Electronic Supplementary Information

Near-Infrared Fluorescein Dyes Containing a Tricoodinate Boron Atom

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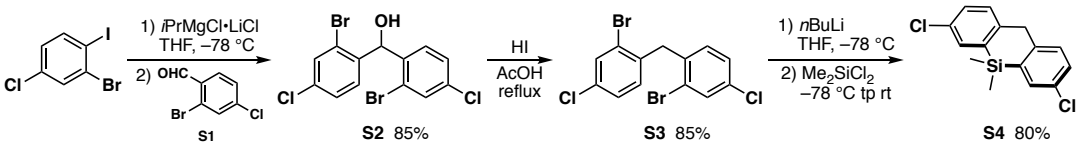
1. Experimental Details

General Procedures. Melting points (mp.) or decomposition temperatures were determined with a Yanaco MP-S3 instrument (MP-S3). ^{1}H, ^{13}C{^{1}H}, ^{11}B{^{1}H}, and ^{29}Si{^{1}H} NMR spectra were recorded with a JEOL AL-400 spectrometer in $CDCl_3$, CD_2Cl_2, CD_3OD, or acetone-d_6, (400 MHz for ^{1}H, 100 MHz for ^{13}C, 128 MHz for ^{11}B, and 79 MHz for ^{29}Si). The chemical shifts in ^{1}H NMR spectra are reported in δ ppm using the residual proton of the solvents, $CHCl_3$ (δ 7.26) in $CDCl_3$, CH_2Cl_2 (δ 5.32) in CD_2Cl_2, CH_3OH (δ 3.31) in CD_3OD, and $(CH_3)_2CO$ (δ 2.05) in acetone-d_6, as an internal standard and those in ^{13}C NMR spectra are reported using the solvent signals of $CDCl_3$ (δ 77.16), CD_2Cl_2 (δ 53.84), CD_3OD (δ 49.00), and acetone-d_6 (δ 29.84) as an internal standard. The chemical shifts in ^{11}B NMR are reported using $BF_3{\cdot}OEt_2$ (δ 0.00) as an external standard. The chemical shifts in ^{29}Si NMR are reported using Me_4Si (δ 0.00) as an external standard. Mass spectra were measured with a Bruker micrOTOF Focus spectrometry system with the ionization method of APCI or a ThermoFisher Scientific Exactive with the ionization method of ESI. Thin layer chromatography (TLC) was performed on plates coated with 0.25 mm thickness of silica gel $60F_{254}$ (Merck). Column chromatography was performed using PSQ100B (Fuji Silysia Chemicals). Recycling preparative gel permeation chromatography (GPC) was performed using LC-918 equipped with polystyrene gel columns (JAIGEL 1H and 2H, Japan Analytical Industry) using chloroform as an eluent. Anhydrous THF, Et_2O, CH_2Cl_2, and toluene were purchased from Kanto Chemicals and Wako Pure Chemical Industries, Ltd. and further purified by Glass Contour Solvent Systems. Anhydrous 1,4-dioxane was purchased from Wako Pure Chemical Industries, Ltd. 2-Bromo-4-chloro-1-iodobenzene,[1] 2-bromo-1,3-di(propen-2-yl)benzene,[2] bis(*t*-butyldimethylsiloxy)xanthone,[3] and bis(*t*-butyldimethylsiloxy)-Si-xanthone[4] were prepared according to the literature methods. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) was distilled prior to use.



Scheme S1 Synthesis of **S4**.

2-Bromo-4-chloro-benzaldehyde (S1). To a solution of 2-bromo-4-chloro-1-iodobenzene (48.8 g, 154 mmol) in anhydrous THF (500 mL) was added a THF solution of *i*PrMgCl·LiCl (2.23 M, 68.9 mL, 154 mmol) dropwise at –78 °C. After stirring at the same temperature for 2 h, anhydrous DMF

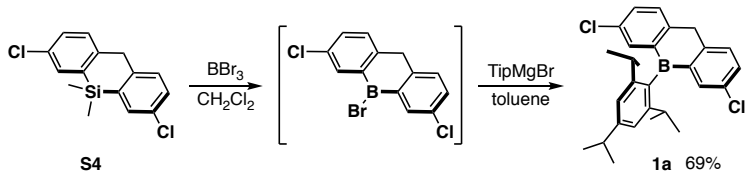
(35.0 mL, 450 mmol) was added to the mixture. The resulting mixture was gradually warmed to room temperature and stirred for 12 h. After removing solvents under reduced pressure, CH_2Cl_2 and a saturated NH_4Cl aqueous solution were added to the mixture. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 three times. The combined organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The mixture was subjected to silica gel column chromatography (CH_2Cl_2, R_f = 0.80) to afford 32.2 g (147 mmol, 95%) of **S1** as yellow solids. Analytical data were consistent with the literature data.[5]

Bis(2-boromo-4-chlorophenyl)methanol (S2). To a solution of 2-bromo-4-chloro-1-iodobenzene (46.8 g, 147 mmol) in anhydrous THF (1 L) was added a THF solution of *i*PrMgCl·LiCl (2.23 M, 66.0 mL, 147 mmol) dropwise at –78 °C. After stirring at the same temperature for 2 h, a solution of **S1** (32.2 g, 147 mmol) in anhydrous THF (200 mL) was added to the mixture at –78 °C. The mixture was gradually warmed to room temperature and stirred for 13 h. After removing the solvents under reduced pressure, Et_2O and a saturated NH_4Cl aqueous solution were added to the mixture. The organic layer was separated and the aqueous layer was extracted with Et_2O three times. The combined organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The mixture was subjected to silica gel column chromatography (CH_2Cl_2, R_f = 0.68). After removal of the solvents under reduced pressure, the resulting solids were washed with hexane to afford 51.3 g (125 mmol, 85%) of **S2** as white solids: mp. 107.3–108.2 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 7.68 (d, J_{HH} = 2.0 Hz, 2H), 7.47–7.40 (m, 4H), 6.28 (d, J_{HH} = 5.2 Hz, 2H), 5.39 (d, J_{HH} = 5.2 Hz, 2H); ^{13}C NMR (100 MHz, acetone-d_6) δ 141.9, 134.5, 133.0, 131.0, 128.7, 124.9, 73.5; HRMS (ESI) *m/z* calcd for $C_{13}H_7{}^{79}Br_2{}^{35}Cl_2O$ $[M]^-$ 408.8215, found: 408.8227.

Bis(2-bromo-4-chlorophenyl)methane (S3). To a solution of **S2** (51.3 g, 125 mmol) in acetic acid (400 mL) was added HI (57 wt% in water, 67.9 g, 303 mmol). The reaction mixture was stirred at reflux for 3 h. After cooling to room temperature, a saturated Na_2SO_3 aqueous solution was added. The mixture was extracted with ethyl acetate five times, neutralized by KOH, and washed with a saturated $NaHCO_3$ aqueous solution. The separated organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The mixture was subjected to silica gel column chromatography (CH_2Cl_2, R_f = 0.91) and further purification by recrystallization from hexane gave 41.8 g (106 mmol, 85%) of **S3** as white solids: mp. 69.2–70.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J_{HH} = 2.0 Hz, 2H), 7.22 (dd, J_{HH} = 8.4 Hz, J_{HH} = 2.0 Hz, 2H), 6.90 (d, J_{HH} = 8.4 Hz, 2H), 4.12 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.1, 133.4, 132.7, 131.4, 128.0, 125.3, 41.1; HRMS

(APCI) m/z calcd for $C_{13}H_8{}^{79}Br_2{}^{35}Cl_2$ $[M]^+$ 391.8364, found: 391.8382.

2,7-Dichloro-9,10-dihydro-9,9-dimethyl-9-silaanthracene (S4). To a solution of **S3** (1.96 g, 4.97 mmol) in anhydrous Et_2O (20 mL) was added a hexane solution of *n*BuLi (1.6 M, 6.40 mL, 10.4 mmol) dropwise at 0 °C. After stirring at the same temperature for 2 h, the mixture was cooled to –78 °C, followed by the addition of Me_2SiCl_2 (0.72 mL, 5.97 mmol) at the same temperature. The mixture was allowed to warm to room temperature and stirred for 2 h. After a saturated NH_4Cl aqueous solution was added, the organic layer was separated and the aqueous layer was extracted with Et_2O three times. The combined organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was subjected to silica gel column chromatography (hexane, R_f = 0.56) to give 1.17 g (4.00 mmol, 80%) of **S4** as white solids: mp. 89.0–89.8 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 7.63 (d, J_{HH} = 1.6 Hz, 2H), 7.40–7.33 (m, 4H), 4.13 (s, 2H), 0.52 (s, 6H); ^{13}C NMR (100 MHz, acetone-d_6) δ 145.2, 138.9, 133.4, 132.6, 130.6, 129.9, 40.2, –3.5; ^{29}Si NMR (79 MHz, acetone-d_6) δ –16.6; HRMS (APCI) *m/z* calcd for $C_{15}H_{15}{}^{35}Cl_2Si$ $[M]^+$ 293.0315, found: 293.0316.



Scheme S2 Synthesis of **1a**.

2,7-Dichloro-9-(2,4,6-triisopropylphenyl)-9,10-dihydro-9-boraanthracene (1a). To a solution of **S4** (1.76 g, 5.99 mmol) in anhydrous CH_2Cl_2 (6.0 mL) was added BBr_3 (1.40 mL, 15.1 mmol) at 0 °C. After stirring at reflux for 91 h, the volatiles were removed in vacuo at 50 °C. The resulting mixture was dissolved in anhydrous toluene (100 mL) and a THF solution of TipMgBr (0.81 M, 11.1 mL, 8.99 mmol) was added to the mixture at 0 °C. After stirring at room temperature for 22 h, water was added. The organic layer was separated and the aqueous layer was extracted with ethyl acetate three times. The combined organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The mixture was subjected to silica gel column chromatography (hexane, R_f = 0.30) to afford 1.85 g (4.11 mmol, 69%) of **1a** as white solids: mp. 213.4–214.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J_{HH} = 2.0 Hz, 2H), 7.54–7.48 (m, 4H), 7.06 (s, 2H), 4.48 (s, 2H), 2.99 (sep, J J_{HH} = 6.8 Hz, 1H), 2.15 (sep, J_{HH} = 6.8 Hz, 2H), 1.37 (d, J_{HH} = 6.8 Hz, 6H), 1.02 (d, J_{HH} = 6.8 Hz,

12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 149.0, 144.8, 137.5, 133.0, 132.1, 129.8, 120.4, 37.3 35.8, 34.4, 24.4, 24.3, two signals for the carbon atoms bound to the boron atom were not observed due to the quadrupolar relaxation; ^{11}B NMR (128 MHz, $CDCl_3$) δ 64.0; HRMS (ESI) *m*/*z* calcd for $C_{28}H_{30}{}^{11}B^{35}Cl_2$ $[M]^-$ 447.1812, found: 447.1826.

2,7-Bis(4,4,5,5-tetramehyl-1,3,3-dioxaborolan-2-yl)-9-(2,4,6-triisopropylphenyl)-9,10-dihydro-9-boraanthracene (2a). A mixture of **1a** (1.13 g, 2.50 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (51.8 mg, 50.0 μmol), XPhos (2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl) (48.0 mg, 0.100 mmol), bis(pinacolato)diboron (1.90 g, 7.48 mmol), and KOAc (1.48 g, 15.1 mmol) in degassed 1,4-dioxane (10 mL) was stirred at reflux for 11 h. After cooling to room temperature, the mixture was filtered through a pad of Celite® and concentrated under reduce pressure. The mixture was subjected to silica gel column chromatography (1/1 hexane/CH_2Cl_2, R_f = 0.40) to afford 967 mg (1.53 mmol, 61%) of **2a** as white solids: mp. 197.9–198.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J_{HH} = 1.2 Hz, 2H), 7.95 (dd, J_{HH} = 7.6 Hz, J_{HH} = 1.2 Hz, 2H), 7.52 (d, J_{HH} = 7.6 Hz, 2H), 7.07 (s, 2H), 4.54 (s, 2H), 3.02 (sep, J_{HH} = 6.8 Hz, 1H), 2.28 (sep, J_{HH} = 6.8 Hz, 2H), 1.39 (d, J_{HH} = 6.8 Hz, 6H), 1.28 (s, 24H), 1.01 (d, J_{HH} = 6.8 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 149.8, 148.0, 145.6, 138.6, 127.3, 120.0, 83.7, 39.2, 35.5, 34.5, 24.9, 24.4, 24.3, three signals for the carbon atoms bound to the boron atom were not observed due to the quadrupolar relaxation; ^{11}B NMR (128 MHz, $CDCl_3$) δ64.4, 30.7; HRMS (ESI) *m*/*z* calcd for C40H55$^{11}B_3O_4$Na $[M+Na]^+$ 655.4272, found: 655.4272.

9-(2,4,6-Triisopropylphenyl)-9,10-dihydro-2,7-dihydroxy-9-boraanthracene (3a). To a solution of **2a** (472 mg, 0.746 mmol) in degassed THF (45 mL)/acetone (6.0 mL)/H_2O (3.0 mL) was added Oxone (972 mg 1.58 mmol) at room temperature. After stirring at room temperature for 20 h, a saturated Na_2SO_3 aqueous solution and a saturated NH_4Cl aqueous solution were successively added. The organic layer was separated and the aqueous layer was extracted with ethyl acetate three times. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The mixture was subjected to silica gel column chromatography (CH_2Cl_2, R_f = 0.41) to afford 298 mg (0.723 mmol, 97%) of **3a** as white solids: mp. 194.3 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J_{HH} = 9.2 Hz, 2H), 7.10–7.08 (m, 4H), 7.05 (s, 2H), 4.58 (s, 2H), 4.42 (s, 2H), 2.98 (sep, J_{HH} = 6.8 Hz, 1H), 2.24 (sep, J_{HH} = 6.8 Hz, 2H), 1.35 (d, J_{HH} = 6.8 Hz, 6H), 1.02 (d, J_{HH} = 6.8 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 149.9, 148.5, 139.9, 129.6, 122.7, 120.7, 120.1, 36.9 35.4, 34.4, 24.5, 24.4, two signals for the carbon atoms bound to the boron atom were not observed due to the quadrupolar relaxation; ^{11}B NMR (128 MHz, $CDCl_3$) δ 63.0; HRMS (APCI) *m*/*z*

calcd for $C_{28}H_{33}{}^{11}BO_2$ $[M]^+$ 412.2568, found: 412.2575.

Dihydroxy-*B*-(2,4,6-triisopropylphenyl)xanthone 4. To a solution of **3a** (273 mg, 0.661 mmol) in MeOH (5.0 mL) was added DDQ (372 mg, 1.64 mmol) at 0 °C. After stirring at room temperature for 5 h, a saturated Na_2SO_3 aqueous solution, ethyl acetate, and a saturated NH_4Cl aqueous solution were added. After filtration, the organic layer was separated and washed with brine twice, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The mixture was subjected to silica gel column chromatography (10/1 CH_2Cl_2/ethyl acetate, R_f = 0.44) to afford 245 mg (0.574 mmol, 87%) of **4** as yellow solids: mp. 271.7 °C (decomp.); ^{1}H NMR (400 MHz, CD_3OD) δ 8.20 (d, J_{HH} = 8.4 Hz, 2H), 7.10–7.06 (m, 4H), 7.00 (d, J_{HH} = 2.8 Hz, 2H), 2.94 (sep, J_{HH} = 6.8 Hz, 1H), 2.26 (sep, J_{HH} = 6.8 Hz, 2H), 1.31 (d, J_{HH} = 6.8 Hz, 6H), 1.09 (d, J_{HH} = 6.8 Hz, 12H), the signal for the OH moiety was not observed; ^{13}C NMR (100 MHz, CD_3OD) δ 188.1, 163.3, 151.1, 150.6, 131.7, 131.5, 125.0, 121.8, 121.2, 37.3, 35.9, 24.7, 24.4, two signals for the carbon atoms bound to the boron atom were not observed due to the quadrupolar relaxation; ^{11}B NMR (128 MHz, CD_3OD) δ 65.7; HRMS (ESI) *m*/*z* calcd for $C_{28}H_{30}{}^{11}BO_3$ $[M]^-$ 425.2282, found: 425.2296.

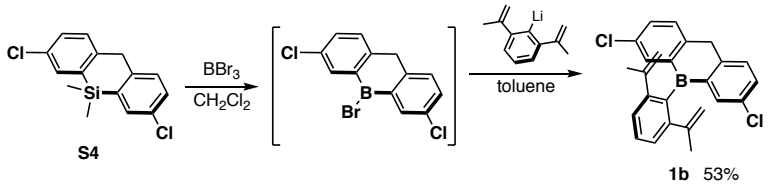
Bis(*t*-butyldimethylsiloxy)-*B*-(2,4,6-triisopropylphenyl)xanthone 5. A mixture of **4** (646 mg, 1.51 mmol), imidazole (512 mg, 7.51 mmol), and *t*-butylchlorodimethylsilane (1.13 g, 7.50 mmol) in anhydrous CH_2Cl_2 (75 mL) was stirred at room temperature for 11 h. After a saturated $NaHCO_3$ aqueous solution was added, the organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 three times. The combined organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The mixture was subjected to silica gel column chromatography (1/1 hexane/CH_2Cl_2, R_f = 0.51) to afford 889 mg (1.36 mmol, 90%) of **5** as yellow solids: mp. 178.6–179.4 °C; 1H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, J_{HH} = 8.8 Hz, 2H), 7.10 (dd, J_{HH} = 8.8 Hz, J_{HH} = 2.4 Hz, 2H), 7.05 (s, 2H), 6.97 (d, J_{HH} = 2.4 Hz, 2H), 2.97 (sep, J_{HH} = 6.8 Hz, 1H), 2.27 (sep, J_{HH} = 6.8 Hz, 2H), 1.32 (d, J_{HH} = 6.8 Hz, 6H), 1.04 (d, J_{HH} = 6.8 Hz, 12H), 0.91 (s, 18H), 0.09 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.9, 160.0, 149.8, 149.3, 132.3, 130.5, 128.1, 125.7, 120.1, 35.9, 34.6, 25.7, 24.4, 24.4, 18.3, –4.2, two signals for the carbon atoms bound to the boron atom were not observed due to the quadrupolar relaxation; ^{11}B NMR (128 MHz, $CDCl_3$) δ 66.1; HRMS (ESI) *m*/*z* calcd for $C_{40}H_{59}{}^{11}BO_3Si_2Na$ $[M+Na]^+$ 677.3988, found: 677.3989.

***o*-Tolyl-substituted *B*-(2,4,6-triisopropylphenyl)-bora-fluorescein BF1.** To a solution of **5** (131 mg, 0.201 mmol) in anhydrous THF (2.0 mL) was added a THF solution of *o*-tolylMgBr (1.62 M, 0.37

mL, 0.60 mmol) at room temperature. After stirring at the same temperature for 14 h, 1 N hydrochloric acid (5.0 mL), CH_2Cl_2 (10 mL), and *p*-toluenesulfonic acid monohydrate (157 mg, 0.825 mmol) were added. After stirring at room temperature for additional 4 h, the organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 three times. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was subjected to silica gel column chromatography (50/1 CH_2Cl_2/ethyl acetate, R_f = 0.46) and recrystallized by slow diffusion of hexane into a solution of crude product in CH_2Cl_2 to afford 59.3 mg (0.118 mmol, 59%) of **BF1** as deep purple solids: mp. 233.7 °C (decomp); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.45–7.34 (m, 3H), 7.23 (d, J_{HH} = 7.6 Hz, 1H), 7.05 (s, 2H), 6.95 (d, J_{HH} = 2.4 Hz, 2H), 6.90 (d, J_{HH} = 9.2 Hz, 2H), 6.53 (d, J_{HH} = 9.2 Hz, 2H), 2.93 (sep, J_{HH} = 6.8 Hz, 1H), 2.32–2.25 (m, 2H), 2.14 (s, 3H), 1.31 (d, J_{HH} = 6.8 Hz, 6H), 1.10–1.08 (m, 12H), the signal for the OH group was not observed; ^{13}C NMR (100 MHz, CD_2Cl_2) δ 155.9, 155.7, 150.5, 149.7, 143.2, 137.8, 137.6, 136.8, 135.1, 131.7, 130.6, 129.7, 128.8, 126.1, 124.7, 120.71, 120.67, 36.6, 36.5, 34.8, 24.32, 24.29, 24.26, 19.8, two signals for the carbon atoms bound to the boron atom were not observed due to the quadrupolar relaxation; ^{11}B NMR (128 MHz, CD_2Cl_2) δ 65.9; HRMS (APCI) *m*/*z* calcd for $C_{35}H_{39}{}^{11}BO_2$ [*M*+H]+ 501.2959, found: 501.2974.

2,6-Dimethoxyphenyl-substituted *B*-(2,4,6-triisopropylphenyl)-bora-fluorescein BF2. To a solution of **5** (524 mg, 0.800 mmol) in anhydrous THF (8.0 mL) was added a THF solution of 2,6-dimethoxyphenylMgBr (0.86 M, 2.80 mL, 2.41 mmol) at room temperature. After stirring for 14 h at the same temperature, 1 N hydrochloric acid (10 mL), CH_2Cl_2 (30 mL), and *p*-toluenesulfonic acid monohydrate (528 mg, 2.78 mmol) were added. After stirring at room temperature for additional 4 h, the organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 three times. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was subjected to silica gel column chromatography (10/1 CH_2Cl_2/ethyl acetate, R_f = 0.71) and recrystallized by slow diffusion of hexane into a solution of crude product in CH_2Cl_2 to afford 346 mg (0.632 mmol, 79%) of **BF2** as deep purple solids: mp. >300 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 9.03 (s, 1H), 7.52 (t, J_{HH} = 8.4 Hz, 1H), 7.16–7.14 (m, 3H), 7.03 (d, J_{HH} = 10.0 Hz, 1H), 6.97–6.92 (m, 2H), 6.88 (d, J_{HH} = 8.0 Hz, 2H), 6.60 (d, J_{HH} = 2.0 Hz, 1H), 6.14 (dd, J_{HH} = 10.0 Hz, J_{HH} = 2.0 Hz, 1H), 3.73 (s, 6H), 2.99 (sep, J_{HH} = 6.8 Hz, 1H), 2.35 (sep, J_{HH} = 6.8 Hz, 2H), 1.33 (d, J_{HH} = 6.8 Hz, 6H), 1.14–1.11 (m, 12H); ^{13}C NMR (100 MHz, acetone-d_6) δ 187.8, 160.0, 158.9, 150.9, 150.3, 150.0, 143.5, 141.6, 135.0, 133.3, 131.5, 129.8, 128.0, 126.9, 122.4, 121.1, 115.2, 105.0, 56.4, 36.8, 35.2, 24.52, 24.46, 24.2, three signals for the carbon atoms bound to

the boron atom were not observed due to the quadrupolar relaxation, one signal for the aromatic carbon atom was not observed due to the overlap with other signals; ^{11}B NMR (128 MHz, acetone-d_6) δ 66.6; HRMS (ESI) *m*/*z* calcd for $C_{36}H_{38}{}^{11}BO_4$ $[M]^-$ 545.2858, found: 545.2872.



Scheme S3 Synthesis of **1b**

2,7-Dichloro-9-[2,6-di(propen-2-yl)phenyl]-9,10-dihydro-9-boraanthracene (1b). To a solution of **S4** (1.48 g, 5.05 mmol) in anhydrous CH_2Cl_2 (5.0 mL) was added BBr_3 (1.20 mL, 12.9 mmol) at 0 °C. After stirring at reflux for 90 h, the volatiles were removed in vacuo at 50 °C. The resulting mixture was dissolved in anhydrous toluene (20 mL) and a toluene solution of 2,6-di(propen-2-yl)phenyllithium, which was prepared from 2-bromo-1,3-di(propen-2-yl)benzene (1.33 g, 5.63 mmol) and *n*BuLi (1.6 M, 3.50 mL, 5.60 mmol) in anhydrous toluene (20 mL),[2] was added at room temperature. The mixture was then stirred at 50 °C for 15 h. After a saturated NH_4Cl aqueous solution was added, the organic layer was separated and the aqueous layer was extracted with ethyl acetate three times. The combined organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The mixture was subjected to silica gel column chromatography (hexane, R_f = 0.33) followed by preparative GPC ($CHCl_3$) to afford 1.09 g (2.69 mmol, 53%) of **1b** as white solids: mp. 197.0–197.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J_{HH} = 2.0 Hz, 2H),7.47–7.37 (m, 9H), 4.62 (s, 2H), 4.41 (s, 2H), 4.34 (s, 2H), 1.97 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 147.1, 143.7, 136.0, 131.9, 131.8, 129.7, 127.8, 125.6, 117.3, 37.2, 24.0, two signals for the carbon atoms bound to the boron atom were not observed due to the quadrupolar relaxation; ^{11}B NMR (128 MHz, $CDCl_3$) δ 58.4; HRMS (ESI) *m*/*z* calcd for $C_{25}H_{20}{}^{11}B^{35}Cl_2$ $[M]^-$ 401.1030, found: 401.1046.

2,7-Bis(4,4,5,5-tetramehyl-1,3,3-dioxaborolan-2-yl)-9-[2,6-di(propen-2-yl)phenyl]-9,10-dihydro-9-boraanthracene (2b). A mixture of **1b** (763 mg, 1.89 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (39.5 mg, 38.2 μmol), XPhos (35.8 mg, 75.1 μmmol), bis(pinacolato)diboron (1.45 g, 5.69 mmol), and KOAc (1.12 g, 11.4 mmol) in degassed 1,4-dioxane (8.0 mL) was stirred at reflux for 18 h. After cooling to room temperature, the mixture was filtered through a pad of Celite® and concentrated under reduce pressure. The mixture was subjected to silica gel column chromatography (1/1 hexane/CH_2Cl_2, R_f =

0.37) to afford 852 mg (1.45 mmol, 77%) of **2b** as white solids: mp. 231.0 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J_{HH} = 1.2 Hz, 2H), 7.89 (dd, J_{HH} = 7.6 Hz, J_{HH} = 1.2 Hz, 2H), 7.45–7.42 (m, 3H), 7.38–7.36 (m, 2H), 4.55 (s, 2H), 4.43–4.42 (m, 4H), 1.97 (s, 6H), 1.30 (s, 24H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 148.2, 147.6, 144.2, 137.5, 127.2, 127.0, 125.3, 117.1, 83.7, 39.0, 24.9, 23.7, three signals for the carbon atoms bound to the boron atom were not observed due to the quadrupolar relaxation; ^{11}B NMR (128 MHz, $CDCl_3$) δ 59.0, 30.3; HRMS (ESI) *m*/*z* calcd for $C_{37}H_{45}{}^{11}B_3O_4Na$ $[M+Na]^+$ 609.3489, found: 609.3494.

2,7-Hydroxy-9-[2,6-Di(propen-2-yl)phenyl]-9,10-dihydro-9-bora-anthracene (3b). To a solution of **2b** (616 mg, 1.05 mmol) in a degassed THF (60 mL)/acetone (8.0 mL)/H_2O (4.0 mL) mixed solvent was added Oxone (1.36 g 2.21 mmol) at room temperature. After stirring at same temperature for 14 h, a saturated Na_2SO_3 aqueous solution and a saturated NH_4Cl aqueous solution were added. The organic layer was separated and the aqueous layer was extracted with ethyl acetate three times. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was subjected to silica gel column chromatography (30/1 CH_2Cl_2, R_f = 0.47) to afford 345 mg (0.942 mmol, 90%) of **3b** as pale yellow solids: mp. 217.6 °C (decomp); ^{1}H NMR (400 MHz, acetone-d_6) δ 8.05 (s, 2H), 7.46–7.42 (m, 1H), 7.39–7.35 (m, 4H), 7.03–7.00 (m, 4H), 4.59–4.58 (m, 2H), 4.47 (m, 2H), 4.25 (s, 2H), 1.94–1.93 (m, 6H); ^{13}C NMR (100 MHz, acetone-d_6) δ 155.7, 148.5, 147.4, 138.6, 130.1, 127.8, 126.0, 122.0, 120.7, 116.7, 37.1, 24.2, two signals for the carbon atoms bound to the boron atom were not observed due to the quadrupolar relaxation; ^{11}B NMR (128 MHz, acetone-d_6) δ 59.4; HRMS (APCI) *m*/*z* calcd for $C_{25}H_{22}{}^{11}BO_2$ $[M]^-$ 365.1707, found: 365.1723.

