Supplementary Information

Metal-free Synthesis of 2,2-disubstituted Indolin-3-ones

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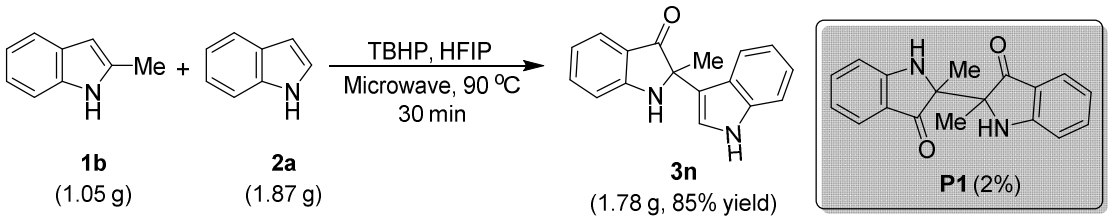
Table of Contents

1. General information

Commercially available reagents and solvents were used without any purification. 1-methyl-1*H*-indole **2b**,[1] 1-methyl-5-carbonitrile-1*H*-indole **2c**,[1] 1-isopropyl-1*H*-indole **2d**,[2] 1-phenyl-1*H*-indole **2e**,[3] 1-benzyl-1*H*-indole **2f**,[4] 1-methyl-2-phenyl-1*H*-indole **1c**,[1] 1-ethyl-2-phenyl-1*H*-indole **1d**[2] and 1-(2-Phenyl-1*H*-indol-1-yl)ethanone **1e**[5] were synthesized according to the literature procedure. Melting points were determined using a Büchi B-540 capillary melting point apparatus. NMR spectra were recorded using Varian Mercury Plus 400 MHz, Bruker Avance III 500MHz or Bruker Avance III 600 MHz spectrometers. Chemical shifts of ^{1}H-NMR were reported relative to the solvent signal ($CDCl_3$: δ = 7.26 ppm; DMSO-d_6: δ =2.50 ppm). Chemical shifts of ^{13}C NMR were reported relative to the solvent signal ($CDCl_3$: δ = 77.00 ppm; DMSO-d_6: δ = 39.50 ppm). HRMS spectra were recorded on an electrospray ionization quadrupole time-of-flight (ESI-Q-TOF) mass spectrometer. Column chromatography was performed on silica gel (300-400 mesh). The synthesis was carried out in CEM Discover 908010 microwave reactor with IR-monitored temperature control.

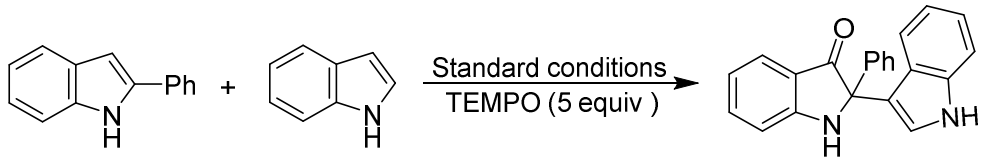
2. Procedure for gram-scale reaction



TBHP (6.4 mL, 70% aqueous, 48 mmol) and HFIP (16.0 mL) were added to a microwave tube (80 mL). After stirring well, 2-methylindole **1b** (1.049 g, 8 mmol) and indole **2a** (1.874 g, 16 mmol) were added in sequence. The resultant reaction mixture was subjected to microwave irradiation at 90 °C for 30 min (150 W of initial power). After the reaction mixture cooled to room temperature, it was quenched with saturated $NaHCO_3$ solution (40 ml) and extracted with ethyl acetate (80 ml x 3). The combined organic phase was washed with water and brine, dried over Na_2SO_4, filtered, and then concentrated in vacuum. Chromatography on silica gel with hexane/ethyl acetate (20:1 to 10:1) to give **3n** as a yellow solid (1.784 g, 85% yield) and **P1** was isolated as a yellow solid (38 mg, 2%). **P1** might formed by dimerization of intermediate B.

3. Procedure for control experiments

a) Radica inhibiting experiment

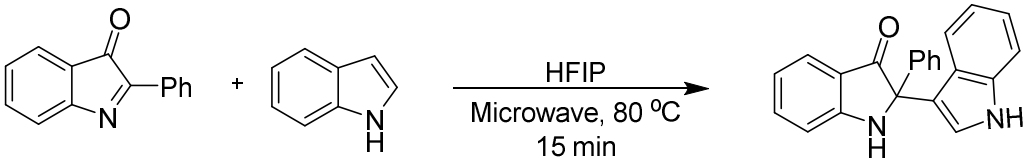


1a **2a** **3a**

TBHP (0.4 mL, 70% aqueous, 3.0 mmol) and HFIP (1.0 mL) were added to a microwave tube (10 mL). After stirring well, TEMPO (391mg, 2.5 mmol), 2-phenylindole **1a** (97 mg, 0.5 mmol) and indole **2a** (117 mg, 1.0 mmol) were added in sequence. The resultant reaction mixture was subjected to microwave irradiation at 90 °C for 30 min (150 W of initial power). After the reaction mixture cooled to room temperature, it was quenched with saturated $NaHCO_3$ solution (5 ml) and extracted with ethyl acetate (15 ml x 3). The combined organic phase was washed with water and brine, dried over Na_2SO_4, filtered, and then concentrated in vacuum. Chromatography on silica gel with hexane/ethyl acetate (20:1 to 10:1) to give product **3a** as a yellow solid (46 mg, 28% yield).

b) Intermediate experiments

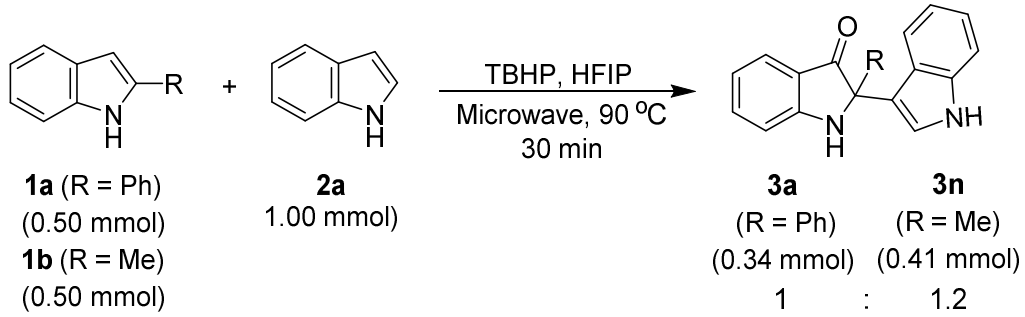
Product 4 was synthesized following literature reported method.[6] Compound 4 was isolated as a red solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, J = 6.9 Hz, 2H), 7.64-7.46 (m, 5H), 7.42 (d, J = 7.2 Hz, 1H), 7.30-7.23 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.5, 161.1, 159.7, 136.7, 132.1, 129.9, 129.2, 128.8, 128.3, 124.6, 123.1, 121.9. ESI-MS *m/z* 208.1 $[M+H]^+$. The spectroscopic data of 4 were compared with the reported values.[7]



4a **2a** **3a**
98%

HFIP (1.0 mL) was added to the microwave tube (10 mL). Next, 2-phenyl-3*H*-indol-3-one **4** (104 mg, 0.5 mmol) and indole **2a** (117 mg, 1.0 mmol) were added in sequence. The resultant reaction mixture was subjected to microwave irradiation at 80 °C for 15 min (150 W of initial power). After the reaction mixture cooled to room temperature, it was quenched with saturated $NaHCO_3$ solution (5 ml) and extracted with ethyl acetate (15 ml x 3). The combined organic phase was washed with water and brine, dried over Na_2SO_4, filtered, and then concentrated in vacuum. Chromatography on silica gel with hexane/ethyl acetate (20:1 to 10:1) to give product **3a** as a yellow solid (159 mg, 98%).

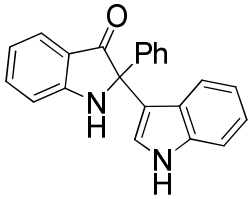
c) Intermolecular competition experiment



TBHP (0.4 mL, 70% aqueous, 3.0 mmol) and HFIP (1.0 mL) were added to a microwave tube (10 mL). After stirring well, 2-methylindole **1b** (66 mg, 0.5 mmol), 2-phenylindole **1a** (97 mg, 0.5 mmol) and indole **2a** (117 mg, 1.0 mmol) were added in sequence. The resultant reaction mixture was subjected to microwave irradiation at 90 °C for 30 min (150 W of initial power). After the reaction mixture cooled to room temperature, it was quenched with saturated $NaHCO_3$ solution (5 ml) and extracted with ethyl acetate (15 ml x 3). The combined organic phase was washed with water and brine, dried over Na_2SO_4, filtered, and then concentrated in vacuum. Chromatography on silica gel with hexane/ethyl acetate (20:1 to 10:1) to give **3a** (109 mg, 0.34 mmol) and **3n** (108 mg, 0.41 mmol).

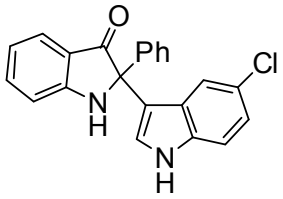
4. Characterization of products

2-(1*H*-indol-3-yl)-2-phenylindolin-3-one (3a)



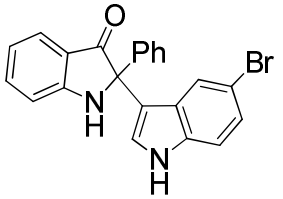
Compound **3a** was isolated as a yellow solid (136 mg, 84%). M.p. 214-216 ˚C (CH_2Cl_2/*n*-hexane); ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.08 (bs, 1H), 8.34 (bs, 1H), 7.55-7.43 (m, 4H), 7.39 (d, J = 8.2 Hz, 1H), 7.35-7.25 (m, 3H), 7.10 (d, J = 8.0 Hz, 1H), 7.08-7.03 (m, 2H), 6.99 (d, J = 8.3 Hz, 1H), 6.88-6.82 (m, 1H), 6.74 (t, J = 7.4 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 200.3, 160.9, 140.0, 137.7, 136.9, 128.1, 127.4, 126.6, 125.5, 124.6, 124.1, 121.3, 120.0, 118.6, 117.5, 117.4, 114.5, 111.9, 111.7, 70.6; IR (KBr): ν (cm^{-1}) = 3423, 3303, 2924, 1660, 1616, 1492, 1333, 1153, 1116, 1053, 890, 746, 688; HRMS (ESI) *m/z*: calcd for $C_{22}H_{16}N_2ONa$ $[M+Na]^+$ 347.1155, found 347.1149.

2-(5-chloro-1*H*-indol-3-yl)-2-phenylindolin-3-one (3b)



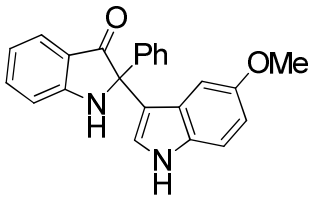
Compound **3b** was isolated as a yellow solid (151 mg, 84%). M.p. 120-122 ˚C (CH_2Cl_2/*n*-hexane); ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.32 (bs, 1H), 8.44 (bs, 1H), 7.55-7.50 (m, 1H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.44-7.37 (m, 3H), 7.35-7.27 (m, 3H), 7.22 (d, *J* = 2.5 Hz, 1H), 7.12 (d, *J* = 1.7 Hz, 1H), 7.07 (dd, *J* = 8.6, 2.0 Hz, 1H), 6.99 (d, *J* = 8.3 Hz, 1H), 6.75 (t, *J* = 7.4 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 200.0, 160.9, 139.8, 137.9, 135.4, 128.3, 127.5, 126.6, 126.5, 125.7, 124.7, 123.2, 121.3, 119.2, 117.6, 117.2, 114.1, 113.3, 111.9, 70.4; IR(KBr): ν (cm^{-1}) = 3395, 3296, 2923, 1692, 1615, 1483, 1466, 1323, 1151, 1114, 1061, 912, 895, 808, 751, 703, 641; HRMS (ESI) *m/z*: calcd For $C_{22}H_{16}ClN_2O$ $[M+H]^+$ 359.0946, found 359.0963.

2-(5-bromo-1*H*-indol-3-yl)-2-phenylindolin-3-one (3c)



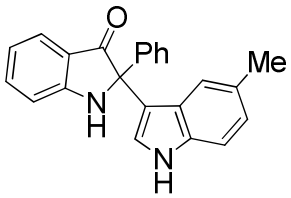
Compound **3c** was isolated as a yellow solid (155 mg, 77%). M.p. 130-132 ˚C (CH_2Cl_2/*n*-hexane); ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.34 (bs, 1H), 8.46 (bs, 1H), 7.55-7.48 (m, 2H), 7.44-7.36 (m, 3H), 7.36 -7.26 (m, 4H), 7.23 (d, *J* = 2.4 Hz, 1H), 7.22-7.17 (m, 1H), 7.01 (d, *J* = 8.3 Hz, 1H), 6.75 (t, *J* = 7.4 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 200.0, 160.9, 139.8, 137.9, 135.6, 128.3, 127.5, 127.3, 126.5, 125.6, 124.7, 123.9, 122.2, 117.7, 117.2, 114.0, 113.8, 111.9, 111.4, 70.4; IR (KBr): ν (cm^{-1}) = 3416, 3280, 1690, 1616, 1483, 1385, 1241, 1150, 999, 887, 800, 751, 701, 640; HRMS (ESI) *m/z*: calcd For $C_{22}H_{16}BrN_2O$ $[M+H]^+$ 403.0441, found 403.0436.

2-(5-methoxy-1*H*-indol-3-yl)-2-phenylindolin-3-one (3d)



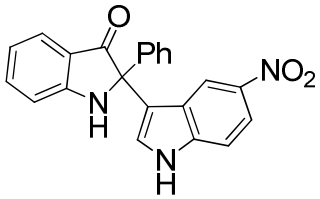
Compound **3d** was isolated as a yellow solid (133 mg, 75%). M.p. 92-94 ˚C (CH_2Cl_2/*n*-hexane); ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.93 (bs, 1H), 8.35 (bs, 1H), 7.56-7.45 (m, 4H), 7.38-7.31 (m, 2H), 7.31-7.25 (m, 2H), 7.02 (d, *J* = 2.3 Hz, 1H), 7.00 (d, *J* = 8.3 Hz, 1H), 6.74 (t, *J* = 7.6 Hz, 2H), 6.59-6.55 (m, 1H), 3.52 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 200.3, 160.9, 152.8, 139.9, 137.7, 132.0, 128.1, 127.3, 126.6, 125.9, 124.7, 124.6, 117.5, 117.5, 114.2, 112.3, 111.9, 110.9, 102.5, 70.6, 55.1; IR (KBr): ν (cm^{-1}) = 3450, 1696, 1619, 1485, 1218, 1110, 993, 799, 755, 700, 620; HRMS (ESI) *m/z*: calcd for $C_{23}H_{19}N_2O_2$ $[M+H]^+$ 355.1441, found: 355.1445.

2-(5-methyl-1*H*-indol-3-yl)-2-phenylindolin-3-one (3e)



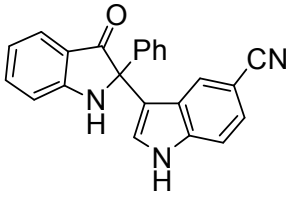
Compound **3e** was isolated as a yellow solid (107 mg, 63%). M.p. 197-198 ˚C (CH_2Cl_2/*n*-hexane); ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.94 (bs, 1H), 8.28 (bs, 1H), 7.53-7.49 (m, 1H), 7.47 (d, *J* = 7.7 Hz, 1H), 7.45-7.40 (m, 2H), 7.35-7.23 (m, 4H), 7.02 (d, *J* = 2.6 Hz, 1H), 6.98 (d, *J* = 8.3 Hz, 1H), 6.92-6.84 (m, 2H), 6.76-6.72 (m, 1H), 2.21 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 200.2, 160.9, 140.1, 137.6, 135.3, 128.1, 127.3, 126.9, 126.5, 125.7, 124.6, 124.0, 122.9, 119.5, 117.4, 117.3, 113.7, 112.0, 111.4, 70.7, 21.4; IR (KBr): ν (cm^{-1}) = 3379, 3329, 2920, 1691, 1615, 1487, 1326, 1150, 1113, 890, 797, 754, 640; HRMS (ESI) *m/z*: calcd for $C_{23}H_{19}N_2O$ $[M+H]^+$ 339.1492, found: 339.1498.

[8]**2-(5-nitro-1*H*-indol-3-yl)-2-phenylindolin-3-one (3f)**



Compound **3f** was isolated as a yellow solid (37 mg, 20%). M.p. 252-254 ˚C (CH_2Cl_2/*n*-hexane); ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.86 (bs, 1H), 8.56 (bs, 1H), 8.14 (d, *J* = 2.1 Hz, 1H), 7.97 (dd, *J* = 9.0, 2.2 Hz, 1H), 7.58-7.52 (m, 2H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.43 (d, *J* = 2.5 Hz, 1H), 7.40 (d, *J* = 7.2 Hz, 2H), 7.37–7.28 (m, 3H), 6.99 (d, *J* = 8.3 Hz, 1H), 6.77 (t, *J* = 7.3 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 199.8, 160.1, 140.3, 140.1, 139.6, 138.0, 128.4, 127.8, 127.7, 126.5, 124.8, 124.7, 117.9, 117.3, 117.08, 117.05, 116.8, 112.4, 112.0, 70.2 ; IR (KBr): ν (cm^{-1}) = 3414, 3313, 2926, 1676, 1623, 1467, 1325, 1230, 1135, 1107, 1086, 1063, 996, 888, 738, 702, 639; HRMS (ESI) *m/z*: calcd for $C_{22}H_{16}N_3O_3$ $[M+H]^+$ 370.1186, found: 370.1197. The NMR data were consistent with those in a literature report.[8]

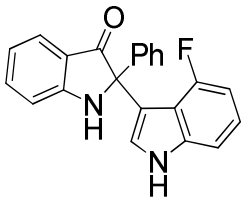
[8]**1-methyl-3-(3-oxo-2-phenylindolin-2-yl)-1*H*-indole-5-carbonitrile (3g)**



Compound **3g** was isolated as a yellow solid (51 mg, 29%). M.p. 201-203 ˚C (CH_2Cl_2/*n*-hexane); ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.72 (s, 1H), 8.52 (s, 1H), 7.62-7.56 (m, 2H), 7.56-7.52 (m, 1H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.46-7.40 (m, 2H), 7.40-7.36 (m, 2H), 7.36-7.28 (m, 3H), 7.00 (d, *J* = 8.3 Hz, 1H), 6.77 (t, *J* = 7.4 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 199.7, 160.9, 139.6,

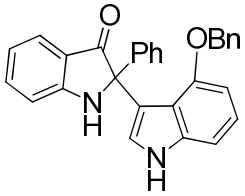
138.7, 138.0, 128.4, 127.7, 126.5, 126.4, 125.6, 125.3, 124.8, 124.0, 120.6, 117.8, 117.0, 115.2, 113.2, 111.9, 100.7, 70.2; IR (KBr): ν (cm^{-1}) = 3349, 3268, 2925, 2224, 1681, 1619, 1493, 1467, 1329, 1149, 1106, 1075, 1001, 886, 811, 745, 700; HRMS (ESI) *m/z*: calcd for $C_{23}H_{16}N_3O$ $[M+H]^+$ 350.1288, found: 350.1283. The NMR data were consistent with those in a literature report.[8]

2-(4-fluoro-1*H*-indol-3-yl)-2-phenylindolin-3-one (3h)



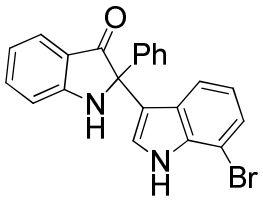
Compound **3h** was isolated as a yellow solid (82 mg, 48%). M.p. 223-225 ˚C (CH_2Cl_2/*n*-hexane); ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.43 (bs, 1H), 7.91 (bs, 1H), 7.52-7.47 (m, 2H), 7.39 (d, *J* = 7.6 Hz, 2H), 7.30-7.25 (m, 3H), 7.25-7.21 (m, 1H), 7.13-7.04 (m, 3H), 6.75 (t, *J* = 7.4 Hz, 1H), 6.66 (dd, *J* = 10.9, 7.9 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 199.7, 160.9, 155.37 (d, *J* = 245.7 Hz), 140.6, 139.94 (d, *J* = 11.6 Hz) , 137.5, 128.0, 127.1, 126.2, 124.8, 124.6, 122.29 (d, *J* = 7.5 Hz), 117.6, 117.4 , 114.24 (d, *J* = 20.8 Hz), 112.6, 112.54 (d, *J* = 3.4 Hz), 108.21 (d, *J* = 3.4 Hz), 104.05 (d, *J* = 19.5 Hz), 70.5; ^{19}F NMR (565 MHz, DMSO-d_6) δ -116.7; IR (KBr): ν (cm^{-1}) = 3446, 3056, 2363, 1686, 1619, 1487, 1326, 1223, 1146, 997, 847, 739, 700, 621; HRMS (ESI) *m/z*: calcd for $C_{22}H_{16}FN_2O$ $[M+H]^+$ 343.1241, found 343.1234.

2-(4-(benzyloxy)-1*H*-indol-3-yl)-2-phenylindolin-3-one (3i)



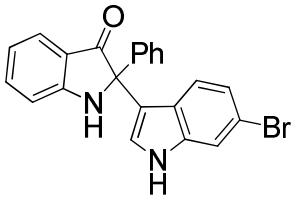
Compound **3i** was isolated as a yellow solid (124 mg, 57%). M.p. 206-208 ˚C (CH_2Cl_2/*n*-hexane); ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.12 (bs, 1H), 7.52-7.41 (m, 3H), 7.32-7.27 (m, 3H), 7.19-7.10 (m, 5H), 7.10-7.07 (m, 2H), 7.06 (d, *J* = 2.5 Hz, 1H), 7.03-6.96 (m, 2H), 6.94 (t, *J* = 7.9 Hz, 1H), 6.70 (t, *J* = 7.4 Hz, 1H), 6.40 (d, *J* = 7.6 Hz, 1H), 5.05 (d, *J* = 12.1 Hz, 1H), 4.85 (d, *J* = 12.1 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 199.2, 160.0, 151.3, 141.2, 138.9, 137.3, 136.8, 128.1, 128.0, 127.8, 127.6, 126.6, 126.2, 124.6, 123.0, 122.4, 117.5, 117.3, 115.9, 112.9, 112.0, 105.0, 100.5, 70.7, 68.8; IR (KBr): ν (cm^{-1}) = 3416, 3313, 3050, 2923, 1678, 1620, 1493, 1463, 1358, 1329, 1237, 1152, 1071, 915, 783, 756, 741, 697; HRMS (ESI) *m/z*: calcd for $C_{29}H_{23}N_2O_2$ $[M+H]^+$ 431.1754, found: 431.1745.

2-(7-bromo-1*H*-indol-3-yl)-2-phenylindolin-3-one (3j)



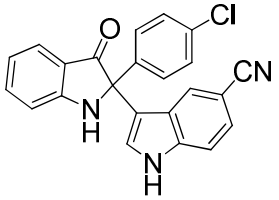
Compound **3j** was isolated as a yellow solid (126 mg, 62%). M.p. 158-159 ˚C (CH_2Cl_2/*n*-hexane); ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.34 (bs, 1H), 8.40 (bs, 1H), 7.55-7.50 (m, 1H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.45-7.38 (m, 2H), 7.36-7.25 (m, 4H), 7.13-7.06 (m, 2H), 6.98 (d, *J* = 8.3 Hz, 1H), 6.83 (t, *J* = 7.8 Hz, 1H), 6.75 (t, *J* = 7.4 Hz, 1H); ^{13}C NMR (151 MHz, DMSO) δ 200.0, 160.9, 139.7, 137.9, 135.1, 128.2, 127.5, 127.2, 126.5, 125.2, 124.7, 124.0, 120.2, 119.6, 117.7, 117.2, 115.9, 111.9, 104.4, 70.5; IR (KBr): ν (cm^{-1}) = 3408, 2923, 2362, 1686, 1616, 1488, 1466, 1323, 1148, 1000, 881, 780, 752, 620; HRMS (ESI) *m/z*: calcd For $C_{22}H_{16}BrN_2O$ $[M+H]^+$ 403.0441, found 403.0429.

