Supplementary Information (SI) for Green Chemistry.

Supporting Information

Metal-free and visible photons for the dehydrogenative N-N coupling of amines: Powerful methods to optoelectronic materials

Linjie Li,[‡a] Yunyi Shang,[‡a] Yujia Gao,[a] Yanfeng Zhang,[b] Chao Xu,[b] Qichun Zhang[*c] and Hui Wang[*a]

[a]*Key Laboratory of Synthetic and Natural Functional Molecule of the Ministry of Education, College of Chemistry & Materials Science, Northwest University, Xi'an 710127, China*
[b]*Xi'an Oude Optoelectronic Materials Co., Ltd., Xi'an 710199, China*
[c]*Department of Materials Science and Engineering, City University of Hong Kong, Kowloon, Hong Kong, SAR 999077, P. R. China*
Corresponding authors: Hui Wang, E-mail: whui210@nwu.edu.cn;
Qichun Zhang, qiczhang@cityu.edu.hk.

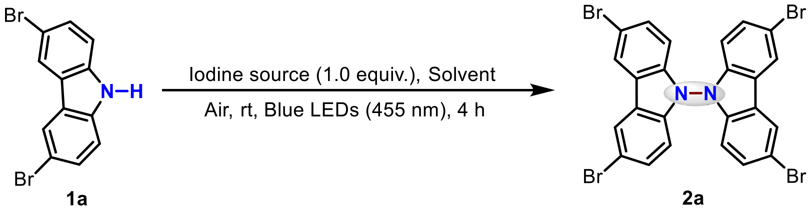
Table of contents

1. General information

All reagents were purchased from commercial suppliers and used without further purification. Flash chromatography was carried out with silica gel (200-300 mesh). Analytical TLC was performed with silica gel GF254 plates, and the products were visualized by UV detection. ^{1}H NMR, ^{13}C NMR (400 MHz and 101 MHz respectively) spectra were measured in $CDCl_3$, DMSO-d_6 recorded on JNM-ECZL400R/S1 spectrometer. All chemical shifts (δ) were reported in ppm and coupling constants (J) in Hz. NMR Spectra recorded in $CDCl_3$ were referenced to tetramethylsilane at 0 ppm for ^{1}H or referenced to residual $CHCl_3$ at 77.16 ppm for ^{13}C. NMR Spectra recorded in DMSO-d_6 were referenced to residual DMSO at 2.50 ppm for ^{1}H or 39.52 ppm for ^{13}C. The following abbreviations are used: m (multiplet), s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), etc. The high resolution mass spectra (HRMS) were measured on a Bruker Daltonics MicroTof-Q Ⅱ spectrometer by ESI. Photoluminescence spectra was performed in Spectrofluorometer FS5 v2. X-ray diffraction experiment was carried out at room temperature on a Bruker D8 QUEST and the data obtained were deposited at the Cambridge Crystallographic Data Centre.

2. Reaction optimization

Table S1. Optimization of the Reaction Conditions[a]

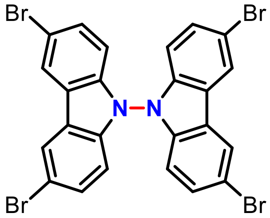


Entry	Iodine sources (equiv.)	Solvent	Yield (%)[b]
1	KIO_4 (1.0)	DMF	5
2	DPIHFP (1.0)	DMF	13
3	PIDA (1.0)	DMF	15
4	NIS (1.0)	DMF	54

[a] Reaction conditions: **1a** (0.2 mmol), iodine sources (1.0 equiv.), solvent (1 mL), air, blue LEDs for 4 h at room temperature. [b] Isolated yields.

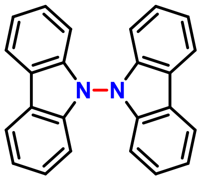
3. Substrates preparation

3,3',6,6'-tetrabromo-9,9'-bicarbazole (2a)



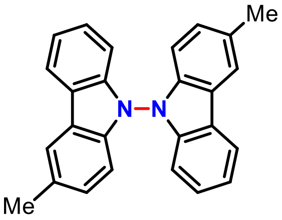
A 10 mL Pyrex tube was charged with substrate 1a (0.2 mmol, 1 equiv.) and NIS (0.3 mmol, 1.5 equiv.) in DMF (1 mL). The sample was then irradiated by blue LEDs for 4 h. After the reaction, quenched with water, extracted with ethyl acetate, washed the organic phase with a large amount of water 3 - 5 times, dried with anhydrous $MgSO_4$ and filtered. The solvent was then removed under vacuum, and obtain white solid 2a by petroleum ether column chromatography (55.4 mg, 0.086 mmol, 86% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 1.7 Hz, 4H), 7.46 (dd, *J* = 8.6, 1.7 Hz, 4H), 6.74 (d, *J* = 8.7 Hz, 4H).[S1] **HRMS** (ESI) m/z calculated for $C_{24}H_{12}Br_4N_2$ $[M]^+$ 643.7728, found 643.7741.

9,9'-bicarbazole (2b)



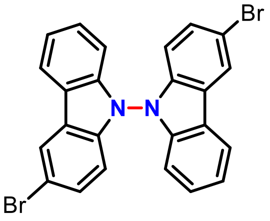
A 10 mL Pyrex tube was charged with substrate 1b (0.2 mmol, 1 equiv.) and NIS (0.3 mmol, 1.5 equiv.) in DMF (1 mL). The sample was then irradiated by blue LEDs for 4 h. After the reaction, quenched with water, extracted with ethyl acetate, washed the organic phase with a large amount of water 3 - 5 times, dried with anhydrous $MgSO_4$ and filtered. The solvent was then removed under vacuum, and obtain white solid 2b by petroleum ether column chromatography (26.6 mg, 0.080 mmol, 80% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 7.0 Hz, 4H), 7.39 - 7.29 (m, 8H), 6.91 (d, *J* = 5.5 Hz, 4H).[S2] **HRMS** (ESI) m/z calculated for $C_{24}H_{17}N_2$ $[M+H]^+$ 333.1386, found 333.1337.

3,3'-dimethyl-9,9'-bicarbazole (2c)



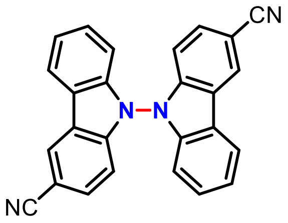
A 10 mL Pyrex tube was charged with substrate 1c (0.2 mmol, 1 equiv.) and NIS (0.3 mmol, 1.5 equiv.) in DMF (1 mL). The sample was then irradiated by blue LEDs for 4 h. After the reaction, quenched with water, extracted with ethyl acetate, washed the organic phase with a large amount of water 3 - 5 times, dried with anhydrous $MgSO_4$ and filtered. The solvent was then removed under vacuum, and obtain white solid 2c by petroleum ether column chromatography (25.6 mg, 0.071 mmol, 71% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.23 - 8.13 (m, 2H), 8.00 (s, 2H), 7.38 - 7.28 (m, 4H), 7.15 (d, *J* = 10.1 Hz, 2H), 6.95 - 6.85 (m, 2H), 6.79 (d, *J* = 8.3 Hz, 2H), 2.55 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.26, 138.22, 130.74, 127.87, 126.47, 122.20, 121.91, 121.05, 120.76, 120.64, 109.17, 108.90, 21.55. **HRMS** (ESI) m/z calculated for $C_{26}H_{21}N_2$ $[M+H]^+$ 361.1699, found 361.1697.

3,3'-dibromo-9,9'-bicarbazole (2d)



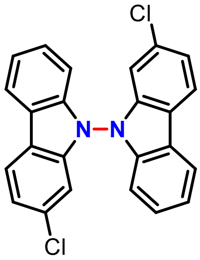
A 10 mL Pyrex tube was charged with substrate 1d (0.2 mmol, 1 equiv.) and NIS (0.3 mmol, 1.5 equiv.) in DMF (1 mL). The sample was then irradiated by blue LEDs for 4 h. After the reaction, quenched with water, extracted with ethyl acetate, washed the organic phase with a large amount of water 3 - 5 times, dried with anhydrous $MgSO_4$ and filtered. The solvent was then removed under vacuum, and obtain white solid 2d by petroleum ether column chromatography (39.0 mg, 0.080 mmol, 80% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 1.9 Hz, 2H), 8.18 - 8.10 (m, 2H), 7.42 (dd, *J* = 8.6, 1.9 Hz, 2H), 7.39 - 7.32 (m, 4H), 6.90 - 6.84 (m, 2H), 6.76 (d, *J* = 8.6 Hz, 2H).[S1] **HRMS** (ESI) m/z calculated for $C_{24}H_{15}Br_2N_2$ $[M+H]^+$ 488.9596, found 488.9526.

[9,9'-bicarbazole]-3,3'-dicarbonitrile (2e)



A 10 mL Pyrex tube was charged with substrate 1e (0.2 mmol, 1 equiv.) and NIS (0.3 mmol, 1.5 equiv.) in DMF (1 mL). The sample was then irradiated by blue LEDs for 24 h. After the reaction, quenched with water, extracted with ethyl acetate, washed the organic phase with a large amount of water 3 - 5 times, dried with anhydrous $MgSO_4$ and filtered. The solvent was then removed under vacuum, and obtain yellow solid 2e by petroleum ether/ethyl acetate = 10/1 column chromatography (16.4 mg, 0.043 mmol, 43% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.53 (s, 2H), 8.23 (d, *J* = 5.2 Hz, 2H), 7.63 (d, *J* = 10.0 Hz, 2H), 7.52 - 7.39 (m, 4H), 7.00 - 6.86 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.31, 139.86, 130.36, 128.54, 125.82, 123.07, 122.49, 121.45, 121.00, 119.67, 109.70, 109.32, 105.26. **HRMS** (ESI) m/z calculated for $C_{26}H_{15}N_4$ $[M+H]^+$ 383.1291, found 383.1266.

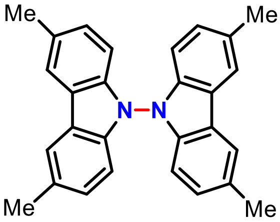
2,2'-dichloro-9,9'-bicarbazole (2f)



A 10 mL Pyrex tube was charged with substrate 1f (0.2 mmol, 1 equiv.) and NIS (0.3 mmol, 1.5 equiv.) in DMF (1 mL). The sample was then irradiated by blue LEDs for 4 h. After the reaction, quenched with water, extracted with ethyl acetate, washed the organic phase with a large amount of water 3 - 5 times, dried with anhydrous $MgSO_4$ and filtered. The solvent was then removed under vacuum, and obtain white solid 2f by petroleum ether column chromatography (27.6 mg, 0.069 mmol, 69% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 - 8.14 (m, 2H), 8.10 (d, *J* = 8.4 Hz, 2H), 7.38 - 7.36 (m, 2H), 7.35 (dd, *J* = 3.0, 1.3 Hz, 2H), 7.34 - 7.31 (m, 2H), 6.90 (d, *J* = 1.8 Hz, 2H), 6.88 -

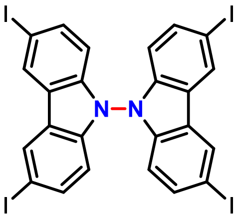
6.84 (m, 2H).[S3] **HRMS** (ESI) m/z calculated for $C_{24}H_{15}Cl_2N_2$ $[M+H]^+$ 401.0607, found 401.0617.

3,3',6,6'-tetramethyl-9,9'-bicarbazole (2g)



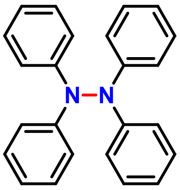
A 10 mL Pyrex tube was charged with substrate 1g (0.2 mmol, 1 equiv.) and NIS (0.3 mmol, 1.5 equiv.) in DMF (1 mL). The sample was then irradiated by blue LEDs for 4 h. After the reaction, quenched with water, extracted with ethyl acetate, washed the organic phase with a large amount of water 3 - 5 times, dried with anhydrous $MgSO_4$ and filtered. The solvent was then removed under vacuum, and obtain white solid 2g by petroleum ether column chromatography (30.3 mg, 0.078 mmol, 78% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (s, 4H), 7.13 (d, *J* = 8.3 Hz, 4H), 6.78 (d, *J* = 8.3 Hz, 4H), 2.57 (s, 12H).[S3] **HRMS** (ESI) m/z calculated for $C_{28}H_{25}N_2$ $[M+H]^+$ 389.2012, found 389.2003.

3,3',6,6'-tetraiodo-9,9'-bicarbazole (2h)



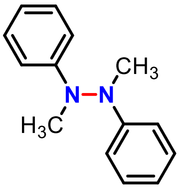
A 10 mL Pyrex tube was charged with substrate 1h (0.2 mmol, 1 equiv.) and NIS (0.3 mmol, 1.5 equiv.) in DMF (1 mL). The sample was then irradiated by blue LEDs for 4 h. After the reaction, quenched with water, extracted with ethyl acetate, washed the organic phase with a large amount of water 3 - 5 times, dried with anhydrous $MgSO_4$ and filtered. The solvent was then removed under vacuum, and obtain white solid 2h by petroleum ether column chromatography (71.0 mg, 0.085 mmol, 85% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 1.1 Hz, 4H), 7.62 (dd, *J* = 8.6, 1.7 Hz, 4H), 6.62 (d, *J* = 8.4 Hz, 4H).[S1] **HRMS** (ESI) m/z calculated for $C_{24}H_{13}I_4N_2$ $[M+H]^+$ 836.7252, found 836.7236.

1,1,2,2-tetraphenylhydrazine (2j)



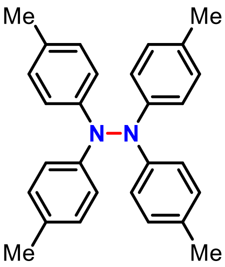
A 10 mL Pyrex tube was charged with substrate 1j (0.2 mmol, 1 equiv.) and NIS (0.3 mmol, 1.5 equiv.) in DMF (1 mL). The sample was then irradiated by blue LEDs for 4 h. After the reaction, quenched with water, extracted with ethyl acetate, washed the organic phase with a large amount of water 3 - 5 times, dried with anhydrous $MgSO_4$ and filtered. The solvent was then removed under vacuum, and obtain white solid 2j by petroleum ether column chromatography (18.2 mg, 0.054 mmol, 54% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.3 Hz, 8H), 7.23 - 7.15 (m, 8H), 6.93 - 6.86 (m, 4H).[S1] **HRMS** (ESI) m/z calculated for $C_{24}H_{21}N_2$ $[M+H]^+$ 337.1699, found 337.1674.

1,2-dimethyl-1,2-diphenylhydrazine (2k)



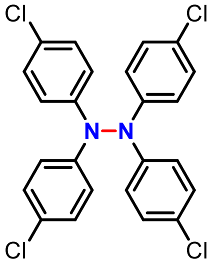
A 10 mL Pyrex tube was charged with substrate 1k (1 mmol, 1 equiv.) and NIS (1.5 mmol, 1.5 equiv.) in EtOH (1 mL). The sample was then stired for 10 min. After the reaction, the solvent was then removed under vacuum, and obtain white solid 2k by petroleum ether column chromatography (53.0 mg, 0.25 mmol, 50% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 - 7.22 (m, 4H), 6.86 - 6.77 (m, 6H), 2.99 (s, 6H).[S3] **HRMS** (ESI) m/z calculated for $C_{14}H_{17}N_2$ $[M+H]^+$ 213.1386, found 213.1358.

1,1,2,2-tetra-p-tolylhydrazine (2l)



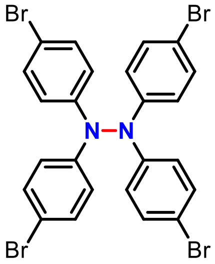
A 10 mL Pyrex tube was charged with substrate 1l (0.2 mmol, 1 equiv.) and NIS (0.3 mmol, 1.5 equiv.) in DMF (1 mL). The sample was then irradiated by blue LEDs for 4 h. After the reaction, quenched with water, extracted with ethyl acetate, washed the organic phase with a large amount of water 3 - 5 times, dried with anhydrous $MgSO_4$ and filtered. The solvent was then removed under vacuum, and obtain white solid 2l by petroleum ether column chromatography (20.8 mg, 0.053 mmol, 53% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.6 Hz, 8H), 6.97 (d, *J* = 8.6 Hz, 8H), 2.21 (s, 12H).[S1] **HRMS** (ESI) m/z calculated for $C_{28}H_{29}N_2$ $[M+H]^+$ 393.2325, found 393.2330.

1,1,2,2-tetrakis(4-chlorophenyl)hydrazine (2m)



A 10 mL Pyrex tube was charged with substrate 1m (0.2 mmol, 1 equiv.) and NIS (0.3 mmol, 1.5 equiv.) in DMF (1 mL). The sample was then irradiated by blue LEDs for 4 h. After the reaction, quenched with water, extracted with ethyl acetate, washed the organic phase with a large amount of water 3 - 5 times, dried with anhydrous $MgSO_4$ and filtered. The solvent was then removed under vacuum, and obtain white solid 2m by petroleum ether column chromatography (41.1 mg, 0.087 mmol, 87% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20 - 7.15 (m, 8H), 7.15 - 7.09 (m, 8H).[S4] **HRMS** (ESI) m/z calculated for $C_{24}H_{17}Cl_4N_2$ $[M+H]^+$ 473.0140, found 473.0126.

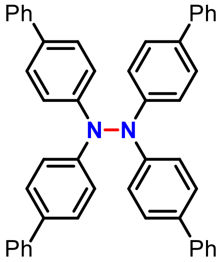
1,1,2,2-tetrakis(4-bromophenyl)hydrazine (2n)



A 10 mL Pyrex tube was charged with substrate 1n (0.2 mmol, 1 equiv.) and NIS (0.3 mmol, 1.5 equiv.) in DMF (1 mL). The sample was then irradiated by blue LEDs for

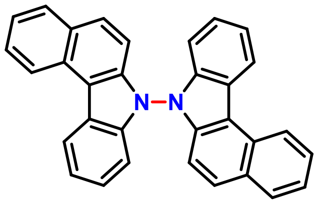
4 h. After the reaction, quenched with water, extracted with ethyl acetate, washed the organic phase with a large amount of water 3 - 5 times, dried with anhydrous $MgSO_4$ and filtered. The solvent was then removed under vacuum, and obtain white solid 2n by petroleum ether column chromatography (60.2 mg, 0.093 mmol, 93% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 - 7.28 (m, 8H), 7.11 - 7.05 (m, 8H).[S1] **HRMS** (ESI) m/z calculated for $C_{24}H_{17}Br_4N_2$ $[M+H]^+$ 648.8120, found 648.8197.

1,1,2,2-tetra([1,1'-biphenyl]-4-yl)hydrazine (2o)



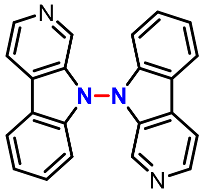
A 10 mL Pyrex tube was charged with substrate 1o (0.2 mmol, 1 equiv.) and NIS (0.3 mmol, 1.5 equiv.) in DMF (1 mL). The sample was then irradiated by blue LEDs for 4 h. After the reaction, quenched with water, extracted with ethyl acetate, washed the organic phase with a large amount of water 3 - 5 times, dried with anhydrous $MgSO_4$ and filtered. The solvent was then removed under vacuum, and obtain white solid 2o by petroleum ether column chromatography (57.6 mg, 0.090mmol, 90% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 - 7.53 (m, 8H), 7.52 – 7.49 (m, 8H), 7.49 – 7.45 (m, 8H), 7.42 - 7.36 (m, 8H), 7.31 - 7.26 (m, 4H).[S5] **HRMS** (ESI) m/z calculated for $C_{48}H_{37}N_2$ $[M+H]^+$ 641.2951, found 641.2919.

7,7'-bibenzo[c]carbazole (2q)



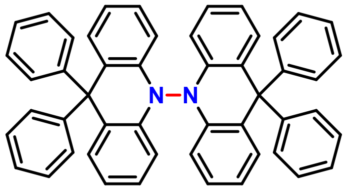
A 10 mL Pyrex tube was charged with substrate 1q (0.2 mmol, 1 equiv.) and NIS (0.3 mmol, 1.5 equiv.) in DMF (1 mL). The sample was then irradiated by blue LEDs for 22 h. After the reaction, quenched with water, extracted with ethyl acetate, washed the organic phase with a large amount of water 3 - 5 times, dried with anhydrous $MgSO_4$ and filtered. The solvent was then removed under vacuum, and obtain white solid 2q by petroleum ether column chromatography (39.3 mg, 0.091 mmol, 91% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.92 (d, *J* = 8.6 Hz, 2H), 8.72 (d, *J* = 3.8 Hz, 2H), 8.01 (d, *J* = 8.1 Hz, 2H), 7.86 - 7.74 (m, 4H), 7.60 - 7.48 (m, 4H), 7.41 - 7.33 (m, 2H), 7.11 - 6.98 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.25, 138.05, 130.23, 129.86, 129.58, 128.50, 127.57, 125.44, 123.92, 123.62, 122.74, 122.56, 122.13, 114.68, 110.28, 109.53. **HRMS** (ESI) m/z calculated for $C_{32}H_{21}N_2$ $[M+H]^+$ 433.1699, found 433.1930.

