

Metal-Free Base-Mediated Oxidative Annulation Cascades to 3-Substituted-3-Hydroxyoxindole and its 3-Spirocyclic Derivative

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Supporting Information

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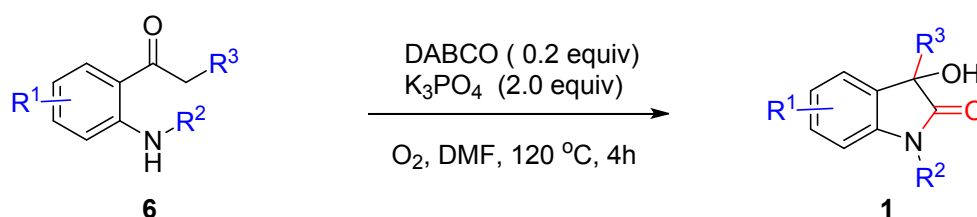
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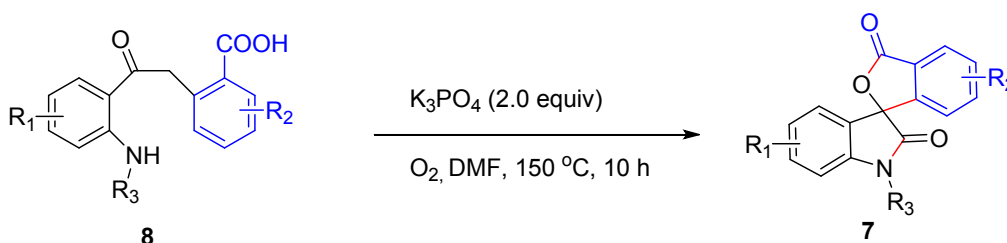
1. General information

All reagents were obtained from commercial suppliers and used without further purification. The starting materials were prepared according to the reported procedures.¹⁻³ Yields for all compounds were determined by the column chromatography which was generally performed on silica gel (200-300 mesh) using petroleum ether 40-60 (PE)/EtOAc as eluent, and reactions were monitored by thin layer chromatography (TLC) on a glass plate coated with silica gel with fluorescent indicator (GF254) using UV light. The ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker ADNANCE III 500 MHz using CDCl₃ as solvent with TMS as internal standard. Chemical shifts are given in ppm (δ) referenced to CDCl₃ with 7.26 for ¹H and 77.16 for ¹³C, and to DMSO-d₆ with 2.50 for ¹H and 39.52 for ¹³C. Signals are abbreviated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, and coupling constants are expressed in hertz. Melting points were measured on a SGW[®] X-4B apparatus and uncorrected. HRMS were recorded on Agilent 6210TOF LC/MS mass spectrometer.

2. General methods of synthesizing the products



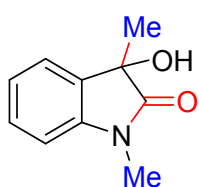
General procedure A: In a 10 mL microwave tube was charged with substrate **6** (0.2 mmol), anhydrous Potassium phosphate (0.4 mmol), DABCO (0.04 mmol), and anhydrous DMF 1.0 mL. The reaction mixture was evacuated and refilled with O₂ for 3 times before it was stirred at 120 °C for 4 h. The reaction mixture was then cooled to rt and diluted with water (5 mL) before it was extracted with EtOAc (30 mL). The combined organic phase were washed with water (3 x 5 mL) and saturated brine (10 mL), dried over anhydrous magnesium sulfate and concentrated in vacuo. The residue was purified by column chromatography (PE/EtOAc = 3:1) on silica gel to provide the desired product **1**.



General procedure B: In a 10 mL microwave tube was charged with substrate **8** (0.2 mmol), anhydrous Potassium phosphate (0.4 mmol), and anhydrous DMF 1.0 mL. The reaction mixture was evacuated and refilled with O₂ for 3 times before it was stirred at 150 °C for 10 h. The reaction mixture was then cooled to rt and diluted with water (5 mL) before it was

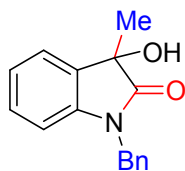
extracted with EtOAc (30 mL). The combined organic phase were washed with water (3 x 5 mL) and saturated brine (10 mL), dried over anhydrous magnesium sulfate and concentrated in vacuo. The residue was purified by column chromatography (PE/EtOAc = 3:1) on silica gel to provide the desired product **7**.

3.Synthesis and characterization of the products:



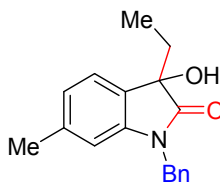
3-hydroxy-1,3-dimethylindolin-2-one (**1a**):

Following the general procedure **A** (150 °C for 24h), **1a** which was purified by PE/EtOAc (3:1) and obtained as a yellow solid (29.7 mg, 84% yield). M_p = 148.2-149.0 °C; R_f = 0.15 (PE/EtOAc = 2:1); ^1H NMR (500 MHz, CDCl_3) δ 7.43 (dd, J = 7.3, 0.6 Hz, 1H), 7.34 (td, J = 7.8, 1.2 Hz, 1H), 7.15 – 7.09 (m, 1H), 6.86 (d, J = 7.8 Hz, 1H), 3.21 (s, 3H), 1.62 (s, 3H) ppm. The spectra data are matched with those reported.⁴



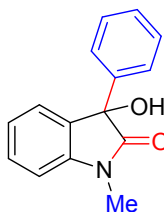
1-benzyl-3-hydroxy-3-methylindolin-2-one (**1b**):

Following the general procedure **A** (150 °C for 24h), **1b** was purified by PE/EtOAc (3:1) and obtained as a white solid (47.0 mg, 93% yield). M_p = 144.1-145.0 °C; R_f = 0.22 (PE/EtOAc = 2:1); ^1H NMR (500 MHz, CDCl_3) δ 7.44 (dd, J = 7.3, 0.5 Hz, 1H), 7.36 – 7.25 (m, 5H), 7.22 (td, J = 7.8, 1.2 Hz, 1H), 7.12 – 7.05 (m, 1H), 6.74 (d, J = 7.8 Hz, 1H), 4.98 (d, J = 15.7 Hz, 1H), 4.84 (d, J = 15.7 Hz, 1H), 3.26 (s, 1H), 1.69 (s, 3H) ppm. The spectra data are matched with those reported.⁵



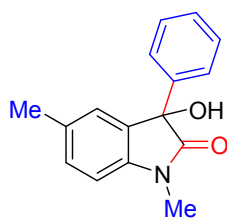
1-benzyl-3-ethyl-3-hydroxy-6-methylindolin-2-one (**1c**):

Following the general procedure **A** (150 °C for 24h), **1c** was purified by PE/EtOAc (3:1) and obtained as a white solid (30.9 mg, 55% yield). M_p = 141.1-142.1 °C; R_f = 0.27 (PE/EtOAc = 2:1); ^1H NMR (500 MHz, CDCl_3) δ 7.40 – 7.22 (m, 6H), 6.95 – 6.84 (m, 1H), 6.56 (s, 1H), 5.02 (d, J = 15.7 Hz, 1H), 4.75 (d, J = 15.7 Hz, 1H), 3.38 – 2.63 (m, 1H), 2.30 (s, 3H), 2.06 (t, J = 7.5 Hz, 2H), 0.80 (t, J = 7.5 Hz, 3H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 178.65, 142.97, 139.89, 135.75, 2x128.82, 127.64, 127.19, 126.75, 123.73, 123.67, 110.24, 43.76, 31.69, 21.90, 7.80. HRMS m/z (ESI): calcd for $\text{C}_{18}\text{H}_{20}\text{NO}_2[\text{M} + \text{H}]^+$ 282.1489, found 282.1487.



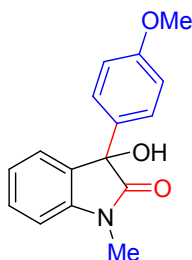
3-hydroxy-1-methyl-3-phenylindolin-2-one (**1d**):

Following the general procedure **A**, **1d** was purified by PE/EtOAc (3:1) and obtained as a yellow solid (38.2 mg, 80% yield). M_p = 137.5-138.4 °C; R_f = 0.20 (PE/EtOAc = 2:1); ^1H NMR (500 MHz, CDCl_3) δ 7.40 (ddd, J = 6.6, 3.7, 1.5 Hz, 2H), 7.38 – 7.28 (m, 5H), 7.10 (td, J = 7.6, 0.9 Hz, 1H), 6.92 (d, J = 7.8 Hz, 1H), 3.55 (s, 1H), 3.26 (s, 3H). The spectra data are matched with those reported.⁴



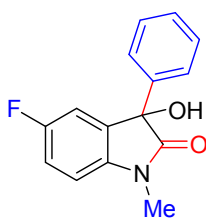
3-hydroxy-1,5-dimethyl-3-phenylindolin-2-one (1e):

Following the general procedure A, **1e** was purified by PE/EtOAc (3:1) and obtained as a yellow solid (41.5 mg, 82% yield). M_p = 116.2-117.1 °C; R_f = 0.20 (PE/EtOAc = 2:1); ^1H NMR (500 MHz, CDCl_3) δ 7.43 – 7.37 (m, 2H), 7.37 – 7.29 (m, 3H), 7.16 (ddd, J = 7.9, 1.6, 0.7 Hz, 1H), 7.13 – 7.08 (m, 1H), 6.81 (d, J = 7.9 Hz, 1H), 3.25 (s, 3H), 2.31 (s, 3H) ppm. The spectra data are matched with those reported.⁴



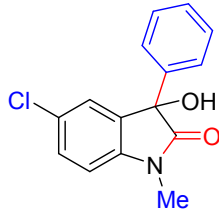
3-hydroxy-3-(4-methoxyphenyl)-1-methylindolin-2-one (1f):

Following the general procedure A, **1f** was purified by PE/EtOAc (3:1) and obtained as a yellow solid (43.0 mg, 80% yield). M_p = 142.5-143.7 °C; R_f = 0.15 (PE/EtOAc = 2:1); ^1H NMR (500 MHz, CDCl_3): δ 7.40 – 7.30 (m, 4H), 7.11 (td, J = 7.6, 0.9 Hz, 1H), 6.91 (d, J = 7.8 Hz, 1H), 6.88 – 6.84 (m, 2H), 3.79 (s, 3H), 3.41 (s, 1H), 3.25 (s, 3H) ppm. The spectra data are matched with those reported.⁶



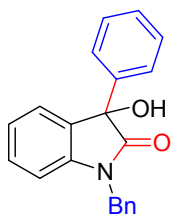
5-fluoro-3-hydroxy-1-methyl-3-phenylindolin-2-one (1g):

Following the general procedure A, **1g** was purified by PE/EtOAc (3:1) and obtained as a yellow solid (37.5 mg, 73% yield). M_p = 159.2-161.0 °C; R_f = 0.17 (PE/EtOAc = 2:1); ^1H NMR (500 MHz, CDCl_3) δ 7.42 – 7.30 (m, 5H), 7.09 – 7.02 (m, 2H), 6.85 (dd, J = 8.4, 4.0 Hz, 1H), 3.26 (s, 3H) ppm. The spectra data are matched with those reported.⁴



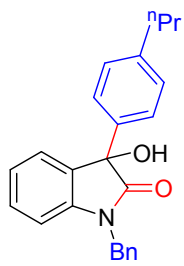
5-chloro-3-hydroxy-1-methyl-3-phenylindolin-2-one (1h):

Following the general procedure A, **1h** was purified by PE/EtOAc (3:1) and obtained as a yellow solid (43.7 mg, 80% yield). M_p = 169.5-171.0 °C; R_f = 0.22 (PE/EtOAc = 2:1); ^1H NMR (500 MHz, CDCl_3) δ 7.40 – 7.31 (m, 6H), 7.29 – 7.25 (m, 1H), 6.85 (d, J = 8.3 Hz, 1H), 3.63 (s, 1H), 3.25 (s, 3H) ppm. The spectra data are matched with those reported.⁴



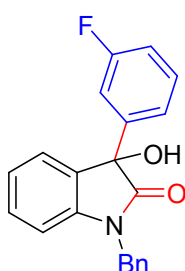
1-benzyl-3-hydroxy-3-phenylindolin-2-one (1i):

Following the general procedure A, **1i** was purified by PE/EtOAc (3:1) and obtained as a white solid (51.0 mg, 81% yield). M_p = 139.2-140.1 °C; R_f = 0.32 (PE/EtOAc = 2:1); ^1H NMR (500 MHz, CDCl_3) δ 7.45 – 7.41 (m, 2H), 7.39 – 7.33 (m, 6H), 7.33 – 7.30 (m, 2H), 7.30 – 7.28 (m, 1H), 7.24 (td, J = 7.8, 1.3 Hz, 1H), 7.06 (td, J = 7.6, 0.9 Hz, 1H), 6.81 (d, J = 7.8 Hz, 1H), 5.07 (d, J = 15.7 Hz, 1H), 4.85 (d, J = 15.7 Hz, 1H), 3.48 (s, 1H) ppm. The spectra data are matched with those reported.⁷



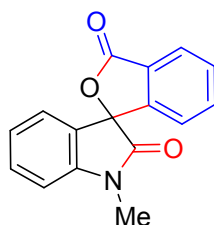
1-benzyl-3-hydroxy-3-(4-propylphenyl)indolin-2-one (1j):

Following the general Procedure A, **1j** was purified by PE/EtOAc (3:1) and obtained as a white solid (53.5 mg, 75% yield). M_p = 137.2–138.1 °C; R_f = 0.42 (PE/EtOAc = 2:1); ^1H NMR (500 MHz, CDCl_3) δ 7.38 – 7.28 (m, 7H), 7.23 (td, J = 7.8, 1.1 Hz, 1H), 7.17 (d, J = 8.2 Hz, 2H), 7.06 (t, J = 7.5 Hz, 1H), 6.79 (d, J = 7.9 Hz, 1H), 5.06 (d, J = 15.7 Hz, 1H), 4.85 (d, J = 15.7 Hz, 1H), 3.45 (s, 1H), 2.66 – 2.49 (m, 2H), 1.63 (dd, J = 15.1, 7.5 Hz, 2H), 0.95 (t, J = 7.3 Hz, 3H) ppm; ^{13}C NMR (126 MHz, CDCl_3) δ 177.76, 142.99, 142.67, 137.43, 135.49, 131.67, 129.71, 128.89, 128.80, 127.78, 127.30, 125.26, 125.02, 123.51, 109.73, 77.92, 44.05, 37.72, 24.42, 13.85. HRMS m/z (ESI): calcd for $\text{C}_{24}\text{H}_{23}\text{NNaO}_2$ $[\text{M} + \text{Na}]^+$ 380.1621, found 380.1613.



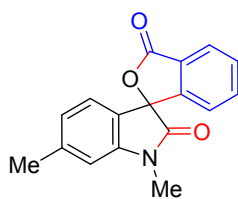
1-benzyl-3-(3-fluorophenyl)-3-hydroxyindolin-2-one (1k):

Following the general Procedure A, **1k** was purified by PE/EtOAc (3:1) and obtained as a white solid (45.9 mg, 69% yield). M_p = 174.2–175.3 °C; R_f = 0.40 (PE/EtOAc = 2:1); ^1H NMR (500 MHz, CDCl_3) δ 7.40 – 7.22 (m, 8H), 7.21 – 7.16 (m, 1H), 7.14 (d, J = 7.9 Hz, 1H), 7.07 (dd, J = 11.1, 4.0 Hz, 1H), 7.01 (td, J = 8.3, 1.9 Hz, 1H), 6.82 (d, J = 7.8 Hz, 1H), 5.04 (d, J = 15.6 Hz, 1H), 4.85 (d, J = 15.6 Hz, 1H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 177.19 (s), 162.95 (d, J = 246.8 Hz), 142.77 (s), 142.59 (s), 135.29 (s), 131.29 (s), 130.23 (d, J = 8.0 Hz), 130.05 (s), 128.94 (s), 127.98 (d, J = 2.9 Hz), 127.33 (s), 124.96 (s), 123.74 (s), 120.97 (s), 115.29 (d, J = 21.1 Hz), 112.80 (d, J = 24.2 Hz), 109.91 (s), 77.66 (s), 44.15 (s). HRMS m/z (ESI): calcd for $\text{C}_{21}\text{H}_{16}\text{FNNaO}_2$ $[\text{M} + \text{Na}]^+$ 356.1057, found 356.1064.



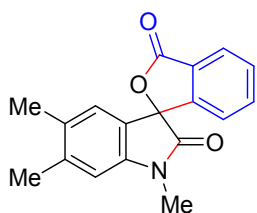
1-methyl-3'H-spiro[indoline-3,1'-isobenzofuran]-2,3'-dione (7a):

Following the general procedure B, **7a** was purified by PE/EtOAc (3:1) and obtained as a white solid (38.2 mg, 72% yield); M_p = 202.5–203.5 °C; R_f = 0.20 (PE/EtOAc = 3:1); ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ 8.04 (d, J = 7.4 Hz, 1H), 7.78 (td, J = 7.4, 1.1 Hz, 1H), 7.73 (td, J = 7.4, 0.9 Hz, 1H), 7.54 (td, J = 7.8, 1.2 Hz, 1H), 7.32 (d, J = 7.5 Hz, 1H), 7.28 (d, J = 7.9 Hz, 1H), 7.22–7.17 (m, 1H), 7.11 (td, J = 7.5, 0.6 Hz, 1H), 3.26 (s, 3H) ppm; ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) δ 170.6, 169.2, 146.5, 144.6, 135.5, 131.8, 130.7, 125.5, 125.0, 125.0, 124.1, 123.6, 122.3, 110.1, 84.2, 26.9 ppm; HRMS m/z (ESI) : calcd for $\text{C}_{16}\text{H}_{11}\text{NO}_3$ $[\text{M} + \text{H}]^+$ 266.0812, found 266.0812.



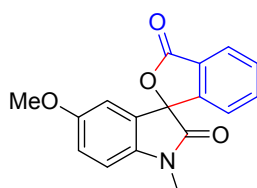
1,6-dimethyl-3'H-spiro[indoline-3,1'-isobenzofuran]-2,3'-dione (7b):

Following the general procedure B, **7b** was purified by PE/EtOAc (3:1) and obtained as a white solid (28.4 mg, 51% yield); M_p = 209.6–210.6 °C; R_f = 0.20 (PE/EtOAc = 3:1); ^1H NMR (500 MHz, CDCl_3) δ 8.01 (dd, J = 6.1, 2.1 Hz, 1H), 7.64–7.60 (m, 2H), 7.10 (dd, J = 5.9, 1.8 Hz, 1H), 6.90 (s, 2H), 6.82 (s, 1H), 3.29 (s, 3H), 2.44 (s, 3H) ppm; ^{13}C NMR (126 MHz, CDCl_3) δ 171.5, 169.6, 147.0, 144.7, 142.4, 134.7, 130.2, 126.1, 126.0, 125.0, 124.3, 121.9, 121.8, 110.0, 84.5, 26.9, 22.1 ppm; HRMS m/z (ESI) calcd for $\text{C}_{17}\text{H}_{14}\text{NO}_3$ $[\text{M} + \text{H}]^+$ 280.0971, found 280.0968.



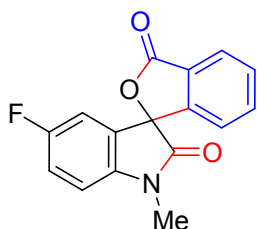
1,5,6-trimethyl-3'H-spiro[indoline-3,1'-isobenzofuran]-2,3'-dione (7c):

Following the general procedure **B**, with the addition of anhydrous Potassium phosphate (84.8 mg, 0.4 mmol) and DABCO (22.4mg, 0.2 mmol). **7c** was purified by column chromatography (PE/EtOAc = 3:1) on silica gel and obtained as a white solid (31.6 mg, 54% yield); M_p = 205.1-206.1 °C; R_f = 0.22 (PE/EtOAc = 3:1); ^1H NMR (500 MHz, CDCl_3) δ 8.04–7.99 (m, 1H), 7.66–7.56 (m, 2H), 7.10 (dd, J = 5.9, 1.8 Hz, 1H), 6.79 (d, J = 2.1 Hz, 2H), 3.28 (s, 3H), 2.35 (s, 3H), 2.17 (s, 3H) ppm; ^{13}C NMR (126 MHz, CDCl_3) δ 171.4, 169.7, 147.2, 142.6, 140.5, 134.7, 132.0, 130.2, 126.2, 126.1, 126.0, 121.9, 121.9, 110.6, 84.8, 27.0, 20.5, 19.3 ppm; HRMS m/z (ESI): calcd for $\text{C}_{18}\text{H}_{15}\text{NO}_3$ $[\text{M} + \text{H}]^+$ 294.1139, found 294.1125.



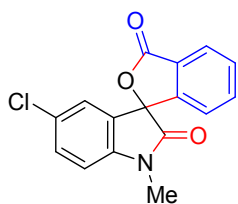
5-methoxy-1-methyl-3'H-spiro[indoline-3,1'-isobenzofuran]-2,3'-dione (7d):

Following the general procedure **B**, with the addition of anhydrous Potassium phosphate (42.4 mg, 0.2 mmol) and DABCO (22.4mg, 0.2 mmol). **7d** was purified by column chromatography (PE/EtOAc = 3:1) on silica gel and obtained as a white solid (31.3 mg, 53% yield); M_p = 161-162 °C; R_f = 0.21 (PE/EtOAc = 2:1); ^1H NMR (500 MHz, CDCl_3) δ 8.01 (dd, J = 6.2, 1.8 Hz, 1H), 7.65–7.59 (m, 2H), 7.11 (dd, J = 6.2, 1.5 Hz, 1H), 6.97 (dd, J = 8.6, 2.5 Hz, 1H), 6.91 (d, J = 8.6 Hz, 1H), 6.61 (d, J = 2.5 Hz, 1H), 3.71 (s, 3H), 3.28 (s, 3H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 171.0, 169.6, 156.8, 147.0, 137.9, 134.9, 130.4, 126.2, 126.0, 125.9, 121.9, 116.6, 111.8, 109.8, 84.8, 55.9, 27.1 ppm; HRMS m/z (ESI) calcd for $\text{C}_{17}\text{H}_{14}\text{NO}_4$ $[\text{M} + \text{H}]^+$ 296.0911, found 296.0917.



5-fluoro-1-methyl-3'H-spiro[indoline-3,1'-isobenzofuran]-2,3'-dione (7e):

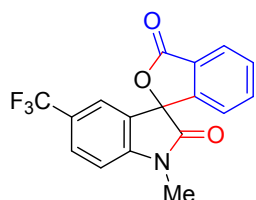
Following the general procedure **B**, **7e** was purified by PE/EtOAc (3:1) and obtained as a white solid (31.7 mg, 56% yield); M_p = 193-194 °C; R_f = 0.24 (PE/EtOAc = 3:1); ^1H NMR (500 MHz, CDCl_3) δ 7.67 (dd, J = 7.0, 2.3 Hz, 1H), 7.48 (td, J = 7.8, 1.3 Hz, 1H), 7.35 (td, J = 8.5, 2.4 Hz, 1H), 7.13–7.10 (m, 1H), 7.09 (t, J = 4.2 Hz, 1H), 7.04 (dd, J = 7.5, 0.9 Hz, 1H), 7.01 (d, J = 7.9 Hz, 1H), 3.31 (s, 3 H) ppm; ^{13}C NMR (126 MHz, CDCl_3) δ 171.0 (s), 169.2 (s), 160.5 (s), 158.6 (s), 146.3 (s), 140.5 (d, J = 2.2 Hz), 134.9 (s), 130.6 (s), 126.3 (d, J = 9.5 Hz), 125.7 (s), 121.8 (s), 118.1 (d, J = 23.6 Hz), 113.3 (d, J = 25.3 Hz), 101.0 (d, J = 7.9 Hz), 84.1 (s), 27.2 (s) ppm; HRMS m/z (ESI) calcd for $\text{C}_{16}\text{H}_{10}\text{FNO}_3$ $[\text{M} + \text{H}]^+$ 284.0720, found 284.0717.



