

**Supporting information**

**Synthesis of Carbonyl-Containing Oxindoles via Ni-Catalyzed Reductive Aryl-Acylation and Aryl-Esterification of Alkenes**

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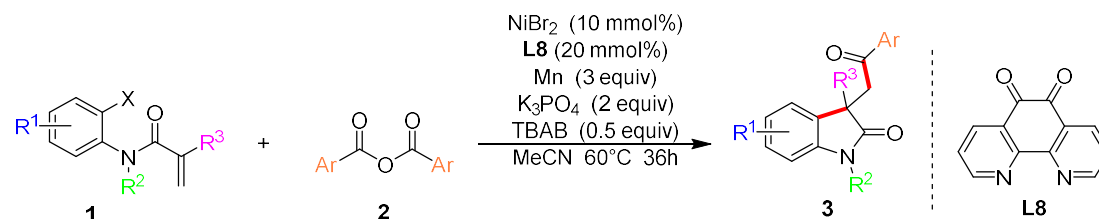
## 1. General information

$^1\text{H}$  and  $^{13}\text{C}$  NMR data were recorded with Bruker ADVANCE III (600 MHz) or JNM-ECZ400S/L1 (400 MHz) spectrometers. Chemical shifts are given in ppm. The spectra are calibrated to the residual  $^1\text{H}$  and  $^{13}\text{C}$  signals of the solvents. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), doublet-doublet (dd), quintet (quint), septet (sept), multiplet (m), and broad (b).  $^{19}\text{F}$  NMR spectra were recorded using  $\text{CFCl}_3$  as internal standard. Gas chromatography were determined with a SHIMADZU Nexis GC 2030 gas chromatography instrument with an FID detector. High-resolution mass spectra (HRMS) were recorded on Thermo Fisher Orbitrap Elite mass spectrometer. Column and elution details were specified in each entry.

Unless otherwise stated, starting materials were purchased from commercial suppliers (Energy Chemical, Alfa, Aldrich and so on). All reactions dealing with air- or moisture-sensitive compounds were performed in the argon-filled glove box or by standard Schlenk techniques in oven-dried reaction vessels under argon atmosphere. Solvents were purchased in HPLC quality, degassed by purging thoroughly with argon and dried over activated molecular sieves of appropriate size. More sensitive compounds were stored in a desiccator or in a glove-box if required. Reactions were monitored by thin layer chromatography (TLC) using glass 0.25 mm silica gel plates. Compounds were visualized by UV-light at 254 nm and by dipping the plates in an aqueous potassium permanganate solution followed by heating. Flash column chromatography was performed over silica gel (200-400 mesh).

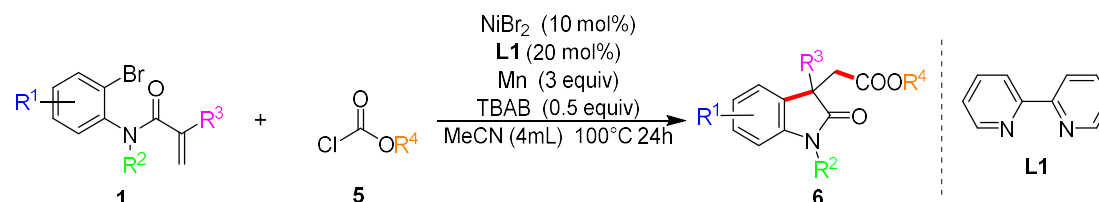
## 2. General procedure

### 2.1 General Procedure for the synthesis of ketones



An oven-dried sealed tube equipped with a PTFE-coated stir bar was charged with  $NiBr_2$  (10 mol%), 1,10-phenanthroline-5,6-dione (**L8**) (20 mol%), **1** (0.1 mmol, 1.0 equiv), manganese powder (3.0 equiv), TBAB (0.5 equiv) and  $K_3PO_4$  (2.0 equiv). The sealed tube was evacuated and backfilled with argon (this process was repeated for three times) and then MeCN (0.05 M) was added. This reaction mixture was stirred at room temperature for 15 minutes and then aryl anhydride **2** (2.0 equiv) was added. The reaction was heated at 60 °C until the reaction was complete (monitored by TLC). The resulting mixture was purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:20~1:5 (v/v) to afford the corresponding products **3**.

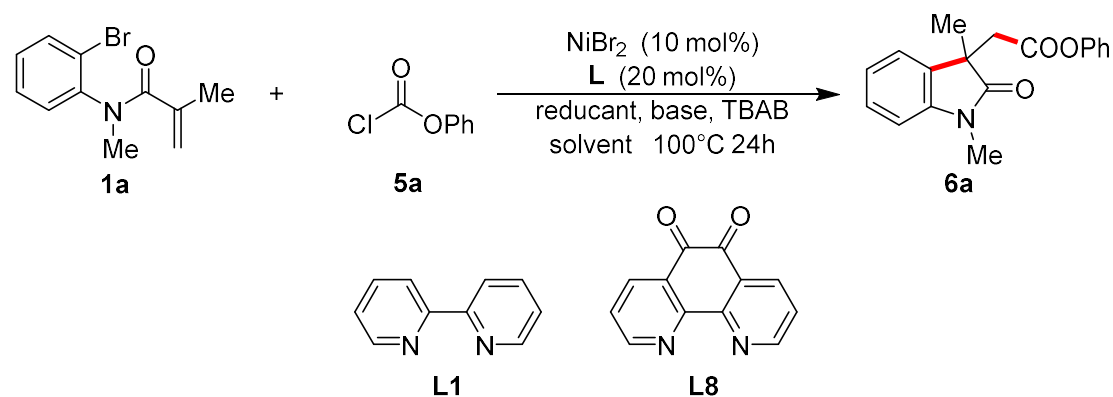
### 2.2 General Procedure for the synthesis of esters



An oven-dried sealed tube equipped with a PTFE-coated stir bar was charged with  $NiBr_2$  (10 mol%), bpy (**L1**) (20 mol%), **1** (0.1 mmol, 1.0 equiv), manganese powder (3.0 equiv) and TBAB (0.5 equiv). The sealed tube was evacuated and backfilled with argon (this process was repeated for three times) and then MeCN (0.025 M) was added. This reaction mixture was stirred at room temperature for 15 minutes and then acid chloride **5** (2.0~4.0 equiv) was added. Then, the reaction heated at 100 °C until the reaction was complete (monitored by TLC). The resulting mixture was purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:20~1:5 (v/v) to afford the corresponding products **6**.

### 3. Optimization of reaction conditions

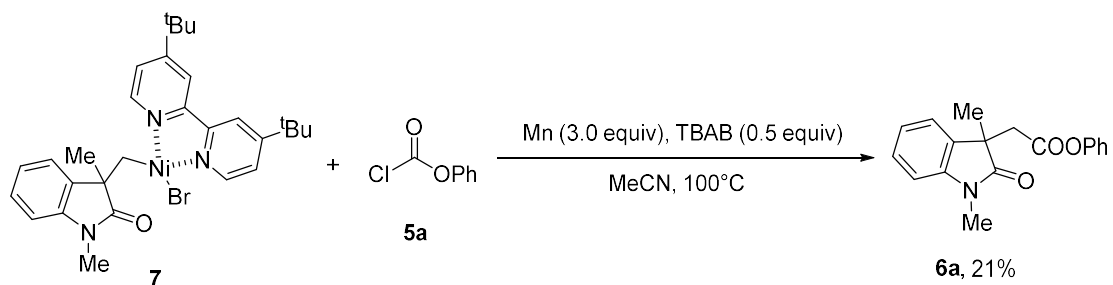
**Table S1: Optimization reaction conditions for the synthesis of esters**



entry	<b>L</b>	reductant	solvent	base	yield of <b>6a</b> (%) <sup>b</sup>
1	<b>L8</b>	Mn	MeCN	K <sub>3</sub> PO <sub>4</sub>	51
2	<b>L8</b>	Mn	DMF	K <sub>3</sub> PO <sub>4</sub>	<1
3	<b>L8</b>	Mn	DMAc	K <sub>3</sub> PO <sub>4</sub>	<1
4	<b>L8</b>	Zn	MeCN	K <sub>3</sub> PO <sub>4</sub>	17
5	<b>L8</b>	Mn	MeCN	K <sub>3</sub> CO <sub>4</sub>	42
6	<b>L8</b>	Mn	MeCN	Cs <sub>2</sub> CO <sub>3</sub>	52
7	<b>L8</b>	Mn	MeCN	-	53
8 <sup>c</sup>	<b>L8</b>	Mn	MeCN	-	58
9 <sup>c</sup>	<b>L1</b>	Mn	MeCN	-	75
10 <sup>c,d</sup>	<b>L1</b>	Mn	MeCN	-	51
11 <sup>d,e</sup>	<b>L1</b>	Mn	MeCN	-	55

<sup>a</sup> Unless indicated otherwise, reactions of **1a** (0.10 mmol), **5a** (0.40 mmol), NiBr<sub>2</sub> (0.01 mmol), ligand (0.02 mmol), reductant (0.30 mmol), TBAB (0.05 mmol), and K<sub>3</sub>PO<sub>4</sub> (0.20 mmol) were carried out in solvent (2 mL) at 100 °C for 24h. <sup>b</sup>Isolated yields. <sup>c</sup>4mL MeCN was used. <sup>d</sup>80 °C. <sup>e</sup>Without TBAB.

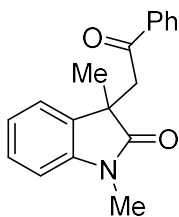
#### 4. Control experiments



**Experimental procedure<sup>[1]</sup>:** An oven-dried seal-tube equipped with a PTFE-coated stir bar was charged with TBAB (0.025 mmol, 8.1 mg), Mn<sup>0</sup> (0.15 mmol, 9.8 mg), complex **7** (0.05 mmol, 29.1 mg) and phenyl carbonochloridate (0.1 mmol, 15.7 mg) in anhydrous MeCN (1 mL). The seal-tube was sealed and removed from the glovebox. Then the reaction was stirred at 100 °C for overnight. The resulting mixture was purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v) to afford the corresponding products **6a** (3.1 mg, 21% yield).

## 5. Characterization data of products

### 1,3-dimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3a)



Chemical Formula: C<sub>18</sub>H<sub>17</sub>NO<sub>2</sub>

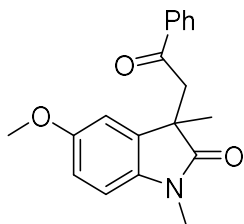
Exact Mass: 279.1259

**3a** was prepared according to general procedure **2.1** using *N*-(2-bromophenyl)-*N*-methylmethacrylamide (0.1 mmol, 25.4 mg) and benzoic anhydride (0.2 mmol, 45.2 mg) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1~5/1) to obtain **3a** as yellow oil (23.7 mg, 85% yield). TLC (petroleum ether: ethyl acetate, 5:1 v/v): R<sub>f</sub> = 0.4. The <sup>1</sup>H NMR data matched those reported in the literature.<sup>[2]</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.87-7.80 (m, 2H), 7.56-7.48 (m, 1H), 7.45-7.36 (m, 2H), 7.28-7.22 (m, 1H), 7.16-7.12 (m, 1H), 7.01-6.95 (m, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 3.72 (d, *J* = 17.9 Hz, 1H), 3.65 (d, *J* = 17.8 Hz, 1H), 3.31 (s, 3H), 1.44 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 196.1, 180.6, 143.8, 136.4, 133.7, 133.2, 128.5, 128.0, 127.8, 122.2, 121.8, 108.2, 46.0, 45.3, 26.5, 24.9.

### 5-methoxy-1,3-dimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3b)



Chemical Formula: C<sub>19</sub>H<sub>19</sub>NO<sub>3</sub>

Exact Mass: 309.14

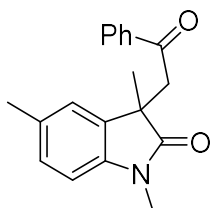
**3b** was prepared according to general procedure **2.1** using *N*-(2-bromo-4-methoxyphenyl)-*N*-methylmethacrylamide (0.1 mmol, 28.4 mg) and benzoic anhydride (0.2 mmol, 45.2 mg) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to obtain **3b** as brown oil (22.9 mg, 74% yield). TLC (petroleum ether: ethyl acetate, 5:1 v/v): R<sub>f</sub>

= 0.3. The  $^1\text{H}$  NMR data matched those reported in the literature.<sup>[2]</sup>

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91-7.79 (m, 2H), 7.57-7.46 (m, 1H), 7.46-7.32 (m, 2H), 6.86-6.79 (m, 1H), 6.79-6.71 (m, 2H), 3.73 (s, 3H), 3.67 (s, 2H), 3.29 (s, 3H), 1.43 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  196.0, 155.6, 137.4, 136.2, 135.1, 133.2, 128.4, 127.9, 111.3, 109.8, 108.3, 55.6, 45.9, 45.6, 26.5, 25.0.

### 1,3,5-trimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3c)



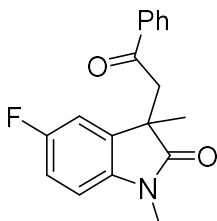
Chemical Formula:  $\text{C}_{19}\text{H}_{19}\text{NO}_2$   
Exact Mass: 293.1416

**3c** was prepared according to general procedure **2.1** using *N*-(2-bromo-4-methylphenyl)-*N*-methylmethacrylamide (0.1 mmol, 26.8 mg) and benzoic anhydride (0.2 mmol, 45.2 mg) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate =5/1) to obtain **3c** as yellow oil (23.7 mg, 81% yield). TLC (petroleum ether: ethyl acetate, 5:1 v/v):  $R_f$  = 0.4. The  $^1\text{H}$  NMR data matched those reported in the literature.<sup>[3]</sup>

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90-7.81 (m, 2H), 7.56-7.48 (m, 1H), 7.44-7.36 (m, 2H), 7.09-7.02 (m, 1H), 6.97-6.92 (m, 1H), 6.79 (d,  $J$  = 7.9 Hz, 1H), 3.75-3.59 (m, 2H), 3.29 (s, 3H), 2.27 (s, 3H), 1.43 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  196.1, 180.5, 141.4, 136.4, 133.7, 133.1, 131.6, 128.5, 128.1, 128.0, 122.7, 107.8, 46.0, 45.3, 26.5, 25.0, 21.1.

### 5-fluoro-1,3-dimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3d)



Chemical Formula:  $\text{C}_{18}\text{H}_{16}\text{FNO}_2$   
Exact Mass: 297.12



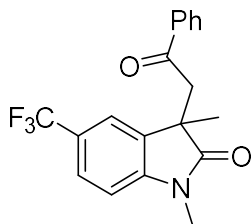
**3d** was prepared according to general procedure **2.1** using *N*-(2-bromo-4-fluorophenyl)-*N*-methylethylmethacrylamide (0.1 mmol, 27.2 mg) and benzoic anhydride (0.2 mmol, 45.2 mg) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate =10:1~5/1) to obtain **3d** as yellow oil (26.7 mg, 90% yield). TLC (petroleum ether: ethyl acetate, 5:1 v/v): R<sub>f</sub> = 0.4. The <sup>1</sup>H NMR data matched those reported in the literature.<sup>[4]</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.89-7.79 (m, 2H), 7.58-7.49 (m, 1H), 7.46-7.37 (m, 2H), 7.02-6.92 (m, 1H), 6.90 (dd, *J* = 8.0, 2.5 Hz, 1H), 6.82 (dd, *J* = 8.5, 4.2 Hz, 1H), 3.67 (s, 2H), 3.30 (s, 3H), 1.44 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 195.9, 180.2, 157.9, 139.8, 136.1, 135.4 (d, *J* = 7.8 Hz), 133.3, 128.6, 127.9, 113.8 (d, *J* = 23.3 Hz), 110.1 (d, *J* = 24.9 Hz), 108.5 (d, *J* = 8.2 Hz), 46.0, 45.7, 26.6, 24.8.

<sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) δ -121.1 (s).

### 1,3-dimethyl-3-(2-oxo-2-phenylethyl)-5-(trifluoromethyl)indolin-2-one (**3e**)



Chemical Formula: C<sub>19</sub>H<sub>16</sub>F<sub>3</sub>NO<sub>2</sub>  
Exact Mass: 347.11

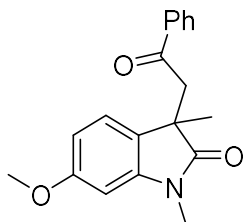
**3e** was prepared according to general procedure **2.1** using *N*-(2-bromo-4-(trifluoromethyl)phenyl)-*N*-methylethylmethacrylamide (0.1 mmol, 32.2 mg) and benzoic anhydride (0.2 mmol, 45.2 mg) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate =10:1~5/1) to obtain **3e** as yellow solid (18.0 mg, 52% yield). TLC (petroleum ether: ethyl acetate, 5:1 v/v): R<sub>f</sub> = 0.4. m.p. 114.5-115.9 °C. The <sup>1</sup>H NMR data matched those reported in the literature.<sup>[5]</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.90-7.80 (m, 2H), 7.59-7.50 (m, 2H), 7.46-7.38 (m, 2H), 7.34 (d, *J* = 1.8 Hz, 1H), 6.98 (d, *J* = 8.2 Hz, 1H), 3.75 (s, 2H), 3.36 (s, 3H), 1.45 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 195.8, 180.5, 146.9, 135.8, 134.4, 133.5, 128.6, 127.9, 125.7 (d, *J* = 4.0 Hz), 118.5, 107.9, 46.1, 45.1, 26.7, 24.9.

$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -61.2 (s).

**6-methoxy-1,3-dimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3f)**



Chemical Formula:  $\text{C}_{19}\text{H}_{19}\text{NO}_3$

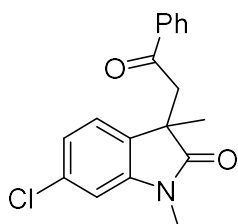
Exact Mass: 309.14

**3f** was prepared according to general procedure **2.1** using *N*-(2-bromo-5-methoxyphenyl)-*N*-methylmethacrylamide (0.1 mmol, 28.4 mg) and benzoic anhydride (0.2 mmol, 45.2 mg) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1~5/1) to obtain **3f** as yellow oil (19.5 mg, 63% yield). TLC (petroleum ether: ethyl acetate, 5:1 v/v):  $R_f$  = 0.3. The  $^1\text{H}$  NMR data matched those reported in the literature.<sup>[5]</sup>

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88-7.80 (m, 2H), 7.54-7.48 (m, 1H), 7.43-7.36 (m, 2H), 7.03 (d,  $J$  = 8.0 Hz, 1H), 6.52-6.44 (m, 2H), 3.80 (s, 3H), 3.69 (d,  $J$  = 17.9 Hz, 1H), 3.60 (d,  $J$  = 17.9 Hz, 1H), 3.29 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  196.3, 181.1, 159.9, 145.0, 136.3, 133.1, 128.4, 127.9, 125.6, 122.3, 105.8, 96.2, 55.4, 46.0, 44.8, 26.4, 25.0.

**6-chloro-1,3-dimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3g)**



Chemical Formula:  $\text{C}_{18}\text{H}_{16}\text{ClNO}_2$

Exact Mass: 313.09

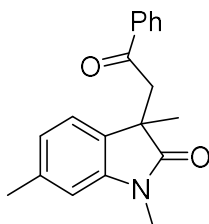
**3g** was prepared according to general procedure **2.1** using *N*-(2-bromo-5-chlorophenyl)-*N*-methylmethacrylamide (0.1 mmol, 28.9 mg) and benzoic anhydride (0.2 mmol, 45.2 mg) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1~5/1) to obtain **3g** as white solid (24.4 mg, 78% yield). TLC (petroleum ether: ethyl acetate, 5:1 v/v):

R<sub>f</sub> = 0.4. m.p. 142.1-143.4 °C. The <sup>1</sup>H NMR data matched those reported in the literature.<sup>[8]</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.88-7.79 (m, 2H), 7.57-7.48 (m, 1H), 7.46-7.35 (m, 2H), 7.03 (d, *J* = 7.8 Hz, 1H), 6.94 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.90 (d, *J* = 1.8 Hz, 1H), 3.69 (dd, *J* = 21.7, 18.1 Hz, 2H), 3.30 (s, 3H), 1.42 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 195.9, 180.5, 145.0, 136.0, 133.5, 133.3, 132.1, 128.5, 127.9, 122.5, 121.9, 108.9, 46.0, 44.9, 26.5, 24.8.

### 1,3,6-trimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3h)



Chemical Formula: C<sub>19</sub>H<sub>19</sub>NO<sub>2</sub>

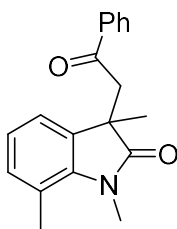
Exact Mass: 293.14

**3h** was prepared according to general procedure **2.1** using *N*-(2-bromo-5-methylphenyl)-*N*-methylmethacrylamide (0.1 mmol, 26.8 mg) and benzoic anhydride (0.2 mmol, 45.2 mg) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1~5/1) to obtain **3h** as colorless oil (24.3 mg, 83% yield). TLC (petroleum ether: ethyl acetate, 5:1 v/v): R<sub>f</sub> = 0.4. The <sup>1</sup>H NMR data matched those reported in the literature.<sup>[4]</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.91-7.78 (m, 2H), 7.58-7.46 (m, 1H), 7.45-7.34 (m, 2H), 7.02 (d, *J* = 7.5 Hz, 1H), 6.81-6.76 (m, 1H), 6.73 (s, 1H), 3.65 (dd, *J* = 29.9, 17.9 Hz, 2H), 3.29 (s, 3H), 2.37 (s, 3H), 1.42 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 196.2, 180.9, 143.9, 137.8, 136.4, 133.1, 130.8, 128.4, 128.0, 122.6, 121.5, 109.2, 46.0, 45.1, 26.4, 25.0, 21.8.

### 1,3,7-trimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3i)



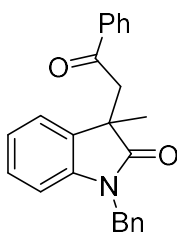
Chemical Formula: C<sub>19</sub>H<sub>19</sub>NO<sub>2</sub>  
Exact Mass: 293.14

**3i** was prepared according to general procedure **2.1** using *N*-(2-bromo-6-methylphenyl)-*N*-methylethylmethacrylamide (0.1 mmol, 26.8 mg) and benzoic anhydride (0.2 mmol, 45.2 mg) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1~5/1) to obtain **3i** as brown oil (14.9 mg, 51% yield). TLC (petroleum ether: ethyl acetate, 5:1 v/v): R<sub>f</sub> = 0.4. The <sup>1</sup>H NMR data matched those reported in the literature.<sup>[4]</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.92-7.78 (m, 2H), 7.58-7.47 (m, 1H), 7.47-7.33 (m, 2H), 7.02-6.90 (m, 2H), 6.89-6.81 (m, 1H), 3.67 (d, *J* = 0.8 Hz, 2H), 3.59 (s, 3H), 2.62 (s, 3H), 1.41 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 196.2, 181.4, 141.6, 136.4, 134.3, 133.1, 131.6, 128.4, 128.0, 122.1, 119.8, 119.5, 46.3, 44.7, 29.8, 25.5, 19.1.

### 1-benzyl-3-methyl-3-(2-oxo-2-phenylethyl)indolin-2-one (**3j**)



Chemical Formula: C<sub>24</sub>H<sub>21</sub>NO<sub>2</sub>  
Exact Mass: 355.16

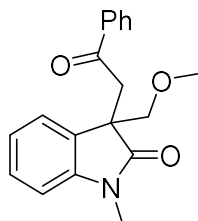
**3j** was prepared according to general procedure **2.1** using *N*-benzyl-*N*-(2-bromophenyl)methacrylamide (0.1 mmol, 33.0 mg) and benzoic anhydride (0.2 mmol, 45.2 mg) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to obtain **3j** as yellow solid (30.2 mg, 85% yield). TLC (petroleum ether: ethyl acetate, 5:1 v/v): R<sub>f</sub> = 0.4. m.p. 146.4-148.8 °C. The <sup>1</sup>H NMR data matched those reported in the literature.<sup>[5]</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.94-7.85 (m, 2H), 7.58-7.49 (m, 1H), 7.48-7.39 (m, 4H), 7.39-7.32 (m, 2H), 7.32-7.26 (m, 1H), 7.18-7.08 (m, 2H), 6.99-6.90 (m, 1H), 6.78-6.71 (m, 1H), 5.10

(d,  $J = 15.8$  Hz, 1H), 4.98 (d,  $J = 15.8$  Hz, 1H), 3.75 (dd,  $J = 23.3, 18.0$  Hz, 2H), 1.51 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  195.9, 180.7, 142.9, 136.31, 136.28, 133.8, 133.3, 128.8, 128.5, 128.1, 127.7, 127.4, 127.3, 122.2, 121.7, 109.3, 45.9, 45.4, 44.0, 25.6.

### 3-(methoxymethyl)-1-methyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3k)



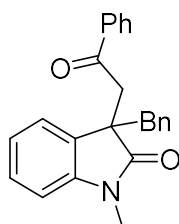
Chemical Formula:  $\text{C}_{19}\text{H}_{19}\text{NO}_3$   
Exact Mass: 309.14

**3k** was prepared according to general procedure **2.1** using *N*-(2-bromophenyl)-2-(methoxymethyl)-*N*-methylacrylamide (0.1 mmol, 28.4 mg) and benzoic anhydride (0.2 mmol, 45.2 mg) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to obtain **3k** as yellow solid (23.8 mg, 77% yield). TLC (petroleum ether: ethyl acetate, 5:1 v/v):  $R_f = 0.3$ . m.p. 126.3-128.6 °C. The  $^1\text{H}$  NMR data matched those reported in the literature.<sup>[5]</sup>

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92-7.79 (m, 2H), 7.56-7.46 (m, 1H), 7.45-7.34 (m, 2H), 7.32-7.21 (m, 2H), 7.04-6.94 (m, 1H), 6.90 (d,  $J = 7.7$  Hz, 1H), 3.96 (d,  $J = 18.1$  Hz, 1H), 3.74 (d,  $J = 8.8$  Hz, 1H), 3.64 (d,  $J = 18.1$  Hz, 1H), 3.44 (d,  $J = 8.7$  Hz, 1H), 3.31 (s, 3H), 3.30 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  196.0, 177.9, 144.4, 136.3, 133.1, 130.8, 128.4, 128.1, 128.0, 123.1, 122.0, 108.0, 59.6, 50.5, 42.2, 29.7, 26.5.

### 3-benzyl-1-methyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3l)



Chemical Formula:  $\text{C}_{24}\text{H}_{21}\text{NO}_2$   
Exact Mass: 355.16

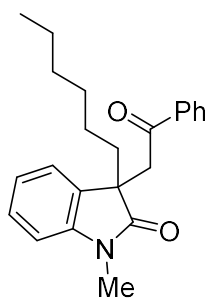
**3l** was prepared according to general procedure **2.1** using 2-benzyl-*N*-(2-bromophenyl)-*N*-

methylacrylamide (0.1 mmol, 33.0 mg) and benzoic anhydride (0.2 mmol, 45.2 mg) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to obtain **3l** as yellow solid (21.3 mg, 60% yield). TLC (petroleum ether: ethyl acetate, 5:1 v/v): R<sub>f</sub> = 0.4. m.p. 142.6-144.7 °C. The <sup>1</sup>H NMR data matched those reported in the literature.<sup>[5]</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.88-7.82 (m, 2H), 7.57-7.49 (m, 1H), 7.44-7.37 (m, 2H), 7.18 (td, *J* = 7.7, 1.3 Hz, 1H), 7.14-7.01 (m, 4H), 6.95 (td, *J* = 7.5, 1.0 Hz, 1H), 6.88-6.80 (m, 2H), 6.66-6.60 (m, 1H), 3.81 (d, *J* = 2.7 Hz, 2H), 3.15 (d, *J* = 12.7 Hz, 1H), 3.09 (d, *J* = 12.7 Hz, 1H), 3.04 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 195.8, 179.1, 144.3, 136.4, 134.8, 133.2, 130.9, 130.0, 128.5, 128.0, 127.9, 127.4, 126.7, 122.7, 121.7, 107.8, 50.9, 44.9, 44.5, 26.0.

### 3-hexyl-1-methyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3m)



Chemical Formula: C<sub>23</sub>H<sub>27</sub>NO<sub>2</sub>

Exact Mass: 349.2042

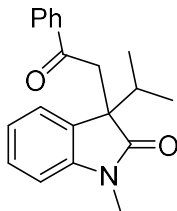
**3m** was prepared according to general procedure **2.1** using *N*-(2-bromophenyl)-*N*-methyl-2-methyleneoctanamide (0.1 mmol, 32.4 mg) and benzoic anhydride (0.2 mmol, 45.2 mg) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1~5/1) to obtain **3m** as yellow oil (20.9 mg, 60% yield). TLC (petroleum ether: ethyl acetate, 5:1 v/v): R<sub>f</sub> = 0.4.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.85-7.78 (m, 2H), 7.54-7.47 (m, 1H), 7.42-7.35 (m, 2H), 7.28-7.22 (m, 1H), 7.12-7.07 (m, 1H), 7.00-6.94 (m, 1H), 6.87 (d, *J* = 7.6 Hz, 1H), 3.72 (d, *J* = 17.8 Hz, 1H), 3.62 (d, *J* = 17.8 Hz, 1H), 3.29 (s, 3H), 1.95-1.79 (m, 2H), 1.24-0.98 (m, 8H), 0.85-0.77 (m, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 196.2, 180.1, 144.6, 136.5, 133.1, 132.1, 128.4, 127.9, 127.8, 122.03, 121.99, 107.9, 49.4, 45.8, 38.7, 31.5, 29.3, 26.3, 23.2, 22.5, 14.0.

HRMS: (ESI) calcd for  $C_{23}H_{27}NO_2H^+[M+H]^+$  350.2115; found 350.2106.

**3-isopropyl-1-methyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3n)**



Chemical Formula:  $C_{20}H_{21}NO_2$

Exact Mass: 307.1572

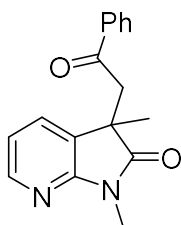
**3n** was prepared according to general procedure **2.1** using *N*-(2-bromophenyl)-*N*,3-dimethyl-2-methylenebutanamide (0.1 mmol, 28.2 mg) and benzoic anhydride (0.2 mmol, 45.2 mg) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1~5/1) to obtain **3n** as colorless oil (19.0 mg, 62% yield). TLC (petroleum ether: ethyl acetate, 5:1 v/v):  $R_f$  = 0.4.

$^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.85-7.78 (m, 2H), 7.55-7.47 (m, 1H), 7.42-7.35 (m, 2H), 7.28-7.22 (m, 1H), 7.11-7.05 (m, 1H), 6.95 (td,  $J$  = 7.5, 1.0 Hz, 1H), 6.87 (d,  $J$  = 7.8 Hz, 1H), 3.84 (d,  $J$  = 17.7 Hz, 1H), 3.64 (d,  $J$  = 17.7 Hz, 1H), 3.28 (s, 3H), 2.32-2.11 (m, 1H), 1.03 (d,  $J$  = 6.9 Hz, 3H), 0.74 (d,  $J$  = 6.7 Hz, 3H).

$^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  196.4, 180.1, 145.1, 136.6, 133.0, 130.5, 128.4, 127.9, 127.8, 122.8, 121.7, 107.7, 52.5, 44.1, 35.8, 26.2, 17.3, 16.8.

HRMS: (ESI) calcd for  $C_{20}H_{21}NO_2H^+[M+H]^+$  308.1645; found 308.1646.

**1,3-dimethyl-3-(2-oxo-2-phenylethyl)-1,3-dihydro-2H-pyrrolo[2,3-b]pyridin-2-one (3o)**



Chemical Formula:  $C_{17}H_{16}N_2O_2$

Exact Mass: 280.12

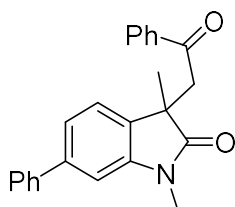
**3o** was prepared according to general procedure **2.1** using *N*-(3-bromopyridin-2-yl)-*N*-methylmethacrylamide (0.1 mmol, 25.5 mg) and benzoic anhydride (0.2 mmol, 45.2 mg) and

was purified by silica gel column chromatography (petroleum ether/ethyl acetate =10:1~5/1) to obtain **3o** as yellow oil (17.1 mg, 61% yield). TLC (petroleum ether: ethyl acetate, 5:1 v/v): R<sub>f</sub> = 0.3. The <sup>1</sup>H NMR data matched those reported in the literature.<sup>[5]</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.17 (dd, *J* = 5.2, 1.5 Hz, 1H), 7.93-7.78 (m, 2H), 7.59-7.49 (m, 1H), 7.47-7.34 (m, 3H), 6.87 (dd, *J* = 7.2, 5.3 Hz, 1H), 3.69 (dd, *J* = 21.3, 18.2 Hz, 2H), 3.39 (s, 3H), 1.47 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 195.8, 180.2, 157.3, 146.6, 136.1, 133.4, 129.3, 128.6, 128.2, 128.0, 117.8, 45.6, 45.0, 25.6, 24.1.

### 1,3-dimethyl-3-(2-oxo-2-phenylethyl)-6-phenylindolin-2-one (3p)



Chemical Formula: C<sub>24</sub>H<sub>21</sub>NO<sub>2</sub>

Exact Mass: 355.1572

**3p** was prepared according to general procedure **2.1** using 3-(*N*-methylmethacrylamido)-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate (0.1 mmol, 39.9 mg) and benzoic anhydride (0.2 mmol, 45.2 mg) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate =10:1~5/1) to obtain **3p** as yellow oil (18.1 mg, 51% yield). TLC (petroleum ether: ethyl acetate, 5:1 v/v): R<sub>f</sub> = 0.3.

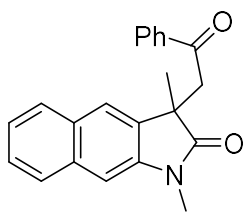
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.88-7.83 (m, 2H), 7.61-7.56 (m, 2H), 7.56-7.49 (m, 1H), 7.47-7.38 (m, 4H), 7.38-7.32 (m, 1H), 7.21-7.18 (m, 2H), 7.11-7.07 (m, 1H), 3.76 (d, *J* = 18.0 Hz, 1H), 3.68 (d, *J* = 18.0 Hz, 1H), 3.37 (s, 3H), 1.48 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 196.2, 180.8, 144.4, 141.4, 141.3, 136.3, 133.2, 132.8, 128.7, 128.5, 128.0, 127.4, 127.2, 122.0, 121.2, 107.2, 46.0, 45.2, 26.5, 25.0.

HRMS: (ESI) calcd for C<sub>24</sub>H<sub>21</sub>NO<sub>2</sub>H<sup>+</sup> [M+H]<sup>+</sup> 356.1645; found 356.1645.

### 1,3-dimethyl-3-(2-oxo-2-phenylethyl)-1,3-dihydro-2H-benzo[f]indol-2-one (3q)





Chemical Formula: C<sub>22</sub>H<sub>19</sub>NO<sub>2</sub>

Exact Mass: 329.1416

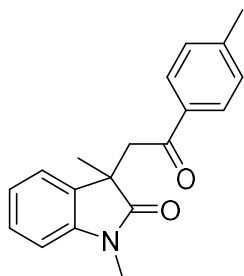
**3q** was prepared according to general procedure **2.1** using 3-(*N*-methylmethacrylamido)naphthalen-2-yl trifluoromethanesulfonate (0.1 mmol, 37.3 mg) and benzoic anhydride (0.2 mmol, 45.2 mg) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to obtain **3q** as white solid (19.7 mg, 60% yield). TLC (petroleum ether: ethyl acetate, 5:1 v/v): R<sub>f</sub> = 0.3. m.p. 147.2-149.0 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.86-7.82 (m, 2H), 7.78 (d, *J* = 7.7 Hz, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.54-7.48 (m, 2H), 7.45-7.36 (m, 3H), 7.34-7.28 (m, 1H), 7.18 (s, 1H), 3.84 (d, *J* = 18.1 Hz, 1H), 3.78 (d, *J* = 18.1 Hz, 1H), 3.42 (s, 3H), 1.52 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 196.0, 180.2, 142.4, 136.2, 135.0, 133.8, 133.2, 130.2, 128.5, 128.0, 127.8, 127.1, 126.2, 123.9, 120.7, 103.8, 46.6, 44.7, 26.7, 25.5.

HRMS: (ESI) calcd for C<sub>22</sub>H<sub>19</sub>NO<sub>2</sub>H<sup>+</sup> [M+H]<sup>+</sup> 330.1489; found 330.1488.

### 1,3-dimethyl-3-(2-oxo-2-(*p*-tolyl)ethyl)indolin-2-one (**3r**)



Chemical Formula: C<sub>19</sub>H<sub>19</sub>NO<sub>2</sub>

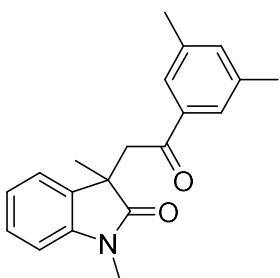
Exact Mass: 293.1416

**3r** was prepared according to general procedure **2.1** using *N*-(2-bromophenyl)-*N*-methylmethacrylamide (0.1 mmol, 25.4 mg) and 4-methylbenzoic anhydride (0.2 mmol, 50.8 mg) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1~5/1) to obtain **3r** as colorless oil (26.7 mg, 91% yield). TLC (petroleum ether: ethyl acetate, 5:1 v/v): R<sub>f</sub> = 0.4. The <sup>1</sup>H NMR data matched those reported in the literature.<sup>[4]</sup>

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.77-7.70 (m, 2H), 7.25 (td,  $J = 7.7, 1.3$  Hz, 1H), 7.21-7.16 (m, 2H), 7.15-7.11 (m, 1H), 6.97 (td,  $J = 7.6, 1.0$  Hz, 1H), 6.89 (d,  $J = 8.1$  Hz, 1H), 3.70 (d,  $J = 17.2$  Hz, 1H), 3.61 (d,  $J = 17.6$  Hz, 1H), 3.31 (s, 3H), 2.37 (s, 3H), 1.43 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  195.7, 180.7, 144.0, 143.8, 133.9, 133.8, 129.1, 128.1, 127.8, 122.1, 121.7, 108.1, 45.9, 45.3, 26.4, 24.9, 21.6.

