Supporting Information

Metal-free catalyzed oxidative trimerization of indoles by using TEMPO in air: a biomimetic approach to 2-(1*H*-indol-3-yl)-2,3'-biindolin-3-ones

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CONTENTS

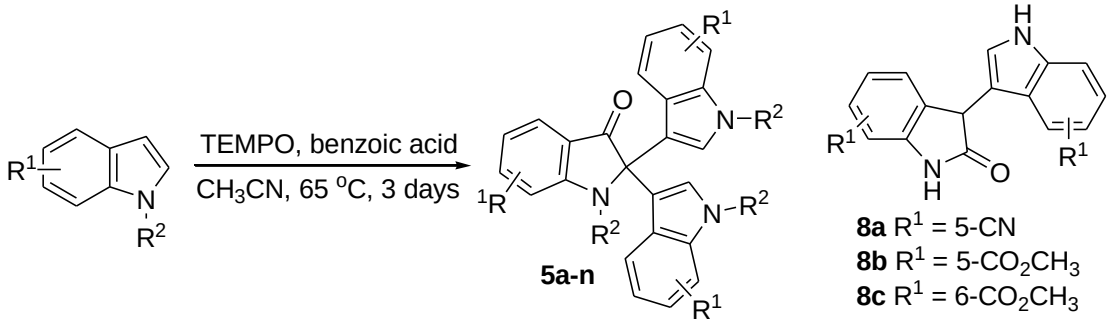
1. General Methods

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. $CDCl_3$ or DMSO-*d6* was used as the NMR solvent. Mass spectra were recorded with Bruker Dalton Esquire 3000 plus LC-MS apparatus. Elemental analysis were 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.

Materials

Commercially available starting materials and solvents were used as supplied, without further purification.

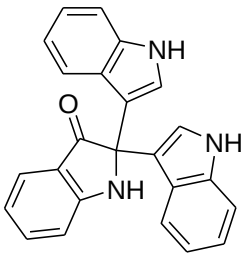
2. General Procedure for the Preparation of 5 and 8a-c.



To a solution of indole (1.0 mmol) and TEMPO (0.7 mmol) in CH_3CN (0.6 mL) was added benzoic acid (0.5 mmol) under atmosphere and the mixture was stirred at 65 °C for 3 days. The reaction mitxure 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.

Spectroscopic Data of the Products 5 and 8.

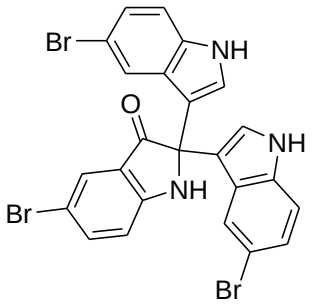
2-(1*H*-Indol-3-yl)-2,3'-biindolin-3-one (**5a**)



Yellow solid, mp: 241.5-244 °C (from EtOAc/PE = 1:2) (lit.[1] mp: 243-245.5). IR (KBr) ν_{max}: 3375, 3296, 1677, 1612, 1462, 1328, 1098, 746 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.94 (s, 1H, NH, D_2O exchangeable), 10.93 (s, 1H, NH, D_2O exchangeable), 8.10 (s, 1H, NH, D_2O exchangeable), 7.45 (t, *J* = 8.0 Hz, 1H, Ar-H), 7.43 (d, *J* = 7.6 Hz, 1H, Ar-H), 7.32 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.28 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.05 (d, *J* = 2.5 Hz, 2H, Ar-H), 6.99 (dt, *J* = 1.0, 8.0 Hz, 2H, Ar-H), 6.91 (d, *J* = 8.0 Hz, 1H, Ar-H)，6.78 (dt, *J* = 1.0, 8.0 Hz, 2H, Ar-H), 6.69 (dt, *J* = 1.0, 7.6 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 201.3, 161.0, 137.9, 137.4, 126.1, 124.9, 124.5, 121.5, 121.0, 118.8, 118.2, 117.5, 114.4, 112.3, 112.1, 68.1. HRESIMS calcd for

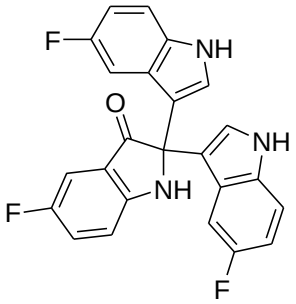
$[C_{24}H_{17}ON_3 + H]^+$ 364.1450, found 364.1443. These assignments matched with those previously published.[2]

5,5'-Dibromo-2-(5-bromo-1*H*-indol-3-yl)-2,3'-biindolin-3-one (**5b**)



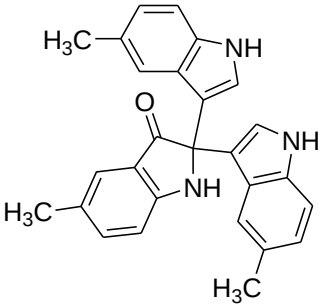
Yellow solid, mp: 247-249 °C (from EtOAc/PE = 1:2). IR (KBr) ν_{max}: 3448, 3395, 3318, 1682, 1623, 1494, 1427, 1103, 795 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 11.27 (s, 1H, NH), 11.26 (s, 1H, NH), 8.51 (s, 1H, NH), 7.62 (dd, *J* = 8.6, 2.4 Hz, 1H, Ar-H), 7.58 (d, *J* = 2.0 Hz, 1H, Ar-H), 7.36 (d, *J* = 2.0 Hz, 2H, Ar-H), 7.32 (d, *J* = 8.6 Hz, 2H, Ar-H), 7.19 (d, *J* = 2.4 Hz, 2H, Ar-H), 7.13 (dd, *J* = 8.6, 2.0 Hz, 2H, Ar-H), 6.92 (d, *J* = 8.6 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 199.5, 159.6, 140.5, 136.2, 127.6, 127.1, 125.9, 124.3, 122.8, 119.4, 114.6, 114.4, 113.3, 111.8, 108.8, 68.2. HRESIMS calcd for $[C_{24}H_{14}ON_3Br_3 + H]^+$ 597.8765, 599.8745, 601.8724, found 597.8759, 599.8732, 601.8708.

5,5'-Difluoro-2-(5-fluoro-1*H*-indol-3-yl)-2,3'-biindolin-3-one (**5c**)



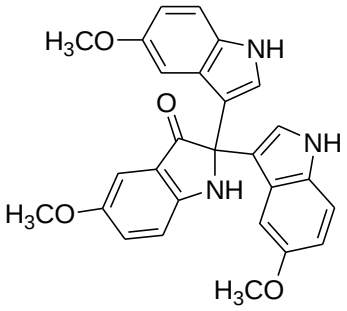
Yellow solid, mp: 90-92 °C (from EtOAc/PE = 1:4). IR (KBr) ν_{max}: 3406 (br s), 1692, 1489, 1455, 1255, 1177, 802 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 8.26 (s, 2H, NH), 7.33 (dd, *J* = 8.8, 2.6 Hz, 1H, Ar-H), 7.26 (dt, *J* = 2.6, 8.8 Hz, 1H, Ar-H), 7.19 (d, *J* = 8.8 Hz, 1H, Ar-H), 7.18 (d, *J* = 8.8 Hz, 1H, Ar-H), 7.07 (d, *J* = 2.6 Hz, 2H, Ar-H), 7.01 (d, *J* = 2.4 Hz, 1H, Ar-H), 6.98 (d, *J* = 2.4 Hz, 1H, Ar-H), 6.87 (dd, *J* = 9.0, 3.0 Hz, 2H, Ar-H), 6.84 (dd, *J* = 9.0, 3.0 Hz, 1H, Ar-H), 5.3 (s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.0, 158.8, 157.0, 156.5, 133.5, 126.0 (d, *J* = 26.0 Hz), 125.7 (d, *J* = 9.9 Hz), 125.5, 120.2 (d, *J* = 7.3 Hz), 114.5 (d, *J* = 4.7 Hz), 114.3 (d, *J* = 7.3 Hz), 112.2 (d, *J* = 9.9 Hz), 110.9 (d, *J* = 26.0 Hz), 110.1 (d, *J* = 23.4 Hz), 105.2 (d, *J* = 23.4 Hz), 69.0. HRESIMS calcd for $[C_{24}H_{14}ON_3F_3 + H]^+$ 418.1167, found 418.1162.

5,5'-Dimethyl-2-(5-methyl-1*H*-indol-3-yl)-2,3'-biindolin-3-one (**5d**)



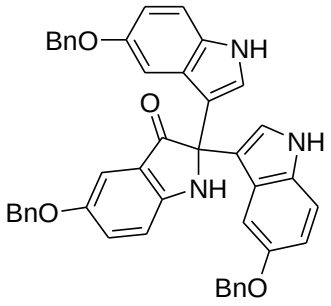
Yellow solid, mp: 161-163 °C (from EtOAc/PE = 1:2). IR (KBr) ν_{max}: 3449, 3385, 3322, 1683, 1623, 1494, 1427, 796 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 10.77 (s, 1H, NH), 10.76 (s, 1H, NH), 7.79 (s, 1H, NH), 7.31 (dd, J = 8.4, 1.7 Hz, 1H, Ar-H), 7.23 (s, 1H, Ar-H), 7.20 (d, J = 8.1 Hz, 2H, Ar-H), 7.07 (s, 2H, Ar-H), 6.98 (d, J = 2.5 Hz, 2H, Ar-H), 6.85 (d, J = 8.4 Hz, 1H, Ar-H), 6.82 (dd, J = 8.4, 1.3 Hz, 2H, Ar-H), 2.21 (s, 3H, CH_3), 2.18 (s, 6H, $2CH_3$). ^{13}C NMR (100 MHz, DMSO-d_6): δ 201.3, 159.6, 139.1, 135.8, 126.9, 126.4, 126.3, 124.5, 124.1, 123.1, 120.7, 118.5, 114.1, 112.4, 111.7, 68.5, 21.9, 20.6. HRESIMS calcd for $[C_{27}H_{23}ON_3 + H]^+$ 406.1919, found 406.1905.

5,5'-Dimethoxy-2-(5-methoxy-1*H*-indol-3-yl)-2,3'-biindolin-3-one (**5e**)



Yellow solid, mp: 226-228 °C (from EtOAc/PE = 1:3) (lit.[1] mp: 201-203). IR (KBr) ν_{max}: 3404, 3033, 1679, 1489, 1445, 1214, 1022 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 10.77 (s, 1H, NH), 10.76 (s, 1H, NH), 7.77 (s, 1H, NH), 7.23 (s, J = 8.8 Hz, 2H, Ar-H), 7.19 (d, J = 2.7 Hz, 1H, Ar-H), 7.02 (d, J = 2.6 Hz, 2H, Ar-H), 6.95 (d, J = 2.6 Hz, 1H, Ar-H), 6.92 (d, J = 8.8 Hz, 1H, Ar-H), 6.79 (d, J = 2.4 Hz, 2H, Ar-H), 6.69 (d, J = 2.4 Hz, 1H, Ar-H), 6.66 (d, J = 2.4 Hz, 1H, Ar-H), 3.69 (s, 3H, CH_3), 3.51 (s, 6H, $2CH_3$). ^{13}C NMR (100 MHz, DMSO-d_6): δ 201.7, 157.3, 153.0, 152.2, 132.6, 128.2, 126.5, 125.2, 118.5, 114.1, 113.9, 112.5, 111.0, 105.0, 103.5, 68.9, 56.0, 55.5. HRESIMS calcd for $[C_{27}H_{23}O_4N_3 + H]^+$ 454.1767, found 454.1749.

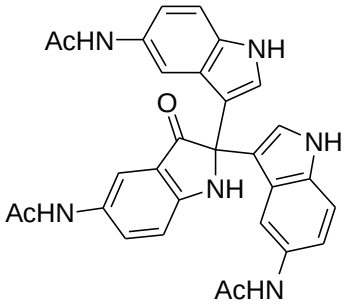
5,5'-Bis(benzyloxy)-2-(5-benzyloxy-1*H*-indol-3-yl)-2,3'-biindolin-3-one (**5f**)



Yellow solid, mp: 91-92 °C (from EtOAc/PE = 1:2). IR (KBr) ν_{max}: 3399 (br s), 1688, 1488, 1455, 1203 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 8.04 (s, 2H, NH), 7.40-7.35 (m, 3H, Ar-H), 7.33 (s, 1H,

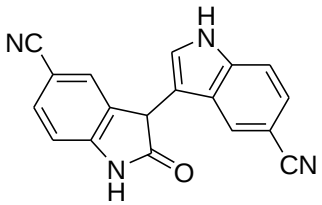
NH), 7.32-7.24 (m, 13H, Ar-H), 7.22 (d, *J* = 2.4 Hz, 1H, Ar-H), 7.13 (d, *J* = 8.8 Hz, 2H, Ar-H), 6.92 (d, *J* = 2.3 Hz, 2H, Ar-H), 6.90 (d, *J* = 2.3 Hz, 2H, Ar-H), 6.86 (d, *J* = 2.4 Hz, 1H, Ar-H), 6.84 (d, *J* = 2.4 Hz, 1H, Ar-H), 6.80 (d, *J* = 8.8 Hz, 1H, Ar-H), 4.96 (s, 2H, CH_2), 4.82 (s, 4H, $2CH_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.1, 156.4, 153.0, 152.9, 137.5, 136.7, 132.3, 128.8, 128.6, 128.5, 128.1, 127.7, 127.6, 127.5, 126.0, 125.0, 120.5, 114.7, 114.4, 113.0, 112.3, 106.4, 103.8, 70.7, 70.6, 69.3. HRESIMS calcd for $[C_{45}H_{35}O_4N_3 + H]^+$ 682.2706, found 682.2692.

N,*N*'-(2-(5-acetamido-1*H*-indol-3-yl)-3-oxo-2,3'-biindoline-5,5'-diyl)diacetamide (**5g**)



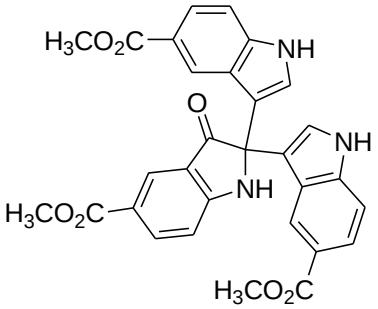
Yellow solid, mp: 153-155 °C (from EtOAc/EtOH = 10:1). IR (KBr) ν_{max}: 3271 (br s), 1662, 1621, 1553, 1492, 1375 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.90 (s, 2H, NH), 9.88 (s, 1H, NH), 9.61 (s, 2H, NH), 7.75 (d, *J* = 1.8 Hz, 1H, Ar-H), 7.64 (s, 1H, NH), 7.56 (dd, *J* = 8.8, 2.0 Hz, 1H, Ar-H), 7.39 (dd, *J* = 8.8, 1.8 Hz, 2H, Ar-H), 7.29 (s, 2H, Ar-H), 7.22 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.01 (d, *J* = 2.4 Hz, 2H, Ar-H), 6.89 (d, *J* = 8.8 Hz, 1H, Ar-H), 1.99 (s, 3H, CH_3), 1.89 (s, 6H, $2CH_3$). ^{13}C NMR (100 MHz, DMSO-d_6): δ 201.1, 168.2, 168.0, 157.8, 134.3, 131.3, 130.5, 129.7, 128.8, 125.9, 125.3, 117.8, 116.2, 114.3, 112.7, 112.1, 111.5, 68.9, 24.2, 24.1. HRESIMS calcd for $[C_{30}H_{26}O_4N_6 + H]^+$ 535.2094, found 535.2084.

2-Oxo-3,3'-biindoline-5,5'-dicarbonitrile (**8a**)



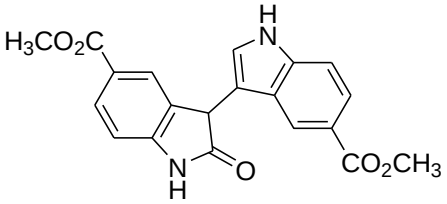
White solid, mp: 67-68 °C (from EtOAc/PE = 1:1). IR (KBr) ν_{max}: 3322 (br s), 2225, 1728, 1619, 1484, 1122 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.67 (s, 1H, NH), 10.90 (s, 1H, NH), 8.22 (s, 1H, Ar-H), 7.79 (dd, *J* = 8.1, 1.6 Hz, 1H, Ar-H), 7.75 (d, *J* = 2.5 Hz, 1H, Ar-H), 7.53 (d, *J* = 8.5 Hz, 1H, Ar-H), 7.45 (dd, *J* = 8.5, 1.6 Hz, 1H, Ar-H), 7.09 (d, *J* = 2.5 Hz, 1H, Ar-H), 7.06 (d, *J* = 8.1 Hz, 1H, Ar-H), 6.78 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 178.4, 146.5, 139.2, 135.3, 133.9, 128.8, 127.5, 126.9, 125.4, 124.5, 121.2, 119.8, 115.6, 113.6, 111.2, 104.5, 101.3, 74.6. MS (ESI): 299 ($M+H^+$, 100), 321 ($M+Na^+$, 10). Anal calcd for $C_{18}H_{10}N_4O$: C, 72.23; H, 3.70; N, 18.72. Found C, 72.05; H, 4.07; N, 18.45.