9,9'-bipyrido[3,4-b]indole (2r)



A 10 mL Pyrex tube was charged with substrate 1r (0.2 mmol, 1 equiv.) and NIS (0.3 mmol, 1.5 equiv.) in DMF (1 mL). The sample was then irradiated by blue LEDs for 4 h. After 4 hours, the sample was added 1.0 equivalent of NIS and then continued the reaction for another 20 hours. After the reaction, quenched with water, extracted with ethyl acetate, washed the organic phase with a large amount of water 3 - 5 times, dried with anhydrous $MgSO_4$ and filtered. The solvent was then removed under vacuum, and obtain tan solid 2r by petroleum ether/ethyl acetate = 5/1 column chromatography (10.4 mg, 0.031 mmol, 31% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 5.3 Hz, 2H), 8.37 (s, 2H), 8.28 (d, *J* = 7.9 Hz, 2H), 8.12 (d, *J* = 5.0 Hz, 2H), 7.52 - 7.42 (m, 4H), 6.94 (d, *J* = 7.9 Hz, 2H).[S2] **HRMS** (ESI) m/z calculated for $C_{22}H_{15}N_4$ $[M+H]^+$ 335.1291, found 335.1209.

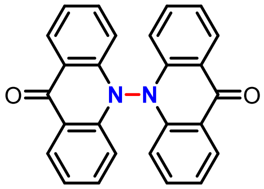
1,1,2,2-tetra([1,1'-biphenyl]-4-yl)hydrazine (2s)



A 10 mL Pyrex tube was charged with substrate 1s (0.2 mmol, 1 equiv.) and NIS (0.3 mmol, 1.5 equiv.) in DMF (1 mL). The sample was then irradiated by blue LEDs for 4 h. After the reaction, quenched with water, extracted with ethyl acetate, washed the organic phase with a large amount of water 3 - 5 times, dried with anhydrous

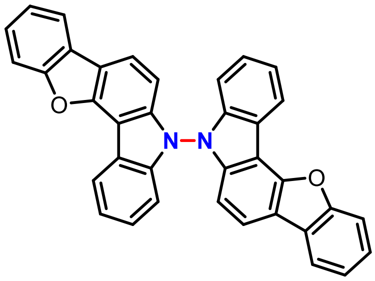
$MgSO_4$ and filtered. The solvent was then removed under vacuum, and obtain yellow solid 2s by petroleum ether column chromatography (30.6 mg, 0.046 mmol, 46% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 - 7.28 (m, 7H), 7.23 (d, *J* = 8.1 Hz, 5H), 7.10 - 6.98 (m, 6H), 6.95 (dd, *J* = 7.9, 1.7 Hz, 4H), 6.94 - 6.89 (m, 7H), 6.89 - 6.83 (m, 3H), 6.78 (d, *J* = 6.3 Hz, 2H), 6.52 (d, *J* = 7.8 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.85, 146.23, 141.56, 131.38, 130.36, 129.94, 129.57, 128.48, 127.77, 127.40, 126.92, 126.82, 126.72, 126.47, 120.92, 120.31, 120.13, 113.97, 56.90. **HRMS** (ESI) m/z calculated for $C_{50}H_{37}N_2$ $[M+H]^+$ 665.2951, found 665.2917.

9H,9'H-[10,10'-biacridine]-9,9'-dione (2t)



A 10 mL Pyrex tube was charged with substrate 1t (0.2 mmol, 1 equiv.) and NIS (0.3 mmol, 1.5 equiv.) in DMF (1 mL). The sample was then irradiated by blue LEDs for 18 h. After the reaction, quenched with water, extracted with ethyl acetate, washed the organic phase with a large amount of water 3 - 5 times, dried with anhydrous $MgSO_4$ and filtered. The solvent was then removed under vacuum, and obtain yellow solid 2t by petroleum ether/ethyl acetate = 5/1 column chromatography (22.5 mg, 0.058 mmol, 58% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.66 (dd, *J* = 8.1, 1.6 Hz, 4H), 7.52 (ddd, *J* = 8.7, 7.0, 1.6 Hz, 4H), 7.39 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 4H), 6.75 (dd, *J* = 8.6, 0.9 Hz, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.47, 140.93, 135.26, 128.54, 123.73, 122.67, 113.68. **HRMS** (ESI) m/z calculated for $C_{26}H_{17}N_2O_2$ $[M+H]^+$ 389.1285, found 389.1299.

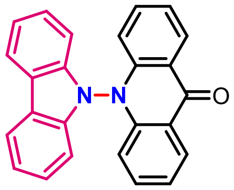
5,5'-bibenzofuro[3,2-c]carbazole (2u)



A 10 mL Pyrex tube was charged with substrate 1u (0.2 mmol, 1 equiv.) and NIS (0.3 mmol, 1.5 equiv.) in DMF (1 mL). The sample was then irradiated by blue LEDs for

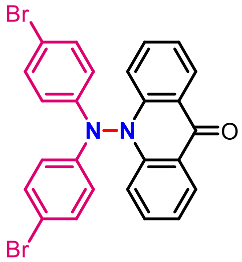
4 h. After the reaction, quenched with water, extracted with ethyl acetate, washed the organic phase with a large amount of water 3 - 5 times, dried with anhydrous $MgSO_4$ and filtered. The solvent was then removed under vacuum, and obtain white solid 2u by petroleum ether column chromatography (36.9 mg, 0.072 mmol, 72% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.65 (d, *J* = 6.7 Hz, 2H), 7.96 (d, *J* = 9.3 Hz, 2H), 7.87 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 8.1 Hz, 2H), 7.54 - 7.45 (m, 4H), 7.40 (q, *J* = 6.9 Hz, 4H), 7.01 (d, *J* = 8.1 Hz, 2H), 6.92 (d, *J* = 8.4 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.47, 151.22, 140.31, 139.57, 126.67, 125.94, 124.87, 123.28, 123.19, 122.15, 120.04, 119.75, 118.94, 118.23, 111.91, 109.19, 107.60, 104.62. **HRMS** (ESI) m/z calculated for $C_{36}H_{21}N_2O_2$ $[M+H]^+$ 513.1598, found 513.1605.

10-(9H-carbazol-9-yl)acridin-9(10H)-one (2bt)



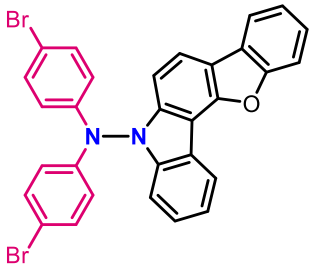
A 10 mL Pyrex tube was charged with substrate 1b (0.2 mmol, 1 equiv.), 1t (0.3 mmol, 1.5 equiv.) and NIS (0.6 mmol, 3 equiv.) in DMF (2 mL). The sample was then irradiated by blue LEDs for 4 h. After the reaction, quenched with water, extracted with ethyl acetate, washed the organic phase with a large amount of water 3 - 5 times, dried with anhydrous $MgSO_4$ and filtered. The solvent was then removed under vacuum, and obtain yellow solid 2bt by petroleum ether/ethyl acetate = 10/1 column chromatography (54.0 mg, 0.15mmol, 75% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.72 - 8.58 (m, 2H), 8.25 (d, *J* = 6.7 Hz, 2H), 7.47 - 7.39 (m, 4H), 7.39 - 7.32 (m, 4H), 7.06 - 6.91 (m, 2H), 6.49 (dd, *J* = 8.5, 1.0 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.95, 142.19, 138.31, 134.83, 128.00, 127.19, 123.16, 122.45, 121.96, 121.90, 121.17, 114.00, 108.95. **HRMS** (ESI) m/z calculated for $C_{25}H_{17}N_2O$ $[M+H]^+$ 361.1335, found 361.1345.

10-(bis(4-bromophenyl)amino)acridin-9(10H)-one (2nt)



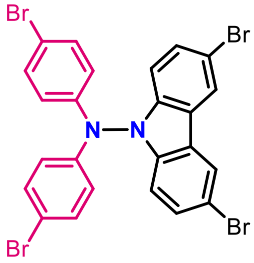
A 10 mL Pyrex tube was charged with substrate 1n (0.2 mmol, 1 equiv.), 1t (0.3 mmol, 1.5 equiv.) and NIS (0.6 mmol, 3 equiv.) in DMF (2 mL). The sample was then irradiated by blue LEDs for 4 h. After the reaction, quenched with water, extracted with ethyl acetate, washed the organic phase with a large amount of water 3 - 5 times, dried with anhydrous $MgSO_4$ and filtered. The solvent was then removed under vacuum, and obtain yellow solid 2nt by petroleum ether/ethyl acetate = 10/1 column chromatography (71.5 mg, 0.138 mmol, 69% yield). **^{1}H NMR** (400 MHz,$CDCl_3$) δ 8.57 (d, *J* = 6.6 Hz, 2H), 7.66 - 7.58 (m, 2H), 7.41 (d, *J* = 8.7 Hz, 2H), 7.36 (d, *J* = 10.2 Hz, 6H), 7.03 (d, *J* = 5.7 Hz, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.60, 142.22, 141.74, 134.87, 132.94, 128.27, 123.13, 122.69, 119.37, 116.20, 114.36. **HRMS** (ESI) m/z calculated for $C_{25}H_{17}Br_2N_2O$ $[M+H]^+$ 518.9702, found 518.9692.

N,N-bis(4-bromophenyl)-5H-benzofuro[3,2-c]carbazol-5-amine (2nu)



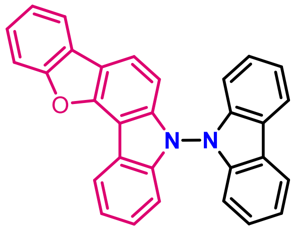
A 10 mL Pyrex tube was charged with substrate 1n (0.2 mmol, 1 equiv.), 1u (0.3 mmol, 1.5 equiv.) and NIS (0.6 mmol, 3 equiv.) in DMF (2 mL). The sample was then irradiated by blue LEDs for 4 h. After the reaction, quenched with water, extracted with ethyl acetate, washed the organic phase with a large amount of water 3 - 5 times, dried with anhydrous $MgSO_4$ and filtered. The solvent was then removed under vacuum, and obtain white solid 2nu by petroleum ether column chromatography (52.2 mg, 0.090 mmol, 45% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 7.0 Hz, 1H), 7.95 (dd, *J* = 11.2, 8.0 Hz, 2H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.46 (dd, *J* = 10.4, 7.2 Hz, 3H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.36 - 7.29 (m, 5H), 6.98 (d, *J* = 6.7 Hz, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.35, 151.21, 143.18, 139.59, 138.73, 132.63, 126.56, 125.84, 124.85, 123.27, 123.15, 121.77, 120.23, 119.92, 119.26, 118.83, 117.87, 116.04, 111.84, 109.18, 107.05, 104.65. **HRMS** (ESI) m/z calculated for $C_{30}H_{19}Br_2N_2O$ $[M+H]^+$ 580.9859, found 580.9885.

3,6-dibromo-N,N-bis(4-bromophenyl)-9H-carbazol-9-amine (2an)



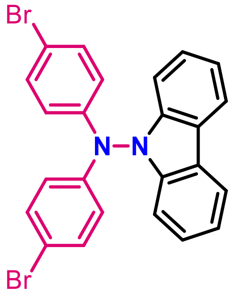
A 10 mL Pyrex tube was charged with substrate 1n (0.2 mmol, 1 equiv.), 1a (0.3 mmol, 1.5 equiv.) and NIS (0.6 mmol, 3 equiv.) in DMF (2 mL). The sample was then irradiated by blue LEDs for 4 h. After the reaction, quenched with water, extracted with ethyl acetate, washed the organic phase with a large amount of water 3 - 5 times, dried with anhydrous $MgSO_4$ and filtered. The solvent was then removed under vacuum, and obtain white solid 2an by petroleum ether column chromatography (81.4 mg, 0.126 mmol, 63% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 1.8 Hz, 2H), 7.49 (dd, *J* = 8.6, 1.9 Hz, 2H), 7.32 (d, *J* = 9.2 Hz, 4H), 7.17 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 6.9 Hz, 4H).[S1] **HRMS** (ESI) m/z calculated for $C_{24}H_{15}Br_4N_2$ $[M+H]^+$ 646.7963, found 646.7915.

5-(9H-carbazol-9-yl)-5H-benzofuro[3,2-c]carbazole (2bu)



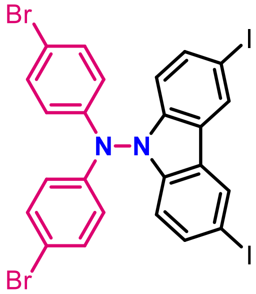
A 10 mL Pyrex tube was charged with substrate 1b (0.2 mmol, 1 equiv.), 1u (0.3 mmol, 1.5 equiv.) and NIS (0.6 mmol, 3 equiv.) in DMF (2 mL). The sample was then irradiated by blue LEDs for 4 h. After the reaction, quenched with water, extracted with ethyl acetate, washed the organic phase with a large amount of water 3 - 5 times, dried with anhydrous $MgSO_4$ and filtered. The solvent was then removed under vacuum, and obtain white solid 2bu by petroleum ether column chromatography (34.6 mg, 0.082 mmol, 41% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 7.0 Hz, 1H), 8.23 (dt, *J* = 6.4, 1.1 Hz, 2H), 7.96 (d, *J* = 7.6 Hz, 1H), 7.87 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.78 (d, *J* = 8.3 Hz, 1H), 7.48 (t, *J* = 7.3 Hz, 2H), 7.43 - 7.30 (m, 6H), 7.01 - 6.86 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.46, 151.22, 140.38, 139.92, 139.56, 126.80, 126.60, 125.87, 124.92, 123.20, 122.16, 122.03, 122.00, 121.49, 120.83, 120.00, 119.68, 118.83, 118.10, 111.88, 109.21, 109.18, 107.51, 104.66. **HRMS** (ESI) m/z calculated for $C_{30}H_{19}N_2O$ $[M+H]^+$ 423.1492, found 423.1485.

N,N-bis(4-bromophenyl)-9H-carbazol-9-amine (2bn)



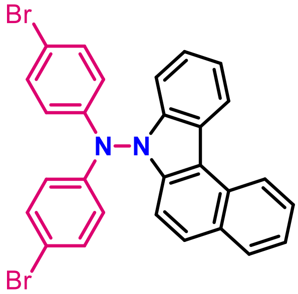
A 10 mL Pyrex tube was charged with substrate 1n (0.2 mmol, 1 equiv.), 1b (0.3 mmol, 1.5 equiv.) and NIS (0.6 mmol, 3 equiv.) in DMF (2 mL). The sample was then irradiated by blue LEDs for 4 h. After the reaction, quenched with water, extracted with ethyl acetate, washed the organic phase with a large amount of water 3 - 5 times, dried with anhydrous $MgSO_4$ and filtered. The solvent was then removed under vacuum, and obtain white solid 2bn by petroleum ether column chromatography (78.4 mg, 0.160 mmol, 80% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.6 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 8H), 6.94 (d, *J* = 9.0 Hz, 4H).[S3] **HRMS** (ESI) m/z calculated for $C_{24}H_{17}Br_2N_2$ $[M+H]^+$ 490.9753, found 490.9759.

N,N-bis(4-bromophenyl)-3,6-diiodo-9H-carbazol-9-amine (2hn)



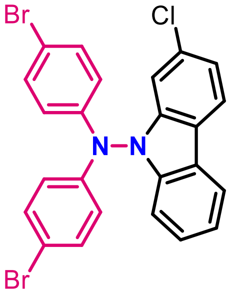
A 10 mL Pyrex tube was charged with substrate 1n (0.2 mmol, 1 equiv.), 1h (0.3 mmol, 1.5 equiv.) and NIS (0.6 mmol, 3 equiv.) in DMF (2 mL). The sample was then irradiated by blue LEDs for 4 h. After the reaction, quenched with water, extracted with ethyl acetate, washed the organic phase with a large amount of water 3 - 5 times, dried with anhydrous $MgSO_4$ and filtered. The solvent was then removed under vacuum, and obtain white solid 2hn by petroleum ether column chromatography (97.9 mg, 0.132 mmol, 66% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.37 (s, 2H), 7.66 (d, *J* = 8.6 Hz, 2H), 7.34 - 7.28 (m, 4H), 7.07 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 9.0 Hz, 4H).[S3] **HRMS** (ESI) m/z calculated for $C_{24}H_{15}Br_2I_2N_2$ $[M+H]^+$ 742.7686, found 742.7681.

N,N-bis(4-bromophenyl)-7H-benzo[c]carbazol-7-amine (2nq)



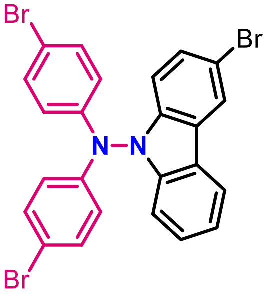
A 10 mL Pyrex tube was charged with substrate 1n (0.2 mmol, 1 equiv.), 1q (0.3 mmol, 1.5 equiv.) and NIS (0.6 mmol, 3 equiv.) in DMF (2 mL). The sample was then irradiated by blue LEDs for 4 h. After the reaction, quenched with water, extracted with ethyl acetate, washed the organic phase with a large amount of water 3 - 5 times, dried with anhydrous $MgSO_4$ and filtered. The solvent was then removed under vacuum, and obtain white solid 2nq by petroleum ether column chromatography (81.0mg, 0.150 mmol, 75% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.82 (d, *J* = 8.4 Hz, 1H), 8.62 (d, *J* = 4.6 Hz, 1H), 8.01 (d, *J* = 8.3 Hz, 1H), 7.85 (d, *J* = 7.0 Hz, 1H), 7.79 - 7.68 (m, 1H), 7.53 (d, *J* = 7.8 Hz, 2H), 7.48 - 7.41 (m, 3H), 7.32 (d, *J* = 9.0 Hz, 4H), 6.96 (d, *J* = 9.0 Hz, 4H). **^{13}C NMR** (101 MHz CDCl$_3$) δ 143.37, 138.05, 137.10, 132.66, 130.03, 129.89, 129.57, 128.45, 127.56, 125.36, 123.82, 123.50, 122.59, 122.33, 121.84, 120.13, 115.99, 114.21, 110.45, 109.64. **HRMS** (ESI) m/z calculated for $C_{28}H_{19}Br_2N_2$ [M+H]$^+$ 540.9909, found 540.9913.

N,N-bis(4-bromophenyl)-2-chloro-9H-carbazol-9-amine (2fn)



A 10 mL Pyrex tube was charged with substrate 1n (0.2 mmol, 1 equiv.), 1f (0.3 mmol, 1.5 equiv.) and NIS (0.6 mmol, 3 equiv.) in DMF (2 mL). The sample was then irradiated by blue LEDs for 4 h. After the reaction, quenched with water, extracted with ethyl acetate, washed the organic phase with a large amount of water 3 - 5 times, dried with anhydrous MgSO$_4$ and filtered. The solvent was then removed under vacuum, and obtain white solid 2fn by petroleum ether column chromatography (74.4 mg, 0.142 mmol, 71% yield). **^{1}H NMR** (400 MHz, CDCl$_3$) δ 8.07 (d, *J* = 7.8 Hz, 1H), 8.01 (d, *J* = 8.2 Hz 1H), 7.40 (t, *J* = 8.4 Hz, 1H), 7.33 (d, *J* = 7.2 Hz, 4H), 7.32 - 7.24 (m, 4H), 6.92 (d, *J* = 7.9 Hz, 4H).[S3] **HRMS** (ESI) m/z calculated for $C_{24}H_{16}Br_2ClN_2$ [M+H]$^+$ 524.9363, found 524.9368.

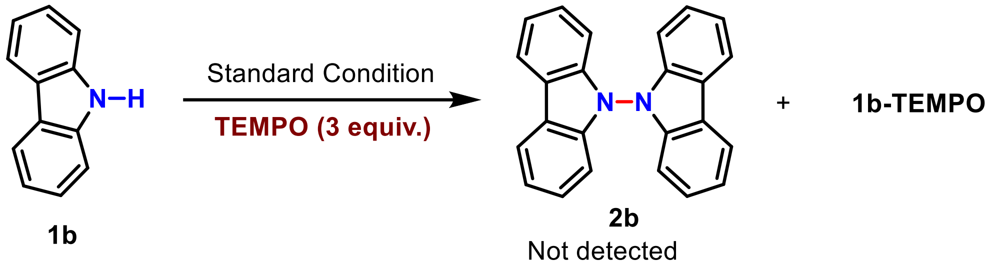
3-bromo-N,N-bis(4-bromophenyl)-9H-carbazol-9-amine (2dn)



A 10 mL Pyrex tube was charged with substrate 1n (0.2 mmol, 1 equiv.), 1d (0.3 mmol, 1.5 equiv.) and NIS (0.6 mmol, 3 equiv.) in DMF (2 mL). The sample was then irradiated by blue LEDs for 4 h. After the reaction, quenched with water, extracted with ethyl acetate, washed the organic phase with a large amount of water 3 - 5 times, dried with anhydrous $MgSO_4$ and filtered. The solvent was then removed under vacuum, and obtain white solid 2dn by petroleum ether column chromatography (79.5 mg, 0.140 mmol, 70% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 4.0 Hz, 1H), 8.06 (d, *J* = 7.6 Hz, 1H), 7.47 (d, *J* = 10.4 Hz, 1H), 7.44 - 7.40 (m, 1H), 7.34 - 7.30 (m, 6H), 7.18 (d, *J* = 8.6 Hz, 1H), 6.91 (d, *J* = 9.0 Hz, 4H).[S3] **HRMS** (ESI) m/z calculated for $C_{24}H_{16}Br_3N_2$ $[M+H]^+$ 568.8858, found 568.8861.

