Supporting Information for

Regioselective Synthesis of 2,3′-Biindoles Mediated by an NBS-Promoted Homo-coupling of Indoles

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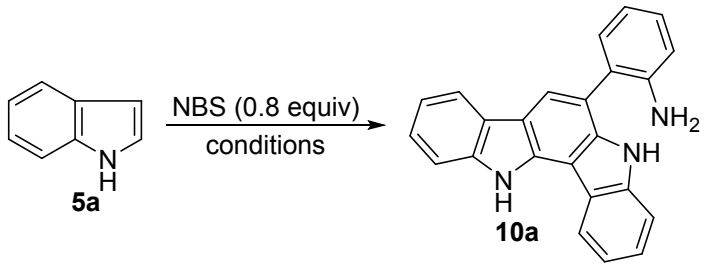
1. General Methods

^{1}H and ^{13}C NMR spectra were recorded on a Bruker spectrometers at 400 and 100 MHz, respectively. 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.

2. Table S1 Condition optimization of the NBS-promoted homo-coupling of indoles for the synthesis of 2-(5,12-dihydroindolo[3,2-*a*]carbazol-6-yl)anilines 10.[a]



entry	catalyst (0.2 equiv)	solvent	temp. (°C)	yield (%)[b]
1	CuI	$CHCl_3$	15	trace
2	$CuSO_4$	$CHCl_3$	15	trace
3	$Pd(OAc)_2$	$CHCl_3$	15	10
4	$NiSO_4$	$CHCl_3$	15	13
5	$FeCl_2$	$CHCl_3$	15	trace
6	$FeCl_3$	$CHCl_3$	15	trace
7	-	DMSO	15	trace
8	-	DMF	15	trace
9	-	DCE	15	15
10	-	$CH_3CO_2C_2H_5$	15	27
11	-	H_2O	15	trace
12	-	CH_3CN	15	35
13	-	Pyridine	15	trace
14	-	EtOH	15	trace
15	-	$CHCl_3$	15	45
16	-	CH_2Cl_2	15	38
17	-	$CHCl_3$	5	5
18	-	$CHCl_3$	15	8
19	-	$CHCl_3$	25	35
20	-	$CHCl_3$	35	61
21	-	$CHCl_3$	40	36
22	-	$CHCl_3$	45	20

[a] Conditions: **5** (0.3 mmol) and NBS (0.24 mmol), in $CHCl_3$ (1 mL), 12 h, under open air. [b]Isolated yield.

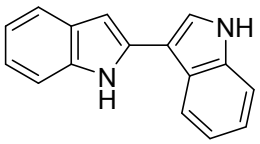
3.1 General Procedure for the Preparation of 6.

To a solution of indole (0.3 mmol) in $CHCl_3$ (1 mL) was added NBS (0.24 mmol) under an air atmosphere and the mixture was stirred at 15 °C for 6 h. The reaction mixture was concentrated

under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EtOAc/PE = 1:1) to yield the corresponding product **6**.

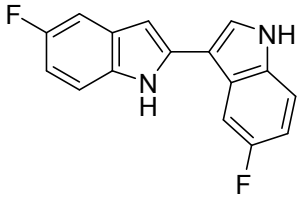
3.2 Spectroscopic Data of the Products 6 and 9.

1*H*,1'*H*-2,3′-Biindole (**6a**)



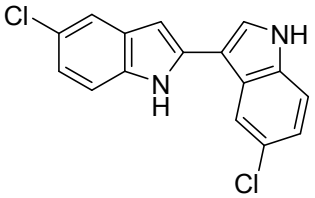
Yellow amorphous solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.38 (s, 1H), 11.18 (s, 1H), 8.00 (d, J = 7.5 Hz, 1H), 7.86 (d, J = 2.6 Hz, 1H), 7.48 (dd, J = 11.8, 7.6 Hz, 2H), 7.35 (d, J = 7.8 Hz, 1H), 7.19 – 7.14 (m, 2H), 7.02 (dd, J = 11.0, 4.0 Hz, 1H), 6.96 (dd, J = 10.8, 3.9 Hz, 1H), 6.75 (d, J = 1.5 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 137.1, 136.5, 134.6, 129.7, 125.1, 123.6, 122.2, 120.7, 120.2, 120.1, 119.5, 119.3, 112.4, 110.9, 108.9, 97.3. MS (ESI): 233 (M+H$^+$, 100). These assignments matched with those previously published.[1]

5,5′-Difluoro-1*H*,1'*H*-2,3′-biindole (**6b**)



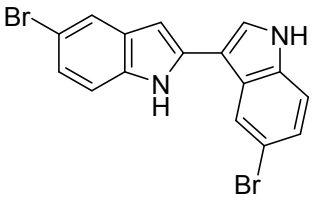
Yellow amorphous solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.56 (s, 1H), 11.31 (s, 1H), 7.94 (d, J = 2.6 Hz, 1H), 7.71 (dd, J = 10.3, 2.3 Hz, 1H), 7.48 (dd, J = 8.8, 4.7 Hz, 1H), 7.32 (dd, J = 8.6, 4.6 Hz, 1H), 7.22 (dd, J = 10.0, 2.4 Hz, 1H), 7.04 (dt, J = 2.4, 9.1 Hz, 1H), 6.85 (dt, J = 2.5, 9.4 Hz, 1H), 6.75 (d, J = 1.4 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 158.0 (d, J = 231.4 Hz), 157.5 (d, J = 230.5 Hz), 136.1, 133.8, 133.2, 130.0 (d, J = 10.5 Hz), 125.9, 125.1 (d, J = 10.2 Hz), 113.5 (d, J = 9.9 Hz), 111.6 (d, J = 9.9 Hz), 110.5 (d, J = 26.0 Hz), 108.9 (d, J = 4.6 Hz), 108.5 (d, J = 25.8 Hz), 104.8 (d, J = 24.0 Hz), 104.2 (d, J = 23.2 Hz), 97.6 (d, J = 4.5 Hz). MS (ESI): 269 (M+H$^+$, 100). Anal calcd for $C_{16}H_{10}F_2N_2$: C, 71.64; H, 3.76; N, 10.44. Found C, 71.37; H, 4.13; N, 10.18.

5,5′-Dichloro-1*H*,1'*H*-2,3′-biindole (**6c**)



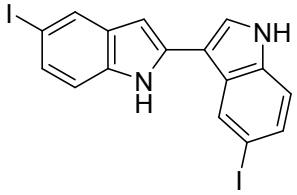
Yellow amorphous solid.^{1}H NMR (400 MHz, DMSO-d_6): δ 11.65 (s, 1H), 11.43 (s, 1H), 8.08-7.81 (m, 2H), 7.49 (d, J = 10.7 Hz, 2H), 7.35 (d, J = 8.5 Hz, 1H), 7.19 (dd, J = 8.6, 1.4 Hz, 1H), 7.02 (dd, J = 8.5, 1.6 Hz, 1H), 6.76 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 137.6, 137.0, 135.1, 128.4, 127.0, 125.4, 125.0, 123.8, 121.4, 120.8, 120.6, 119.7, 112.1, 110.5, 108.8, 97.7. MS (ESI): 301 (M+H$^+$, 100), 303 (M+H$^+$, 30). These assignments matched with those previously published.[2]

5,5′-Dibromo-1*H*,1'*H*-2,3′-biindole (**6d**)



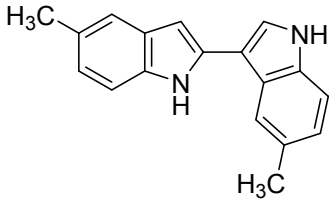
Yellow amorphous solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.66 (s, 1H), 11.43 (s, 1H), 8.10 (s, 1H), 7.92 (d, J = 2.6 Hz, 1H), 7.66 (d, J = 1.7 Hz, 1H), 7.45 (d, J = 8.6 Hz, 1H), 7.38-7.26 (m, 2H), 7.13 (dd, J = 8.5, 1.9 Hz, 1H), 6.75 (d, J = 1.2 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 135.9, 135.4, 135.3, 131.6, 126.7, 125.7, 124.9, 123.3, 122.1, 121.8, 114.5, 113.1, 112.9, 111.9, 108.2, 97.3. MS (ESI): 391 (M+H$^+$, 100). These assignments matched with those previously published.[2]

5,5'-Diiodo-1*H*,1'*H*-2,3′-biindole (**6e**)



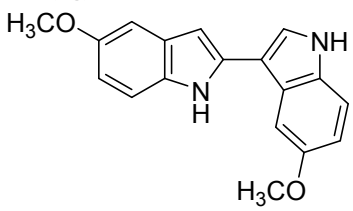
Yellow amorphous solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.64 (s, 1H), 11.42 (s, 1H), 8.26 (s, 1H), 7.86 (d, J = 7.9 Hz, 2H), 7.45 (d, J = 8.5 Hz, 1H), 7.33 (d, J = 8.5 Hz, 1H), 7.28 (d, J = 8.3 Hz, 1H), 7.20 (d, J = 8.3 Hz, 1H), 6.71 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 136.2, 135.7, 134.9, 132.5, 130.4, 128.8, 128.2, 128.1, 127.6, 125.2, 115.0, 113.4, 107.8, 96.9, 84.4, 83.0. MS (ESI): 485 (M+H$^+$, 100). Anal calcd for $C_{16}H_{10}I_2N_2$: C, 39.70; H, 2.08; N, 5.79. Found C, 40.05; H, 2.30; N, 5.48.

5,5'-Dimethyl-1*H*,1'*H*-2,3′-biindole (**6f**)



Yellow amorphous solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.21 (s, 1H), 10.99 (s, 1H), 7.77 (d, J = 2.7 Hz, 2H), 7.33 (d, J = 8.2 Hz, 1H), 7.26 (s, 1H), 7.21 (d, J = 8.1 Hz, 1H), 6.99 (dd, J = 8.3, 1.1 Hz, 1H), 6.83 (dd, J = 8.2, 1.2 Hz, 1H), 6.64 (d, J = 1.4 Hz, 1H), 2.45 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 135.5, 134.9, 134.8, 130.0, 128.8, 127.5, 125.4, 123.7, 123.5, 122.2, 119.7, 119.2, 112.0, 110.5, 108.6, 96.8, 21.8, 21.7. MS (ESI): 261 (M+H$^+$, 100). Anal calcd for $C_{18}H_{16}N_2$: C, 83.04; H, 6.19; N, 10.76. Found C, 82.87; H, 6.01; N, 10.83.

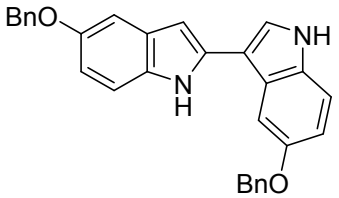
5,5'-Dimethoxy-1*H*,1'*H*-2,3′-biindole (**6g**)



Yellow amorphous solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.22 (s, 1H), 10.97 (s, 1H), 7.76 (d, J = 2.7 Hz, 1H), 7.36 (dd, J = 14.7, 5.6 Hz, 2H), 7.21 (d, J = 8.7 Hz, 1H), 7.01 (d, J = 2.4 Hz, 1H), 6.82 (dd, J = 8.8, 2.3 Hz, 1H), 6.69-6.61 (m, 2H), 3.83 (s, 3H), 3.74 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 154.5, 153.8, 135.4, 132.2, 131.6, 130.2, 125.5, 124.1, 113.1, 112.3, 111.4, 110.3,

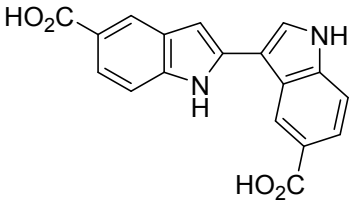
110.2, 108.9, 101.9, 97.1, 60.2, 55.9. MS (ESI): 293 ($M+H^+$, 100). These assignments matched with those previously published.[2]

5,5'-Bis(benzyloxy)-1*H*,1'*H*-2,3′-biindole (**6h**)



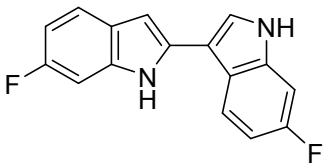
Yellow amorphous solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.25 (d, J = 2.0 Hz, 1H), 11.01 (s, 1H), 7.80 (d, J = 2.6 Hz, 1H), 7.56-7.50 (m, 3H), 7.47 (d, J = 7.2 Hz, 2H), 7.39 (dd, J = 14.2, 7.5 Hz, 5H), 7.32 (dd, J = 7.3, 4.6 Hz, 2H), 7.25 (d, J = 8.6 Hz, 1H), 7.10 (d, J = 2.2 Hz, 1H), 6.92 (dd, J = 8.8, 2.3 Hz, 1H), 6.76 (dd, J = 8.6, 2.4 Hz, 1H), 6.64 (d, J = 1.1 Hz, 1H), 5.19 (s, 2H), 5.10 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 153.6, 152.9, 138.5, 138.3, 135.5, 132.4, 131.8, 130.2, 129.0, 128.9, 128.8, 128.7, 128.2, 128.1, 128.0, 127.9, 125.5, 124.2, 113.1, 112.9, 111.4, 111.1, 108.9, 103.8, 103.5, 97.2, 70.6, 70.4. MS (ESI): 445 ($M+H^+$, 100). Anal calcd for $C_{30}H_{24}N_2O_2$: C, 81.06; H, 5.44; N, 6.30. Found C, 80.73; H, 5.46; N, 6.51.

1*H,*1′*H*-[3, 3′-Biindole]-5,5′-dicarboxylic acid (**6i**)



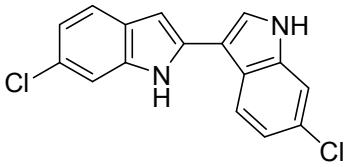
Yellow amorphous solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.50 (s, 2H), 11.81 (d, J = 2.2 Hz, 1H), 11.68 (d, J = 1.2 Hz, 1H), 8.64 (s, 1H), 8.27-8.24 (m, 1H), 7.99 (d, J = 2.6 Hz, 1H), 7.83 (dd, J = 8.6, 1.5 Hz, 1H), 7.71 (dd, J = 8.5, 1.6 Hz, 1H), 7.55 (d, J = 8.6 Hz, 1H), 7.43 (d, J = 8.5 Hz, 1H), 6.89 (d, J = 1.4 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 168.9, 168.7, 139.6, 139.2, 135.4, 129.2, 125.6, 124.7, 123.6, 123.0, 122.6, 122.5, 122.4, 122.0, 112.3, 110.7, 109.7, 98.8. MS (ESI): 321 ($M+H^+$, 100). Anal calcd for $C_{18}H_{12}N_2O_4$: C, 67.50; H, 3.78; N, 8.75. Found C, 67.84; H, 3.60; N, 9.02.

6,6′-Difluoro-1*H*,1'*H*-2,3′-biindole (**6j**)



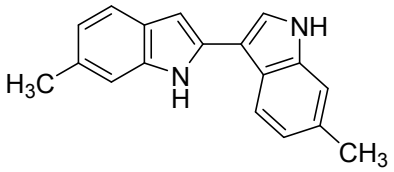
Yellow amorphous solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.46 (s, 1H), 11.34 (s, 1H), 7.96 (dd, J = 8.6, 5.4 Hz, 1H), 7.84 (d, J = 2.3 Hz, 1H), 7.47 (dd, J = 8.4, 5.5 Hz, 1H), 7.25 (dd, J = 9.9, 2.1 Hz, 1H), 7.10 (d, J = 10.0 Hz, 1H), 7.03-6.97 (m, 1H), 6.83 (dd, J = 13.2, 5.3 Hz, 1H), 6.77 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 159.5 (d, J = 235.4 Hz), 159.0 (d, J = 233.3 Hz), 137.1 (d, J = 12.6 Hz), 136.4 (d, J = 12.7 Hz), 134.8 (d, J = 3.5 Hz), 126.4, 124.2 (d, J = 3.1 Hz), 121.9, 121.1 (d, J = 10.2 Hz), 120.4 (d, J = 10.0 Hz), 108.9, 108.7 (d, J = 24.3 Hz), 107.5 (d, J = 24.0 Hz), 98.4 (d, J = 25.5 Hz), 97.4, 97.1 (d, J = 25.6 Hz). MS (ESI): 269 ($M+H^+$, 100). Anal calcd for $C_{16}H_{10}F_2N_2$: C, 71.64; H, 3.76; N, 10.44. Found C, 71.79; H, 3.92; N, 10.25.

6,6′-Dichloro-1*H*,1'*H*-2,3′-biindole (**6k**)



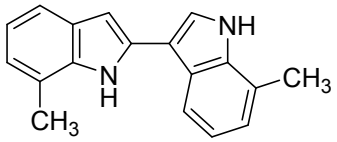
Yellow amorphous solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.56 (s, 1H), 11.41 (s, 1H), 7.98 (d, J = 8.6 Hz, 1H), 7.90 (d, J = 2.5 Hz, 1H), 7.51 (dd, J = 14.9, 5.0 Hz, 2H), 7.35 (s, 1H), 7.16 (dd, J = 8.4, 1.5 Hz, 1H), 6.98 (dd, J = 8.3, 1.6 Hz, 1H), 6.79 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 137. 5, 137.0, 135.0, 128.4, 127.0, 125.4, 125.0, 123.8, 121.4, 120.8, 120.6, 119.6, 112.1, 110.5, 108.8, 97.7. MS (ESI): 301 (M+H$^+$, 100), 303 (M+H$^+$, 30). Anal calcd for $C_{16}H_{10}Cl_2N_2$: C, 63.81; H, 3.35; N, 9.30. Found C, 64.20; H, 3.48; N, 9.17.

6,6'-Dimethyl-1*H*,1'*H*-2,3′-biindole (**6l**)



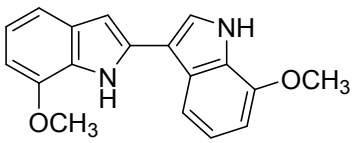
Yellow amorphous solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.18 (s, 1H), 10.98 (s, 1H), 7.84 (d, J = 8.2 Hz, 1H), 7.73 (d, J = 2.6 Hz, 1H), 7.35 (d, J = 7.9 Hz, 1H), 7.23 (s, 1H), 7.12 (s, 1H), 6.96 (dd, J = 8.2, 1.0 Hz, 1H), 6.78 (dd, J = 8.0, 0.9 Hz, 1H), 6.65 (d, J = 1.4 Hz, 1H), 2.42 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 137.6, 136.9, 134.1, 131.2, 129.6, 127.6, 123.1, 122.6, 121.9, 120.9, 119.8, 119.2, 112.1, 110.8, 109.0, 97.0, 22.0, 21.8. MS (ESI): 261 (M+H$^+$, 100). Anal calcd for $C_{18}H_{16}N_2$: C, 83.04; H, 6.19; N, 10.76. Found C, 82.96; H, 5.82; N, 10.49.

