Supporting Information

Three-component assembly of 2,3-disubstituted benzo[*e*]indoles from 1,2-diketones, 2-tetralones, and NH_4OAc

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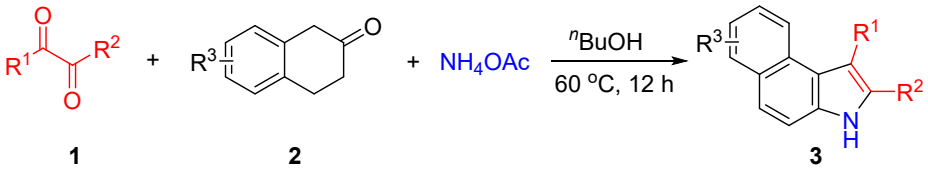
1. General information

All reactions were carried out in well-cleaned and oven-dried glassware with magnetic stirring in an oil bath. All chemical reagents were used as received from commercial suppliers (Adamas and Bide) without further purification. Thin layer chromatography was performed using silica gel (HSGF254) using UV light for detection. The products were isolated by column chromatography (200−300 mesh silica gel) using petroleum ether and ethyl acetate as the eluent. ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectra were recorded on Bruker-AV (400 and 101 MHz, respectively) instrument using chloroform-*d* or DMSO-d_6 as solvent and TMS as an internal standard. To display multiplicities and signal forms correctly, the following abbreviations were used: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Chemical shifts (δ) were given in parts per million (ppm), and coupling constants (*J*) were reported in hertz (Hz). High-resolution mass spectra (ESI) were obtained with the Agilent Technologies QTOF6550.

2. Experimental section

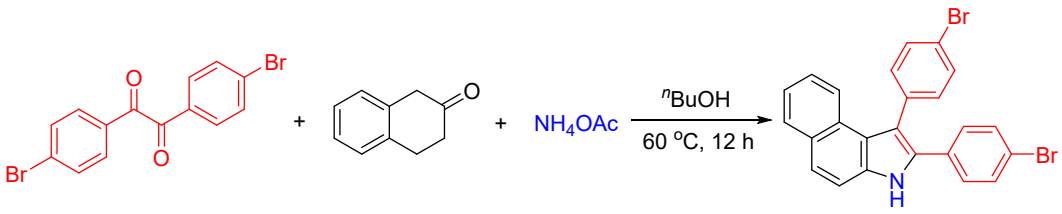
2.1 General procedure for the synthesis of products 3.



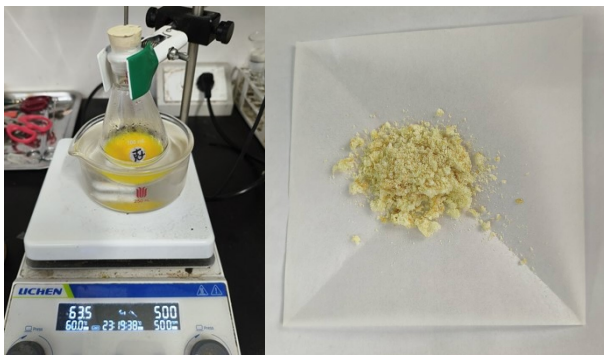
1 **2** **3**

An oven-dried vial equipped with a magnetic stirring bar was charged with 1,2-diketone **1** (0.2 mmol), 2-tetralone **2** (0.5 mmol), NH_4OAc (0.6 mmol) and ^{n}BuOH (1 mL). The vial was then sealed and placed into an oil bath. The reaction mixture was stirred at 60 °C for 12 h. After the reaction was completed, the mixture was cooled to room temperature and filtered through a pad of silica gel by washing with ethyl acetate. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography (silica gel, PE/EA) to yield the desired product **3**.

2.2 Procedure for the gram-scale synthesis of product 3ae.

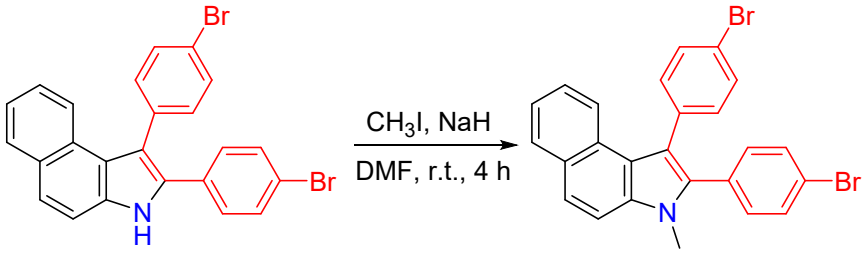


1e, 4 mmol **2a**, 10 mmol 12 mmol **3ae**, 1.8773 g, 98%



An oven-dried 100 mL round-bottom flask equipped with a magnetic stirring bar was charged with **1e** (4 mmol), **2a** (10 mmol), NH_4OAc (12 mmol) and ^nBuOH (20 mL). The flask was then sealed and placed into an oil bath. The reaction mixture was stirred at 60 ℃ for 12 h. After the reaction was completed, the mixture was cooled to room temperature and filtered through a pad of silica gel by washing with ethyl acetate. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography (silica gel, PE/EA = 95:5) to yield the desired product **3ae** (1.8773 g, 98% yield).

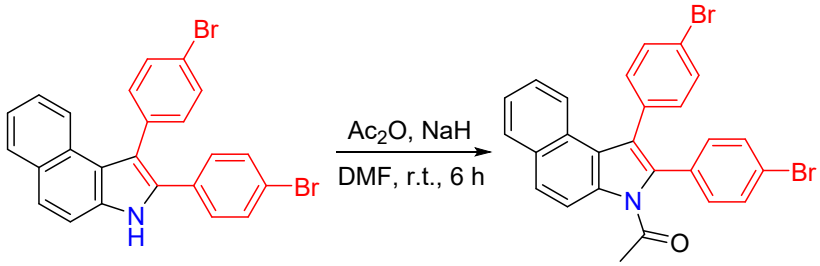
2.3 Procedure for the synthesis of compound 4a.



3ae, 0.2 mmol **4a**, 95%

To a solution of **3ae** (0.2 mmol) in DMF (2.0 mL) was added NaH (0.3 mmol, 1.5 equiv) at 0 °C. After 10 min, CH_3I was added and the mixture was stirred at r.t. for 4 h. The reaction was quenched by NH_4Cl solution, extracted with EA (2×30 mL) and dried ($MgSO_4$). The combined extracts were concentrated under vacuum and purified by column chromatography on silica gel with PE/EA = 95:5, affording product **4a** as a white solid in 95% yield (93.3 mg).

2.4 Procedure for the synthesis of compound 4b.

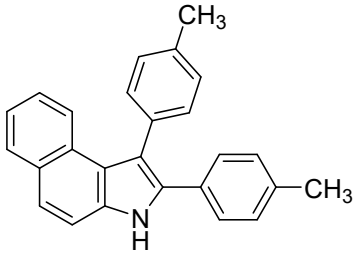


3ae, 0.2 mmol **4b**, 72%

To a solution of **3ae** (0.2 mmol) in DMF (2.0 mL) was added NaH (0.3 mmol, 1.5 equiv) at 0 °C. After 10 min, Ac_2O was added and the mixture was stirred at r.t. for 6 h. The reaction was quenched by NH_4Cl solution, extracted with EA (2×30 mL) and dried ($MgSO_4$). The combined extracts were concentrated under vacuum and purified by column chromatography on silica gel with PE/EA = 95:5, affording product **4b** as a white solid in 72% yield (74.8 mg).

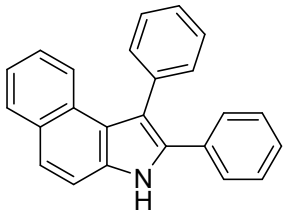
3. Characterization data of products

1,2-di-*p*-tolyl-3*H*-benzo[*e*]indole (3aa)



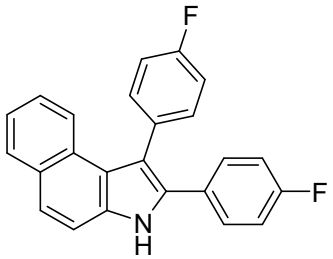
Yield: 62.2 mg, 90% (yellow liquid, PE/EA = 95:5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.78 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.63 (d, *J* = 8.8 Hz, 1H), 7.55 (d, *J* = 8.8 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.37−7.31 (m, 1H), 7.31−7.21 (m, 5H), 7.09 (d, *J* = 8.0 Hz, 2H), 2.49 (s, 3H), 2.33 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 136.9, 136.7, 134.2, 132.9, 132.2, 131.4, 130.1, 130.1, 129.7, 129.4, 129.0, 128.9, 127.4, 125.4, 123.8, 123.4, 123.2, 122.2, 117.6, 112.5, 21.6, 21.3. **HRMS (ESI) m/z**: calcd. for $C_{26}H_{22}N^+$ $(M+H)^+$ 348.1747, found 348.1745.

1,2-diphenyl-3*H*-benzo[*e*]indole (3ab)



Yield: 59.5 mg, 93% (yellow liquid, PE/EA = 95:5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.78 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.66−7.61 (m, 1H), 7.53 (d, *J* = 8.7 Hz, 1H), 7.45−7.34 (m, 6H), 7.26−7.11 (m, 7H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 137.3, 132.8, 132.7, 132.4, 131.6, 130.1, 128.9, 128.7, 127.6, 127.3, 127.2, 125.6, 124.1, 123.3, 122.1, 118.1, 112.6. **HRMS (ESI) m/z**: calcd. for $C_{24}H_{18}N^+$ $(M+H)^+$ 320.1434, found 320.1431.

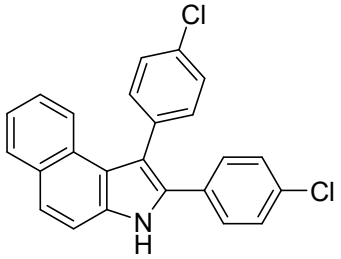
1,2-bis(4-fluorophenyl)-3*H*-benzo[*e*]indole (3ac)



Yield: 47.3 mg, 67% (brown solid, PE/EA = 9:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 7.89 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.70 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.65 (d, *J* = 8.8 Hz, 1H), 7.56 (d, *J* = 8.8 Hz, 1H), 7.48–7.42 (m, 2H), 7.38–7.33 (m, 1H), 7.29–7.25 (m, 3H), 7.18 (t, *J* = 8.7 Hz, 2H), 6.99 (t, *J* = 8.7 Hz, 2H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 163.5 (d, *J* = 32.0 Hz), 161.0 (d, *J* = 33.0 Hz), 133.1 (d, *J* = 8.0 Hz), 132.9 (d, *J* = 3.0 Hz), 132.3, 132.2, 130.2, 129.4 (d, *J* = 8.0 Hz), 129.0, 128.83 (d, *J* = 3.0 Hz), 128.76, 125.7, 124.3, 123.5, 123.1, 122.0, 116.8,

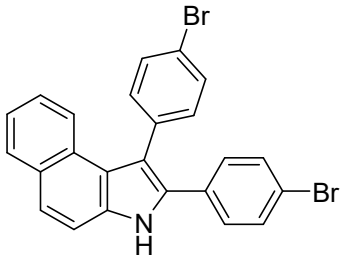
116.0 (d, *J* = 15.0 Hz), 115.8 (d, *J* = 16.0 Hz), 112.5. **HRMS (ESI) m/z**: calcd. for $C_{24}H_{16}F_2N^+$ $(M+H)^+$ 356.1245, found 356.1247.

1,2-bis(4-chlorophenyl)-3*H*-benzo[*e*]indole (3ad)



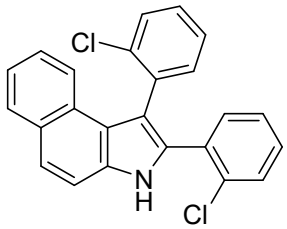
Yield: 63 mg, 81% (faint-yellow liquid, PE/EA = 95:5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.81–7.77 (m, 1H), 7.61 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.54 (d, *J* = 8.8 Hz, 1H), 7.41 (d, *J* = 8.8 Hz, 1H), 7.37–7.33 (m, 2H), 7.32–7.24 (m, 3H), 7.21–7.13 (m, 3H), 7.10 – 7.05 (m, 2H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 135.5, 133.5, 133.3, 132.8, 132.6, 131.8, 130.9, 130.2, 129.3, 129.1, 129.0, 128.8, 128.7, 125.8, 124.6, 123.6, 123.1, 121.8, 117.0, 112.5. **HRMS (ESI) m/z**: calcd. for $C_{24}H_{16}Cl_2N^+$ $(M+H)^+$ 388.0654, found 388.0658.

1,2-bis(4-bromophenyl)-3*H*-benzo[*e*]indole (3ae)



Yield: 81.1mg, 85% (yellow solid, PE/EA = 95:5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.66 (d, *J* = 8.8 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.8 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 3H), 7.34 (d, *J* = 8.4 Hz, 3H), 7.08 (d, *J* = 8.4 Hz, 2H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 135.9, 133.1, 132.6, 132.2, 131.9, 131.7, 131.3, 130.1, 129.1, 129.0, 128.6, 125.8, 124.6, 123.6, 123.1, 121.7, 121.7, 121.4, 117.0, 112.5. **HRMS (ESI) m/z**: calcd. for $C_{24}H_{16}Br_2N^+$ $(M+H)^+$ 475.9644, found 475.9648.

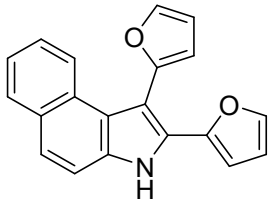
1,2-bis(2-chlorophenyl)-3*H*-benzo[*e*]indole (3af)



Yield: 58.4 mg, 75% (brown liquid, PE/EA = 95:5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.84 (s, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.68 (d, *J* = 8.8 Hz, 1H), 7.62−7.51 (m, 3H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.40−7.21 (m, 7H), 7.10 (t, *J* = 7.5 Hz, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 136.2, 135.8, 133.6, 133.5, 132.8, 132.2, 131.2, 131.0, 130.1, 130.0, 129.7, 129.4, 129.0, 128.8,

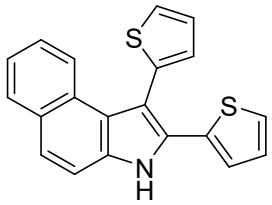
127.0, 126.8, 125.9, 124.4, 123.5, 122.9, 121.0, 116.5, 112.8. **HRMS (ESI) m/z**: calcd. for $C_{24}H_{16}Cl_2N^+$ $(M+H)^+$ 388.0654, found 388.0652.

1,2-di(furan-2-yl)-3*H*-benzo[*e*]indole (3ag)



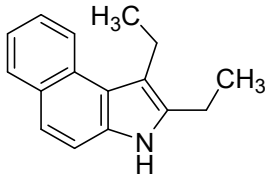
Yield: 26.1 mg, 43% (brown liquid, PE/EA = 95:5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.03 (s, 1H), 7.93−7.84 (m, 1H), 7.79−7.68 (m, 2H), 7.63 (d, *J* = 8.8 Hz, 1H), 7.53 (d, *J* = 8.7 Hz, 1H), 7.44 (dd, *J* = 1.8, 0.7 Hz, 1H), 7.41−7.34 (m, 2H), 6.69 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.63 (dd, *J* = 3.2, 0.8 Hz, 1H), 6.42 (dd, *J* = 3.5, 1.8 Hz, 1H), 6.15 (dd, *J* = 3.4, 0.7 Hz, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 148.5, 146.5, 142.7, 141.5, 132.1, 130.2, 128.9, 128.2, 127.7, 126.1, 124.6, 123.8, 123.2, 123.0, 112.5, 112.3, 111.6, 110.8, 107.0, 104.8. **HRMS (ESI) m/z**: calcd. for $C_{20}H_{14}NO_2^+$ $(M+H)^+$ 300.1019, found 300.1015.

1,2-di(thiophen-2-yl)-3*H*-benzo[*e*]indole (3ah)



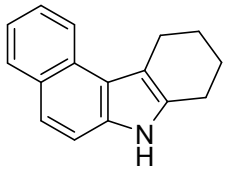
Yield: 44.1 mg, 66% (faint-yellow liquid, PE/EA = 9:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 7.87 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.73 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.60 (d, *J* = 8.7 Hz, 1H), 7.53 (dd, *J* = 4.9, 3.0 Hz, 1H), 7.48 (d, *J* = 8.8 Hz, 1H), 7.38−7.27 (m, 3H), 7.25−7.20 (m, 2H), 7.06 (dd, *J* = 3.0, 1.4 Hz, 1H), 6.94 (dd, *J* = 5.1, 1.3 Hz, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 136.9, 133.5, 132.0, 130.4, 130.1, 129.7, 128.9, 128.8, 126.3, 126.0, 126.0, 125.8, 124.7, 124.0, 123.5, 123.2, 122.5, 120.5, 112.5, 111.7. **HRMS (ESI) m/z**: calcd. for $C_{20}H_{14}NS_2^+$ $(M+H)^+$ 332.0562, found 332.0561.

1,2-diethyl-3*H*-benzo[*e*]indole (3ai)



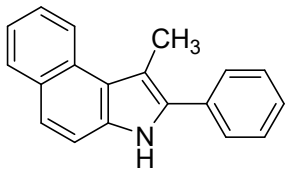
Yield: 32.5 mg, 73% (yellow liquid, PE/EA = 95:5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.4 Hz, 1H), 8.08 (s, 1H), 7.91 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.57−7.51 (m, 2H), 7.45 (d, *J* = 8.7 Hz, 1H), 7.42−7.37 (m, 1H), 3.09 (q, *J* = 7.5 Hz, 2H), 2.85 (q, *J* = 7.6 Hz, 2H), 1.40−1.32 (m, 6H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 134.8, 131.7, 129.9, 129.0, 128.9, 125.5, 123.3, 122.6, 122.2, 121.0, 116.1, 112.6, 19.4, 19.3, 15.8, 14.9. **HRMS (ESI) m/z**: calcd. for $C_{16}H_{18}N^+$ $(M+H)^+$ 224.1434, found 224.1435.

8,9,10,11-tetrahydro-7*H*-benzo[*c*]carbazole (3aj)



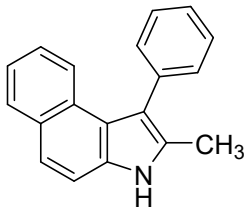
Yield: 27.1mg, 54% (yellow solid, PE/EA = 95:5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.3 Hz, 1H), 7.99 (s, 1H), 7.92 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.57−7.50 (m, 2H), 7.45−7.37 (m, 2H), 3.21 (t, *J* = 5.6 Hz, 2H), 2.81 (t, *J* = 5.6 Hz, 2H), 2.04−1.92 (m, 4H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 132.4, 131.8, 129.7, 129.2, 128.7, 125.3, 123.7, 122.6, 121.9, 121.0, 112.6, 112.4, 24.4, 23.9, 23.7, 22.9. **HRMS (ESI) m/z**: calcd. for $C_{16}H_{16}N^+$ $(M+H)^+$ 222.1277, found 222.1278.

1-methyl-2-phenyl-3*H*-benzo[*e*]indole (3ak)



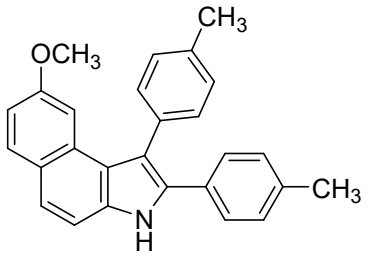
Yield: 23.3 mg, 45% (yellow liquid, PE/EA = 98:2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.60 (dd, *J* = 8.4, 1.1 Hz, 1H), 8.35 (s, 1H), 7.95 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.64−7.48 (m, 7H), 7.47−7.36 (m, 2H), 2.85 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 133.4, 133.4, 132.6, 130.0, 129.8, 129.0, 129.0, 128.7, 127.5, 125.7, 123.6, 123.4, 123.0, 122.5, 112.7, 111.3, 13.4. **HRMS (ESI) m/z**: calcd. for $C_{19}H_{16}N^+$ $(M+H)^+$ 258.1277, found 258.1273.

2-methyl-1-phenyl-3*H*-benzo[*e*]indole (3ak')



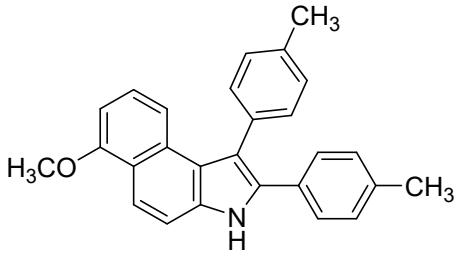
Yield: 23.6 mg, 45% (yellow liquid, PE/EA = 98:2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.92−7.81 (m, 2H), 7.60−7.41 (m, 7H), 7.35−7.30 (m, 1H), 7.27−7.21 (m, 1H), 2.36 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 137.3, 131.4, 131.3, 130.4, 129.9, 128.8, 128.5, 128.4, 126.9, 125.2, 123.3, 123.0, 122.6, 121.1, 117.4, 112.3, 12.1. **HRMS (ESI) m/z**: calcd. for $C_{19}H_{16}N^+$ $(M+H)^+$ 258.1277, found 258.1275.

8-methoxy-1,2-di-*p*-tolyl-3*H*-benzo[*e*]indole (3ba)



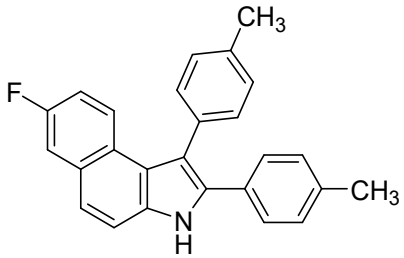
Yield: 70.6 mg, 94% (yellow liquid, PE/EA = 95:5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 7.79 (d, *J* = 8.9 Hz, 1H), 7.56 (d, *J* = 8.7 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.6 Hz, 1H), 7.30 (dd, *J* = 13.9, 8.0 Hz, 4H), 7.15−7.09 (m, 3H), 7.02 (dd, *J* = 8.9, 2.6 Hz, 1H), 3.50 (s, 3H), 2.48 (s, 3H), 2.35 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 157.3, 136.8, 136.7, 134.4, 132.6, 132.3, 131.7, 130.1, 130.0, 129.9, 129.5, 129.4, 127.2, 124.8, 123.5, 121.9, 117.3, 114.9, 110.1, 103.2, 54.7, 21.4, 21.3. **HRMS (ESI) m/z**: calcd. for $C_{27}H_{24}NO^+$ $(M+H)^+$ 378.1852 found 378.1853.

6-methoxy-1,2-di-*p*-tolyl-3*H*-benzo[*e*]indole (3bb)



Yield: 41.9 mg, 56% (white solid, PE/EA = 95:5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.14 (d, *J* = 9.0 Hz, 1H), 7.53 (d, *J* = 9.1 Hz, 1H), 7.42−7.37 (m, 3H), 7.28 (d, *J* = 7.7 Hz, 2H), 7.23−7.16 (m, 3H), 7.09 (d, *J* = 8.0 Hz, 2H), 6.76 (d, *J* = 7.4 Hz, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 156.1, 136.9, 136.7, 134.3, 132.9, 132.8, 131.4, 130.1, 130.0, 129.6, 129.4, 127.4, 125.6, 122.1, 121.3, 117.6, 117.3, 116.2, 111.6, 102.4, 55.6, 21.6, 21.3. **HRMS (ESI) m/z**: calcd. for $C_{27}H_{24}NO^+$ $(M+H)^+$ 378.1852, found 378.1853.

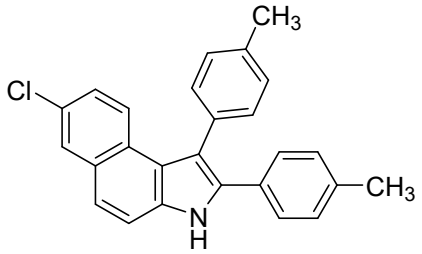
7-fluoro-1,2-di-*p*-tolyl-3*H*-benzo[*e*]indole (3bc)



Yield: 66.1 mg, 90% (faint-yellow liquid, PE/EA = 95:5).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.76 (dd, *J* = 9.2, 5.7 Hz, 1H), 7.61−7.48 (m, 3H), 7.38 (d, *J* = 7.7 Hz, 2H), 7.29 (d, *J* = 7.6 Hz, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 7.10 (d, *J* = 7.9 Hz, 2H), 7.03 (td, *J* = 8.8, 2.7 Hz, 1H), 2.50 (s, 3H), 2.33 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 159.1 (d, *J* = 240.0 Hz), 137.1, 136.9, 134.0, 133.3, 131.7 (d, *J* = 2.0 Hz), 131.3, 131.0 (d, *J* = 8.0 Hz), 129.9, 129.8, 129.5, 127.4, 125.7, 125.4 (d, *J* = 8.0 Hz), 122.8 (d, *J* = 4.0 Hz), 122.4, 117.2, 114.7 (d, *J* = 24.0 Hz),

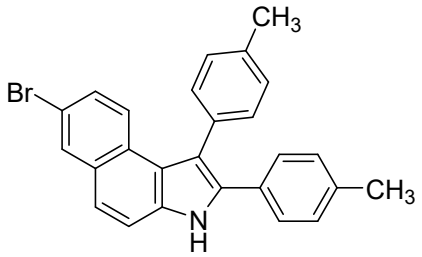
113.7, 112.2 (d, J = 20.0 Hz), 21.6, 21.3. **HRMS (ESI) m/z**: calcd. for $C_{26}H_{21}FN^+$ $(M+H)^+$ 366.1653, found 366.1657.

7-chloro-1,2-di-*p*-tolyl-3*H*-benzo[*e*]indole (3bd)



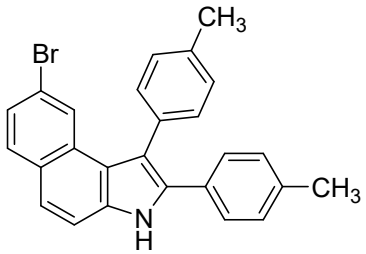
Yield: 49.7 mg, 65% (yellow solid, PE/EA = 95:5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 7.85 (d, J = 2.2 Hz, 1H), 7.71 (d, J = 9.0 Hz, 1H), 7.57−7.50 (m, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 7.8 Hz, 2H), 7.22 (d, J = 8.2 Hz, 3H), 7.10 (d, J = 8.0 Hz, 2H), 2.49 (s, 3H), 2.33 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 137.2, 137.0, 133.8, 133.4, 132.2, 131.2, 131.0, 129.8, 129.5, 128.7, 127.5, 127.4, 127.1, 125.9, 124.9, 122.7, 122.2, 117.4, 113.6, 21.6, 21.3. **HRMS (ESI) m/z**: calcd. for $C_{26}H_{21}ClN^+$ $(M+H)^+$ 382.1357, found 382.1358.

7-bromo-1,2-di-*p*-tolyl-3*H*-benzo[*e*]indole (3be)



Yield: 48.3 mg, 57% (faint-yellow liquid, PE/EA = 95:5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.93 (d, J = 2.1 Hz, 1H), 7.56 (d, J = 9.0 Hz, 1H), 7.46−7.38 (m, 2H), 7.30−7.16 (m, 5H), 7.12 (d, J = 8.1 Hz, 2H), 7.00 (d, J = 8.0 Hz, 2H), 2.40 (s, 3H), 2.24 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 137.1, 137.0, 133.8, 133.4, 132.2, 131.5, 131.2, 130.7, 129.8, 129.7, 129.5, 128.4, 127.4, 127.3, 125.1, 122.6, 122.1, 117.4, 116.7, 113.6, 21.6, 21.3. **HRMS (ESI) m/z**: calcd. for $C_{26}H_{21}BrN^+$ $(M+H)^+$ 426.0852, found 426.0855.

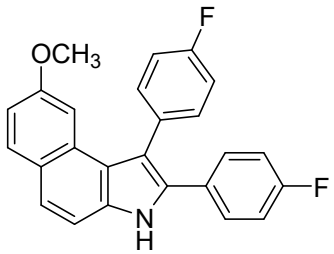
8-bromo-1,2-di-*p*-tolyl-3*H*-benzo[*e*]indole (3bf)



Yield: 44.5 mg, 52% (brown liquid, PE/EA = 98:2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 7.91 (d, J = 1.9 Hz, 1H), 7.73 (d, J = 8.6 Hz, 1H), 7.57−7.51 (m, 2H), 7.41 (dd, J = 8.6, 2.0 Hz, 1H), 7.38 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 7.8 Hz, 2H), 7.23 (d, J = 8.1 Hz, 2H), 7.10

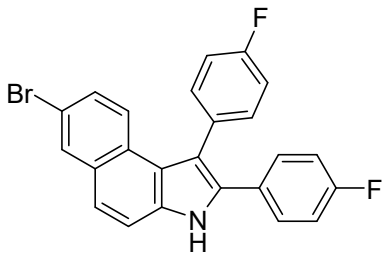
(d, J = 8.0 Hz, 2H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 137.2, 137.1, 133.4, 133.2, 132.6, 131.1, 130.3, 130.1, 129.8, 129.5, 128.5, 127.4, 126.4, 125.9, 123.3, 121.4, 119.5, 117.5, 112.9, 21.6, 21.3. **HRMS (ESI) m/z**: calcd. for $C_{26}H_{21}BrN^+$ $(M+H)^+$ 426.0852, found 426.0855.

1,2-bis(4-fluorophenyl)-8-methoxy-3*H*-benzo[*e*]indole (3bg)



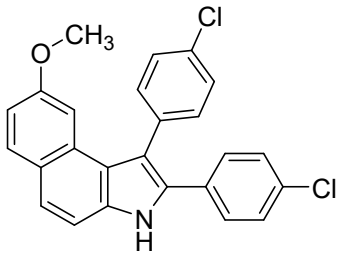
Yield: 59.0 mg, 61% (yellow solid, PE/EA = 95:5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.57 (d, J = 9.1 Hz, 1H), 7.36 (d, J = 8.7 Hz, 1H), 7.30−7.24 (m, 2H), 7.17 (dt, J = 8.8, 2.0 Hz, 1H), 7.08−7.03 (m, 2H), 6.97 (t, J = 8.5 Hz, 2H), 6.87−6.75 (m, 4H), 3.30 (d, J = 1.7 Hz, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 163.4 (d, J = 31.0 Hz), 161.0 (d, J = 32.0 Hz), 157.5, 133.4 (d, J = 8.0 Hz), 133.1 (d, J = 3.0 Hz), 132.8, 131.7, 130.4, 129.8, 129.2 (d, J = 8.0 Hz), 128.8 (d, J = 4.0 Hz), 124.9, 124.0, 121.5, 116.5, 115.9 (d, J = 4.0 Hz), 115.7 (d, J = 4.0 Hz), 115.1, 110.1, 103.0, 54.8. **HRMS (ESI) m/z**: calcd. for $C_{25}H_{18}F_2NO^+$ $(M+H)^+$ 386.1351, found 386.1354.

7-bromo-1,2-bis(4-fluorophenyl)-3*H*-benzo[*e*]indole (3bh)



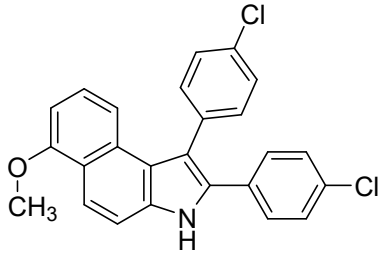
Yield: 77.7 mg, 84% (white solid, PE/EA = 95:5). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.17 (s, 1H), 8.14 (d, J = 2.1 Hz, 1H), 7.72 (d, J = 8.8 Hz, 1H), 7.60 (d, J = 8.9 Hz, 1H), 7.47−7.30 (m, 8H), 7.17 (t, J = 8.9 Hz, 2H). **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6) δ 162.7 (d, J = 35.0 Hz), 160.2 (d, J = 36.0 Hz), 133.1 (d, J = 3.0 Hz), 133.0 (d, J = 8.0 Hz), 132.6 (d, J = 10.0 Hz), 131.1, 130.6, 129.5 (d, J = 8.0 Hz), 128.7 (d, J = 3.0 Hz), 127.8, 126.7, 124.1, 122.1, 120.7, 116.1 (d, J = 21.0 Hz), 115.6, 115.6, 115.4, 115.2, 114.7. **HRMS (ESI) m/z**: calcd. for $C_{24}H_{15}BrF_2N^+$ $(M+H)^+$ 434.0350, found 434.0351.

1,2-bis(4-chlorophenyl)-8-methoxy-3*H*-benzo[*e*]indole (3bi)



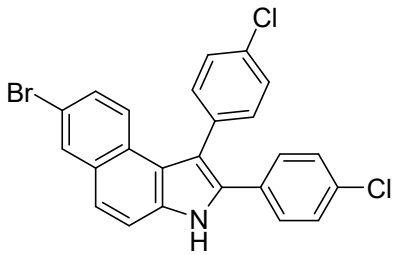
Yield: 41.9 mg, 50% (yellow solid, PE/EA = 95:5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.77 (d, *J* = 9.3 Hz, 1H), 7.58 (d, *J* = 8.6 Hz, 1H), 7.50−7.36 (m, 5H), 7.24 (d, *J* = 9.1 Hz, 4H), 7.06−6.95 (m, 2H), 3.51 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 157.6, 135.6, 133.5, 133.2, 133.1, 131.3, 131.0, 130.4, 129.7, 129.1, 129.1, 128.7, 124.9, 124.4, 121.4, 116.8, 115.2, 110.1, 103.1, 54.8. **HRMS (ESI) m/z**: calcd. for $C_{25}H_{18}Cl_2NO^+$ $(M+H)^+$ 418.0760, found 418.0762.

1,2-bis(4-chlorophenyl)-6-methoxy-3*H*-benzo[*e*]indole (3bj)



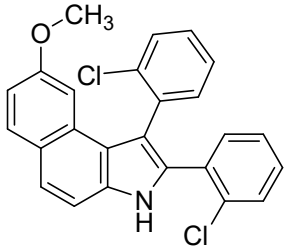
Yield: 46.3 mg, 54% (faint-yellow solid, PE/EA = 95:5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 3.4 Hz, 1H), 8.16 (d, *J* = 9.1 Hz, 1H), 7.53−7.47 (m, 1H), 7.47−7.42 (m, 2H), 7.41−7.37 (m, 2H), 7.32−7.28 (m, 1H), 7.26−7.14 (m, 5H), 6.78 (dd, *J* = 7.7, 1.0 Hz, 1H), 4.01 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 156.2, 135.5, 133.4, 133.2, 133.1, 132.9, 131.8, 131.0, 129.7, 129.2, 129.0, 128.8, 126.0, 121.7, 121.3, 118.1, 117.0, 115.9, 111.5, 102.8, 55.7. **HRMS (ESI) m/z**: calcd. for $C_{25}H_{18}Cl_2NO^+$ $(M+H)^+$ 418.0760, found 418.0762.

7-bromo-1,2-bis(4-chlorophenyl)-3*H*-benzo[*e*]indole (3bk)



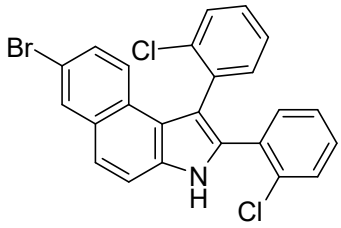
Yield: 57.2 mg, 62% (faint-brown solid, PE/EA = 95:5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 7.90 (d, *J* = 2.1 Hz, 1H), 7.46−7.39 (m, 3H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.28−7.20 (m, 3H), 7.15 (d, *J* = 8.2 Hz, 2H), 7.07 (d, *J* = 8.8 Hz, 2H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 135.0, 133.7, 133.6, 132.7, 132.6, 132.4, 131.6, 131.0, 130.7, 129.4, 129.1, 128.9, 128.8, 127.1, 124.8, 123.5, 121.7, 117.1, 116.9, 113.6. **HRMS (ESI) m/z**: calcd. for $C_{24}H_{15}BrCl_2N^+$ $(M+H)^+$465.9759, found 465.9755.

1,2-bis(2-chlorophenyl)-8-methoxy-3*H*-benzo[*e*]indole (3bl)



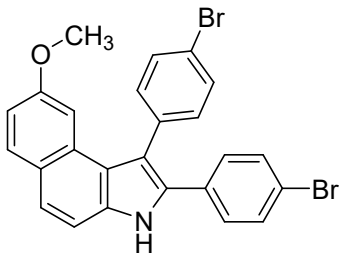
Yield: 53.5mg, 64% (faint yellow solid, PE/EA = 95:5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 7.66 (d, *J* = 8.8 Hz, 1H), 7.48 (d, *J* = 8.8 Hz, 1H), 7.42 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.35−7.28 (m, 3H), 7.22−7.07 (m, 4H), 6.99 (td, *J* = 7.6, 1.3 Hz, 1H), 6.88 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.81 (d, *J* = 2.6 Hz, 1H), 3.36 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 157.8, 136.5, 136.0, 133.9, 133.4, 132.8, 132.7, 131.2, 130.5, 130.1, 130.1, 129.9, 129.5, 129.4, 129.0, 126.9, 126.8, 124.7, 124.1, 120.6, 116.3, 115.1, 110.3, 102.5, 54.8. **HRMS (ESI) m/z**: calcd. for $C_{25}H_{18}Cl_2NO^+$ $(M+H)^+$ 418.0760, found 418.0762.

7-bromo-1,2-bis(2-chlorophenyl)-3*H*-benzo[*e*]indole (3bm)



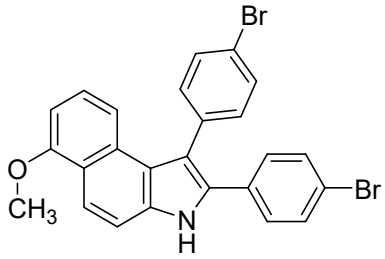
Yield: 57.9 mg, 62% (yellow liquid, PE/EA = 95:5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.69 (s, 1H), 7.92 (d, *J* = 2.1 Hz, 1H), 7.47−7.39 (m, 3H), 7.35−7.29 (m, 2H), 7.27−7.19 (m, 3H), 7.15−7.07 (m, 3H), 6.98 (t, *J* = 7.5 Hz, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 136.1, 135.3, 133.4, 133.4, 132.8, 132.2, 131.5, 131.3, 130.9, 130.7, 130.1, 129.7, 129.6, 129.2, 128.9, 127.3, 127.1, 126.8, 124.6, 123.2, 120.9, 117.0, 116.4, 113.9. **HRMS (ESI) m/z**: calcd. for $C_{24}H_{15}BrCl_2N^+$ $(M+H)^+$ 465.9759, found 465.9755.

