*Electronic Supporting Information for*

# Chiral Bowl-Shaped Thiazole-Embedded B(III)-Azatriphyrins(2.1.1): A Nonaromatic Platform via Triple Core-Modification

Lei Zhang,[a] Qinghua Wu,[a,b] Zhongxin Li,[*a,c] Wenxin Gu,[a] Zhengxin Kang,[a] Hua Wang,[a] Long Wang,[a] Yingjian Shang,[a] Lijuan Jiao,[*a] Erhong Hao[*a]

[a]Anhui Laboratory of Molecule-Based Materials; The Key Laboratory of Functional Molecular Solids of Ministry of Education; School of Chemistry and Materials Science, Anhui Normal University, Wuhu 241002, China.

[b]School of Pharmacy, Anhui University of Chinese Medicine, Hefei 230012, China

[c]College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

[*]E-mail: lizhongxin@pku.edu.cn, haoehong@ahnu.edu.cn, jiao421@ahnu.edu.cn

***Contents:***

## 1. General information

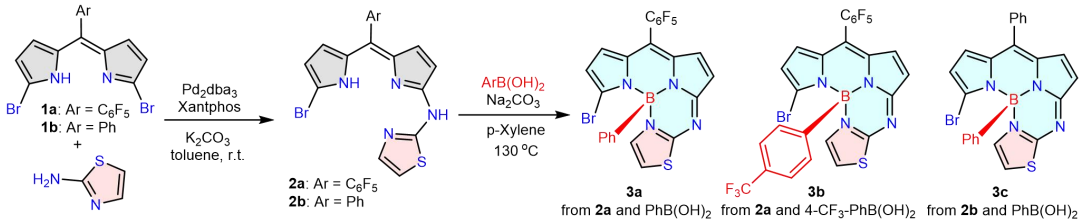
Reagents and solvents were used as received from commercial suppliers (Energy Chemicals, Shanghai, China) unless noted otherwise. All reactions were performed in oven-dried or flame-dried glassware unless stated otherwise and were monitored by TLC using 0.25 mm silica gel plates with UV indicator (60F-254). Liquid metal bath was used for all heating reactions. $^{1}$H, $^{11}$B and $^{13}$C NMR spectra were recorded on a 400 or 500 MHz NMR spectrometer at room temperature. Chemical shifts ($\delta$) are given in ppm relative to $CDCl_3$ (7.26 ppm for $^{1}$H and 77 ppm for $^{13}$C) or to internal TMS ($\delta$ = 0 ppm) as internal standard. High-resolution mass spectra (HRMS) were obtained using ESI-TOF or MAlDI-TOF in positive mode. UV-visible absorption spectra were recorded on a Shimadzu UV-2450 spectrophotometer. All measurements were made at 25 °C, using 5 × 10 mm cuvettes.

**Crystallography.** Crystals of compound **5a** suitable for X-ray analysis were obtained *via* the slow diffusion of petroleum ether into their dichloromethane solutions. The vials containing these solutions were placed, loosely capped, to promote the crystallization. Single-crystal X-ray diffraction data collection was performed at 293(2) K in beamline station BL17B at the Shanghai Synchrotron Radiation Facility in the scan range of $2.112° < 2\theta < 51°$. The structure was solved by the direct method using the SHELXS-97[1] program and refined by least squares method on $F^2$, SHELXL-2018/3[2], incorporated in SHELXTL V5.10[3], CCDC-2531362 (**5a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

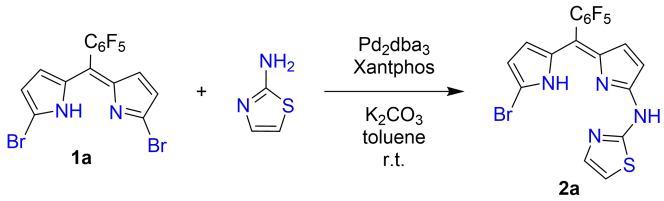
**Electrochemical measurements.** Cyclic voltammogram (CV) was obtained on a CH Instruments electrochemical workstation (CHI 610E, USA). CV was performed on 1.0 mM solutions of selected compounds in dichloromethane, containing 0.1 M $TBAPF_6$ as the supporting electrolyte. Measurements were carried out at room temperature using a standard three-electrode configuration: a 3 mm diameter glassy

carbon working electrode (geometric area: 0.071 $cm^2$), a Pt wire counter electrode, and saturated calomel electrode (SCE) as reference electrode. The scan rate was 100 mV $s^{-1}$. Prior to measurement, solutions were deoxygenated by argon bubbling. Before each experiment, the working electrode was polished on a felt pad with 0.3 μm alumina (Buehler, Ltd., Lake Bluff, IL) and sonicated in Milli-Q deionized water and then in ethanol. The counter and reference electrodes were cleaned by rinsing and sonicating in water, and ethanol. Potentials were recorded versus the ferrocene/ferrocenium (Fc/Fc+) couple. The HOMO and LUMO energy levels were estimated from the onset potentials of oxidation and reduction waves, respectively. The CV was plotted following the IUPAC convention.

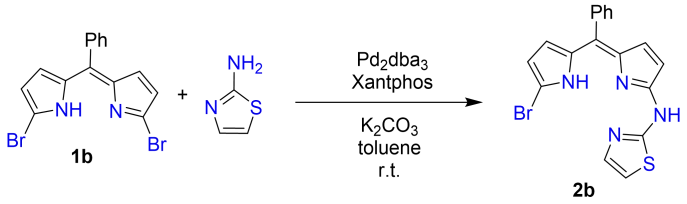
## 2. Synthesis and characterization



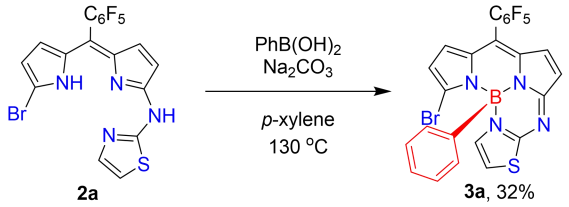

**Scheme S1.** Synthesis of compounds **3a-c**.




Synthesis of **2a**: Synthesis of **2a**: To a solution of the limiting reactant **1a** (93 mg, 0.20 mmol, 1.0 equiv) in anhydrous toluene (5 mL, concentration of **1a** = 0.04 M) were added 2-thiazolamine (30 mg, 0.30 mmol, 1.5 equiv), $Pd_2(dba)_3$ (9 mg, 0.01 mmol, 5 mol%), Xantphos (12 mg, 0.02 mmol, 10 mol%), and $K_2CO_3$ (83 mg, 0.60 mmol, 3.0 equiv). The reaction mixture was stirred at room temperature under an argon atmosphere for 12 h. After completion (monitored by TLC), the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 4:1, *v*/*v*) to afford **2a** as a yellow solid (70 mg, 0.14 mmol, 72% yield). $^1$H NMR (400 MHz, DMSO-$d_6$) δ 12.37 (brs, 2H, NH), 7.62 (d, $J$ = 3.5 Hz, 1H, thiazole-H), 7.44 (d, $J$ = 3.4 Hz, 1H, thiazole-H), 7.04 (d, $J$ = 4.7 Hz, 1H, pyrrole-H), 6.63 (brs, 1H, pyrrole-H), 6.45 (brs, 1H, pyrrole-H), 6.38 (brs, 1H, pyrrole-H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 161.6, 158.5, 148.0, 144.8 (d, $J$ = 235.4 Hz*), 140.97 (d, J = 248.5 Hz*), 139.0, 137.4 (d, $J$ = 227.1 Hz*), 136.1, 131.2, 121.8, 116.8, 113.0, 112.8, 111.5, 110.3 (t, $J$ = 19.9 Hz*), 105.6. (*These signals showed further long-range coupling with the fluorine atoms and would be less accurate). HRMS (ESI) m/z calcd for $C_{18}H_9BrF_5N_4S^+$ $(M+H)^+$ 486.9651, found 486.9658.

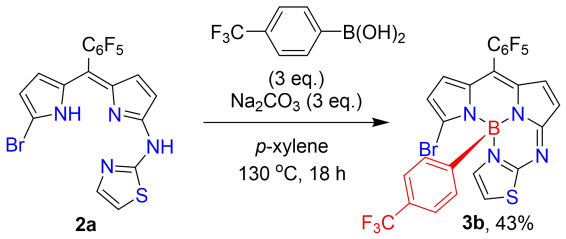



Compound **2b** was obtained as yellow solid in 68% yield (54 mg) from compound **1b** (75 mg, 0.2 mmol) and 2-thiazolamine (30 mg, 0.3 mmol) using the same procedure described above for the synthesis of **2a**. Upon the completion of the reaction, the solvent was evaporated under vacuum and the crude product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 4:1, *v*/*v*). $^{1}$H NMR (400 MHz, DMSO-$d_6$) δ 12.89 (brs, 1H, NH), 12.10 (brs, 1H, NH), 7.62-7.35 (m, 7H, *meso*-Ph-H and thiazole-H), 6.77 (brs, 1H, pyrrole-H), 6.55 (d, $J$ = 4.4 Hz, 1H, pyrrole-H), 6.34 (brs, 1H, pyrrole-H), 6.07 (brs, 1H, pyrrole-H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 159.8, 158.8, 145.5, 138.8, 136.4, 135.8, 133.5, 130.5, 129.9, 128.6, 128.0, 119.4, 117.8, 112.6, 111.8, 105.8. HRMS (ESI) m/z calcd for $C_{18}H_{14}BrN_4S^+$ $(M+H)^+$ 397.0123, found 397.0126.

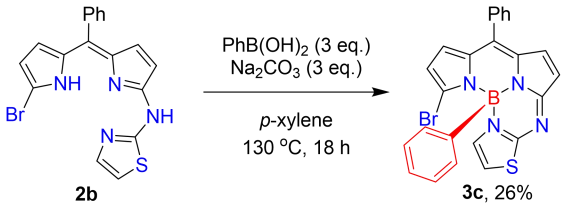



Synthesis of **3a**: To a solution of the limiting reactant **2a** (97 mg, 0.20 mmol, 1.0 equiv) in *p*-xylene (8 mL, concentration of **2a** = 0.025 M) were added phenylboronic acid (73 mg, 0.6 mmol, 3.0 equiv) and $Na_2CO_3$ (64 mg, 0.60 mmol, 3.0 equiv). The reaction mixture was stirred at 130 °C for 18 h and monitored by TLC. After completion, the solvent was removed under reduced pressure. The crude residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 8:1, *v*/*v*) to afford product **3a** as a black solid (37 mg, 0.064 mmol) in 32% yield. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, $J$ = 4.5 Hz, 1H, thiazole-H), 7.19-7.08 (m, 3H, B-Ar-H), 6.97 (brs, 1H, thiazole-H), 6.76 (d, $J$ = 5.0 Hz, 1H, pyrrole-H), 6.61 (d, $J$ = 4.2 Hz, 2H, B-Ar-H), 6.51 (d, $J$ = 5.1 Hz, 1H, pyrrole-H), 6.43 (d, $J$ = 4.0 Hz, 1H, pyrrole-H), 6.36 (d, $J$ = 3.8 Hz, 1H, pyrrole-H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ

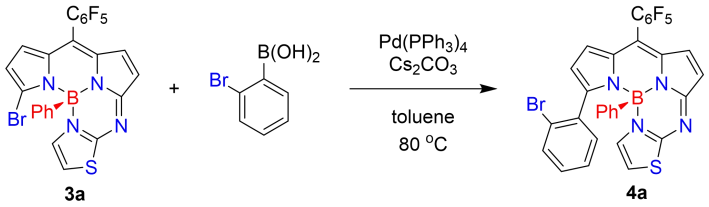
173.3, 161.1, 145.3 (d, $J$ = 248.0 Hz*), 141.8 (d, $J$ = 264.9 Hz*), 137.8 (d, $J$ = 247.5 Hz*), 135.4, 135.0, 133.9, 130.6, 130.5, 127.6, 127.5, 123.6, 118.7, 118.4, 118.1, 115.3, 110.2, 108.6 (t, $J$ = 19.0 Hz*), *carbon attached to boron not observed*. (*These signals showed further long-range coupling with the fluorine atoms and would be less accurate). $^{11}$B NMR (128 MHz, $CDCl_3$) δ 1.8 (brs). HRMS (ESI) m/z calcd for $C_{24}H_{12}BBrF_5N_4S^+$ $(M+H)^+$ 572.9979, found 572.9990.




Compound **3b** was obtained as a black solid in 43% yield (55 mg) from **2a** (97 mg, 0.2 mmol) and 4-(trifluoromethyl)phenylboronic acid (114 mg, 0.6 mmol) using the same procedure described above for the synthesis of **3a** and purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 7:1, v/v). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, $J$ = 4.5 Hz, 1H, thiazole-H), 7.37 (d, $J$ = 7.9 Hz, 2H, B-Ar-H), 7.04 (d, $J$ = 4.5 Hz, 1H, thiazole-H), 6.80 (d, $J$ = 5.0 Hz, 1H, pyrrole-H), 6.71 (d, $J$ = 7.9 Hz, 2H, B-Ar-H), 6.54 (d, $J$ = 5.1 Hz, 1H, pyrrole-H), 6.45 (d, $J$ = 3.9 Hz, 1H, pyrrole-H), 6.39 (d, $J$ = 3.8 Hz, 1H, pyrrole-H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 173.1, 160.9, 145.1 (d, $J$ = 246.8 Hz*), 141.8 (d, $J$ = 244.2 Hz*), 137.8 (d, $J$ = 253.8 Hz*), 135.3, 134.7, 133.7, 130.8, 129.4 (q, $J$ = 32.3 Hz*), 127.1 (q, $J$ = 272.7 Hz*), 124.4 (q, $J$ = 4.0 Hz*), 123.5, 123.0, 119.0, 118.4, 115.3, 110.7, 110.5, 108.3 (t, $J$ = 18.8 Hz*), *carbon attached to boron not observed*. (*These signals showed further long-range coupling with the fluorine atoms and would be less accurate). $^{11}$B NMR (128 MHz, $CDCl_3$) δ 1.4 (brs). HRMS (ESI) m/z calcd for $C_{25}H_{11}BBrF_8N_4S^+$ $(M+H)^+$ 640.9853, found 640.9867.

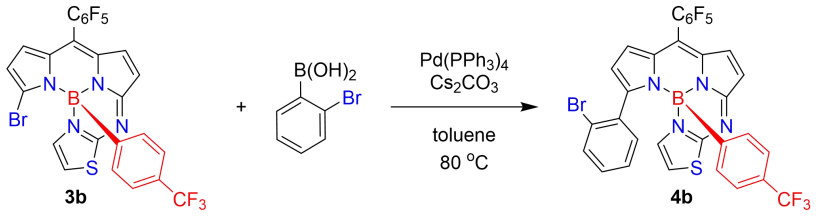


Compound **3c** was obtained as a black solid in 26% yield (31 mg) from **2b** (100 mg, 0.25 mmol), phenylboronic acid (114 mg, 0.6 mmol) and $Na_2CO_3$ (64 mg, 0.6 mmol) using the same procedure described above for the synthesis of **3a** and purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 8:1, *v*/*v*). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 4.5 Hz, 1H, thiazole-H), 7.57 (dd, *J* = 6.1, 2.7 Hz, 2H, *meso*-Ar-H), 7.50-7.49 (m, 3H, *meso*-Ar-1H and B-Ar-2H), 7.13-7.12 (m, 3H, thiazole-H and *meso*-Ar-2H), 6.90 (dd, *J* = 9.7, 4.8 Hz, 2H, pyrrole-1H and B-Ar-1H), 6.65 (d, *J* = 3.9 Hz, 1H, pyrrole-H), 6.62 (d, *J* = 4.8 Hz, 2H, B-Ar-H), 6.46 (dd, *J* = 8.5, 4.5 Hz, 2H, pyrrole-H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 172.4, 159.5, 137.0, 134.4, 133.9, 132.4, 131.8, 130.8, 130.3, 129.3, 128.4, 127.6, 127.3, 121.2, 120.7, 118.1, 116.0, 113.7, 109.1, *carbon attached to boron not observed*. $^{11}$B NMR (128 MHz, $CDCl_3$) δ 1.4 (brs). HRMS (ESI) m/z calcd for $C_{24}H_{17}BBrN_4S^+$ $(M+H)^+$ 483.0450, found 483.0460.

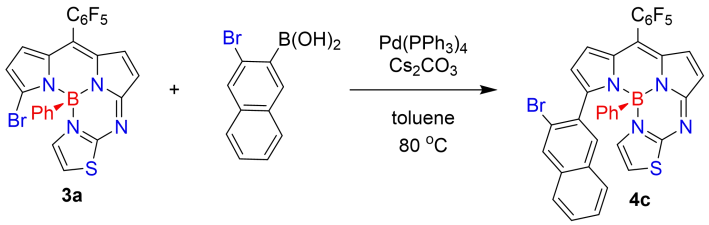



Synthesis of **4a**: Compound **3a** (57 mg, 0.1 mmol), 2-bromophenylboronic acid (40 mg, 0.4 mmol), $Pd(PPh_3)_4$ (23 mg, 0.02 mmol), and $Cs_2CO_3$ (65 mg, 0.2 mmol) were dissolved in 4 mL of toluene. The reaction mixture was stirred at 80 °C under argon for 2 hours. Upon the completion of the reaction, the solvent was evaporated under vacuum and the crude product was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 8:1, v/v) to give product **4a** as black solid (58 mg, 0.09 mmol) in 85% yield. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.9 Hz, 1H, thiazole-H), 7.23-7.05 (m, 5H, B-Ar-H), 6.83 (d, *J* = 4.3 Hz, 1H, *α*-Ar-H), 6.79 (d, *J* = 7.4 Hz, 1H, thiazole-H), 6.57 (d, *J* = 5.7 Hz, 2H, *α*-Ar-H), 6.51-6.41 (m, 2H, pyrrole-H and *α*-Ar-H), 6.42-6.27 (m, 2H, pyrrole-H), 5.50 (d, *J* = 4.3 Hz, 1H, pyrrole-H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 173.2, 160.3, 148.6 (d, *J* = 251.0 Hz*), 145.0 (d, *J* = 224.6 Hz*), 144.8, 140.0, 139.8 (d, *J* = 151.7 Hz*), 136.5, 136.1, 133.8, 132.7, 132.5, 131.7, 130.7, 130.2, 127.8, 127.6, 127.4, 126.8, 121.7, 121.2, 117.3,

116.9, 112.7, 109.4, *carbon attached to boron not observed*. (*These signals showed further long-range coupling with the fluorine atoms and would be less accurate). $^{11}$B NMR (128 MHz, $CDCl_3$) δ 2.4 (brs). HRMS (ESI) m/z calcd for $C_{30}H_{16}BBrF_5N_4S^+$ $(M+H)^+$ 649.0292, found 649.0305.

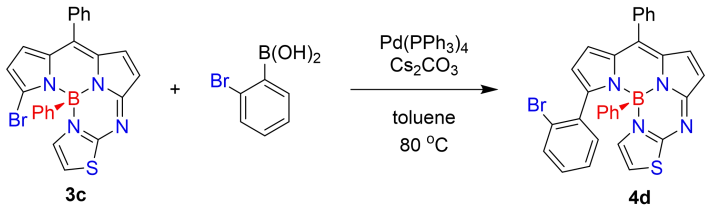



Compound **4b** was obtained as a black solid in 62% yield (89 mg) from **3b** (128 mg, 0.2 mmol) and 2-bromophenylboronic acid (40 mg, 0.4 mmol) using the same procedure described above for the synthesis of **4a** and purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 7:1, v/v). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.9 Hz, 1H, thiazole-H), 7.38 (d, *J* = 7.7 Hz, 2H, B-Ar-H), 7.23-7.08 (m, 2H, B-Ar-H), 6.83 (brs, 2H, thiazole-H and *α*-Ar-H), 6.64 (d, *J* = 7.4 Hz, 2H, *α*-Ar-H), 6.47 (brs, 2H, *α*-Ar-H and pyrrole-H), 6.40 (brs, 2H, pyrrole-H ), 5.41 (brs, 1H, pyrrole-H). $^{13}$C NMR (101 MHz, CDCl3) δ 173.4, 160.3, 147.8 (d, *J* = 243.4 Hz*), 144.8, 144.7 (d, *J* = 238.4 Hz*), 137.8 (d, *J* = 246.4*), 136.3, 136.1, 134.1, 133.4, 132.7, 132.4, 132.0, 131.2, 130.4, 130.3, 129.9 (q, *J* = 30.6 Hz*), 126.9, 126.7, 124.5, 124.4 (q, *J* = 272.2 Hz*), 121.8, 117.9, 117.6, 116.9, 109.7, 109.1 (q, *J* = 20.2 Hz*), *carbon attached to boron not observed*. (*These signals showed further long-range coupling with the fluorine atoms and would be less accurate). $^{11}$B NMR (128 MHz, $CDCl_3$) δ 2.0 (brs). HRMS (MALDI-TOF) m/z calcd for $C_{31}H_{15}BBrF_8N_4S^+$ $(M+H)^+$ 717.0166, found 717.0155.



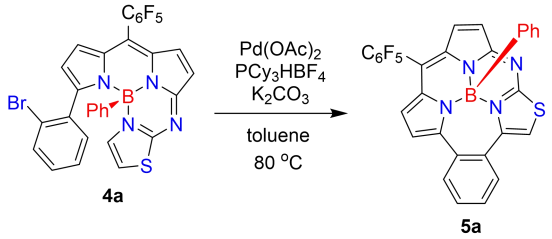

Compound **4c** was obtained as a black solid in 81% yield (87 mg) from **3a** (96 mg, 0.2 mmol) and (3-bromonaphthalen-2-yl)boronic acid (100 mg, 0.4 mmol) using the

same procedure described above for the synthesis of **4a** and purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 7:1, v/v). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H, *α*-Ar-H), 7.75 (d, *J* = 8.2 Hz, 1H, thiazole-H), 7.51 (t, *J* = 7.8 Hz, 1H, *α*-Ar-H), 7.42 (t, *J* = 7.5 Hz, 1H, B-Ar-H), 7.25-7.09 (m, 3H, B-Ar-2H and thiazole-H), 6.83 (brs, 2H, B-Ar-H), 6.58 (d, *J* = 7.0 Hz, 3H, *α*-Ar-3H), 6.53 (s, 1H, *α*-Ar-H), 6.50-6.41 (m, 2H, pyrrole-H), 6.30 (d, *J* = 3.9 Hz, 1H, pyrrole-H), 5.67 (d, *J* = 4.1 Hz, 1H, pyrrole-H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 172.5, 160.2, 145.3 (d, *J* = 245.4 Hz*), 144.8, 141.5 (d, *J* = 218.4 Hz*), 137.7 (d, *J* = 243.3 Hz*), 135.5, 133.8, 133.7, 132.8, 132.3, 131.4, 131.1, 130.9, 130.8, 130.1, 128.6, 128.1, 127.9, 127.6, 127.0, 126.5, 122.9, 121.7, 121.6, 118.3, 117.8, 110.0, 109.3 (t, *J* = 17.7 Hz*), *carbon attached to boron not observed*. (*These signals showed further long-range coupling with the fluorine atoms and would be less accurate). $^{11}$B NMR (128 MHz, CDCl3) δ 2.4 (brs). HRMS (MALDI-TOF) m/z calcd for $C_{34}H_{18}BBrF_5N_4S^+$ $(M+H)^+$ 699.0449, found 699.0425.

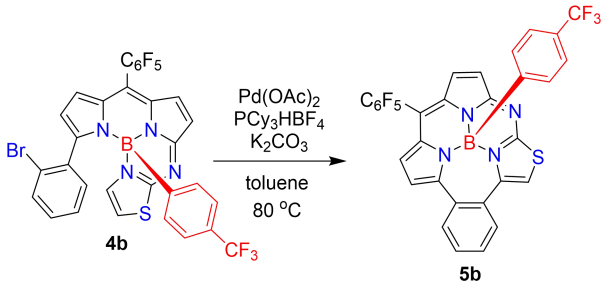



Compound **4d** was obtained as a black solid in 78% yield (87 mg) from **1c** (114 mg, 0.2 mmol) and 2-bromophenylboronic acid (40 mg, 0.4 mmol) using the same procedure described above for the synthesis of **4a** and purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 7:1, v/v). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.56-7.62 (m, 2H, thiazole-H and *meso*-Ph-H), 7.17-7.02 (m, 4H, *meso*-Ph-H), 7.23-7.18 (m, 1H, B-Ar-H), 7.12 (d, *J* = 3.6 Hz, 4H, B-Ar-H), 6.91 (d, *J* = 4.9 Hz, 2H, *α*-Ar-H), 6.76 (d, *J* = 3.4 Hz, 1H, thiazole-H), 6.54 (d, *J* = 4.5 Hz, 2H, *α*-Ar-H), 6.37 (d, *J* = 4.5 Hz, 2H, pyrrole-H), 6.20 (d, *J* = 4.4 Hz, 1H, pyrrole-H), 5.34 (d, *J* = 4.5 Hz, 1H, pyrrole-H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 172.8, 160.9, 145.0, 137.8, 136.8, 134.8, 133.6, 133.3, 132.8, 132.5, 132.3, 130.3(9), 130.3(6), 130.0, 129.1, 128.2, 127.7, 127.3, 126.8, 126.7, 119.6, 119.2, 117.5, 116.4, 107.8, *carbon attached to boron not observed*. $^{11}$B NMR (128 MHz, $CDCl_3$) δ 2.0

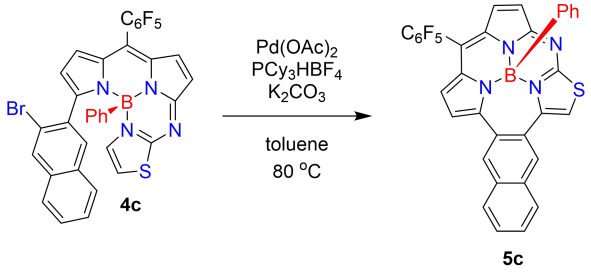
(brs). HRMS (MALDI-TOF) m/z calcd for $C_{30}H_{21}BBrN_4S^+$ $(M+H)^+$ 559.0763, found 559.0751.




Synthesis of **5a**: To a solution of the limiting reactant **4a** (65 mg, 0.10 mmol, 1.0 equiv) in toluene (5 mL) were added $Pd(OAc)_2$ (7 mg, 0.03 mmol, 30 mol%), $PCy_3{\cdot}HBF_4$ (22 mg, 0.06 mmol, 60 mol%), and $K_2CO_3$ (41 mg, 0.30 mmol, 3 equiv). The reaction mixture was stirred at 80 °C under an argon atmosphere for 48 hours and monitored by TLC. After completion, the solvent was evaporated under vacuum. The crude residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 8:1, v/v) to afford product **5a** as a black solid (7 mg, 0.006 mmol) in 13% yield. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.0 Hz, 2H, B-Ar-H), 7.33 (t, *J* = 7.2 Hz, 2H, B-Ar-H), 7.28 (d, *J* = 7.3 Hz, 1H, B-Ar-H), 7.18 (d, *J* = 7.8 Hz, 1H, $C_2$-*meso*-Ph-H), 7.08 (t, *J* = 7.2 Hz, 1H, $C_2$-*meso*-Ph-H), 7.04-6.94 (m, 2H, $C_2$-*meso*-Ph-H), 6.45 (s, 1H, thiazole-H), 6.39 (dd, *J* = 8.2, 4.5 Hz, 2H, pyrrole-H), 6.08 (d, *J* = 3.4 Hz, 1H, pyrrole-H), 6.04 (d, *J* = 4.8 Hz, 1H, pyrrole-H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ174.0, 164.0, 162.3, 147.5 (d, *J* = 214.12 Hz*), 147.4, 145.0, 144.8 (d, *J* = 214.0 Hz*), 137.7 (d, *J* = 254.5 Hz*), 136.3, 135.2, 132.7, 132.0, 131.5, 131.3, 130.9, 130.4, 129.6, 129.1, 128.1, 127.7, 121.7, 117.6, 113.8, 109.3, 108.3 (t, *J* = 22.1 Hz*), *carbon attached to boron not observed*. (*These signals showed further long-range coupling with the fluorine atoms and would be less accurate). $^{11}$B NMR (128 MHz, $CDCl_3$) δ 3.4 (brs). HRMS (ESI) m/z calcd for $C_{30}H_{15}BF_5N_4S^+(M+H^+)$: 569.1031, found 569.1046. UV/Vis [($CH_2Cl_2$): $\lambda_{max}$(nm) ($\varepsilon/10^5$ $M^{-1}cm^{-1}$)]: 324 (0.34), 380 (0.18), 673 (0.07).