7,7'-Dimethyl-1*H*,1'*H*-2,3′-biindole (**6m**)



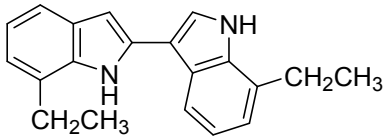
Yellow amorphous solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.36 (s, 1H), 10.78 (s, 1H), 8.03 (d, J = 2.7 Hz, 1H), 7.81 (d, J = 7.9 Hz, 1H), 7.32 (d, J = 7.6 Hz, 1H), 7.05 (t, J = 7.8 Hz, 1H), 6.98 (d, J = 7.0 Hz, 1H), 6.87 (t, J = 7.2 Hz, 1H), 6.81 (d, J = 7.0 Hz, 1H), 6.75 (t, J = 2.0 Hz, 1H), 2.51 (s, 3H), 2.49 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 136.6, 135.8, 134.6, 129.4, 125.0, 123.8, 122.6, 121.6, 121.4, 120.3, 120.1, 119.5, 117.8, 117.2, 109.3, 98.0, 17.6, 17.2. MS (ESI): 261 (M+H$^+$, 100). These assignments matched with those previously published.[2]

7,7'-Dimethoxy-1*H*,1'*H*-2,3′-biindole (**6n**)



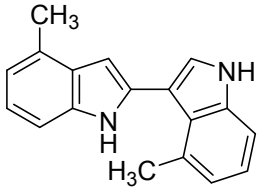
Yellow amorphous solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.41 (s, 1H), 11.13 (s, 1H), 8.00 (s, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.12-7.00 (m, 2H), 6.90 – 6.83 (m, 1H), 6.72 (d, J = 6.8 Hz, 2H), 6.60 (d, J = 7.5 Hz, 1H), 3.92 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 146.8, 146.1, 134.6, 131.2, 127.2, 126.8, 126.2, 123.7, 120.8, 119.8, 112.9, 112.7, 109.2, 102.6, 101.9, 98.0, 55.7, 55.5. HRESIMS calcd for [$C_{18}H_{16}N_2O_2$ + H]$^+$ 293.12900, found 293.12859.

7,7'-Diethyl-1*H*,1'*H*-2,3′-biindole (**6o**)



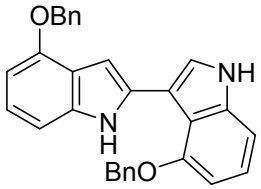
Yellow amorphous solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.35 (s, 1H), 10.76 (s, 1H), 8.02 (d, J = 2.5 Hz, 1H), 7.80 (d, J = 7.9 Hz, 1H), 7.32 (d, J = 7.5 Hz, 1H), 7.07 (t, J = 7.5 Hz, 1H), 7.00 (d, J = 7.0 Hz, 1H), 6.95-6.79 (m, 2H), 6.74 (d, J = 1.6 Hz, 1H), 2.94 (q, J = 7.5 Hz, 2H), 2.90 (q, J = 7.5 Hz, 2H), 1.31 (t, J = 7.5 Hz, 3H), 1.30 (t, J = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 135.8, 135.1, 134.6, 129.6, 127.8, 126.6, 125.3, 123.8, 120.8, 120.5, 119.65 (d, J = 8.4 Hz), 117.8, 117.2, 109.3, 98.1, 24.2, 24.1, 15.1, 14.9. MS (ESI): 289 (M+H$^+$, 100). Anal calcd for $C_{20}H_{20}N_2$: C, 83.30; H, 6.99; N, 9.71. Found C, 83.04; H, 6.83; N, 9.39.

4,4'-Dimethyl-1*H*,1'*H*-2,3′-biindole (**6p**)



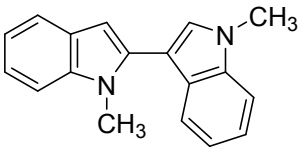
Yellow amorphous solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.31 (s, 1H), 11.09 (s, 1H), 7.44 (d, J = 2.5 Hz, 1H), 7.28 (d, J = 8.1 Hz, 1H), 7.16 (d, J = 8.1 Hz, 1H), 7.07-6.99 (m, 1H), 6.97-6.88 (m, 1H), 6.78 (dd, J = 9.5, 7.2 Hz, 2H), 6.40 (d, J = 1.5 Hz, 1H), 2.47 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 136.8, 136.3, 134.1, 130.3, 128.8, 128.4, 125.9, 125.7, 122.0, 121.2, 120.8, 119.3, 110.1, 109.4, 108.9, 100.4, 20.3, 19.1. MS (ESI): 261 (M+H$^+$, 100). Anal calcd for $C_{18}H_{16}N_2$: C, 83.04; H, 6.19; N, 10.76. Found C, 82.87; H, 5.95; N, 10.38.

4,4′-Bis(benzyloxy)- 1*H*,1'*H*-2,3′-biindole (**6q**)



Yellow amorphous solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.53 (d, J = 2.2 Hz, 1H), 10.65 (d, J = 1.5 Hz, 1H), 7.84 (d, J = 2.6 Hz, 1H), 7.58-7.55 (m, 2H), 7.48 (d, J = 7.2 Hz, 2H), 7.40-7.33 (m, 5H), 7.10 (d, J = 4.1 Hz, 2H), 6.81-6.76 (m, 4H), 6.49 (d, J = 7.8 Hz, 1H), 6.32 (d, J = 8.0 Hz, 1H), 5.27 (s, 2H), 5.18 (s, 2H), 3.37 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 152.5, 151.4, 139.0, 138.3, 137.4, 137.0, 133.3, 129.1, 129.0, 128.8, 128.6, 128.0, 127.8, 124.2, 122.8, 120.8, 120.1, 114.8, 108.7, 106.4, 104.8, 101.9, 101.2, 95.3, 70.6, 69.5. MS (ESI): 445 (M+H$^+$, 100). Anal calcd for $C_{30}H_{24}N_2O_2$: C, 81.06; H, 5.44; N, 6.30. Found C, 80.91; H, 5.28; N, 6.03.

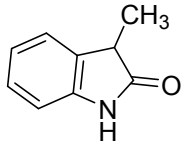
1,1'-Dimethyl-1*H*,1'*H*-2,3′-biindole (**6r**)



Yellow amorphous solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.71 (s, 1H), 7.68 (s, 1H), 7.53 (s, 1H), 7.44 (s, 1H), 7.24 (d, J = 7.3 Hz, 2H), 7.14 (d, J = 4.6 Hz, 2H), 7.04 (t, J = 7.4 Hz, 2H), 3.87

(s, 3H), 3.76 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 138.0, 137.2, 135.4, 129.7, 128.4, 127.3, 122.4, 121.0, 120.5, 120.0, 119.9, 119.7, 110.6, 110.1, 106.2, 100.6, 33.1, 31.3. MS (ESI): 261 (M+H$^+$, 100). Anal calcd for $C_{18}H_{16}N_2$: C, 83.04; H, 6.19; N, 10.76. Found C, 82.76; H, 5.84; N, 10.59.

3-Methylindolin-2-one (**9**)



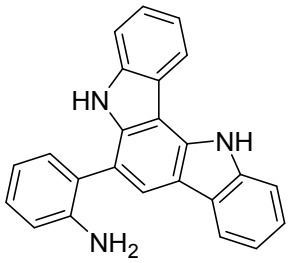
White amorphous solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.31 (s, 1H), 7.22 (d, J = 7.4 Hz, 1H), 7.15 (t, J = 7.7 Hz, 1H), 6.93 (t, J = 7.4 Hz, 1H), 6.81 (d, J = 7.7 Hz, 1H), 3.38 (q, J = 7.6 Hz, 1H), 1.30 (d, J = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 180.1, 142.8, 131.8, 128.0, 124.1, 121.7, 109.6, 40.6, 15.5. MS (ESI): 148 (M+H$^+$, 100).

3.3 General Procedure for the Preparation of 10.

To a solution of indole (0.3 mmol) in CH_3CN (1 mL) was added NBS (0.24 mmol) under an air atmosphere and the mixture was stirred at room temperature for 12 h. The reaction mixture was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EtOAc/PE = 1:2) to yield the corresponding product **10**.

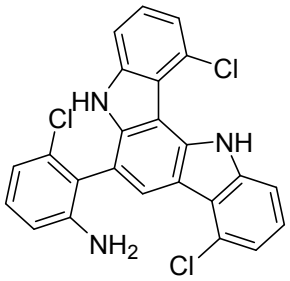
3.4 Spectroscopic Data of the Products 10

2-(5,12-Dihydroindolo[3,2-*a*]carbazol-6-yl)aniline (**10a**)



Yellow amorphous solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.74 (s, 1H), 10.81 (s, 1H), 8.66 (d, J = 7.8 Hz, 1H), 8.11 (d, J = 7.7 Hz, 1H), 8.02 (s, 1H), 7.62 (dd, J = 14.1, 8.0 Hz, 2H), 7.32-7.14 (m, 6H), 6.90 (dd, J = 8.1, 1.0 Hz, 1H), 6.75 (dt, J = 1.2, 7.4 Hz,1H), 4.64 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 149.5, 139.9, 139.6, 137.7, 133.7, 131.5, 128.6, 124.5, 124.2, 124.1, 123.9, 122.0, 121.5, 119.5, 119.4, 119.3, 119.1, 117.1, 115.7, 115.6, 115.4, 111.9, 111.5, 107.1. MS (ESI): 348 (M+H$^+$, 100). These assignments matched with those previously published.[3]

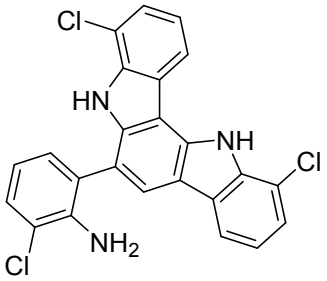
3-Chloro-2-(1,8-dichloro-5,12-dihydroindolo[3,2-*a*]carbazol-6-yl)aniline (**10b**)



Yellow amorphous solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.39 (s, 1H), 10.93 (s, 1H), 8.38 (s, 1H), 7.92 (d, J = 7.7 Hz, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.44-7.26 (m, 5H), 7.25-7.15 (m, 2H), 4.64

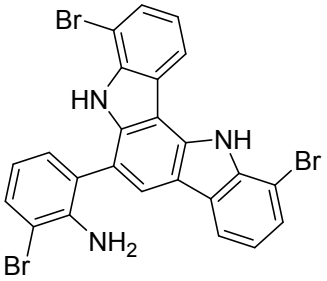
(s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 149.4, 141.1, 140.4, 138.7, 135.0, 133.8, 130.1, 125.9,125.8, 125.1, 124.8, 122.9, 121.0, 120.5, 120.4, 120.3, 119.8, 117.0, 115.2, 113.8, 113.0, 111.7, 111.1, 105.5. MS (ESI): 450 (M+H$^+$, 100). Anal calcd for $C_{24}H_{14}Cl_3N_3$: C, 63.95; H, 3.13; N, 9.32. Found C, 64.07; H, 3.28; N, 9.01.

2-Chloro-6-(4,11-dichloro-5,12-dihydroindolo[3,2-*a*]carbazol-6-yl)aniline (**10c**)



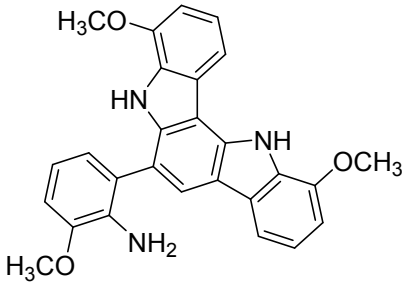
Yellow amorphous solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.74 (s, 1H), 10.94 (s, 1H), 9.05 (d, J = 7.8 Hz, 1H), 8.20-8.10 (m, 2H), 7.48 (dd, J = 7.7, 0.8 Hz, 1H), 7.42 (dd, J = 7.7, 0.9 Hz, 1H), 7.36 (dd, J = 8.0, 1.4 Hz, 1H), 7.31 (t, J = 7.8 Hz, 1H), 7.24-7.17 (m, 2H), 6.77 (t, J = 7.8 Hz, 1H), 4.69 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 142.9, 138.6, 136.9, 136.4, 134.3, 130.7, 129.0, 126.5, 125.9, 124.8, 124.3, 124.1, 121.8, 121.1, 121.0, 120.3, 118.8, 118.5, 117.7, 116.9, 116.7, 116.1, 115.7, 108.4. MS (ESI): 450 (M+H$^+$, 100). Anal calcd for $C_{24}H_{14}Cl_3N_3$: C, 63.95; H, 3.13; N, 9.32. Found C, 63.80; H, 3.32; N, 8.96.

2-Bromo-6-(4,11-dibromo-5,12-dihydroindolo[3,2-*a*]carbazol-6-yl)aniline (**10d**)



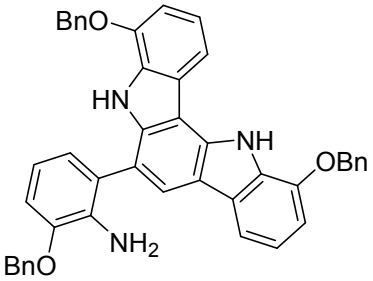
Yellow amorphous solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.54 (s, 1H), 10.53 (s, 1H), 9.07 (d, J = 7.8 Hz, 1H), 8.43-7.94 (m, 2H), 7.63 (d, J = 7.7 Hz, 1H), 7.60-7.47 (m, 2H), 7.33-7.19 (m, 2H), 7.15 (t, J = 7.7 Hz, 1H), 6.72 (t, J = 7.7 Hz, 1H), 4.70 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 143.7, 138.5, 138.3, 137.8, 134.4, 132.2, 131.4, 127.9, 127.5, 126.4, 125.9, 123.9, 122.5, 121.5, 121.2, 120.8, 119.0, 118.5, 117.2, 116.9, 109.5, 108.6, 104.3, 103.9, 56.3, 56.1, 56.0. MS (ESI): 584 (M+H$^+$, 100). Anal calcd for $C_{24}H_{14}Br_3N_3$: C, 49.35; H, 2.42; N, 7.19. Found C, 49.69; H, 2.16; N, 6.83.

2-(4,11-Dimethoxy-5,12-dihydroindolo[3,2-*a*]carbazol-6-yl)-6-methoxyaniline (**10e**)



Yellow amorphous solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.40 (s, 1H), 10.39 (s, 1H), 8.14 (s, 1H), 7.77 (d, J = 7.8 Hz, 1H), 7.44 (d, J = 8.4 Hz, 1H), 7.16 (t, J = 7.8 Hz, 1H), 7.00-7.92 (m, 4H), 6.90 (dd, J = 7.8, 1.0 Hz, 1H), 6.78 (t, J = 7.8 Hz, 1H), 4.33 (s, 2H), 4.04 (s, 3H), 3.95 (s, 3H), 3.89 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 147.5, 146.1, 145.8, 137.7, 135.2, 131.9, 131.2, 128.0, 124.8, 124.3, 124.2, 124.1, 122.7, 121.3, 120.7, 117.4, 117.1, 117.0, 112.4, 110.2, 107.4, 106.6, 105.5, 104.0, 56.3, 56.1, 56.0. MS (ESI): 438 (M+H$^+$, 100). Anal calcd for $C_{27}H_{23}N_3O_3$: C, 74.13; H, 5.30; N, 9.60. Found C, 73.85; H, 5.21; N, 9.29.

2-(Benzyloxy)-6-(4,11-bis(benzyloxy)-5,12-dihydroindolo[3,2-*a*]carbazol-6-yl)aniline (**10f**)



Yellow amorphous solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.50 (s, 1H), 11.15 (s, 1H), 8.12 (dd, J = 5.0, 2.6 Hz, 1H), 7.60-7.55 (m, 8H), 7.44-7.33 (m, 9H), 7.12 (t, J = 8.1 Hz, 1H), 7.06 (d, J = 8.1 Hz, 2H), 6.88-6.85 (m, 2H), 6.77 (d, J = 1.9 Hz, 1H), 6.67 (d, J = 7.8 Hz, 1H), 5.35-5.27 (m, 8H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 145.9, 145.8, 145.0, 144.6, 138.1, 137.8, 137.7, 137.6, 135.8, 134.7, 131.4, 128.9, 128.8, 128.3, 128.2, 128.1, 128.0, 127.9, 127.4, 127.0, 126.9, 126.5, 124.8, 124.2, 121.1, 120.8, 119.8, 113.1, 112.8, 109.2, 108.4, 104.9, 104.0, 103.4, 98.1, 97.6, 70.0, 69.7, 69.6. MS (ESI): 666 (M+H$^+$, 100). Anal calcd for $C_{45}H_{35}N_3O_3$: C, 81.18; H, 5.30; N, 6.31. Found C, 80.83; H, 5.09; N, 6.12.

3.5 General Procedure for the Preparation of 11.

To a solution of indole (0.3 mmol) and morpholine (0.6 mmol) in CH_3CN (1 mL) was added NBS (0.24 mmol) under an air atmosphere and the mixture was stirred at room temperature for 3 h. The reaction mixture was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EtOAc/PE = 1:4) to yield the corresponding product **11**.

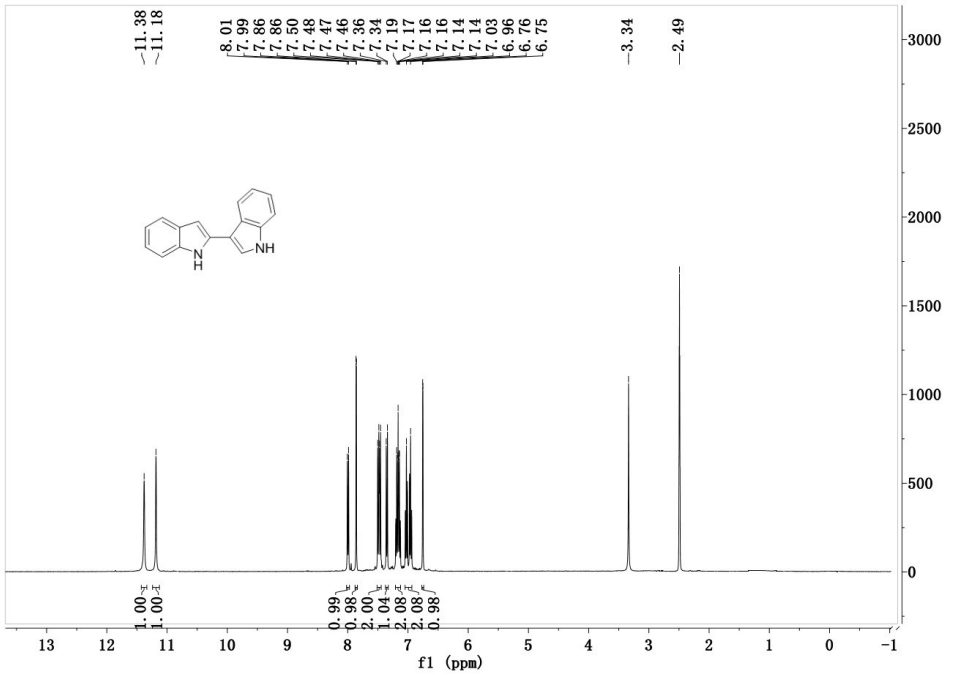
3.6 Spectroscopic Data of the Products 11.

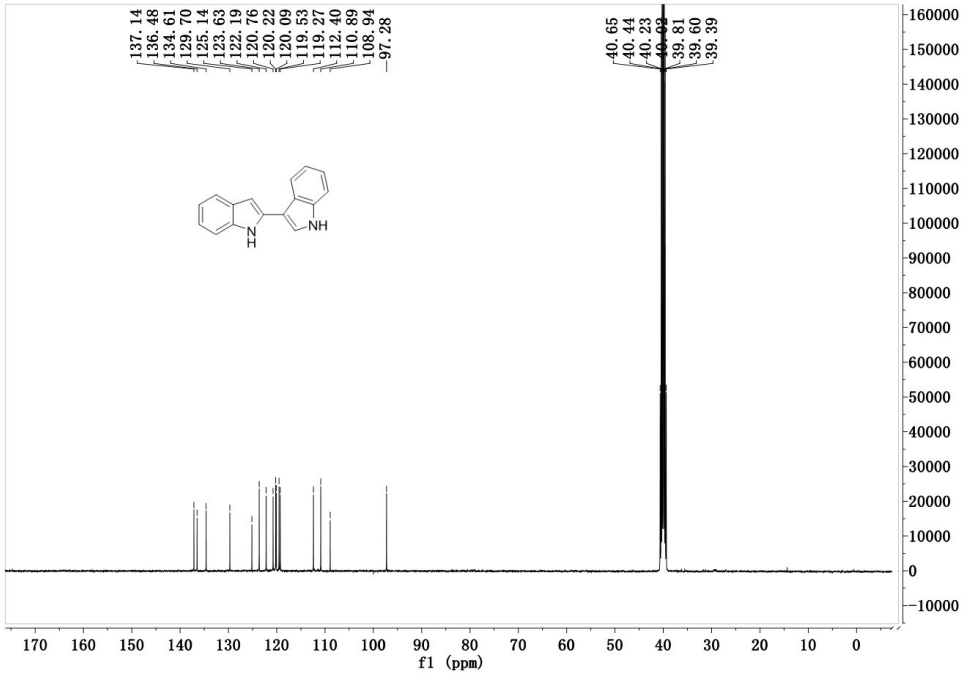
3-Bromo-1*H*-indole (**11**)

White amorphous solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.45 (s, 1H), 7.52 (d, J = 2.6 Hz, 1H), 7.40 (t, J = 8.2 Hz, 2H), 7.18-7.14 (m, 1H), 7.11-7.07 (m, 1H). ^{1}H NMR (400 MHz, DMSO-d_6): δ 135.8, 126.5, 125.2, 122.6, 120.3, 118.3, 112.5, 89.1.