Dihydroxy-substituted *B*-phenyl-planarized xanthone 6. A mixture of **3b** (210 mg, 0.574 mmol) and $Sc(OTf)_3$ (286 mg, 0.580 mmol) in anhydrous 1,2-dichloroethane (150 mL) was stirred at reflux for 1 h. After cooling to room temperature, the solvents were removed under reduced pressure. After addition of ethyl acetate and H_2O, the organic layer was separated, and the aqueous layer was extracted with ethyl acetate three times. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting mixture was dissolved into MeOH (10 mL) followed by addition of DDQ (323 mg, 1.42 mmol) at 0 °C. After stirring at room temperature for 10 h, a saturated Na_2SO_3 aqueous solution, ethyl acetate, and a saturated NH_4Cl aqueous solution were successively added. After filtration, the organic layer was separated and washed with brine three times, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The mixture was

subjected to silica gel column chromatography (10/2/1 CH_2Cl_2/ethyl acetate/MeOH, R_f = 0.53) to afford 179 mg (0.472 mmol, 82%) of **6** as yellow solids: mp. >300 °C; ^{1}H NMR (400 MHz, CD_3OD) δ 8.14 (d, J_{HH} = 8.4 Hz, 2H), 7.82–7.78 (m, 1H), 7.74–7.72 (m, 2H), 7.17 (d, J_{HH} = 8.4 Hz, 2H), 1.92 (s, 12H), the signal for the OH moiety was not observed; ^{13}C NMR (100 MHz, CD_3OD) δ 189.9, 161.5, 160.7, 141.8, 135.3, 131.6, 129.3, 125.0, 122.0, 44.0, 29.1, two signals for the carbon atoms bound to the boron atom were not observed due to the quadrupolar relaxation; ^{11}B NMR (128 MHz, CD_3OD) δ 46.8; HRMS (ESI) *m*/*z* calcd for $C_{25}H_{20}{}^{11}BO_3$ $[M]^-$ 379.1500, found: 379.1510.

Bis(trimethylsiloxy)-substituted *B*-phenyl-planarized xanthone 7. To a mixture of **6** (287 mg, 0.755 mmol) and imidazole (260 mg, 3.82 mmol) in anhydrous CH_2Cl_2 (80 mL) was added chlorotrimethylsilane (0.48 mL, 3.80 mmol) at room temperature. After stirring at the same temperature for 16 h, the mixture was filtered through a pad of Celite®. After removal of solvents, the mixture was passed through a short silica gel column (CH_2Cl_2) to afford 272 mg (0.519 mmol, 69%) of **7** as pale yellow solids: mp. 194.1 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, J_{HH} = 8.4 Hz, 2H), 7.82–7.78 (m, 1H), 7.68 (d, J_{HH} = 7.6 Hz, 2H), 7.15 (d, J_{HH} = 8.4 Hz, 2H), 1.89 (s, 12H), 0.48 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.0, 159.1, 157.8, 143.7, 134.0, 131.8, 128.3, 124.0, 123.5, 42.9, 29.2, 0.94, two signals for the carbon atoms bound to the boron atom were not observed due to the quadrupolar relaxation; ^{11}B NMR (128 MHz, $CDCl_3$) δ 45.6; HRMS (APCI) *m*/*z* calcd for $C_{31}H_{38}{}^{11}BO_3Si_2$ $[M+H]^+$ 525.2447, found: 525.2444.

2,6-Dimethoxyphenyl-substituted *B*-phenyl-planarized bora-fluorescein BF3. To a solution of **7** (79.9 mg, 0.152 mmol) in anhydrous THF (2.0 mL) was added a THF solution of 2,6-dimethoxyphenylMgBr (0.91 M, 0.49 mL, 0.45 mmol) at room temperature. After stirring at the same temperature for 9 h, 1 N hydrochloric acid (5 mL), CH_2Cl_2 (10 mL), and *p*-toluenesulfonic acid monohydrate (101 mg, 0.533 mmol) were successively added. After stirring at room temperature for 3 h, the organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 three times. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The mixture was subjected to silica gel column chromatography (20/1 CH_2Cl_2/ethyl acetate, R_f = 0.64) and further purified by recrystallization from hexane and CH_2Cl_2 to afford 19.3 mg (38.6 μmol, 25%) of **BF3** as purple solids: mp. 228.7 °C (decomp); ^{1}H NMR (400 MHz, acetone-d_6) δ 9.45 (s, 1H), 7.89–7.80 (m, 3H), 7.51 (t, J_{HH} = 8.4 Hz, 1H), 7.06 (d, J_{HH} = 8.4 Hz, 1H), 7.00 (d, J_{HH} = 10.0 Hz, 1H), 6.90–6.87 (m, 3H), 6.23 (d, J_{HH} = 10.0 Hz, 1H), 3.69 (s, 6H), 1.97 (s, 6H), 1.82 (s, 6H); ^{13}C NMR (100 MHz, acetone-d_6) δ 186.6, 160.1, 159.8, 159.1, 158.0, 156.9, 150.5, 143.5, 139.1,

134.7, 134.1, 131.2, 130.8, 130.5, 128.9, 124.6, 124.4, 122.6, 115.7, 104.9, 56.3, 44.7, 43.9, two signals for the carbon atoms bound to the boron atom were not observed due to the quadrupolar relaxation; ^{11}B NMR (128 MHz, acetone-d_6) δ 46.3; HRMS (ESI) *m*/*z* calcd for $C_{33}H_{28}{}^{11}BO_4$ $[M]^-$ 499.2075, found: 499.2087.

2,6-Dimethoxyphenyl-substituted fluorescein OF. To a solution of bis(*t*-butyldimethysiloxy)xanthone (184 mg, 0.402 mmol) in anhydrous THF (10 mL) was added a THF solution of 2,6-dimethoxyphenylMgBr (0.91 M, 2.20 mL, 2.00 mmol) at 0 °C. After stirring at room temperature for 15 h, the mixture was concentrated to a ca. 1/5 volume under reduced pressure and 2 N hydrochloric acid (10 mL) was added. The solid was collected by filtration, and washed with H_2O and Et_2O. The resulting solid was recrystallized by slow diffusion of Et_2O into a solution of crude product in MeOH to afford 130 mg (0.373 mmol, 93%) of **OF** as yellow solids: mp. >300 °C; ^{1}H NMR (400 MHz, CD_3OD) δ 7.72–7.67 (m, 3H), 7.34 (d, J_{HH} = 2.0 Hz, 2H), 7.22 (dd, J_{HH} = 9.6 Hz, J_{HH} = 2.0 Hz, 2H), 6.98 (d, J_{HH} = 8.4 Hz, 2H), 3.69 (s, 6H), the signal for the OH moiety was not observed; ^{13}C NMR (100 MHz, CD_3OD) δ 172.9, 164.9, 161.0, 158.9, 134.8, 134.6, 121.3, 118.6, 109.3, 105.6, 103.2, 56.6; HRMS (ESI) *m*/*z* calcd for $C_{21}H_{15}O_5$ $[M]^-$ 347.0914, found: 347.0925.

2,6-Dimethoxyphenyl-substituted sila-fluorescein SiF. To a solution of bis(*t*-butyldimethysiloxy)-Si-xanthone (97.7 mg, 0.196 mmol) in anhydrous THF (5.0 mL) was added a THF solution of 2,6-dimethoxyphenylMgBr (0.86 M, 1.16 mL, 1.00 mmol) at room temperature. The mixture was stirred at the same temperature for 15 h. After 1 N hydrochloric acid (10 mL) was added, the organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 three times. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The mixture was subjected to silica gel column chromatography (ethyl acetate, R_f = 0.75). Further purification by recrystallization from hexane and CH_2Cl_2 afforded 63.1 mg (0.162 mmol, 83%) of **SiF** as red solids: mp. 244.9–245.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (t, J_{HH} = 8.4 Hz, 2H), 7.04 (d, J_{HH} = 9.2 Hz, 2H), 6.99 (d, J_{HH} = 2.4 Hz, 2H), 6.66 (d, J_{HH} = 8.4 Hz, 2H), 6.51 (dd, J_{HH} = 9.2 Hz, J_{HH} = 2.4 Hz, 2H), 3.65 (s, 6H), 0.39 (s, 6H), the signal for the OH moiety was not observed; ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 157.7, 145.1, 139.3, 131.1, 130.3, 128.6, 122.2, 116.9, 104.0, 56.2, –1.4; ^{29}Si NMR (79 MHz, $CDCl_3$) δ –20.5; HRMS (ESI) *m*/*z* calcd for $C_{23}H_{21}O_4Si$ $[M]^-$ 389.1204, found: 389.1216.

2. X-ray Crystallographic Analysis

Structural analysis of BF2. Plate-shape purple single crystals of **BF2** were obtained by slow diffusion of hexane into a solution of **BF2** in dichloromethane. The intensity data were collected at 93 K. A total of 24549 reflections were measured at the maximum 2θ angle of 55°, of which 10095 were independent reflections (R_{int} = 0.0419). The structure was solved by direct methods (SHELXL-2017/1)[6] and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-2017/1). All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: $C_{36}H_{39}BO_4$; FW = 546.48, Monoclinic, $P\,2_1$, a = 10.3101(3) Å, b = 18.3821(5) Å, c = 16.3489(4) Å, β = 93.091(2)°, V = 3093.96(14) Å^3, Z = 4, D_c = 1.173 g cm^{-3}, μ = 0.091 mm^{-1}, R_1 = 0.0425 ($I > 2\sigma(I)$), wR_2 = 0.1110 (all data), GOF = 1.134. CCDC 1913398 contains the supplementary crystallographic data for this compound. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

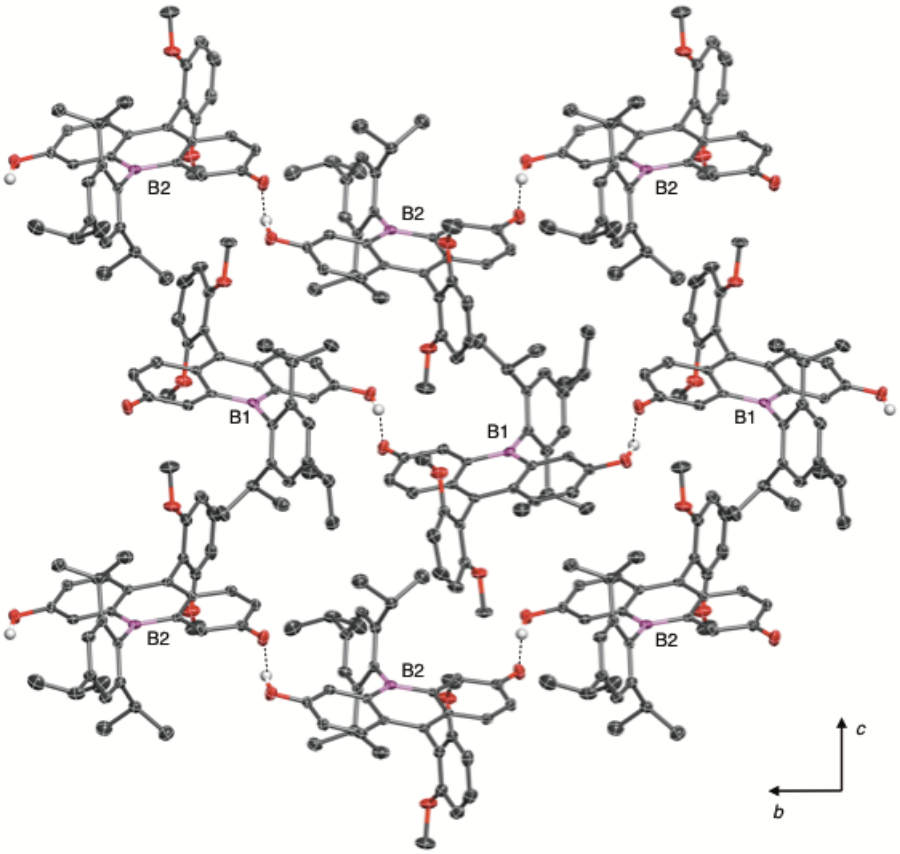


Fig. S1 Packing structure of **BF2**.

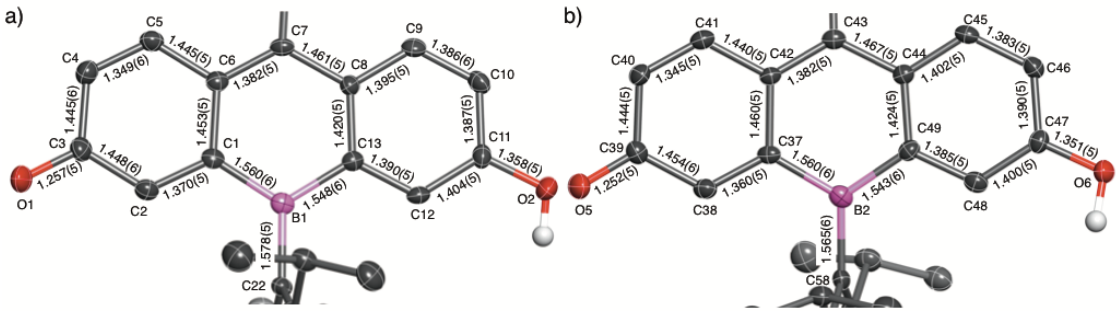


Fig. S2 Selected bond lengths (Å) of **BF2**: a) molecule A and b) molecule B.

Structural analysis of BF3. Plate-shape purple single crystals of **BF3** were obtained by slow diffusion of hexane into a solution of **BF3** in ethyl acetate. The intensity data were collected at 123 K. A total of 43491 reflections were measured at the maximum 2θ angle of 55°, of which 7766 were independent reflections (R_{int} = 0.0773). The structure was solved by direct methods (SHELXL-2017/1)[6] and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-2017/1). All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: $C_{35.4}H_{34.6}BO_4$; FW = 534.84, Orthorhombic, *Pna* 2_1, a = 13.313(2) Å, b = 11.317(2) Å, c = 22.471(4) Å, V = 3385.5(11) Å^3, Z = 4, Dc = 1.049 g cm^{-3}, μ = 0.067 mm^{-1}, R_1 = 0.0616 ($I > 2\sigma(I)$), wR_2 = 0.1706 (all data), GOF = 1.026. CCDC 1913399 contains the supplementary crystallographic data for this compound. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

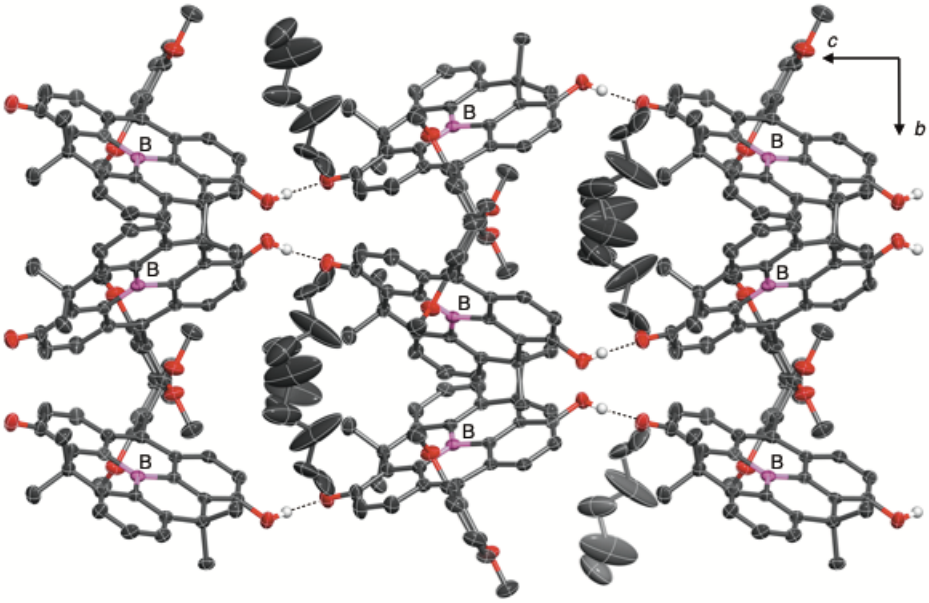


Fig. S3 Packing structure of **BF3**.

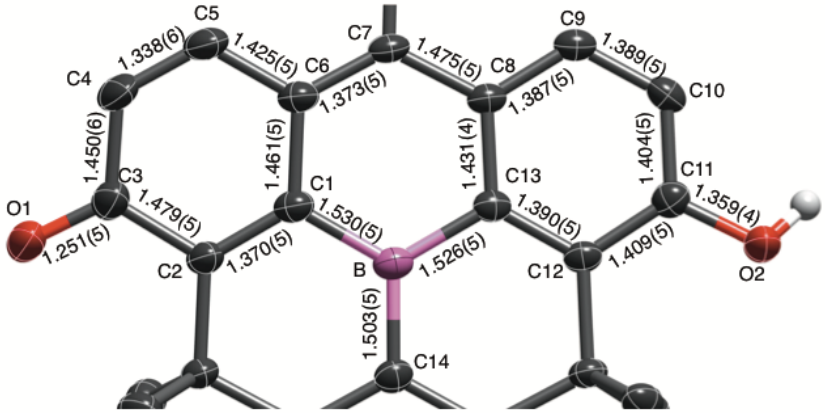


Fig. S4 Selected bond lengths (Å) of **BF3**.

3. Photophysical Properties

Methods. UV-vis-NIR absorption spectra were measured with a Shimadzu UV-3600 Plus spectrometer using dilute sample solutions in dried and degassed CH_3CN in a 1 cm square quartz cuvette. Fluorescence spectra were recorded on a JASCO FP-8500 spectrofluorometer. NIR emission spectra were measured with a Horiba SPEX Fluorolog 3 spectrofluorometer equipped with a Hamamatsu PMA R5509-73 and a cooling system C9940-01. Fluorescence quantum yields were determined with a Hamamatsu photonics C9920-02 calibrated integrating sphere system, with a multichannel spectrometer PMA12 for borate-anion $[\mathbf{BF}\cdot F]^{2-}$ in CH_3CN with an excess amount of TBAF, and with two photonic multichannel analyzers C10027-02 and C10028-01 for the others.

Chemical Stability of BF1 and BF2. The chemical stability of neutral **BF1** and **BF2** were compared by UV-vis absorption spectra in CH_2Cl_2 and CH_3CN without any additives (Fig. S5).

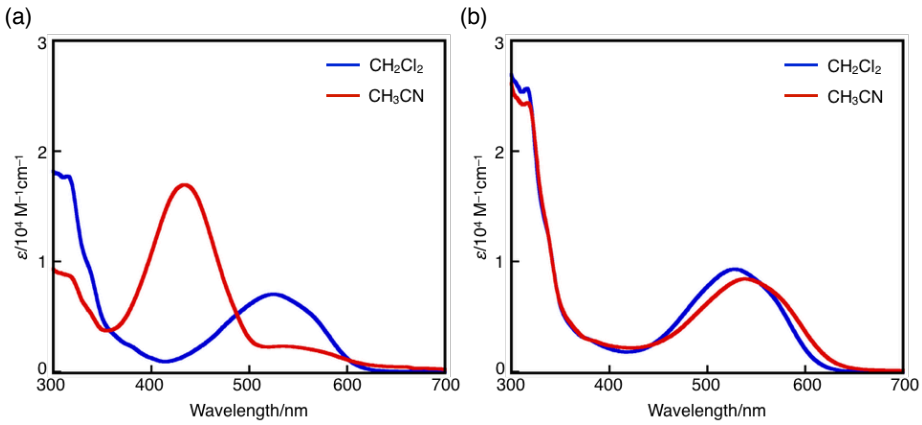


Fig. S5 UV-vis absorption spectra of (a) **BF1** in CH_2Cl_2 (2.3×10^{-5} M, blue) and CH_3CN (2.4×10^{-5} M, red), and (b) **BF2** in CH_2Cl_2 (3.1×10^{-5} M, blue) and CH_3CN (3.2×10^{-5} M, red).

Monitoring the deprotonation of BFs by UV-vis Absorption Spectroscopy. To a dried and degassed CH_3CN solution of **BF**s in a 1 cm square quartz cuvette was added an CH_3CN solution of DBU. UV-vis-NIR absorption spectra were measured with a Shimadzu UV-3600 Plus spectrometer.

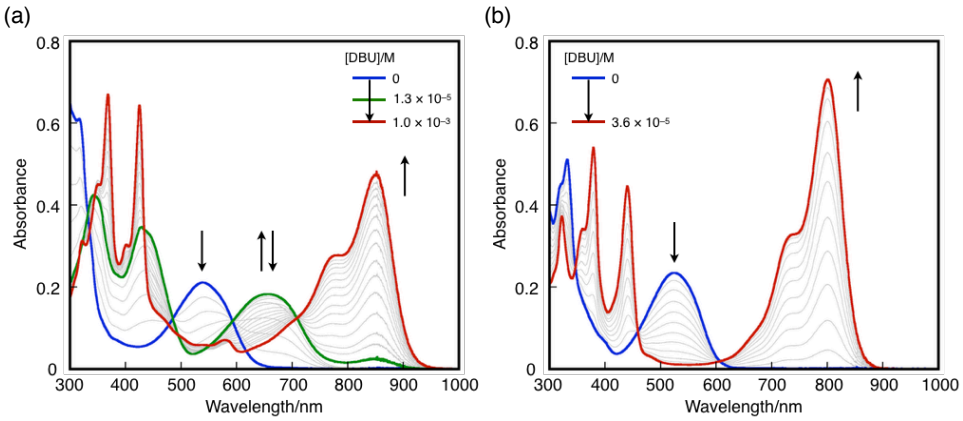


Fig. S6 UV-vis absorption spectral changes upon addition of DBU to an acetonitrile solution of (a) **BF2** (2.5×10^{-5} M) and (b) **BF3** (2.1×10^{-5} M).

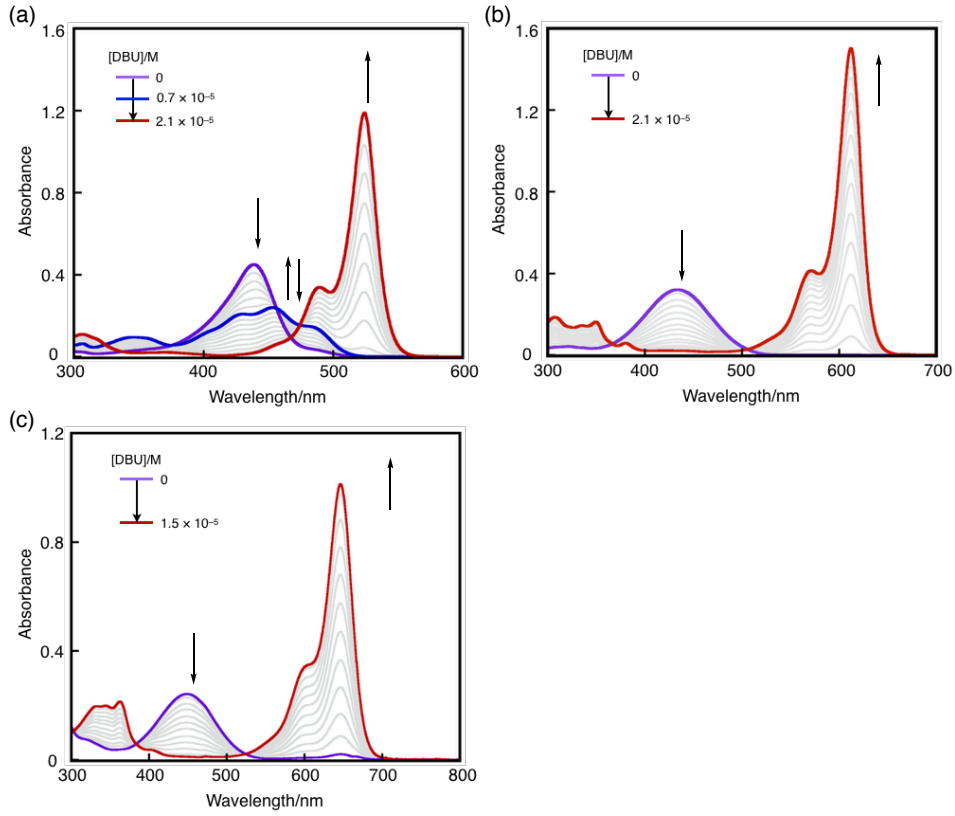


Fig. S7 UV-vis absorption spectral changes upon addition of DBU to an acetonitrile solution of (a) **OF** (1.2×10^{-5} M), (b) **SiF** (1.2×10^{-5} M), and (c) **POF** (1.2×10^{-5} M).

Monitoring the Response of BFs to TBAF by UV-vis Absorption Spectroscopy. The dried and degassed CH_3CN solution of **BF**s in a 1 cm square quartz cuvette was added the CH_3CN solution of TABF. UV-vis-NIR absorption spectra were measured with a Shimadzu UV-3600 Plus spectrometer. Possible equilibriums observed in **BF3** (Fig. S8) was represented in Scheme S4.

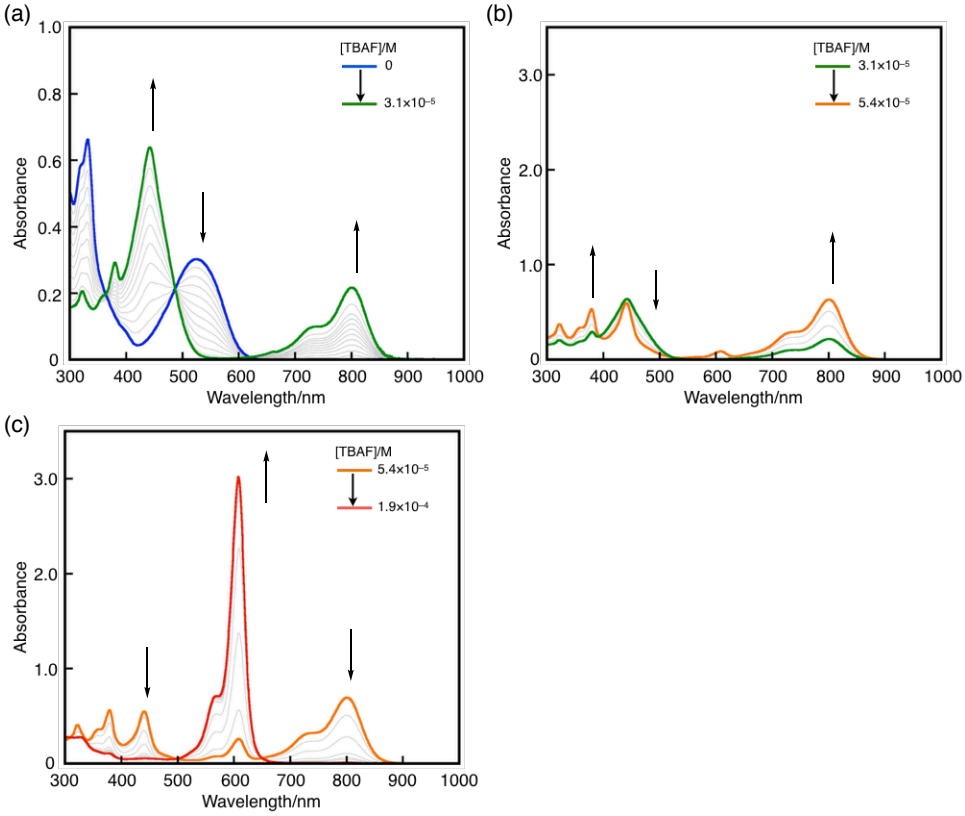
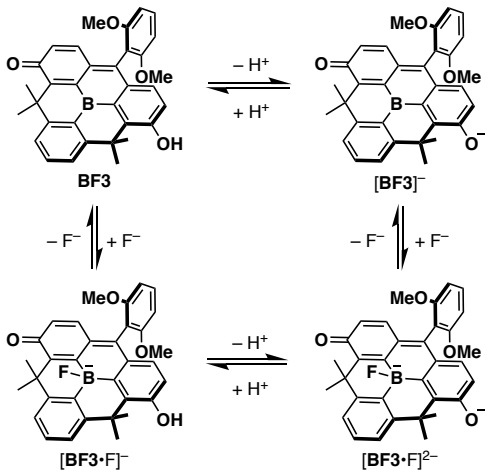


Fig. S8 UV-vis-NIR absorption spectral changes of **BF3** in acetonitrile (2.8×10^{-5} M) upon addition of TBAF: (a) [TBAF] = 0–3.1×10^{-5} M^{-1}, (b) 3.1×10^{-5}–5.4×10^{-4} M^{-1}, (c) 5.4×10^{-5}–1.9×10^{-4} M^{-1}.



