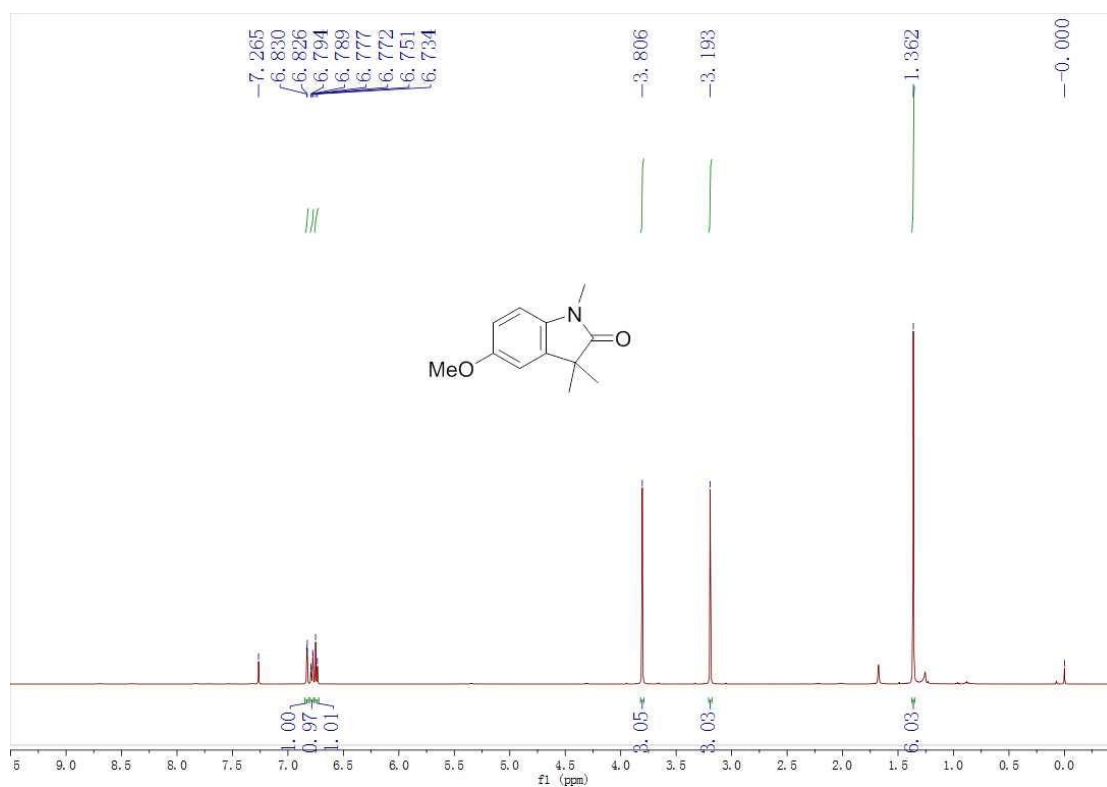


**5-Fluoro-1-(4-fluorophenyl)-3,3-dimethylindolin-2-one (3ia)**

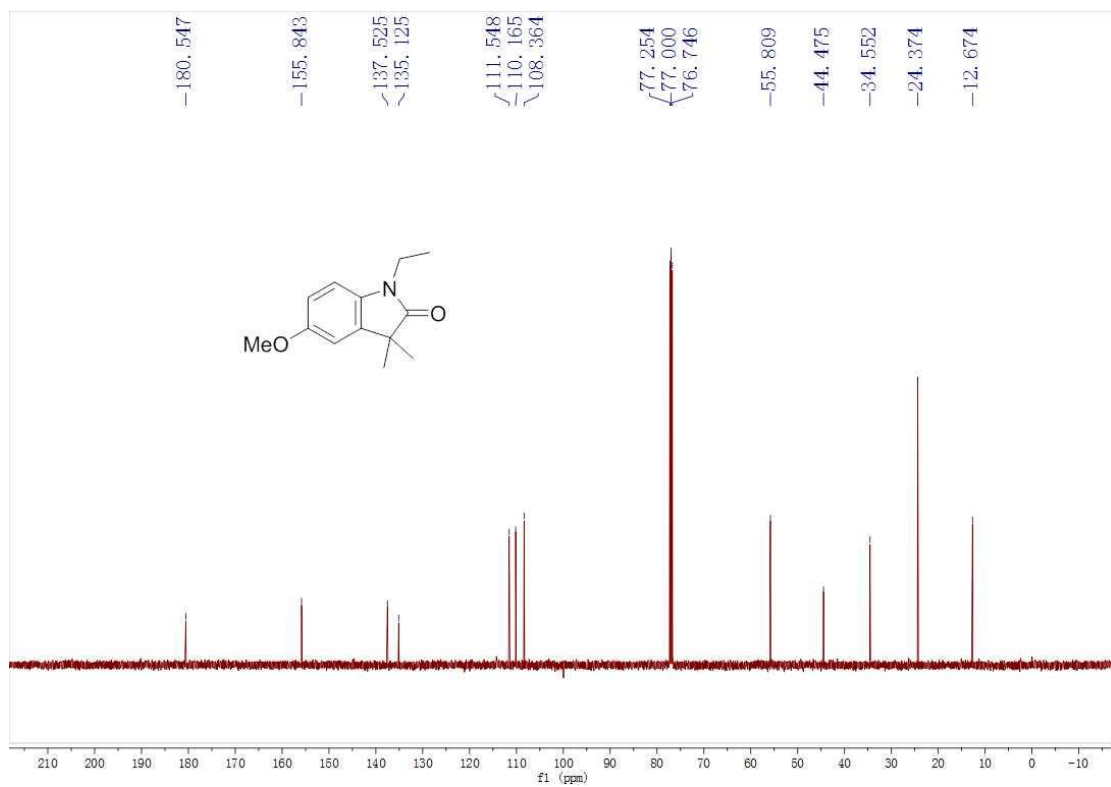
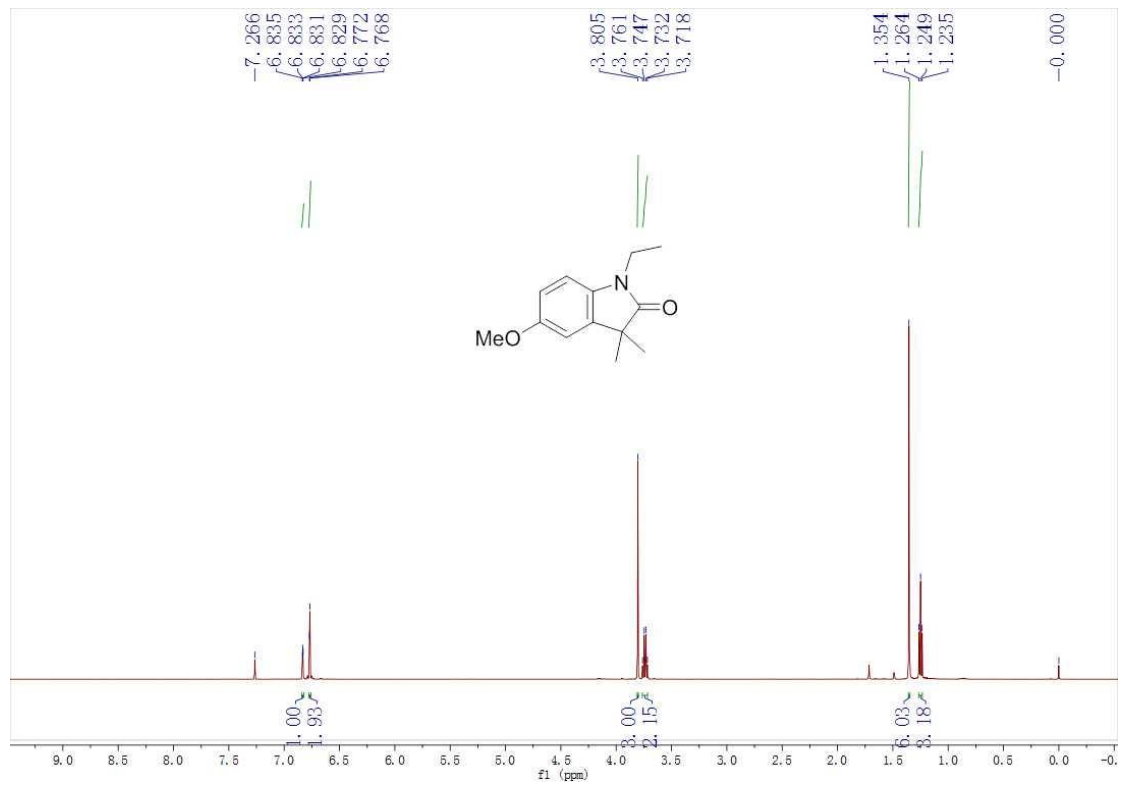




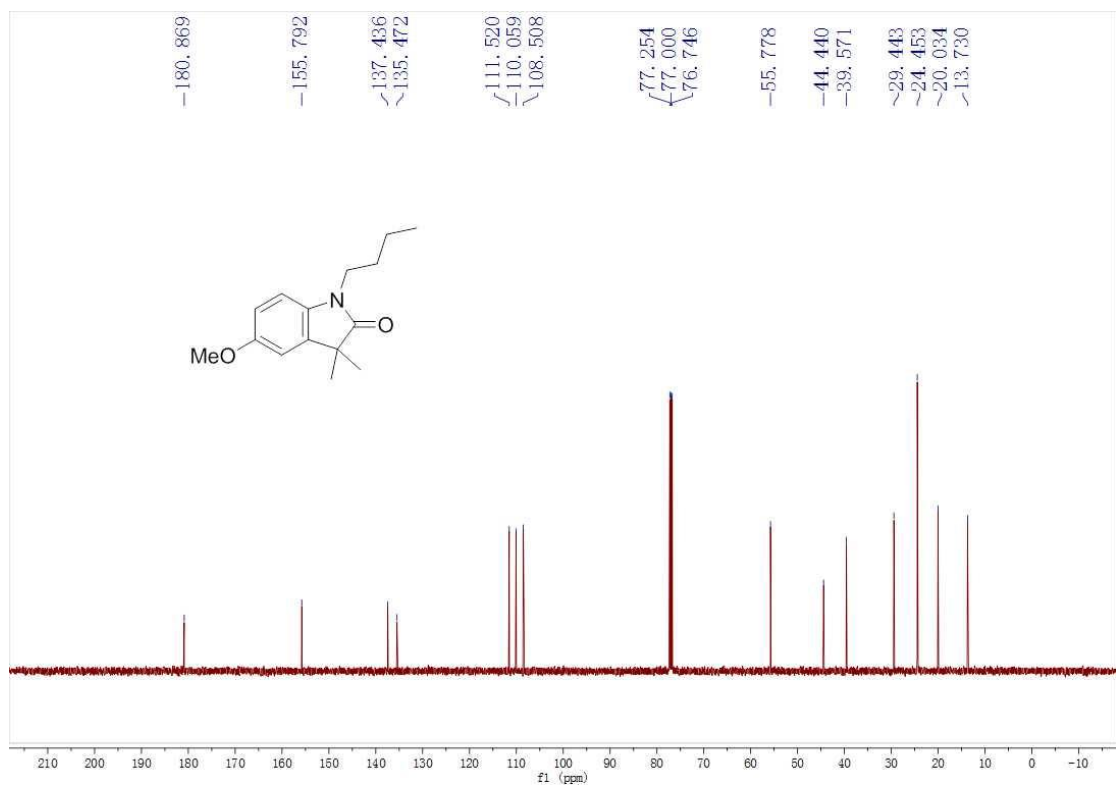
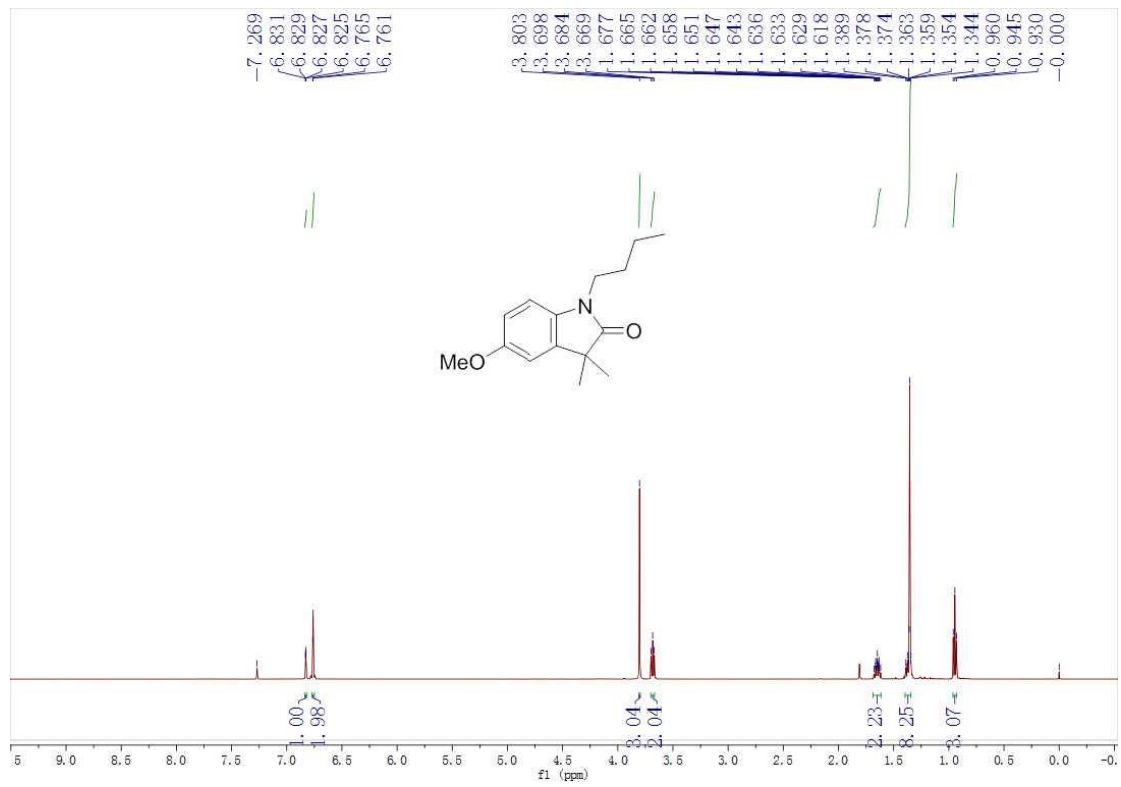
### 5-Methoxy-1,3,3-trimethylindolin-2-one (3ka)