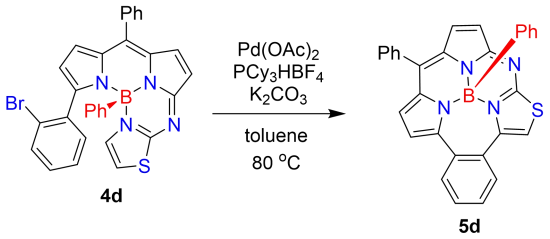



Compound **5b** was obtained as a black solid in 11% yield (3 mg) from **4b** (36 mg, 0.05 mmol) using the same procedure described above for the synthesis of **5a** and purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 8:1, v/v). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.7 Hz, 2H, B-Ar-H), 7.57 (d, *J* = 7.9 Hz, 2H, B-Ar-H), 7.18 (d, *J* = 7.8 Hz, 1H, $C_2$-*meso*-Ph-H), 7.11 (t, *J* = 7.5 Hz, 1H, $C_2$-*meso*-Ph-H), 7.04 (t, *J* = 7.2 Hz, 1H, $C_2$-*meso*-Ph-H), 6.97 (d, *J* = 7.8 Hz, 1H, $C_2$-*meso*-Ph-H), 6.46 (s, 1H, thiazole-H), 6.42 (d, *J* = 3.7 Hz, 1H, pyrrole-H), 6.39 (d, *J* = 4.0 Hz, 1H, pyrrole-H), 6.09 (d, *J* = 3.8 Hz, 1H, pyrrole-H), 6.05 (d, *J* = 5.0 Hz, 1H, pyrrole-H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 173.9, 162.0, 147.2, 145.2 (d, *J* = 266.6 Hz*), 145.1, 141.7 (d, *J* = 273.4 Hz*), 137.9 (d, *J* = 267.5 Hz*), 136.3, 135.0, 134.4, 132.5, 132.2, 131.6, 131.4, 131.1, 130.7, 130.0, 129.4 (q, *J* = 32.3 Hz*), 124.9 (q, *J* = 4.0 Hz*), 124.5 (q, *J* = 272.7 Hz*), 123.6, 121.6, 118.1, 114.2, 109.7, 108.0 (t, *J* = 19.2 Hz*), *carbon attached to boron not observed*. (*These signals showed further long-range coupling with the fluorine atoms and would be less accurate). $^{11}$B NMR (128 MHz, $CDCl_3$) δ 2.6 (brs). HRMS (MALDI-TOF) m/z calcd for $C_{31}H_{13}BF_8N_4S$: 636.0826, found 636.0820. UV/Vis [($CH_2Cl_2$): $\lambda_{max}$(nm) (ε/$10^5$ $M^{-1}cm^{-1}$)]: 325 (0.34), 380 (0.13), 675 (0.05).




Compound **5c** was obtained as a black solid in 16% yield (5 mg) from **4c** (35 mg, 0.05 mmol) using the same procedure described above for the synthesis of **5a** and purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 7:1, v/v).$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H, $C_2$-*meso*-Nph-H),

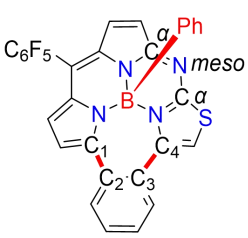
7.64-7.53 (m, 3H, $C_2$-*meso*-Nph-H), 7.41 (d, *J* = 7.0 Hz, 2H, B-Ar-H), 7.39-7.28 (m, 2H, B-Ar-H), 7.25-7.08 (m, 3H, B-Ar-1H and $C_2$-*meso*-Nph-2H), 6.78 (brs, 1H, pyrrole-H), 6.69 (brs, 1H, pyrrole-H), 6.52 (s, 1H, thiazole-H), 6.24 (brs, 1H, pyrrole-H), 6.17 (d, *J* = 4.4 Hz, 1H, pyrrole-H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 174.3, 160.4, 147.1 (d, *J* = 255.5 Hz*), 146.9, 144.0 (d, *J* = 236.3 Hz*), 137.8 (d, *J* = 239.4 Hz*), 136.2, 134.5, 134.0, 133.6, 131.7, 131.1, 130.7, 130.5, 129.5, 129.3, 128.0(3), 127.9(6), 127.9, 127.6, 127.2, 127.1(2), 127.0(7), 122.3, 121.1, 117.8, 116.2, 113.9, 109.8, *carbon attached to boron not observed*. (*These signals showed further long-range coupling with the fluorine atoms and would be less accurate). $^{11}$B NMR (128 MHz, $CDCl_3$) δ 2.6 (brs). HRMS (MALDI-TOF) m/z calcd for $C_{34}H_{17}BF_5N_4S^+$ $(M+H)^+$ 619.1187, found 619.1171. UV/Vis [($CH_2Cl_2$): $\lambda_{max}$(nm) (ε/$10^5$ $M^{-1}cm^{-1}$)]: 309 (0.26), 363 (0.30), 656 (0.09).



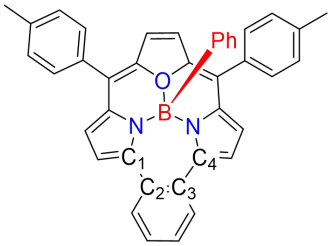

Compound **5d** was obtained as a black solid in 21% yield (5 mg) from **4d** (28 mg, 0.05 mmol) using the same procedure described above for the synthesis of **5a** and purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 7:1, *v*/*v*). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.5 Hz, 2H, B-Ph-H), 7.42 (brs, 5H, B-Ph-3H and *meso*-Ph-2H), 7.30 (dd, *J* = 10.5, 3.9 Hz, 2H, *meso*-Ph-H), 7.24 (d, *J* = 7.6 Hz, 2H, *meso*-Ph-H and $C_2$-*meso*-Nph-H), 7.08 (t, *J* = 7.0 Hz, 1H, $C_2$-*meso*-Nph-H), 6.97 (brs, 2H, $C_2$-*meso*-Ph-H), 6.58-6.49 (m, 1H, pyrrole-H), 6.41 (d, *J* = 1.5 Hz, 1H, pyrrole-H), 6.38 (s, 1H, thiazole-H), 6.29 (d, *J* = 1.3 Hz, 1H, pyrrole-H), 6.06-5.93 (m, 1H, pyrrole-H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 173.9, 161.8, 146.9, 144.8, 137.5, 134.0, 133.49, 133.46, 132.9, 131.6, 131.1, 130.8, 130.6, 130.2, 129.9, 129.4, 129.3, 129.2, 128.4, 127.9, 127.4, 119.7, 119.4, 113.5, 107.7, *carbon attached to boron not observed*. $^{11}$B NMR (128 MHz, $CDCl_3$) δ 2.8 (s). HRMS (MALDI-TOF) m/z calcd for $C_{30}H_{19}BN_4S$: 478.1424, found 478.1419. UV/Vis [($CH_2Cl_2$): $\lambda_{max}$(nm) (ε/$10^5$ $M^{-1}cm^{-1}$)]: 327 (0.35), 382 (0.19), 655 (0.08).

## 3. Crystal data

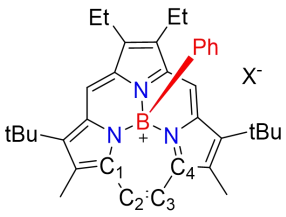
**Table S1.** Selected geometrical parameters of **5a** obtained from crystallography.




**5a**




**TRP1**




**TRP2**

| dyes | $N_{meso}$-$C_\alpha$ (Å) | B-C (Å) | B-N (Å) | α[a] (deg) | Bowl-depth(Å)[b] | $C_1$-$C_2$, $C_3$-$C_4$ |
|---|---|---|---|---|---|---|
| **5a** | 1.331(5), 1.337(5) | 1.603(6) | 1.533(5), 1.557(6), 1.556(6) | 75.54(18) | 1.103(5) | 1.458(6), 1.506(6) |
| **TRP1**[4] | - | 1.581(9) | 1.531(7), 1.510(8) | 48.8(2) | 0.991(3) | 1.475(4), 1.477(3) |
| **TRP2**[5] | - | 1.617(3) | 1.523(3), 1.529(3), 1.529(3) | - | 0.934(3) | 1.405(3), 1.398(5) |

[a]Angle α is defined by the dihedral angle between the plane of $C_\alpha$-$C_{meso}$-$C'_\alpha$ and the mean plane of *meso*-aryl group. [b]Bowl-depth is defined by the distance from the axial boron atom to the mean plane of peripheral *β*-carbons.

**Table S2.** Crystal data and structure refinement for **5a**.

| dyes | **5a** |
|---|---|
| CCDC number | 2531362 |
| Chemical formula | $C_{30}H_{14}BF_5N_4S$ |
| $M_r$ | 568.32 |
| Crystal system, space group | monoclinic, $P_{21}/c$ |
| Temperature (K) | 293 |
| $a$, $b$, $c$ (Å) | 19.8353(3)<br>16.2211(2)<br>16.1661(3) |
| $\alpha$, $\beta$, $\gamma$ (°) | 90<br>109.5130(10)<br>90 |
| $V$ (Å$^3$) | 4902.71(14) |
| $Z$ | 8 |
| $\rho_{calc}$(g·cm$^{-3}$) | 1.540 |
| $\mu$ (mm$^{-1}$) | 0.186 |
| Crystal size (mm) | 0.19 × 0.17 × 0.13 |
| 2Θ range for date collection/$^o$ | 2.112 to 51 |
| Reflections collected | 63767 |
| Independent reflections | 10026 [$R_{int}$ = 0.0899, $R_{sigma}$ = 0.1537] |
| Date/restraints/parameters | 10026/0/739 |
| Goodness-of-fit on $F^2$ | 0.777 |
| Final R indexes [I> =2σ (I)] | $R_1$ = 0.0580, w$R_2$ = 0.1339 |
| Final R indexes [all date] | $R_1$ = 0.1099, w$R_2$ = 0.1435 |
| Largest diff. Peak/hole/ e Å$^{-3}$ | 0.42/-0.39 |

## 4. Analysis of inherent chirality of compound 5a

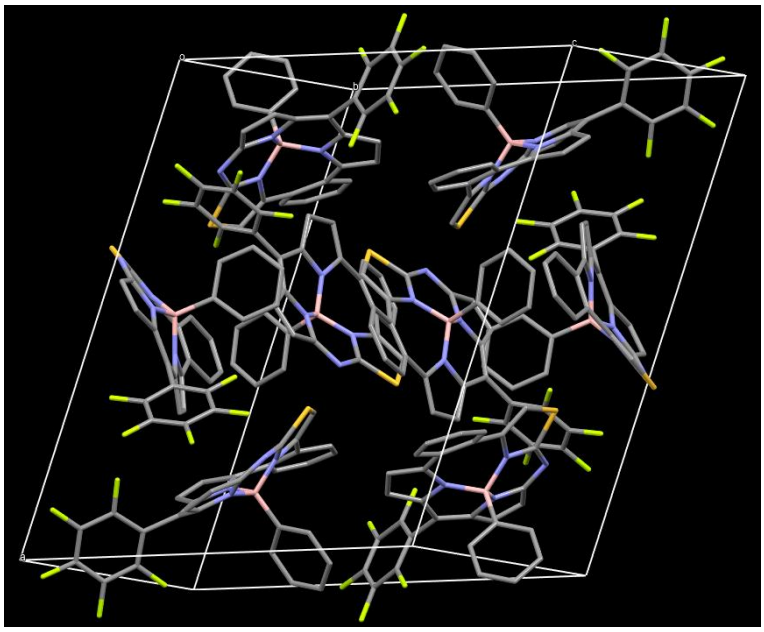


**Figure S1.** View of the unit cell of compound **5a** in X-ray crystal structure. C, gray; N, blue, B, pink; F, light yellow; S, orange. Hydrogen atoms are removed for clarity. The thermal ellipsoids shown at the 50% probability level.

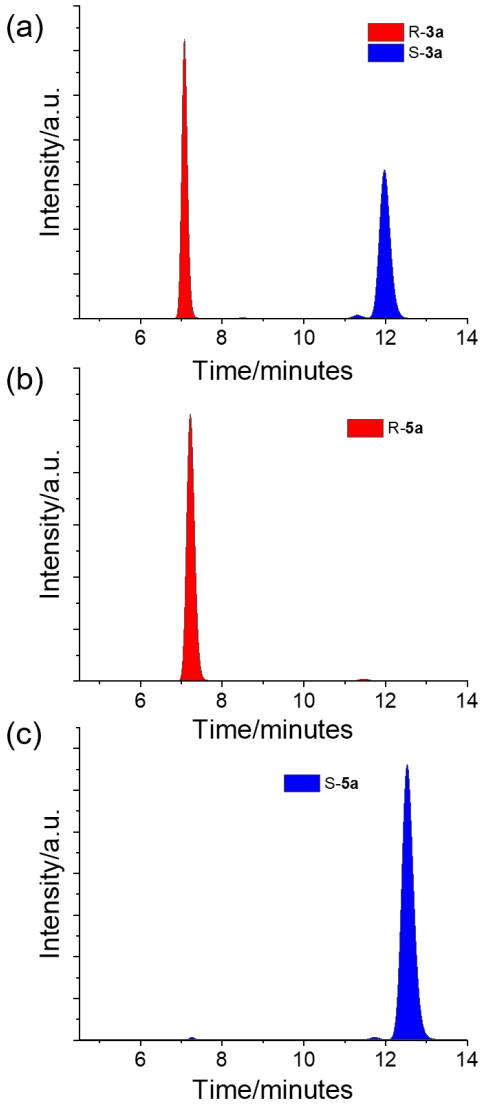



**Figure S2.** Chiral HPLC chromatogram of racemate **5a** (a), the first (b) and second (c) eluted fractions. Resolution of **5a** by chiral HPLC monitored at 500 nm was performed with a CHIRALPAK IE column (4.6 cm I.D.×250 mmL). Injection volume was 20 μL, and a mixture of *n*-hexane/*i*-PrOH = 80/20 (v/v) was used as the eluent with a flow rate of 1.0 mL/min at 25 ºC.

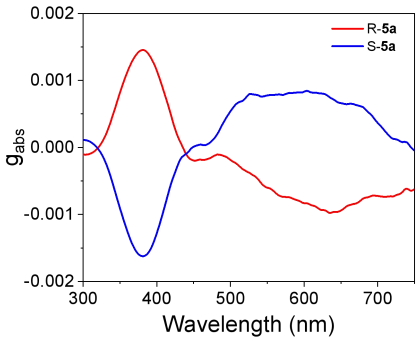



**Figure S3.** The $g_{abs}$ spectra of R/S-**5a** in hexane.

## 5. Electrochemical data

**Table S3.** Electrochemical data and HOMO-LUMO gaps determined from spectroscopy of **5a-d**.

| dyes | $E_{red,3}$ (V) | $E_{red,2}$ (V) | $E_{red,1}$ (V) | $E_{ox,1}$ (V) | $E_{ox,2}$ (V) | $E_{red}^{onset}$ (V) | $E_{ox}^{onset}$ (V) | LUMO (eV) | HOMO (eV) | $E_g^e$ (eV) |
|---|---|---|---|---|---|---|---|---|---|---|
| **5a** | -1.88[b] | -1.73[b] | -1.13 | 0.84[b] | 1.31[b] | -1.01 | 0.71 | -3.79 | -5.51 | 1.72 |
| **5b** | -1.85[b] | -1.571[b] | -1.10 | 0.89[b] | 1.38[b] | -0.90 | 0.76 | -3.90 | -5.56 | 1.66 |
| **5c** | - | -1.70[b] | -1.12 | 0.87[b] | 1.33[b] | -0.99 | 0.73 | -3.81 | -5.53 | 1.72 |
| **5d** | - | -1.89[b] | -1.27 | 0.73[b] | 1.28[b] | -1.05 | 0.62 | -3.75 | -5.42 | 1.67 |

[a]$E_{red}^{onset}$ = the onset reduction potentials; $E_{ox}^{onset}$ = the onset oxidation potentials; $E_{LUMO}$ = -e($E_{red}^{onset}$ + 4.8); $E_{HOMO}$ = -e($E_{ox}^{onset}$ + 4.8); $E_g^e$ = bandgap, obtained from the intercept of the electrochemical data, $E_g^e = E_{LUMO} - E_{HOMO}$; [b]irreversible peaks.

## 6. Theoretical calculation

The ground state geometry was optimized by using density functional theory (DFT) method at B3LYP/6-31G(d,p) level. The same method was adopted for vibrational analysis to verify that the optimized structures correspond to local minima on the energy surface. TD-DFT computations were used the optimized ground state geometries under the B3LYP/6-31G(d,p) theoretical level. All of the calculations were carried out by the methods implemented in Gaussian 09 package.[6]

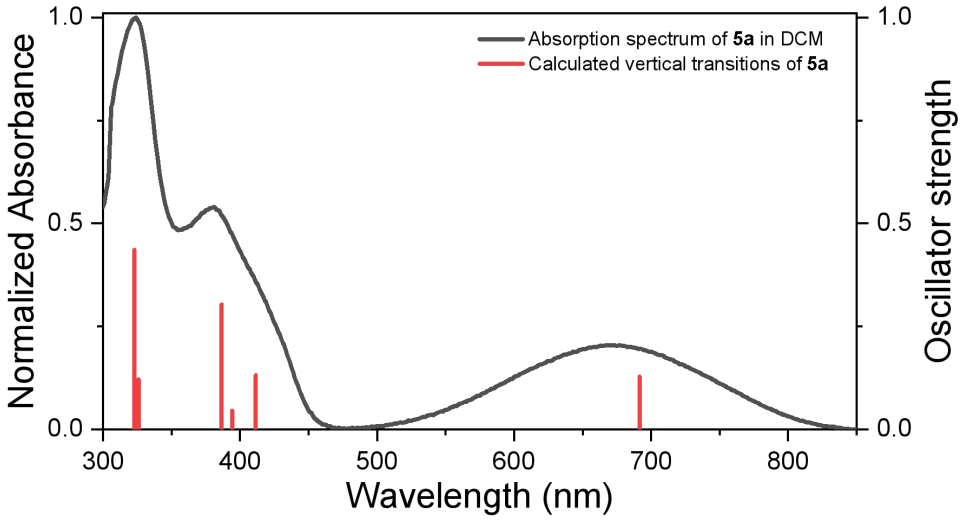



**Figure S4.** Calculated vertical transition of **5a** from TD-DFT calculations (TD//B3LYP/6-31G(d,p)).

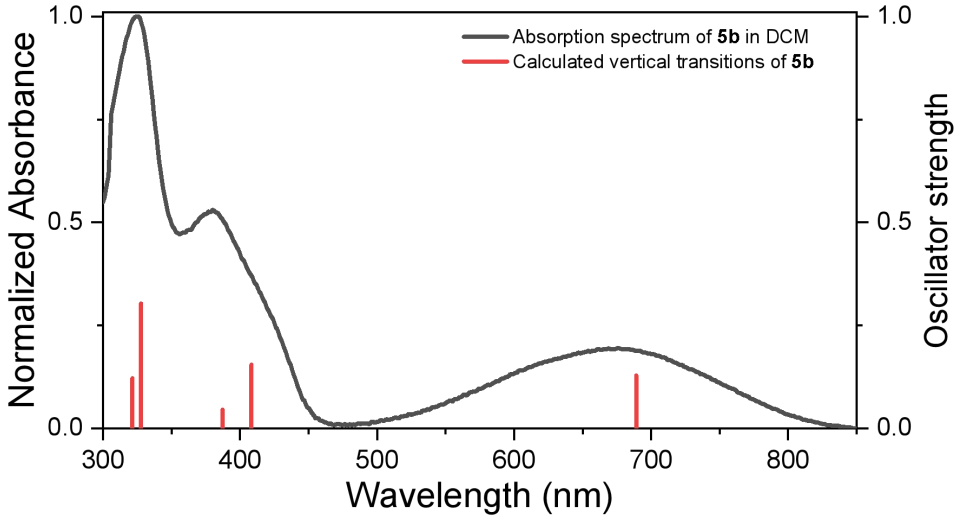



**Figure S5.** Calculated vertical transition of **5b** from TD-DFT calculations (TD//B3LYP/6-31G(d,p)).

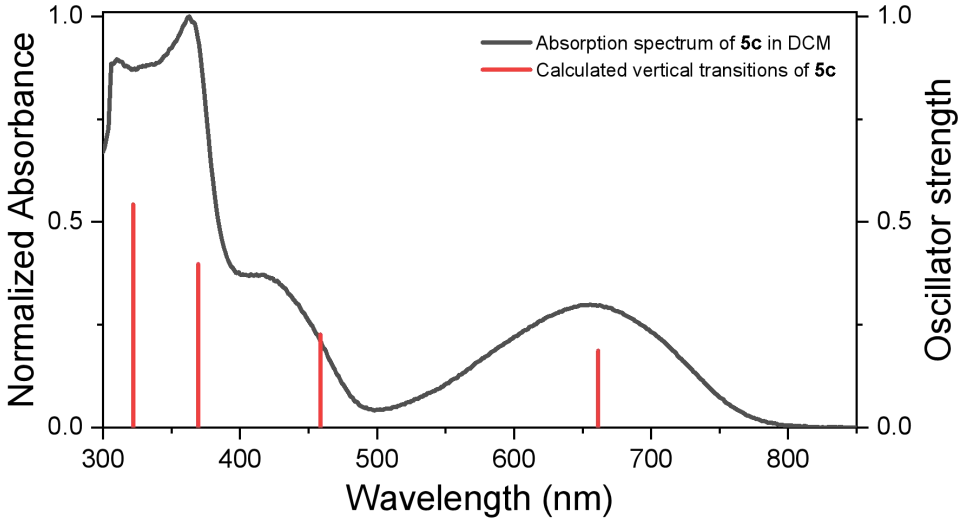



**Figure S6.** Calculated vertical transition of **5c** from TD-DFT calculations (TD//B3LYP/6-31G(d,p)).

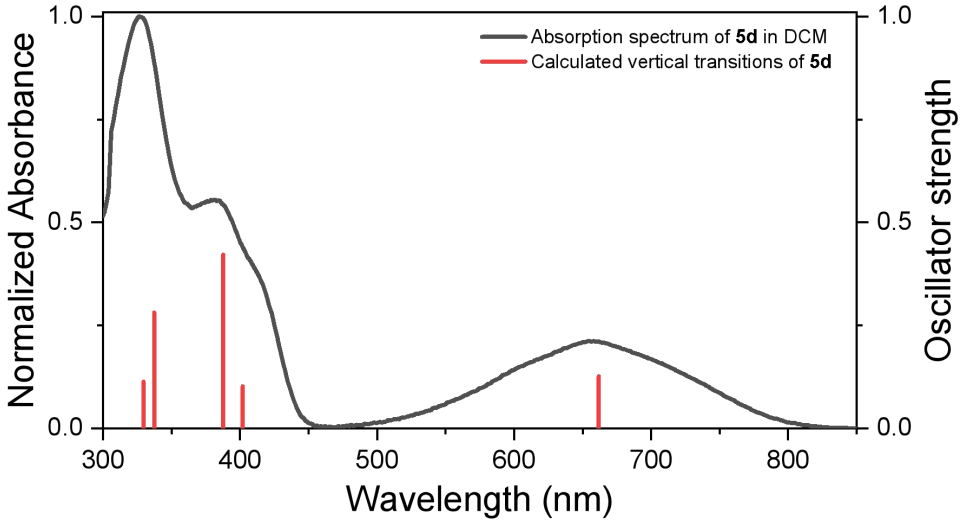



**Figure S7.** Calculated vertical transition of **5d** from TD-DFT calculations (TD//B3LYP/6-31G(d,p)).

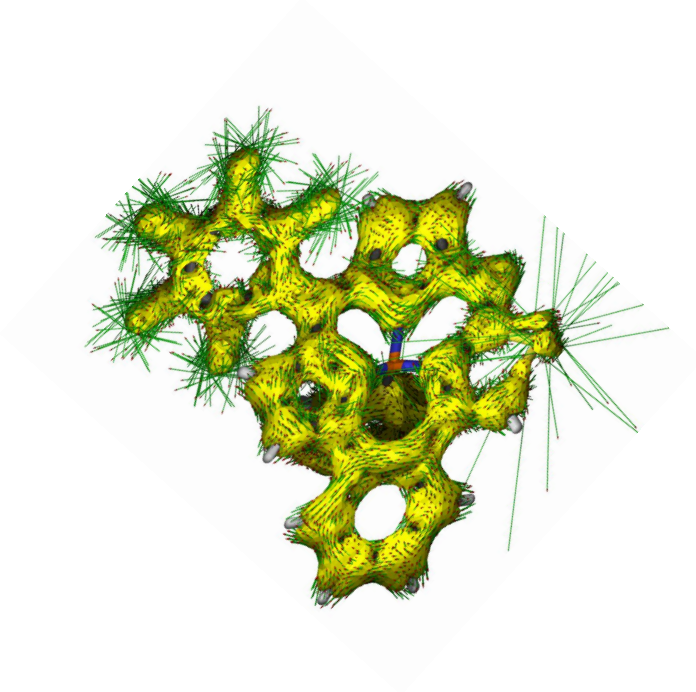


**Figure S8.** ACID plots of **5a**. Direction of the applied magnetic field is perpendicular to the paper and pointing outward. The current density vectors indicate clockwise current.

