Supporting Information

The rapid construction of bis-BN dipyrrolyl[*a,j*]anthracenes and a direct comparison with a carbonaceous analogue

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Contents

1. General

All oxygen-sensitive and moisture-sensitive manipulations were carried out under an inert atmosphere using either standard Schlenk techniques or a nitrogen-filled drybox. THF and toluene was purified by sodium absorption under argon. All other chemicals and solvents were purchased and used as received. 1,5-difluoro-2,4-dinitrobenzene, m-phenylenediamine, dimethyl sulfoxide, pyrrole, sodium borohydride, N,N-dimethylformamide, N-iodosuccinimide, dichlorophenylborane, triethylamine (extra dry, with molecular sieves), boron trichloride (1.0 M in toluene), methylmagnesium (3.00 M in diethyl ether), 1-bromohexane, n-BuLi (2.5 M in hexane), chlorobenzene, *o*-dichlorobenzene, 1,2-dichloroethane, bis(triphenylphosphine)palladium(II) chloride, acetonitrile, phenylacetylene, indium chloride were purchased from Energy Chemical (Shanghai, China). Bismuth trichloride, copper iodide was purchased from Heowns Biochemical Technology Co., Ltd. (Tianjin, China). Mesitylmagnesium bromide (1.00 M solution in THF) was purchased from J&K Chemical (Beijing, China). Sodium hydroxide was purchased from FuChen chemical reagent Co., Ltd. (Tianjin, China). Petroleum ether, ethyl acetate, dichloromethane, ethanol and THF were purchased from Hengshan Chemical (Tianjin, China). Acetic acid was purchased from Tianjin Chemical Reagent Company.

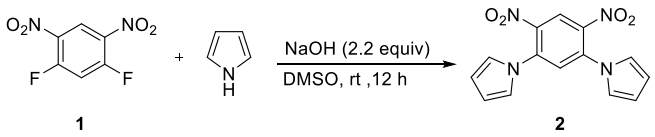
^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM-400 spectrometer. The reported chemical shifts were against TMS. ^{11}B spectra were recorded on a Bruker AM-400 spectrometer. The reported chemical shifts were against $BF_3 \cdot Et_2O$. HMRS were obtained on Waters Xevo Q-TOF MS with ESI. 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 Thermo Scientific Evolution 201 spectrophotometer. Fluorescence measurements were carried out with an F-7000 fluorescence spectrophotometer. Absolute quantum yields were measured by SPECORD 210 PLUS and Spectrofluorometer FLS1000.

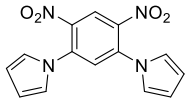
Data collections for compounds **4b, 4d**, **4e** and **9** were performed at 113 K on a Rigaku Saturn CCD diffractometer using graphite-monochromated MoK radiation (λ = 0.71073 Å).

2. Synthetic Procedures

Synthesis of bis-BN dipyrrolyl[*a,j*]anthracenes **4a-4f**:

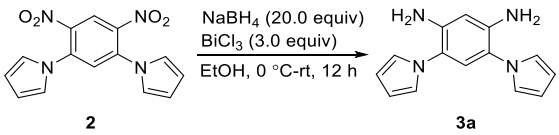


Scheme S1. Synthesis of **2**.

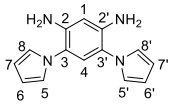


To a solution of 1,5-difluoro-2,4-dinitrobenzene (6.00 g, 29.40 mmol, 1.00 equiv) and sodium hydroxide (2.59 g, 64.68 mmol, 2.20 equiv) in dimethyl sulfoxide under N_2 was added pyrrole (4.49 ml, 64.68 mmol, 2.20 equiv).The reaction mixture was stirred at room temperature for 12 hours. Then, the mixture was quenched with water, and extracted with ethyl acetate three times. Combined organic layer was dried over $MgSO_4$. After removal of the solvents, the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1) to afford the title compound **2** as yellow solid (5.75 g, yield = 65%).

M.p.180-182 ºC.^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (s, 1H, Ar), 7.54 (s, 1H, Ar), 6.83 (t, *J* = 2.4 Hz, 4H, Ar), 6.45 (t, *J* = 2.4 Hz, 4H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.5, 138.0, 125.1, 123.6, 121.0, 113.1. FTIR (thin film): 2920, 2851, 1614, 1593, 1520, 1495, 1317, 1081, 1063, 909, 729. m/z calcd for ($C_{14}H_{10}N_4O_4$) $[M+H]^+$, 299.0775; found, 299.0780.



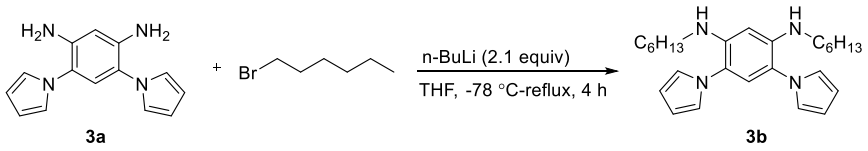
Scheme S2. Synthesis of **3a**.



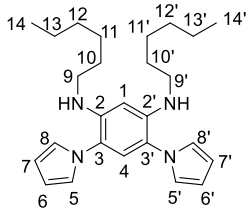
To a solution of **2** (586 mg, 1.97 mmol, 1.00 equiv) in ethanol (20 ml) was added $BiCl_3$ (1.86 g, 5.91 mmol, 3.00 equiv). Then, sodium borohydride (1.49 g, 39.40 mmol, 20.00 eqiuv) was added portion wise at 0 ºC to the reaction mixture. The reaction mixture was stirred at room temperature for 12 hours. Ethanol was evaporated under reduced pressure. The reaction was quenched with water and extracted with ethyl acetate three times. The combined organic layer was dried over $MgSO_4$. After removal of solvents under reduced pressure, the reside was purified by column chromatography on silica gel (using petroleum ether/ethyl acetate = 4/1 as eluent) to give **3a** as yellow solid (293 mg, yield = 63%).

M.p.106-108 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.00 (s, 1H, Ar, H-4), 6.79 (t, *J* = 2.0 HZ, 4H, Ar, H-5, H-5′, H-8, H-8′), 6.32 (t, *J* = 2.0 Hz, 4H, Ar, H-6, H-6′, H-7, H-7′),

6.16 (s, 1H, Ar, H-1), 3.68 (br, 4H, NH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.6 (C-2, C-2′), 126.1 (C-4), 122.1 (C-5, C-5′, C-8, C-8′), 118.6 (C-3), 109.2 (C-6, C-6′, C-7, C-7′), 101.4 (C-1). FTIR (thin film): 3344, 2919, 1631, 1611, 1525, 1490, 1296, 1061, 1001, 735, 702. m/z cacld for ($C_{14}H_{14}N_4$) $[M+H]^+$, 239.1297; found, 239.1303.

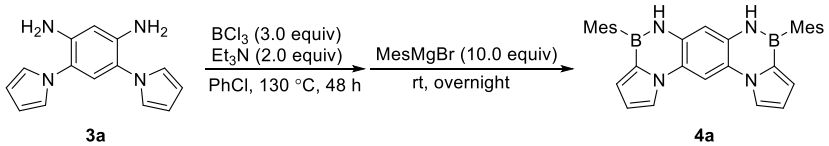


Scheme S3. Synthesis of **3b**.

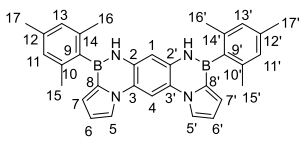


To a solution of **3a** (500 mg, 2.10 mml, 1.00 equiv) in THF (10 ml) under N_2 was added n-BuLi (2.5 M in hexane, 1.76 ml, 4.41 mmol, 2.10 equiv) dropwise at -78° C. After the mixture being stirred at -78° C for 1 hour, 1-bromohexane (1.39 g, 8.40 mmol, 4.00 equiv) was added under N_2. Then, the reaction mixture was heated at reflux for 4 hours. After removing the solvents under reduced pressure, the reddish-brown oil was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 80/1-50/1) to afford compound **3b** as yellow oil (436 mg, yield = 51%).

^1H NMR (400 MHz, $CDCl_3$): δ 6.97 (s, 1H, Ar, H-4), 6.75 (t, J = 2.0 Hz, 4H, Ar, H-5, H-5′, H-8, H-8′), 6.31 (t, J = 2.0 Hz, 4H, Ar, H-6, H-6′, H-7, H-7′), 5.98 (s, 1H, Ar, H-1), 3.72 (br, 2H, NH), 3.12 (t, J = 6.8 Hz, 4H, CH_2, H-9, H-9′), 1.53-1.56 (m, 4H, CH_2, H-10, H-10′), 1.28-1.38 (m, 12H, CH_2, H-11, H-11′, H-12, H-12′, H-13, H-13′), 0.91 (t, J = 6.4 Hz, 6H, CH_3, H-14, H-14′). ^{13}C NMR(100 MHz, $CDCl_3$): δ 144.8 (C-2, C-2′), 125.8 (C-4), 122.4 (C-5, C-5′, C-8, C-8′), 115.8 (C-3), 109.0 (C-6, C-6′, C-7, C-7′), 92.6 (C-1), 43.5 (C-9, C-9′), 31.4 (C-13, C-13′), 29.1 (C-10, C-10′), 26.6 (C-11, C-11′), 22.5 (C-12, C-12′), 14.0 (C-14, C-14′). FTIR (thin film): 3415, 2956, 2927, 2857, 1624, 1589, 1541, 1464, 1299, 1068, 726. m/z cacld for ($C_{26}H_{38}N_4$) $[M+H]^+$, 407.3175;found, 407.3176.



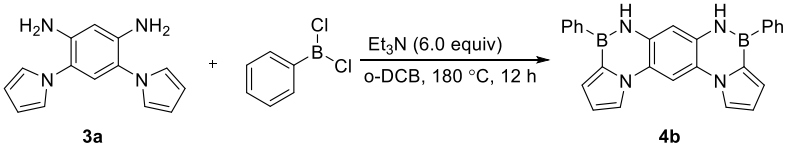
Scheme S4. Synthesis of **4a**.



To a solution of **3a** (500 mg, 2.10 mmol, 1.00 equiv) in chlorobenzene (10 ml) under N_2 was added boron trichloride solution (1.0 M in toluene, 6.30 mmol, 6.30 ml, 3.00 equiv) and triethylamine (584 μl, 4.20 mmol, 2.00 equiv). The reaction mixture was heated at reflux for 48 hours. After the reaction cooling down,

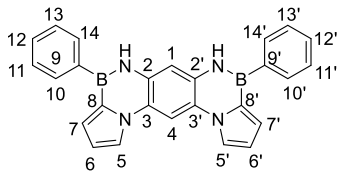
mesitylmagnesium bromide (1.0 M in THF, 21.00 mmol, 21.00 ml, 10.00 equiv) was added to the reaction mixture at room temperature. After stirring at the room temperature overnight, the mixture was quenched with water, and extracted with ethyl acetate three times, the combined organic layer was dried over $MgSO_4$. After removal of the solvents, the yellow oil was first purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50/1-20/1) then recrystallization from CH_2Cl_2 and hexane to give **4a** as pale-yellow crystals (659 mg, yield = 64%).

M.p. 210-212 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (s, 1H, Ar, H-4), 8.02 (d, *J* = 1.6 Hz, 2H, Ar, H-5, H-5′), 6.95 (s, 4H, Ar, H-11, H-11′, H-13, H-13′), 6.88 (br, 2H, NH), 6.85 (s, 1H, Ar, H-1), 6.82 (t, *J* = 2.4 Hz, 2H, Ar, H-7, H-7′), 6.74 (t, *J* = 2.4 Hz, 2H, Ar, H-6, H-6′), 2.38 (s, 6H, CH_3, H-17, H-17′), 2.27 (s, 12H, CH_3, H-15, H-15′, H-16, H-16′). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.4 (C-10, C-10′, C-14, C-14′), 137.8 (C-12, C-12′), 135.0 (C-9, C-9′), 132.3 (C-8, C-8′), 128.6 (C-2, C-2′), 127.1 (C-11, C-11′, C-13, C-13′), 123.0 (C-3, C-3′), 119.0 (C-7, C-7′), 117.2 (C-5, C-5′), 112.6 (C-6, C-6′), 108.3 (C-1), 102.2 (C-4), 22.6 (C-15, C-15′, C-16, C-16′), 21.2 (C-17, C-17′). ^{11}B NMR (128MHz, $BF_3{\cdot}OEt_2$): δ 35.3. FTIR (thin film): 3361, 2916, 2857, 1545, 1463, 1333, 1296, 1031, 891, 849, 730, 707. m/z cacld for ($C_{32}H_{32}B_2N_4$) $[M+H]^+$, 495.2902; found, 495.2903.



3a 4b

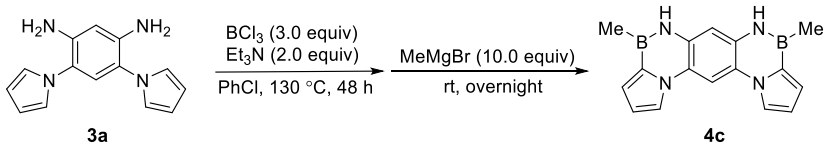
Scheme S5. Synthesis of **4b**.



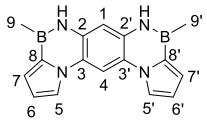
To a solution of **3a** (200 mg, 0.84 mmol, 1.00 equiv) in *o*-dichlorobenzene (5 ml) under N_2 was added phenyldichloroborane (327 µl, 2.52 mmol, 3.00 equiv) and triethylamine (701 µl, 5.04 mmol, 6.00 equiv). The reaction mixture was refluxed for 12 hours. The mixture was quenched with water, and extracted with ethyl acetate three times. Combined organic layer was dried over $MgSO_4$. After removal of the solvents, the reside was first purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1) then recrystallization from mixture of CH_2Cl_2 and hexane to give **4b** as yellow crystals (265 mg, yield = 77%).

M.p. 217-219 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (s, 1H, H-4), 7.97-7.98 (m, 2H, H-5, H-5′), 7.93-7.96 (m, 4H, H-10, H-10′, H-14, H-14′), 7.50-7.53 (m, 6H, H-10, H-10′, H-11, H-11′, H-12, H-12′), 7.22 (d, *J* = 2.8 Hz, H-7, H-7′), 7.02 (br, 2H, NH), 6.96 (s, 1H, H-1), 6.79 (t, *J* = 2.8 Hz, H-6, H-6′). ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.0 (C-10, C-10′, C-14, C-14′), 129.8 (C-12, C-12′), 128.8 (C-2, C-2′), 128.2 (C-11, C-11′, C-13, C-13′), 122.9 (C-3, C-3′), 119.0 (C-7, C-7′), 117.5 (C-5, C-5′), 112.8 (C-6, C-6′), 108.3 (C-1, C-1′), 102.2 (C-4, C-4′) (B-aryl carbon signals were not observed). ^{11}B NMR (128MHz, $BF_3{\cdot}OEt_2$): δ 33.0. FTIR (thin film): 3397, 2923, 2852, 1545, 1499,

1464, 1338, 1299, 725, 701, 648. m/z cacld for ($C_{26}H_{20}B_2N_4$) $[M+H]^+$, 411.1961; found, 411.1957.

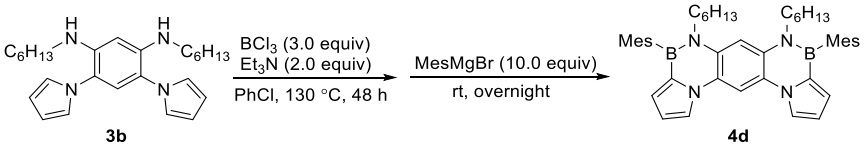


Scheme S6. Synthesis of **4c**.

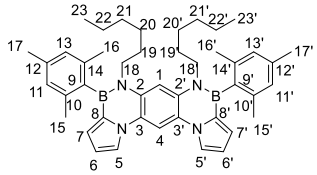


To a solution of **3a** (500 mg, 2.10 mmol, 1.00 equiv) in chlorobenzene (10 ml) under N_2 was added boron trichloride solution (1.0 M in toluene, 6.30 ml, 6.30 mmol, 3.00 equiv) and triethylamine (584.00 µl, 4.20 mmol, 2.00 equiv). The reaction mixture was refluxed for 48 hours. Methylmagnesium bromide (3.0 M in diethyl ether, 7.00 ml, 21.00 mmol, 10.00 equiv) was added to the reaction mixture at room temperature. After stirring at the same temperature overnight, the mixture was quenched with water, and extracted with ethyl acetate three times. The combined organic layer was dried over $MgSO_4$. After removal of the solvents, the reside was first purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1-4/1) then recrystallization from mixture of CH_2Cl_2 and hexane to give **4c** as white crystals (380 mg, yield = 63%).

M.p. 210-212 °C. ^{1}H NMR (400 MHz, d_6-DMSO): δ 9.26 (s, 2H, NH), 8.54 (s, 1H, Ar, H-4), 8.44 (d, J = 1.6 Hz, 2H, Ar, H-5, H-5′), 7.26 (s, 1H, Ar, H-1), 6.83 (dd, J_1 = 0.8 Hz, J_2 = 3.2 Hz, 2H, Ar, H-7, H-7′), 6.59-6.62 (m, 2H, Ar, H-6, H-6′), 0.76 (s, 6H, H-9, H-9′). ^{13}C NMR (100 MHz, d_6-DMSO): δ 129.8 (C-2, C-2′), 122.1 (C-3, C-3′), 118.8 (C-5, C-5′), 116.8 (C-7, C-7′), 112.1 (C-6, C-6′), 108.2 (C-1), 102.9 (C-4), 0.2 (C-9, C-9′**)** (B-aryl carbon signals were not observed). ^{11}B NMR (128 MHz, $BF_3{\cdot}OEt_2$): δ 36.3. FTIR (thin film): 3346, 2959, 2931, 1544, 1414, 1350, 1297, 1162, 1104, 848, 792, 700. m/z cacld for ($C_{16}H_{16}B_2N_4$) $[M+H]^+$, 287.1634; found, 287.1632.



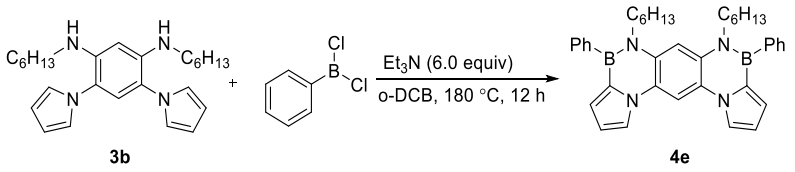
Scheme S7. Synthesis of **4d**.



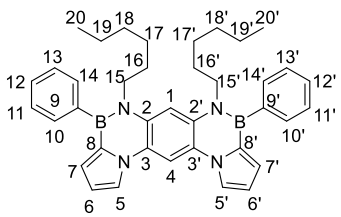
To a solution of **3b** (511 mg, 1.26 mmol, 1.00 equiv) in chlorobenzene (8 ml) under N_2 was added boron trichloride solution (1.0 M in toluene, 3.80 ml, 3.80 mmol, 3.00 equiv) and triethylamine (350 µl, 2.52 mmol, 2.00 equiv). The reaction mixture was refluxed for 48 hours.

Methylmagnesium bromide (1.0 M in diethyl ether, 13.00 ml, 12.60 mmol, 10.00 equiv) was added to the reaction mixture at room temperature. After stirring at room temperature overnight, the mixture was quenched with water, and extracted with ethyl acetate three times. The combined organic layer was dried over $MgSO_4$. After removal of the solvents, the reside was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1) to afford **4d** as yellow solid (634 mg, yield = 76 %).

M.p. 170-172 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (s, 1H, Ar, H-4), 7.97 (d, *J* = 1.2 Hz, 2H, Ar, H-5, H-5′), 7.43 (s, 1H, Ar, H-1), 6.92 (s, 4H, Ar, H-11, H-11′, H-13, H-13′), 6.67 (t, *J* = 3.2 Hz, 2H, Ar, H-6, H-6′), 6.60 (d, *J* = 2.4 Hz, 2H, Ar, H-7, H-7′), 3.78 (t, *J* = 8.0 Hz, 4H, CH_2, H-18, H-18′), 2.37 (s, 6H, CH_3, H-17, H-17′), 2.20 (s, 12H, CH_3, H-15, H-15′, H-16, H-16′), 1.70-1.78 (m, 4H, CH_2, H-19, H-19′), 1.13-1.27 (m, 12H, CH_2, H-20, H-20′, H-21, H-21′, H-22, H-22′), 0.81 (t, *J* = 6.4 Hz, 6H, CH_3, H-23, H-23′). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.4 (C-10, C-10′, C-14, C-14′), 137.1 (C-12, C-12′), 136.0 (C-9, C-9′), 132.6 (C-8, C-8′), 129.9 (C-2, C-2′), 127.2 (C-11, C-11′, C-13, C-13′), 123.8 (C-3, C-3′), 118.5 (C-7, C-7′), 116.5 (C-5, C-5′), 112.6 (C-6, C-6′), 104.9 (C-1), 102.5 (C-4), 47.8 (C-18, C-18′), 31.4 (C-22, C-22′), 29.2 (C-19, C-19′), 27.0 (C-20, C-20′), 22.5 (C-15, C-15′, C-16, C-16′, C-21, C-21′), 21.3 (C-17, C-17′), 13.9 (C-23, C-23′). ^{11}B NMR (128MHz, $BF_3{\cdot}OEt_2$): δ 36.3. FTIR (thin film): 2956, 2927, 2857, 1069, 1588, 1439, 1383, 1316, 1183, 1031, 726. m/z cacld for ($C_{44}H_{56}B_2N_4$) $[M+H]^+$, 663.4783; found, 663.4779.



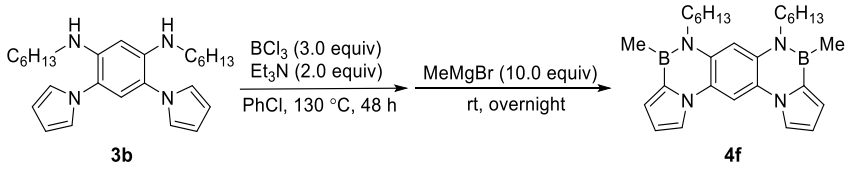
Scheme S8. Synthesis of **4e**.



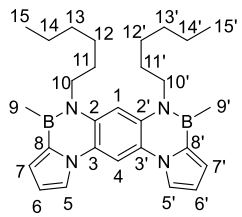
To a solution of **3b** (300 mg, 0.74 mmol, 1.00 equiv) in *o*-dichlorobenzene (5 ml) under N_2 was added phenyldichloroborane (287 µl, 2.22 mmol, 3.00 equiv) and triethylamine (617 µl, 4.44 mmol, 6.00 equiv). The reaction mixture was refluxed for 12 hours. The mixture was quenched with water, and extracted with ethyl acetate three times; the combined organic layer was dried over $MgSO_4$. After removal of the solvents, the reside was first purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1-4/1) then recrystallization from mixture of CH_2Cl_2 and hexane to give **4e** as pale yellow crystals (190 mg, yield = 44%).

M.p. 120-122 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (s, 1H, H-4), 7.98 (t, *J* = 2.0 Hz, 2H, H-5), 7.65-7.68 (m, 4H, H-10, H-10′, H-14, H-14′), 7.45-7.52 (m, 7H, H-11, H-11′, H-12, H-12′, H-13, H-13′, H-1), 6.72 (d, *J* = 1.6 Hz, 4H, H-6, H-6′, H-7, H-7′), 4.00 (t, *J* = 7.6 Hz, 4H, H-15, H-15′), 1.79-1.86 (m, 4H, H-16, H-16′), 1.19-1.31 (m,

12H, H-17, H-17′, H-18, H-18′, H-19, H-19′), 0.85 (t, J = 6.4 Hz, 6H, H-20, H-20′). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.3 (C-9, C-9′), 133.3 (C-8, C-8′), 132.3 (C-12, C-12′, C-14, C-14′), 129.8 (C-2, C-2′), 128.0 (C-12, C-12′), 127.7 (C-11, C-11′, C-13, C-13′), 123.8 (C-3, C-3′), 119.3 (C-6/C-6′ or C-7/C-7′), 116.8 (C-5, C-5′), 112.7 (C-6/C-6′ or C-7/C-7′), 105.4 (C-1, C-1′), 102.5 (C-4, C-4′), 47.5 (C-15, C-15′), 31.5 (C-19, C-19′), 29.8 (C-16, C-16′), 26.8 (C-17, C-17′), 22.6 (C-18, C-18′), 13.9 (C-20, C-20′). ^{11}B NMR (128MHz, $BF_3{\cdot}OEt_2$): δ 35.7. FTIR (thin film): 2956, 2928, 2856, 1590, 1520, 1387, 1182, 1031, 845, 754. m/z cacld for ($C_{38}H_{44}B_2N_4$) $[M+H]^+$, 579.3843; found, 579.3842.

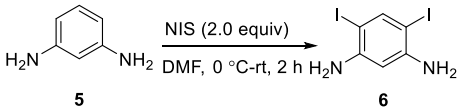


Scheme S9. Synthesis of **4f**.

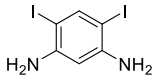


To a solution of **3b** (213 mg, 0.52 mmol, 1.00 equiv) in chlorobenzene (10 ml) under N_2 was added boron trichloride solution (1.0 M in hexane, 1.57 ml, 1.57 mmol, 3.00 equiv) and triethylamine (145 μl, 1.04 mmol, 2.00 equiv). The reaction mixture was refluxed for 48 hours. Methylmagnesium bromide (3.0 M in diethyl ether, 1.80 ml, 5.20 mmol, 10.00 equiv) was added to the reaction mixture at room temperature. After stirring at the room temperature overnight, the mixture was quenched with water, and extracted with ethyl acetate three times; the combined organic layer was dried over $MgSO_4$. After removal of the solvents, the reside was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1) to afford compound **4f** (231 mg, yield = 98 %). M.p. 136-138 °C.^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (s, 1H, Ar, H-4), 7.81 (d, J = 1.2 Hz, 2H, Ar, H-5, H-5′), 7.18 (s, 1H, Ar, H-1), 6.96 (dd, J_1 = 3.2 Hz, J_2 = 0.8 Hz, 2H, Ar, H-7, H-7′), 6.68 (dd, J_1 = 3.6 Hz, J_2 = 2.4 Hz, 2H, Ar, H-6, H-6′), 3.86 (t, J = 7.6 Hz, 4H, CH_2, H-10, H-10′), 1.72-1.78 (m, 4H, CH_2, H-11, H-11′), 1.41-1.46 (m, 4H, CH_2, H-12, H-12′), 1.34-1.38 (m, 8H, CH_2, H-13, H-13′, H-14, H-14′), 0.94 (t, J = 6.4 Hz, 6H, CH_3, H-15, H-15′), 0.93 (s, 6H, BCH_3, H-9, H-9′). ^{13}C NMR (100 MHz, $CDCl_3$): δ 129.9 (C-2, C-2′), 122.8 (C-3, C-3′), 116.8 (C-7, C-7′), 116.3 (C-5, C-5′), 112.1 (C-6, C-6′), 103.4 (C-1), 102.2 (C-4), 46.7 (C-10, C-10′), 31.8 (C-14, C-14′), 29.5 (C-11, C-11′), 27.1 (C-12, C-12′), 22.8 (C-13, C-13′), 14.1 (C-15, C-15′), 0.4 (C-9, C-9′) (B-aryl carbon signals were not observed). ^{11}B NMR (128MHz, $BF_3{\cdot}OEt_2$): δ 37.2. FTIR (thin film): 2956, 2924, 2855, 1549, 1520, 1464, 1417, 1386, 840, 782. m/z cacld for ($C_{28}H_{40}B_2N_4$) $[M+H]^+$, 455.3527; found, 455.3524.

Synthesis of dipyrrolyl[*a*,*j*]anthracene **9**:

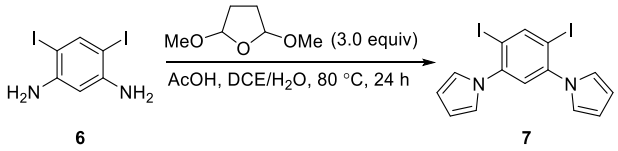


Scheme S10. Synthesis of **6**.

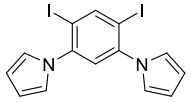


A solution of 1,3-benzenediamine (200 mg, 1.85 mmol, 1.00 equiv) in N,N-dimethylformamide was cooled to 0 ºC. N-iodosuccinimide (832 mg, 3.70 mmol, 2.00 equiv) was added slowly at 0 ºC, then it was allowed to room temperature and stirred at room temperature for 2 hours. Then, the mixture was quenched with water, extracted with ethyl acetate three times. Combined organic layer was dried over $MgSO_4$. After removal of the solvents, the residue was purified by column chromatography on silica gel (eluent: dichloromethane) to afford the title compound **6** as white solid (415mg, yield = 62%). The ^1H NMR was identical to the reported data. [1]

^1H NMR (400 MHz, $CDCl_3$): δ 7.75 (s, 1H, Ar), 6.21 (s, 1H, Ar), 4.00 (br, 4H, NH_2).

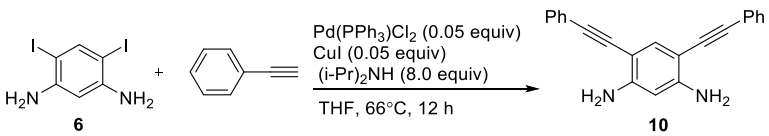


Scheme S11. Synthesis of **7**.

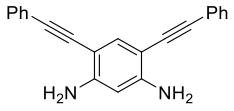


A mixture of 1,3-diiodo-4,6-diaminobenzene (394 mg, 1.07 mmol, 1.00 equiv), 2,5-dimethoxytetrahydrofuran (415 µl, 3.19 mmol, 3.00 equiv) and acetic acid (172 µl, 3.00 mmol, 2.80 equiv) in 1,2-dichloroethane (10 ml) and H_2O (6 ml) was heated at 80 ºC for 24 hours. Then, the mixture was quenched with water, and extracted with ethyl acetate three times. Combined organic layer was dried over $MgSO_4$. After removal of the solvents, the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 80/1) to afford the title compound **7** (98 mg, yield = 20%) as white solid.

M.p. 108-110ºC. ^1H NMR (400 MHz, $CDCl_3$): δ 8.51 (s, 1H, Ar), 7.21 (s, 1H, Ar), 6.83-6.84 (m, 4H, Ar), 6.33-6.36 (m, 4H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.6, 144.7, 126.5, 121.8, 110.0, 94.6. FTIR (thin film): 3098, 1487, 1453, 1382, 1303, 1265, 1118, 1073, 959, 891, 876, 726. m/z calcd for ($C_{14}H_{10}I_2N_2$) $[M+H]^+$, 460.9012; found, 460.9015.

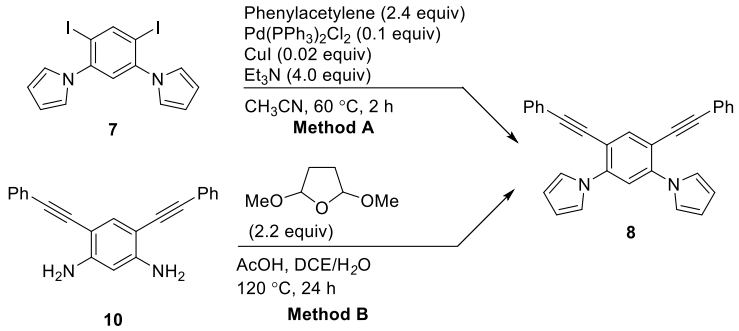


Scheme S12. Synthesis of **10**.

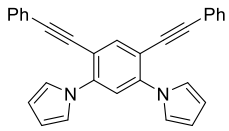


To a solution of **6** (2.56 g, 7.10 mmol, 1.00 equiv) bis(triphenylphosphine)palladium(II) chloride (249 mg, 0.36 mmol, 0.05 equiv) and copper iodide (68 mg, 0.36 mmol, 0.05equiv) in THF under N_2 was added diisopropylamine (8.00 ml, 56.80 mmol, 8.00 equiv) and phenylacetylene (2.00 ml, 17.03 mmol, 2.40 equiv).The reaction mixture was stirred at 66 ºC for 12 hours. THF was evaporated under reduced pressure, the reside was quenched with water, and extracted with ethyl acetate three times. Combined organic layer was dried over $MgSO_4$. After removal of the solvents, the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1-3/1) to give the title compound **10** as yellow solid (1.34 g, yield = 61%). The procedure is following literature's procedure. [2]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 4H, Ar), 7.45 (s, 1H, Ar),7.30-7.37 (m, 6H, Ar), 6.03 (s, 1H, Ar), 4.36 (s, 4H, NH_2).



Scheme S13. Synthesis of **8**.

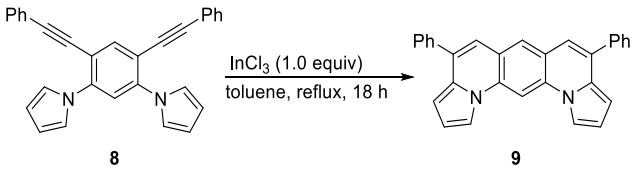


Method A: To a solution of **7** (360 mg, 0.78 mmol, 1.00 equiv) bis(triphenylphosphine)palladium(II) chloride (55 mg, 0.078 mmol, 0.10 equiv) and copper iodide (3 mg, 0.016 mmol, 0.02 equiv) in acetonitrile under N_2 was added triethylamine (260 µl, 1.87 mmol, 4.00 equiv) and phenylacetylene (206 µl, 1.88 mmol, 2.40 equiv).The reaction mixture was stirred at 60 ºC for 2 hours. Then, the mixture was quenched with water, and extracted with ethyl acetate three times. Combined organic layer was dried over $MgSO_4$. After removal of the solvents, the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50/1) to give the title compound **8** as white solid (263 mg, yield = 83%).

Method B: A mixture of **10** (1.34 g, 4.35 mmol, 1.00 equiv) and 2,5-dimethoxytetrahydrofuran (1.30 ml, 9.57 mmol, 2.20 equiv) in acetic acid (30 ml), 1,2-dichloroethane (30 ml) and H_2O (30 ml) was heated at 120 ºC for 24 hours. Then, the mixture was quenched with water, and extracted with ethyl acetate three times. Combined organic layer was dried over $MgSO_4$. After removal of the solvents, the residue was purified by column chromatography on silica gel (eluent: petroleum

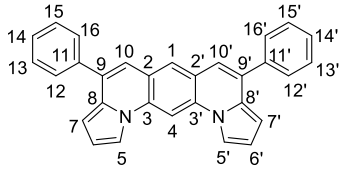
ether/ethyl acetate = 60/1) to afford the title compound **8** as white solid (728 mg, yield = 41%).

M.p. 48-50 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (s, 1H, Ar), 7.45-7.50 (m, 4H, Ar), 7.33-7.38 (m, 6H, Ar), 7.34 (s, 1H, Ar), 7.25-7.26 (m, 4H, Ar), 6.39-6.41 (m, 4H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$): 142.0, 138.8, 131.5, 128.8, 128.4, 122.6, 121.5, 120.5, 115.5, 110.1, 94.7, 85.3. FTIR (thin film): 2922, 2850, 1625, 1491, 1446, 1359, 1343, 1294, 895, 762, 698. m/z calcd for ($C_{30}H_{20}N_2$) $[M+H]^+$, 409.1705; found, 409.1708.



8 **9**

Scheme S14. Synthesis of **9**.



A solution of **8** (237 mg, 0.58 mmol, 1.00 equiv) and indium chloride (128 mg, 0.58 mmol, 1.00 equiv) in toluene was heated at reflux for 18 hours. Then, the mixture was quenched with water, and extracted with ethyl acetate three times. Combined organic layer was dried over $MgSO_4$. After removal of the solvents, the residue was first purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate=50:1) then recrystallization from mixture of CH_2Cl_2/hexane to give **9** as yellow crystals (108 mg, yield = 46%).

M.p. 192-194 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (s, 1H, H-4), 8.03-8.04 (m, 2H, H-5, H-5′), 7.94 (s, 1H, H-1), 7.74 (d, J = 6.8 Hz, 4H, H-12, H-12′, H-16, H-16′), 7.49-7.53 (m, 4H, H-13, H-13′, H-15, H-15′), 7.43-7.48 (m, 2H, H-14, H-14′), 7.06 (s, 2H, H-10, H-10′), 6.86 (t, J = 6.8 Hz, 2H, H-6, H-6′), 6.66-6.67 (m, 2H, H-7, H-7′). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.8 (H-11, H-11′), 132.4 (H-2, H-2′), 132.0 (H-9, H-9′), 130.9 (H-8, H-8′), 128.6 (H-13, H-13′, H-15, H-15′), 128.34 (H-12, H-12′, H-16, H-16′), 128.25 (H-1), 128.1 (H-14, H-14′), 121.2 (H-3, H-3′), 117.7 (H-10, H-10′), 113.2 (H-5/H-5′ or H-6/H-6′), 113.2 (H-5/H-5′ or H-6/H-6′), 104.3 (H-7, H-7′), 98.4 (H-4, H-4′). FTIR (thin film): 2922, 2850, 1624, 1600, 1491, 1446, 1419, 1359, 1343, 1295, 1105, 893, 826, 781, 726, 735. m/z calcd for ($C_{30}H_{20}N_2$) $[M+H]^+$, 409.1705; found, 409.1697.

3. Thermogravimetric Analysis

In the range of 40 °C to 800 °C, TA 209F3A thermogravimeter of NETZSCH (in Germany) was selected to perform the thermogravimetric analysis (TGA) of target molecules, under nitrogen atmosphere at a heating rate of 10 °C min^{-1}.

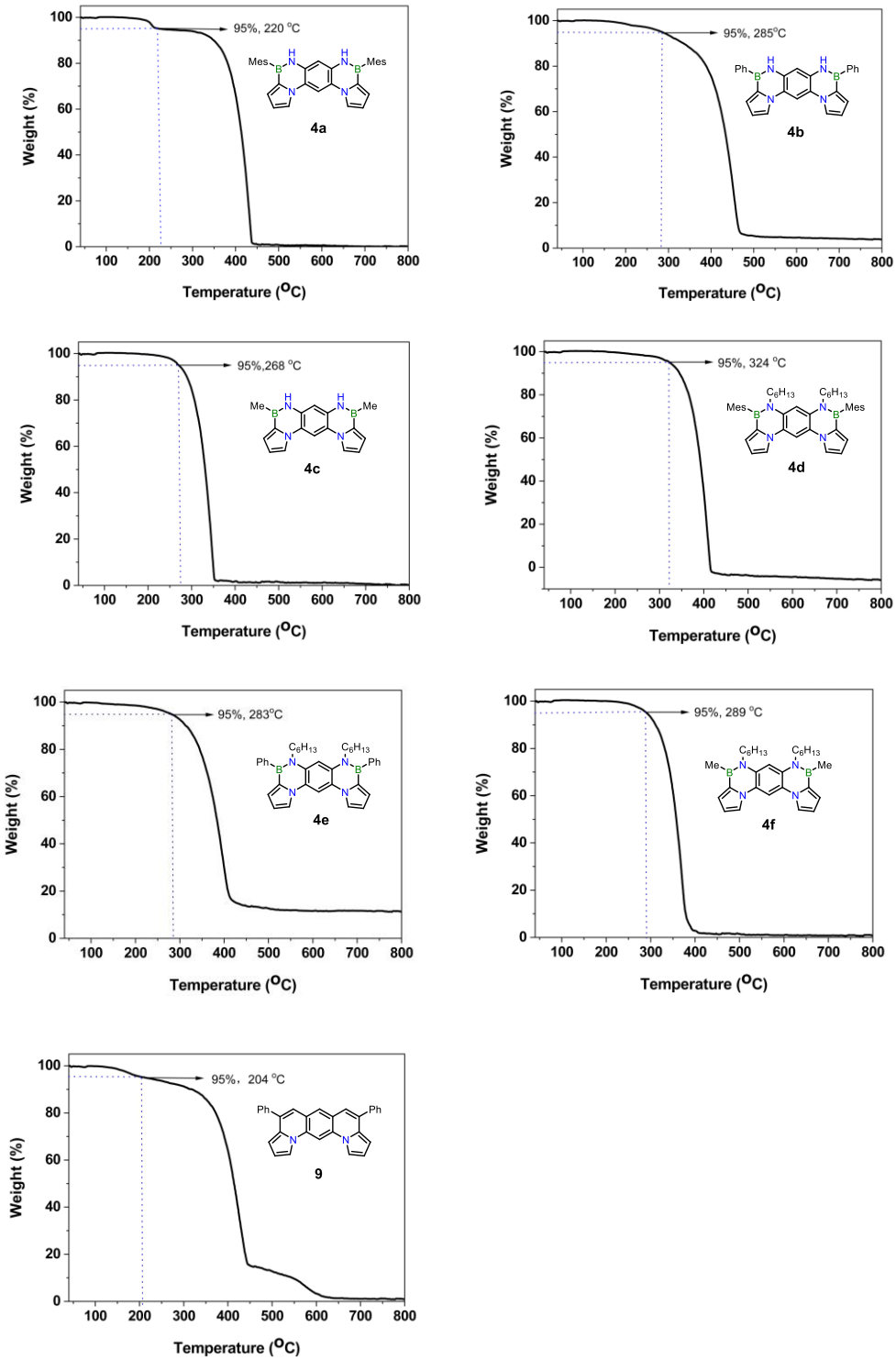


Figure S1. TG curves of Bis-BN dipyrrolyl[*a,j*]anthracenes **4a**-**4f** and dipyrrolyl[*a,j*]anthracene **9**.

4. Photophysical Properties

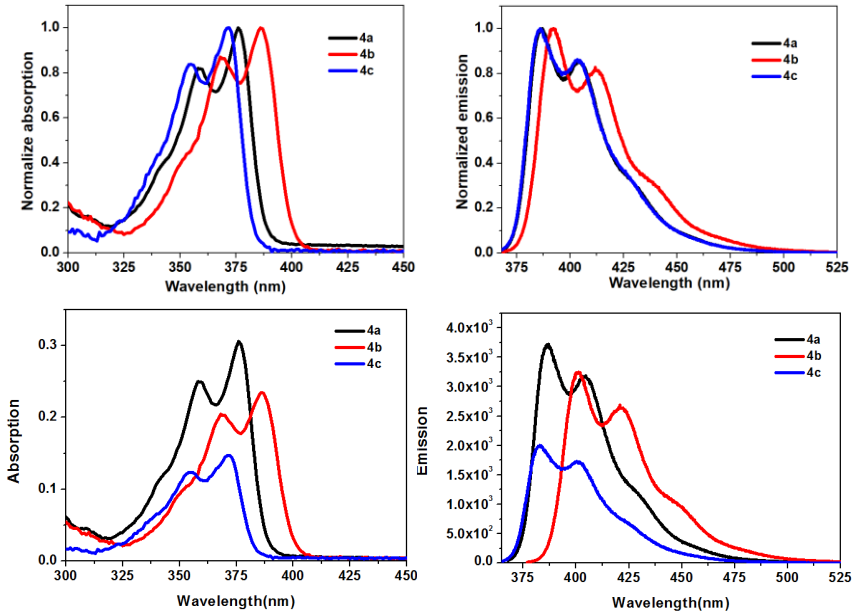


Figure S2. Normalized absorption (top left) and emission (top right) spectra of bis-BN dipyrrolyl[*a,j*]anthracenes **4a**, **4b** and **4c** in dichloromethane at a concentration of 1×10^{-5}M. Absorption (bottom left) and emission (bottom right) spectra of bis-BN dipyrrolyl[*a,j*]anthracenes **4a**, **4b** and **4c** in dichloromethane at a concentration of 1×10^{-5}M.

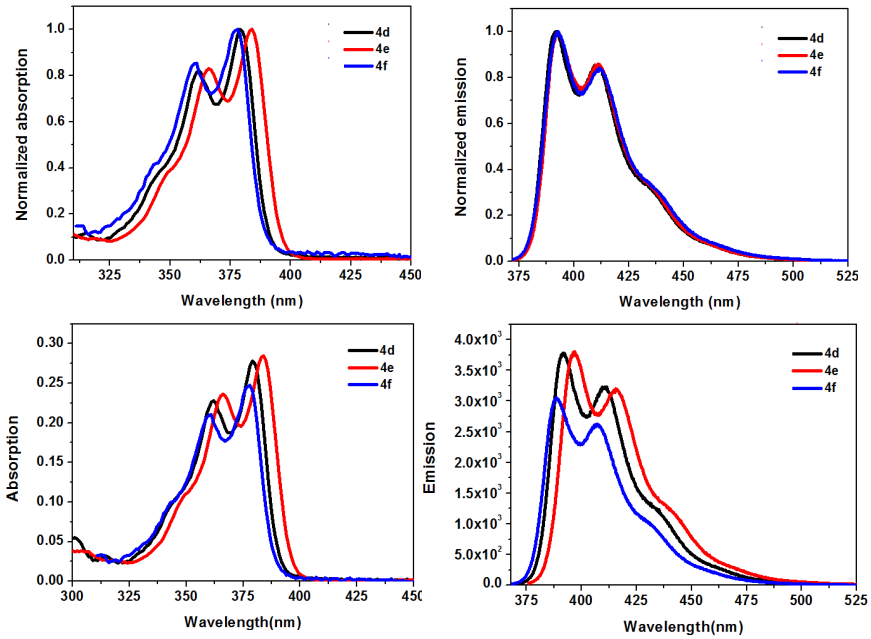


Figure S3. Normalized absorption (top left) and emission (top right) spectra of bis-BN dipyrrolyl[*a,j*]anthracenes **4d**, **4e** and **4f** in dichloromethane at a concentration of 1×10^{-5}M. Absorption (bottom left) and emission (bottom right) spectra of bis-BN dipyrrolyl[*a,j*]anthracenes **4d**, **4e** and **4f** in dichloromethane at a concentration of 1×10^{-5}M.