5-chloro-1-methyl-3'H-spiro[indoline-3,1'-isobenzofuran]-2,3'-dione (7f):

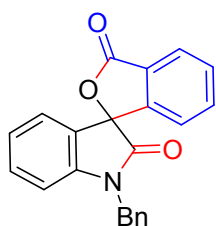
Following the general procedure **B**, **7f** was purified by PE/EtOAc (3:1) and obtained as a white solid (33.5 mg, 56% yield); M_p = 177-178 °C; R_f = 0.23 (PE/EtOAc = 3:1); ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ 8.05–8.02 (m, 1H), 7.78 (td, J = 7.5, 1.3 Hz, 1H), 7.74 (td, J = 7.4, 1.1 Hz,

1H), 7.61 (dd, $J = 8.4, 2.2$ Hz, 1H), 7.46 (d, $J = 2.2$ Hz, 1H), 7.36 (dd, $J = 4.6, 3.7$ Hz, 1H), 7.31 (d, $J = 8.5$ Hz, 1H), 3.26 (s, 3 H) ppm; ^{13}C NMR (126 MHz, CDCl_3) δ 170.8, 169.1, 146.2, 143.2, 135.0, 131.6, 130.7, 129.2, 126.4, 126.3, 125.7, 125.6, 121.8, 110.3, 83.9, 27.2 ppm; HRMS m/z (ESI) calcd for $\text{C}_{16}\text{H}_{10}\text{ClNO}_3$ $[\text{M} + \text{H}]^+$ 322.0246, found 322.0241.



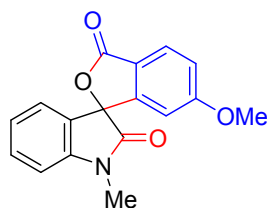
1-methyl-5-(trifluoromethyl)-3'H-spiro[indoline-3,1'-isobenzofuran]-2,3'-dione (7g):

Following the general procedure **B**, **7g** was purified by PE/EtOAc (3:1) and obtained as a white solid (37.3 mg, 56% yield). $M_p = 200.1$ – 200.8 °C; $R_f = 0.25$ (PE/EtOAc = 3:1); ^1H NMR (500 MHz, CDCl_3) δ 8.10–8.00 (m, 1 H), 7.75 (dd, $J = 8.3, 0.9$ Hz, 1 H), 7.71–7.62 (m, 2 H), 7.27 (d, $J = 1.9$ Hz, 1 H), 7.19–7.04 (m, 2 H), 3.35 (s, 3 H) ppm; ^{13}C NMR (126 MHz, CDCl_3) δ 171.2 (s), 169.0 (s), 147.6 (s), 145.9 (s), 135.1 (s), 130.8 (s), 129.4 (q, $J = 3.9$ Hz), 126.4 (s), 126.1 (s), 125.8 (s), 125.6 (s), 123.7 (d, $J = 271.9$ Hz), 122.4 (q, $J = 3.7$ Hz), 121.8 (s), 109.2 (s), 83.5 (s), 27.3 (s) ppm; HRMS m/z (ESI): calcd for $\text{C}_{17}\text{H}_{10}\text{F}_3\text{NO}_3$ $[\text{M} + \text{H}]^+$ 334.0690, found 334.0686.



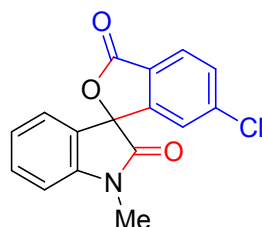
1-benzyl-3'H-spiro[indoline-3,1'-isobenzofuran]-2,3'-dione (7h):

Following the general procedure **B**, **7h** was purified by PE/EtOAc (3:1) and obtained as a white solid (40.9 mg, 60% yield). $M_p = 163.5$ – 164.5 °C; $R_f = 0.23$ (PE/EtOAc = 3:1); ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ 8.07 (d, $J = 7.5$ Hz, 1H), δ 7.84–7.79 (m, 1H), 7.76 (t, $J = 7.4$ Hz, 1H), 7.46 (td, $J = 7.9, 1.0$ Hz, 1H), 7.43–7.30 (m, 5H), 7.29 (d, $J = 7.5$ Hz, 1H), 7.24 (d, $J = 7.3$ Hz, 1H), 7.21 (d, $J = 7.9$ Hz, 1H), 7.09 (t, $J = 7.5$ Hz, 1H), 5.02 (d, $J = 3.3$ Hz, 2H) ppm; ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) δ 170.9, 169.1, 146.4, 143.5, 135.7, 135.6, 131.8, 130.8, 128.9, 127.7, 127.2, 125.7, 125.4, 125.0, 124.1, 123.8, 122.1, 110.7, 84.1, 43.5 ppm; HRMS m/z (ESI): calcd for $\text{C}_{22}\text{H}_{15}\text{NO}_3$ $[\text{M} + \text{H}]^+$ 342.1128, found 342.1125.



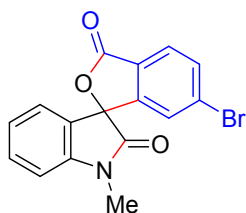
6'-methoxy-1-methyl-3'H-spiro(indoline-3,1'-isobenzofuran)-2,3'-dione (7i):

Following the general procedure **B**, **7i** was purified by PE/EtOAc (2:1) and obtained as a white solid (32.4 mg, 55% yield); $M_p = 187.5$ – 188.5 °C; $R_f = 0.21$ (PE/EtOAc = 2:1); ^1H NMR (500 MHz, CDCl_3) δ 7.90 (d, $J = 8.5$ Hz, 1H), 7.46 (td, $J = 7.8, 1.2$ Hz, 1H), 7.14–7.07 (m, 2H), 7.04 (dd, $J = 7.4, 0.8$ Hz, 1H), 7.00 (d, $J = 7.9$ Hz, 1H), 6.47 (d, $J = 2.0$ Hz, 1H), 3.80 (s, 3H), 3.31 (s, 3H) ppm; ^{13}C NMR (126 MHz, CDCl_3) δ 171.3, 169.2, 165.26, 149.5, 144.6, 131.6, 127.5, 125.2, 125.0, 123.8, 118.2, 117.9, 109.1, 105.6, 83.8, 55.9, 27.0 ppm; HRMS m/z (ESI): calcd for $\text{C}_{17}\text{H}_{13}\text{NO}_4$ $[\text{M} + \text{H}]^+$ 296.0920, found 296.0917.



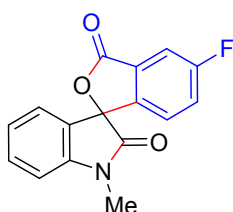
6'-chloro-1-methyl-3'H-spiro[indoline-3,1'-isobenzofuran]-2,3'-dione (7j):

Following the general procedure **B**, **7j** was purified by PE/EtOAc (3:1) and obtained as a white solid (29.9 mg, 50% yield); M_p = 203.5-204.5 °C; R_f = 0.23 (PE/EtOAc = 3:1); ^1H NMR (500 MHz, CDCl_3) δ 7.95 (d, J = 8.1 Hz, 1H), 7.59 (dd, J = 8.2, 1.7 Hz, 1H), 7.49 (td, J = 7.8, 1.3 Hz, 1H), 7.12 (td, J = 7.6, 0.8 Hz, 1H), 7.09 (d, J = 1.4 Hz, 1H), 7.05 (dd, J = 7.4, 0.9 Hz, 1H), 7.02 (d, J = 7.9 Hz, 1H), 3.32 (s, 3H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 170.6, 168.3, 148.3, 144.6, 141.5, 132.0, 131.1, 127.2, 125.2, 124.5, 124.1, 124.0, 122.3, 109.3, 83.9, 27.1 ppm; HRMS m/z (ESI) : calcd for $\text{C}_{16}\text{H}_{10}\text{ClNO}_3$ $[\text{M} + \text{H}]^+$ 300.0424, found 300.0422.



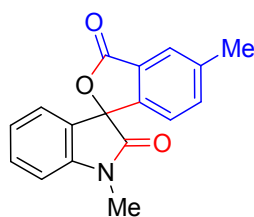
6'-bromo-1-methyl-3'H-spiro[indoline-3,1'-isobenzofuran]-2,3'-dione (7k):

Following the general procedure **B**, with the addition of anhydrous Potassium phosphate (42.4 mg, 0.2 mmol) and DABCO (22.4mg, 0.2 mmol). **7k** was purified by column chromatography (PE/EtOAc = 3:1) on silica gel and obtained as a white solid (37.6 mg, 55% yield); M_p = 224.8-225.8 °C; R_f = 0.21 (PE/EtOAc = 3:1); ^1H NMR (500 MHz, CDCl_3) δ 7.67 (dd, J = 7.0, 2.3 Hz, 1H), 7.48 (td, J = 7.8, 1.3 Hz, 1H), 7.35 (td, J = 8.5, 2.4 Hz, 1H), 7.14–7.11 (m, 1H), 7.09 (t, J = 4.2 Hz, 1H), 7.04 (dd, J = 7.5, 0.9 Hz, 1H), 7.01 (d, J = 7.9 Hz, 1H), 3.31 (s, 3H) ppm; ^{13}C NMR (126 MHz, CDCl_3) δ 170.6, 168.5, 148.4, 144.6, 134.0, 132.0, 130.0, 127.3, 125.3, 125.3, 125.0, 124.1, 124.0, 109.3, 83.9, 27.1 ppm; HRMS m/z (ESI): calcd for $\text{C}_{16}\text{H}_{10}\text{BrNO}_3$ $[\text{M} + \text{H}]^+$ 343.9923, found 343.9917.



5'-fluoro-1-methyl-3'H-spiro[indoline-3,1'-isobenzofuran]-2,3'-dione (7l):

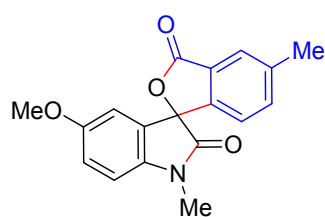
Following the general procedure **B**, with the addition of anhydrous Potassium phosphate (42.4 mg, 0.2 mmol) and DABCO (22.4mg, 0.2 mmol). **7l** was purified by column chromatography (PE/EtOAc = 3:1) on silica gel and obtained as a white solid (33.9 mg, 60% yield); M_p = 193-194 °C; R_f = 0.23 (PE/EtOAc = 3:1); ^1H NMR (500 MHz, CDCl_3) δ 7.89–7.87 (m, 1H), 7.75 (dd, J = 8.2, 1.6 Hz, 1H), 7.49 (td, J = 7.8, 1.3 Hz, 1H), 7.26–7.26 (m, 1H), 7.12 (td, J = 7.6, 0.9 Hz, 1H), 7.05 (dd, J = 7.5, 0.8 Hz, 1H), 7.02 (d, J = 7.9 Hz, 1H), 3.32 (s, 3H) ppm; ^{13}C NMR (126 MHz, CDCl_3) δ 169.5 (d, J = 322.9 Hz), 163.8 (d, J = 251.5 Hz), 144.6 (s), 142.3 (d, J = 2.3 Hz), 131.9 (s), 128.3 (d, J = 9.3 Hz), 125.2 (s), 124.3 (s), 123.9 (s), 123.8 (d, J = 8.8 Hz), 122.8 (d, J = 24.3 Hz), 112.6 (s), 112.4 (s), 109.3 (s), 84.3 (s), 27.0 (s) ppm; HRMS m/z (ESI) calcd for $\text{C}_{16}\text{H}_{10}\text{FNO}_3$ $[\text{M} + \text{H}]^+$ 284.0720, found 284.0717.



1,5'-dimethyl-3'H-spiro[indoline-3,1'-isobenzofuran]-2,3'-dione (7m):

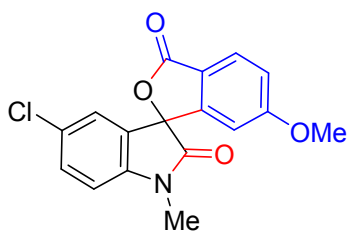
Following the general procedure **B**, **7m** was purified by PE/EtOAc (3:1) and obtained as a white solid (38.5 mg, 69% yield); M_p = 218.7-219.4 °C; R_f = 0.21 (PE/EtOAc = 3:1); ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ 7.84 (s, 1H), 7.58 (dd, J = 7.9, 0.7 Hz, 1H), 7.53 (td, J = 7.8, 1.3 Hz, 1H), 7.27 (d, J = 7.9 Hz, 1H), 7.19 (d, J = 7.9 Hz, 1H), 7.16 (dd, J = 7.4, 0.9 Hz, 1H), 7.10 (td, J = 7.5, 0.7 Hz, 1H), 3.25 (s, 3H), 2.46 (s, 3H) ppm; ^{13}C NMR (126 MHz, CDCl_3) δ

171.4, 169.7, 144.6, 144.2, 140.9, 135.9, 131.6, 126.2, 126.1, 125.2, 125.0, 123.7, 121.5, 109.1, 84.3, 27.0, 21.3 ppm; HRMS m/z (ESI): calcd for $C_{17}H_{14}NO_3$ $[M + H]^+$ 280.0966, found 280.0968



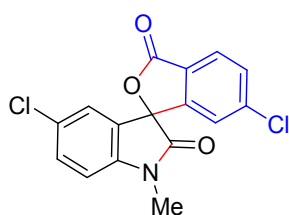
5-methoxy-1,5'-dimethyl-3'H-spiro[indoline-3,1'-isobenzofuran]-2,3'-dione (7n):

Following the general procedure **B**, with the addition of anhydrous Potassium phosphate (42.4 mg, 0.2 mmol) and DABCO (22.4mg, 0.2 mmol). **7n** was purified by column chromatography (PE/EtOAc = 3:1) on silica gel and obtained as a white solid (27.8 mg 45% yield); M_p = 145.5-146.5 °C; R_f = 0.20 (PE/EtOAc = 2:1); 1H NMR (500 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.46–7.43 (m, 1H), 7.00 (d, J = 7.9 Hz, 1H), 6.97 (dd, J = 8.6, 2.5 Hz, 1H), 6.90 (d, J = 8.6 Hz, 1H), 6.61 (d, J = 2.5 Hz, 1H), 3.72 (s, 3H), 3.28 (s, 3H), 2.49 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.1, 169.7, 156.7, 144.3, 140.9, 137.8, 135.9, 126.1, 126.1, 121.5, 116.5, 111.7, 109.7, 84.6, 55.9, 27.0, 21.4 ppm; HRMS m/z (ESI): calcd for $C_{18}H_{16}NO_4$ $[M + H]^+$ 310.1081, found 310.1074.



5-chloro-6'-methoxy-1-methyl-3'H-spiro[indoline-3,1'-isobenzofuran]-2,3'-dione (7o):

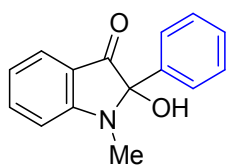
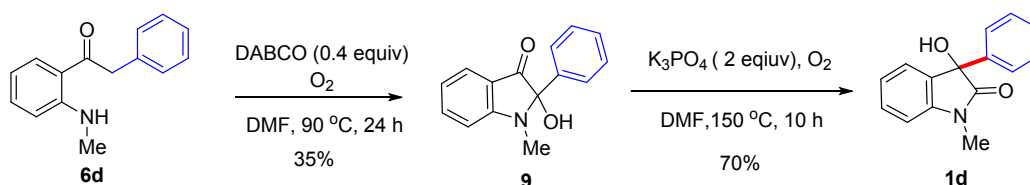
Following the general procedure **B**, **7o** was purified by PE/EtOAc (2:1) and obtained as a white solid (28.3 mg, 43% yield); M_p = 234.1-235.0 °C; R_f = 0.2 (PE/EtOAc = 2:1); 1H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, J = 8.5 Hz, 1H), 7.43 (dd, J = 8.3, 2.0 Hz, 1H), 7.12 (dd, J = 8.6, 2.0 Hz, 1H), 7.03 (d, J = 2.0 Hz, 1H), 6.94 (d, J = 8.4 Hz, 1H), 6.48 (d, J = 1.9 Hz, 1H), 3.82 (s, 3H), 3.30 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.9, 168.8, 165.4, 148.9, 143.1, 131.5, 129.3, 127.8, 126.7, 125.7, 118.0, 118.0, 110.2, 105.7, 83.3, 56.0, 27.2 ppm; HRMS m/z (ESI): calcd for $C_{17}H_{12}ClNO_4$ $[M + H]^+$ 330.0529, found 330.0528.



5,6'-dichloro-1-methyl-3'H-spiro[indoline-3,1'-isobenzofuran]-2,3'-dione (7p):

Following the general procedure **B**, with the addition of anhydrous Potassium phosphate (42.4 mg, 0.2 mmol) and DABCO (22.4mg, 0.2 mmol). **7p** was purified by column chromatography (PE/EtOAc = 3:1) on silica gel and obtained as a white solid (35.3 mg, 53% yield); M_p = 238.9-239.9 °C; R_f = 0.21 (PE/EtOAc = 3:1); 1H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, J = 8.2 Hz, 1H), 7.61 (dd, J = 8.2, 1.7 Hz, 1H), 7.46 (dd, J = 8.4, 2.1 Hz, 1H), 7.10 (d, J = 1.3 Hz, 1H), 7.04 (d, J = 2.1 Hz, 1H), 6.96 (d, J = 8.4 Hz, 1H), 3.31 (s, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.2, 167.9, 147.7, 141.8, 131.9, 131.4, 129.5, 127.4, 125.7, 125.7, 124.3, 122.3, 110.4, 83.3, 27.2 ppm; HRMS m/z (ESI): calcd for $C_{16}H_9Cl_2NO_3$ $[M + H]^+$ 334.0034, found 334.0032.

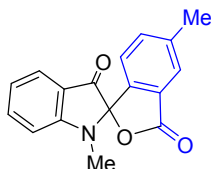
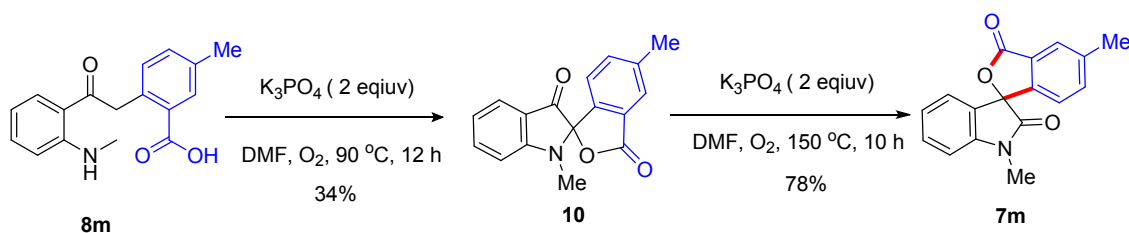
4.Reaction intermediates confirmation



2-hydroxy-1-methyl-2-phenylindolin-3-one (9):

In a 10 mL microwave tube was charged with 1-(2-(methylamino)phenyl)-2-phenylethanone (112.5 mg, 0.5 mmol), DABCO (22.4 mg, 0.2 mmol), and anhydrous DMF 2.0 mL. The reaction mixture was evacuated and refilled with O₂ for 3 times before it was stirred at 90 °C for 24 h. The reaction mixture was then cooled to rt and diluted with water (10 mL) before it was extracted with EtOAc (60 mL). The residue was purified by column chromatography (PE/EtOAc = 3:1) on silica gel to provide **9** as a yellow solid (41.8 mg, 35% yield); *M_p* = 104.1–105.1 °C; *R_f* = 0.21 (PE/EtOAc = 3:1); ¹H NMR (500 MHz, CDCl₃) δ 7.58 – 7.52 (m, 2H), 7.44 – 7.40 (m, 2H), 7.36 (m, *J* = 7.1, 4.6, 2.4 Hz, 3H), 6.82 – 6.73 (m, 2H), 2.86 (s, 3H) ppm. ¹³C NMR (126 MHz, CDCl₃) δ 199.88, 161.16, 138.85, 135.83, 128.89, 128.85, 126.11, 126.10, 118.14, 117.26, 107.95, 90.90, 27.53 ppm. The spectra data are matched with those reported.⁸

In a 10 mL microwave tube was charged with 2-hydroxy-1-methyl-2-phenylindolin-3-one (**9**) (23.9 mg, 0.1 mmol), K₃PO₄ (42.4 mg, 0.2 mmol) and anhydrous DMF 0.5 mL. The reaction mixture was evacuated and refilled with O₂ for 3 times before it was stirred at 150 °C for 10 h. The reaction mixture was then cooled to rt and diluted with water (10 mL) before it was extracted with EtOAc (60 mL). The residue was purified by column chromatography (PE/EtOAc = 3:1) on silica gel to provide **1d** as a yellow solid (17.7 mg, 70% yield).



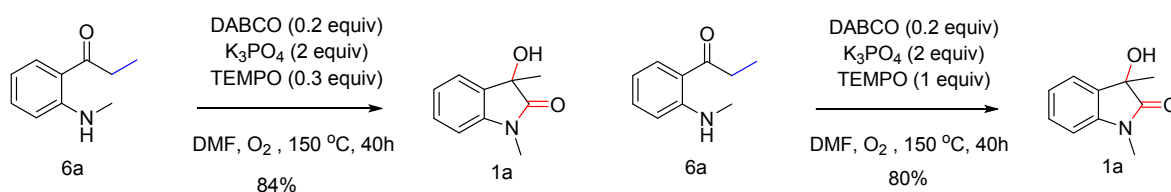
1,5'-dimethyl-3'H-spiro[indoline-2,1'-isobenzofuran]-3,3'-dione (10):

In a 10 mL microwave tube was charged with 5-methyl-2-(2-(2-(methylamino)phenyl)-2-oxoethyl)benzoic acid (**8m**) (141.5 mg, 0.5 mmol), anhydrous Potassium phosphate (212 mg, 1.0 mmol), and anhydrous DMF 2.5 mL. The reaction mixture was evacuated and refilled with O₂ for 3 times before it was stirred at 90 °C for 12 h. The reaction mixture was then cooled to rt and diluted with water (10 mL) before it was extracted with EtOAc (60 mL). The residue was purified by column chromatography (PE/EtOAc = 3:1) on silica gel to provide **10** as a yellow solid (47.4 mg, 34% yield). *M_p* = 113.5–114.9 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.81 (s, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.63 – 7.58 (m, 1H), 7.51 (dd, *J* = 7.8, 0.7 Hz, 1H),

7.19 (d, $J = 7.8$ Hz, 1H), 6.91 (t, $J = 7.5$ Hz, 1H), 6.86 (d, $J = 8.2$ Hz, 1H), 2.75 (s, 3H), 2.51 (s, 3H) ppm. ^{13}C NMR (151 MHz, CDCl_3) δ 192.11, 167.36, 160.11, 140.87, 138.46, 137.94, 134.85, 127.74, 125.15, 124.93, 120.98, 118.49, 117.30, 107.94, 95.50, 76.24, 76.03, 75.81, 26.68, 20.41 ppm. HRMS m/z (EI): calcd for $\text{C}_{17}\text{H}_{13}\text{NO}_3$ [M] 279.0895, found 279.0906.

