Electronic Supplementary Material (ESI) for RSC Advances.


# Fridel-Crafts Alkylation of Arenes with Indolyl Alcohols for Construction of 3,3-Disubstituted Oxindoles

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## Supporting Information

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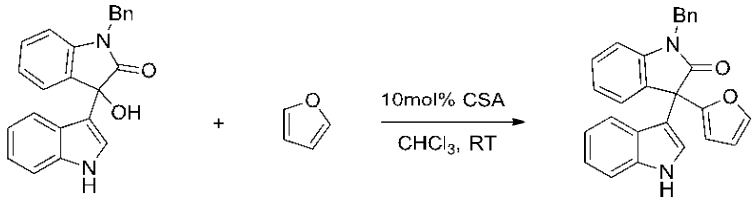
## 1. General Information

Proton nuclear magnetic resonance spectra ($^1$H NMR) were recorded on a Bruker AMX 500 spectrophotometer ($CDCl_3$ as solvent). Chemical shifts were reported in ppm using tetramethylsilane (TMS, δ (ppm) = 0.00 ppm) as the internal standard, and relative to the signal of chloroform-d (7.26, singlet). The number of protons for a given resonance was indicated by nH. Coupling constants were reported as a *J* value in Hz. The following abbreviations were used to indiδcate the multiplicity: singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), and multiplet (m). Carbon nuclear magnetic resonance spectra ($^{13}$C NMR) were reported in ppm using solvent $CDCl_3$ (δ (ppm) = 77.10 ppm) as an internal standard. X-ray structure for compounds was determined on X-ray single crystal diffractometer (Model Specifications: D8 QUEST). HRMS analyses were performed on a Waters XEVO QTOF mass spectrometer.

All the chemical reagents, unless otherwise noted, were purchased from commercial companies and used without further purification. All reactions were performed in flask and monitored by TLC (0.2 mm silica gel-coated HSGF 254 plate). The reaction mixtures were purified by flash column chromatography (200-300 mesh silica gel) eluted with the gradient of petroleum ether and ethyl acetate.

## 2. General Procedure

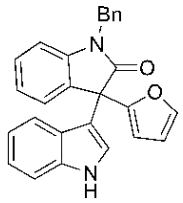



**1a** **2a** **3a**

To a tube sealing charged with **1a** (35.4 mg, 0.10 mmol), **2a** (20.5 mg, 0.3 mmol) and catalyst CSA (2.32 mg, 0.01 mmol) were dissolved in 1.5 mL $CHCl_3$, and the resulting solution was stirred at room temperature. The reaction was monitored by TLC until starting material **1** was consumed up. The resultant solution was concentrated under the reduced pressure to give the residue, which was purified through flash column chromatography on silica gel to afford the pure products **3a** (34.4 mg, 85% yield) as a white solid.

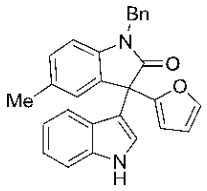
## 3. Characterization of Products

**1-benzyl-3-(furan-2-yl)-3-(1H-indol-3-yl)indolin-2-one (3a)**



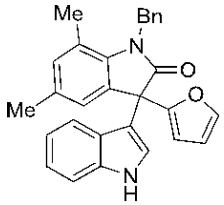

**Physical Appearance:** white solid; 34.4 mg, 85%yield; **m.p.:**191.0 – 192.3℃.
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.46 (dd, *J* = 7.4, 0.7 Hz, 1H), 7.41 (dd, *J* = 1.7, 0.8 Hz, 1H), 7.32 – 7.25 (m, 6H), 7.24-7.19 (m, 1H), 7.13-7.08 (m, 2H), 7.03 (td, *J* = 7.6, 0.8 Hz, 1H), 6.94 – 6.89 (m, 1H), 6.85 (d, *J* = 2.6 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 6.39-6.35 (m, 2H), 5.01 (q, *J* = 15.7 Hz, 2H) ; **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 175.54, 152.25, 142.93, 142.30, 136.95, 135.80, 131.30, 128.85, 128.61, 127.68, 127.39, 125.84, 125.65, 124.13, 122.98, 122.28, 120.76, 119.82, 114.11, 111.40, 110.32, 109.53, 108.35, 53.59, 44.20 ; **HRMS (ESI)** calculated for $C_{27}H_{20}N_2O_2Na[M+Na]^+$ : 427.1422, found: 427.1426.

**1-benzyl-3-(furan-2-yl)-3-(1H-indol-3-yl)-5-methylindolin-2-one (3b)**




**Physical Appearance:** white solid; 35.9 mg, 86% yield; **m.p.:**240.8 – 243.3℃.
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.42 (s, 1H), 7.32-7.222 (m, 7H), 7.11 (t, *J* = 7.4 Hz, 2H), 7.01 (d, *J* = 7.9 Hz, 1H), 6.92 (t, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 2.5 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 6.39-6.35 (m, 2H), 4.99 (q, *J* = 15.7 Hz, 2H), 2.25 (s, 3H); **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 154.51, 139.84, 137.76, 135.26, 130.46, 130.29, 130.13, 129.41, 128.91, 128.81, 128.06, 127.63, 127.59, 127.22, 127.19, 127.15, 126.00, 119.09, 118.72, 85.10, 84.55, 43.49, 43.24, 34.88 ; **HRMS (ESI)** calculated for $C_{28}H_{22}N_2O_2$ $Na[M+Na]^+$ : 441.1579, found: 441.1585.

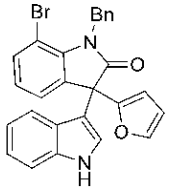
**1-benzyl-3-(furan-2-yl)-3-(1H-indol-3-yl)-5,7-dimethylindolin-2-one (3c)**




**Physical Appearance:** white solid; 37.6 mg, 87% yield; **m.p.:**248.9 – 250.7℃.
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.43 (dd, *J* = 1.5, 0.8 Hz, 1H), 7.32 – 7.26 (m, 3H), 7.25 -7.19 (m, 2H), 7.19 -7.14 (m, 4H), 7.01 – 6.95 (m, 1H), 6.89 (d, *J*

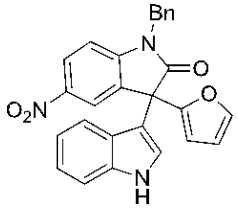
= 2.4 Hz, 1H), 6.81 (s, 1H), 6.38 – 6.35 (m, 2H), 5.25 (q, *J* = 15.7 Hz, 2H), 2.29 (s, 3H), 2.24 (s, 3H); **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 176.48, 152.80, 142.85, 137.91, 137.79, 136.96, 133.09, 132.44, 131.96, 128.86, 127.12, 125.81, 125.78, 124.50, 124.18, 122.22, 121.16, 119.77, 114.50, 111.34, 110.26, 108.41, 58.56, 53.19, 45.36, 20.94, 18.87 ; **HRMS (ESI)** calculated for $C_{29}H_{24}N_2O_2Na[M+Na]^+$ : 455.1735, found: 455.1739.

**1-benzyl-7-bromo-3-(furan-2-yl)-3-(1H-indol-3-yl)indolin-2-one (3d)**



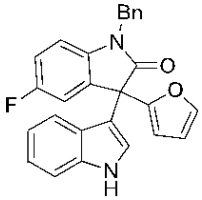

**Physical Appearance:** white solid; 42.5 mg, 88% yield; **m.p.:**114.4 – 115.9℃.
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.42 (t, *J* = 9.8 Hz, 3H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.25-7.17 (m, 5H), 7.16 – 7.11 (m, 1H), 7.00-6.90 (m, 2H), 6.84 (s, 1H), 6.36 (d, *J* = 9.3 Hz, 2H), 5.49 (s, 2H); **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 176.10, 151.62, 143.06, 139.84, 137.38, 136.86, 134.55, 134.28, 128.52, 127.02, 126.40, 125.44, 125.06, 124.15, 124.03, 122.43, 120.80, 119.96, 113.73, 111.36, 110.34, 108.73, 102.60, 53.19, 44.89 ; **HRMS (ESI)** calculated for $C_{27}H_{19}N_2O_2NaBr[M+Na]^+$ : 505.0528, found: 505.0526.

**1-benzyl-3-(furan-2-yl)-3-(1H-indol-3-yl)-5-nitroindolin-2-one (3e)**



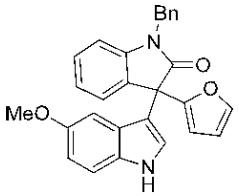

**Physical Appearance:** yellow solid; 38.7 mg, 86% yield; **m.p.:**88.7 – 94.5℃.
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.33 (d, *J* = 2.2 Hz, 1H), 8.25 (s, 1H), 8.20 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.45 (d, *J* = 0.9 Hz, 1H), 7.40 – 7.28 (m, 6H), 7.18 – 7.09 (m, 2H), 6.98 – 6.87 (m, 3H), 6.44 (d, *J* = 3.2 Hz, 1H), 6.41 (dd, *J* = 3.2, 1.9 Hz, 1H), 5.11 – 4.99 (m, 2H); **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 175.60, 150.46, 147.93, 143.52, 137.03, 134.69, 132.09, 129.49, 129.20, 128.29, 127.45, 125.85, 125.20, 124.23, 122.78, 121.70, 120.38, 120.26, 112.73, 111.70, 110.64, 109.25, 109.18, 53.41, 44.64 ; **HRMS (ESI)** calculated for $C_{27}H_{19}N_3O_4$ Na$[M+Na]^+$ : 472.1273, found: 472.1274.

**1-benzyl-5-fluoro-3-(furan-2-yl)-3-(1H-indol-3-yl)indolin-2-one (3f)**



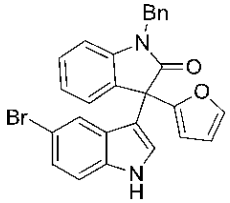
**Physical Appearance:** white solid; 35.9 mg, 85% yield; **m.p.:**191.6 – 195.0℃.
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.42 (s, 1H), 7.36 – 7.04 (m, 9H), 6.98 – 6.68 (m, 4H), 6.39 (d, *J* = 11.8 Hz, 2H), 4.99 (q, *J* = 15.7 Hz, 2H); **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 175.34, 160.34, 158.42, 151.51, 143.11, 138.15, 136.92, 135.44, 132.84, 128.92, 127.36, 125.40, 124.16, 122.39, 120.46, 119.92, 115.10, 114.01, 113.47, 111.51, 110.41, 110.08, 108.56, 53.88, 44.34 ; **HRMS (ESI)** calculated for $C_{27}H_{19}N_2O_2F$ Na[M+Na]$^+$ : 445.1328, found: 445.1333.

**1-benzyl-3-(furan-2-yl)-3-(5-methoxy-1H-indol-3-yl)indolin-2-one (3g)**



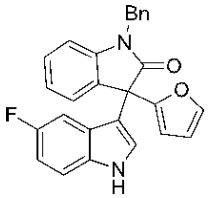

**Physical Appearance:** white solid; 36.9 mg, 85% yield; **m.p.:**231.8 – 233.0℃.
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.48 (d, *J* = 7.4 Hz, 1H), 7.42 (s, 1H), 7.31 – 7.15 (m, 7H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.85 (d, *J* = 2.0 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 6.77 (dd, *J* = 8.8, 2.2 Hz, 1H), 6.49 (s, 1H), 6.42 (d, *J* = 2.9 Hz, 1H), 6.37 (d, *J* = 1.7 Hz, 1H), 5.00 (q, *J* = 15.7 Hz, 2H), 3.50 (s, 3H); **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 175.60, 153.89, 152.18, 142.96, 142.38, 135.78, 131.98, 131.22, 128.87, 128.61, 127.68, 127.32, 126.05, 125.95, 124.71, 123.02, 113.70, 112.79, 112.02, 110.26, 109.47, 108.36, 102.19, 55.43, 53.51, 44.15 ; **HRMS (ESI)** calculated for $C_{28}H_{22}N_2O_3$ Na[M+Na]$^+$ : 457.1528, found: 457.1535.

**1-benzyl-3-(5-bromo-1H-indol-3-yl)-3-(furan-2-yl)indolin-2-one (3h)**



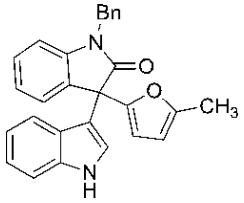

**Physical Appearance:** white solid; 38.1 mg, 79% yield; **m.p.:**234.1 – 236.3℃.
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.34 (d, *J* = 19.8 Hz, 1H), 7.44-7.40 (m, 2H), 7.35 – 7.20 (m, 8H), 7.18 – 7.03 (m, 3H), 6.85-6.79 (m, 2H), 6.38-6.34 (m, 1H), 4.98 (d, *J* = 40.4 Hz, 2H)**$^{13}$**; **C NMR** (125 MHz, $CDCl_3$) δ 176.23, 151.75, 143.19, 139.97, 137.51, 136.99, 134.68, 134.41, 128.64, 127.15, 126.53, 125.57, 125.19, 124.28, 124.16, 122.55, 120.93, 120.09, 113.86, 111.49, 110.47, 108.86, 102.73, 53.32, 45.01 ; **HRMS (ESI)** calculated for $C_{27}H_{19}N_2O_2Br$ Na[M+Na]$^+$ : 505.0528, found: 505.0530.

**1-benzyl-3-(5-fluoro-1H-indol-3-yl)-3-(furan-2-yl)indolin-2-one (3i)**



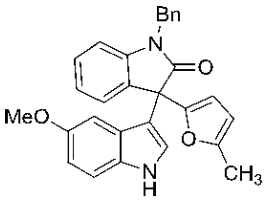

**Physical Appearance:** white solid; 34.6 mg, 82% yield; **m.p.:**197.6 – 199.8℃.
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.46 (d, *J* = 7.4 Hz, 1H), 7.42 (d, *J* = 1.1 Hz, 1H), 7.30 (d, *J* = 4.4 Hz, 4H), 7.23 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.21 – 7.16 (m, 1H), 7.11 – 7.01 (m, 1H), 6.92 – 6.75 (m, 5H), 6.37 (d, *J* = 0.9 Hz, 2H), 5.01 (q, *J* = 15.7 Hz, 2H) ; **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 175.41, 159.62, 155.72, 151.85, 143.06, 135.66, 133.44, 130.86, 128.90, 128.37, 127.75, 127.30, 125.74, 123.09, 119.87, 117.36, 114.17, 111.92, 111.02, 110.39, 109.69, 108.43, 105.69, 53.38, 44.20 ; **HRMS (ESI)** calculated for $C_{27}H_{19}N_2O_2F$ Na[M+Na]$^+$ ： 445.1328, found: 445.1327.

**1-benzyl-3-(1H-indol-3-yl)-3-(5-methylfuran-2-yl)indolin-2-one (3j)**




**Physical Appearance:** white solid; 37.7 mg, 90% yield; **m.p.:**210.3 – 213.9℃.
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.44 (dd, *J* = 7.4, 0.8 Hz, 1H), 7.34 – 7.25 (m, 5H), 7.24 – 7.18 (m, 1H), 7.14 (d, *J* = 8.1 Hz, 1H), 7.11 – 7.07 (m, 1H), 7.02 (td, *J* = 7.6, 0.9 Hz, 1H), 6.93 – 6.89 (m, 1H), 6.87 (d, *J* = 2.6 Hz, 1H), 6.80 (d, *J* = 7.8 Hz, 1H), 6.22 (d, *J* = 3.1 Hz, 1H), 5.93 – 5.91 (m, 1H), 5.00 (dd, *J* = 52.3, 15.7 Hz, 2H), 2.23 (d, *J* = 0.5 Hz, 3H) ; **$^3$C NMR** (125 MHz, $CDCl_3$) δ 175.69, 152.58, 150.20, 142.28, 136.95, 135.86, 131.57, 128.79, 128.44, 127.61, 127.36, 125.80, 125.73, 124.15, 122.88, 122.20, 121.00, 119.69, 114.19, 111.30, 109.45, 109.15, 106.23, 53.61, 44.10, 31.02 ; **HRMS (ESI)** calculated for $C_{28}H_{22}N_2O_2Na$[M+Na]$^+$ ： 441.1579, found: 441.1581.

**1-benzyl-3-(5-methoxy-1H-indol-3-yl)-3-(5-methylfuran-2-yl)indolin-2-one (3k)**

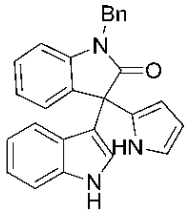



**Physical Appearance:** white solid; 36.8 mg, 82% yield; **m.p.:**232.9 – 234.4℃.
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.46 (dd, *J* = 7.4, 0.8 Hz, 1H), 7.32-7.26 (m, 4H), 7.25 – 7.19 (m, 2H), 7.17 (d, *J* = 8.8 Hz, 1H), 7.04 (td, *J* = 7.6, 0.9 Hz, 1H), 6.89 (d, *J* = 2.6 Hz, 1H), 6.81 – 6.74 (m, 2H), 6.53 (d, *J* = 2.3 Hz, 1H), 6.27 (d, *J* = 3.1 Hz, 1H), 5.94 – 5.92 (m, 1H), 5.00 (q, *J* = 15.7 Hz 2H), 3.51 (s, 3H), 2.25 (s, 3H) ; **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 175.78, 153.79, 152.59, 150.12, 142.38, 135.84, 132.00, 131.54, 128.81, 128.45, 127.62, 127.29, 126.13, 125.94, 124.77,

122.92,

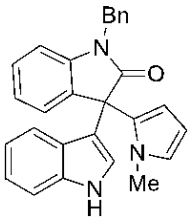
113.80, 112.74, 111.93, 109.40, 109.18, 106.18, 102.41, 55.46, 53.58, 44.07, 13.84 ; **HRMS (ESI)** calculated for $C_{29}H_{24}N_2O_3$ Na[M+Na]$^+$ : 471.1685, found: 471.1685.

**1-benzyl-3-(1H-indol-3-yl)-3-(1H-pyrrol-2-yl)indolin-2-one (5a)**



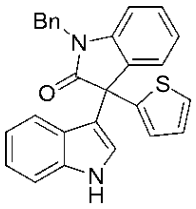

**Physical Appearance:** dark green solid; 27.0 mg, 67% yield; **m.p.:**223.4 – 227.3℃. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 9.09 (s, 1H), 8.08 (s, 1H), 7.42 – 7.39 (m, 1H), 7.36 – 7.27 (m, 6H), 7.22 (td, *J* = 7.8, 1.1 Hz, 1H), 7.12 – 7.08 (m, 1H), 7.02 (td, *J* = 7.6, 0.8 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 6.85 – 6.81 (m, 3H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.18 (dd, *J* = 6.0, 2.8 Hz, 1H), 6.06 – 6.04 (m, 1H), 5.15 (d, *J* = 15.5 Hz, 1H), 4.88 (d, *J* = 15.5 Hz, 1H) ; **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 177.59, 142.06, 136.76, 135.77, 132.51, 128.89, 128.66, 128.32, 127.82, 127.71, 125.47, 124.24, 123.17, 122.32, 119.94, 119.66, 118.69, 116.86, 111.38, 109.57, 107.89, 107.52, 53.51, 44.36 ; **HRMS (ESI)** calculated for $C_{27}H_{21}N_3O$ Na[M+Na]$^+$ : 426.1582, found: 426.1584.