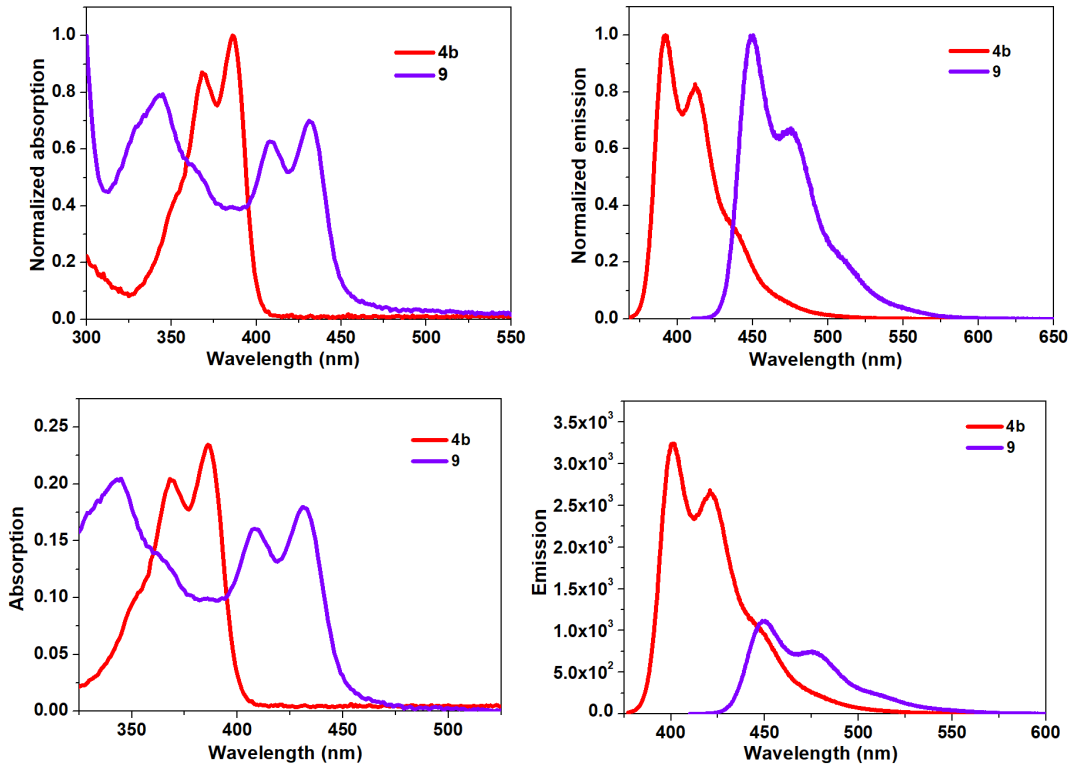


Figure S4. Normalized absorption (top left) and emission (top right) spectra of bis-BN dipyrrolyl[*a,j*]anthracene **4b** and dipyrrolyl[*a,j*]anthracene **9** in dichloromethane at a concentration of 1×10^{-5}M. Absorption (bottom left) and emission (bottom right) spectra of bis-BN dipyrrolyl[*a,j*]anthracene **4b** and dipyrrolyl[*a,j*]anthracene **9** in dichloromethane at a concentration of 1×10^{-5}M.

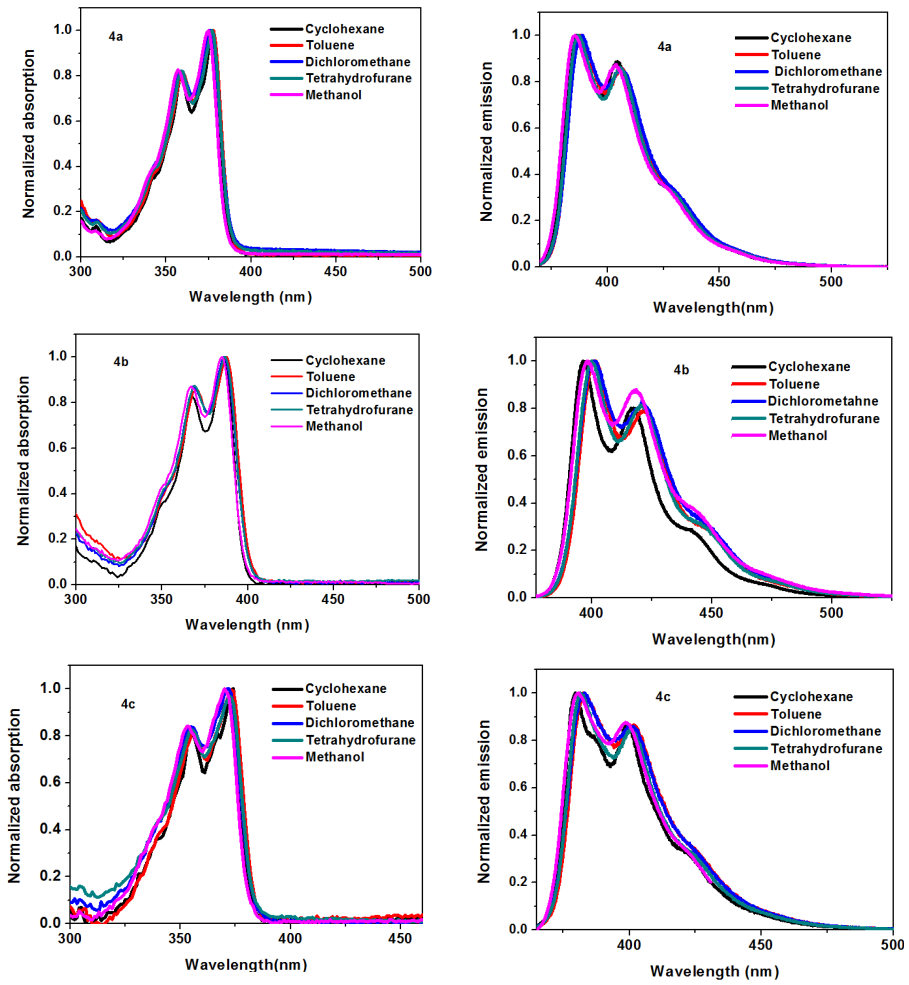


Figure S5. Normalized absorption (left) and emission spectra (right) of bis-BN dipyrrolyl[*a,j*]anthracenes **4a**, **4b** and **4c** in different solvents.

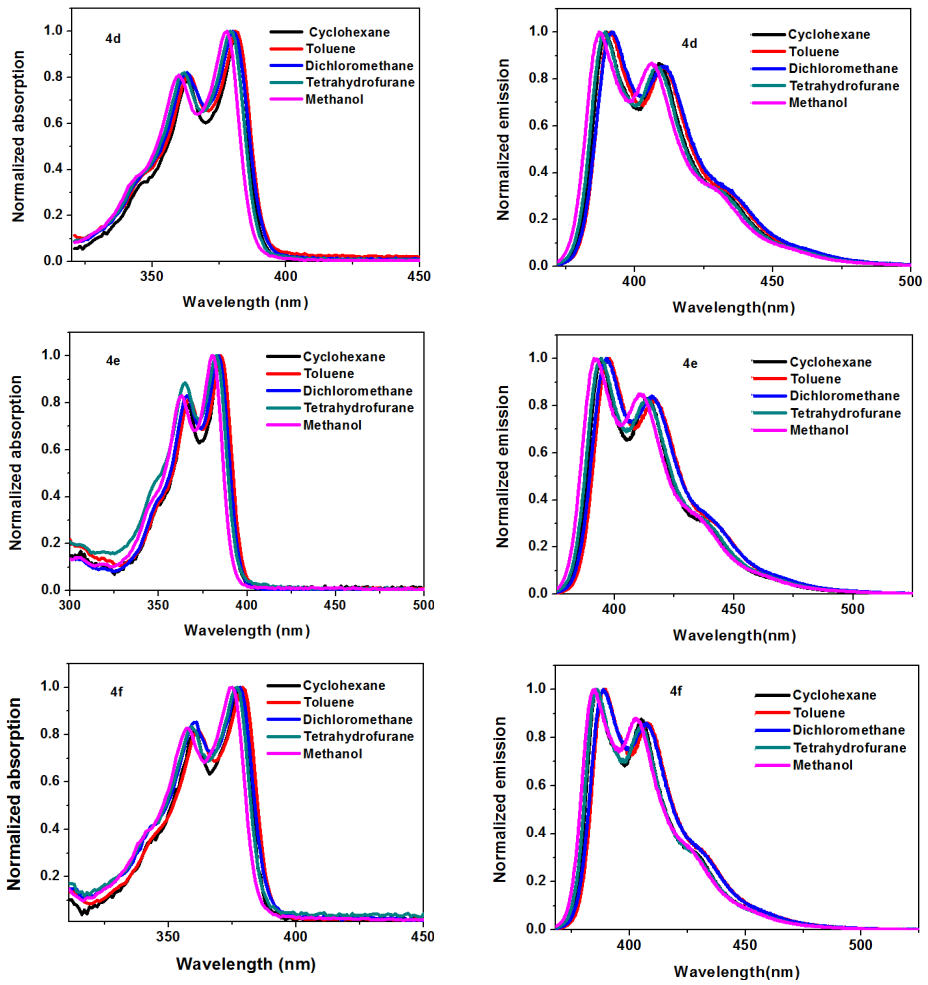


Figure S6. Normalized absorption (left) and emission spectra (right) of bis-BN dipyrrolyl[*a,j*]anthracenes **4d**, **4e** and **4f** in different solvents.

Table S1. Photophysical properties of bis-BN dipyrrolyl[*a,j*]anthracenes (**4a-4f**) and dipyrrolyl[*a,j*]anthracene (**9**).

Compound	λ_{abs} (nm)	ε ($M^{-1}cm^{-1}$)[a]	λ_{onset} (nm)	λ_{ex}(nm)	λ_{em} (nm)[b]	Φ_{pl}[c]	E_G^{opt}(eV)[d]
4a	359, 376	31068 (376)	393	360	386	0.73 (350)	3.15
4b	368, 386	24457 (386)	408	366	392	0.82 (350)	3.04
4c	355, 372	14709 (372)	390	355	386	0.65 (350)	3.18
4d	363, 380	27816 (380)	399	362	392	0.72 (350)	3.11
4e	366, 384	28463 (384)	404	366	393	0.72 (350)	3.07
4f	360, 378	26233 (378)	399	358	392	0.65 (350)	3.11
9	408, 432	16878 (432)	517	400	450	0.71 (404)	2.40

[a] Molar Absorption Coefficient ε = A/bc. [b] Refer to the highest-energy peak maxima values.
[c] Absolute quantum yields in the solution of dichloromethane , excitation wavelengths (nm) used are included in the parentheses.
[d] Optical band gap $E_G^{opt} = 1240/\lambda_{onset}$.

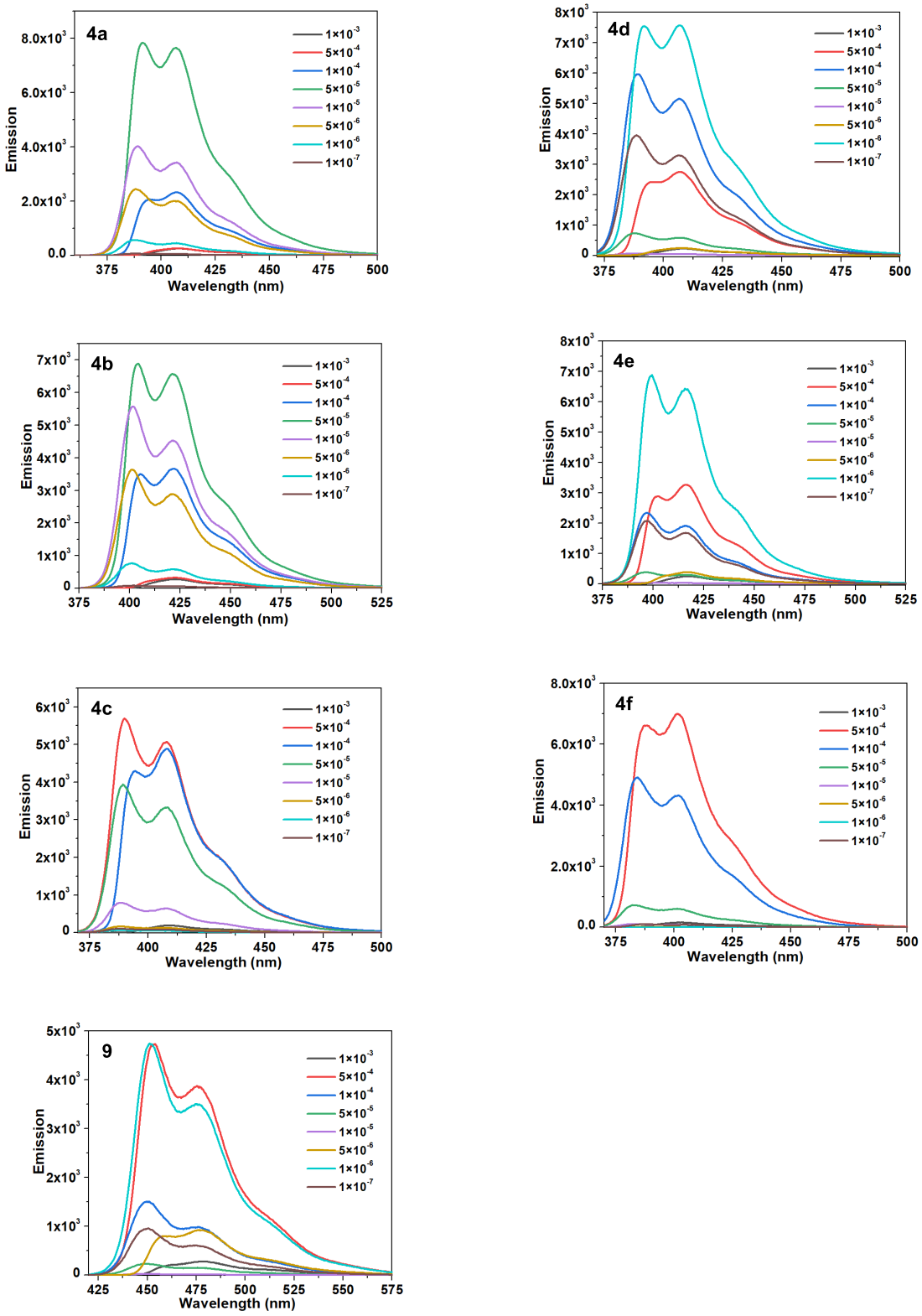


Figure S7. Emission spectra of compounds **4a**-**4f** and **9** at different concentrations in CH_2Cl_2.

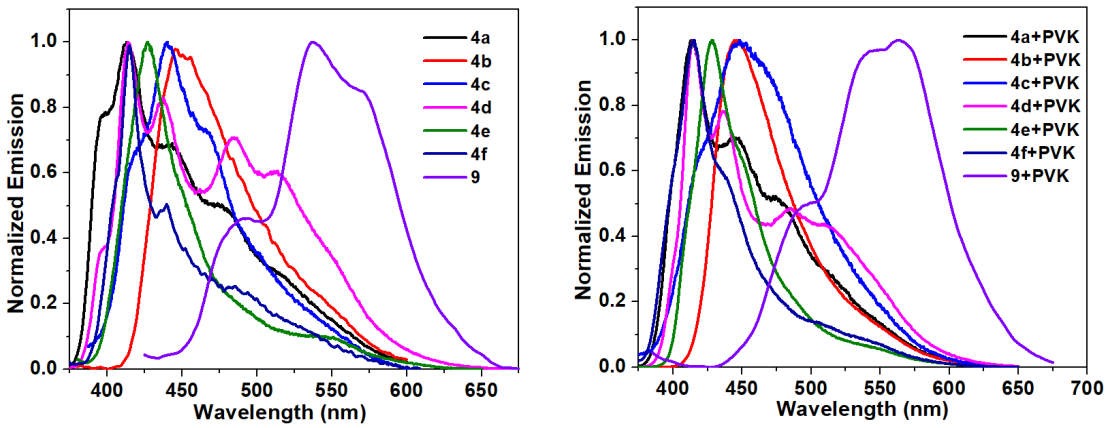


Figure S8. Left: Photoluminescence spectrum of **4a-4f** and **9** in thin film; Right: Photoluminescence spectrum of **4a-4f** and **9** doping with PVK in thin film.

Table S2: The photophysical properties of **4** and **9** in thin films.

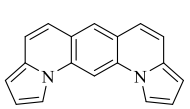
Compound	λ_{ex}(nm)	λ_{em} (nm)[a]	Φ_{pl}[b]	τ (ns)
4a	360	412	0.127 (0.109)	4.43
4b	366	446	0.170 (0.150)	2.62
4c	355	440	0.059 (0.076)	3.79
4d	362	415	0.101 (0.122)	1.55
4e	366	427	0.074 (0.108)	1.03
4f	358	415	0.140 (0.123)	0.96
9	400	537	0.109 (0.117)	2.22

[a] Refer to the highest-intensity peak maxima values. [b] Absolute quantum yields in thin film, absolute quantum yields doping with PVK in thin film are included in the parentheses.

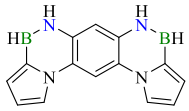
5. Computational Details

Calculations were performed in gas phase using the Gaussian 09 computational programme.[3] Geometrical optimizations were carried out using the B3LYP density functional method[4] and 6-31+G(d,p) basis set. Nucleus independent chemical shifts (NICS) were calculated using the gauge invariant atomic orbital (GIAO) approach at the B3LYP/6-311+G(2d,p) level of theory. NICS(1) values were averaged by two positions (above and below the plane) of all the equivalent rings. The excitation data were calculated using the TD-DFT method at the B3LYP/6-311+G(2d,p) level of theory.

Table S3. Cartesian coordinates for dipyrrolyl[a,j]anthracene (**9′**) and bis-BN dipyrrolyl[*a,j*]anthracene (**4′**).



9′



4′

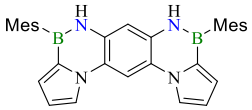
Compound	Cartesian Coordinates			
9′	6	-3.670596000	0.048887000	0.000076000
	6	-1.211821000	0.034404000	0.000000000
	6	-1.230192000	1.460477000	0.000166000
	6	-2.491408000	2.162511000	0.000294000
	6	-3.666239000	1.475634000	0.000267000
	6	-0.000003000	-0.660094000	-0.000101000
	6	0.000000000	2.128948000	0.000209000
	6	1.230197000	1.460460000	0.000105000
	6	1.211819000	0.034406000	-0.000053000
	6	3.670594000	0.048885000	-0.000103000
	6	3.666248000	1.475631000	0.000057000
	6	2.491409000	2.162505000	0.000157000
	1	0.000012000	-1.741970000	-0.000219000
	1	-2.479320000	3.248887000	0.000417000
	1	-4.622617000	1.989943000	0.000362000
	1	0.000016000	3.216946000	0.000336000
	1	4.622623000	1.989940000	0.000092000
	1	2.479317000	3.248880000	0.000277000
	6	4.682215000	-0.904713000	-0.000241000
	1	5.742863000	-0.691605000	-0.000251000
	7	2.440738000	-0.636409000	-0.000156000
	6	4.064639000	-2.179106000	-0.000360000
	6	2.694733000	-1.993990000	-0.000301000
	1	4.562789000	-3.139911000	-0.000478000
	1	1.898039000	-2.720985000	-0.000356000
	7	-2.440748000	-0.636400000	-0.000053000

	6	-4.682180000	-0.904686000	-0.000033000
	1	-5.742813000	-0.691536000	-0.000048000
	6	-4.064654000	-2.179109000	0.000122000
	6	-2.694743000	-1.994043000	-0.000060000
	1	-4.562858000	-3.139893000	0.000205000
	1	-1.898072000	-2.721067000	-0.000094000
4´	6	-3.694239000	0.019156000	0.000125000
	6	-1.220961000	0.039524000	0.000062000
	6	-1.224063000	1.456493000	0.000171000
	6	0.000001000	-0.638713000	-0.000040000
	6	-0.000011000	2.129389000	0.000185000
	6	1.224051000	1.456499000	0.000087000
	6	1.220956000	0.039520000	-0.000031000
	6	3.694316000	0.019169000	-0.000130000
	1	-0.000019000	-1.720150000	-0.000131000
	1	-0.000006000	3.218175000	0.000271000
	6	4.674184000	-0.969930000	-0.000248000
	1	5.740268000	-0.782882000	-0.000268000
	7	2.451241000	-0.648887000	-0.000139000
	6	4.035028000	-2.231082000	-0.000339000
	6	2.668253000	-2.004929000	-0.000271000
	1	4.506748000	-3.205190000	-0.000443000
	1	1.855962000	-2.715627000	-0.000308000
	7	-2.451234000	-0.648925000	0.000044000
	6	-4.674179000	-0.969878000	0.000167000
	1	-5.740251000	-0.782777000	0.000278000
	6	-4.035061000	-2.231062000	-0.000158000
	6	-2.668272000	-2.004968000	-0.000064000
	1	-4.506811000	-3.205157000	-0.000316000
	1	-1.855992000	-2.715678000	-0.000159000
	5	-3.710623000	1.537222000	0.000244000
	1	-4.693388000	2.212012000	0.000353000
	5	3.710658000	1.537220000	-0.000003000
	1	4.693285000	2.212205000	0.000019000
	7	-2.432170000	2.157844000	0.000264000
	1	-2.337636000	3.166417000	0.000355000
	7	2.432159000	2.157816000	0.000098000
	1	2.337686000	3.166400000	0.000185000

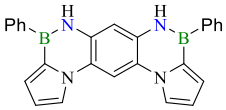
Table S4. Vertical excitation energies (λ), oscillator strengths (f) and orbital transitions of the two absorptions for dipyrrolyl[*a,j*]anthracene (**9´**) and bis-BN dipyrrolyl[*a,j*]anthracene (**4´)** predicted by DFT calculations.

Compound	**Major Transitions**		**λ (nm)**	**f**
9´	67 → 68	0.679	409.23(1)	0.173

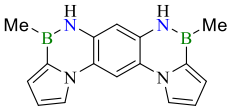
	66 → 69	0.639	332.94(4)	0.190
	65 → 68	0.626	292.65(5)	0.255
	64 → 69	0.618	256.10(11)	0.488
4′	67 → 68	0.693	363.41(1)	0.330
	65 → 68	0.679	294.34(3)	0.050
	66 → 69 67 → 72	−0.451 0.499	265.25(8)	0.199
	64 → 69	0.529	238.02(15)	0.459



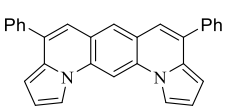
4a



4b



4c



9

Table S5. Cartesian coordinates for compounds **4a, 4b, 4c and 9**.

Compound	Cartesian Coordinates			
4a	6	-3.682138000	1.574210000	-0.000114000
	6	-1.215863000	1.558515000	-0.000086000
	6	-1.219356000	0.147918000	0.000035000
	6	-0.000251000	2.234477000	-0.000037000
	6	0.000248000	-0.522024000	0.000145000
	6	1.219605000	0.148363000	0.000170000
	6	1.215609000	1.558962000	0.000112000
	6	3.681879000	1.575556000	0.000062000
	1	-0.000446000	3.313115000	-0.000121000
	1	0.000445000	-1.607563000	0.000213000
	7	2.424517000	-0.551345000	0.000232000
	1	2.332253000	-1.557394000	0.000378000
	7	-2.424008000	-0.552231000	0.000047000
	1	-2.331316000	-1.558239000	0.000053000
	5	3.711497000	0.052970000	0.000102000
	5	-3.711209000	0.051621000	0.000013000
	6	5.013080000	-0.834201000	0.000001000
	6	5.609748000	-1.232740000	-1.211894000
	6	5.610095000	-1.232569000	1.211764000
	6	6.765864000	-2.012412000	-1.193684000
	6	6.766221000	-2.012240000	1.193323000
	6	7.358974000	-2.417075000	-0.000232000
	1	7.218389000	-2.305593000	-2.136275000
	1	7.219018000	-2.305293000	2.135824000
	6	-5.012839000	-0.835488000	0.000072000
	6	-5.606790000	-1.238330000	-1.211731000
	6	-5.606733000	-1.238223000	1.211903000
	6	-6.759275000	-2.023335000	-1.193367000

	6	-6.759271000	-2.023207000	1.193641000
	6	-7.353849000	-2.425560000	0.000176000
	1	-7.205227000	-2.326518000	-2.135942000
	1	-7.205234000	-2.326248000	2.136253000
	6	5.014118000	-0.820697000	-2.539880000
	1	4.029372000	-1.271008000	-2.696589000
	1	4.881971000	0.262722000	-2.600385000
	1	5.652353000	-1.127801000	-3.369718000
	6	5.014727000	-0.820548000	2.539873000
	1	4.880832000	0.262685000	2.599737000
	1	4.030836000	-1.272405000	2.697567000
	1	5.654023000	-1.126059000	3.369481000
	6	8.592602000	-3.284873000	-0.000361000
	1	9.207423000	-3.103876000	0.883532000
	1	8.326607000	-4.346944000	-0.000531000
	1	9.207430000	-3.103602000	-0.884195000
	6	-5.007138000	-0.832293000	2.539995000
	1	-4.025168000	-1.289151000	2.695352000
	1	-4.868068000	0.250162000	2.601856000
	1	-5.646691000	-1.136327000	3.369953000
	6	-5.007312000	-0.832333000	-2.539854000
	1	-4.870097000	0.250329000	-2.602382000
	1	-4.024477000	-1.287553000	-2.694481000
	1	-5.645999000	-1.138023000	-3.369868000
	6	-8.620278000	-3.244817000	0.000168000
	1	-9.505422000	-2.600497000	-0.002502000
	1	-8.681252000	-3.884620000	-0.882452000
	1	-8.683722000	-3.880805000	0.885348000
	7	2.444458000	2.242604000	0.000198000
	7	-2.444964000	2.241714000	-0.000251000
	6	4.659684000	2.558567000	0.000173000
	6	4.023931000	3.816720000	0.000391000
	1	5.721530000	2.369267000	0.000137000
	1	4.495455000	4.786790000	0.000525000
	6	-4.660298000	2.556873000	-0.000329000
	6	-4.025007000	3.815255000	-0.000584000
	1	-5.722062000	2.367155000	-0.000308000
	1	-4.496869000	4.785161000	-0.000790000
	6	2.662860000	3.594940000	0.000402000
	6	-2.663859000	3.593966000	-0.000535000
	1	1.855798000	4.306256000	0.000560000
	1	-1.857056000	4.305576000	-0.000679000
4b	6	-3.685260000	1.230198000	0.062316000
	6	-1.215514000	1.208728000	0.024650000

	6	-1.219225000	-0.201573000	0.024400000
	6	-0.000017000	1.884326000	0.000090000
	6	0.000001000	-0.871967000	0.000103000
	6	1.219221000	-0.201553000	-0.024203000
	6	1.215495000	1.208742000	-0.024461000
	6	3.685259000	1.230225000	-0.062248000
	1	-0.000028000	2.962776000	0.000081000
	1	0.000007000	-1.957487000	0.000115000
	7	2.422580000	-0.899423000	-0.038899000
	1	2.329202000	-1.904063000	0.010583000
	7	-2.422575000	-0.899446000	0.039048000
	1	-2.329219000	-1.904081000	-0.010586000
	5	3.710159000	-0.293785000	-0.040340000
	5	-3.710154000	-0.293789000	0.040360000
	6	4.990528000	-1.194688000	-0.027510000
	6	5.043148000	-2.392209000	-0.758994000
	6	6.123906000	-0.852906000	0.726739000
	6	6.169148000	-3.207855000	-0.742869000
	6	7.248813000	-1.669704000	0.757633000
	6	7.275923000	-2.849160000	0.019977000
	1	6.185281000	-4.120801000	-1.327121000
	1	8.106172000	-1.385936000	1.357198000
	6	-4.990533000	-1.194685000	0.027519000
	6	-6.123893000	-0.852832000	-0.726716000
	6	-5.043133000	-2.392274000	0.758893000
	6	-7.248788000	-1.669653000	-0.757714000
	6	-6.169140000	-3.207909000	0.742699000
	6	-7.275899000	-2.849158000	-0.020140000
	1	-8.106117000	-1.385875000	-1.357319000
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	7	2.444268000	1.892447000	-0.052501000
	7	-2.444278000	1.892432000	0.052621000
	6	4.655658000	2.219943000	-0.124356000
	6	4.013023000	3.473871000	-0.145644000
	1	5.718232000	2.042813000	-0.164239000
	1	4.479111000	4.445337000	-0.192919000
	6	-4.655663000	2.219902000	0.124565000
	6	-4.013041000	3.473853000	0.145307000
	1	-5.718215000	2.042745000	0.164773000
	1	-4.479135000	4.445321000	0.192521000
	6	2.654606000	3.245057000	-0.101526000
	6	-2.654628000	3.245037000	0.101255000
	1	1.843350000	3.951327000	-0.108905000
	1	-1.843371000	3.951309000	0.108604000

	1	8.154362000	-3.483689000	0.037909000
	1	4.197319000	-2.683850000	-1.374120000
	1	6.118352000	0.058914000	1.312690000
	1	-4.197295000	-2.683943000	1.373984000
	1	-8.154326000	-3.483701000	-0.038137000
	1	-6.118322000	0.059016000	-1.312615000
4c	6	3.681819000	0.250217000	0.000049000
	6	1.215878000	0.232217000	0.000000000
	6	1.219711000	-1.178011000	-0.000022000
	6	-0.000002000	0.907659000	0.000037000
	6	-0.000013000	-1.847735000	-0.000034000
	6	-1.219731000	-1.178003000	-0.000016000
	6	-1.215887000	0.232225000	0.000038000
	6	-3.681824000	0.250241000	0.000016000
	1	-0.000002000	1.986228000	0.000077000
	1	-0.000017000	-2.933401000	-0.000063000
	7	-2.424488000	-1.877632000	-0.000058000
	1	-2.327539000	-2.883038000	-0.000090000
	7	2.424464000	-1.877648000	-0.000029000
	1	2.327508000	-2.883054000	-0.000053000
	5	-3.712280000	-1.274838000	-0.000057000
	5	3.712260000	-1.274862000	0.000039000
	7	-2.444920000	0.915882000	0.000071000
	7	2.444919000	0.915865000	-0.000019000
	6	-4.657682000	1.234599000	0.000126000
	6	-4.020697000	2.492899000	0.000010000
	1	-5.720820000	1.051870000	0.000220000
	1	-4.491403000	3.463346000	0.000022000
	6	4.657700000	1.234583000	0.000040000
	6	4.020755000	2.492904000	-0.000177000
	1	5.720834000	1.051837000	0.000095000
	1	4.491488000	3.463340000	-0.000282000
	6	-2.660788000	2.269267000	0.000025000
	6	2.660828000	2.269297000	-0.000088000
	1	-1.852390000	2.978894000	-0.000113000
	1	1.852454000	2.978950000	0.000153000
	6	-5.019480000	-2.152973000	-0.000079000
	1	-5.640768000	-1.935774000	0.874810000
	1	-5.640802000	-1.935681000	-0.874920000
	1	-4.819092000	-3.228483000	-0.000139000
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	1	5.640895000	-1.935662000	-0.874632000
	1	5.640627000	-1.935878000	0.875098000
	1	4.819054000	-3.228517000	-0.000050000

	6	-3.662748000	1.075400000	0.065409000
	6	-1.205975000	1.098096000	0.023135000
	6	-1.224331000	-0.320370000	0.022620000
	6	0.000007000	1.790839000	0.000006000
	6	-0.000007000	-0.988538000	0.000023000
	6	1.224323000	-0.320386000	-0.022582000
	6	1.205980000	1.098079000	-0.023120000
	6	3.662742000	1.075357000	-0.065362000
	1	0.000020000	2.869548000	0.000003000
	1	-0.000015000	-2.073111000	0.000030000
	6	4.956622000	-1.098715000	-0.023735000
	6	5.183980000	-2.139144000	-0.931206000
	6	5.954070000	-0.802086000	0.912566000
	6	6.370017000	-2.863974000	-0.902232000
	6	7.137530000	-1.529736000	0.943897000
	6	7.351343000	-2.562363000	0.035871000
	1	6.529670000	-3.661073000	-1.618861000
	1	7.892993000	-1.292767000	1.683919000
	6	-4.956619000	-1.098698000	0.023737000
	6	-5.953901000	-0.802366000	-0.912837000
	6	-5.184142000	-2.138859000	0.931478000
9	6	-7.137338000	-1.530054000	-0.944184000
	6	-6.370156000	-2.863724000	0.902488000
	6	-7.351305000	-2.562418000	-0.035897000
	1	-7.892658000	-1.293323000	-1.684428000
	1	-6.529934000	-3.660601000	1.619336000
	7	2.434509000	1.758354000	-0.051141000
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	6	4.663988000	2.030687000	-0.138193000
	6	4.044037000	3.298506000	-0.161488000
	1	5.720147000	1.826812000	-0.182813000
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	6	-2.683272000	3.112003000	0.107805000
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	1	-1.887944000	3.835056000	0.113990000
	1	8.276249000	-3.126221000	0.058819000
	1	4.430088000	-2.367420000	-1.675237000
	1	5.790227000	-0.010254000	1.632901000
	1	-4.430405000	-2.366886000	1.675741000

	1	-8.276196000	-3.126300000	-0.058856000
	1	-5.789935000	-0.010762000	-1.633392000
	6	-2.479162000	-1.018008000	0.030041000
	1	-2.461178000	-2.100521000	-0.005291000
	6	-3.670088000	-0.359071000	0.039002000
	6	2.479154000	-1.018040000	-0.029991000
	1	2.461156000	-2.100555000	0.005305000
	6	3.670075000	-0.359108000	-0.038960000

Table S6. Vertical excitation energies (λ), oscillator strengths (f) and orbital transitions of the four strongest absorptions for compounds **4a, 4b, 4c and 9**, predicted by DFT calculations.

Compound	**Major Transition**		**Excited State**	**λ (nm)**	**f**
4a	131 → 132	0.694	1	357.74	0.437
	130 → 132	0.638	2	311.12	0.021
	129 → 132	0.684	3	290.06	0.105
	131 → 138	0.653	14	262.23	0.184
4b	107 → 108	0.696	1	373.27	0.496
	105 → 108	0.648	4	303.85	0.110
	107 → 110	0.624	5	293.35	0.070
	104 → 109	0.661	12	261.09	0.423
4c	75 → 76	0.693	1	354.71	0.355
	73 → 76	0.685	3	289.43	0.063
	75 → 81	0.661	9	259.04	0.177
	74 → 79	0.615	14	239.49	0.132
9	107 → 108	0.682	1	420.47	0.277
	106 → 109	0.658	4	349.56	0.382
	105 → 108 107 → 110	0.527 0.428	5	301.70	0.236
	104 → 109	0.615	14	270.90	0.606

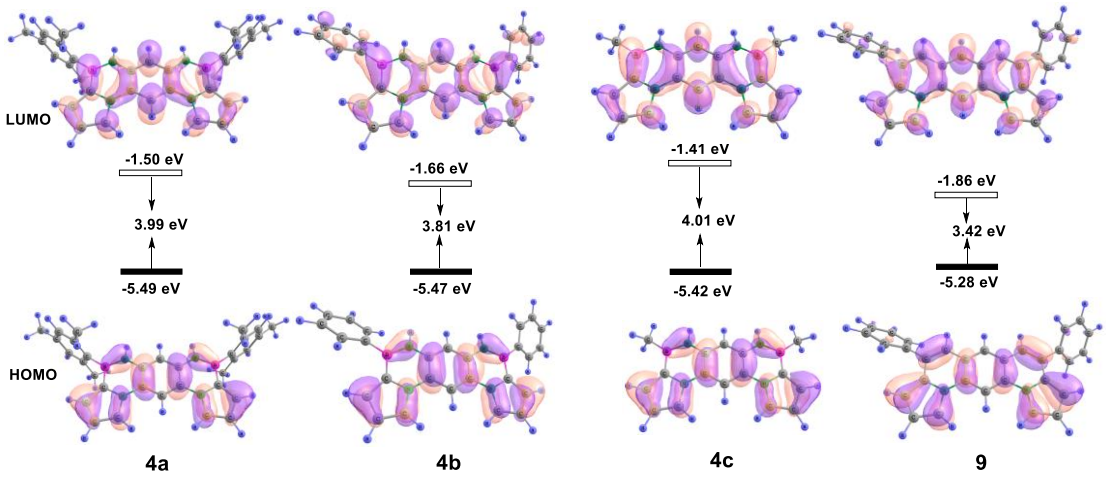


Figure S9. Selected molecular orbitals and the corresponding energy levels for bis-BN dipyrrolyl[*a,j*]anthracenes (**4a-4c)** and dipyrrolyl[*a,j*]anthracene (**9**).

6. Single-Crystal X-ray Analysis

The single crystals of bis-BN dipyrrolyl[*a,j*]anthracenes **4b**, **4d**, **4e** and **9** suitable for X-ray analysis were obtained by slow diffusion of hexane into concentrated solution of CH_2Cl_2. Detailed characterizations and data are shown as follow.

Table S7. Crystal data and structure refinement for **4b**.

Identification code	lmy-3-75_a	
Empirical formula	$C_{26}H_{20}B_2N_4$	
Formula weight	410.08	
Temperature	293(2) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 16.2099(3) Å	α= 90°.
	b = 10.1372(2) Å	β= 97.930(2)°.
	c = 13.0144(2) Å	γ= 90°.
Volume	2118.11(7) $Å^3$	
Z	4	
Density (calculated)	1.286 Mg/m3	
Absorption coefficient	0.590 mm^{-1}	
F(000)	856	
Crystal size	0.120 x 0.100 x 0.080 mm^3	
Theta range for data collection	5.160 to 79.696°.	
Index ranges	-20<=h<=20, -12<=k<=11, -16<=l<=13	
Reflections collected	14331	
Independent reflections	4507 [R(int) = 0.0292]	
Completeness to theta = 67.684°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4507 / 0 / 289	
Goodness-of-fit on F^2	1.069	
Final R indices [I>2sigma(I)]	R1 = 0.0488, wR2 = 0.1320	
R indices (all data)	R1 = 0.0553, wR2 = 0.1385	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.180 and -0.266 e.$Å^{-3}$	

Table S8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **4b**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
B(1)	8055(1)	4067(2)	3644(1)	54(1)

B(2)	4132(1)	2622(1)	5750(1)	47(1)
C(1)	8603(1)	3805(1)	2767(1)	55(1)
C(2)	8637(1)	2572(2)	2304(1)	64(1)
C(3)	9141(1)	2334(2)	1547(1)	72(1)
C(4)	9616(1)	3340(2)	1222(1)	72(1)
C(5)	9590(1)	4571(2)	1658(1)	71(1)
C(6)	9093(1)	4803(2)	2419(1)	64(1)
C(7)	8306(1)	4986(1)	4559(1)	54(1)
C(8)	8996(1)	5749(2)	4910(1)	64(1)
C(9)	8871(1)	6364(2)	5830(1)	71(1)
C(10)	8109(1)	5988(2)	6056(1)	64(1)
C(11)	6751(1)	3628(1)	4395(1)	48(1)
C(12)	6990(1)	4487(1)	5230(1)	47(1)
C(13)	6465(1)	4679(1)	5971(1)	50(1)
C(14)	5702(1)	4043(1)	5899(1)	46(1)
C(15)	5457(1)	3173(1)	5076(1)	45(1)
C(16)	5990(1)	2984(1)	4336(1)	50(1)
C(17)	5274(1)	5118(2)	7453(1)	59(1)
C(18)	4608(1)	5018(2)	7983(1)	62(1)
C(19)	4069(1)	4076(1)	7488(1)	55(1)
C(20)	4401(1)	3595(1)	6636(1)	47(1)
C(21)	3330(1)	1742(1)	5657(1)	48(1)
C(22)	2647(1)	2057(2)	6159(1)	63(1)
C(23)	1964(1)	1232(2)	6122(1)	76(1)
C(24)	1933(1)	75(2)	5573(1)	77(1)
C(25)	2587(1)	-262(2)	5053(1)	75(1)
C(26)	3275(1)	561(2)	5102(1)	61(1)
N(1)	7277(1)	3436(1)	3644(1)	55(1)
N(2)	7761(1)	5147(1)	5297(1)	52(1)
N(3)	4696(1)	2514(1)	5016(1)	49(1)
N(4)	5160(1)	4259(1)	6644(1)	48(1)

Table S9. Bond Lengths [Å] for **4b**.

Atom	Length/ Å	Atom	Length/ Å
B(1)-N(1)	1.4142(19)	C(12)-N(2)	1.4096(16)
B(1)-C(7)	1.523(2)	C(13)-C(14)	1.3857(17)
B(1)-C(1)	1.5630(19)	C(13)-H(13)	0.9300

B(2)-N(3)	1.4151(16)	C(14)-C(15)	1.4018(17)
B(2)-C(20)	1.5351(19)	C(14)-N(4)	1.4122(14)
B(2)-C(21)	1.5674(19)	C(15)-C(16)	1.3921(16)
C(1)-C(2)	1.392(2)	C(15)-N(3)	1.3954(15)
C(1)-C(6)	1.398(2)	C(16)-H(16)	0.9300
C(2)-C(3)	1.3855(19)	C(17)-N(4)	1.3592(16)
C(2)-H(2)	0.9300	C(17)-C(18)	1.3639(19)
C(3)-C(4)	1.378(2)	C(17)-H(17)	0.9300
C(3)-H(3)	0.9300	C(18)-C(19)	1.390(2)
C(4)-C(5)	1.374(2)	C(18)-H(18)	0.9300
C(4)-H(4)	0.9300	C(19)-C(20)	1.3859(16)
C(5)-C(6)	1.3795(19)	C(19)-H(19)	0.9300
C(5)-H(5)	0.9300	C(20)-N(4)	1.4010(16)
C(6)-H(6)	0.9300	C(21)-C(26)	1.3949(19)
C(7)-C(8)	1.384(2)	C(21)-C(22)	1.3975(17)
C(7)-N(2)	1.4016(16)	C(22)-C(23)	1.383(2)
C(8)-C(9)	1.389(2)	C(22)-H(22)	0.9300
C(8)-H(8)	0.9300	C(23)-C(24)	1.370(3)
C(9)-C(10)	1.364(2)	C(23)-H(23)	0.9300
C(9)-H(9)	0.9300	C(24)-C(25)	1.377(2)
C(10)-N(2)	1.3667(18)	C(24)-H(24)	0.9300
C(10)-H(10)	0.9300	C(25)-C(26)	1.388(2)
C(11)-C(16)	1.3885(17)	C(25)-H(25)	0.9300
C(11)-N(1)	1.3968(15)	C(26)-H(26)	0.9300
C(11)-C(12)	1.4050(17)	N(1)-H(1)	0.8600
C(12)-C(13)	1.3848(17)	N(3)-H(3A)	0.8600

Table S10. Bond Angles [°] for **4b**.

