

Supporting Information

Synthesis, Characterization and Properties of Aryl-Fused Bis-BN Dihydropyrenes

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1. General

Materials and Methods

Oxygen-sensitive reactions were performed under dry nitrogen atmosphere. Oxygen- and moisture-sensitive reactions were performed under dry nitrogen atmosphere and with anhydrous solvents.

THF, toluene were purified by sodium absorption under argon. We have phenyl dichloroborane, triethylamine and chlorobenzene (extra dry, with molecular sieves) through commercial channels and use them as received. We purchase o-phenylenediamine, bromine, hydrobromic acid, sodium borohydride, glyoxal, phenylboronic acid, tetrakis(triphenylphosphine)palladium and palladium on carbon from Energy Chemical (China) and 2-Thiopheneboronic acid, 3-Thiopheneboronic acid, Benzo[b]thiophene-2-boronic acid and Benzo[b]thiophen-3-ylboronic acid from Tianjin Heowns Biochemical Technology Co., Ltd. (China). Petroleum ether, ethyl acetate, ethyl alcohol and dichloromethane were purchased from Hengshan Chemical (China).

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AM-400 or AM-600 spectrometer. The reported chemical shifts were against TMS. ^{11}B spectra were recorded on a Bruker AM-400 spectrometer. The reported chemical shifts were against $\text{BF}_3\text{-Et}_2\text{O}$. High-resolution mass spectra were obtained with a Micro mass GCT-TOF mass spectrometer.

IR spectra were recorded on a Tensor 27 instrument with a Bruker OPTIK GmbH (Made in Germany) spectrometer.

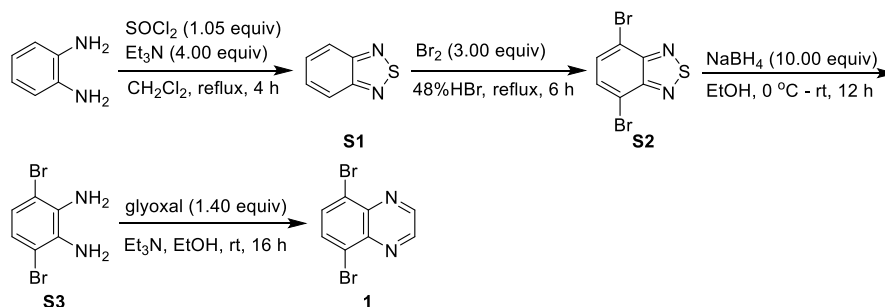
The absorption spectra of all compounds were measured by HITACHI U-3900H spectrophotometer. Fluorescence measurements were carried out with an F-7000 fluorescence spectrophotometer. Fluorescence quantum yields were determined using the comparative method, Quinine sulfate were referenced to 0.5 N H_2SO_4 ($\Phi_{\text{F}} = 0.546$).¹

UV-vis absorption spectra in solid state were obtained on a PekinElmer Lambda 750 UV/VIS/NIR spectrometer. Photoluminescent (PL) spectra in solid state were recorded on a Hitachi F-7000 spectrometer.

Cyclic voltammetry (CV) were recorded on an electrochemical work station of Shanghai (in China) ChenHua by CHI660E B14511.

The single-crystal X-ray diffraction data of **4a**, **4c** and **4d** were collected on a Rigaku SCX-mini diffractometer at 293(2)K. The program CrystalClear² was used for the integration of the diffraction profiles. The structure was solved by direct method using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL (semi-empirical absorption corrections were applied by using the SADABS program).³ The non-hydrogen atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on F2. All hydrogen atoms were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors.

2. Synthetic Procedures



Scheme S1. Synthesis of 5,8-dibromoquinoxaline.

Synthesis of **S1**:

Triethylamine (4.00 equiv, 369.98 mmol, 37.4 g) was added to commercially available o-phenylenediamine (1.00 equiv, 92.47 mmol, 10.0 g) in CH_2Cl_2 (300 mL). The color of the reaction mixture turned brown after stirring at room temperature for 10 minutes. Thionyl chloride (1.05 equiv, 1.05 mmol, 0.13 g) was placed in a constant pressure funnel and added dropwise. After that, the mixture was refluxed for 4 hours. The solvent was removed under reduced pressure, and 700 mL of water was added. Subsequently, concentrated HCl was added to acidified the mixture ($\text{pH} = 2$). The mixture was extracted three times with 100 mL of CH_2Cl_2 , dried over MgSO_4 , and filtered. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography to give **S1** as white solid (6.04 g, yield = 48 %). The ^1H NMR of **S1** is identical to the reported data.⁴

^1H NMR (400 MHz, CDCl_3): δ 8.02 (dd, $J_1 = 6.8$ Hz, $J_2 = 3.2$ Hz, 2H, Ar), 7.60 (dd, $J_1 = 6.8$ Hz, $J_2 = 3.2$ Hz, 2H, Ar).

Synthesis of **S2**:

Br_2 (3.00 equiv, 220.32 mmol, 35.2 g) in 100 mL of 48% HBr was added very slowly to the solution of benzothiadiazole **S1** (1.00 equiv, 73.44 mmol, 10.0 g) in 150 mL of 48% HBr. After refluxing for 6 hours, an orange solid precipitated. Saturated solution of NaHSO_3 was added to neutralize the

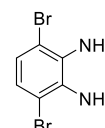
remaining Br₂ after the mixture was cooled to room temperature. The mixture was filtered and washed repeatedly with water. The solid was purified by crystallization in CH₂Cl₂ (9.5 g, yield = 44 %). The ¹H NMR of **S2** is identical to the reported data.⁴

¹H NMR (400 MHz, CDCl₃): δ 7.73 (s, 2H, Ar).

Synthesis of **S3**:

Sodium borohydride (10.00 equiv, 0.10 mol, 3.80 g) was added portion-wise to a stirred suspension of **S2** (1.00 equiv, 10.00 mmol, 2.94 g) in ethanol (100 mL) under N₂ at 0 °C. After stirring for 5 minutes at 0 °C, the reaction mixture was allowed to stir at room temperature for 12 hours. After the reaction completed, solvent was removed by reduced pressure. Then 100 mL of distilled water was added to the above reaction mixture at room temperature. The mixture was extracted with 100 mL ethyl acetate. The organic phase was collected and washed with 50 mL saturated brine and dried over anhydrous MgSO₄. After removal of solvent, the residual was purified by silica gel chromatography with petroleum ether/ ethyl acetate (v:v = 10:1) as eluent to afford **S3** as a pale white solid (1.6 g, yield = 61%) . The ¹H NMR of **S3** is identical to the reported data.⁵

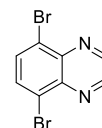
¹H NMR (400 MHz, CDCl₃): δ 6.85 (s, 2H, Ar), 3.90 (s, 4H, NH₂).

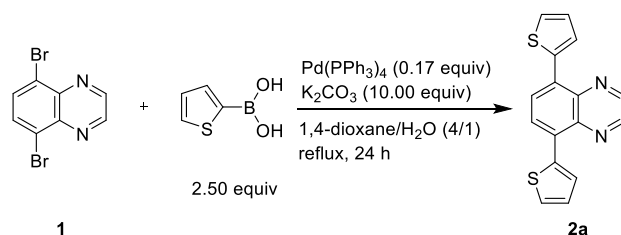


Synthesis of **1**:

Glyoxal (40 wt% aqueous solution, 1.40 equiv, 1.40 mmol, 0.20 mL) was added to a solution of **S3** (1.00 equiv, 1.00 mmol, 266 mg) in anhydrous ethanol (7 mL) under N₂. Then, triethylamine (0.25 equiv, 0.25 mmol, 25.3 mg) was added to the above reaction mixture. This resulting mixture was stirred overnight at room temperature. The white precipitate was collected by filtration under vacuum. The wet filter cake was recrystallized from 500 mL anhydrous ethanol to give compound **1** as white solid (184.0 mg, yield = 64%). The ¹H NMR of **1** is identical to the reported data.⁵

¹H NMR (400 MHz, CDCl₃): δ 9.02 (s, 2H, Ar), 8.01 (s, 2H, Ar).



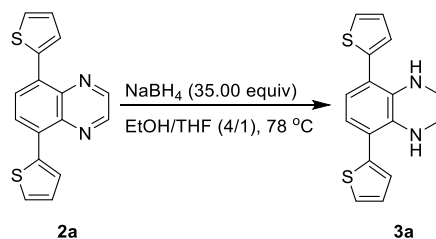


Scheme S2. Synthesis of **2a**.

Synthesis of **2a**:

Following a similar procedure based on a literature method. 5,8-dibromoquinoxaline (1.00 equiv, 1.00 mmol, 288 mg), thiophene-2-boronic acid (2.50 equiv, 2.50 mmol, 320 mg) and potassium carbonate (10.00 equiv, 10.00 mmol, 3.68 g) were added in a 200 mL dried flask fit with a condenser under N_2 . Then $\text{Pd(PPh}_3)_4$ (0.17 equiv, 0.17 mmol, 196 mg) was added under N_2 . The reaction mixture was allowed to dissolve in dioxane/water 4:1 (20 mL) under N_2 . The reaction was stirred at 110°C for 24 hours. Then 40 mL of water was added after the reaction mixture was cooled to room temperature. The mixture was extracted with dichloromethane three times. The combined organic phase was dried over MgSO_4 . After the solvents were removed, the orange oil was purified by silica gel chromatography with petroleum ether/dichloromethane ($v/v = 10:1$) to afford title compound **2a** as yellow powder (221 mg, yield = 75%). The $^1\text{H NMR}$ of **2a** is identical to the reported data.⁶

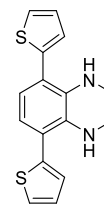
$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.99 (s, 2H, Ar), 8.14 (s, 2H, Ar), 7.83 (dd, $J_1 = 3.7$ Hz, $J_2 = 1.0$ Hz, 2H, Ar), 7.52 (dd, $J_1 = 5.1$ Hz, $J_2 = 1.0$ Hz, 2H, Ar), 7.20 (dd, $J_1 = 5.1$ Hz, $J_2 = 3.7$ Hz, 2H, Ar).



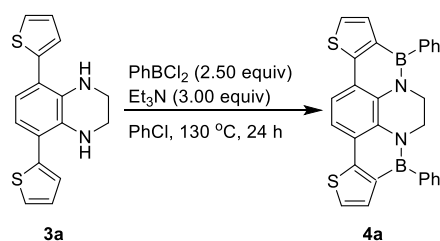
Scheme S3. Synthesis of **3a**.

Synthesis of **3a**:

NaBH₄ (35.00 equiv, 35.00 mmol, 1.32 g) was added to **2a** (1.00 equiv, 1.00 mmol, 294 mg) in mixture of ethanol (80 mL) and THF (40 mL) under argon. The reaction mixture was heated at 78 °C overnight. The reaction process was monitored by TLC, water was added (20 mL) when the reaction almost completed. The crude product was extracted by 3×50 mL of ethyl acetate, the organic phase was collected and dried over MgSO₄. After quick filtration and evaporation of the solvent, the residue was purified by column chromatography to provide **3a** as yellow powder (131 mg, yield = 44%). We found that **3a** could be oxidized slowly when it was exposed to air. So it should be purified quickly and stored under N₂.



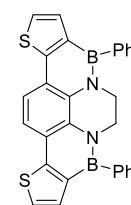
m.p. 129-131 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.37 (dd, *J* = 4.8 Hz, 2H, Ar), 7.22 (dt, *J*₁ = 6.3 Hz, *J*₂ = 3.4 Hz, 2H, Ar), 7.14 (dt, *J*₁ = 12.4 Hz, *J*₂ = 6.3 Hz, 2H, Ar), 6.78-6.71 (m, 2H, Ar), 4.48 (s, 2H, NH), 3.44 (s, 4H, CH₂). ¹³C NMR (100 MHz, CDCl₃): δ 140.9, 131.2, 127.4, 125.9, 125.2, 119.8, 118.8, 40.8. FTIR (thin film): 3453, 2921, 2851, 1636, 1476, 1436, 1406, 1343 cm⁻¹. *m/z* (C₁₆H₁₄N₂S₂) calcd for [M+H]⁺, 299.0677; found, 299.0697.



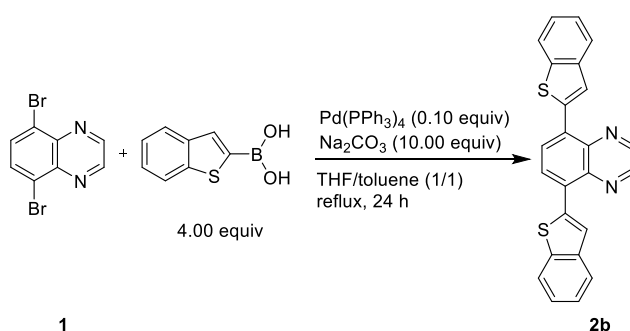
Scheme S4. Synthesis of **4a**.

Synthesis of **4a**:

3a (1.00 equiv, 1.00 mmol, 294 mg), anhydrous triethylamine (3.00 equiv, 3.00 mmol, 304 mg) and phenyldichloroborane (2.50 equiv, 2.50 mmol, 398 mg) in chlorobenzene (21 mL) were placed in a sealed tube under N₂ atmosphere. The reaction mixture was heated at 130 °C for 24 hours. After cooling to room temperature, the solvent was evaporated and the residue was purified by column chromatography to provide title compound **4a** as pale green powder (400 mg, yield = 85%).



m.p. 242-244 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.96 (s, 2H, Ar), 7.63 (d, *J*₁ = 6.8 Hz, 4H, Ar), 7.51-7.34 (m, 10H, Ar), 4.35 (s, 4H, CH₂). ¹³C NMR (100 MHz, CDCl₃): δ 151.2, 139.5, 139.0, 132.9, 132.2, 128.7, 127.9, 127.8, 124.3, 121.2, 119.2, 46.8. ¹¹B NMR (128 MHz, BF₃·OEt₂): δ 38.4. FTIR (thin film): 3453, 2924, 2859, 2357, 2313, 1637, 1512, 1421, 1368, 1263, 1086, 1016, 798, 740, 698 cm⁻¹. m/z (C₂₈H₂₀B₂N₂S₂) calcd for [M+H]⁺, 471.1342; found, 471.1393.

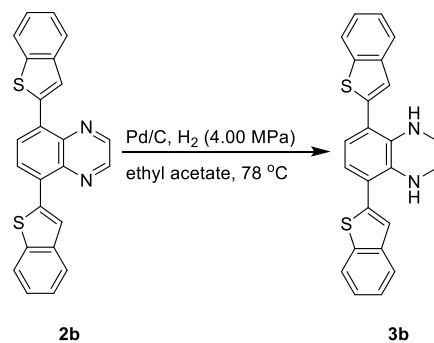


Scheme S5. Synthesis of **2b**.

Synthesis of **2b**:

5,8-dibromoquinoxaline (1.00 equiv, 1.00 mmol, 288 mg), 2-benzothiénylboronic acid (4.00 equiv, 4.00 mmol, 712 mg), sodium carbonate (4.00 equiv, 424 mg) and Pd(PPh₃)₄ (0.10 equiv, 0.10 mmol, 116 mg) in THF/toluene (v/v = 1:1) were placed in a 200 mL dried flask fit with a condenser under N₂. The suspension was heated at 110 °C for 24 hours. After the reaction completed, it was allowed to cool to room temperature. The precipitate was filtered off and washed with dichloromethane and petroleum ether to afford title compound **2b** as yellow solid (331 mg, yield = 84%).

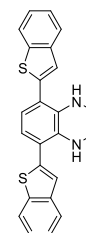
m.p. 247-249 °C. ¹H NMR (400 MHz, CDCl₃): δ 9.06 (s, 2H, Ar), 8.28 (s, 2H, Ar), 8.18 (s, 2H, Ar), 7.88-7.93 (m, 4H, Ar), 7.33-7.42 (m, 4H, Ar). ¹³C NMR (100 MHz, CDCl₃): Carbon NMR was not recorded due to limited solubility. FTIR (thin film): 3454, 2921, 2851, 2360, 2341, 2026, 1638, 1468, 1425, 1330, 1075, 1050, 1016, 929, 846, 734 cm⁻¹. m/z (C₂₄H₁₄N₂S₂) calcd for [M+H]⁺, 395.0677; found, 395.0690.



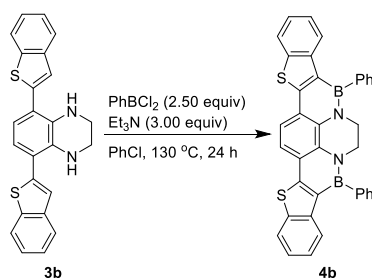
Scheme S6. Synthesis of **3b**.

Synthesis of **3b**:

Pd/C (10 wt %, 0.50 equiv, 0.50 mmol, 53 mg) was added to **2b** (1.00 equiv, 1.00 mmol, 394 mg) in ethyl acetate (10 mL). The flask was vacuumed and recharged with hydrogen (4.00 MPa). The reaction mixture was heated at 78 °C for 14 hours. The reaction progress is monitored by TLC. After the reaction completed, Pd/C was removed by filtration. Removal of solvent by vacuum gave the title compound **3b**, and it was used directly without further purification.



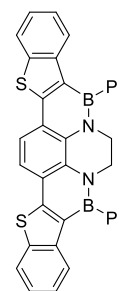
m.p. 218-220 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.86 (d, *J* = 8.0 HZ, 2H, Ar), 7.79 (d, *J* = 7.6 HZ, 2H, Ar), 7.44 (s, 2H, Ar), 7.34-7.40 (m, 4H, Ar), 6.85 (s, 2H, Ar), 4.69 (br, 2H, NH), 3.47 (s, 4H, CH₂). ¹³C NMR (100 MHz, CDCl₃): δ 141.3, 140.3, 139.8, 131.5, 124.4, 124.2, 123.4, 122.6, 122.1, 120.0, 118.9, 40.7. FTIR (thin film): 3451, 2923, 2854, 2031, 1638, 1474, 1439, 1356, 1296, 1227, 1172, 1116, 1010, 946, 781, 738 cm⁻¹. *m/z* (C₂₄H₁₈N₂S₂) calcd for [M+H]⁺, 399.0990; found, 399.0998.



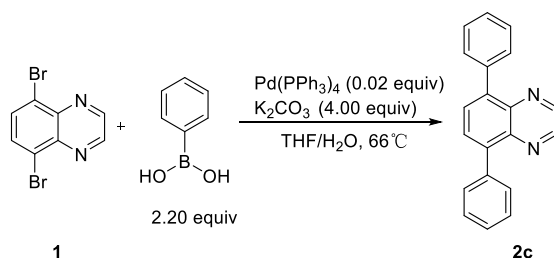
Scheme S7. Synthesis of **4b**.

Synthesis of **4b**:

3b (1.00 equiv, 1.00 mmol, 398 mg), anhydrous triethylamine (3.00 equiv, 3.00 mmol, 304 mg) and phenyldichloroborane (2.50 equiv, 2.50 mmol, 398 mg) in chlorobenzene (21 mL) were placed in a sealed tube under N₂ atmosphere. The reaction mixture was heated at 130 °C for 24 hours. After cooling to room temperature, the solvent was removed under vacuum, and the crude mixture was triturated in hexanes to provide title compound **4b** as white solid (342 mg, yield = 60%).



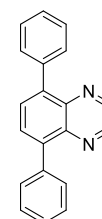
m.p. > 305 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.04 (s, 2H, Ar), 7.94 (d, *J* = 7.6 Hz, 2H, Ar), 7.46-7.55 (m, 10H, Ar), 7.32 (d, *J* = 7.6 Hz, 2H, Ar), 7.28 (d, *J* = 8.8 Hz, 2H, Ar), 7.13 (dd, *J*₁ = 7.6 Hz, *J*₂ = 7.6 Hz, 2H, Ar), 4.20 (s, 4H, CH₂). ¹³C NMR (100 MHz, CDCl₃): δ 152.4, 143.3, 140.0, 131.4, 129.6, 128.4, 127.9, 125.2, 125.0, 124.4, 122.0, 121.6, 120.0, 46.7 (The B-aryl carbons were not observed). ¹¹B NMR (128 MHz, BF₃·OEt₂): δ 29.9. FTIR (thin film): 3450, 2925, 2857, 2033, 1638, 1458, 1412, 1301, 1265, 1229, 1176, 1008, 955, 744 cm⁻¹. *m/z* (C₃₆H₂₄B₂N₂S₂) calcd for [M+H]⁺, 571.1645; found, 571.1655.



Scheme S8. Synthesis of **2c**.

Synthesis of **2c**:

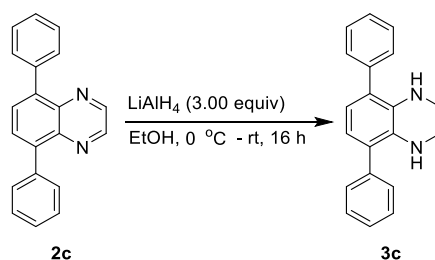
5,8-dibromoquinoxaline (1.00 equiv, 1.00 mmol, 288 mg), phenyl-2-boronic acid (2.20 equiv, 2.20 mmol, 268 mg), Pd(PPh₃)₄ (0.02 equiv, 0.02 mmol, 23 mg) and potassium carbonate (4.00 equiv, 4.00 mmol, 1.22 g) were placed in a 200 mL flask with 20 mL of THF/water (4:1) under



N₂. The suspension was heated at 66 °C for 24 hours, the color turned from white to orange during the reaction. After the reaction cooled to room temperature, the

precipitation was collected and recrystallized to afford title compound **2c** (234 mg, yield = 83%). The ^1H NMR is identical to the reported data.⁷

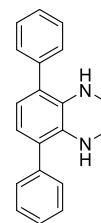
^1H NMR (400 MHz, CDCl_3): δ 8.89 (s, 2H, Ar), 7.88 (s, 2H, Ar), 7.72 (d, $J = 8.0$ Hz, 4H, Ar), 7.54 (dd, $J_1 = 7.5$ Hz, $J_2 = 7.5$ Hz, 4H, Ar), 7.44-7.48 (m, 2H, Ar).



Scheme S9. Synthesis of **3c**.

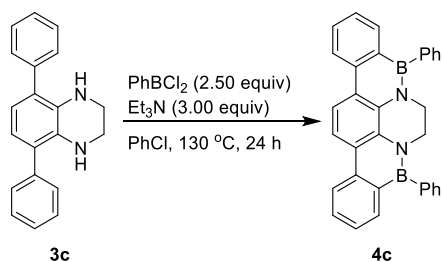
Synthesis of **3c**:

LiAlH_4 (3.00 equiv, 2.10 mmol, 81 mg) in THF 10 mL was added slowly to **2c** (1.00 equiv, 0.70 mmol, 200 mg) in 10 mL THF under argon. The reaction mixture was stirred overnight at 0 °C. After reaction completed, water was added slowly to quench the reaction.



The mixture was extracted with ethyl acetate three times, and the organic phase was combined and dried over MgSO_4 . After quick filtration and evaporation of the solvent, the residue was purified by column chromatography to provide **3c** as yellow solid (163 mg, yield = 57%).

m.p. 82-84 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.51 (d, $J = 7.0$ Hz, 4H, Ar), 7.45 (dd, $J_1 = 7.6$ Hz, $J_2 = 7.6$ Hz, 4H, Ar), 7.32-7.37 (dd, $J_1 = 7.6$ Hz, $J_2 = 7.0$ Hz, 2H, Ar), 6.62 (s, 2H, Ar), 4.06 (br, 2H, NH), 3.38 (s, 4H, CH_2). ^{13}C NMR (100 MHz, CDCl_3): δ 139.4, 130.3, 129.3, 128.7, 127.0, 126.3, 119.4, 40.9. FTIR (thin film): 3444, 2923, 2851, 2349, 2027, 1639, 1476, 1425, 1351, 1265, 1228, 1072, 740, 703 cm^{-1} . m/z ($\text{C}_{20}\text{H}_{18}\text{N}_2\text{S}_2$) calcd for $[\text{M}+\text{H}]^+$, 287.1548; found, 287.1593.

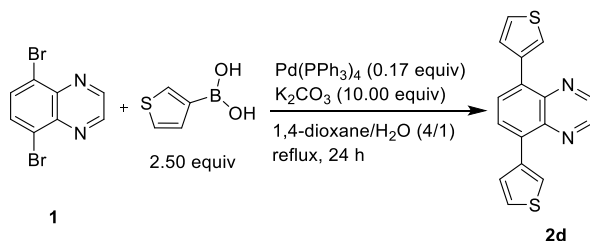


Scheme S10. Synthesis of **4c**.

Synthesis of **4c**:

3c (1.00 equiv, 1.00 mmol, 286 mg), anhydrous triethylamine (3.00 equiv, 3.00 mmol, 304 mg) and phenyldichloroborane (2.50 equiv, 2.50 mmol, 398 mg) in chlorobenzene (21 mL) were placed in a sealed tube under N_2 atmosphere. The reaction mixture was heated at $130\text{ }^\circ\text{C}$ for 24 hours. After cooling to room temperature, the solvent was evaporated and the residue was purified by column chromatography to provide the title compound **4c** as white powder (389 mg, yield = 85%).

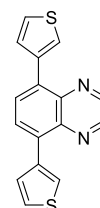
m.p. $247\text{--}249\text{ }^\circ\text{C}$. ^1H NMR (400 MHz, CDCl_3): δ 8.62 (d, $J = 8.3$ Hz, 2H, Ar), 8.51 (s, 2H, Ar), 7.76–7.83 (m, 4H, Ar), 7.53 (d, $J = 6.4$ Hz, 4H, Ar), 7.41–7.48 (m, 8H, Ar), 4.19 (s, 4H, CH_2). ^{13}C NMR (100 MHz, CDCl_3): δ 138.5, 136.7, 132.5, 131.1, 127.8, 127.7, 126.2, 124.2, 122.5, 117.5, 47.5 (The B-aryl carbons were not observed). ^{11}B NMR (128 MHz, $\text{BF}_3\cdot\text{OEt}_2$): δ 42.0. FTIR (thin film): 3449, 2924, 2861, 2033, 1637, 1497, 1460, 1395, 1336, 1305, 1263, 1227, 1168, 1109, 745.1, 704 cm^{-1} . m/z ($\text{C}_{32}\text{H}_{24}\text{B}_2\text{N}_2$) calcd for $[\text{M}+\text{H}]^+$: 459.2215 ; found, 459.2225.



Scheme S11. Synthesis of **2d**.

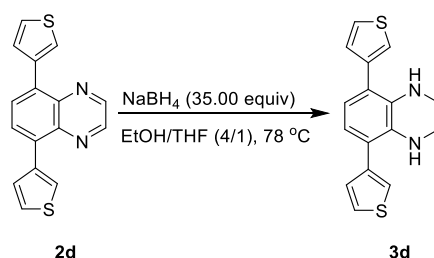
Synthesis of **2d**:

5,8-dibromoquinoxaline (1.00 equiv, 1.00 mmol, 288 mg), thiophene-3-boronic acid (2.50 equiv, 2.50 mmol, 320 mg) and potassium



carbonate (10.00 equiv, 10.00 mmol, 3.68 g) were placed in a 200 mL dried flask fit with a condenser under N₂, Then Pd(PPh₃)₄ (0.17 equiv, 0.17 mmol, 196 mg) was added under N₂, followed by adding 20 mL of dioxane/water (v/v = 4/1) under N₂. Subsequently, the reaction mixture was heated at 110 °C for 24 hours, and monitored the reaction by TLC. Then 40 mL of water was added after the reaction mixture was cooled to room temperature. The mixture was extracted with dichloromethane three times. The combined organic phase was dried over MgSO₄. After the solvents was removed under vacuum, the orange oil was purified by silica gel chromatography using petroleum ether/dichloromethane (v/v = 10:1) as eluent to afford title compound **2d** as green powder (185 mg, yield = 63%).