Scheme S4 Possible equilibriums of **BF3** in the presence of fluoride ion.

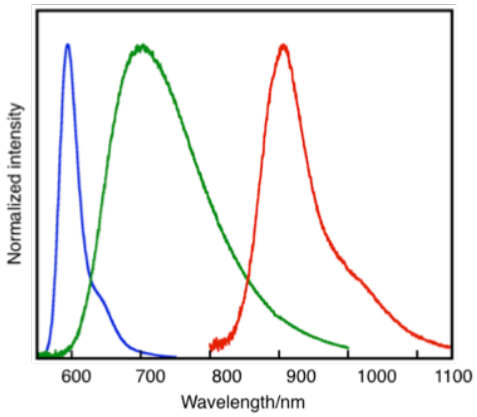


Fig. S9 Fluorescence spectra of neutral **BF2** (green), deprotonated [**BF2**]$^{-}$ (red), and borate fluorescein anion [**BF2**·F]$^{2-}$ (blue) in acetonitrile.

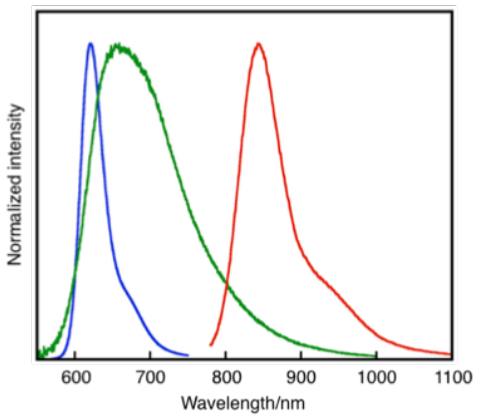


Fig. S10 Fluorescence spectra of neutral **BF3** (green), deprotonated [**BF3**]$^{-}$ (red), and borate fluorescein anion [**BF3**·F]$^{2-}$ (blue) in acetonitrile.

Table S1 Photophysical Properties of **BF2** and its Related Species Generated by the Addition of Additives in Acetonitrile

Compound	additive	λ_{abs} [nm]	ε [10^4 $M^{-1}cm^{-1}$]	λ_{em} [nm]	Φ_F [a]	Stokes shift [cm^{-1}]
BF2	None	538	0.84	704	0.011	4400
[**BF2**]$^-$	DBU	851	1.90	907	0.003	730
[**BF2**·F]$^-$	TBAF	436	2.80	–	–	–
[**BF2**·F]$^{2-}$	TBAF (excess)	585	14.5	595	0.89	290

[a] Absolute fluorescence quantum yields determined by a calibrated integrating sphere system.

Table S2 Photophysical Properties of **BF3** and its Related Species Generated by the Addition of Additives in Acetonitrile

Compound	additive	λ_{abs} [nm]	ε [10^4 $M^{-1}cm^{-1}$]	λ_{em} [nm]	Φ_F [a]	Stokes shift [cm^{-1}]
BF3	None	524	1.10	660	0.004	3900
[**BF3**]$^-$	DBU	801	3.40	843	0.029	620
[**BF3**·F]	TBAF	–	–	–	–	–
[**BF3**·F]$^{2-}$	TBAF (excess)	608	8.56	621	0.87	340

[a] Absolute fluorescence quantum yields determined by a calibrated integrating sphere system.

UV-via Absorption Titration Experiments with Pyridine. UV-vis absorption spectra were measured with a Shimadzu UV-3600 Plus spectrometer using dried and degassed sample solutions in a 1 cm square quartz cuvette. The titration experiments were conducted according to the literature method.[7]

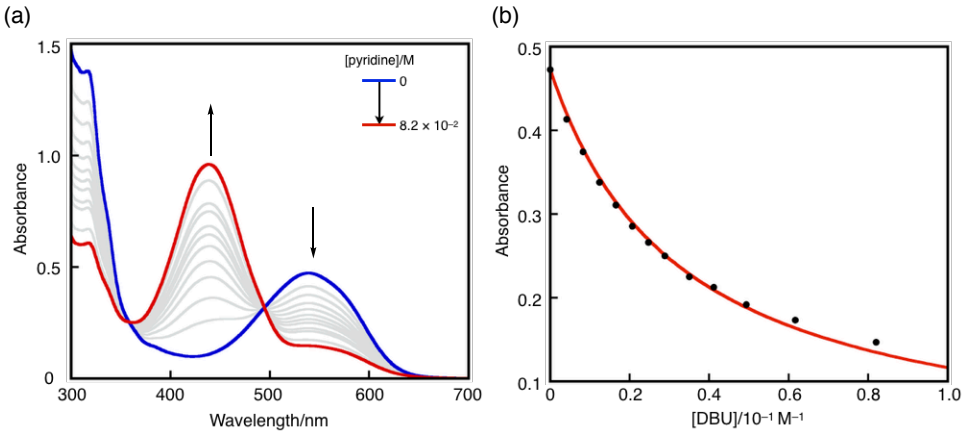


Fig. S11 (a) UV-vis absorption spectral changes upon addition of pyridine to an acetonitrile solution of **BF2** (5.6×10^{-5} M) and (b) plots of the absorbance at 540 nm with a fitting curve for the binding constants toward pyridine. The binding constant was estimated to be 31 M^{-1} ($R^2 = 0.99654$).

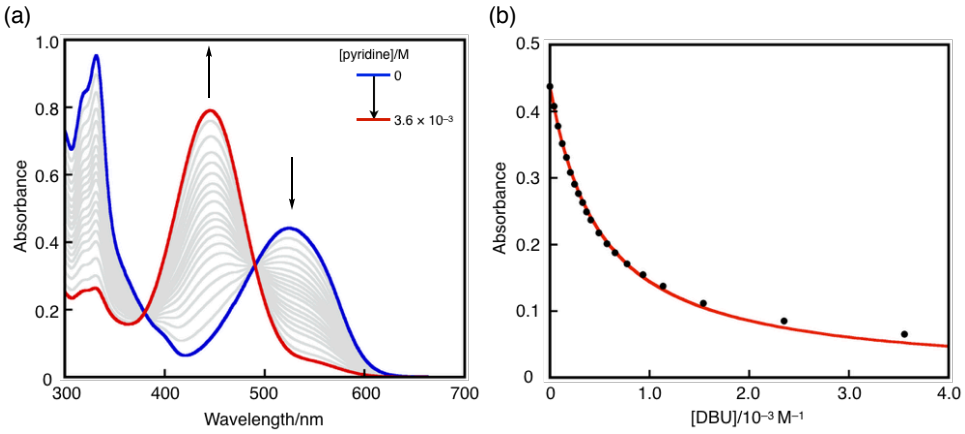


Fig. S12 (a) UV-vis absorption spectral changes upon addition of pyridine to an acetonitrile solution of **BF3** (4.0×10^{-5} M) and (b) plots of the absorbance at 530 nm with a fitting curve for the binding constants toward pyridine. The binding constant was estimated to be 2.1×10^{3} M^{-1} ($R^2 = 0.99793$).

4. Theoretical Calculations

Computational Methods. Geometry optimizations were performed using the Gaussian 09 program[8] at the B3LYP/6-31+G(d) level of theory. The optimized geometry at the same level were employed for the TD-DFT calculations at the B3LYP/6-31+G(d) level of theory. The Cartesian coordinates are shown in Tables S3–S13.

Table S3 Cartesian Coordinates for the Neutral Form of **BF2**

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
B	0.62784454	-0.02686766	0.05618007	H	2.15839428	2.12922164	2.95507586
C	-0.19938621	1.29158435	0.03465394	C	2.25200738	-0.03696670	-2.45958379
C	-1.70532428	3.67644179	-0.00479252	H	1.16838576	-0.02616213	-2.27215777
C	0.42875566	2.54490959	0.05334450	C	2.55413594	-1.32332033	-3.25282003
C	-1.62347990	1.23044909	-0.00478570	H	1.98880404	-1.33819070	-4.19317886
C	-2.34549895	2.44183347	-0.02362657	H	2.28462591	-2.21709490	-2.67947253
C	-0.30849933	3.73273107	0.03397243	H	3.61985959	-1.39516080	-3.50230460
H	1.51706903	2.58695171	0.08344533	C	2.56957120	1.21586413	-3.29879556
H	-3.42988406	2.42136105	-0.05359950	H	2.00662905	1.20198830	-4.24056136
H	-2.27358440	4.60196577	-0.01980281	H	3.63617441	1.26927866	-3.54891412
C	-2.33136845	-0.05620248	-0.02483692	H	2.30537341	2.13301053	-2.75970556
C	-1.67555278	-1.27384009	-0.00877743	C	6.57324563	-0.00418294	0.21829257
C	-0.21376729	-1.34260982	0.03191591	H	6.85813260	-0.00003629	1.27989433
C	0.39382322	-2.56743201	0.04888711	C	7.17453551	-1.27559742	-0.41311209
H	1.47773826	-2.65167097	0.07904412	H	8.26620981	-1.28274043	-0.30137046
C	-2.41396366	-2.52428565	-0.03030784	H	6.94905726	-1.33339916	-1.48518601
C	-1.80289568	-3.73630261	-0.01362488	H	6.77659421	-2.18028104	0.06046848
H	-3.49864332	-2.47533715	-0.06097843	C	7.17250204	1.26347067	-0.42233976
H	-2.36952491	-4.66326236	-0.03022822	H	8.26447855	1.27169856	-0.31386013
C	-0.34541627	-3.84627923	0.02790685	H	6.77638826	2.17132836	0.04759877
O	0.25153521	-4.93242839	0.04494160	H	6.94440357	1.31470966	-1.49425848
O	0.27620648	4.96947718	0.05124041	C	-3.83031637	-0.01861851	-0.06137112
H	1.24204338	4.87609488	0.07616918	C	-6.63137914	0.07092589	-0.12759917
C	2.20826316	-0.02713084	0.09905917	C	-4.51960079	0.00830016	-1.28827615
C	5.04993951	-0.00714921	0.16760391	C	-4.57704024	0.00574141	1.13149096
C	2.95788517	-0.02105639	-1.10186289	C	-5.97926851	0.04927555	1.10515234
C	2.89601087	-0.02379094	1.33365769	C	-5.92149993	0.05159982	-1.32807704
C	4.29782747	-0.01340258	1.34625684	H	-6.55645341	0.06513218	2.02187971
C	4.35652163	-0.01084617	-1.04925500	H	-6.45475814	0.06916126	-2.27098831
H	4.82455140	-0.01552674	2.29945858	H	-7.71753026	0.10326574	-0.15340576
H	4.92080689	-0.01106065	-1.97971378	O	-3.83916578	-0.01664963	2.27948004
C	2.12766620	-0.04134274	2.65653899	O	-3.72791099	-0.01146824	-2.39988551
H	1.05387651	-0.03558718	2.41886919	C	-4.34158175	0.00430702	-3.68325650
C	2.39922512	-1.32503517	3.46501694	H	-3.52018813	-0.02095797	-4.40106152
H	3.45266407	-1.39089821	3.76340465	H	-4.92989616	0.91877365	-3.83297897
H	2.16120161	-2.22091480	2.88117322	H	-4.98131796	-0.87530608	-3.82955191
H	1.79115565	-1.34179355	4.37829746	C	-4.51364576	-0.00355040	3.53196476
C	2.40177819	1.21412082	3.50725658	H	-5.10794607	0.91094810	3.65536323
H	3.45596475	1.27229827	3.80451046	H	-3.72767128	-0.03106550	4.28831283
H	1.79721786	1.19953148	4.42286217	H	-5.16019602	-0.88305795	3.64511572

Table S4 Cartesian Coordinates for the Neutral Form of **BF3**

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
B	1.25309257	-0.02840272	-0.00015413	C	3.21323973	3.32738573	1.28019021
C	0.49025445	1.29995310	-0.00004885	H	2.92209304	2.76978600	2.17763427
C	-0.96809132	3.65504612	0.00043319	H	2.77561934	4.32557842	1.33009268
C	-0.93311425	1.24013712	0.00001165	H	4.30226267	3.43402531	1.29215017
C	1.20229935	2.51552920	0.00003993	C	3.21318264	3.32706593	-1.28048899
C	0.42956909	3.70513611	0.00035646	H	2.77566185	4.32528551	-1.33058619
C	-1.65053264	2.44564721	0.00023816	H	2.92190344	2.76928614	-2.17777845
H	-1.52937136	4.58930960	0.00067273	H	4.30221479	3.43359878	-1.29258124
C	0.47266892	-1.34985757	-0.00023189	C	-1.63311976	-0.05164955	-0.00010645
C	-1.08366986	-3.71066320	-0.00028400	C	-3.13308863	-0.01306057	-0.00001380
C	1.15935119	-2.54362958	-0.00026186	C	-5.93614035	0.07420821	0.00014858
C	-0.98519181	-1.27709137	-0.00022884	C	-3.85198454	0.01217199	-1.20982337
C	-1.72545918	-2.51842772	-0.00020586	C	-3.85185532	0.01182470	1.20987802
C	0.37496578	-3.82437718	-0.00057740	C	-5.25457339	0.05415767	1.21691806
H	-1.62474046	-4.65293259	-0.00020888	C	-5.25470440	0.05448945	-1.21670183
C	2.76374389	-0.03679614	-0.00002866	H	-5.80968588	0.06943193	2.14721570
C	5.53603319	-0.06347998	0.00022762	H	-5.80992333	0.06993239	-2.14693197
C	3.46258146	1.19547455	0.00007373	H	-7.02269772	0.10496072	0.00021240
C	3.44028211	-1.28145686	-0.00002415	O	1.05344134	4.93093010	0.00067492
C	4.84147631	-1.27253560	0.00011784	H	0.38247209	5.63161446	0.00098608
C	4.86154983	1.15971120	0.00019191	O	0.90248984	-4.94849422	-0.00006583
H	5.40817323	-2.19852516	0.00013845	H	-2.73544831	2.44874733	0.00033102
H	5.44745204	2.07392580	0.00025640	H	-2.81118492	-2.48643474	-0.00010465
H	6.62391758	-0.07224437	0.00032657	O	-3.08720776	-0.00926561	2.34018030
C	2.74863764	2.56736668	-0.00004190	O	-3.08744802	-0.00874622	-2.34020617
C	2.69399736	-2.62952058	-0.00016210	C	-3.73072039	-0.00693160	3.60832038
C	3.13633614	-3.41205886	-1.27795211	H	-4.32580036	0.90419600	3.75266779
H	2.85447159	-2.85797264	-2.18094873	H	-2.92628661	-0.03601993	4.34500629
H	2.67008927	-4.39772791	-1.30175047	H	-4.37102620	-0.88970088	3.73183691
H	4.22293995	-3.54203764	-1.29015630	C	-3.73103948	-0.00454818	-3.60830003
C	3.13618559	-3.41223998	1.27756797	H	-2.92665495	-0.03269620	-4.34507644
H	2.85413634	-2.85832390	2.18061189	H	-4.32603427	0.90684194	-3.75131376
H	4.22279666	-3.54213991	1.28992609	H	-4.37144173	-0.88707876	-3.73303917
H	2.67000983	-4.39794726	1.30112594				

Table S5 Cartesian Coordinates for the Deprotonated Form of **BF2** ([**BF2**]$^-$)

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
B	-0.59519530	0.03310419	0.03876819	C	-2.26785343	-0.17530735	-2.44348538
C	0.24726980	-1.27710572	0.09687038	H	-1.18341905	-0.15521007	-2.27285323
C	1.82436006	-3.63913167	0.23349595	C	-2.59996312	1.03517076	-3.33764799
C	-0.35349035	-2.51723102	0.21261026	H	-2.05252304	0.97363285	-4.28759113
C	1.69149060	-1.18712017	0.03734682	H	-2.32487660	1.97531887	-2.84746828
C	2.42861560	-2.41100668	0.11703942	H	-3.67190646	1.07656922	-3.57113078
C	0.38141224	-3.77912982	0.28489993	C	-2.57921196	-1.50130363	-3.16466025
H	-1.43800954	-2.59642474	0.25603728	H	-2.02454079	-1.56311204	-4.11037069
H	3.51539830	-2.36857897	0.08697281	H	-3.64827083	-1.58781928	-3.39863654
H	2.41608583	-4.55031212	0.29352864	H	-2.29839298	-2.36204928	-2.54792930
C	2.33916490	0.07227088	-0.08746802	C	-6.54774395	-0.03628942	0.29446489
C	1.65468868	1.31113244	-0.14421965	H	-6.81573650	0.02788791	1.35916843
C	0.20771260	1.36302803	-0.08221724	C	-7.17350112	1.18444882	-0.40928285
C	-0.42982879	2.58800750	-0.12832518	H	-8.26511875	1.18875895	-0.28532755
H	-1.51582698	2.64282518	-0.08338012	H	-6.95893880	1.17458213	-1.48525760
C	2.35506764	2.55544522	-0.25411945	H	-6.77730982	2.12139843	-0.00118649

C	1.71408114	3.76764869	-0.29594521	C	-7.14770998	-1.34812830	-0.24931585
H	3.44108093	2.53885301	-0.30816290	H	-8.23872212	-1.35971518	-0.12104843
H	2.27570666	4.69558857	-0.38011688	H	-6.73128743	-2.21846375	0.27083222
C	0.26817862	3.86963006	-0.23376396	H	-6.93607363	-1.46831410	-1.31917515
O	-0.35049545	4.96240506	-0.26637529	C	3.84208022	0.08774146	-0.14634099
O	-0.20280967	-4.88748338	0.38560407	C	6.66297525	0.11241531	-0.23454448
C	-2.18174807	0.01293432	0.10548843	C	4.53271905	0.09954937	-1.36573453
C	-5.02541872	-0.02333016	0.21856865	C	4.60865356	0.09336953	1.04190265
C	-2.95160056	-0.08658738	-1.07775427	C	6.00892821	0.10241236	1.00230762
C	-2.85436641	0.09385219	1.34524874	C	5.93426744	0.11440824	-1.41911540
C	-4.25586421	0.07332128	1.38130468	H	6.59114034	0.10761118	1.91690158
C	-4.34975944	-0.10276778	-1.00505951	H	6.42448216	0.14570131	-2.38796011
H	-4.76779983	0.13555030	2.34119201	H	7.75007159	0.12874928	-0.26335581
H	-4.92593225	-0.17817649	-1.92588885	O	3.88771931	0.09102569	2.20185385
C	-2.06901123	0.20170192	2.65334754	O	3.82781018	0.16975710	-2.55098887
H	-1.00151685	0.22674376	2.39803824	C	3.57882886	-1.08179578	-3.19691312
C	-2.37549707	1.50865632	3.41030789	H	3.05329237	-0.84272889	-4.12473190
H	-3.42503010	1.54915134	3.72961982	H	2.95155127	-1.72949047	-2.57452049
H	-2.17979987	2.38461571	2.78230328	H	4.52144485	-1.59720308	-3.43213629
H	-1.74959328	1.58693080	4.30914936	C	4.57705083	0.08302215	3.43911619
C	-2.28299072	-1.02737260	3.55858529	H	5.20393394	-0.81345504	3.54431120
H	-3.33256148	-1.11626227	3.86806788	H	3.80191066	0.07431568	4.20783854
H	-1.67122013	-0.94707784	4.46707530	H	5.19900405	0.98112007	3.55908620
H	-2.00443163	-1.95202386	3.04156279				

Table S6 Cartesian Coordinates for the Deprotonated Form of **BF3** ([**BF3**]$^{-}$)

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
B	0.00000000	0.00000000	-1.24919393	H	1.30073333	-4.35280182	-2.69063600
C	0.00000328	1.32920084	-0.48299634	C	1.27468313	3.37352141	-3.17216360
C	-0.00000812	3.69247685	1.02145222	H	2.17659153	2.81203673	-2.89941936
C	0.00000000	1.25934414	0.95934418	H	1.30082835	4.35276187	-2.69061520
C	0.00000830	2.53200184	-1.17943725	H	1.28199609	3.51359126	-4.25945237
C	0.00000774	3.81001428	-0.42278511	C	-1.27461305	3.37355832	-3.17218021
C	-0.00000614	2.49036988	1.67767086	H	-1.30073333	4.35280182	-2.69063600
H	-0.00001856	4.63200848	1.57001813	H	-2.17654191	2.81210255	-2.89944417
C	-0.00000328	-1.32920084	-0.48299634	H	-1.28190901	3.51362465	-4.25946955
C	0.00000812	-3.69247685	1.02145222	C	0.00000000	0.00000000	1.61850541
C	-0.00000830	-2.53200184	-1.17943725	C	0.00000000	0.00000000	3.12270242
C	0.00000000	-1.25934414	0.95934418	C	0.00000000	0.00000000	5.93624873
C	0.00000614	-2.49036988	1.67767086	C	1.20607613	-0.00000542	3.84718854
C	-0.00000774	-3.81001428	-0.42278511	C	-1.20607613	0.00000542	3.84718854
H	0.00001856	-4.63200848	1.57001813	C	-1.21508711	0.00000502	5.25181058
C	0.00000000	0.00000000	-2.76800167	C	1.21508711	-0.00000502	5.25181058
C	0.00000000	0.00000000	-5.54307776	H	-2.14671821	0.00000537	5.80574431
C	0.00000815	1.23808255	-3.45521310	H	2.14671821	-0.00000537	5.80574431
C	-0.00000815	-1.23808255	-3.45521310	H	0.00000000	0.00000000	7.02395891
C	-0.00000749	-1.21574865	-4.85713734	O	-0.00002848	4.94750502	-0.96666461
C	0.00000749	1.21574865	-4.85713734	O	0.00002848	-4.94750502	-0.96666461
H	-0.00001404	-2.13880556	-5.43020277	H	-0.00001166	2.47881296	2.76551608
H	0.00001404	2.13880556	-5.43020277	H	0.00001166	-2.47881296	2.76551608
H	0.00000000	0.00000000	-6.63228340	O	-2.34212186	0.00000337	3.08915918
C	0.00002061	2.59475720	-2.72035102	O	2.34212186	-0.00000337	3.08915918
C	-0.00002061	-2.59475720	-2.72035102	C	-3.60150190	0.00008305	3.73616649
C	-1.27468313	-3.37352141	-3.17216360	H	-3.73622716	-0.89716347	4.35640256
H	-2.17659153	-2.81203673	-2.89941936	H	-4.34326730	0.00011733	2.93501970
H	-1.30082835	-4.35276187	-2.69061520	H	-3.73612172	0.89735742	4.35638444

H	-1.28199609	-3.51359126	-4.25945237	C	3.60150190	-0.00008305	3.73616649
C	1.27461305	-3.37355832	-3.17218021	H	4.34326730	-0.00011733	2.93501970
H	2.17654191	-2.81210255	-2.89944417	H	3.73612172	-0.89735742	4.35638444
H	1.28190901	-3.51362465	-4.25946955	H	3.73622716	0.89716347	4.35640256

Table S7 Cartesian Coordinates for the Deprotonated Form of **OF** ([**OF**]$^-$)

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
H	1.00141706	-2.48350600	0.00000000	O	1.81110691	2.03163775	0.00000000
C	1.71937516	-1.66588644	0.00000000	C	-1.18839627	-1.05206111	0.00000000
C	3.55525614	0.46457314	0.00000000	C	-3.10736537	-3.12425362	0.00000000
C	1.21539619	-0.32440043	0.00000000	C	-1.68955413	-1.58007939	1.20484351
C	3.05932343	-1.94327353	0.00000000	C	-1.68955413	-1.58007939	-1.20484351
C	4.07477442	-0.88768339	0.00000000	C	-2.63914329	-2.60766198	-1.20873146
C	2.20470808	0.71597614	0.00000000	C	-2.63914329	-2.60766198	1.20873146
H	3.41981399	-2.96946224	0.00000000	H	-3.01681597	-2.97198055	-2.16020739
H	4.26025041	1.29044411	0.00000000	H	-3.01681597	-2.97198055	2.16020739
C	-0.15088377	0.02823815	0.00000000	H	-3.85567248	-3.91336344	0.00000000
C	-0.53308414	1.37692319	0.00000000	O	-1.29358669	-1.02295191	2.40301571
C	0.48445867	2.39275496	0.00000000	O	-1.29358669	-1.02295191	-2.40301571
C	-1.88970756	1.84219456	0.00000000	C	-0.31013203	-1.75378907	-3.14074767
H	-2.68364398	1.09912316	0.00000000	H	0.63670404	-1.80127586	-2.59121134
C	-2.19943796	3.17141852	0.00000000	H	-0.16456908	-1.20437173	-4.07377879
H	-3.23342088	3.50798991	0.00000000	H	-0.65890959	-2.77183309	-3.36556796
C	0.19920443	3.73395799	0.00000000	C	-0.31013203	-1.75378907	3.14074767
H	1.00420915	4.46256971	0.00000000	H	-0.16456908	-1.20437173	4.07377879
C	-1.16885964	4.21397710	0.00000000	H	0.63670404	-1.80127586	2.59121134
O	-1.46347198	5.43433168	0.00000000	H	-0.65890959	-2.77183309	3.36556796
O	5.30348974	-1.15147046	0.00000000				

Table S8 Cartesian Coordinates for the Deprotonated Form of **SiF** ([**SiF**]$^-$)

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
H	-1.81395375	2.15550392	0.00000000	C	1.03968843	3.89580887	-1.20843492
C	-2.16604570	1.12761951	0.00000000	C	1.03968843	3.89580887	1.20843492
C	-3.10250085	-1.48550056	0.00000000	H	1.18519253	4.40240182	-2.15864983
C	-1.19821560	0.06332955	0.00000000	H	1.18519253	4.40240182	2.15864983
C	-3.52192836	0.91815957	0.00000000	H	1.44236744	5.63498368	0.00000000
C	-4.09341416	-0.41602685	0.00000000	O	0.65699542	1.84379986	2.39751668
C	-1.73988050	-1.28033690	0.00000000	O	0.65699542	1.84379986	-2.39751668
H	-4.21430125	1.75796263	0.00000000	C	-0.50301959	2.09008968	-3.19450739
H	-3.51287196	-2.49592691	0.00000000	H	-0.59731691	3.15571670	-3.44755775
C	0.20418862	0.35580256	0.00000000	H	-1.40963083	1.75273917	-2.67881306
C	1.29237954	-0.55902684	0.00000000	H	-0.36638363	1.51145814	-4.11132442
C	1.13160739	-2.00080441	0.00000000	C	-0.50301959	2.09008968	3.19450739
C	2.64827886	-0.07269436	0.00000000	H	-0.59731691	3.15571670	3.44755775
H	2.81633707	1.00032452	0.00000000	H	-0.36638363	1.51145814	4.11132442
C	3.74149268	-0.89522927	0.00000000	H	-1.40963083	1.75273917	2.67881306
H	4.74904590	-0.48466224	0.00000000	Si	-0.58333708	-2.75556303	0.00000000
C	2.23464377	-2.82239900	0.00000000	C	-0.85276117	-3.83261440	-1.54010146
H	2.12426698	-3.90723896	0.00000000	H	-1.87224802	-4.23909981	-1.56600595
C	3.61312777	-2.34198472	0.00000000	H	-0.14949298	-4.67533955	-1.55831182
O	4.59765946	-3.12071723	0.00000000	H	-0.69972184	-3.24733352	-2.45463050
O	-5.33086969	-0.63592276	0.00000000	C	-0.85276117	-3.83261440	1.54010146
C	0.56393900	1.82091799	0.00000000	H	-1.87224802	-4.23909981	1.56600595
C	1.18698980	4.57784237	0.00000000	H	-0.69972184	-3.24733352	2.45463050
C	0.73116015	2.53089588	1.20293006	H	-0.14949298	-4.67533955	1.55831182