Atom	Angles/°	Atom	Angles/°
N(1)-B(1)-C(7)	114.74(12)	C(16)-C(15)-N(3)	121.56(11)
N(1)-B(1)-C(1)	121.34(13)	C(16)-C(15)-C(14)	118.51(11)
C(7)-B(1)-C(1)	123.91(12)	N(3)-C(15)-C(14)	119.93(10)
N(3)-B(2)-C(20)	114.41(11)	C(11)-C(16)-C(15)	121.90(11)
N(3)-B(2)-C(21)	120.73(11)	C(11)-C(16)-H(16)	119.1
C(20)-B(2)-C(21)	124.79(11)	C(15)-C(16)-H(16)	119.1
C(2)-C(1)-C(6)	116.84(12)	N(4)-C(17)-C(18)	108.18(12)
C(2)-C(1)-B(1)	121.90(13)	N(4)-C(17)-H(17)	125.9

C(6)-C(1)-B(1)	121.26(13)	C(18)-C(17)-H(17)	125.9
C(3)-C(2)-C(1)	121.74(14)	C(17)-C(18)-C(19)	107.85(12)
C(3)-C(2)-H(2)	119.1	C(17)-C(18)-H(18)	126.1
C(1)-C(2)-H(2)	119.1	C(19)-C(18)-H(18)	126.1
C(4)-C(3)-C(2)	119.89(15)	C(20)-C(19)-C(18)	108.93(12)
C(4)-C(3)-H(3)	120.1	C(20)-C(19)-H(19)	125.5
C(2)-C(3)-H(3)	120.1	C(18)-C(19)-H(19)	125.5
C(5)-C(4)-C(3)	119.66(13)	C(19)-C(20)-N(4)	105.23(11)
C(5)-C(4)-H(4)	120.2	C(19)-C(20)-B(2)	136.54(12)
C(3)-C(4)-H(4)	120.2	N(4)-C(20)-B(2)	118.19(10)
C(4)-C(5)-C(6)	120.34(15)	C(26)-C(21)-C(22)	116.19(13)
C(4)-C(5)-H(5)	119.8	C(26)-C(21)-B(2)	121.37(11)
C(6)-C(5)-H(5)	119.8	C(22)-C(21)-B(2)	122.38(12)
C(5)-C(6)-C(1)	121.52(15)	C(23)-C(22)-C(21)	121.76(15)
C(5)-C(6)-H(6)	119.2	C(23)-C(22)-H(22)	119.1
C(1)-C(6)-H(6)	119.2	C(21)-C(22)-H(22)	119.1
C(8)-C(7)-N(2)	105.50(12)	C(24)-C(23)-C(22)	120.53(15)
C(8)-C(7)-B(1)	135.70(12)	C(24)-C(23)-H(23)	119.7
N(2)-C(7)-B(1)	118.77(11)	C(22)-C(23)-H(23)	119.7
C(7)-C(8)-C(9)	109.05(13)	C(23)-C(24)-C(25)	119.54(15)
C(7)-C(8)-H(8)	125.5	C(23)-C(24)-H(24)	120.2
C(9)-C(8)-H(8)	125.5	C(25)-C(24)-H(24)	120.2
C(10)-C(9)-C(8)	107.83(14)	C(24)-C(25)-C(26)	119.79(16)
C(10)-C(9)-H(9)	126.1	C(24)-C(25)-H(25)	120.1
C(8)-C(9)-H(9)	126.1	C(26)-C(25)-H(25)	120.1
C(9)-C(10)-N(2)	108.26(13)	C(25)-C(26)-C(21)	122.17(14)
C(9)-C(10)-H(10)	125.9	C(25)-C(26)-H(26)	118.9
N(2)-C(10)-H(10)	125.9	C(21)-C(26)-H(26)	118.9
C(16)-C(11)-N(1)	121.31(11)	C(11)-N(1)-B(1)	124.61(12)
C(16)-C(11)-C(12)	118.81(11)	C(11)-N(1)-H(1)	117.7
N(1)-C(11)-C(12)	119.88(11)	B(1)-N(1)-H(1)	117.7
C(13)-C(12)-C(11)	119.70(11)	C(10)-N(2)-C(7)	109.35(11)
C(13)-C(12)-N(2)	121.02(11)	C(10)-N(2)-C(12)	127.92(11)
C(11)-C(12)-N(2)	119.28(11)	C(7)-N(2)-C(12)	122.72(11)
C(12)-C(13)-C(14)	121.02(12)	C(15)-N(3)-B(2)	125.05(10)
C(12)-C(13)-H(13)	119.5	C(15)-N(3)-H(3A)	117.5
C(14)-C(13)-H(13)	119.5	B(2)-N(3)-H(3A)	117.5
C(13)-C(14)-C(15)	120.05(11)	C(17)-N(4)-C(20)	109.79(10)

C(13)-C(14)-N(4)	120.99(11)	C(17)-N(4)-C(14)	126.84(11)
C(15)-C(14)-N(4)	118.96(11)	C(20)-N(4)-C(14)	123.36(10)

Table S11. Crystal data and structure refinement for **4d**.

Identification code	1_a	
Empirical formula	$C_{44}H_{56}B_2N_4$	
Formula weight	662.54	
Temperature	293(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 9.4761(2) Å	α= 90°.
	b = 32.5624(8) Å	β= 95.109(3)°.
	c = 13.4595(4) Å	γ= 90°.
Volume	4136.62(18) $Å^3$	
Z	4	
Density (calculated)	1.064 Mg/m3	
Absorption coefficient	0.461 mm^{-1}	
F(000)	1432	
Crystal size	0.220 x 0.200 x 0.180 mm^3	
Theta range for data collection	2.714 to 79.746°.	
Index ranges	-12<=h<=11, -41<=k<=37, -16<=l<=17	
Reflections collected	31495	
Independent reflections	8787 [R(int) = 0.0461]	
Completeness to theta = 67.684°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8787 / 25 / 459	
Goodness-of-fit on F^2	1.085	
Final R indices [I>2sigma(I)]	R1 = 0.0826, wR2 = 0.2503	
R indices (all data)	R1 = 0.0966, wR2 = 0.2698	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.481 and -0.561 e.$Å^{-3}$	

Table S12. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **4d**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
B(1)	7524(3)	8074(1)	5094(2)	64(1)
B(2)	3736(2)	6094(1)	5271(2)	60(1)
C(1)	8894(4)	8265(1)	7109(2)	107(1)

C(2)	8458(3)	8612(1)	6404(2)	78(1)
C(3)	8731(3)	9013(1)	6695(2)	94(1)
C(4)	8346(4)	9341(1)	6085(3)	103(1)
C(5)	7650(4)	9260(1)	5149(2)	97(1)
C(6)	7353(3)	8861(1)	4834(2)	81(1)
C(7)	7766(2)	8530(1)	5458(2)	69(1)
C(8)	8667(6)	9784(1)	6404(4)	152(2)
C(9)	6580(4)	8786(1)	3822(2)	109(1)
C(10)	8524(2)	7869(1)	4419(2)	65(1)
C(11)	9726(3)	7996(1)	3988(2)	78(1)
C(12)	10224(3)	7666(1)	3453(2)	81(1)
C(13)	9353(2)	7338(1)	3561(2)	71(1)
C(14)	6240(2)	7414(1)	5088(1)	55(1)
C(15)	7192(2)	7229(1)	4476(1)	56(1)
C(16)	7048(2)	6816(1)	4236(1)	57(1)
C(17)	5989(2)	6576(1)	4572(1)	54(1)
C(18)	5007(2)	6751(1)	5178(1)	54(1)
C(19)	5172(2)	7168(1)	5412(1)	57(1)
C(20)	6767(2)	5922(1)	3811(2)	79(1)
C(21)	6278(3)	5528(1)	3789(2)	86(1)
C(22)	5056(3)	5518(1)	4293(2)	73(1)
C(23)	4815(2)	5909(1)	4637(2)	61(1)
C(24)	2477(2)	5833(1)	5624(2)	69(1)
C(25)	2609(3)	5628(1)	6542(2)	77(1)
C(26)	1449(4)	5411(1)	6848(3)	99(1)
C(27)	168(4)	5393(1)	6270(3)	112(1)
C(28)	72(3)	5581(1)	5363(3)	112(1)
C(29)	1188(3)	5802(1)	5013(2)	88(1)
C(30)	1024(4)	6001(1)	4002(3)	115(1)
C(31)	3974(4)	5641(1)	7181(2)	99(1)
C(32)	-1103(5)	5171(2)	6629(5)	171(2)
C(33)	5320(3)	8006(1)	5980(2)	69(1)
C(34)	3924(3)	8120(1)	5377(2)	93(1)
C(35)	2845(5)	8297(2)	6000(4)	156(1)
C(36)	3058(9)	8686(2)	6408(6)	216(2)
C(37)	3161(9)	9036(3)	5716(7)	225(2)
C(38)	3422(9)	9448(3)	6181(7)	242(2)
C(39)	2976(2)	6712(1)	6214(2)	61(1)

C(40)	1805(2)	6973(1)	5683(2)	75(1)
C(41)	654(3)	7077(1)	6363(2)	96(1)
C(42)	-322(3)	6712(1)	6535(2)	96(1)
C(43)	-1501(4)	6800(2)	7174(3)	127(1)
C(44)	-2403(4)	6441(2)	7337(4)	159(2)
N(1)	6389(2)	7830(1)	5374(1)	60(1)
N(2)	8312(2)	7462(1)	4145(1)	60(1)
N(3)	3916(2)	6516(1)	5537(1)	58(1)
N(4)	5890(2)	6156(1)	4330(1)	59(1)

Table S13. Bond Lengths [Å] for **4d**.

Atom	Length/ Å	Atom	Length/ Å
B(1)-N(1)	1.417(3)	C(25)-C(26)	1.399(4)
B(1)-C(10)	1.524(3)	C(25)-C(31)	1.488(4)
B(1)-C(7)	1.573(3)	C(26)-C(27)	1.383(5)
B(2)-N(3)	1.427(3)	C(26)-H(26)	0.9300
B(2)-C(23)	1.513(3)	C(27)-C(28)	1.362(6)
B(2)-C(24)	1.572(3)	C(27)-C(32)	1.520(4)
C(1)-C(2)	1.509(4)	C(28)-C(29)	1.394(4)
C(1)-H(1A)	0.9600	C(28)-H(28)	0.9300
C(1)-H(1B)	0.9600	C(29)-C(30)	1.503(5)
C(1)-H(1C)	0.9600	C(30)-H(30A)	0.9600
C(2)-C(3)	1.380(3)	C(30)-H(30B)	0.9600
C(2)-C(7)	1.404(3)	C(30)-H(30C)	0.9600
C(3)-C(4)	1.377(5)	C(31)-H(31A)	0.9600
C(3)-H(3)	0.9300	C(31)-H(31B)	0.9600
C(4)-C(5)	1.395(5)	C(31)-H(31C)	0.9600
C(4)-C(8)	1.528(4)	C(32)-H(32A)	0.9600
C(5)-C(6)	1.387(3)	C(32)-H(32B)	0.9600
C(5)-H(5)	0.9300	C(32)-H(32C)	0.9600
C(6)-C(7)	1.400(3)	C(33)-N(1)	1.473(2)
C(6)-C(9)	1.508(4)	C(33)-C(34)	1.535(4)
C(8)-H(8A)	0.9600	C(33)-H(33A)	0.9700
C(8)-H(8B)	0.9600	C(33)-H(33B)	0.9700
C(8)-H(8C)	0.9600	C(34)-C(35)	1.494(4)
C(9)-H(9A)	0.9600	C(34)-H(34A)	0.9700
C(9)-H(9B)	0.9600	C(34)-H(34B)	0.9700

C(9)-H(9C)	0.9600	C(35)-C(36)	1.389(8)
C(10)-C(11)	1.387(3)	C(35)-H(35A)	0.9700
C(10)-N(2)	1.388(3)	C(35)-H(35B)	0.9700
C(11)-C(12)	1.399(4)	C(36)-C(37)	1.481(10)
C(11)-H(11)	0.9300	C(36)-H(36A)	0.9700
C(12)-C(13)	1.367(3)	C(36)-H(36B)	0.9700
C(12)-H(12)	0.9300	C(37)-C(38)	1.491(10)
C(13)-N(2)	1.375(3)	C(37)-H(37A)	0.9700
C(13)-H(13)	0.9300	C(37)-H(37B)	0.9700
C(14)-C(19)	1.392(2)	C(38)-H(38A)	0.9600
C(14)-C(15)	1.409(3)	C(38)-H(38B)	0.9600
C(14)-N(1)	1.411(2)	C(38)-H(38C)	0.9600
C(15)-C(16)	1.385(3)	C(39)-N(3)	1.475(2)
C(15)-N(2)	1.409(2)	C(39)-C(40)	1.524(3)
C(16)-C(17)	1.380(3)	C(39)-H(39A)	0.9700
C(16)-H(16)	0.9300	C(39)-H(39B)	0.9700
C(17)-N(4)	1.406(2)	C(40)-C(41)	1.523(3)
C(17)-C(18)	1.412(2)	C(40)-H(40A)	0.9700
C(18)-C(19)	1.398(3)	C(40)-H(40B)	0.9700
C(18)-N(3)	1.407(2)	C(41)-C(42)	1.537(5)
C(19)-H(19)	0.9300	C(41)-H(41A)	0.9700
C(20)-N(4)	1.363(3)	C(41)-H(41B)	0.9700
C(20)-C(21)	1.366(3)	C(42)-C(43)	1.497(4)
C(20)-H(20)	0.9300	C(42)-H(42A)	0.9700
C(21)-C(22)	1.393(4)	C(42)-H(42B)	0.9700
C(21)-H(21)	0.9300	C(43)-C(44)	1.475(6)
C(22)-C(23)	1.380(3)	C(43)-H(43A)	0.9700
C(22)-H(22)	0.9300	C(43)-H(43B)	0.9700
C(23)-N(4)	1.390(2)	C(44)-H(44A)	0.9600
C(24)-C(25)	1.401(3)	C(44)-H(44B)	0.9600
C(24)-C(29)	1.414(4)	C(44)-H(44C)	0.9600

Table S14. Bond Angles [°] for **4d**.

Atom	Angles/°	Atom	Angles/°
N(1)-B(1)-C(10)	116.03(18)	C(29)-C(30)-H(30A)	109.5
N(1)-B(1)-C(7)	122.72(19)	C(29)-C(30)-H(30B)	109.5
C(10)-B(1)-C(7)	121.24(18)	H(30A)-C(30)-H(30B)	109.5

N(3)-B(2)-C(23)	116.91(17)	C(29)-C(30)-H(30C)	109.5
N(3)-B(2)-C(24)	121.45(18)	H(30A)-C(30)-H(30C)	109.5
C(23)-B(2)-C(24)	121.64(17)	H(30B)-C(30)-H(30C)	109.5
C(2)-C(1)-H(1A)	109.5	C(25)-C(31)-H(31A)	109.5
C(2)-C(1)-H(1B)	109.5	C(25)-C(31)-H(31B)	109.5
H(1A)-C(1)-H(1B)	109.5	H(31A)-C(31)-H(31B)	109.5
C(2)-C(1)-H(1C)	109.5	C(25)-C(31)-H(31C)	109.5
H(1A)-C(1)-H(1C)	109.5	H(31A)-C(31)-H(31C)	109.5
H(1B)-C(1)-H(1C)	109.5	H(31B)-C(31)-H(31C)	109.5
C(3)-C(2)-C(7)	119.9(2)	C(27)-C(32)-H(32A)	109.5
C(3)-C(2)-C(1)	119.7(2)	C(27)-C(32)-H(32B)	109.5
C(7)-C(2)-C(1)	120.5(2)	H(32A)-C(32)-H(32B)	109.5
C(4)-C(3)-C(2)	122.0(3)	C(27)-C(32)-H(32C)	109.5
C(4)-C(3)-H(3)	119.0	H(32A)-C(32)-H(32C)	109.5
C(2)-C(3)-H(3)	119.0	H(32B)-C(32)-H(32C)	109.5
C(3)-C(4)-C(5)	118.1(2)	N(1)-C(33)-C(34)	113.85(19)
C(3)-C(4)-C(8)	122.0(3)	N(1)-C(33)-H(33A)	108.8
C(5)-C(4)-C(8)	119.9(3)	C(34)-C(33)-H(33A)	108.8
C(6)-C(5)-C(4)	121.3(3)	N(1)-C(33)-H(33B)	108.8
C(6)-C(5)-H(5)	119.3	C(34)-C(33)-H(33B)	108.8
C(4)-C(5)-H(5)	119.3	H(33A)-C(33)-H(33B)	107.7
C(5)-C(6)-C(7)	119.9(2)	C(35)-C(34)-C(33)	113.4(3)
C(5)-C(6)-C(9)	119.8(3)	C(35)-C(34)-H(34A)	108.9
C(7)-C(6)-C(9)	120.3(2)	C(33)-C(34)-H(34A)	108.9
C(6)-C(7)-C(2)	118.7(2)	C(35)-C(34)-H(34B)	108.9
C(6)-C(7)-B(1)	120.85(19)	C(33)-C(34)-H(34B)	108.9
C(2)-C(7)-B(1)	120.3(2)	H(34A)-C(34)-H(34B)	107.7
C(4)-C(8)-H(8A)	109.5	C(36)-C(35)-C(34)	119.3(6)
C(4)-C(8)-H(8B)	109.5	C(36)-C(35)-H(35A)	107.5
H(8A)-C(8)-H(8B)	109.5	C(34)-C(35)-H(35A)	107.5
C(4)-C(8)-H(8C)	109.5	C(36)-C(35)-H(35B)	107.5
H(8A)-C(8)-H(8C)	109.5	C(34)-C(35)-H(35B)	107.5
H(8B)-C(8)-H(8C)	109.5	H(35A)-C(35)-H(35B)	107.0
C(6)-C(9)-H(9A)	109.5	C(35)-C(36)-C(37)	117.9(7)
C(6)-C(9)-H(9B)	109.5	C(35)-C(36)-H(36A)	107.8
H(9A)-C(9)-H(9B)	109.5	C(37)-C(36)-H(36A)	107.8
C(6)-C(9)-H(9C)	109.5	C(35)-C(36)-H(36B)	107.8
H(9A)-C(9)-H(9C)	109.5	C(37)-C(36)-H(36B)	107.8

H(9B)-C(9)-H(9C)	109.5	H(36A)-C(36)-H(36B)	107.2
C(11)-C(10)-N(2)	106.20(18)	C(38)-C(37)-C(36)	116.5(8)
C(11)-C(10)-B(1)	134.1(2)	C(38)-C(37)-H(37A)	108.2
N(2)-C(10)-B(1)	119.65(17)	C(36)-C(37)-H(37A)	108.2
C(10)-C(11)-C(12)	108.3(2)	C(38)-C(37)-H(37B)	108.2
C(10)-C(11)-H(11)	125.9	C(36)-C(37)-H(37B)	108.2
C(12)-C(11)-H(11)	125.9	H(37A)-C(37)-H(37B)	107.3
C(13)-C(12)-C(11)	108.16(19)	C(37)-C(38)-H(38A)	109.5
C(13)-C(12)-H(12)	125.9	C(37)-C(38)-H(38B)	109.5
C(11)-C(12)-H(12)	125.9	H(38A)-C(38)-H(38B)	109.5
C(12)-C(13)-N(2)	107.6(2)	C(37)-C(38)-H(38C)	109.5
C(12)-C(13)-H(13)	126.2	H(38A)-C(38)-H(38C)	109.5
N(2)-C(13)-H(13)	126.2	H(38B)-C(38)-H(38C)	109.5
C(19)-C(14)-C(15)	117.25(16)	N(3)-C(39)-C(40)	114.04(17)
C(19)-C(14)-N(1)	121.64(16)	N(3)-C(39)-H(39A)	108.7
C(15)-C(14)-N(1)	121.09(16)	C(40)-C(39)-H(39A)	108.7
C(16)-C(15)-N(2)	120.63(16)	N(3)-C(39)-H(39B)	108.7
C(16)-C(15)-C(14)	119.77(16)	C(40)-C(39)-H(39B)	108.7
N(2)-C(15)-C(14)	119.56(16)	H(39A)-C(39)-H(39B)	107.6
C(17)-C(16)-C(15)	122.23(17)	C(41)-C(40)-C(39)	112.0(2)
C(17)-C(16)-H(16)	118.9	C(41)-C(40)-H(40A)	109.2
C(15)-C(16)-H(16)	118.9	C(39)-C(40)-H(40A)	109.2
C(16)-C(17)-N(4)	120.76(16)	C(41)-C(40)-H(40B)	109.2
C(16)-C(17)-C(18)	119.63(16)	C(39)-C(40)-H(40B)	109.2
N(4)-C(17)-C(18)	119.60(16)	H(40A)-C(40)-H(40B)	107.9
C(19)-C(18)-N(3)	121.47(16)	C(40)-C(41)-C(42)	113.0(2)
C(19)-C(18)-C(17)	117.23(16)	C(40)-C(41)-H(41A)	109.0
N(3)-C(18)-C(17)	121.30(16)	C(42)-C(41)-H(41A)	109.0
C(14)-C(19)-C(18)	123.89(17)	C(40)-C(41)-H(41B)	109.0
C(14)-C(19)-H(19)	118.1	C(42)-C(41)-H(41B)	109.0
C(18)-C(19)-H(19)	118.1	H(41A)-C(41)-H(41B)	107.8
N(4)-C(20)-C(21)	108.3(2)	C(43)-C(42)-C(41)	115.3(3)
N(4)-C(20)-H(20)	125.8	C(43)-C(42)-H(42A)	108.4
C(21)-C(20)-H(20)	125.8	C(41)-C(42)-H(42A)	108.4
C(20)-C(21)-C(22)	107.8(2)	C(43)-C(42)-H(42B)	108.4
C(20)-C(21)-H(21)	126.1	C(41)-C(42)-H(42B)	108.4
C(22)-C(21)-H(21)	126.1	H(42A)-C(42)-H(42B)	107.5
C(23)-C(22)-C(21)	108.2(2)	C(44)-C(43)-C(42)	114.0(4)

C(23)-C(22)-H(22)	125.9	C(44)-C(43)-H(43A)	108.8
C(21)-C(22)-H(22)	125.9	C(42)-C(43)-H(43A)	108.8
C(22)-C(23)-N(4)	106.58(18)	C(44)-C(43)-H(43B)	108.8
C(22)-C(23)-B(2)	134.14(19)	C(42)-C(43)-H(43B)	108.8
N(4)-C(23)-B(2)	119.21(16)	H(43A)-C(43)-H(43B)	107.7
C(25)-C(24)-C(29)	118.9(2)	C(43)-C(44)-H(44A)	109.5
C(25)-C(24)-B(2)	120.9(2)	C(43)-C(44)-H(44B)	109.5
C(29)-C(24)-B(2)	120.2(2)	H(44A)-C(44)-H(44B)	109.5
C(24)-C(25)-C(26)	119.3(3)	C(43)-C(44)-H(44C)	109.5
C(24)-C(25)-C(31)	120.1(2)	H(44A)-C(44)-H(44C)	109.5
C(26)-C(25)-C(31)	120.7(3)	H(44B)-C(44)-H(44C)	109.5
C(27)-C(26)-C(25)	122.0(3)	C(14)-N(1)-B(1)	121.81(17)
C(27)-C(26)-H(26)	119.0	C(14)-N(1)-C(33)	117.97(15)
C(25)-C(26)-H(26)	119.0	B(1)-N(1)-C(33)	120.22(17)
C(28)-C(27)-C(26)	118.1(3)	C(13)-N(2)-C(10)	109.77(16)
C(28)-C(27)-C(32)	120.5(4)	C(13)-N(2)-C(15)	128.42(17)
C(26)-C(27)-C(32)	121.5(4)	C(10)-N(2)-C(15)	121.78(16)
C(27)-C(28)-C(29)	122.8(3)	C(18)-N(3)-B(2)	120.95(16)
C(27)-C(28)-H(28)	118.6	C(18)-N(3)-C(39)	118.59(15)
C(29)-C(28)-H(28)	118.6	B(2)-N(3)-C(39)	120.45(16)
C(28)-C(29)-C(24)	118.8(3)	C(20)-N(4)-C(23)	109.07(17)
C(28)-C(29)-C(30)	120.5(3)	C(20)-N(4)-C(17)	128.99(17)
C(24)-C(29)-C(30)	120.6(2)	C(23)-N(4)-C(17)	121.93(15)

Table S15. Crystal data and structure refinement for **4e**.

Identification code	0510-4_a	
Empirical formula	$C_{38}H_{44}B_2N_4$	
Formula weight	578.39	
Temperature	293(2) K	
Wavelength	1.54184Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.2471(3) Å	α= 66.723(2)°.
	b = 12.1079(3) Å	β= 84.175(2)°.
	c = 13.8717(3) Å	γ= 70.607(2)°.
Volume	1635.86(8) $Å^3$	
Z	2	
Density (calculated)	1.174 Mg/m3	
Absorption coefficient	0.516 mm^{-1}	

F(000)	620
Crystal size	0.220 x 0.200 x 0.180 mm^3
Theta range for data collection	3.471 to 79.408°.
Index ranges	-12<=h<=14, -15<=k<=15, -17<=l<=17
Reflections collected	21494
Independent reflections	6917 [R(int) = 0.0553]
Completeness to theta = 67.684°	99.8 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6917 / 0 / 399
Goodness-of-fit on F^2	1.066
Final R indices [I>2sigma(I)]	R1 = 0.0667, wR2 = 0.1811
R indices (all data)	R1 = 0.0729, wR2 = 0.1900
Extinction coefficient	n/a
Largest diff. peak and hole	0.191 and -0.414 e.$Å^{-3}$

Table S16. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **4e**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
B(1)	6059(1)	4415(2)	6875(1)	34(1)
B(2)	10172(1)	5713(2)	2343(1)	35(1)
C(1)	4999(2)	5324(2)	8276(2)	58(1)
C(2)	3968(2)	5717(2)	8841(2)	65(1)
C(3)	2812(2)	5691(2)	8644(2)	55(1)
C(4)	2684(2)	5268(2)	7891(2)	57(1)
C(5)	3715(2)	4869(2)	7330(1)	46(1)
C(6)	4895(1)	4893(1)	7508(1)	35(1)
C(7)	6689(1)	3005(1)	7127(1)	35(1)
C(8)	6541(1)	1913(1)	7899(1)	40(1)
C(9)	7516(2)	866(1)	7831(1)	44(1)
C(10)	8251(2)	1316(1)	7014(1)	39(1)
C(11)	8170(1)	3492(1)	5726(1)	30(1)
C(12)	7585(1)	4810(1)	5471(1)	30(1)
C(13)	8023(1)	5638(1)	4605(1)	32(1)
C(14)	8984(1)	5243(1)	3978(1)	31(1)
C(15)	9551(1)	3924(1)	4260(1)	31(1)
C(16)	9135(1)	3081(1)	5117(1)	32(1)
C(17)	11221(1)	2241(1)	3809(1)	41(1)
C(18)	11985(1)	2259(2)	2968(1)	44(1)

C(19)	11728(1)	3524(2)	2266(1)	41(1)
C(20)	10806(1)	4284(1)	2682(1)	35(1)
C(21)	10356(1)	6679(1)	1226(1)	35(1)
C(22)	11003(2)	7537(2)	1056(1)	47(1)
C(23)	11084(2)	8421(2)	62(1)	53(1)
C(24)	10515(2)	8465(2)	-788(1)	50(1)
C(25)	9879(2)	7620(2)	-649(1)	51(1)
C(26)	9811(2)	6731(2)	344(1)	44(1)
C(27)	8740(1)	7482(1)	2846(1)	35(1)
C(28)	7479(1)	8062(1)	2242(1)	38(1)
C(29)	6892(1)	9457(1)	2057(1)	42(1)
C(30)	5714(2)	10122(1)	1351(1)	48(1)
C(31)	5152(2)	11520(2)	1129(2)	63(1)
C(32)	3983(2)	12176(2)	414(2)	69(1)
C(33)	6026(1)	6639(1)	5761(1)	34(1)
C(34)	5048(1)	7254(1)	4861(1)	38(1)
C(35)	4439(2)	8685(1)	4580(1)	45(1)
C(36)	3628(2)	9041(1)	5430(1)	46(1)
C(37)	2443(2)	8660(2)	5625(2)	50(1)
C(38)	1643(2)	9019(2)	6471(2)	62(1)
N(1)	6585(1)	5257(1)	6061(1)	32(1)
N(2)	7750(1)	2616(1)	6581(1)	33(1)
N(3)	9344(1)	6118(1)	3076(1)	33(1)
N(4)	10506(1)	3471(1)	3640(1)	33(1)

Table S17. Bond Lengths [Å] for **4e**.

Atom	Length/ Å	Atom	Length/ Å
B(1)-N(1)	1.4214(19)	C(22)-C(23)	1.389(2)
B(1)-C(7)	1.521(2)	C(22)-H(22)	0.9300
B(1)-C(6)	1.577(2)	C(23)-C(24)	1.372(3)
B(2)-N(3)	1.4277(19)	C(23)-H(23)	0.9300
B(2)-C(20)	1.526(2)	C(24)-C(25)	1.377(3)
B(2)-C(21)	1.573(2)	C(24)-H(24)	0.9300
C(1)-C(6)	1.388(2)	C(25)-C(26)	1.387(2)
C(1)-C(2)	1.390(2)	C(25)-H(25)	0.9300
C(1)-H(1)	0.9300	C(26)-H(26)	0.9300
C(2)-C(3)	1.368(3)	C(27)-N(3)	1.4752(16)

C(2)-H(2)	0.9300	C(27)-C(28)	1.524(2)
C(3)-C(4)	1.370(3)	C(27)-H(27A)	0.9700
C(3)-H(3)	0.9300	C(27)-H(27B)	0.9700
C(4)-C(5)	1.388(2)	C(28)-C(29)	1.5180(19)
C(4)-H(4)	0.9300	C(28)-H(28A)	0.9700
C(5)-C(6)	1.386(2)	C(28)-H(28B)	0.9700
C(5)-H(5)	0.9300	C(29)-C(30)	1.515(2)
C(7)-C(8)	1.384(2)	C(29)-H(29A)	0.9700
C(7)-N(2)	1.3941(17)	C(29)-H(29B)	0.9700
C(8)-C(9)	1.403(2)	C(30)-C(31)	1.509(2)
C(8)-H(8)	0.9300	C(30)-H(30A)	0.9700
C(9)-C(10)	1.374(2)	C(30)-H(30B)	0.9700
C(9)-H(9)	0.9300	C(31)-C(32)	1.514(3)
C(10)-N(2)	1.3735(17)	C(31)-H(31A)	0.9700
C(10)-H(10)	0.9300	C(31)-H(31B)	0.9700
C(11)-C(16)	1.3886(18)	C(32)-H(32A)	0.9600
C(11)-N(2)	1.4064(17)	C(32)-H(32B)	0.9600
C(11)-C(12)	1.4174(17)	C(32)-H(32C)	0.9600
C(12)-C(13)	1.3959(19)	C(33)-N(1)	1.4746(16)
C(12)-N(1)	1.4091(16)	C(33)-C(34)	1.525(2)
C(13)-C(14)	1.3963(18)	C(33)-H(33A)	0.9700
C(13)-H(13)	0.9300	C(33)-H(33B)	0.9700
C(14)-N(3)	1.4087(17)	C(34)-C(35)	1.535(2)
C(14)-C(15)	1.4111(18)	C(34)-H(34A)	0.9700
C(15)-C(16)	1.3855(19)	C(34)-H(34B)	0.9700
C(15)-N(4)	1.4100(17)	C(35)-C(36)	1.525(2)
C(16)-H(16)	0.9300	C(35)-H(35A)	0.9700
C(17)-N(4)	1.3730(18)	C(35)-H(35B)	0.9700
C(17)-C(18)	1.375(2)	C(36)-C(37)	1.516(2)
C(17)-H(17)	0.9300	C(36)-H(36A)	0.9700
C(18)-C(19)	1.400(2)	C(36)-H(36B)	0.9700
C(18)-H(18)	0.9300	C(37)-C(38)	1.518(2)
C(19)-C(20)	1.3859(19)	C(37)-H(37A)	0.9700
C(19)-H(19)	0.9300	C(37)-H(37B)	0.9700
C(20)-N(4)	1.3945(18)	C(38)-H(38A)	0.9600
C(21)-C(22)	1.393(2)	C(38)-H(38B)	0.9600
C(21)-C(26)	1.395(2)	C(38)-H(38C)	0.9600

Table S18. Bond Angles [°] for **4e**.

Atom	Length/ Å	Atom	Length/ Å
N(1)-B(1)-C(7)	116.61(12)	N(3)-C(27)-C(28)	114.21(11)
N(1)-B(1)-C(6)	122.59(13)	N(3)-C(27)-H(27A)	108.7
C(7)-B(1)-C(6)	120.79(12)	C(28)-C(27)-H(27A)	108.7
N(3)-B(2)-C(20)	116.09(12)	N(3)-C(27)-H(27B)	108.7
N(3)-B(2)-C(21)	121.83(13)	C(28)-C(27)-H(27B)	108.7
C(20)-B(2)-C(21)	121.98(13)	H(27A)-C(27)-H(27B)	107.6
C(6)-C(1)-C(2)	121.65(16)	C(29)-C(28)-C(27)	111.57(12)
C(6)-C(1)-H(1)	119.2	C(29)-C(28)-H(28A)	109.3
C(2)-C(1)-H(1)	119.2	C(27)-C(28)-H(28A)	109.3
C(3)-C(2)-C(1)	120.00(18)	C(29)-C(28)-H(28B)	109.3
C(3)-C(2)-H(2)	120.0	C(27)-C(28)-H(28B)	109.3
C(1)-C(2)-H(2)	120.0	H(28A)-C(28)-H(28B)	108.0
C(2)-C(3)-C(4)	119.53(15)	C(30)-C(29)-C(28)	113.91(13)
C(2)-C(3)-H(3)	120.2	C(30)-C(29)-H(29A)	108.8
C(4)-C(3)-H(3)	120.2	C(28)-C(29)-H(29A)	108.8
C(3)-C(4)-C(5)	120.43(16)	C(30)-C(29)-H(29B)	108.8
C(3)-C(4)-H(4)	119.8	C(28)-C(29)-H(29B)	108.8
C(5)-C(4)-H(4)	119.8	H(29A)-C(29)-H(29B)	107.7
C(6)-C(5)-C(4)	121.34(16)	C(31)-C(30)-C(29)	114.29(15)
C(6)-C(5)-H(5)	119.3	C(31)-C(30)-H(30A)	108.7
C(4)-C(5)-H(5)	119.3	C(29)-C(30)-H(30A)	108.7
C(5)-C(6)-C(1)	117.05(14)	C(31)-C(30)-H(30B)	108.7
C(5)-C(6)-B(1)	120.49(13)	C(29)-C(30)-H(30B)	108.7
C(1)-C(6)-B(1)	122.45(13)	H(30A)-C(30)-H(30B)	107.6
C(8)-C(7)-N(2)	106.47(12)	C(30)-C(31)-C(32)	113.74(18)
C(8)-C(7)-B(1)	133.99(13)	C(30)-C(31)-H(31A)	108.8
N(2)-C(7)-B(1)	119.12(12)	C(32)-C(31)-H(31A)	108.8
C(7)-C(8)-C(9)	108.41(13)	C(30)-C(31)-H(31B)	108.8
C(7)-C(8)-H(8)	125.8	C(32)-C(31)-H(31B)	108.8
C(9)-C(8)-H(8)	125.8	H(31A)-C(31)-H(31B)	107.7
C(10)-C(9)-C(8)	107.76(13)	C(31)-C(32)-H(32A)	109.5
C(10)-C(9)-H(9)	126.1	C(31)-C(32)-H(32B)	109.5
C(8)-C(9)-H(9)	126.1	H(32A)-C(32)-H(32B)	109.5
N(2)-C(10)-C(9)	107.94(13)	C(31)-C(32)-H(32C)	109.5
N(2)-C(10)-H(10)	126.0	H(32A)-C(32)-H(32C)	109.5

C(9)-C(10)-H(10)	126.0	H(32B)-C(32)-H(32C)	109.5
C(16)-C(11)-N(2)	120.77(12)	N(1)-C(33)-C(34)	112.69(11)
C(16)-C(11)-C(12)	119.56(12)	N(1)-C(33)-H(33A)	109.1
N(2)-C(11)-C(12)	119.66(11)	C(34)-C(33)-H(33A)	109.1
C(13)-C(12)-N(1)	121.76(12)	N(1)-C(33)-H(33B)	109.1
C(13)-C(12)-C(11)	117.34(12)	C(34)-C(33)-H(33B)	109.1
N(1)-C(12)-C(11)	120.89(12)	H(33A)-C(33)-H(33B)	107.8
C(12)-C(13)-C(14)	123.89(12)	C(33)-C(34)-C(35)	112.27(13)
C(12)-C(13)-H(13)	118.1	C(33)-C(34)-H(34A)	109.1
C(14)-C(13)-H(13)	118.1	C(35)-C(34)-H(34A)	109.1
C(13)-C(14)-N(3)	121.70(12)	C(33)-C(34)-H(34B)	109.1
C(13)-C(14)-C(15)	117.20(12)	C(35)-C(34)-H(34B)	109.1
N(3)-C(14)-C(15)	121.05(12)	H(34A)-C(34)-H(34B)	107.9
C(16)-C(15)-N(4)	120.28(12)	C(36)-C(35)-C(34)	114.84(13)
C(16)-C(15)-C(14)	120.05(12)	C(36)-C(35)-H(35A)	108.6
N(4)-C(15)-C(14)	119.62(12)	C(34)-C(35)-H(35A)	108.6
C(15)-C(16)-C(11)	121.94(12)	C(36)-C(35)-H(35B)	108.6
C(15)-C(16)-H(16)	119.0	C(34)-C(35)-H(35B)	108.6
C(11)-C(16)-H(16)	119.0	H(35A)-C(35)-H(35B)	107.5
N(4)-C(17)-C(18)	107.87(13)	C(37)-C(36)-C(35)	113.78(14)
N(4)-C(17)-H(17)	126.1	C(37)-C(36)-H(36A)	108.8
C(18)-C(17)-H(17)	126.1	C(35)-C(36)-H(36A)	108.8
C(17)-C(18)-C(19)	107.87(13)	C(37)-C(36)-H(36B)	108.8
C(17)-C(18)-H(18)	126.1	C(35)-C(36)-H(36B)	108.8
C(19)-C(18)-H(18)	126.1	H(36A)-C(36)-H(36B)	107.7
C(20)-C(19)-C(18)	108.42(13)	C(36)-C(37)-C(38)	113.29(16)
C(20)-C(19)-H(19)	125.8	C(36)-C(37)-H(37A)	108.9
C(18)-C(19)-H(19)	125.8	C(38)-C(37)-H(37A)	108.9
C(19)-C(20)-N(4)	106.36(12)	C(36)-C(37)-H(37B)	108.9
C(19)-C(20)-B(2)	134.40(13)	C(38)-C(37)-H(37B)	108.9
N(4)-C(20)-B(2)	119.16(12)	H(37A)-C(37)-H(37B)	107.7
C(22)-C(21)-C(26)	116.76(13)	C(37)-C(38)-H(38A)	109.5
C(22)-C(21)-B(2)	123.84(13)	C(37)-C(38)-H(38B)	109.5
C(26)-C(21)-B(2)	119.36(13)	H(38A)-C(38)-H(38B)	109.5
C(23)-C(22)-C(21)	121.90(15)	C(37)-C(38)-H(38C)	109.5
C(23)-C(22)-H(22)	119.0	H(38A)-C(38)-H(38C)	109.5
C(21)-C(22)-H(22)	119.0	H(38B)-C(38)-H(38C)	109.5
C(24)-C(23)-C(22)	119.90(16)	C(12)-N(1)-B(1)	121.48(12)

C(24)-C(23)-H(23)	120.0	C(12)-N(1)-C(33)	118.19(11)
C(22)-C(23)-H(23)	120.0	B(1)-N(1)-C(33)	120.17(11)
C(23)-C(24)-C(25)	119.68(15)	C(10)-N(2)-C(7)	109.41(11)
C(23)-C(24)-H(24)	120.2	C(10)-N(2)-C(11)	128.86(12)
C(25)-C(24)-H(24)	120.2	C(7)-N(2)-C(11)	121.72(11)
C(24)-C(25)-C(26)	120.28(16)	C(14)-N(3)-B(2)	121.39(11)
C(24)-C(25)-H(25)	119.9	C(14)-N(3)-C(27)	118.13(11)
C(26)-C(25)-H(25)	119.9	B(2)-N(3)-C(27)	120.19(11)
C(25)-C(26)-C(21)	121.45(15)	C(17)-N(4)-C(20)	109.48(12)
C(25)-C(26)-H(26)	119.3	C(17)-N(4)-C(15)	128.71(12)
C(21)-C(26)-H(26)	119.3	C(20)-N(4)-C(15)	121.72(11)

Table S19. Crystal data and structure refinement for **9**.

Identification code	3-143	
Empirical formula	C30 H20 N2	
Formula weight	408.48	
Temperature	293(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 16.1159(3) Å	a= 90°.
	b = 7.5077(2) Å	b= 90°.
	c = 35.1802(8) Å	g = 90°.
Volume	4256.57(17) $Å^3$	
Z	8	
Density (calculated)	1.275 Mg/m^3	
Absorption coefficient	0.574 mm^{-1}	
F(000)	1712	
Crystal size	0.200 x 0.200 x 0.200 mm^3	
Theta range for data collection	2.512 to 68.195°.	
Index ranges	-19<=h<=19, -6<=k<=9, -42<=l<=33	
Reflections collected	35384	
Independent reflections	3852 [R(int) = 0.0713]	
Completeness to theta = 67.679°	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3852 / 0 / 289	

Goodness-of-fit on F^2	1.017
Final R indices [I>2sigma(I)]	R1 = 0.0506, wR2 = 0.1247
R indices (all data)	R1 = 0.0839, wR2 = 0.1459
Extinction coefficient	n/a
Largest diff. peak and hole	0.124 and -0.241 e.$Å^{-3}$

Table S20. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **9**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	8821(1)	3506(3)	4544(1)	61(1)
C(2)	9242(2)	3278(3)	4884(1)	79(1)
C(3)	8909(2)	3934(3)	5217(1)	88(1)
C(4)	8165(2)	4813(3)	5211(1)	78(1)
C(5)	7741(1)	5046(3)	4873(1)	63(1)
C(6)	8064(1)	4394(2)	4534(1)	52(1)
C(7)	5495(1)	4832(3)	3862(1)	61(1)
C(8)	5370(1)	4138(3)	4214(1)	69(1)
C(9)	6136(1)	3944(3)	4395(1)	62(1)
C(10)	6745(1)	4555(2)	4149(1)	49(1)
C(11)	7632(1)	4709(2)	4167(1)	48(1)
C(12)	8051(1)	5203(2)	3850(1)	48(1)
C(13)	7634(1)	5663(2)	3503(1)	45(1)
C(14)	6759(1)	5688(2)	3493(1)	44(1)
C(15)	6334(1)	6270(2)	3175(1)	45(1)
C(16)	6771(1)	6759(2)	2852(1)	43(1)
C(17)	7646(1)	6682(2)	2842(1)	43(1)
C(18)	8053(1)	6158(2)	3174(1)	46(1)
C(19)	8074(1)	7098(2)	2494(1)	47(1)
C(20)	7667(1)	7583(2)	2173(1)	45(1)
C(21)	6780(1)	7773(2)	2186(1)	45(1)
C(22)	6184(1)	8323(2)	1930(1)	55(1)
C(23)	5411(1)	8206(2)	2110(1)	61(1)
C(24)	5527(1)	7606(2)	2470(1)	57(1)
C(25)	8120(1)	7875(2)	1810(1)	48(1)
C(26)	7832(1)	7155(3)	1469(1)	60(1)

C(27)	8277(2)	7370(3)	1137(1)	73(1)
C(28)	9006(2)	8317(3)	1138(1)	79(1)
C(29)	9300(1)	9042(3)	1471(1)	71(1)
C(30)	8859(1)	8822(2)	1806(1)	54(1)
N(1)	6335(1)	5086(2)	3816(1)	49(1)
N(2)	6365(1)	7340(2)	2524(1)	46(1)

Table S21. Bond Lengths [Å] for **9**.

Atom	Length/ Å	Atom	Length/ Å
C(1)-C(2)	1.384(3)	C(15)-H(15)	0.9300
C(1)-C(6)	1.390(3)	C(16)-N(2)	1.398(2)
C(1)-H(1)	0.9300	C(16)-C(17)	1.412(2)
C(2)-C(3)	1.381(3)	C(17)-C(18)	1.396(2)
C(2)-H(2)	0.9300	C(17)-C(19)	1.439(2)
C(3)-C(4)	1.369(3)	C(18)-H(18)	0.9300
C(3)-H(3)	0.9300	C(19)-C(20)	1.356(2)
C(4)-C(5)	1.382(3)	C(19)-H(19)	0.9300
C(4)-H(4)	0.9300	C(20)-C(21)	1.438(2)
C(5)-C(6)	1.391(3)	C(20)-C(25)	1.486(2)
C(5)-H(5)	0.9300	C(21)-C(22)	1.380(2)
C(6)-C(11)	1.485(2)	C(21)-N(2)	1.400(2)
C(7)-C(8)	1.360(3)	C(22)-C(23)	1.401(3)
C(7)-N(1)	1.377(2)	C(22)-H(22)	0.9300
C(7)-H(7)	0.9300	C(23)-C(24)	1.357(3)
C(8)-C(9)	1.398(3)	C(23)-H(23)	0.9300
C(8)-H(8)	0.9300	C(24)-N(2)	1.378(2)
C(9)-C(10)	1.387(2)	C(24)-H(24)	0.9300
C(9)-H(9)	0.9300	C(25)-C(30)	1.387(2)
C(10)-N(1)	1.402(2)	C(25)-C(26)	1.395(3)
C(10)-C(11)	1.436(2)	C(26)-C(27)	1.381(3)
C(11)-C(12)	1.356(2)	C(26)-H(26)	0.9300
C(12)-C(13)	1.436(2)	C(27)-C(28)	1.373(3)
C(12)-H(12)	0.9300	C(27)-H(27)	0.9300
C(13)-C(18)	1.392(2)	C(28)-C(29)	1.378(3)
C(13)-C(14)	1.411(2)	C(28)-H(28)	0.9300
C(14)-C(15)	1.382(2)	C(29)-C(30)	1.386(3)
C(14)-N(1)	1.400(2)	C(29)-H(29)	0.9300

C(15)-C(16)	1.385(2	C(30)-H(30)	0.9300

Table S22. Bond Angles [°] for **9**.