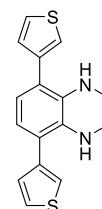
m.p. 199-201 °C. ¹H NMR (600 MHz, CDCl₃): δ 8.93 (s, 2H, Ar), 7.96 (s, 2H, Ar), 7.93 (d, *J* = 3.0 Hz, 2H, Ar), 7.65 (d, *J* = 4.8 Hz, 2H, Ar), 7.47 (dd, *J*₁ = 4.8 Hz, *J*₂ = 3.0 Hz, 2H, Ar). ¹³C NMR (100 MHz, CDCl₃): δ 144.0, 141.1, 138.3, 134.5, 129.4, 129.4, 125.2, 124.9. FTIR (thin film): 3454, 3092, 2920, 2849, 1637, 1482, 1265, 780, 740 cm⁻¹. m/z (C₁₆H₁₀N₂S₂) calcd for [M+H]⁺, 295.0397; found, 295.0364.



Scheme S12. Synthesis of **3d**

Synthesis of **3d**:

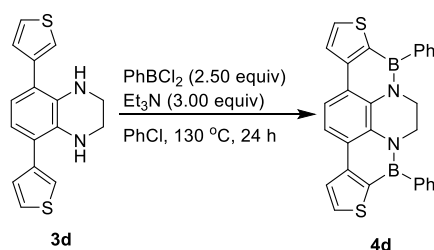
NaBH₄ (35.00 equiv, 35.00 mmol, 1.32 g) was added to **2d** (1.0 equiv, 1.00 mmol, 294 mg) in mixture of ethanol (80 mL) and THF (40 mL) under N₂. The reaction mixture was heated at 78 °C overnight. The reaction process was monitored by TLC, water was added (20 mL)



when the reaction almost completed. The reaction mixture was extracted with ethyl acetate three times, the organic phase was combined and dried over MgSO₄. After quick filtration and evaporation of the solvent, the residue was purified by column

chromatography to provide **3d** as white powder (164 mg, yield = 55%). We found that **3d** could be oxidized slowly when it was exposed to air. So it should be purified as quickly as possible and stored under N₂.

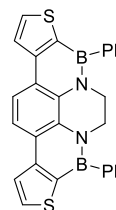
m.p. 161-163 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.42-7.44 (m, 2H, Ar), 7.39-7.40 (m, 2H, Ar), 7.30 (d, *J* = 5.2 Hz, 2H, Ar), 6.69 (s, 2H, Ar), 4.20 (br, 2H, NH), 3.42 (s, 4H, CH₂). ¹³C NMR (100 MHz, CDCl₃): δ 139.6, 130.8, 128.6, 125.8, 122.5, 121.2, 119.2, 41.0. FTIR (thin film): 3450, 2920, 2850, 2361, 2342, 2027, 1633, 1470, 1347, 1266, 1123, 1084, 851, 782, 741 cm⁻¹. m/z (C₁₆H₁₄N₂S₂) calcd for [M+H]⁺, 299.0677; found, 299.0683.



Scheme S13. Synthesis of **4d**.

Synthesis of **4d**:

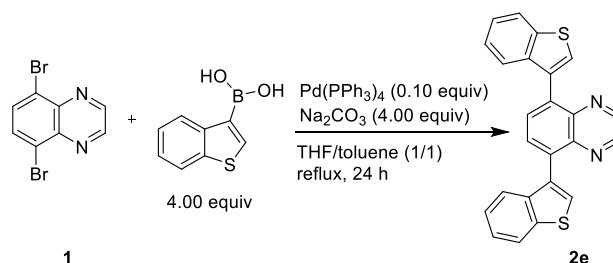
3d (1.00 equiv, 1.00 mmol, 294 mg), anhydrous triethylamine (3.00 equiv, 3.00 mmol, 304 mg) and phenyldichloroborane (2.50 equiv, 2.50 mmol, 398 mg) in chlorobenzene (21 mL) were placed in a sealed tube under N₂ atmosphere. The reaction mixture was heated at 130 °C for 24



hours. After cooling to room temperature, the solvent was evaporated and the residue was purified by column chromatography to provide the title compound **4d** as white powder (376 mg, yield = 80%).

m.p. 237-239 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.19 (s, 2H, Ar), 8.11 (d, *J* = 5.2 Hz, 2H, Ar), 7.94 (d, *J* = 5.2 Hz, 2H, Ar), 7.71 (d, *J* = 6.8 Hz, 4H, Ar), 7.44-7.51 (m, 6H, Ar), 4.41 (s, 4H, CH₂). ¹³C NMR (100 MHz, CDCl₃): δ 146.4, 134.5, 132.9, 129.7, 128.4, 128.0, 123.9, 121.4, 118.8, 47.1 (The B-aryl carbons were not observed). ¹¹B NMR (128 MHz, BF₃·OEt₂): δ 34.2. FTIR (thin film): 3453, 1639, 1251, 1483, 1451,

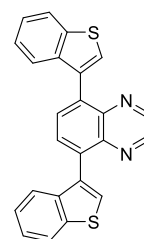
1429, 1385, 1343, 1322, 1265, 1250, 1122, 743, 704 cm^{-1} . m/z ($\text{C}_{28}\text{H}_{20}\text{B}_2\text{N}_2\text{S}_2$) calcd for $[\text{M}+\text{H}]^+$, 471.1342; found, 471.1373.



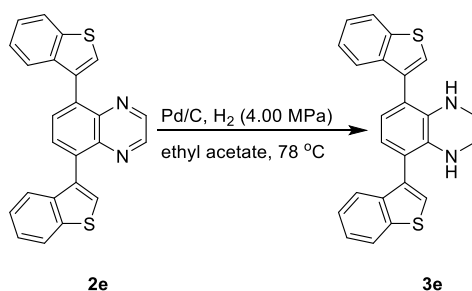
Scheme S14. Synthesis of **2e**.

Synthesis of **2e**:

5,8-Dibromoquinoxaline (1.00 equiv, 1.00 mmol, 288 mg), 2-benzothiophenylboronic acid (4.00 equiv, 4.00 mmol, 712 mg) and sodium carbonate (4.00 equiv, 4.00 mmol, 424 mg) was placed in a 200 mL dried flask fit with a condenser. Then $\text{Pd}(\text{PPh}_3)_4$ (0.10 equiv, 0.10 mmol, 116 mg) was added under N_2 . The reaction mixture was allowed to dissolve in THF/toluene 1:1 (90 mL) under N_2 . The reaction mixture was stirred at reflux for 24 hours. The reaction mixture was cooled to room temperature. The precipitate was filtered off and washed with dichloromethane and petroleum ether to afford the title compound **2e** as light green solid (233 mg, yield = 59%).



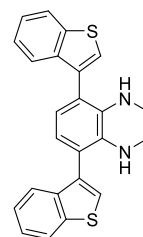
m.p. 257-259 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3): δ 8.86 (s, 2H, Ar), 8.03 (s, 2H, Ar), 7.98 (d, $J = 8.0$ Hz, 2H, Ar), 7.73 (s, 2H, Ar), 7.62 (d, $J = 8.0$ Hz, 2H, Ar), 7.33-7.45 (m, 4H, Ar). ^{13}C NMR (100 MHz, CDCl_3): δ 144.6, 142.0, 140.1, 139.2, 135.4, 133.8, 130.9, 126.8, 124.4, 124.2, 123.4, 122.9. FTIR (solid): 3710, 3088, 2380, 2345, 2310, 1911, 1427, 1333, 1073, 849, 819, 779, 759, 738 cm^{-1} . m/z ($\text{C}_{24}\text{H}_{14}\text{N}_2\text{S}_2$) calcd for $[\text{M}+\text{H}]^+$, 395.0677; found, 395.0695.



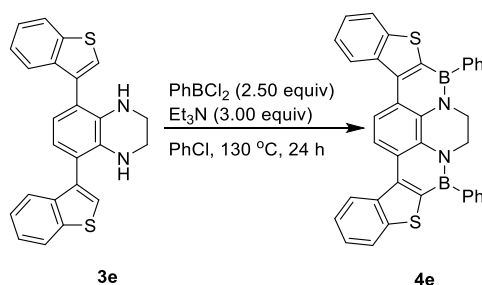
Scheme S15. Synthesis of **3e**.

Synthesis of **3e**:

Pd/C (10 wt %, 0.50 equiv, 0.50 mmol, 53 mg) was added to **2e** (1.00 equiv, 1.00 mmol, 394 mg) in ethyl acetate (10 mL). The flask was vacuumed and recharged with hydrogen gas (4.00 MPa). The reaction mixture was heated at 78 °C for 14 hours. The reaction progress was monitored by TLC. After the reaction completed, Pd/C was removed by filtration. Removal of solvent by vacuum gave the title compound **3e**, and it was used directly without further purification.



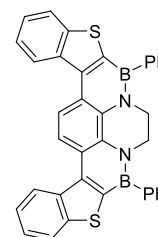
m.p. 200-202 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.93-7.96 (m, 2H, Ar), 7.76-7.79 (m, 2H, Ar), 7.51 (s, 2H, Ar), 7.39-7.42 (m, 4H, Ar), 6.71 (s, 2H, Ar), 3.87 (br, 2H, NH), 3.35 (s, 4H, CH₂). ¹³C NMR (100 MHz, CDCl₃): δ 140.3, 138.3, 134.9, 131.6, 124.7, 124.5, 124.2, 123.7, 122.8, 119.8, 119.7, 40.9. FTIR (solid): 3712, 2851, 2972, 1477, 1351, 1225, 761, 735 cm⁻¹. m/z (C₂₄H₁₈N₂S₂) calcd for [M+H]⁺, 399.0990; found, 399.1000.



Scheme S16. Synthesis of **4e**.

Synthesis of **4e**:

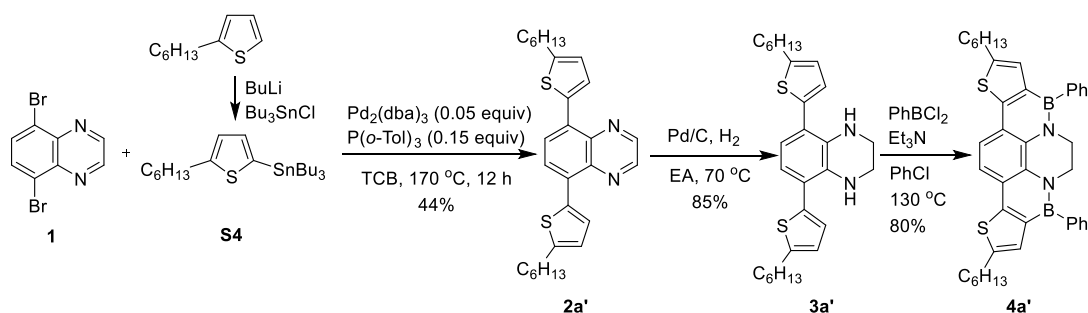
3e (1.00 equiv, 1.00 mmol, 398 mg), anhydrous triethylamine (3.00 equiv, 3.00 mmol, 304 mg) and phenyldichloroborane (2.50 equiv,



2.50 mmol, 398 mg) in chlorobenzene (21 mL) were placed in a sealed tube under N₂ atmosphere. The reaction mixture was heated at 130 °C for 24 hours. After cooling to room temperature, the solvent was removed under vacuum, and the crude mixture was triturated in hexanes to provide the title compound **4e** (473 mg, yield = 83%). The solubility of **4e** is poor in common solvents, such as, CHCl₃, THF, CH₃CN, toluene and hexanes.

m.p. >305 °C. ¹H NMR (400 MHz, *d*₆-DMSO): δ 9.11-9.14 (m, 4H, Ar), 8.25 (d, *J* = 8.0 Hz, 2H), 7.82 (d, *J* = 6.8 Hz, 4H, Ar), 7.74 (dd, *J*₁ = 7.5 Hz, *J*₂ = 7.5 Hz, 2H, Ar), 7.66 (dd, *J*₁ = 7.5 Hz, *J*₂ = 7.5 Hz, 2H, Ar), 7.75-7.58 (m, 6H, Ar), 4.48 (s, 4H, CH₂). ¹³C NMR (100 MHz, CDCl₃): Carbon NMR was not recorded due to limited solubility. FTIR (solid): 3714, 2920, 1507, 1321, 1251, 1240, 1139, 1110, 1027, 960, 850 cm⁻¹. *m/z* (C₃₆H₂₄B₂N₂S₂) calcd for [M+H]⁺, 571.1645; found, not found.

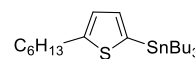
Synthesis of analogue of **4a** with a long alkyl chain attached to terminal thiophene **4a'**



Scheme S17. Synthesis of **4a'**.

Synthesis of **S4**:

n-Butyllithium (5.05 mL, 1.6 M in hexanes, 8.08 mol) was added to a stirring solution of 2-hexylthiophene **1** (1.00 equiv, 2.97 mmol, 500 mg) in anhydrous diethyl ether (5 mL) at -78 °C. The temperature was allowed to to room temperature slowly and the reaction mixture was stirred for 2 h. Then , tributyltin chloride (1.10 equiv, 3.27 mmol, 1.10 g) was added and the mixture was stirred at room temperature for 24 h. The reaction mixture was then poured onto water and extracted with DCM. The organic phase was collected and dried over magnesium sulfate, the solvent was removed to afford the title compound 1.36 g (~ 95% purity),

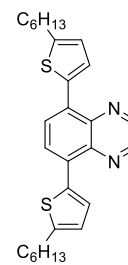


which was used without further purification. The ^1H NMR is identical to the reported data.⁸

^1H NMR (400 MHz, CDCl_3): δ 7.01 (d, $J = 3.0$ Hz, 1H), 6.93 (d, $J = 3.0$ Hz, 1H), 2.88 (t, $J = 7.7$ Hz, 2H), 0.90-1.70 (m, 38H, CH_2/CH_3).

Synthesis of **2a'**:

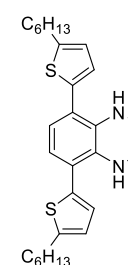
A mixture of compound **1** (1.00 equiv, 1.00 mmol, 288 mg), butylthiophenium reagent **S4** (5.00 equiv, 3.30 mmol, 1.53 g), $\text{P}(o\text{-Tol})_3$ (0.15 equiv, 0.10 mmol, 31.00 mg), in 1,2,4-trichlorobenzene (40 mL) were heated at 170 °C for 12 hours. The solvent was removed by vacuum. The mixture was purified by column chromatography (eluent: petroleum ether/methylene chloride = 10/1) to give 1.53 g of **2a'** as a yellow solid (yield = 44%).



m.p. 135-137 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.95 (s, 2H, Ar), 8.05 (s, 2H, Ar), 7.64 (d, $J = 3.7$ Hz, 2H, Ar), 6.86 (d, $J = 3.7$ Hz, 2H, Ar), 2.89 (t, $J = 7.6$ Hz, 4H, CH_2), 1.72-1.80 (m, 4H, CH_2), 1.40-1.45 (m, 4H, CH_2), 1.31-1.37 (m, 8H, CH_2), 0.90 (t, $J = 7.0$ Hz, 6H, CH_3). ^{13}C NMR (100 MHz, CDCl_3): δ 149.1, 143.3, 139.9, 136.0, 132.0, 127.4, 127.0, 124.1, 31.6, 30.2, 28.9, 22.6, 14.1. FTIR (thin film): 3454, 922, 2851, 2307, 1632, 1265, 740, 705, 516. m/z ($\text{C}_{28}\text{H}_{34}\text{N}_2\text{S}_2$) calcd for $[\text{M}+\text{H}]^+$, 463.2242; found, 463.2264.

Synthesis of **3a'**:

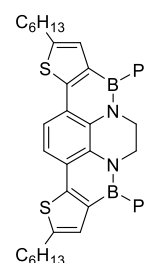
Pd/C (10% wt, 0.50 equiv, 0.50 mmol, 53 mg) was added to **2a'** (1.00 equiv, 1.00 mmol, 462 mg) in ethyl acetate (10 mL). The flask was vacuumed and recharged with hydrogen gas (4.00 MPa). The reaction mixture was heated at 78 °C for 14 hours. The reaction progress was monitored by TLC. After the reaction completed, Pd/C was removed by filtration. Removal of solvent by vacuum gave the title compound 396.3 mg of **3a'** (yield = 85%), and it was pure enough and was used directly without further purification.



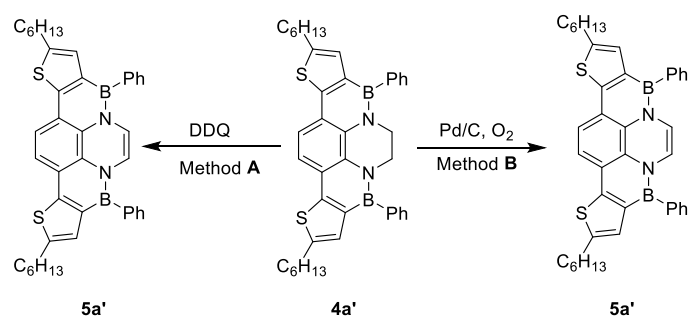
m.p. 100-102 °C. ^1H NMR (400 MHz, CDCl_3): δ 6.98 (d, $J = 3.5$ Hz, 2H, Ar), 6.76 (d, $J = 3.4$ Hz, 2H, Ar), 6.69 (s, 2H, Ar), 4.58 (s, 2H, NH), 3.43 (s, 4H, CH_2), 2.82 (t, $J = 7.6$ Hz, 4H, CH_2), 1.70 (dt, $J_1 = 15.2$, $J_2 = 7.5$ Hz, 4H, CH_2), 1.43-1.23 (m, 12H, CH_2), 0.90 (t, $J = 6.9$ Hz, 6H, CH_3). ^{13}C NMR (100 MHz, CDCl_3): δ 145.90, 138.23, 130.96, 125.55, 124.24, 121.30, 120.33, 119.72, 77.32, 77.20, 77.00, 76.68, 40.80, 31.63, 31.58, 30.16, 28.88, 22.58, 14.08. FTIR (thin film): 3406, 3131, 2927, 2854, 1725, 1617, 1585, 1482, 1463, 1401, 1354, 1301, 1231, 1131, 866, 790. m/z ($\text{C}_{28}\text{H}_{38}\text{N}_2\text{S}_2$) calcd for $[\text{M}+\text{H}]^+$, 467.2555; found, 467.2577.

Synthesis of **4a'**:

3a' (1.00 equiv, 1.00 mmol, 466 mg), anhydrous triethylamine (3.00 equiv, 3.00 mmol, 304 mg) and phenyldichloroborane (2.50 equiv, 2.50 mmol, 398 mg) in chlorobenzene (21 mL) were placed in a sealed tube under N_2 atmosphere. The reaction mixture was heated at 130 °C for 24 hours. After cooling to room temperature, the solvent was removed under vacuum, the mixture was purified by column chromatography (eluent: petroleum ether/methylene chloride = 10/1) to give 510 mg of **4a'** as white solid (yield = 80%).



m.p. 104-106 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.83 (s, 2H, Ar), 7.60 (d, $J = 7.4$ Hz, 4H, Ar), 7.39-7.49 (m, 6H, Ar), 7.00 (s, 2H, Ar), 4.30 (s, 4H, CH_2), 2.90 (t, $J = 7.6$ Hz, 4H, CH_2), 1.73-1.77 (m, 4H, CH_2), 1.26-1.41 (m, 12H, CH_2), 0.90 (t, $J = 6.5$ Hz, 6H, CH_3). ^{13}C NMR (100 MHz, CDCl_3): δ 149.9, 145.6, 132.9, 128.8, 128.4, 127.8, 127.8, 121.1, 119.0, 47.0, 31.8, 31.6, 30.4, 28.9, 22.6, 14.1 (The B-aryl carbons were not observed). ^{11}B NMR (128 MHz, $\text{BF}_3\cdot\text{OEt}_2$): δ 34.6. FTIR (thin film): 3442, 2923, 2851, 1632, 1485, 1320, 1231, 1115, 1009, 845, 795, 745, 705. m/z ($\text{C}_{40}\text{H}_{44}\text{B}_2\text{N}_2\text{S}_2$) calcd for $[\text{M}+\text{H}]^+$, 639.3210; found, not found.



Scheme S18. Attempt to dehydrogenation of **4a'** to **5a'**.

Synthesis of **5a'**.

We screened several reaction conditions to dehydrogenate **4a'**, the typical two methods are shown below. Extremely low yields were obtained in both cases, which made the isolation and purification of **5a'** very challenge.

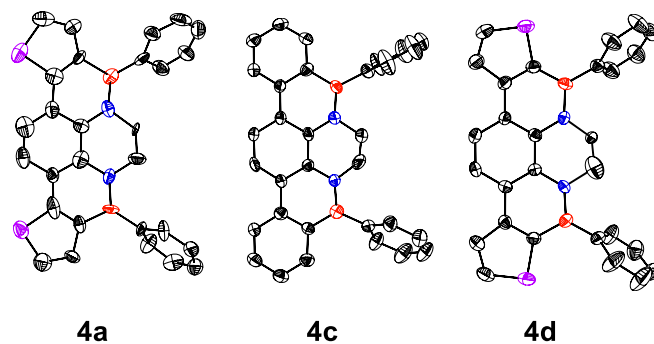
Method A: To a solution of **4a'** (1.00 equiv, 0.05 mmol, 30 mg) in cyclohexene (1 mL) was added 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (1.00 equiv, 0.05 mmol, 11 mg). The reaction mixture was heated at reflux overnight, then the solvent was evaporated under vacuum and the residue was purified by chromatography on silica gel to give product **5a'** as an orange solid (5 mg, yield \approx 17%).

Method B: To a solution of **4a'** (1.00 equiv, 0.05 mmol, 30 mg) in cyclohexene (1 mL) was added Pd/C (10 wt %, 0.05 mmol, 5 mg). The reaction mixture was heated at reflux overnight, then the solvent was evaporated under vacuum and the residue was purified by chromatography on silica gel to give product **5a'** as an orange solid (4 mg, yield \approx 14%).

m.p. 220-222 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.74 (s, 2H, Ar), 7.42 (s, 2H, Ar), 7.11-7.15 (m, 10H, Ar), 6.98 (s, 2H, Ar), 2.89 (t, $J = 7.7$ Hz, 4H, CH₂), 1.76-1.80 (m, 4H, CH₂), 1.33-1.46 (m, 12H, CH₂), 0.90 (t, $J = 6.5$ Hz, 6H, CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 147.2, 143.9, 141.6, 140.8, 137.0, 133.5, 132.2, 130.5, 128.7, 128.1, 126.5, 31.6, 31.4, 30.2, 29.0, 22.6, 14.1 (The B-aryl carbons were not observed). ¹¹B NMR (128 MHz, BF₃·OEt₂): δ 28.6. FTIR (thin film): 3422, 2922, 1628, 1492, 1384, 1260, 1173, 1097, 799, 697, 615. m/z (C₄₀H₄₂B₂N₂S₂) calcd for [M+H]⁺, 637.3054; found, not found. It should be noted that the dehydrogenation product **5a'** was not fully characterized at current stage.

3. Single-Crystal X-ray Analysis

The single crystals of **4a**, **4c** and **4d** suitable for X-ray analysis were obtained by slow diffusion of hexane into concentrated solution of CH₂Cl₂. Detailed characterizations and data are shown as follow.



4a

Table S1. Crystal data and structure refinement for **4a**

Identification code	4a
Empirical formula	C ₅₆ H ₄₀ B ₄ N ₄ S ₄
Formula weight	940.4
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	Pna21
a/Å	12.195(4)
b/Å	12.807(5)
c/Å	30.751(9)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	4803(3)
Z	4
ρ _{calc} /cm ³	1.301
μ/mm ⁻¹	0.242
F(000)	1952
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.612 to 50.012
Index ranges	-13 ≤ h ≤ 14, -15 ≤ k ≤ 9, -36 ≤ l ≤ 36
Reflections collected	16615
Independent reflections	8208 [Rint = 0.2188, Rsigma = 0.3525]

Data/restraints/parameters	8208/1/613
Goodness-of-fit on F2	0.975
Final R indexes [$I \geq 2\sigma(I)$]	R1 = 0.1143, wR2 = 0.2275
Final R indexes [all data]	R1 = 0.3408, wR2 = 0.3613
Largest diff. peak/hole / e Å ⁻³	0.39/-0.29
Flack parameter	-0.2(4)

Table S2. Bond Lengths for **4a**

Atom	Length/Å	Atom	Atom	Length/Å
S3-C32	1.77(3)	C45	C50	1.42(3)
S3-C31	1.73(3)	C45	C46	1.40(4)
S2-C11	1.76(3)	C45	B3	1.61(4)
S2-C14	1.76(3)	C52	C53	1.45(4)
S1-C3	1.82(4)	C52	C51	1.35(4)
S1-C4	1.80(3)	C23	C28	1.38(4)
S4-C39	1.76(3)	C23	C24	1.45(3)
S4-C42	1.72(3)	C23	B2	1.58(4)
N1-C6	1.39(3)	C43	C44	1.38(4)
N1-B1	1.44(5)	C29	C32	1.43(4)
N1-C15	1.50(3)	C29	B3	1.62(4)
C39-C40	1.39(4)	C20	C19	1.38(4)
C39-c36	1.39(4)	C20	C21	1.37(4)
N2-c7	1.45(3)	C49	C50	1.46(4)
N2-B2	1.46(3)	C40	C41	1.46(4)
N2-C16	1.47(3)	C40	B4	1.55(5)
N3-C43	1.57(3)	C9	C10	1.35(4)
N3-C34	1.40(3)	C33	C38	1.45(4)
N3-B3	1.40(4)	C33	C32	1.40(4)
C7-C6	1.47(3)	C33	C34	1.49(3)
C7-C8	1.40(3)	C47	C46	1.41(5)
C6-C5	1.45(4)	C2	C3	1.33(4)
C5-C10	1.40(4)	C18	C19	1.37(4)
C5-C4	1.46(4)	C35	N4	1.41(3)
C17-B1	1.58(4)	C35	C34	1.48(3)
C17-C18	1.38(4)	C35	C36	1.42(4)
C17-C22	1.45(4)	C14	C13	1.36(4)
B1-C1	1.60(4)	C28	C27	1.39(5)
C8-C11	1.46(4)	C53	C54	1.45(5)
C8-C9	1.50(4)	C24	C25	1.37(3)
C12-C11	1.37(4)	C25	C26	1.38(4)
C12-C13	1.51(4)	N4	C44	1.52(4)
C12-B2	1.55(4)	N4	B4	1.48(4)

C1-C2	1.39(4)	C56	C51	1.45(4)
C1-C4	1.37(4)	C56	C55	1.44(5)
C48-C49	1.41(4)	C41	C42	1.33(4)
C48-C47	1.39(5)	C51	B4	1.55(4)
C37-C38	1.43(4)	C16	C15	1.38(4)
C37-C36	1.41(4)	C22	C21	1.35(4)
C30-C29	1.44(4)	C27	C26	1.45(5)
C30-C31	1.46(4)	C55	C54	1.32(5)

Table S3. Bond Angles for **4a**

Atom	Angle/°	Atom	Atom	Atom	Angle/°
C31-S3-C32	92.0(15)	C10	C9	C8	117(3)
C14-S2-C11	92.4(17)	C38	C33	C34	115(3)
C4-S1-C3	89.9(16)	C32	C33	C38	127(3)
C42-S4-C39	90.6(14)	C32	C33	C34	118(3)
C6-N1-B1	128(2)	C37	C38	C33	122(3)
C6-N1-C15	111(2)	C48	C47	C46	120(4)
B1-N1-C15	121(2)	C3	C2	C1	116(3)
C40-C39-S4	110(2)	C45	C50	C49	122(3)
C36-C39-S4	124(2)	C19	C18	C17	121(3)
C36-C39-C4-	126(3)	N4	C35	C34	120(2)
C7-N2-B2	124(2)	N4	C35	C36	122(3)
C7-N2-C16	115(2)	C36	C35	C34	118(3)
B2-N2-C16	121(2)	C13	C14	S2	110(3)
C34-N3-C43	114(2)	C45	C46	C47	121(3)
B3-N3-C43	121(3)	C23	C28	C27	121(3)
B3-N3-C34	125(2)	C52	C53	C54	114(3)
N2-C7-C6	120(3)	C25	C24	C23	121(3)
C8-C7-N2	120(2)	C24	C25	C26	121(3)
C8-C7-C6	120(2)	C9	C10	C5	126(4)
N1-C6-C7	124(2)	C2	C3	S1	110(3)
N1-C6-C5	118(2)	C29	C32	S3	108.4(18)
C5-C6-C7	118(3)	C33	C32	S3	123(2)
C6-C5-C4	116(3)	C33	C32	C29	128(3)
C10-C5-C6	118(3)	C14	C13	C12	114(3)
C10-C5-C4	126(3)	N2	B2	C12	114(2)
C18-C17-B1	123(2)	N2	B2	C23	124(2)
C18-C17-C22	116(3)	C12	B2	C23	122(2)
C22-C17-B1	121(3)	C35	N4	C44	117(2)
N1-B1-C17	125(2)	C35	N4	B4	122(2)
N1-B1-C1	115(3)	B4	N4	C44	120(2)
C17-B1-C1	120(3)	C55	C56	C51	120(3)
C7-C8-C11	119(2)	C42	C41	C40	111(4)
C7-C8-C9	120(3)	C18	C19	C20	124(3)