Dimethyl 2-(5-(methoxycarbonyl)-1*H*-indol-3-yl)-3-oxo-2,3'-biindoline-5,5'-dicarboxylate (**5i**)



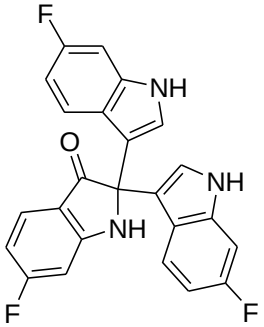
Yellow solid, mp: 111-113 °C (from EtOAc/PE = 1:2). IR (KBr) ν_{max}: 3337 (br s), 1702, 1618, 1436, 1310, 1249 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 11.48 (s, 1H, NH), 11.47 (s, 1H, NH), 9.16 (s, 1H, NH), 8.08 (dd, J = 8.7, 1.6 Hz, 1H, Ar-H), 8.03 (s, 1H, Ar-H), 8.00 (s, 2H, Ar-H), 7.67 (dd, J = 8.6, 1.6 Hz, 2H, Ar-H), 7.43 (d, J = 8.6 Hz, 2H, Ar-H), 7.27 (d, J = 2.4 Hz, 2H, Ar-H), 6.99 (d, J = 8.7 Hz, 1H, Ar-H), 3.78 (s, 3H, CH_3), 3.69 (s, 6H, $2CH_3$). ^{13}C NMR (100 MHz, DMSO-d_6): δ 199.9, 167.5, 166.2, 162.8, 140.1, 129.0, 127.4, 126.5, 125.3, 123.6, 122.8, 120.7, 118.7, 117.4, 114.9, 112.3, 112.0, 68.6, 52.3, 52.1. HRESIMS calcd for $[C_{30}H_{23}O_7N_3 + H]^+$ 538.1614, found 538.1597.

Dimethyl 2-oxo-3,3'-biindoline-5,5'-dicarboxylate (**8b**)



White solid, mp: 144-146 °C (from EtOAc/PE = 1:2). IR (KBr) ν_{max}: 3332 (br s), 1705, 1620, 1435, 1315, 1256 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 11.40 (d, J = 2.3 Hz, 1H, NH), 10.79 (s, 1H, NH), 8.36 (s, 1H, Ar-H), 7.92 (dd, J = 8.2, 1.8 Hz, 1H, Ar-H), 7.81 (d, J = 1.8 Hz, 1H, Ar-H), 7.67 (dd, J = 8.6, 1.8 Hz, 1H, Ar-H), 7.40 (d, J = 8.6 Hz, 1H, Ar-H), 7.03 (d, J = 2.3 Hz, 1H, Ar-H), 7.00 (d, J = 8.2 Hz, 1H, Ar-H), 6.64 (s, 1H), 3.78 (s, 3H, CH_3), 3.75 (s, 3H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ 178.8, 167.7, 166.5, 146.8, 140.0, 133.7, 132.1, 126.0, 125.8, 125.1, 124.3, 123.6, 122.7, 120.6, 116.7, 112.1, 110.2, 74.9, 52.3, 52.1. MS (ESI): 365 ($M+H^+$, 100), 387 ($M+Na^+$, 25). Anal calcd for $C_{20}H_{16}N_2O_5$: C, 65.93; H, 4.43; N, 7.69. Found C, 66.12; H, 4.29; N, 7.92.

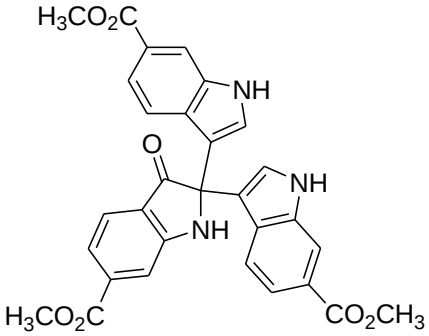
6,6'-Difluoro-2-(6-fluoro-1*H*-indol-3-yl)-2,3'-biindolin-3-one (**5j**)



Yellow solid, mp: 78-79 °C (from EtOAc/PE = 1:1). IR (KBr) ν_{max}: 3469, 3355 (br s), 1675, 1625, 1592, 1457, 1300, 1144, 1096 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 11.12 (s, 2H, NH), 8.54 (s, 1H, NH), 7.55 (dd, J = 8.6, 5.8 Hz, 1H, Ar-H), 7.24 (dd, J = 8.6, 5.8 Hz, 2H, Ar-H), 7.16 (dd, J =

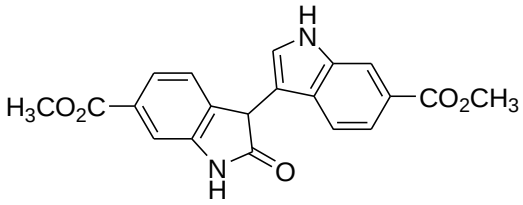
10.2, 2.4 Hz, 2H, Ar-H), 7.12 (d, *J* = 2.4 Hz, 2H, Ar-H), 6.75 (dt, *J* = 2.4, 9.4 Hz, 2H, Ar-H), 6.64 (dd, *J* = 10.2, 2.1 Hz, 1H, Ar-H), 6.54 (dt, *J* = 2.1, 9.4 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 199.1, 162.3 (d, *J* = 14.6 Hz), 158.0, 137.2 (d, *J* = 12.8 Hz), 129.7, 129.0, 127.9 (d, *J* = 12.8 Hz), 125.1, 122.7, 121.7 (d, *J* = 10.1 Hz), 114.9, 114.2, 107.6 (d, *J* = 14.6 Hz), 106.1 (d, *J* = 25.0 Hz), 98.0 (d, *J* = 25.0 Hz), 68.5. HRESIMS calcd for $[C_{24}H_{14}ON_3F_3 + H]^+$ 418.1167, found 418.1162.

Dimethyl 2-(6-(methoxycarbonyl)-1*H*-indol-3-yl)-3-oxo-2,3'-biindoline-6,6'-dicarboxylate (**5k**)



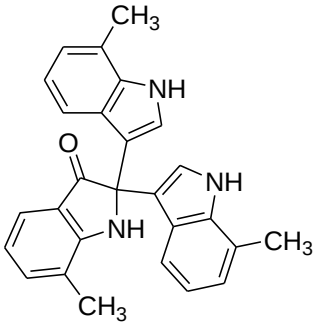
Yellow solid, mp: 154-156 °C (from EtOAc/PE = 1:2). IR (KBr) ν_{max}: 3349 (br s), 1708, 1621, 1454, 1319, 1277, 1218 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.48 (s, 1H, NH), 11.47 (s, 1H, NH), 8.50 (s, 1H, NH), 7.58 (d, *J* = 8.0 Hz, 1H, Ar-H), 8.02 (s, 2H, Ar-H), 7.50 (s, 1H, Ar-H), 7.44 (dd, *J* = 8.5, 1.2 Hz, 2H, Ar-H), 7.38 (d, *J* = 2.5 Hz, 2H, Ar-H), 7.27 (d, *J* = 8.5 Hz, 2H, Ar-H), 7.25 (dd, *J* = 8.0, 1.2 Hz, 1H, Ar-H), 3.84 (s, 3H, CH_3), 3.78 (s, 6H, $2CH_3$). ^{13}C NMR (100 MHz, DMSO-d_6): δ 200.8, 167.5, 166.4, 160.5, 138.0, 136.8, 129.4, 129.0, 128.5, 125.6, 122.8, 120.9, 120.5, 119.7, 118.1, 114.3, 113.2, 68.4, 53.0, 52.3. HRESIMS calcd for $[C_{30}H_{23}O_7N_3 + H]^+$ 538.1614, found 538.1600.

Dimethyl 2-oxo-3,3'-biindoline-6,6'-dicarboxylate (**8c**)



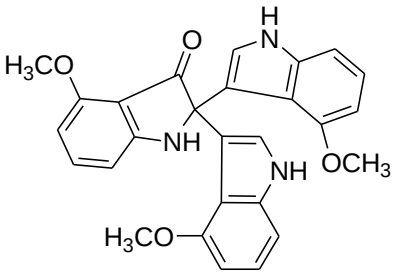
White solid, mp: 240-242 °C (from EtOAc/PE = 1:2). IR (KBr) ν_{max}: 3329 (br s), 1703, 1617, 1436, 1312, 1253 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.43 (d, *J* = 2.3 Hz, 1H, NH), 10.57 (s, 1H, NH), 8.00 (s, 1H, Ar-H), 7.60 (dd, *J* = 7.7, 1.2 Hz, 1H, Ar-H), 7.56 (dd, *J* = 8.5, 1.0 Hz, 1H, Ar-H), 7.51 (dd, *J* = 8.5, 1.2 Hz, 1H, Ar-H), 7.41 (d, *J* = 1.0 Hz, 1H, Ar-H), 7.38 (d, *J* = 7.7 Hz, 1H, Ar-H), 7.25 (d, *J* = 2.3 Hz, 1H, Ar-H), 6.64 (s, 1H), 3.82 (s, 3H, CH_3), 3.79 (s, 3H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ 178.4, 167.6, 166.4, 142.5, 138.6, 136.6, 130.9, 128.9, 127.9, 125.4, 123.9, 122.8, 120.8, 119.7, 115.7, 114.1, 110.3, 75.0, 52.7, 52.2. MS (ESI): 365 (M+H$^+$, 100), 387 (M+Na$^+$, 25). Anal calcd for $C_{20}H_{16}N_2O_5$: C, 65.93; H, 4.43; N, 7.69. Found C, 65.79; H, 4.71; N, 7.60.

7,7'-Dimethyl-2-(7-methyl-1*H*-indol-3-yl)-2,3'-biindolin-3-one (**5l**)



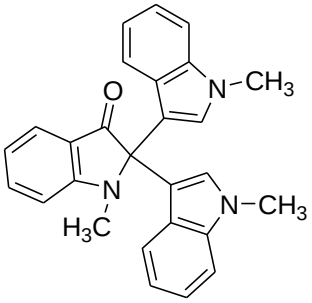
Yellow solid, mp: 121-123 °C (from EtOAc/PE = 1:2). IR (KBr) ν_{max}: 3410 (br s), 1692, 1606, 1498, 1433, 786, 749 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 8.08 (s, 1H, NH), 8.07 (s, 1H, NH), 7.59 (d, J = 7.5 Hz, 1H, Ar-H), 7.33 (d, J = 7.0 Hz, 1H, Ar-H), 7.23 (d, J = 8.8 Hz, 2H, Ar-H), 6.96-6.87 (m, 6H, Ar-H), 6.83 (t, J = 7.5 Hz, 1H, Ar-H), 5.28 (s, 1H), 2.39 (s, 6H, $2CH_3$), 2.19 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.0, 159.7, 137.5, 136.6, 125.3, 124.3, 122.8, 122.6, 122.0, 120.8, 120.0, 119.6, 119.5, 118.0, 115.3, 68.5, 16.6, 15.8. HRESIMS calcd for $[C_{27}H_{23}ON_3 + H]^+$ 406.1919, found 406.1905.

4,4'-Dimethoxy-2-(4-methoxy-1*H*-indol-3-yl)-2,3'-biindolin-3-one (**5m**)



Red solid, mp: 185-187 °C (from EtOAc/PE = 2:1). IR (KBr) ν_{max}: 3389 (br s), 1687, 1613, 1501, 1262, 1088 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 8.26 (s, 2H, NH), 7.25 (t, J = 8.1 Hz, 1H, Ar-H), 7.04 (s, 1H, N-H), 6.94 (t, J = 7.8 Hz, 2H, Ar-H), 6.76 (d, J = 8.1 Hz, 2H, Ar-H), 6.53 (s, 2H, Ar-H), 6.38 (d, J = 7.8 Hz, 2H, Ar-H), 6.31 (d, J = 8.1 Hz, 1H, Ar-H), 6.12 (d, J = 8.1 Hz, 1H, Ar-H), 3.88 (s, 3H, CH_3), 3.46 (s, 6H, $2CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.6, 161.1, 159.3, 153.0, 138.7, 137.5, 125.2, 122.4, 116.4, 114.5, 109.9, 105.1, 104.8, 100.2, 98.2, 67.5, 55.6, 54.9. HRESIMS calcd for $[C_{27}H_{23}O_4N_3 + H]^+$ 454.1767, found 454.1754.

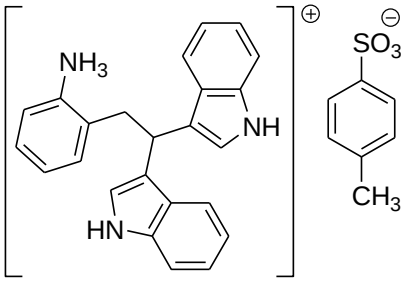
1,1'-Dimethyl-2-(1-methyl-1*H*-indol-3-yl)-2,3'-biindolin-3-one (**5n**)



Yellow solid, mp: 271-273 °C (from EtOAc/PE = 1:4). IR (KBr) ν_{max}: 3050, 1697, 1614, 1325, 1293 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.61 (dt, J = 7.3, 1.0 Hz, 2H, Ar-H), 7.35 (d, J = 8.1 Hz, 2H, Ar-H), 7.29 (d, J = 8.1 Hz, 2H, Ar-H), 7.17 (dt, J = 8.1, 1.0 Hz, 2H, Ar-H), 6.99 (s, 2H, Ar-H), 6.96 (dt, J = 8.1, 1.0 Hz, 2H, Ar-H), 6.82 (d, J = 8.1 Hz, 1H, Ar-H), 6.73 (t, J = 7.3 Hz, 1H, Ar-H), 3.71 (s, 6H, $2CH_3$), 2.95 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.8, 159.8, 137.8, 137.7,

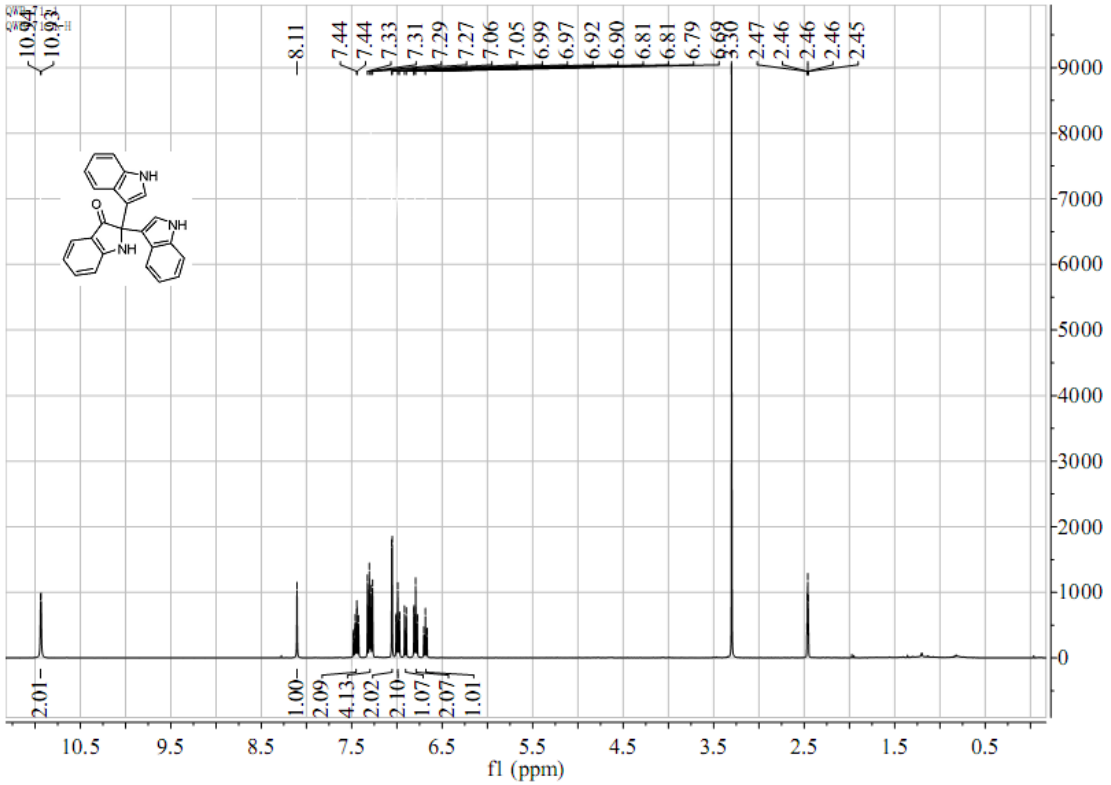
129.3, 126.3, 125.7, 121.7, 121.6, 119.4, 118.6, 116.8, 111.3, 109.4, 107.9, 72.8, 32.9, 29.5. HRESIMS calcd for $[C_{27}H_{23}ON_3 + Na]^+$ 428.1739, found 428.1709.