### 1-Ethyl-5-methoxy-3,3-dimethylindolin-2-one (31a)

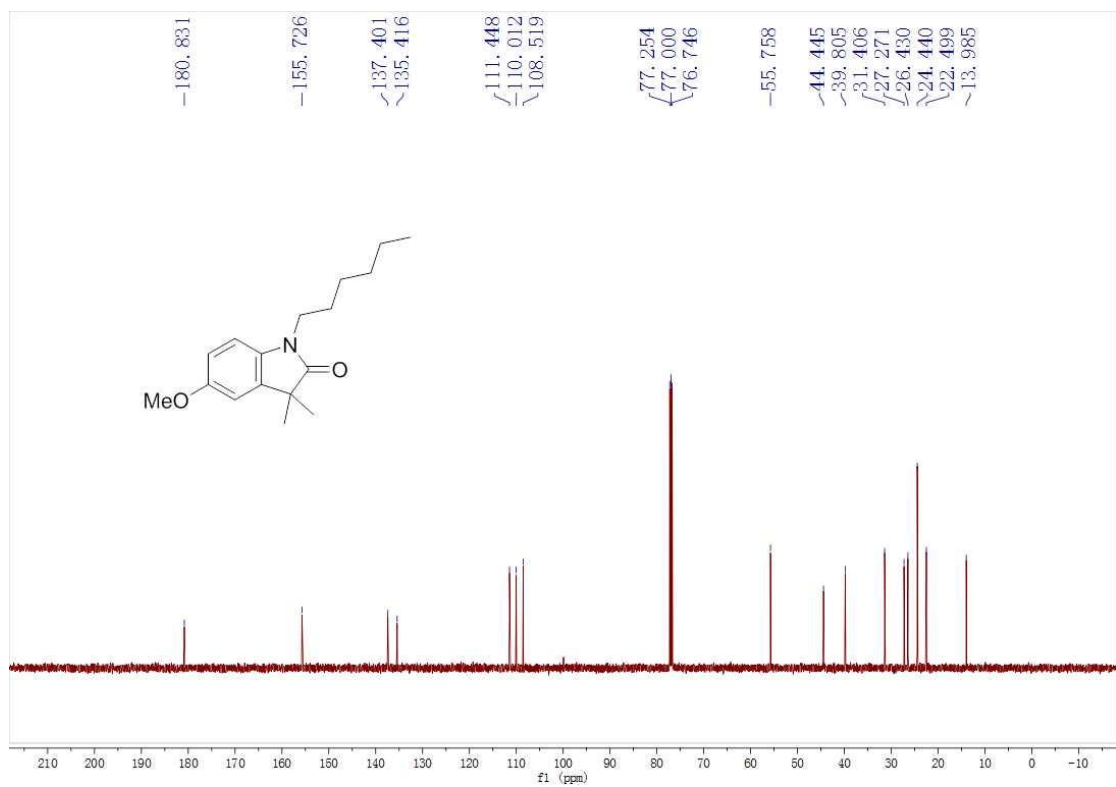
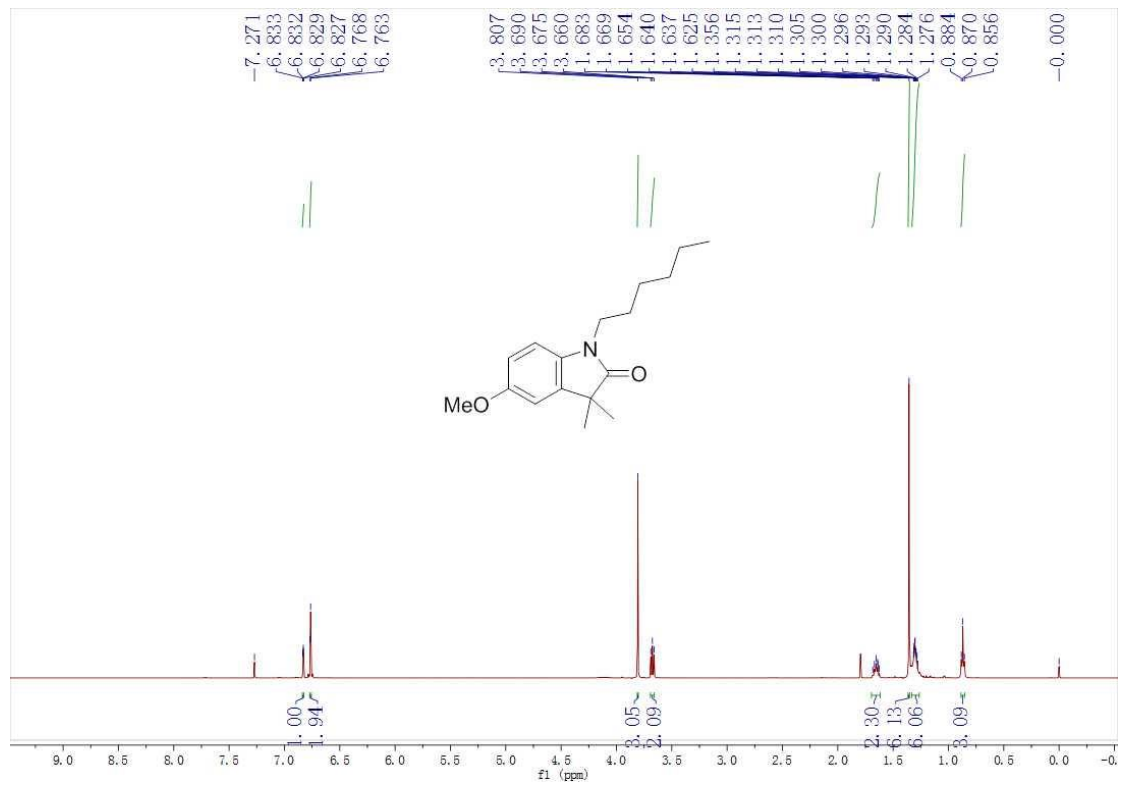


### 1-Butyl-5-methoxy-3,3-dimethylindolin-2-one (3ma)

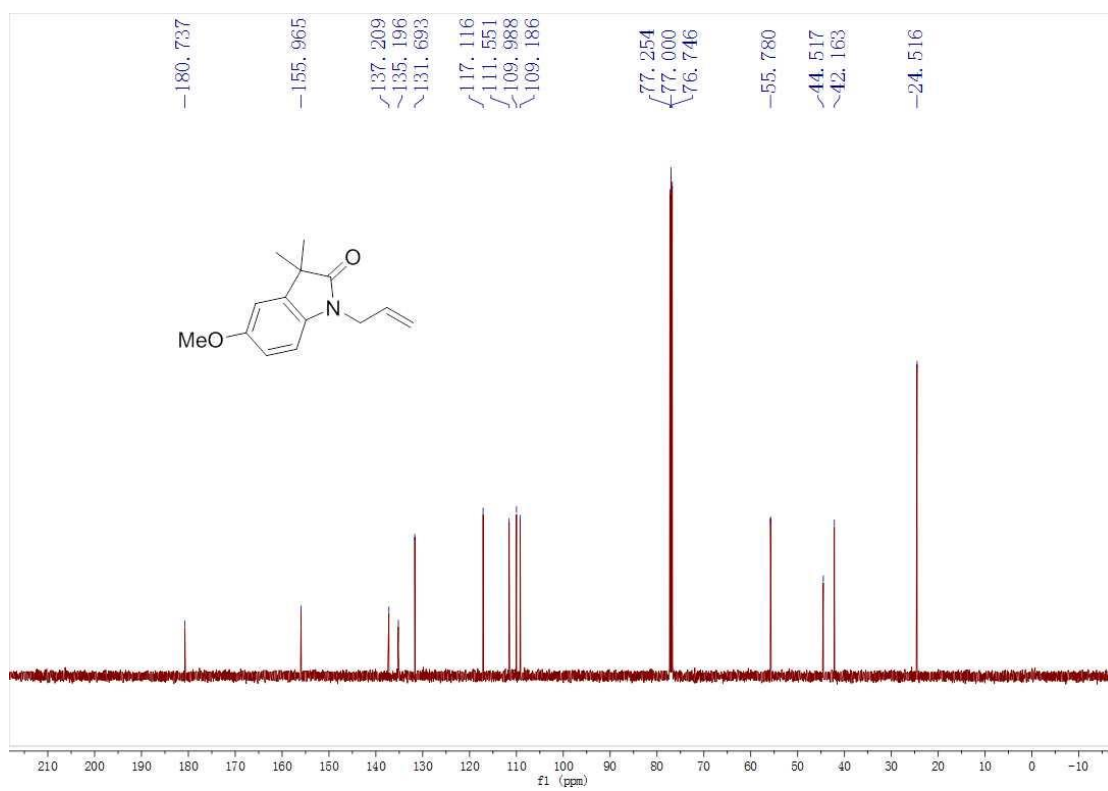
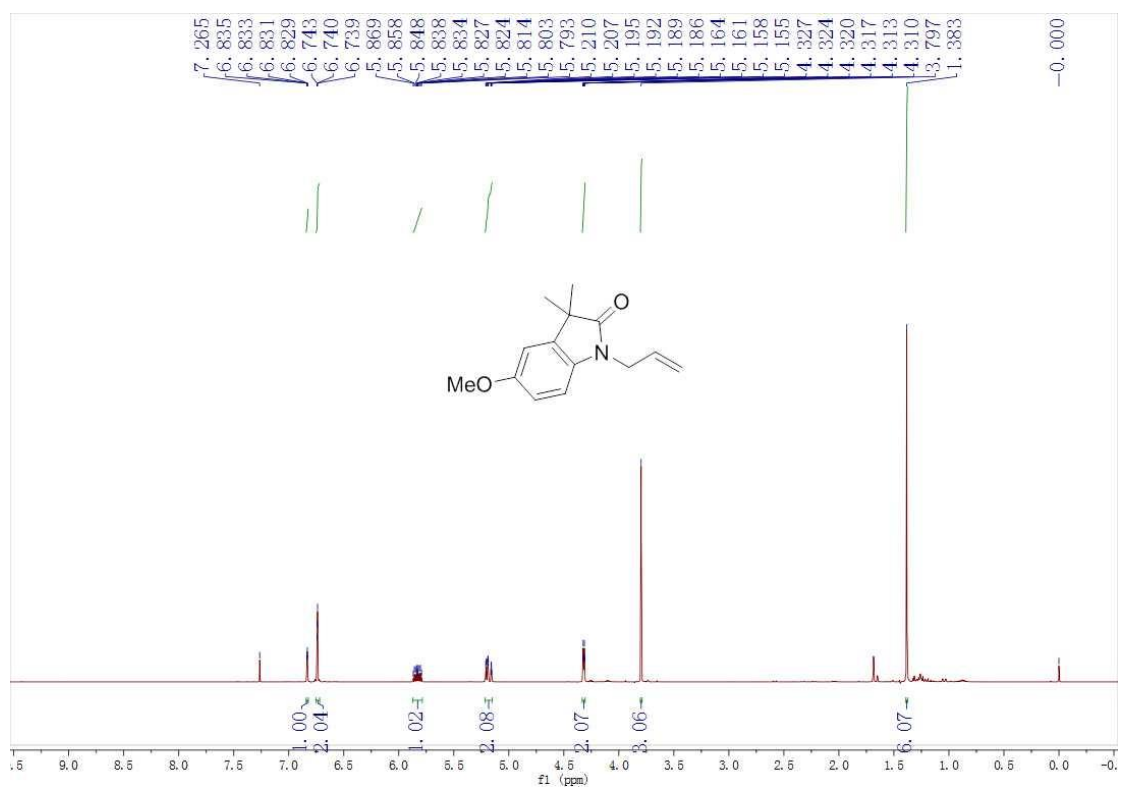




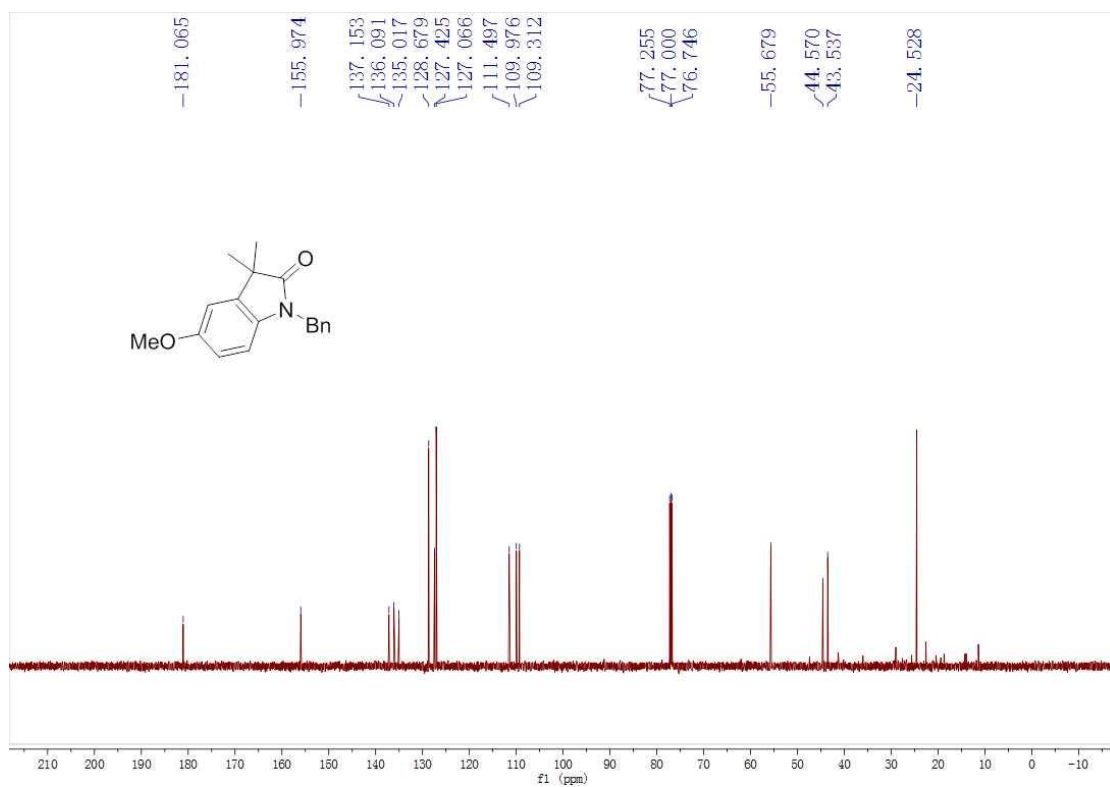
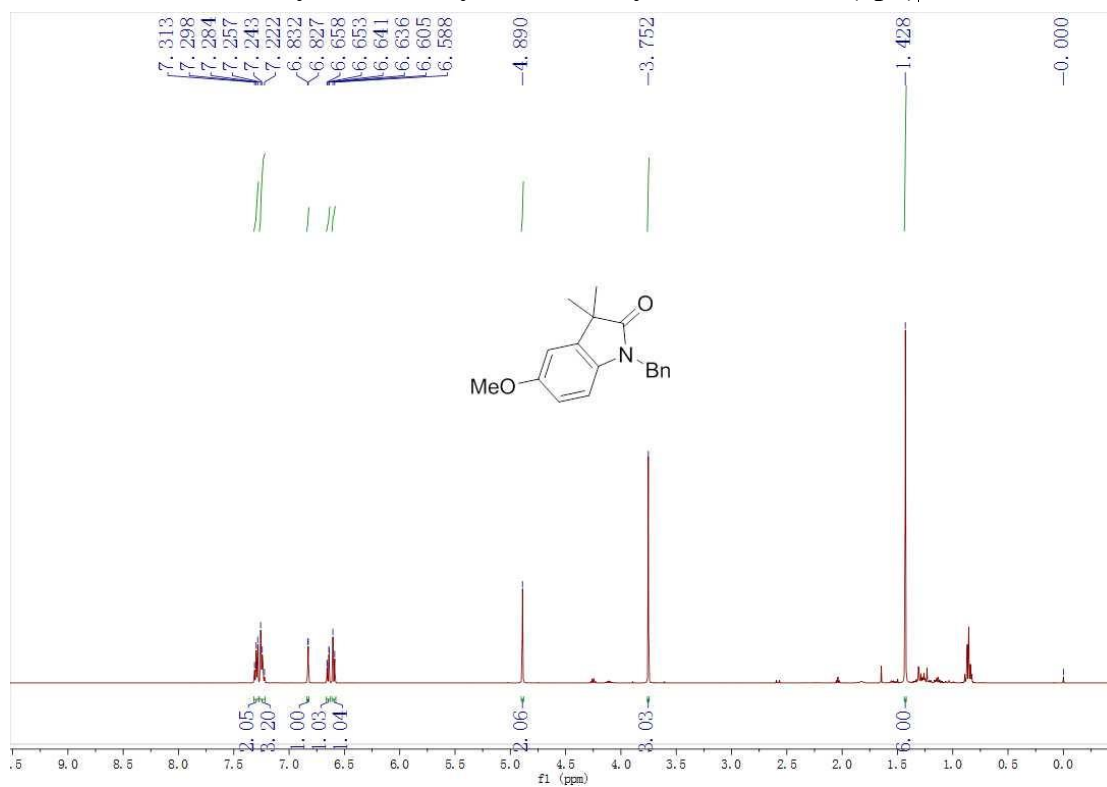
### 1-Hexyl-5-methoxy-3,3-dimethylindolin-2-one (3na)



