Supporting Information for

TEMPO-Catalyzed Oxidative Homocoupling Route to 3,2'-Biindolin-2-ones via an Indolin-3-one Intermediate

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CONTENTS

1. General Methods

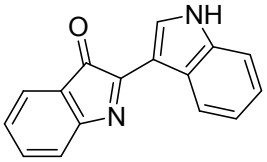
Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. Infrared spectra were measured with a Nicolet Avatar 360 FT-IR spectrometer using film KBr pellet techniques. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker spectrometers at 400 and 100 MHz, respectively. Chemical shifts were reported in ppm relative to TMS for ^{1}H and ^{13}C NMR spectra. DMSO-d_6 was used as the NMR solvent. Mass spectra were recorded with Bruker Dalton Esquire 3000 plus LC-MS apparatus. Elemental analysis was carried out on a Perkin-Elmer 240B instrument. HRFABMS spectra were recorded on a FTMS apparatus. Silica gel (300-400 mesh) was used for flash column chromatography, eluting (unless otherwise stated) with an ethyl acetate/petroleum ether (PE) (60-90 °C) mixture.

2. General Procedure for the Preparation of 9.

To a solution of indole (0.3 mmol), Ag_2CO_3 (0.105 mmol), and NaOAc (0.03 mmol) in DMF (1 mL) was added TEMPO (0.045 mmol) under an air atmosphere and the mixture was stirred at 80 ^{o}C for 12 h. The reaction mixture was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EtOAc/PE = 1:4) to yield the corresponding product **9**.

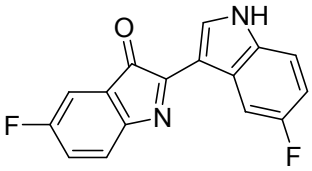
Spectroscopic Data of the Products 9.

2,3'-Bi(3*H*-indol)-3-one (**9a**)



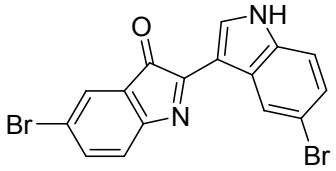
Red solid, mp: 214-215 °C (from EtOAc/PE = 1:4). IR (KBr) ν_{max}: 3187, 1719, 1604, 1559, 1447, 1368, 1240, 1135 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.14 (s, 1H, NH), 8.50 (d, J = 3.0 Hz, 1H, Ar-H), 8.40 (dd, J = 7.0, 2.5 Hz, 1H, Ar-H), 7.59-7.50 (m, 3H, Ar-H), 7.34 (d, J = 7.5 Hz, 1H, Ar-H), 7.28-7.24 (m, 2H, Ar-H), 7.18 (dt, J = 0.5, 7.5 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 195.7, 163.4, 158.5, 137.8, 137.3, 133.7, 126.8, 126.4, 124.9, 123.9, 123.0, 122.9, 122.2, 121.1, 113.0, 106.9. HRESIMS calcd for $[C_{16}H_{10}N_2O + H]^+$ 247.08714, found 247.08625.

5,5'-Difluoro-2,3'-bi(3*H*-indol)-3-one (**9b**)



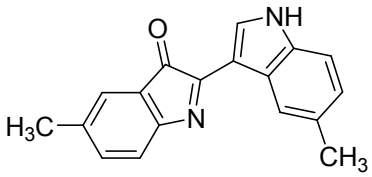
Red solid, mp: 193-195 °C (from EtOAc/PE = 1:4). IR (KBr) ν_{max}: 3460, 1723, 1626, 1572, 1469, 1358, 1263, 1125, cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.23 (s, 1H, NH), 8.49 (s, 1H, Ar-H), 8.02 (d, J = 8.7 Hz, 1H, Ar-H), 7.53 (q, J = 4.3 Hz, 1H, Ar-H), 7.38 (d, J = 4.3 Hz, 2H, Ar-H), 7.37 (s, 1H, Ar-H), 7.11 (t, J = 8.7 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 194.2, 161.2 (d, J = 237.05 Hz), 159.0 (d, J = 2.3 Hz), 158.9 (d, J = 227.8 Hz), 158.8 (d, J = 4.0 Hz), 134.9, 133.8, 126.9 (d, J = 11.0 Hz), 124.2 (d, J = 7.9 Hz), 123.0 (d, J = 23.7 Hz), 122.2 (d, J = 7.6 Hz), 114.3 (d, J = 9.8 Hz), 112.5 (d, J = 25.3 Hz), 112.0 (d, J = 25.9 Hz), 107.6 (d, J = 24.7 Hz), 106.8 (d, J = 4.3 Hz). HRESIMS calcd for $[C_{16}H_8F_2N_2O + H]^+$ 283.06829, found 283.06662.

5,5'-Dibromo-2,3'-bi(3*H*-indol)-3-one (**9c**)



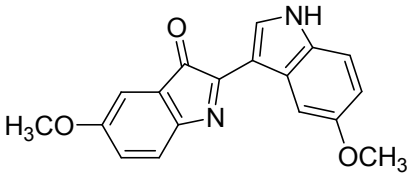
Red solid, mp: 157-159 °C (from EtOAc/PE = 1:4). IR (KBr) ν_{max}: 3409, 1728, 1560, 1440, 1351, 1286, 1104, 1019 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 12.32 (s, 1H, NH), 8.46 (s, 2H, Ar-H), 7.70 (dd, J = 8.0, 1.6 Hz, 1H, Ar-H), 7.59 (s, 1H, Ar-H), 7.49 (d, J = 8.5 Hz, 1H, Ar-H), 7.38 (dd, J = 8.5, 1.6 Hz, 1H, Ar-H), 7.32 (d, J = 8.0 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 193.3, 161.4, 157.7, 139.0, 135.6, 134.5, 127.6, 126.9, 126.0, 124.4, 124.3, 122.5, 118.4, 114.6, 114.5, 105.8. HRESIMS calcd for $[C_{16}H_8Br_2N_2O + H]^+$ 402.90816 (51%), 404.90612 (100%), found 402.90646 (51%), 404.90418 (100%).

5,5'-Dimethyl-2,3'-bi(3*H*-indol)-3-one (**9d**)



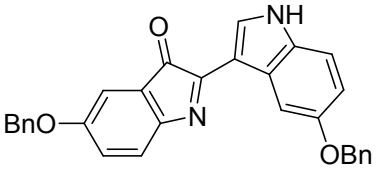
Red amorphous solid. IR (KBr) ν_{max}: 3415, 1719, 1611, 1559, 1473, 1354, 1207, 1105 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 11.99 (s, 1H, NH), 8.41 (s, 1H, Ar-H), 8.17 (s, 1H, Ar-H), 7.39 (d, J = 8.2 Hz, 1H, Ar-H), 7.31 (d, J = 7.5 Hz, 1H, Ar-H), 7.28 (s, 1H, Ar-H), 7.21 (d, J = 7.5 Hz, 1H, Ar-H), 7.07 (d, J = 8.2 Hz, 1H, Ar-H), 2.43 (s, 3H, CH_3), 2.27 (s, 3H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ 196.0, 161.3, 158.0, 137.7, 136.2, 135.5, 133.3, 131.0, 125.7, 125.4, 125.3, 123.0, 122.6, 120.7, 112.6, 106.6, 21.8, 20.9. HRESIMS calcd for $[C_{18}H_{14}N_2O + H]^+$ 275.11844, found 275.11810.

5,5'-Dimethoxy-2,3'-bi(3*H*-indol)-3-one (**9e**)



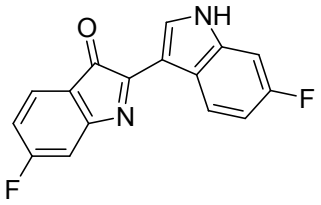
Red solid, mp: 198-199 °C (from EtOAc/PE = 1:4). IR (KBr) ν_{max}: 3429, 1724, 1619, 1557, 1477, 1360, 1216, 1135, 1029 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 11.93 (s, 1H, NH), 8.37 (d, J = 3.0 Hz, 1H, Ar-H), 7.87 (d, J = 2.5 Hz, 1H, Ar-H), 7.41 (d, J = 8.8 Hz, 1H, Ar-H), 7.24 (d, J = 7.9 Hz, 1H, Ar-H), 7.06 (s, 1H, Ar-H), 7.05 (dd, J = 3.0, 7.9 Hz, 1H, Ar-H), 6.89 (dd, J = 8.8, 2.5 Hz, 1H, Ar-H), 3.81 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ 195.9, 158.6, 157.7, 156.3, 155.8, 133.0, 132.0, 127.1, 123.9, 121.7, 121.4, 113.6, 113.2, 111.2, 106.8, 105.2, 56.3, 55.9. HRESIMS calcd for $[C_{18}H_{14}N_2O_3 + H]^+$ 307.10827, found 307.10690.

5,5'-Bis(benzyloxy)-2,3'-bi(3*H*-indol)-3-one (**9f**)



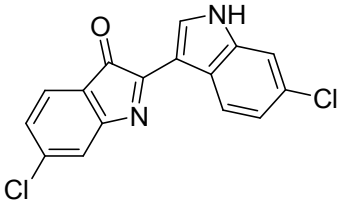
Red solid, mp: 167-169 °C (from EtOAc/PE = 1:3). IR (KBr) ν_{max}: 3419, 1719, 1617, 1562, 1470, 1382, 1270, 1126, 1018 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 11.96 (s, 1H, NH), 8.37 (d, J = 2.6 Hz, 1H, Ar-H), 7.98 (d, J = 2.3 Hz, 1H, Ar-H), 7.51 (d, J = 7.4 Hz, 2H, Ar-H), 7.46-7.38 (m, 7H, Ar-H), 7.35-7.30 (m, 2H, Ar-H), 7.26 (d, J = 8.9 Hz, 1H, Ar-H), 7.16 (s, 1H, Ar-H), 7.14 (d, J = 6.9 Hz, 1H, Ar-H), 6.98 (dd, J = 8.9, 2.3 Hz, 1H, Ar-H), 5.14 (s, 4H, OCH_2). ^{13}C NMR (100 MHz, DMSO-d_6): δ 195.8, 157.8, 157.6, 156.6, 154.8, 137.9, 137.3, 133.1, 132.2, 128.9, 128.8, 128.4, 128.3, 128.2, 128.1, 127.1, 123.8, 122.6, 121.7, 113.6, 113.5, 112.0, 107.0, 106.8, 70.5, 70.4. HRESIMS calcd for $[C_{30}H_{22}N_2O_3 + H]^+$ 459.17087, found 459.17087.

6,6'-Difluoro-2,3'-bi(3*H*-indol)-3-one (**9g**)



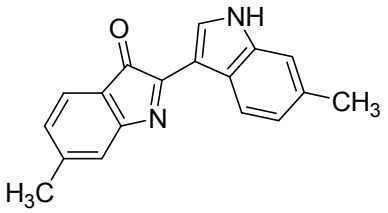
Red solid, mp: 203-205 °C (from EtOAc/PE = 1:4). IR (KBr) ν_{max}: 3381, 1717, 1615, 1563, 1422, 1366, 1232, 1122, 1084 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 12.24 (s, 1H, NH), 8.50 (s, 1H, Ar-H), 8.31 (t, J = 6.2 Hz, 1H, Ar-H), 7.55 (t, J = 6.2 Hz, 1H, Ar-H), 7.32 (d, J = 8.9 Hz, 1H, Ar-H), 7.18 (d, J = 8.9 Hz, 1H, Ar-H), 7.10 (t, J = 8.4 Hz, 1H, Ar-H), 6.95 (t, J = 8.4 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 193.3, 168.4 (d, J = 254.3 Hz), 166.2 (d, J = 13.6 Hz), 160.2 (d, J = 237.9 Hz), 159.8, 137.5 (d, J = 12.8 Hz), 135.2, 126.9 (d, J = 11.5 Hz), 124.0 (d, J = 10.0 Hz), 123.0, 119.5 (d, J = 2.5 Hz), 112.8 (d, J = 23.6 Hz), 110.6 (d, J = 24.0 Hz), 109.5 (d, J = 25.1 Hz), 106.8, 99.5 (d, J = 26.0 Hz). HRESIMS calcd for $[C_{16}H_8F_2N_2O + H]^+$ 283.06829, found 283.06872.

6,6'-Dichloro-2,3'-bi(3*H*-indol)-3-one (**9h**)



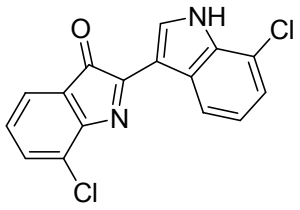
Red solid, mp: 210-212 °C (from EtOAc/PE = 1:4). IR (KBr) ν_{max}: 3397, 1717, 1559, 1406, 1356, 1256, 1128, 1057 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 12.25 (s, 1H, NH), 8.49 (s, 1H, Ar-H), 8.29 (d, J = 8.4 Hz, 1H, Ar-H), 7.55 (s, 1H, Ar-H), 7.47 (d, J = 7.6 Hz, 1H, Ar-H), 7.36 (s, 1H, Ar-H), 7.26 (d, J = 8.4 Hz, 1H, Ar-H), 7.19 (d, J = 7.6 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 193.6, 164.6, 159.5, 142.0, 137.8, 135.3, 128.6, 126.5, 125.9, 125.1, 124.1, 122.6, 121.7, 121.4, 112.9, 106.9. HRESIMS calcd for $[C_{16}H_8Cl_2N_2O + H]^+$ 315.00919 (100%), 317.00624 (64%), found 315.00980 (100%), 317.00684 (64%).

6,6'-Dimethyl-2,3'-bi(3*H*-indol)-3-one (**9i**)



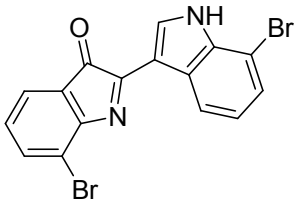
Red amorphous solid. IR (KBr) ν_{max}: 3421, 1721, 1611, 1561, 1415, 1367, 1275, 1122 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 12.03 (s, 1H, NH), 8.43 (s, 1H, Ar-H), 8.23 (d, J = 8.0 Hz, 1H, Ar-H), 7.38 (d, J = 7.3 Hz, 1H, Ar-H), 7.31 (s, 1H, Ar-H), 7.15 (s, 1H, Ar-H), 7.08 (d, J = 8.0 Hz, 1H, Ar-H), 6.96 (d, J = 7.3 Hz, 1H, Ar-H), 2.45 (s, 3H, CH_3), 2.42 (s, 3H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ 195.0, 163.9, 158.9, 149.1, 137.7, 133.6, 133.4, 126.8, 124.8, 124.2, 123.9, 122.6, 121.9, 120.6, 112.9, 107.1, 22.4, 21.8. HRESIMS calcd for $[C_{18}H_{14}N_2O + H]^+$ 275.11844, found 275.11914.

7,7'-Dichloro-2,3'-bi(3*H*-indol)-3-one (**9j**)



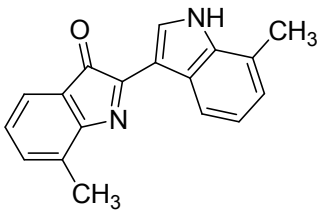
Red solid, mp: 222-224 °C (from EtOAc/PE = 1:4). IR (KBr) ν_{max}: 3417, 1719, 1566, 1412, 1369, 1263, 1125, 1013 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 12.61 (s, 1H, NH), 8.42 (s, 1H, Ar-H), 8.35 (d, J = 7.8 Hz, 1H, Ar-H), 7.58 (d, J = 7.8 Hz, 1H, Ar-H), 7.44 (d, J = 7.2 Hz, 1H, Ar-H), 7.35 (d, J = 7.6 Hz, 1H, Ar-H), 7.27 (t, J = 7.8 Hz, 1H, Ar-H), 7.17 (t, J = 7.2 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 194.0, 158.7, 137.5, 134.6, 134.2, 128.4, 128.3, 128.2, 125.5, 125.1, 123.7, 123.6. 123.5, 121.9, 117.4, 108.0. HRESIMS calcd for $[C_{16}H_8Cl_2N_2O + H]^+$ 315.00919 (100%), 317.00624 (64%), found 315.01022 (100%), 317.00720 (64%).

7,7'-Dibromo-2,3'-bi(3*H*-indol)-3-one (**9k**)



Red solid, mp: 224-226 °C (from EtOAc/PE = 1:4). IR (KBr) ν_{max}: 3418, 1717, 1563, 1430, 1368, 1261, 1114, 1048 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 12.44 (s, 1H, NH), 8.41 (s, 1H, Ar-H), 8.40 (d, J = 7.0 Hz, 1H, Ar-H), 7.71 (d, J = 7.8 Hz, 1H, Ar-H), 7.49 (d, J = 7.6 Hz, 1H, Ar-H), 7.46 (d, J = 7.0 Hz, 1H, Ar-H), 7.21 (t, J = 7.8 Hz, 1H, Ar-H), 7.09 (t, J = 7.6 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 194.3, 160.4, 158.8, 140.2, 135.8, 134.6, 128.7, 128.0, 126.8, 125.2, 123.9, 123.8, 122.4, 115.3, 108.0, 105.6. HRESIMS calcd for $[C_{16}H_8Br_2N_2O + H]^+$ 402.90816 (51%), 404.90612 (100%), found 402.90848 (51%), 404.90631 (100%).

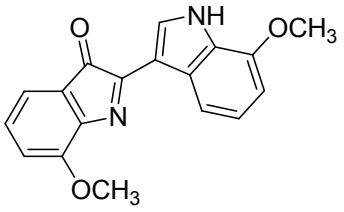
7,7'-Dimethyl-2,3'-bi(3*H*-indol)-3-one (**9l**)



Red solid, mp: 208-209 °C (from EtOAc/PE = 1:4). IR (KBr) ν_{max}: 3378, 1707, 1623, 1567, 1441, 1373, 1241, 1129 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 12.12 (s, 1H, NH), 8.41 (d, J = 3.0 Hz,

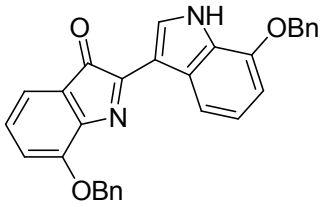
1H, Ar-H), 8.28 (d, J = 7.6 Hz, 1H, Ar-H), 7.37 (d, J = 7.6 Hz, 1H, Ar-H), 7.30 (d, J = 6.9 Hz, 1H, Ar-H), 7.16 (t, J = 7.6 Hz, 1H, Ar-H), 7.06 (d, J = 7.6 Hz, 1H, Ar-H), 7.04 (t, J = 6.9 Hz, 1H, Ar-H), 2.51 (s, 3H, CH_3), 2.42 (s, 3H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ 196.2, 161.1, 157.6, 139.1, 136.7, 132.8, 130.3, 126.4, 126.3, 124.5, 122.6, 122.4, 122.3, 122.2, 120.7, 107.6, 17.1, 15.3. HRESIMS calcd for $[C_{18}H_{14}N_2O + H]^+$ 275.11844, found 275.11698.