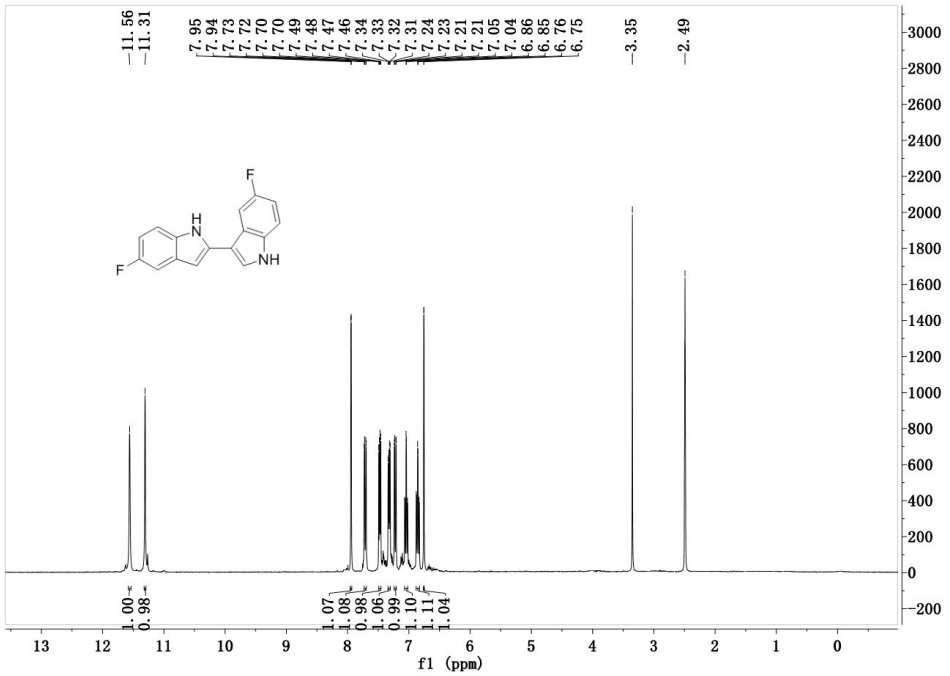
4. Copies of ^{1}H, ^{13}C Spectra

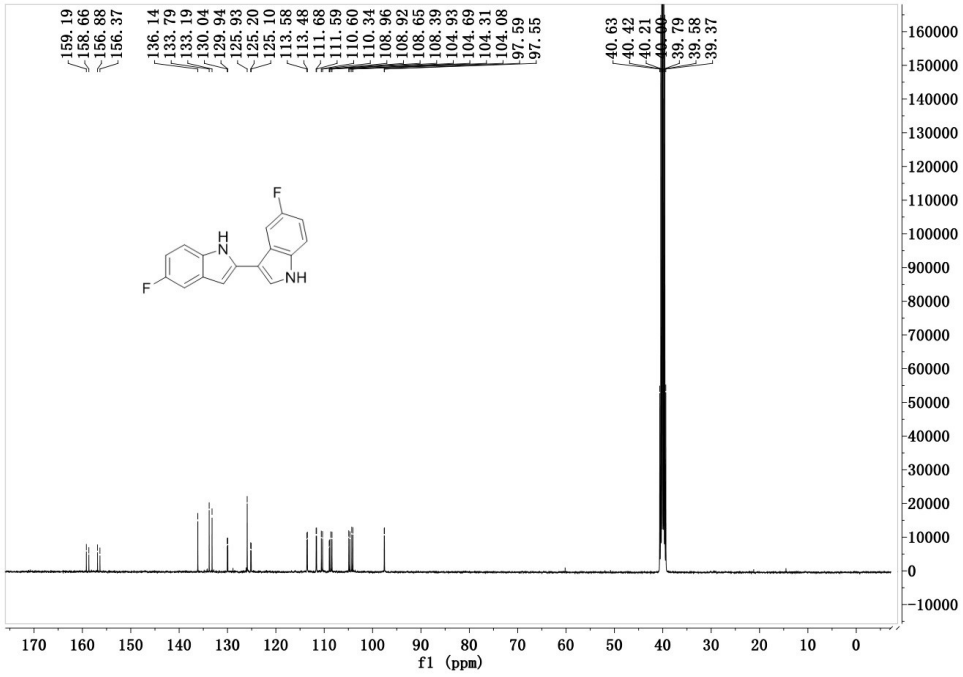
^{1}H and ^{13}C NMR Spectra for **6a**



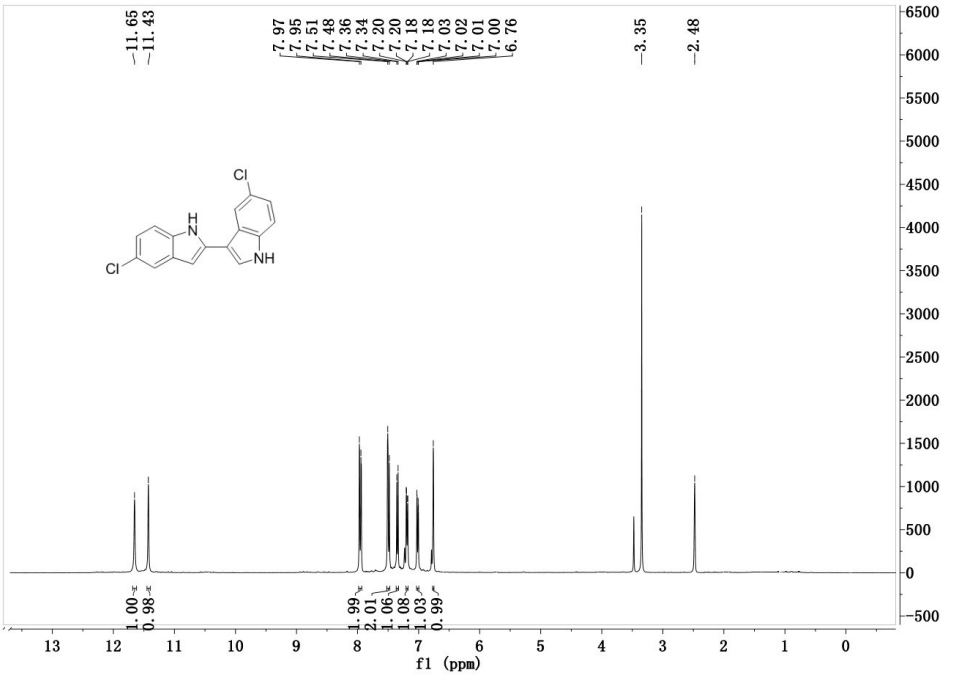


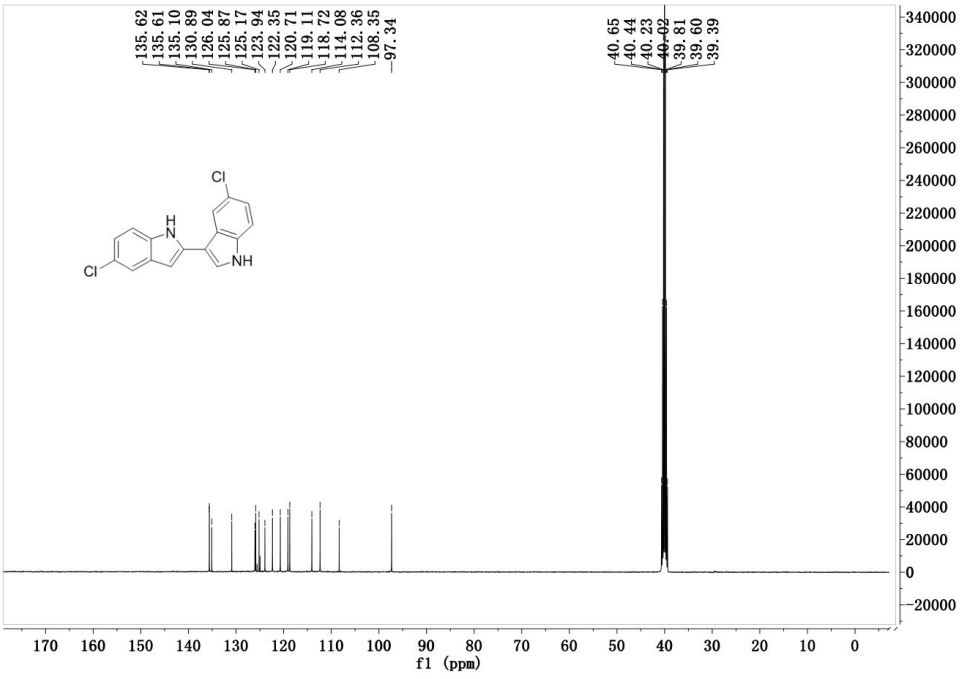
^{1}H and ^{13}C NMR Spectra for **6b**



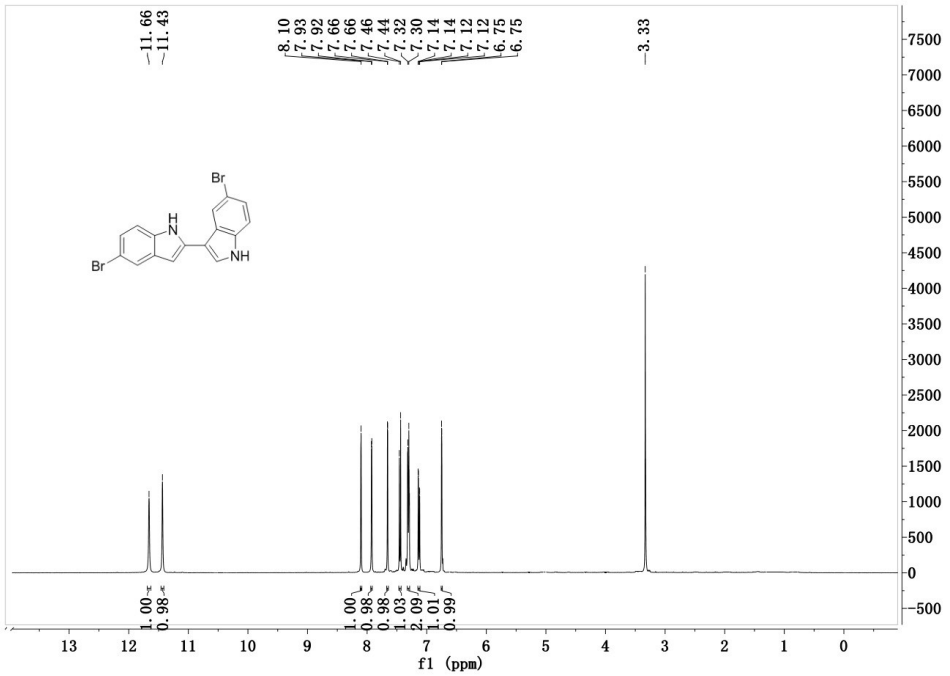


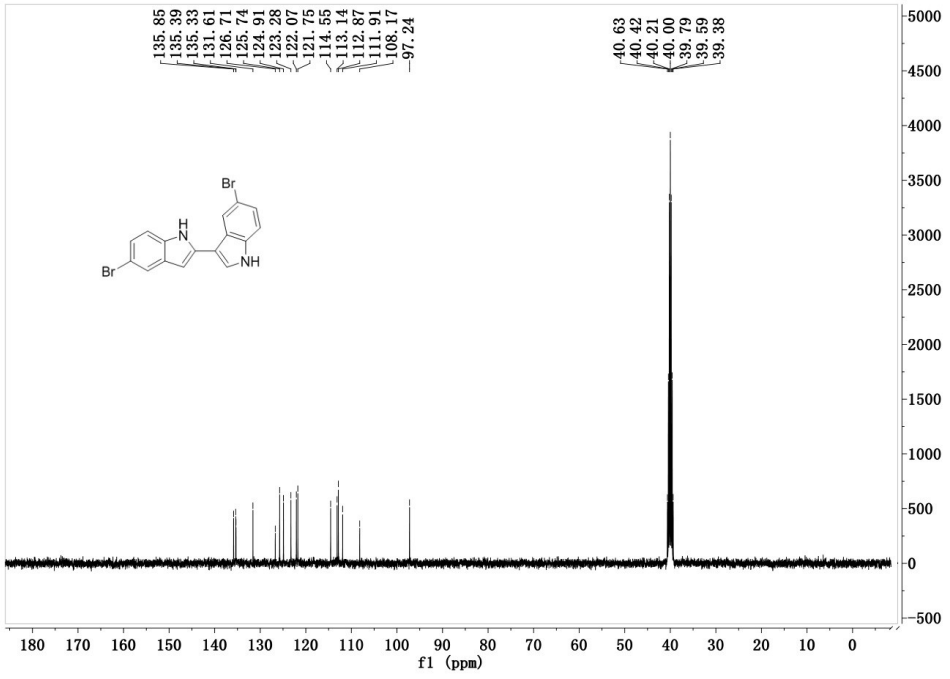
^{1}H and ^{13}C NMR Spectra for **6c**



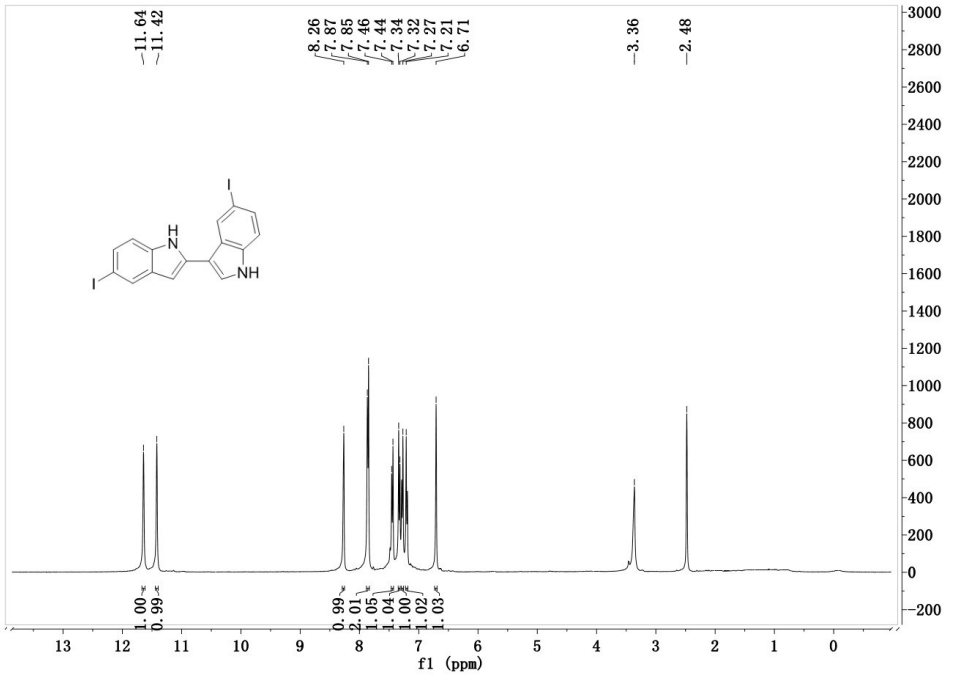


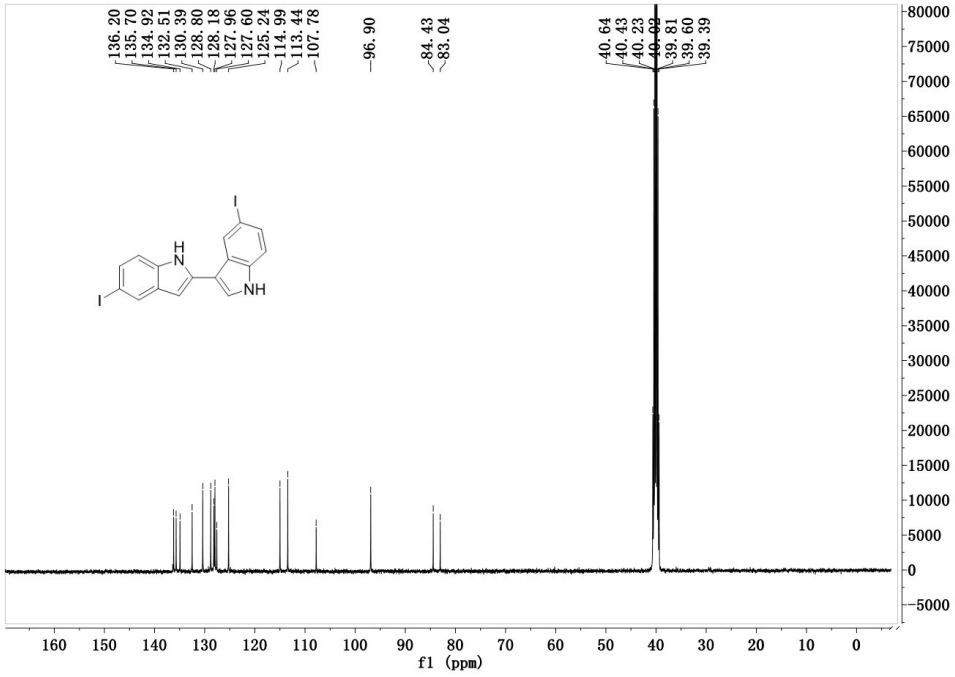
^{1}H and ^{13}C NMR Spectra for **6d**



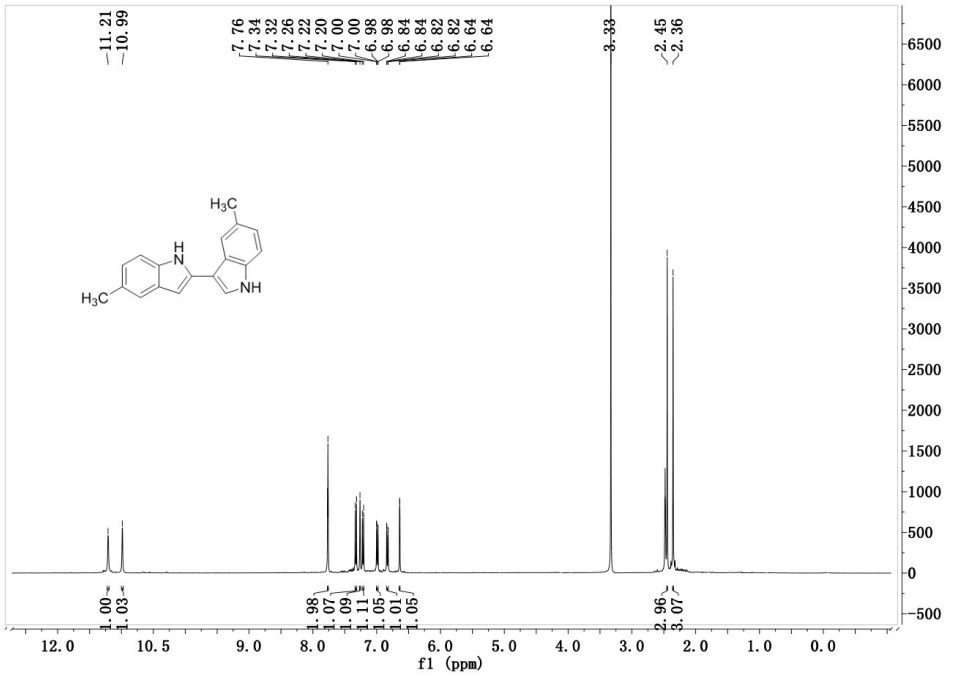