4. Mechanism study

4.1 TEMPO capture experiment



A 10 mL Pyrex tube was charged with substrate 1b (0.2 mmol, 1 equiv.), NIS (0.3 mmol, 1.5 equiv.) and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (0.6 mmol, 3 equiv.) in DMF (1 mL). The sample was then irradiated by blue LEDs for 4 h. After the reaction, quenched with water, extracted with ethyl acetate, washed the organic phase with a large amount of water 3 - 5 times, dried with anhydrous $MgSO_4$ and filtered. The solvent was then removed under vacuum, and obtain red solid 1b-TEMPO by petroleum ether column chromatography. **HRMS** (ESI) m/z calculated for $C_{21}H_{26}N_2O$ $[M]^+$ 322.2045, found 322.1994.

4.2 ESI-HRMS spectra of 1b-TEMPO

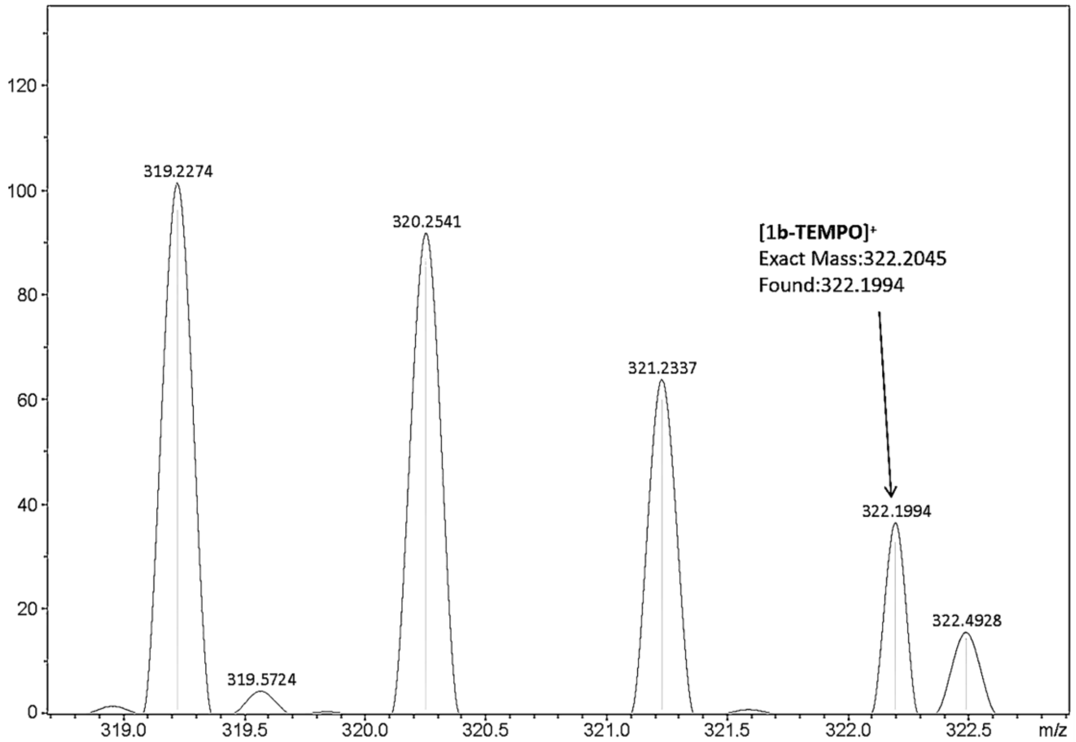
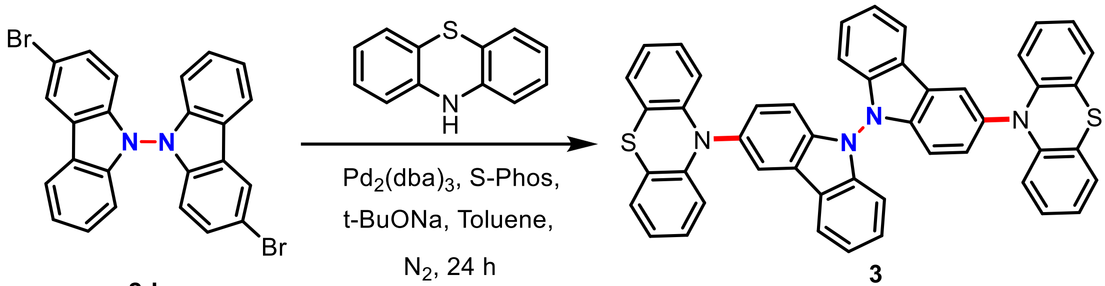


Fig.S1 ESI-HRMS spectra of 1b-TEMPO

5. Synthesis of 3



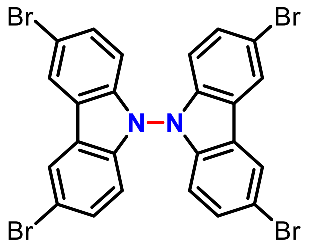
2d

3
OLED Host

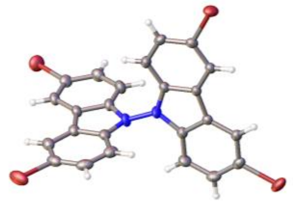
Compound 2d (98.4 mg, 0.2 mmol), POT (87.6 mg, 4.4 mmol), [$Pd_2(dba)_3$] (11 mg, 0.012 mmol), and S-Phos (8.2 mg, 0.02 mmol) were dissolved in dry toluene (4 mL) under N_2 before the addition of tBuONa (76.9 mg, 20 mmol). Then the mixture was heated to reflux for 24 h. After cooling to room temperature, the reaction mixture was diluted with CH_2Cl_2. After filtration, the filtrate was concentrated under reduced pressure to give acrude product, which was subjected to column chromatography (petroleum ether/CH_2Cl_2 = 10/1, v/v) to afford pure 3 as a white solid (77.0 mg, 53%). **^{1}H NMR** (400 MHz, DMSO-*d₆*) δ 8.52 (s, 2H), 8.44 (d, *J* = 6.9 Hz, 2H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.41 - 7.35 (m, 4H), 7.26 (d, *J* = 8.5 Hz, 2H), 7.03 (dd, *J* = 13.4, 7.6 Hz, 6H), 6.86 (t, *J* = 8.5 Hz, 4H), 6.80 (t, *J* = 7.4 Hz, 4H), 6.19 (d, *J* = 9.6 Hz, 4H). **^{13}C NMR** (101 MHz, DMSO-*d₆*) δ 144.77, 140.20, 139.13, 134.29, 130.20, 128.25, 127.83, 127.08, 124.24, 123.08, 122.39, 121.89, 119.16, 116.41, 111.52, 109.53.[S6] **HRMS** (ESI) m/z calculated for $C_{48}H_{31}N_4S_2$ $[M+H]^+$ 727.1985, found 727.1994.

6. Crystal structures and crystal data

Method of crystallization: compound 2a was crystallized as yellow block from n-hexane /DCM (2:1, v/v) by slowly evaporating the solvent.



2a

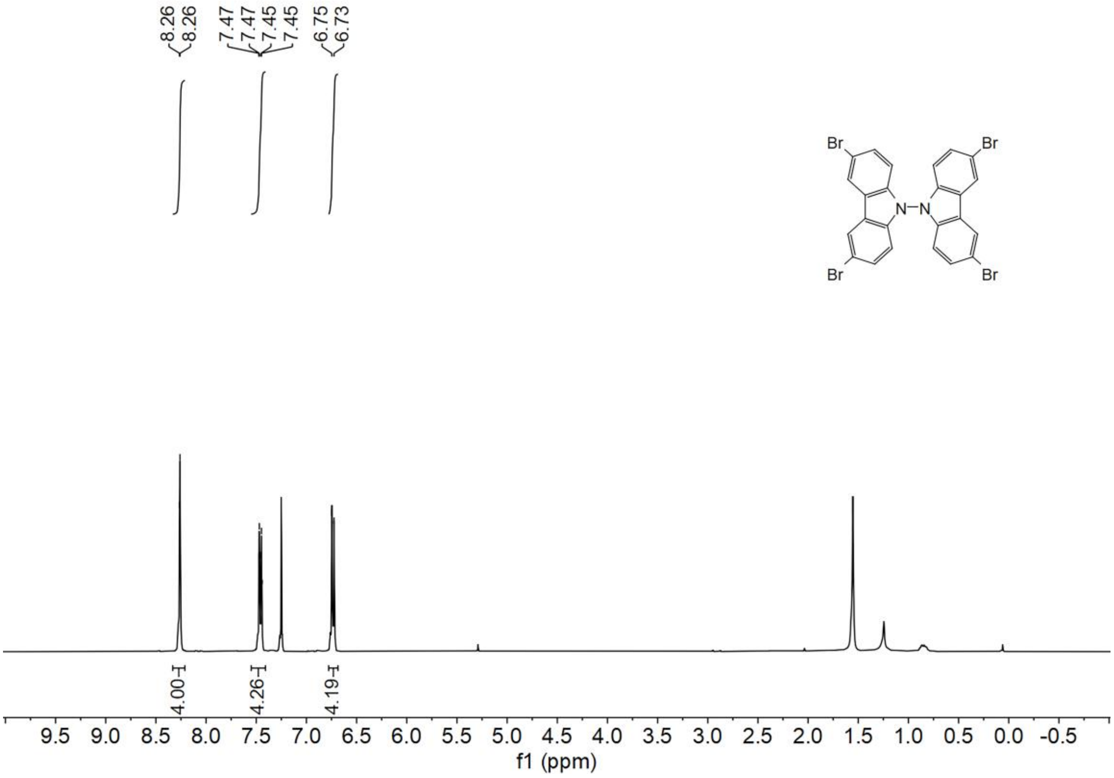


CCDC: 2488431

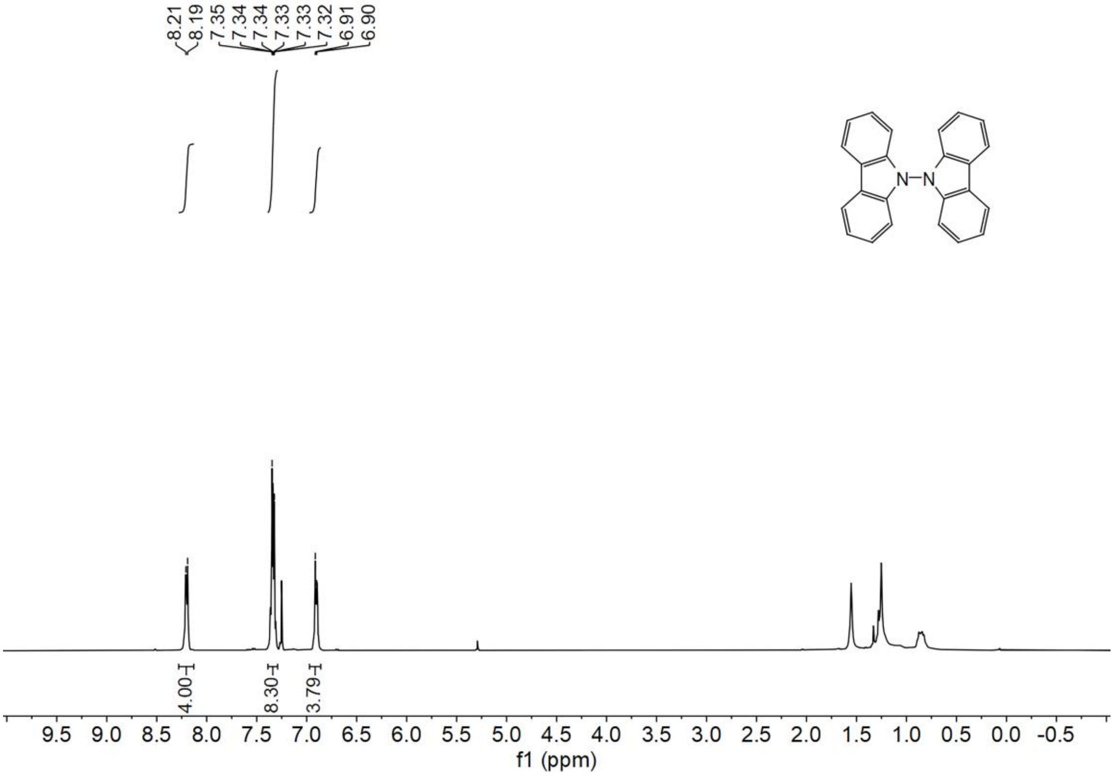
Identification code	2a
Empirical formula	$C_{24}H_{12}Br_4N_2$
Formula weight	648.00
Temperature/K	230.15
Crystal system	orthorhombic
Space group	Pbca
a/Å	10.5240(3)
b/Å	15.0537(5)
c/Å	27.8000(8)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4404.2(2)
Z	8
ρ_{calc}g/cm^3	1.955
μ/mm^{-1}	9.030
F(000)	2480.0
Crystal size/mm^3	0.3 × 0.2 × 0.1
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	6.358 to 136.626
Index ranges	$-11 \leq h \leq 12$, $-18 \leq k \leq 18$, $-33 \leq l \leq 33$
Reflections collected	63304
Independent reflections	4001 [R_{int} = 0.0471, R_{sigma} = 0.0178]
Data/restraints/parameters	4001/0/271
Goodness-of-fit on F^2	1.107

Final R indexes [I>=2σ (I)]	R_1 = 0.0351, wR_2 = 0.0845
Final R indexes [all data]	R_1 = 0.0359, wR_2 = 0.0851
Largest diff. peak/hole / e Å^{-3}	1.35/-1.59

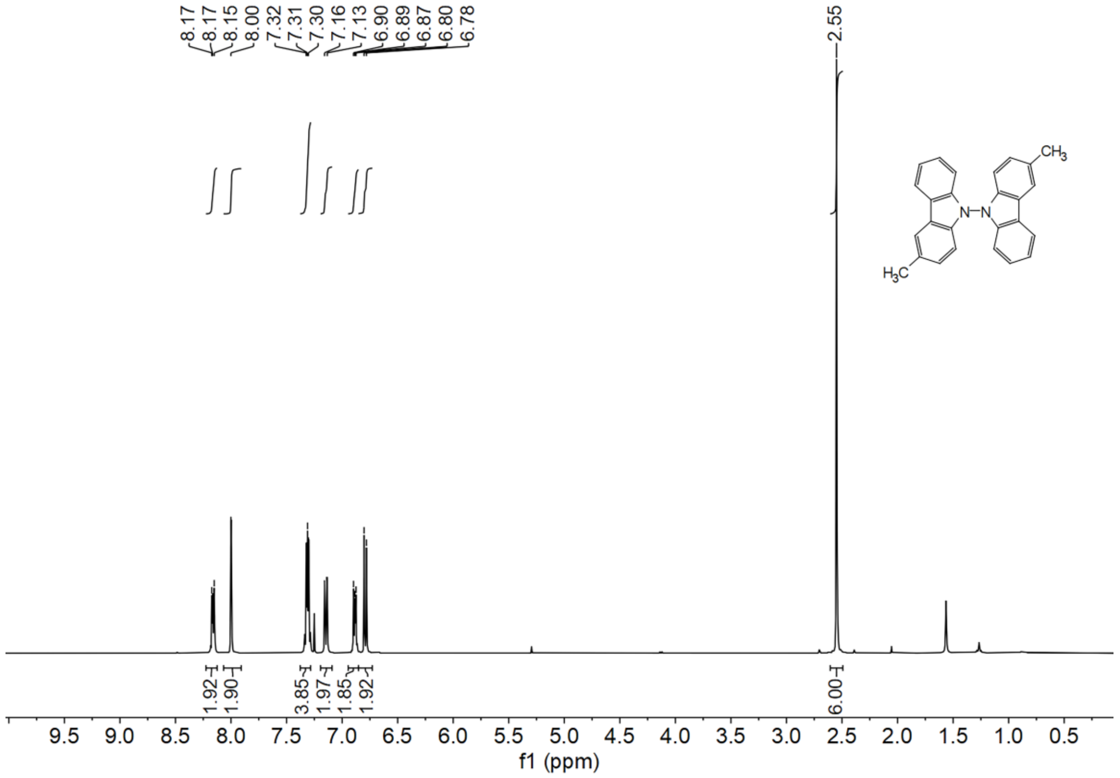
7. Characterization Data for Compounds



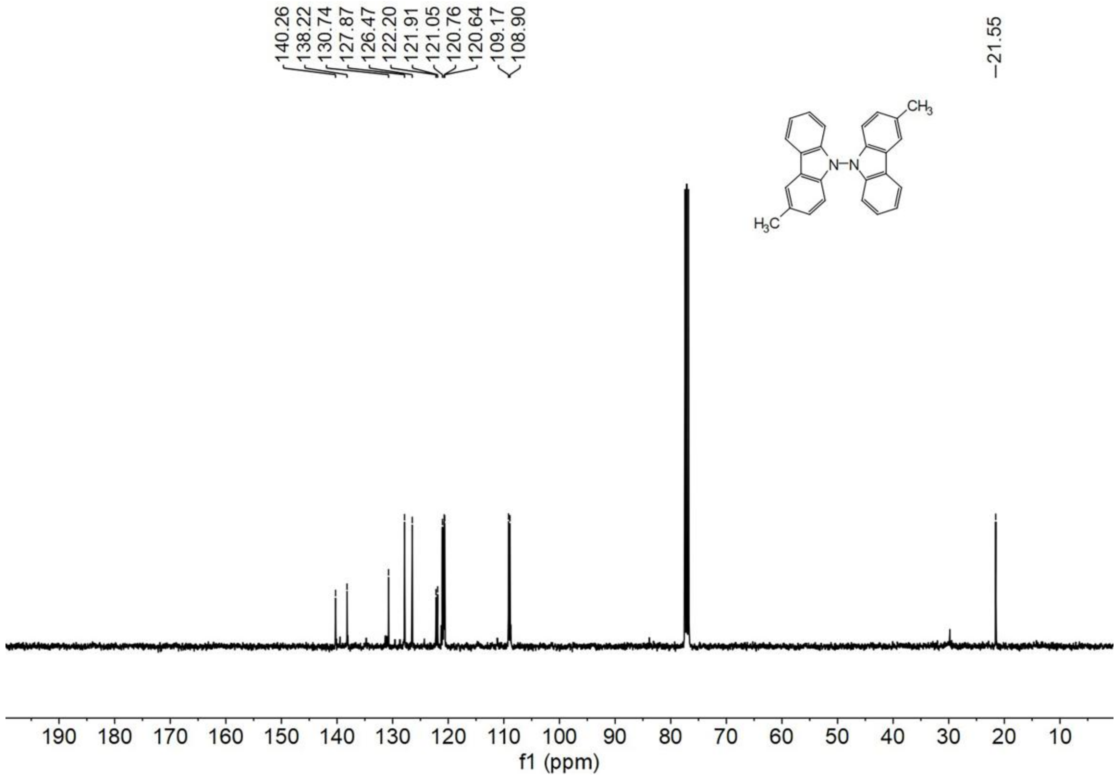
^{1}H NMR spectrum (400 MHz) of 2a in CDCl$_3$ at 298K



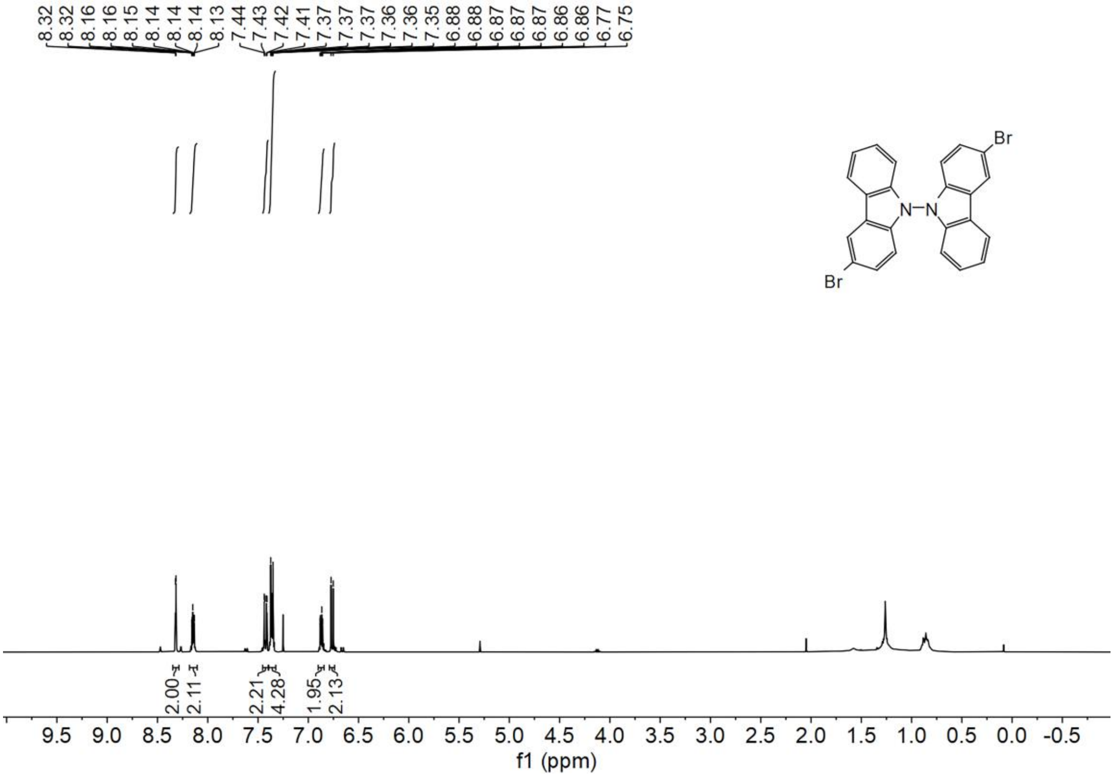
^{1}H NMR spectrum (400 MHz) of 2b in CDCl$_3$ at 298K