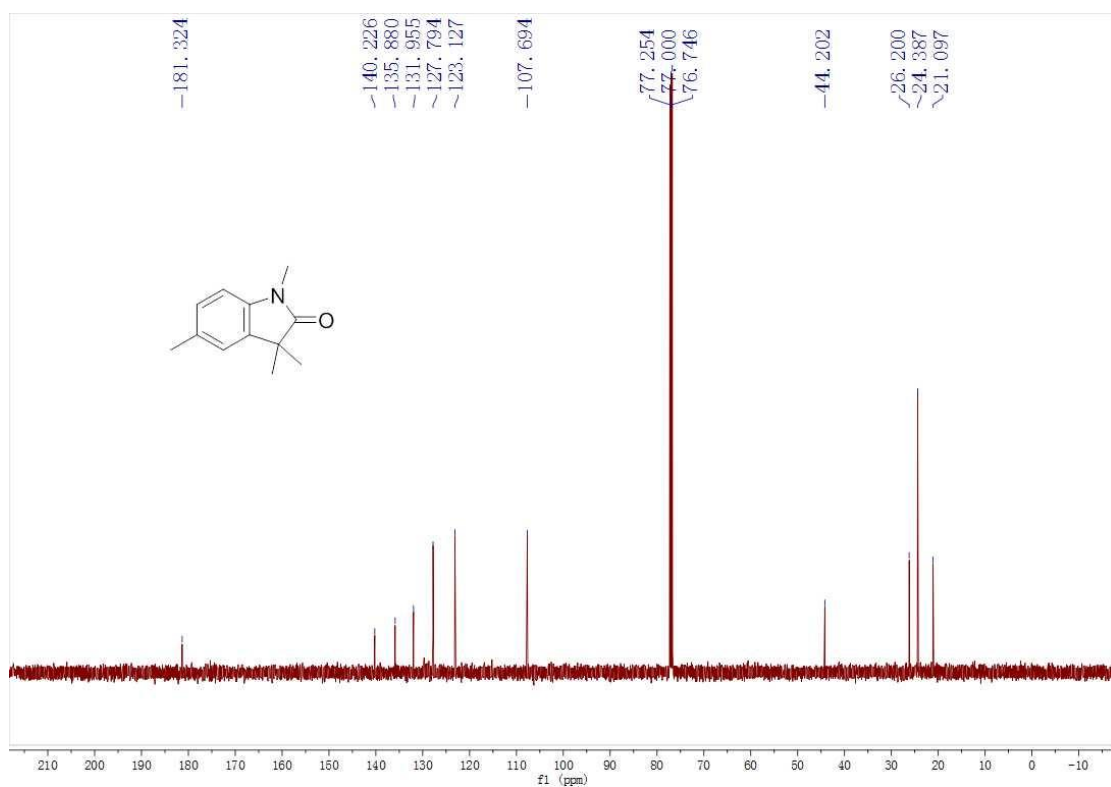
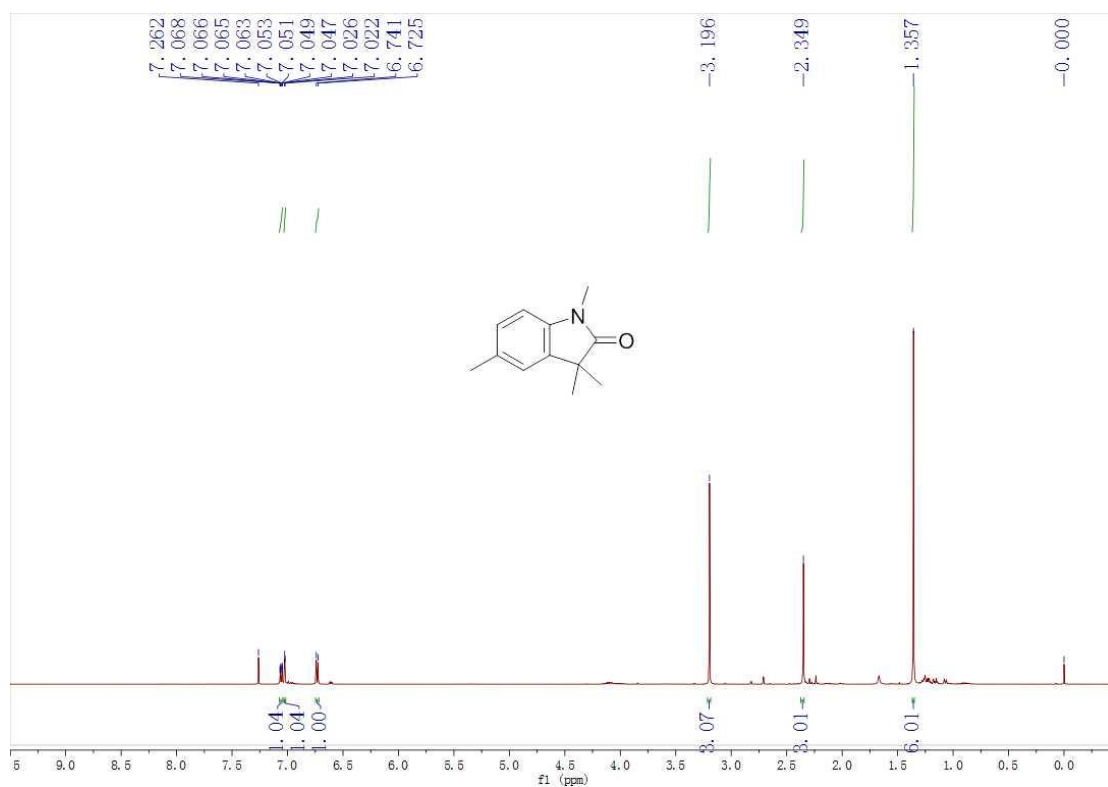
**1-Allyl-5-methoxy-3,3-dimethylindolin-2-one (30a)**



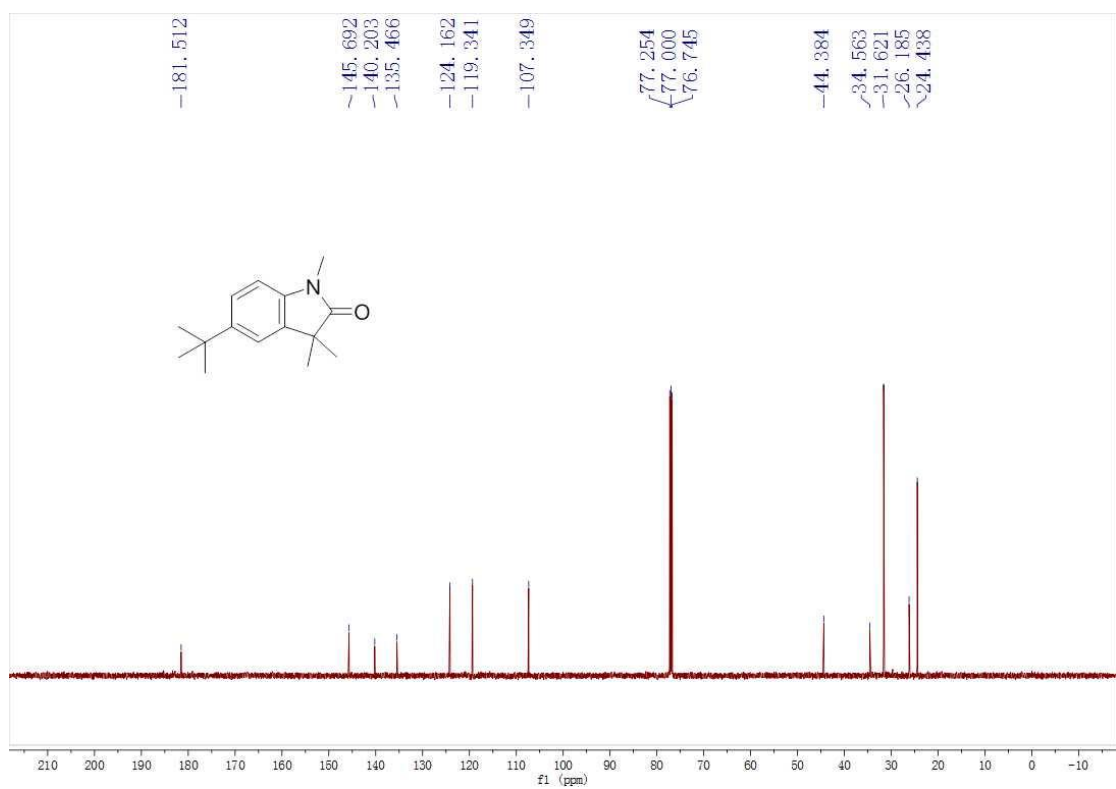
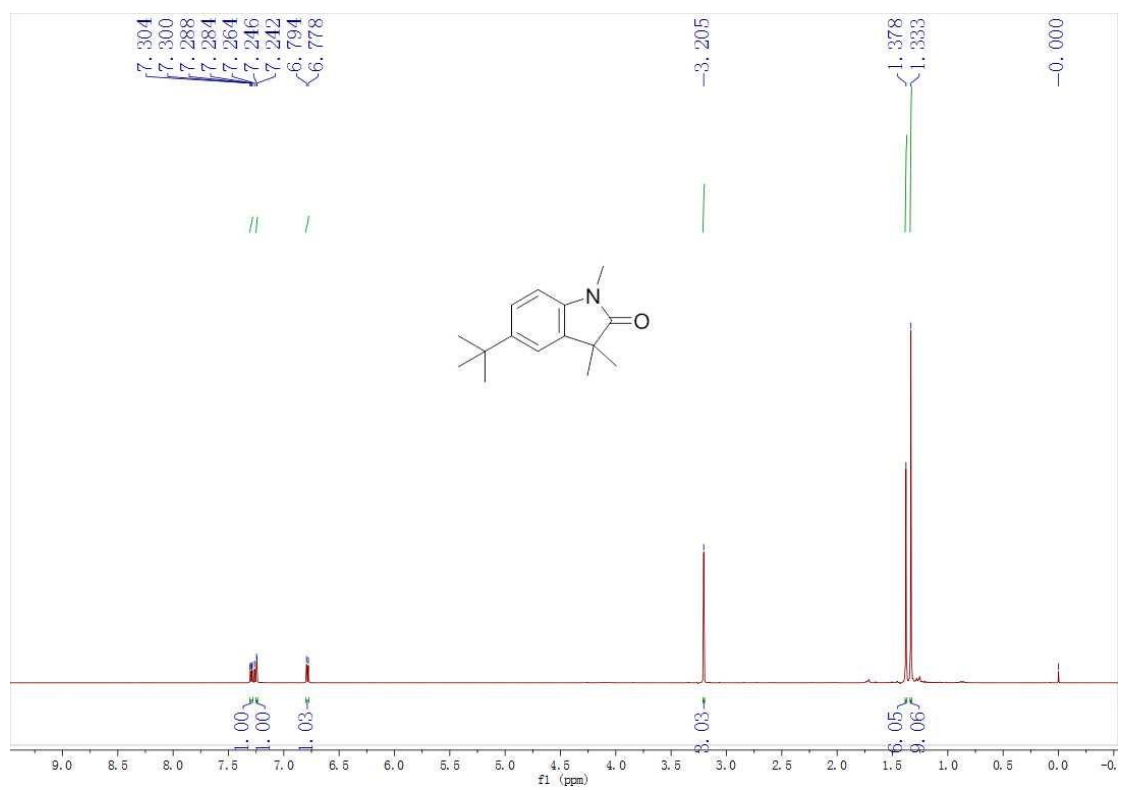
### 1-Benzyl-5-methoxy-3,3-dimethylindolin-2-one (3pa)