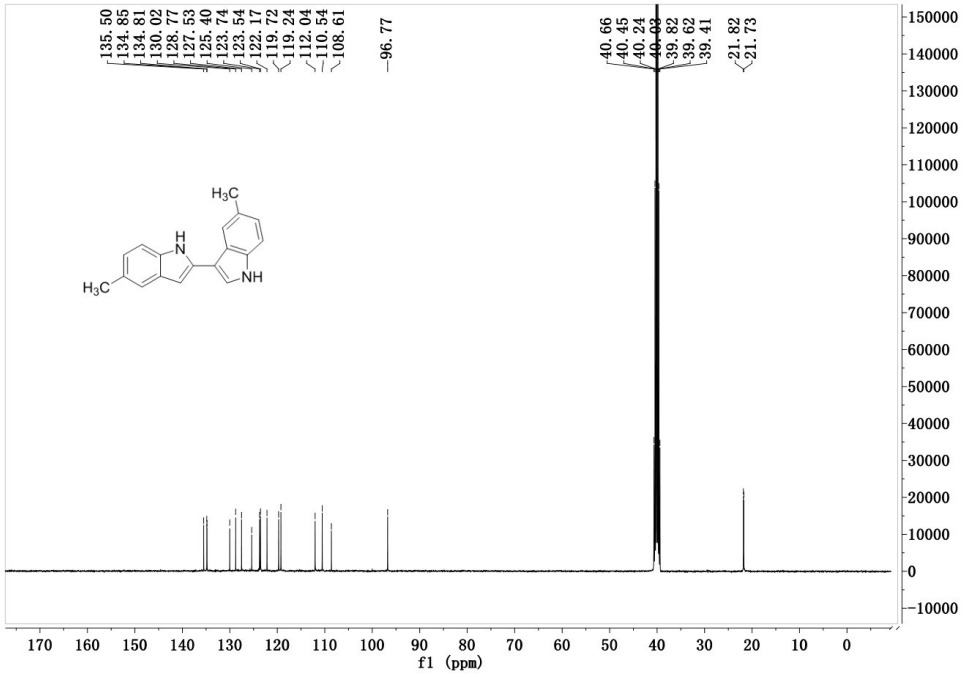
^{1}H and ^{13}C NMR Spectra for **6e**



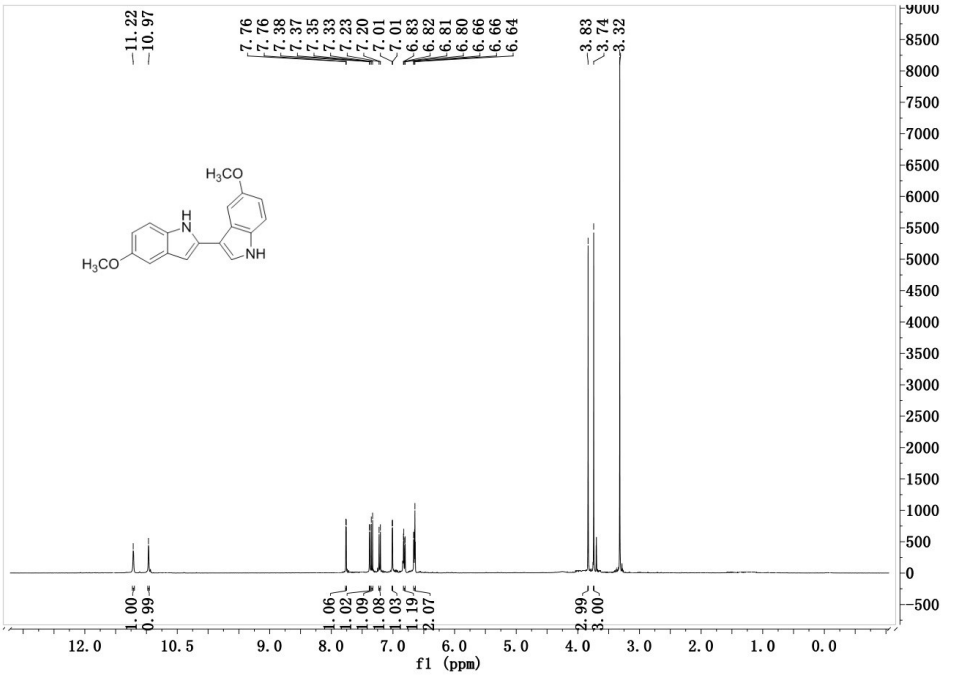


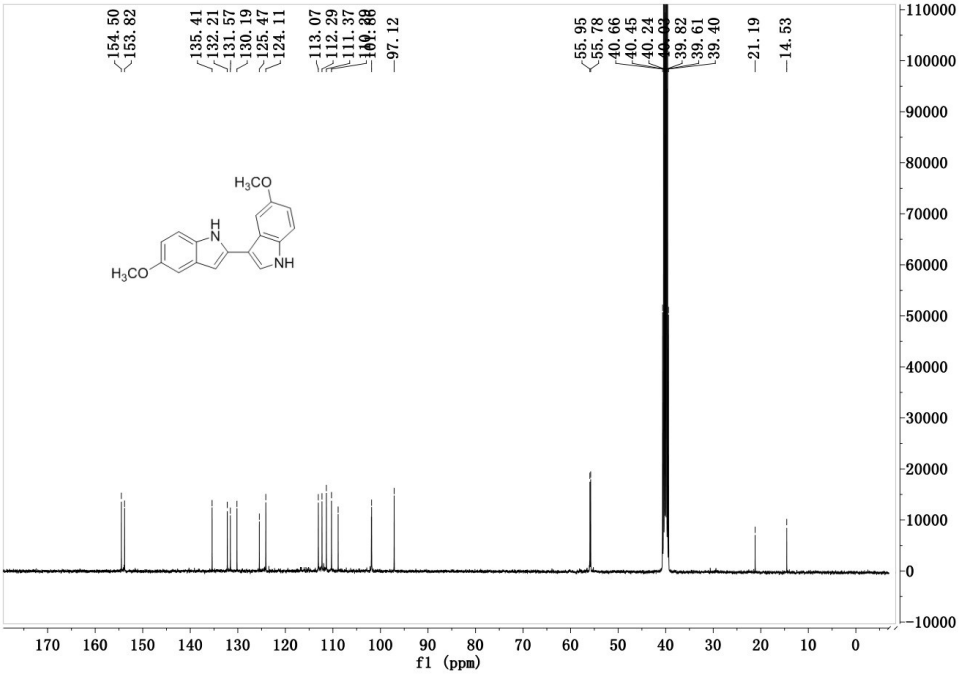
^{1}H and ^{13}C NMR Spectra for **6f**



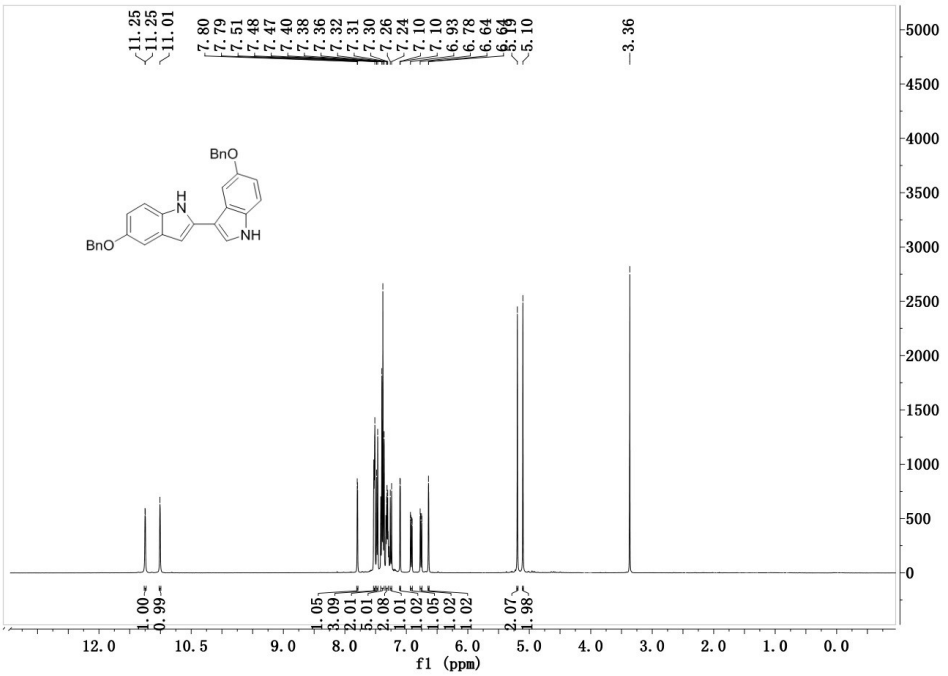


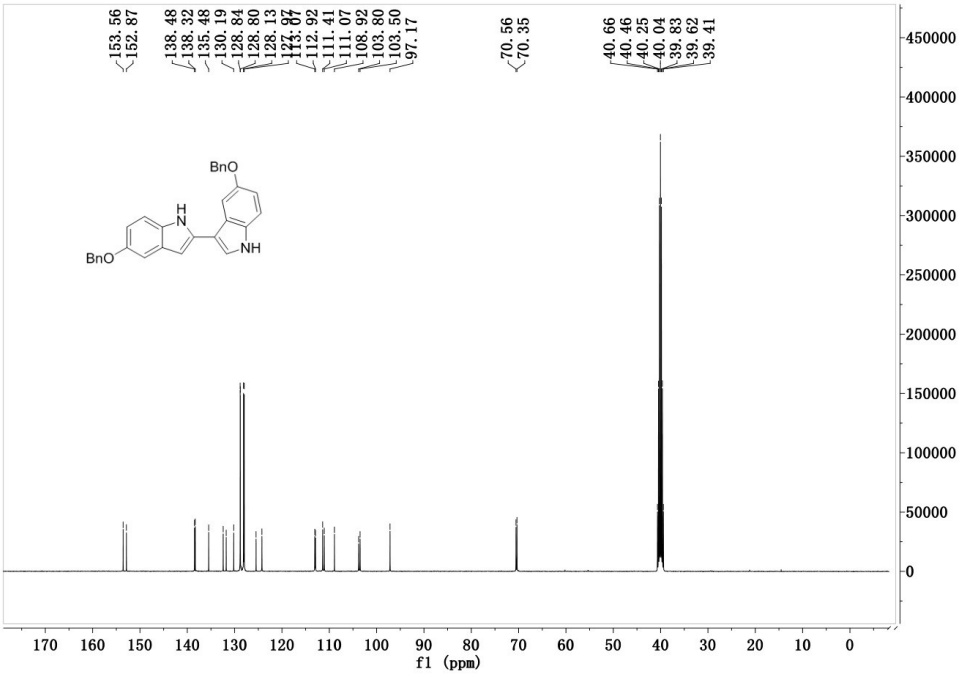
^{1}H and ^{13}C NMR Spectra for **6g**



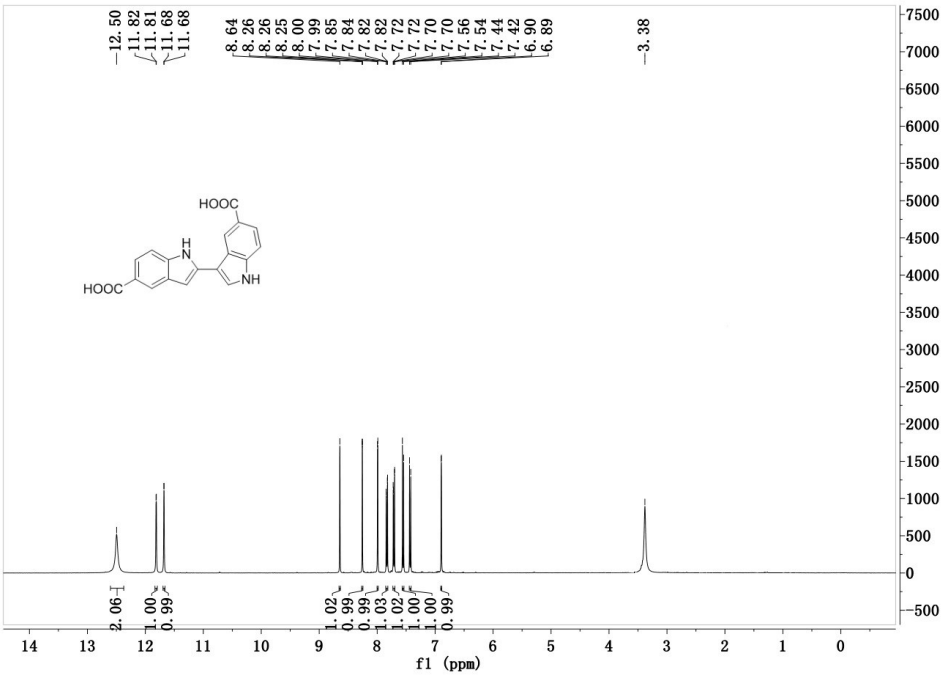


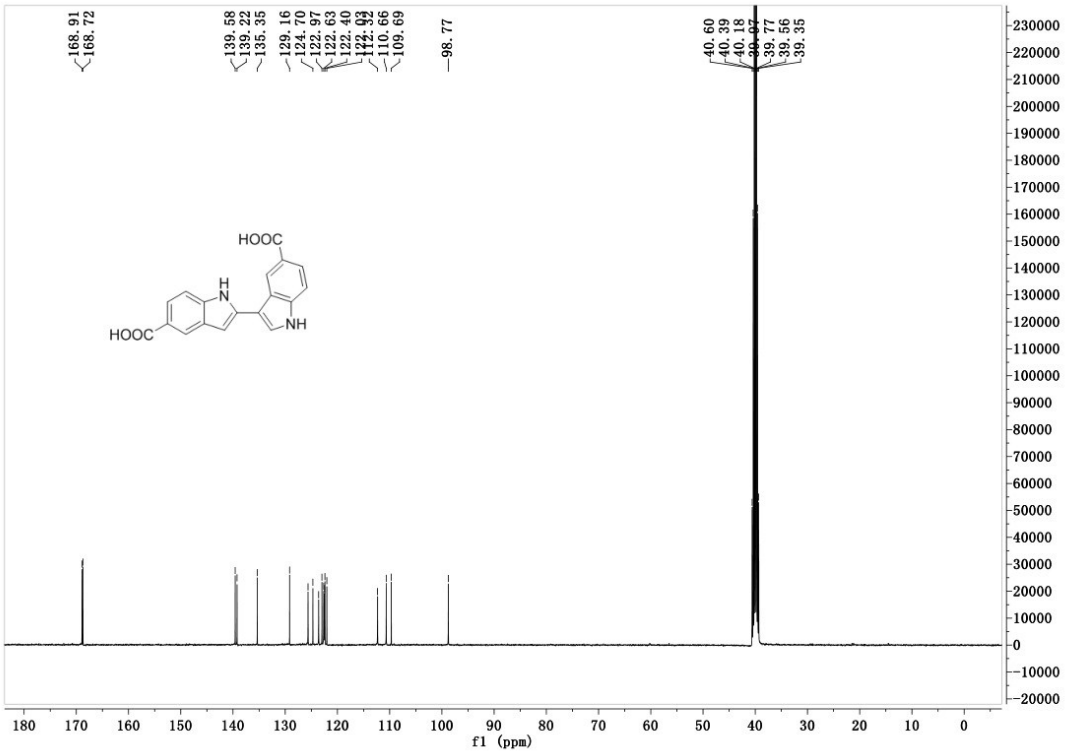
^{1}H and ^{13}C NMR Spectra for **6h**



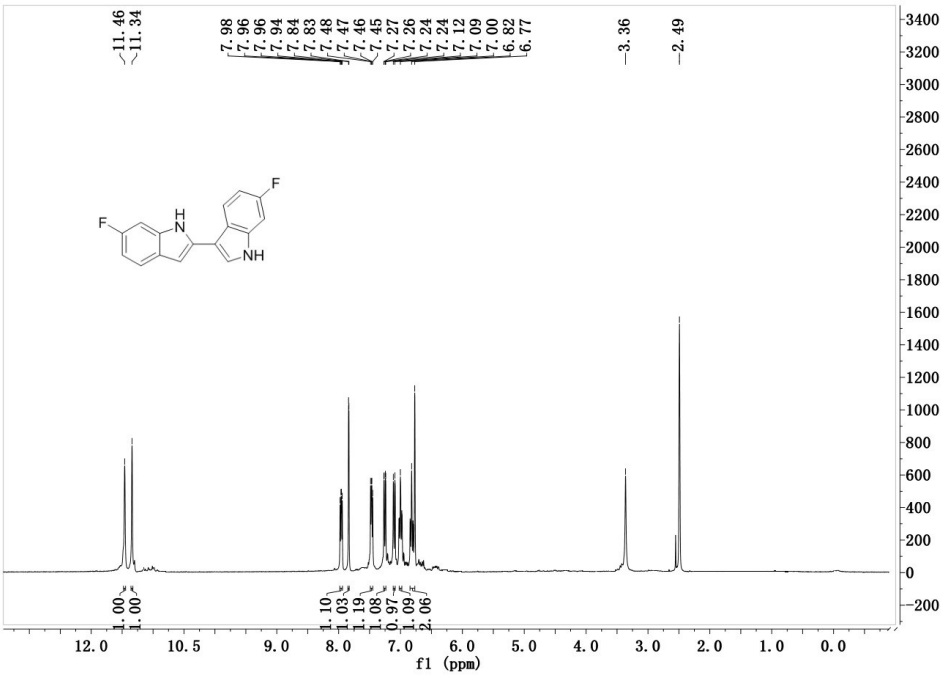


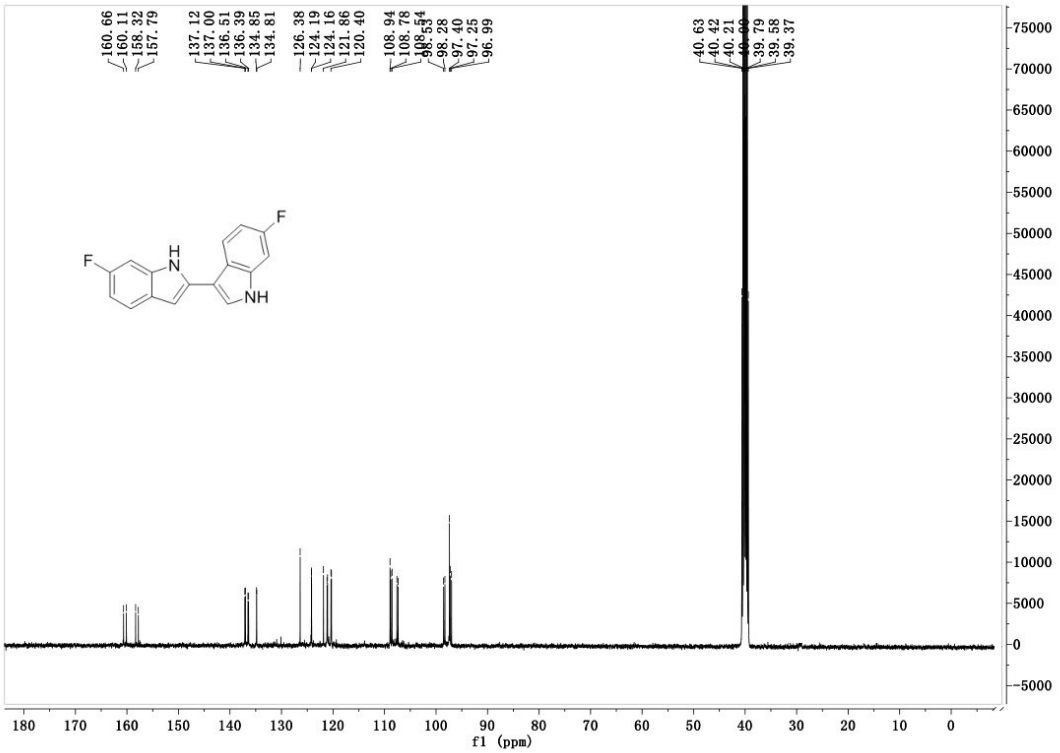