In a 10 mL microwave tube was charged with 1,5'-dimethyl-3'H-spiro[indoline-2,1'-isobenzofuran]-3,3'-dione (**10**) (27.9 mg, 0.1 mmol), anhydrous Potassium phosphate (42.4 mg, 0.2 mmol), and anhydrous DMF 0.5 mL. The reaction mixture was evacuated and refilled with O_2 for 3 times before it was stirred at 150 °C for 10 h. The reaction mixture was then cooled to rt and diluted with water (10 mL) before it was extracted with EtOAc (60 mL). The residue was purified by column chromatography (PE/EtOAc = 3:1) on silica gel to provide **7m** as a yellow solid (21.8 mg, 78% yield).

5. Reactions in the presence of TEMPO



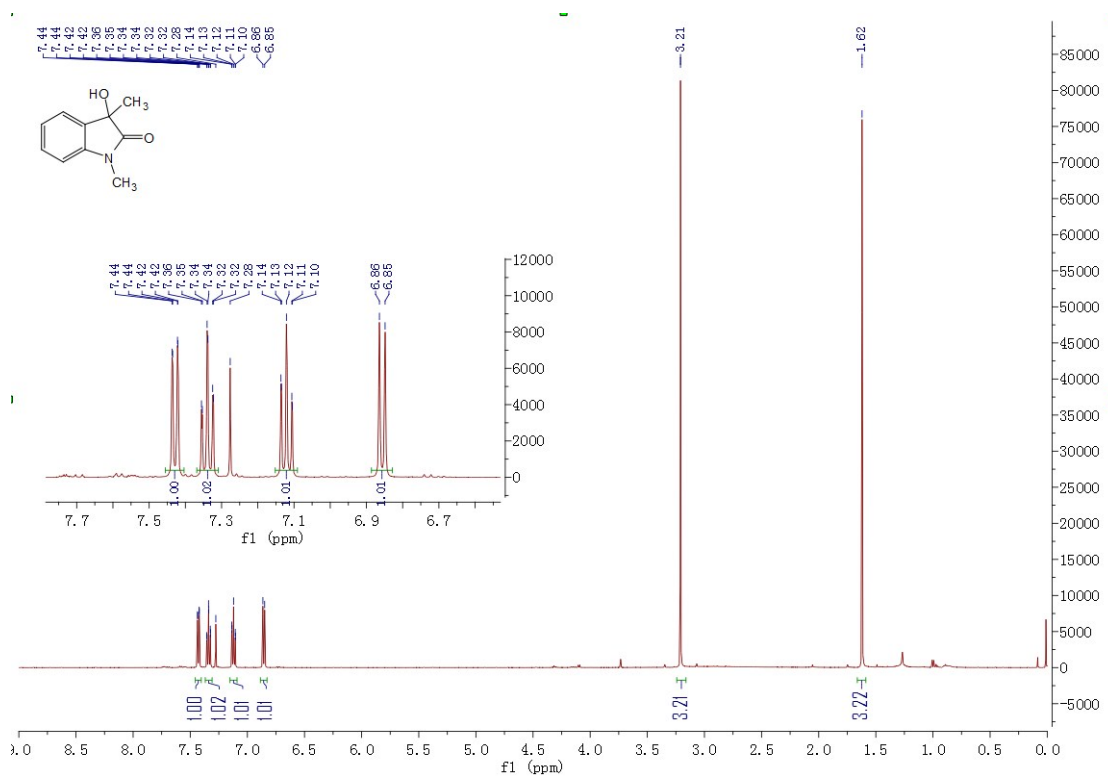
Following the general procedure A, with the addition of either 0.3 equiv of TEMPO (9.3 mg, 0.06 mmol) or 1.0 equiv of TEMPO (31.2 mg, 0.2 mmol), then the reactions were stirred at 150 °C for 40 hours, which afforded the product **1a** in 84% yield (29.9 mg) and 80% yield (28.5 mg), respectively.

Reference:

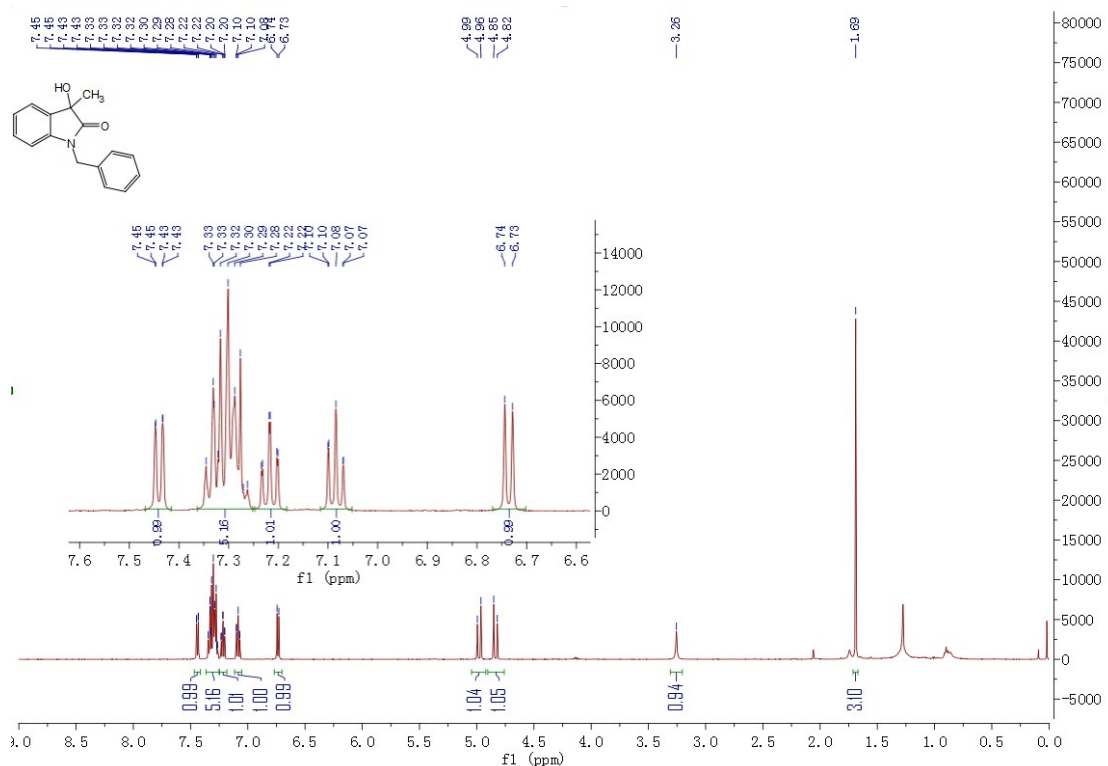
1. K. Okuma, S. Ozaki. *Heterocycles*. 2010, **81**, 935.
2. Y. Zhu, M. M. Alam, and S. A. Jenekhe. *Macromolecules*. 2003, **36**, 8958-8968.
3. R. M. Letcher, N. C. Kwok. *J. Chem. Soc., Perkin Trans. 1*. 1998, 1715-1720.
4. J. P. Zhu. *Org. Biomol. Chem.* 2013, **11**, 1533-1536.
5. A. D. Smith. *Synthesis*. 2008, **17**, 2805-2818.
6. P. J. Jones, E. C. Merrick. *J Pharmacol. Exp. Ther.* 2009, **328**, 201-212.
7. J. L. Zhang, J. X. Chen. *Tetrahedron*. 2011, **67**, 9347-9351.
8. K. Q. Ling. *Chin. J. Chem.* 1996, **14**, 265-270.

6. NMR spectra of all the indolin-2-one

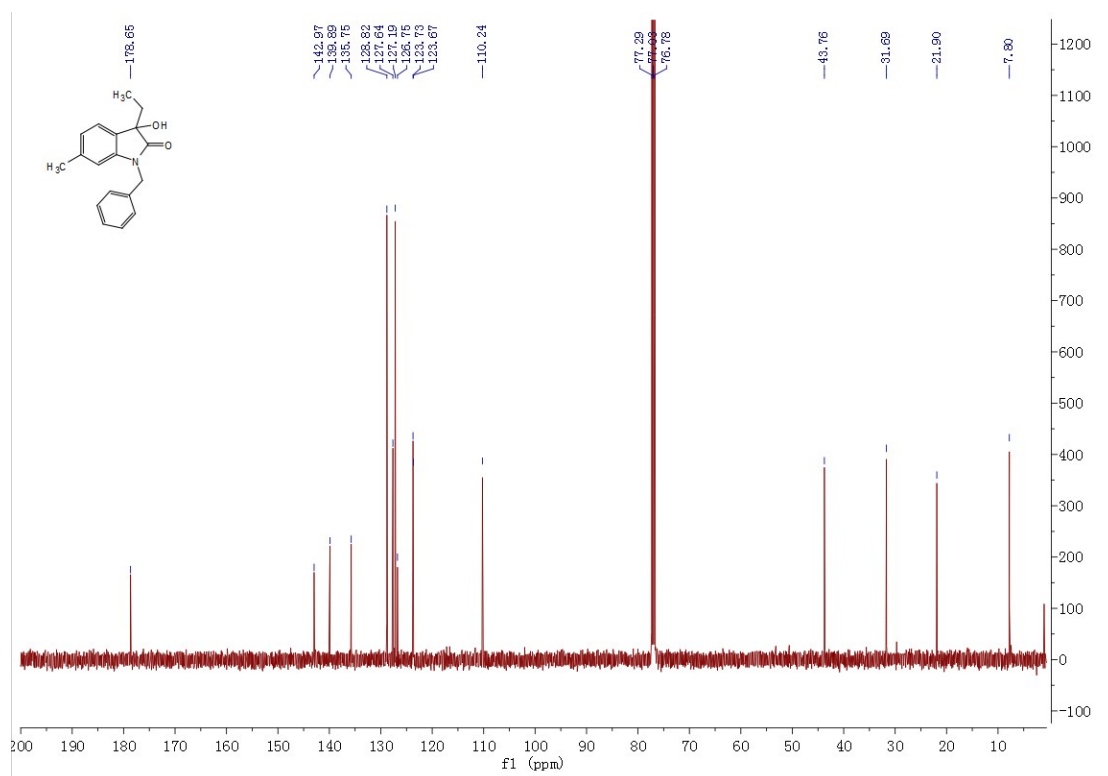
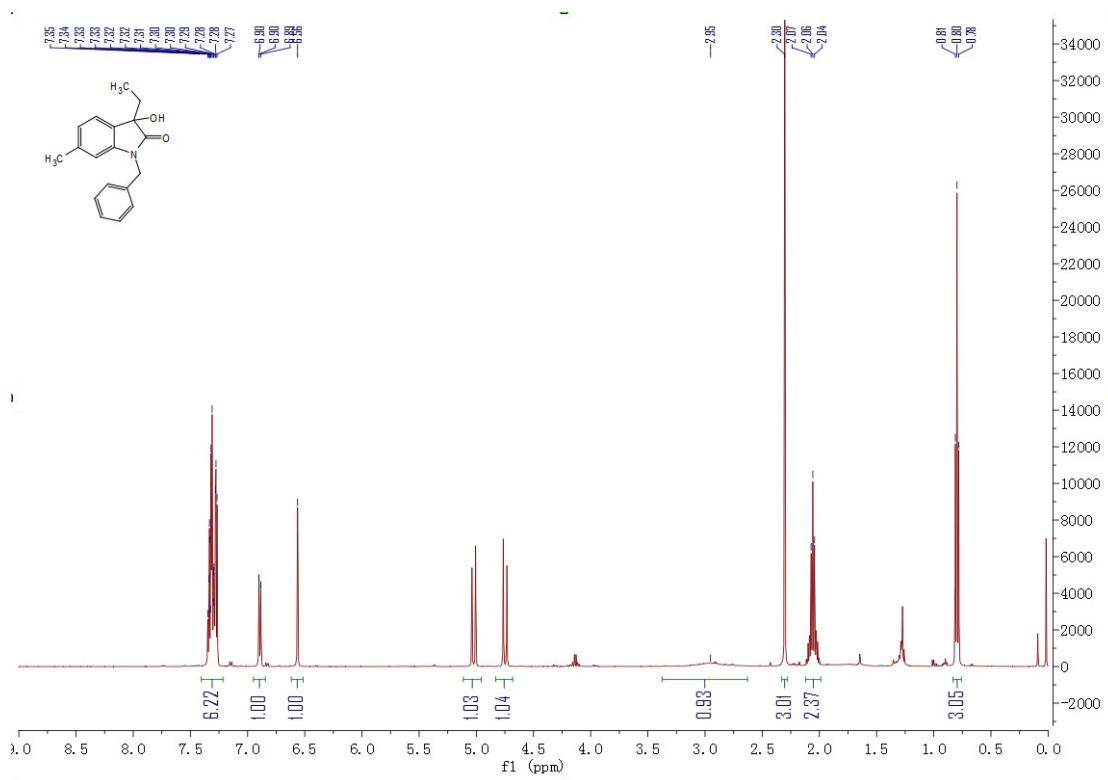
3-hydroxy-1,3-dimethylindolin-2-one (**1a**)



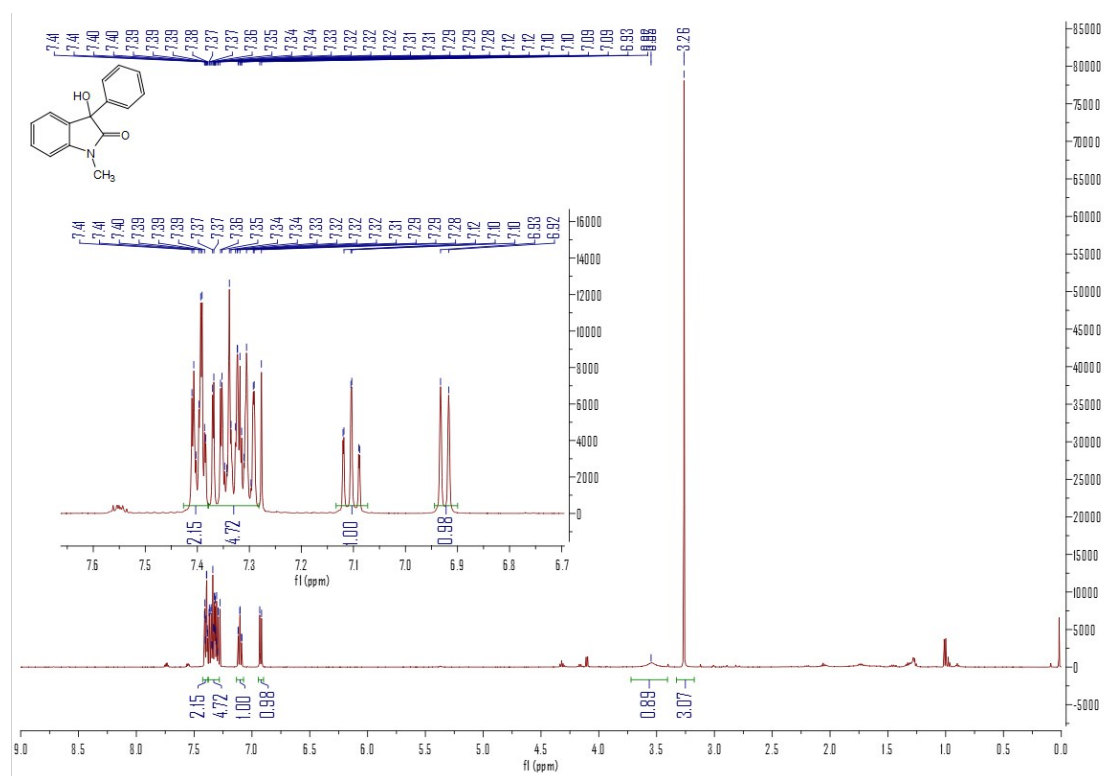
1-benzyl-3-hydroxy-3-methylindolin-2-one (1b)



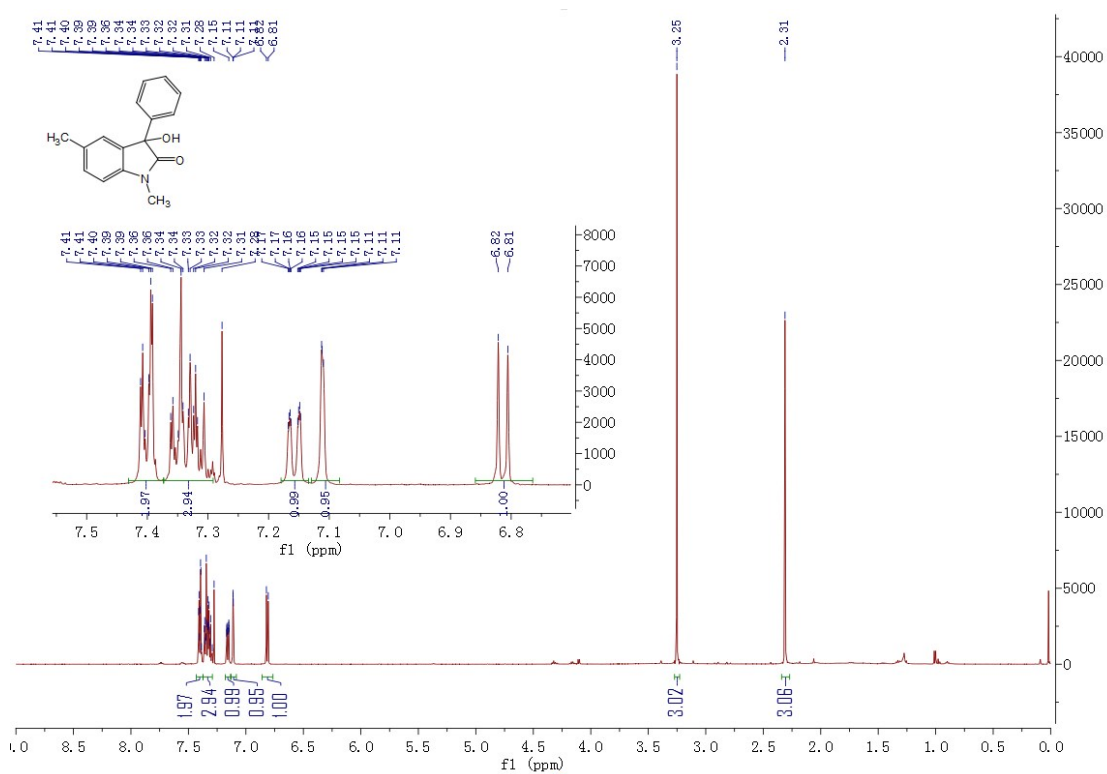
1-benzyl-3-ethyl-3-hydroxy-6-methylindolin-2-one (1c)



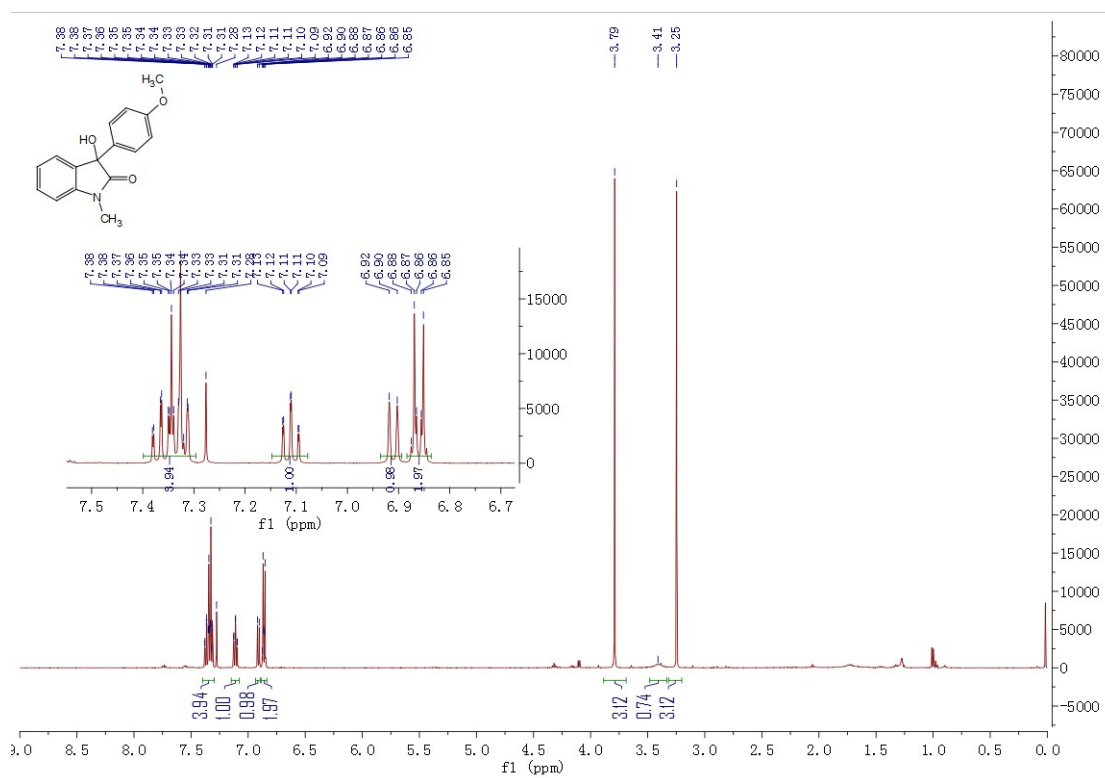
3-hydroxy-1-methyl-3-phenylindolin-2-one (1d)



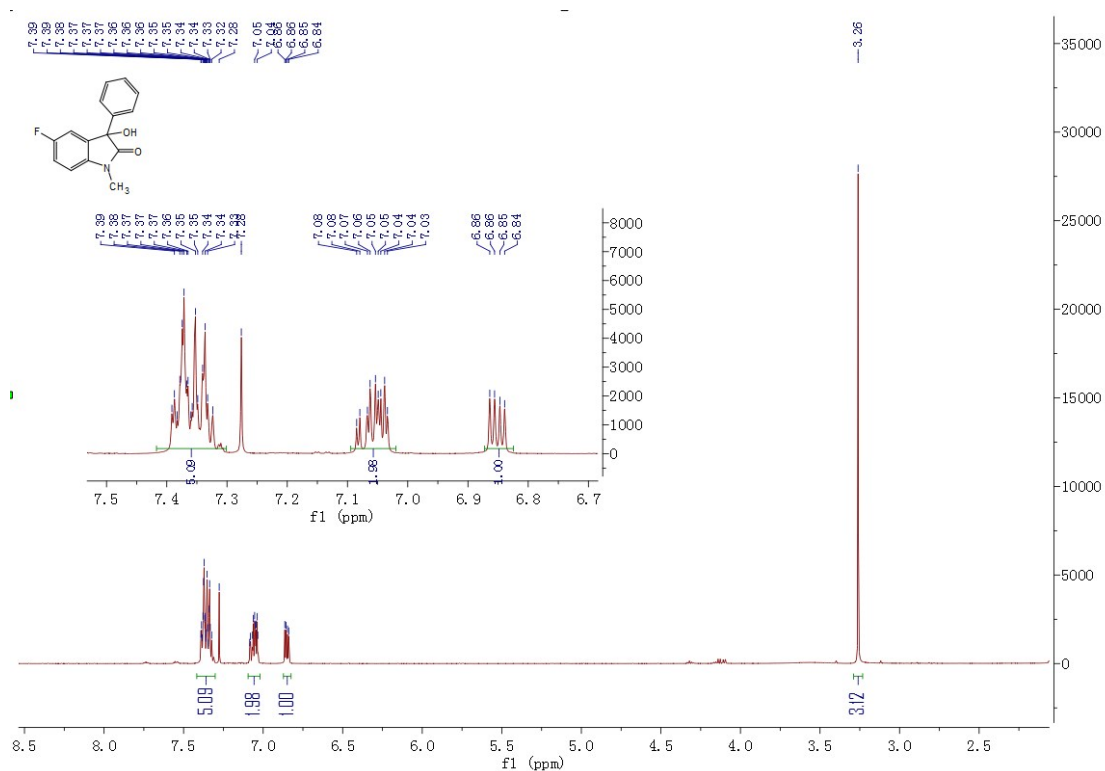
3-hydroxy-1,5-dimethyl-3-phenylindolin-2-one (1e)