7,7'-Dimethoxy-2,3'-bi(3*H*-indol)-3-one (**9m**)



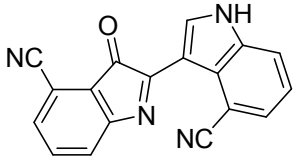
Red solid, mp: 179-181 °C (from EtOAc/PE = 1:4). IR (KBr) ν_{max}: 3348, 1726, 1622, 1561, 1442, 1371, 1263, 1129, 1069 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.29 (s, 1H, NH), 8.29 (s, 1H, Ar-H), 7.95 (d, J = 7.9 Hz, 1H, Ar-H), 7.25 (dt, J = 3.5, 2.3 Hz, 1H, Ar-H), 7.18 (t, J = 7.9 Hz, 1H, Ar-H), 7.12 (d, J = 2.3 Hz, 1H, Ar-H), 7.11 (t, J = 3.5 Hz, Ar-H), 6.84 (d, J = 7.9 Hz, 1H, Ar-H), 4.02 (s, 3H, OCH_3), 3.95 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ 196.5, 156.6, 150.9, 149.6, 146.9, 132.0, 128.2, 127.9, 127.1, 124.5, 124.0, 123.0 117.4, 115.5, 107.7, 104.8, 57.5, 55.8. HRESIMS calcd for $[C_{18}H_{14}N_2O_3 + H]^+$ 307.10827, found 307.10628.

7,7'-Bis(benzyloxy)-2,3'-bi(3*H*-indol)-3-one (**9n**)



Red solid, mp: 183-185 °C (from EtOAc/PE = 1:4). IR (KBr) ν_{max}: 3438, 1709, 1569, 1429, 1376, 1249, 1116, 1089 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.31 (s, 1H, NH), 8.32 (s, 1H, Ar-H), 7.94 (d, J = 7.7 Hz, 1H, Ar-H), 7.57 (d, J = 6.9 Hz, 2H, Ar-H), 7.52 (d, J = 6.9 Hz, 2H, Ar-H), 7.44-7.30 (m, 6H, Ar-H), 7.27 (d, J = 7.7 Hz, 1H, Ar-H), 7.14 (d, J = 6.0 Hz, 2H, Ar-H), 7.09 (d, J = 7.4 Hz, 1H, Ar-H), 6.94 (d, J = 7.4 Hz, 1H, Ar-H), 5.51 (s, 2H, OCH_2), 5.29 (s, 2H, OCH_2). ^{13}C NMR (100 MHz, DMSO-d_6): δ 195.3, 156.6, 149.9, 149.8, 145.9, 137.8, 137.5, 132.3, 129.0, 128.9. 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.3, 126.6, 124.9, 123.0, 118.2, 115.6, 107.7, 106.1, 72.0, 69.9. HRESIMS calcd for $[C_{30}H_{22}N_2O_3 + H]^+$ 459.17087, found 459.17139.

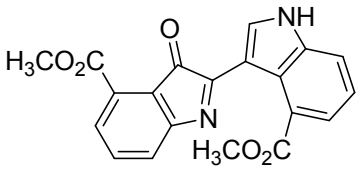
3-Oxo-2,3'-bi(3*H*-indole)-4,4'-dicarbonitrile (**9o**)



Brown amorphous solid. IR (KBr) ν_{max}: 3413, 1729, 1610, 1561, 1421, 1356, 1251, 1129, 1038 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.73 (s, 1H, NH), 8.61 (s, 1H, Ar-H), 7.89 (dd, J = 7.9, 1.0 Hz, 1H, Ar-H), 7.76 (t, J = 7.7 Hz, 1H, Ar-H), 7.73 (d, J = 7.3 Hz, 1H, Ar-H), 7.63 (d, J = 7.3 Hz, 1H, Ar-H), 7.60 (d, J = 7.7 Hz, 1H, Ar-H), 7.43 (t, J = 7.9 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 191.0, 162.6, 158.0, 138.2, 138.0, 136.7, 130.6, 130.4, 125.8, 124.6, 124.0,

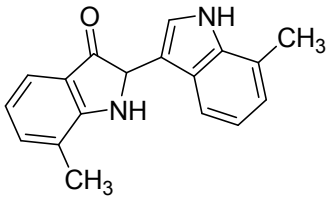
123.8, 119.6, 118.5, 115.6, 106.8, 106.4, 104.8. MS (ESI): 297 ($M+H^+$, 100), 319 ($M+Na^+$, 15). Anal calcd for $C_{18}H_8N_4O$: C, 72.97; H, 2.72; N, 18.91. Found C, 72.75; H, 3.02; N, 18.69.

Dimethyl 3-oxo-2,3'-bi(3*H*-indole)-6,6'-dicarboxylate (**9p**)



Red solid, mp: 177-179 °C (from EtOAc/PE = 1:1). IR (KBr) ν_{max}: 3306, 1728, 1561, 1428, 1355, 1279, 1139, 1022 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 12.43 (s, 1H, NH), 8.35 (d, J = 3.0 Hz, 1H, Ar-H), 7.72 (d, J = 8.0 Hz, 1H, Ar-H), 7.68 (d, J = 7.7 Hz, 1H, Ar-H), 7.50 (d, J = 7.4 Hz, 1H, Ar-H), 7.45 (d, J = 7.4 Hz, 2H, Ar-H), 7.33 (t, J = 7.7 Hz, 1H, Ar-H), 3.87 (s, 3H, OCH_3), 2.72 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ 191.5, 169.3, 166.0, 162.9, 159.6, 138.1, 137.6, 134.6, 130.0, 126.9, 126.6, 124.1, 123.0, 122.8, 122.7, 120.4, 116.2, 106.9, 52.9, 52.3. HRESIMS calcd for $[C_{20}H_{14}N_2O_5 - H]^+$ 361.08245, found 361.08298.

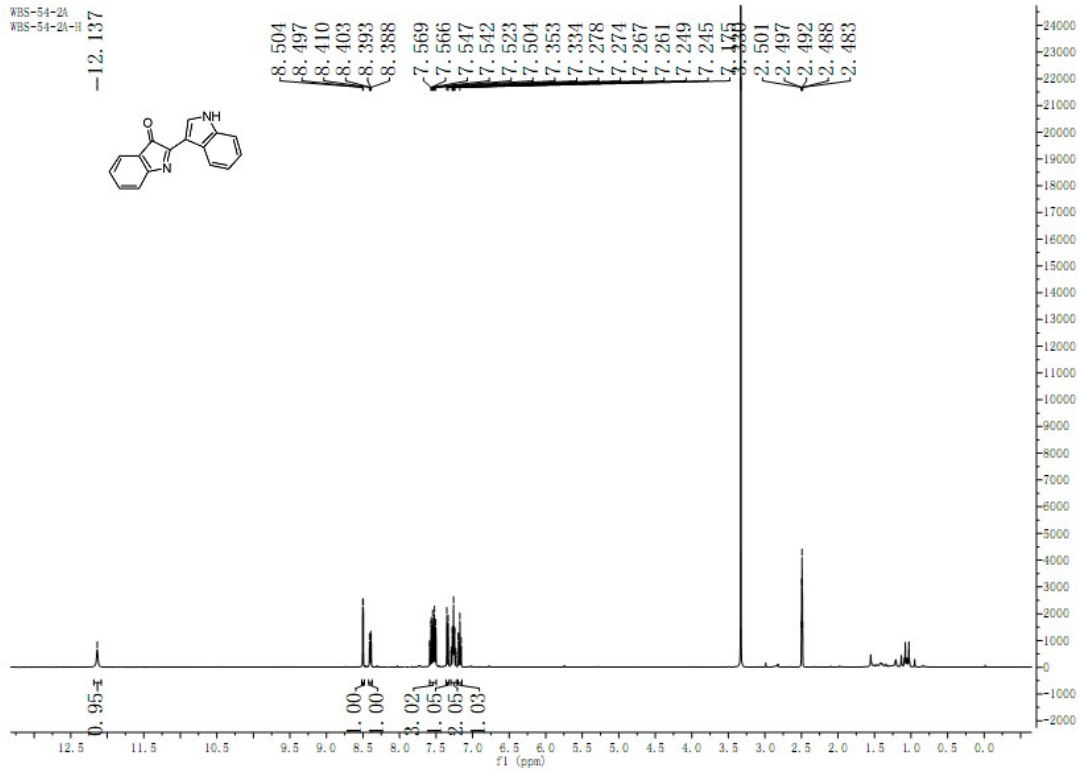
7-Methyl-2-(7-methyl-1*H*-indol-3-yl)indolin-3-one (**13**)

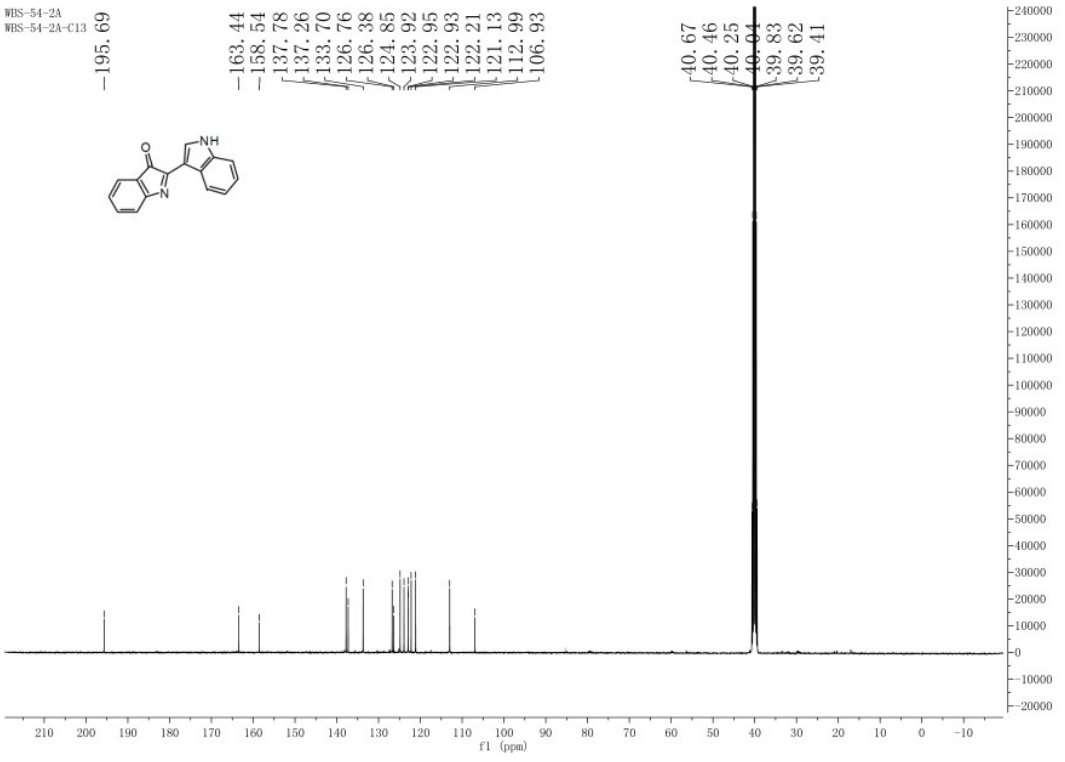


White amorphous solid. IR (KBr) ν_{max}: 3375, 1716, 1620, 1569, 1236, 1125 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 12.13 (s, 1H, NH), 7.72 (s, 1H, Ar-H), 7.60 (s, 1H, Ar-H), 7.21 (s, 1H, Ar-H), 7.12 (d, J = 6.3 Hz, 1H, Ar-H), 6.99 (s, 1H, Ar-H), 6.81 (s, 1H, Ar-H), 6.60 (d, J = 6.3 Hz, 1H, Ar-H), 5.93 (s, 2H), 3.94 (s, 3H, CH_3), 3.83 (s, 3H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ 192.1, 147.4, 146.7, 139.6, 133.9, 128.4, 127.0, 123.7, 122.7, 121.4, 117.2, 114.6, 114.5, 114.4, 113.0, 104.0, 56.2, 55.8. MS (ESI): 277 ($M+H^+$, 100). Anal calcd for $C_{18}H_{16}N_2O_1$: C, 78.24; H, 5.84; N, 10.14. Found C, 77.89; H, 6.07; N, 9.83.