**1-benzyl-3-(1H-indol-3-yl)-3-(1-methyl-1H-pyrrol-2-yl)indolin-2-one (5b)**



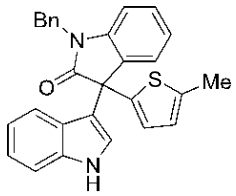

**Physical Appearance:** white solid; 30.9 mg, 74% yield; **m.p.:**220.4 – 221.3℃. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.41 (d, *J* = 7.0 Hz, 1H), 7.36 – 7.27 (m, 7H), 7.17 (t, *J* = 7.1 Hz, 2H), 7.04 – 6.95 (m, 2H), 6.89 (s, 1H), 6.81 (d, *J* = 7.2 Hz, 1H), 6.58 (s, 1H), 6.02 (s, 1H), 5.78 (s, 1H), 5.05 (d, *J* = 15.7 Hz, 1H), 4.92 (d, *J* = 16.7 Hz, 1H), 3.34 (s, 3H) ; **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 176.89, 141.52, 136.88, 136.06, 135.30, 133.86, 129.57, 128.86, 128.09, 127.68, 127.46, 126.41, 125.55, 125.23, 125.13, 122.86, 122.44, 122.15, 121.13, 120.16, 111.23, 110.38, 109.32, 106.10, 53.27, 44.11, 32.30 ; **HRMS (ESI)** calculated for $C_{28}H_{23}N_3O$ Na[M+Na]$^+$ : 440.1739, found: 440.1741.

**1-benzyl-3-(1H-indol-3-yl)-3-(thiophen-2-yl)indolin-2-one (5c)**



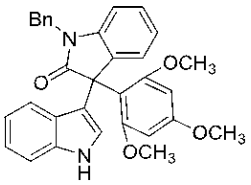
**Physical Appearance:** white solid; 21.9 mg, 52% yield; **m.p.:**110.4 – 114.1℃.
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.39 (d, *J* = 7.2 Hz, 1H), 7.22 – 7.11 (m, 7H), 7.03 (dd, *J* = 15.6, 5.1 Hz, 2H), 6.98 – 6.85 (m, 5H), 6.84 – 6.75 (m, 2H), 4.94 (s, 2H) ;**$^1$ $^3$C NMR** (125 MHz, $CDCl_3$) δ 176.79, 143.89, 141.98, 137.03, 135.87, 135.30, 133.48, 128.87, 128.57, 127.75, 127.55, 126.66, 126.47, 125.61, 125.54, 125.13, 124.17, 122.99, 122.40, 120.83, 119.88, 111.39, 109.59, 54.59, 44.33 ; **HRMS (ESI)** calculated for $C_{27}H_{20}N_2OS$ Na[M+Na]$^+$ : 443.1194, found: 443.1199.

**1-benzyl-3-(1H-indol-3-yl)-3-(5-methylthiophen-2-yl)indolin-2-one (5d)**



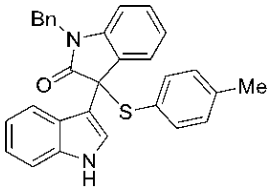

**Physical Appearance:** white solid; 25.2 mg, 58% yield; **m.p.:**125.9 – 127.1℃.
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.37 (d, *J* = 7.3 Hz, 1H), 7.25 -7.15 (m, 6H), 7.14 -7.10 (m, 1H), 7.04 – 6.98 (m, 2H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 2.4 Hz, 1H), 6.81 (dd, *J* = 13.1, 5.5 Hz, 2H), 6.75 (d, *J* = 7.8 Hz, 1H), 6.54 – 6.52 (m, 1H), 4.93 (t,*J* = 16 Hz, 2H), 2.34 (s, 3H) ; **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 176.92, 141.89, 141.02, 140.01, 136.96, 135.84, 133.51, 128.80, 128.38, 127.66, 127.49, 126.24, 125.64, 125.52, 124.61, 124.29, 122.88, 122.18, 120.69, 119.67, 116.41, 111.39, 109.49, 54.69, 44.26, 29.73 ; **HRMS (ESI)** calculated for $C_{28}H_{22}N_2OS$ Na[M+Na]$^+$ : 457.1351, found: 457.1354.

**1-benzyl-3-(1H-indol-3-yl)-3-(2,4,6-trimethoxyphenyl)indolin-2-one (5e)**



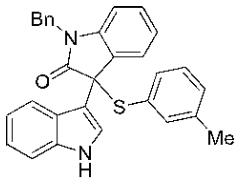

**Physical Appearance:** white solid; 31.3 mg, 62% yield; **m.p.:**122.5 – 124.2℃.
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.51 (s, 1H), 7.37 (d, *J* = 7.2 Hz, 1H), 7.31 (d, *J* = 7.0 Hz, 2H), 7.27 – 7.18 (m, 5H), 7.07 (t, *J* = 7.3 Hz, 1H), 6.99 (t, *J* = 7.3 Hz, 1H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.80 (d, *J* = 7.8 Hz, 1H), 6.33 (s, 1H), 6.14 (d, *J* = 2.1 Hz, 1H), 6.06 (d, *J* = 2.0 Hz, 1H), 4.86 (q, *J* = 15.7 Hz, 2H), 3.77 (s, 3H), 3.36 (s, 3H), 2.90 (s, 3H) ; **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 178.09, 161.08, 160.25, 158.90, 143.07, 137.10, 137.04, 133.33, 128.50, 127.78, 127.63, 127.20, 127.04, 125.12, 122.05, 121.69, 120.75, 119.01, 118.93, 110.65, 110.17, 108.44, 92.98, 92.55, 55.99, 55.82, 52.99, 43.83 ; **HRMS (ESI)** calculated for $C_{32}H_{27}N_2O_4$ Na[M+Na]$^+$ : 526.1869, found: 526.1867.

**1-benzyl-3-(1H-indol-3-yl)-3-(p-tolylthio)indolin-2-one (5f)**



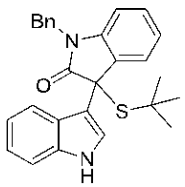

**Physical Appearance:** white solid; 31.3 mg, 68% yield; **m.p.:**192.3 – 194.8℃.
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.55 (s, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.49 (d, *J* = 7.3 Hz, 1H), 7.28 (d, *J* = 8.1 Hz, 1H), 7.20 -7.13 (m, 3H), 7.13 – 7.09 (m, 5H), 7.07 – 7.01 (m, 2H), 6.92 (d, *J* = 6.6 Hz, 2H), 6.87 (d, *J* = 7.9 Hz, 2H), 6.48 (d, *J* = 7.8 Hz, 1H), 4.64 (t, *J* = 16.5 Hz, 2H), 2.26 (s, 3H).
**$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 175.37, 142.14, 139.61, 137.09, 136.72, 135.48, 131.10, 129.25, 128.66, 128.58, 127.37, 127.17, 126.63, 125.79, 125.54, 124.80, 122.75, 122.33, 121.94, 119.69, 111.67, 111.11, 109.20, 59.38, 44.15, 21.40 ; **HRMS (ESI)** calculated for $C_{30}H_{24}N_2OS$ Na[M+Na]$^+$ : 483.1507, found: 483.1511.

**1-benzyl-3-(1H-indol-3-yl)-3-(m-tolylthio)indolin-2-one (5g)**




**Physical Appearance:** white solid; 31.8 mg, 59% yield; **m.p.:**156.0 – 158.0℃.
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.55 (d, *J* = 7.2 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.23 – 7.16 (m, 5H), 7.14 – 7.02 (m, 6H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 6.1 Hz, 2H), 6.47 (d, *J* = 7.7 Hz, 1H), 4.63 (dd, *J* = 53.2, 15.8 Hz, 2H), 2.13 (s, 3H) ; **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 175.14, 142.28, 138.17, 137.28, 137.05, 135.47, 133.61, 131.02, 130.21, 129.80, 128.65, 128.61, 128.16, 127.33, 126.99, 125.83, 125.56, 124.56, 122.67, 122.46, 122.12, 119.78, 111.48, 111.34, 109.14, 59.36, 44.10, 21.07 ; **HRMS (ESI)** calculated for $C_{30}H_{24}N_2OS$ Na[M+Na]$^+$ : 483.1507, found: 483.1506.

**1-benzyl-3-(tert-butylthio)-3-(1H-indol-3-yl)indolin-2-one (5h)**

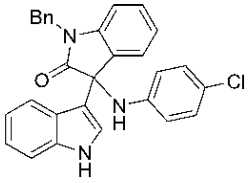



**Physical Appearance:** yellow solid; 26.9 mg, 63% yield; **m.p.:**217.0 – 220.3℃.
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.36 (d, *J* = 7.2 Hz, 2H), 7.25 – 7.17 (m, 4H), 7.12 (t, *J* = 7.8 Hz, 1H), 7.01 (t, *J* =7.5 Hz, 1H), 6.93 (d, *J* = 7.3 Hz, 1H), 6.88 – 6.79 (m, 2H), 6.66 (t, *J* = 7.2 Hz, 1H), 6.41 (d, *J* = 7.7 Hz, 1H), 5.27 (s, 1H), 5.09 (d, *J* = 15.3 Hz, 1H), 4.83 (d, *J* = 15.2 Hz, 1H), 1.40 (s, 9H) ; **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 176.45, 143.25, 136.82, 136.19, 129.38, 128.76, 128.01, 127.81, 127.74, 127.65, 124.69, 123.39, 122.65, 119.87, 119.34, 118.76, 118.72, 110.90,

108.91, 48.52,

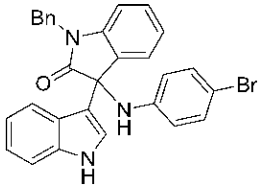
44.70, 44.27, 31.45 **;HRMS (ESI)** calculated for $C_{27}H_{26}N_2OS$ Na$[M+Na]^+$ :449.1664, found: 449.1663.

**1-benzyl-3-((4-chlorophenyl)amino)-3-(1H-indol-3-yl)indolin-2-one (5i)**




**Physical Appearance:** white solid; 28.8 mg, 62% yield; **m.p.:**94.0 – 96.7℃.
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 7.9 Hz, 1H), 8.19 (s, 1H), 7.50 (d, *J* = 7.1 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.29 – 7.26 (m, 4H), 7.25 – 7.21 (m, 3H), 7.19 (d, *J* = 7.0 Hz, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.92 – 6.88 (m, 2H), 6.86 (d, *J* = 7.8 Hz, 1H), 6.78 (d, *J* = 2.6 Hz, 1H), 6.27 – 6.23 (m, 2H), 5.11 (d, *J* = 15.4 Hz, 1H), 4.95 (d, *J* = 4.6 Hz, 1H), 4.73 (d, *J* = 15.4 Hz, 1H) ; **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 176.34, 143.87, 142.08, 137.14, 135.63, 129.92, 129.27, 128.96, 128.74, 127.83, 127.81, 124.78, 124.70, 124.01, 123.37, 123.09, 122.91, 121.56, 120.43, 116.75, 115.61, 111.72, 109.82, 53.45, 44.26 ; **HRMS (ESI)** calculated for $C_{29}H_{22}N_3OCl$ Na $[M+Na]^+$ : 486.1349, found: 486.1354.

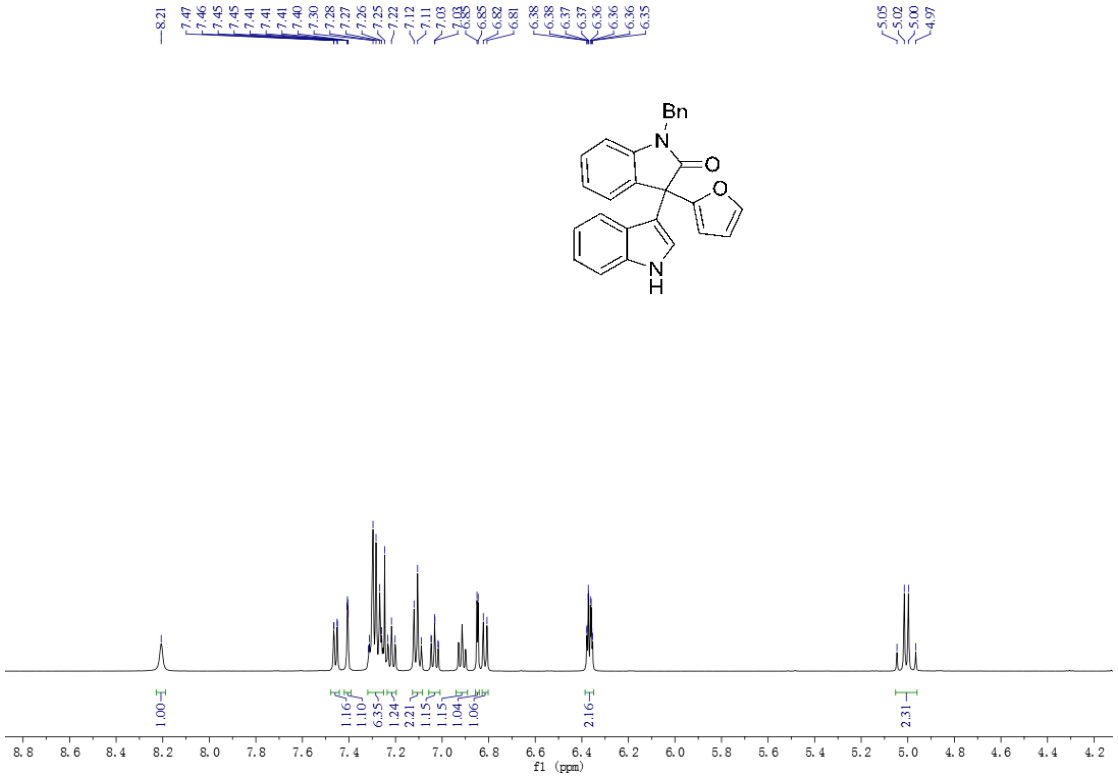
**1-benzyl-3-((4-bromophenyl)amino)-3-(1H-indol-3-yl)indolin-2-one (5j)**

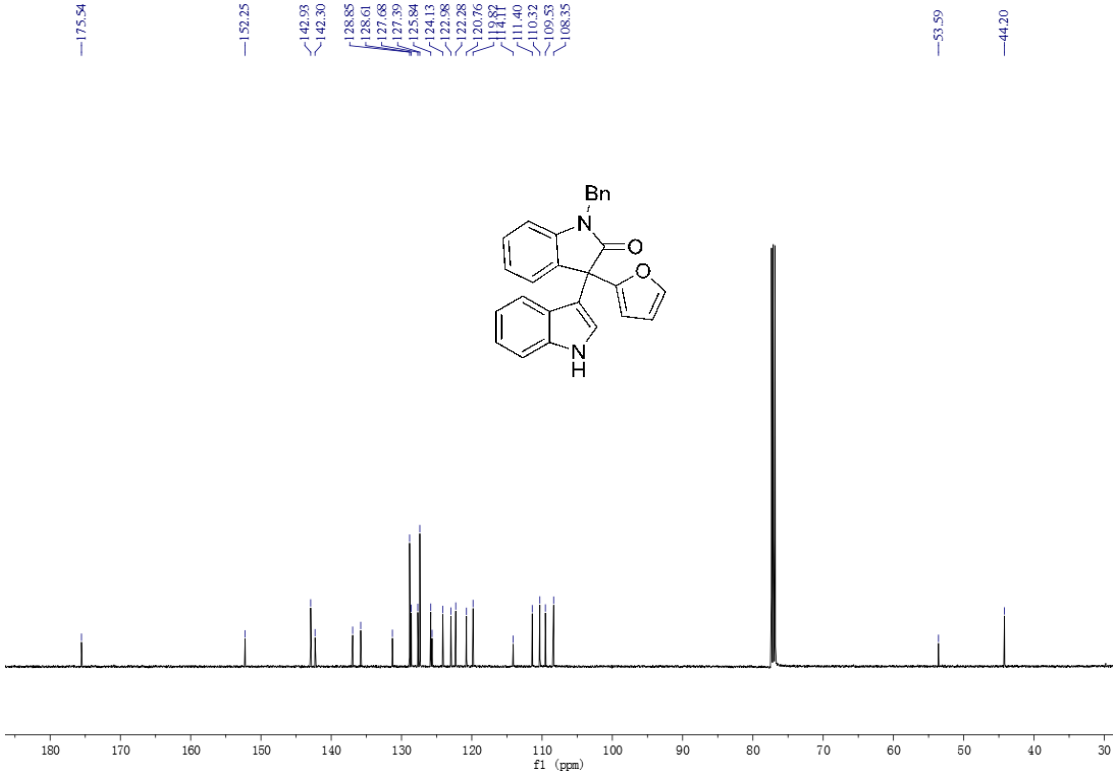



**Physical Appearance:** white solid; 30.0 mg, 59% yield; **m.p.:**107.3 – 109.8℃.
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.24 (d, *J* = 7.9 Hz, 1H), 8.11 (s, 1H), 7.50 (dd, *J* = 7.4, 0.7 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.30 -7.27 (m,4H), 7.25 - 7.21 (m, 3H), 7.21 – 7.19 (m, 1H), 7.09 – 7.06 (m, 1H), 7.06 – 7.04 (m, 1H), 7.03 – 7.02 (m, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 6.79 (d, *J* = 2.7 Hz, 1H), 6.21 – 6.18 (m, 2H), 5.11 (d, *J* = 15.4 Hz, 1H), 4.97 (s, 1H), 4.73 (d, *J* = 15.4 Hz, 1H) ; **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 176.20, 144.32, 142.08, 137.13, 135.64, 131.84, 129.82, 129.28, 128.74, 127.85, 127.82, 124.75, 124.71, 123.32, 123.06, 122.97, 121.63, 120.49, 117.04, 115.69, 111.66, 111.16, 109.81, 53.44, 44.27 **;HRMS (ESI)** calculated for $C_{29}H_{22}N_3OBr$ Na$[M+Na]^+$ : 530.0844, found: 530.0837.