2-(6-bromo-1*H*-indol-3-yl)-2-phenylindolin-3-one (3k)



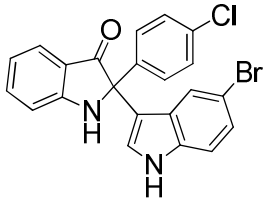
Compound **3k** was isolated as a yellow solid (155 mg, 77%). M.p. 137-139 ˚C (CH_2Cl_2/*n*-hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (bs, 1H), 7.67 (d, J = 7.7 Hz, 1H), 7.57-7.44 (m, 4H), 7.37-7.26 (m, 3H), 7.10 (d, J = 2.5 Hz, 1H), 7.07-7.01 (m, 1H), 7.01-6.85 (m, 3H), 5.32 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.7, 160.4, 139.2, 137.75, 137.71, 128.5, 127.9, 126.7, 125.6, 124.5, 124.4, 123.3, 121.1, 119.8, 119.4, 116.0, 115.8, 114.6, 112.8, 71.1; IR (KBr): ν (cm^{-1}) = 3404, 2958, 1685, 1617, 1487, 1466, 1326, 1150, 1052, 886, 803, 752, 697; HRMS (ESI) *m/z*: calcd For $C_{22}H_{16}BrN_2O$ $[M+H]^+$ 403.0441, found 403.0431.

3-(2-(4-chlorophenyl)-3-oxoindolin-2-yl)-1*H*-indole-5-carbonitrile (3l)



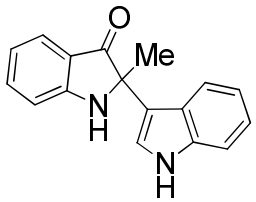
Compound **3l** was isolated as a yellow solid (80 mg, 42%). M.p. 143-145 ˚C (CH_2Cl_2/*n*-hexane); ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.75 (bs, 1H), 8.55 (bs, 1H), 7.60-7.53 (m, 3H), 7.51 (d, *J* = 7.7 Hz, 1H), 7.46-7.43 (m, 1H), 7.43-7.36 (m, 5H), 7.00 (d, *J* = 8.3 Hz, 1H), 6.78 (t, *J* = 7.4 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 199.4, 160.9, 138.8, 138.6, 138.2, 132.5, 128.4, 128.3, 126.7, 125.4, 125.1, 124.8, 124.2, 120.5, 118.1, 116.9, 114.8, 113.3, 112.0, 100.9, 69.7; IR (KBr): ν (cm^{-1}) = 3415, 2923, 2426, 2222, 1684, 1618, 1488, 1468, 1385, 1351, 1326, 1147, 1014, 892, 755, 620; HRMS (ESI) *m/z*: calcd for $C_{23}H_{15}ClN_3O$ $[M+H]^+$ 384.0898, found: 384.0890.

2-(5-bromo-1*H*-indol-3-yl)-2-(4-chlorophenyl)indolin-3-one (3m)



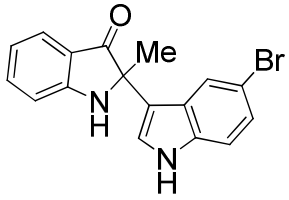
Compound **3m** was isolated as a yellow solid (125 mg, 58%). M.p. 187-189 ˚C (CH_2Cl_2/*n*-hexane); ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.37 (bs, 1H), 8.47 (bs, 1H), 7.56-7.52 (m, 1H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.44-7.38 (m, 4H), 7.37 (d, *J* = 8.6 Hz, 1H), 7.29-7.24 (m, 1H), 7.22-7.17 (m, 2H), 6.99 (d, *J* = 8.3 Hz, 1H), 6.77 (t, *J* = 7.4 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 199.6, 160.9, 138.8, 138.0, 135.6, 132.3, 128.4, 128.3, 127.1, 125.7, 124.7, 124.0, 122.0, 117.9, 117.0, 113.9, 113.6, 112.0, 111.5, 69.9; IR (KBr): ν (cm^{-1}) = 3408, 2922, 1683, 1616, 1487, 1465, 1325, 1241, 1151, 1092, 1055, 1013, 885, 799, 751, 704; HRMS (ESI) *m/z*: calcd for $C_{22}H_{15}BrClN_2O$ $[M+H]^+$ 437.0051, found: 437.0050.

2-(1*H*-indol-3-yl)-2-methylindolin-3-one (3n)



Compound **3n** was isolated as a yellow solid (124 mg, 94%). M.p. 210-212 ˚C (CH_2Cl_2/*n*-hexane); ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.06 (bs, 1H), 7.76 (bs, 1H), 7.54-7.50 (m, 1H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.41 (d, *J* = 2.5 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 1H), 7.08-7.01 (m, 1H), 6.94 (d, *J* = 8.3 Hz, 1H), 6.88-6.81 (m, 1H), 6.74 (t, *J* = 7.3 Hz, 1H), 1.67 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 203.3, 160.6, 137.5, 136.8, 124.9, 124.4, 123.5, 121.1, 119.6, 118.6, 117.9, 117.1, 114.5, 112.0, 111.6, 65.1, 23.3; IR (KBr): ν (cm^{-1}) = 3407, 3275, 2424, 1652, 1620, 1500, 1385, 1336, 1122, 997, 882, 757, 737, 696, 641, 620; HRMS (ESI) *m/z*: calcd for $C_{17}H_{14}N_2ONa$ $[M+Na]^+$ 285.0998, found: 285.0993.

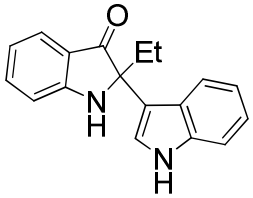
2-(5-bromo-1*H*-indol-3-yl)-2-methylindolin-3-one (3o)



Compound **3o** was isolated as a yellow solid (161 mg, 94%). M.p. 224-226 ˚C (CH_2Cl_2/*n*-hexane); ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.30 (bs, 1H), 7.82 (bs, 1H), 7.56-7.52 (m, 1H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.49 (d, *J* = 2.6 Hz, 1H), 7.41 (d, *J* = 1.9 Hz, 1H), 7.36 (d, *J* = 8.6 Hz, 1H), 7.18 (dd, *J* = 8.6, 1.9 Hz, 1H), 6.97 (d, *J* = 8.3 Hz, 1H), 6.79-6.71 (m, 1H), 1.67 (s, 3H); ^{13}C NMR (150

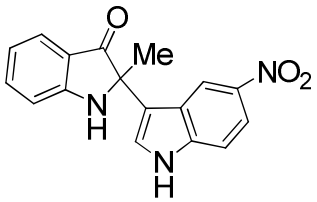
MHz, DMSO-d_6) δ 203.0, 160.6, 137.7, 135.5, 126.6, 125.0, 124.5, 123.6, 122.0, 117.7, 117.4, 114.4, 113.7, 112.0, 111.3, 65.0, 23.5; IR (KBr): ν (cm^{-1}) = 3416, 3281, 2421, 1652, 1619, 1499, 1460, 1333, 1294, 1143, 999, 884, 797, 756, 715; HRMS (ESI) *m/z*: calcd for $C_{17}H_{14}BrN_2O$ $[M+H]^+$ 341.0284, found: 341.0267.

2-ethyl-2-(1*H*-indol-3-yl)indolin-3-one (3p)



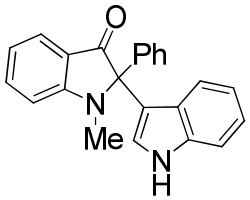
Compound **3p** was isolated as a yellow solid (117 mg, 84%). M.p. 234-236 ˚C (CH_2Cl_2/*n*-hexane); ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.02 (bs, 1H), 7.77 (bs, 1H), 7.50-7.46 (m, 1H), 7.42 (dd, *J* = 16.0, 7.9 Hz, 2H), 7.38-7.30 (m, 2H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 8.3 Hz, 1H), 6.87 (t, *J* = 7.5 Hz, 1H), 6.69 (t, *J* = 7.3 Hz, 1H), 2.21 (dq, *J* = 14.6, 7.3 Hz, 1H), 2.10 (dq, *J* = 14.2, 7.1 Hz, 1H), 0.79 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 202.8, 161.4, 137.4, 136.8, 125.0, 124.0, 123.2, 121.1, 120.2, 118.9, 118.5, 116.9, 113.6, 111.7, 111.6, 69.2, 29.4, 8.1; IR (KBr): ν (cm^{-1}) = 3361, 2973, 2935, 1665, 1613, 1488, 1459, 1325, 1247,1154, 1132, 1099, 1048, 1002, 881, 780, 748, 714; HRMS (ESI) *m/z*: calcd For $C_{18}H_{17}N_2O$ $[M+H]^+$ 277.1335, found 277.1340.

[8]2-methyl-2-(5-nitro-1*H*-indol-3-yl)indolin-3-one (3q)



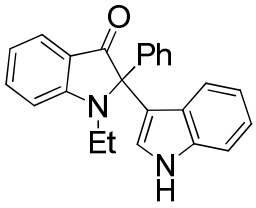
Compound **3q** was isolated as a yellow solid (82 mg, 53%). M.p. 196-198 ˚C (CH_2Cl_2/*n*-hexane); ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.83 (bs, 1H), 8.32 (bs, 1H), 8.00-7.94 (m, 1H), 7.92 (s, 1H), 7.72-7.66 (m,, 1H), 7.60-7.52 (m, 2H), 7.49 (d, *J* = 7.7 Hz, 1H), 6.99 (d, *J* = 8.3 Hz, 1H), 6.78 (t, *J* = 7.4 Hz, 1H), 1.69 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 202.6, 160.7, 140.3, 140.0, 137.9, 127.2, 124.6, 124.0, 117.6, 117.54, 117.48, 116.9, 116.6, 112.2, 112.1, 65.0, 23.6 ; IR (KBr): ν (cm^{-1}) = 3387, 2935, 2405, 1688, 1612, 1518, 1486, 1468, 1326, 1289, 1244, 1154, 1101, 1076, 964, 793, 760, 739, 713, 675; HRMS (ESI) *m/z*: calcd for $C_{17}H_{14}N_3O_3$ $[M+H]^+$ 308.1030, found: 308.1036. The NMR data were consistent with those in a literature report.[8]

2-(1*H*-indol-3-yl)-1-methyl-2-phenylindolin-3-one (3r)



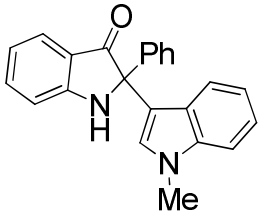
Compound **3r** was isolated as a yellow solid (88 mg, 52%). M.p. 216-220 ˚C (CH_2Cl_2/*n*-hexane); ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.24 (bs, 1H), 7.65-7.58 (m, 1H), 7.50 (d, *J* = 7.5 Hz, 1H), 7.42-7.35 (m, 6H), 7.08 (d, *J* = 2.5 Hz, 1H), 7.07-7.04 (m, 2H), 6.83 – 6.79 (m, 1H), 6.79-6.75 (m, 2H), 2.83 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 199.9, 160.1, 138.3, 137.5, 136.7, 128.5, 127.9, 127.3, 126.5, 125.5, 124.6, 121.3, 119.8, 119.0, 117.6, 117.1, 112.0, 111.7, 108.8, 75.6, 29.2; IR (KBr): ν (cm^{-1}) = 3223, 1671, 1620, 1493, 1467, 1380, 1243, 1197, 1111, 977, 915, 872, 741, 702, 637; HRMS (ESI) *m/z*: calcd for $C_{23}H_{19}N_2O$ $[M+H]^+$ 339.1492, found: 339.1495.

2-(1*H*-indol-3-yl)-1-ethyl-2-phenylindolin-3-one (3s)



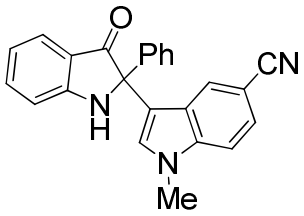
Compound **3s** was isolated as a yellow solid (63 mg, 36%). M.p. 210-212 ˚C (CH_2Cl_2/*n*-hexane); ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.22 (s, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.39 (d, *J* = 8.2 Hz, 1H), 7.38-7.30 (m, 5H), 7.08 (d, *J* = 2.5 Hz, 1H), 7.07-7.03 (m, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 6.85-6.78 (m, 2H), 6.74 (t, *J* = 7.4 Hz, 1H), 3.61 (dq, *J* = 13.9, 6.8 Hz, 1H), 3.41 (dq, *J* = 14.4, 7.0 Hz, 1H), 0.43 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 199.8, 158.7, 138.04, 138.02, 136.6, 128.4, 127.9, 127.6, 126.3, 125.6, 124.8, 121.3, 120.0, 118.8, 117.5, 116.7, 112.1, 111.9, 108.9, 75.7, 37.5, 12.6; IR (KBr): ν (cm^{-1}) = 3241, 1673, 1618, 1498, 1470, 1326, 1313, 1164, 1124, 929, 747, 738, 701, 634; HRMS (ESI) *m/z*: calcd for $C_{24}H_{21}N_2O$ $[M+H]^+$ 353.1648, found: 353.1640.

2-(1-methyl-1*H*-indol-3-yl)-2-phenylindolin-3-one (3t)



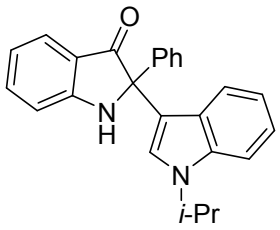
Compound **3t** was isolated as a yellow solid (98 mg, 58%). M.p. 206-208 ˚C (CH_2Cl_2/*n*-hexane); ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.35 (s, 1H), 7.55-7.45 (m, 4H), 7.41 (d, *J* = 8.2 Hz, 1H), 7.35-7.25 (m, 3H), 7.16-7.06 (m, 3H), 6.99 (d, *J* = 8.3 Hz, 1H), 6.92-6.87 (m, 1H), 6.77-6.72 (m, 1H), 3.74 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 200.1, 160.9, 139.9, 137.7, 137.3, 128.3, 128.1, 127.4, 126.6, 125.8, 124.6, 121.4, 120.2, 118.7, 117.5, 117.3, 113.7, 112.0, 109.9, 70.5, 32.3; IR (KBr): ν (cm^{-1}) = 3420, 1696, 1612, 1484, 1470, 1446, 1326, 1153, 951, 923, 895, 880, 759, 738, 697; HRMS (ESI) *m/z*: calcd for $C_{23}H_{19}N_2O$ $[M+H]^+$ 339.1492, found: 339.1494.

1-methyl-3-(3-oxo-2-phenylindolin-2-yl)-1*H*-indole-5-carbonitrile (3u)



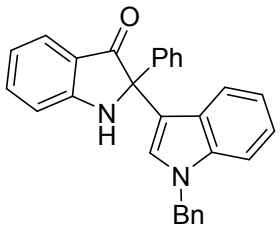
Compound **3u** was isolated as a yellow solid (83 mg, 45%). M.p. 244-246 ˚C (CH_2Cl_2/*n*-hexane); ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.52 (bs, 1H), 7.64 (d, *J* = 8.5 Hz, 1H), 7.58-7.52 (m, 2H), 7.52-7.47 (m, 2H), 7.43-7.40 (m, 1H), 7.39-7.26 (m, 5H), 6.99 (d, *J* = 8.3 Hz, 1H), 6.77 (t, *J* = 7.4 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 199.7, 161.0, 139.5, 139.0, 138.2, 130.8, 128.5, 127.8, 126.4, 125.7, 125.6, 124.8, 124.1, 120.6, 118.0, 117.0, 114.6, 112.0, 111.7, 100.9, 70.2, 32.8; IR (KBr): ν (cm^{-1}) = 3451, 2925, 2216, 1695, 1618, 1485, 1469, 1383, 1297, 1144, 992, 752, 702, 617; HRMS (ESI) *m/z*: calcd for $C_{24}H_{18}N_3O$ $[M+H]^+$ 364.1444, found: 364.1445.

2-(1-isopropyl-1*H*-indol-3-yl)-2-phenylindolin-3-one (3v)



Compound **3v** was isolated as a yellow solid (80 mg, 43%). M.p. 169-173 ˚C (CH_2Cl_2/*n*-hexane); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.35 (s, 1H), 7.56-7.45 (m, 3H), 7.44-7.38 (m, 2H), 7.36-7.23 (m, 3H), 7.16 (s, 1H), 7.13-7.06 (m, 2H), 6.98 (d, *J* = 8.2 Hz, 1H), 6.87 (t, *J* = 7.5 Hz, 1H), 6.74 (t, *J* = 7.4 Hz, 1H), 4.73 (p, *J* = 6.6 Hz, 1H), 1.43 (d, *J* = 6.6 Hz, 3H), 1.40 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 200.1, 160.9, 140.0, 137.8, 136.1, 128.2, 127.4, 126.5, 126.0, 124.7, 122.9, 121.4, 120.4, 118.8, 117.6, 117.2, 113.9, 112.0, 110.2, 70.6, 46.7, 22.34, 22.31; IR (KBr): ν (cm^{-1}) = 3356, 1690, 1619, 1465,1147, 998, 906, 742, 692; HRMS (ESI) *m/z*: calcd for $C_{25}H_{22}N_2ONa$ $[M+Na]^+$ 389.1624, found: 389.1637.

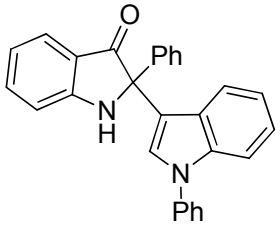
2-(1-benzyl-1*H*-indol-3-yl)-2-phenylindolin-3-one (3w)



Compound **3w** was isolated as a yellow solid (88 mg, 42%). M.p. 128-130 ˚C (CH_2Cl_2/*n*-hexane); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.38 (s, 1H), 7.57-7.37 (m, 5H), 7.36-7.20 (m, 7H), 7.20-7.14 (m, 2H), 7.13-7.03 (m, 2H), 6.98 (d, *J* = 8.4 Hz, 1H), 6.87 (t, *J* = 7.4 Hz, 1H), 6.75 (t, *J* = 7.4 Hz, 1H), 5.41 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 200.1, 160.9, 139.9, 138.1, 137.8, 136.7,

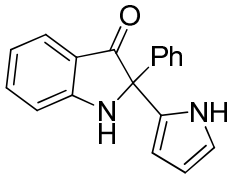
128.5, 128.2, 127.8, 127.4, 127.3, 127.0, 126.5, 126.1, 124.6, 121.6, 120.3, 118.9, 117.6, 117.2, 114.3, 112.0, 110.4, 70.5, 48.9; IR (KBr): ν (cm^{-1}) = 3385, 1686, 1617, 1466, 1324, 1149, 1047, 878, 743, 696; HRMS (ESI) *m/z*: calcd for $C_{29}H_{22}N_2ONa$ $[M+Na]^+$ 437.1624, found: 437.1635.

2-phenyl-2-(1-phenyl-1*H*-indol-3-yl)indolin-3-one (3x)



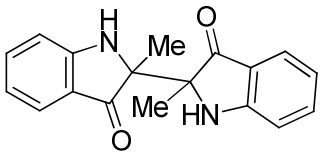
Compound **3x** was isolated as a yellow solid (149 mg, 74%). M.p. 125-128 ˚C (CH_2Cl_2/*n*-hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.6 Hz, 1H), 7.67-7.60 (m, 2H), 7.58-7.45 (m, 6H), 7.38-7.28 (m, 5H), 7.24-7.16 (m, 2H), 7.04 (t, *J* = 7.6 Hz, 1H), 6.98-6.86 (m, 2H), 5.42 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.3, 160.5, 139.3, 139.2, 137.6, 136.9, 129.6, 128.5, 127.8, 127.4, 126.9, 126.8, 126.7, 125.7, 124.4, 122.9, 120.6, 120.2, 119.7, 119.6, 116.4, 112.9, 111.1, 71.2. IR (KBr): ν (cm^{-1}) = 3384, 1686, 1618, 1596, 1142, 884, 847, 744, 697; HRMS (ESI) *m/z*: calcd for $C_{28}H_{20}N_2ONa$ $[M+Na]^+$ 423.1468, found: 423.1477

[9]2-phenyl-2-(1*H*-pyrrol-2-yl)indolin-3-one (3aa)



Compound **3aa** was isolated as a yellow solid (65 mg, 47%). M.p. 133-136 ˚C (CH_2Cl_2/*n*-hexane); 1H NMR (600 MHz, Chloroform-d) δ 8.83 (s, 1H), 7.63 (d, *J* = 7.7 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.31-7.20 (m, 5H), 6.92 (d, *J* = 8.2 Hz, 1H), 6.87 (t, *J* = 7.4 Hz, 1H), 6.81-6.74 (m, 1H), 6.27-6.23 (m, 1H), 6.21-6.17 (m, 1H), 5.34 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 201.0, 160.9, 140.7, 137.9, 129.0, 128.7, 128.3, 126.6, 125.6, 119.8, 119.5, 118.5, 112.6, 108.4, 107.1, 70.8. IR (KBr): ν (cm^{-1}) = 3373, 3276, 1683, 1623, 1494, 1129, 747, 731, 710; HRMS (ESI) *m/z*: calcd for $C_{18}H_{15}N_2O[M+H]^+$ 275.1179, found: 275.1179.

2,2'-dimethyl-[2,2'-biindoline]-3,3'-dione (P1)



Compound **P1** was isolated as a yellow solid (38 mg, 2%). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.60 (d, *J* = 7.8 Hz, 2H), 7.52-7.45 (m, 2H), 6.94 (d, *J* = 8.3 Hz, 2H), 6.80 (t, *J* = 7.4 Hz, 2H), 1.14 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.1, 161.0, 138.1, 124.7, 119.8, 118.5, 112.2, 68.5, 18.2. HRMS (ESI) *m/z*: calcd for $C_{18}H_{16}N_2O_2Na$ $[M+Na]^+$ 315.1104, found: 315.1100.