1,2-bis(4-bromophenyl)-8-methoxy-3*H*-benzo[*e*]indole (3bn)



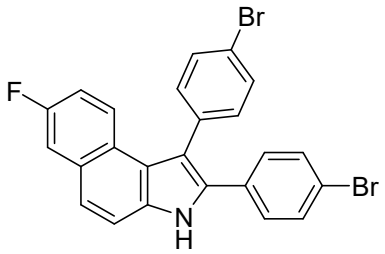
Yield: 84.4 mg, 84% (brown solid, PE/EA = 95:5). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.04 (s, 1H), 7.79 (d, *J* = 8.9 Hz, 1H), 7.72−7.66 (m, 2H), 7.58−7.49 (m, 4H), 7.38 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.6 Hz, 2H), 6.95 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.85 (d, *J* = 2.6 Hz, 1H), 3.44 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6) δ 157.0, 136.7, 133.7, 133.5, 132.1, 131.7, 131.7, 131.1, 130.5, 129.4, 129.4, 124.4, 123.6, 120.9, 120.6, 120.4, 115.8, 113.9, 111.2, 103.0, 54.3. **HRMS (ESI) m/z**: calcd. for $C_{25}H_{18}Br_2NO^+$ $(M+H)^+$ 505.9750, found 505.9753.

1,2-bis(4-bromophenyl)-6-methoxy-3*H*-benzo[*e*]indole (3bo)



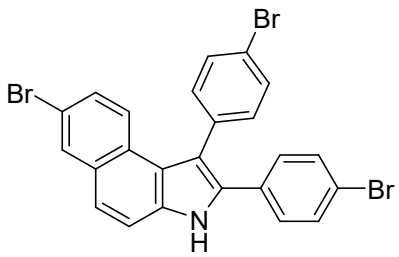
Yield: 46.6 mg, 46% (faint-yellow solid, PE/EA = 95:5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 8.07 (d, *J* = 9.1 Hz, 1H), 7.51 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 9.1 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.27−7.17 (m, 3H), 7.13 (t, *J* = 8.1 Hz, 1H), 7.01 (d, *J* = 8.2 Hz, 2H), 6.89 (d, *J* = 7.8 Hz, 1H), 3.92 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 156.2, 136.0, 133.2, 133.2, 132.2, 132.0, 131.8, 131.4, 129.7, 129.1, 126.1, 121.6, 121.4, 121.3, 118.2, 117.1, 115.9, 111.5, 102.8, 55.7. **HRMS (ESI) m/z**: calcd. for $C_{25}H_{18}Br_2NO^+$ $(M+H)^+$ 505.9750, found 505.9753.

1,2-bis(4-bromophenyl)-7-fluoro-3*H*-benzo[*e*]indole (3bp)



Yield: 78.4 mg, 80% (yellow liquid, PE/EA = 95:5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 7.68 (dd, *J* = 9.2, 5.6 Hz, 1H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.57 (s, 2H), 7.51 (dd, *J* = 10.0, 2.7 Hz, 1H), 7.42 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 8.3 Hz, 2H), 7.13 (d, *J* = 8.5 Hz, 2H), 7.09−7.02 (m, 1H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 159.3 (d, *J* = 242.0 Hz), 135.7, 133.1, 132.4, 132.2, 132.11 (d, *J* = 2.0 Hz), 132.06 , 131.2, 131.1, 129.1, 125.4 (d, *J* = 1.0 Hz), 125.1 (d, *J* = 8.0 Hz), 123.7 (d, *J* = 4.0 Hz), 121.9, 121.8, 121.7, 116.7, 115.2 (d, *J* = 23.0 Hz), 113.7, 112.5 (d, *J* = 20.0 Hz). **HRMS (ESI) m/z**: calcd. for $C_{24}H_{15}Br_2FN^+$ $(M+H)^+$ 493.9550, found 493.9551.

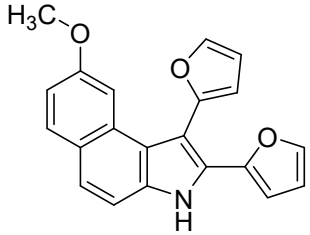
7-bromo-1,2-bis(4-bromophenyl)-3*H*-benzo[*e*]indole (3bq)



Yield: 95.4 mg, 86% (faint-yellow liquid, PE/EA = 95:5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.01 (d, *J* = 2.1 Hz, 1H), 7.62−7.51 (m, 5H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.34 (dd, *J*

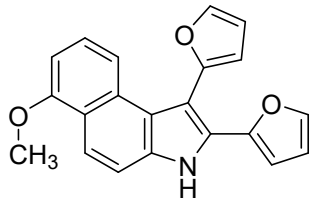
= 8.9, 2.1 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.6 Hz, 2H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 135.5, 133.0, 132.6, 132.4, 132.3, 132.0, 131.6, 131.0, 130.9, 129.1, 128.8, 127.0, 124.7, 123.5, 121.9, 121.7, 121.6, 117.1, 116.8, 113.6. **HRMS (ESI) m/z**: calcd. for $C_{24}H_{15}Br_3N^+$ $(M+H)^+$ 553.8749, found 553.8746.

1,2-di(furan-2-yl)-8-methoxy-3*H*-benzo[*e*]indole (3br)



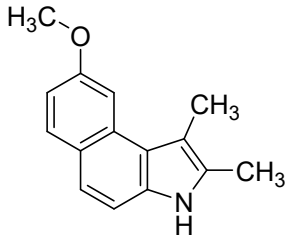
Yield: 34.8 mg, 53% (yellow solid, PE/EA = 95:5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 7.80−7.71 (m, 2H), 7.56 (d, *J* = 8.7 Hz, 1H), 7.43 (d, *J* = 1.7 Hz, 1H), 7.38 (d, *J* = 8.7 Hz, 1H), 7.09 (d, *J* = 2.6 Hz, 1H), 7.03 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.69 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.65 (d, *J* = 3.2 Hz, 1H), 6.42 (dd, *J* = 3.5, 1.8 Hz, 1H), 6.20 (d, *J* = 3.4 Hz, 1H), 3.70 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 157.9, 148.7, 146.6, 142.7, 141.5, 132.5, 130.2, 129.3, 127.3, 125.0, 124.4, 122.5, 115.5, 112.2, 111.6, 110.9, 110.0, 106.8, 104.5, 102.7, 55.1. **HRMS (ESI) m/z**: calcd. for $C_{21}H_{16}NO_3^+$ $(M+H)^+$ 330.1125, found 330.1127.

1,2-di(furan-2-yl)-6-methoxy-3*H*-benzo[*e*]indole (3bs)



Yield: 30.9 mg, 47% (yellow liquid, PE/EA = 95:5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.01 (s, 1H), 8.14 (d, *J* = 9.0 Hz, 1H), 7.74 (dd, *J* = 1.9, 0.9 Hz, 1H), 7.50 (d, *J* = 9.1 Hz, 1H), 7.45−7.40 (m, 1H), 7.35−7.30 (m, 2H), 6.80 (dd, *J* = 5.4, 3.3 Hz, 1H), 6.69 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.64−6.60 (m, 1H), 6.41 (dd, *J* = 3.4, 1.8 Hz, 1H), 6.13 (d, *J* = 3.4 Hz, 1H), 4.01 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 156.2, 148.5, 146.5, 142.6, 141.5, 132.6, 129.3, 127.8, 126.3, 122.9, 121.4, 118.2, 115.7, 112.2, 111.5, 111.5, 110.8, 106.9, 104.8, 102.9, 55.6. **HRMS (ESI) m/z**: calcd. for $C_{21}H_{16}NO_3^+$ $(M+H)^+$ 330.1125, found 330.1127.

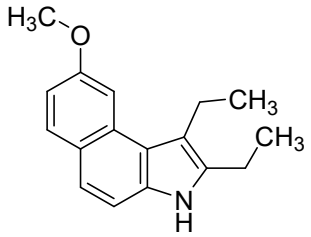
8-methoxy-1,2-dimethyl-3*H*-benzo[*e*]indole (3bt)



Yield: 18.5 mg, 41% (white solid, PE/EA = 95:5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.92 (d, *J* = 2.6 Hz, 1H), 7.82 (d, *J* = 8.9 Hz, 1H), 7.45 (d, *J* = 8.6 Hz, 1H), 7.26 (d, *J* = 8.5 Hz, 1H), 7.08 (dd, *J* = 8.9, 2.6 Hz, 1H), 3.99 (s, 3H), 2.64 (s, 3H), 2.41 (s, 3H). **^{13}C{^{1}H}**

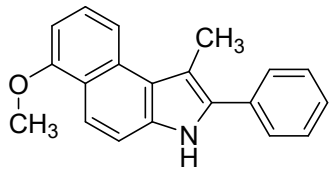
NMR (101 MHz, $CDCl_3$) δ 157.6, 131.9, 130.3, 130.2, 128.7, 124.8, 121.9, 121.4, 113.4, 110.2, 109.5, 103.8, 55.4, 12.4, 11.6. **HRMS (ESI) m/z**: calcd. for $C_{15}H_{16}NO^+$ $(M+H)^+$ 226.1226, found 226.1228.

1,2-diethyl-8-methoxy-3*H*-benzo[*e*]indole (3bu)



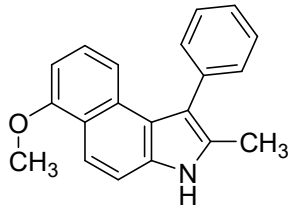
Yield: 18.4 mg, 36% (yellow liquid, PE/EA = 95:5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.84−7.79 (m, 2H), 7.47 (d, *J* = 8.7 Hz, 1H), 7.30 (d, *J* = 8.7 Hz, 1H), 7.08 (dd, *J* = 8.9, 2.5 Hz, 1H), 3.99 (s, 3H), 3.08 (q, *J* = 7.5 Hz, 2H), 2.83 (q, *J* = 7.6 Hz, 2H), 1.41 (t, *J* = 7.5 Hz, 3H), 1.33 (t, *J* = 7.6 Hz, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 157.7, 134.4, 132.2, 130.3, 129.9, 124.8, 122.0, 120.5, 115.7, 113.6, 110.3, 103.7, 55.3, 19.4, 19.3, 15.9, 15.0. **HRMS (ESI) m/z**: calcd. for $C_{17}H_{20}NO^+$ $(M+H)^+$ 254.1539, found 254.1535.

6-methoxy-1-methyl-2-phenyl-3*H*-benzo[*e*]indole (3bv)



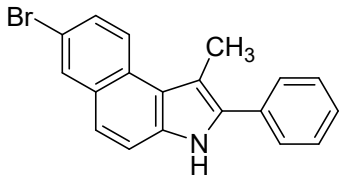
Yield: 27.6 mg, 48% (faint-yellow solid, PE/EA = 9:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 8.21 (d, *J* = 8.4 Hz, 1H), 8.12 (d, *J* = 9.0 Hz, 1H), 7.62−7.55 (m, 2H), 7.55−7.47 (m, 4H), 7.44−7.35 (m, 1H), 6.86 (d, *J* = 7.6 Hz, 1H), 4.05 (s, 3H), 2.83 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 156.3, 133.4, 133.2, 130.9, 128.9, 128.8, 128.7, 127.4, 125.9, 122.4, 121.1, 117.1, 116.1, 111.7, 111.3, 102.3, 55.7, 13.4. **HRMS (ESI) m/z**: calcd. for $C_{20}H_{18}NO^+$ $(M+H)^+$ 288.1383, found 288.1381.

6-methoxy-2-methyl-1-phenyl-3*H*-benzo[*e*]indole (3bv')



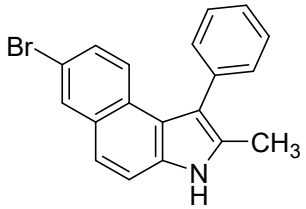
Yield: 27.8 mg, 48% (white solid, PE/EA = 9:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 8.07 (d, *J* = 9.0 Hz, 1H), 7.54−7.40 (m, 7H), 7.17 (t, *J* = 8.1 Hz, 1H), 6.74 (d, *J* = 7.8 Hz, 1H), 4.01 (s, 3H), 2.33 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 156.1, 137.3, 132.0, 131.3, 130.5, 129.4, 128.4, 126.8, 125.3, 121.1, 121.0, 117.4, 116.2, 116.0, 111.4, 102.1, 55.6, 12.1. **HRMS (ESI) m/z**: calcd. for $C_{20}H_{18}NO^+$ $(M+H)^+$ 288.1383, found 288.1381.

7-bromo-1-methyl-2-phenyl-3*H*-benzo[*e*]indole (3bw)



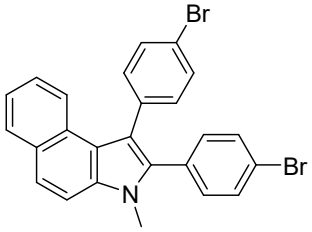
Yield: 24.3 mg, 36% (faint-yellow liquid, PE/EA = 95:5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 8.9 Hz, 1H), 8.38 (s, 1H), 8.07 (d, *J* = 2.1 Hz, 1H), 7.63 (dd, *J* = 8.9, 2.1 Hz, 1H), 7.59−7.48 (m, 6H), 7.43−7.37 (m, 1H), 2.79 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 134.0, 133.0, 132.6, 131.4, 130.9, 129.0, 128.7, 128.2, 127.7, 125.1, 122.5, 122.4, 116.5, 113.8, 111.1, 13.3. **HRMS (ESI) m/z**: calcd. for $C_{19}H_{15}BrN^+$ $(M+H)^+$ 336.0382, found 336.0384.

7-bromo-2-methyl-1-phenyl-3*H*-benzo[*e*]indole (3bw')



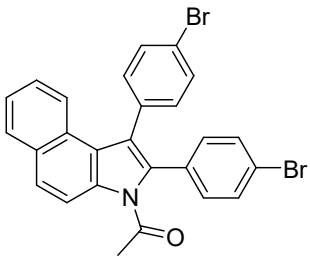
Yield: 24.9 mg, 37% (faint-yellow liquid, PE/EA = 95:5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 8.01 (d, *J* = 2.2 Hz, 1H), 7.70 (d, *J* = 9.0 Hz, 1H), 7.53−7.42 (m, 7H), 7.29 (dd, *J* = 9.0, 2.1 Hz, 1H), 2.36 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 136.8, 131.5, 131.3, 131.1, 131.1, 130.6, 128.7, 128.2, 127.1, 126.8, 125.0, 121.5, 121.1, 117.3, 116.5, 113.4, 12.1. **HRMS (ESI) m/z**: calcd. for $C_{19}H_{15}BrN^+$ $(M+H)^+$ 336.0382, found 336.0384.

1,2-bis(4-bromophenyl)-3-methyl-3*H*-benzo[*e*]indole (4a)



Yield: 93.3 mg, 95% (white solid, PE/EA = 95:5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 8.3 Hz, 1H), 7.57 (d, J = 8.9 Hz, 1H), 7.44 (d, *J* = 8.8 Hz, 1H), 7.35 (dd, *J* = 10.0, 8.3 Hz, 4H), 7.28−7.22 (m, 1H), 7.20−7.15 (m, 1H), 7.11 (d, *J* = 8.3 Hz, 2H), 6.95 (d, *J* = 8.5 Hz, 2H), 3.63 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 13C NMR (101 MHz, CDCl3) δ 135.8, 135.6, 133.8, 133.2, 132.7, 131.62, 131.58, 130.4, 130.0, 129.0, 128.5, 125.7, 123.9, 123.4, 123.2, 122.3, 121.0, 120.2, 117.1, 111.2, 31.5. **HRMS (ESI) m/z**: calcd. for $C_{25}H_{18}Br_2N^+$ $(M+H)^+$ 489.9801, found 489.9805.

1-(1,2-bis(4-bromophenyl)-3*H*-benzo[*e*]indol-3-yl)ethan-1-one (4b)



Yield: 74.8 mg, 72% (white solid, PE/EA = 95:5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 9.1 Hz, 1H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 9.2 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.48−7.40 (m, 3H), 7.32−7.26 (m, 1H), 7.18 (d, *J* = 8.3 Hz, 2H), 7.12 (d, *J* = 8.3 Hz, 2H), 2.11 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 171.8, 134.2, 133.7, 133.5, 132.7, 132.0, 131.9, 131.9, 131.6, 131.3, 128.8, 127.4, 126.7, 126.1, 124.7, 124.1, 123.5, 123.0, 122.5, 122.0, 115.6, 28.5. **HRMS (ESI) m/z**: calcd. for $C_{26}H_{18}Br_2NO^+$ $(M+H)^+$ 517.9750, found 517.9752.

4. The X-ray single-crystal diffraction analysis of product 3bv

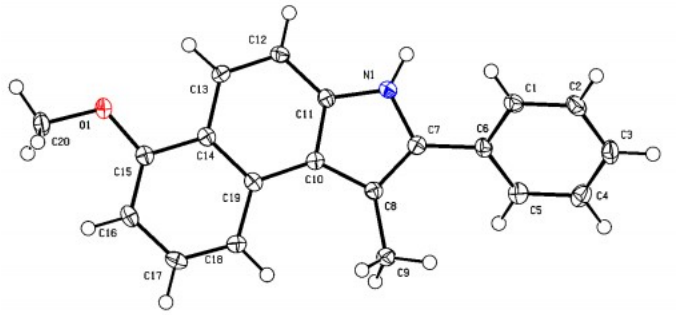


Table 1 Crystal data and structure refinement for 3bv.

Empirical formula	$C_{20}H_{17}NO$
Formula weight	287.35
Temperature/K	100.00
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	7.9657(4)
b/Å	11.4669(5)
c/Å	15.8658(7)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1449.21(12)
Z	4
ρ_{calc}g/cm3	1.317
μ/mm^{-1}	0.081
F(000)	608.0
Crystal size/mm^3	0.15 × 0.13 × 0.12

Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.136 to 52.94
Index ranges	$-9 \le h \le 9$, $-14 \le k \le 14$, $-19 \le l \le 19$
Reflections collected	13384
Independent reflections	2990 [R_{int} = 0.0513, R_{sigma} = 0.0444]
Data/restraints/parameters	2990/0/202
Goodness-of-fit on F^2	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.0335, wR_2 = 0.0834
Final R indexes [all data]	R_1 = 0.0391, wR_2 = 0.0866
Largest diff. peak/hole / e Å^{-3}	0.18/-0.20
Flack parameter	1.6(18)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 3bv. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U(eq)
C1	10548(3)	-128.8(18)	6868.3(12)	18.7(4)
C2	11305(3)	-1148.1(18)	7144.4(13)	21.7(5)
C3	10471(3)	-2206.5(18)	7070.8(13)	23.2(5)
C4	8880(3)	-2242.6(19)	6712.3(13)	23.1(5)
C5	8117(3)	-1218.7(17)	6442.4(13)	20.3(4)
C6	8928(2)	-147.4(17)	6522.2(12)	16.2(4)
C7	8127(3)	954.3(16)	6268.7(12)	16.2(4)
C8	6536(2)	1380.1(16)	6427.2(12)	15.0(4)
C9	5173(3)	757.8(18)	6901.0(13)	19.9(4)
C10	6507(2)	2556.9(16)	6104.9(12)	14.1(4)
C11	8097(3)	2778.2(16)	5758.8(12)	15.1(4)
C12	8539(2)	3842.1(17)	5376.4(13)	17.1(4)
C13	7377(2)	4719.0(17)	5387.4(12)	17.0(4)
C14	5749(2)	4561.3(17)	5748.9(12)	15.1(4)
C15	4565(3)	5493.7(17)	5749.4(12)	16.5(4)
C16	2956(3)	5333.5(17)	6038.0(13)	19.0(4)
C17	2486(2)	4236.2(17)	6356.2(13)	19.3(4)
C18	3597(2)	3326.9(17)	6391.4(12)	17.1(4)
C19	5261(2)	3462.0(16)	6093.5(12)	14.9(4)
C20	4102(3)	7516.8(18)	5498.6(14)	23.5(5)
N1	9064(2)	1807.0(14)	5875.3(10)	16.9(4)
O1	5184.4(18)	6528.0(12)	5448.0(9)	21.2(3)

Table 3 Anisotropic Displacement Parameters (Å^2×10^3) for 3bv. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U11	U22	U33	U23	U13	U12
C1	16.6(10)	21.2(10)	18.4(10)	1.2(8)	3.7(8)	1.4(8)
C2	17.2(10)	27.7(11)	20.3(10)	3.4(9)	4.1(8)	6.5(9)
C3	28.7(11)	19.7(10)	21.2(10)	4.4(8)	7.6(9)	9.6(9)
C4	31.2(12)	16.9(10)	21.2(11)	-0.4(8)	4.7(9)	-0.5(9)
C5	22.2(10)	20.1(9)	18.5(10)	-1.5(8)	-0.4(9)	1.0(9)
C6	18.1(10)	17.1(9)	13.2(9)	0.1(8)	2.9(8)	3.8(8)
C7	16.9(9)	16.5(9)	15.3(9)	-0.6(7)	-1.8(8)	-0.8(8)
C8	13.9(9)	17.2(9)	13.9(9)	0.5(7)	-2.8(7)	-0.8(7)
C9	15.7(9)	20.6(10)	23.4(10)	5.6(8)	-0.6(8)	-0.2(9)
C10	15.1(9)	15.9(9)	11.4(8)	-0.5(7)	-1.3(7)	-0.6(8)
C11	15.0(9)	15.9(9)	14.6(9)	-0.8(7)	-1.1(8)	1.2(8)
C12	13.8(9)	19.4(10)	18.1(10)	1.2(8)	3.0(8)	0.2(8)
C13	16.9(9)	15.3(9)	18.9(10)	1.4(8)	0.6(8)	-2.2(8)
C14	15.0(9)	17.0(9)	13.4(9)	-1.5(7)	-2.5(7)	0.5(8)
C15	16.9(9)	17.1(9)	15.4(9)	-1.6(8)	-2.4(8)	1.0(8)
C16	16.1(9)	21.0(10)	19.9(10)	-1.2(8)	-3.1(8)	5.2(8)
C17	12.6(8)	26.6(10)	18.6(10)	-1.0(8)	-0.4(8)	-0.9(8)
C18	16.1(9)	18.9(9)	16.3(9)	0.5(8)	0.5(8)	-1.6(8)
C19	14.9(9)	17.8(9)	12.0(9)	-1.6(7)	-1.7(7)	1.2(8)
C20	21.2(10)	16.8(10)	32.7(12)	-1.1(9)	-2.8(10)	6.2(9)
N1	13.9(8)	17.8(8)	19.0(9)	1.8(7)	2.7(7)	1.6(7)
O1	19.0(7)	15.3(7)	29.4(8)	2.6(6)	0.9(6)	3.6(6)

Table 4 Bond Lengths for 3bv.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.386(3)	C11	C12	1.407(3)
C1	C6	1.403(3)	C11	N1	1.367(2)
C2	C3	1.388(3)	C12	C13	1.367(3)
C3	C4	1.390(3)	C13	C14	1.429(3)
C4	C5	1.389(3)	C14	C15	1.426(3)
C5	C6	1.393(3)	C14	C19	1.428(3)
C6	C7	1.471(3)	C15	C16	1.373(3)
C7	C8	1.381(3)	C15	O1	1.371(2)
C7	N1	1.379(2)	C16	C17	1.407(3)
C8	C9	1.501(3)	C17	C18	1.369(3)
C8	C10	1.443(3)	C18	C19	1.416(3)
C10	C11	1.404(3)	C20	O1	1.426(2)
C10	C19	1.436(3)			

Table 5 Bond Angles for 3bv.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	C1	C6	120.7(2)	N1	C11	C10	107.98(16)
C1	C2	C3	120.16(19)	N1	C11	C12	128.56(18)
C2	C3	C4	119.78(19)	C13	C12	C11	117.55(17)
C5	C4	C3	120.0(2)	C12	C13	C14	121.77(18)
C4	C5	C6	120.97(19)	C15	C14	C13	120.37(17)
C1	C6	C7	119.53(18)	C15	C14	C19	118.79(17)
C5	C6	C1	118.37(18)	C19	C14	C13	120.82(17)
C5	C6	C7	122.10(17)	C16	C15	C14	121.15(18)
C8	C7	C6	130.66(18)	O1	C15	C14	114.23(16)
N1	C7	C6	119.86(17)	O1	C15	C16	124.62(18)
N1	C7	C8	109.16(16)	C15	C16	C17	119.22(18)
C7	C8	C9	125.93(17)	C18	C17	C16	121.57(18)
C7	C8	C10	106.32(17)	C17	C18	C19	120.57(18)
C10	C8	C9	127.59(17)	C14	C19	C10	117.04(16)
C11	C10	C8	107.03(16)	C18	C19	C10	124.30(17)
C11	C10	C19	119.20(16)	C18	C19	C14	118.65(17)
C19	C10	C8	133.75(17)	C11	N1	C7	109.49(16)
C10	C11	C12	123.46(17)	C15	O1	C20	116.78(16)

Table 6 Torsion Angles for 3bv.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C1	C2	C3	C4	0.6(3)	C11	C10	C19	C18	177.31(18)
C1	C6	C7	C8	-132.6(2)	C11	C12	C13	C14	-1.9(3)
C1	C6	C7	N1	40.1(3)	C12	C11	N1	C7	-179.27(19)
C2	C1	C6	C5	-1.7(3)	C12	C13	C14	C15	-179.94(18)
C2	C1	C6	C7	177.33(18)	C12	C13	C14	C19	-1.8(3)
C2	C3	C4	C5	-1.1(3)	C13	C14	C15	C16	175.21(18)
C3	C4	C5	C6	0.2(3)	C13	C14	C15	O1	-5.2(3)
C4	C5	C6	C1	1.1(3)	C13	C14	C19	C10	3.7(3)
C4	C5	C6	C7	-177.85(19)	C13	C14	C19	C18	-175.70(17)
C5	C6	C7	C8	46.4(3)	C14	C15	C16	C17	1.5(3)
C5	C6	C7	N1	-140.87(19)	C14	C15	O1	C20	-174.89(16)
C6	C1	C2	C3	0.9(3)	C15	C14	C19	C10	-178.12(17)
C6	C7	C8	C9	-2.1(3)	C15	C14	C19	C18	2.5(3)
C6	C7	C8	C10	173.74(19)	C15	C16	C17	C18	0.5(3)
C6	C7	N1	C11	-175.36(16)	C16	C15	O1	C20	4.7(3)
C7	C8	C10	C11	0.5(2)	C16	C17	C18	C19	-1.0(3)
C7	C8	C10	C19	-178.2(2)	C17	C18	C19	C10	-179.90(19)

Table 6 Torsion Angles for 3bv.

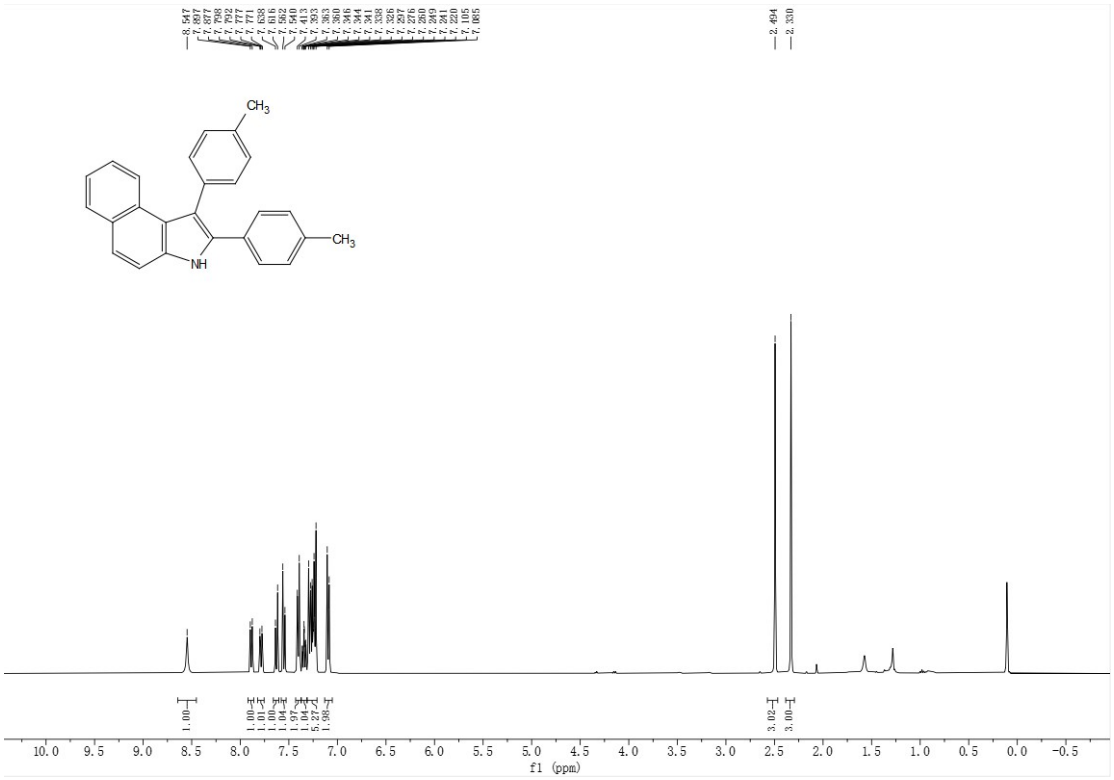
A	B	C	D	Angle/°	A	B	C	D	Angle/°
C8	C7	N1	C11	-1.2(2)	C17	C18	C19	C14	-0.6(3)
C8	C10	C11	C12	179.52(18)	C19	C10	C11	C12	-1.6(3)
C8	C10	C11	N1	-1.2(2)	C19	C10	C11	N1	177.67(16)
C8	C10	C19	C14	176.46(19)	C19	C14	C15	C16	-3.0(3)
C8	C10	C19	C18	-4.2(3)	C19	C14	C15	O1	176.59(17)
C9	C8	C10	C11	176.17(19)	N1	C7	C8	C9	-175.36(18)
C9	C8	C10	C19	-2.5(3)	N1	C7	C8	C10	0.4(2)
C10	C11	C12	C13	3.6(3)	N1	C11	C12	C13	-175.53(19)
C10	C11	N1	C7	1.5(2)	O1	C15	C16	C17	-178.07(18)
C11	C10	C19	C14	-2.0(3)					

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3bv.

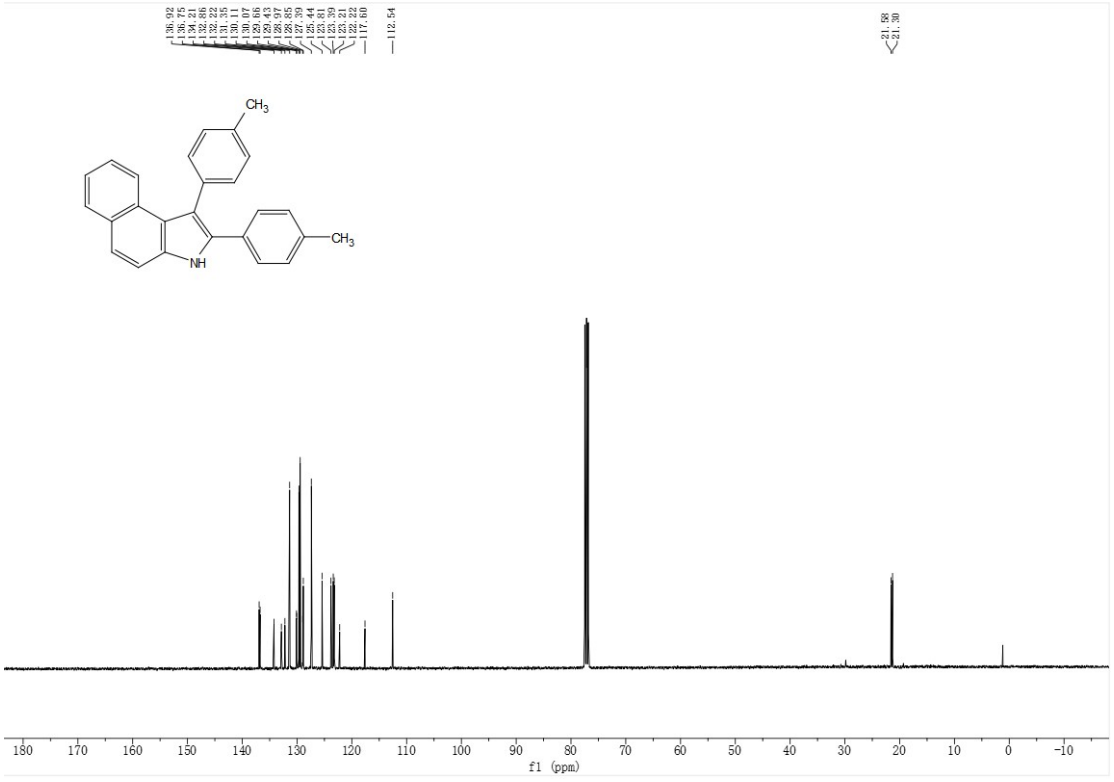
Atom	x	y	z	U(eq)
H1	11133.54	590.28	6913.91	22
H2	12397.01	-1122.41	7384.59	26
H3	10986.83	-2903.71	7264.81	28
H4	8313.42	-2966.95	6651.93	28
H5	7027.87	-1249.44	6199.96	24
H9A	4258.35	560.47	6513.36	30
H9B	4744.5	1264.81	7349.24	30
H9C	5626.59	41.69	7149.7	30
H12	9606.28	3947.02	5120.17	21
H13	7658.15	5452.87	5148.3	20
H16	2170.44	5956.36	6022.97	23
H17	1369.77	4123.37	6551.32	23
H18	3248.99	2599	6617.78	21
H20A	3063.98	7357.36	5188.11	35
H20B	4664.51	8196.22	5252.14	35
H20C	3835.39	7676.18	6090.5	35
H1A	10121.4	1736.66	5722.82	20

5. Copies of NMR spectra

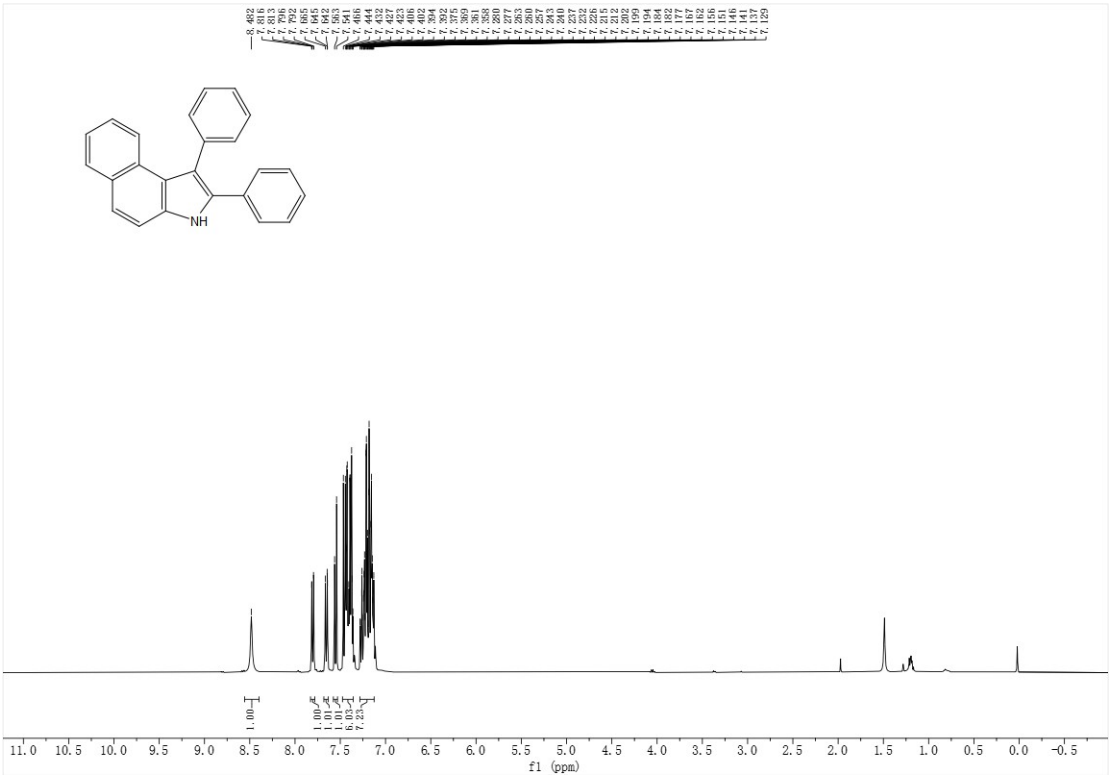
^{1}H NMR spectrum of **3aa** (400 MHz, $CDCl_3$)



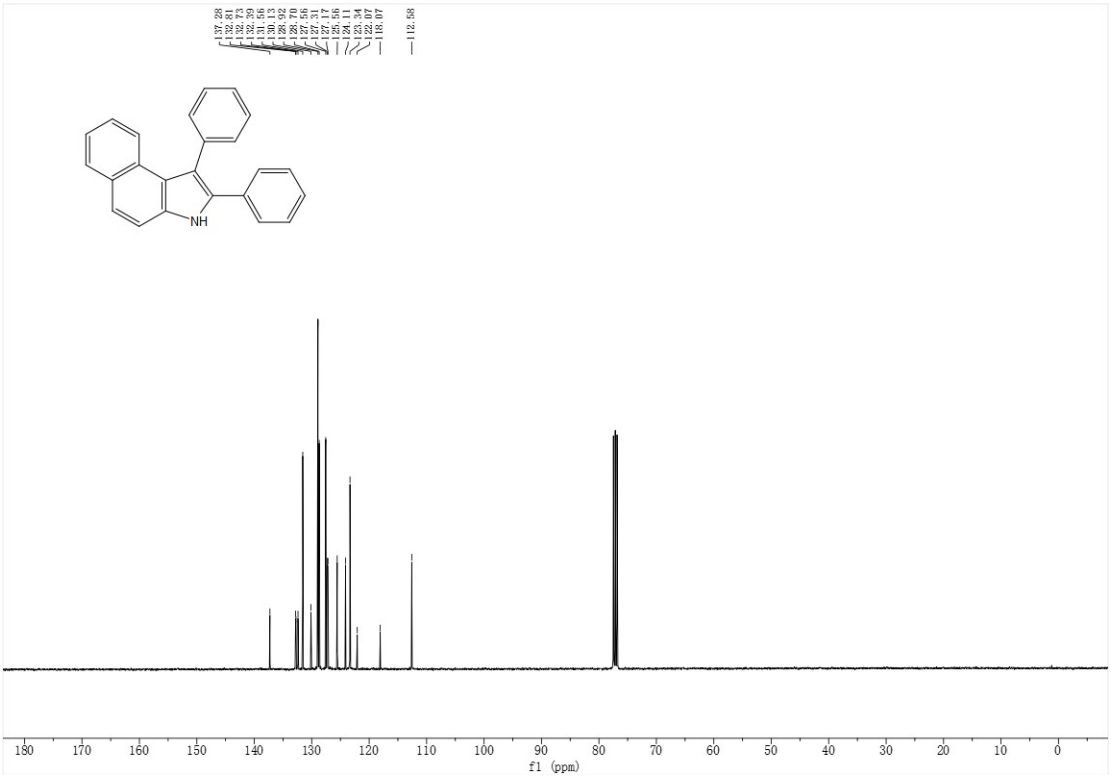
^{13}C NMR spectrum of **3aa** (101 MHz, $CDCl_3$)