C11-C8-C9	121(3)	C52	C51	C56	115(3)
C11-C12-C13	110(3)	C52	C51	B4	126(3)
C11-C12-B2	120(3)	C56	C51	B4	118(3)
C13-C12-B2	129(2)	C43	C44	N4	112(3)
C2-C1-B1	132(3)	C30	C31	S3	116(2)
C4-C1-B1	112(3)	N3	C34	C33	118(3)
C4-C1-C2	116(2)	N3	C34	C35	121(2)
C47-C48-C49	122(3)	C35	C34	C33	121(3)
C36-C37-C38	121(3)	C39	C36	C37	121(3)
C29-C30-C31	106(3)	C39	C36	C35	118(3)
C8-C11-S2	124(2)	C37	C36	C35	121(3)
C12-C11-S2	112(3)	C15	C16	N2	113(2)
C12-C11-C8	124(3)	C16	C15	N1	123(3)
C50-C45-B3	121(2)	C21	C22	C17	119(3)
C46-C45-C50	118(3)	C28	C27	C26	120(3)
C46-C45-B3	121(3)	C54	C55	C56	121(4)
C51-C52-C53	127(3)	C25	C26	C27	118(3)
C28-C23-C25	118(2)	C41	C42	S4	115(3)
C28-C23-B2	118(2)	C22	C21	C20	125(3)
C24-C23-B2	124(2)	N3	B3	C45	127(3)
C44-C43-N3	112(3)	N3	B3	C29	119(3)
C30-C29-B3	130(3)	C45	B3	C29	114(3)
C32-C29-C30	118(2)	N4	B4	C40	114(3)
C32-C29-B3	111(3)	N4	B4	C51	120(3)
C21-C20-C19	115(3)	C51	B4	C40	126(3)
C48-C49-C50	116(3)	C55	C54	C53	122(4)
C39-C40-C41	113(3)	C5	C4	S1	120(2)
C39-C40-B4	118(3)	C1	C4	S1	109(2)
C41-C40-B4	129(3)	C1	C4	C5	131(3)

4c

Table S4. Crystal data and structure refinement for **4c**

Identification code	4c
Empirical formula	C ₁₁ H ₁₀ NOBClO.08
Formula weight	185.96
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	P212121
a/Å	7.742(2)
b/Å	14.293(5)
c/Å	25.540(7)
α/°	90
β/°	90
γ/°	90

Volume/Å ³	2826.3(15)
Z	12
$\rho_{\text{calc}}/\text{cm}^3$	1.311
μ/mm^{-1}	0.105
F(000)	1169
Radiation	MoK α ($\lambda = 0.71073$)
2 θ range for data collection/°	4.278 to 50.012
Index ranges	$-8 \leq h \leq 9, -11 \leq k \leq 17, -30 \leq l \leq 29$
Reflections collected	9465
Independent reflections	4939 [Rint = 0.0754, Rsigma = 0.1172]
Data/restraints/parameters	4939/0/352
Goodness-of-fit on F ²	1.007
Final R indexes [$I \geq 2\sigma(I)$]	R1 = 0.0943, wR2 = 0.2373
Final R indexes [all data]	R1 = 0.1952, wR2 = 0.3236
Largest diff. peak/hole / e Å ⁻³	0.35/-0.40
Flack parameter	0.26(12)

Table S5. Bond Lengths for **4c**

Atom	Length/Å	Atom	Atom	Length/Å
C12-C33	1.889(19)	C2	C1	1.401(11)
C11-C33	1.640(17)	C2	C3	1.347(14)
N2-C9	1.397(11)	C1	B1	1.549(14)
N2-B2	1.422(13)	C5	C4	1.354(12)
N2-C20	1.467(13)	C21	B1	1.593(14)
N1-C8	1.397(11)	C21	C22	1.333(16)
N1-B1	1.409(12)	C21	C26	1.410(17)
N1-C19	1.466(13)	C27	C28	1.386(14)
C9-C8	1.429(12)	C27	C32	1.380(14)
C9-C10	1.399(12)	C27	B2	1.569(15)
C8-C7	1.448(12)	C18	C17	1.375(13)
C7-C6	1.455(11)	C16	C17	1.383(14)
C7-C12	1.411(12)	C3	C4	1.418(15)
C10-C11	1.404(12)	C28	C29	1.385(17)
C10-C13	1.472(12)	C32	C31	1.427(15)
C14-C15	1.426(12)	C31	C30	1.332(16)
C14-C13	1.410(12)	C30	C29	1.358(18)
C14-B2	1.501(14)	C22	C23	1.395(18)
C6-C1	1.433(12)	C19	C20	1.345(16)
C6-C5	1.399(12)	C24	C25	1.34(2)
C11-C12	1.365(12)	C24	C23	1.36(2)
C15-C16	1.383(14)	C26	C25	1.335(18)
C13-C18	1.409(13)			

Table S6. Bond Angles for **4c**

Atom	Angle/°	Atom	Atom	Atom	Angle/°
C9-N2-C20	113.8(7)	C6	C5	C4	122.0(10)
B2-N2C9	122.9(8)	C22	C21	B1	119.8(10)
B2-N2-C20	123.0(8)	C22	C21	C26	115.8(11)
C8-N1-C19	115.0(7)	C26	C21	B1	124.4(10)
B1-N1-C8	124.9(8)	C11	C12	C7	120.1(9)
B1-N1-C19	120.1(8)	C28	C27	C32	115.9(10)
N2-C9-C8	119.1(8)	C28	C27	B2	122.6(10)
N2-C9-C10	119.9(8)	C32	C27	B2	121.4(10)
C10-C9-C8	121.0(8)	C17	C18	C13	120.4(9)
N1-C8-C9	122.4(8)	C15	C16	C17	117.6(10)
N1-C8-C7	118.2(8)	C2	C3	C4	118.5(9)
C9-C8-C7	119.4(8)	C5	C4	C3	121.1(10)
C8-C7-C6	121.2(8)	C18	C17	C16	122.1(10)
C12-C7-C8	117.9(8)	C27	C28	C29	121.5(12)
C12-C7-C6	120.9(8)	C31	C32	C27	121.5(11)
C9-C10-C13	121.0(8)	C30	C31	C32	120.3(12)
C11-C10-C9	117.2(8)	C29	C30	C31	119.2(12)
C11-C10-C13	121.8(8)	N1	B1	C1	117.5(8)
C15-C14-B2	122.2(9)	N1	B1	C21	120.4(9)
C13-C14-C15	116.9(9)	C1	B1	C21	122.1(8)
C13-C14-B2	120.8(8)	C21	C22	C23	121.8(13)
C1-C6-C7	120.4(8)	C20	C19	N1	115.4(11)
C5-C6-C7	122.8(8)	N2	B2	C14	116.3(9)
C5-C6-C7	116.8(8)	N2	B2	C27	118.6(9)
C10-C11-C12	124.2(9)	C14	B2	C27	125.0(9)
C16-C15-C14	123.2(10)	C25	C24	C23	119.5(12)
C14-C13-C10	118.0(8)	C25	C26	C21	122.7(14)
C14-C13-C18	119.8(8)	C24	C25	C26	120.4(14)
C18-C13-C10	122.2(9)	C19	C20	N2	116.4(12)
C3-C2-C1	121.9(10)	C30	C29	C28	121.5(13)
C6-C1-B1	117.5(8)	C24	C23	C22	119.5(14)
C2-C1-C6	119.8(8)	C11	C33	C12	107.2(10)
C2-C1-B1	122.6(9)				

4dTable S7. Crystal data and structure refinement for **4d**

Identification code	4d
Empirical formula	C ₂₈ H ₂₂ B ₂ N ₂ O ₃ S ₂
Formula weight	520.21
Temperature/K	293(2)
Crystal system	monoclinic

Space group	P21
a/Å	13.257(4)
b/Å	8.073(2)
c/Å	13.405(3)
α /°	90
β /°	104.92(3)
γ /°	90
Volume/Å ³	1386.3(7)
Z	2
ρ calc/cm ³	1.246
μ /mm ⁻¹	0.224
F(000)	540
Radiation	MoK α (λ = 0.71073)
2 θ range for data collection/°	3.854 to 50.014
Index ranges	-15 \leq h \leq 9, -4 \leq k \leq 9, -15 \leq l \leq 15
Reflections collected	4286
Independent reflections	3365 [Rint = 0.0297, Rsigma = 0.0609]
Data/restraints/parameters	3365/1/361
Goodness-of-fit on F ²	1.081
Final R indexes [$I \geq 2\sigma(I)$]	R1 = 0.0752, wR2 = 0.2025
Final R indexes [all data]	R1 = 0.1099, wR2 = 0.2410
Largest diff. peak/hole / e Å ⁻³	0.66/-0.28
Flack parameter	-0.01(11)

Table S8. Bond Lengths for **4d**

Atom	Length/Å	Atom	Atom	Length/Å
S1-C1	1.725(7)	C9	C10	1.365(10)
S1-C2	1.703(11)	C6	C5	1.393(11)
S2-C12	1.732(7)	C4	C3	1.423(12)
S2-C13	1.707(12)	C4	C1	1.370(12)
N2-C7	1.411(10)	C4	C5	1.468(10)
N2-B2	1.423(10)	C3	C2	1.353(12)
N2-C30	1.49(3)	C1	B1	1.522(13)
N2-C16	1.491(19)	C17	B1	1.559(13)
N1-C6	1.414(10)	C17	C22	1.369(15)
N1-B1	1.427(11)	C17	C18	1.382(14)
N1-C29	1.46(2)	C5	C10	1.404(11)
N1-C15	1.52(3)	C24	C25	1.382(15)
C12-C11	1.359(12)	C14	C13	1.329(12)
C12-B2	1.502(13)	C26	C25	1.357(15)
C8-C7	1.415(11)	C26	C27	1.344(18)
C8-C11'	1.461(10)	C28	C27	1.372(15)
C8-C9	1.407(12)	C22	C21	1.367(16)
C23-C24	1.368(14)	C20	C19	1.33(2)

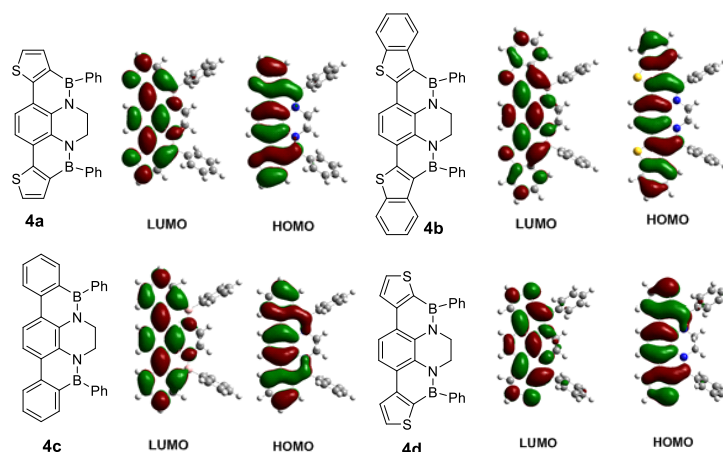
C23-C28	1.376(13)	C20	C21	1.387(16)
C23-B2	1.581(13)	C18	C19	1.387(18)
C7-C6	1.430(9)	C30	C29	1.56(3)
C11-C14	1.443(12)	C16	C15	1.50(4)

Table S9. Bond Angles for **4d**

Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2-S1-C1	92.1(4)	C2	C3	C4	112.3(9)
C13-S2-C12	91.7(4)	C4	C1	S1	110.5(6)
C7-N2-B2	123.4(7)	C4	C1	B1	122.0(6)
C7-N2-C30	113.1(10)	B1	C1	S1	127.3(6)
C7-N2-C16	115.0(9)	C22	C17	B1	122.4(8)
B2-N2-C30	118.5(10)	C22	C17	C18	115.3(10)
B2-N2-C16	120.6(10)	C18	C17	B1	121.9(10)
C6-N1-C29	116.3(9)	C6	C5	C4	120.3(7)
C6-N1-C15	112.8(14)	C6	C5	C10	119.5(6)
B1-N1-C6	123.7(7)	C10	C5	C4	120.2(7)
B1-N1-C29	119.1(10)	C3	C2	S1	112.2(7)
B1-N1-C15	119.3(15)	C23	C24	C25	121.3(10)
C11-C12-S2	110.2(6)	C13	C14	C11	111.7(9)
C11-C12-B2	122.6(6)	N1	B1	C1	114.4(7)
B2-C12-S2	126.9(6)	N1	B1	C17	122.7(8)
C7-C8-C11	119.5(7)	C1	B1	C17	122.9(7)
C9-C8-C7	119.6(7)	C14	C13	S2	113.2(8)
C9-C8-C11	120.9(7)	C27	C26	C25	119.9(11)
C24-C23-28	116.3(9)	C27	C28	C23	122.8(11)
C24-C23-S2	122.8(8)	N2	B2	C12	114.8(8)
C28-C23-B2	120.7(9)	N2	B2	C23	122.3(8)
N2-C7-C6	121.4(7)	C12	B2	C23	122.8(7)
C8-C7-N2	119.7(6)	C26	C25	C24	120.2(12)
C8-C7-C6	118.9(7)	C21	C22	C17	122.8(11)
C12-C11-C8	119.9(7)	C26	C27	C28	119.3(11)
C12-C11-C14	113.2(7)	C19	C20	C21	118.1(12)
C14-C11-C8	126.9(8)	C19	C18	C17	122.0(13)
C10-C9-C8	120.6(8)	C20	C19	C18	121.3(13)
N1-C6-C7	120.0(7)	C22	C21	C20	120.4(13)
C5-C6-N1	120.0(6)	C9	C10	C5	121.4(7)
C5-C6-C7	120.0(7)	N2	C30	C29	105.5(17)
C3-C4-C5	127.5(8)	N2	C16	C15	108.5(19)
C1-C4-C3	112.8(7)	N1	C29	C30	109.7(19)
C1-C4-C5	119.6(7)	C16	C15	N1	106(2)

4. Computational Studies

Calculations were performed using the Gaussian 09 software package.⁹ The geometries were optimized as the B3LYP/6-311+G(2d,p) level, and energies were calculated at the same level of theory. Nucleus independent chemical shifts (NICS) were calculated using the gauge invariant atomic orbital (GIAO) approach at the GIAO-B3LYP/6-311+G(2d,p) level.¹⁰ NICS (1) values were averaged by two positions (above and below the plane) of all the equivalent rings.



Figures S1. Frontier orbital maps of **4a-4d**.

Table S10. Cartesian coordinates for calculations on **4a**

Tag	Symbol	X	Y	Z
1	C	-0.66943	-3.31257	-0.00334
2	C	0.691217	-3.30961	-0.09584
3	C	1.417121	-2.10033	-0.08521
4	C	0.72271	-0.87289	0.011435
5	C	-0.70968	-0.8721	-3.7E-05
6	C	-1.39945	-2.10631	0.042924
7	C	-2.83059	-2.0955	0.119806
8	C	2.848657	-2.07761	-0.16146
9	N	1.44179	0.323816	0.130167
10	C	0.633155	1.479864	0.529375
11	C	-0.63404	1.536548	-0.28625
12	N	-1.43523	0.325651	-0.06797
13	C	-3.59373	-0.93728	0.134955
14	C	-4.99508	-1.22235	0.218262
15	C	-5.27287	-2.55011	0.269018
16	S	-3.83363	-3.52294	0.210359
17	S	3.859075	-3.49373	-0.31811
18	C	5.291371	-2.51011	-0.36093

19	C	5.005876	-1.18671	-0.26003
20	C	3.604735	-0.91447	-0.14041
21	B	-2.86575	0.394491	-0.00408
22	B	2.869608	0.409524	0.03821
23	C	-3.63769	1.766989	-0.10141
24	C	-4.34709	2.2624	1.002666
25	C	-5.06718	3.451375	0.930908
26	C	-5.11256	4.168294	-0.26012
27	C	-4.42988	3.690034	-1.37409
28	C	-3.69992	2.508558	-1.29048
29	C	3.627773	1.789031	0.138424
30	C	3.523404	2.764466	-0.86497
31	C	4.234415	3.958388	-0.79694
32	C	5.066968	4.212993	0.28824
33	C	5.189487	3.261382	1.295233
34	C	4.4857	2.063272	1.213256
35	H	-1.20469	-4.25368	0.016901
36	H	1.228135	-4.24769	-0.16168
37	H	1.216267	2.385356	0.392306
38	H	0.382223	1.396715	1.592656
39	H	-0.38209	1.627602	-1.34845
40	H	-1.22802	2.402462	-0.00649
41	H	-5.76063	-0.45829	0.234219
42	H	-6.23572	-3.0323	0.334302
43	H	6.255819	-2.98303	-0.46111
44	H	5.76578	-0.41691	-0.2698
45	H	-4.33443	1.711717	1.937717
46	H	-5.5976	3.814972	1.80366
47	H	-5.67839	5.090585	-0.32117
48	H	-4.46618	4.237609	-2.30903
49	H	-3.17686	2.153415	-2.1728
50	H	2.882894	2.585481	-1.72317
51	H	4.13963	4.689762	-1.59155
52	H	5.61891	5.143829	0.34625
53	H	5.837763	3.449503	2.143514
54	H	4.604377	1.329329	2.003671
55	Bq	-0.06492	-1.94214	1.050342
56	Bq	-0.05875	-2.17734	-0.93577
57	Bq	-2.1553	-0.71705	1.150565
58	Bq	-2.14571	-0.96428	-0.83407
59	Bq	2.186379	-0.66424	1.091534
60	Bq	2.196649	-0.89117	-0.89552
61	Bq	4.102439	-2.09266	-0.50255
62	Bq	4.105315	-1.85145	1.482851

63	Bq	-4.04429	-2.21952	-0.60673
64	Bq	-4.05485	-1.95012	1.375019

Table S11. Cartesian coordinates for calculations on **4b**.

Row	Symbol	X	Y	Z
1	C	-0.68096	-3.02829	0.02821
2	C	0.680928	-3.02829	-0.02807
3	C	1.409761	-1.81867	-0.02722
4	C	0.715813	-0.58972	0.022844
5	C	-0.71584	-0.58972	-0.02275
6	C	-1.40979	-1.81866	0.027314
7	C	-2.84159	-1.80355	0.066628
8	C	2.841569	-1.80357	-0.06659
9	C	-3.61004	-0.65356	0.046957
10	C	-5.02817	-0.95431	0.122854
11	C	-5.28371	-2.34159	0.19093
12	S	-3.80009	-3.27509	0.164484
13	S	3.800047	-3.27511	-0.16432
14	C	5.283665	-2.34162	-0.19098
15	C	5.028141	-0.95433	-0.12305
16	C	3.610005	-0.65356	-0.04711
17	C	-6.12923	-0.08332	0.141316
18	C	-7.41449	-0.59265	0.222618
19	C	-7.63927	-1.97304	0.286927
20	C	-6.57352	-2.85922	0.271936
21	C	6.573472	-2.85926	-0.27193
22	C	7.639232	-1.97309	-0.28701
23	C	7.414462	-0.59269	-0.22284
24	C	6.1292	-0.08334	-0.1416
25	N	1.436666	0.601367	0.130756
26	C	0.62603	1.790766	0.420151
27	C	-0.62605	1.790808	-0.41992
28	N	-1.43669	0.601374	-0.13065
29	B	-2.86974	0.674762	-0.09278
30	B	2.869716	0.674755	0.092674
31	C	-3.58184	2.080038	-0.21914
32	C	-3.81881	2.877375	0.90994
33	C	-4.45916	4.109242	0.808168
34	C	-4.88138	4.575286	-0.4327
35	C	-4.66036	3.80028	-1.56669
36	C	-4.02073	2.568845	-1.45754
37	C	3.581856	2.080015	0.219048
38	C	3.819365	2.87714	-0.91006
39	C	4.459776	4.108971	-0.80823

40	C	4.881534	4.575186	0.432736
41	C	4.659968	3.800392	1.566766
42	C	4.020264	2.569002	1.457561
43	H	-1.21676	-3.96852	0.056925
44	H	1.216728	-3.96853	-0.05674
45	H	-5.97263	0.985176	0.092493
46	H	-8.25808	0.087026	0.236939
47	H	-8.65164	-2.35352	0.349825
48	H	-6.74197	-3.92797	0.322992
49	H	6.741922	-3.92801	-0.32291
50	H	8.651601	-2.35358	-0.34989
51	H	8.25805	0.086977	-0.23719
52	H	5.972603	0.985156	-0.09289
53	H	1.218312	2.678015	0.216796
54	H	0.357682	1.7995	1.482194
55	H	-1.21834	2.678029	-0.21647
56	H	-0.35769	1.799648	-1.48196
57	H	-3.5043	2.529731	1.889003
58	H	-4.63068	4.703564	1.698429
59	H	-5.38109	5.533373	-0.51502
60	H	-4.98909	4.153322	-2.53751
61	H	-3.86666	1.976673	-2.35389
62	H	3.505236	2.529358	-1.88919
63	H	4.631705	4.703133	-1.69852
64	H	5.381306	5.533233	0.5151
65	H	4.988327	4.15357	2.53766
66	H	3.86574	1.977008	2.353955
67	Bq	0.091482	-1.79499	1.049546
68	Bq	0.063222	-1.83692	-0.94982
69	Bq	2.158529	-0.63023	-0.97036
70	Bq	2.179228	-0.58946	1.029119
71	Bq	-2.10113	-0.64025	-1.05941
72	Bq	-2.08586	-0.59425	0.940005
73	Bq	-6.2924	-1.46968	-0.7771
74	Bq	-6.27568	-1.4473	1.222709
75	Bq	6.386953	-1.42123	-1.21425
76	Bq	6.416464	-1.39571	0.785375
77	Bq	-4.08595	-1.92607	-0.8234
78	Bq	-4.07479	-1.90233	1.176425
79	Bq	4.100375	-1.84888	-1.09865
80	Bq	4.159139	-1.81379	0.900181
81	Bq	-3.35536	3.781025	-0.29687
82	Bq	-5.155	2.926976	-0.47538
83	Bq	3.415493	3.78721	0.414071

Table S12. Cartesian coordinates for calculations on **4c**.

Tag	Symbol	X	Y	Z
1	C	0.681834	-3.41888	-0.04752
2	C	-0.68182	-3.41888	0.047393
3	C	-1.42629	-2.22549	0.065964
4	C	-0.71724	-1.00648	-0.00896
5	C	0.717242	-1.00648	0.008904
6	C	1.4263	-2.22548	-0.06603
7	C	2.889223	-2.25113	-0.1597
8	C	-2.88921	-2.25115	0.159672
9	C	3.611825	-1.0356	-0.14422
10	C	5.014277	-1.06754	-0.25803
11	C	5.701812	-2.25855	-0.38372
12	C	4.985498	-3.45889	-0.39443
13	C	3.608506	-3.45727	-0.28405
14	C	-3.60848	-3.45729	0.28406
15	C	-4.98547	-3.45891	0.394472
16	C	-5.70179	-2.25859	0.38375
17	C	-5.01427	-1.06757	0.258043
18	C	-3.61182	-1.03562	0.144205
19	N	-1.42971	0.202859	-0.1153
20	C	-0.62306	1.386415	-0.42287
21	C	0.623044	1.386403	0.422867
22	N	1.429708	0.202867	0.115251
23	B	2.846499	0.282953	0.033647
24	B	-2.8465	0.282935	-0.03368
25	C	3.584498	1.676895	0.144054
26	C	4.088174	2.144825	1.365781
27	C	4.753981	3.363847	1.458649
28	C	4.939912	4.145972	0.323479
29	C	4.457918	3.698649	-0.90222
30	C	3.790752	2.479788	-0.98702
31	C	-3.58451	1.676874	-0.14407
32	C	-3.79108	2.47955	0.9871
33	C	-4.45824	3.698418	0.902352
34	C	-4.93993	4.145955	-0.32338
35	C	-4.7537	3.364042	-1.45865
36	C	-4.08788	2.145024	-1.36584
37	H	1.19055	-4.37013	-0.08942
38	H	-1.19053	-4.37014	0.089231
39	H	5.560142	-0.1316	-0.24412

40	H	6.781761	-2.26594	-0.47179
41	H	5.510843	-4.40211	-0.49241
42	H	3.09588	-4.40839	-0.30322
43	H	-3.09585	-4.40841	0.303255
44	H	-5.51081	-4.40214	0.492478
45	H	-6.78174	-2.26598	0.471833
46	H	-5.56014	-0.13163	0.244136
47	H	-1.21795	2.275345	-0.23424
48	H	-0.34748	1.380386	-1.48328
49	H	0.347458	1.380325	1.48328
50	H	1.217919	2.275348	0.234273
51	H	3.960721	1.547654	2.263085
52	H	5.130317	3.701421	2.417677
53	H	5.459721	5.094387	0.392763
54	H	4.603222	4.297689	-1.79405
55	H	3.427231	2.148041	-1.95465
56	H	-3.42781	2.147627	1.95476
57	H	-4.60378	4.29729	1.794252
58	H	-5.45975	5.094372	-0.39263
59	H	-5.1298	3.701783	-2.41771
60	H	-3.96017	1.548027	-2.26323
61	Bq	-0.14439	-2.20609	0.924133
62	Bq	-0.08945	-2.07475	-1.06679
63	Bq	2.165783	-0.86928	-0.79952
64	Bq	2.119066	-0.9947	1.022636
65	Bq	-2.26456	-1.08276	1.196243
66	Bq	-2.24274	-0.93309	-1.02207
67	Bq	-4.26788	-2.20485	-0.71345
68	Bq	-4.3118	-2.34291	1.326125
69	Bq	4.217199	-2.26522	0.464801
70	Bq	4.283654	-2.12884	-1.30466
71	Bq	-3.46186	3.485361	-0.18873
72	Bq	-5.20657	2.513276	-0.29368
73	Bq	3.095252	3.212989	0.310191
74	Bq	4.916616	2.397124	0.179812

Table S13. Cartesian coordinates for calculations on **4d**.