5. References

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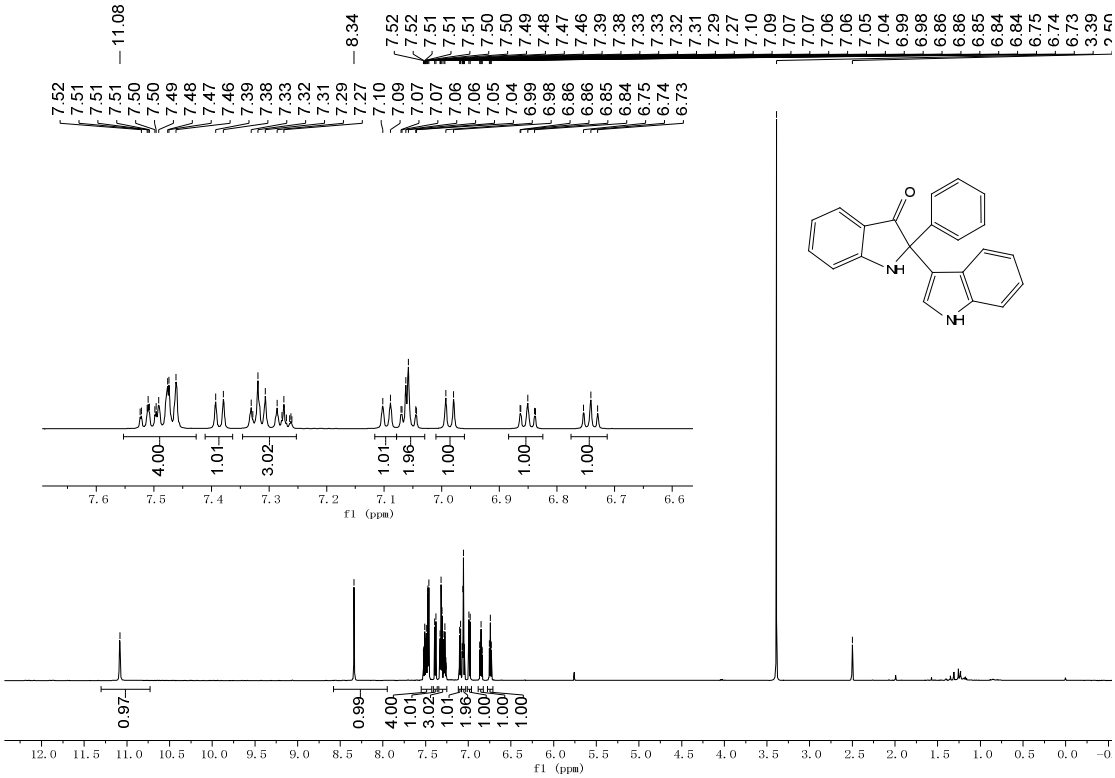
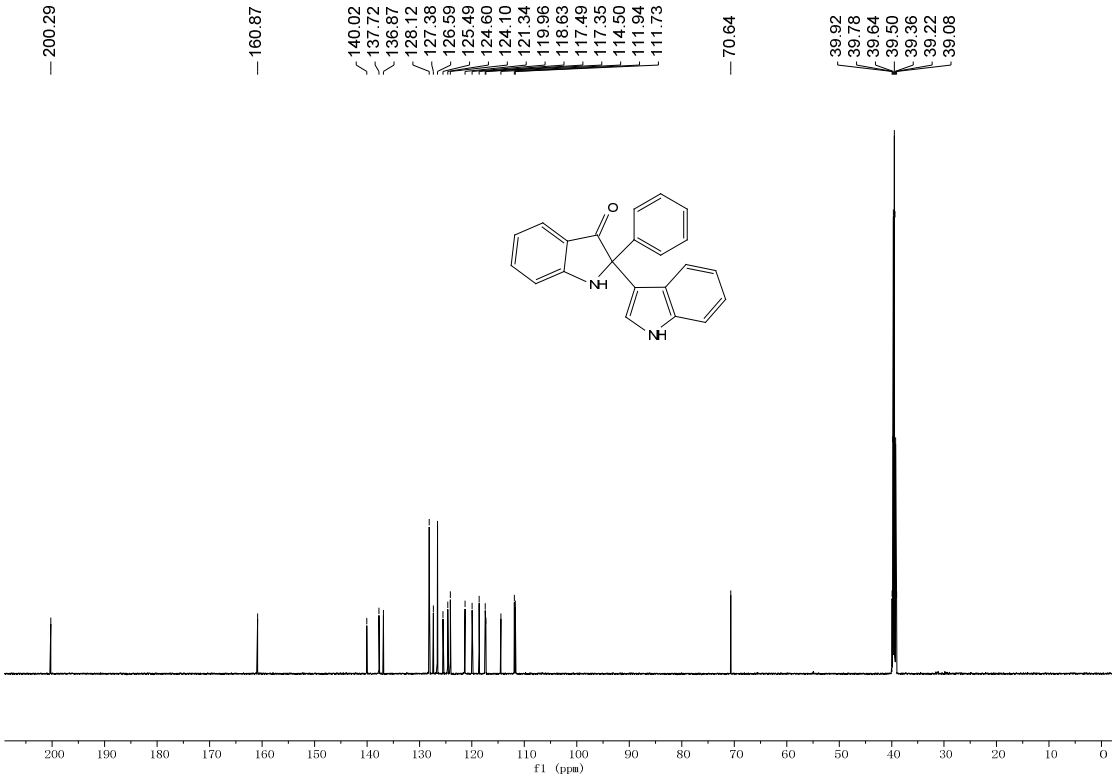
6. Copies of ^{1}H and ^{13}C NMR spectra of all products

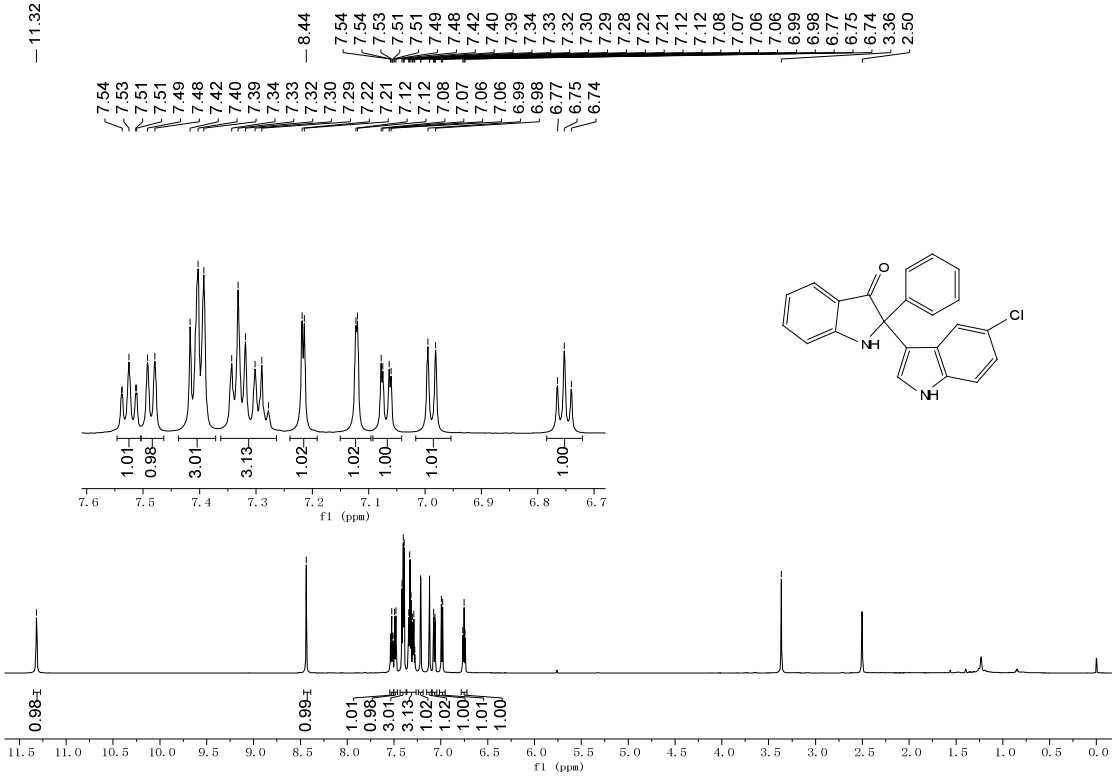
3a: ^{1}H NMR



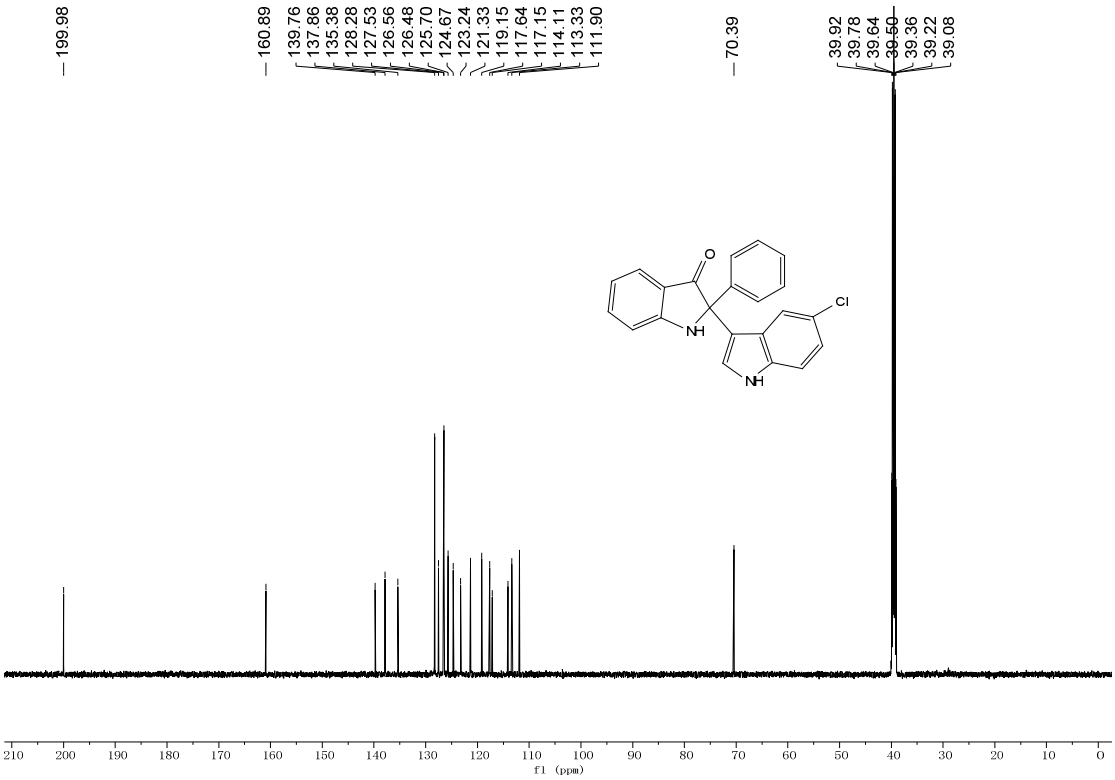
3a: ^{13}C NMR



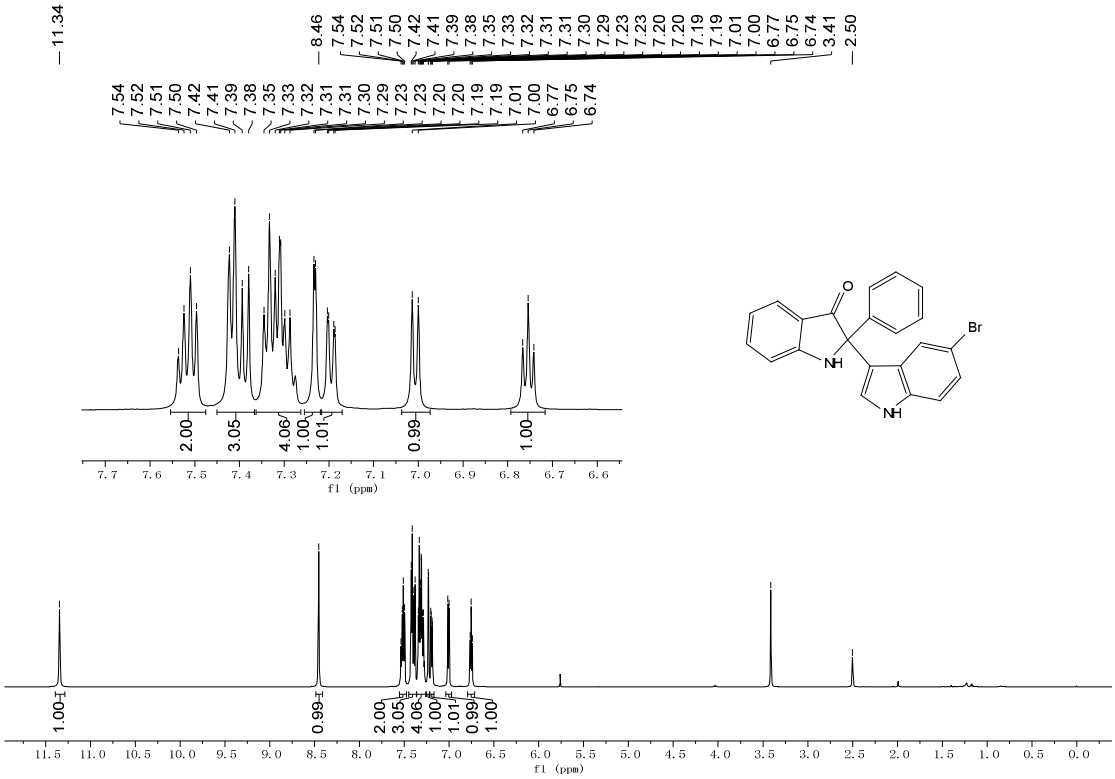
3b: ^{1}H NMR



3b: ^{13}C NMR



3c: ^{1}H NMR



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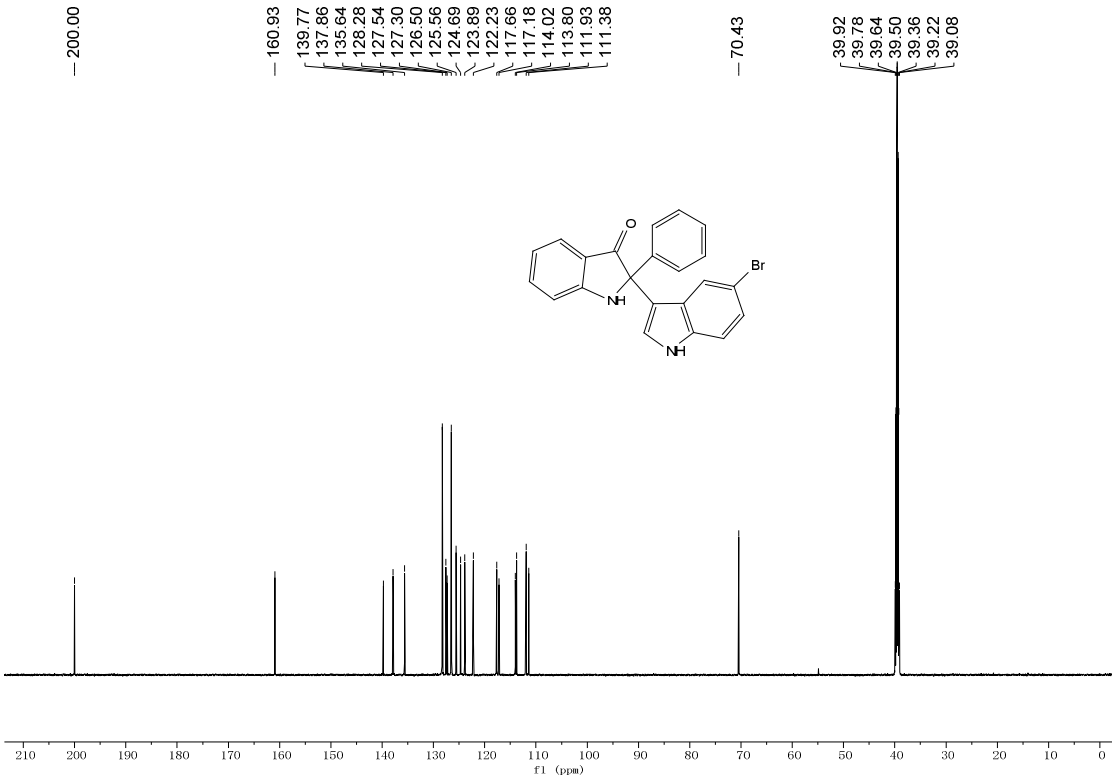
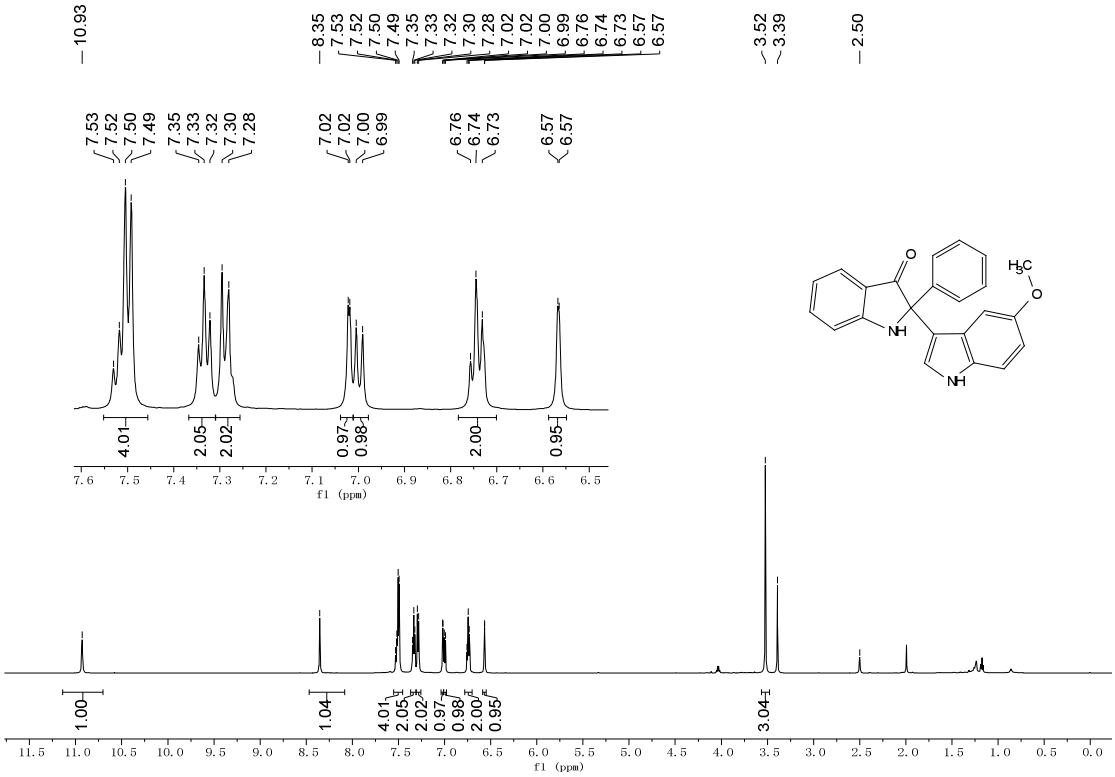


3d: ^{1}H NMR



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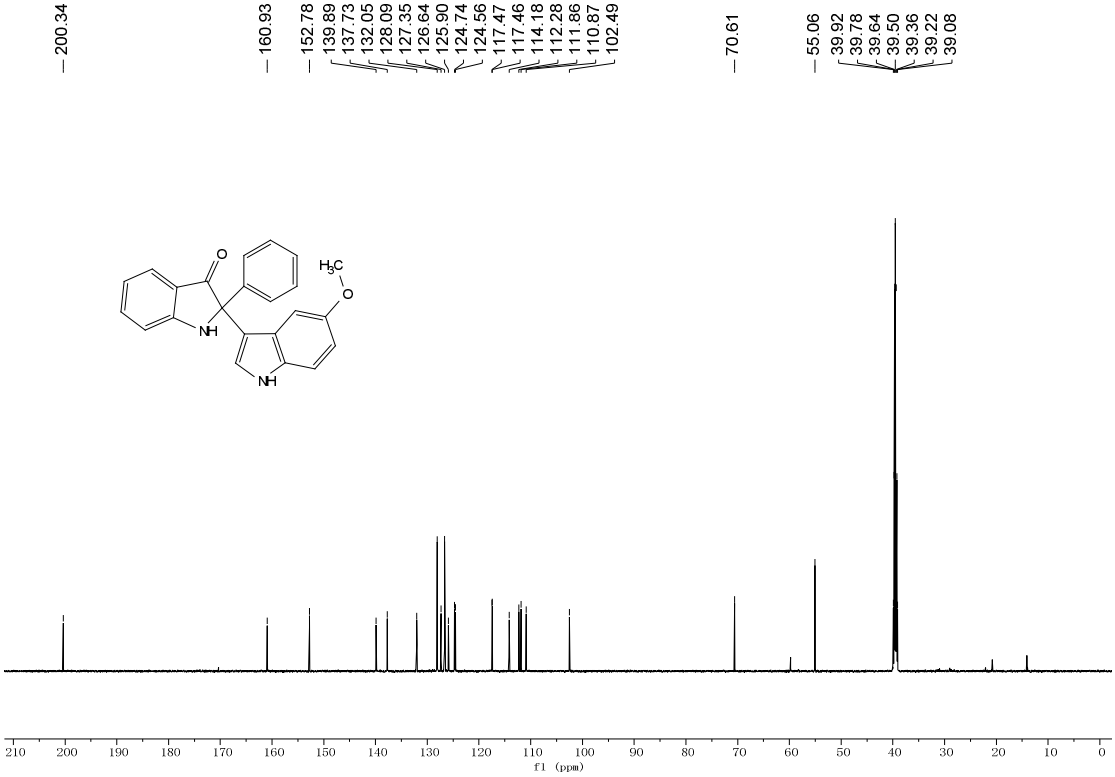
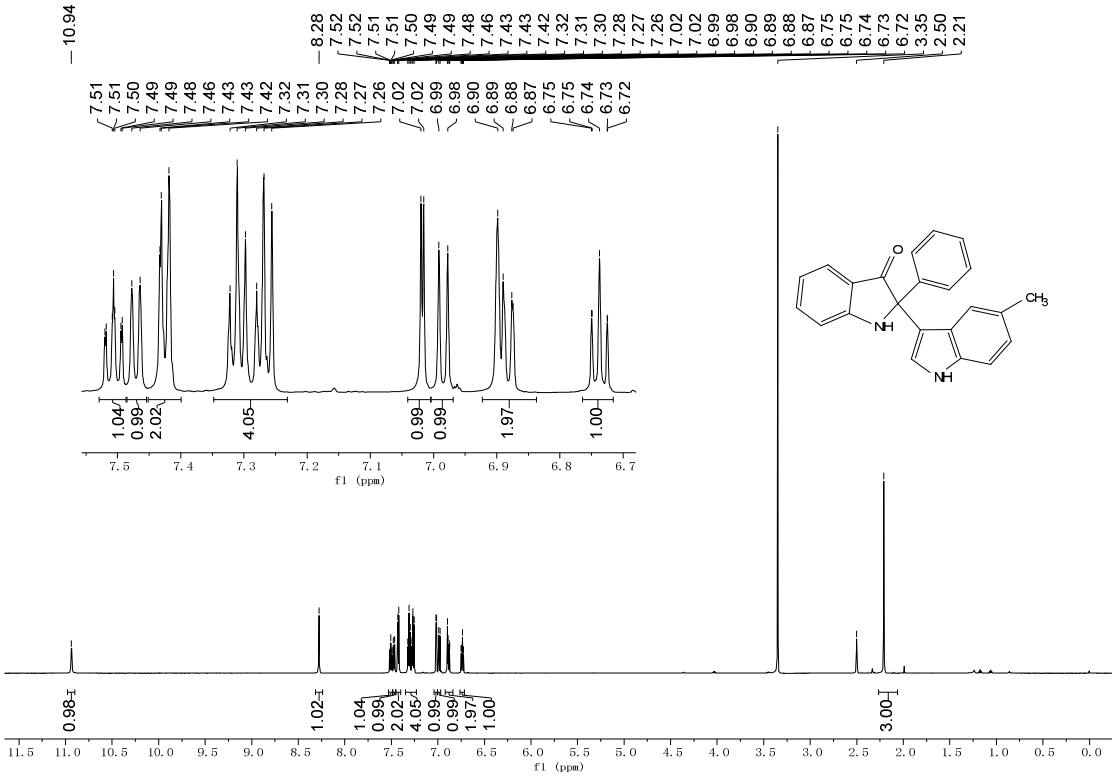