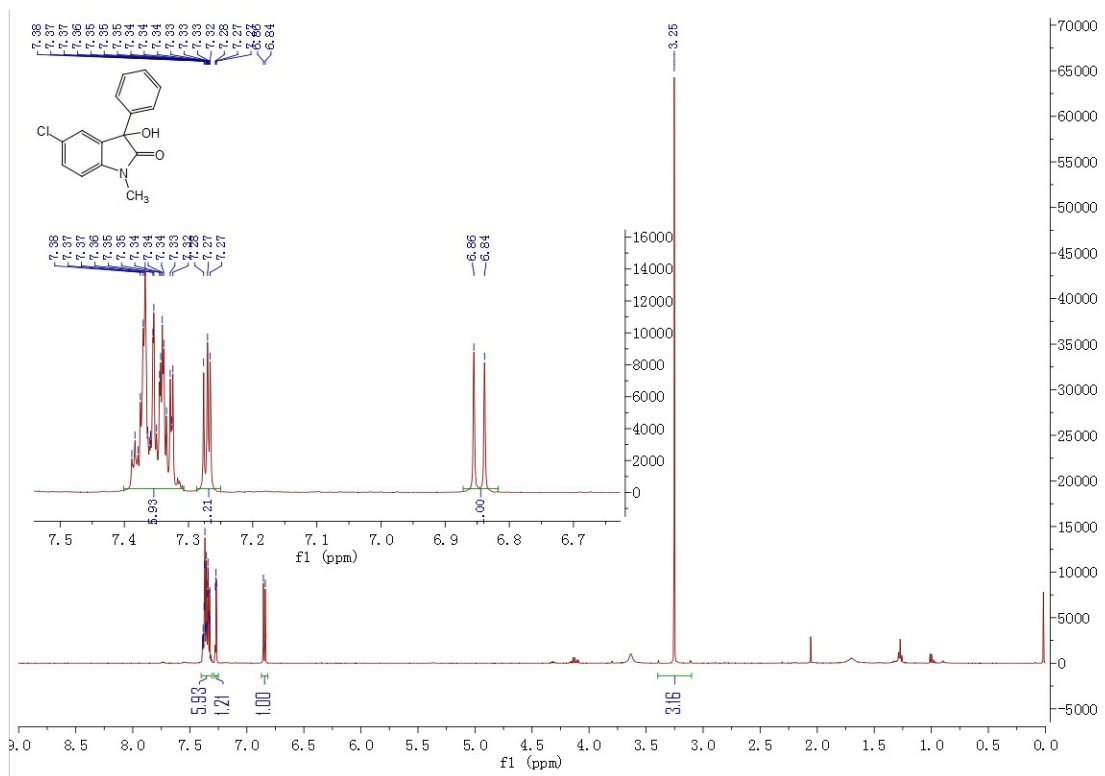
3-hydroxy-3-(4-methoxyphenyl)-1-methylindolin-2-one (1f)



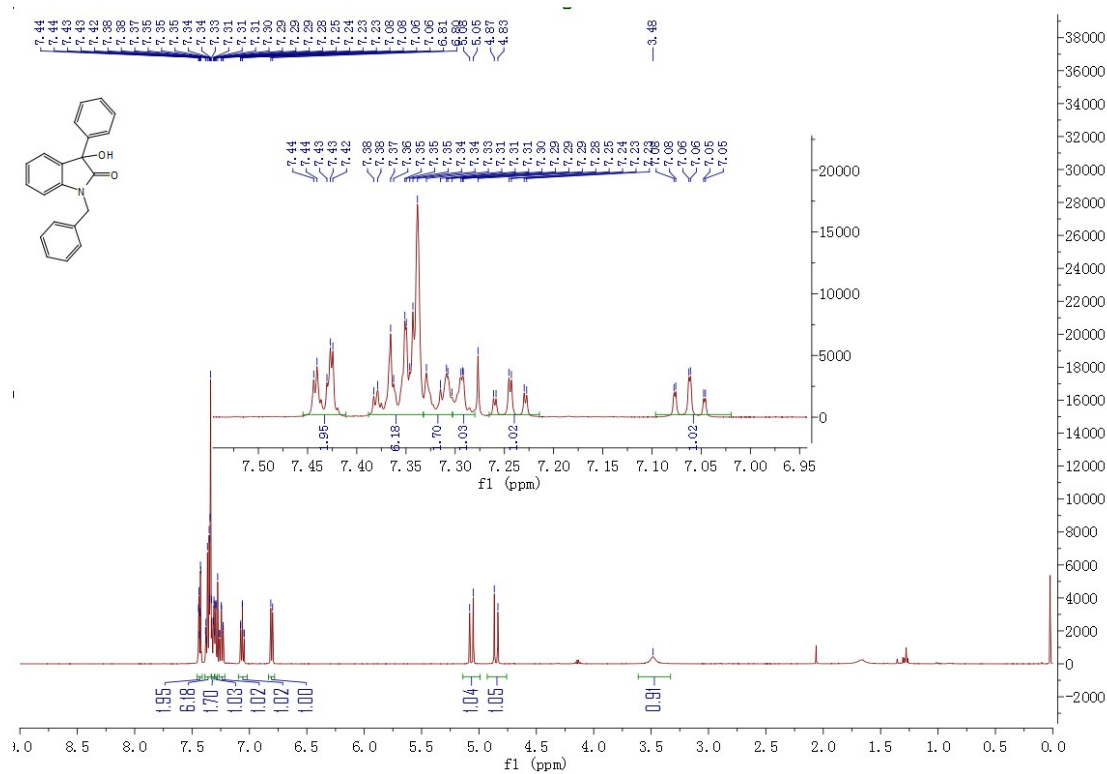
5-fluoro-3-hydroxy-1-methyl-3-phenylindolin-2-one (1g)



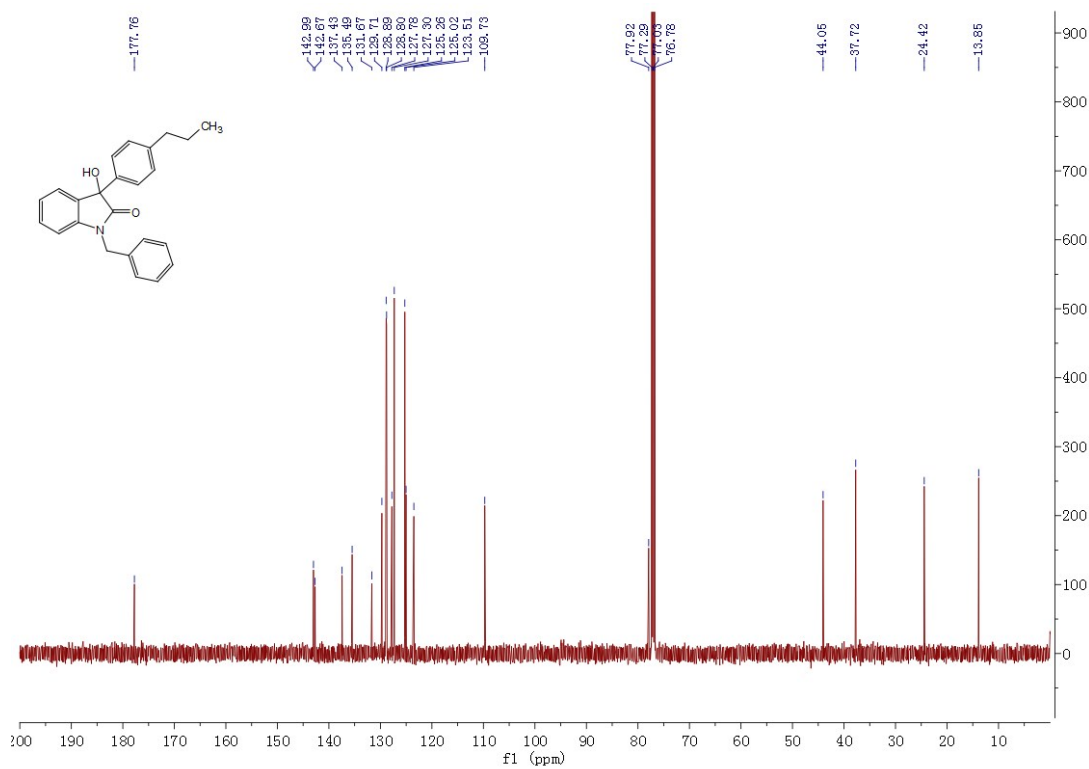
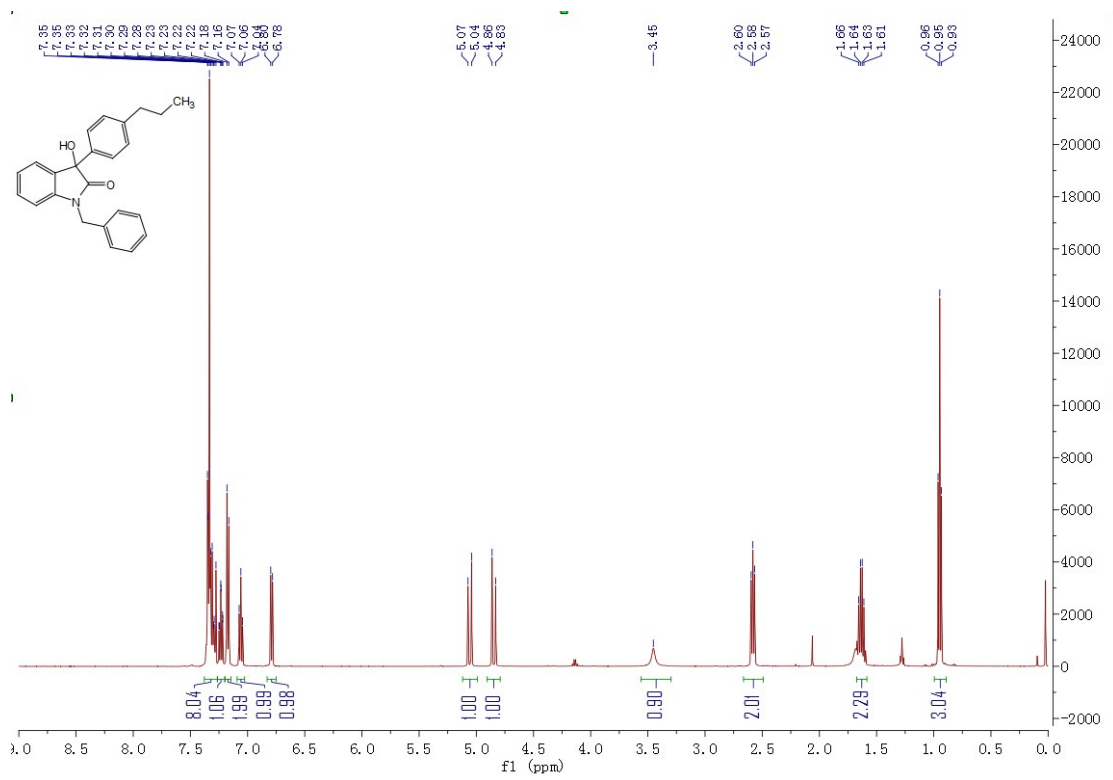
5-chloro-3-hydroxy-1-methyl-3-phenylindolin-2-one (1h)



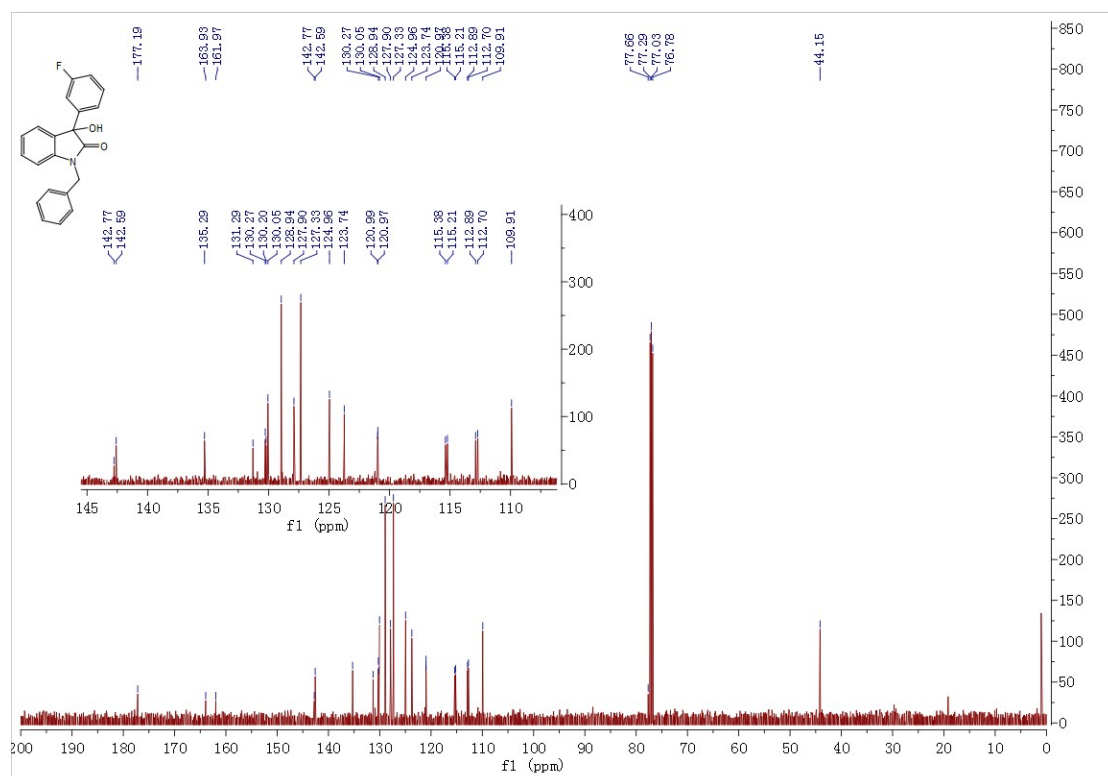
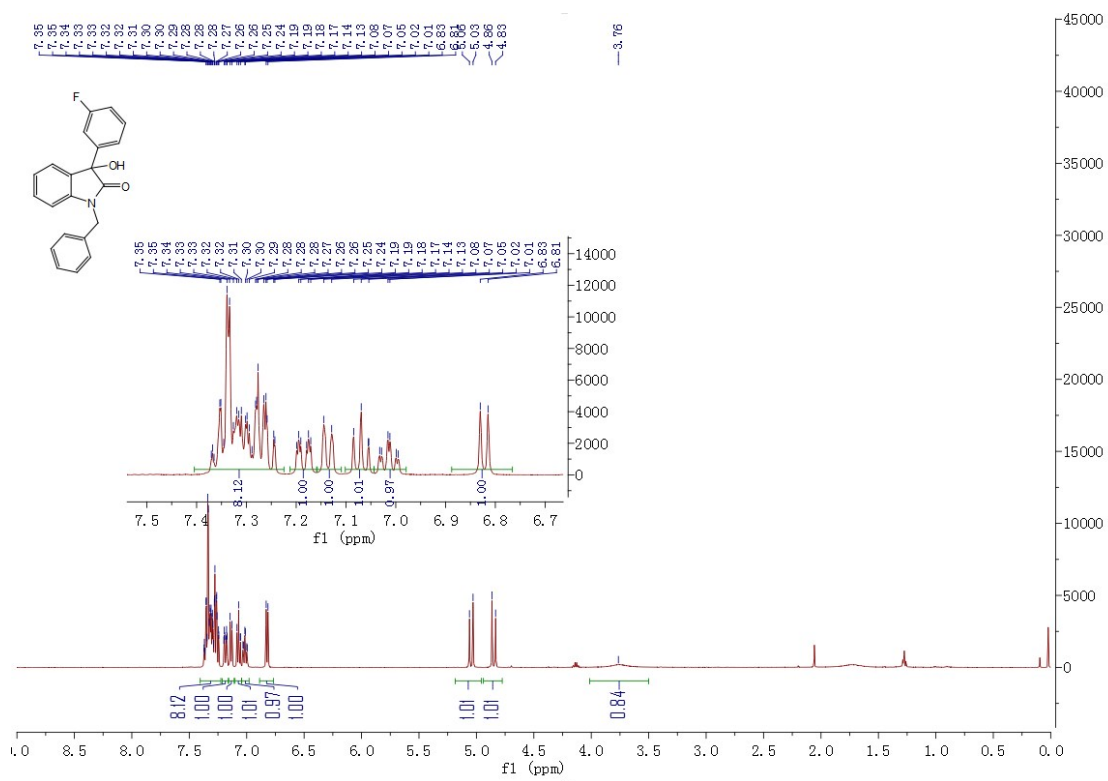
1-benzyl-3-hydroxy-3-phenylindolin-2-one (1i)



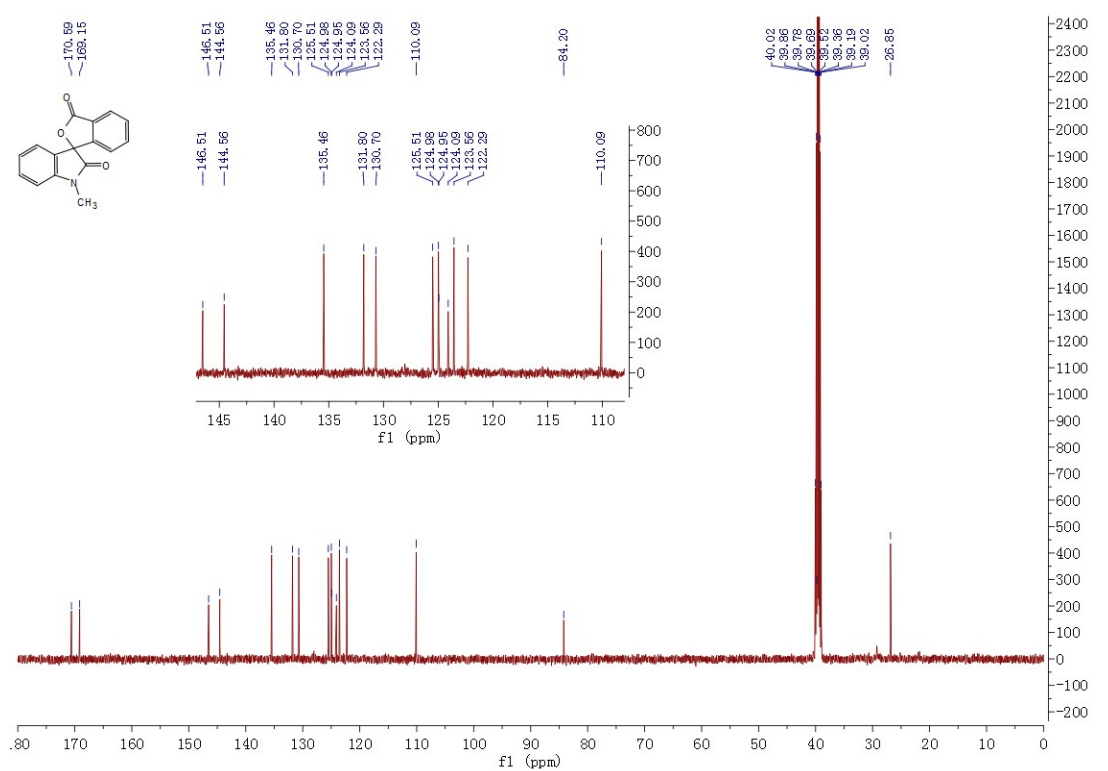
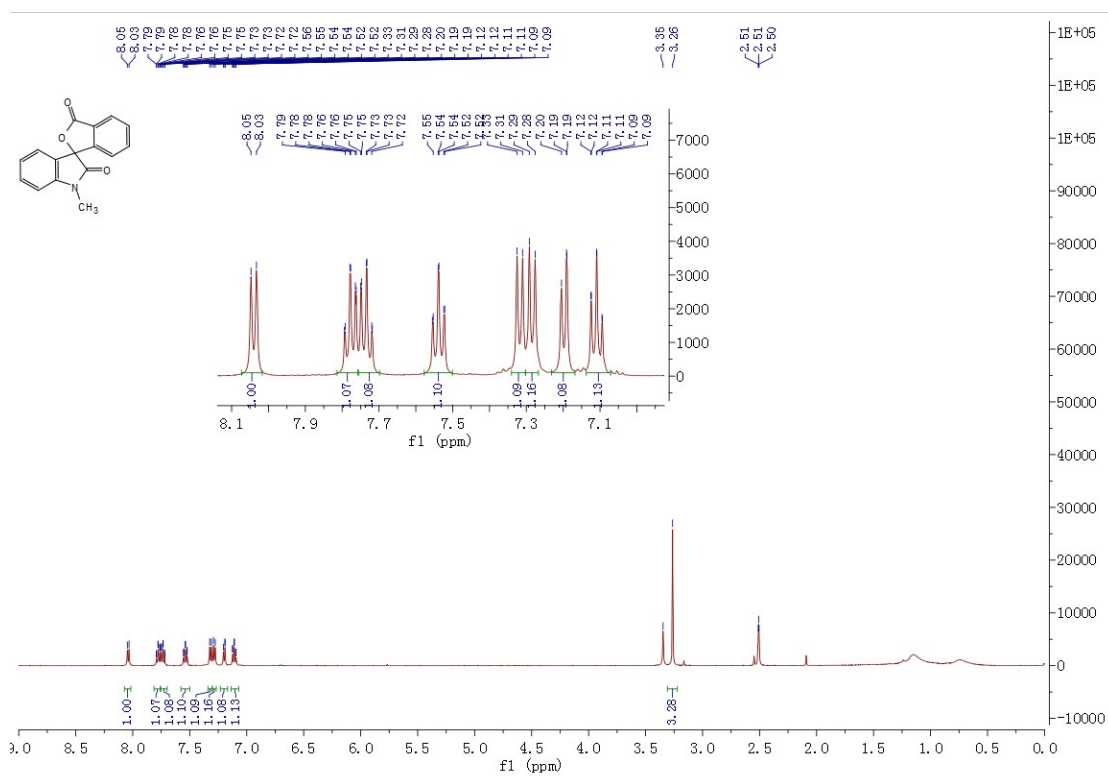
1-benzyl-3-hydroxy-3-(4-propylphenyl)indolin-2-one (1j)



