

**Supporting information for**

**Direct Oxidative Dearomatization of Indoles: Access to Structurally Diverse 2,2-Disubstituted Indolin-3-ones**

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## General information

EtOAc was freshly distilled over CaSO<sub>4</sub> and THF was freshly distilled over Na. CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>CN were freshly distilled over CaH<sub>2</sub>. Other reagents and solvents were used as commercially available products without further purification unless specified. Proton (<sup>1</sup>H) and carbon (<sup>13</sup>C) nuclear magnetic resonance (NMR) spectra were recorded at on an Bruker AVANCE DRX600 NMR spectrometer. The chemical shifts were given in parts per million (ppm) on the delta (δ) scale, and the residual solvent peaks were used as references as follows: CDCl<sub>3</sub> δ<sub>H</sub> 7.26, δ<sub>C</sub> 77.16 ppm; acetone-*d*<sub>6</sub> δ<sub>H</sub> 2.05, δ<sub>C</sub> 29.84 ppm. Analytical TLC was performed on precoated silica gel GF254 plates. Column chromatography was carried out on silica gel (200–300 mesh). ESIMS analyses were performed on an Agilent 1260-6460 Triple Quad LC-MS spectrometer. HR-ESIMS were carried out on an Agilent 6520 Q-TOF MS spectrometer.

## General procedures for synthesis of starting materials.

The C2 substituted indoles were synthesized according to the protocols in previous reports.<sup>1-3</sup>

## General procedures for synthesis of TEMPO oxoammonium salts<sup>4</sup>

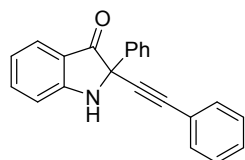
TEMPO (10 g, 64 mmol) was dissolved in water (16.4 mL) and the corresponding acid (64 mmol) was slowly added dropwise over 1 h at room temperature. Then NaOCl (23 mL, 32 mmol) was added over 1 h at 0 °C and stirred for an additional 1 h at 0 °C. The reaction mixture was filtered and the yellow crystalline precipitate was washed with ice-cold 5% NaHCO<sub>3</sub> (20 mL), water (40 mL), and ice-cold Et<sub>2</sub>O (400 mL). The solid was dried over 24 h at 50 °C *in vacuo* to afford the desired product.

## General procedures for oxidative dearomative difunctionalization of indoles

**General procedure:** To a solution of **1** (0.1 mmol) and **2** (0.15 mmol) in EtOAc was added TEMPO<sup>+</sup>ClO<sub>4</sub><sup>-</sup> (0.105 mmol) at room temperature. After 6 h, the solvent was removed and the residue was purified by flash chromatography using acetone-petroleum ether as eluent to afford the desired product.

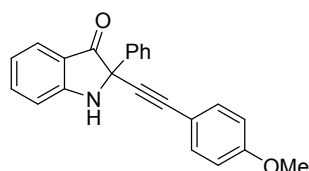
## The analytical and spectral characterization data of the products

### 2-Phenyl-2-(phenylethynyl)indolin-3-one (**3a**)



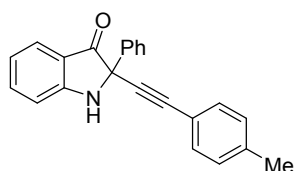
According to general procedure, **3a** was obtained in 93% yield (28.7 mg).  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.73-7.69 (m, 2H), 7.69-7.65 (m, 1H), 7.58-7.53 (m, 1H), 7.50 (d,  $J = 7.2$  Hz, 2H), 7.43-7.29 (m, 6H), 7.02 (d,  $J = 7.6$  Hz, 1H), 6.98-6.89 (m, 1H), 5.31 (s, 1H);  $^{13}\text{C NMR}$  (151 MHz,  $\text{CDCl}_3$ )  $\delta$  196.3, 160.6, 138.0, 137.9, 132.1, 128.9, 128.9, 128.6, 128.4, 126.4, 126.2, 122.1, 120.4, 118.1, 112.8, 86.4, 84.3, 67.1; HR-ESIMS  $m/z$  calcd for  $\text{C}_{22}\text{H}_{16}\text{NO}$   $[\text{M}+\text{H}]^+$  310.1226, found 310.1225.

### 2-((4-Methoxyphenyl)ethynyl)-2-phenylindolin-3-one (**3b**)



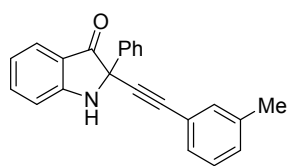
According to general procedure, **3b** was obtained in 94% yield (31.9 mg).  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.73-7.67 (m, 2H), 7.66 (d,  $J = 7.2$  Hz, 1H), 7.57-7.51 (m, 1H), 7.46-7.31 (m, 5H), 7.00 (d,  $J = 8.5$  Hz, 1H), 6.96-6.90 (m, 1H), 6.83 (d,  $J = 8.1$  Hz, 2H), 5.31 (s, 1H), 3.81 (s, 3H);  $^{13}\text{C NMR}$  (151 MHz,  $\text{CDCl}_3$ )  $\delta$  196.5, 160.7, 160.0, 138.1, 137.9, 133.6, 128.8, 128.5, 126.4, 126.2, 120.3, 118.2, 114.2, 114.0, 112.8, 85.0, 84.3, 67.2, 55.4; HR-ESIMS  $m/z$  calcd for  $\text{C}_{23}\text{H}_{18}\text{NO}_2$   $[\text{M}+\text{H}]^+$  340.1332, found 340.1336.

### 2-Phenyl-2-(*p*-tolylethynyl)indolin-3-one (**3c**)



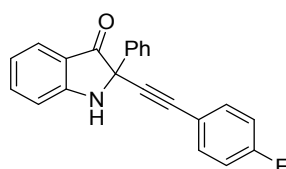
According to general procedure, **3c** was obtained in 88% yield (28.4 mg).  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.73-7.68 (m, 2H), 7.66 (dd,  $J = 7.8, 1.2$  Hz, 1H), 7.55 (ddd,  $J = 8.3, 7.1, 1.3$  Hz, 1H), 7.42-7.32 (m, 5H), 7.12 (d,  $J = 7.9$  Hz, 2H), 7.01 (d,  $J = 8.2$  Hz, 1H), 6.93 (t,  $J = 7.4$  Hz, 1H), 5.30 (s, 1H), 2.35 (s, 3H);  $^{13}\text{C NMR}$  (151 MHz,  $\text{CDCl}_3$ )  $\delta$  196.4, 160.7, 139.1, 138.0, 137.9, 132.0, 129.2, 128.8, 128.6, 126.4, 126.2, 120.4, 119.0, 118.2, 112.8, 85.7, 84.5, 67.2, 21.6; HR-ESIMS  $m/z$  calcd for  $\text{C}_{23}\text{H}_{18}\text{NO}$   $[\text{M}+\text{H}]^+$  324.1383, found 324.1381.

### 2-Phenyl-2-(*m*-tolylethynyl)indolin-3-one (**3d**)



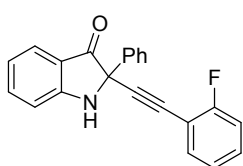
According to general procedure, **3d** was obtained in 90% yield (28.8 mg).  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74-7.69 (m, 2H), 7.67 (dd,  $J = 7.8, 1.3$  Hz, 1H), 7.55 (ddd,  $J = 8.4, 7.1, 1.3$  Hz, 1H), 7.42-7.32 (m, 4H), 7.30 (brd,  $J = 7.6$  Hz, 1H), 7.20 (t,  $J = 7.6$  Hz, 1H), 7.15 (brd,  $J = 7.6$  Hz, 1H), 7.01 (d,  $J = 8.2$  Hz, 1H), 6.95-6.91 (m, 1H), 5.31 (s, 1H), 2.32 (s, 3H);  $^{13}\text{C NMR}$  (151 MHz,  $\text{CDCl}_3$ )  $\delta$  196.3, 160.6, 138.1, 137.9, 137.9, 132.7, 129.7, 129.1, 128.8, 128.5, 128.3, 126.4, 126.2, 121.9, 120.3, 118.1, 112.8, 86.0, 84.4, 67.1, 21.3; HR-ESIMS  $m/z$  calcd for  $\text{C}_{23}\text{H}_{18}\text{NO}$   $[\text{M}+\text{H}]^+$  324.1383, found 324.1384.

### 2-((4-Fluorophenyl)ethynyl)-2-phenylindolin-3-one (**3e**)



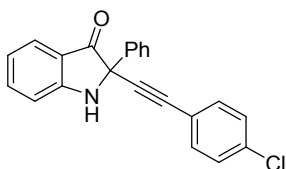
According to general procedure, **3e** was obtained in 91% yield (29.8 mg).  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.72-7.61 (m, 3H), 7.60-7.52 (m, 1H), 7.50-7.44 (m, 2H), 7.42-7.32 (m, 3H), 7.04-6.97 (m, 3H), 6.97-6.90 (m, 1H), 5.32 (s, 1H);  $^{13}\text{C NMR}$  (151 MHz,  $\text{CDCl}_3$ )  $\delta$  196.2, 163.7, 162.0, 160.6, 138.1, 137.8, 134.1, 134.1, 128.9, 128.6, 126.4, 126.1, 120.4, 118.2, 118.2, 118.1, 115.8, 115.7, 112.8, 86.2, 83.2, 67.1; HR-ESIMS  $m/z$  calcd for  $\text{C}_{22}\text{H}_{15}\text{FNO}$   $[\text{M}+\text{H}]^+$  328.1132, found 328.1333.

### 2-((2-Fluorophenyl)ethynyl)-2-phenylindolin-3-one (**3f**)



According to general procedure, **3f** was obtained in 92% yield (30.0 mg).  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.73-7.69 (m, 2H), 7.66 (dd,  $J = 8.3, 2.6$  Hz, 1H), 7.56 (t,  $J = 8.2$  Hz, 1H), 7.50-7.45 (m, 1H), 7.42-7.30 (m, 4H), 7.11-7.05 (m, 2H), 7.02 (dd,  $J = 8.6, 2.7$  Hz, 1H), 6.96-6.91 (m, 1H), 5.36 (s, 1H);  $^{13}\text{C NMR}$  (151 MHz,  $\text{CDCl}_3$ )  $\delta$  196.0, 164.0, 162.4, 160.6, 138.0, 137.6, 133.9, 130.7, 130.6, 128.9, 128.6, 126.4, 126.2, 124.0, 124.0, 120.4, 118.0, 115.7, 115.5, 112.8, 110.8, 110.7, 91.5, 91.5, 77.9, 67.2; HR-ESIMS  $m/z$  calcd for  $\text{C}_{22}\text{H}_{15}\text{FNO}$   $[\text{M}+\text{H}]^+$  328.1132, found 328.1335.

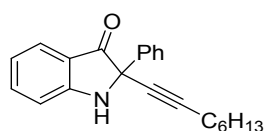
### 2-((4-Chlorophenyl)ethynyl)-2-phenylindolin-3-one (**3g**)



According to general procedure, **3g** was obtained in 90% yield (30.8 mg).  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.70-7.64 (m, 3H),

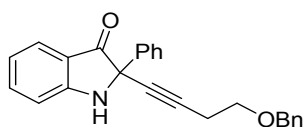
7.56 (ddd,  $J = 8.4, 7.1, 1.3$  Hz, 1H), 7.44-7.34 (m, 5H), 7.31-7.27 (m, 2H), 7.02 (d,  $J = 8.2$  Hz, 1H), 6.94 (t,  $J = 7.4$  Hz, 1H), 5.31 (s, 1H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  196.1, 160.6, 138.1, 137.7, 135.0, 133.4, 128.9, 128.8, 128.7, 126.5, 126.1, 120.6, 120.5, 118.1, 112.8, 87.4, 83.2, 67.1; HR-ESIMS  $m/z$  calcd for  $\text{C}_{22}\text{H}_{15}\text{ClNO}$   $[\text{M}+\text{H}]^+$  344.0837, found 344.0835.

### 2-(Oct-1-yn-1-yl)-2-phenylindolin-3-one (3h)



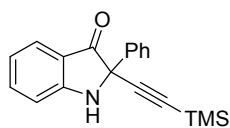
According to general procedure, **3h** was obtained in 87% yield (27.6 mg).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62 (d,  $J = 7.8$  Hz, 3H), 7.53 (t,  $J = 8.2$  Hz, 1H), 7.38-7.28 (m, 3H), 6.97 (d,  $J = 8.2$  Hz, 1H), 6.91 (t,  $J = 7.4$  Hz, 1H), 5.15 (s, 1H), 2.27 (td,  $J = 7.2, 2.1$  Hz, 2H), 1.55 (p,  $J = 7.3$  Hz, 2H), 1.43-1.35 (m, 2H), 1.34-1.26 (m, 4H), 0.89 (t,  $J = 6.9$  Hz, 3H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  197.0, 160.7, 138.3, 137.8, 128.7, 128.4, 126.3, 126.2, 120.2, 118.2, 112.8, 85.6, 77.3, 66.9, 31.4, 28.7, 28.6, 22.6, 19.0, 14.2; HR-ESIMS  $m/z$  calcd for  $\text{C}_{22}\text{H}_{24}\text{NO}$   $[\text{M}+\text{H}]^+$  318.1852, found 318.1854.

### 2-(4-(Benzyloxy)but-1-yn-1-yl)-2-phenylindolin-3-one (3i)



According to general procedure, **3i** was obtained in 86% yield (31.5 mg).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63-7.57 (m, 3H), 7.51 (t,  $J = 7.0$  Hz, 1H), 7.35-7.25 (m, 8H), 6.94 (d,  $J = 5.9$  Hz, 1H), 6.89 (t,  $J = 6.5$  Hz, 1H), 5.16 (s, 1H), 4.53 (s, 2H), 3.61 (t,  $J = 6.6$  Hz, 2H), 2.59 (t,  $J = 6.6$  Hz, 2H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  196.7, 160.6, 138.0, 137.9, 137.8, 128.7, 128.5, 128.4, 127.7, 127.7, 126.2, 126.1, 120.2, 118.0, 112.7, 81.9, 78.4, 73.0, 68.2, 66.7, 20.4; HR-ESIMS  $m/z$  calcd for  $\text{C}_{25}\text{H}_{22}\text{NO}_2$   $[\text{M}+\text{H}]^+$  368.1645, found 368.1644.

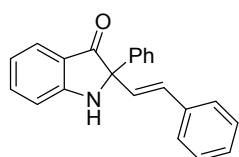
### 2-Phenyl-2-((trimethylsilyl)ethynyl)indolin-3-one (3j)



According to general procedure, **3j** was obtained in 84% yield (25.6 mg).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66-7.60 (m, 3H), 7.55 (t,  $J = 7.0$  Hz, 1H), 7.42-7.30 (m, 3H), 7.00 (brd,  $J = 7.9$  Hz, 1H), 6.93 (t,  $J = 7.2$  Hz, 1H), 5.18 (s, 1H), 0.22 (s, 9H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  195.8, 160.4,

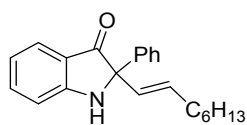
137.7, 137.6, 128.6, 128.4, 126.3, 125.9, 120.2, 117.9, 112.7, 101.8, 89.5, 67.1, -0.2;  
HR-ESIMS  $m/z$  calcd for  $C_{19}H_{20}NOSi$   $[M+H]^+$  306.1309, found 306.1312.

### (*E*)-2-Phenyl-2-styrylindolin-3-one (**3k**)



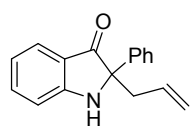
According to general procedure, **3k** was obtained in 92% yield (28.6 mg).  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$  7.68-7.64 (m, 1H), 7.56-7.49 (m, 3H), 7.43-7.23 (m, 8H), 6.99 (d,  $J = 8.2$  Hz, 1H), 6.88 (t,  $J = 7.4$  Hz, 1H), 6.83 (d,  $J = 15.9$  Hz, 1H), 6.64 (d,  $J = 15.9$  Hz, 1H), 5.16 (s, 1H);  $^{13}C$  NMR (151 MHz,  $CDCl_3$ )  $\delta$  200.2, 160.2, 139.7, 137.7, 136.3, 130.5, 128.9, 128.7, 128.5, 128.2, 128.1, 126.8, 126.6, 125.7, 119.7, 119.5, 112.5, 73.4; HR-ESIMS  $m/z$  calcd for  $C_{22}H_{18}NO$   $[M+H]^+$  312.1383, found 312.1386.

### (*E*)-2-(Oct-1-en-1-yl)-2-phenylindolin-3-one (**3l**)



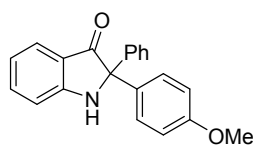
According to general procedure, **3l** was obtained in 86% yield (27.4 mg).  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$  7.63-7.57 (m, 1H), 7.50-7.45 (m, 3H), 7.36-7.24 (m, 3H), 6.93 (d,  $J = 8.1$  Hz, 1H), 6.84 (t,  $J = 7.1$  Hz, 1H), 5.97-5.77 (m, 2H), 4.99 (s, 1H), 2.10-2.05 (m, 2H), 1.42-1.16 (m, 8H), 0.86 (t,  $J = 6.0$  Hz, 3H);  $^{13}C$  NMR (151 MHz,  $CDCl_3$ )  $\delta$  200.6, 160.2, 140.0, 137.5, 132.3, 128.8, 128.6, 127.9, 126.5, 125.7, 119.5, 119.4, 112.4, 73.1, 32.5, 31.8, 29.1, 29.0, 22.7, 14.2; HR-ESIMS  $m/z$  calcd for  $C_{22}H_{26}NO$   $[M+H]^+$  320.2009, found 320.2013.

### 2-Allyl-2-phenylindolin-3-one (**3m**)



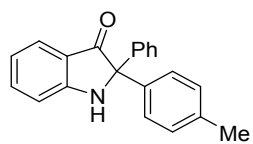
According to general procedure, **3m** was obtained in 86% yield (21.4 mg).  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$  7.65-7.61 (m, 2H), 7.58 (d,  $J = 7.7$  Hz, 1H), 7.49 (ddd,  $J = 8.4, 7.1, 1.4$  Hz, 1H), 7.35 (t,  $J = 7.7$  Hz, 2H), 7.31-7.26 (m, 1H), 6.97 (d,  $J = 8.2$  Hz, 1H), 6.84 (t,  $J = 7.4$  Hz, 1H), 5.63-5.56 (m, 1H), 5.17 (dd,  $J = 17.1, 1.6$  Hz, 1H), 5.13 (s, 1H), 5.11-5.06 (m, 1H), 3.06 (dd,  $J = 14.0, 5.9$  Hz, 1H), 2.65 (dd,  $J = 14.0, 8.4$  Hz, 1H);  $^{13}C$  NMR (151 MHz,  $CDCl_3$ )  $\delta$  201.3, 160.4, 138.6, 137.5, 132.7, 128.7, 127.8, 126.0, 125.5, 119.9, 119.6, 119.4, 112.4, 70.8, 42.9; HR-ESIMS  $m/z$  calcd for  $C_{17}H_{16}NO$   $[M+H]^+$  250.1226, found 250.1230.

### 2-(4-Methoxyphenyl)-2-phenylindolin-3-one (3n)



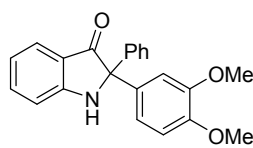
According to general procedure with 1.2 eq oxidant, **3n** was obtained in 85% yield (26.8 mg).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 (d,  $J = 7.8$  Hz, 1H), 7.49 (t,  $J = 7.6$  Hz, 1H), 7.43-7.40 (m, 2H), 7.36-7.27 (m, 5H), 6.92 (d,  $J = 8.2$  Hz, 1H), 6.89-6.83 (m, 3H), 5.26 (s, 1H), 3.78 (s, 3H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  201.2, 160.2, 159.3, 141.4, 137.7, 133.3, 128.7, 128.6, 127.9, 127.5, 125.6, 120.0, 119.7, 114.0, 112.6, 74.7, 55.4; HR-ESIMS  $m/z$  calcd for  $\text{C}_{21}\text{H}_{18}\text{NO}_2$   $[\text{M}+\text{H}]^+$  316.1332, found 316.1334.

### 2-Phenyl-2-(*p*-tolyl)indolin-3-one (3o)



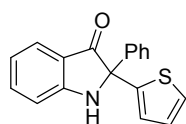
According to general procedure with 1.2 eq oxidant for 12 h, **3o** was obtained in 72% yield (21.5 mg).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66 (dd,  $J = 7.8, 1.3$  Hz, 1H), 7.50 (ddd,  $J = 8.3, 7.0, 1.3$  Hz, 1H), 7.44-7.39 (m, 2H), 7.35-7.27 (m, 5H), 7.14 (d,  $J = 8.0$  Hz, 2H), 6.93 (d,  $J = 8.2$  Hz, 1H), 6.88 (t,  $J = 7.4$  Hz, 1H), 5.19 (s, 1H), 2.34 (s, 3H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  200.9, 160.0, 141.1, 138.2, 137.6, 137.5, 129.3, 128.5, 127.8, 127.4, 127.3, 125.5, 120.0, 119.6, 112.5, 74.8, 21.1; HR-ESIMS  $m/z$  calcd for  $\text{C}_{21}\text{H}_{18}\text{NO}$   $[\text{M}+\text{H}]^+$  300.1383, found 300.1382.

### 2-(3,4-Dimethoxyphenyl)-2-phenylindolin-3-one (3p)



According to general procedure with 1.2 eq oxidant, **3p** was obtained in 82% yield (28.3 mg).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 (d,  $J = 7.6$  Hz, 1H), 7.49 (t,  $J = 7.5$  Hz, 1H), 7.40-7.36 (m, 2H), 7.34-7.27 (m, 3H), 6.99 (d,  $J = 8.3$  Hz, 1H), 6.97-6.91 (m, 2H), 6.87 (t,  $J = 7.1$  Hz, 1H), 6.80 (d,  $J = 8.2$  Hz, 1H), 5.25 (s, 1H), 3.85 (s, 3H), 3.78 (s, 3H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  201.2, 160.2, 149.0, 148.9, 141.5, 137.7, 133.4, 128.7, 128.0, 127.4, 125.6, 120.1, 119.8, 119.8, 112.6, 111.0, 110.9, 74.8, 56.0, 56.0; HR-ESIMS  $m/z$  calcd for  $\text{C}_{22}\text{H}_{20}\text{NO}_3$   $[\text{M}+\text{H}]^+$  346.1438, found 346.1439.

### 2-Phenyl-2-(thiophen-2-yl)indolin-3-one (3s)

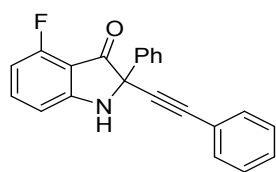


According to general procedure, **3s** was obtained in 71% yield (20.7 mg).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.67 (d,  $J = 7.7$  Hz, 1H), 7.57-7.44



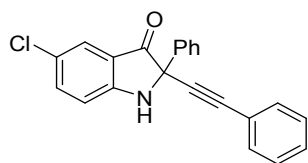
(m, 3H), 7.37-7.29 (m, 3H), 7.25 (d,  $J = 5.2$  Hz, 1H), 7.12 (dd,  $J = 3.7, 1.2$  Hz, 1H), 7.00 (dd,  $J = 5.1, 3.6$  Hz, 1H), 6.96 (d,  $J = 8.2$  Hz, 1H), 6.91 (t,  $J = 7.4$  Hz, 1H), 5.35 (s, 1H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  199.4, 160.0, 144.6, 140.5, 137.9, 128.7, 128.4, 127.3, 126.9, 126.4, 125.9, 125.4, 120.2, 119.4, 112.8, 72.4; HR-ESIMS  $m/z$  calcd for  $\text{C}_{18}\text{H}_{14}\text{NOS}$   $[\text{M}+\text{H}]^+$  292.0791, found 292.0795.

#### 4-Fluoro-2-phenyl-2-(phenylethynyl)indolin-3-one (4a)



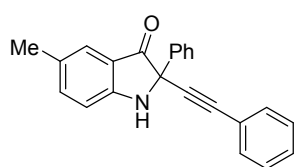
According to general procedure, **4a** was obtained in 86% yield (28.1 mg).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.73-7.67 (m, 2H), 7.52-7.47 (m, 3H), 7.43-7.28 (m, 6H), 6.76 (d,  $J = 8.2$  Hz, 1H), 6.52 (t,  $J = 8.5$  Hz, 1H), 5.46 (s, 1H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  192.2, 161.3, 139.7, 139.7, 137.4, 132.2, 129.0, 128.9, 128.8, 128.4, 126.2, 122.0, 108.3, 108.3, 106.3, 106.2, 85.9, 84.7, 67.5; HR-ESIMS  $m/z$  calcd for  $\text{C}_{22}\text{H}_{15}\text{FNO}$   $[\text{M}+\text{H}]^+$  328.1132, found 328.1133.

#### 5-Chloro-2-phenyl-2-(phenylethynyl)indolin-3-one (4b)



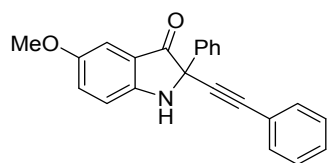
According to general procedure, **4b** was obtained in 90% yield (30.8 mg).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.70-7.64 (m, 2H), 7.61 (s, 1H), 7.51-7.47 (m, 3H), 7.41-7.31 (m, 6H), 6.97 (d,  $J = 8.5$  Hz, 1H), 5.34 (s, 1H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  195.1, 158.9, 137.9, 137.3, 132.1, 129.0, 128.9, 128.8, 128.4, 126.1, 125.6, 121.9, 119.2, 114.0, 85.8, 84.7, 67.8; HR-ESIMS  $m/z$  calcd for  $\text{C}_{22}\text{H}_{15}\text{ClNO}$   $[\text{M}+\text{H}]^+$  344.0837, found 344.0841.

#### 5-Methyl-2-phenyl-2-(phenylethynyl)indolin-3-one (4c)



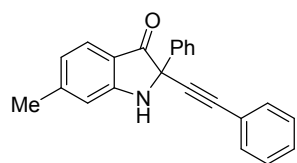
According to general procedure, **4c** was obtained in 95% yield (30.8 mg).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.73-7.67 (m, 2H), 7.51-7.44 (m, 3H), 7.42-7.29 (m, 7H), 6.95 (d,  $J = 8.2$  Hz, 1H), 5.16 (s, 1H), 2.33 (s, 3H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  196.4, 159.1, 139.4, 138.1, 132.1, 130.1, 128.8, 128.8, 128.5, 128.4, 126.2, 125.7, 122.2, 118.4, 112.9, 86.6, 84.2, 67.5, 20.7; HR-ESIMS  $m/z$  calcd for  $\text{C}_{23}\text{H}_{18}\text{NO}$   $[\text{M}+\text{H}]^+$  324.1383, found 324.1388.

### 5-Methoxy-2-phenyl-2-(phenylethynyl)indolin-3-one (4d)



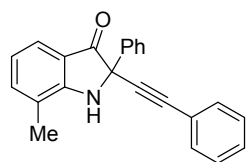
According to general procedure, **4d** was obtained in 94% yield (31.8 mg). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.74-7.68 (m, 2H), 7.49 (d, *J* = 6.9 Hz, 2H), 7.44-7.28 (m, 6H), 7.24 (d, *J* = 8.9 Hz, 1H), 7.09 (s, 1H), 6.99 (d, *J* = 9.0 Hz, 1H), 5.09 (s, 1H), 3.79 (s, 3H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 196.7, 156.4, 154.4, 138.0, 132.1, 128.8, 128.8, 128.5, 128.4, 126.2, 122.1, 118.6, 114.6, 105.9, 86.6, 84.2, 68.0, 55.9; HR-ESIMS *m/z* calcd for C<sub>23</sub>H<sub>18</sub>NO<sub>2</sub> [M+H]<sup>+</sup> 340.1332, found 340.1333.

### 6-Methyl-2-phenyl-2-(phenylethynyl)indolin-3-one (4e)



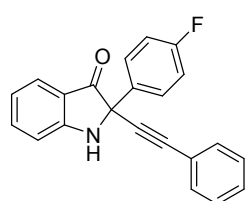
According to general procedure, **4e** was obtained in 91% yield (29.4 mg). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.72-7.66 (m, 2H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.49 (d, *J* = 6.6 Hz, 2H), 7.42-7.28 (m, 6H), 6.82 (s, 1H), 6.76 (d, *J* = 7.8 Hz, 1H), 5.23 (s, 1H), 2.42 (s, 3H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 195.6, 161.2, 149.8, 138.1, 132.1, 128.8, 128.8, 128.5, 128.4, 126.2, 126.1, 122.2, 122.2, 115.9, 112.9, 86.6, 84.3, 67.4, 22.7; HR-ESIMS *m/z* calcd for C<sub>23</sub>H<sub>18</sub>NO [M+H]<sup>+</sup> 324.1383, found 324.1386.

### 7-Methyl-2-phenyl-2-(phenylethynyl)indolin-3-one (4f)



According to general procedure, **4f** was obtained in 90% yield (29.1 mg). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.73-7.67 (m, 2H), 7.54 (brd, *J* = 7.6 Hz, 1H), 7.50 (brd, *J* = 7.4 Hz, 2H), 7.43-7.29 (m, 7H), 6.89 (t, *J* = 7.2 Hz, 1H), 5.13 (s, 1H), 2.34 (s, 3H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 196.7, 159.8, 138.0, 138.0, 132.1, 128.9, 128.8, 128.6, 128.4, 126.2, 123.7, 122.2, 122.0, 120.5, 117.7, 86.6, 84.3, 67.2, 15.9; HR-ESIMS *m/z* calcd for C<sub>23</sub>H<sub>18</sub>NO [M+H]<sup>+</sup> 324.1383, found 324.1385.

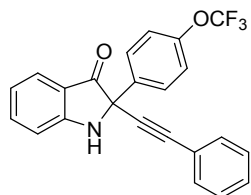
### 2-(4-Fluorophenyl)-2-(phenylethynyl)indolin-3-one (4g)



According to general procedure, **4g** was obtained in 92% yield (30.1 mg). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.72-7.64 (m, 3H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.48 (d, *J* = 7.1 Hz, 2H), 7.36-7.30 (m, 3H), 7.07 (t, *J* = 8.1 Hz, 2H), 7.02 (d, *J* = 8.1 Hz, 1H), 6.95 (t, *J* = 7.2

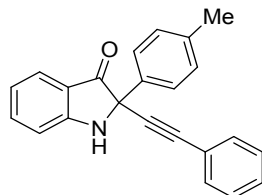
Hz, 1H), 5.31 (s, 1H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  196.1, 163.8, 162.2, 160.6, 138.1, 133.7, 133.7, 132.1, 129.0, 128.4, 128.2, 128.1, 126.5, 121.9, 120.6, 118.0, 115.8, 115.6, 113.0, 86.2, 84.3, 66.6; HR-ESIMS  $m/z$  calcd for  $\text{C}_{22}\text{H}_{15}\text{FNO}$   $[\text{M}+\text{H}]^+$  328.1132, found 328.1130.

### 2-(Phenylethynyl)-2-(4-(trifluoromethoxy)phenyl)indolin-3-one (4h)



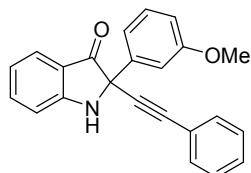
According to general procedure, **4h** was obtained in 90% yield (35.3 mg).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.75 (d,  $J = 8.0$  Hz, 2H), 7.67 (d,  $J = 7.6$  Hz, 1H), 7.57 (t,  $J = 7.4$  Hz, 1H), 7.48 (d,  $J = 7.0$  Hz, 2H), 7.36-7.30 (m, 3H), 7.23 (d,  $J = 8.0$  Hz, 2H), 7.04 (d,  $J = 8.1$  Hz, 1H), 6.96 (t,  $J = 7.2$  Hz, 1H), 5.33 (s, 1H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  195.8, 160.6, 149.4, 138.3, 136.6, 132.1, 129.1, 128.4, 127.9, 126.4, 121.8, 121.3, 121.2, 120.7, 119.6, 117.9, 113.0, 86.0, 84.4, 66.5; HR-ESIMS  $m/z$  calcd for  $\text{C}_{23}\text{H}_{15}\text{F}_3\text{NO}_2$   $[\text{M}+\text{H}]^+$  394.1049, found 394.1051.

### 2-(Phenylethynyl)-2-(*p*-tolyl)indolin-3-one (4i)



According to general procedure, **4i** was obtained in 93% yield (30.0 mg).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63 (d,  $J = 7.7$  Hz, 1H), 7.55 (d,  $J = 7.8$  Hz, 2H), 7.51 (t,  $J = 7.5$  Hz, 1H), 7.46 (d,  $J = 6.8$  Hz, 2H), 7.34-7.25 (m, 3H), 7.17 (d,  $J = 7.7$  Hz, 2H), 6.97 (d,  $J = 8.2$  Hz, 1H), 6.89 (t,  $J = 7.3$  Hz, 1H), 5.28 (s, 1H), 2.33 (s, 3H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  196.5, 160.6, 138.4, 137.9, 134.9, 132.1, 129.6, 128.8, 128.4, 126.4, 126.1, 122.2, 120.3, 118.2, 112.8, 86.6, 84.2, 67.0, 21.2; HR-ESIMS  $m/z$  calcd for  $\text{C}_{23}\text{H}_{18}\text{NO}$   $[\text{M}+\text{H}]^+$  324.1383, found 324.1384.

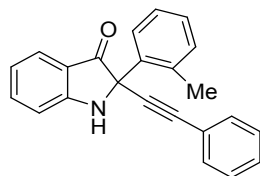
### 2-(3-Methoxyphenyl)-2-(phenylethynyl)indolin-3-one (4j)



According to general procedure, **4j** was obtained in 95% yield (32.2 mg).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63 (d,  $J = 7.6$  Hz, 1H), 7.51 (t,  $J = 7.5$  Hz, 1H), 7.46 (d,  $J = 6.8$  Hz, 2H), 7.34-7.25 (m, 6H), 6.97 (d,  $J = 7.2$  Hz, 1H), 6.93-6.84 (m, 2H), 5.30 (s, 1H), 3.79 (s, 3H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  196.1, 160.6, 156.0, 139.4, 138.0, 132.1,

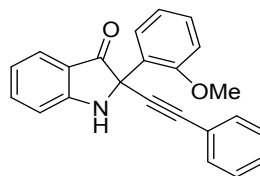
129.9, 128.9, 128.4, 126.4, 122.1, 120.4, 118.4, 118.1, 113.8, 112.8, 112.2, 86.3, 84.2, 67.0, 55.4; HR-ESIMS  $m/z$  calcd for  $C_{23}H_{18}NO_2$   $[M+H]^+$  340.1332, found 340.1335.

### 2-(Phenylethynyl)-2-(*o*-tolyl)indolin-3-one (4k)



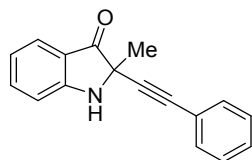
According to general procedure, **4k** was obtained in 94% yield (30.4 mg).  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$  8.03 (d,  $J = 6.6$  Hz, 1H), 7.73 (d,  $J = 7.5$  Hz, 1H), 7.53 (t,  $J = 7.5$  Hz, 1H), 7.47-7.43 (m, 2H), 7.35-7.22 (m, 5H), 7.17-7.013 (m, 1H), 6.97-6.94 (m, 2H), 5.17 (s, 1H), 2.17 (s, 3H);  $^{13}C$  NMR (151 MHz,  $CDCl_3$ )  $\delta$  196.8, 159.6, 137.7, 137.2, 135.1, 132.1, 132.1, 129.7, 128.9, 128.9, 128.4, 126.0, 125.7, 122.1, 120.4, 120.0, 113.3, 86.67, 84.7, 68.6, 20.4; HR-ESIMS  $m/z$  calcd for  $C_{23}H_{18}NO$   $[M+H]^+$  324.1383, found 324.1386.

### 2-(2-Methoxyphenyl)-2-(phenylethynyl)indolin-3-one (4l)



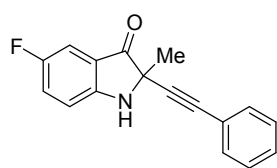
According to general procedure, **4l** was obtained in 93% yield (31.5 mg).  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$  7.95 (dd,  $J = 7.7, 1.7$  Hz, 1H), 7.76 (d,  $J = 7.7$  Hz, 1H), 7.52-7.47 (m, 3H), 7.36-7.27 (m, 4H), 7.04 (td,  $J = 7.6, 1.1$  Hz, 1H), 6.96-6.86 (m, 3H), 5.15 (s, 1H), 3.55 (s, 3H);  $^{13}C$  NMR (151 MHz,  $CDCl_3$ )  $\delta$  197.6, 159.2, 157.2, 137.0, 132.1, 130.3, 130.2, 128.8, 128.3, 127.0, 125.3, 122.2, 121.0, 120.8, 119.8, 113.0, 112.3, 86.0, 85.0, 66.0, 55.8; HR-ESIMS  $m/z$  calcd for  $C_{23}H_{18}NO_2$   $[M+H]^+$  340.1332, found 340.1337.

### 2-Methyl-2-(phenylethynyl)indolin-3-one (4m)



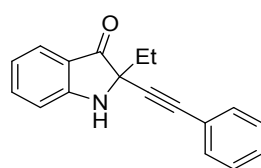
According to general procedure, **4m** was obtained in 92% yield (22.7 mg).  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$  7.68 (d,  $J = 7.7$  Hz, 1H), 7.50 (ddd,  $J = 8.4, 7.1, 1.4$  Hz, 1H), 7.41 (dd,  $J = 8.0, 1.7$  Hz, 2H), 7.32-7.25 (m, 3H), 6.93-6.88 (m, 2H), 4.98 (s, 1H), 1.72 (s, 3H);  $^{13}C$  NMR (151 MHz,  $CDCl_3$ )  $\delta$  198.6, 159.8, 137.8, 132.0, 128.6, 128.3, 125.8, 122.2, 120.0, 119.1, 113.1, 87.1, 82.8, 60.8, 25.5; HR-ESIMS  $m/z$  calcd for  $C_{17}H_{14}NO$   $[M+H]^+$  248.1070, found 248.1073.

### 5-Fluoro-2-methyl-2-(phenylethynyl)indolin-3-one (4n)



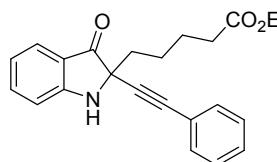
According to general procedure, **4n** was obtained in 90% yield (23.8 mg). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.42-7.37 (m, 2H), 7.34-7.24 (m, 5H), 6.88 (dd, *J* = 8.8, 3.7 Hz, 1H), 4.87 (s, 1H), 1.71 (s, 3H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 198.4, 157.9, 156.4, 156.3, 132.0, 128.8, 128.3, 126.0, 125.8, 122.0, 119.7, 119.6, 114.5, 114.4, 110.6, 110.5, 86.8, 83.1, 61.9, 25.5; HR-ESIMS *m/z* calcd for C<sub>17</sub>H<sub>13</sub>FNO [M+H]<sup>+</sup> 266.0976, found 266.0979.

### 2-Ethyl-2-(phenylethynyl)indolin-3-one (4o)



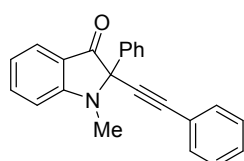
According to general procedure, **4o** was obtained in 90% yield (24.5 mg). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.67 (d, *J* = 7.7 Hz, 1H), 7.52-7.46 (m, 1H), 7.43-7.38 (m, 2H), 7.34-7.22 (m, 3H), 6.97-6.81 (m, 2H), 4.94 (s, 1H), 2.15-2.07 (m, 1H), 1.95-1.89 (m, 1H), 1.11 (t, *J* = 7.4 Hz, 3H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 198.6, 160.3, 137.7, 132.0, 128.6, 128.3, 125.6, 122.3, 119.9, 119.9, 113.1, 86.3, 83.6, 65.0, 31.9, 8.7; HR-ESIMS *m/z* calcd for C<sub>18</sub>H<sub>16</sub>NO [M+H]<sup>+</sup> 262.1226, found 262.1224.

### Ethyl 5-(3-oxo-2-(phenylethynyl)indolin-2-yl)pentanoate (4p)



According to general procedure, **4p** was obtained in 91% yield (32.8 mg). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.66 (d, *J* = 7.7 Hz, 1H), 7.50 (ddd, *J* = 8.3, 7.1, 1.4 Hz, 1H), 7.39 (dd, *J* = 8.0, 1.7 Hz, 2H), 7.30-7.25 (m, 3H), 6.93-6.87 (m, 2H), 4.91 (s, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.32 (t, *J* = 7.2 Hz, 2H), 2.07 (ddd, *J* = 13.4, 11.9, 3.9 Hz, 1H), 1.87 (ddd, *J* = 13.4, 10.9, 4.6 Hz, 1H), 1.75-1.67 (m, 3H), 1.51-1.43 (m, 1H), 1.23 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 198.4, 173.7, 160.3, 137.8, 132.1, 128.7, 128.3, 125.7, 122.2, 120.0, 119.8, 113.2, 86.3, 83.7, 64.4, 60.4, 38.2, 34.2, 24.5, 23.9, 14.4; HR-ESIMS *m/z* calcd for C<sub>23</sub>H<sub>24</sub>NO<sub>3</sub> [M+H]<sup>+</sup> 362.1751, found 362.1753.

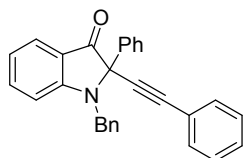
### 1-Methyl-2-phenyl-2-(phenylethynyl)indolin-3-one (4q)



According to general procedure, **4q** was obtained in 92% yield (29.7 mg). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.67-7.63 (m, 1H), 7.60-7.50 (m, 5H), 7.44-7.29 (m, 6H), 6.92 (d, *J* = 8.3 Hz, 1H), 6.83 (t,

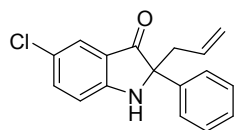
$J = 7.3$  Hz, 1H), 3.07 (s, 3H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  195.8, 161.3, 138.2, 135.9, 132.2, 129.0, 128.9, 128.7, 128.4, 126.7, 126.5, 122.1, 118.3, 117.8, 108.9, 86.0, 84.1, 72.4, 29.4; HR-ESIMS  $m/z$  calcd for  $\text{C}_{23}\text{H}_{18}\text{NO}$   $[\text{M}+\text{H}]^+$  324.1383, found 324.1387.

#### 1-Benzyl-2-phenyl-2-(phenylethynyl)indolin-3-one (4r)



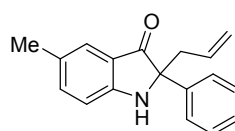
According to general procedure, **4r** was obtained in 94% yield (37.5 mg).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.70 (d,  $J = 7.7$  Hz, 1H), 7.57 (d,  $J = 7.3$  Hz, 2H), 7.45 (t,  $J = 7.7$  Hz, 1H), 7.42-7.22 (m, 13H), 6.84 (t,  $J = 7.4$  Hz, 1H), 6.67 (d,  $J = 8.3$  Hz, 1H), 4.68 (d,  $J = 16.6$  Hz, 1H), 4.56 (d,  $J = 16.6$  Hz, 1H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  195.9, 160.8, 138.1, 137.4, 136.2, 132.0, 129.0, 128.8, 128.8, 128.6, 128.3, 127.3, 127.2, 126.9, 126.4, 122.0, 118.6, 118.2, 109.8, 86.9, 84.3, 72.8, 48.7; HR-ESIMS  $m/z$  calcd for  $\text{C}_{29}\text{H}_{22}\text{NO}$   $[\text{M}+\text{H}]^+$  400.1696, found 400.1701.

#### 2-Allyl-5-chloro-2-phenylindolin-3-one (6b)



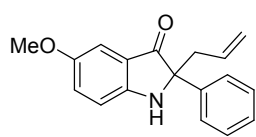
According to general procedure, **6b** was obtained in 92% yield (26.0 mg).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62-7.56 (m, 2H), 7.53 (d,  $J = 2.2$  Hz, 1H), 7.43 (dd,  $J = 8.7, 2.2$  Hz, 1H), 7.38-7.34 (m, 2H), 7.32-7.28 (m, 1H), 6.93 (d,  $J = 8.6$  Hz, 1H), 5.61-5.52 (m, 1H), 5.18 (dd,  $J = 17.0, 1.1$  Hz, 1H), 5.11-5.07 (m, 2H), 3.04 (dd,  $J = 14.0, 5.9$  Hz, 1H), 2.66 (dd,  $J = 14.0, 8.4$  Hz, 1H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  200.1, 158.6, 138.2, 137.4, 132.4, 128.9, 128.0, 125.9, 124.8, 124.6, 120.8, 120.2, 113.6, 71.7, 43.0; HR-ESIMS  $m/z$  calcd for  $\text{C}_{17}\text{H}_{15}\text{ClNO}$   $[\text{M}+\text{H}]^+$  284.0837, found 284.0838.

#### 2-Allyl-5-methyl-2-phenylindolin-3-one (6c)



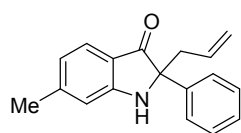
According to general procedure, **6c** was obtained in 85% yield (22.4 mg).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64-7.60 (m, 2H), 7.40-7.30 (m, 4H), 7.29-7.26 (m, 1H), 6.90 (d,  $J = 8.3$  Hz, 1H), 5.63-5.54 (m, 1H), 5.19-5.14 (m, 1H), 5.10-5.05 (m, 1H), 4.94 (s, 1H), 3.07-3.02 (m, 1H), 2.66 (dd,  $J = 14.0, 8.3$  Hz, 1H), 2.29 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  201.4, 158.9, 138.9, 132.8, 129.0, 128.7, 127.7, 126.0, 124.8, 119.9, 119.8, 112.4, 71.1, 43.0, 20.7; HR-ESIMS  $m/z$  calcd for  $\text{C}_{18}\text{H}_{18}\text{NO}$   $[\text{M}+\text{H}]^+$  264.1383, found 264.1381.