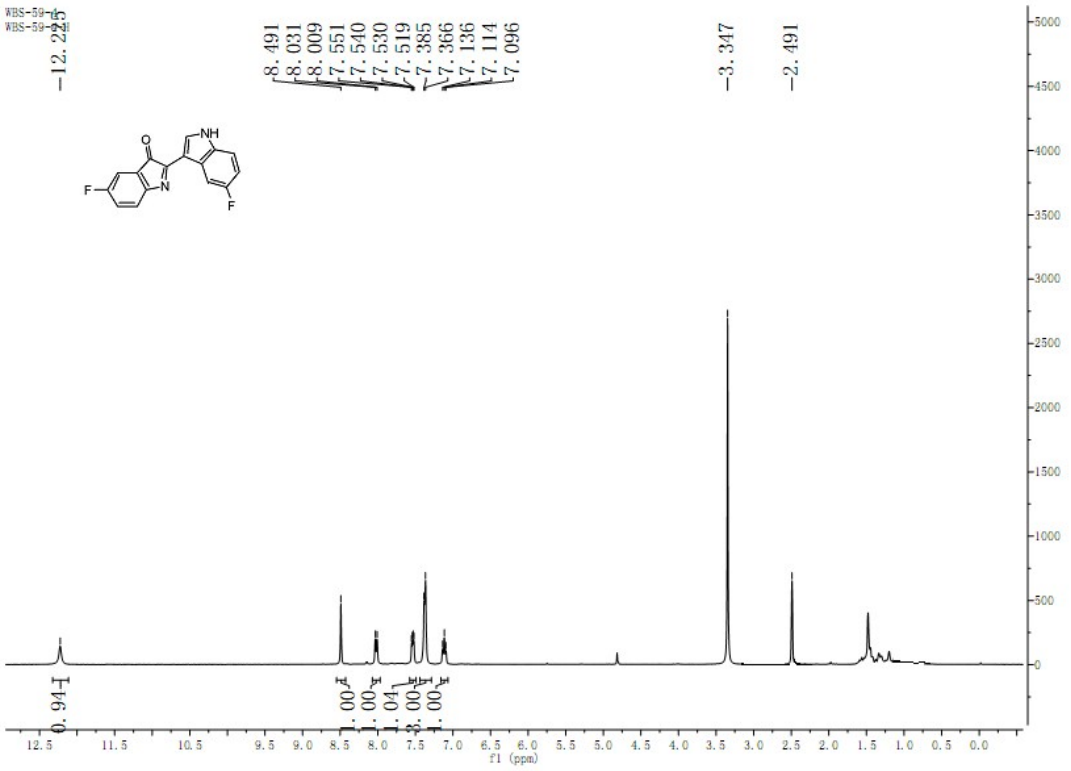
3. Copies of ^1H, ^{13}C Spectra

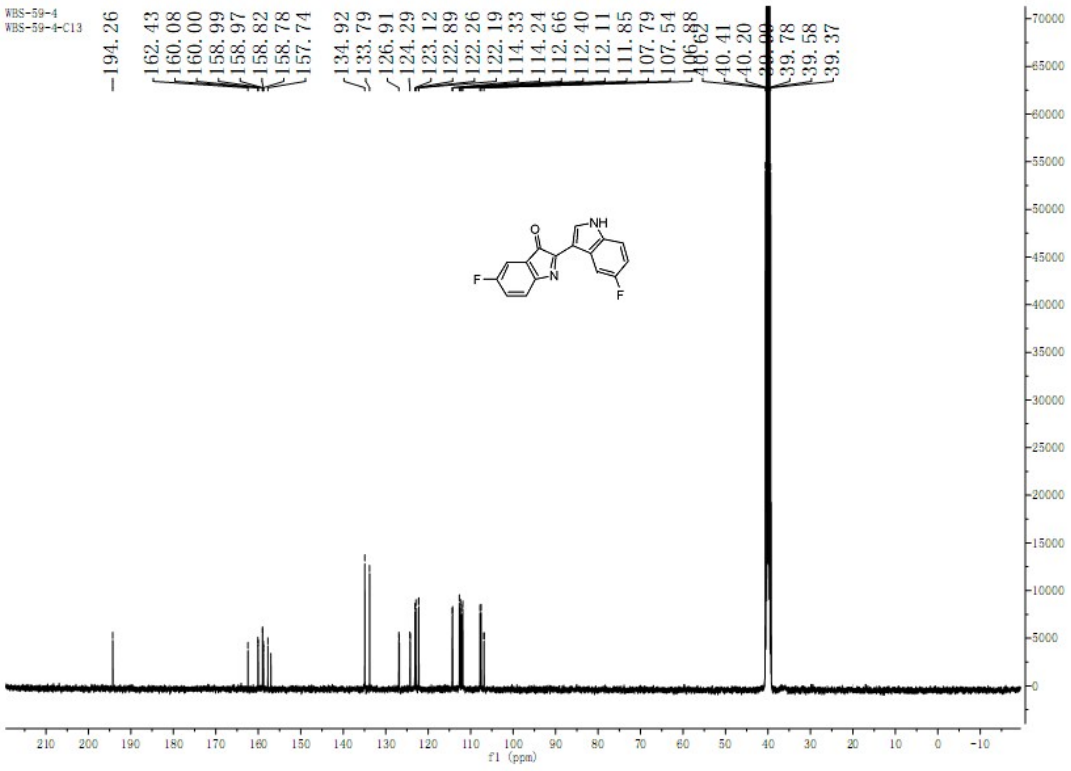
^{1}H and ^{13}C NMR Spectra for **9a**



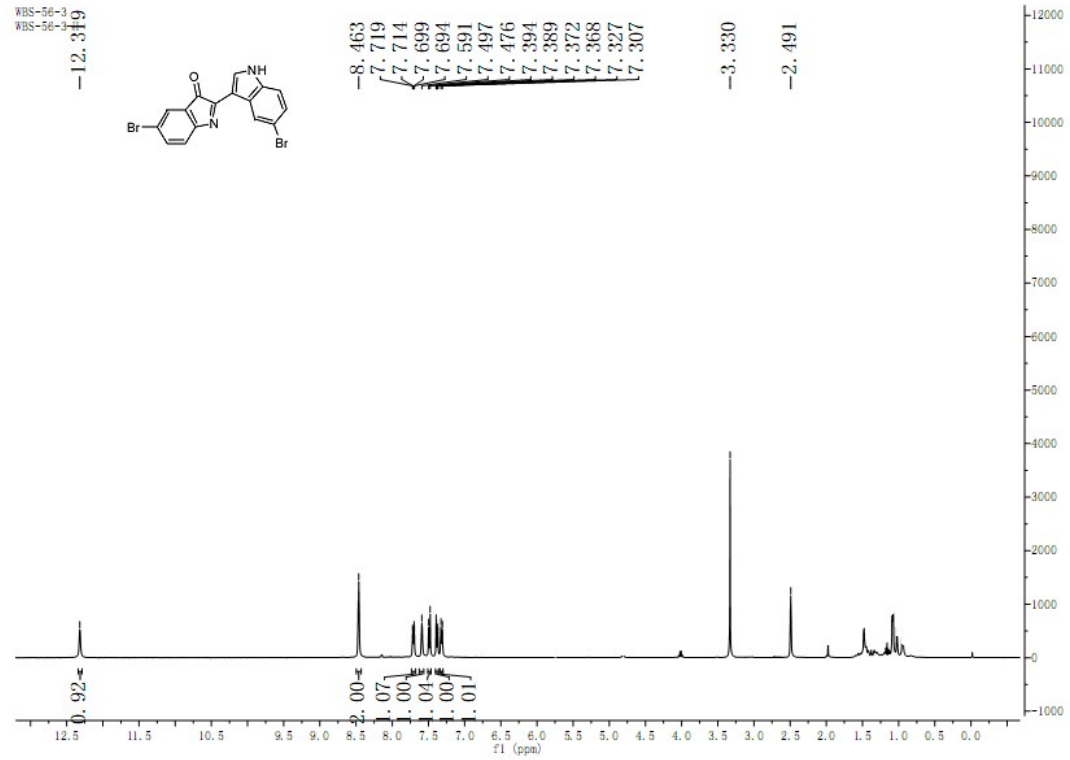


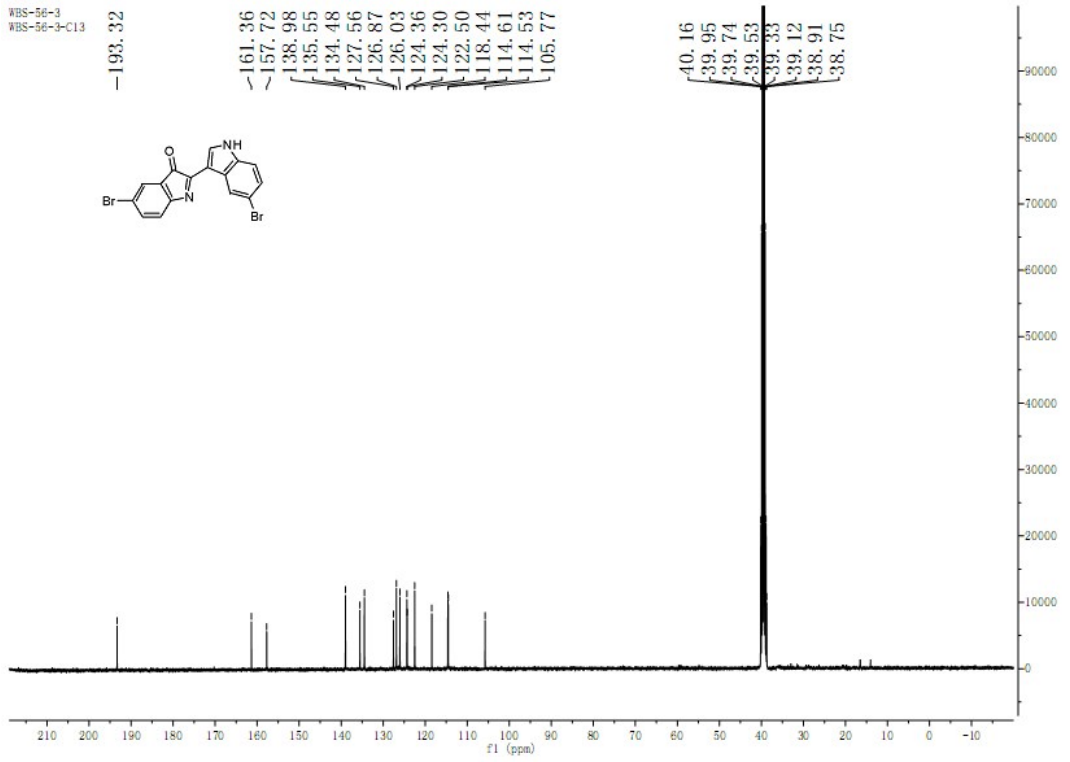
^{1}H and ^{13}C NMR Spectra for **9b**



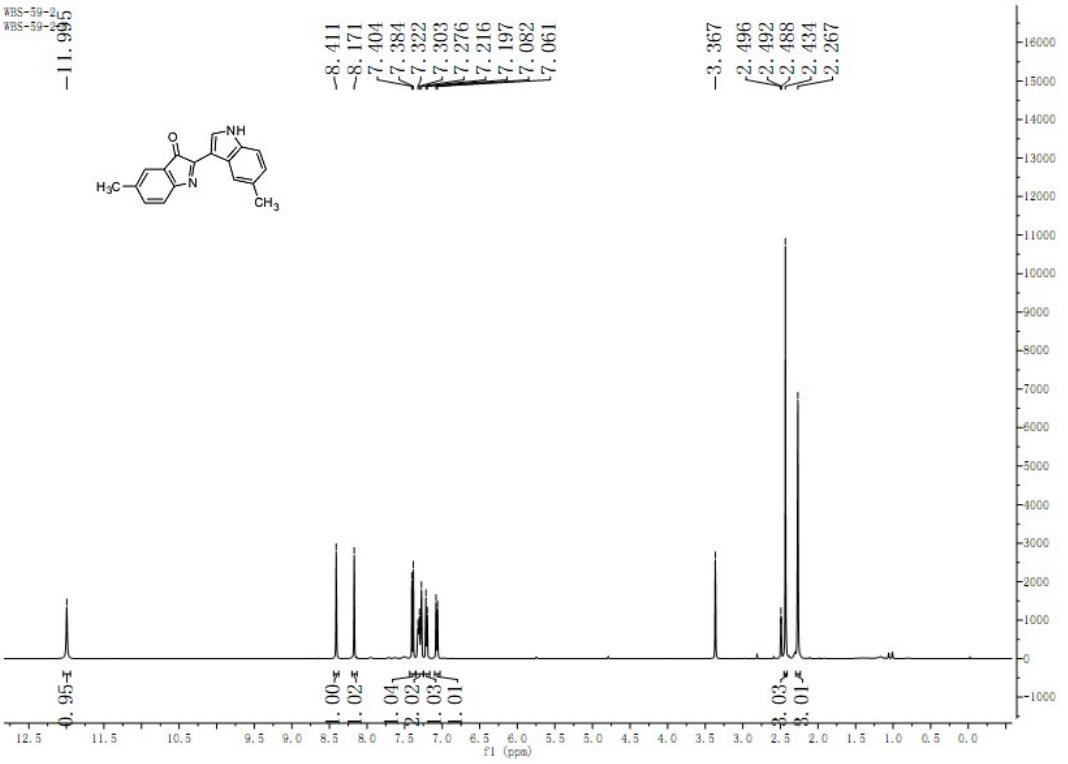


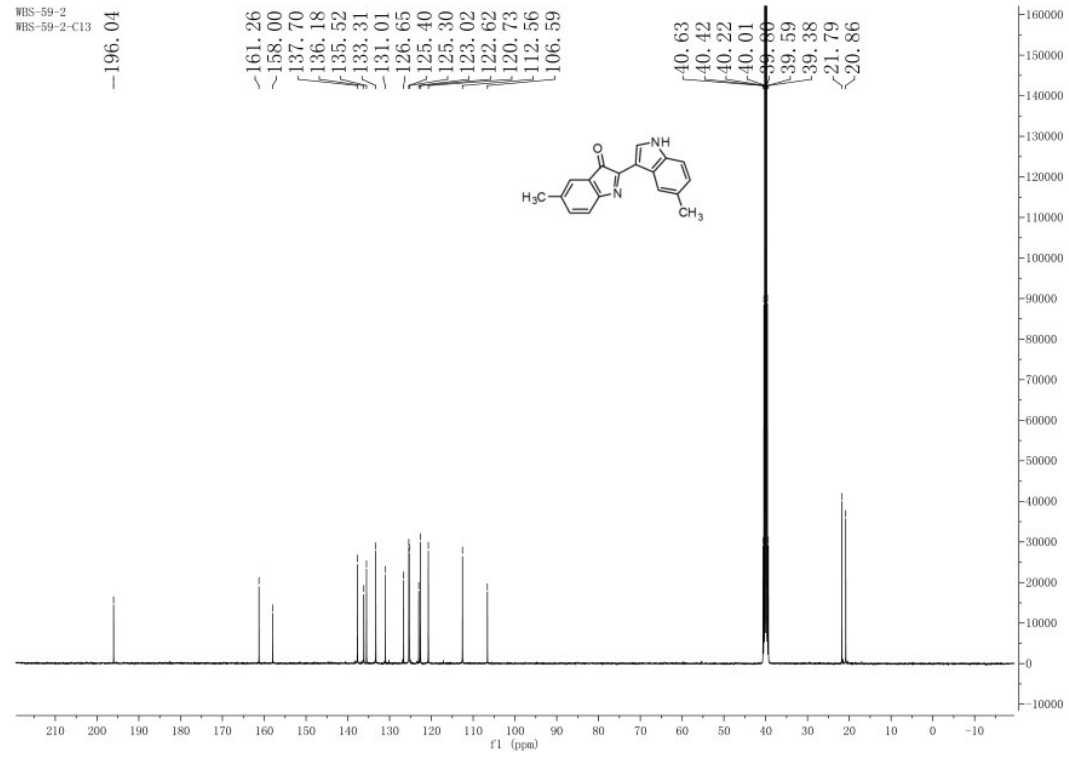
^{1}H and ^{13}C NMR Spectra for **9c**



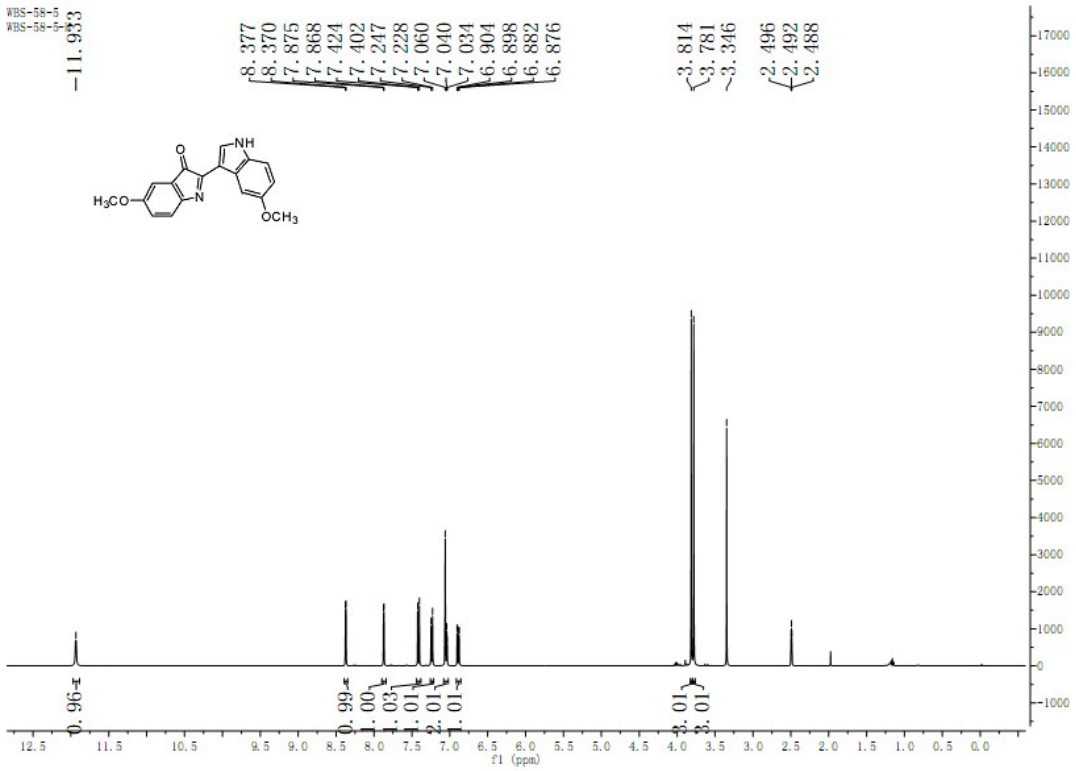


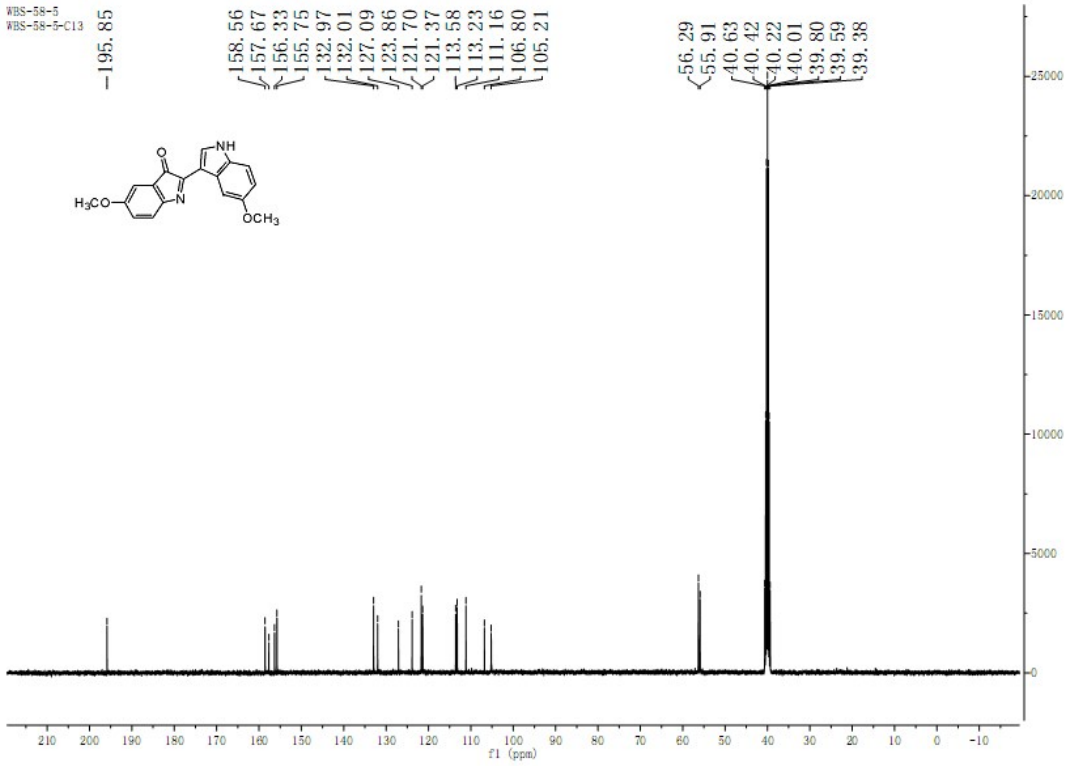