### 3-(2-(3,5-dimethylphenyl)-2-oxoethyl)-1,3-dimethylindolin-2-one (3s)



Chemical Formula:  $\text{C}_{20}\text{H}_{21}\text{NO}_2$

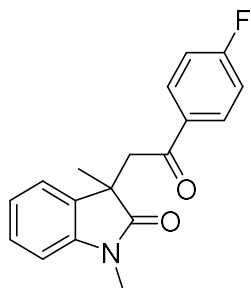
Exact Mass: 307.1572

**3s** was prepared according to general procedure **2.1** using *N*-(2-bromophenyl)-*N*-methylmethacrylamide (0.1 mmol, 25.4 mg) and 3,5-dimethylbenzoic anhydride (0.2 mmol, 56.4 mg) at 80 °C and was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1~5/1) to obtain **3s** as white solid (23.8 mg, 62% yield). TLC (petroleum ether: ethyl acetate, 5:1 v/v):  $R_f = 0.4$ . m.p. 105.2-106.8 °C. The  $^1\text{H}$  NMR data matched those reported in the literature.<sup>[3]</sup>

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 (s, 2H), 7.27-7.22 (m, 1H), 7.17-7.10 (m, 2H), 6.96 (td,  $J = 7.5, 1.0$  Hz, 1H), 6.89 (d,  $J = 7.7$  Hz, 1H), 3.70 (d,  $J = 17.8$  Hz, 1H), 3.61 (d,  $J = 17.6$  Hz, 1H), 3.31 (s, 3H), 2.31 (s, 6H), 1.44 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  196.5, 180.7, 143.9, 138.1, 136.4, 134.8, 133.8, 127.8, 125.8, 122.1, 121.7, 108.1, 46.1, 45.3, 26.4, 24.8, 21.1.

### 3-(2-(4-fluorophenyl)-2-oxoethyl)-1,3-dimethylindolin-2-one (3t)



Chemical Formula: C<sub>18</sub>H<sub>16</sub>FNO<sub>2</sub>

Exact Mass: 297.1165

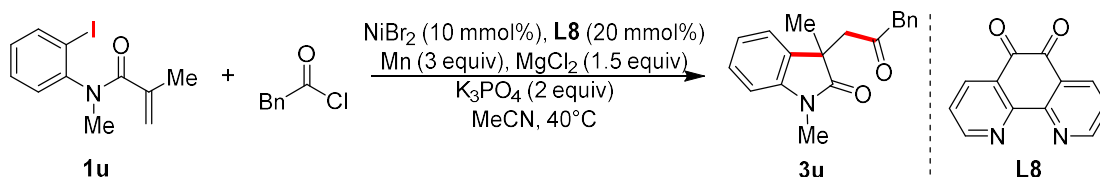
**3t** was prepared according to general procedure **2.1** using *N*-(2-bromophenyl)-*N*-methylethylmethacrylamide (0.1 mmol, 25.4 mg) and 4-fluorobenzoic anhydride (0.2 mmol, 52.4 mg) and was purified by silica gel column chromatography (petroleum ether/ethyl acetate =10:1~5/1) to obtain **3t** as white solid (23.8 mg, 80% yield). TLC (petroleum ether: ethyl acetate, 5:1 v/v): R<sub>f</sub> = 0.4. m.p. 107.8-109.5 °C. The <sup>1</sup>H NMR data matched those reported in the literature.<sup>[4]</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.92-7.80 (m, 2H), 7.29-7.23 (m, 1H), 7.16-7.11 (m, 1H), 7.11-7.02 (m, 2H), 6.98 (td, *J* = 7.5, 1.0 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 3.65 (d, *J* = 2.3 Hz, 2H), 3.31 (s, 3H), 1.44 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 194.5, 180.5, 165.7 (d, *J* = 254.8 Hz), 143.8, 133.6, 132.7 (m), 130.60 (d, *J* = 9.5 Hz), 127.9, 122.2, 121.7, 115.6 (d, *J* = 22.0 Hz), 108.2, 45.9, 45.3, 26.4, 24.9.

<sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) δ -104.8(s).

### 1,3-dimethyl-3-(2-oxo-3-phenylpropyl)indolin-2-one (**3u**)



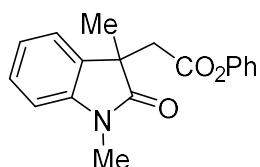
An oven-dried sealed tube equipped with a PTFE-coated stir bar was charged with NiBr<sub>2</sub> (10 mol%), **L8** (20 mol%), *N*-(2-iodophenyl)-*N*-methylethylmethacrylamide (0.1 mmol, 1.0 equiv), manganese powder (3.0 equiv), MgCl<sub>2</sub> (1.5 equiv) and K<sub>3</sub>PO<sub>4</sub> (2.0 equiv). The sealed tube was evacuated and backfilled with argon (this process was repeated for three times) and then MeCN (2 mL) was added. This reaction mixture was stirred at room temperature for 15 minutes and then 2-phenylacetyl chloride (3.0 equiv) was added. Then, the reaction heated at 40 °C for 36

hours. The resulting mixture was purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:20~1:5 (v/v) to afford the corresponding product **3u** as yellow oil (17.9 mg, 61% yield). TLC (petroleum ether: ethyl acetate, 5:1 v/v):  $R_f = 0.5$ . The  $^1\text{H}$  NMR data matched those reported in the literature.<sup>[6]</sup>

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.3-7.2 (m, 4H), 7.1-7.0 (m, 2H), 7.0-6.9 (m, 2H), 6.9-6.8 (m, 1H), 3.5 (d,  $J = 1.2$  Hz, 2H), 3.2 (s, 3H), 3.1 (d,  $J = 3.4$  Hz, 2H), 1.3 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  204.3, 180.4, 143.8, 133.7, 133.4, 129.5, 128.8, 128.0, 127.2, 122.3, 121.9, 108.3, 50.2, 48.8, 45.3, 26.5, 24.5.

#### Phenyl 2-(1,3-dimethyl-2-oxoindolin-3-yl)acetate (**6a**)



Chemical Formula:  $\text{C}_{18}\text{H}_{17}\text{NO}_3$

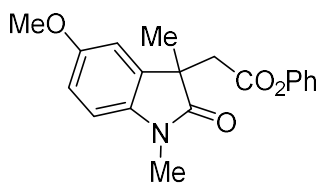
Exact Mass: 295.1208

**6a** was prepared according to general procedure **2.2** using *N*-(2-bromophenyl)-*N*-methylmethacrylamide (0.1 mmol, 25.4 mg) and phenyl carbonochloridate (0.4 mmol, 62.6 mg) and was purified by silica gel column chromatography (PE/EtOAc = 15/1~5/1) to obtain **6a** as colorless oil (22.1 mg, 75% yield). TLC (petroleum ether: ethyl acetate, 5:1 v/v):  $R_f = 0.5$ . The  $^1\text{H}$  NMR data matched those reported in the literature.<sup>[7]</sup>

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.29 (m, 2H), 7.25-7.18 (m, 2H), 7.14-7.04 (m, 2H), 6.90-6.82 (m, 1H), 6.70-6.63 (m, 2H), 3.29 (d,  $J = 16.0$  Hz, 1H), 3.20 (s, 3H), 3.06 (d,  $J = 16.0$  Hz, 1H), 1.45 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  179.6, 168.5, 150.2, 143.7, 132.5, 129.4, 128.5, 125.9, 122.6, 122.6, 121.4, 108.4, 45.8, 41.9, 26.5, 24.4.

#### Phenyl 2-(5-methoxy-1,3-dimethyl-2-oxoindolin-3-yl)acetate (**6b**)



Chemical Formula: C<sub>19</sub>H<sub>19</sub>NO<sub>4</sub>

Exact Mass: 325.1314

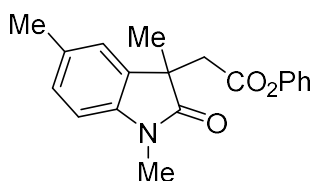
**6b** was prepared according to general procedure **2.2** using *N*-(2-bromo-4-methoxyphenyl)-*N*-methylmethacrylamide (0.1 mmol, 28.4 mg) and phenyl carbonochloridate (0.4 mmol, 62.6 mg) and was purified by silica gel column chromatography (PE/EtOAc = 5/1) to obtain **6b** as brown solid (21.1 mg, 65% yield). TLC (petroleum ether: ethyl acetate, 5:1 v/v): R<sub>f</sub> = 0.4. m.p. 86.0-88.4 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.28-7.22 (m, 2H), 7.16-7.11 (m, 1H), 6.93 (d, *J* = 2.5 Hz, 1H), 6.84-6.80 (m, 1H), 6.78-6.70 (m, 3H), 3.80 (s, 3H), 3.29 (d, *J* = 16.2 Hz, 1H), 3.19 (s, 3H), 3.04 (d, *J* = 16.2 Hz, 1H), 1.45 (s, 3H);

<sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ 179.3, 168.4, 156.0, 150.2, 137.2, 133.9, 129.3, 125.9, 121.4, 112.3, 110.3, 108.6, 55.9, 46.1, 41.8, 26.5, 24.4;

HRMS: (ESI) calcd for C<sub>19</sub>H<sub>19</sub>NNaO<sub>4</sub><sup>+</sup>[M+Na]<sup>+</sup> 348.1212; found 348.1194.

#### Phenyl 2-(1,3,5-trimethyl-2-oxoindolin-3-yl)acetate (**6c**)



Chemical Formula: C<sub>19</sub>H<sub>19</sub>NO<sub>3</sub>

Exact Mass: 309.1365

**6c** was prepared according to general procedure **2.2** using *N*-(2-bromo-4-methylphenyl)-*N*-methylmethacrylamide (0.1 mmol, 26.8 mg) and phenyl carbonochloridate (0.4 mmol, 62.6 mg) and was purified by silica gel column chromatography (PE/EtOAc = 15/1~5/1) to obtain **6c** as yellow solid (19.1 mg, 62% yield). TLC (petroleum ether: ethyl acetate, 5:1 v/v): R<sub>f</sub> = 0.5. m.p. 100.1-103.0 °C.

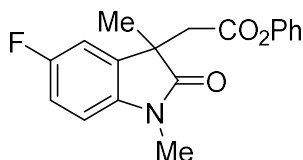
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.28-7.21 (m, 2H), 7.16-7.07 (m, 3H), 6.75 (d, *J* = 7.8 Hz, 1H), 6.71-6.65 (m, 2H), 3.28 (d, *J* = 16.0 Hz, 1H), 3.19 (s, 3H), 3.04 (d, *J* = 16.0 Hz, 1H), 2.35 (s,

3H), 1.45 (s, 3H);

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  179.6, 168.5, 150.2, 141.3, 132.6, 132.1, 129.4, 128.6, 125.9, 123.5, 121.4, 108.1, 45.8, 41.9, 26.5, 24.4, 21.2;

HRMS: (ESI) calcd for  $\text{C}_{19}\text{H}_{19}\text{NNaO}_3^+[\text{M}+\text{Na}]^+$  332.1263; found 332.1261.

**Phenyl 2-(5-fluoro-1,3-dimethyl-2-oxoindolin-3-yl)acetate (6d)**



Chemical Formula:  $\text{C}_{18}\text{H}_{16}\text{FNO}_3$

Exact Mass: 313.1114

**6d** was prepared according to general procedure **2.2** using *N*-(2-bromo-4-fluorophenyl)-*N*-methylmethacrylamide (0.1 mmol, 27.2 mg) and phenyl carbonochloridate (0.4 mmol, 62.6 mg) and was purified by silica gel column chromatography (PE/EtOAc = 15/1~5/1) to obtain **6d** as yellow solid (20.0 mg, 64% yield). TLC (petroleum ether: ethyl acetate, 5:1 v/v):  $R_f$  = 0.5. m.p. 81.4-84.3 °C.

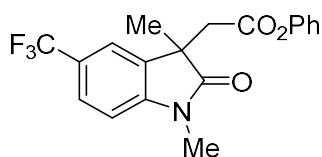
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.31-7.23 (m, 2H), 7.18-7.12 (m, 1H), 7.09–7.05 (m, 1H), 7.04–6.97 (m, 1H), 6.80-6.74 (m, 3H), 3.30 (d,  $J$  = 16.5 Hz, 1H), 3.21 (s, 3H), 3.06 (d,  $J$  = 16.5 Hz, 1H), 1.45 (s, 3H);

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  179.3, 168.3, 159.3 (d,  $J$  = 240.8 Hz), 150.1, 139.7, 134.2, 129.4, 126.0, 121.3, 114.5 (d,  $J$  = 23.4 Hz), 110.8 (d,  $J$  = 24.9 Hz), 108.8 (d,  $J$  = 8.1 Hz), 46.1, 41.6, 26.6, 24.3;

$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -120.5(s).

HRMS: (ESI) calcd for  $\text{C}_{18}\text{H}_{16}\text{FNNaO}_3^+[\text{M}+\text{Na}]^+$  336.1012; found 336.1007.

**Phenyl 2-(1,3-dimethyl-2-oxo-5-(trifluoromethyl)indolin-3-yl)acetate (6e)**



Chemical Formula:  $\text{C}_{19}\text{H}_{16}\text{F}_3\text{NO}_3$

Exact Mass: 363.1082

**6e** was prepared according to general procedure **2.2** using *N*-(2-bromo-4-(trifluoromethyl)phenyl)-*N*-methylmethacrylamide (0.1 mmol, 32.2 mg) and phenyl carbonochloridate (0.4 mmol, 62.6 mg) and was purified by silica gel column chromatography (PE/EtOAc = 15/1~5/1) to obtain **6e** as brown solid (23.9 mg, 66% yield). TLC (petroleum ether: ethyl acetate, 5:1 v/v): R<sub>f</sub> = 0.5. m.p. 86.8-88.6 °C.

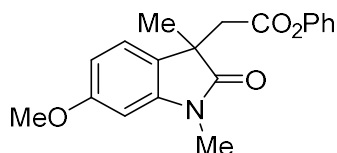
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.62-7.56 (m, 1H), 7.53 (d, *J* = 1.8 Hz, 1H), 7.31-7.23 (m, 2H), 7.18-7.12 (m, 1H), 6.92 (d, *J* = 8.2 Hz, 1H), 6.79-6.77 (m, 1H), 6.76-6.74 (m, 1H), 3.34 (d, *J* = 16.7 Hz, 1H), 3.25 (s, 3H), 3.14 (d, *J* = 16.7 Hz, 1H), 1.47 (s, 3H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 179.6, 168.3, 150.0, 146.8, 133.3, 129.5, 126.2 (q, *J* = 4.0 Hz), 126.1, 125.3 (d, *J* = 91.3 Hz), 123.8 (d, *J* = 147.5 Hz), 121.2, 119.4 (q, *J* = 3.6 Hz), 108.1, 45.6, 41.6, 26.7, 24.3;

<sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) δ -61.2(s).

HRMS: (ESI) calcd for C<sub>19</sub>H<sub>16</sub>F<sub>3</sub>NNaO<sub>3</sub><sup>+</sup>[M+Na]<sup>+</sup> 386.0980; found 386.0976.

#### Phenyl 2-(6-methoxy-1,3-dimethyl-2-oxoindolin-3-yl)acetate (**6f**)



Chemical Formula: C<sub>19</sub>H<sub>19</sub>NO<sub>4</sub>

Exact Mass: 325.1314

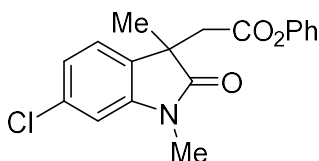
**6f** was prepared according to general procedure **2.2** using *N*-(2-bromo-5-methoxyphenyl)-*N*-methylmethacrylamide (0.1 mmol, 28.4 mg) and phenyl carbonochloridate (0.4 mmol, 62.6 mg) and was purified by silica gel column chromatography (PE/EtOAc =15/1~5/1) to obtain **6f** as colorless oil (19.5 mg, 60% yield). TLC (petroleum ether: ethyl acetate, 5:1 v/v): R<sub>f</sub> = 0.4.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.31-7.22 (m, 2H), 7.20 (d, *J* = 8.1 Hz, 1H), 7.17-7.11 (m, 1H), 6.76-6.68 (m, 2H), 6.62-6.55 (m, 1H), 6.45 (d, *J* = 2.3 Hz, 1H), 3.83 (s, 3H), 3.25 (d, *J* = 15.9 Hz, 1H), 3.20 (s, 3H), 3.03 (d, *J* = 15.9 Hz, 1H), 1.44 (s, 3H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 180.2, 168.6, 160.4, 150.2, 145.0, 129.4, 125.9, 124.4, 123.2, 121.4, 106.2, 96.4, 55.6, 45.3, 42.1, 26.5, 24.5;

HRMS: (ESI) calcd for C<sub>19</sub>H<sub>19</sub>NNaO<sub>4</sub><sup>+</sup>[M+Na]<sup>+</sup> 348.1212; found 348.1208.

**Phenyl 2-(6-chloro-1,3-dimethyl-2-oxoindolin-3-yl)acetate (6g)**



Chemical Formula: C<sub>18</sub>H<sub>16</sub>ClNO<sub>3</sub>

Exact Mass: 329.0819

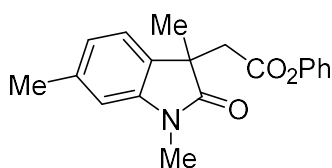
**6g** was prepared according to general procedure **2.2** using *N*-(2-bromo-5-chlorophenyl)-*N*-methylmethacrylamide (0.1 mmol, 28.8 mg) and phenyl carbonochloridate (0.4 mmol, 62.6 mg) and was purified by silica gel column chromatography (PE/EtOAc = 15/1~5/1) to obtain **6g** as white solid (18.7 mg, 57% yield). TLC (petroleum ether: ethyl acetate, 5:1 v/v): R<sub>f</sub> = 0.5. m.p. 113.0-114.6 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.31-7.24 (m, 2H), 7.21 (d, *J* = 7.9 Hz, 1H), 7.18-7.12 (m, 1H), 7.09-7.03 (m, 1H), 6.86 (d, *J* = 1.8 Hz, 1H), 6.77-6.75 (m, 1H), 6.75-6.73 (m, 1H), 3.29 (d, *J* = 16.4 Hz, 1H), 3.20 (s, 3H), 3.06 (d, *J* = 16.4 Hz, 1H), 1.44 (s, 3H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 179.6, 168.3, 150.1, 145.0, 134.2, 131.0, 129.5, 126.0, 123.4, 122.3, 121.3, 109.1, 45.4, 41.7, 26.6, 24.3;

HRMS: (ESI) calcd for C<sub>18</sub>H<sub>16</sub>ClNNaO<sub>3</sub><sup>+</sup>[M+Na]<sup>+</sup> 352.0717; found 352.0709.

**Phenyl 2-(1,3,6-trimethyl-2-oxoindolin-3-yl)acetate (6h)**



Chemical Formula: C<sub>19</sub>H<sub>19</sub>NO<sub>3</sub>

Exact Mass: 309.1365

**6h** was prepared according to general procedure **2.2** using *N*-(2-bromo-5-methylphenyl)-*N*-methylmethacrylamide (0.1 mmol, 26.8 mg) and phenyl carbonochloridate (0.4 mmol, 62.6 mg) and was purified by silica gel column chromatography (PE/EtOAc = 15/1~5/1) to obtain **6h** as white solid (18.8 mg, 61% yield). TLC (petroleum ether: ethyl acetate, 5:1 v/v): R<sub>f</sub> = 0.5. m.p. 77.9-79.3 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.28-7.21 (m, 2H), 7.18 (m, 1H), 7.16-7.10 (m, 1H), 6.93-6.86

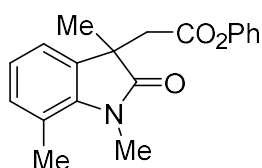


(m, 1H), 6.74-6.66 (m, 3H), 3.26 (d,  $J = 16.1$  Hz, 1H), 3.20 (s, 3H), 3.04 (d,  $J = 16.0$  Hz, 1H), 2.39 (s, 3H), 1.44 (s, 3H);

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  180.0, 168.5, 150.2, 143.8, 138.5, 129.6, 129.3, 125.9, 123.0, 122.3, 121.4, 109.3, 45.6, 41.9, 26.4, 24.4, 21.9;

HRMS: (ESI) calcd for  $\text{C}_{19}\text{H}_{19}\text{NNaO}_3^+[\text{M}+\text{Na}]^+$  332.1263; found 332.1258.

#### Phenyl 2-(1,3,7-trimethyl-2-oxoindolin-3-yl)acetate (**6i**)



Chemical Formula:  $\text{C}_{19}\text{H}_{19}\text{NO}_3$

Exact Mass: 309.1365

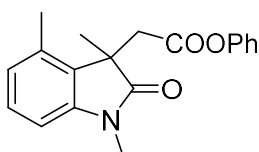
**6i** was prepared according to general procedure **2.2** using *N*-(2-bromo-6-methylphenyl)-*N*-methylmethacrylamide (0.1 mmol, 26.8 mg) and phenyl carbonochloridate (0.4 mmol, 62.6 mg) and was purified by silica gel column chromatography (PE/EtOAc = 15/1~5/1) to obtain **6i** as yellow solid (13.3 mg, 43% yield). TLC (petroleum ether: ethyl acetate, 5:1 v/v):  $R_f = 0.5$ . m.p. 103.4-104.8 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.29–7.22 (m, 2H), 7.17-7.09 (m, 2H), 7.04-7.00 (m, 1H), 7.00–6.94 (m, 1H), 6.71–6.69 (m, 1H), 6.69-6.66 (m, 1H), 3.49 (s, 3H), 3.30 (d,  $J = 16.0$  Hz, 1H), 3.03 (d,  $J = 16.0$  Hz, 1H), 2.56 (s, 3H), 1.43 (s, 3H);

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  180.4, 168.5, 150.2, 141.5, 133.2, 132.1, 129.4, 125.9, 122.5, 121.4, 120.3, 112.0, 45.1, 42.2, 29.8, 24.8, 19.1;

HRMS: (ESI) calcd for  $\text{C}_{19}\text{H}_{19}\text{NNaO}_3^+[\text{M}+\text{Na}]^+$  332.1263; found 332.1260.

#### phenyl 2-(1,3,4-trimethyl-2-oxoindolin-3-yl)acetate (**6j**)



Chemical Formula:  $\text{C}_{19}\text{H}_{19}\text{NO}_3$

Exact Mass: 309.1365

**6j** was prepared according to general procedure **2.2** using *N*-(2-bromo-3-methylphenyl)-*N*-

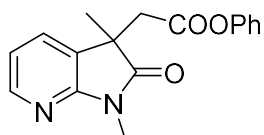
methacrylamide (0.1 mmol, 26.8 mg) and phenyl carbonochloridate (0.4 mmol, 62.6 mg) and was purified by silica gel column chromatography (PE/EtOAc = 15/1~5/1) to obtain **6j** as white solid (13.6 mg, 44% yield). TLC (petroleum ether: ethyl acetate, 5:1 v/v): R<sub>f</sub> = 0.4. m.p. 82.5-84.7 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.24-7.16 (m, 3H), 7.13-7.07 (m, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 6.71 (d, *J* = 7.7 Hz, 1H), 6.53-6.46 (m, 2H), 3.41 (d, *J* = 15.3 Hz, 1H), 3.24-3.18 (m, 4H), 2.46 (s, 3H), 1.52 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 179.6, 168.4, 150.1, 144.1, 134.2, 129.2, 128.3, 125.8, 125.1, 121.2, 106.1, 46.8, 41.3, 26.5, 22.4, 18.2.

HRMS: (ESI) calcd for C<sub>19</sub>H<sub>19</sub>NO<sub>3</sub>H<sup>+</sup>[M+H]<sup>+</sup> 310.1438; found 310.1440.

**phenyl 2-(1,3-dimethyl-2-oxo-2,3-dihydro-1H-pyrrolo[2,3-b]pyridin-3-yl)acetate (6k)**



Chemical Formula: C<sub>17</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub>

Exact Mass: 296.1161

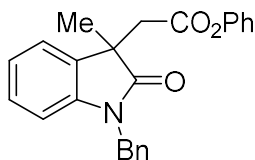
**6k** was prepared according to general procedure **2.2** using *N*-(3-bromopyridin-2-yl)-*N*-methacrylamide (0.1 mmol, 25.5 mg) and phenyl carbonochloridate (0.4 mmol, 62.6 mg) and was purified by silica gel column chromatography (PE/EtOAc = 15/1~5/1) to obtain **6k** as colorless oil (18.0 mg, 61% yield). TLC (petroleum ether: ethyl acetate, 5:1 v/v): R<sub>f</sub> = 0.4.

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.21 (dd, *J* = 5.3, 1.6 Hz, 1H), 7.56 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.30-7.26 (m, 2H), 7.19-7.14 (m, 1H), 6.97 (dd, *J* = 7.3, 5.3 Hz, 1H), 6.81-6.73 (m, 2H), 3.33-3.26 (m, 4H), 3.09 (d, *J* = 16.5 Hz, 1H), 1.49 (s, 3H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 179.2, 168.2, 157.1, 150.0, 147.1, 130.1, 129.4, 127.1, 126.0, 121.2, 118.1, 45.3, 41.3, 25.6, 23.6.

HRMS: (ESI) calcd for C<sub>17</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub>H<sup>+</sup>[M+H]<sup>+</sup> 297.1234; found 297.1236.

**Phenyl 2-(1-benzyl-3-methyl-2-oxoindolin-3-yl)acetate (6l)**



Chemical Formula:  $C_{24}H_{21}NO_3$

Exact Mass: 371.1521

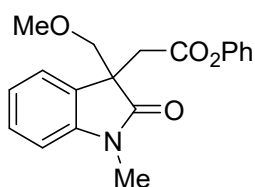
**6l** was prepared according to general procedure **2.2** using *N*-benzyl-*N*-(2-bromophenyl)methacrylamide (0.1 mmol, 33.0 mg) and phenyl carbonochloridate (0.4 mmol, 62.6 mg) and was purified by silica gel column chromatography (PE/EtOAc = 10/1~5/1) to obtain **6l** as yellow oil (16.0 mg, 43% yield). TLC (petroleum ether: ethyl acetate, 5:1 v/v):  $R_f$  = 0.5.

$^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  7.34-7.29 (m, 1H), 7.28-7.24 (m, 2H), 7.24-7.09 (m, 7H), 7.08-7.02 (m, 1H), 6.75-6.70 (m, 1H), 6.61-6.58 (m, 1H), 6.57-6.55 (m, 1H), 4.92 (q,  $J$  = 15.7 Hz, 2H), 3.39 (d,  $J$  = 15.9 Hz, 1H), 3.10 (d,  $J$  = 15.9 Hz, 1H), 1.52 (s, 3H);

$^{13}C$  NMR (101 MHz,  $CDCl_3$ ):  $\delta$  179.7, 168.5, 150.2, 142.8, 135.8, 132.5, 129.3, 128.7, 128.3, 127.5, 127.3, 125.9, 122.7, 122.6, 121.4, 109.5, 45.9, 44.0, 41.8, 25.2;

HRMS: (ESI) calcd for  $C_{24}H_{21}NNaO_3^+[M+Na]^+$  394.1419; found 394.1417.

#### Phenyl 2-(3-(methoxymethyl)-1-methyl-2-oxoindolin-3-yl)acetate (**6m**)



Chemical Formula:  $C_{19}H_{19}NO_4$

Exact Mass: 325.1314

**6m** was prepared according to general procedure **2.2** using *N*-(2-bromophenyl)-2-(methoxymethyl)-*N*-methylacrylamide (0.1 mmol, 28.4 mg) and phenyl carbonochloridate (0.4 mmol, 62.6 mg) and was purified by silica gel column chromatography (PE/EtOAc = 5/1) to obtain **6m** as yellow oil (16.5 mg, 51% yield). TLC (petroleum ether: ethyl acetate, 5:1 v/v):  $R_f$  = 0.4.

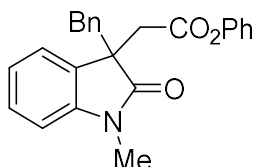
$^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.43-7.38 (m, 1H), 7.36-7.30 (m, 1H), 7.27-7.20 (m, 2H), 7.15-7.05 (m, 2H), 6.86 (d,  $J$  = 7.8 Hz, 1H), 6.68-6.65 (m, 1H), 6.65-6.62 (m, 1H), 3.71 (d,  $J$  = 8.8

Hz, 1H), 3.52 (d,  $J$  = 8.8 Hz, 1H), 3.30 (s, 3H), 3.26 (s, 2H), 3.21 (s, 3H);

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  177.1, 168.4, 150.2, 144.4, 129.7, 129.3, 128.7, 125.9, 123.8, 122.5, 121.3, 108.2, 76.2, 59.7, 50.9, 37.9, 26.5.

HRMS: (ESI) calcd for  $\text{C}_{19}\text{H}_{19}\text{NNaO}_4^+[\text{M}+\text{Na}]^+$  348.1212; found 348.1212.

### Phenyl 2-(3-benzyl-1-methyl-2-oxoindolin-3-yl)acetate (**6n**)



Chemical Formula:  $\text{C}_{24}\text{H}_{21}\text{NO}_3$

Exact Mass: 371.1521

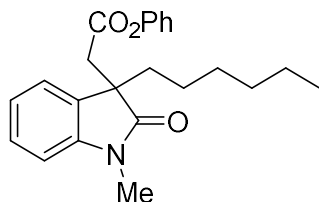
**6n** was prepared according to general procedure **2.2** using 2-benzyl-*N*-(2-bromophenyl)-*N*-methylacrylamide (0.1 mmol, 33.0 mg) and phenyl carbonochloridate (0.4 mmol, 62.6 mg) and was purified by silica gel column chromatography (PE/EtOAc = 15/1~5/1) to obtain **6n** as yellow oil (26.1 mg, 70% yield). TLC (petroleum ether: ethyl acetate, 5:1 v/v):  $R_f$  = 0.5.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.27-7.18 (m, 4H), 7.14-7.03 (m, 5H), 6.89-6.84 (m, 2H), 6.66-6.63 (m, 1H), 6.63-6.59 (m, 2H), 3.44 (d,  $J$  = 15.9 Hz, 1H), 3.17 (d,  $J$  = 16.0 Hz, 1H), 3.12 (s, 2H), 2.97 (s, 3H);

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  178.2, 168.4, 150.2, 144.26, 134.7, 130.1, 129.8, 129.3, 128.5, 127.6, 126.9, 125.9, 123.5, 122.1, 121.3, 108.0, 51.4, 44.0, 40.6, 26.1.

HRMS: (ESI) calcd for  $\text{C}_{24}\text{H}_{21}\text{NNaO}_3^+[\text{M}+\text{Na}]^+$  394.1419; found 394.1416.

### Phenyl 2-(3-hexyl-1-methyl-2-oxoindolin-3-yl)acetate (**6o**)



Chemical Formula:  $\text{C}_{23}\text{H}_{27}\text{NO}_3$

Exact Mass: 365.1991

**6o** was prepared according to general procedure **2.2** using *N*-(2-bromophenyl)-*N*-methyl-2-methyloctanamide (0.1 mmol, 32.4 mg) and phenyl carbonochloridate (0.4 mmol, 62.6 mg)

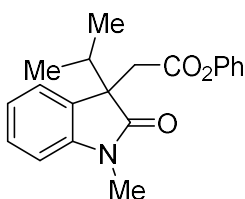
and was purified by silica gel column chromatography (PE/EtOAc = 15/1~5/1) to obtain **6o** as brown oil (22.2 mg, 63% yield). TLC (petroleum ether: ethyl acetate, 5:1 v/v): R<sub>f</sub> = 0.5.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.35-7.18 (m, 4H), 7.15-7.05 (m, 2H), 6.85 (d, *J* = 7.8 Hz, 1H), 6.65-6.58 (m, 2H), 3.28 (d, *J* = 15.8 Hz, 1H), 3.20 (s, 3H), 3.06 (d, *J* = 15.8 Hz, 1H), 1.86 (dtd, *J* = 45.9, 12.9, 4.4 Hz, 2H), 1.36-0.70 (m, 13H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 179.1, 168.5, 150.2, 144.5, 130.9, 129.3, 128.37, 125.8, 122.8, 122.5, 121.3, 108.1, 50.0, 41.7, 38.3, 31.5, 29.3, 26.4, 23.6, 22.6, 14.0;

HRMS: (ESI) calcd for C<sub>23</sub>H<sub>27</sub>NNaO<sub>3</sub><sup>+</sup>[M+Na]<sup>+</sup> 388.1889; found 388.1881.

#### Phenyl 2-(3-isopropyl-1-methyl-2-oxoindolin-3-yl)acetate (**6p**)



Chemical Formula: C<sub>20</sub>H<sub>21</sub>NO<sub>3</sub>

Exact Mass: 323.1521

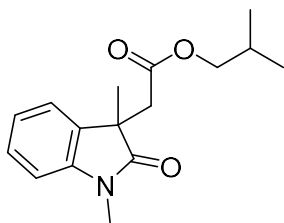
**6p** was prepared according to general procedure **2.2** using *N*-(2-bromophenyl)-*N*,3-dimethyl-2-methylenebutanamide (0.1 mmol, 29.6 mg) and phenyl carbonochloridate (0.4 mmol, 62.6 mg) and was purified by silica gel column chromatography (PE/EtOAc = 15/1~5/1) to obtain **6p** as yellow solid (21.4 mg, 66% yield). TLC (petroleum ether: ethyl acetate, 5:1 v/v): R<sub>f</sub> = 0.5. m.p. 75.8-78.2 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.35-7.29 (m, 1H), 7.28-7.25 (m, 1H), 7.24-7.18 (m, 2H), 7.14-7.04 (m, 2H), 6.87-6.81 (m, 1H), 6.61-6.58 (m, 1H), 6.58-6.55 (m, 1H), 3.32 (d, *J* = 15.8 Hz, 1H), 3.20 (d, *J* = 9.1 Hz, 4H), 2.20 (p, *J* = 6.8 Hz, 1H), 0.99 (d, *J* = 6.9 Hz, 3H), 0.81 (d, *J* = 6.7 Hz, 3H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 179.1, 168.8, 150.2, 144.9, 129.7, 129.3, 128.4, 125.8, 123.5, 122.1, 121.3, 108.0, 53.2, 39.9, 35.6, 26.2, 17.3, 16.9.

HRMS: (ESI) calcd for C<sub>20</sub>H<sub>21</sub>NNaO<sub>3</sub><sup>+</sup>[M+Na]<sup>+</sup> 346.1419; found 346.1410.

#### isobutyl 2-(1,3-dimethyl-2-oxoindolin-3-yl)acetate (**6q**)

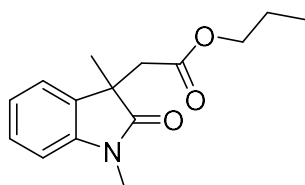


Chemical Formula:  $C_{16}H_{21}NO_3$   
Exact Mass: 275.1521

**6q** was prepared according to general procedure **2.2** using *N*-(2-bromophenyl)-*N*-methylmethacrylamide (0.1 mmol, 25.4 mg) and isobutyl carbonochloridate (0.4 mmol, 54.6 mg) and was purified by silica gel column chromatography (PE/EtOAc = 15/1~5/1) to obtain **6q** as yellow oil (16.5 mg, 60% yield). TLC (petroleum ether: ethyl acetate, 5:1 v/v):  $R_f$  = 0.5.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.30-7.23 (m, 1H), 7.20 (d,  $J$  = 7.0 Hz, 1H), 7.03 (t,  $J$  = 7.5 Hz, 1H), 6.85 (d,  $J$  = 7.8 Hz, 1H), 3.61 (d,  $J$  = 6.6 Hz, 2H), 3.25 (s, 3H), 3.04 (d,  $J$  = 16.2 Hz, 1H), 2.86 (d,  $J$  = 16.2 Hz, 1H), 1.74-1.65 (m, 1H), 1.37 (s, 3H), 0.75 (t,  $J$  = 7.1 Hz, 6H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  179.9, 169.9, 143.5, 133.0, 128.1, 122.4, 122.2, 108.1, 70.7, 45.5, 41.6, 27.5, 26.3, 24.5, 18.9.

HRMS: (ESI) calcd for  $C_{16}H_{21}NO_3H^+$   $[M+H]^+$  276.1594; found 276.1593.

#### propyl 2-(1,3-dimethyl-2-oxoindolin-3-yl)acetate (**6r**)

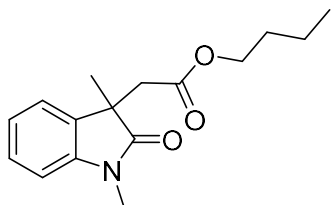


Chemical Formula:  $C_{15}H_{19}NO_3$   
Exact Mass: 261.1365

**6r** was prepared according to general procedure **2.2** using *N*-(2-bromophenyl)-*N*-methylmethacrylamide (0.1 mmol, 25.4 mg) and propyl carbonochloridate (0.4 mmol, 49.0 mg) and was purified by silica gel column chromatography (PE/EtOAc = 15/1~5/1) to obtain **6r** as yellow oil (17.7 mg, 68% yield). TLC (petroleum ether: ethyl acetate, 5:1 v/v):  $R_f$  = 0.5. The  $^1H$  NMR data matched those reported in the literature.<sup>[7]</sup>  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.30-7.23 (m, 1H), 7.22-7.17 (m, 1H), 7.03 (td,  $J$  = 7.5, 1.0 Hz, 1H), 6.85 (d,  $J$  = 7.8 Hz, 1H), 3.86-3.72 (m, 2H), 3.25 (s, 3H), 3.03 (d,  $J$  = 16.2 Hz, 1H), 2.84 (d,  $J$  = 16.2 Hz, 1H), 1.45-1.36 (m, 5H), 0.76 (t,  $J$  = 7.4 Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  179.9, 169.9, 143.6, 133.0, 128.1, 122.4, 122.3, 108.1, 66.1, 45.5, 41.7, 26.3, 24.5, 21.7, 10.2.