Atom	Angles/°	Atom	Angles/°
C(2)-C(1)-C(6)	120.7(2)	C(18)-C(17)-C(16)	117.43(16)
C(2)-C(1)-H(1)	119.6	C(18)-C(17)-C(19)	123.19(16)
C(6)-C(1)-H(1)	119.6	C(16)-C(17)-C(19)	119.36(16)
C(3)-C(2)-C(1)	119.9(2)	C(13)-C(18)-C(17)	122.89(17)
C(3)-C(2)-H(2)	120.1	C(13)-C(18)-H(18)	118.6
C(1)-C(2)-H(2)	120.1	C(17)-C(18)-H(18)	118.6
C(4)-C(3)-C(2)	120.0(2)	C(20)-C(19)-C(17)	122.41(17)
C(4)-C(3)-H(3)	120.0	C(20)-C(19)-H(19)	118.8
C(2)-C(3)-H(3)	120.0	C(17)-C(19)-H(19)	118.8
C(3)-C(4)-C(5)	120.4(2)	C(19)-C(20)-C(21)	118.69(17)
C(3)-C(4)-H(4)	119.8	C(19)-C(20)-C(25)	121.25(17)
C(5)-C(4)-H(4)	119.8	C(21)-C(20)-C(25)	120.05(16)
C(4)-C(5)-C(6)	120.6(2)	C(22)-C(21)-N(2)	106.95(16)
C(4)-C(5)-H(5)	119.7	C(22)-C(21)-C(20)	134.42(18)
C(6)-C(5)-H(5)	119.7	N(2)-C(21)-C(20)	118.63(15)
C(1)-C(6)-C(5)	118.38(18)	C(21)-C(22)-C(23)	107.70(18)
C(1)-C(6)-C(11)	120.65(18)	C(21)-C(22)-H(22)	126.1
C(5)-C(6)-C(11)	120.91(18)	C(23)-C(22)-H(22)	126.1
C(8)-C(7)-N(1)	107.83(18)	C(24)-C(23)-C(22)	108.70(17)
C(8)-C(7)-H(7)	126.1	C(24)-C(23)-H(23)	125.6
N(1)-C(7)-H(7)	126.1	C(22)-C(23)-H(23)	125.6
C(7)-C(8)-C(9)	108.91(19)	C(23)-C(24)-N(2)	108.08(17)
C(7)-C(8)-H(8)	125.5	C(23)-C(24)-H(24)	126.0
C(9)-C(8)-H(8)	125.5	N(2)-C(24)-H(24)	126.0
C(10)-C(9)-C(8)	107.78(19)	C(30)-C(25)-C(26)	118.39(18)
C(10)-C(9)-H(9)	126.1	C(30)-C(25)-C(20)	120.37(17)
C(8)-C(9)-H(9)	126.1	C(26)-C(25)-C(20)	121.20(18)
C(9)-C(10)-N(1)	106.50(17)	C(27)-C(26)-C(25)	120.6(2)
C(9)-C(10)-C(11)	134.57(19)	C(27)-C(26)-H(26)	119.7
N(1)-C(10)-C(11)	118.93(16)	C(25)-C(26)-H(26)	119.7
C(12)-C(11)-C(10)	118.72(17)	C(28)-C(27)-C(26)	120.3(2)
C(12)-C(11)-C(6)	121.60(18)	C(28)-C(27)-H(27)	119.8
C(10)-C(11)-C(6)	119.64(17)	C(26)-C(27)-H(27)	119.8

C(11)-C(12)-C(13)	122.10(18)	C(27)-C(28)-C(29)	120.0(2)
C(11)-C(12)-H(12)	118.9	C(27)-C(28)-H(28)	120.0
C(13)-C(12)-H(12)	118.9	C(29)-C(28)-H(28)	120.0
C(18)-C(13)-C(14)	117.38(16)	C(28)-C(29)-C(30)	120.0(2)
C(18)-C(13)-C(12)	122.95(17)	C(28)-C(29)-H(29)	120.0
C(14)-C(13)-C(12)	119.62(16)	C(30)-C(29)-H(29)	120.0
C(15)-C(14)-N(1)	121.20(16)	C(29)-C(30)-C(25)	120.70(19)
C(15)-C(14)-C(13)	121.36(16)	C(29)-C(30)-H(30)	119.7
N(1)-C(14)-C(13)	117.44(16)	C(25)-C(30)-H(30)	119.7
C(14)-C(15)-C(16)	119.72(16)	C(7)-N(1)-C(14)	128.21(16)
C(14)-C(15)-H(15)	120.1	C(7)-N(1)-C(10)	108.98(15)
C(16)-C(15)-H(15)	120.1	C(14)-N(1)-C(10)	122.74(15)
C(15)-C(16)-N(2)	121.49(16)	C(24)-N(2)-C(16)	128.13(16)
C(15)-C(16)-C(17)	121.10(16)	C(24)-N(2)-C(21)	108.55(15)
N(2)-C(16)-C(17)	117.42(15)	C(16)-N(2)-C(21)	123.32(15)

7. Electrochemical Properties

Cyclic voltammetry (CV) measurements were performed in a three-electrode cell in CH_2Cl_2 solution (oxidation waves) or THF solution (reduction waves) of 0.1 M *n*-Bu_4NPF_6 with a scan rate of 100 mV/s at room temperature, using glassy carbon 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.

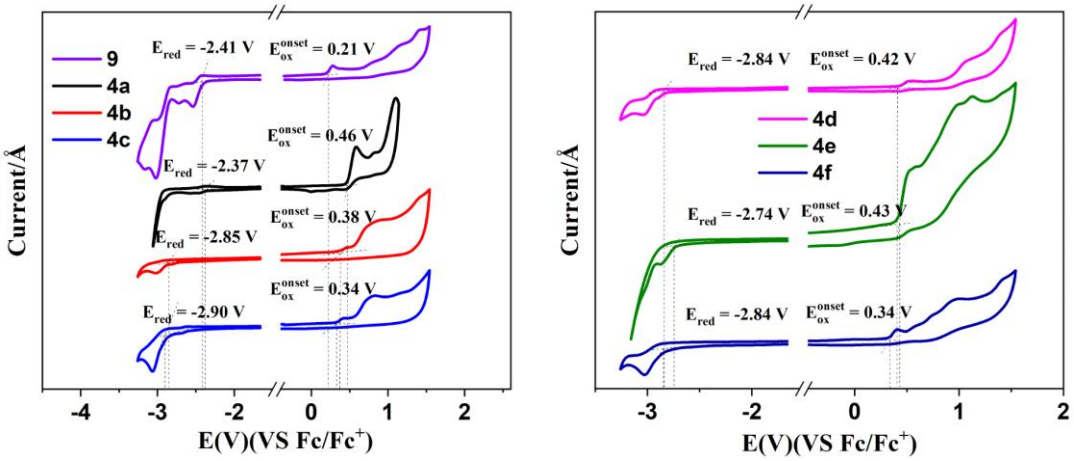


Figure S10. Cyclic voltammogram of **4a-4f** and **9** measured in CH_2Cl_2 (oxidation waves) and THF (reduction waves) at a scan rate of 100 mV/S.

Table S23. Electrochemical properties of **4a-4f** and **9**.

Compounds	E_{ox}^{onset} (V)	E_{red}^{onset} (V)	E_{HOMO}(eV)[a]	E_{LUMO}(eV)[b]	E_G (eV)[c]
4a	0.46	-2.37	-5.26	-2.43	2.83
4b	0.38	-2.85	-5.18	-1.95	3.23
4c	0.34	-2.90	-5.14	-1.90	3.24
4d	0.42	-2.84	-5.22	-1.96	3.26
4e	0.43	-2.74	-5.23	-2.06	3.17
4f	0.34	-2.84	-5.14	-1.96	3.18
9	0.21	-2.41	-5.01	-2.39	2.62

HOMO and LUMO energy levels were calculated from the onset potentials of the first oxidation the first reduction wave according to the following equations: [a] E_{HOMO} = –4.8 eV–E_{ox}^{onset}. [b] E_{LUMO}= –4.8 eV–E_{red}^{onset}. [c] E_G= E_{LUMO}–E_{HOMO}, where the potentials are referred to E_{Fc/Fc^+}.

8. Device performance

OLED fabrication.

The devices **I** to **VII** were fabricated by the following processes. The Indium Tin Oxide (ITO)-coated glass substrates with a sheet resistance of about 20 Ω/square were used as anodes. Before spin-coating, the ITO substrates were ultrasonically cleaned with non-ionic detergent, deionized water, acetone and isopropyl alcohol for 15 minutes at each step, and dried with nitrogen gas. Then, the ITO substrates were treated by ultraviolet ozone for 15 minutes. After that, Poly (3,4-ethylenedioxythiophene) (PEDOT): Polystyrene Sulfonate (PSS, Baytron PVP AI 4083) was spin coated on pre-cleaned ITO substrates to form a 40 nm hole transport layer and baked at 100 ºC for 20 minutes. Compounds **4** or **9** (9 mg) and PVK (2 mg, 99%, Acros) were dissolved in 1 mL toluene to obtain the required solution. The prepared mixtures filtered with a pore filter was spin coated at 2000 rpm for 30 seconds on PEDOT:PSS layer to form a 50 nm EML (Emitting Layer) and baked for 10 min at 80 ºC. Doping polymer PVK could obviously improve the film-forming quality of EML. 4,7-Diphnenyl-1,10-phe-nanthroline (Bphen, 30nm, 99.5%, Lumitec), LiF (Lithium Fluoride, 1nm) and Al (Aluminum, 120 nm) were successively deposited by the vacuum thermal evaporation (Edwards Auto-500 evaporation system integrated with M. Braun 20 G glove-box) under a base vacuum of about 7×10^{-5} Pa. The film thickness and deposition rate were monitored and controlled in situ by using an oscillating quartz thickness monitor. The evaporation rates for Bphen, LiF and Al are 0.20 nm/s, 0.05 nm/s and 5 nm/s, respectively. Current density-voltage (*J-V*), luminance-voltage (*L-V*), current efficiency-current density, power efficiency-current density and external quantum efficiency-current density characteristics were measured with a Keithley 2400 Source Meter and a PhotoResearch SpectraScan PR-650 Colorimeter. The EQE (External Quantum Efficiency) and the power efficiency of OLEDs were calculated from the current density, the luminance, the electroluminescence spectra, and the angular distribution of the electroluminescence intensity.

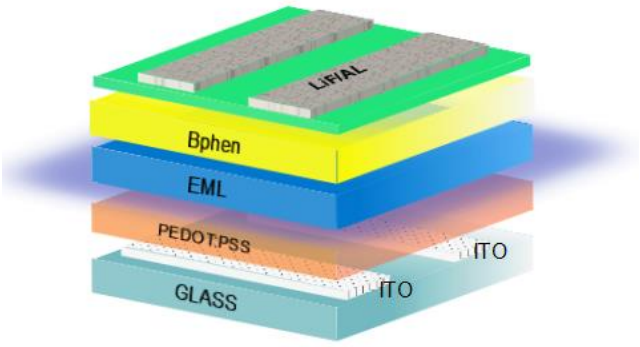


Figure S11. Schematic structure of OLEDs device.

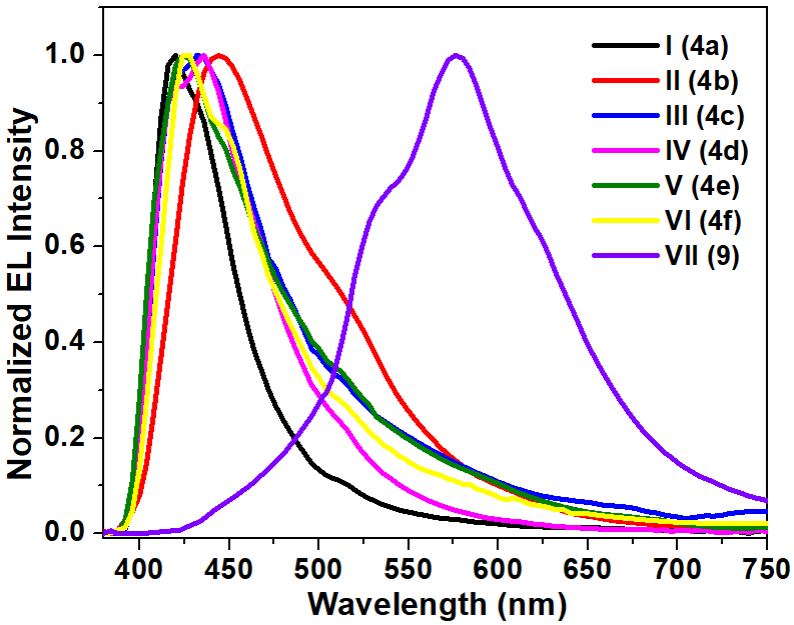


Figure S12. Normalized electroluminescence spectra of devices **I** to **VII**.

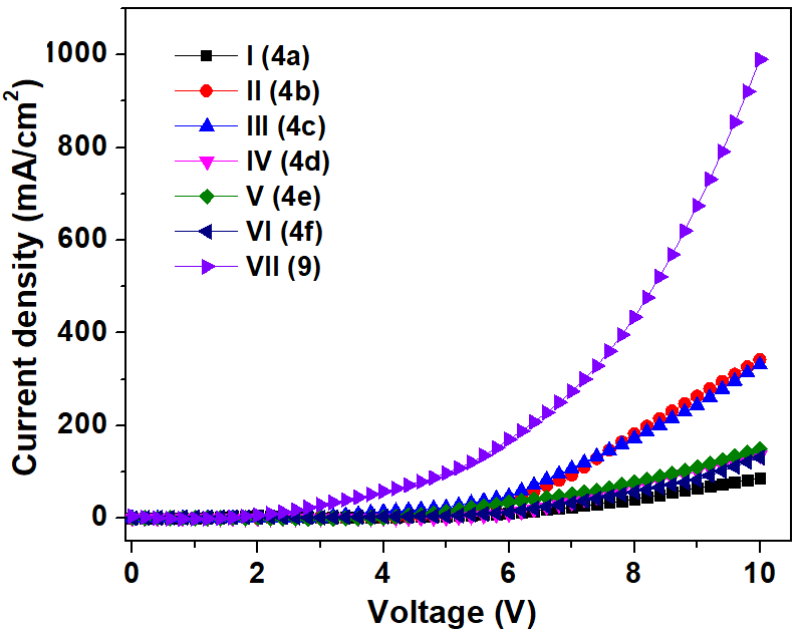


Figure S13. Current density−voltage (*J*-*V*) curves of devices **I** to **VII**.

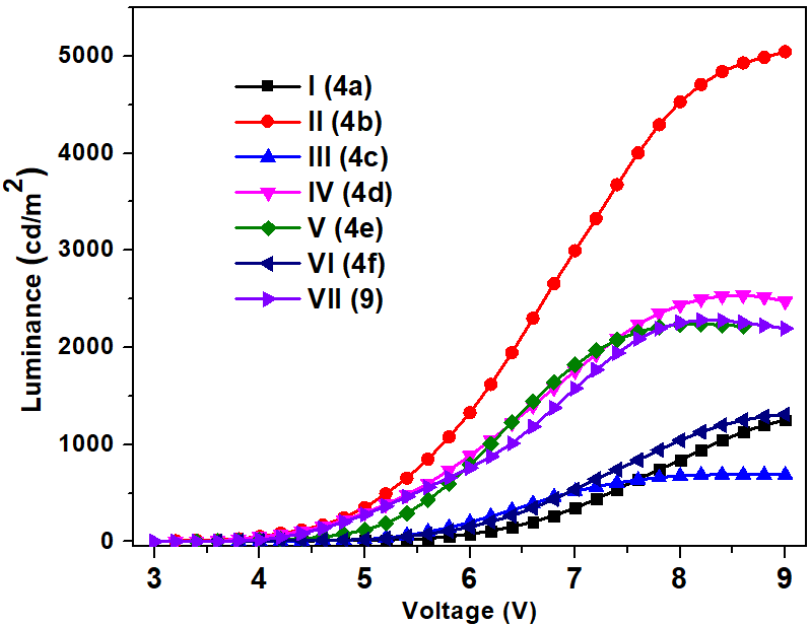


Figure S14. Luminescence-voltage (*L*-*V*) curves of devices **I** to **VII**.

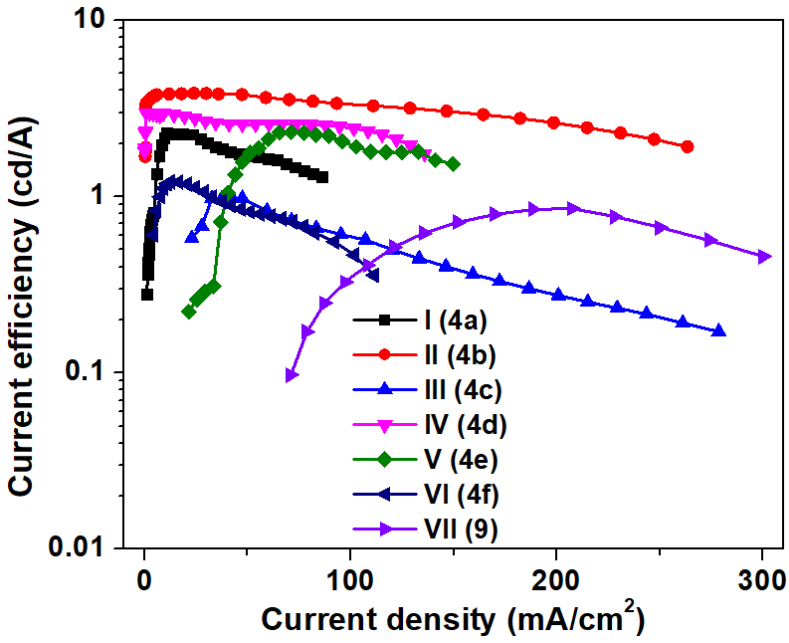


Figure S15. Current efficiency-current density curves of devices **I** to **VII**.

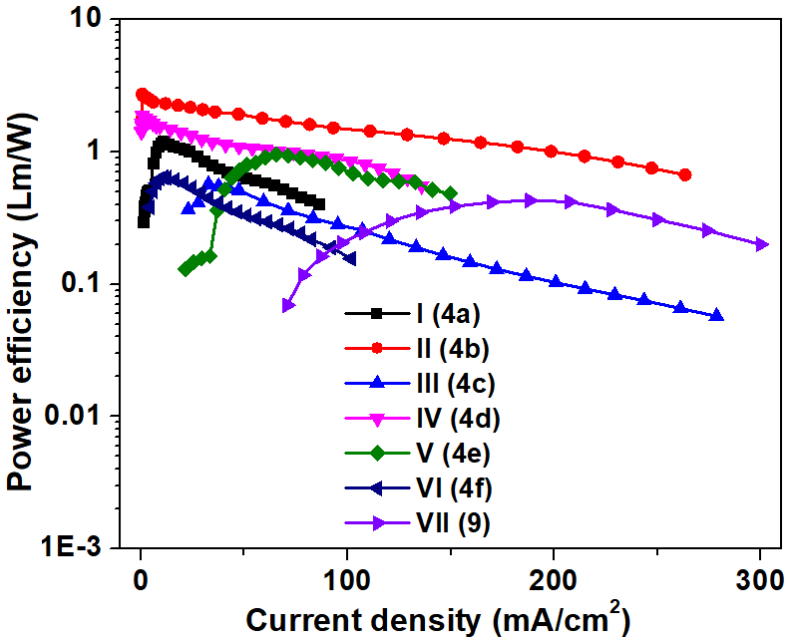


Figure S16. Power efficiency-current density curves of devices **I** to **VII**.

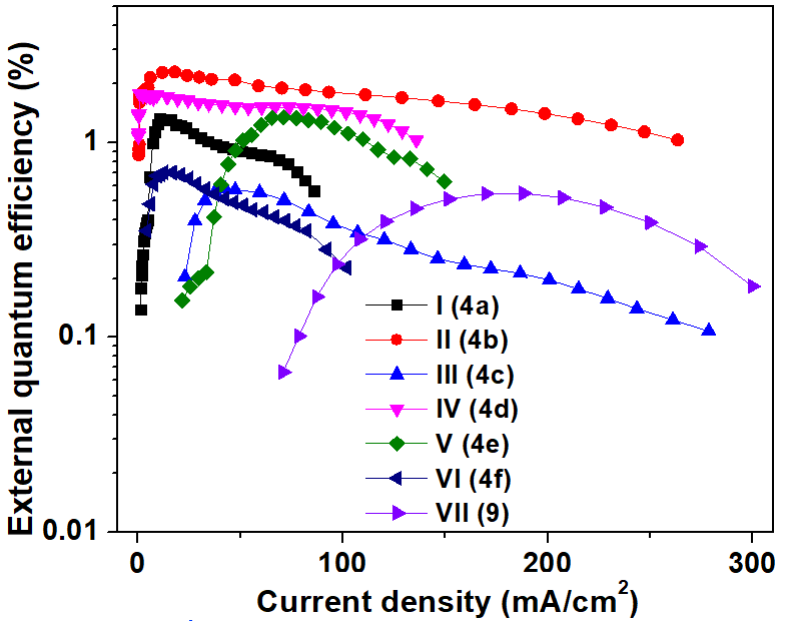
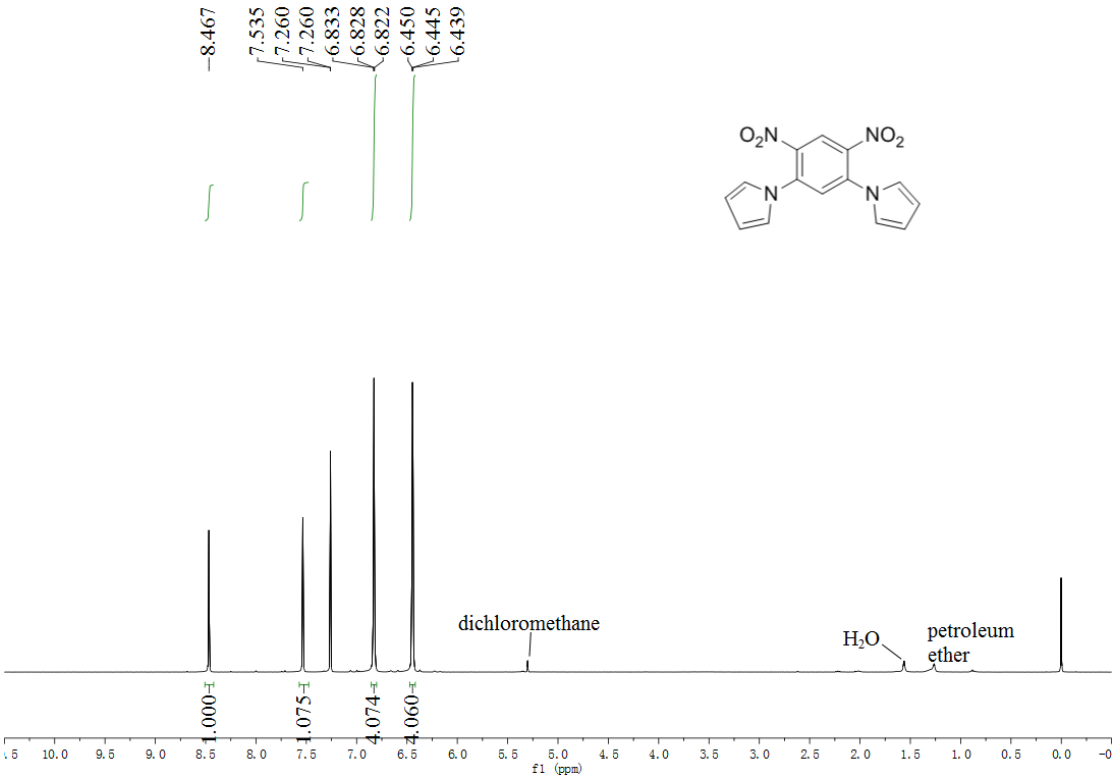


Figure S17. External quantum efficiency-current density curves of devices **I** to **VII**.

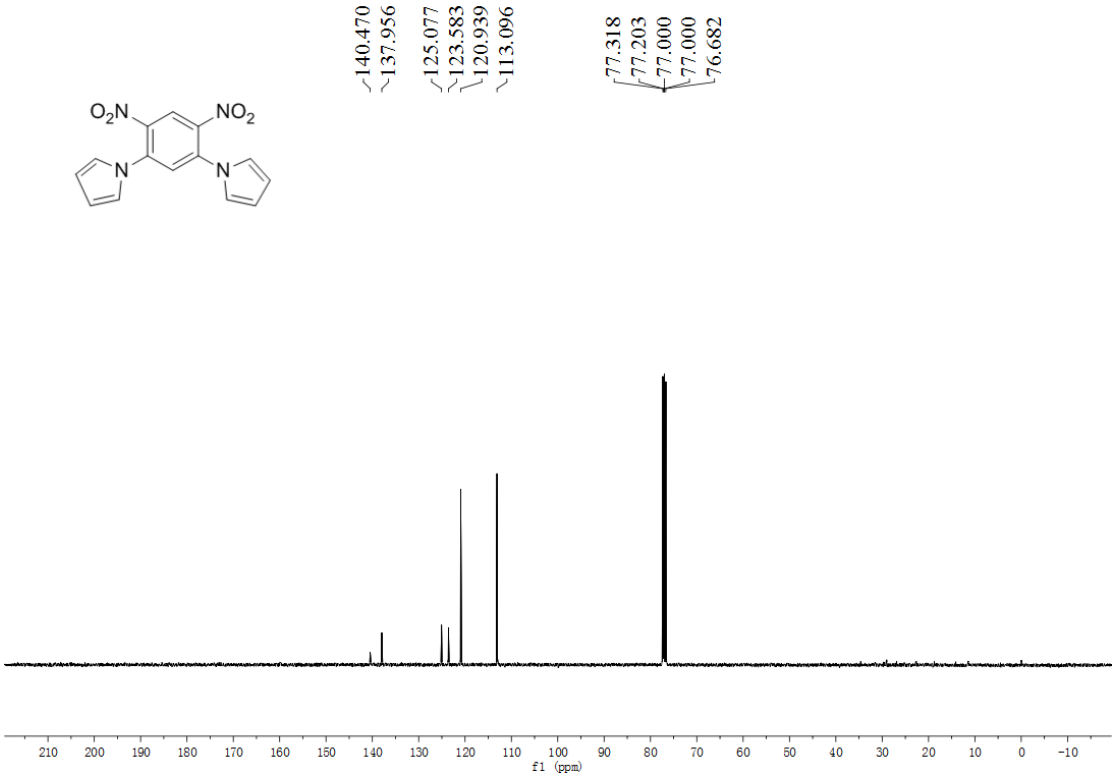
9. References

[1] W. Z. Zhang, F. Zhang, R. Z. Tang, W. B. Fu, X. Y. Wang, X. D. Zhuang, G. F. He, X. L. Feng, *Org. Lett.* 2016, **18**, 3618-3621.
[2] Y. Xing, B. Hu, Q. Yao, P. Lu, Y. Wang, *Chem. Eur. J.* 2013, **19**, 12788-12793.
[3] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, Jr. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega,N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian 09, Revision A.02*; Gaussian, Inc., Wallingford, CT, 2009.
[4] A. D. Becke, *J. Chem. Phys.* 1993, **98**, 5648−5652.

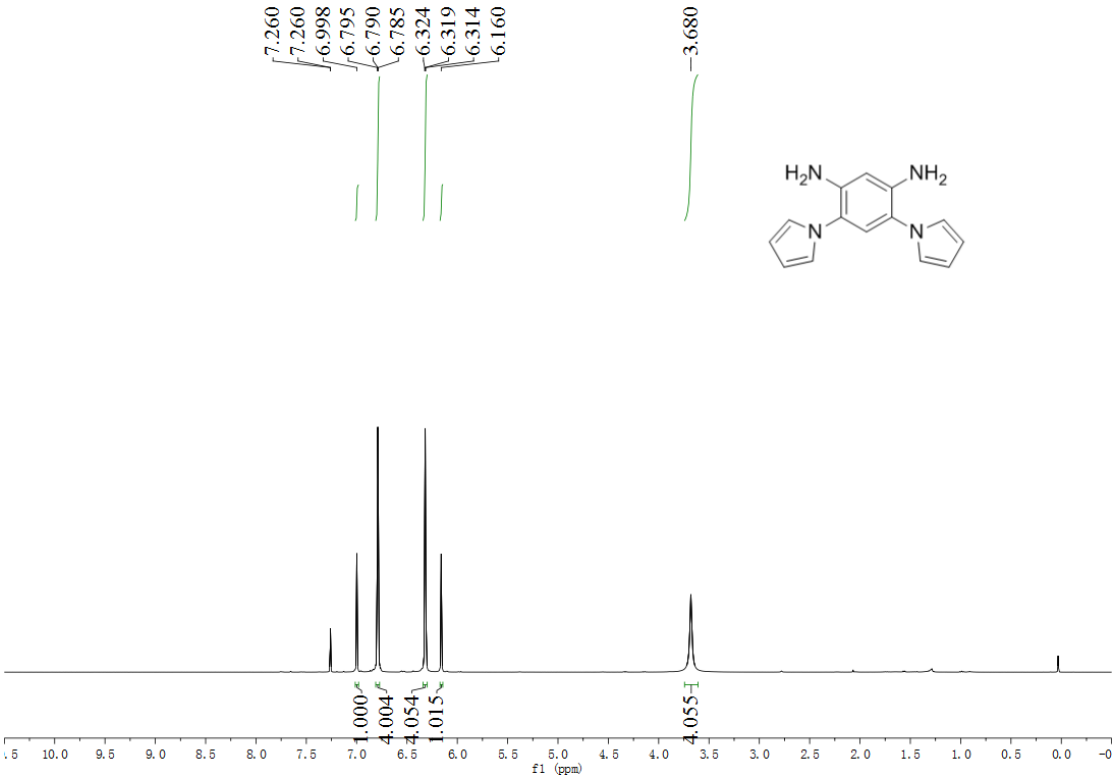
10. NMR Spectra



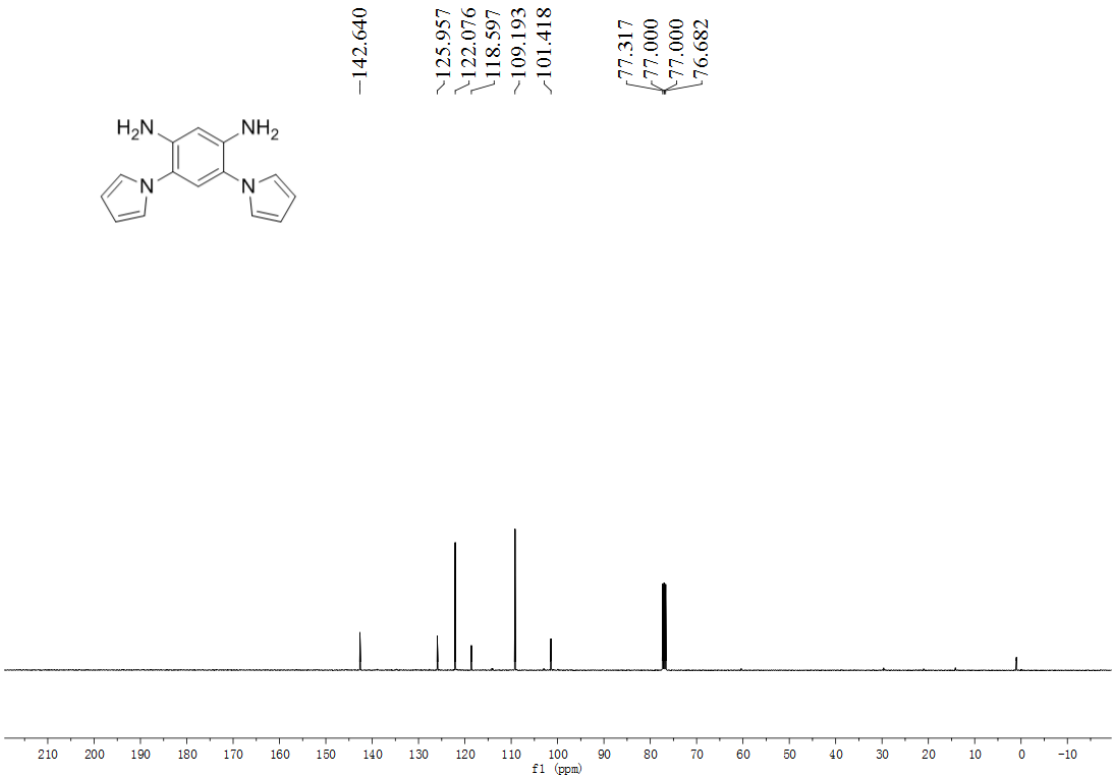
^{1}H NMR spectra of **2** (400 MHz, $CDCl_3$)



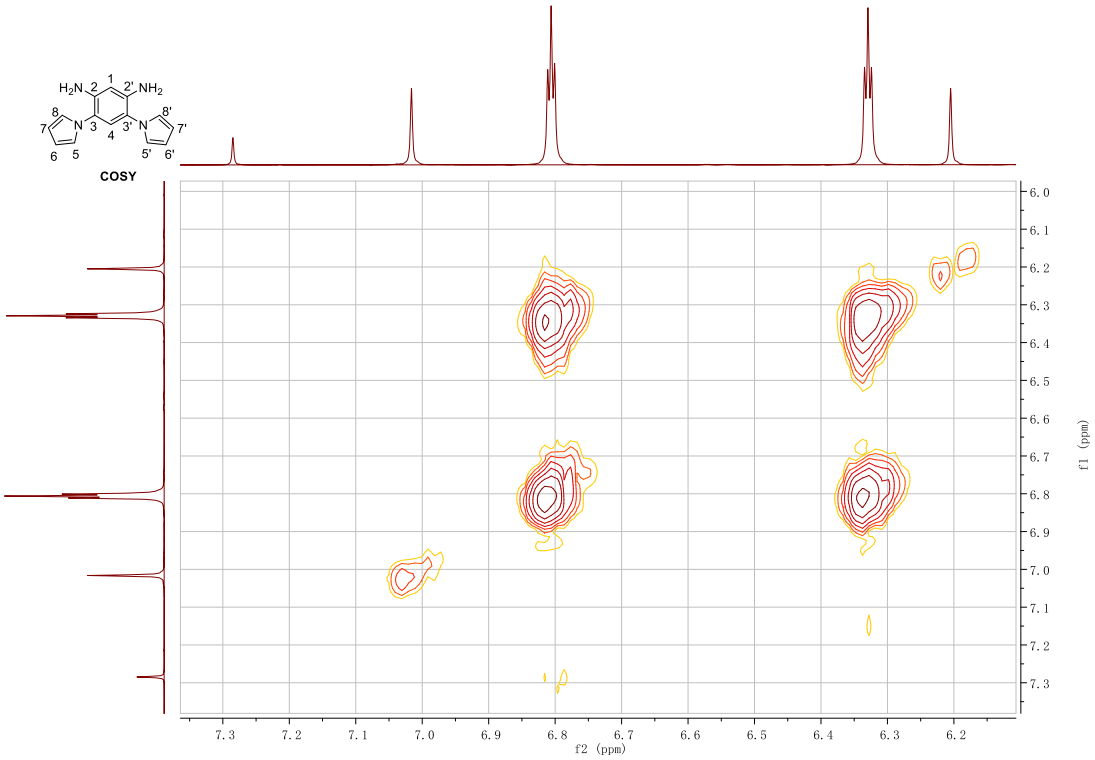
^{13}C NMR spectra of **2** (100 MHz, $CDCl_3$)



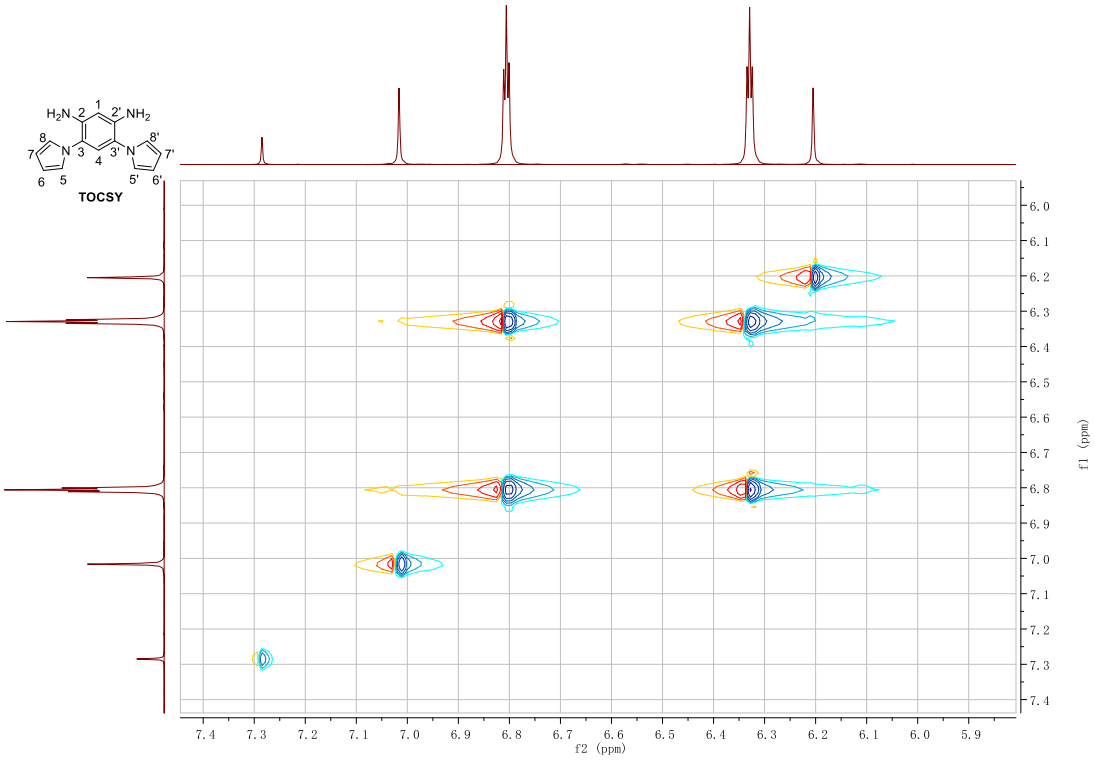
^{1}H NMR spectra of **3a** (400 MHz, $CDCl_3$)



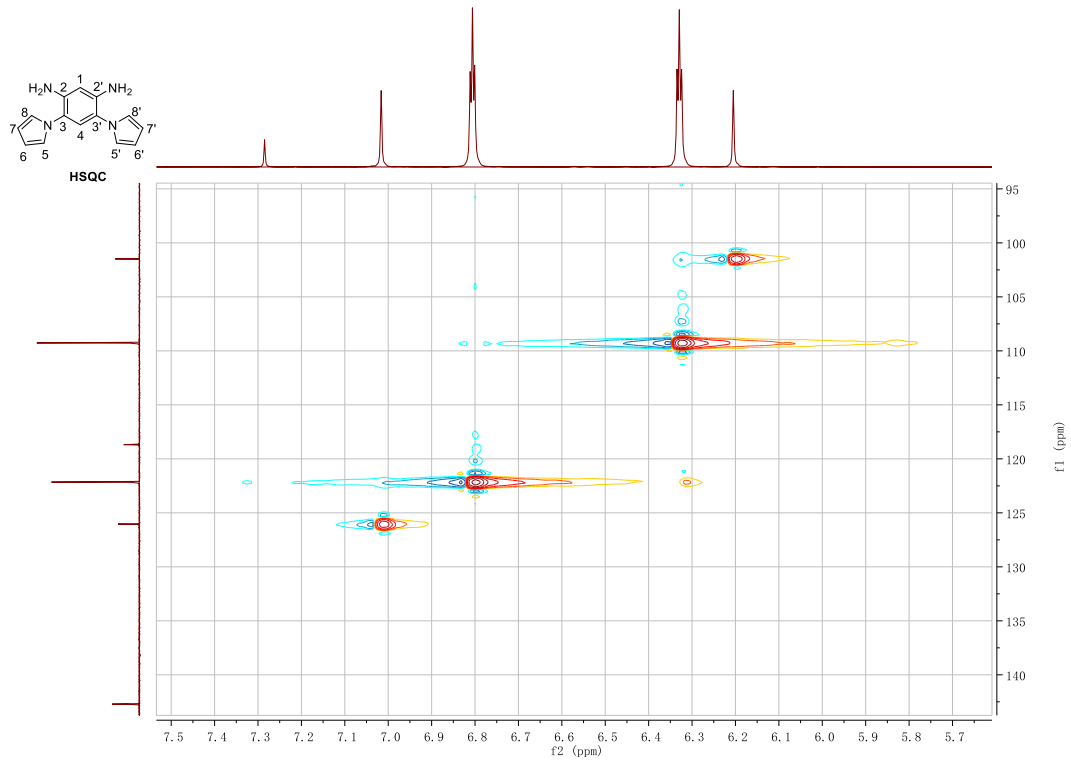
^{13}C NMR spectra of **3a** (100 MHz, $CDCl_3$)



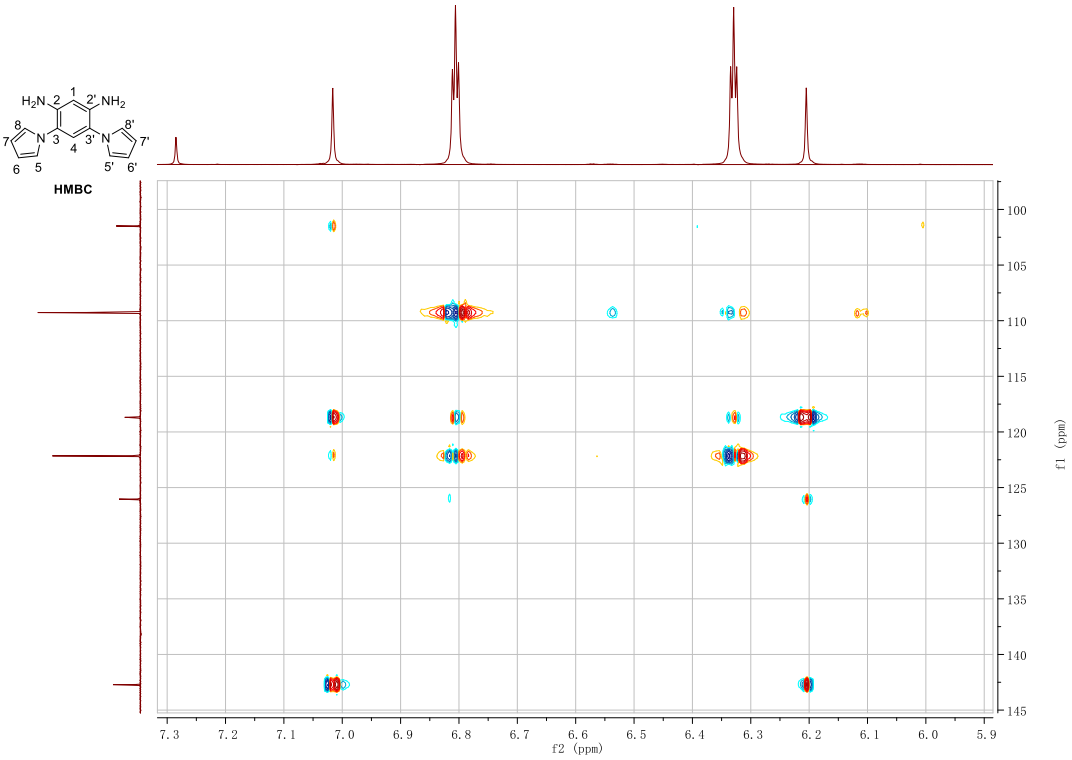
COSY NMR spectra of **3a** ($CDCl_3$)



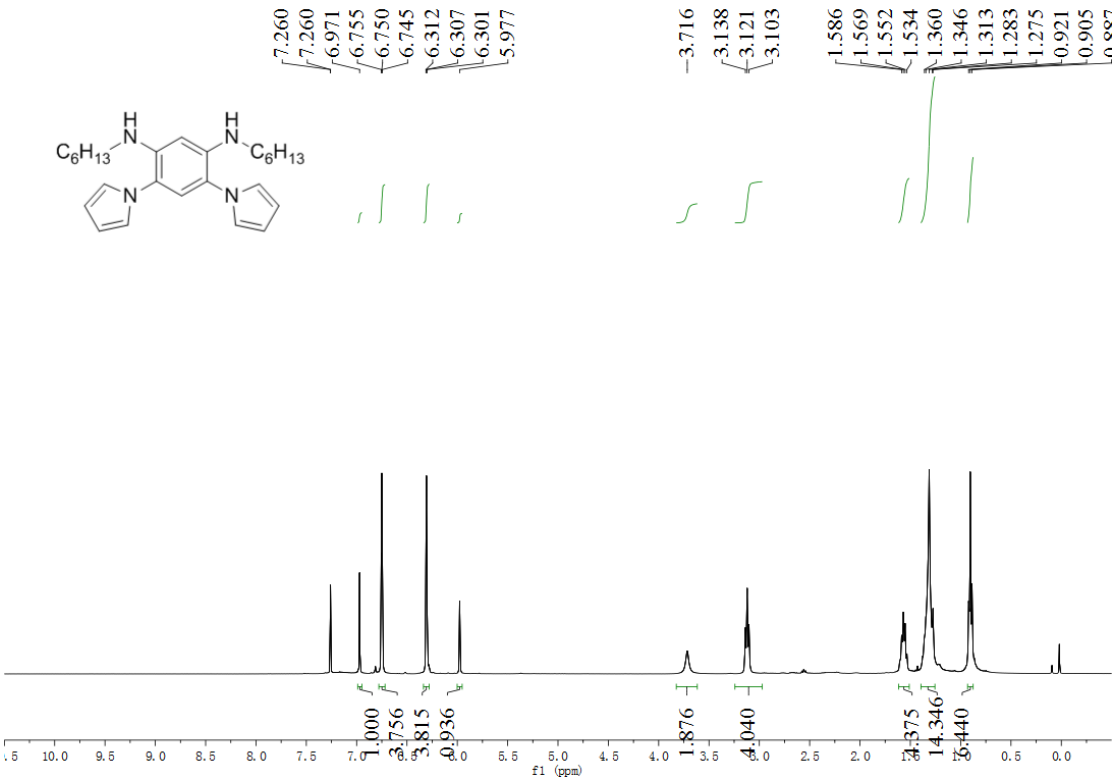
TOCSY NMR spectra of **3a** ($CDCl_3$)