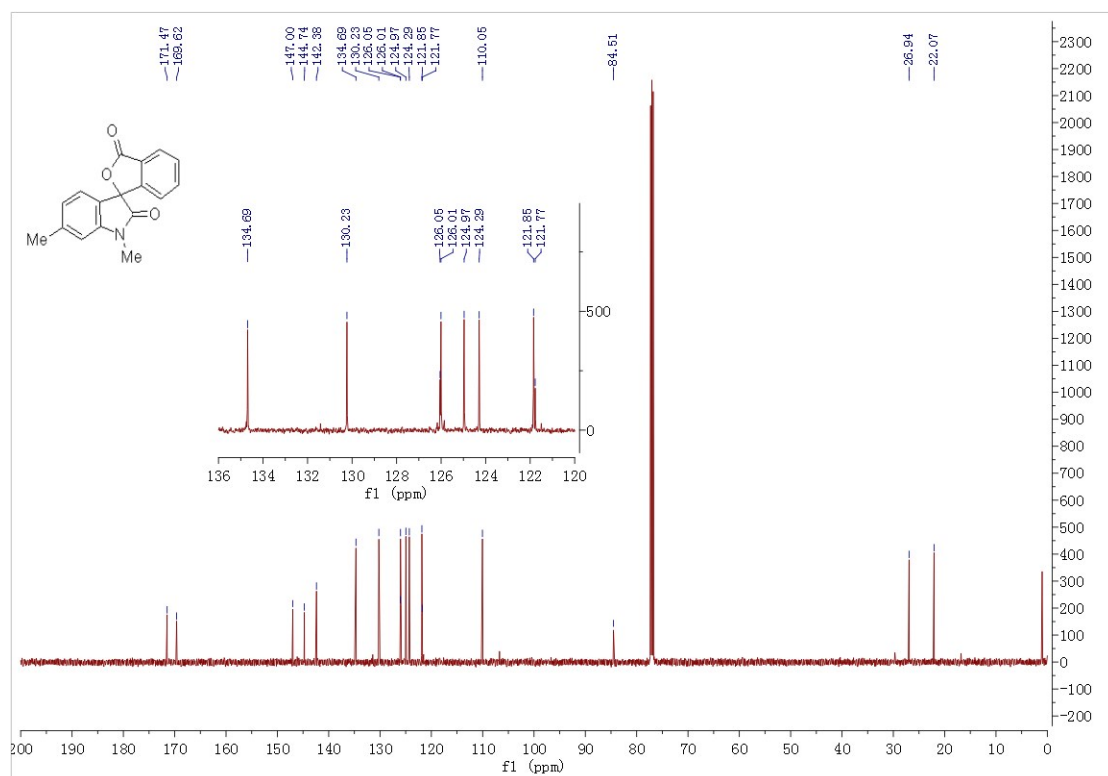
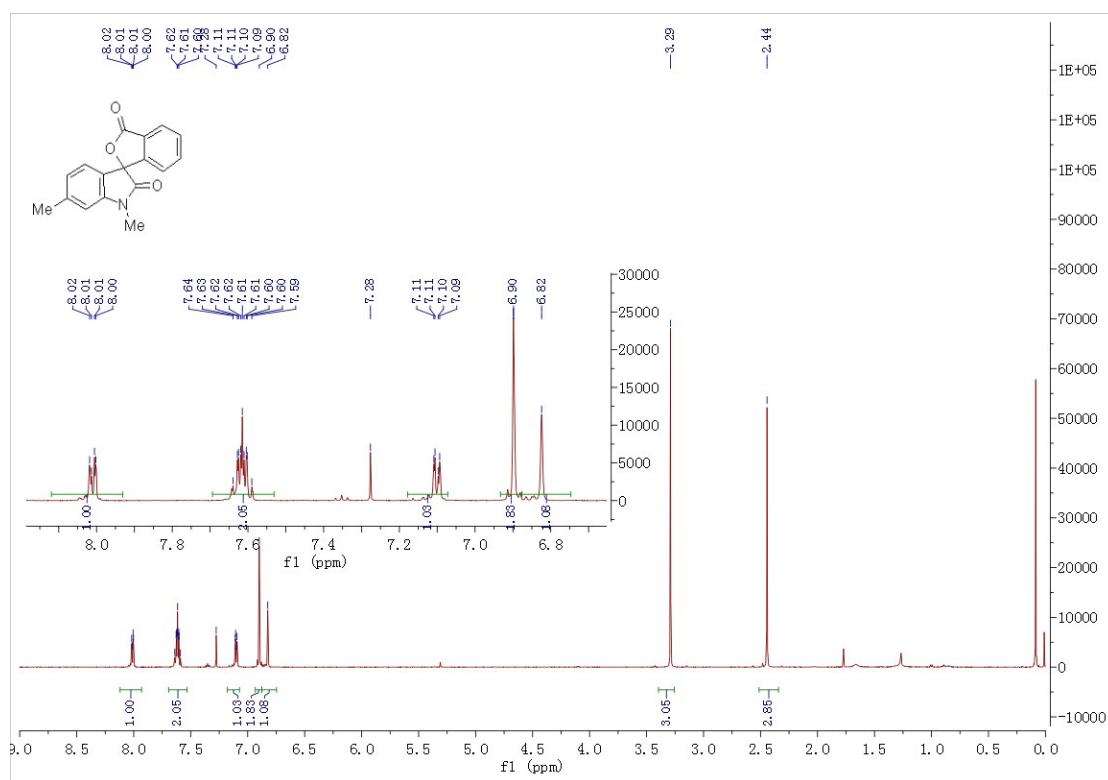
1-benzyl-3-(3-fluorophenyl)-3-hydroxyindolin-2-one (1k)



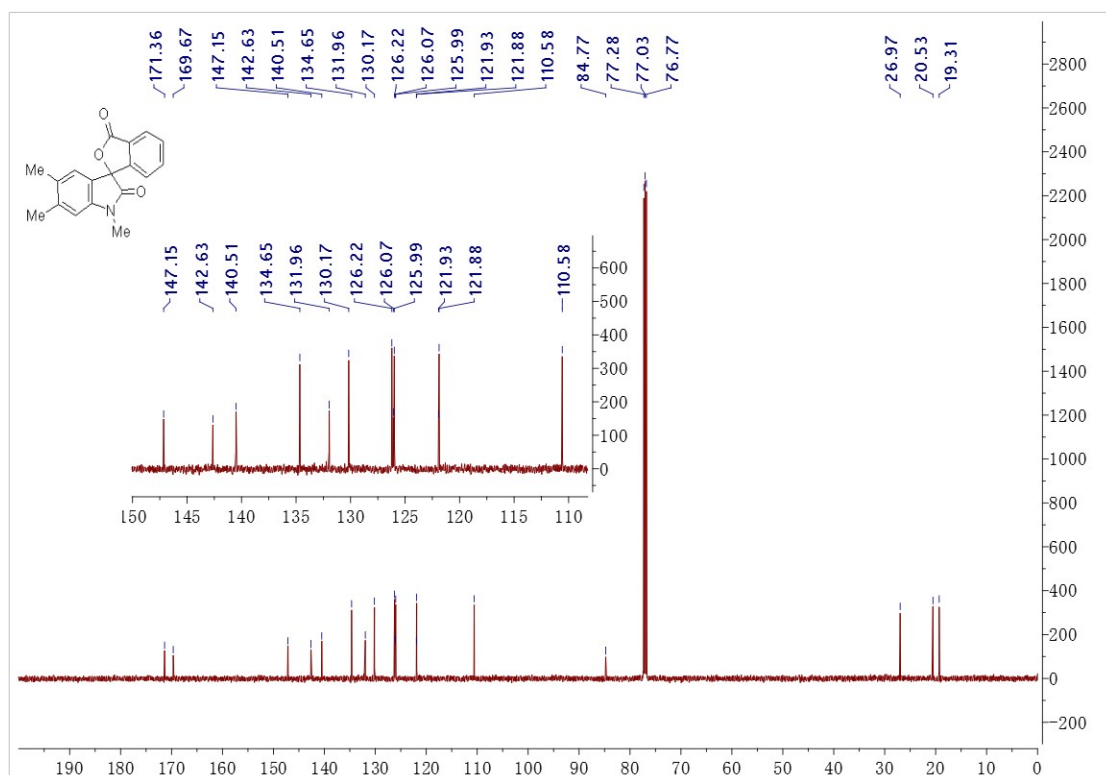
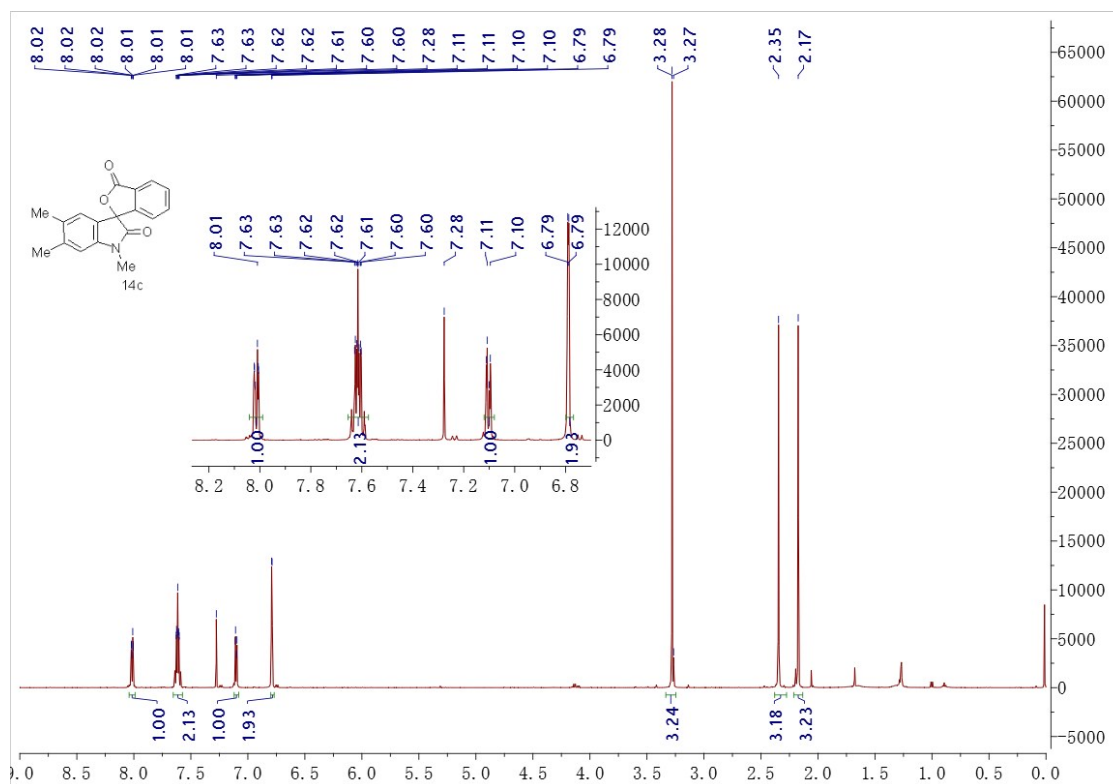
1-methyl-3'H-spiro[indoline-3,1'-isobenzofuran]-2,3'-dione (7a)



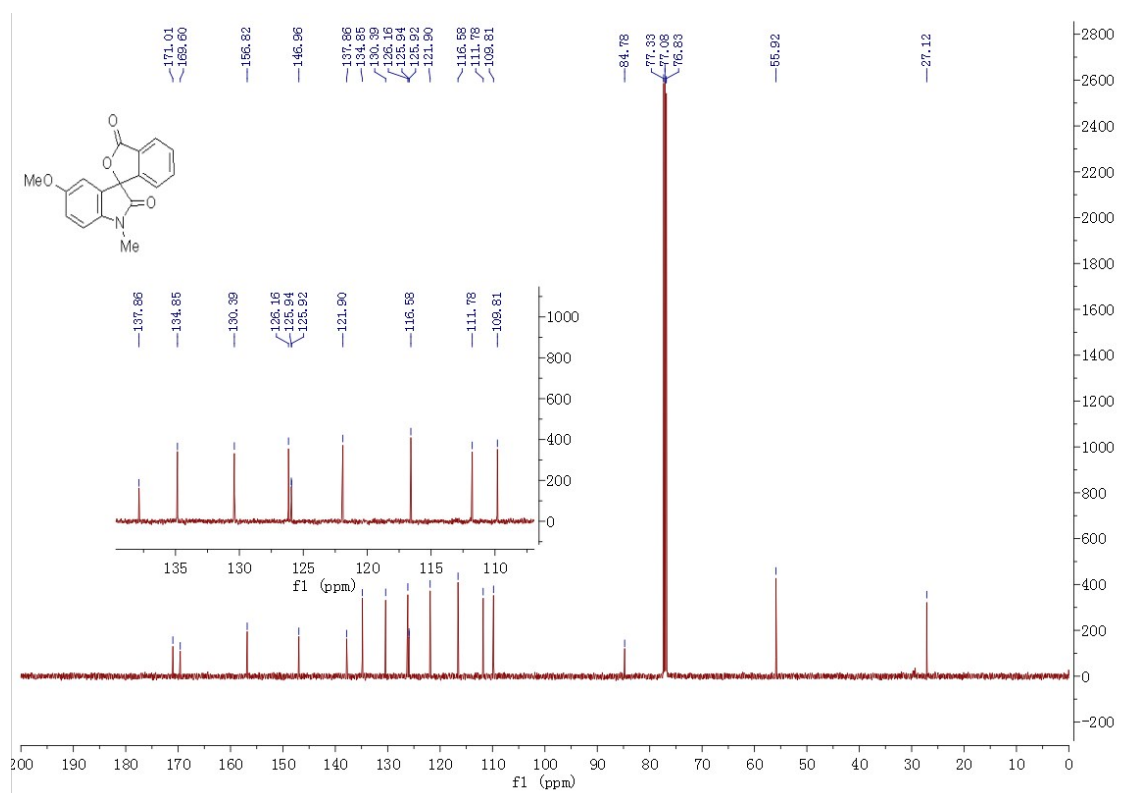
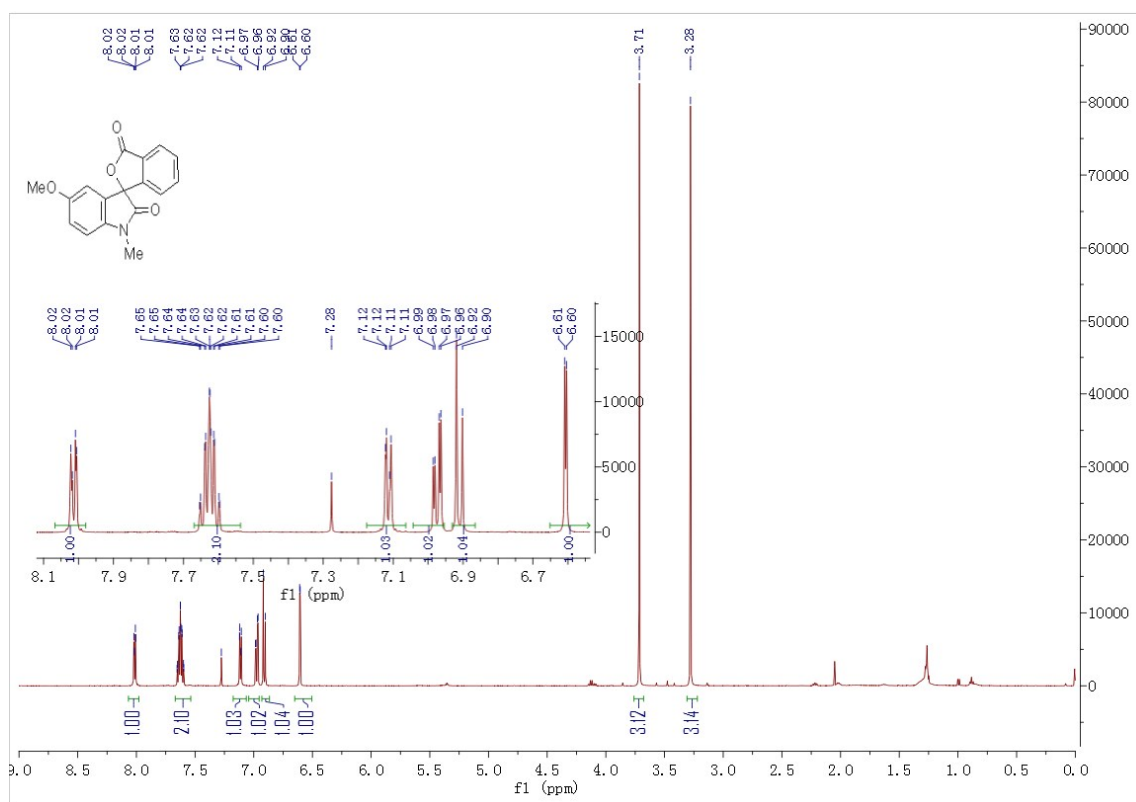
1,6-dimethyl-3'H-spiro[indoline-3,1'-isobenzofuran]-2,3'-dione (7b)



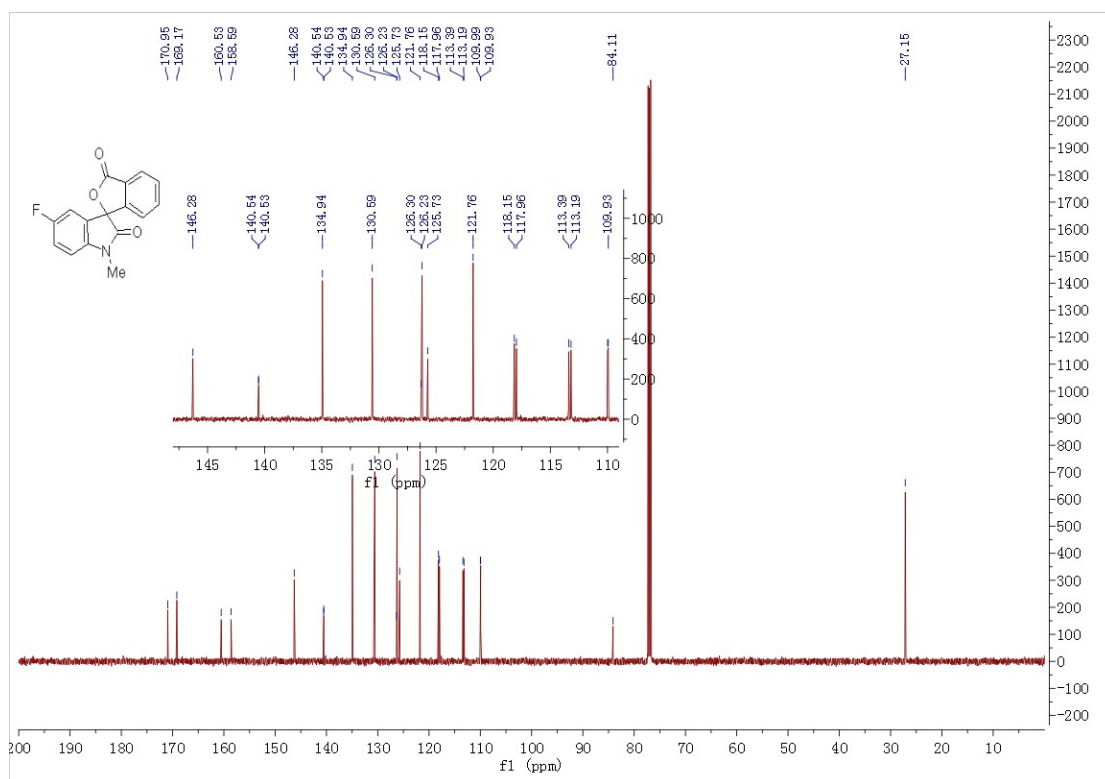
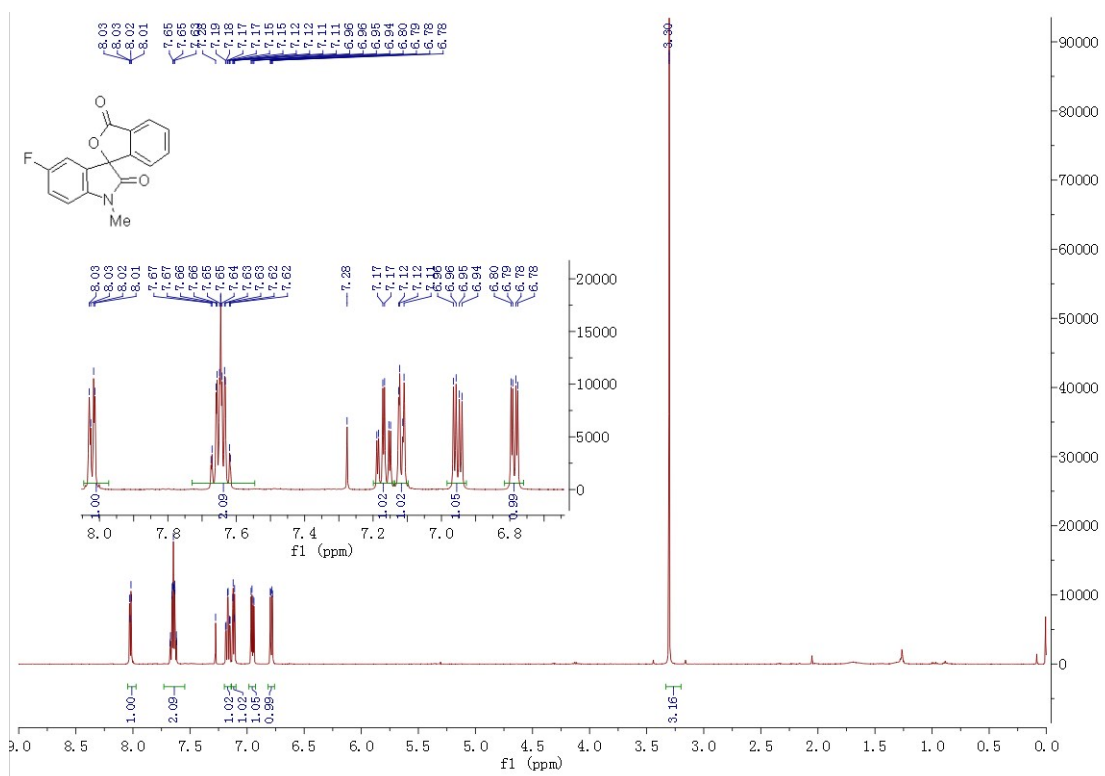
1,5,6-trimethyl-3'H-spiro(indoline-3,1'-isobenzofuran)-2,3'-dione (7c)