**butyl 2-(1,3-dimethyl-2-oxoindolin-3-yl)acetate (6s)**



Chemical Formula:  $\text{C}_{16}\text{H}_{21}\text{NO}_3$

Exact Mass: 275.1521

**6s** was prepared according to general procedure **2.2** using *N*-(2-bromophenyl)-*N*-methylmethacrylamide (0.1 mmol, 25.4 mg) and butyl carbonochloridate (0.4 mmol, 54.6 mg) and was purified by silica gel column chromatography (PE/EtOAc = 15/1~5/1) to obtain **6s** as yellow oil (15.7mg, 57% yield). TLC (petroleum ether: ethyl acetate, 5:1 v/v):  $R_f$  = 0.5.

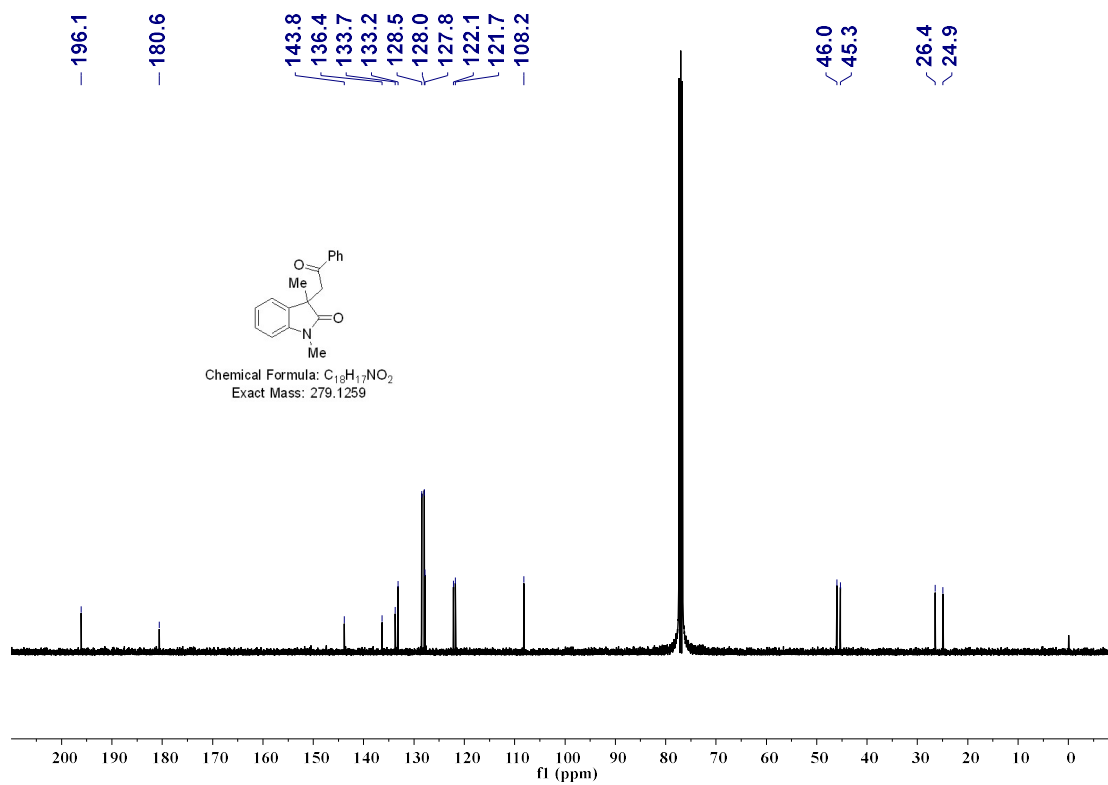
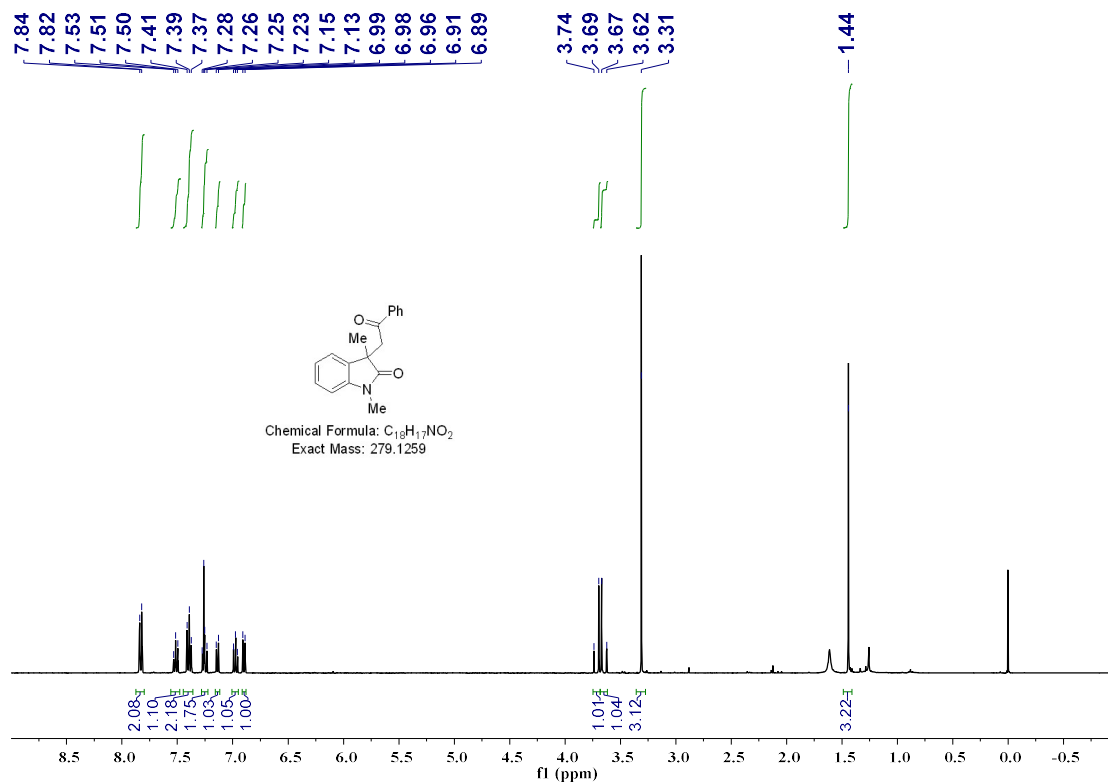
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32-7.23 (m, 1H), 7.23-7.16 (m, 1H), 7.03 (td,  $J$  = 7.5, 1.0 Hz, 1H), 6.85 (d,  $J$  = 7.8 Hz, 1H), 3.91-3.75 (m, 2H), 3.25 (s, 3H), 3.03 (d,  $J$  = 16.2 Hz, 1H), 2.83 (d,  $J$  = 16.2 Hz, 1H), 1.40-1.30 (m, 5H), 1.22-1.11 (m, 2H), 0.82 (t,  $J$  = 7.3 Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  179.9, 169.9, 143.6, 133.0, 128.1, 122.3, 122.3, 108.1, 64.4, 45.5, 41.7, 30.4, 26.3, 24.5, 18.9, 13.6.

HRMS: (ESI) calcd for  $\text{C}_{16}\text{H}_{21}\text{NO}_3\text{H}^+[\text{M}+\text{H}]^+$  276.1594; found 276.1595.

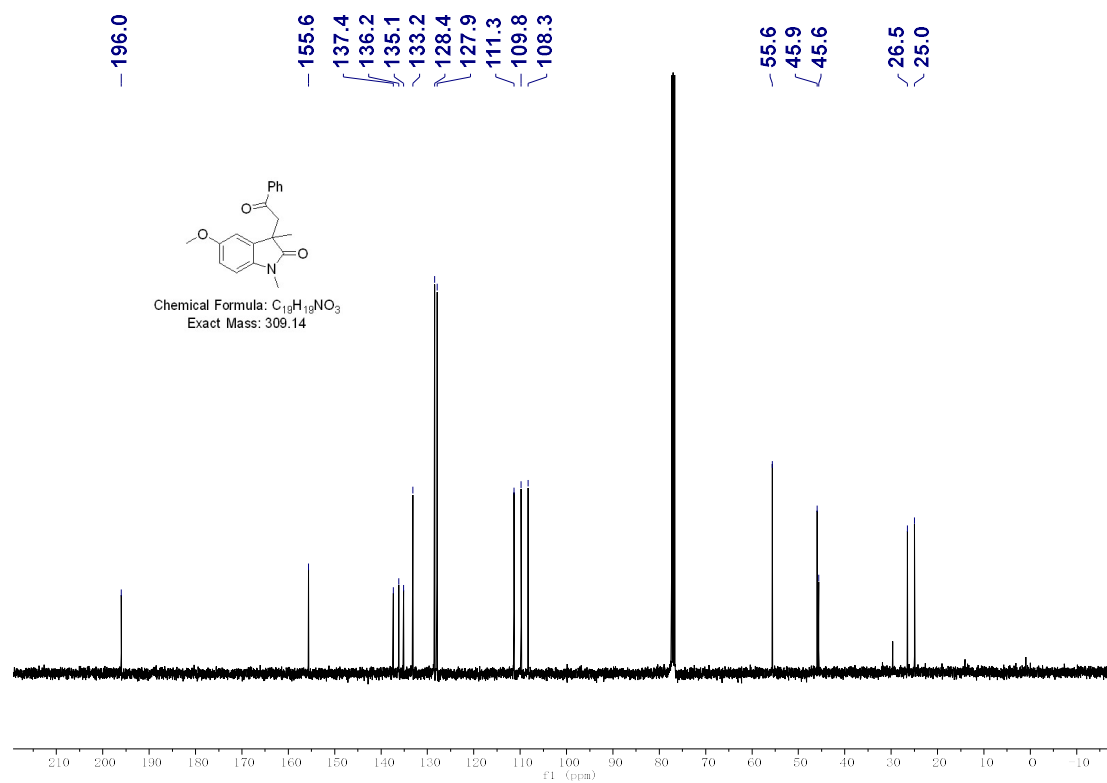
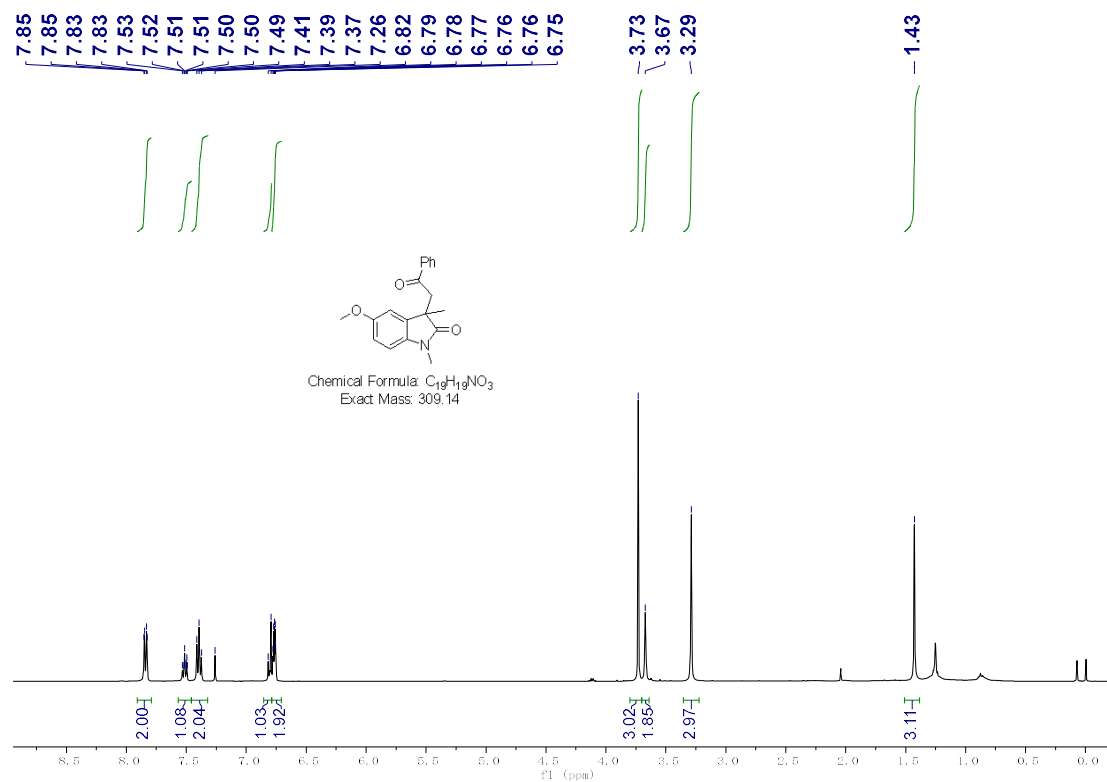
## 6. Copies of the $^1\text{H}$ , $^{19}\text{F}$ and $^{13}\text{C}$ NMR spectra

**3a**

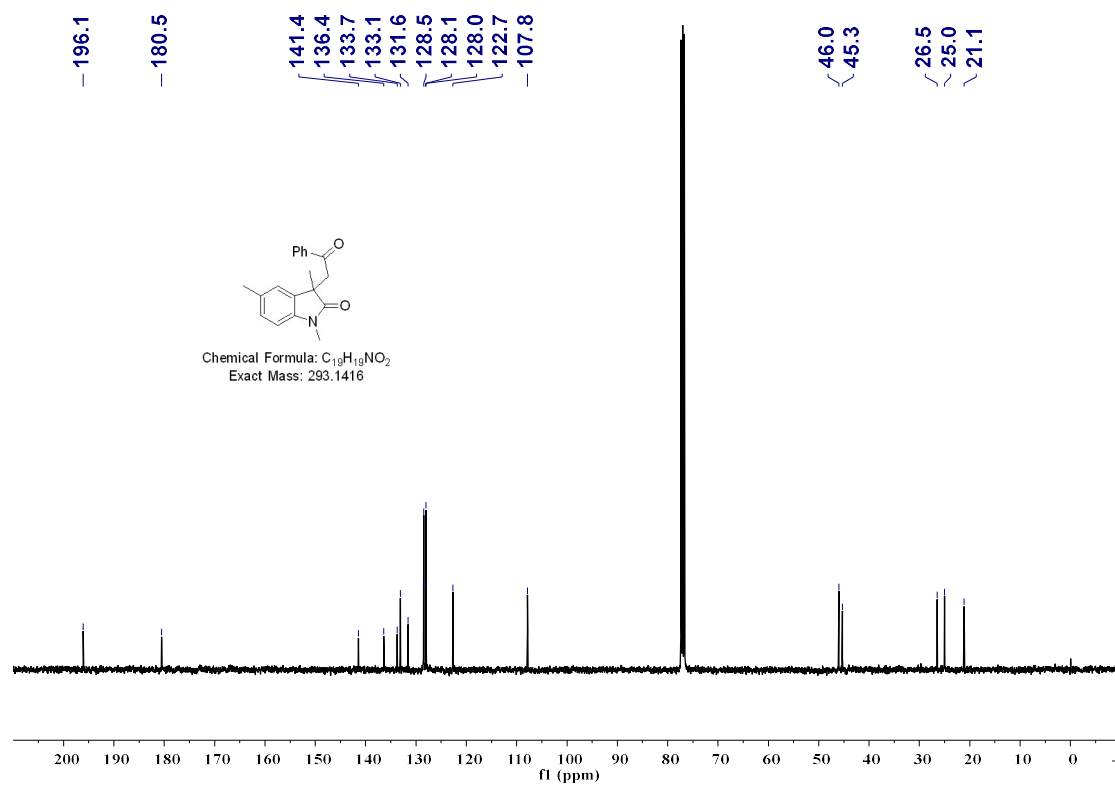
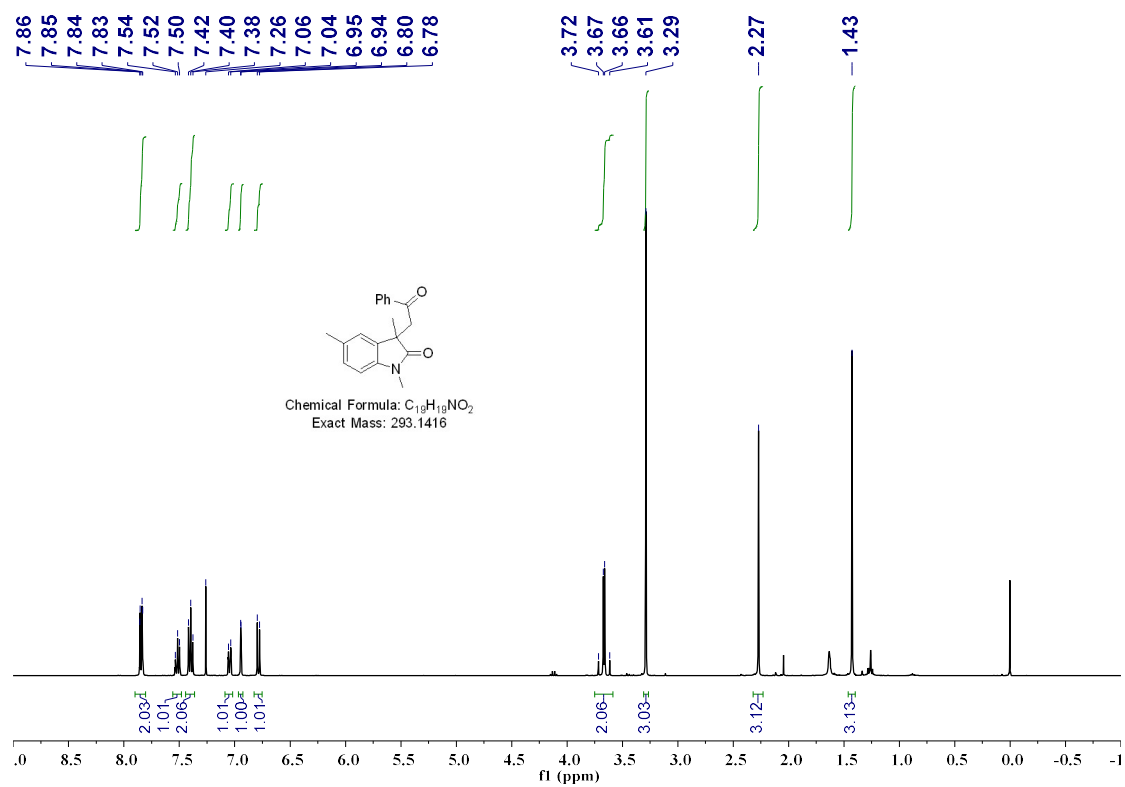




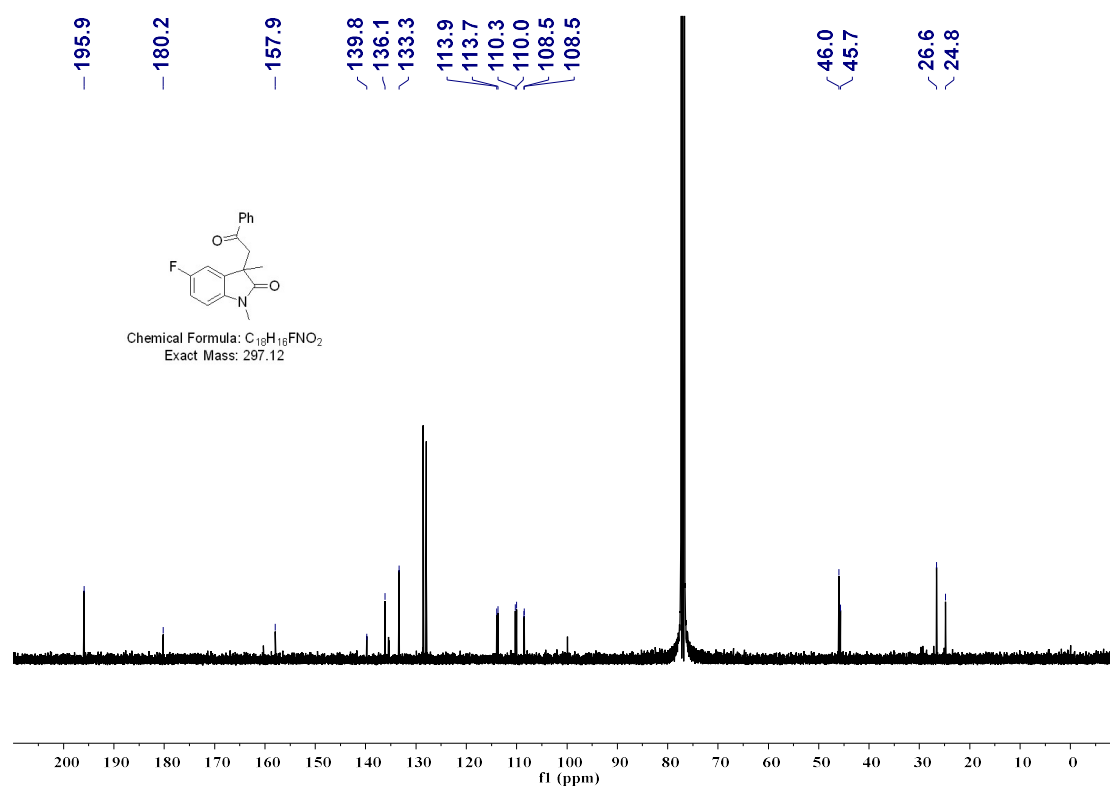
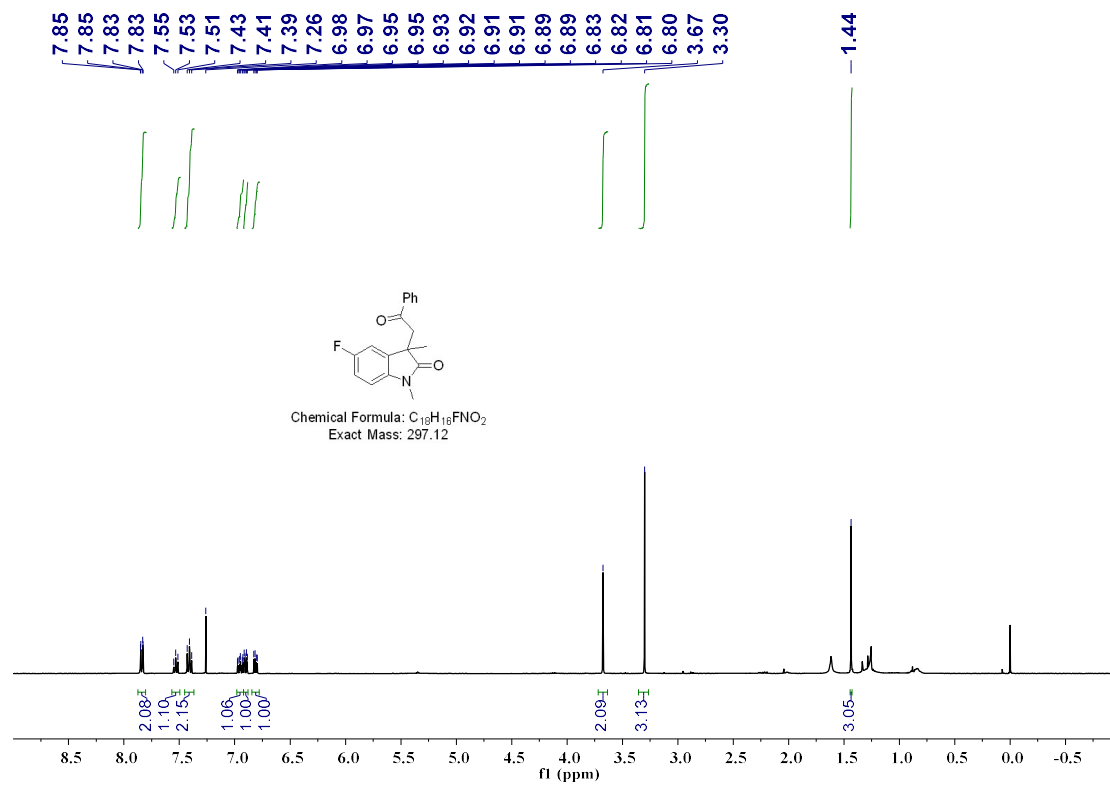
3b



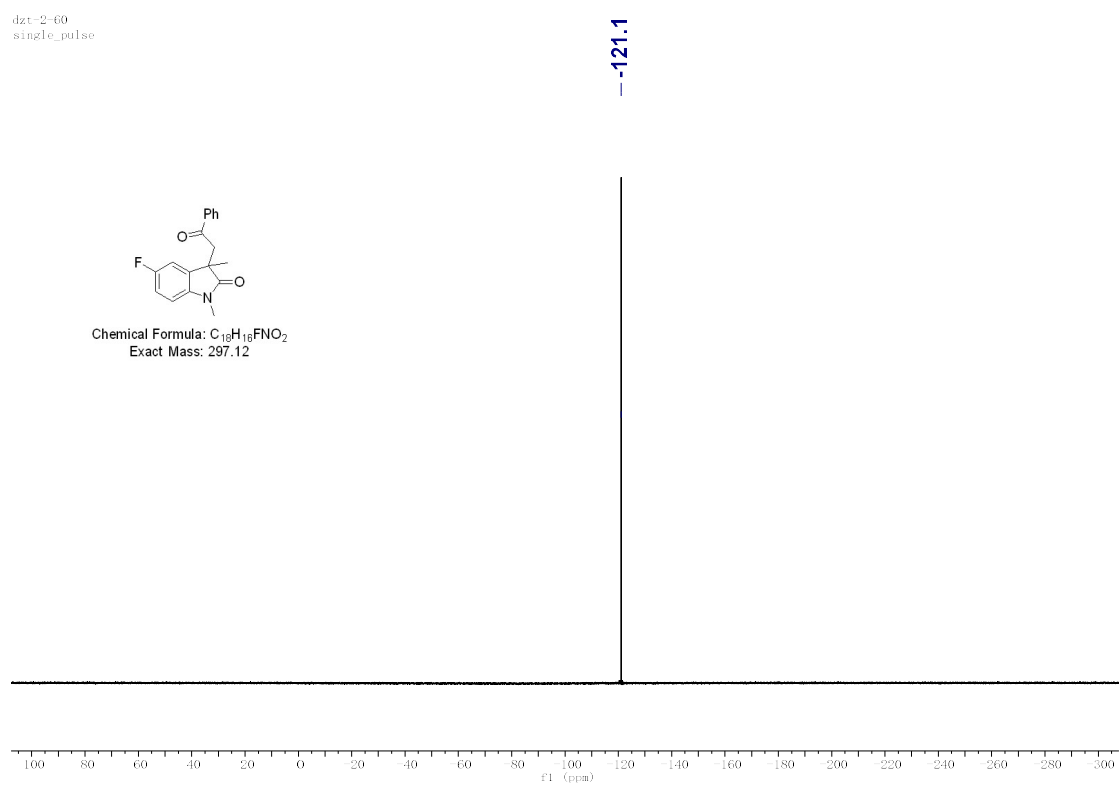
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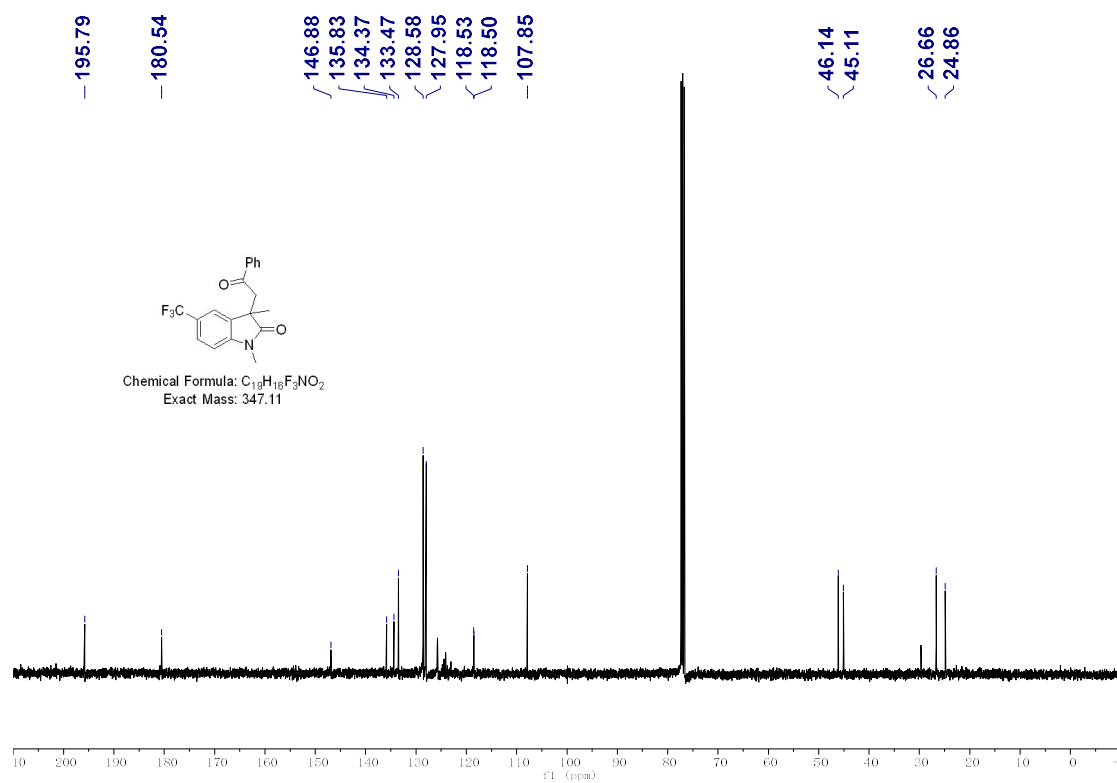
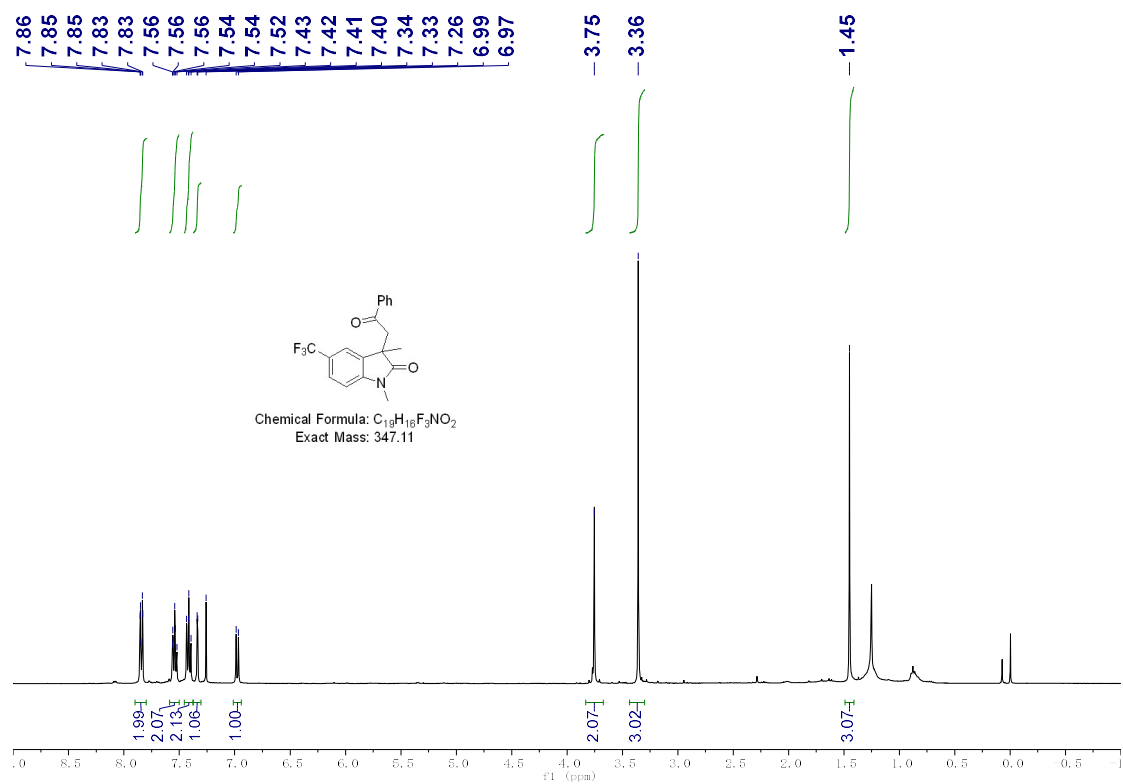
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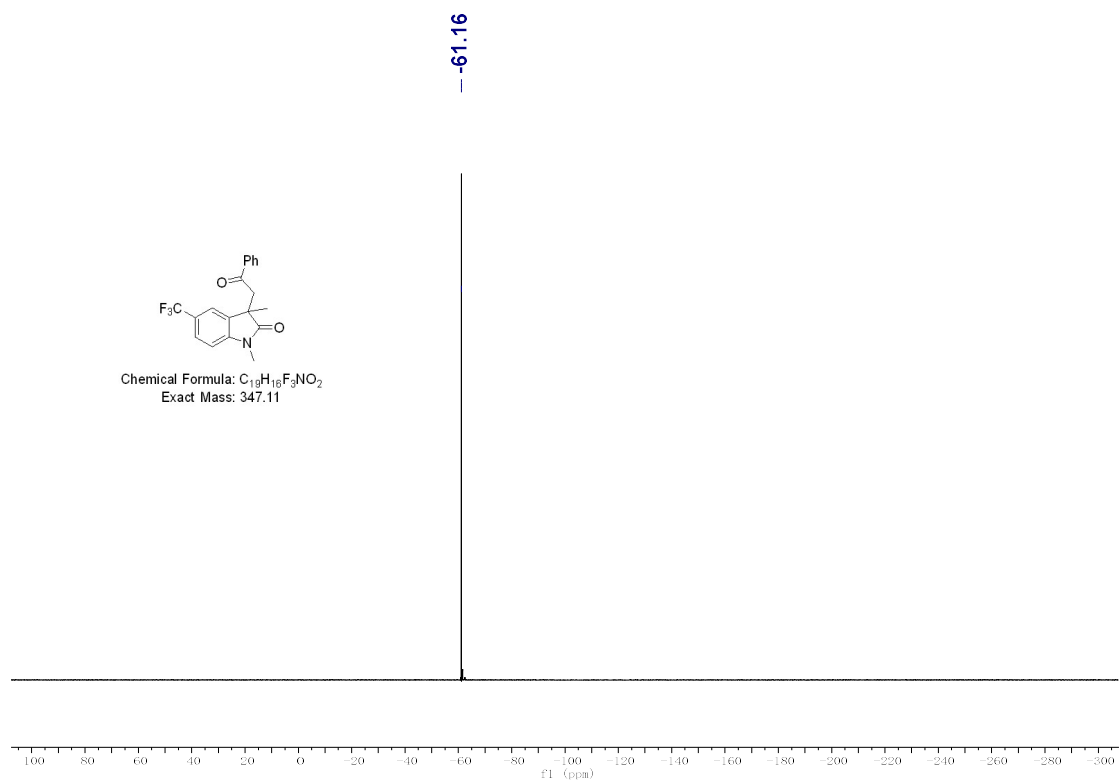


dzt-2-60  
single\_pulse

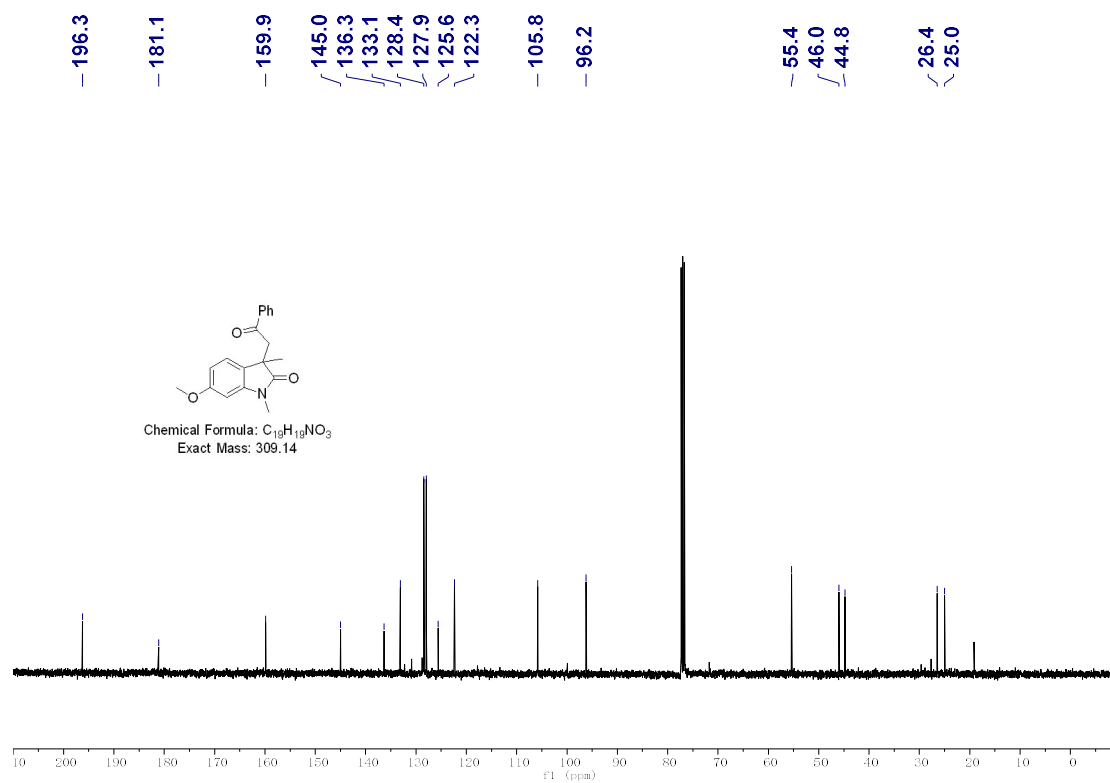
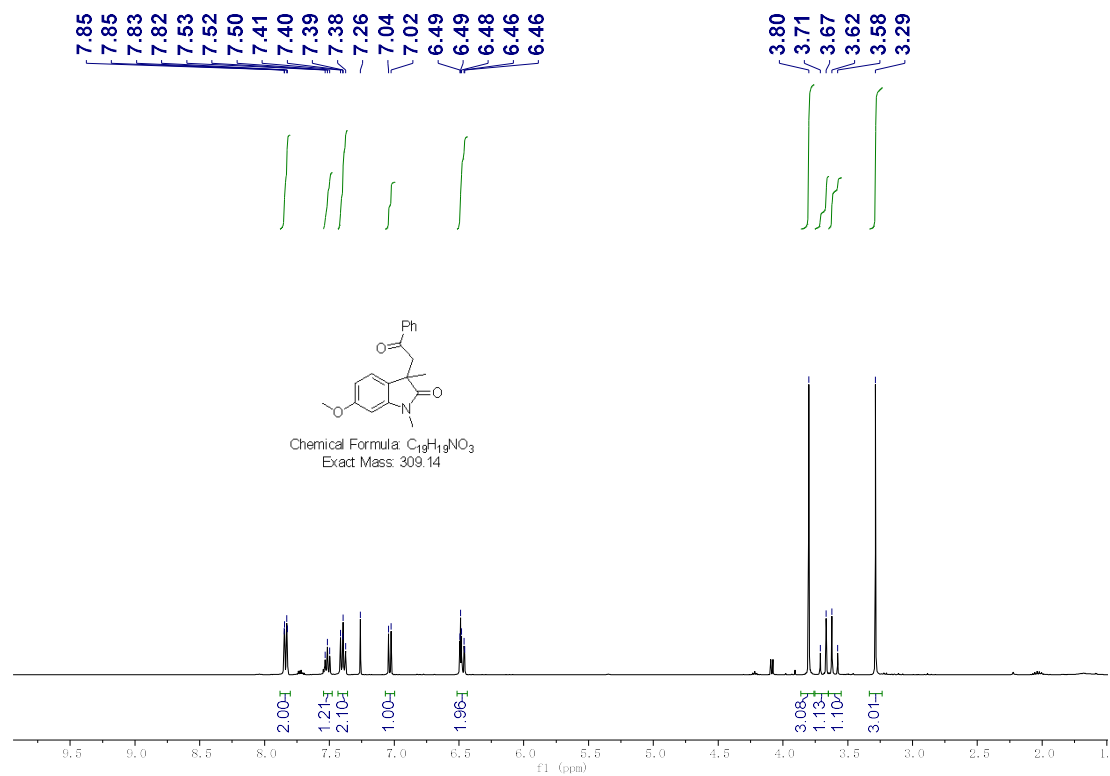