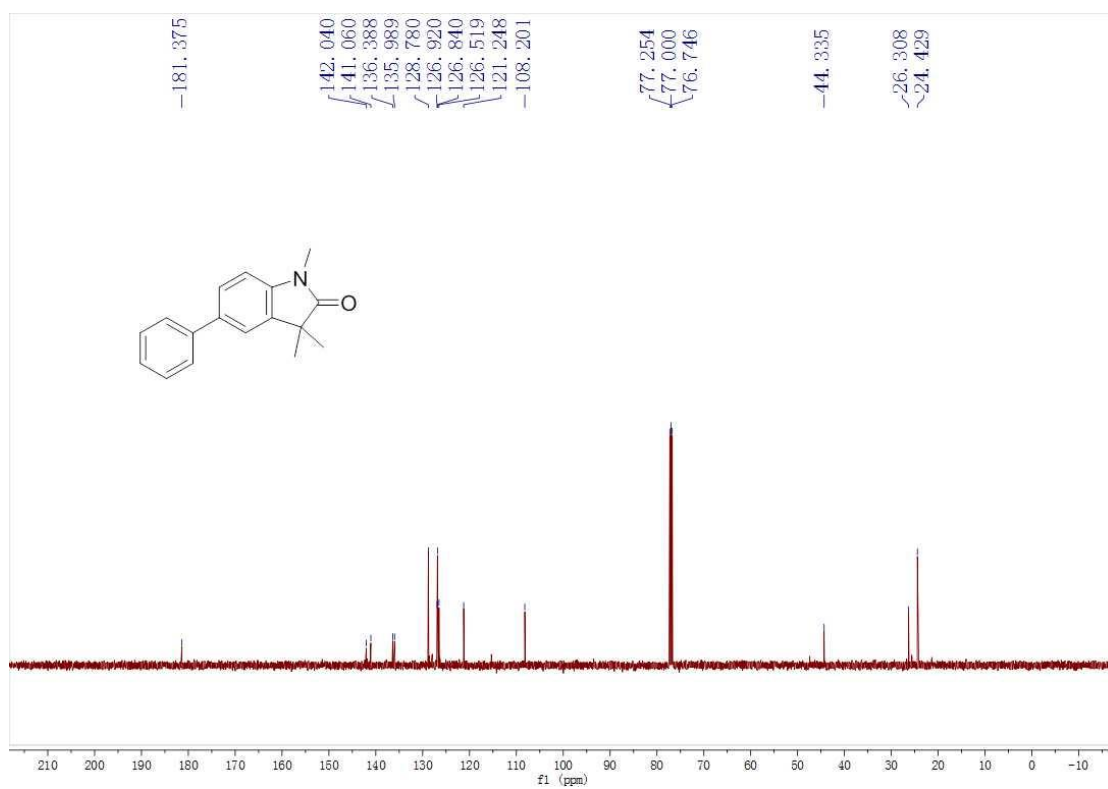
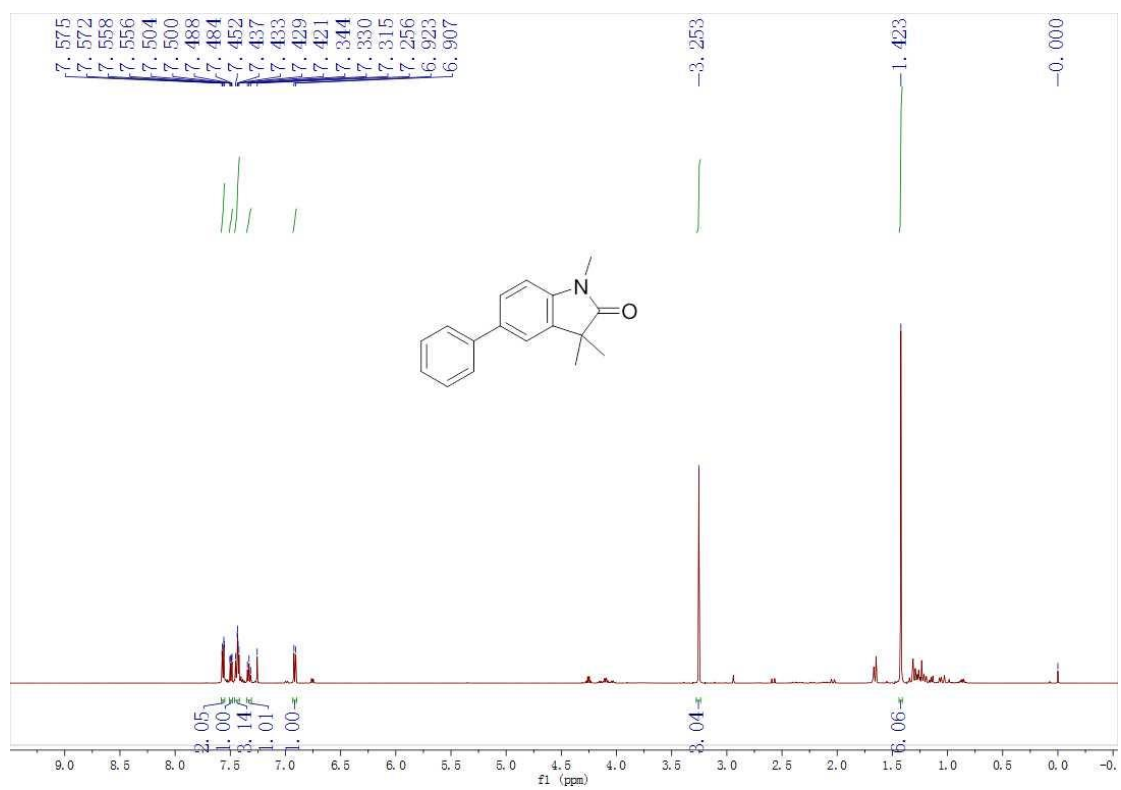
### 1,3,3,5-Tetramethylindolin-2-one (3qa)



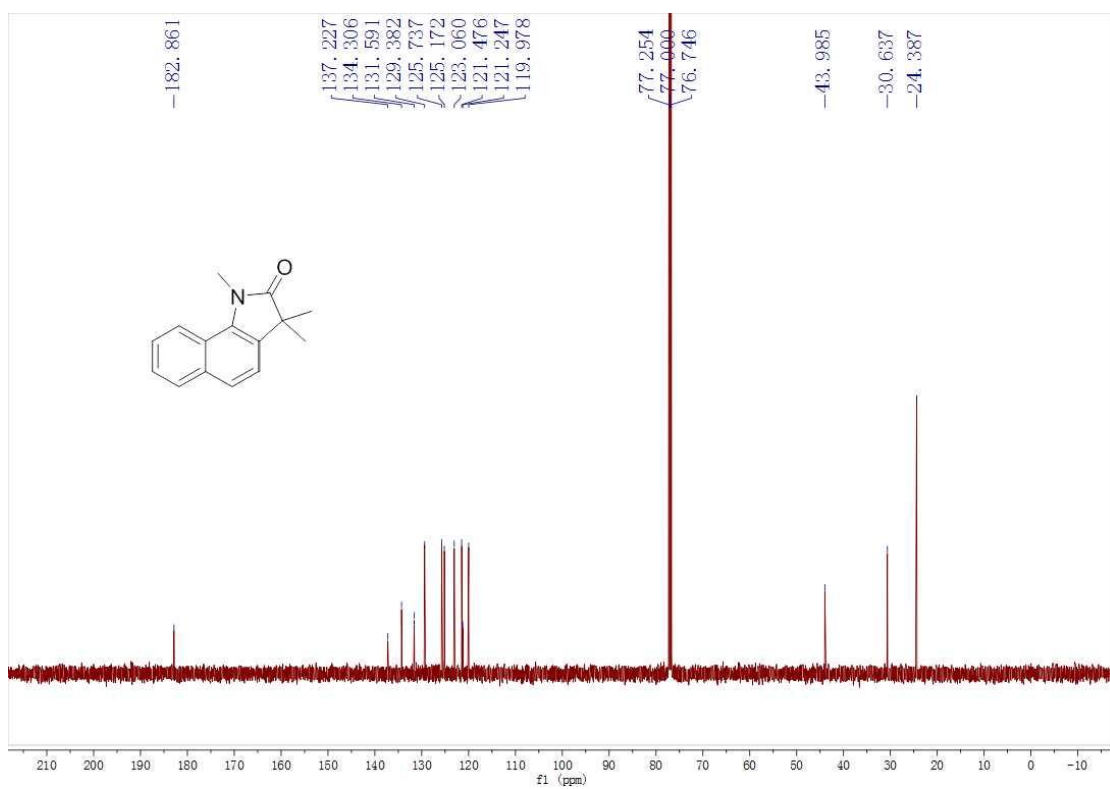
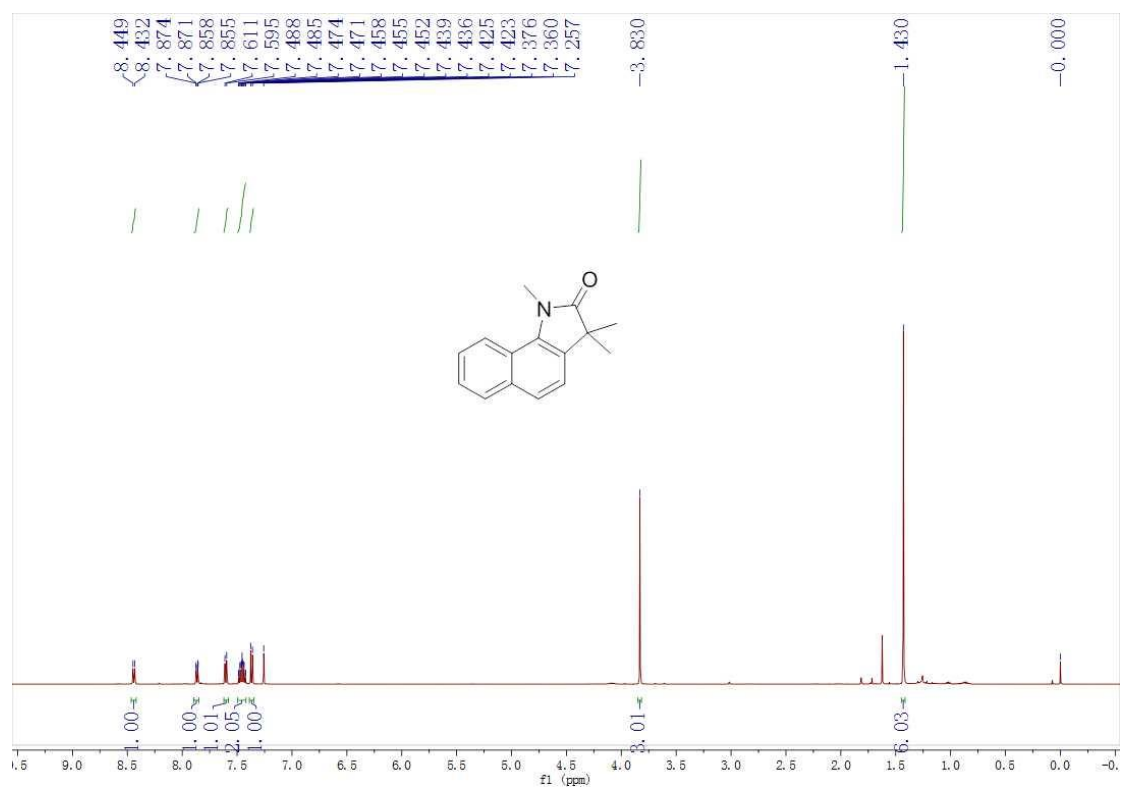
**5-(Tert-butyl)-1,3,3-trimethylindolin-2-one (3ra)**



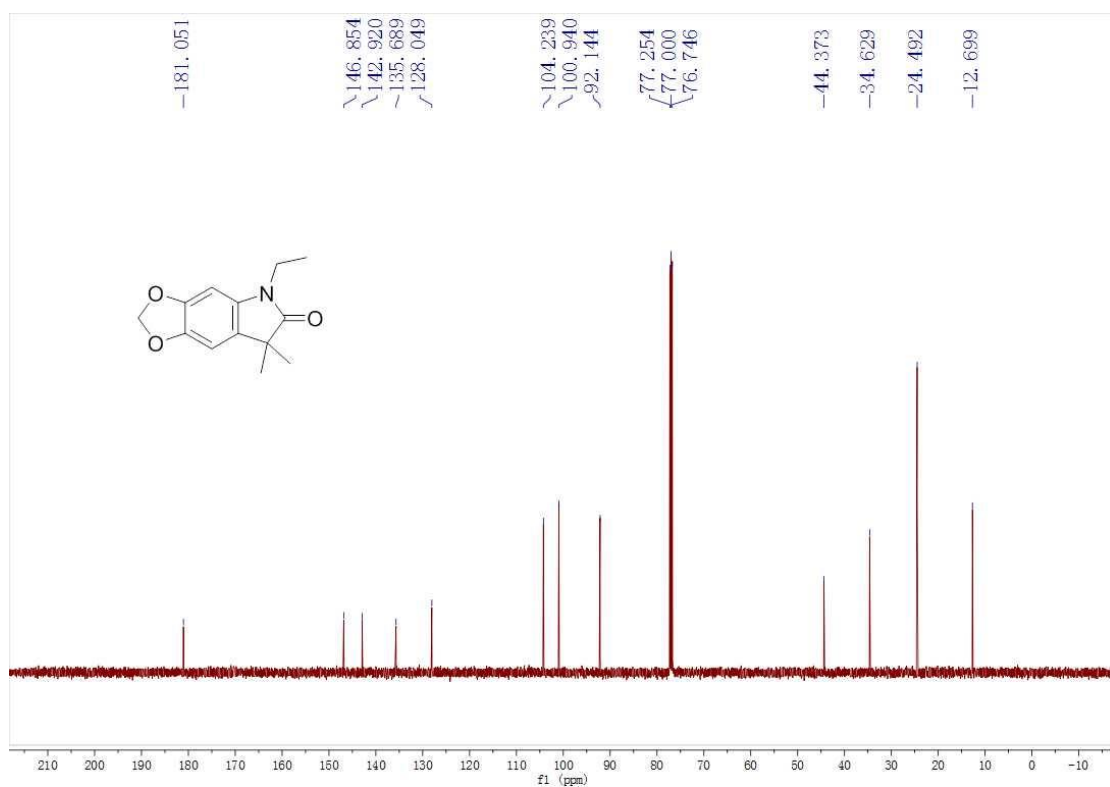
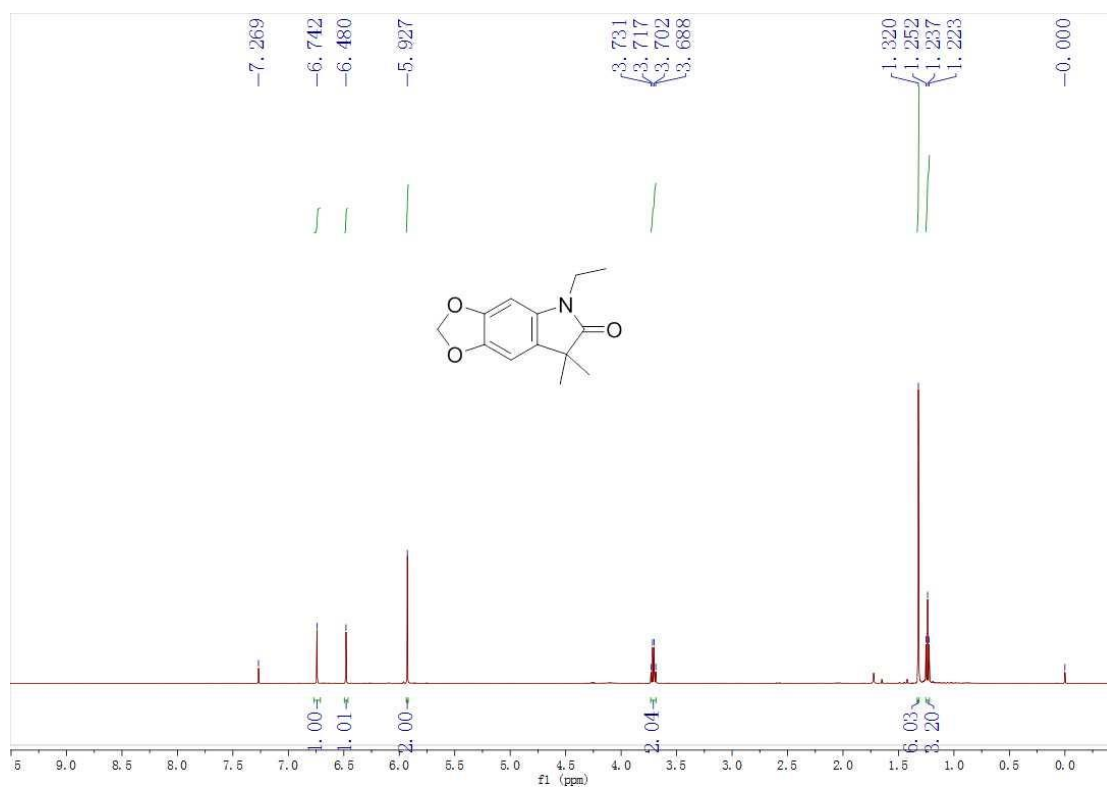
### 1,3,3-Trimethyl-5-phenylindolin-2-one (3sa)