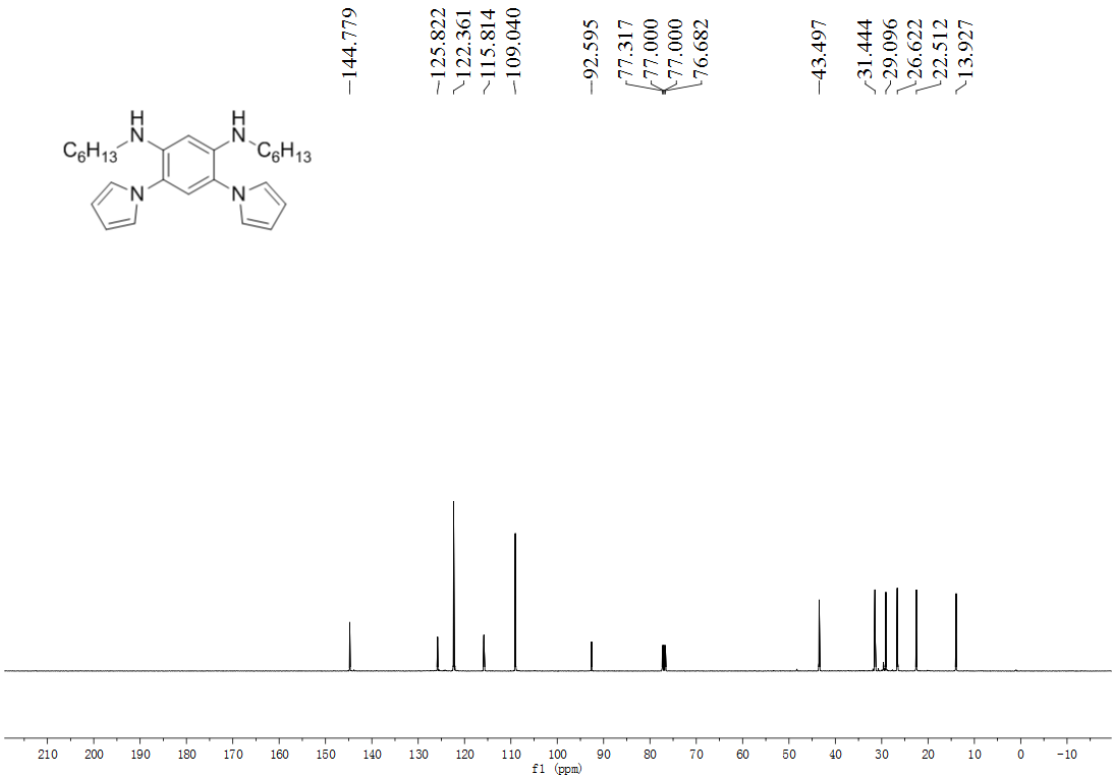
HSQC NMR spectra of **3a** ($CDCl_3$)



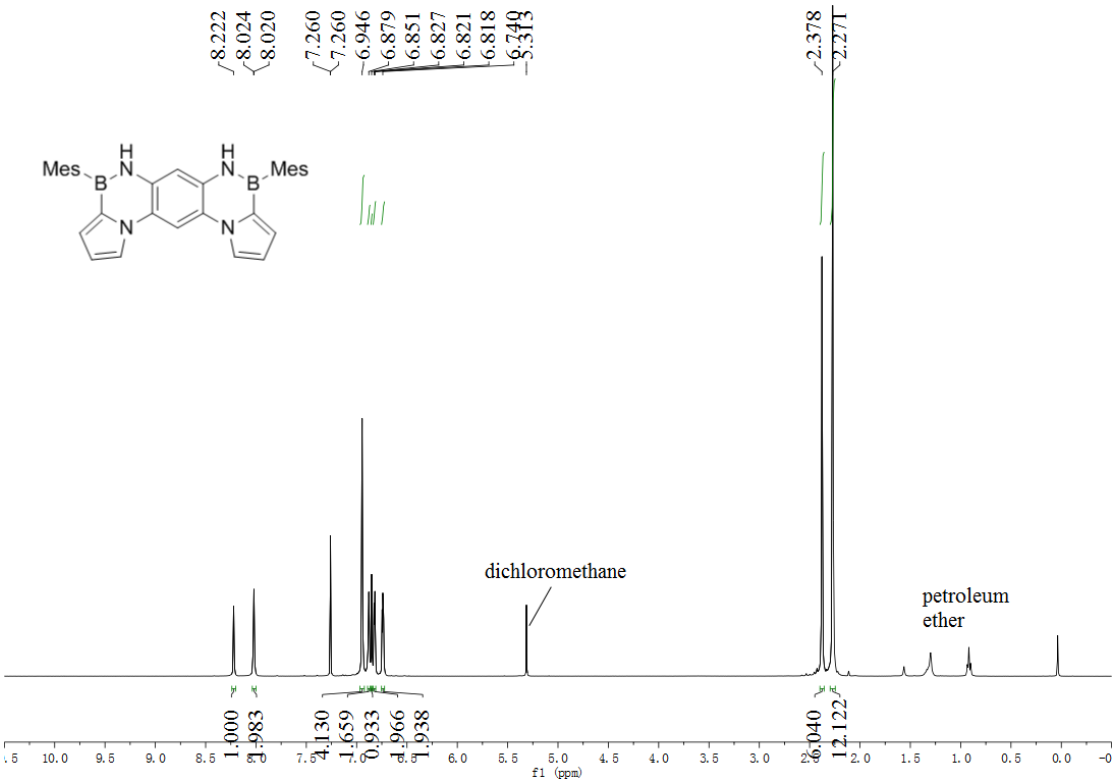
HMBC NMR spectra of **3a** ($CDCl_3$)



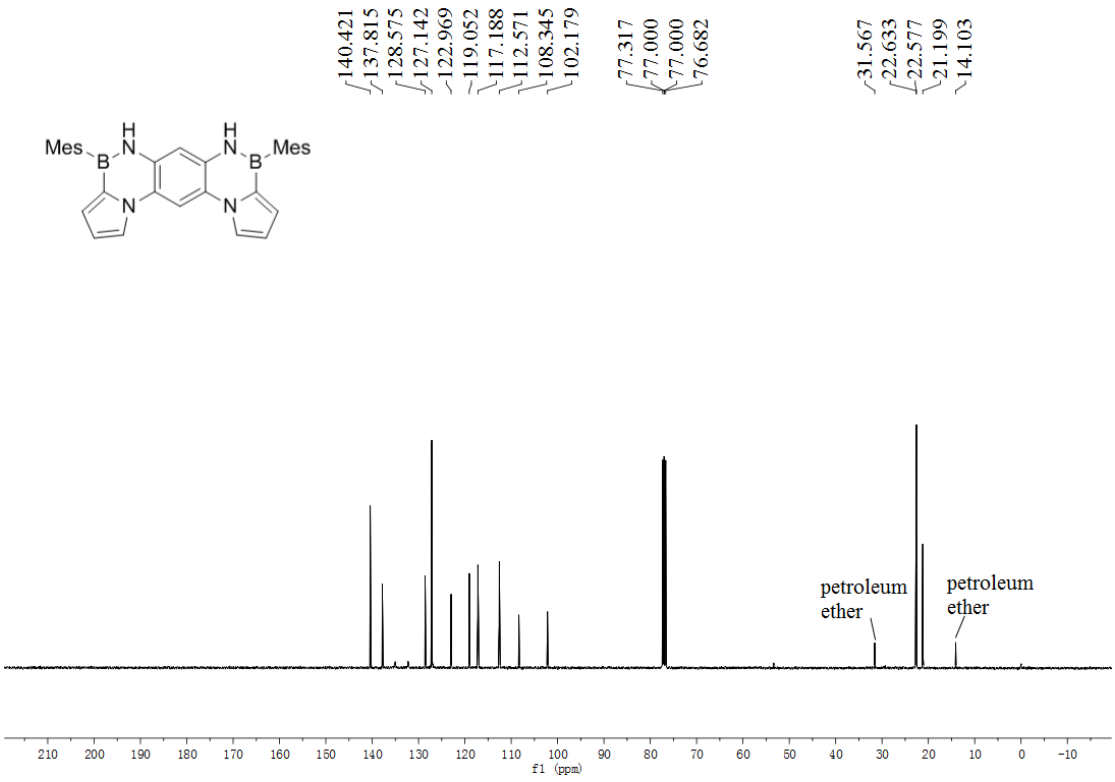
^{1}H NMR spectra of **3b** (400 MHz, $CDCl_3$)



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



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



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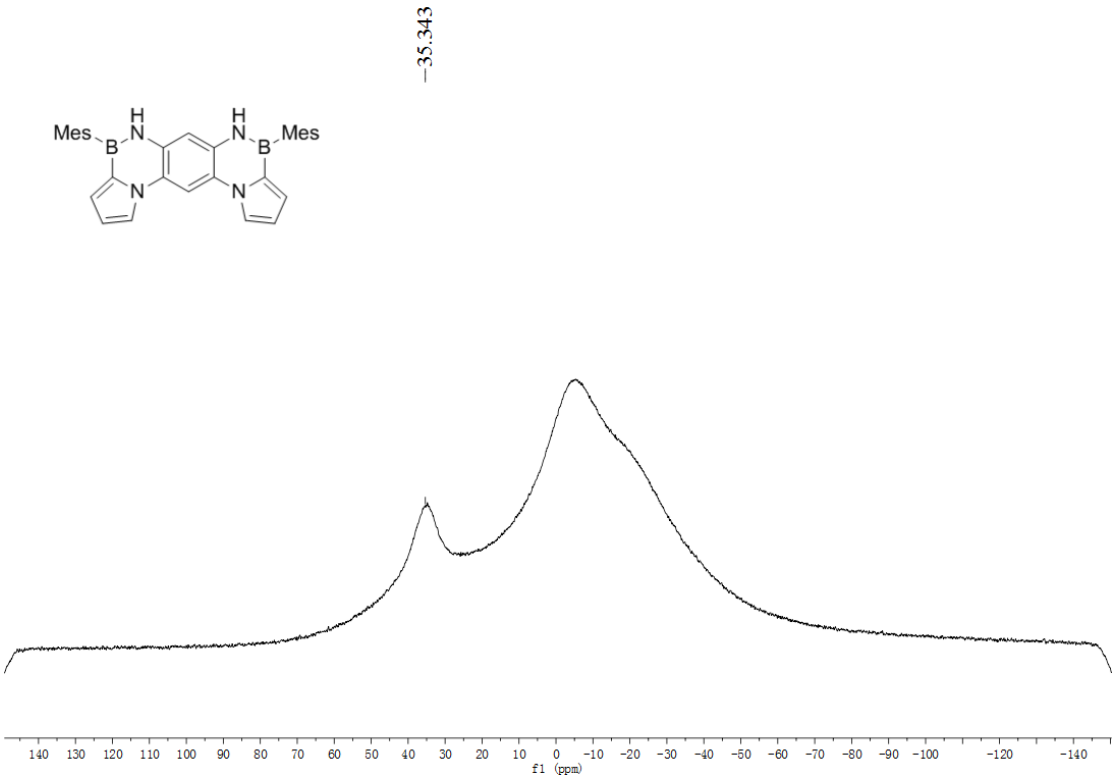
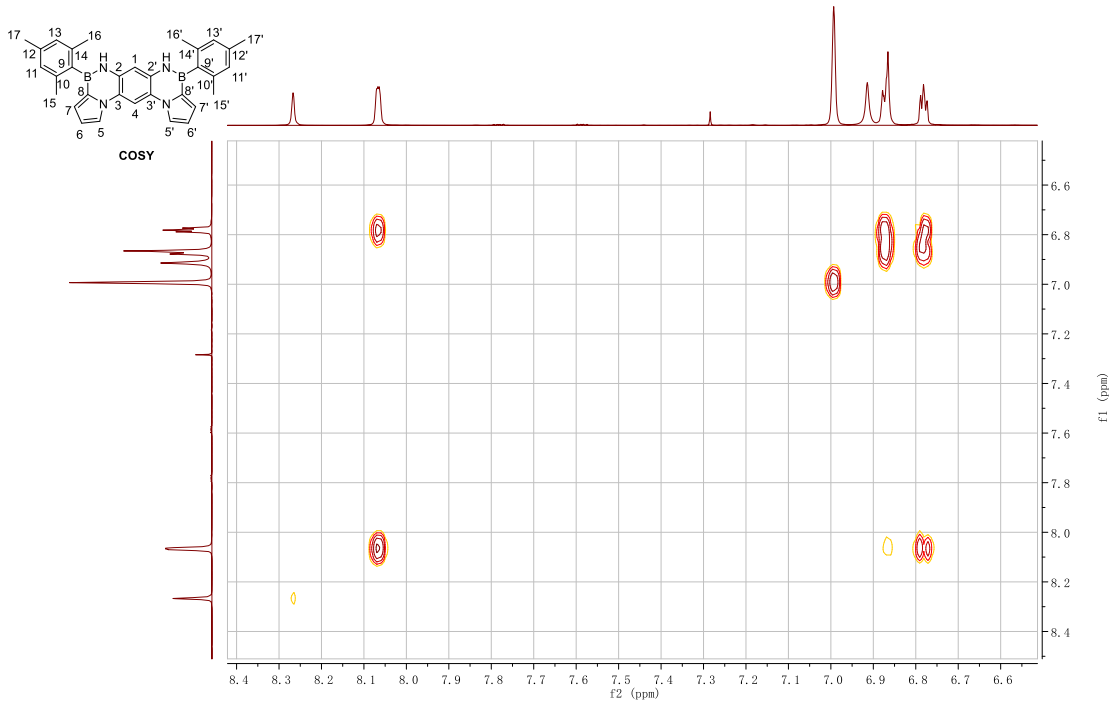
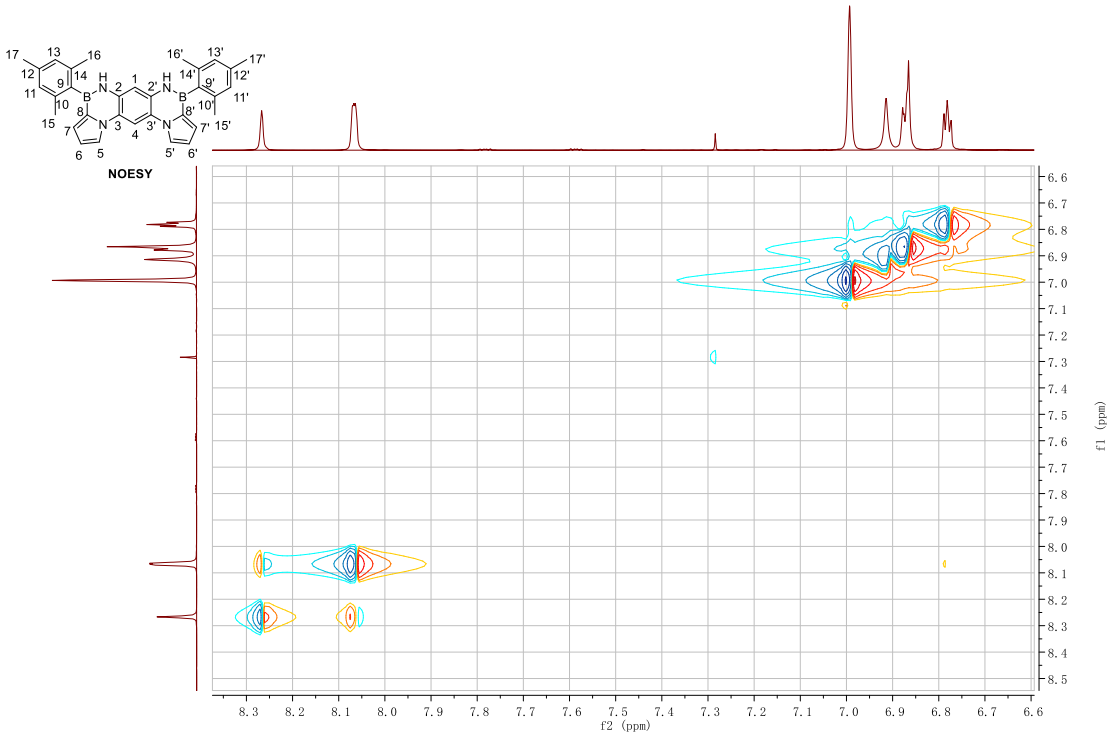


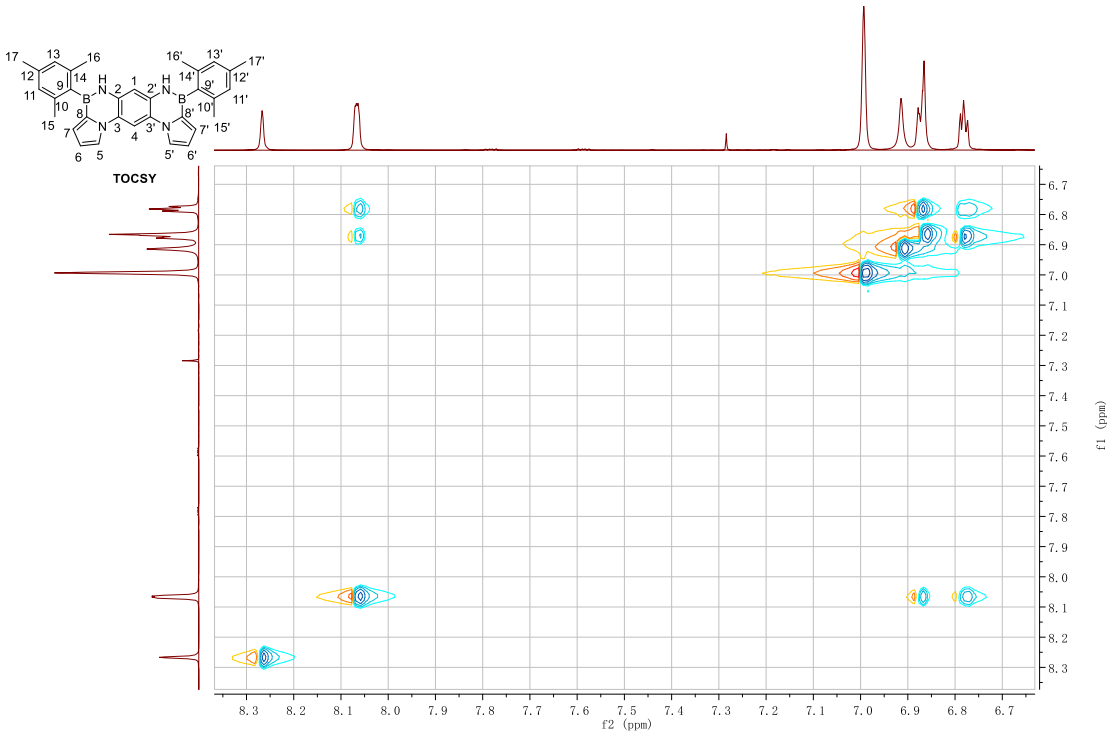
^{11}B NMR spectra of **4a** (128 MHz, $CDCl_3$)



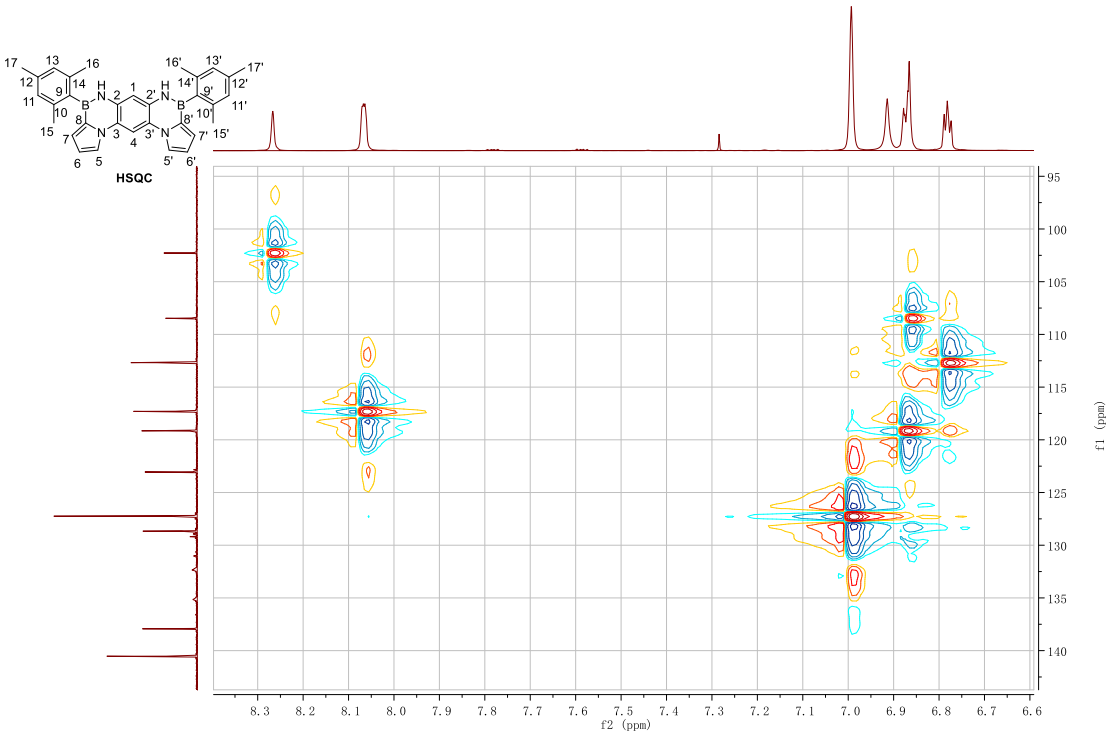
TOCSY NMR spectra of **4a** ($CDCl_3$)



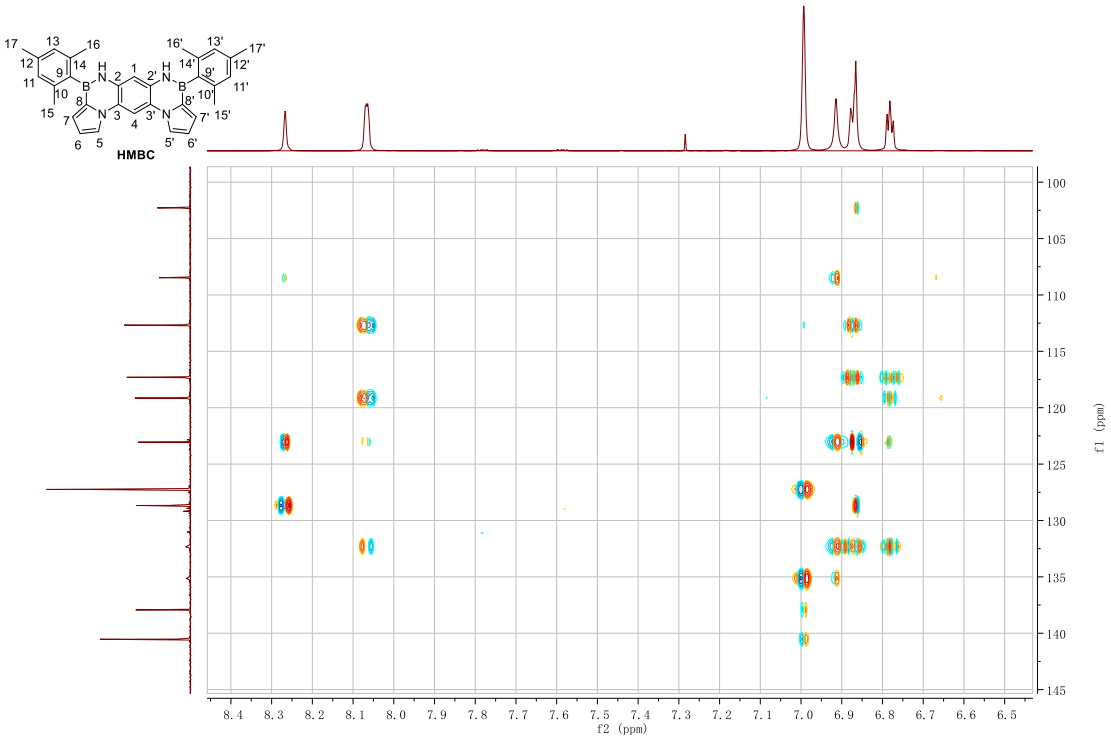
NOESY NMR spectra of **4a** ($CDCl_3$)



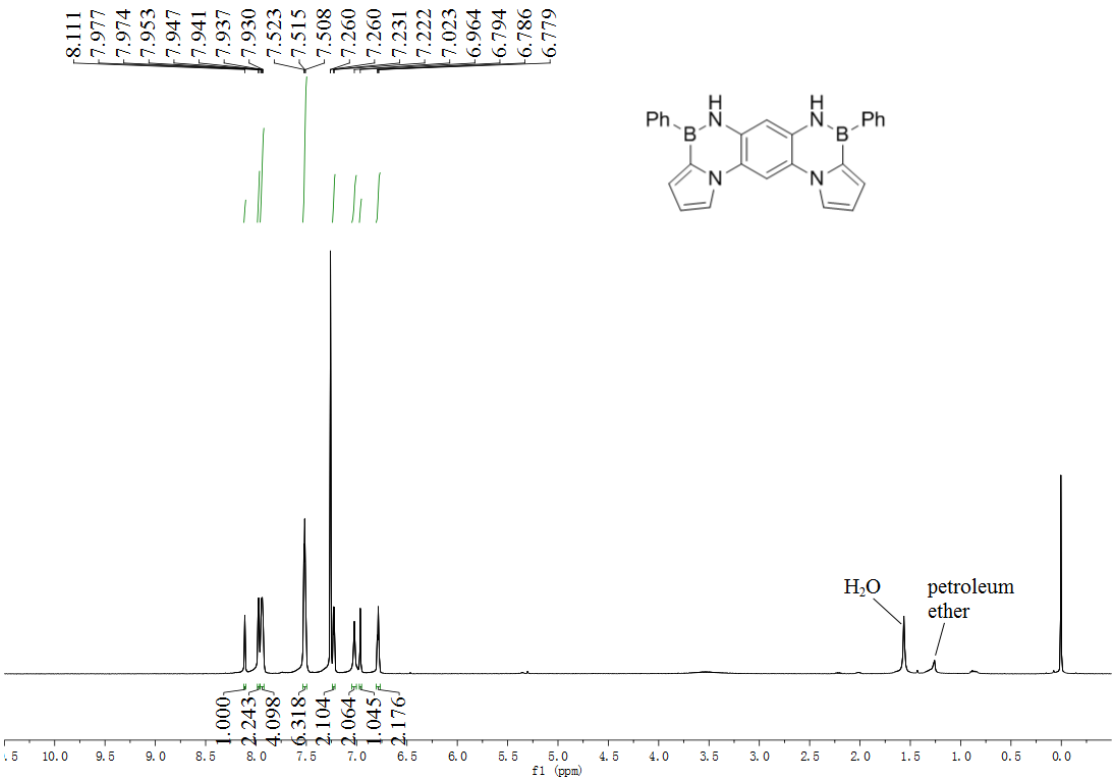
TOCSY NMR spectra of **4a** ($CDCl_3$)



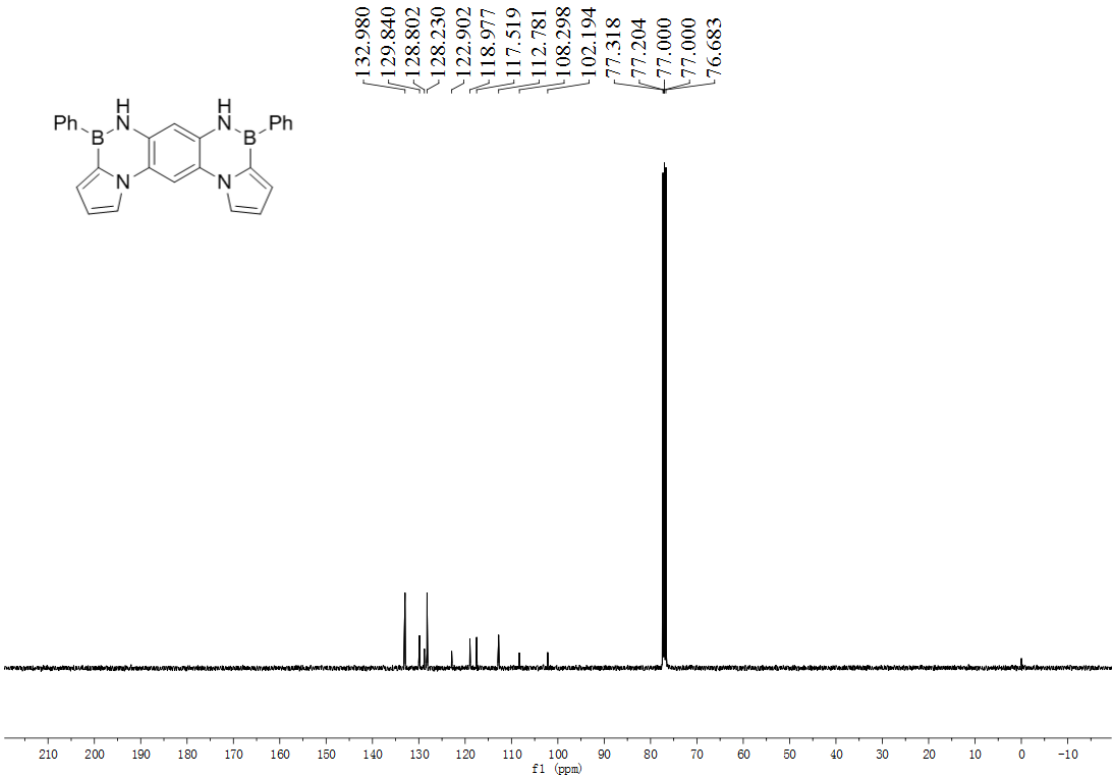
HSQC NMR spectra of **4a** ($CDCl_3$)



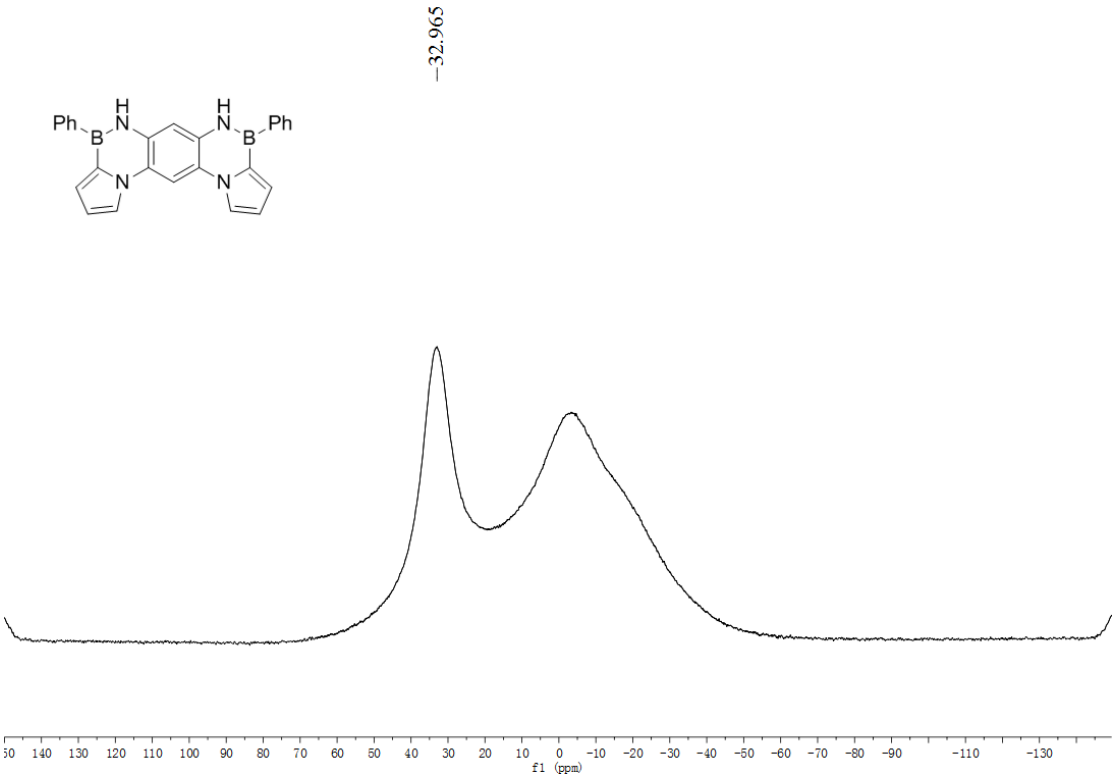
HMBC NMR spectra of **4a** ($CDCl_3$)



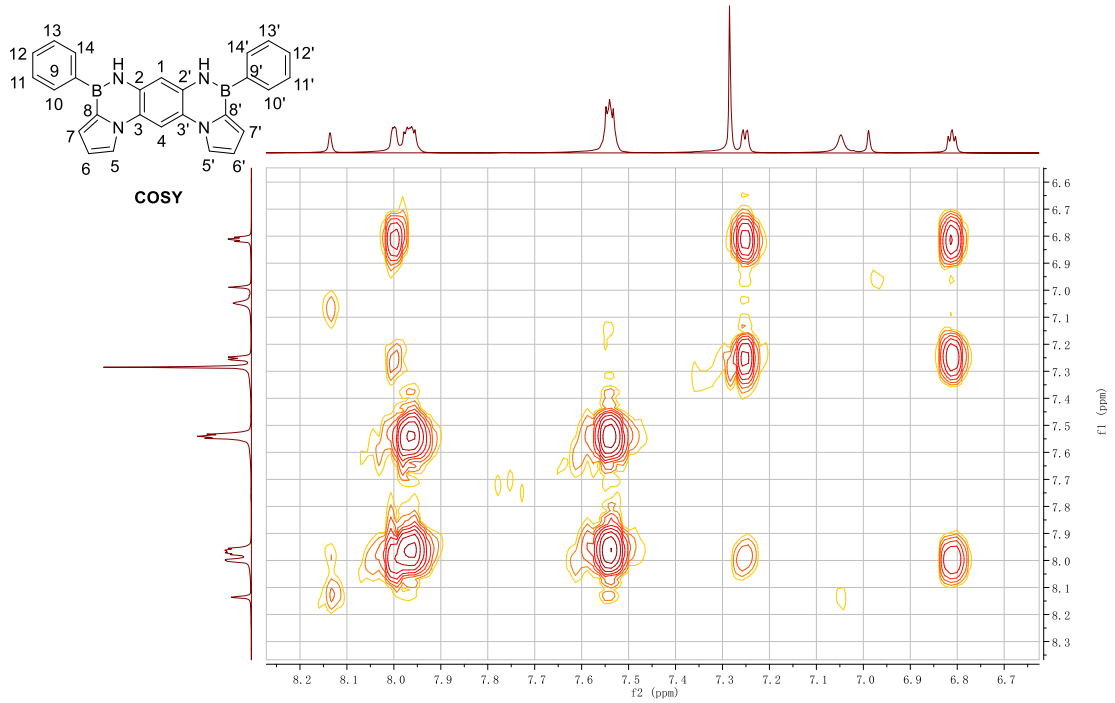
^{13}H NMR spectra of **4b** (400 MHz, $CDCl_3$)



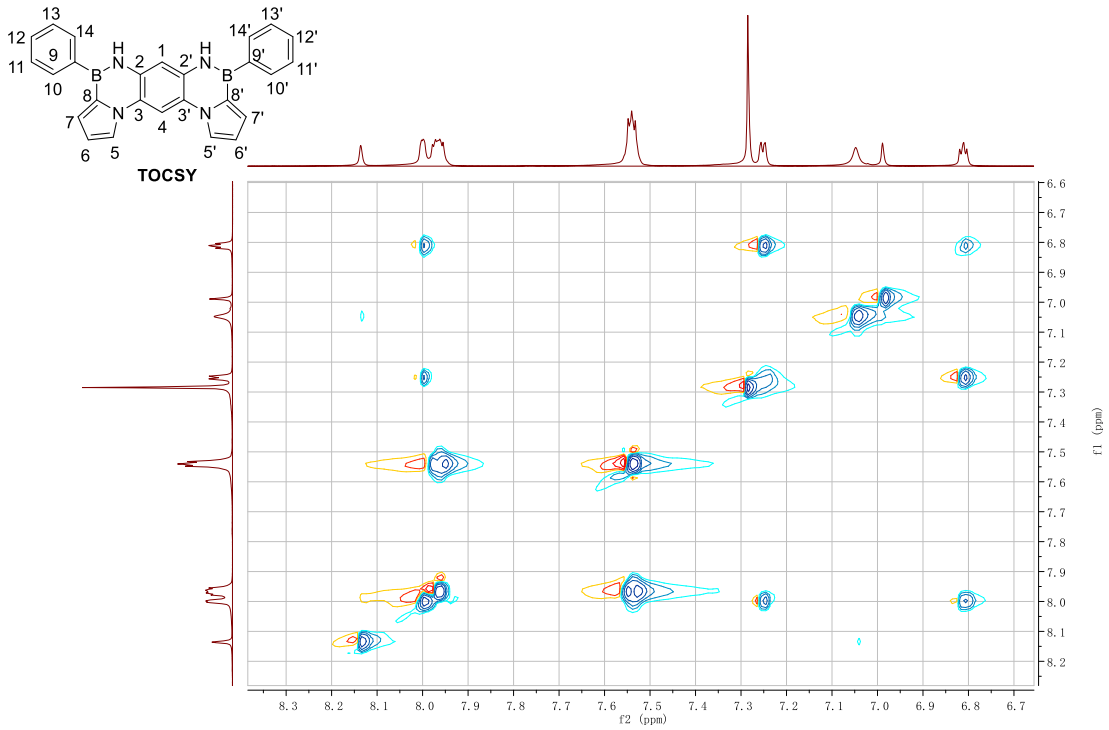
^{13}C NMR spectra of **4b** (100 MHz, $CDCl_3$)



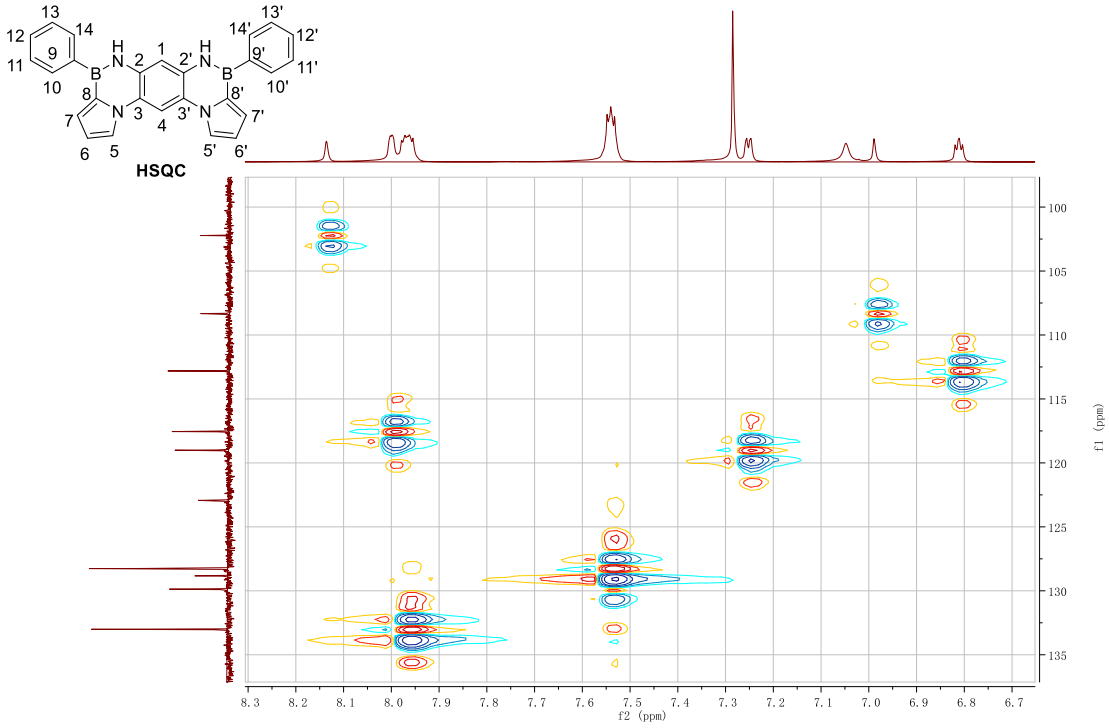
^{11}B NMR spectra of **4b** (128 MHz, $CDCl_3$)



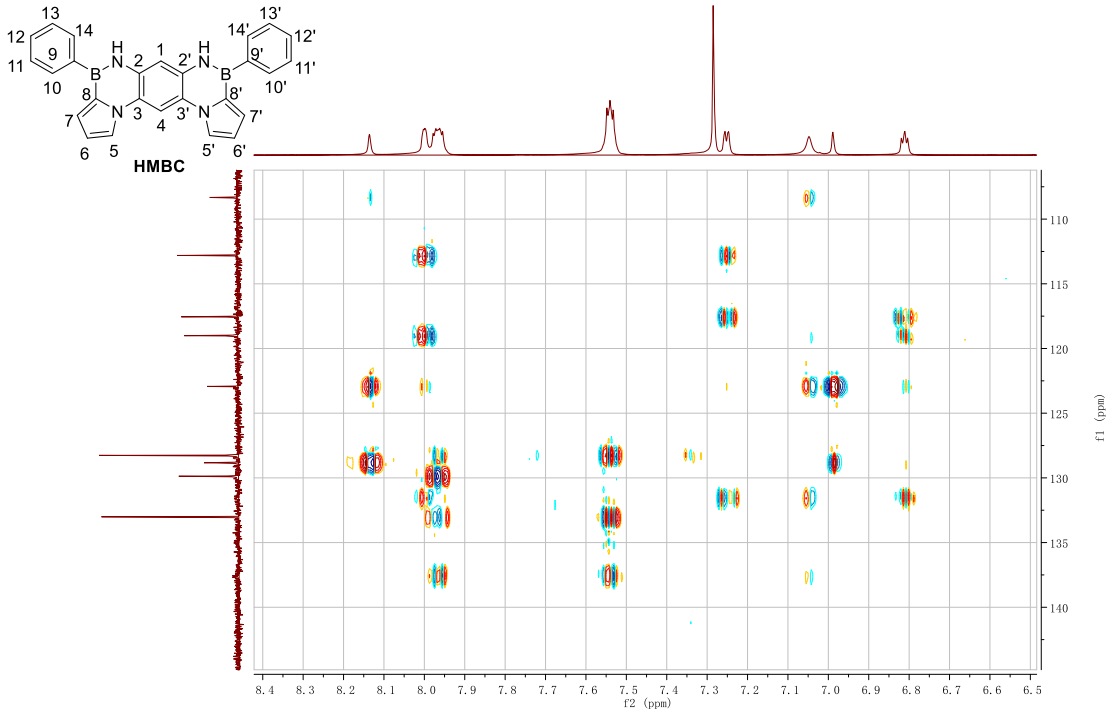
COSY NMR spectra of **4b** ($CDCl_3$)



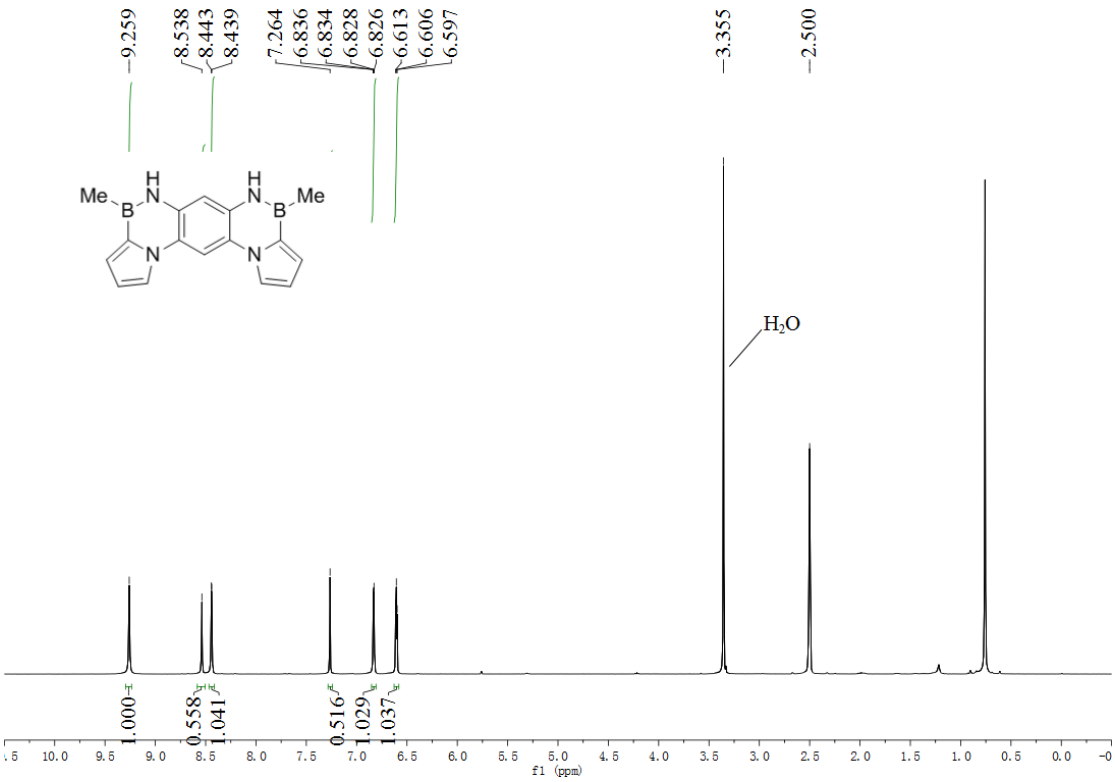
TOCSY NMR spectra of **4b** ($CDCl_3$)