^{1}H and ^{13}C NMR Spectra for **9d**



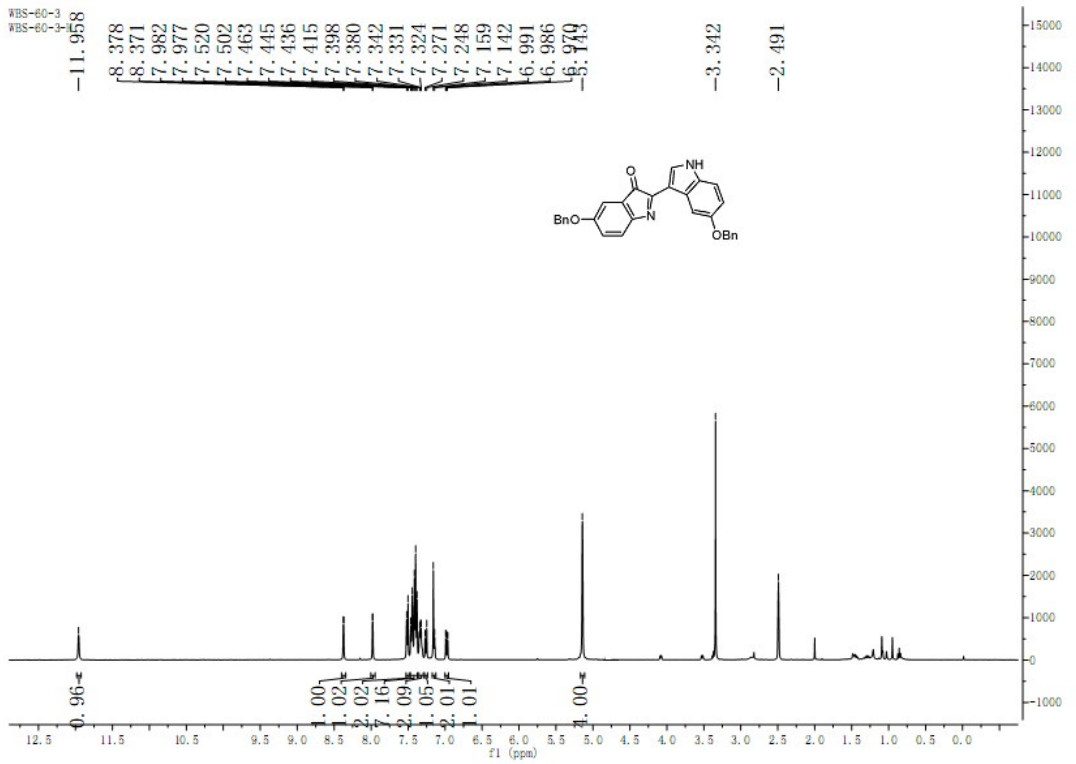


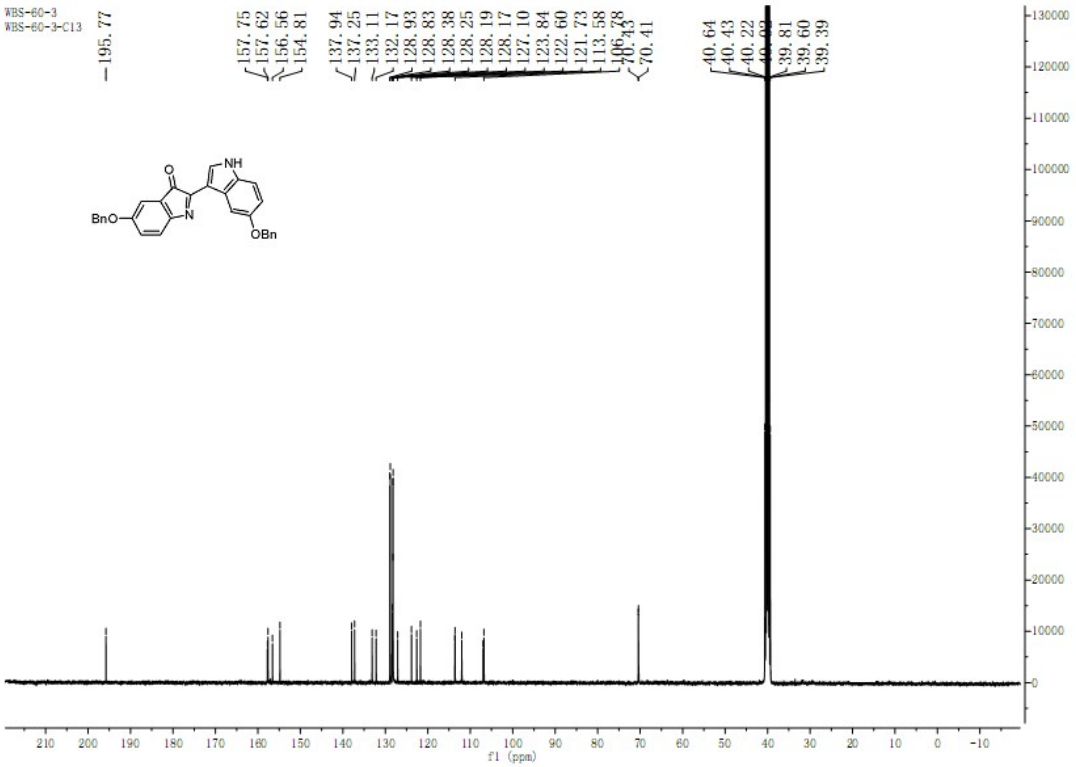
^{1}H and ^{13}C NMR Spectra for **9e**



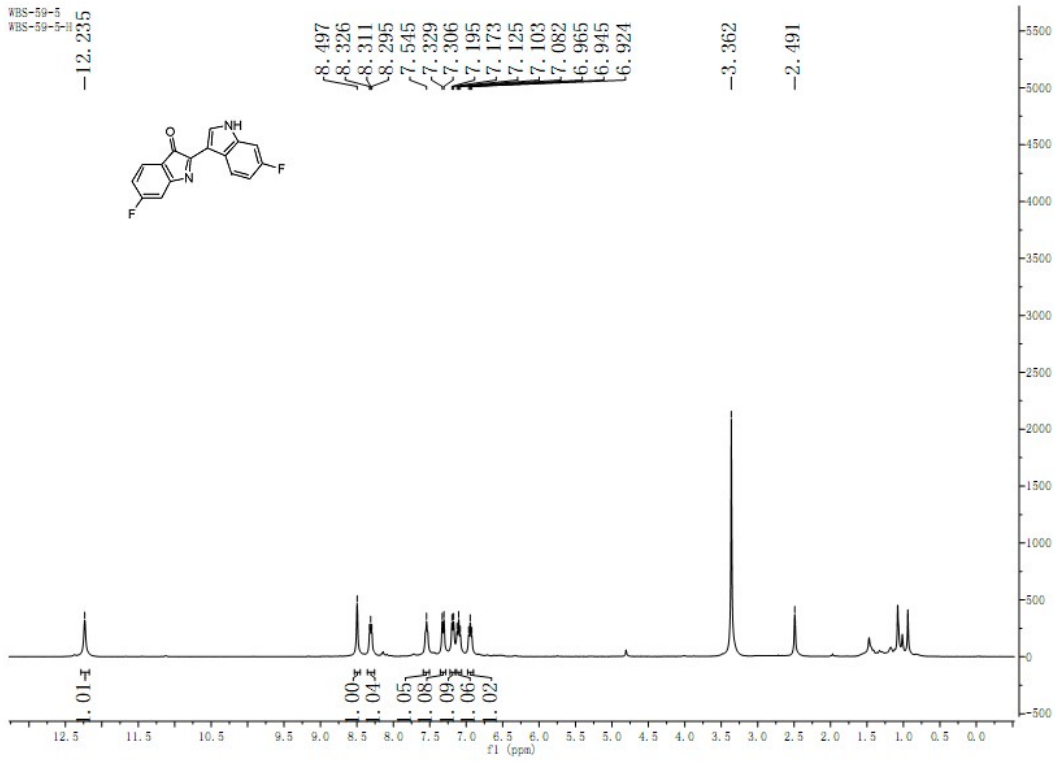


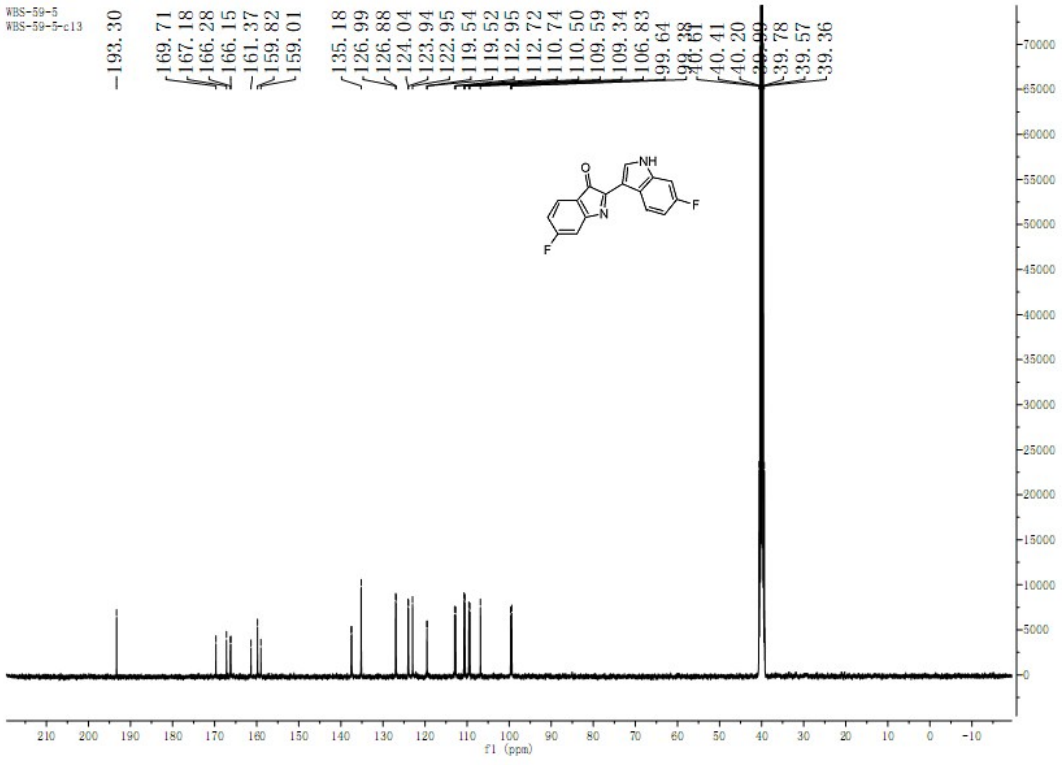
^{1}H and ^{13}C NMR Spectra for **9f**



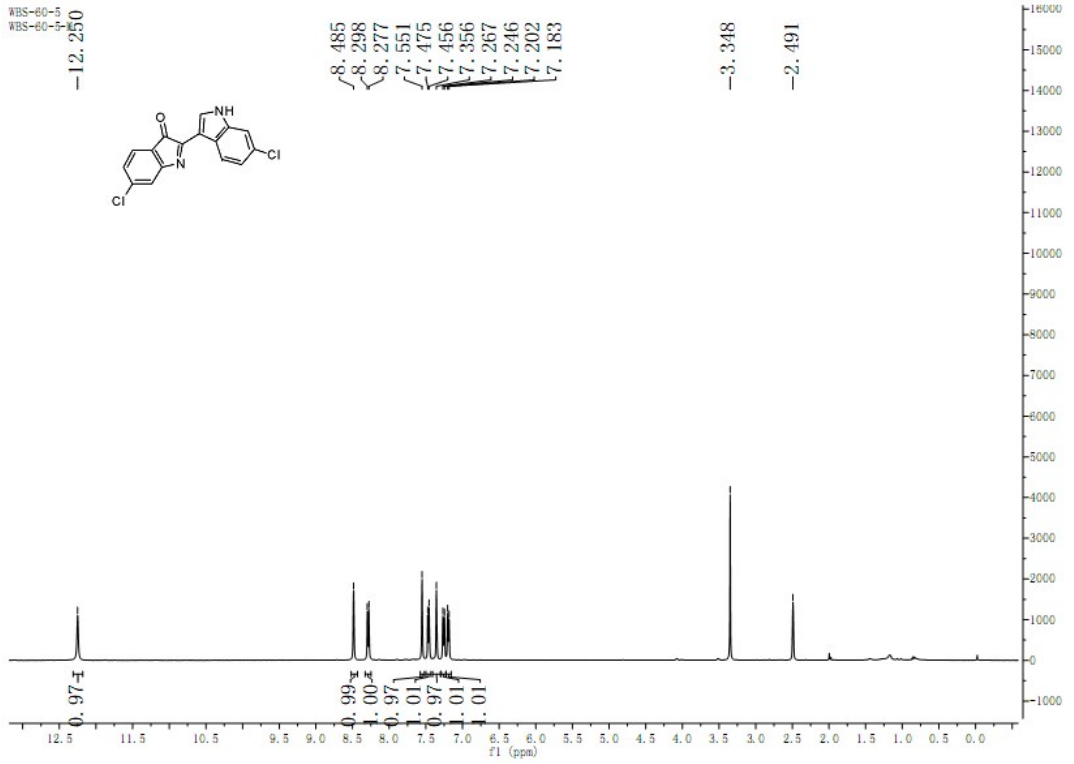


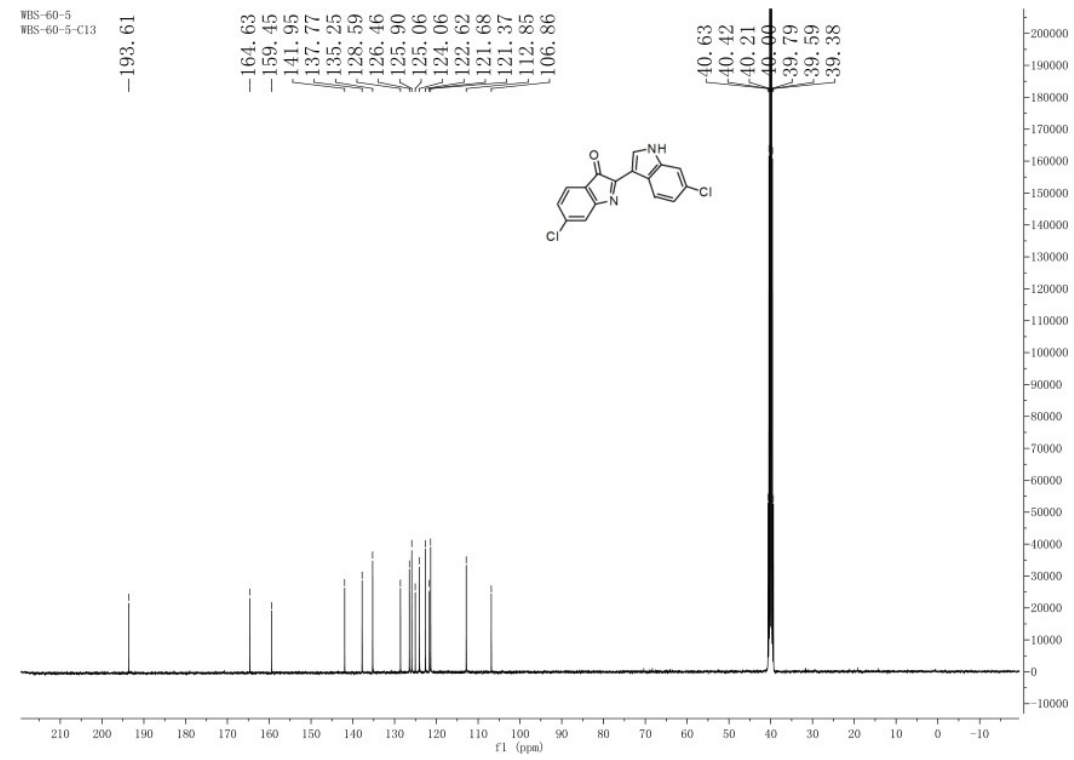
^{1}H and ^{13}C NMR Spectra for **9g**



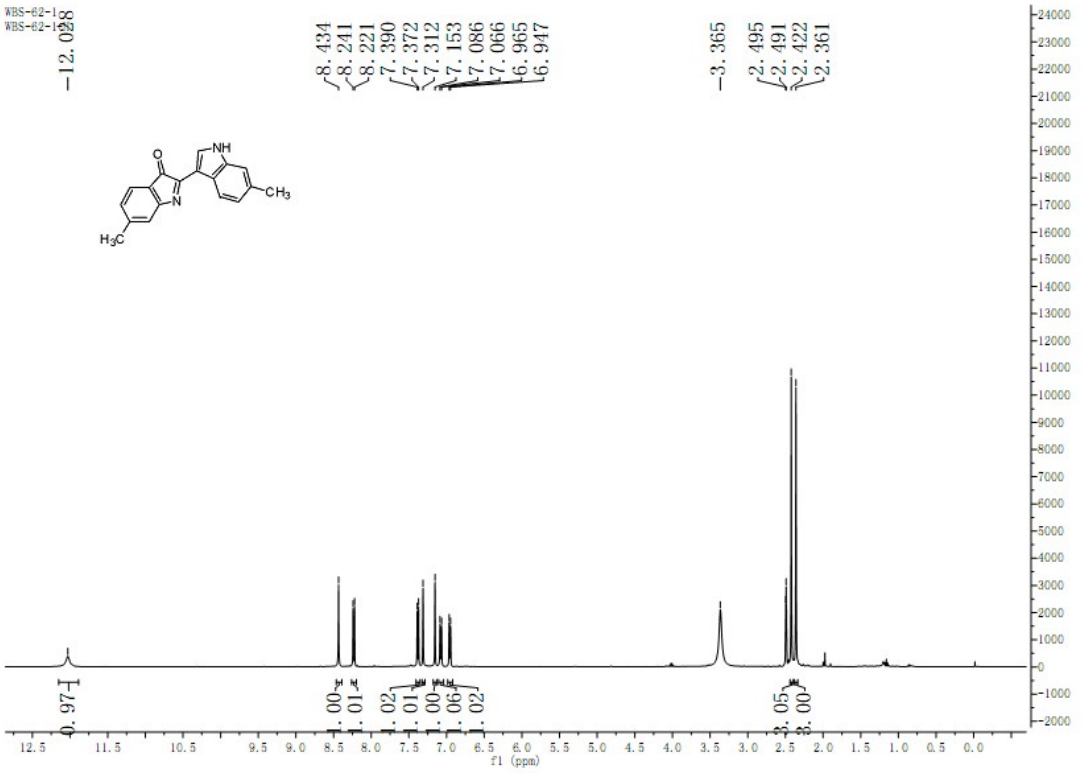


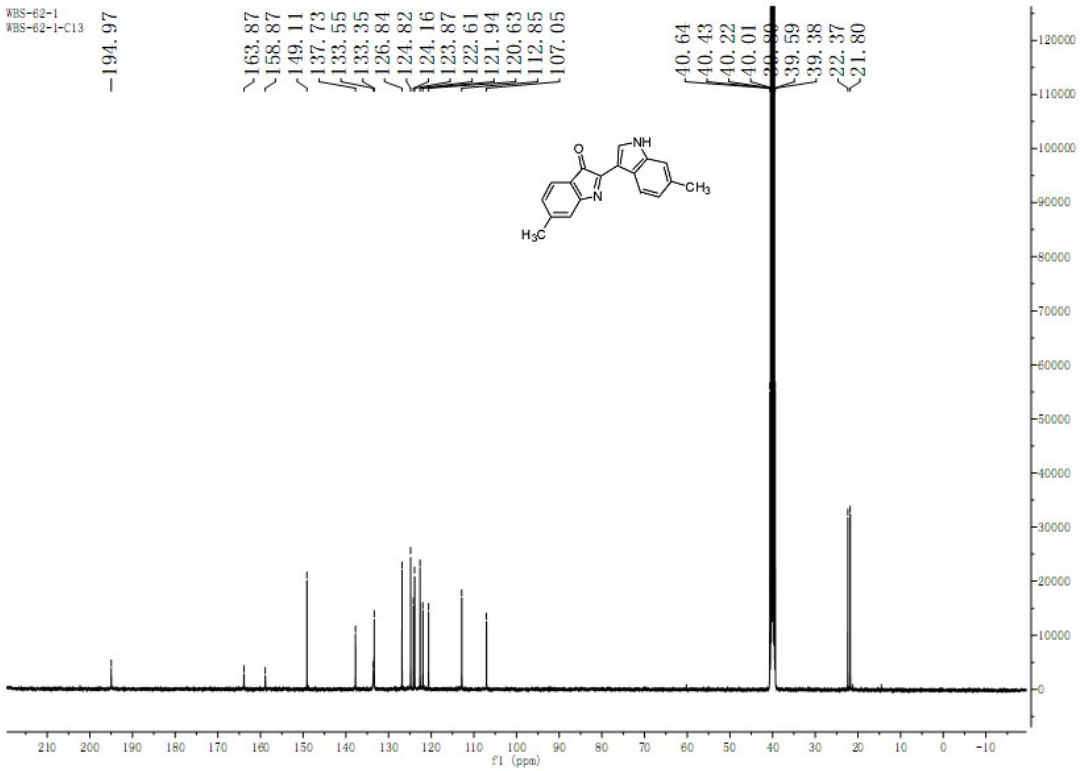
^{1}H and ^{13}C NMR Spectra for **9h**