### 2-Allyl-5-methoxy-2-phenylindolin-3-one (6d)



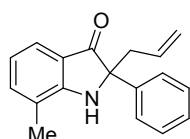
According to general procedure, **6d** was obtained in 90% yield (25.1 mg). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.66-7.61 (m, 2H), 7.37-7.33 (m, 2H), 7.29-7.26 (m, 1H), 7.18 (dd, *J* = 8.8, 2.7 Hz, 1H), 7.01 (d, *J* = 2.7 Hz, 1H), 6.94 (d, *J* = 8.8 Hz, 1H), 5.63-5.54 (m, 1H), 5.17 (dd, *J* = 17.0, 1.2 Hz, 1H), 5.10-5.06 (m, 1H), 4.83 (s, 1H), 3.76 (s, 3H), 3.04 (dd, *J* = 14.0, 6.0 Hz, 1H), 2.67 (dd, *J* = 14.0, 8.3 Hz, 1H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 201.7, 156.2, 153.8, 139.0, 132.8, 128.7, 128.1, 127.1, 126.1, 120.1, 119.8, 114.1, 105.2, 71.7, 55.9, 43.1; HR-ESIMS *m/z* calcd for C<sub>18</sub>H<sub>18</sub>NO<sub>2</sub> [M+H]<sup>+</sup> 280.1332, found 280.1333.

### 2-Allyl-6-methyl-2-phenylindolin-3-one (6e)



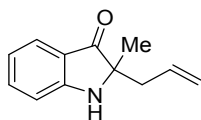
According to general procedure, **6e** was obtained in 87% yield (22.9 mg). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.60 (d, *J* = 7.6 Hz, 2H), 7.45 (d, *J* = 7.9 Hz, 1H), 7.36-7.31 (m, 2H), 7.26 (dd, *J* = 8.4, 6.2 Hz, 1H), 6.76 (s, 1H), 6.65 (d, *J* = 7.9 Hz, 1H), 5.62-5.53 (m, 1H), 5.15 (d, *J* = 17.0 Hz, 1H), 5.06 (d, *J* = 10.1 Hz, 1H), 5.01 (s, 1H), 3.03 (dd, *J* = 14.0, 5.9 Hz, 1H), 2.64 (dd, *J* = 14.0, 8.4 Hz, 1H), 2.38 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 200.5, 160.9, 149.2, 138.9, 132.8, 128.7, 127.7, 126.0, 125.3, 121.2, 119.8, 117.4, 112.4, 71.0, 42.9, 22.6; HR-ESIMS *m/z* calcd for C<sub>18</sub>H<sub>18</sub>NO [M+H]<sup>+</sup> 264.1383, found 264.1381.

### 2-Allyl-7-methyl-2-phenylindolin-3-one (6f)



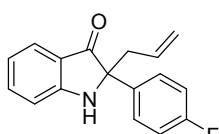
According to general procedure, **6f** was obtained in 90% yield (23.7 mg). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.66-7.62 (m, 2H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.38-7.34 (m, 2H), 7.33 (d, *J* = 7.1 Hz, 1H), 7.30-7.27 (m, 1H), 6.80 (t, *J* = 7.4 Hz, 1H), 5.64-5.56 (m, 1H), 5.17 (dd, *J* = 17.0, 1.2 Hz, 1H), 5.11-5.07 (m, 1H), 4.85 (s, 1H), 3.10-3.06 (m, 1H), 2.65 (dd, *J* = 14.0, 8.4 Hz, 1H), 2.32 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 201.6, 159.6, 138.8, 137.4, 132.9, 128.7, 127.8, 126.0, 122.9, 121.5, 119.8, 119.6, 119.2, 70.8, 43.0, 15.9; HR-ESIMS *m/z* calcd for C<sub>18</sub>H<sub>18</sub>NO [M+H]<sup>+</sup> 264.1383, found 264.1381.

### 2-Allyl-2-methylindolin-3-one (6g)



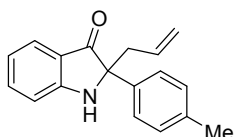
According to general procedure, **6g** was obtained in 91% yield (17.0 mg). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.61 (d, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.3 Hz, 1H), 6.92-6.76 (m, 2H), 5.77-5.70 (m, 1H), 5.15-5.08 (m, 2H), 4.66 (s, 1H), 2.45-2.39 (m, 1H), 2.39-2.32 (m, 1H), 1.32 (s, 3H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 204.6, 160.0, 137.4, 132.5, 125.0, 120.4, 119.5, 119.0, 112.6, 66.4, 42.1, 22.5; HR-ESIMS *m/z* calcd for C<sub>12</sub>H<sub>14</sub>NO [M+H]<sup>+</sup> 188.1070, found 188.1071.

### 2-Allyl-2-(4-fluorophenyl)indolin-3-one (6h)



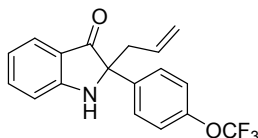
According to general procedure, **6h** was obtained in 92% yield (24.5 mg). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.65-7.56 (m, 3H), 7.50 (ddd, *J* = 8.3, 7.1, 1.3 Hz, 1H), 7.06-7.01 (m, 2H), 6.98 (d, *J* = 8.2 Hz, 1H), 6.88-6.84 (m, 1H), 5.60-5.52 (m, 1H), 5.17 (dd, *J* = 17.0, 1.1 Hz, 1H), 5.12-5.08 (m, 1H), 5.06 (s, 1H), 3.06-2.96 (m, 1H), 2.61 (dd, *J* = 14.1, 8.5 Hz, 1H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 201.2, 163.3, 161.7, 160.3, 137.6, 134.4, 134.4, 132.4, 127.9, 127.8, 125.6, 120.2, 119.7, 119.6, 115.6, 115.5, 112.6, 70.2, 43.1; HR-ESIMS *m/z* calcd for C<sub>17</sub>H<sub>15</sub>FNO [M+H]<sup>+</sup> 268.1132, found 268.1134.

### 2-Allyl-2-(*p*-tolyl)indolin-3-one (6i)



According to general procedure, **6i** was obtained in 88% yield (23.1 mg). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.57 (d, *J* = 7.7 Hz, 1H), 7.51-7.46 (m, 3H), 7.16 (d, *J* = 8.1 Hz, 2H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.83 (t, *J* = 7.4 Hz, 1H), 5.64-5.57 (m, 1H), 5.17 (dd, *J* = 17.0, 1.2 Hz, 1H), 5.10-5.05 (m, 2H), 3.04 (dd, *J* = 14.0, 5.9 Hz, 1H), 2.63 (dd, *J* = 14.0, 8.4 Hz, 1H), 2.33 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 201.4, 160.4, 137.5, 137.4, 135.6, 132.8, 129.5, 125.9, 125.6, 119.8, 119.7, 119.3, 112.3, 70.7, 42.7, 21.1; HR-ESIMS *m/z* calcd for C<sub>18</sub>H<sub>18</sub>NO [M+H]<sup>+</sup> 264.1383, found 264.1383.

### 2-Allyl-2-(4-(trifluoromethoxy)phenyl)indolin-3-one (6j)

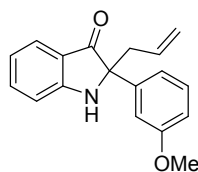


According to general procedure, **6j** was obtained in 93% yield (30.9 mg). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.70-7.67 (m, 2H), 7.59 (d, *J* = 7.7 Hz, 1H), 7.51 (ddd, *J* = 8.3, 7.1, 1.3 Hz, 1H), 7.20 (d,



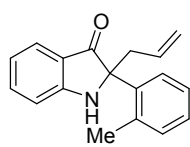
$J = 8.1$  Hz, 2H), 6.99 (d,  $J = 8.3$  Hz, 1H), 6.89-6.85 (m, 1H), 5.60-5.51 (m, 1H), 5.18 (dd,  $J = 17.0, 1.1$  Hz, 1H), 5.13-5.10 (m, 1H), 5.05 (s, 1H), 3.05-3.01 (m, 1H), 2.62 (dd,  $J = 14.1, 8.5$  Hz, 1H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  200.8, 160.3, 148.9, 137.8, 137.4, 132.2, 127.7, 125.6, 121.4, 121.1, 120.4, 119.8, 119.6, 112.7, 70.2, 43.2; HR-ESIMS  $m/z$  calcd for  $\text{C}_{18}\text{H}_{15}\text{F}_3\text{NO}_2$   $[\text{M}+\text{H}]^+$  334.1049, found 334.1052.

### 2-Allyl-2-(3-methoxyphenyl)indolin-3-one (6k)



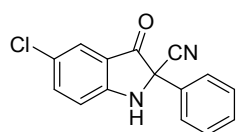
According to general procedure, **6k** was obtained in 95% yield (26.5 mg).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57-7.54 (m, 1H), 7.46 (ddd,  $J = 8.3, 7.1, 1.3$  Hz, 1H), 7.26-7.24 (m, 1H), 7.21-7.16 (m, 2H), 6.94 (d,  $J = 8.2$  Hz, 1H), 6.83-6.79 (m, 2H), 5.62-5.54 (m, 1H), 5.15 (dd,  $J = 17.0, 1.2$  Hz, 1H), 5.09-5.03 (m, 2H), 3.79 (s, 3H), 3.05-3.01 (m, 1H), 2.60 (dd,  $J = 14.0, 8.5$  Hz, 1H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  201.0, 160.3, 159.9, 140.3, 137.5, 132.8, 129.8, 125.6, 119.9, 119.7, 119.4, 118.4, 112.8, 112.4, 112.2, 70.7, 55.4, 43.0; HR-ESIMS  $m/z$  calcd for  $\text{C}_{18}\text{H}_{18}\text{NO}_2$   $[\text{M}+\text{H}]^+$  280.1332, found 280.1331.

### 2-Allyl-2-(*o*-tolyl)indolin-3-one (6l)



According to general procedure, **6l** was obtained in 94% yield (24.7 mg).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66 (d,  $J = 7.7$  Hz, 1H), 7.59 (dd,  $J = 7.3, 1.9$  Hz, 1H), 7.49 (ddd,  $J = 8.3, 7.2, 1.3$  Hz, 1H), 7.25-7.19 (m, 2H), 7.16-7.12 (m, 1H), 6.90-6.86 (m, 2H), 5.81-5.69 (m, 1H), 5.17 (dd,  $J = 17.0, 1.5$  Hz, 1H), 5.11-5.04 (m, 1H), 4.99 (s, 1H), 3.15 (dd,  $J = 14.0, 6.3$  Hz, 1H), 2.78 (dd,  $J = 14.0, 7.7$  Hz, 1H), 2.17 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  202.5, 159.8, 137.8, 137.4, 136.9, 132.5, 132.4, 128.1, 128.0, 126.0, 124.8, 121.3, 120.0, 119.4, 112.5, 71.5, 41.9, 21.4; HR-ESIMS  $m/z$  calcd for  $\text{C}_{18}\text{H}_{18}\text{NO}$   $[\text{M}+\text{H}]^+$  264.1383, found 264.1385.

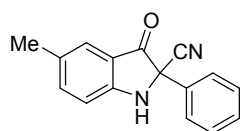
### 5-Chloro-3-oxo-2-phenylindoline-2-carbonitrile (6m)



According to general procedure, **6m** was obtained in 92% yield (24.6 mg).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.61 (d,  $J = 2.1$  Hz, 1H), 7.56 (dd,  $J = 8.7, 2.2$  Hz, 1H), 7.54-7.50 (m, 2H), 7.45-7.41 (m, 3H), 7.02 (d,  $J = 8.7$  Hz, 1H), 5.47 (s, 1H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  189.8, 158.6,

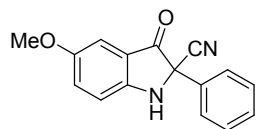
139.0, 132.8, 130.1, 129.6, 127.0, 125.9, 125.4, 118.1, 116.4, 114.1, 66.2; HR-ESIMS  $m/z$  calcd for  $C_{15}H_{10}ClN_2O$   $[M+H]^+$  269.0476, found 269.0477.

### 5-Methyl-3-oxo-2-phenylindoline-2-carbonitrile (6n)



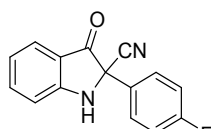
According to general procedure, **6n** was obtained in 85% yield (21.1 mg).  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$  7.58-7.53 (m, 2H), 7.49-7.40 (m, 6H), 6.98 (d,  $J = 8.5$  Hz, 1H), 2.35 (s, 3H).  $^{13}C$  NMR (151 MHz,  $CDCl_3$ )  $\delta$  190.9, 158.6, 140.2, 133.4, 131.4, 129.6, 129.3, 125.8, 125.3, 117.1, 116.8, 112.77, 65.9, 20.5; HR-ESIMS  $m/z$  calcd for  $C_{16}H_{13}N_2O$   $[M+H]^+$  249.1022, found 249.1024.

### 5-Methoxy-3-oxo-2-phenylindoline-2-carbonitrile (6o)



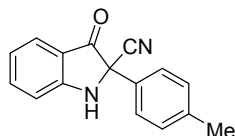
According to general procedure, **6o** was obtained in 90% yield (23.7 mg).  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$  7.56-7.53 (m, 2H), 7.45-7.40 (m, 3H), 7.29 (dd,  $J = 8.9, 2.7$  Hz, 1H), 7.05 (d,  $J = 2.6$  Hz, 1H), 7.02 (d,  $J = 8.9$  Hz, 1H), 5.18 (s, 1H), 3.80 (s, 3H).  $^{13}C$  NMR (151 MHz,  $CDCl_3$ )  $\delta$  191.2, 156.0, 155.2, 133.5, 129.8, 129.6, 129.5, 125.5, 117.6, 117.0, 114.5, 106.1, 66.6, 56.0; HR-ESIMS  $m/z$  calcd for  $C_{16}H_{13}N_2O_2$   $[M+H]^+$  265.0972, found 265.0971.

### 2-(4-Fluorophenyl)-3-oxoindoline-2-carbonitrile (6p)



According to general procedure, **6p** was obtained in 92% yield (23.1 mg).  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$  7.65 (dd,  $J = 7.8, 0.5$  Hz, 1H), 7.62 (ddd,  $J = 8.4, 7.2, 1.3$  Hz, 1H), 7.56-7.52 (m, 2H), 7.13-7.08 (m, 2H), 7.06-7.00 (m, 2H), 5.44 (s, 1H).  $^{13}C$  NMR (151 MHz,  $CDCl_3$ )  $\delta$  190.7, 164.4, 162.8, 160.1, 139.2, 129.1, 129.1, 127.6, 127.6, 126.8, 121.8, 116.9, 116.8, 116.3, 116.5, 113.0, 64.9; HR-ESIMS  $m/z$  calcd for  $C_{15}H_{10}FN_2O$   $[M+H]^+$  253.0772, found 253.0771.

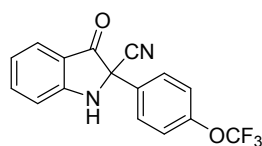
### 3-Oxo-2-(p-tolyl)indoline-2-carbonitrile (6q)



According to general procedure, **6q** was obtained in 88% yield (21.8 mg).  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$  7.66 (d,  $J = 7.8$  Hz, 1H),

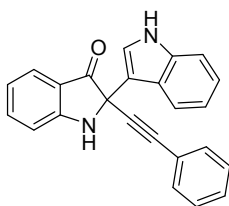
7.61 (ddd,  $J = 8.4, 7.3, 1.3$  Hz, 1H), 7.42 (d,  $J = 8.3$  Hz, 2H), 7.22 (d,  $J = 8.0$  Hz, 2H), 7.06-6.98 (m, 2H), 5.36 (s, 1H), 2.36 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  191.2, 160.3, 140.0, 139.0, 130.3, 130.2, 126.8, 125.4, 121.6, 117.1, 116.9, 112.8, 65.5, 21.3; HR-ESIMS  $m/z$  calcd for  $\text{C}_{16}\text{H}_{13}\text{N}_2\text{O}$   $[\text{M}+\text{H}]^+$  249.1022, found 249.1025.

### 3-Oxo-2-(4-(trifluoromethoxy)phenyl)indoline-2-carbonitrile (**6r**)



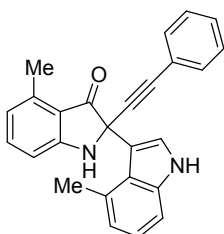
According to general procedure, **6r** was obtained in 93% yield (29.5 mg).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.70-7.60 (m, 4H), 7.28 (d,  $J = 8.8$  Hz, 2H), 7.10-7.02 (m, 2H), 5.45 (s, 1H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  190.3, 160.1, 150.3, 139.3, 131.9, 127.4, 126.9, 122.0, 121.8, 121.3, 116.8, 116.6, 113.0, 64.8; HR-ESIMS  $m/z$  calcd for  $\text{C}_{16}\text{H}_{10}\text{F}_3\text{N}_2\text{O}_2$   $[\text{M}+\text{H}]^+$  319.0689, found 319.0688.

### 2-(1*H*-Indol-3-yl)-2-(phenylethynyl)indolin-3-one (**8a**)



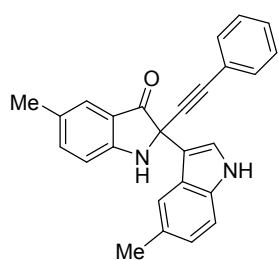
According to general procedure, **8a** was obtained in 66% yield (22.9 mg).  $^1\text{H}$  NMR (600 MHz, acetone- $d_6$ )  $\delta$  10.34 (s, 1H), 7.65-7.57 (m, 3H), 7.51-7.49 (m, 3H), 7.45-7.34 (m, 4H), 7.27 (s, 1H), 7.14-7.06 (m, 2H), 6.97-6.89 (m, 2H);  $^{13}\text{C}$  NMR (151 MHz, acetone- $d_6$ )  $\delta$  197.4, 161.8, 138.8, 138.5, 132.6, 129.6, 129.5, 126.0, 125.8, 125.4, 123.5, 122.7, 120.9, 120.1, 119.7, 119.1, 114.0, 113.6, 112.6, 88.5, 83.2, 64.0; HR-ESIMS  $m/z$  calcd for  $\text{C}_{24}\text{H}_{17}\text{N}_2\text{O}$   $[\text{M}+\text{H}]^+$  349.1335, found 349.1339.

### 4-Methyl-2-(4-methyl-1*H*-indol-3-yl)-2-(phenylethynyl)indolin-3-one (**8b**)



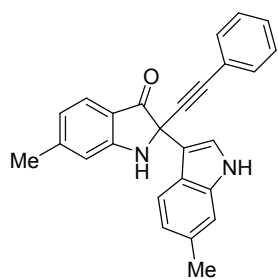
According to general procedure, **8b** was obtained in 60% yield (22.5 mg).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.21 (s, 1H), 7.52 (d,  $J = 2.6$  Hz, 1H), 7.45-7.42 (m, 2H), 7.37 (t,  $J = 7.7$  Hz, 1H), 7.30-7.26 (t,  $J = 8.3$  Hz, 3H), 7.22 (d,  $J = 8.1$  Hz, 1H), 7.09 (t,  $J = 7.7$  Hz, 1H), 6.91 (d,  $J = 7.1$  Hz, 1H), 6.74 (d,  $J = 8.1$  Hz, 1H), 6.71 (d,  $J = 7.3$  Hz, 1H), 5.20 (s, 1H), 2.67 (s, 3H), 2.65 (s, 3H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  197.6, 160.1, 141.2, 138.1, 137.1, 132.1, 130.4, 128.6, 128.3, 125.7, 124.6, 122.8, 122.6, 122.6, 122.0, 118.5, 113.5, 110.9, 109.5, 89.2, 82.9, 63.6, 22.1, 18.6; HR-ESIMS  $m/z$  calcd for  $\text{C}_{26}\text{H}_{21}\text{N}_2\text{O}$   $[\text{M}+\text{H}]^+$  377.1648, found 377.1645.

### 5-Methyl-2-(5-methyl-1*H*-indol-3-yl)-2-(phenylethynyl)indolin-3-one (**8c**)



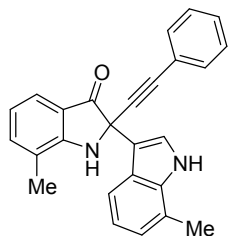
According to general procedure, **8c** was obtained in 68% yield (25.5 mg). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.08 (s, 1H), 7.55 (s, 1H), 7.49-7.45 (m, 3H), 7.41 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.31-7.27 (m, 3H), 7.24 (d, *J* = 8.3 Hz, 1H), 7.22-7.20 (m, 1H), 6.99 (dd, *J* = 8.3, 1.6 Hz, 1H), 6.91 (d, *J* = 8.3 Hz, 1H), 5.12 (s, 1H), 2.36 (s, 3H), 2.33 (s, 3H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 197.3, 158.7, 139.5, 135.5, 132.2, 129.9, 129.6, 128.7, 128.4, 125.4, 124.9, 124.4, 124.4, 122.5, 119.6, 119.5, 113.3, 113.2, 111.3, 87.0, 83.3, 63.7, 21.8, 20.8; HR-ESIMS *m/z* calcd for C<sub>26</sub>H<sub>21</sub>N<sub>2</sub>O [M+H]<sup>+</sup> 377.1648, found 377.1648.

### 6-Methyl-2-(6-methyl-1*H*-indol-3-yl)-2-(phenylethynyl)indolin-3-one (**8d**)



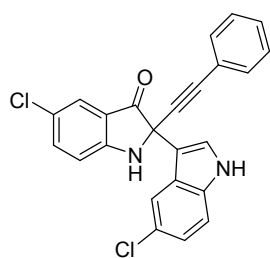
According to general procedure, **8d** was obtained in 62% yield (23.3 mg). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.11 (s, 1H), 7.63 (d, *J* = 7.9 Hz, 1H), 7.48-7.45 (m, 2H), 7.41 (d, *J* = 2.6 Hz, 1H), 7.33-7.27 (m, 3H), 7.25 (s, 1H), 7.13 (s, 1H), 6.84 (dd, *J* = 8.2, 1.4 Hz, 1H), 6.78 (d, *J* = 7.9 Hz, 1H), 6.76 (s, 1H), 5.18 (s, 1H), 2.43 (s, 3H), 2.38 (s, 3H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 196.6, 160.7, 149.9, 137.6, 132.5, 132.2, 128.7, 128.4, 125.8, 124.0, 122.5, 122.4, 122.1, 121.9, 119.4, 117.1, 113.6, 113.1, 111.6, 86.9, 83.4, 63.6, 22.8, 21.8; HR-ESIMS *m/z* calcd for C<sub>26</sub>H<sub>21</sub>N<sub>2</sub>O [M+H]<sup>+</sup> 377.1648, found 377.1647.

### 7-Methyl-2-(7-methyl-1*H*-indol-3-yl)-2-(phenylethynyl)indolin-3-one (**8e**)



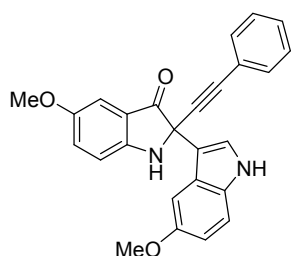
According to general procedure, **8e** was obtained in 64% yield (24.1 mg). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.26 (s, 1H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.51 (d, *J* = 2.7 Hz, 1H), 7.49-7.45 (m, 2H), 7.42-7.40 (m, 1H), 7.33-7.26 (m, 3H), 7.18 (d, *J* = 7.7 Hz, 1H), 6.96-6.90 (m, 3H), 5.09 (s, 1H), 2.44 (s, 3H), 2.27 (s, 3H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 197.7, 159.5, 138.2, 136.8, 132.2, 128.7, 128.4, 124.4, 124.0, 123.4, 123.2, 122.4, 122.2, 120.9, 120.6, 120.3, 118.8, 117.4, 114.1, 86.8, 83.5, 63.5, 16.7, 15.9; HR-ESIMS *m/z* calcd for C<sub>26</sub>H<sub>21</sub>N<sub>2</sub>O [M+H]<sup>+</sup> 377.1648, found 377.1649.

### 5-Chloro-2-(5-chloro-1*H*-indol-3-yl)-2-(phenylethynyl)indolin-3-one (**8f**)



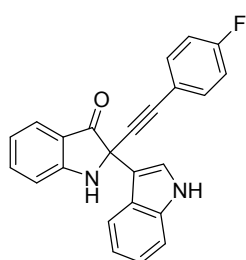
According to general procedure, **8f** was obtained in 60% yield (24.9 mg). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.37 (s, 1H), 7.70 (d, *J* = 2.2 Hz, 1H), 7.54 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.47-7.41 (m, 4H), 7.34-7.27 (m, 3H), 7.24 (s, 1H), 7.09 (dd, *J* = 8.7, 2.0 Hz, 1H), 6.96 (d, *J* = 8.6 Hz, 1H), 5.26 (s, 1H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 195.8, 158.4, 138.3, 135.5, 132.2, 129.1, 128.5, 126.1, 125.8, 125.7, 125.5, 125.5, 123.2, 121.9, 120.0, 119.3, 114.4, 112.9, 112.8, 85.6, 84.0, 63.9; HR-ESIMS *m/z* calcd for C<sub>24</sub>H<sub>15</sub>Cl<sub>2</sub>N<sub>2</sub>O [M+H]<sup>+</sup> 417.0556, found 417.0556.

### 5-Methoxy-2-(5-methoxy-1*H*-indol-3-yl)-2-(phenylethynyl)indolin-3-one (**8g**)



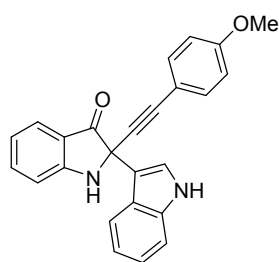
According to general procedure, **8g** was obtained in 67% yield (27.3 mg). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.15 (s, 1H), 7.51-7.44 (m, 3H), 7.33-7.27 (m, 3H), 7.23 (d, *J* = 8.8 Hz, 2H), 7.19 (d, *J* = 2.7 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 1H), 6.84 (d, *J* = 2.4 Hz, 1H), 6.80 (dd, *J* = 8.8, 2.5 Hz, 1H), 5.04 (s, 1H), 3.82 (s, 3H), 3.62 (s, 3H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 197.6, 156.1, 154.4, 154.3, 132.3, 132.2, 128.8, 128.7, 128.4, 125.1, 124.9, 122.4, 119.9, 114.9, 113.4, 112.9, 112.4, 105.6, 101.6, 86.6, 83.6, 64.3, 56.0, 55.6; HR-ESIMS *m/z* calcd for C<sub>26</sub>H<sub>21</sub>N<sub>2</sub>O<sub>3</sub> [M+H]<sup>+</sup> 409.1547, found 409.1545.

### 2-((4-Fluorophenyl)ethynyl)-2-(1*H*-indol-3-yl)indolin-3-one (**8h**)



According to general procedure, **8h** was obtained in 64% yield (23.4 mg). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.29 (s, 1H), 7.75 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.58 (ddd, *J* = 8.4, 7.1, 1.4 Hz, 1H), 7.47-7.43 (m, 3H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.15 (ddd, *J* = 8.2, 7.0, 1.1 Hz, 1H), 7.03-6.95 (m, 5H), 5.27 (s, 1H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 197.2, 163.7, 162.0, 160.2, 138.3, 137.2, 134.2, 134.1, 126.1, 124.6, 124.5, 122.8, 120.4, 120.3, 119.7, 119.2, 118.4, 118.4, 115.8, 115.6, 113.4, 113.1, 111.8, 86.3, 82.5, 63.3; HR-ESIMS *m/z* calcd for C<sub>24</sub>H<sub>16</sub>FN<sub>2</sub>O [M+H]<sup>+</sup> 367.1241, found 367.1239.

## 2-(1*H*-Indol-3-yl)-2-((4-methoxyphenyl)ethynyl)indolin-3-one (**8i**)

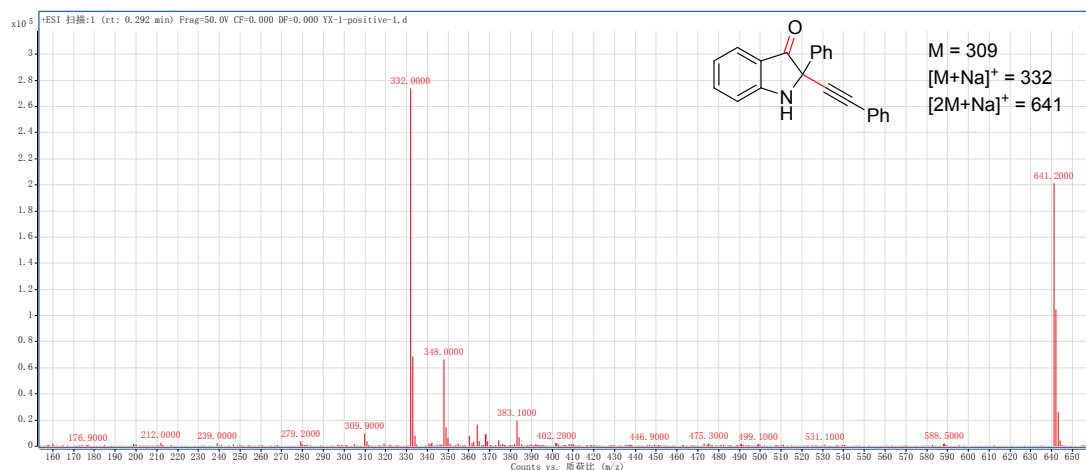


According to general procedure, **8i** was obtained in 62% yield (23.4 mg). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.20 (s, 1H), 7.78-7.73 (m, 1H), 7.60-7.56 (m, 1H), 7.51 (s, 1H), 7.43-7.39 (m, 3H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 7.7 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 5.25 (s, 1H), 3.81 (s, 3H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 197.3, 160.2, 159.9, 138.1, 137.1, 133.6, 126.0, 124.6, 124.5, 122.6, 120.2, 120.1, 119.7, 119.2, 114.3, 113.9, 113.8, 113.0, 111.7, 85.0, 83.4, 63.3, 55.4; HR-ESIMS *m/z* calcd for C<sub>25</sub>H<sub>19</sub>N<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup> 379.1441, found 379.1444.

## Mechanism studies

### ESI-MS analysis

ESI-MS analysis of the product by adding H<sub>2</sub><sup>18</sup>O, and no <sup>18</sup>O labeling product was detected.



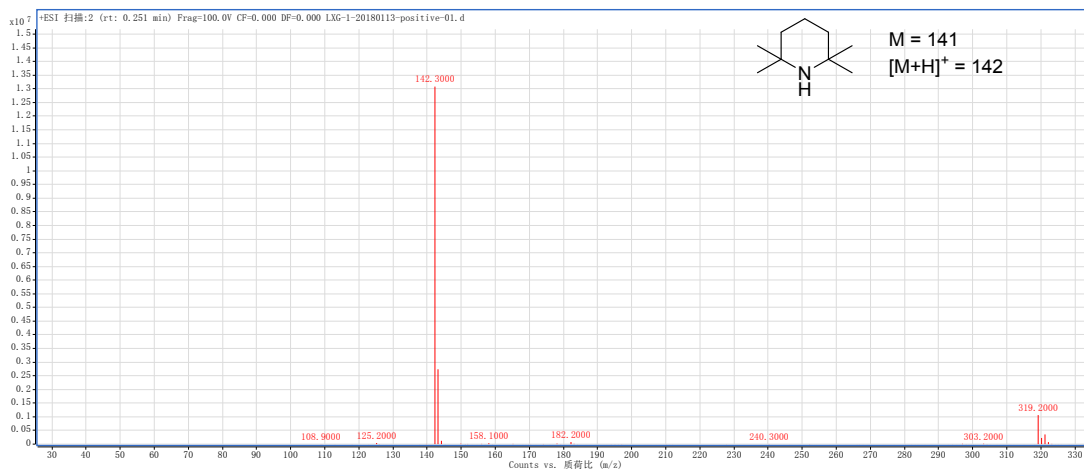
### ESI-MS analysis of the reaction solution.

The reaction of **1a** with **2a** was performed under standard conditions and then ESI-MS analysis was performed with 2,2,6,6-tetramethylpiperidine (**9**) being detected.

### 2,2,6,6-Tetramethylpiperidine (**9**).

The solution of the reaction was filtered and the residue was dissolved in 1.0 mL water. After that, 1 N NaOH was added, and then the mixture was extracted with CHCl<sub>3</sub> (1

mL × 3). The organic solution was evaporated *in vacuum* to give 2,2,6,6-tetramethylpiperidine **9**.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  1.69-1.64 (m, 2H), 1.40-1.33 (m, 4H), 1.20 (s, 12H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  49.6, 38.2, 31.1, 18.0.



## References

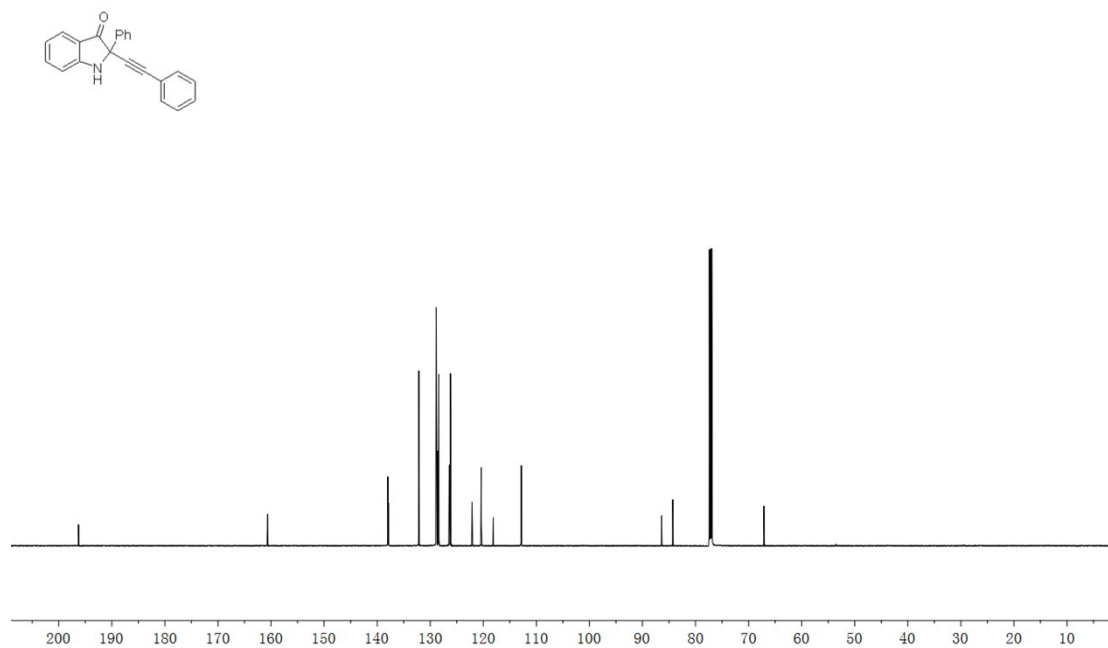
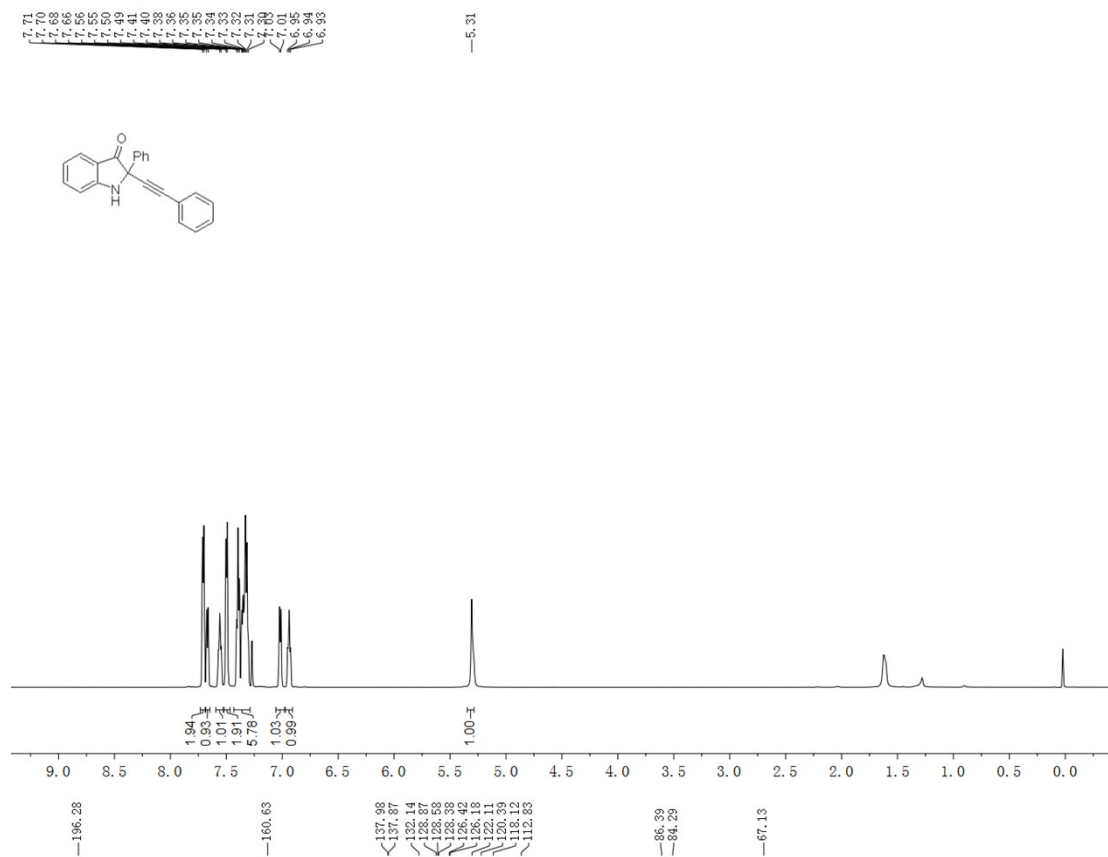
- [1] S. D. Yang, C. L. Sun, Z. Fang, B. J. Li, Y. Z. Li, Z. J. Shi, *Angew. Chem. Int. Ed.* **2008**, *47*, 1473.
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- [5] a) N. Anderton, P. A. Cockrum, S. M. Colegate, J. A. Edgar, K. Flower, D. Gardner, R. I. Willing, *Phytochemistry*. **1999**, *51*, 153; b) J. D. Trzuppek, D. Lee, B. M. Crowley, V. M.

Marathias, S. J. Danishefsky, *J. Am. Chem. Soc.* **2010**, *132*, 8506; c) H. Ding, D. Y. K. Chen, *Angew. Chem. Int. Ed.* **2011**, *50*, 676.

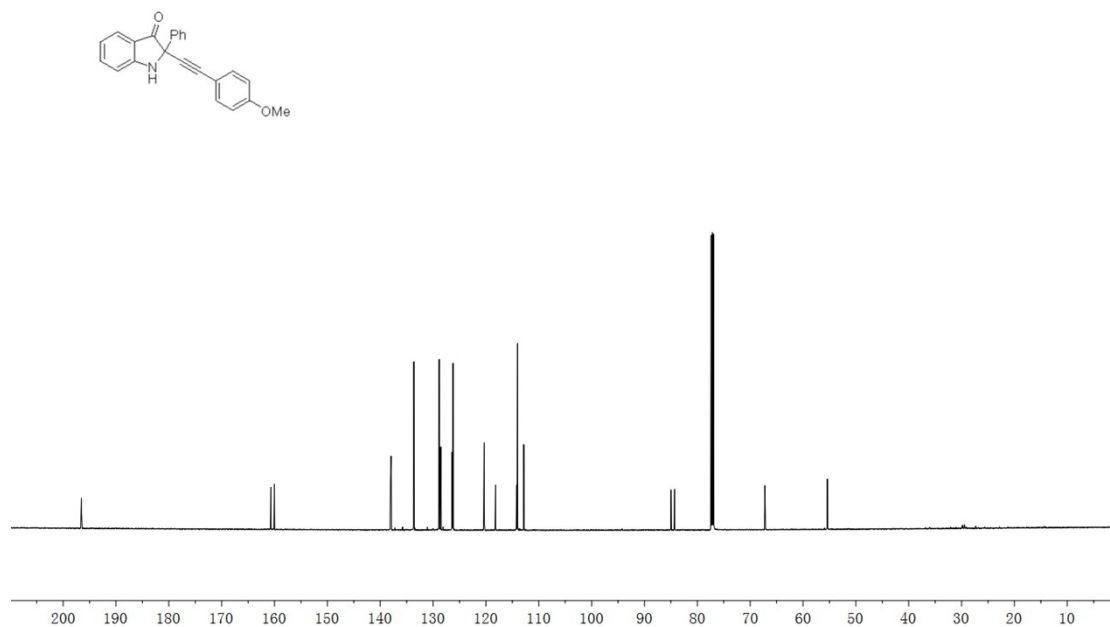
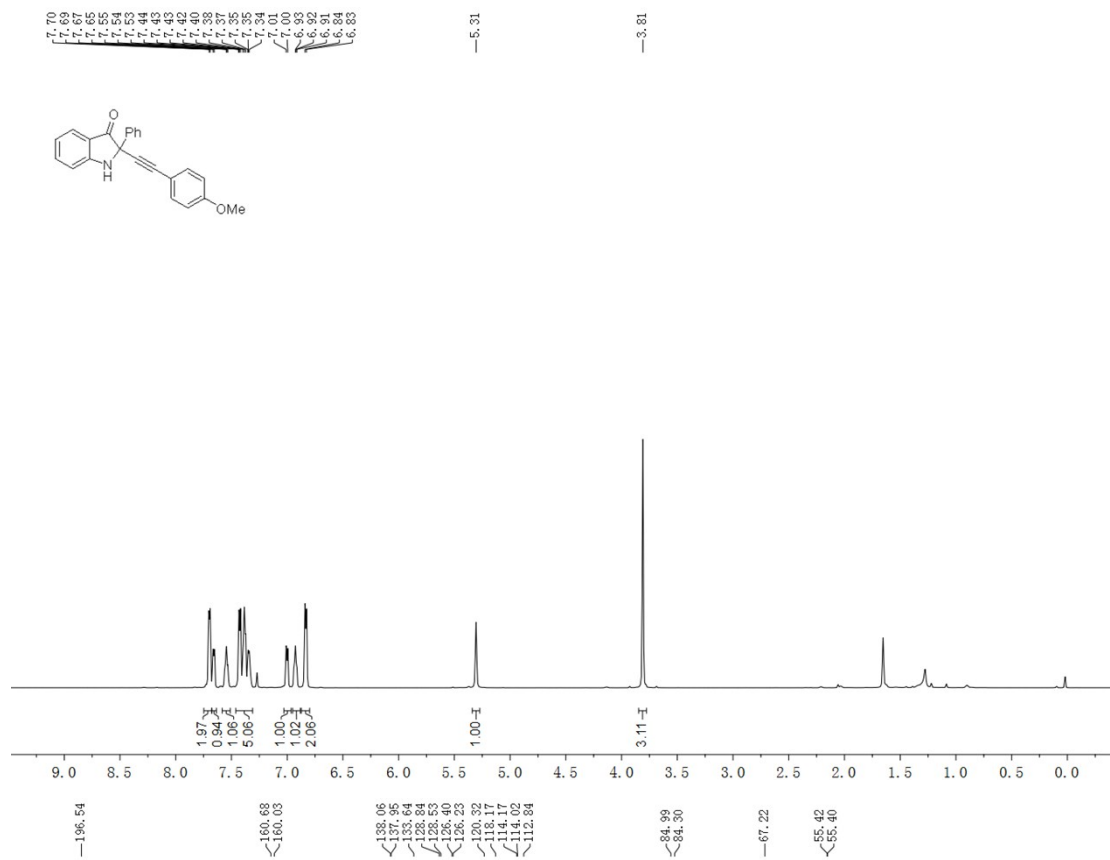