C	0.73116015	2.53089588	-1.20293006				

Table S9 Cartesian Coordinates for the Deprotonated Form of **POF** ([**POF**]$^-$)

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
H	-2.23239479	-2.27699258	0.09667518	H	-4.01318485	-0.15013702	3.37688538
C	-1.23957553	-2.37211228	-0.33496240	H	-5.63609082	0.55694224	-0.55014587
C	1.30967582	-2.62844452	-1.44370235	H	-5.96378341	0.20715708	1.90789643
C	-0.45134118	-1.18284406	-0.50274721	P	2.05385993	-0.01421473	-1.13996624
C	-0.80858043	-3.61781427	-0.70833247	C	2.99100892	-0.09878200	0.44703509
C	0.49561881	-3.83487849	-1.31305043	C	4.52887829	-0.21533782	2.79019131
C	0.86866046	-1.39008335	-1.05014512	C	2.36471939	-0.10291617	1.70268508
H	-1.44125022	-4.49148859	-0.56741711	C	4.38871807	-0.15398536	0.37301250
H	2.30362400	-2.74962261	-1.86798940	C	5.15520762	-0.21240235	1.54123701
C	-0.97973693	0.10555984	-0.20377858	C	3.13278940	-0.16034823	2.86761299
C	-0.33470855	1.34818988	-0.43135075	H	1.28066305	-0.06087348	1.77290870
C	1.00226855	1.45913758	-0.96962827	H	4.86005665	-0.14890365	-0.60607825
C	-1.00994799	2.59498897	-0.19301923	H	6.24025635	-0.25441912	1.47402085
H	-2.01171631	2.56635611	0.22592935	H	2.64194626	-0.16056853	3.83869005
C	-0.46046842	3.81204166	-0.48968259	H	5.12386284	-0.25946375	3.70006539
H	-1.00884176	4.73224181	-0.30141584	O	3.00714670	-0.02792449	-2.30868750
C	1.55888953	2.67012023	-1.29019558	O	-3.34075810	0.61481256	-1.77513981
H	2.56057253	2.72390018	-1.71014074	O	-1.43985806	-0.21246088	2.50363076
C	0.86178700	3.93871256	-1.08135598	C	-1.56252183	-0.43615476	3.89820394
O	1.37627843	5.04094939	-1.37927352	H	-0.54393741	-0.57380009	4.26594540
O	0.90025106	-4.96206375	-1.68227542	H	-2.14951793	-1.34047551	4.10887279
C	-2.36970816	0.14728301	0.37412595	H	-2.01912075	0.42516064	4.40505535
C	-4.96559905	0.18668778	1.47683662	C	-3.46869743	-0.50769607	-2.65393174
C	-3.49923697	0.35184311	-0.43108870	H	-2.68718871	-1.25070904	-2.46206715
C	-2.57401951	-0.03021244	1.76121273	H	-3.35639818	-0.11054868	-3.66534482
C	-3.86155371	-0.01471990	2.31210032	H	-4.45767293	-0.97686905	-2.55028752
C	-4.79290331	0.37413943	0.10961776				

Table S10 Cartesian Coordinates for the Borate Form of **BF2** ([**BF2**·**F**]$^-$)

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
C	-0.21243139	1.17707529	0.66167154	H	0.38199588	0.28325359	-1.55743471
C	-1.57464537	3.67170409	0.68149180	C	1.44039953	-0.67376702	-3.13790264
C	0.45301535	2.37246532	0.94392263	H	0.62588502	-0.53926462	-3.86367861
C	-1.60648688	1.23851465	0.38269197	H	1.35750239	-1.68135946	-2.71715645
C	-2.25826072	2.49476780	0.40105670	H	2.38959145	-0.61276828	-3.68652584
C	-0.20563676	3.60436840	0.95739607	C	1.39530498	1.81133200	-2.63971364
H	1.52145063	2.33912979	1.16363633	H	0.56182301	1.94560817	-3.34249023
H	-3.31981284	2.55842113	0.18376913	H	2.32652954	1.99423826	-3.19189553
H	-2.08077356	4.63309417	0.68568182	H	1.30525809	2.57776302	-1.86261829
C	-2.36319988	0.01423710	0.09644906	C	6.29022359	0.33710366	-0.96210441
C	-1.78583908	-1.24208944	-0.04447697	H	6.92891900	0.07778792	-0.10472154
C	-0.34615231	-1.44957935	0.14993049	C	6.68780155	-0.59330370	-2.12534670
C	0.17530942	-2.68435609	-0.11239229	H	7.74963253	-0.46996736	-2.38080864
H	1.24094333	-2.86713583	0.01542596	H	6.09981207	-0.37573327	-3.02583315
C	-2.59991695	-2.38954214	-0.42127449	H	6.51642591	-1.64392689	-1.86405611
C	-2.05883199	-3.60884052	-0.66615128	C	6.58007419	1.80865360	-1.31949481
H	-3.67366502	-2.25634730	-0.52340105	H	7.63976306	1.95024702	-1.57461617
H	-2.67196457	-4.45826674	-0.95919902	H	6.33761972	2.47193836	-0.48072180
C	-0.61323684	-3.83645674	-0.54867449	H	5.98190429	2.13111262	-2.18098962
O	-0.10822672	-4.94931584	-0.79898007	C	-3.85437864	0.14340065	-0.06109078
O	0.45238503	4.78255732	1.23495179	C	-6.64948806	0.30515007	-0.49558499

H	1.38661920	4.57897187	1.40228923	C	-4.39189470	0.58134855	-1.28933485
C	2.12407740	-0.22815785	0.37413825	C	-4.77038096	-0.19429750	0.96262532
C	4.84737293	0.12669854	-0.51947259	C	-6.15436728	-0.11800873	0.73422500
C	2.43919440	0.17378847	-0.96093201	C	-5.76727085	0.66800270	-1.51466776
C	3.23332183	-0.52050083	1.21980964	H	-6.81822289	-0.39752354	1.54689723
C	4.54982538	-0.31787721	0.76706234	H	-6.12367680	1.02638913	-2.47633139
C	3.76604824	0.34641577	-1.37650203	H	-7.72353378	0.36734120	-0.65507807
H	5.37893010	-0.52422005	1.44241556	O	-4.43022146	-0.68736011	2.19351272
H	3.95988954	0.65822539	-2.40191144	O	-3.52881732	0.98198990	-2.29291528
C	3.08483828	-1.06625336	2.64850713	C	-3.24825559	-0.00052123	-3.29351418
H	2.06303800	-1.41987364	2.76264091	H	-2.59715666	0.48760296	-4.02268407
C	4.00939729	-2.26670219	2.93935892	H	-4.17143451	-0.33228952	-3.78970837
H	5.07151501	-1.99030244	2.97791730	H	-2.73224661	-0.86564463	-2.86215743
H	3.89431655	-3.04893994	2.17943120	C	-3.33465387	-0.13407175	2.94389772
H	3.75304777	-2.70382707	3.91419855	H	-2.37341037	-0.54946199	2.63631642
C	3.29449669	0.04276174	3.69914662	H	-3.53761532	-0.40908117	3.98233554
H	4.30661806	0.46764510	3.63469080	H	-3.31238059	0.95655830	2.84934255
H	3.15794020	-0.35213635	4.71609128	B	0.53433315	-0.26567178	0.84469731
H	2.57120424	0.85251651	3.55432761	F	0.36300418	-0.49910179	2.29852685
C	1.35930365	0.39612562	-2.02911221				

Table S11 Cartesian Coordinates for the Borate-anion Form of **BF2** ([**BF2**·**F**]$^{2-}$)

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
C	-0.32372900	1.41867577	-0.01161434	H	0.45622990	-0.46535686	-1.57299606
C	-1.90474573	3.56277091	-1.04142885	C	1.53802856	-2.04045408	-2.51417621
C	0.25196258	2.62320116	-0.35286187	H	0.74016806	-2.24094181	-3.24402073
C	-1.75094221	1.24933365	-0.21511202	H	1.42548059	-2.74856558	-1.68690678
C	-2.49784001	2.37136113	-0.71173785	H	2.49757031	-2.24115096	-3.01107625
C	-0.47186946	3.76419138	-0.89389792	C	1.54313429	0.40959118	-3.18259391
H	1.32243381	2.77130191	-0.21036537	H	0.75776626	0.20440776	-3.92499863
H	-3.57359278	2.27161949	-0.84473814	H	2.51272709	0.33855387	-3.69546364
H	-2.49142741	4.39726824	-1.42414152	H	1.41646648	1.43844995	-2.83014488
C	-2.38179978	-0.00425877	0.01764007	C	6.33655952	-0.33645217	-0.79290632
C	-1.70139777	-1.20186473	0.37583834	H	6.93912111	-0.04840210	0.08226492
C	-0.27559562	-1.19883973	0.65165207	C	6.67074659	-1.80733809	-1.11362051
C	0.33416662	-2.39126893	0.97676609	H	7.74324399	-1.93268048	-1.32659557
H	1.40196833	-2.41187677	1.19393216	H	6.11066211	-2.15598508	-1.99041927
C	-2.40688142	-2.44821306	0.48882420	H	6.40591285	-2.46048505	-0.27408086
C	-1.77831683	-3.62321639	0.81136085	C	6.75908141	0.58113122	-1.95841108
H	-3.47853824	-2.46743859	0.30124912	H	7.83218646	0.47378136	-2.17797437
H	-2.33317117	-4.55840645	0.87872622	H	6.55796283	1.63235363	-1.72098178
C	-0.34853361	-3.67302994	1.07239289	H	6.20318743	0.33762333	-2.87267625
O	0.24340868	-4.75219176	1.36314153	C	-3.88475017	-0.06153171	-0.12031758
O	0.08889082	4.85301742	-1.20907318	C	-6.72588400	-0.12321670	-0.32248489
C	2.10954510	0.17531685	0.38440052	C	-4.53932617	-0.58612783	-1.26128737
C	4.87489688	-0.14733739	-0.40610639	C	-4.71827098	0.43225564	0.91732553
C	2.48378578	-0.27404155	-0.91963955	C	-6.11745669	0.40436480	0.81323824
C	3.18724046	0.51689587	1.25438888	C	-5.94000954	-0.62025193	-1.35734619
C	4.52320493	0.33210084	0.85425099	H	-6.69702083	0.80202653	1.64146403
C	3.82767202	-0.42792762	-1.28635463	H	-6.37772617	-1.03886456	-2.25916864
H	5.32482183	0.57629654	1.55084361	H	-7.81155363	-0.14694560	-0.40092679
H	4.06021847	-0.77850845	-2.29168482	O	-4.26480926	1.02966693	2.06504207
C	2.97397721	1.08296268	2.66692128	O	-3.91474127	-1.15663867	-2.34505402
H	1.95941035	1.47230765	2.71111380	C	-2.69723305	-0.62796158	-2.88603546
C	3.07182979	-0.02864316	3.73114671	H	-1.82707534	-0.98708196	-2.33366928
H	4.07397593	-0.48342706	3.73983378	H	-2.70482865	0.46618663	-2.88682592

H	2.33868892	-0.81607962	3.53097359	H	-2.66183099	-1.00006678	-3.91507049
H	2.87260283	0.37387196	4.73621564	C	-3.19381161	0.46070502	2.84314323
C	3.91954043	2.25019750	3.01797885	H	-3.36259054	0.82985603	3.86024251
H	4.96505087	1.93458676	3.14353613	H	-2.21335737	0.78359293	2.49122400
H	3.60485328	2.70708513	3.96739504	H	-3.24450441	-0.63269233	2.83409102
H	3.89320423	3.02814853	2.24500887	B	0.49247063	0.24352551	0.78048332
C	1.44854331	-0.58689576	-2.00871451	F	0.27820306	0.57889690	2.21869069
H	0.45622990	-0.46535686	-1.57299606				

Table S12 Cartesian Coordinates for the Borate Form of **BF3** ([**BF3·F**]$^{-}$)

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
C	-0.42875336	-1.31823089	0.04646284	H	-2.81596688	-2.35209224	2.16148620
C	0.93910992	-3.72562259	-0.31452764	H	-2.72291683	-4.02435466	1.58168028
C	0.98721560	-1.31962596	-0.06343155	H	-4.24951583	-3.12178339	1.44717899
C	-1.17844408	-2.49816575	-0.08719815	C	-3.31111686	-3.39664443	-1.15944202
C	-0.45892097	-3.71189938	-0.23073668	H	-2.59916336	-3.50541037	-1.98420044
C	1.65897197	-2.54513534	-0.24664696	H	-4.22330676	-2.97995398	-1.58701996
H	1.43467653	-4.68448746	-0.44097498	H	-3.59345126	-4.40222682	-0.80730002
C	-0.31010618	1.34002443	0.10210415	C	1.73327977	-0.05920717	0.02264449
C	1.35605679	3.62029822	-0.03673763	C	3.23551666	-0.14221729	0.03266400
C	-0.92888270	2.55806139	-0.03074624	C	6.06683957	-0.17254630	-0.06450505
C	1.14344943	1.20049555	0.06368743	C	3.93598227	-0.30773533	-1.18021696
C	1.94755939	2.40444785	0.02633562	C	4.00491873	-0.01456599	1.21306908
C	-0.10167157	3.79235925	-0.06540940	C	5.40867621	-0.02307234	1.15244492
H	1.93590363	4.54004400	-0.06331687	C	5.33102458	-0.32639003	-1.24083667
C	-2.64220526	0.11336372	0.00927268	H	5.95663978	0.08853835	2.08338955
C	-5.39814035	0.25589291	-0.42691056	H	5.81654524	-0.47113543	-2.20193447
C	-3.38404828	-1.07438912	-0.14652272	H	7.15401724	-0.18548244	-0.09456247
C	-3.25640277	1.37368446	-0.15106620	O	-1.02647107	-4.96792766	-0.28269304
C	-4.64445976	1.42672526	-0.36025215	H	-1.98992090	-4.89585997	-0.27877818
C	-4.77317776	-0.98792304	-0.33651199	O	-0.56075546	4.95479068	-0.08578507
H	-5.15834175	2.37961556	-0.45625269	H	2.74008027	-2.58169813	-0.33684579
H	-5.39358032	-1.87986791	-0.39690949	H	3.03187506	2.32942076	0.03828107
H	-6.47745206	0.31108461	-0.56204750	O	3.49761949	0.20205761	2.46504667
C	-2.73373510	-2.48337582	-0.01682167	O	3.21891161	-0.50316621	-2.34673223
C	-2.46816553	2.70561420	-0.07583484	C	2.33140156	-0.50131184	2.93213411
C	-2.83326922	3.54036365	-1.34153853	H	2.35947321	-1.54828541	2.61266717
H	-2.56005362	2.98758302	-2.24920036	H	1.40369482	-0.03771221	2.59246930
H	-2.30767978	4.49597903	-1.33355522	H	2.39042997	-0.44801874	4.02253096
H	-3.90886638	3.74275987	-1.38589121	C	3.01758299	0.66028125	-3.15272966
C	-2.93143605	3.46292491	1.20373507	H	2.47166120	0.32363649	-4.03751211
H	-2.70169141	2.86669162	2.09413167	H	3.97831693	1.09897228	-3.45859693
H	-4.01513059	3.63437700	1.18065193	H	2.42391972	1.41189182	-2.62048720
H	-2.42744576	4.43016213	1.27843884	B	-1.14195831	0.03642087	0.49658409
C	-3.15785921	-3.03604775	1.37893631	F	-1.13534864	-0.00590124	1.99907378

Table S13 Cartesian Coordinates for the Borate-anion Form of **BF3** ([**BF3·F**]$^{2-}$)

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
C	-0.34656503	1.34131393	0.06361037	H	-2.77060382	2.84112328	-2.25204118
C	1.18552520	3.67990735	-0.23017079	H	-2.50228710	4.37279389	-1.37457715
C	1.09507604	1.25937426	-0.01356577	H	-4.09704906	3.59133129	-1.34675097
C	-1.02242402	2.54036965	-0.08231597	C	-3.03007146	3.36942504	1.19806319
C	-0.26239453	3.80352928	-0.18404885	H	-2.55408674	4.35378599	1.23893467
C	1.83232451	2.47721583	-0.15124664	H	-2.75149845	2.79469002	2.08905859
H	1.73768398	4.61446886	-0.31968140	H	-4.12162146	3.50116992	1.20527300

C	-0.35978791	-1.33632021	0.08046313	C	1.74319417	-0.00851134	-0.01779920
C	1.14639547	-3.69659382	-0.16425542	C	3.25132792	-0.01130077	-0.04760683
C	-1.04840777	-2.53340592	-0.01673653	C	6.09811759	0.01286442	-0.05561823
C	1.08102454	-1.26993342	-0.02293619	C	3.99749459	0.23516804	1.13404862
C	1.80498181	-2.49775092	-0.14064957	C	3.99384675	-0.24441923	-1.23091299
C	-0.30085694	-3.80610346	-0.08192601	C	5.39816807	-0.23668488	-1.23218220
H	1.68863929	-4.63803563	-0.24132759	C	5.40116369	0.25052117	1.12602357
C	-2.63147254	0.01242214	0.05792228	H	5.90763146	-0.42508878	-2.17301604
C	-5.39452665	0.02026828	-0.36427632	H	5.91324079	0.44849389	2.06340550
C	-3.30433585	1.24161794	-0.11500189	H	7.18691746	0.02204960	-0.05953239
C	-3.31760101	-1.21464472	-0.07480996	O	-0.78188246	4.95968269	-0.21165198
C	-4.70978903	-1.19232210	-0.26893047	O	-0.83004184	-4.95789531	-0.05035273
C	-4.69667807	1.22774110	-0.30972031	H	2.91981025	2.45342382	-0.19642987
H	-5.27849032	-2.11696746	-0.33902324	H	2.89065560	-2.48618616	-0.21612437
H	-5.25507043	2.15569490	-0.41231613	O	3.45710017	-0.55130386	-2.45892469
H	-6.47721515	0.02385886	-0.49907817	O	3.45194422	0.53868840	2.35445228
C	-2.57205612	2.60955007	-0.08159339	C	2.26181849	0.07360451	-2.94805021
C	-2.59861930	-2.58765479	0.00601721	H	1.36593015	-0.40935249	-2.55341480
C	-3.04892205	-3.28940023	1.32117854	H	2.30465212	-0.05443767	-4.03471748
H	-2.75370162	-2.68182915	2.18450471	H	2.24197139	1.13919130	-2.70021386
H	-2.58297814	-4.27661899	1.39662267	C	2.32813566	-0.19030532	2.88731501
H	-4.14179090	-3.40832525	1.34556349	H	2.39845389	-0.05229194	3.97128297
C	-3.06403915	-3.43603371	-1.21734578	H	2.40723187	-1.25485429	2.64467483
H	-2.82704650	-2.90864808	-2.15057577	H	1.37388023	0.19652187	2.52736165
H	-4.14735018	-3.60899077	-1.19767959	B	-1.11416273	0.00954972	0.50421272
H	-2.55969200	-4.40388652	-1.21253434	F	-1.07700156	0.01959572	2.01742456
C	-3.01493874	3.40973024	-1.34522833				

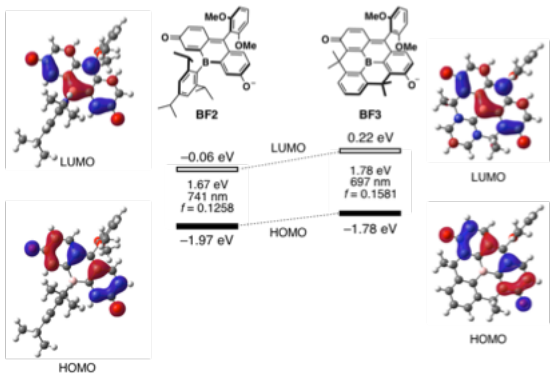


Fig. S13 Energy diagrams and Kohn–Sham plots of HOMOs and LUMOs for the deprotonated [**BF2**]$^-$ and [**BF3**]$^-$ calculated at the B3LYP/6-31+G(d) level of theory.

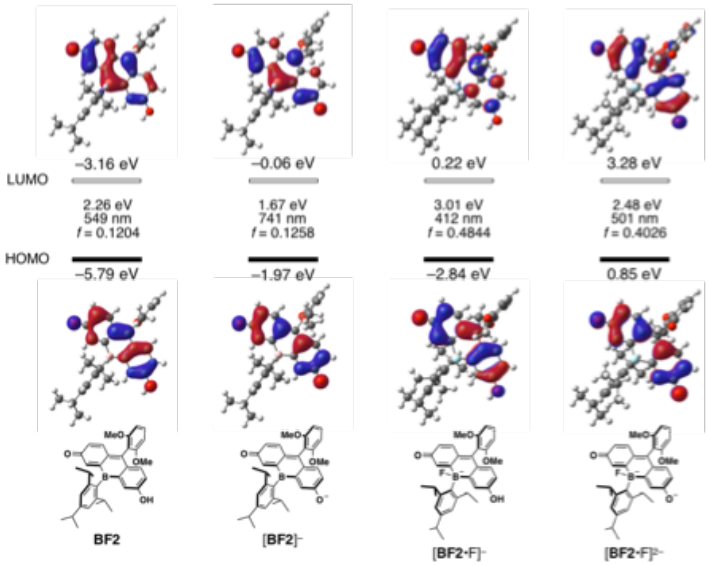


Fig. S14 Energy diagrams and Kohn–Sham plots of HOMOs and LUMOs for neutral **BF2**, deprotonated [**BF2**]$^{-}$, borate [**BF2**·F]$^{-}$, and borate fluorescein anion [**BF2**·F]$^{2-}$ calculated at the B3LYP/6-31G+(d) level of theory. The results of TD-DFT calculations at the same level of theory are also shown.

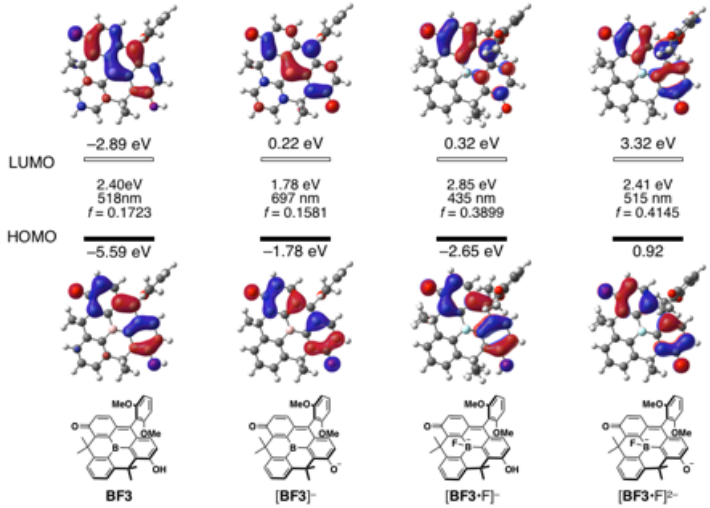


Fig. S15 Energy diagrams and Kohn–Sham plots of HOMOs and LUMOs for neutral **BF3**, deprotonated [**BF3**]$^{-}$, borate [**BF3**·F]$^{-}$, and borate fluorescein anion [**BF3**·F]$^{2-}$ calculated at the B3LYP/6-31+G(d) level of theory. The results of TD-DFT calculations at the same level of theory are also shown.

Table S14 Excited Energies of **BF2** and its Related Species[a]

Compound	Excited state	transition energy [eV] (wavelength [nm])	main CI coefficient	oscillator strength *f*
BF2	1	2.23 (557)	0.51463 (HOMO–4→LUMO)	0.0000
			0.42885 (HOMO–1→LUMO)	
	2	2.26 (549)	0.68292 (HOMO→LUMO)	0.1204
	3	2.47 (503)	–0.41435 (HOMO–4→LUMO)	0.0000
			0.55519 (HOMO–1→LUMO)	
[**BF2**]$^-$	1	1.67 (741)	0.69224 (HOMO→LUMO)	0.1258
	2	2.27 (548)	0.70189 (HOMO–1→LUMO)	0.0000
	3	2.42 (513)	0.70127 (HOMO–2→LUMO)	0.0000
[**BF2**·F]$^-$	1	2.53 (491)	0.32493 (HOMO–3→LUMO)	0.0002
			–0.22977 (HOMO–2→LUMO)	
			0.57759 (HOMO–1→LUMO)	
	2	2.94 (422)	0.47658 (HOMO–3→LUMO)	0.0013
			–0.31134 (HOMO–2→LUMO)	
			–0.39950 (HOMO–1→LUMO)	
	3	3.01 (412)	0.69187 (HOMO→LUMO)	0.4844
[**BF2**·F]$^{2-}$	1	2.41 (514)	0.70231 (HOMO–1→LUMO)	0.0034
	2	2.48 (501)	0.64897 (HOMO→LUMO)	0.4026
			0.24257 (HOMO→LUMO+4)	
	3	2.59 (478)	0.70145 (HOMO→LUMO+2)	0.0000

[a] Calculated at the B3LYP/6-31+G(d) level using TD-DFT method.

Table S15 Excited Energies of the **BF3** and its Related Species[a]

Compound	Excited state	transition energy [eV] (wavelength [nm])	main CI coefficient	oscillator strength *f*
BF3	1	2.34 (530)	0.69168 (HOMO–1→LUMO)	0.0000
	2	2.40 (518)	0.68179 (HOMO→LUMO)	0.1723
	3	2.90 (427)	0.70504 (HOMO–1→LUMO)	0.0003
[**BF3**]$^-$	1	1.78 (697)	0.68848 (HOMO→LUMO)	0.1581
	2	2.41 (514)	0.70225 (HOMO–1→LUMO)	0.0000
	3	2.54 (488)	0.70127 (HOMO–2→LUMO)	0.0000
[**BF3**·F]$^-$	1	2.50 (495)	0.69027 (HOMO–1→LUMO)	0.0005
	2	2.85 (435)	0.68385 (HOMO→LUMO)	0.3899
	3	3.14 (395)	0.68042 (HOMO-2→LUMO)	0.0426
[**BF3**·F]$^{2-}$	1	2.41 (515)	0.67614 (HOMO→LUMO)	0.4145
	2	2.56 (484)	0.70397 (HOMO→LUMO+1)	0.0002
	3	2.62 (474)	0.69196 (HOMO–1→LUMO)	0.0061

[a] Calculated at the B3LYP/6-31+G(d) level using TD-DFT method.

5. References

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6. NMR Spectra

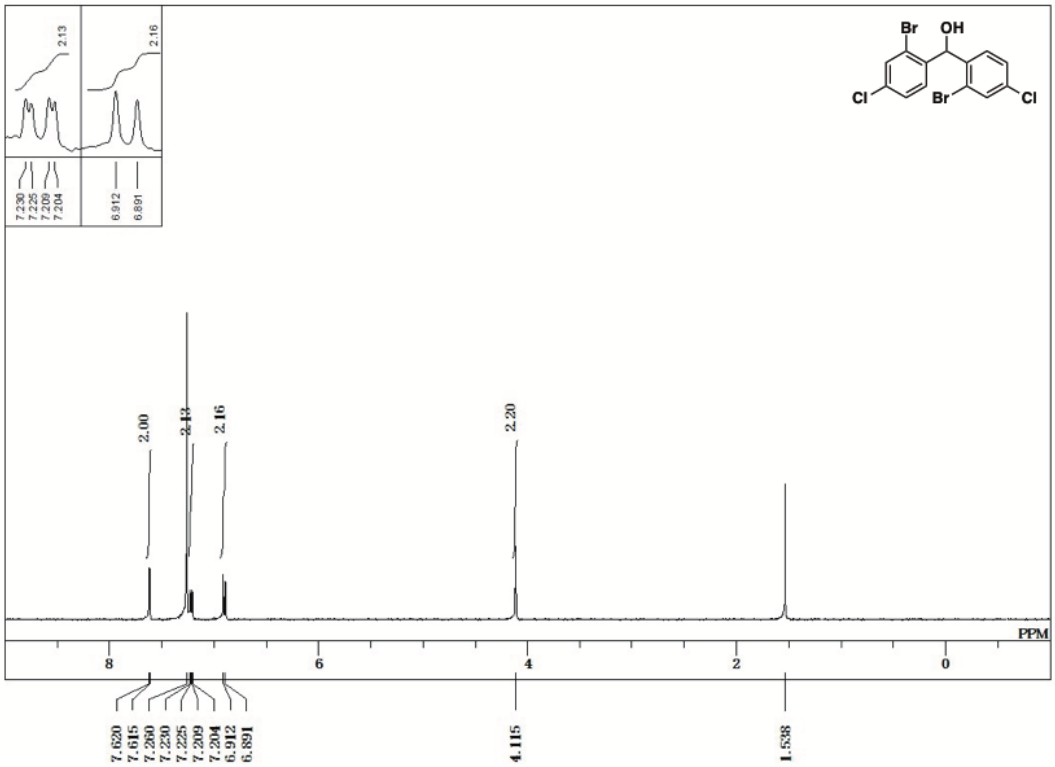

Fig. S16 ^{1}H NMR spectrum of **S2** (400 MHz, acetone-d_6).