**Table S4.** Selected electronic excitation energies (eV) and oscillator strengths (*f*), configurations of the low-lying singlet excited states of **5a-d** calculated by TD//B3LYP/6-31G(d, p), based on the optimized ground state geometries.

| | Electronic transition | TD//B3LYP/6-31+G(d, p) | | | |
|---|---|---|---|---|---|
| | | Energy/ eV [a] | *f* [b] | Composition [c] | CI [d] |
| **5a** | S0→S1 | 1.7931 eV<br>691.46 nm | 0.1285 | HOMO→LUMO | 0.7003 |
| | S0→S2 | 3.1031 eV<br>411.49 nm | 0.1317 | HOMO-2→LUMO | 0.2559 |
| | | | | HOMO-1→LUMO | 0.5910 |
| | | | | HOMO→LUMO+1 | 0.2495 |
| | S0→S3 | 3.1453 eV<br>394.19 nm | 0.0458 | HOMO-2→LUMO | 0.6496 |
| | | | | HOMO-1→LUMO | 0.2025 |
| | | | | HOMO→LUMO+1 | 0.1557 |
| | S0→S4 | 3.2077 eV<br>386.52 nm | 0.3035 | HOMO-1→LUMO | 0.2666 |
| | | | | HOMO→LUMO+1 | 0.6277 |
| | S0→S11 | 3.8042 eV<br>325.92 nm | 0.1219 | HOMO→LUMO+5 | 0.4621 |
| | | | | HOMO→LUMO+4 | 0.3332 |

| | | | | | |
|---|---|---|---|---|---|
| | | | | HOMO-4→LUMO | 0.2058 |
| | S0→S12 | 3.8395 eV<br>322.92 nm | 0.4361 | HOMO→LUMO+5 | 0.4693 |
| | | | | HOMO-4→LUMO | 0.2624 |
| | | | | HOMO-5→LUMO | 0.3815 |
| **5b** | S0→S1 | 1.7994 eV<br>689.05 nm | 0.1287 | HOMO→LUMO | 0.7003 |
| | S0→S2 | 3.0366 eV<br>408.30 nm | 0.1550 | HOMO-1→LUMO | 0.6097 |
| | | | | HOMO→LUMO+1 | 0.3122 |
| | S0→S3 | 3.2018 eV<br>387.23 nm | 0.3020 | HOMO-3→LUMO | 0.1136 |
| | | | | HOMO→LUMO+1 | 0.6194 |
| | S0→S11 | 3.7828 eV<br>327.75 nm | 0.1800 | HOMO-1→LUMO | 0.2976 |
| | | | | HOMO→LUMO+5 | 0.4008 |
| | S0→S13 | 3.8578 eV<br>321.39 nm | 0.2323 | HOMO-5→LUMO | 0.3879 |
| | | | | HOMO-7→LUMO | 0.2565 |
| | | | | HOMO-6→LUMO | 0.2590 |
| | | | | HOMO→LUMO+6 | 0.5622 |
| | | | | HOMO→LUMO+5 | 0.1569 |
| | | | | HOMO-7→LUMO | 0.2380 |
| **5c** | S0→S1 | 1.8748 eV<br>661.34 nm | 0.1871 | HOMO→LUMO | 0.7002 |
| | S0→S2 | 2.7036 eV<br>458.58 nm | 0.2267 | HOMO-1→LUMO | 0.6880 |
| | | | | HOMO→LUMO+2 | 0.1020 |
| | S0→S6 | 3.3562 eV<br>369.42 nm | 0.3977 | HOMO-6→LUMO | 0.1402 |
| | | | | HOMO→LUMO+2 | 0.6624 |
| | S0→S14 | 3.8498 eV<br>322.05 nm | 0.5430 | HOMO-1→LUMO+1 | 0.5423 |
| | | | | HOMO-4→LUMO | 0.1055 |
| | | | | HOMO-7→LUMO | 0.3227 |
| **5d** | S0→S1 | 1.8734 eV<br>661.81 nm | 0.1270 | HOMO→LUMO | 0.7000 |
| | S0→S14 | 3.0845 eV<br>401.96 nm | 0.1025 | HOMO-1→LUMO | 0.4951 |
| | | | | HOMO→LUMO+1 | 0.4787 |
| | | | | HOMO-2→LUMO | 0.1133 |
| | S0→S3 | 3.1973 eV<br>387.78 nm | 0.4222 | HOMO-1→LUMO | 0.4540 |

| | | | | | |
|---|---|---|---|---|---|
| | | | | HOMO→LUMO+1 | 0.5054 |
| | S0→S8 | 3.6760 eV<br>337.28 nm | 0.2815 | HOMO→LUMO+2 | 0.5911 |
| | | | | HOMO-5→LUMO | 0.3217 |
| | S0→S9 | 3.7635 eV<br>329.44 nm | 0.1138 | HOMO-5→LUMO | 0.3140 |
| | | | | HOMO-4→LUMO | 0.6084 |

[a] Only the selected low-lying excited states are presented. [b] Oscillator strength. [c] Only the main configurations are presented. [d] The CI coefficients are in absolute values.

DFT optimized coordinates for **5a** optimized S0 state Geometry by B3LYP/6-31G(d).

| | | | |
|---|---|---|---|
| S | 4.1499 | 3.12146 | -0.83663 |
| F | -2.78424 | -1.99069 | 0.95971 |
| F | -5.42432 | -2.52783 | 0.90413 |
| F | -3.58533 | 2.08599 | -1.33869 |
| F | -7.15967 | -0.76409 | -0.24569 |
| F | -6.22112 | 1.54326 | -1.35873 |
| N | 0.27128 | 1.61105 | 0.44998 |
| N | 2.51549 | 1.21271 | -0.30796 |
| N | 0.62867 | -0.47556 | -0.71448 |
| N | 1.82219 | 3.38624 | 0.49407 |
| C | 0.5913 | 2.89781 | 0.70633 |
| C | -1.10872 | 1.45535 | 0.4569 |
| C | -1.63291 | 0.33471 | -0.15514 |
| C | 1.6528 | -0.28029 | 1.67592 |
| C | -3.08933 | 0.06896 | -0.1839 |
| C | -0.75517 | -0.57993 | -0.81936 |
| C | -3.60483 | -1.10798 | 0.37185 |
| C | -1.66464 | 2.71166 | 0.90071 |
| H | -2.71869 | 2.92181 | 1.00659 |
| C | 1.20687 | -1.47955 | -1.43129 |
| C | -0.62961 | 3.59895 | 1.04853 |
| H | -0.68325 | 4.64835 | 1.29876 |
| C | 2.66188 | 2.54712 | -0.11108 |
| C | 0.81086 | -1.27981 | 2.19249 |
| H | -0.07887 | -1.57049 | 1.64043 |
| C | 3.56911 | 0.60518 | -0.98874 |
| C | -4.96438 | -1.39753 | 0.35591 |
| C | -4.00639 | 0.94816 | -0.76704 |
| C | 4.52031 | 1.50156 | -1.37366 |
| H | 5.42179 | 1.30278 | -1.93153 |
| C | -5.85151 | -0.49776 | -0.22745 |
| C | 0.1808 | -2.21895 | -2.05757 |

| | | | |
|---|---|---|---|
| H | 0.32574 | -3.04635 | -2.73635 |
| C | -1.04002 | -1.66661 | -1.66608 |
| H | -2.0268 | -1.97665 | -1.97818 |
| C | 2.79063 | 0.05344 | 2.42521 |
| H | 3.4708 | 0.8162 | 2.05557 |
| C | 2.64105 | -1.78448 | -1.40211 |
| C | 3.69646 | -0.86314 | -1.15006 |
| C | 1.08845 | -1.91317 | 3.40317 |
| H | 0.41942 | -2.68319 | 3.77785 |
| C | 3.0817 | -0.57734 | 3.63605 |
| H | 3.97401 | -0.30092 | 4.19121 |
| C | 2.2288 | -1.56434 | 4.12969 |
| H | 2.45122 | -2.05997 | 5.07046 |
| C | -5.37145 | 0.68089 | -0.78878 |
| C | 5.01331 | -1.35482 | -1.08747 |
| H | 5.8091 | -0.664 | -0.83436 |
| B | 1.28563 | 0.47154 | 0.2998 |
| C | 2.98203 | -3.13457 | -1.61935 |
| H | 2.18145 | -3.84595 | -1.78301 |
| C | 5.3221 | -2.68982 | -1.31454 |
| H | 6.35209 | -3.02551 | -1.25308 |
| C | 4.29366 | -3.58699 | -1.59462 |
| H | 4.50532 | -4.63816 | -1.76228 |

SCF done: -2293.06080617 a.u.

No imaginary Frequency.

DFT optimized coordinates for **5b** optimized S0 state Geometry by B3LYP/6-31G(d).

| | | | |
|---|---|---|---|
| S | 3.1745 | -3.8885 | -1.80828 |
| F | -2.72459 | 1.95838 | 1.10425 |
| F | -5.26117 | 2.79067 | 1.48241 |
| F | -4.35072 | -2.00513 | -0.94086 |
| F | -7.34955 | 1.25213 | 0.63896 |
| F | -6.87553 | -1.14284 | -0.57902 |
| N | -0.19242 | -1.14816 | -1.4444 |
| N | 1.87931 | -2.02689 | -0.60462 |
| N | 0.12574 | -0.98004 | 0.94534 |
| N | 1.15214 | -2.4593 | -2.87003 |
| C | 0.04439 | -1.74102 | -2.63536 |
| C | -1.52157 | -0.75083 | -1.36865 |
| C | -2.04655 | -0.49477 | -0.11808 |
| C | 1.58293 | 0.58524 | -0.54288 |
| C | -3.44737 | -0.05127 | 0.0649 |
| C | -1.23471 | -0.70071 | 1.04225 |
| C | -3.72706 | 1.16921 | 0.69049 |

| | | | |
|---|---|---|---|
| C | -2.09649 | -0.98176 | -2.67234 |
| H | -3.12279 | -0.78143 | -2.94247 |
| C | 0.64517 | -1.10834 | 2.19867 |
| C | -1.14498 | -1.5925 | -3.44853 |
| H | -1.2499 | -1.97202 | -4.45432 |
| C | 1.92999 | -2.65585 | -1.80648 |
| C | 0.94669 | 1.74622 | -0.07051 |
| H | -0.01307 | 1.66856 | 0.43157 |
| C | 2.82694 | -2.46141 | 0.32144 |
| C | -5.02874 | 1.61481 | 0.88886 |
| C | -4.54104 | -0.81503 | -0.3528 |
| C | 3.58549 | -3.48555 | -0.15979 |
| H | 4.37063 | -4.01735 | 0.35389 |
| C | -6.09555 | 0.83269 | 0.45595 |
| C | -0.40782 | -0.96312 | 3.12655 |
| H | -0.32086 | -1.06588 | 4.19814 |
| C | -1.57443 | -0.69714 | 2.40706 |
| H | -2.5686 | -0.5541 | 2.80498 |
| C | 2.826 | 0.74202 | -1.17216 |
| H | 3.35697 | -0.13039 | -1.54147 |
| C | 2.07973 | -1.22635 | 2.47999 |
| C | 3.06624 | -1.78536 | 1.61933 |
| C | 1.51846 | 3.00526 | -0.2229 |
| H | 1.0132 | 3.88776 | 0.15531 |
| C | 3.41602 | 1.99468 | -1.33013 |
| H | 4.38297 | 2.09088 | -1.81188 |
| C | 2.76011 | 3.12973 | -0.8527 |
| C | -5.85146 | -0.38571 | -0.16936 |
| C | 4.41155 | -1.74748 | 2.02999 |
| H | 5.16899 | -2.11871 | 1.34952 |
| B | 0.87465 | -0.85793 | -0.3871 |
| C | 2.50396 | -0.70189 | 3.71732 |
| H | 1.76268 | -0.2476 | 4.36375 |
| C | 4.80086 | -1.23307 | 3.26011 |
| H | 5.85065 | -1.22125 | 3.53402 |
| C | 3.83289 | -0.7137 | 4.11695 |
| H | 4.11151 | -0.29201 | 5.07729 |
| C | 3.3543 | 4.48942 | -1.06364 |
| F | 2.89262 | 5.07687 | -2.19744 |
| F | 3.06117 | 5.3377 | -0.04941 |
| F | 4.70281 | 4.45017 | -1.17398 |

SCF done: -2293.06080617 a.u.

No imaginary Frequency.

DFT optimized coordinates for **5c** optimized S0 state Geometry by B3LYP/6-31G(d).

| | | | |
|---|---|---|---|
| S | 2.80678 | 4.0921 | -1.1579 |
| F | -2.95555 | -2.12442 | 1.24873 |
| F | -5.41538 | -3.22716 | 1.17512 |
| F | -4.42139 | 1.29576 | -1.69852 |
| F | -7.39148 | -2.07356 | -0.31039 |
| F | -6.87782 | 0.1929 | -1.73959 |
| N | -0.69853 | 1.94708 | 0.28723 |
| N | 1.61479 | 1.96248 | -0.35821 |
| N | 0.17032 | -0.14768 | -0.55314 |
| N | 0.41735 | 4.01553 | 0.08495 |
| C | -0.68443 | 3.29684 | 0.35016 |
| C | -2.00917 | 1.48858 | 0.28213 |
| C | -2.24081 | 0.20709 | -0.17727 |
| C | 1.00095 | 0.59617 | 1.80198 |
| C | -3.60286 | -0.37233 | -0.21786 |
| C | -1.15043 | -0.57073 | -0.67567 |
| C | -3.89886 | -1.53849 | 0.49701 |
| C | -2.85132 | 2.63621 | 0.51743 |
| H | -3.93017 | 2.61508 | 0.56658 |
| C | 0.99118 | -1.08929 | -1.09732 |
| C | -2.0456 | 3.74605 | 0.55455 |
| H | -2.34199 | 4.78109 | 0.64167 |
| C | 1.45059 | 3.3098 | -0.36944 |
| C | 0.36929 | -0.48495 | 2.44015 |
| H | -0.41403 | -1.03121 | 1.92144 |
| C | 2.80793 | 1.51681 | -0.92296 |
| C | -5.16268 | -2.11708 | 0.47243 |
| C | -4.63732 | 0.19022 | -0.9709 |
| C | 3.55138 | 2.538 | -1.43431 |
| H | 4.49827 | 2.46546 | -1.94575 |
| C | -6.17286 | -1.52846 | -0.28262 |
| C | 0.18538 | -2.11729 | -1.63399 |
| H | 0.54507 | -2.97725 | -2.17951 |
| C | -1.14516 | -1.80145 | -1.35832 |
| H | -2.02286 | -2.3623 | -1.64557 |
| C | 2.00872 | 1.26383 | 2.5132 |
| H | 2.52654 | 2.1002 | 2.05125 |
| C | 2.45219 | -1.06877 | -0.97974 |
| C | 3.27386 | 0.11277 | -0.84046 |
| C | 0.72439 | -0.87918 | 3.72939 |
| H | 0.21945 | -1.71983 | 4.19764 |
| C | 2.37651 | 0.87495 | 3.80247 |
| H | 3.16588 | 1.40791 | 4.32563 |

| | | | |
|---|---|---|---|
| C | 1.73354 | -0.20016 | 4.41546 |
| C | -5.9104 | -0.36949 | -1.00583 |
| C | 4.63839 | -0.04481 | -0.65545 |
| H | 5.2487 | 0.83618 | -0.48982 |
| B | 0.54752 | 1.05499 | 0.32624 |
| C | 3.08146 | -2.30686 | -0.97131 |
| H | 2.4728 | -3.20119 | -1.04263 |
| C | 5.28028 | -1.30377 | -0.65435 |
| C | 4.47663 | -2.4695 | -0.83212 |
| H | 2.01726 | -0.50881 | 5.41766 |
| C | 5.10076 | -3.74473 | -0.83002 |
| H | 4.48626 | -4.6305 | -0.96281 |
| C | 6.4624 | -3.85336 | -0.66114 |
| H | 6.93347 | -4.83141 | -0.66142 |
| C | 7.2591 | -2.69547 | -0.48202 |
| C | 6.68019 | -1.44634 | -0.47635 |
| H | 7.2858 | -0.55519 | -0.33774 |
| H | 8.33116 | -2.79912 | -0.34672 |

SCF done: -2446.71657997 a.u.

No imaginary Frequency.

DFT optimized coordinates for **5d** optimized S0 state Geometry by B3LYP/6-31G(d).

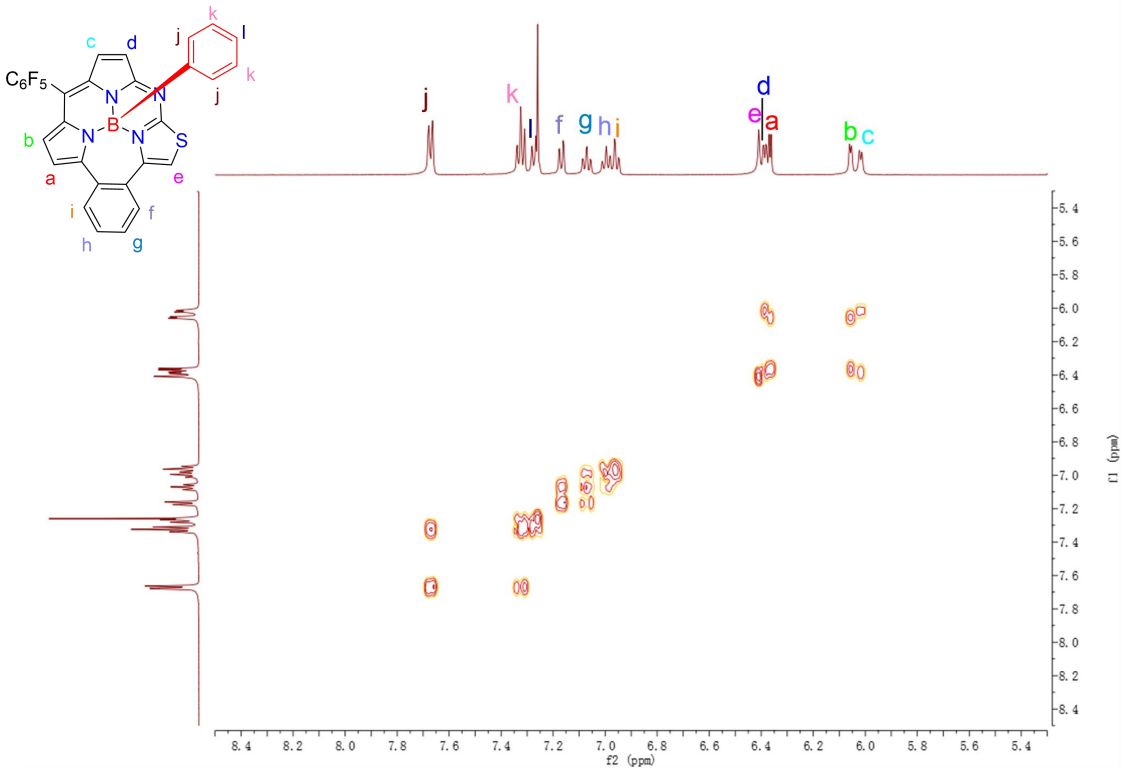
| | | | |
|---|---|---|---|
| S | 3.12557 | 3.04215 | -1.45796 |
| N | -0.66856 | 1.54422 | 0.08136 |
| N | 1.61635 | 1.16813 | -0.55251 |
| N | -0.13138 | -0.71299 | -0.59018 |
| N | 0.75049 | 3.40301 | -0.23706 |
| C | -0.45085 | 2.87648 | 0.06567 |
| C | -2.03462 | 1.2848 | 0.11457 |
| C | -2.47063 | 0.02363 | -0.25561 |
| C | 0.82591 | 0.08173 | 1.70224 |
| C | -3.90843 | -0.32379 | -0.29744 |
| C | -1.50222 | -0.94282 | -0.68659 |
| C | -4.37009 | -1.48435 | 0.34538 |
| C | -2.68731 | 2.55718 | 0.2943 |
| H | -3.75457 | 2.69966 | 0.37758 |
| C | 0.5402 | -1.79046 | -1.08399 |
| C | -1.72237 | 3.53565 | 0.25387 |
| H | -1.85907 | 4.60661 | 0.28968 |
| C | 1.65949 | 2.52296 | -0.64458 |
| C | 0.35385 | -1.09444 | 2.30415 |
| H | -0.26881 | -1.77374 | 1.72848 |
| C | 2.73347 | 0.51447 | -1.06955 |
| C | -5.72356 | -1.81277 | 0.32528 |

| | | | |
|---|---|---|---|
| C | -4.83234 | 0.48872 | -0.97389 |
| C | 3.62867 | 1.37736 | -1.6256 |
| H | 4.55787 | 1.13331 | -2.1156 |
| C | -6.63526 | -0.99429 | -0.34368 |
| C | -0.40946 | -2.7182 | -1.56098 |
| H | -0.18403 | -3.64997 | -2.05874 |
| C | -1.67911 | -2.19379 | -1.30828 |
| H | -2.63084 | -2.63167 | -1.56991 |
| C | 1.63725 | 0.92247 | 2.48202 |
| H | 2.02739 | 1.84129 | 2.05174 |
| C | 1.99226 | -1.9714 | -0.97486 |
| C | 2.97127 | -0.94015 | -0.91345 |
| C | 0.6703 | -1.41939 | 3.62403 |
| H | 0.29257 | -2.33946 | 4.06207 |
| C | 1.96069 | 0.60941 | 3.80188 |
| H | 2.59219 | 1.27879 | 4.37982 |
| C | 1.47689 | -0.56667 | 4.37811 |
| H | 1.72909 | -0.81684 | 5.40478 |
| C | -6.18506 | 0.15474 | -0.99504 |
| C | 4.31829 | -1.30669 | -0.73535 |
| H | 5.05542 | -0.51947 | -0.62783 |
| B | 0.42797 | 0.48066 | 0.19181 |
| C | 2.43523 | -3.30711 | -0.89538 |
| H | 1.69194 | -4.09523 | -0.91087 |
| C | 4.72854 | -2.63191 | -0.67099 |
| H | 5.77837 | -2.86752 | -0.53012 |
| C | 3.77489 | -3.6436 | -0.76276 |
| H | 4.066 | -4.68733 | -0.70054 |
| H | -6.8862 | 0.78854 | -1.52934 |
| H | -7.68952 | -1.25288 | -0.3609 |
| H | -6.0668 | -2.70709 | 0.8363 |
| H | -3.66328 | -2.11353 | 0.87537 |
| H | -4.48038 | 1.36569 | -1.50587 |

SCF done: -1796.90578407 a.u.

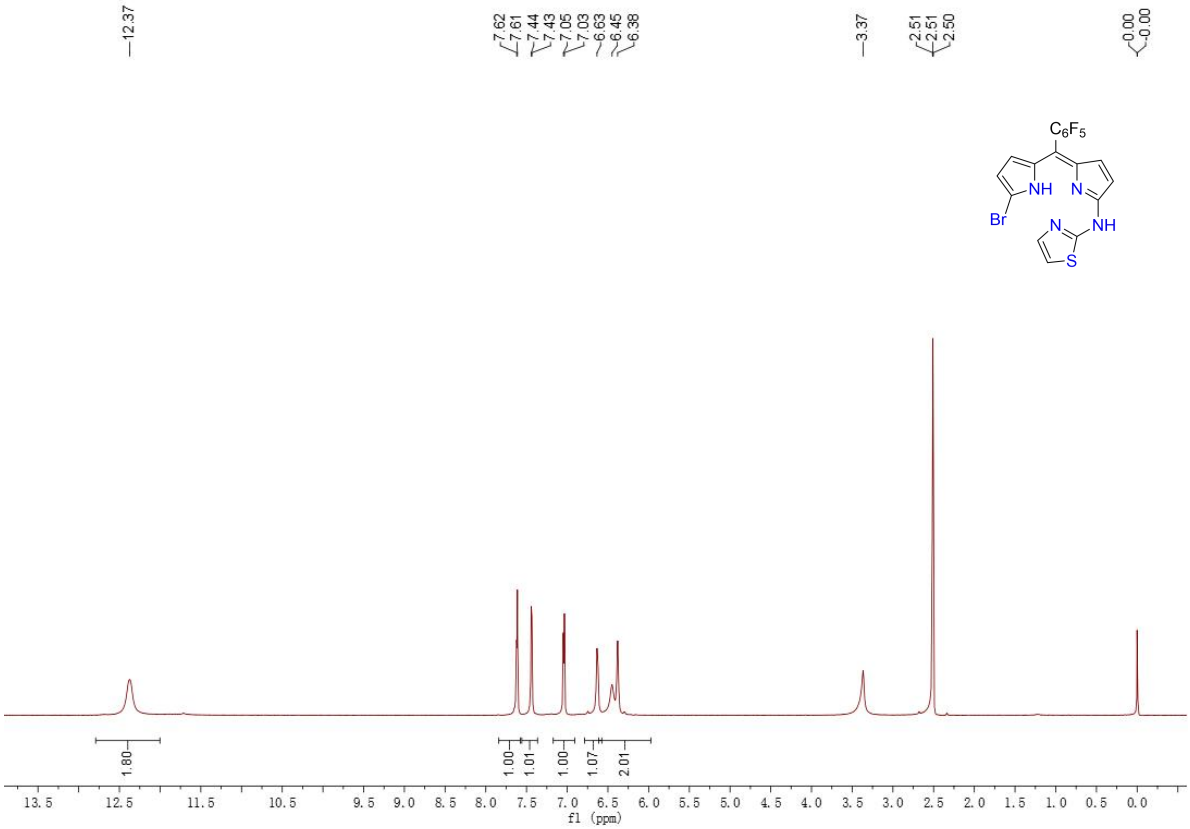
No imaginary Frequency.