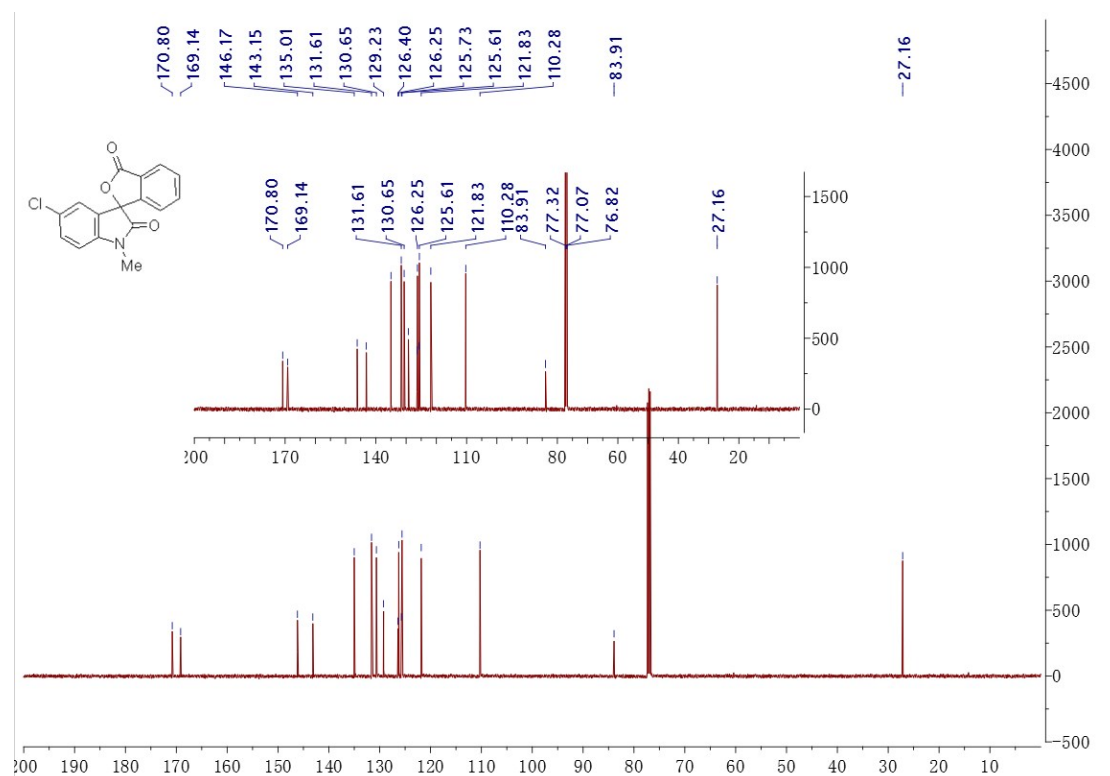
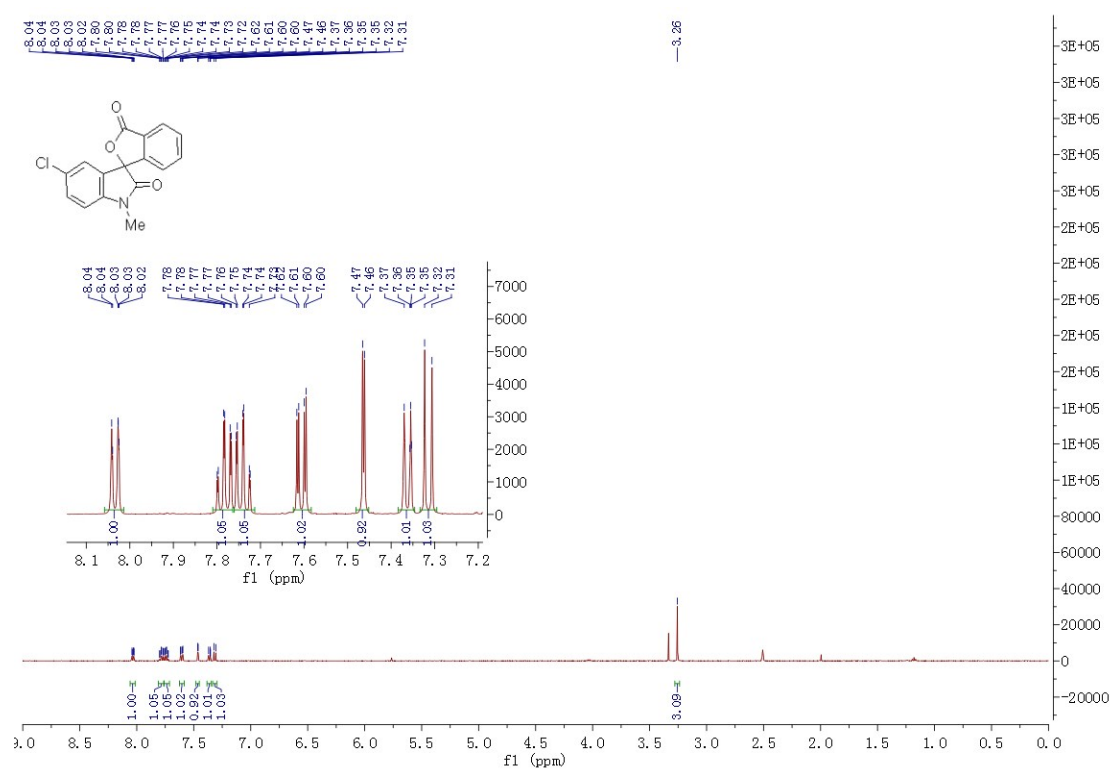
5-methoxy-1-methyl-3'H-spiro[indoline-3,1'-isobenzofuran]-2,3'-dione (7d)



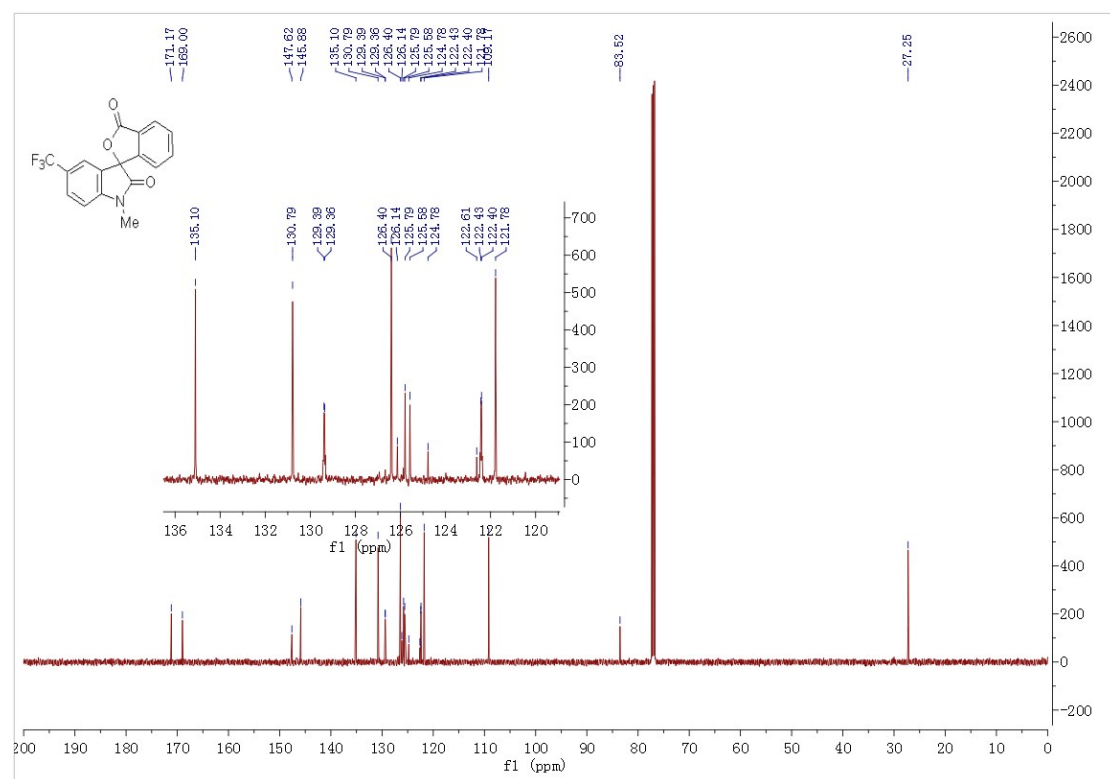
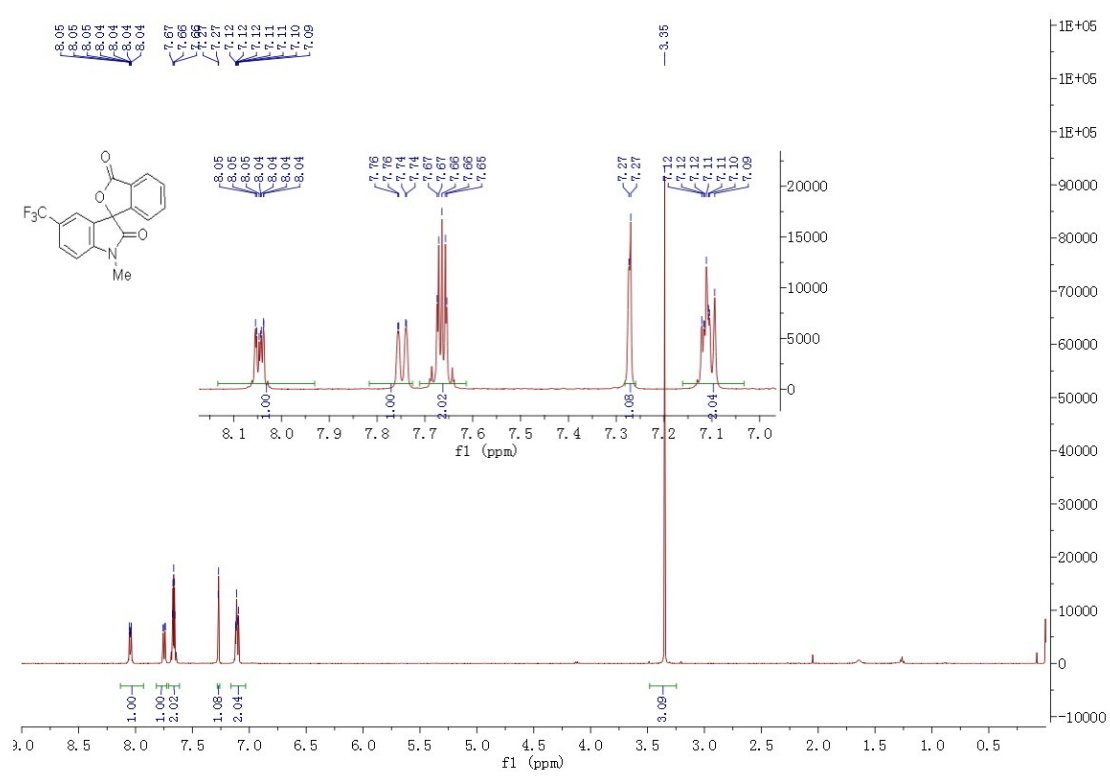
5-fluoro-1-methyl-3'H-spiro[indoline-3,1'-isobenzofuran]-2,3'-dione (7e)



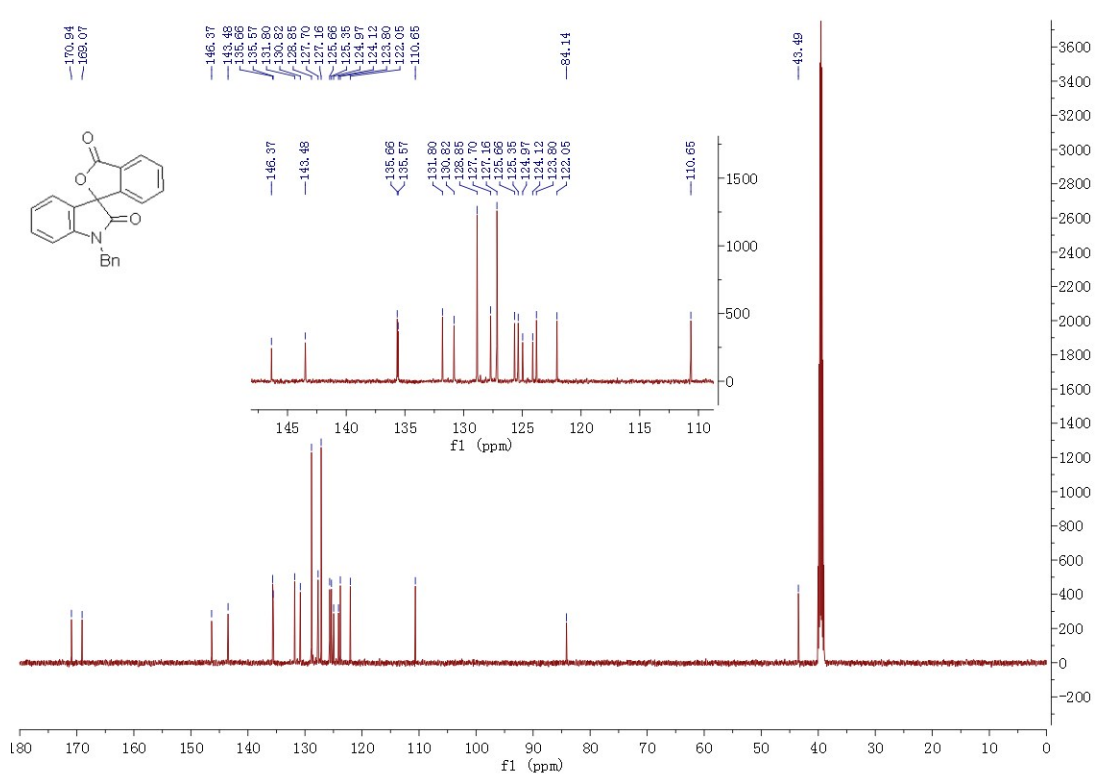
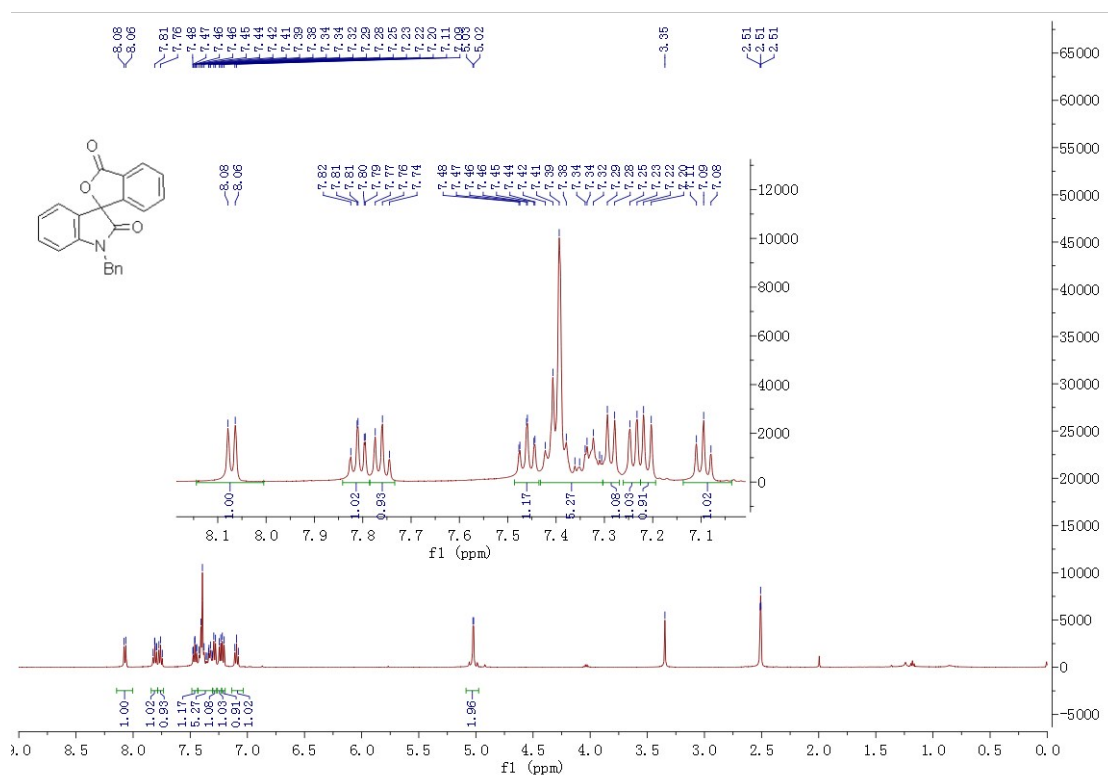
5-chloro-1-methyl-3'-H-spiro[indoline-3,1'-isobenzofuran]-2,3'-dione (7f)



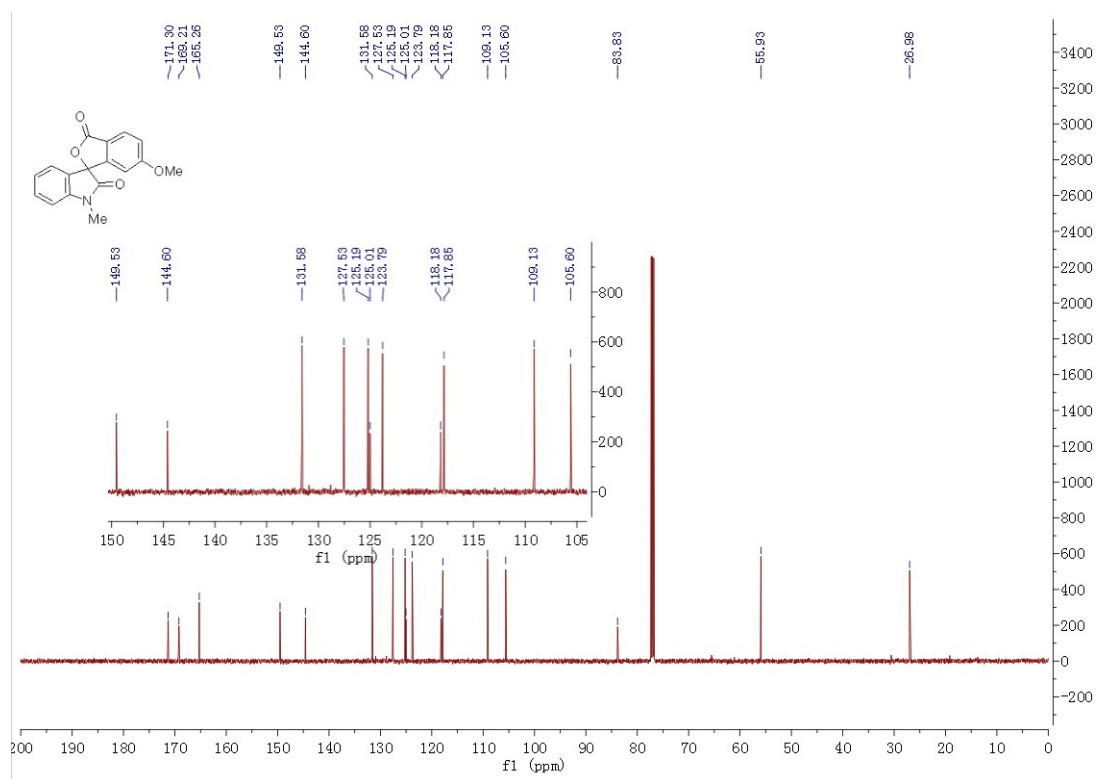
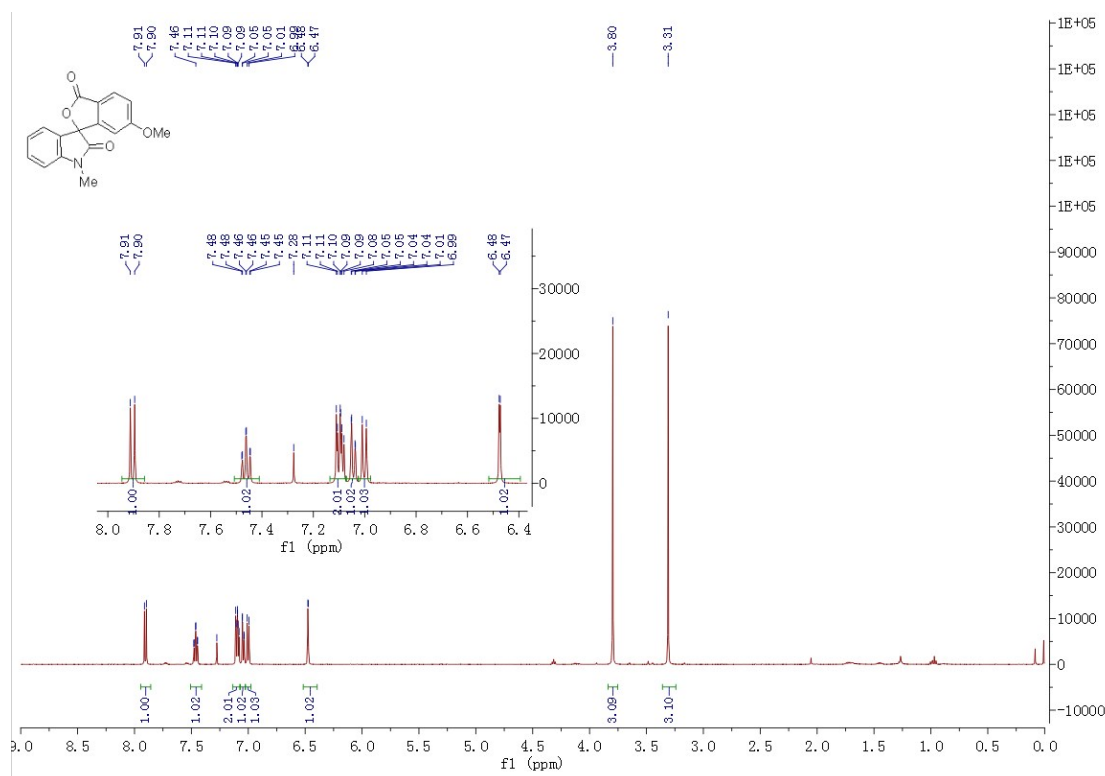
1-methyl-5-(trifluoromethyl)-3'H-spiro[indoline-3,1'-isobenzofuran]-2,3'-dione (7g)