# $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectral data

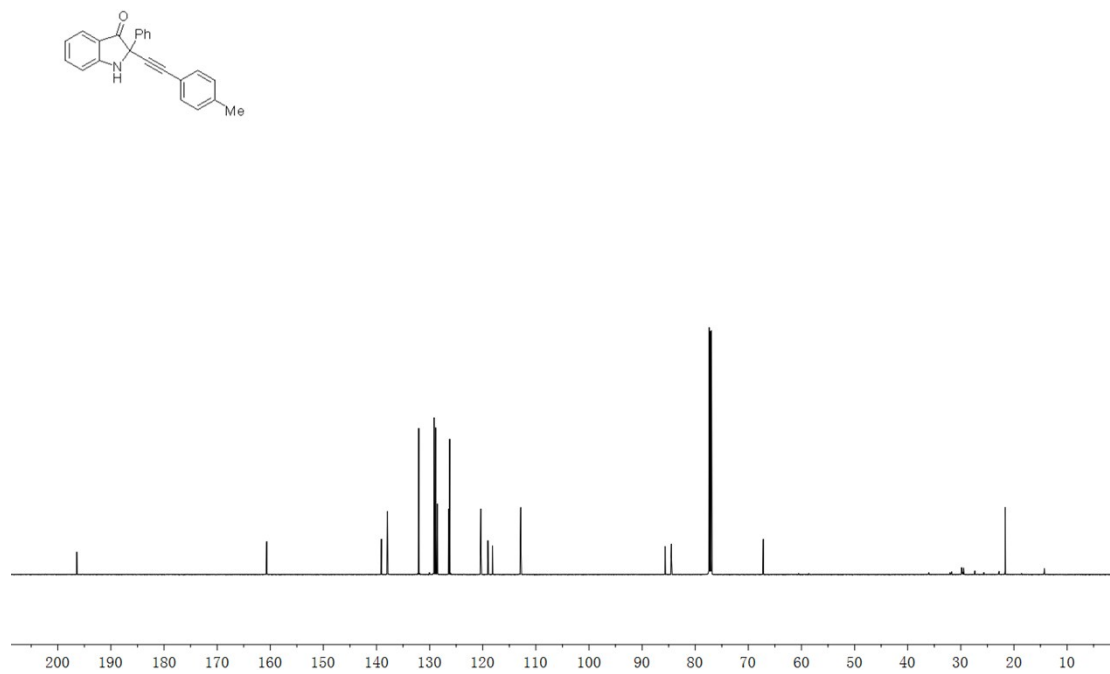
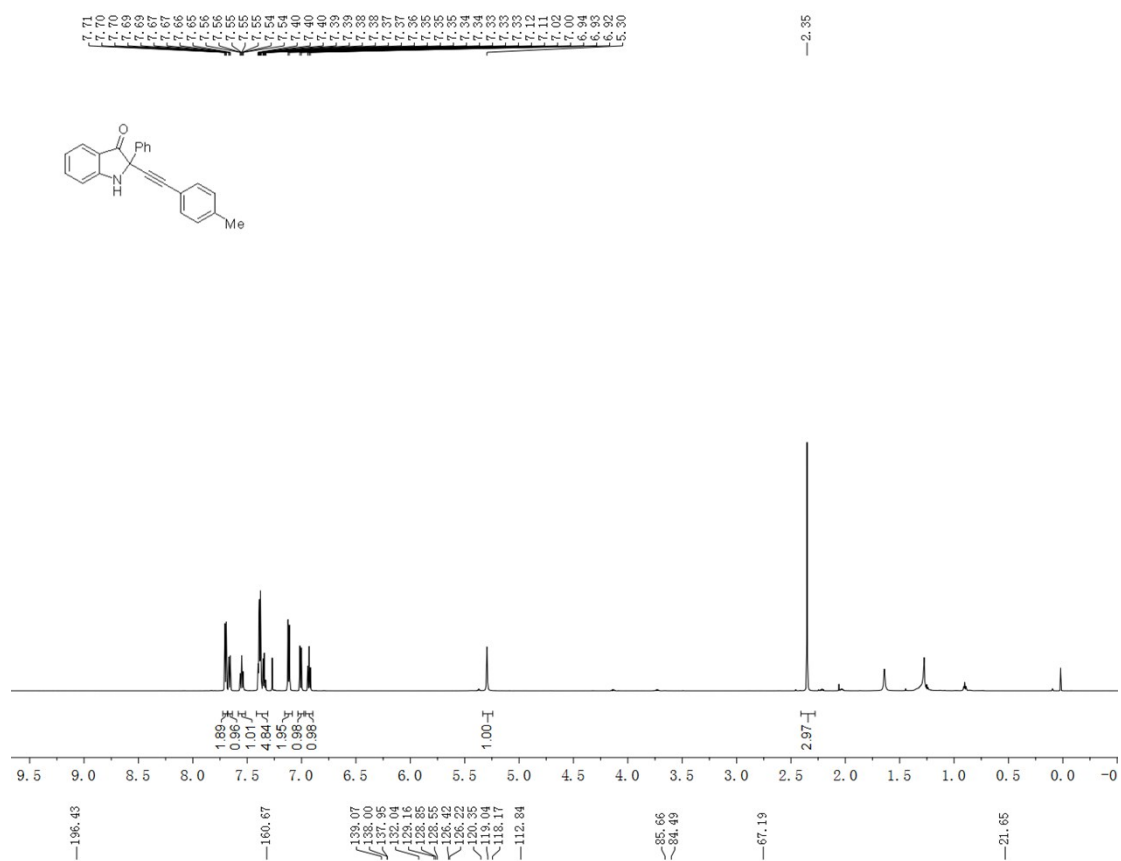
## $^1\text{H}$ and $^{13}\text{C}$ NMR data of compound 3a



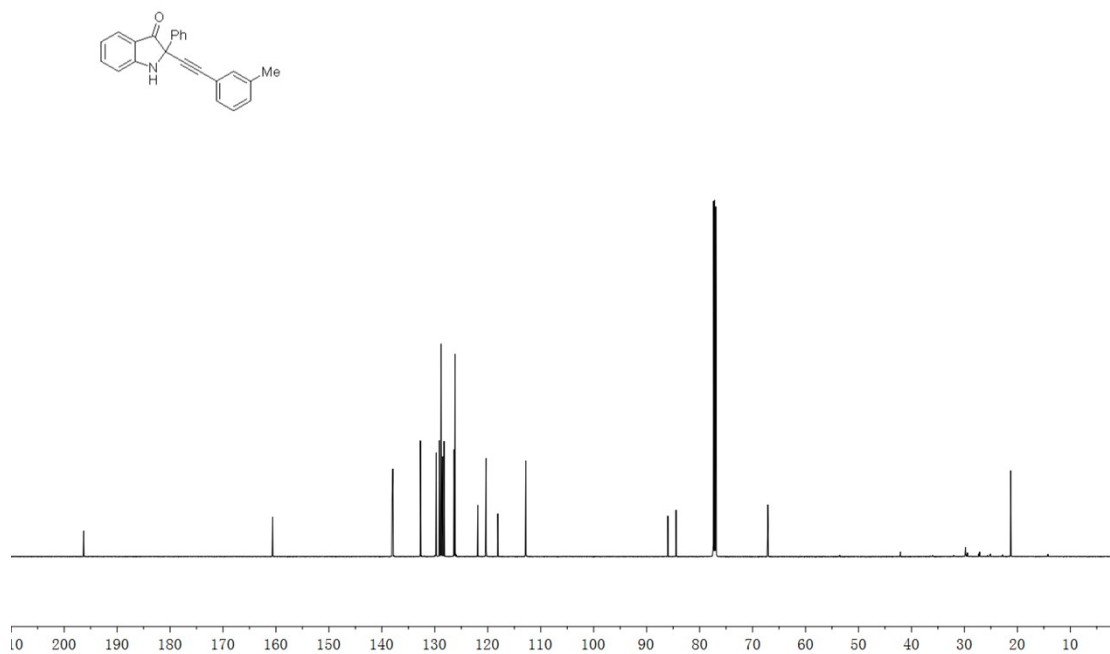
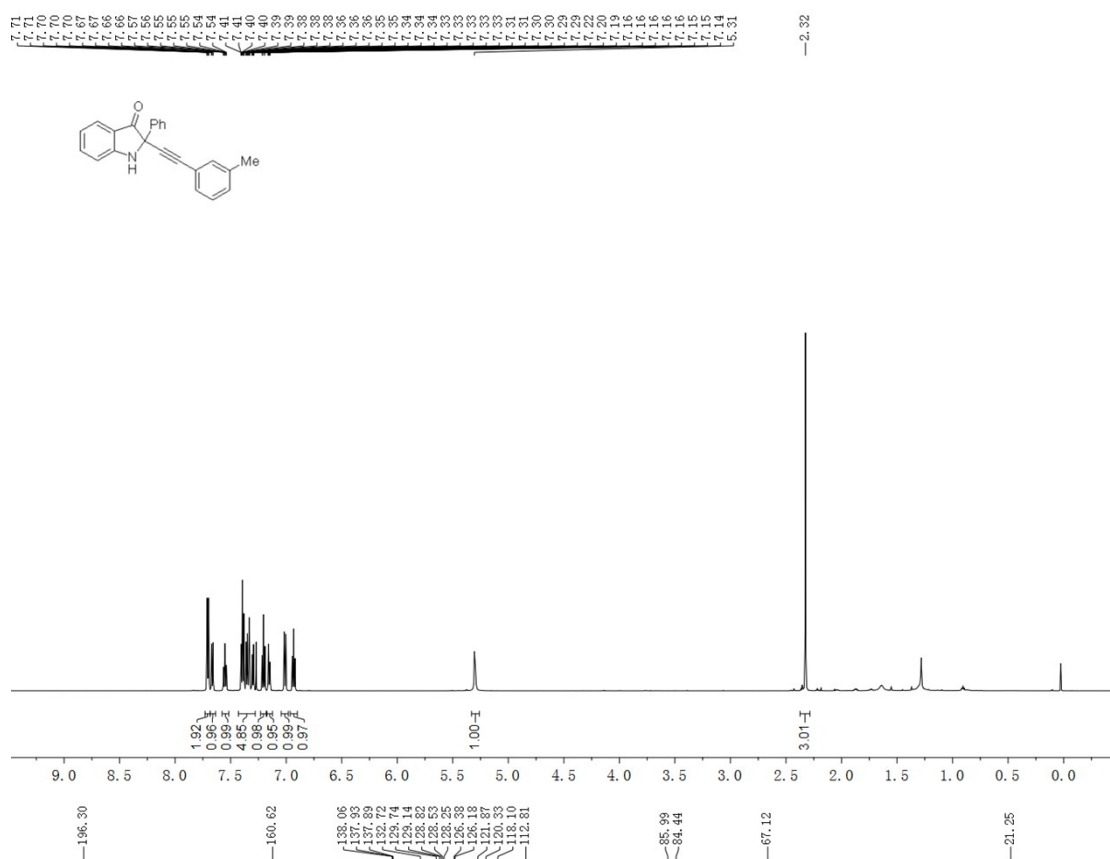
# <sup>1</sup>H and <sup>13</sup>C NMR data of compound 3b



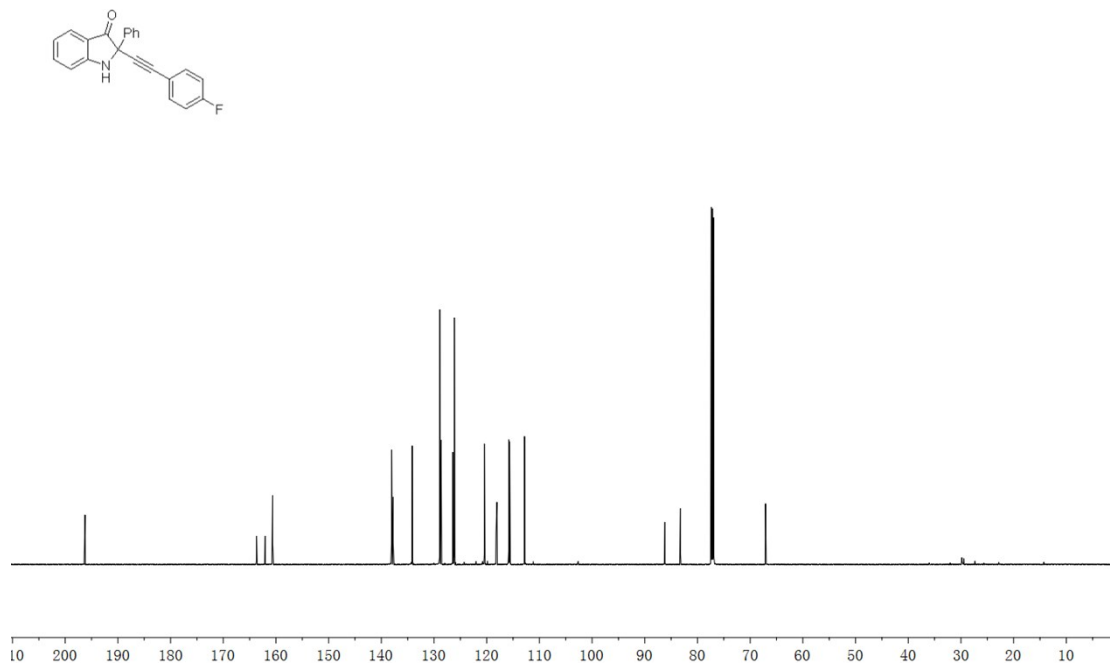
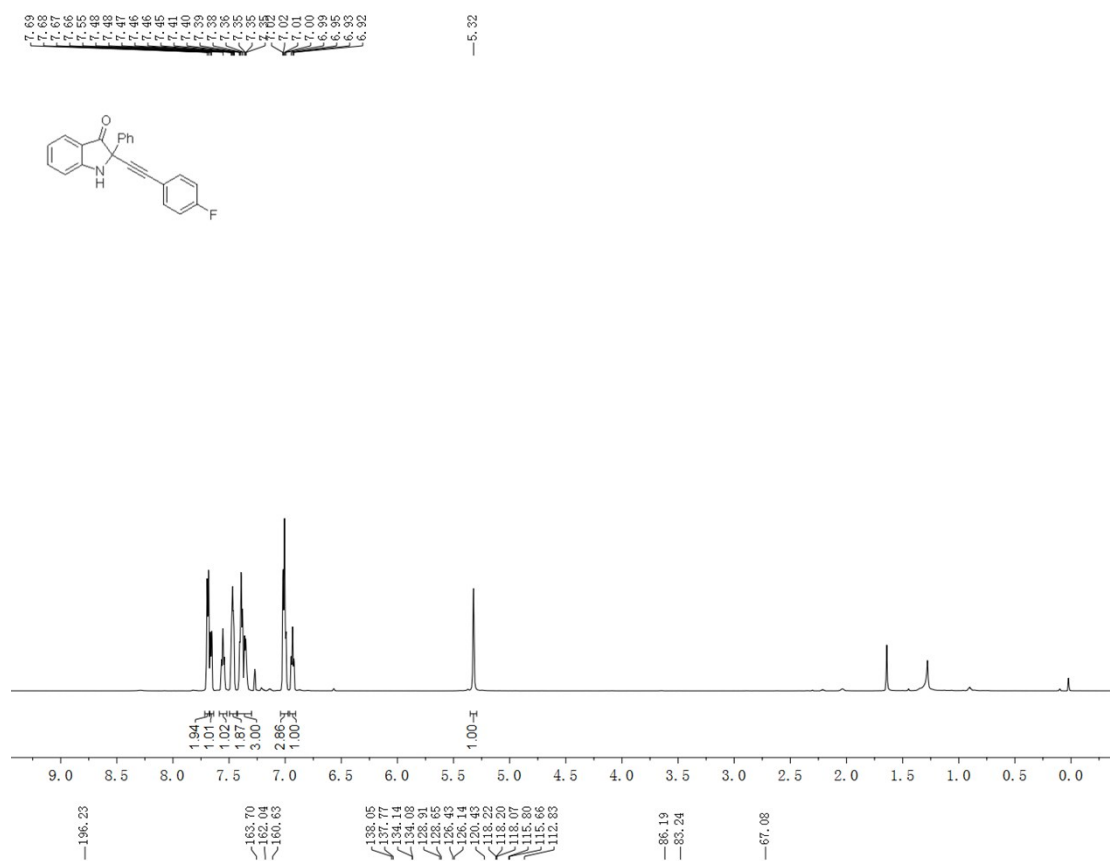
# <sup>1</sup>H and <sup>13</sup>C NMR data of compound 3c



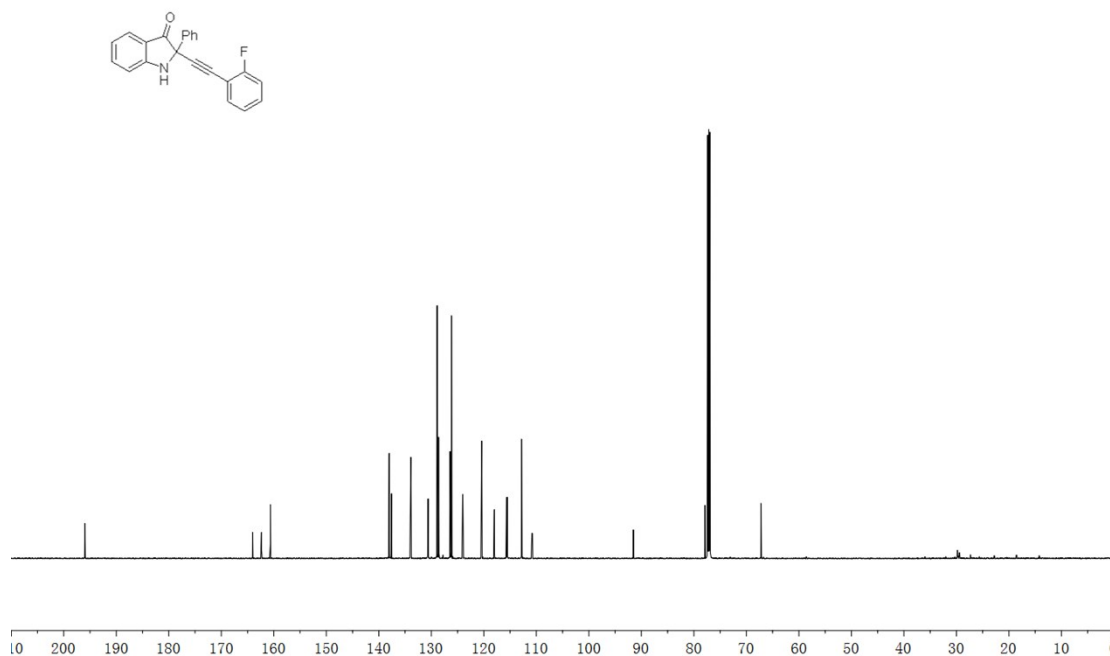
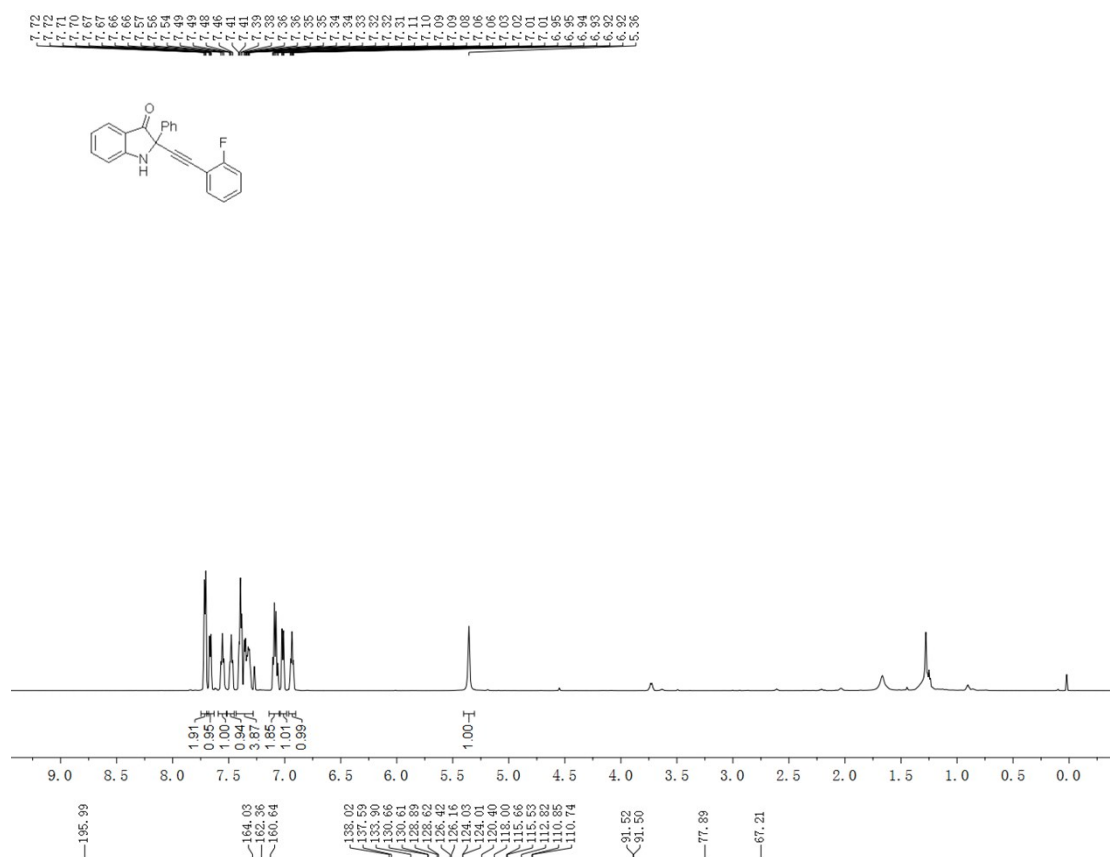
# <sup>1</sup>H and <sup>13</sup>C NMR data of compound 3d



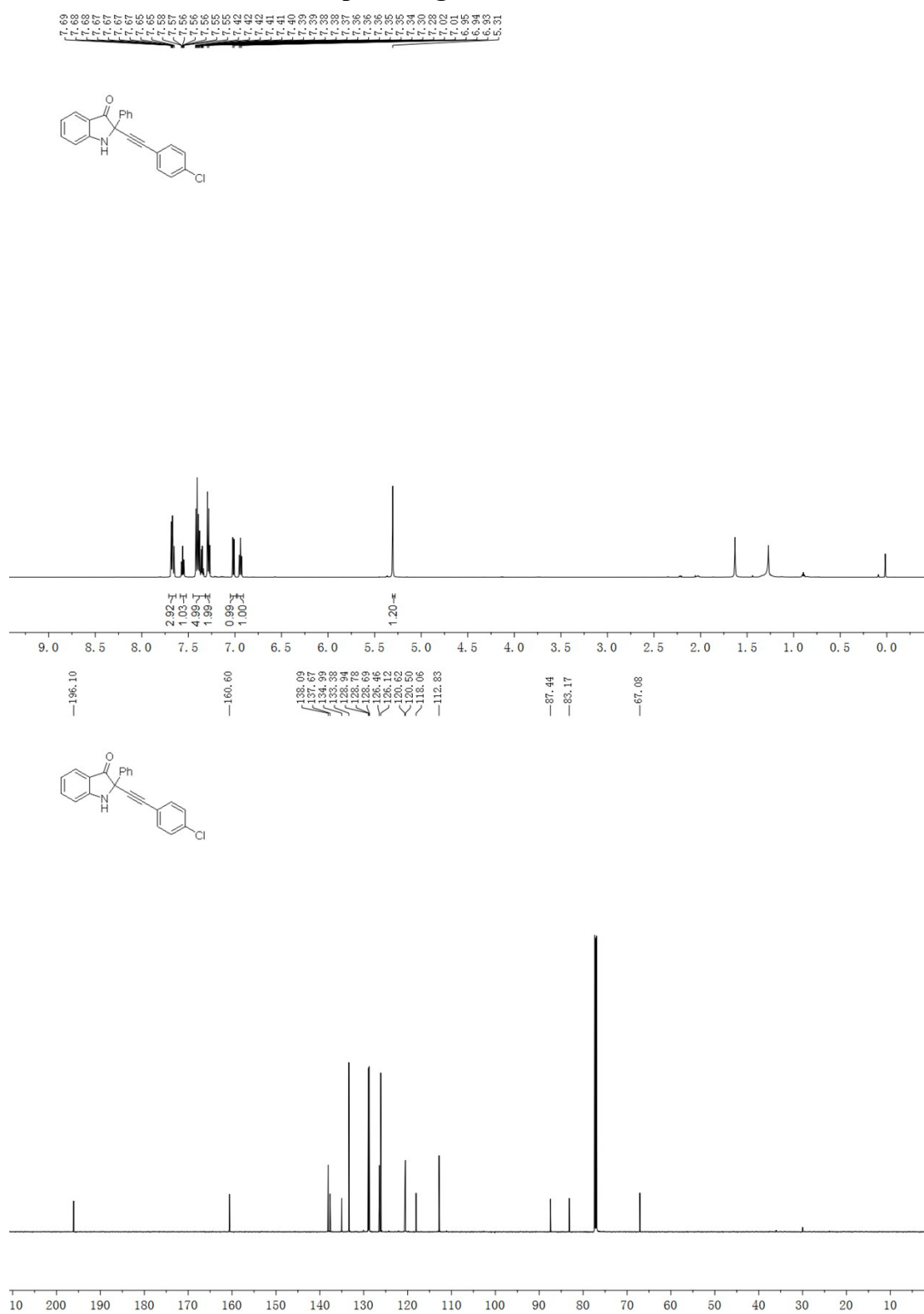
# <sup>1</sup>H and <sup>13</sup>C NMR data of compound 3e



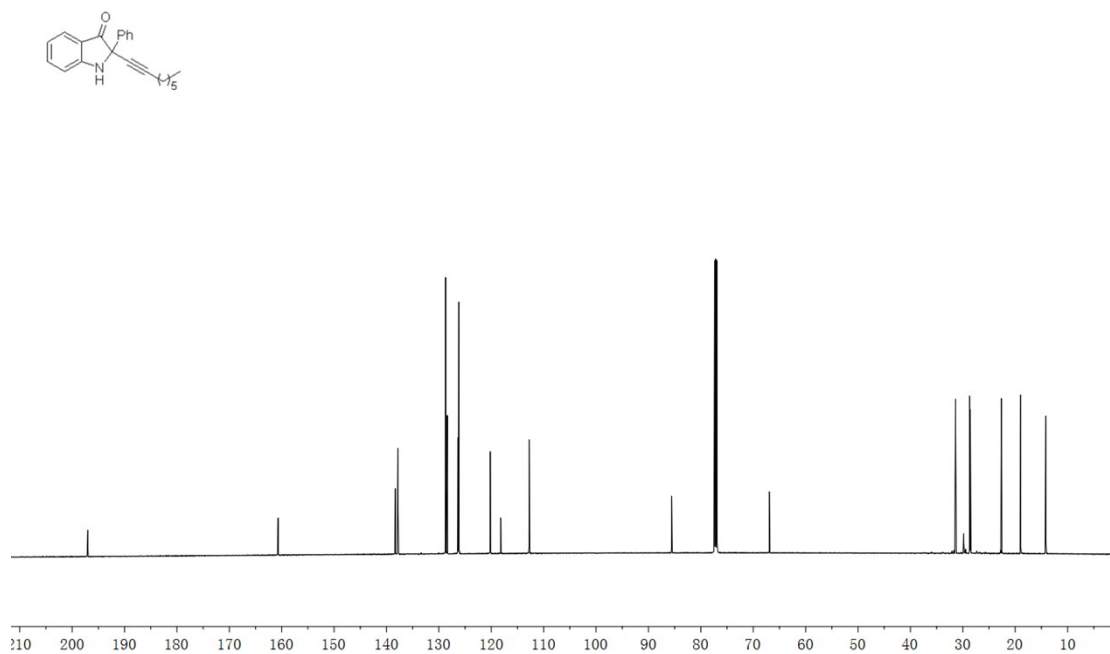
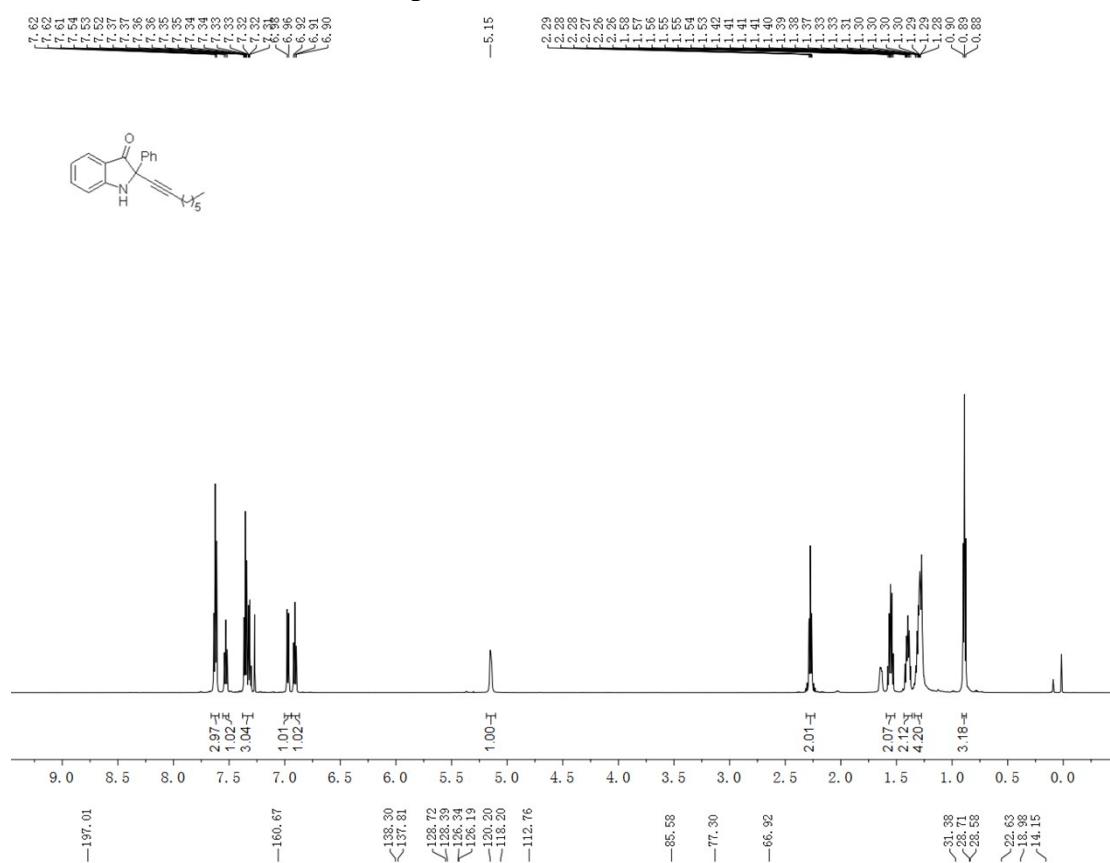
# <sup>1</sup>H and <sup>13</sup>C NMR data of compound 3f



# <sup>1</sup>H and <sup>13</sup>C NMR data of compound 3g

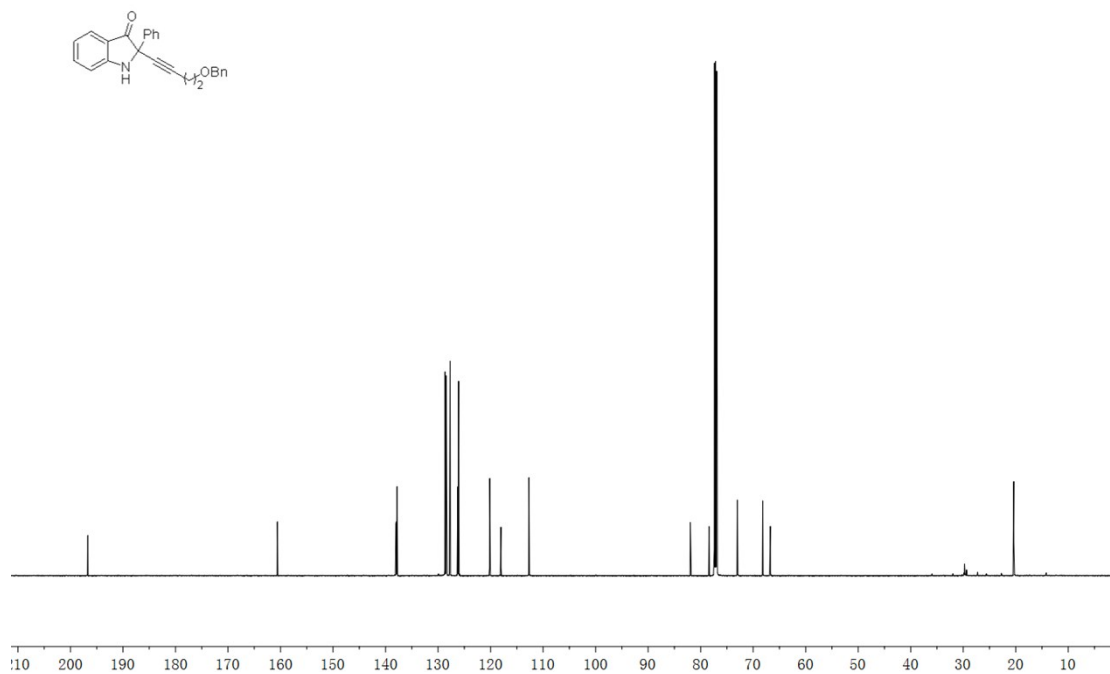
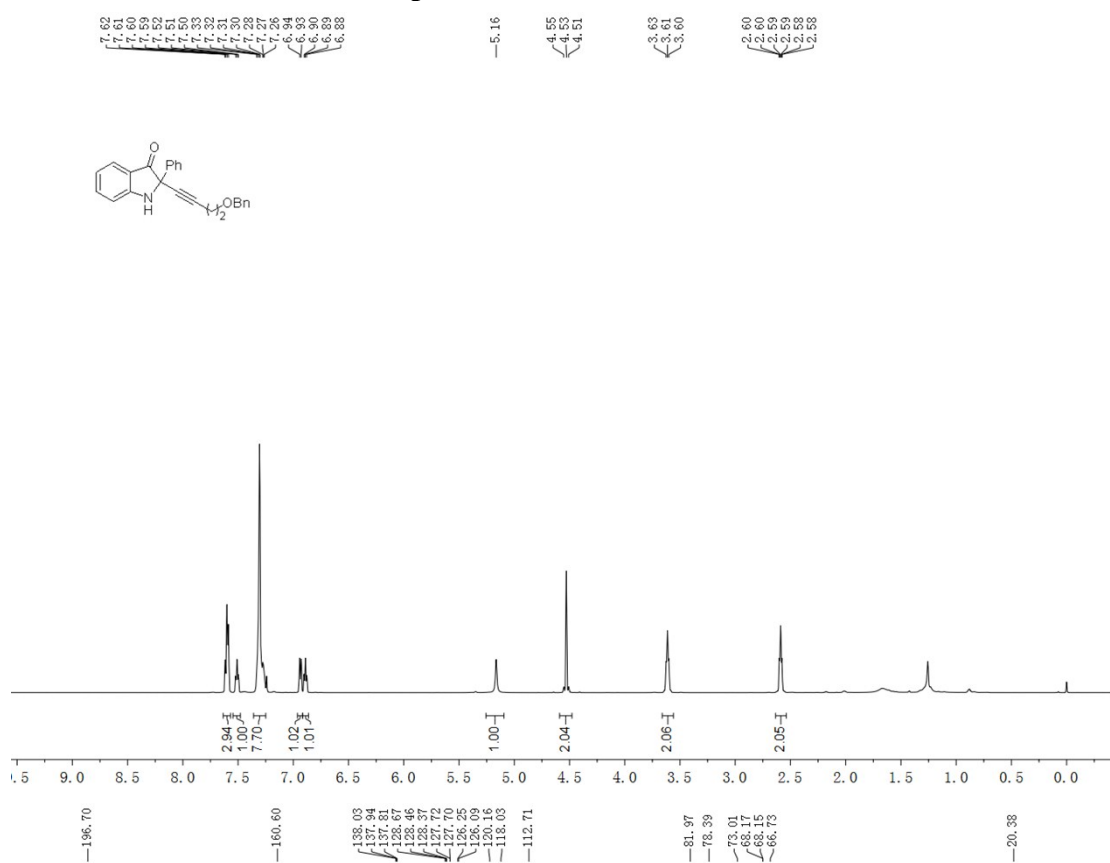


# <sup>1</sup>H and <sup>13</sup>C NMR data of compound 3h

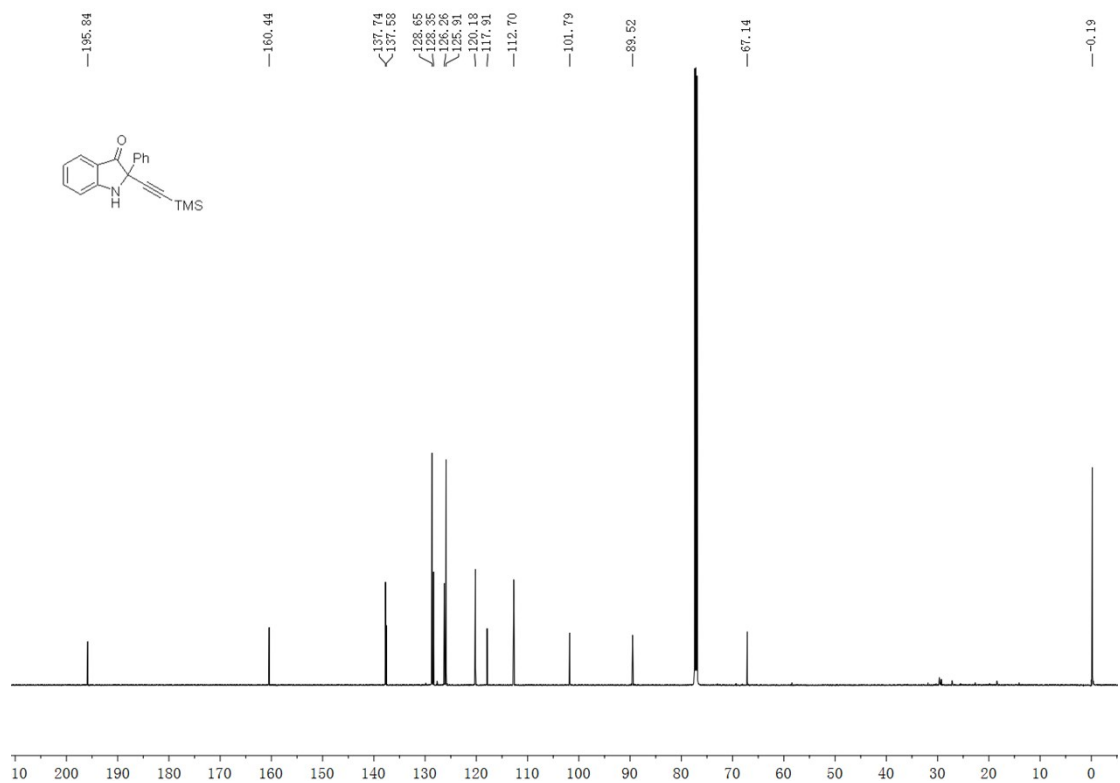
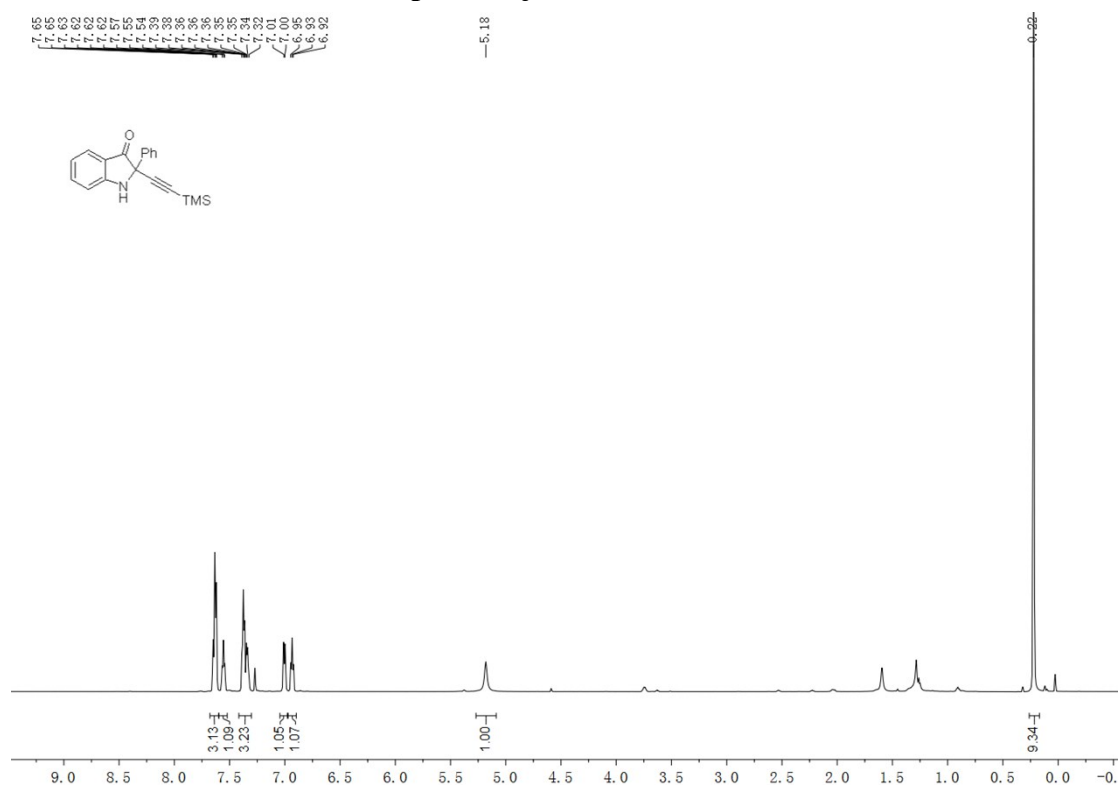




# <sup>1</sup>H and <sup>13</sup>C NMR data of compound 3i

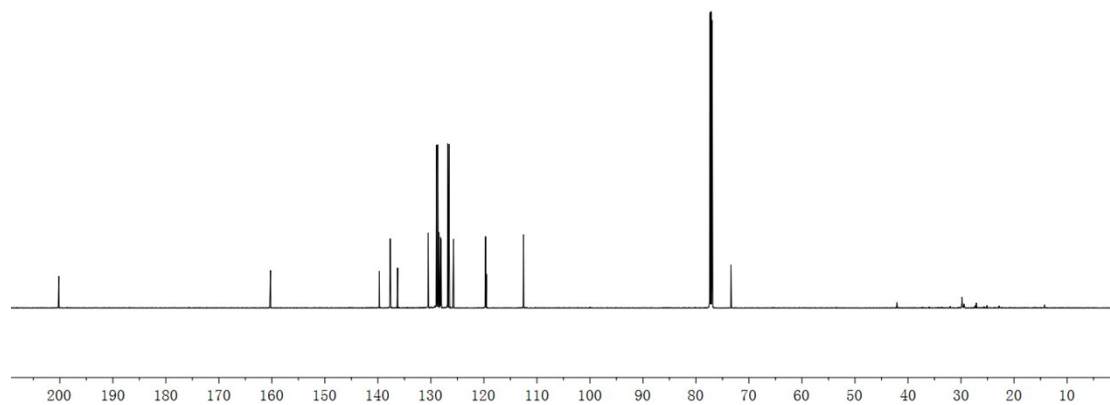
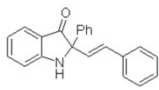
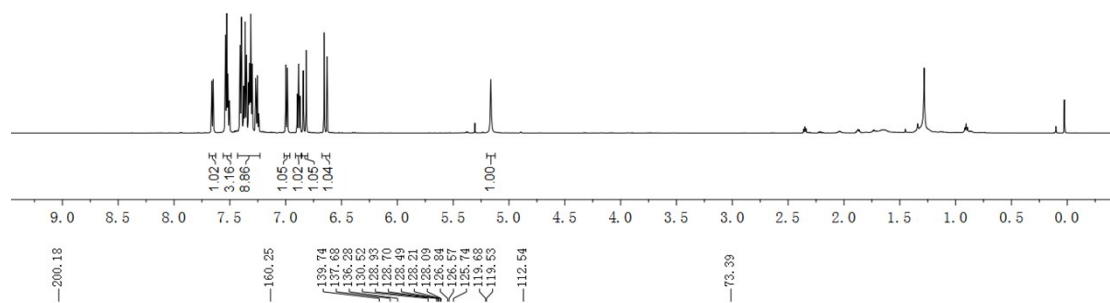
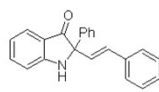


# <sup>1</sup>H and <sup>13</sup>C NMR data of compound 3j

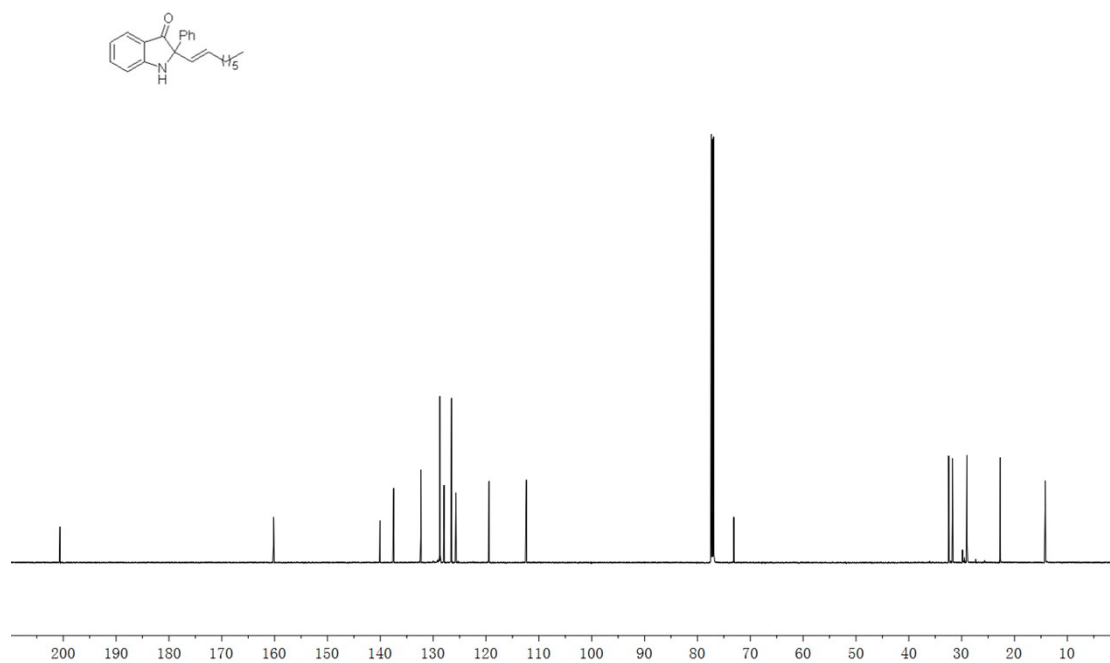
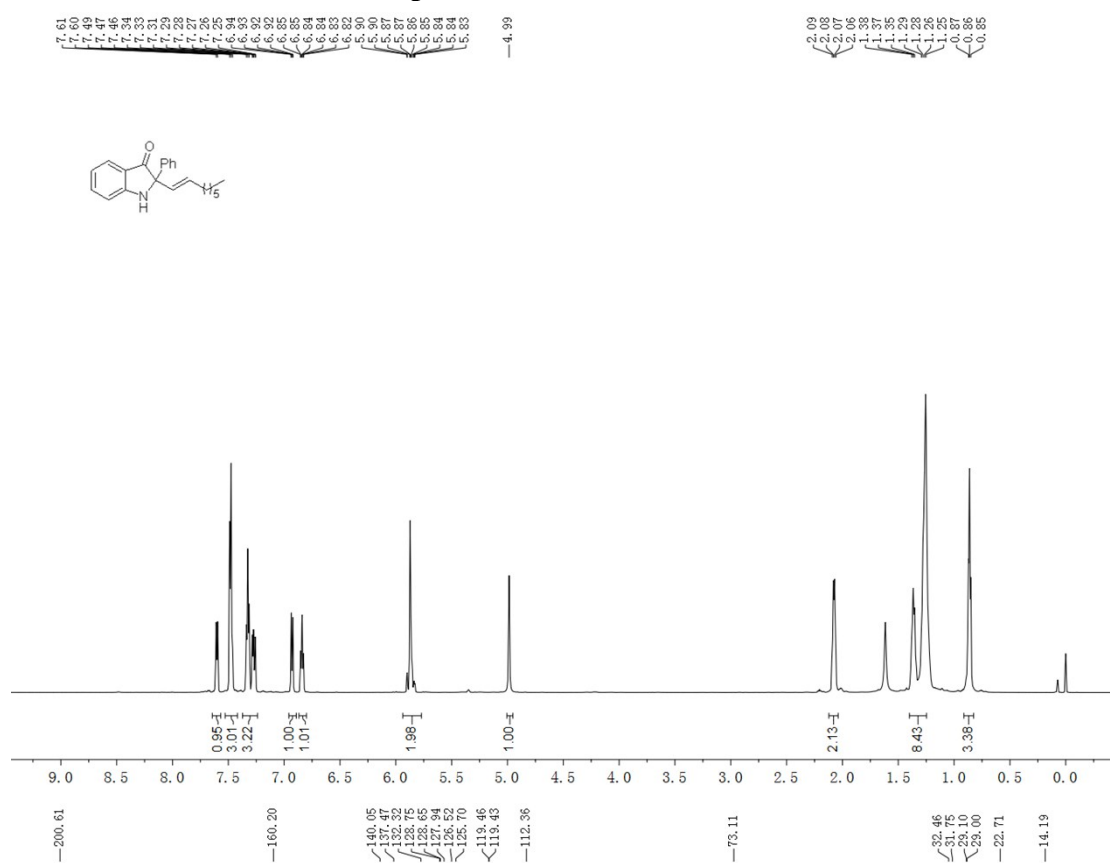