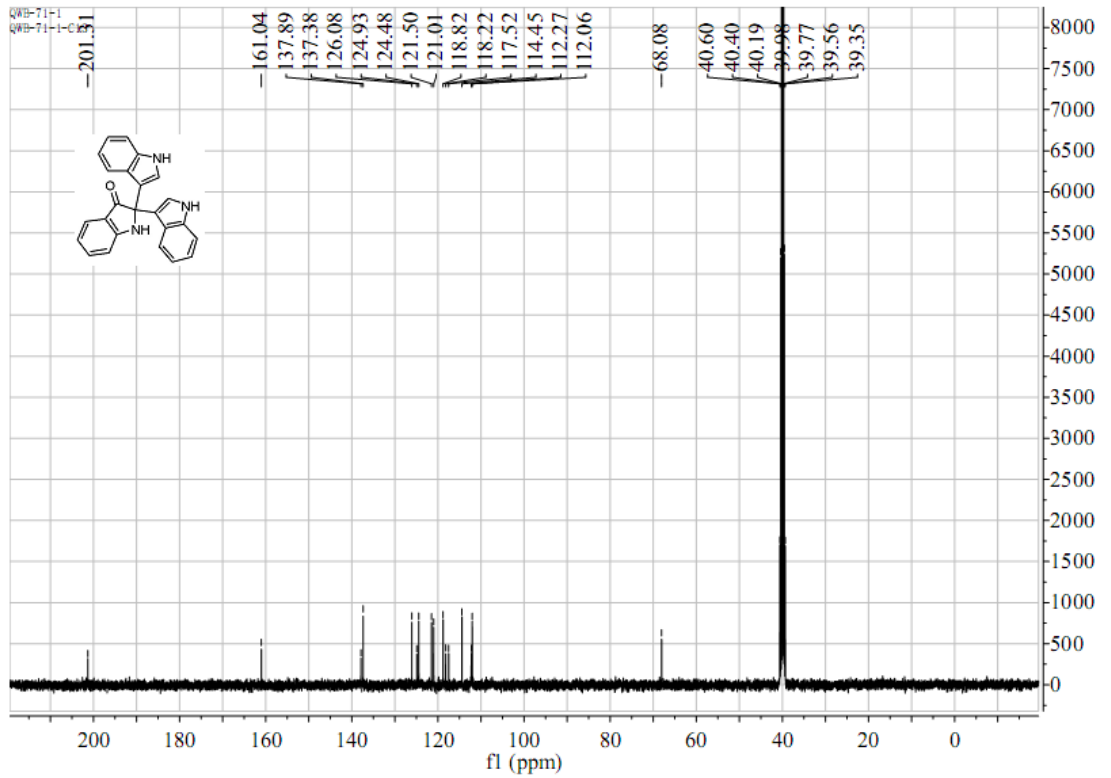
2-(2,2-Di(1*H*-indol-3-yl)ethyl)benzenaminium benzenesulfonate (**7**)

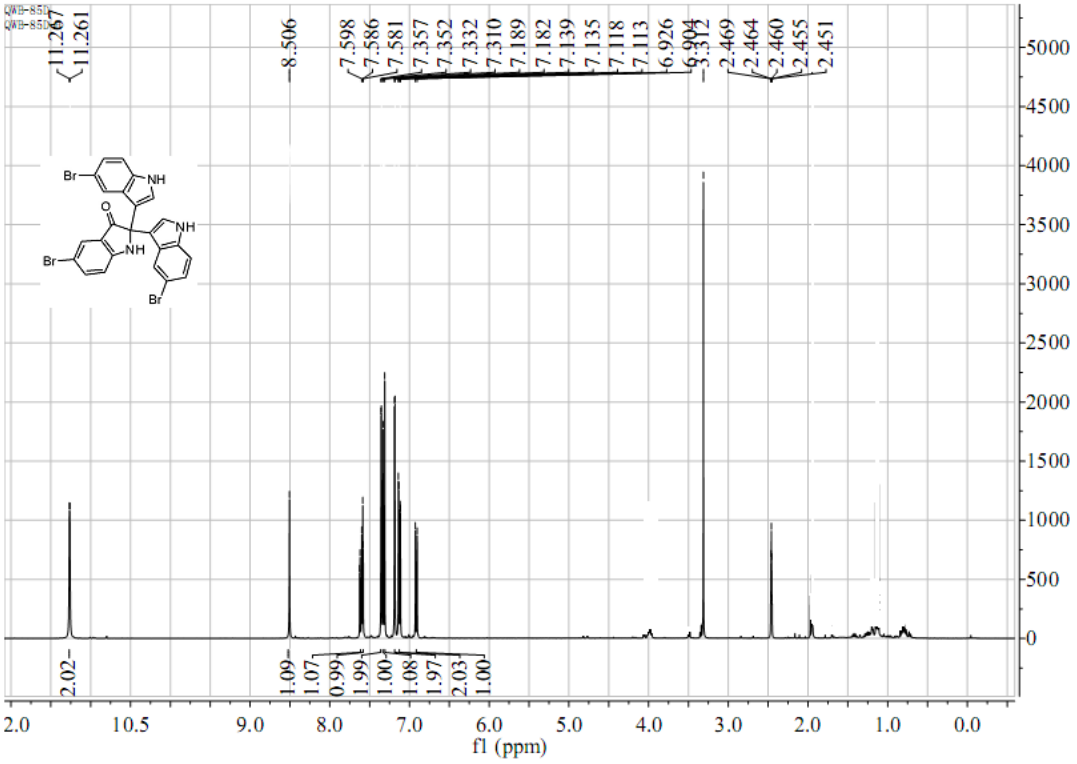


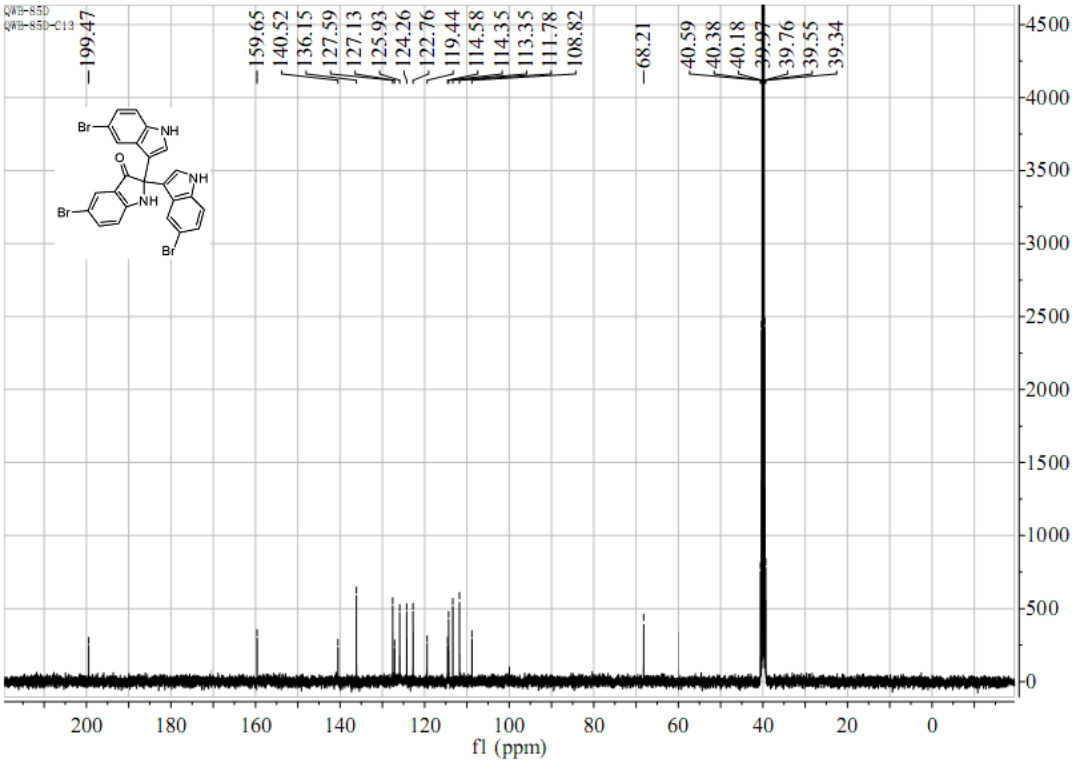
Waxy solid. IR (KBr) ν_{max}: 3250 (br s), 1603, 1496, 1450, 1078 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 10.72 (s, 1H, NH), 10.71 (s, 1H, NH), 9.90-9.30 (s, 3H, NH), 7.51 (d, J = 8.0 Hz, 2H, Ar-H), 7.46 (d, J = 8.0 Hz, 2H, Ar-H), 7.27 (d, J = 8.0 Hz, 1H, Ar-H), 7.25 (d, J = 8.0 Hz, 2H, Ar-H), 7.21 (d, J = 2.2 Hz, 2H, Ar-H), 7.15 (dt, J = 2.2, 8.0 Hz, 1H, Ar-H), 7.07 (d, J = 8.0 Hz, 2H, Ar-H), 7.03 (s, 2H, Ar-H), 6.96 (t, J = 7.3 Hz, 2H, Ar-H), 6.83 (t, J = 7.3 Hz, 2H, Ar-H), 4.94 (t, J = 7.8 Hz, 1H), 3.58 (d, J = 7.8 Hz, 2H), 2.25 (s, 3H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ 145.9, 138.3, 136.9, 134.4, 131.6, 130.5, 128.6, 127.6, 127.3, 127.0, 126.0, 123.2, 122.8, 121.1, 119.5, 118.4, 118.3, 111.8, 35.5, 32.3, 21.2. MS (ESI): 524 ($M+H^+$, 100).

