Supporting Information for

Multifunctionalized Strategy of Indoles to C2-Quaternary Indolin-3-ones *via* a TEMPO/Pd-catalyzed Cascade Process

Zhongfu Deng[a], Xiangjun Peng[b], Panpan Huang[a], Lili Jiang[a],
Dongnai Ye*[a], Liangxian Liu*[a]

[a] Department of Chemistry and Chemical Engineering, Gannan Normal University, Ganzhou 341000, PR China

[b] School of Pharmaceutical Science, Gannan Medical University, Ganzhou, Jiangxi 341000, P. R. China

E-mail: lxliu@xmu.edu.cn

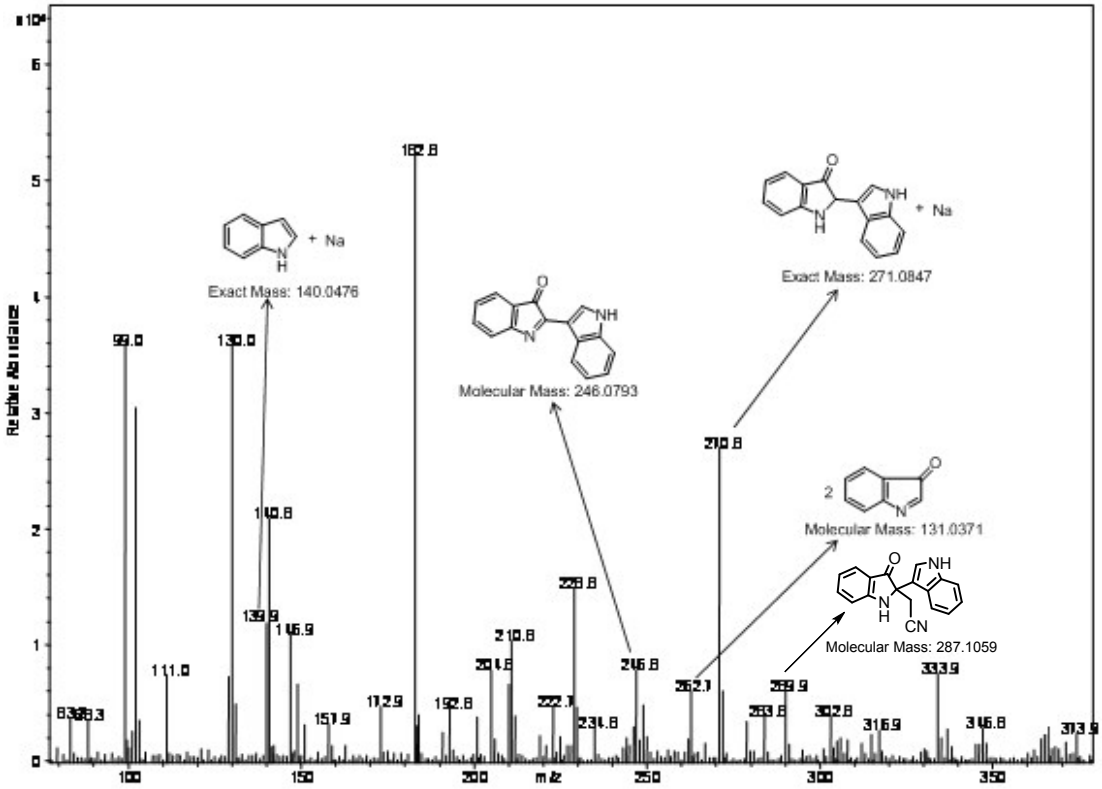
CONTENTS

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. $CDCl_3$ or 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. ESI-MS Investigation

ESI-MS of crude mixtures after 30 min of the onset of reaction for identifiying the possible intermediates

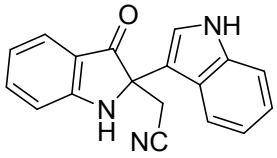


3. General Procedure for the Preparation of 6 and **7.**

To a solution of indole (0.3 mmol), $Pd(OAc)_2$ (0.015 mmol), Ag_2CO_3 (0.105 mmol), CH_3CN (1.5 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 24 h. The reaction mixture was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EtOAc/PE = 1:2) to yield the corresponding product **6**.

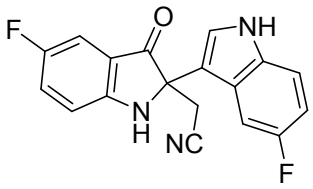
Spectroscopic Data of the Products 6, 7 and **9.**

2-(2-(1*H*-Indol-3-yl)-3-oxoindolin-2-yl)acetonitrile (6a)



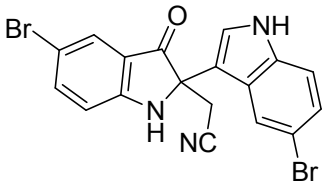
Yellow amorphous solid. IR (KBr) ν_{max}: 3400, 2253, 1692, 1615 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 8.35 (s, 1H, NH), 7.70 (d, J = 7.8 Hz, 1H, Ar-H), 7.59 (dt, J = 1.2, 7.1 Hz, 1H, Ar-H), 7.41 (d, J = 8.2 Hz, 1H, Ar-H), 7.37 (d, J = 8.2 Hz, 1H, Ar-H), 7.25-7.18 (m, 2H, Ar-H), 7.07 (dt, J = 1.2, 7.1 Hz, 1H, Ar-H), 7.00 (d, J = 7.8 Hz, 1H, Ar-H), 6.96 (d, J = 8.2 Hz, 1H, Ar-H), 5.41 (s, 1H, NH), 3.38 (d, J = 16.6 Hz, 1H, CH_2), 3.30 (d, J = 16.6 Hz, 1H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.2, 160.3, 138.5, 136.9, 125.6, 124.3, 123.0, 122.9, 120.6, 120.4, 119.5, 119.3, 116.8, 113.0, 111.9, 111.5, 65.7, 26.6. HRESIMS calcd for $[C_{18}H_{13}N_3O_1 + H]^+$ 288.11369, found 288.10602.

2-(5-Fluoro-2-(5-fluoro-1*H*-indol-3-yl)-3-oxoindolin-2-yl)acetonitrile (6b)



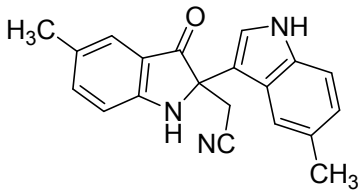
Orange amorphous solid. IR (KBr) ν_{max}: 3395, 2253, 1697, 1630, 1493 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 11.38 (s, 1H, NH), 8.10 (s, 1H, NH), 7.58 (d, J = 2.8 Hz, 1H, Ar-H), 7.51 (dt, J = 4.2, 7.6 Hz, 1H, Ar-H), 7.38 (dd, J = 9.0, 4.2 Hz, 1H, Ar-H), 7.29 (dd, J = 7.6, 2.8 Hz, 1H, Ar-H), 7.08 (dd, J = 9.0, 4.2 Hz, 1H, Ar-H), 7.03 (dd, J = 10.5, 2.4 Hz, 1H, Ar-H), 6.94 (dt, J = 9.0, 2.4 Hz, 1H, Ar-H), 3.50 (d, J = 16.7 Hz, 1H, CH_2), 3.33 (d, J = 16.7 Hz, 1H, CH_2). ^{13}C NMR (100 MHz, DMSO-d_6): δ 200.0 (d, J = 3.4 Hz), 158.8, 157.1 (d, J = 231.6 Hz), 155.8 (d, J = 236.5 Hz), 133.9, 126.9 (d, J = 25.5 Hz), 126.6, 124.7 (d, J = 10.3 Hz), 118.2 (d, J = 12.6 Hz), 118.1 (d, J = 6.1 Hz), 114.2 (d, J = 7.6 Hz), 113.4 (d, J = 9.9 Hz), 111.3 (d, J = 4.5 Hz), 110.2 (d, J = 26.2 Hz), 109.6 (d, J = 22.5 Hz), 104.8 (d, J = 24.3 Hz), 66.9, 25.8. HRESIMS calcd for $[C_{18}H_{11}F_2N_3O + Na]^+$ 346.07679, found 346.06770.

2-(5-Bromo-2-(5-bromo-1*H*-indol-3-yl)-3-oxoindolin-2-yl)acetonitrile (6c)



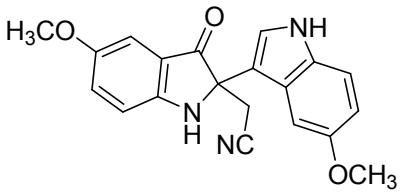
Yellow amorphous solid. IR (KBr) ν_{max}: 3403, 2252, 1700, 1612, 1471 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 11.50 (d, J = 1.8 Hz, 1H, NH), 8.42 (s, 1H, NH), 7.71 (dd, J = 6.8, 1.8, Hz, 1H, Ar-H), 7.63 (d, J = 2.4 Hz, 1H, Ar-H), 7.56 (d, J = 2.4 Hz, 1H, Ar-H), 7.51 (s, 1H, Ar-H), 7.36 (d, J = 8.6 Hz, 1H, Ar-H), 7.21 (dd, J = 6.8, 1.8 Hz, 1H, Ar-H), 7.03 (d, J = 8.6 Hz, 1H, Ar-H), 3.52 (d, J = 16.7 Hz, 1H, CH_2), 3.36 (d, J = 16.7 Hz, 1H, CH_2). ^{13}C NMR (100 MHz, DMSO-d_6): δ 198.8, 160.4, 141.0, 136.0, 127.1, 126.3, 126.2, 124.6, 122.3, 119.7, 117.9, 114.9, 114.4, 112.3, 110.7, 109.8, 66.5, 25.9. HRESIMS calcd for $[C_{18}H_{11}Br_2N_3O_1 + Na]^+$ 467.91461, found 467.90000.

2-(5-Methyl-2-(5-methyl-1*H*-indol-3-yl)-3-oxoindolin-2-yl)acetonitrile (6d)



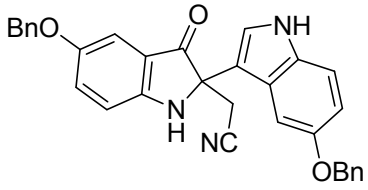
Orange amorphous solid. IR (KBr) ν_{max}: 3390, 2250, 1694, 1626, 1499 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 11.07 (s, 1H, NH), 7.85 (s, 1H, NH), 7.41 (d, J = 8.3 Hz, 1H, Ar-H), 7.38 (d, J = 2.6 Hz, 1H, Ar-H), 7.27 (s, 1H, Ar-H), 7.23 (d, J = 8.3 Hz, 1H, Ar-H), 7.11 (s, 1H, Ar-H), 6.95 (d, J = 8.3 Hz, 1H, Ar-H), 6.88 (d, J = 8.3 Hz, 1H, Ar-H), 3.43 (d, J = 16.6 Hz, 1H, CH_2), 3.26 (d, J = 16.6 Hz, 1H, CH_2), 2.25 (s, 3H, CH_3), 2.23 (s, 3H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ 200.3, 160.4, 139.9, 135.6, 127.7, 127.5, 125.0, 124.3, 124.1, 123.4, 119.8, 118.5, 118.2, 112.7, 112.0, 111.1, 66.4, 26.0, 21.9, 20.5. HRESIMS calcd for $[C_{20}H_{17}N_3O + H]^+$ 316.14499, found 316.13557.

2-(5-Methoxy-2-(5-methoxy-1*H*-indol-3-yl)-3-oxoindolin-2-yl)acetonitrile (6e)



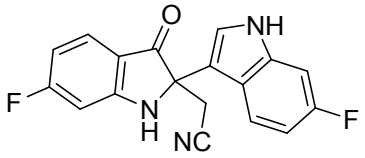
Yellow amorphous solid. IR (KBr) ν_{max}: 3362, 2250, 1689, 1627, 1494, 1217 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 8.26 (s, 1H, NH), 7.29-7.26 (m, 2H, Ar-H), 7.23 (d, J = 2.8 Hz, 1H, Ar-H), 7.13 (d, J = 2.6 Hz, 1H, Ar-H), 7.00 (d, J = 8.8 Hz, 1H, Ar-H), 6.86 (dd, J = 8.8, 2.3 Hz, 1H, Ar-H), 6.76 (d, J = 2.3 Hz, 1H, Ar-H), 5.14 (s, 1H, NH), 3.81 (s, 3H, OCH_3), 3. 67 (s, 3H, OCH_3), 3.37 (d, J = 16.5 Hz, 1H, CH_2), 3.01 (d, J = 16.5 Hz, 1H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.6, 158.7, 156.3, 131.9, 129.9, 129.0, 124.6, 123.4, 120.3, 116.9, 114.7, 113.1, 112.6, 111.4, 105.0, 101.1, 66.6, 55.8, 55.6, 26.4. HRESIMS calcd for $[C_{20}H_{17}N_3O_3 + Na]^+$ 370.11676, found 370.10627.

2-(5-(Benzyloxy)-2-(5-(benzyloxy)-1*H*-indol-3-yl)-3-oxoindolin-2-yl)acetonitrile (6f)



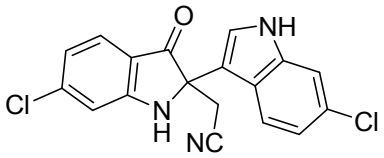
Green amorphous solid. IR (KBr) ν_{max}: 3367, 2249, 1693, 1491, 1220 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 11.08 (d, J = 1.9 Hz, 1H, NH), 7.72 (s, 1H, NH), 7.45-7.30 (m, 12H, Ar-H), 7.25 (d, J = 8.8 Hz, 1H, Ar-H), 7.05 (d, J = 2.3 Hz, 1H, Ar-H), 7.03 (d, J = 8.8 Hz, 1H, Ar-H), 6.81 (s, 1H, Ar-H), 6.78 (dd, J = 8.8, 2.3 Hz, 1H, Ar-H). 5.07 (s, 2H, OCH_2), 4.83 (s, 2H, OCH_2), 3.46 (d, J = 16.6 Hz, 1H, CH_2), 3.26 (d, J = 16.6 Hz, 1H, CH_2). ^{13}C NMR (100 MHz, DMSO-d_6): δ 200.5, 158.0, 152.5, 151.9, 137.9, 137.6, 132.5, 129.5, 128.9, 128.8, 128.2, 128.1, 128.0, 127.9, 125.1, 125.0, 118.7, 118.3, 114.4, 112.9, 112.6, 111.3, 106.5, 103.6, 70.4, 70.0, 66.9, 25.7. HRESIMS calcd for $[C_{32}H_{25}N_3O_3 + H]^+$ 500.19742, found 500.18283.

2-(6-Fluoro-2-(6-fluoro-1*H*-indol-3-yl)-3-oxoindolin-2-yl)acetonitrile (6g)



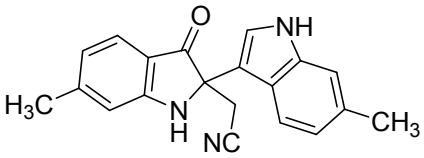
Orange amorphous solid. IR (KBr) ν_{max}: 3344, 2254, 1694, 1626, 1306 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 11.34 (s, 1H, NH), 8.47 (s, 1H, NH), 7.57 (dd, J = 8.5, 6.0 Hz, 1H, Ar-H), 7.51 (d, J = 2.5 Hz, 1H, Ar-H), 7.25 (dd, J = 8.5, 6.0 Hz, 1H, Ar-H), 7.16 (dd, J = 10.0, 2.3 Hz, 1H, Ar-H), 6.83 (dt, J = 2.3, 9.6 Hz, 1H, Ar-H), 6.77 (dd, J = 10.0, 8.5 Hz, 1H, Ar-H), 6.62 (dt, J = 2.5, 9.6 Hz, 1H, Ar-H), 3.50 (d, J = 16.7 Hz, 1H, CH_2), 3.35 (d, J = 16.7 Hz, 1H, CH_2). ^{13}C NMR (100 MHz, DMSO-d_6): δ 198.3, 169.7 (d, J = 253.0 Hz), 163.2 (d, J = 14.9 Hz), 159.2 (d, J = 235.5 Hz), 137.2 (d, J = 12.5 Hz), 127.9 (d, J = 13.0 Hz), 125.4 (d, J = 3.1 Hz), 121.4, 121.0 (d, J = 10.2 Hz), 118.0, 115.1, 111.4, 108.2 (d, J = 24.4 Hz), 107.2 (d, J = 25.0 Hz), 98.5 (d, J = 16.9 Hz), 98.2 (d, J = 16.3 Hz), 66.6, 25.8. HRESIMS calcd for $[C_{18}H_{11}F_2N_3O + Na]^+$ 346.07679, found 346.06745.

2-(6-Chloro-2-(6-chloro-1*H*-indol-3-yl)-3-oxoindolin-2-yl)acetonitrile (6h)



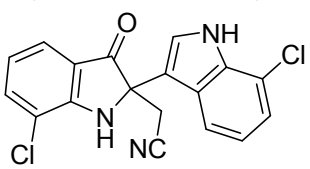
Yellow amorphous solid. IR (KBr) ν_{max}: 3339, 3215, 2254, 1731, 1610 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 11.42 (d, J = 1.5 Hz, 1H, NH), 8.44 (s, 1H, NH), 7.56 (d, J = 2.6 Hz, 1H, Ar-H), 7.50 (d, J = 8.4 Hz, 1H, Ar-H), 7.43 (d, J = 1.7 Hz, 1H, Ar-H), 7.30 (d, J = 8.4 Hz, 1H, Ar-H), 7.06 (d, J = 1.5 Hz, 1H, Ar-H), 6.97 (dd, J = 6.6, 1.7 Hz, 1H, Ar-H), 6.81 (dd, J = 6.6, 1.7 Hz, 1H, Ar-H), 3.52 (d, J = 16.7 Hz, 1H, CH_2), 3.36 (d, J = 16.7 Hz, 1H, CH_2). ^{13}C NMR (100 MHz, DMSO-d_6): δ 198.8, 161.9, 143.6, 137.7, 126.9, 126.8, 125.9, 123.4, 121.3, 120.0, 119.0, 117.9, 117.0, 112.0, 111.9, 111.4, 66.4, 25.8. HRESIMS calcd for $[C_{18}H_{11}Cl_2N_3O + Na]^+$ 378.01769, found 378.00797.