3e: ^{1}H NMR



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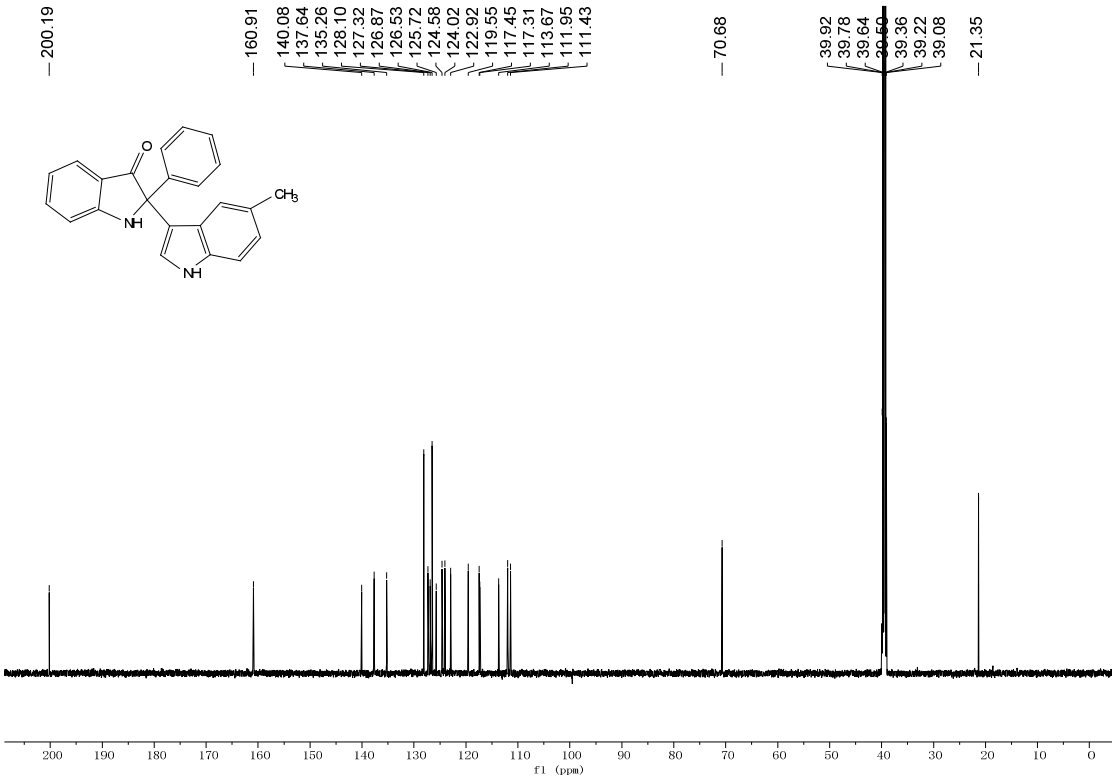
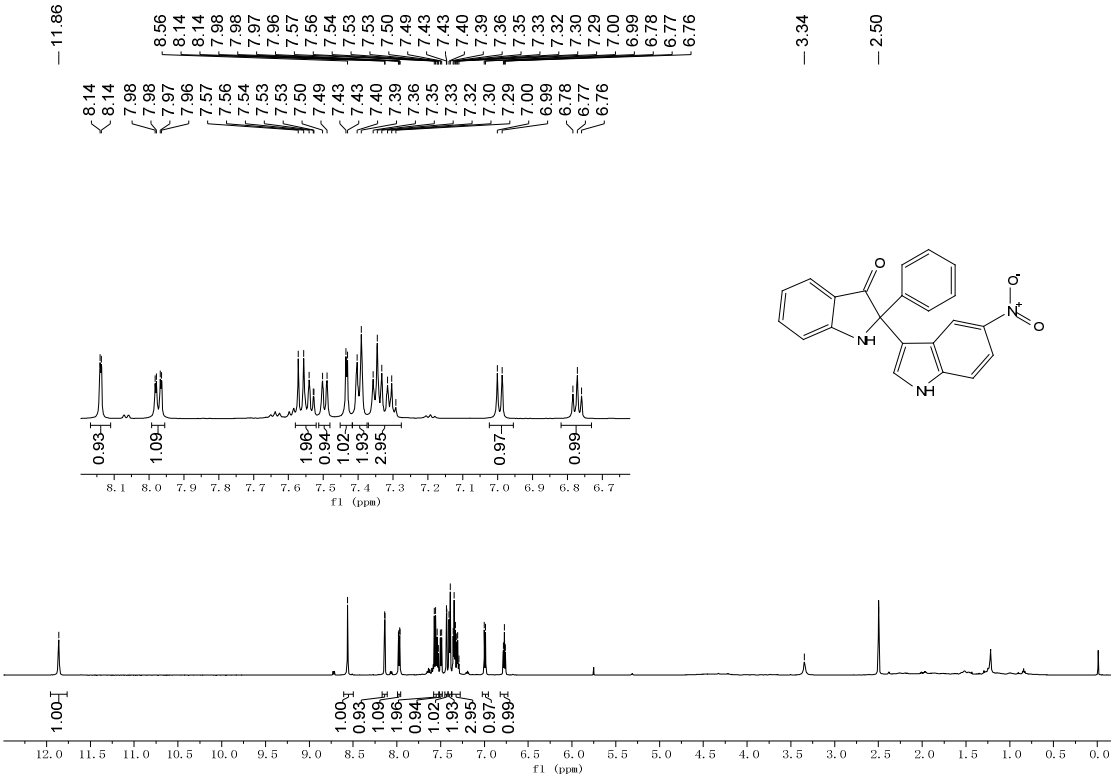
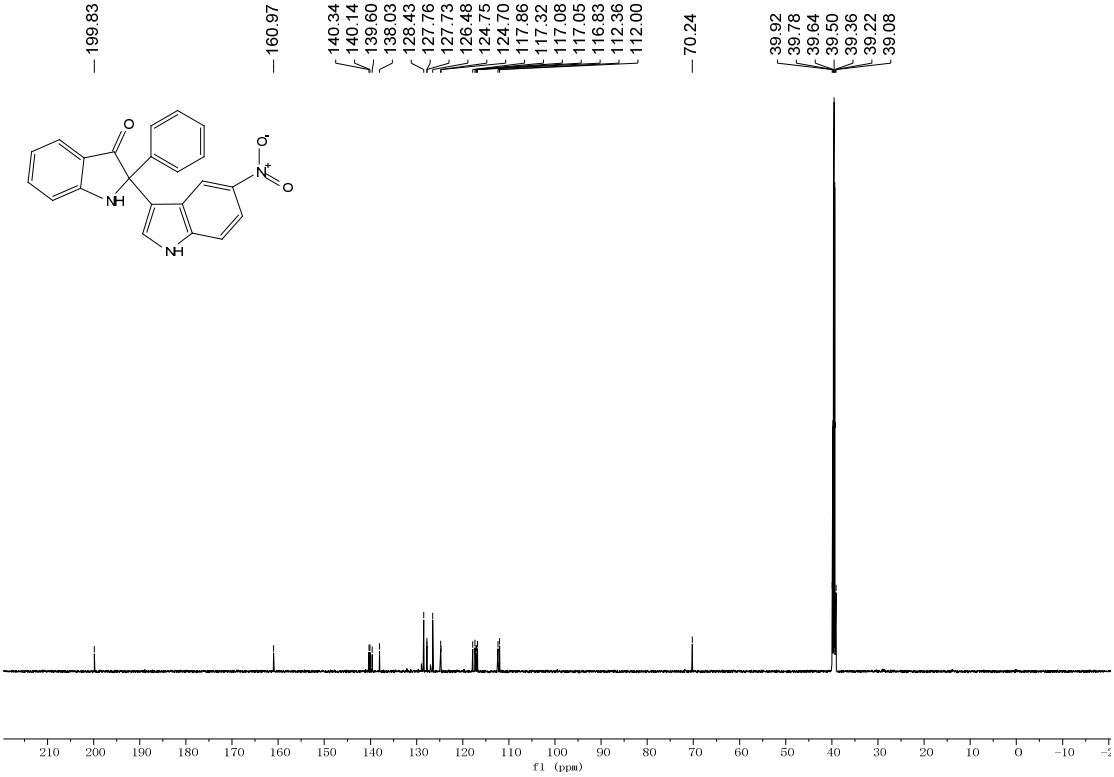


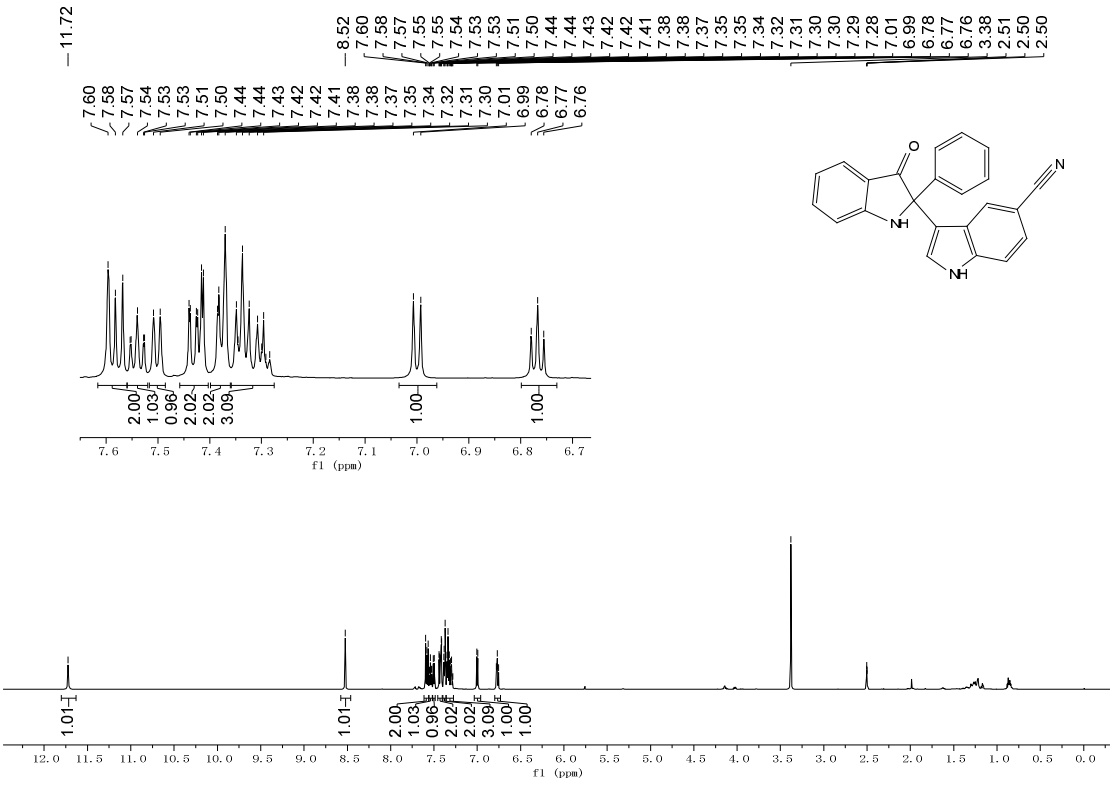
3f: ^{1}H NMR



3f: ^{13}C NMR



3g: ^{1}H NMR



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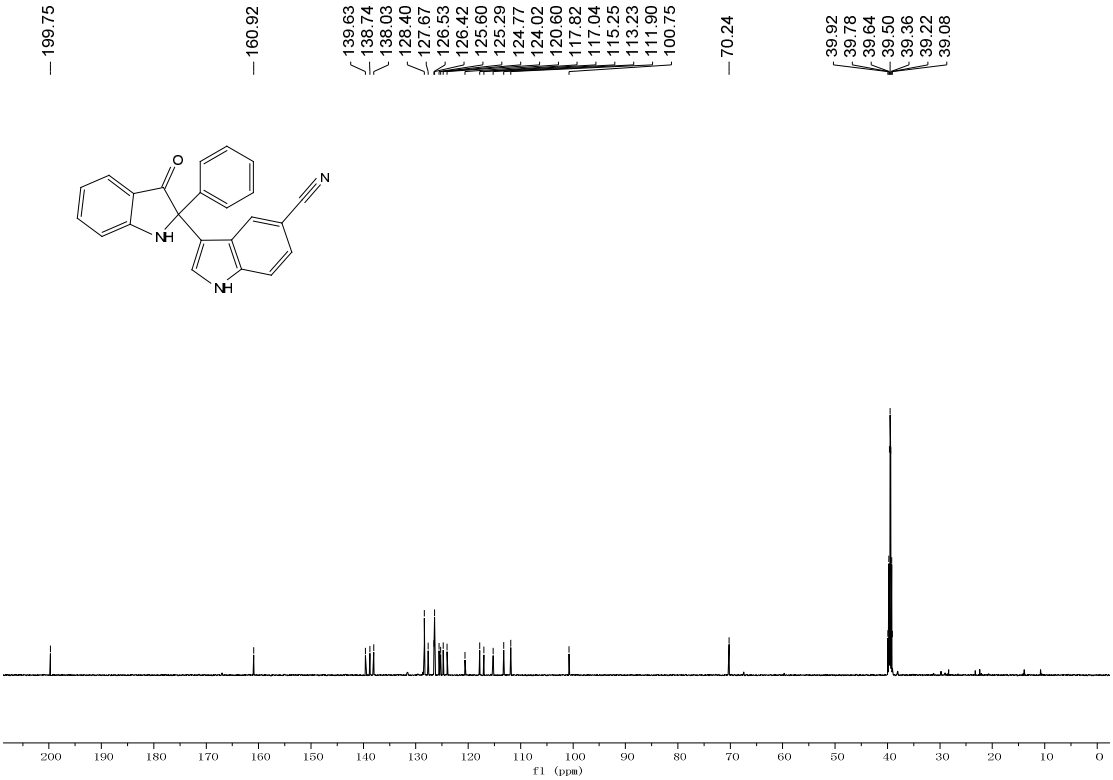
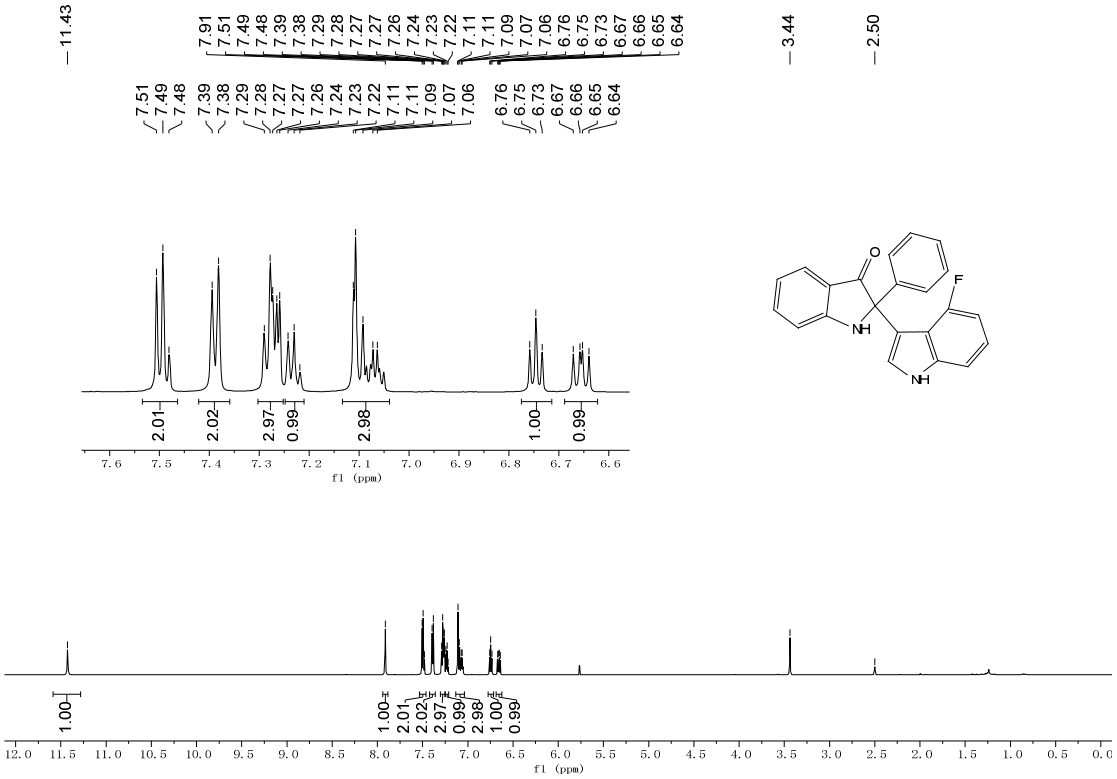


3h: ^{1}H NMR



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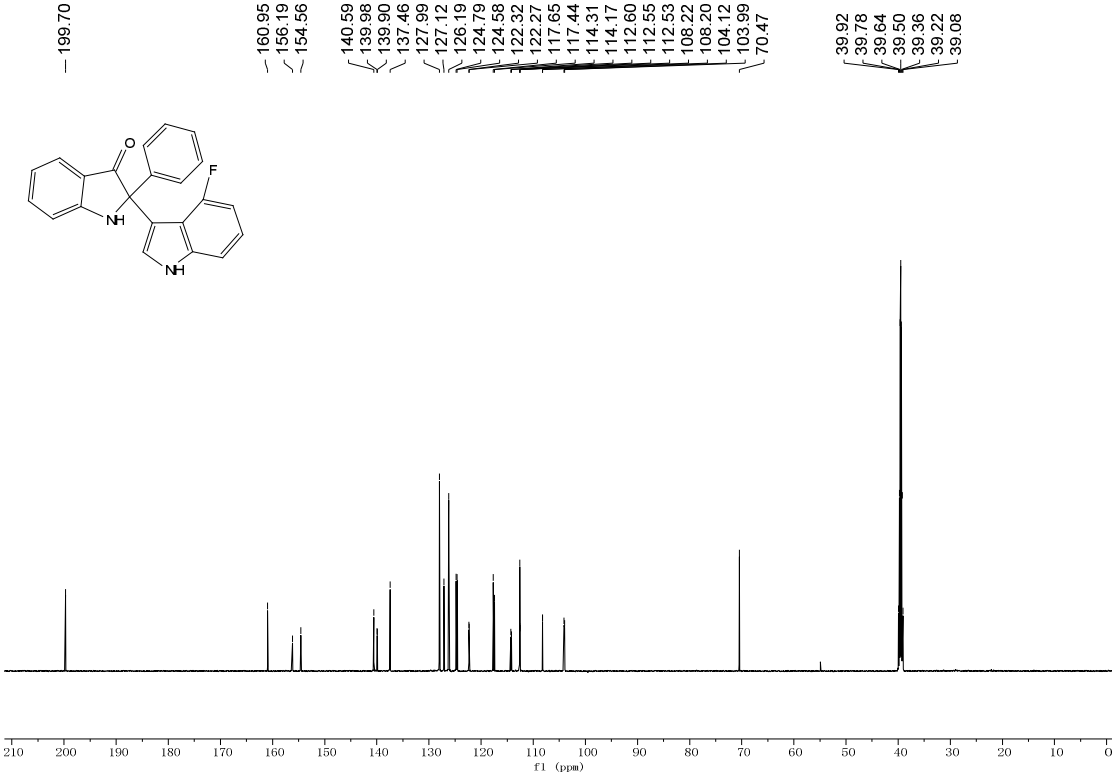
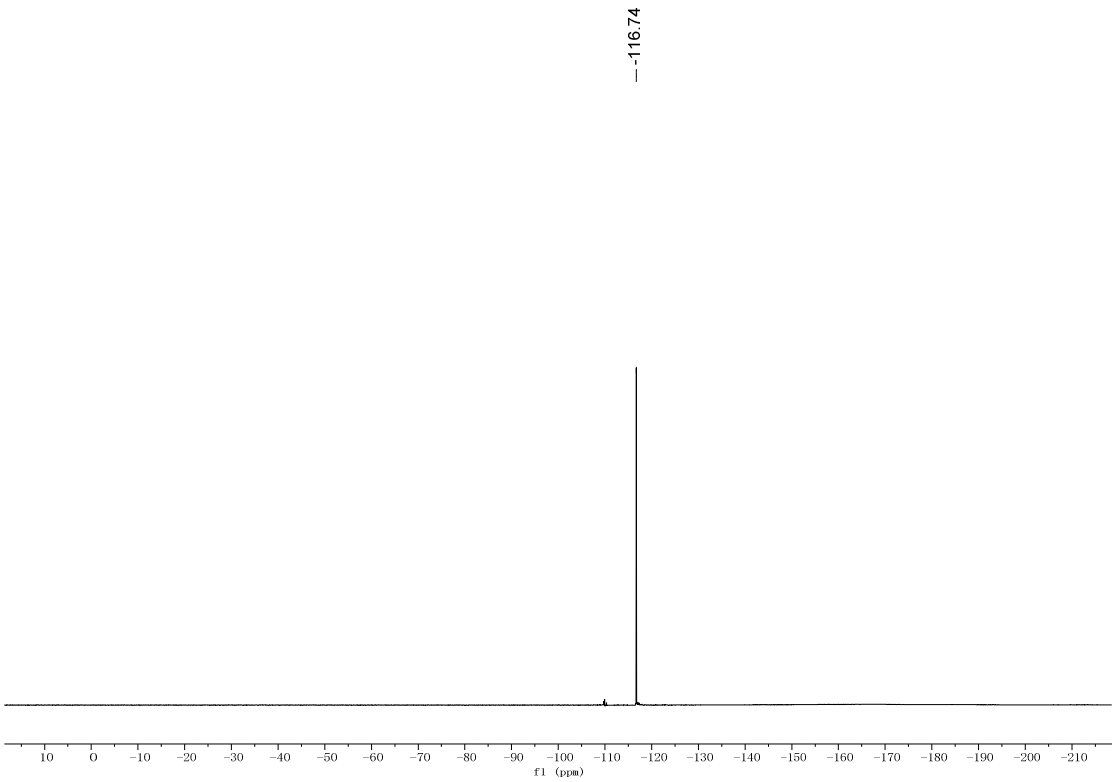
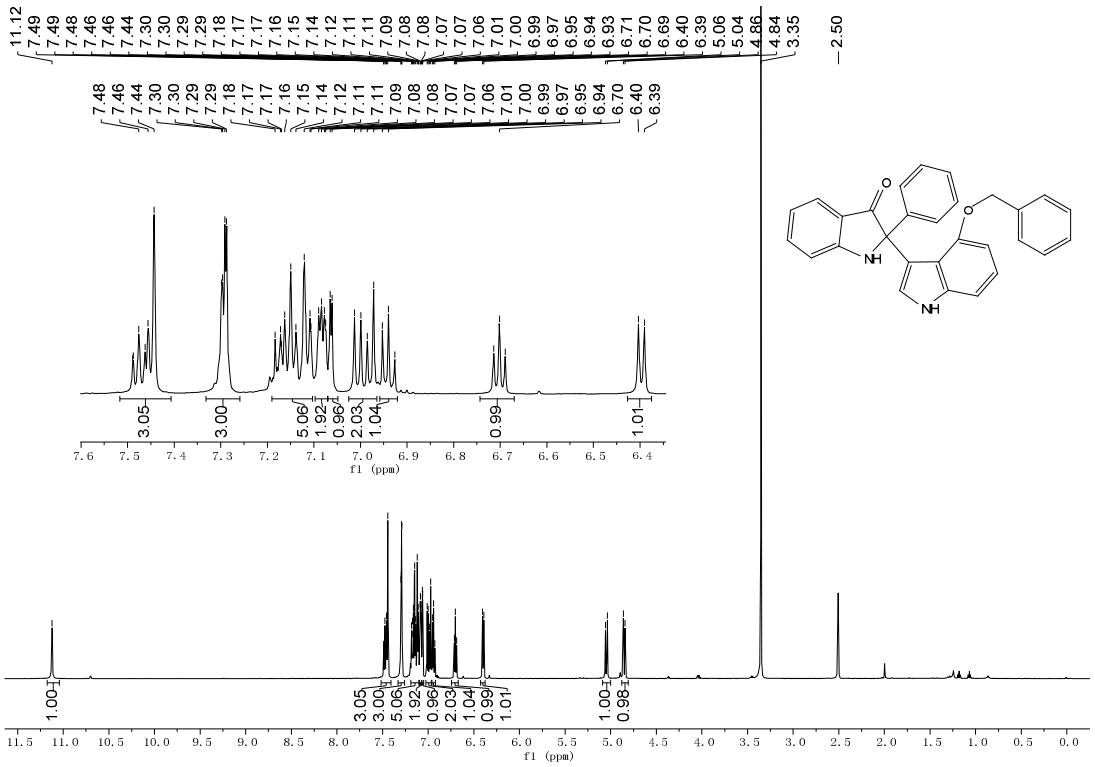