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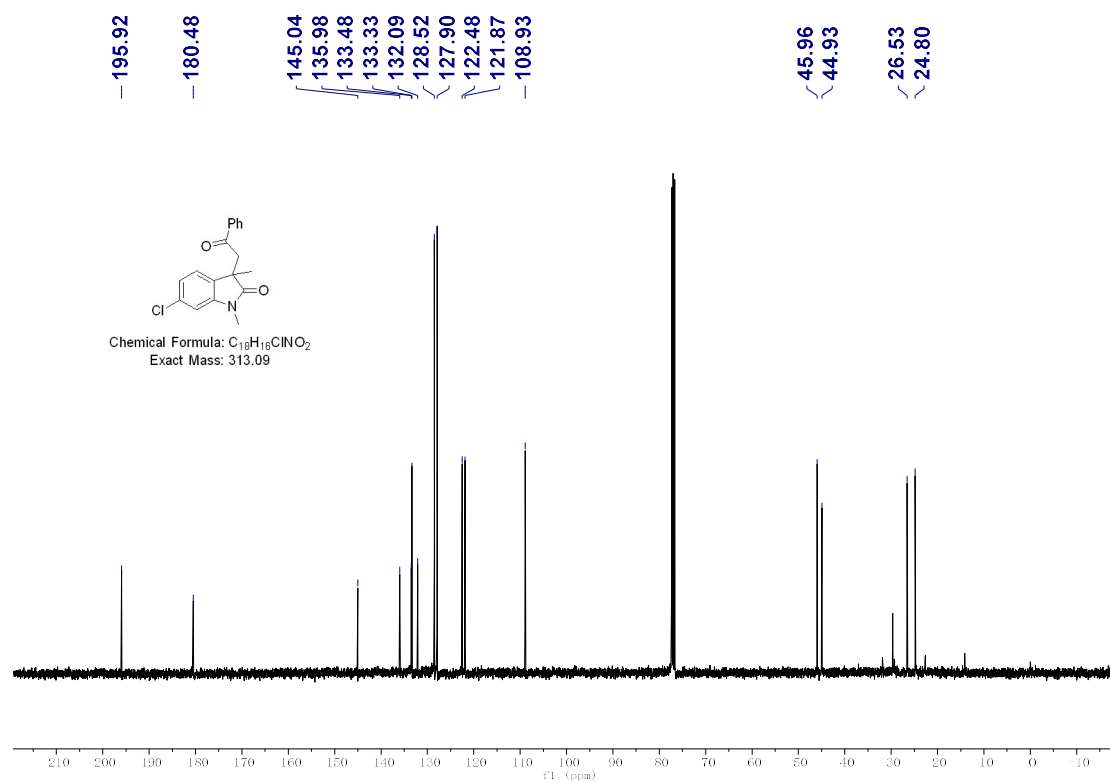
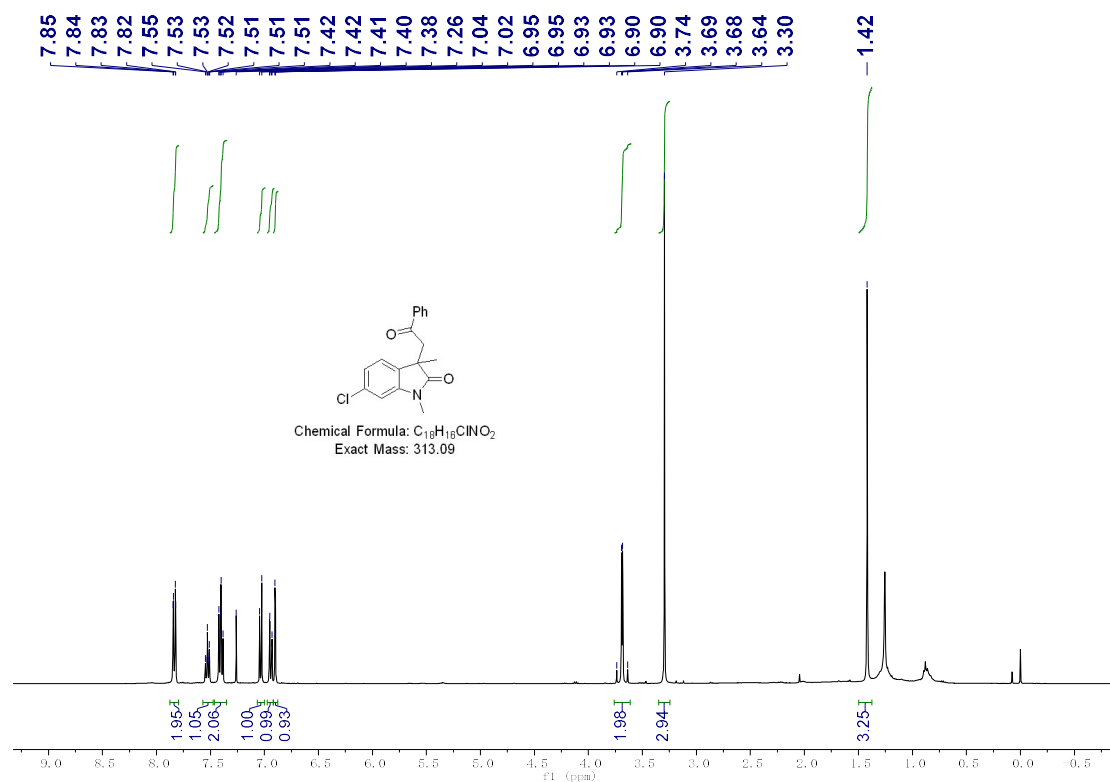




3f

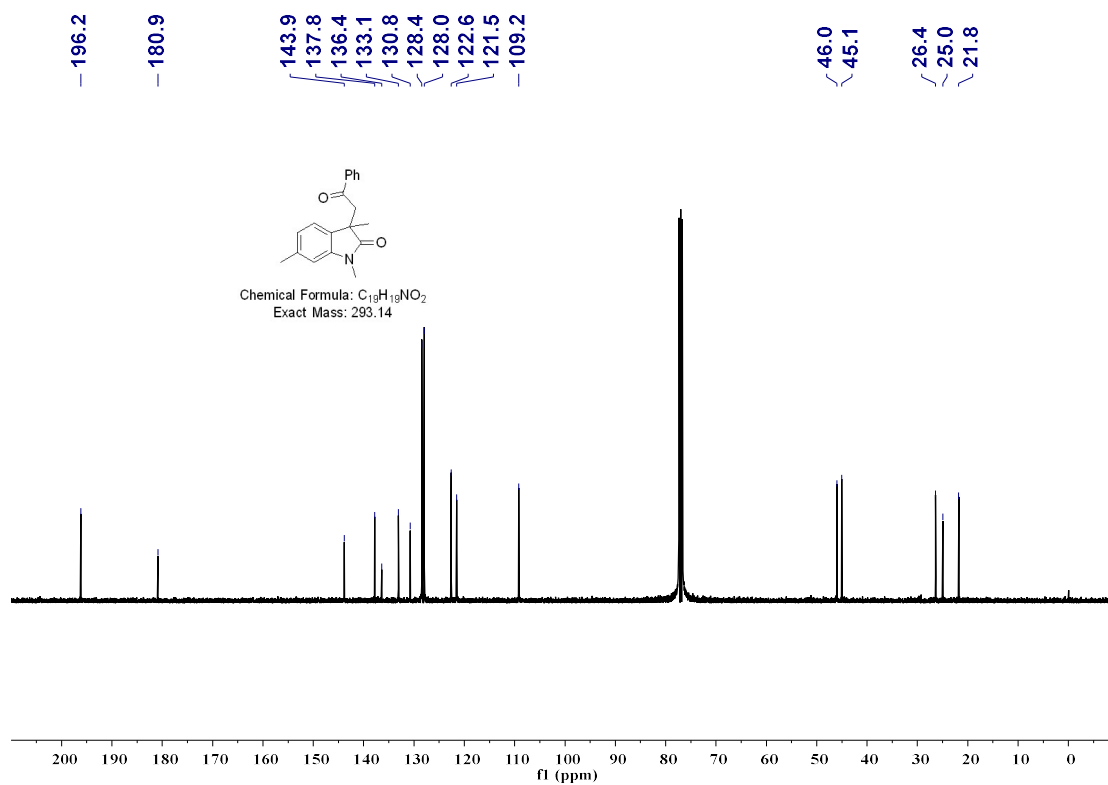
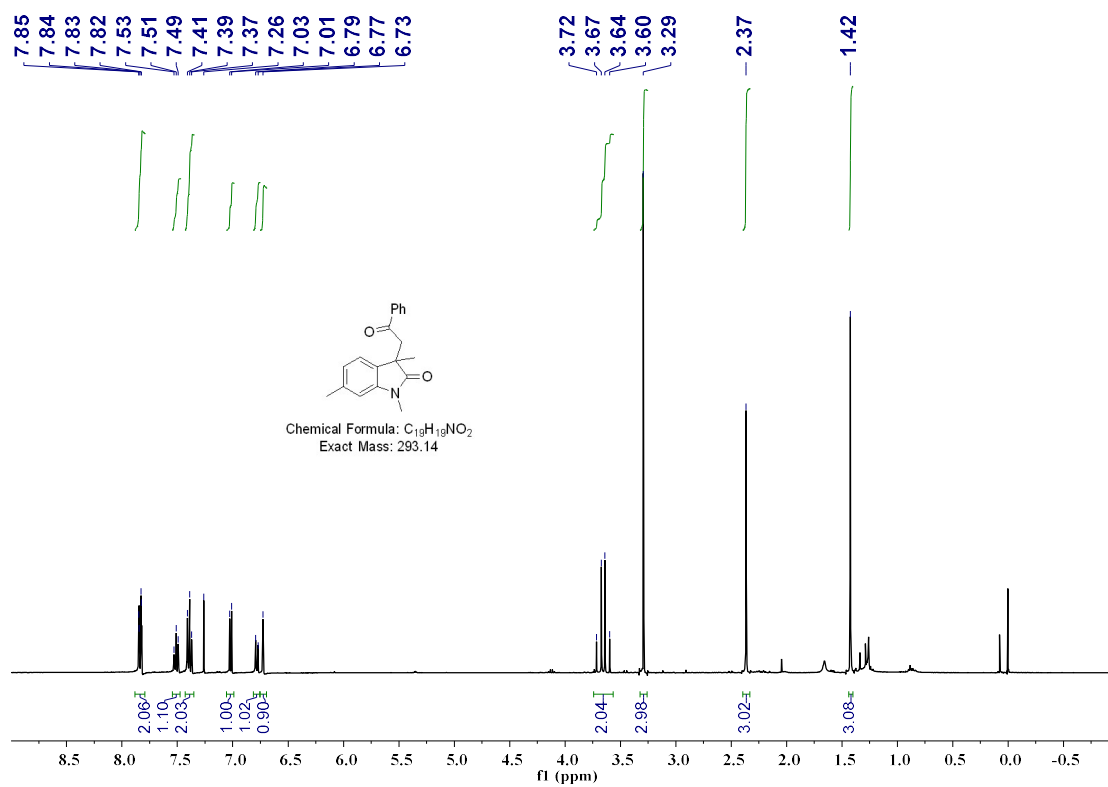


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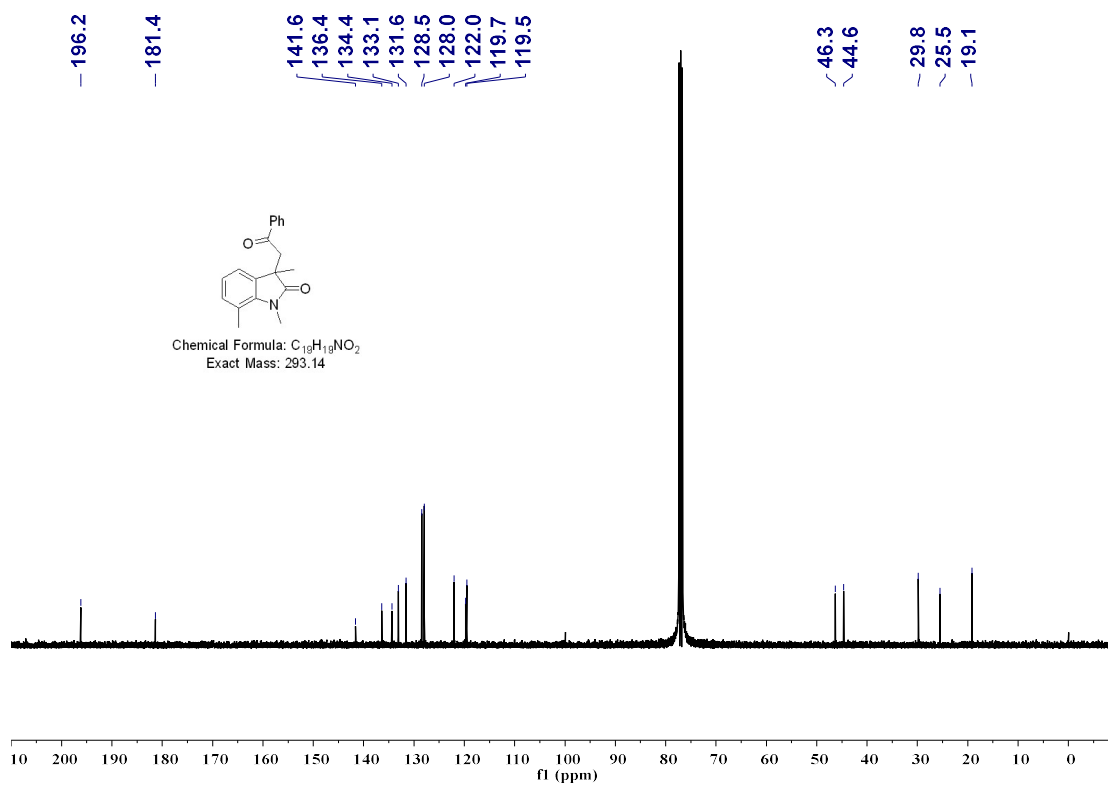
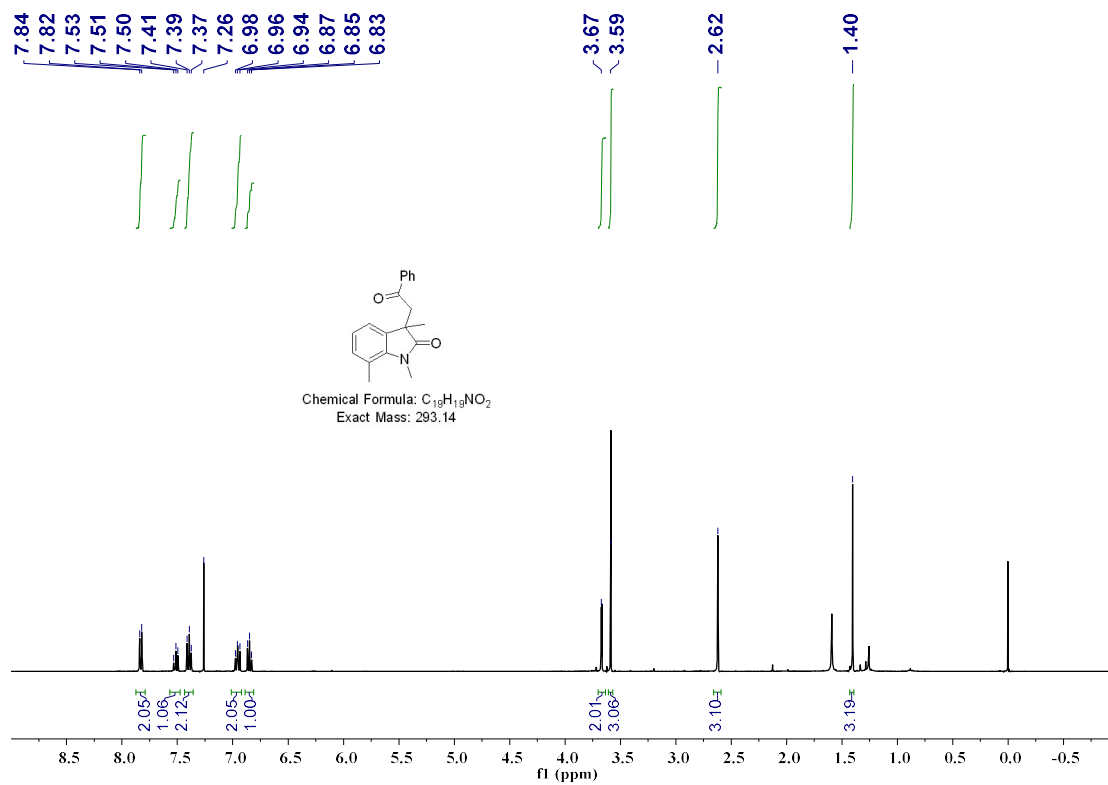




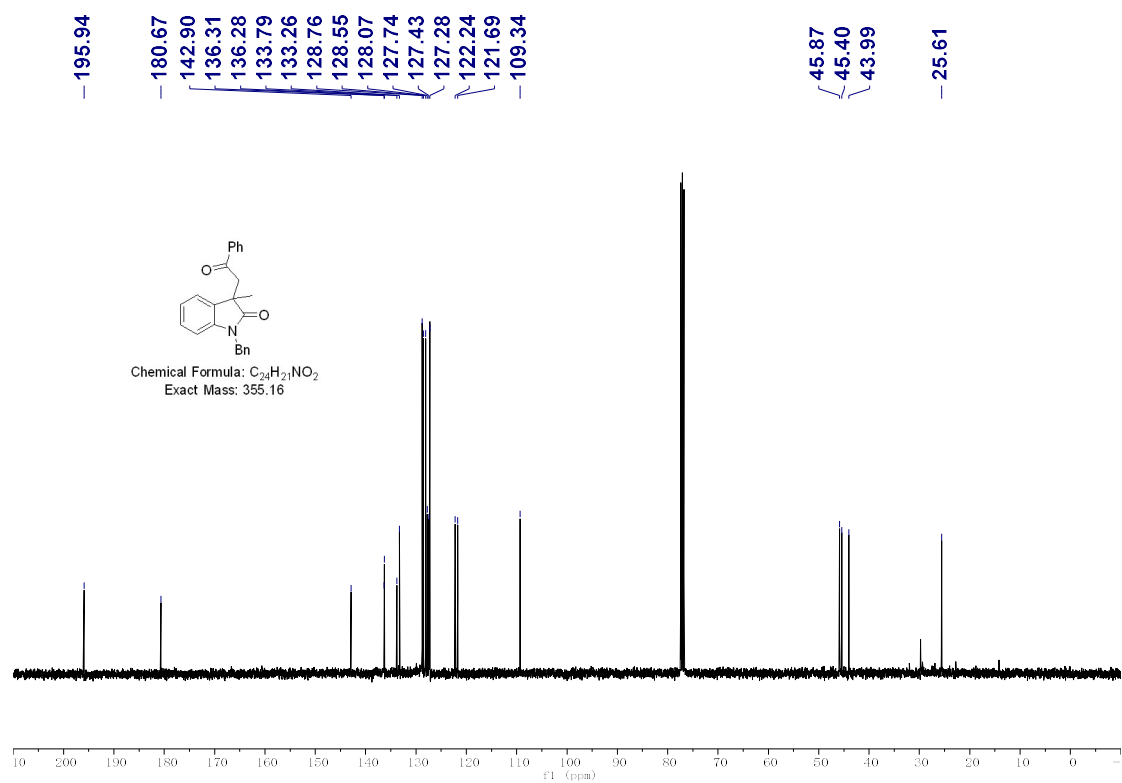
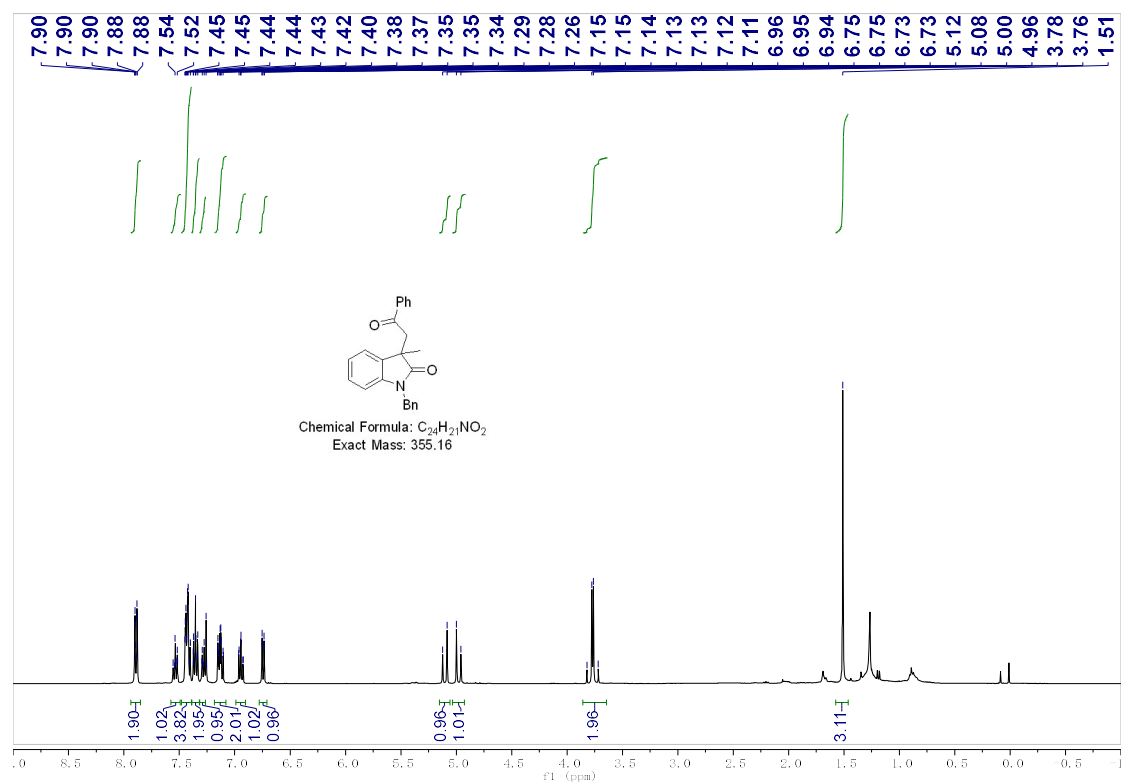
3h



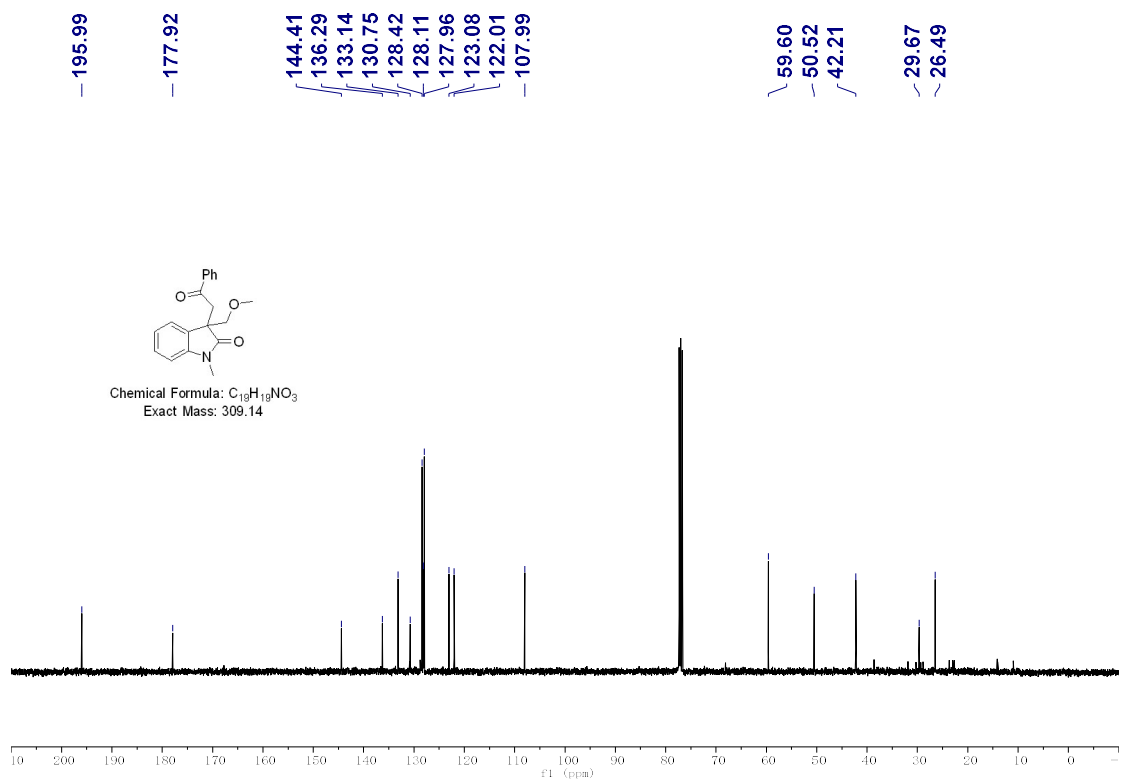
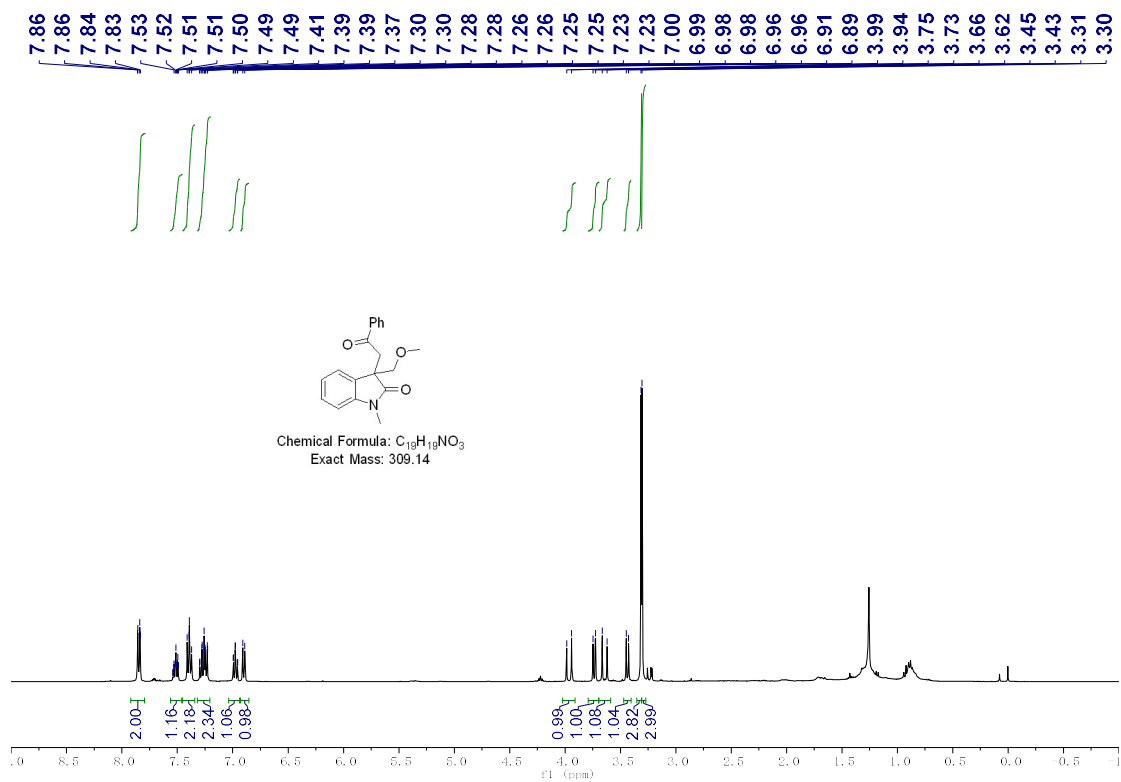
3i

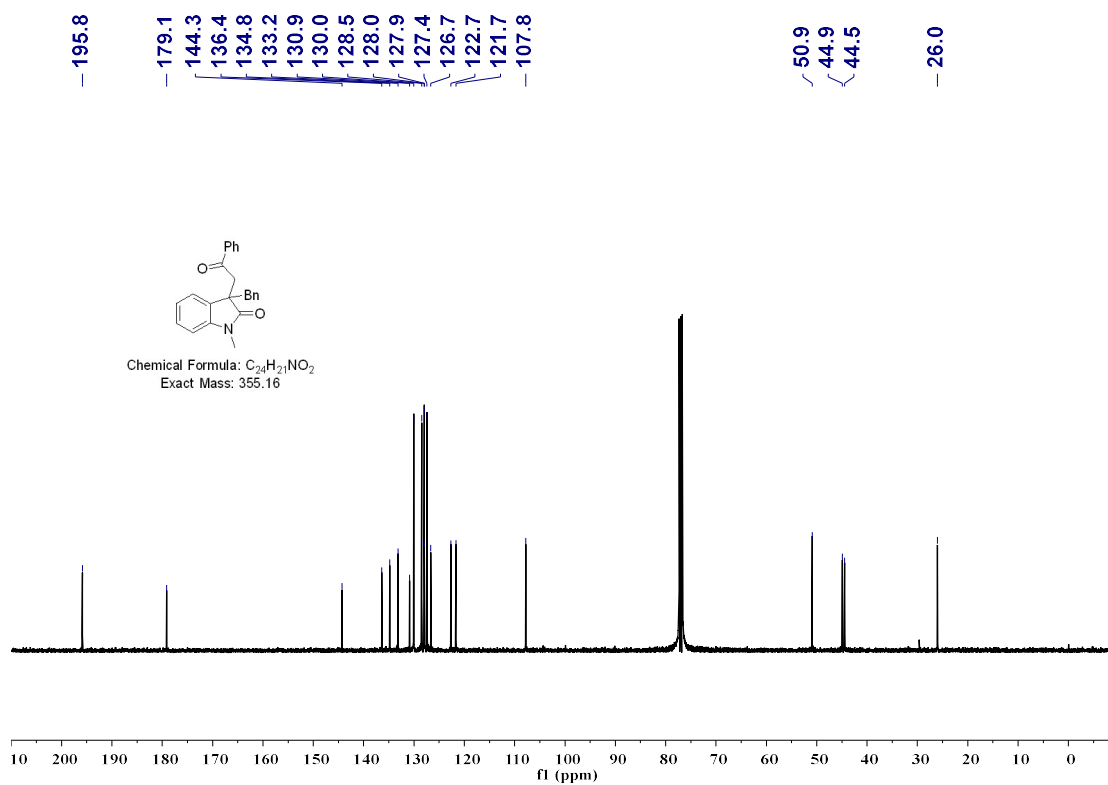
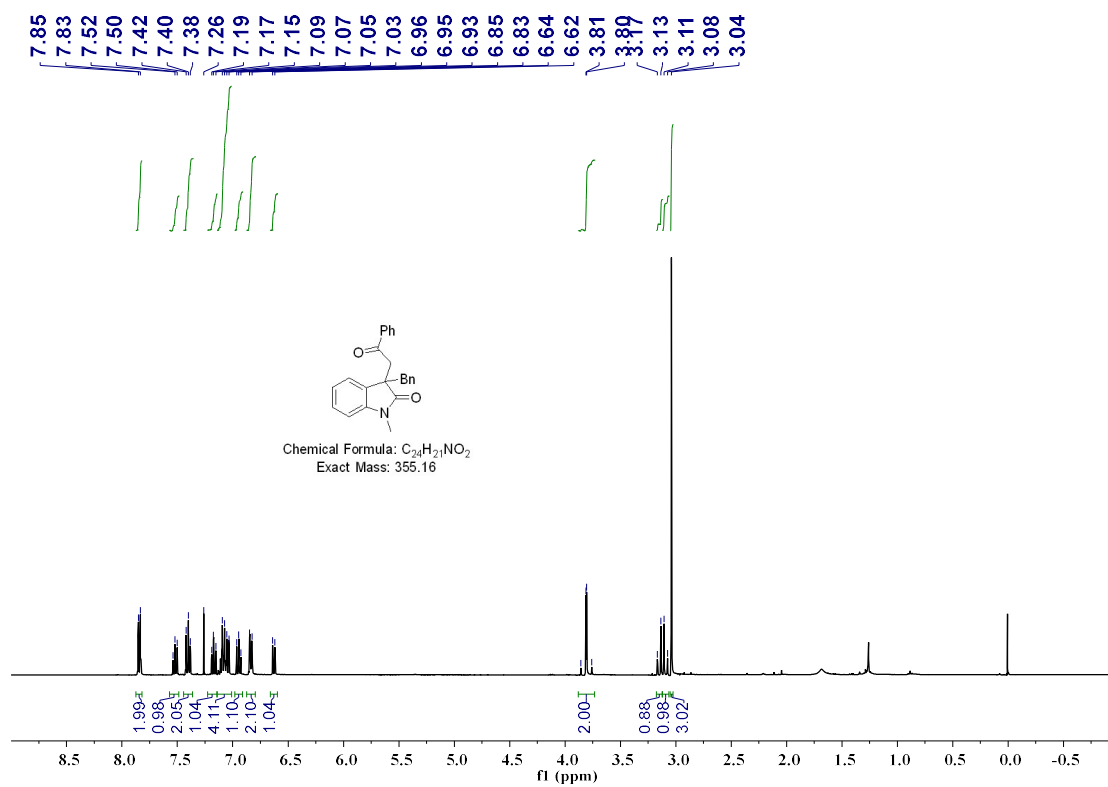