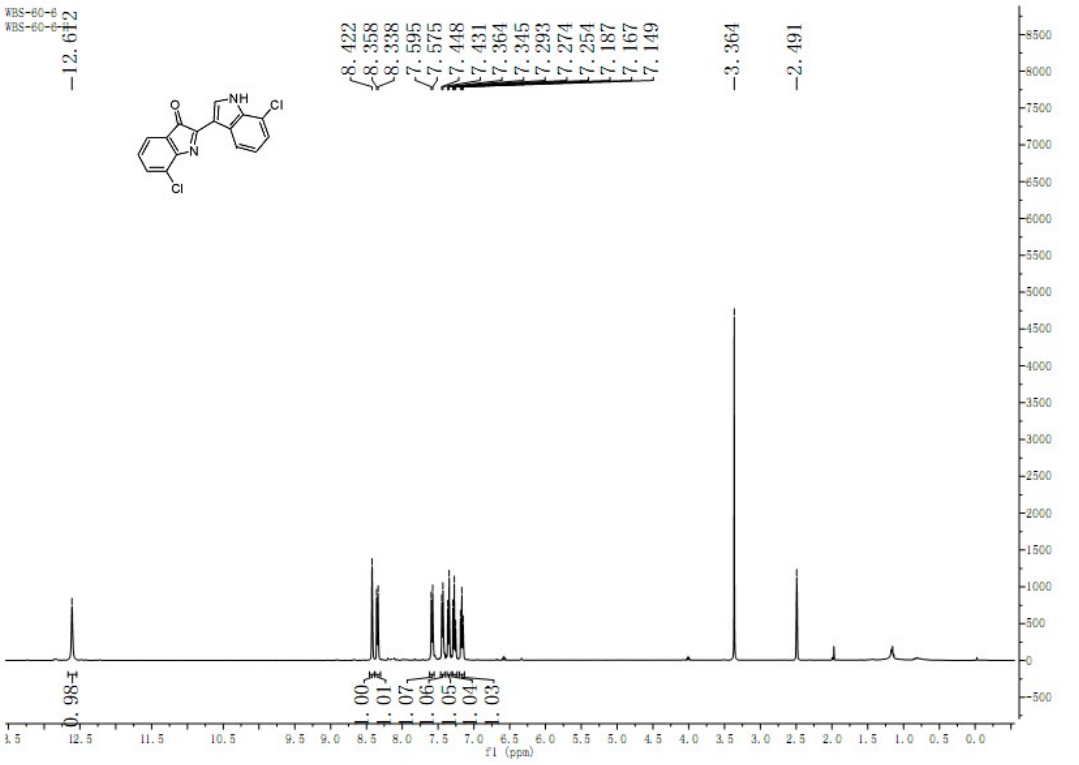


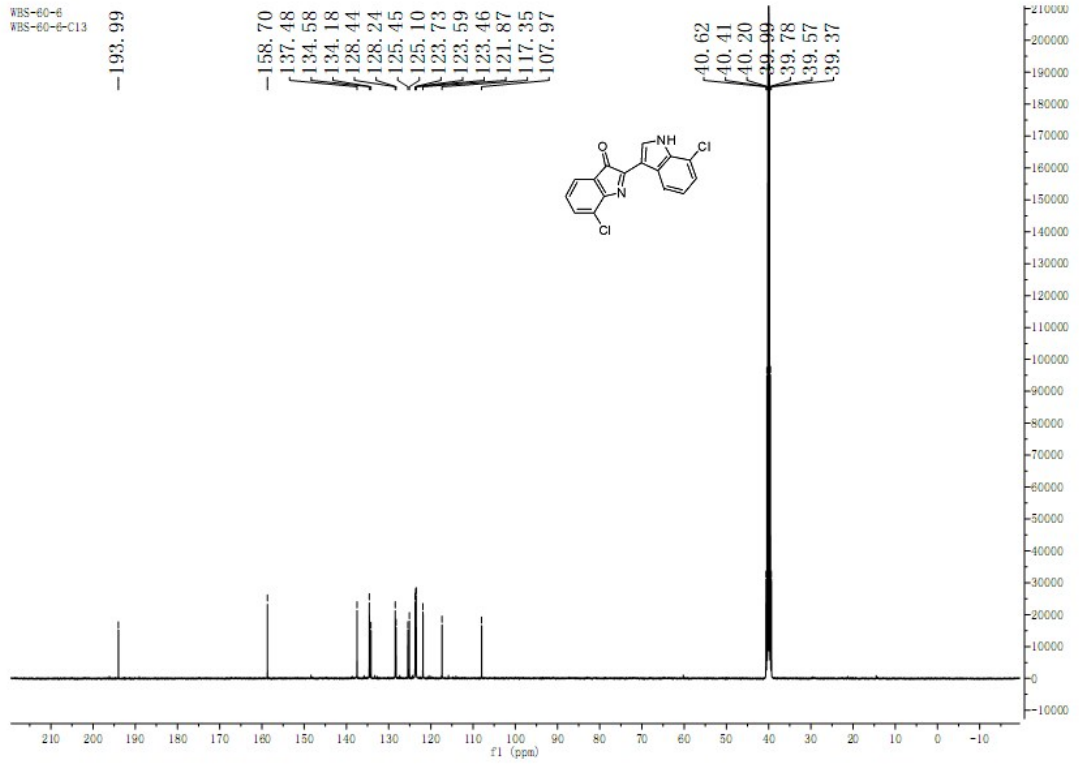
^{1}H and ^{13}C NMR Spectra for **9i**



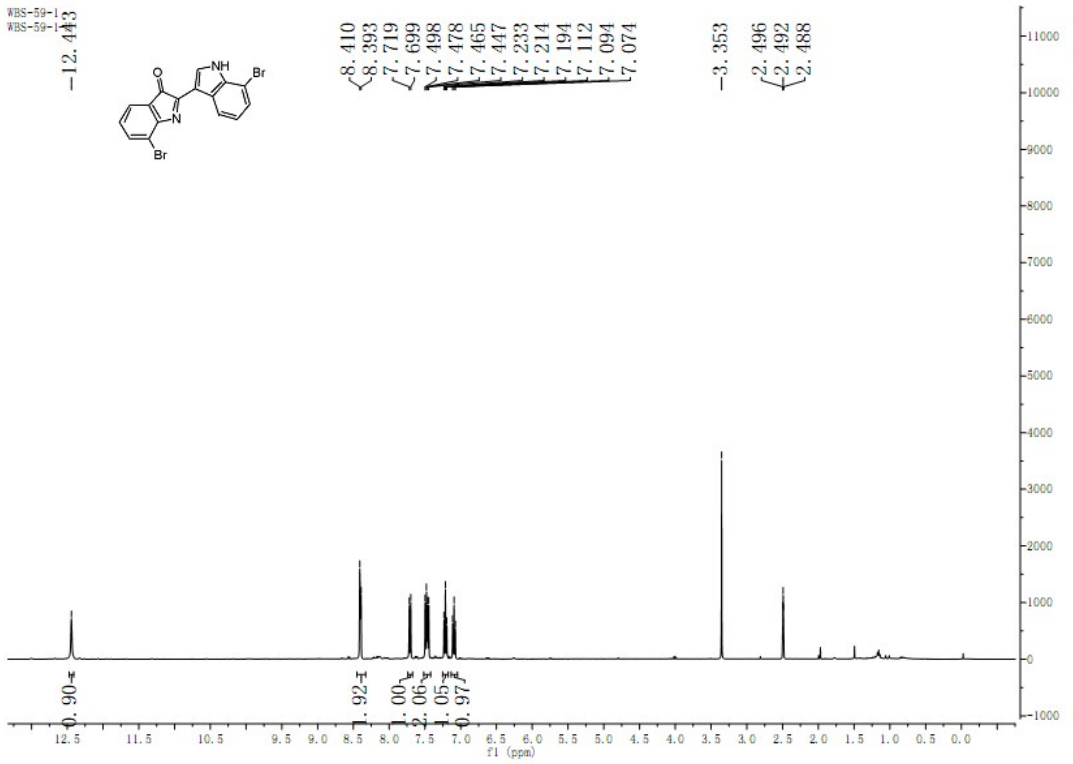


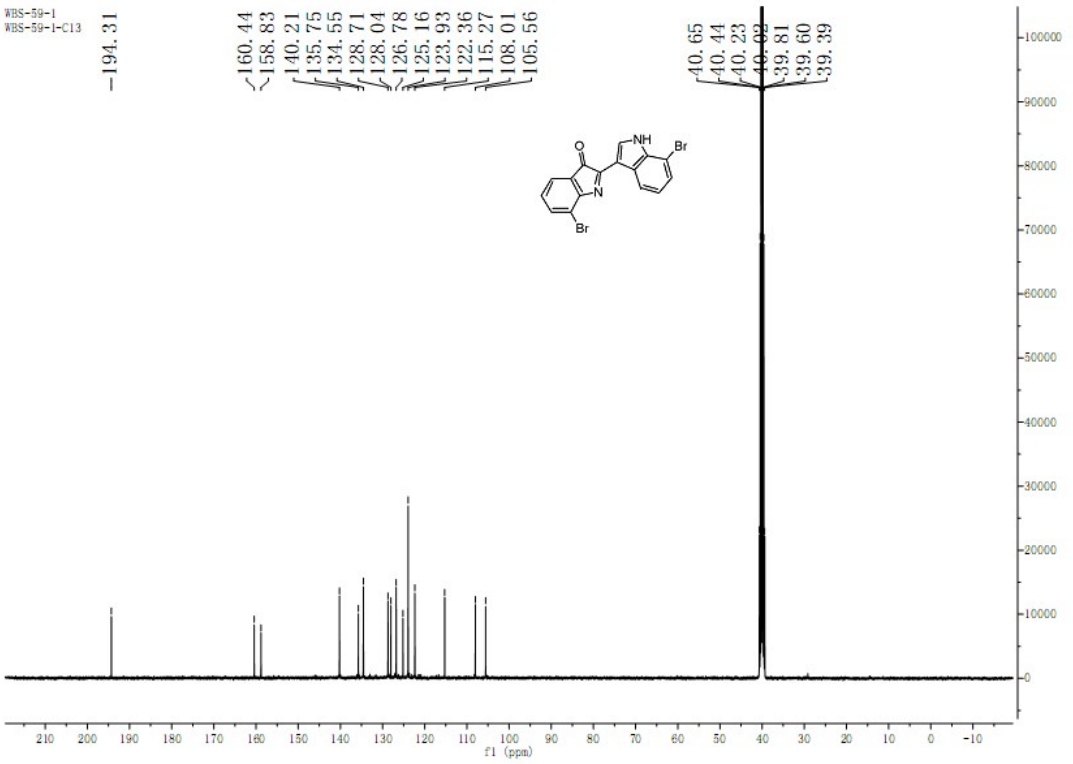
^{1}H and ^{13}C NMR Spectra for **9j**



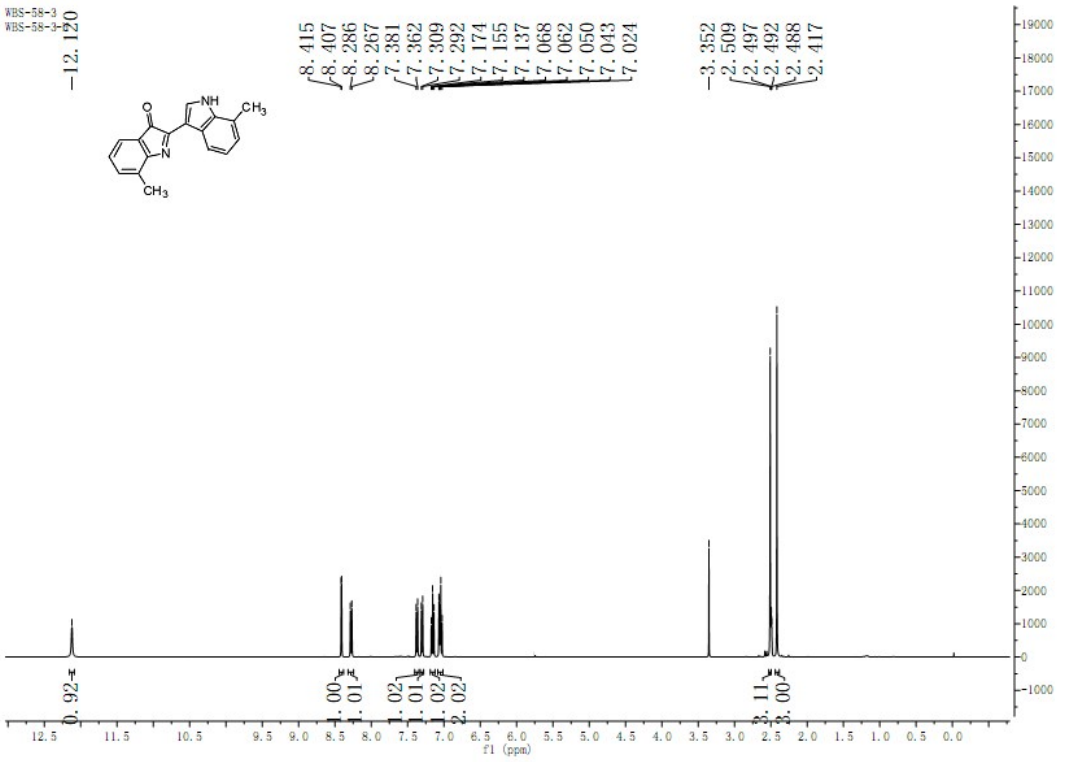


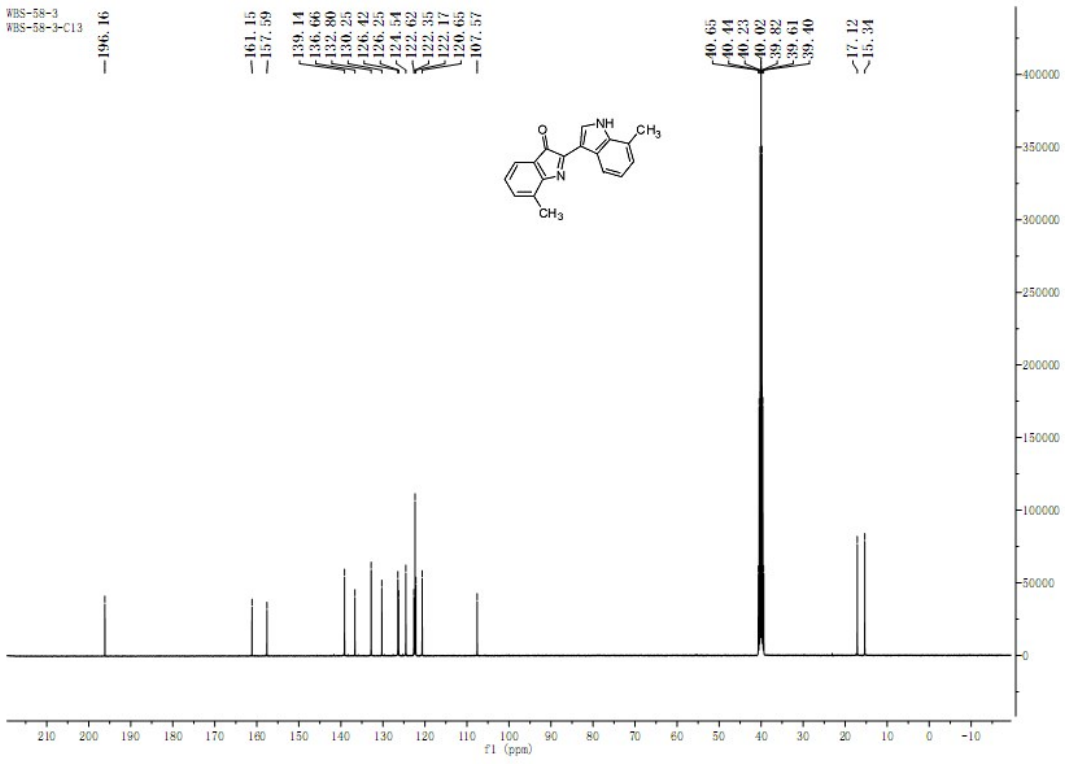
^{1}H and ^{13}C NMR Spectra for **9k**



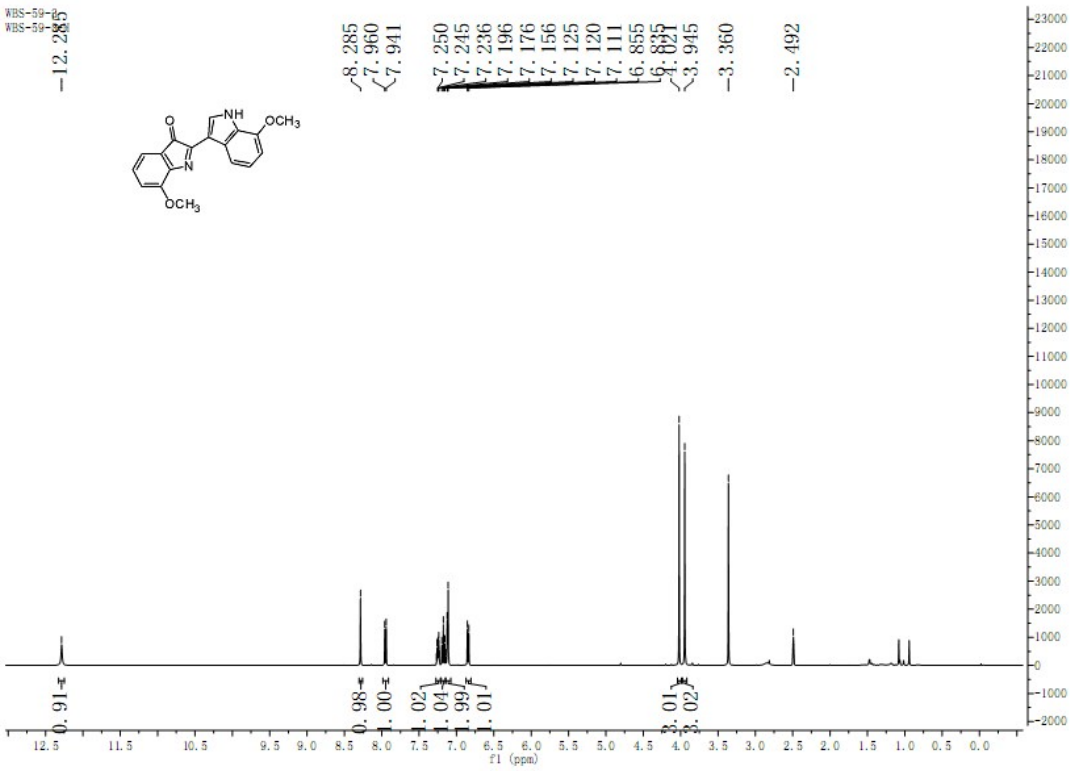


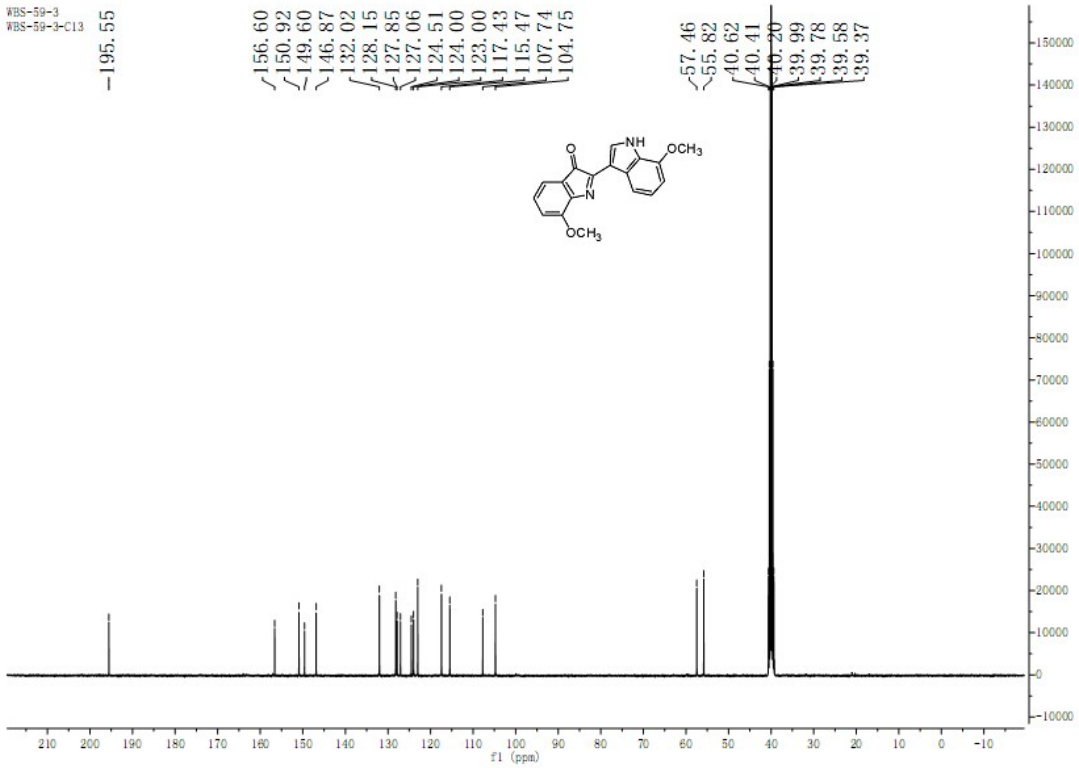
^{1}H and ^{13}C NMR Spectra for **9l**