^{1}H and ^{13}C NMR Spectra for **6i**



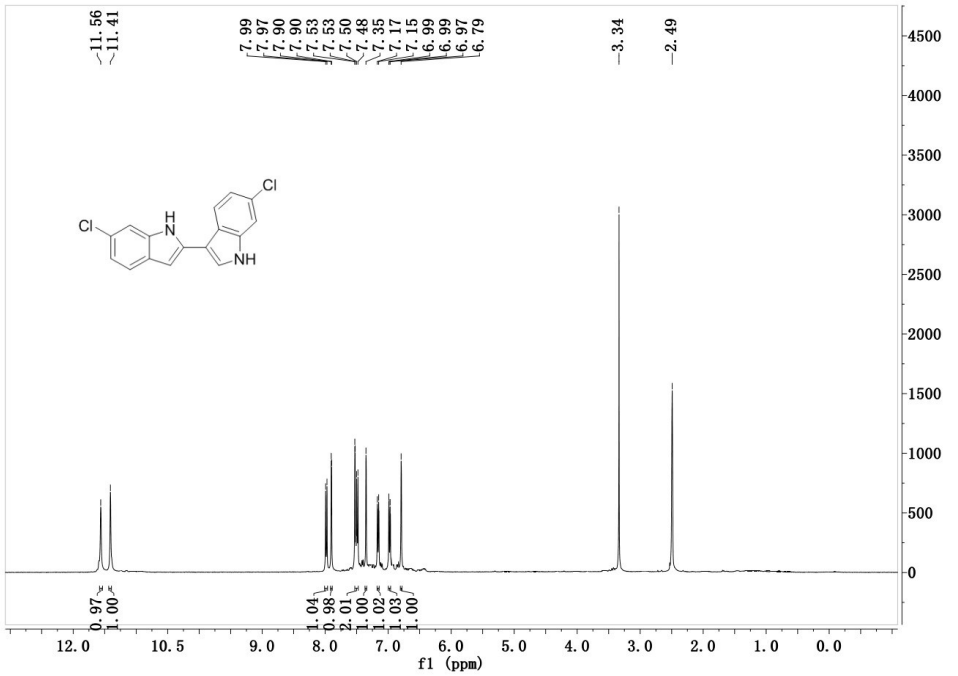


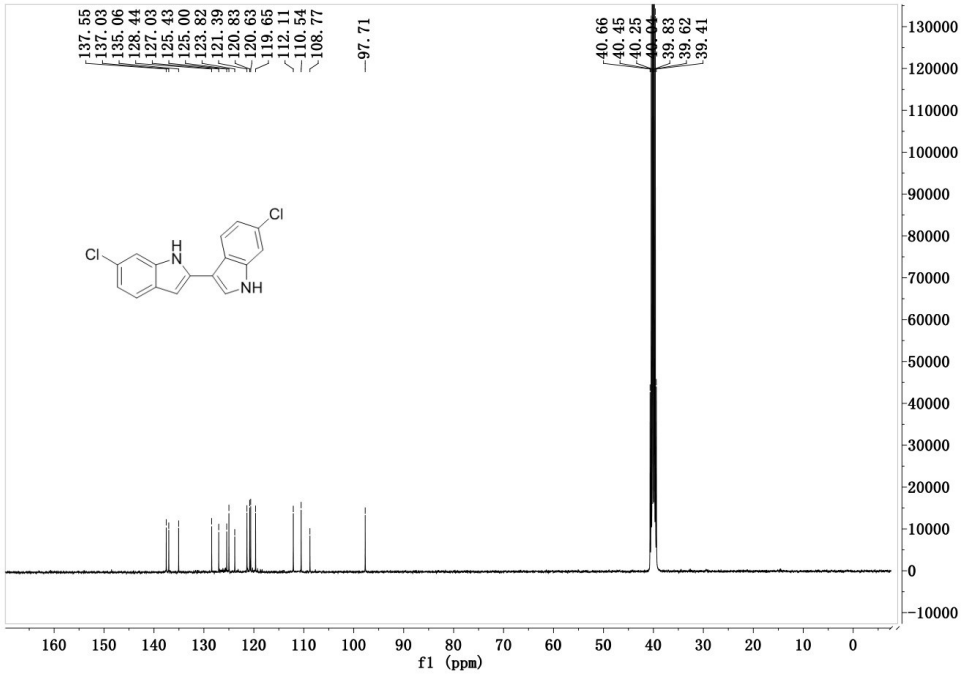
^{1}H and ^{13}C NMR Spectra for **6j**



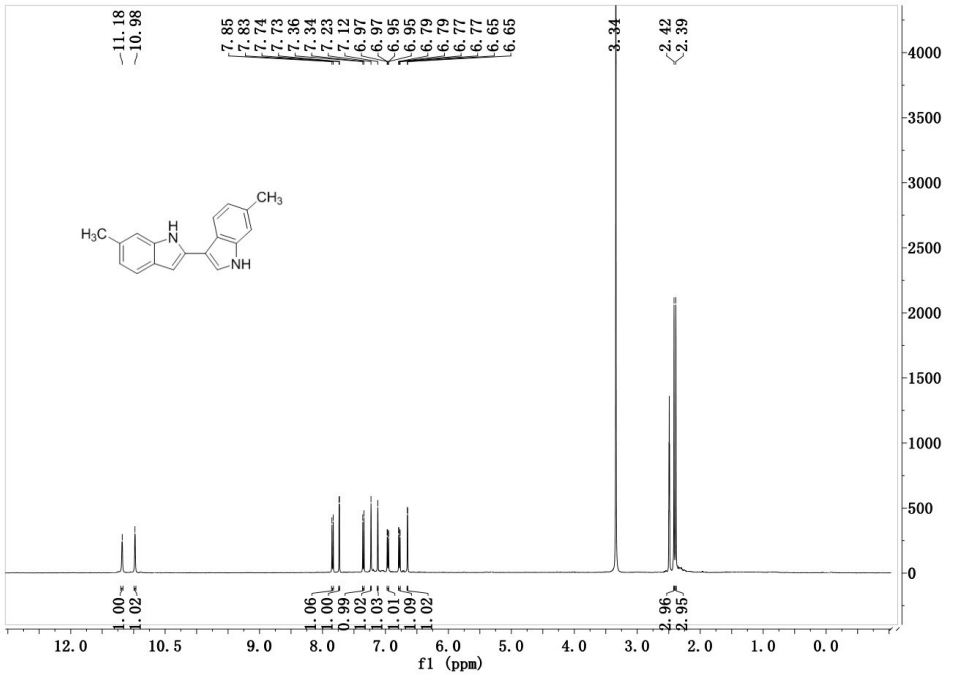


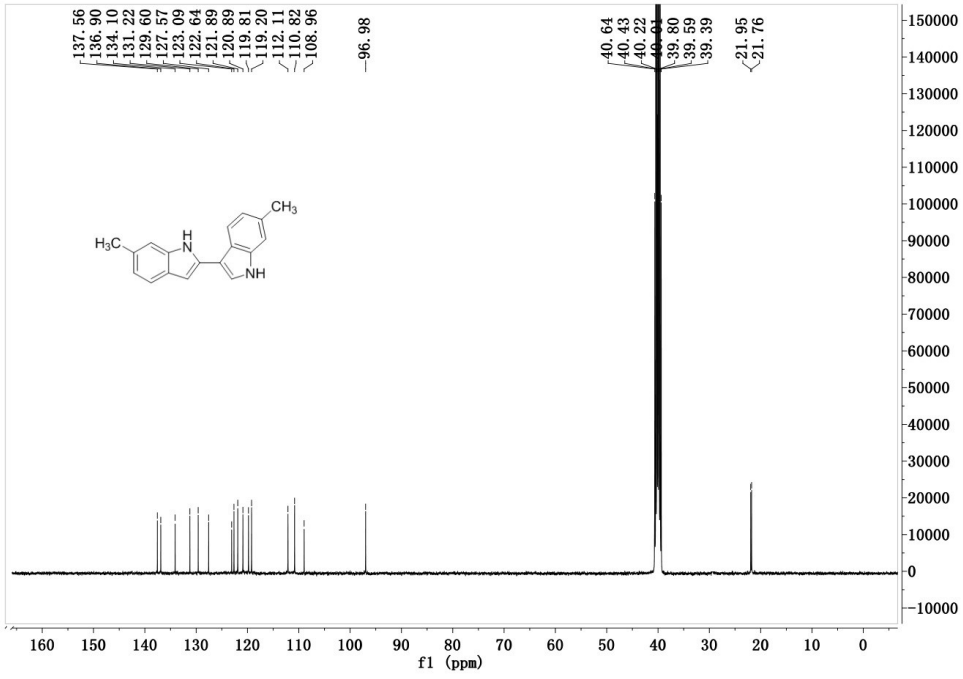
^{1}H and ^{13}C NMR Spectra for **6k**



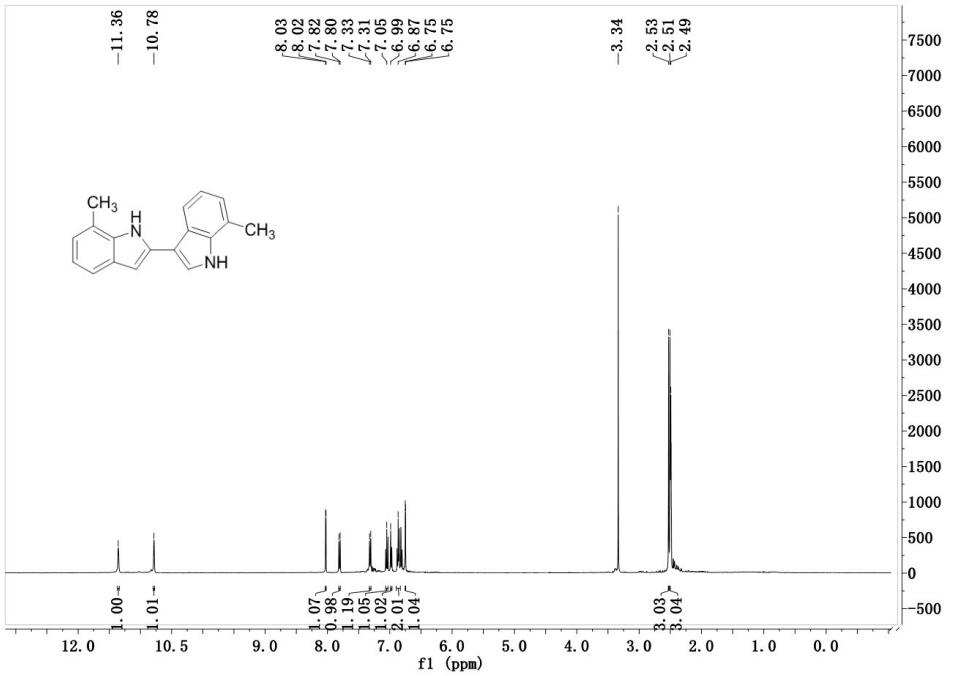


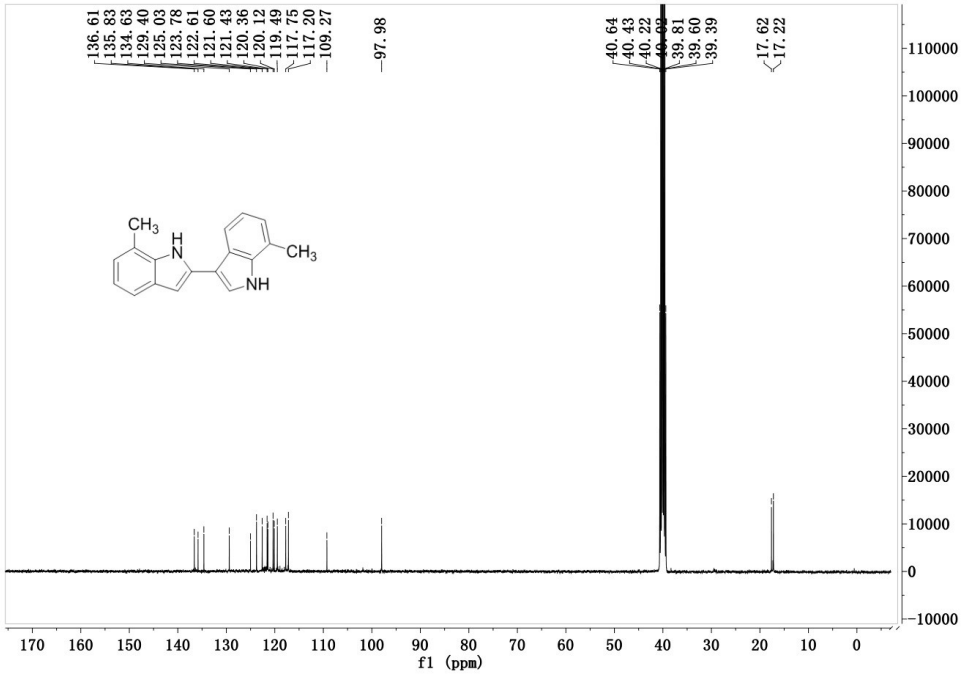
^{1}H and ^{13}C NMR Spectra for **6l**



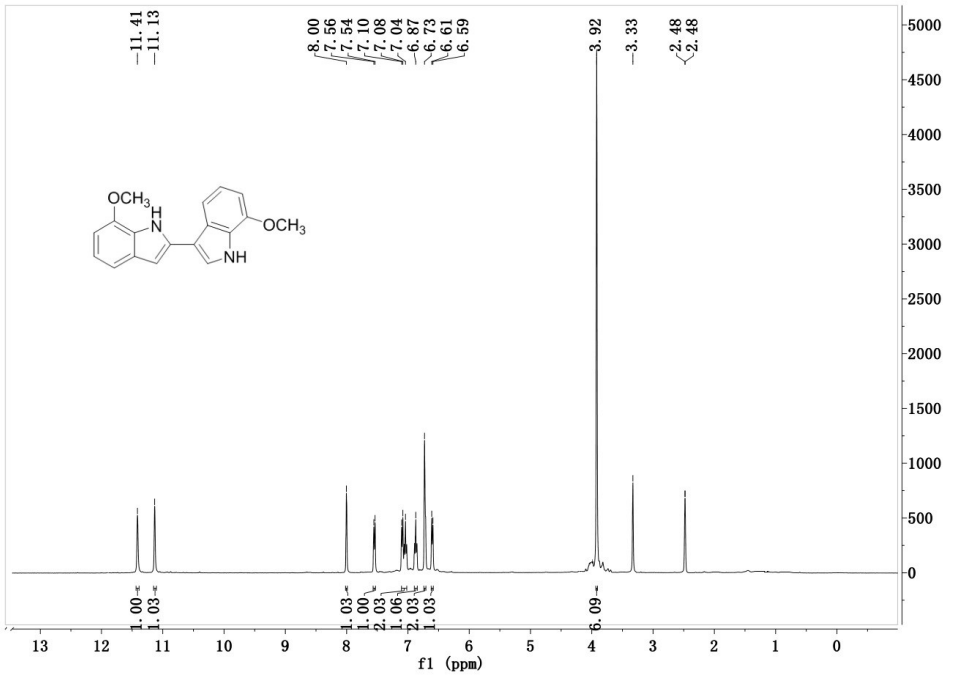


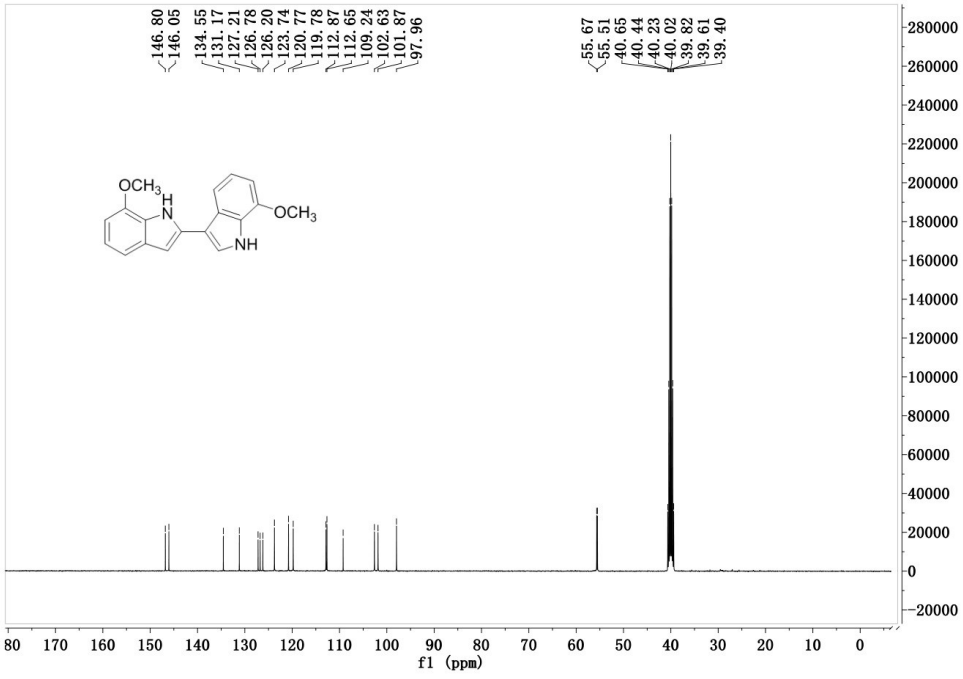
^{1}H and ^{13}C NMR Spectra for **6m**