# <sup>1</sup>H and <sup>13</sup>C NMR data of compound 3k

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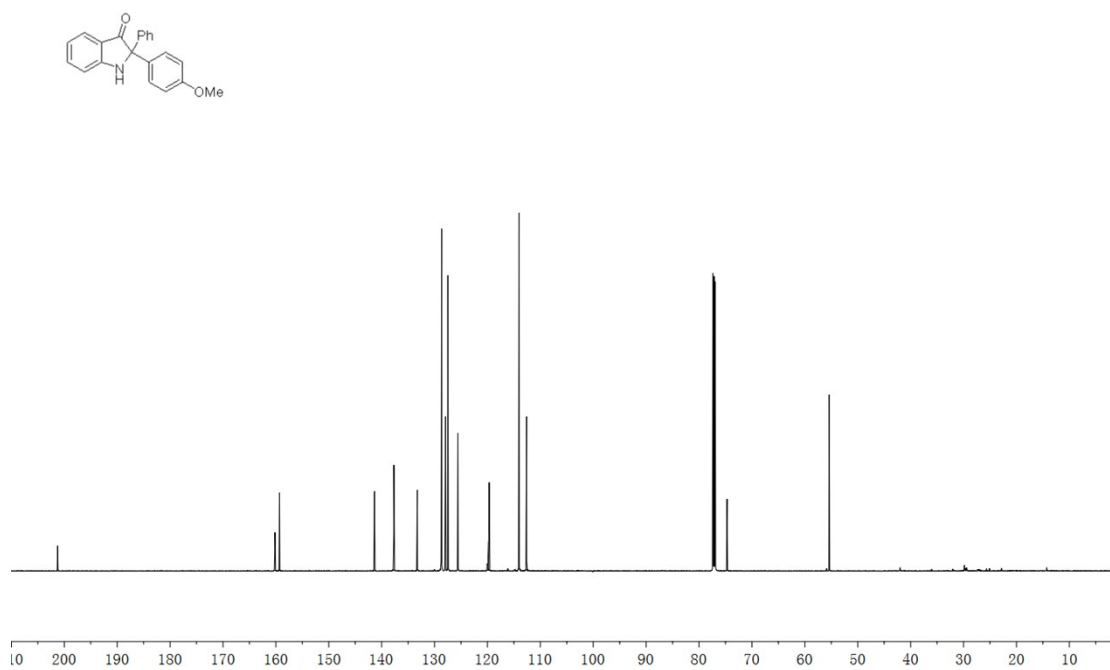
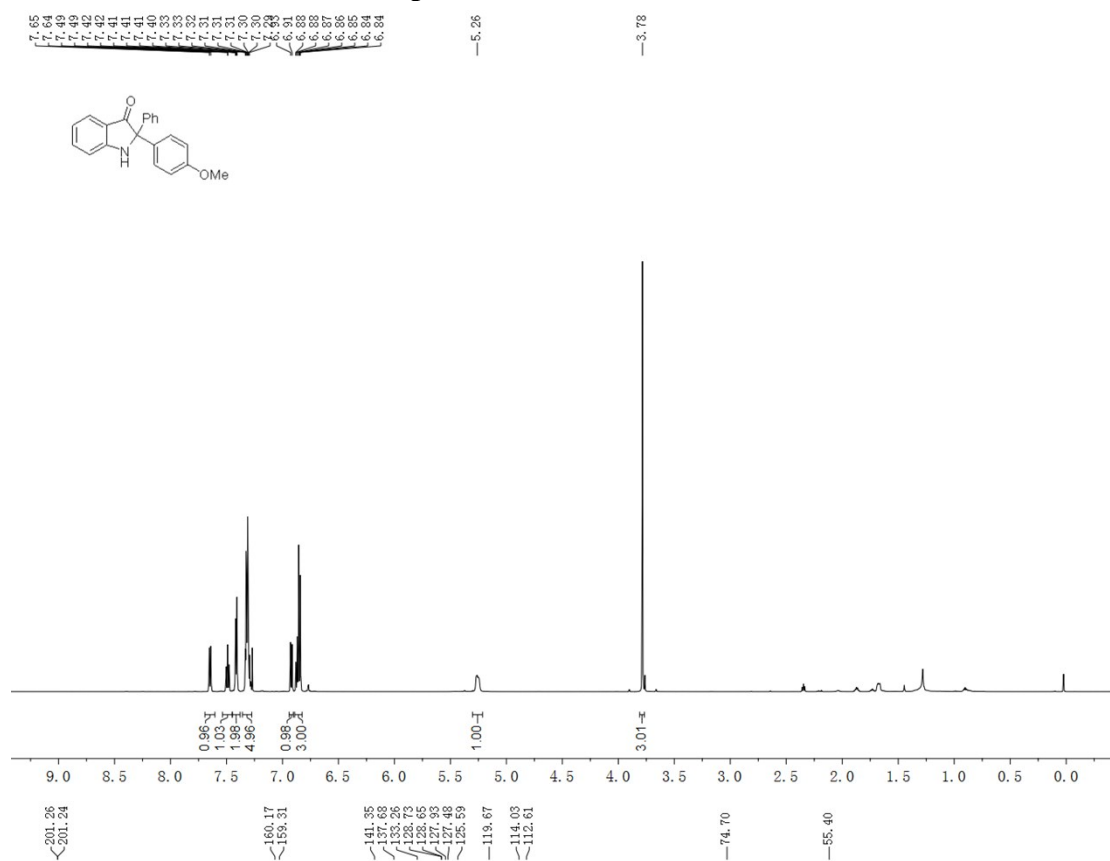


# <sup>1</sup>H and <sup>13</sup>C NMR data of compound 3l

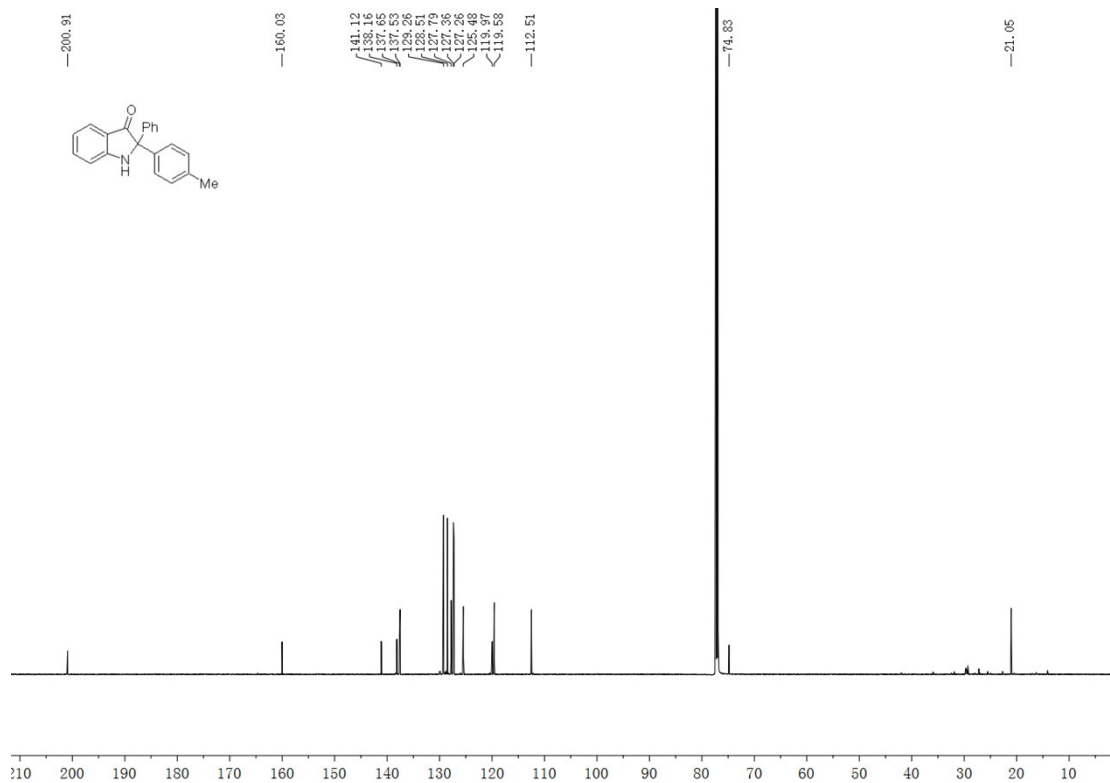
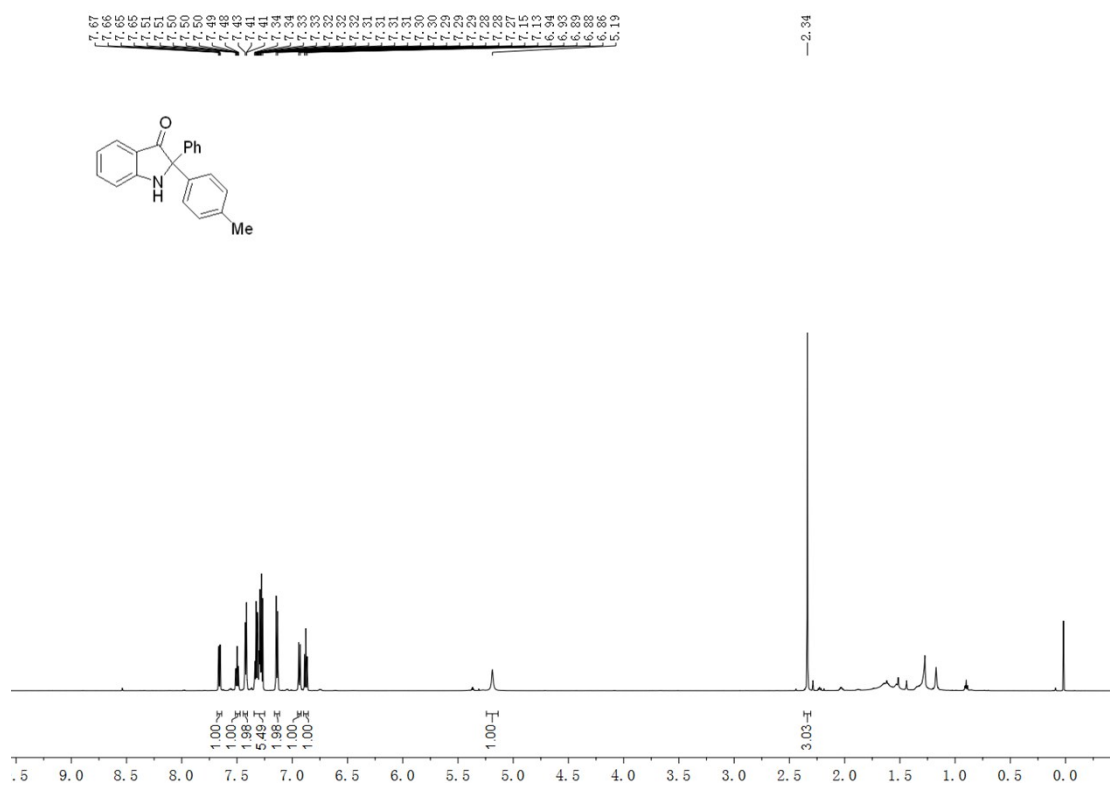




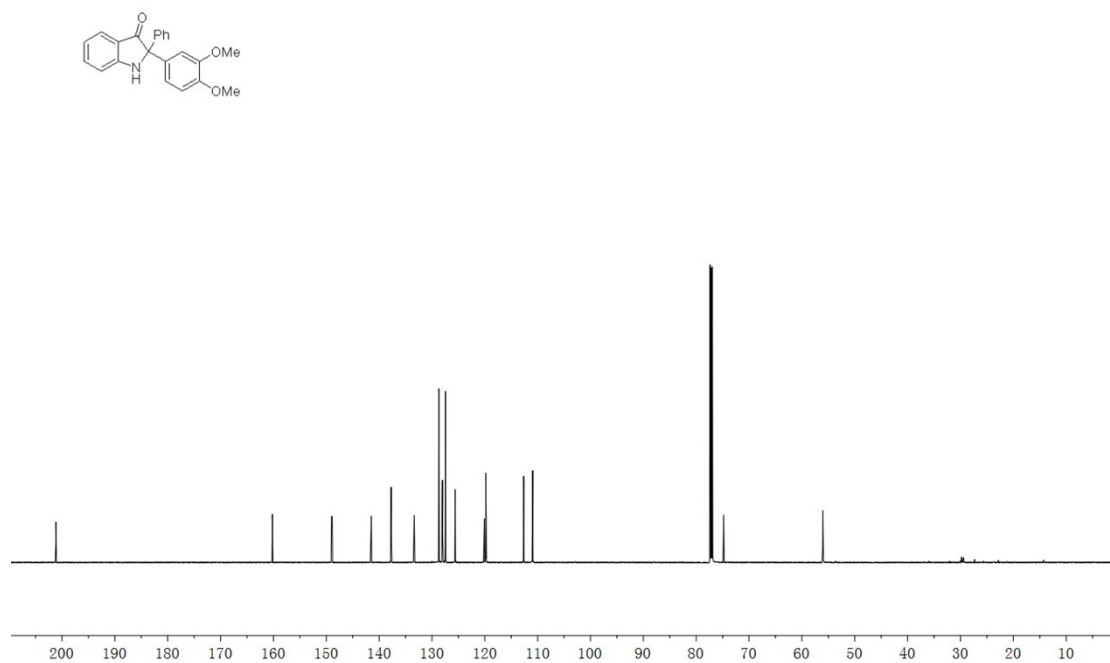
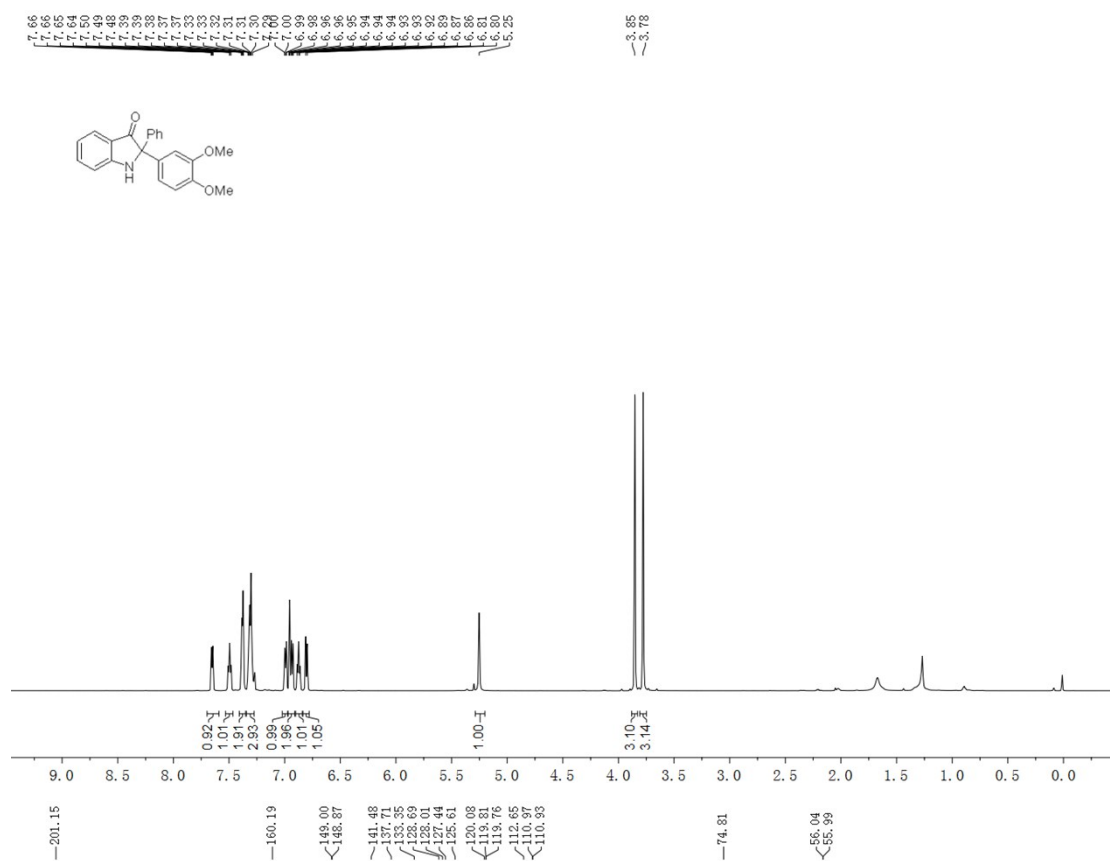
# <sup>1</sup>H and <sup>13</sup>C NMR data of compound 3n



# <sup>1</sup>H and <sup>13</sup>C NMR data of compound 3o

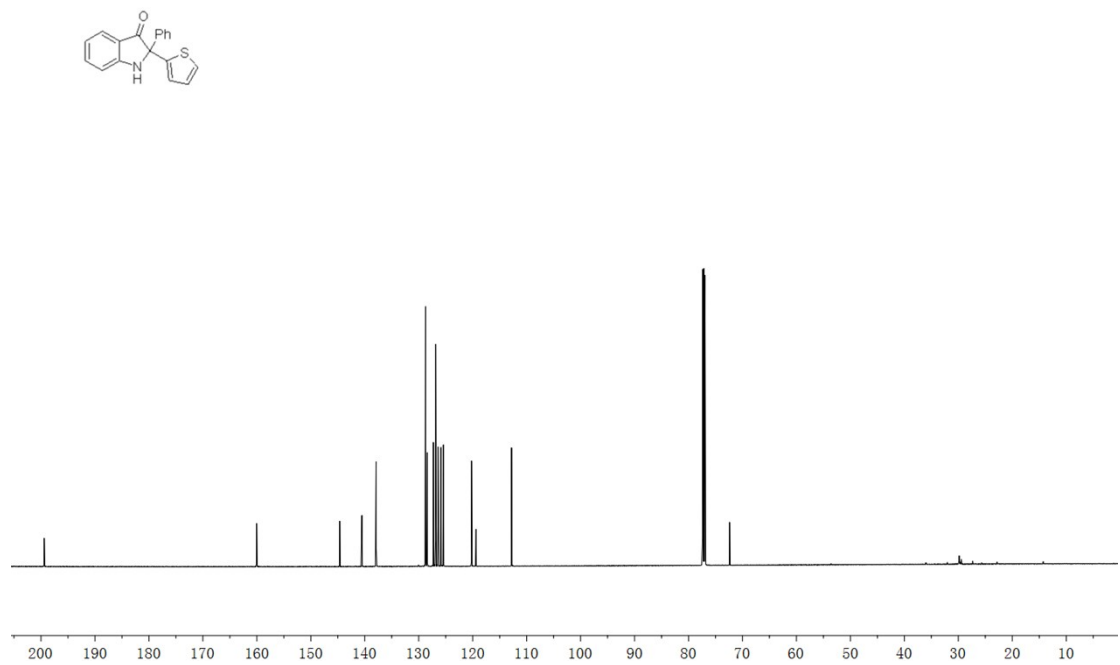
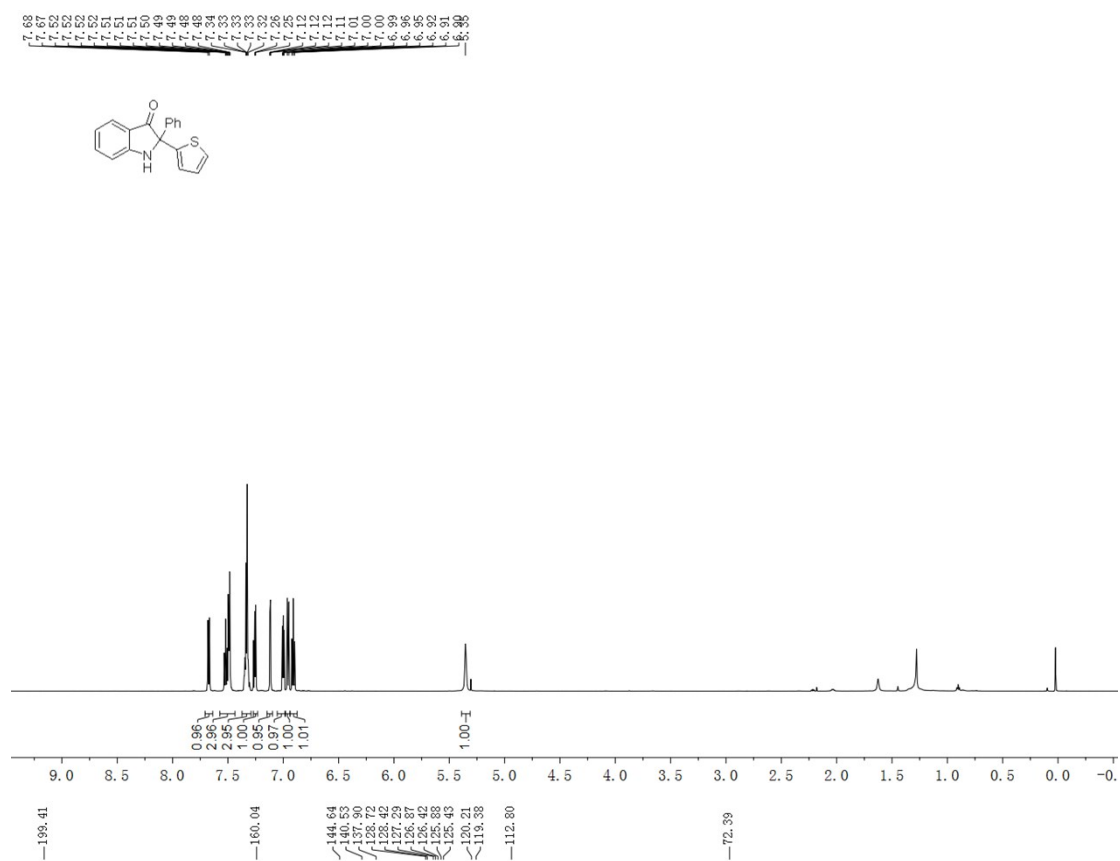


# <sup>1</sup>H and <sup>13</sup>C NMR data of compound 3p

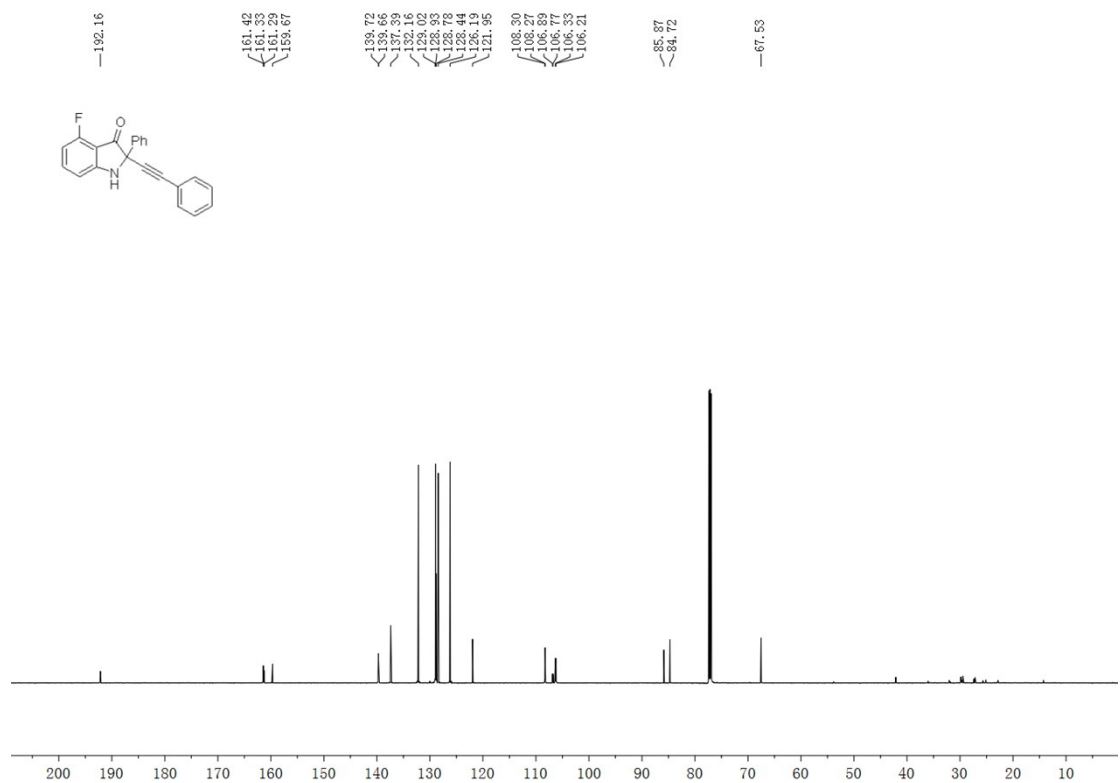
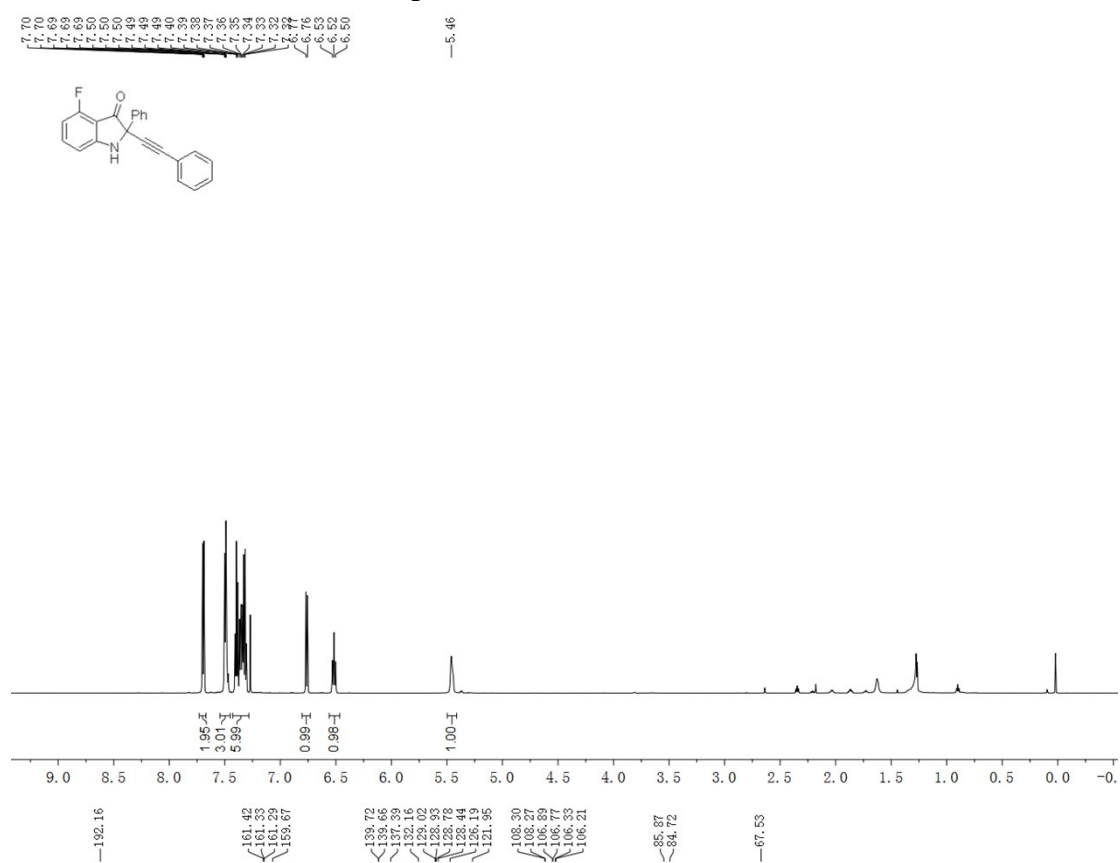




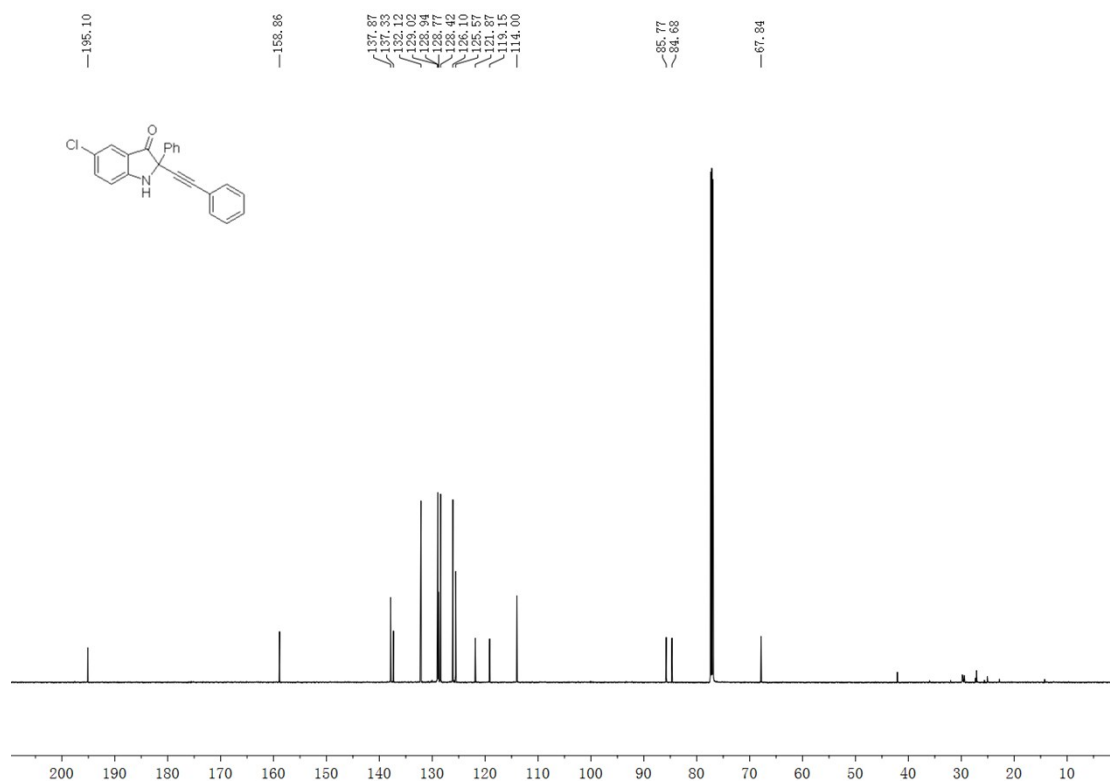
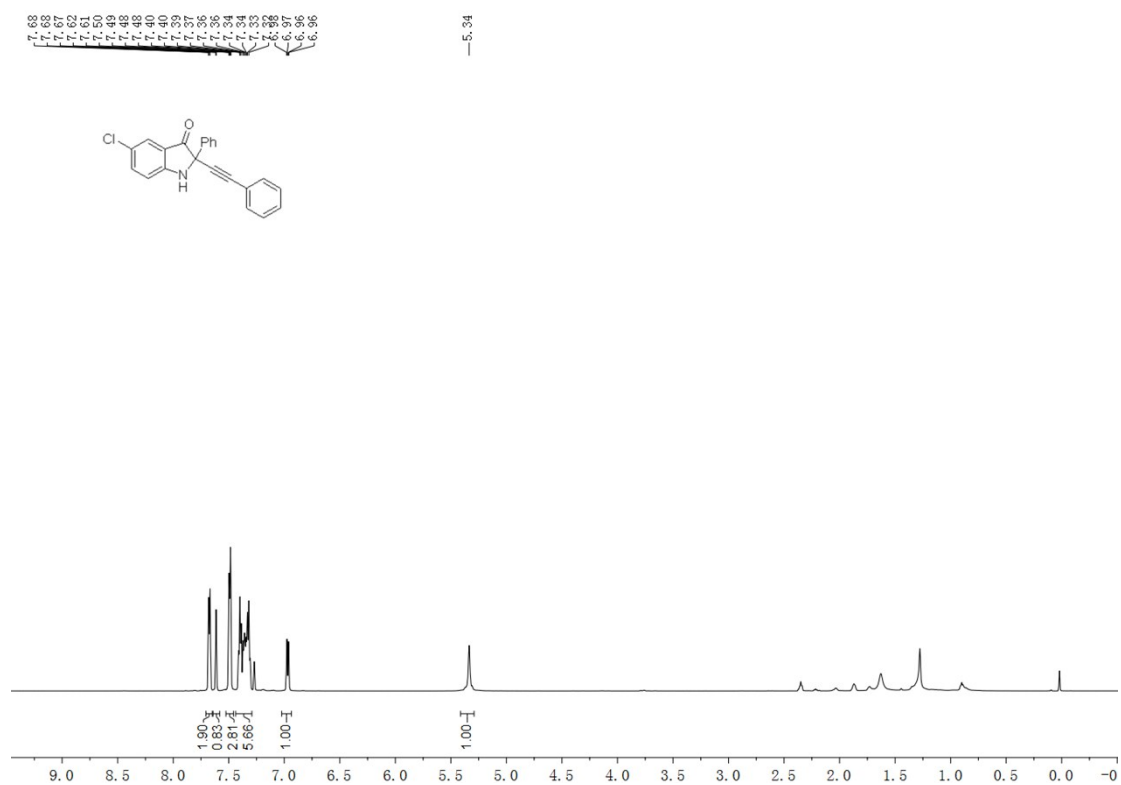
# <sup>1</sup>H and <sup>13</sup>C NMR data of compound 3s



# <sup>1</sup>H and <sup>13</sup>C NMR data of compound 4a

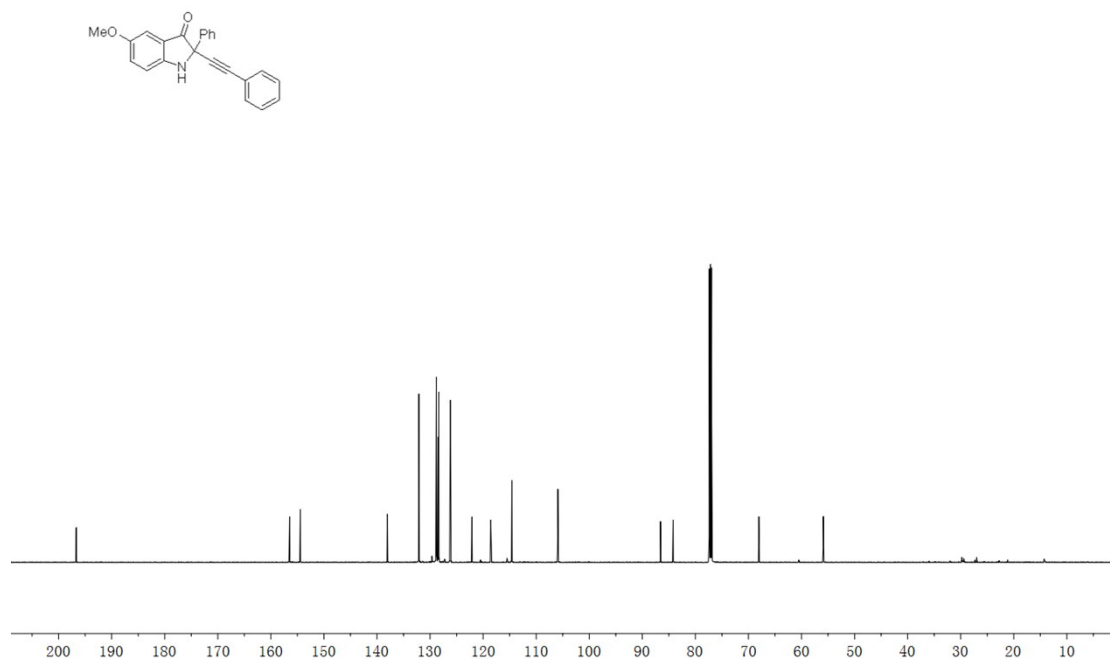
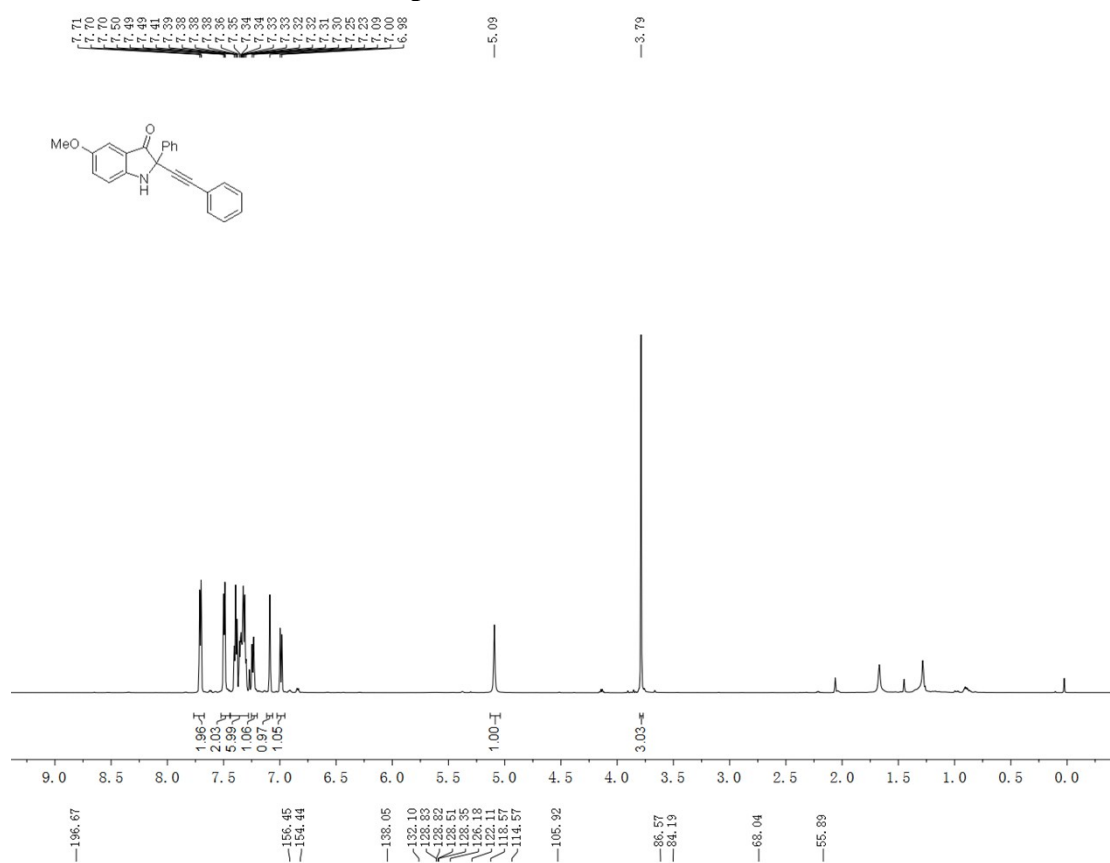


# <sup>1</sup>H and <sup>13</sup>C NMR data of compound 4b

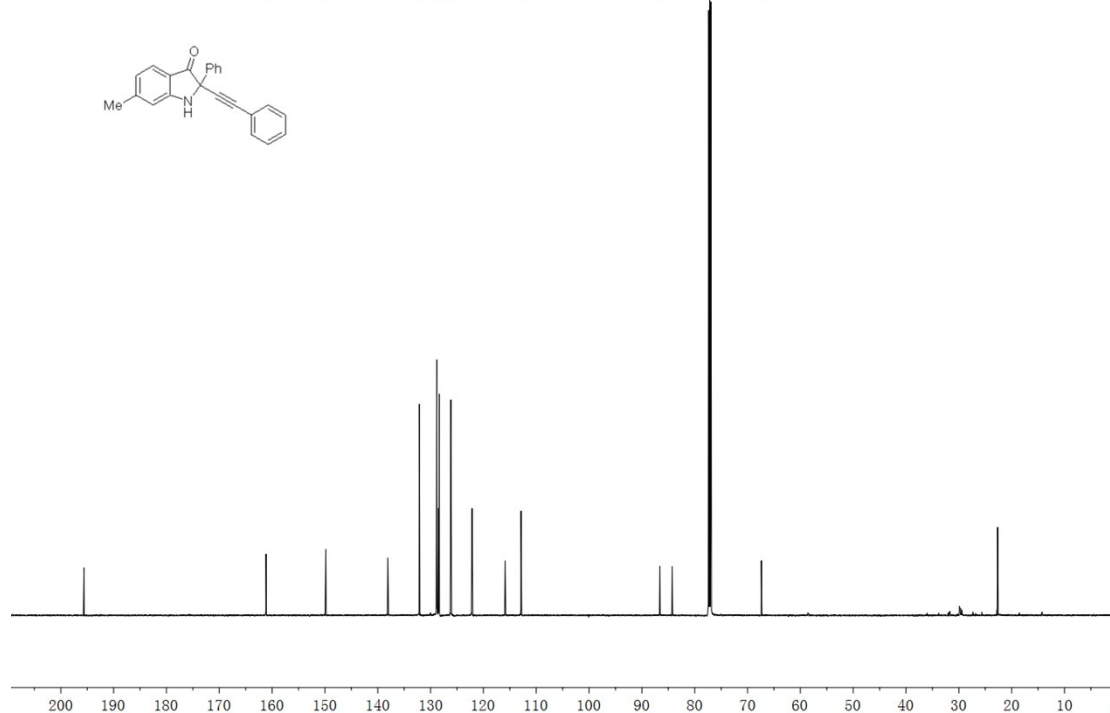
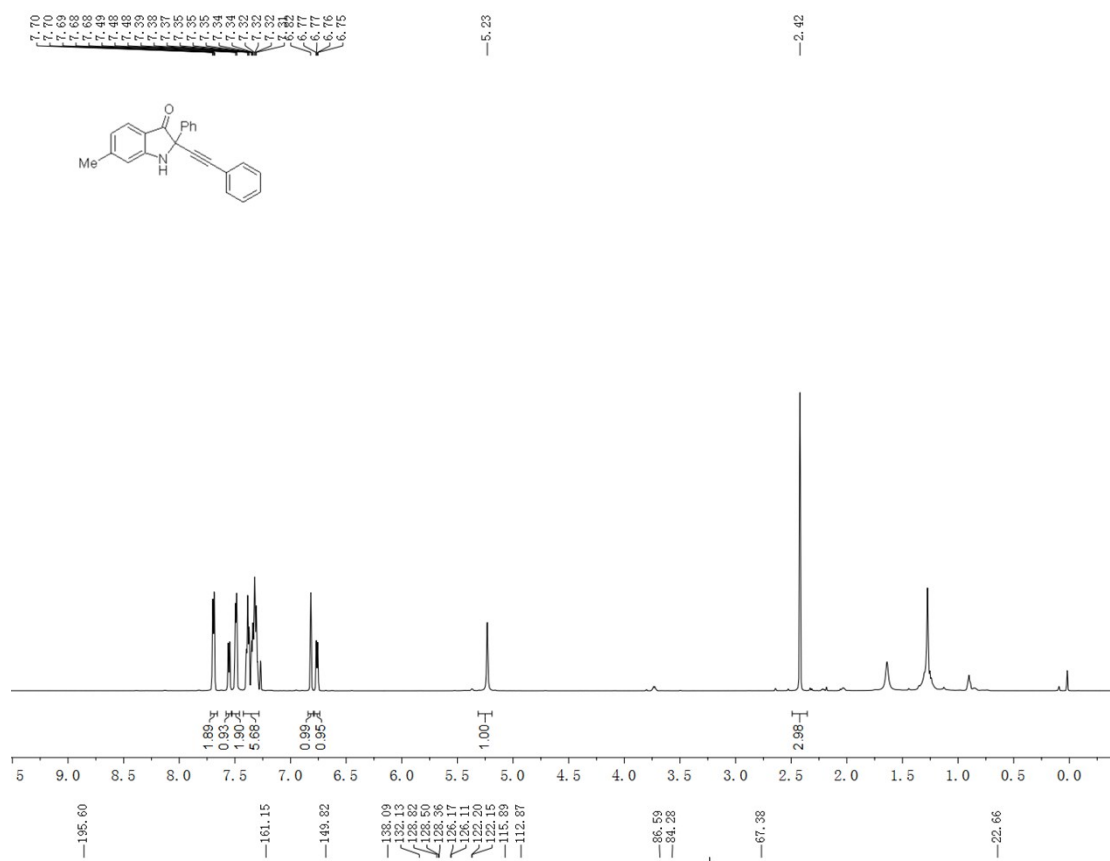