Tag	Symbol	X	Y	Z
1	C	-0.69085	-3.45164	-0.11081
2	C	0.671782	-3.45371	-0.01355
3	C	1.403612	-2.25126	0.040201
4	C	0.709349	-1.01972	-9.2E-05
5	C	-0.72451	-1.02234	0.012345
6	C	-1.42101	-2.24741	-0.0945

7	C	-2.85263	-2.23568	-0.19226
8	C	2.847208	-2.26703	0.122754
9	N	1.430243	0.183747	-0.0684
10	C	0.626753	1.394202	-0.27573
11	C	-0.63241	1.329043	0.550681
12	N	-1.44127	0.177238	0.143194
13	C	-3.57137	-1.05674	-0.137
14	S	-5.27852	-1.34182	-0.29331
15	C	-5.03486	-3.04835	-0.40523
16	C	-3.7202	-3.39112	-0.33048
17	C	3.558496	-1.07404	0.13147
18	B	-2.86792	0.271235	0.052979
19	C	3.69874	-3.41577	0.20524
20	C	5.016072	-3.08288	0.27369
21	S	5.267467	-1.37413	0.232754
22	B	2.859958	0.261841	-0.01117
23	C	-3.63022	1.64699	0.160654
24	C	-3.51671	2.631879	-0.83264
25	C	-4.22708	3.825402	-0.7586
26	C	-5.06833	4.069696	0.322405
27	C	-5.19985	3.108784	1.318993
28	C	-4.496	1.911124	1.23168
29	C	3.635971	1.630268	-0.11651
30	C	3.66524	2.383777	-1.29959
31	C	4.39747	3.562612	-1.39315
32	C	5.115907	4.026009	-0.2953
33	C	5.103583	3.297334	0.889025
34	C	4.380265	2.111046	0.970987
35	H	-1.22111	-4.3913	-0.18281
36	H	1.202446	-4.39572	0.002901
37	H	0.364456	1.48992	-1.3351
38	H	1.221563	2.259925	0.002974
39	H	-1.21762	2.235479	0.429353
40	H	-0.37161	1.233417	1.610607
41	H	-5.87899	-3.71029	-0.5226
42	H	-3.38262	-4.41612	-0.38749
43	H	3.356913	-4.44084	0.219086
44	H	5.858345	-3.75335	0.348202
45	H	-2.86955	2.460283	-1.68729
46	H	-4.12573	4.564365	-1.54529
47	H	-5.62034	5.000218	0.384806
48	H	-5.85538	3.288794	2.163358
49	H	-4.62183	1.170161	2.014151
50	H	3.114574	2.039509	-2.16924

51	H	4.408345	4.119576	-2.32313
52	H	5.684191	4.946245	-0.36422
53	H	5.662568	3.649161	1.748581
54	H	4.393463	1.551374	1.900431
55	Bq	-0.16589	-2.31808	0.931582
56	Bq	0.219316	-2.10393	-0.97882
57	Bq	-2.31218	-1.08576	0.64293
58	Bq	-1.91834	-0.87184	-1.30621
59	Bq	1.977713	-1.09657	1.21726
60	Bq	2.34519	-0.87563	-0.73624
61	Bq	3.931359	-2.31716	1.238523
62	Bq	4.32128	-2.09729	-0.71074
63	Bq	-4.26901	-2.29673	0.702028
64	Bq	-3.86871	-2.08413	-1.24593

5. Photophysical Properties

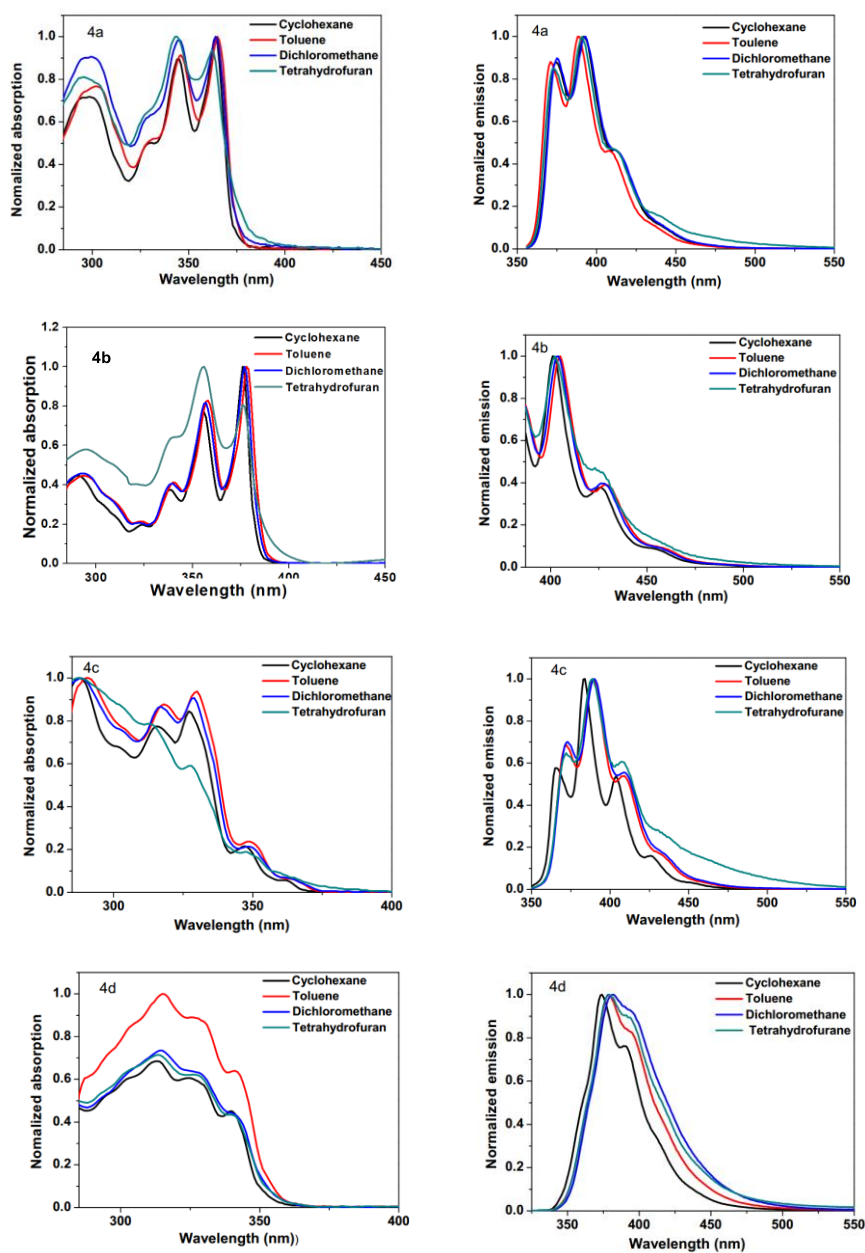


Figure S2. UV-vis absorption (left) and emission (right) spectra of **4a-4d**. (Excitation wavelength: **4a**, $\lambda_{\text{ex}} = 345$ nm; **4b**, $\lambda_{\text{ex}} = 349$ nm; **4c**, $\lambda_{\text{ex}} = 329$ nm; **4d**, $\lambda_{\text{ex}} = 320$ nm). All experiments were performed in a solution at 1×10^{-5} M.

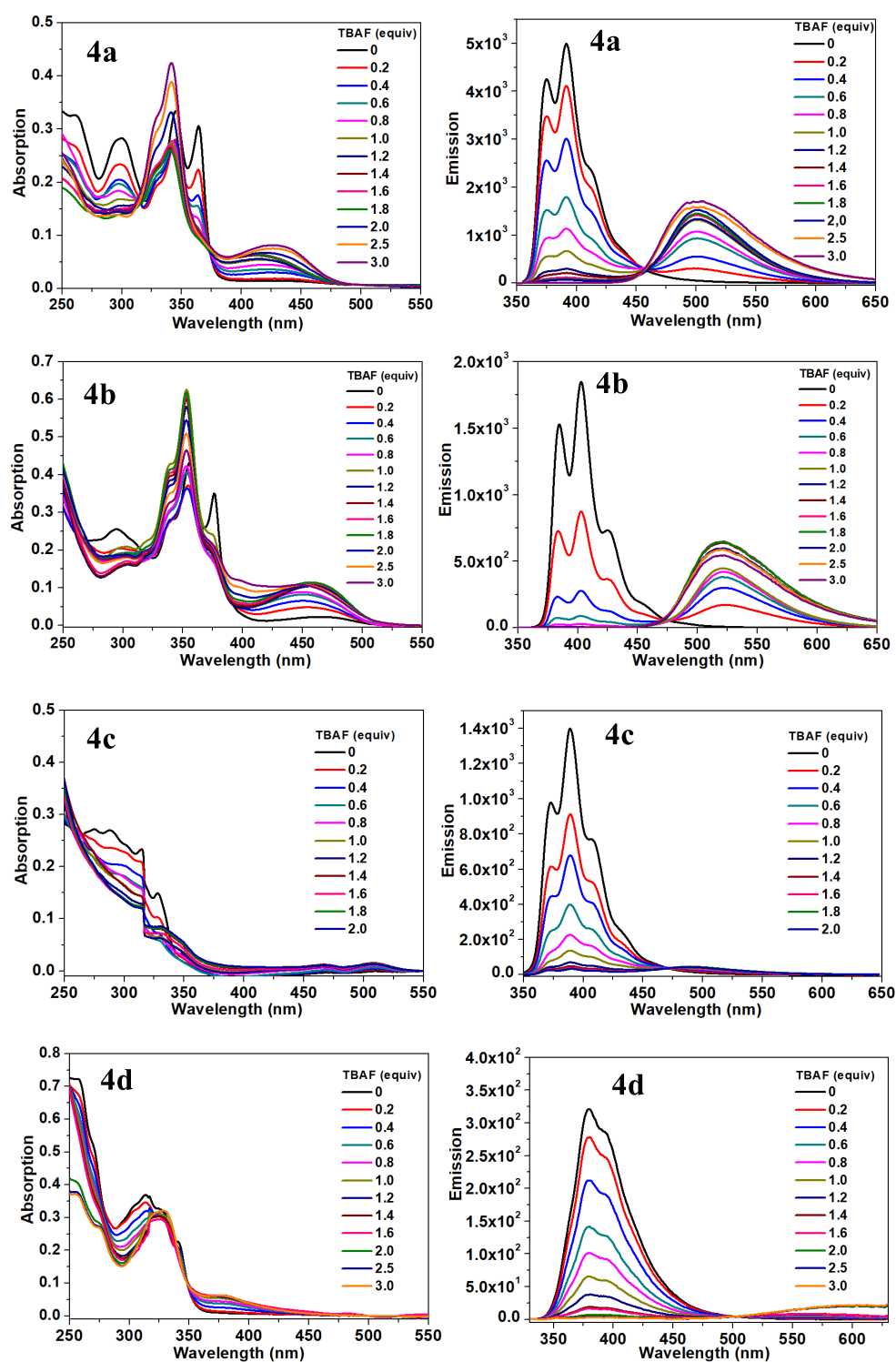


Figure S3. UV-vis (left) and emission (right) spectra change of **4a-4d** by adding TBAF gradually. All experiments were performed in THF at a concentration of 1×10^{-5} M. (Excitation wavelength: **4a**, $\lambda_{\text{ex}} = 345$ nm; **4b**, $\lambda_{\text{ex}} = 349$ nm; **4c**, $\lambda_{\text{ex}} = 329$ nm; **4d**, $\lambda_{\text{ex}} = 320$ nm). The binding constants of **4a-4d** are as follows: **4a** $\log K_a \approx 5.6 \pm 0.2$; **4b** $\log K_a \approx 6.4 \pm 0.3$; **4c** $\log K_a \approx 5.1 \pm 0.1$; **4d** $\log K_a \approx 4.7 \pm 0.1$.

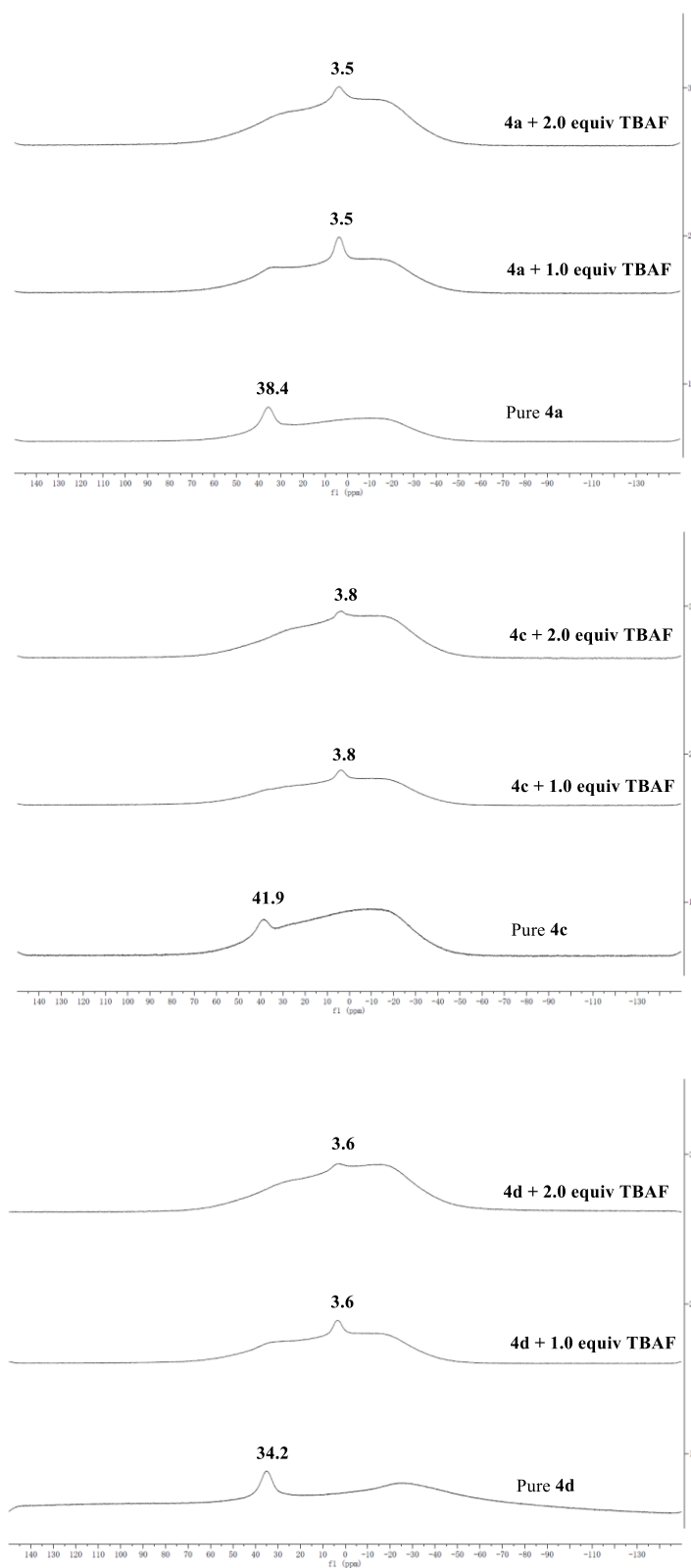


Figure S4. ^{11}B NMR spectra of **4a**, **4c** and **4d** after addition of 1 and 2 equivalents of TBAF. Titration of **4b** by TBAF was not monitored by ^{11}B NMR due to its weak boron signal.

Photophysical properties of **4a-4e** in solid state.

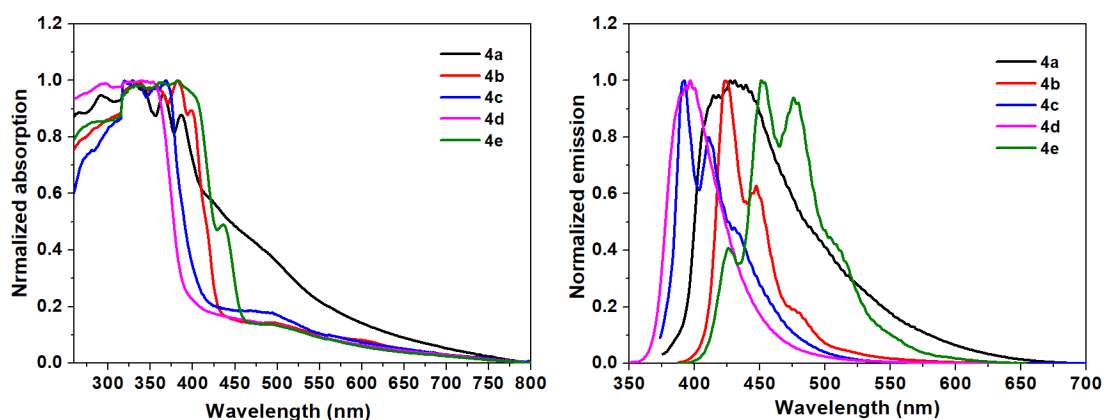


Figure S5. Absorption and emission spectra of **4a-4e** in solid state. (Excitation wavelength: **4a**, λ_{ex} = 365 nm; **4b**, λ_{ex} = 377 nm; **4c**, λ_{ex} = 363 nm; **4d**, λ_{ex} = 341 nm; **4e**, λ_{ex} = 377 nm).

Table S14. Photophysical properties of **4a-4e** in solid state.

Compd	λ_{abs} (nm)	λ_{em} (nm)	$\Phi_{\text{pl}}^{\text{a}}$
4a	329, 366, 386	429	0.49
4b	357, 384, 398, 494	424, 447, 480	0.22
4c	354, 368, 492	392, 412	0.61
4d	350, 498	397	0.15
4e	381, 437, 498	426, 453, 477	0.34

^a Crystalline state FL efficiencies were measured using an integrating sphere (C-701, Labsphere Inc.), with a 365 nm Ocean Optics LLS-LED as the excitation source, and the light was introduced into the integrating sphere through optical fiber.¹¹

6. Electrochemical Properties

Cyclic voltammetry (CV) measurements were performed in a three-electrode cell in dichloromethane solution of 0.1 M *n*-Bu₄NPF₆ with a scan rate of 100 mV/s at room temperature, using A2 mm Pt button electrode was used as the working electrode, Pt wire as the counter electrode, Ag/AgCl electrode as the reference electrode. Cyclic voltammograms were performed using analyte concentrations of 2.5 mM. The ferrocene/ferrocenium as an external potential marker (The Fc/Fc⁺ oxidation onset potential vs. the reference electrode Ag/AgCl is +0.46 V).

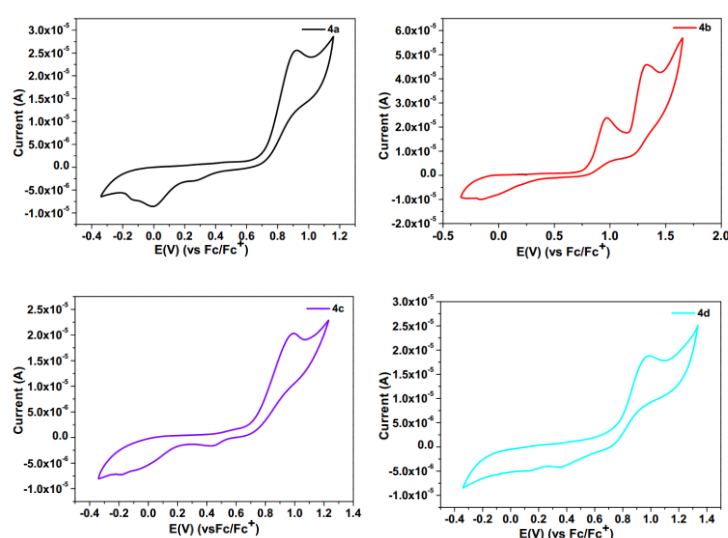


Figure S6. CV of **4a-4d** measured in dichloromethane at a scan rate of 100 mV·S⁻¹.

Table S15. Electrochemical properties of **4a-4d**

Compound	E _{ox} (V)	E _{HOMO} (eV) ^a	E _{LUMO} (eV) ^b	E _G ^{opt} (eV) ^c	E _{HOMO} ^{cal} (eV) ^d	E _{LUMO} ^{cal} (eV) ^d	E _G ^{cal} (eV) ^d
4a	0.7229	-5.5229	-2.3008	3.221	-5.4926	-1.4669	4.0257
4b	0.8240	-5.6240	-2.4850	3.139	-5.5680	-1.6655	3.9025
4c	0.7124	-5.5124	-2.1794	3.333	-5.5984	-1.1551	4.4433
4d	0.7607	-5.5607	-2.1827	3.378	-5.6319	-1.2258	4.4061

$$^a E_{\text{HOMO}} = -4.8 \text{ eV} - E_{\text{ox}}$$

$$^b E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{G}}^{\text{opt}}$$

$$^c E_{\text{G}}^{\text{opt}} = 1240 / \lambda_{\text{onset}}$$

^d Calculations were performed using the Gaussian 09 software package. The geometries were optimized as the B3LYP/6-311+G (2d,p) level, and energies were calculated at the same level of theory.⁹

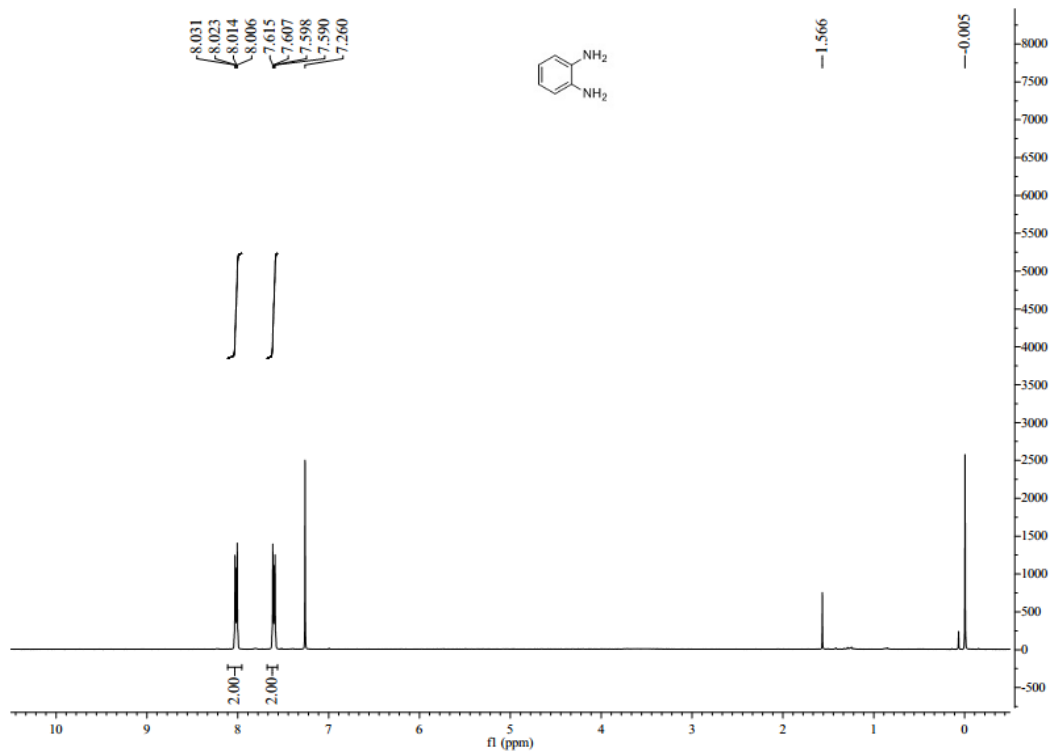
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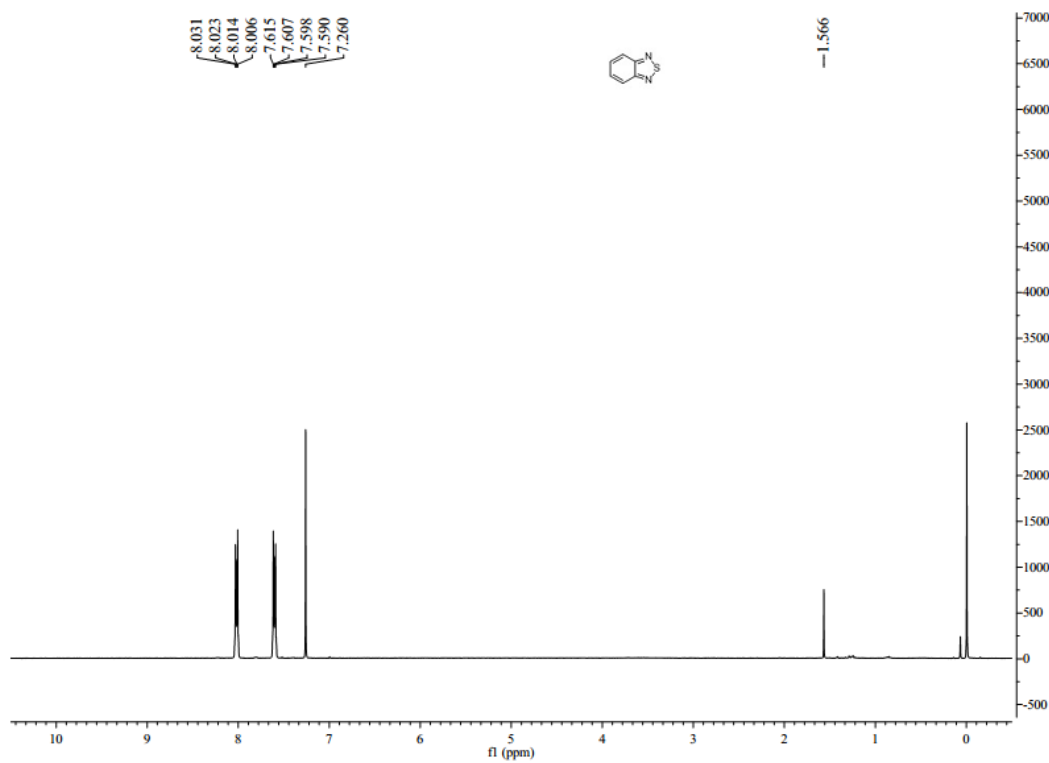
Rev. 2005, **105**, 3842. (b) P. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N. J. R. E. Hommes, *J. Am. Chem. Soc.* 1996, **118**, 6317. (c) K. Wolinski, J. F. Hinton, P. Pulay, *J. Am. Chem. Soc.* 1990, **112**, 8251.

(11) J. Zhang, B. Xu, J. Chen, S. Ma, Y. Dong, L. Wang, B. Li, L. Ye, W. Tian, *Adv. Mater.* 2014, **26**, 739.