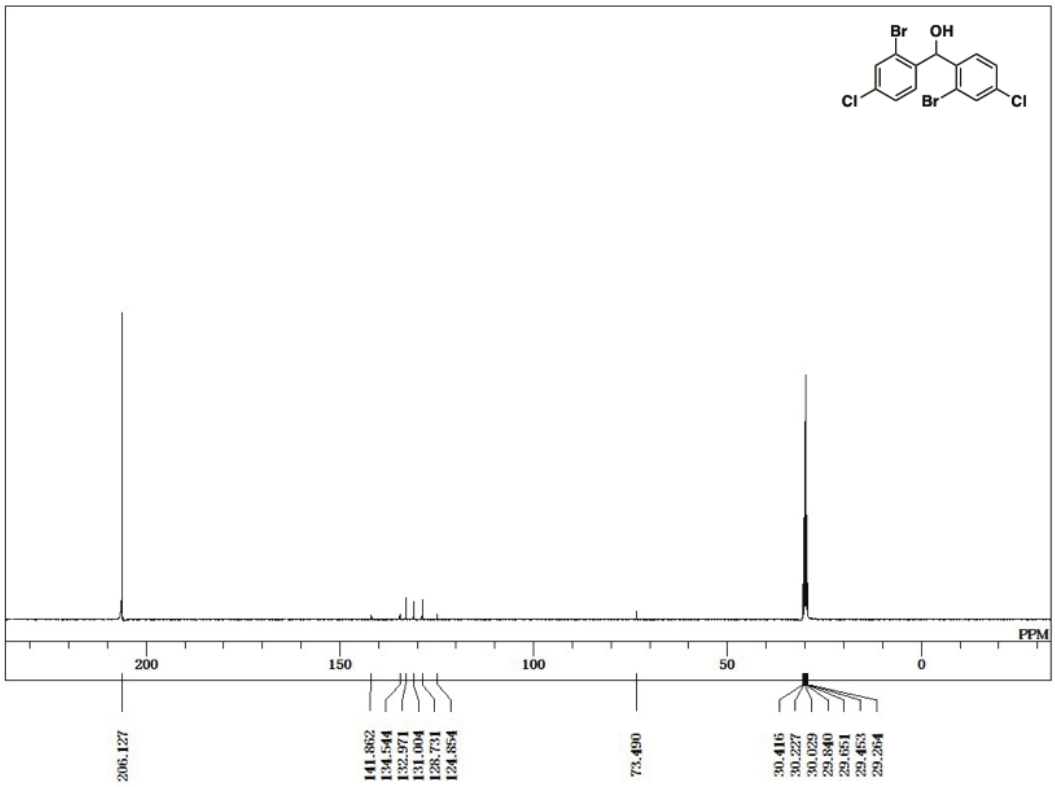

Fig. S17 $^{13}C\{^{1}H\}$ NMR spectrum of **S2** (100 MHz, acetone-d_6).

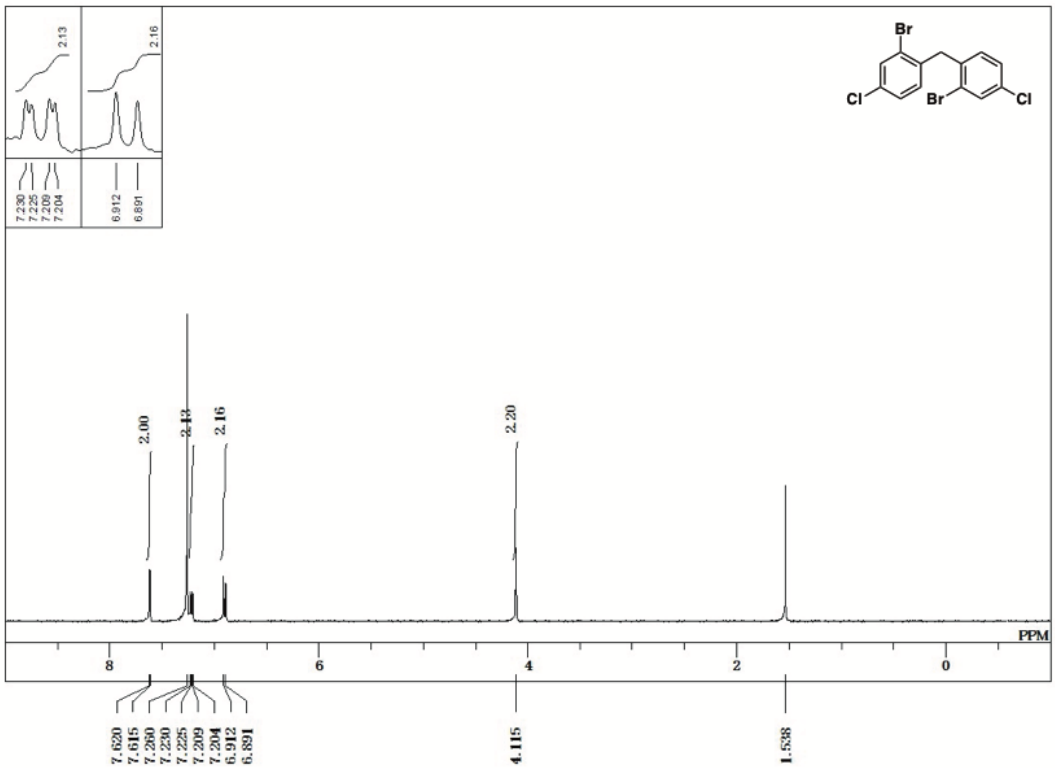

Fig. S18 ^{1}H NMR spectrum of **S3** (400 MHz, $CDCl_3$).

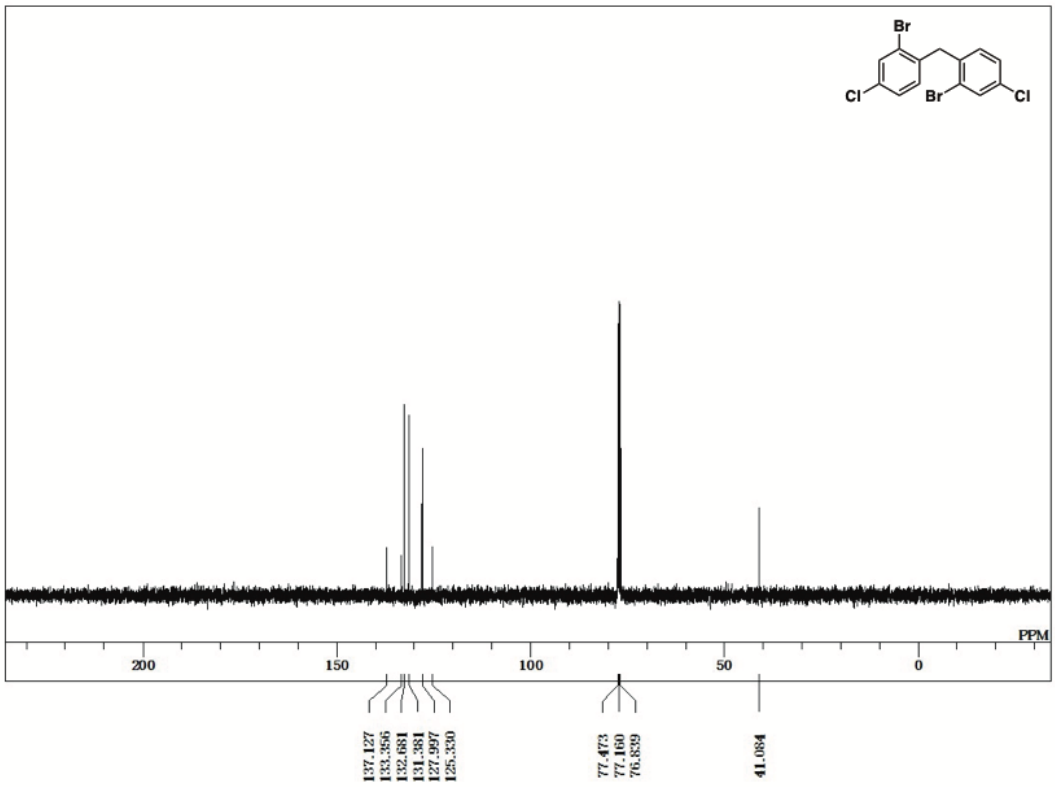

Fig. S19 $^{13}C\{^{1}H\}$ NMR spectrum of **S3** (100 MHz, $CDCl_3$).

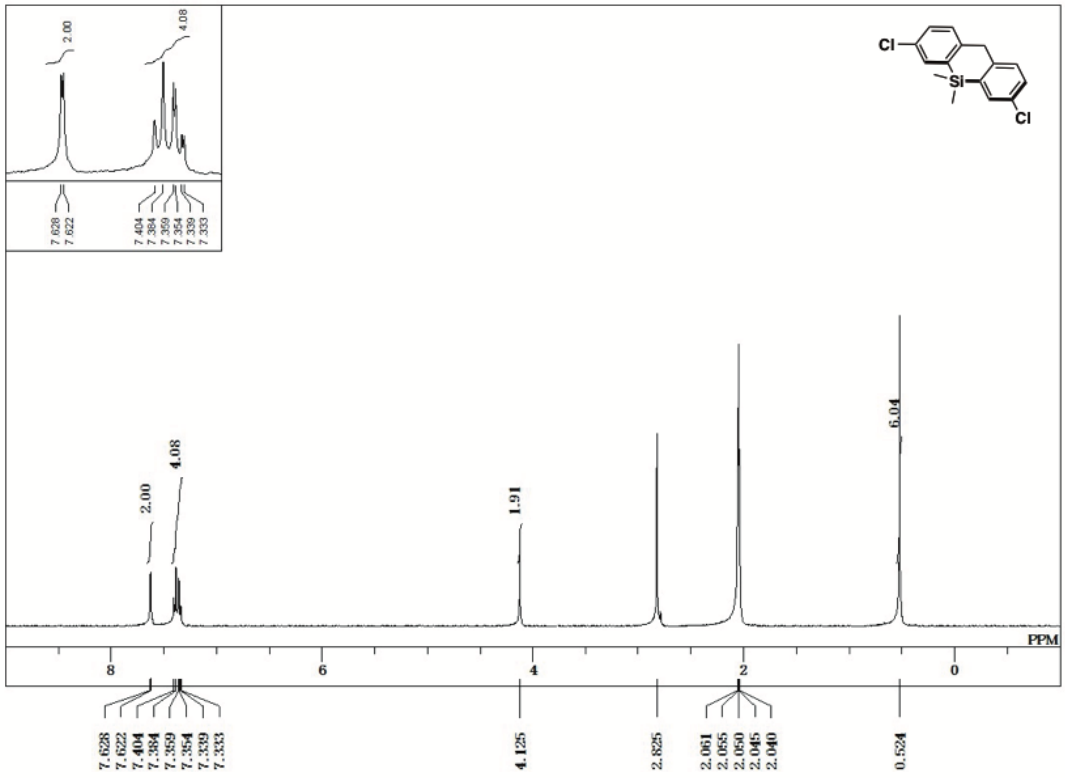

Fig. S20 ^{1}H NMR spectrum of **S4** (400 MHz, acetone-d_6).

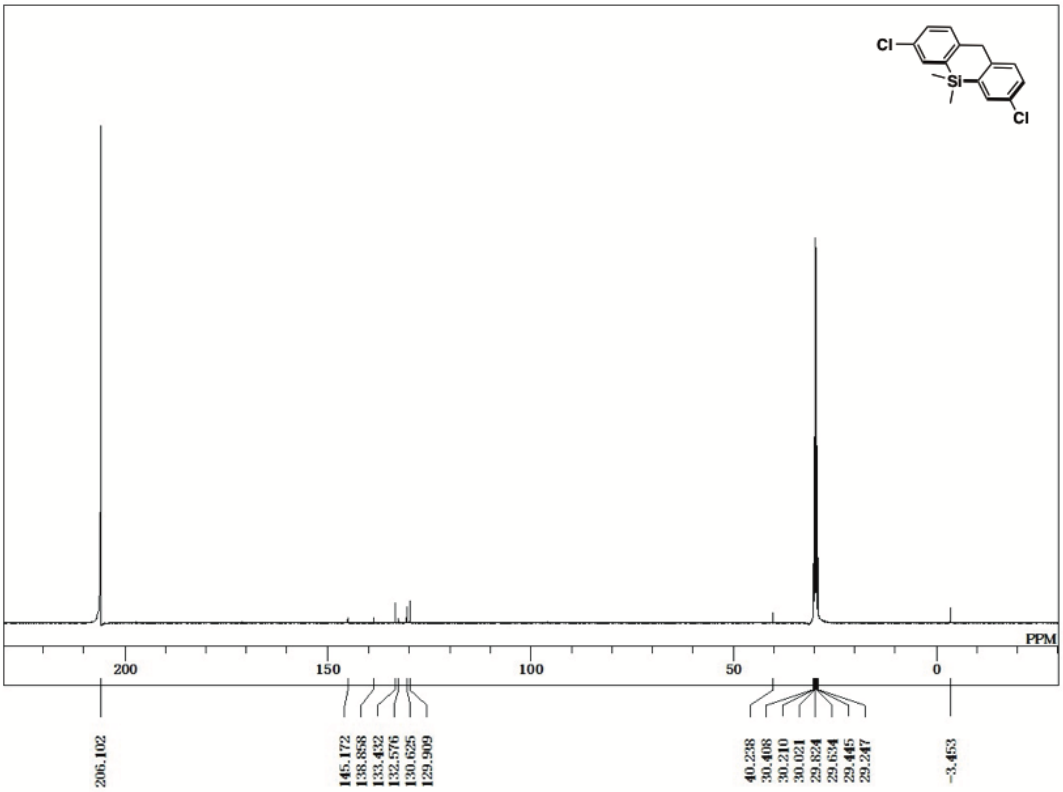

Fig. S21 $^{13}C\{^{1}H\}$ NMR spectrum of **S4** (100 MHz, acetone-d_6).

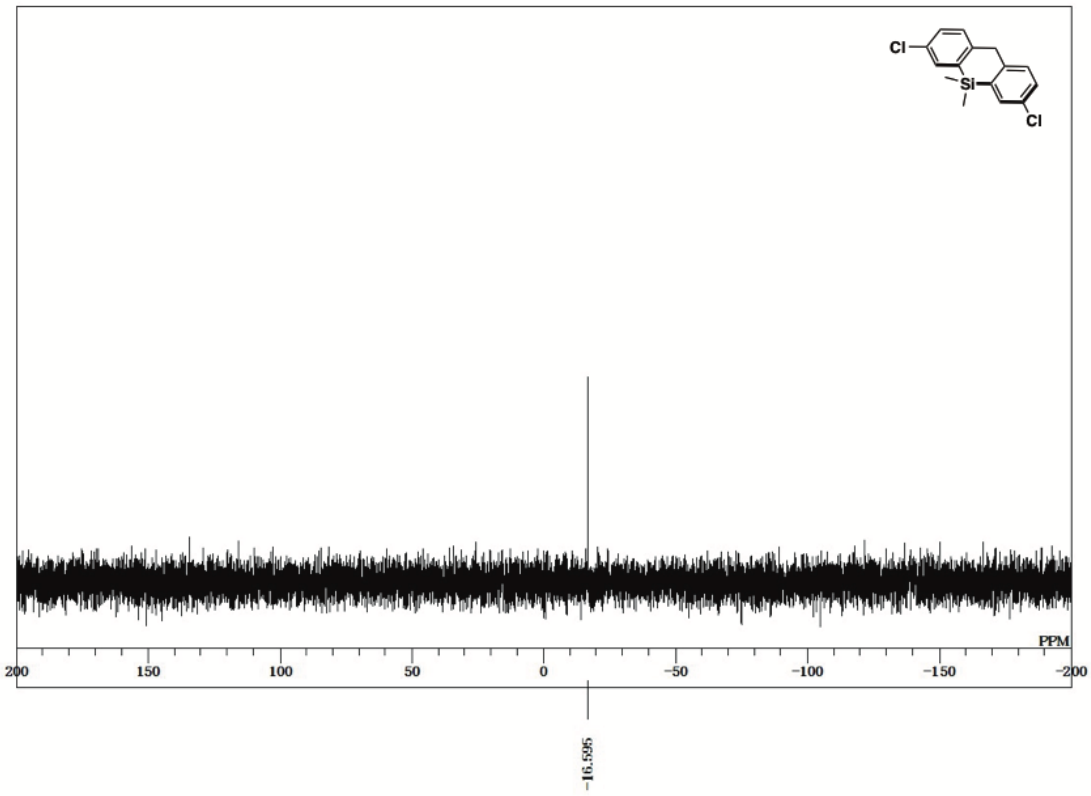

Fig. S22 $^{29}Si\{^{1}H\}$ NMR spectrum of **S4** (79 MHz, acetone-d_6).

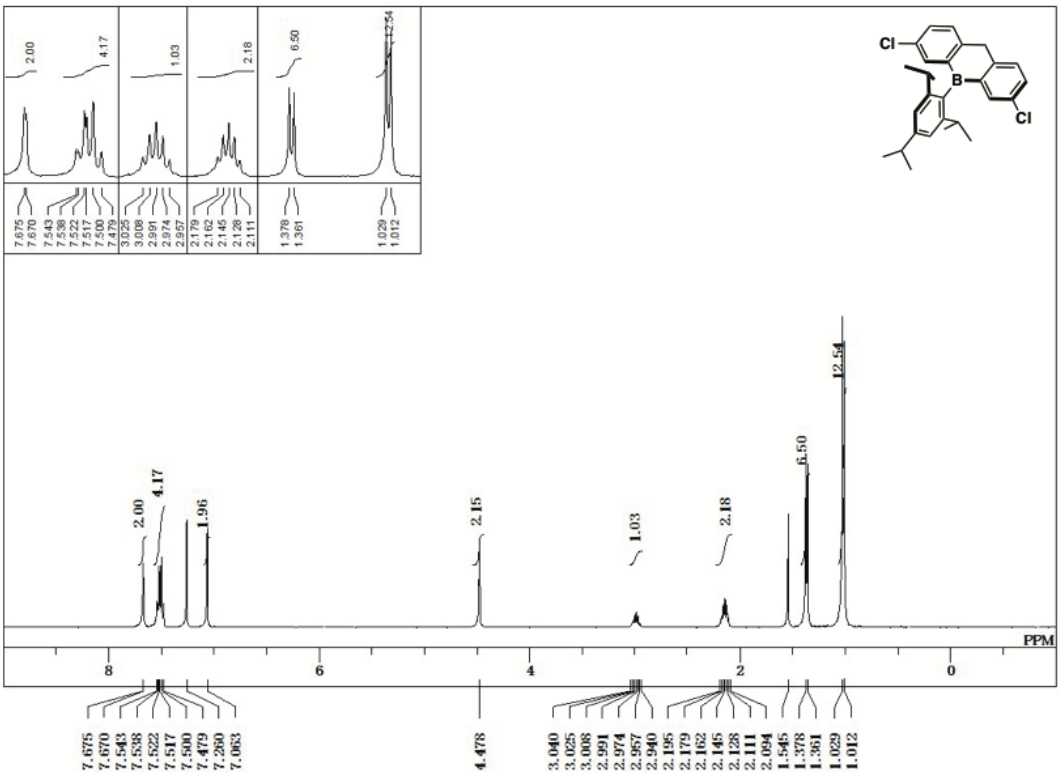

Fig. S23 ^{1}H NMR spectrum of **1a** (400 MHz, $CDCl_3$).

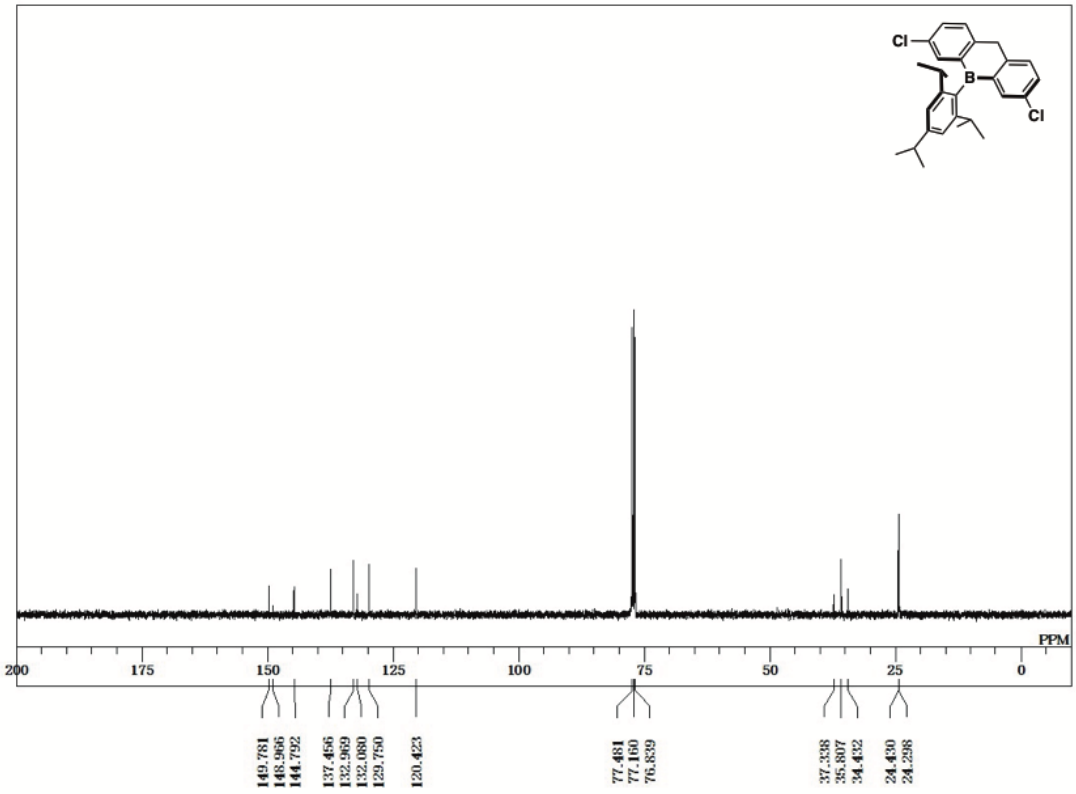

Fig.S24 $^{13}C\{^{1}H\}$ NMR spectrum of **1a** (100 MHz, $CDCl_3$).

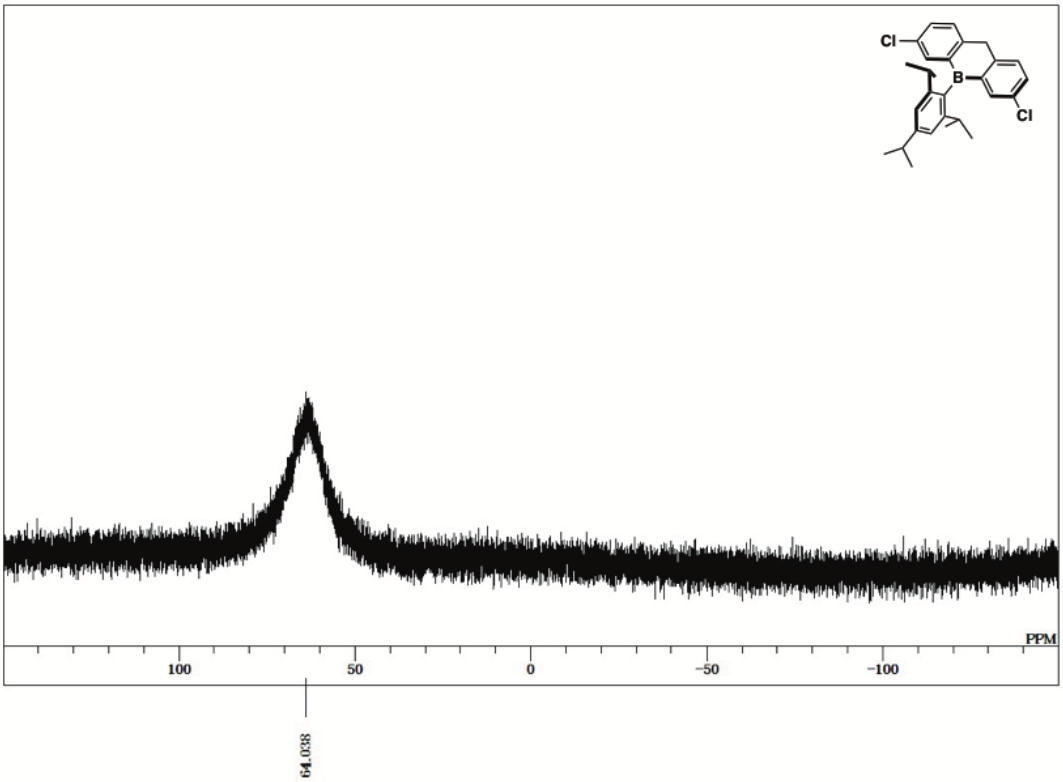

Fig. S25 $^{11}B\{^{1}H\}$ NMR spectrum of **1a** (128 MHz, $CDCl_3$).

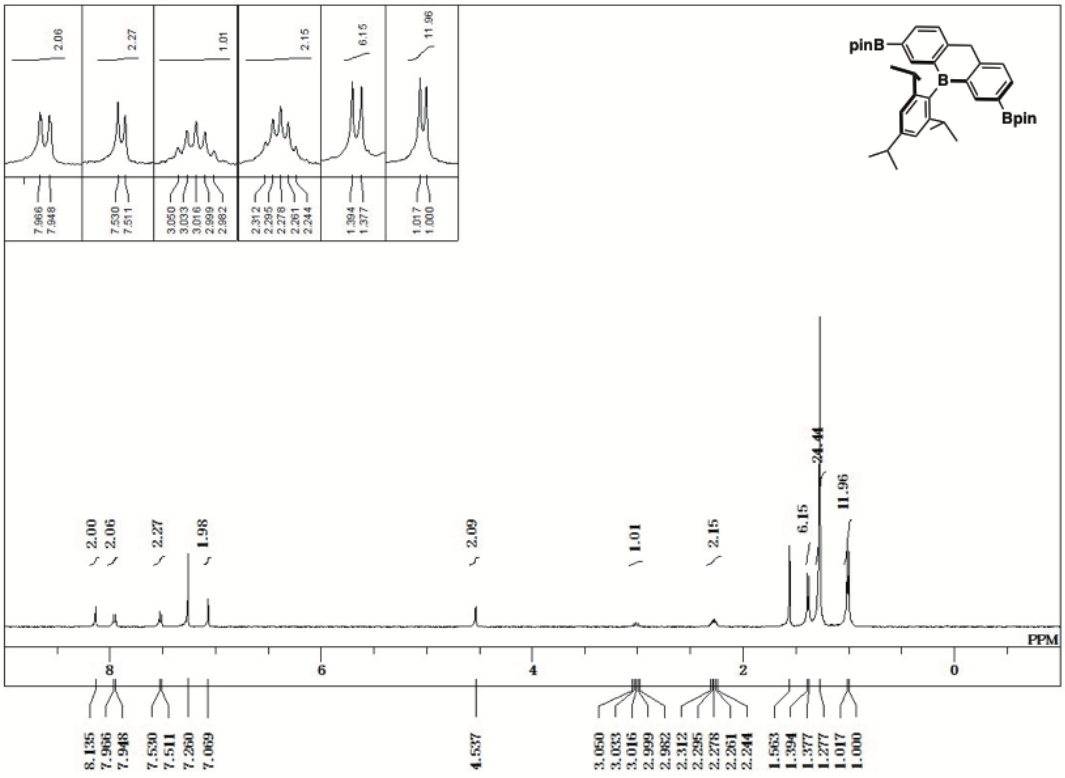

Fig. S26 ^{1}H NMR spectrum of **2a** (400 MHz, $CDCl_3$).