3h: ^{19}F NMR


-116.74
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

3i: ^{1}H NMR



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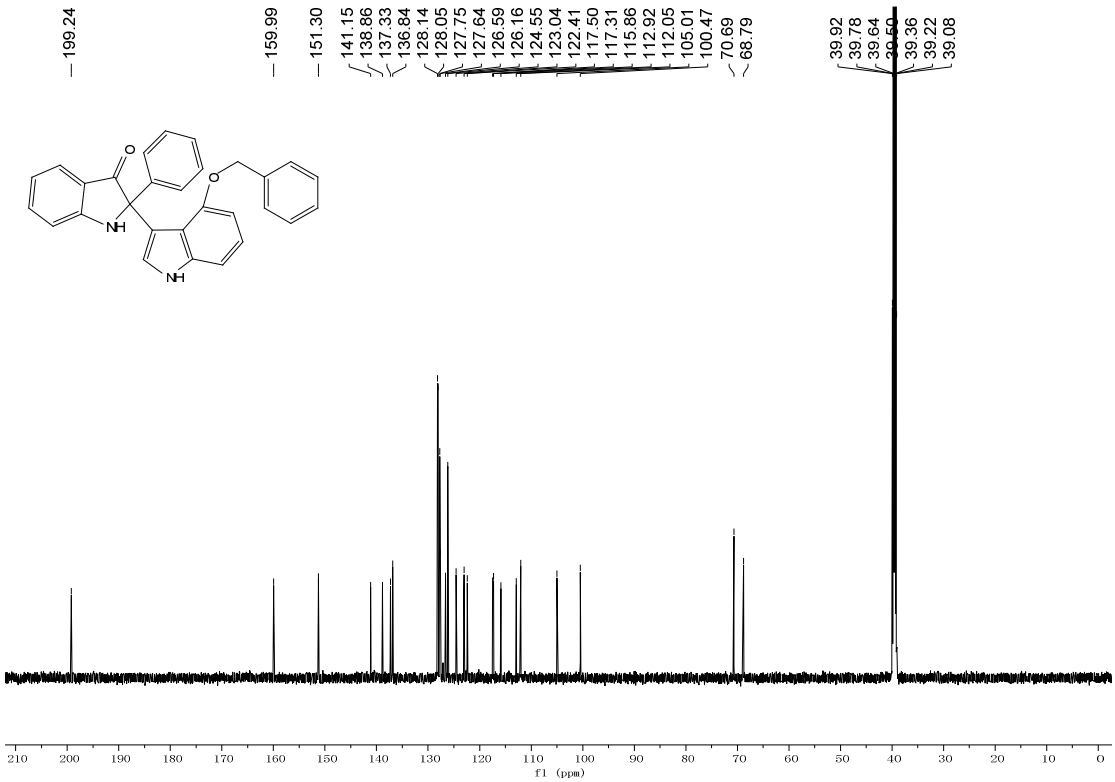

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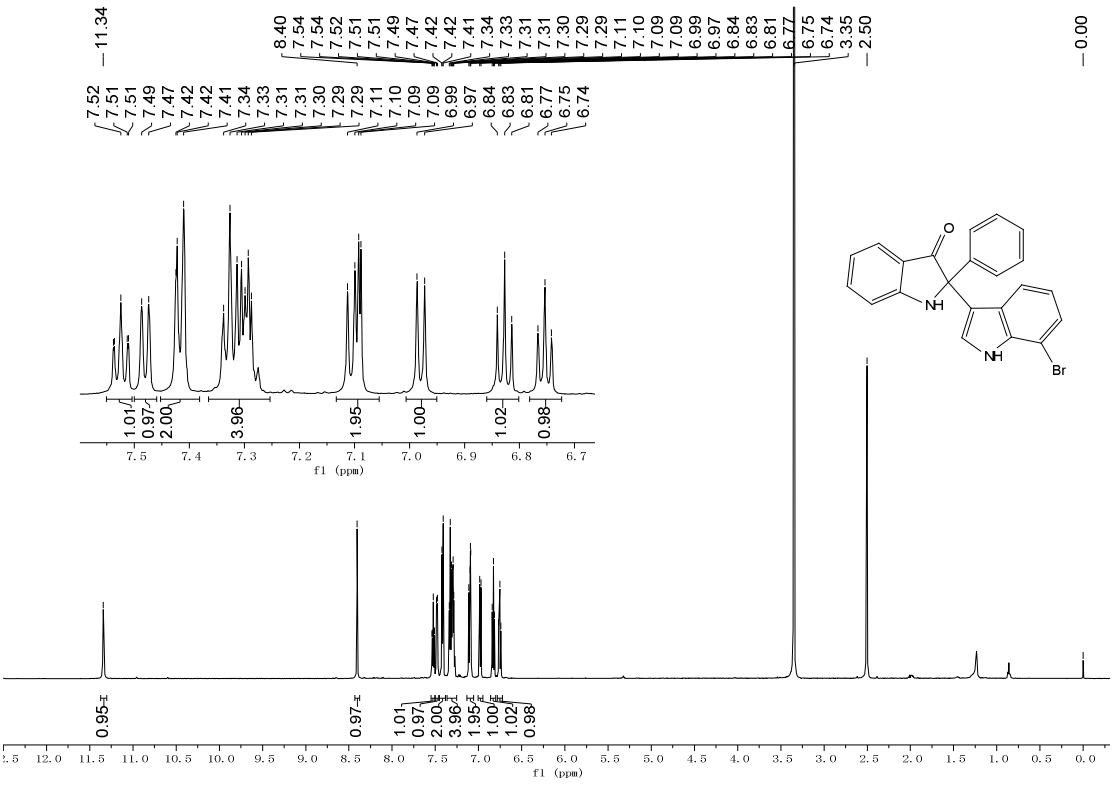

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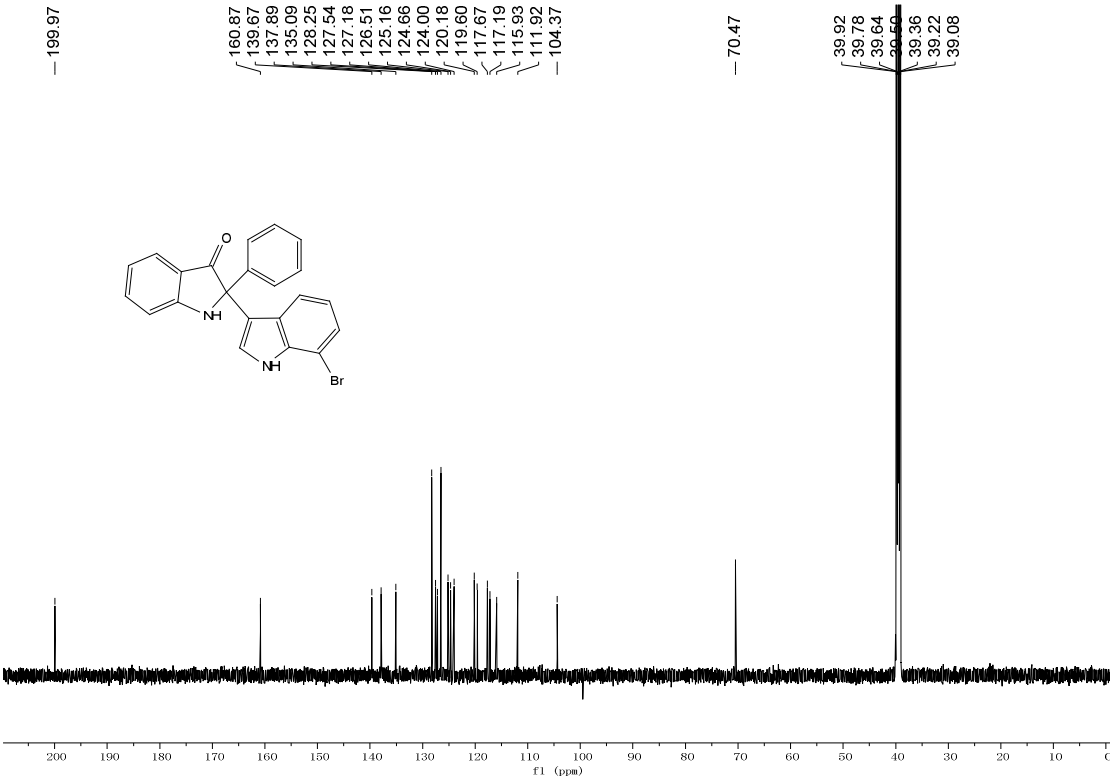
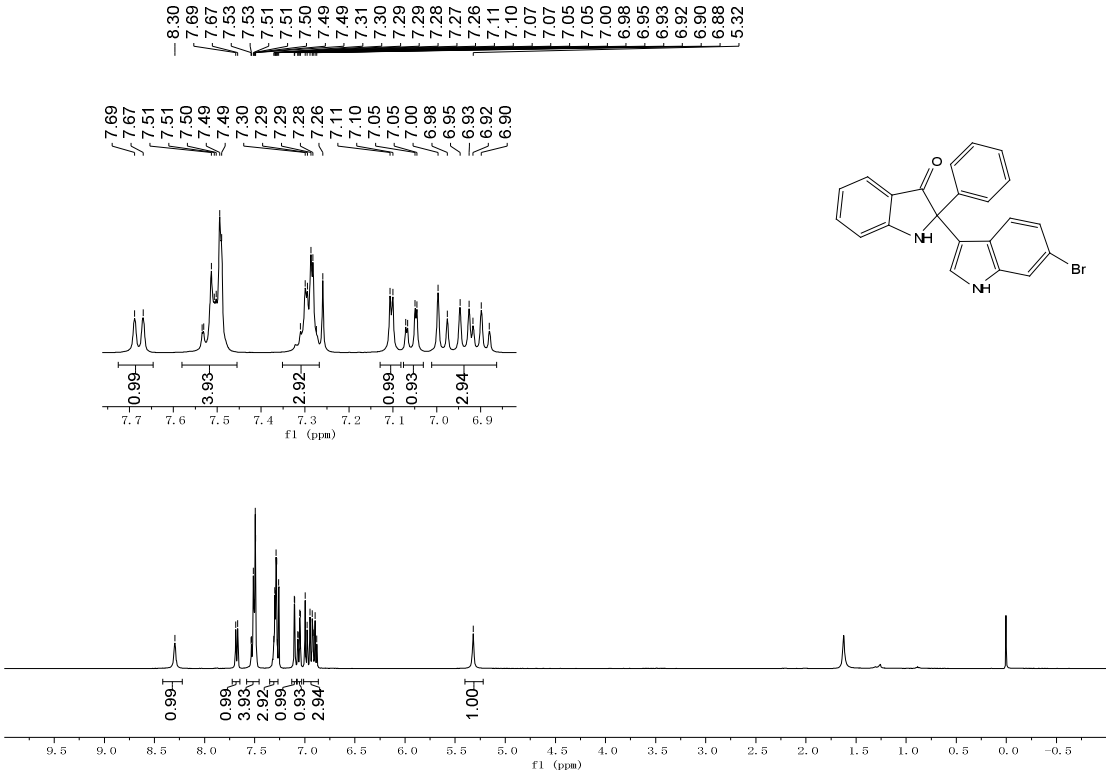


3k: ^{1}H NMR



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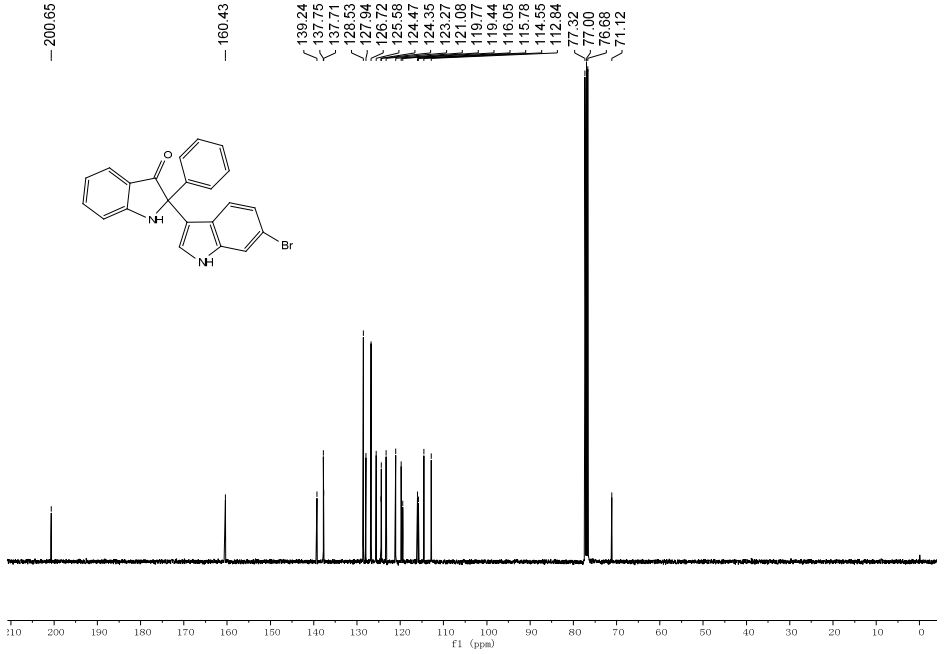

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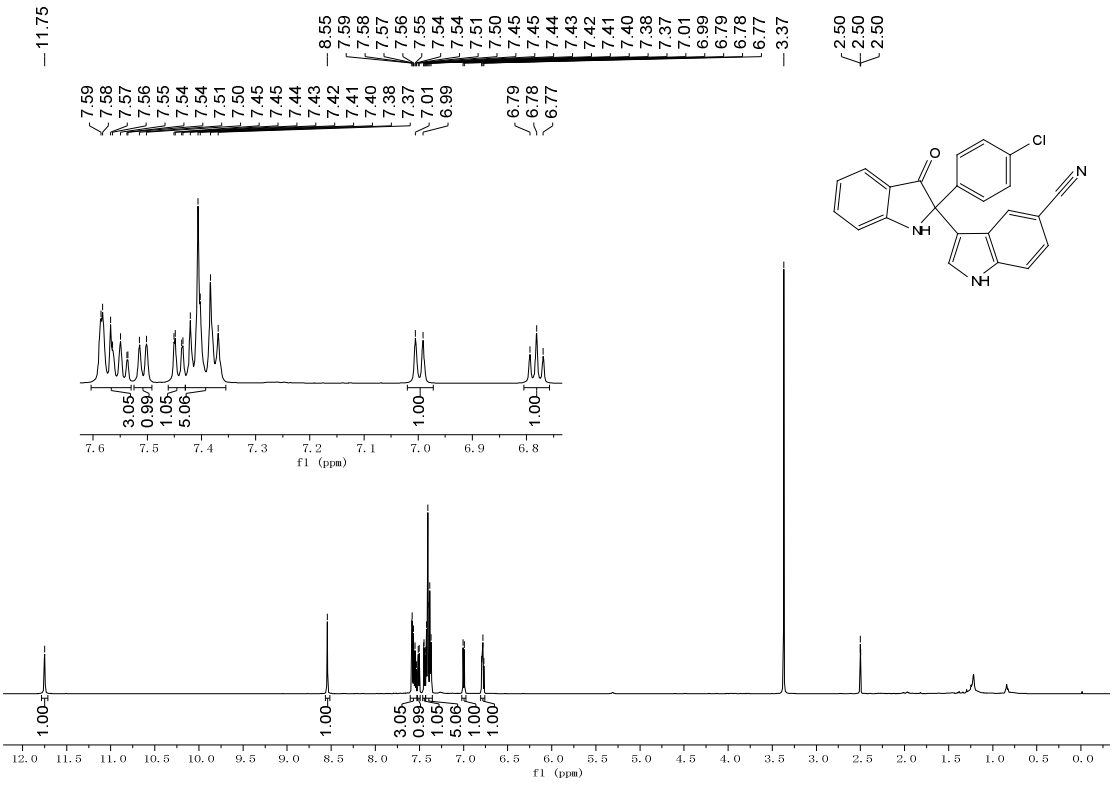

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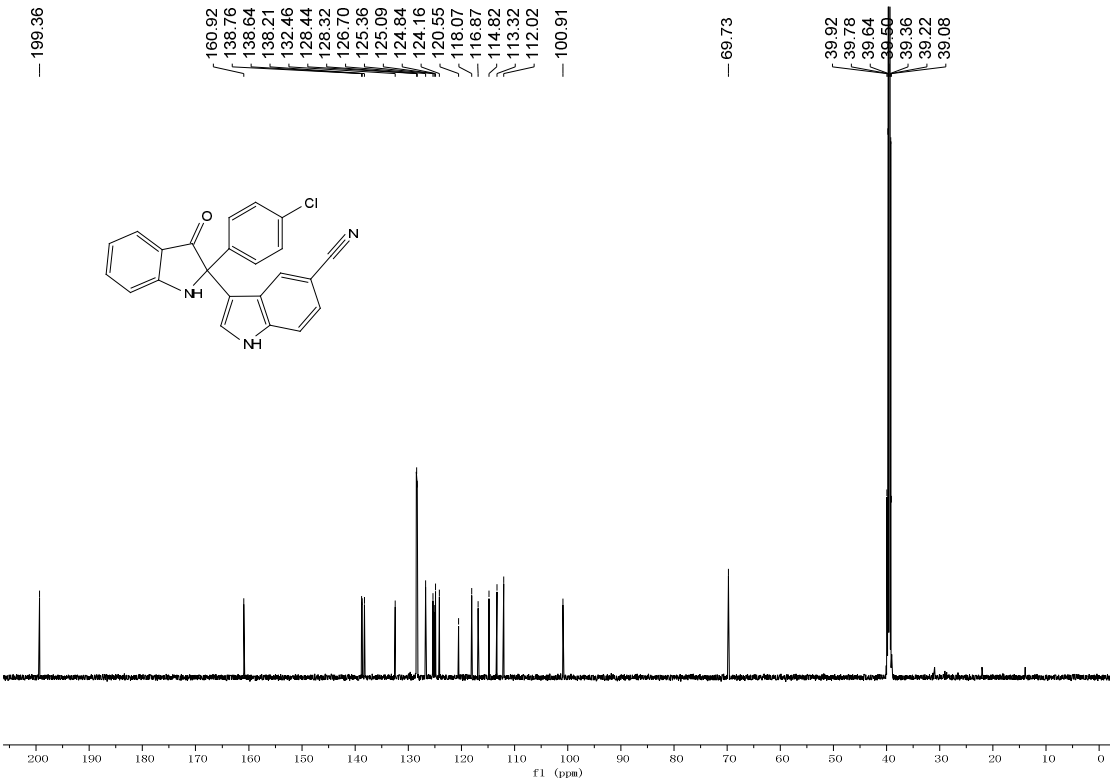
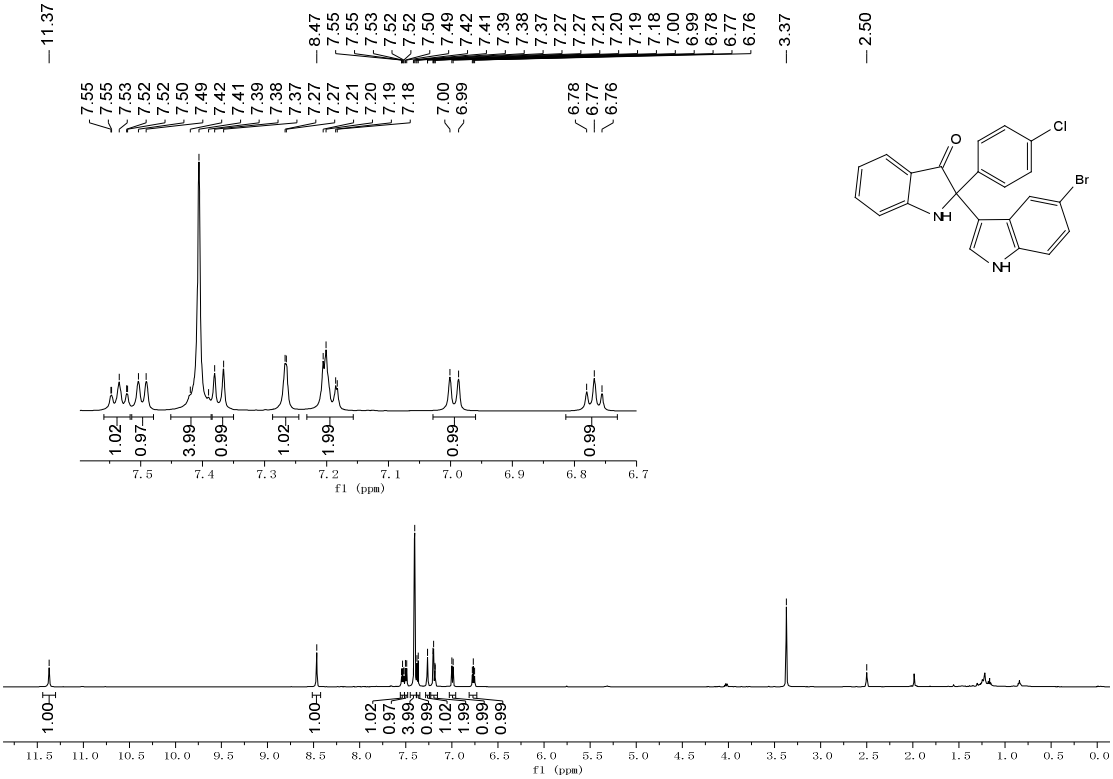


3m: ^{1}H NMR



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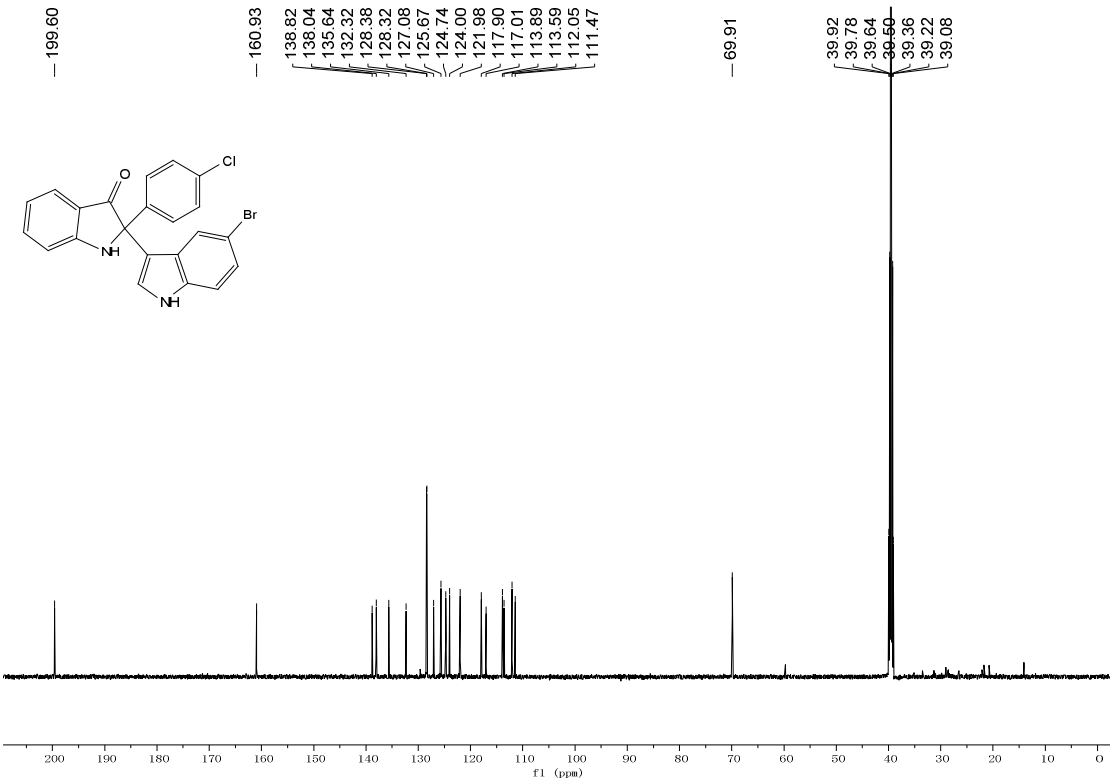

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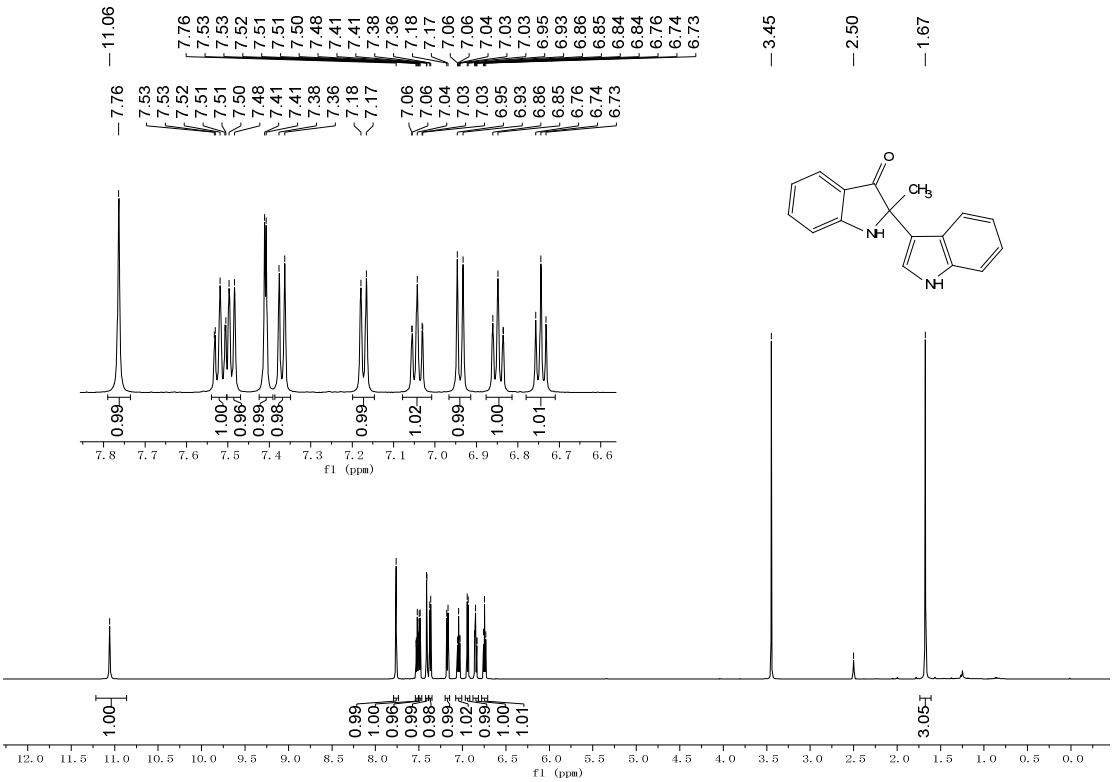