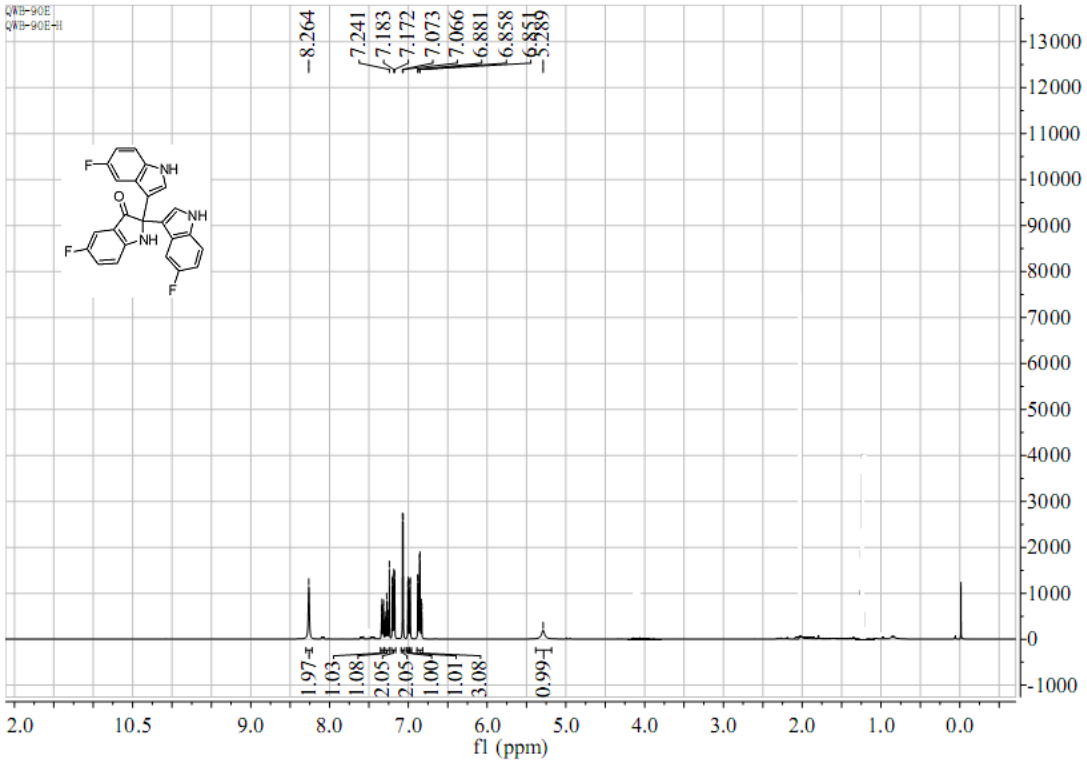
3. Copies of ^{1}H, ^{13}C NMR Spectra

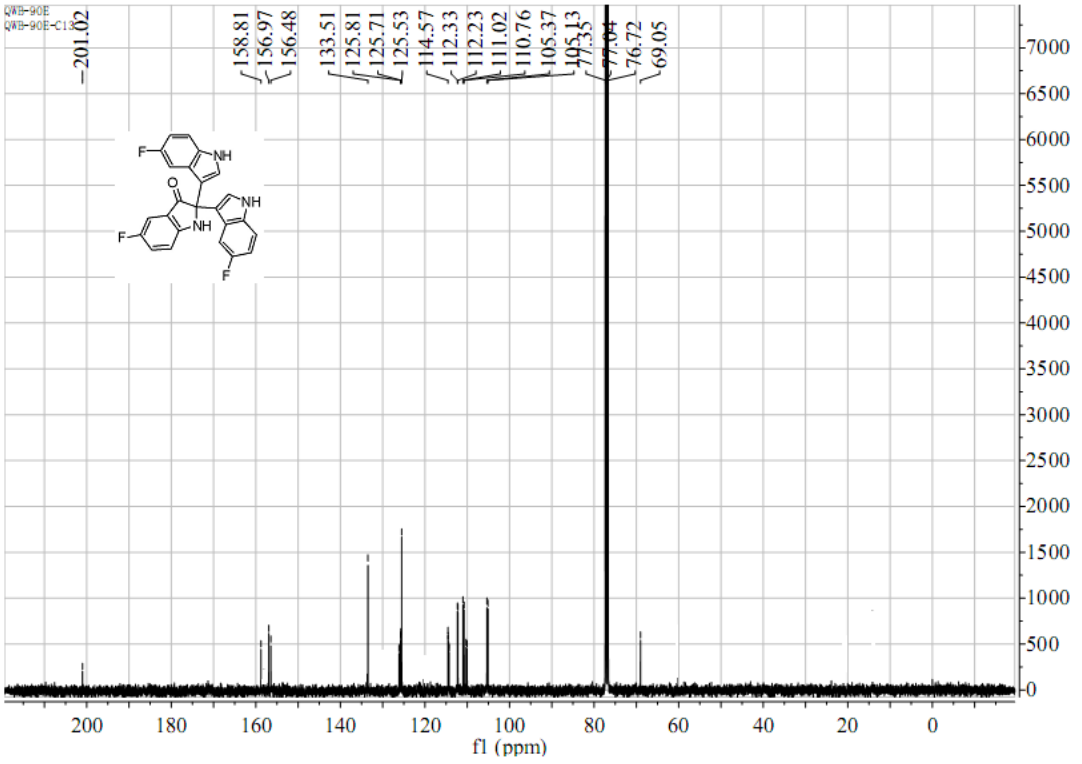


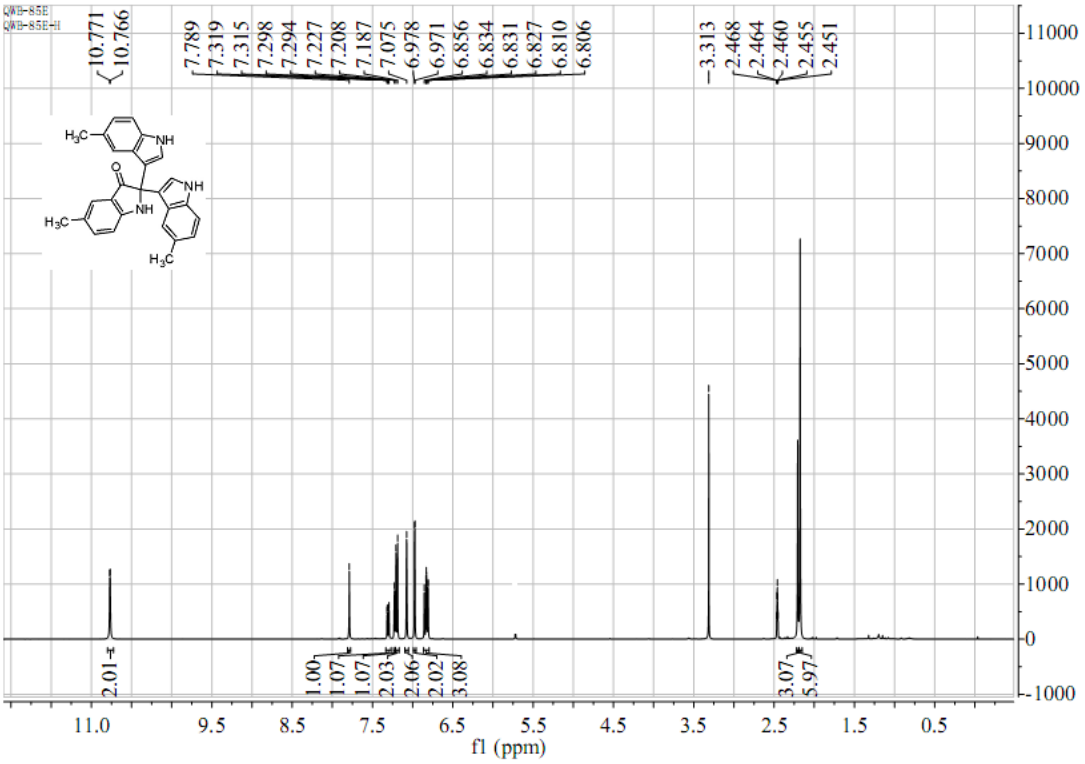


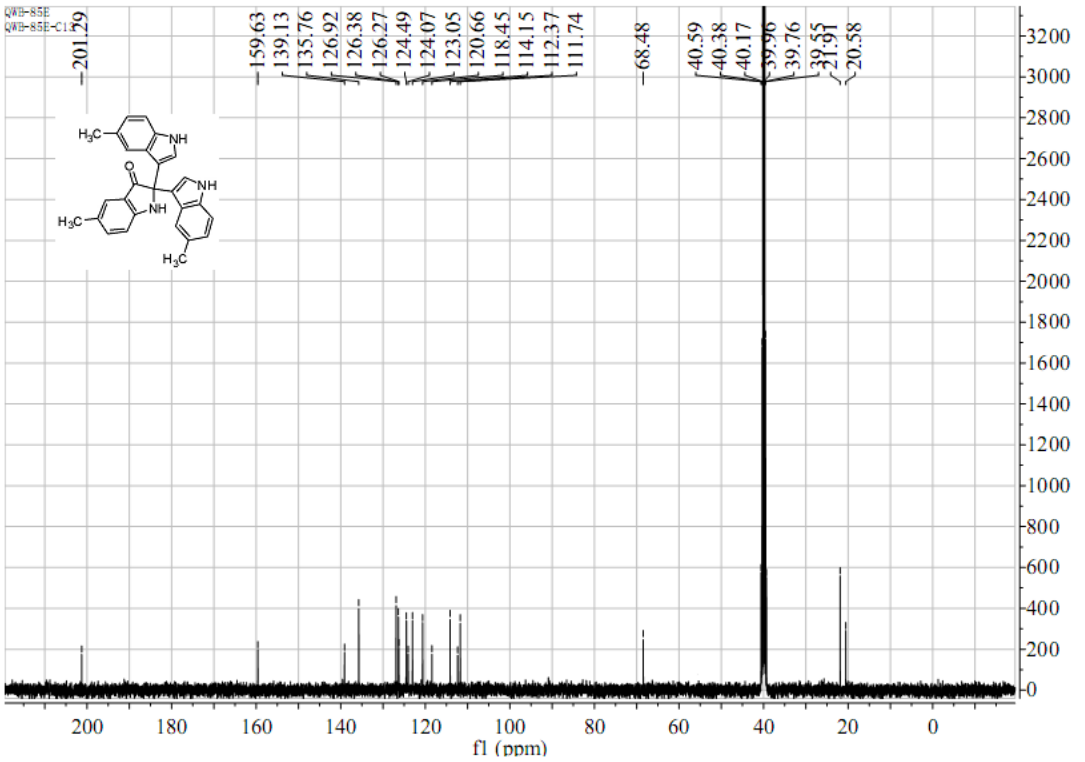


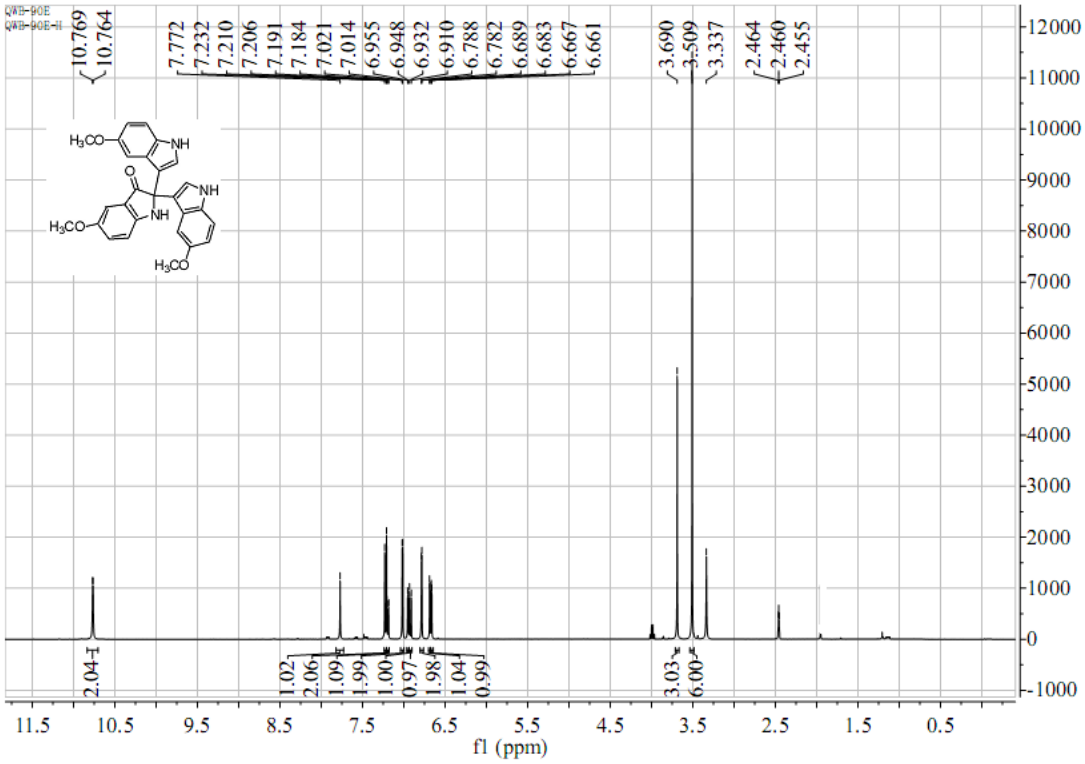



QWB-90E
QWB-90E-H
8.264
7.241
7.183
7.172
7.073
7.066
6.881
6.858
6.851
5.289
F
NH
O
NH
NH
F
F
1.97
1.03
1.08
2.05
2.05
1.00
1.01
3.08
0.99
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
2.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


QWB-90E
QWB-90E-C13
201.02
158.81
156.97
156.48
133.51
125.81
125.71
125.53
114.57
112.33
112.23
111.02
110.76
105.37
105.13
77.35
77.04
76.72
69.05
F
NH
O
NH
NH
F
F
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)






10.769
10.764
7.772
7.232
7.210
7.206
7.191
7.184
7.021
7.014
6.955
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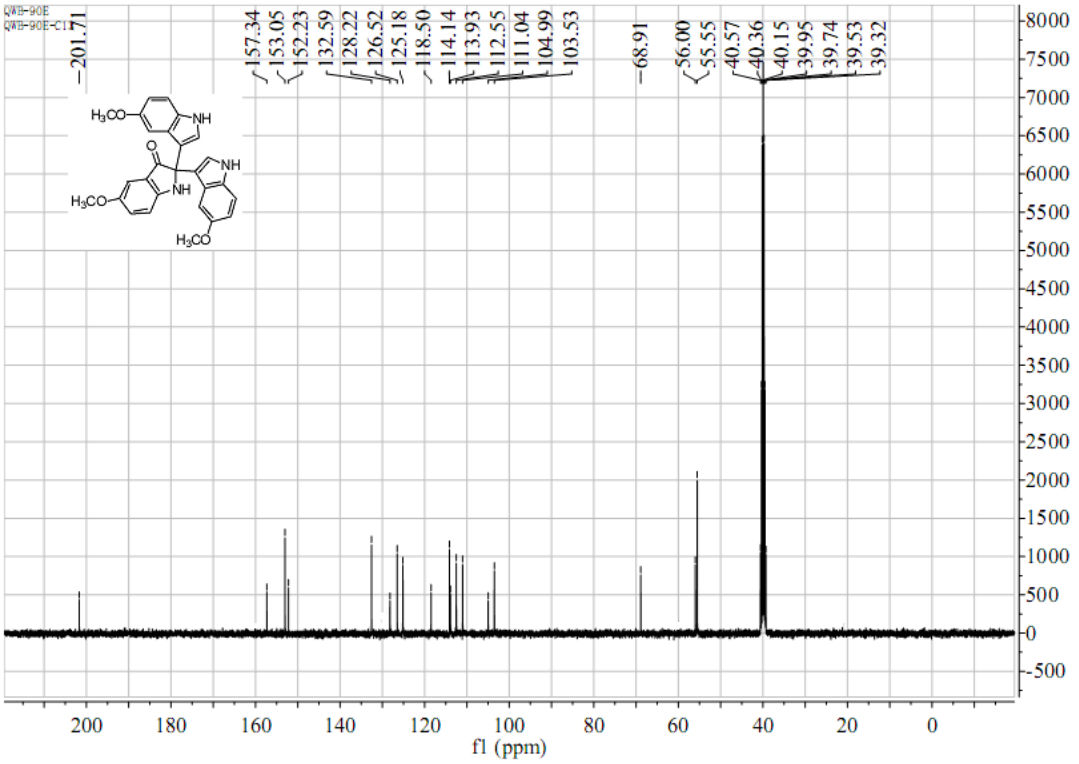
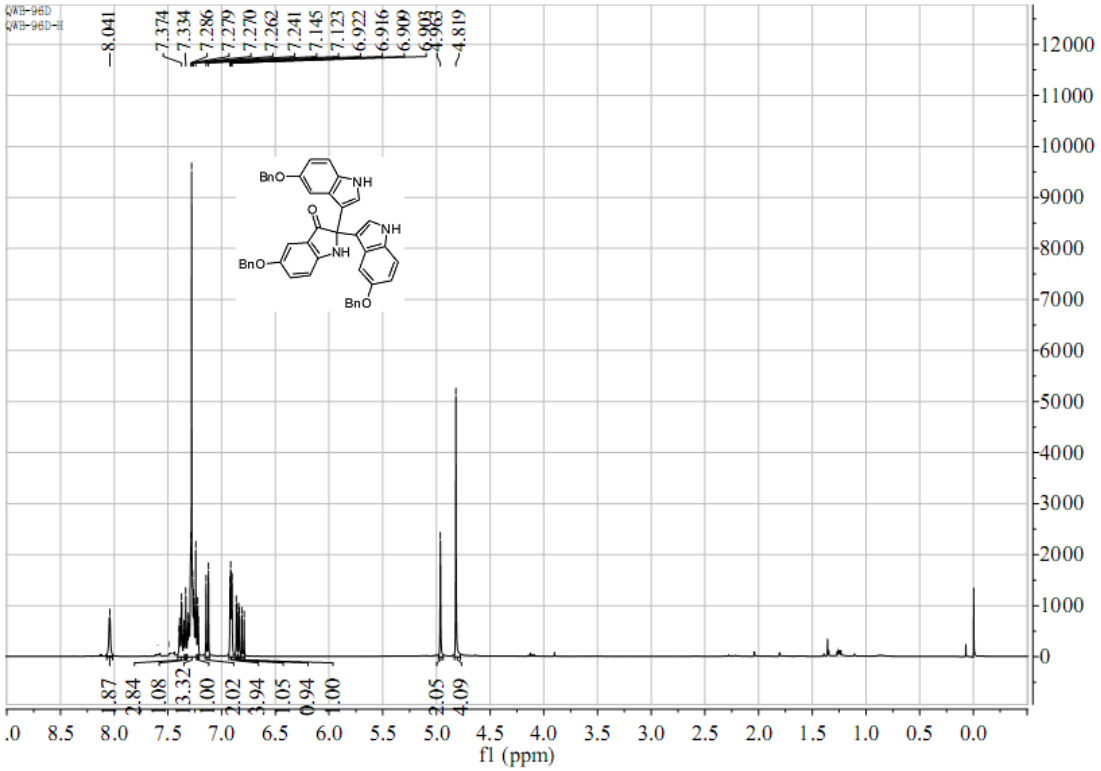
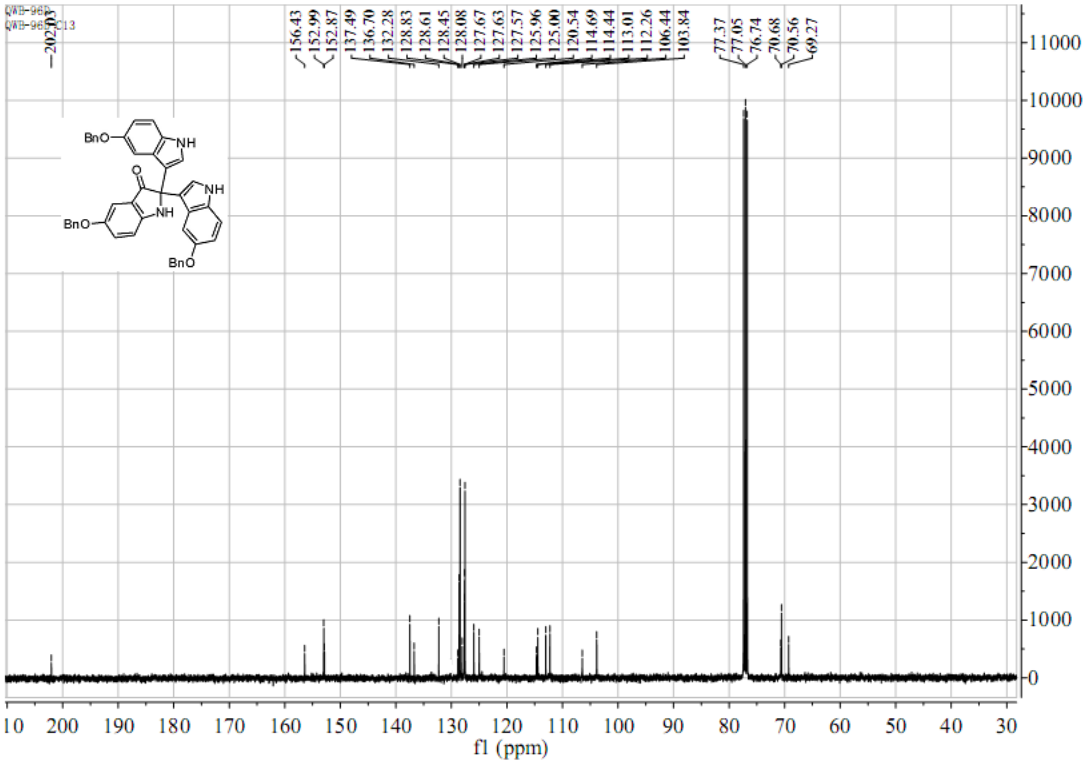
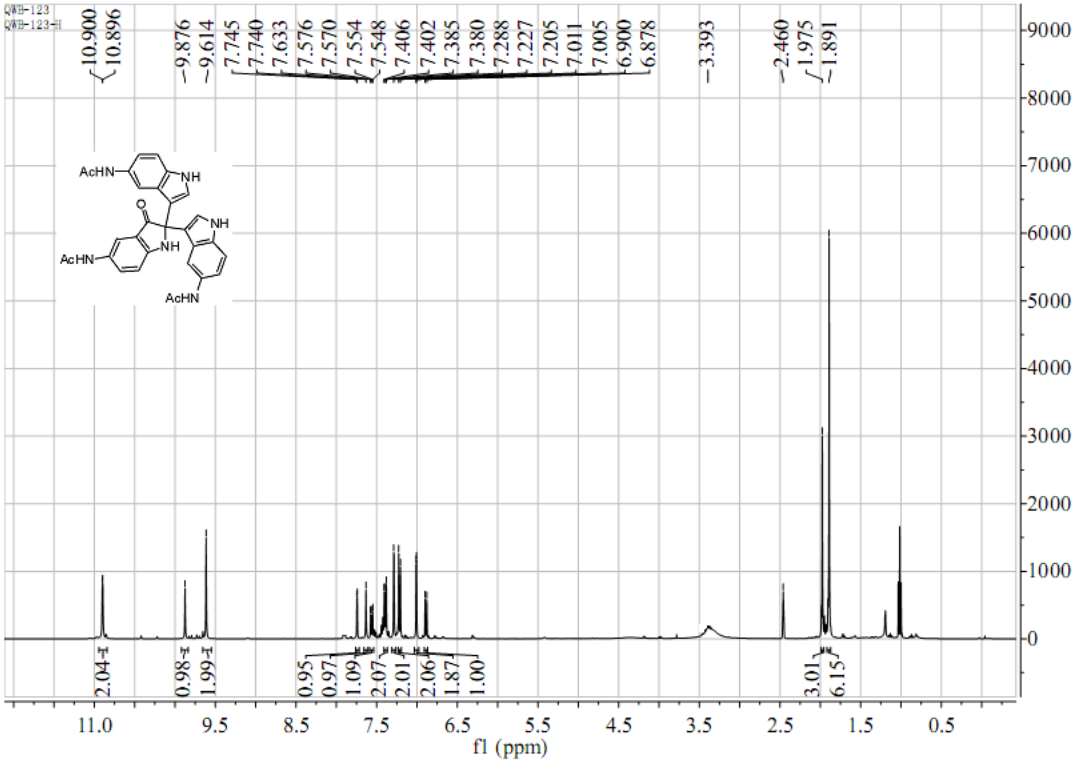
6.932
6.910
6.788
6.782
6.689
6.683
6.667
6.661
3.690
3.509
3.337
2.464
2.460
2.455
2.04
1.02
2.06
1.09
1.99
1.00
0.97
1.98
1.04
0.99
3.03
6.00
fl (ppm)