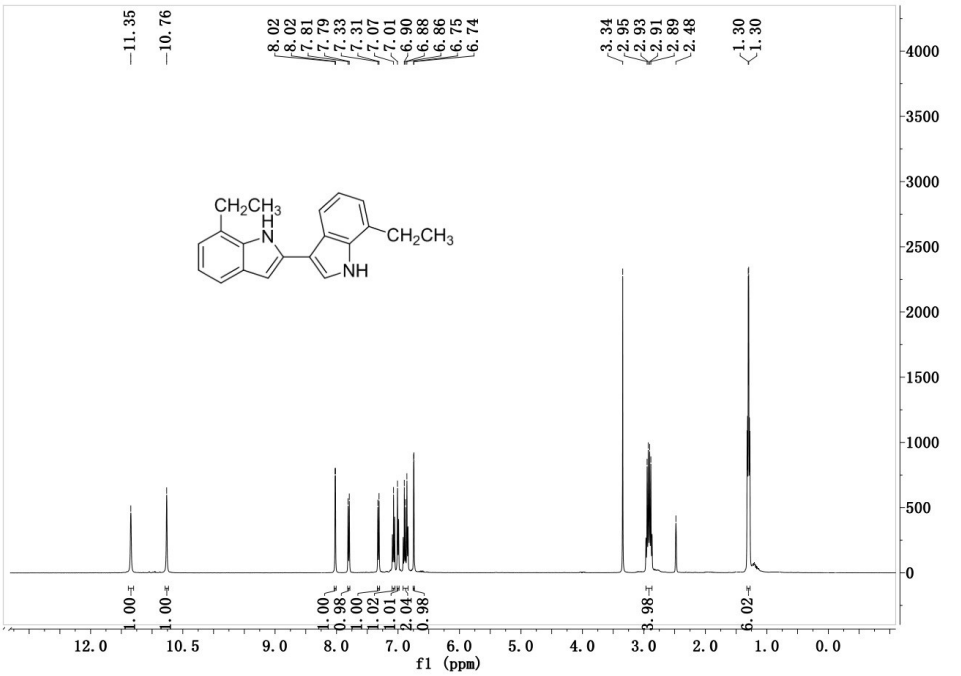


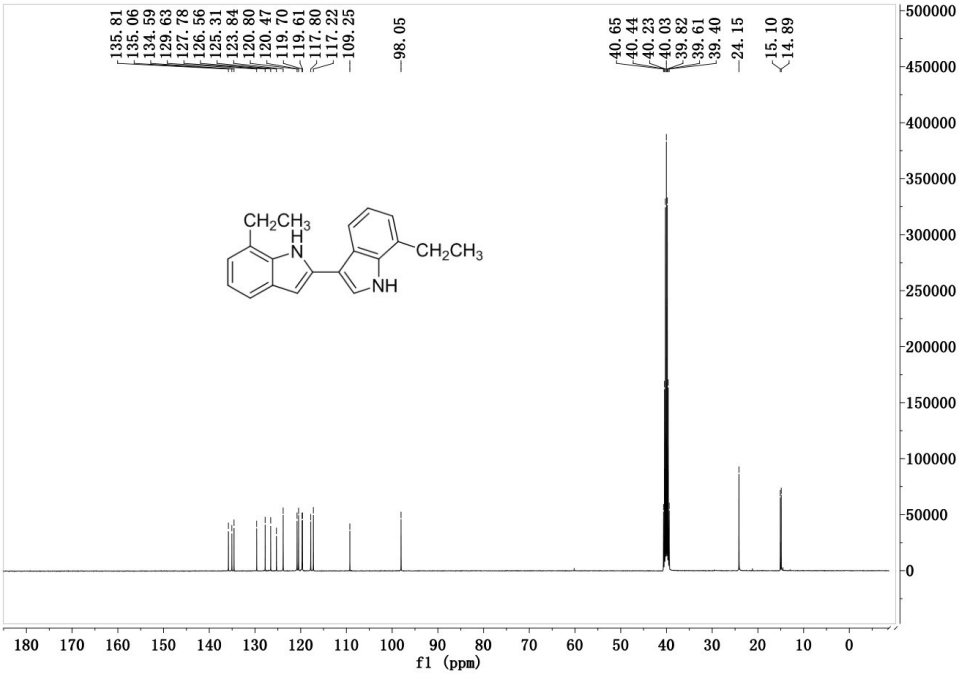
^{1}H and ^{13}C NMR Spectra for **6n**



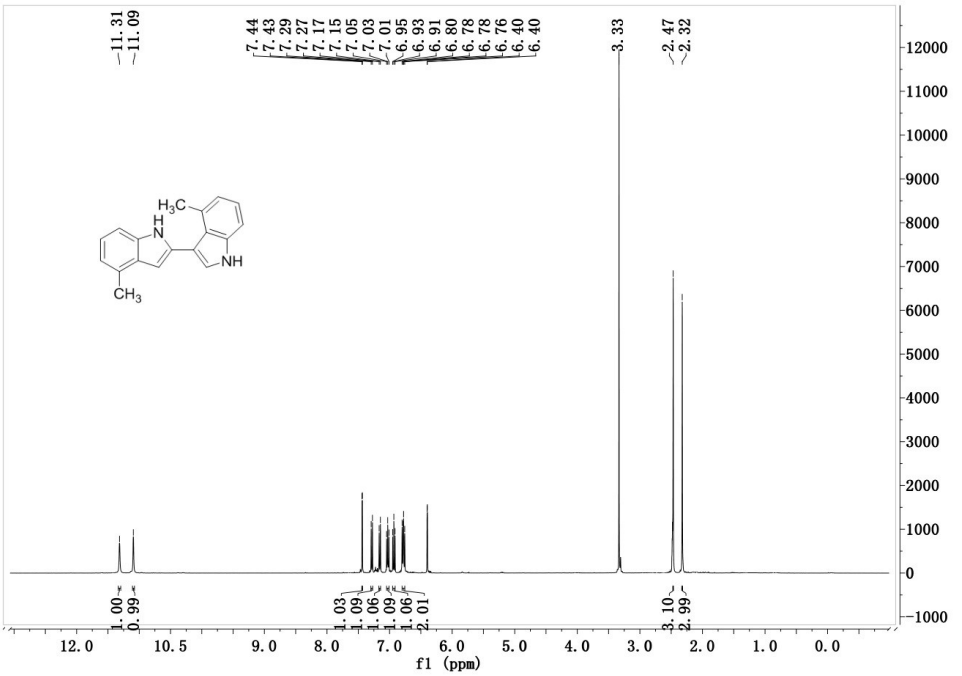


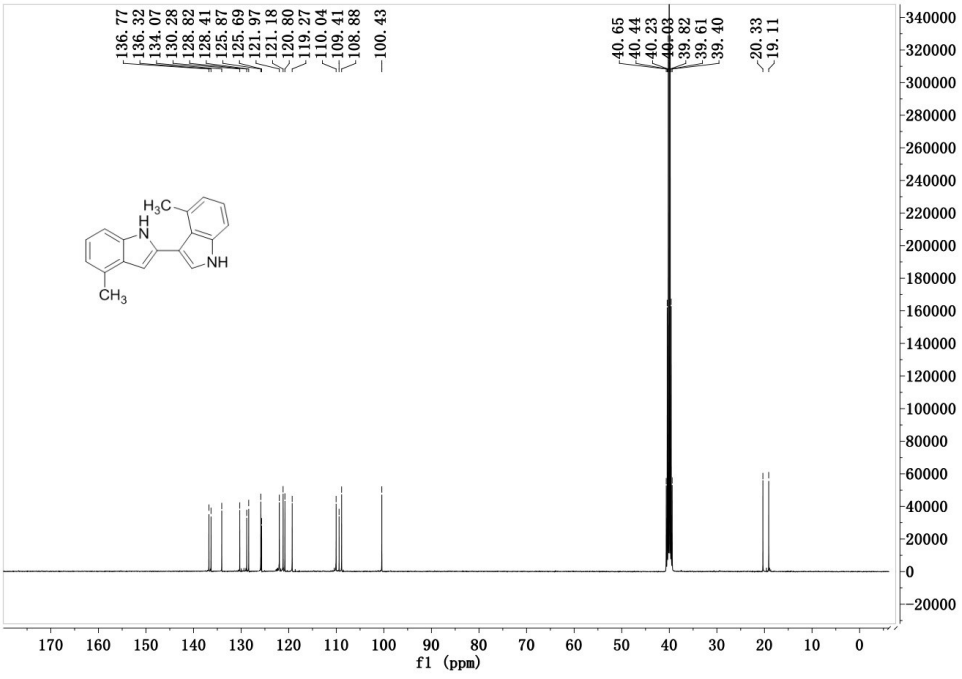
^{1}H and ^{13}C NMR Spectra for **6o**



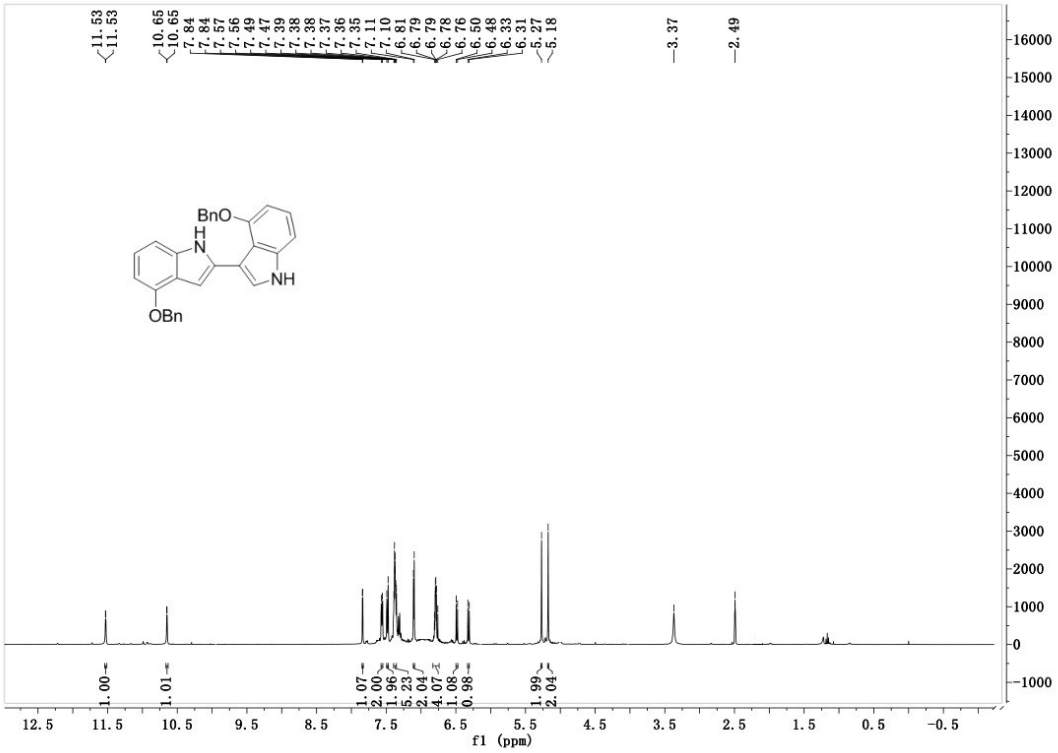


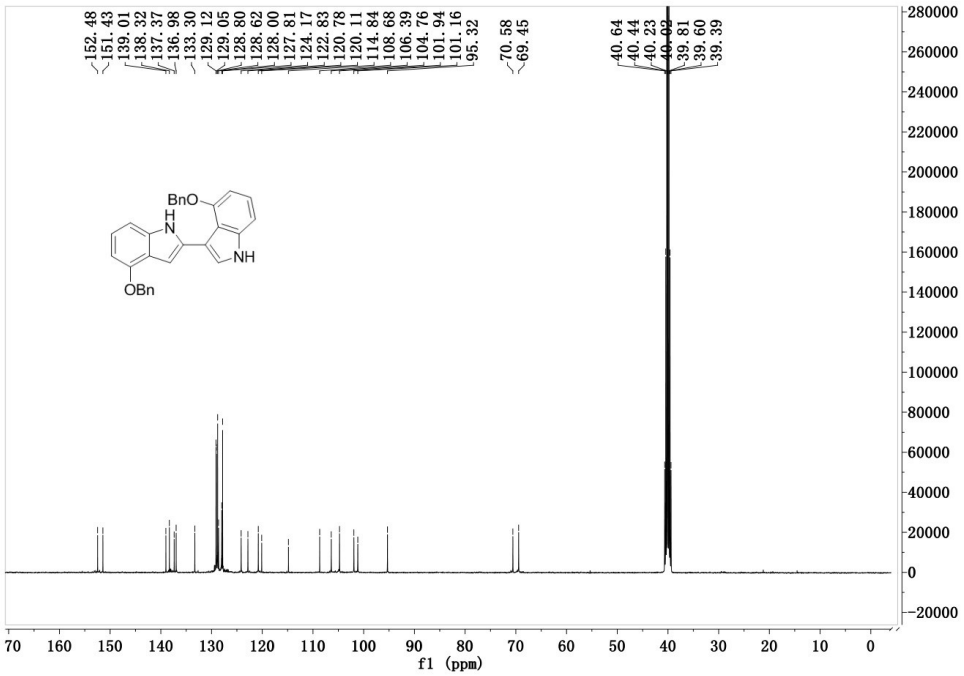
^{1}H and ^{13}C NMR Spectra for **6p**



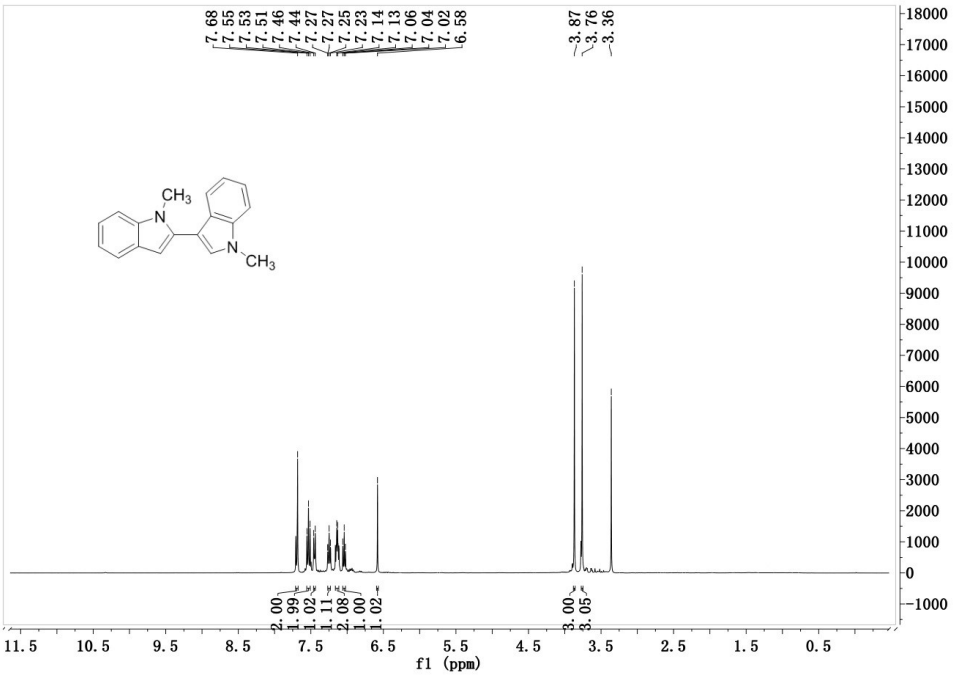


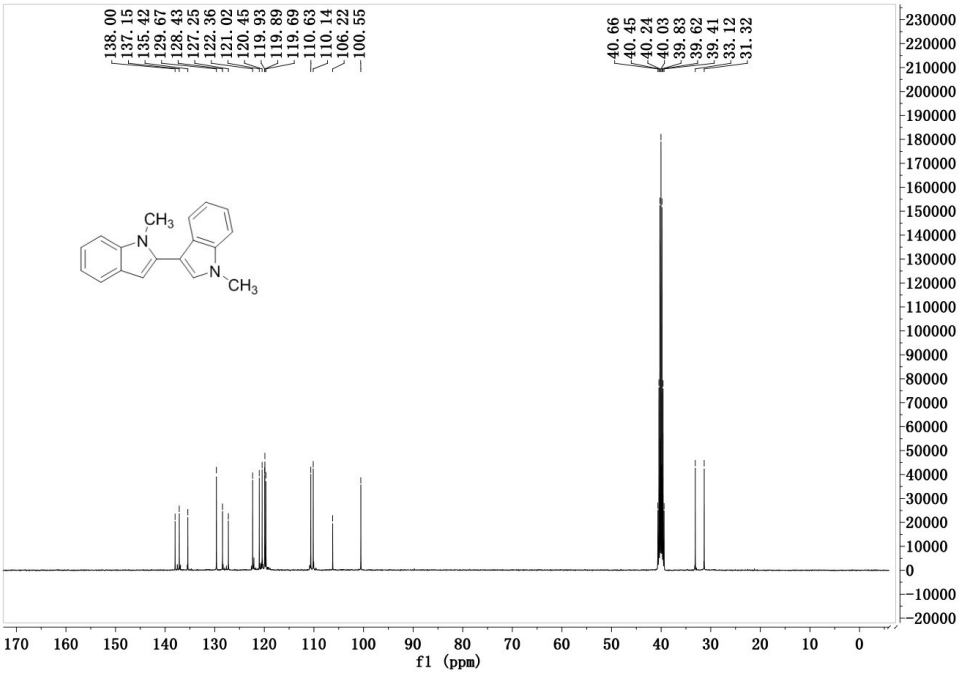
^{1}H and ^{13}C NMR Spectra for **6q**



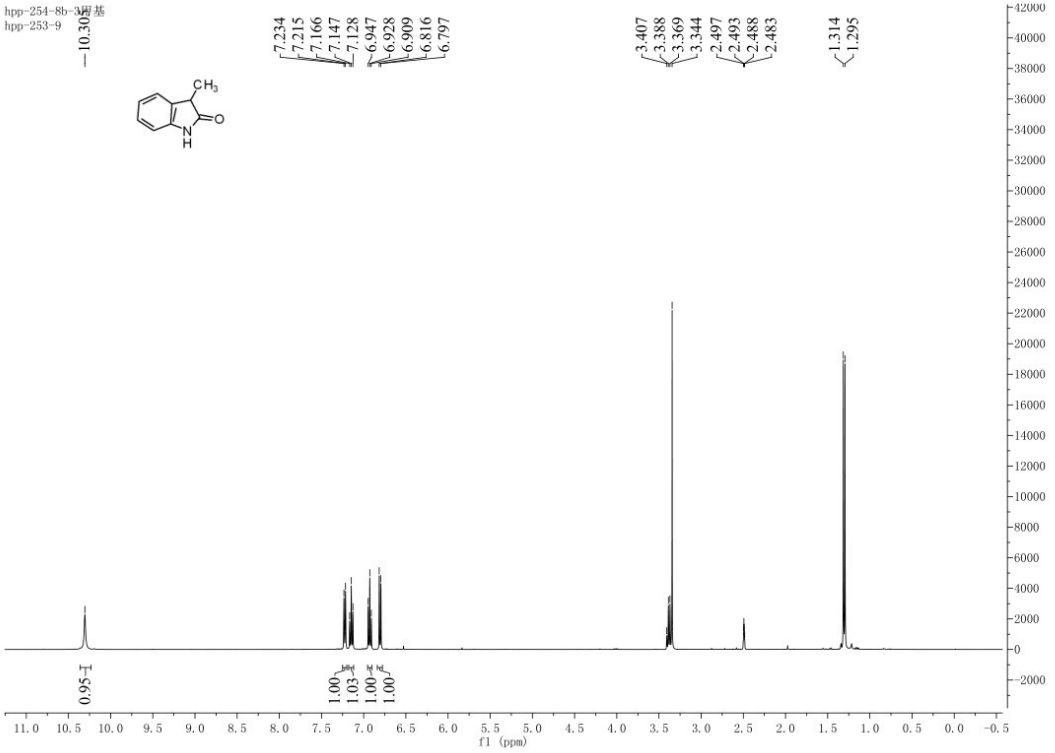


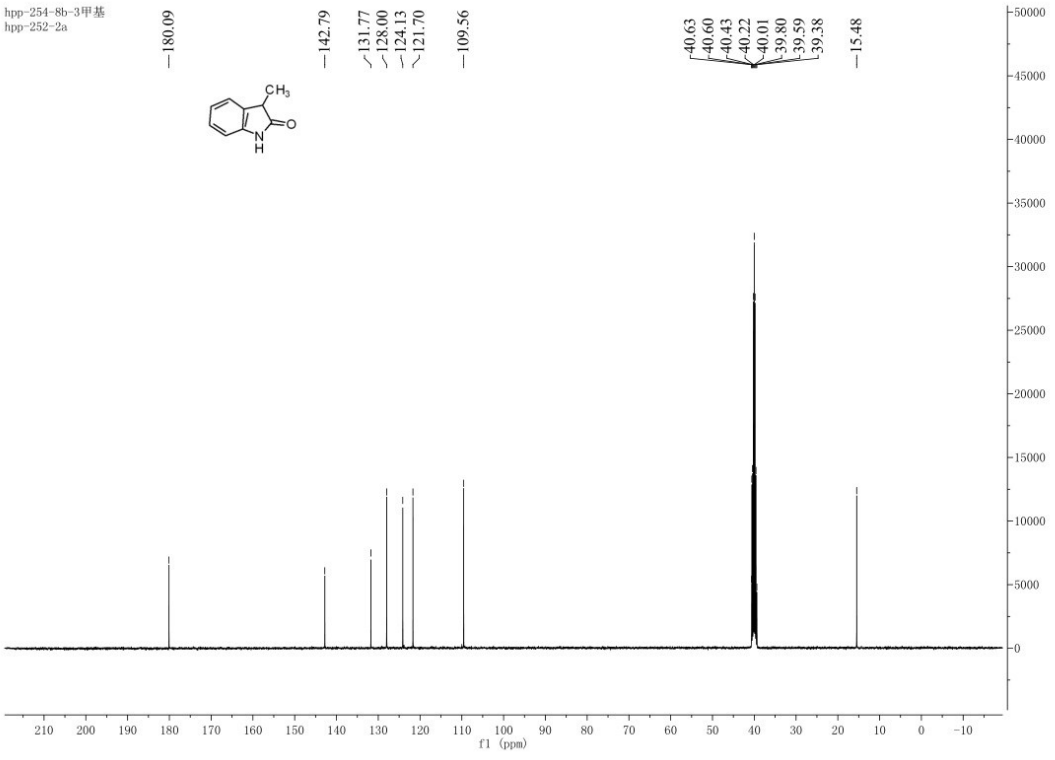