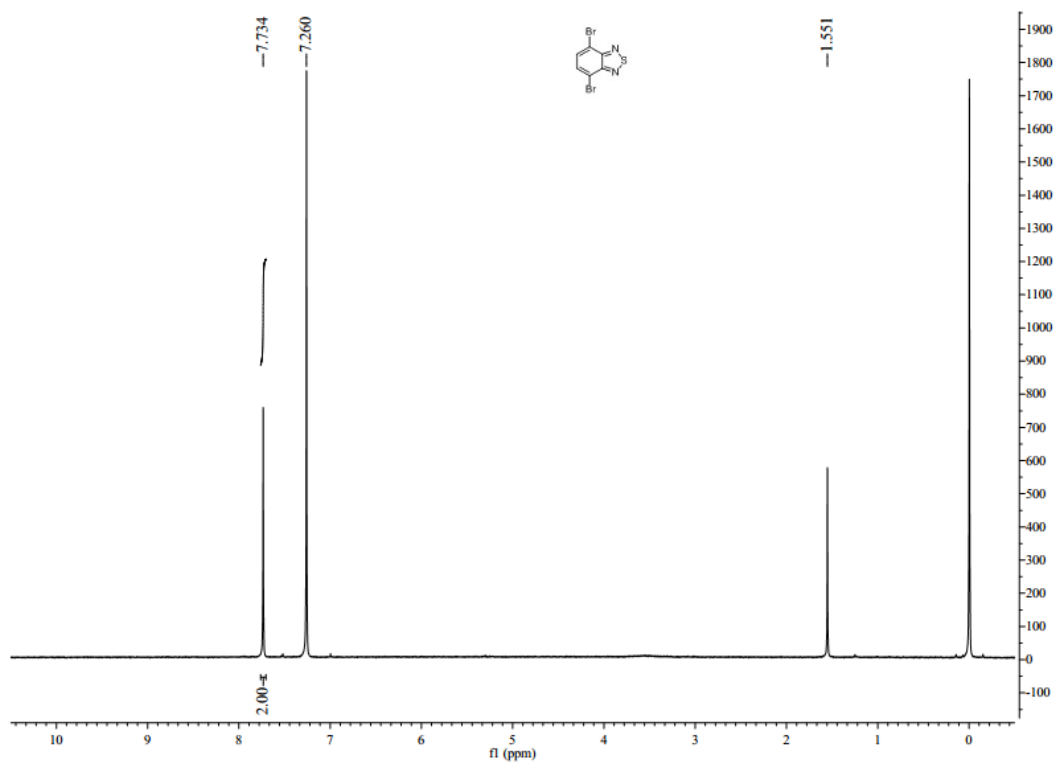
8. NMR spectra



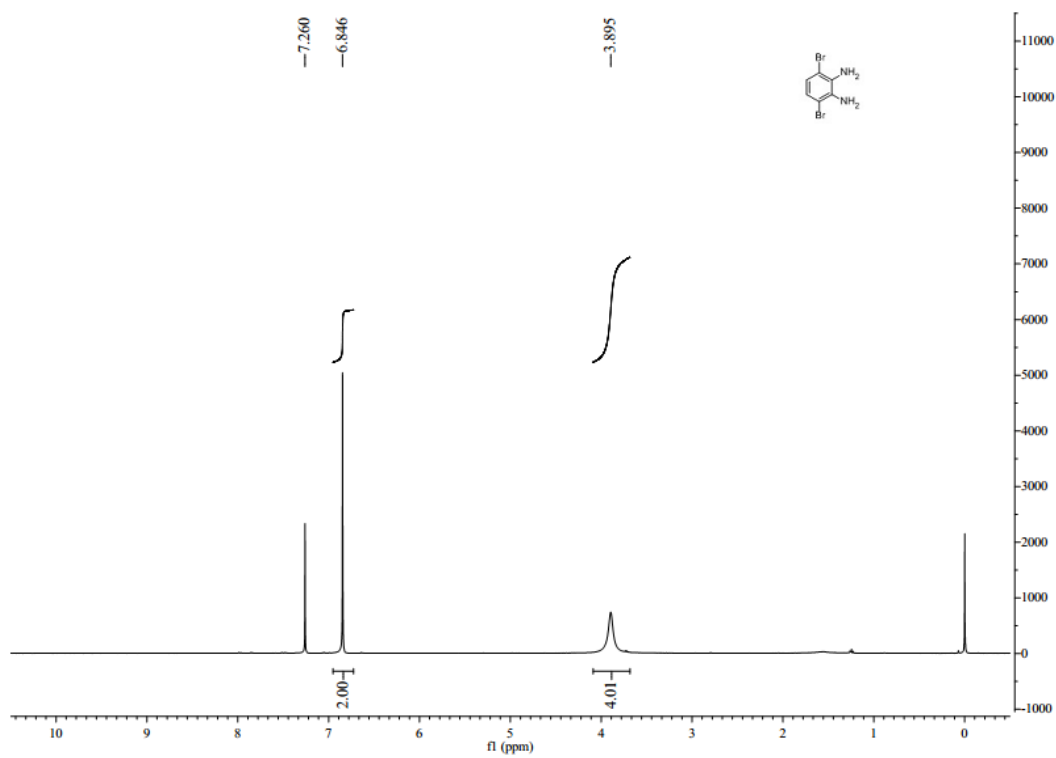
¹H NMR spectra of p-Phenylenediamine (400 MHz, CDCl₃)



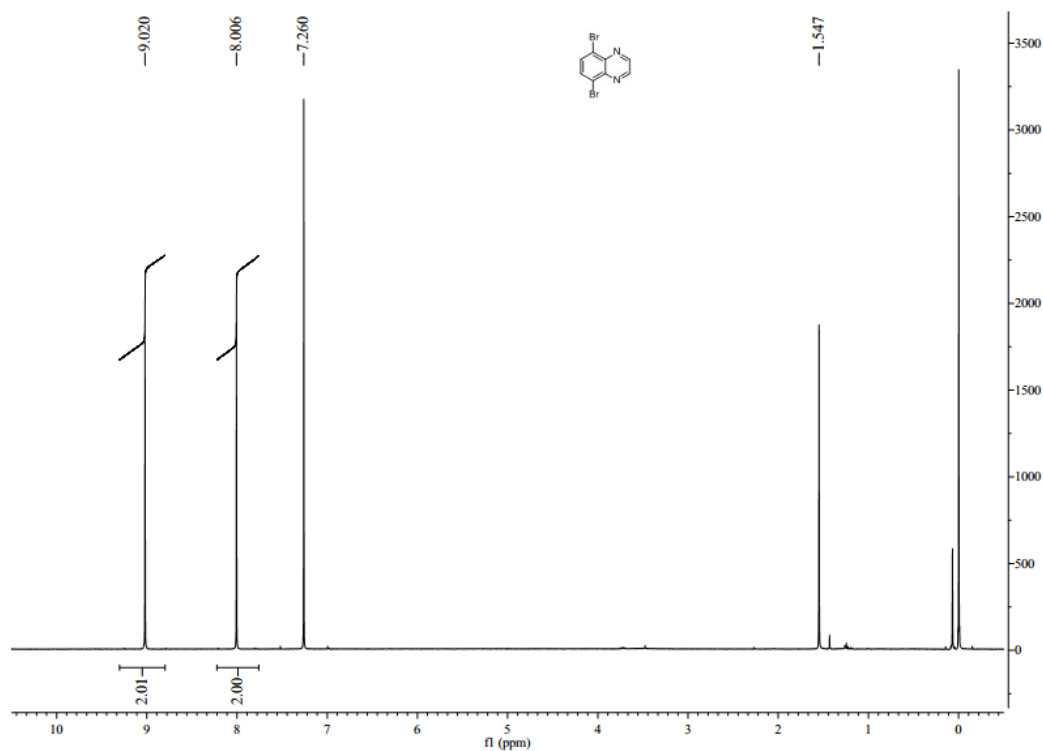
¹H NMR spectra of 2,1,3-Benzothiadiazole **S1** (400 MHz, CDCl₃)



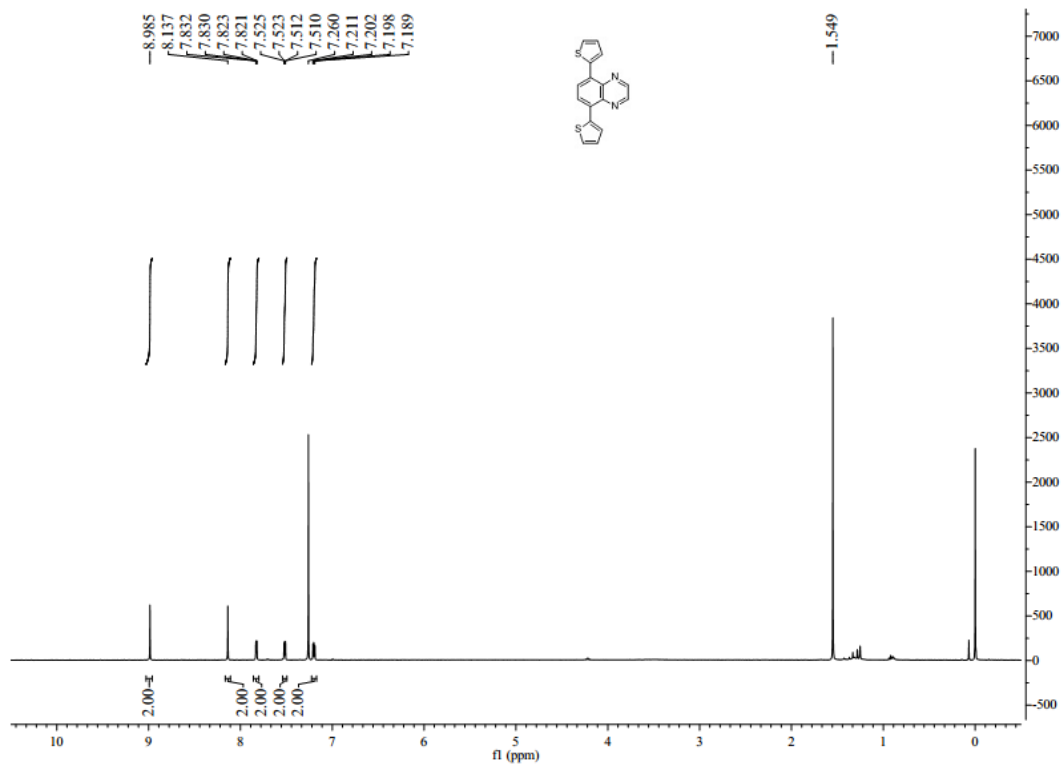
^1H NMR spectra of 4,7-Dibromo-2,1,3-benzothiadiazole **S2** (400 MHz, CDCl_3)



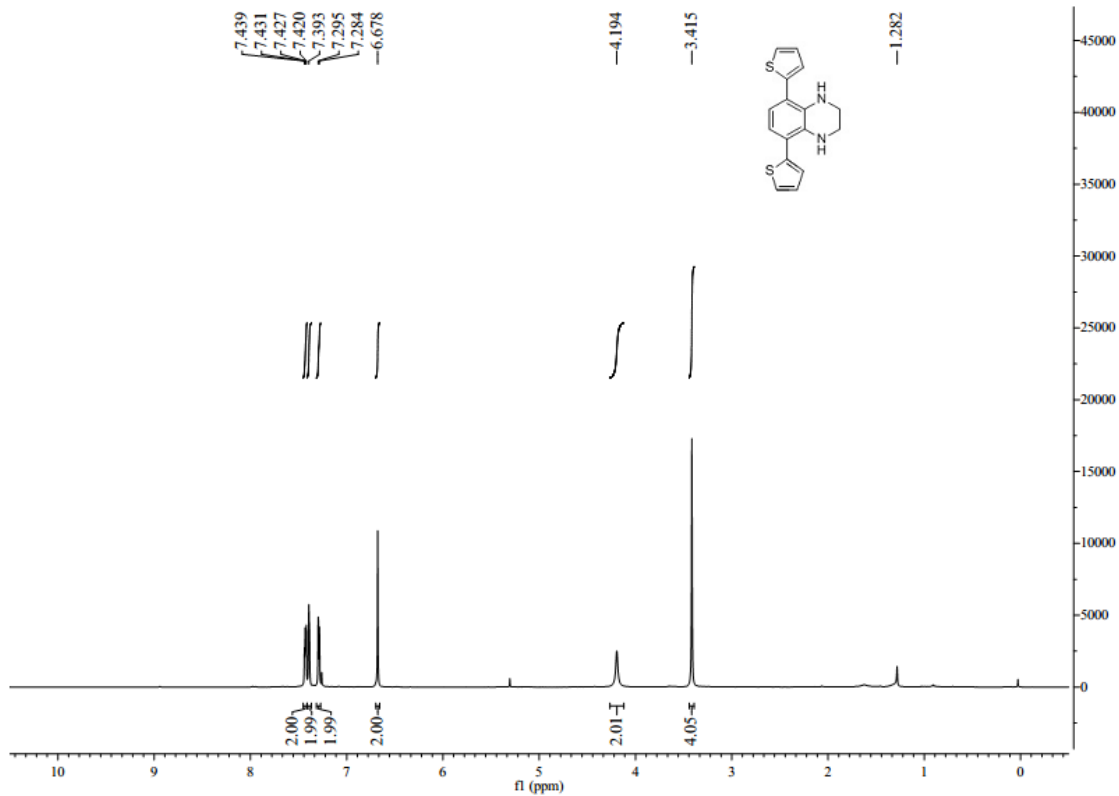
^1H NMR spectra of 4,7-dibromo- Phenylenediamine **S3** (400 MHz, CDCl_3)



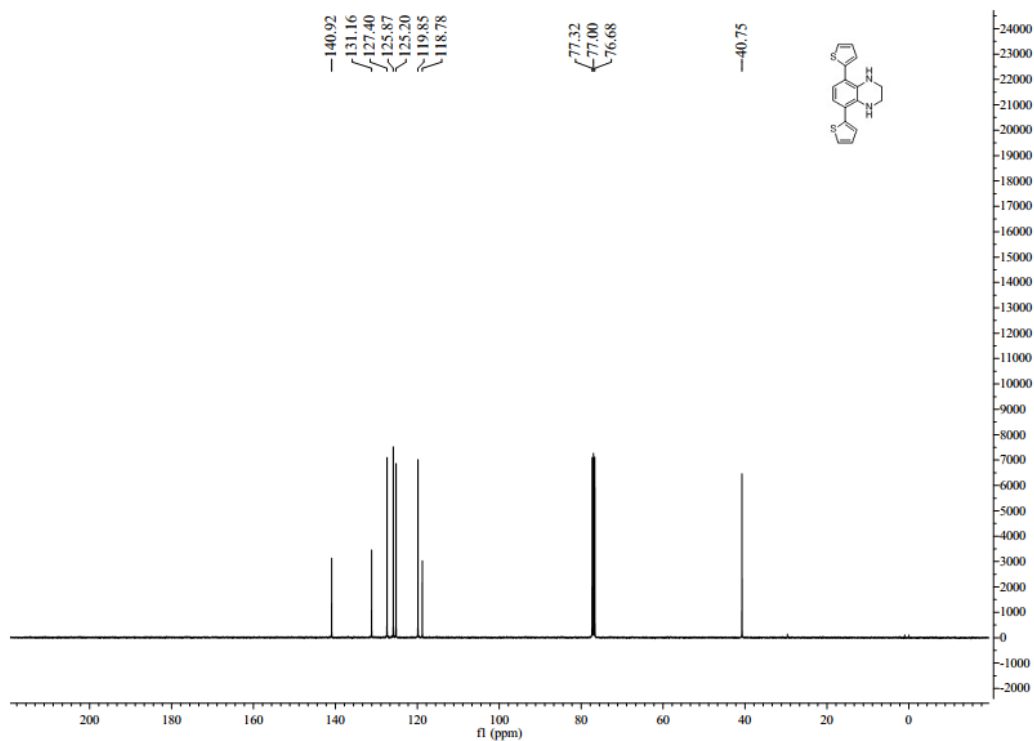
^1H NMR spectra of 5,8-dibromoquinoxaline **1** (400 MHz, CDCl_3)



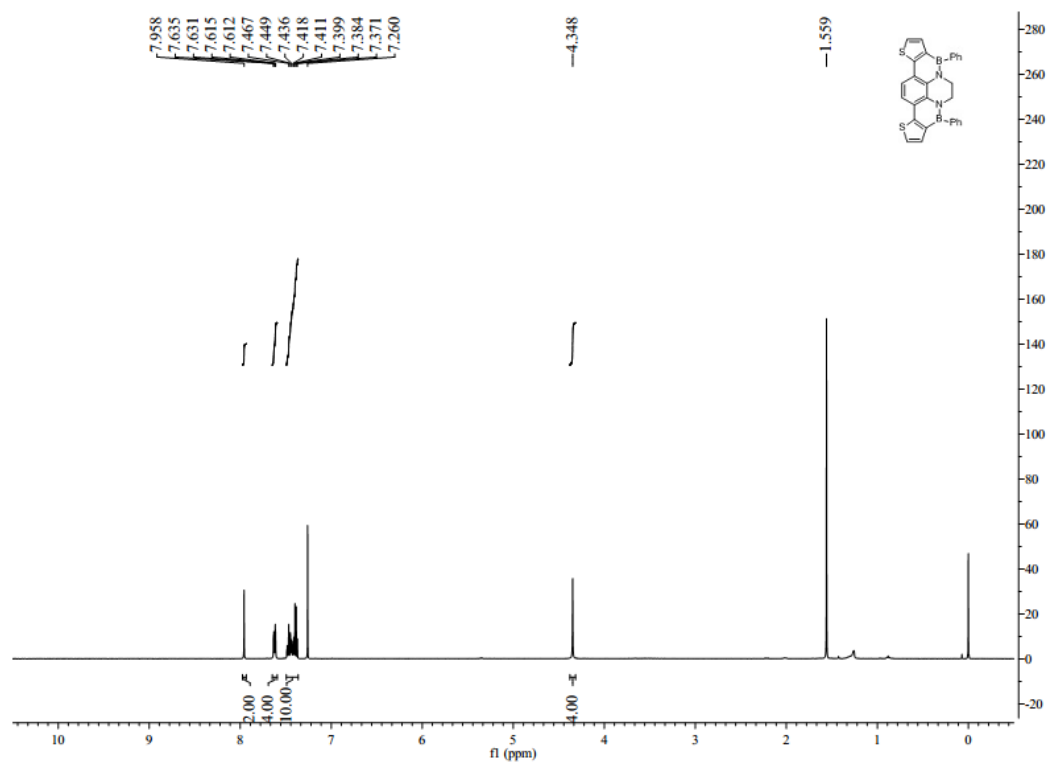
^1H NMR spectra of 5,8-dithienylquinoxaline **2a** (400 MHz, CDCl_3)



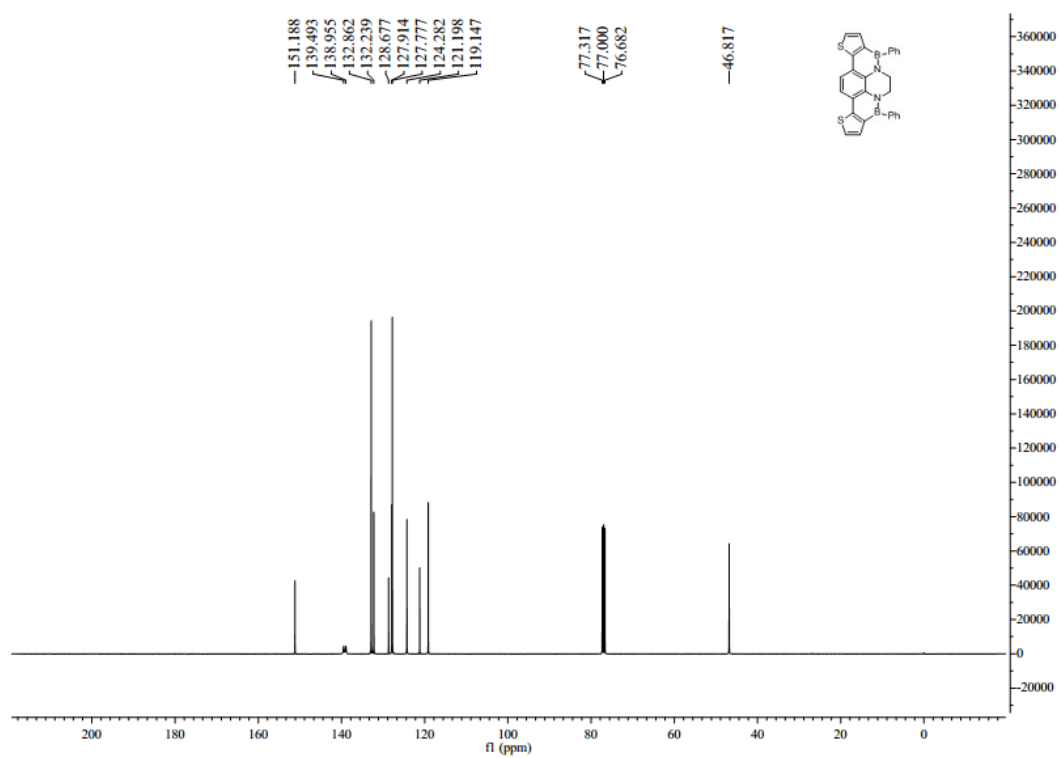
^1H NMR spectra of **3a** (400 MHz, CDCl_3)



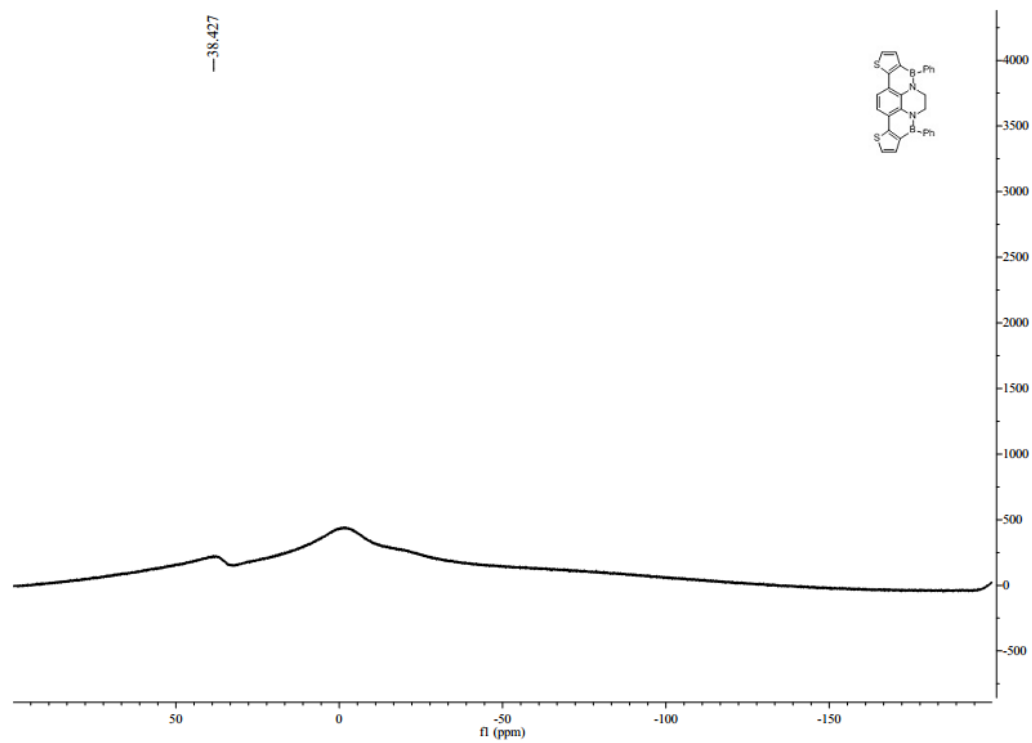
^{13}C NMR spectra of **3a** (100 MHz, CDCl_3)



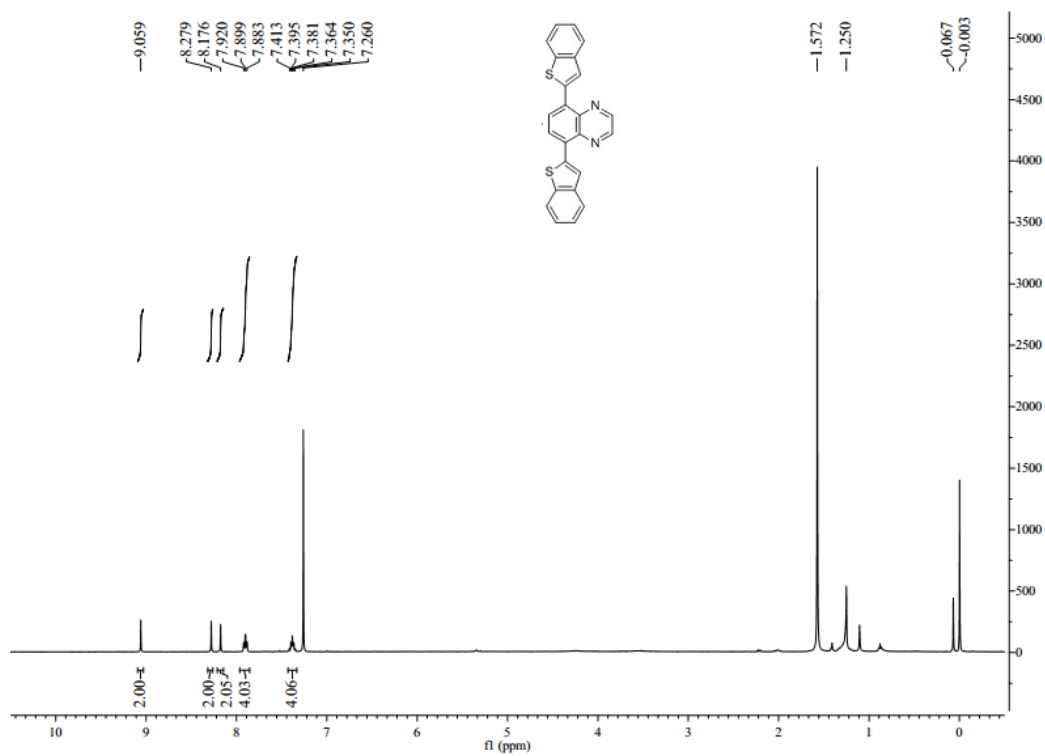
^1H NMR spectra of **4a** (400 MHz, CDCl_3)



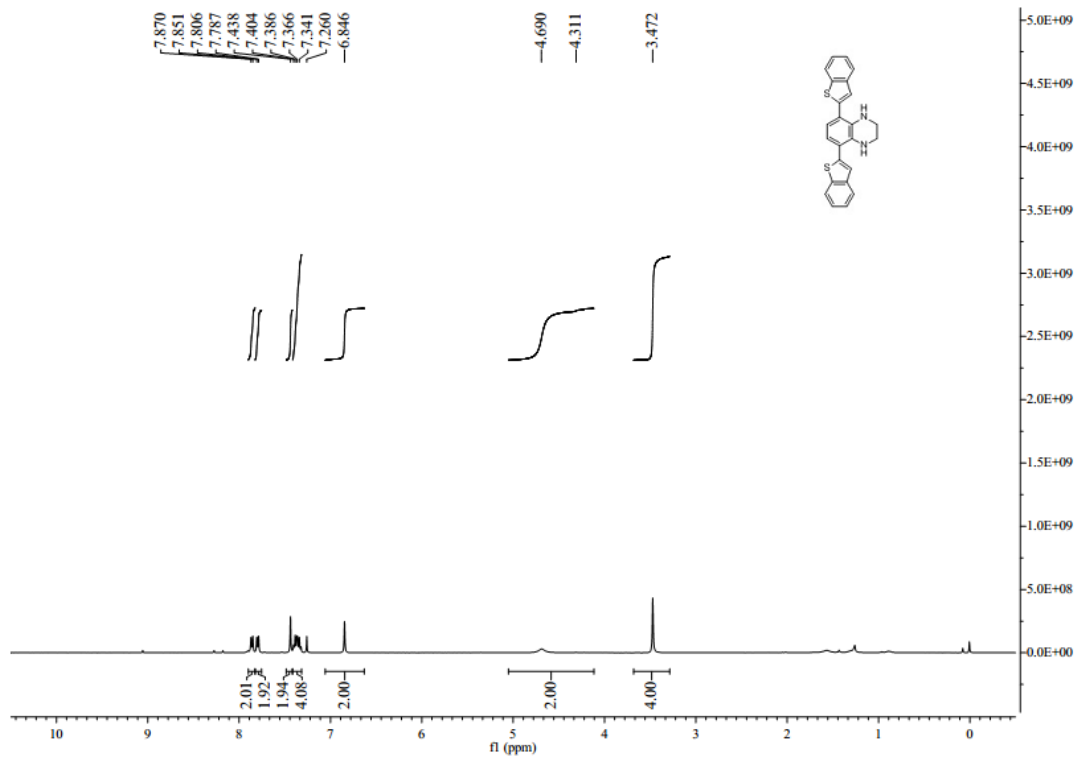
^{13}C NMR spectra of **4a** (100 MHz, CDCl_3)



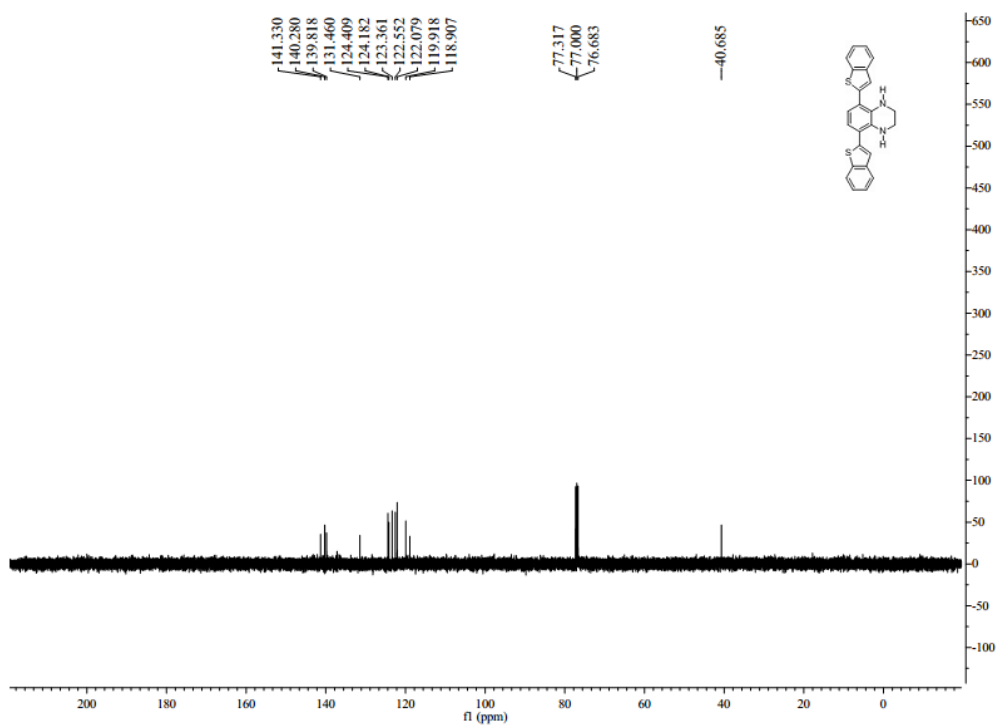
^{11}B NMR spectra of **4a** (128 MHz)