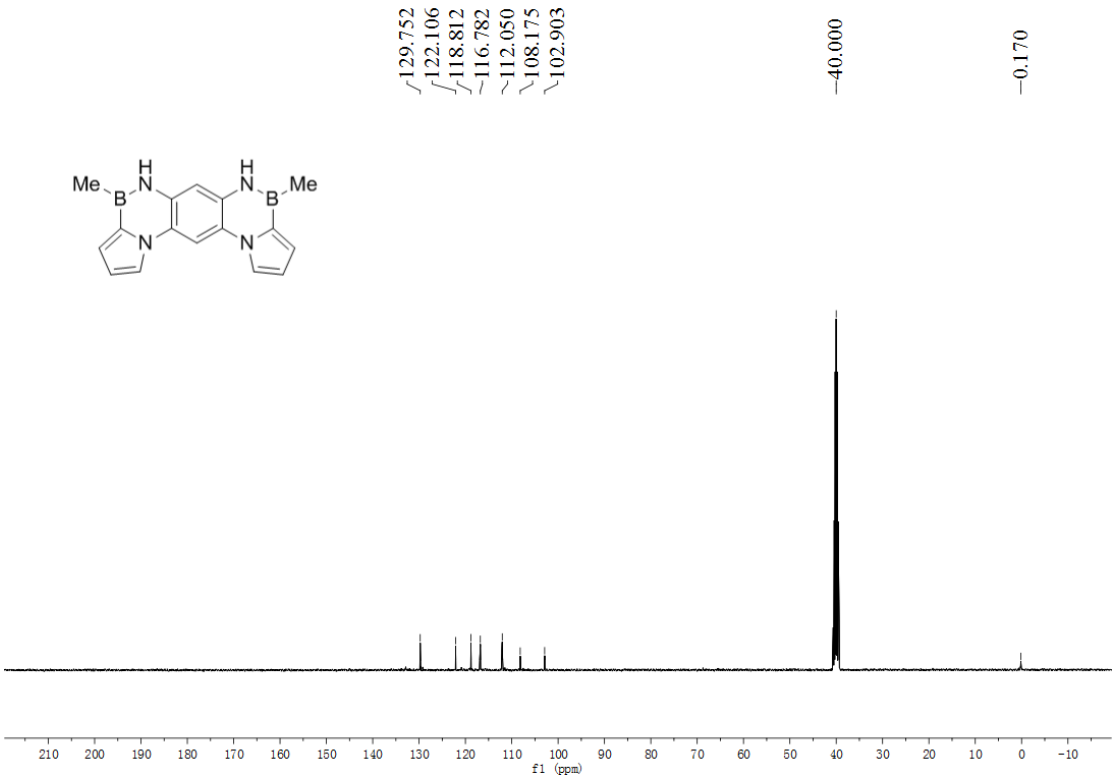
HSQC NMR spectra of **4b** ($CDCl_3$)



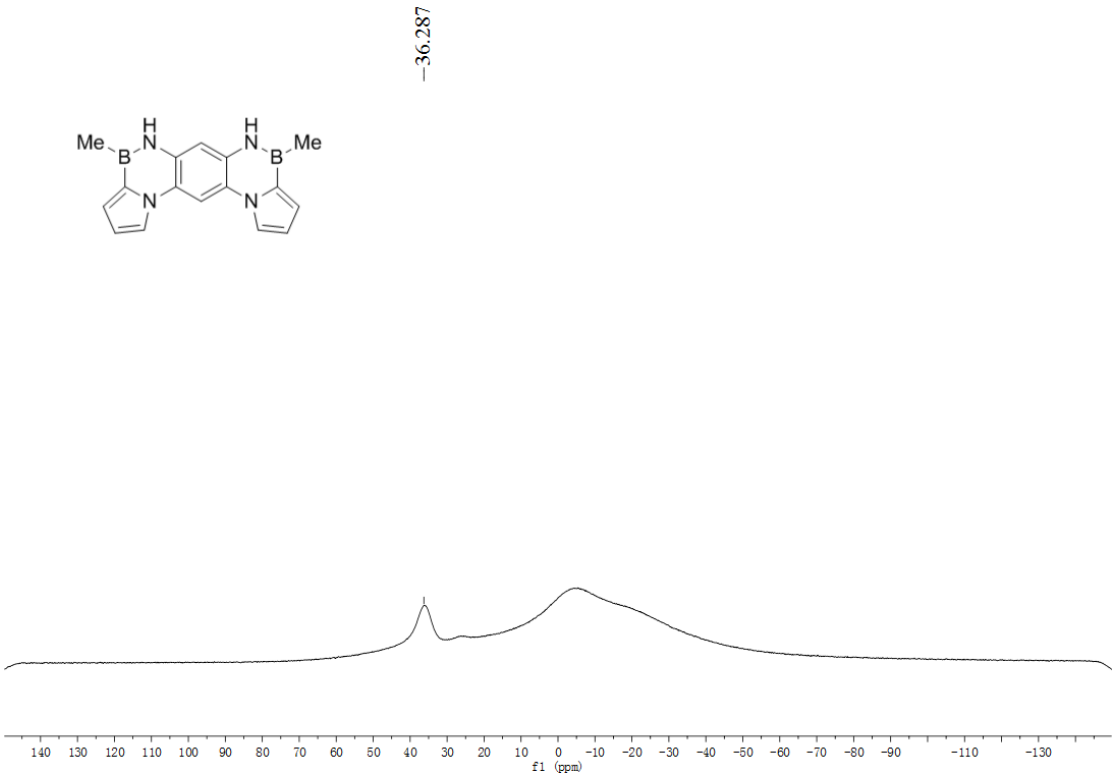
HMBC NMR spectra of **4b** ($CDCl_3$)



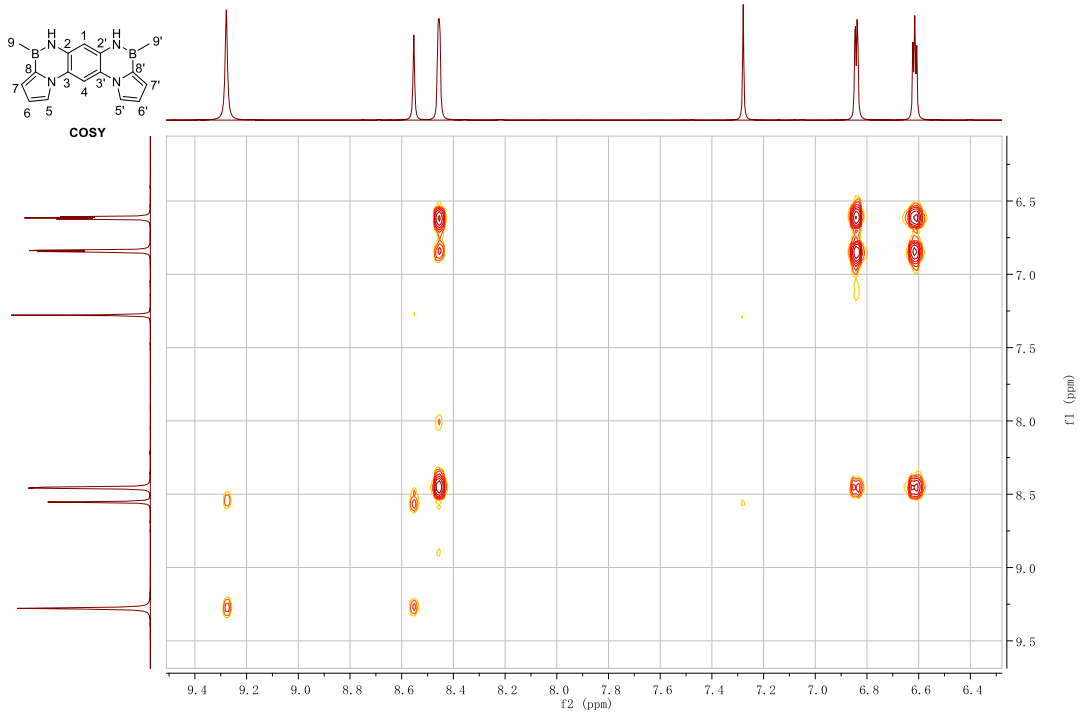
^{13}H NMR spectra of **4c** (400 MHz, d_6-DMSO)



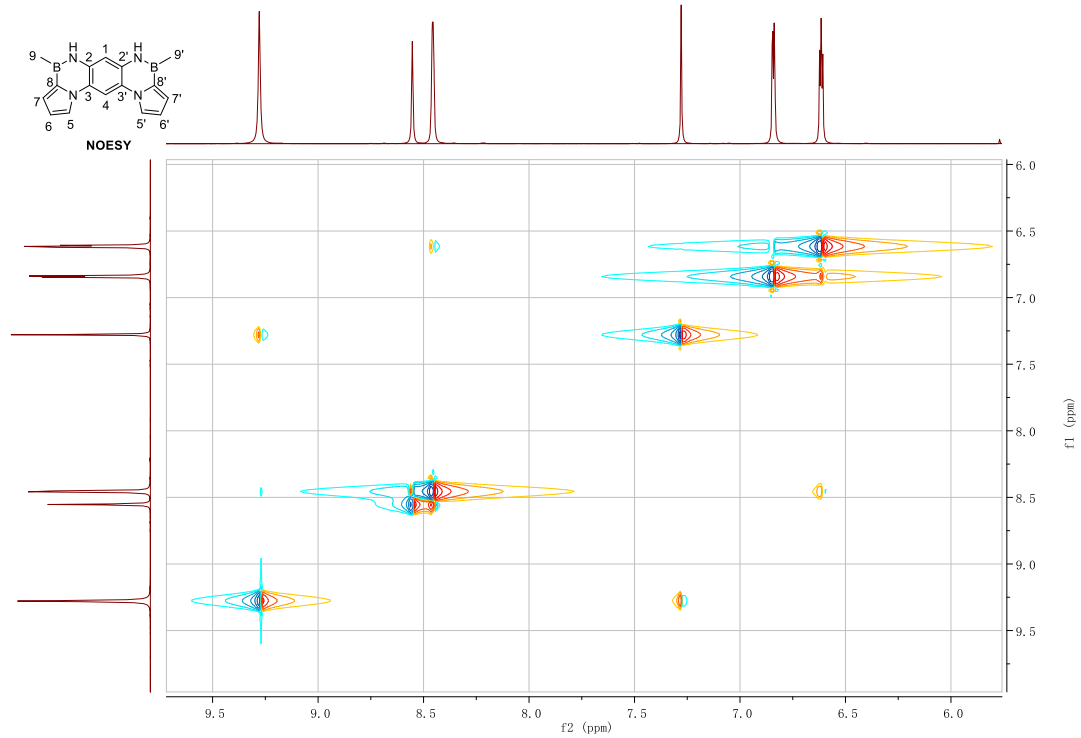
^{13}C NMR spectra of **4c** (100 MHz, d_6-DMSO)



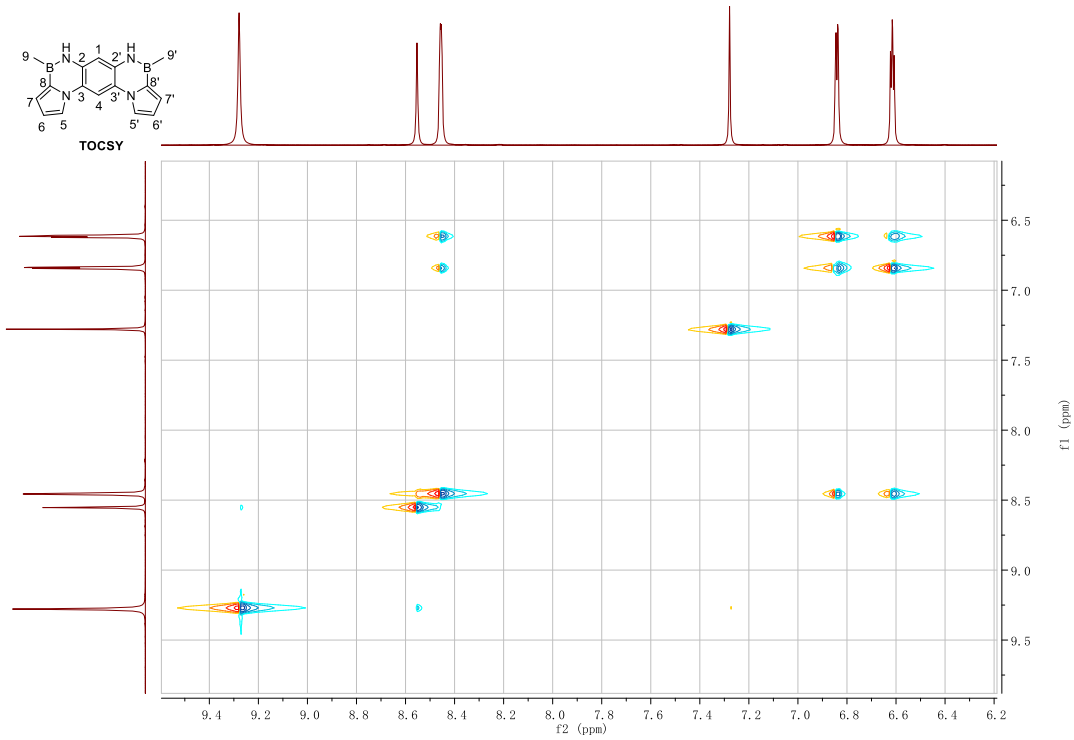
^{11}B NMR spectra of **4c** (128 MHz, $CDCl_3$)



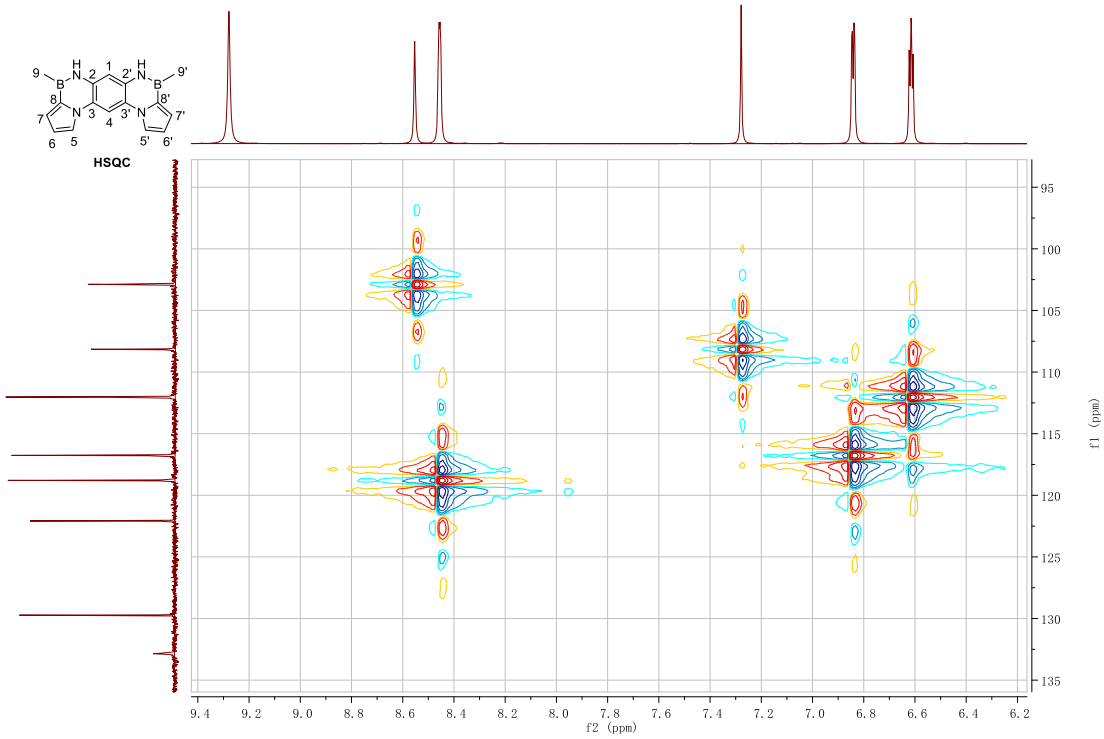
COSY NMR spectra of **4c** ($CDCl_3$)



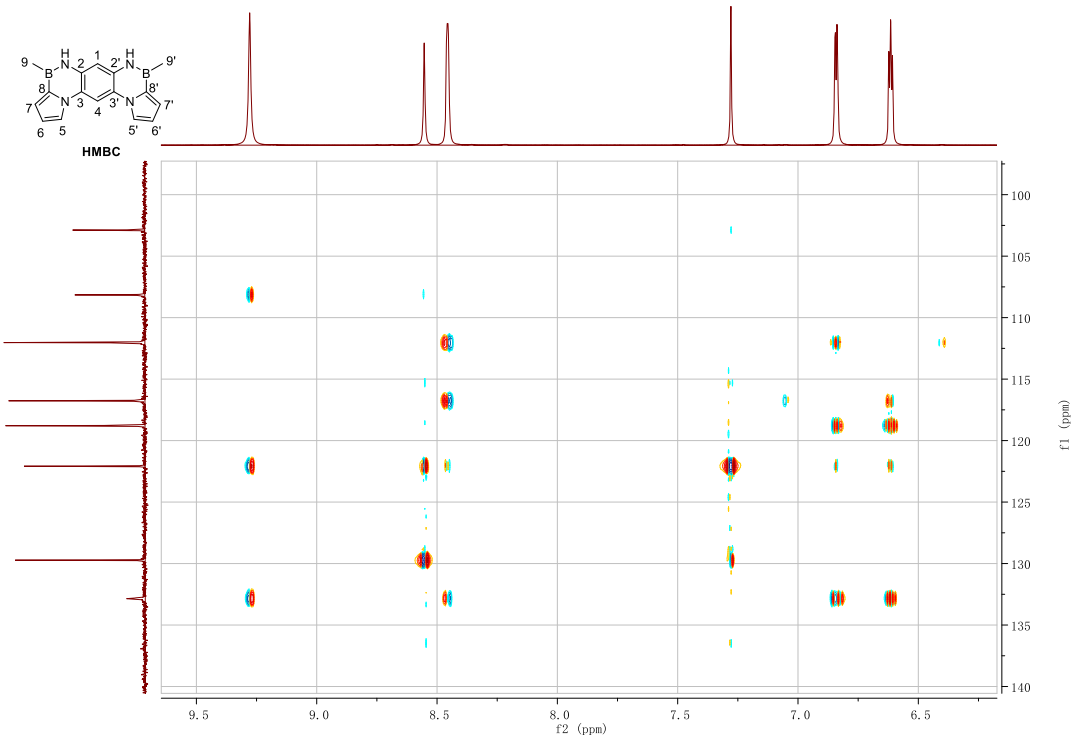
NOESY NMR spectra of **4c** ($CDCl_3$)



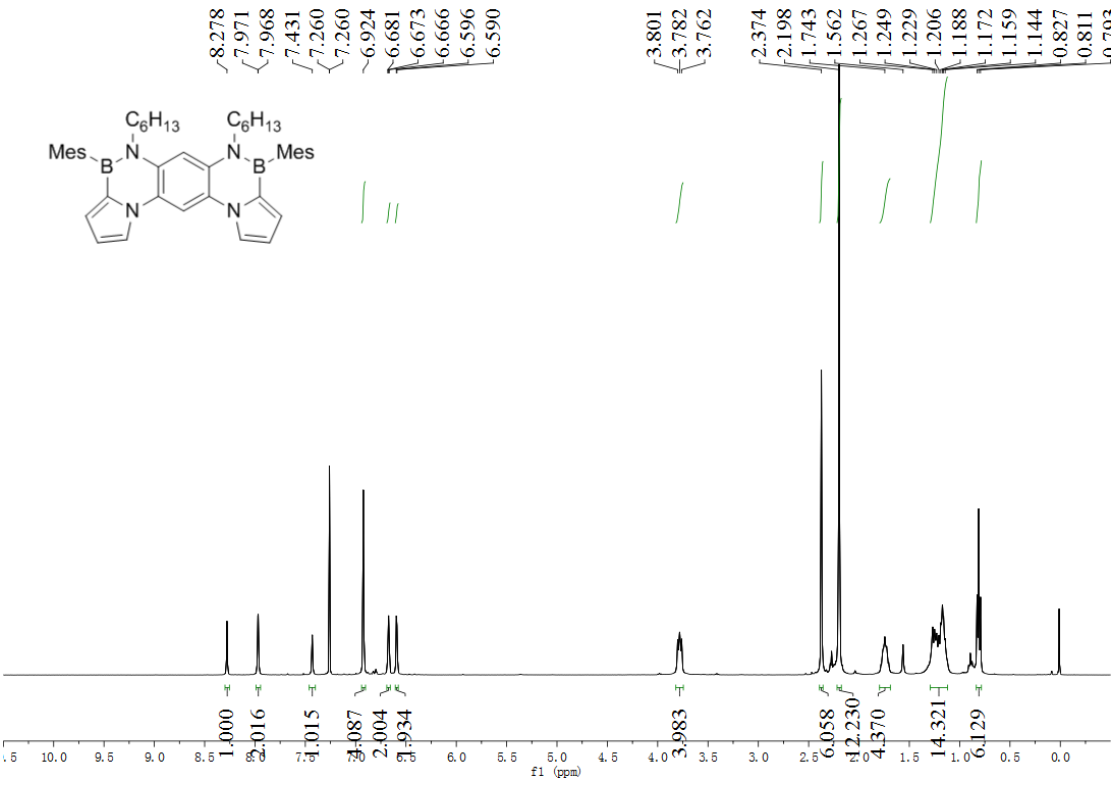
TOCSY NMR spectra of **4c** ($CDCl_3$)



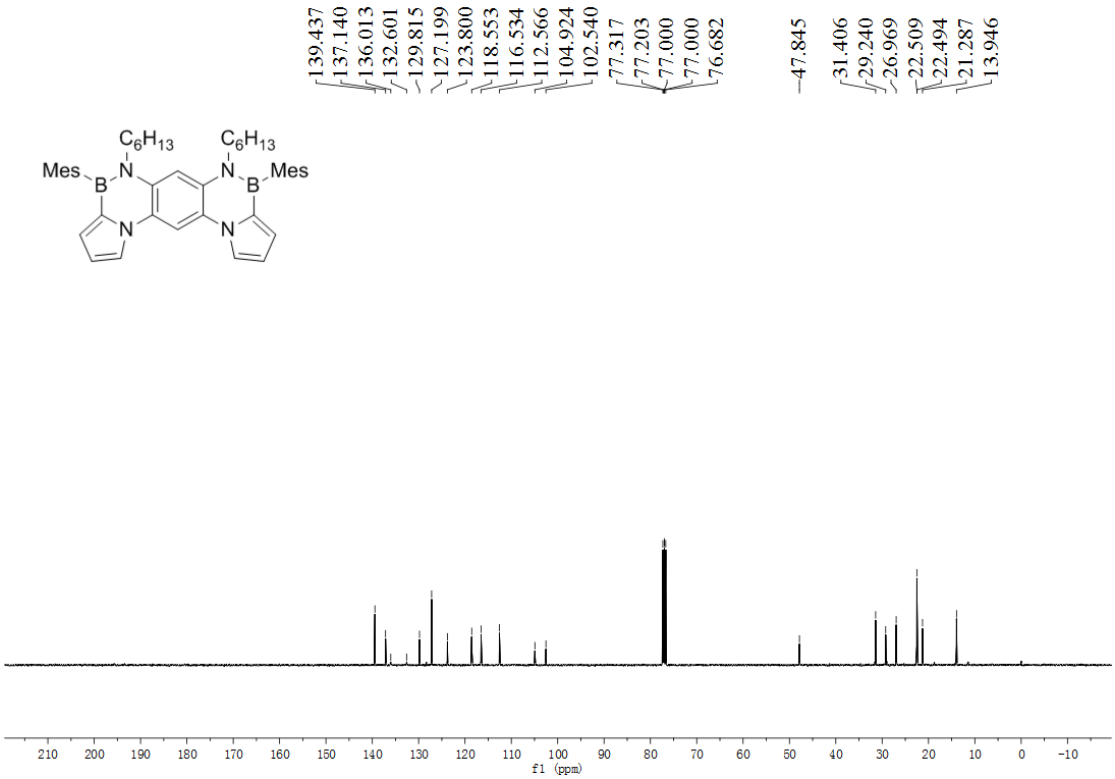
HSQC NMR spectra of **4c** ($CDCl_3$)



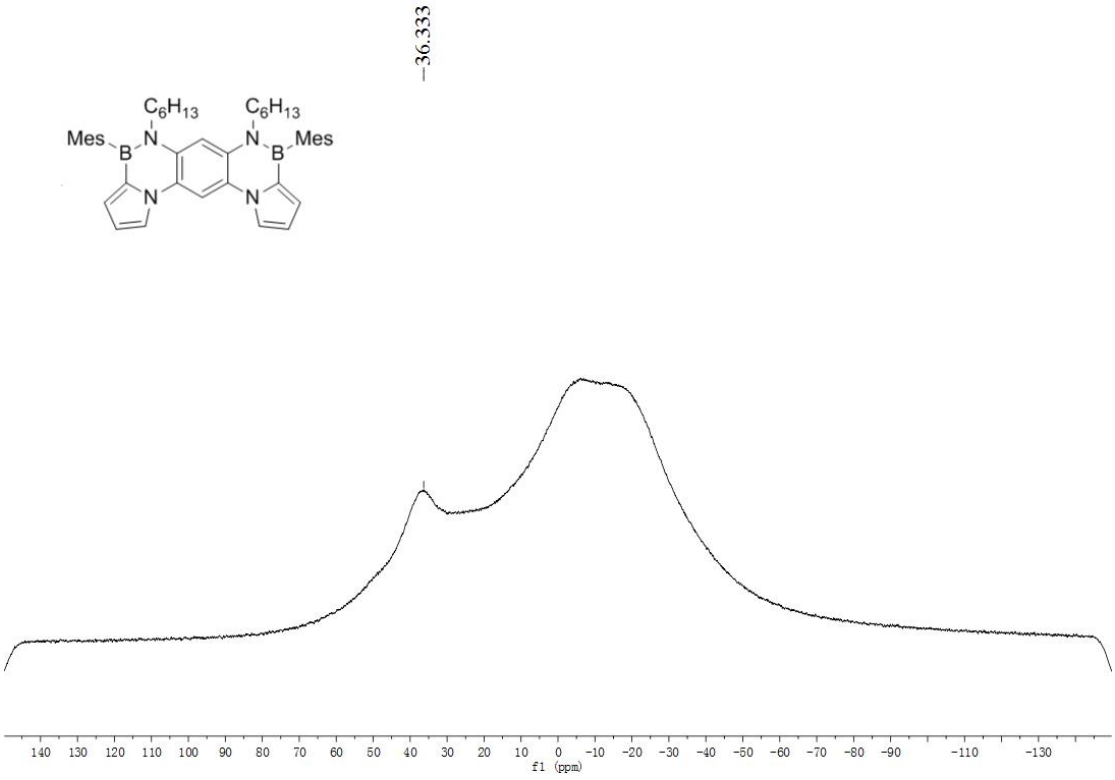
HMBC NMR spectra of **4c** ($CDCl_3$)



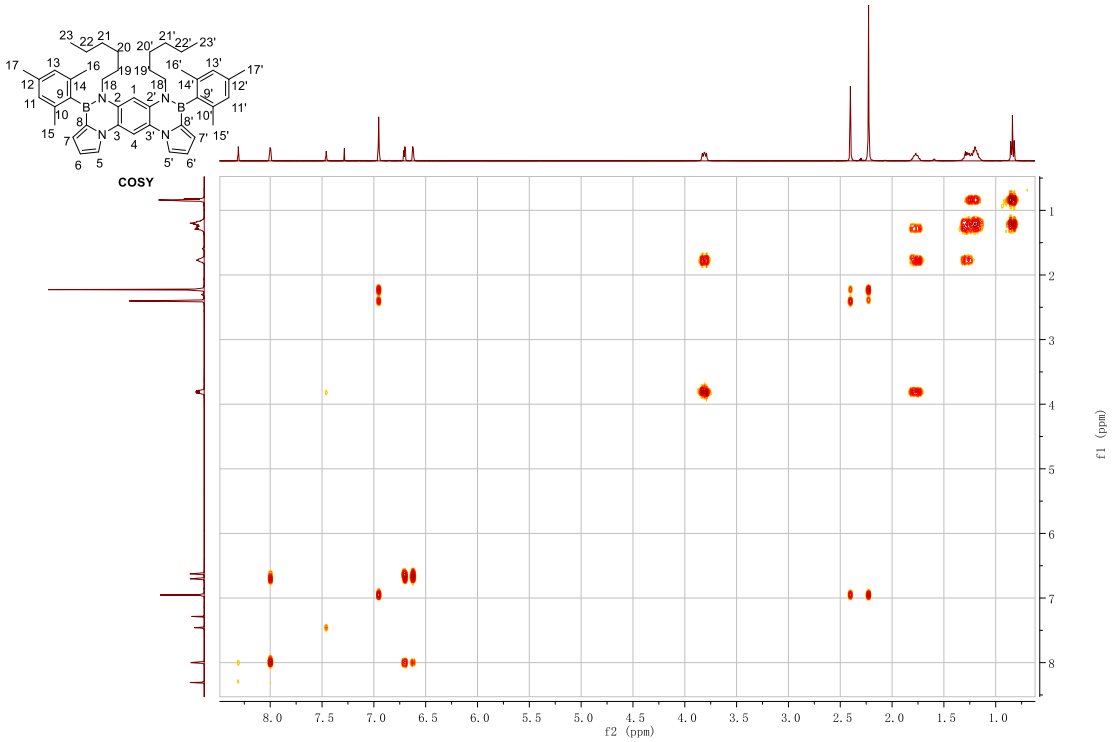
^{1}H NMR spectra of **4d** (400 MHz, $CDCl_3$)



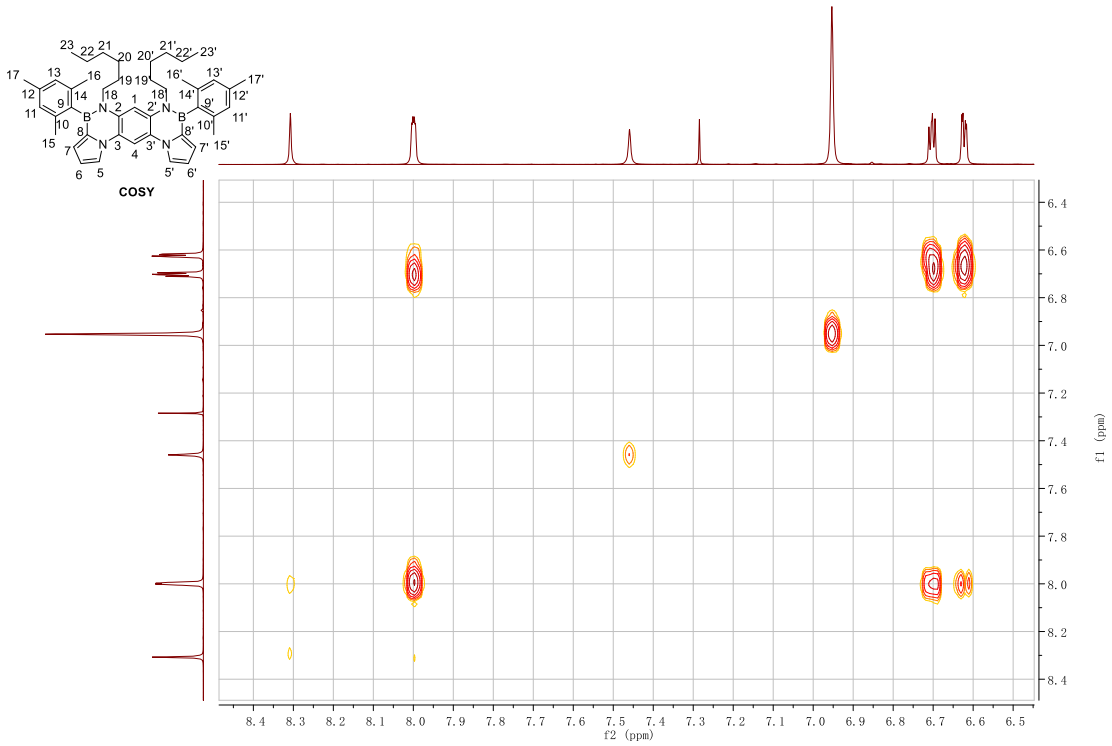
^{13}C NMR spectra of **4d** (100 MHz, $CDCl_3$)



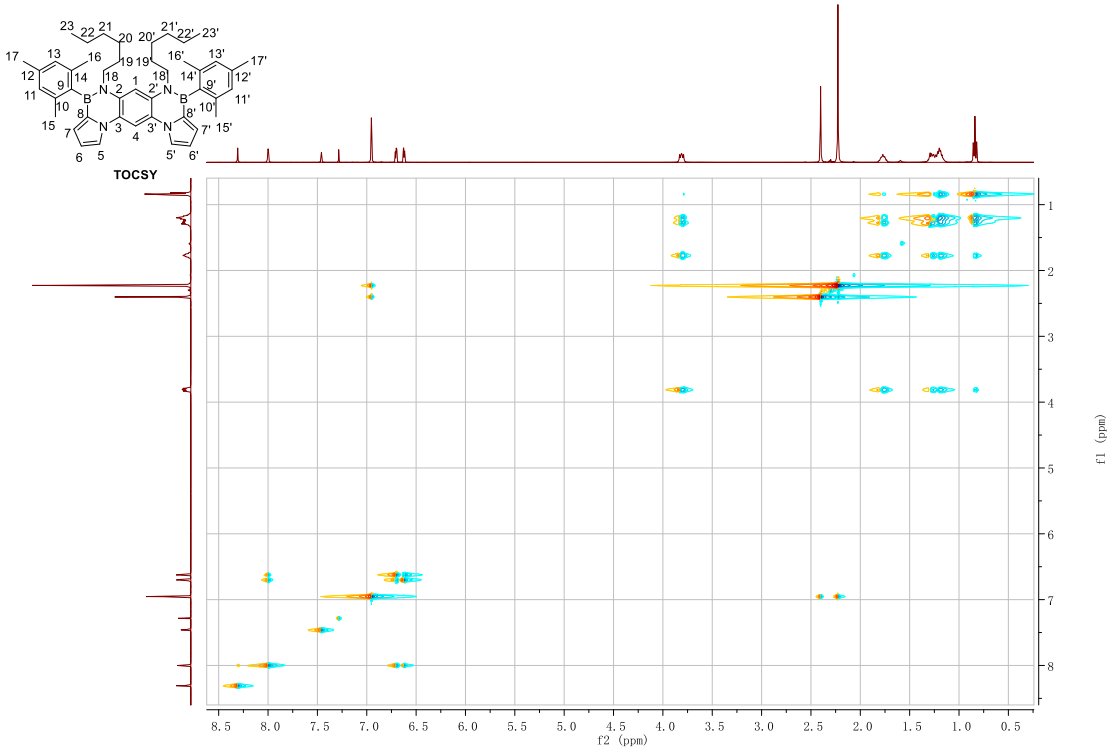
^{11}B NMR spectra of **4d** (128 MHz, $CDCl_3$)



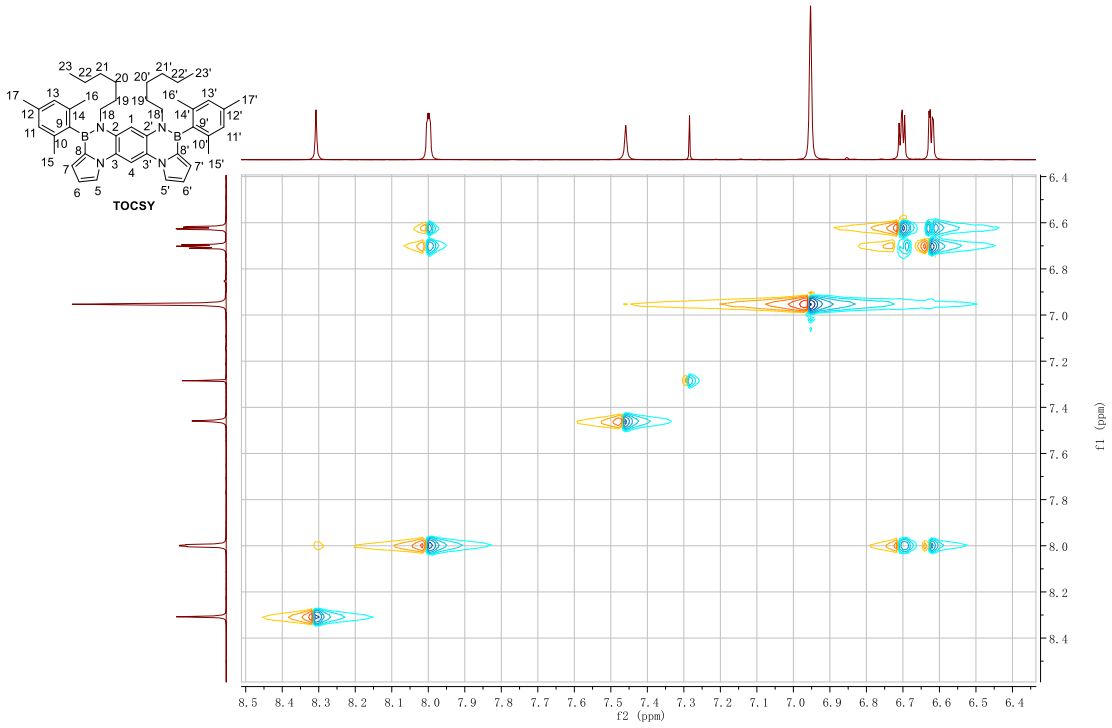
COSY NMR spectra of **4d** ($CDCl_3$)



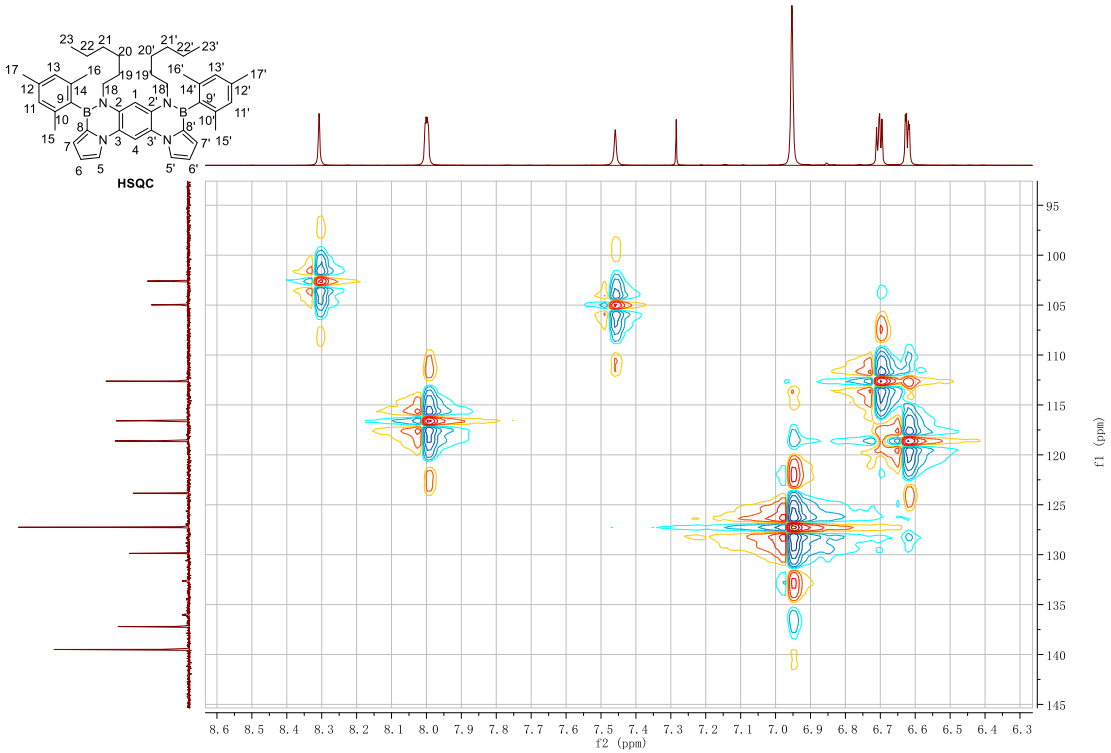
COSY NMR spectra (zoom, aromatic region) of **4d** ($CDCl_3$)



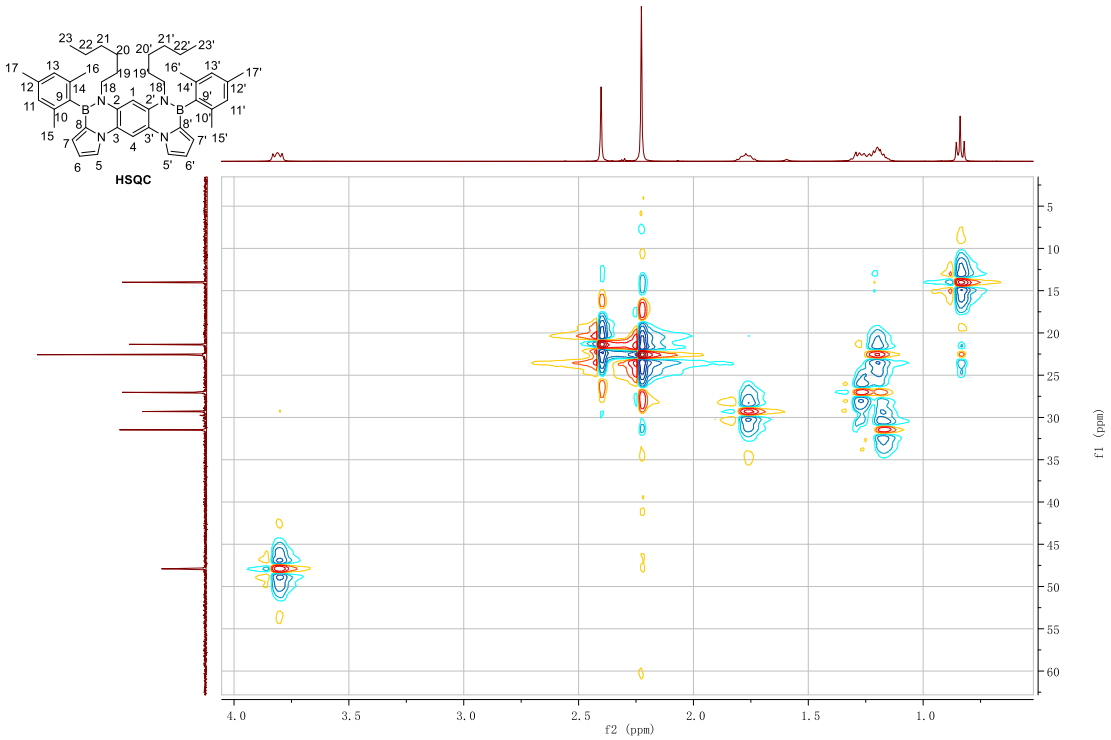
TOCSY NMR spectra of **4d** ($CDCl_3$)



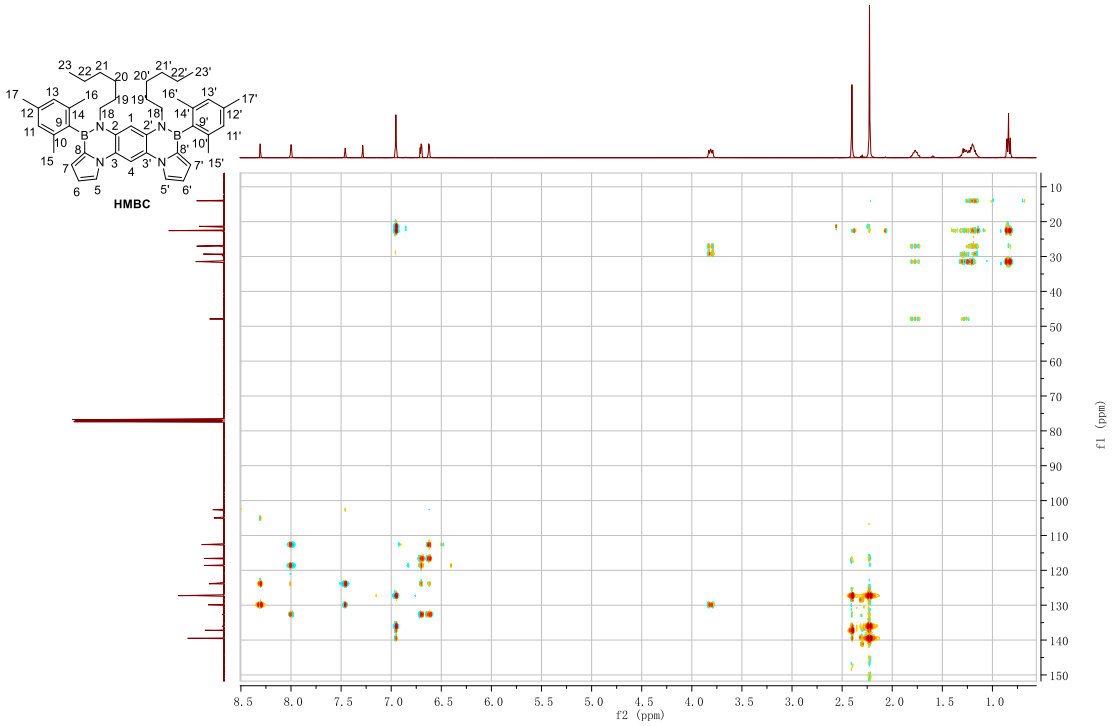
TOCSY NMR spectra (zoom, aromatic region) of **4d** ($CDCl_3$)