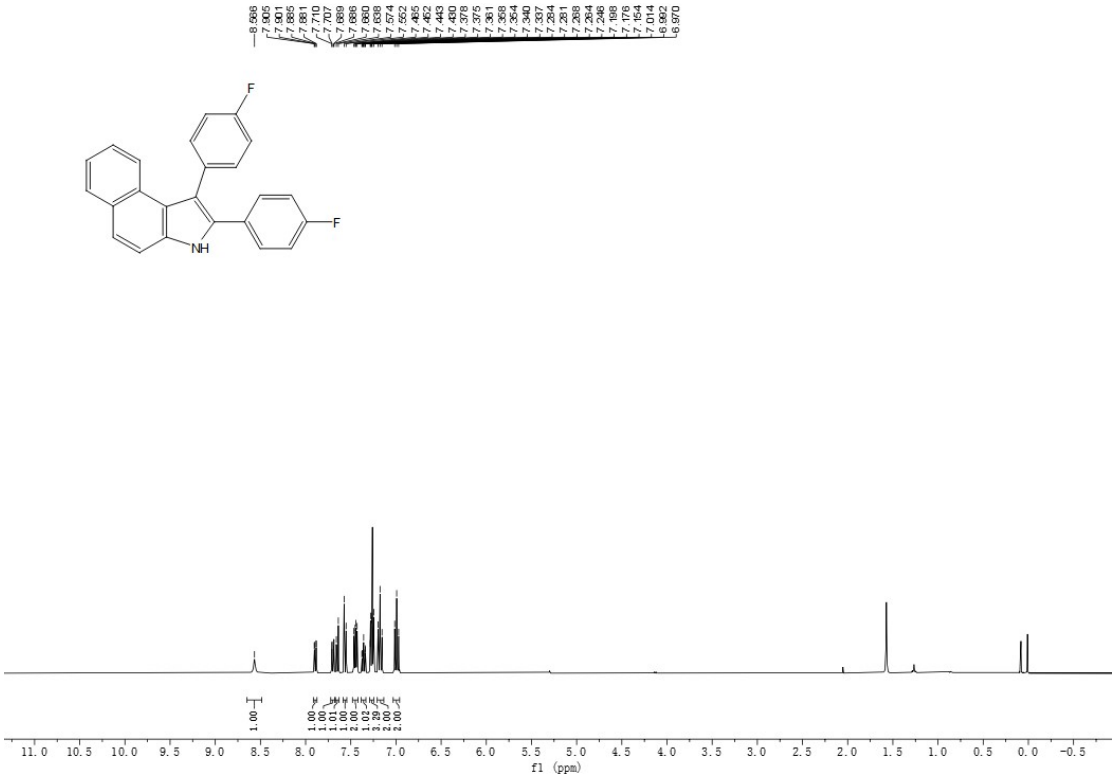
^{1}H NMR spectrum of **3ab** (400 MHz, $CDCl_3$)



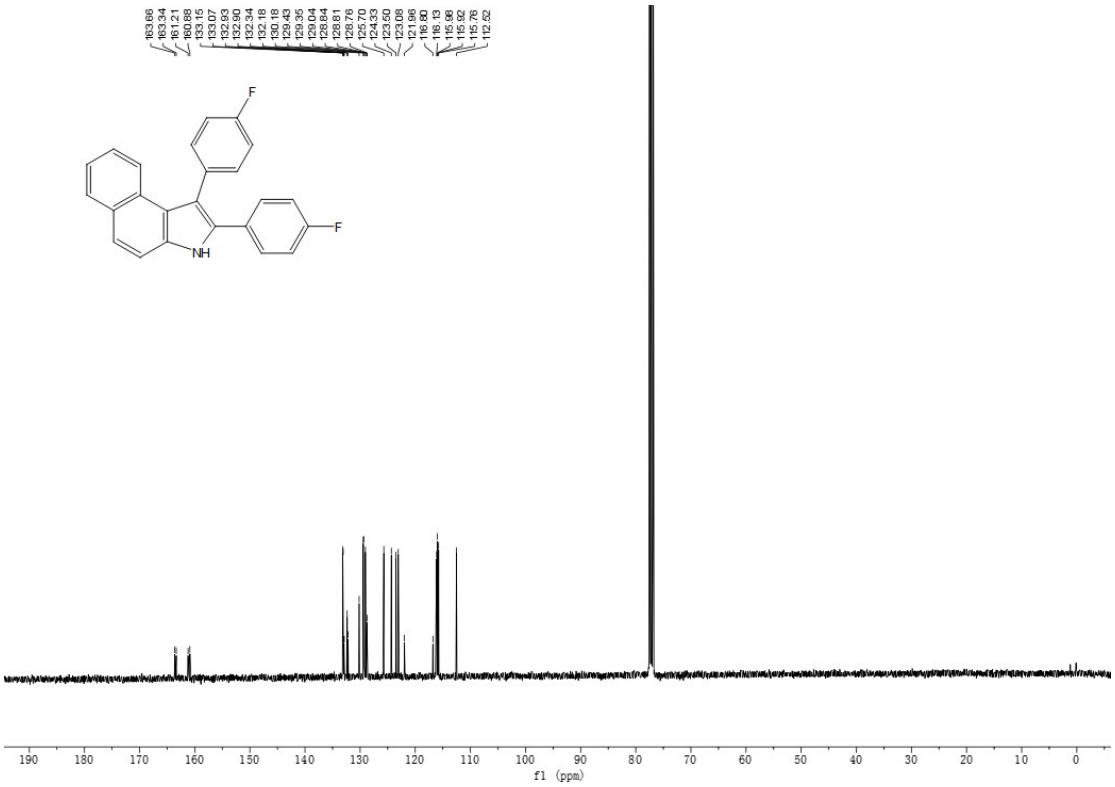
^{13}C NMR spectrum of **3ab** (101 MHz, $CDCl_3$)



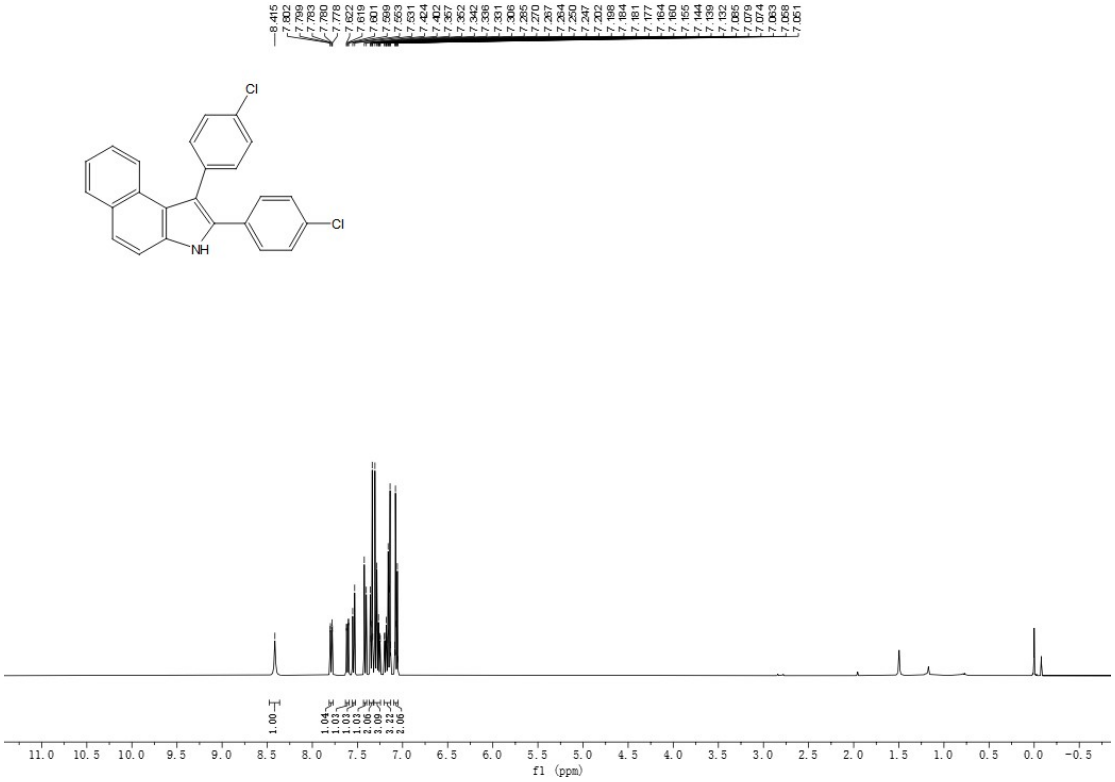
^{1}H NMR spectrum of **3ac** (400 MHz, $CDCl_3$)



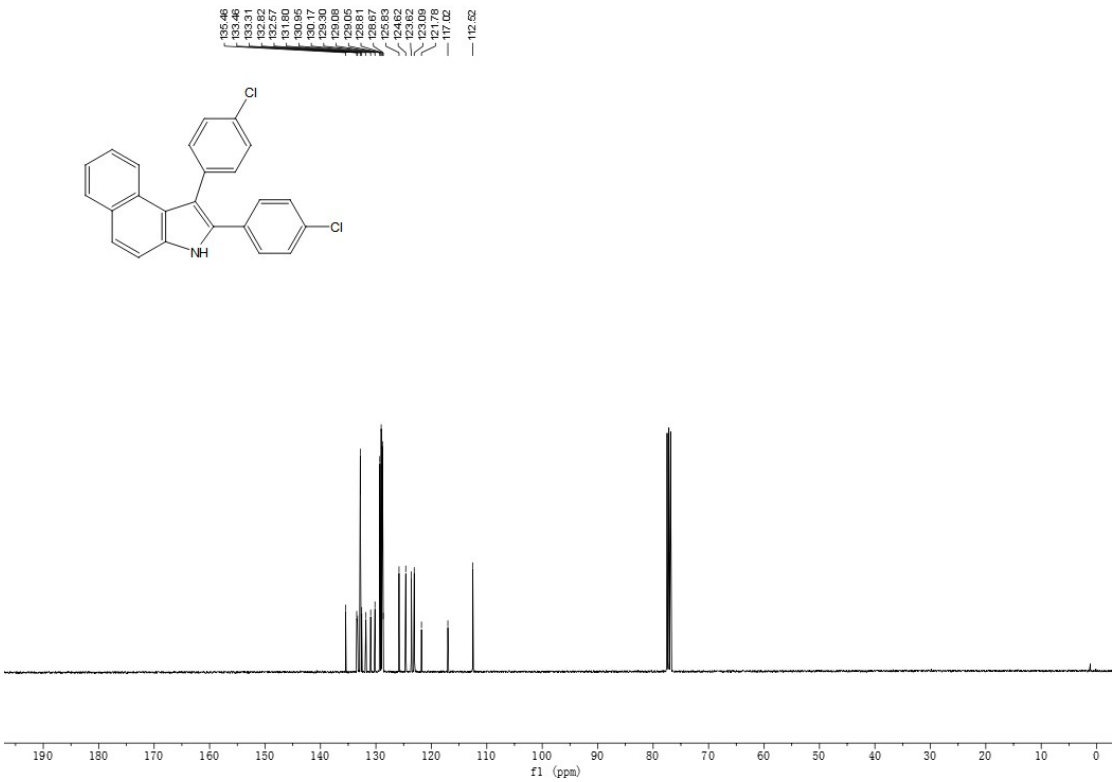
^{13}C NMR spectrum of **3ac** (101 MHz, $CDCl_3$)



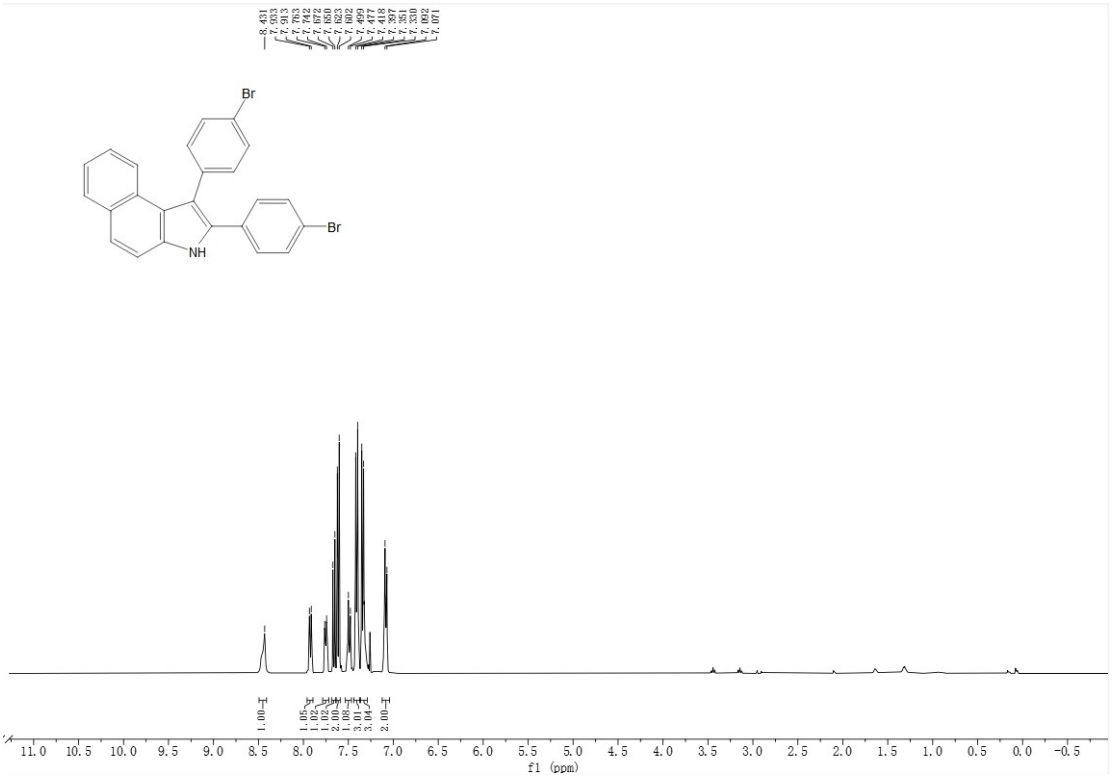
^{1}H NMR spectrum of **3ad** (400 MHz, $CDCl_3$)



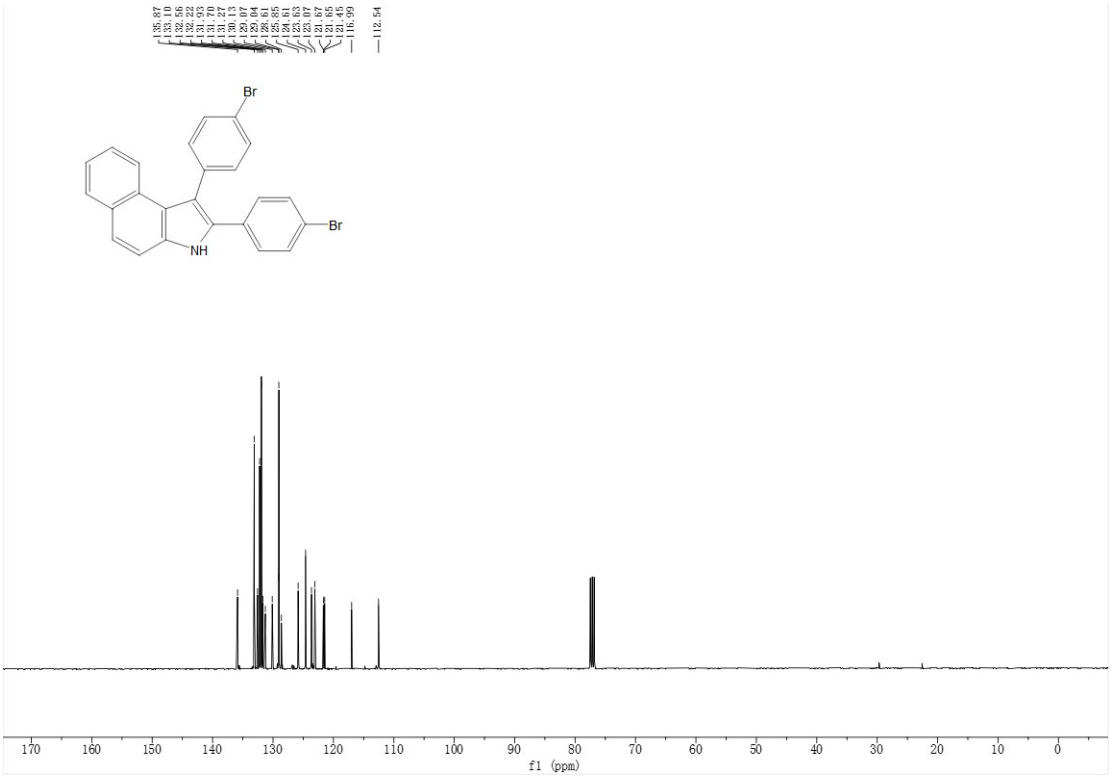
^{13}C NMR spectrum of **3ad** (101 MHz, $CDCl_3$)



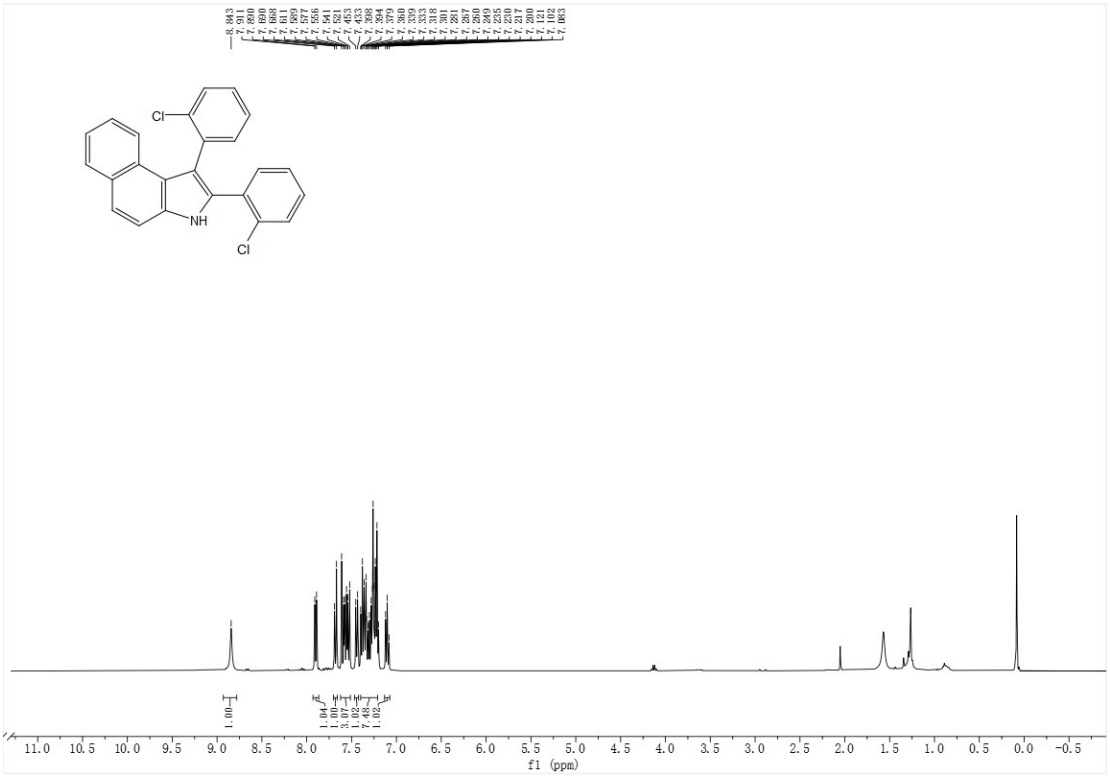
^{1}H NMR spectrum of **3ae** (400 MHz, $CDCl_3$)



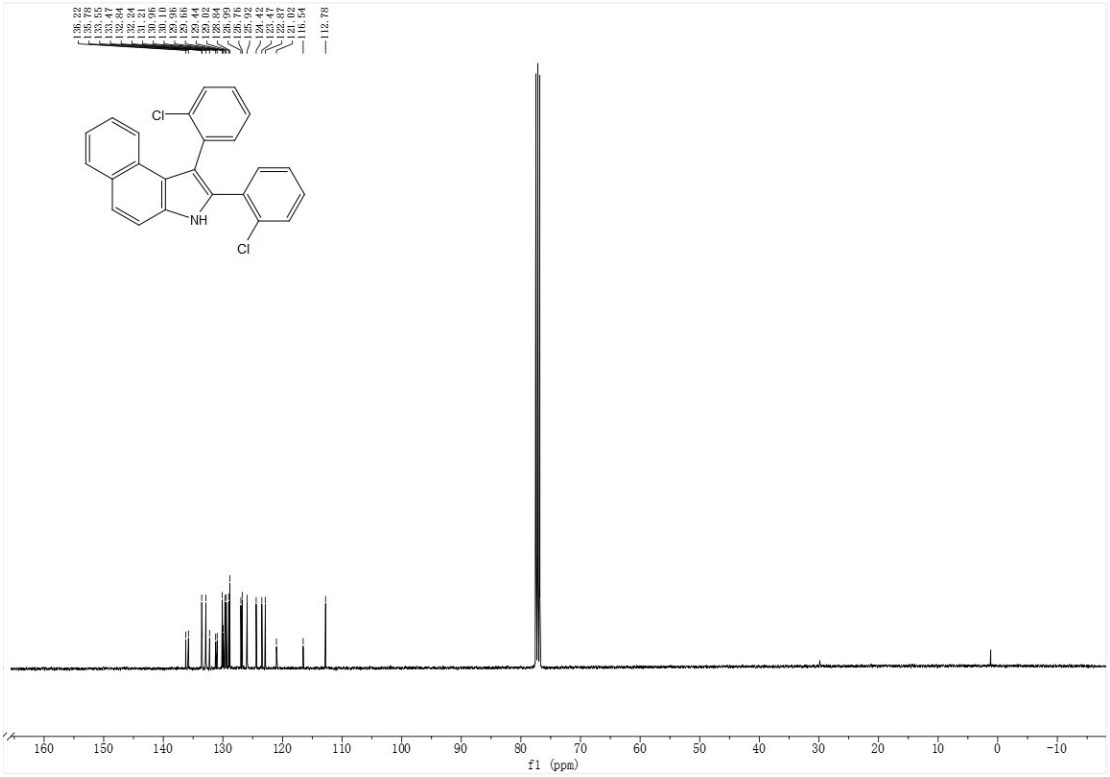
^{13}C NMR spectrum of **3ae** (101 MHz, $CDCl_3$)



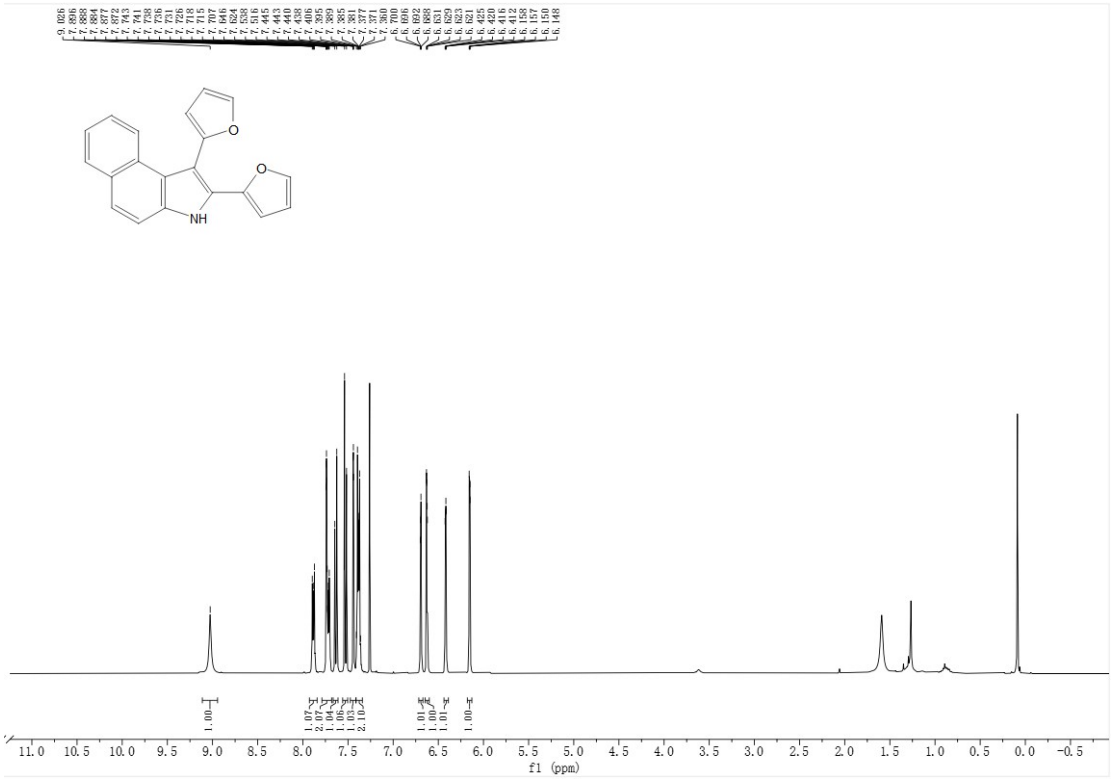
^{1}H NMR spectrum of **3af** (400 MHz, $CDCl_3$)



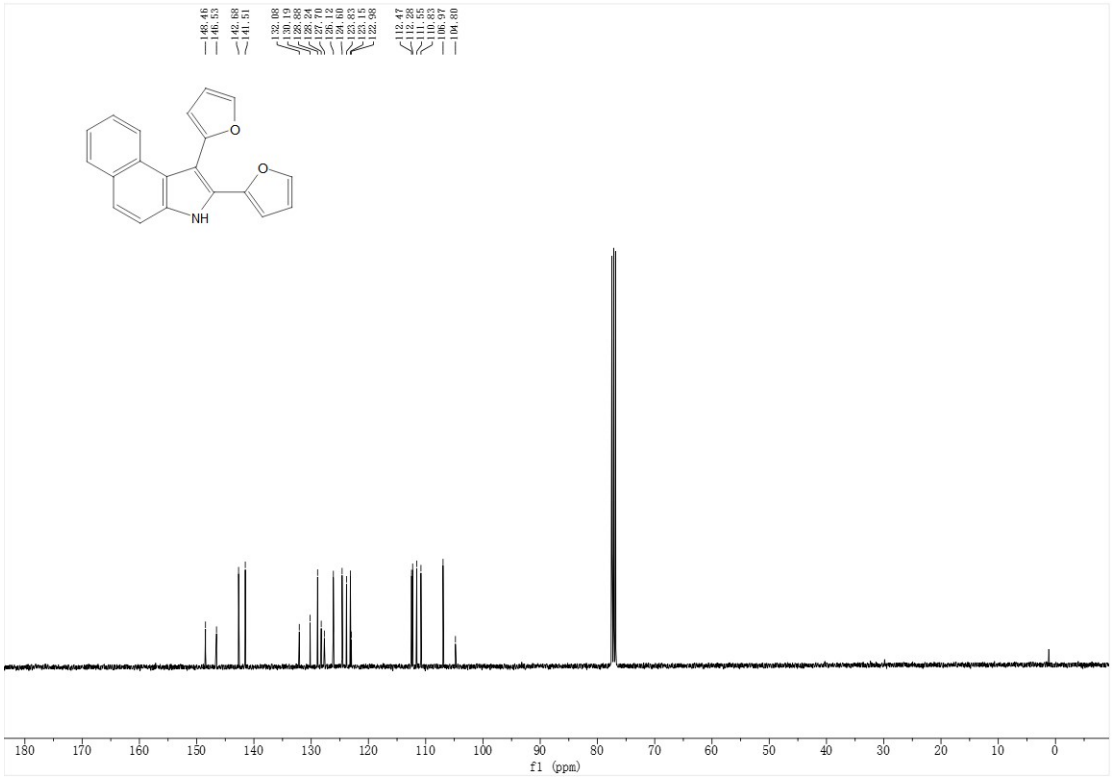
^{13}C NMR spectrum of **3af** (101 MHz, $CDCl_3$)



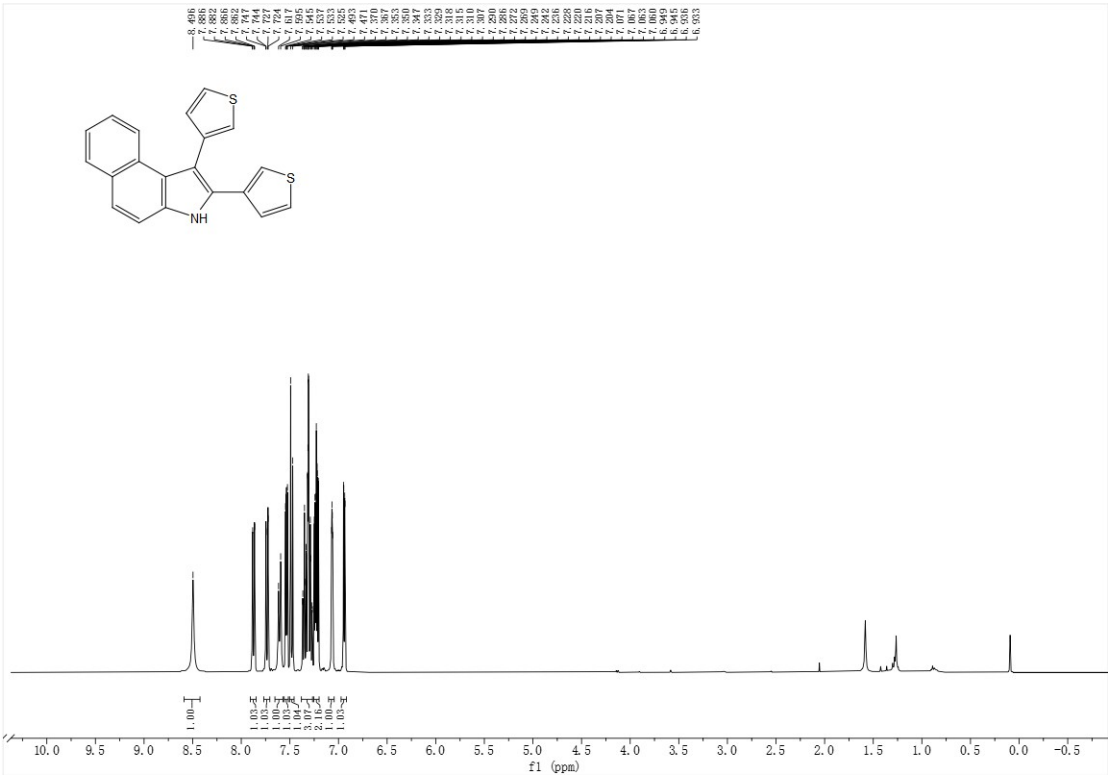
^{1}H NMR spectrum of **3ag** (400 MHz, $CDCl_3$)



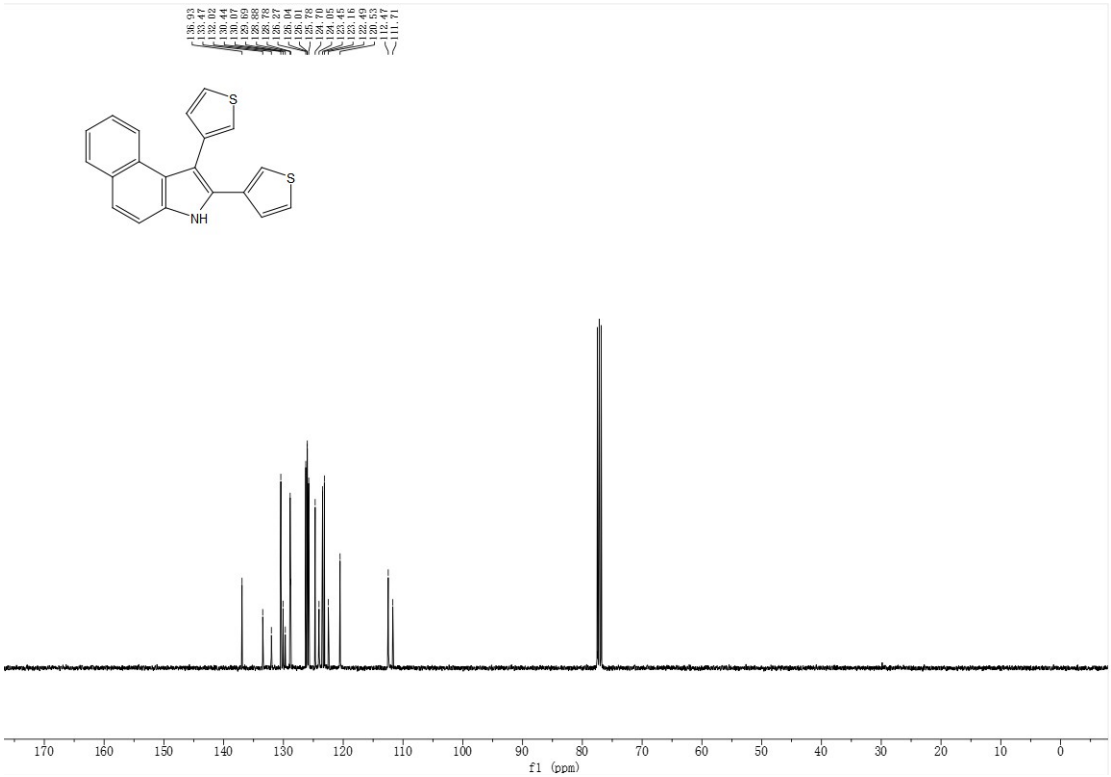
^{13}C NMR spectrum of **3ag** (101 MHz, $CDCl_3$)



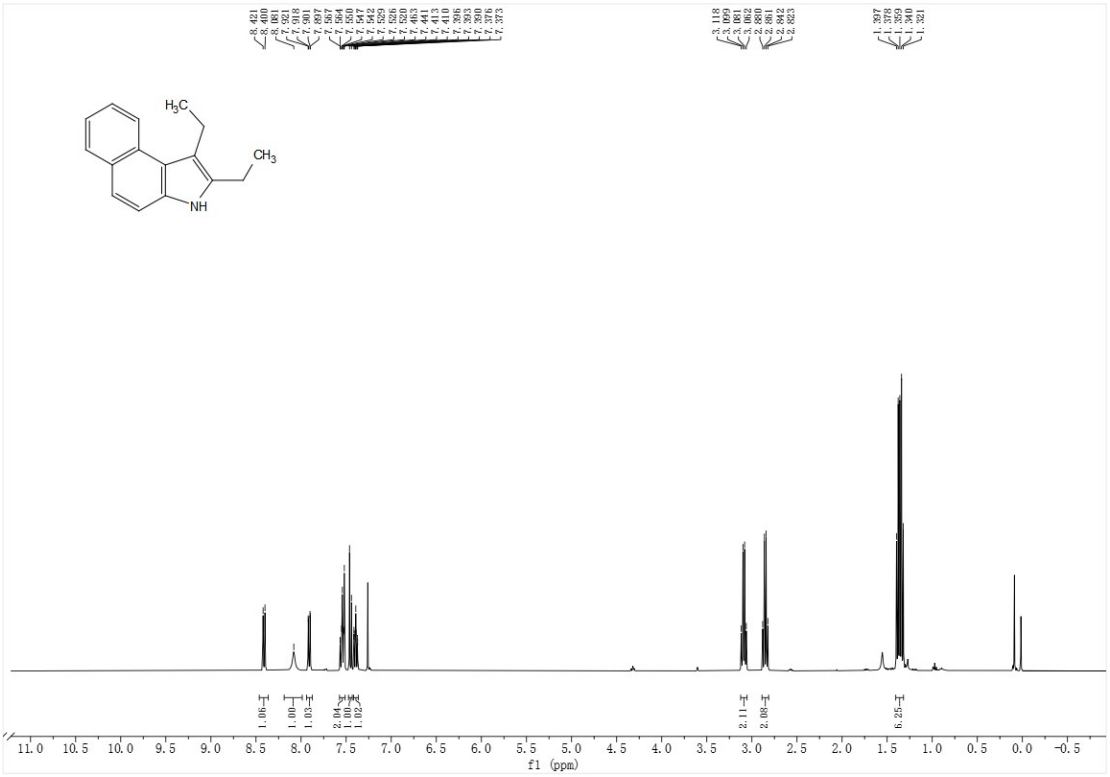
^{1}H NMR spectrum of **3ah** (400 MHz, $CDCl_3$)



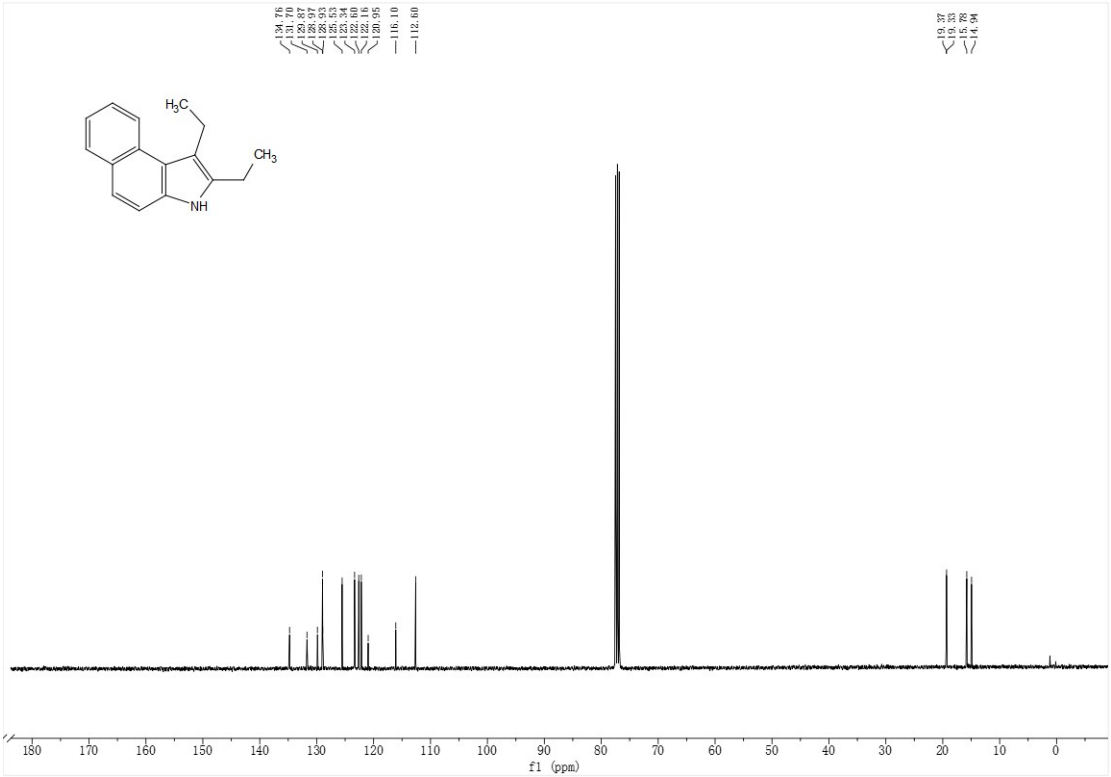
^{13}C NMR spectrum of **3ah** (101 MHz, $CDCl_3$)