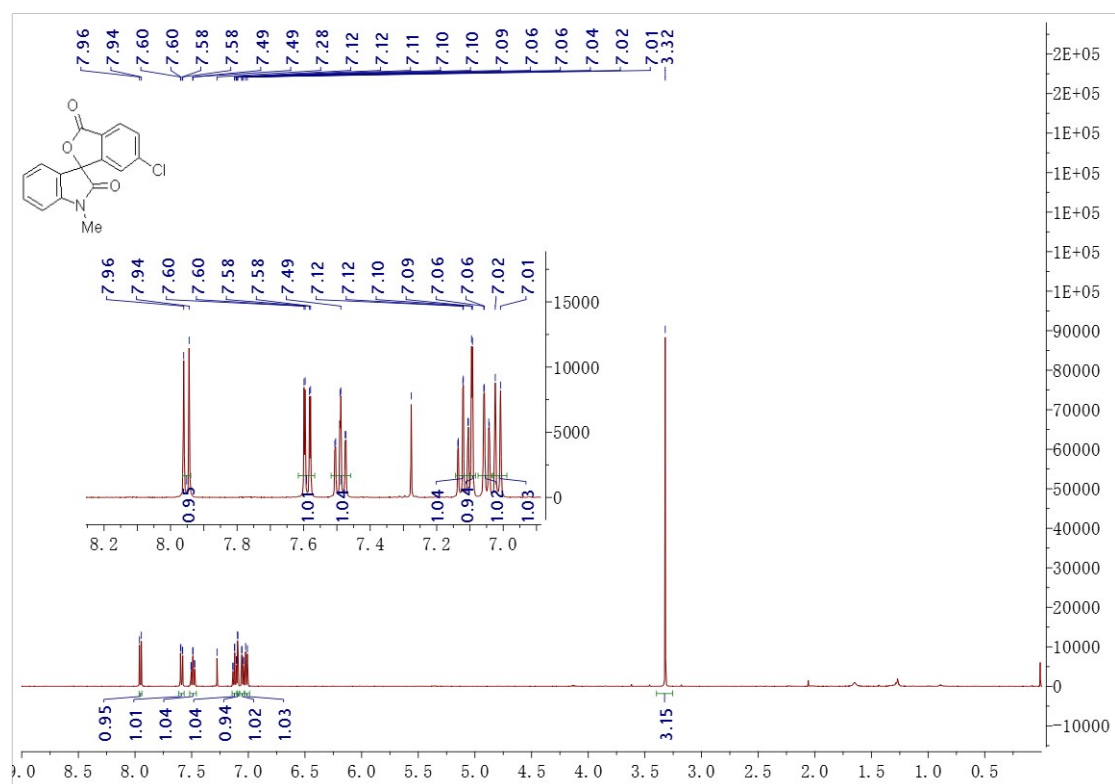
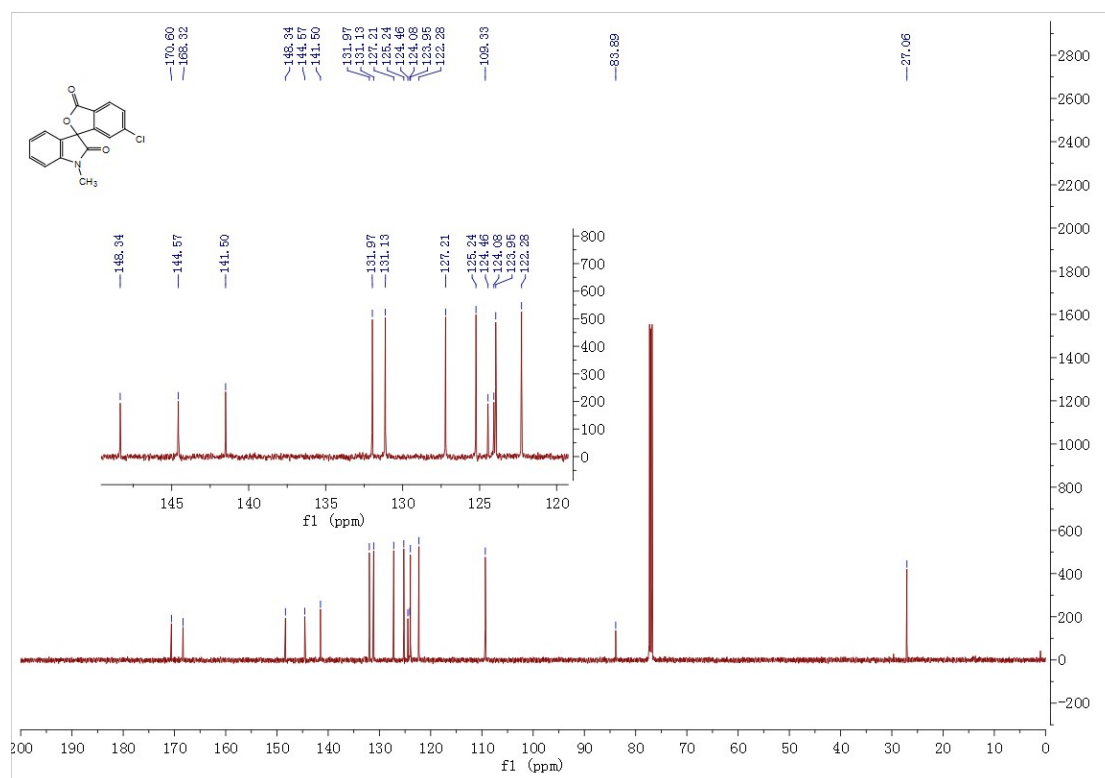
1-benzyl-3'H-spiro[indoline-3,1'-isobenzofuran]-2,3'-dione (7h)



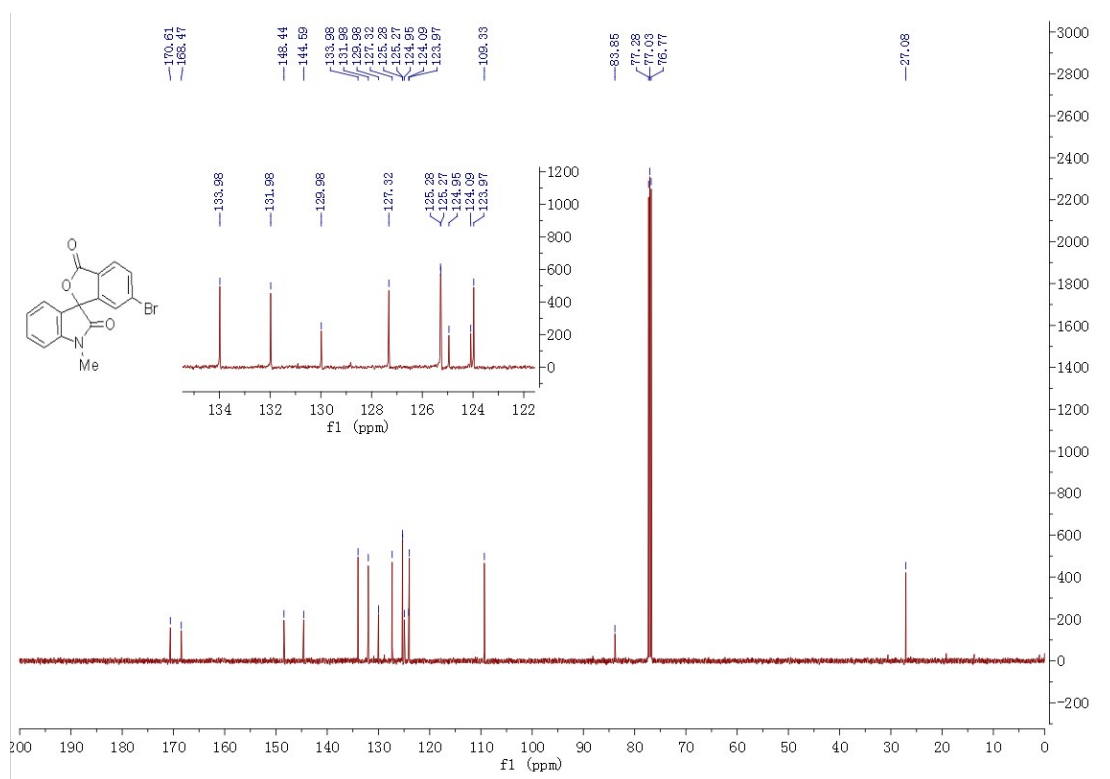
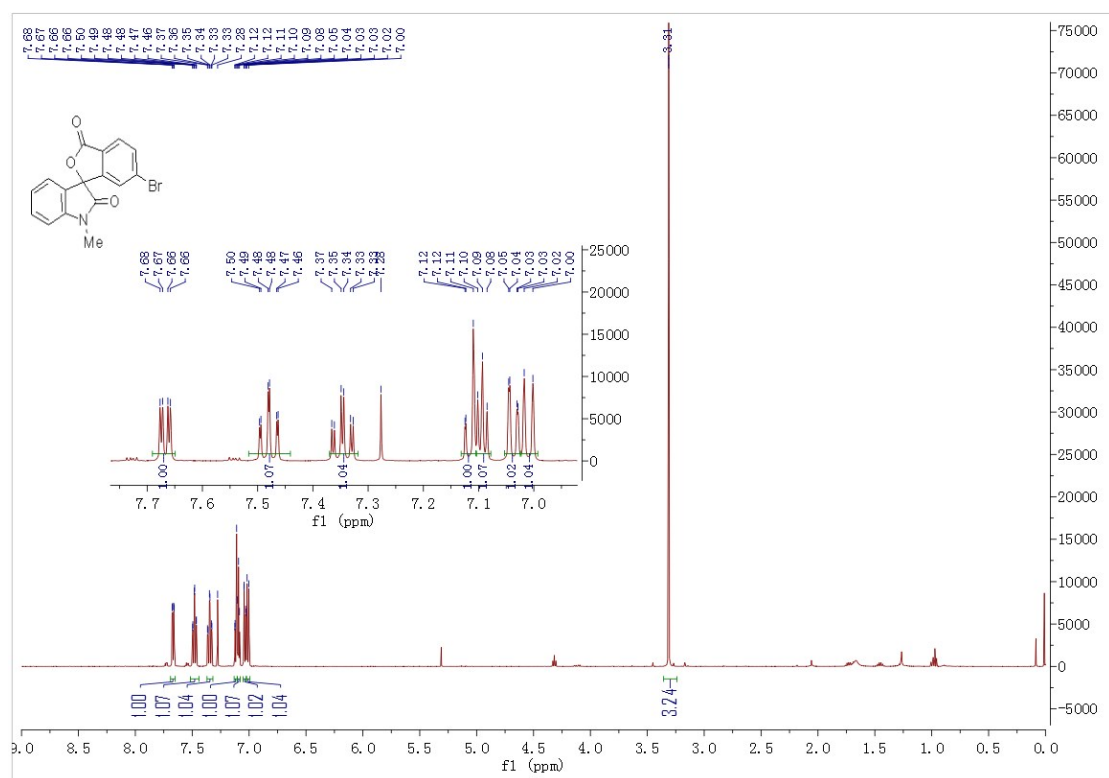
6'-methoxy-1-methyl-3'*H*-spiro(indoline-3,1'-isobenzofuran)-2,3'-dione (7i):



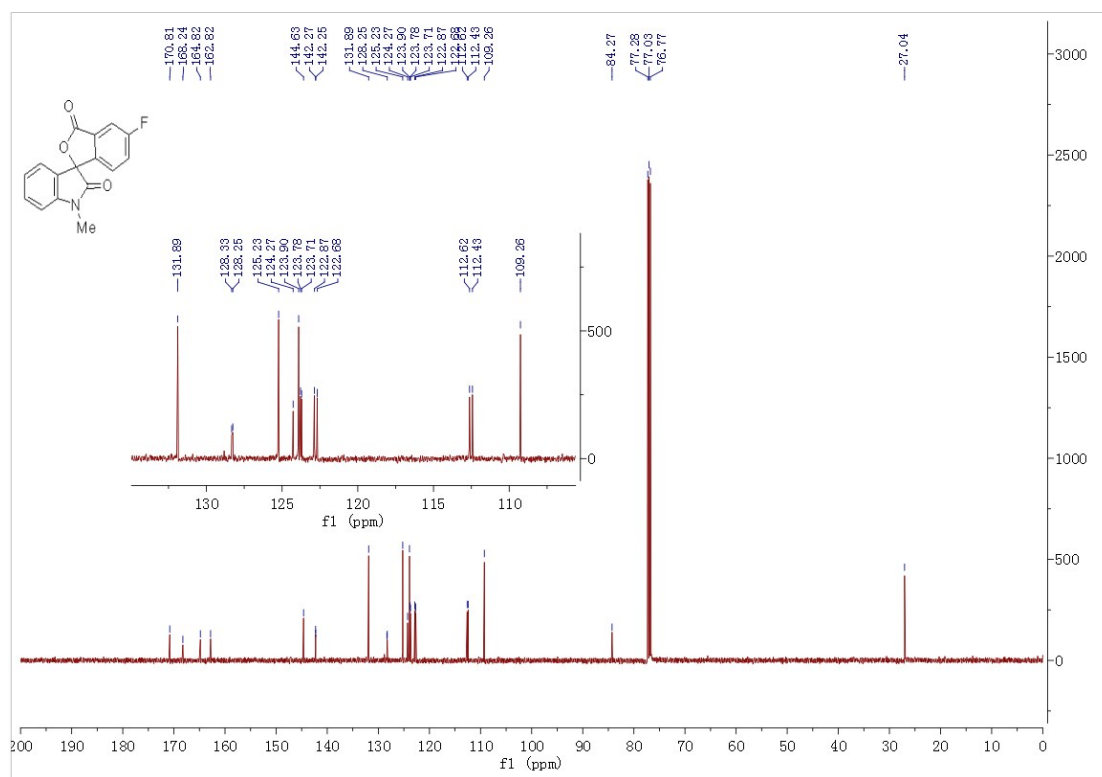
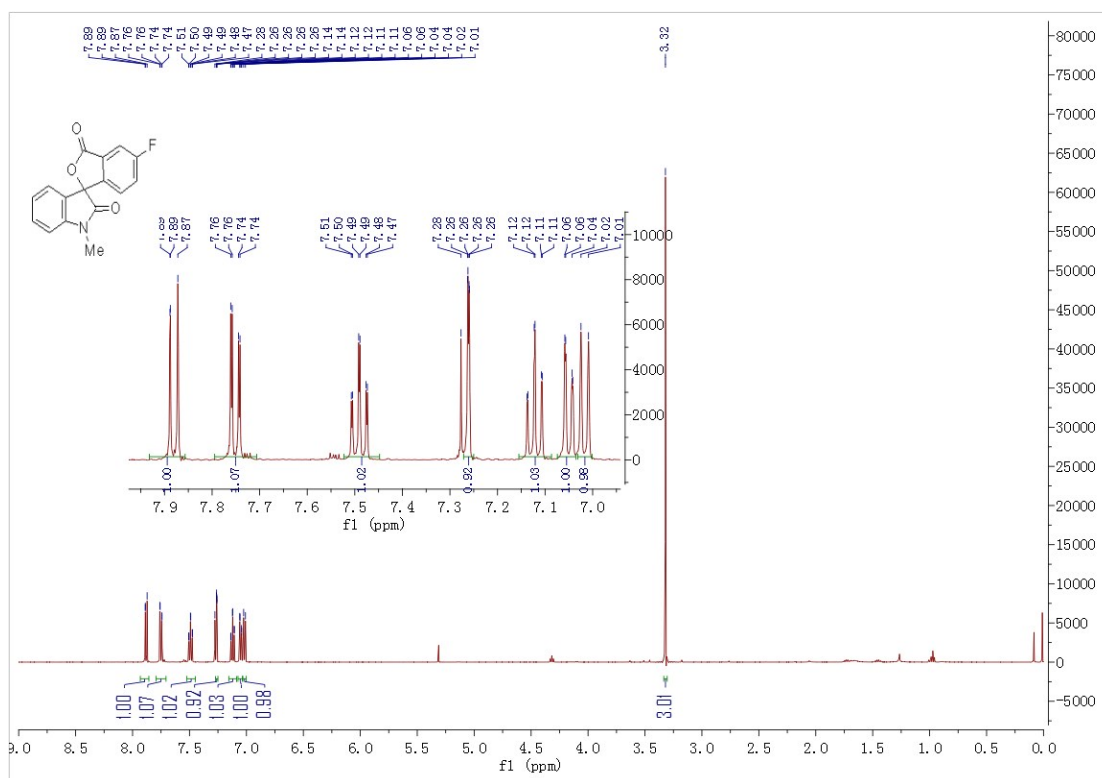
6'-chloro-1-methyl-3'H-spiro[indoline-3,1'-isobenzofuran]-2,3'-dione (7j)



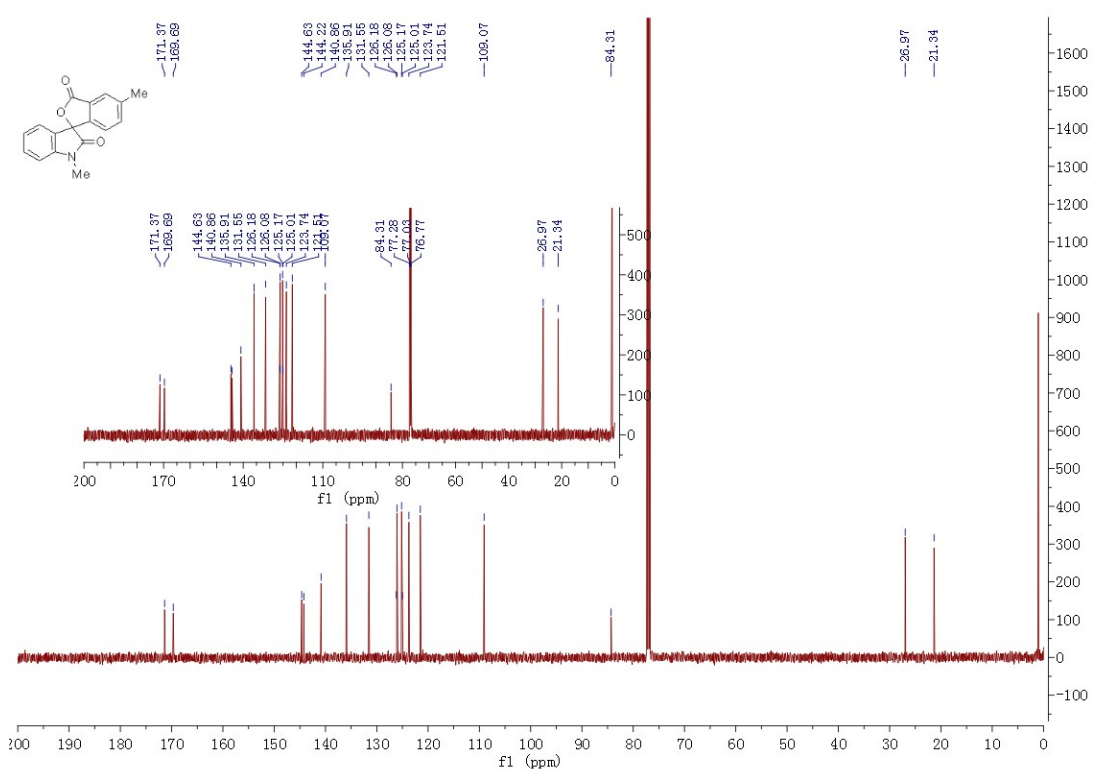
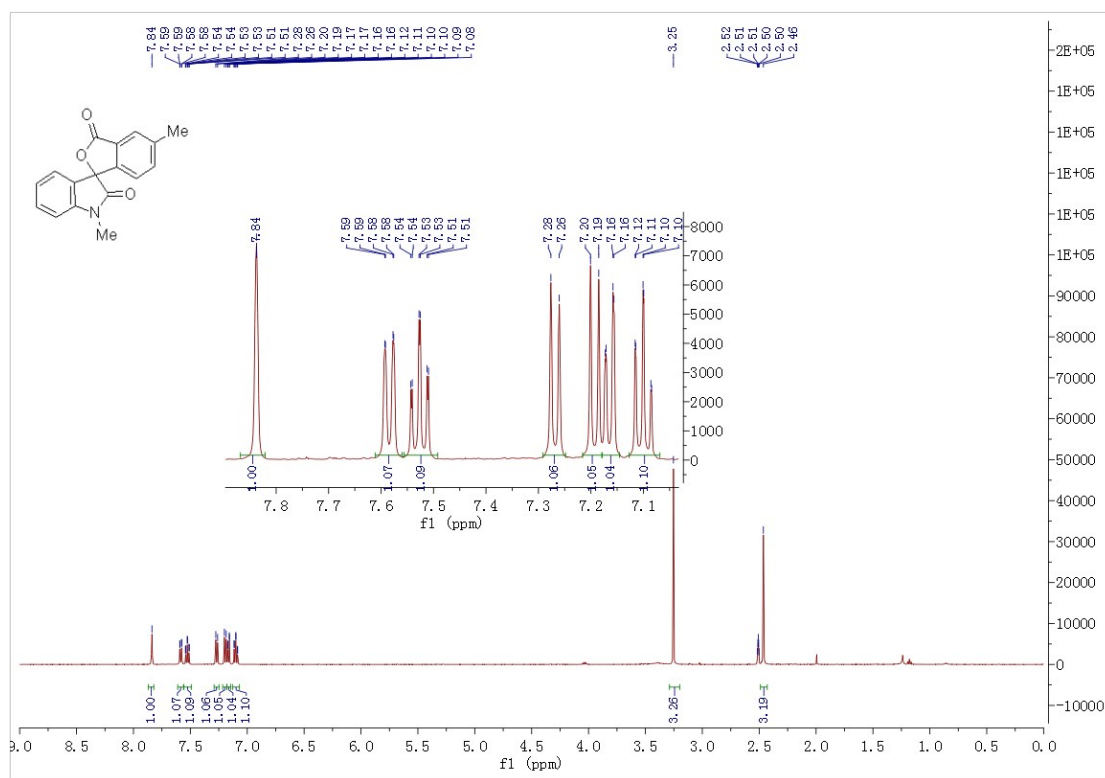
6'-bromo-1-methyl-3'H-spiro[indoline-3,1'-isobenzofuran]-2,3'-dione (7k)



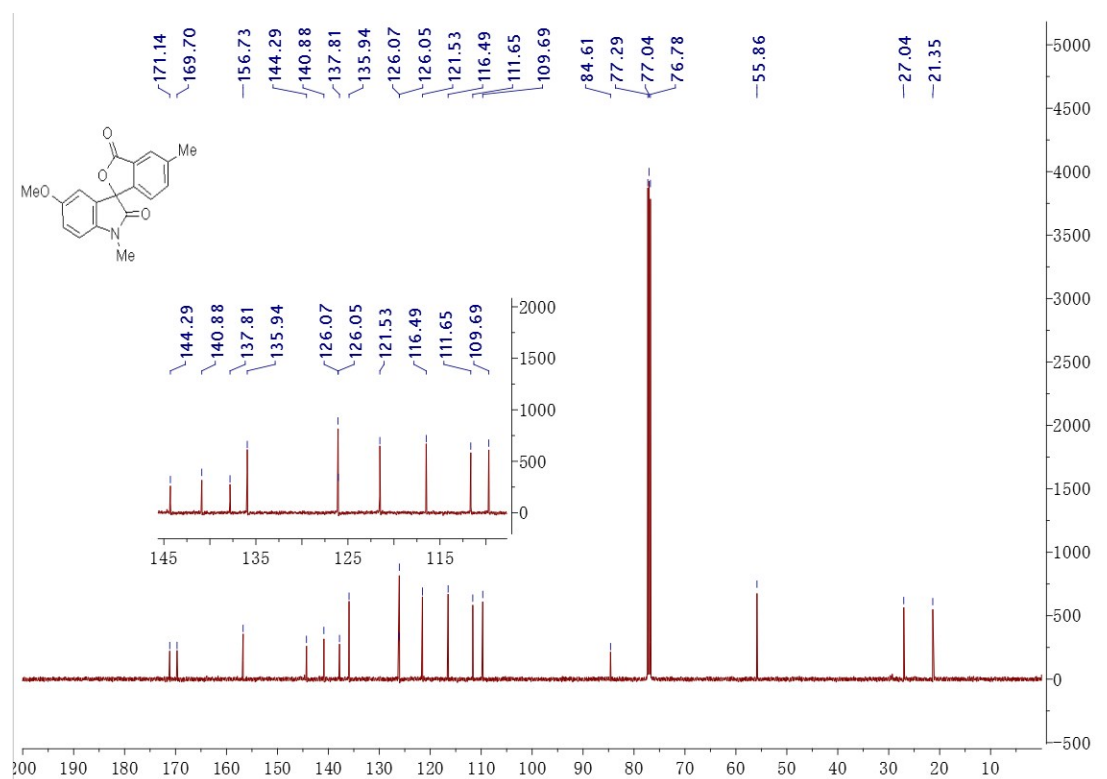
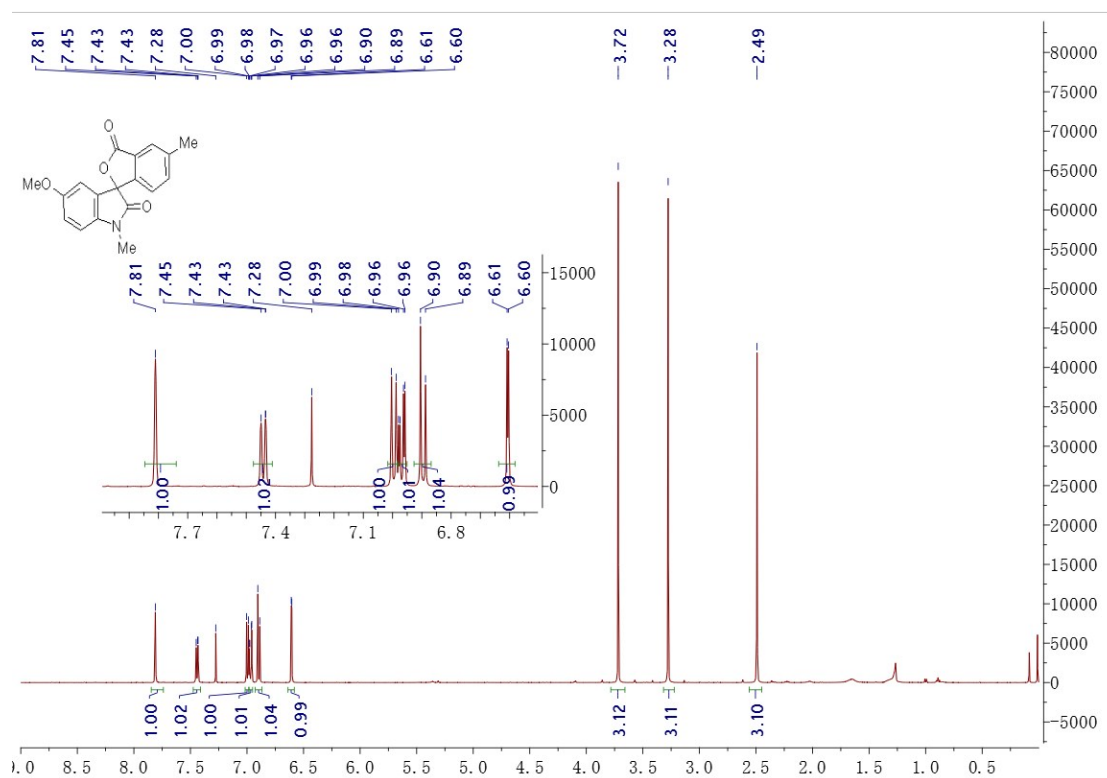
5'-fluoro-1-methyl-3'H-spiro[indoline-3,1'-isobenzofuran]-2,3'-dione (7I)