^{1}H and ^{13}C NMR Spectra for **6r**



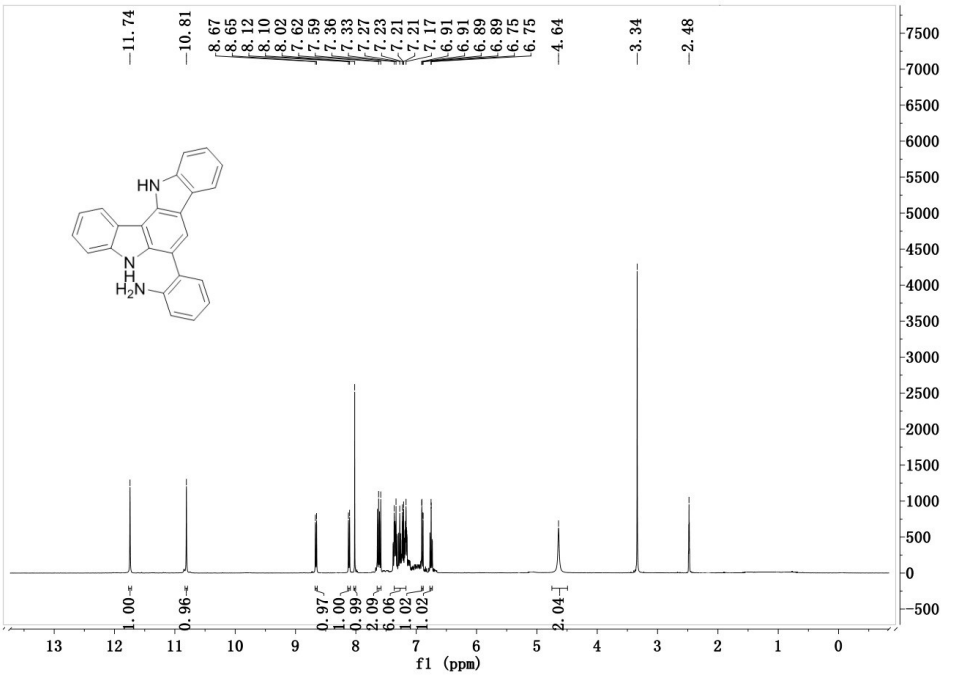


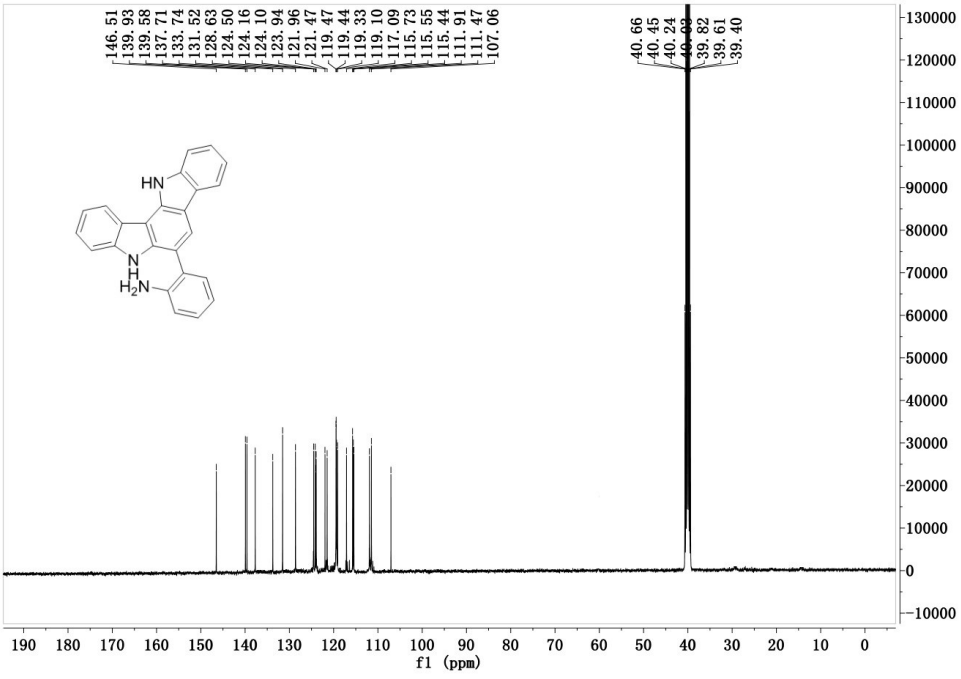
^{1}H and ^{13}C NMR Spectra for **9**



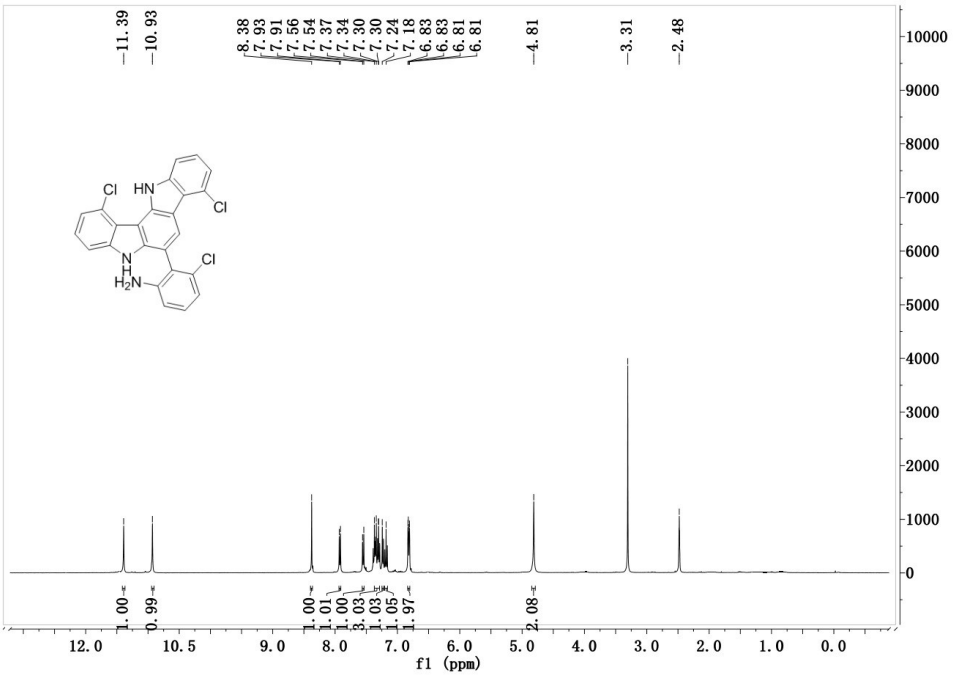


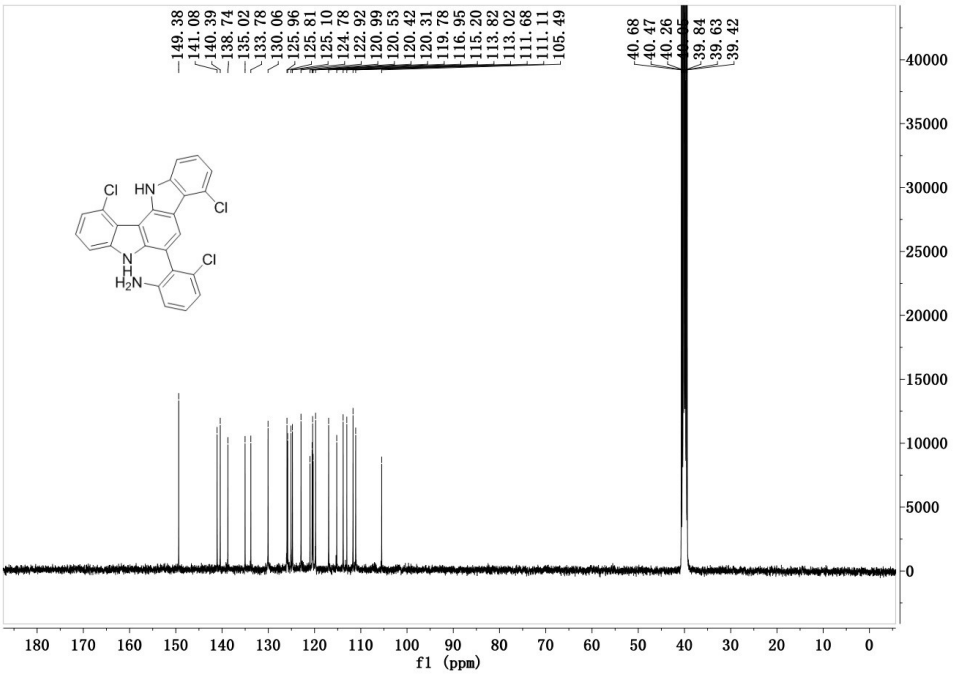
^{1}H and ^{13}C NMR Spectra for **10a**



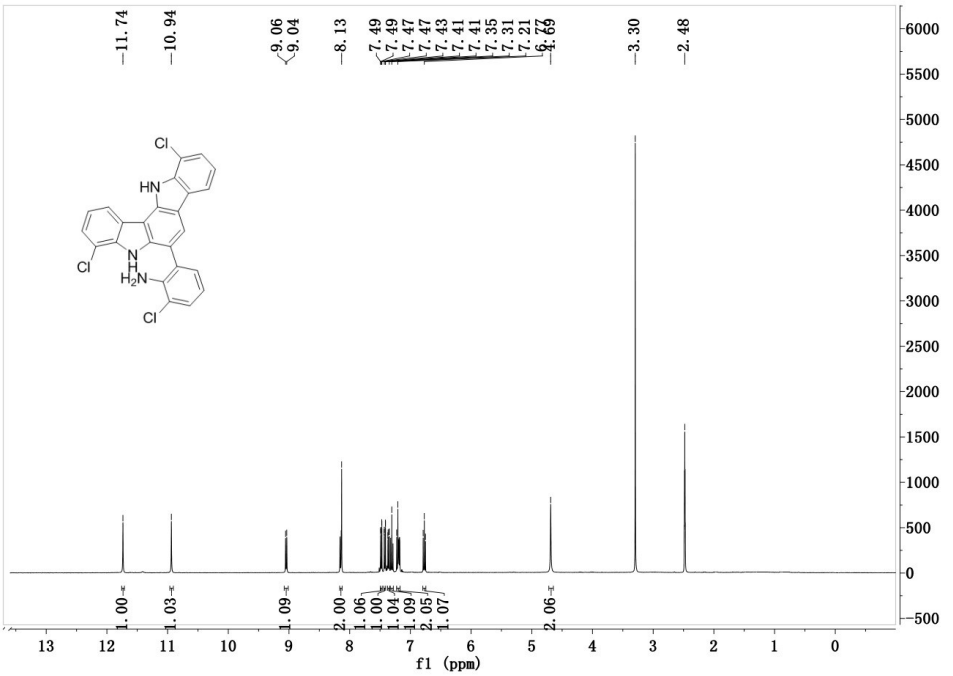


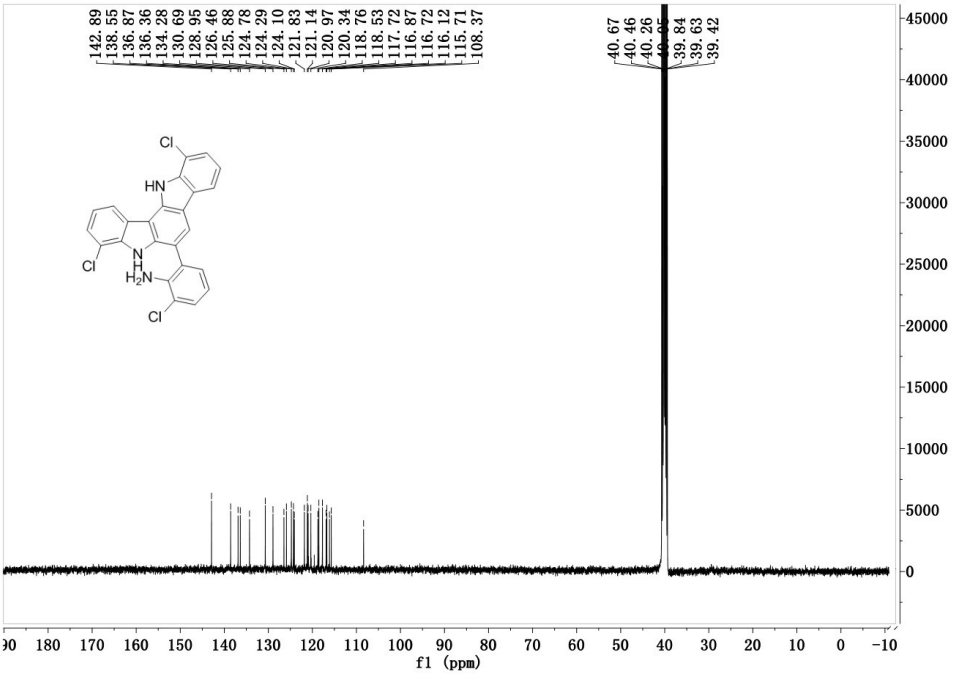
^{1}H and ^{13}C NMR Spectra for **10b**



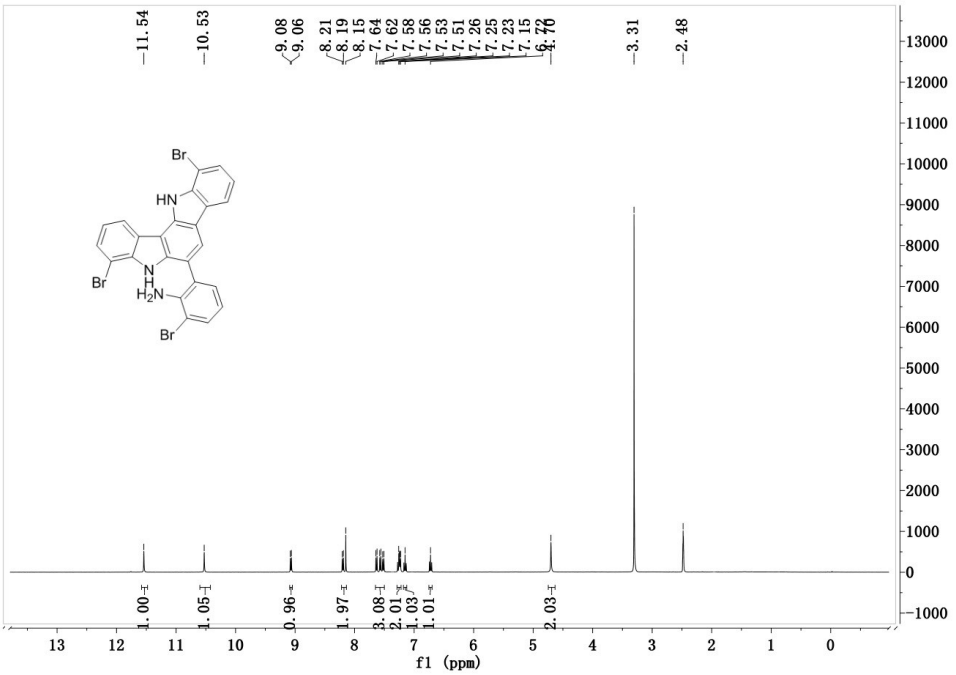


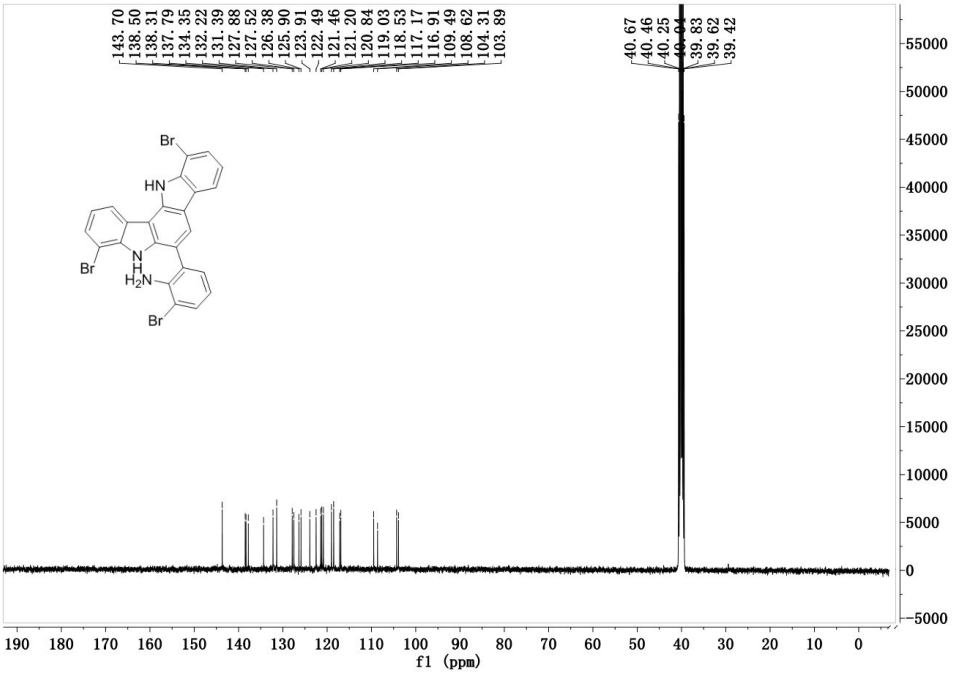
^{1}H and ^{13}C NMR Spectra for **10c**