### 1,3,3-Trimethyl-1,3-dihydro-2H-benzo[g]indol-2-one (3ta)

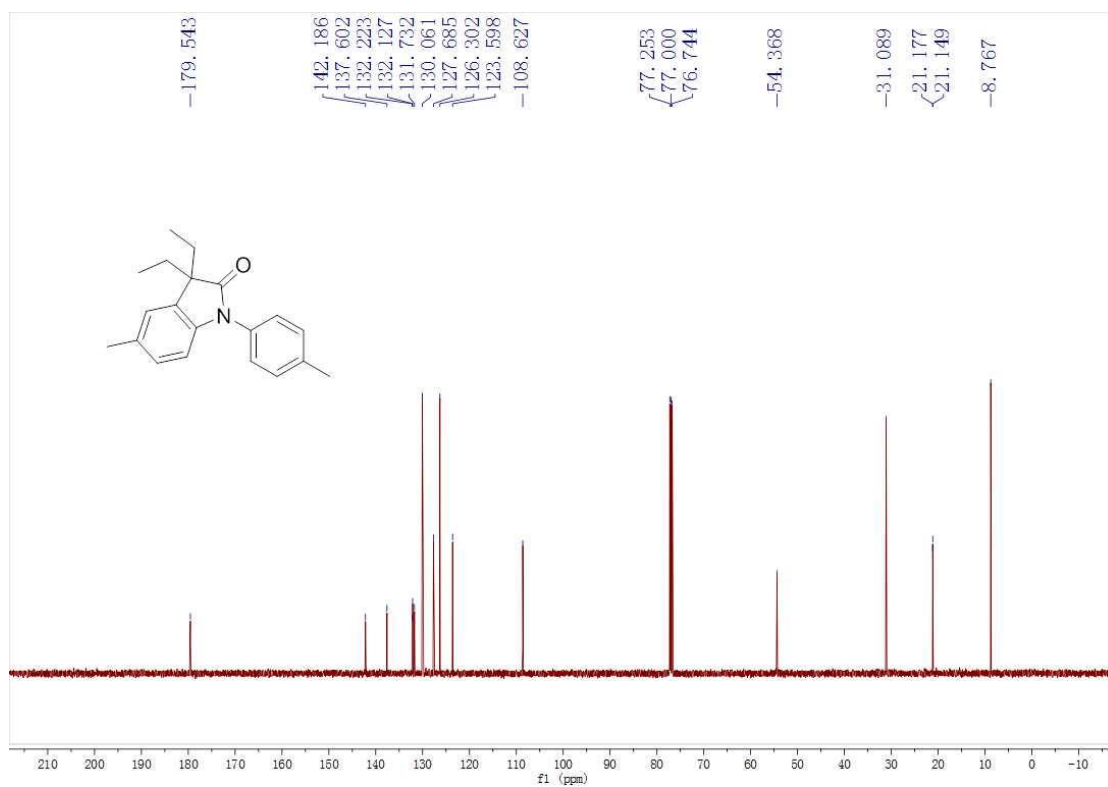
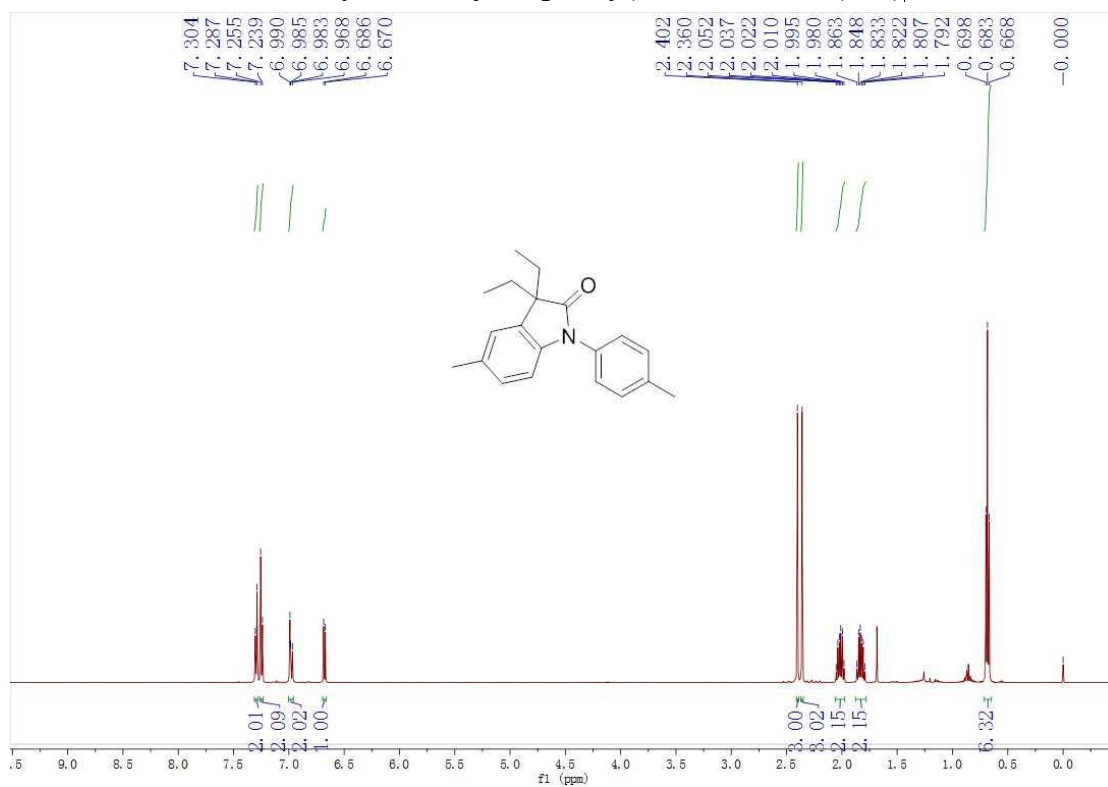


**5-Ethyl-7,7-dimethyl-5,7-dihydro-6H-[1,3]dioxolo[4,5-f]indol-6-one (3ua):**

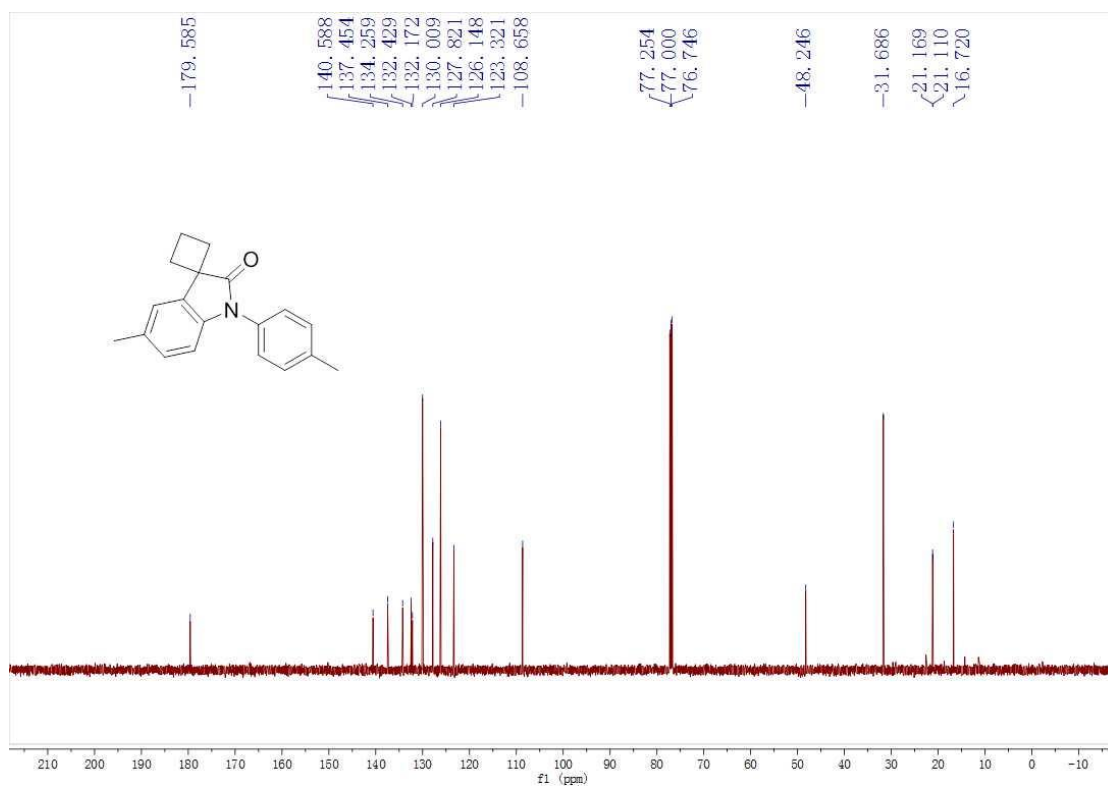
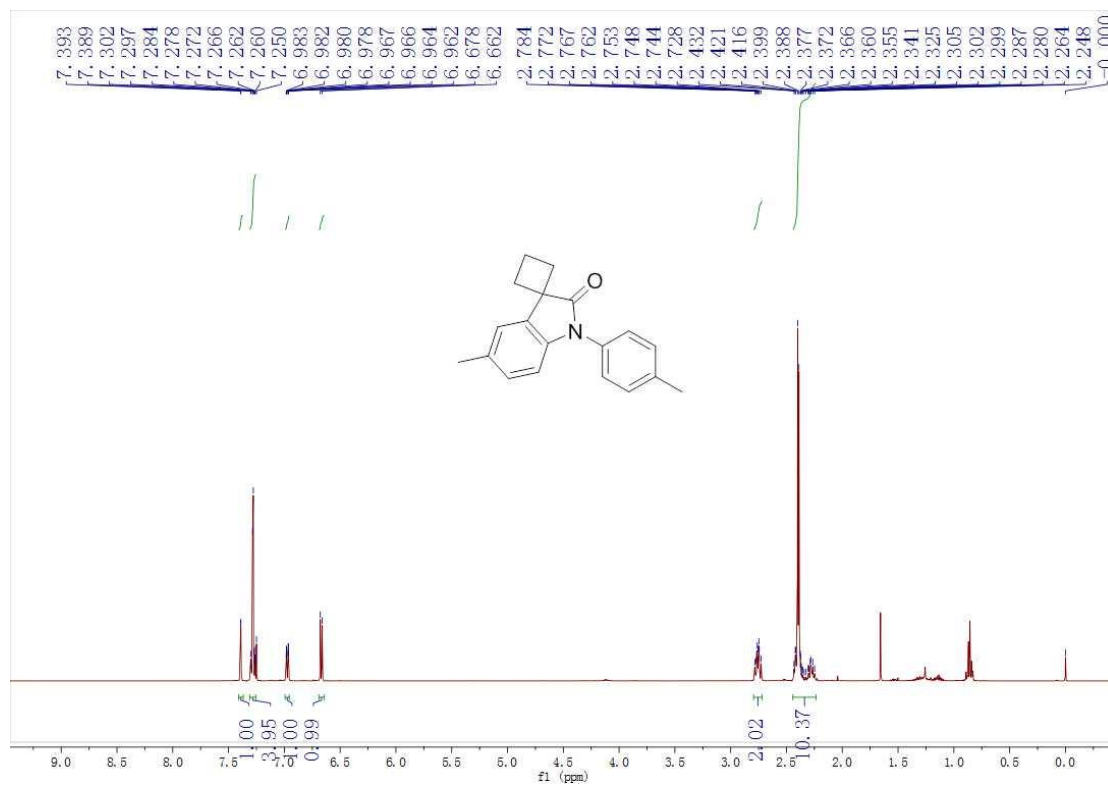