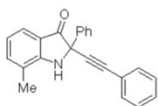
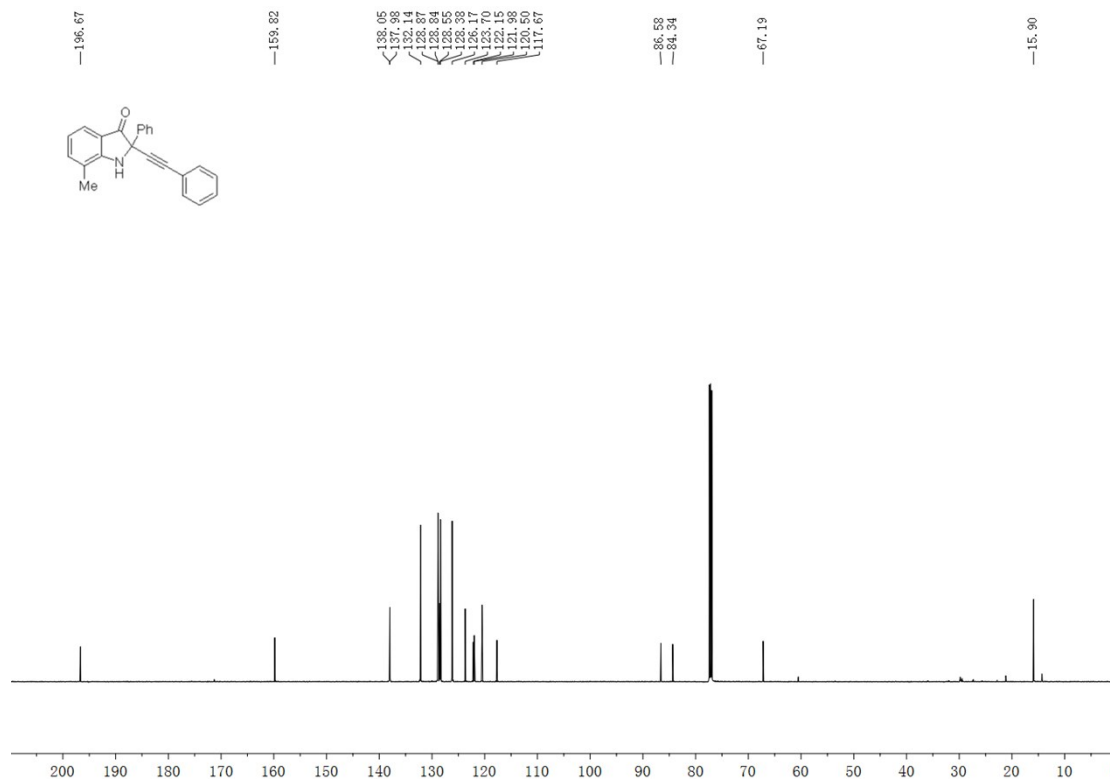
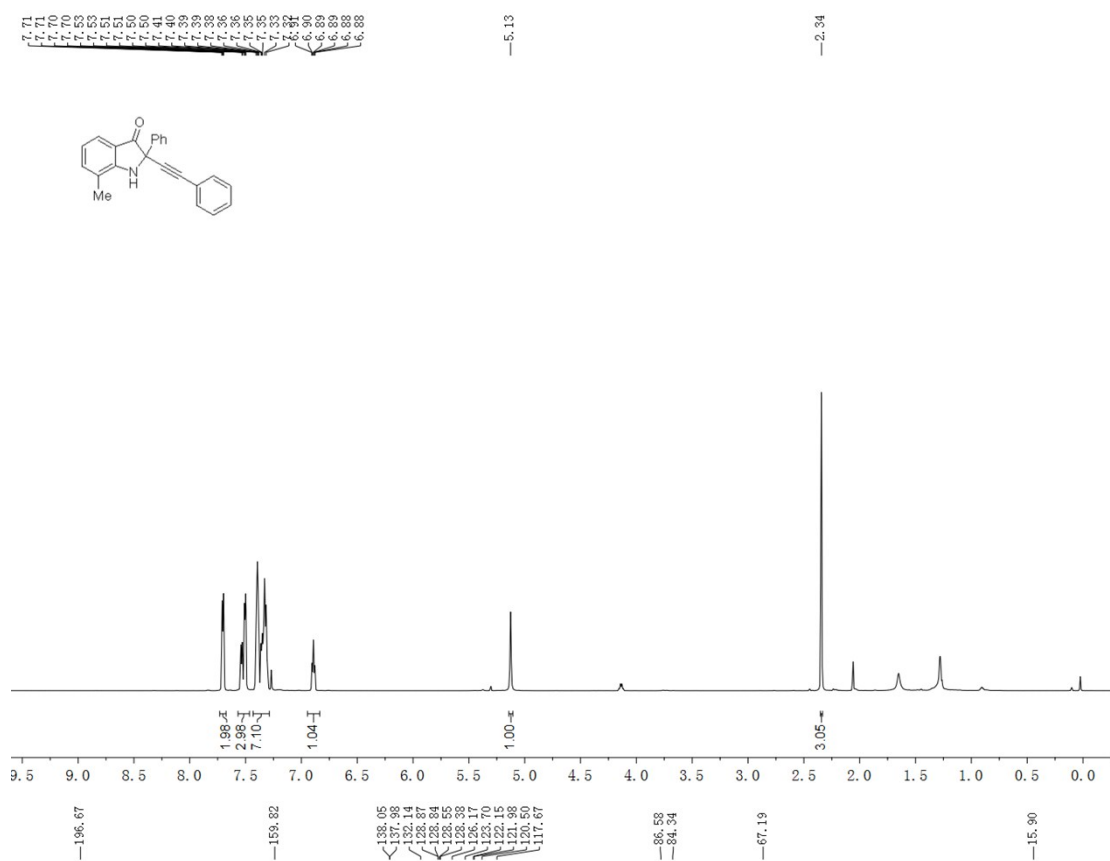
# <sup>1</sup>H and <sup>13</sup>C NMR data of compound 4d



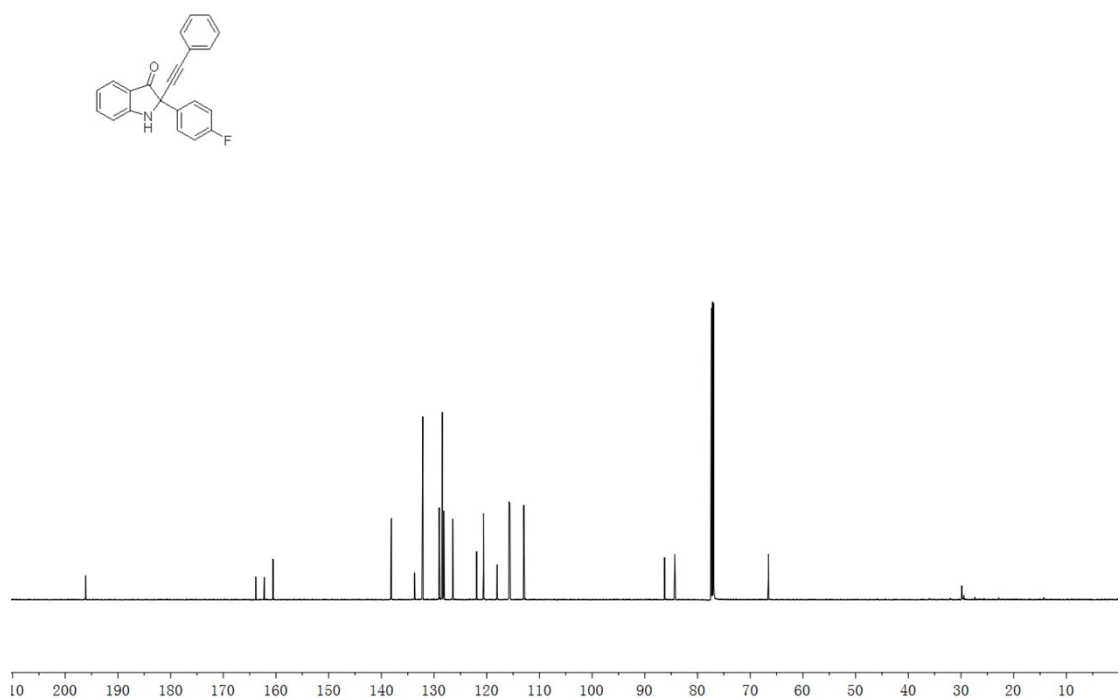
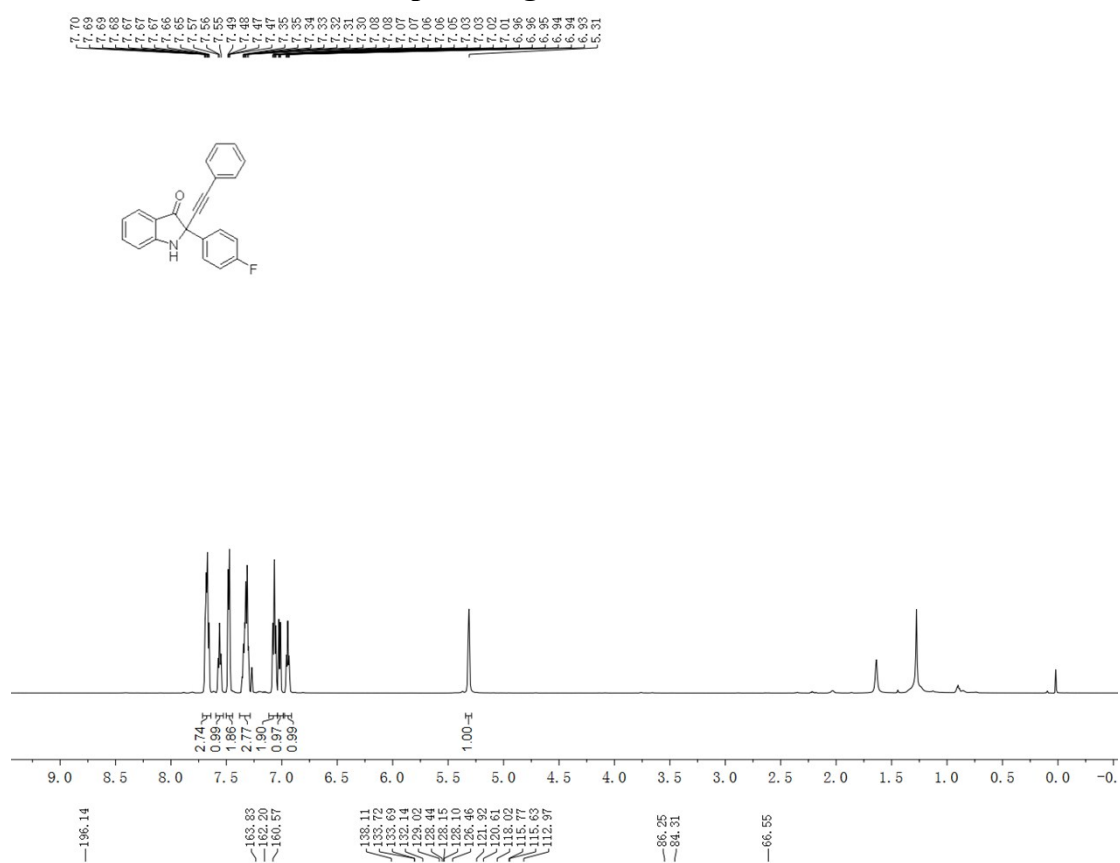
# <sup>1</sup>H and <sup>13</sup>C NMR data of compound 4e



# <sup>1</sup>H and <sup>13</sup>C NMR data of compound 4f

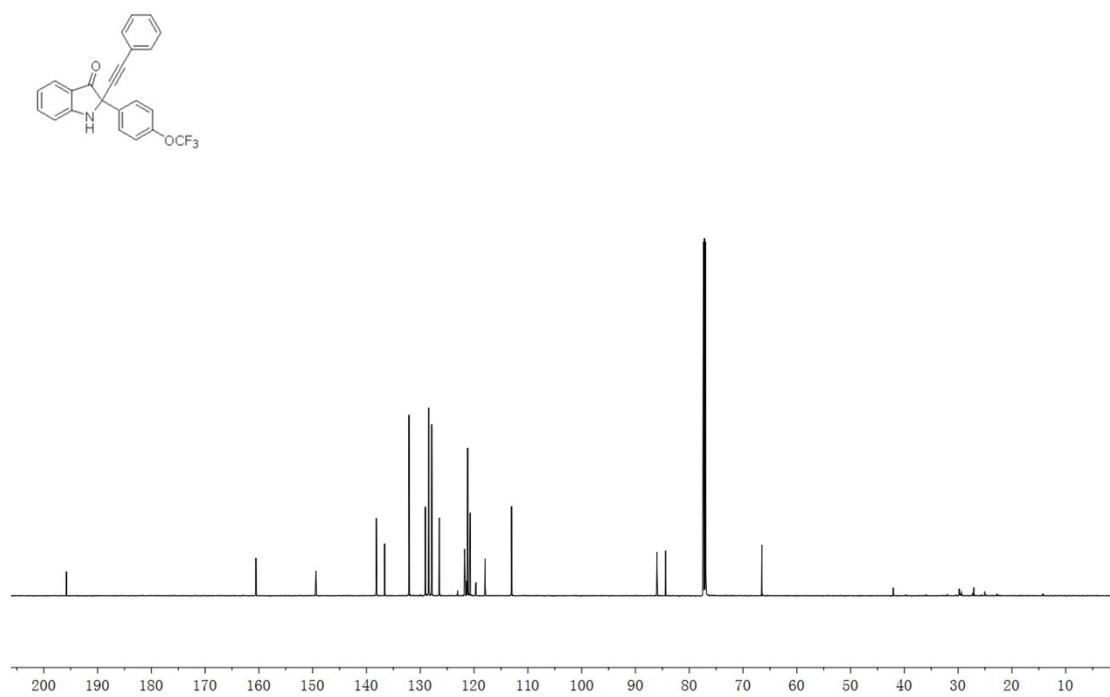
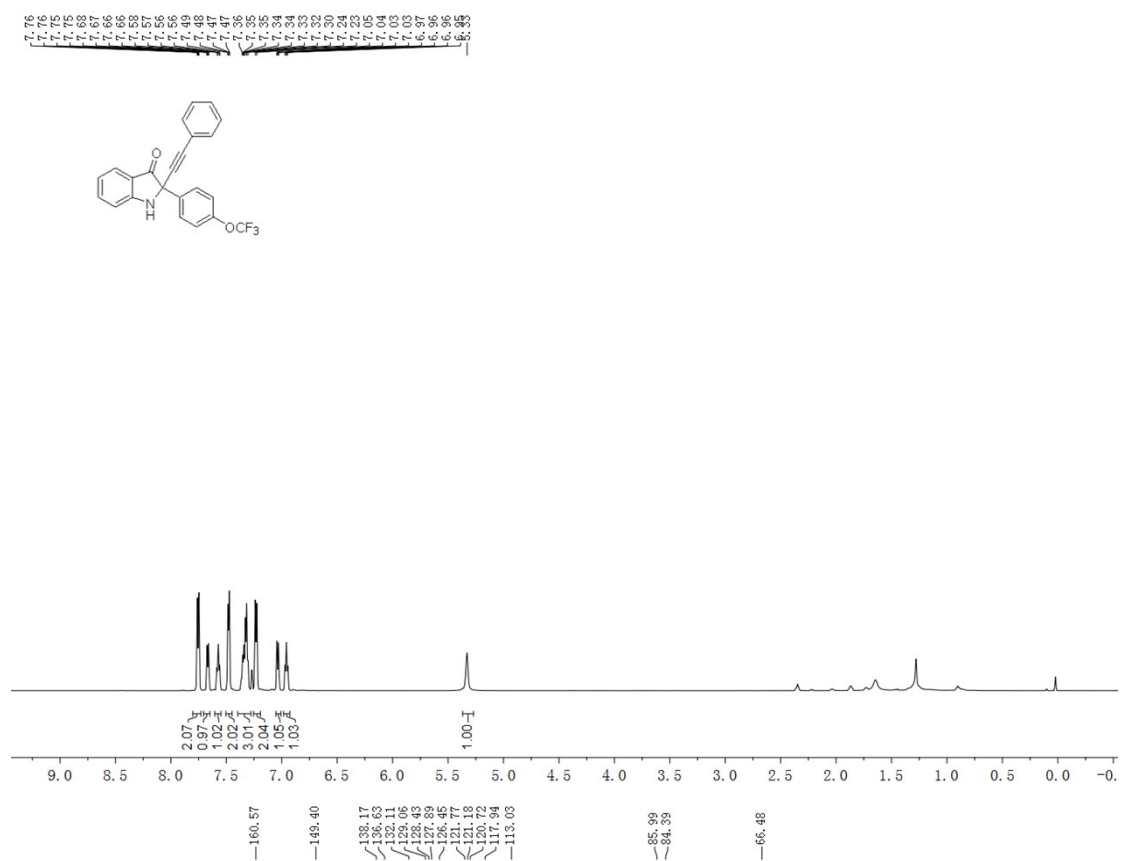


# <sup>1</sup>H and <sup>13</sup>C NMR data of compound 4g

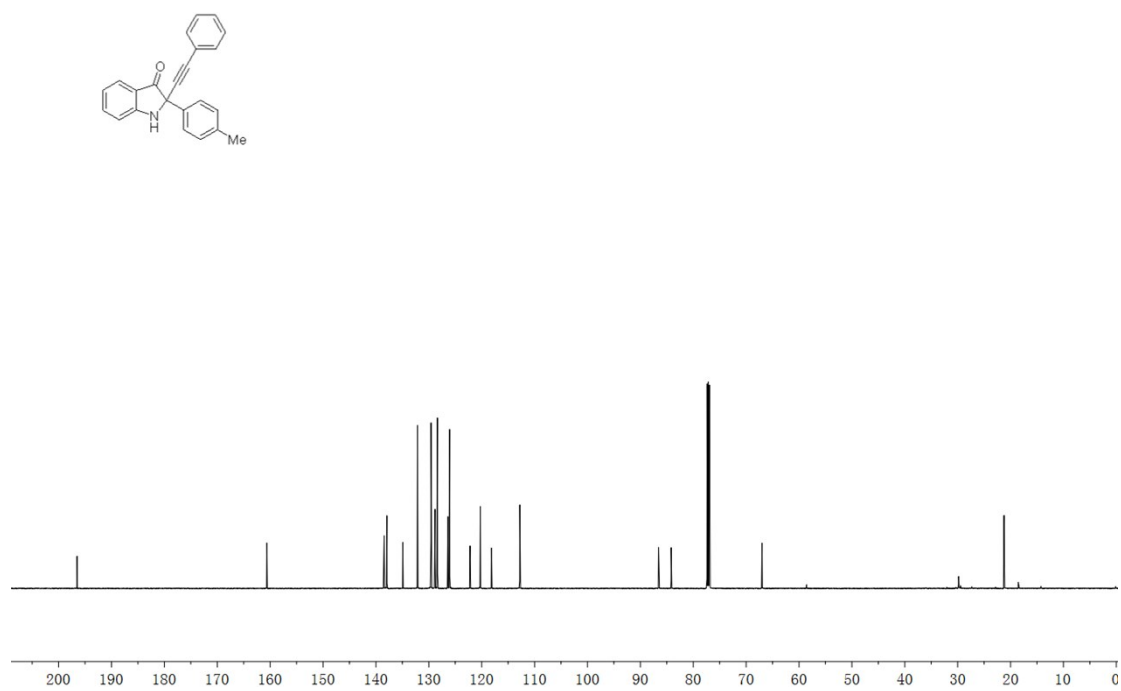
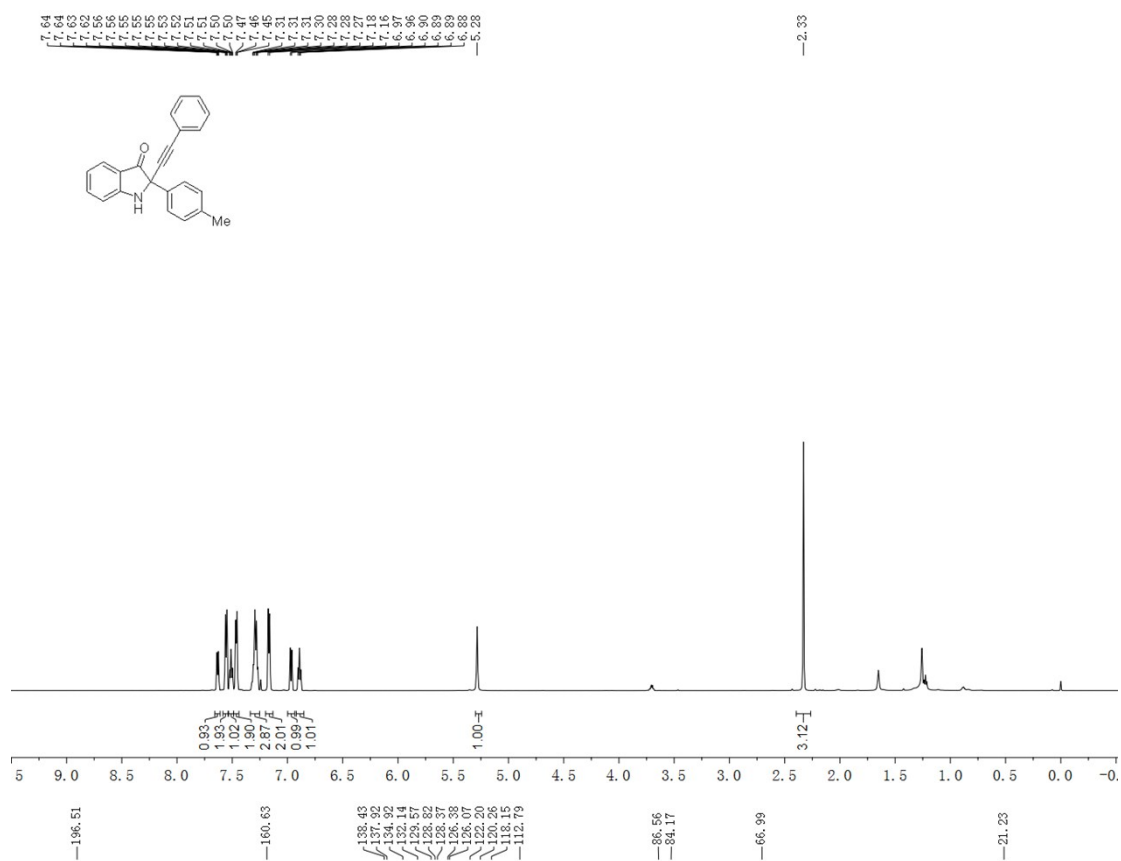




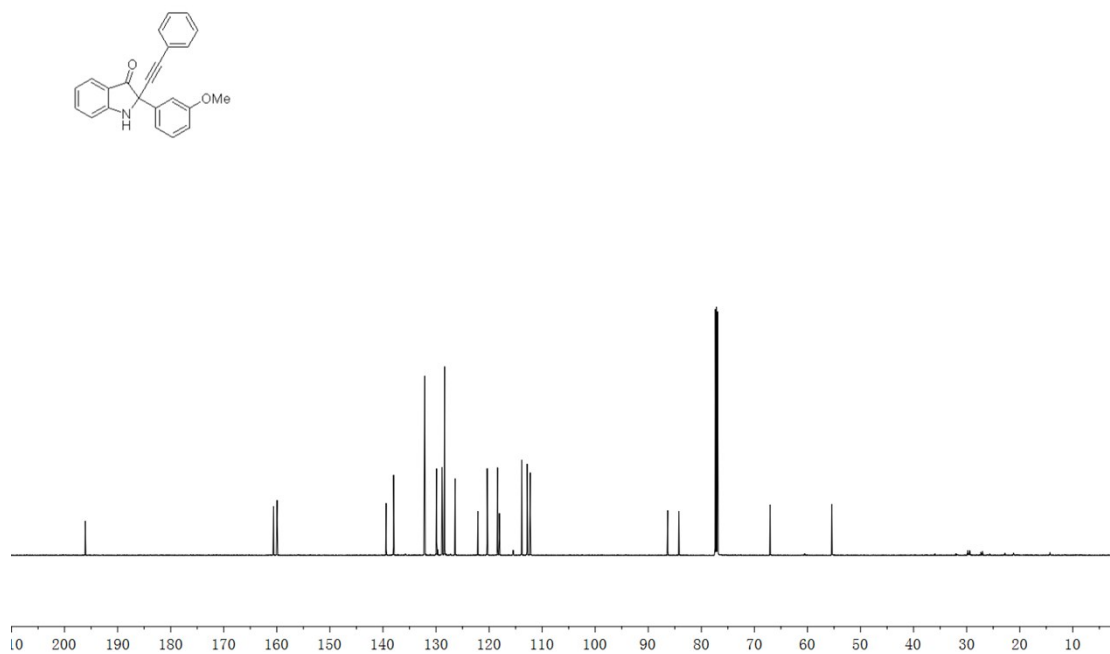
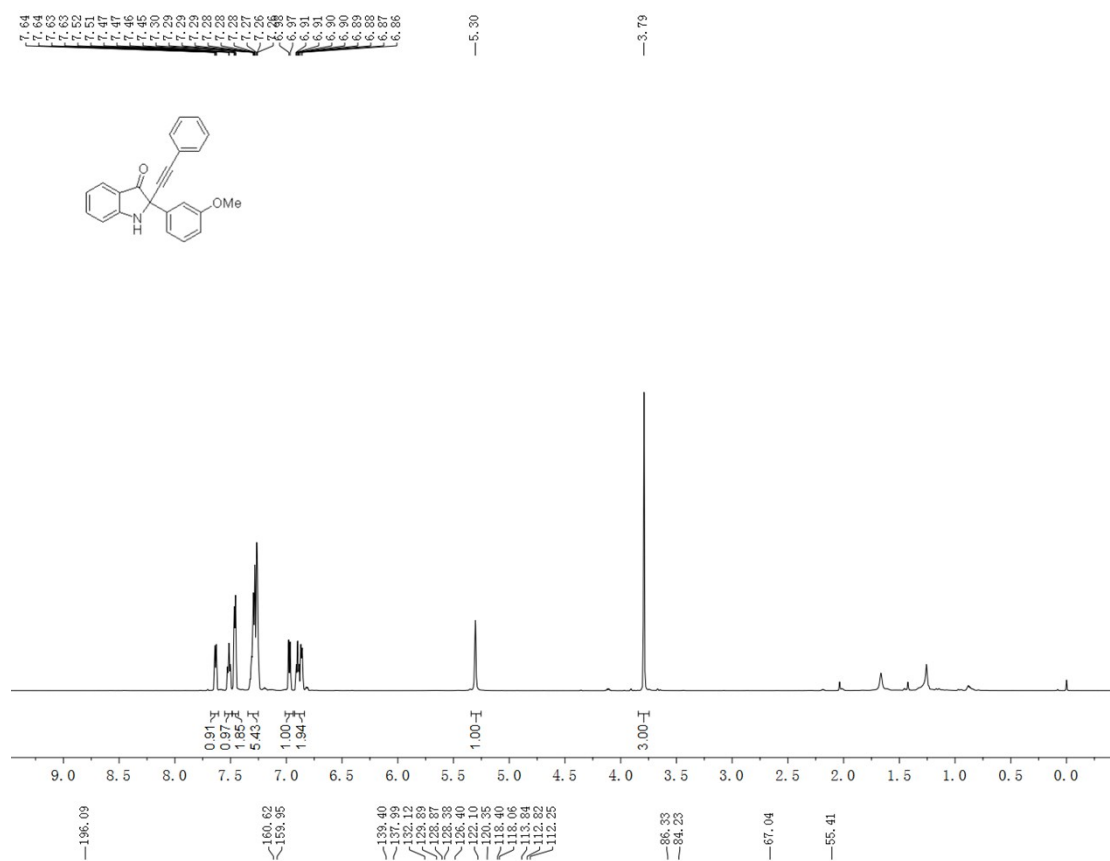
# <sup>1</sup>H and <sup>13</sup>C NMR data of compound 4h



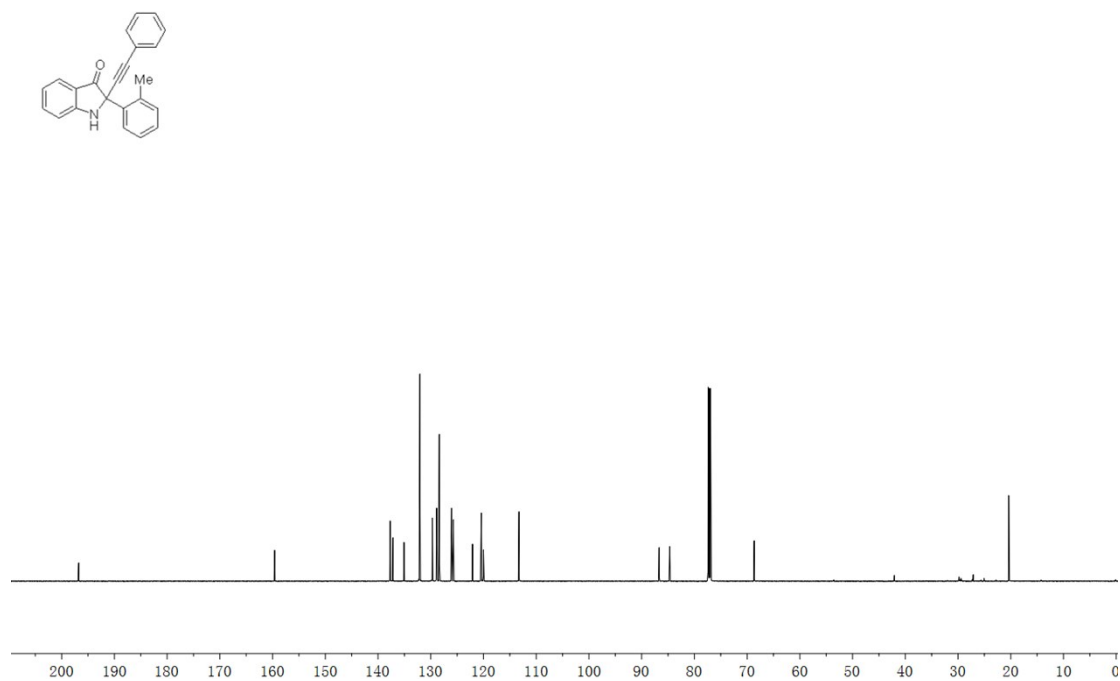
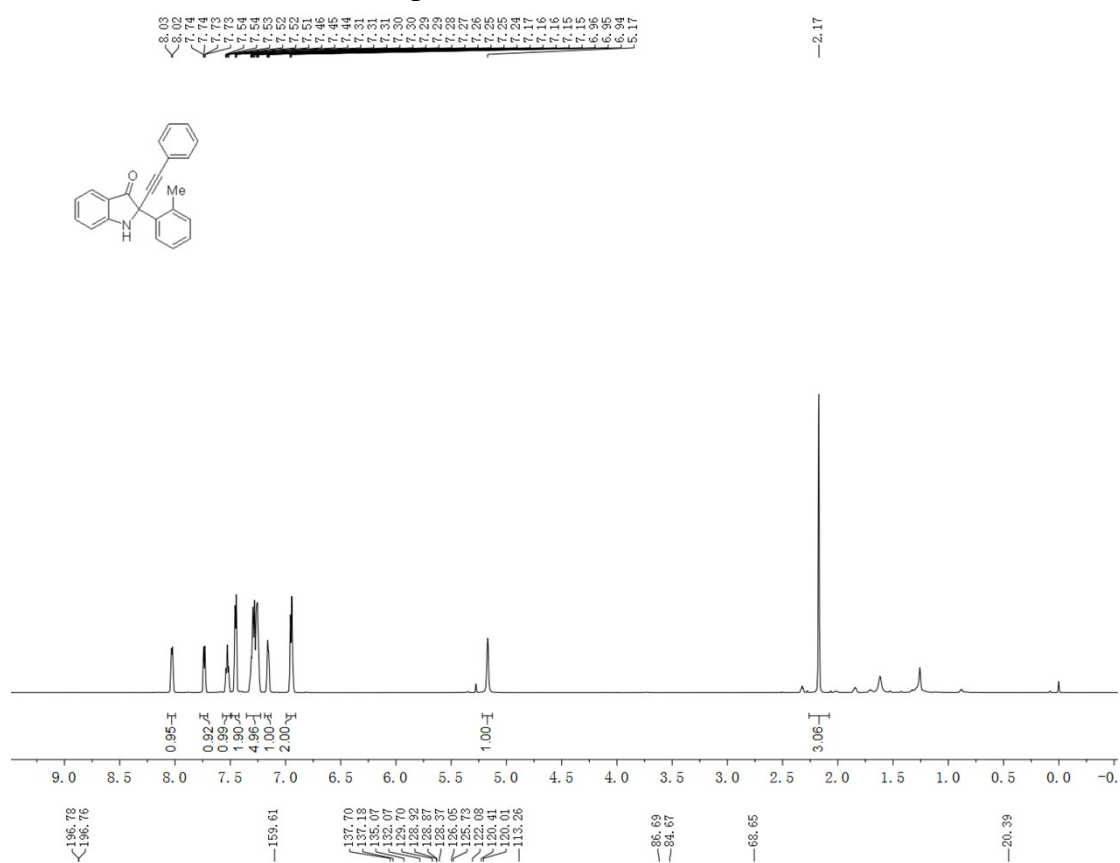
# <sup>1</sup>H and <sup>13</sup>C NMR data of compound 4i



# <sup>1</sup>H and <sup>13</sup>C NMR data of compound 4j

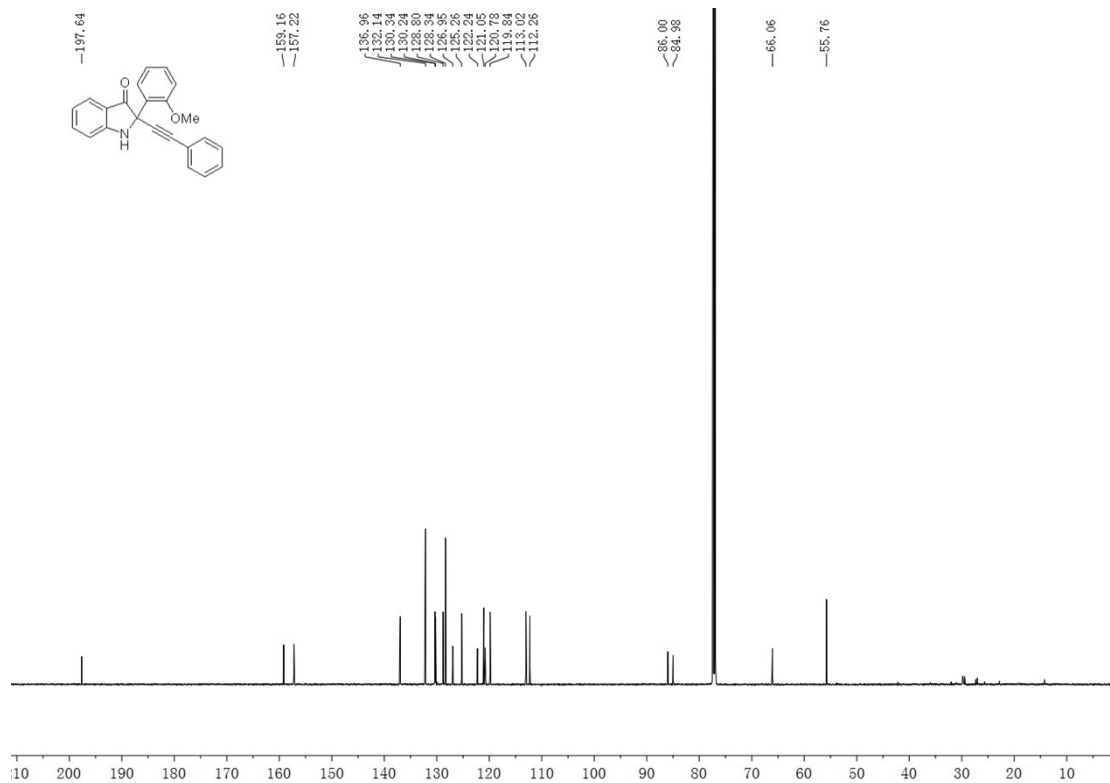
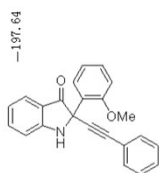
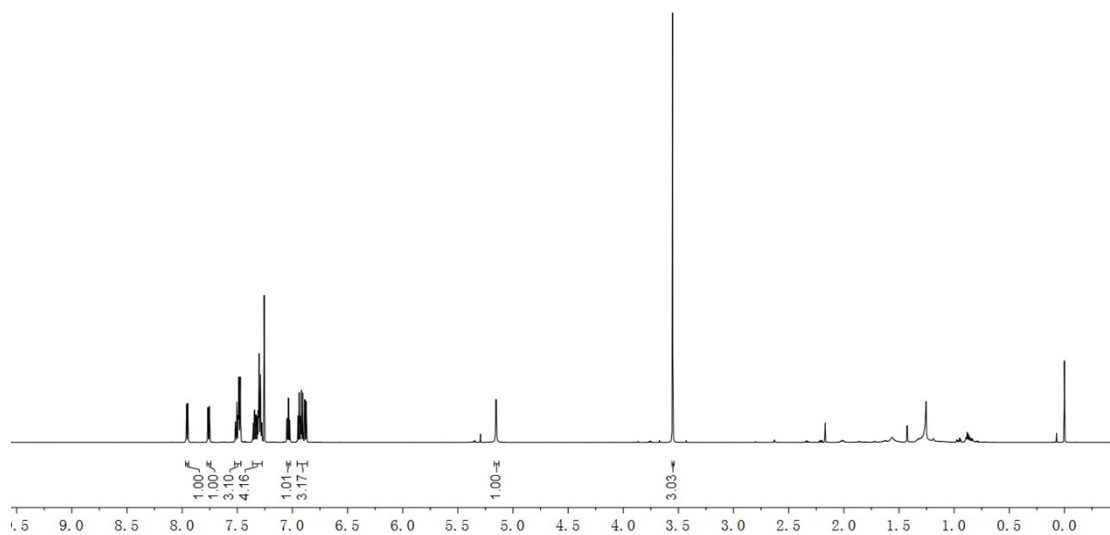
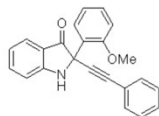


# <sup>1</sup>H and <sup>13</sup>C NMR data of compound 4k

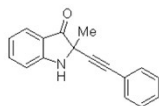
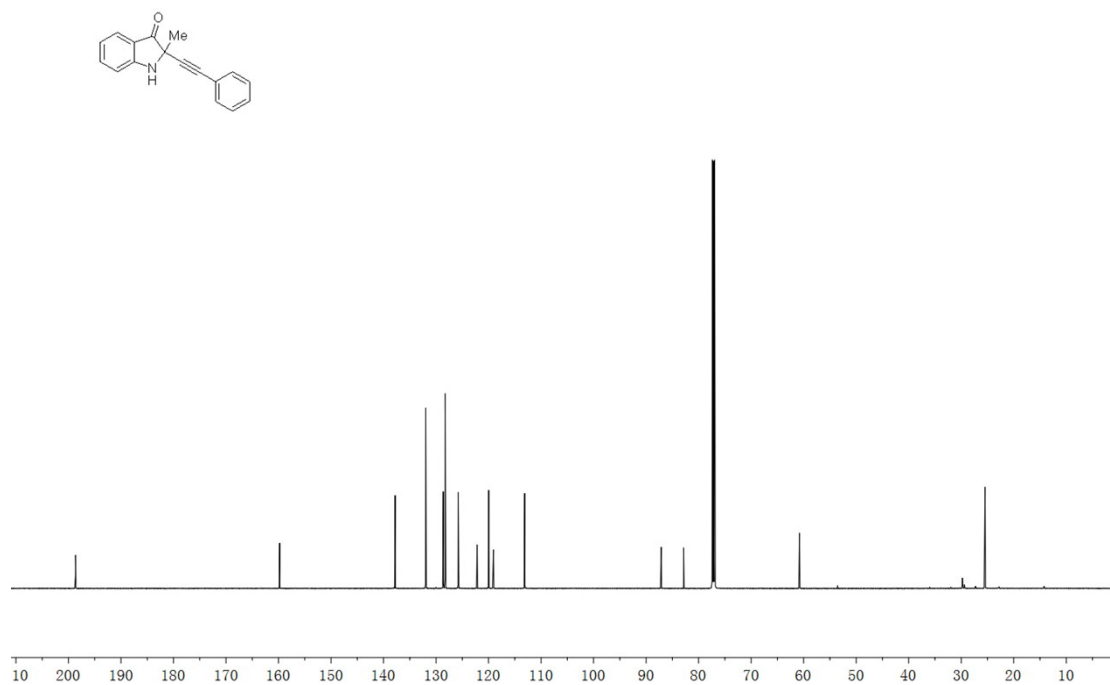
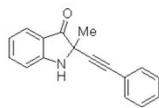
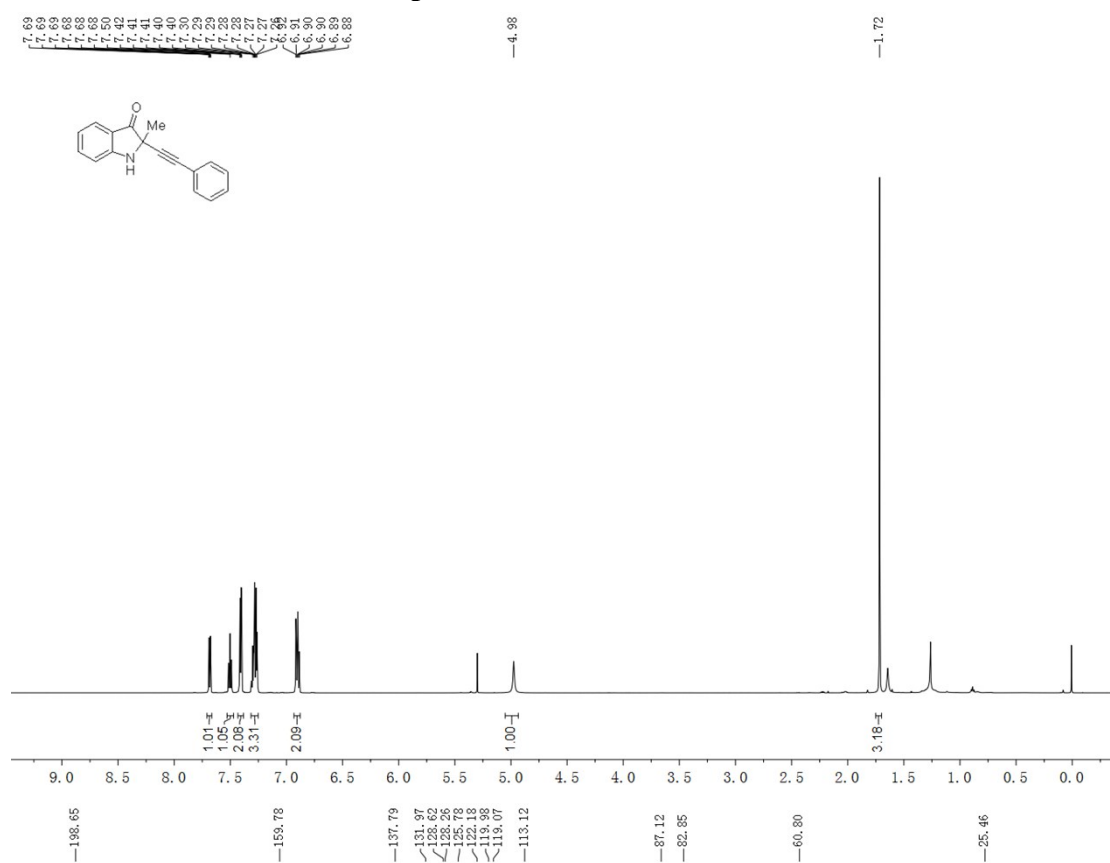