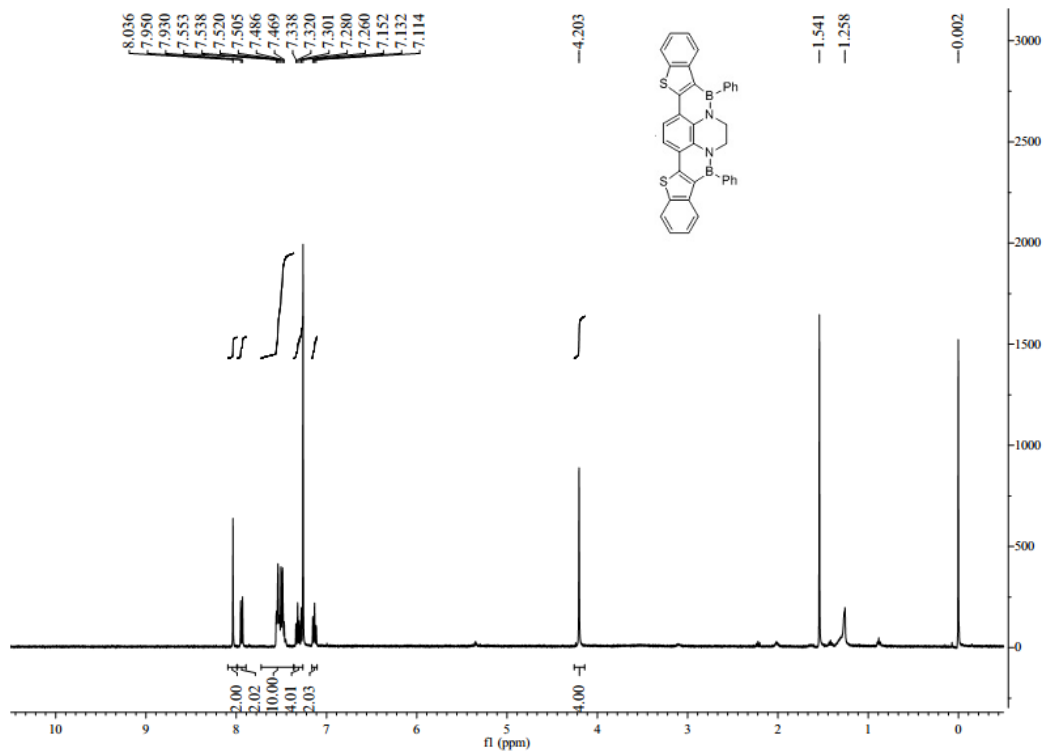
^1H NMR spectra of **2b** (400 MHz, CDCl_3)



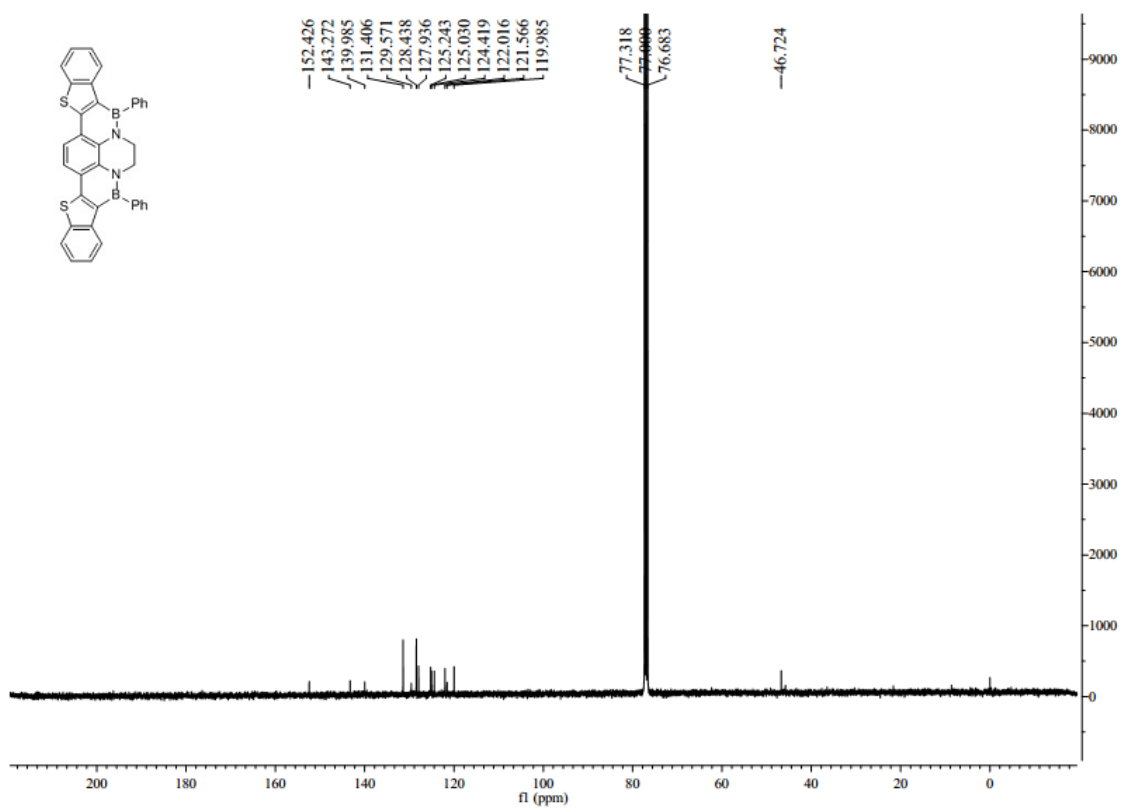
^1H NMR spectra of **3b** (400 MHz, CDCl_3)



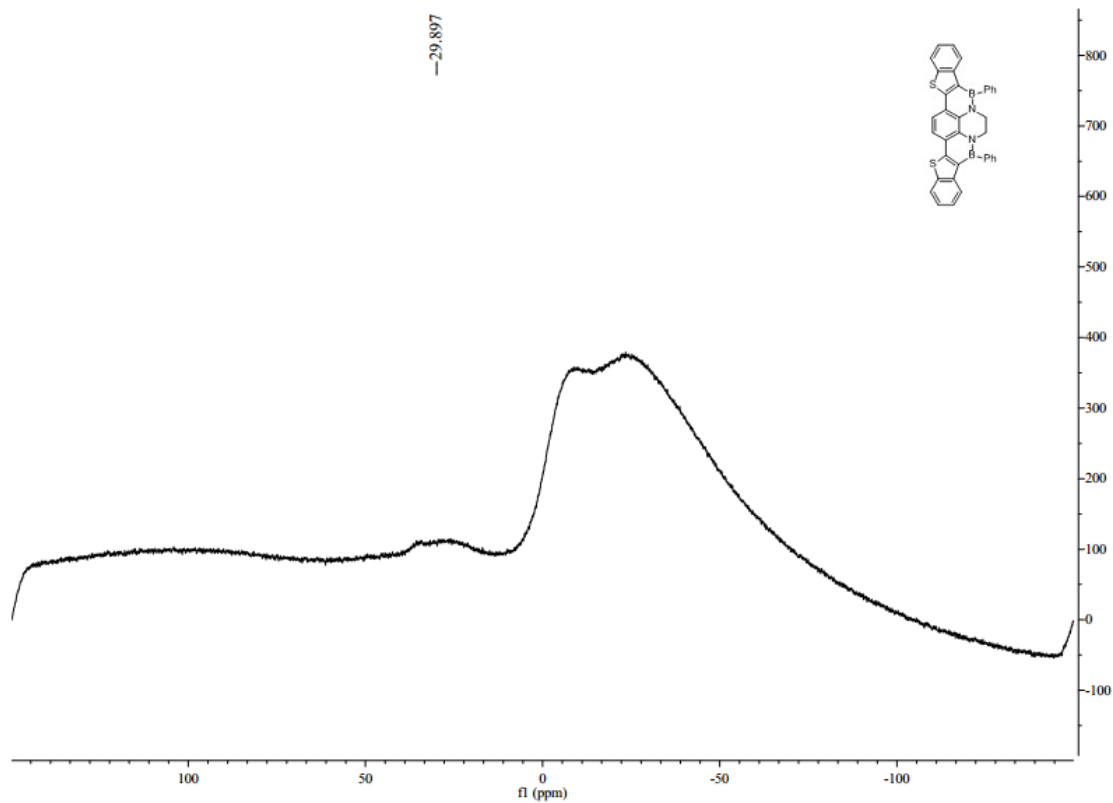
^{13}C NMR spectra of **3b** (100 MHz, CDCl_3)



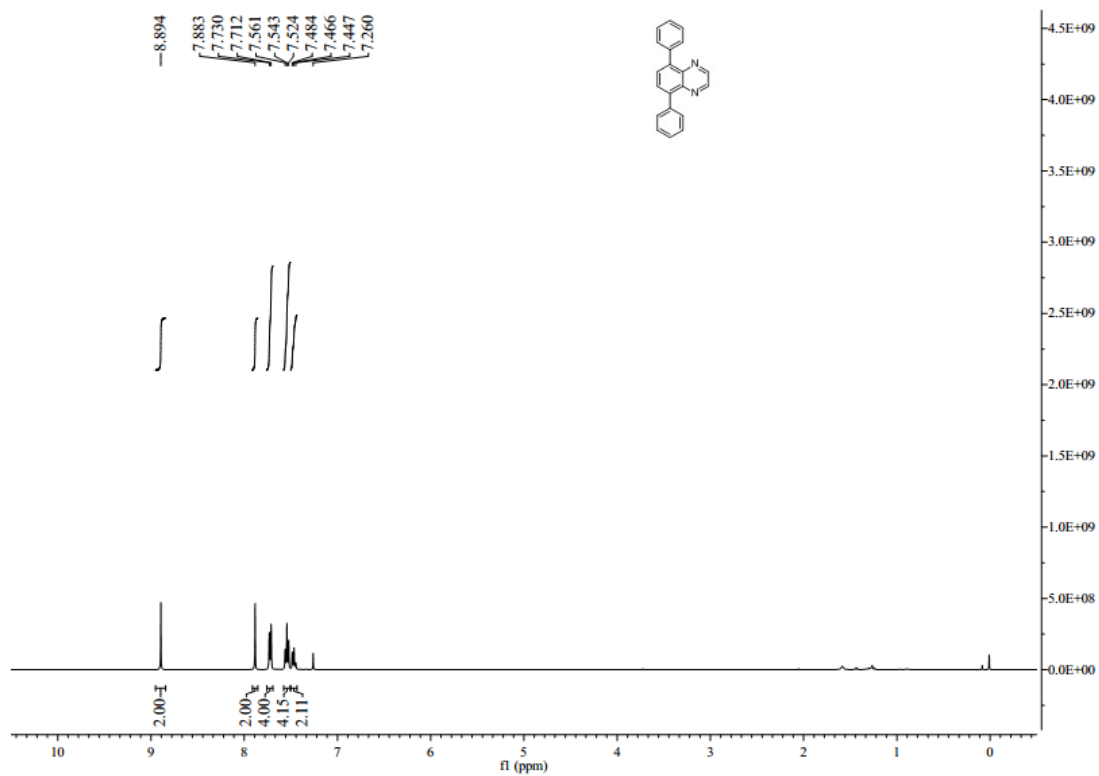
^1H NMR spectra of **4b** (400 MHz, CDCl_3)



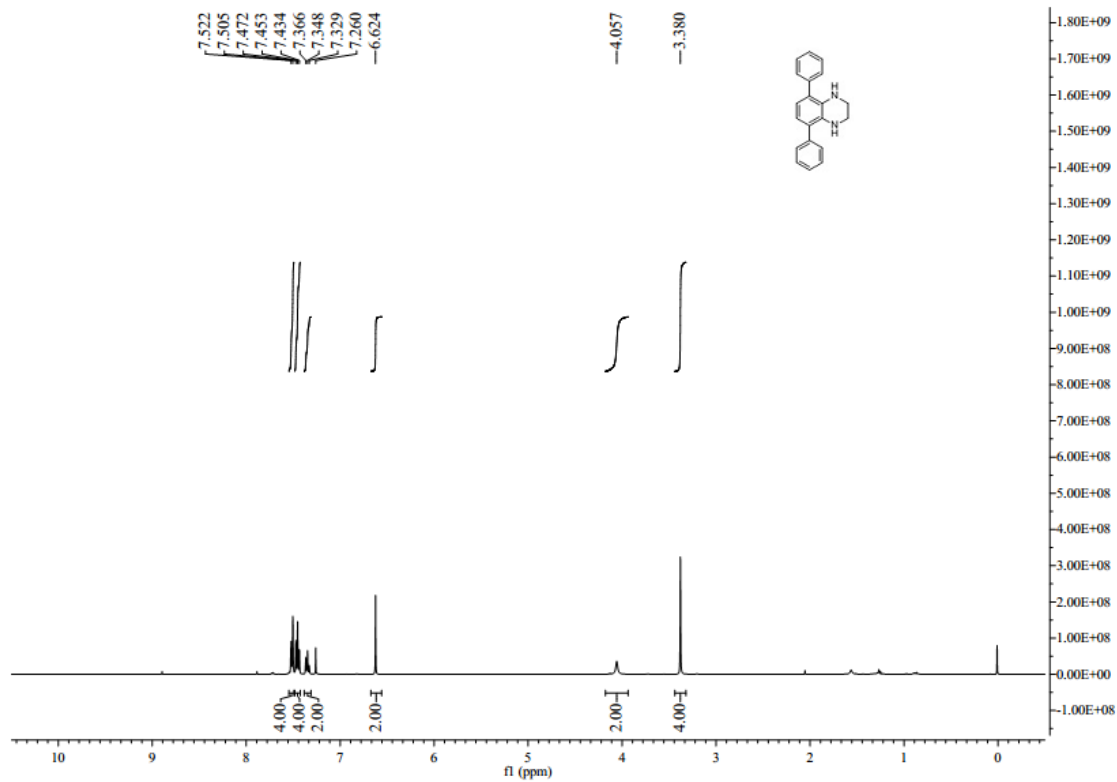
^{13}C NMR spectra of **4b** (100 MHz, CDCl_3)



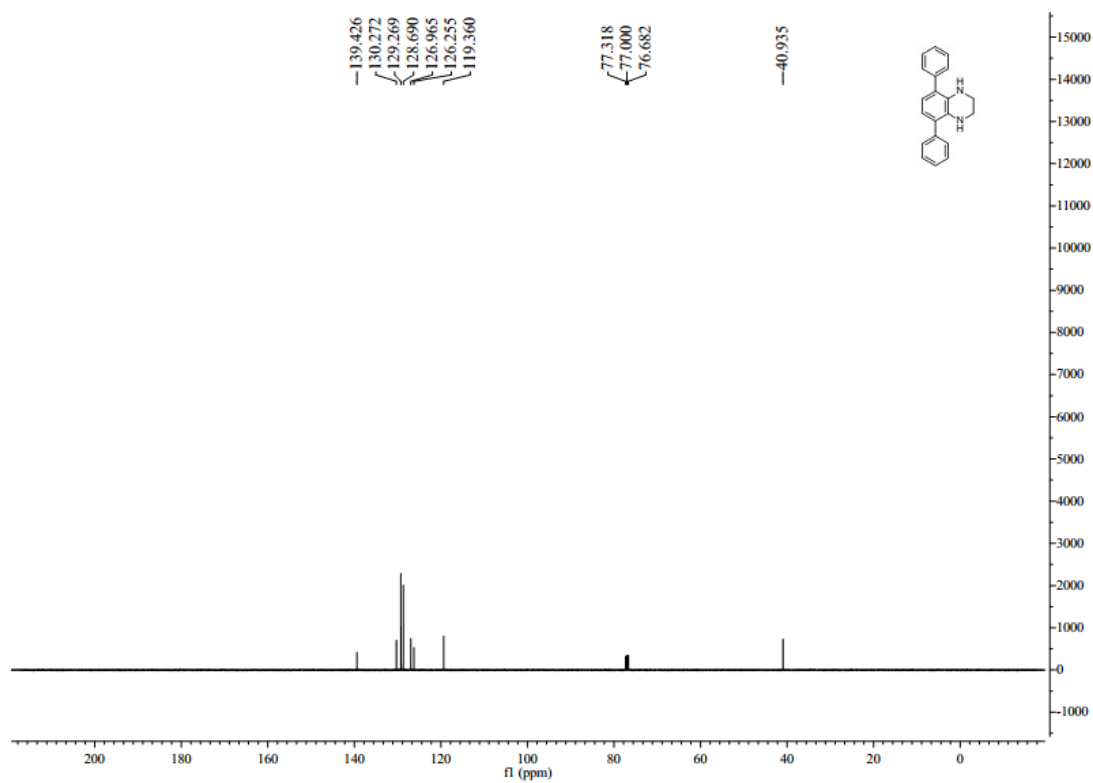
¹¹B NMR spectra of **4b** (128 MHz)



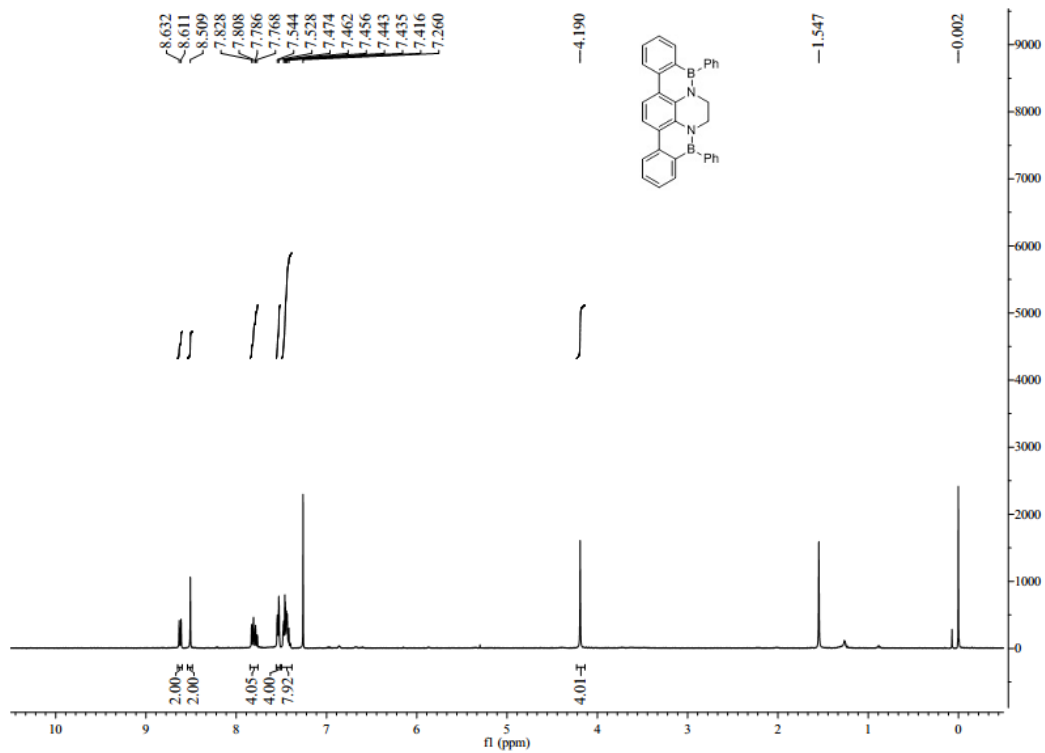
¹H NMR spectra of **2c** (400 MHz, CDCl₃)



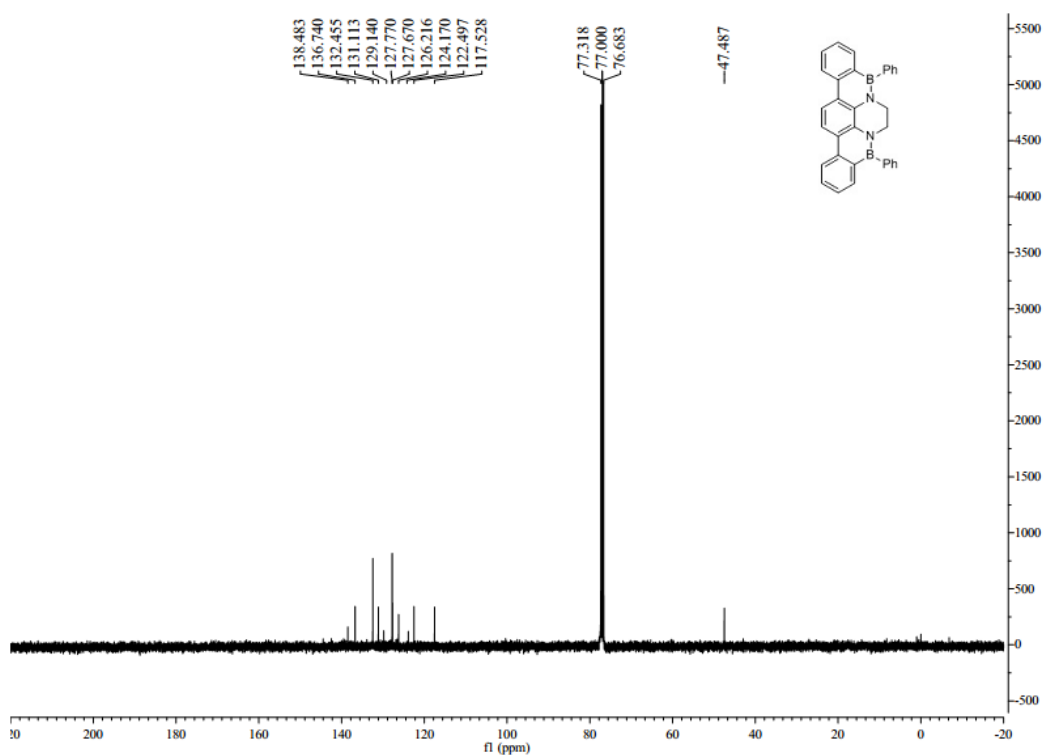
^1H NMR spectra of **3c** (400 MHz, CDCl_3)



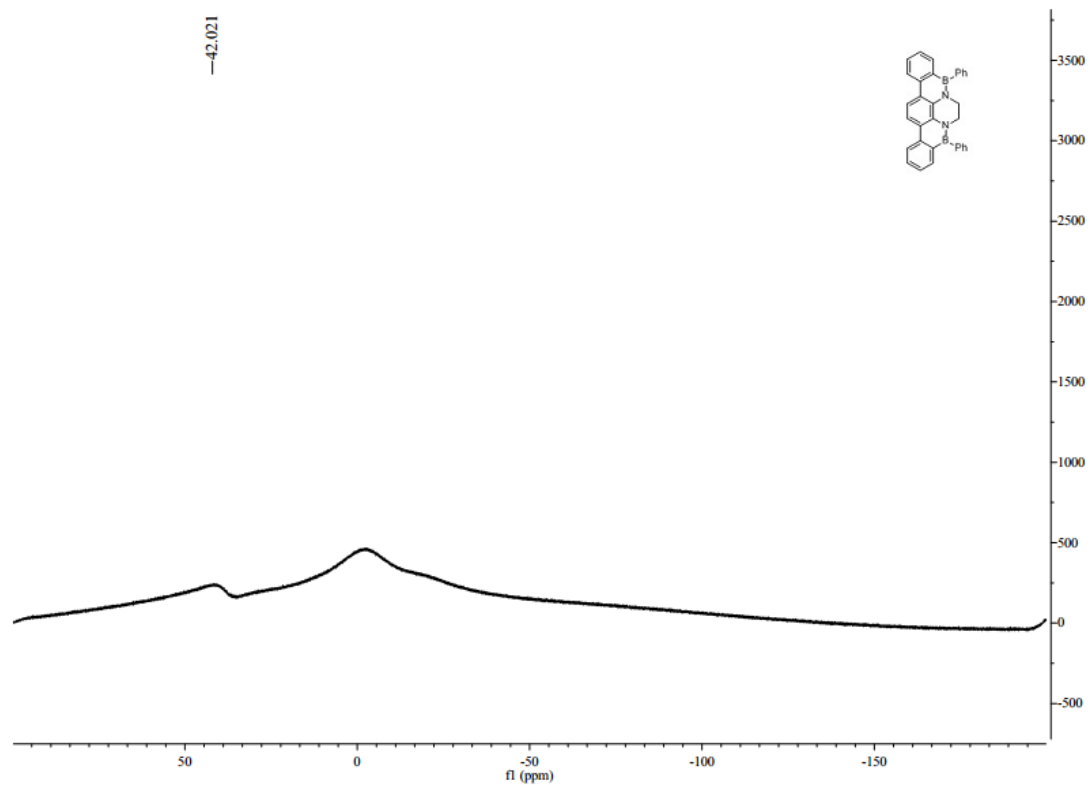
^{13}C NMR spectra of **3c** (100 MHz, CDCl_3)



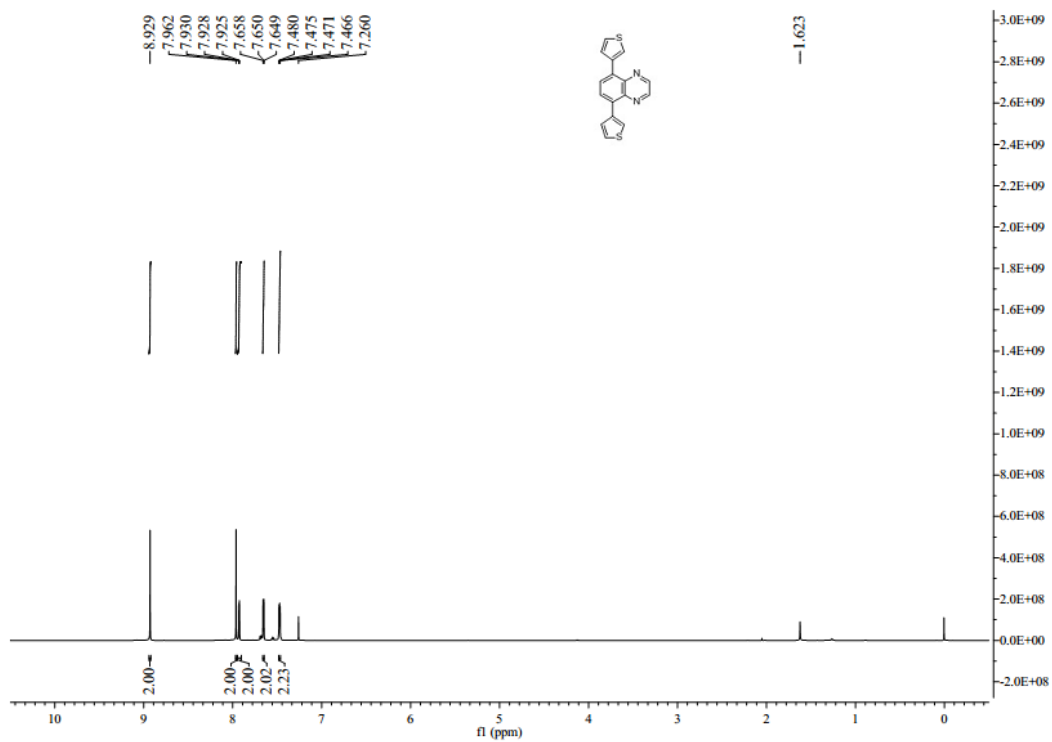
^1H NMR spectra of **4c** (400 MHz, CDCl_3)