2-(6-Methyl-2-(6-methyl-1*H*-indol-3-yl)-3-oxoindolin-2-yl)acetonitrile (6i)



Yellow amorphous solid. IR (KBr) ν_{max}: 3384, 2252, 1689, 1462, 1334 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 11.05 (s, 1H, NH), 8.01 (s, 1H, NH), 7.38 (d, J = 2.0 Hz, 1H, Ar-H), 7.35 (d, J = 8.0 Hz, 1H, Ar-H), 7.14 (s, 1H, Ar-H), 7.12 (s, 1H, Ar-H), 6.81 (s, 1H, Ar-H), 6.71 (d, J = 8.0 Hz, 1H, Ar-H), 6.62 (d, J = 8.0 Hz, 1H, Ar-H), 3.43 (d, J = 16.7 Hz, 1H, CH_2), 3.26 (d, J = 16.7 Hz, 1H, CH_2), 2.35 (s, 3H, CH_3), 2.32 (s, 3H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ 199.5, 162.2, 149.7, 137.7, 131.0, 124.7, 123.7, 122.7, 121.2, 120.3, 119.8, 118.2, 116.2, 112.4, 111.9, 111.6, 66.2, 25.9, 22.6, 21.7. HRESIMS calcd for $[C_{20}H_{17}N_3O + H]^+$ 316.14499, found 316.13694.

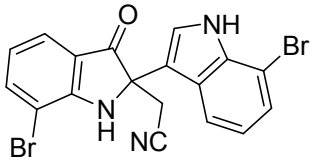
2-(7-Chloro-2-(7-chloro-1*H*-indol-3-yl)-3-oxoindolin-2-yl)acetonitrile (6j)



Yellow amorphous solid. IR (KBr) ν_{max}: 3337, 3201, 2252, 1706, 1613 cm^{-1}. ^1H NMR (400 MHz,

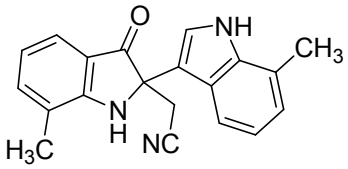
DMSO-d_6): δ 11.67 (s, 1H, NH), 8.48 (s, 1H, NH), 7.73 (d, J = 7.6 Hz, 1H, Ar-H), 7.60 (d, J = 2.6 Hz, 1H, Ar-H), 7.51 (d, J = 7.6 Hz, 1H, Ar-H), 7.17 (d, J = 7.6 Hz, 1H, Ar-H), 7.12 (d, J = 7.8 Hz, 1H, Ar-H), 6.91 (t, J = 7.8 Hz, 1H, Ar-H), 6.84 (t, J = 7.8 Hz, 1H, Ar-H), 3.57 (d, J = 16.6 Hz, 1H, CH_2), 3.47 (d, J = 16.6 Hz, 1H, CH_2). ^{13}C NMR (100 MHz, DMSO-d_6): δ 199.8, 157.6, 137.9, 134.0, 126.6, 126.1, 123.9, 121.6, 120.8, 120.5, 119.6, 118.7, 117.4, 116.8, 116.6, 112.6, 66.2, 25.6. HRESIMS calcd for $[C_{18}H_{11}Cl_2N_3O + Na]^+$ 378.01769, found 378.00878.

2-(7-Bromo-2-(7-bromo-1*H*-indol-3-yl)-3-oxoindolin-2-yl)acetonitrile (6k)



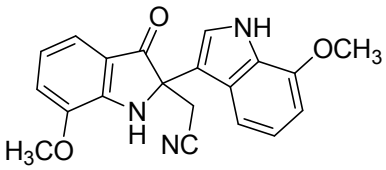
Orange amorphous solid. IR (KBr) ν_{max}: 3391, 2250, 1707, 1610 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.52 (s, 1H, NH), 8.32 (s, 1H, NH), 7.87 (d, J = 7.6 Hz, 1H, Ar-H), 7.57 (s, 1H, Ar-H), 7.55 (d, J = 8.0 Hz, 1H, Ar-H), 7.30 (d, J = 7.6 Hz, 1H, Ar-H), 7.17 (d, J = 8.0 Hz, 1H, Ar-H), 6.86 (t, J = 7.7 Hz, 1H, Ar-H), 6.78 (t, J = 7.7 Hz, 1H, Ar-H), 3.59 (d, J = 16.6 Hz, 1H, CH_2), 3.47 (d, J = 16.6 Hz, 1H, CH_2). ^{13}C NMR (100 MHz, DMSO-d_6): δ 200.0, 158.9, 141.0, 135.4, 126.3, 126.1, 124.6, 124.4, 121.1, 120.4, 120.0, 119.2, 117.4, 112.7, 105.2, 105.1, 66.2, 25.5. HRESIMS calcd for $[C_{18}H_{11}Br_2N_3O_1 + H]^+$ 445.93267, found 445.91940.

2-(7-Methyl-2-(7-methyl-1*H*-indol-3-yl)-3-oxoindolin-2-yl)acetonitrile (6l)



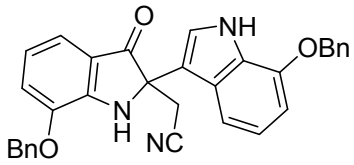
Yellow amorphous solid. IR (KBr) ν_{max}: 3370, 2253, 1690, 1607 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (s, 1H, NH), 7.56 (d, J = 7.8 Hz, 1H, Ar-H), 7.42 (d, J = 7.1 Hz, 1H, Ar-H), 7.29 (s, 1H, Ar-H), 7.17 (d, J = 7.5 Hz, 1H, Ar-H), 7.02-6.96 (m, 2H, Ar-H), 6.91 (t, J = 7.5 Hz, 1H, Ar-H), 5.21 (s, 1H, NH), 3.40 (d, J = 16.6 Hz, 1H, CH_2), 3.01 (d, J = 16.6 Hz, 1H, CH_2), 2.45 (s, 3H, CH_3), 2.29 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.7, 159.6, 138.4, 136.5, 123.9, 123.4, 122.9, 122.7, 122.2, 121.2, 120.9, 120.6, 119.2, 116.9, 116.7, 112.0, 65.9, 26.7, 16.5, 15.7. HRESIMS calcd for $[C_{20}H_{17}N_3O + H]^+$ 316.14499, found 316.13577.

2-(7-Methoxy-2-(7-methoxy-1*H*-indol-3-yl)-3-oxoindolin-2-yl)acetonitrile (6m)



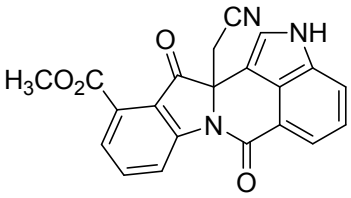
Orange amorphous solid. IR (KBr) ν_{max}: 3445, 2254, 1694, 1626, 1461, 1306 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.29 (s, 1H, NH), 7.92 (s, 1H, NH), 7.35 (d, J = 2.3 Hz, 1H, Ar-H), 7.16 (d, J = 7.8 Hz, 1H, Ar-H), 7.07 (d, J = 7.8 Hz, 1H, Ar-H), 6.80-6.73 (m, 3H, Ar-H), 6.68 (dd, J = 5.6, 2.3 Hz, 1H, Ar-H), 3.90 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 3.43 (d, J = 16.6 Hz, 1H, CH_2), 3.36 (d, J = 16.6 Hz, 1H, CH_2). ^{13}C NMR (100 MHz, DMSO-d_6): δ 200.5, 153.0, 146.7, 146.3, 127.3, 126.2, 124.1, 120.0, 119.1, 118.8, 117.7, 117.5, 116.0, 112.7, 112.3, 102.3, 66.1, 56.0, 55.6, 25.6. HRESIMS calcd for $[C_{20}H_{17}N_3O_3 + Na]^+$ 370.11676, found 370.10588.

2-(7-(Benzyloxy)-2-(7-(benzyloxy)-1*H*-indol-3-yl)-3-oxoindolin-2-yl)acetonitrile (6n)



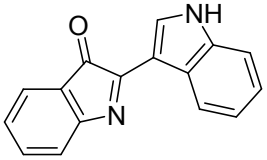
Yellow amorphous solid. IR (KBr) ν_{max}: 3396, 2252, 1702, 1617, 1263, 1052 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 11.33 (d, J = 2.0 Hz, 1H, NH), 8.00 (s, 1H, NH), 7.57-7.49 (m, 4H, Ar-H), 7.42-7.36 (m, 5H, Ar-H), 7.32 (t, J = 6.0 Hz, 2H, Ar-H), 7.25 (d, J = 7.8 Hz, 1H, Ar-H), 7.08 (d, J = 7.8 Hz, 1H, Ar-H), 6.75-6.68 (m, 4H, Ar-H), 5.27 (s, 2H, OCH_2), 5.22 (s, 2H, OCH_2), 3.43 (d, J = 16.7 Hz, 1H, CH_2), 3.36 (d, J = 16.7 Hz, 1H, CH_2). ^{13}C NMR (100 MHz, DMSO-d_6): δ 200.5, 153.3, 145.6, 145.1, 137.7, 137.2, 128.9, 128.8, 128.3, 128.2, 128.0, 127.9, 127.6, 127.5, 126.4, 124.3, 112.0, 119.4, 119.2, 118.8, 116.4, 112.8, 112.4, 103.8, 69.9, 69.6, 66.2, 25.6. HRESIMS calcd for $[C_{32}H_{25}N_3O_3 + H]^+$ 500.19742, found 500.18442.

Methyl 12a-(cyanomethyl)-6,12-dioxo-2,6,12,12a-tetrahyroindolo[1,2-*b*]pyrrolo[4,3,2-*de*] isoquioline-11-carboxylate (**7**)



Yellow amorphous solid. IR (KBr) ν_{max}: 3351, 2253, 1739, 1712, 1665, 1613, 1226 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 11.73 (s, 1H, NH), 8.73 (d, J = 8.5 Hz, 1H, NH), 7.92 (t, J = 8.0 Hz, 1H, Ar-H), 7.72 (s, 1H, Ar-H), 7.71 (d, J = 7.7 Hz, 2H, Ar-H), 7.48 (d, J = 7.4 Hz, 1H, Ar-H), 7.37 (t, J = 7.7 Hz, 1H, Ar-H), 3.89 (s, 3H, OCH_3), 3.46 (d, J = 16.7 Hz, 1H, CH_2), 3.37 (d, J = 16.7 Hz, 1H, CH_2). ^{13}C NMR (100 MHz, DMSO-d_6): δ 194.7, 166.7, 162.7, 153.9, 138.5, 134.0, 131.0, 128.4, 124.2, 123.7, 122.8, 120.1, 119.9, 118.8, 118.0, 117.4, 116.4, 104.4, 69.3, 53.1, 32.1. HRESIMS calcd for $[C_{21}H_{13}N_3O_4 + Na]^+$ 394.08038, found 394.06886.

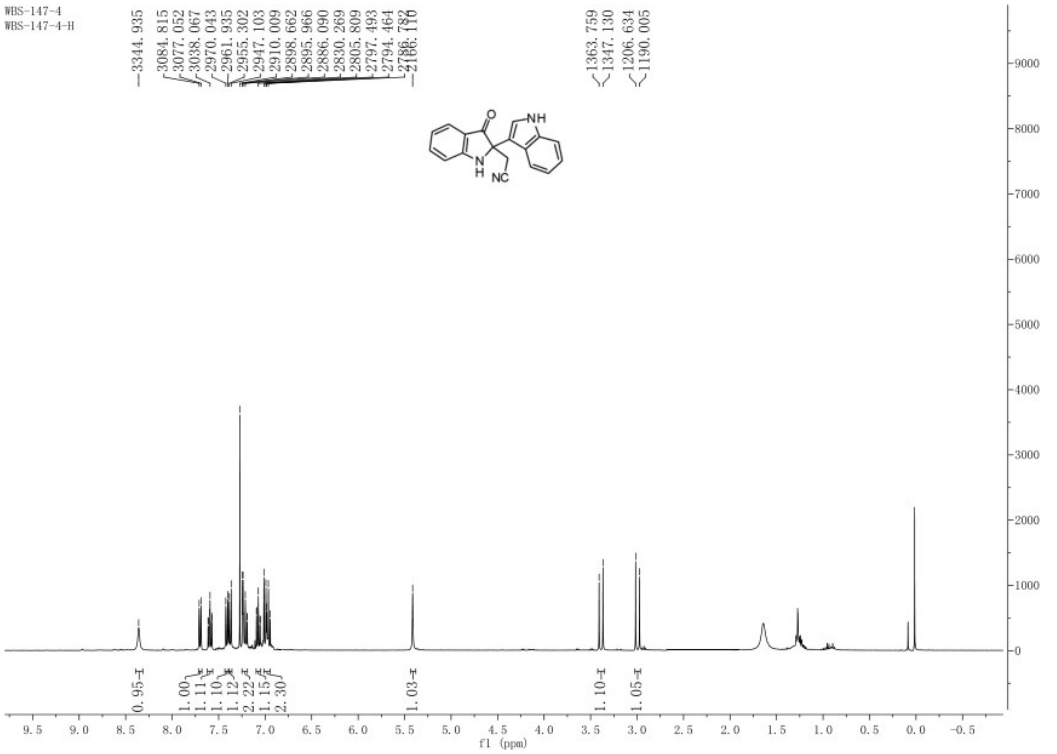
2,3'-Bi(3*H*-indol)-3-one (**9**)

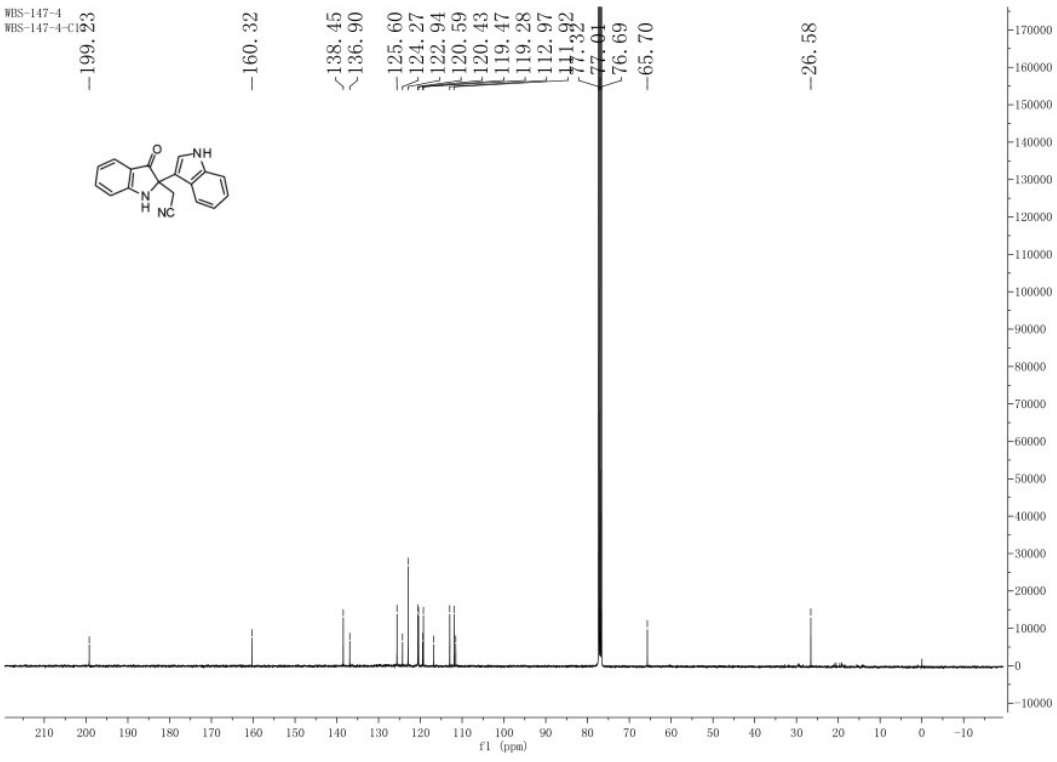


Red solid, mp: 214-215 °C (from EtOAc/PE = 1:4). IR (KBr) ν_{max}: 3187, 1719, 1604, 1559, 1447, 1368, 1240, 1135 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 12.14 (s, 1H, NH), 8.50 (d, J = 3.0 Hz, 1H, Ar-H), 8.40 (dd, J = 7.0, 2.5 Hz, 1H, Ar-H), 7.59-7.50 (m, 3H, Ar-H), 7.34 (d, J = 7.5 Hz, 1H, Ar-H), 7.28-7.24 (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.