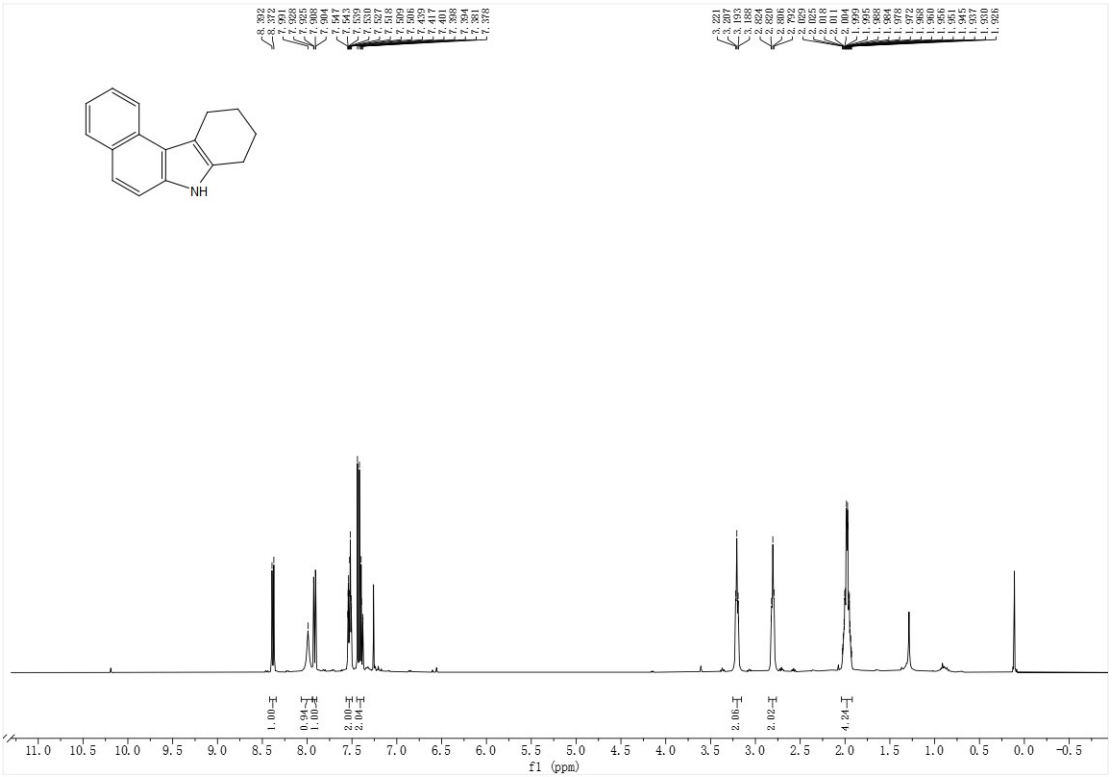
^{1}H NMR spectrum of **3ai** (400 MHz, $CDCl_3$)



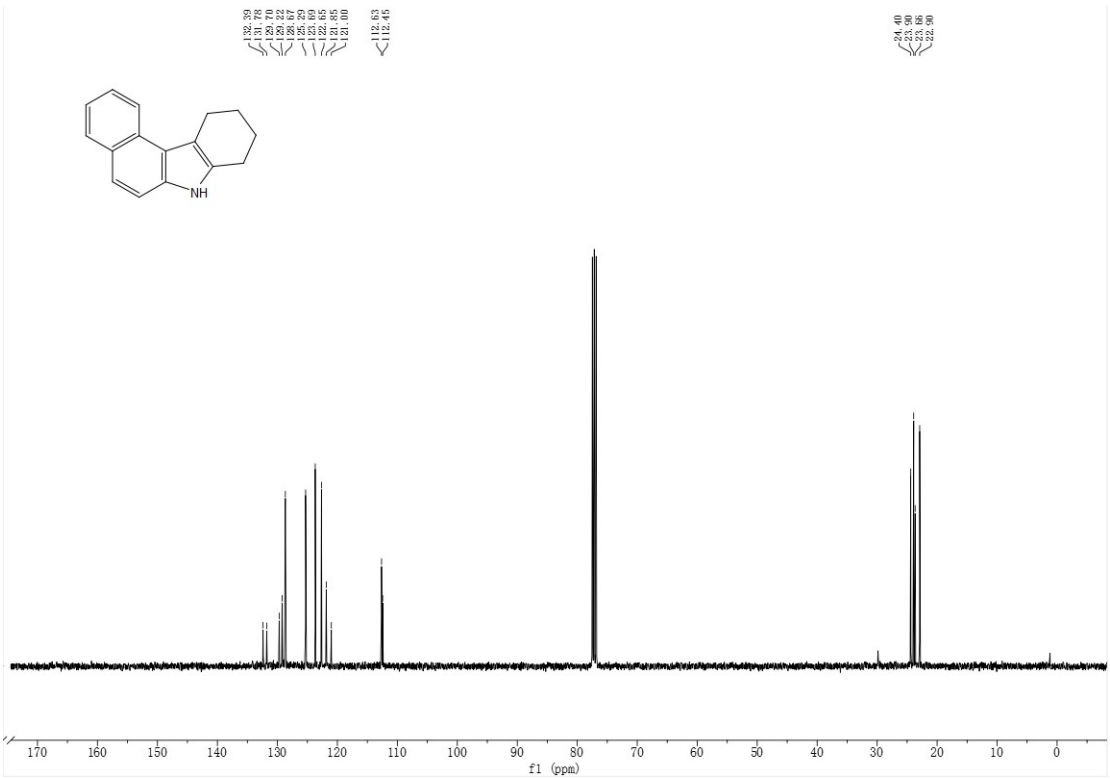
^{13}C NMR spectrum of **3ai** (101 MHz, $CDCl_3$)



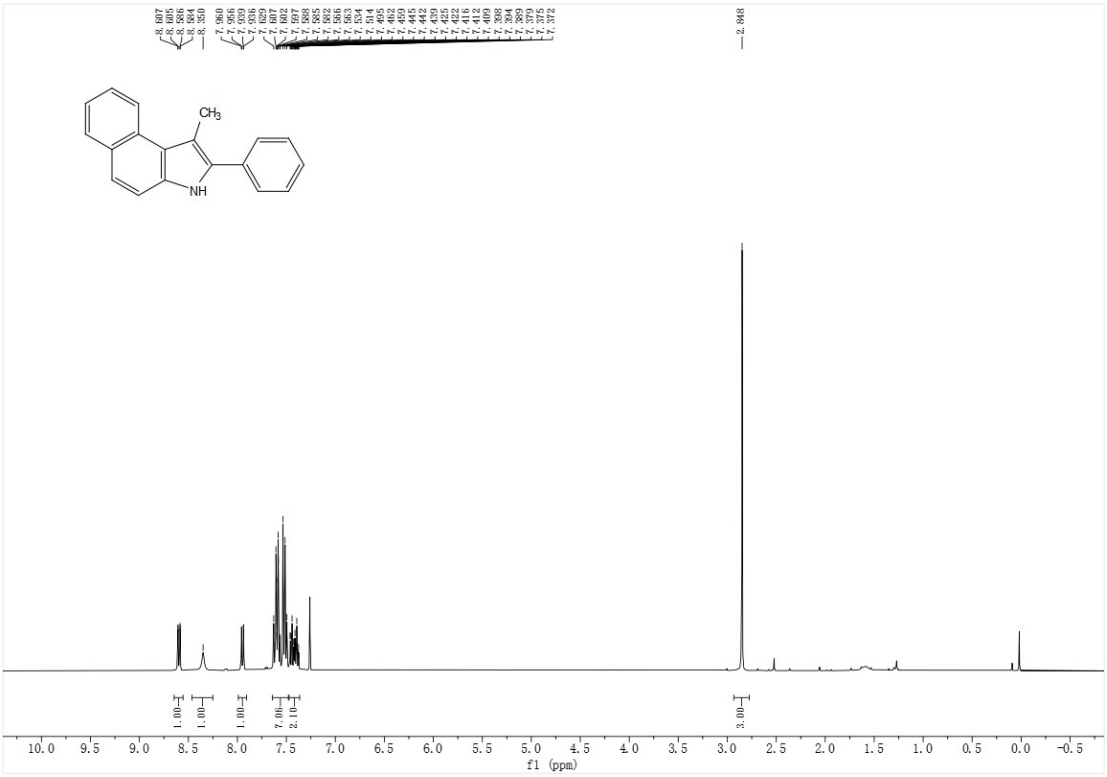
^{1}H NMR spectrum of **3aj** (400 MHz, $CDCl_3$)



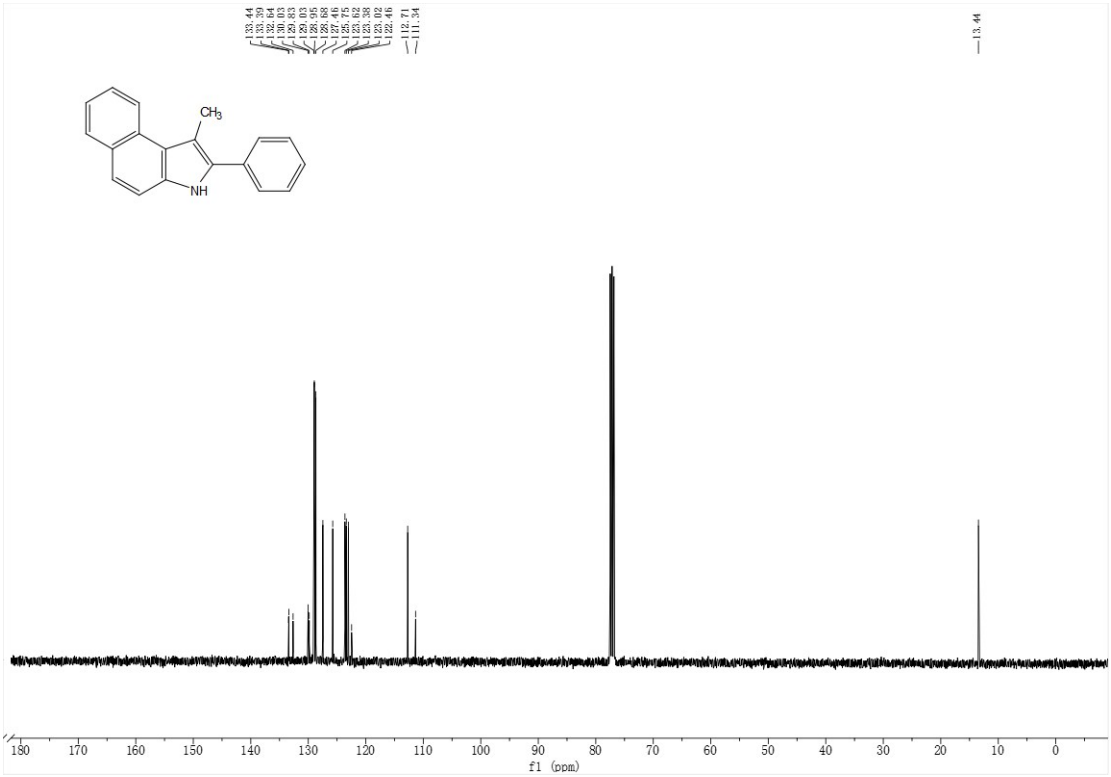
^{13}C NMR spectrum of **3aj** (101 MHz, $CDCl_3$)



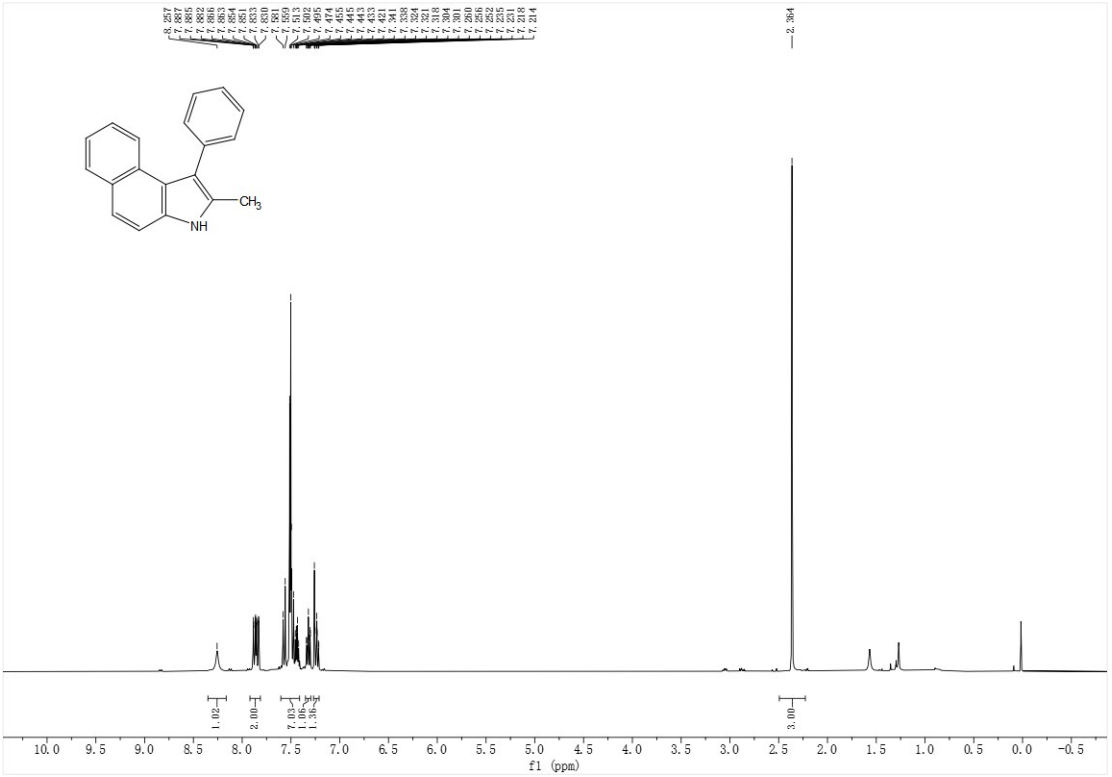
^{1}H NMR spectrum of **3ak** (400 MHz, $CDCl_3$)



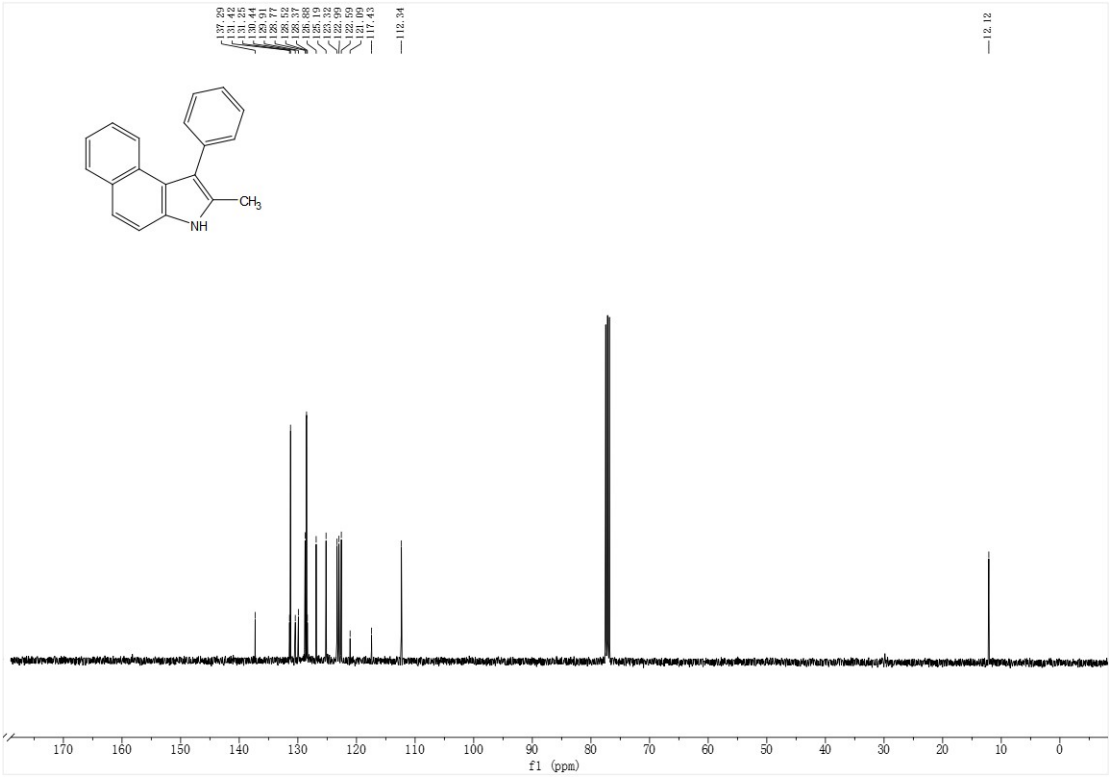
^{13}C NMR spectrum of **3ak** (101 MHz, $CDCl_3$)



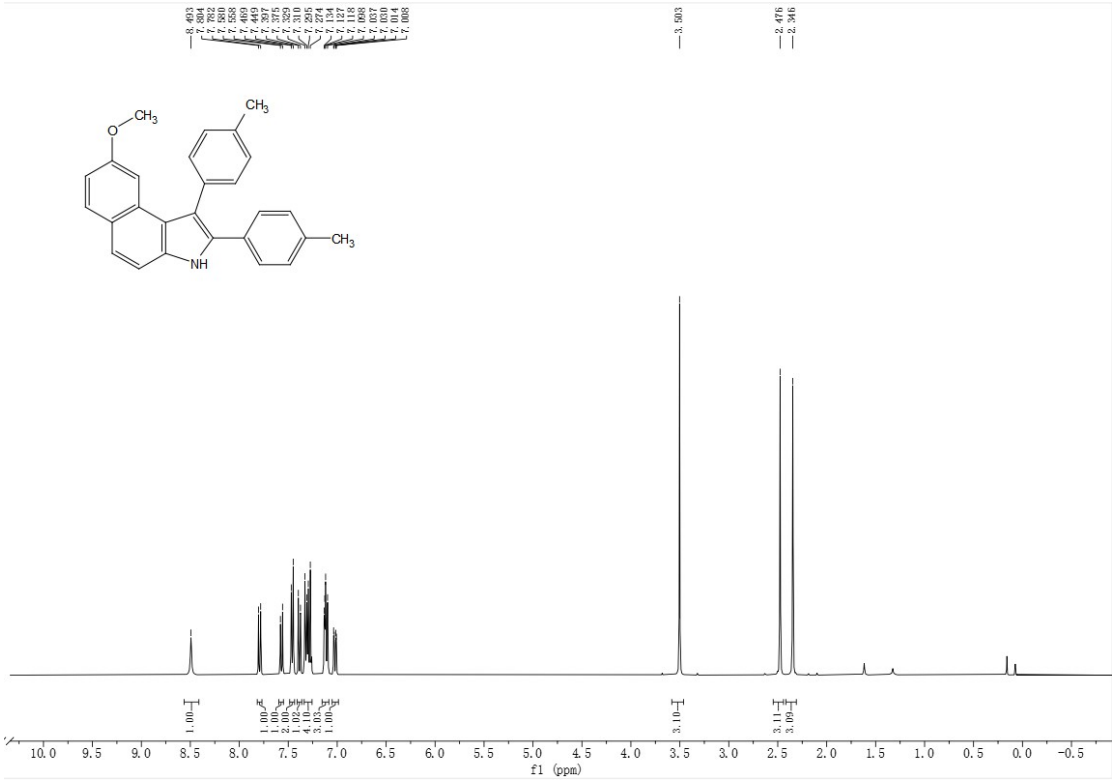
^{1}H NMR spectrum of **3ak'** (400 MHz, $CDCl_3$)



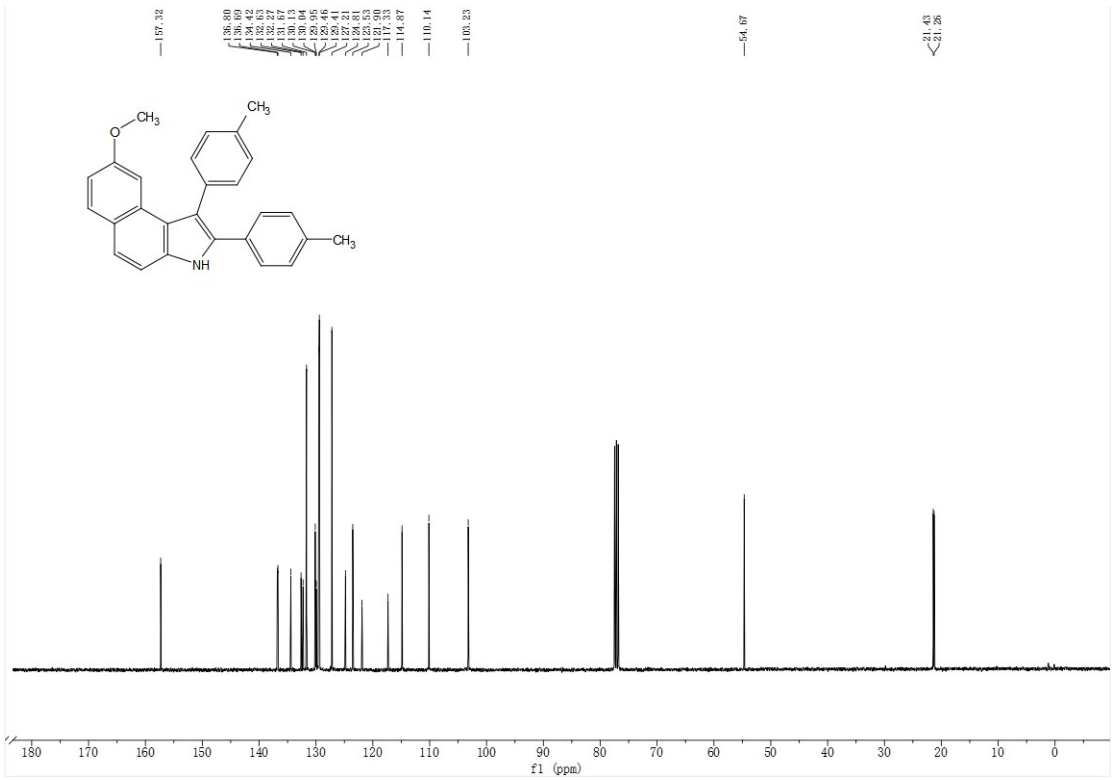
^{13}C NMR spectrum of **3ak'** (101 MHz, $CDCl_3$)



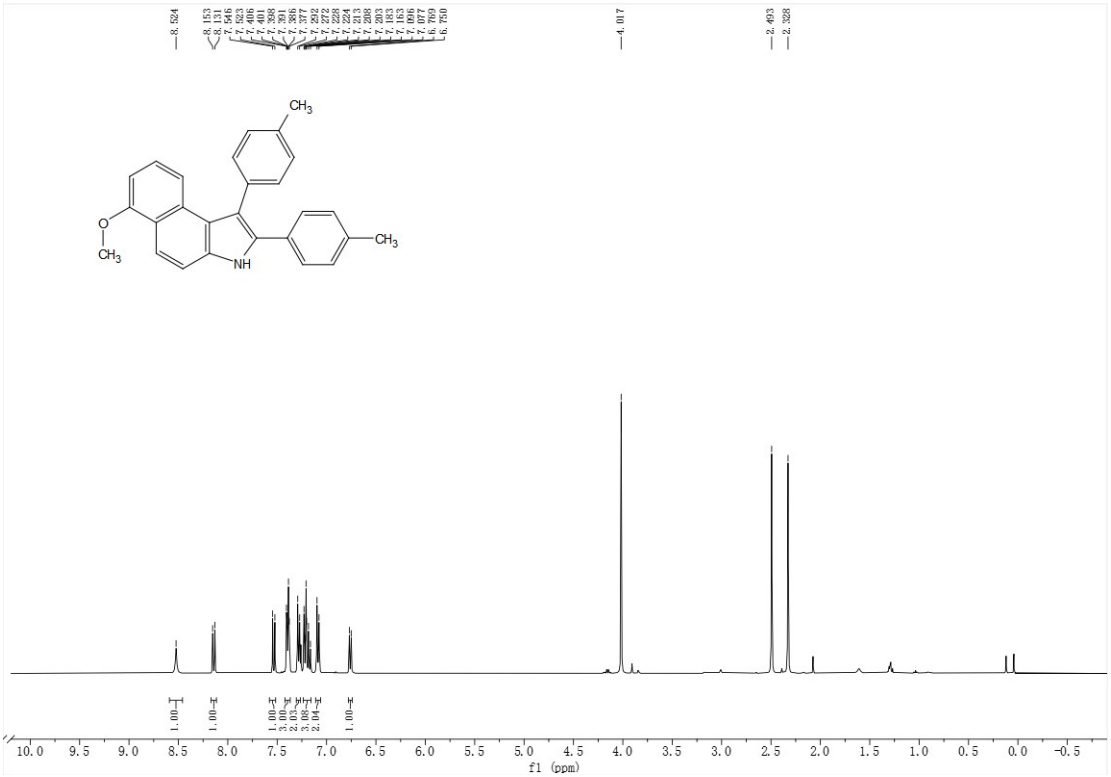
^{1}H NMR spectrum of **3ba** (400 MHz, $CDCl_3$)



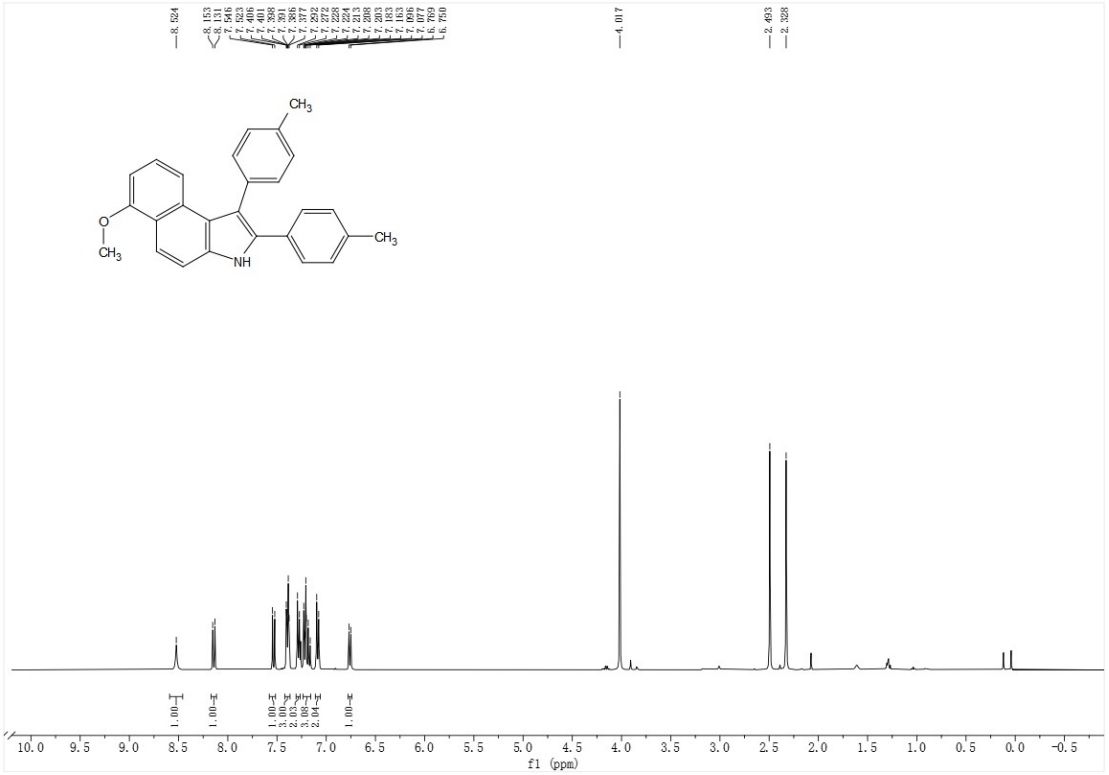
^{13}C NMR spectrum of **3ba** (101 MHz, $CDCl_3$)



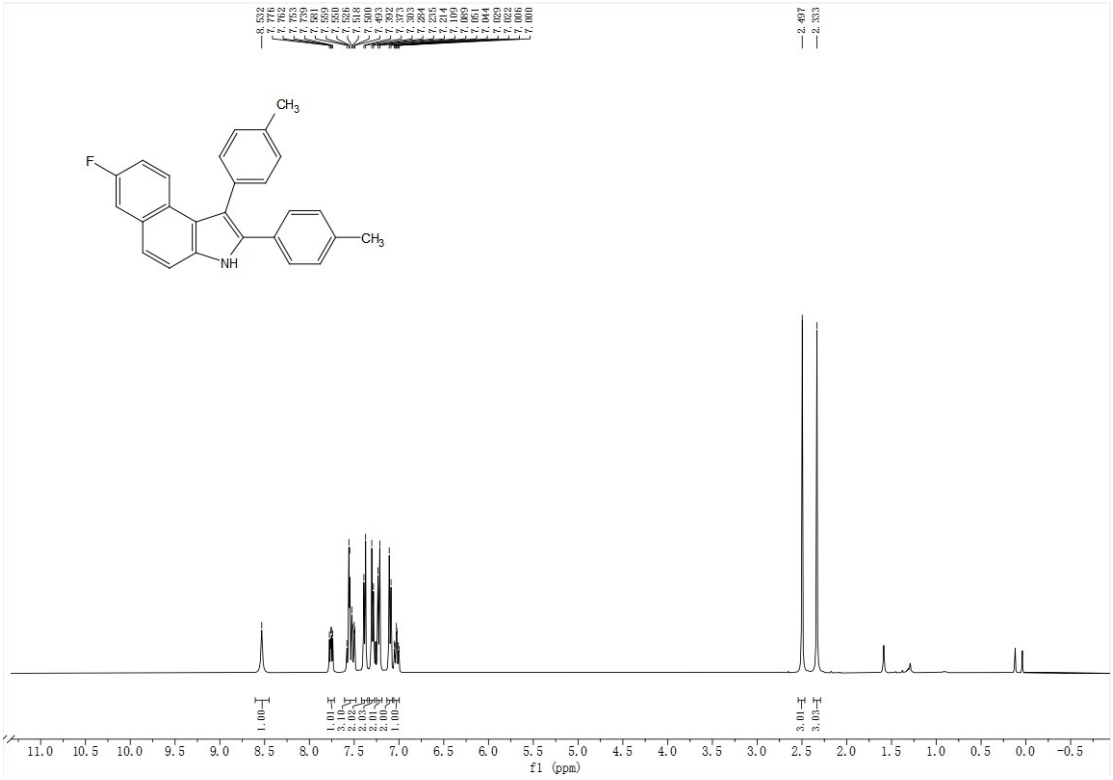
^{1}H NMR spectrum of **3bb** (400 MHz, $CDCl_3$)



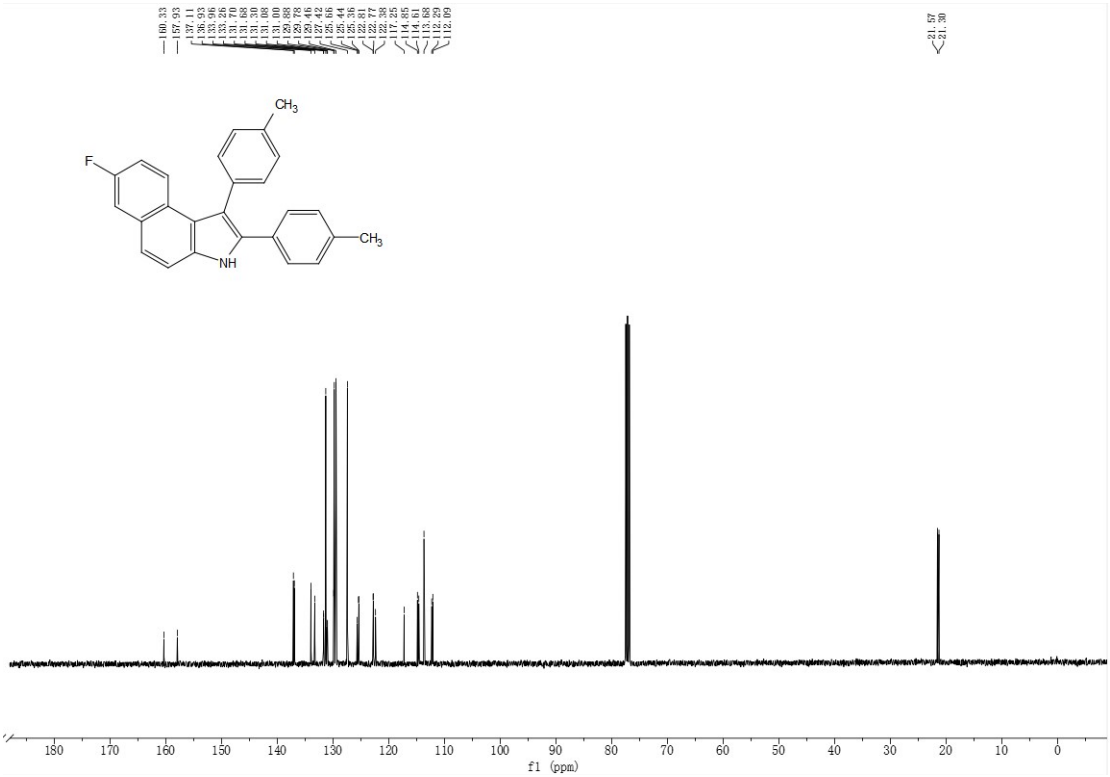
^{13}C NMR spectrum of **3bb** (101 MHz, $CDCl_3$)



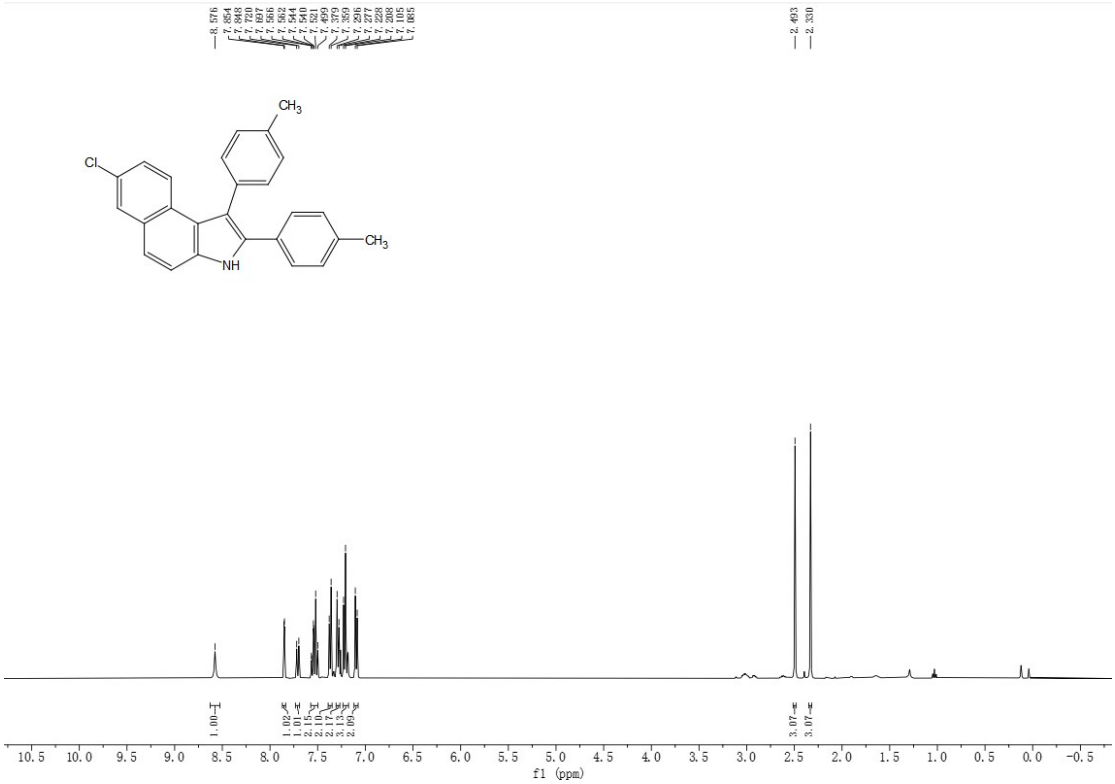
^{1}H NMR spectrum of **3bc** (400 MHz, $CDCl_3$)



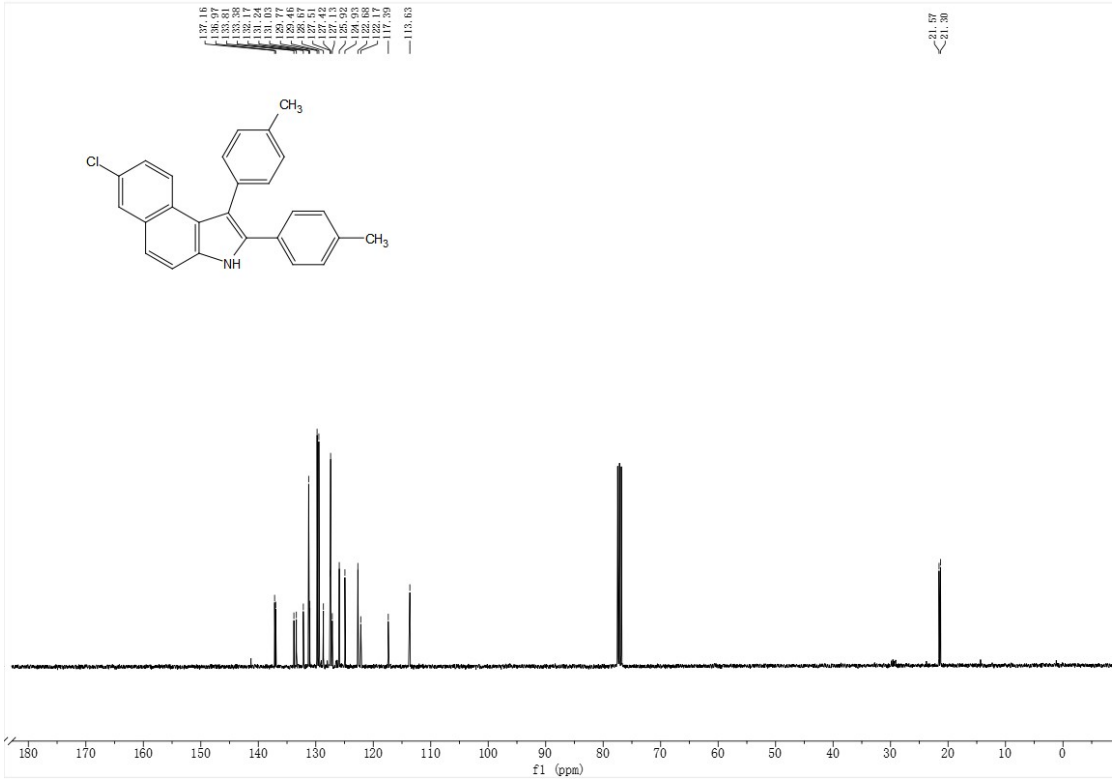
^{13}C NMR spectrum of **3bc** (101 MHz, $CDCl_3$)