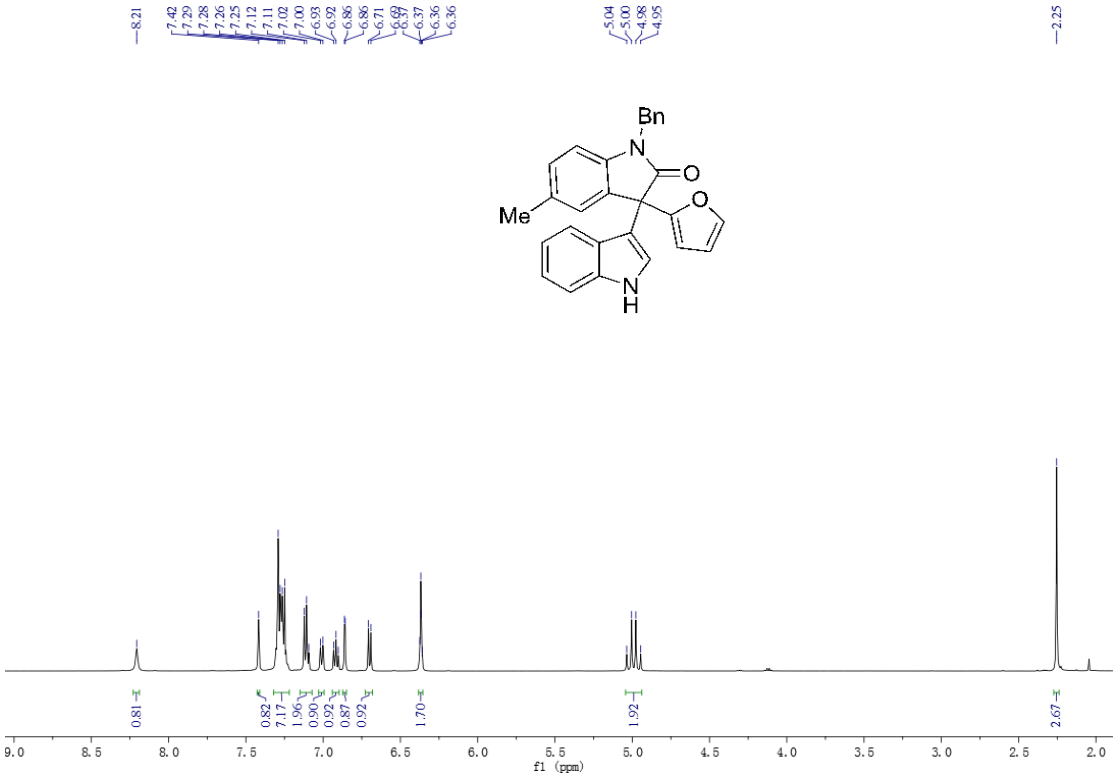
## 4. $^{1}$H NMR and $^{13}$C NMR Spectra

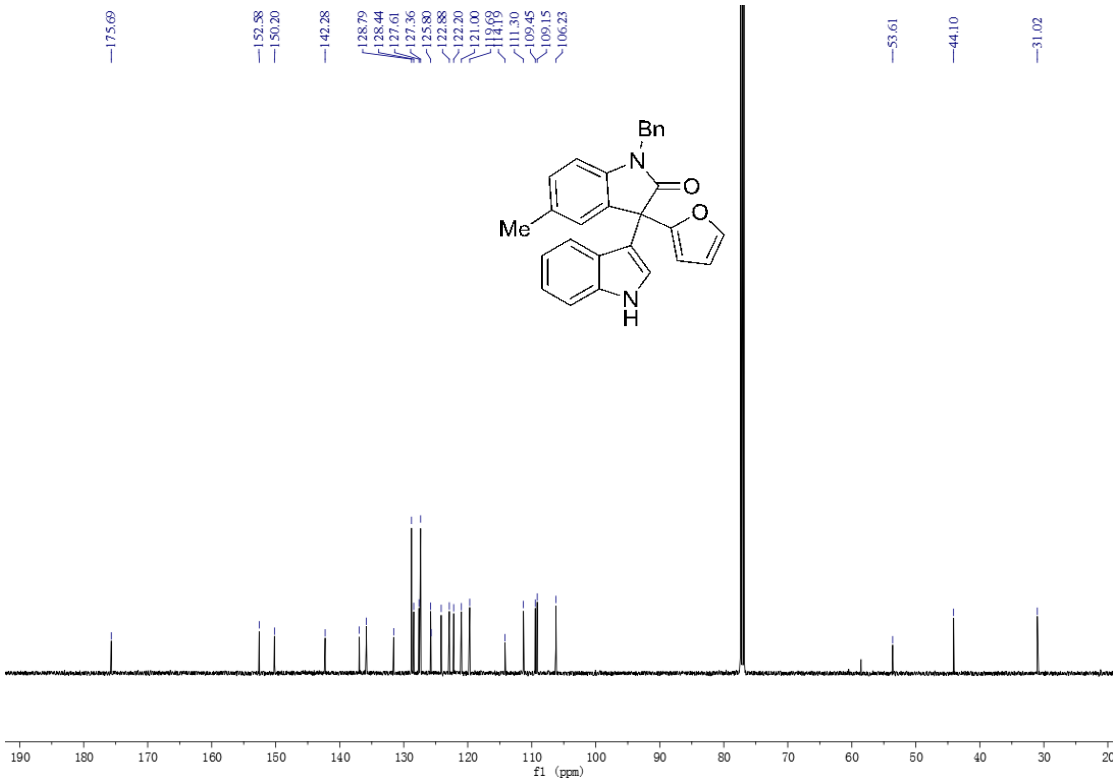
1-benzyl-3-(furan-2-yl)-3-(1H-indol-3-yl)indolin-2-one **(3a)**



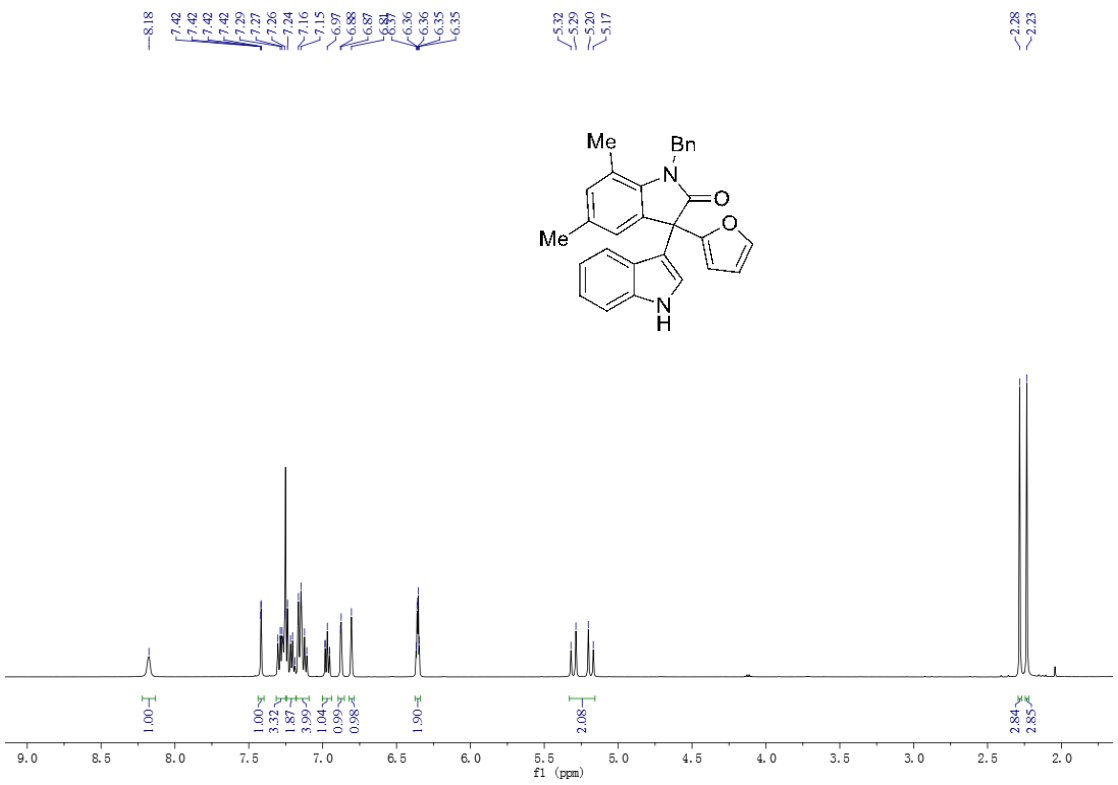



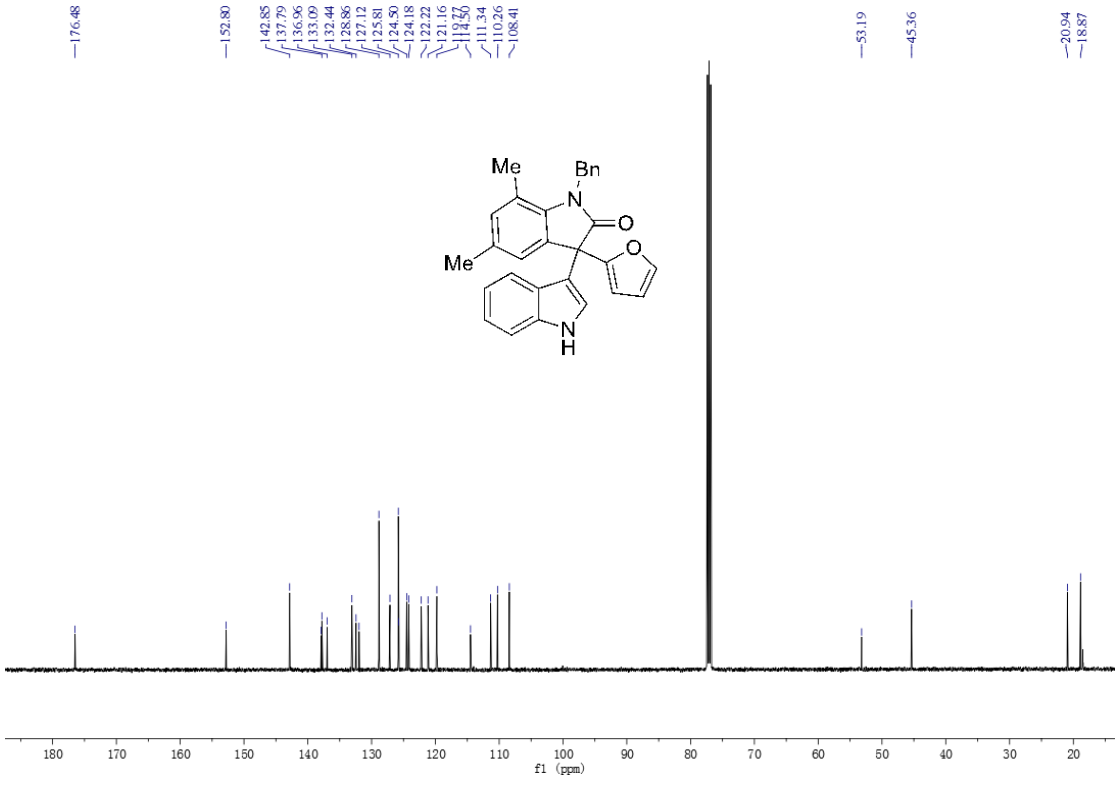
1-benzyl-3-(furan-2-yl)-3-(1H-indol-3-yl)-5-methylindolin-2-one **(3b)**



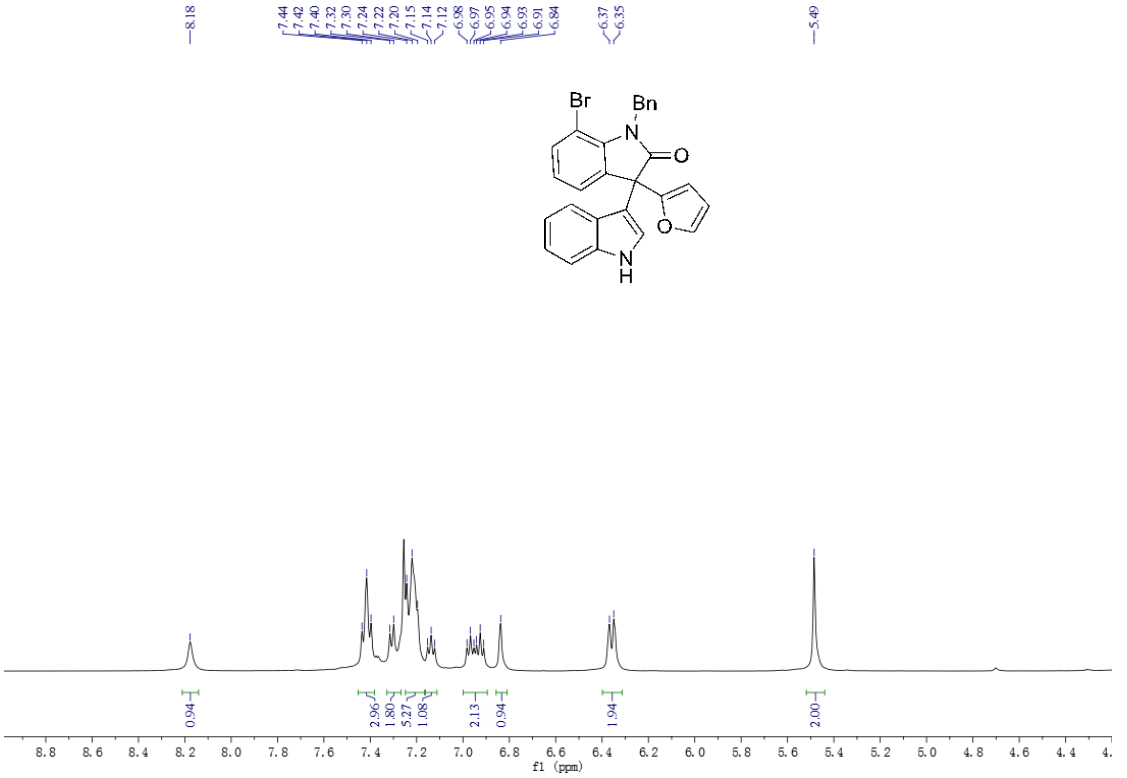



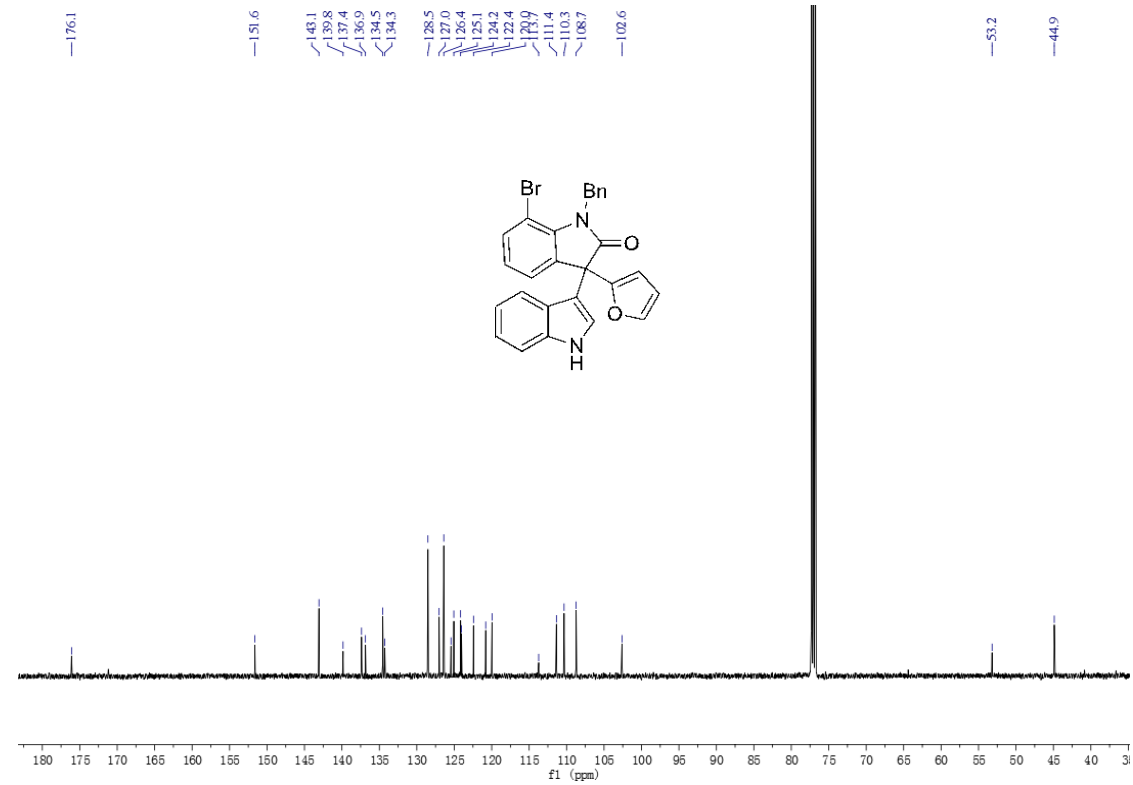
1-benzyl-3-(furan-2-yl)-3-(1H-indol-3-yl)-5,7-dimethylindolin-2-one **(3c)**