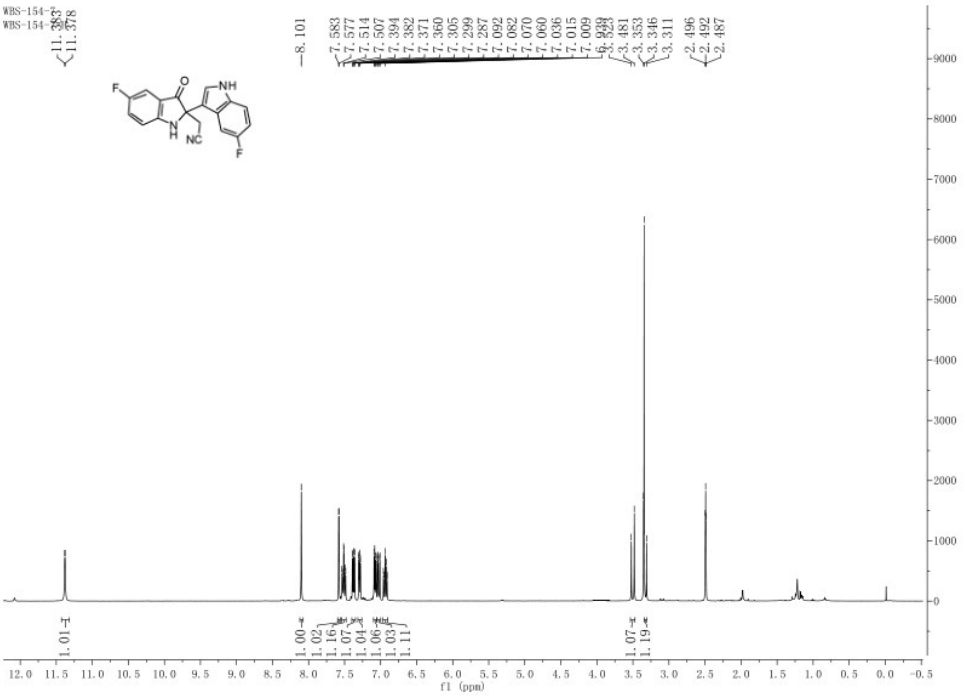
4. Copies of ^1H and ^{13}C Spectra

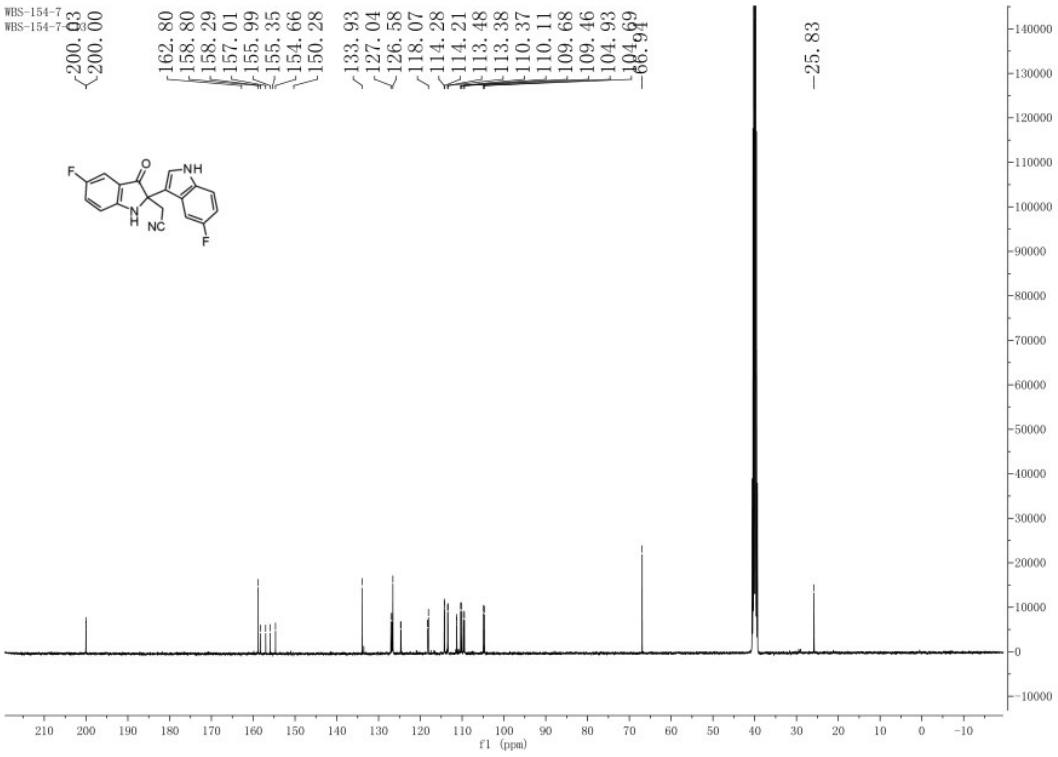
^{1}H and ^{13}C NMR Spectra for **6a**



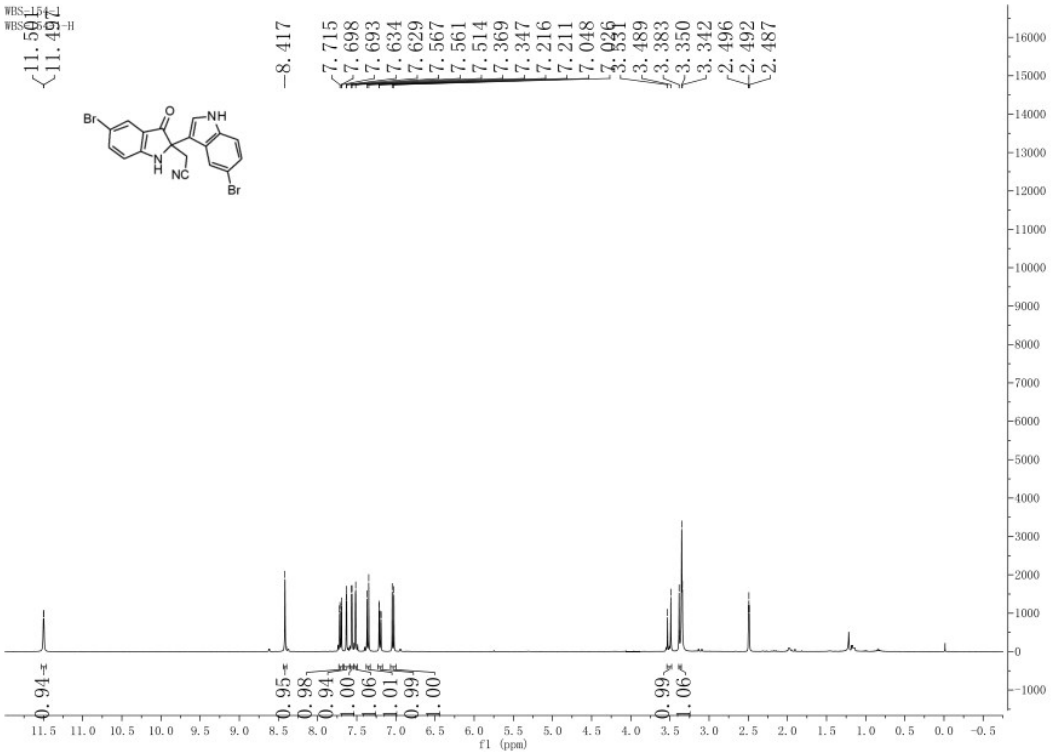


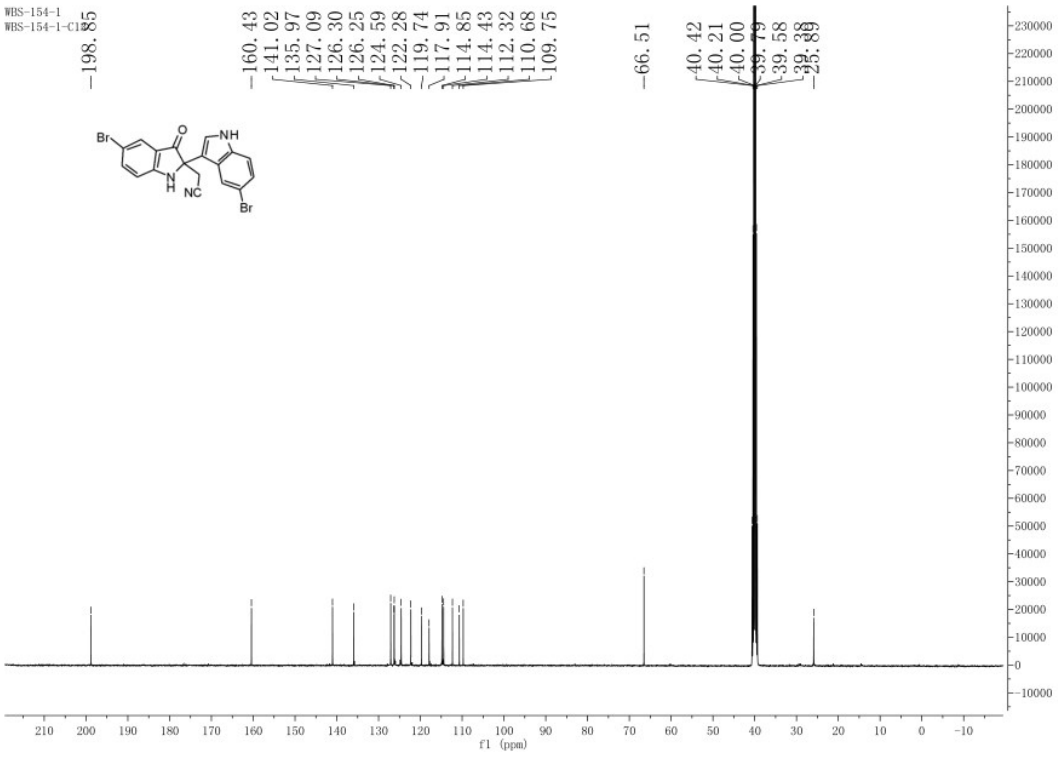
^{1}H and ^{13}C NMR Spectra for **6b**



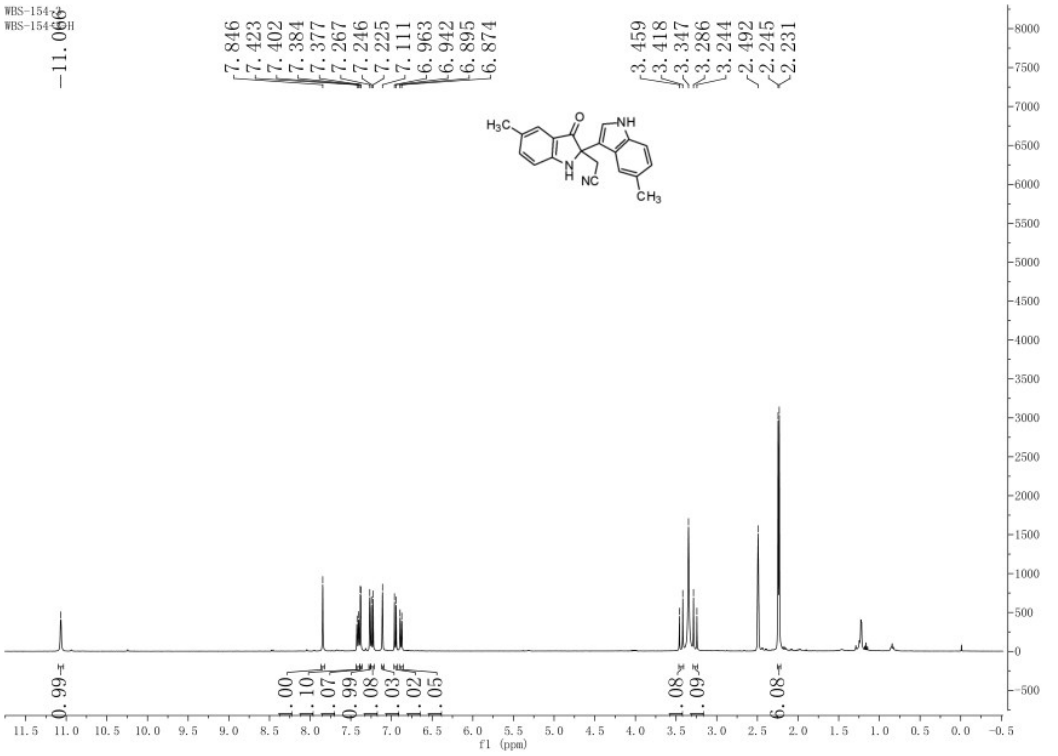


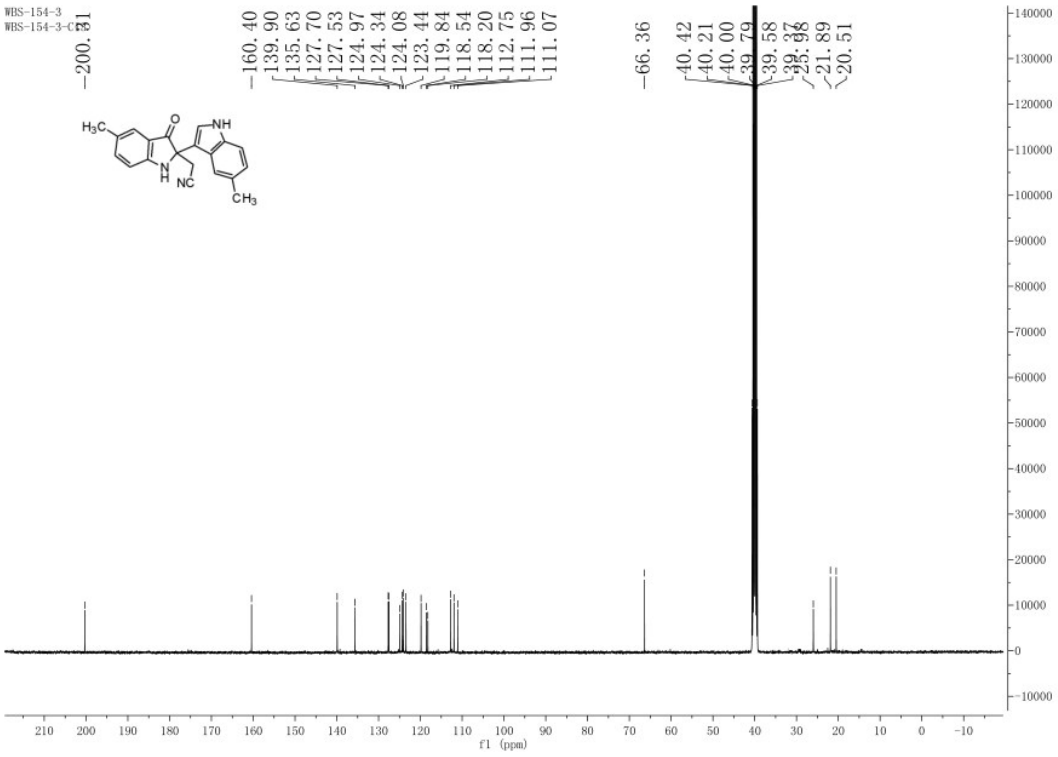
^{1}H and ^{13}C NMR Spectra for **6c**



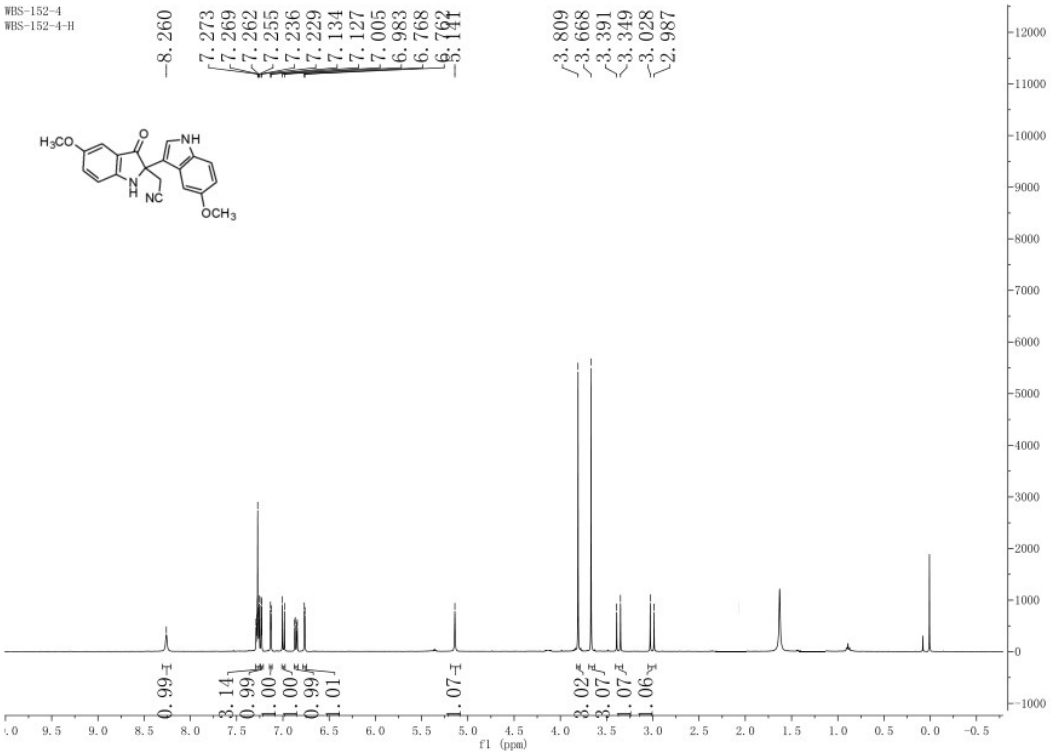


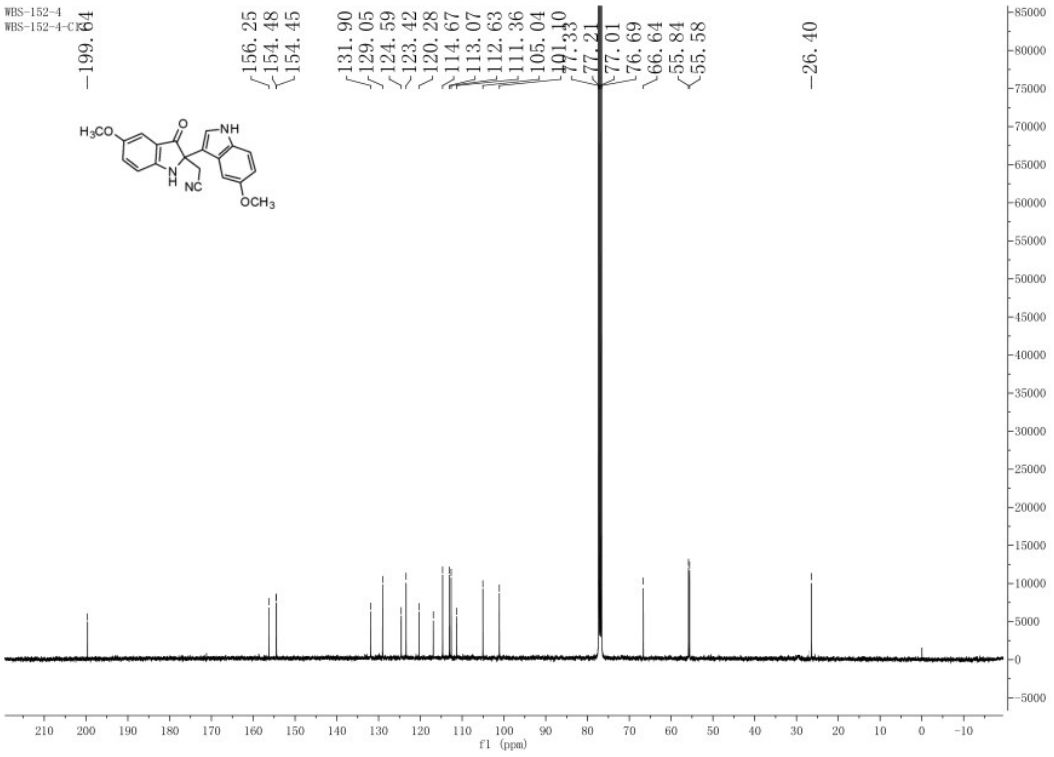
^{1}H and ^{13}C NMR Spectra for **6d**



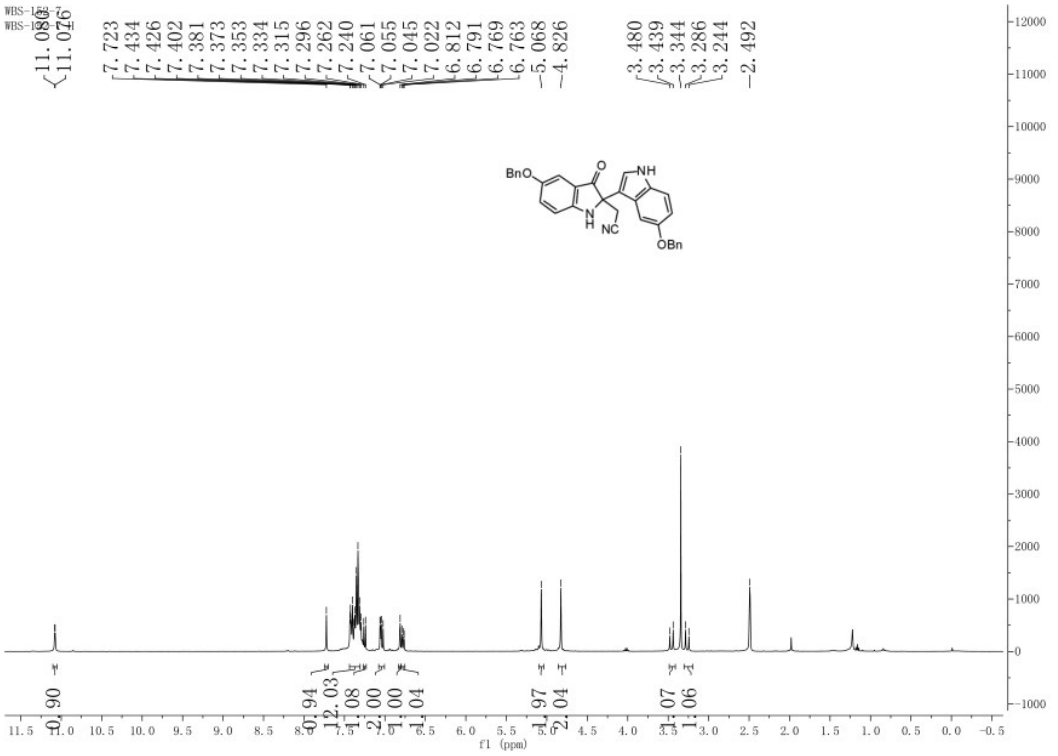