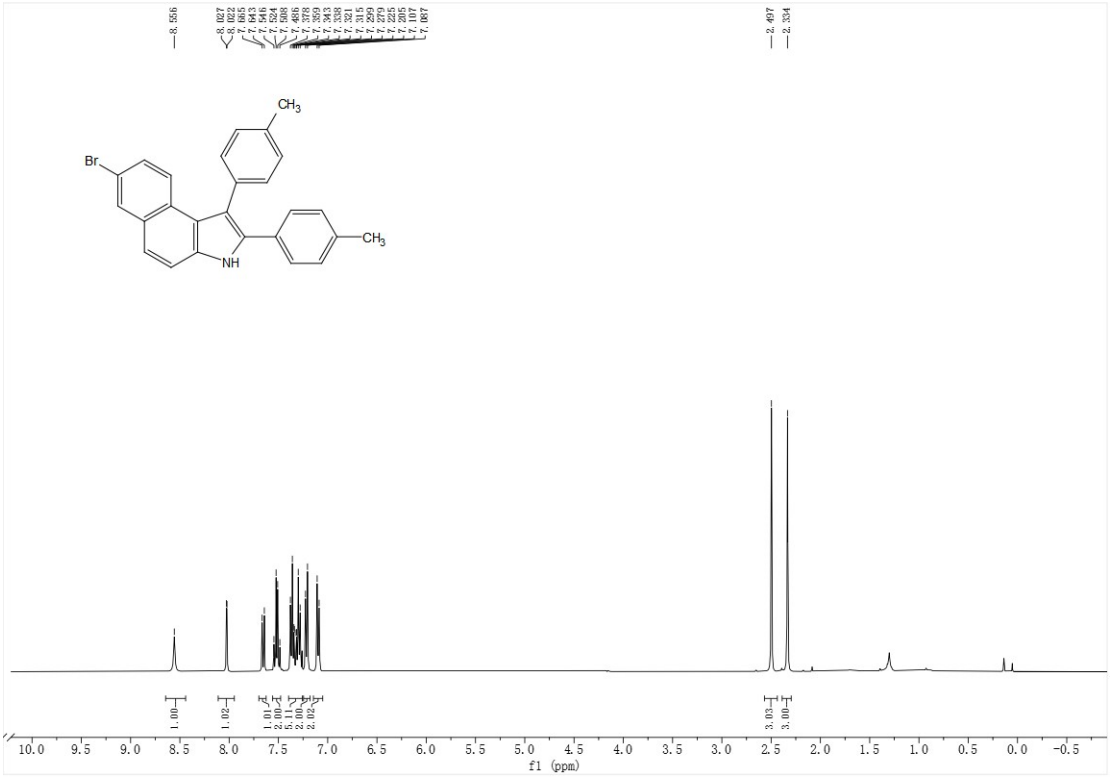
^{1}H NMR spectrum of **3bd** (400 MHz, $CDCl_3$)



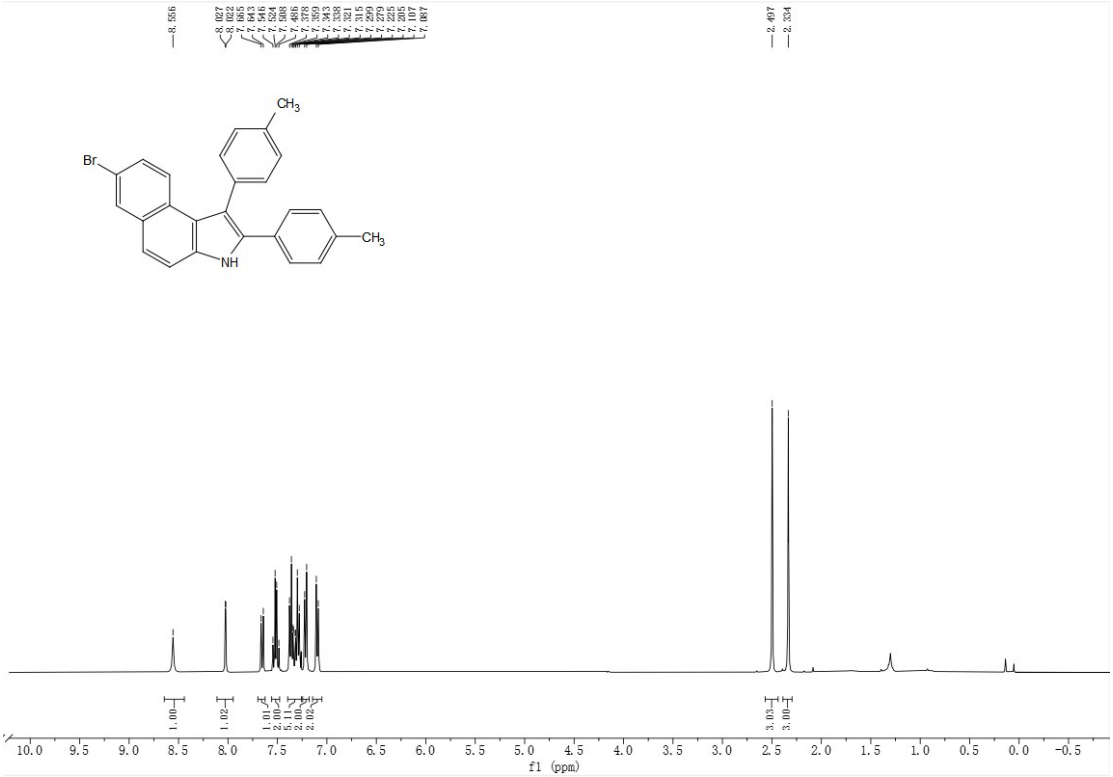
^{13}C NMR spectrum of **3bd** (101 MHz, $CDCl_3$)



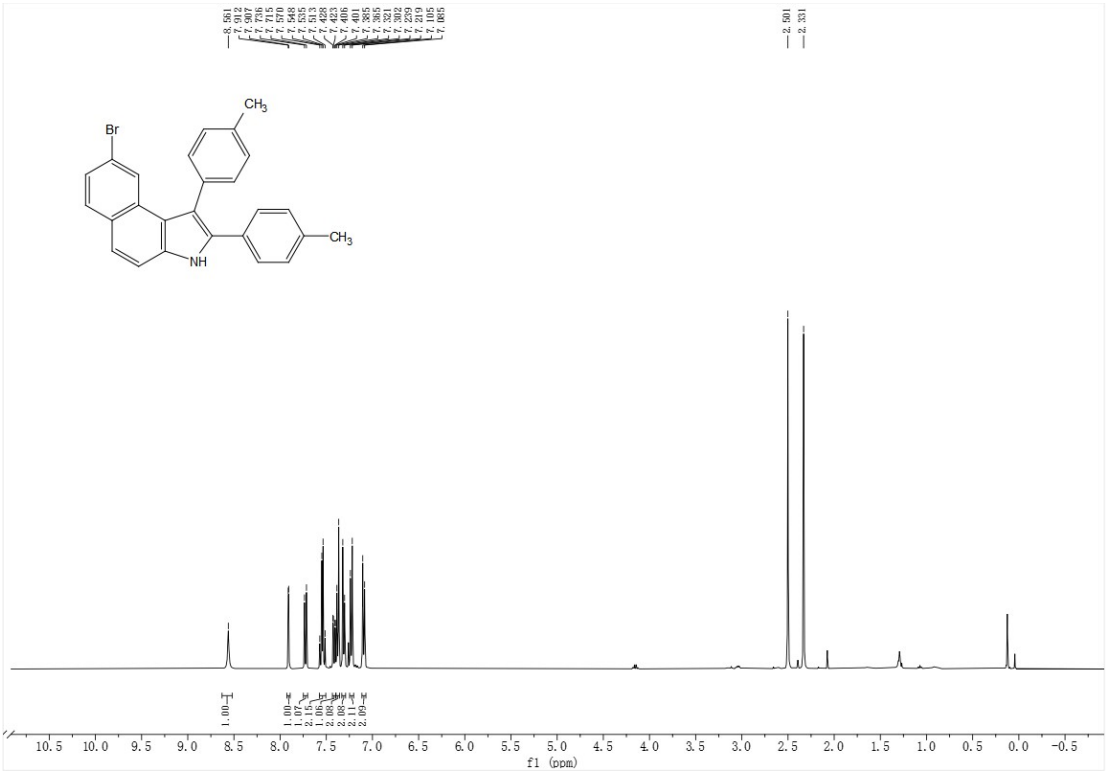
^{1}H NMR spectrum of **3be** (400 MHz, $CDCl_3$)



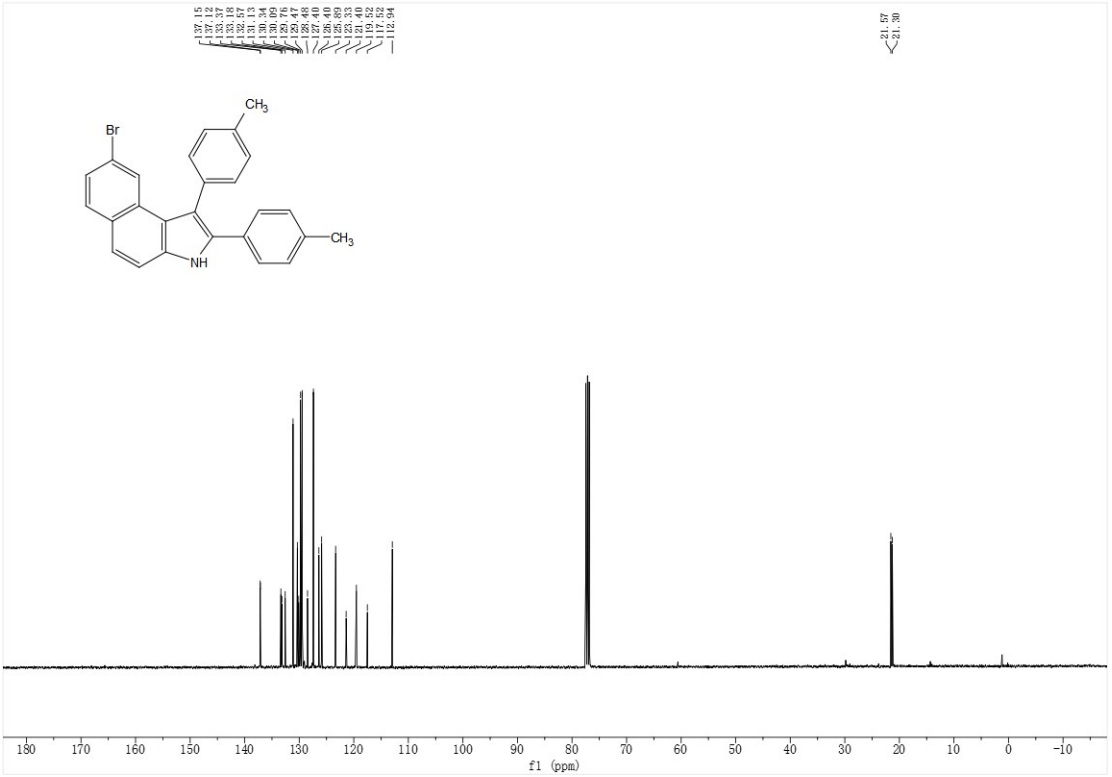
^{13}C NMR spectrum of **3be** (101 MHz, $CDCl_3$)



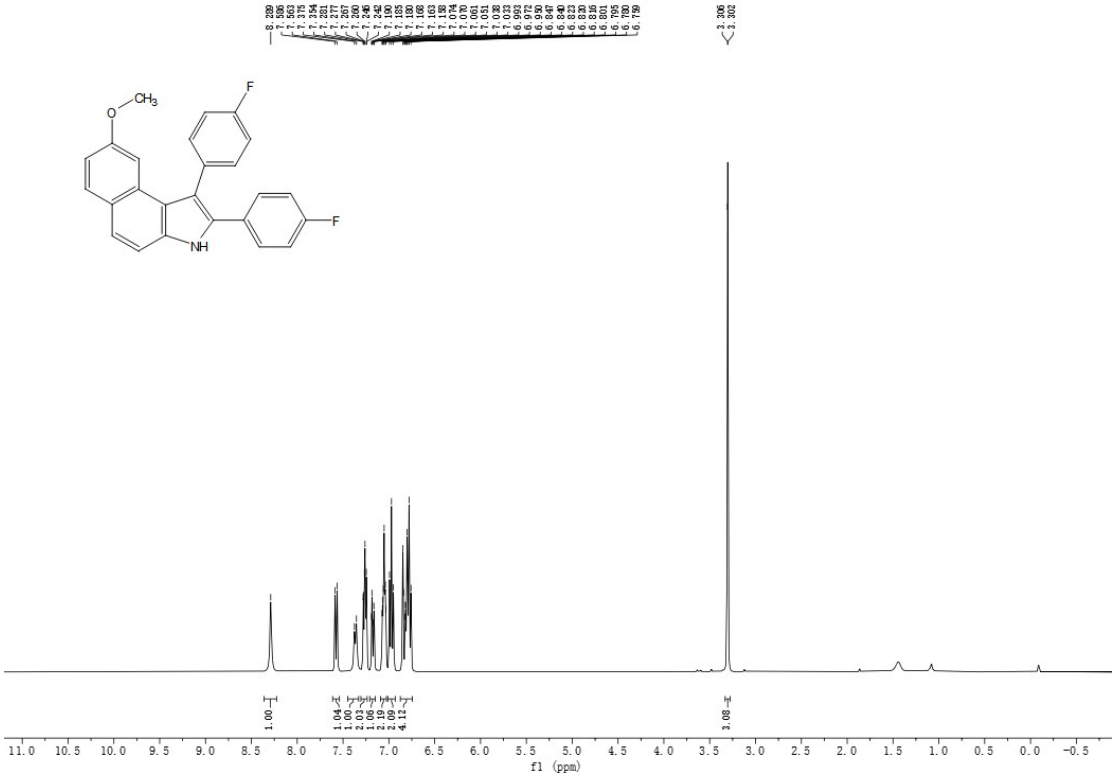
^{1}H NMR spectrum of **3bf** (400 MHz, $CDCl_3$)



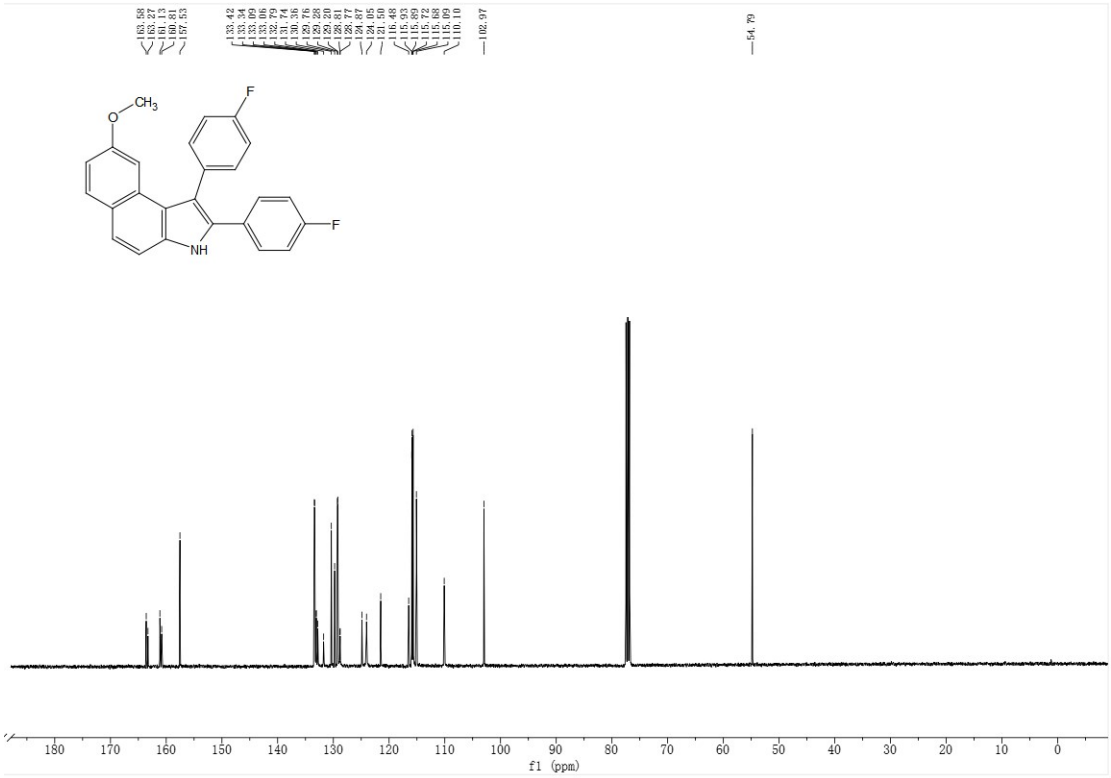
^{13}C NMR spectrum of **3bf** (101 MHz, $CDCl_3$)



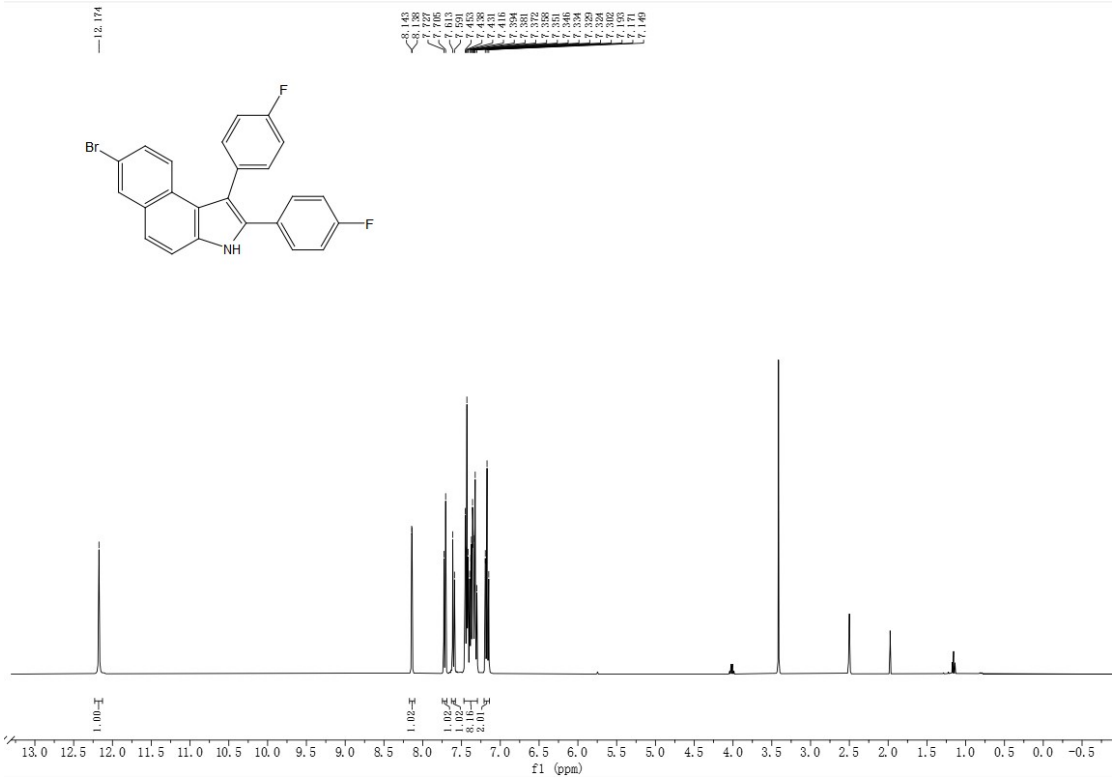
^{1}H NMR spectrum of **3bg** (400 MHz, $CDCl_3$)



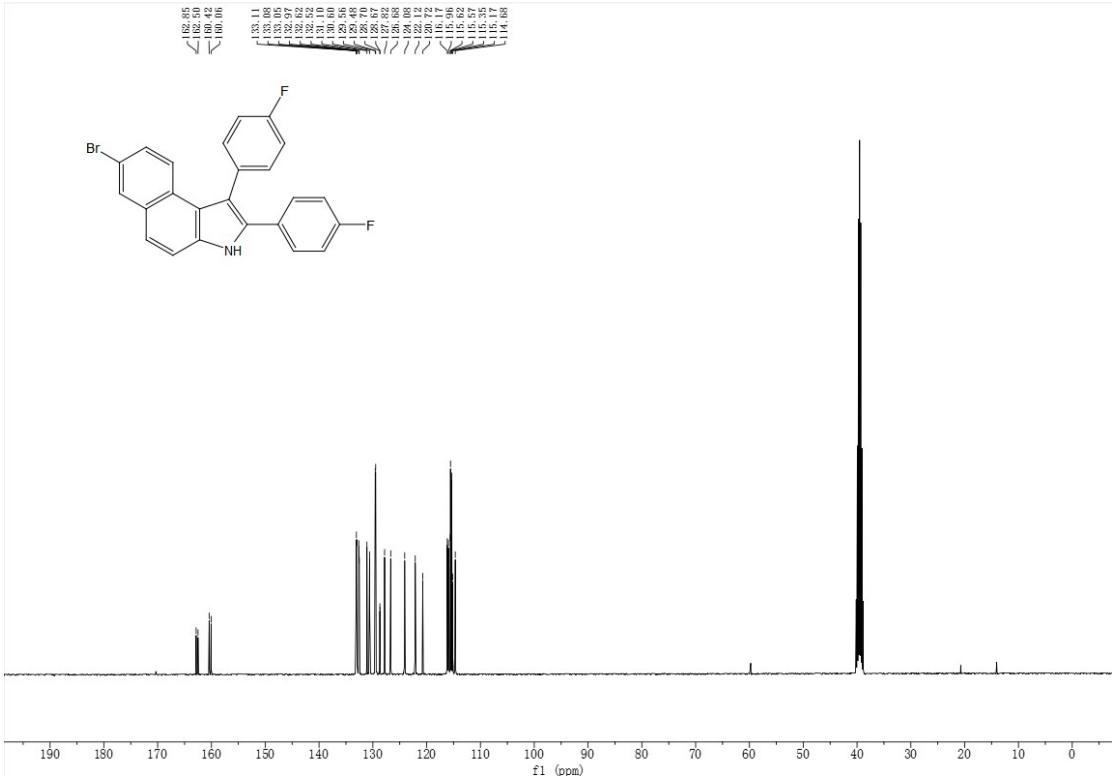
^{13}C NMR spectrum of **3bg** (101 MHz, $CDCl_3$)



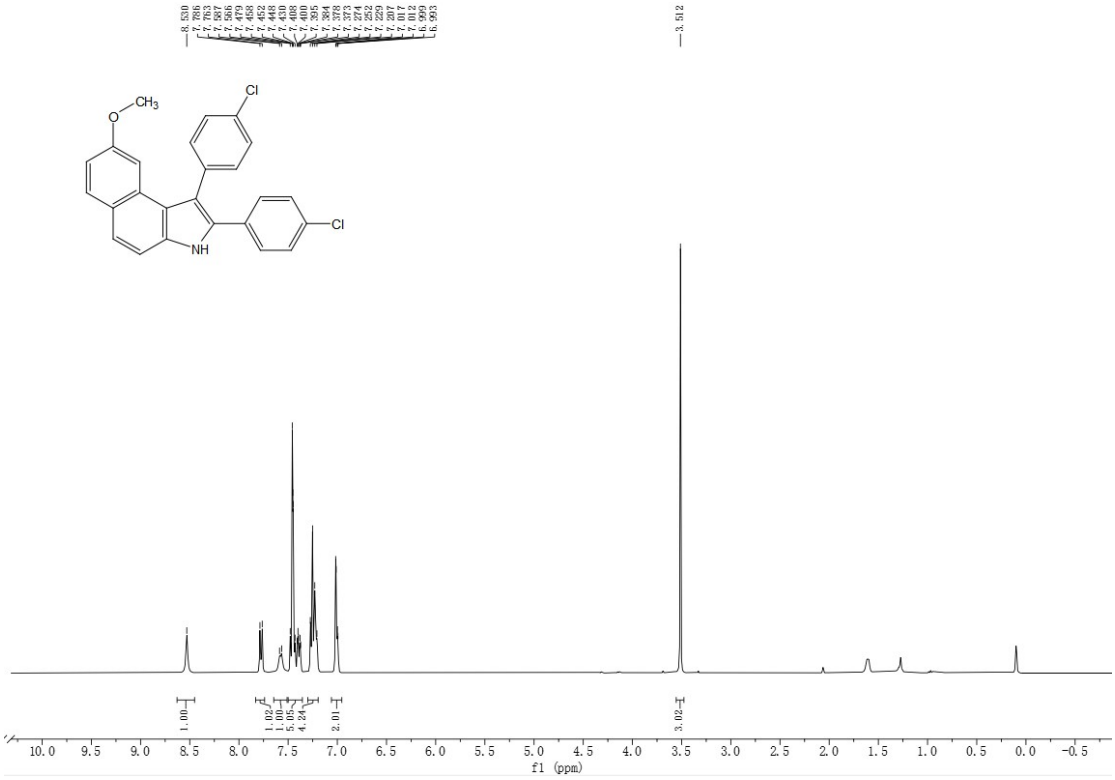
^{1}H NMR spectrum of **3bh** (400 MHz, DMSO-d_6)



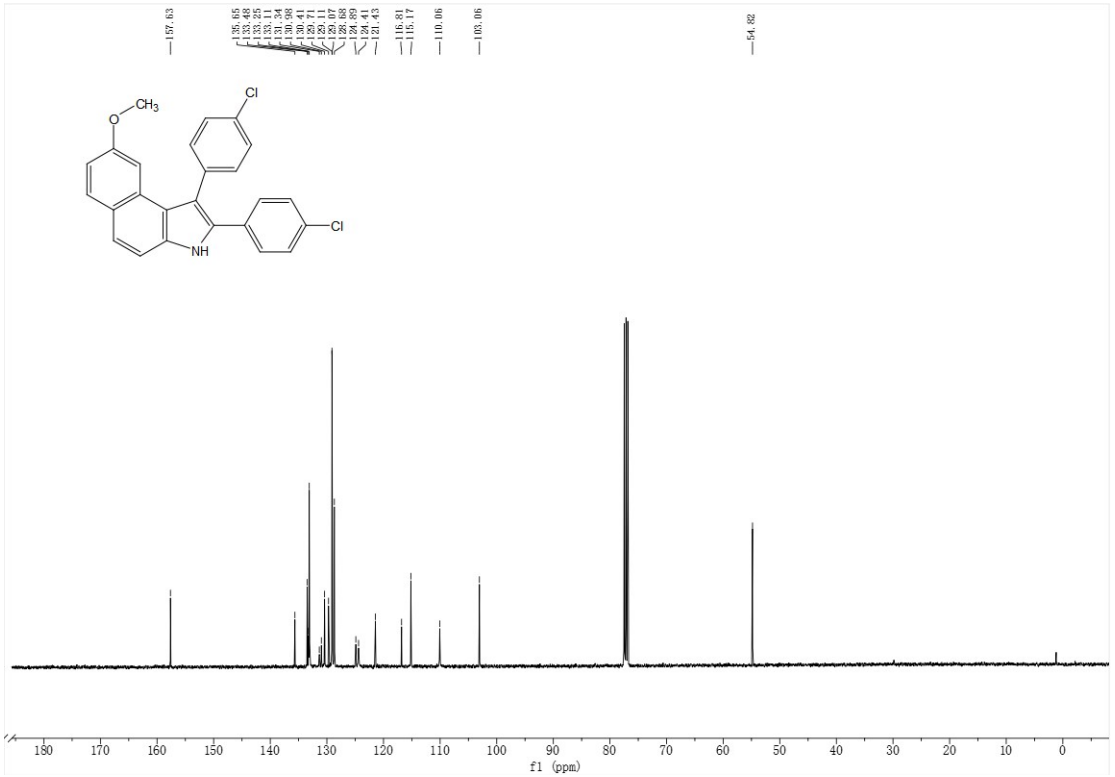
^{13}C NMR spectrum of **3bh** (101 MHz, DMSO-d_6)



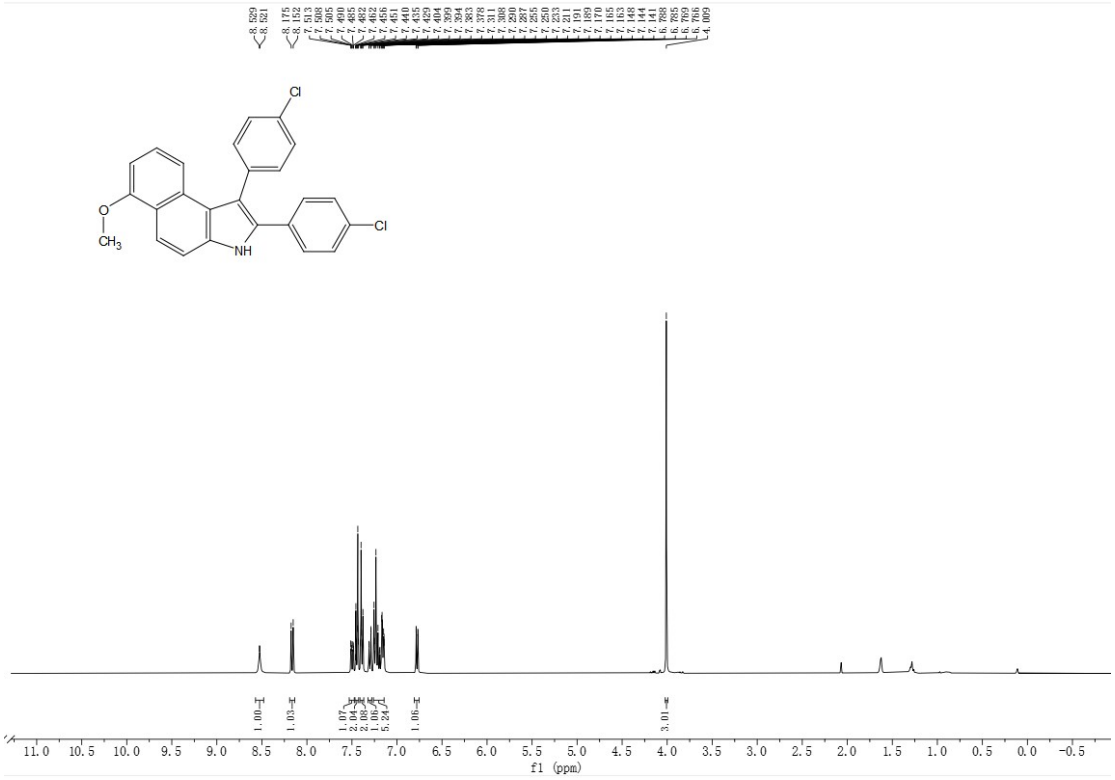
^{1}H NMR spectrum of **3bi** (400 MHz, $CDCl_3$)



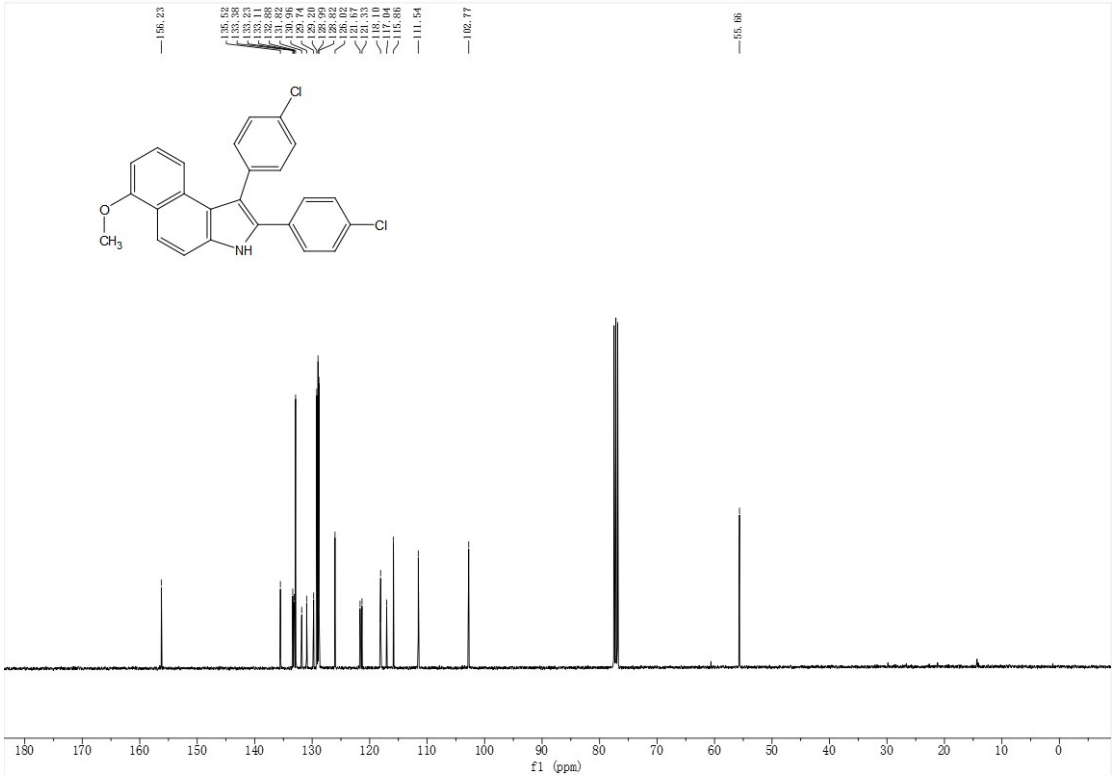
^{13}C NMR spectrum of **3bi** (101 MHz, $CDCl_3$)



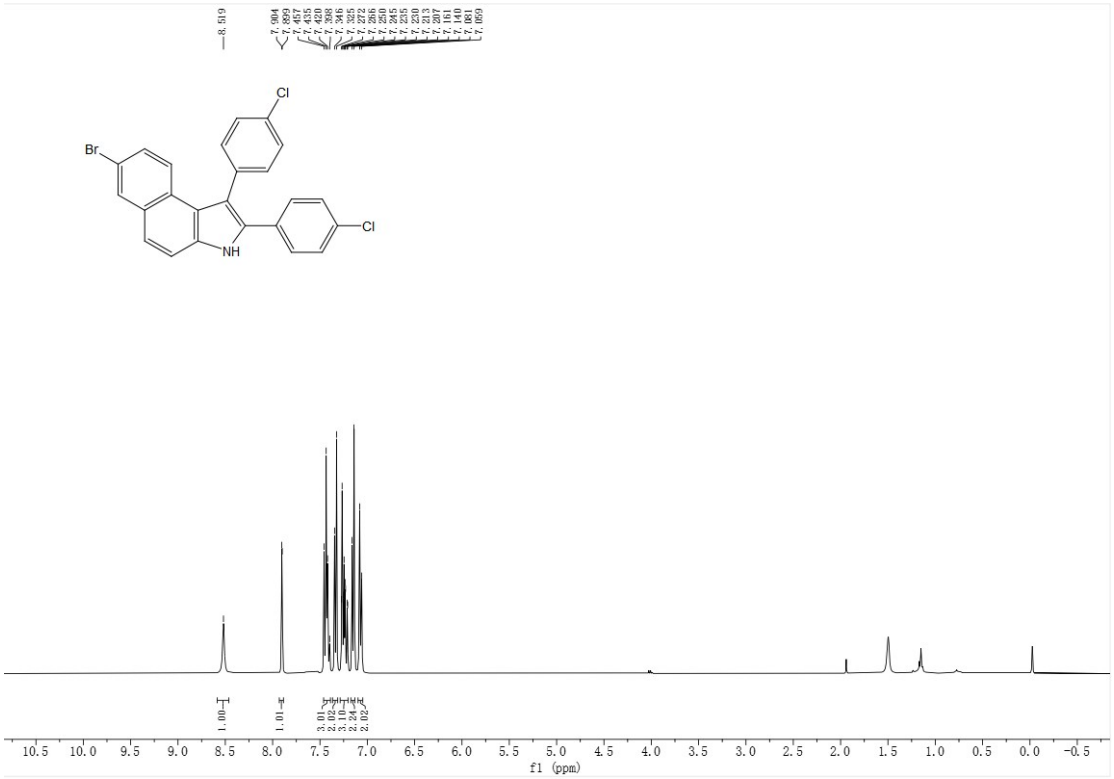
^{1}H NMR spectrum of **3bj** (400 MHz, $CDCl_3$)



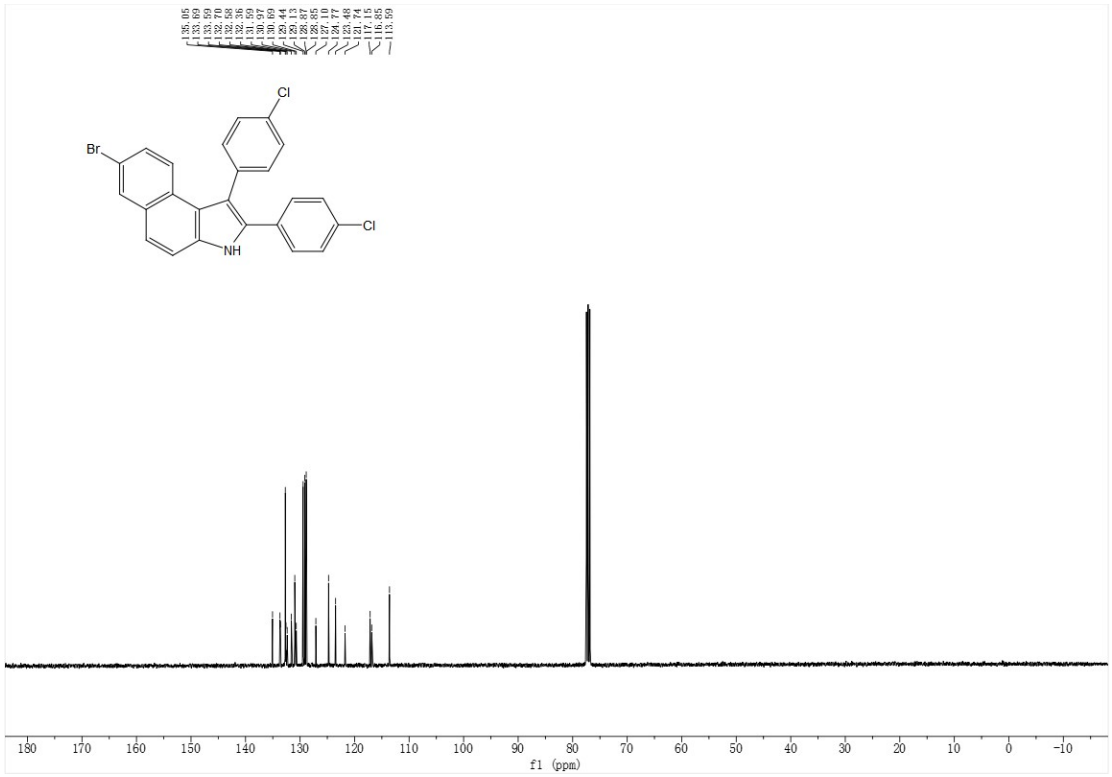
^{13}C NMR spectrum of **3bj** (101 MHz, $CDCl_3$)