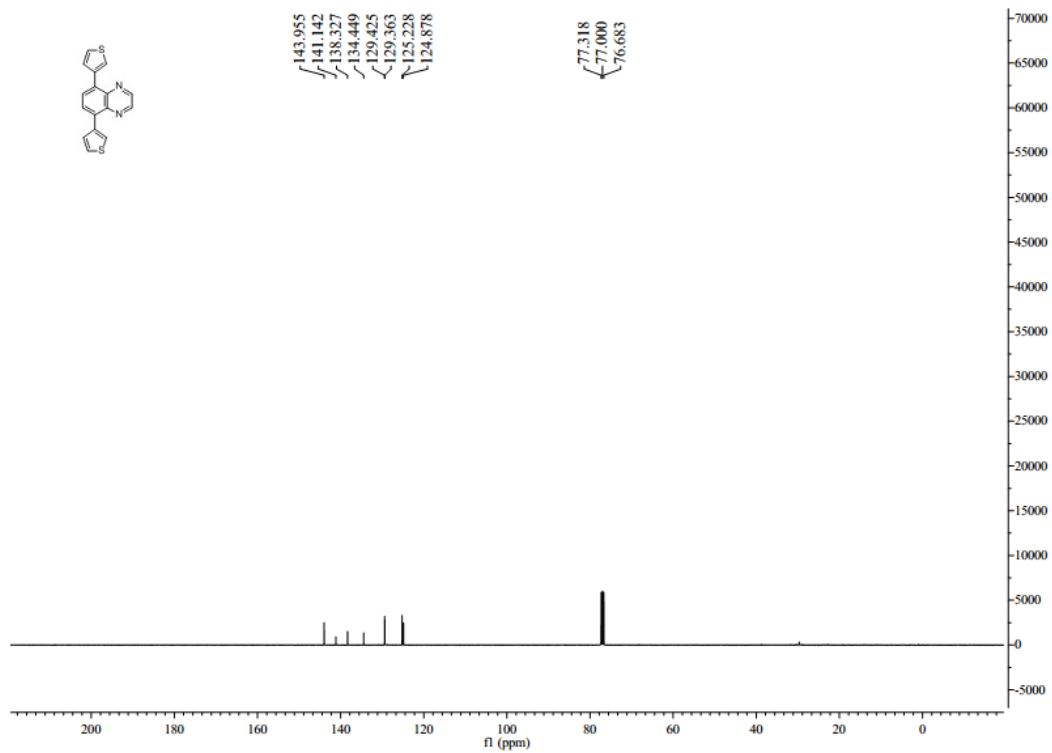
^{13}C NMR spectra of **4c** (100 MHz, CDCl_3)



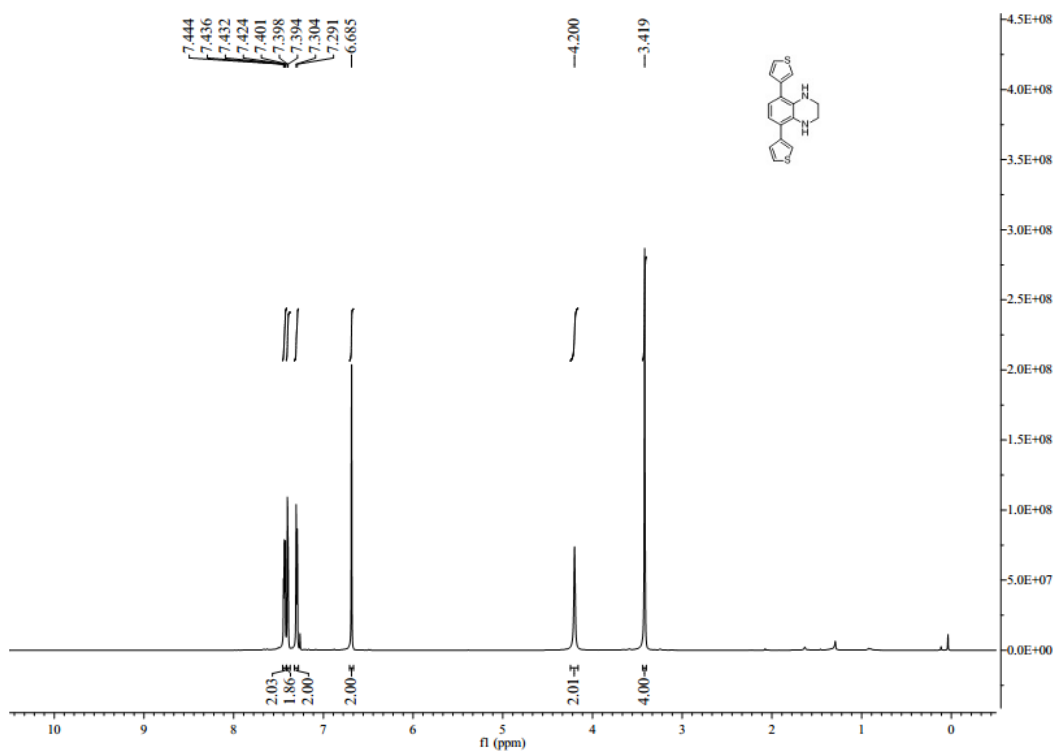
^{11}B NMR spectra of **4c** (128 MHz)



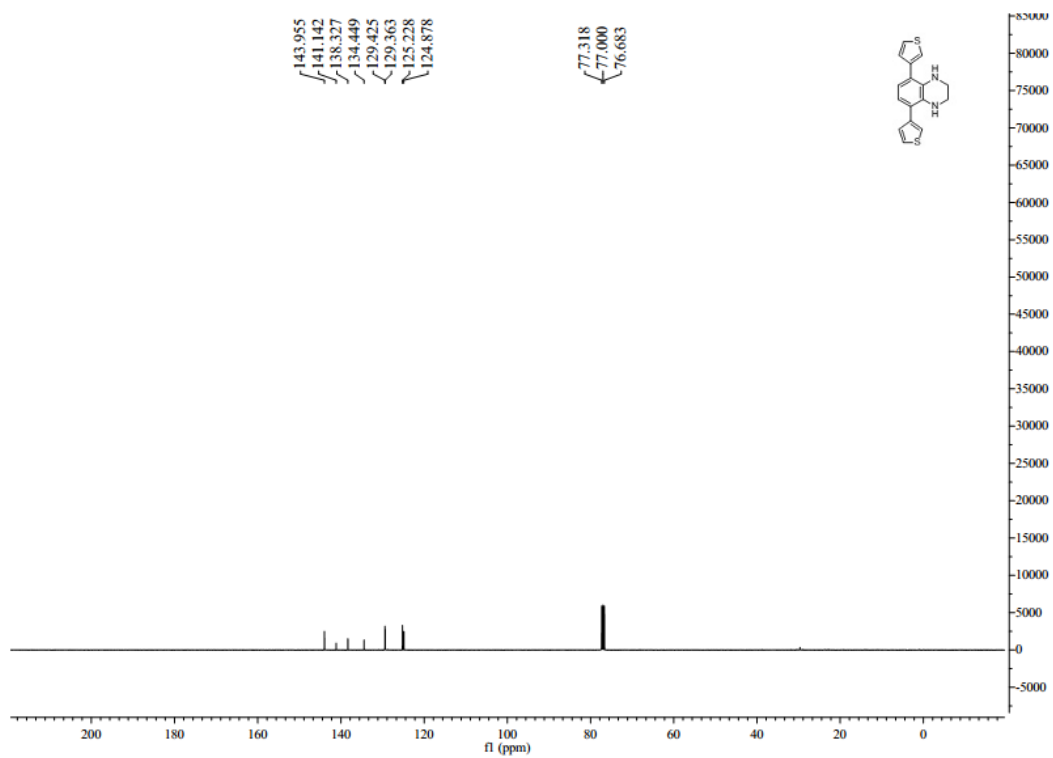
^1H NMR spectra of **2d** (400 MHz, CDCl_3)



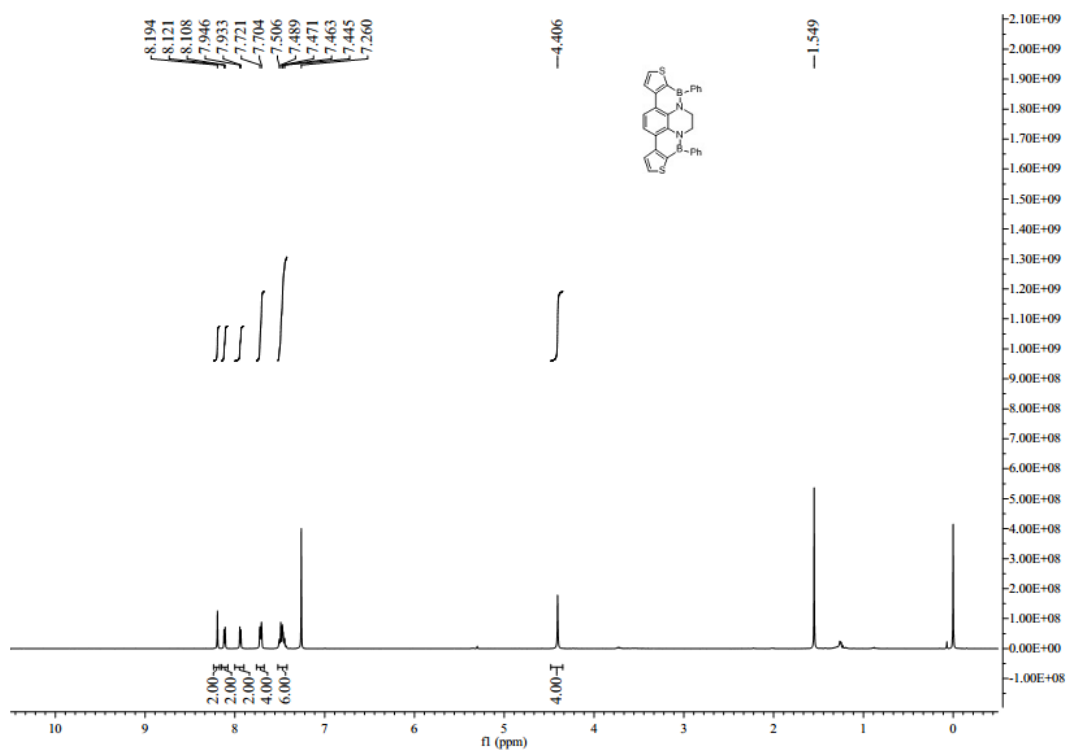
^{13}C NMR spectra of **2d** (100 MHz, CDCl_3)



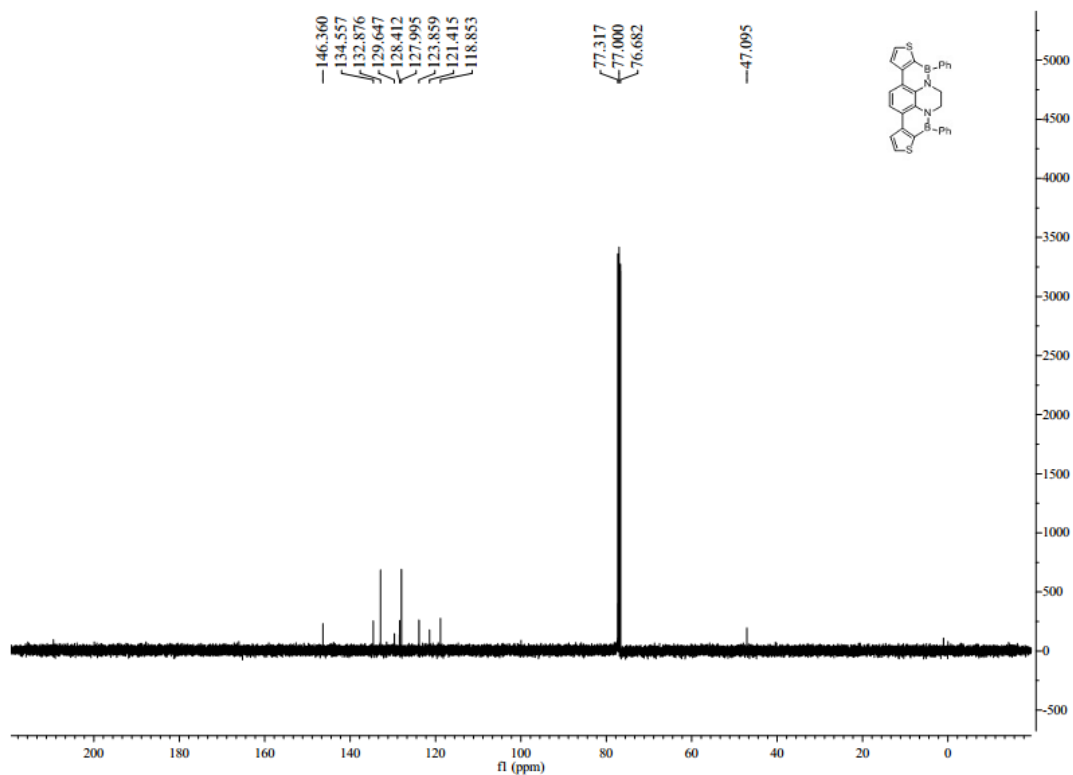
^1H NMR spectra of **3d** (400 MHz, CDCl_3)



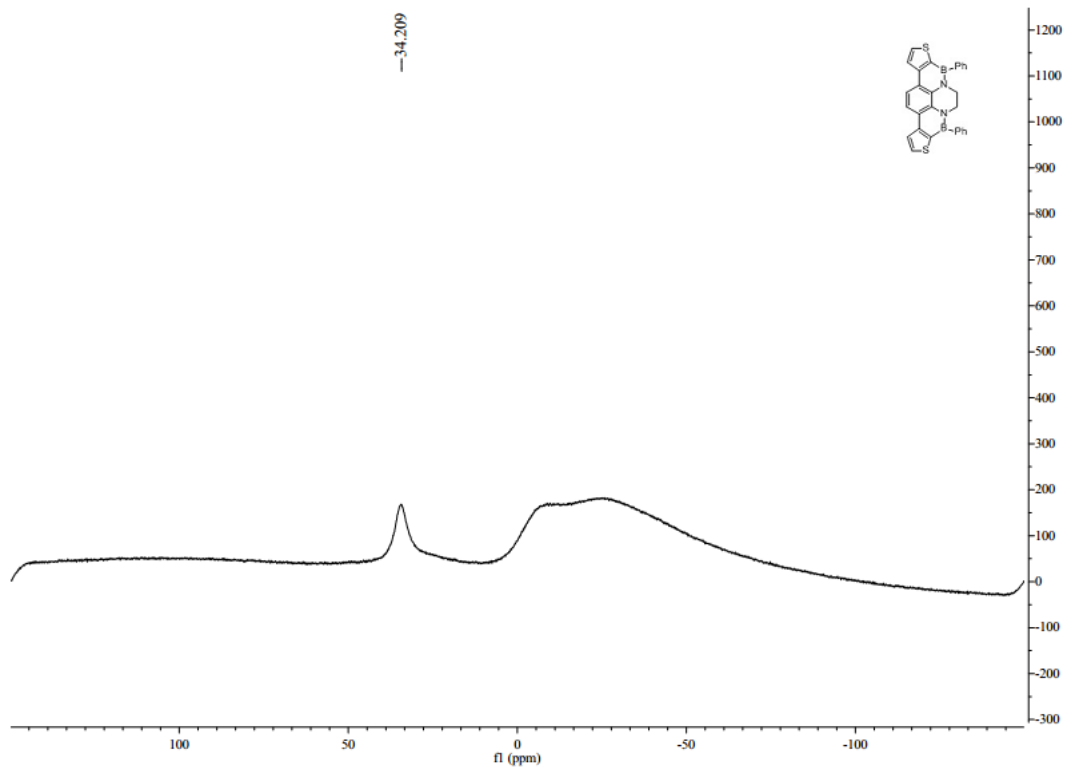
^{13}C NMR spectra of **3d** (100 MHz, CDCl_3)



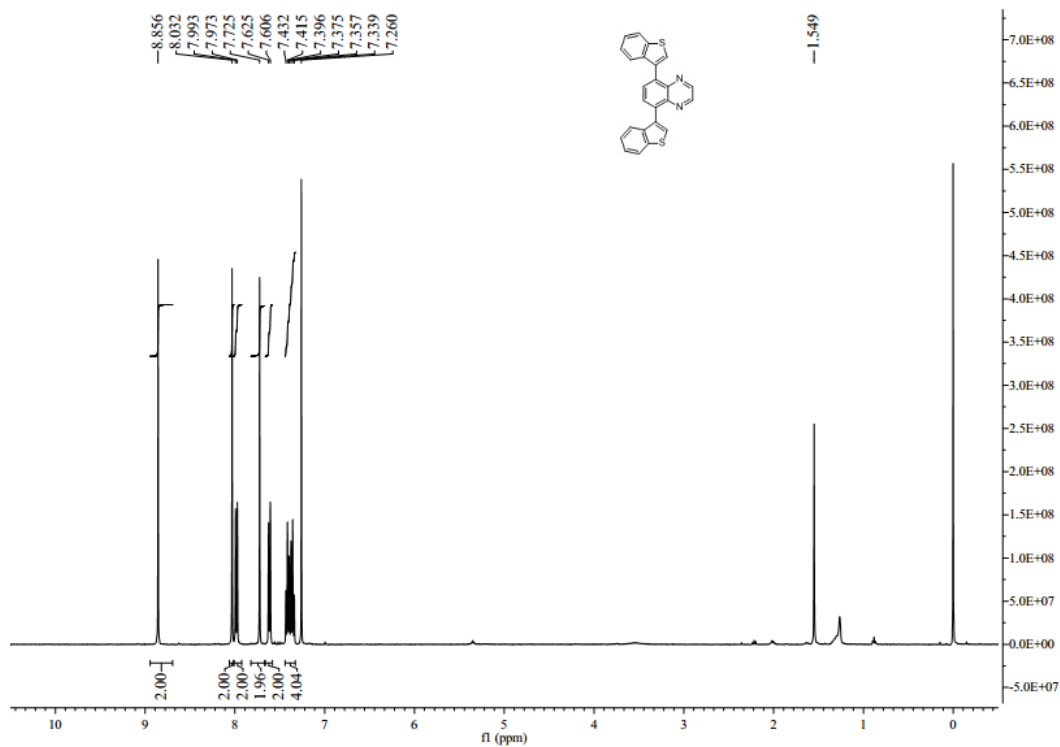
^1H NMR spectra of **4d** (400 MHz, CDCl_3)



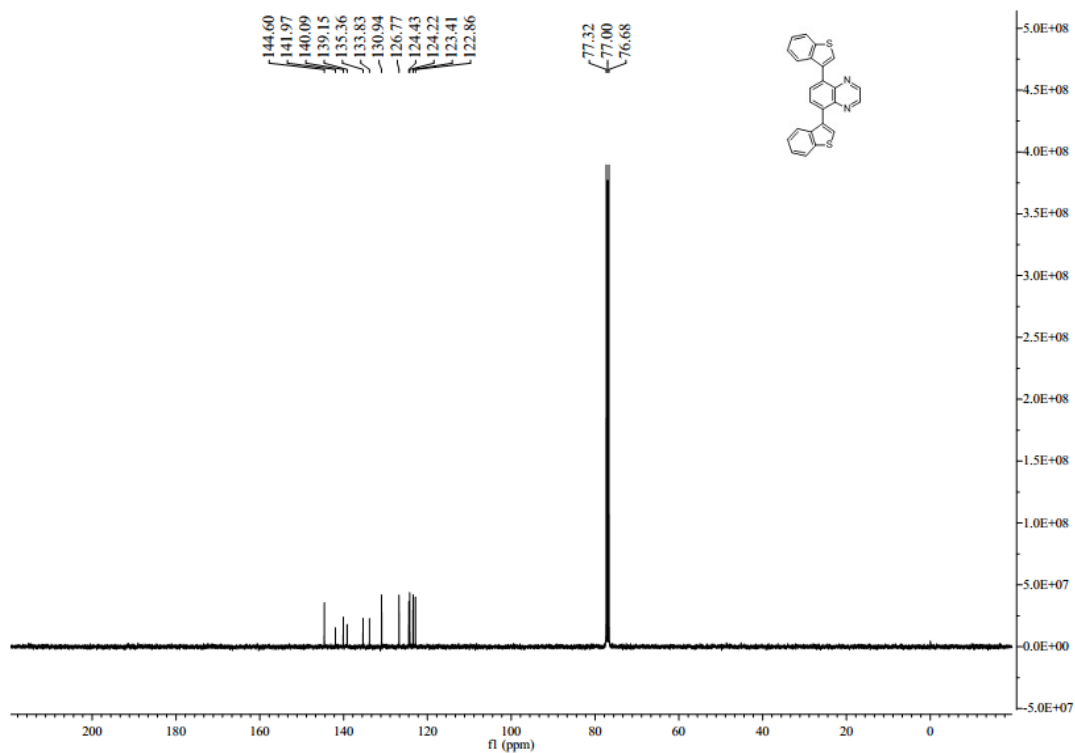
^{13}C NMR spectra of **4d** (100 MHz, CDCl_3)



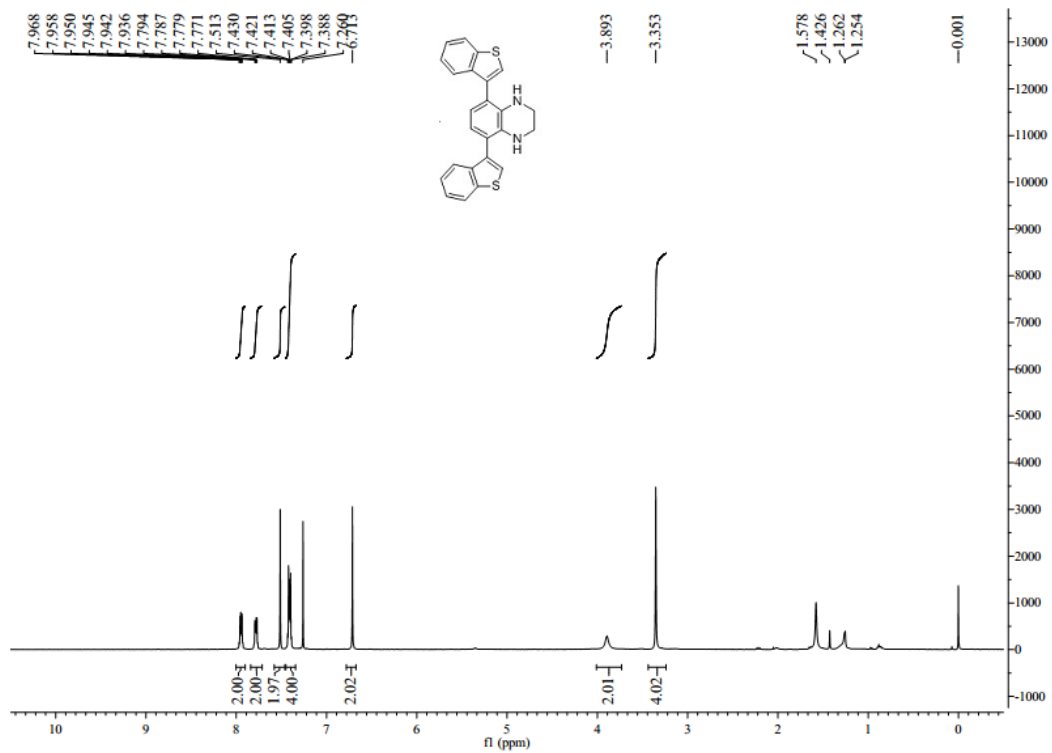
^{11}B NMR spectra of **4d** (128 MHz)



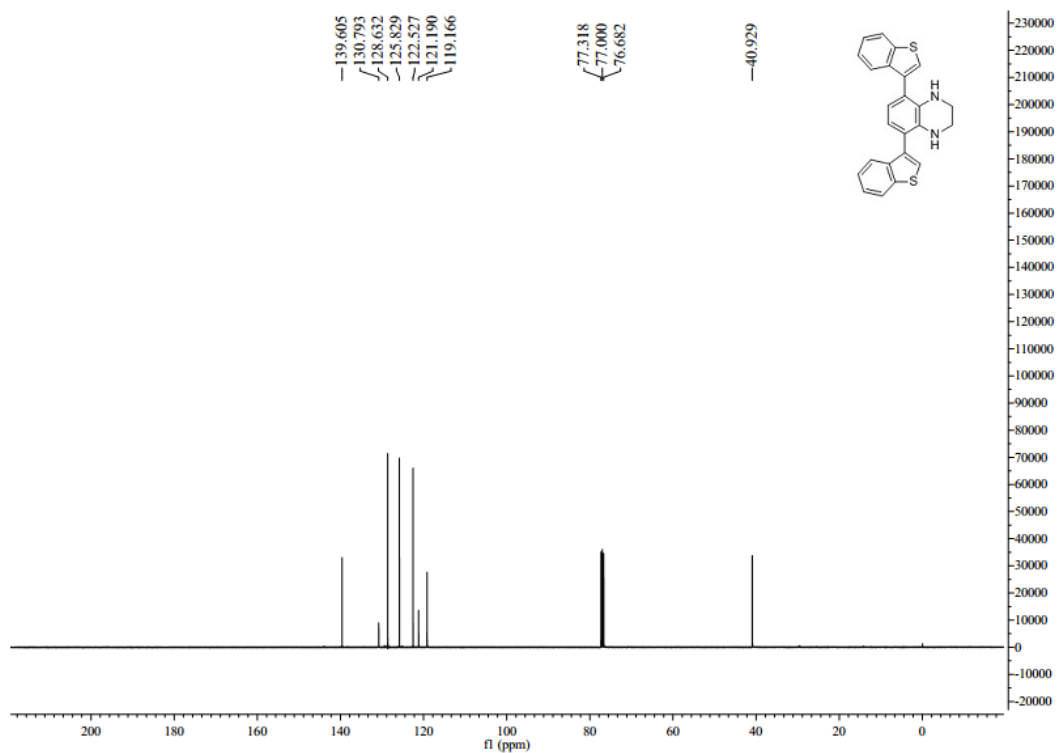
^1H NMR spectra of **2e** (400 MHz, CDCl_3)



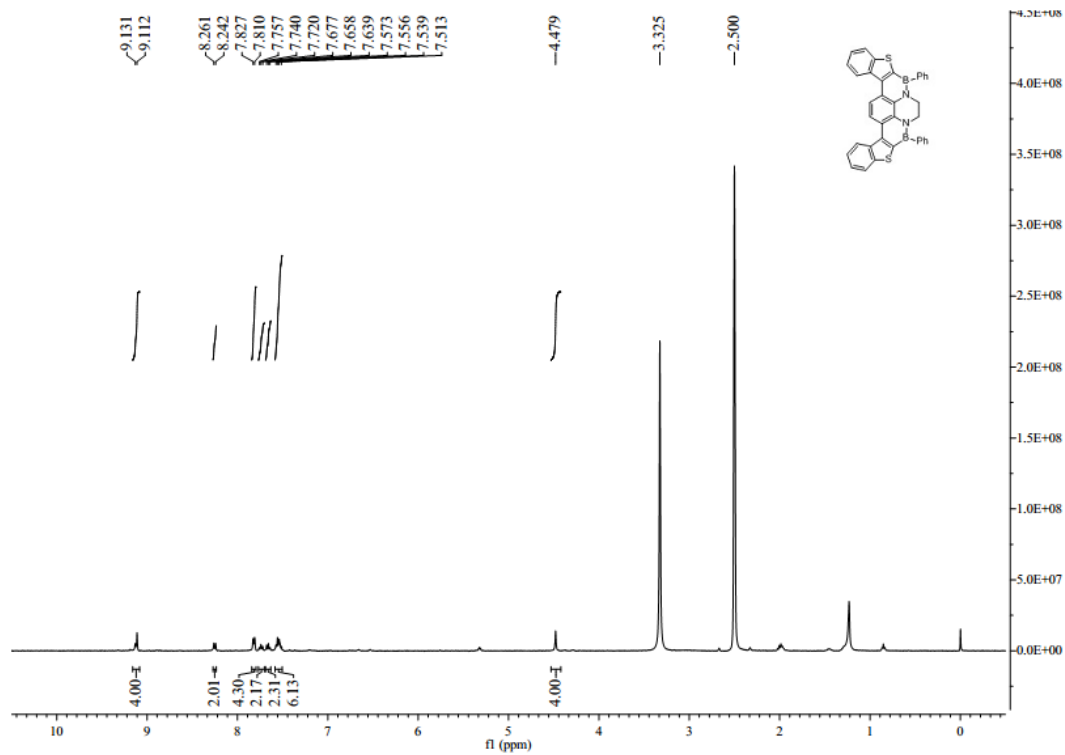
^{13}C NMR spectra of **2e** (100 MHz, CDCl_3)