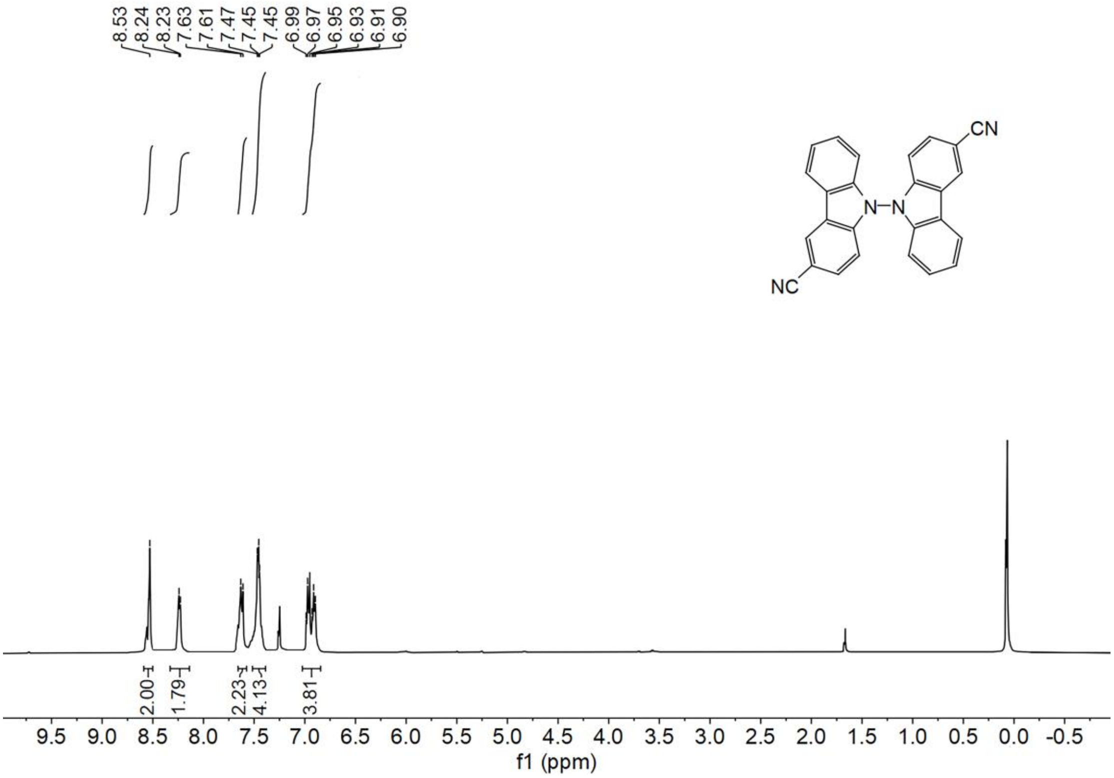
^{1}H NMR spectrum (400 MHz) of 2c in $CDCl_3$ at 298K



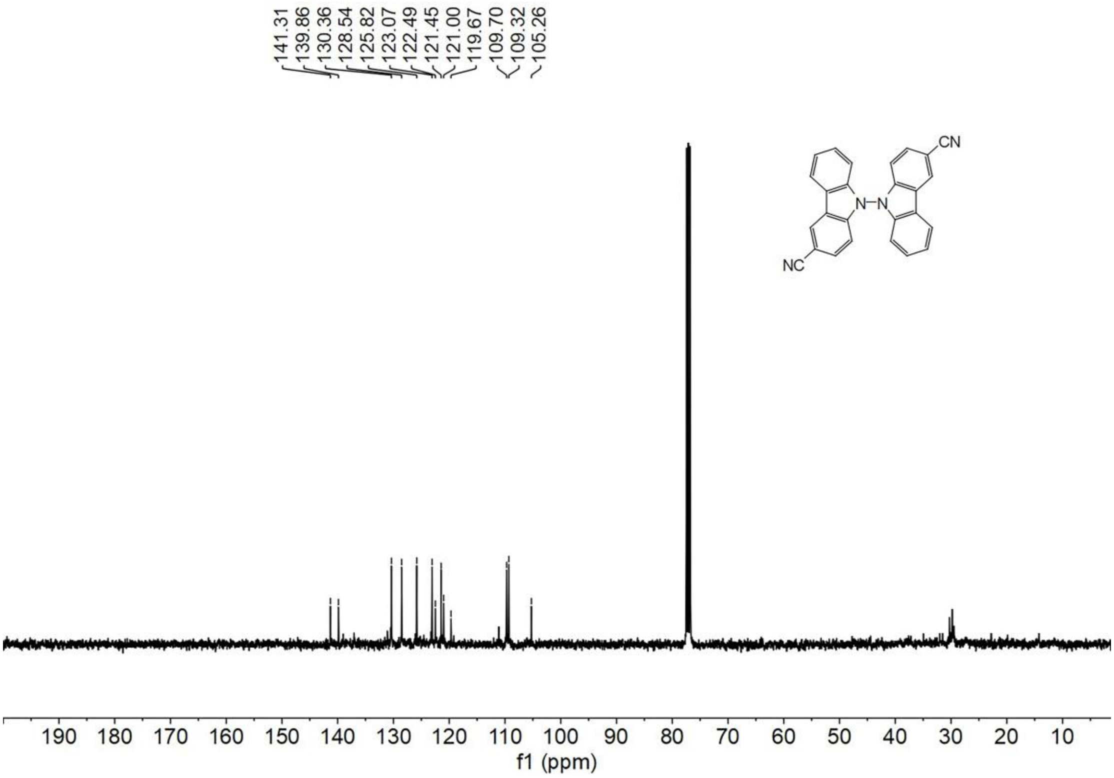
^{13}C NMR spectrum (101 MHz) of 2c in $CDCl_3$ at 298K



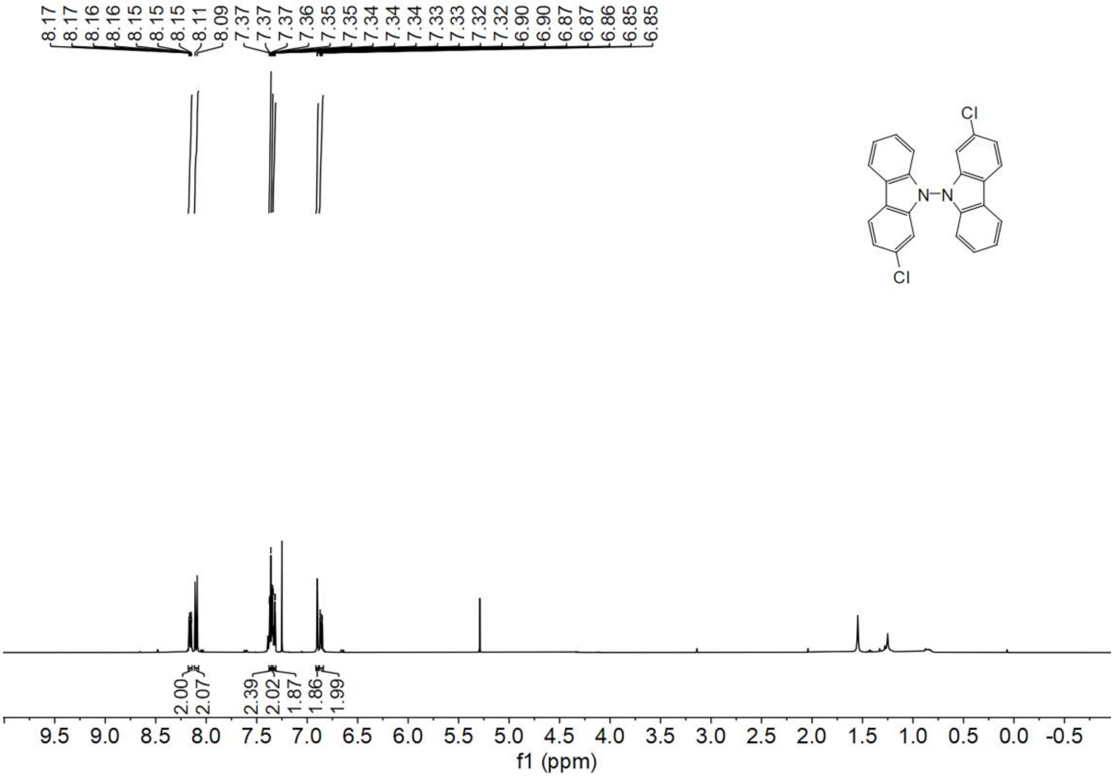
^{1}H NMR spectrum (400 MHz) of 2d in $CDCl_3$ at 298K



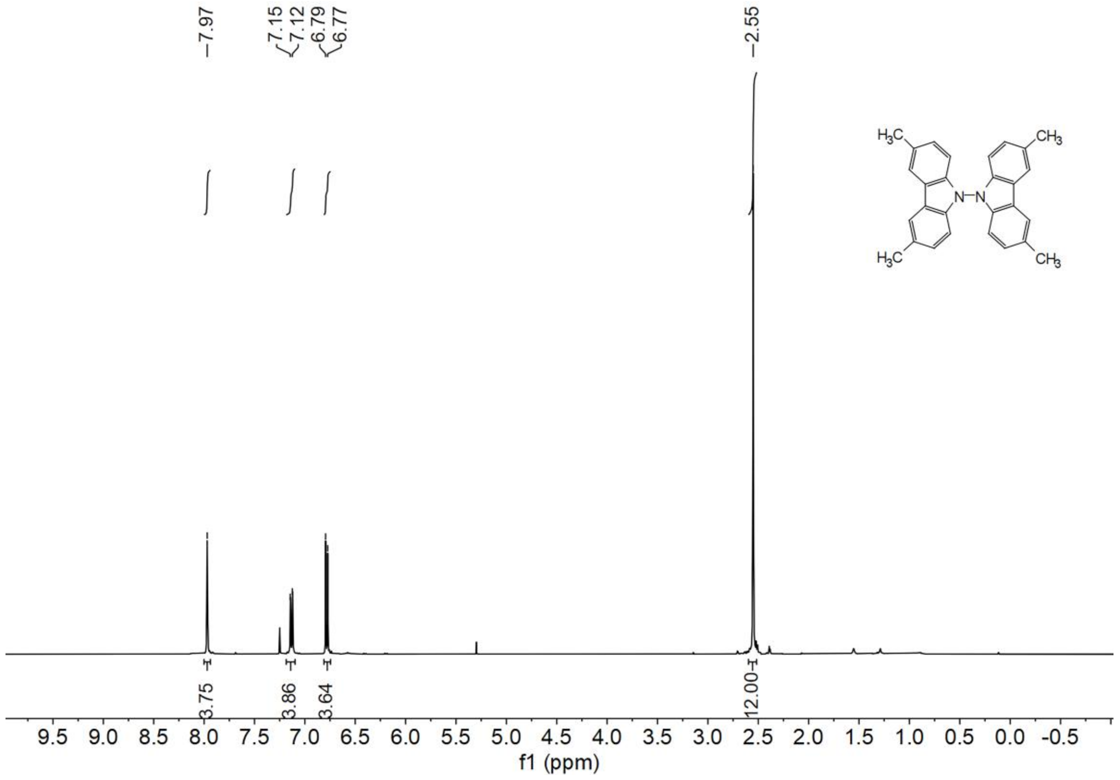
^{1}H NMR spectrum (400 MHz) of 2e in $CDCl_3$ at 298K



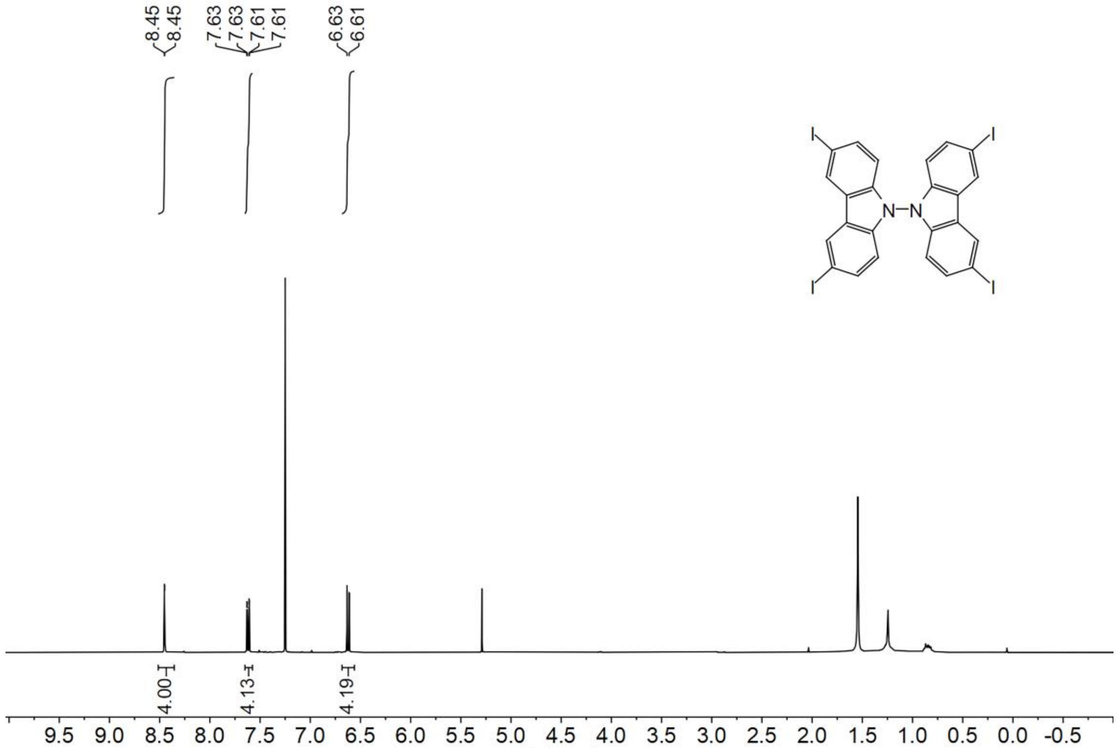
^{13}C NMR spectrum (101 MHz) of 2e in $CDCl_3$ at 298K



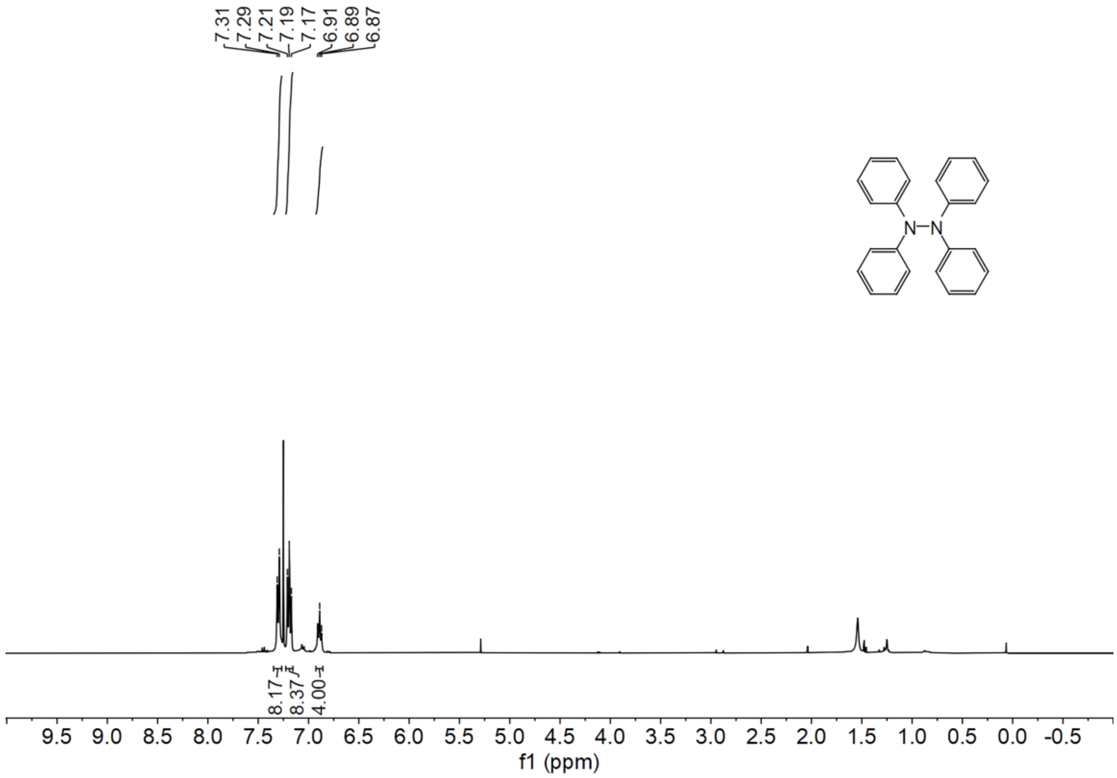
^{1}H NMR spectrum (400 MHz) of 2f in $CDCl_3$ at 298K



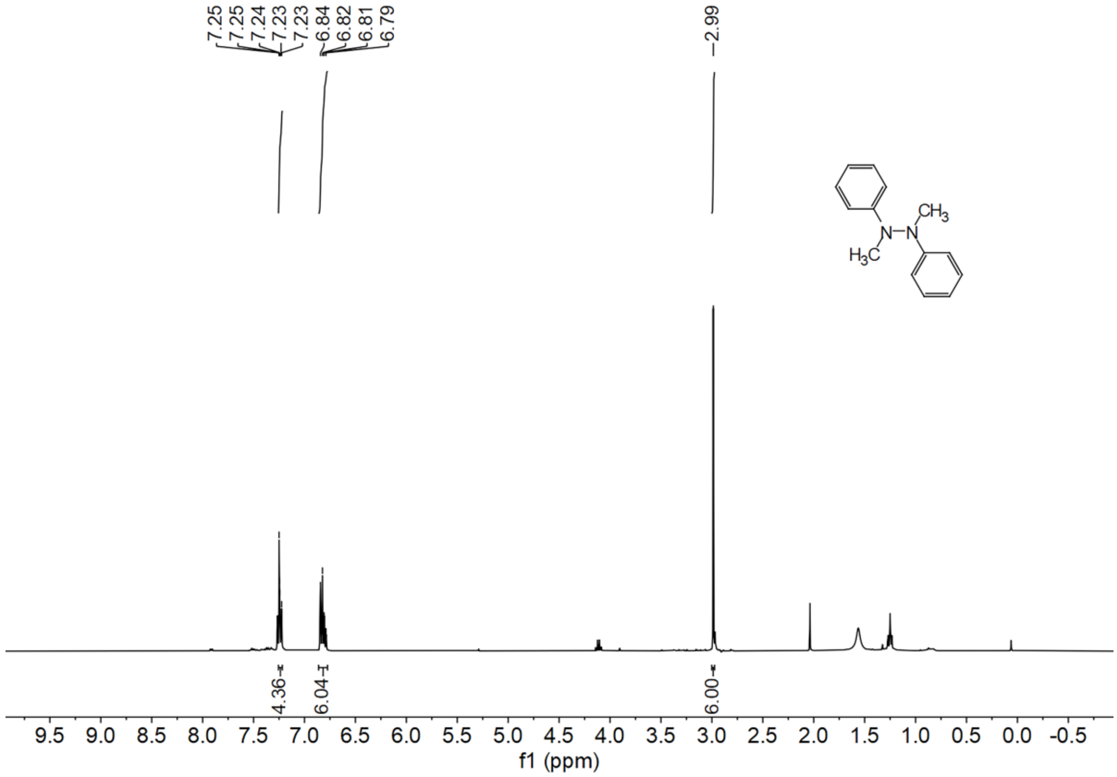
^{1}H NMR spectrum (400 MHz) of 2g in CDCl$_3$ at 298K