## 7. H-H COSY spectra of new compound 5a

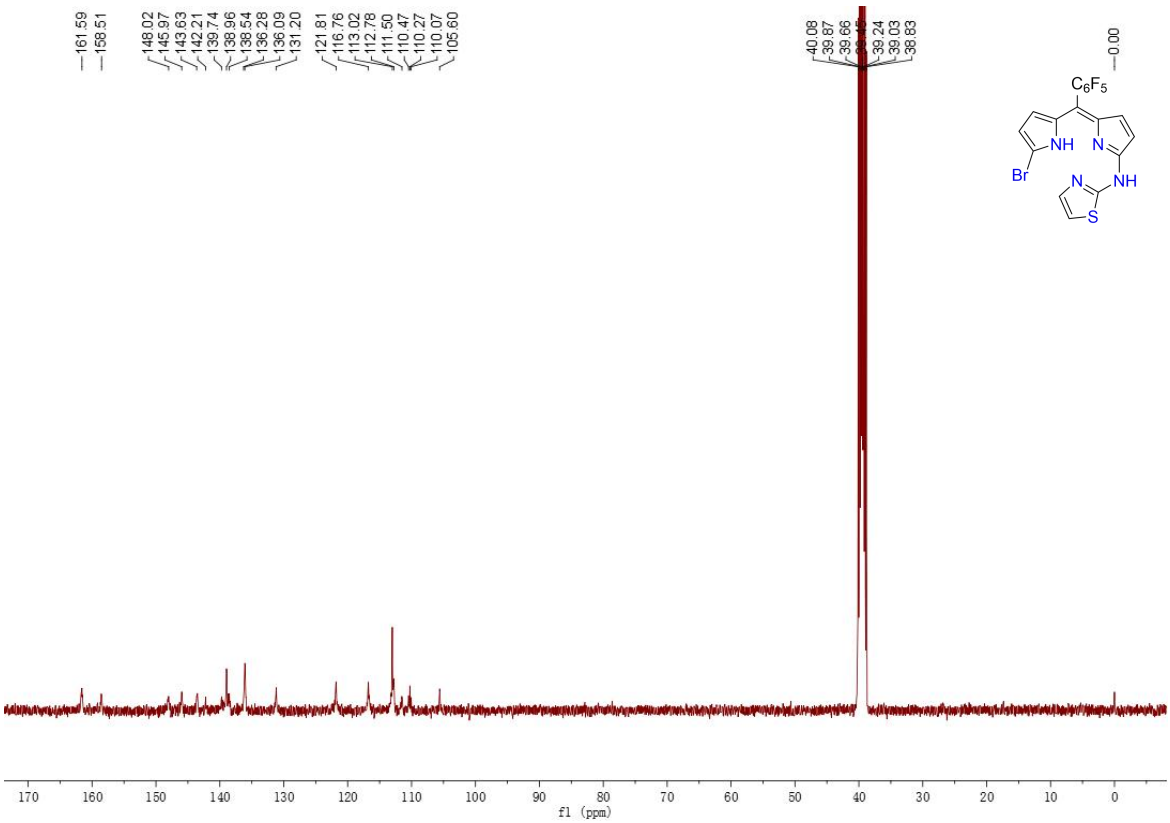



H-H COSY spectra of **5a** in $CDCl_3$ (500 MHz)

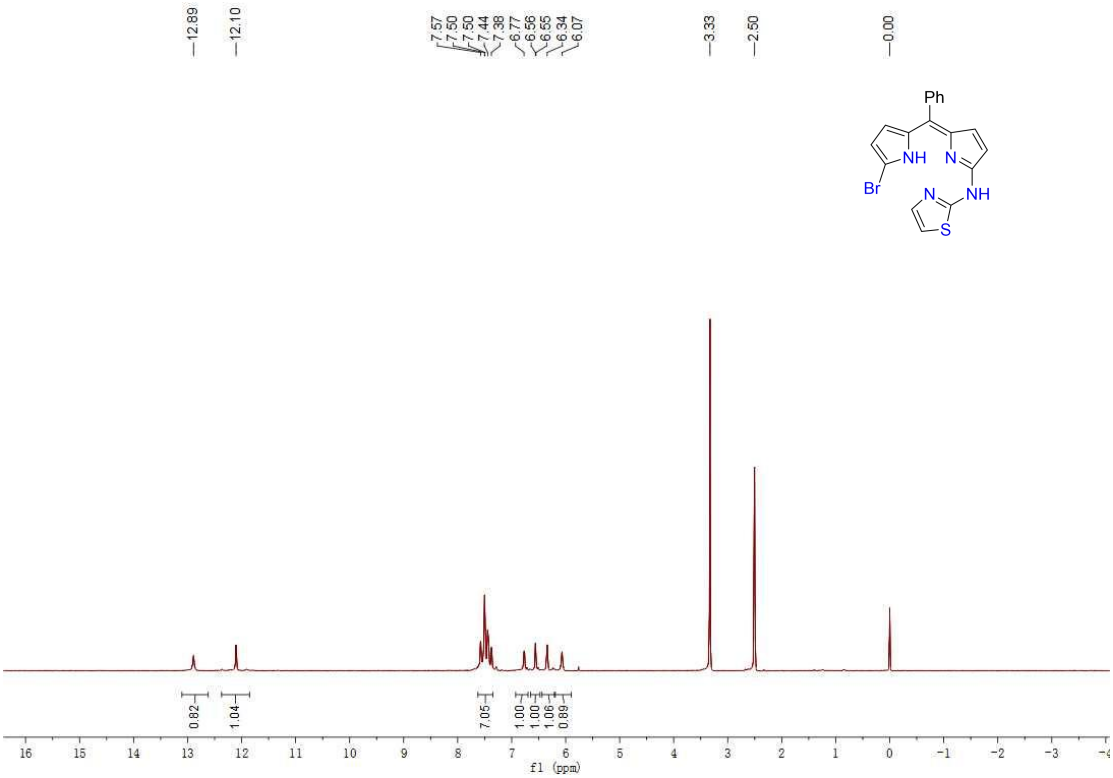
## 8. $^{1}$H, $^{13}$C NMR and HRMS spectra for all new compounds



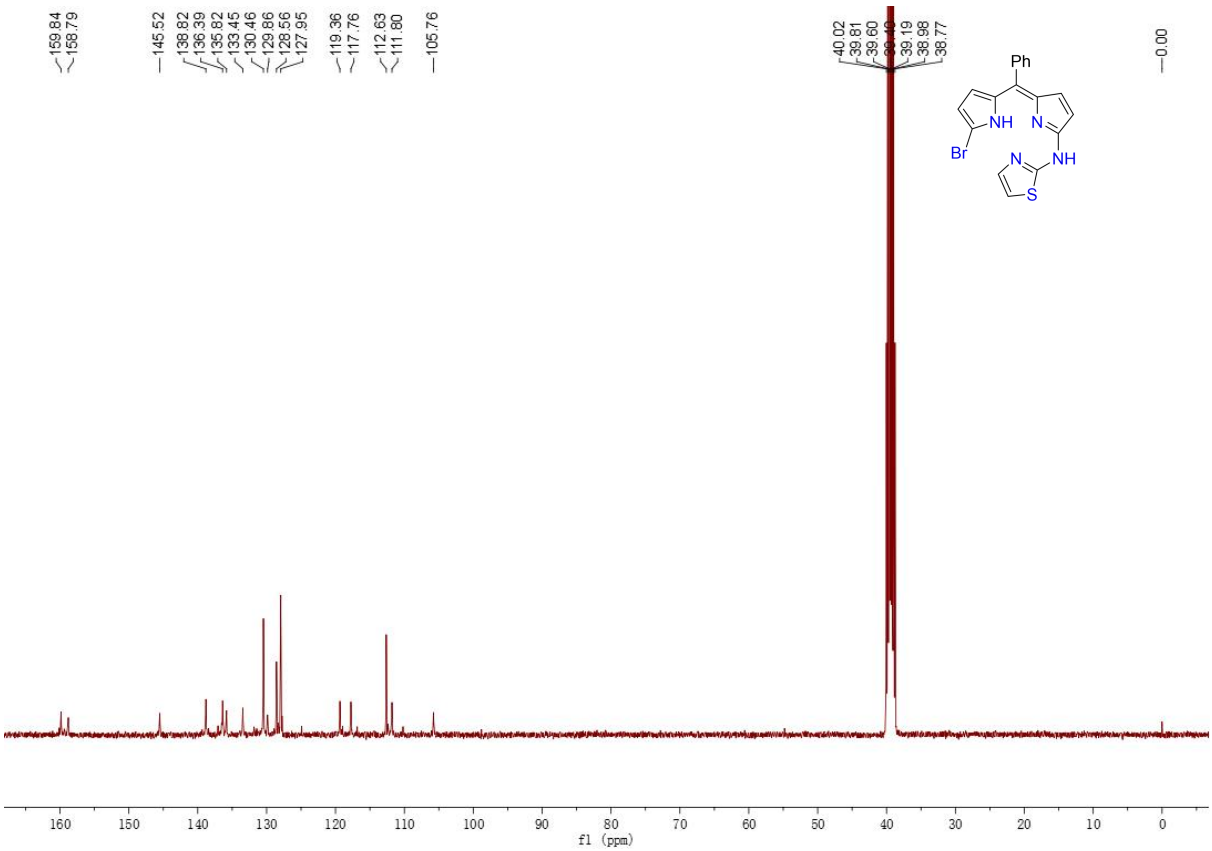

$^{1}$H NMR spectrum of **2a** in DMSO-$d_6$ (400 MHz)



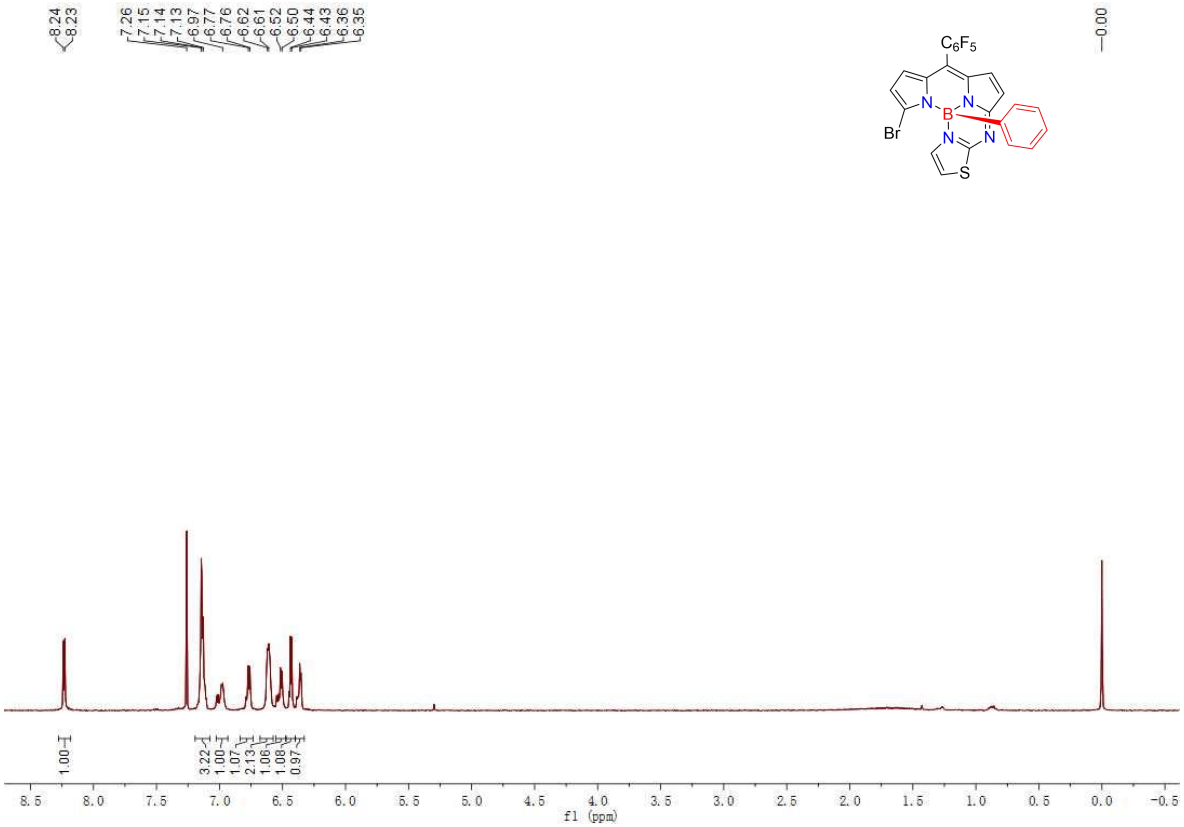

$^{13}$C NMR spectrum of **2a** in DMSO-$d_6$ (101 MHz)



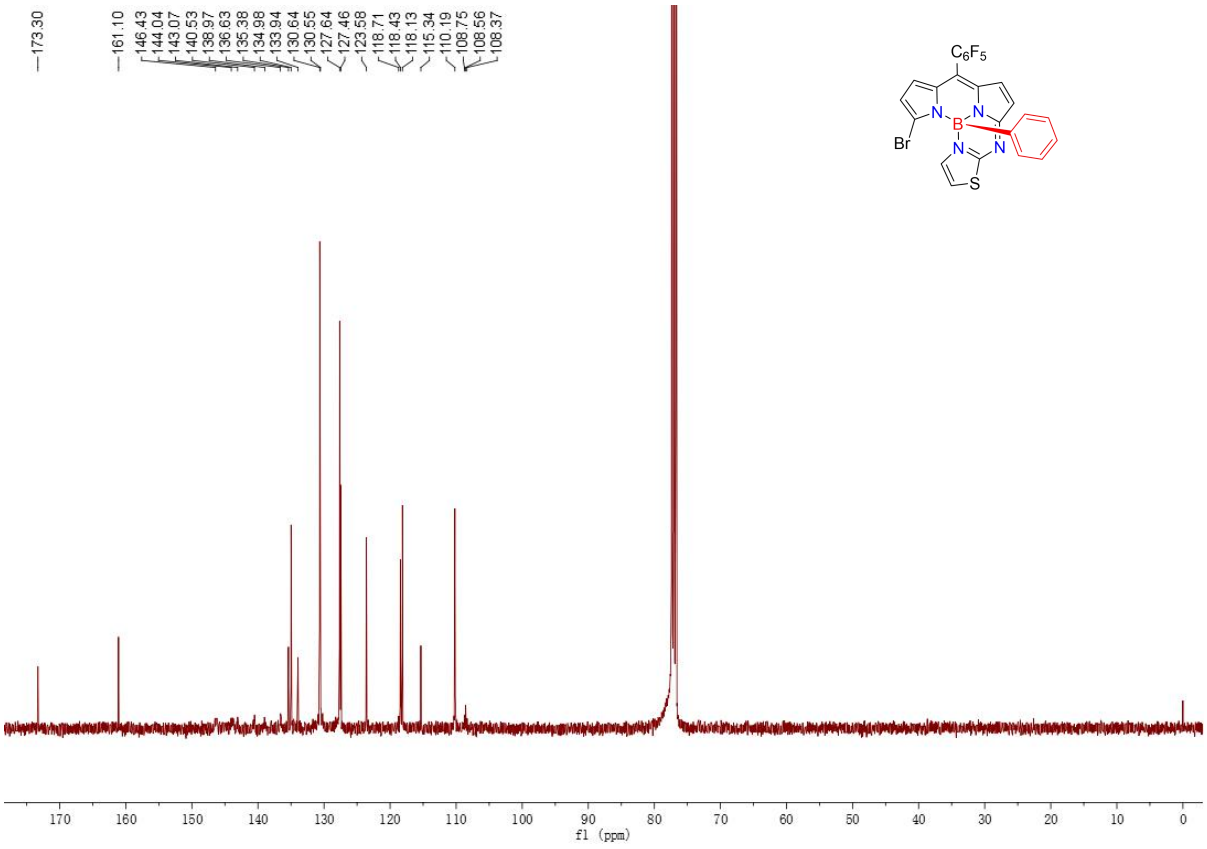

$^{1}$H NMR spectrum of **2b** in DMSO-$d_6$ (400 MHz)



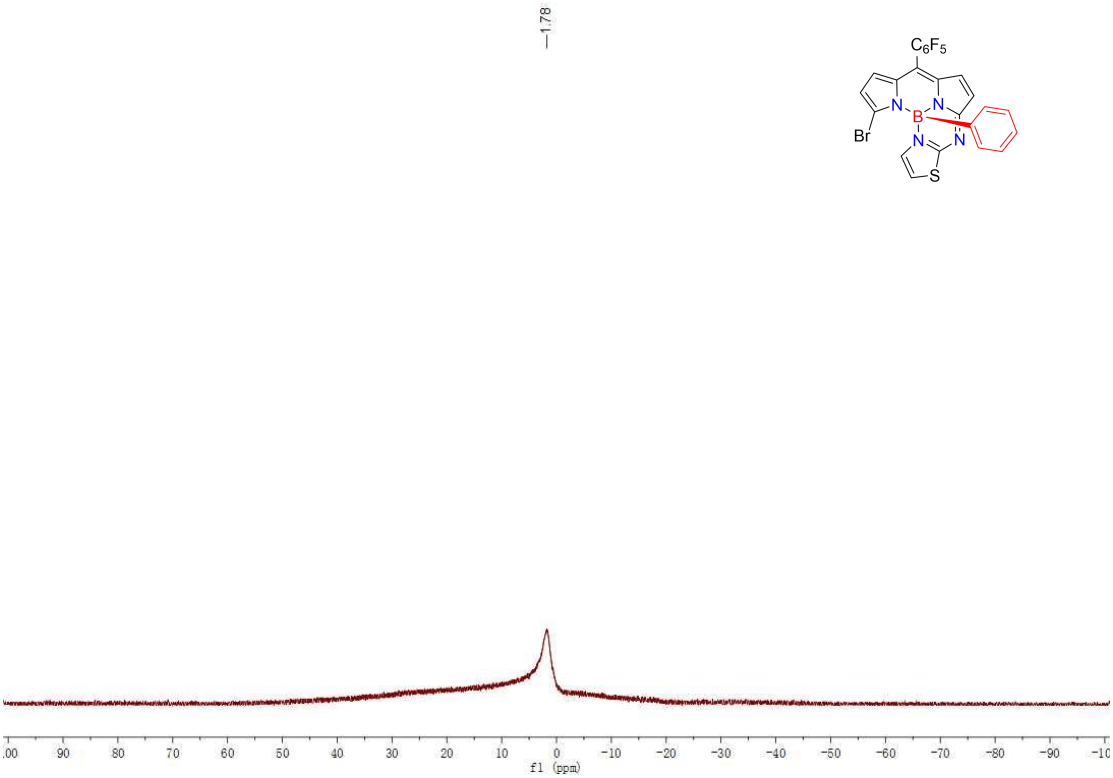

$^{13}$C NMR spectrum of **2b** in DMSO-$d_6$ (101 MHz)



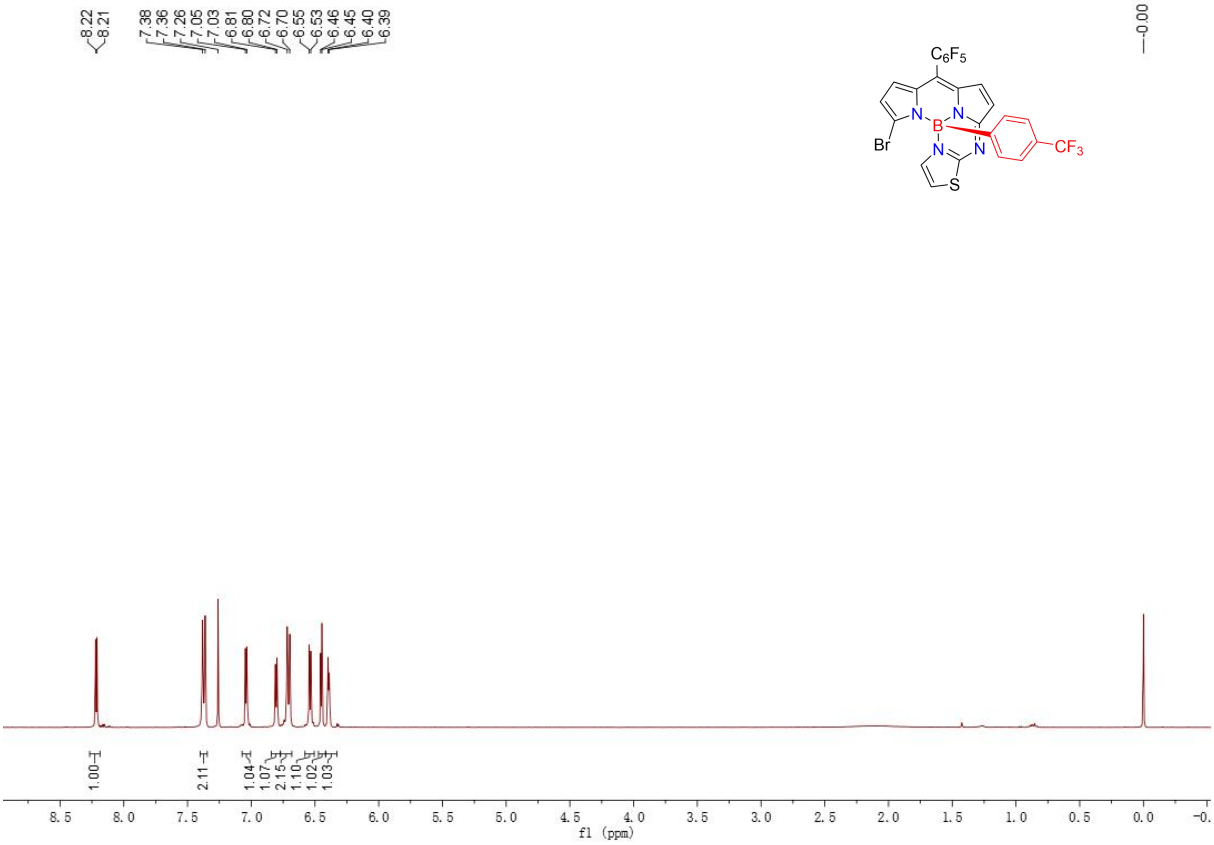

$^{1}$H NMR spectrum of **3a** in $CDCl_3$ (400 MHz)



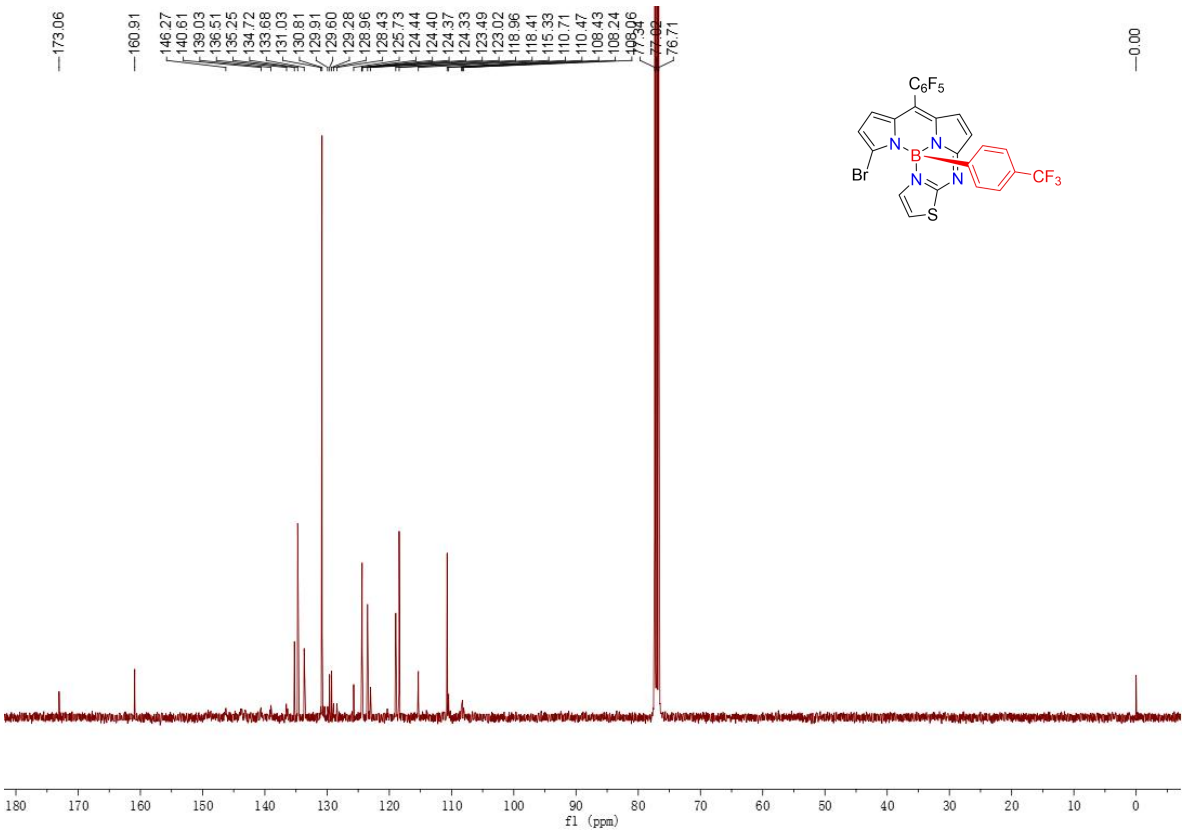

$^{13}$C NMR spectrum of **3a** in $CDCl_3$ (101 MHz)



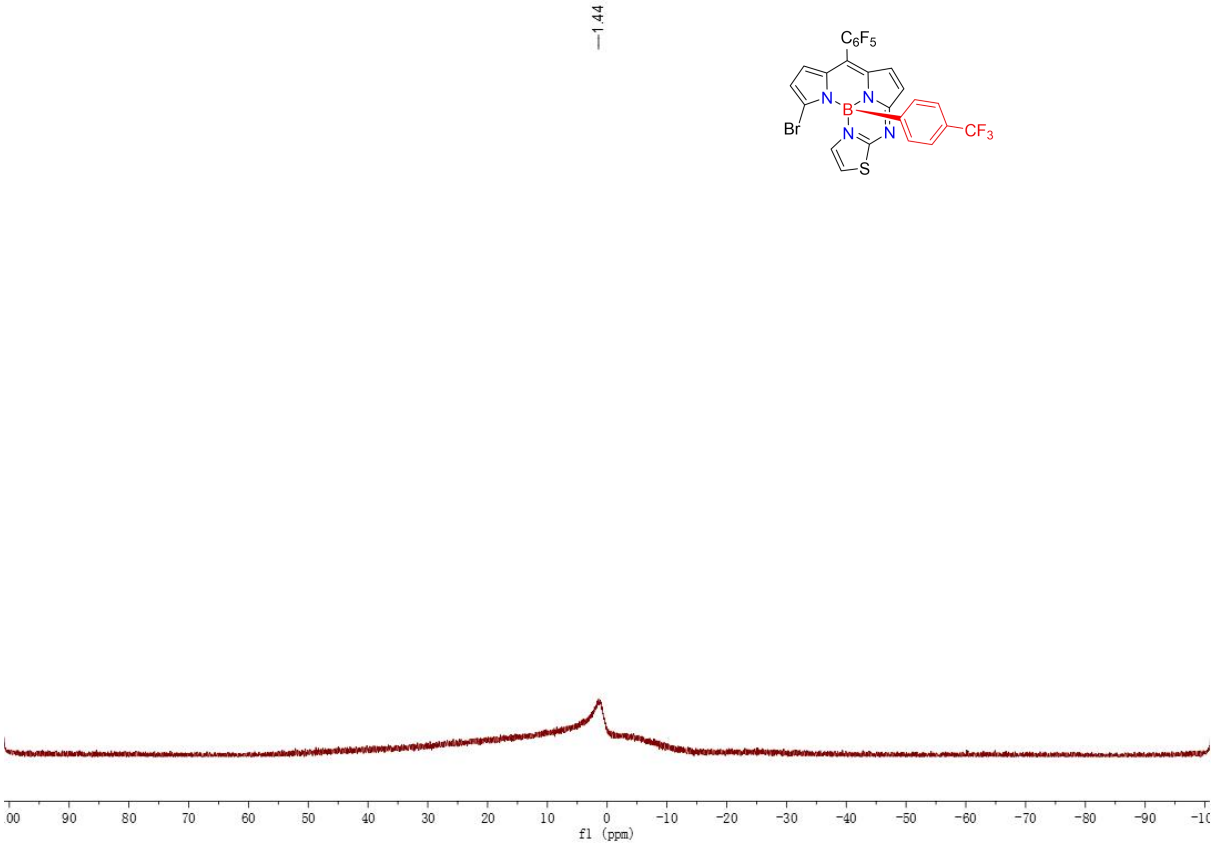

$^{11}$B NMR spectrum of **3a** in $CDCl_3$ (128 MHz)



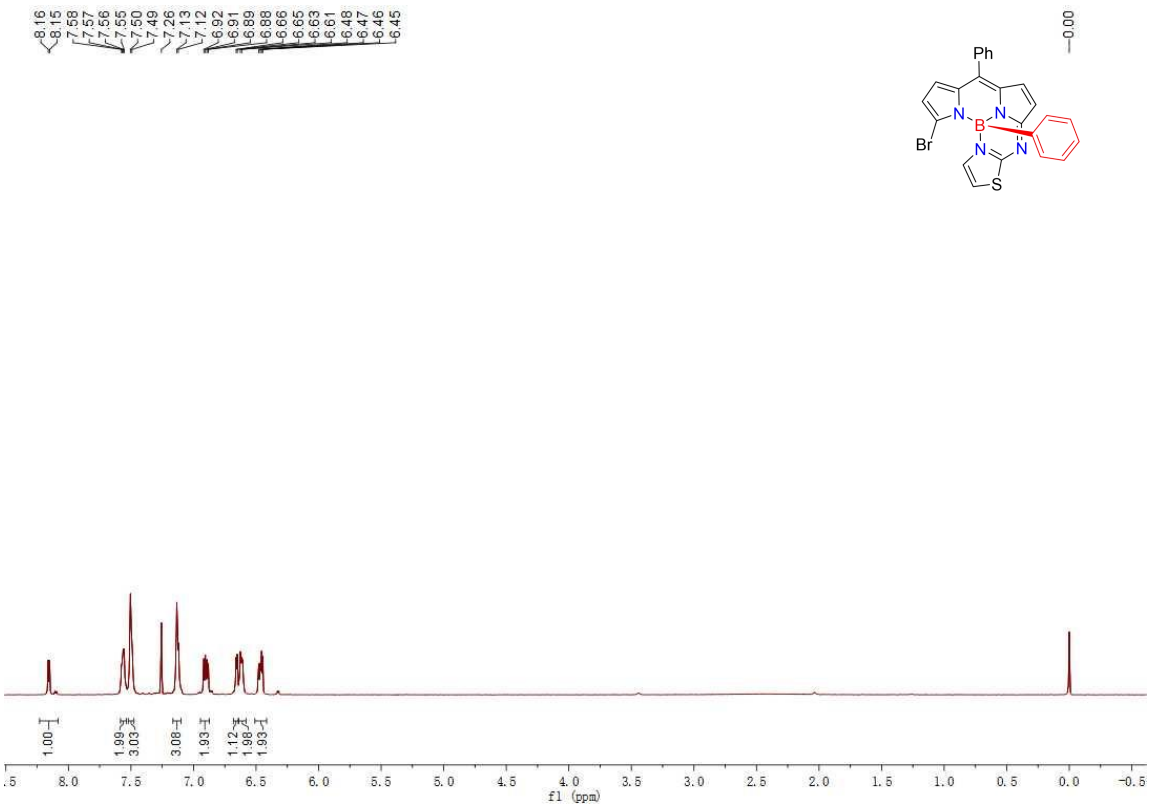

$^{1}$H NMR spectrum of **3b** in $CDCl_3$ (400 MHz)