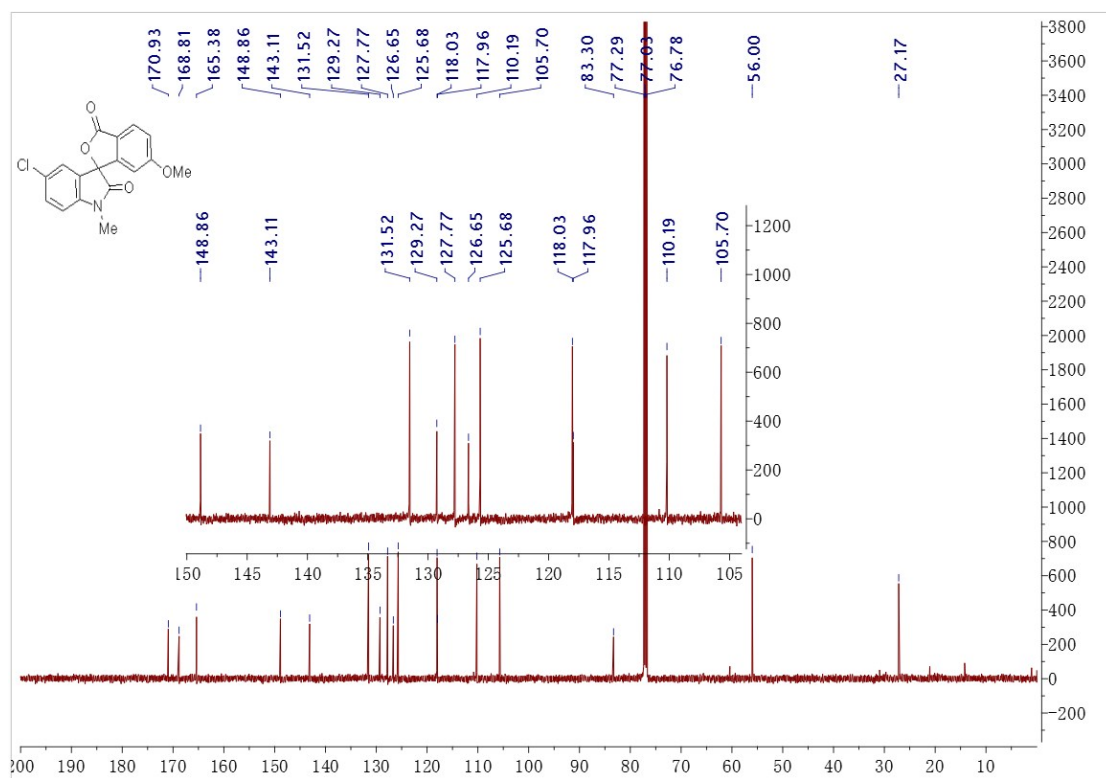
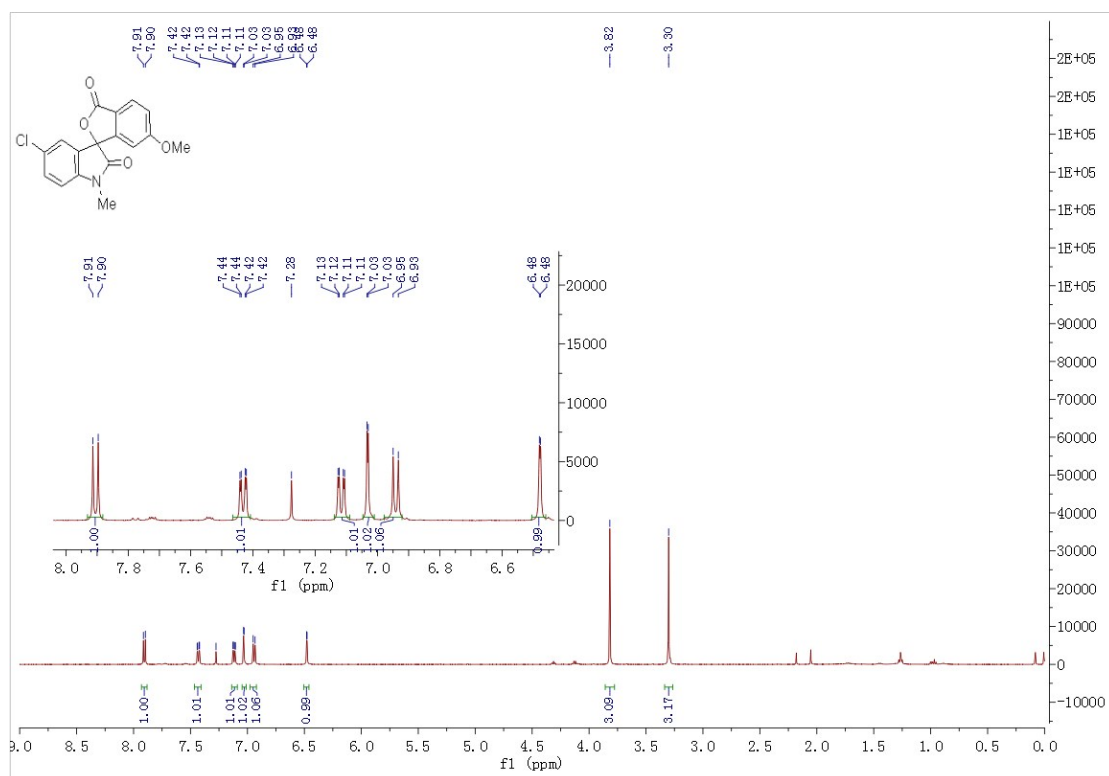
1,5'-dimethyl-3'H-spiro[indoline-3,1'-isobenzofuran]-2,3'-dione (7m)



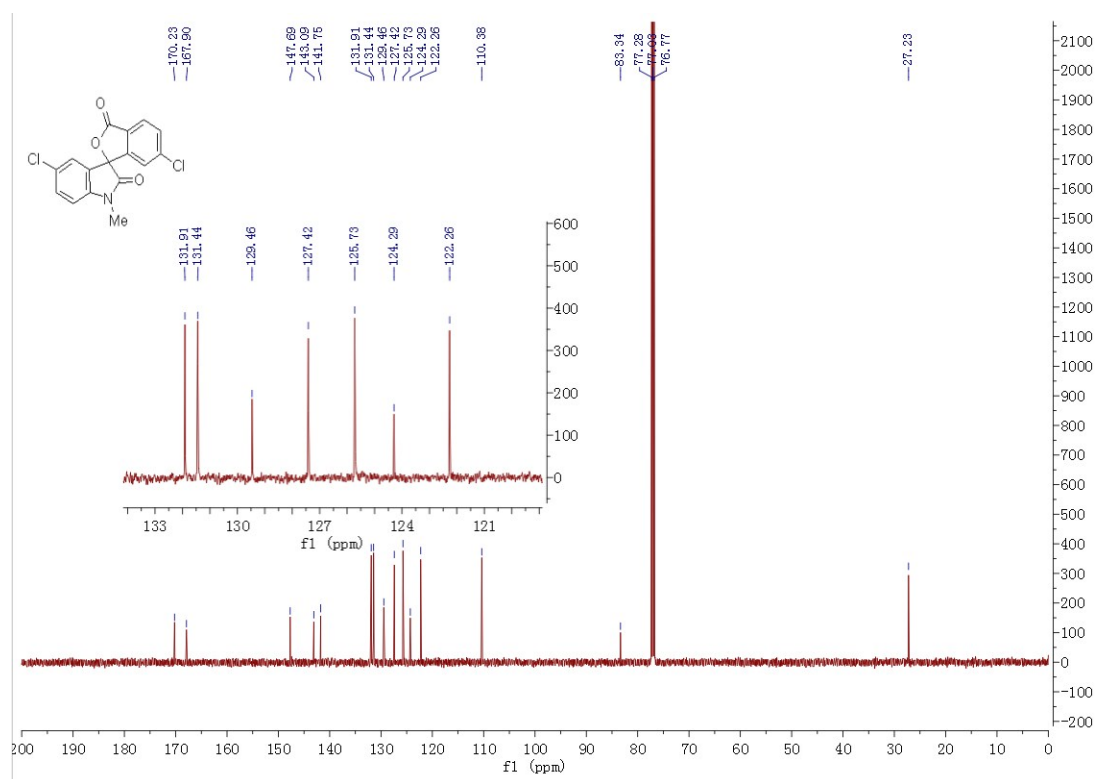
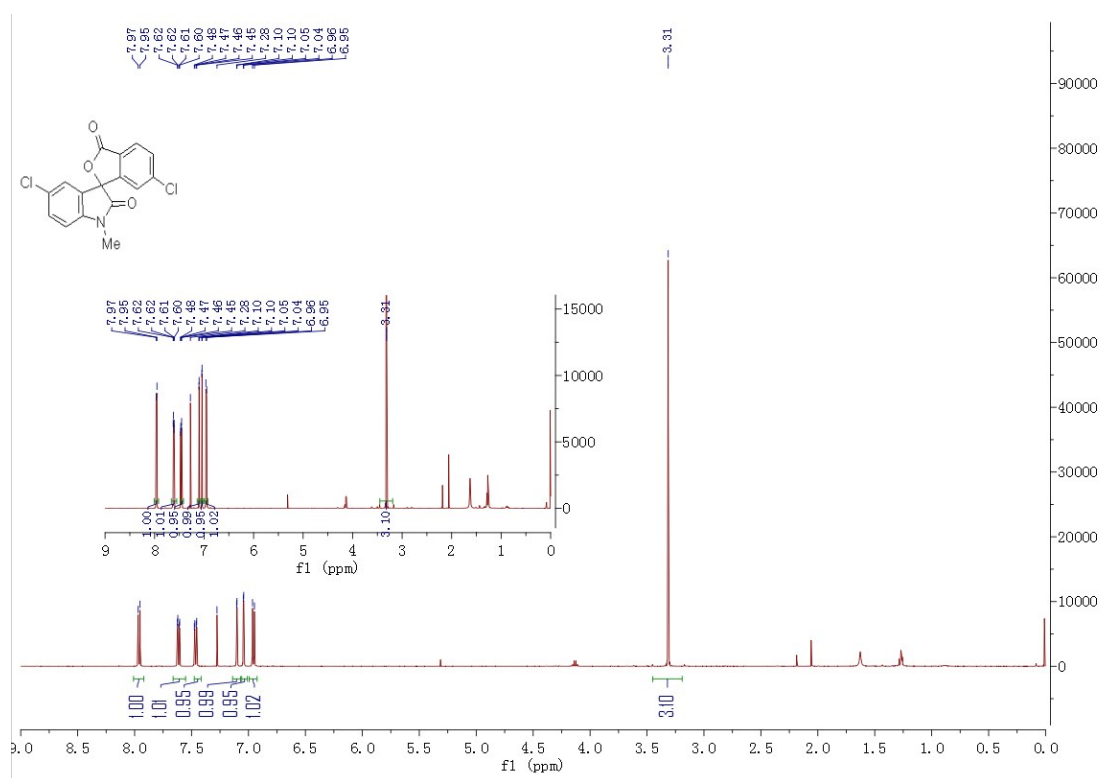
5-methoxy-1,5'-dimethyl-3'H-spiro[indoline-3,1'-isobenzofuran]-2,3'-dione (7n)



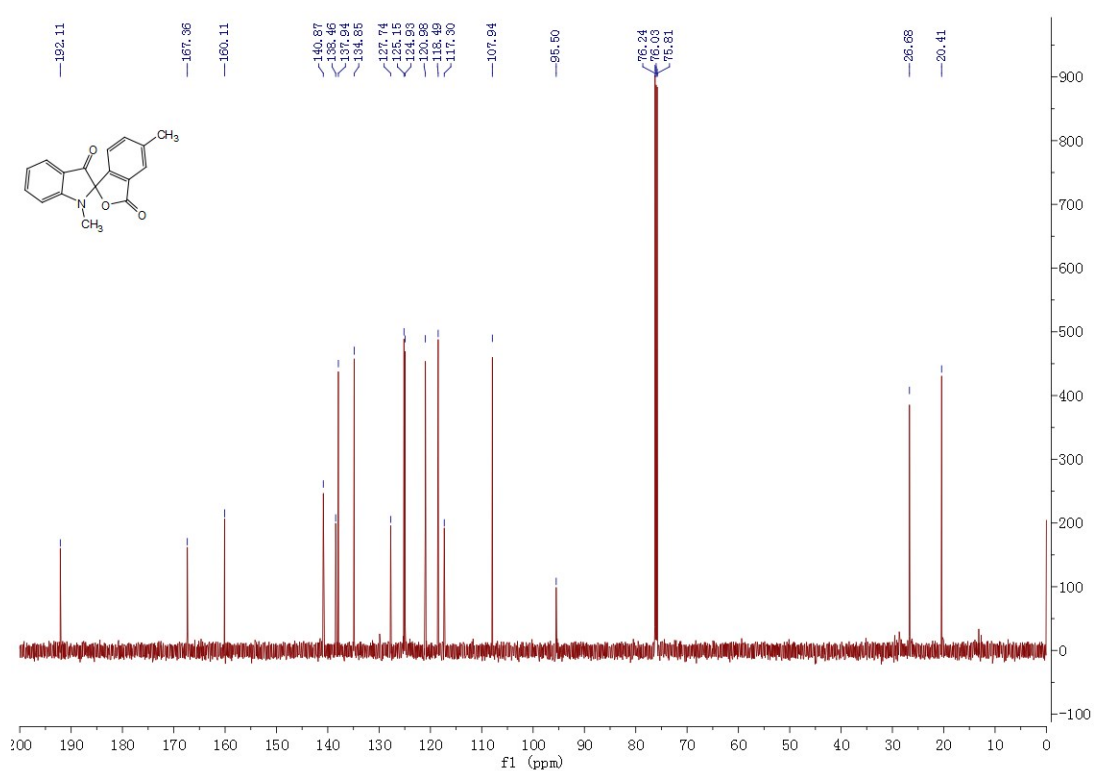
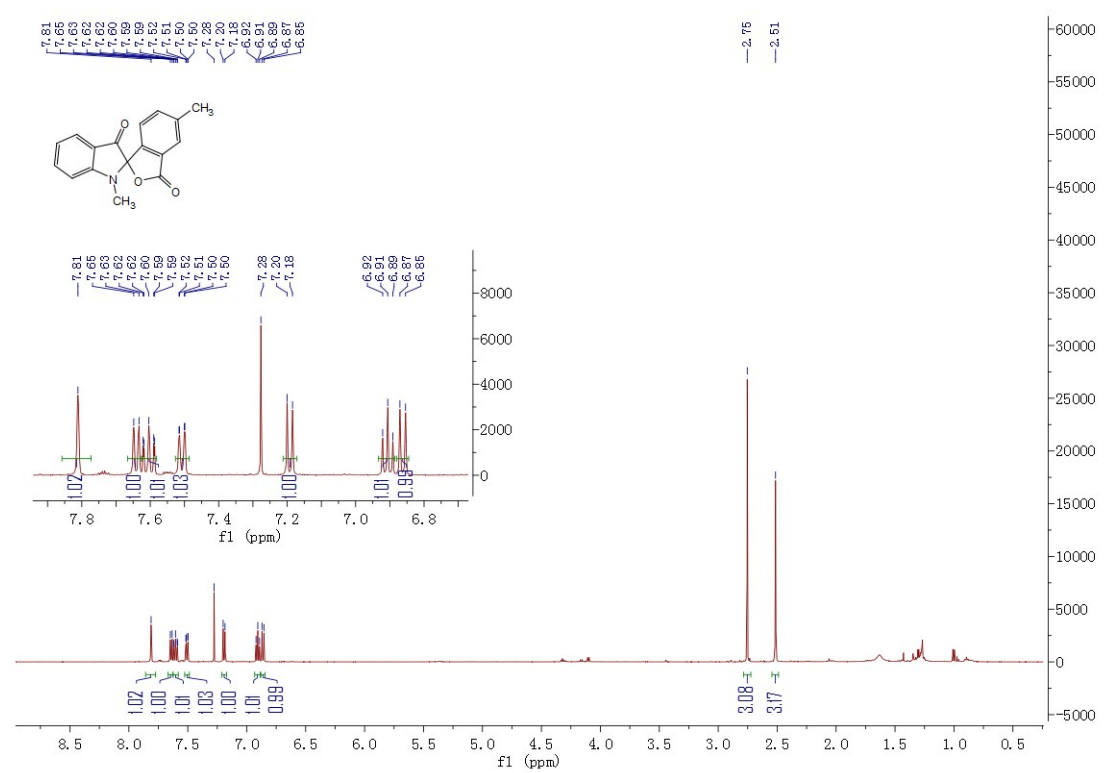
5-chloro-6'-methoxy-1-methyl-3'H-spiro[indoline-3,1'-isobenzofuran]-2,3'-dione (7o)



5,6'-dichloro-1-methyl-3'H-spiro[indoline-3,1'-isobenzofuran]-2,3'-dione (7p)

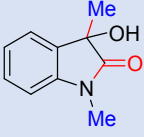
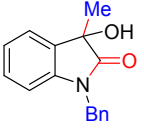
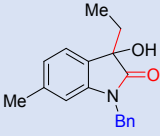
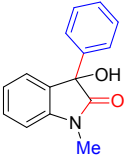
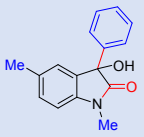
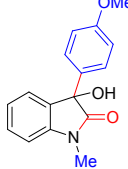
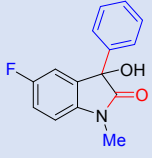
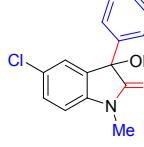
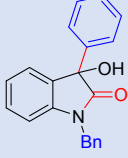


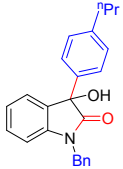
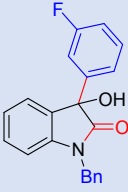
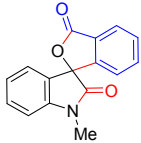
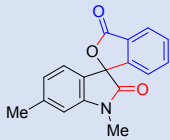
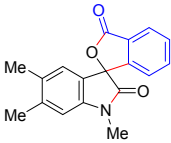
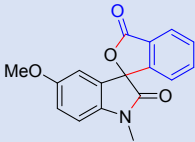
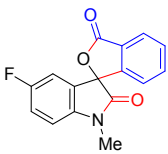
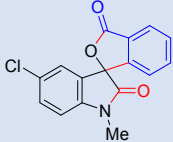
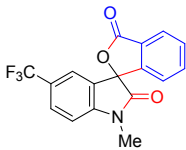
2-hydroxy-1-methyl-2-phenylindolin-3-one (9)

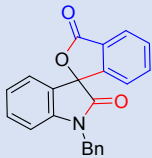
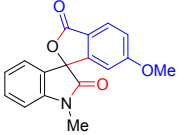
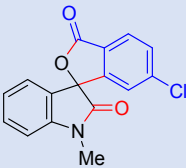
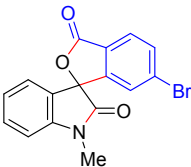
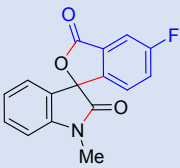
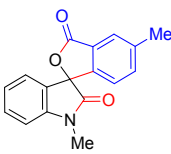
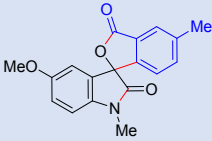
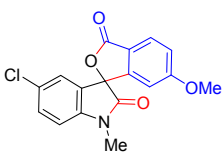
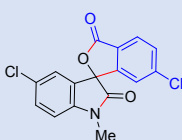


Ref. Scheme: New/Known ¹HNMR ¹³CNMR LRMS HRMS IR Mp:

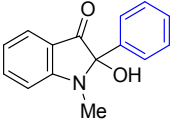
No.:

1a		Known	✓				✓
1b		Known	✓				✓
1c		new	✓	✓		✓	✓
1d		Known	✓				✓
1e		Known	✓				✓
1f		Known	✓				✓
1g		Known	✓				✓
1h		Known	✓				✓
1i		Known	✓				✓

1j		New	✓	✓		✓
1k		Known	✓	✓	✓	✓
7a		New	✓	✓	✓	✓
7b		New	✓	✓	✓	✓
7c		New	✓	✓	✓	✓
7d		New	✓	✓	✓	✓
7e		New	✓	✓	✓	✓
7f		New	✓	✓	✓	✓
7g		New	✓	✓	✓	✓

7h		New	✓	✓	✓	✓
7i		New	✓	✓	✓	✓
7j		New	✓	✓	✓	✓
7k		New	✓	✓	✓	✓
7l		New	✓	✓	✓	✓
7m		New	✓	✓	✓	✓
7n		New	✓	✓	✓	✓
7o		New	✓	✓	✓	✓
7p		New	✓	✓	✓	✓

9		known	✓	✓	✓	✓
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known

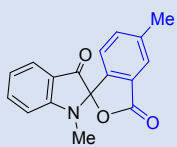
✓

✓

✓

✓

10



New

✓

✓

✓

✓