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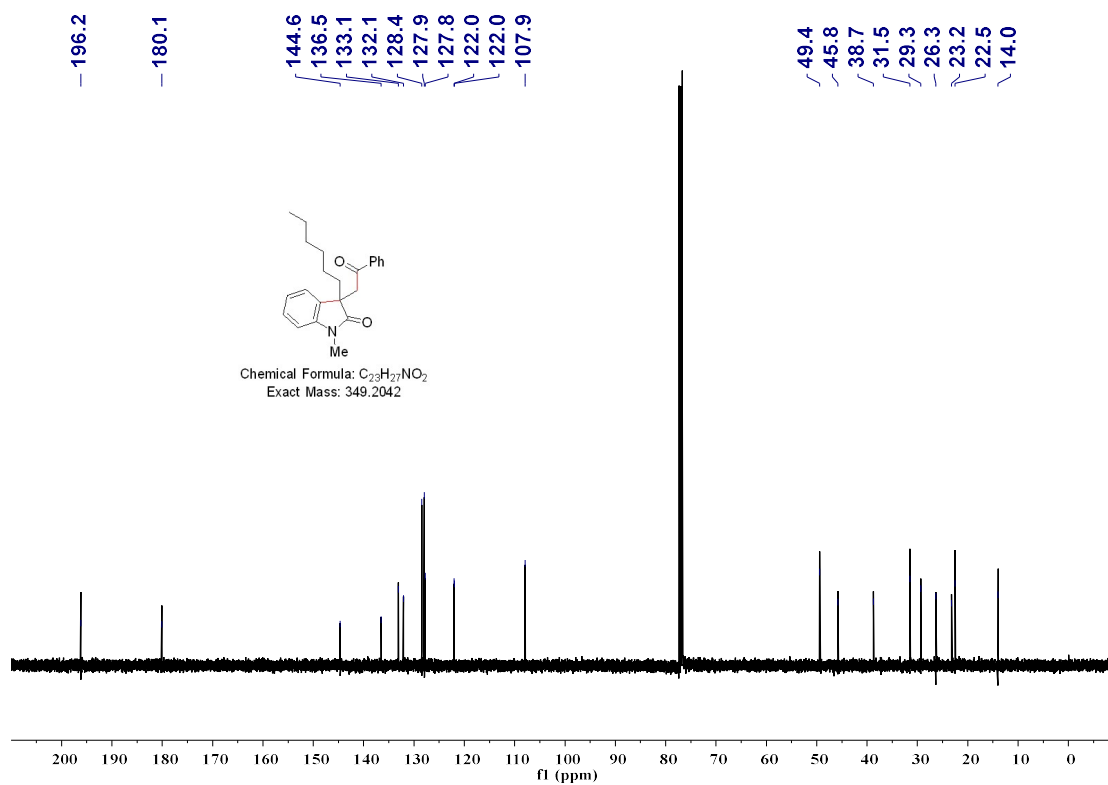
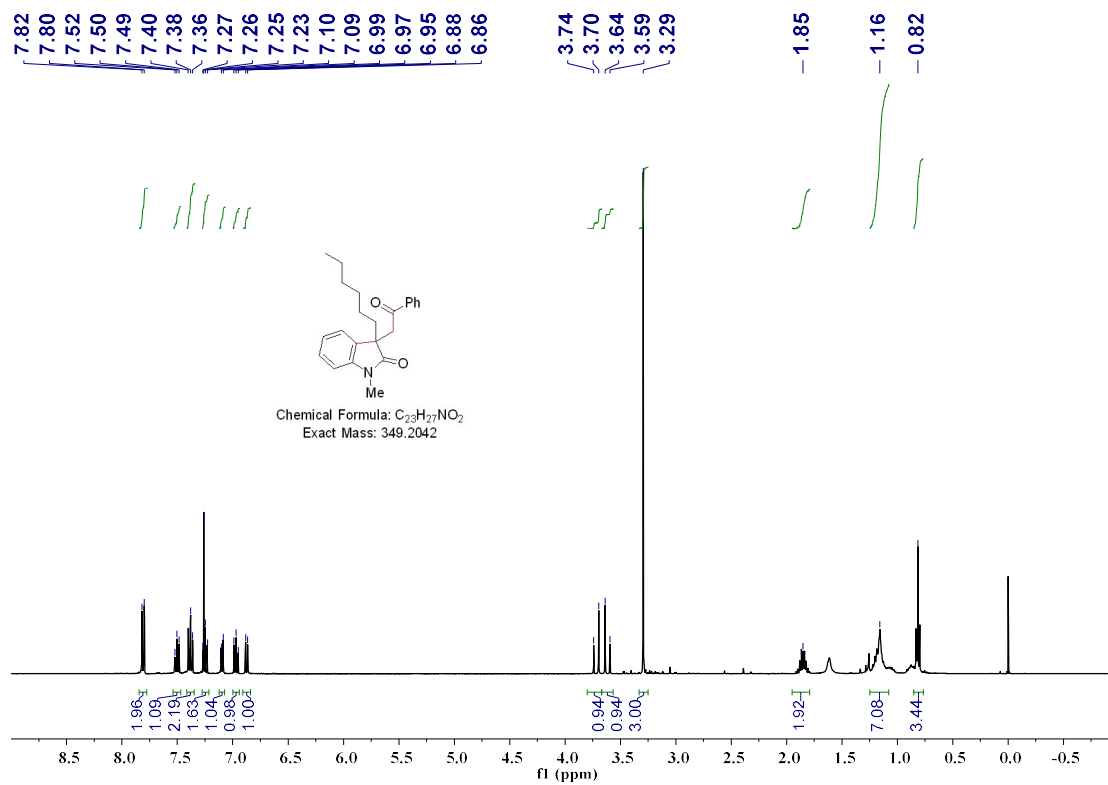


3k





3m

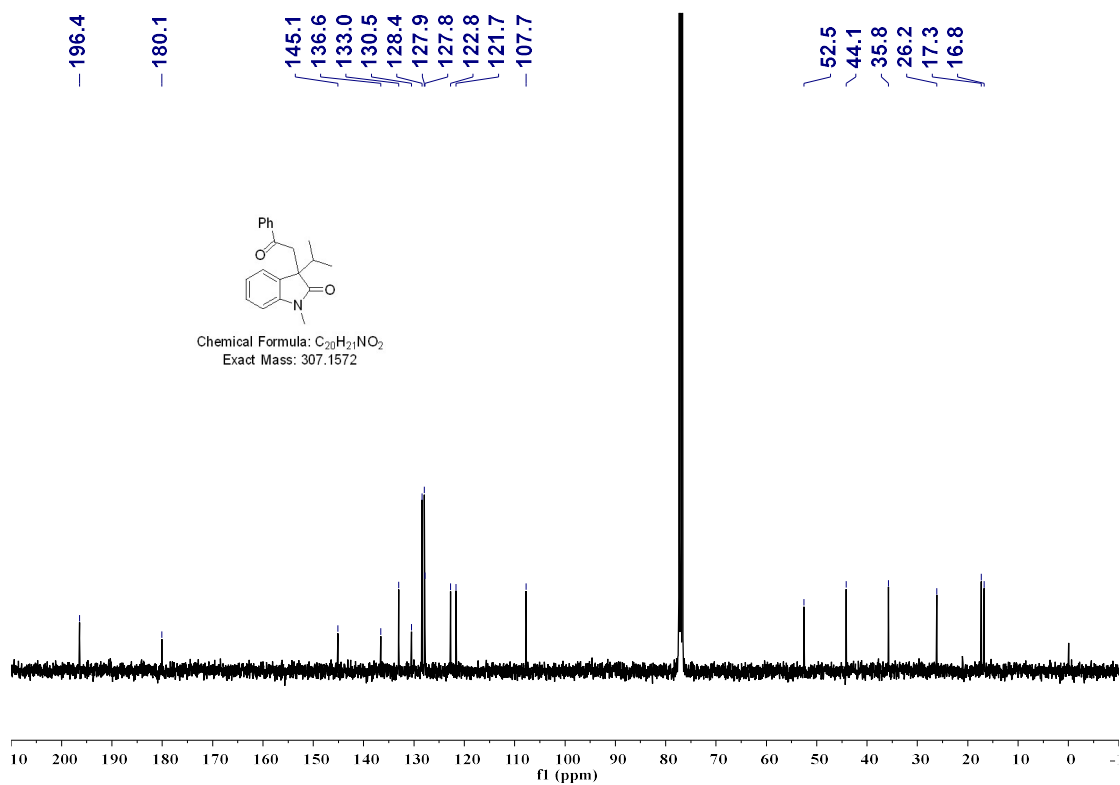


Chemical Formula:  $C_{20}H_{21}NO_2$   
Exact Mass: 307.1572

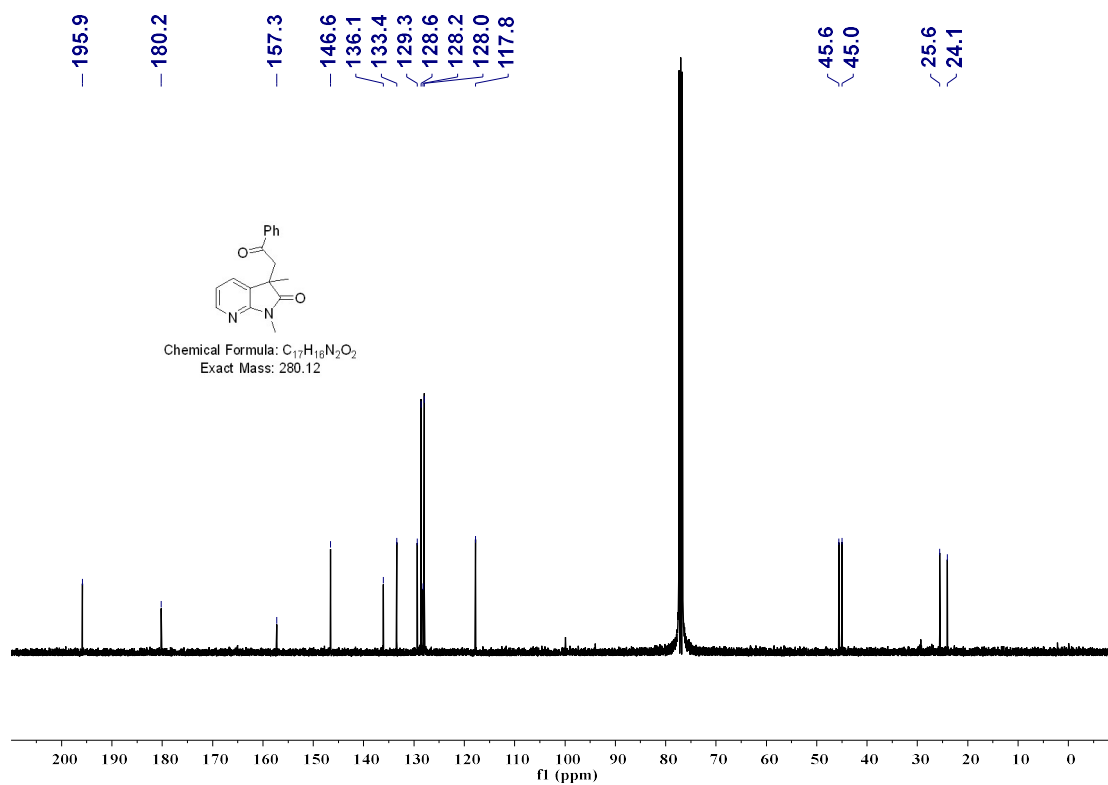
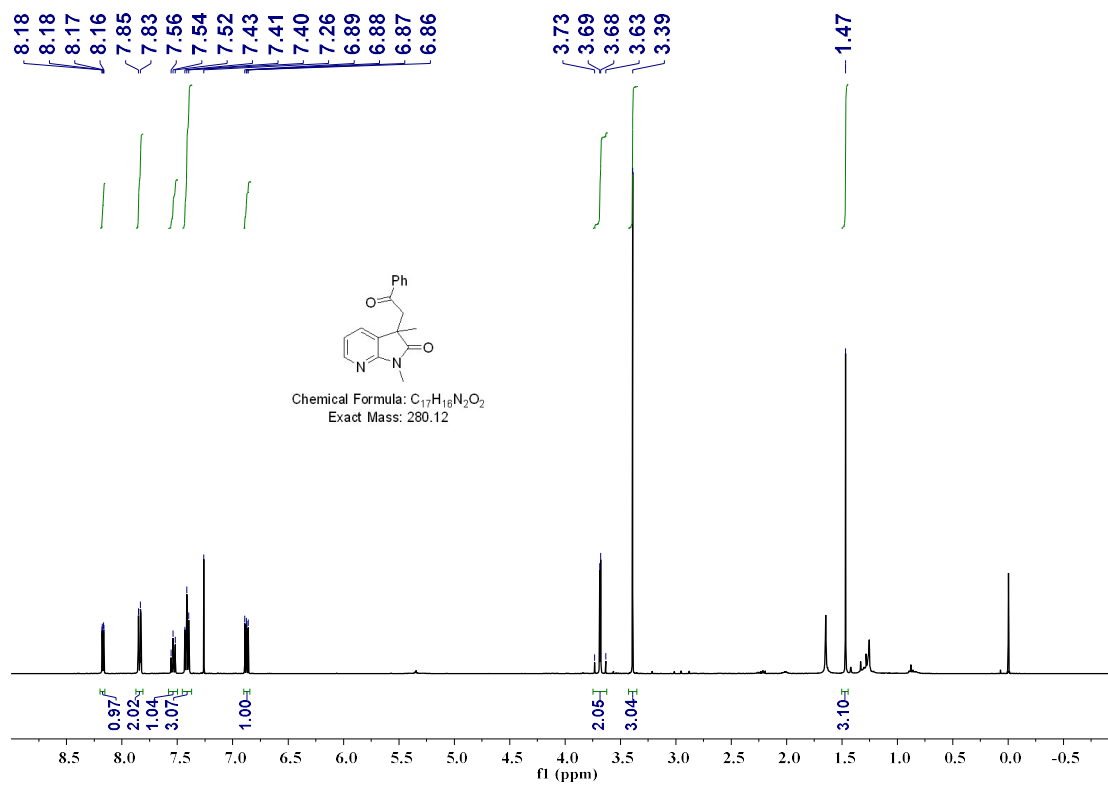
Chemical structure: CC1(C)C(=O)Nc2ccccc2C1=O

$^1H$  NMR spectrum (ppm):

- 7.83, 7.82, 7.81, 7.80, 7.80 (m, 2H, integration 2.00)
- 7.50, 7.48, 7.40, 7.38, 7.36, 7.28, 7.26, 7.24, 7.09, 7.07, 6.97, 6.95, 6.93, 6.93, 6.88, 6.86, 6.86, 3.82, 3.67, 3.62, 3.28, 3.23, 2.21, 2.19 (m, 10H, integration 10.00)
- 7.26 (s, 1H, integration 1.03)
- 1.04, 1.02, 0.74, 0.73 (m, 10H, integration 10.00)

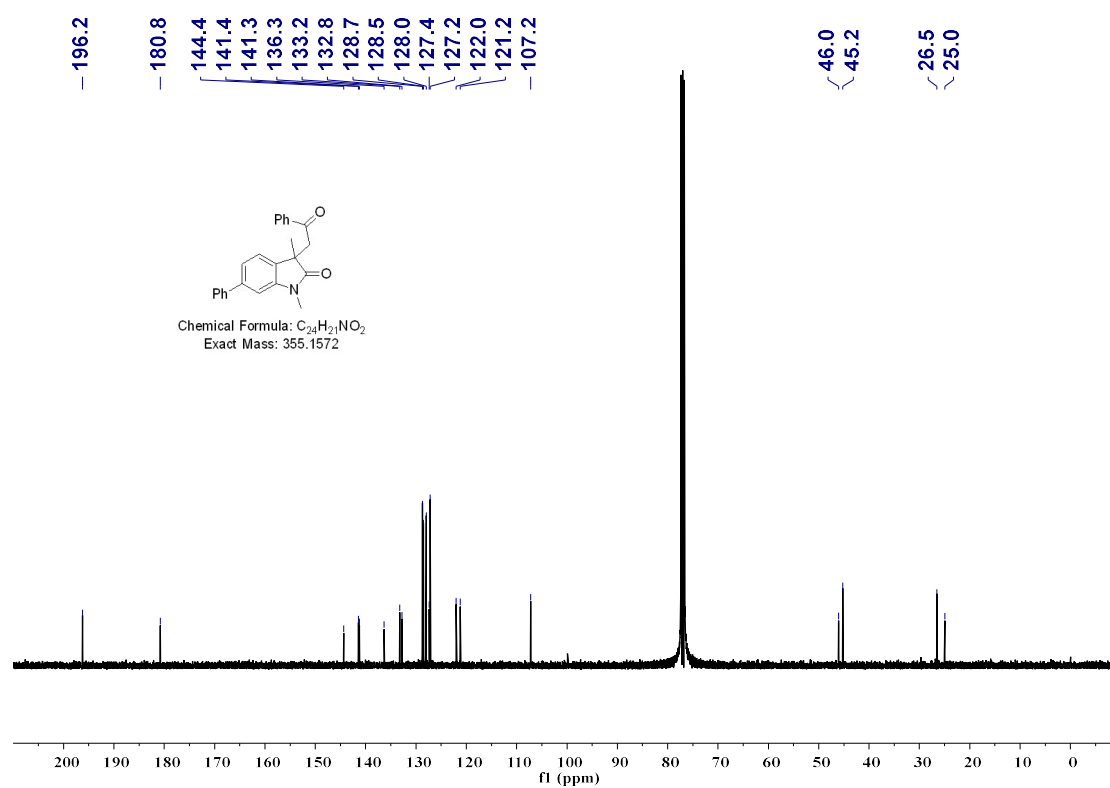
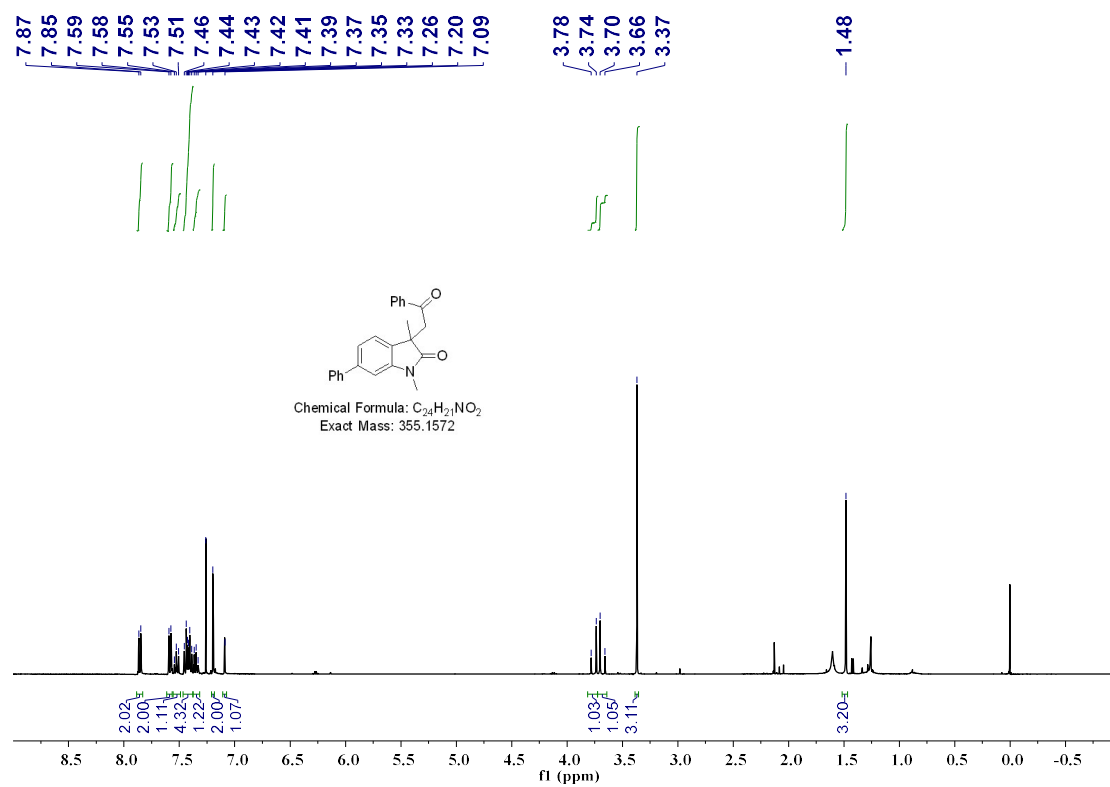


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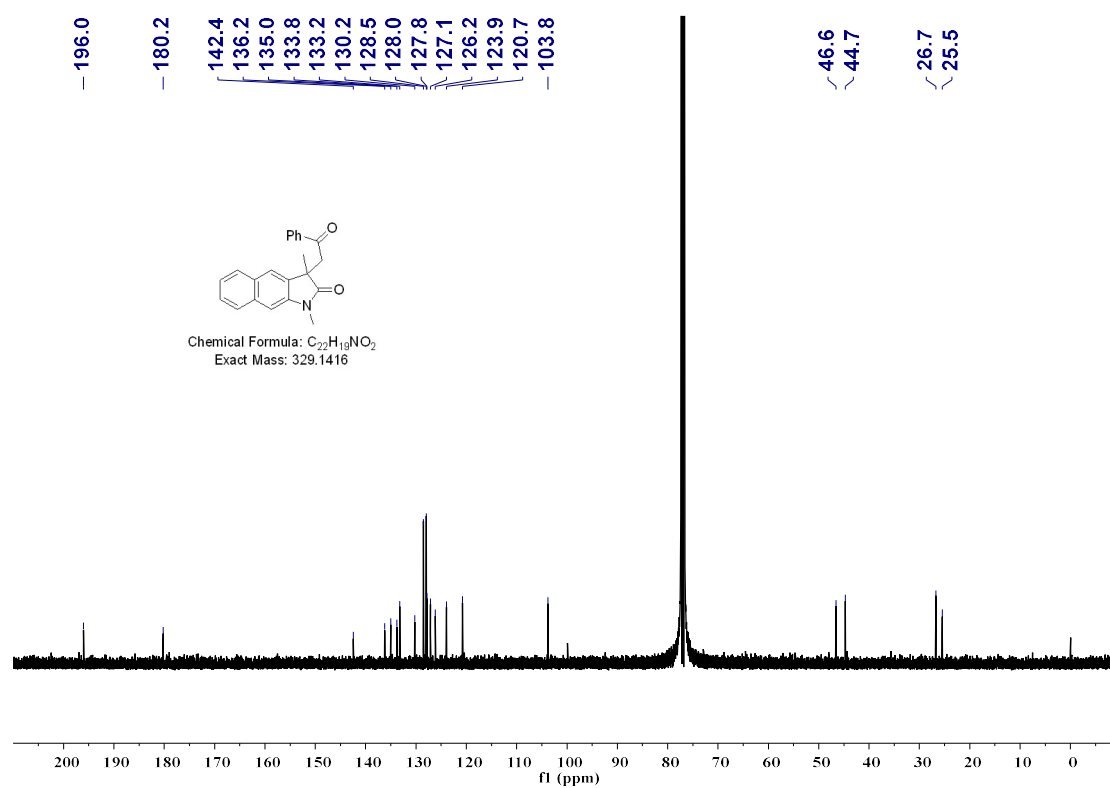
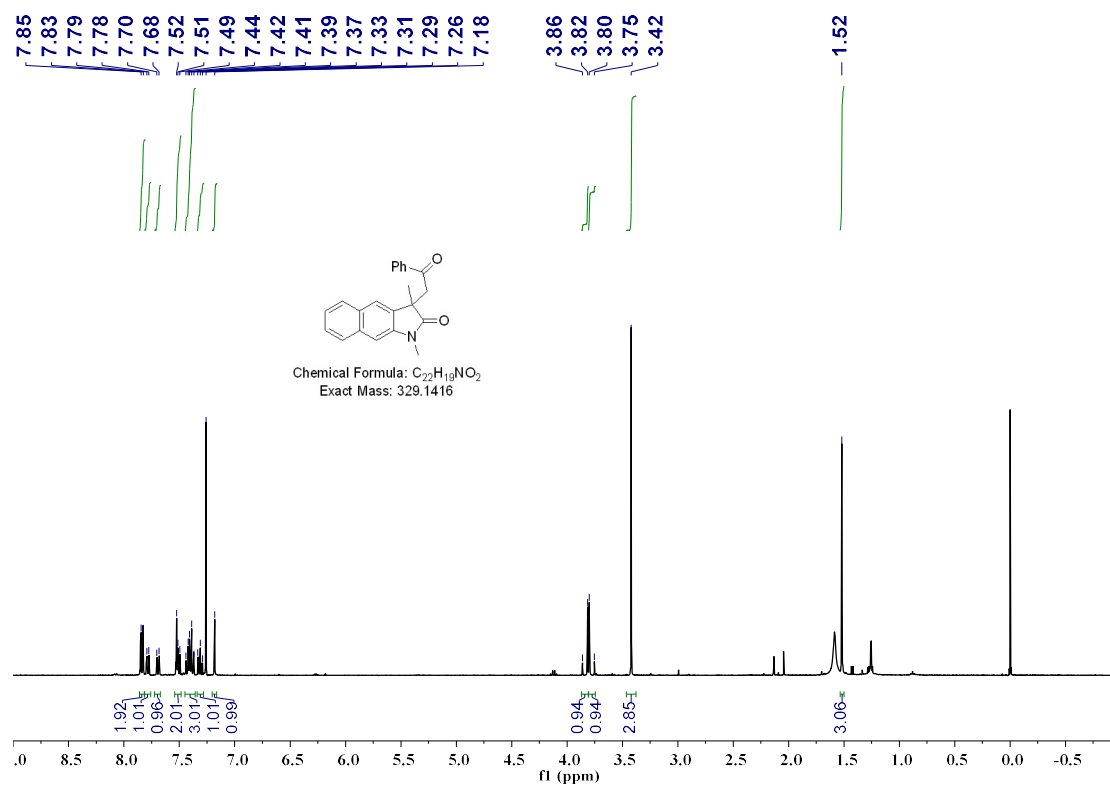




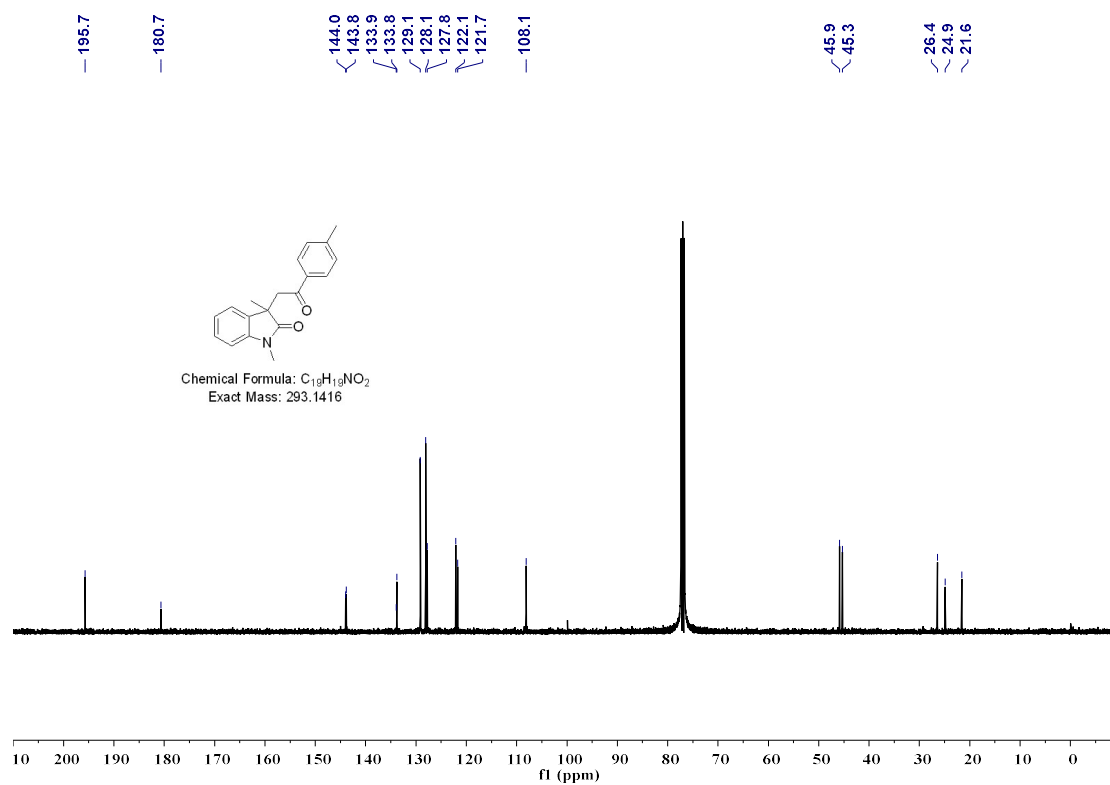
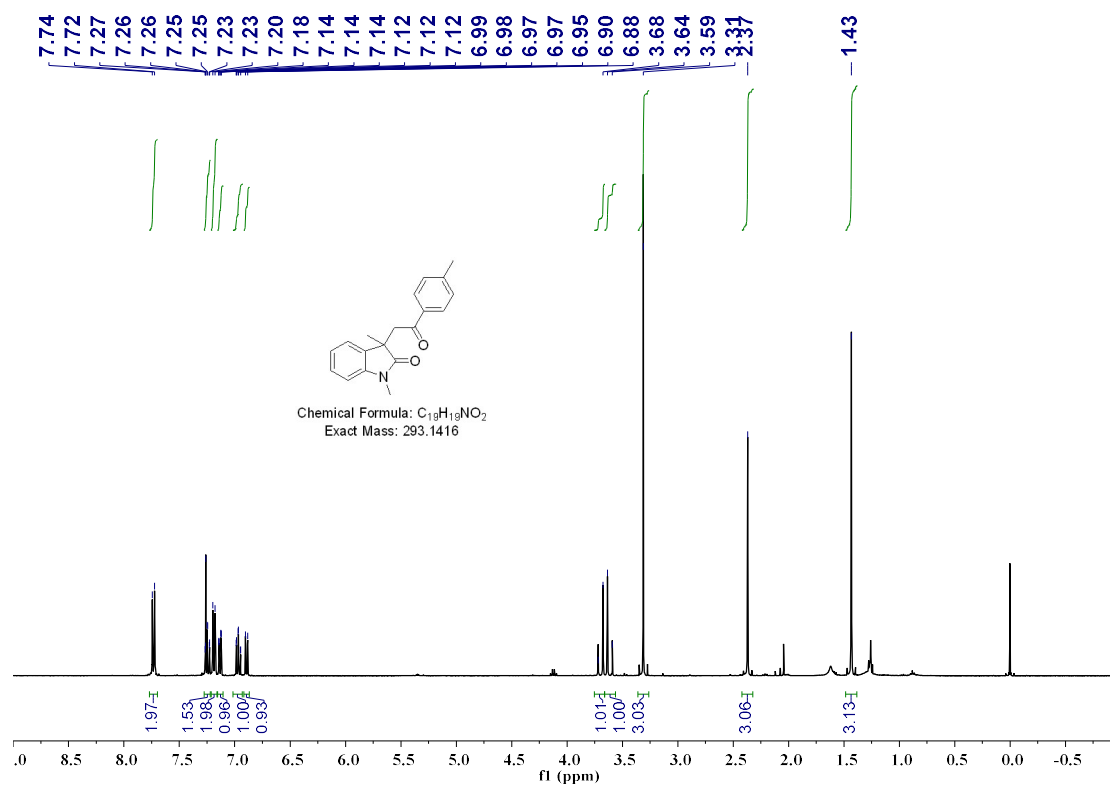
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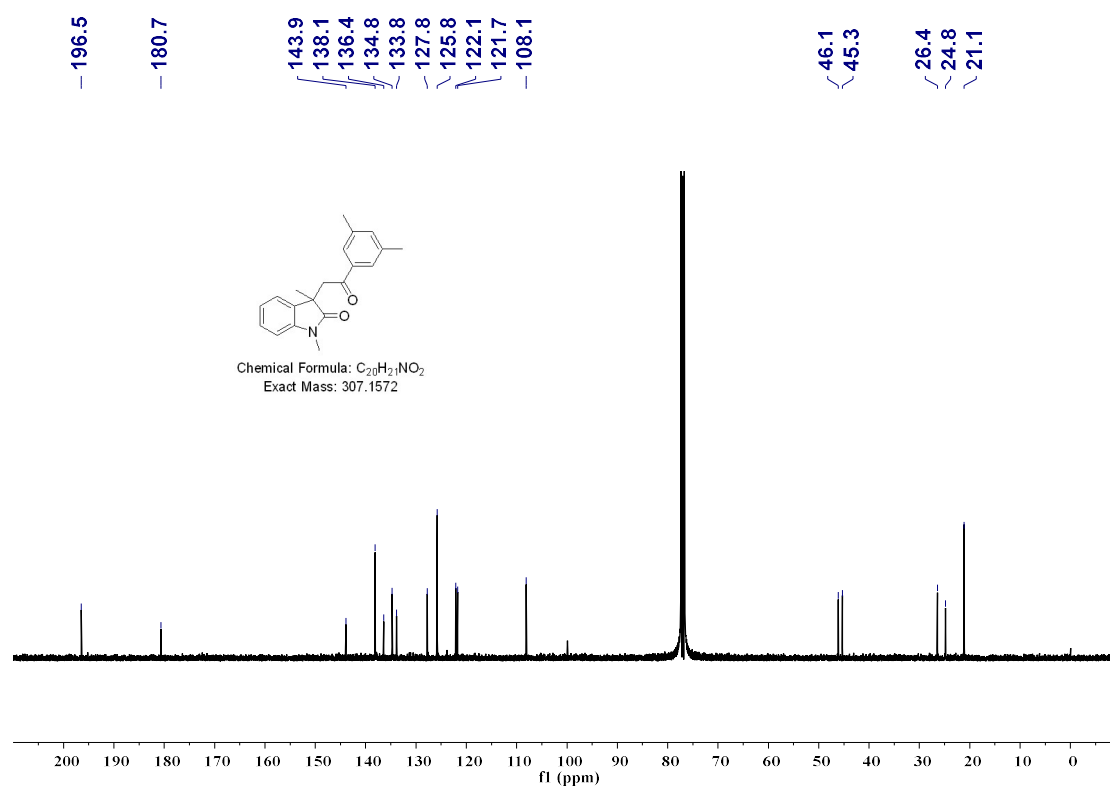
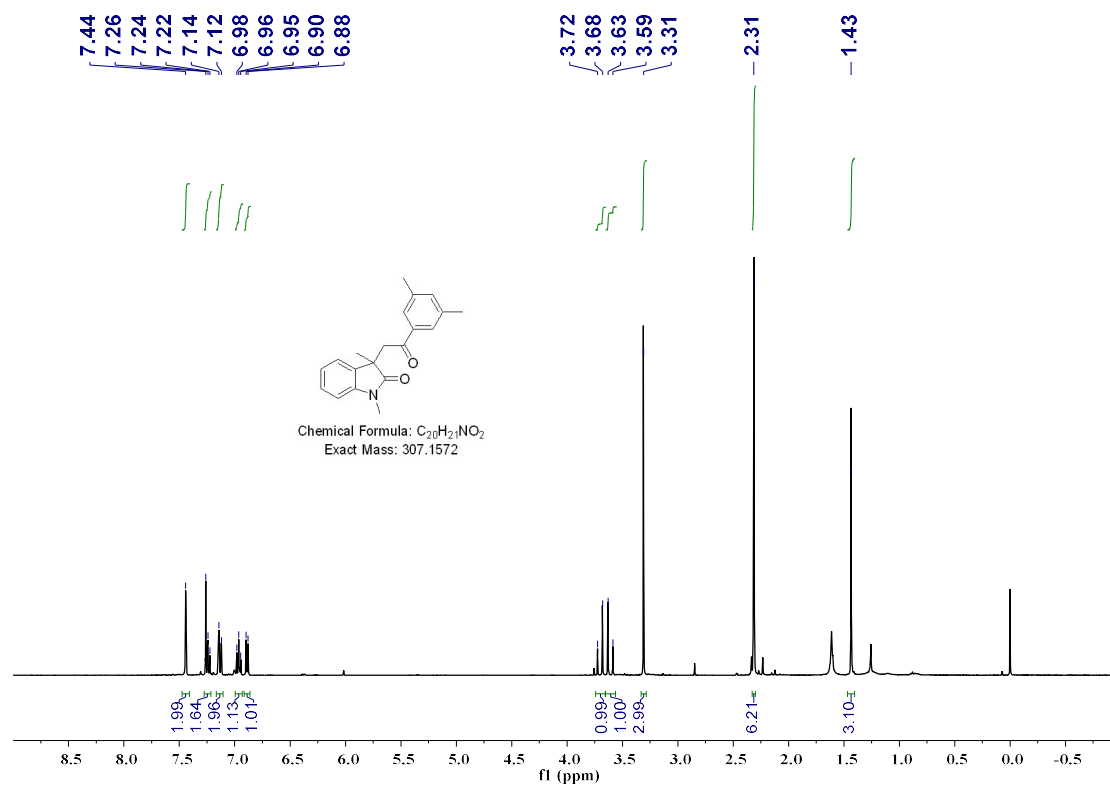
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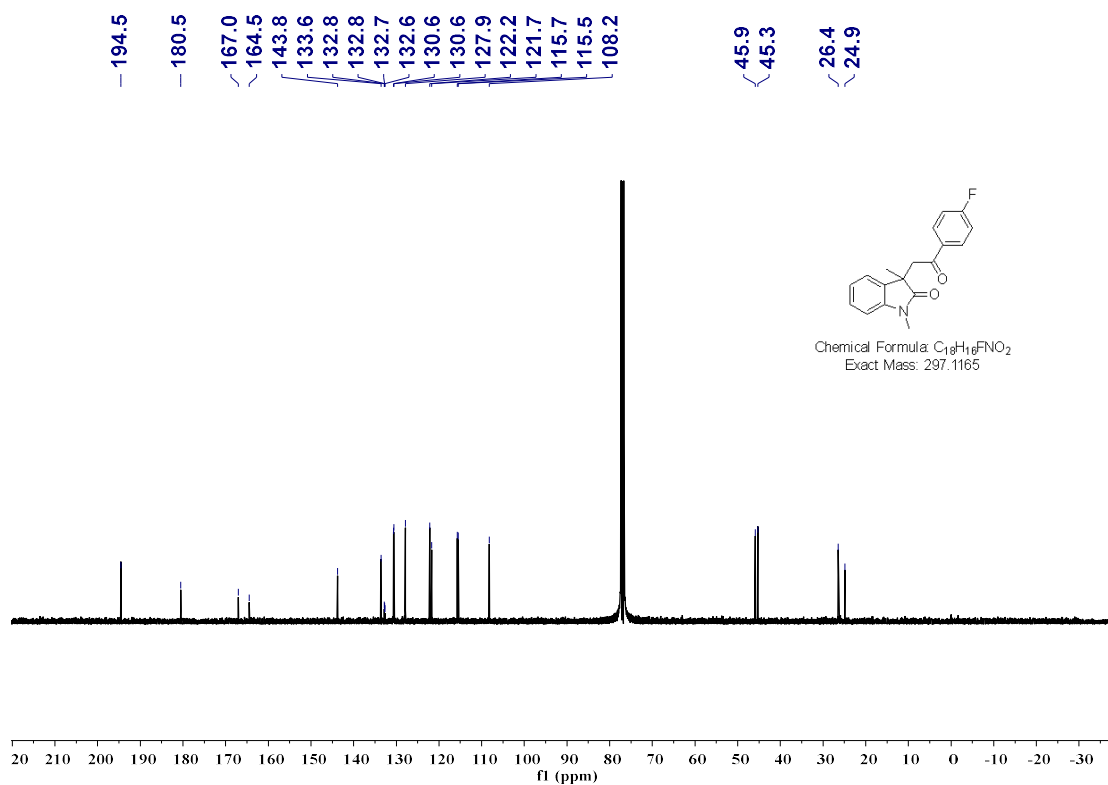
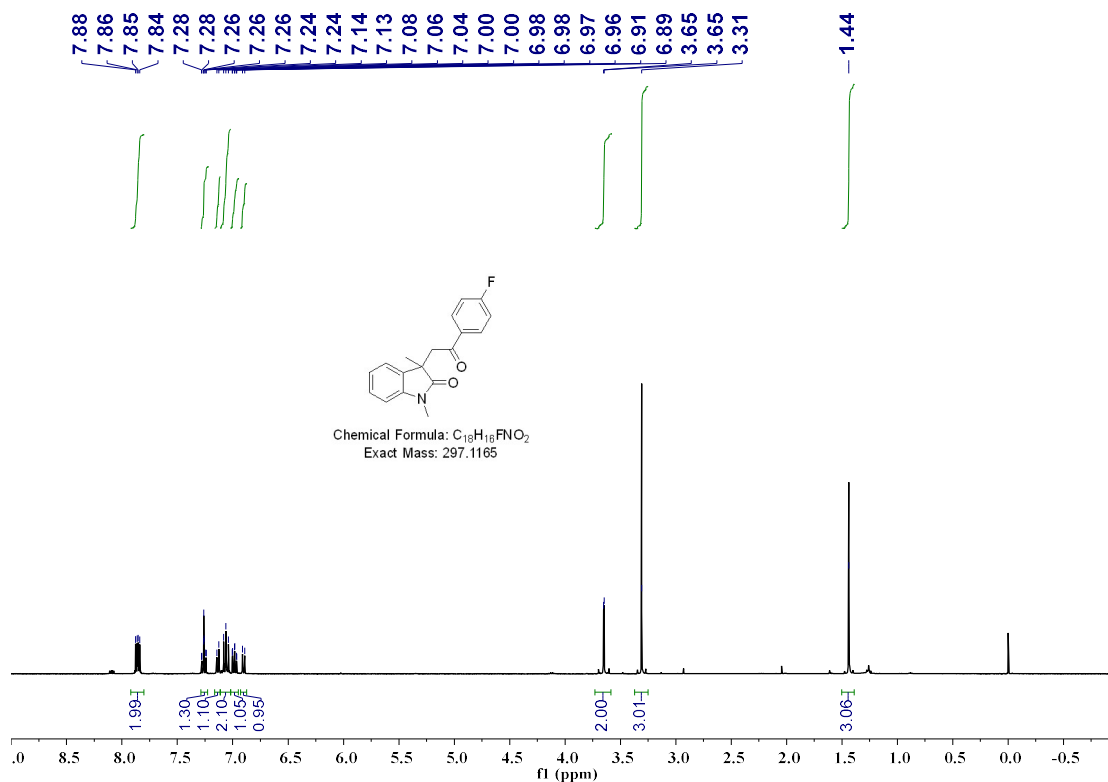
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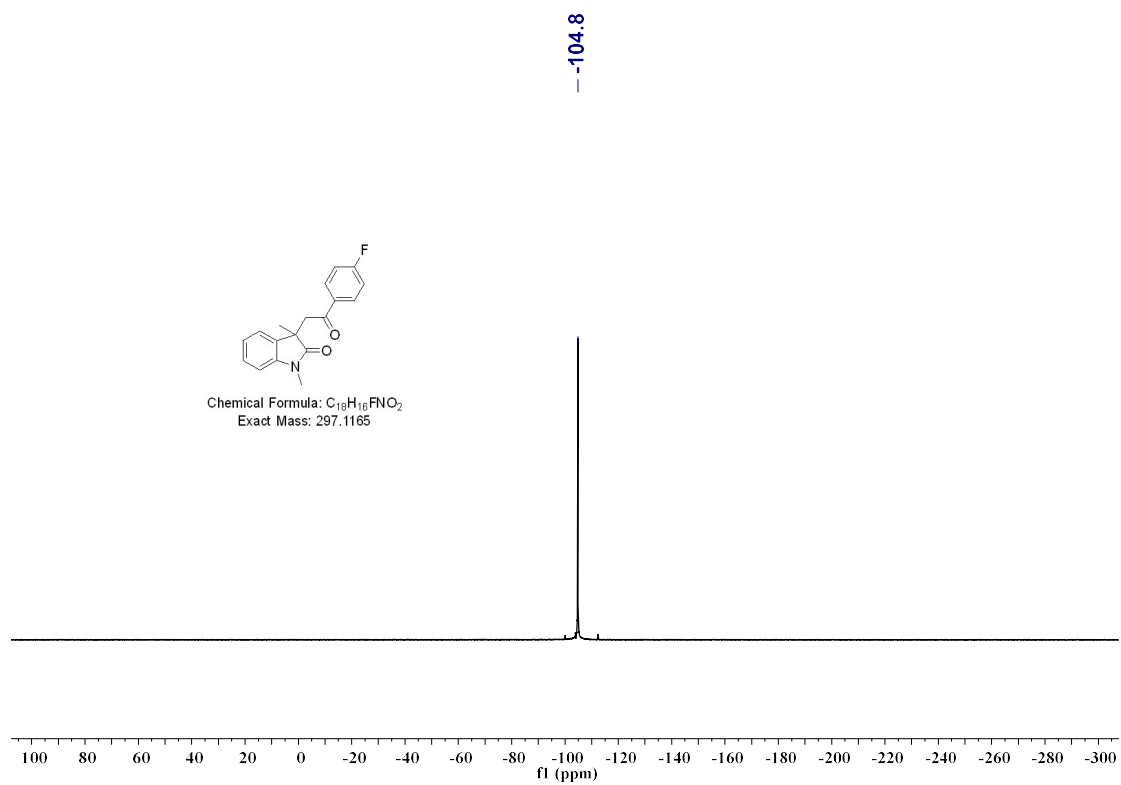