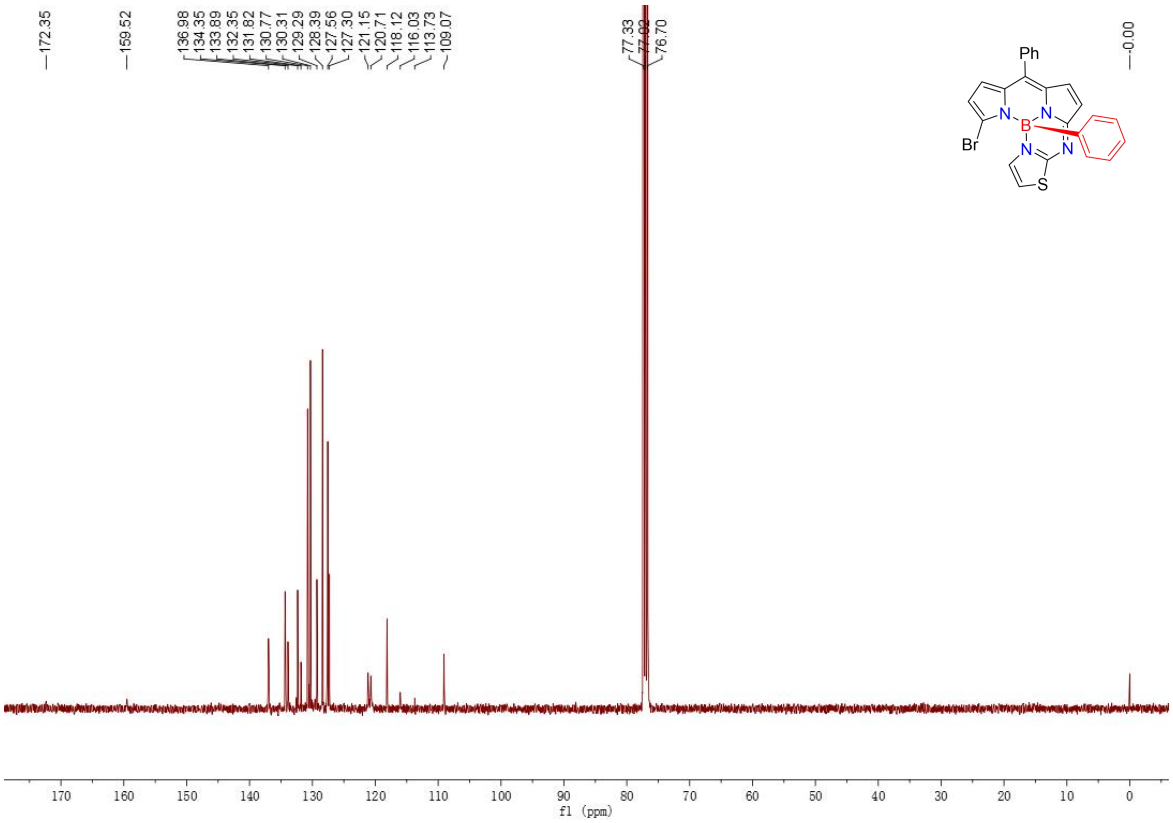

$^{13}$C NMR spectrum of **3b** in $CDCl_3$ (101 MHz)



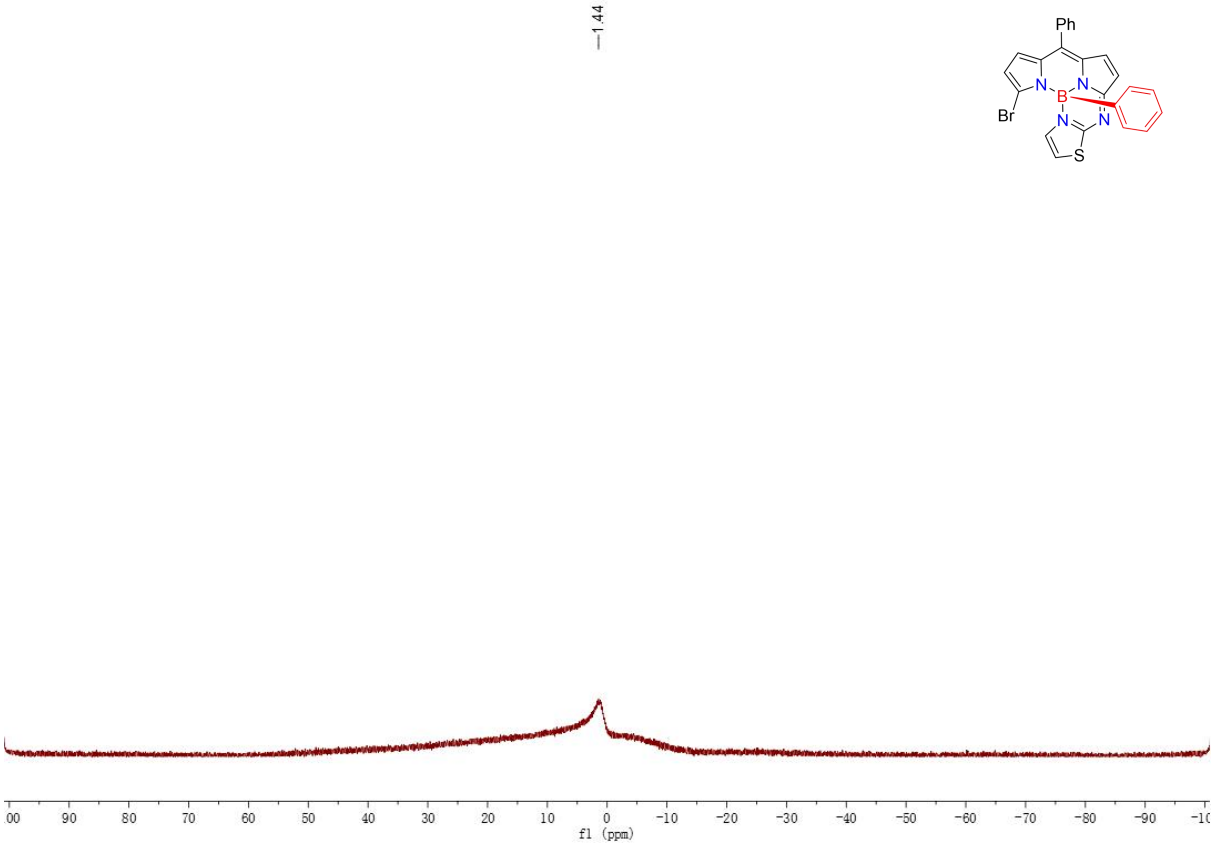

$^{11}$B NMR spectrum of **3b** in $CDCl_3$ (128 MHz)



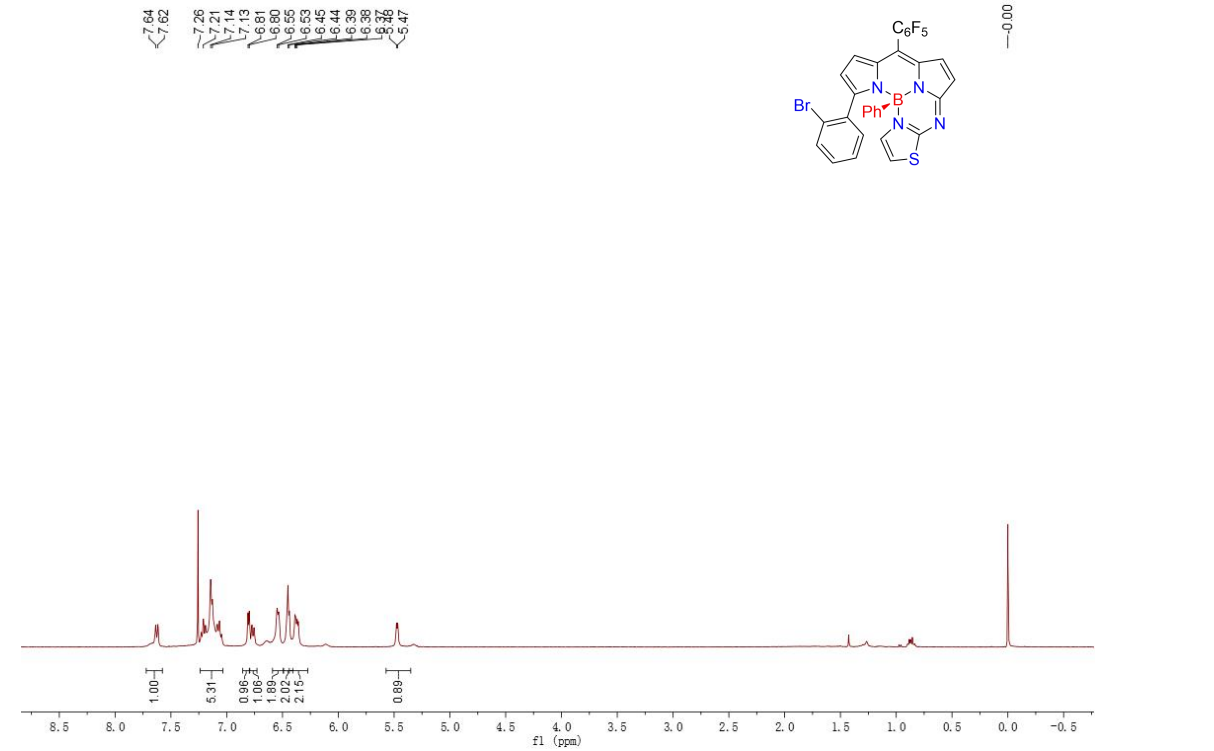

$^{1}$H NMR spectrum of **3c** in $CDCl_3$ (400 MHz)



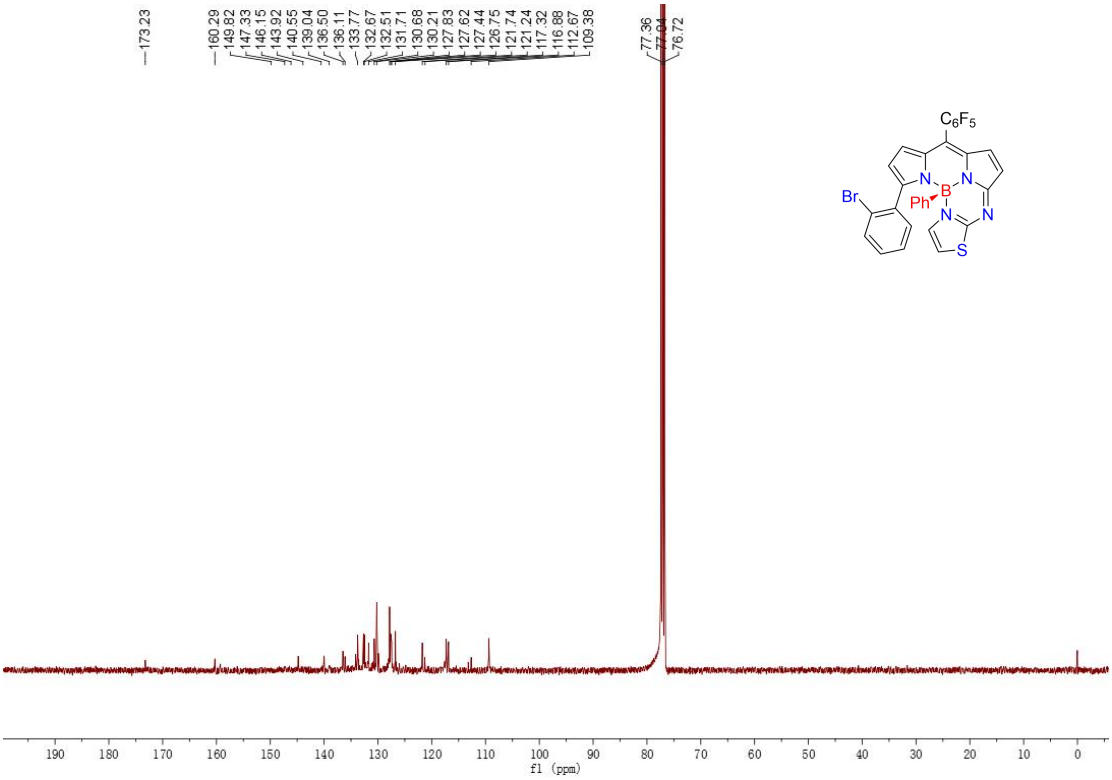

$^{13}$C NMR spectrum of **3c** in $CDCl_3$ (101 MHz)



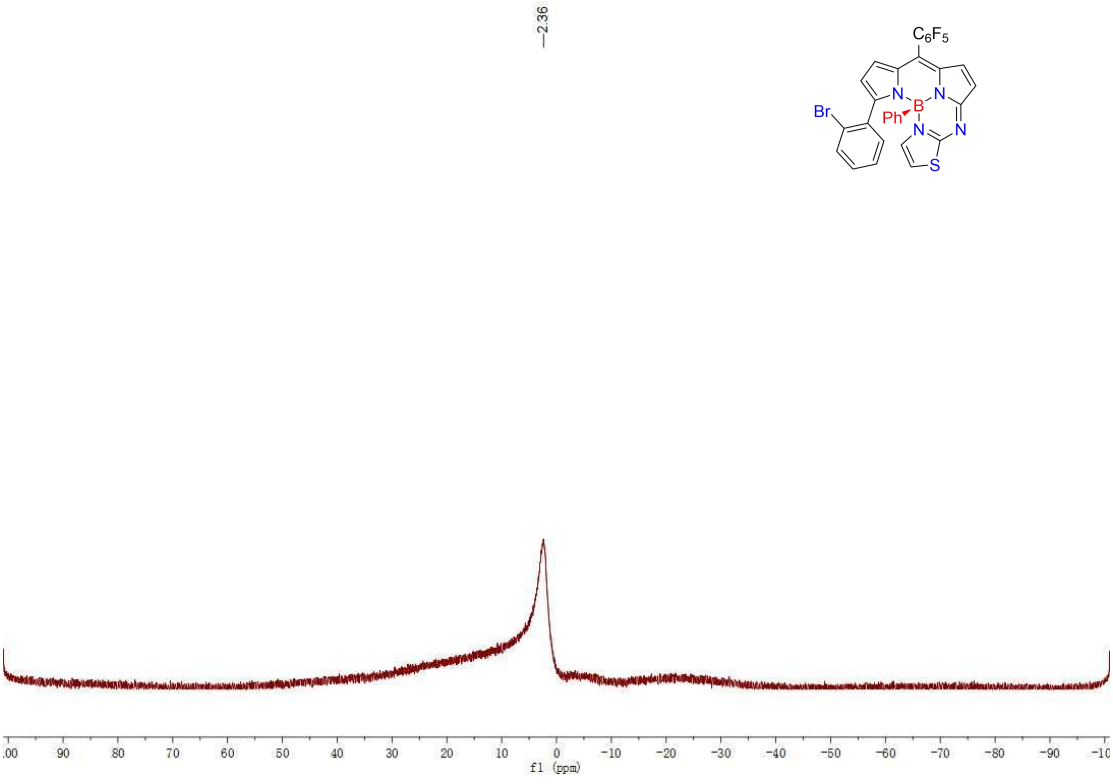

$^{11}$B NMR spectrum of **3c** in $CDCl_3$ (128 MHz)



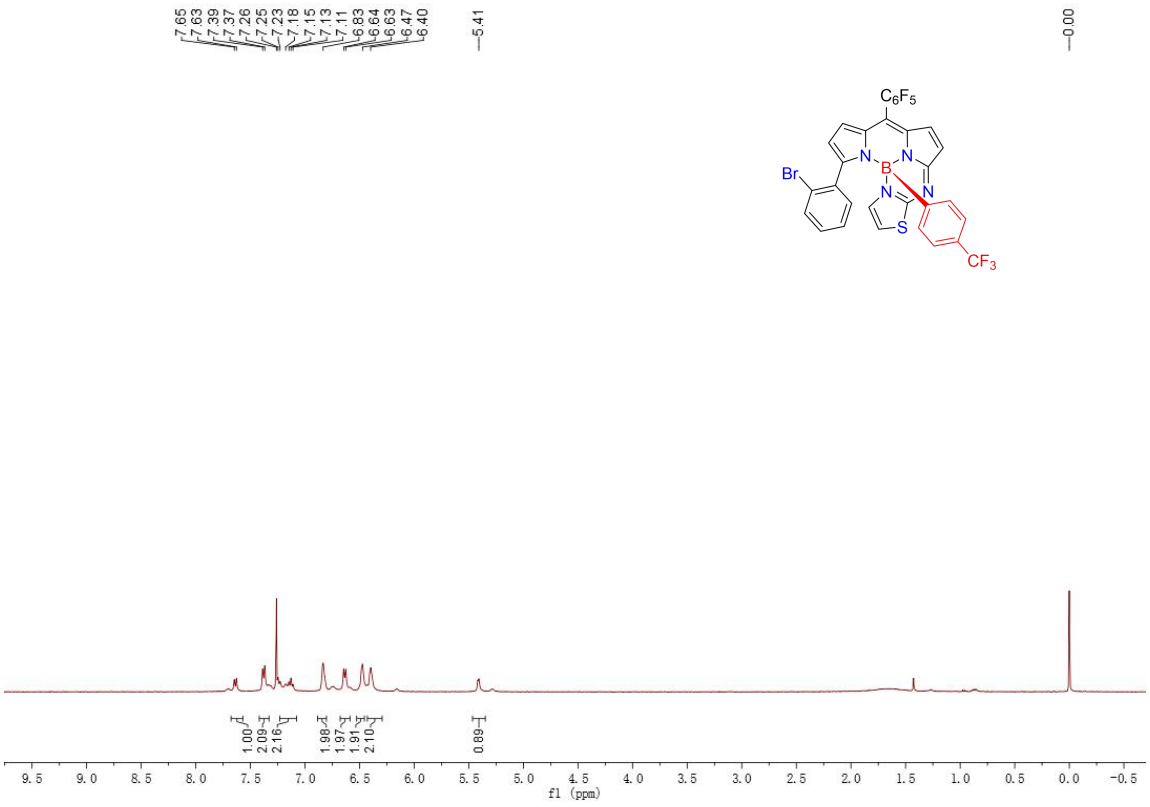

$^{1}$H NMR spectrum of **4a** in $CDCl_3$ (400 MHz)



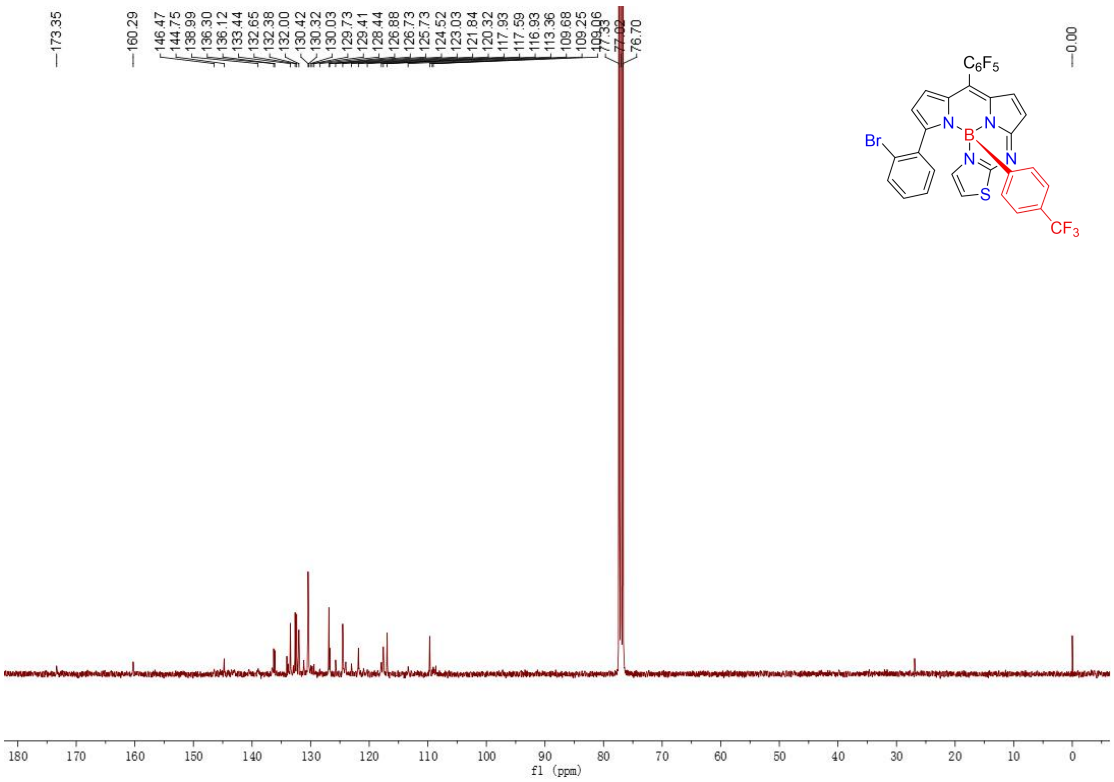

$^{13}$C NMR spectrum of **4a** in $CDCl_3$ (101 MHz)



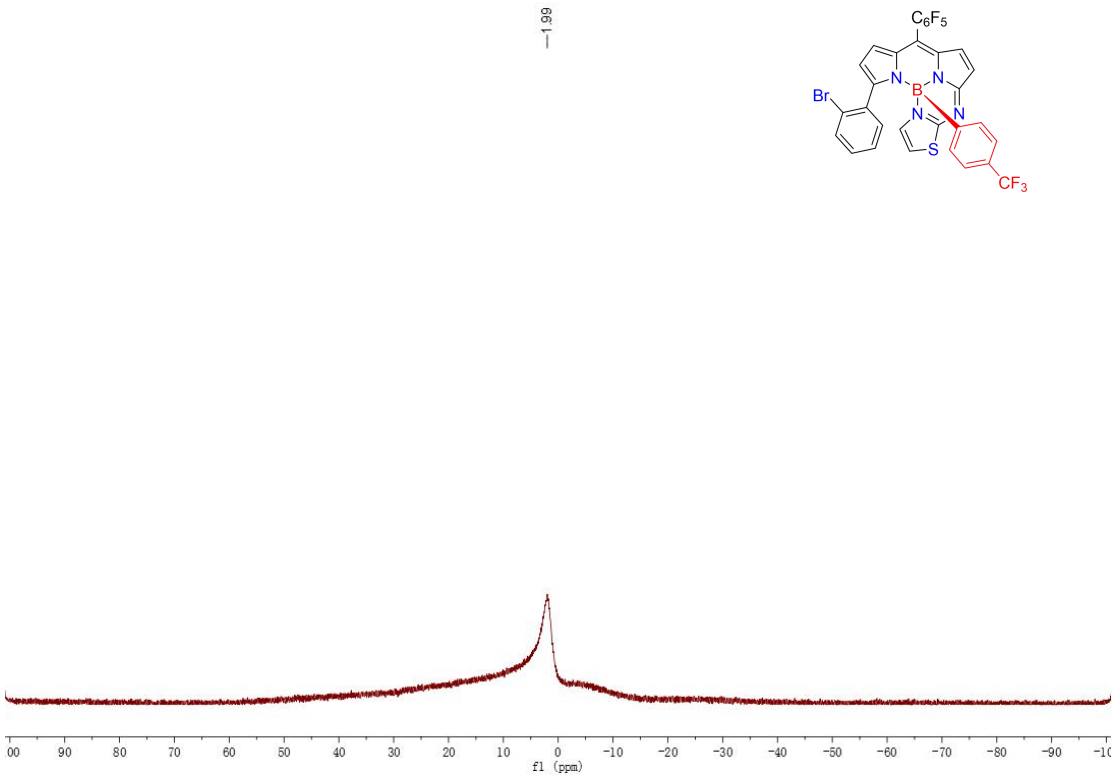

$^{11}$B NMR spectrum of **4a** in $CDCl_3$ (128 MHz)



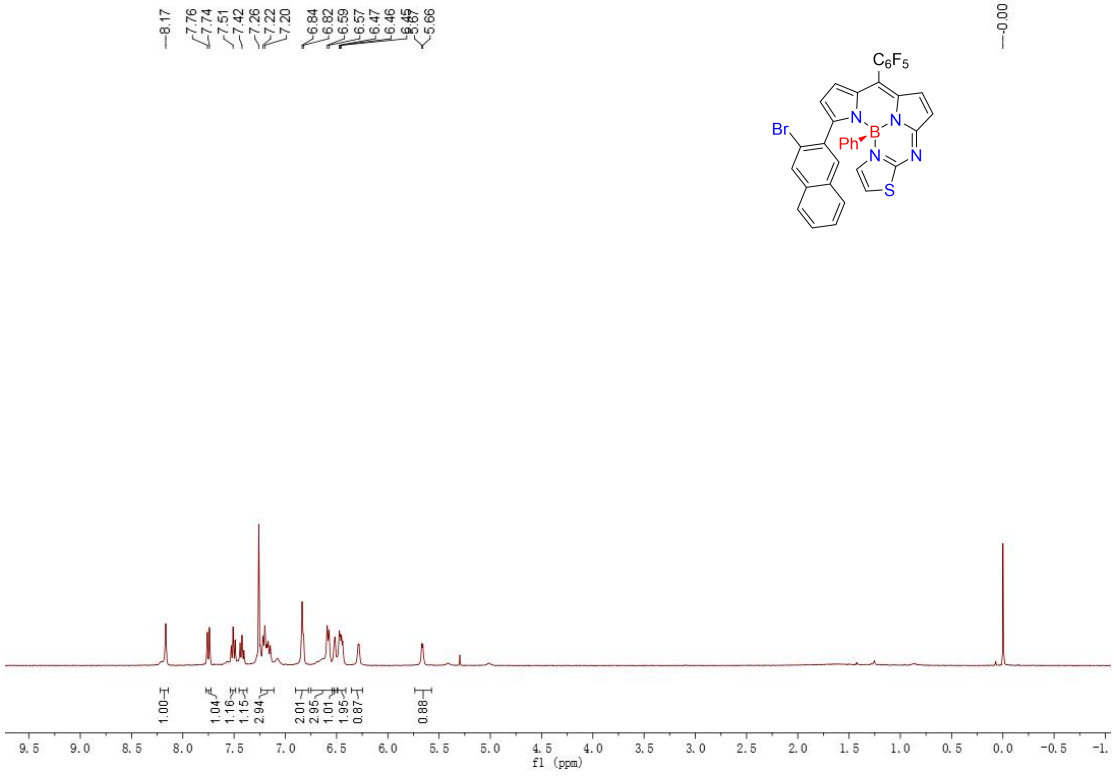

$^{1}$H NMR spectrum of **4b** in $CDCl_3$ (400 MHz)