201.71
157.34
153.05
152.23
132.59
128.22
126.52
125.18
118.50
114.14
113.93
112.55
111.04
104.99
103.53
68.91
56.00
55.55
40.57
40.36
40.15
39.95
39.74
39.53
39.32
fl (ppm)


8.041
7.374
7.334
7.286
7.279
7.270
7.262
7.241
7.145
7.123
6.922
6.916
6.909
4.819
BnO
NH
NH
NH
BnO
BnO
1.87
2.84
1.08
13.32
1.00
2.02
3.94
1.05
0.94
1.00
2.05
4.09
f1 (ppm)


202.03
156.43
152.99
152.87
137.49
136.70
132.28
128.83
128.61
128.45
128.08
127.67
127.63
127.57
125.96
125.00
120.54
114.69
114.44
113.01
112.26
106.44
103.84
77.37
77.05
76.74
70.68
70.56
69.27
BnO
NH
NH
NH
BnO
BnO
f1 (ppm)


QWB-123
QWB-123-H1
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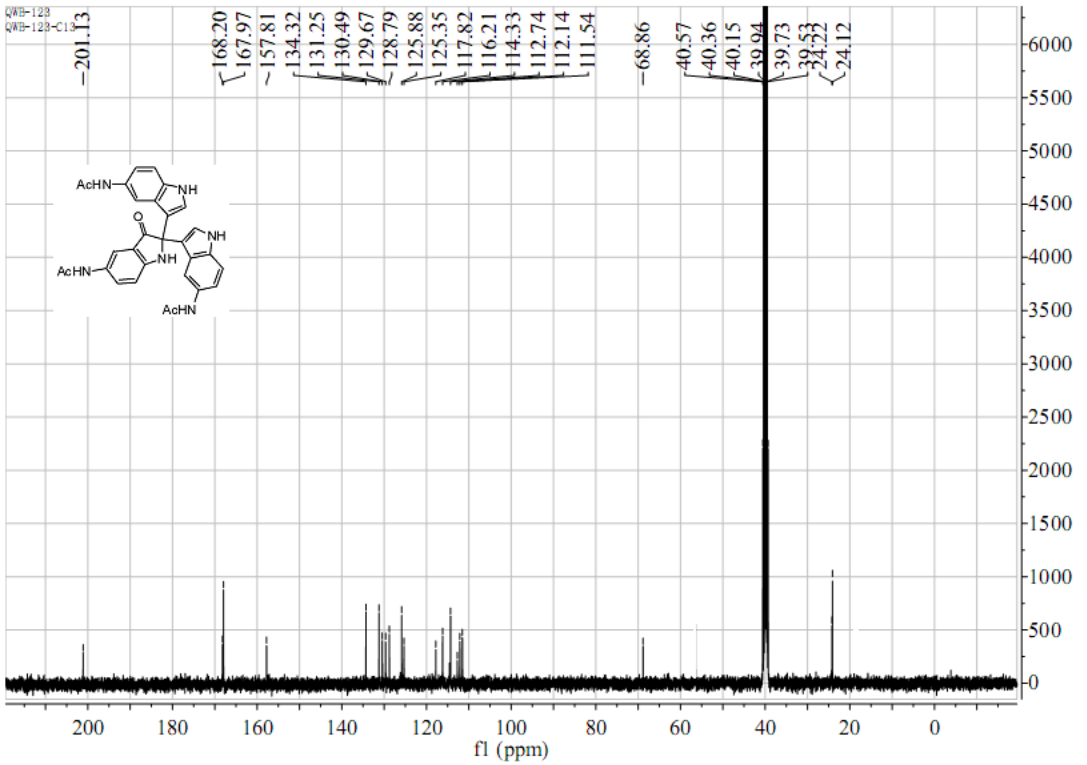
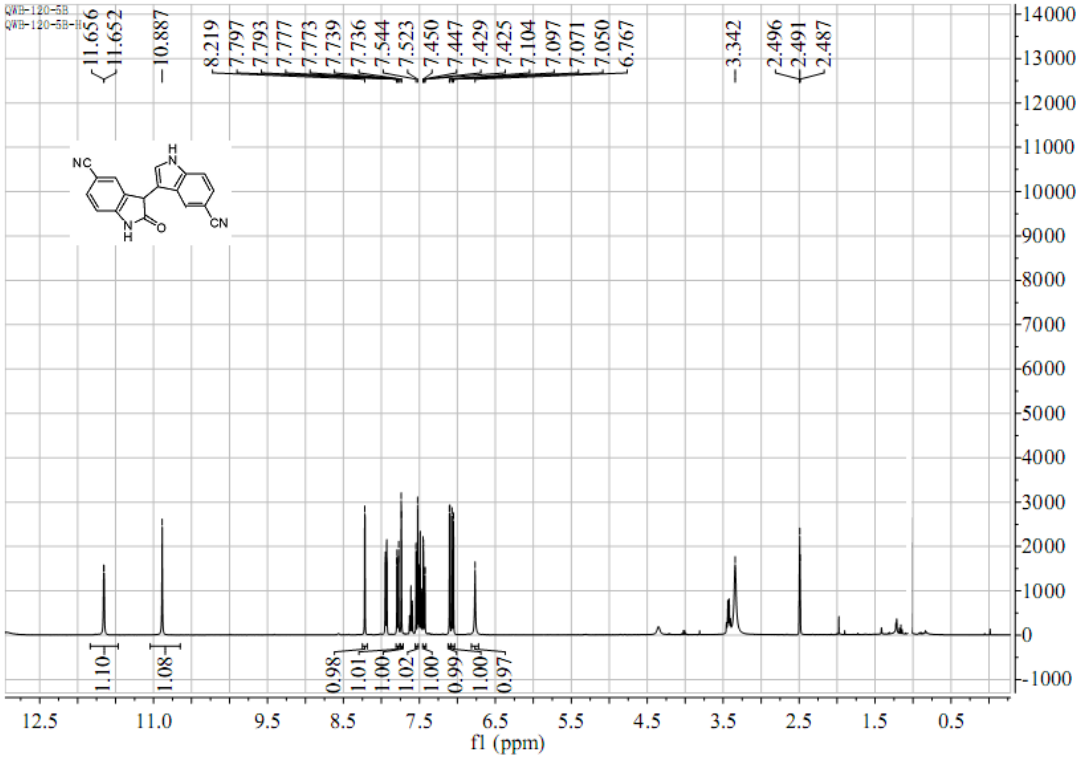
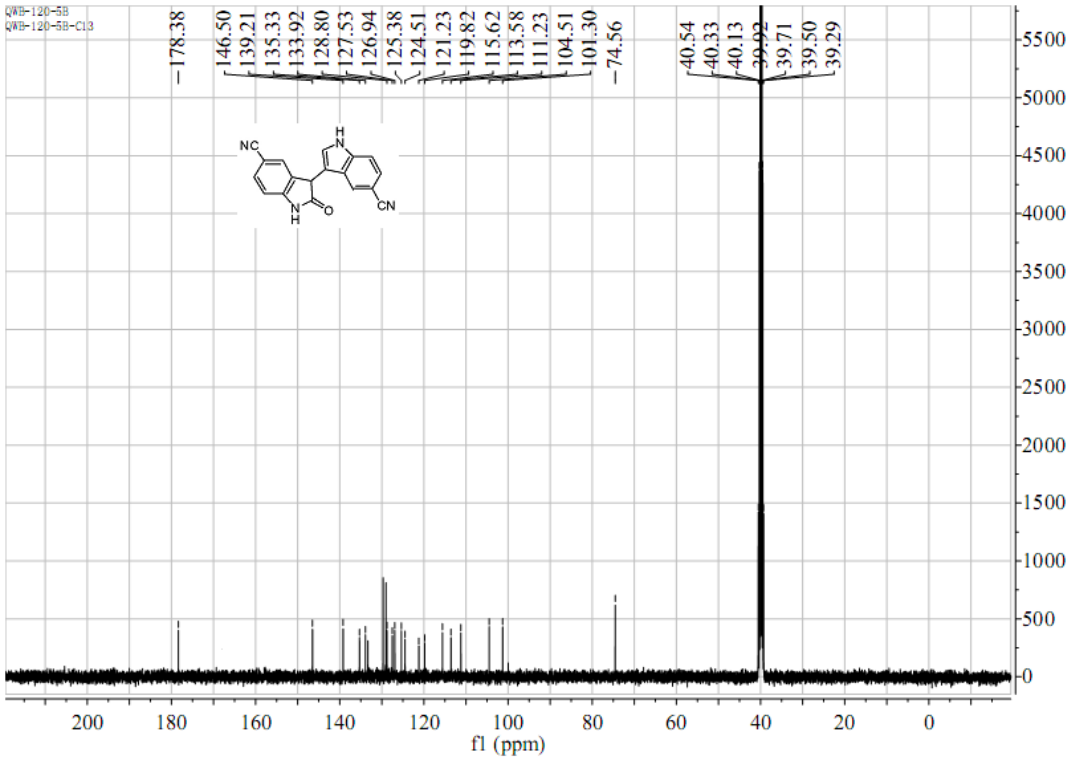
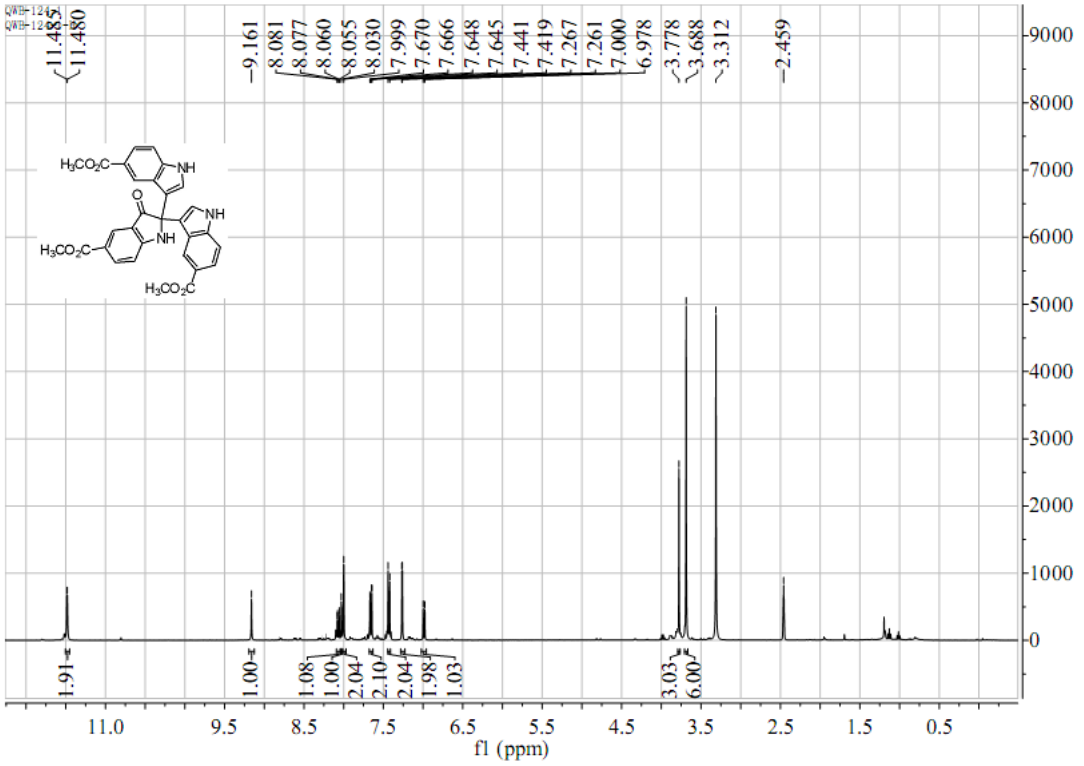
10.896
9.876
9.614
7.745
7.740
7.633
7.576
7.570
7.554
7.548
7.406
7.402
7.385
7.380
7.288
7.227
7.205
7.011
7.005
6.900
6.878
3.393
2.460
1.975
1.891
AcHN
NH
AcHN
NH
NH
AcHN
2.04
0.98
1.99
0.95
0.97
1.09
2.07
2.01
2.06
1.87
1.00
3.01
6.15
11.0
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


QWB-123
QWB-123-C13
201.13
168.20
167.97
157.81
134.32
131.25
130.49
129.67
128.79
125.88
125.35
117.82
116.21
114.33
112.74
112.14
111.54
68.86
40.57
40.36
40.15
39.94
39.73
39.53
24.22
24.12
AcHN
NH
AcHN
NH
NH
AcHN
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


11.656
11.652
10.887
8.219
7.797
7.793
7.777
7.773
7.739
7.736
7.544
7.523
7.450
7.447
7.429
7.425
7.104
7.097
7.071
7.050
6.767
3.342
2.496
2.491
2.487
1.10
1.08
0.98
1.01
1.00
1.02
1.00
0.99
1.00
0.97
f1 (ppm)


178.38
146.50
139.21
135.33
133.92
128.80
127.53
126.94
125.38
124.51
121.23
119.82
115.62
113.58
111.23
104.51
101.30
74.56
40.54
40.33
40.13
39.92
39.71
39.50
39.29
f1 (ppm)