3s

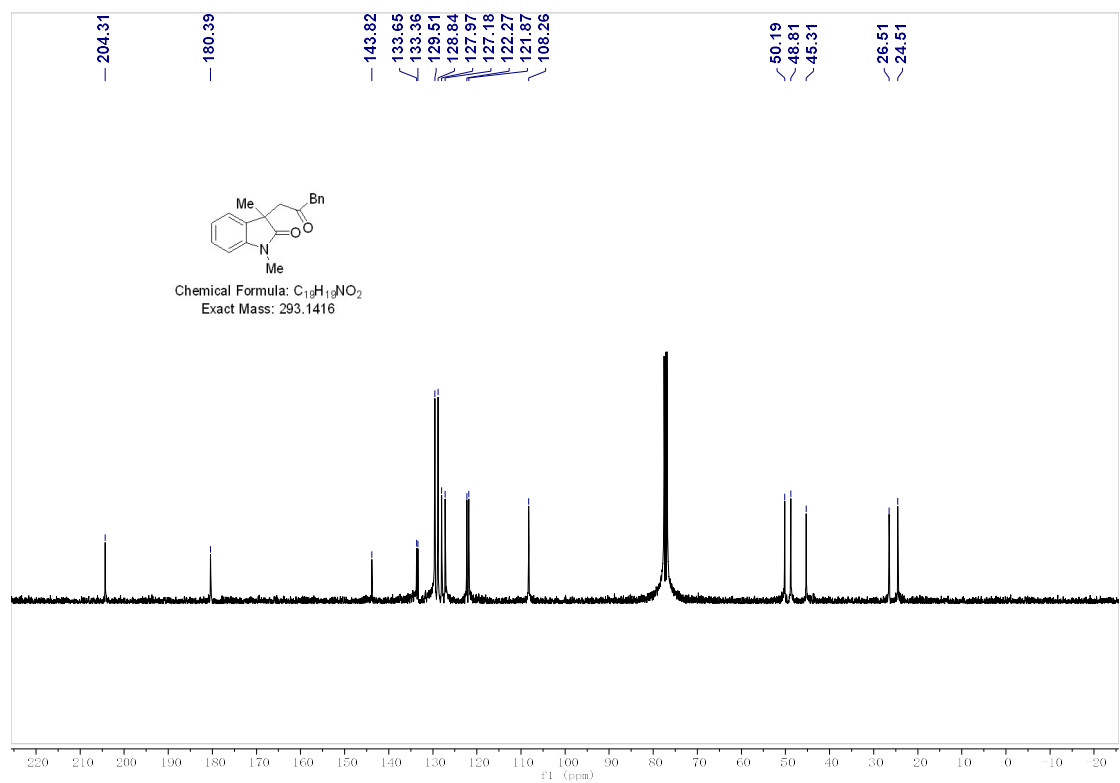
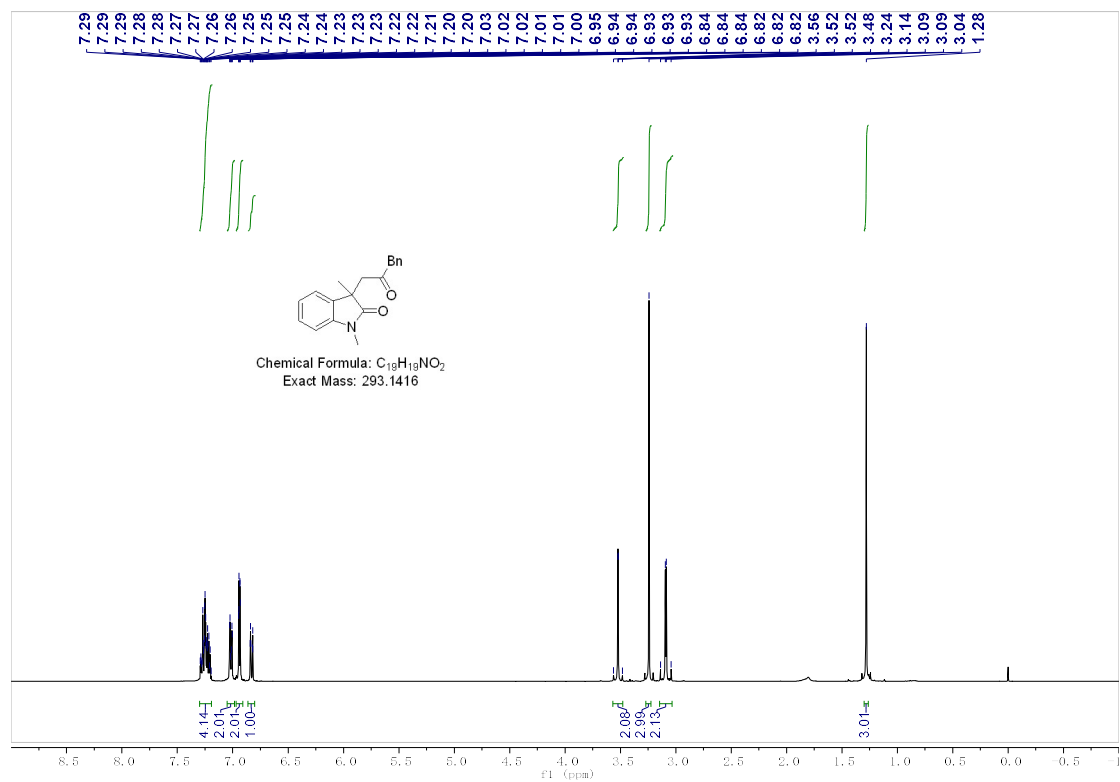


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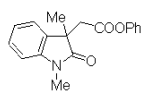
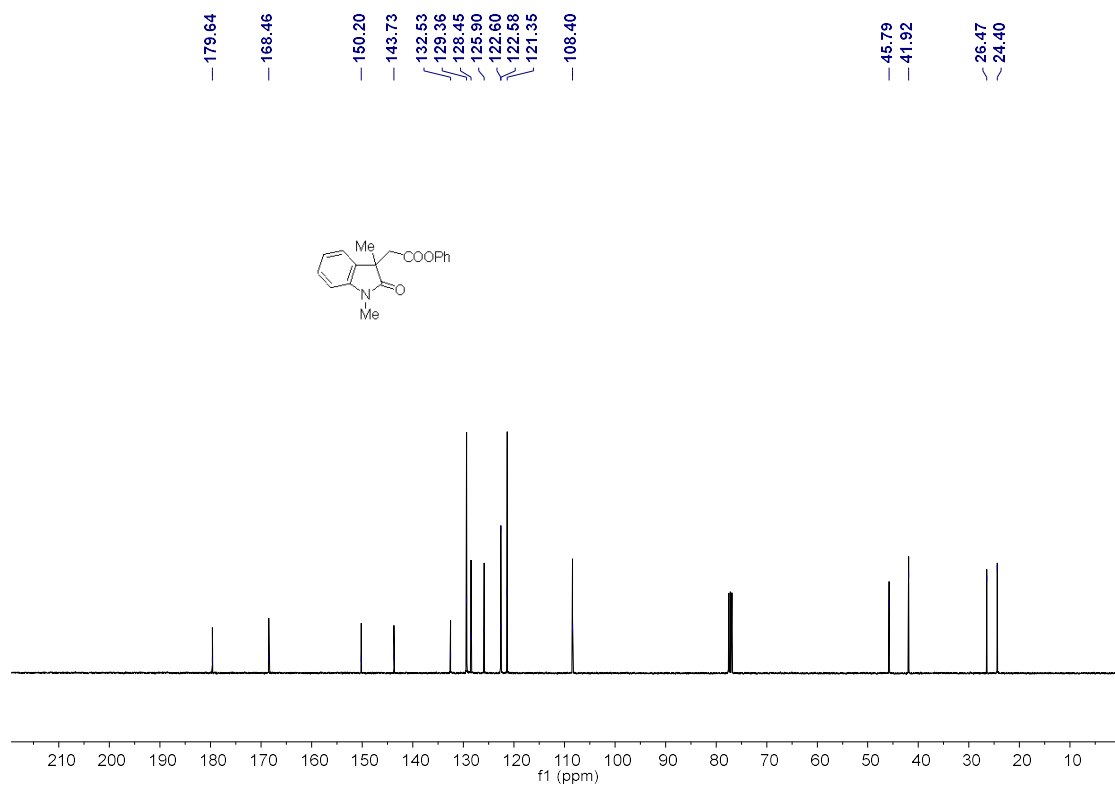
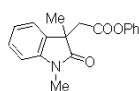
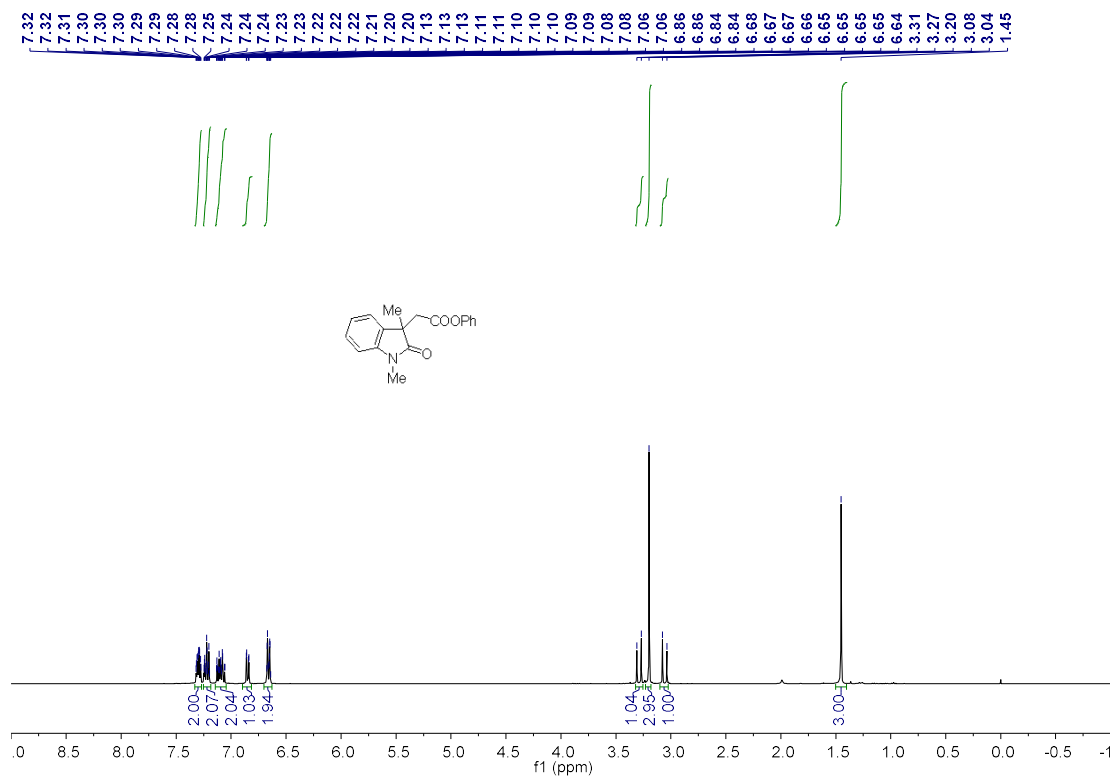




3u

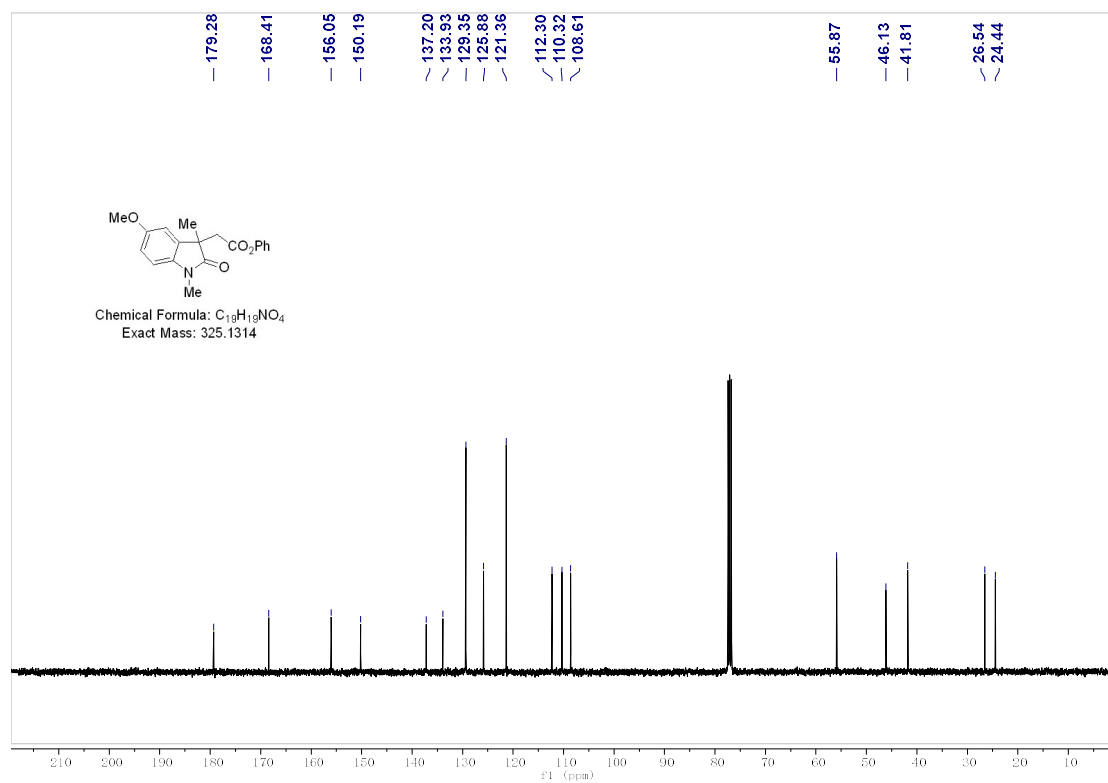
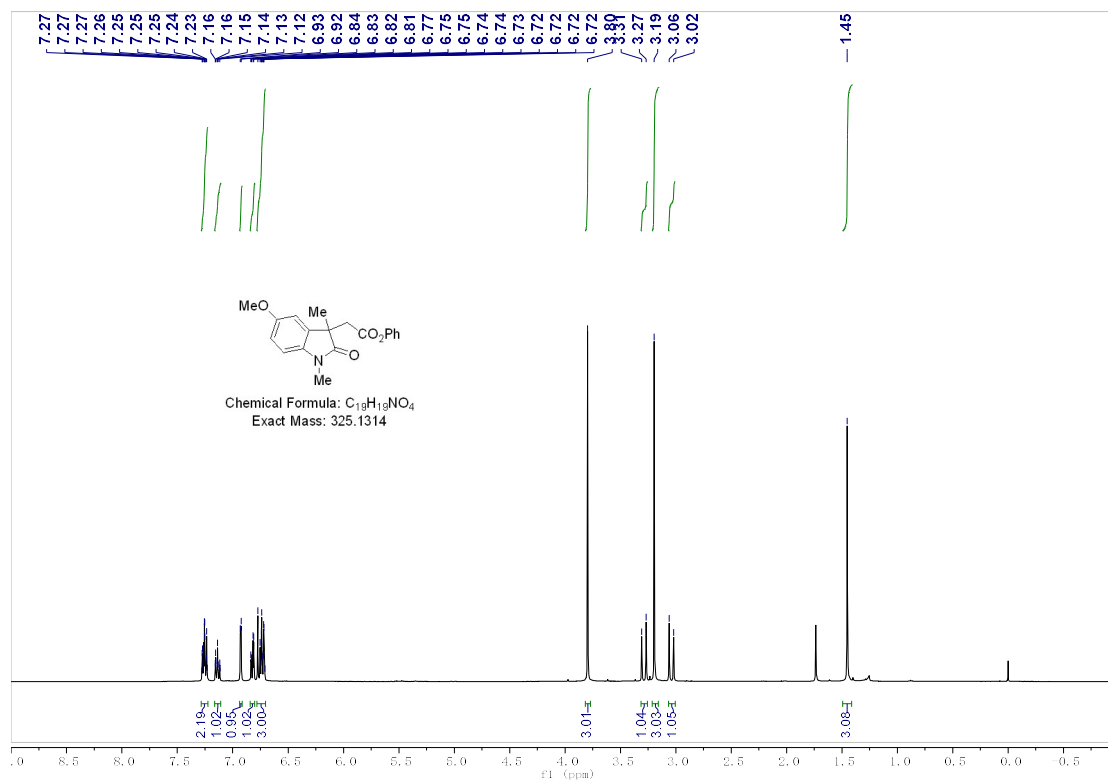


6a

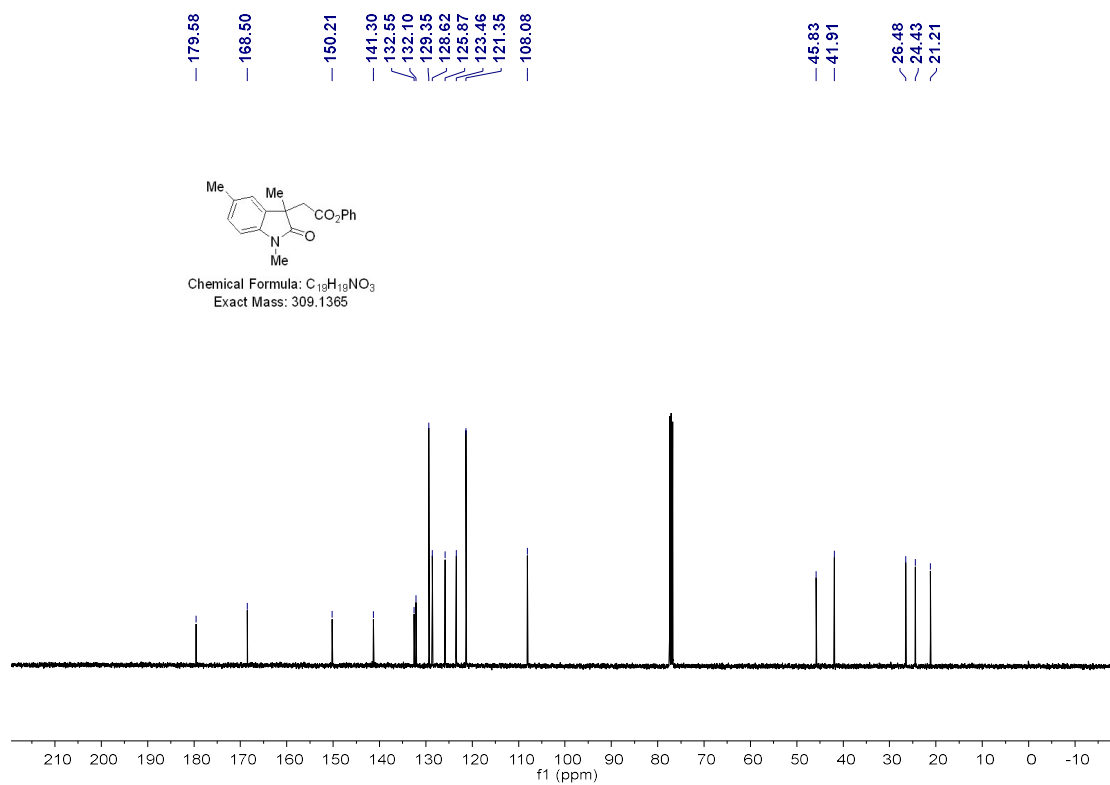
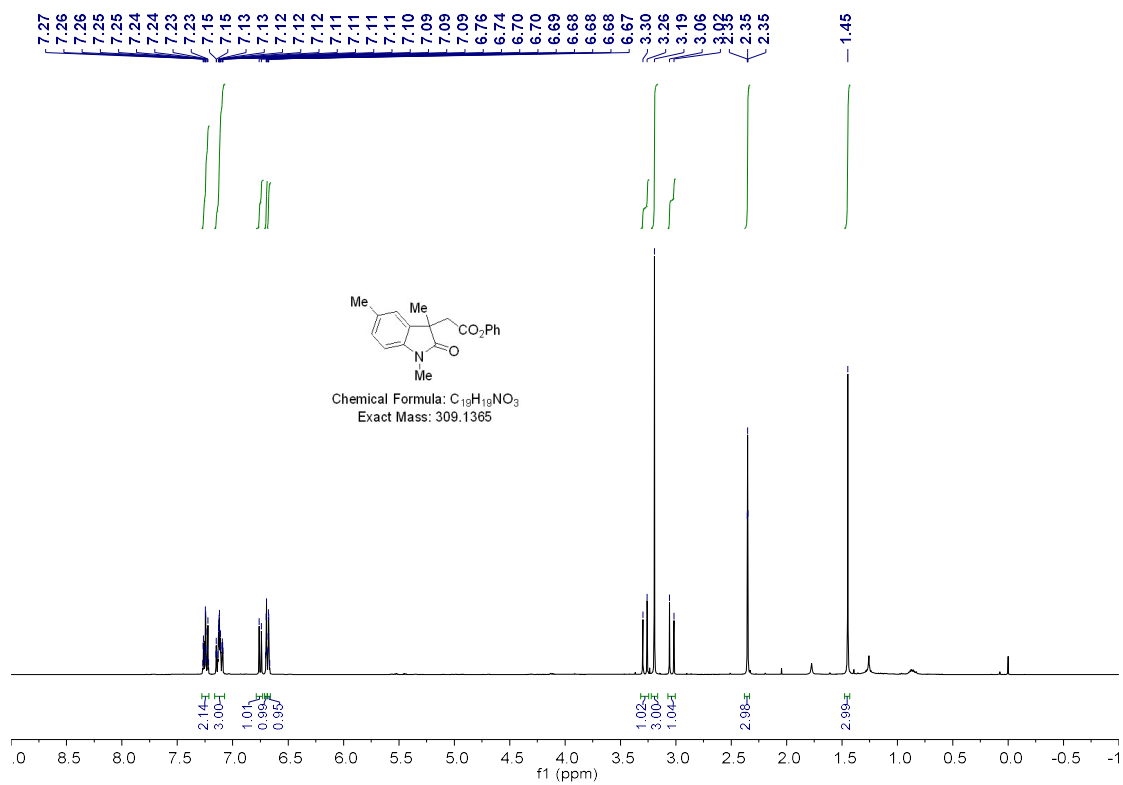




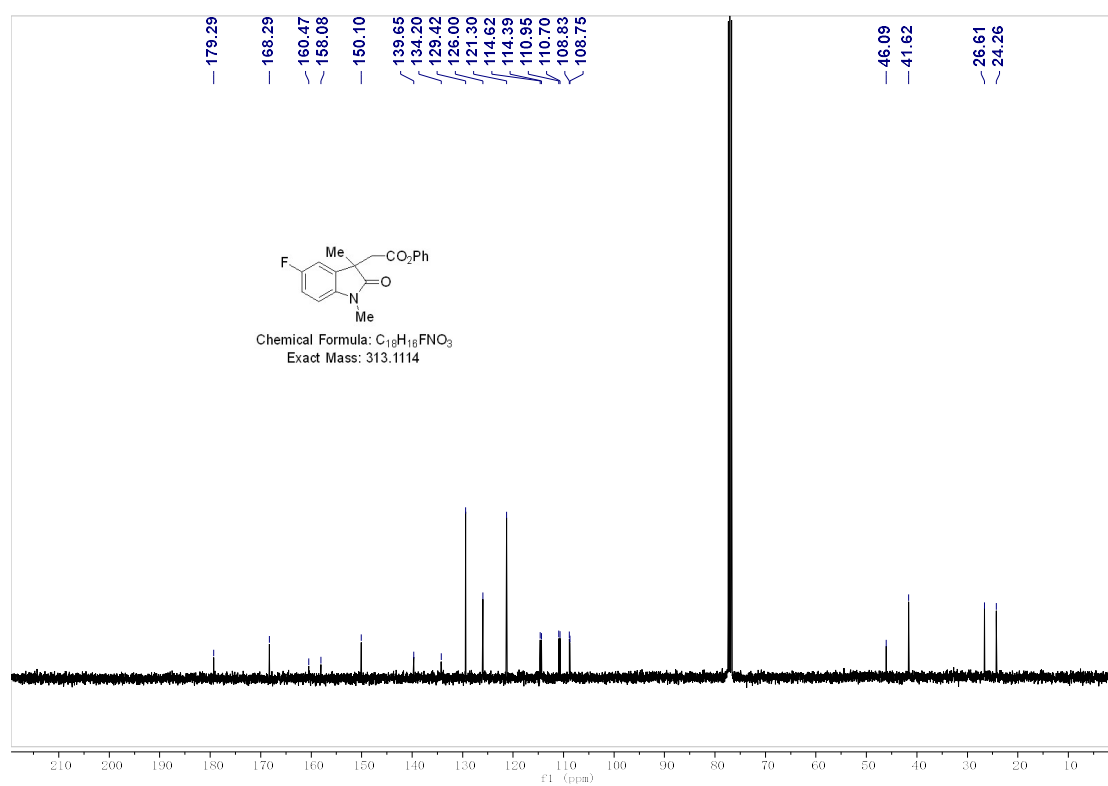
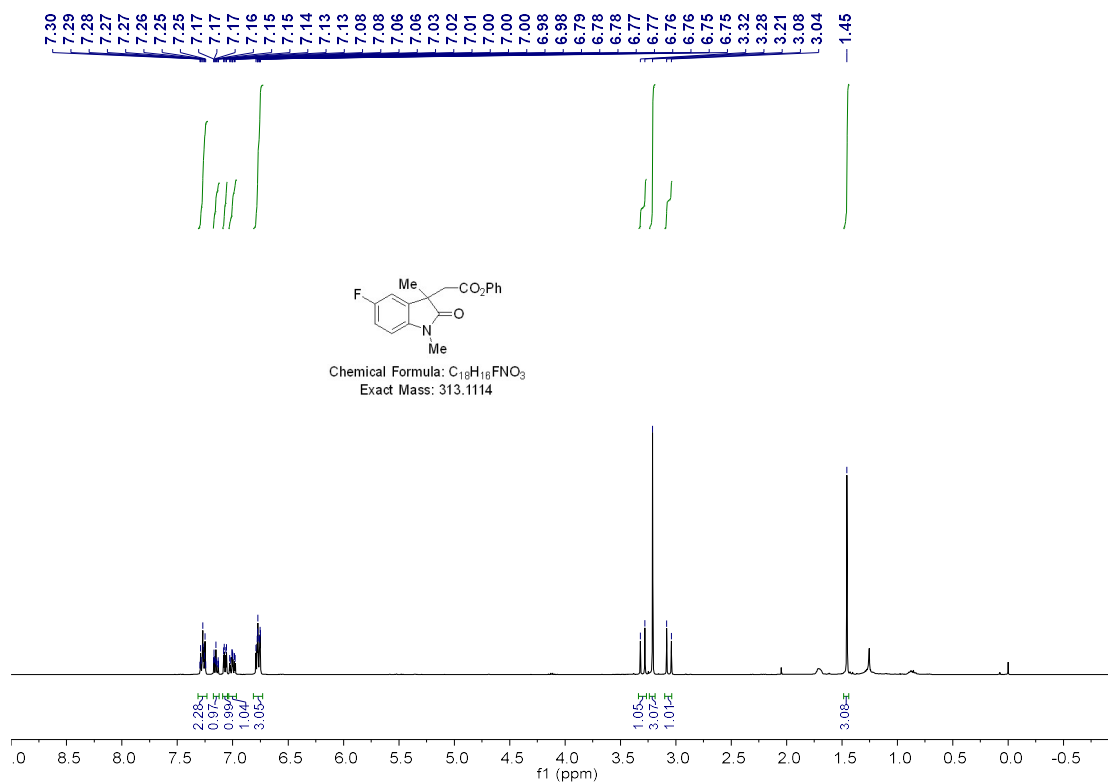
6b

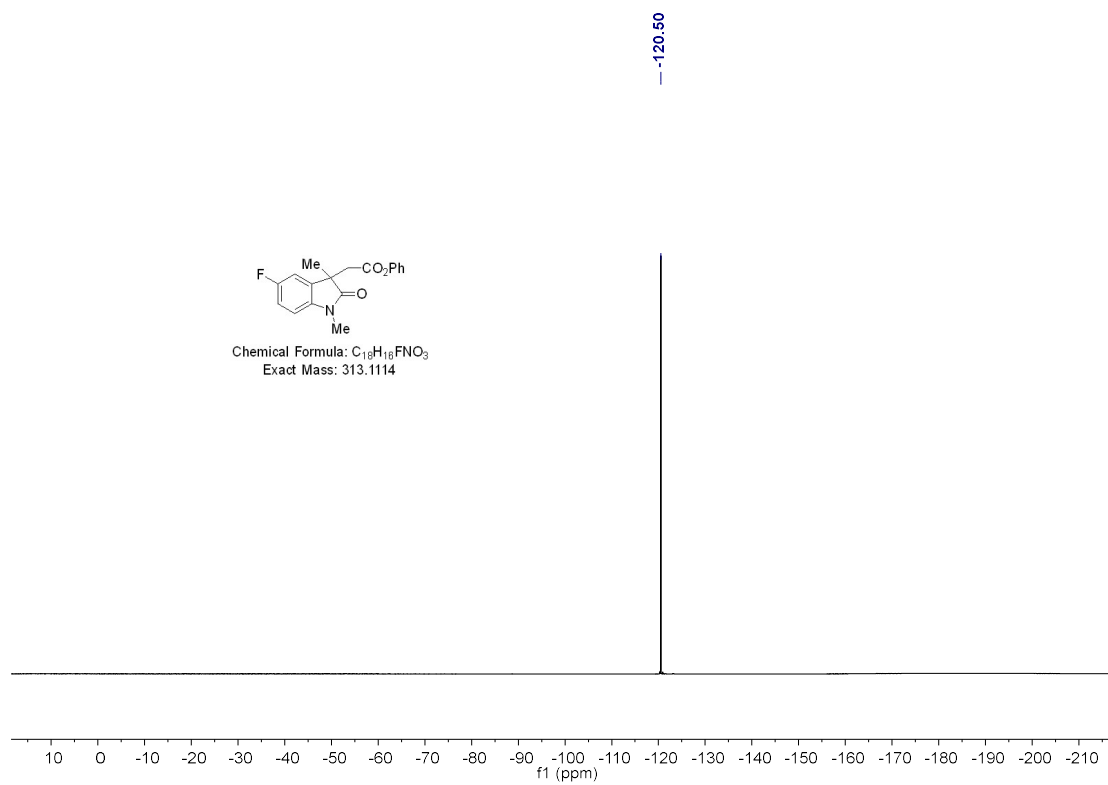


6c

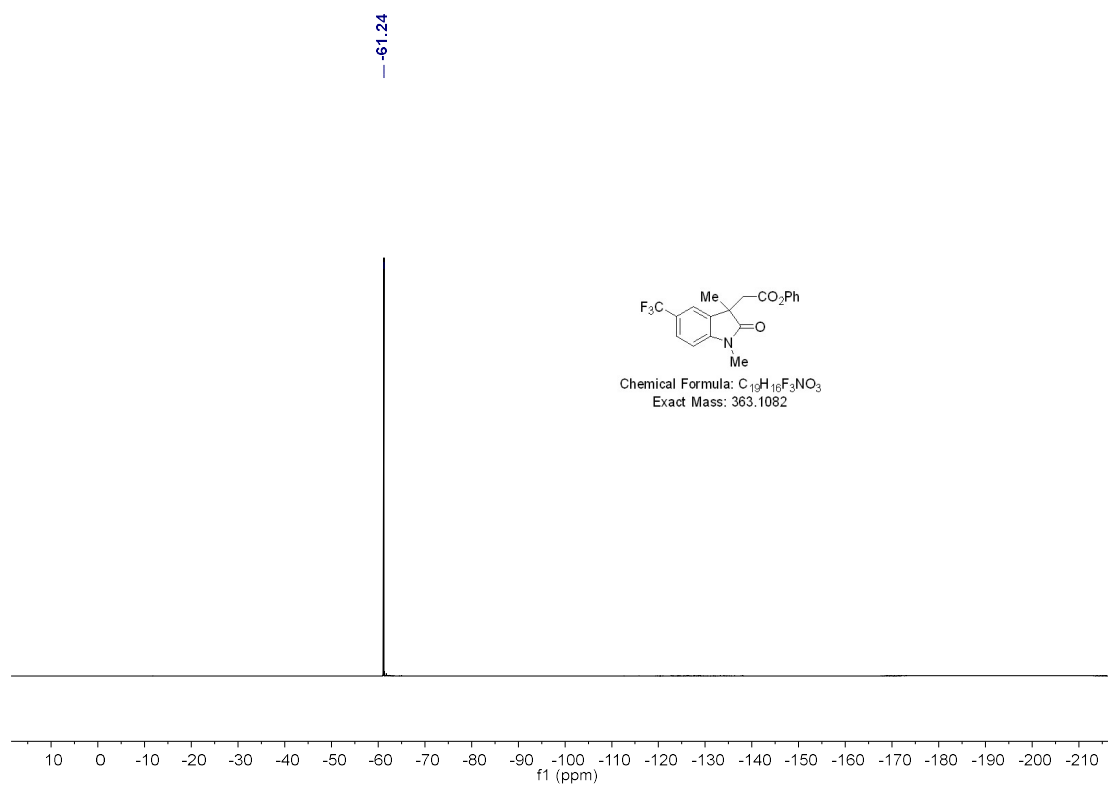


6d

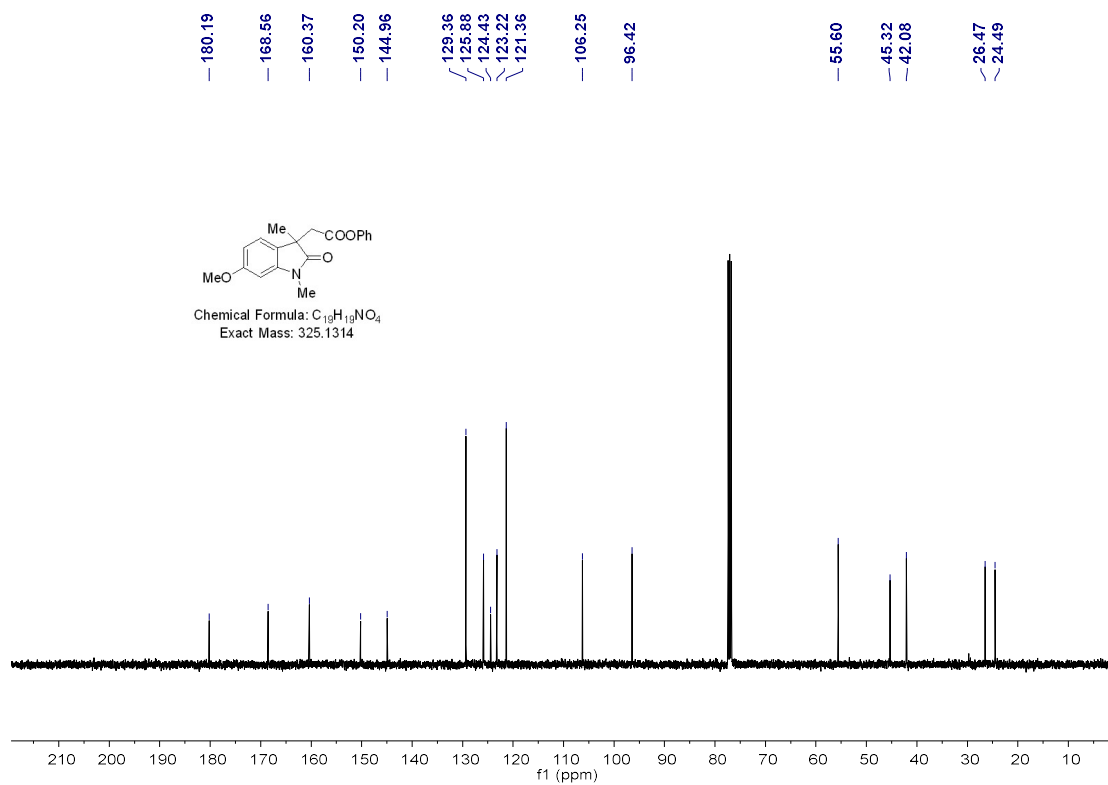
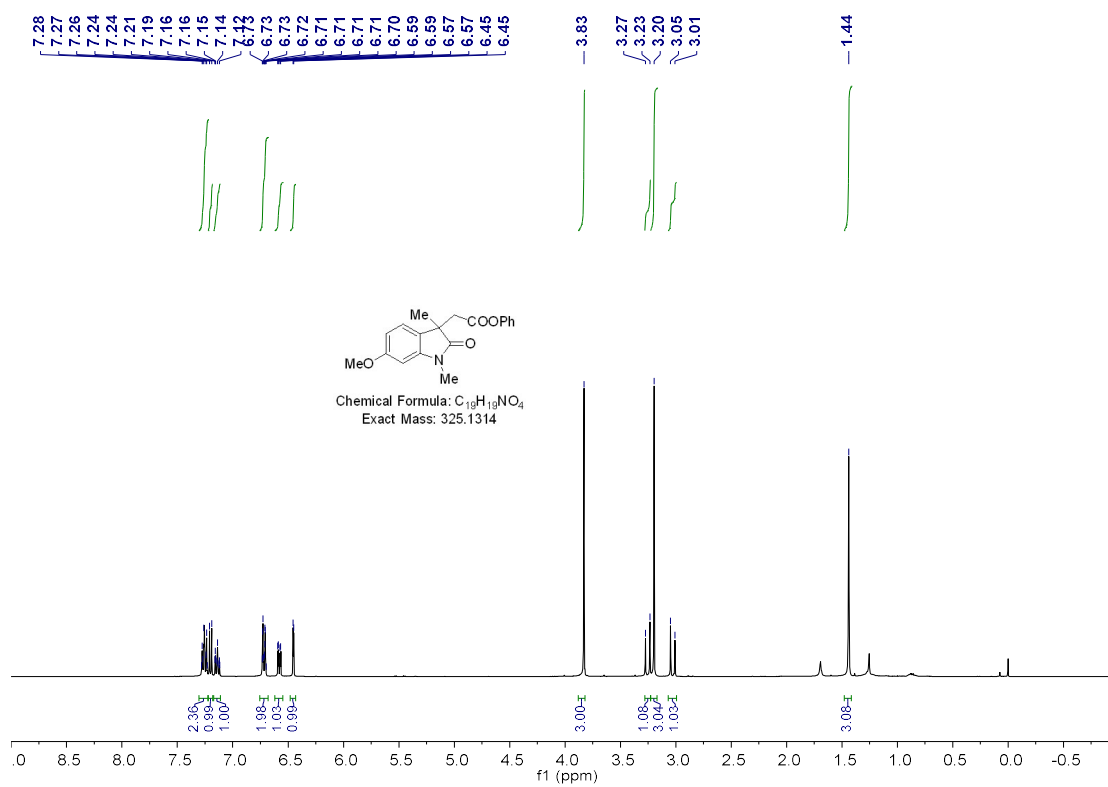