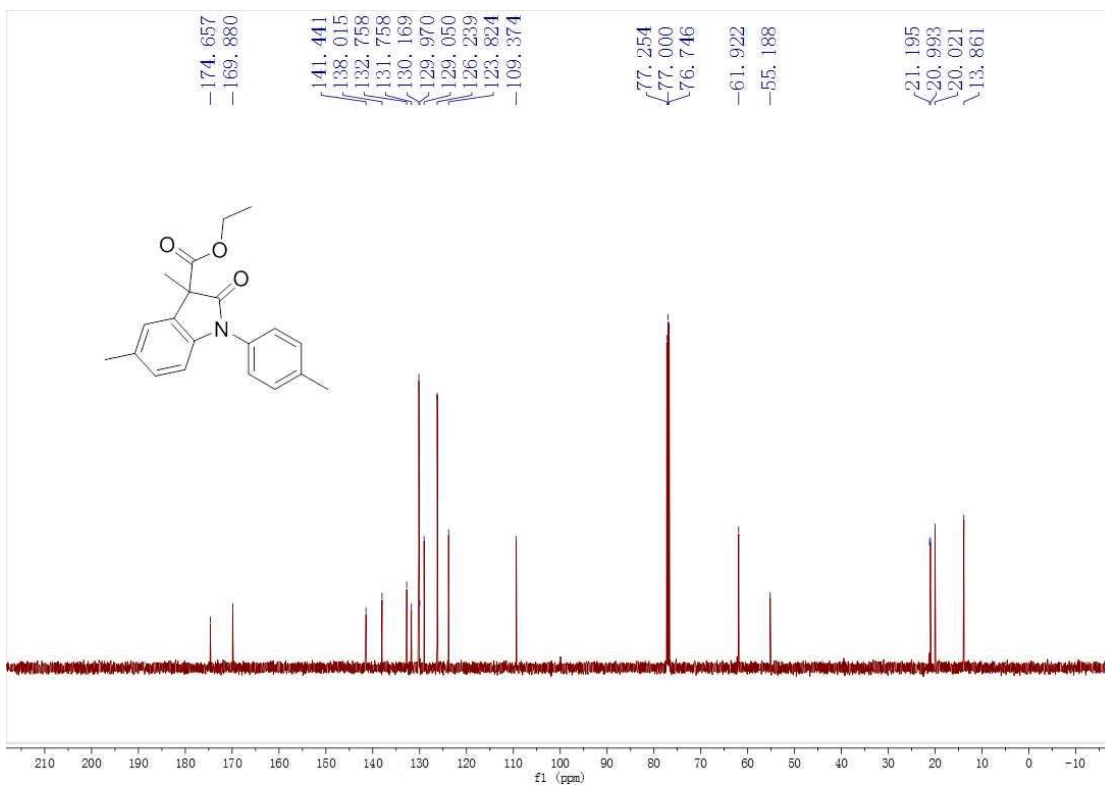
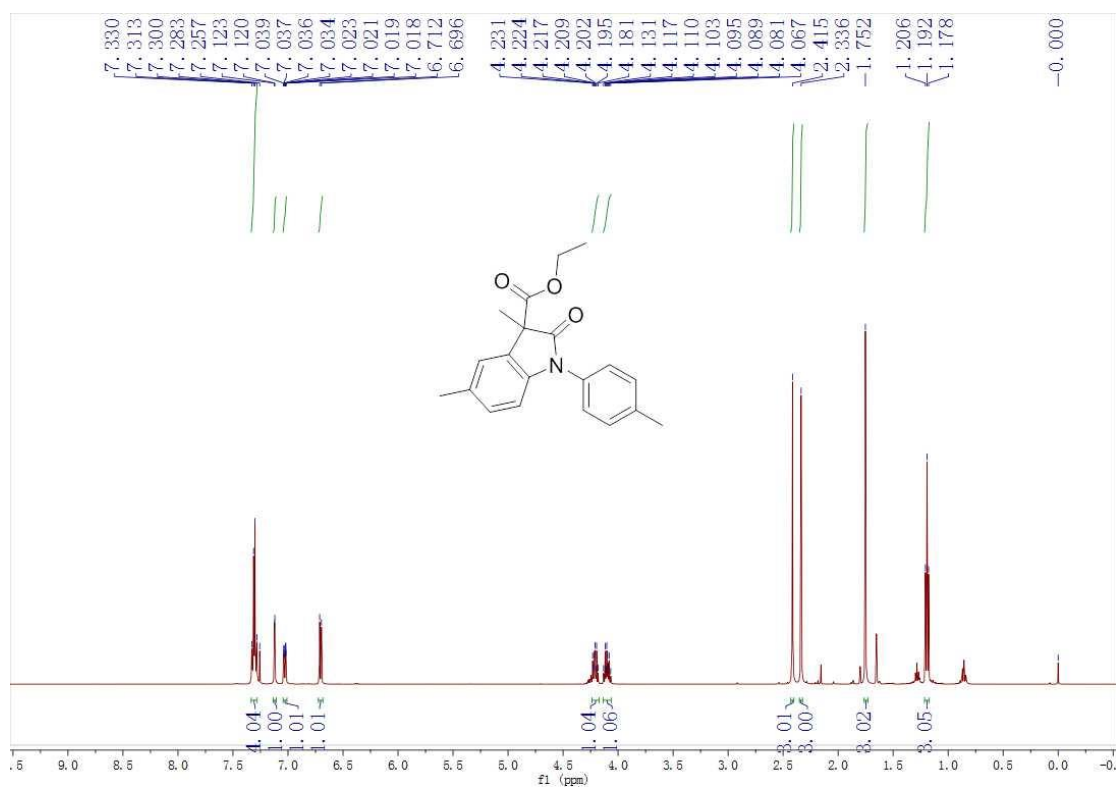
### 3,3-Diethyl-5-methyl-1-(*p*-tolyl)indolin-2-one (3ab)



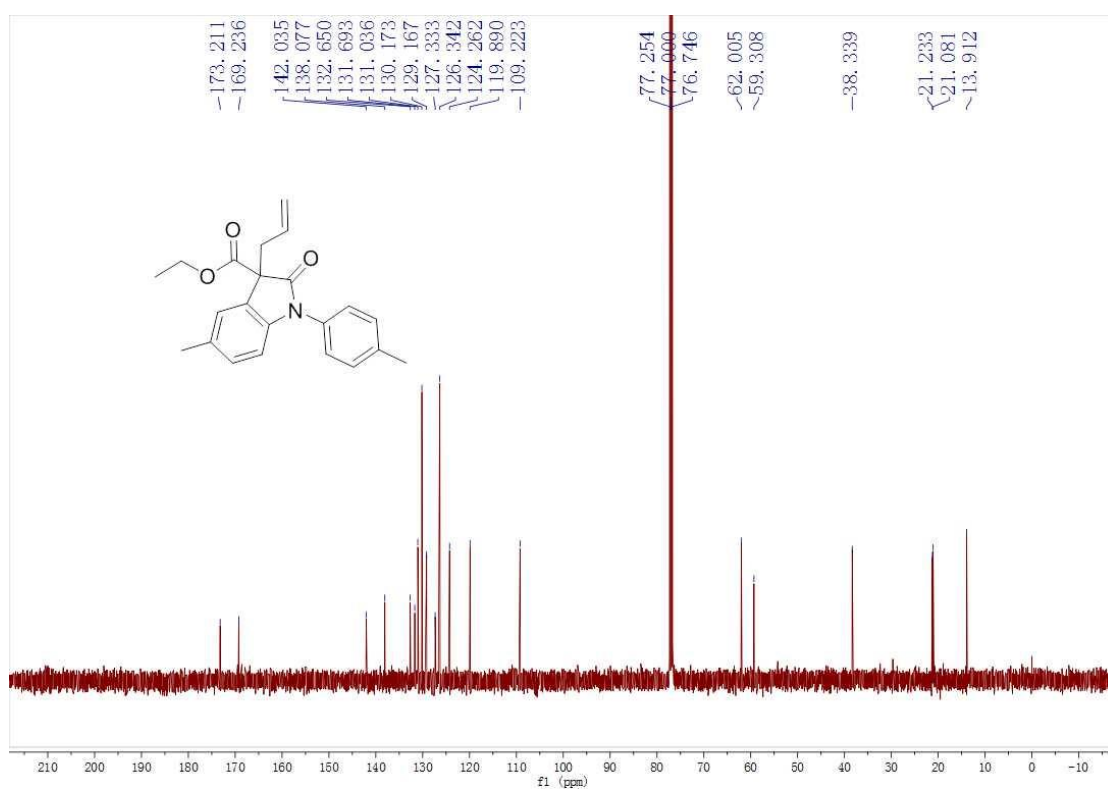
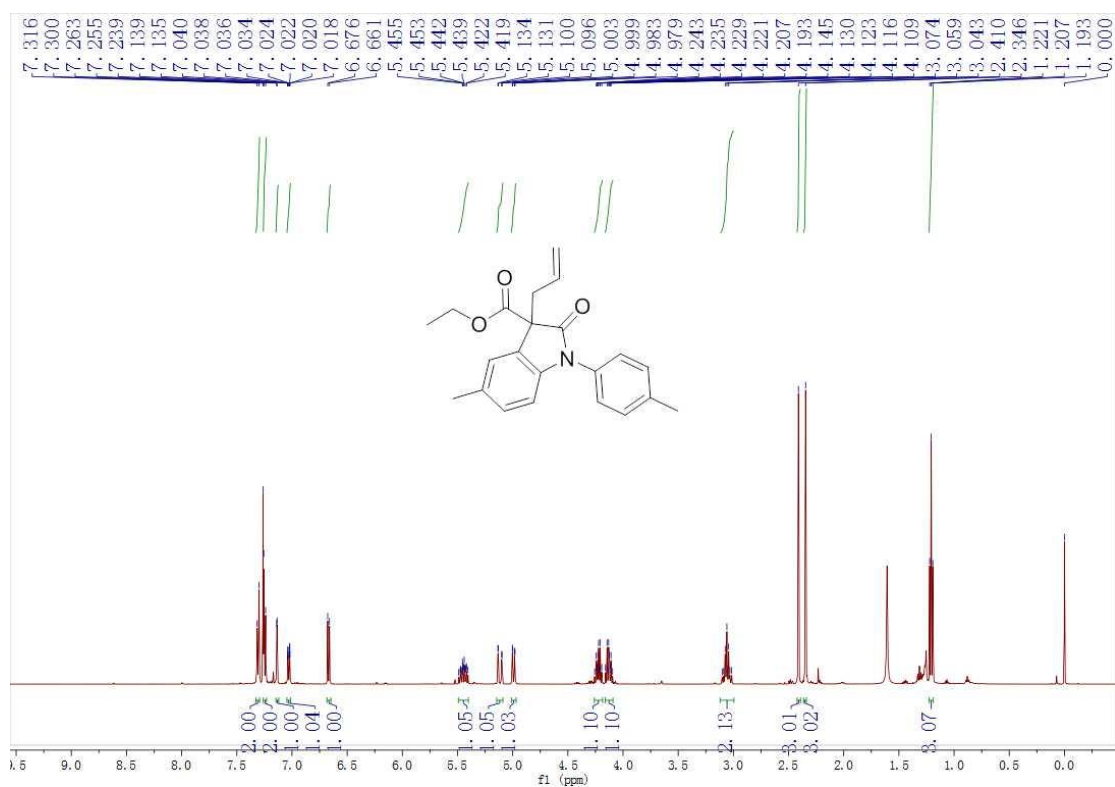
**5'-Methyl-1'-(*p*-tolyl)spiro[cyclobutane-1,3'-indolin]-2'-one (3ac)**



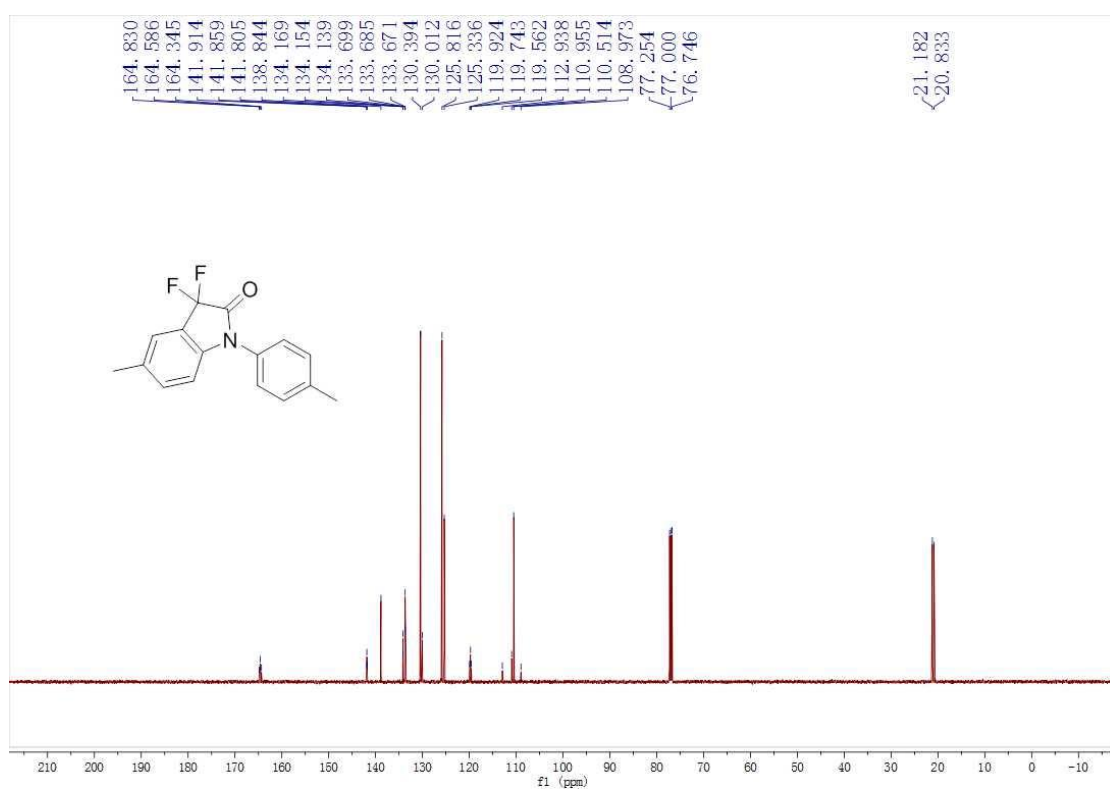
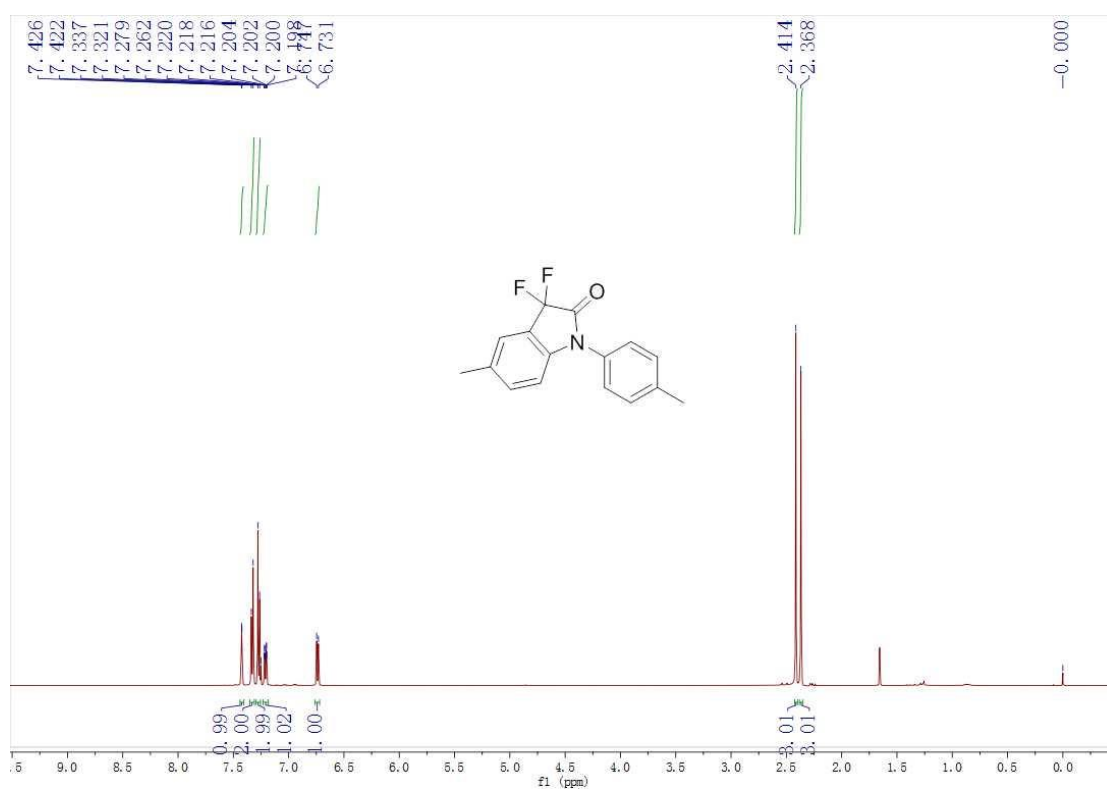
**Ethyl 3,5-dimethyl-2-oxo-1-(*p*-tolyl)indoline-3-carboxylate (3ad)**