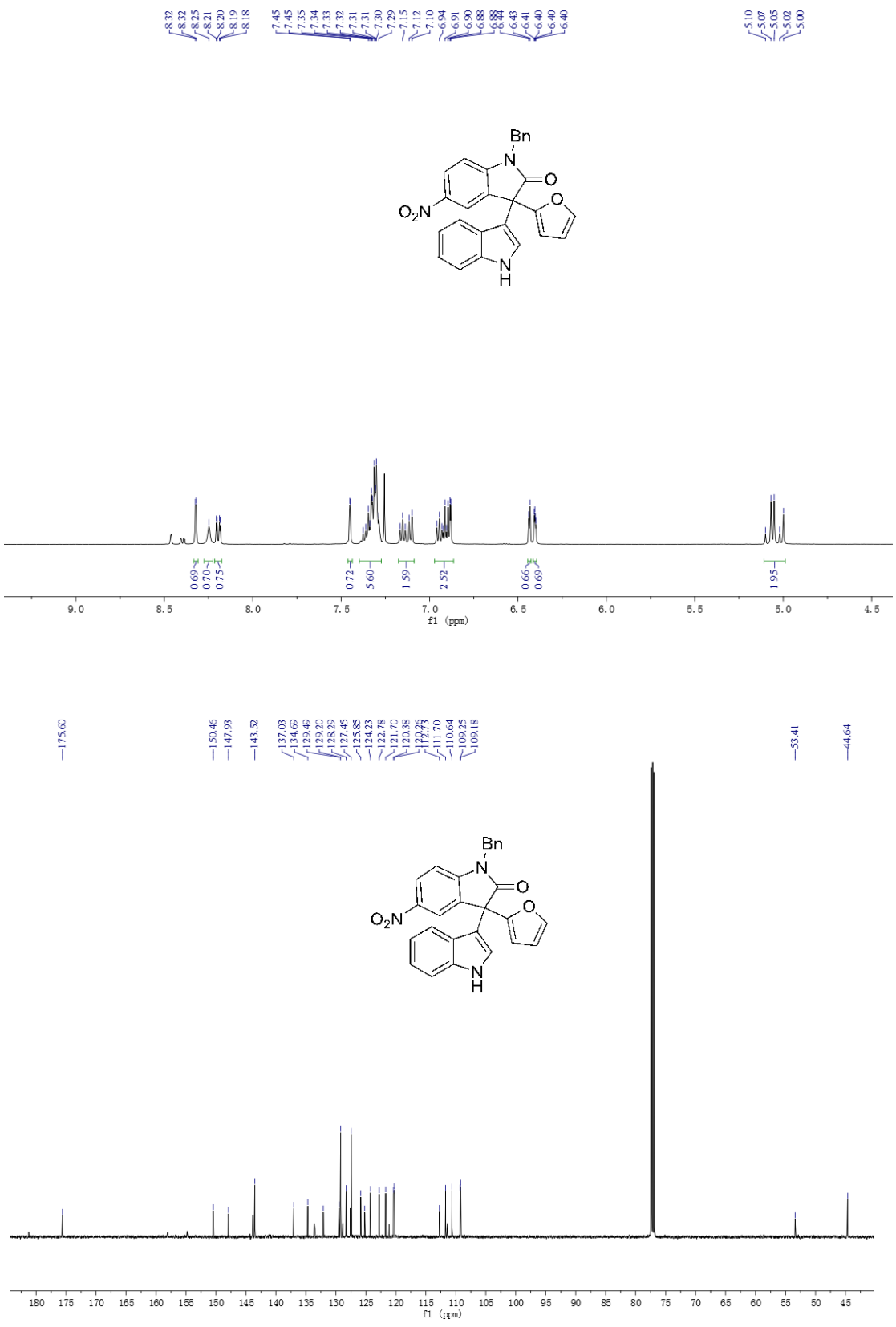



1-benzyl-7-bromo-3-(furan-2-yl)-3-(1H-indol-3-yl)indolin-2-one **(3d)**

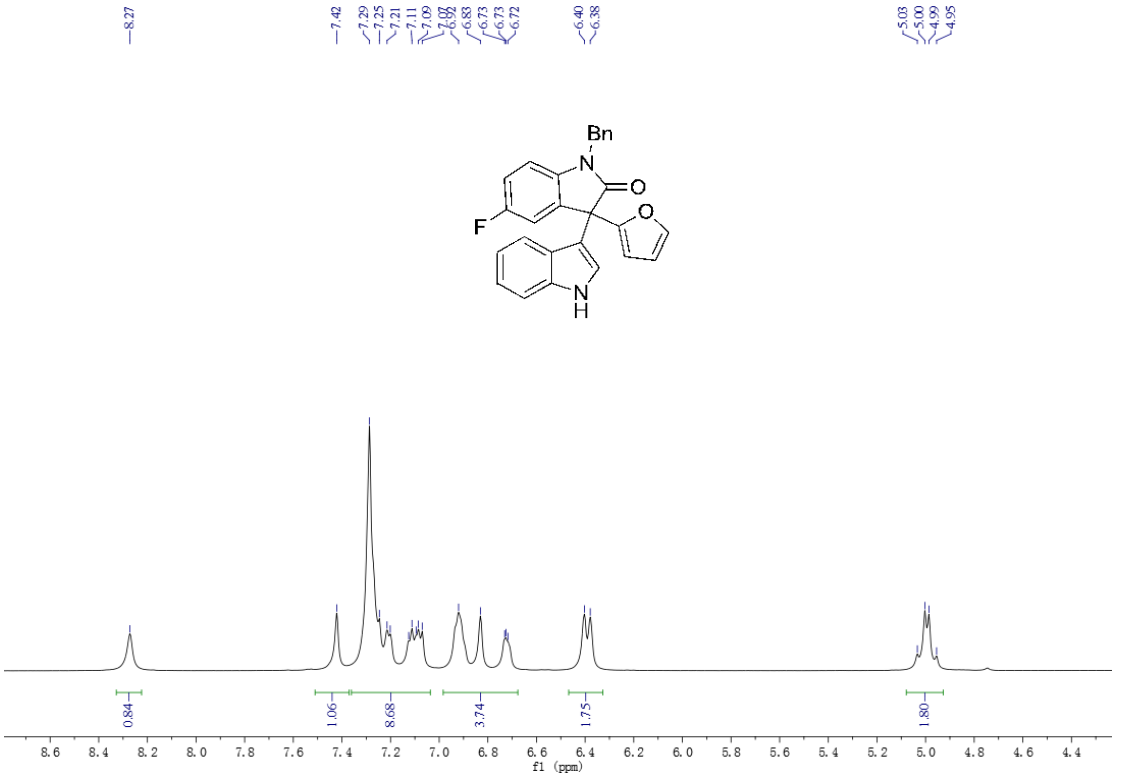


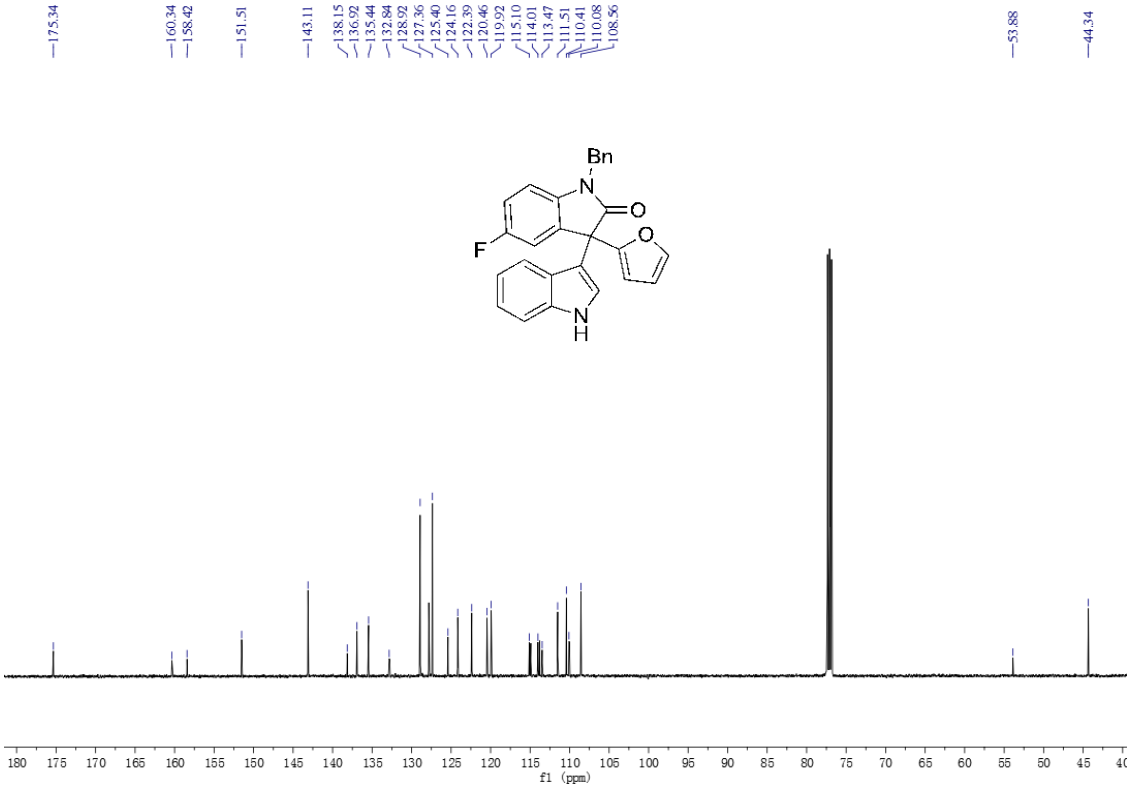



1-benzyl-3-(furan-2-yl)-3-(1H-indol-3-yl)-5-nitroindolin-2-one **(3e)**

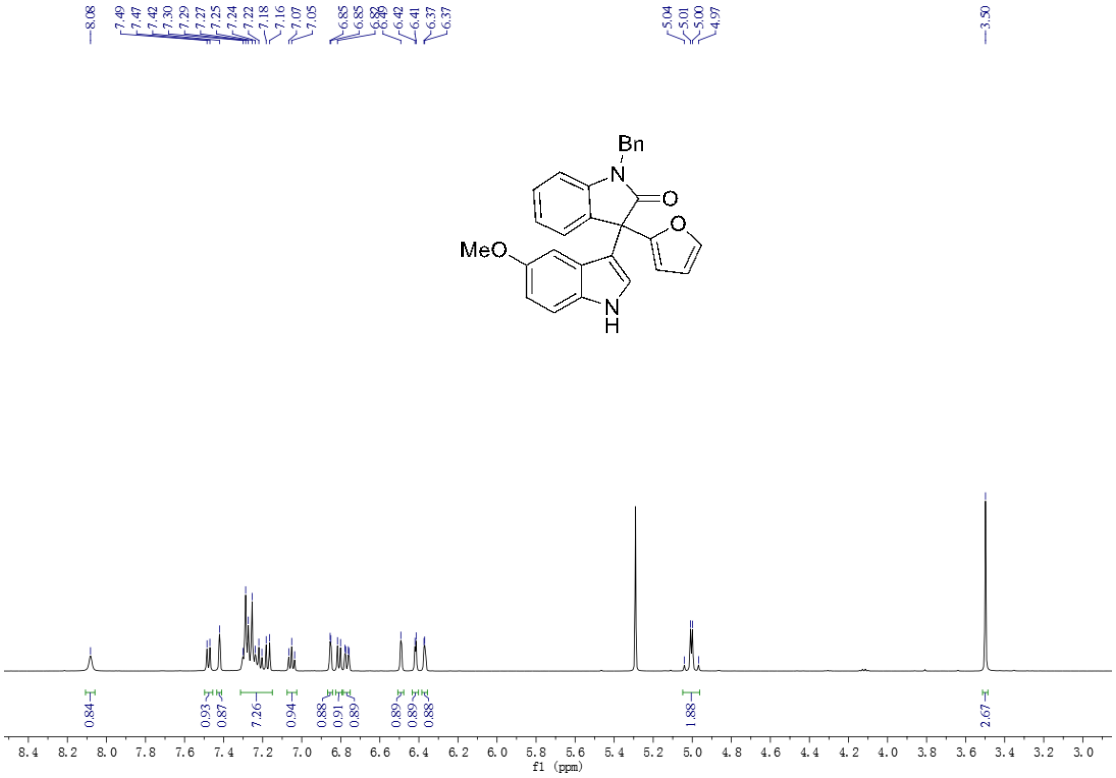


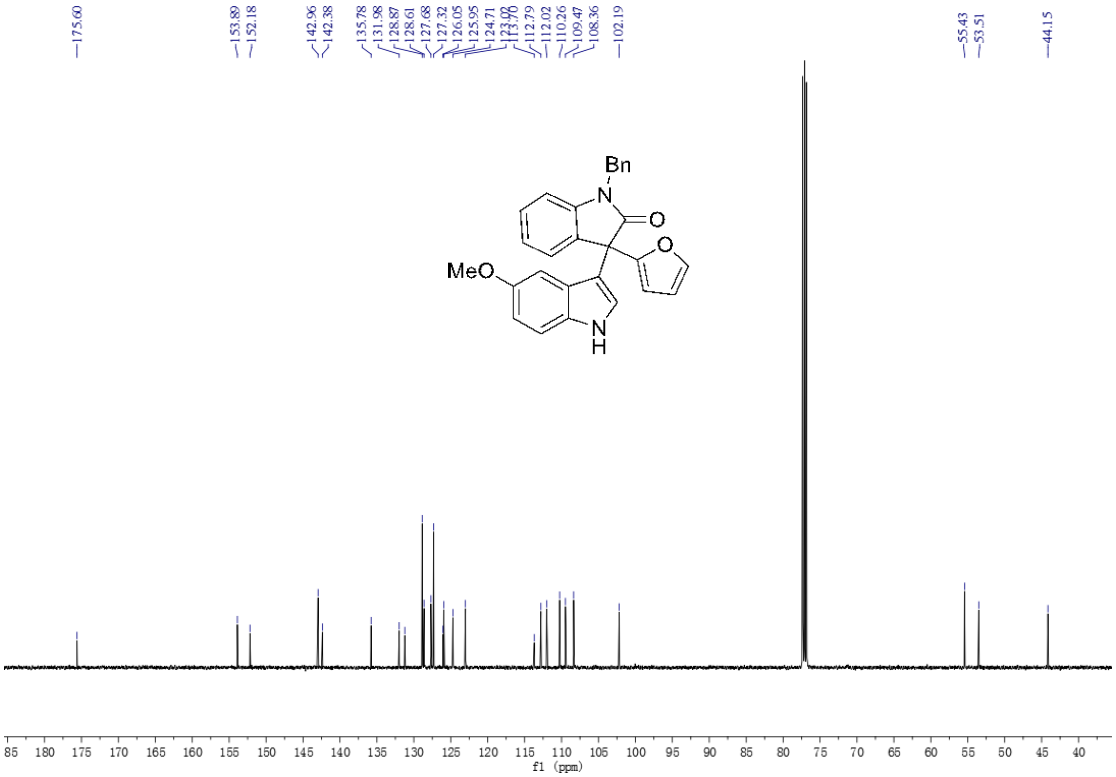
1-benzyl-5-fluoro-3-(furan-2-yl)-3-(1H-indol-3-yl)indolin-2-one **(3f)**



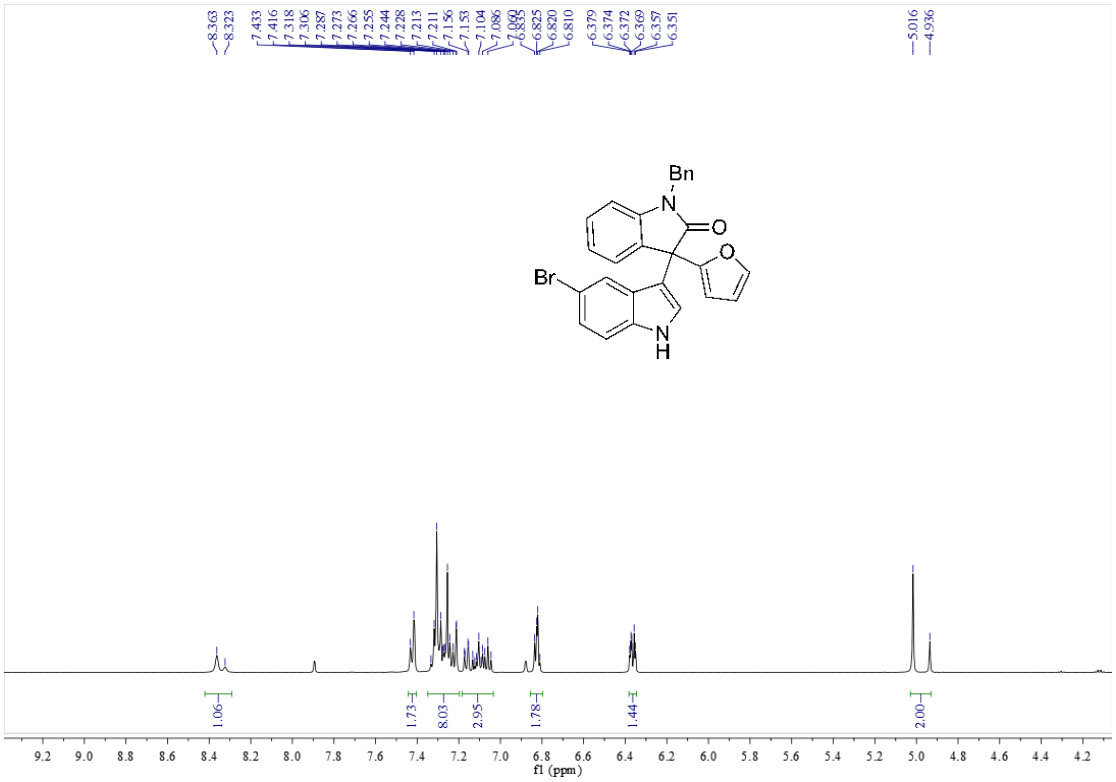



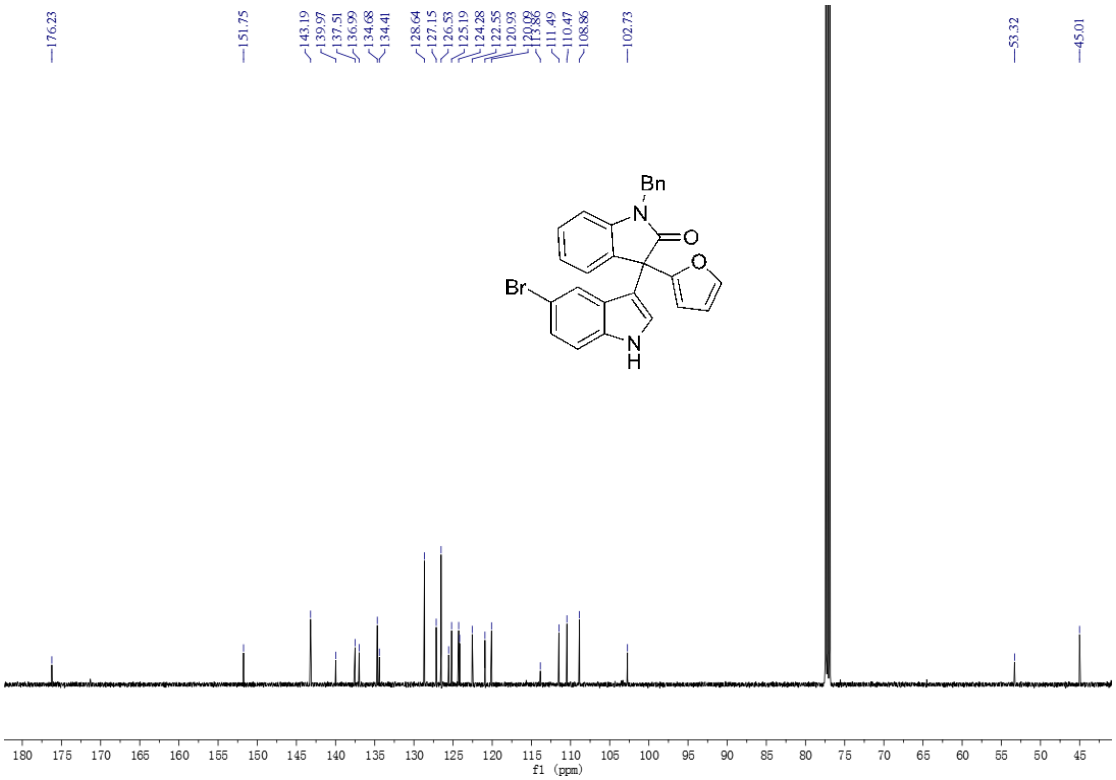
1-benzyl-3-(furan-2-yl)-3-(5-methoxy-1H-indol-3-yl)indolin-2-one **(3g)**