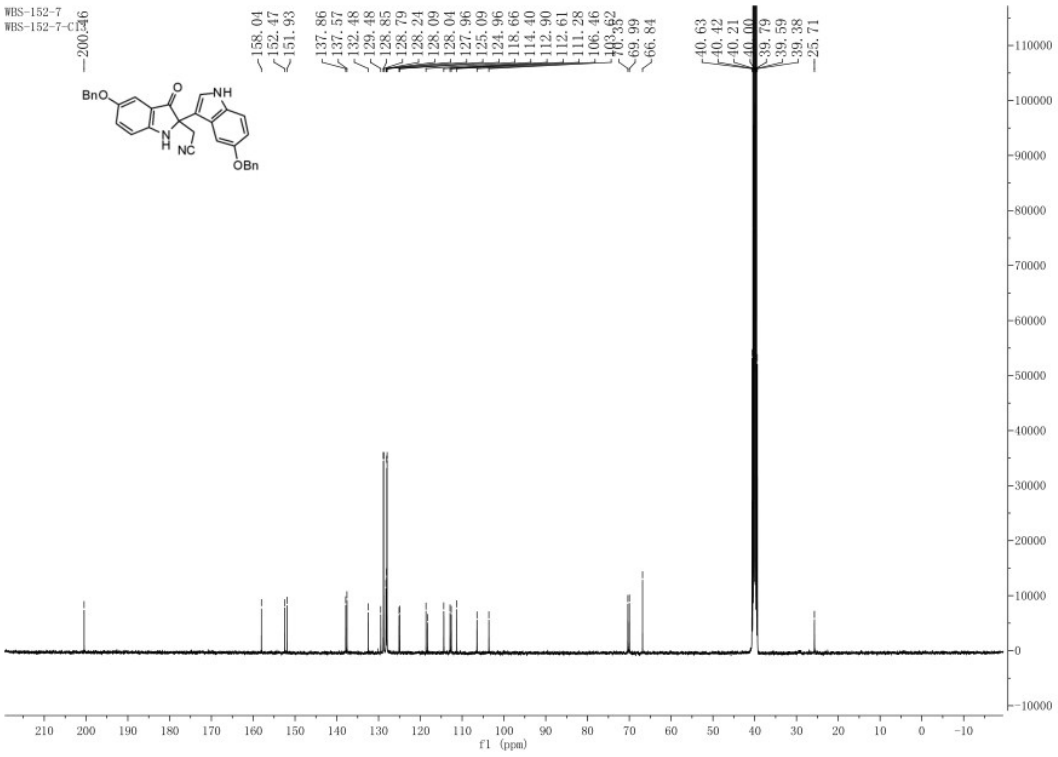
^{1}H and ^{13}C NMR Spectra for **6e**



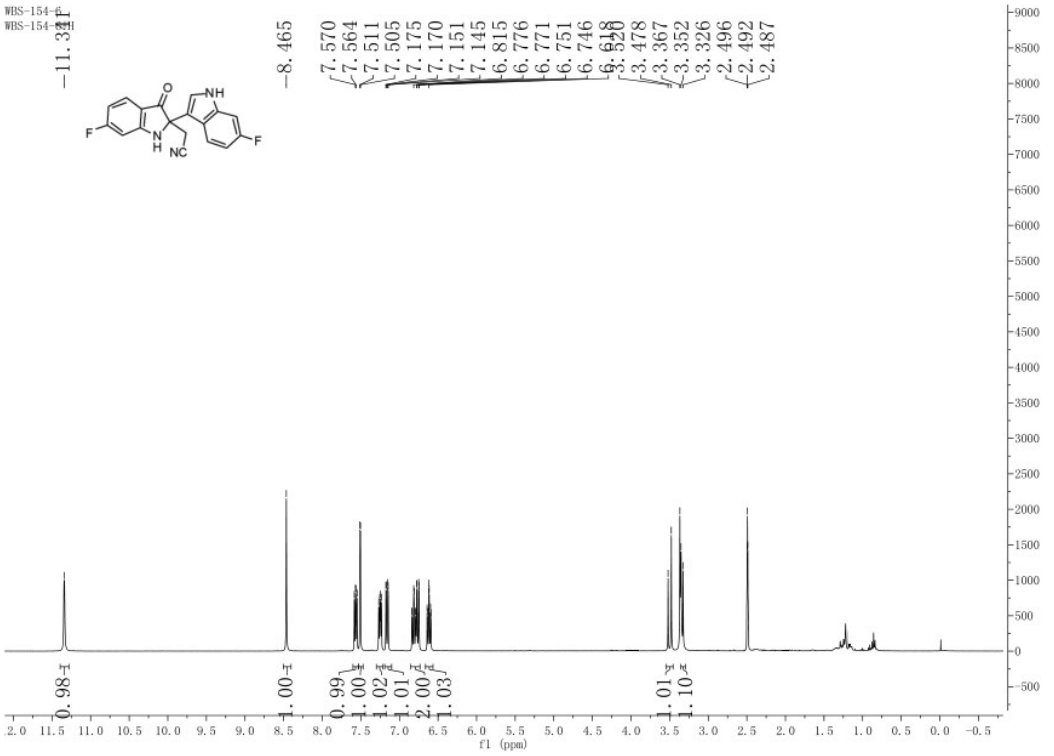


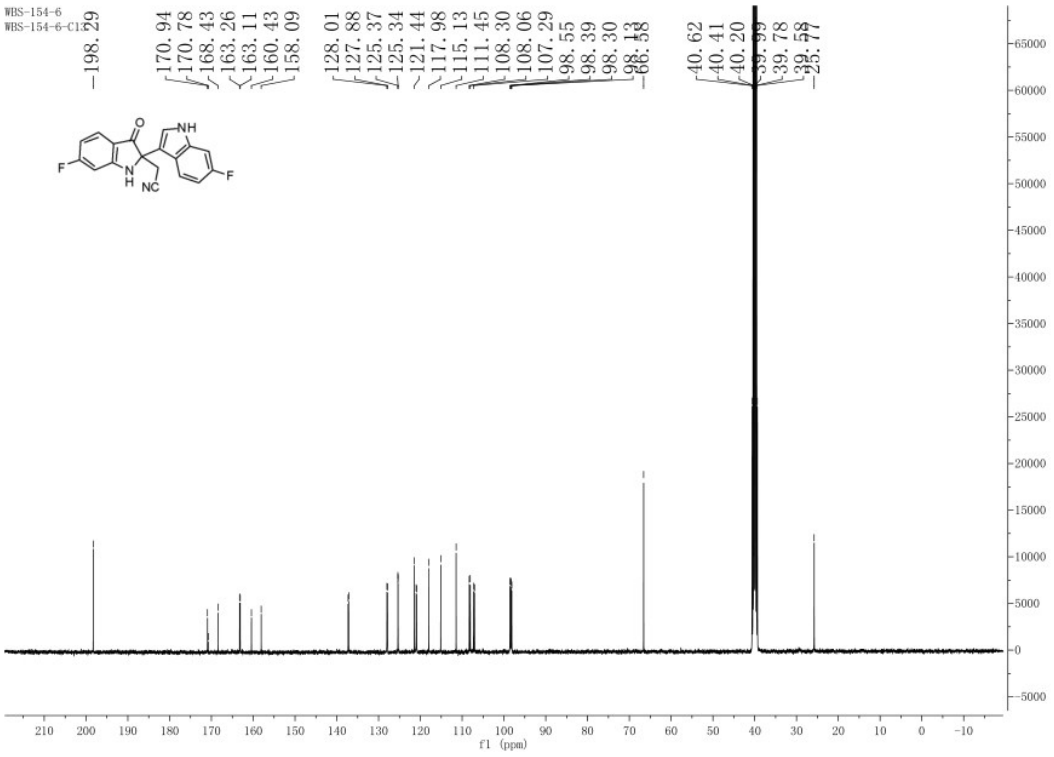
^{1}H and ^{13}C NMR Spectra for **6f**



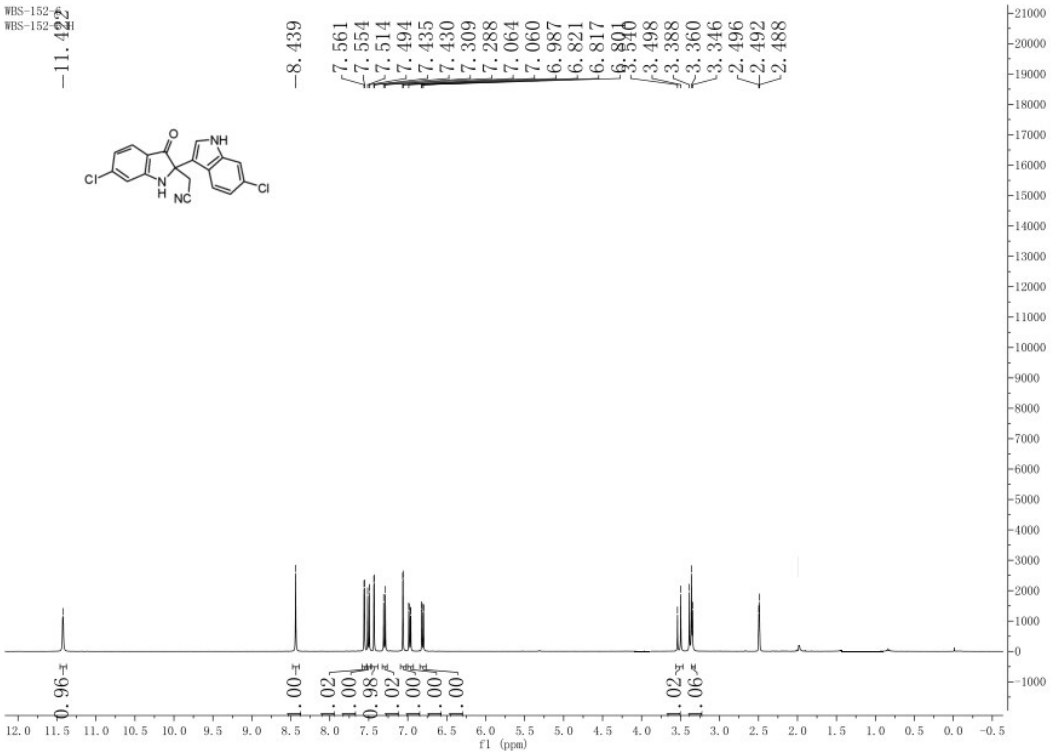


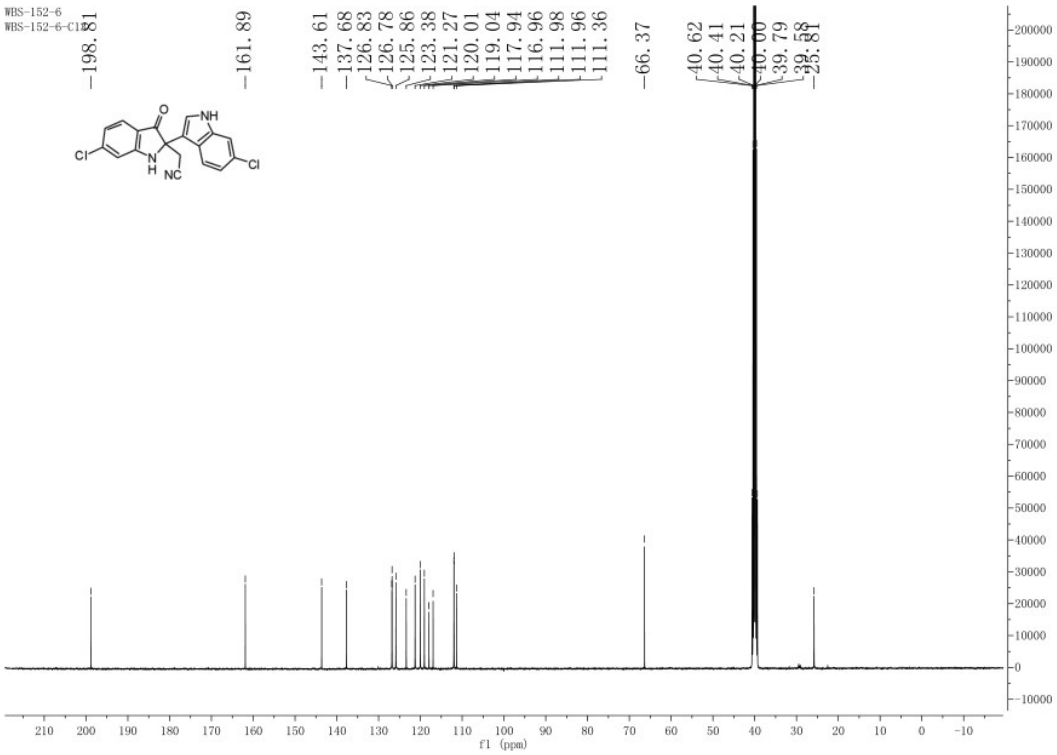
^{1}H and ^{13}C NMR Spectra for **6g**



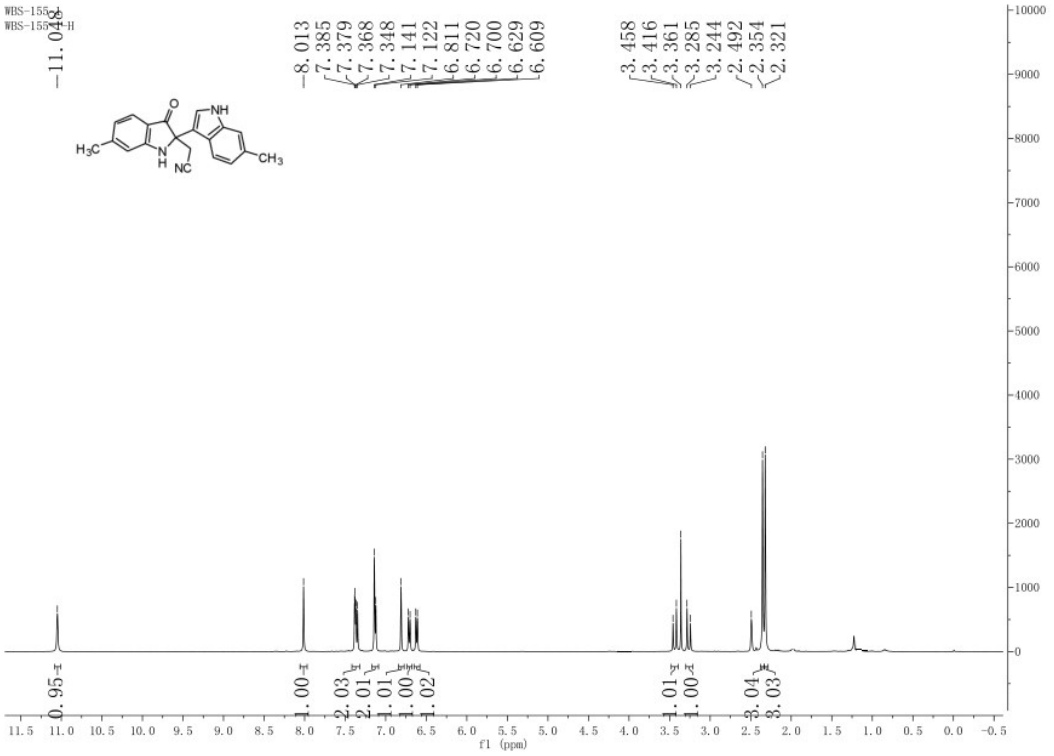


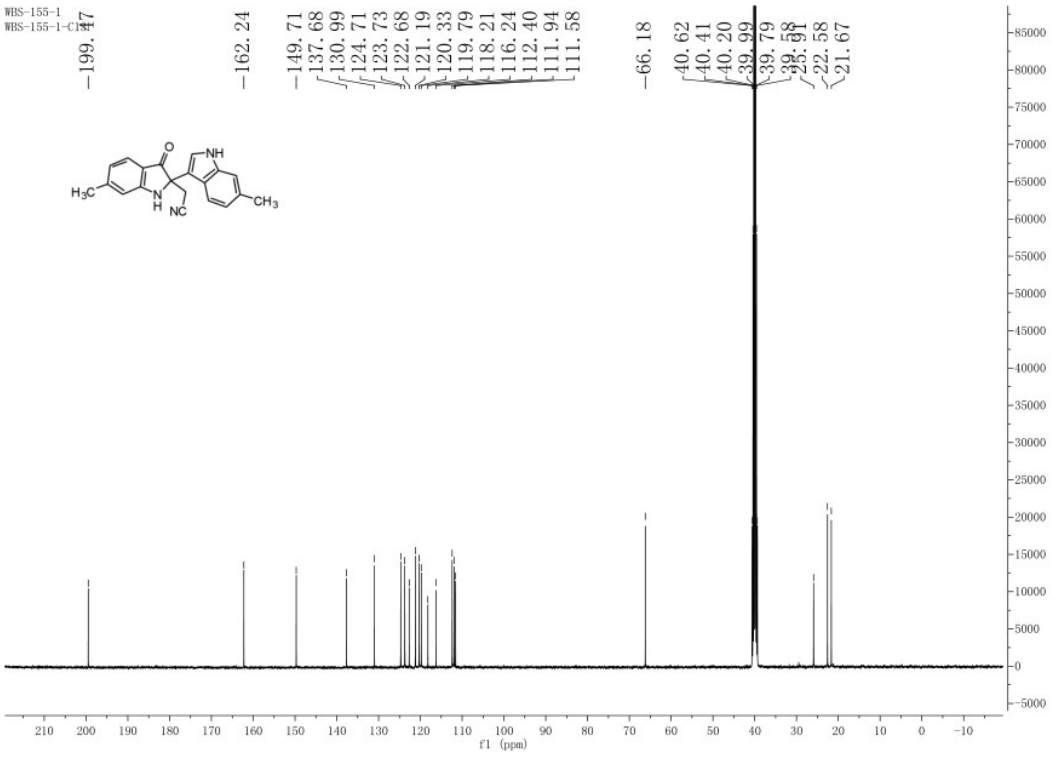
^{1}H and ^{13}C NMR Spectra for **6h**



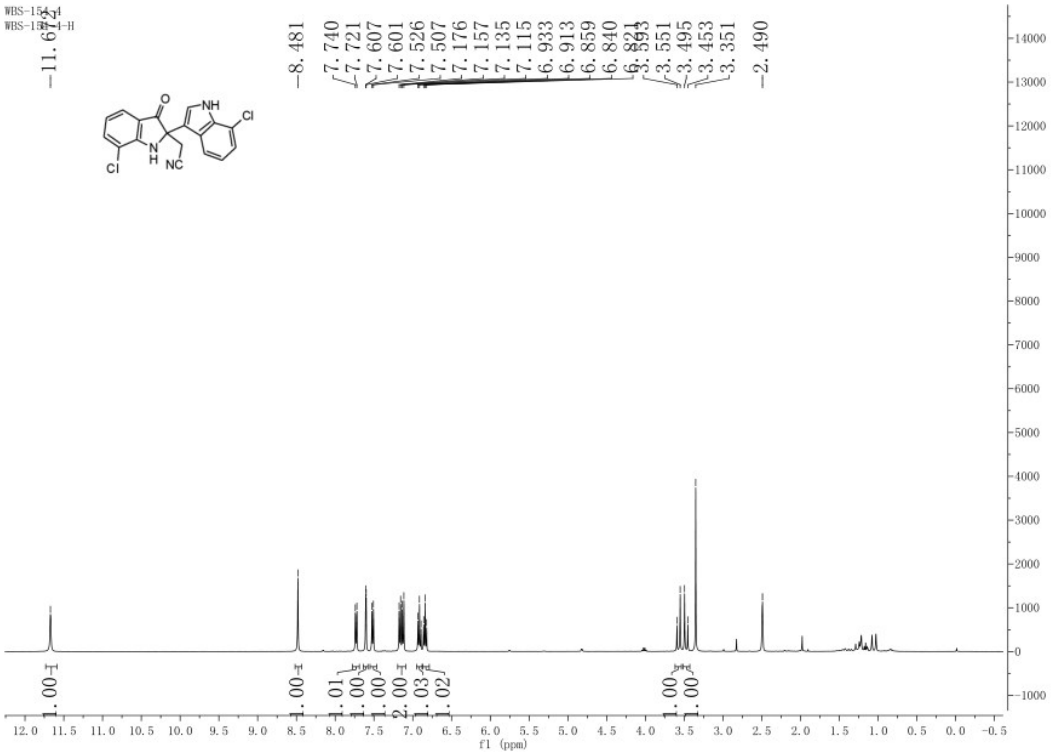


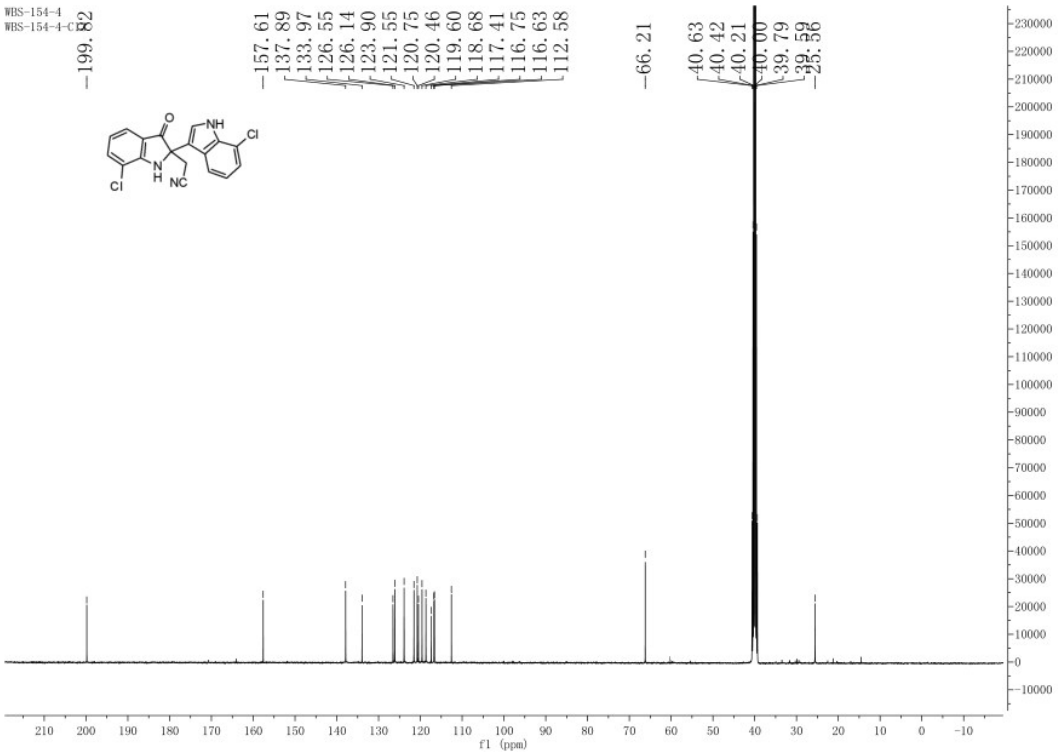