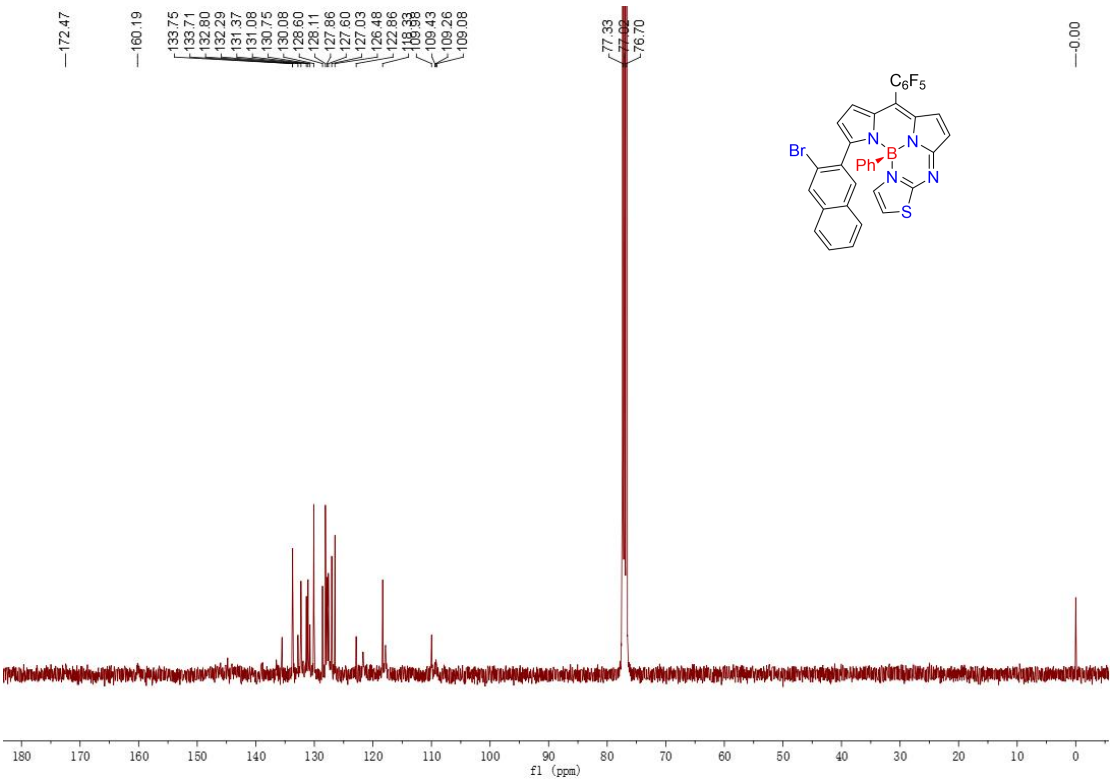

$^{13}$C NMR spectrum of **4b** in $CDCl_3$ (101 MHz)



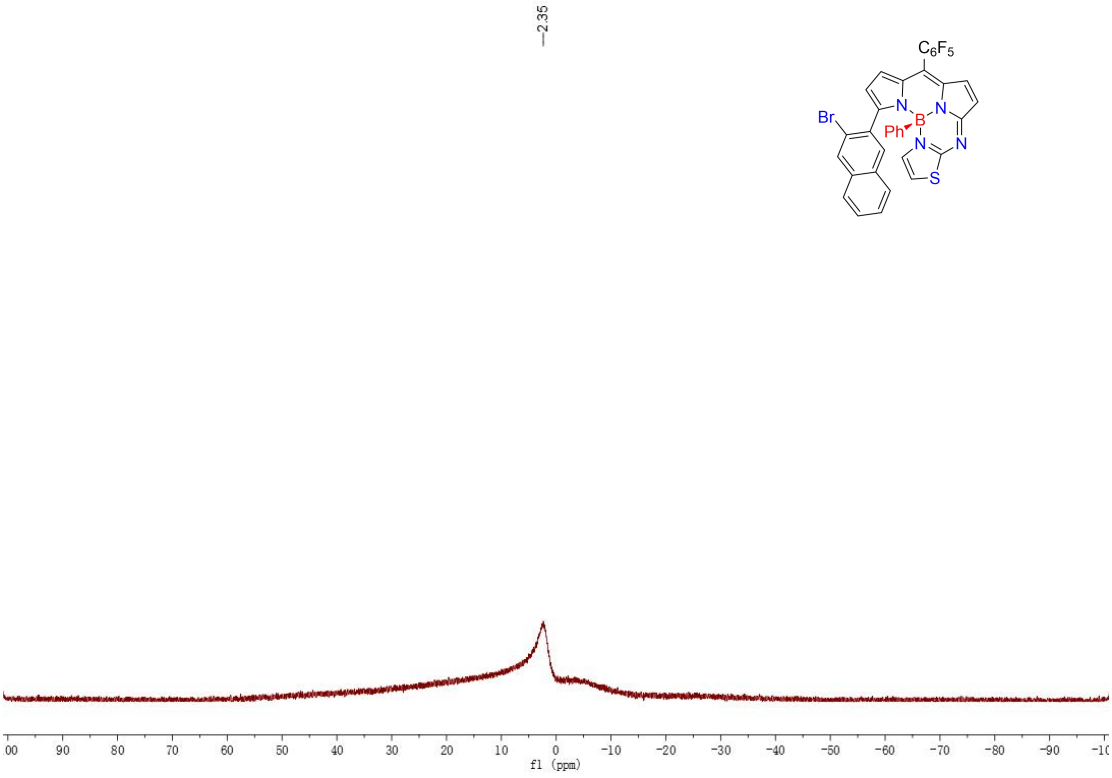

$^{11}$B NMR spectrum of **4b** in $CDCl_3$ (128 MHz)



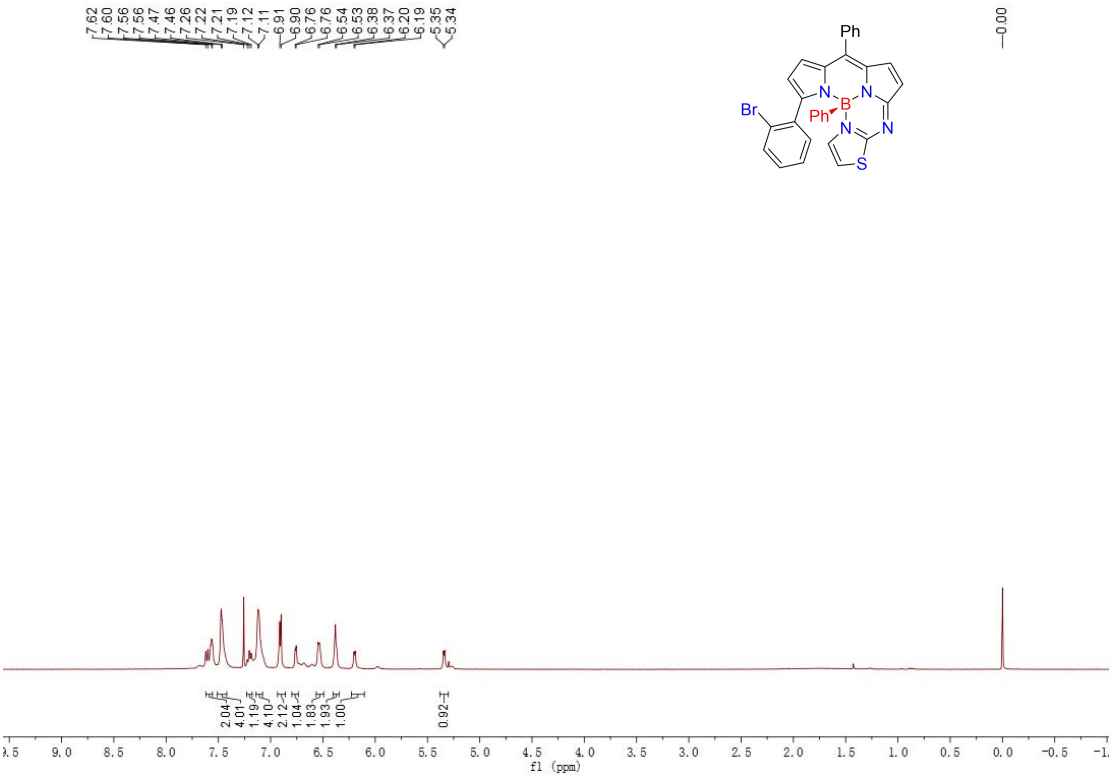

$^{1}$H NMR spectrum of **4c** in $CDCl_3$ (400 MHz)



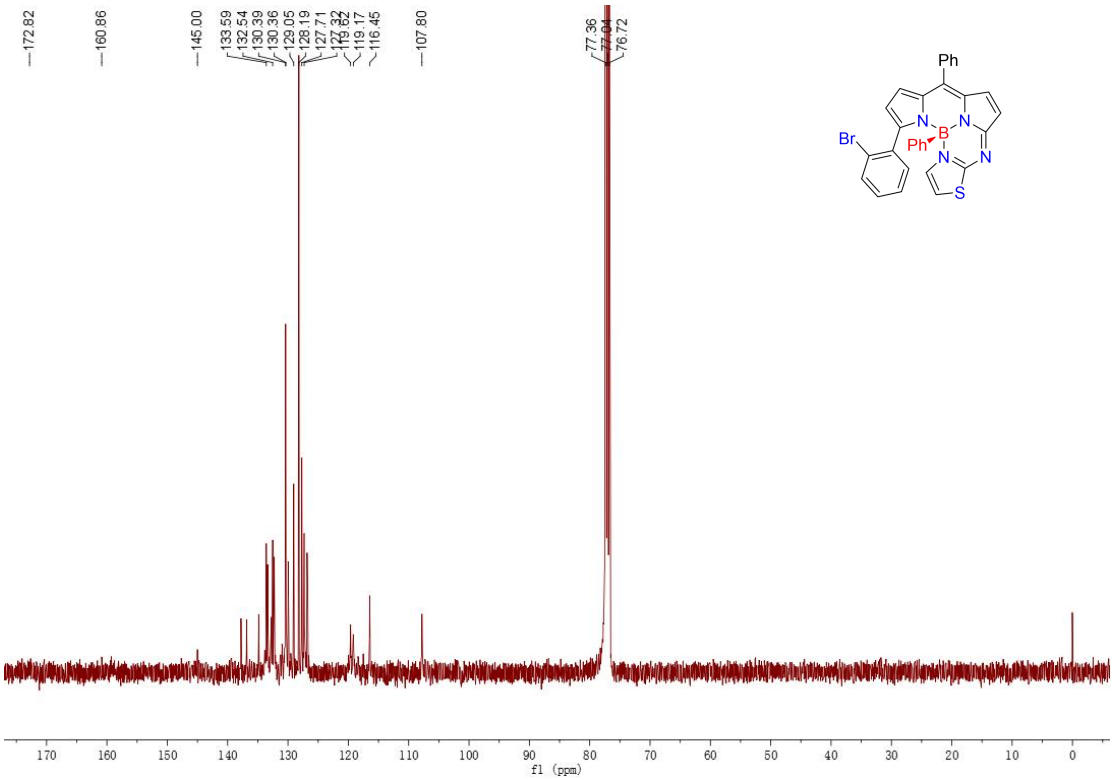

$^{13}$C NMR spectrum of **4c** in $CDCl_3$ (101 MHz)



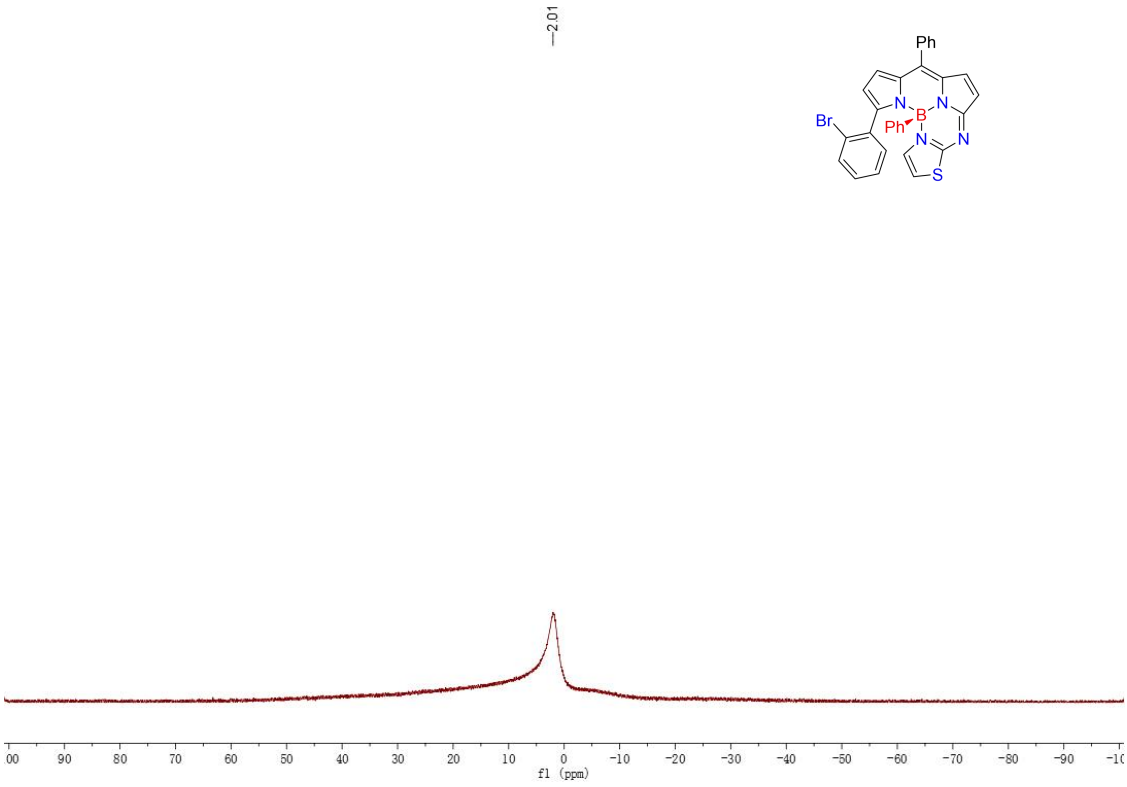

$^{11}$B NMR spectrum of **4c** in $CDCl_3$ (128 MHz)



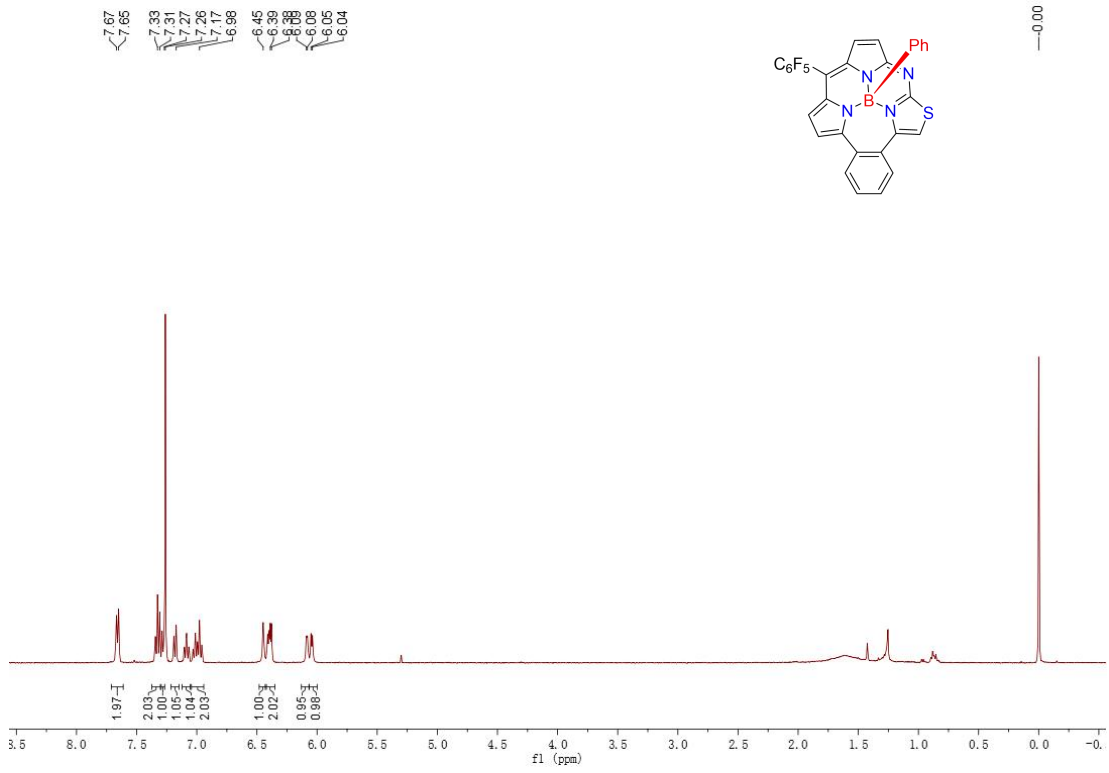

$^{1}$H NMR spectrum of **4d** in $CDCl_3$ (400 MHz)



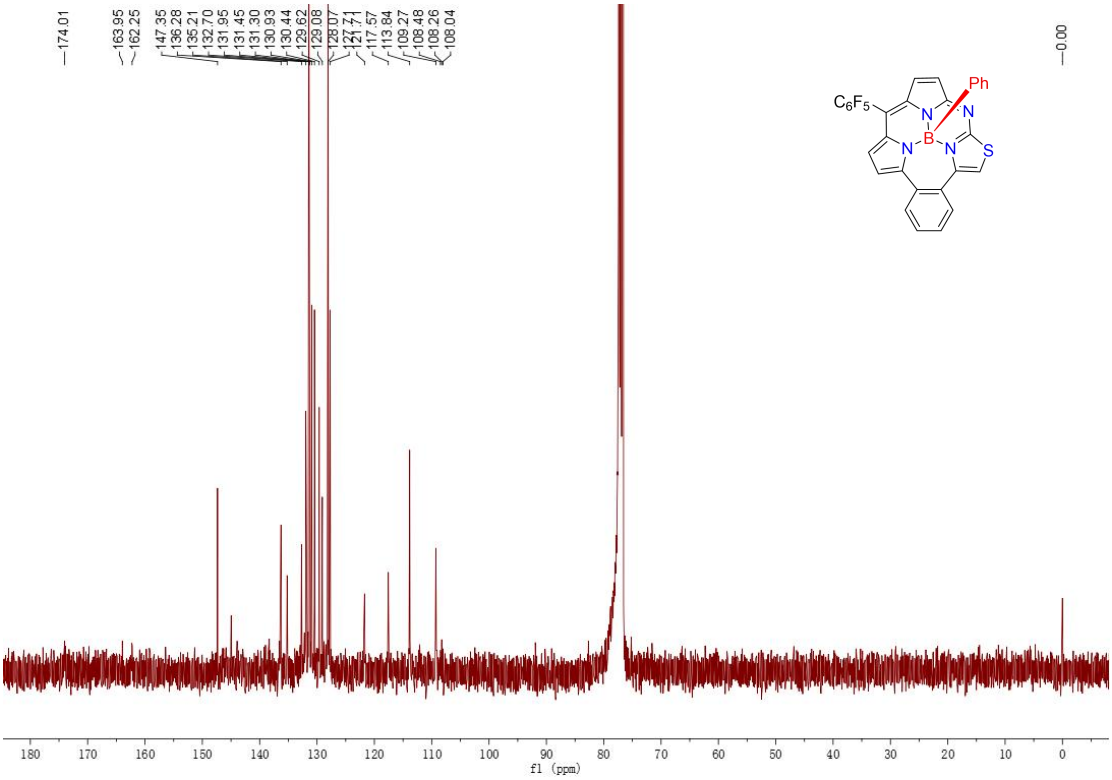

$^{13}$C NMR spectrum of **4d** in $CDCl_3$ (101 MHz)



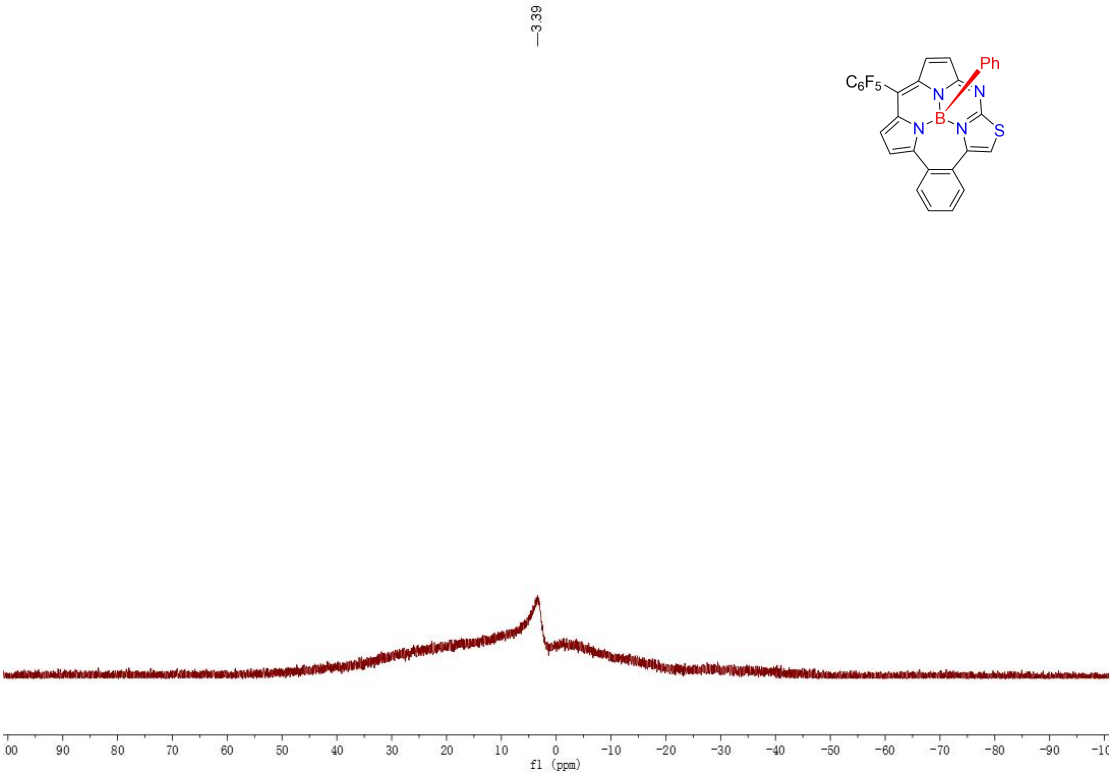

$^{11}$B NMR spectrum of **4d** in $CDCl_3$ (128 MHz)



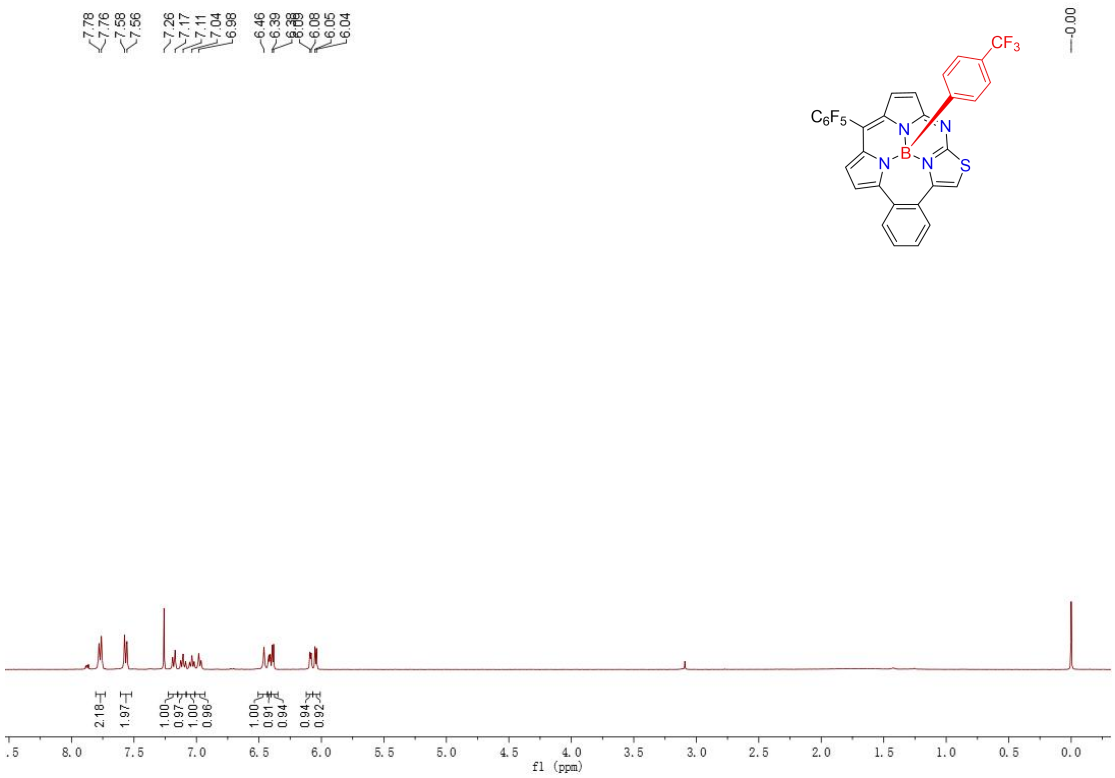

$^{1}$H NMR spectrum of **5a** in $CDCl_3$ (400 MHz)



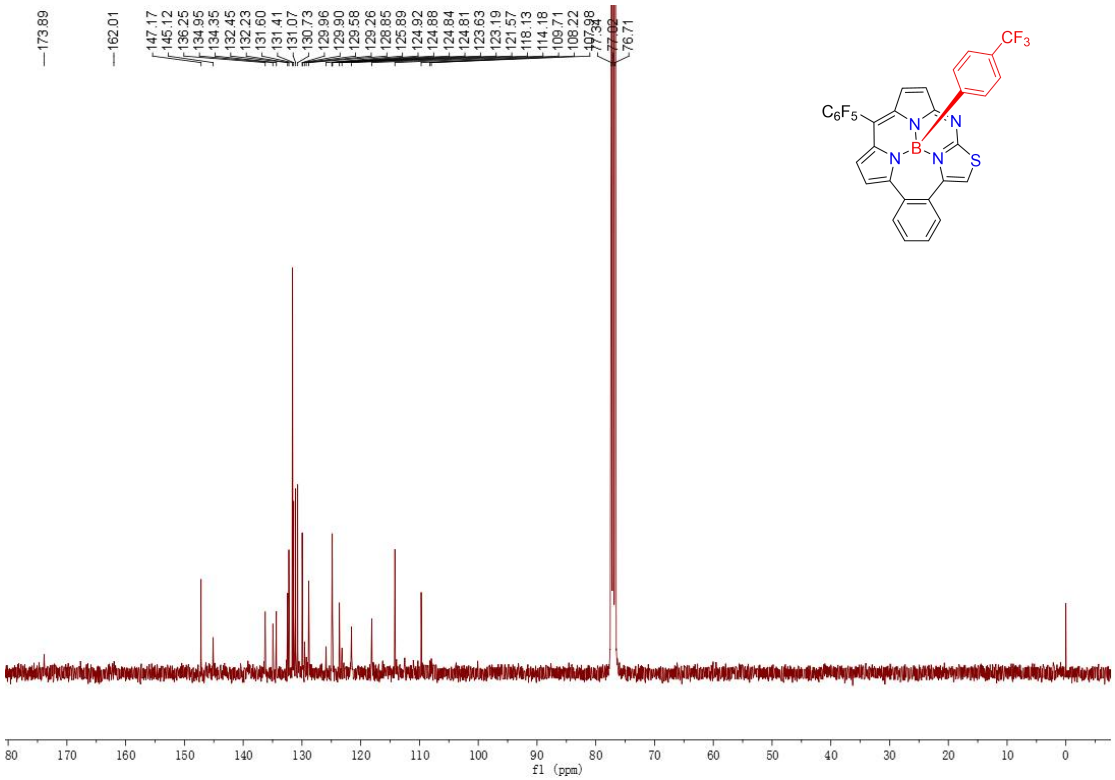

$^{13}$C NMR spectrum of **5a** in $CDCl_3$ (101 MHz)