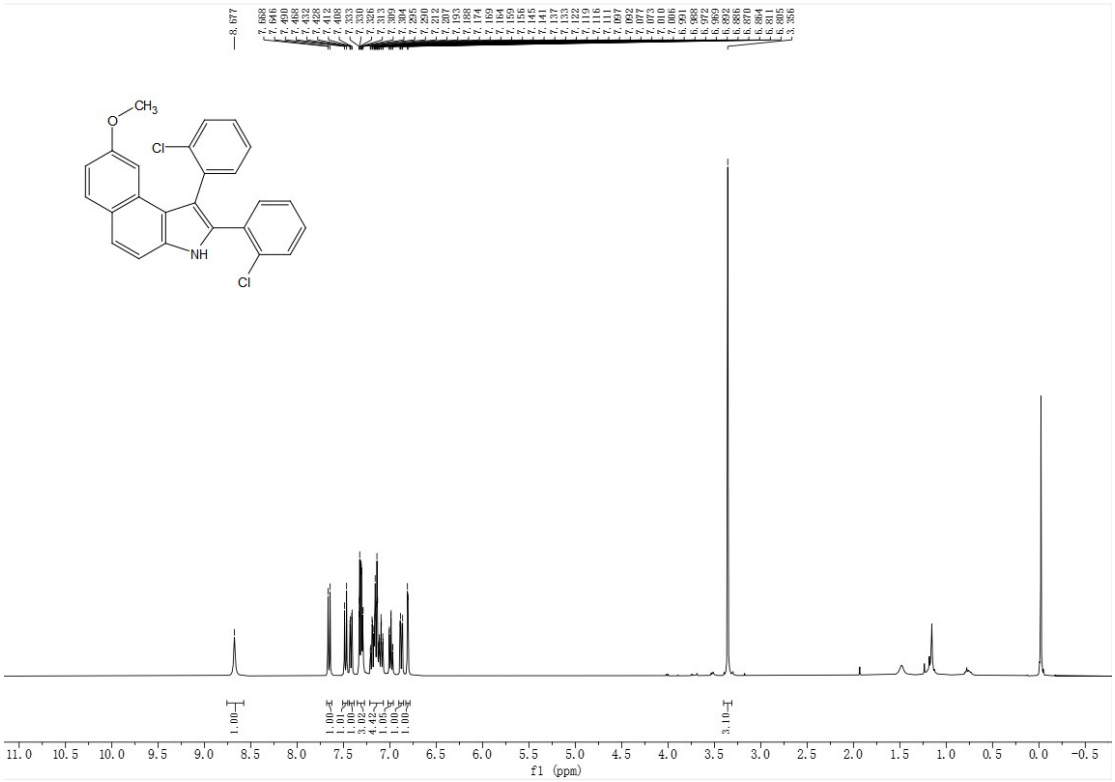
^{1}H NMR spectrum of **3bk** (400 MHz, $CDCl_3$)



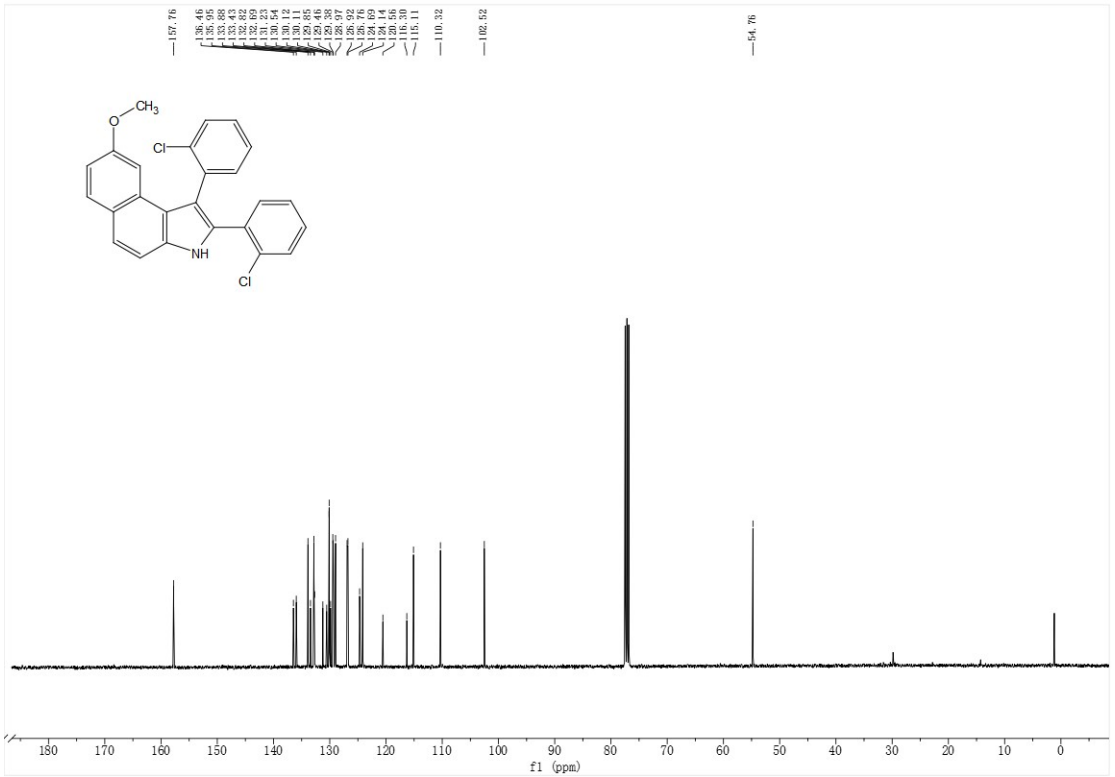
^{13}C NMR spectrum of **3bk** (101 MHz, $CDCl_3$)



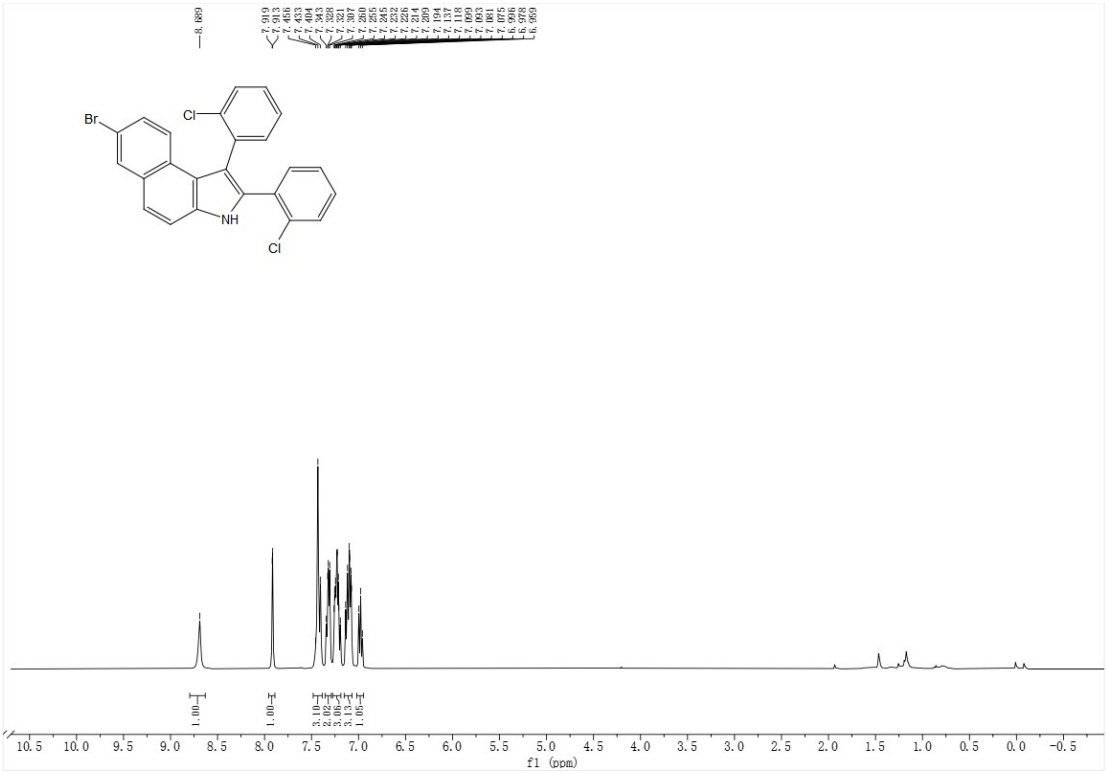
^{1}H NMR spectrum of **3bl** (400 MHz, $CDCl_3$)



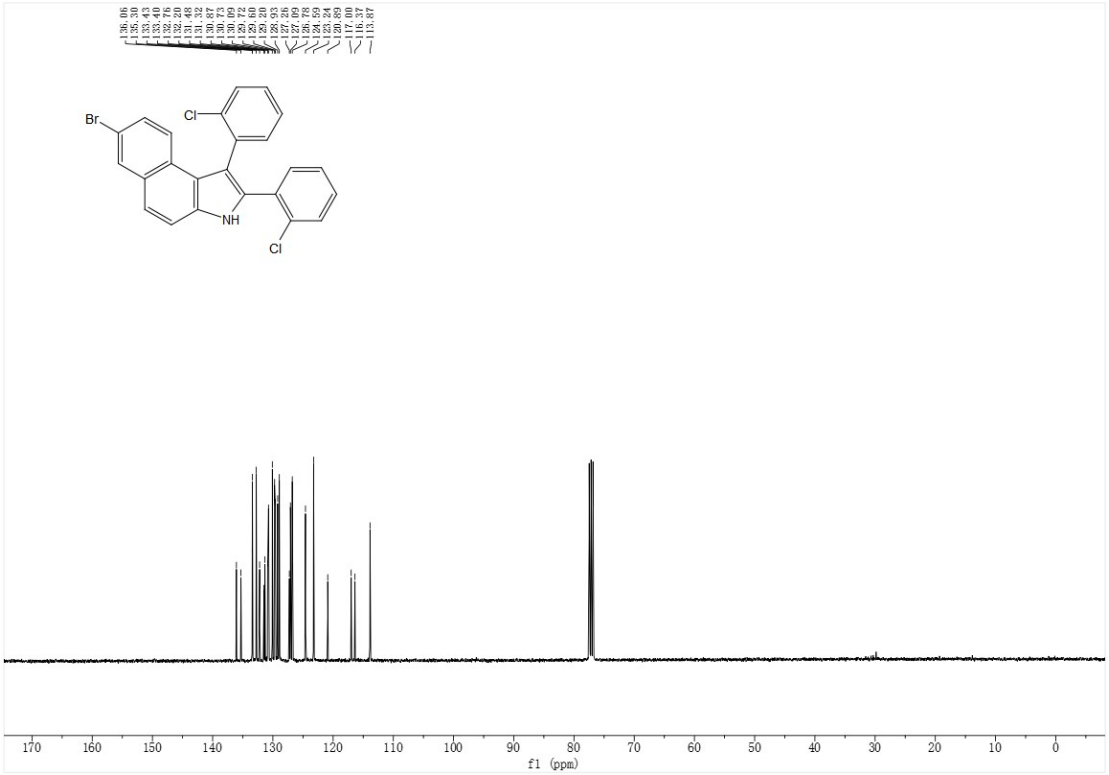
^{13}C NMR spectrum of **3bl** (101 MHz, $CDCl_3$)



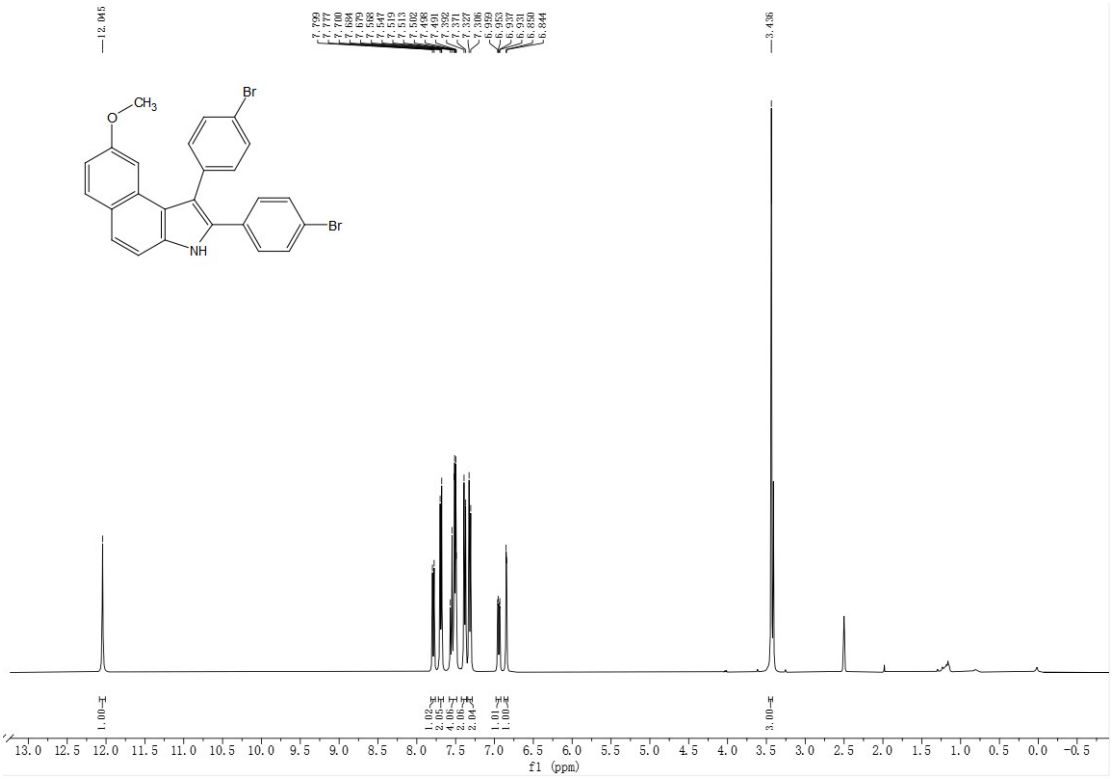
^{1}H NMR spectrum of **3bm** (400 MHz, $CDCl_3$)



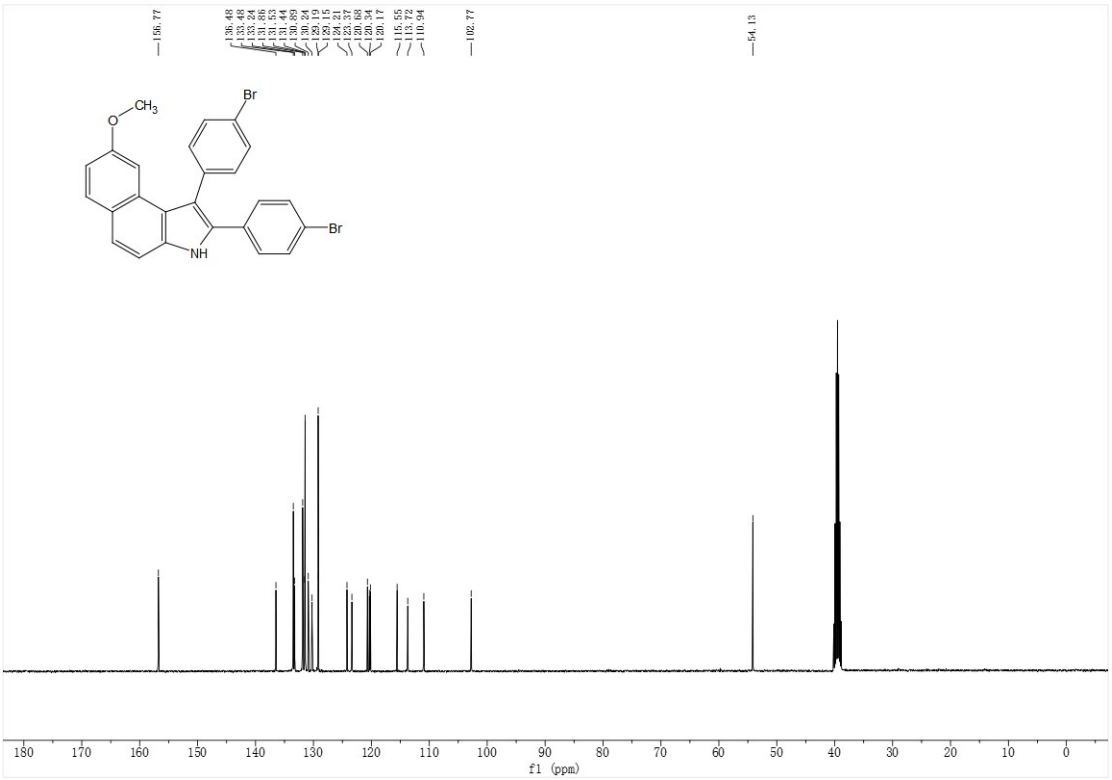
^{13}C NMR spectrum of **3bm** (101 MHz, $CDCl_3$)



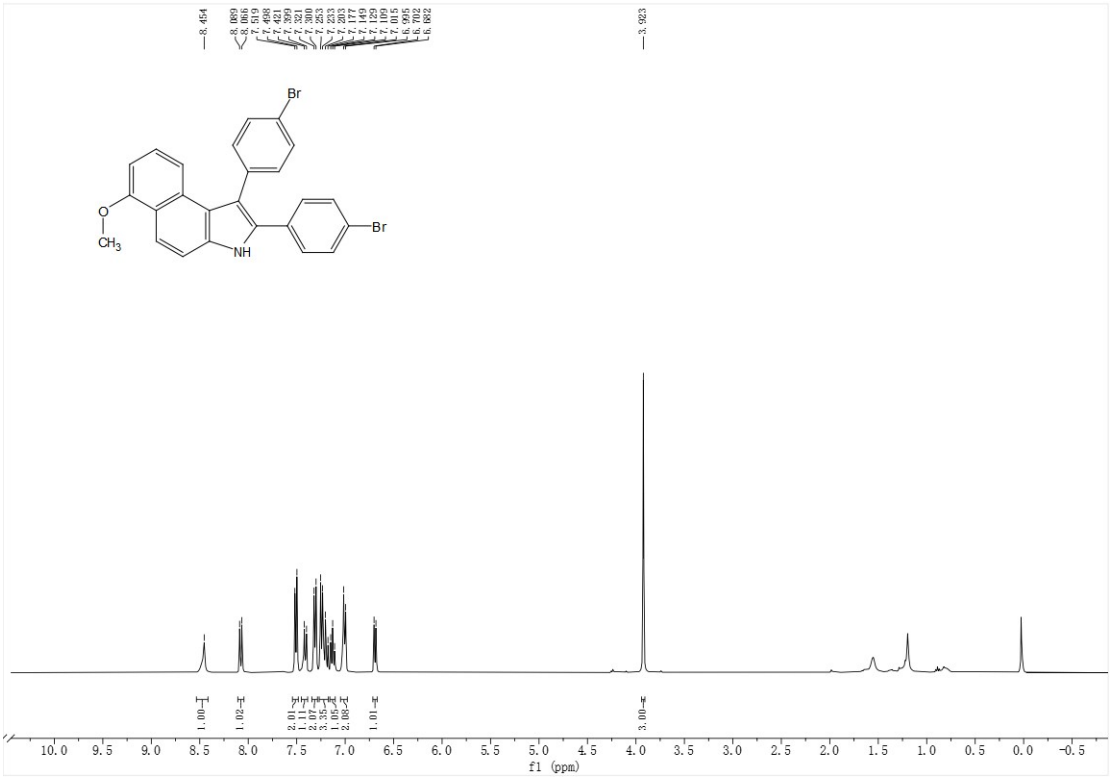
^{1}H NMR spectrum of **3bn** (400 MHz, DMSO-d_6)



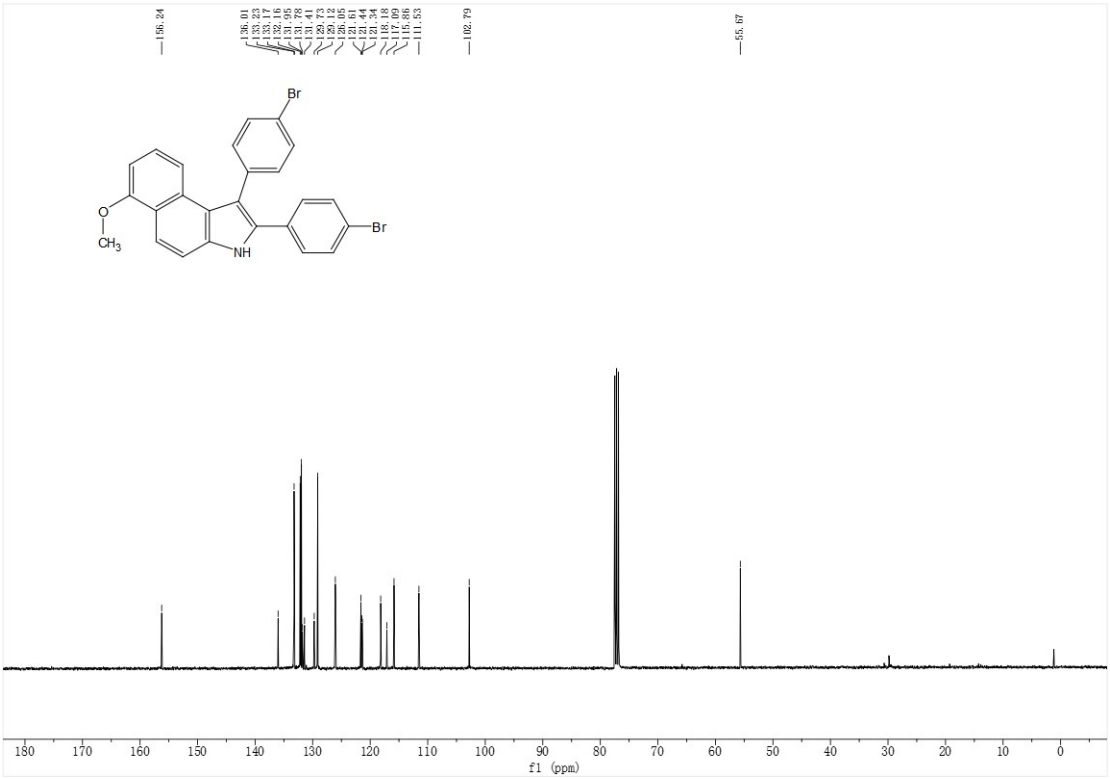
^{13}C NMR spectrum of **3bn** (101 MHz, DMSO-d_6)



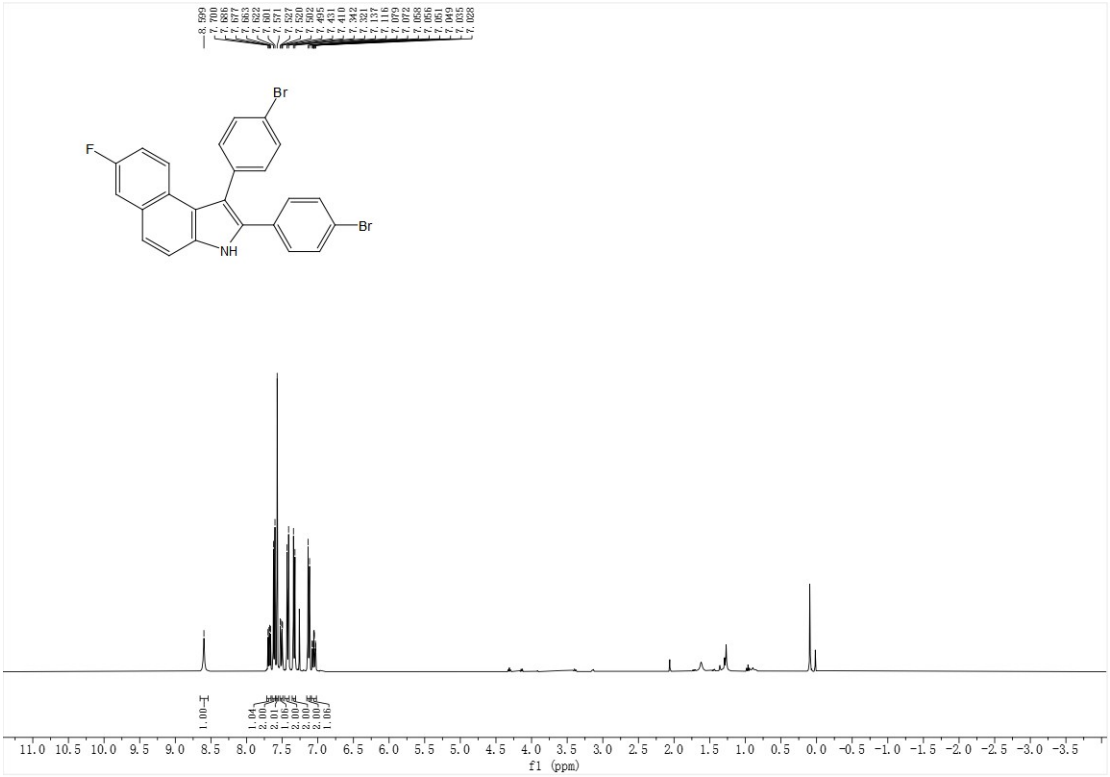
^{1}H NMR spectrum of **3bo** (400 MHz, $CDCl_3$)



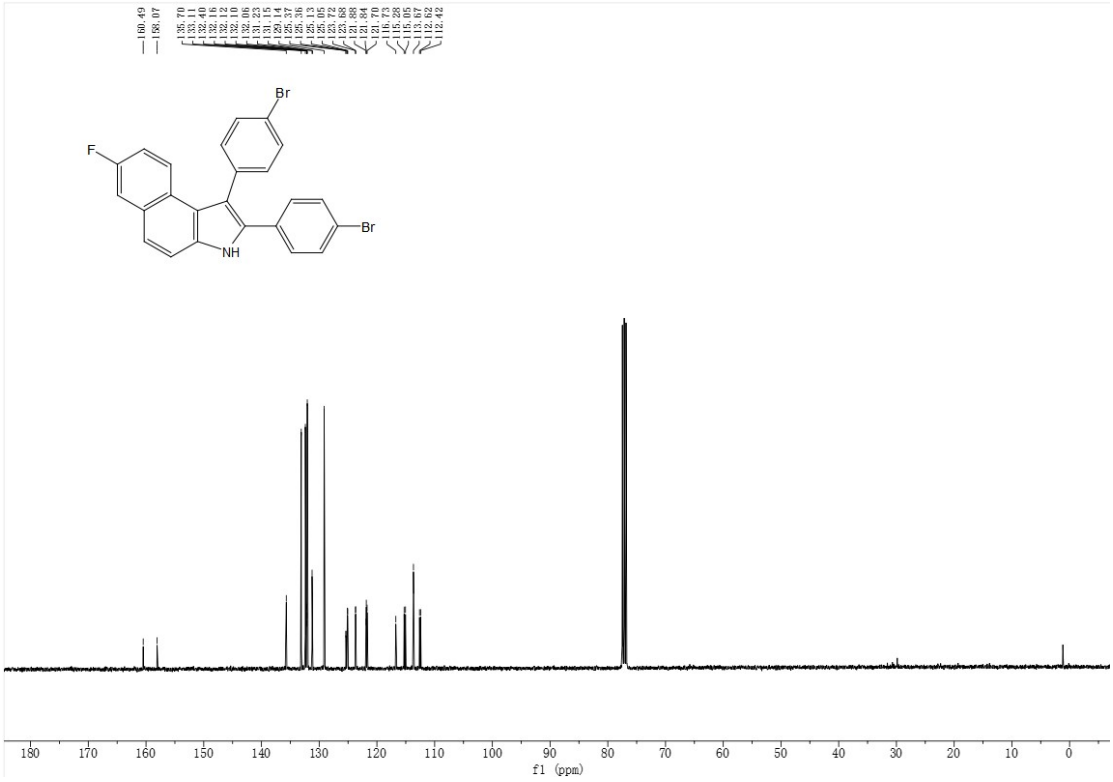
^{13}C NMR spectrum of **3bo** (101 MHz, $CDCl_3$)



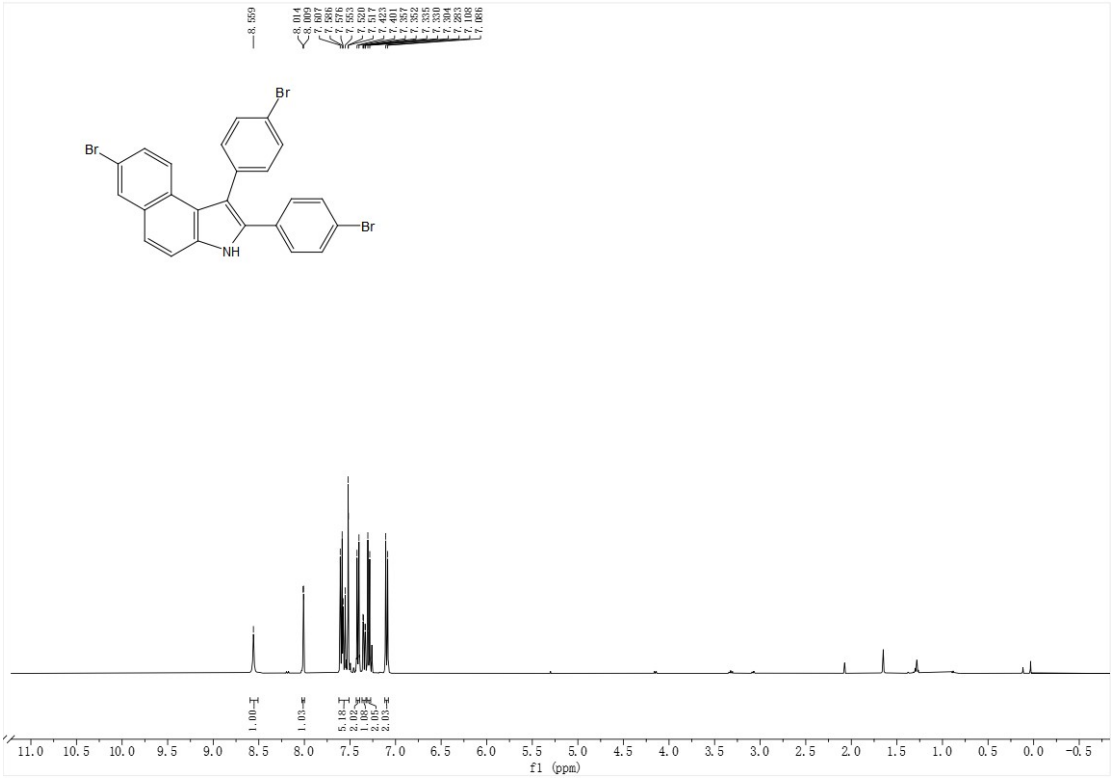
^{1}H NMR spectrum of **3bp** (400 MHz, $CDCl_3$)



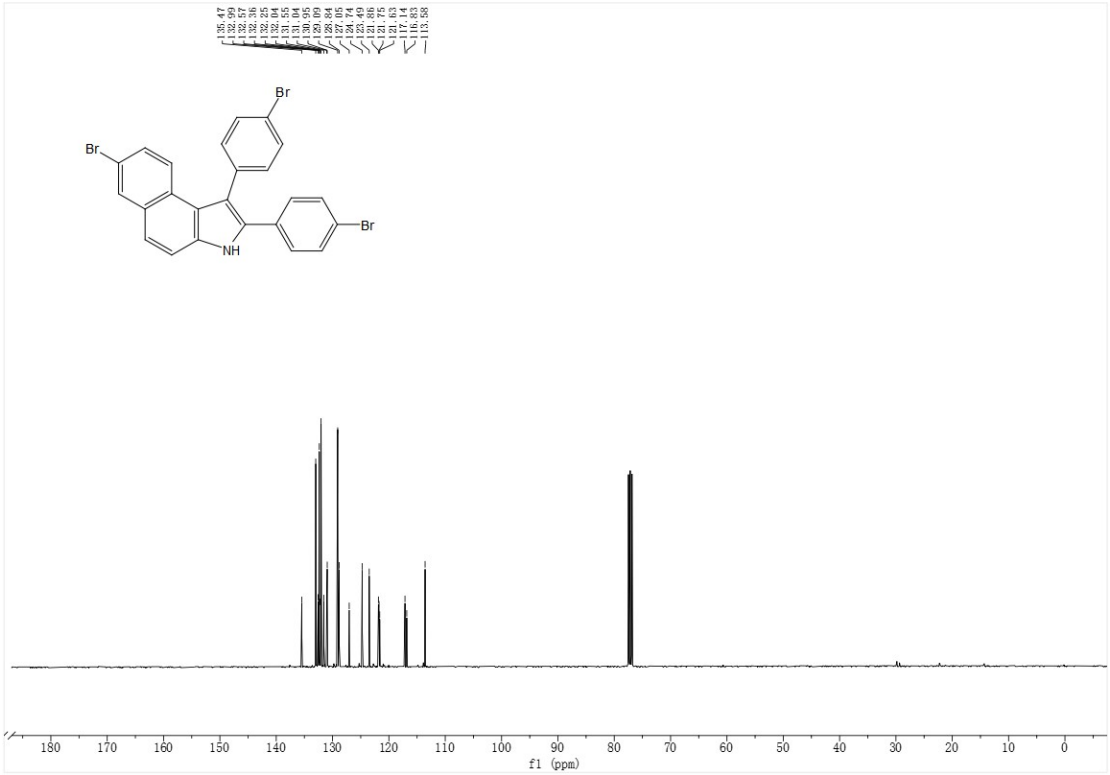
^{13}C NMR spectrum of **3bp** (101 MHz, $CDCl_3$)



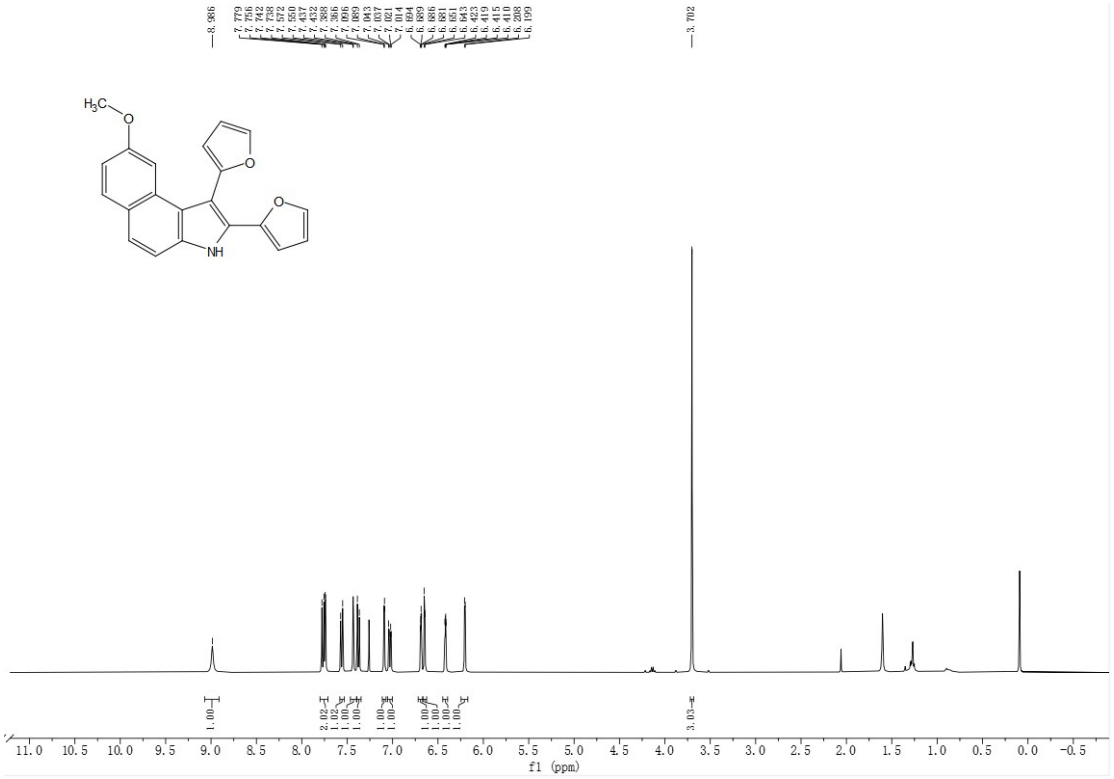
^{1}H NMR spectrum of **3bq** (400 MHz, $CDCl_3$)