^{1}H and ^{13}C NMR Spectra for **6i**



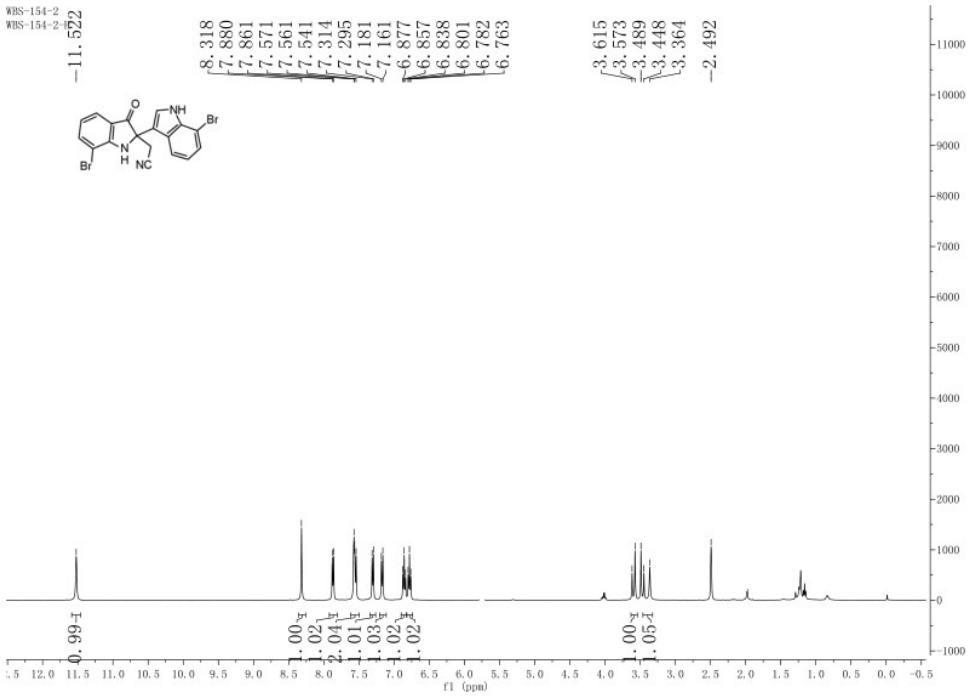


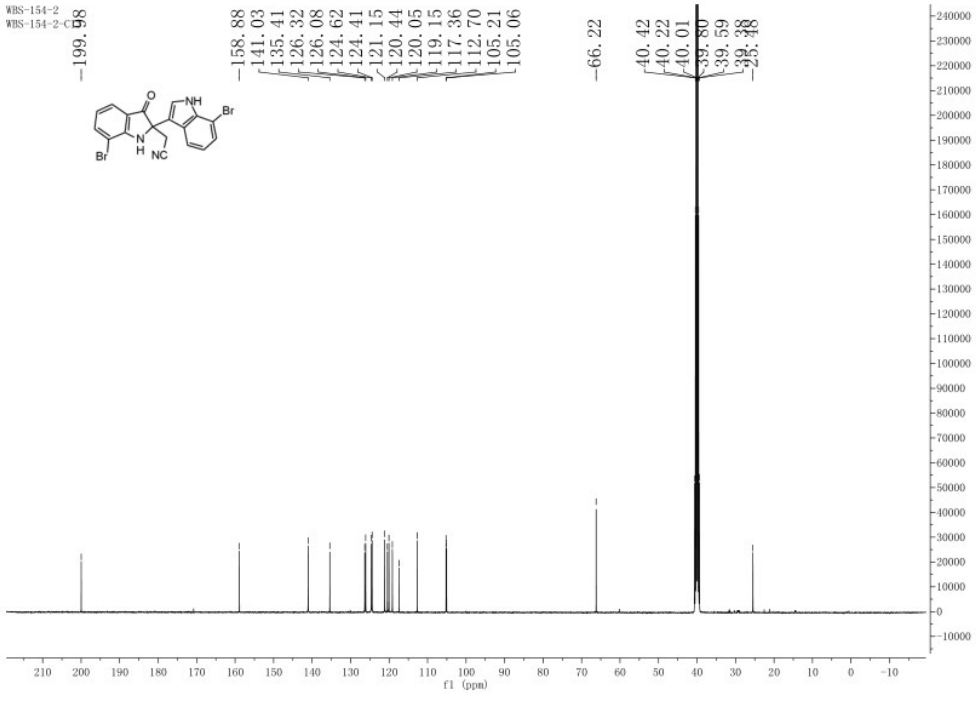
^{1}H and ^{13}C NMR Spectra for **6j**



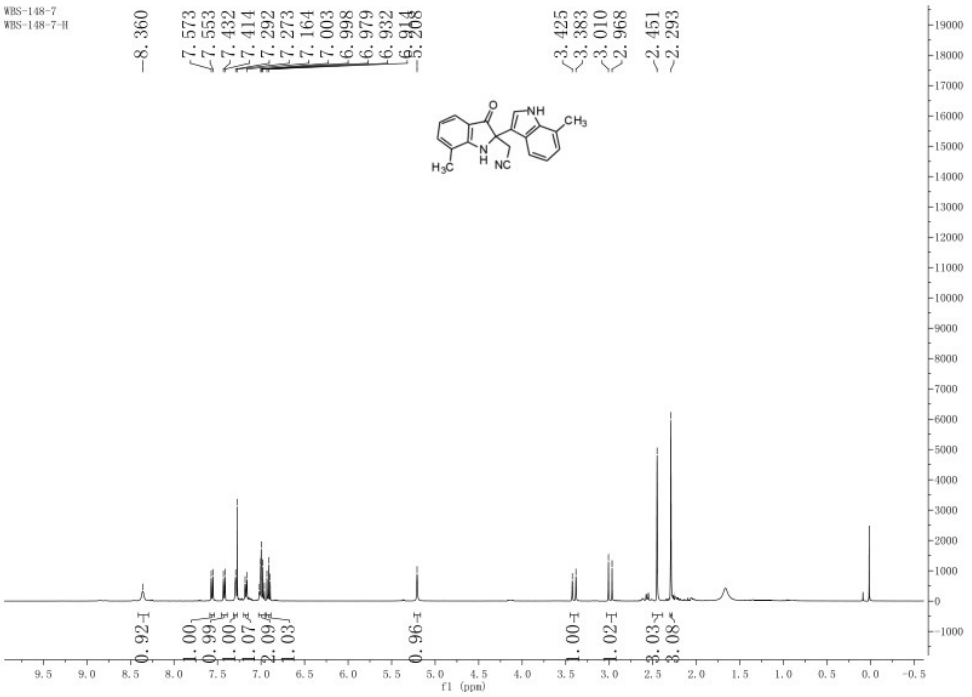


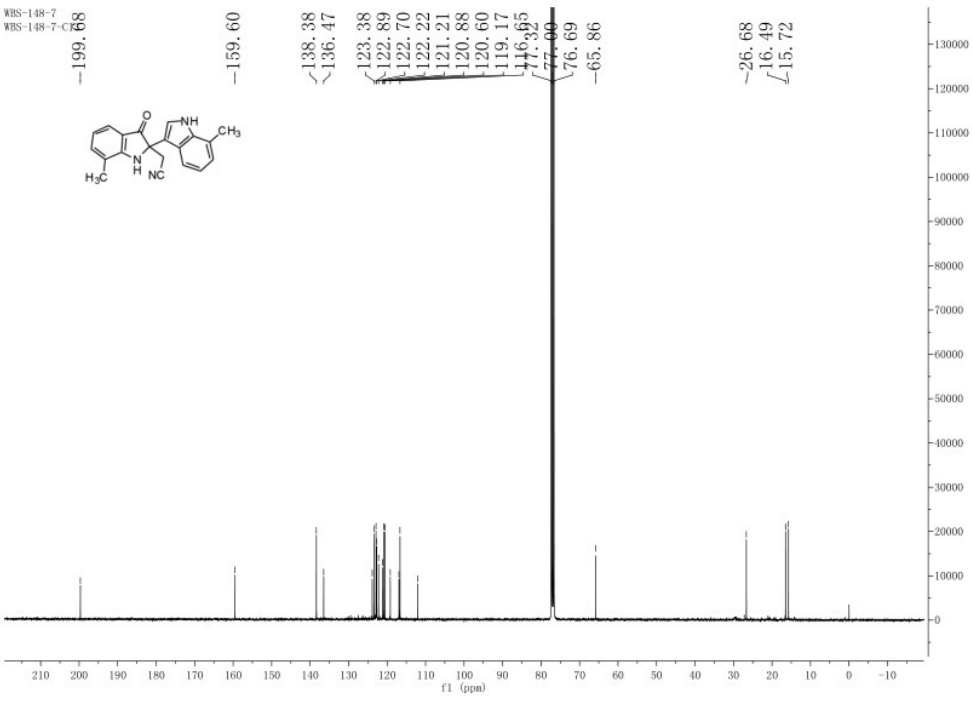
^{1}H and ^{13}C NMR Spectra for **6k**



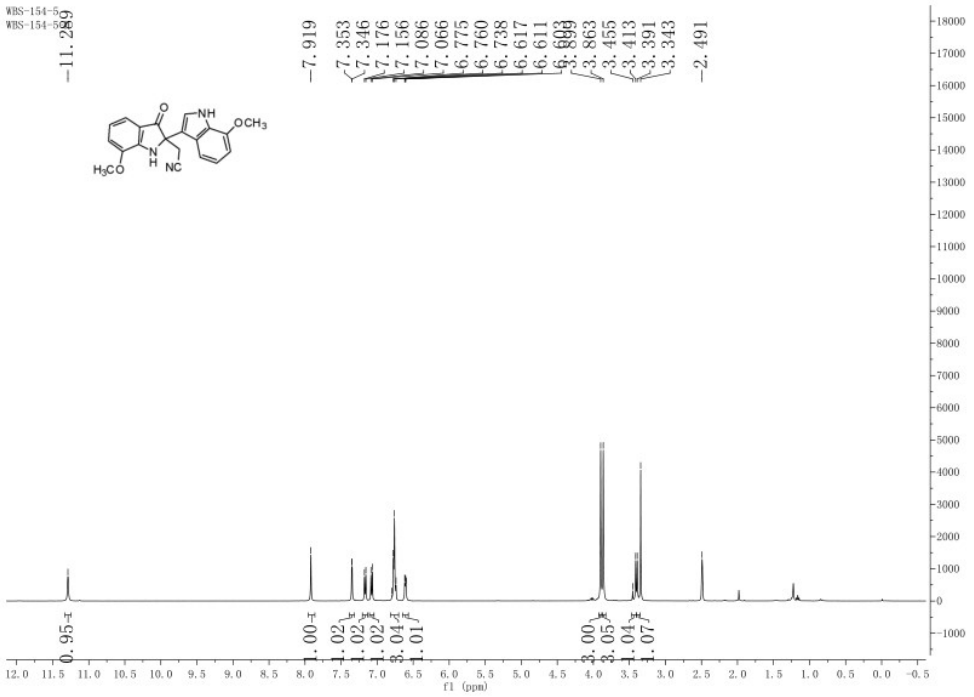


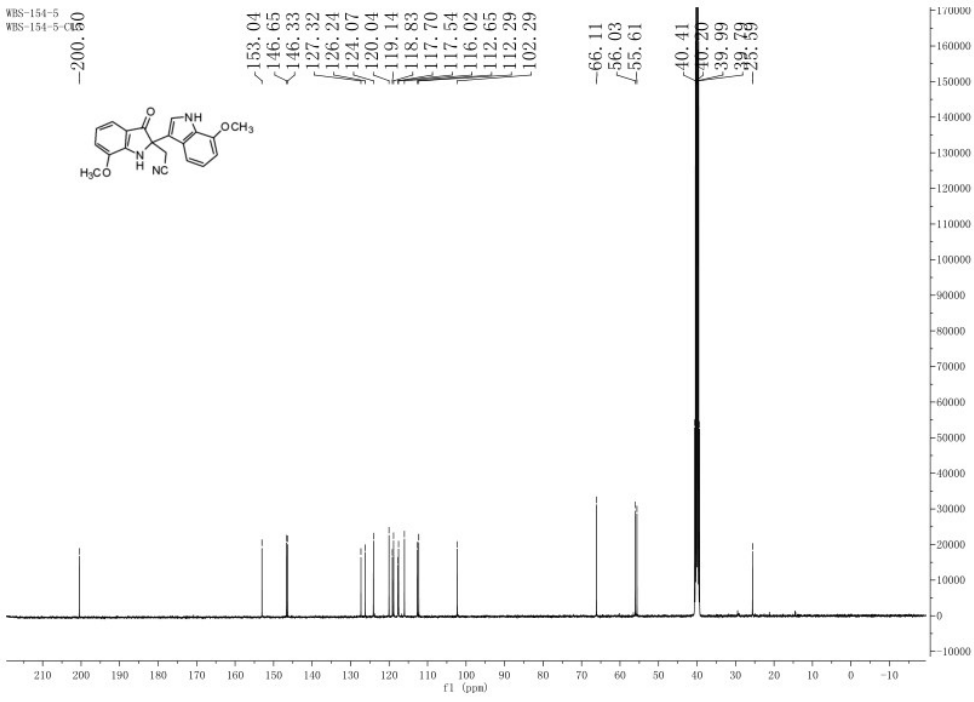
^{1}H and ^{13}C NMR Spectra for **6l**



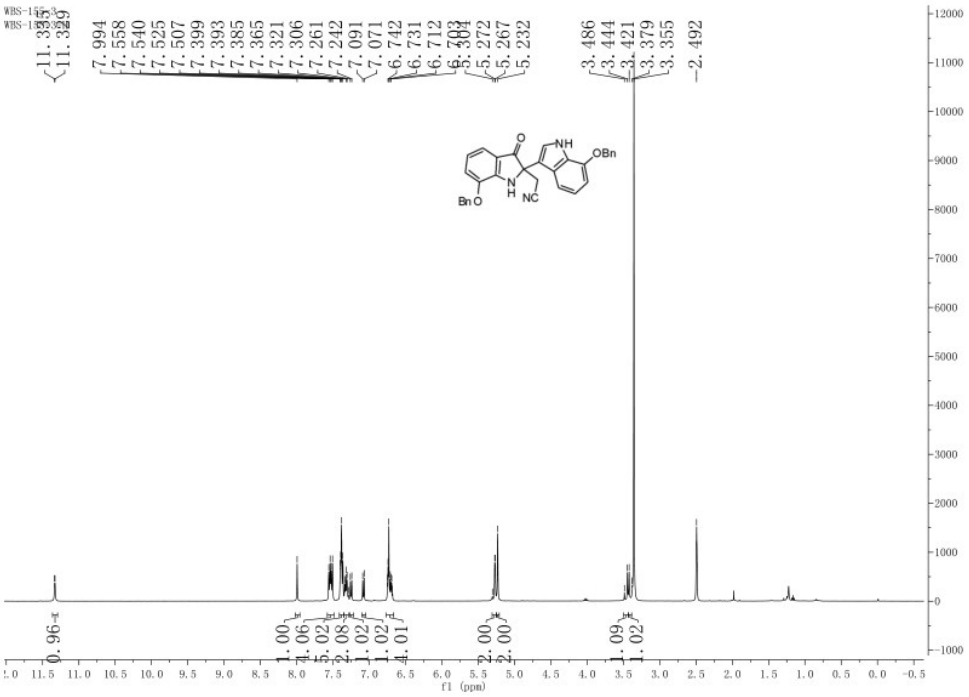


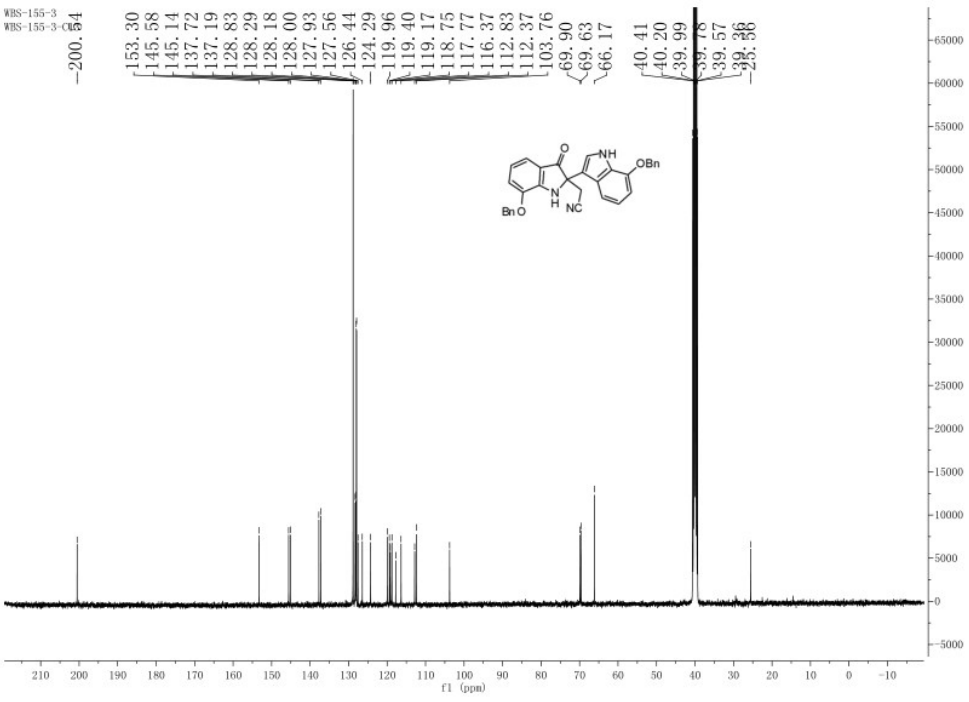
^{1}H and ^{13}C NMR Spectra for **6m**