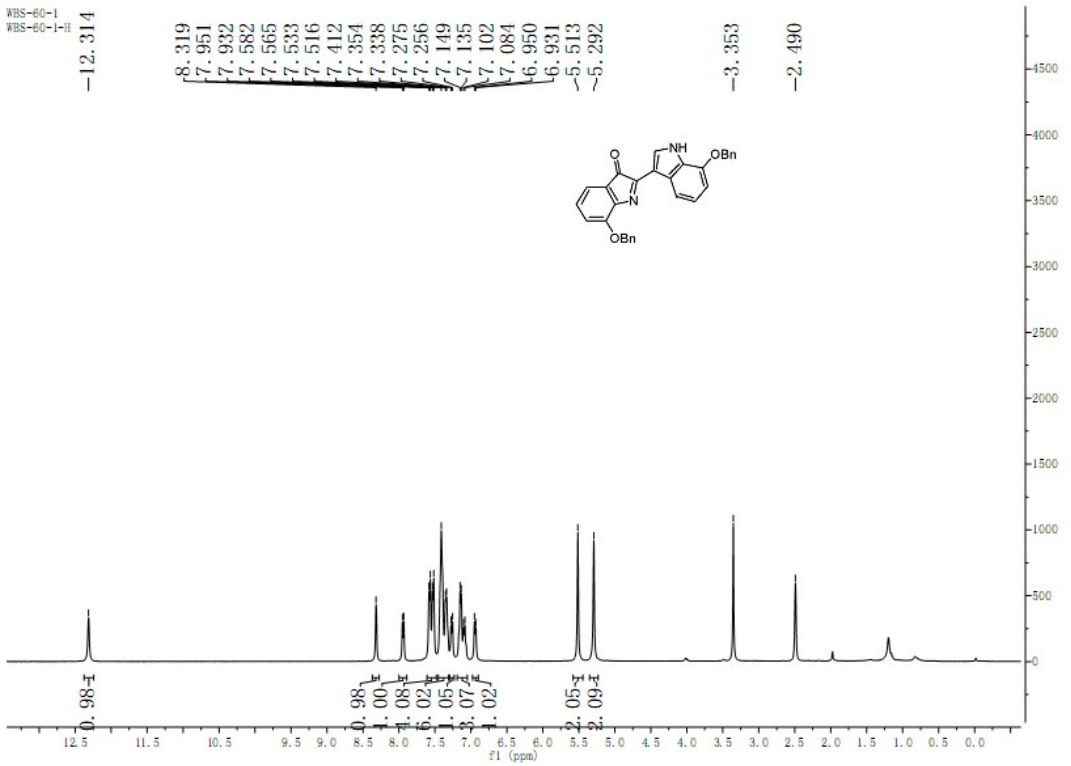


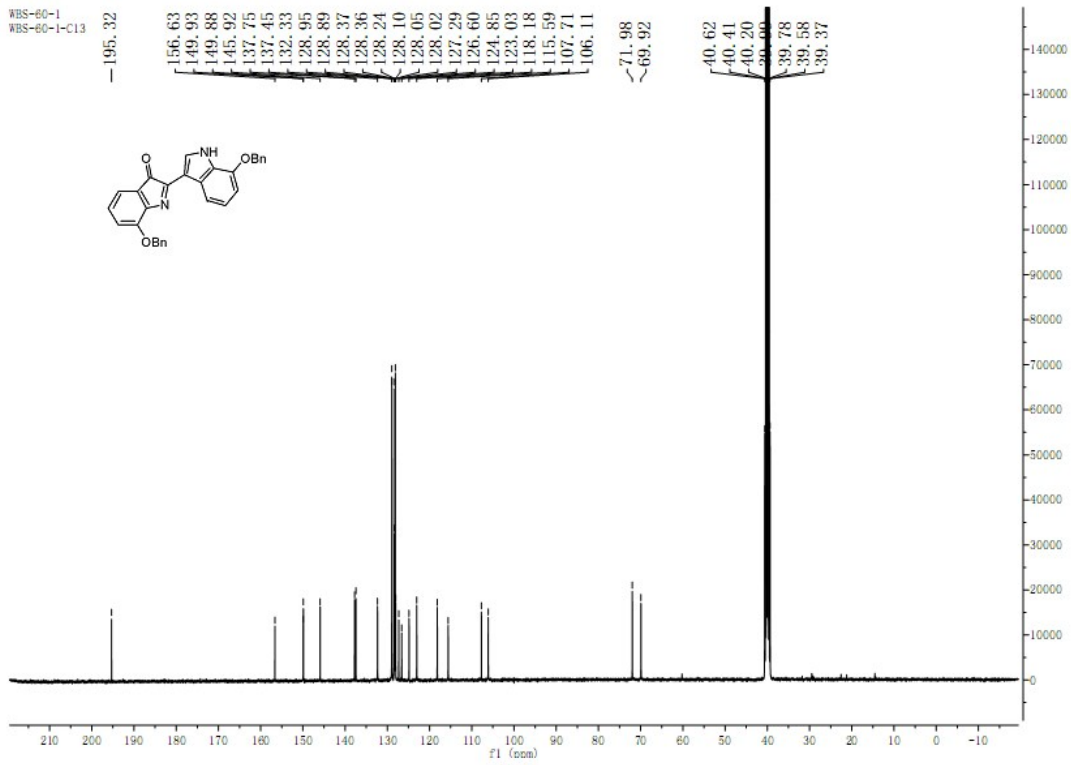
^{1}H and ^{13}C NMR Spectra for **9m**



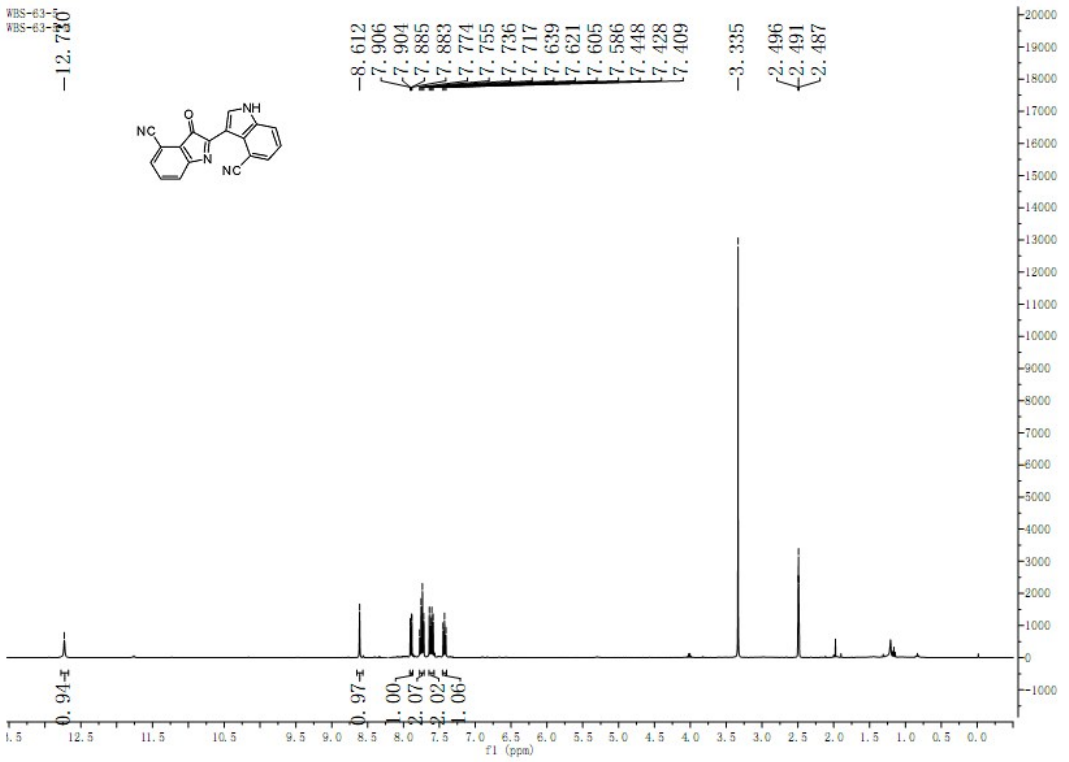


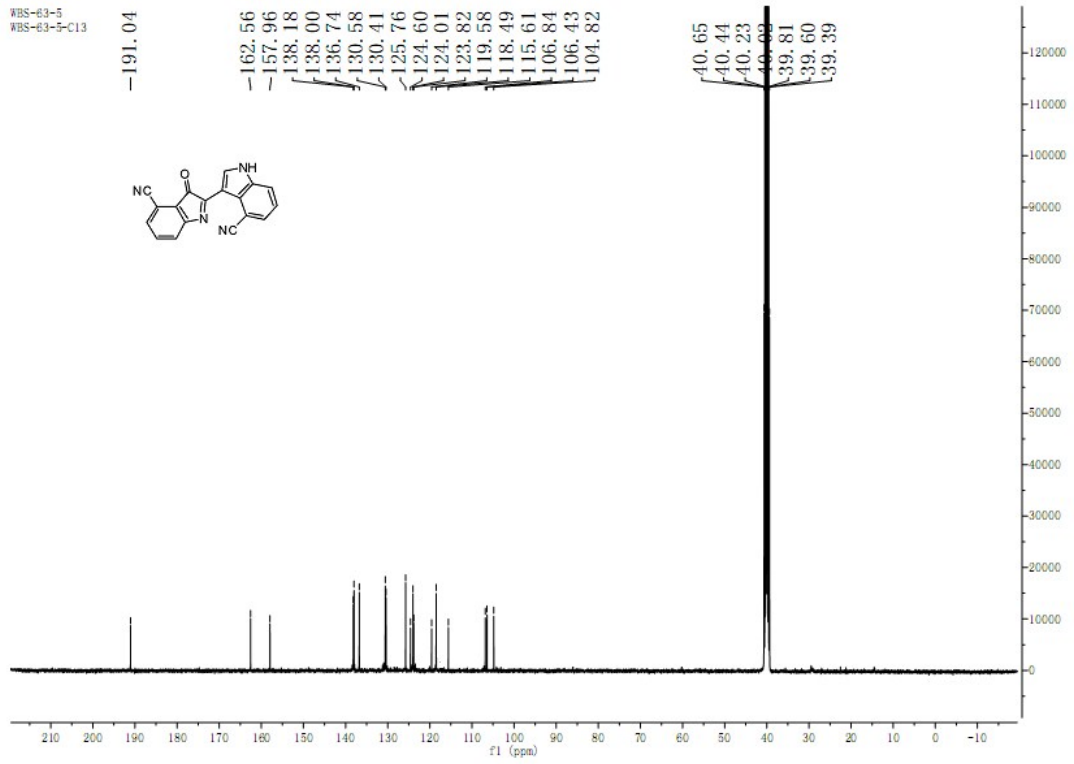
^{1}H and ^{13}C NMR Spectra for **9n**



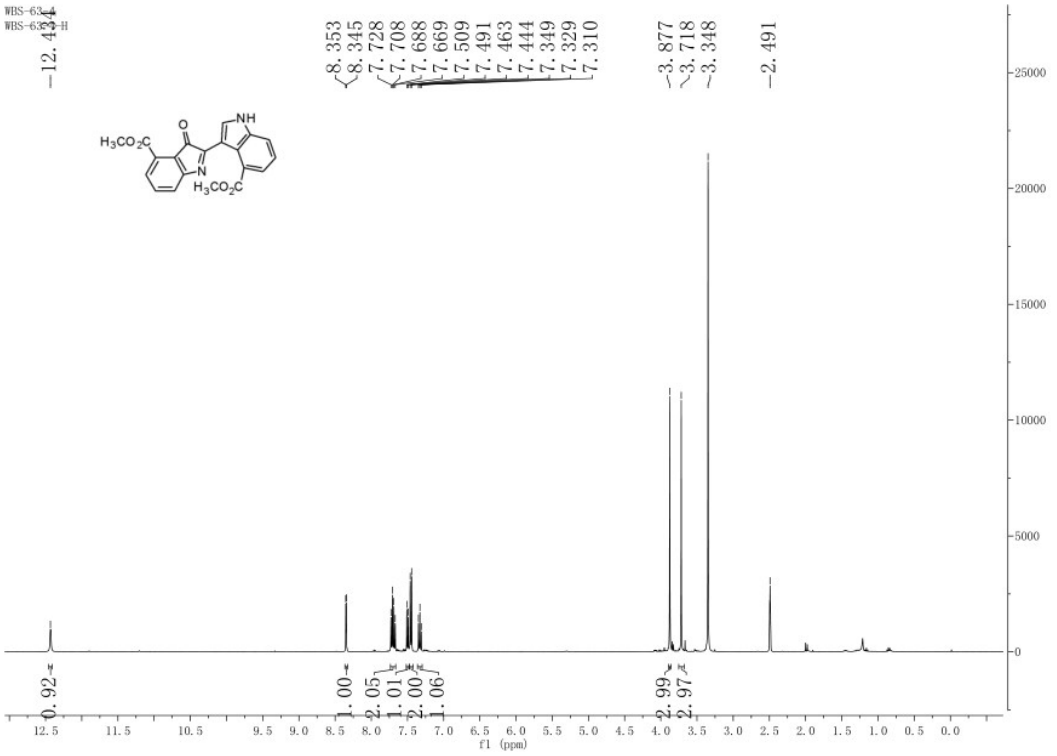


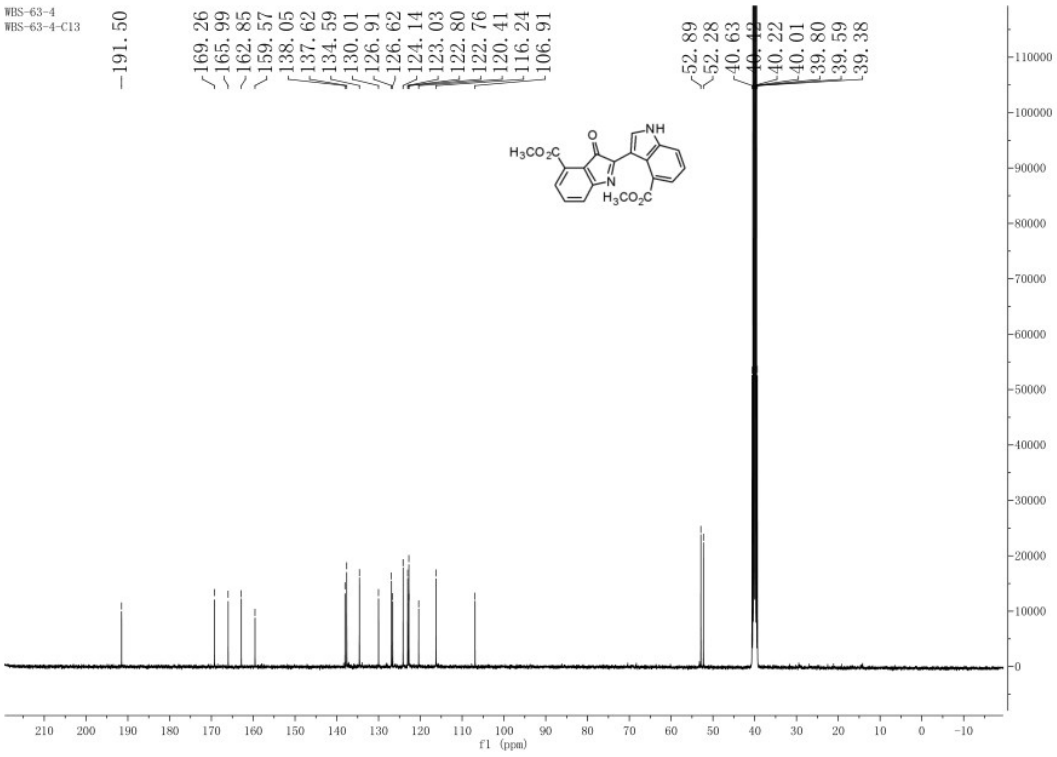
^{1}H and ^{13}C NMR Spectra for **9o**



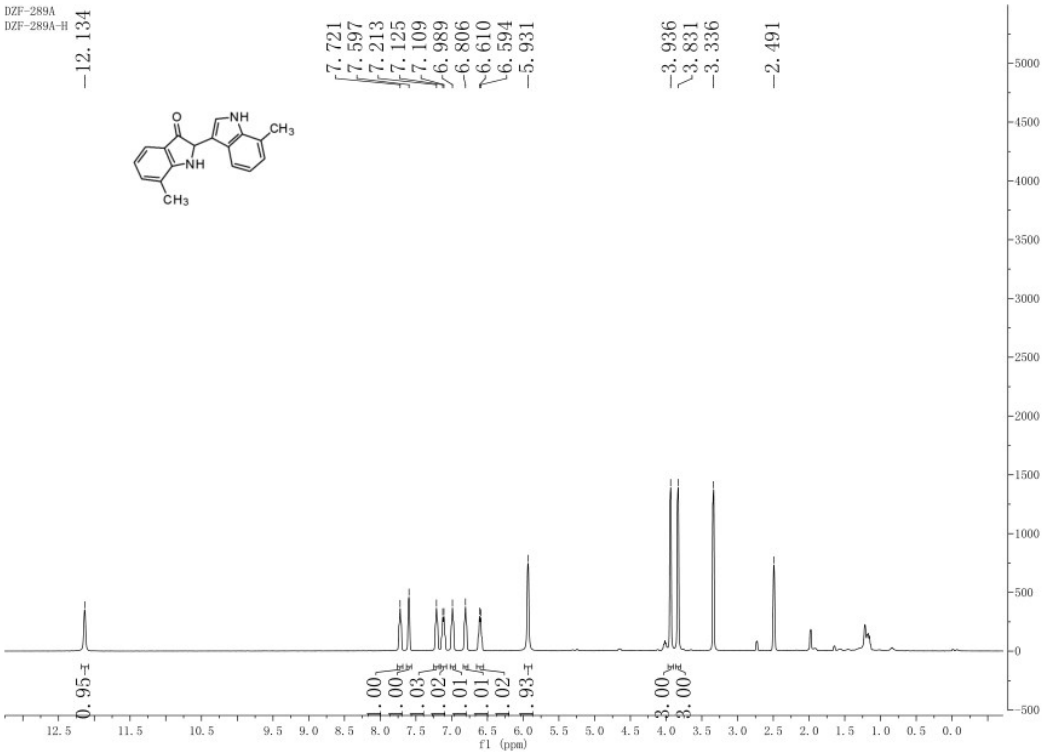


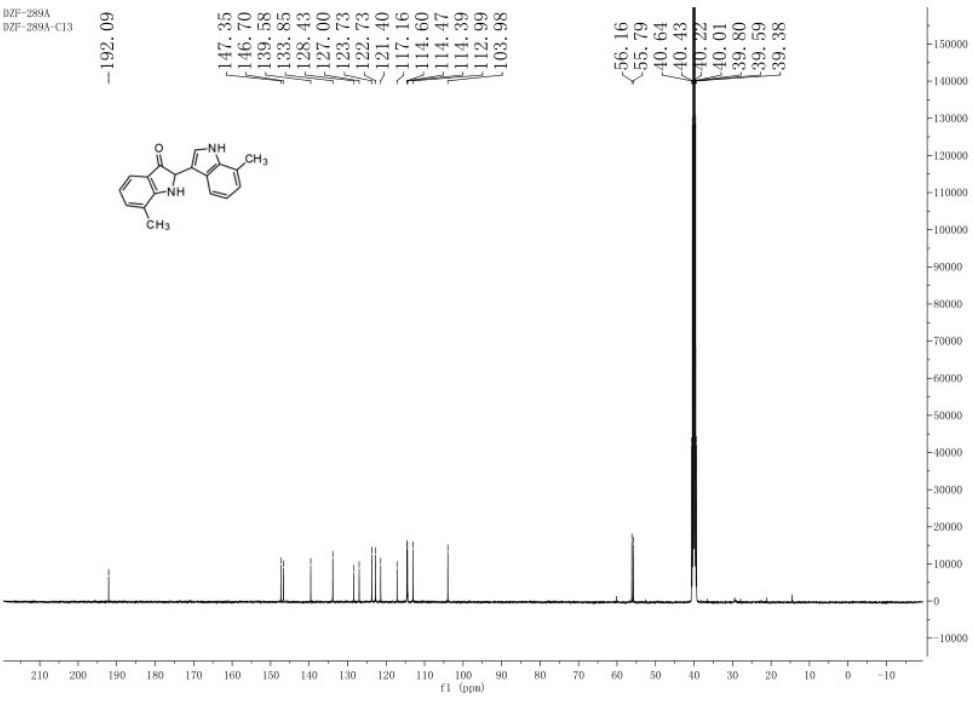
^{1}H and ^{13}C NMR Spectra for **9p**