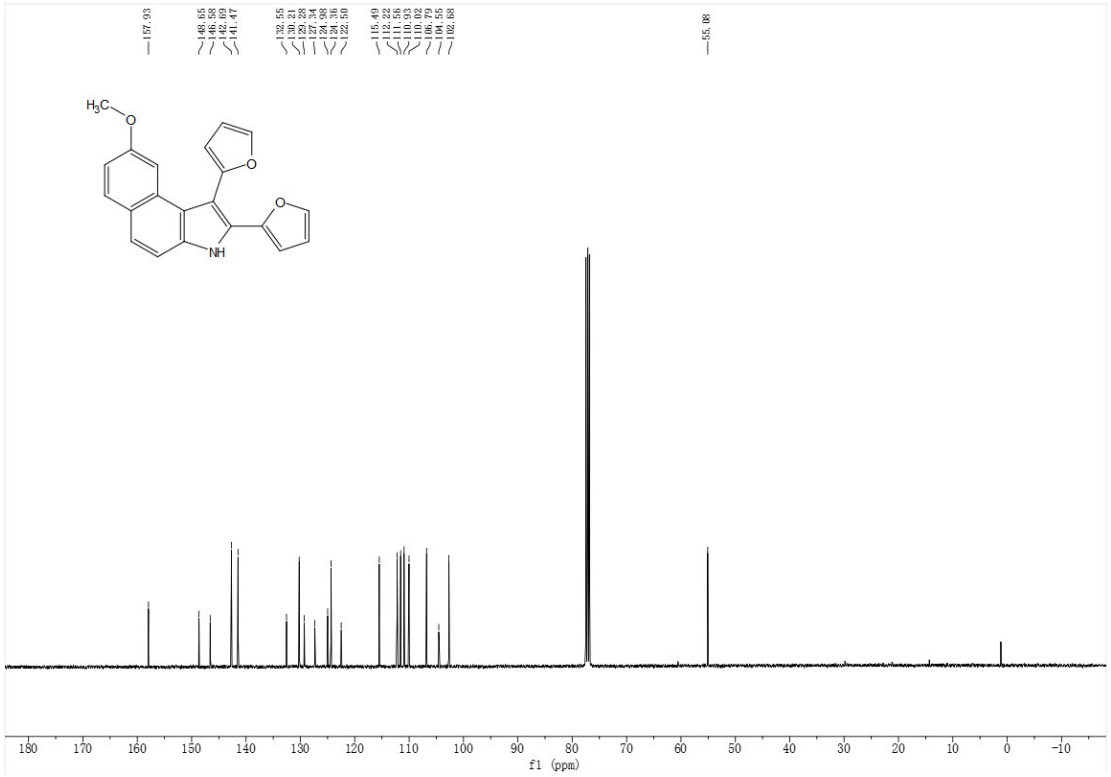
^{13}C NMR spectrum of **3bq** (101 MHz, $CDCl_3$)



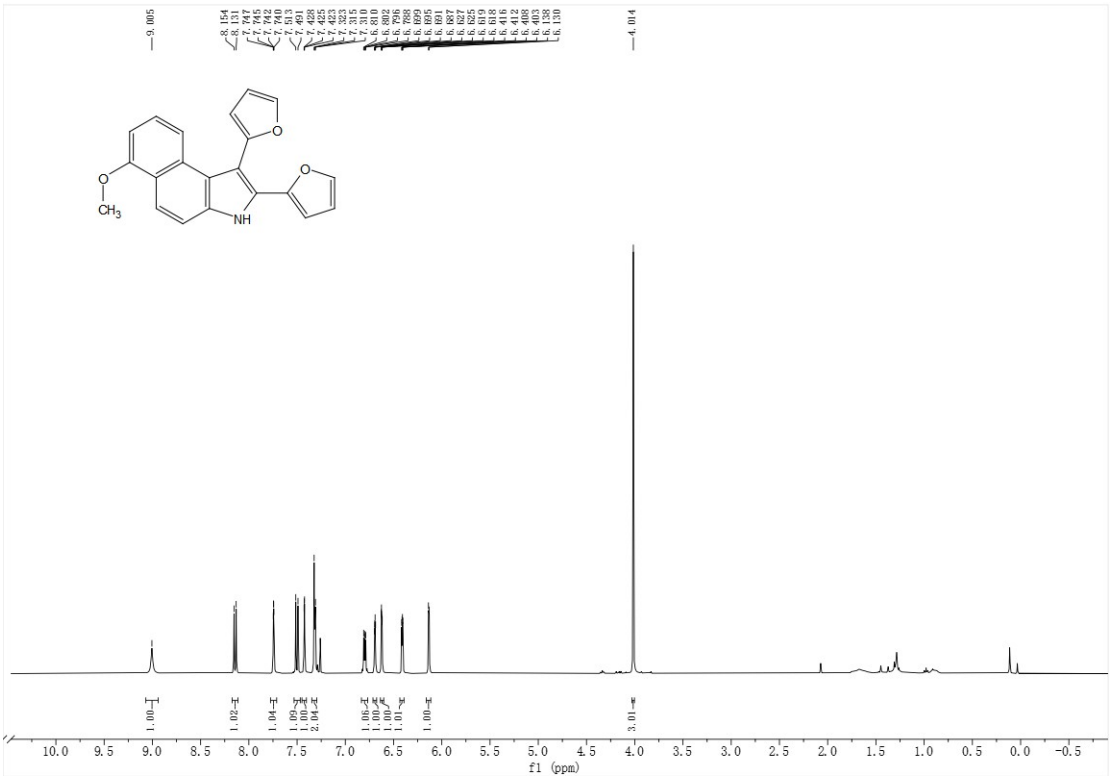
^{1}H NMR spectrum of **3br** (400 MHz, $CDCl_3$)



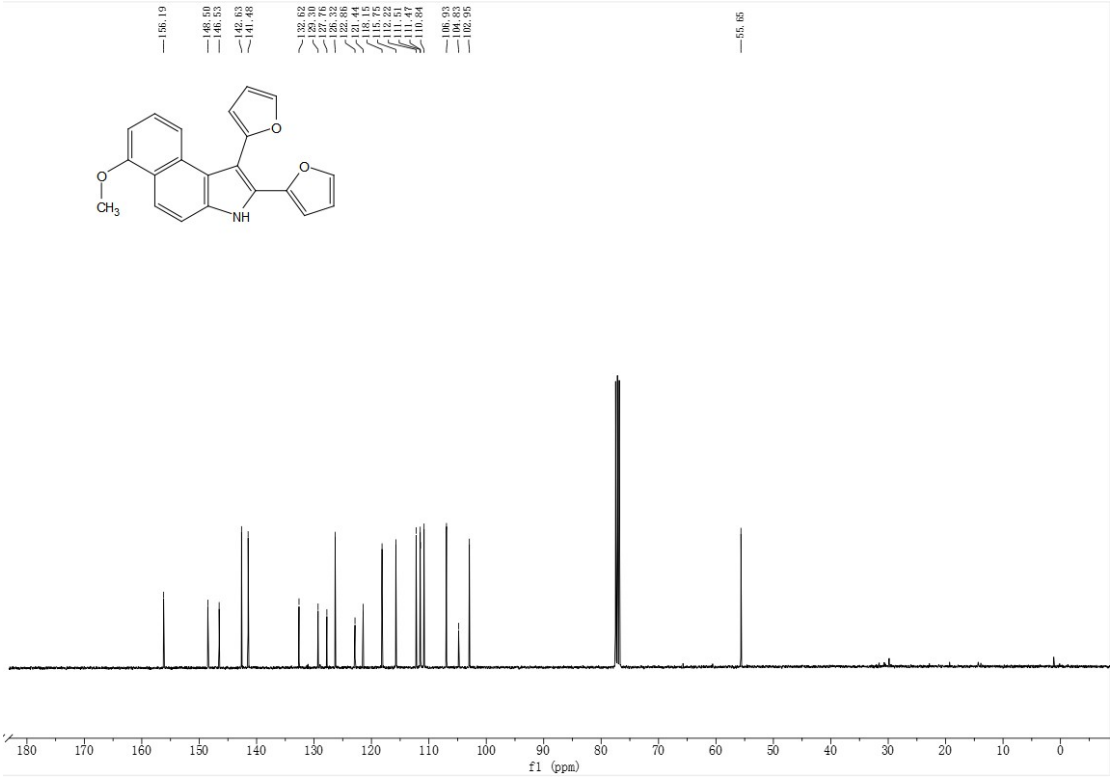
^{13}C NMR spectrum of **3br** (101 MHz, $CDCl_3$)



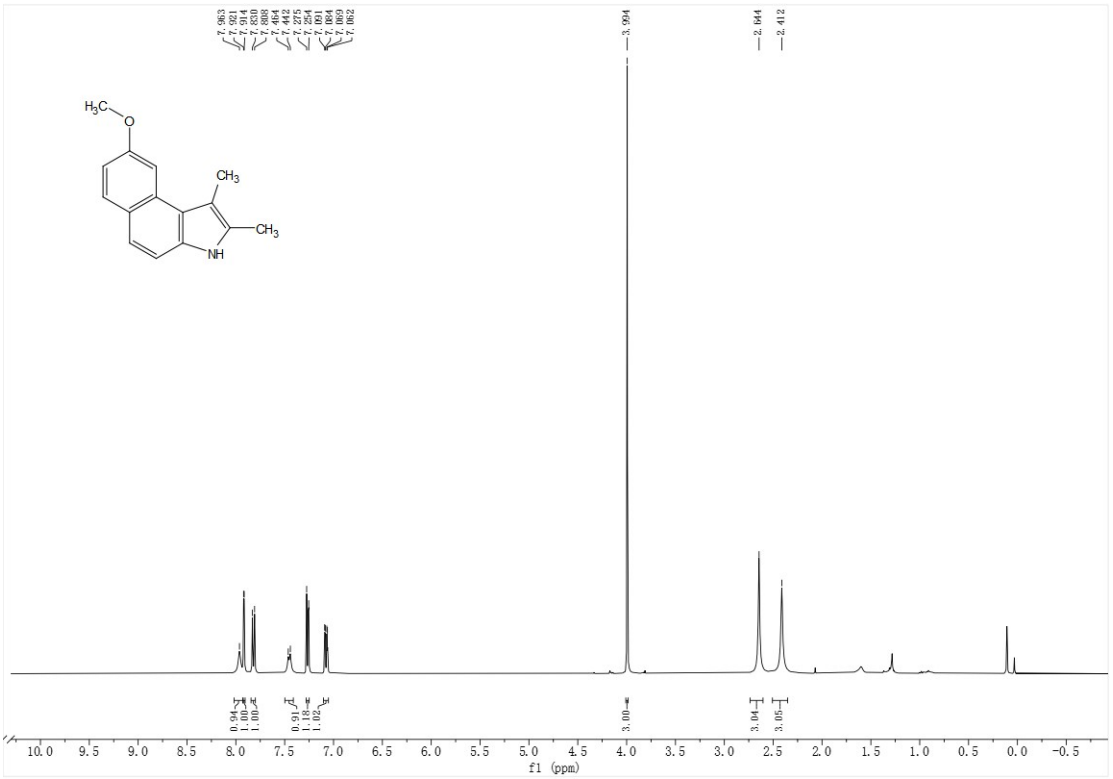
^{1}H NMR spectrum of **3bs** (400 MHz, $CDCl_3$)



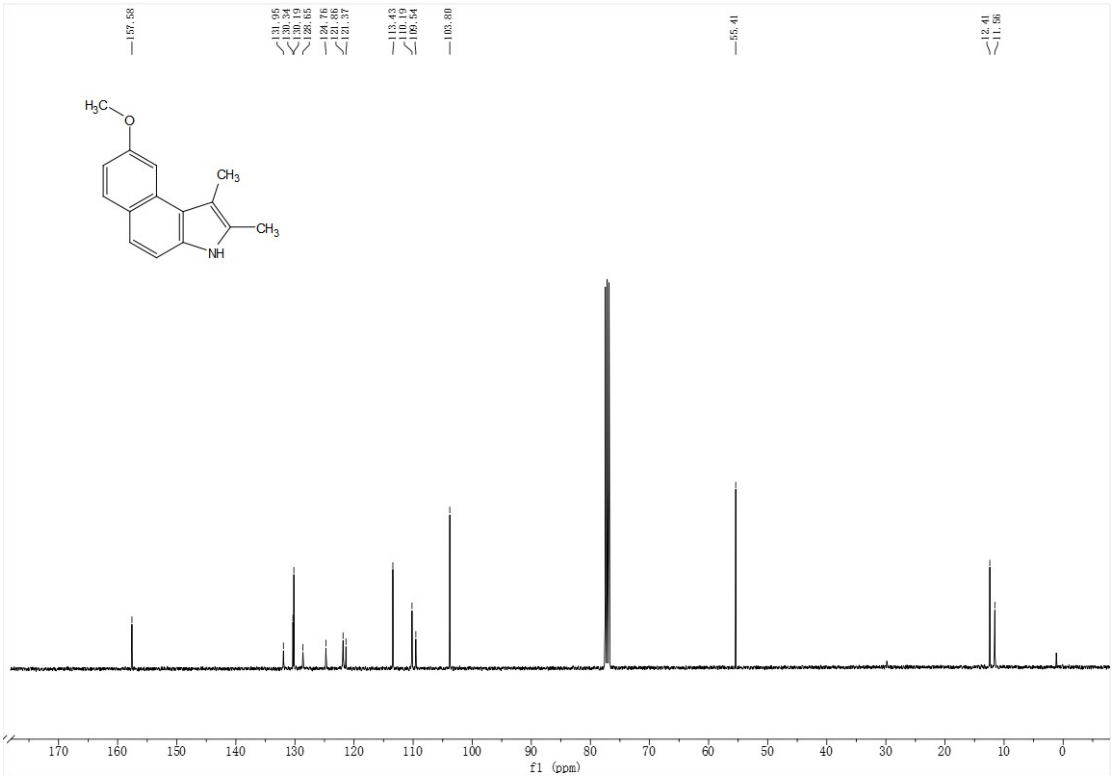
^{13}C NMR spectrum of **3bs** (101 MHz, $CDCl_3$)



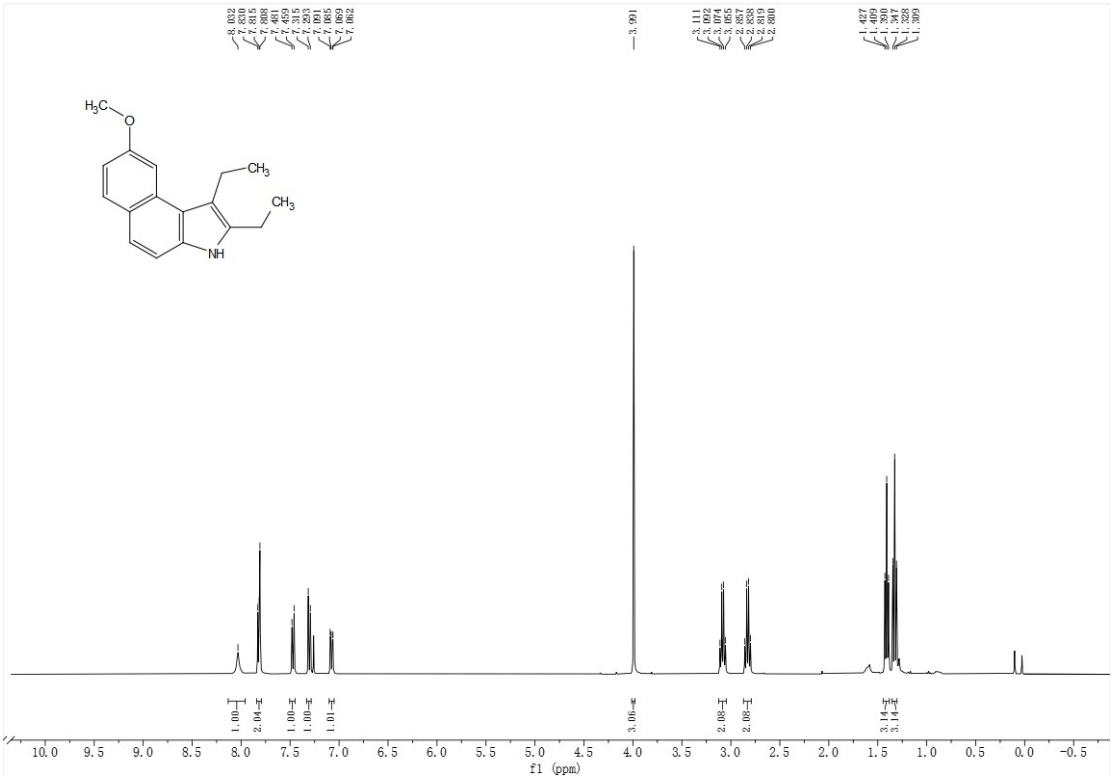
^{1}H NMR spectrum of **3bt** (400 MHz, $CDCl_3$)



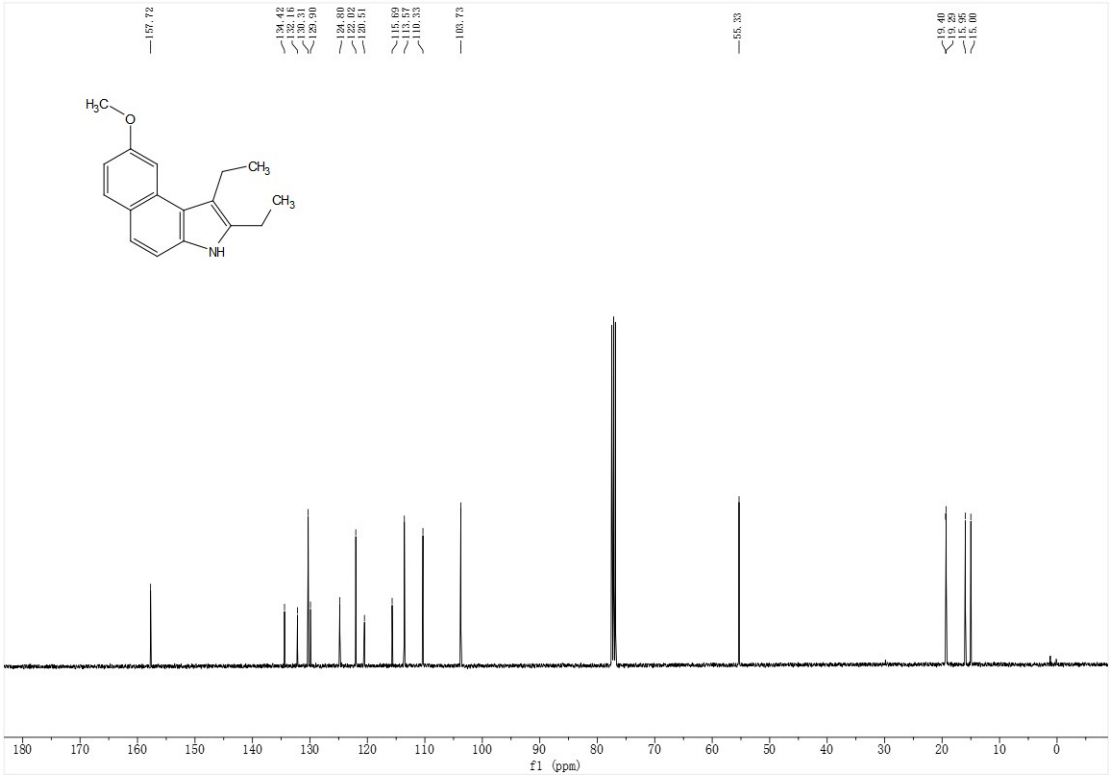
^{13}C NMR spectrum of **3bt** (101 MHz, $CDCl_3$)



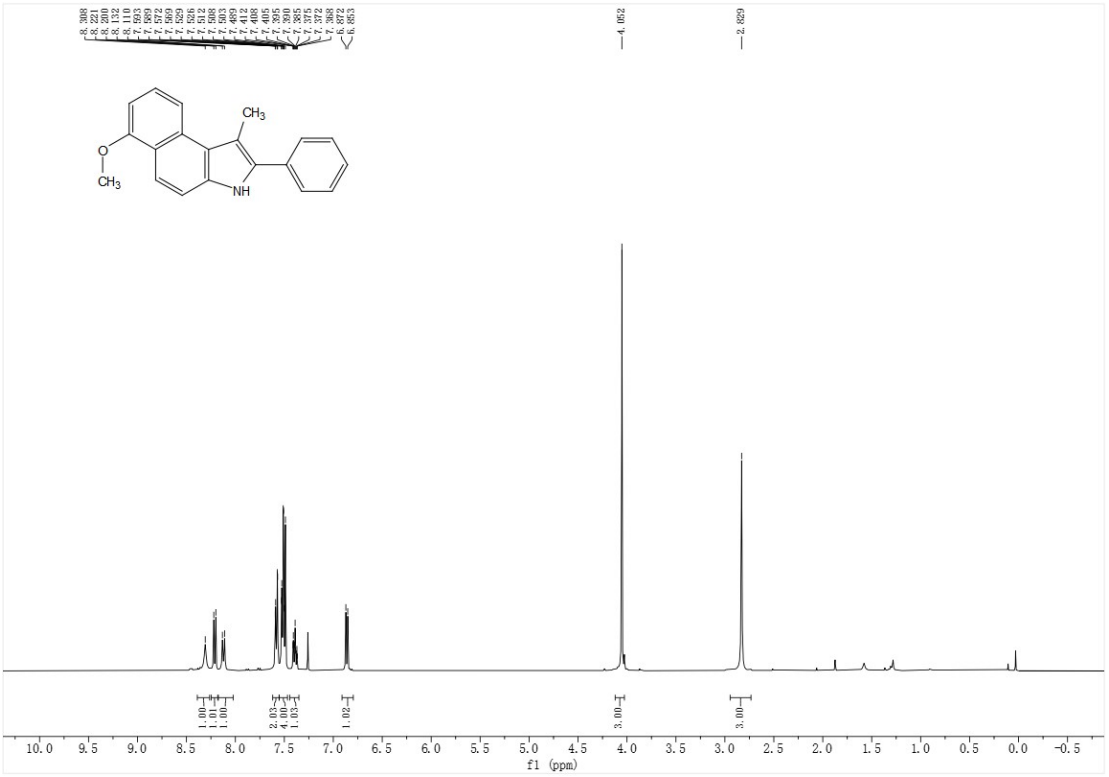
^{1}H NMR spectrum of **3bu** (400 MHz, $CDCl_3$)



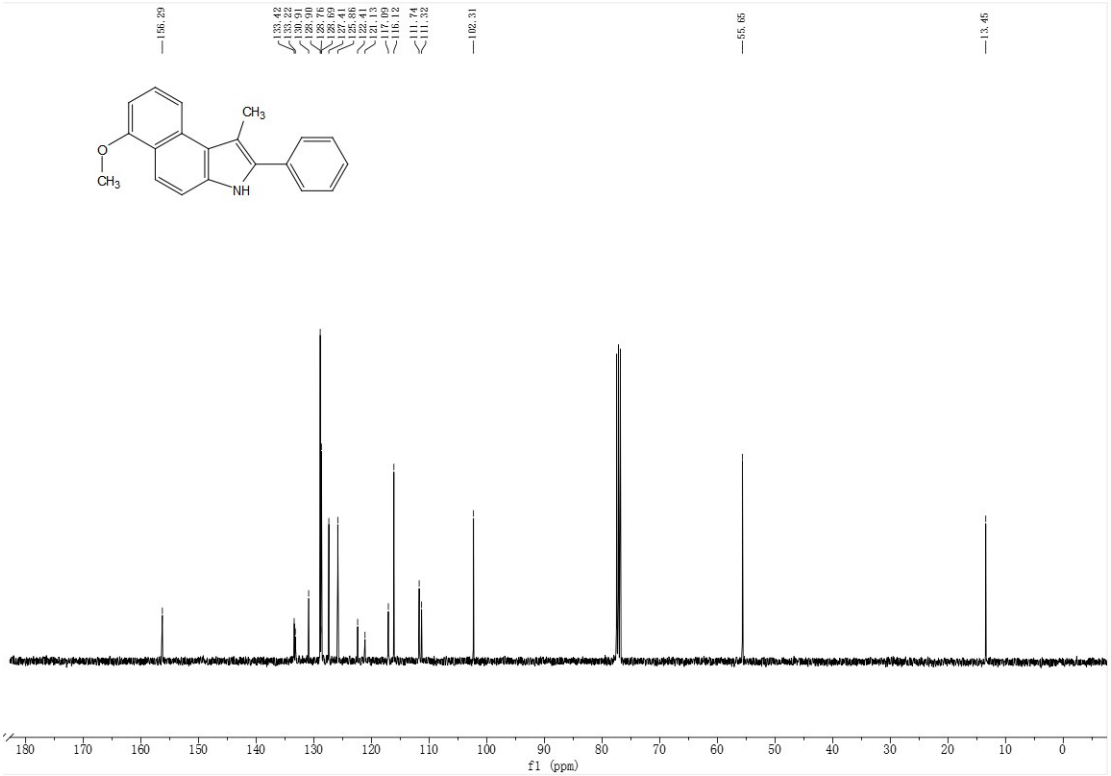
^{13}C NMR spectrum of **3bu** (101 MHz, $CDCl_3$)



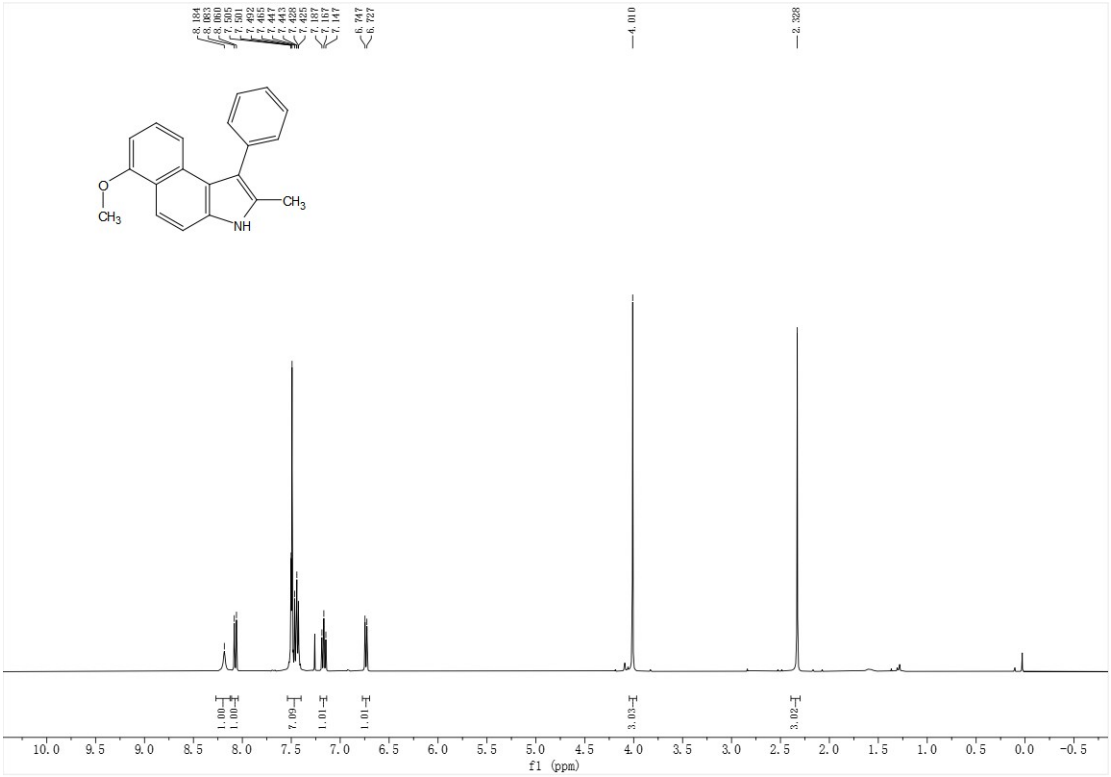
^{1}H NMR spectrum of **3bv** (400 MHz, $CDCl_3$)



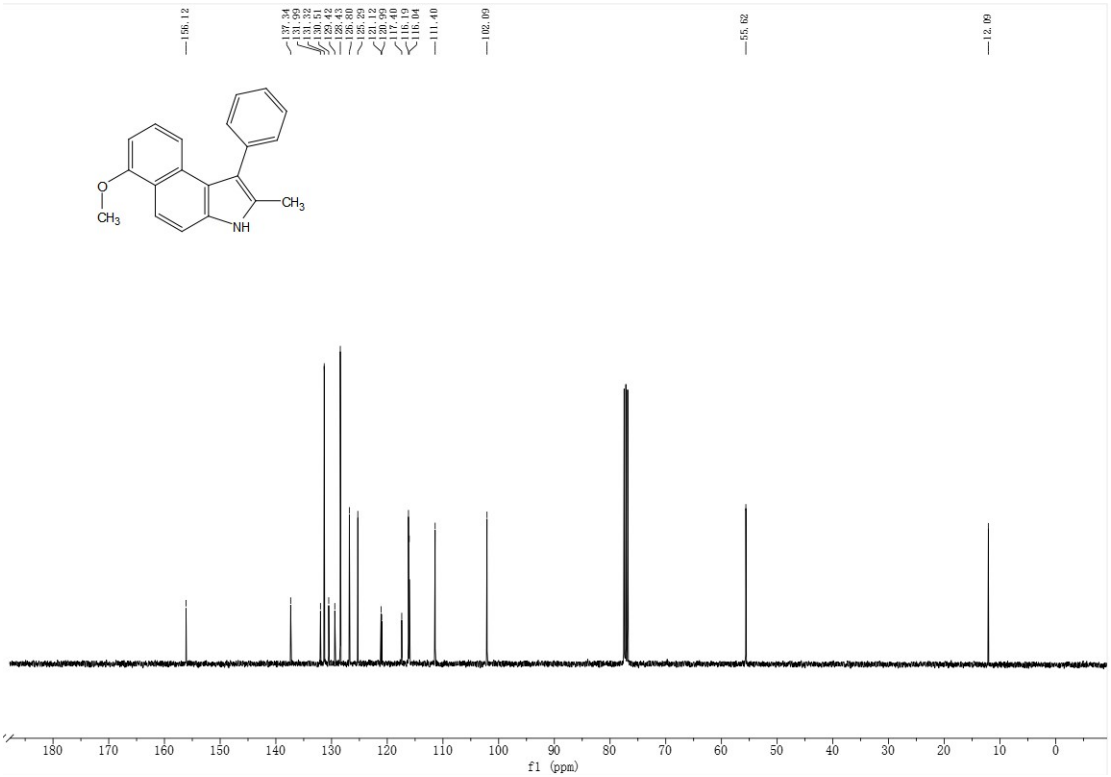
^{13}C NMR spectrum of **3bv** (101 MHz, $CDCl_3$)



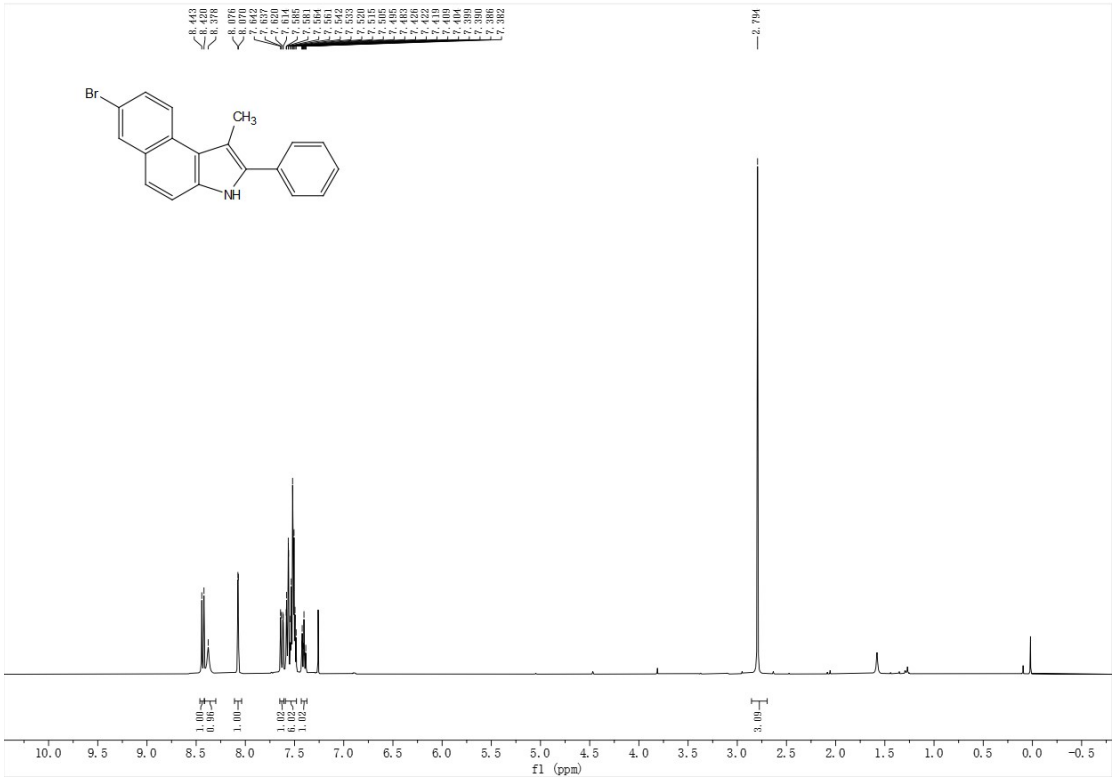
^{1}H NMR spectrum of **3bv'** (400 MHz, $CDCl_3$)



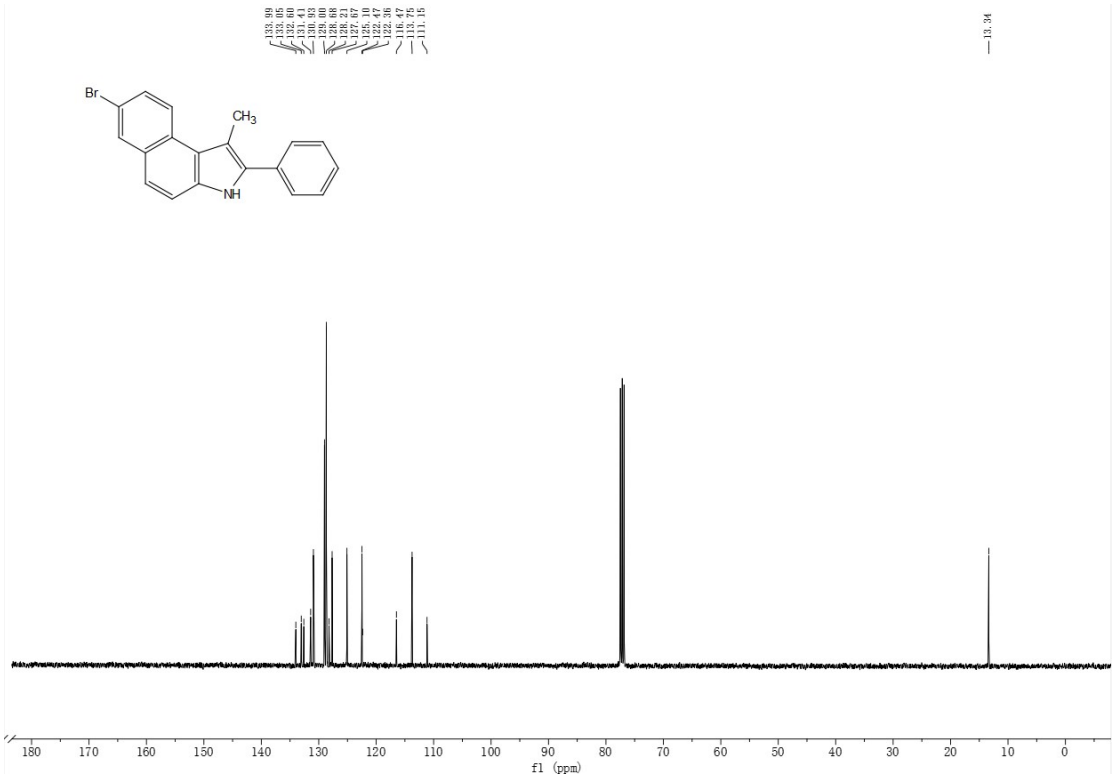
^{13}C NMR spectrum of **3bv'** (101 MHz, $CDCl_3$)



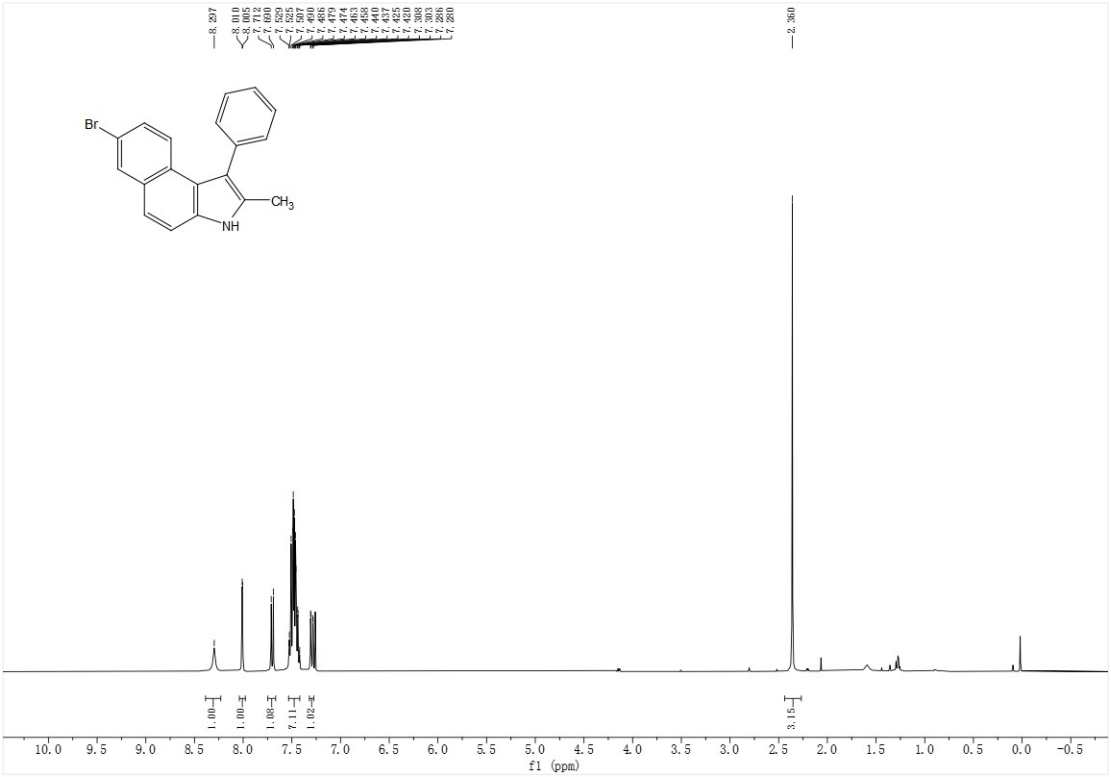
^{1}H NMR spectrum of **3bw** (400 MHz, $CDCl_3$)