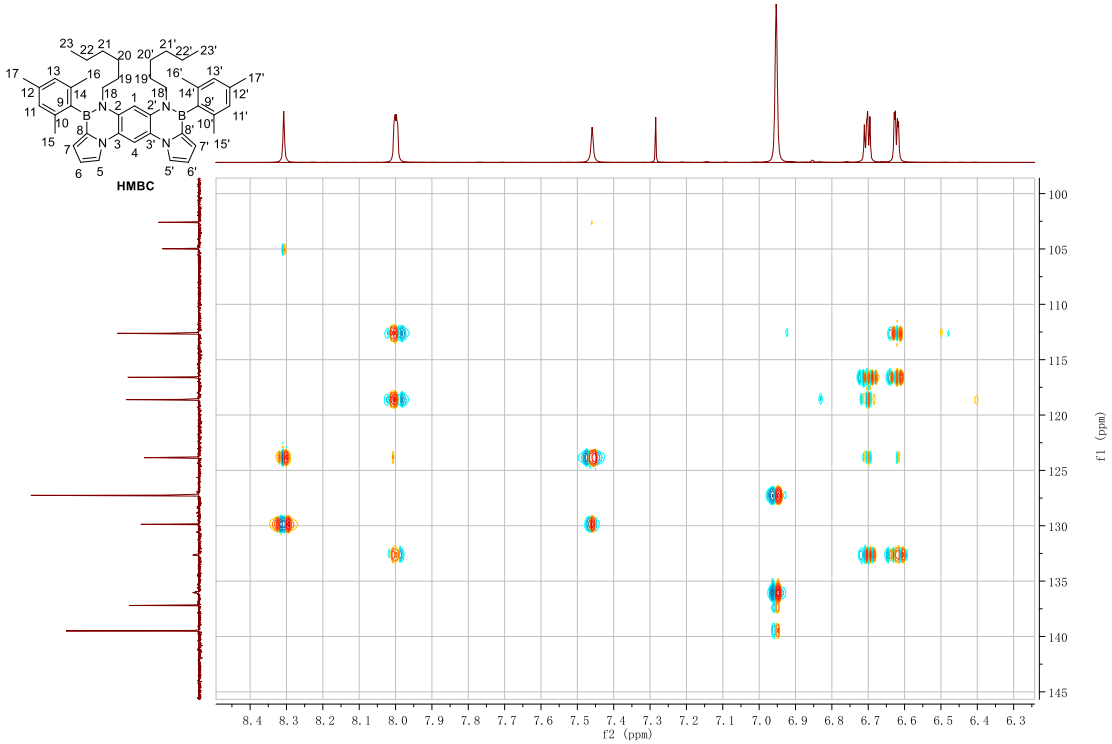
HSQC NMR (zoom, aromatic region) spectra of **4d** ($CDCl_3$)



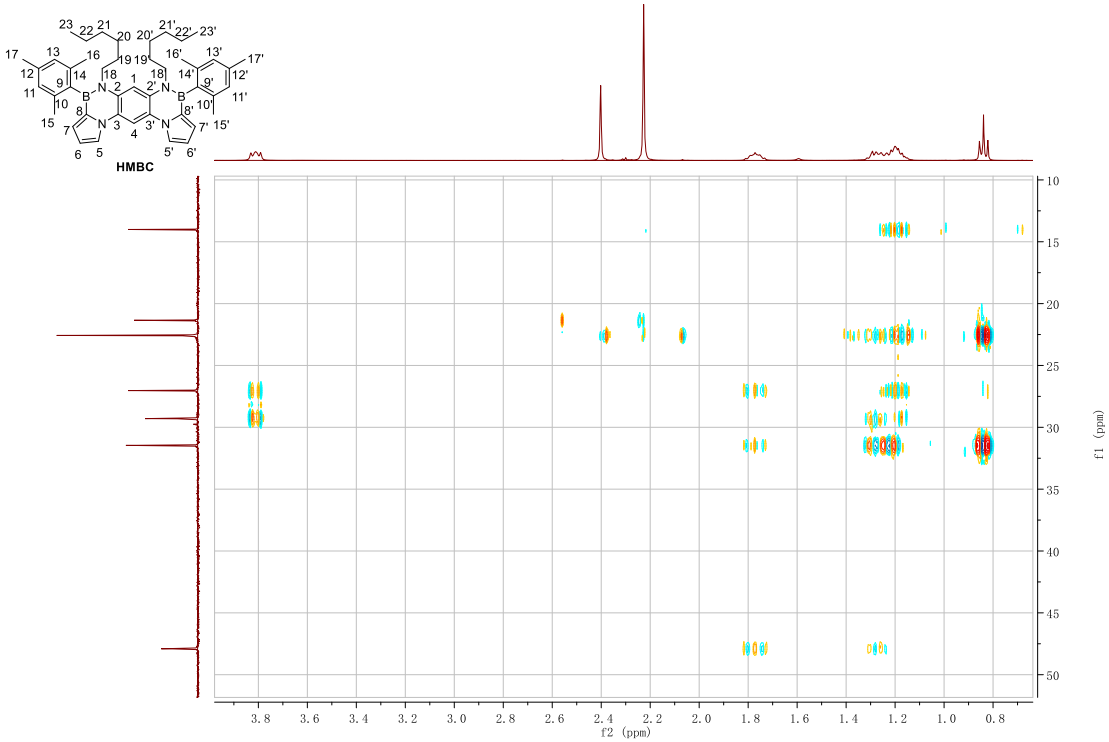
HSQC NMR spectra (zoom, aliphatic region) of **4d** ($CDCl_3$)



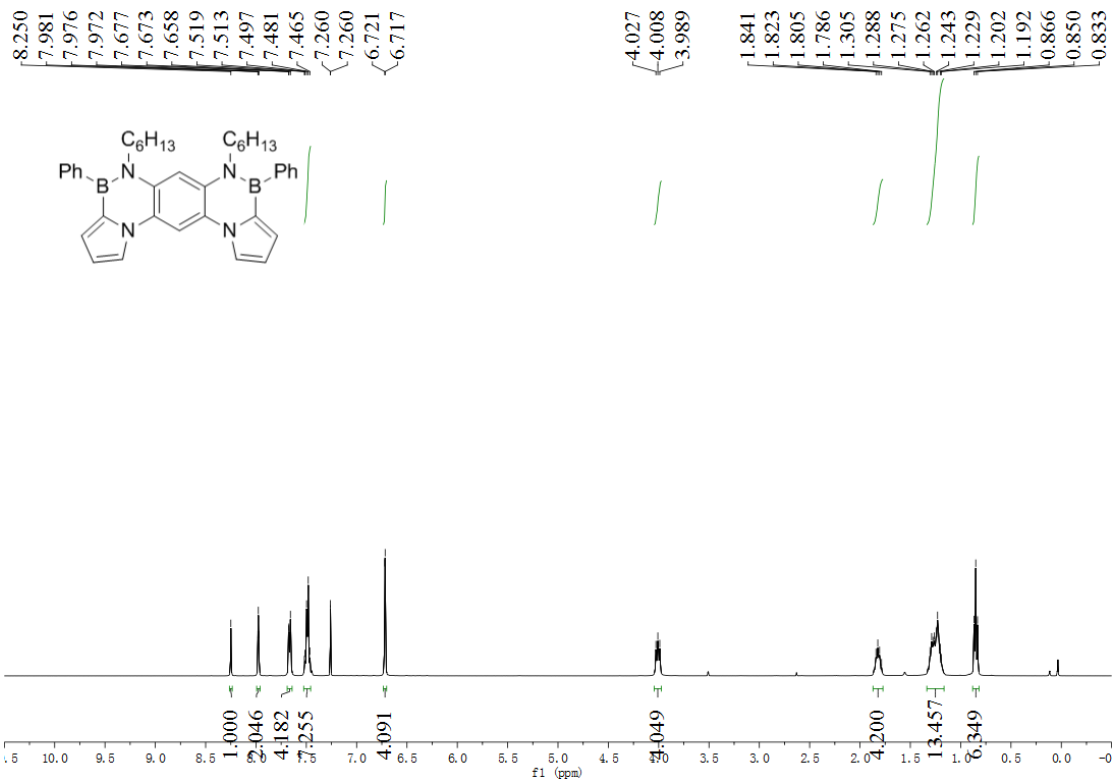
HMBC NMR spectra of **4d** ($CDCl_3$)



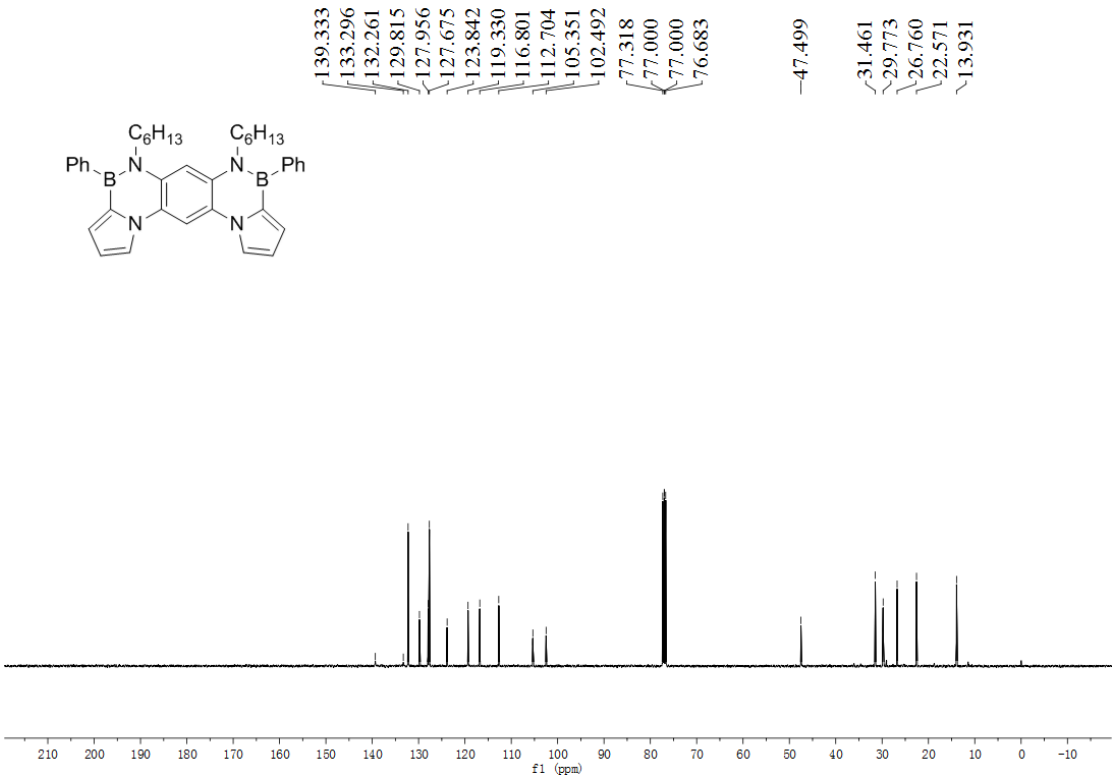
HMBC NMR spectra (zoom, aromatic region) of **4d** ($CDCl_3$)



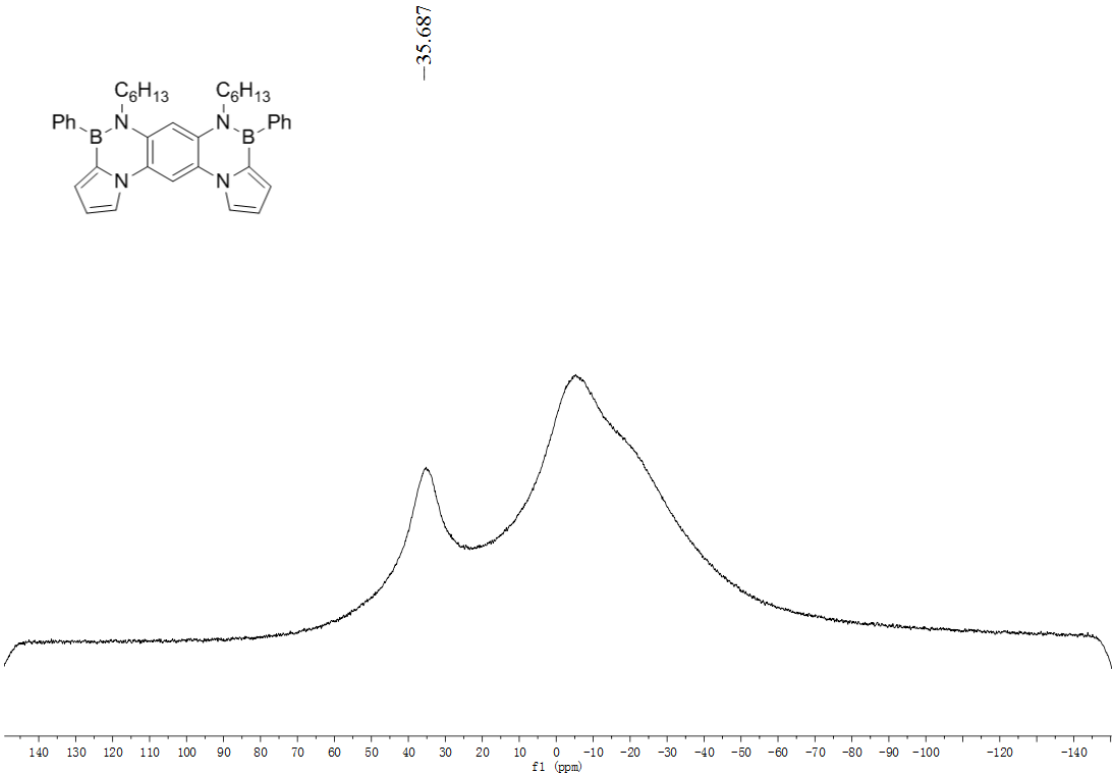
HMBC NMR spectra (zoom, aromatic region) of **4d** ($CDCl_3$)



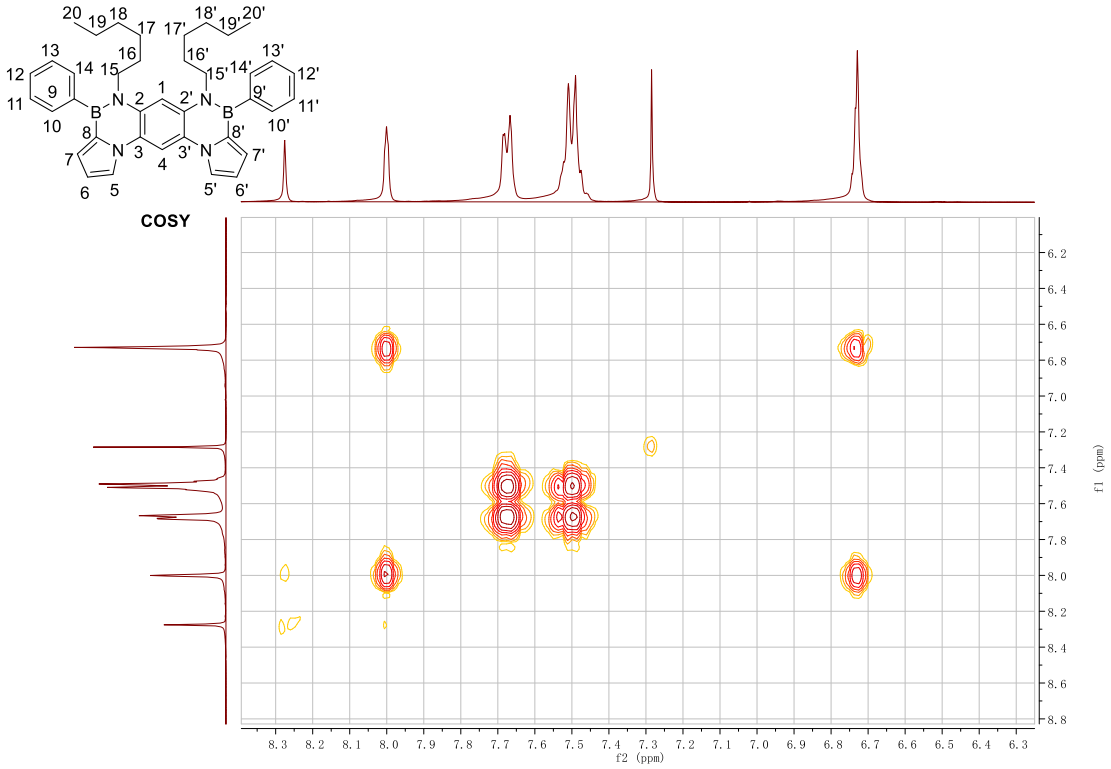
^{1}H NMR spectra of **4e** (400 MHz, $CDCl_3$)



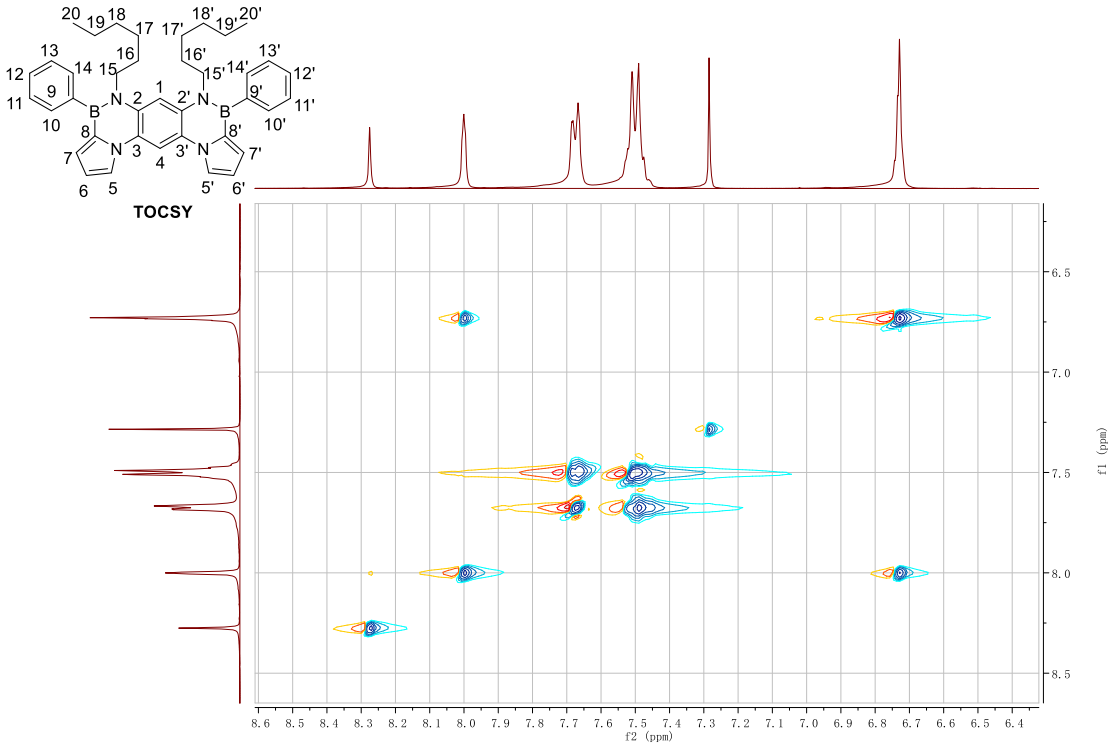
^{13}C NMR spectra of **4e** (100 MHz, $CDCl_3$)



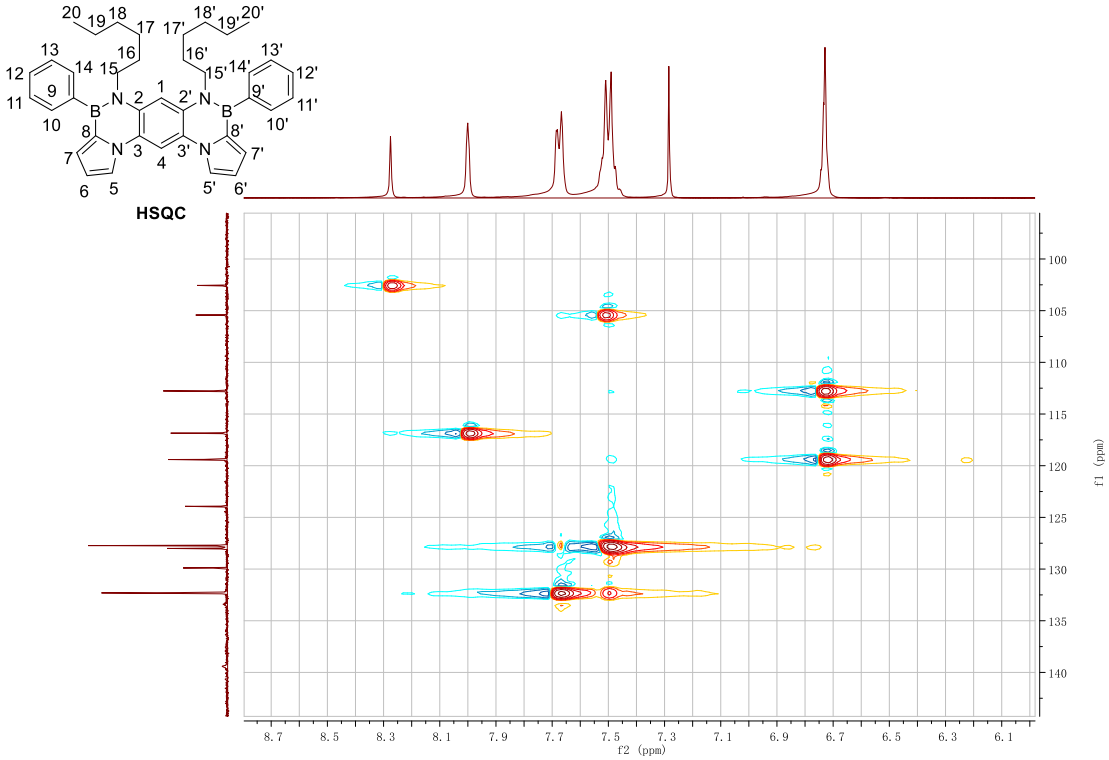
^{11}B NMR spectra of **4e** (128 MHz, $CDCl_3$)



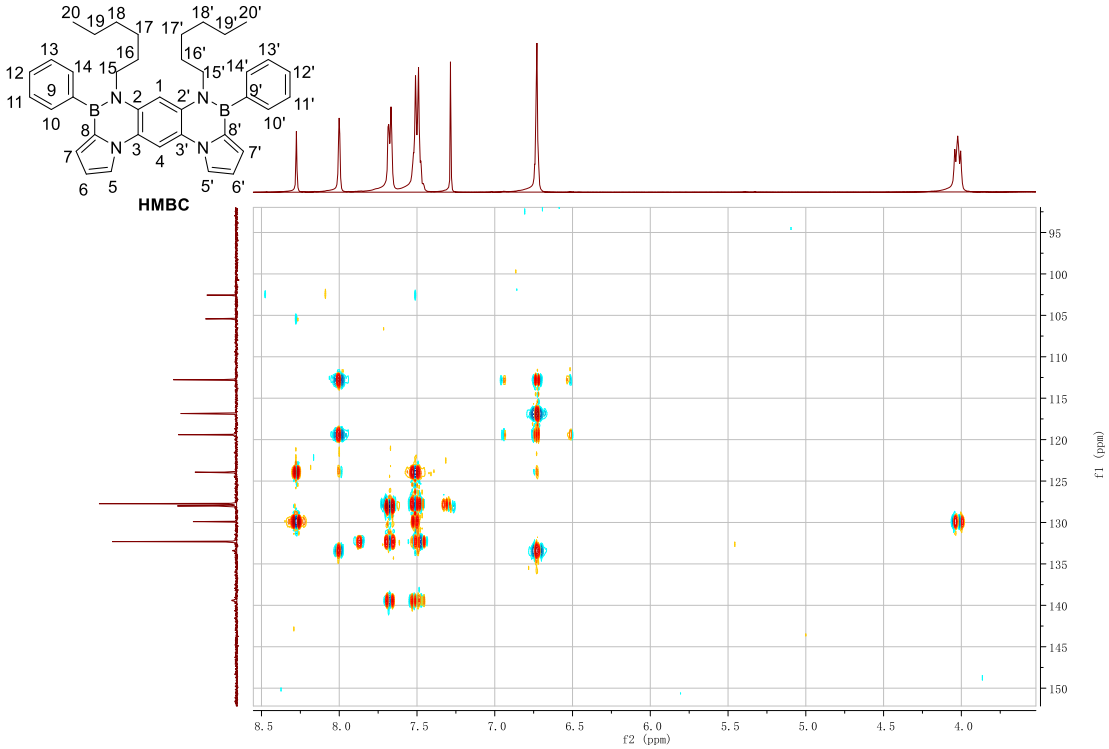
COSY NMR spectra of **4e** ($CDCl_3$)



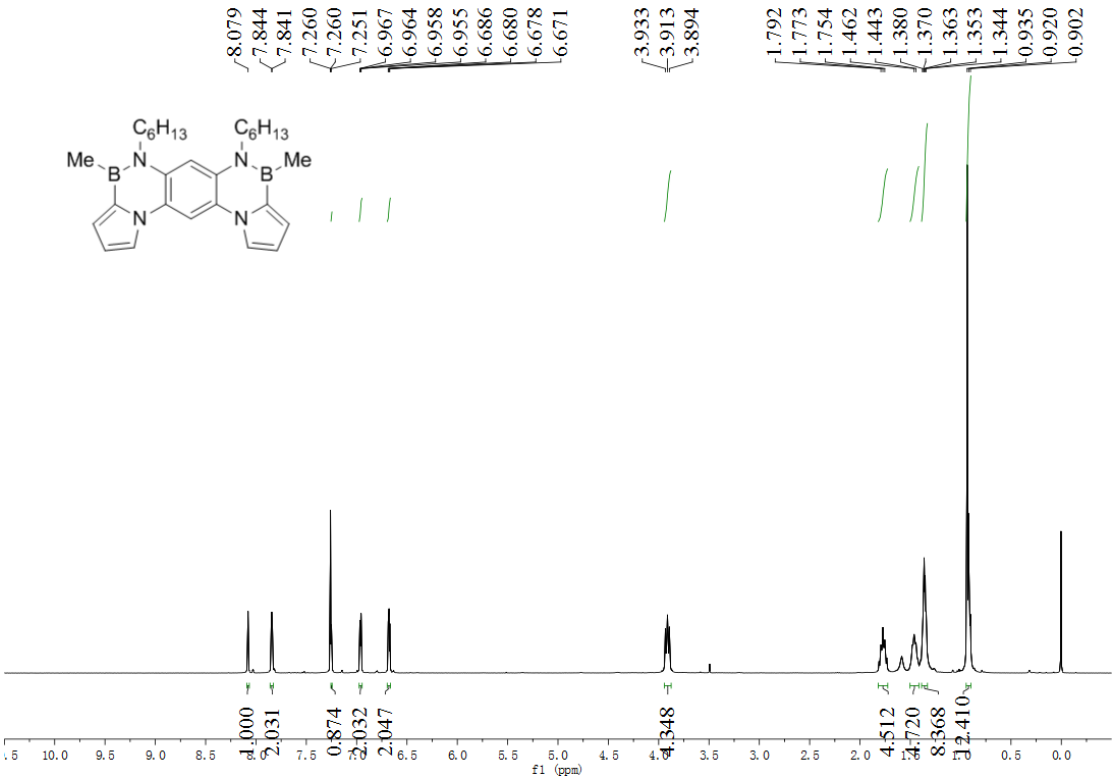
TOCSY NMR spectra of **4e** ($CDCl_3$)



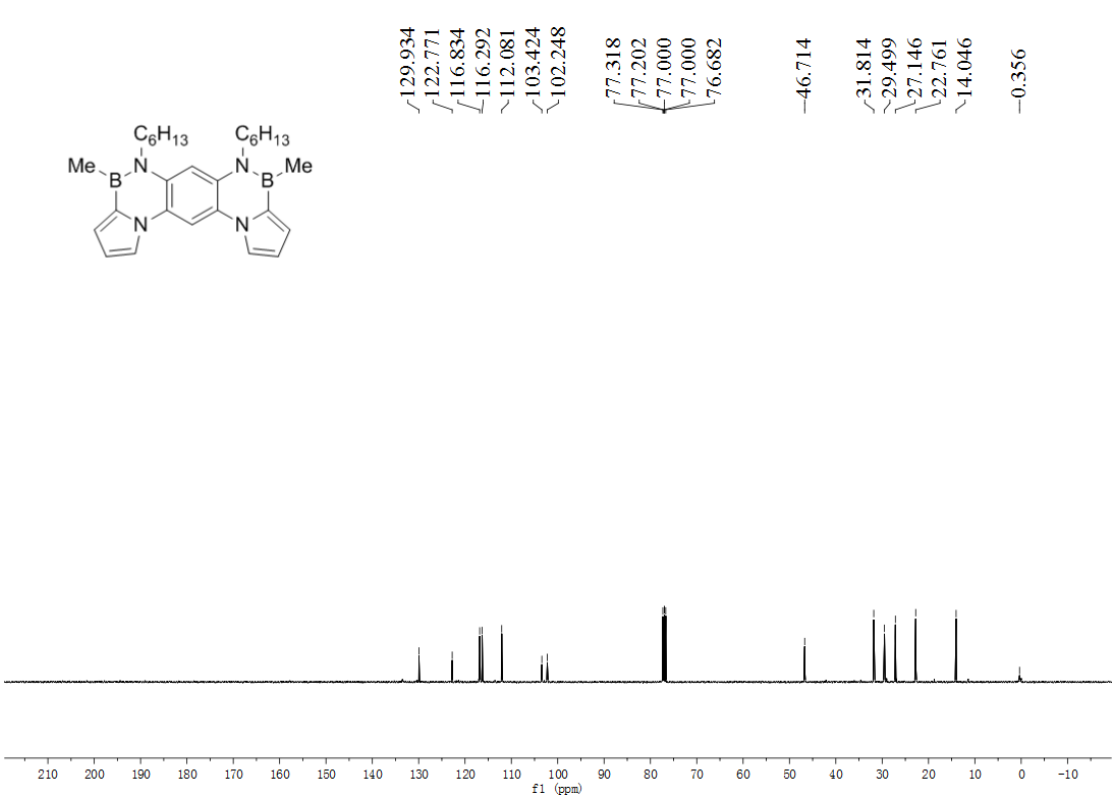
HSQC NMR spectra of **4e** ($CDCl_3$)



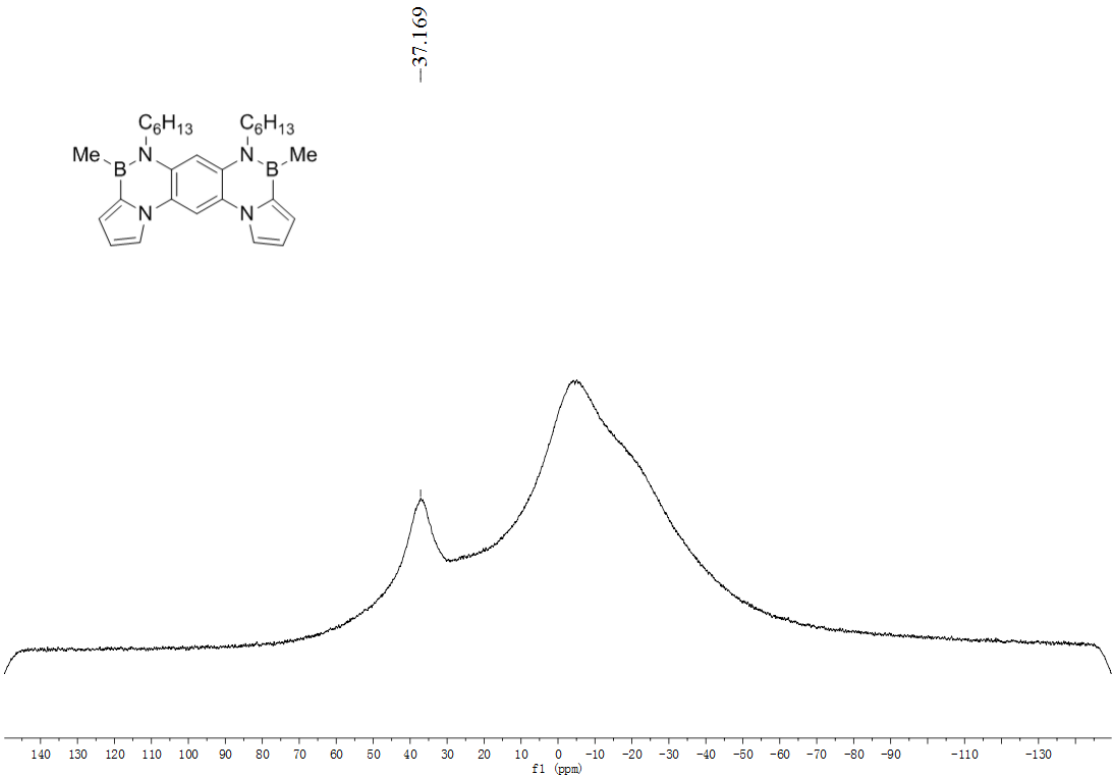
HMBC NMR spectra of **4e** ($CDCl_3$)



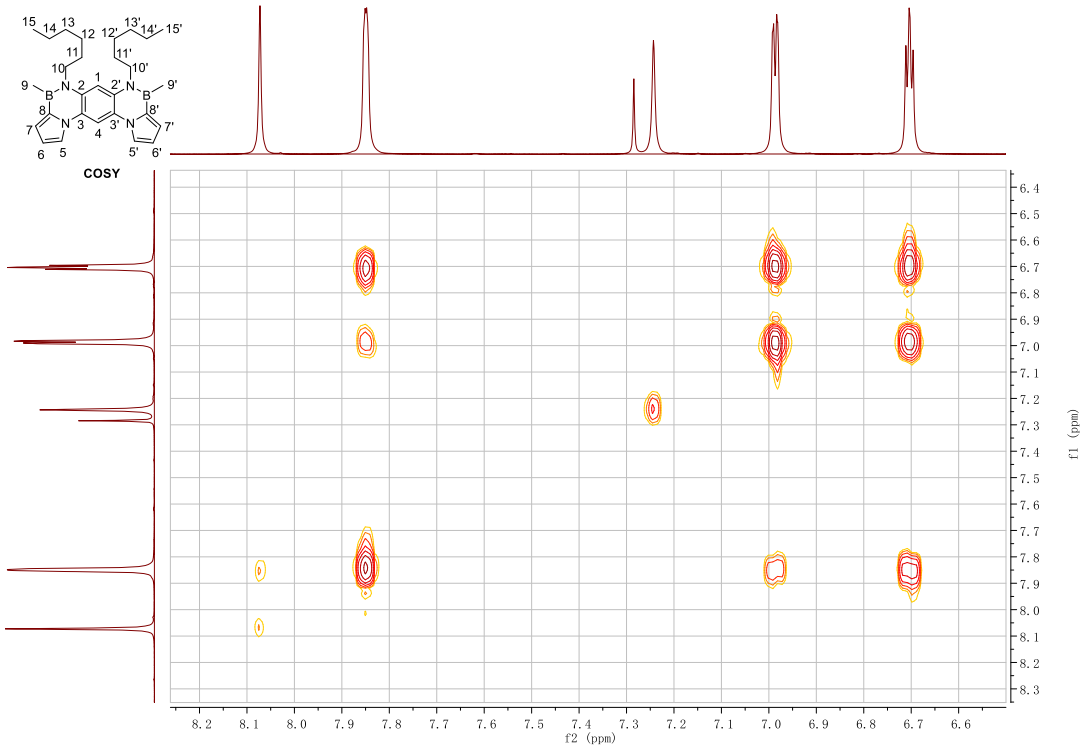
^{1}H NMR spectra of **4f** (400 MHz, $CDCl_3$)



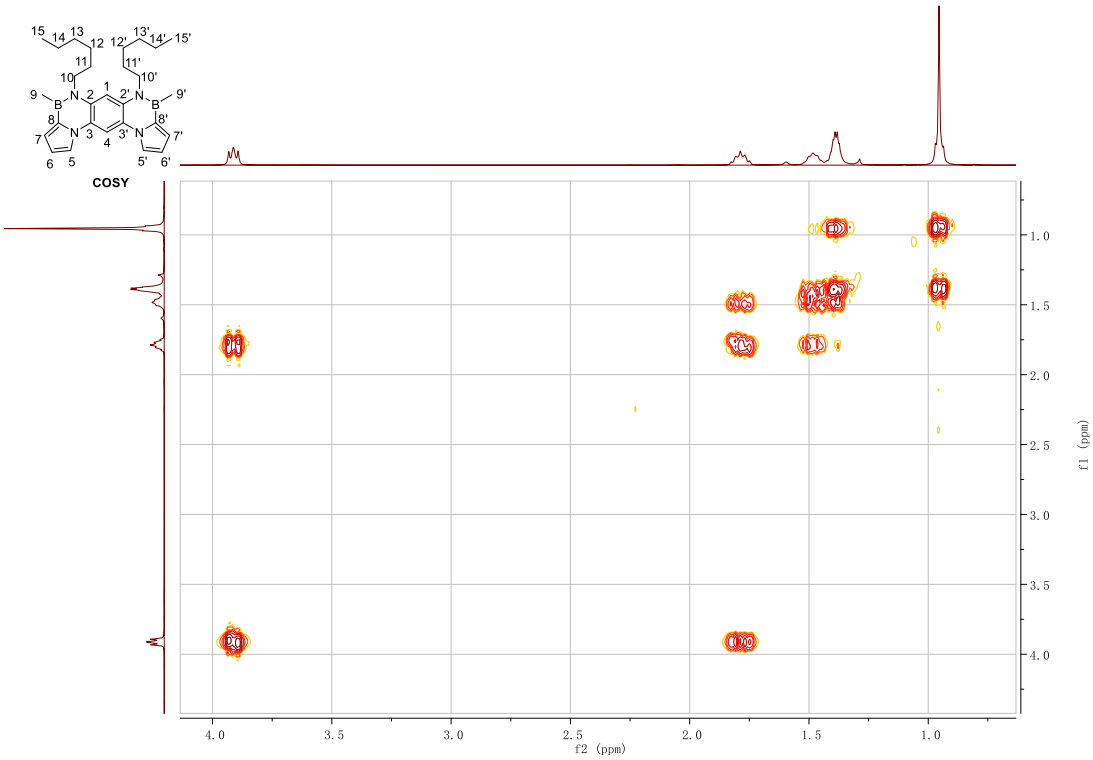
^{13}C NMR spectra of **4f** (100 MHz, $CDCl_3$)



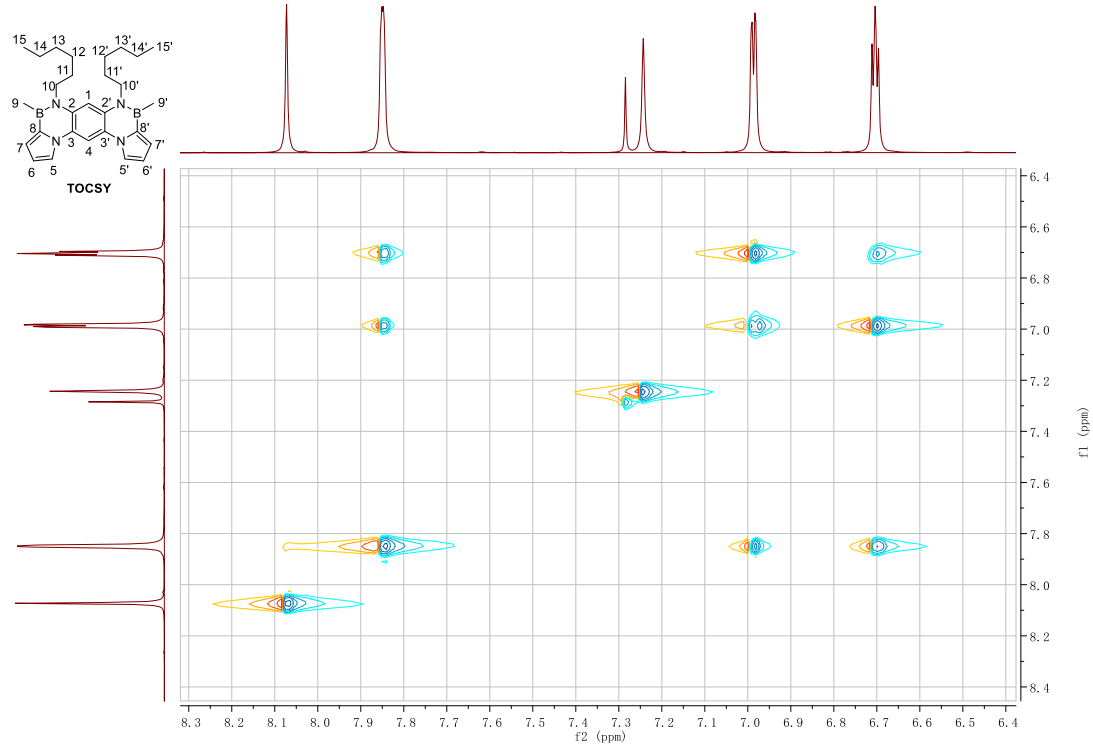
^{11}B NMR spectra of **4f** (128 MHz, $CDCl_3$)



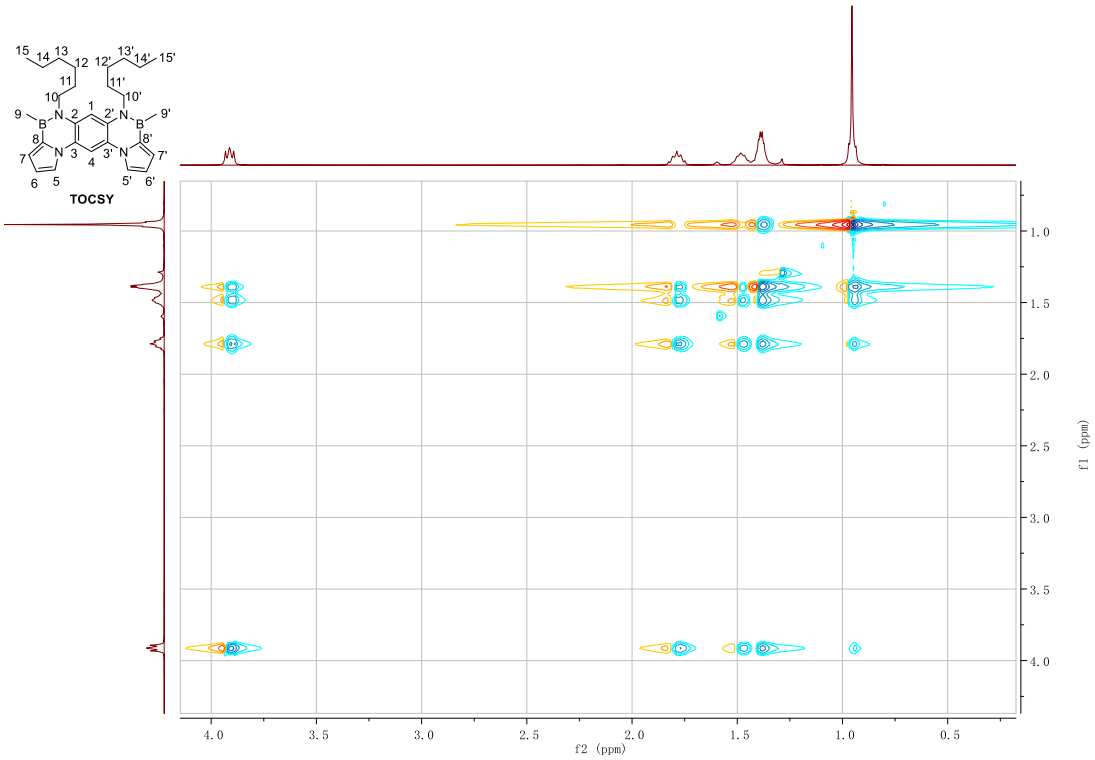
COSY NMR spectra (zoom, aromatic region) of **4f** ($CDCl_3$)