11.485
11.480
9.161
8.081
8.077
8.060
8.055
8.030
7.999
7.670
7.666
7.648
7.645
7.441
7.419
7.267
7.261
7.000
6.978
3.778
3.688
3.312
2.459
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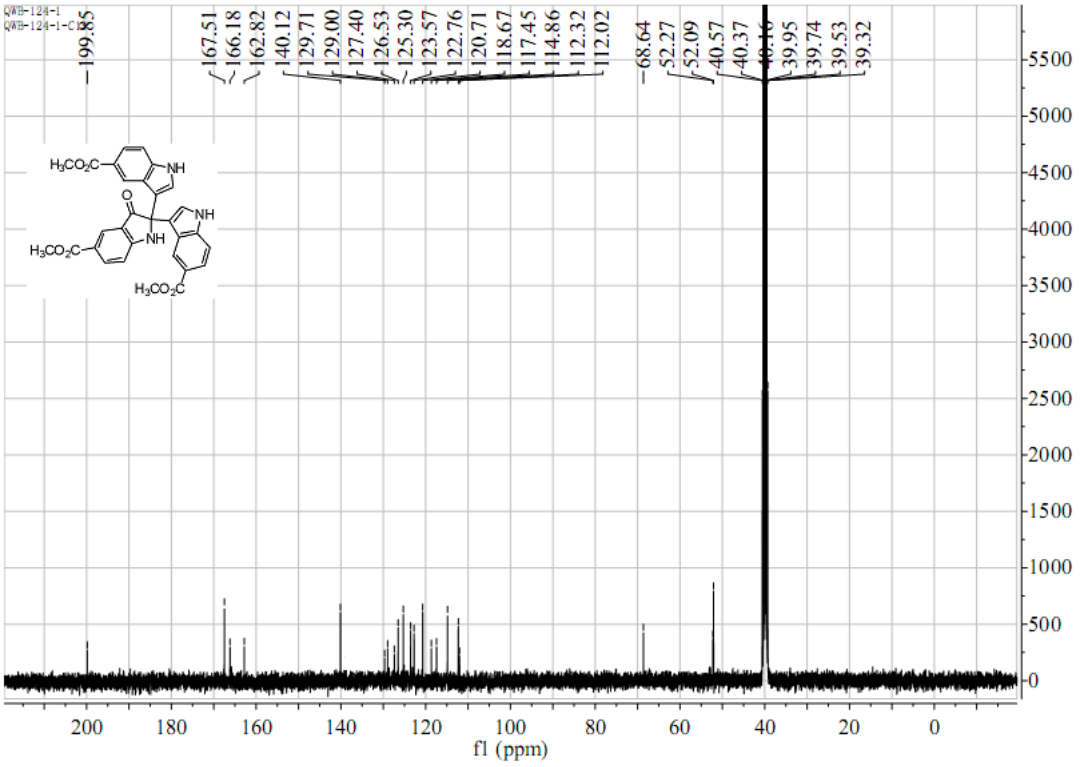
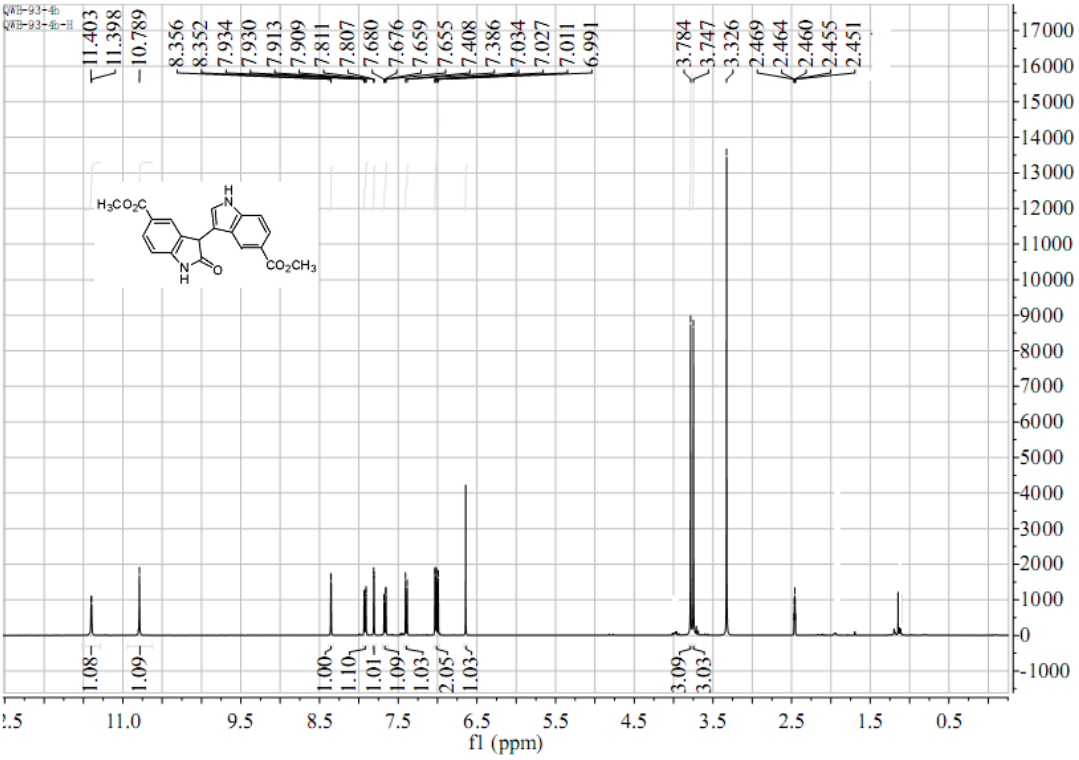
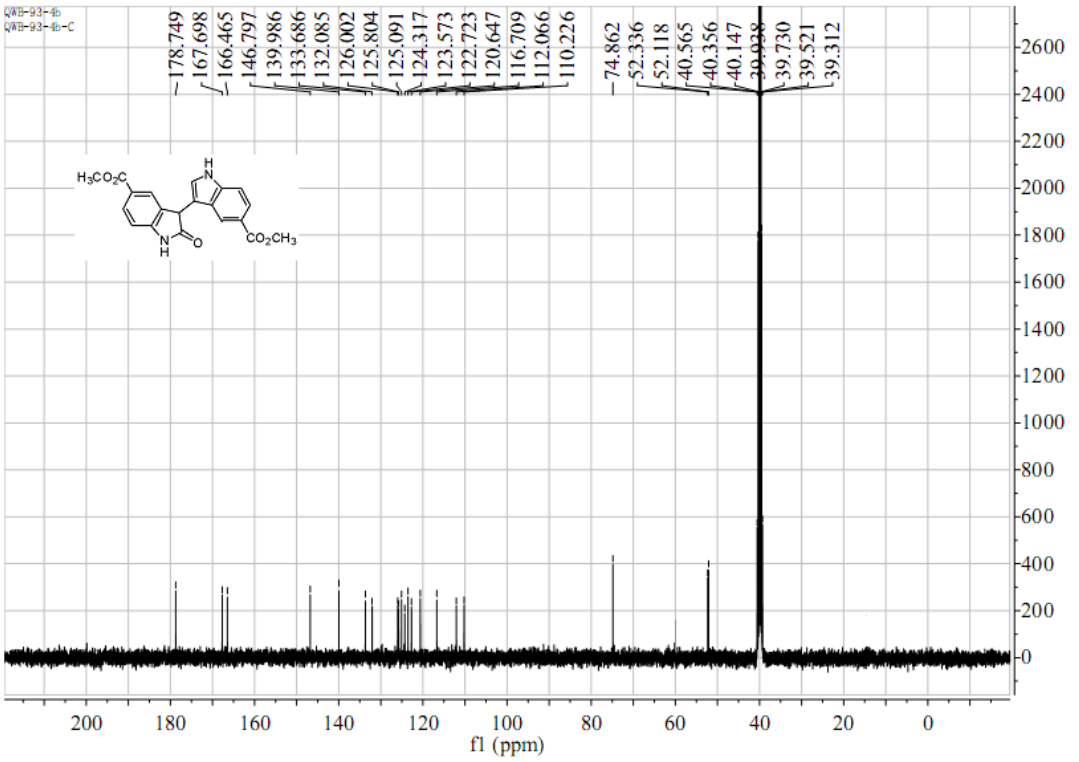
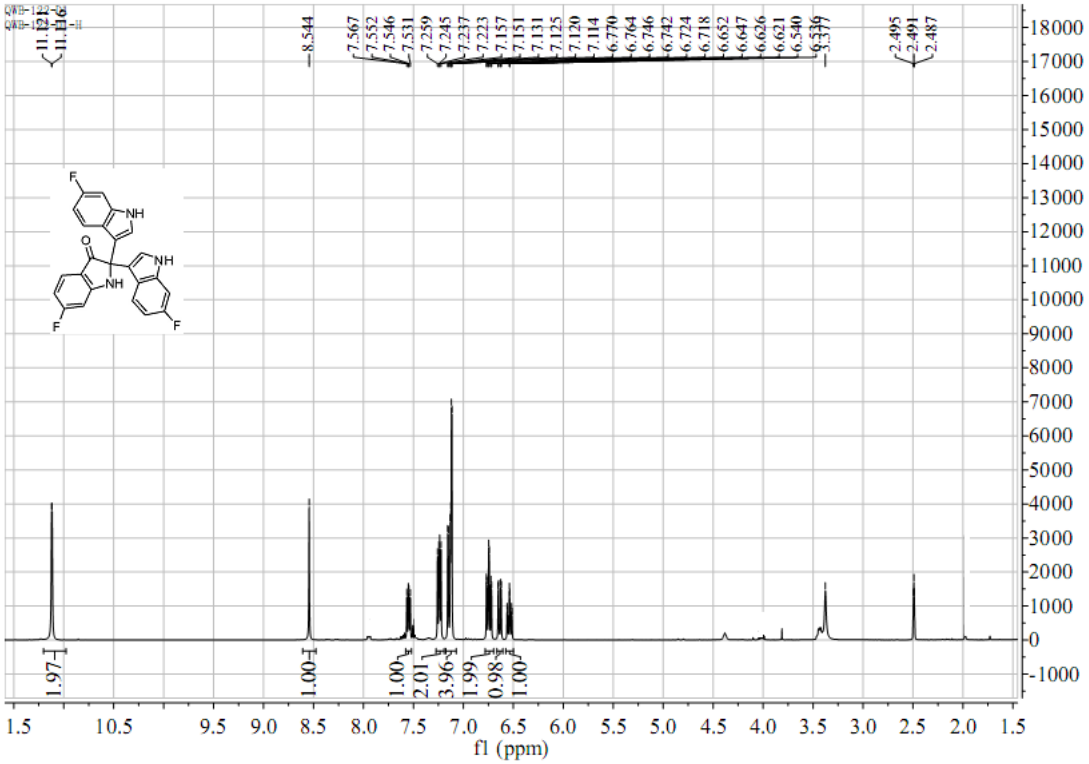
1.00
2.04
2.10
2.04
1.98
1.03
3.03
6.00
fl (ppm)


199.85
167.51
166.18
162.82
140.12
129.71
129.00
127.40
126.53
125.30
123.57
122.76
120.71
118.67
117.45
114.86
112.32
112.02
68.64
52.27
52.09
40.57
40.37
39.95
39.74
39.53
39.32
fl (ppm)






11.621
11.116
8.544
7.567
7.552
7.546
7.531
7.259
7.245
7.237
7.223
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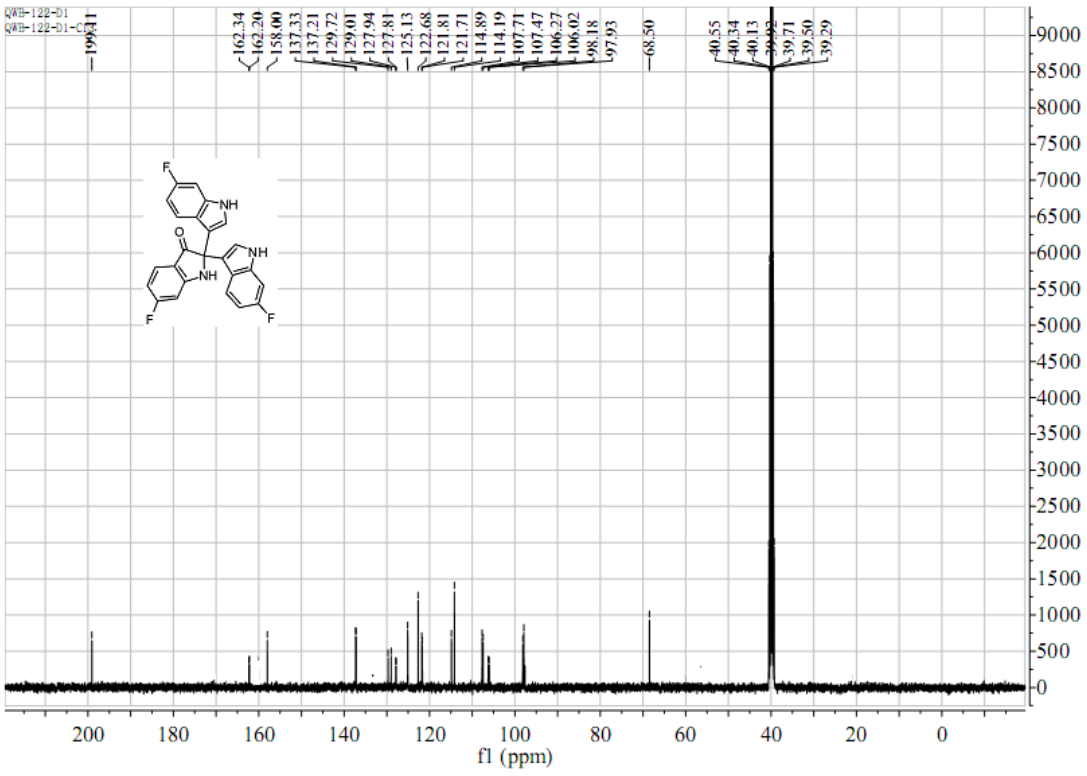
7.131
7.125
7.120
7.114
6.770
6.764
6.746
6.742
6.724
6.718
6.652
6.647
6.626
6.621
6.540
6.536
3.377
2.495
2.491
2.487
1.97
1.00
1.00
2.01
3.96
1.99
0.98
1.00
f1 (ppm)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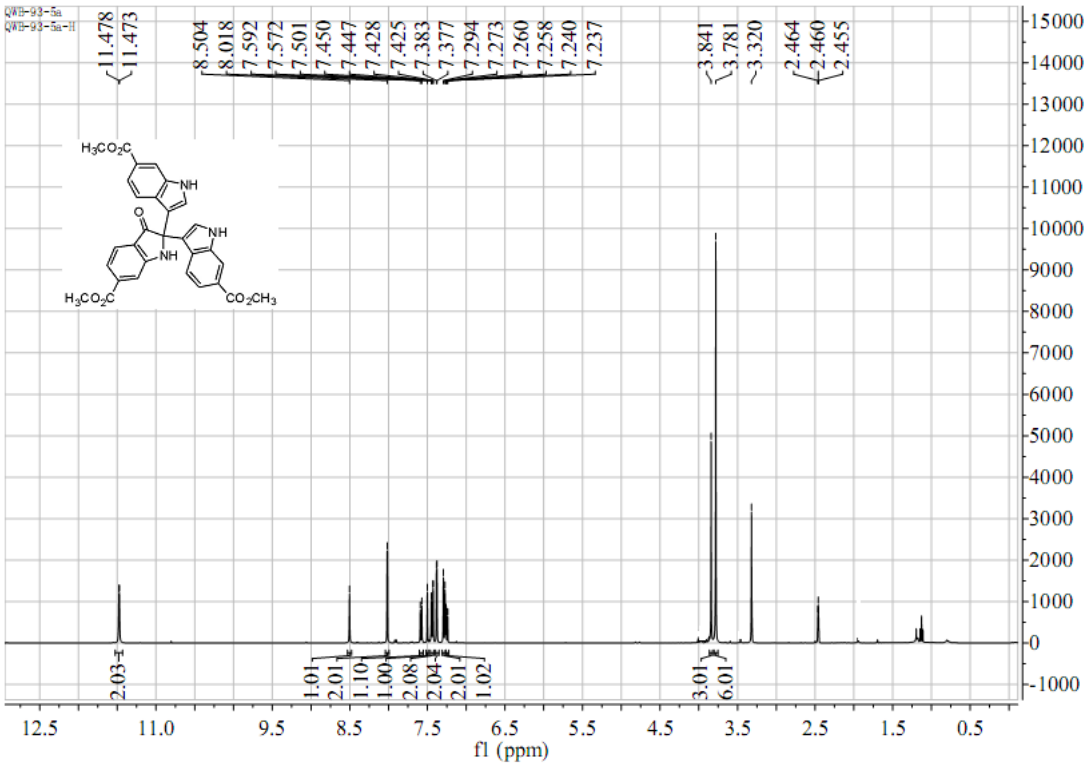
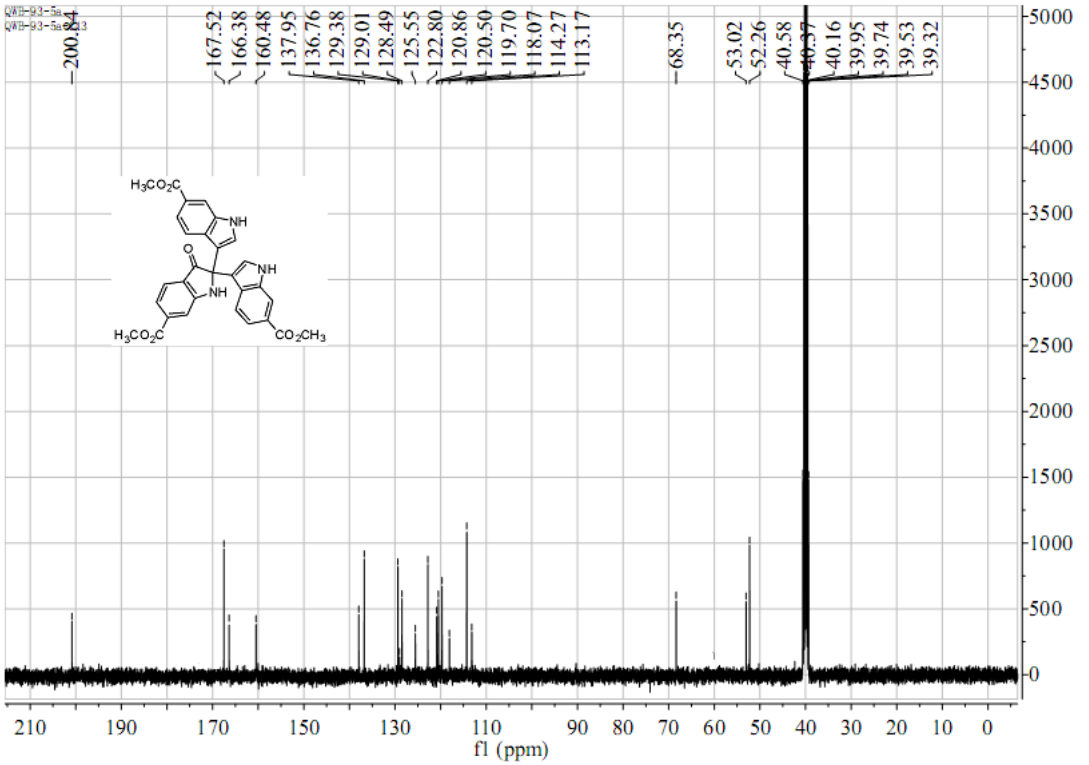
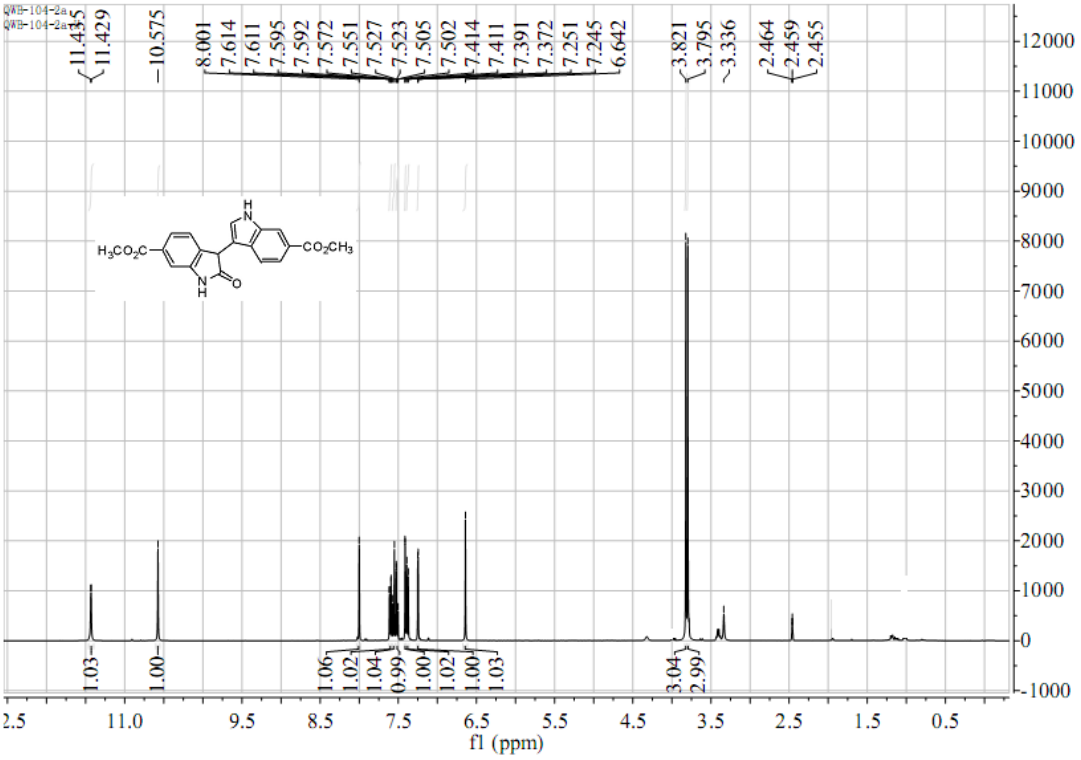
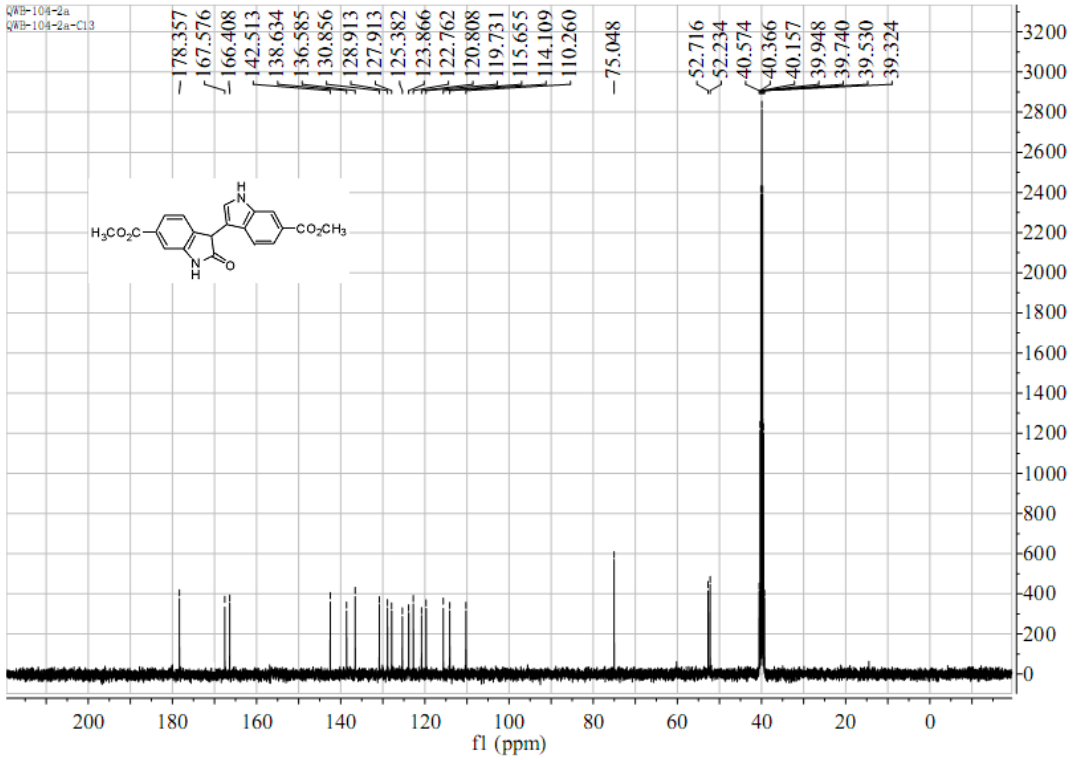
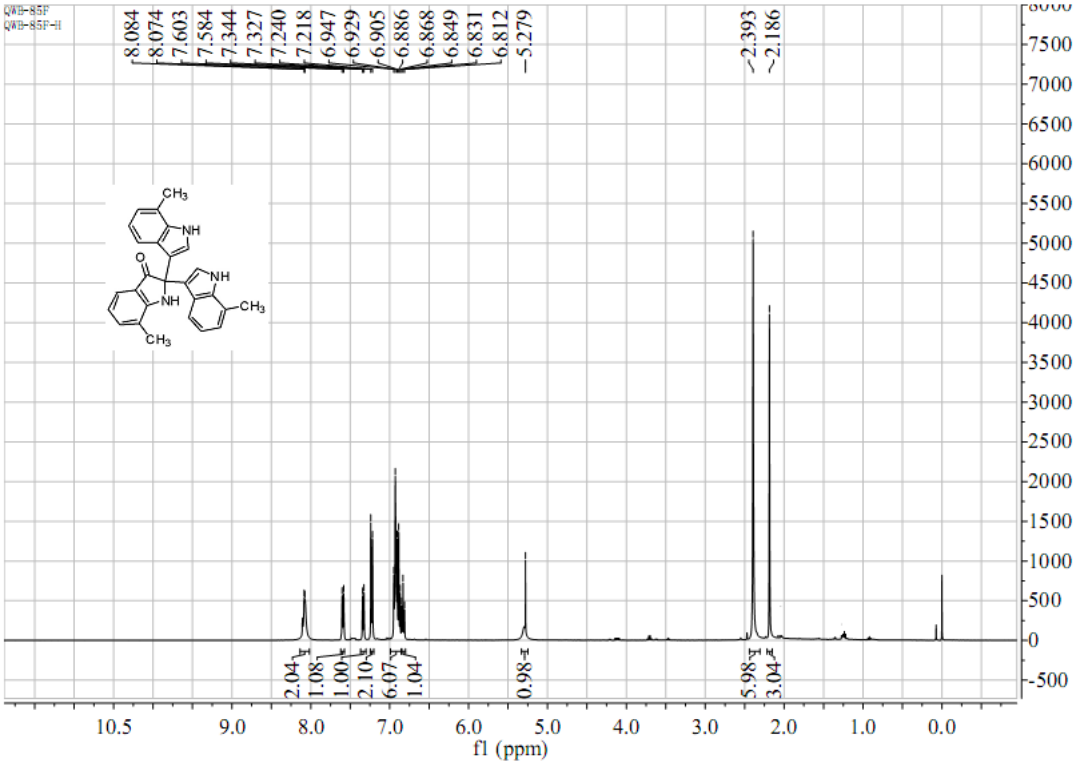
162.34
162.20
158.00
137.33
137.21
129.72
129.01
127.94
127.81
125.13
122.68
121.81
121.71
114.89
114.19
107.71
107.47
106.27
106.02
98.18
97.93
68.50
40.55
40.34
40.13
39.92
39.71
39.50
39.29
f1 (ppm)