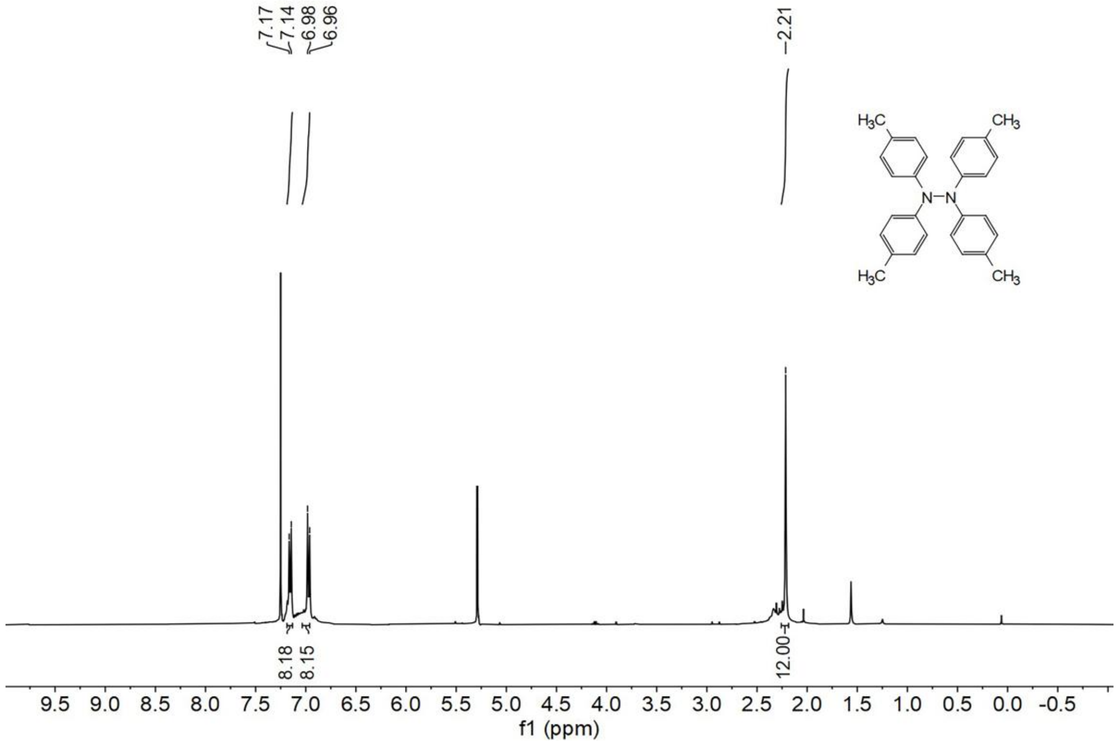
^{1}H NMR spectrum (400 MHz) of 2h in CDCl$_3$ at 298K



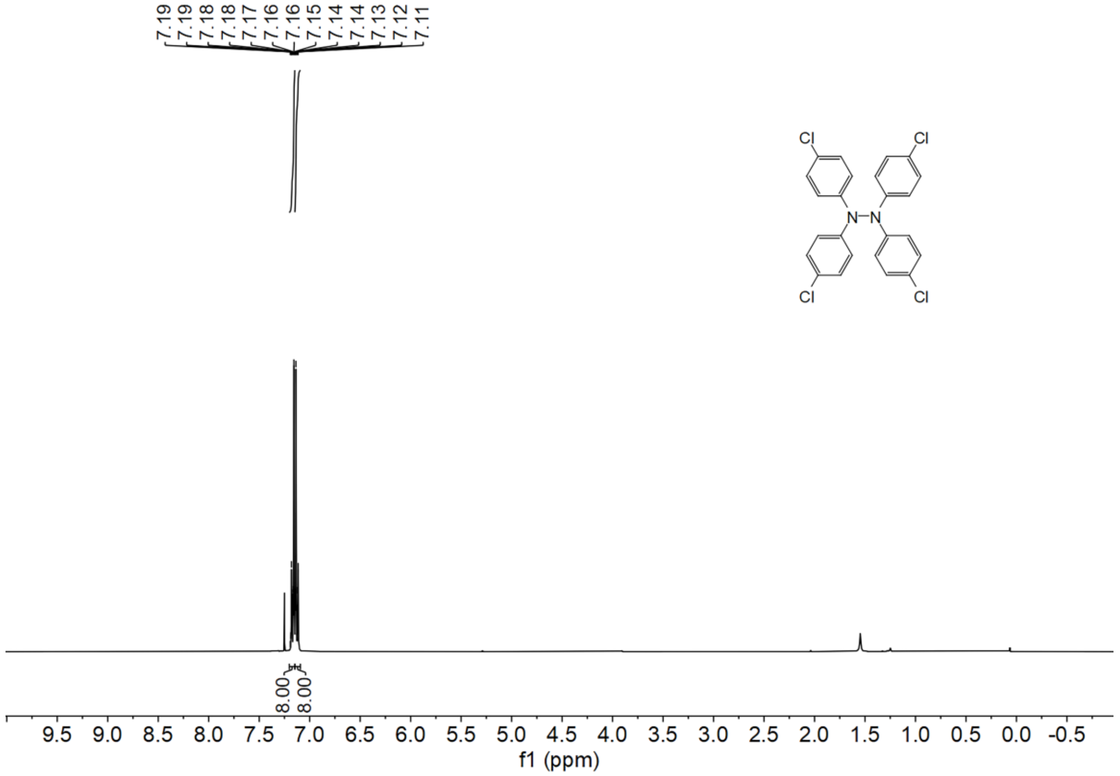
^{1}H NMR spectrum (400 MHz) of 2j in $CDCl_3$ at 298K



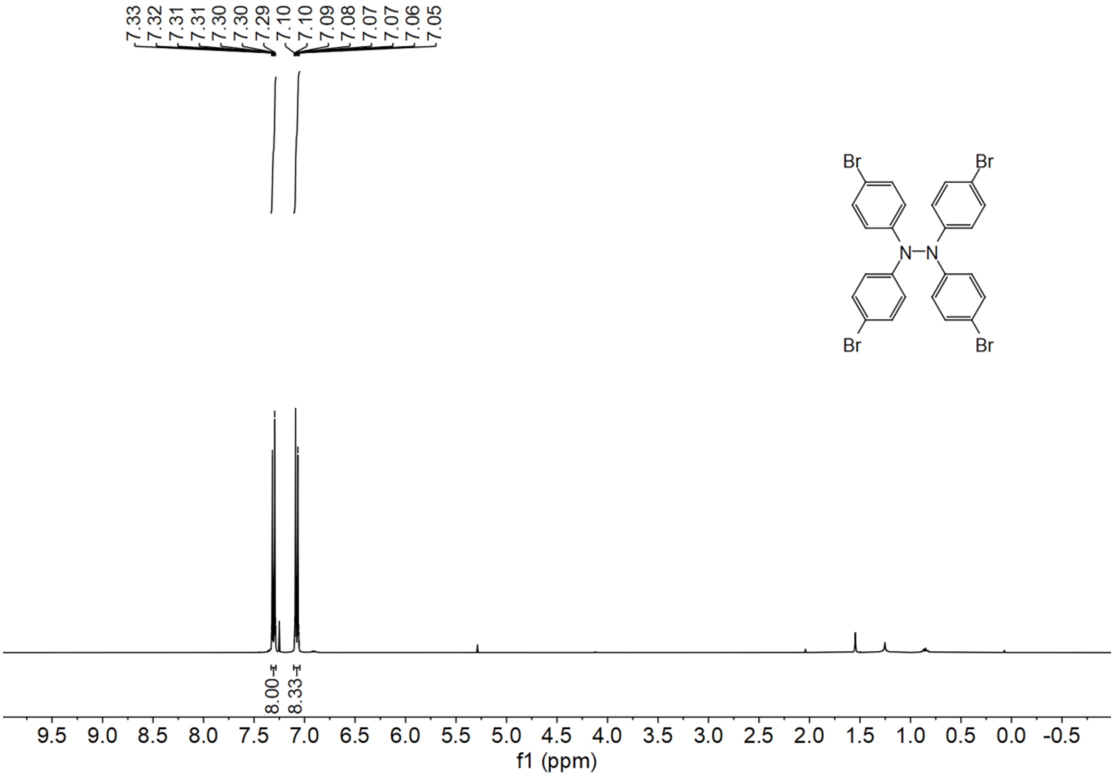
^{1}H NMR spectrum (400 MHz) of 2k in $CDCl_3$ at 298K



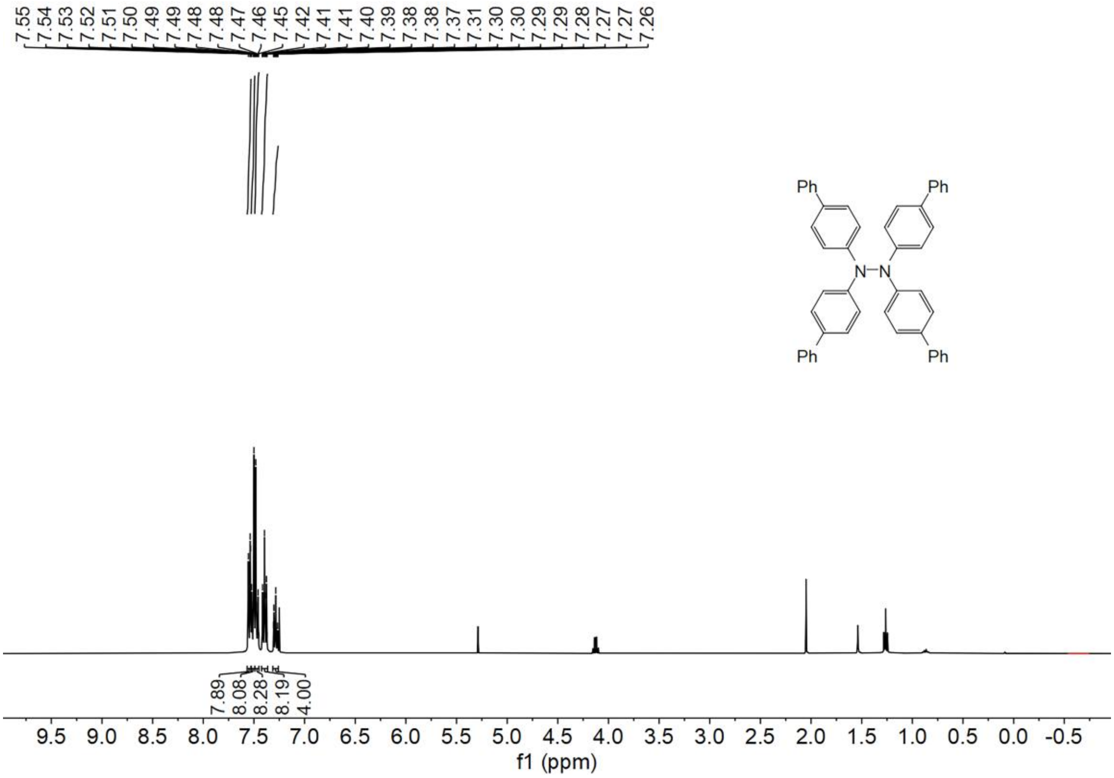
^{1}H NMR spectrum (400 MHz) of 2l in $CDCl_3$ at 298K



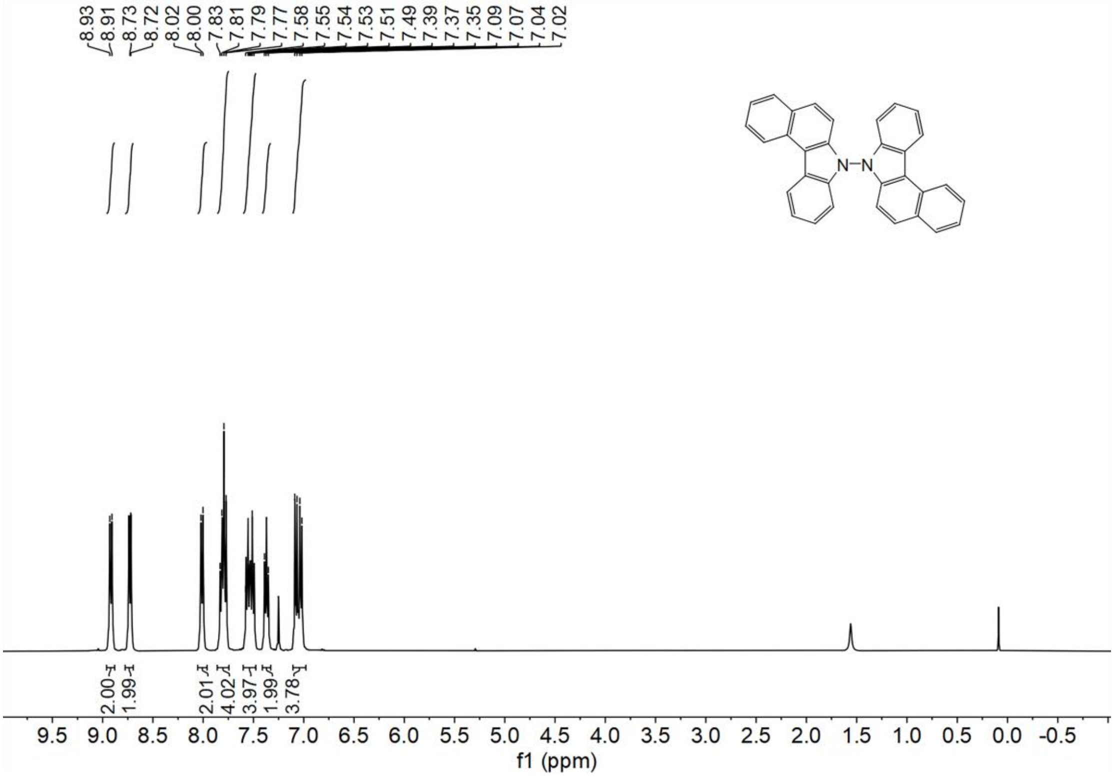
^{1}H NMR spectrum (400 MHz) of 2m in $CDCl_3$ at 298K



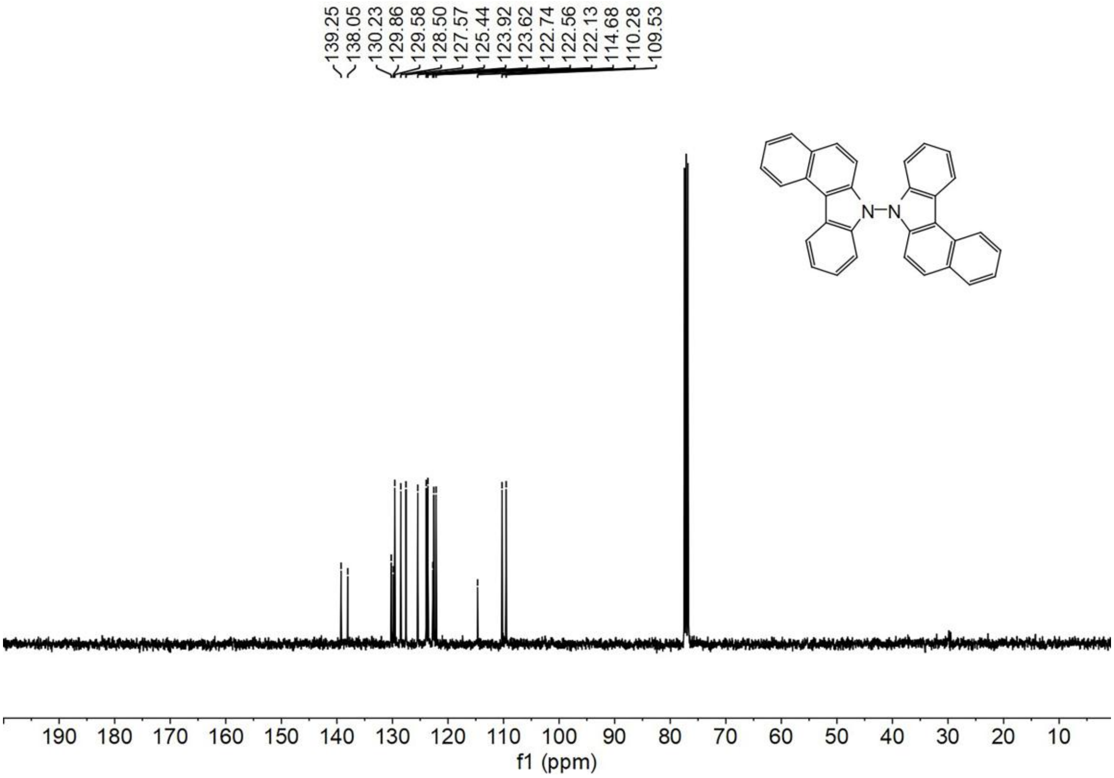
^{1}H NMR spectrum (400 MHz) of 2n in $CDCl_3$ at 298K



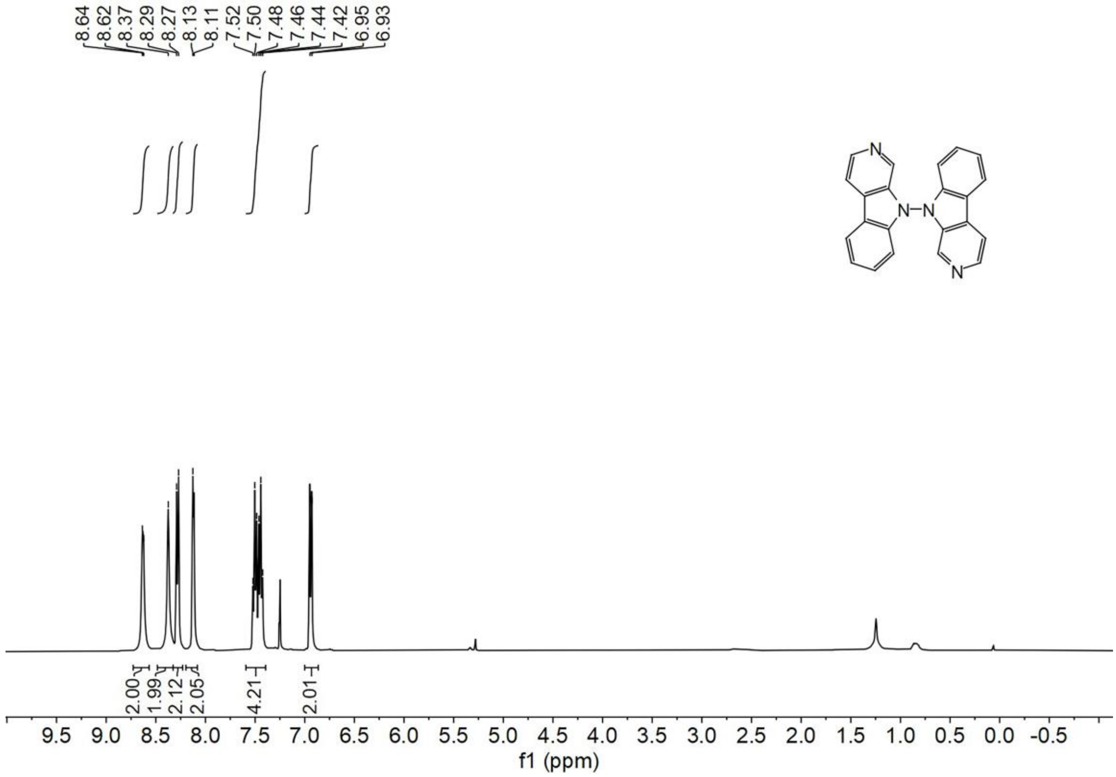
^{1}H NMR spectrum (400 MHz) of 2o in $CDCl_3$ at 298K



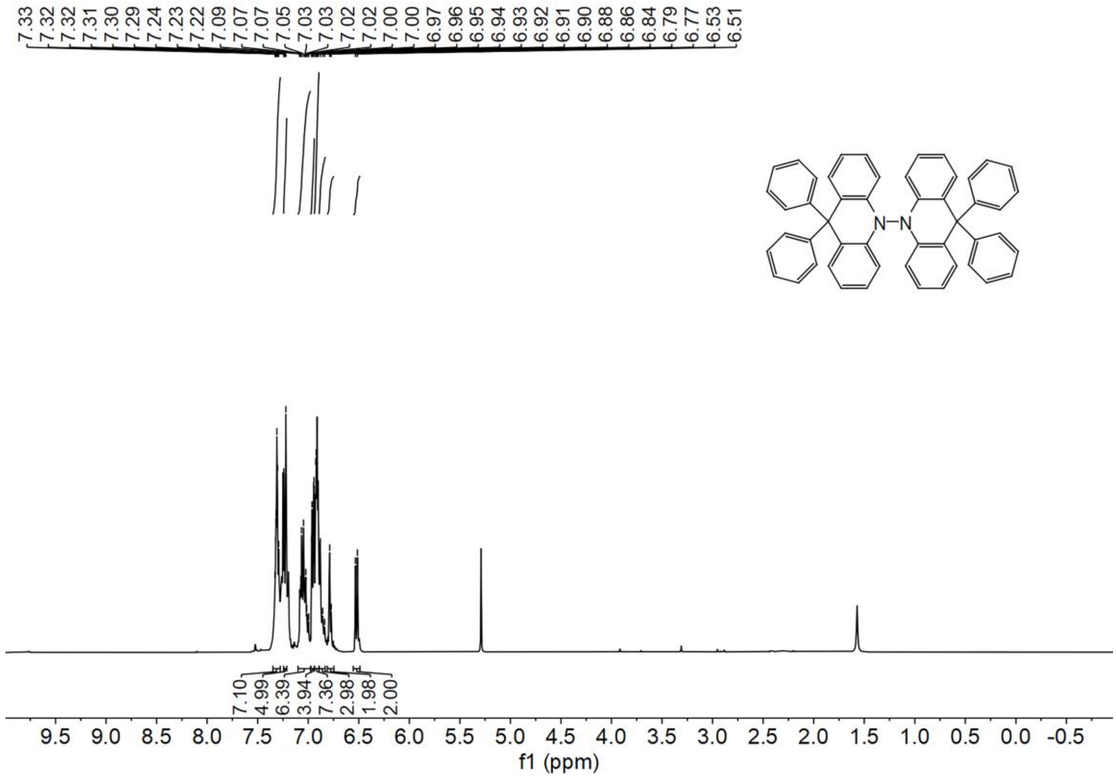
^{1}H NMR spectrum (400 MHz) of 2q in $CDCl_3$ at 298K