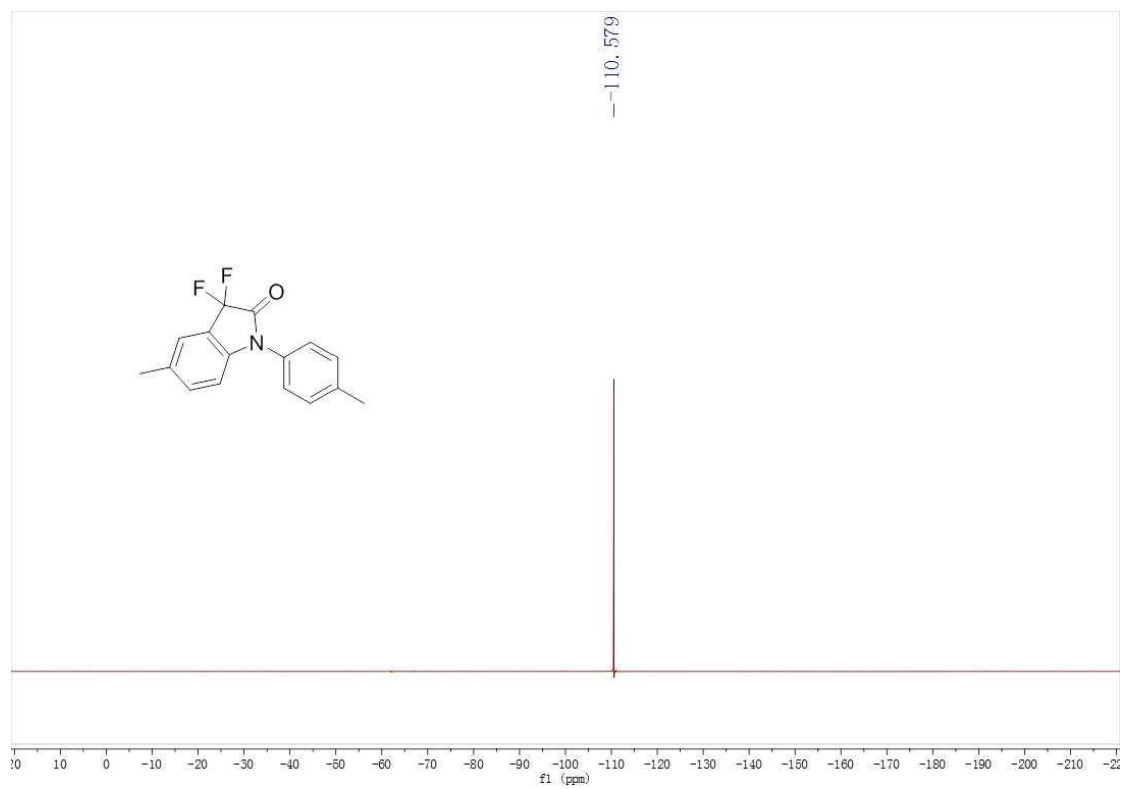


**Ethyl 3-allyl-5-methyl-2-oxo-1-(*p*-tolyl)indoline-3-carboxylate (3ae)**

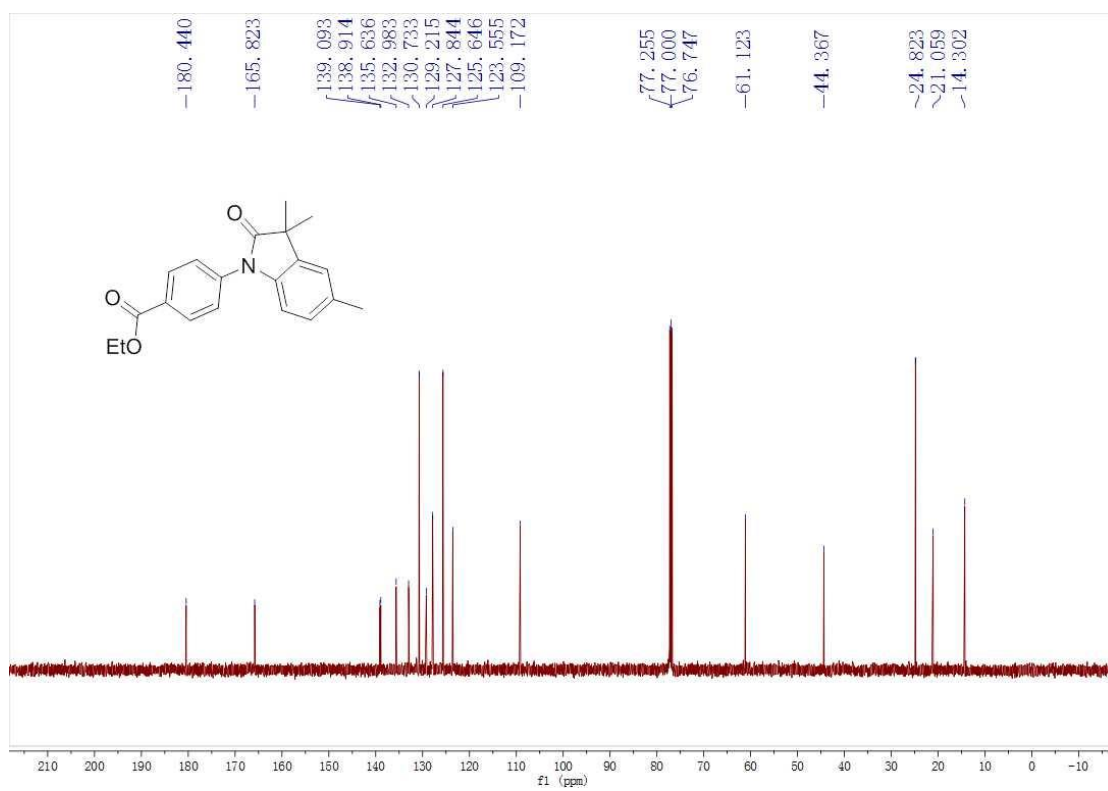
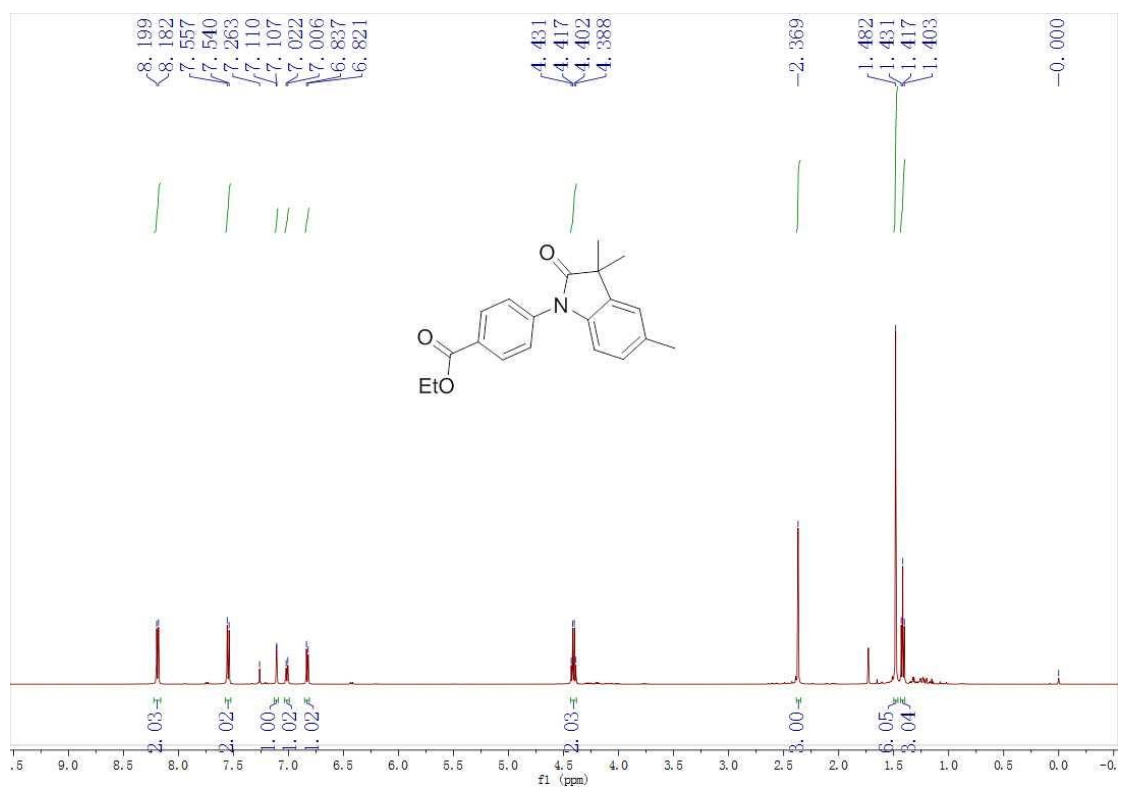


### 3,3-Difluoro-5-methyl-1-(*p*-tolyl)indolin-2-one (3af)

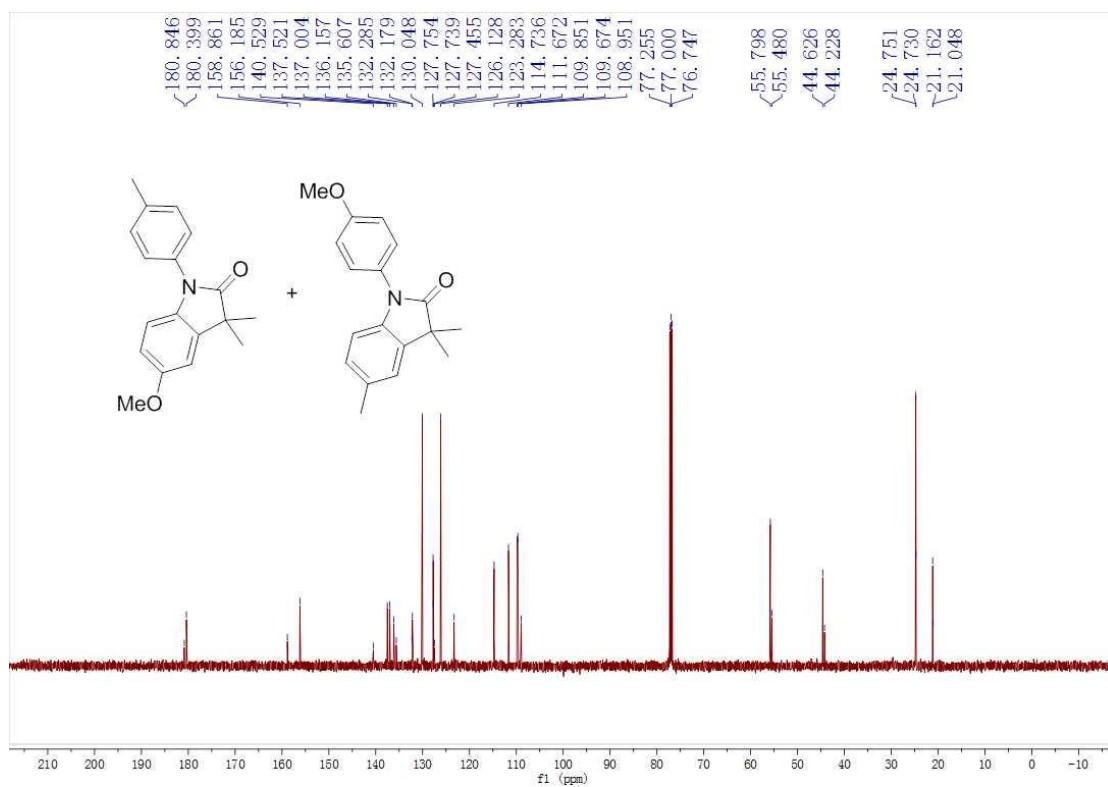
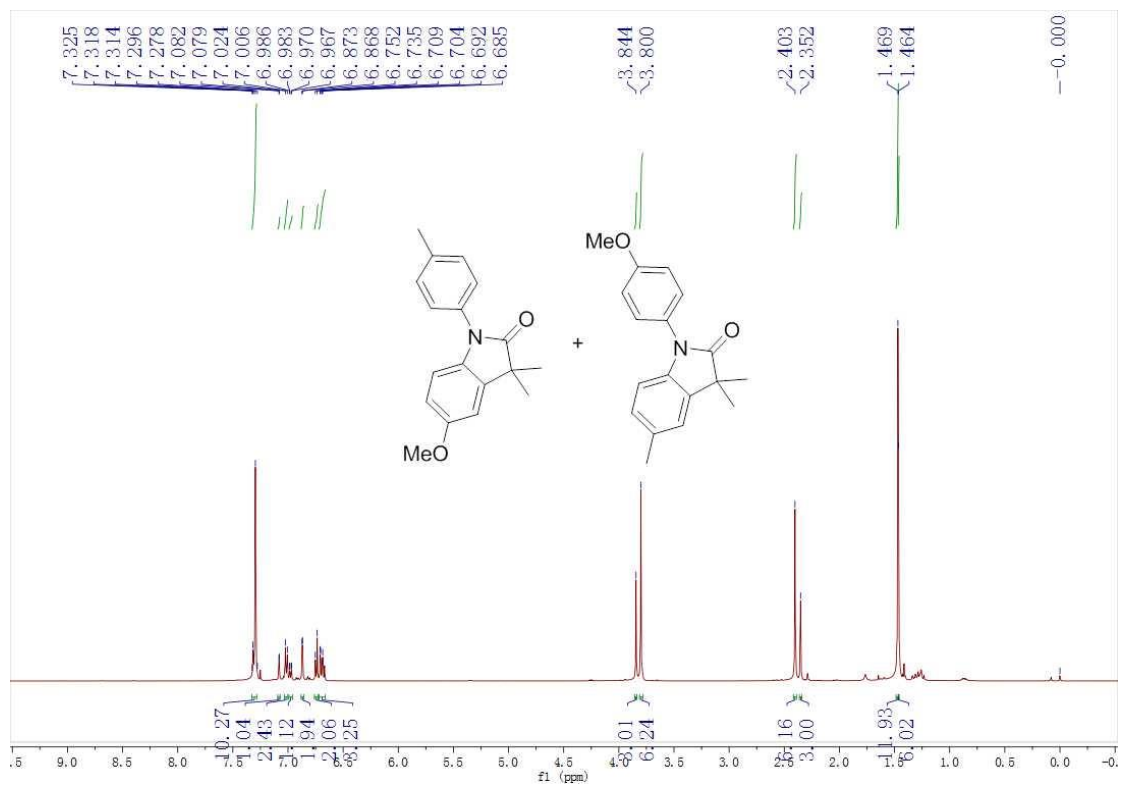