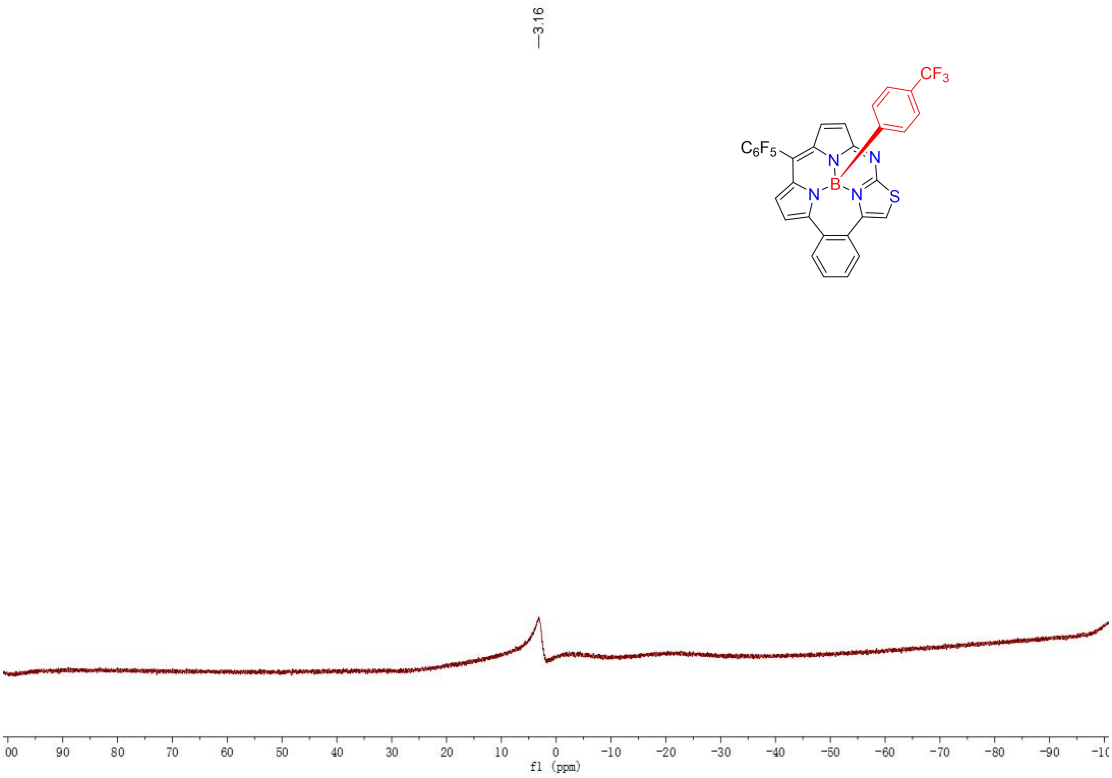

$^{11}$B NMR spectrum of **5a** in $CDCl_3$ (128 MHz)



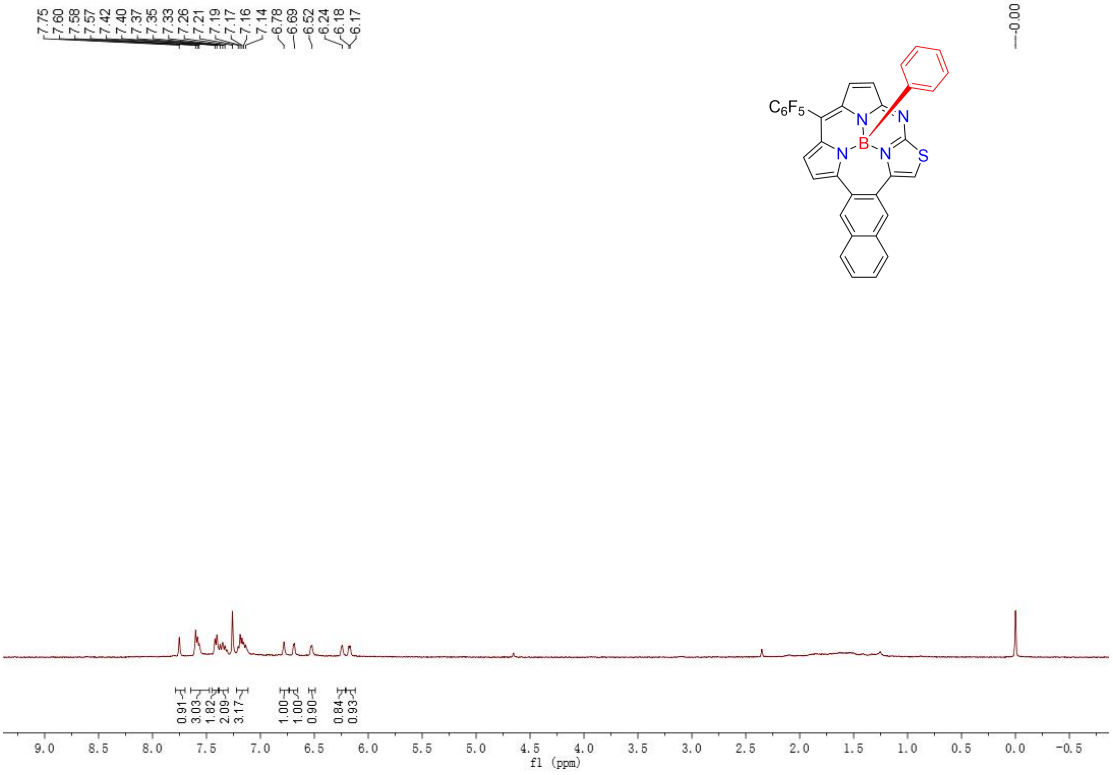

$^{1}$H NMR spectrum of **5b** in $CDCl_3$ (400 MHz)



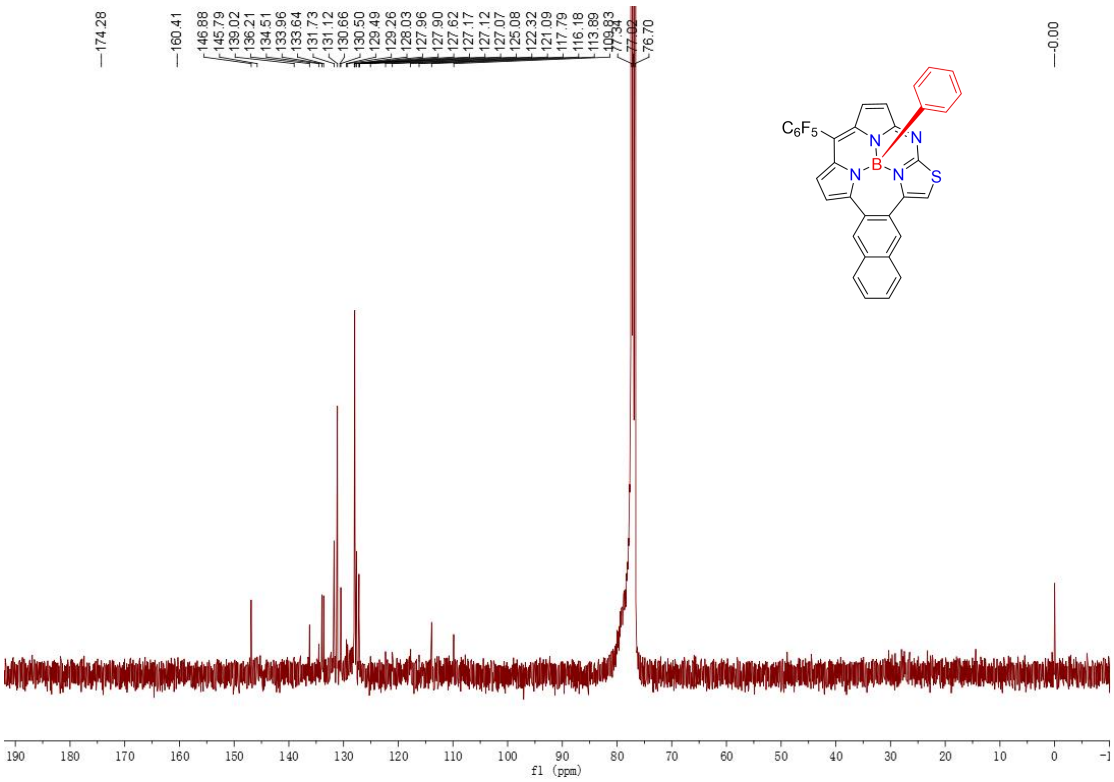

$^{13}$C NMR spectrum of **5b** in $CDCl_3$ (101 MHz)



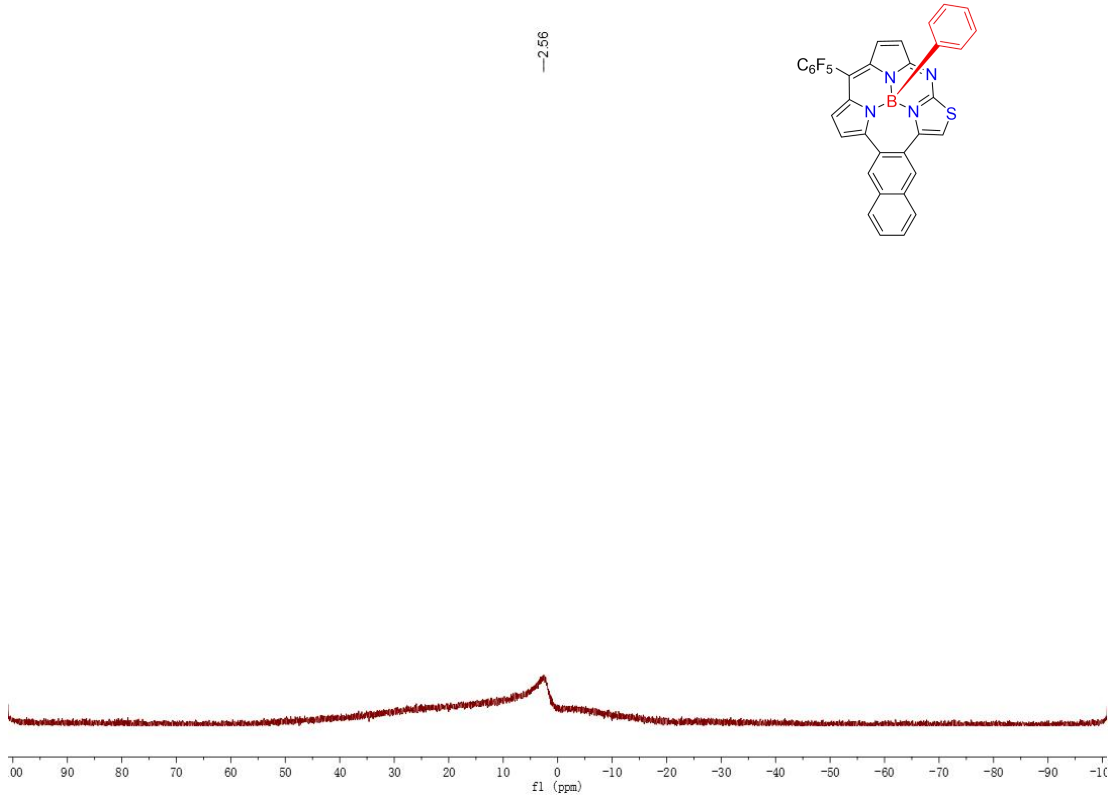

$^{11}$B NMR spectrum of **5b** in $CDCl_3$ (128 MHz)



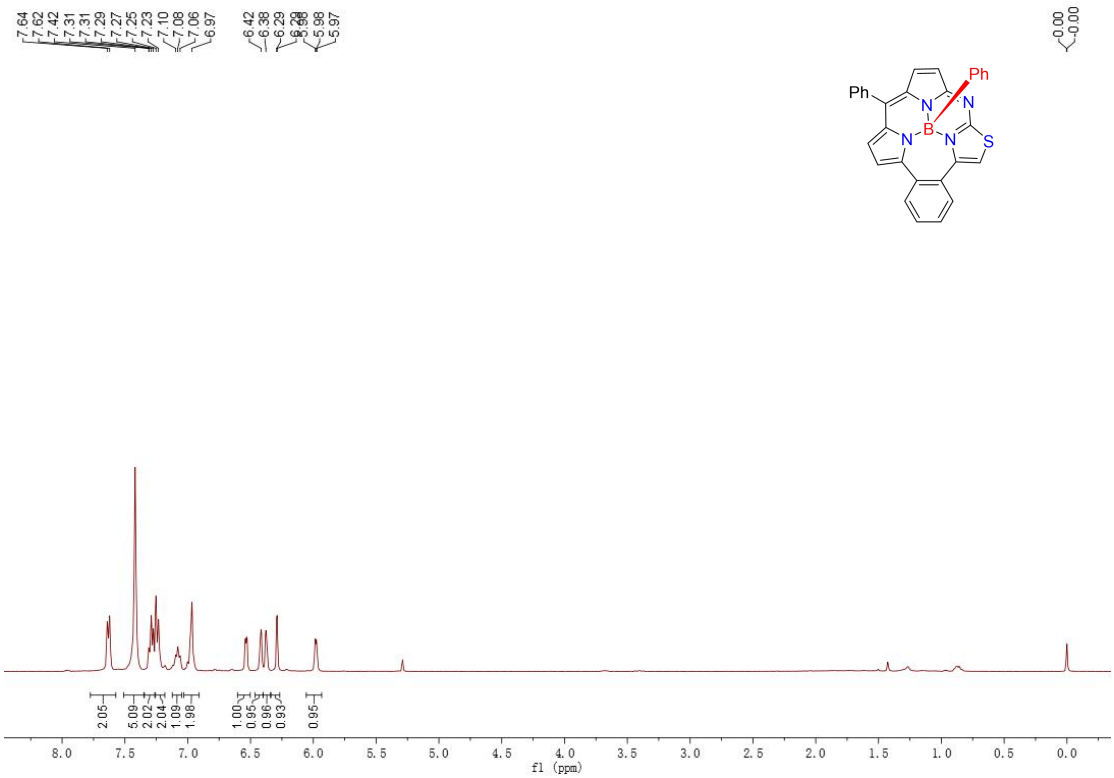

$^{1}$H NMR spectrum of **5c** in $CDCl_3$ (400 MHz)



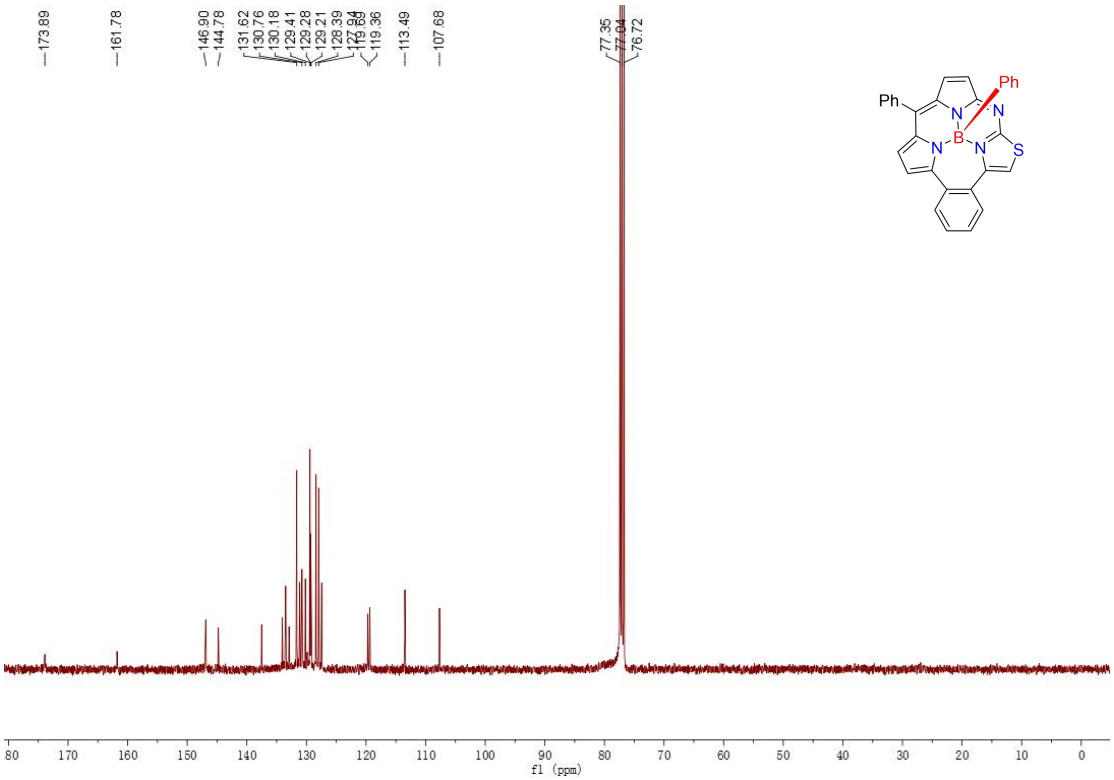

$^{13}$C NMR spectrum of **5c** in $CDCl_3$ (101 MHz)



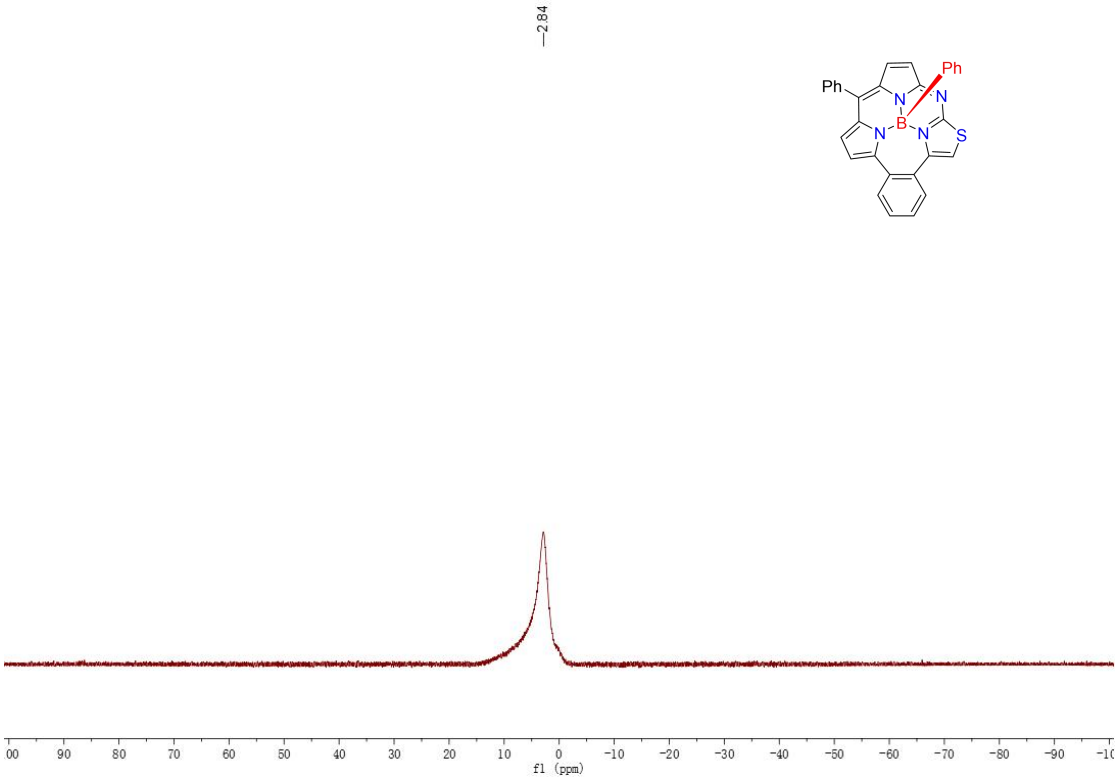

$^{11}$B NMR spectrum of **5c** in $CDCl_3$ (128 MHz)



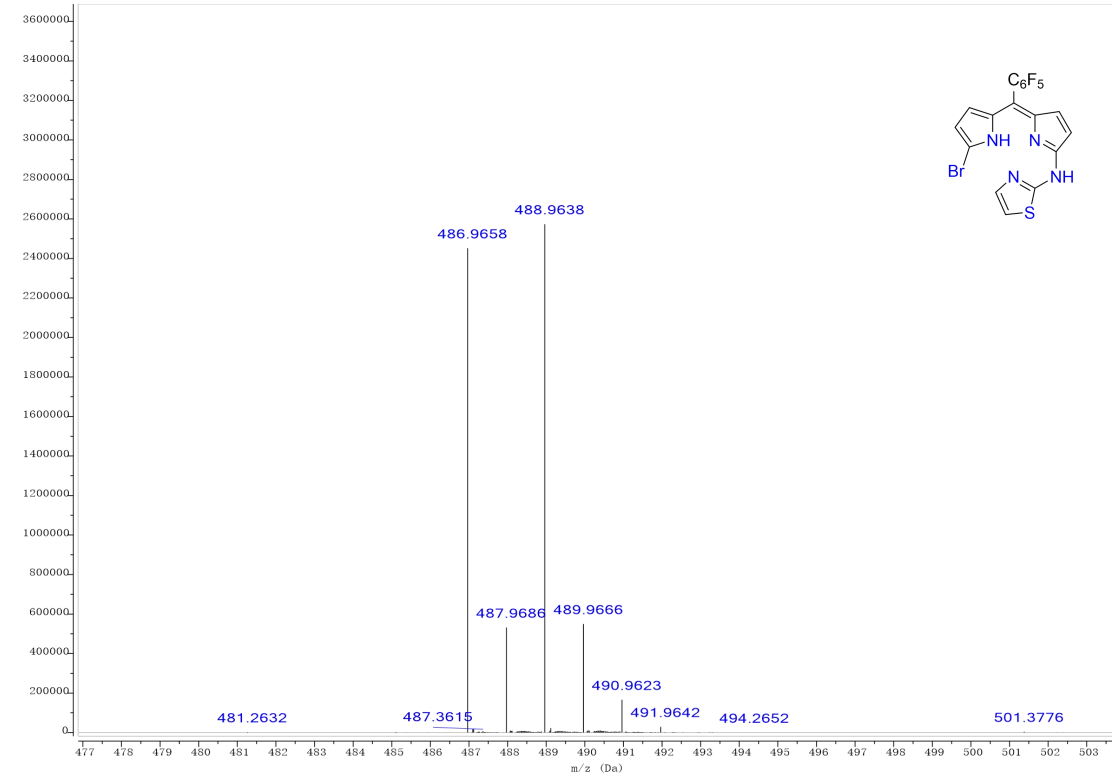

$^{1}$H NMR spectrum of **5d** in $CDCl_3$ (400 MHz)



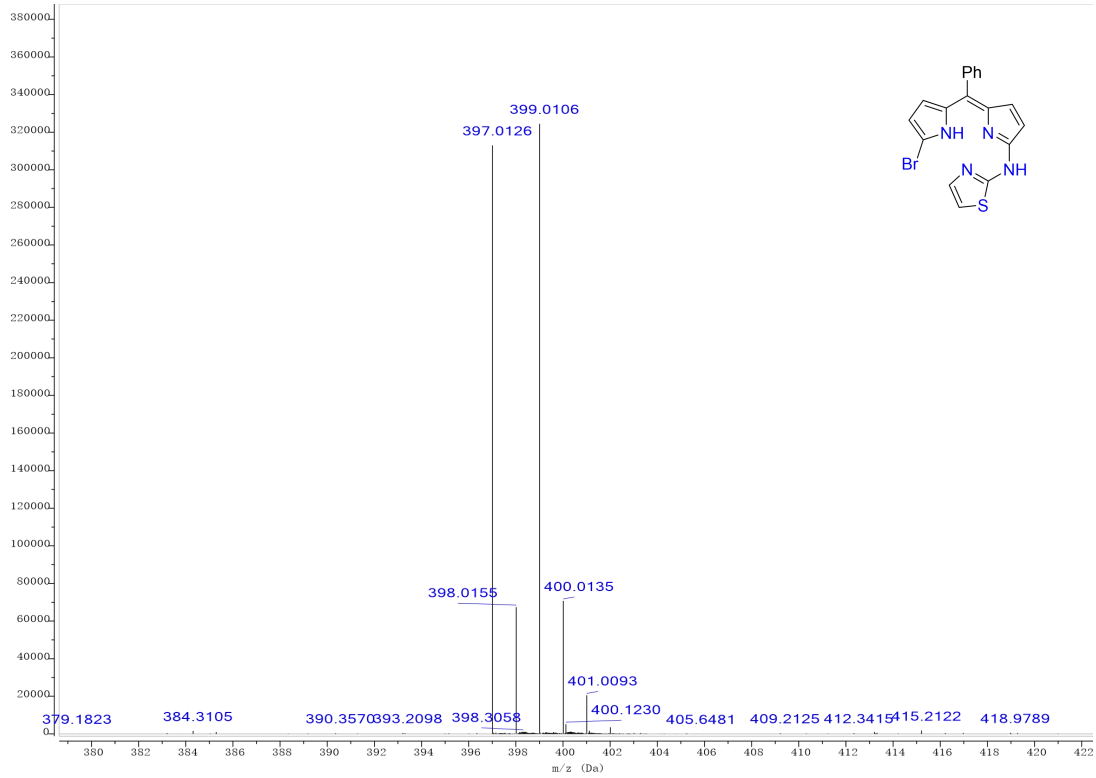

$^{13}$C NMR spectrum of **5d** in $CDCl_3$ (101 MHz)



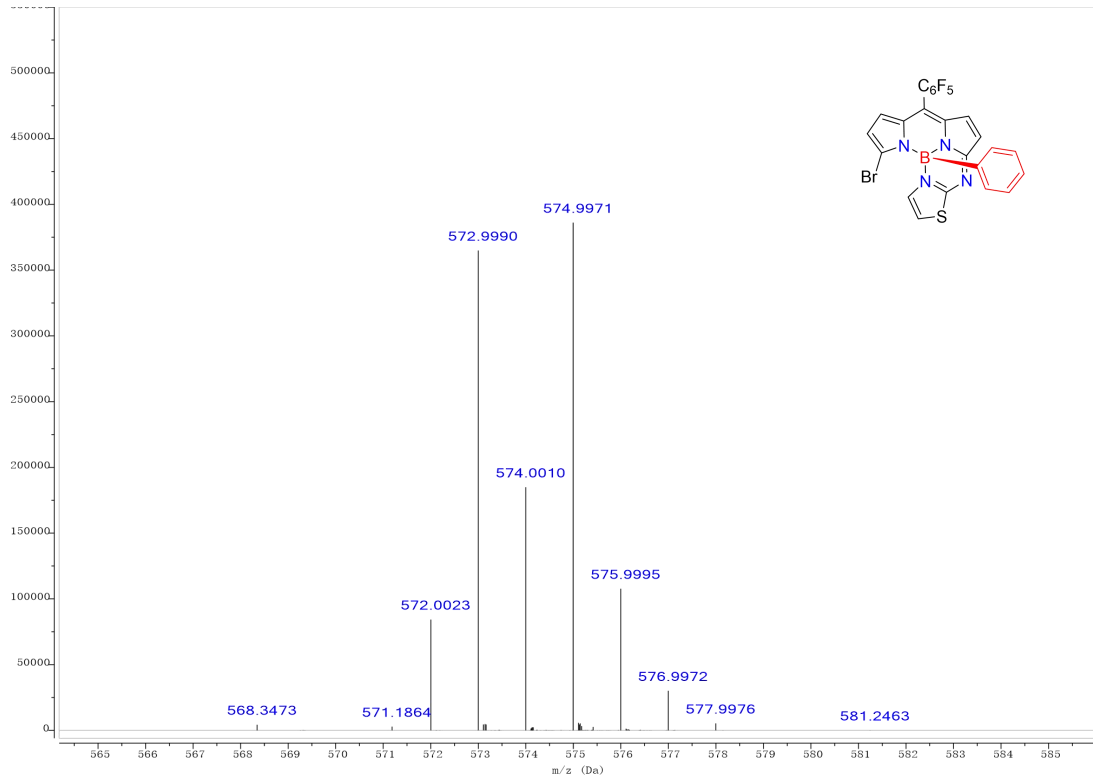

$^{11}$B NMR spectrum of **5d** in $CDCl_3$ (128 MHz)