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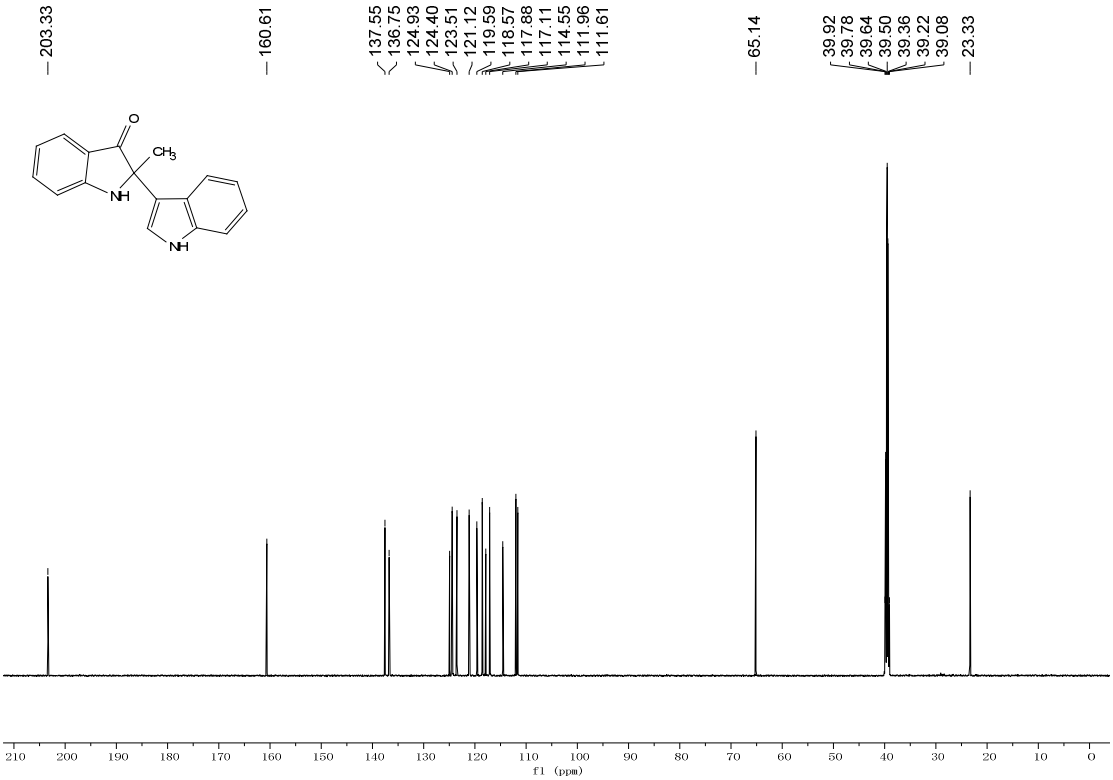

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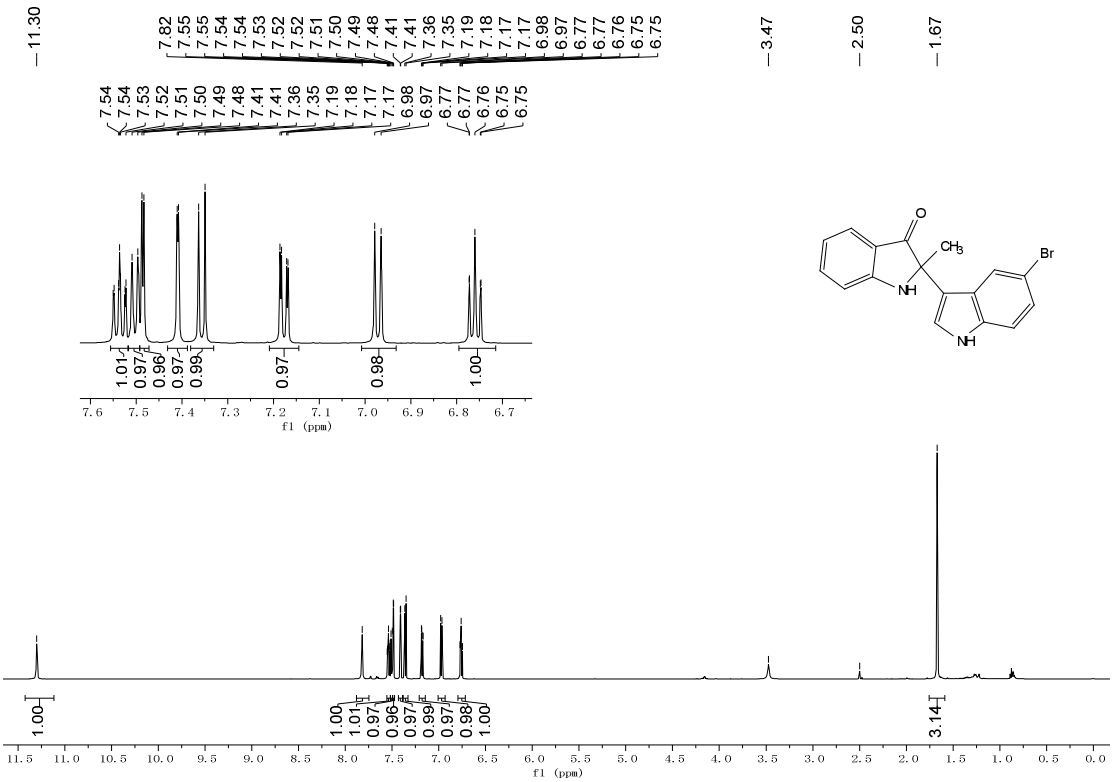

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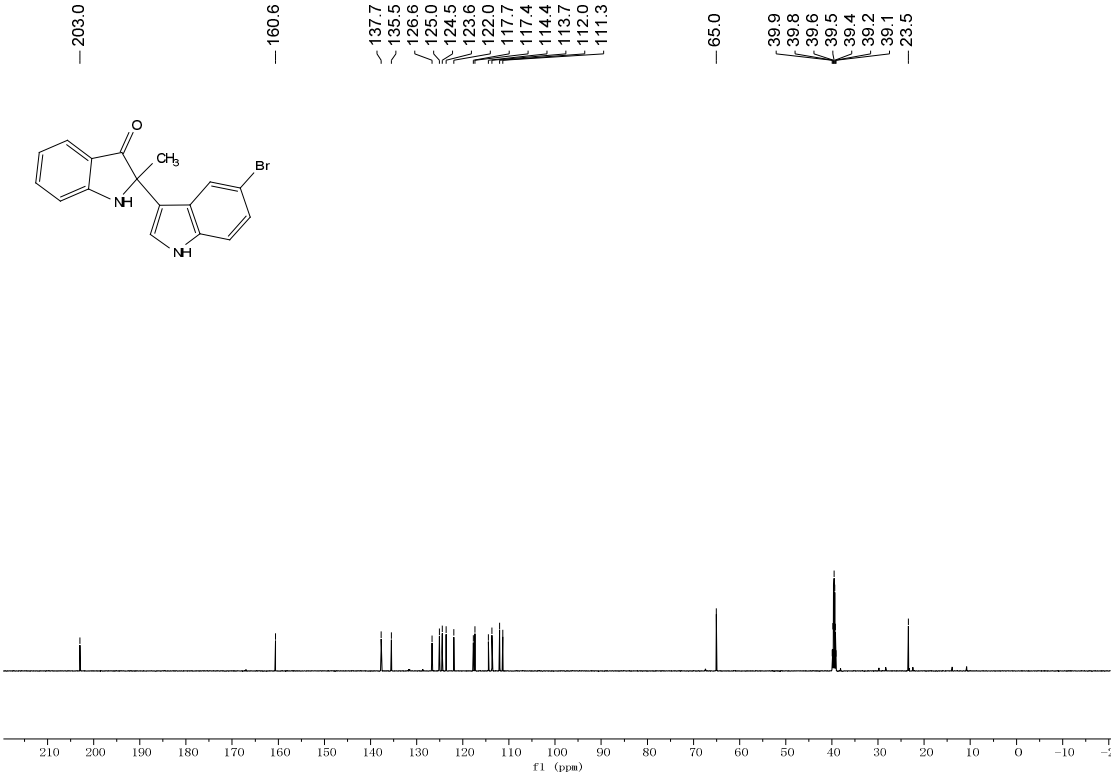
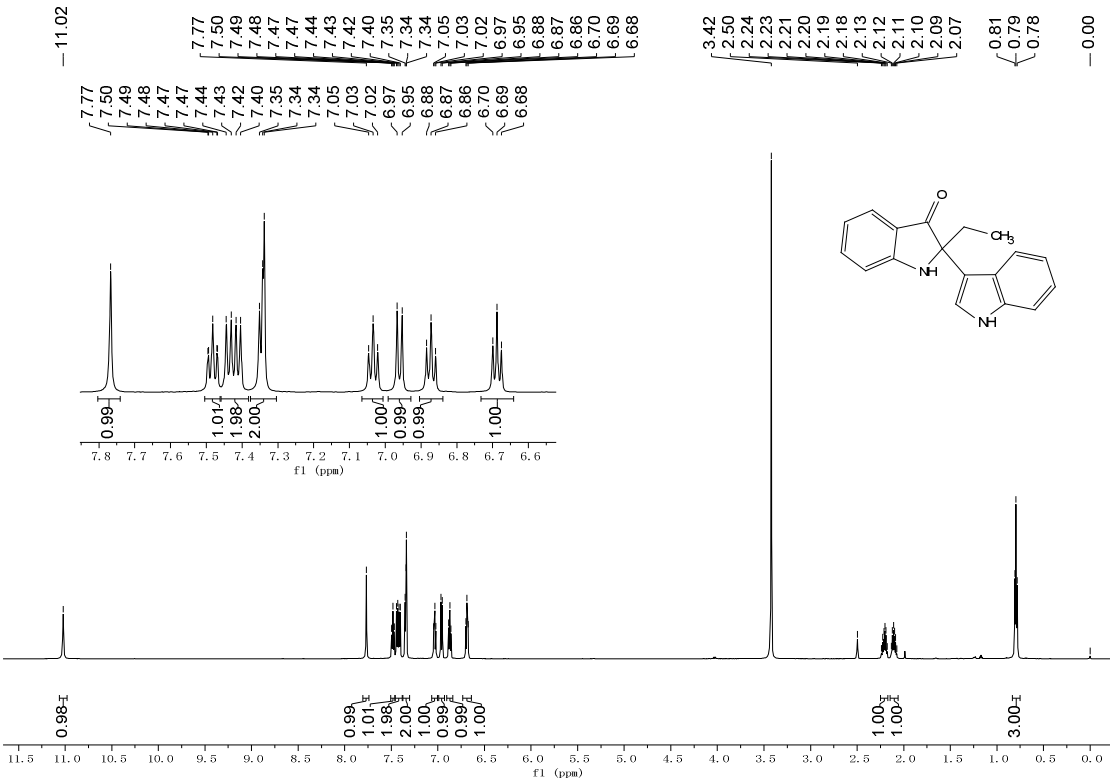
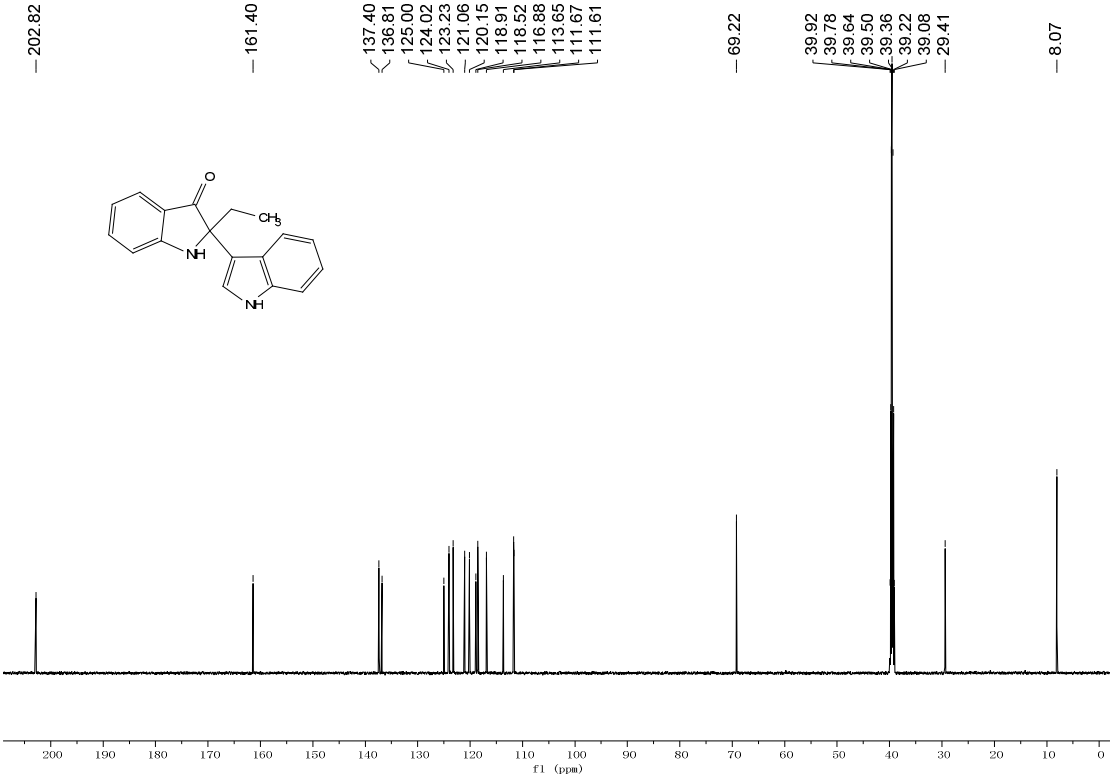


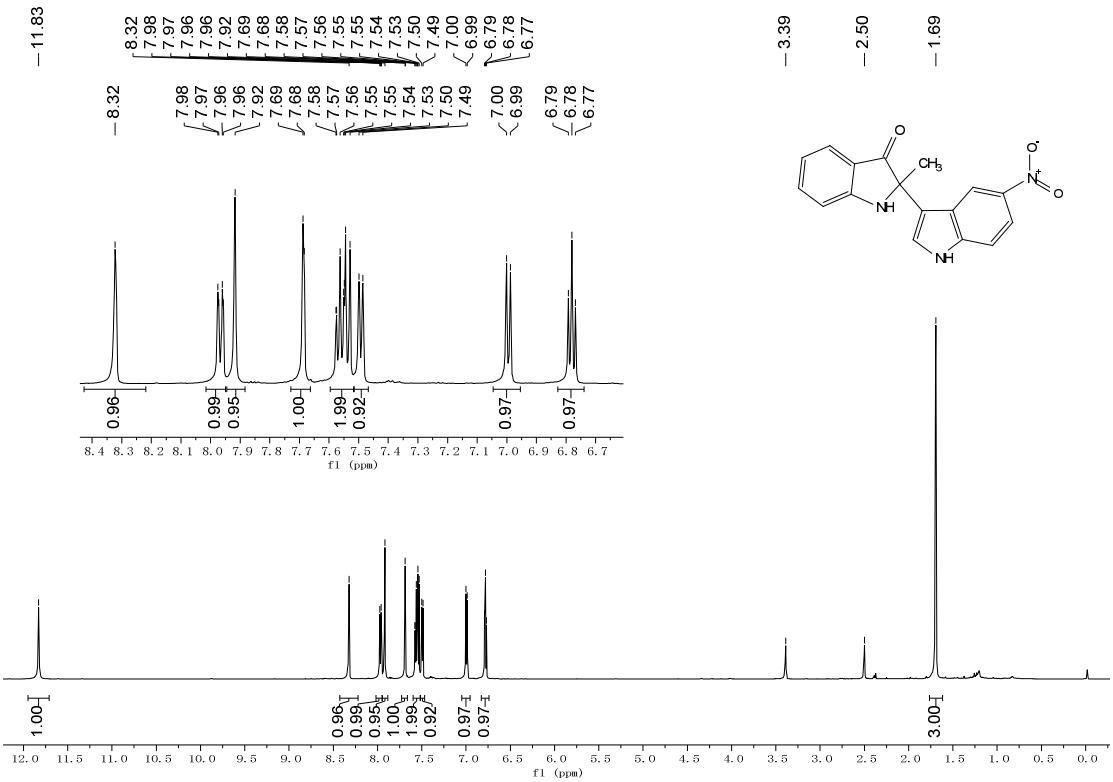
3p: ^{1}H NMR



3p: ^{13}C NMR



3q: ^{1}H NMR



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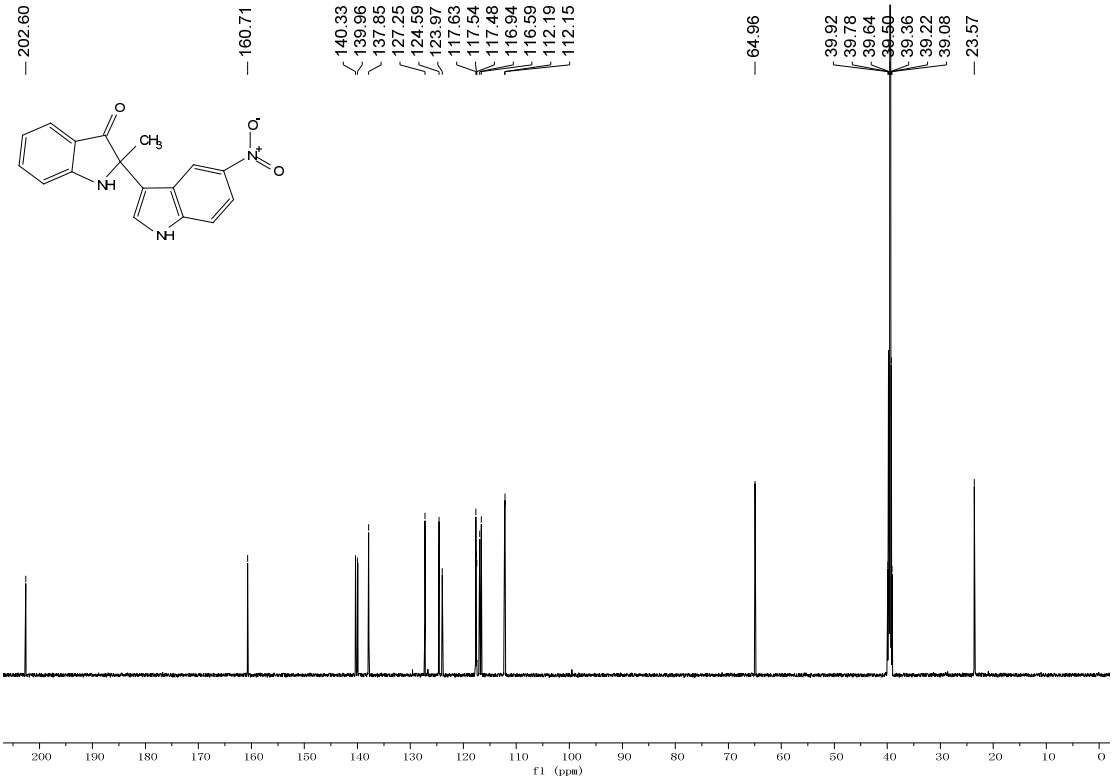
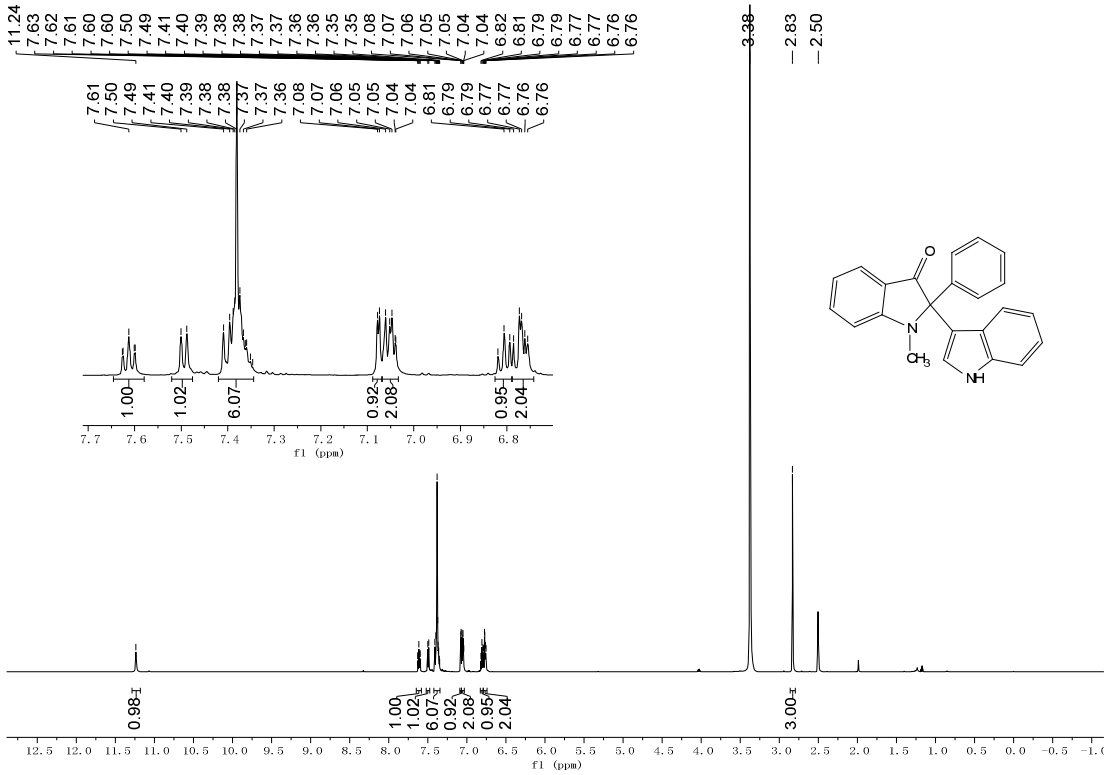