### Ethyl 4-(3,3,5-trimethyl-2-oxindolin-1-yl)benzoate (3va)

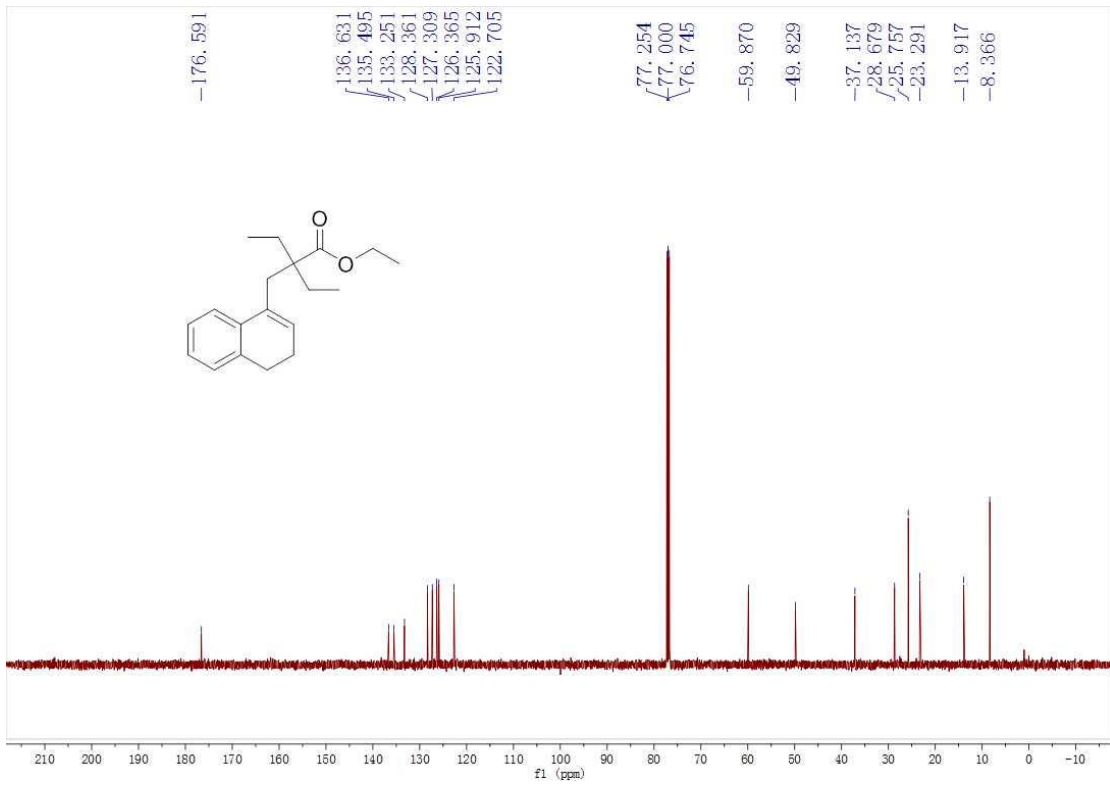
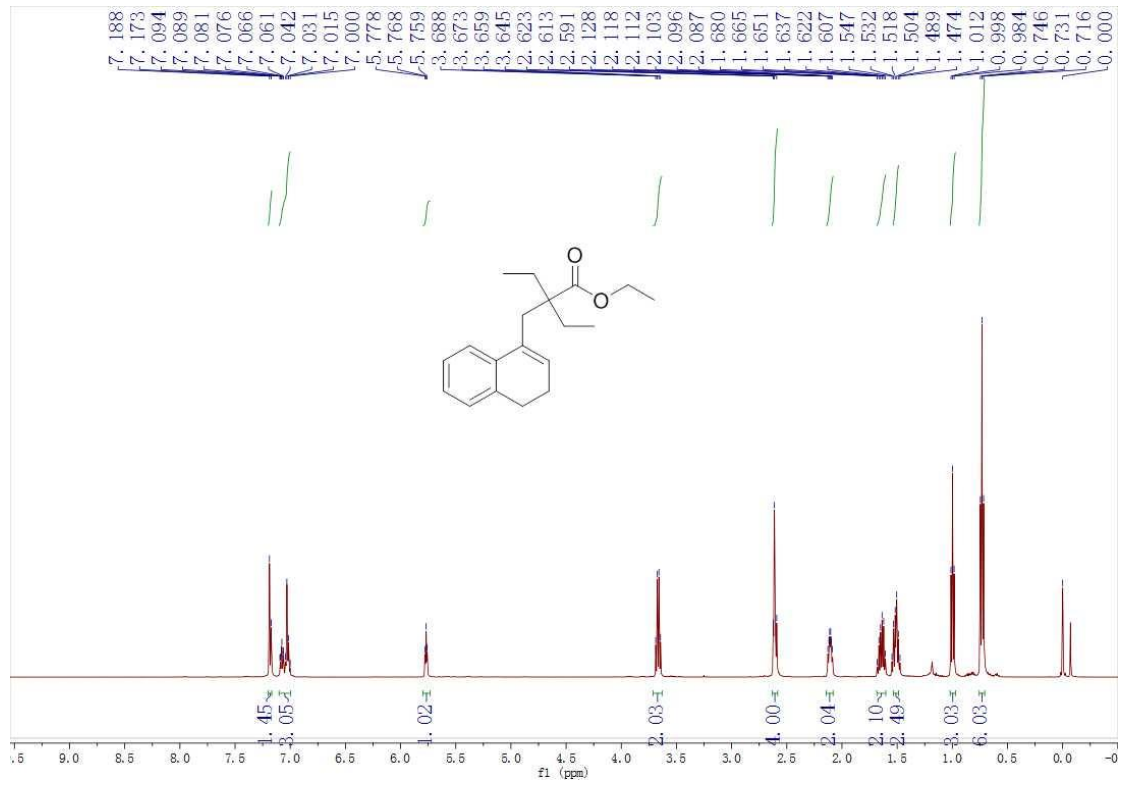


**5-Methoxy-3,3-dimethyl-1-(*p*-tolyl)indolin-2-one (3wa) and  
1-(4-Methoxyphenyl)-3,3,5-trimethylindolin-2-one (3wa')**

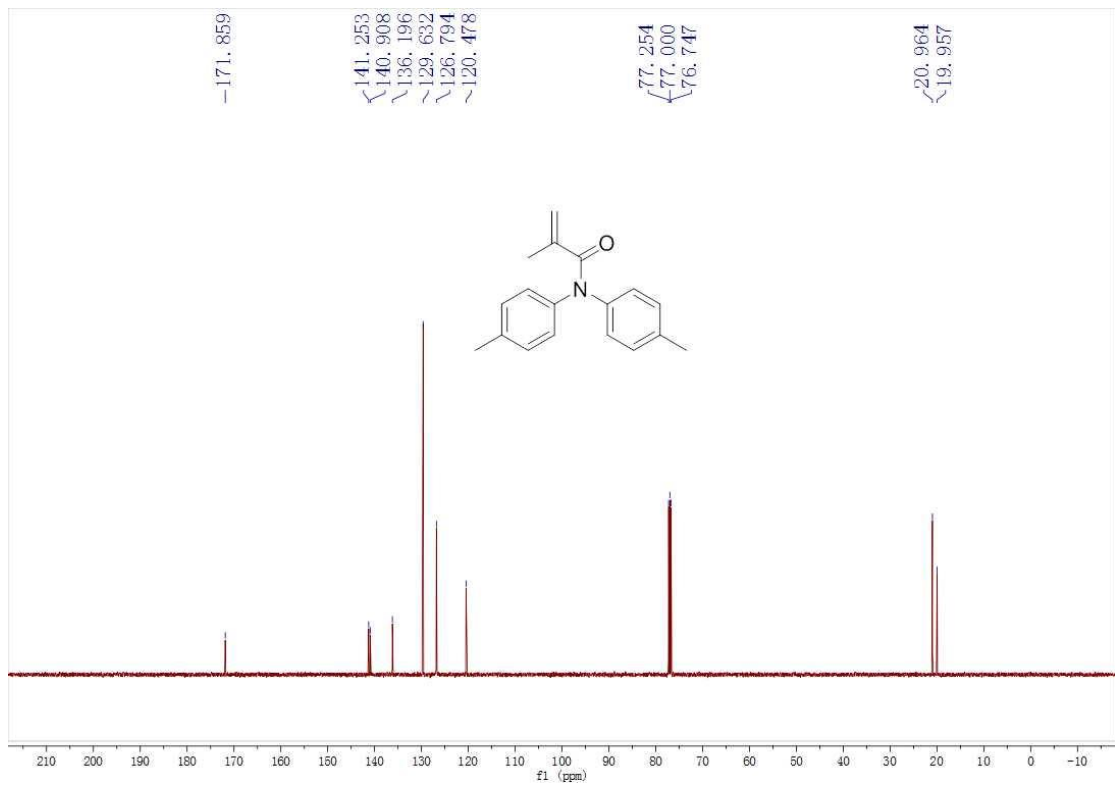
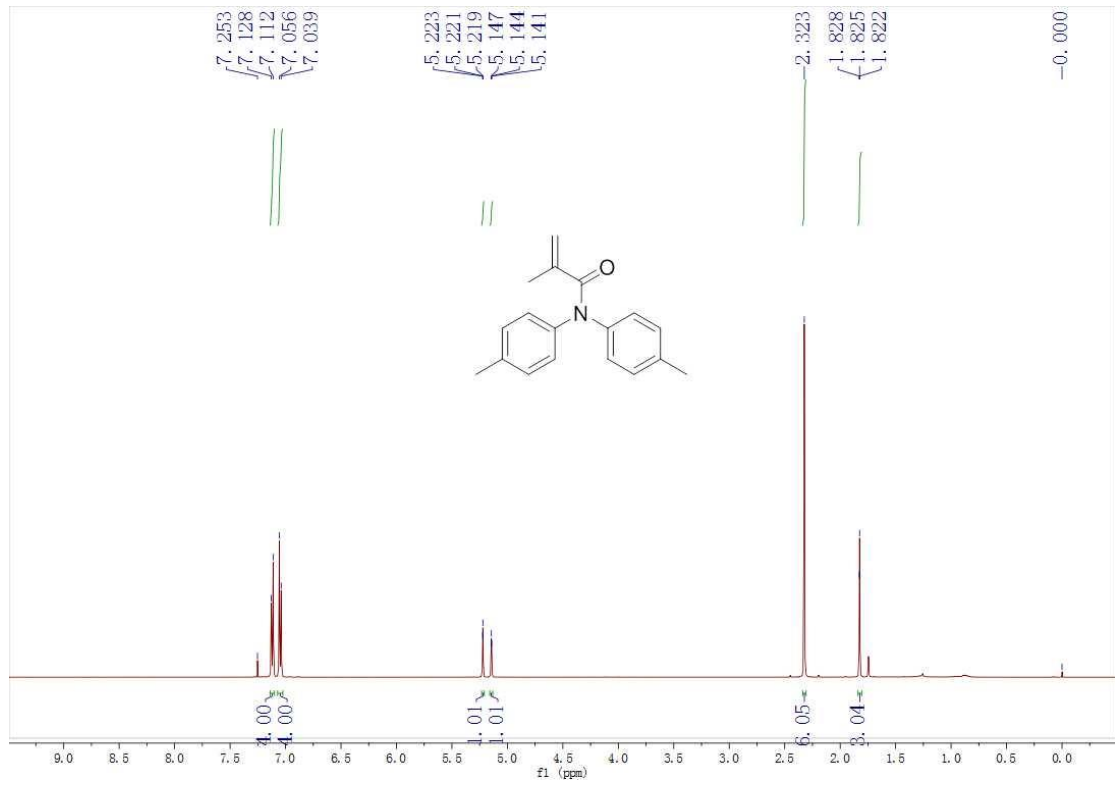




**Ethyl 2-((3,4-dihydronaphthalen-1-yl)methyl)-2-ethylbutanoate (4)**



**N,N-di-*p*-tolylmethacrylamide (6)**



**(D) The X-ray single-crystal diffraction analysis of 3ba**

**(CCDC 1963875)**