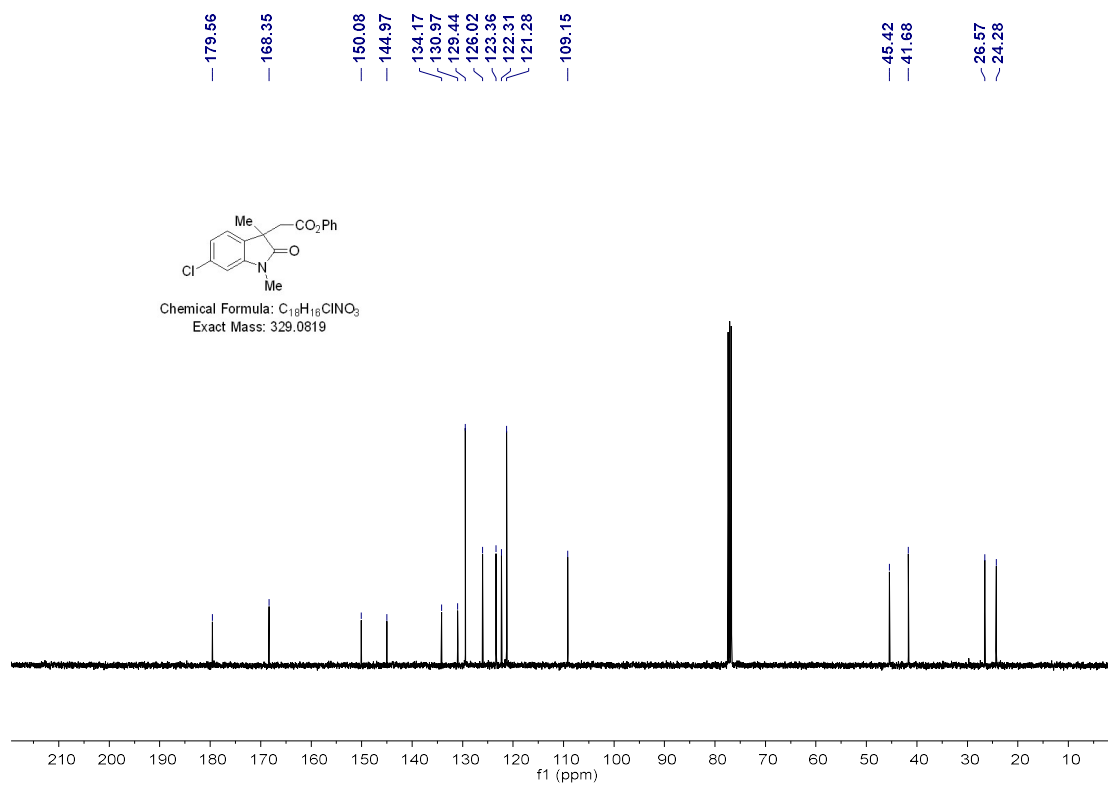
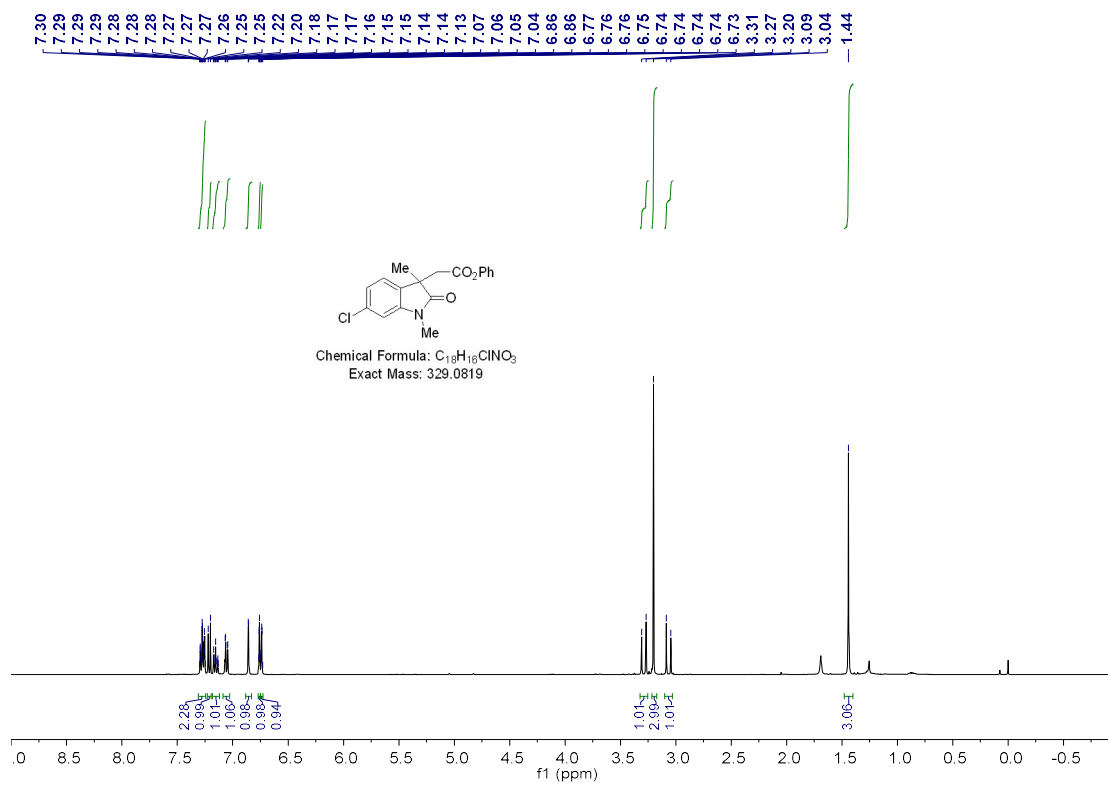




6f

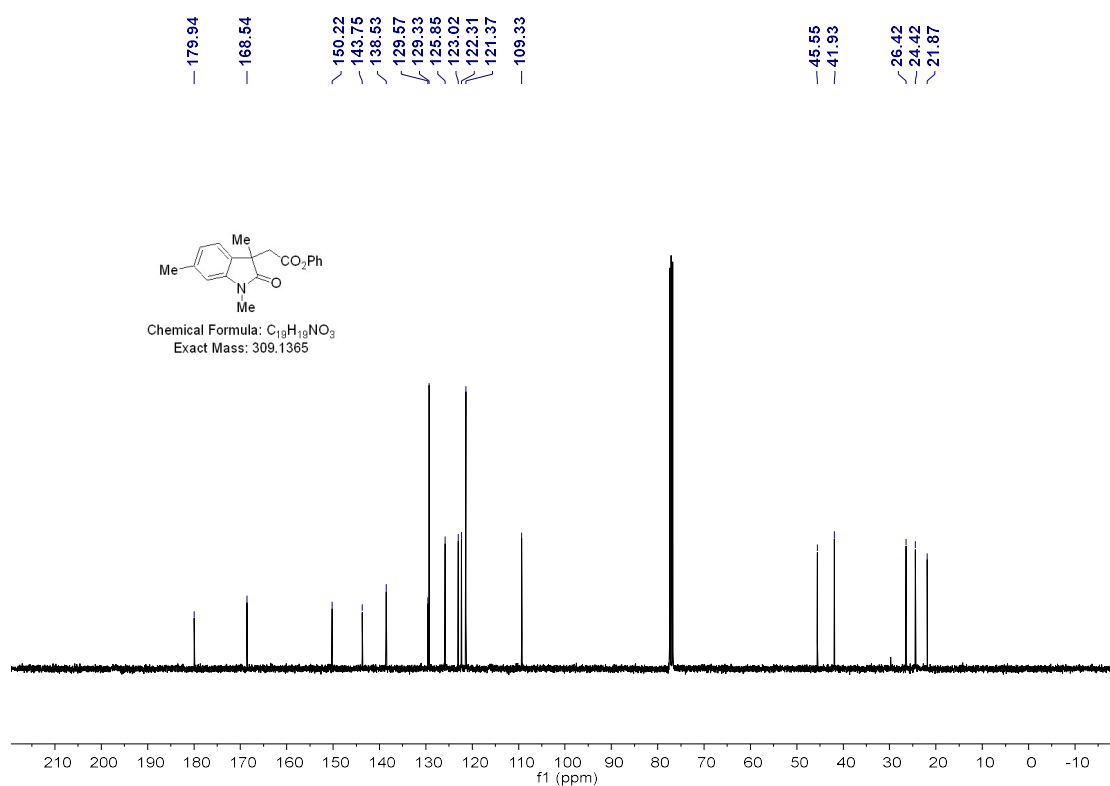
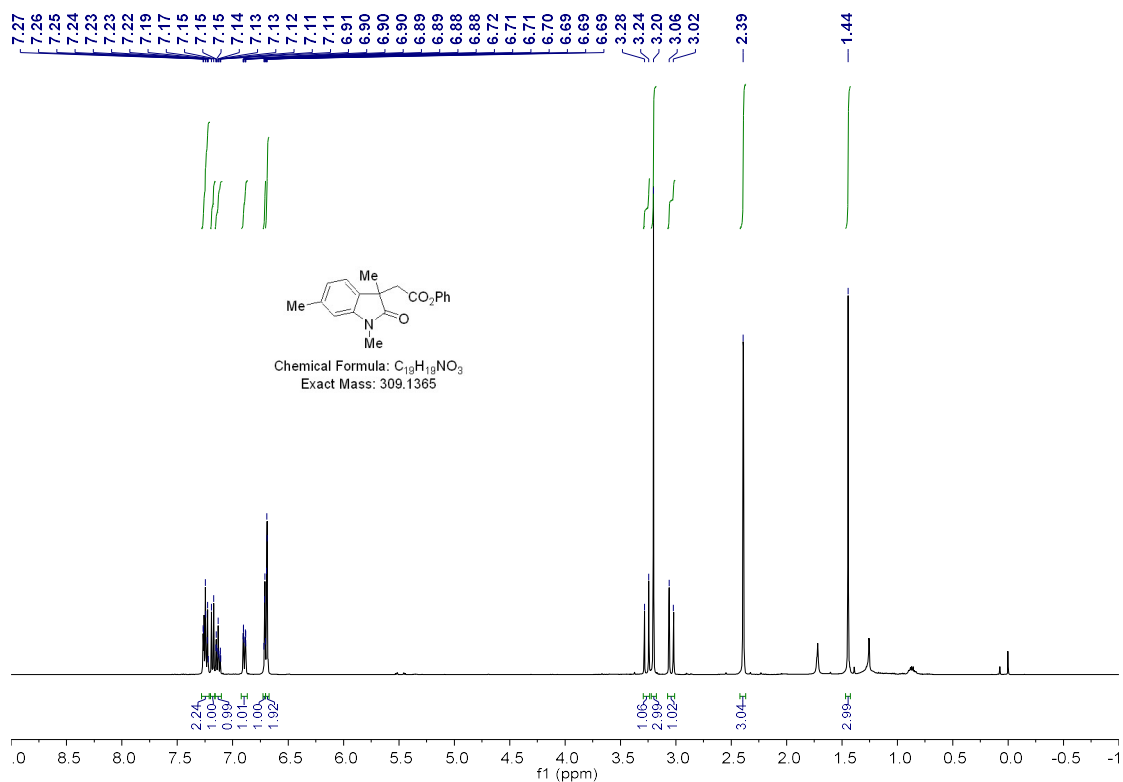


6g

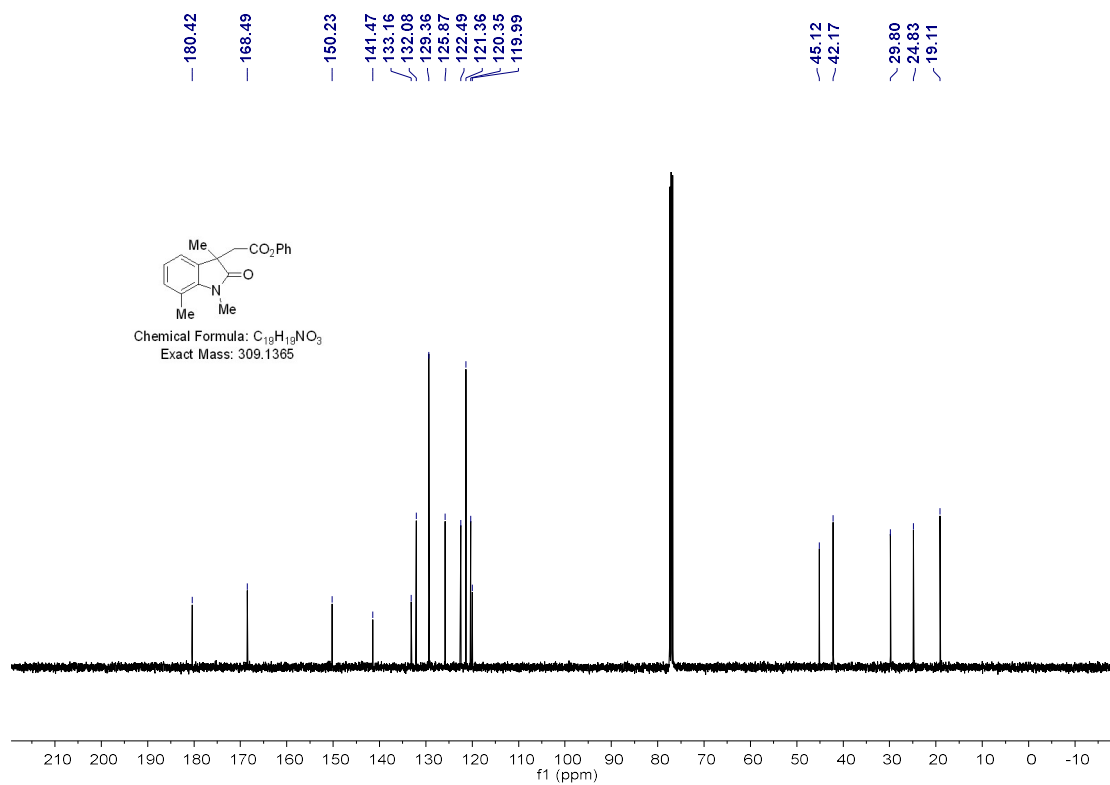
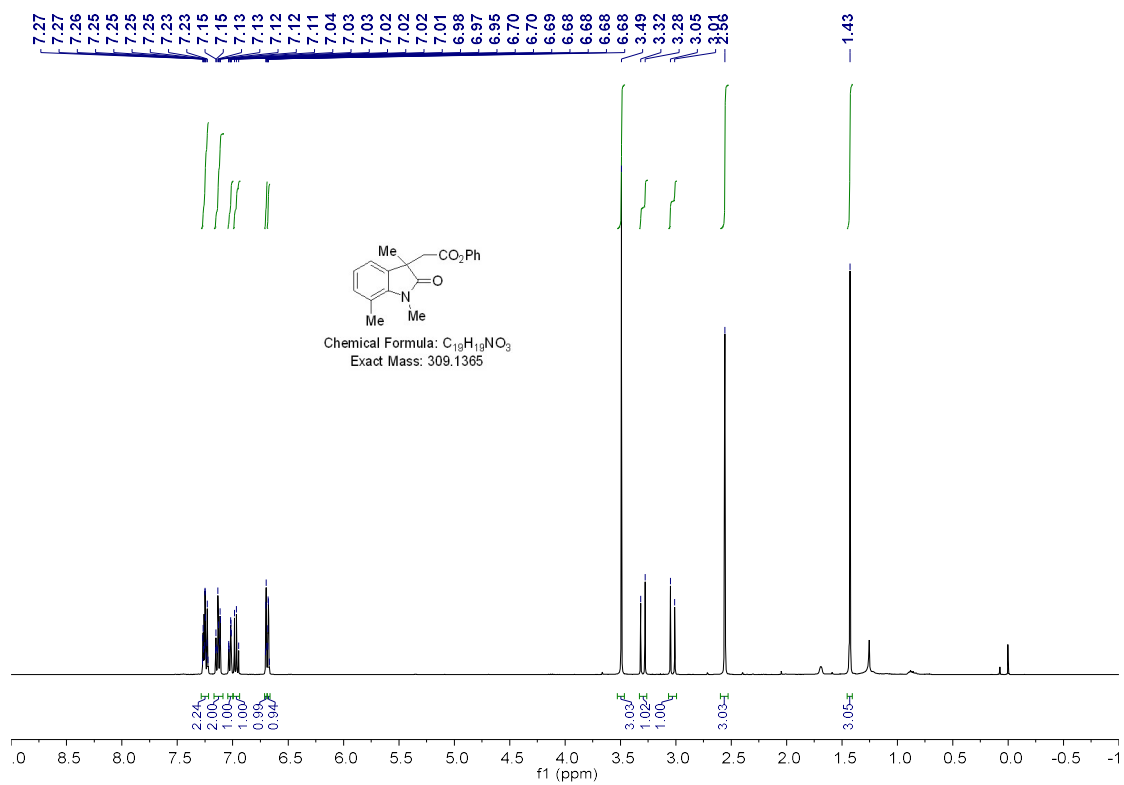




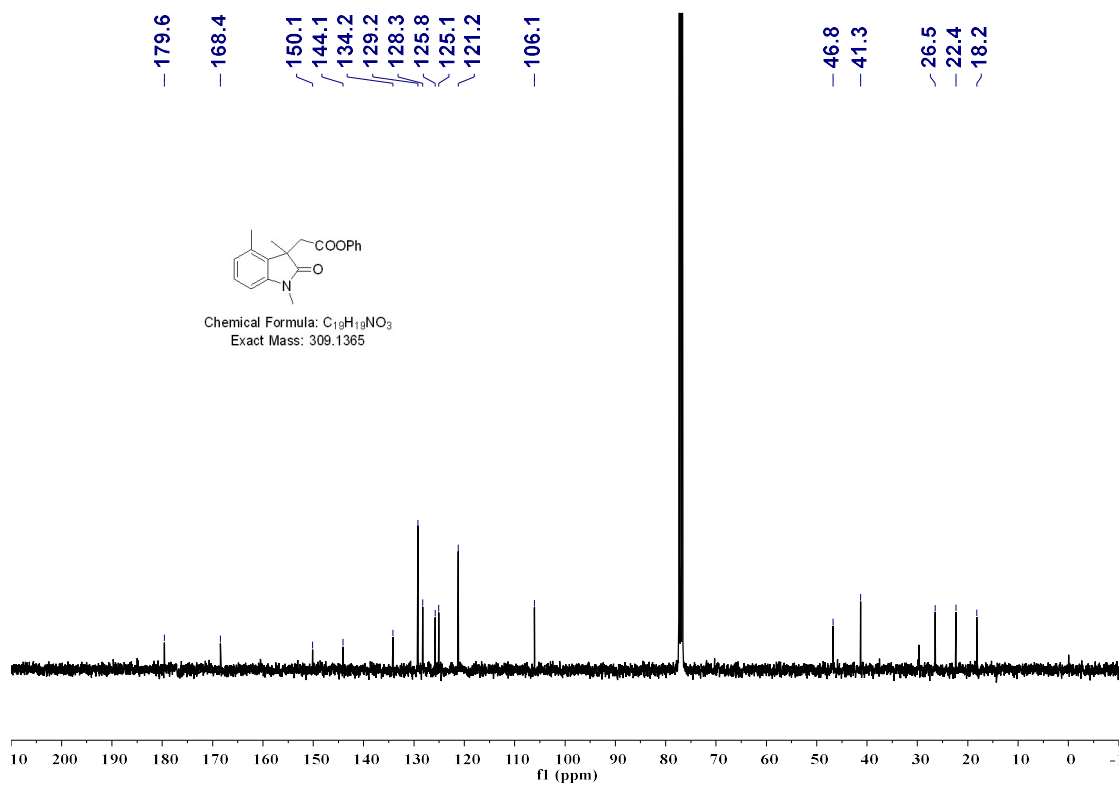
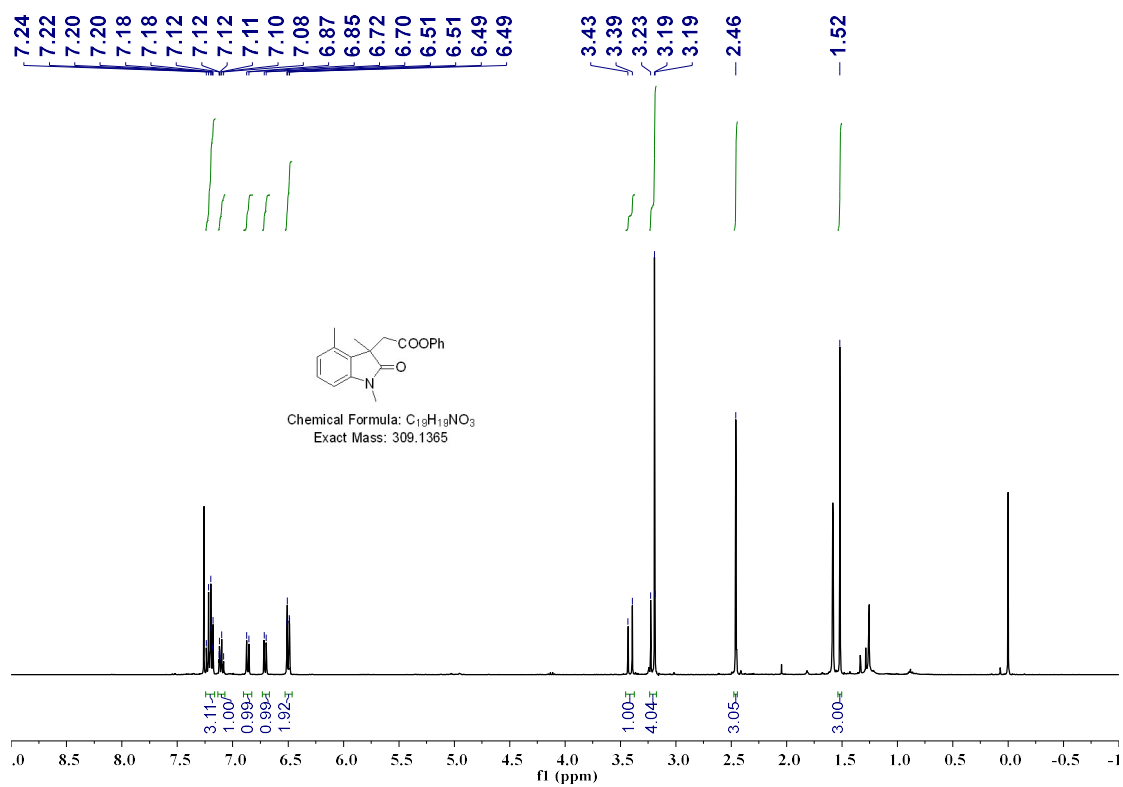
6h



6i



6j



Chemical structure: CC(=O)OCC1C(=O)N2C=CC=CC=C2N1

Chemical Formula:  $C_{17}H_{16}N_2O_3$   
Exact Mass: 296.1161

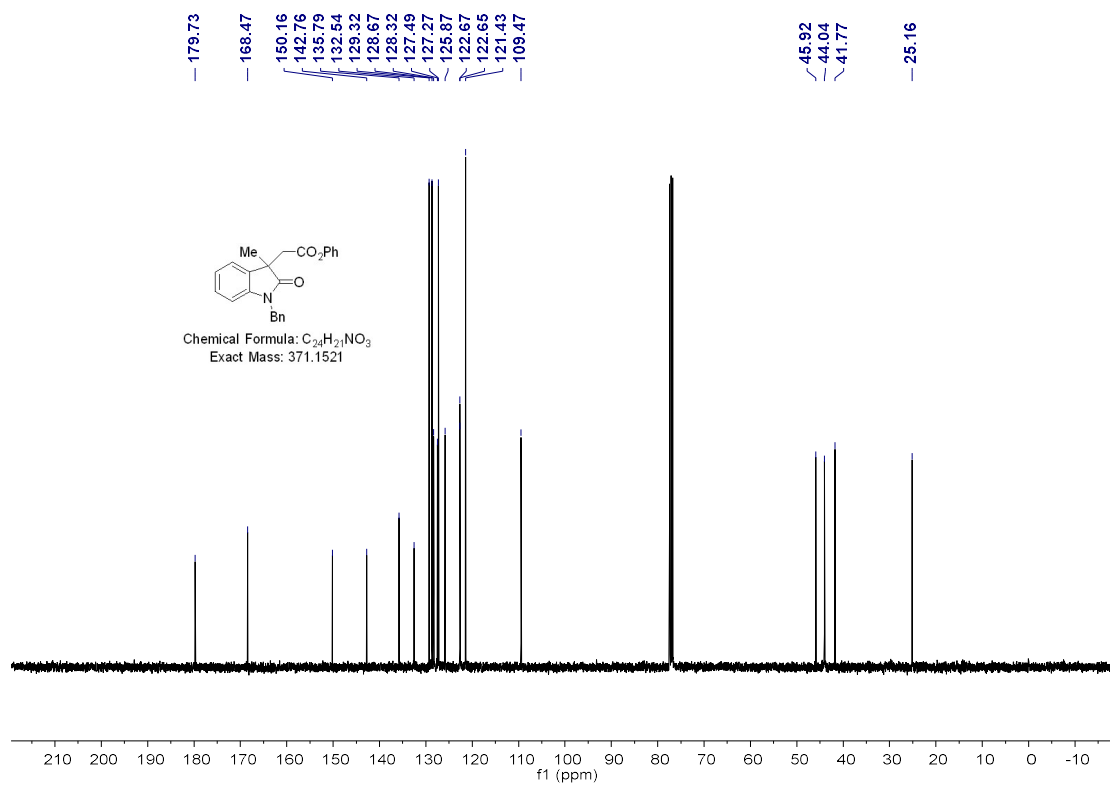
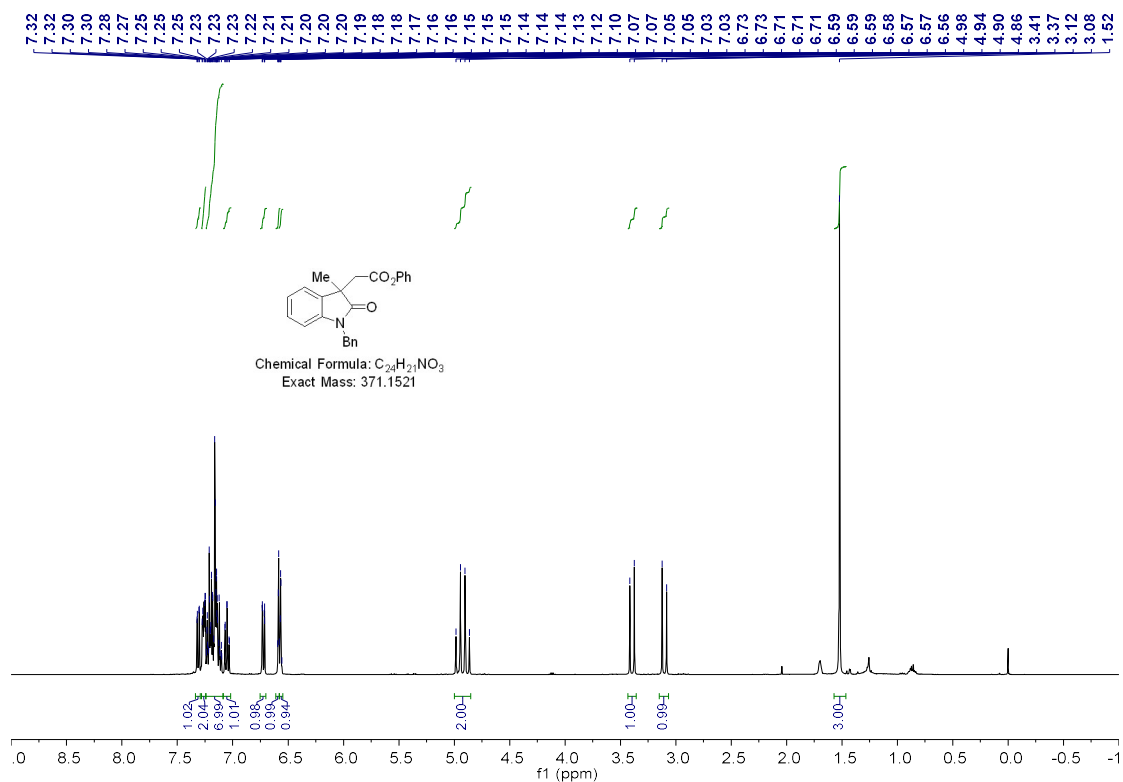
$^1H$  NMR spectrum (ppm):

- 8.22, 8.21, 8.21, 8.21
- 7.56, 7.56, 7.55, 7.55, 7.29, 7.29, 7.29, 7.28, 7.28, 7.27, 7.27, 7.26, 7.17, 7.17, 7.17, 7.16, 7.16, 7.16, 7.15, 6.98, 6.97, 6.97, 6.96, 6.78, 6.77, 6.77, 6.77, 6.77, 6.76, 6.76, 6.76, 6.76, 3.31, 3.30, 3.27, 3.07, 1.49

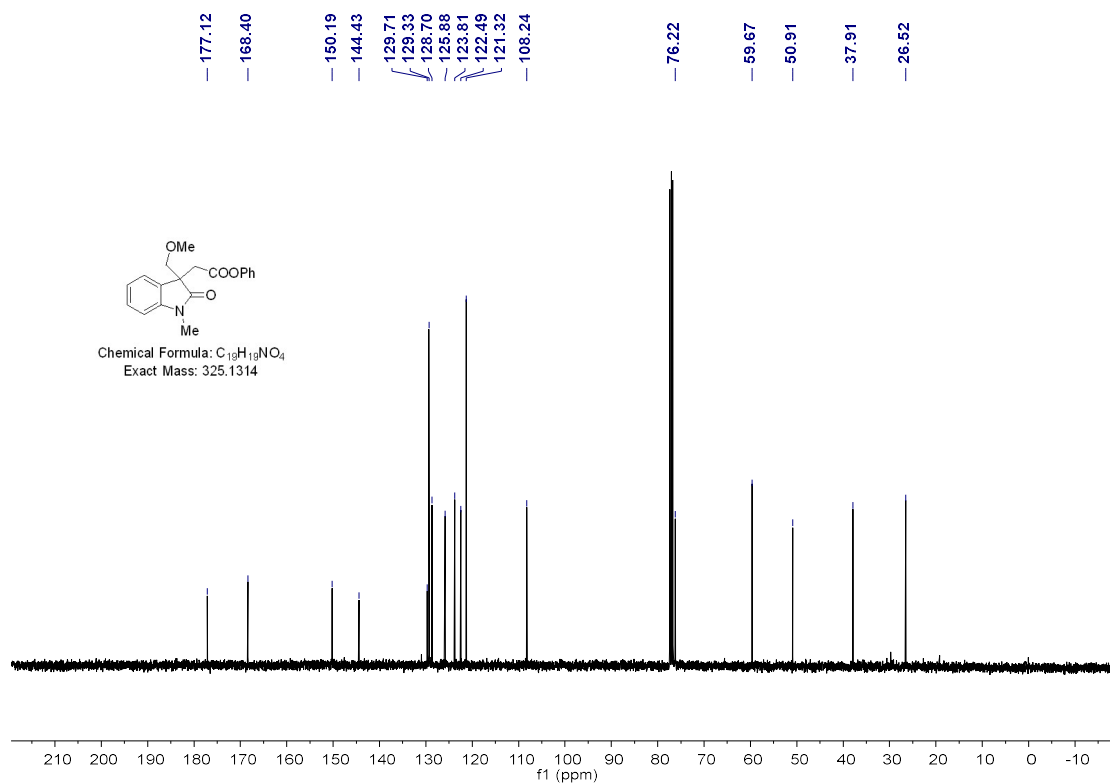
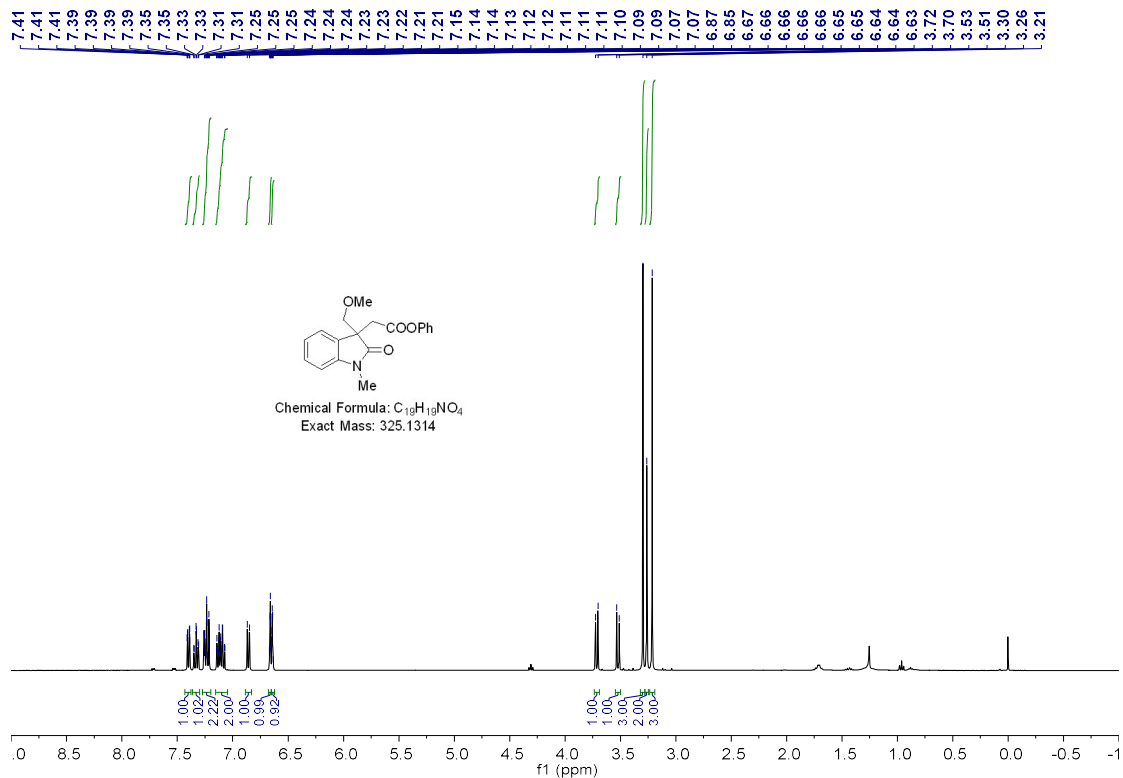
Integration values:

- 1.03
- 1.03, 2.01, 1.05, 1.05, 2.00
- 3.00, 1.07, 1.06
- 3.04

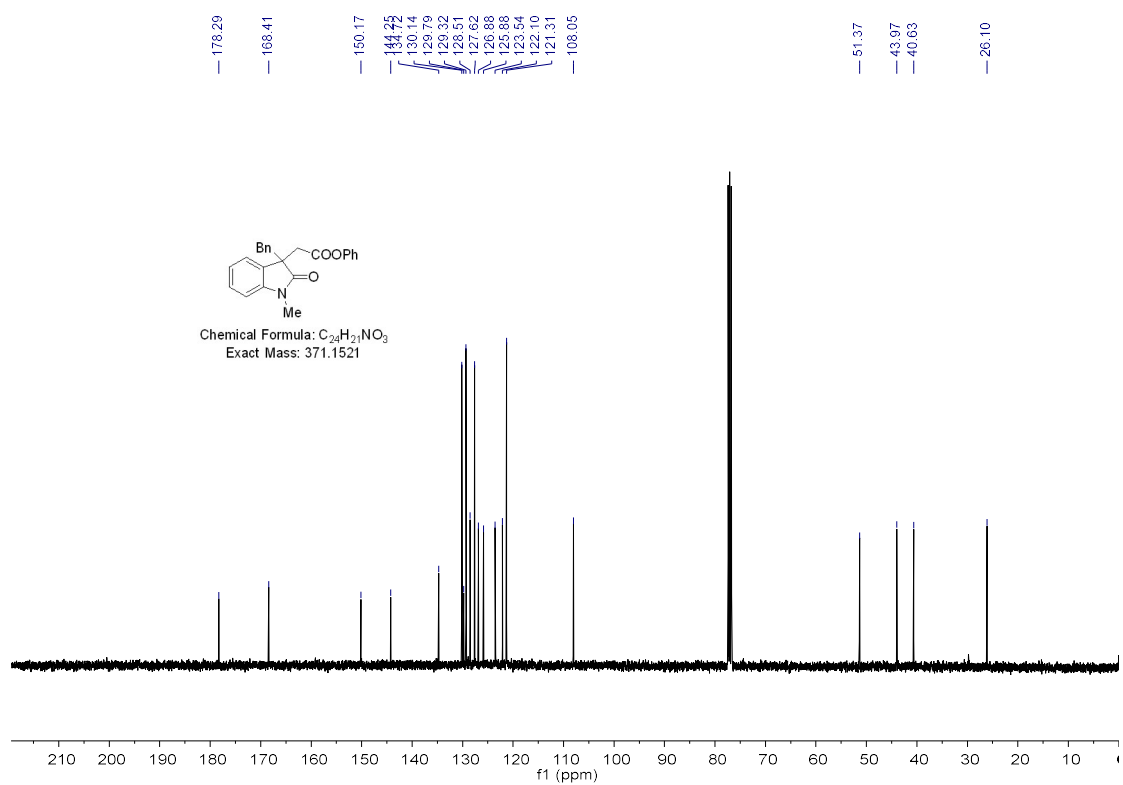
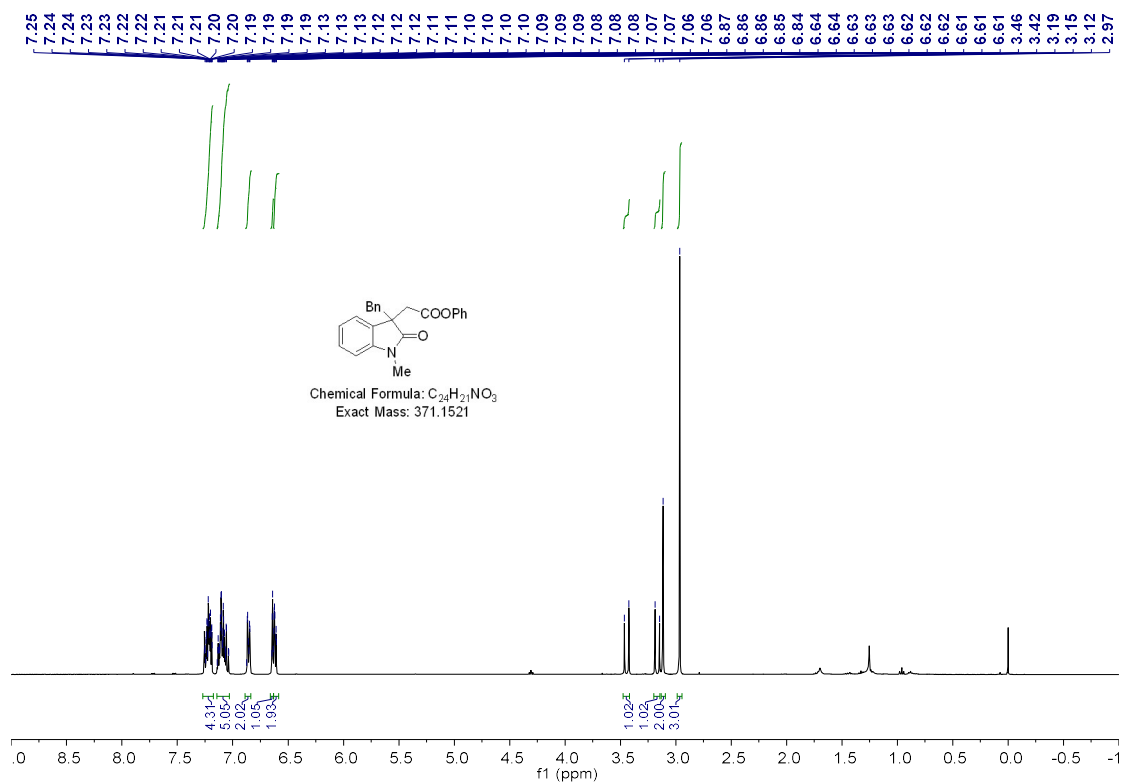


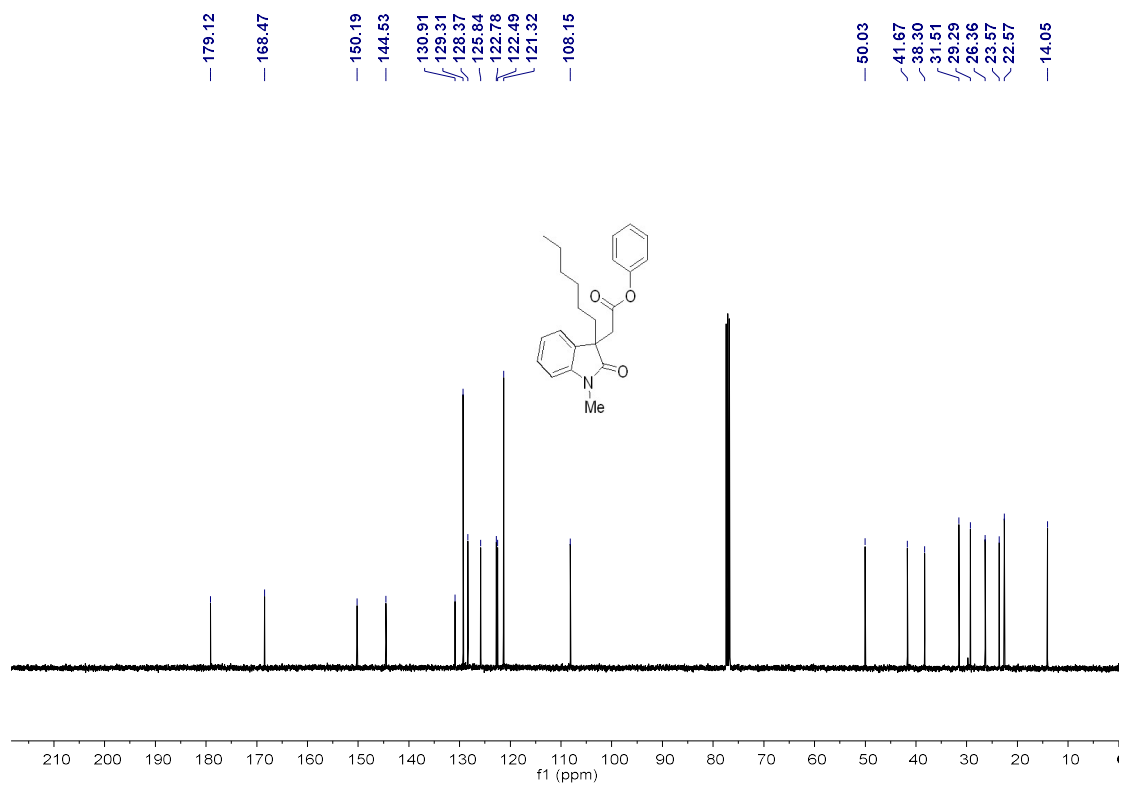
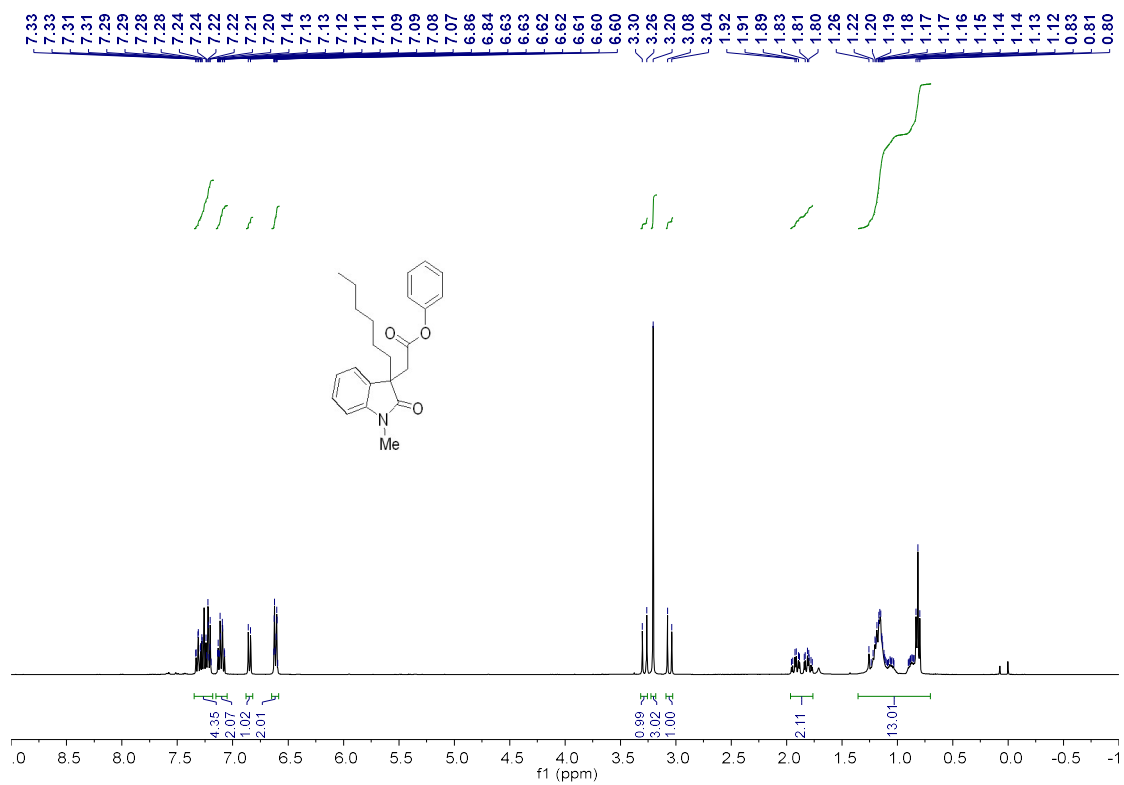


6m



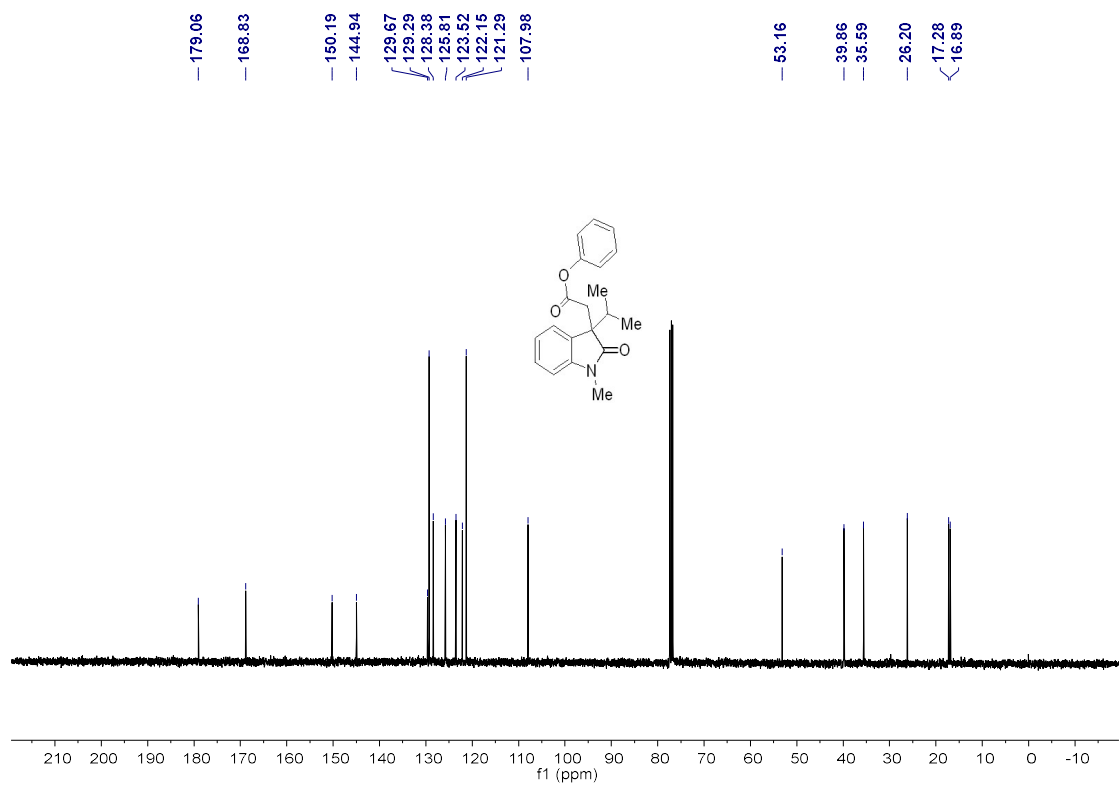
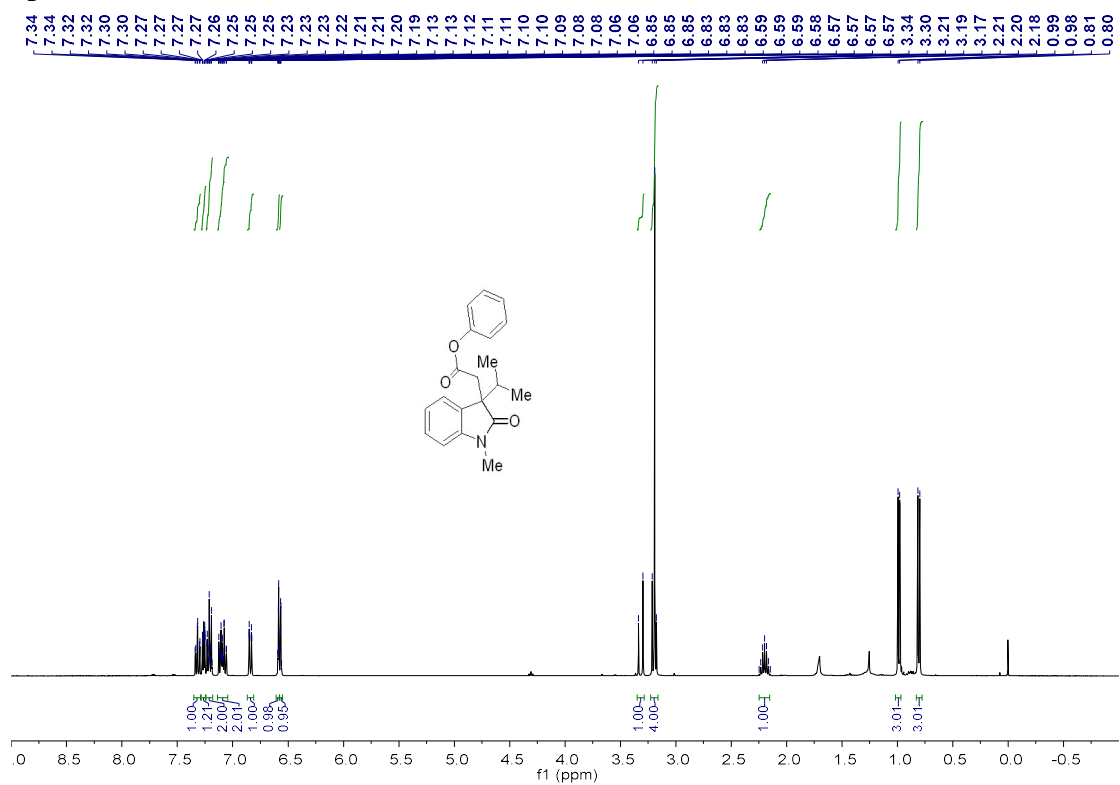
6n



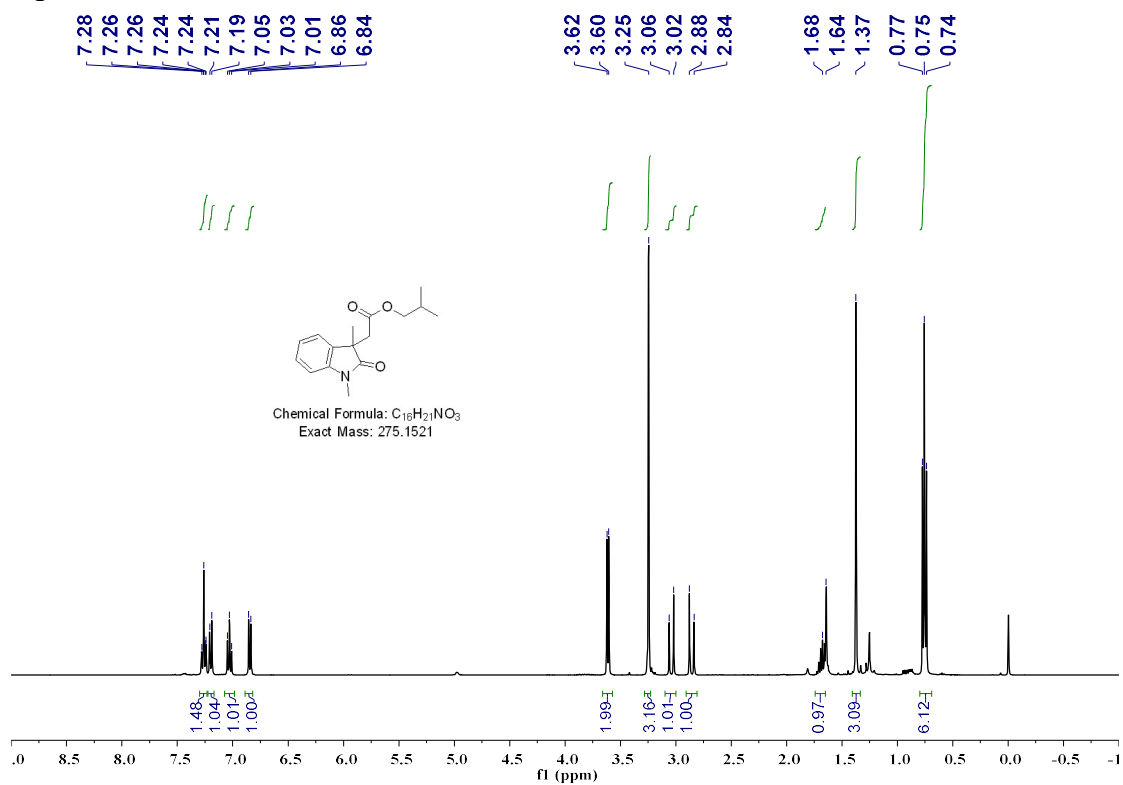




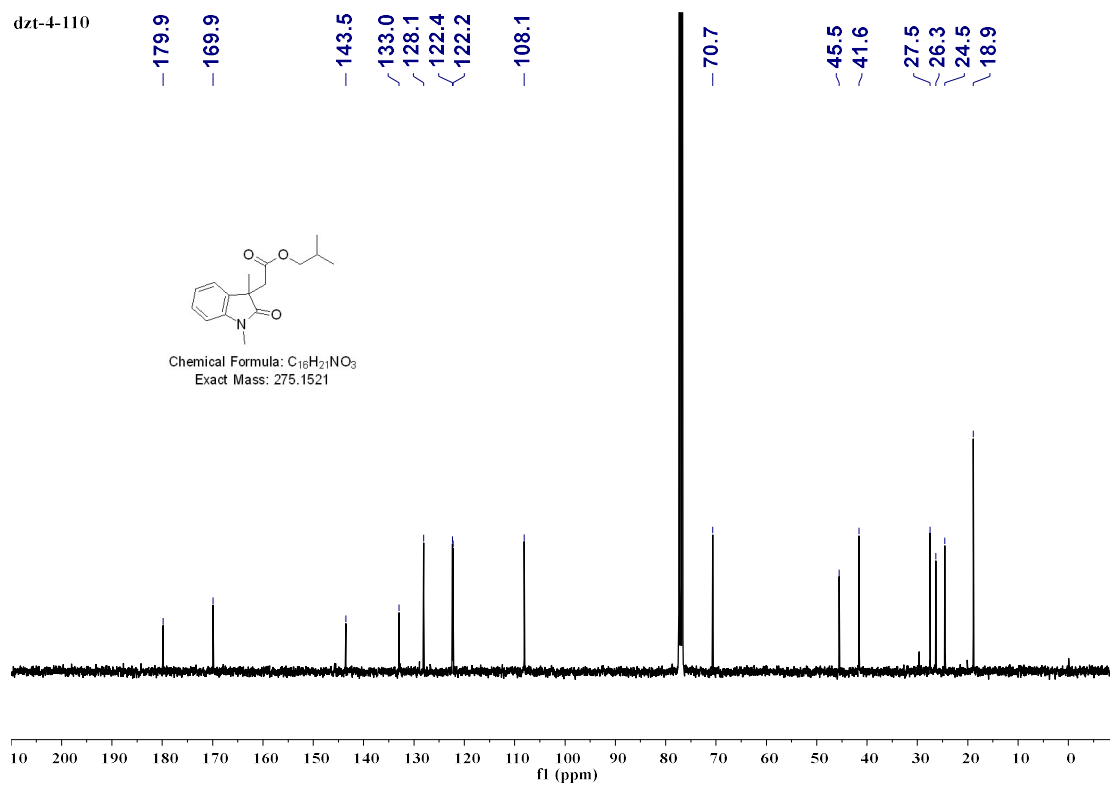
6p



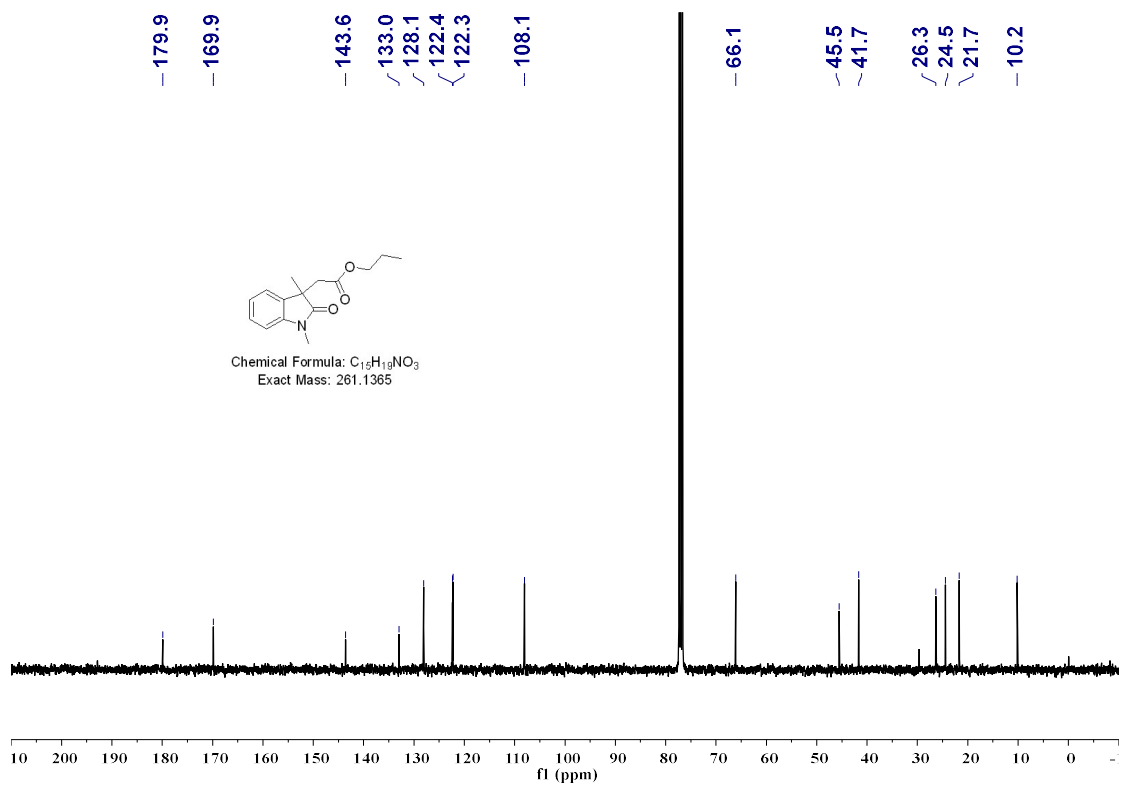
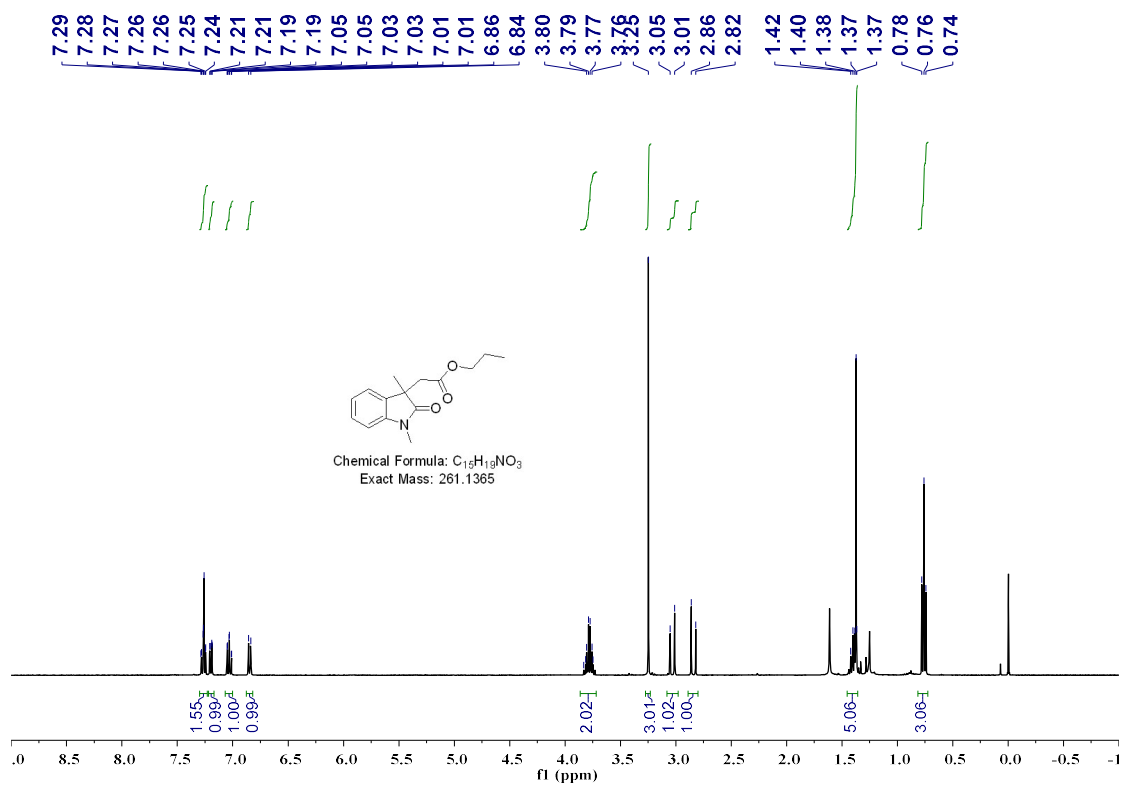
6q



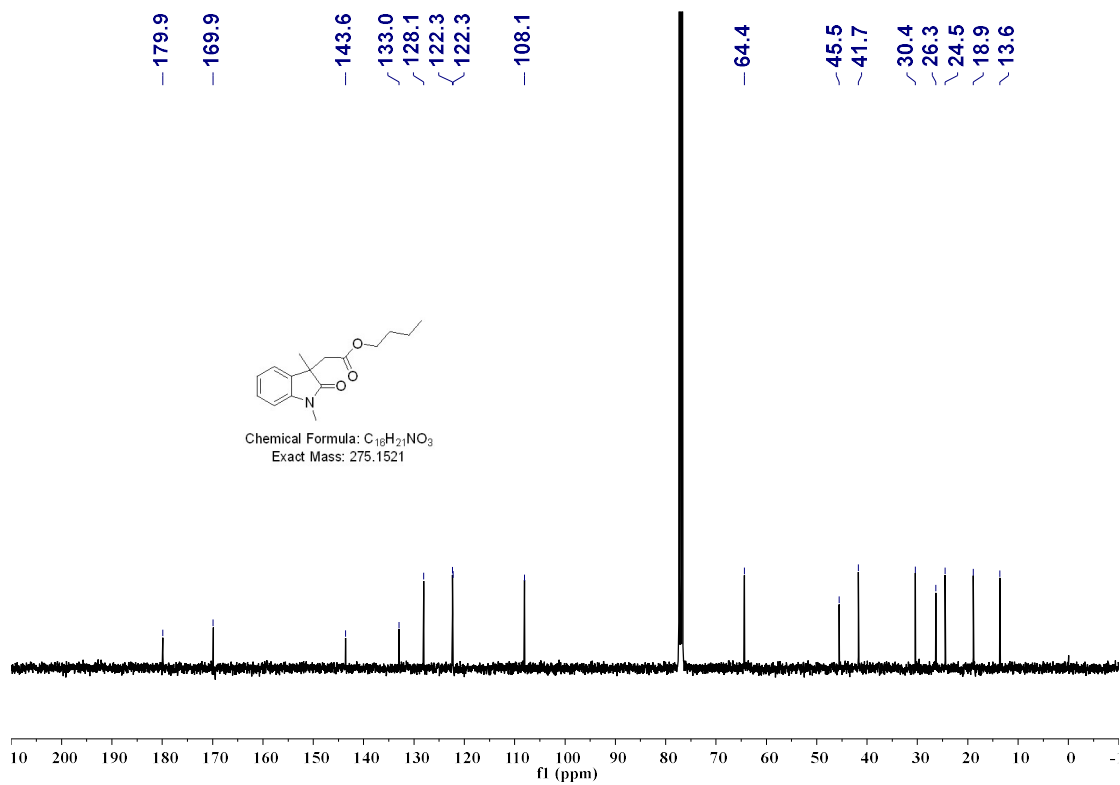
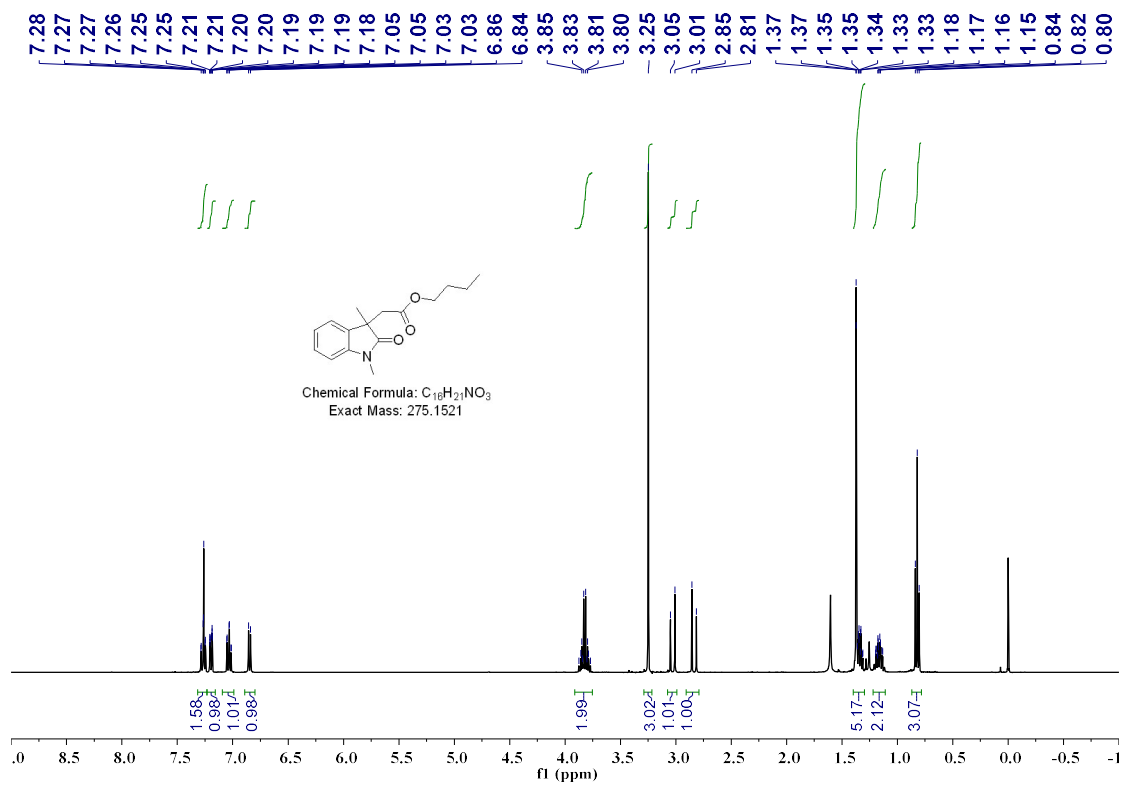
dzt-4-110



6r



6s



## 7. References

- [1] Wang, K.; Ding, Z.; Zhou, Z.; Kong, W. Ni-Catalyzed Enantioselective Reductive Diarylation of Activated Alkenes by Domino Cyclization/Cross-Coupling. *J. Am. Chem. Soc.* **2018**, *140*, 12364-12368.
- [2] Bergonzini, G.; Cassani, C.; Lorimer-Olsson, H.; H  rberg, J.; Wallentin, C. Visible-Light-Mediated Photocatalytic Difunctionalization of Olefins by Radical Acylarylation and Tandem Acylation/Semipinacol Rearrangement. *Chem. Eur. J.* **2016**, *22*, 3292-3295.
- [3] Xu, S.; Chen, J.; Liu, D.; Bao, Y.; Liang, Y.; Xu, P. Aryl chlorides as novel acyl radical precursors via visible-light photoredox catalysis. *Org. Chem. Front.*, **2017**, *4*, 1331-1335.
- [4] Ji, W.; Tan, H. Wang, M. Lia, P.; Wang, L. Photocatalyst-free hypervalent iodine reagent catalyzed decarboxylative acylarylation of acrylamides with  $\alpha$ -oxocarboxylic acids driven by visible-light irradiation *Chem. Commun.* **2016**, *52*, 1462-1465.
- [5] Zheng, L.; Huang, H.; Yang, C.; Xia, W. UV Light-Mediated Difunctionalization of Alkenes through Aryl Radical Addition/1,4-/1,2-Aryl Shift Cascade Reactions. *Org. Lett.* **2015**, *17*, 1034-1037.
- [6] Xu, S.; Wang, k.; Kong W. Ni-Catalyzed Reductive Arylacylation of Alkenes toward Carbonyl-Containing Oxindoles. *Org. Lett.* **2019**, *21*, 7498-7503.
- [7] Wang, G.; Wang, S.; Wang, J.; Chen, S.; Yu, X. Synthesis of oxindole-3-acetates through iron-catalyzed oxidative arylalkoxycarbonylation of activated alkenes. *Tetrahedron*, **2014**, *70*, 3466-3470.
- [8] Wang, H.; Guo, L.; Duan, X. Silver-Catalyzed Decarboxylative Acylarylation of Acrylamides with  $\alpha$ -Oxocarboxylic Acids in Aqueous Media. *Adv. Synth. Catal.* **2013**, *355*, 2222-2226.