3r: ^{1}H NMR



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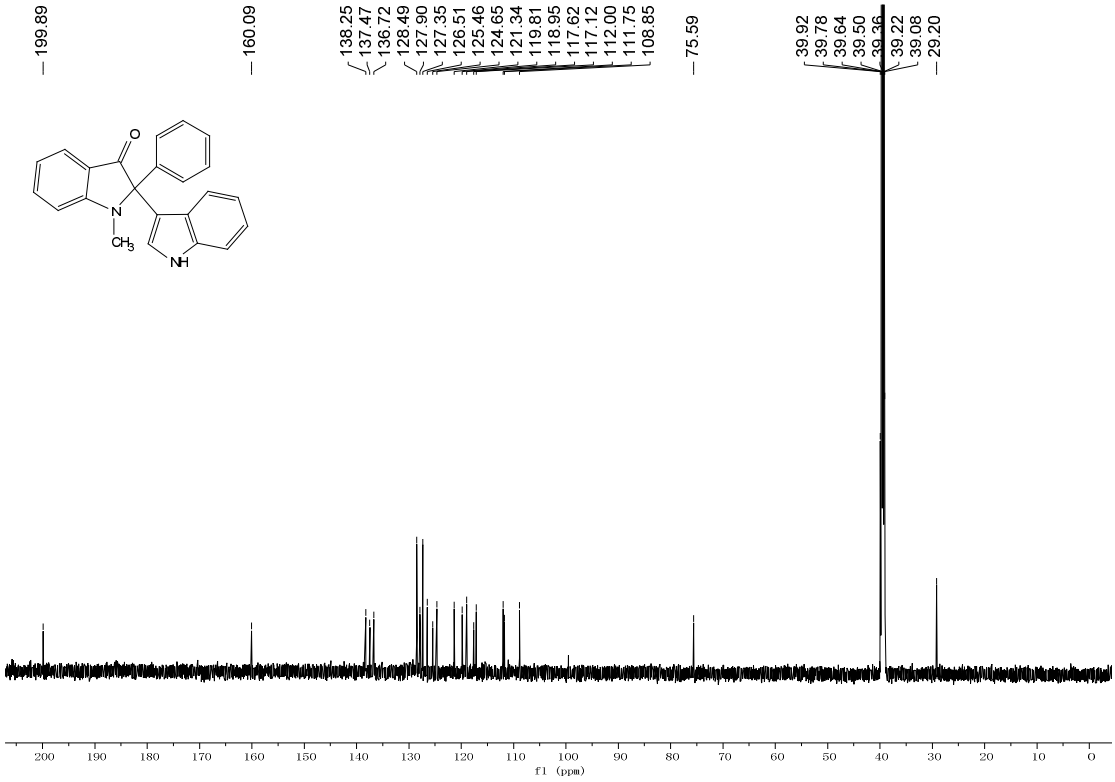

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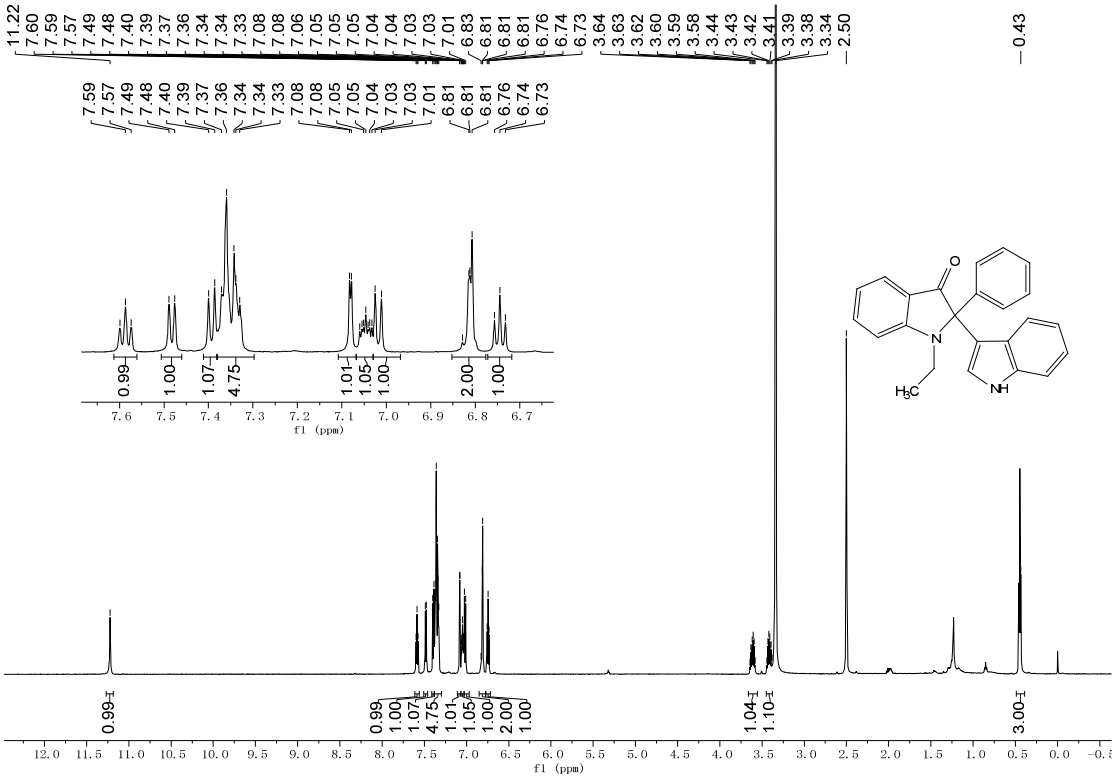

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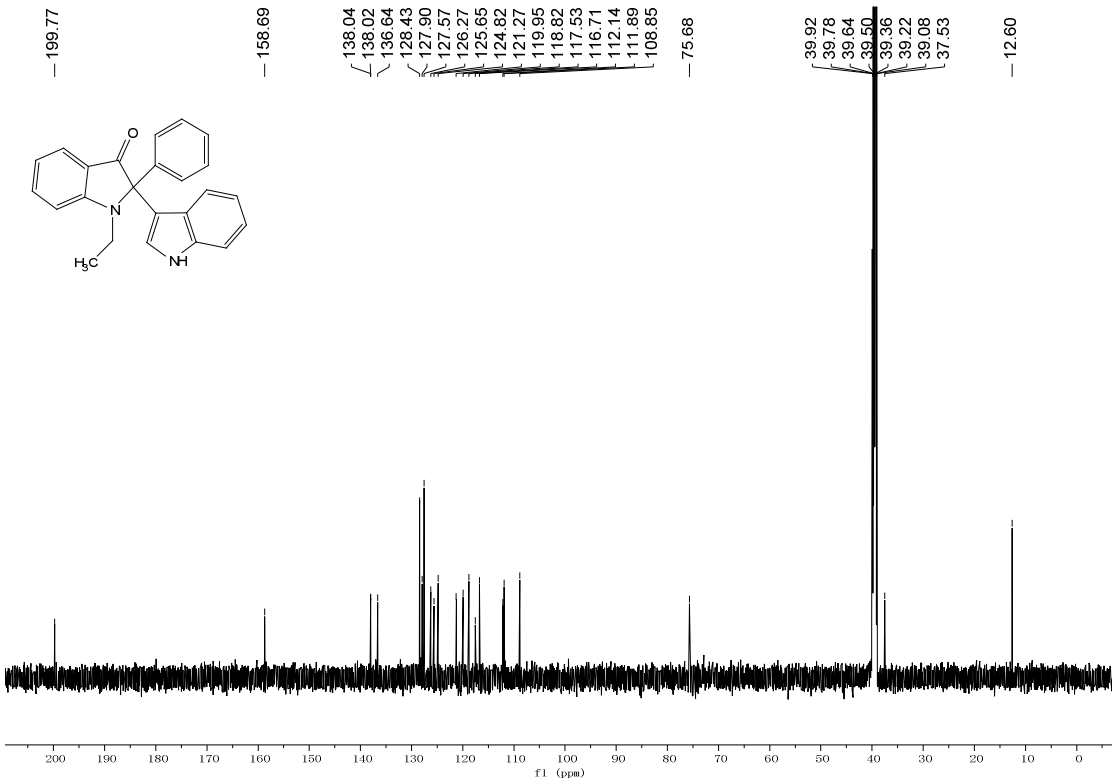
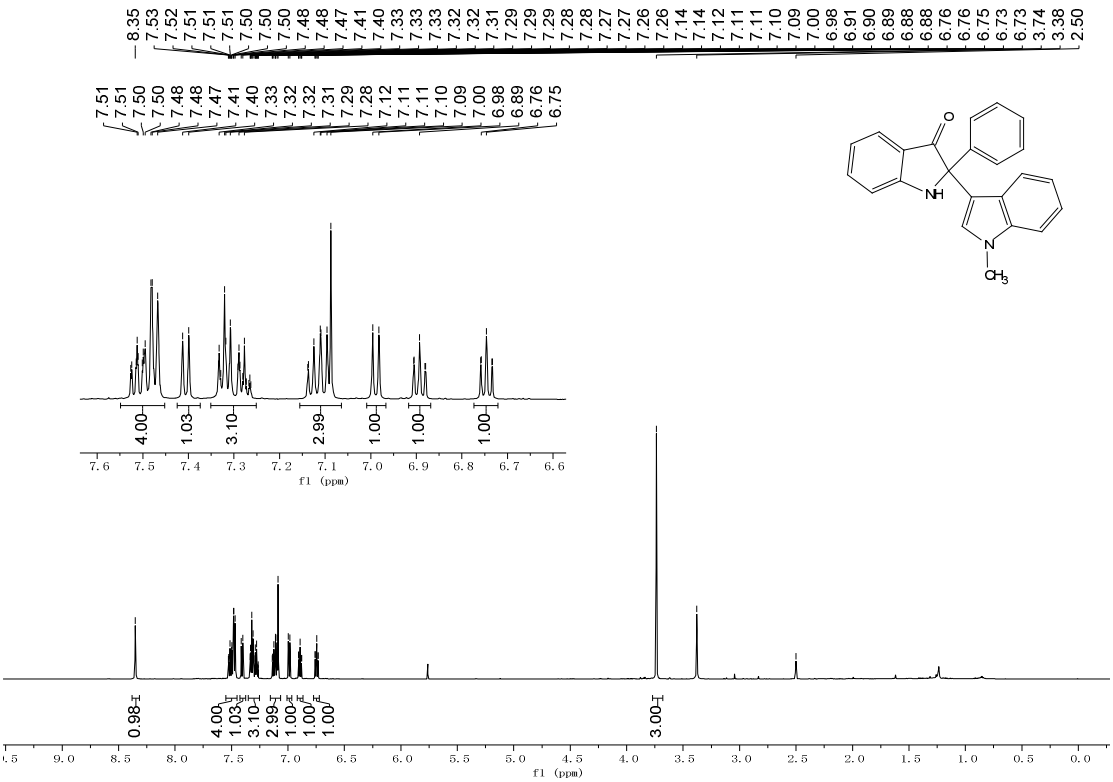


3t: ^{1}H NMR



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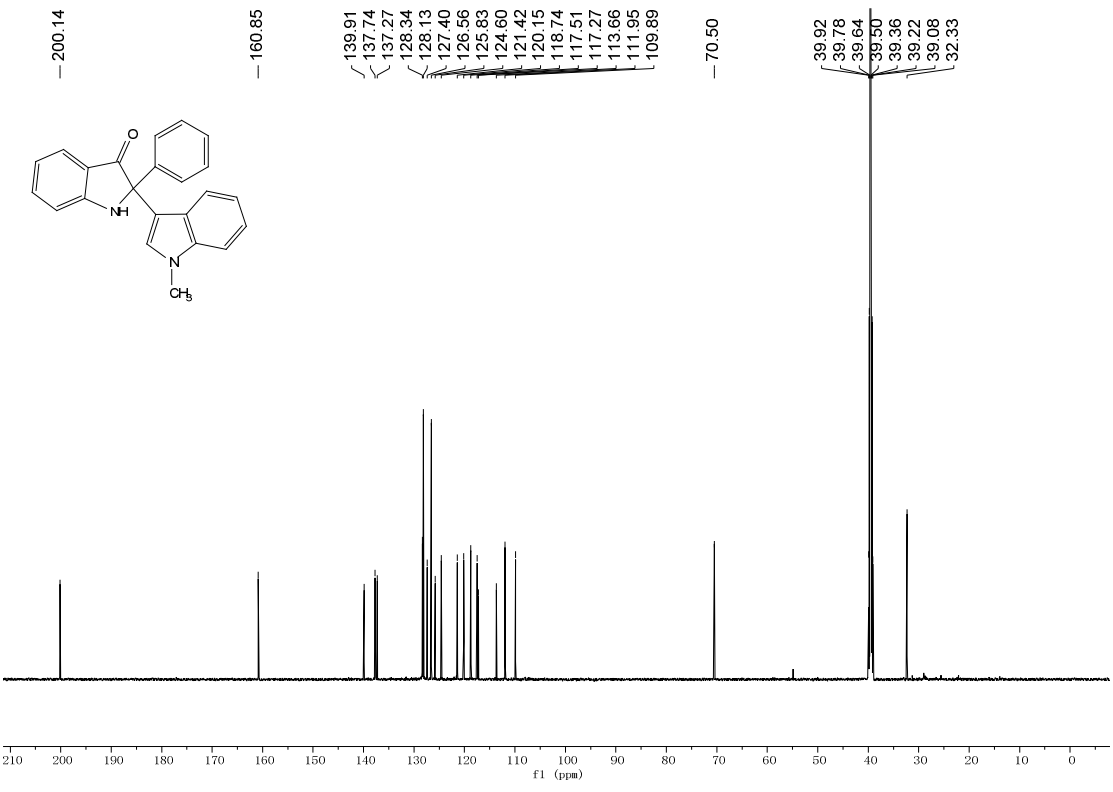
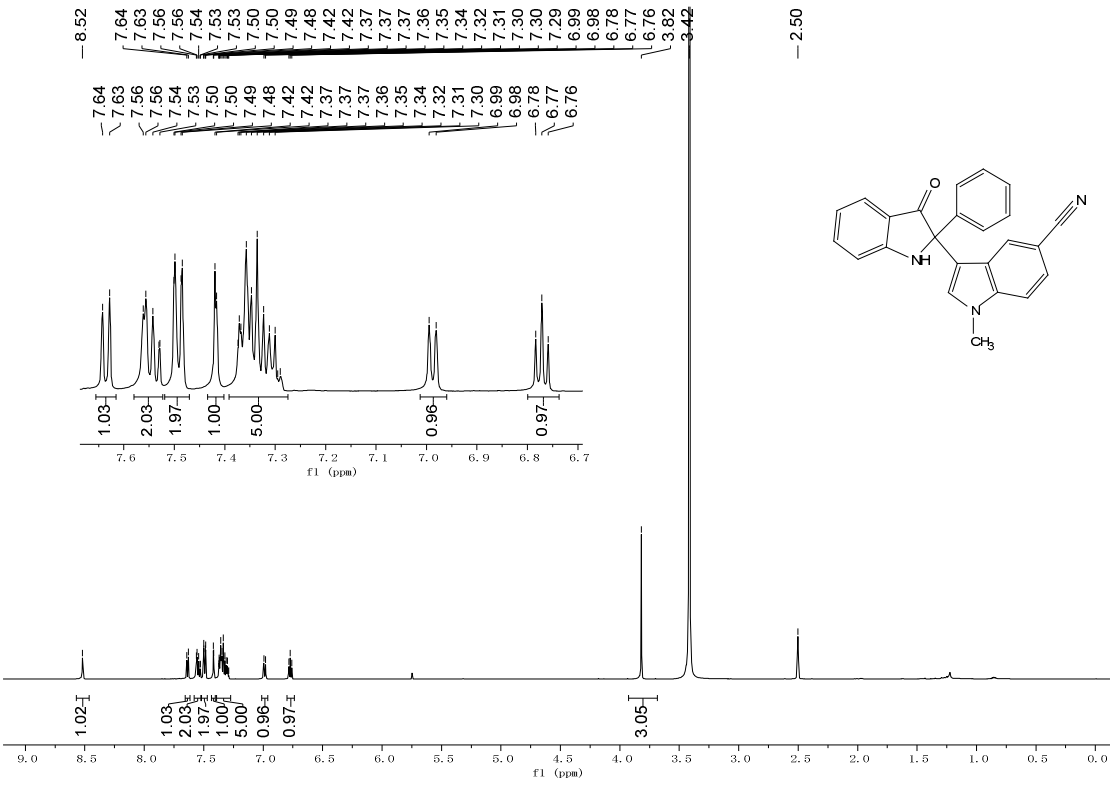


3u: ^{1}H NMR



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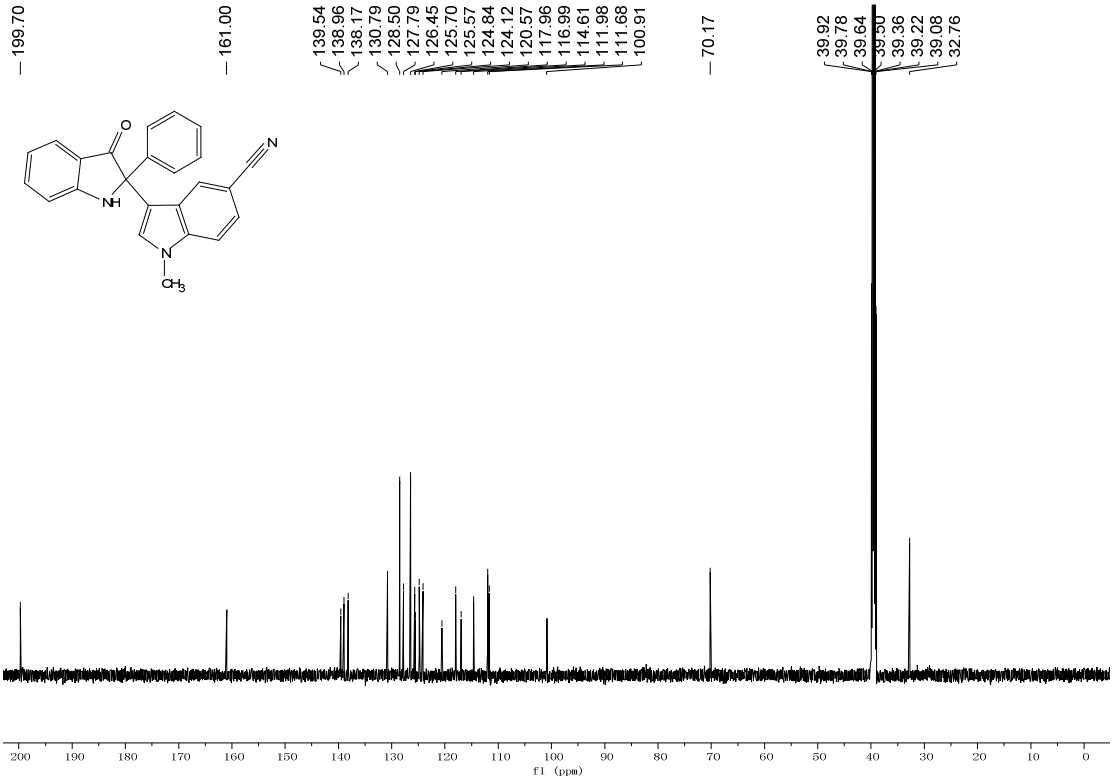
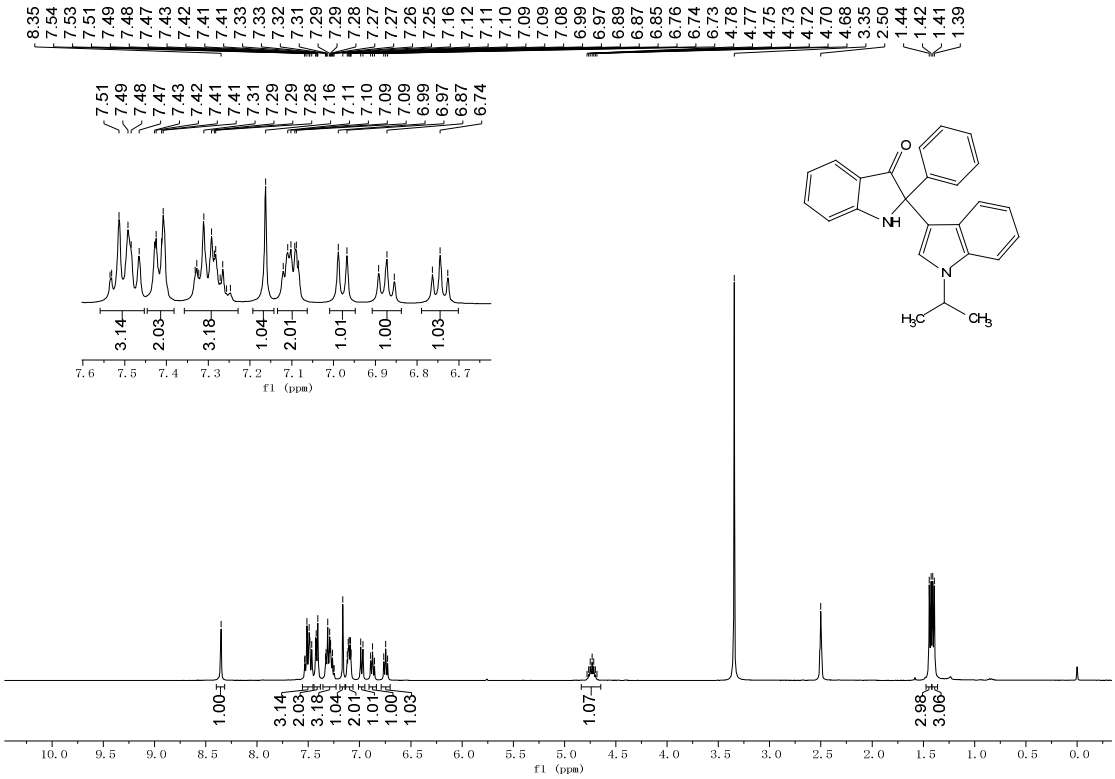
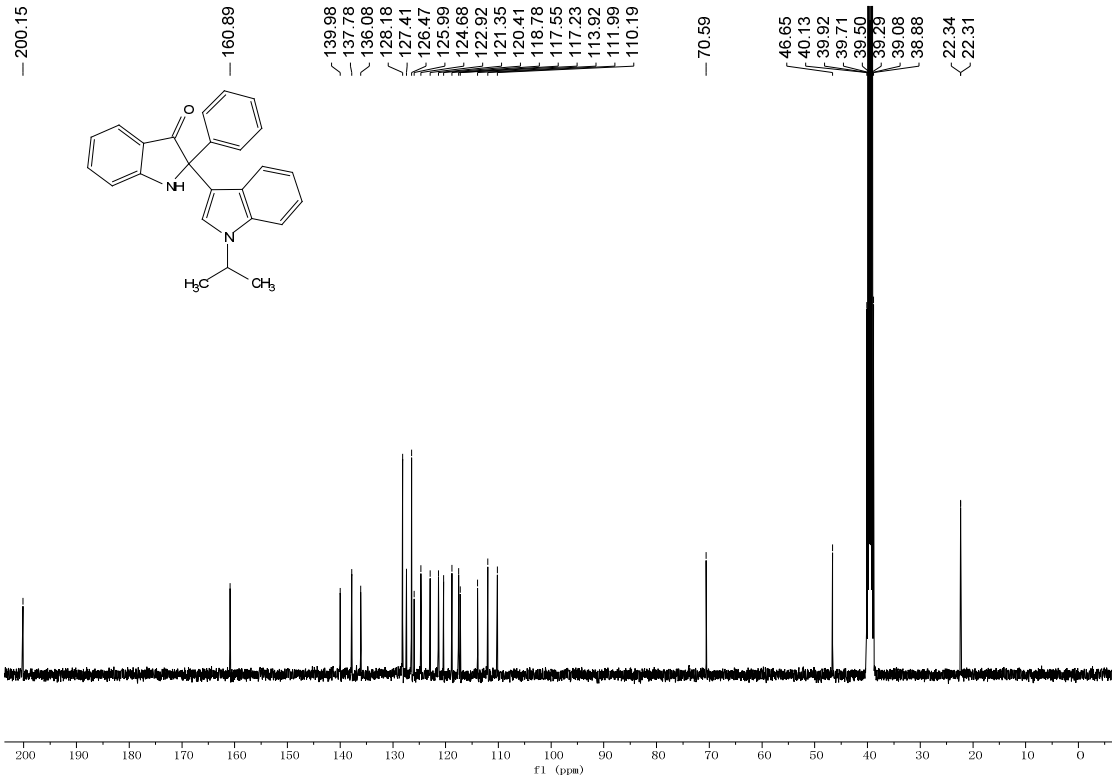