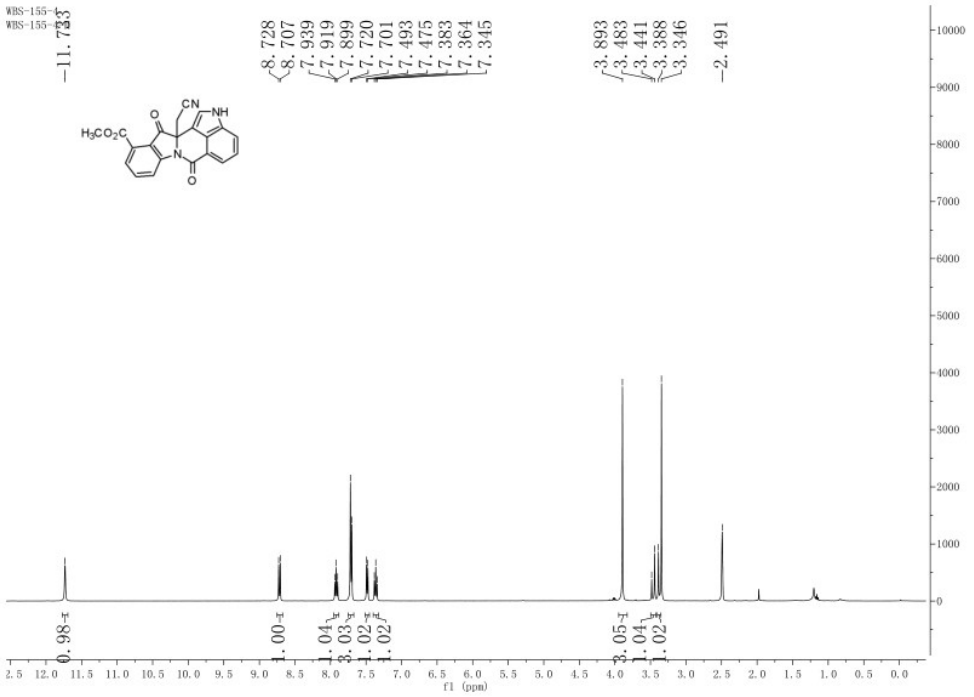


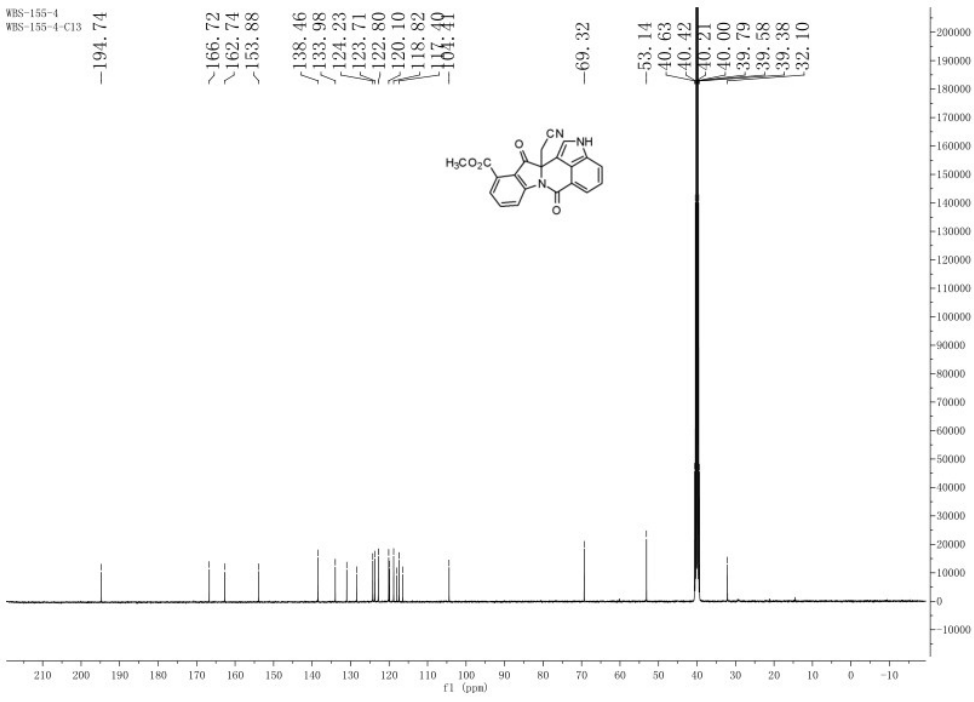
^{1}H and ^{13}C NMR Spectra for **6n**



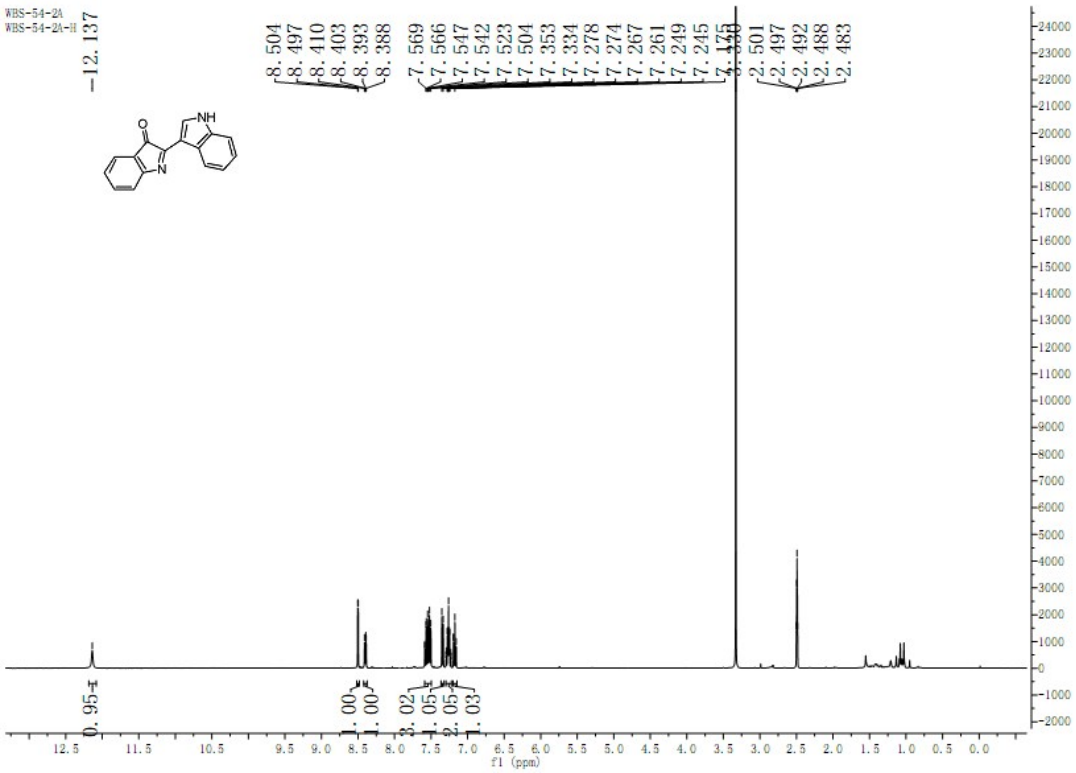


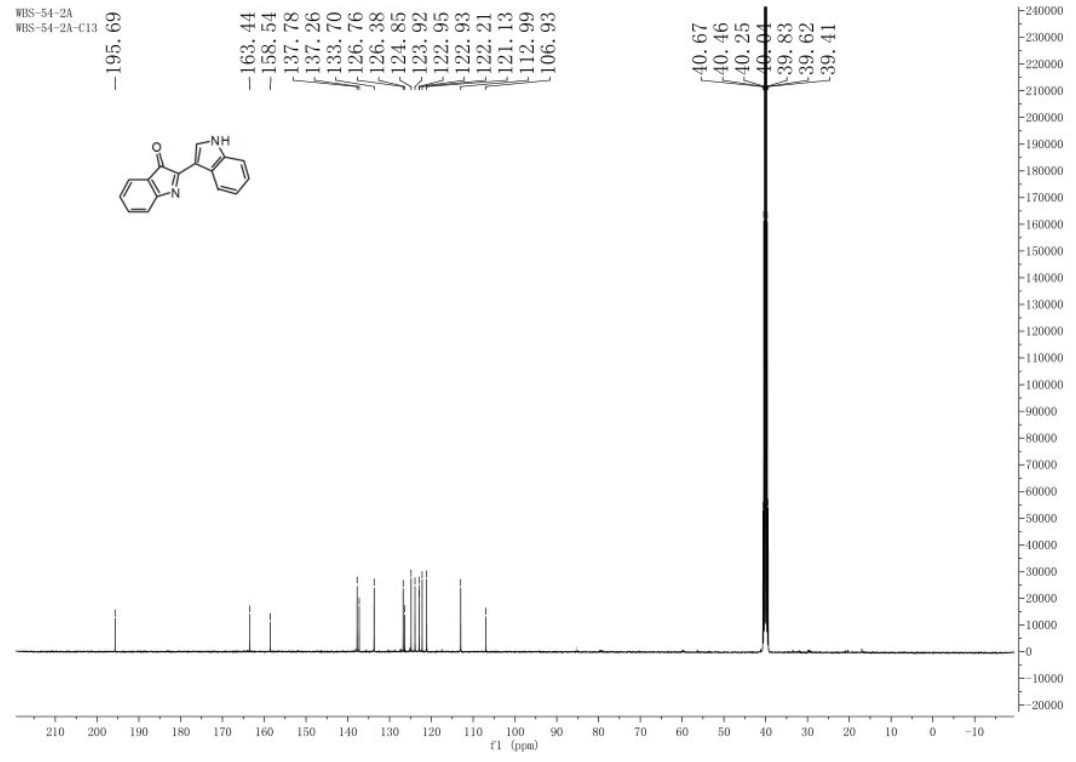
^{1}H and ^{13}C NMR Spectra for **7**





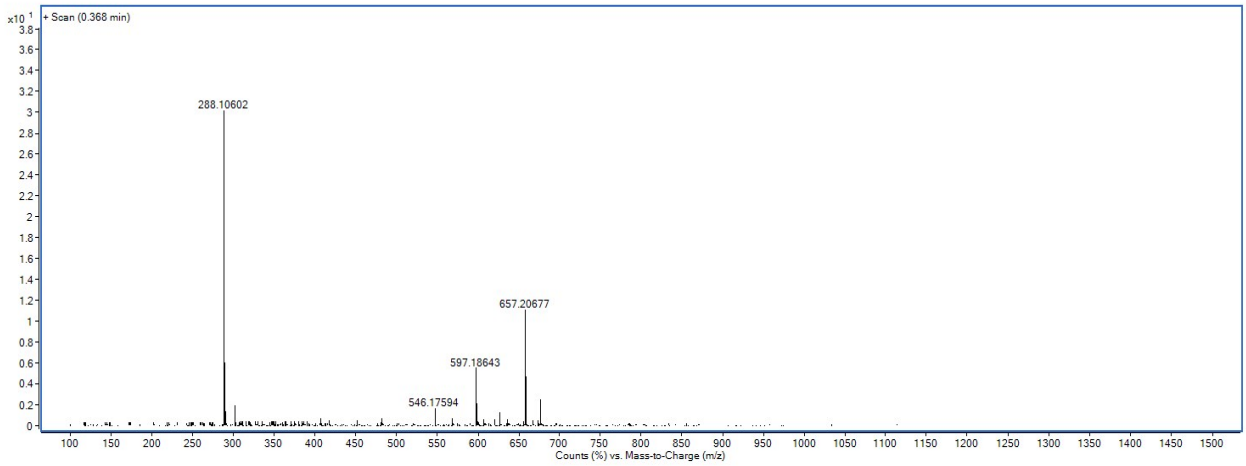
^{1}H and ^{13}C NMR Spectra for **9**



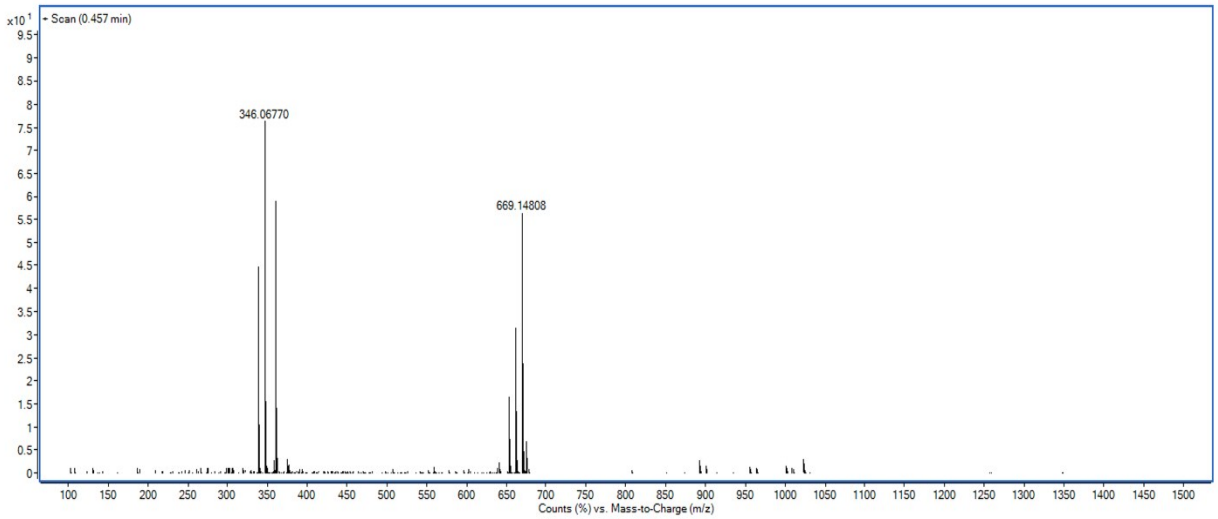


5. Copies of HRESIMS Spectra

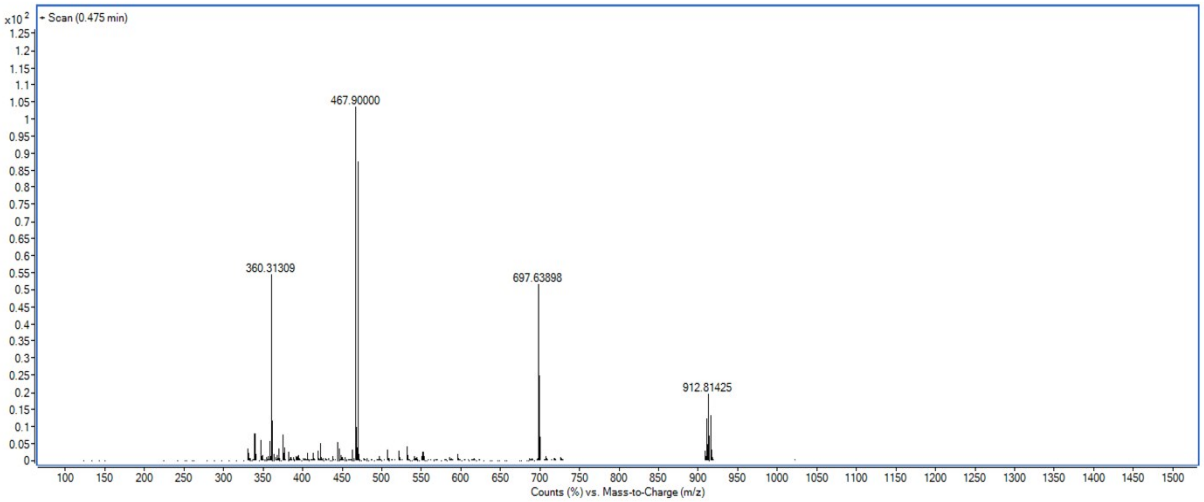
2-(2-(1H-Indol-3-yl)-3-oxoindolin-2-yl)acetonitrile (**6a**)



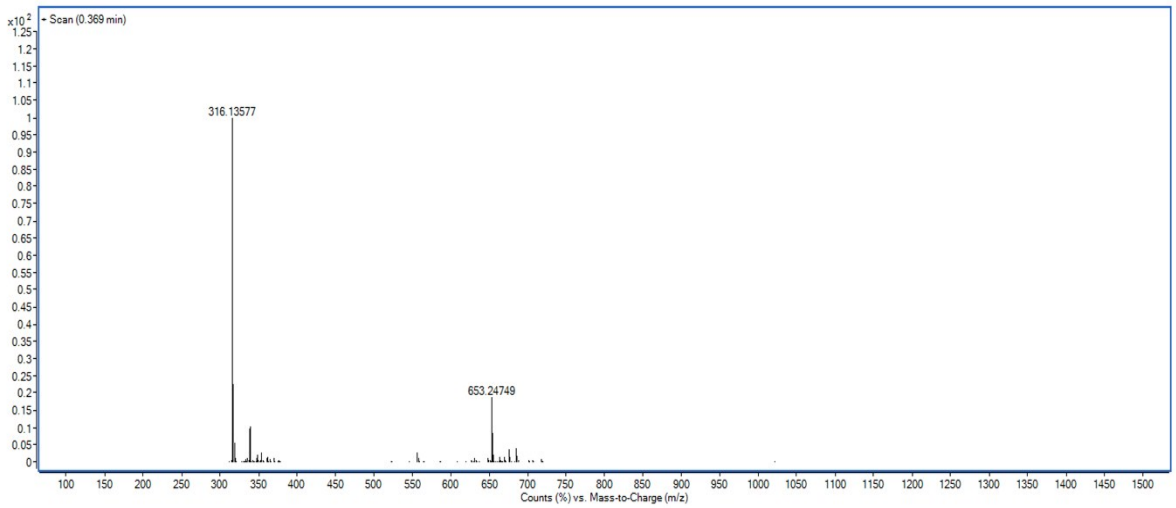