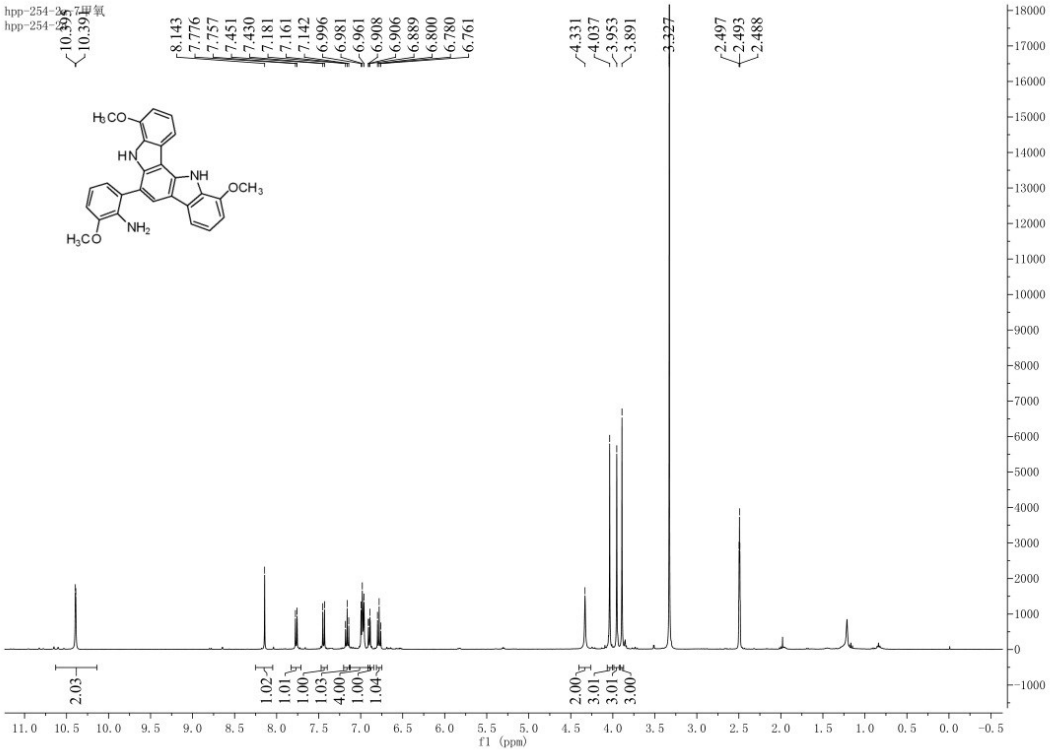


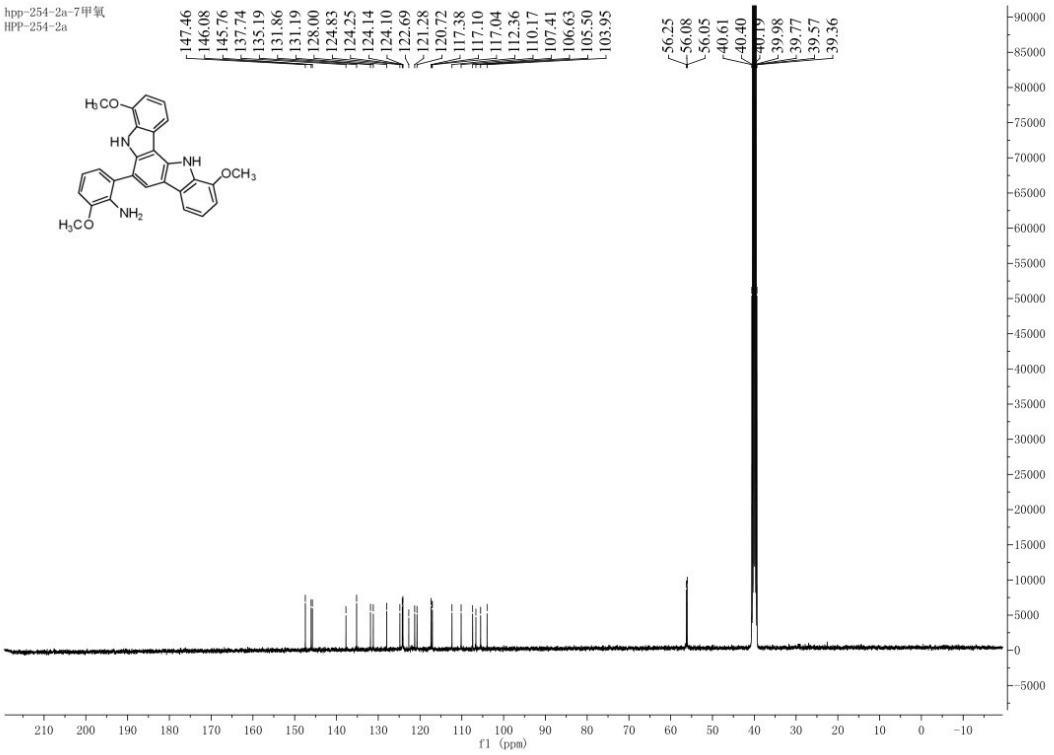
^{1}H and ^{13}C NMR Spectra for **10d**



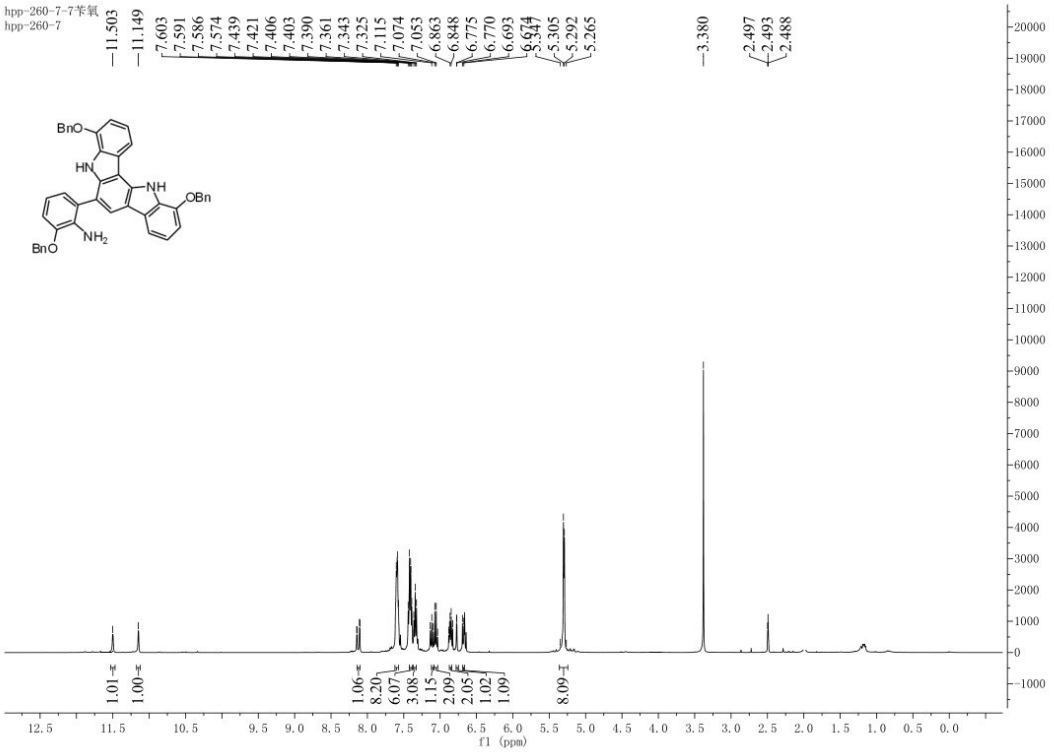


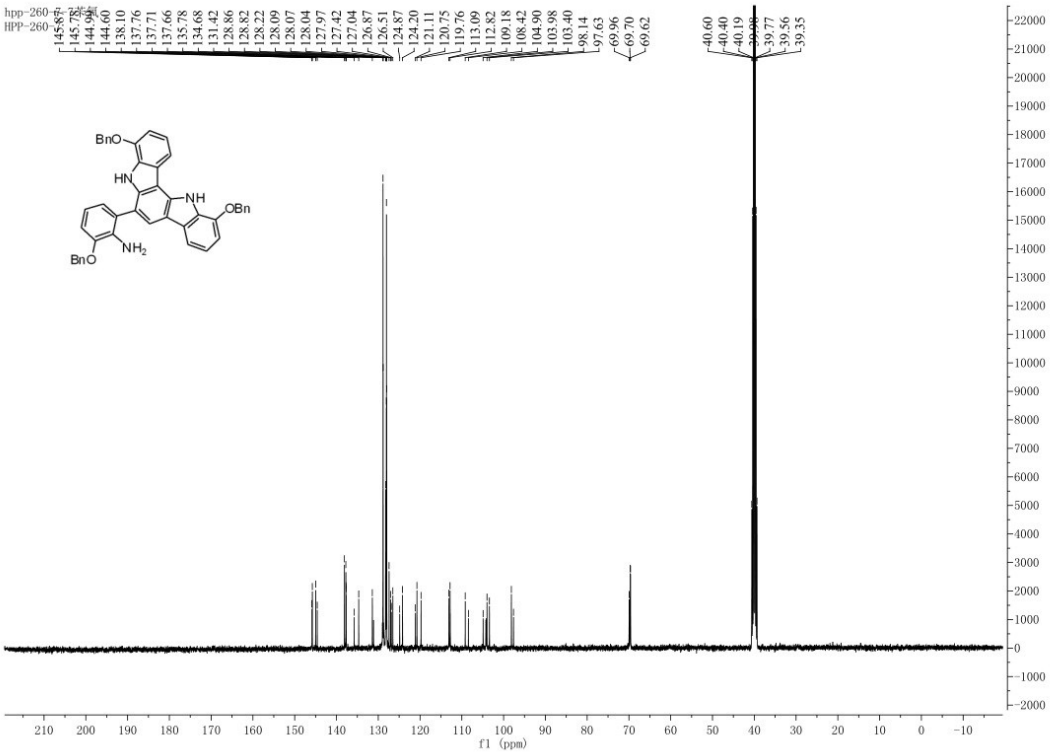
^{1}H and ^{13}C NMR Spectra for **10e**



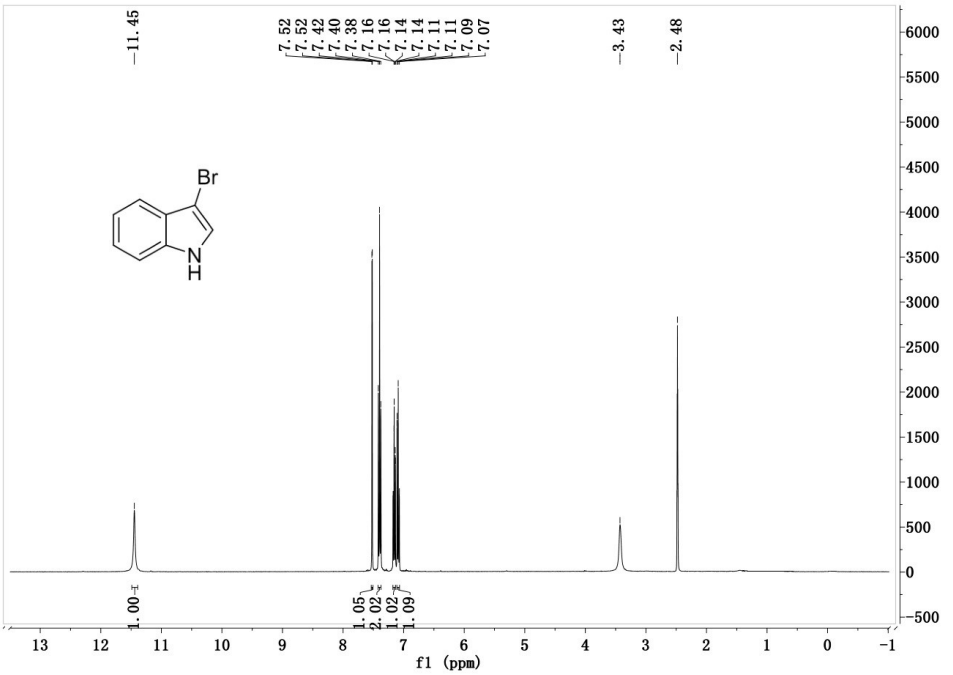


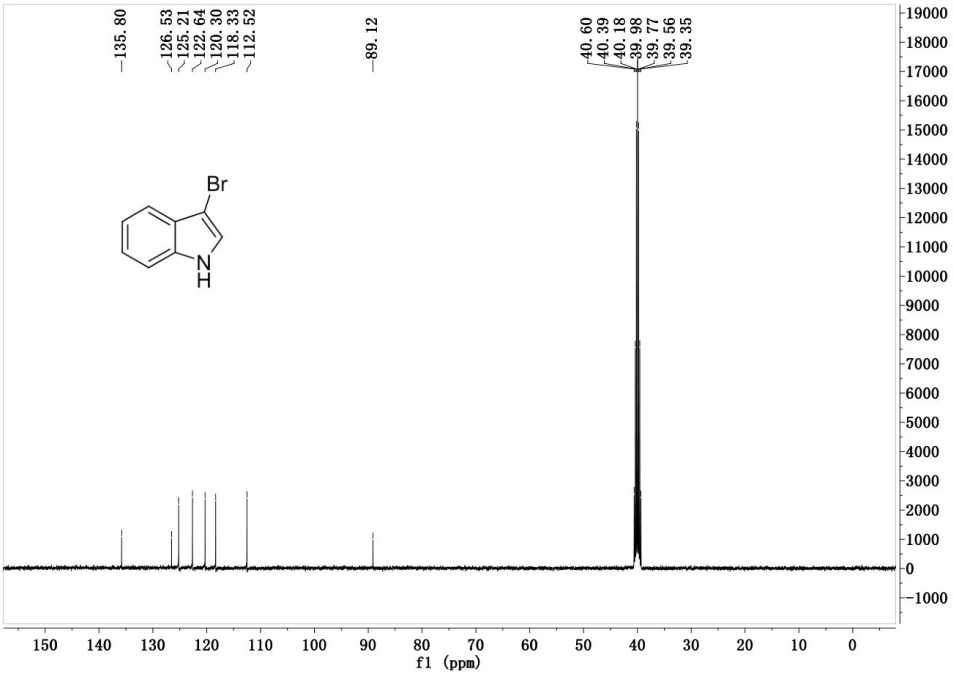
^{1}H and ^{13}C NMR Spectra for **10f**



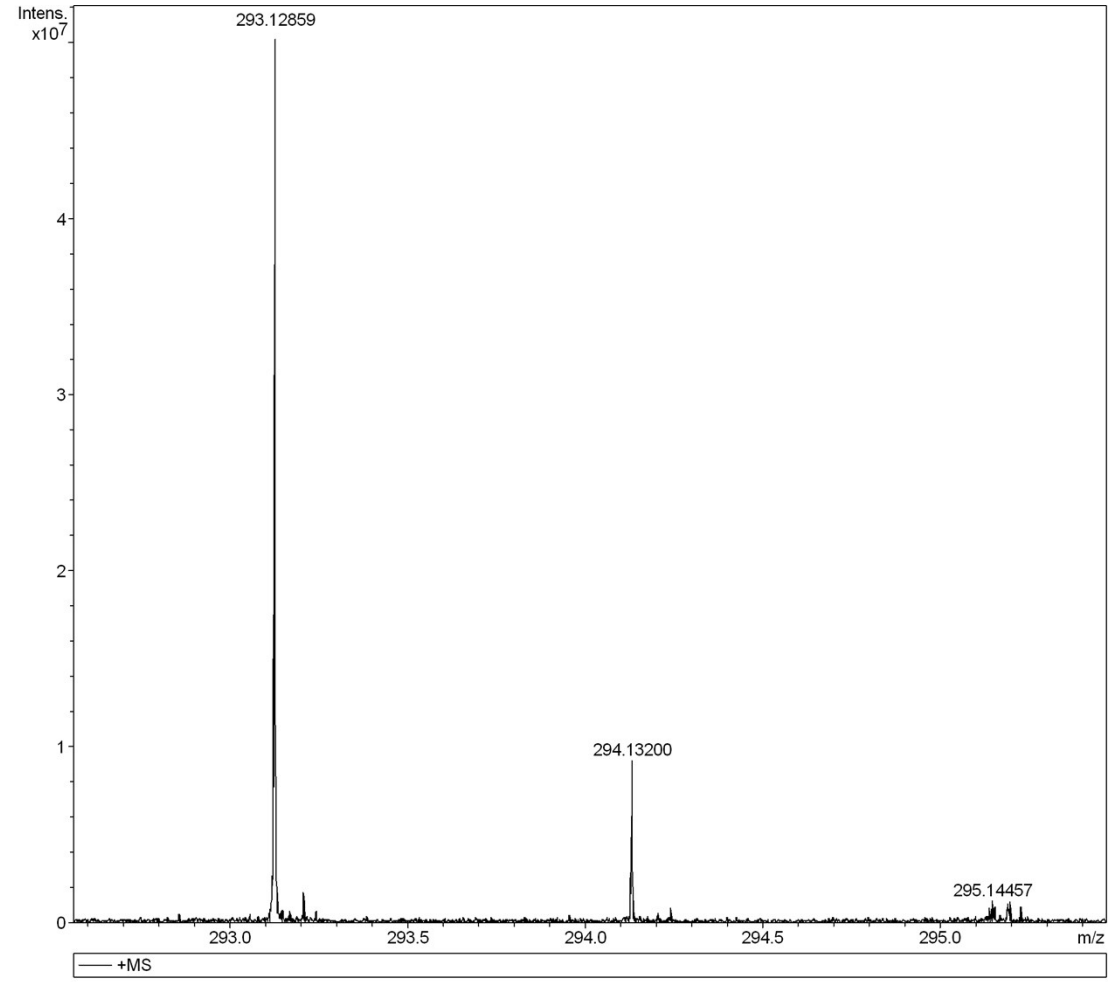


^{1}H and ^{13}C NMR Spectra for **11**





5. Copies of HRESIMS Spectra for 6n



6. X-ray Data of Compound 10b

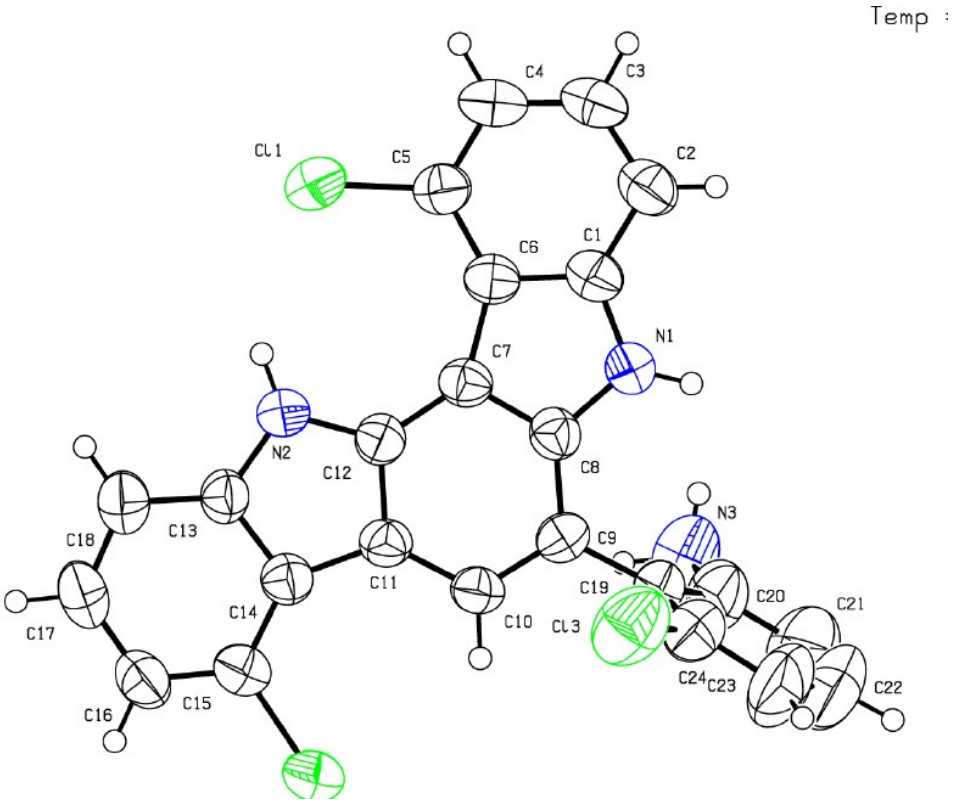


Figure 1. ORTEP representation of the molecular structure of **10b**.
The data have been assigned the following deposition numbers, **CCDC** 1574092.

7. References

1. N. H. Ansari, C. A. Dacko, N. G. Akhmedov and B. C. G. Söderberg, *J. Org. Chem*. **2016**, *81*, 9337–9349.
2. T. Guo, S. L. Han, Y. C. Liu, Y. Liu and H. M. Liu, *Tetrahedron Lett*. **2016**, *57*, 1097–1099.
3. V. Bocchi and G. Palla, *Tetrahedron* **1986**, *42*, 5019–5024.