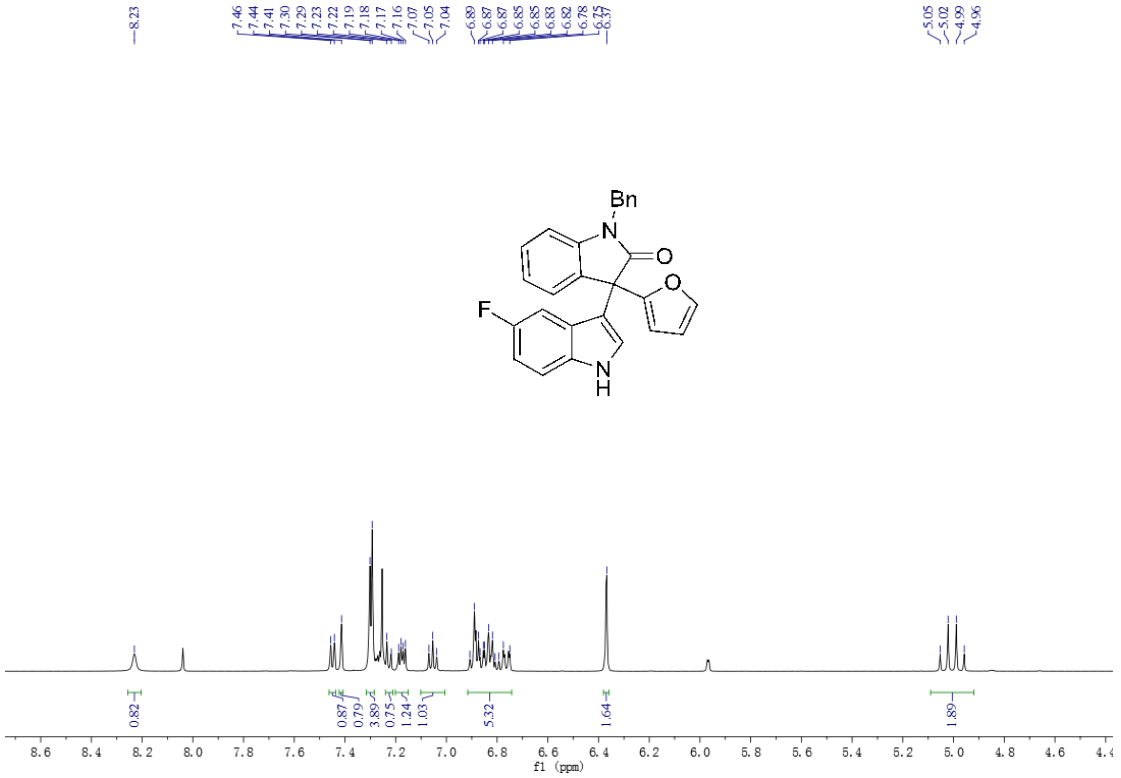



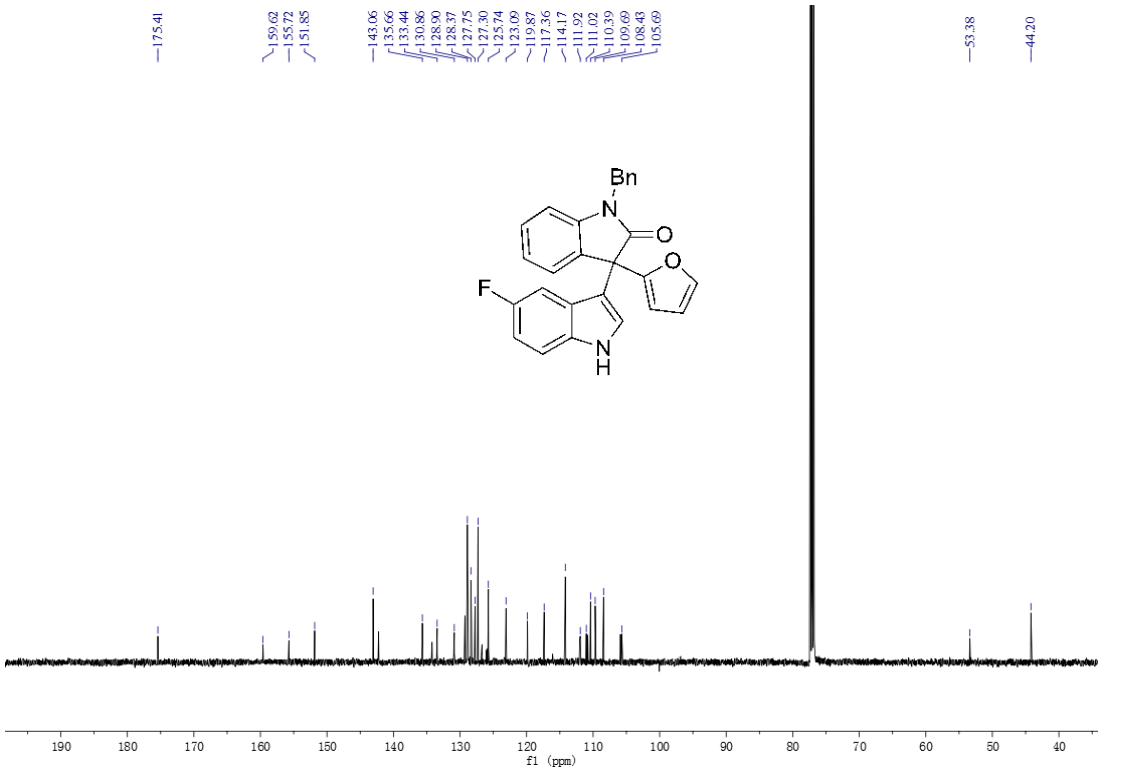
1-benzyl-3-(5-bromo-1H-indol-3-yl)-3-(furan-2-yl)indolin-2-one **(3h)**



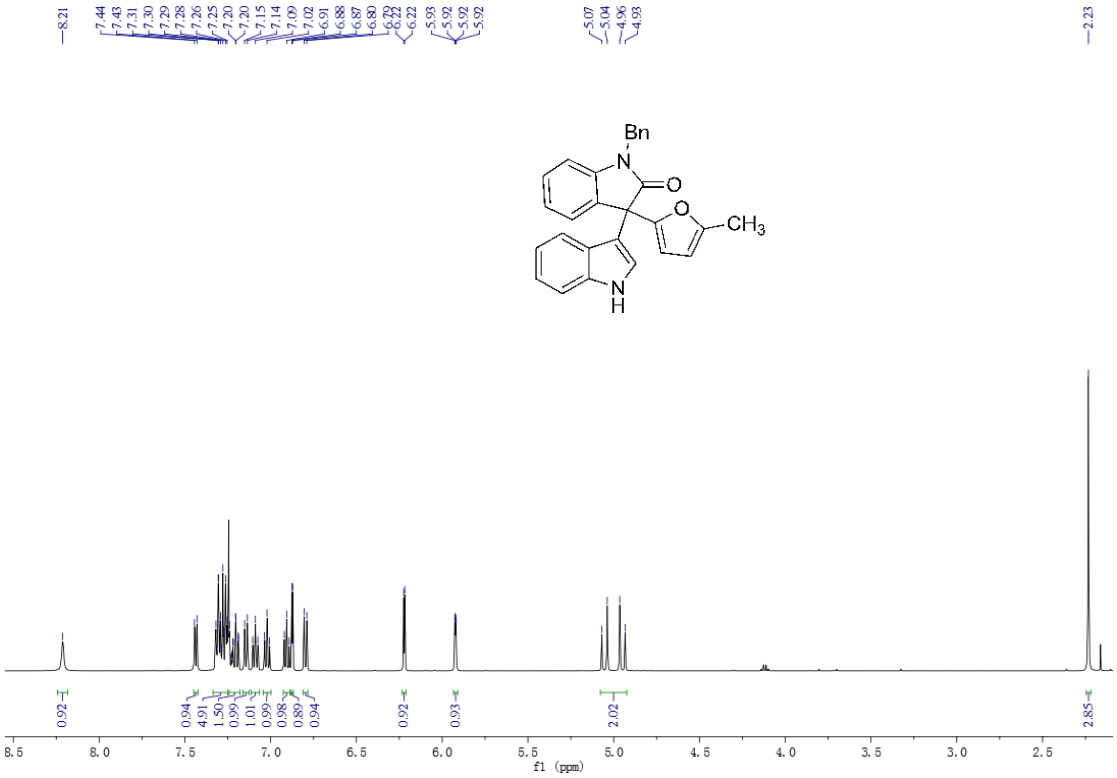



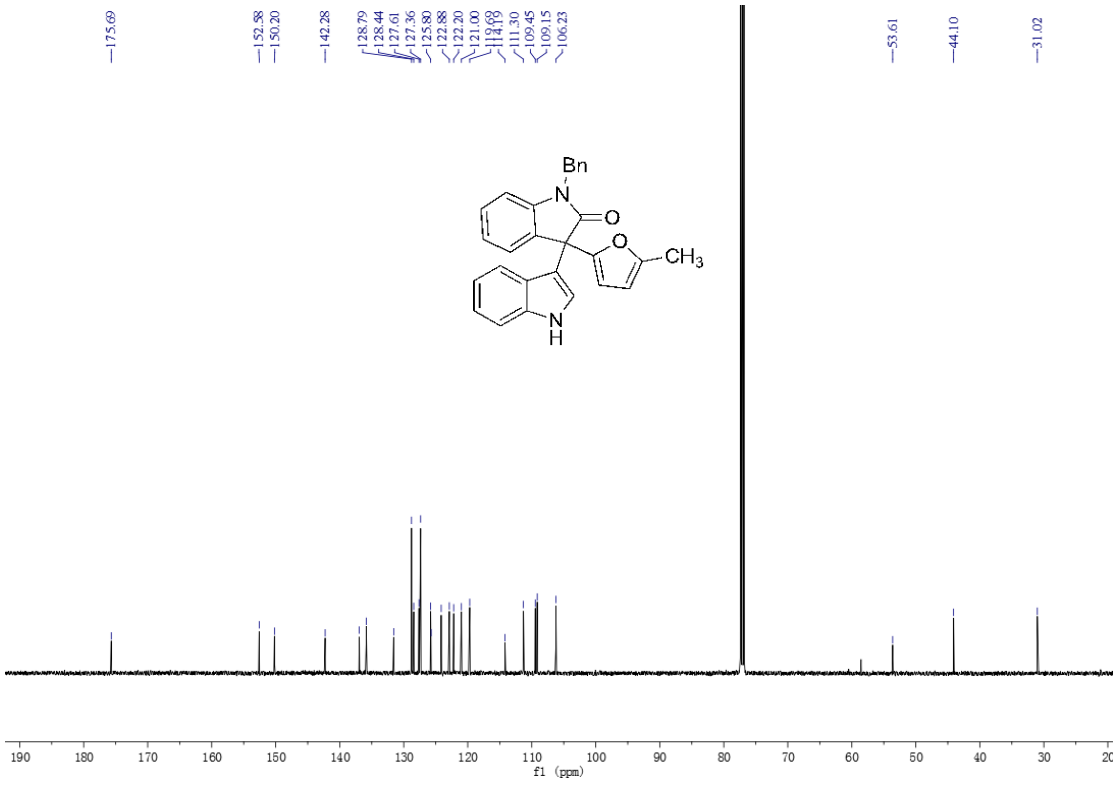
**1-benzyl-3-(5-fluoro-1H-indol-3-yl)-3-(furan-2-yl)indolin-2-one (3i)**



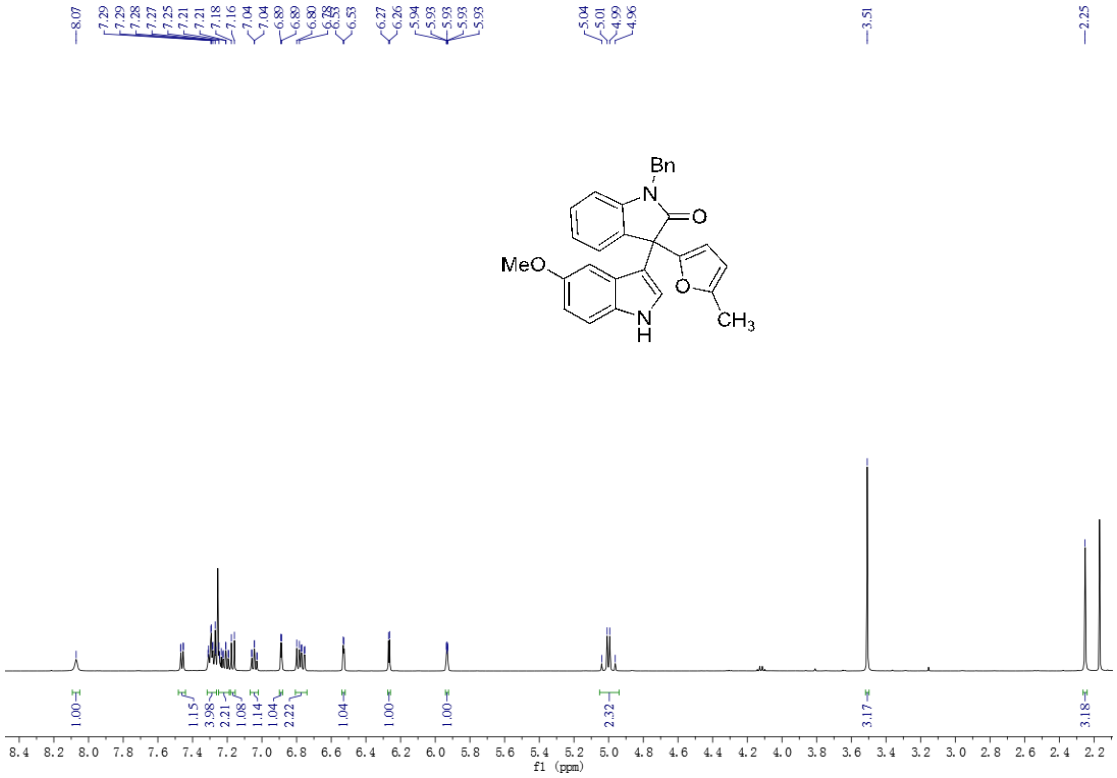



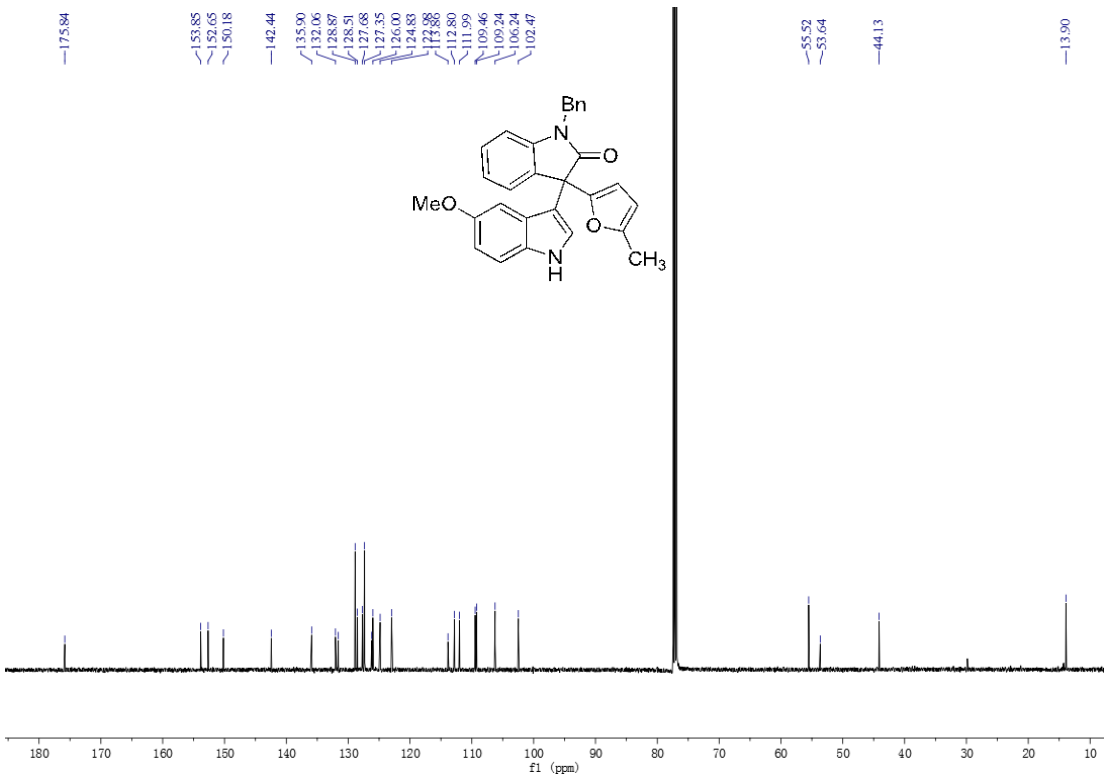
1-benzyl-3-(1H-indol-3-yl)-3-(5-methylfuran-2-yl)indolin-2-one **(3j)**