2-(5-Fluoro-2-(5-fluoro-1H-indol-3-yl)-3-oxoindolin-2-yl)acetonitrile (**6b**).



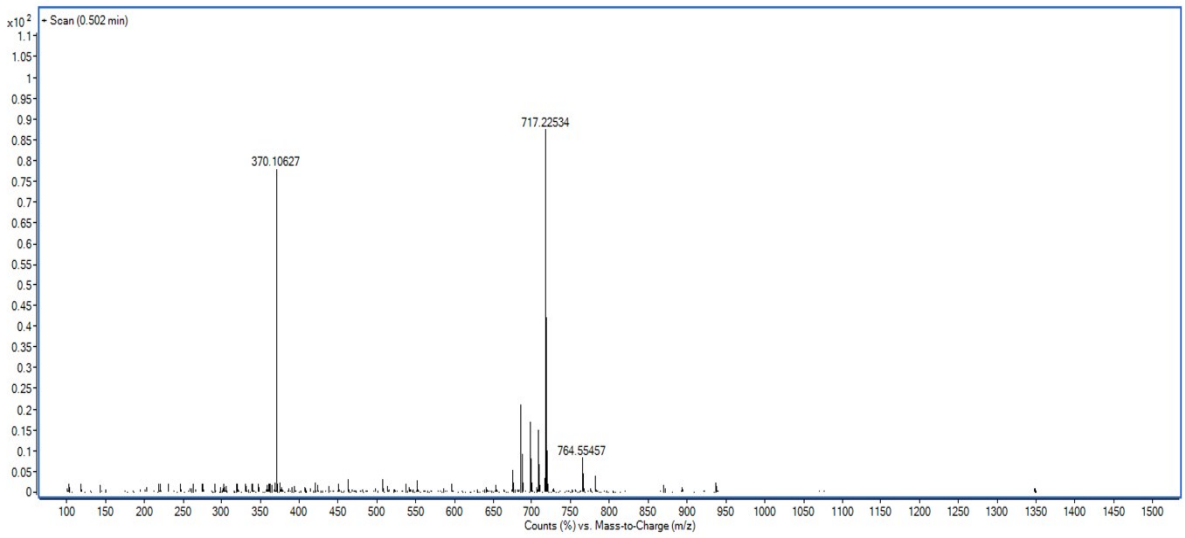
2-(5-Bromo-2-(5-bromo-1H-indol-3-yl)-3-oxoindolin-2-yl)acetonitrile (**6c**).



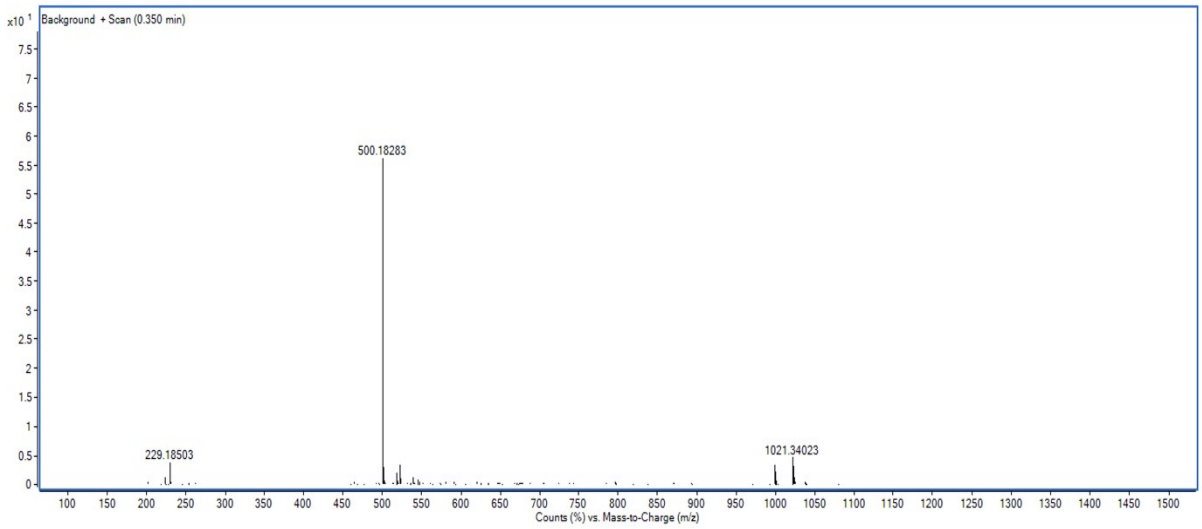
2-(5-Methyl-2-(5-methyl-1H-indol-3-yl)-3-oxoindolin-2-yl)acetonitrile (**6d**)



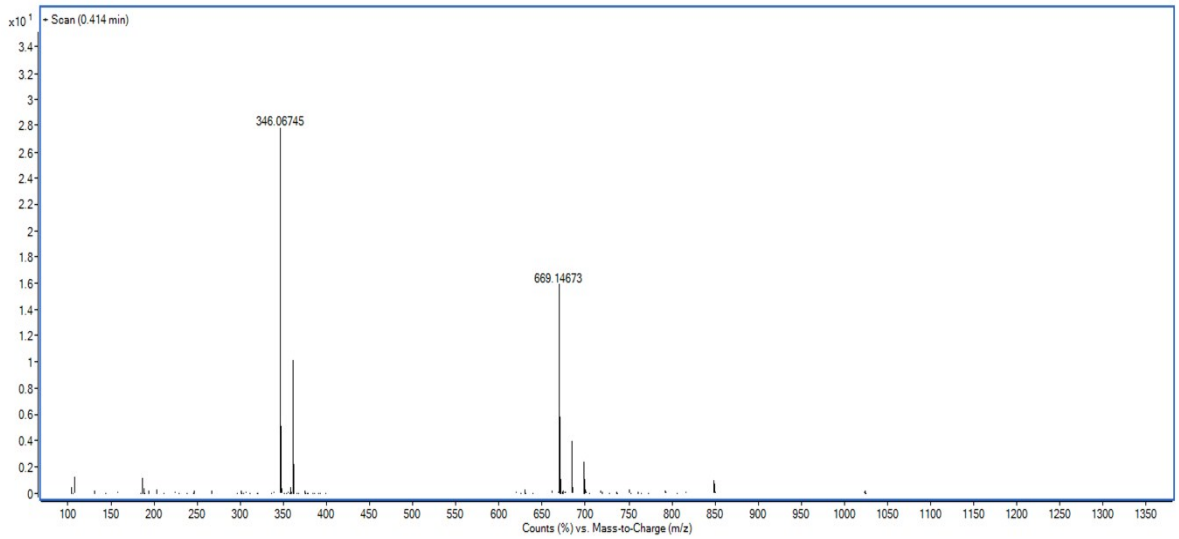
2-(5-Methoxy-2-(5-methoxy-1H-indol-3-yl)-3-oxoindolin-2-yl)acetonitrile (**6e**)



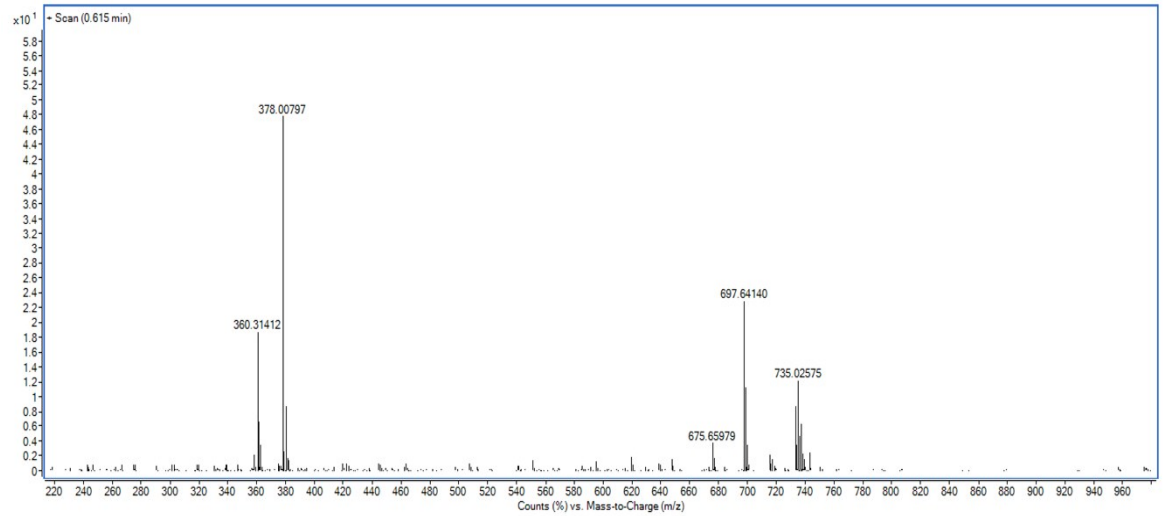
2-(5-(Benzyloxy)-2-(5-(benzyloxy)-1H-indol-3-yl)-3-oxoindolin-2-yl)acetonitrile (**6f**)