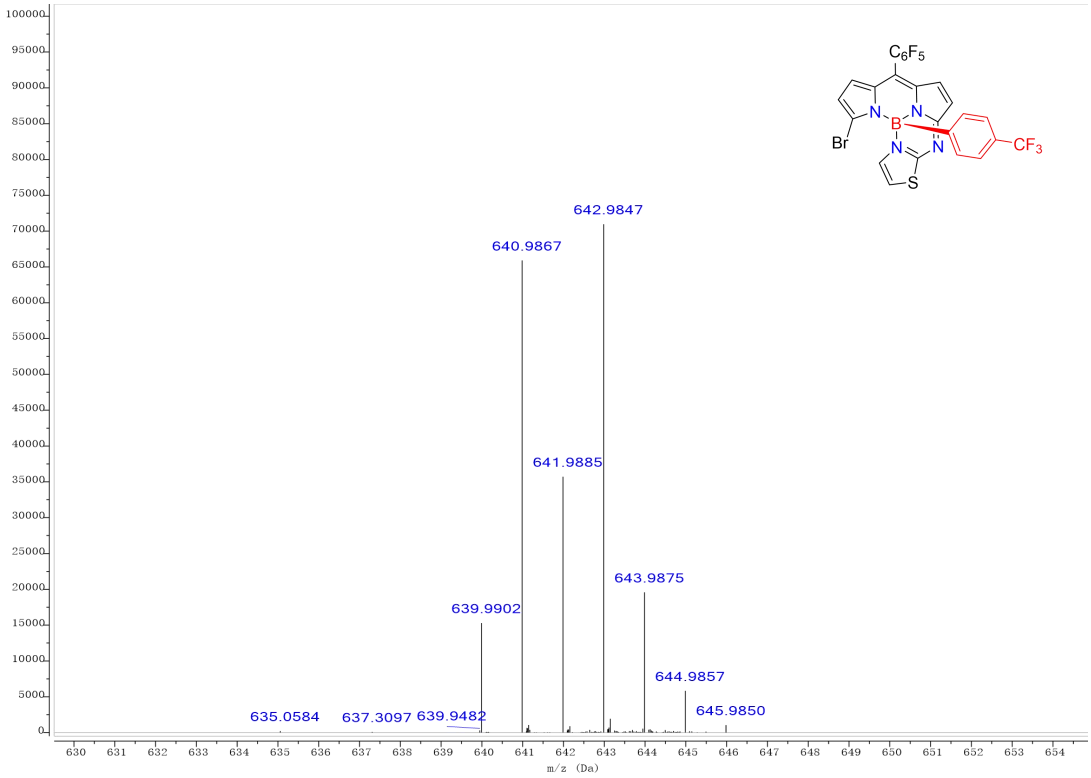

Observed HRMS for **2a**



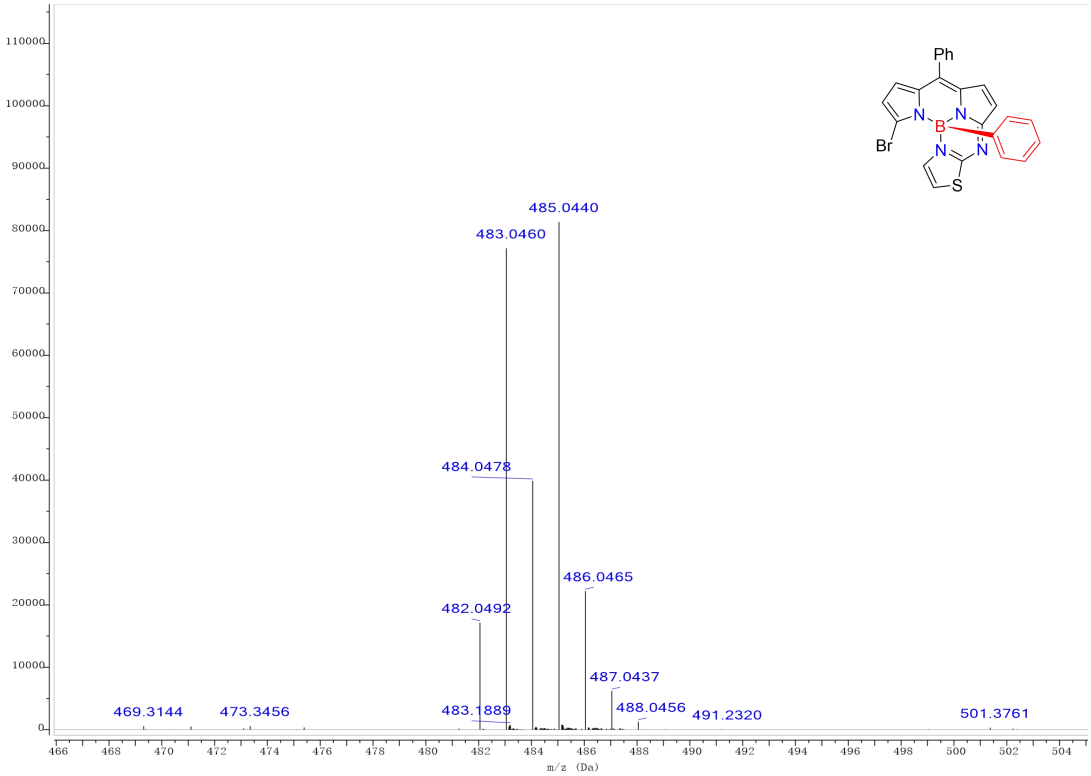

Observed HRMS for **2b**



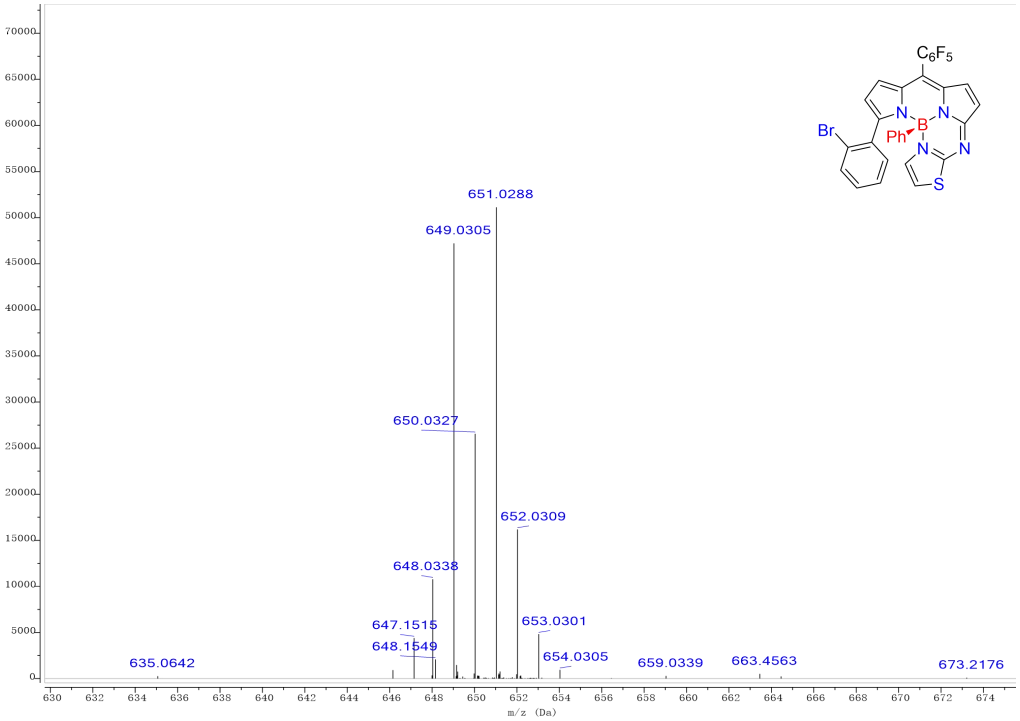

Observed HRMS for **3a**



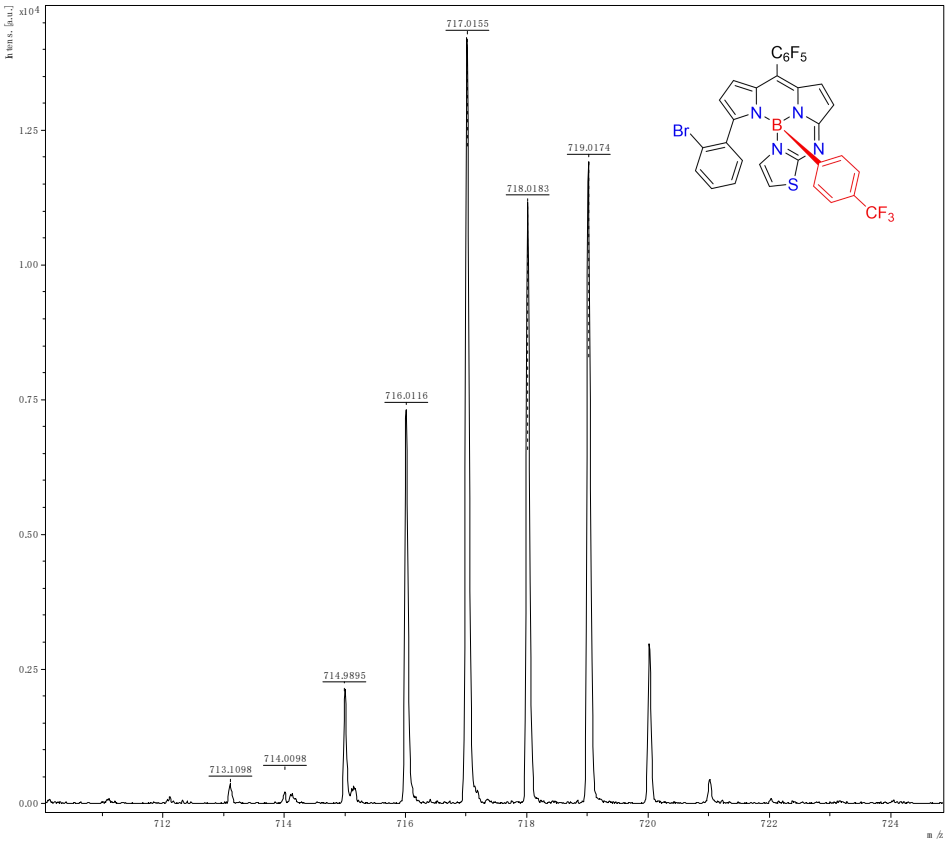

Observed HRMS for **3b**




Observed HRMS for **3c**




Observed HRMS for **4a**

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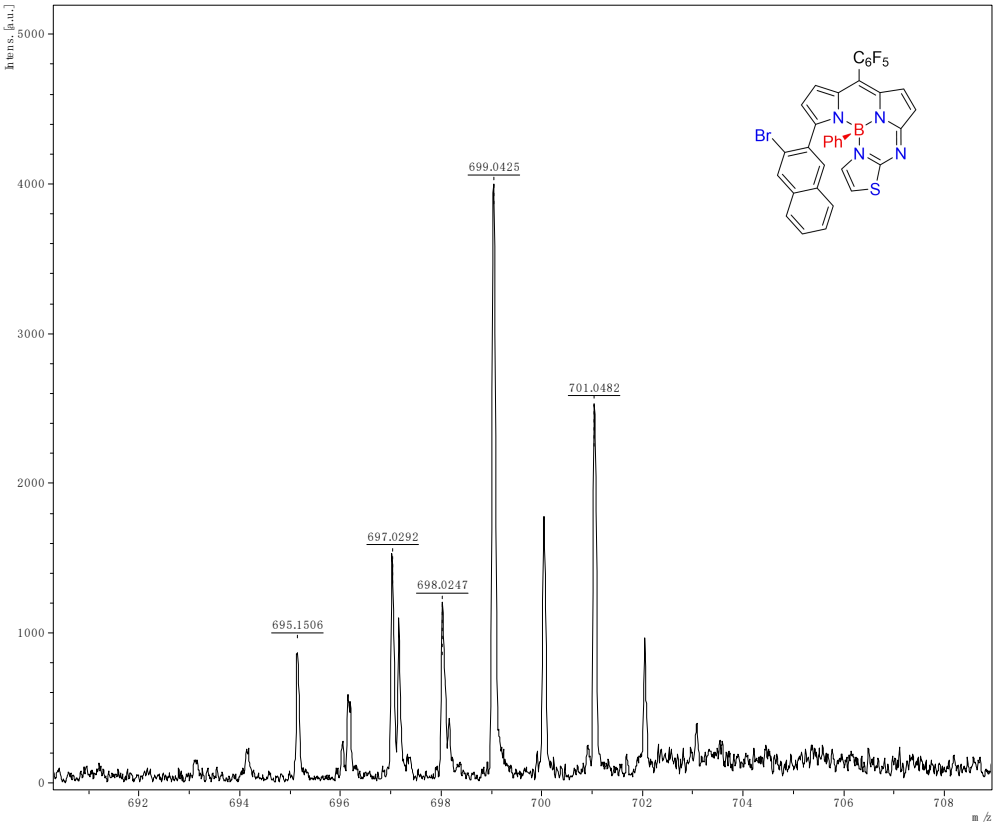
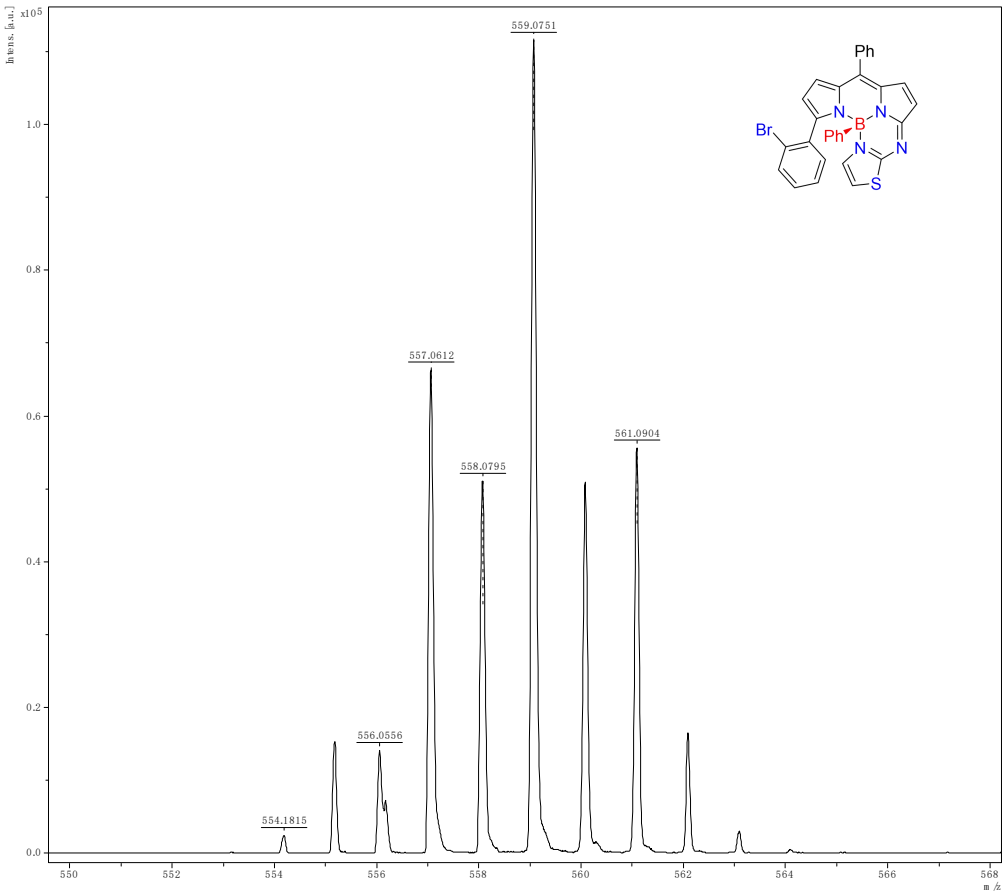
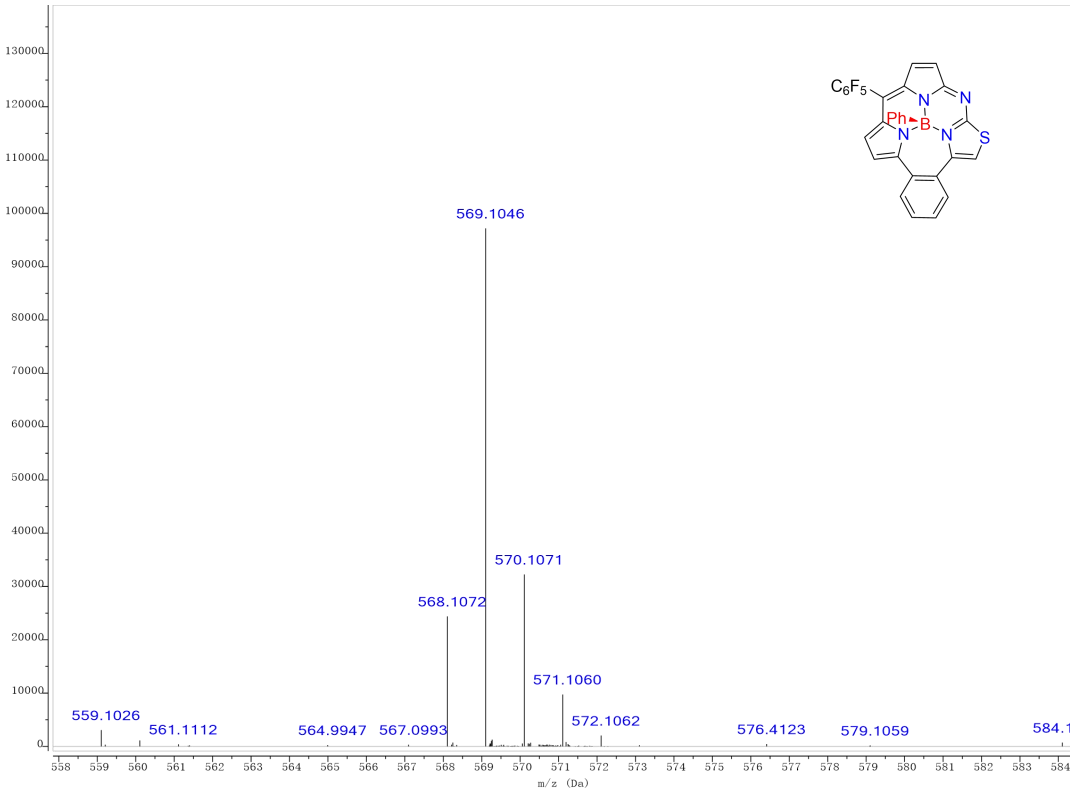


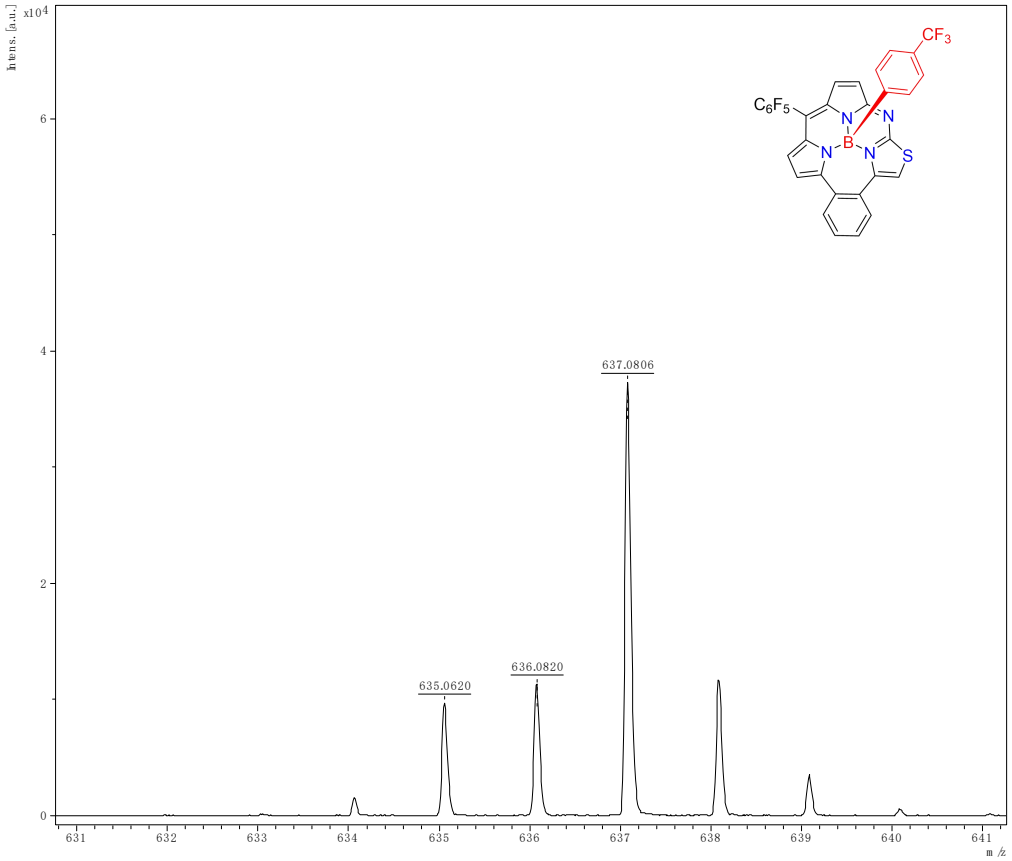

Observed HRMS for **4c**




Observed HRMS for **4d**




Observed HRMS for **5a**

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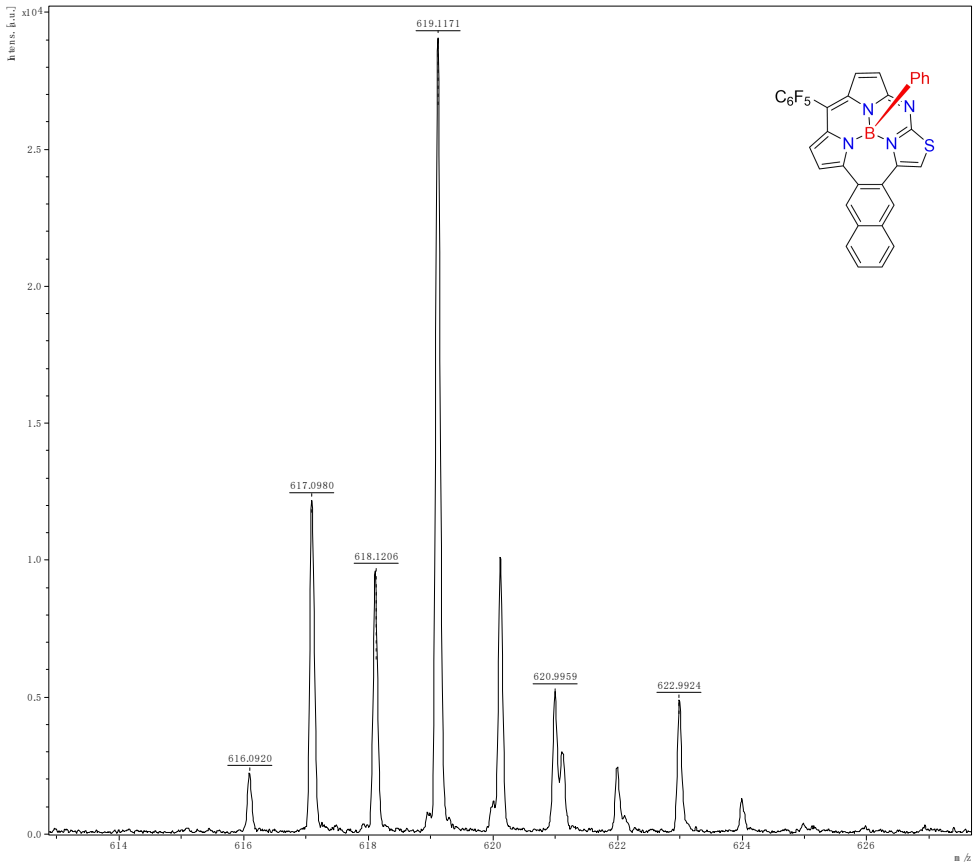
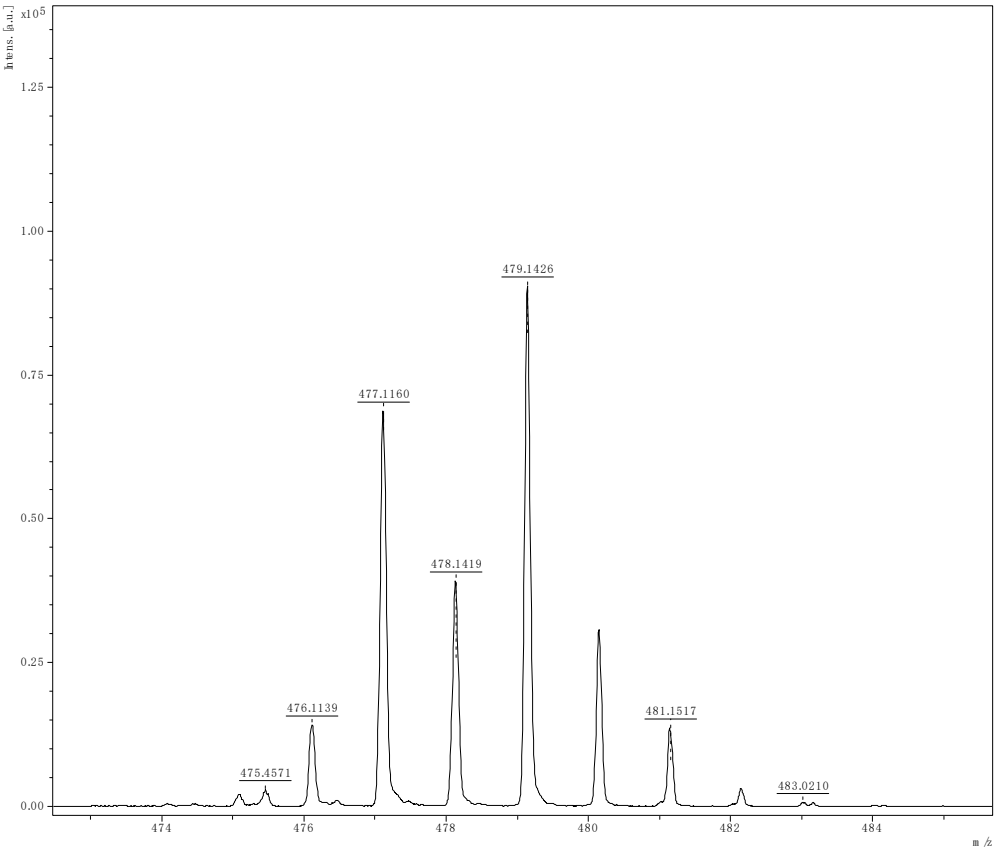



Observed HRMS for **5c**




Observed HRMS for **5d**

## 9. References

1) SAINT V 6.01 (NT) *Software for the CCD Detector System*, Bruker Analytical X-ray Systems, Madison, WI 1999.
2) SHELXL-97, *Program for the Refinement of Crystal Structure*, University of Göttingen, Germany, 1997.
3) SHELXTL 5.10 (PC/NT-Version), *Program library for Structure Solution and Molecular Graphics*, Bruker Analytical X-ray Systems, Madison, WI 1998.
4) Pawlicki, M.; Garbicz, M.; Szterenberg, L.; Latos-Grażyński, L. Oxatriphyrins(2.1.1) incorporating an ortho-phenylene motif. *Angew. Chem. Int. Ed.*, 2015, **54**, 1906.
5) Kuzuhara, D.; Xue, Z.; Mori, S.; Okujima, T.; Uno, H.; Aratania, N.; Yamada, H. Synthesis and properties of boron complexes of [14]triphyrins(2.1.1). *Chem. Commun.*, 2013, **49**, 8955.
6) Gaussian 09, Revision D.01, 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, J. A.; Montgomery, Jr., Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; R. L.; Martin, Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2013.