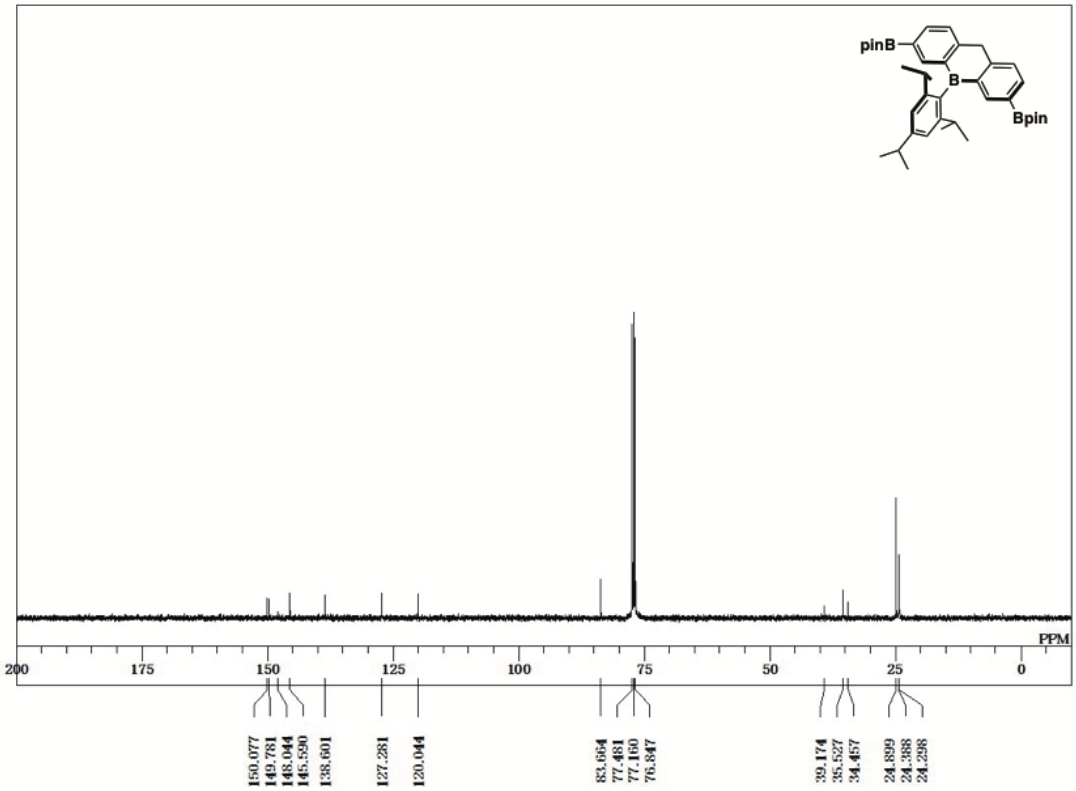

Fig. S27 $^{13}C\{^{1}H\}$ NMR spectrum of **2a** (100 MHz, $CDCl_3$).

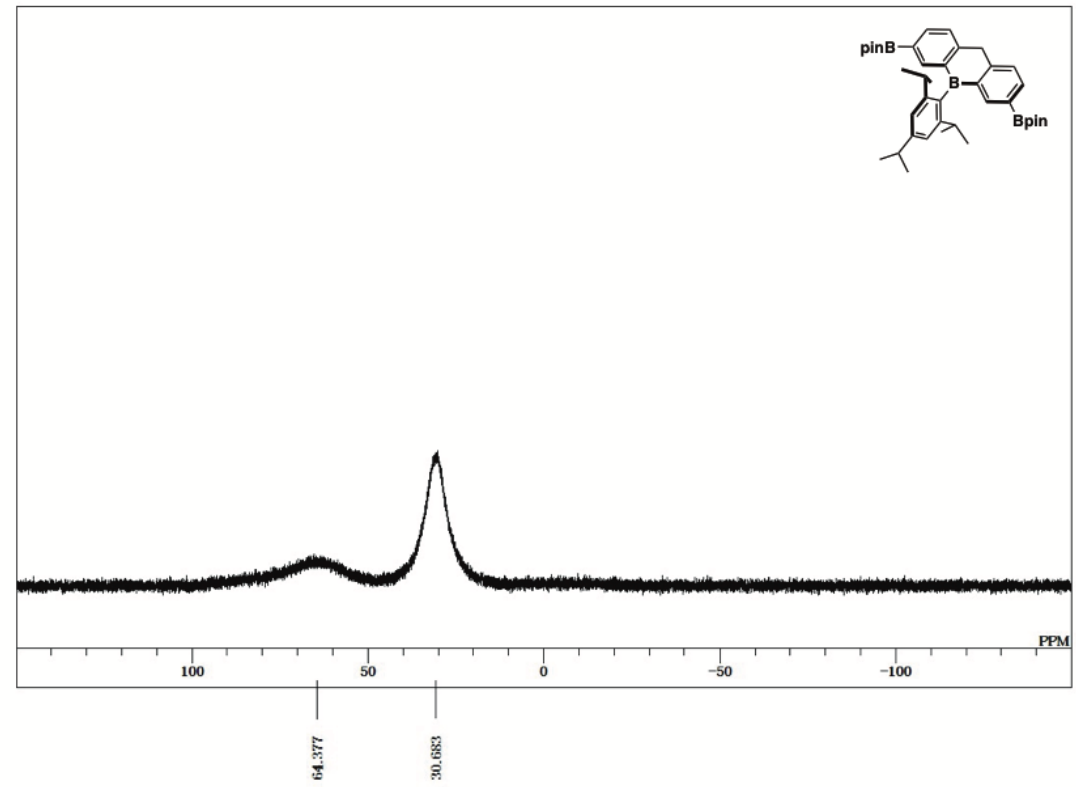

Fig. S28 $^{11}B\{^{1}H\}$ NMR spectrum of **2a** (128 MHz, $CDCl_3$).

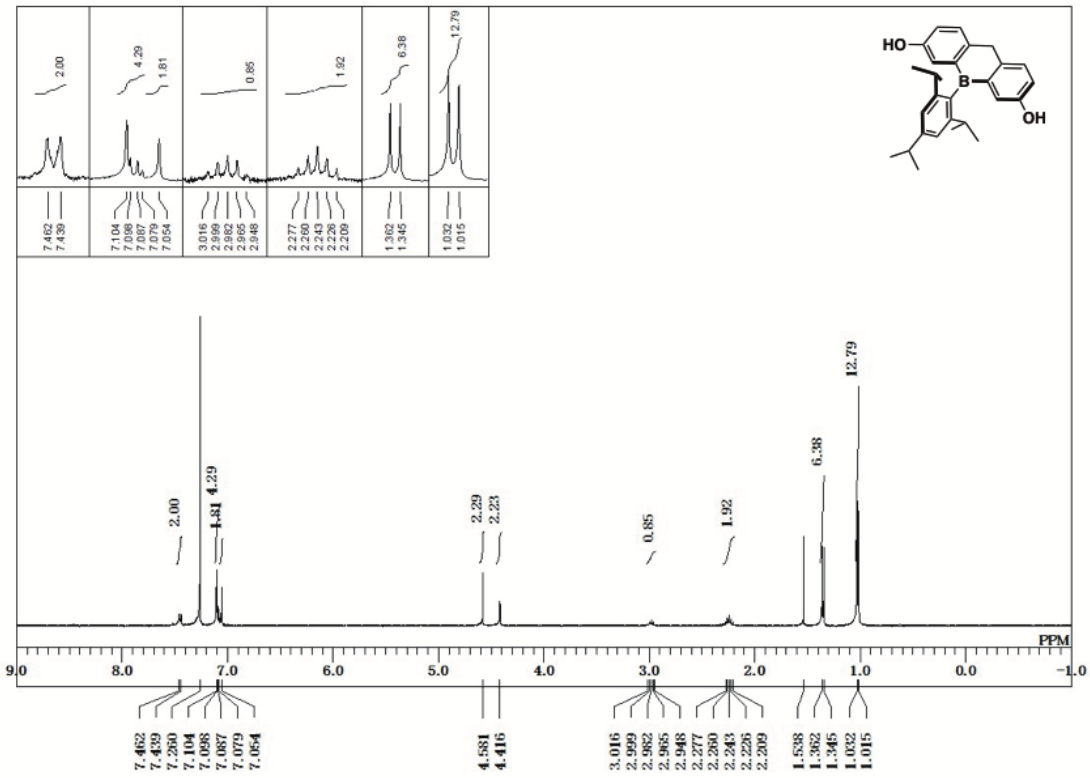

Fig. S29 ^{1}H NMR spectrum of **3a** (400 MHz, $CDCl_3$).

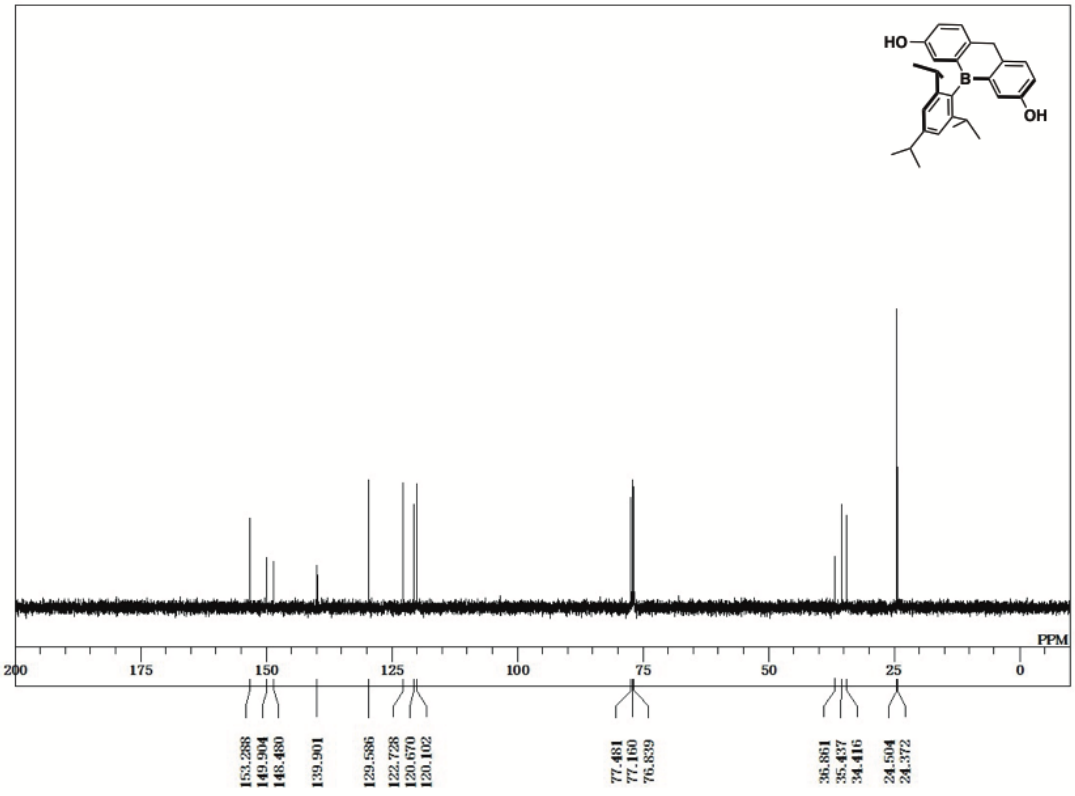

Fig. S30 $^{13}C\{^{1}H\}$ NMR spectrum of **3a** (100 MHz, $CDCl_3$).

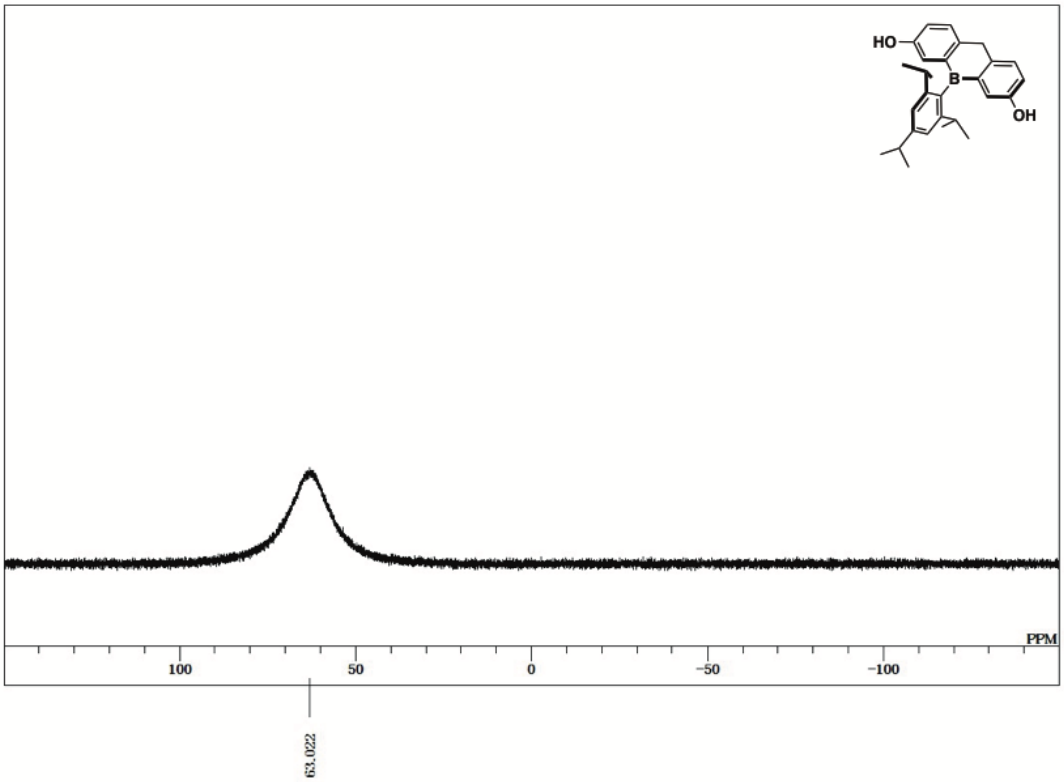

Fig. S31 $^{11}B\{^{1}H\}$ NMR spectrum of **3a** (128 MHz, $CDCl_3$).

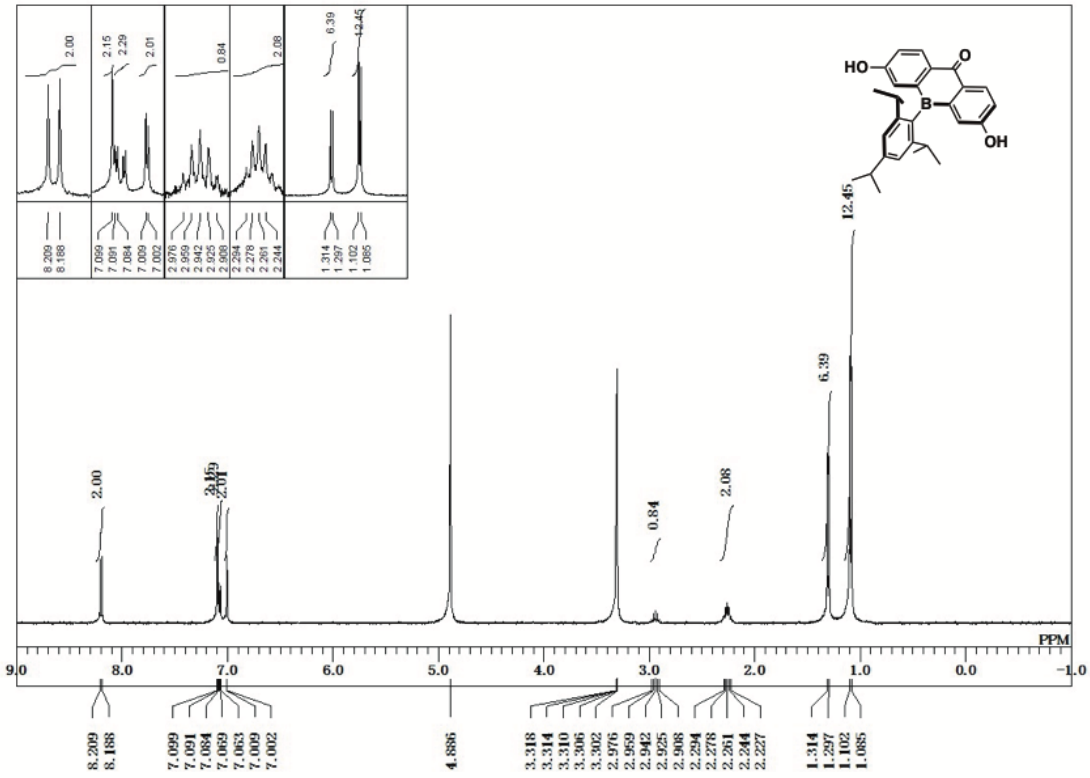

Fig. S32 ^{1}H NMR spectrum of **4** (400 MHz, CD_3OD).

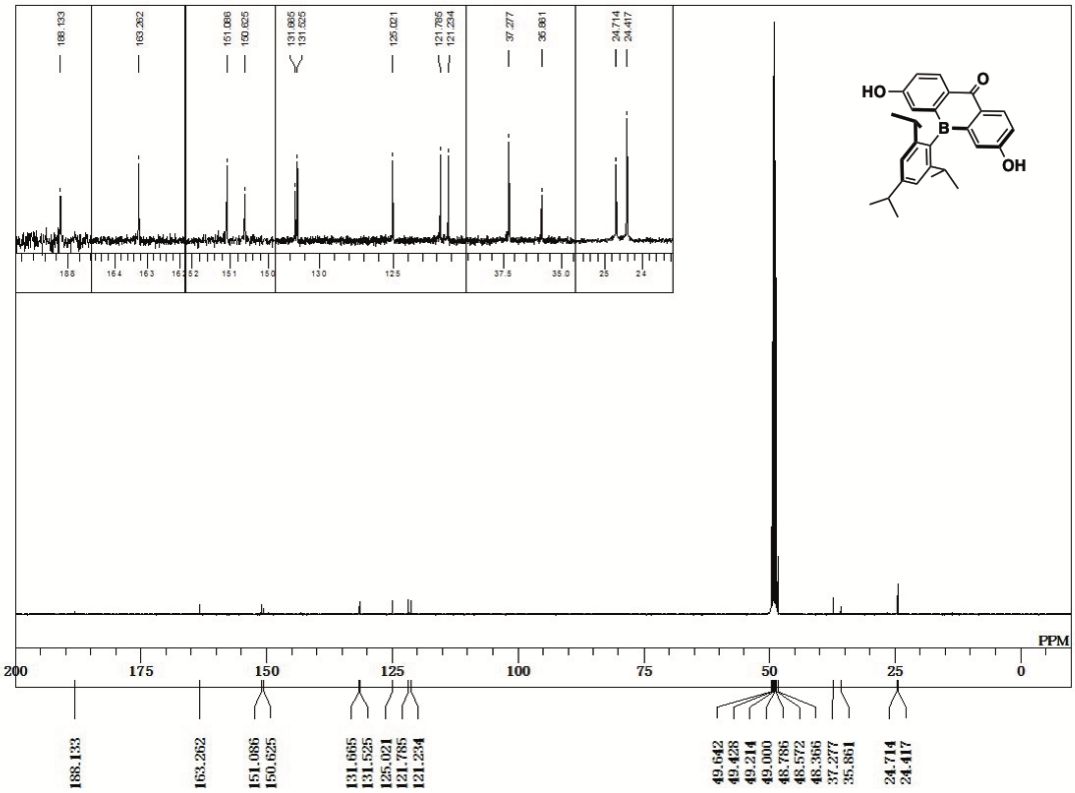

Figure S33 $^{13}C\{^{1}H\}$ NMR spectrum of **4** (100 MHz, CD_3OD).

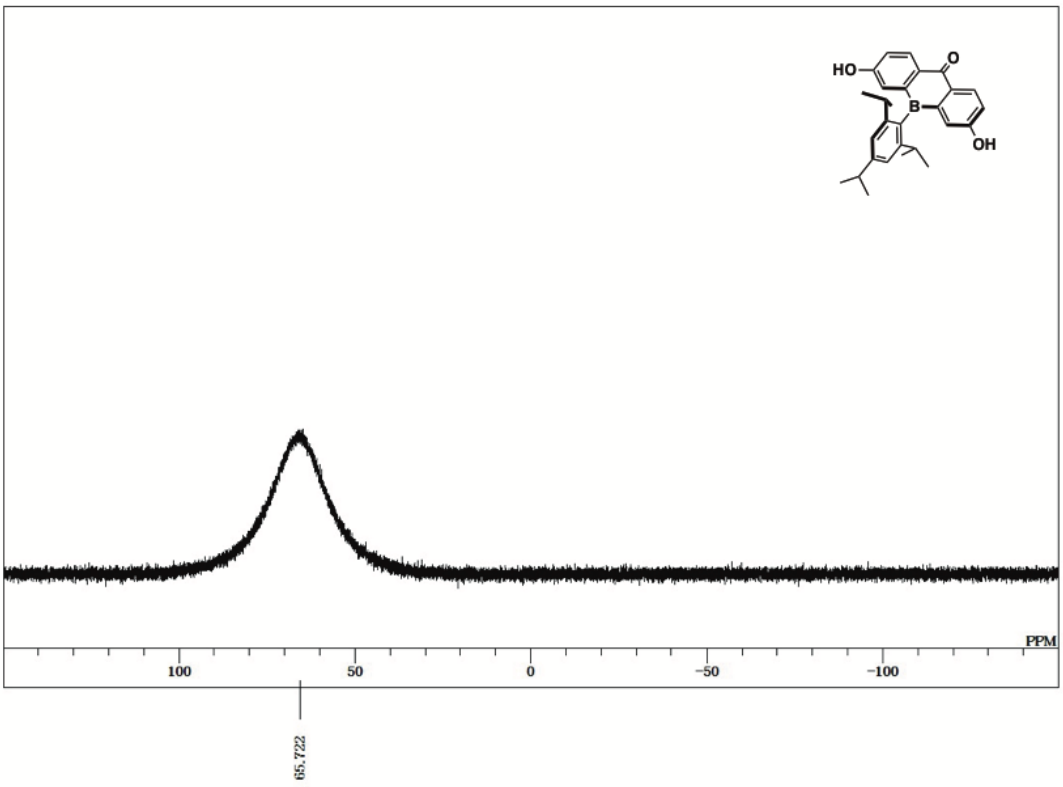

Fig. S34 $^{11}B\{^{1}H\}$ NMR spectrum of **4** (128 MHz, CD_3OD).

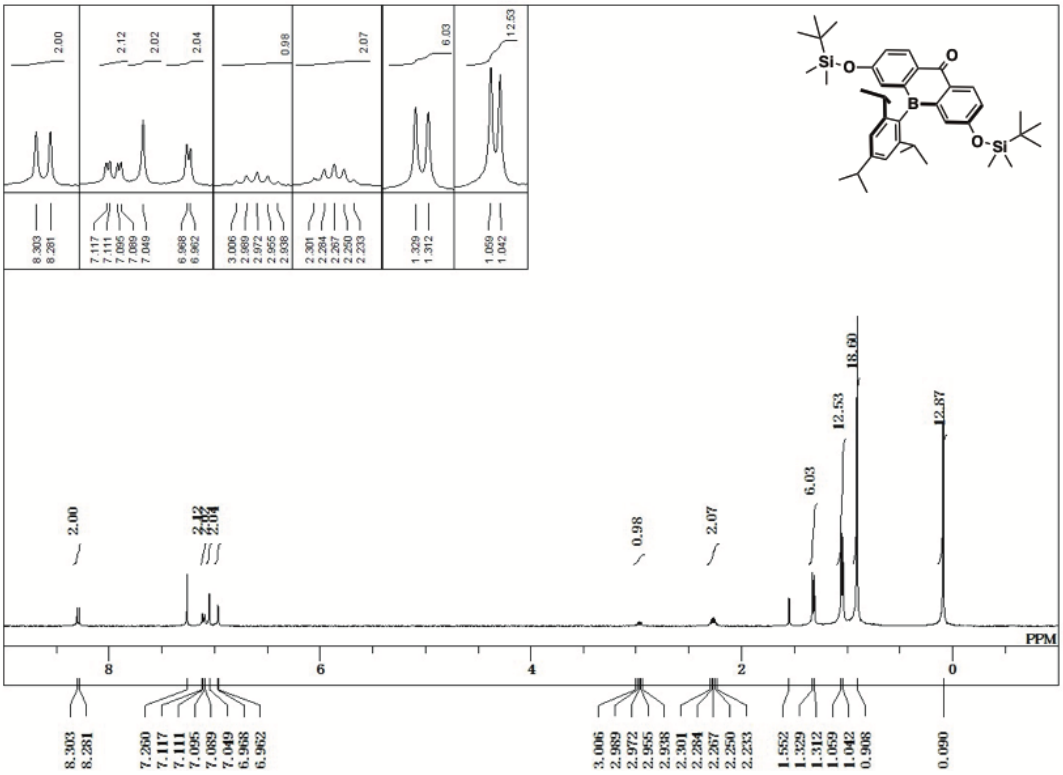

Fig. S35 ^{1}H NMR spectrum of **5** (400 MHz, $CDCl_3$).

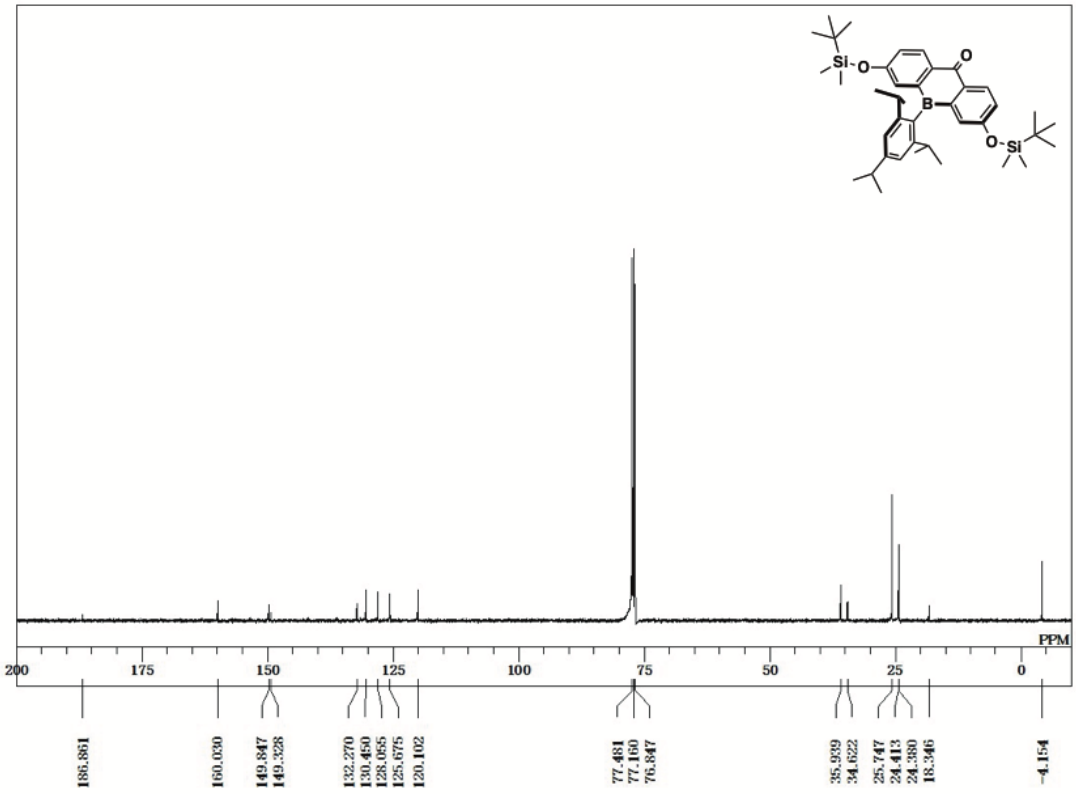

Fig. S36 $^{13}C\{^{1}H\}$ NMR spectrum of **5** (100 MHz, $CDCl_3$).