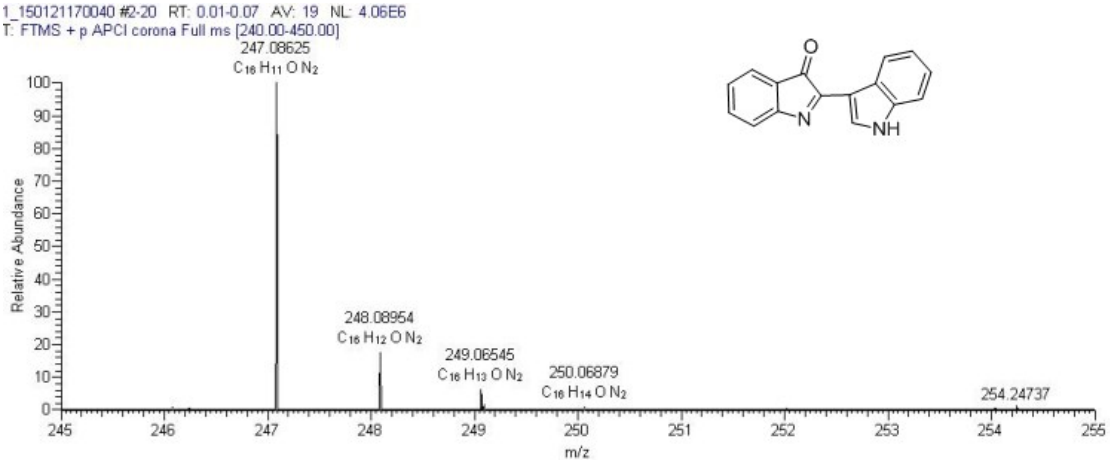
^{1}H and ^{13}C NMR Spectra for **13**



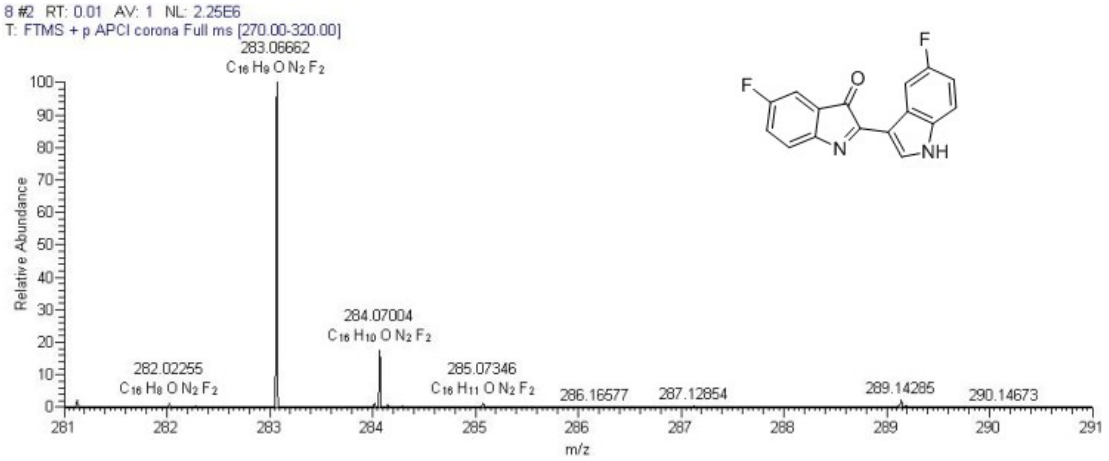


4. Copies of HRESIMS Spectra

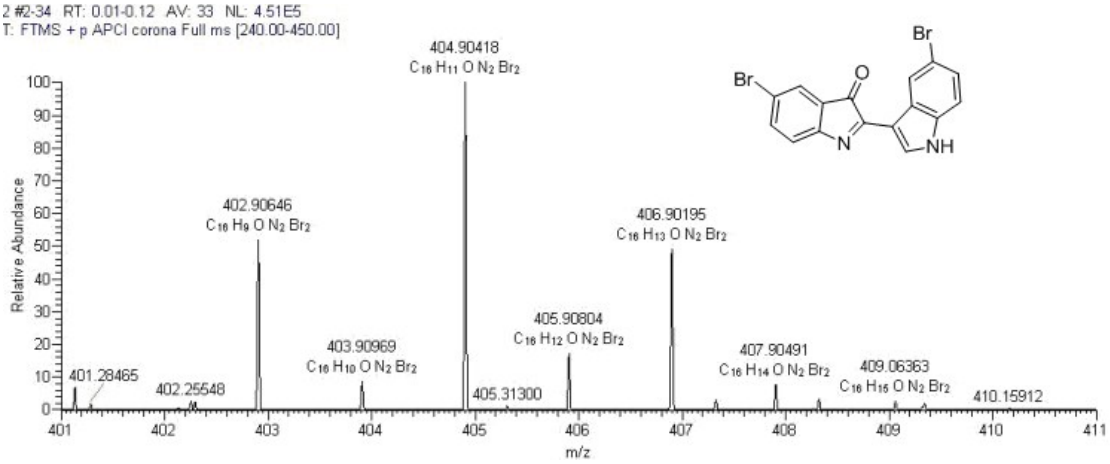
2,3'-Bi(3*H*-indol)-3-one (**9a**)



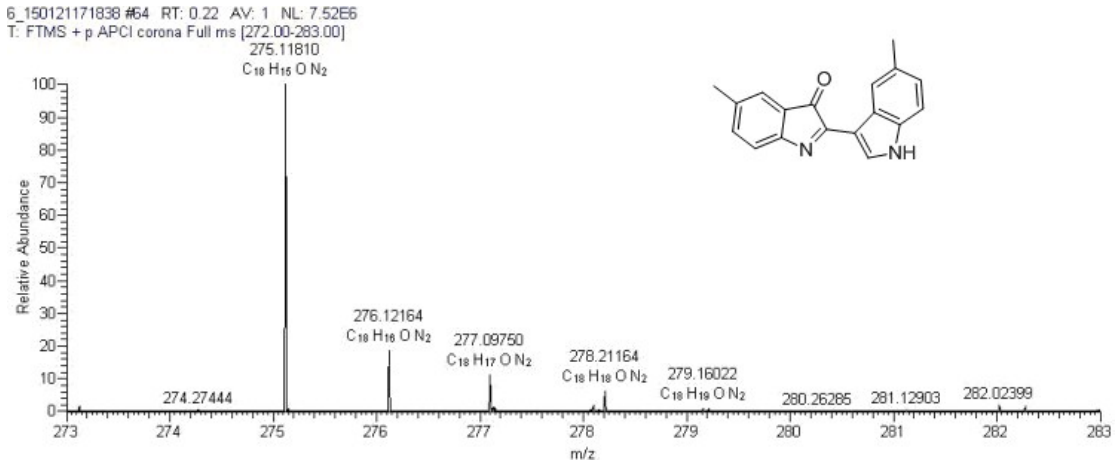
5,5'-Difluoro-2,3'-bi(3*H*-indol)-3-one (**9b**)



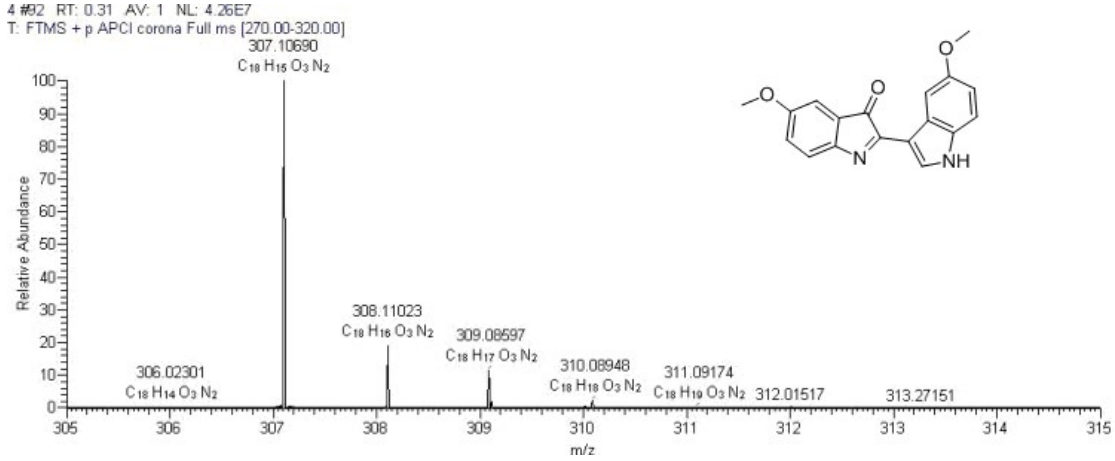
5,5'-Dibromo-2,3'-bi(3*H*-indol)-3-one (**9c**)



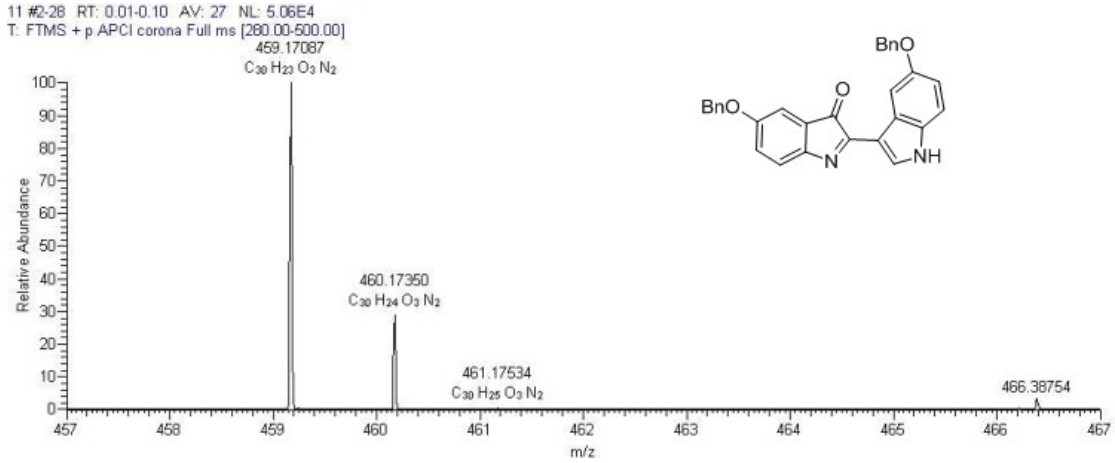
5,5'-Dimethyl-2,3'-bi(3*H*-indol)-3-one (**9d**)