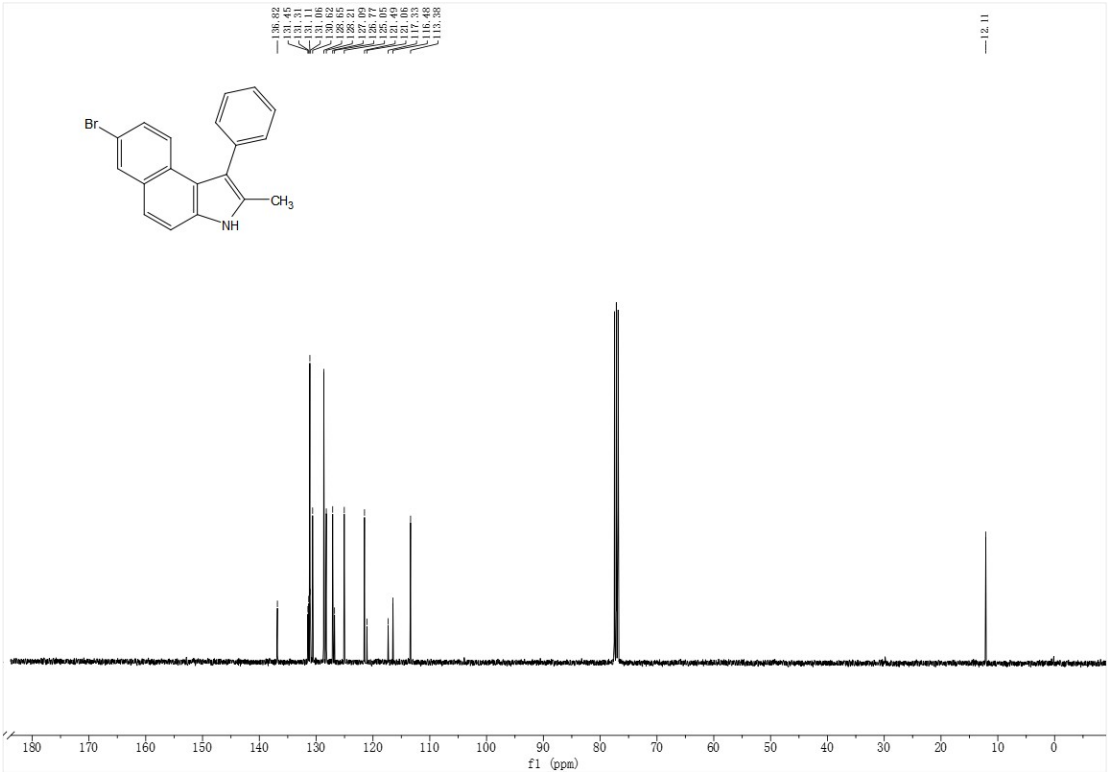
^{13}C NMR spectrum of **3bw** (101 MHz, $CDCl_3$)



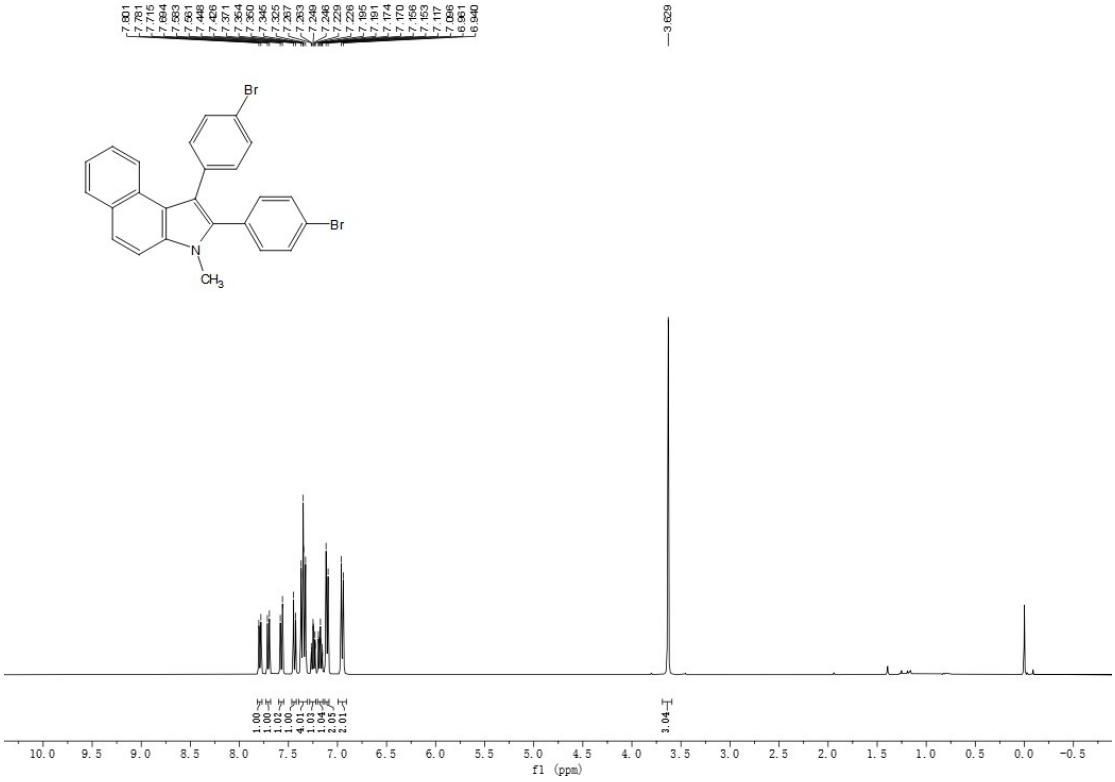
^{1}H NMR spectrum of **3bw'** (400 MHz, $CDCl_3$)



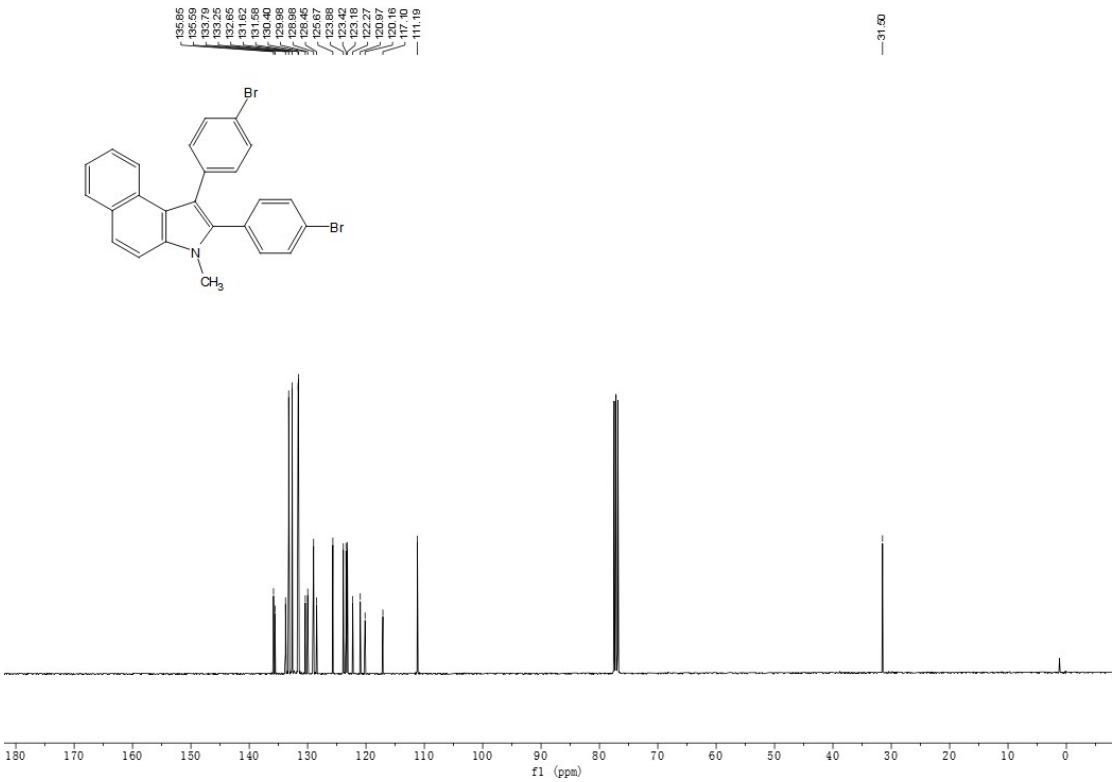
^{13}C NMR spectrum of **3bw'** (101 MHz, $CDCl_3$)



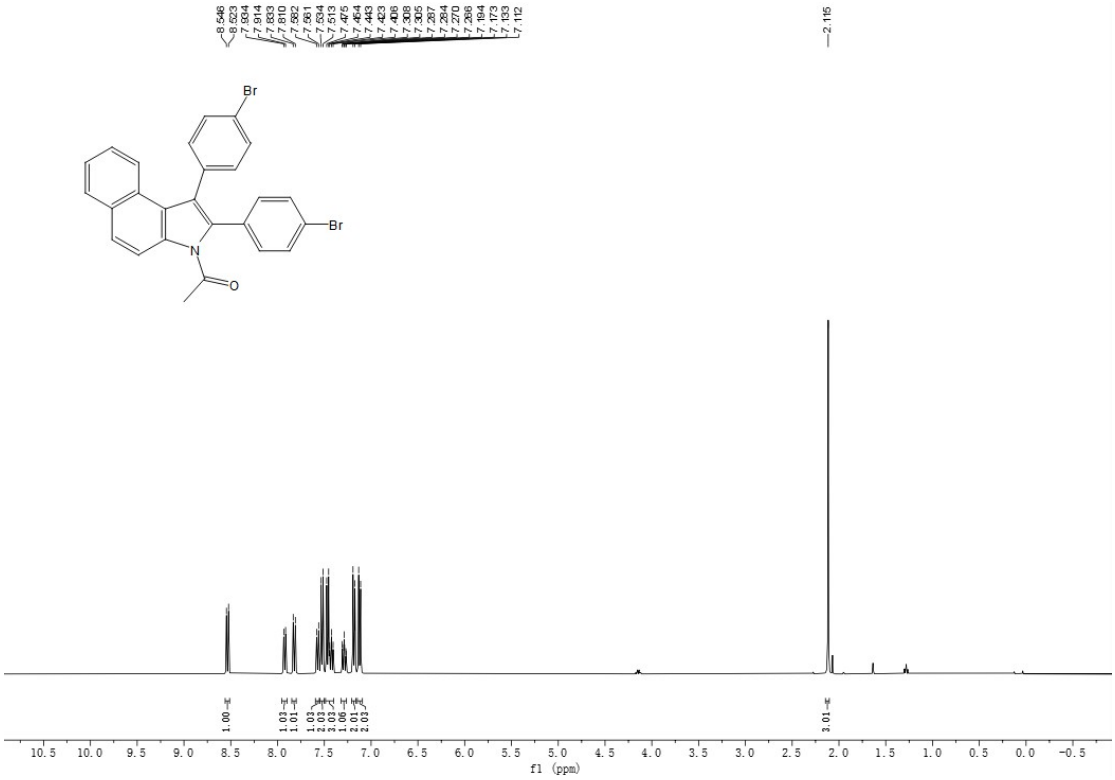
^{1}H NMR spectrum of **4a** (400 MHz, $CDCl_3$)



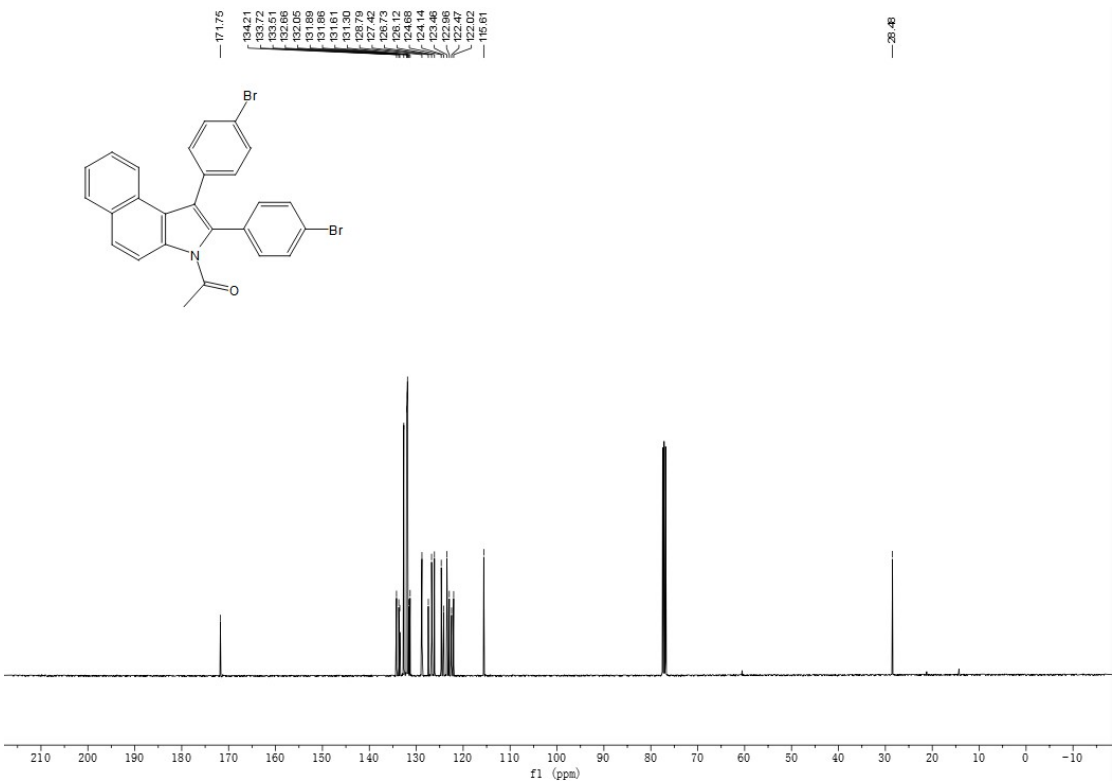
^{13}C NMR spectrum of **4a** (101 MHz, $CDCl_3$)



^{1}H NMR spectrum of **4b** (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of **4b** (101 MHz, $CDCl_3$)



6. UV-vis absorption and fluorescence emission spectra

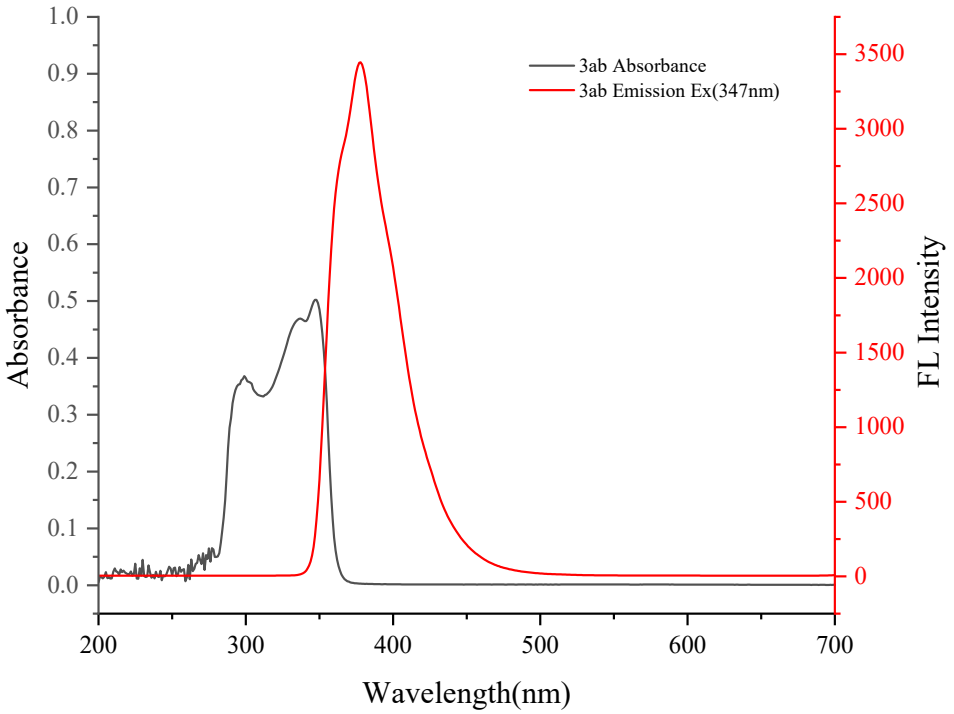


Figure S1. UV-vis absorption and fluorescence emission spectra of **3ab** in MeOH at RT (10^{-5} M).

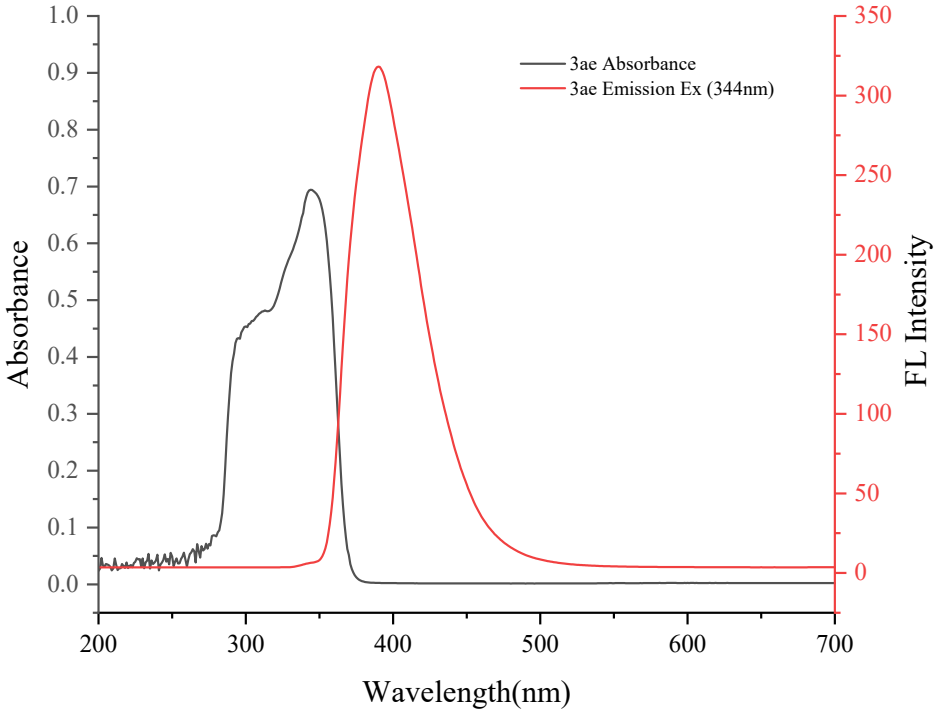


Figure S2. UV-vis absorption and fluorescence emission spectra of **3ae** in MeOH at RT (10^{-5} M).

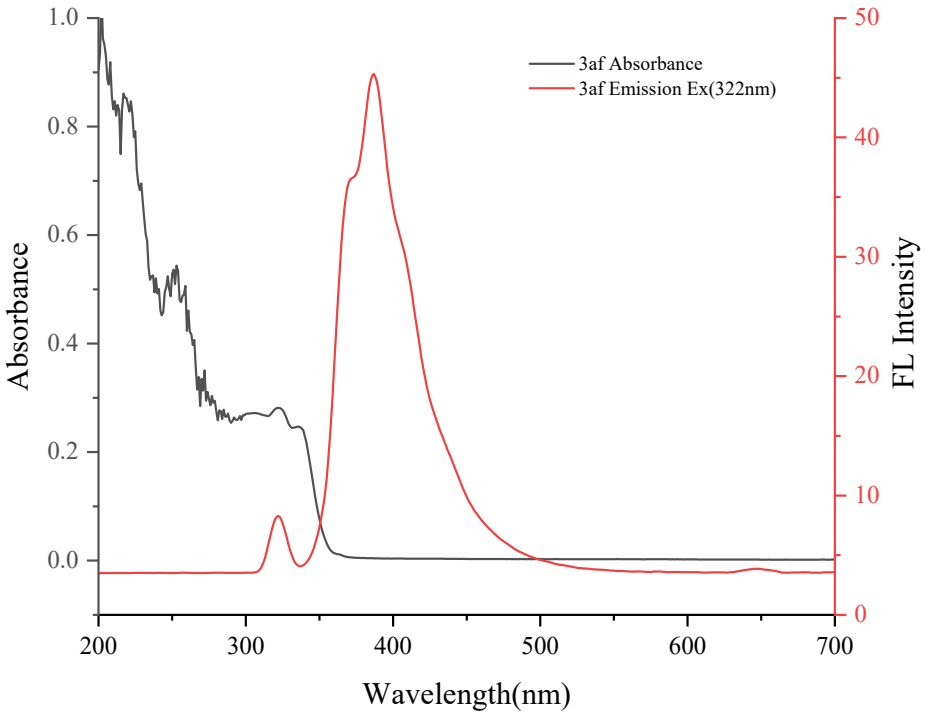


Figure S3. UV-vis absorption and fluorescence emission spectra of **3af** in MeOH at RT (10^{-5} M).

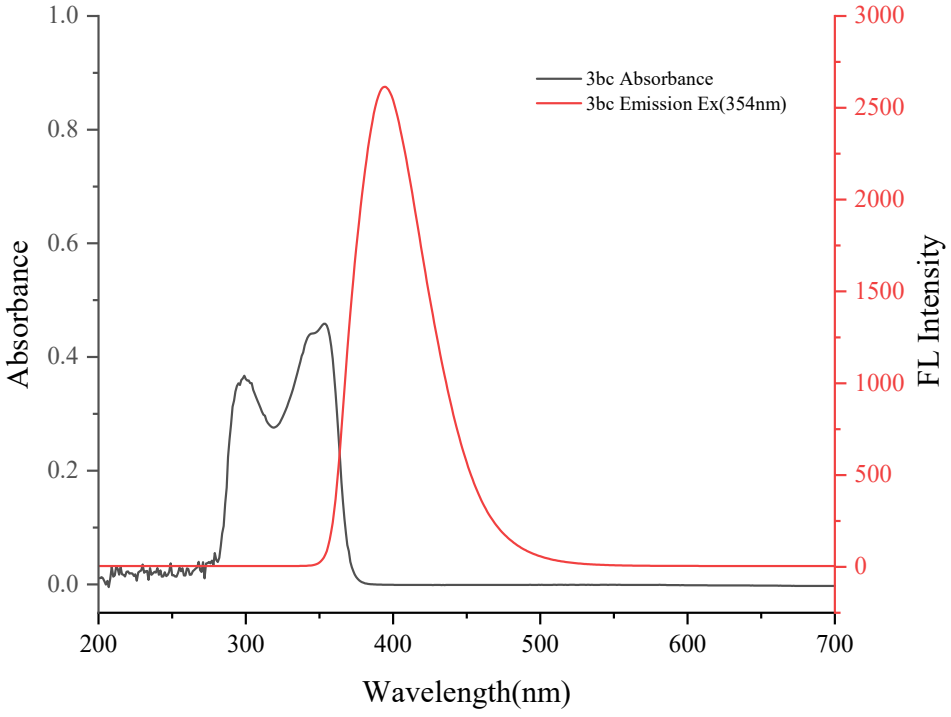


Figure S4. UV-vis absorption and fluorescence emission spectra of **3bc** in MeOH at RT (10^{-5} M).

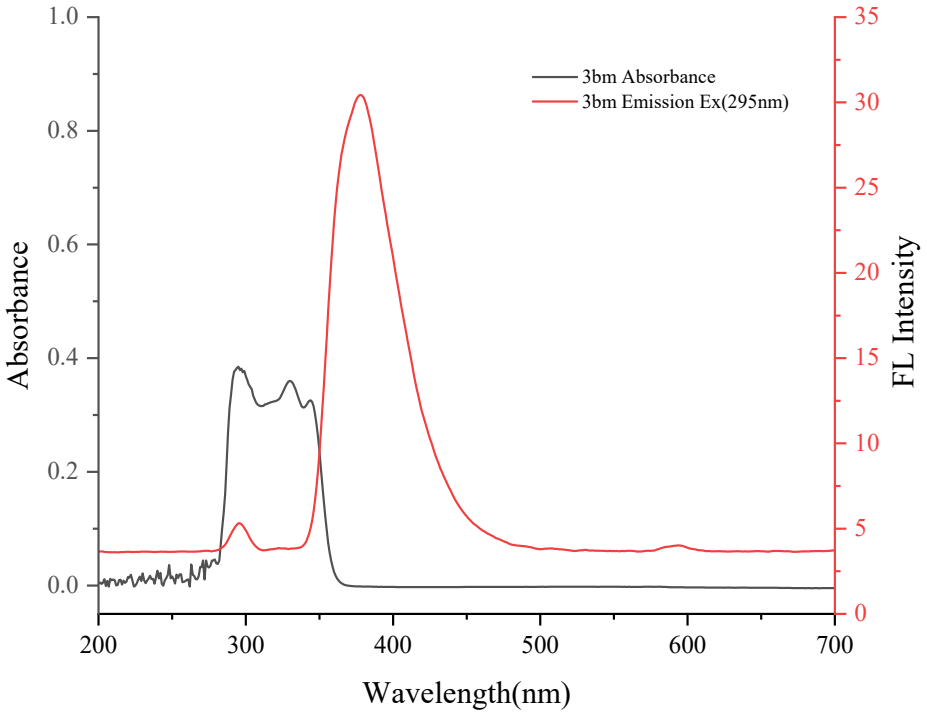


Figure S5. UV-vis absorption and fluorescence emission spectra of **3bm** in MeOH at RT (10^{-5} M).

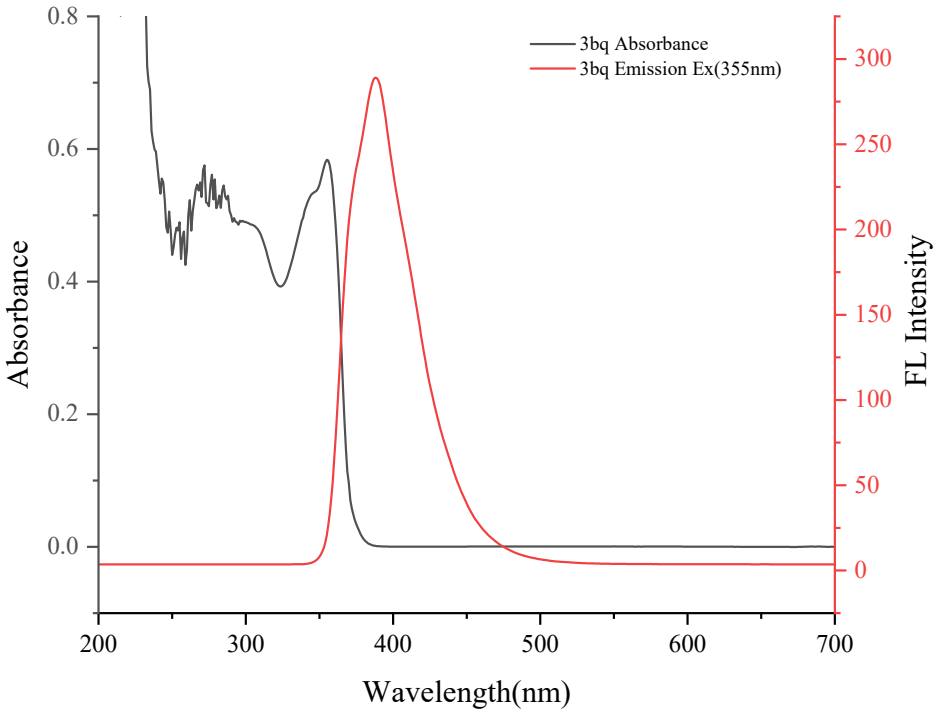


Figure S6. UV-vis absorption and fluorescence emission spectra of **3bq** in MeOH at RT (10^{-5} M).

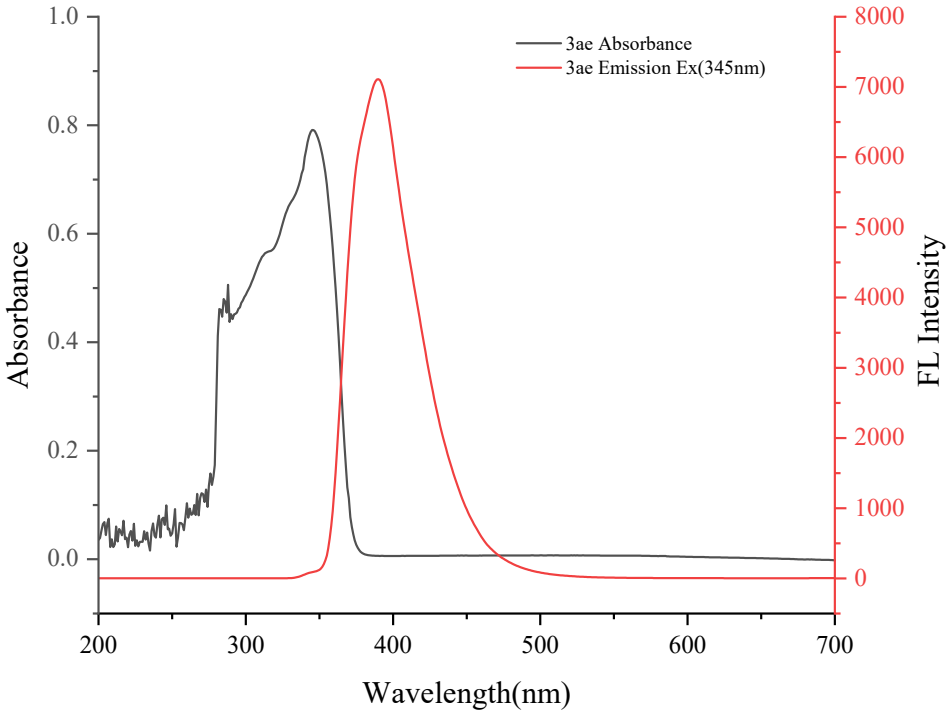


Figure S7. UV-vis absorption and fluorescence emission spectra of **3ae** in toluene at RT (10^{-5} M).

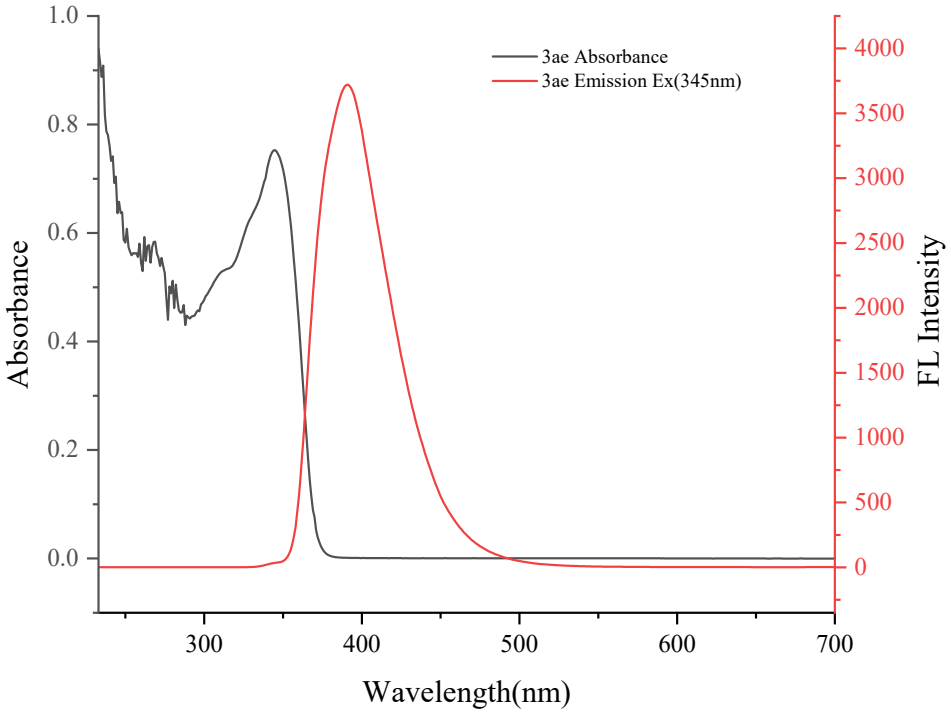


Figure S8. UV-vis absorption and fluorescence emission spectra of **3ae** in DCM at RT (10^{-5} M).

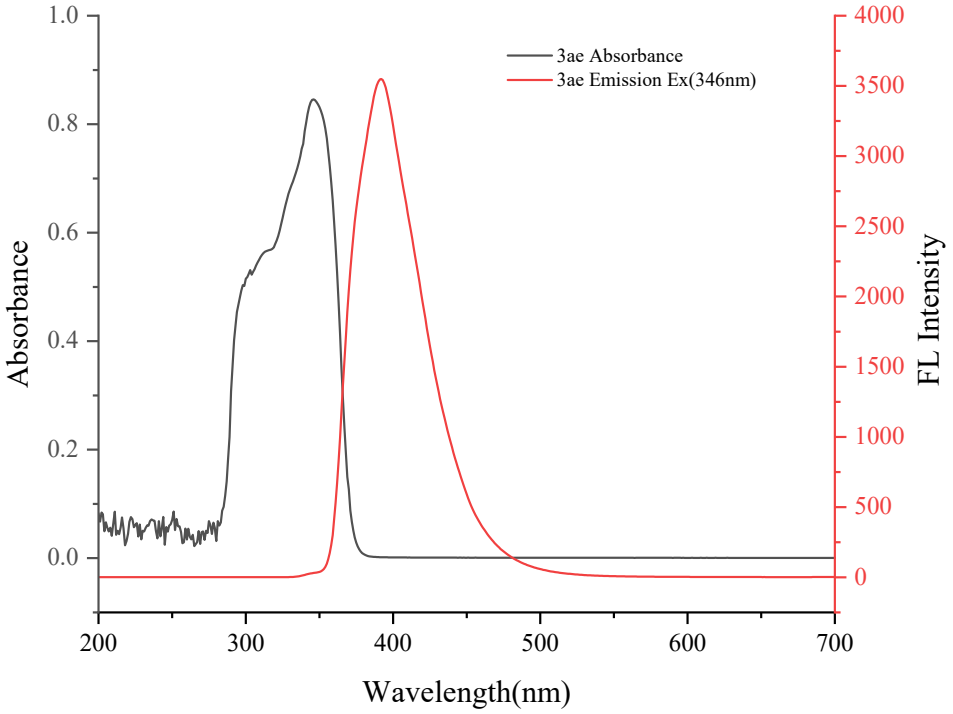


Figure S9. UV-vis absorption and fluorescence emission spectra of **3ae** in THF at RT (10^{-5} M).

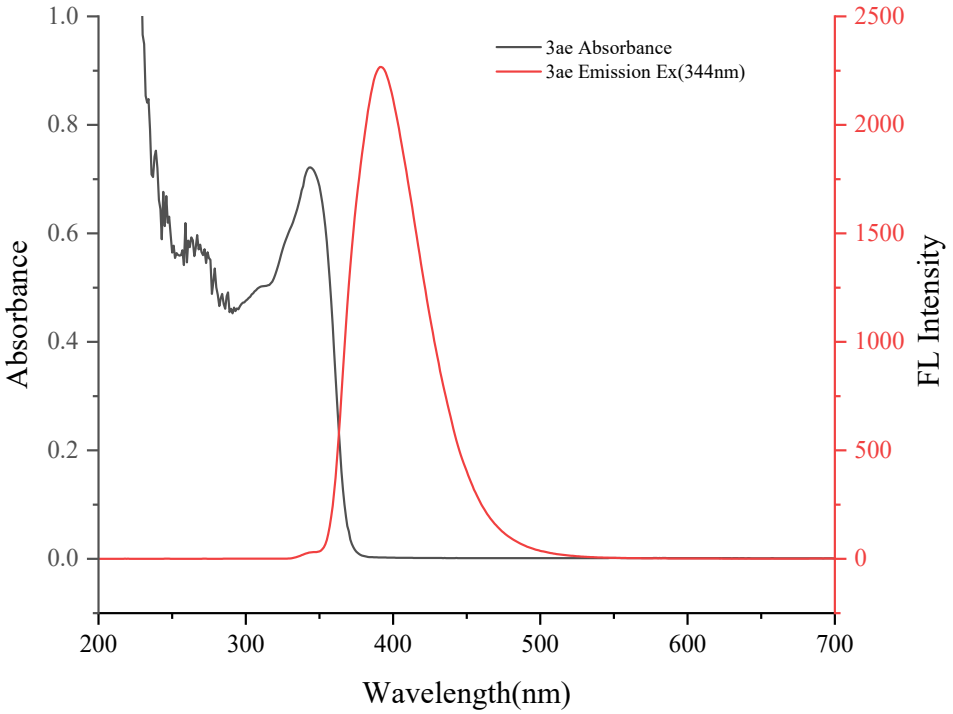


Figure S10. UV-vis absorption and fluorescence emission spectra of **3ae** in MeCN at RT (10^{-5} M).

7. HRMS of the imine/enamine intermediate

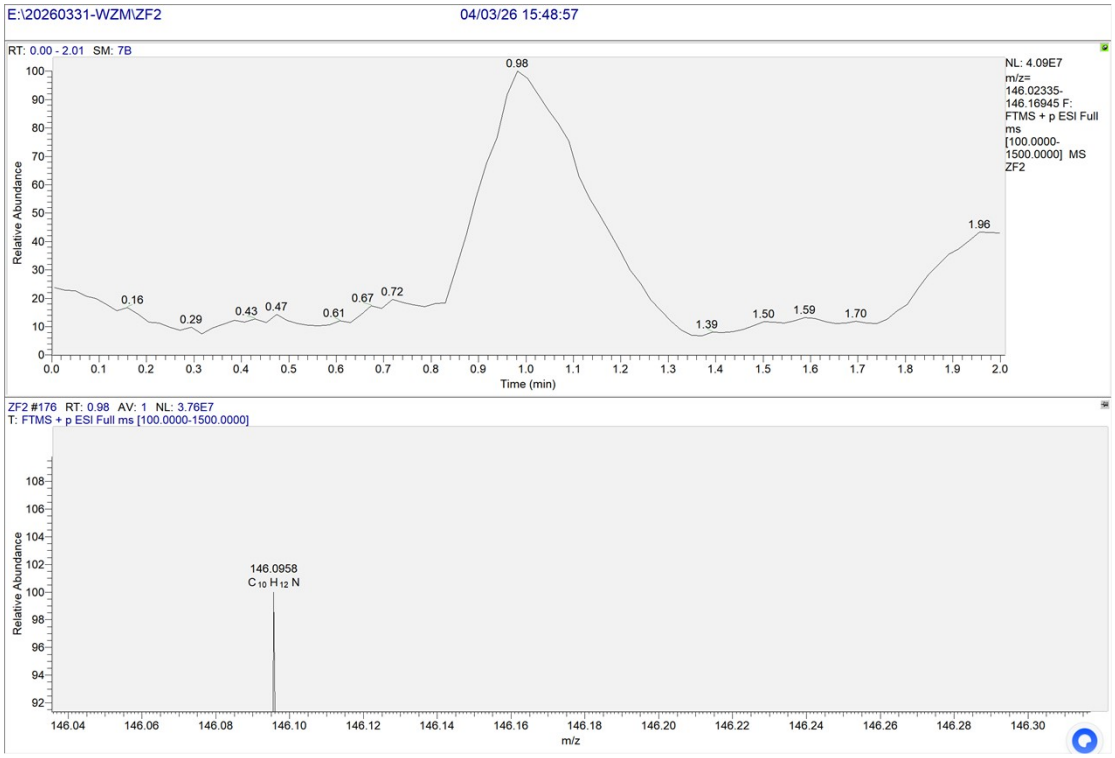


Figure S11. The picture of HRMS of the imine/enamine intermediate (the reaction of 2-tetralone with NH_4OAc within 10 min. Calcd. for $C_{10}H_{12}N^+$ $(M+H)^+$ 146.0964, found 146.0958)