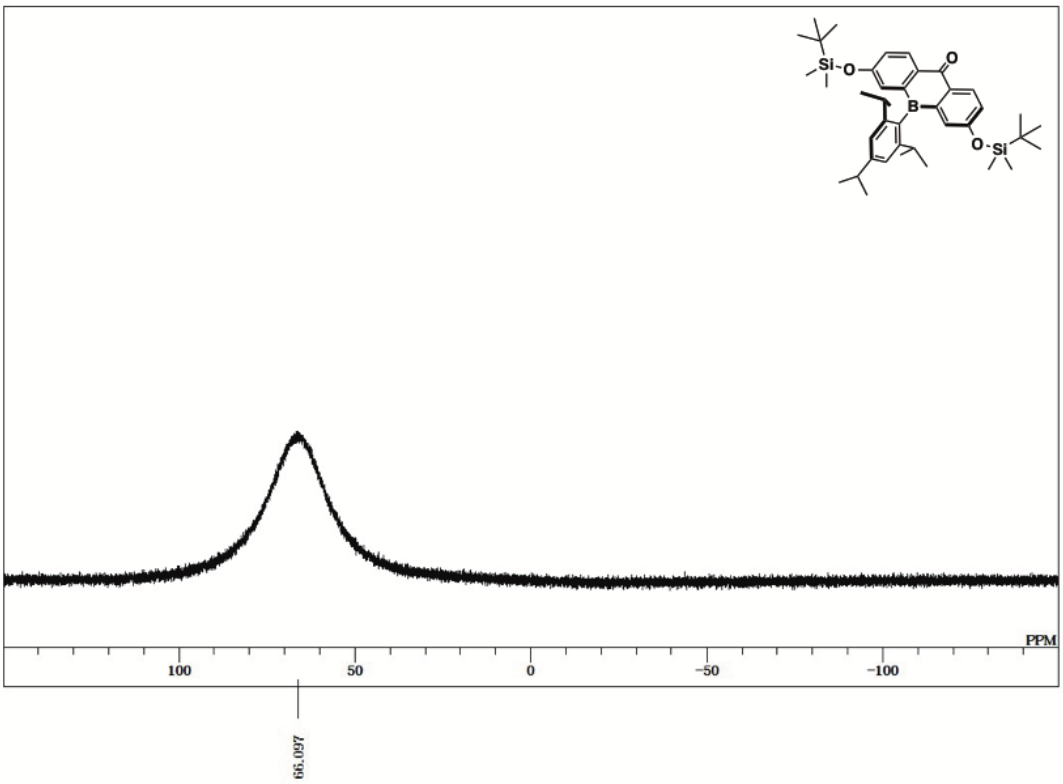

Fig. S37 $^{11}B\{^{1}H\}$ NMR spectrum of **5** (128 MHz, $CDCl_3$).

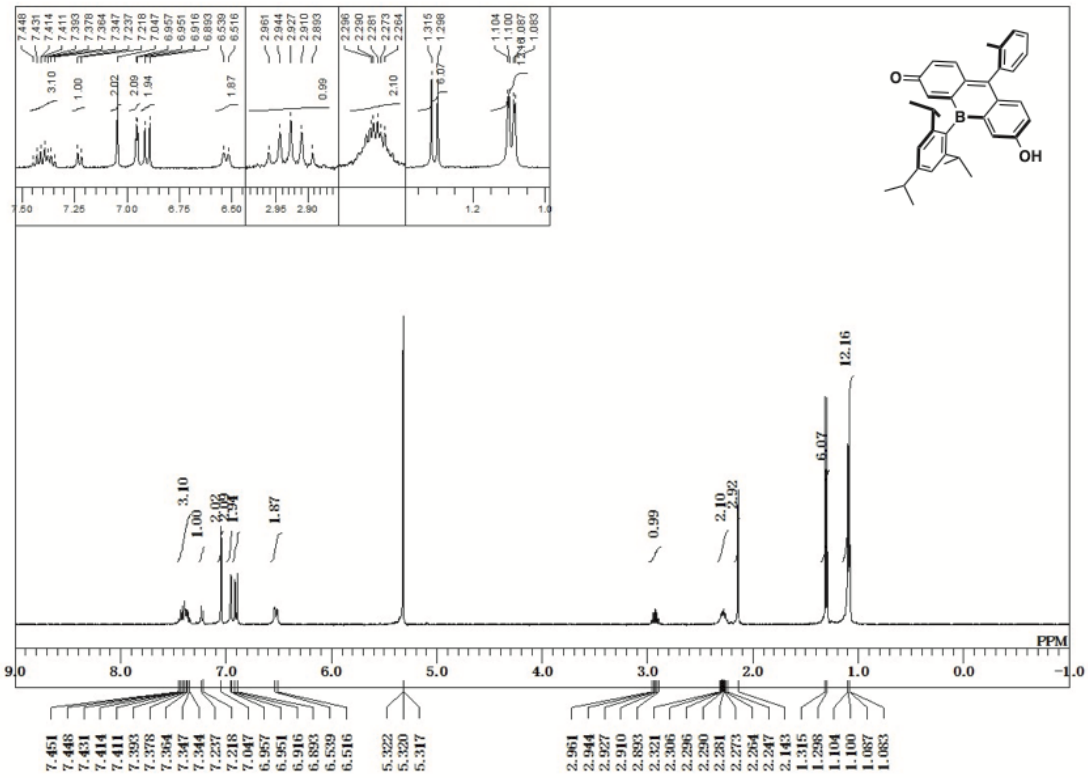

Fig. S38 ^{1}H NMR spectrum of **BF1** (400 MHz, CD_2Cl_2).

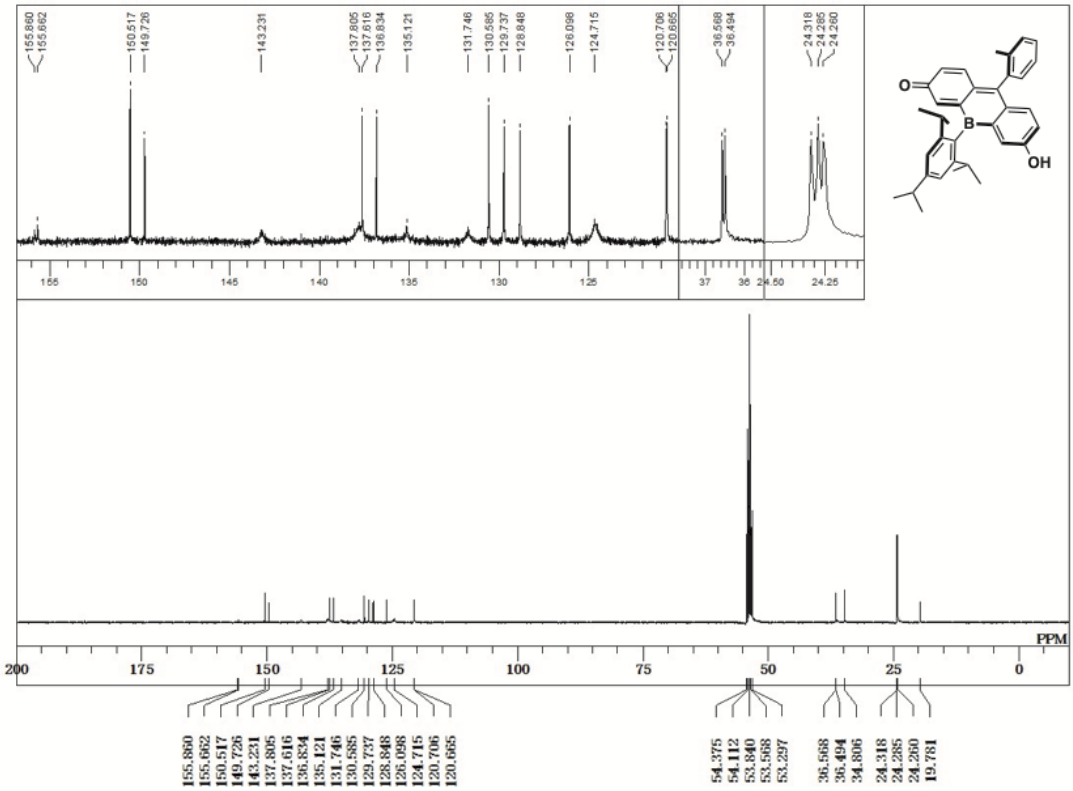

Figure S39 $^{13}C\{^{1}H\}$ NMR spectrum of **BF1** (100 MHz, CD_2Cl_2).

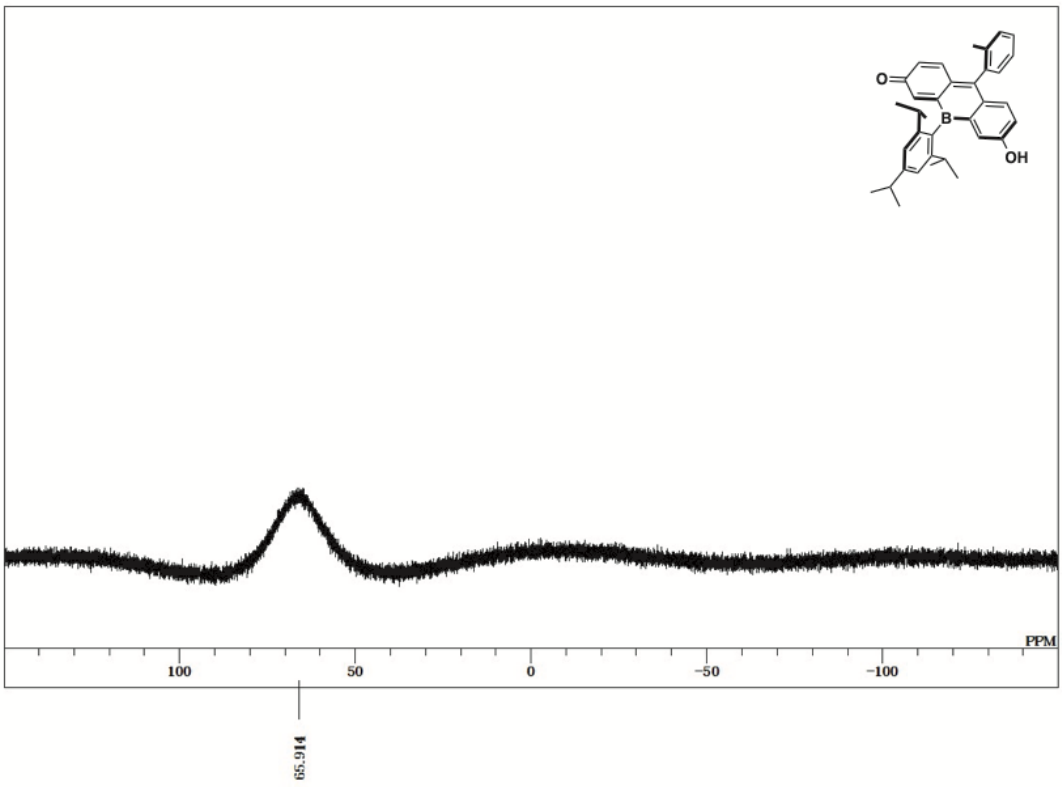

Fig. S40 $^{11}B\{^{1}H\}$ NMR spectrum of **BF1** (128 MHz, CD_2Cl_2).

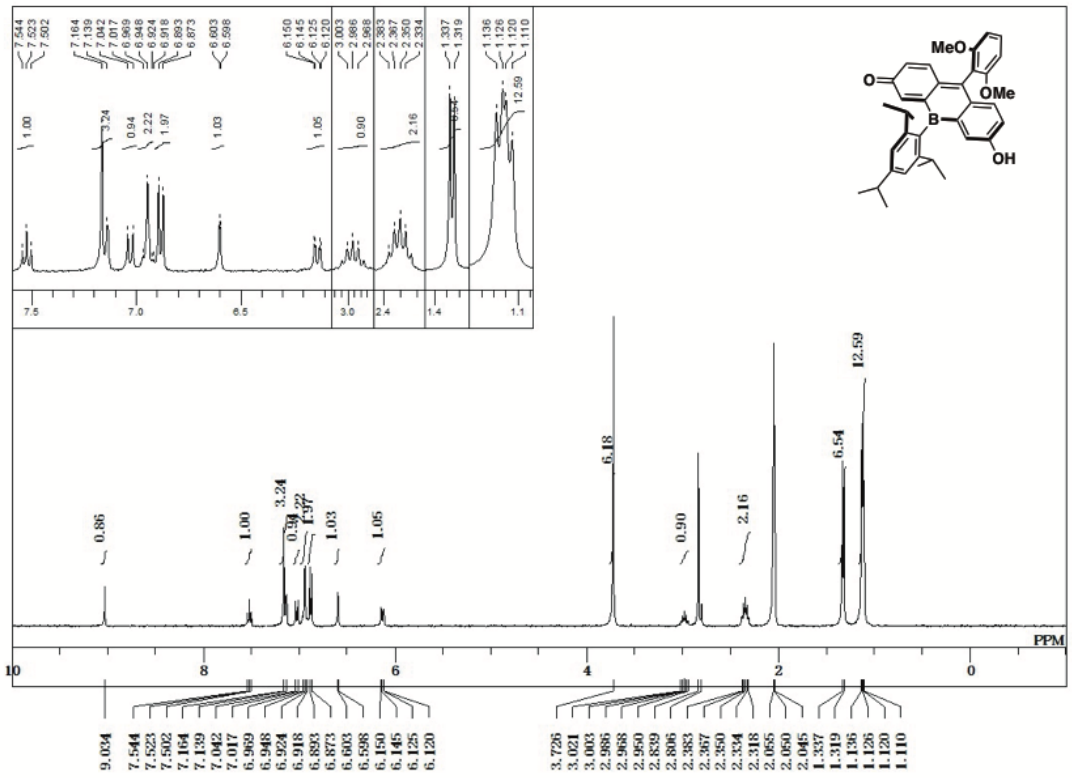

Fig. S41 ^{1}H NMR spectrum of **BF2** (400 MHz, acetone-d_6).

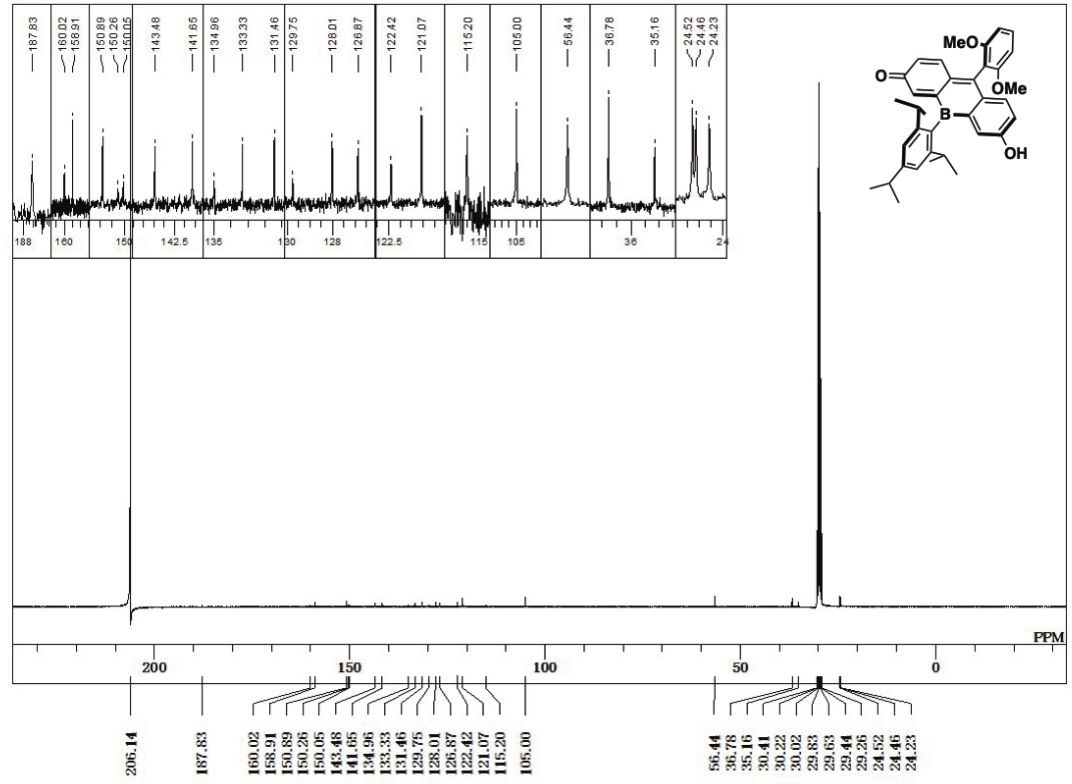

Fig. S42 ^{13}C{^{1}H} NMR spectrum of **BF2** (100 MHz, acetone-d_6).

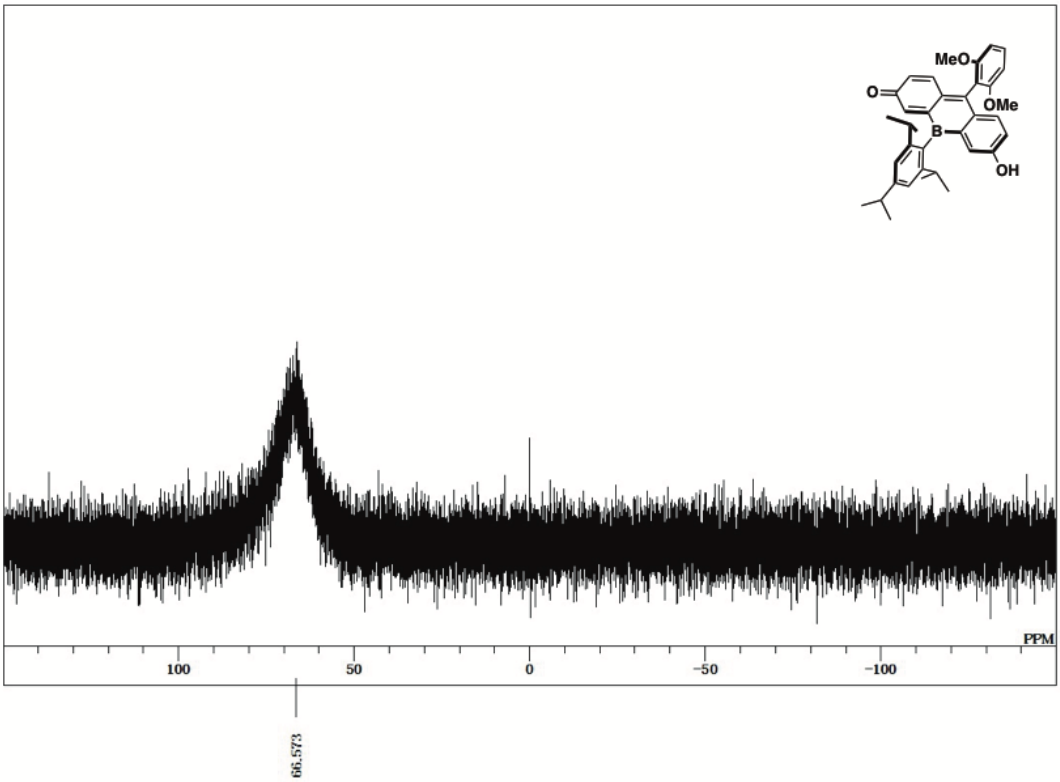

Fig. S43 $^{11}B\{^{1}H\}$ NMR spectrum of **BF2** (128 MHz, acetone-d_6).

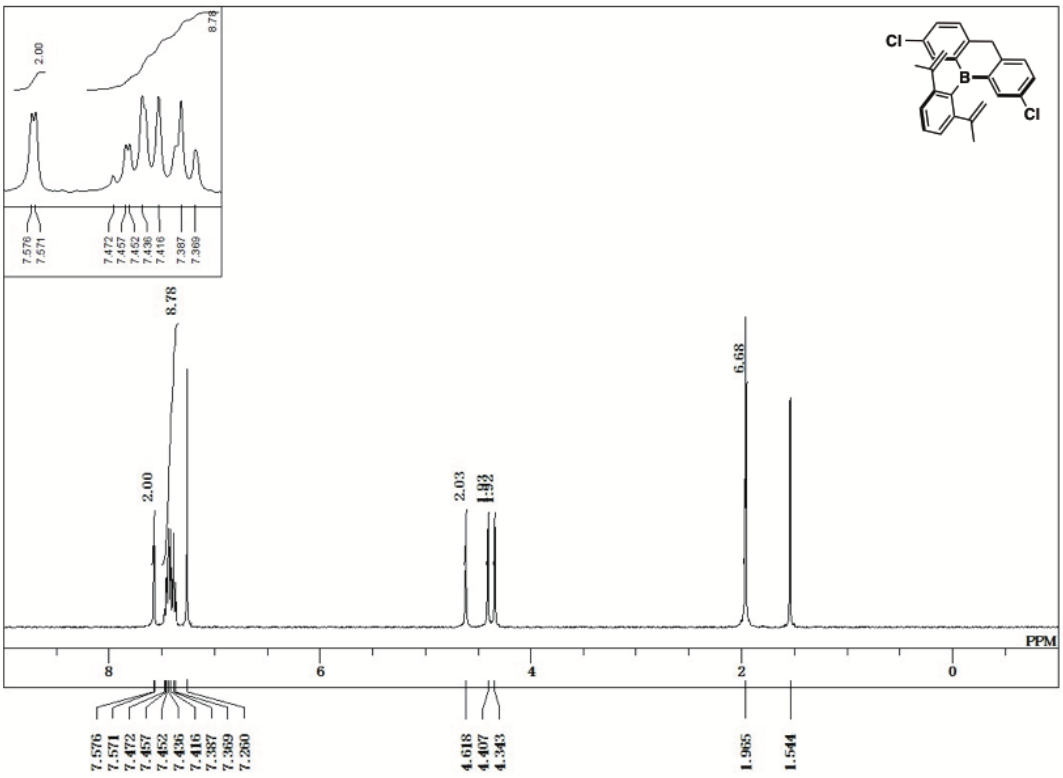

Fig S44. ^{1}H NMR spectrum of **1b** (400 MHz, $CDCl_3$).

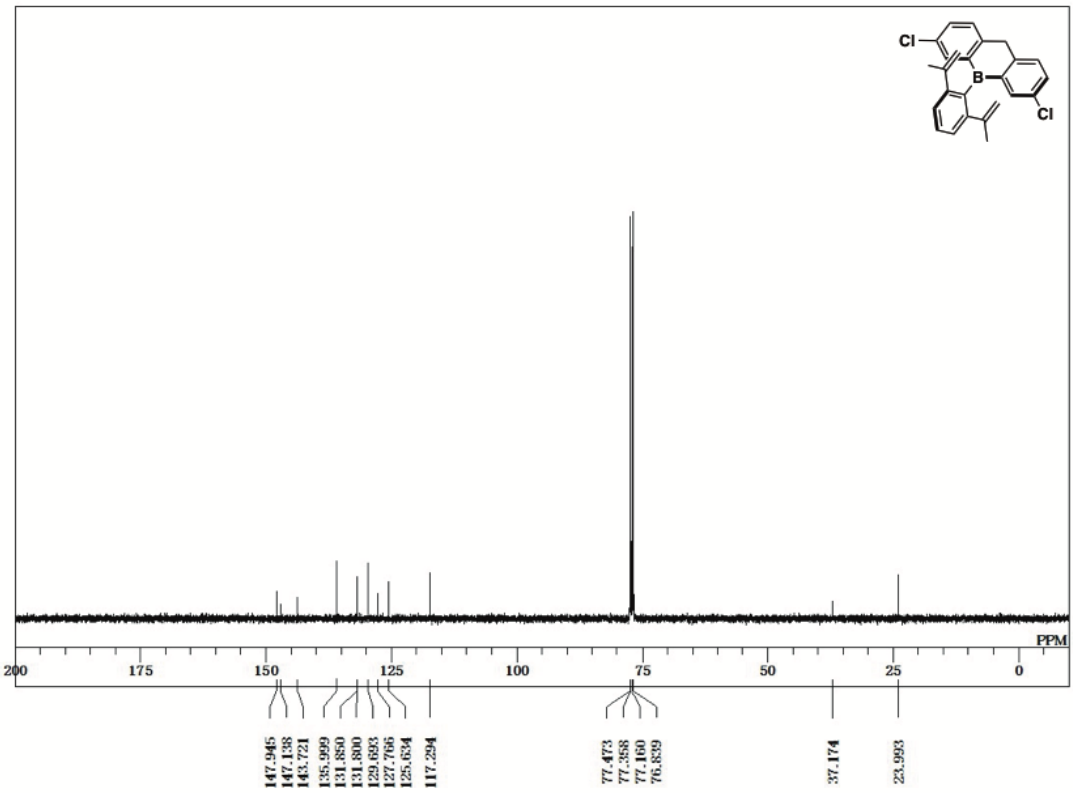

Fig. S45 $^{13}C\{^{1}H\}$ NMR spectrum of **1b** (100 MHz, $CDCl_3$).

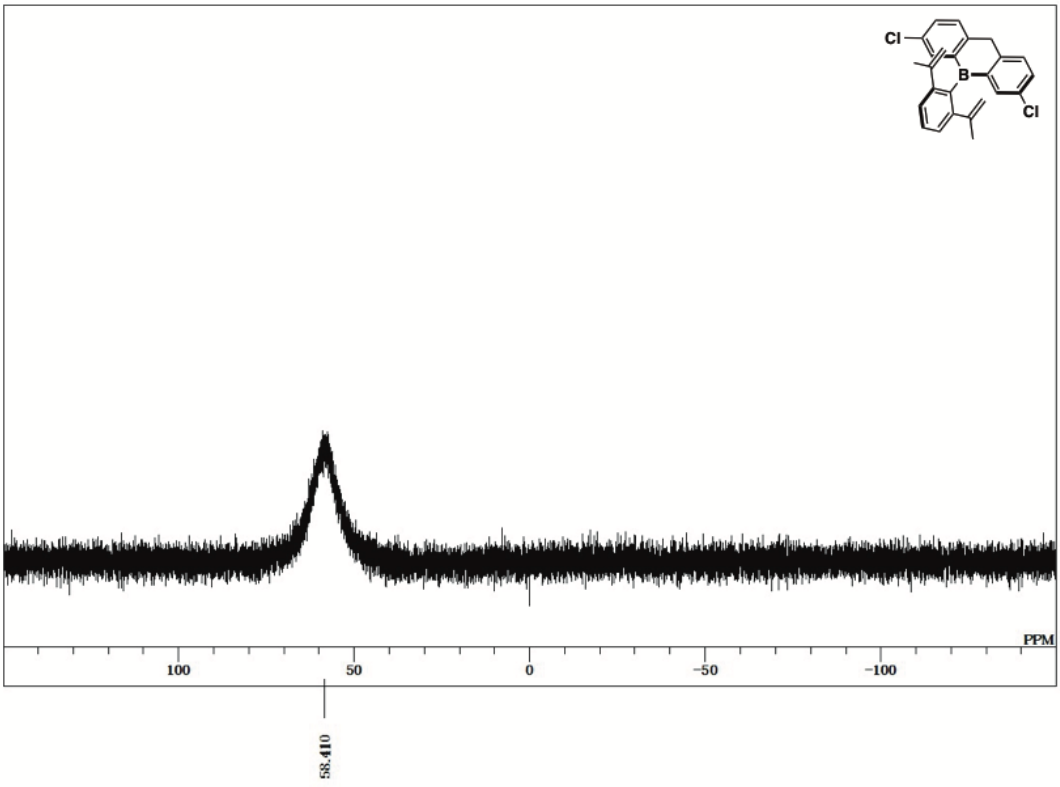

Fig. S46 $^{11}B\{^{1}H\}$ NMR spectrum of **1b** (128 MHz, $CDCl_3$).