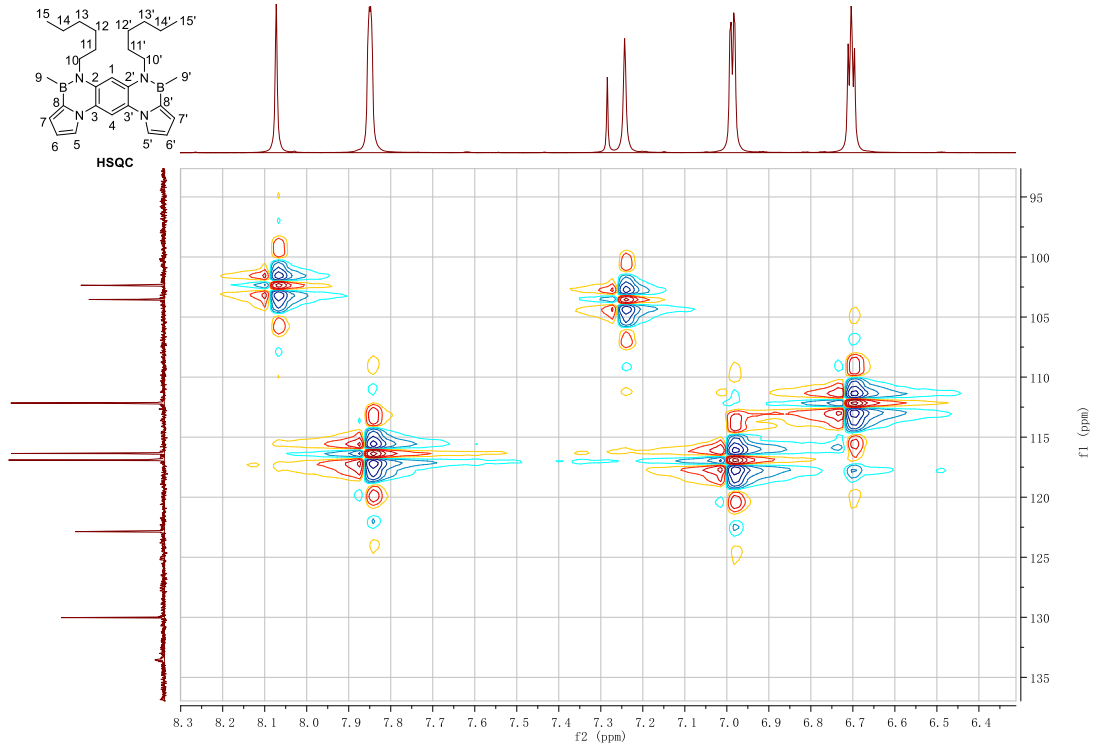
COSY NMR spectra (zoom, aliphatic region) of **4f** ($CDCl_3$)



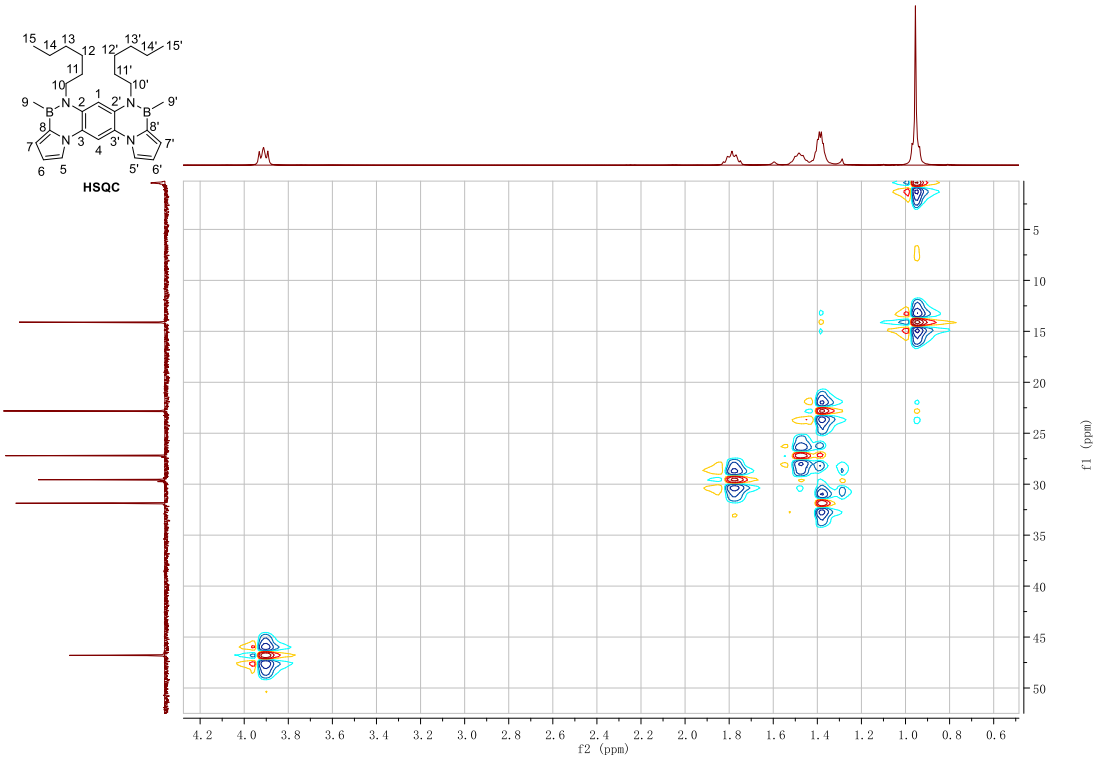
TOCSY NMR (zoom, aromatic region) spectra of **4f** ($CDCl_3$)



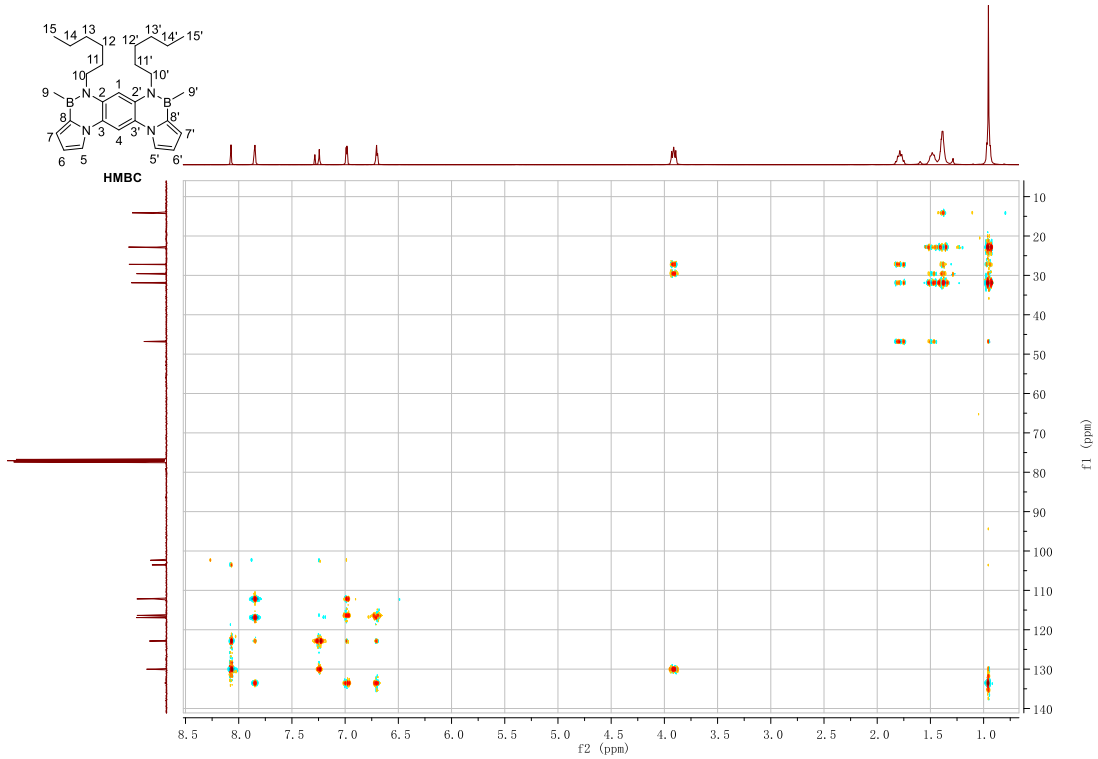
TOCSY NMR (zoom, aliphatic region) spectra of **4f** ($CDCl_3$)



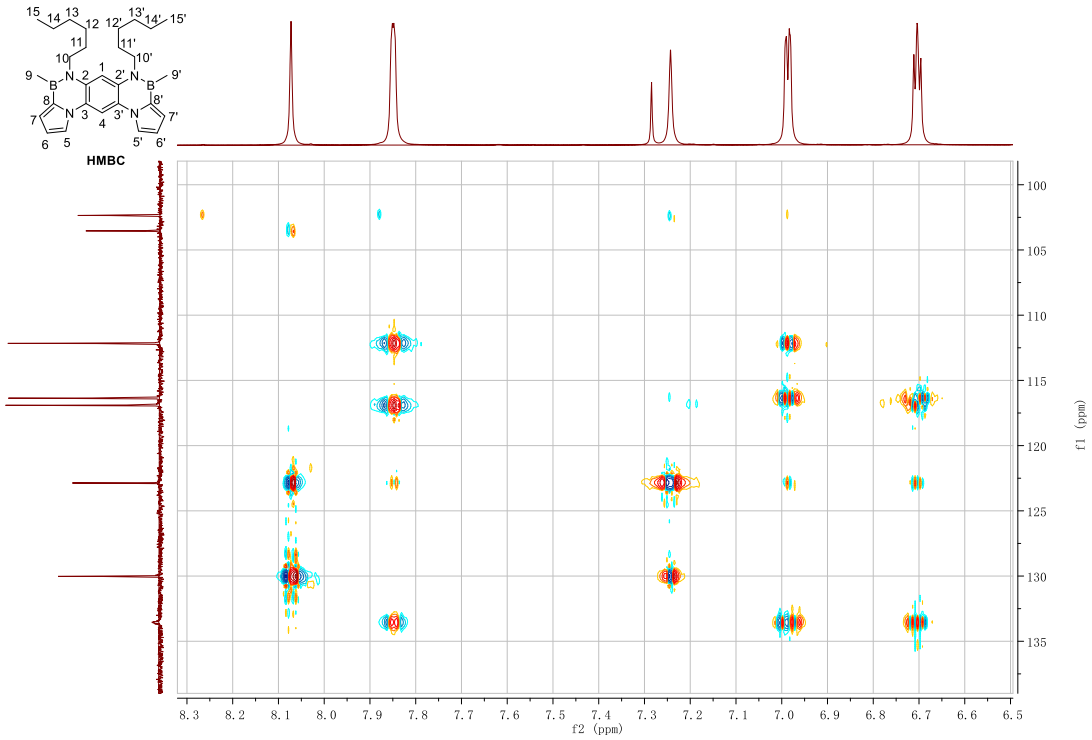
HSQC NMR spectra (zoom, aromatic region) of **4f** ($CDCl_3$)



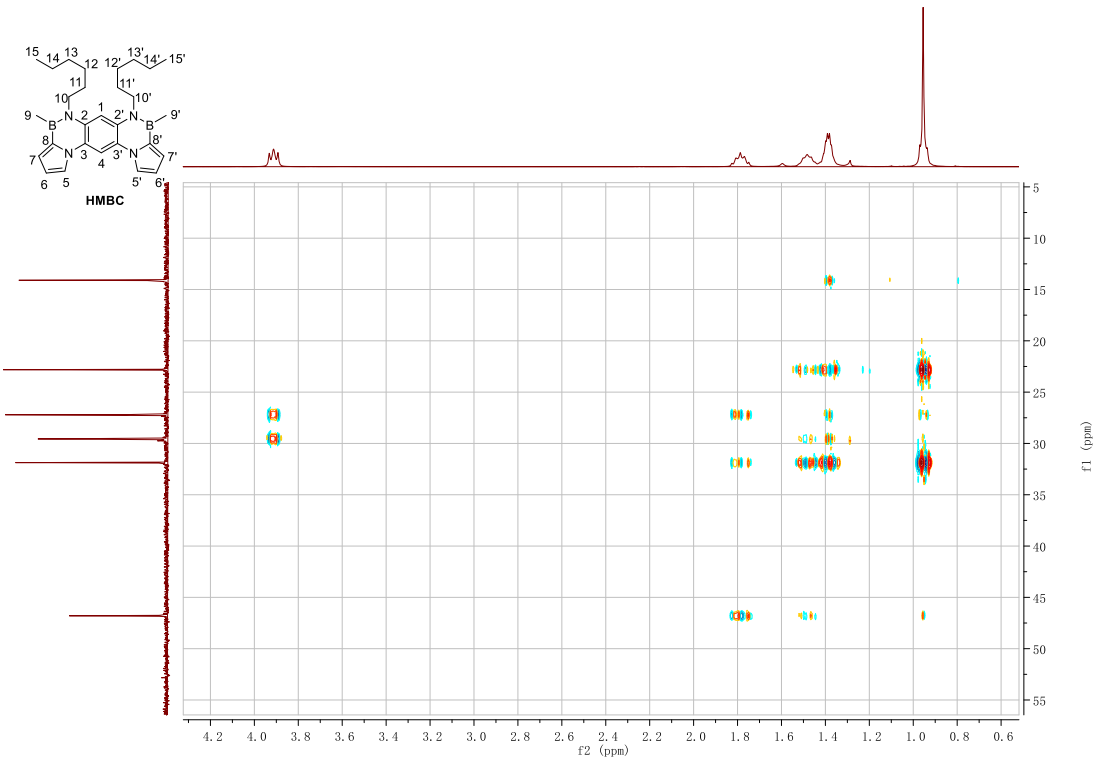
HSQC NMR spectra (zoom, aliphatic region) of **4f** ($CDCl_3$)



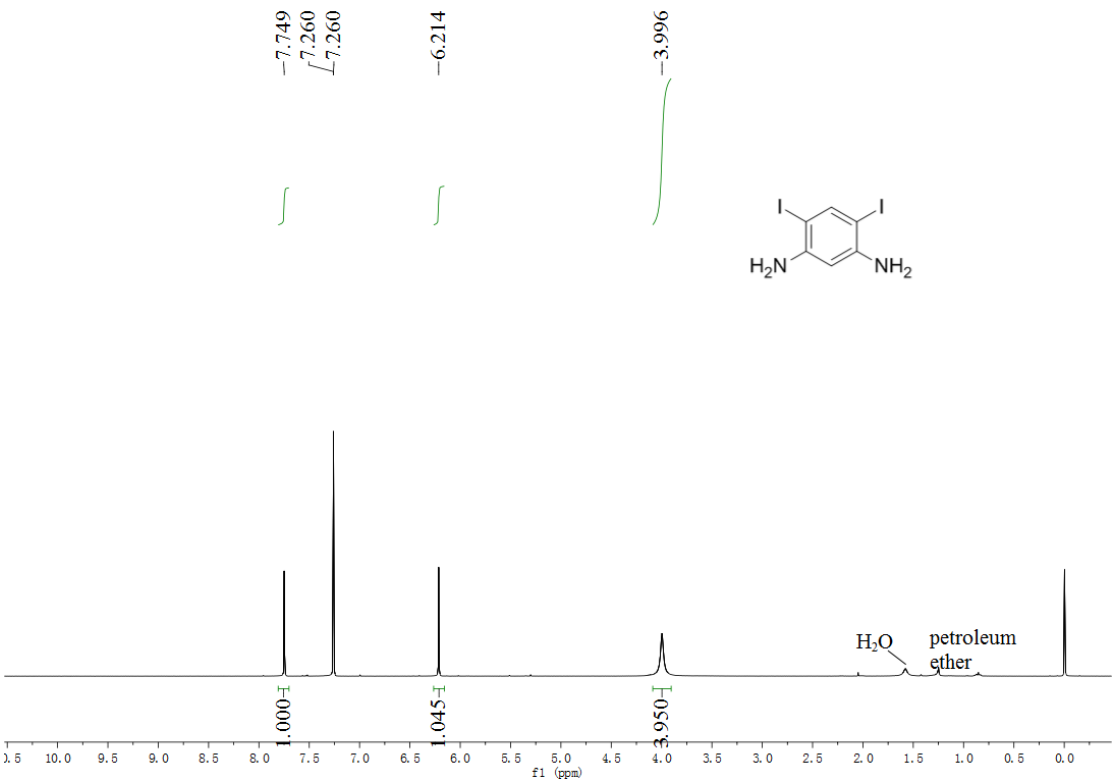
HMBC NMR spectra of **4f** ($CDCl_3$)



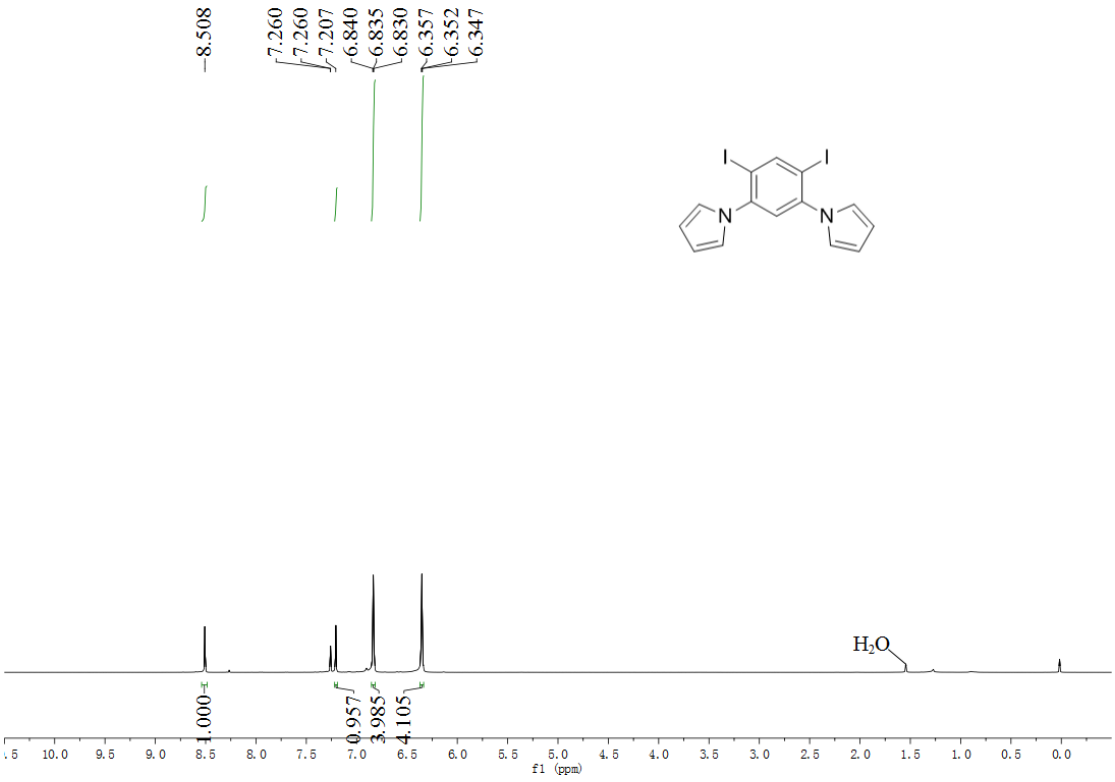
HMBC NMR spectra (zoom, aromatic region) of **4f** ($CDCl_3$)



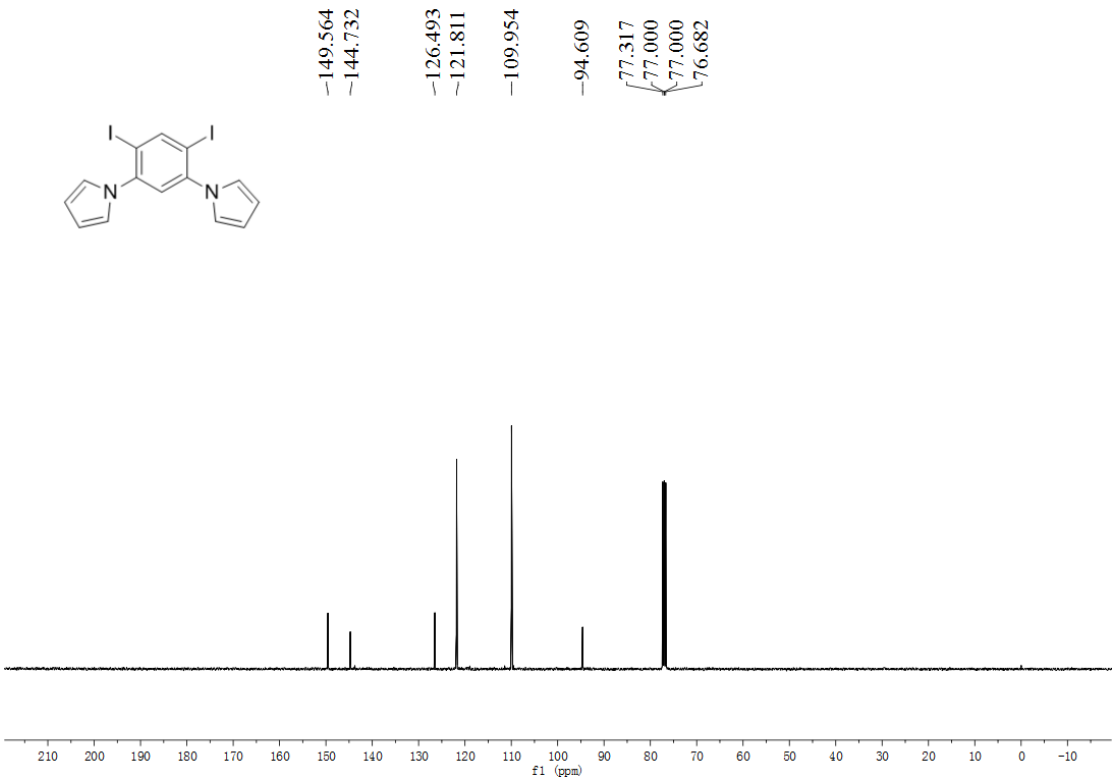
HMBC NMR spectra (zoom, aliphatic region) of **4f** ($CDCl_3$)



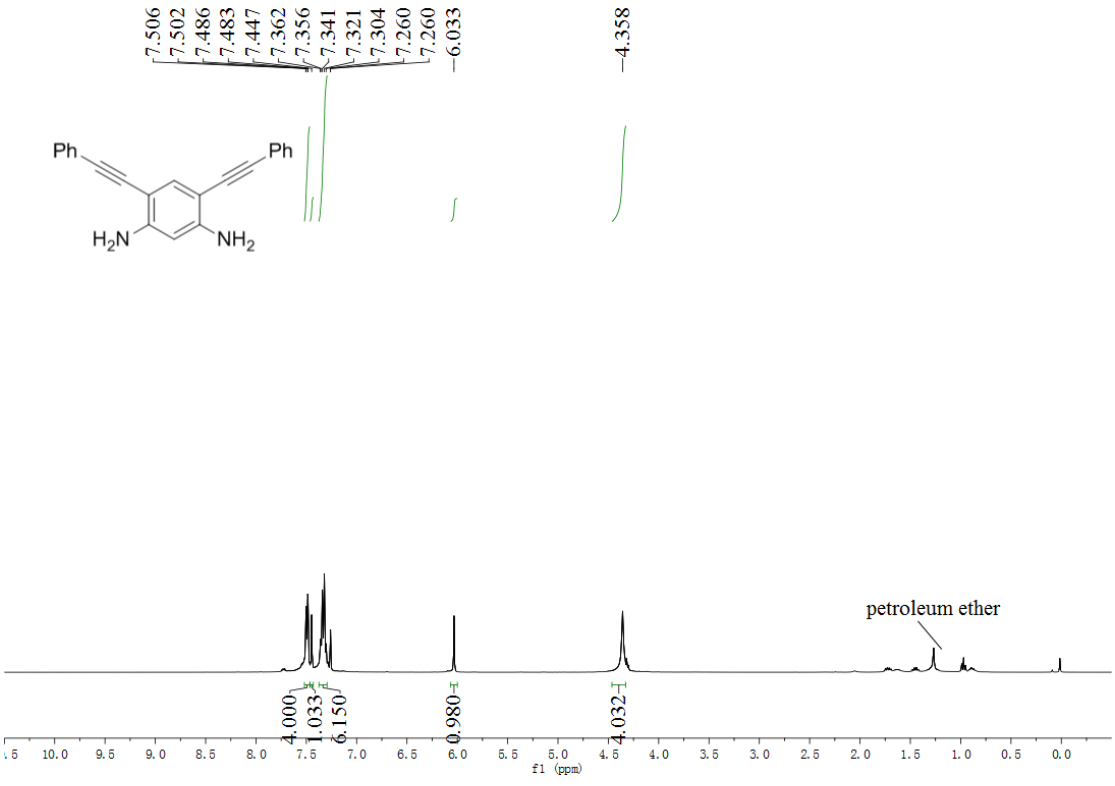
^{1}H NMR spectra of **6** (400 MHz, $CDCl_3$)



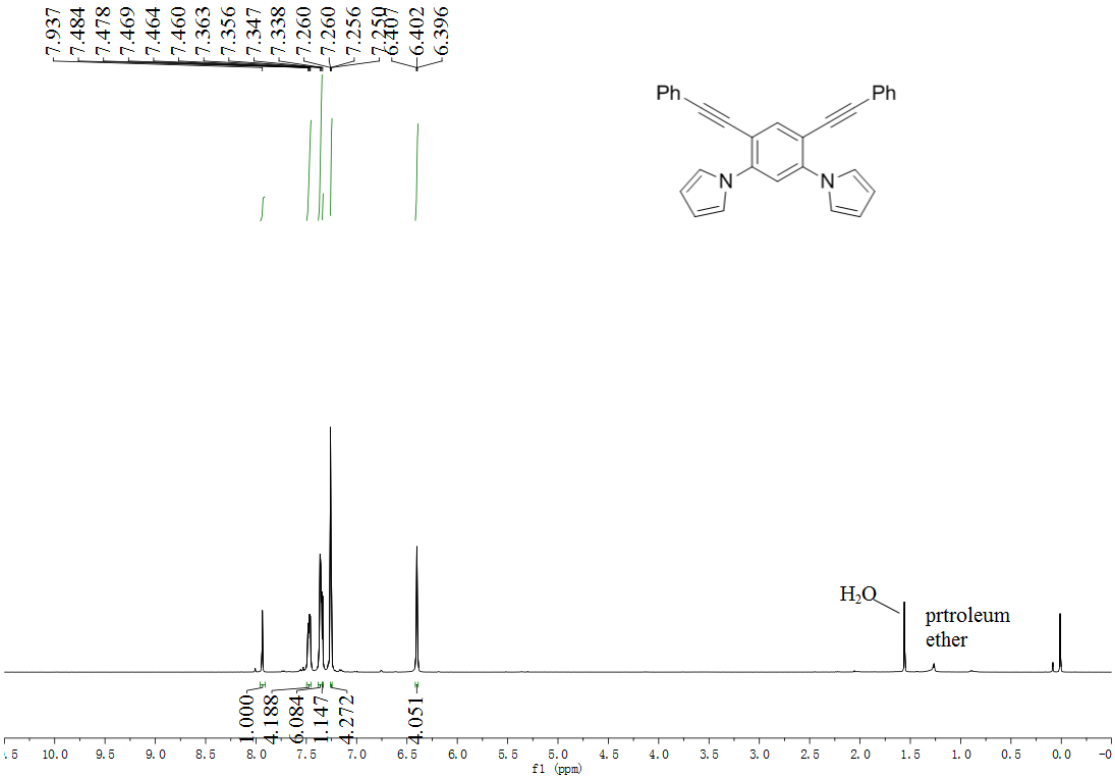
^{1}H NMR spectra of **7** (400 MHz, $CDCl_3$)



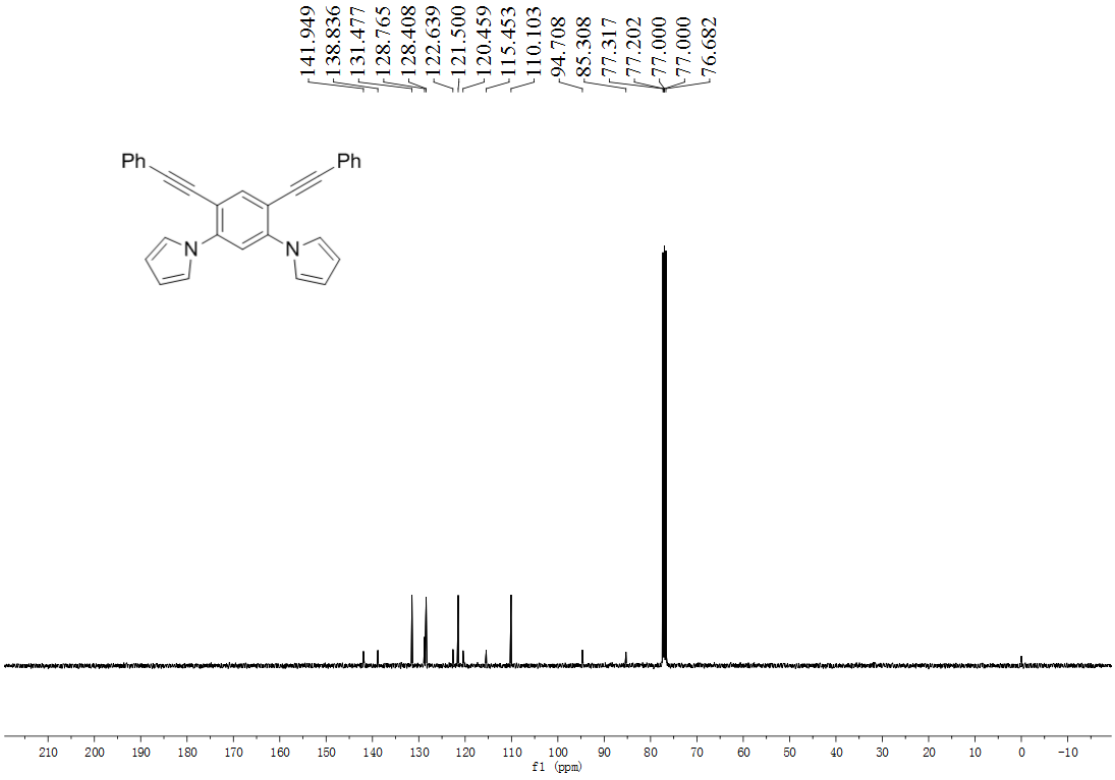
^{13}C NMR spectra of **7** (100 MHz, $CDCl_3$)



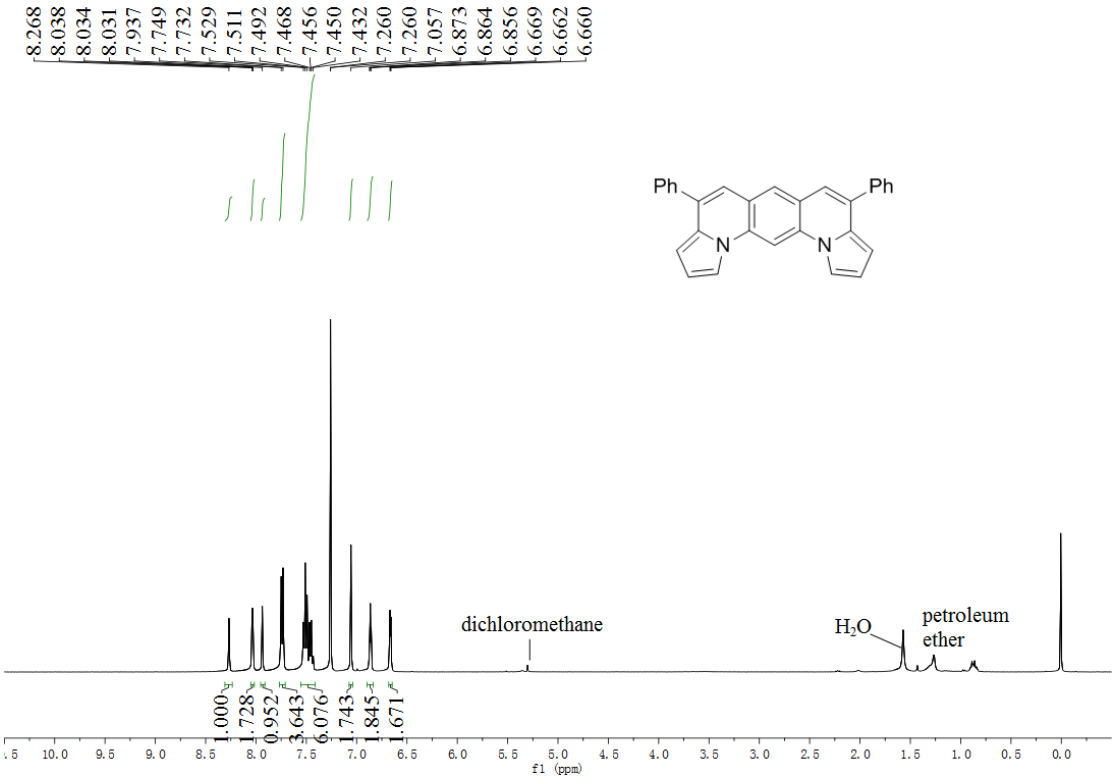
^{1}H NMR spectra of **10** (400 MHz, $CDCl_3$)



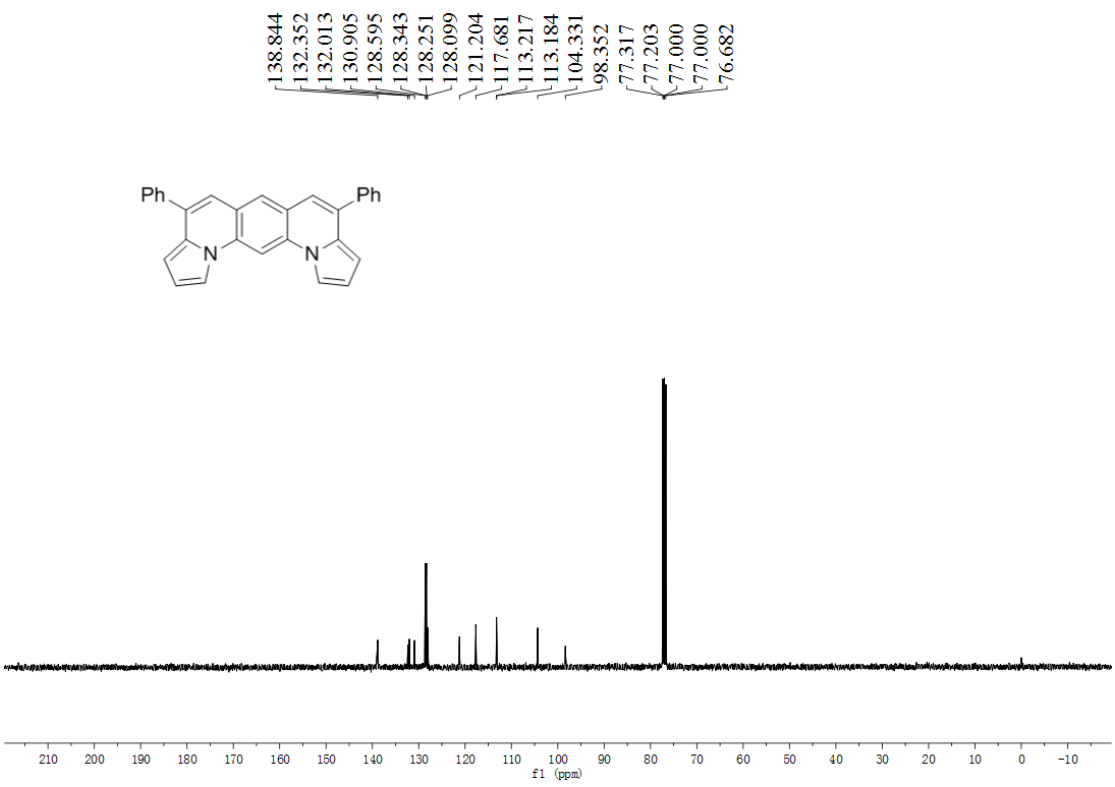
^{1}H NMR spectra of **8** (400 MHz, $CDCl_3$)



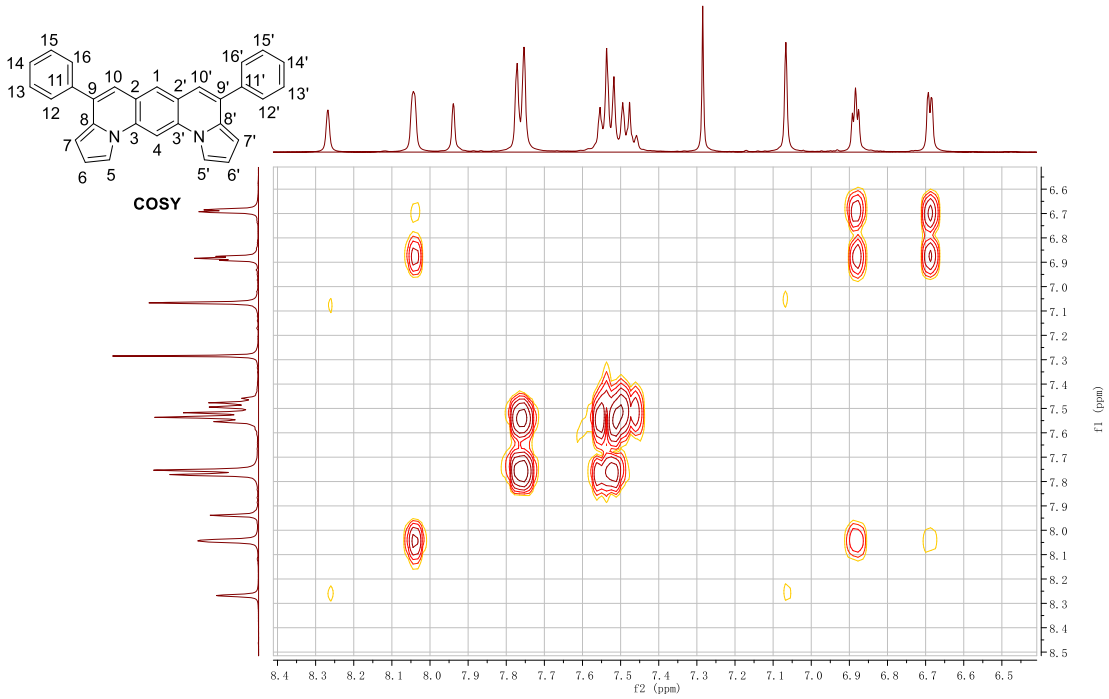
^{13}C NMR spectra of **8** (100 MHz, $CDCl_3$)



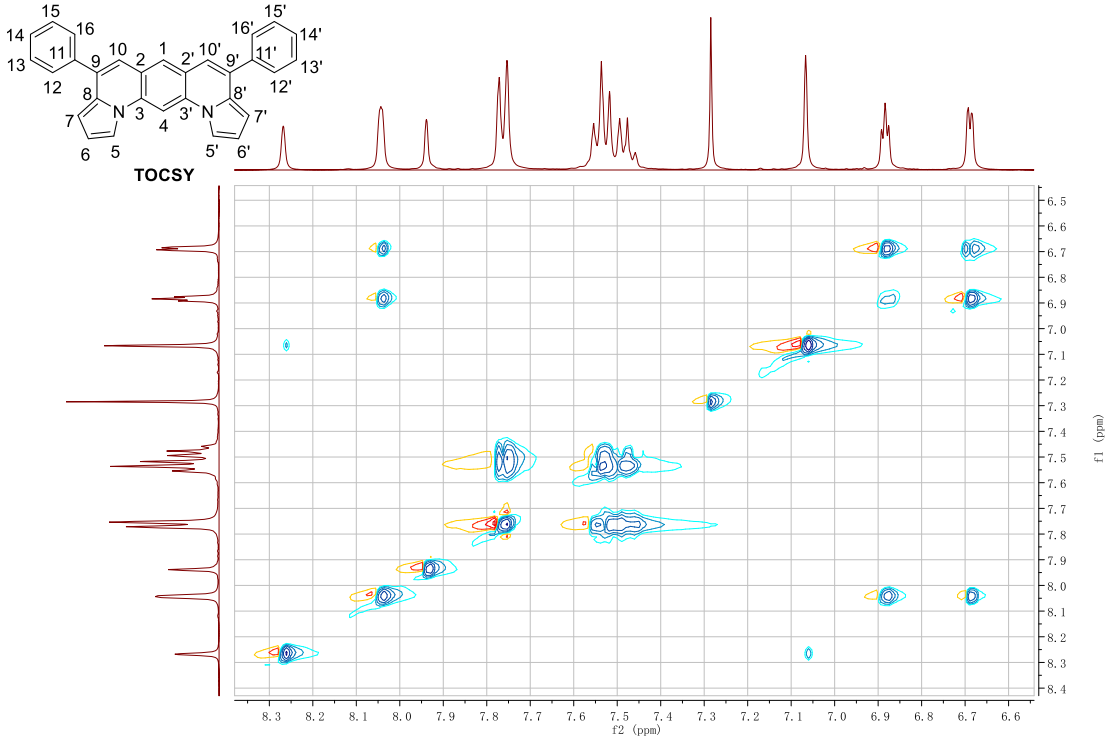
^{1}H NMR spectra of **9** (400 MHz, $CDCl_3$)



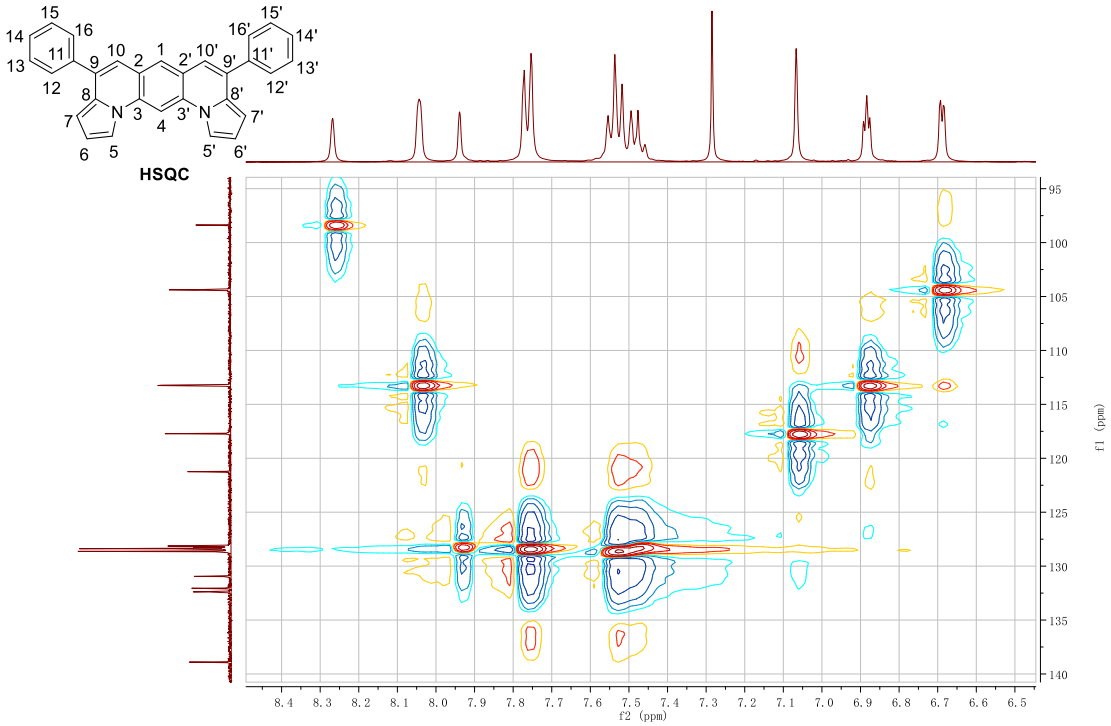
^{13}C NMR spectra of **9** (100 MHz, $CDCl_3$)



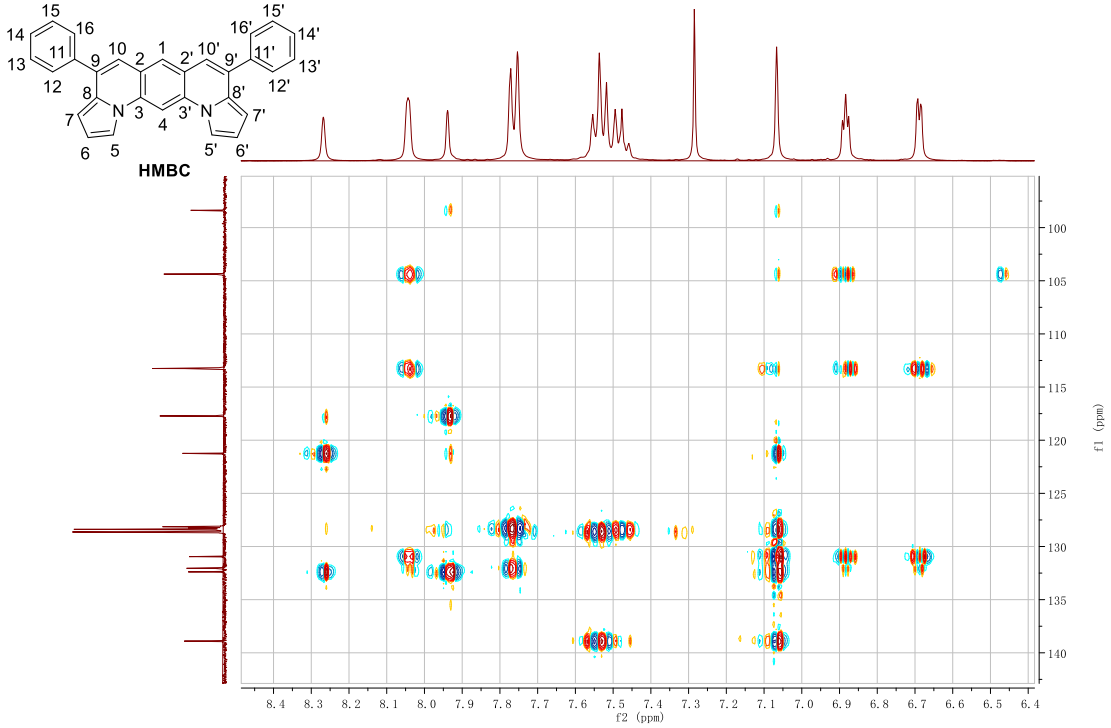
COSY NMR spectra of **9** ($CDCl_3$)



TOCSY NMR spectra of **9** ($CDCl_3$)



HSQC NMR spectra of **9** ($CDCl_3$)



HMBC NMR spectra of **9** ($CDCl_3$)