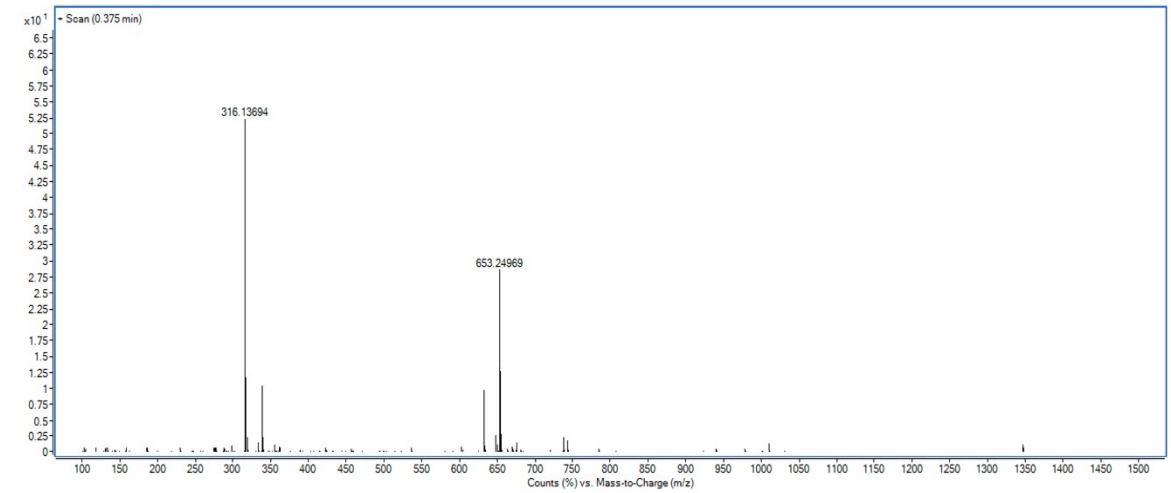
2-(6-Fluoro-2-(6-fluoro-1H-indol-3-yl)-3-oxoindolin-2-yl)acetonitrile (**6g**)



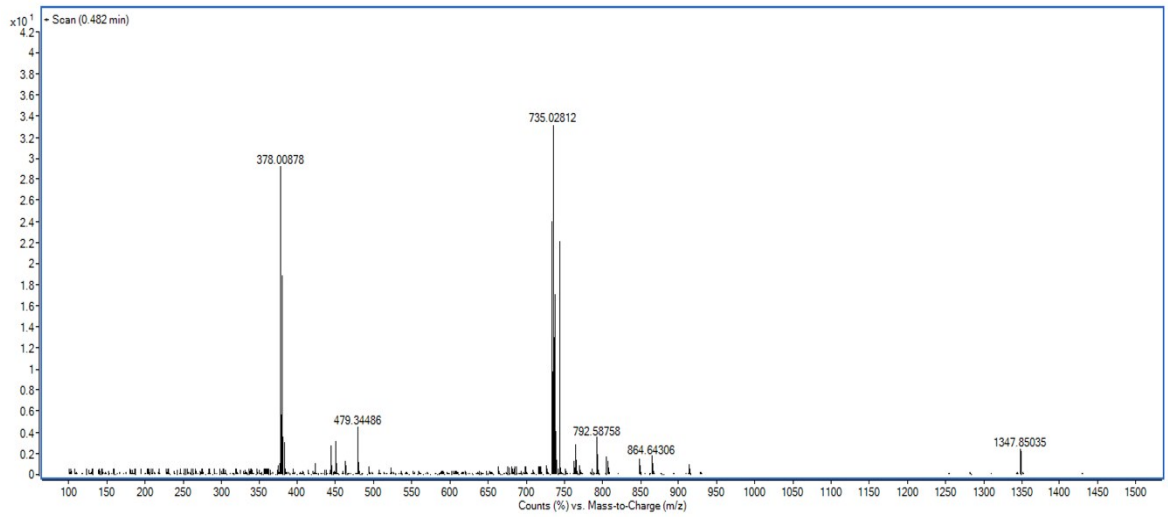
2-(6-Chloro-2-(6-chloro-1H-indol-3-yl)-3-oxoindolin-2-yl)acetonitrile (**6h**)



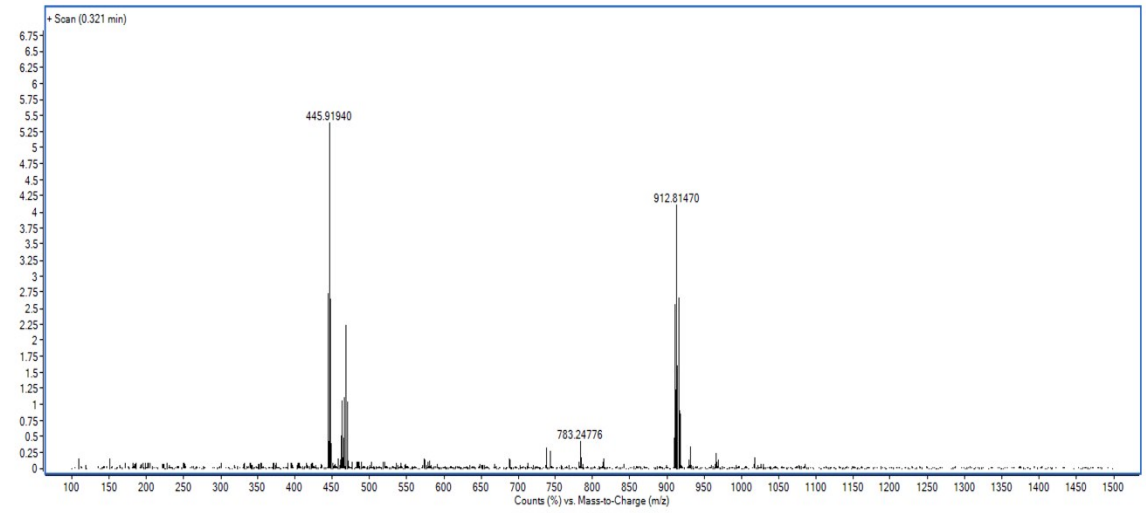
2-(6-Methyl-2-(6-methyl-1H-indol-3-yl)-3-oxoindolin-2-yl)acetonitrile (**6i**)



2-(7-Chloro-2-(7-chloro-1H-indol-3-yl)-3-oxoindolin-2-yl)acetonitrile (**6j**)

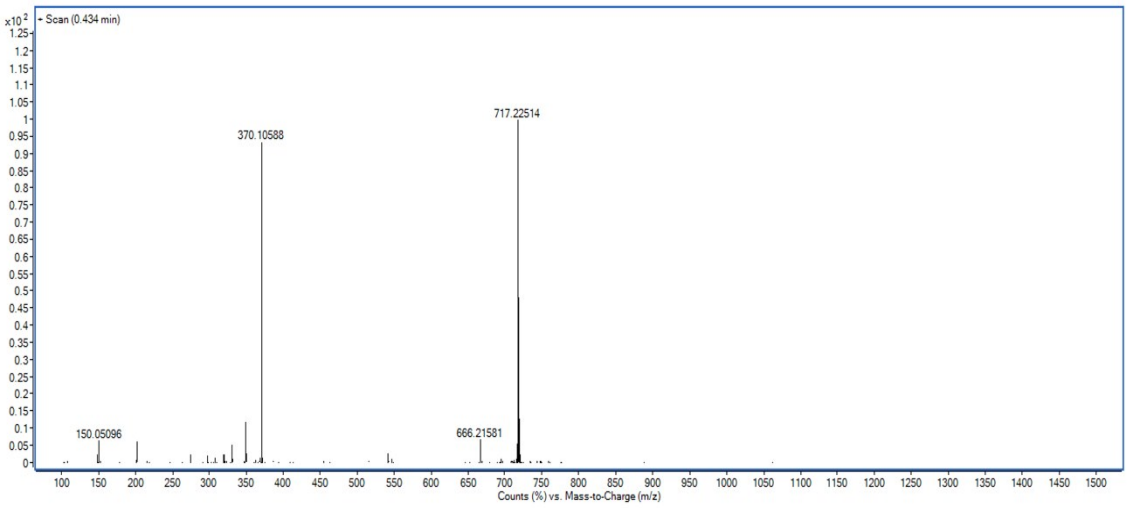


2-(7-Bromo-2-(7-bromo-1H-indol-3-yl)-3-oxoindolin-2-yl)acetonitrile (**6k**)

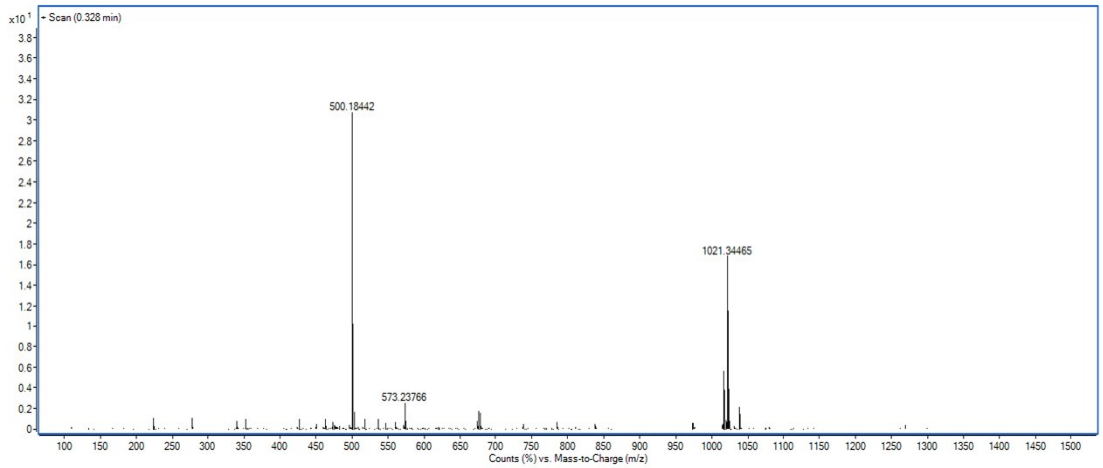


2-(7-Methyl-2-(7-methyl-1H-indol-3-yl)-3-oxoindolin-2-yl)acetonitrile (**6l**)

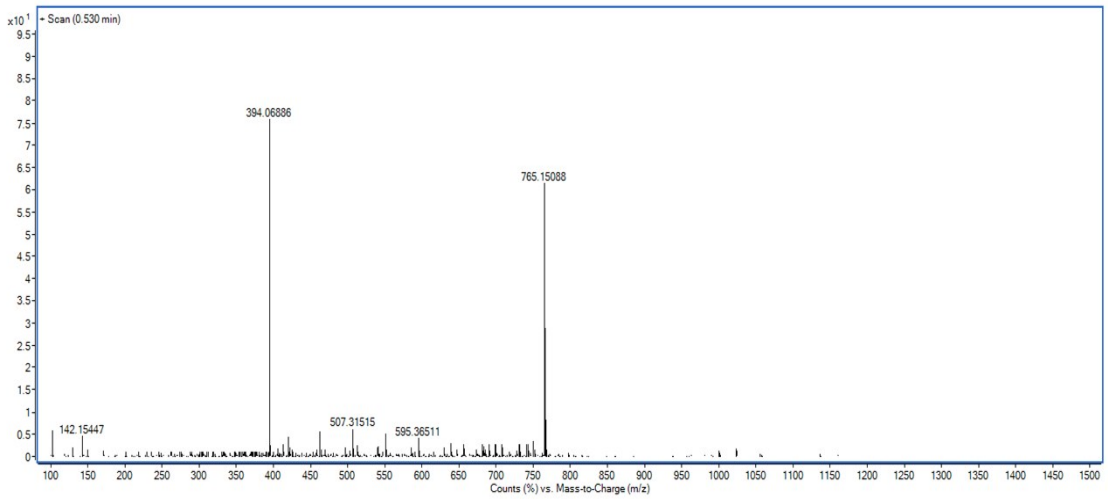
2-(7-Methoxy-2-(7-methoxy-1H-indol-3-yl)-3-oxoindolin-2-yl)acetonitrile (**6m**)



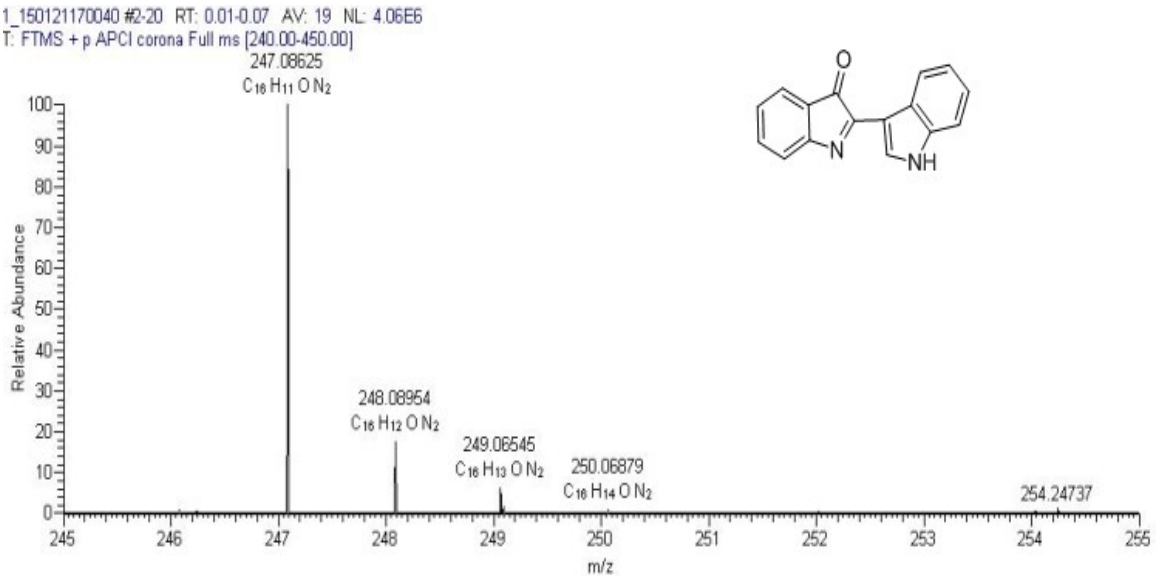
2-(7-(Benzyloxy)-2-(7-(benzyloxy)-1H-indol-3-yl)-3-oxoindolin-2-yl)acetonitrile (**6n**)



Methyl 12a-(cyanomethyl)-6,12-dioxo-2,6,12,12a-tetrahyroindolo[1,2-b]pyrrolo[4,3,2-de] isoquioline-11-carboxylate (**7**)



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



6. X-ray Data of Compound 9

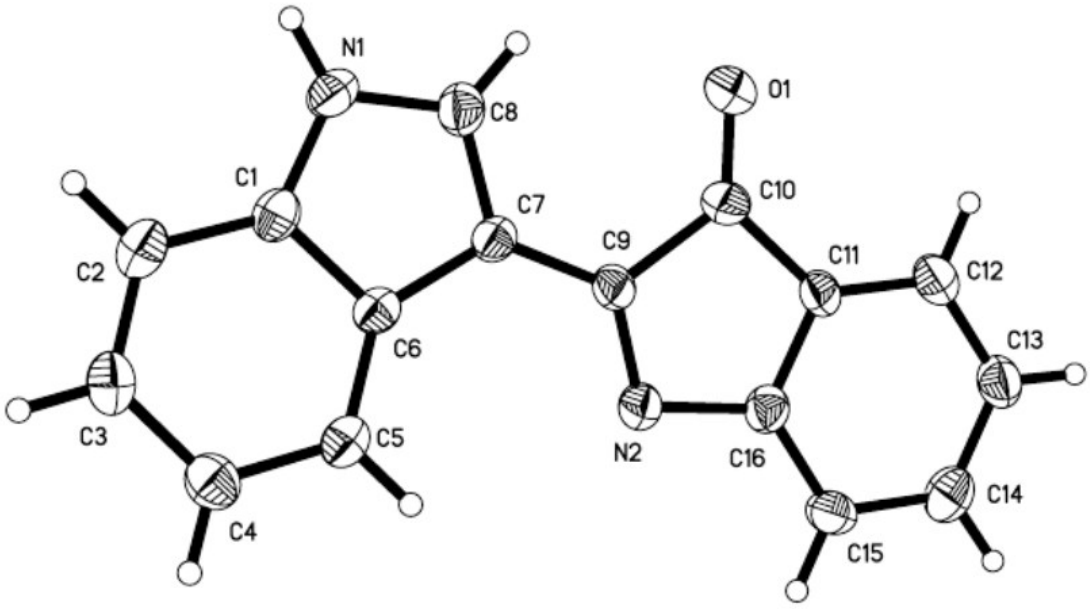


Figure 1. ORTEP representation of the molecular structure of **9**.

The data have been assigned the following deposition numbers, **CCDC 1453369**.