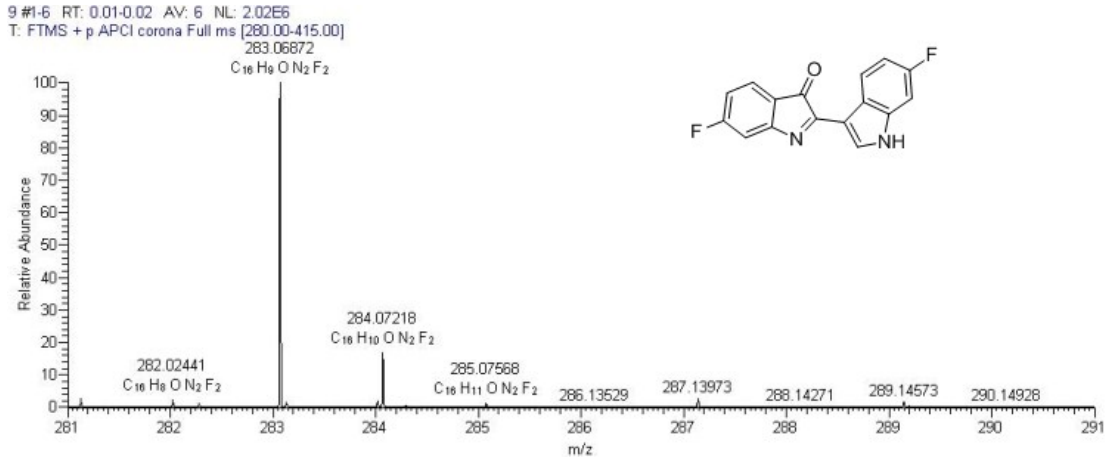
5,5'-Dimethoxy-2,3'-bi(3*H*-indol)-3-one (**9e**)



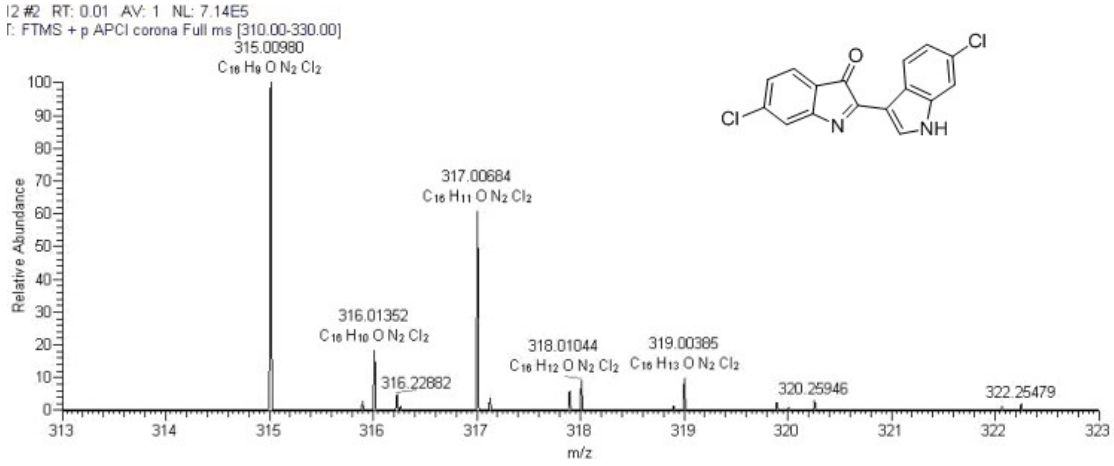
5,5'-Bis(benzyloxy)-2,3'-bi(3*H*-indol)-3-one (**9f**)



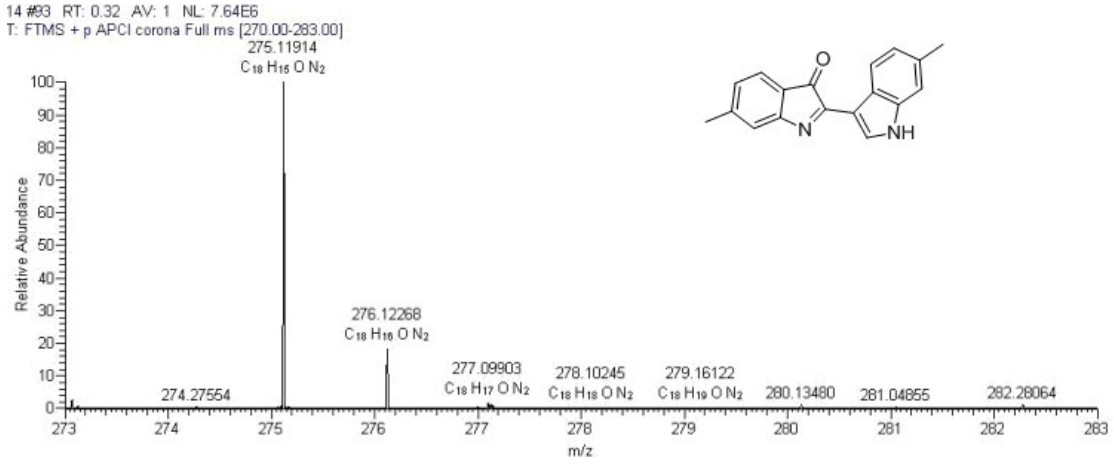
6,6'-Difluoro-2,3'-bi(3*H*-indol)-3-one (**9g**)



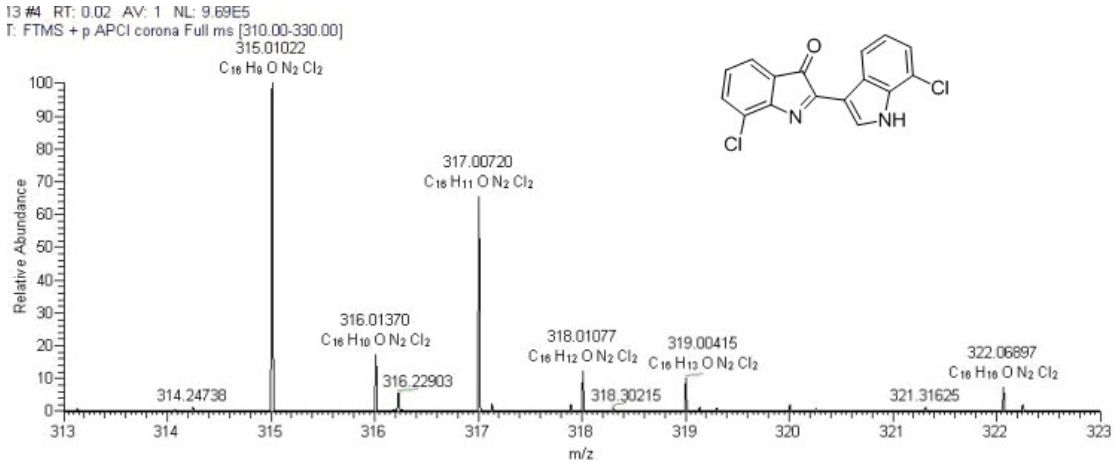
6,6'-Dichloro-2,3'-bi(3*H*-indol)-3-one (**9h**)



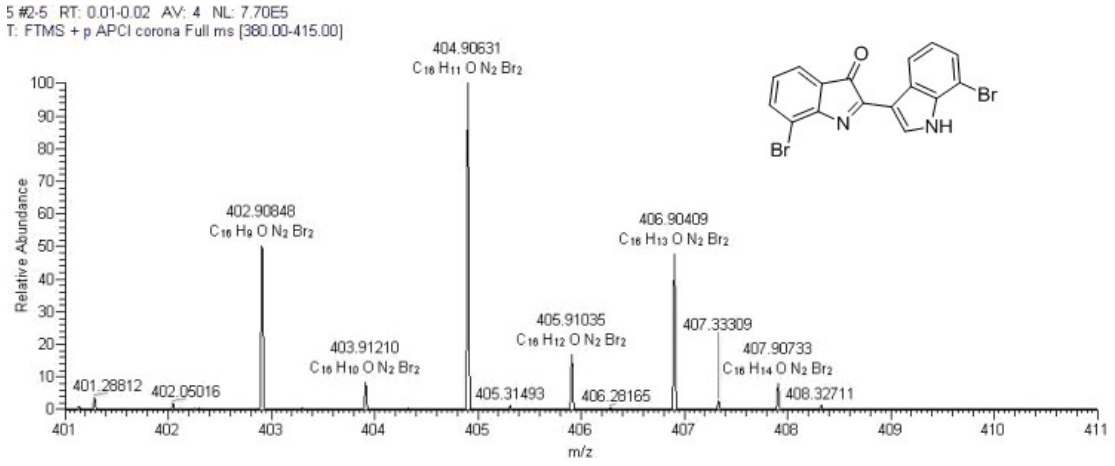
6,6'-Dimethyl-2,3'-bi(3*H*-indol)-3-one (**9i**)



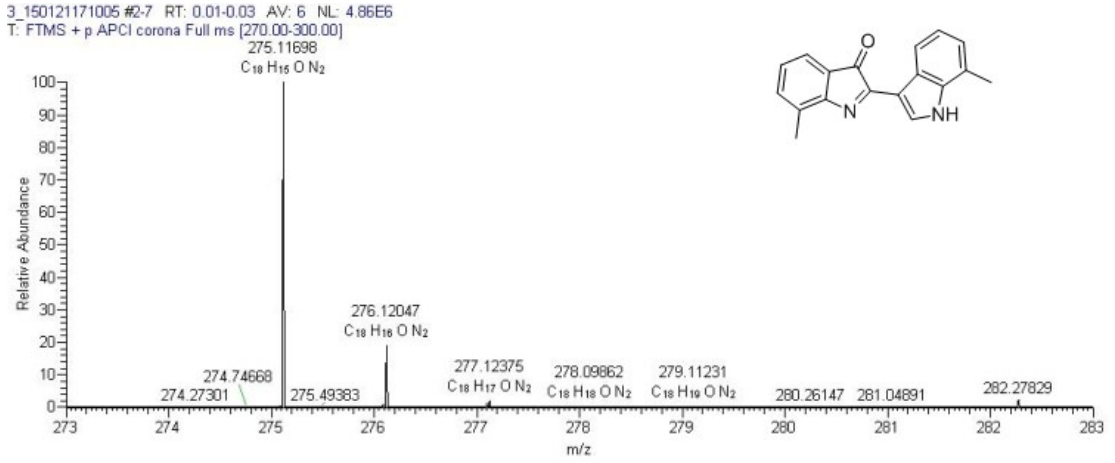
7,7'-Dichloro-2,3'-bi(3*H*-indol)-3-one (**9j**)



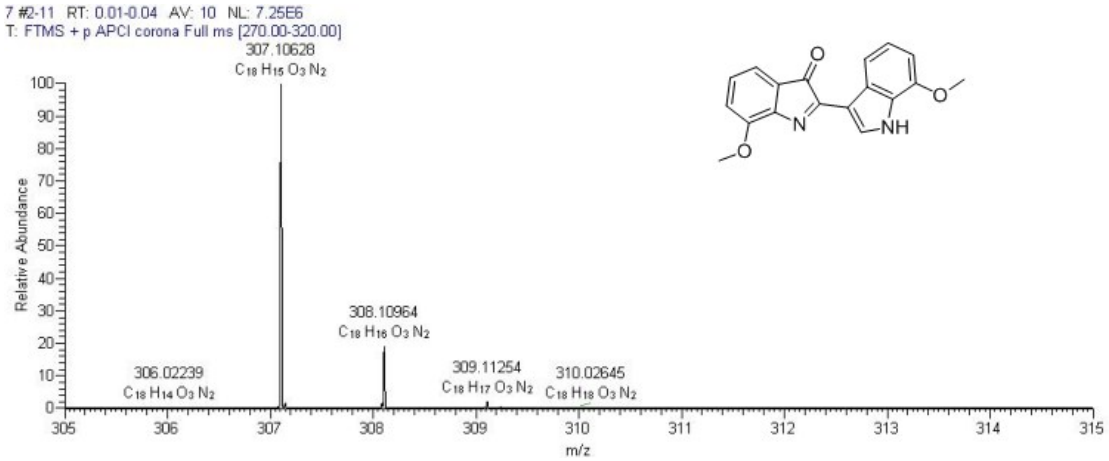
7,7'-Dibromo-2,3'-bi(3*H*-indol)-3-one (**9k**)



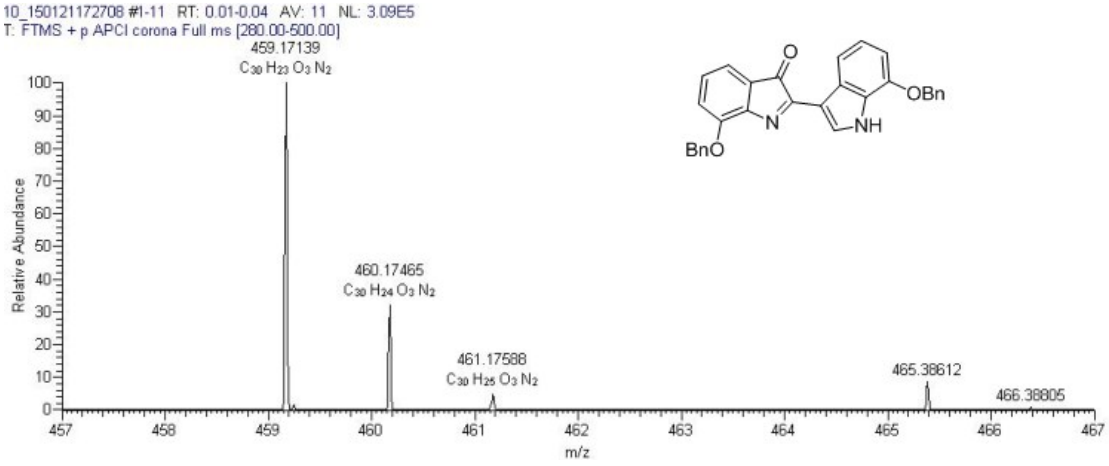
7,7'-Dimethyl-2,3'-bi(3*H*-indol)-3-one (**9l**)



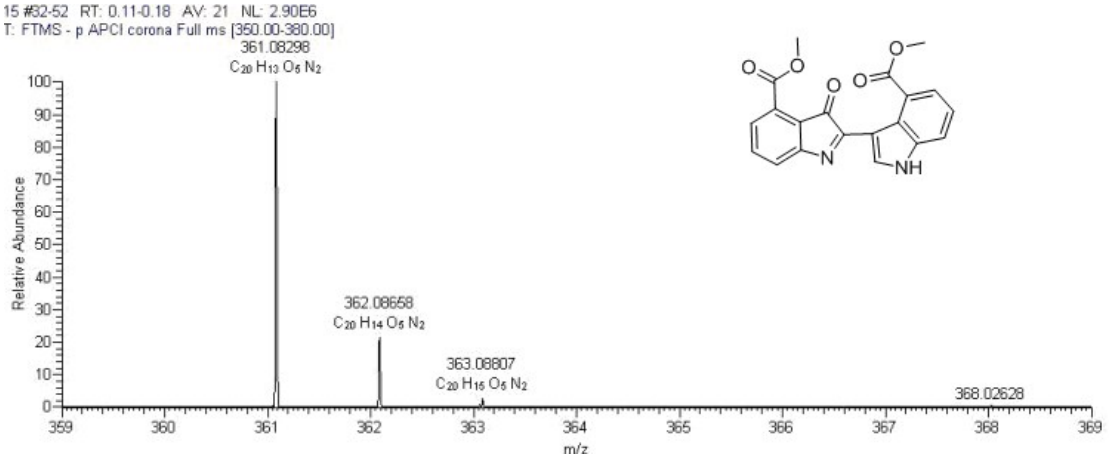
7,7'-Dimethoxy-2,3'-bi(3*H*-indol)-3-one (**9m**)



7,7'-Bis(benzyloxy)-2,3'-bi(3*H*-indol)-3-one (**9n**)



Dimethyl 3-oxo-2,3'-bi(3*H*-indole)-6,6'-dicarboxylate (**9p**)



5. X-ray Data of Compound 9a

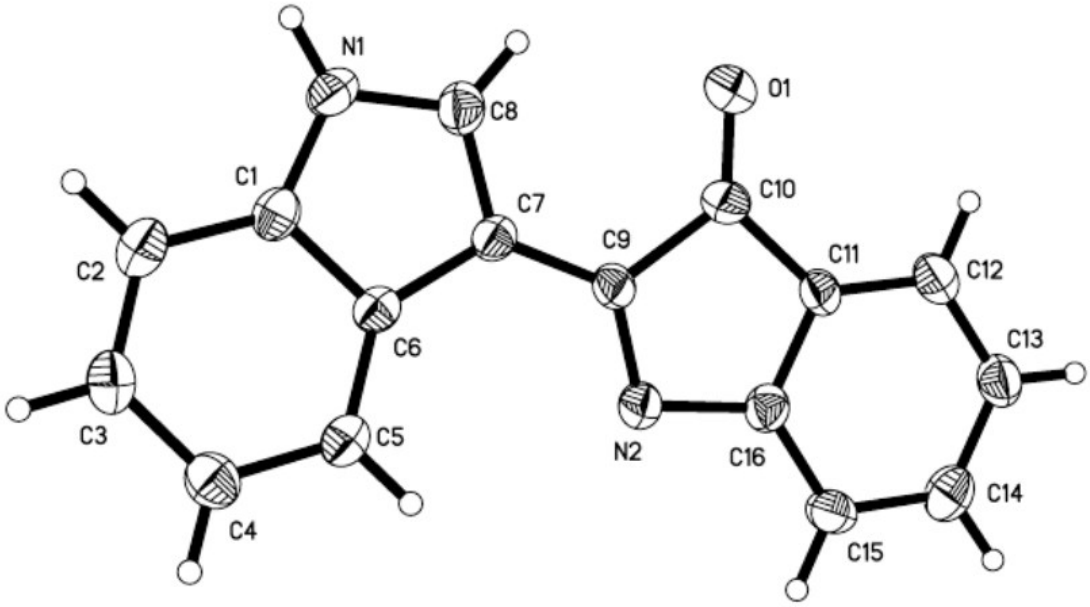


Figure 1. ORTEP representation of the molecular structure of **9a**.
The data have been assigned the following deposition numbers, **CCDC 1453369**.