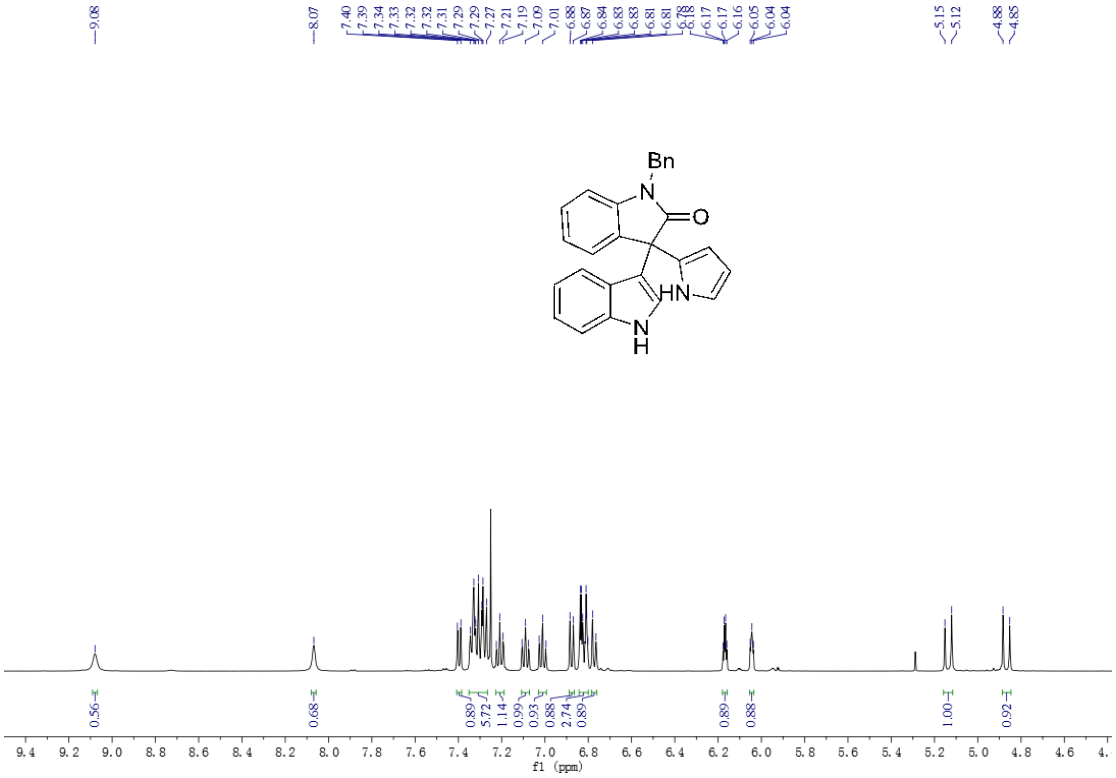



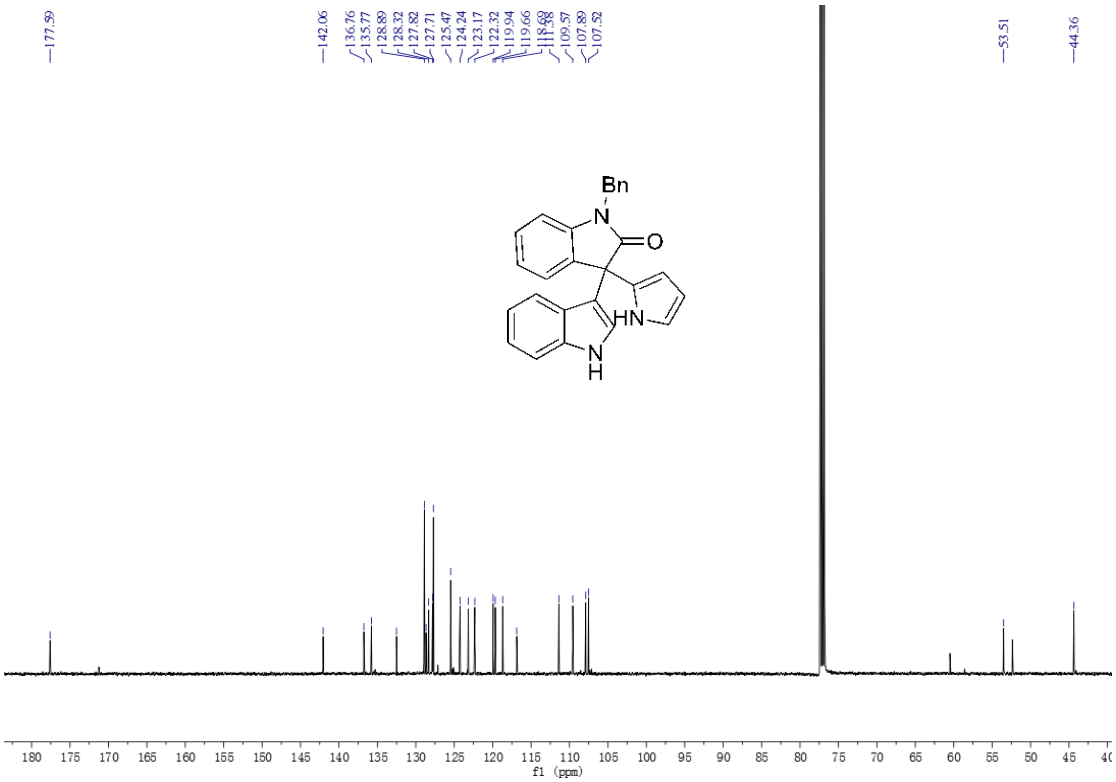
1-benzyl-3-(5-methoxy-1H-indol-3-yl)-3-(5-methylfuran-2-yl)indolin-2-one **(3k)**



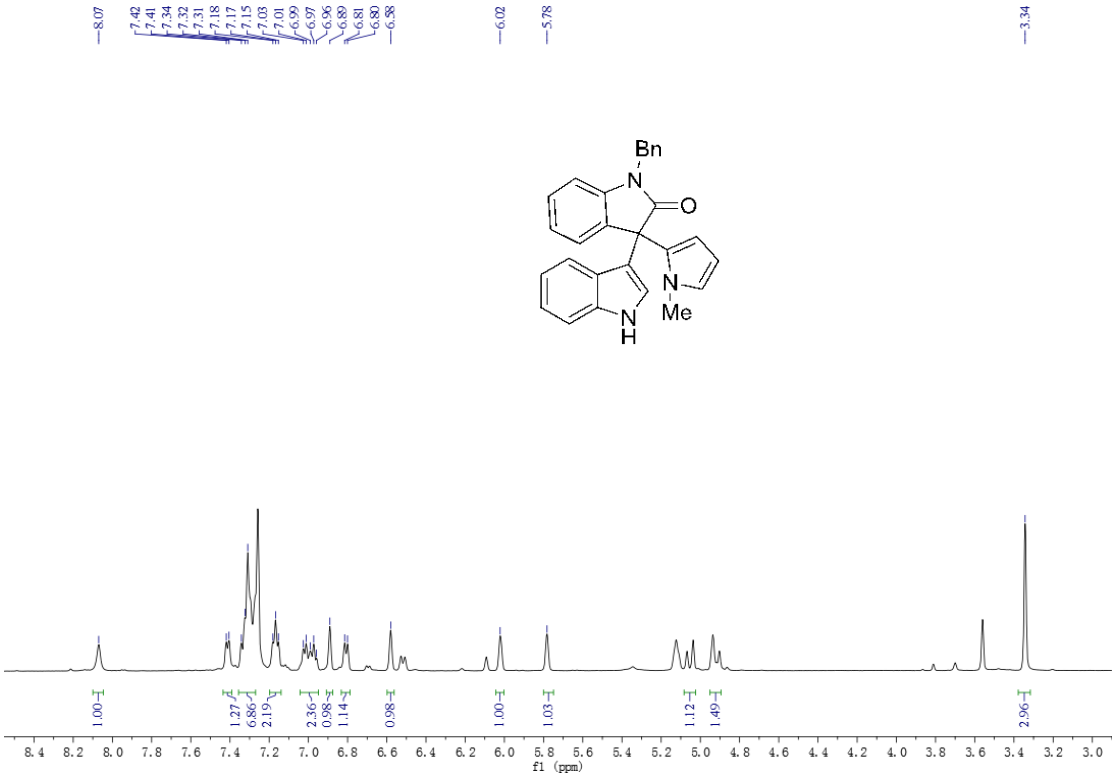



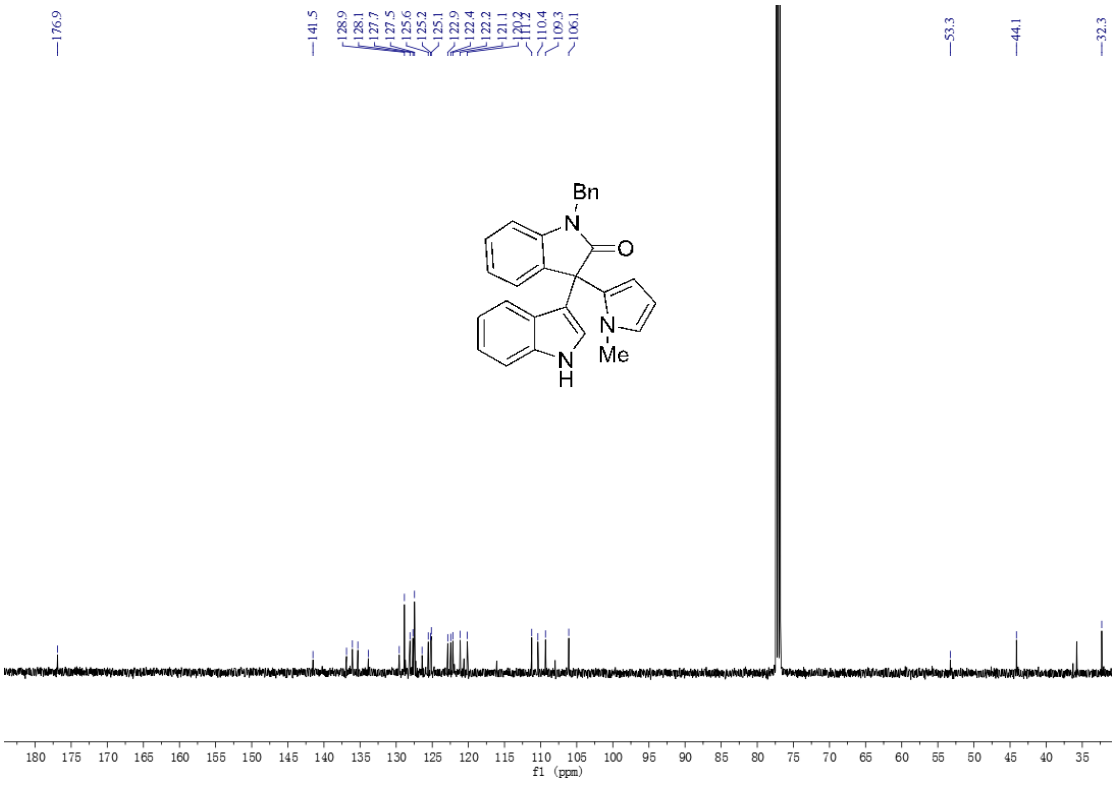
1-benzyl-3-(1H-indol-3-yl)-3-(1H-pyrrol-2-yl)indolin-2-one **(5a)**



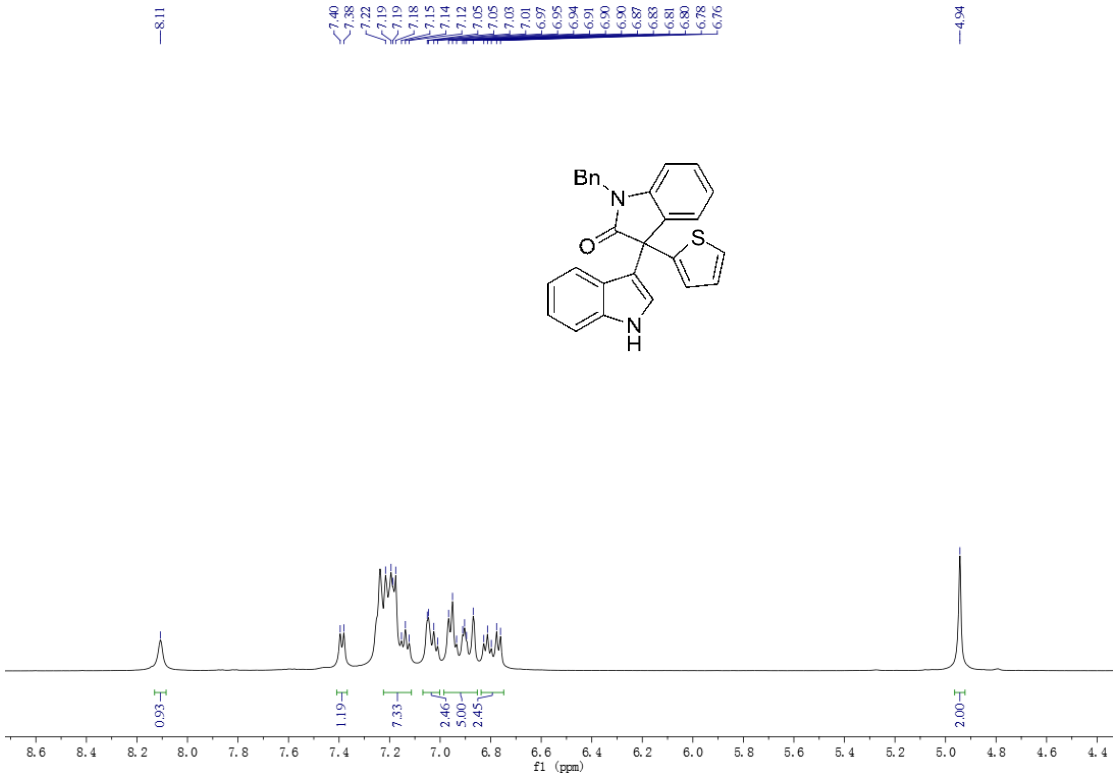



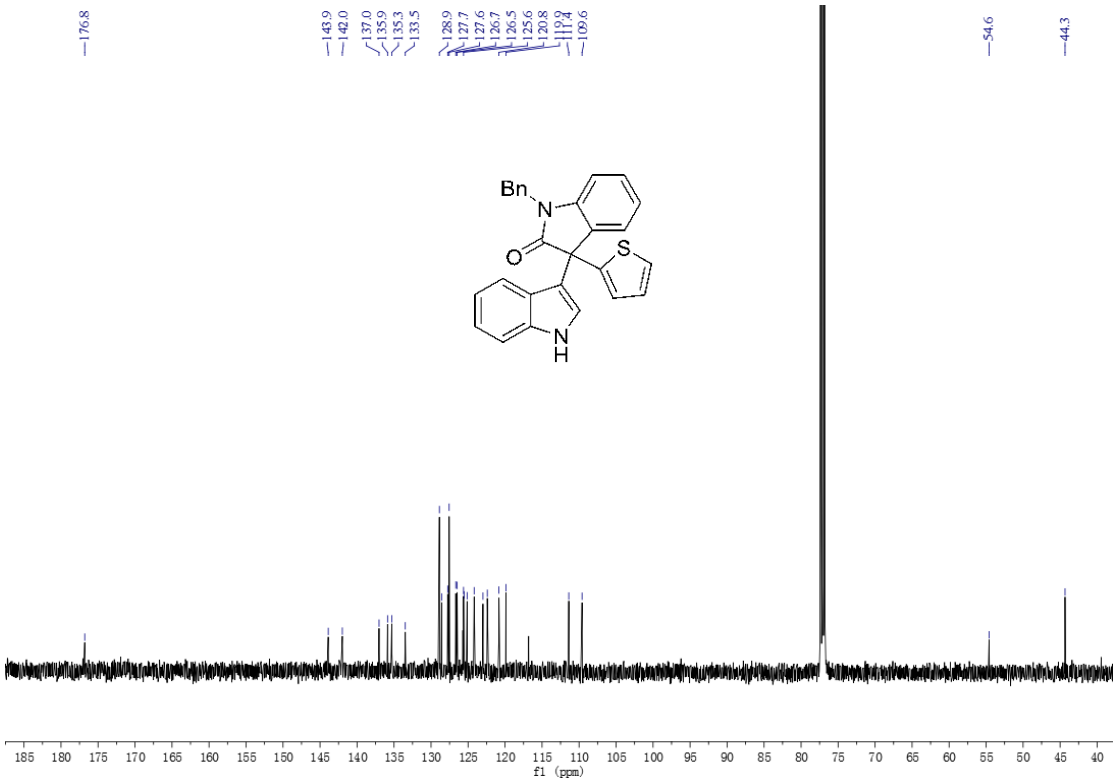
1-benzyl-3-(1H-indol-3-yl)-3-(1-methyl-1H-pyrrol-2-yl)indolin-2-one **(5b)**



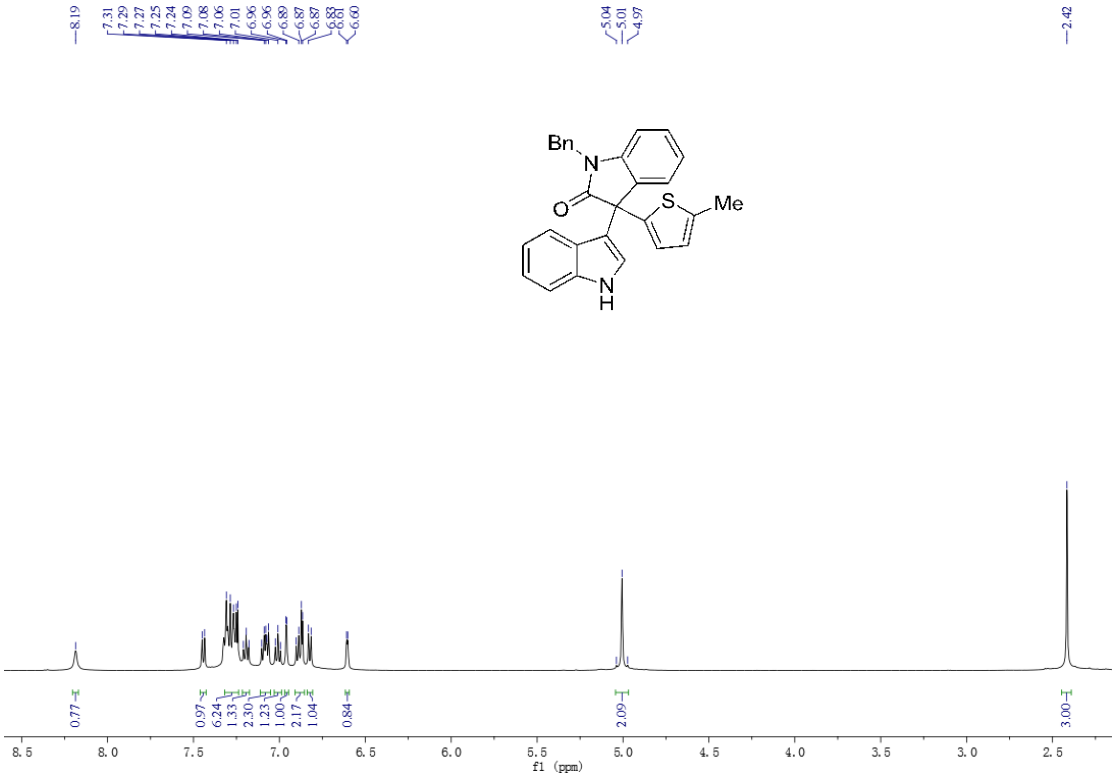



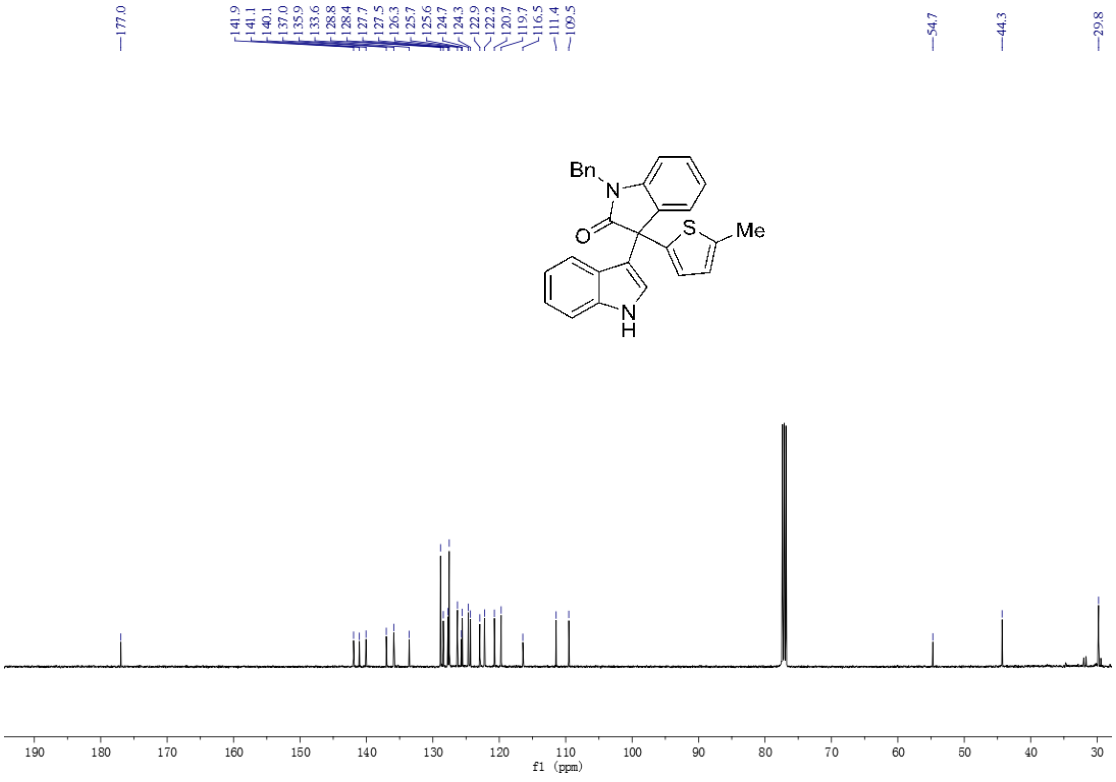
1-benzyl-3-(1H-indol-3-yl)-3-(thiophen-2-yl)indolin-2-one **(5c)**