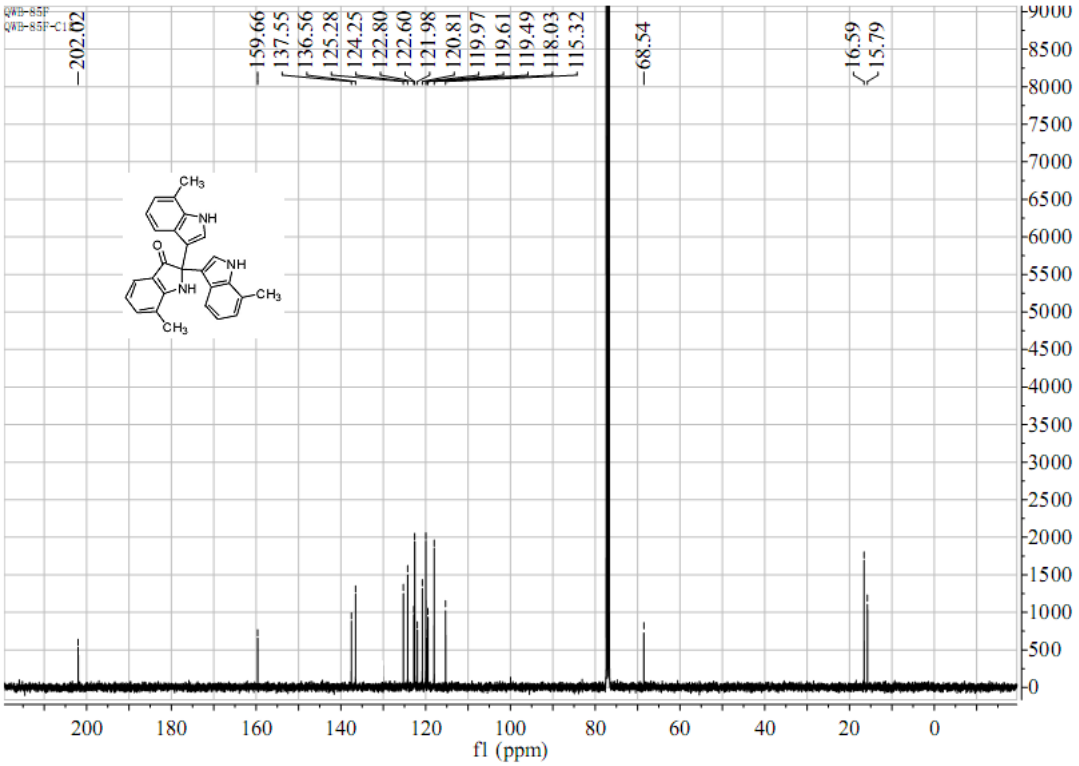

11.478
11.473
8.504
8.018
7.592
7.572
7.501
7.450
7.447
7.428
7.425
7.383
7.377
7.294
7.273
7.260
7.258
7.240
7.237
3.841
3.781
3.320
2.464
2.460
2.455
2.03
1.01
2.01
1.10
1.00
2.08
2.04
2.01
1.02
3.01
6.01
fl (ppm)

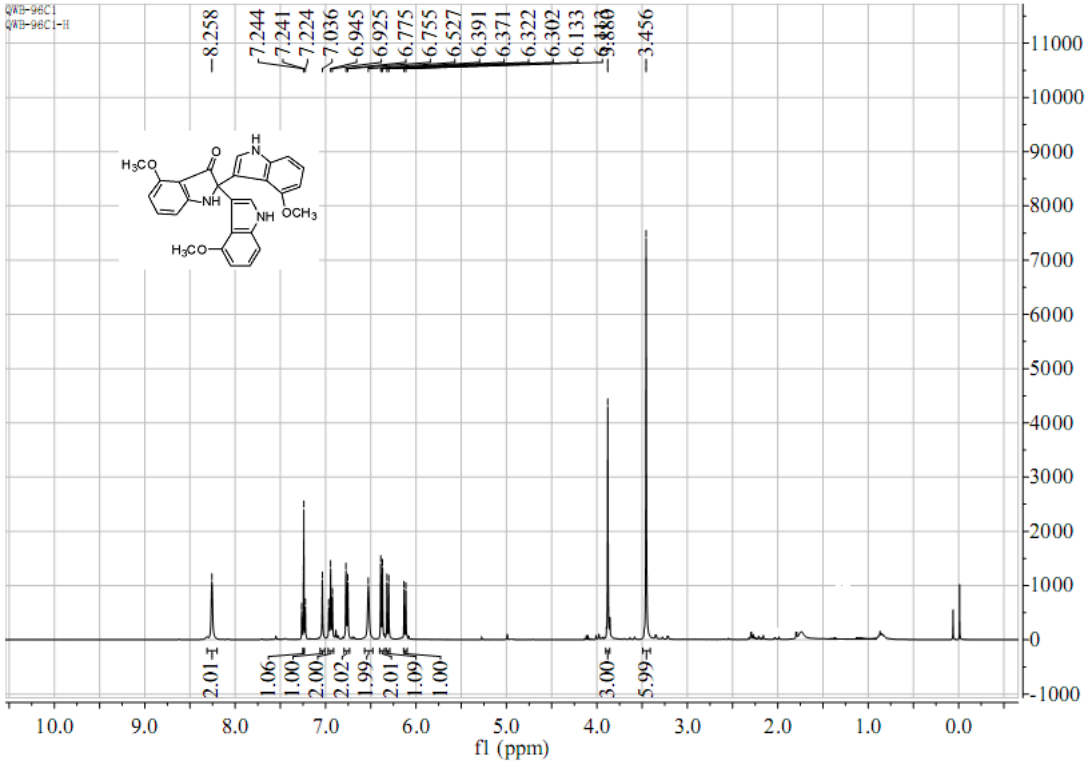

200.84
167.52
166.38
160.48
137.95
136.76
129.38
129.01
128.49
125.55
122.80
120.86
120.50
119.70
118.07
114.27
113.17
68.35
53.02
52.26
40.58
40.37
40.16
39.95
39.74
39.53
39.32
fl (ppm)

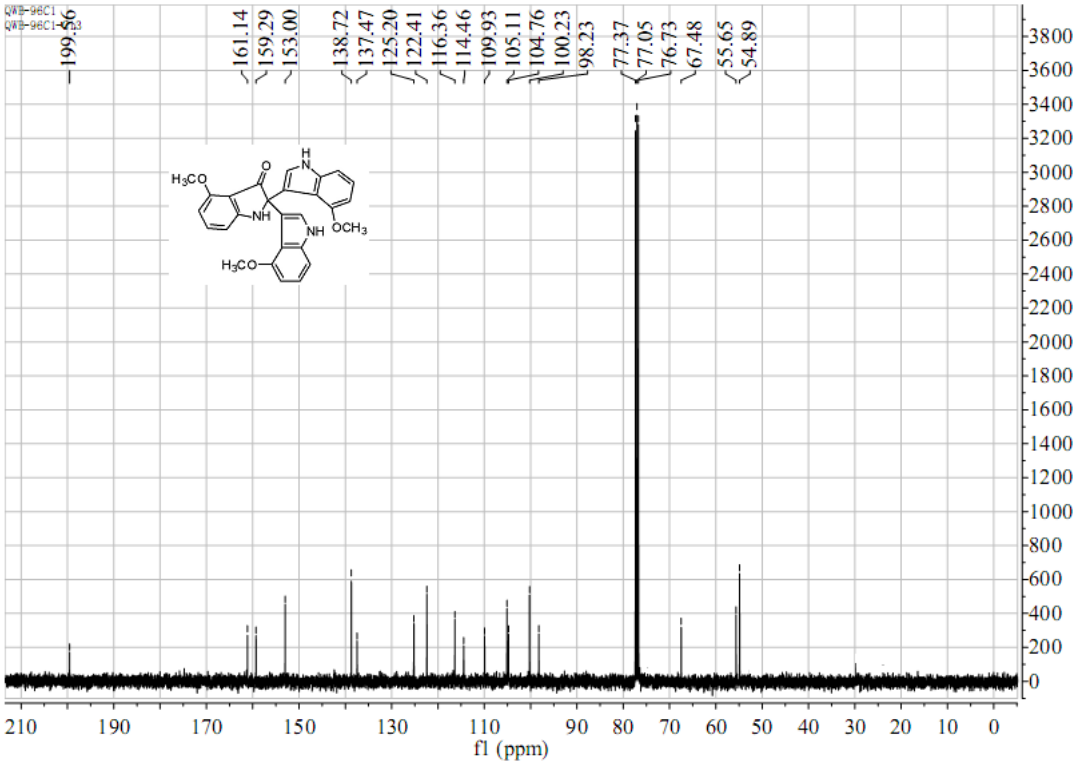

11.435
11.429
10.575
8.001
7.614
7.611
7.595
7.592
7.572
7.551
7.527
7.523
7.505
7.502
7.414
7.411
7.391
7.372
7.251
7.245
6.642
3.821
3.795
3.336
2.464
2.459
2.455
1.03
1.00
1.06
1.02
1.04
0.99
1.00
1.02
1.00
1.03
3.04
2.99
f1 (ppm)

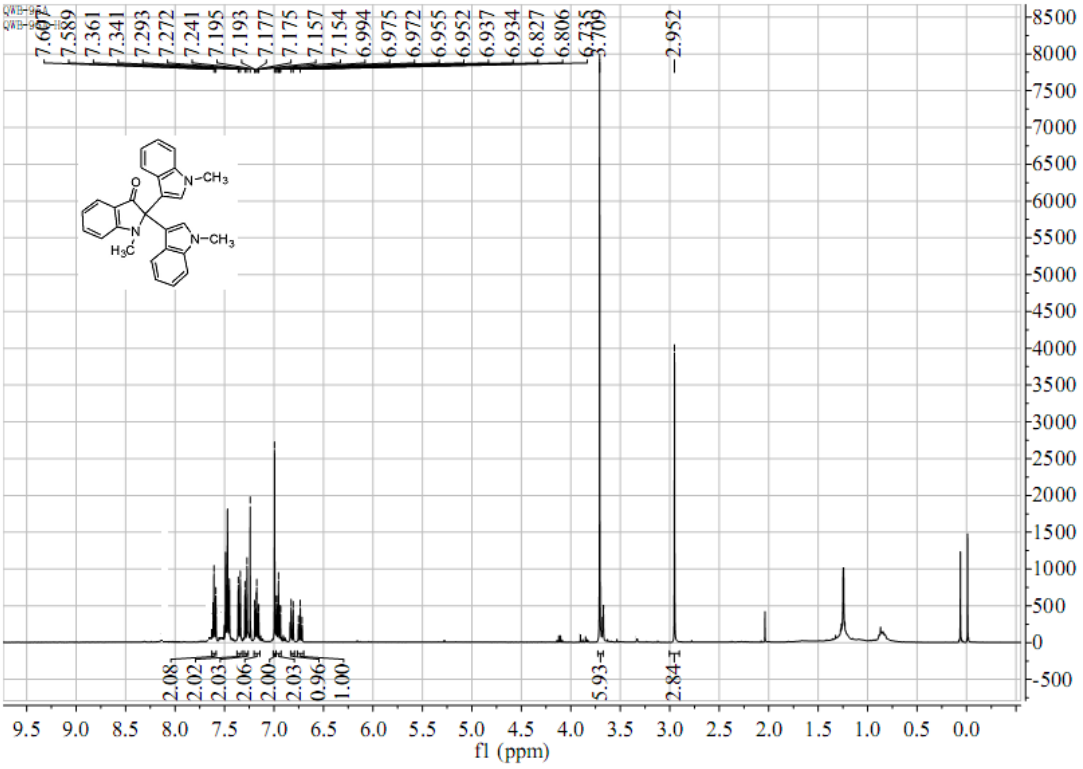

178.357
167.576
166.408
142.513
138.634
136.585
130.856
128.913
127.913
125.382
123.866
122.762
120.808
119.731
115.655
114.109
110.260
75.048
52.716
52.234
40.574
40.366
40.157
39.948
39.740
39.530
39.324
f1 (ppm)