# <sup>1</sup>H and <sup>13</sup>C NMR data of compound 4l

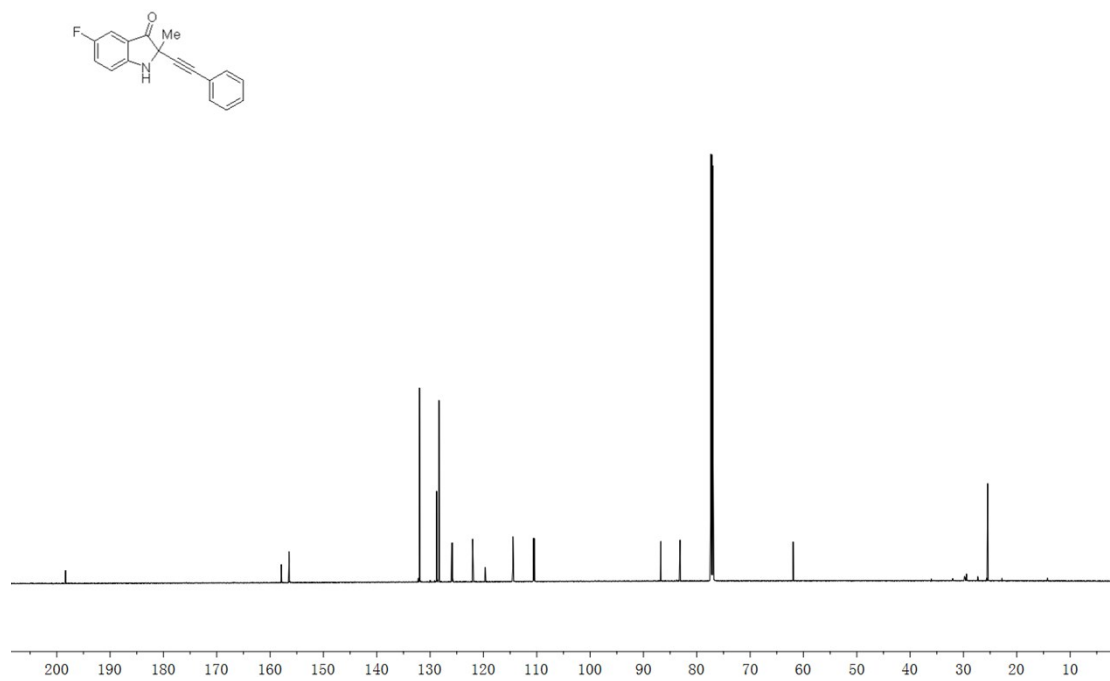
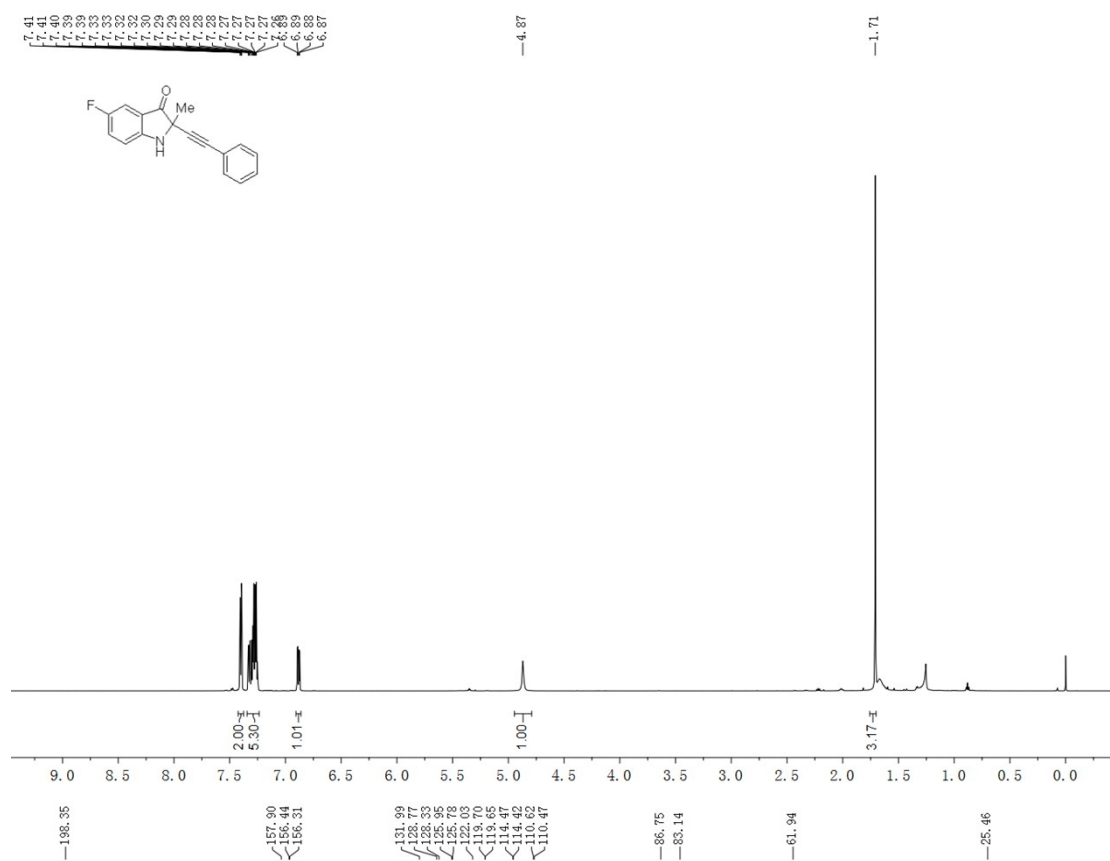
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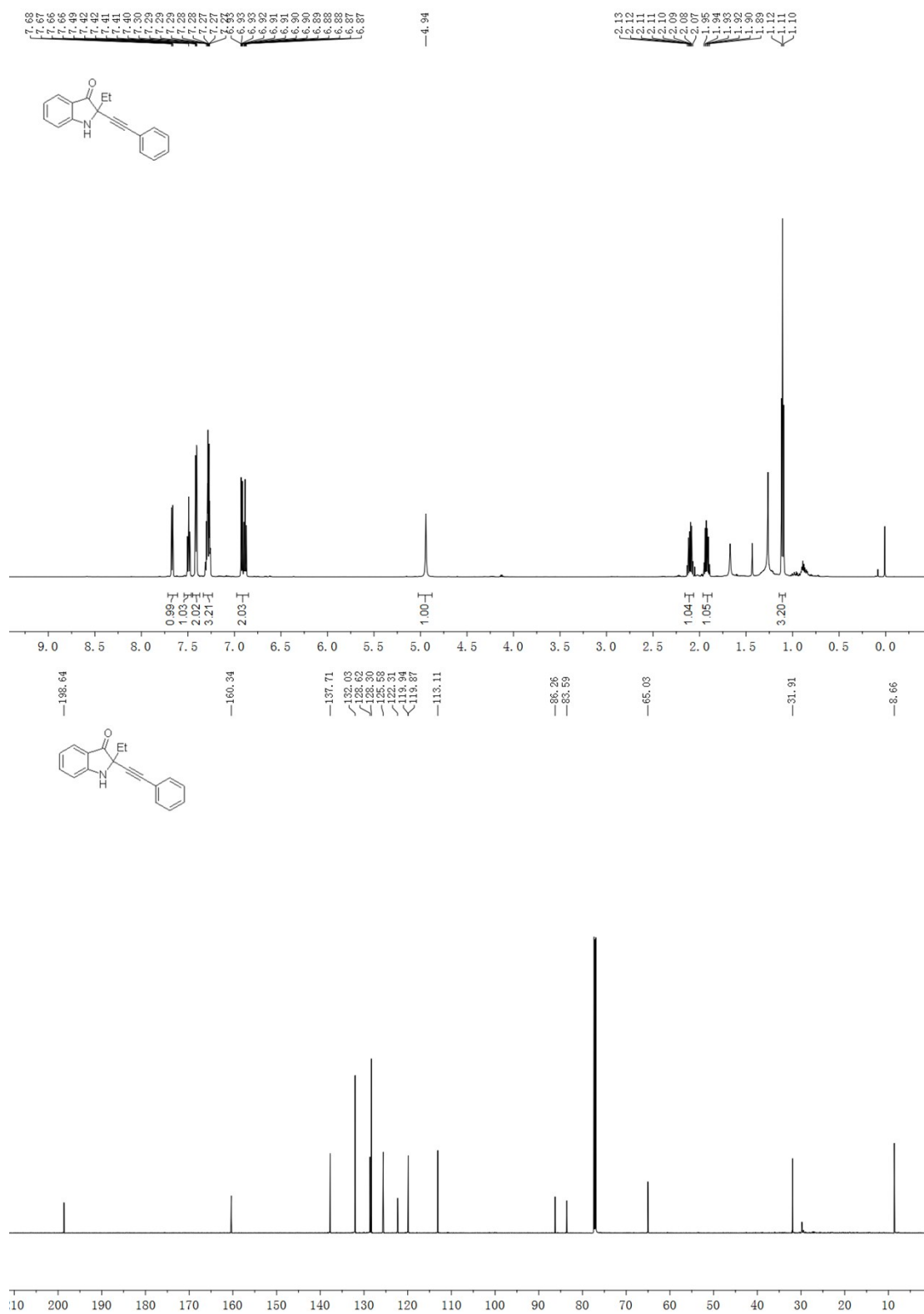
# <sup>1</sup>H and <sup>13</sup>C NMR data of compound 4m



# <sup>1</sup>H and <sup>13</sup>C NMR data of compound 4n

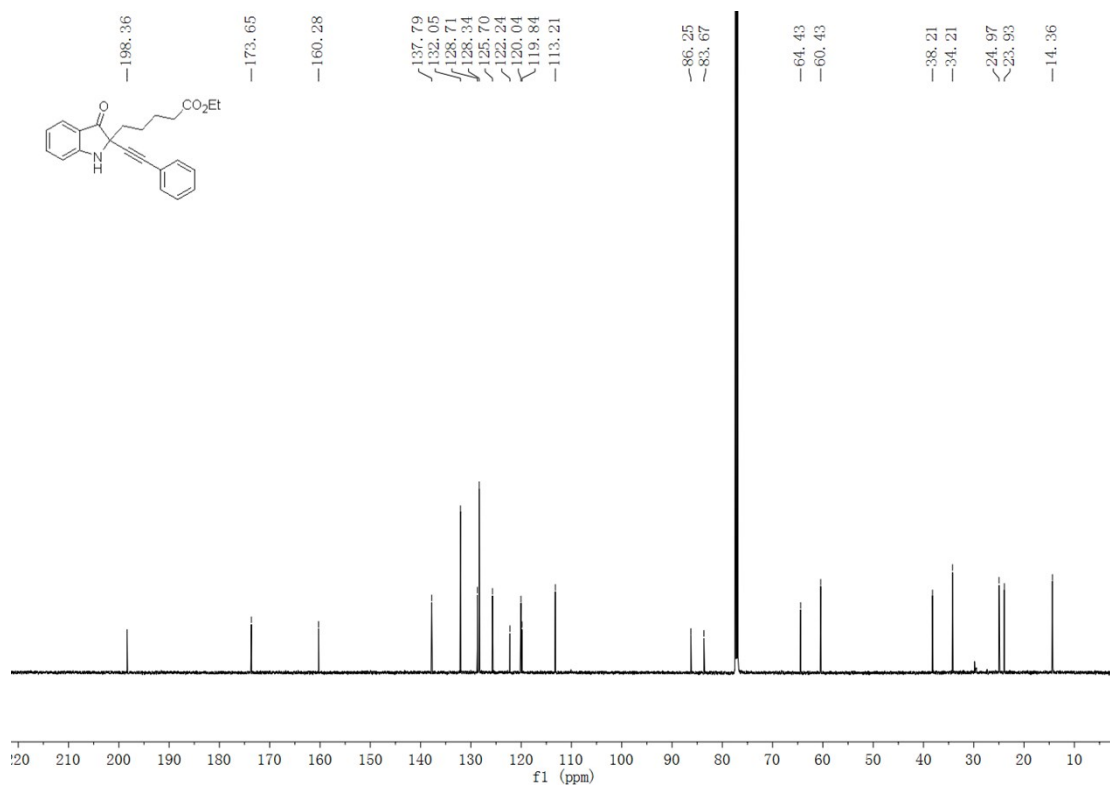
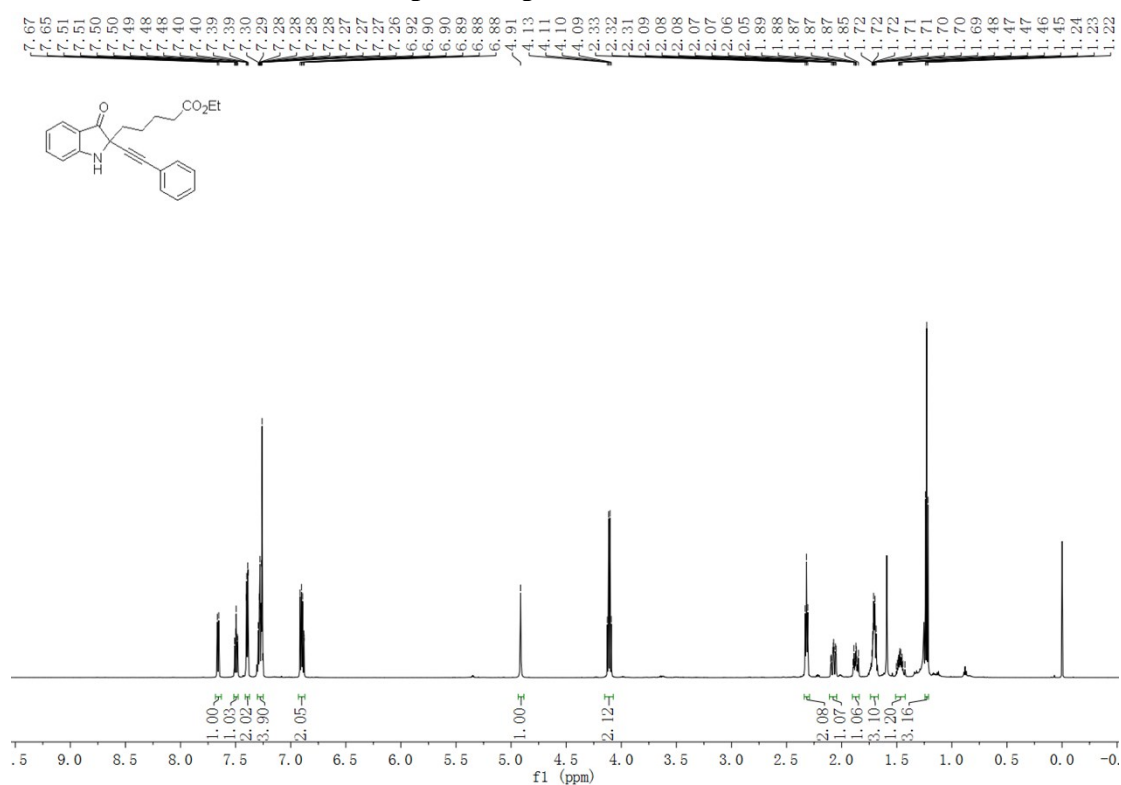


# <sup>1</sup>H and <sup>13</sup>C NMR data of compound 4o





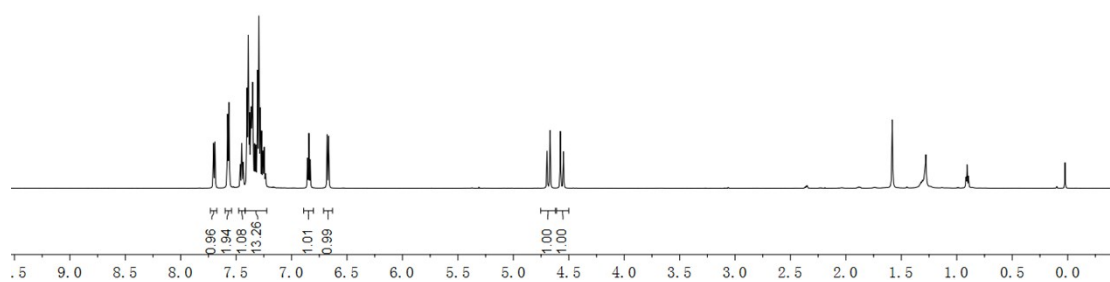
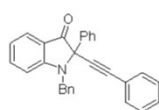
# <sup>1</sup>H and <sup>13</sup>C NMR data of compound 4p



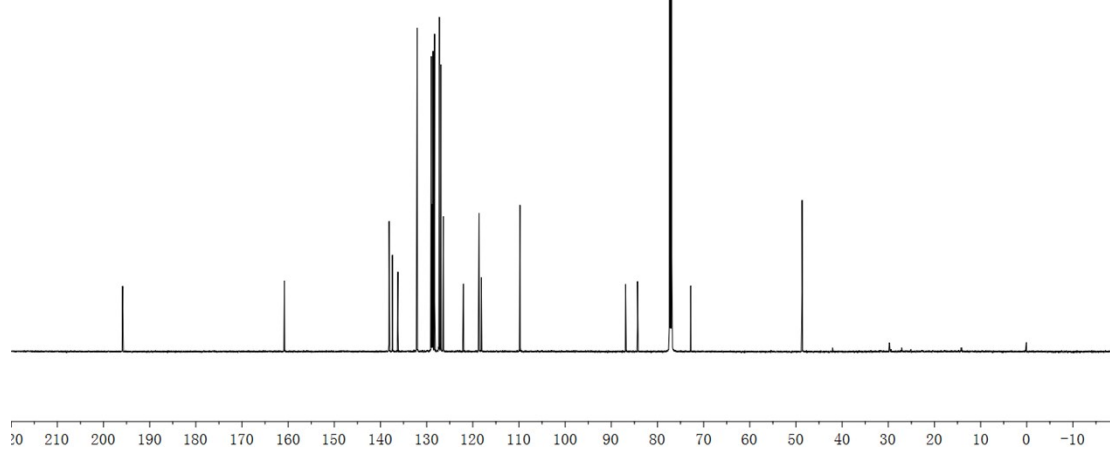
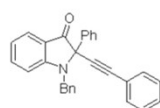


# <sup>1</sup>H and <sup>13</sup>C NMR data of compound 4r

7.70  
7.69  
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7.57  
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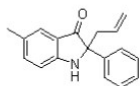
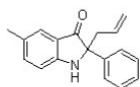
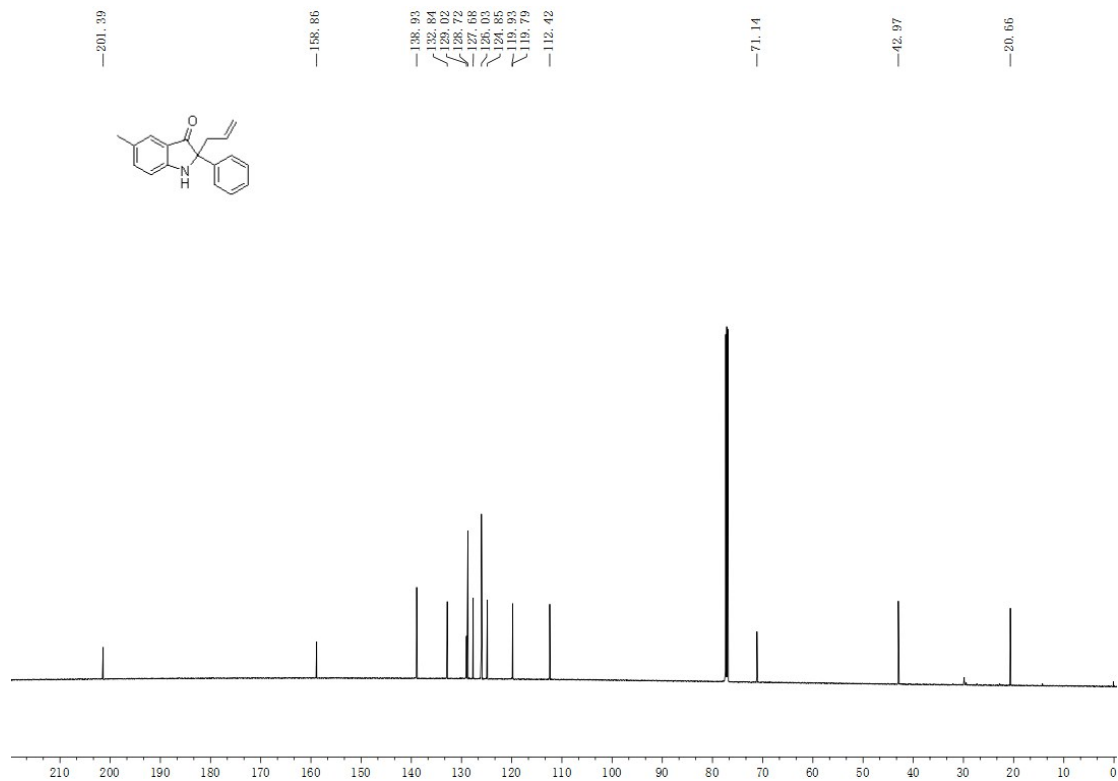
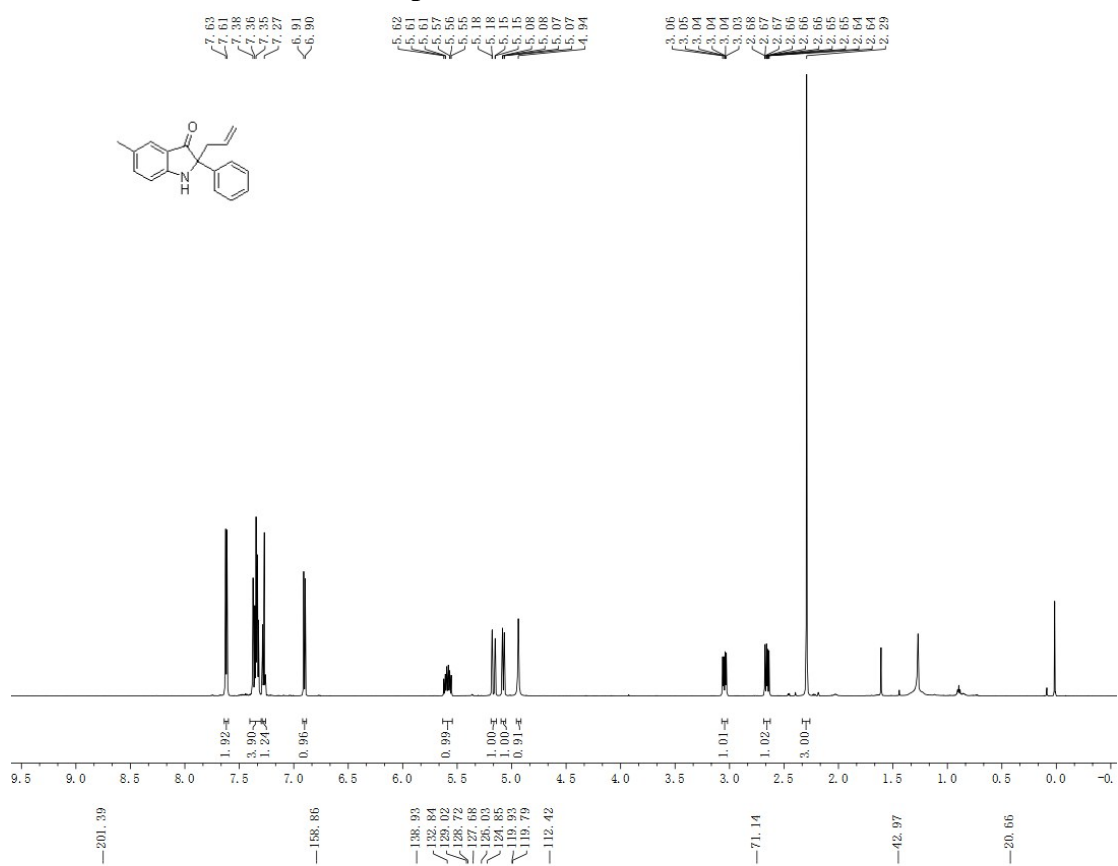


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48.67

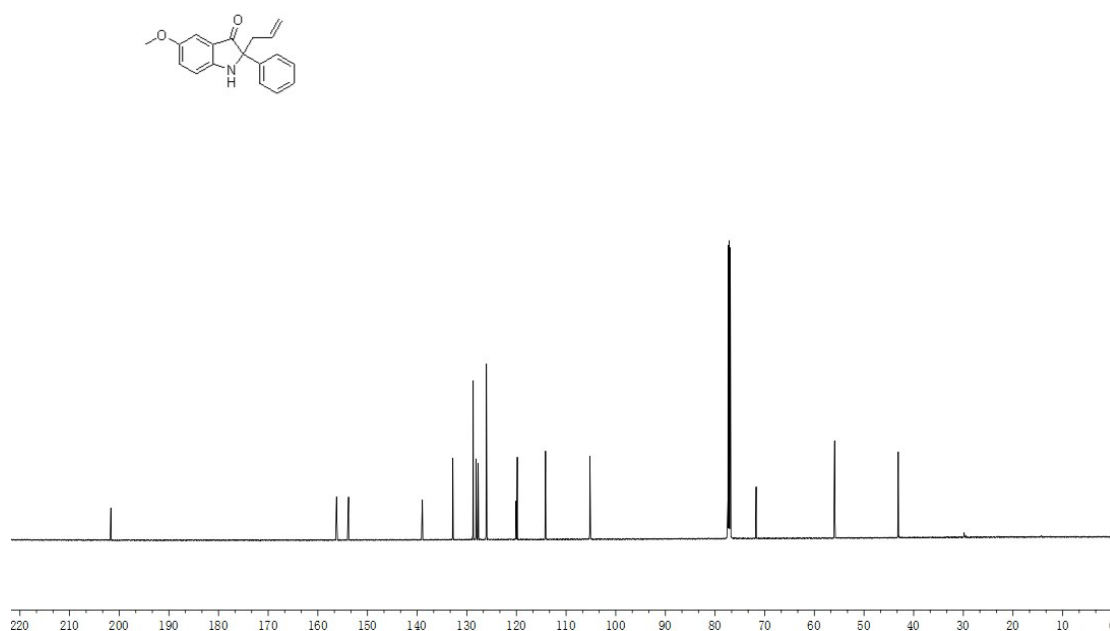
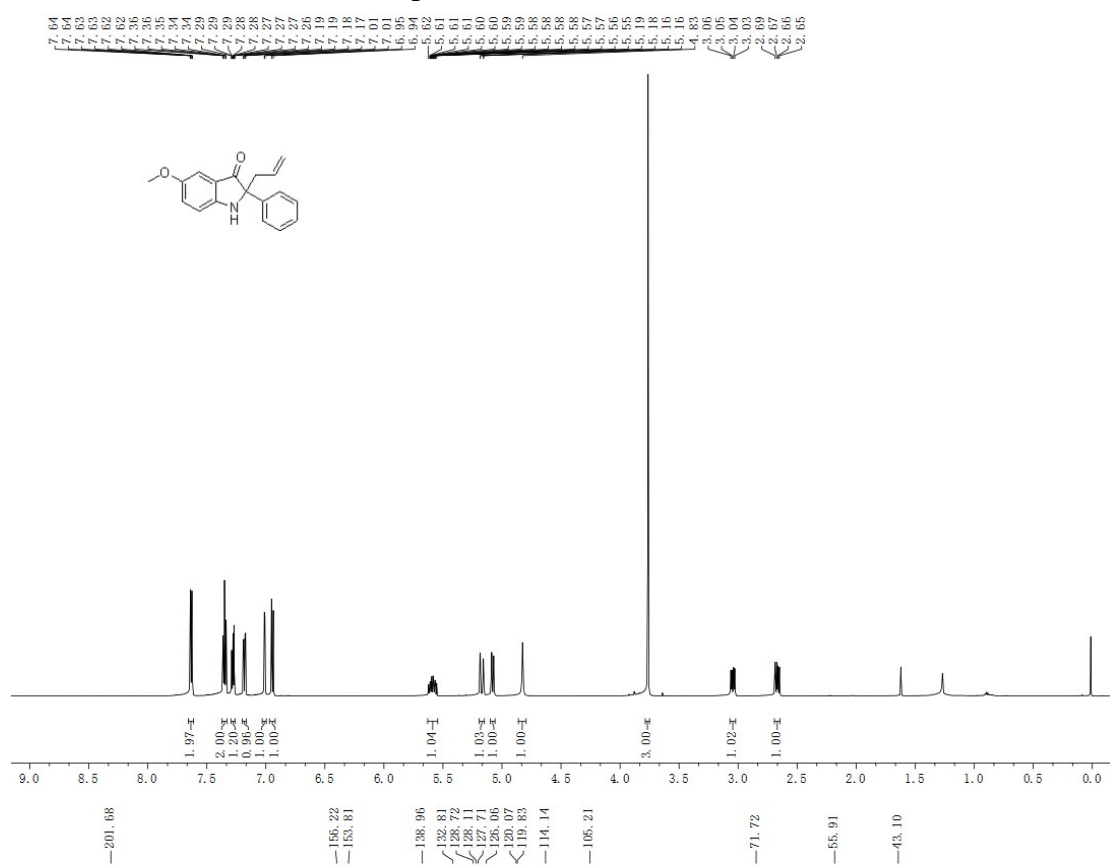




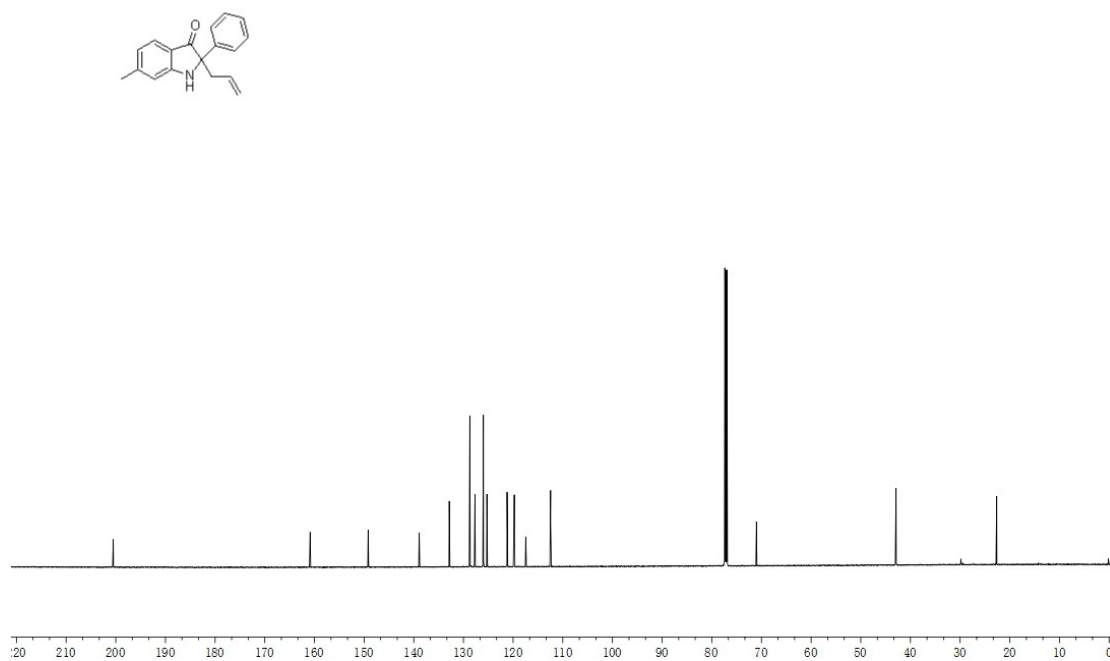
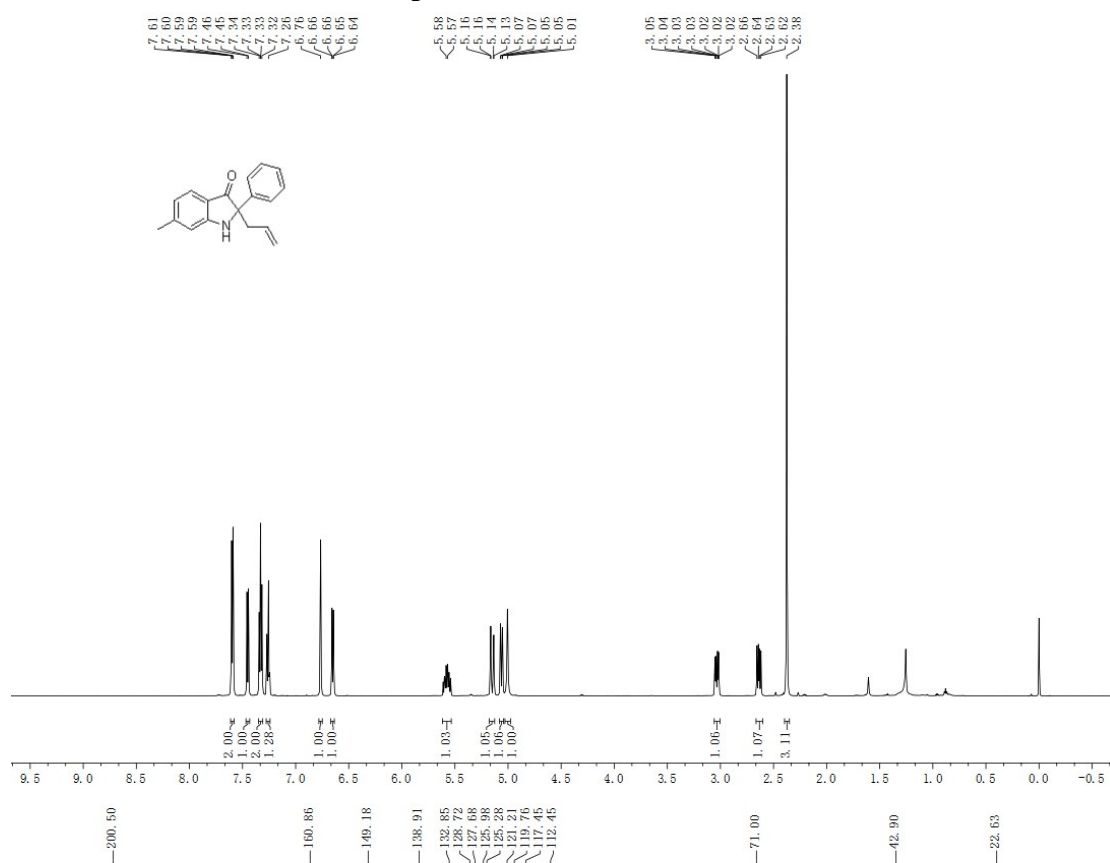
# <sup>1</sup>H and <sup>13</sup>C NMR data of compound 6c



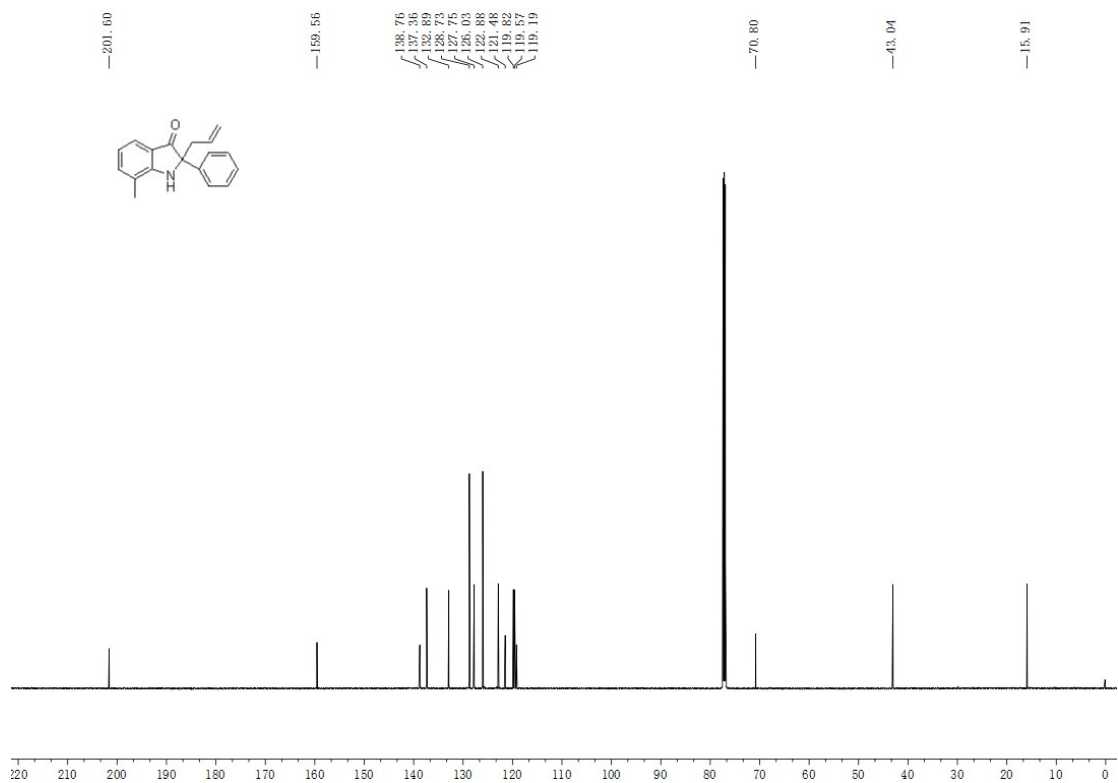
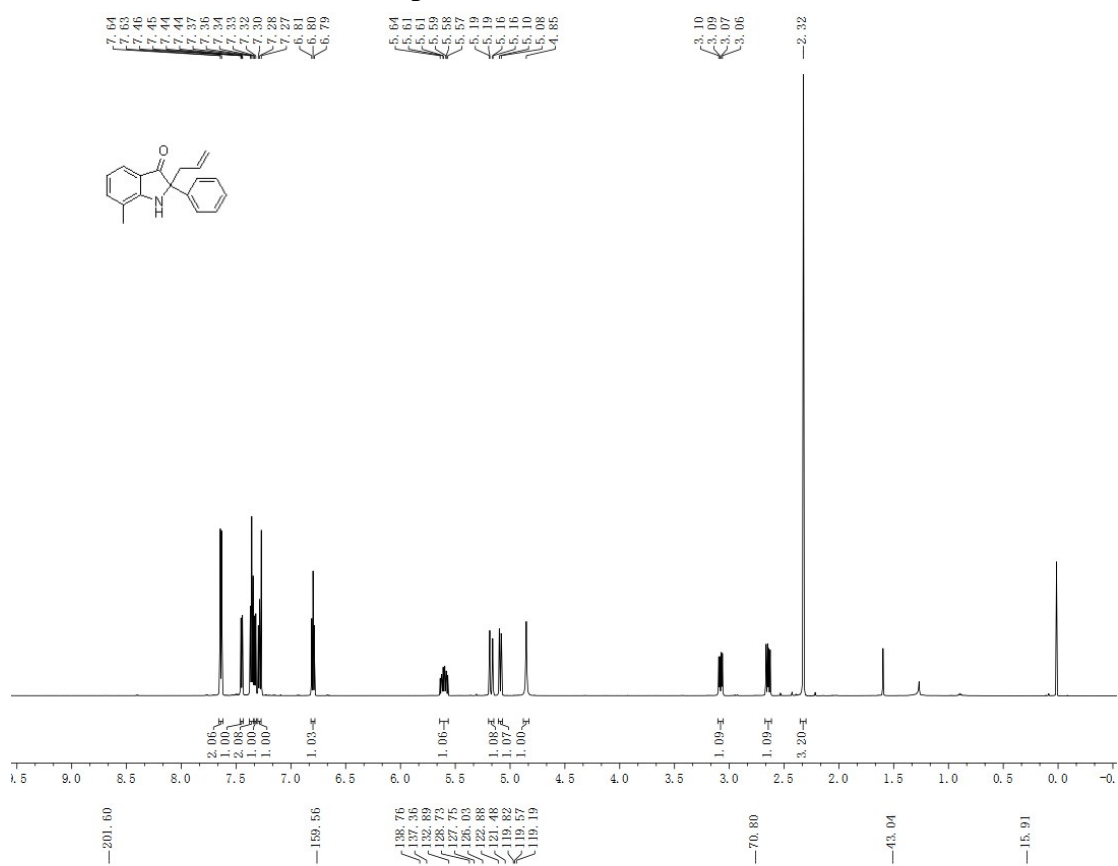
# <sup>1</sup>H and <sup>13</sup>C NMR data of compound 6d



# <sup>1</sup>H and <sup>13</sup>C NMR data of compound 6e

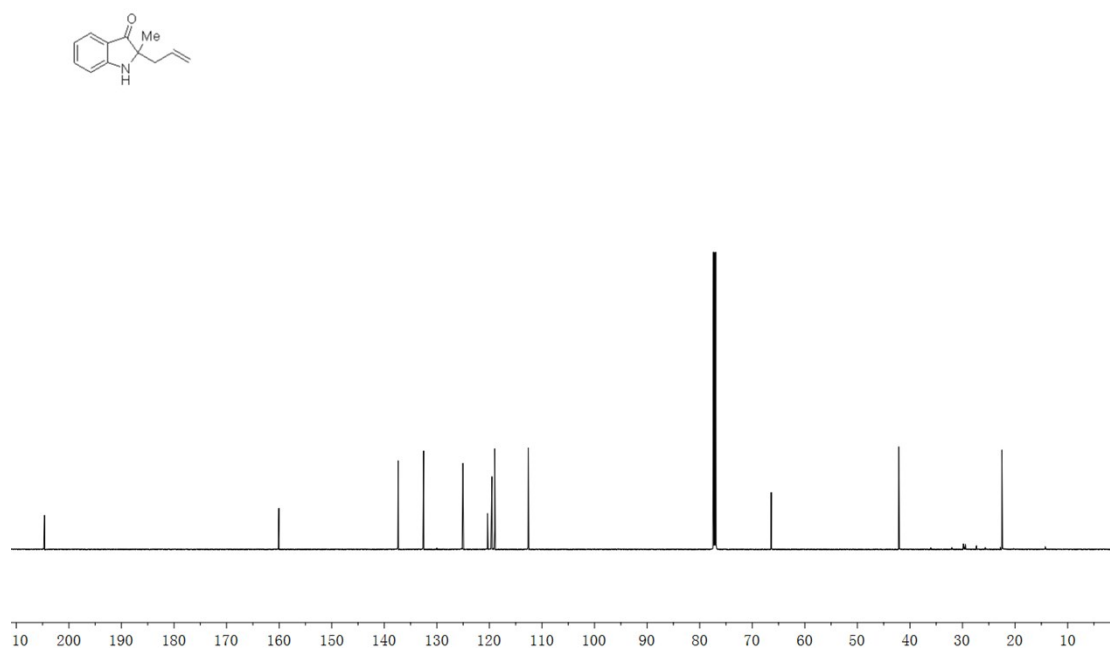
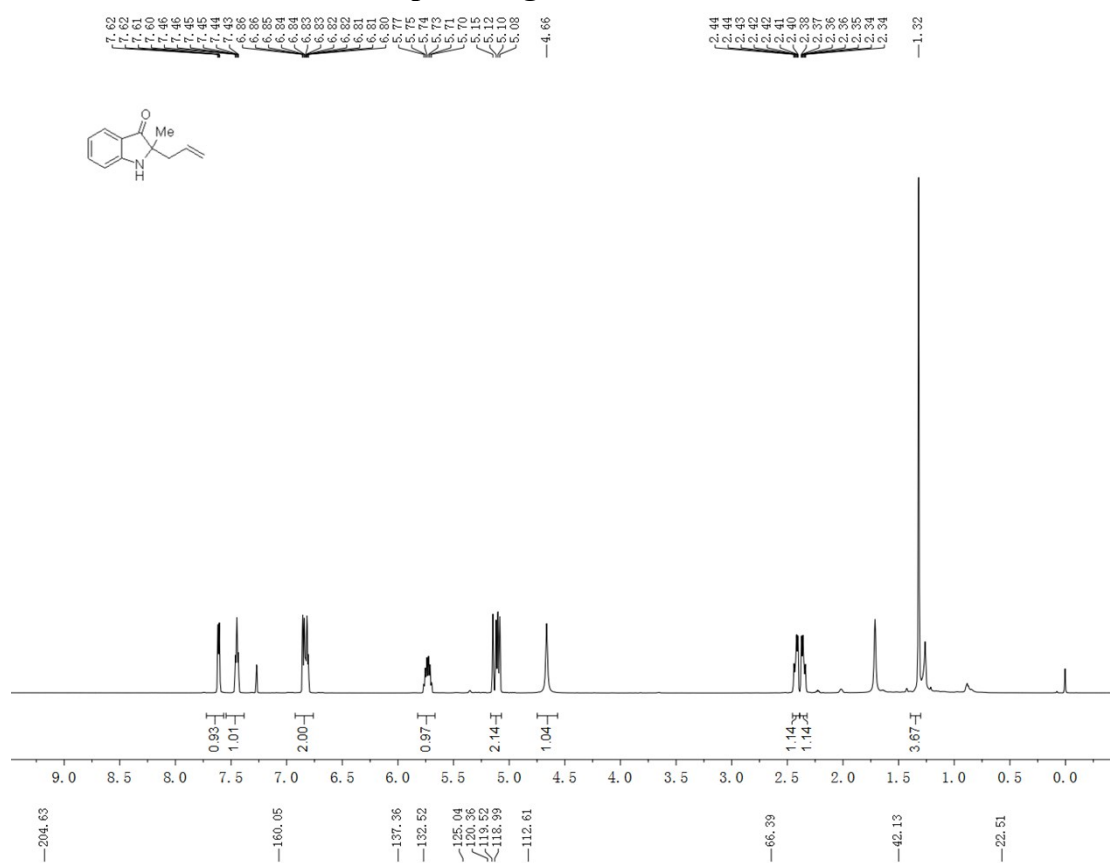