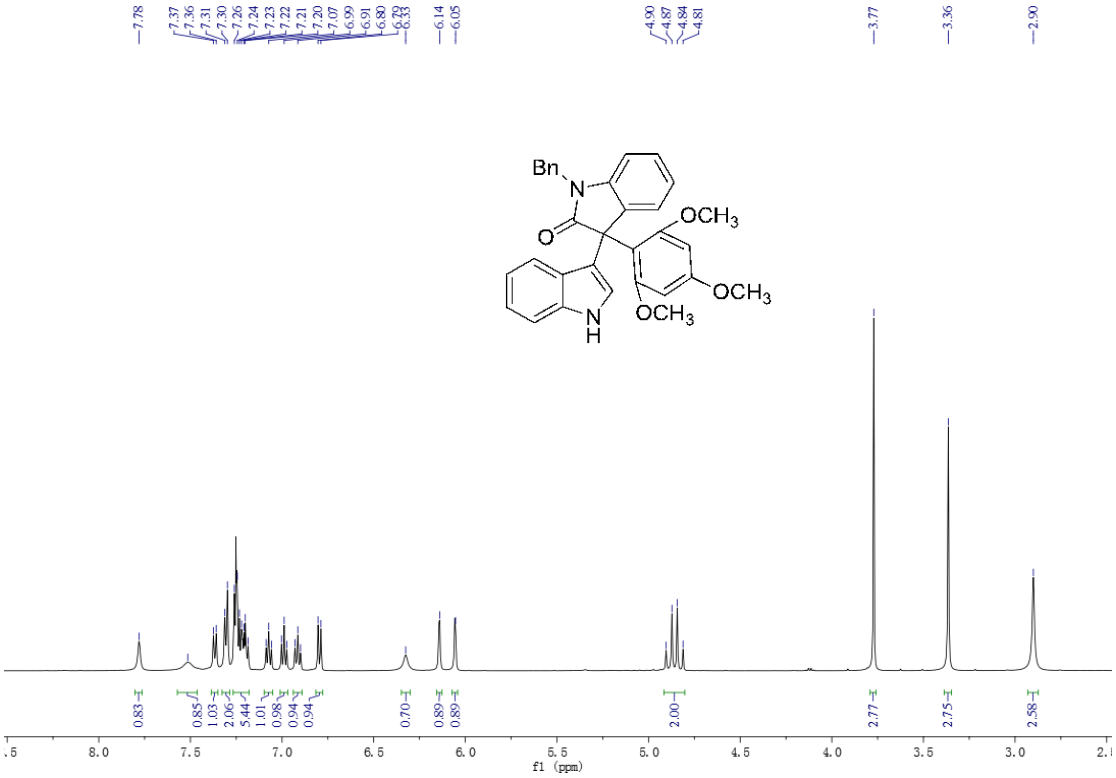



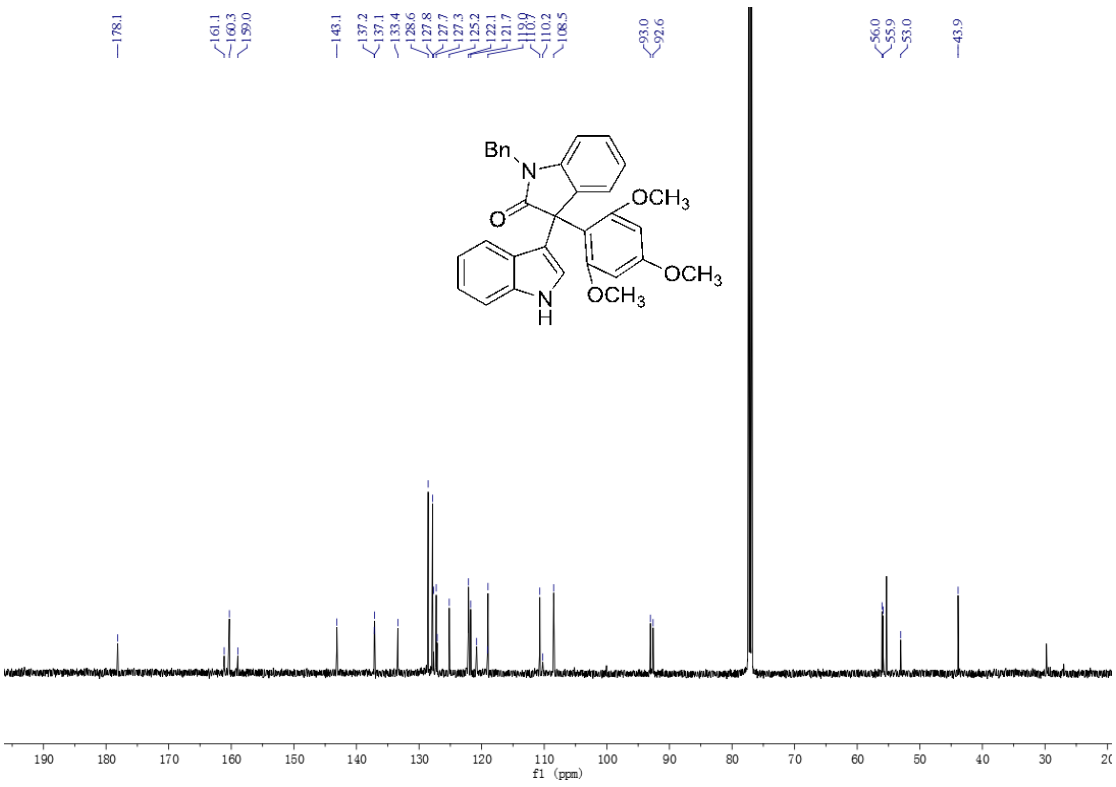
1-benzyl-3-(1H-indol-3-yl)-3-(5-methylthiophen-2-yl)indolin-2-one **(5d)**



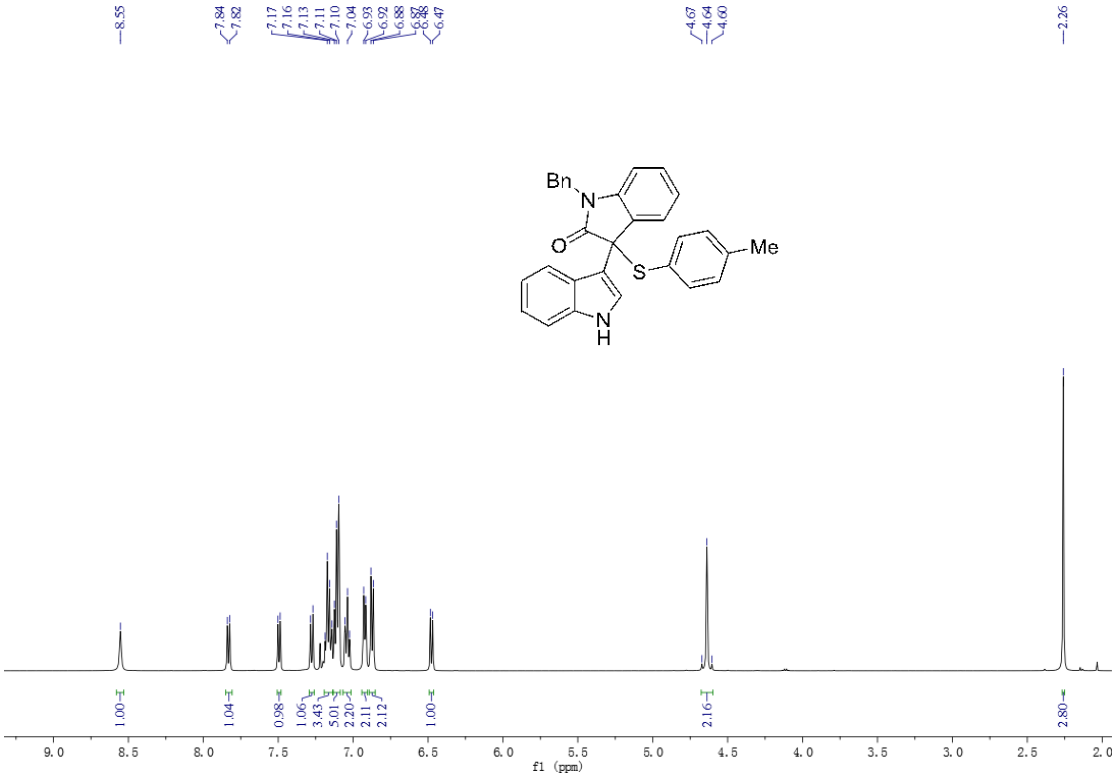



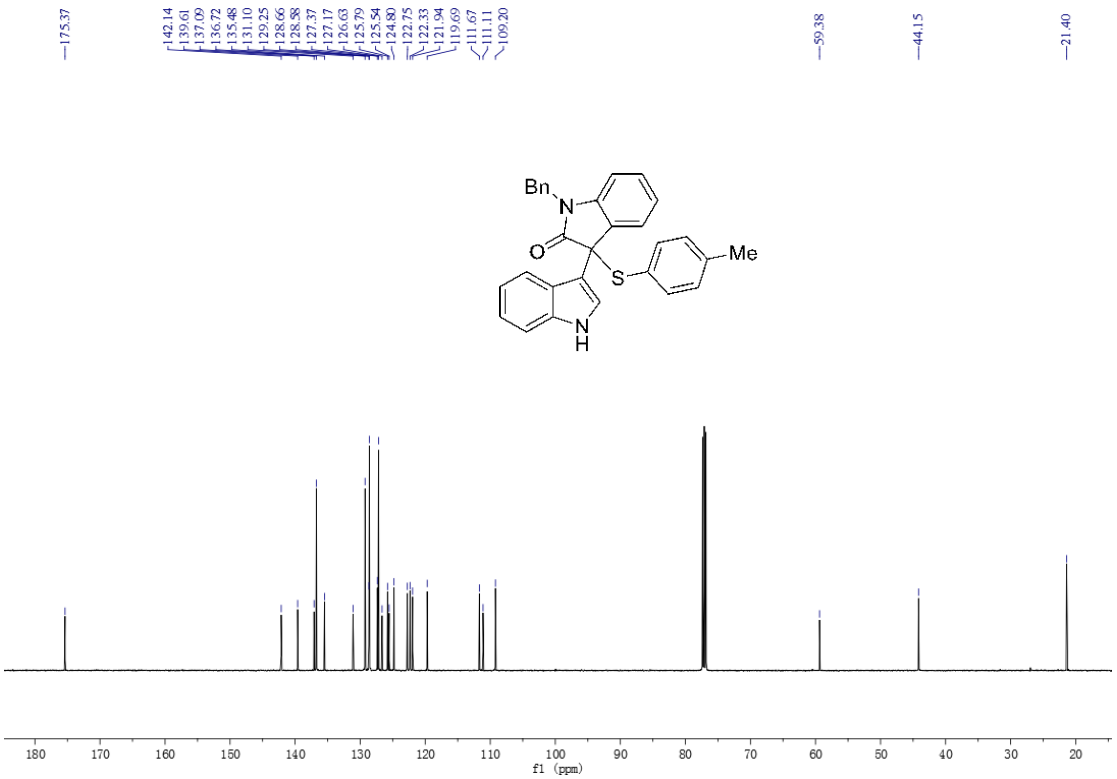
1-benzyl-3-(1H-indol-3-yl)-3-(2,4,6-trimethoxyphenyl)indolin-2-one **(5e)**



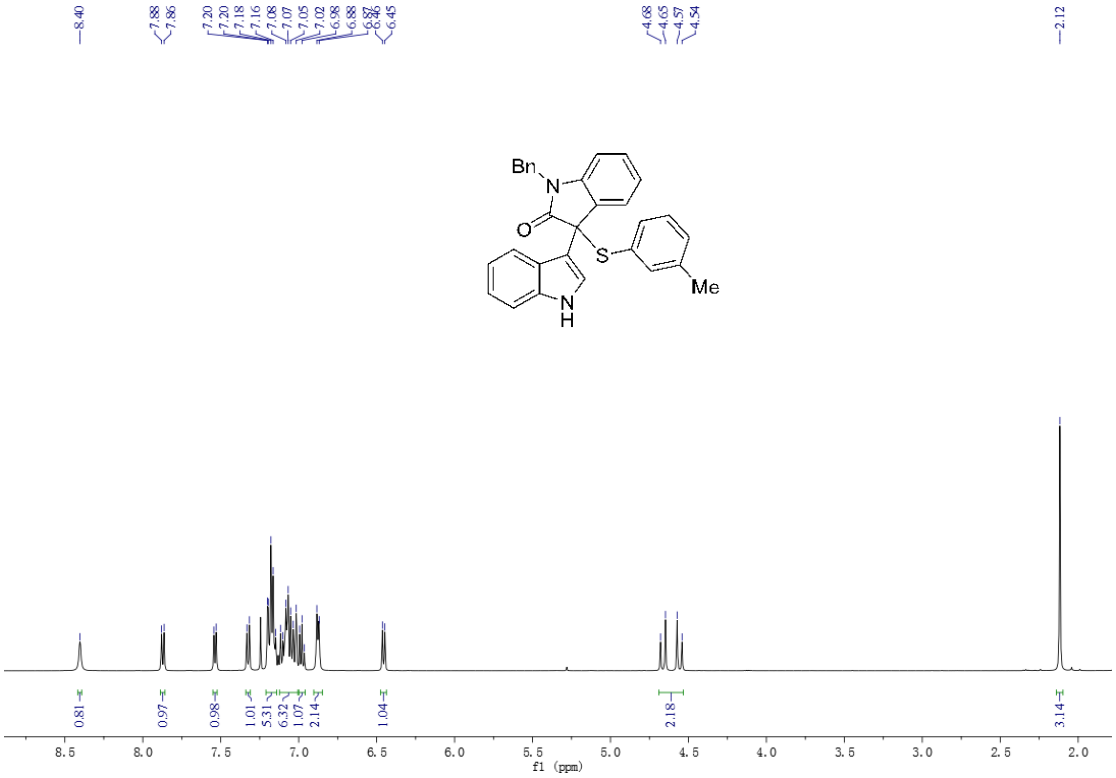



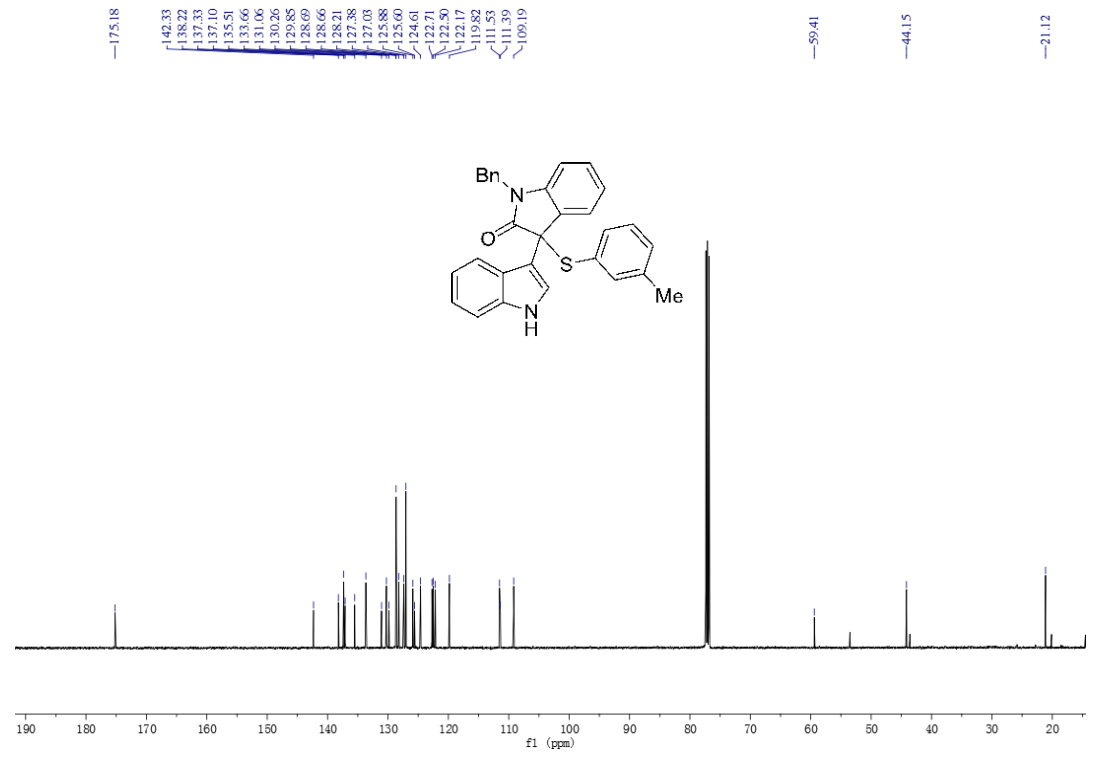
1-benzyl-3-(1H-indol-3-yl)-3-(p-tolylthio)indolin-2-one **(5f)**