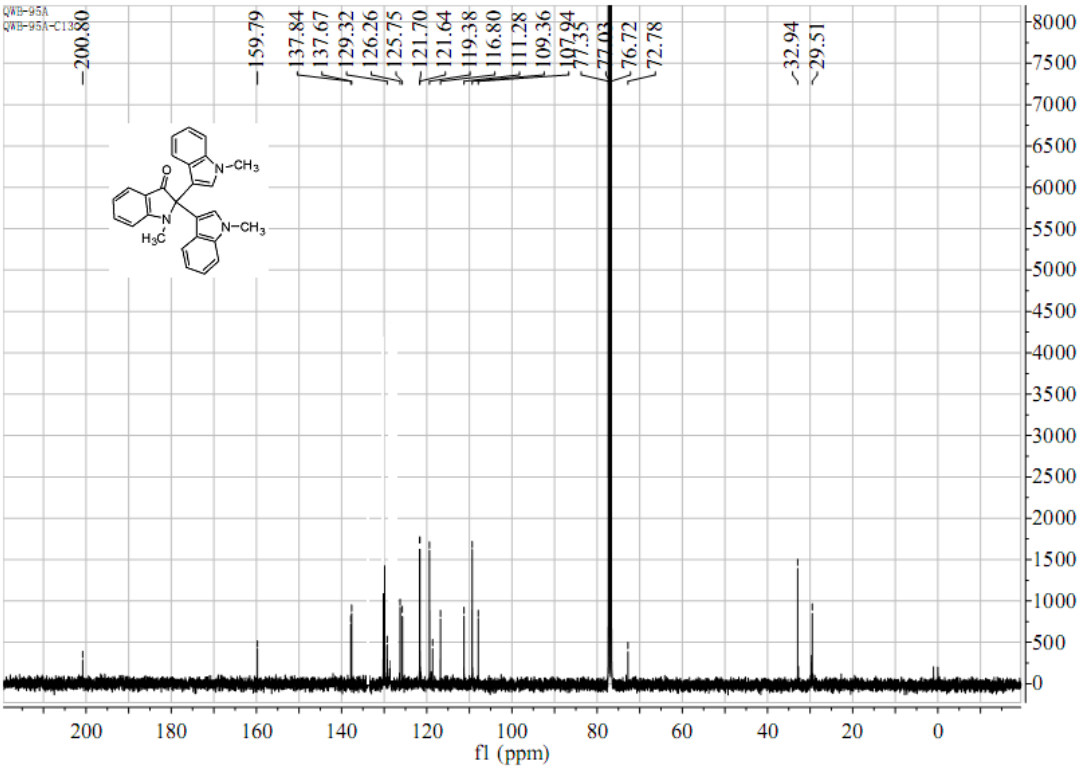

8.084
8.074
7.603
7.584
7.344
7.327
7.240
7.218
6.947
6.929
6.905
6.886
6.868
6.849
6.831
6.812
5.279
2.393
2.186
2.04
1.08
1.00
2.10
6.07
1.04
0.98
5.98
3.04
fl (ppm)

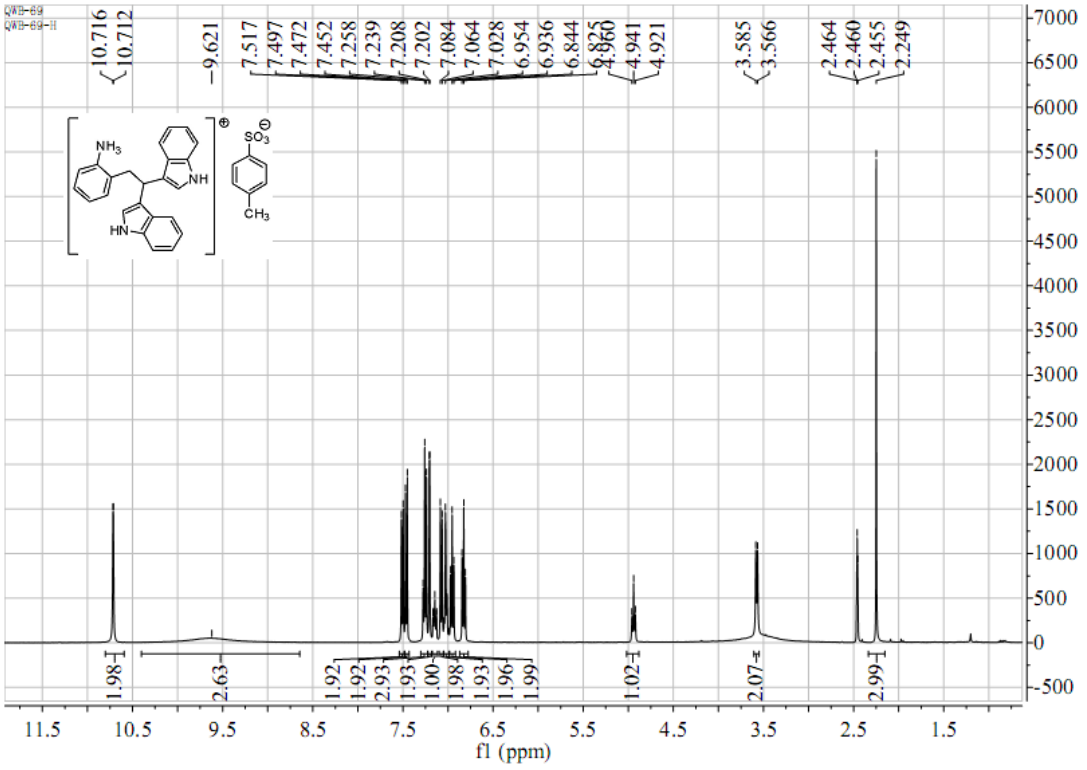

202.02
159.66
137.55
136.56
125.28
124.25
122.80
122.60
121.98
120.81
119.97
119.61
119.49
118.03
115.32
68.54
16.59
15.79
fl (ppm)

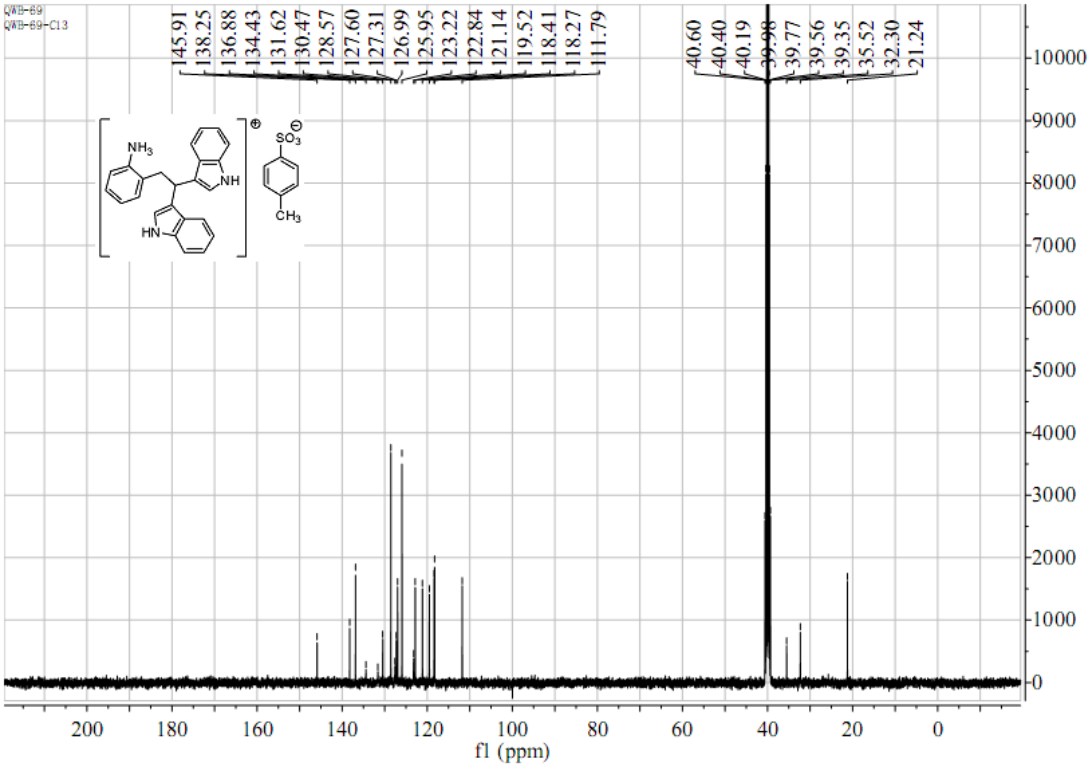

8.258
7.244
7.241
7.224
7.036
6.945
6.925
6.775
6.755
6.527
6.391
6.371
6.322
6.302
6.133
3.880
3.456
2.01
1.06
1.00
2.00
2.02
1.99
2.01
1.09
1.00
3.00
5.99
fl (ppm)


199.56
161.14
159.29
153.00
138.72
137.47
125.20
122.41
116.36
114.46
109.93
105.11
104.76
100.23
98.23
77.37
77.05
76.73
67.48
55.65
54.89
fl (ppm)

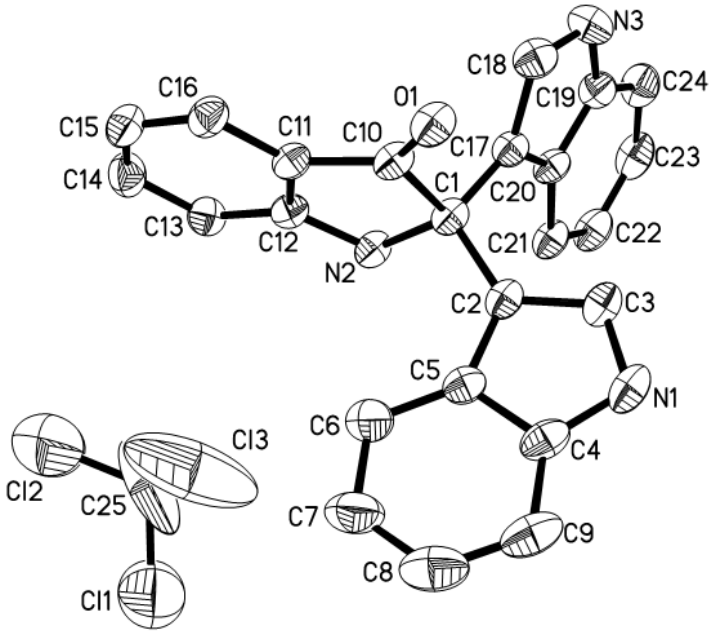

7.607
7.589
7.361
7.341
7.293
7.272
7.241
7.195
7.193
7.177
7.175
7.157
7.154
6.994
6.975
6.972
6.955
6.952
6.937
6.934
6.827
6.806
6.735
3.709
2.952
N–CH3
N–CH3
H3C
2.08
2.02
2.03
2.06
2.00
2.03
0.96
1.00
5.93
2.84
f1 (ppm)


200.80
159.79
137.84
137.67
129.32
126.26
125.75
121.70
121.64
119.38
116.80
111.28
109.36
107.94
77.35
77.03
76.72
72.78
32.94
29.51
N–CH3
N–CH3
H3C
f1 (ppm)


10.716
10.712
9.621
7.517
7.497
7.472
7.452
7.258
7.239
7.208
7.202
7.084
7.064
7.028
6.954
6.936
6.844
4.960
4.941
4.921
3.585
3.566
2.464
2.460
2.455
2.249
NH3
NH
HN
SO3
CH3
1.98
2.63
1.92
1.92
2.93
1.93
1.00
1.98
1.93
1.96
1.99
1.02
2.07
2.99
f1 (ppm)


145.91
138.25
136.88
134.43
131.62
130.47
128.57
127.60
127.31
126.99
125.95
123.22
122.84
121.14
119.52
118.41
118.27
111.79
40.60
40.40
40.19
39.98
39.77
39.56
39.35
35.52
32.30
21.24
NH3
NH
HN
SO3
CH3
f1 (ppm)

4. X-ray Data of Compound 5a.



Datablock: I

Bond precision: C-C = 0.0061 A Wavelength=0.71073

Cell: a=13.85200 b=14.99000 c=11.59400
alpha=90 beta=107.5900 gamma=90

Temperature: 293 K

	Calculated	Reported
Volume	2294.834	2295
Space group	P 21/c	P21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C24 H17 N3 O, C H Cl3	C25 H18 Cl3 N3 O
Sum formula	C25 H18 Cl3 N3 O	C25 H18 Cl3 N3 O
Mr	482.77	482.77
Dx,g cm-3	1.397	1.397
Z	4	4
Mu (mm-1)	0.423	0.423
F000	992.0	992.0
F000'	994.08	
h,k,lmax	17,19,15	17,19,15
Nref	5240	5082
Tmin,Tmax	0.859,0.975	0.314,0.346
Tmin'	0.844	

Correction method= MULTI-SCAN

Data completeness= 0.970 Theta(max)= 27.430

R(reflections)= 0.1007(2579) wR2(reflections)= 0.3389(5082)

S = 1.105 Npar= 290

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

```
RFACG01_ALERT_3_C  The value of the R factor is > 0.10
           R factor given   0.101
RFACR01_ALERT_3_C  The value of the weighted R factor is > 0.25
           Weighted R factor given   0.339
PLAT029_ALERT_3_C _diffrn_measured_fraction_theta_full Low .......      0.970
PLAT084_ALERT_2_C High wR2 Value ................................       0.34
PLAT141_ALERT_4_C su on a - Axis Small or Missing ................    0.00000 Ang.
PLAT142_ALERT_4_C su on b - Axis Small or Missing ................    0.00000 Ang.
PLAT143_ALERT_4_C su on c - Axis Small or Missing ................    0.00000 Ang.
PLAT145_ALERT_4_C su on beta     Small or Missing ................     0.0000 Deg.
PLAT151_ALERT_1_C No su (esd) Given on Volume ....................          ?
PLAT244_ALERT_4_C Low   'Solvent' Ueq as Compared to Neighbors of        C25
PLAT340_ALERT_3_C Low Bond Precision on  C-C Bonds ...............     0.0061 Ang
PLAT420_ALERT_2_C D-H Without Acceptor       N3     -   H3A    ...          ?
```

Alert level G

```
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite         4
PLAT005_ALERT_5_G No _iucr_refine_instructions_details in CIF ....         ?
PLAT007_ALERT_5_G Note: Number of Unrefined D-H Atoms ............         3
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings  Differ         ?
PLAT072_ALERT_2_G SHELXL First  Parameter in WGHT Unusually Large.      0.20
PLAT194_ALERT_1_G Missing _cell_measurement_reflns_used datum ....         ?
PLAT199_ALERT_1_G Check the Reported _cell_measurement_temperature       293 K
PLAT200_ALERT_1_G Check the Reported   _diffrn_ambient_temperature       293 K
PLAT860_ALERT_3_G Note: Number of Least-Squares Restraints .......         3
```

```
  1 ALERT level A = Most likely a serious problem - resolve or explain
  0 ALERT level B = A potentially serious problem, consider carefully
 12 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  9 ALERT level G = General information/check it is not something unexpected

  5 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
  4 ALERT type 2 Indicator that the structure model may be wrong or deficient
  5 ALERT type 3 Indicator that the structure quality may be low
  6 ALERT type 4 Improvement, methodology, query or suggestion
  2 ALERT type 5 Informative message, check
```

5. References

1. P. Manini, M. d'Ischia, M. Milosa and G. Prota, *J. Org. Chem*. **1998**, *63*, 7002-7008.
2. T. L. Stull, L. Hyun, C. Sharetzshy, J. Wooten, J. P. McCauley and A. B. Smith Ⅲ, *J. Biol. Chem*. **1995**, *270*, 5-8.