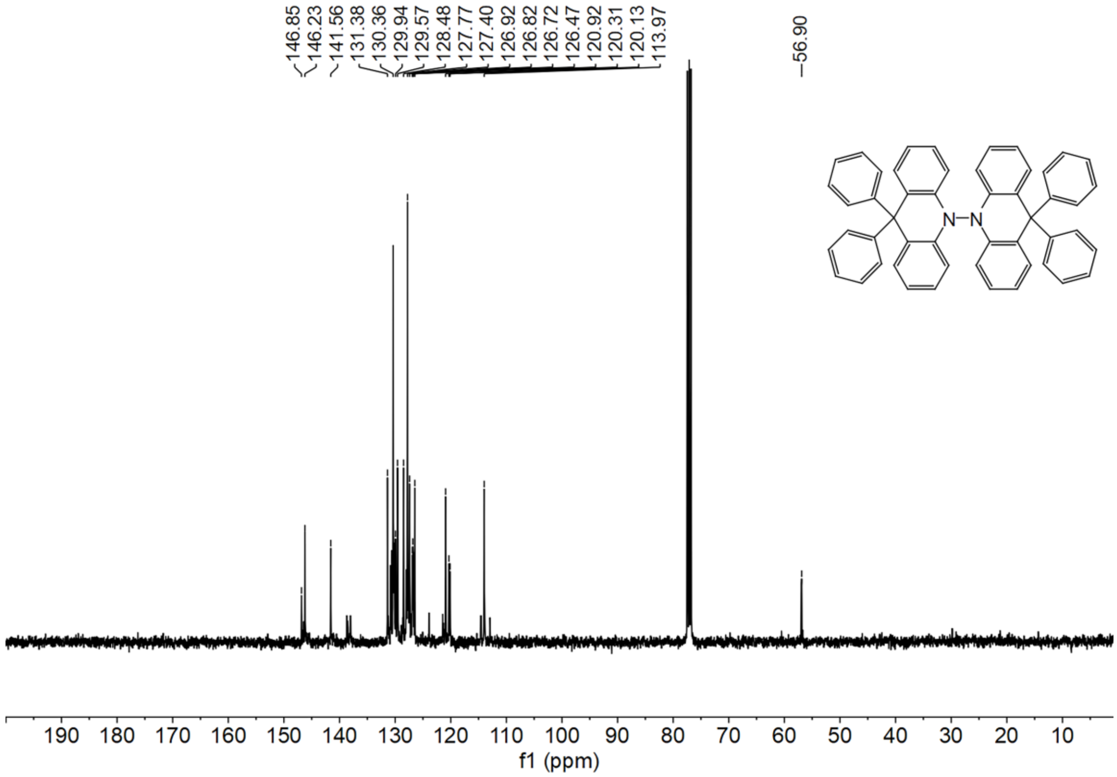
^{13}C NMR spectrum (101 MHz) of 2q in $CDCl_3$ at 298K



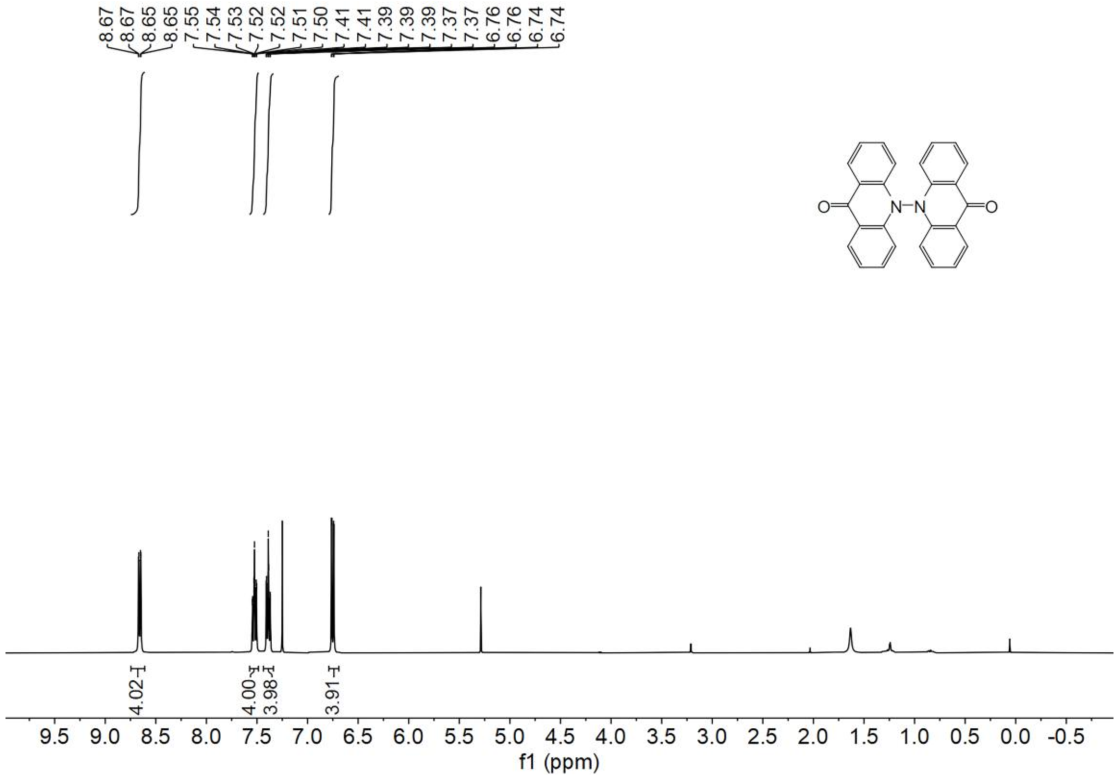
^{1}H NMR spectrum (400 MHz) of 2r in $CDCl_3$ at 298K



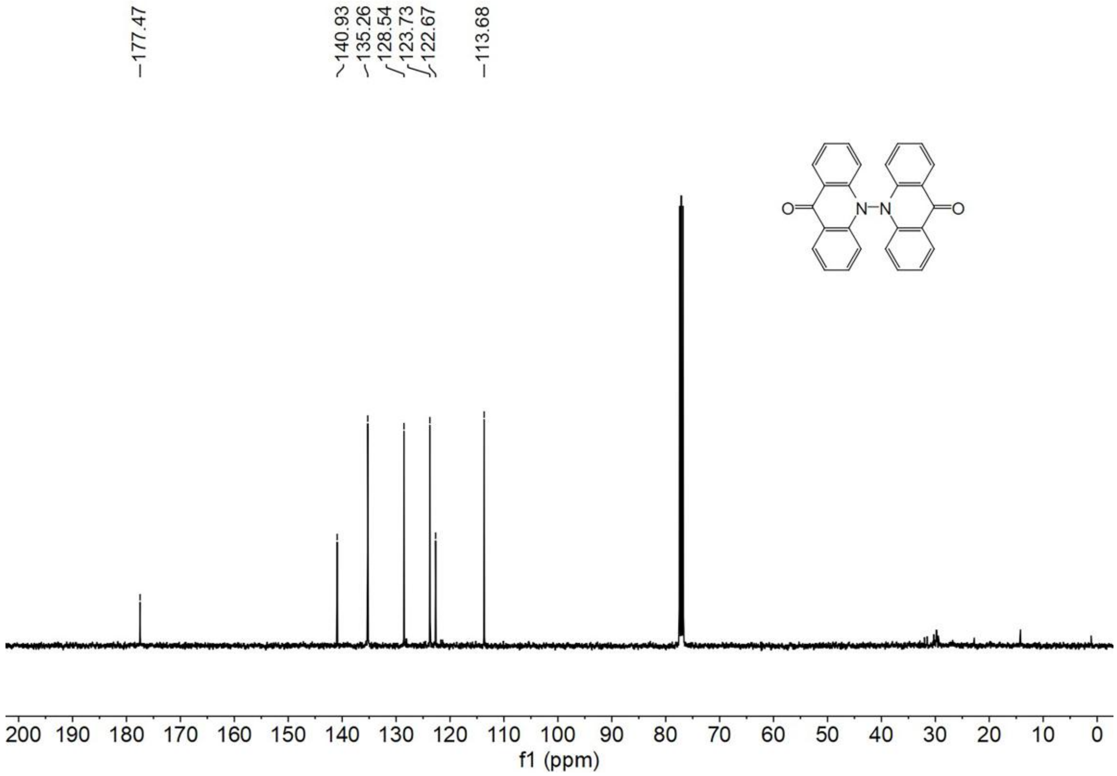
^{1}H NMR spectrum (400 MHz) of 2s in $CDCl_3$ at 298K



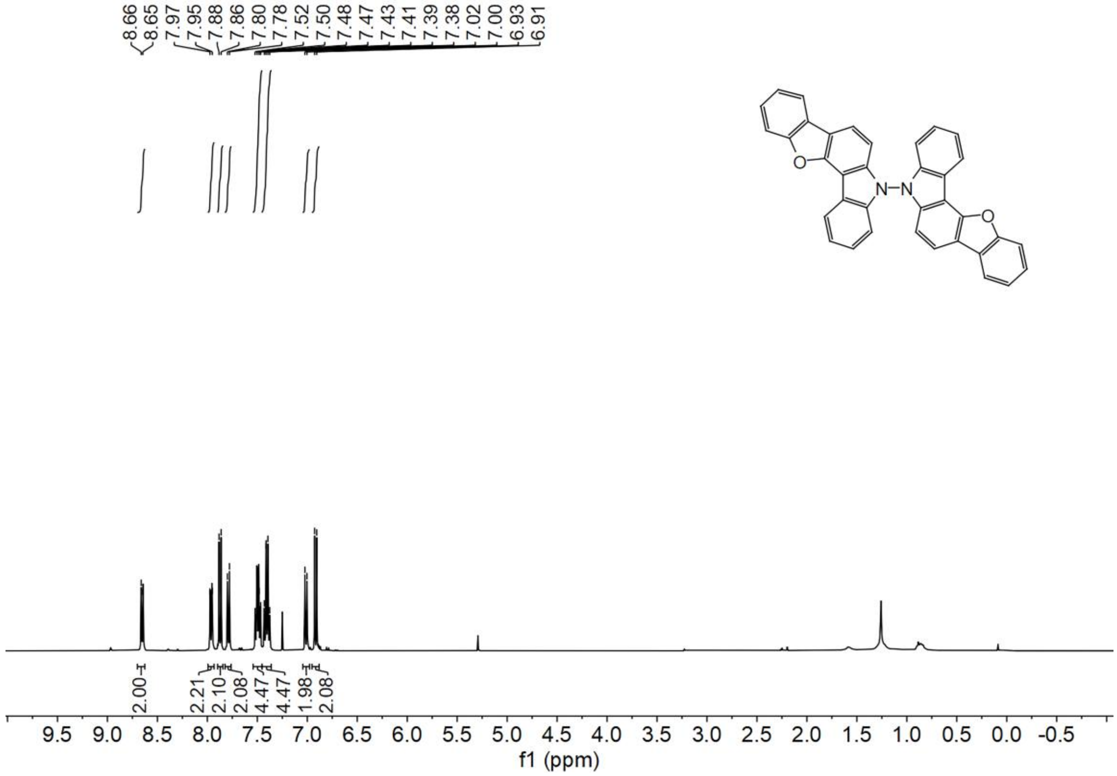
^{13}C NMR spectrum (101 MHz) of 2s in $CDCl_3$ at 298K



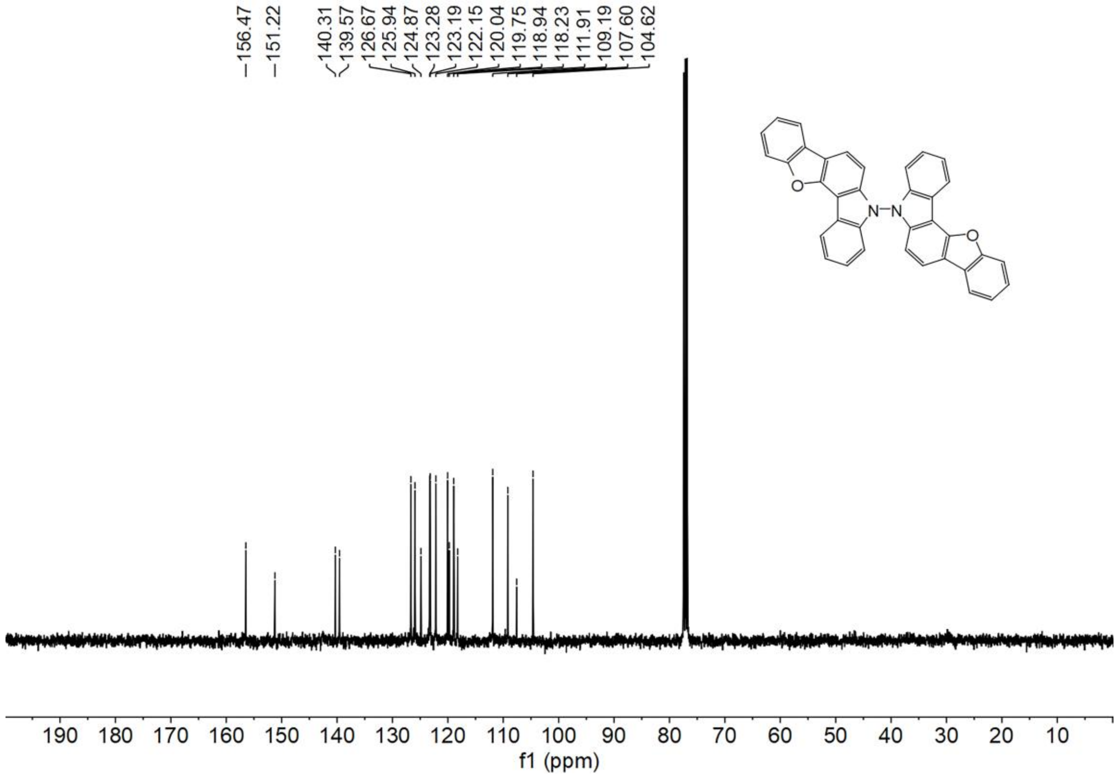
^{1}H NMR spectrum (400 MHz) of 2t in $CDCl_3$ at 298K



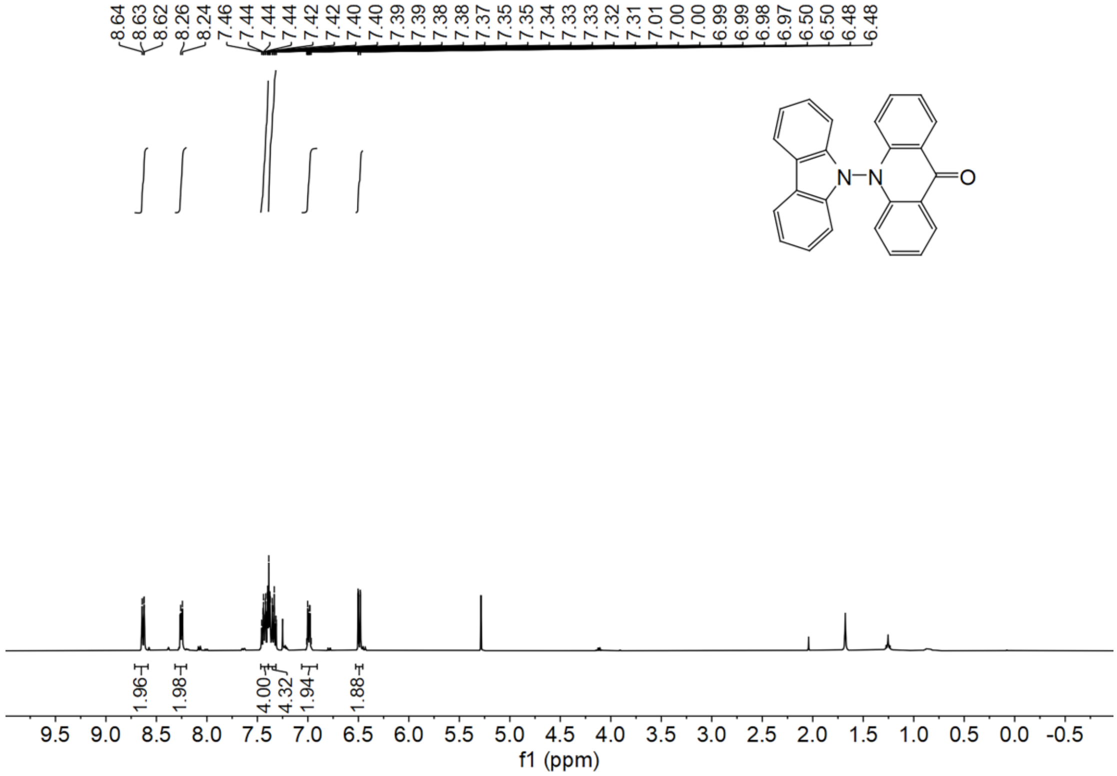
^{13}C NMR spectrum (101 MHz) of 2t in $CDCl_3$ at 298K



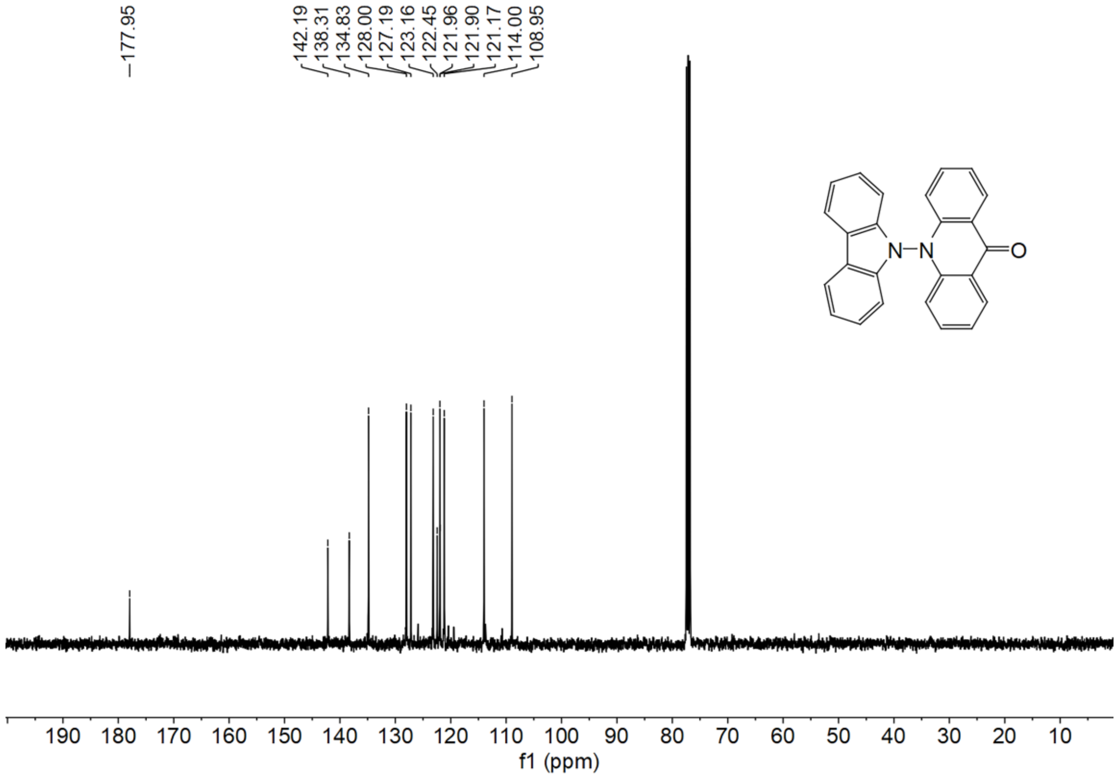
^{1}H NMR spectrum (400 MHz) of 2u in $CDCl_3$ at 298K