# <sup>1</sup>H and <sup>13</sup>C NMR data of compound 6f

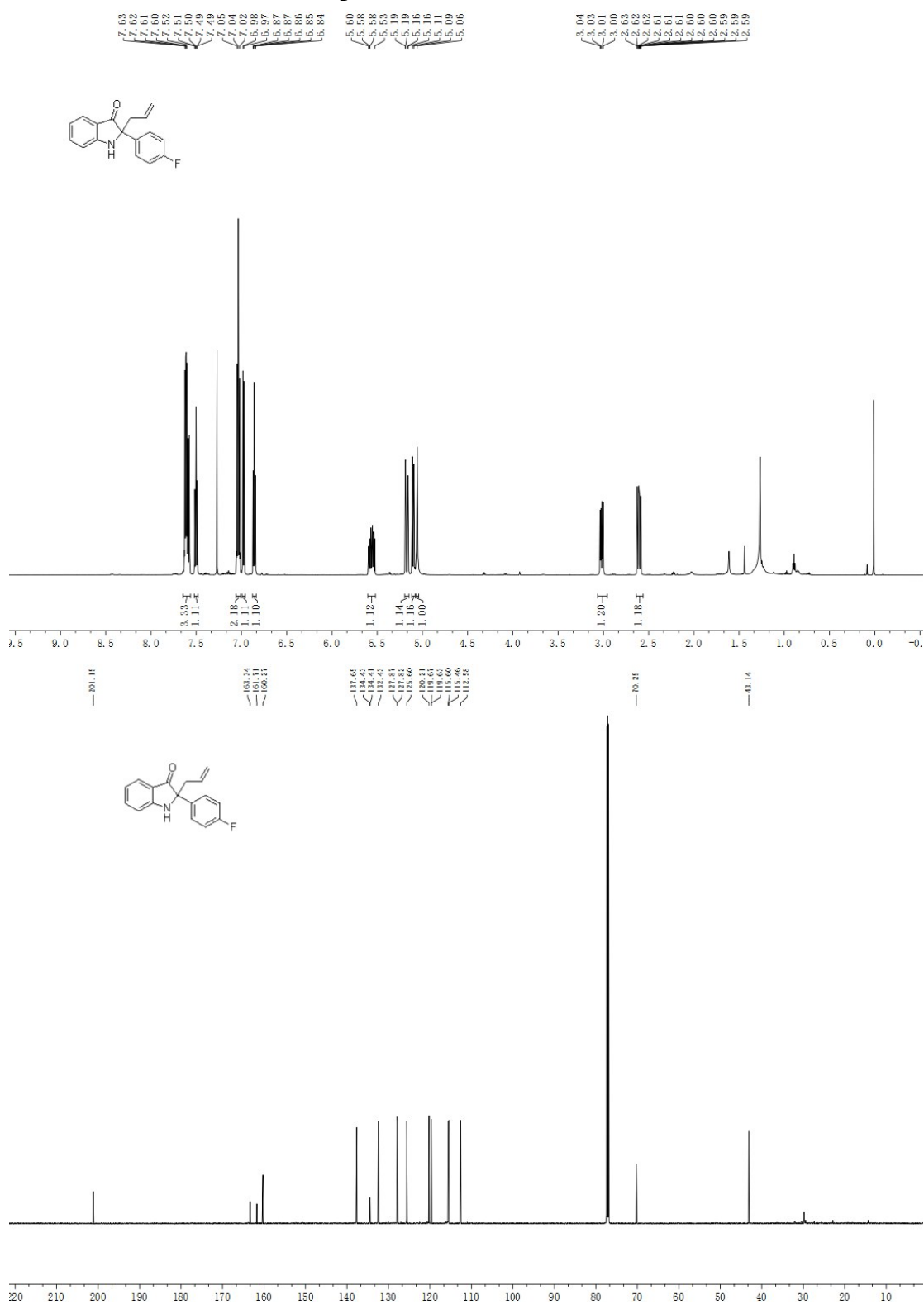




# <sup>1</sup>H and <sup>13</sup>C NMR data of compound 6g

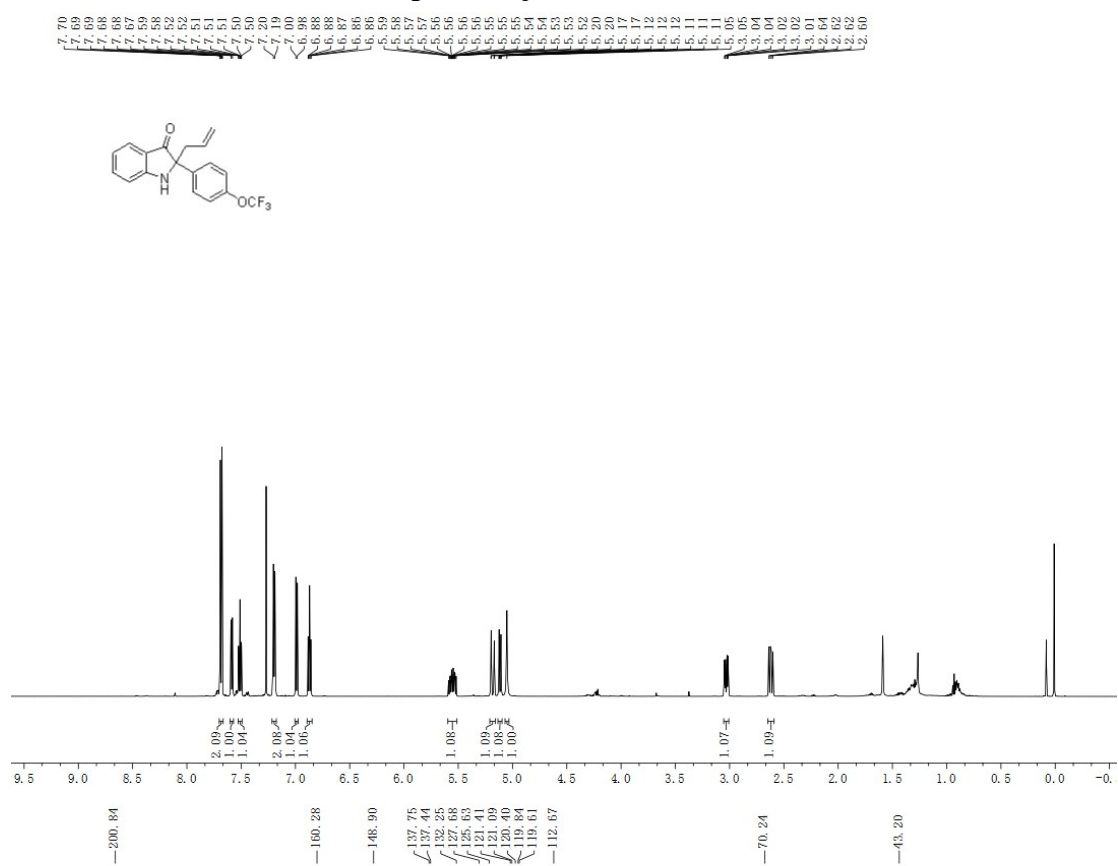


# <sup>1</sup>H and <sup>13</sup>C NMR data of compound 6h

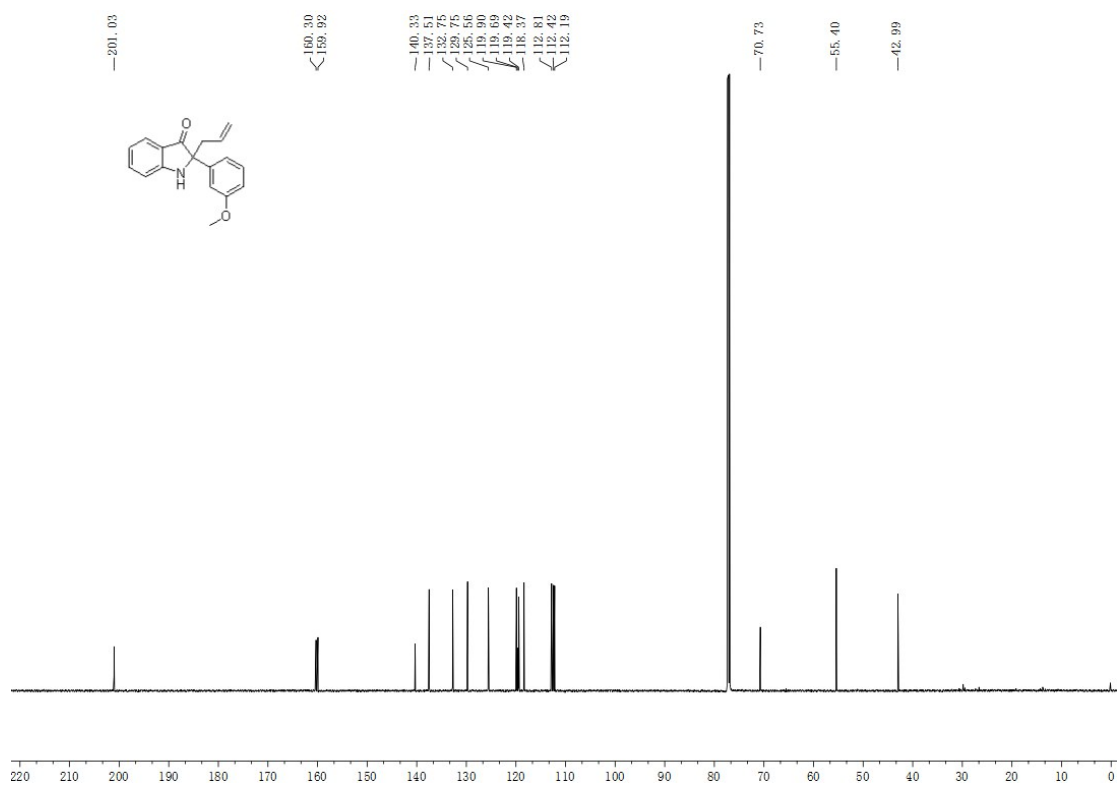
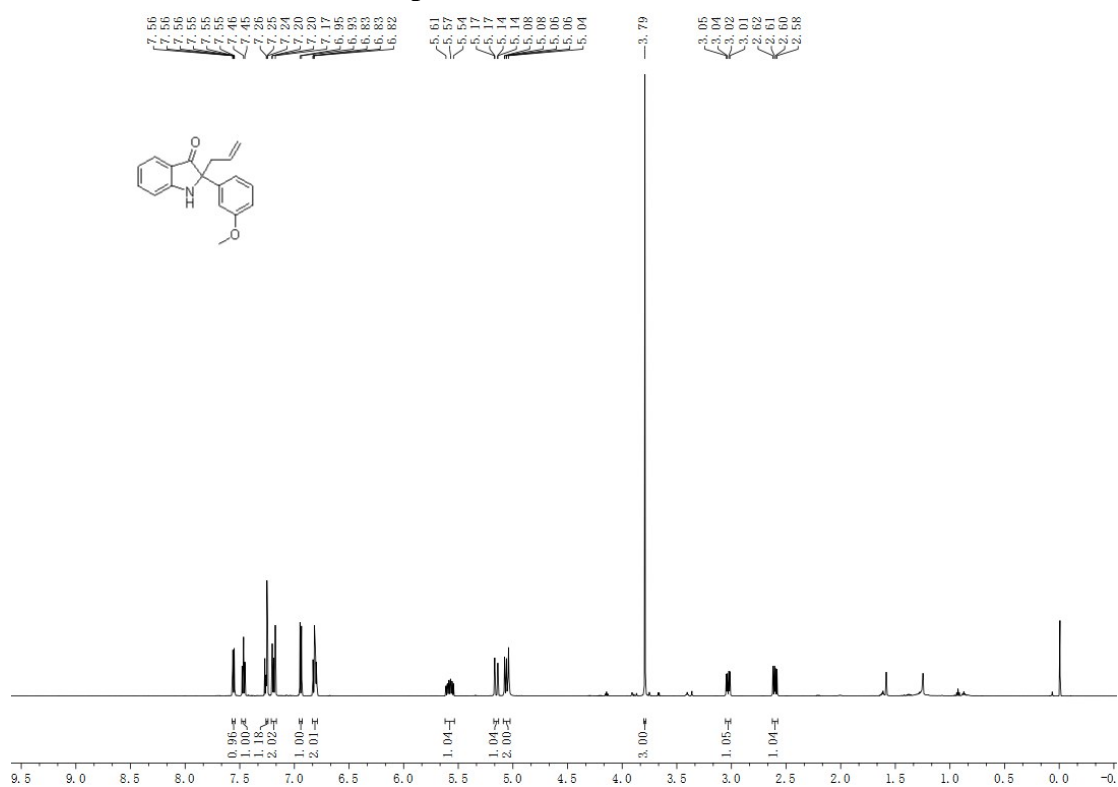




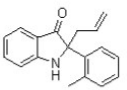
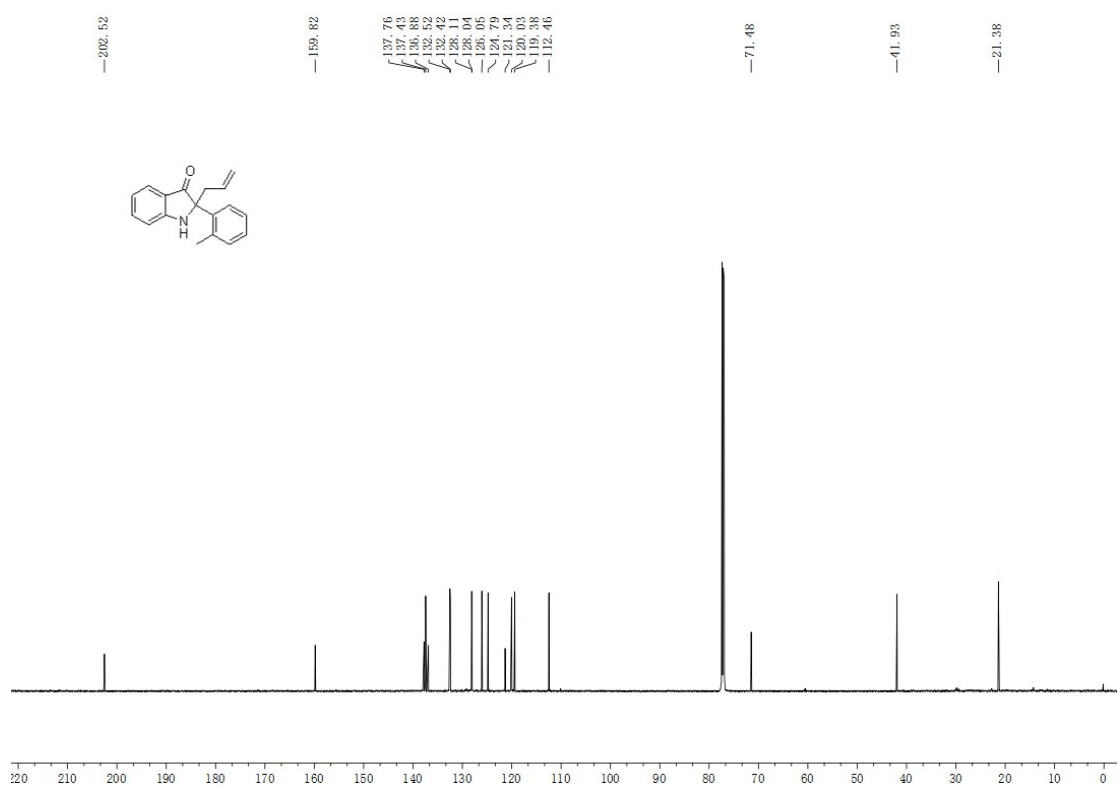
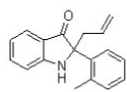
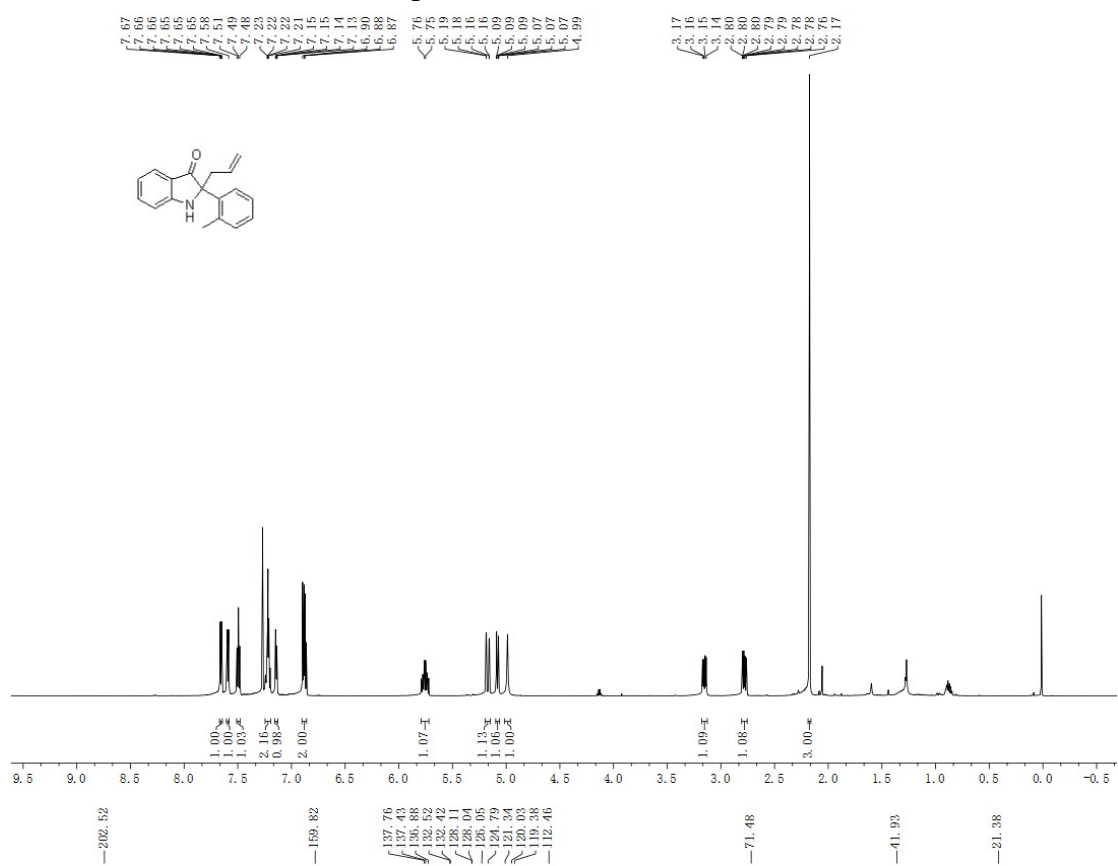
# <sup>1</sup>H and <sup>13</sup>C NMR data of compound 6j



# $^1\text{H}$ and $^{13}\text{C}$ NMR data of compound 6k



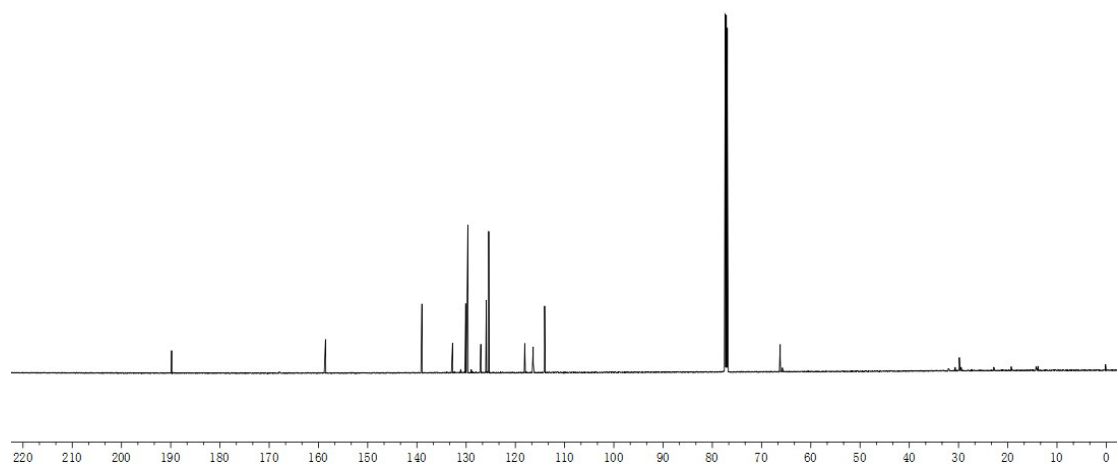
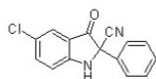
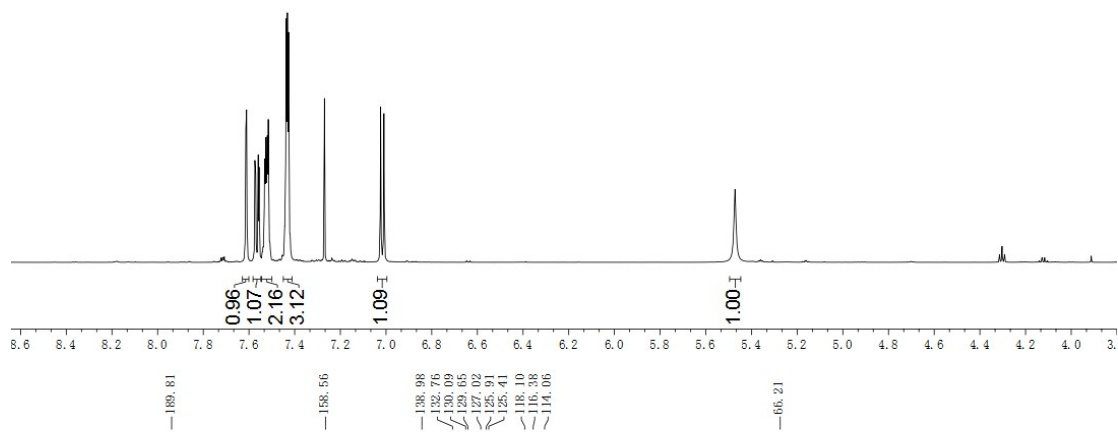
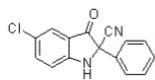
# <sup>1</sup>H and <sup>13</sup>C NMR data of compound 6l



# <sup>1</sup>H and <sup>13</sup>C NMR data of compound 6m

7.61  
7.57  
7.56  
7.56  
7.53  
7.52  
7.52  
7.43  
7.43  
7.09  
7.01

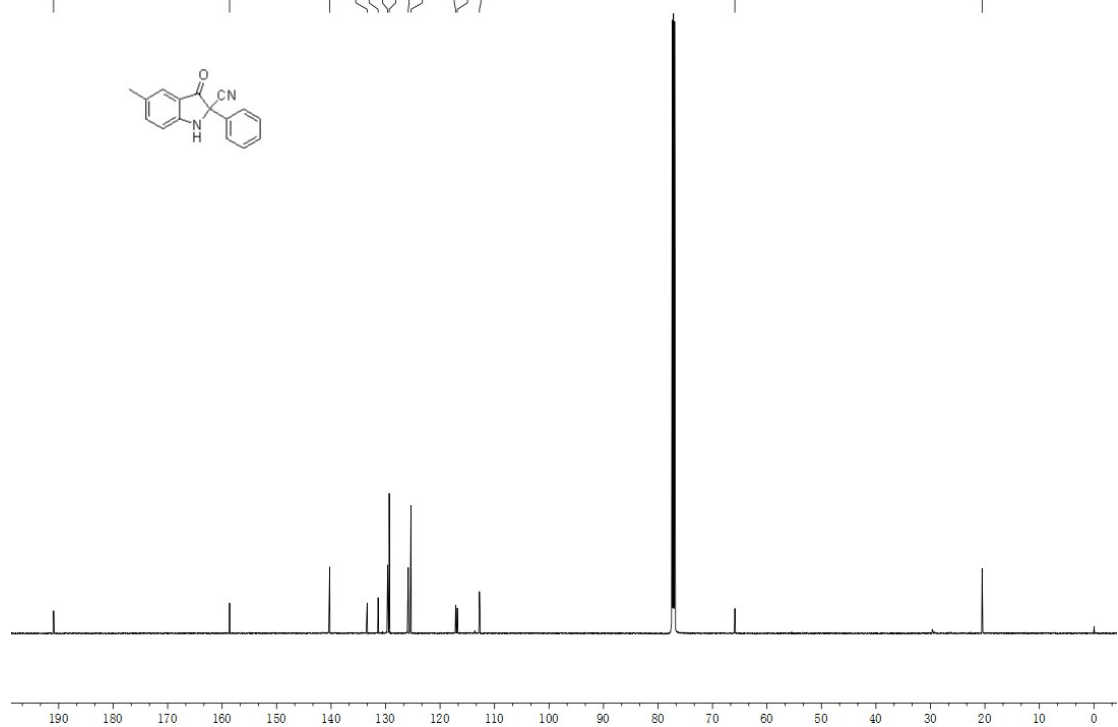
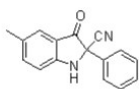
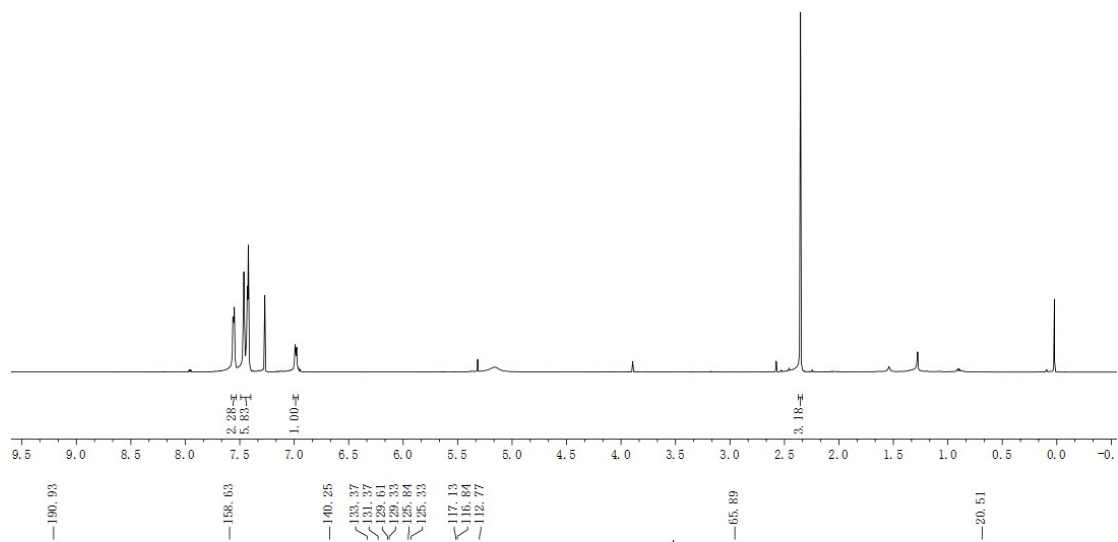
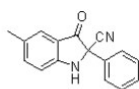
5.47



# <sup>1</sup>H and <sup>13</sup>C NMR data of compound 6n

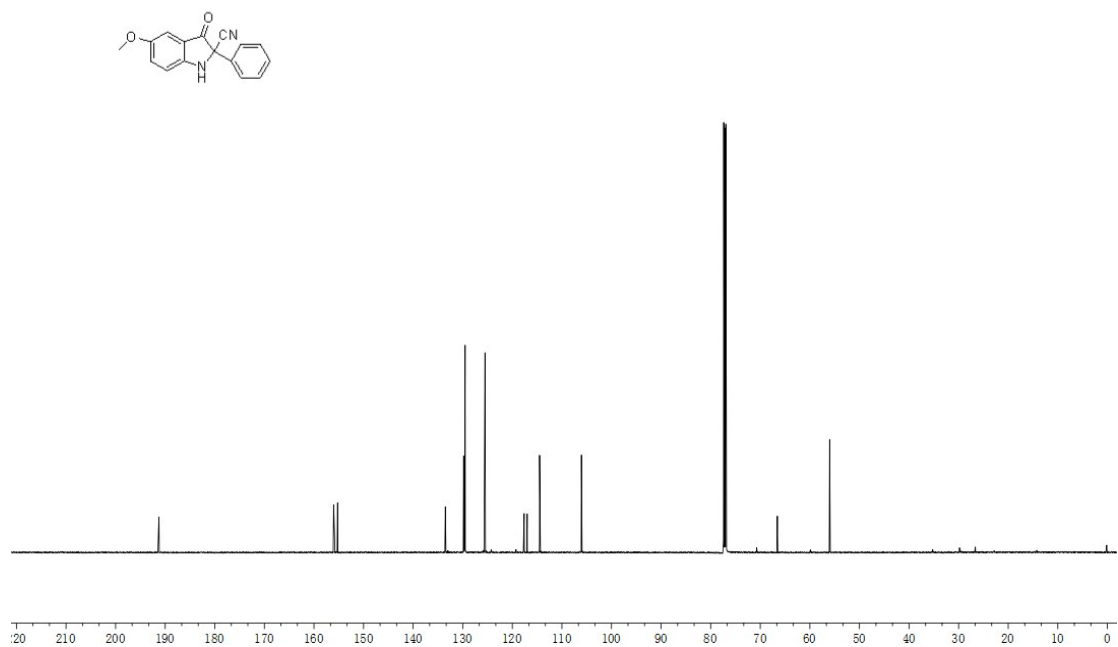
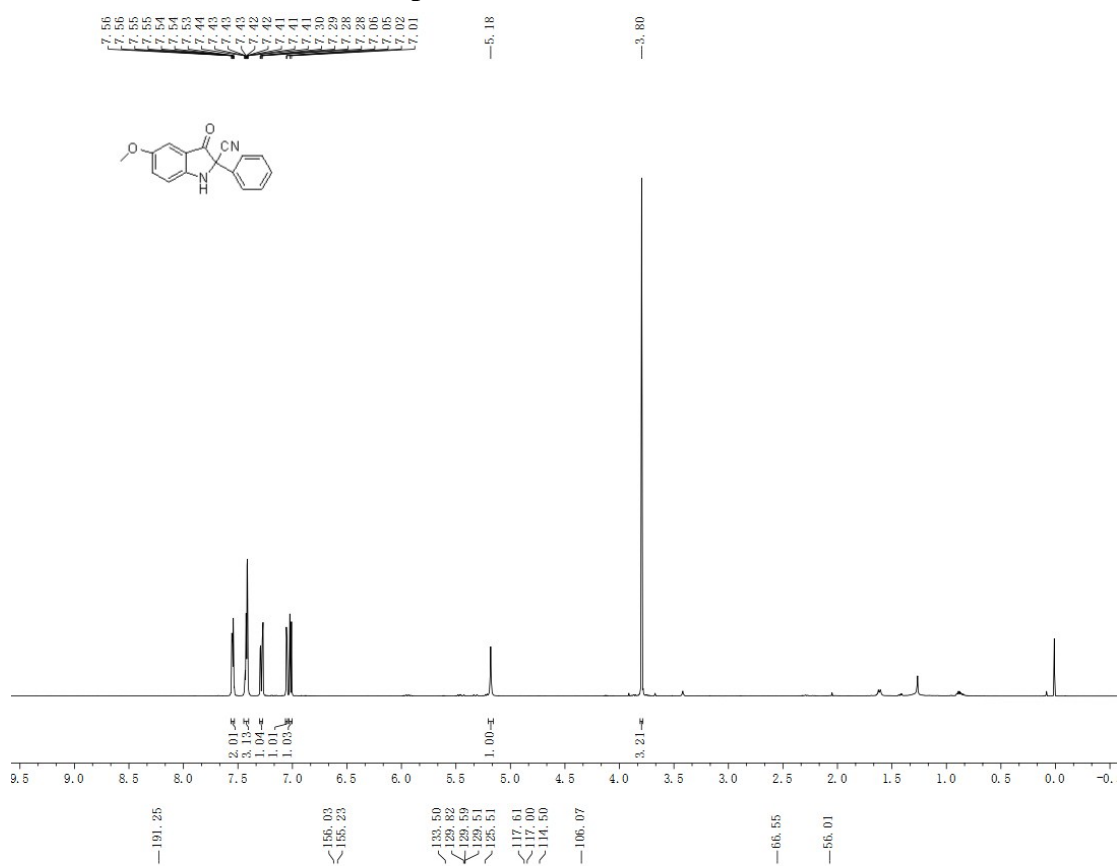
7.56  
7.50  
7.48  
7.43  
7.42  
6.99  
6.98

2.35

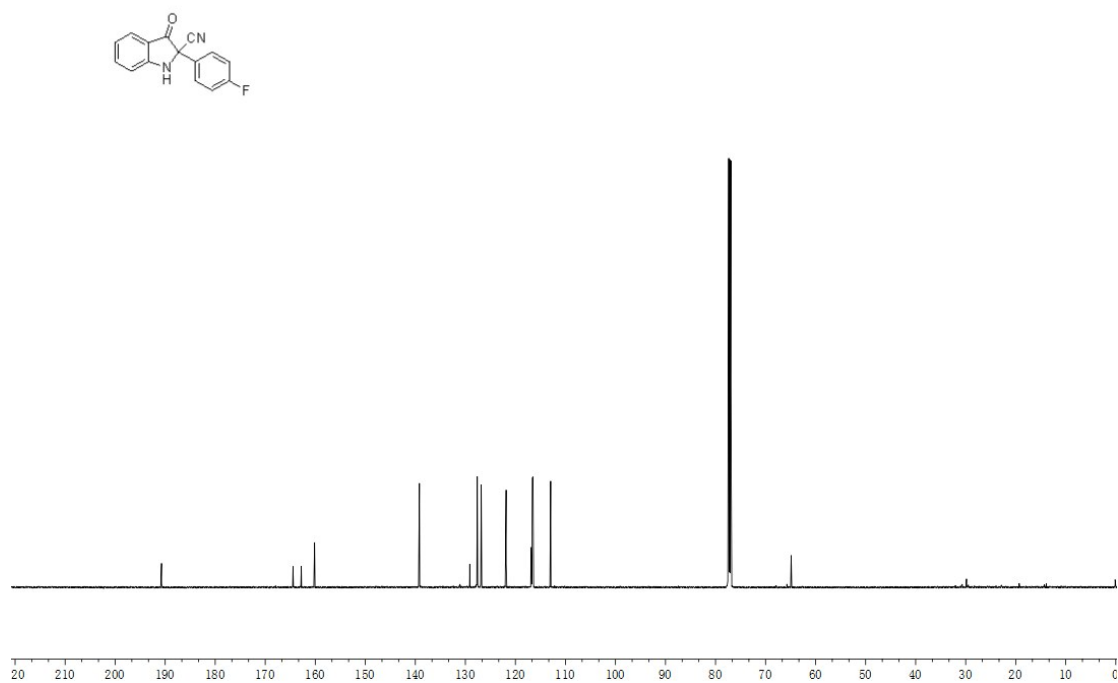
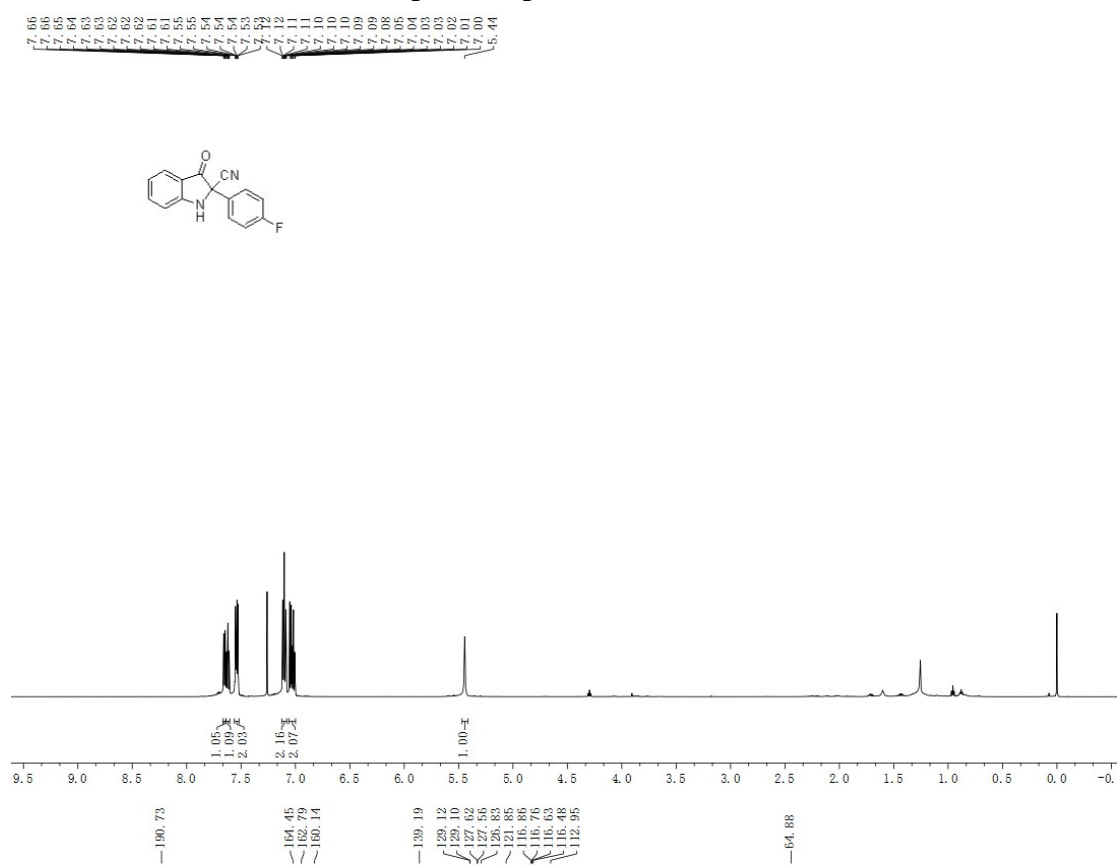




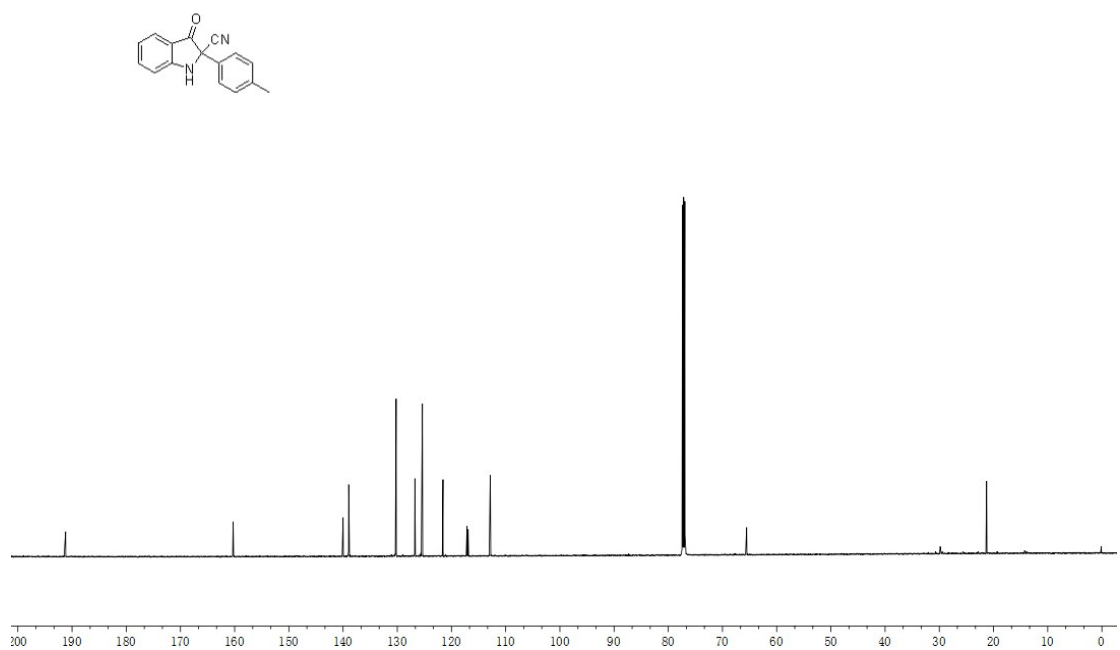
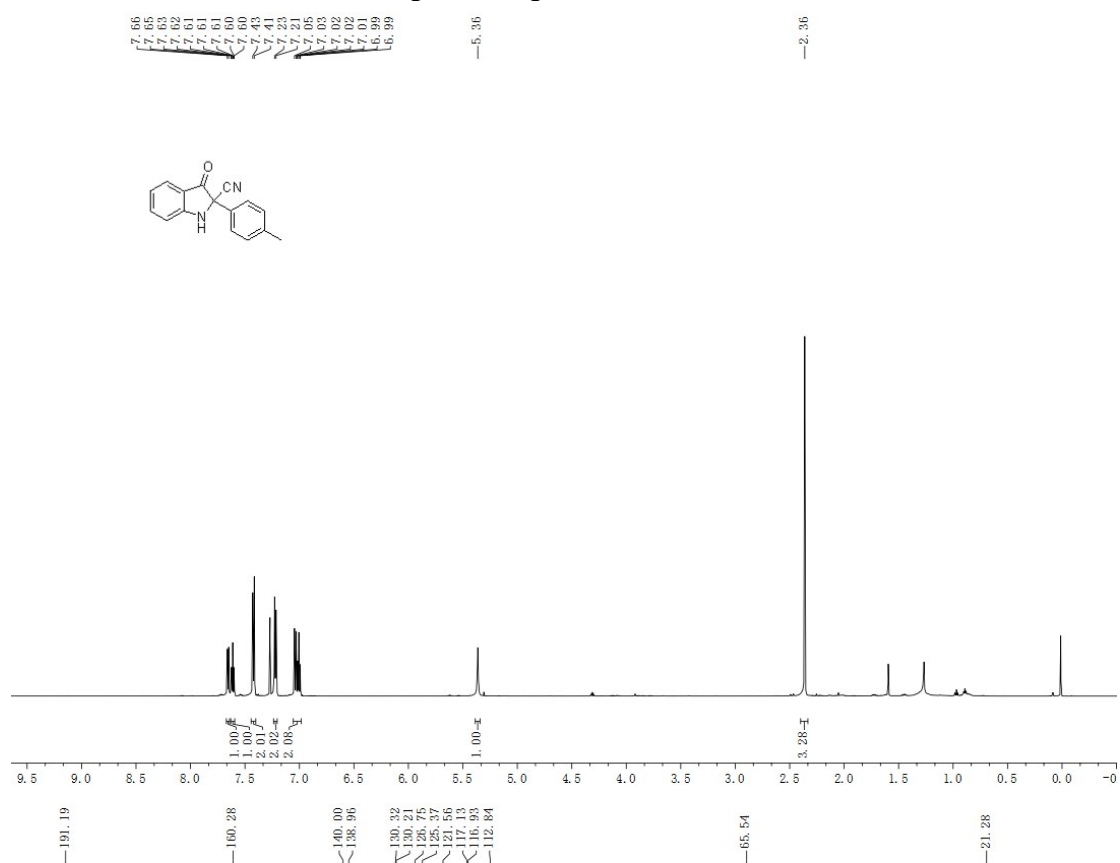
**<sup>1</sup>H and <sup>13</sup>C NMR data of compound 6o**



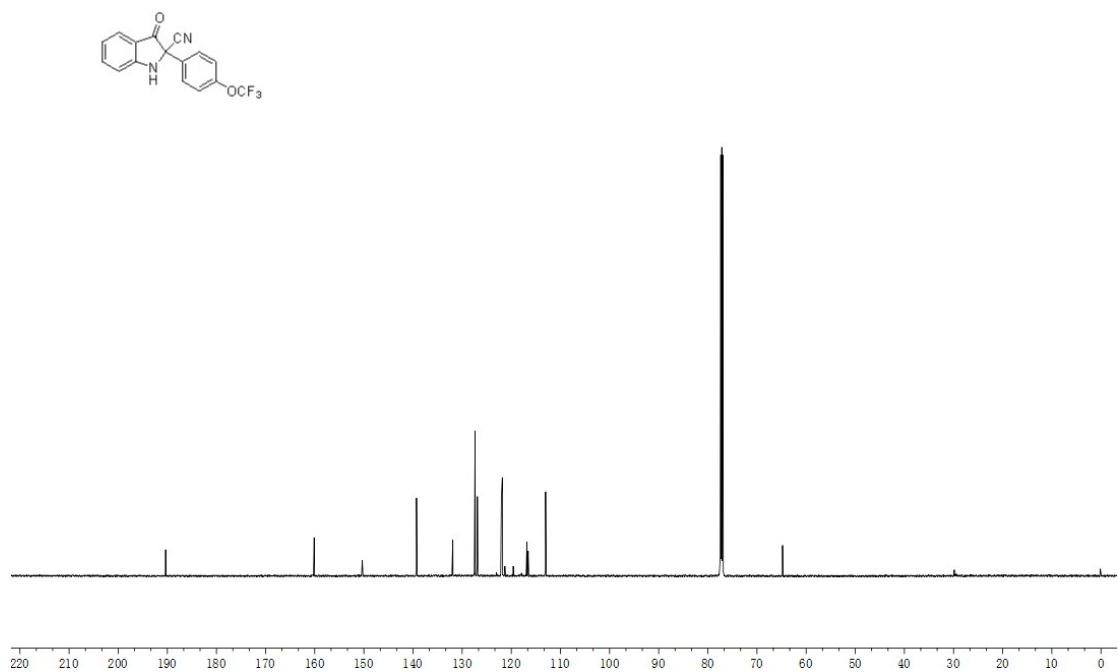
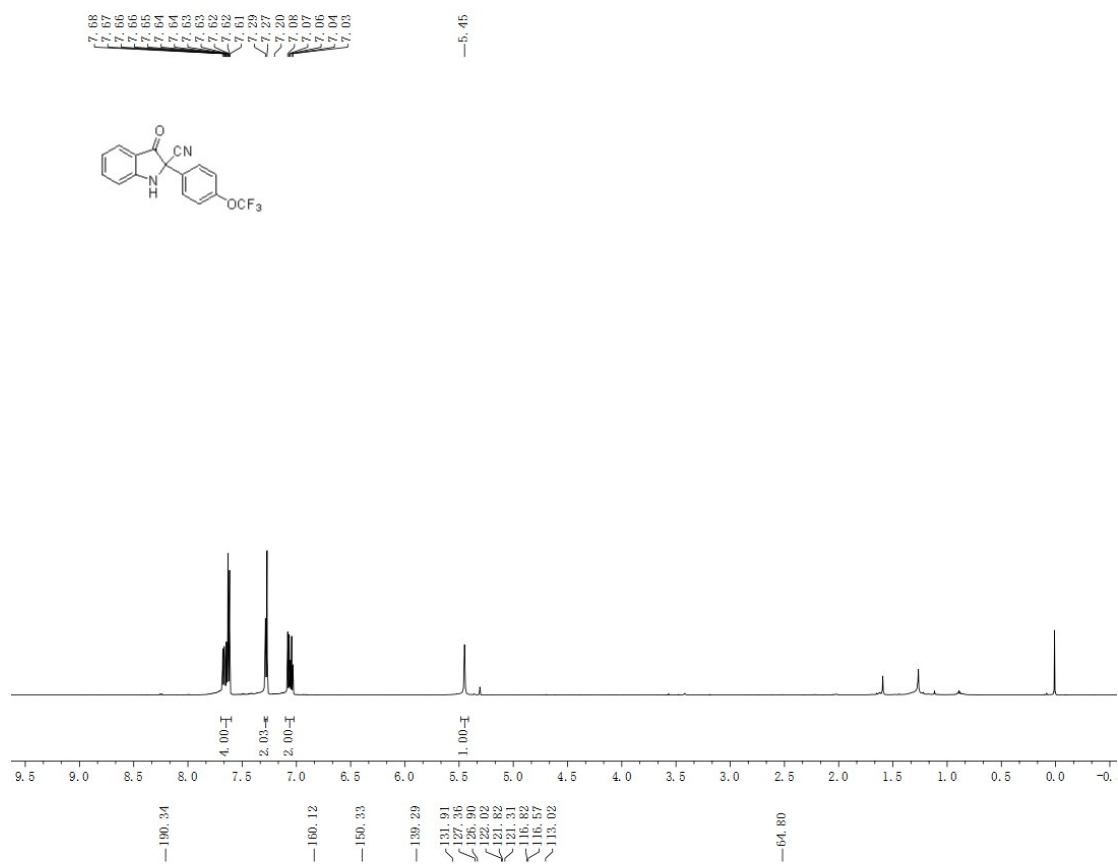
# <sup>1</sup>H and <sup>13</sup>C NMR data of compound 6p