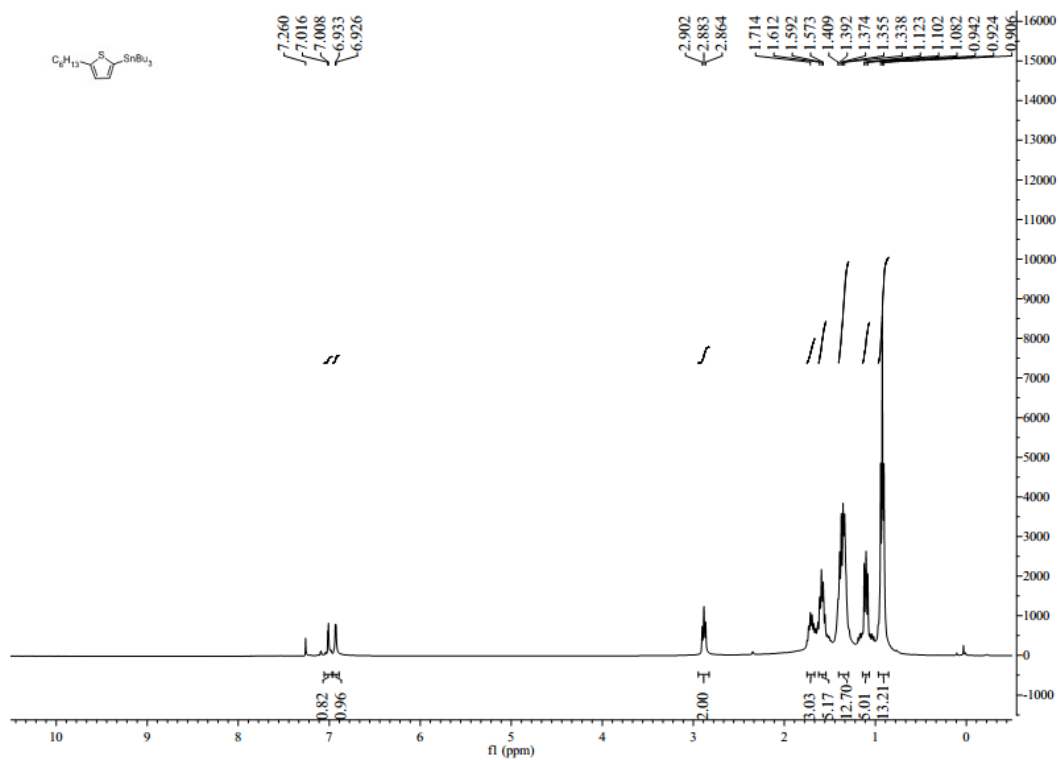
¹H NMR spectra of **3e** (400 MHz, CDCl₃)



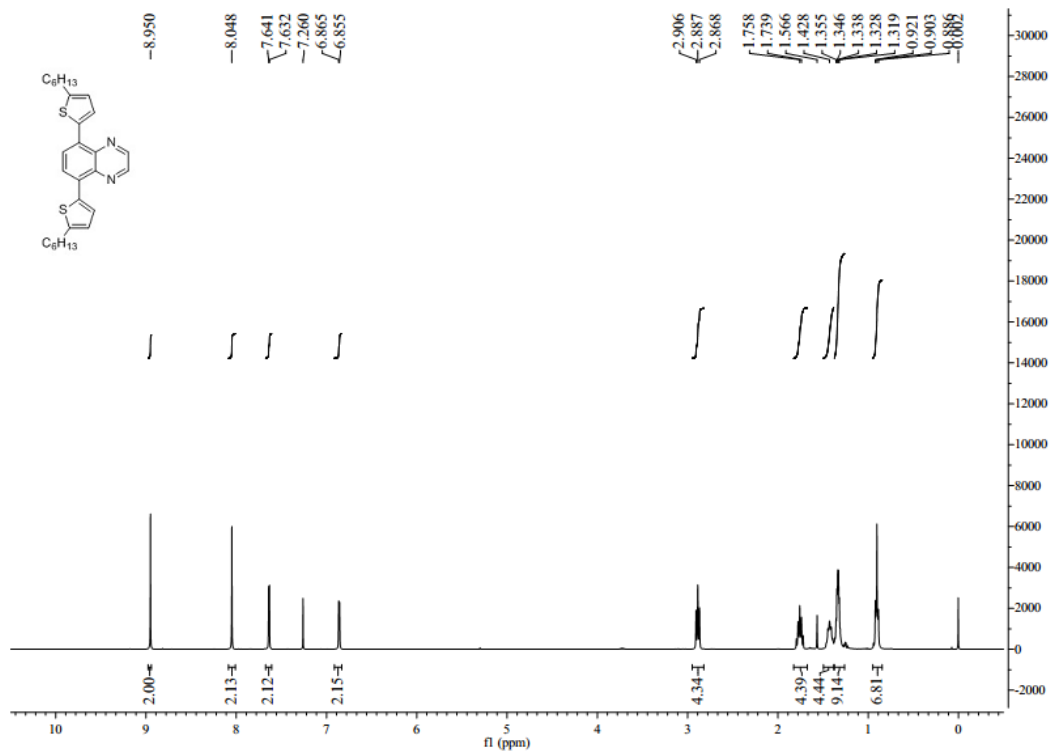
¹³C NMR spectra of **3e** (100 MHz, CDCl₃)



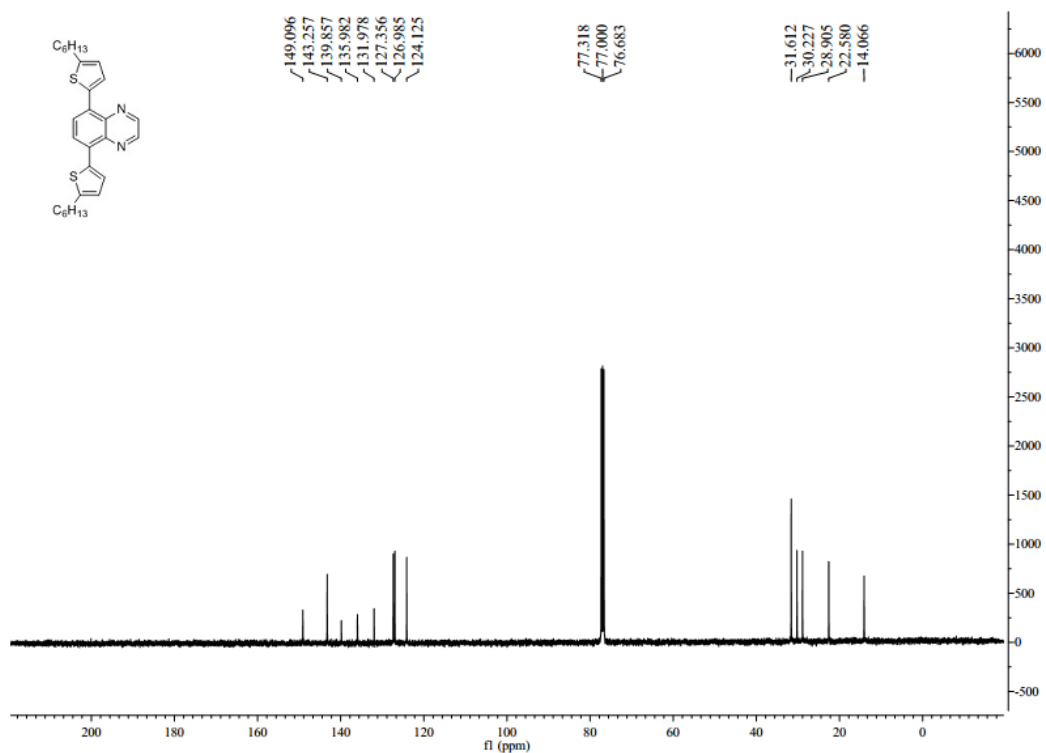
^1H NMR spectra of **4e** (400 MHz, DMSO- d_6)



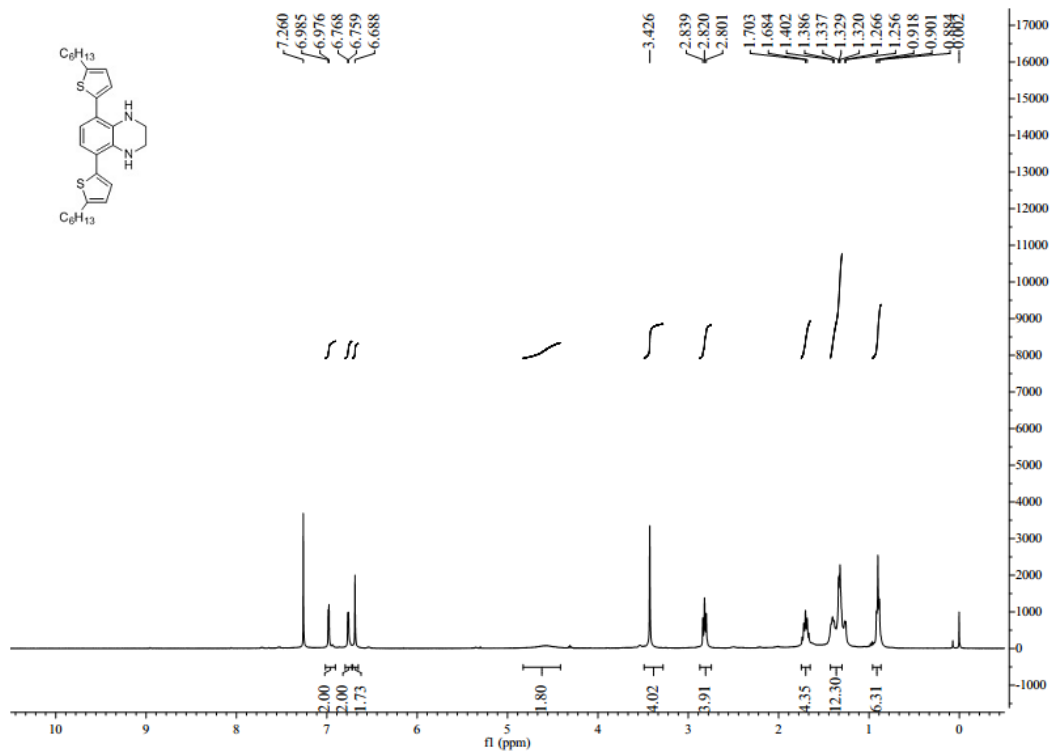
^1H NMR spectra (~90% purity) of **S4** (400 MHz, CDCl_3)



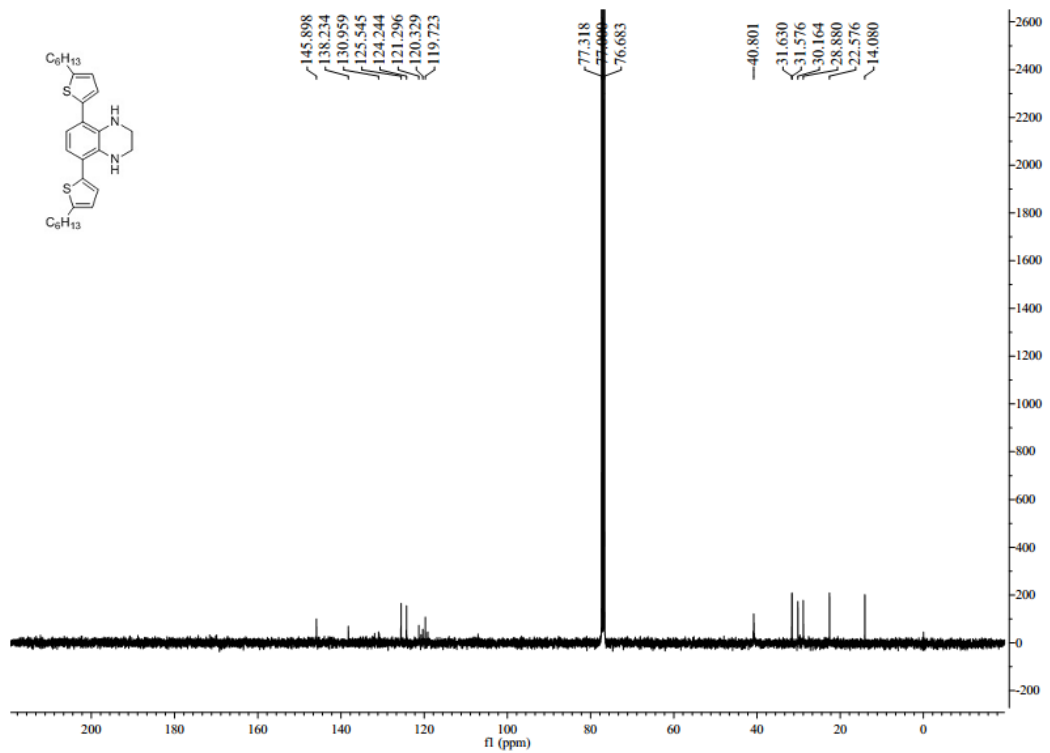
^1H NMR spectra of **2a'** (400 MHz, CDCl_3)



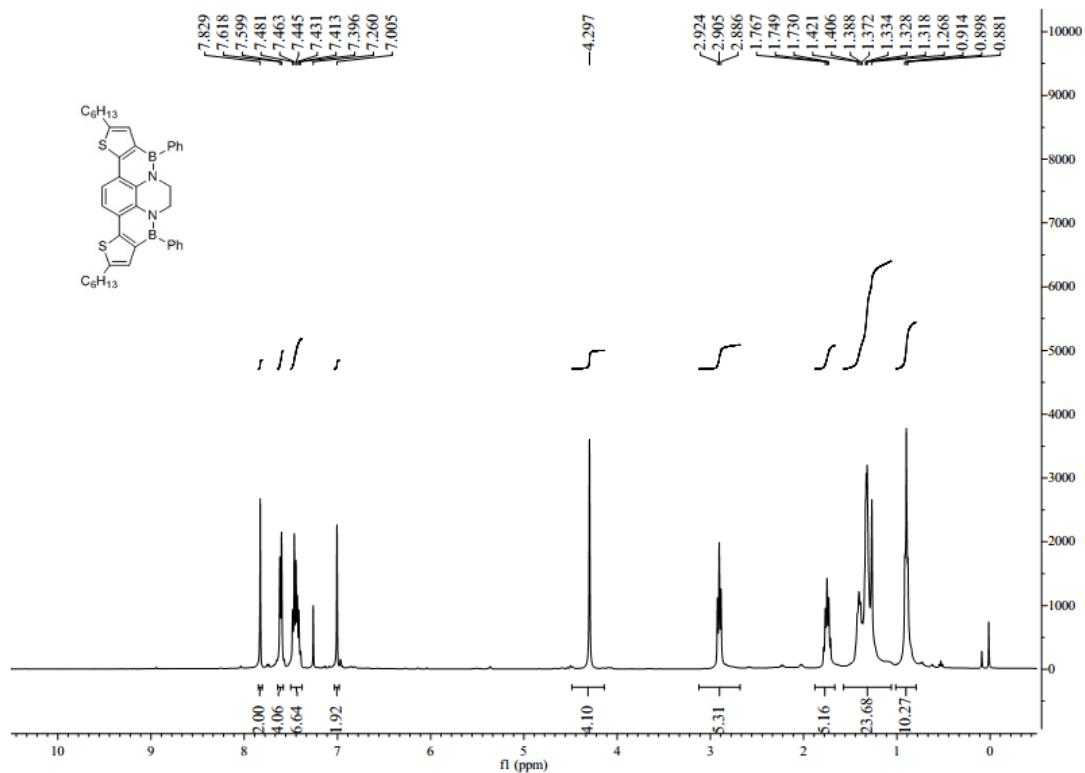
^{13}C NMR spectra of **2a'** (100 MHz, CDCl_3)



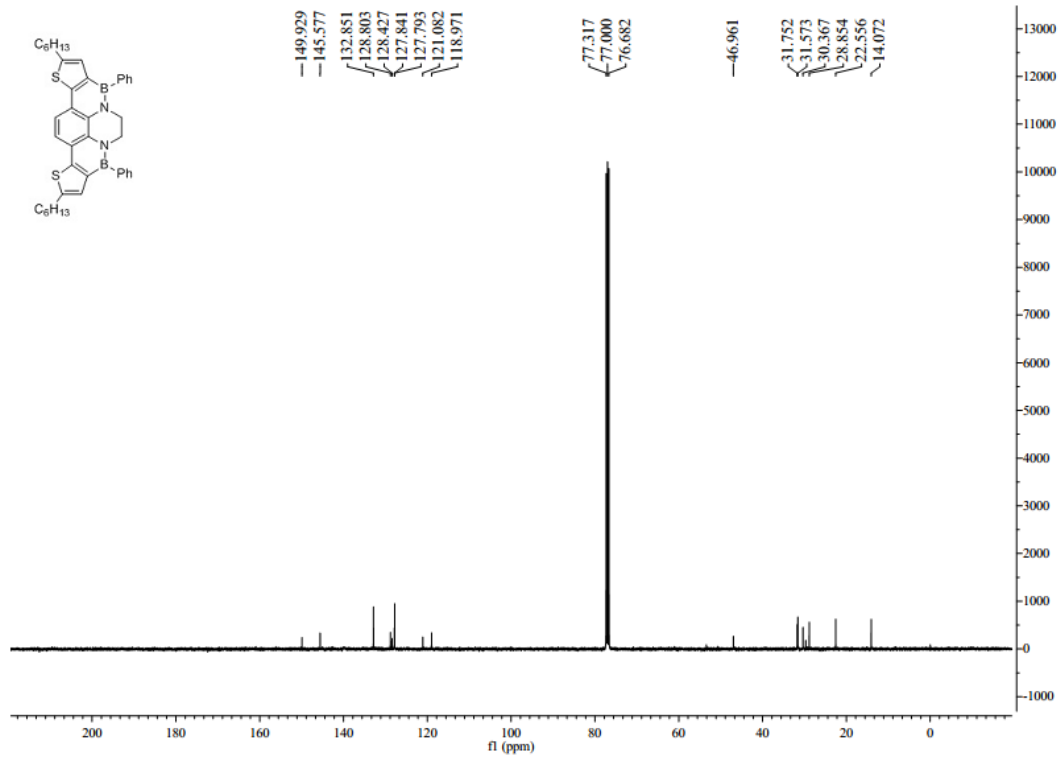
¹H NMR spectra of **3a'** (400 MHz, CDCl₃)



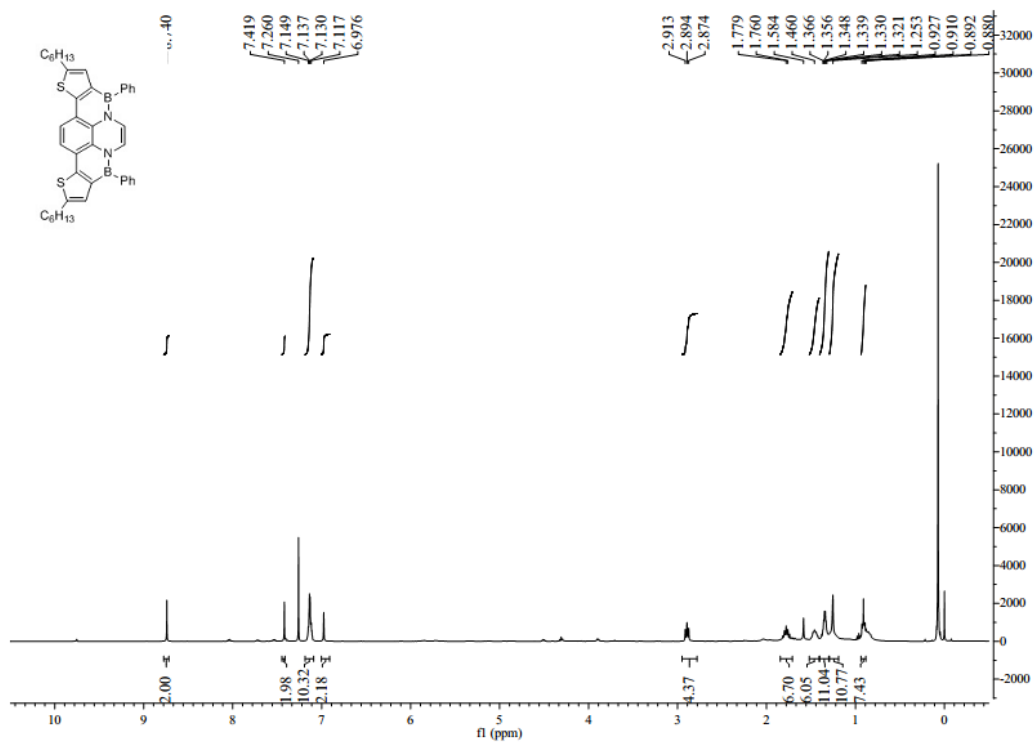
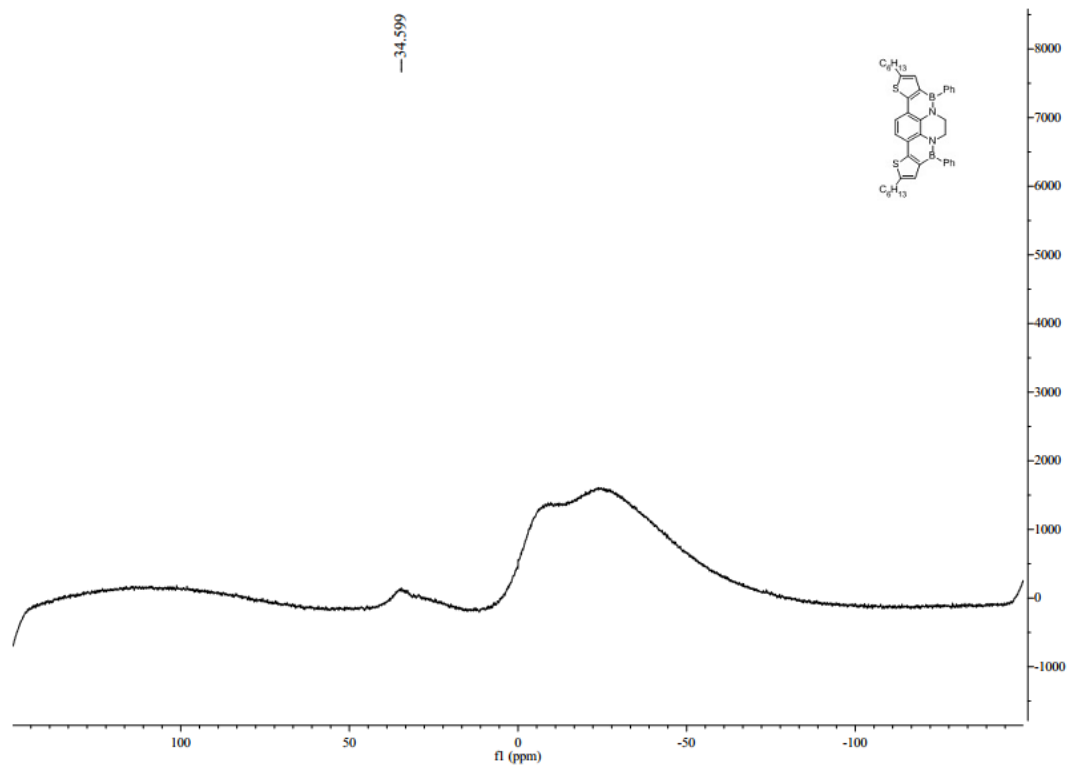
¹³C NMR spectra of **3a'** (100 MHz, CDCl₃)

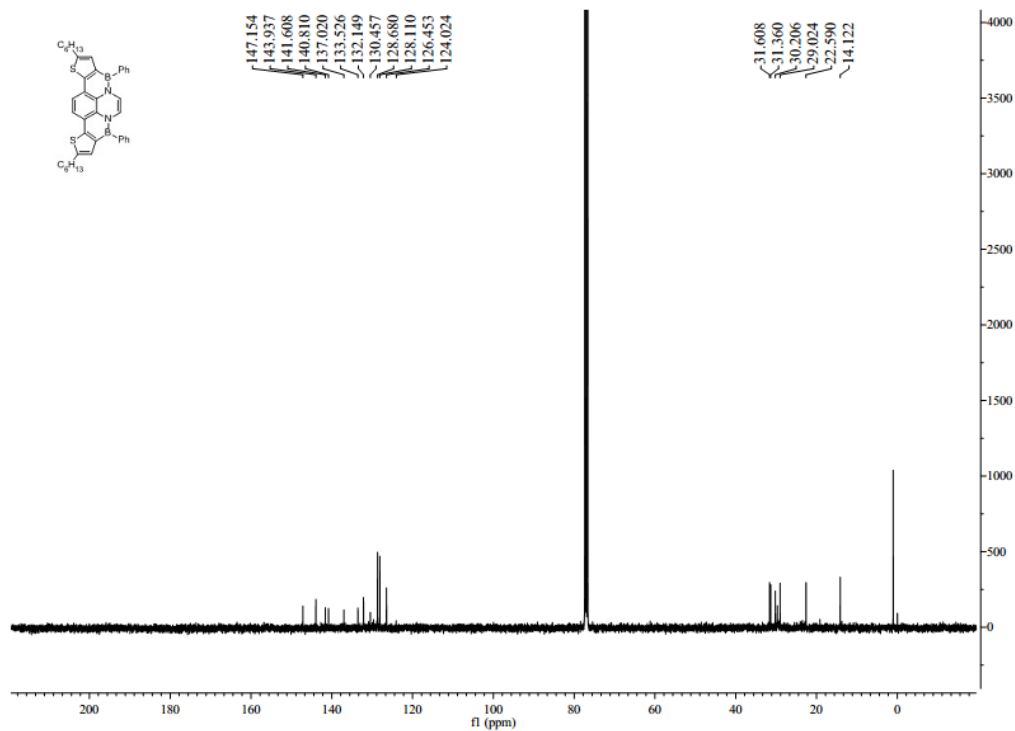


¹H NMR spectra of **4a'** (400 MHz, CDCl₃)

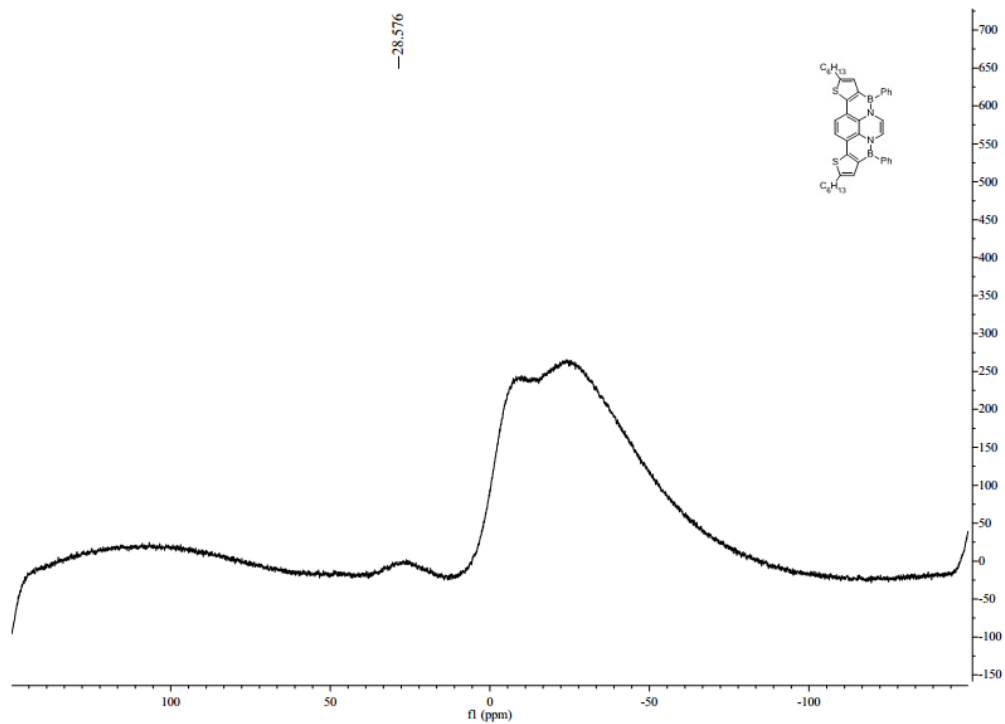


¹³C NMR spectra of **4a'** (100 MHz, CDCl₃)





¹³C NMR spectra of **5a'** (100 MHz, CDCl₃)



¹¹B NMR spectra of **5a'** (128 MHz)