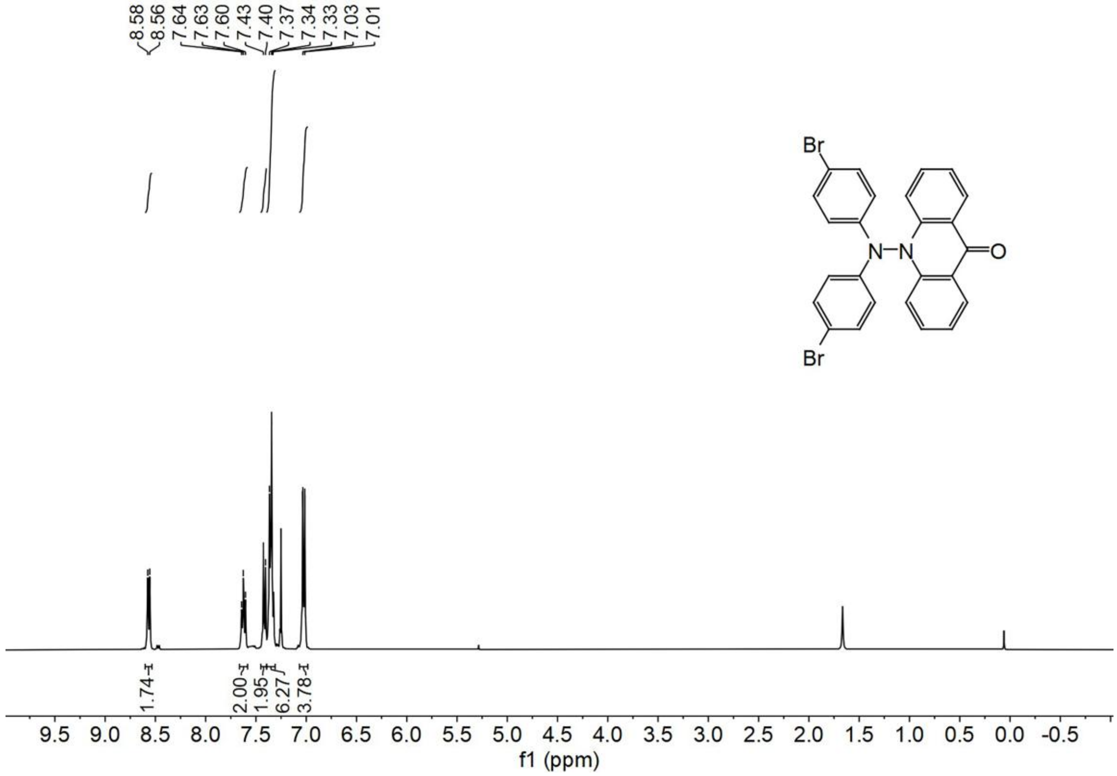
^{13}C NMR spectrum (101 MHz) of 2u in $CDCl_3$ at 298K



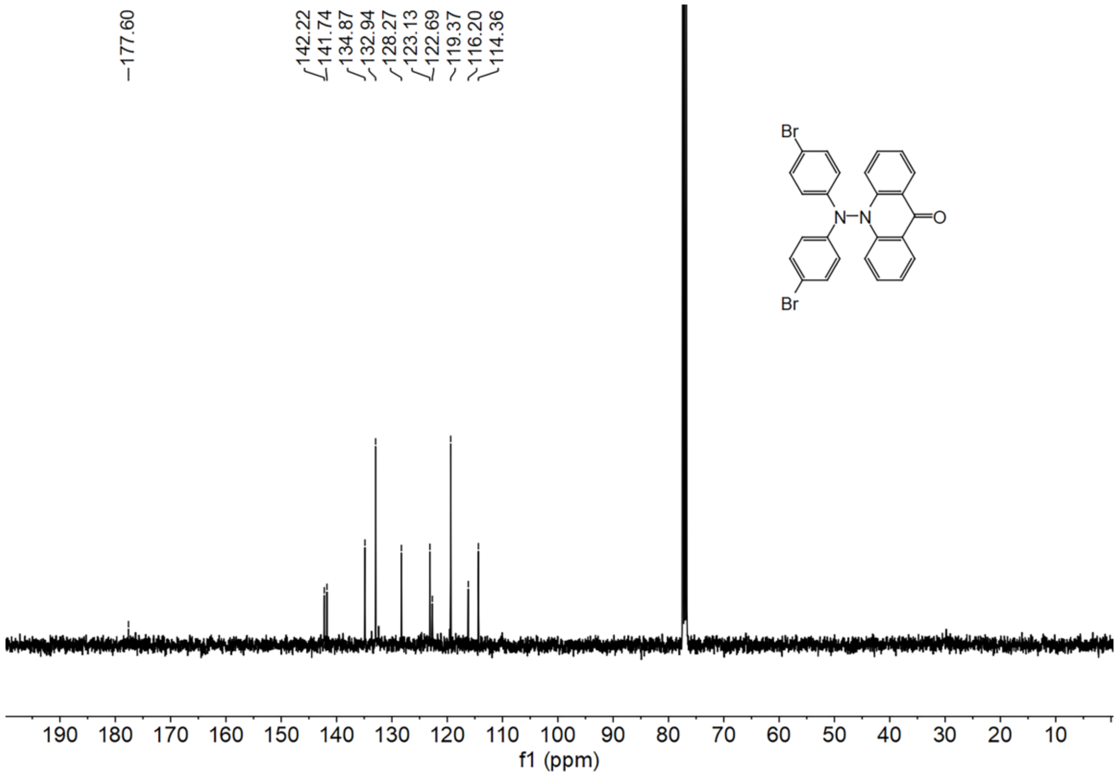
^{1}H NMR spectrum (400 MHz) of 2bt in $CDCl_3$ at 298K



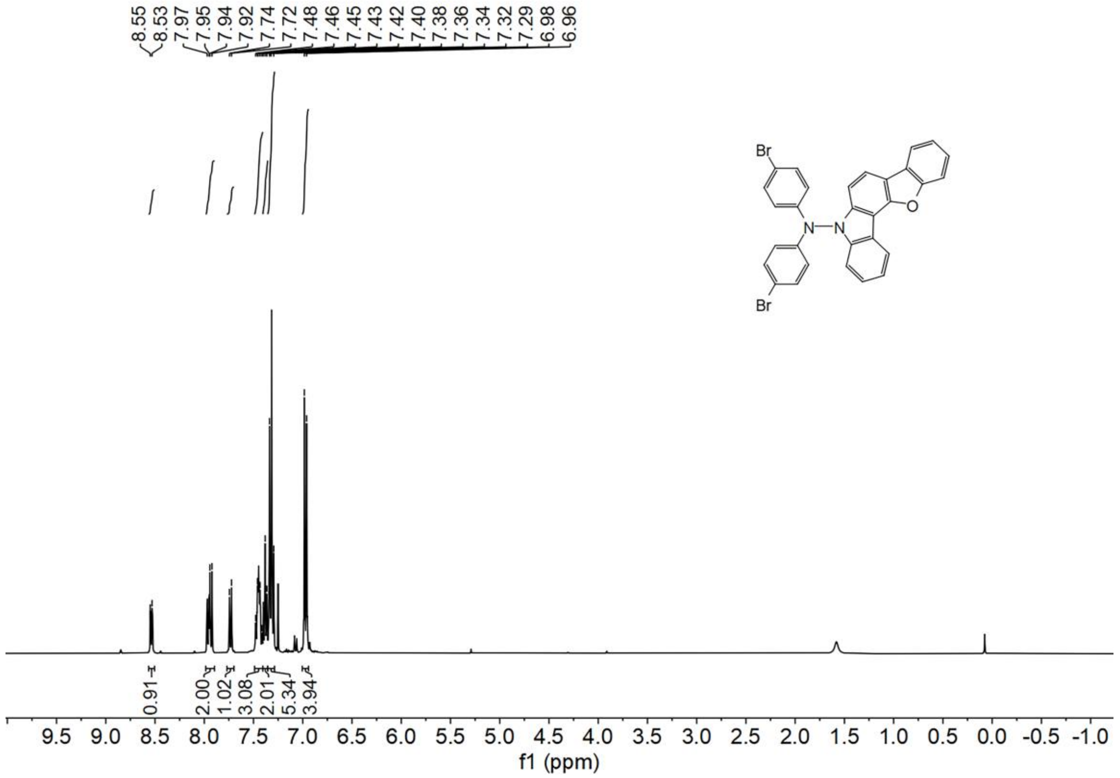
^{13}C NMR spectrum (101 MHz) of 2bt in $CDCl_3$ at 298K



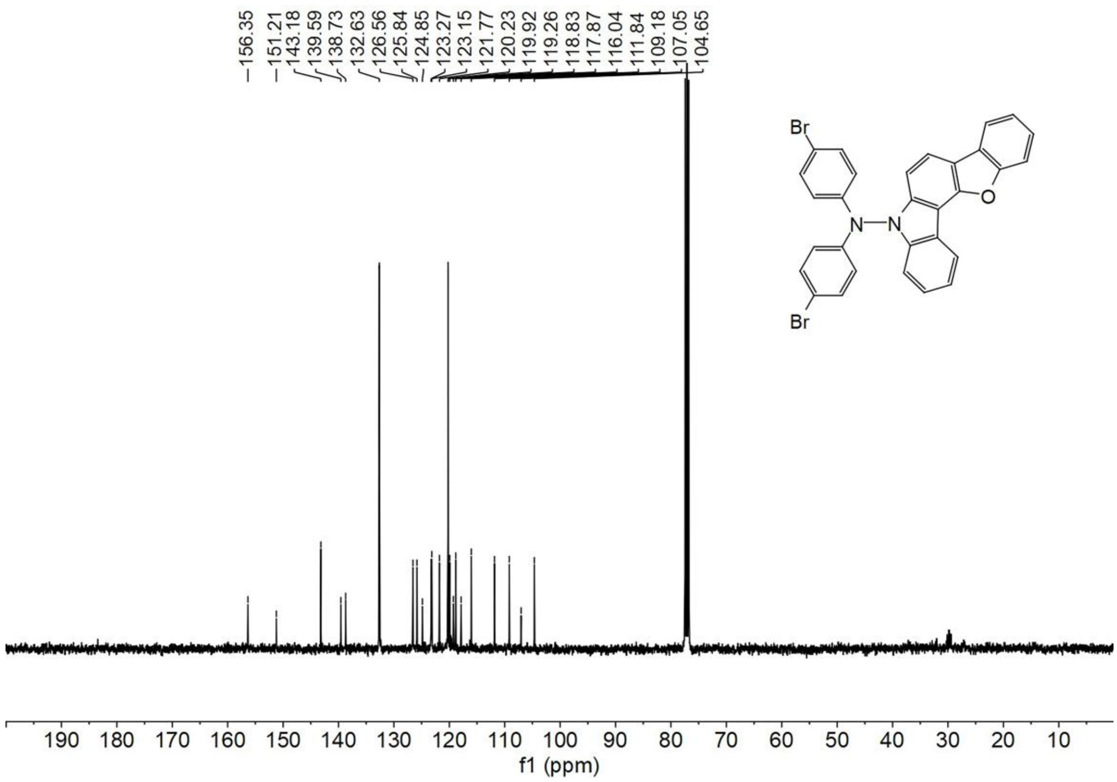
^{1}H NMR spectrum (400 MHz) of 2nt in $CDCl_3$ at 298K



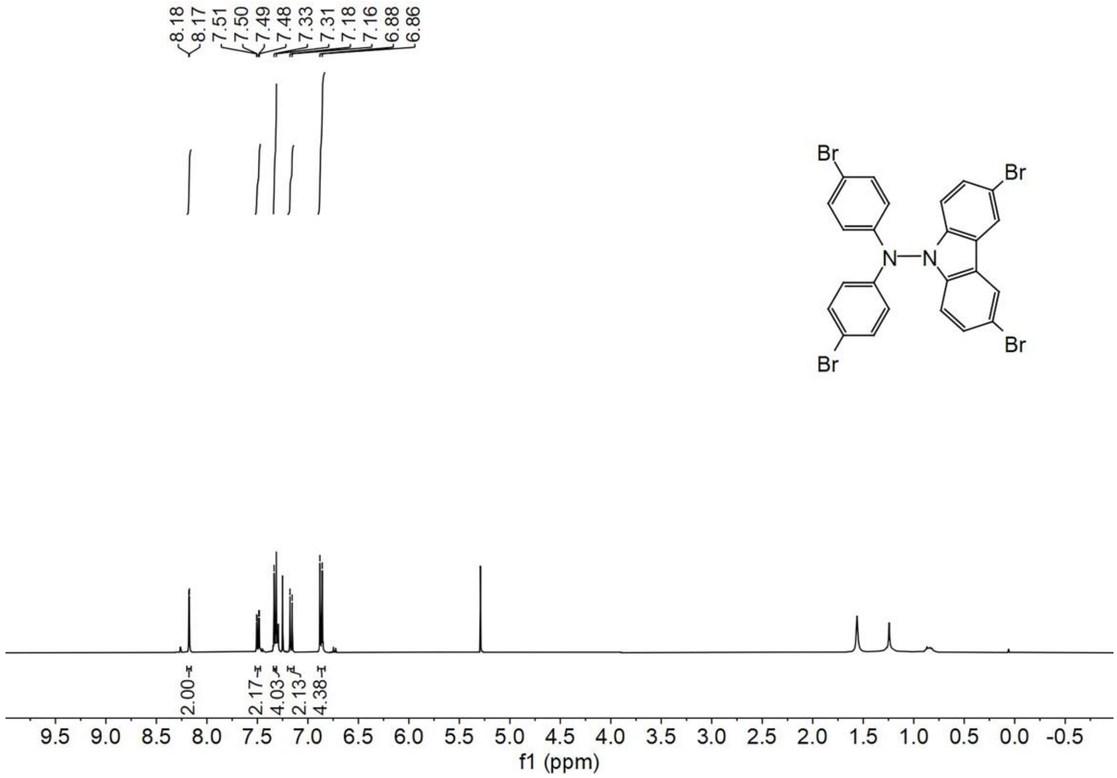
^{13}C NMR spectrum (101 MHz) of 2nt in $CDCl_3$ at 298K



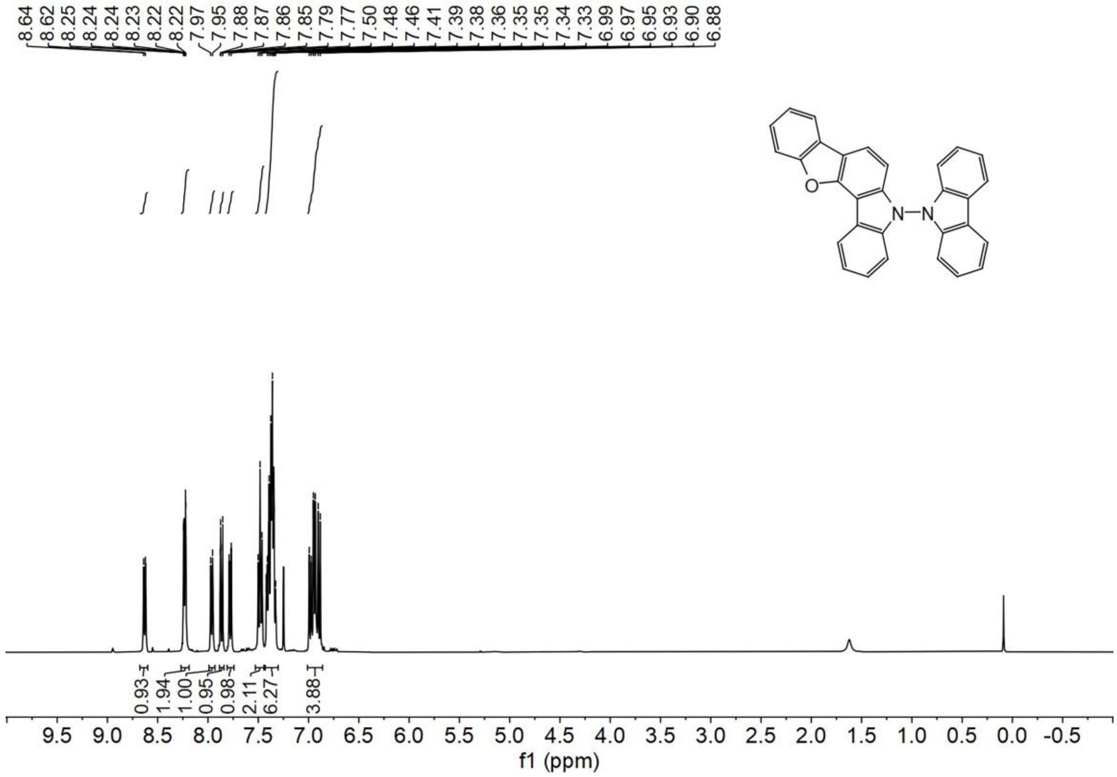
^{1}H NMR spectrum (400 MHz) of 2nu in $CDCl_3$ at 298K



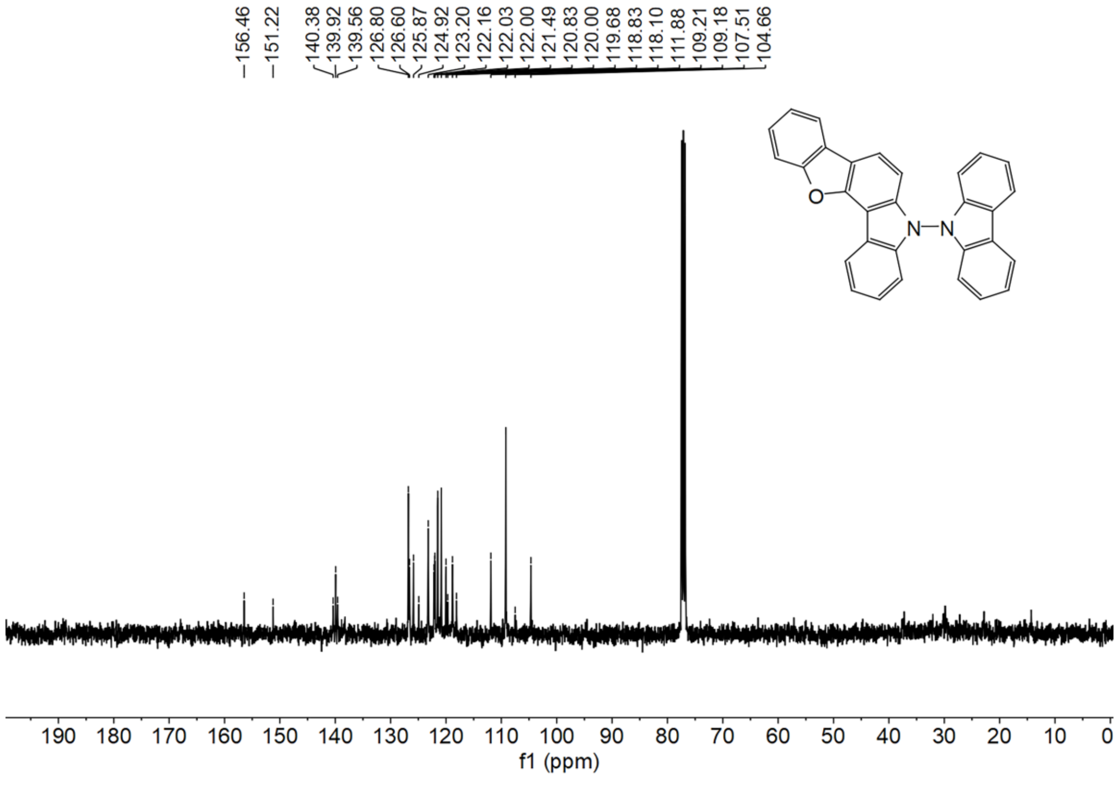
^{13}C NMR spectrum (101 MHz) of 2nu in $CDCl_3$ at 298K



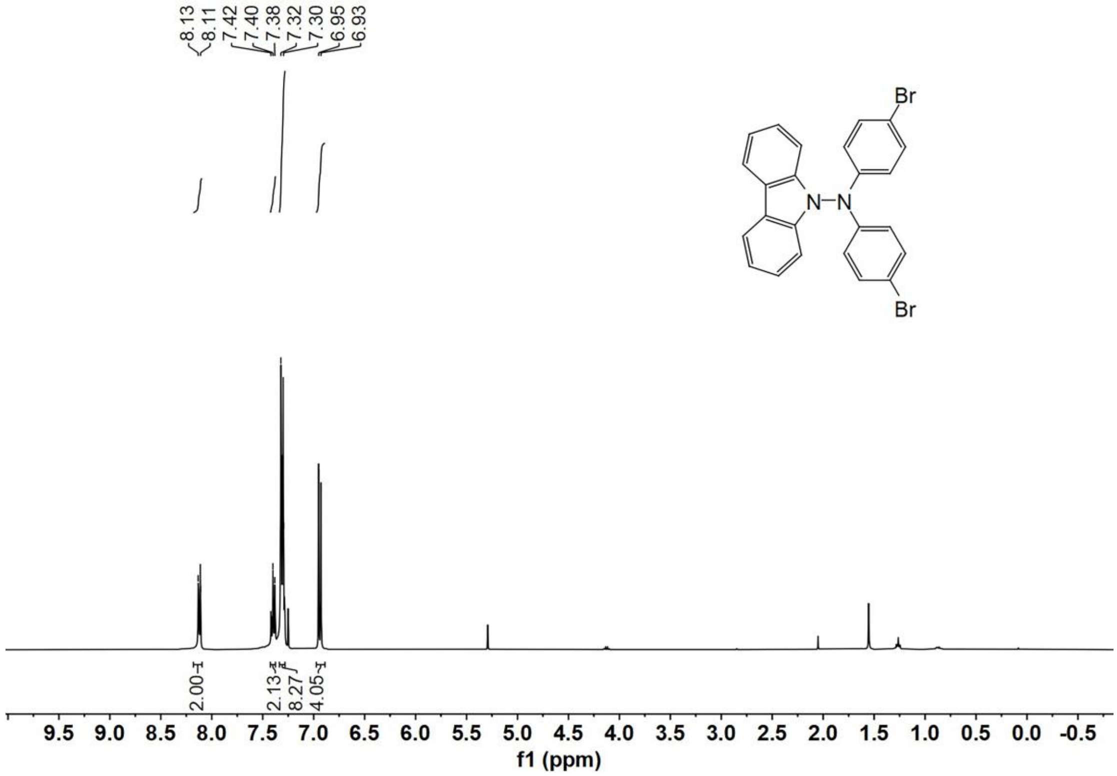
^{1}H NMR spectrum (400 MHz) of 2an in $CDCl_3$ at 298K