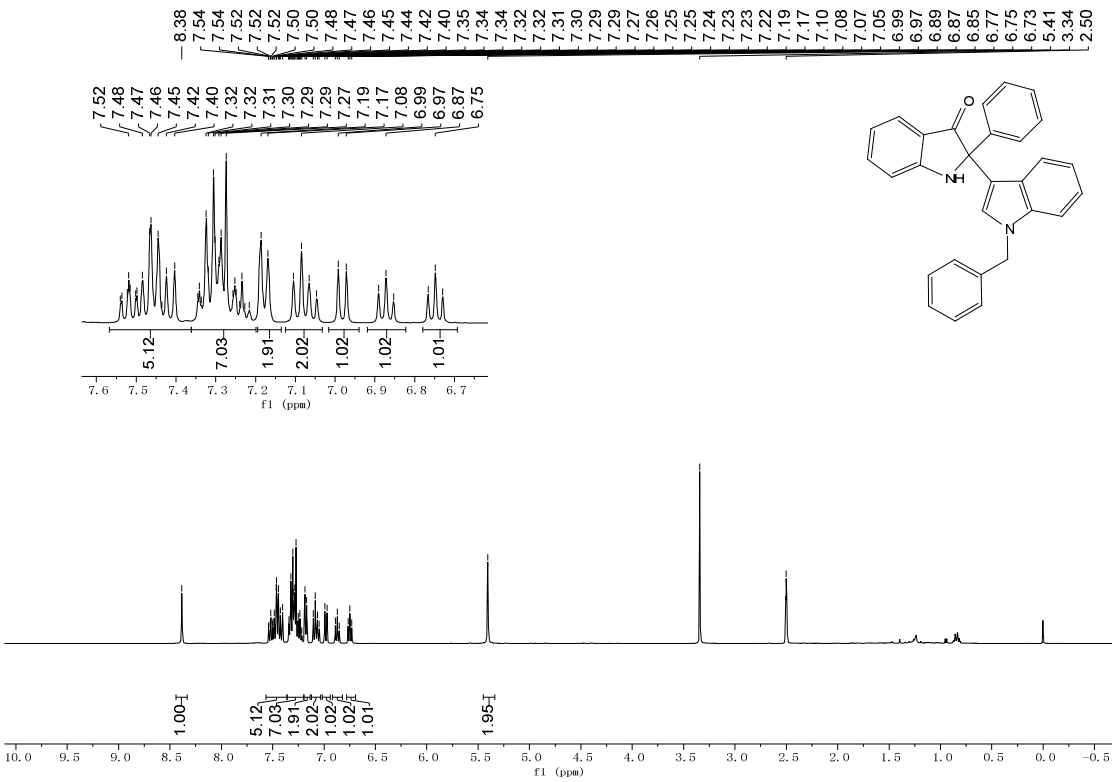
3v: ^{1}H NMR



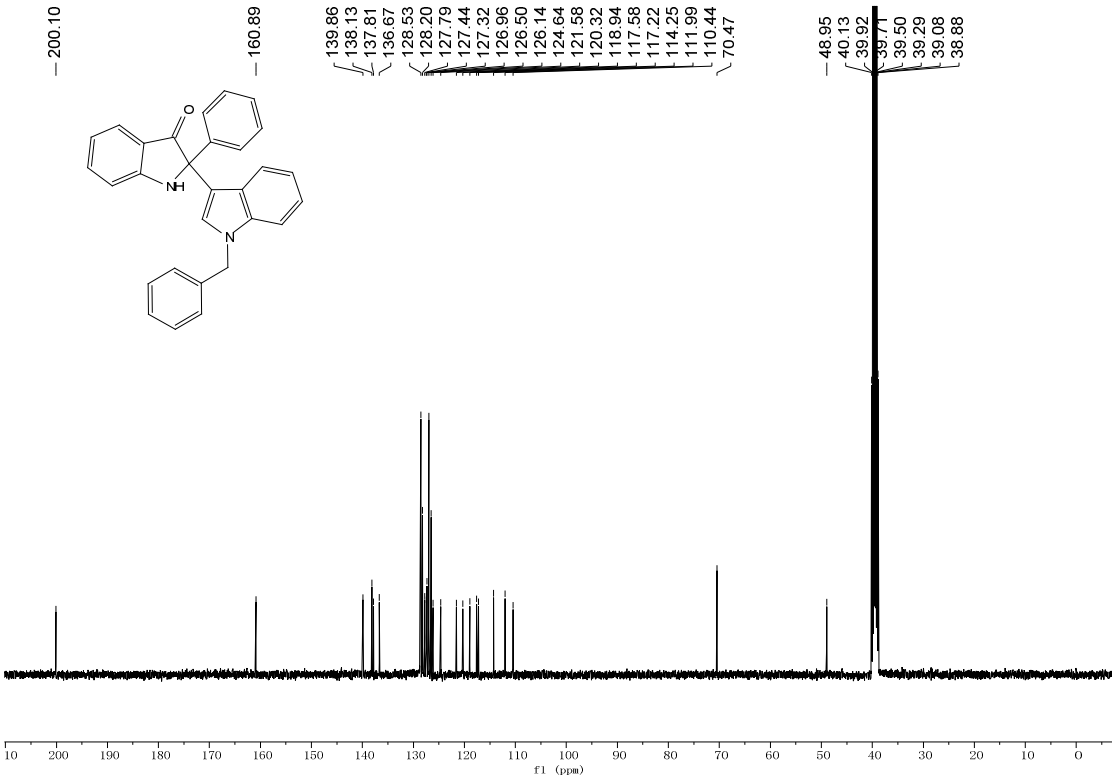
3v: ^{13}C NMR



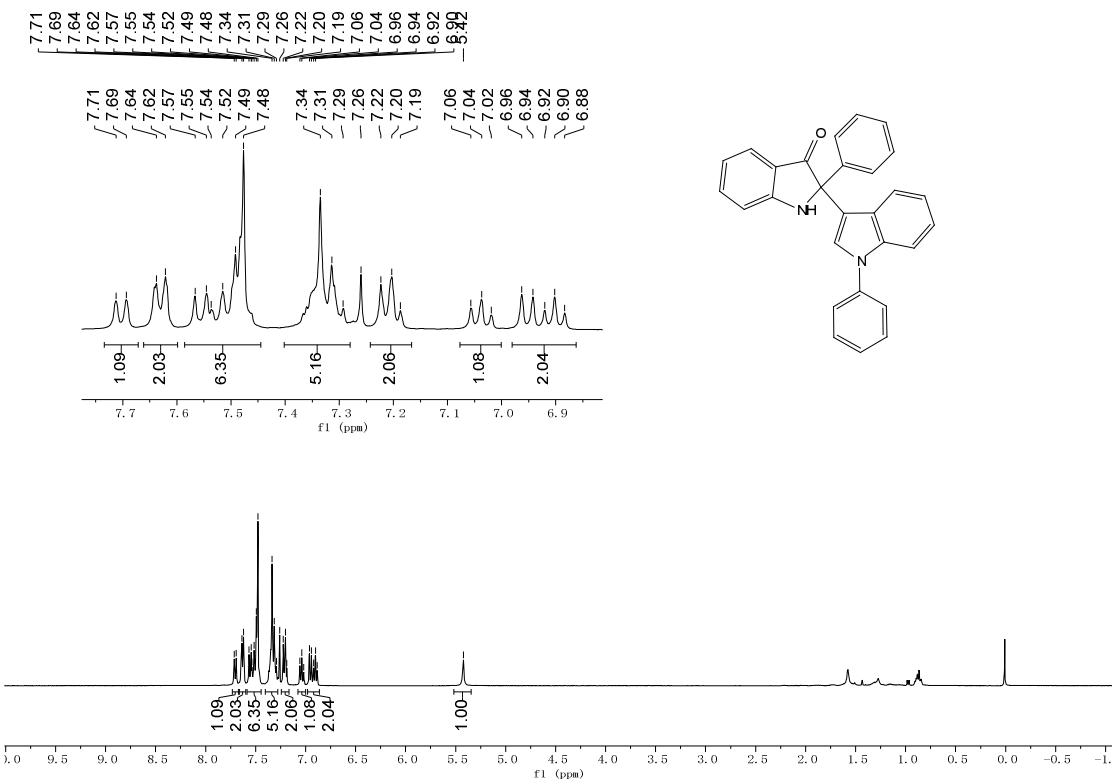
3w: ^{1}H NMR



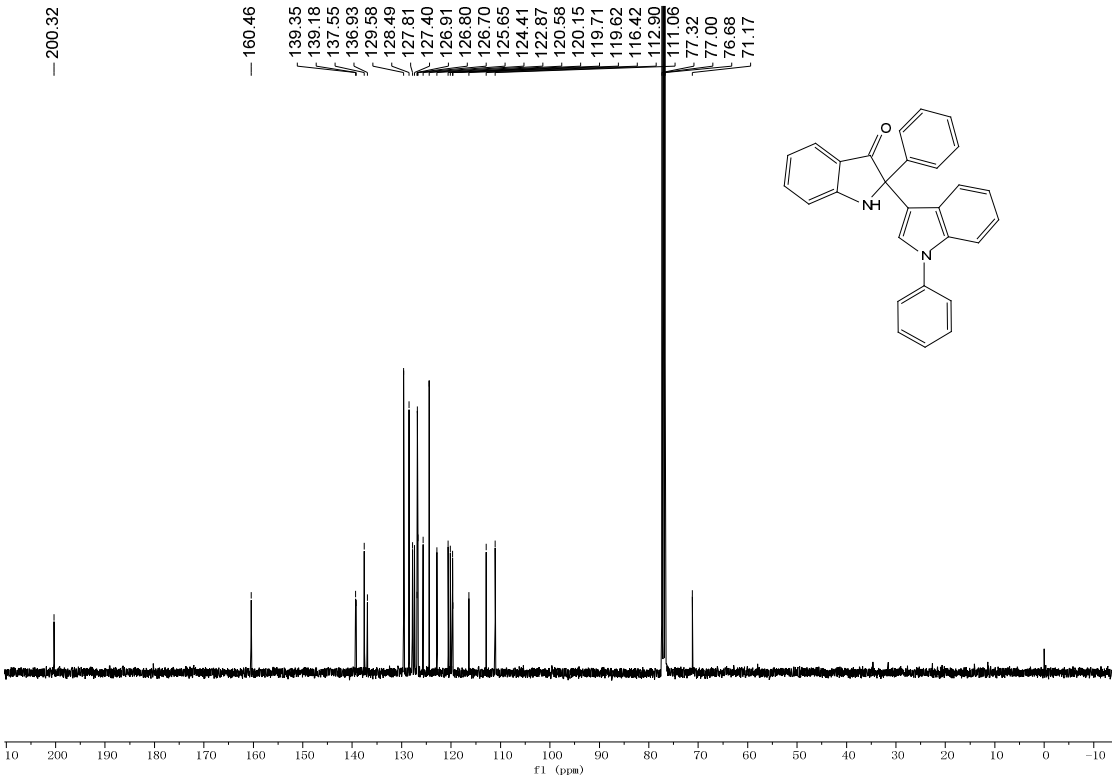
3w: ^{13}C NMR



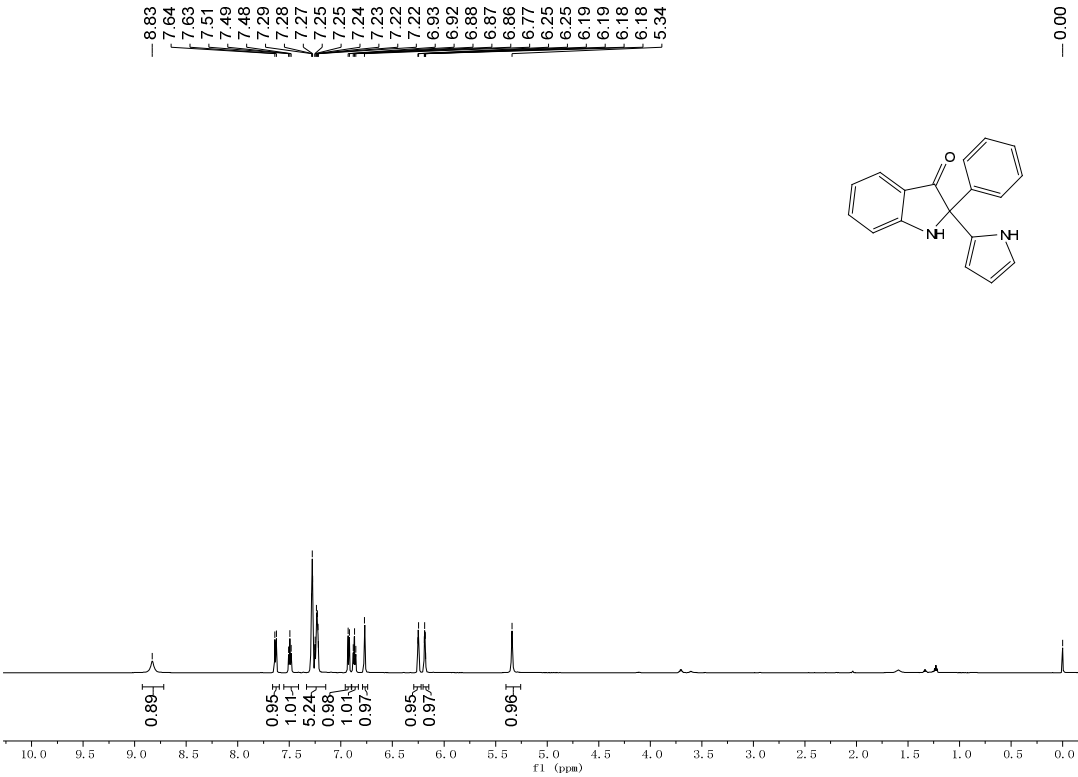
3x: ^{1}H NMR



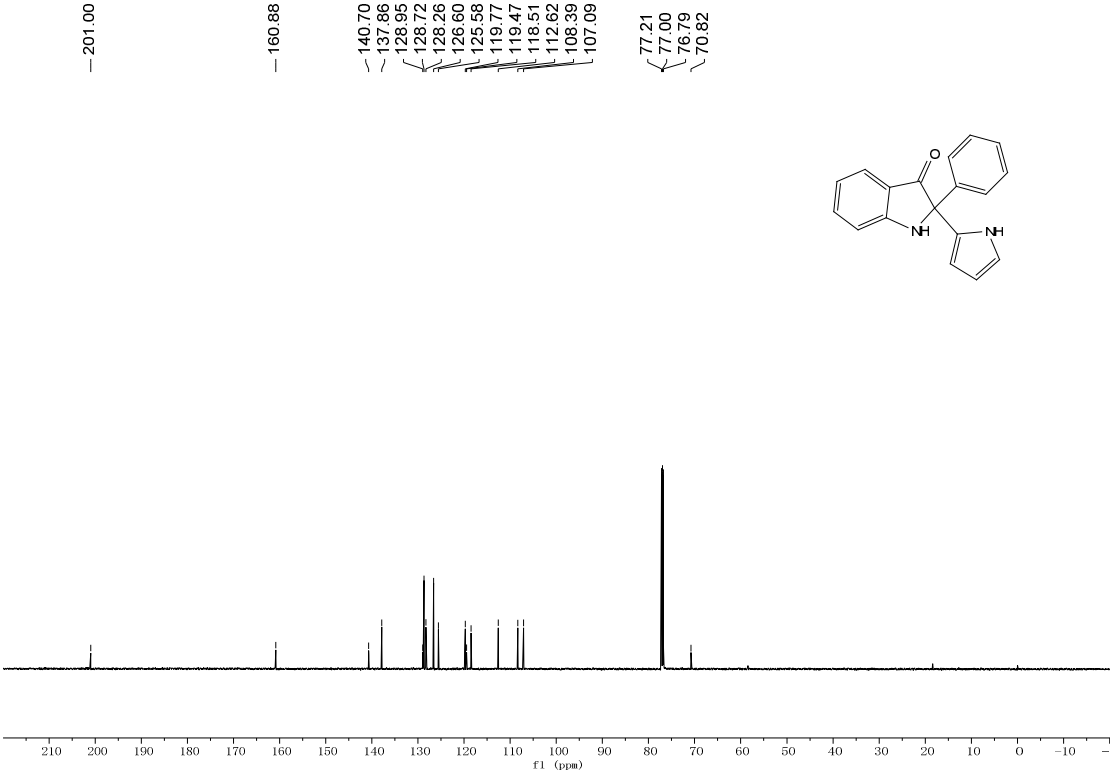
3x: ^{13}C NMR



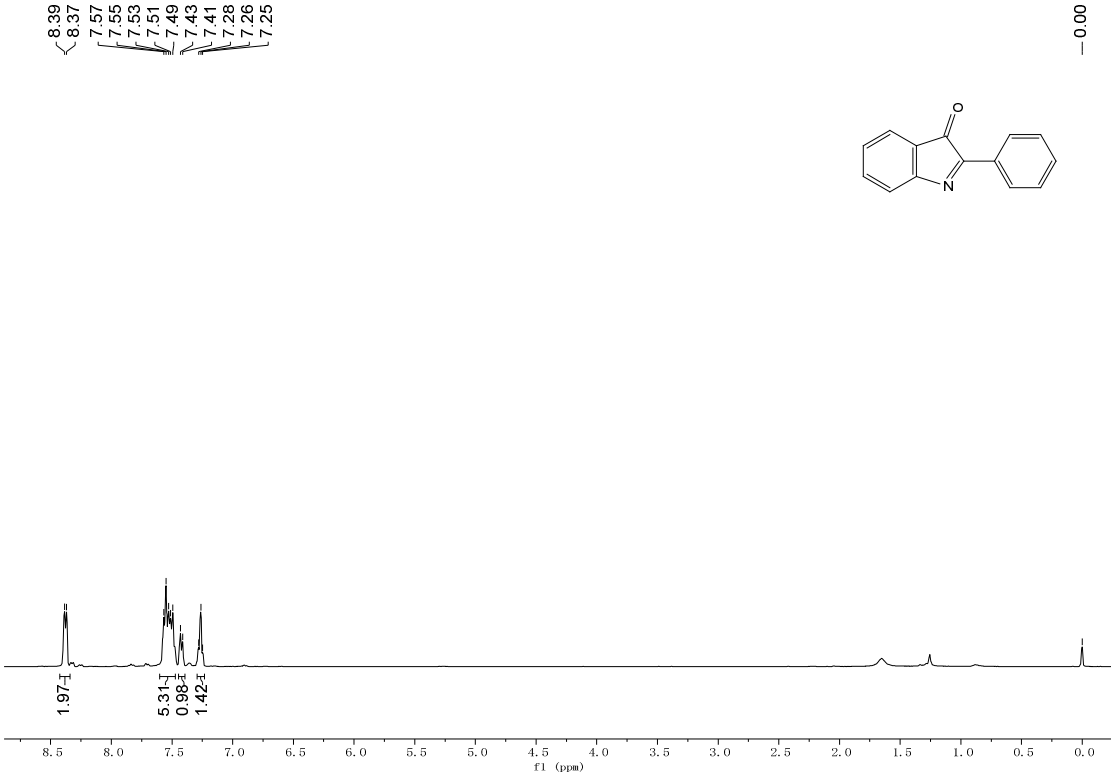
3aa: ^{1}H NMR



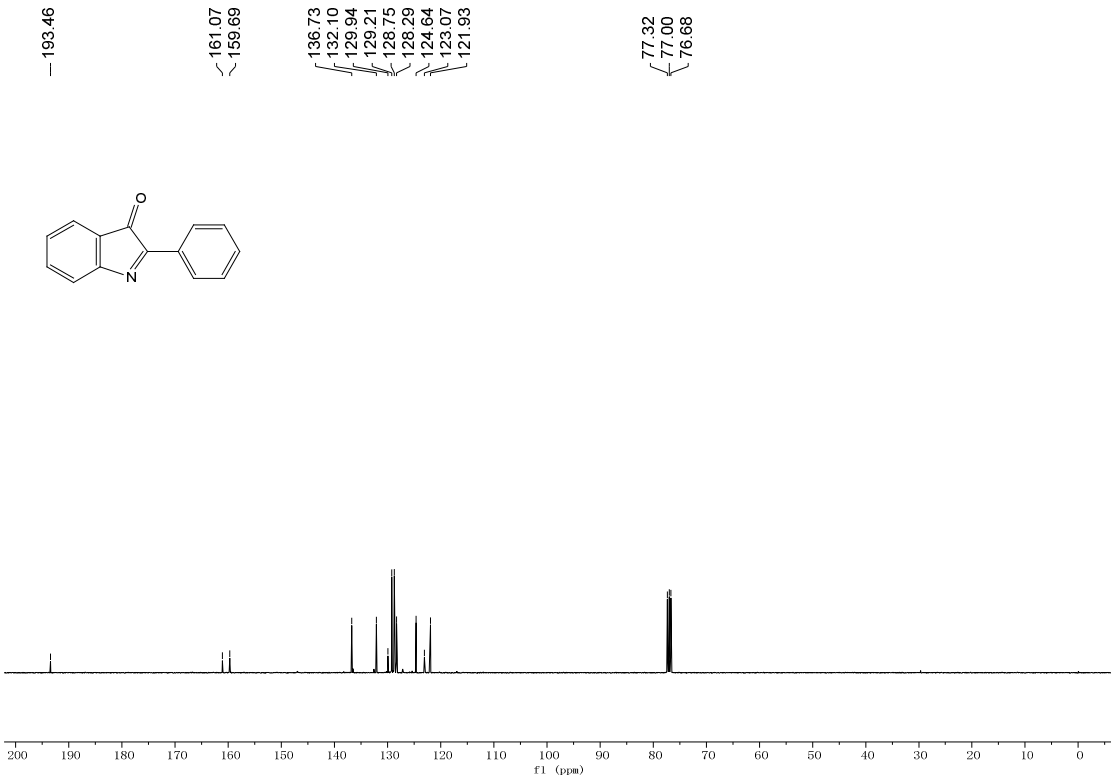
3aa: ^{13}C NMR



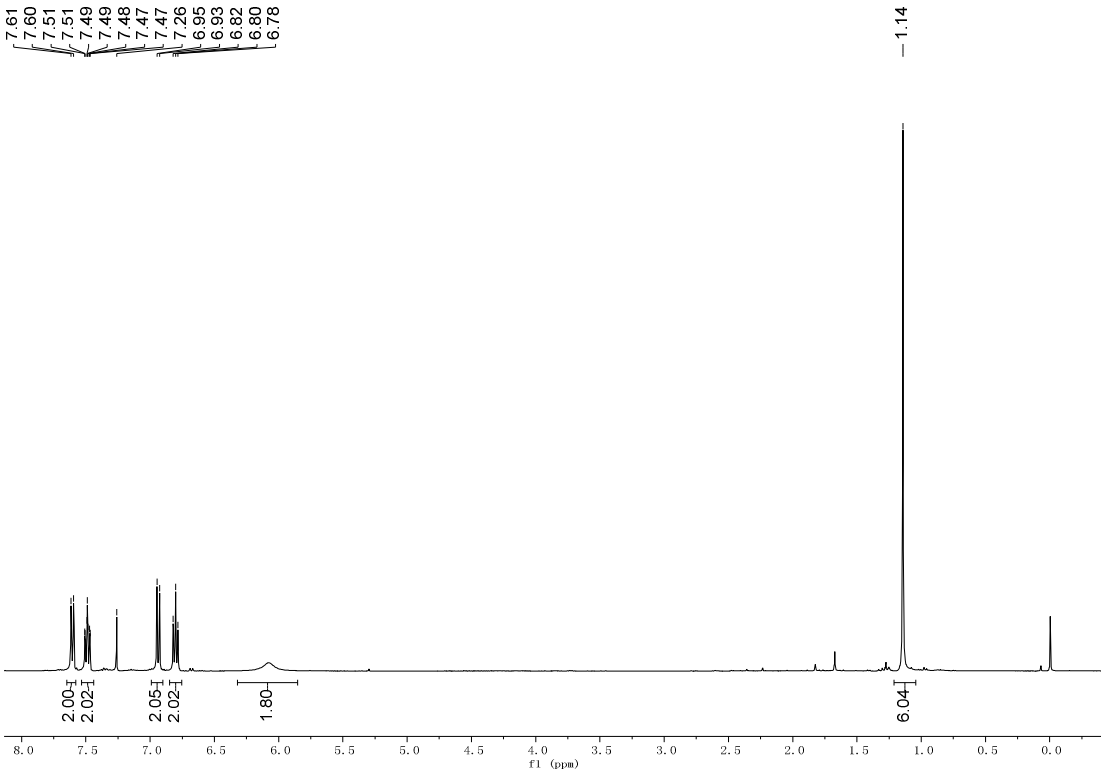
4: ^{1}H NMR



4: ^{13}C NMR



P1: ^{1}H NMR



P1: ^{13}C NMR