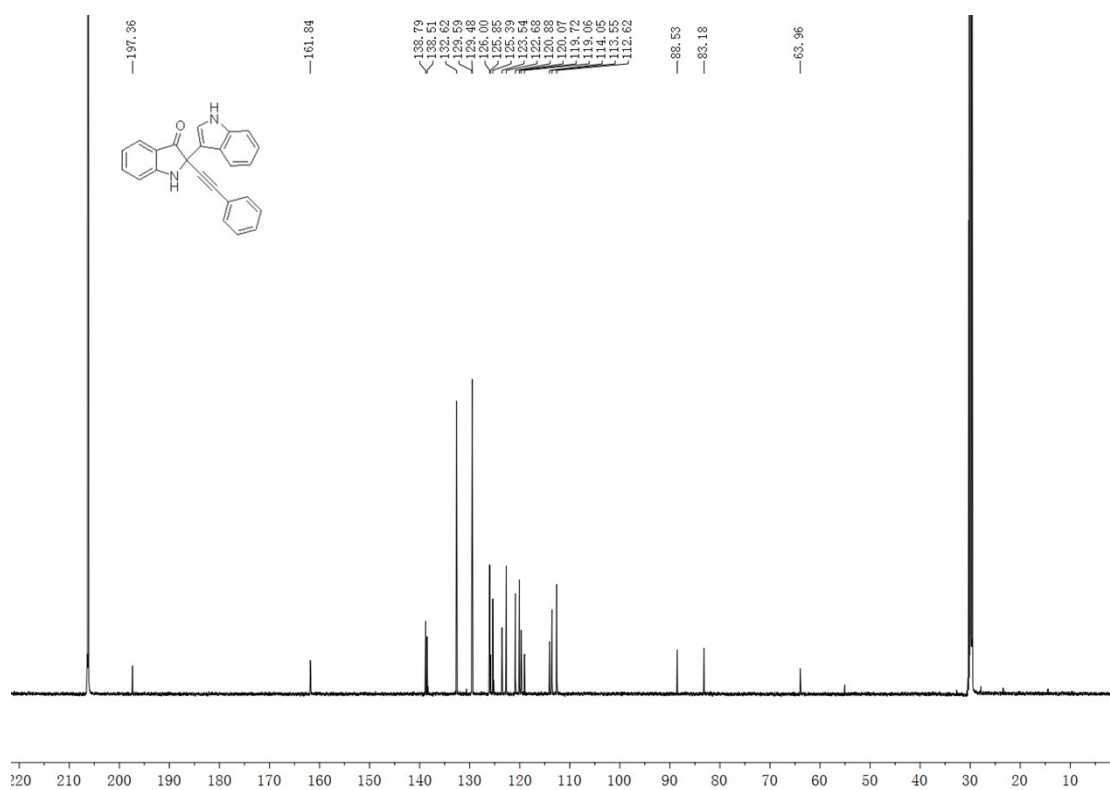
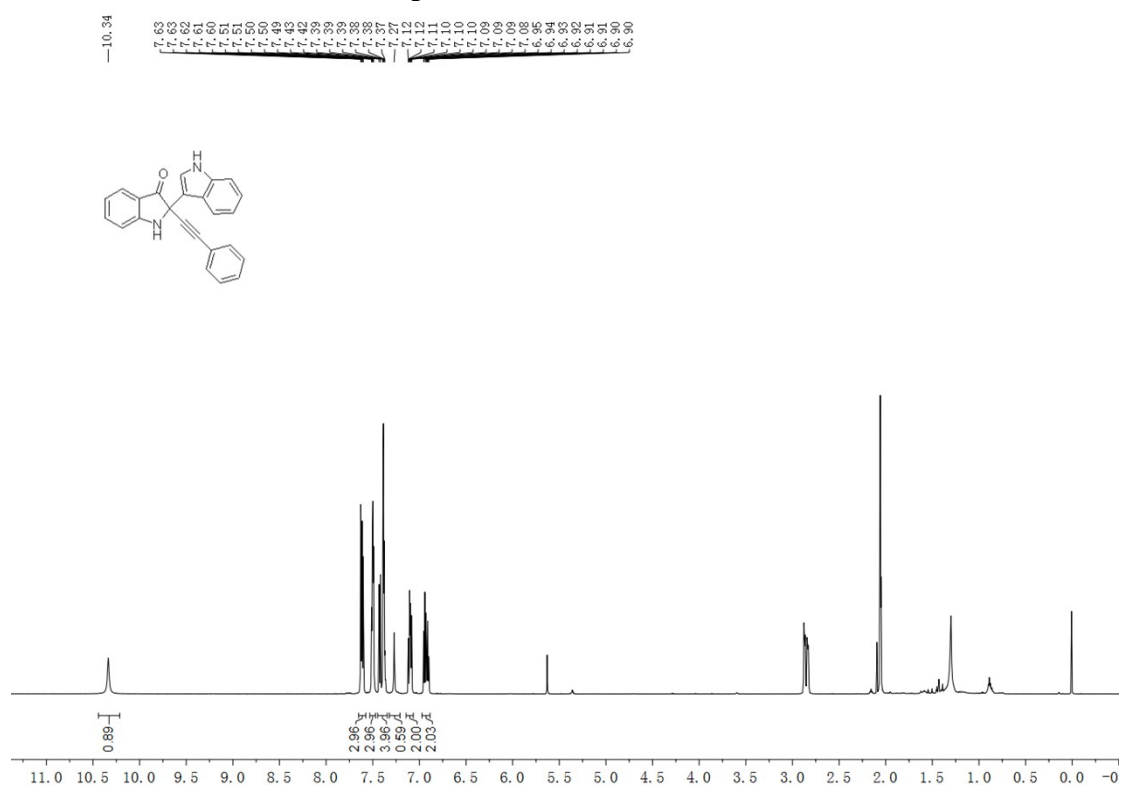
# <sup>1</sup>H and <sup>13</sup>C NMR data of compound 6q



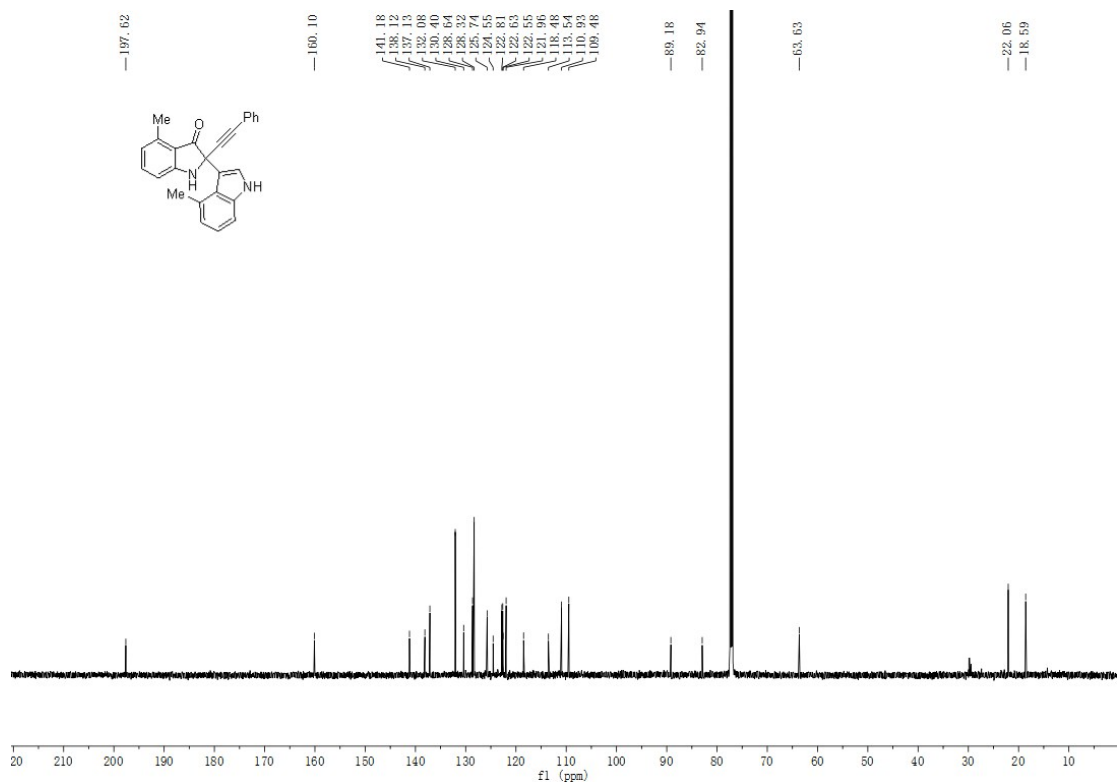
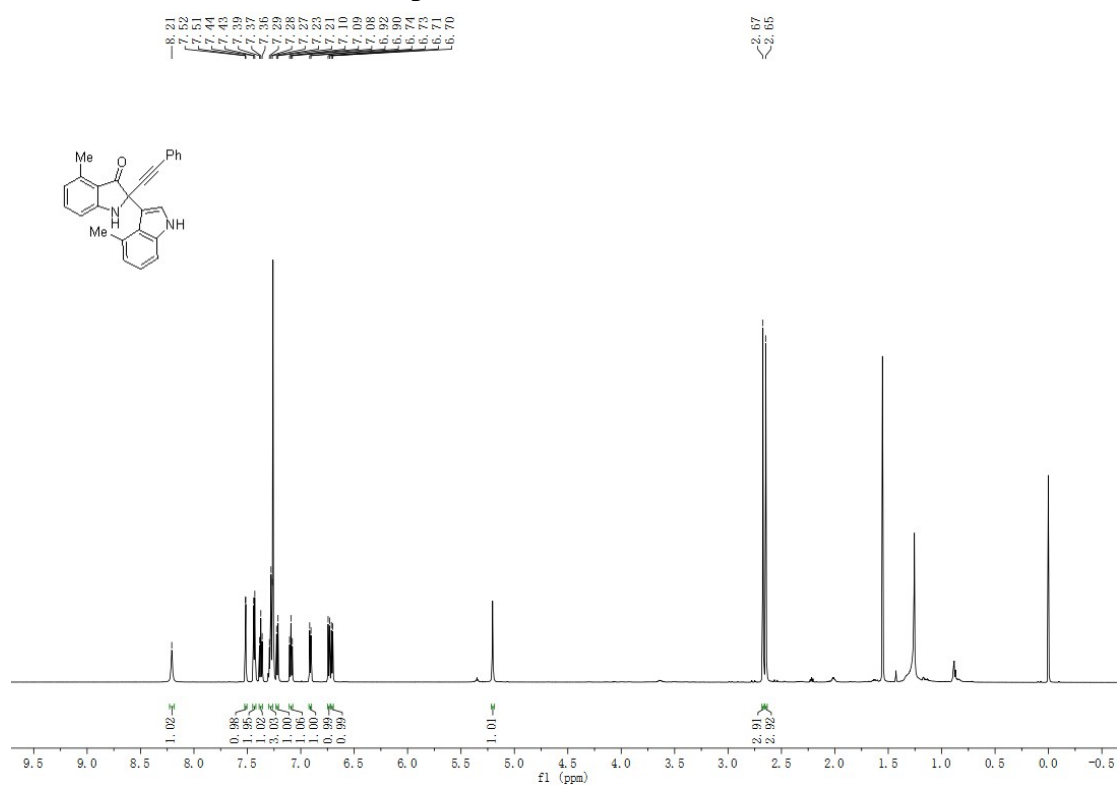
# <sup>1</sup>H and <sup>13</sup>C NMR data of compound 6r



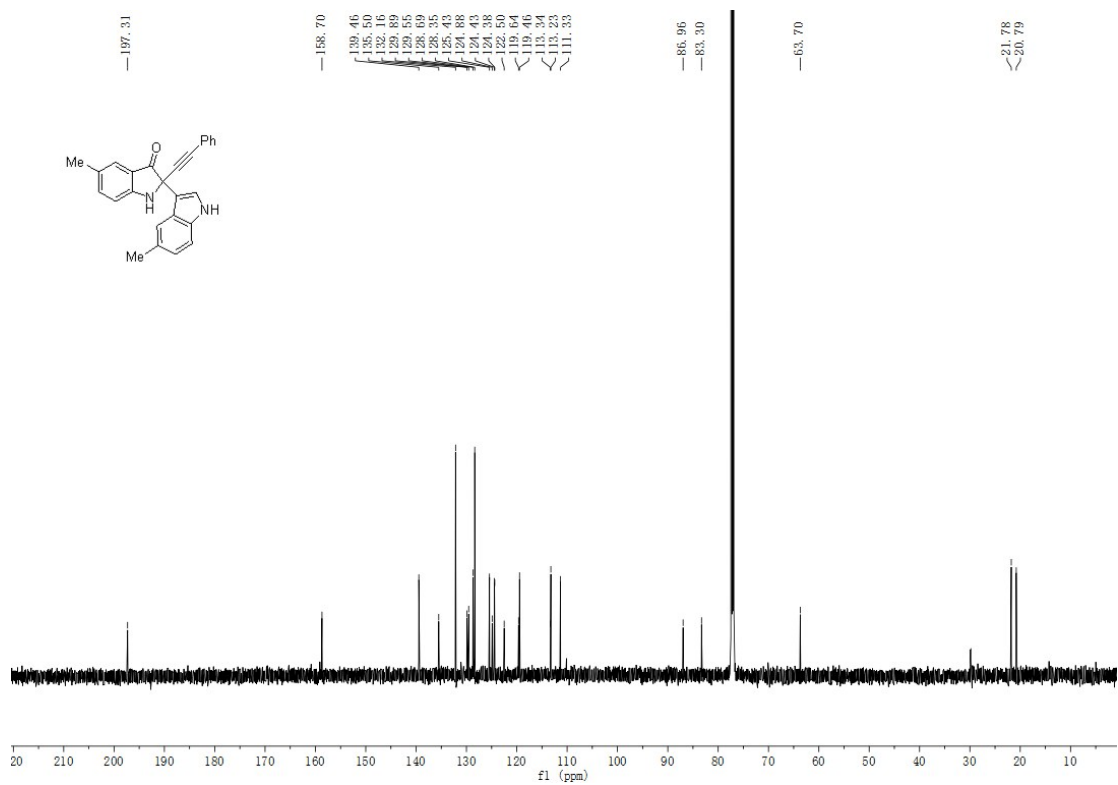
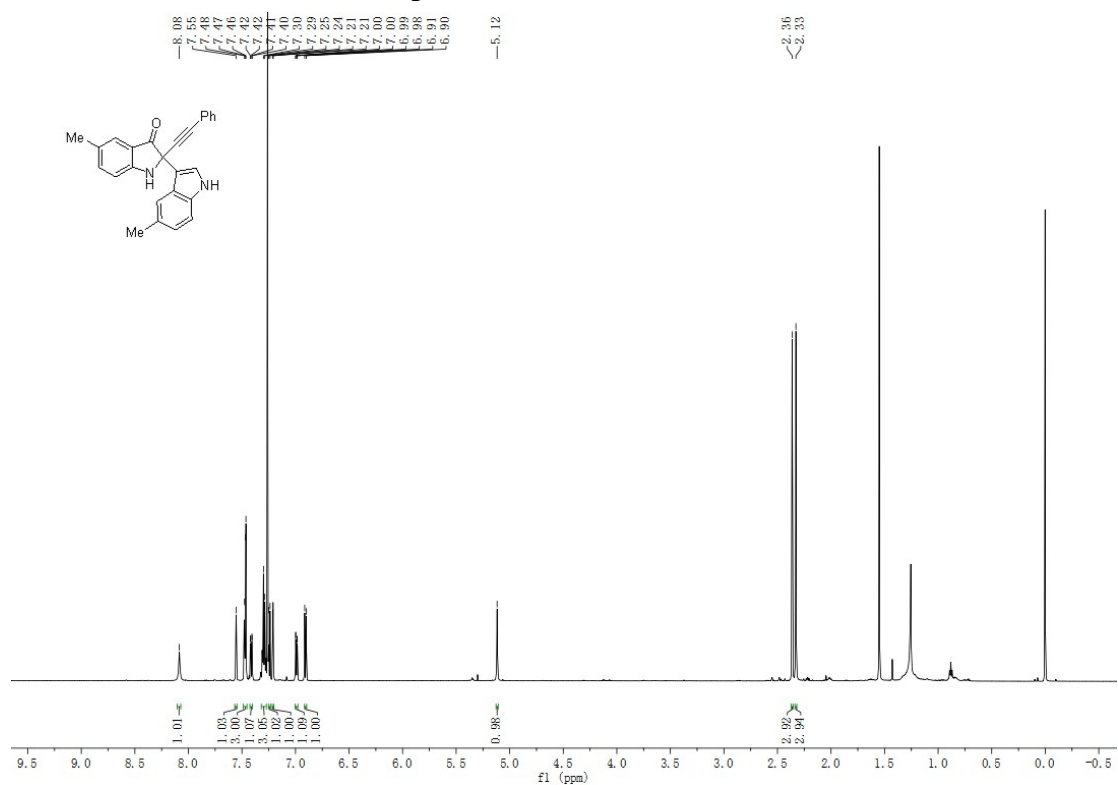
# <sup>1</sup>H and <sup>13</sup>C NMR data of compound 8a



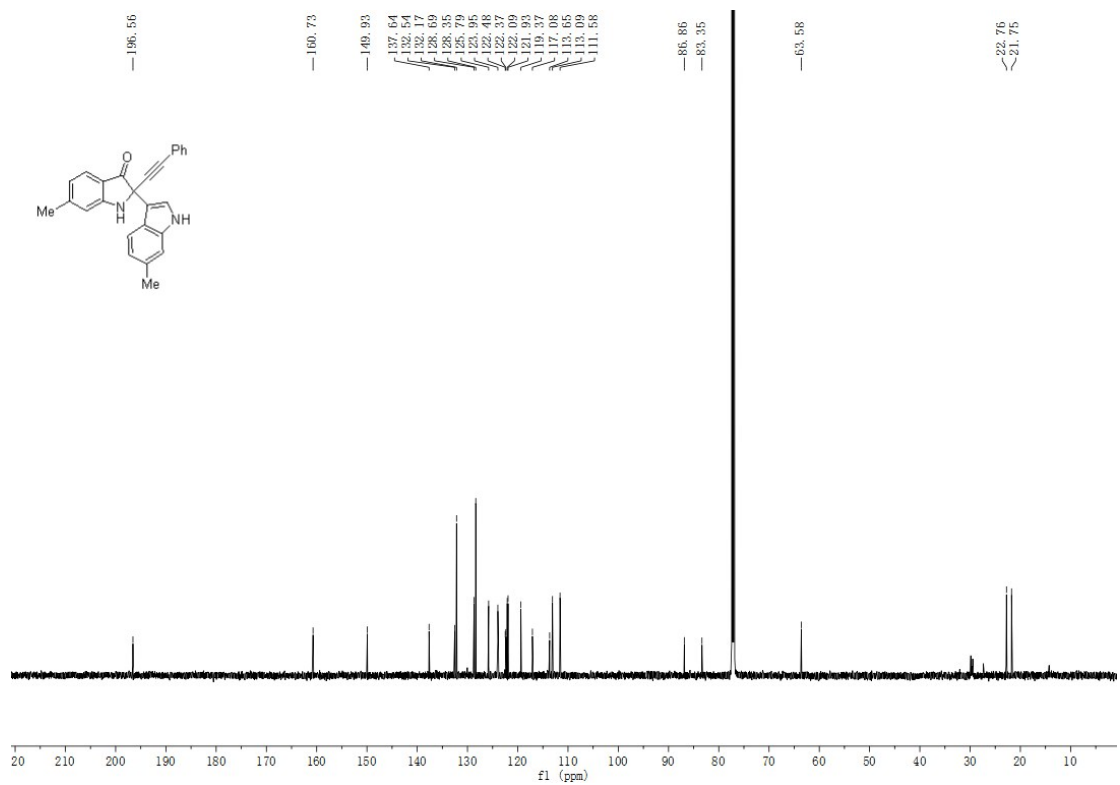
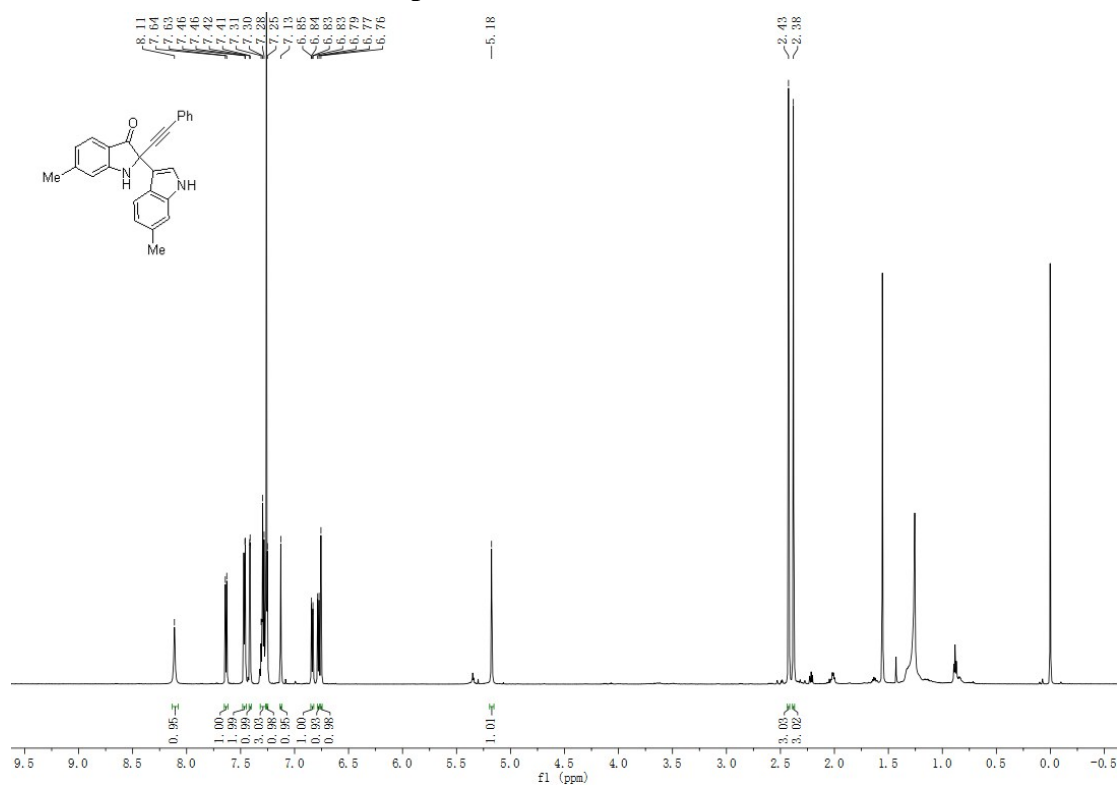
# <sup>1</sup>H and <sup>13</sup>C NMR data of compound 8b



# <sup>1</sup>H and <sup>13</sup>C NMR data of compound 8c

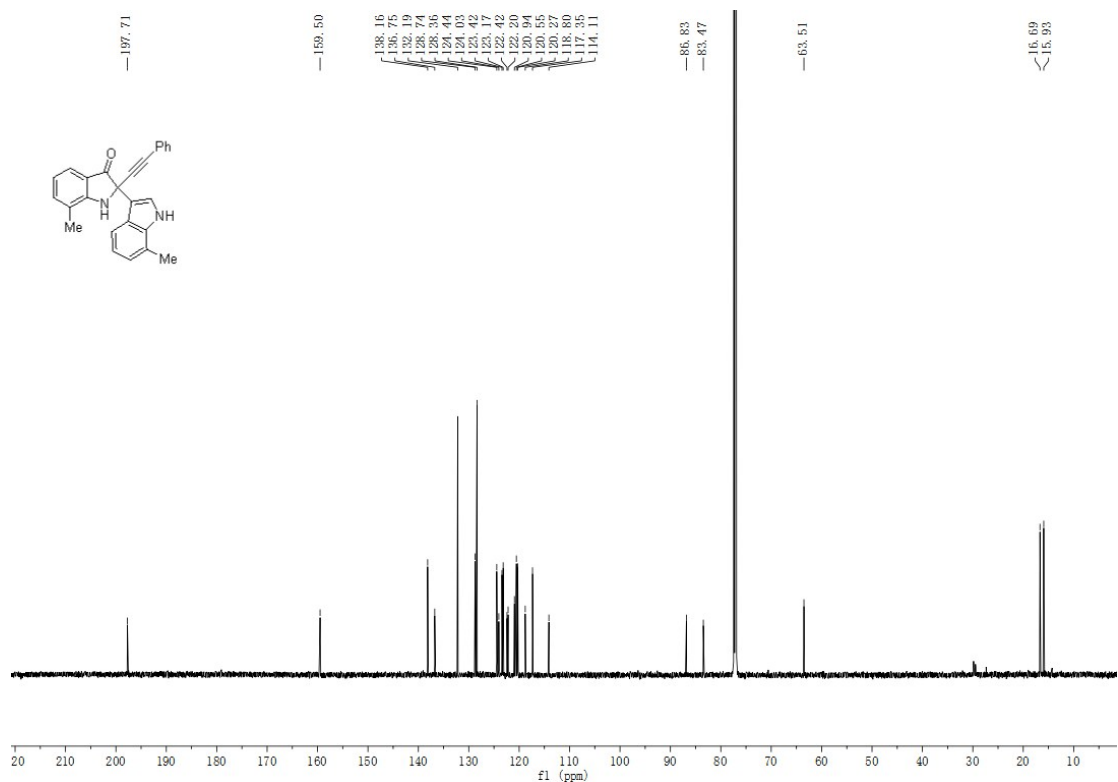
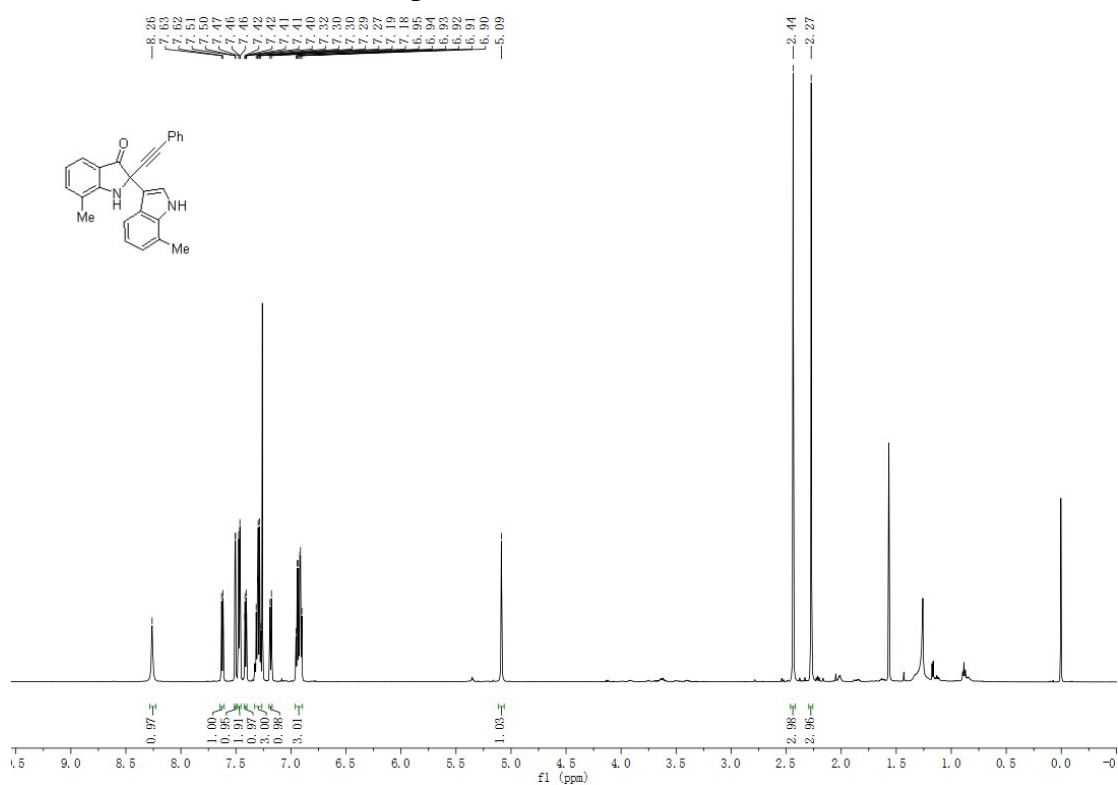


# <sup>1</sup>H and <sup>13</sup>C NMR data of compound 8d

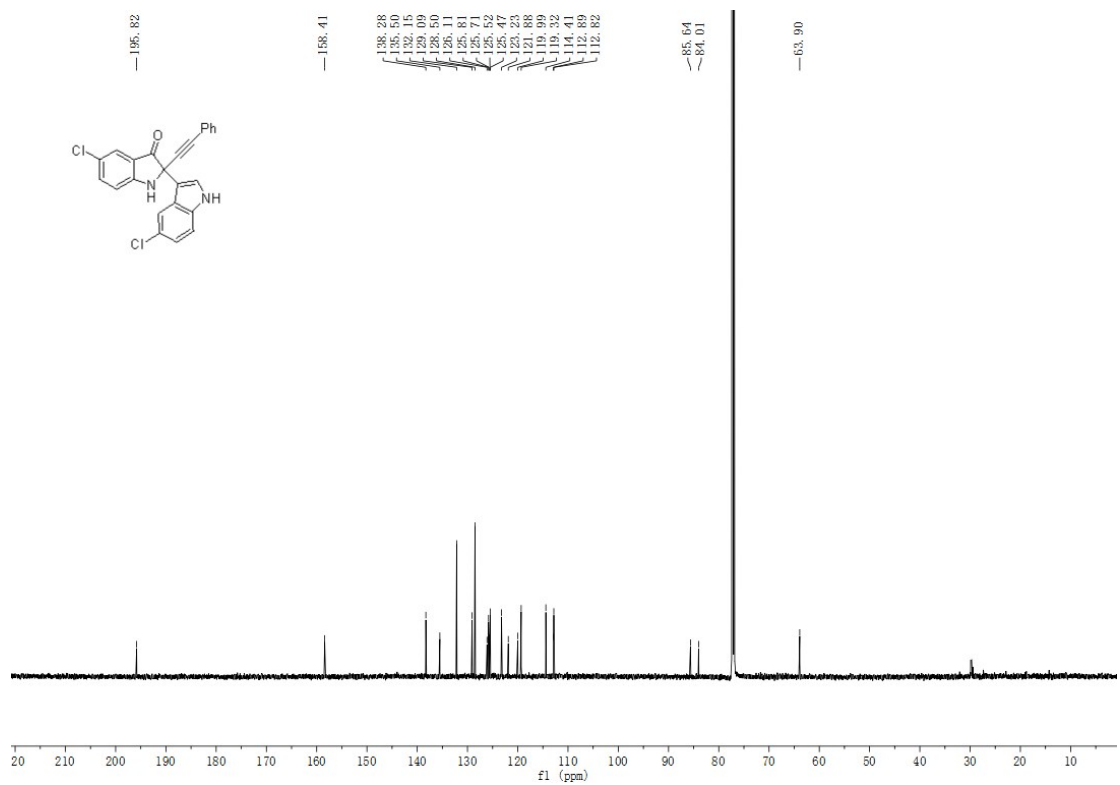
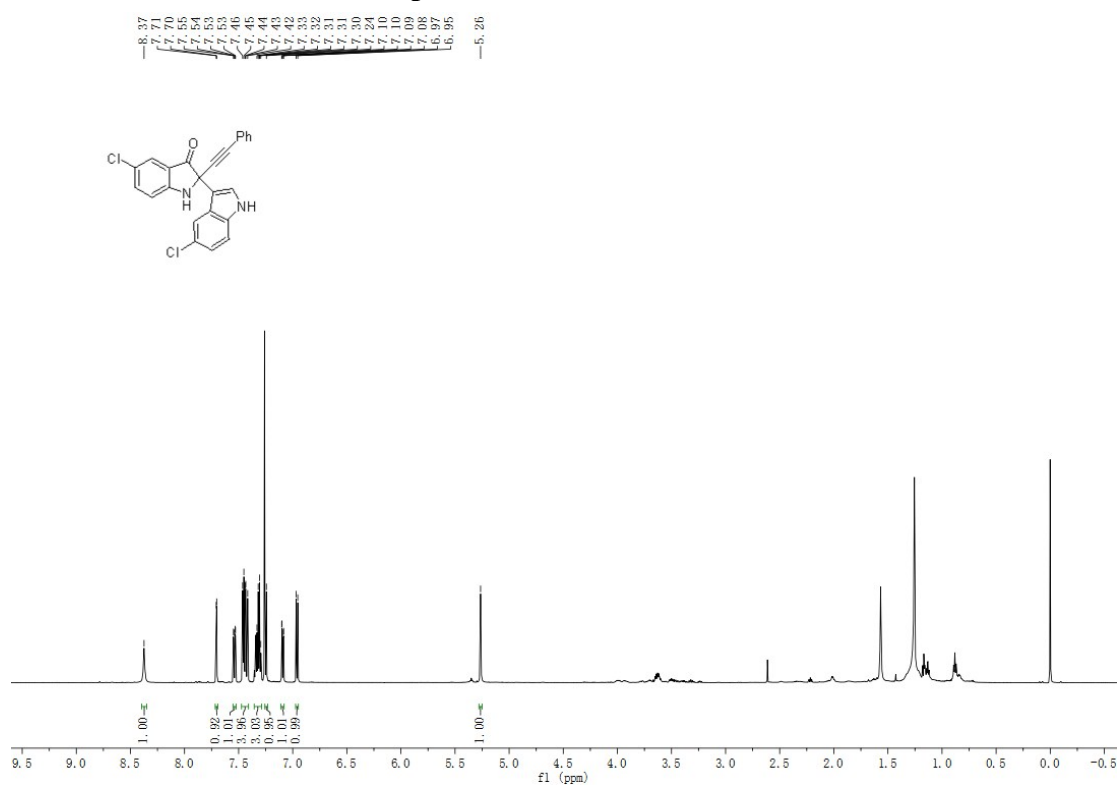




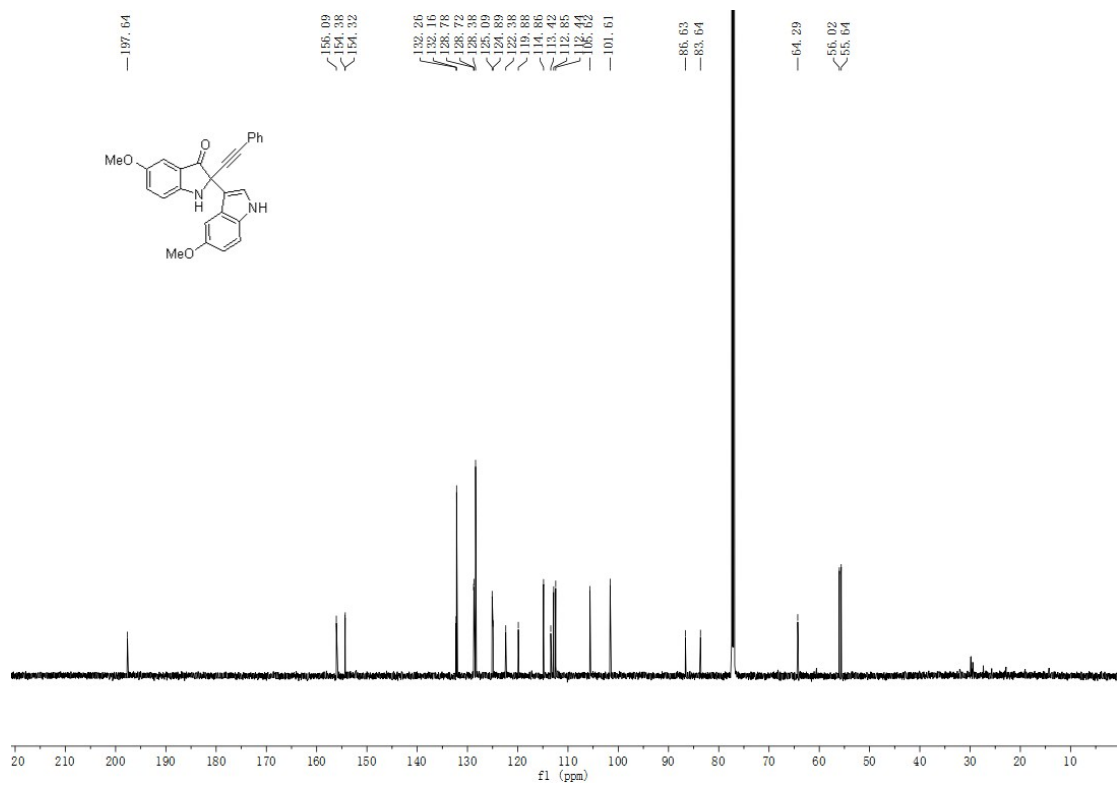
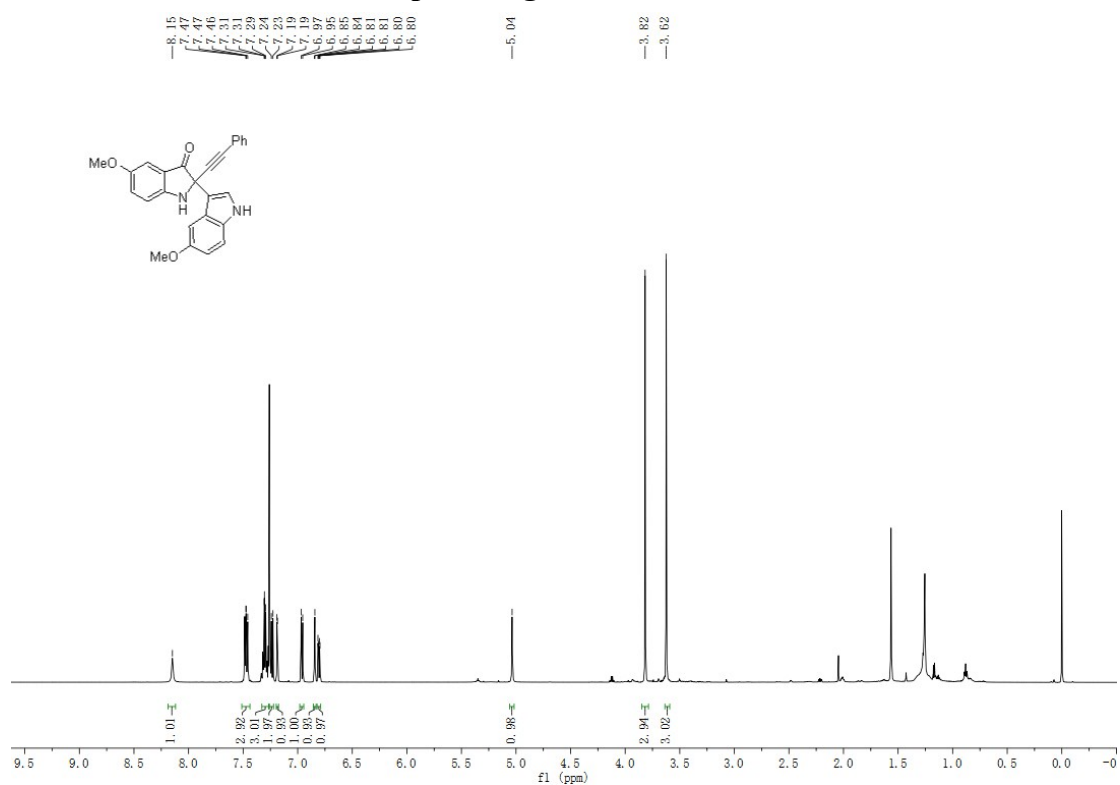
# <sup>1</sup>H and <sup>13</sup>C NMR data of compound 8e



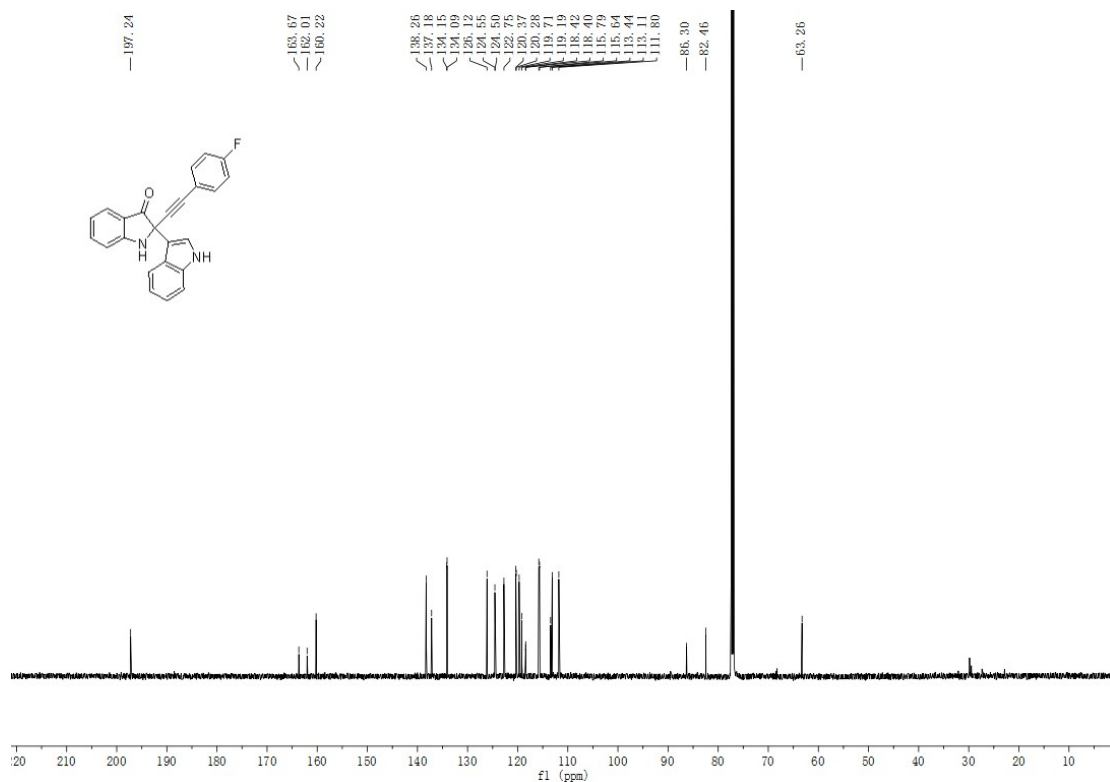
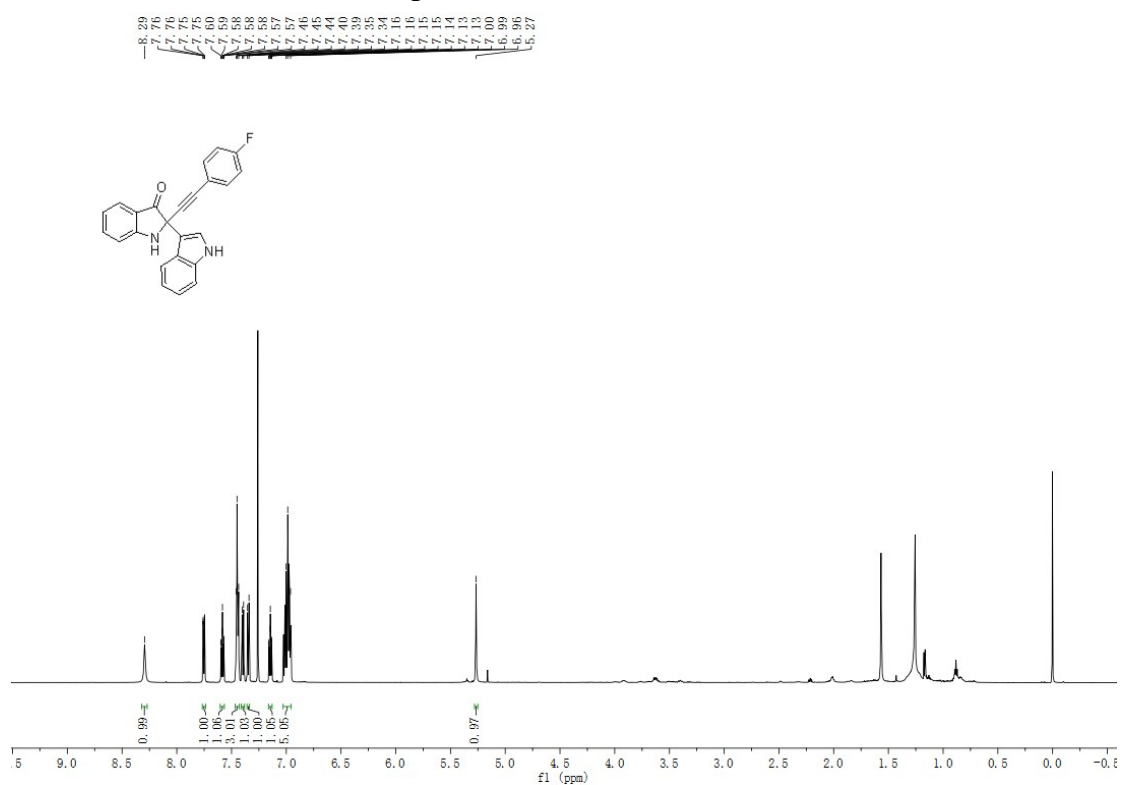
# <sup>1</sup>H and <sup>13</sup>C NMR data of compound 8f



# <sup>1</sup>H and <sup>13</sup>C NMR data of compound 8g



# <sup>1</sup>H and <sup>13</sup>C NMR data of compound 8h



# <sup>1</sup>H and <sup>13</sup>C NMR data of compound 8i