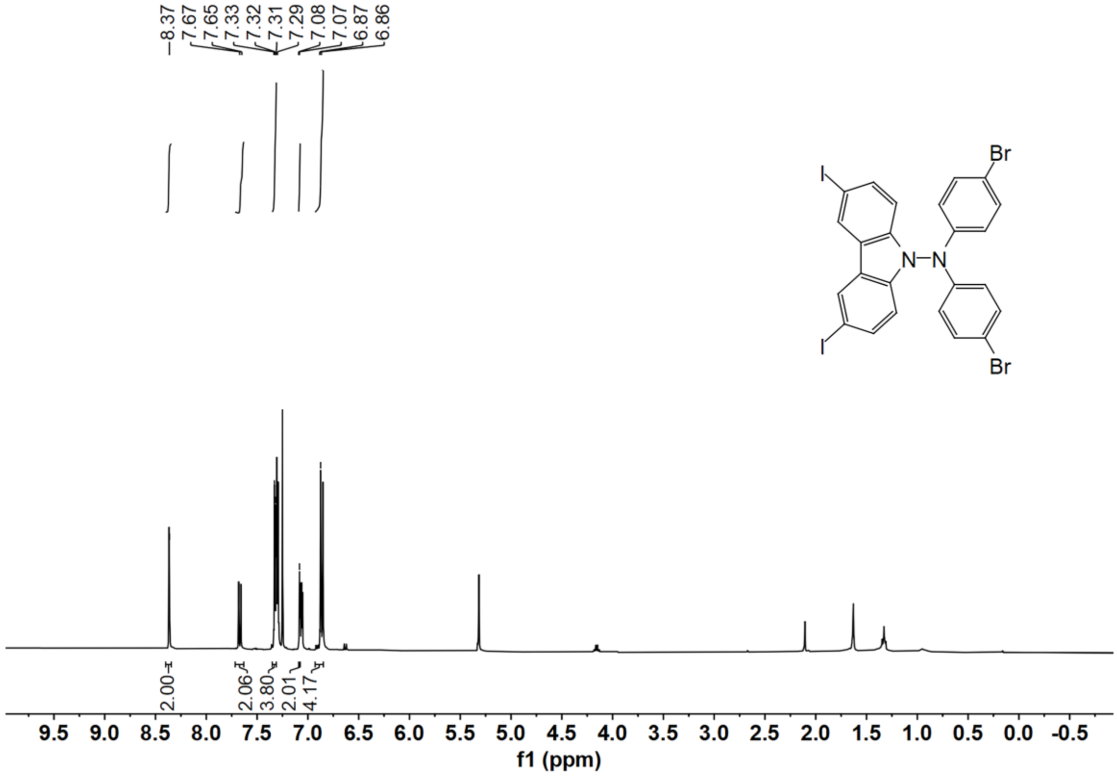
^{1}H NMR spectrum (400 MHz) of 2bu in $CDCl_3$ at 298K



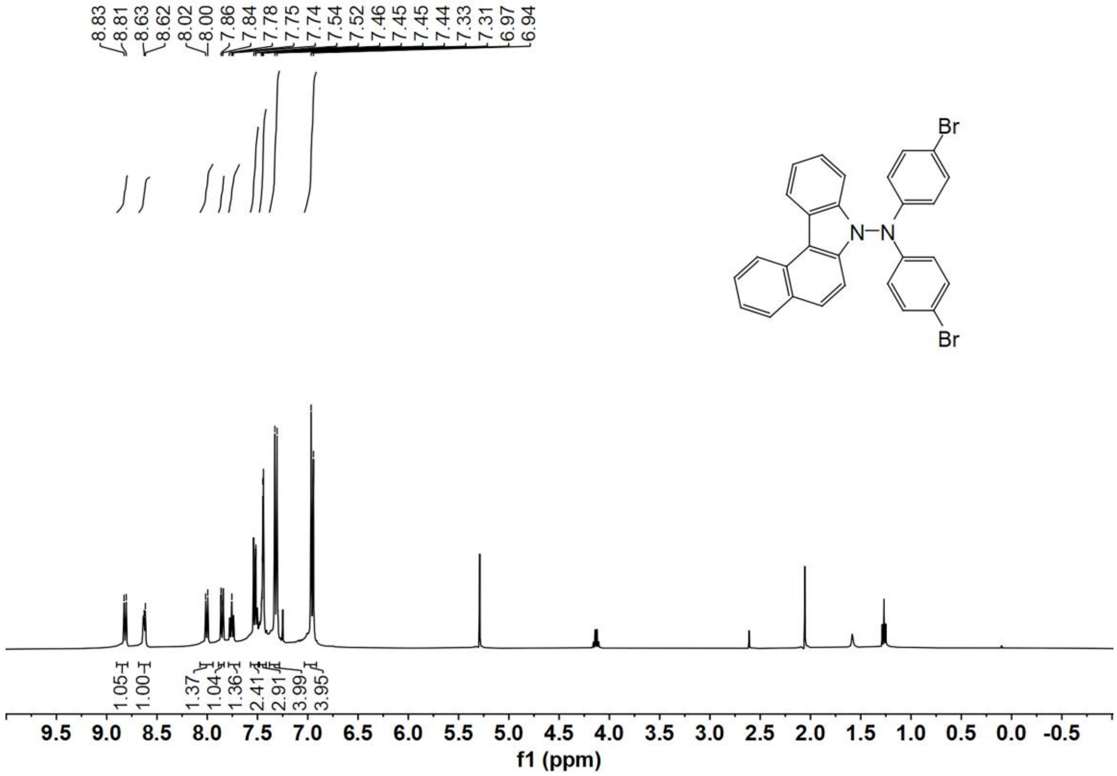
^{13}C NMR spectrum (101 MHz) of 2bu in $CDCl_3$ at 298K



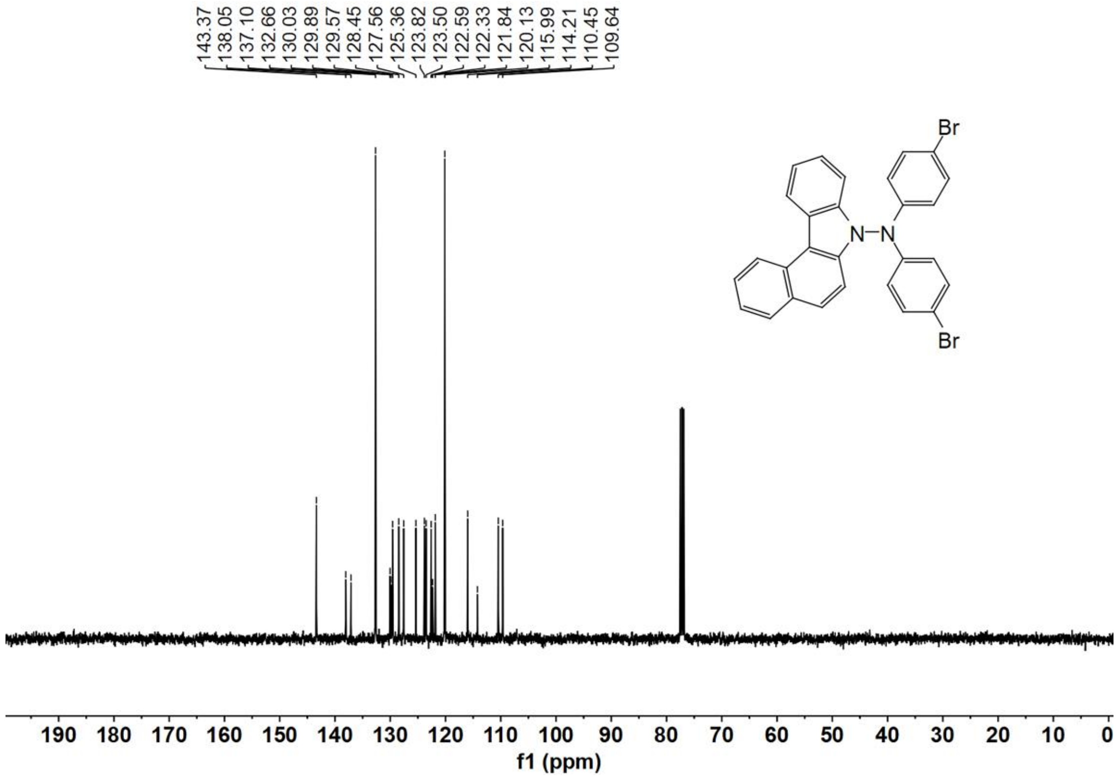
^{1}H NMR spectrum (400 MHz) of 2bn in $CDCl_3$ at 298K



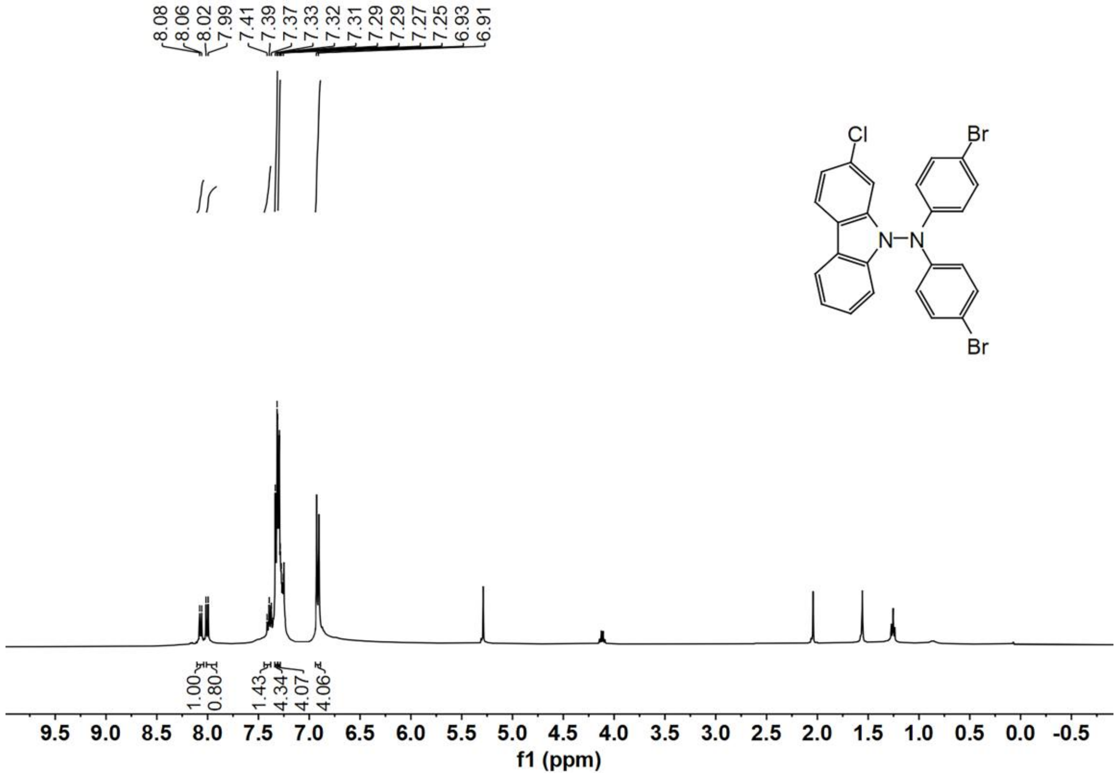
^{1}H NMR spectrum (400 MHz) of 2hn in $CDCl_3$ at 298K



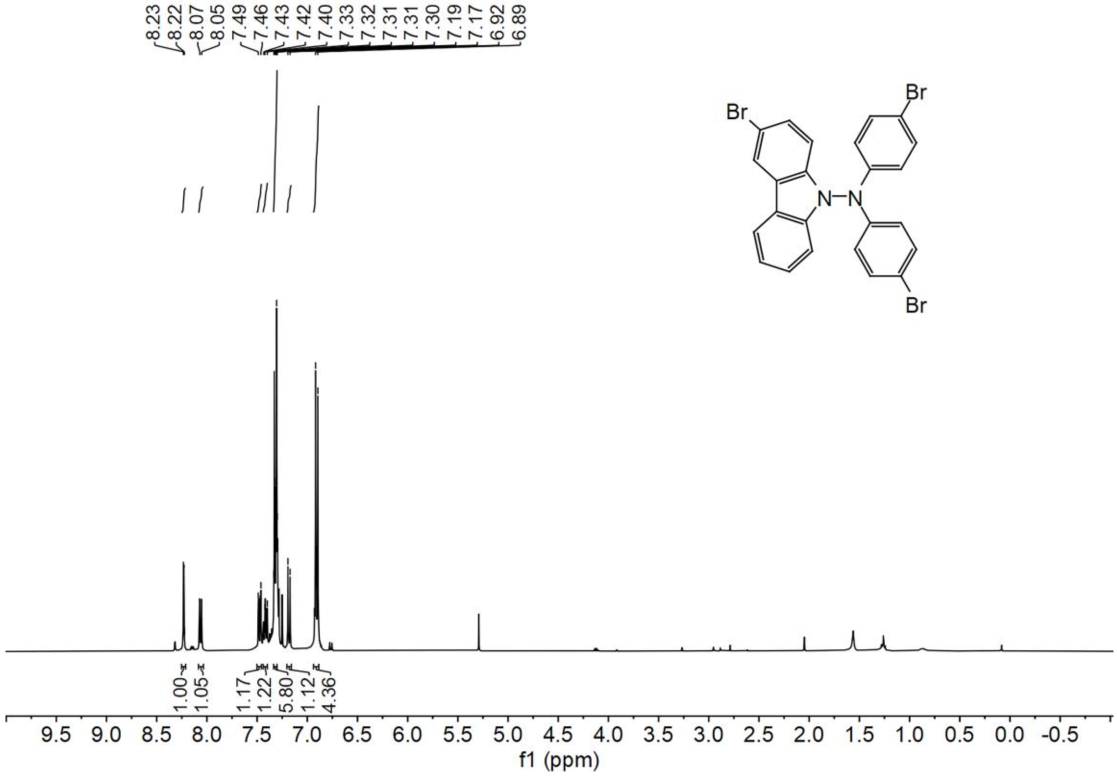
^{1}H NMR spectrum (400 MHz) of 2nq in $CDCl_3$ at 298K



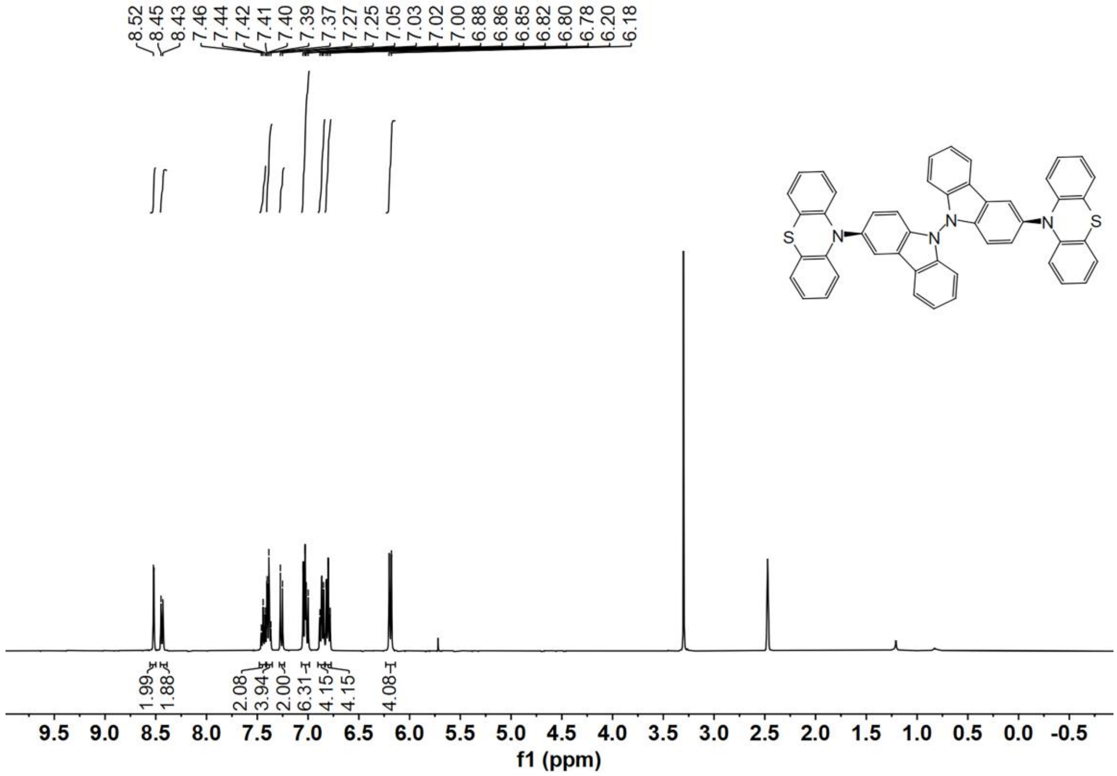
^{13}C NMR spectrum (101 MHz) of 2nq in $CDCl_3$ at 298K



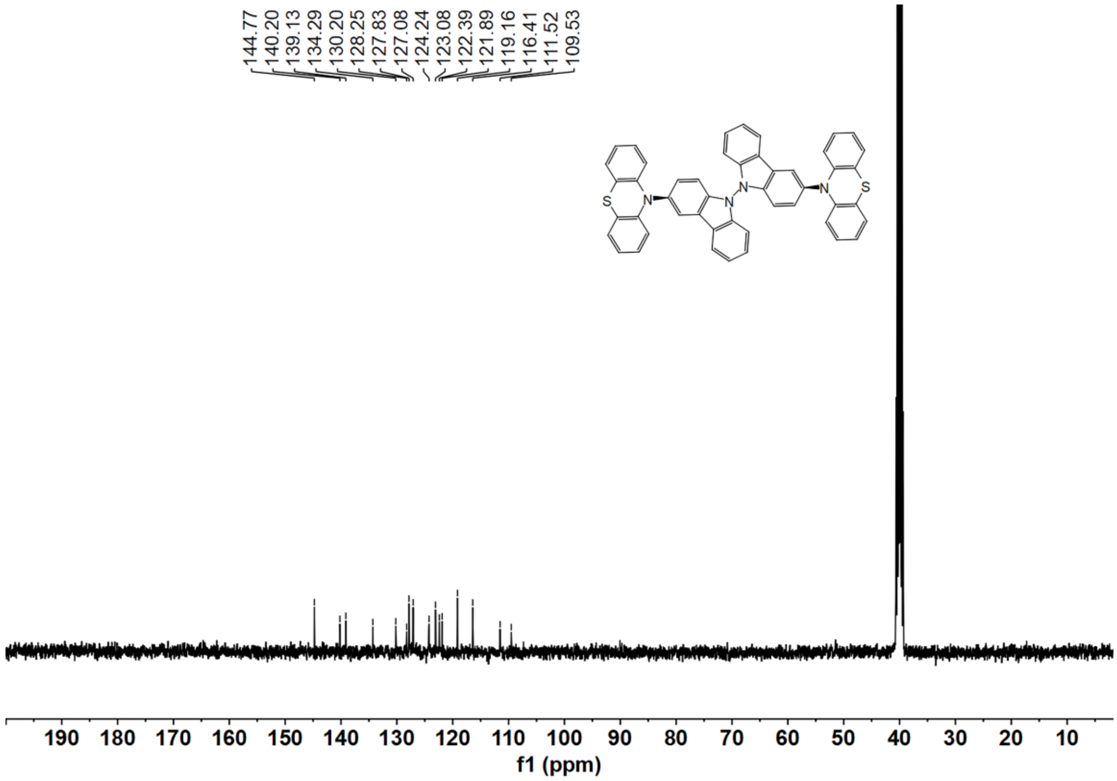
^{1}H NMR spectrum (400 MHz) of 2fn in $CDCl_3$ at 298K



^{1}H NMR spectrum (400 MHz) of 2dn in $CDCl_3$ at 298K



^{1}H NMR spectrum (400 MHz) of 3 in DMSO-d_6 at 298K



^{13}C NMR spectrum (101 MHz) of 3 in DMSO-d_6 at 298K

8. References

[S1] M. C. Ryan, J. R. Martinelli and S. S. Stahl, *J. Am. Chem. Soc.*, 2018, **140**, 9074-9077.

[S2] B. R. Rosen, E. W. Werner, A. G. O'Brien and P. S. Baran, *J. Am. Chem. Soc.*, 2014, **136**, 5571-5574.

[S3] D. Yin and J. Jin, *Eur. J. Org. Chem.*, **2019**, 5646-5649.

[S4] S. I. Thomas and D. E. Falvey, *J. Org. Chem.*, 2007, **72**, 4626-4634.

[S5] E. Feng, Z. Hou and H.-C. Xu, *Chin. J. Org. Chem.*, 2019, **39**, 1424-1428.

[S6] X.-Y. Liu, Y.-L. Zhang, X. Fei, L.-S. Liao and J. Fan, *Chem. Eur. J.*, 2019, **25**, 4501-4508.