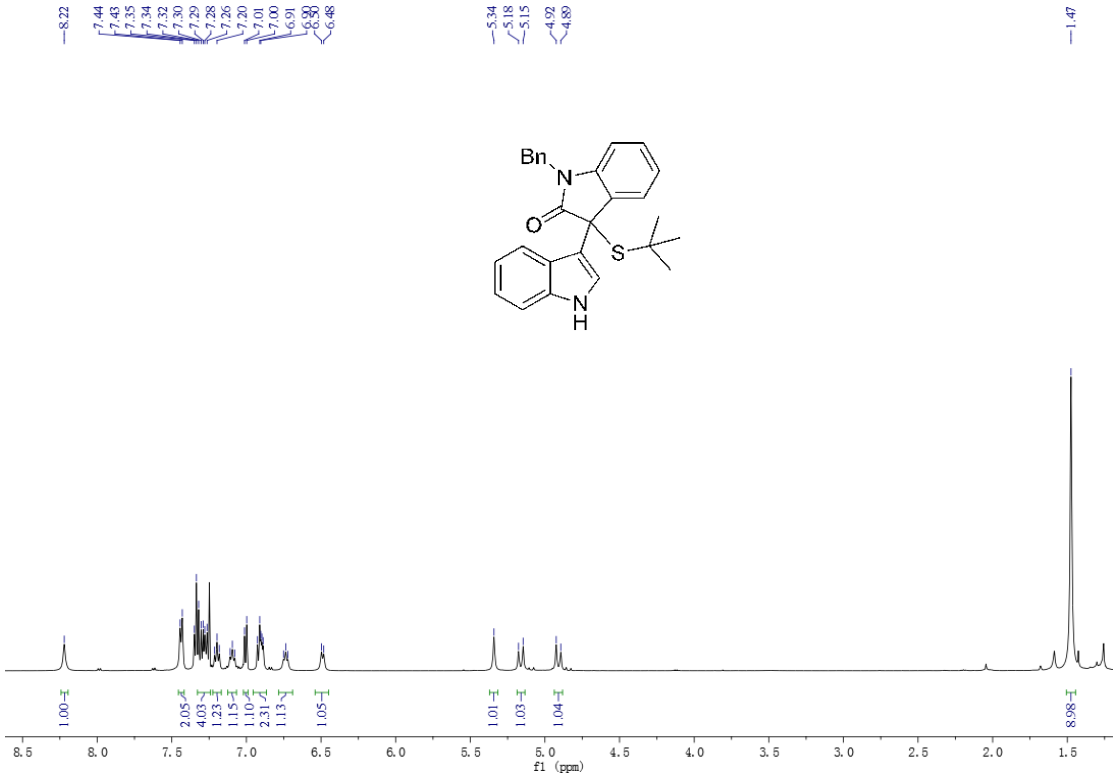



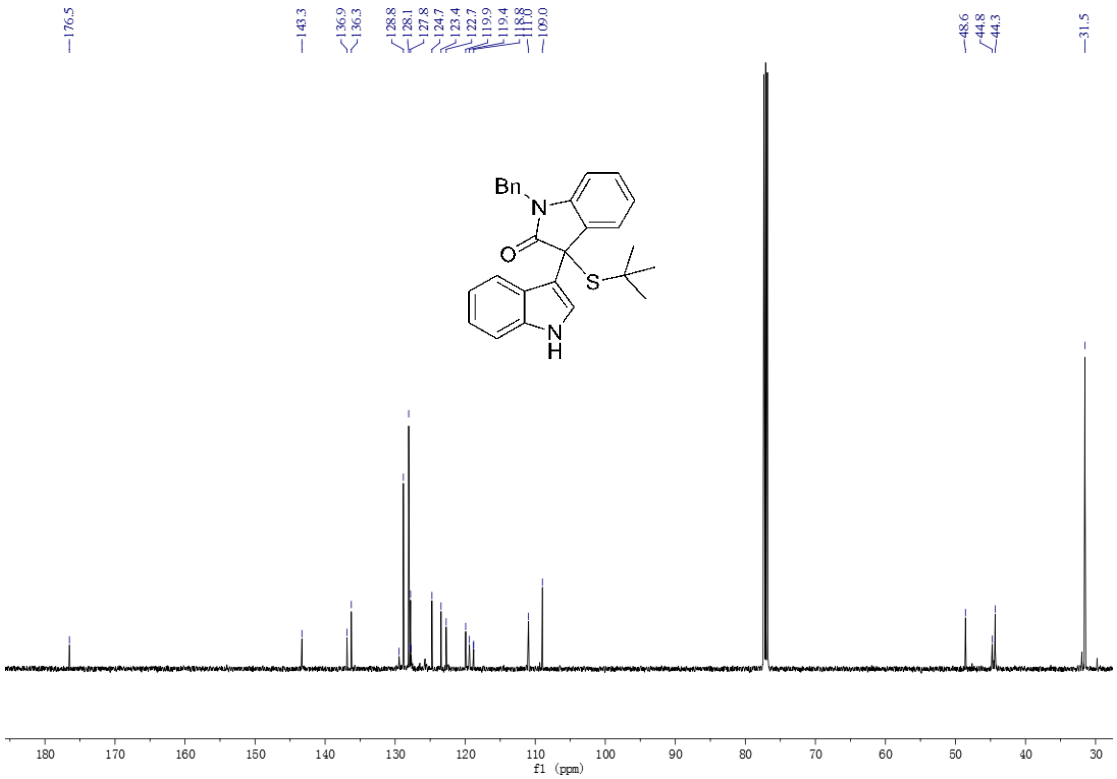
1-benzyl-3-(1H-indol-3-yl)-3-(m-tolylthio)indolin-2-one **(5g)**



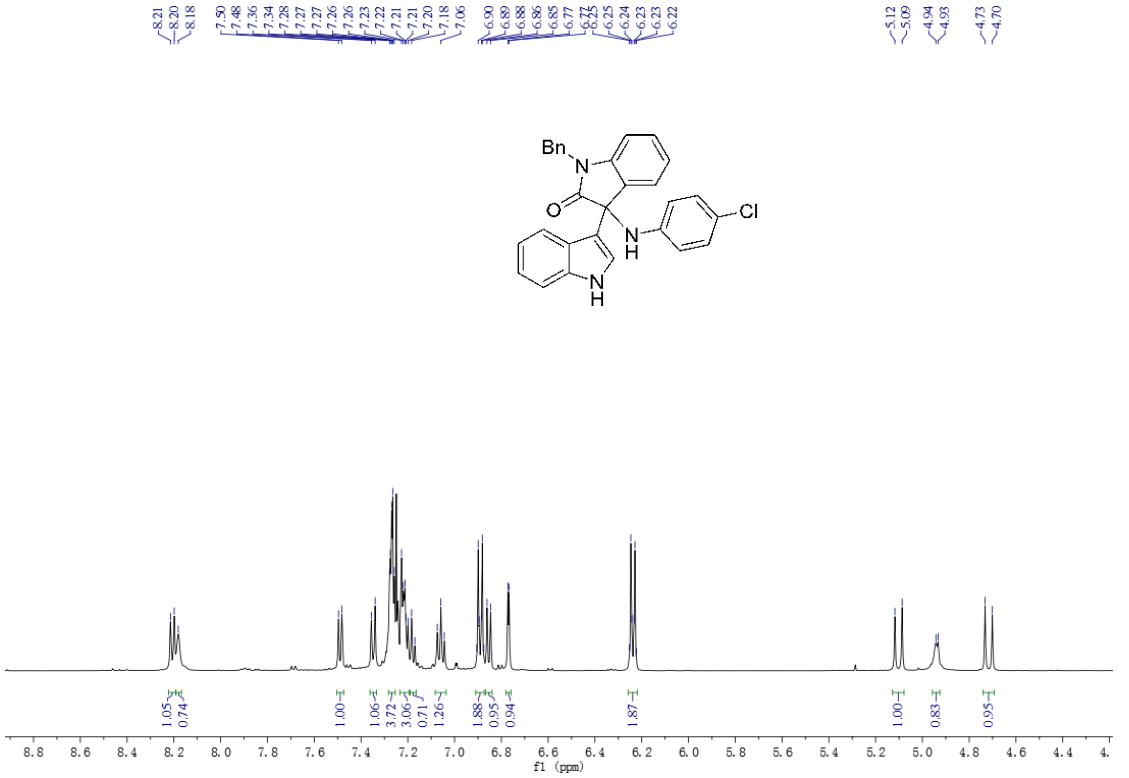



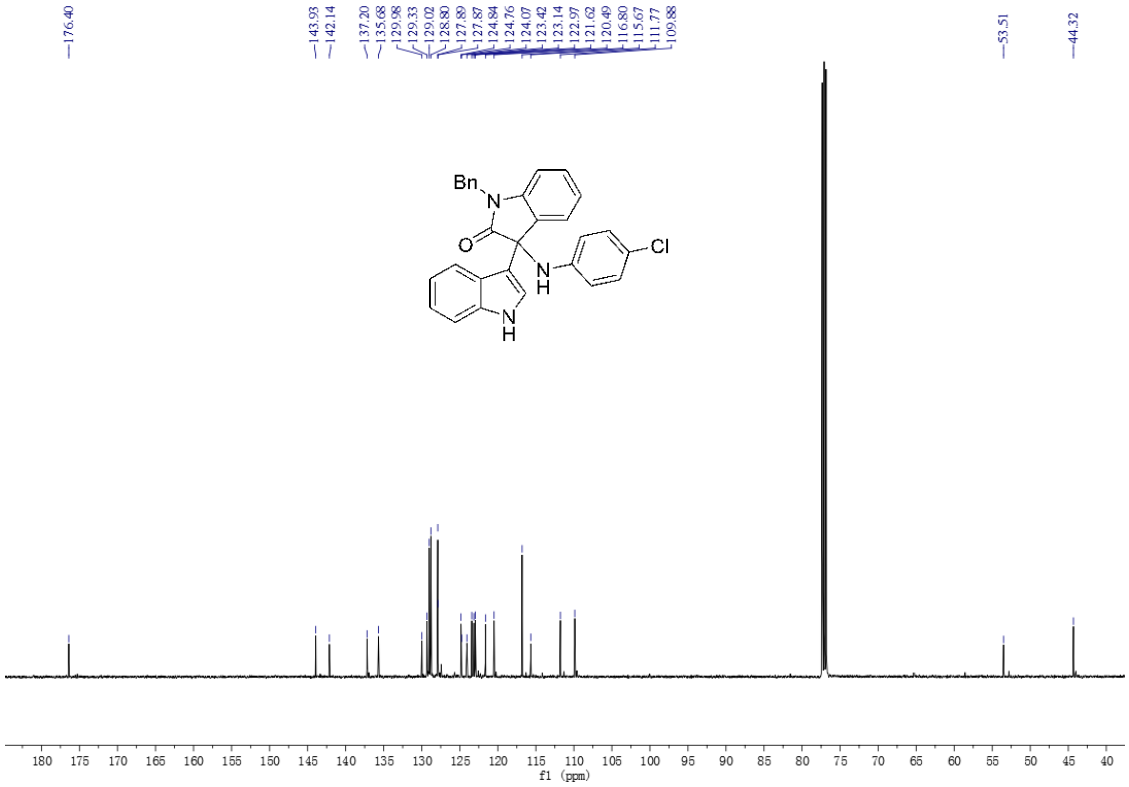
1-benzyl-3-(tert-butylthio)-3-(1H-indol-3-yl)indolin-2-one **(5h)**



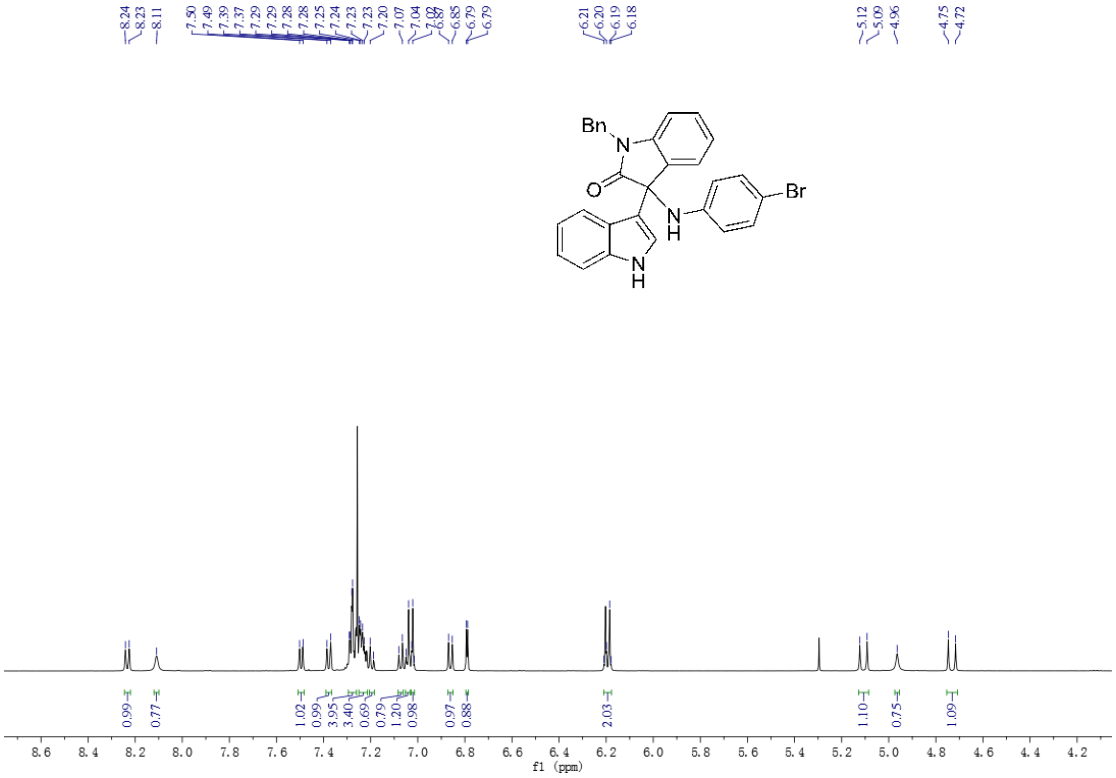



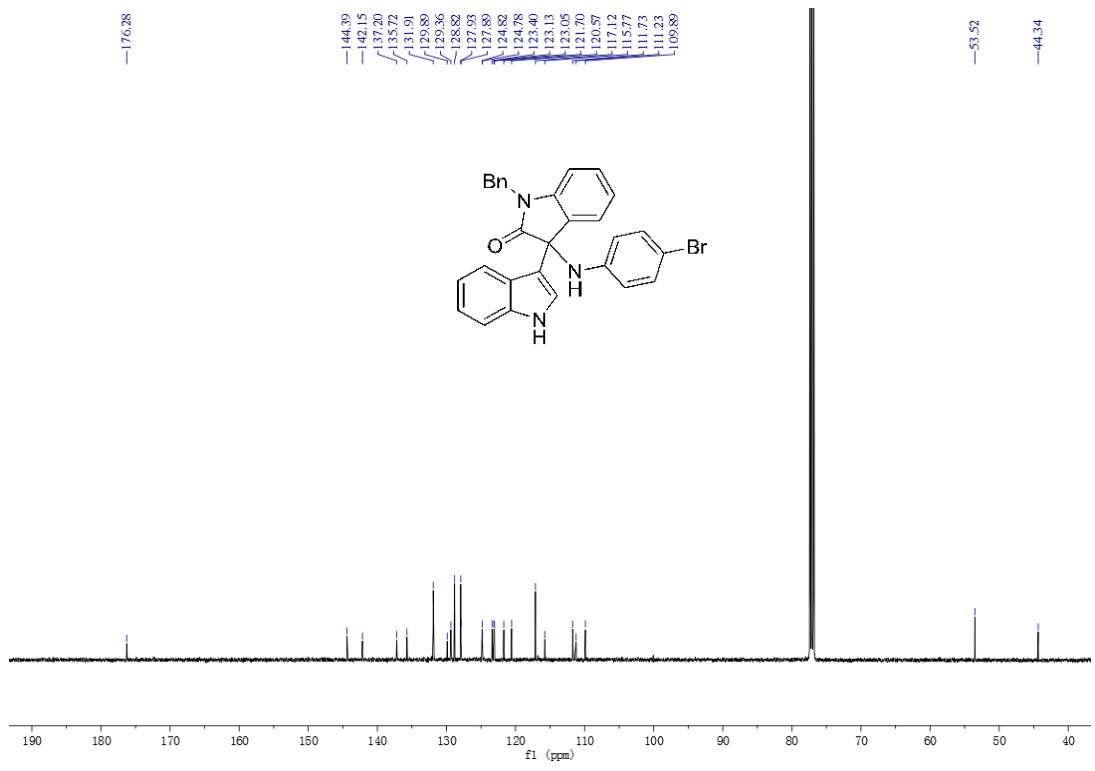
1-benzyl-3-((4-chlorophenyl)amino)-3-(1H-indol-3-yl)indolin-2-one **(5i)**



1-benzyl-3-((4-bromophenyl)amino)-3-(1H-indol-3-yl)indolin-2-one **(5j)**



## 5. X-ray Data for Compound 3a


Table 1. Crystal data and structure refinement for **3a** (ellipsoids depicted at the 50% probability level).

| | | |
|---|---|---|
| Identification code | 1RAW | |
| Empirical formula | C27 H19 N2 O2 | |
| Formula weight | 403.44 | |
| Temperature | 296(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Triclinic | |
| Space group | P -1 | |
| Unit cell dimensions | a = 9.1713(12) Å | a= 87.145(4)° |
| | b = 10.4692(14) Å | b= 75.225(4)° |
| | c = 11.6564(16) Å | g = 84.729(4)° |
| Volume | 1077.2(3) $Å^3$ | |
| Z | 2 | |
| Density (calculated) | 1.244 $Mg/m^3$ | |
| Absorption coefficient | 0.079 $mm^{-1}$ | |
| F(000) | 422 | |
| Crystal size | 0.498 x 0.359 x 0.297 $mm^3$ | |
| Theta range for data collection | 3.061 to 27.530° | |
| Index ranges | -11<=h<=11, -13<=k<=13, -15<=l<=15 | |
| Reflections collected | 22099 | |
| Independent reflections | 4941 [R(int) = 0.0391] | |
| Completeness to theta = 25.242° | 99.8 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 4941 / 0 / 281 | |
| Goodness-of-fit on $F^2$ | 1.016 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0561, wR2 = 0.1473 | |
| R indices (all data) | R1 = 0.0781, wR2 = 0.1646 | |
| Extinction coefficient | 0.015(4) | |
| Largest diff. peak and hole | 0.556 and -0.188 $e.Å^{-3}$ | |