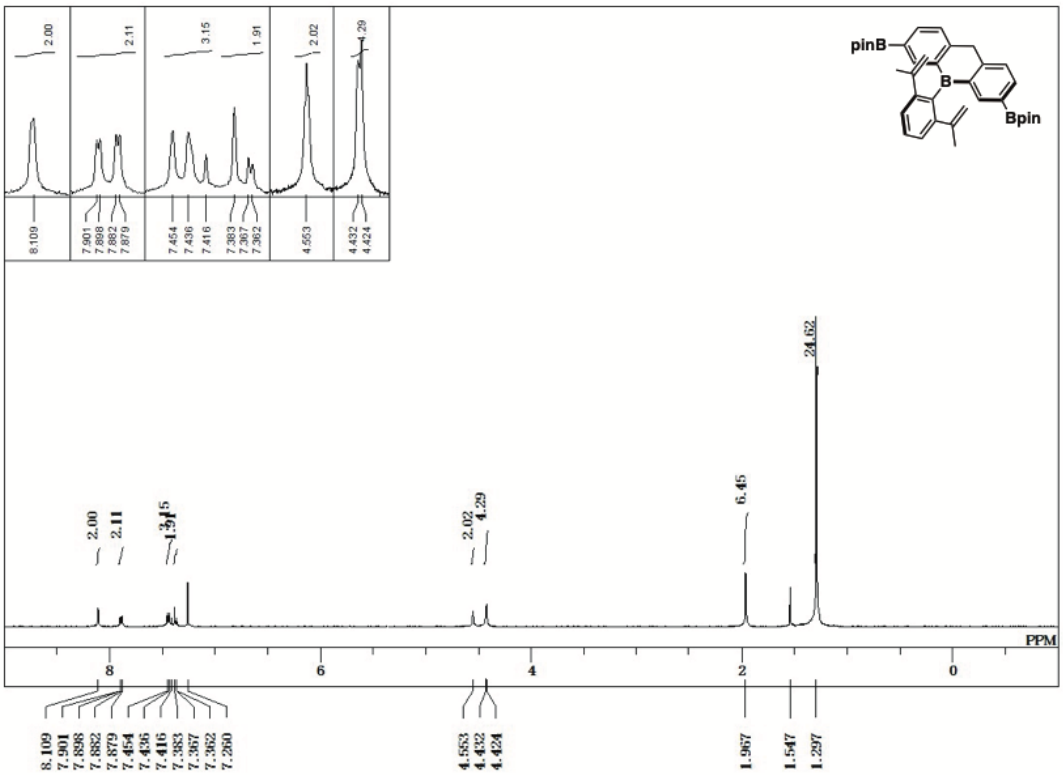

Fig. S47 ^{1}H NMR spectrum of **2b** (400 MHz, $CDCl_3$).

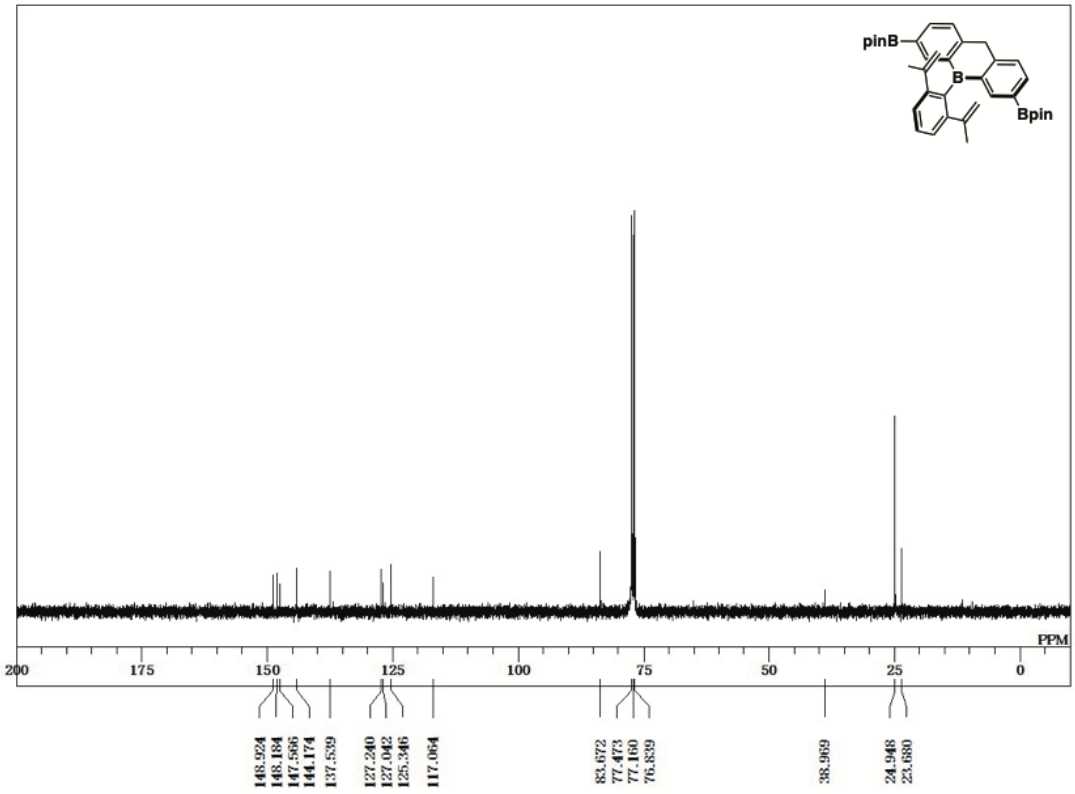

Fig. S48 $^{13}C\{^{1}H\}$ NMR spectrum of **2b** (100 MHz, $CDCl_3$).

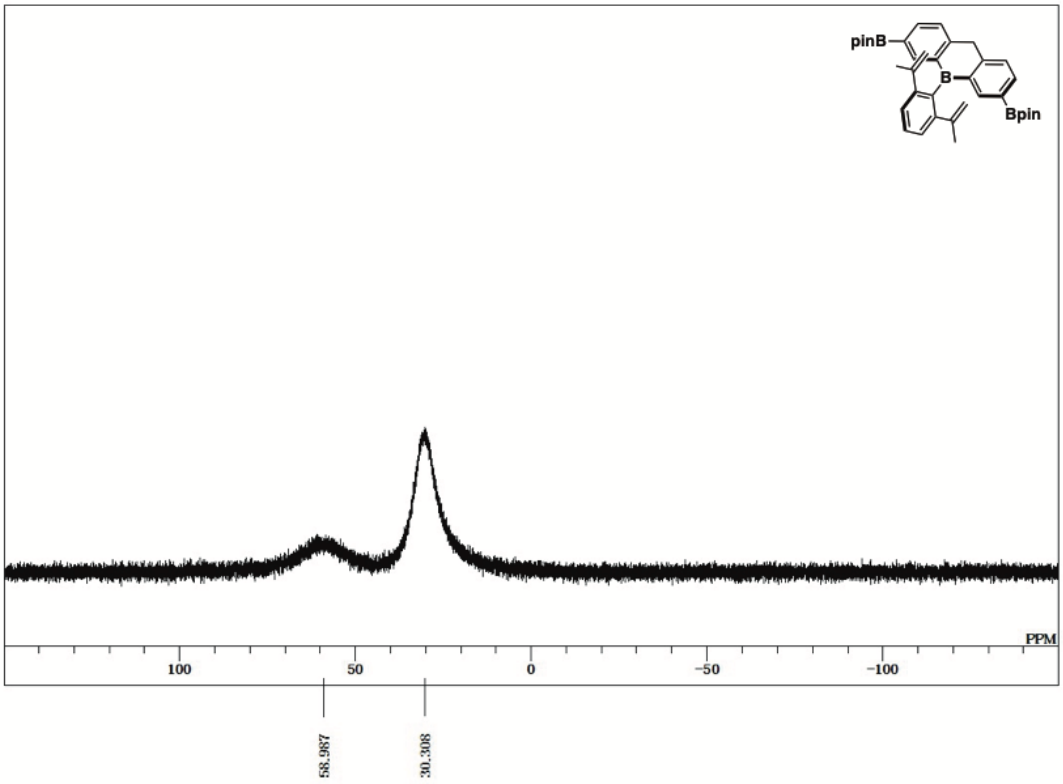

Fig. S49 $^{11}B\{^{1}H\}$ NMR spectrum of **2b** (128 MHz, $CDCl_3$).

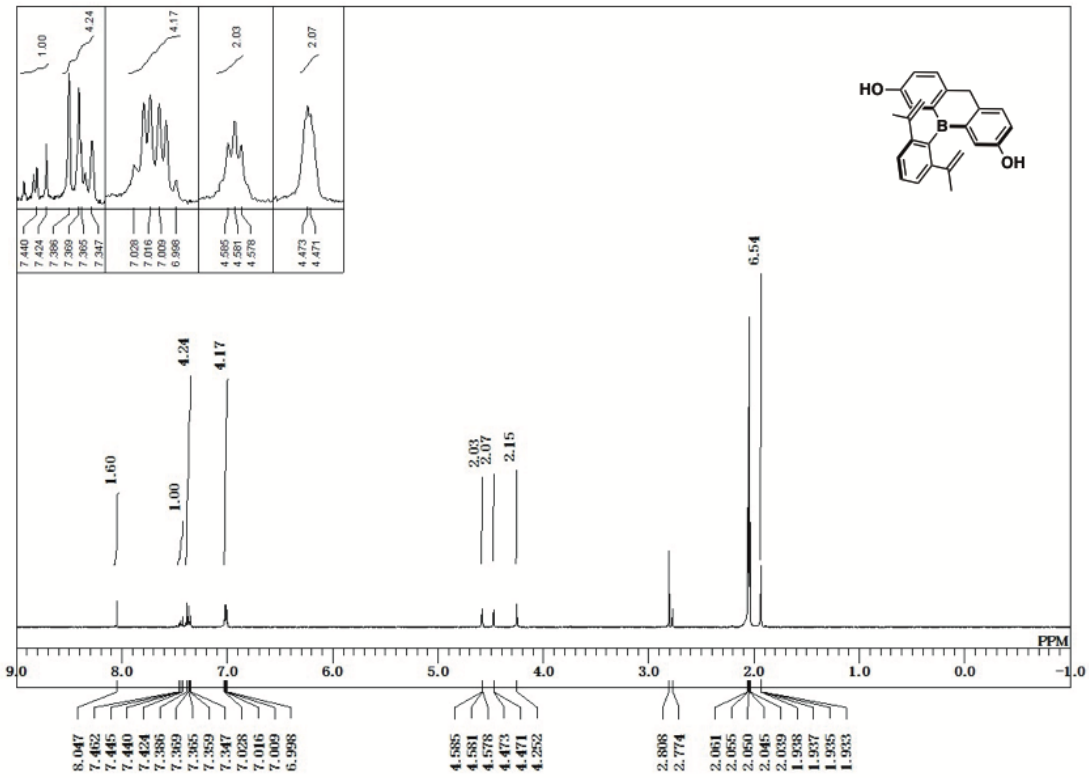

Fig. S50 ^{1}H NMR spectrum of **3b** (400 MHz, acetone-d_6).

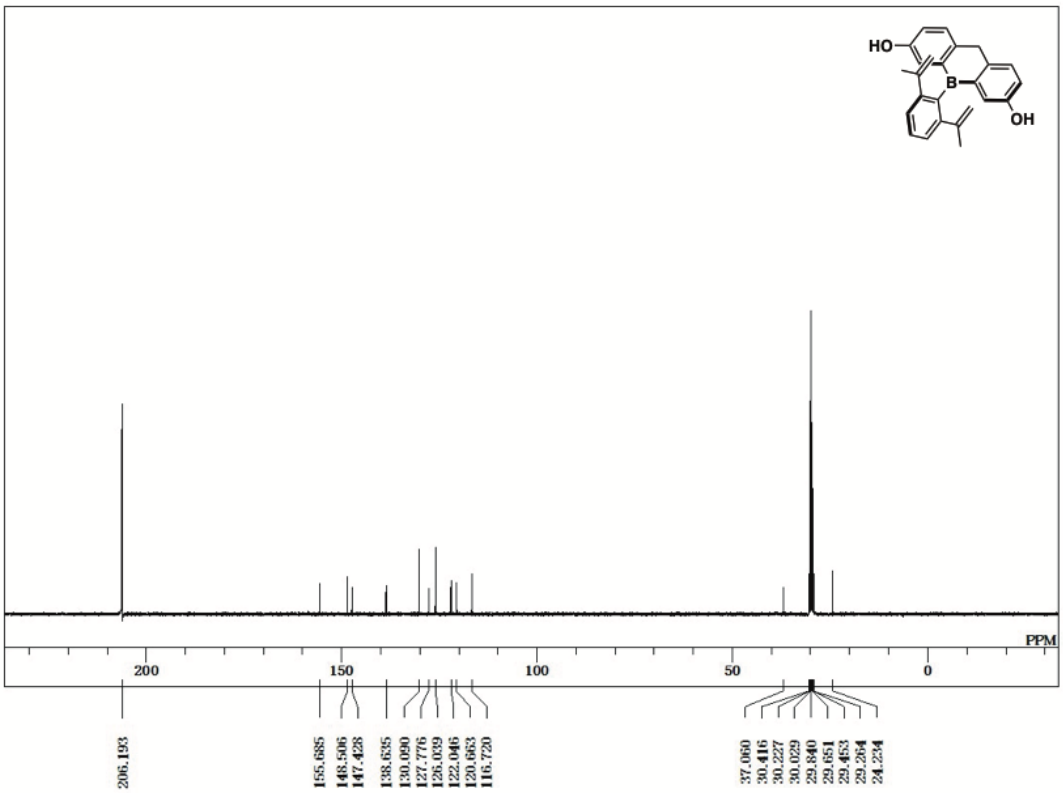

Fig. S51 $^{13}C\{^{1}H\}$ NMR spectrum of **3b** (100 MHz, acetone-d_6).

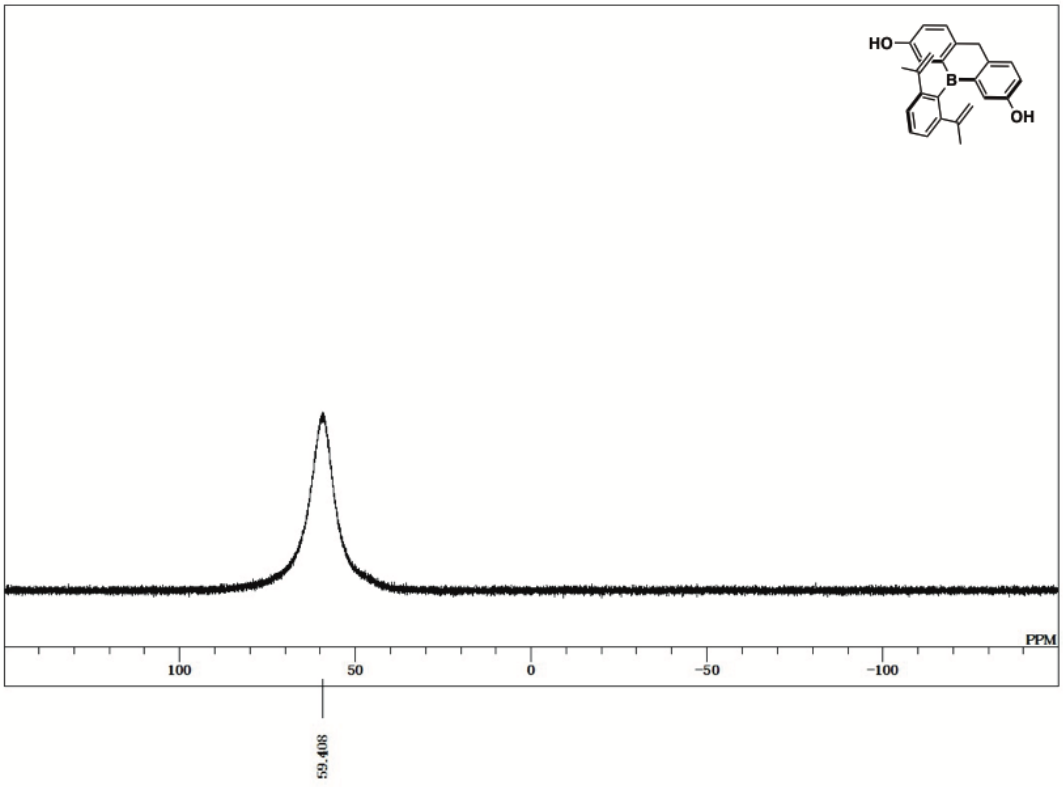

Fig. S52 $^{11}B\{^{1}H\}$ NMR spectrum of **3b** (128 MHz, acetone-d_6).

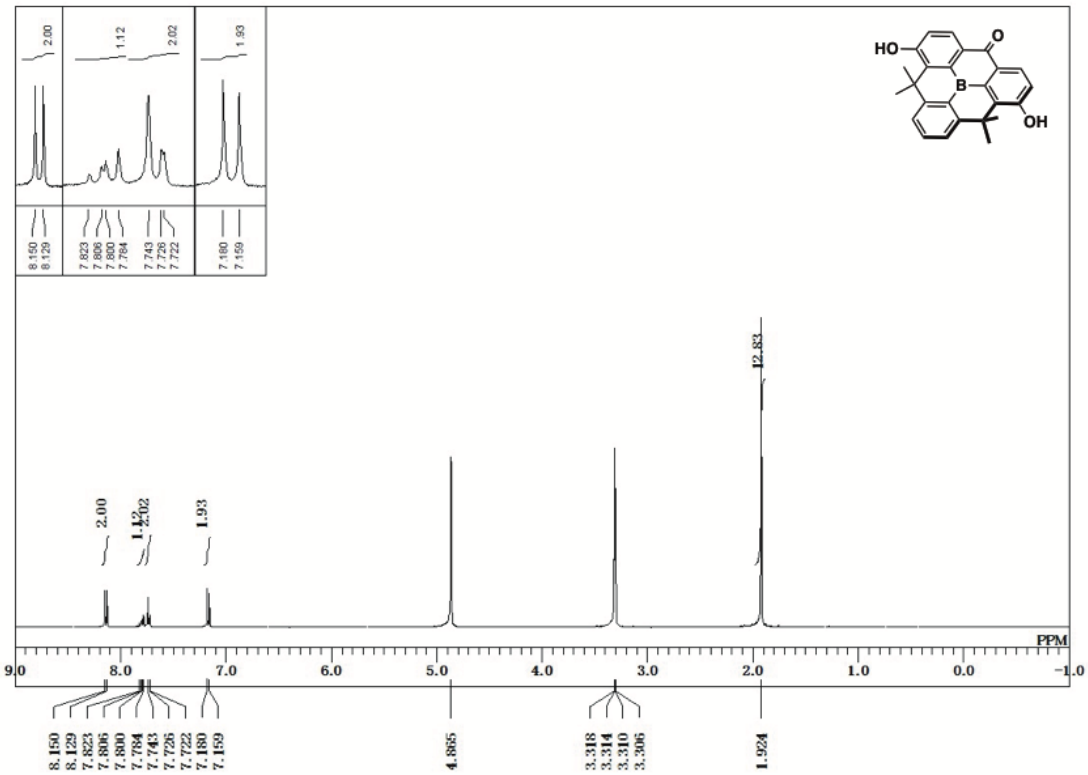

Fig. S53 ^{1}H NMR spectrum of **6** (400 MHz, CD_3OD).

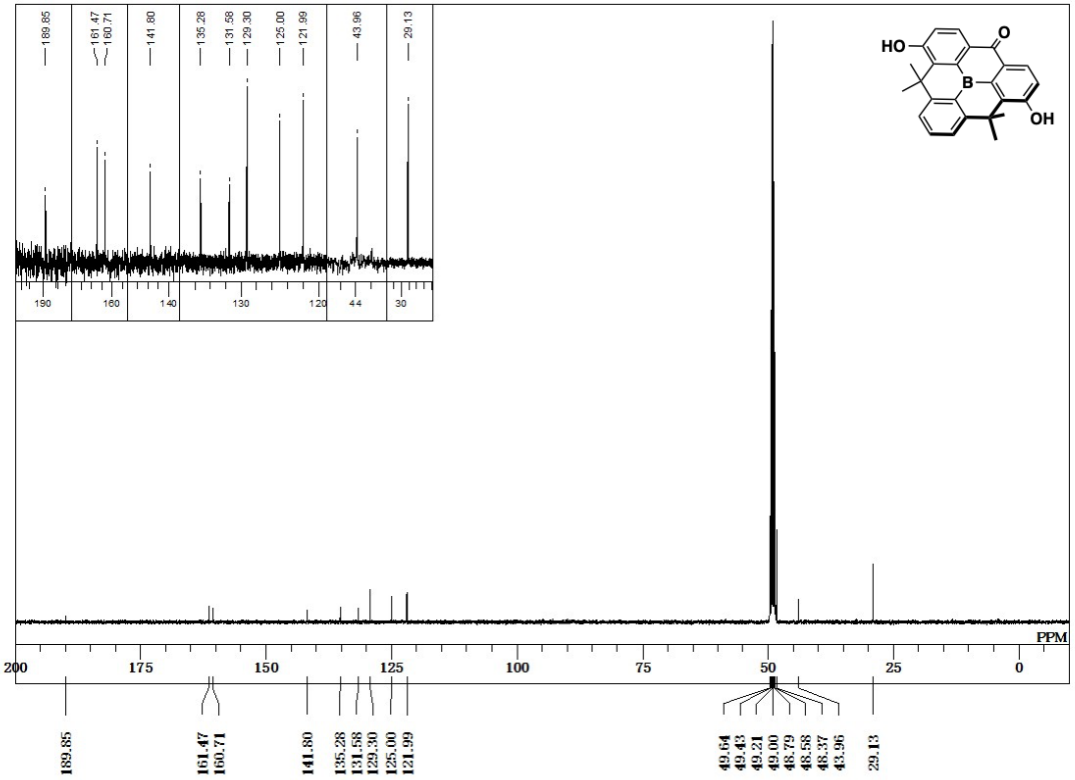

Fig. S54 $^{13}C\{^{1}H\}$ NMR spectrum of **6** (100 MHz, CD_3OD).

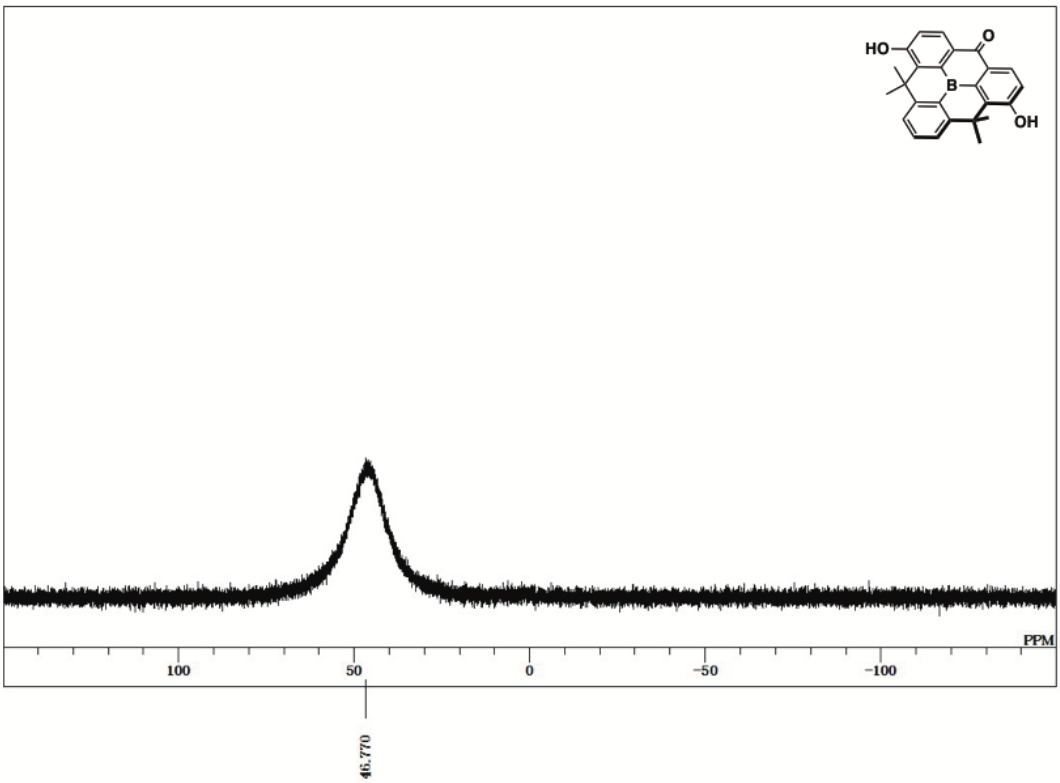

Fig. S55 $^{11}B\{^{1}H\}$ NMR spectrum of **6** (128 MHz, CD_3OD).

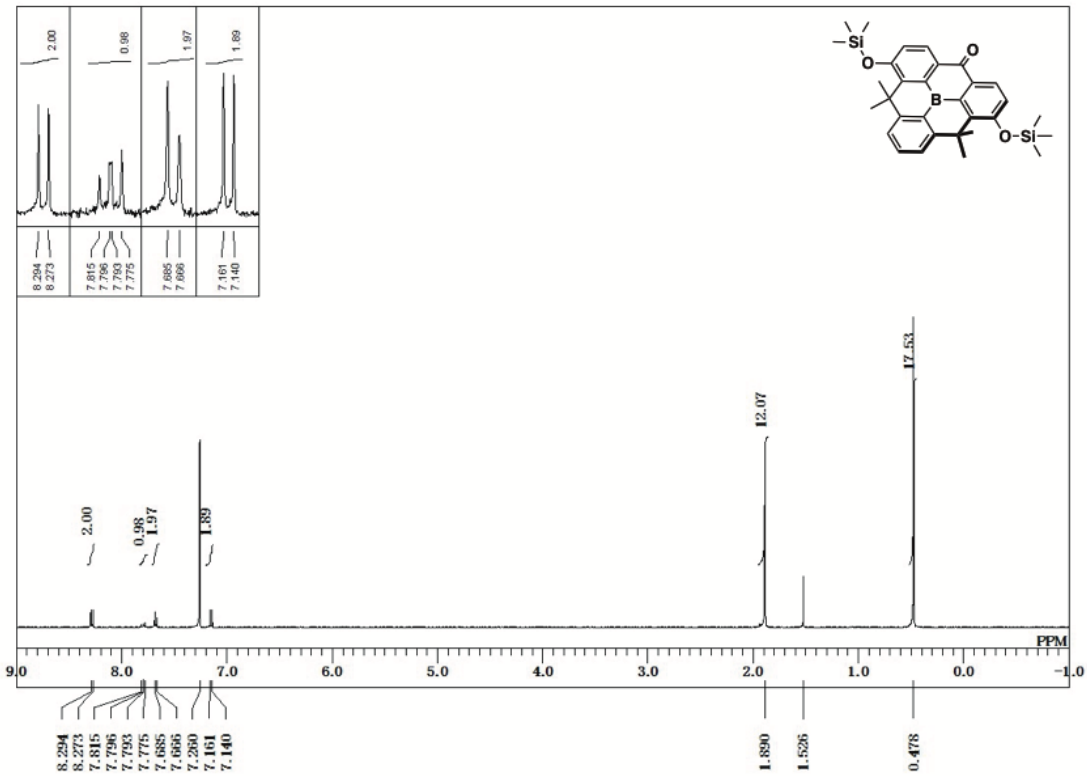

Fig. S56 ^{1}H NMR spectrum of **7** (400 MHz, $CDCl_3$).

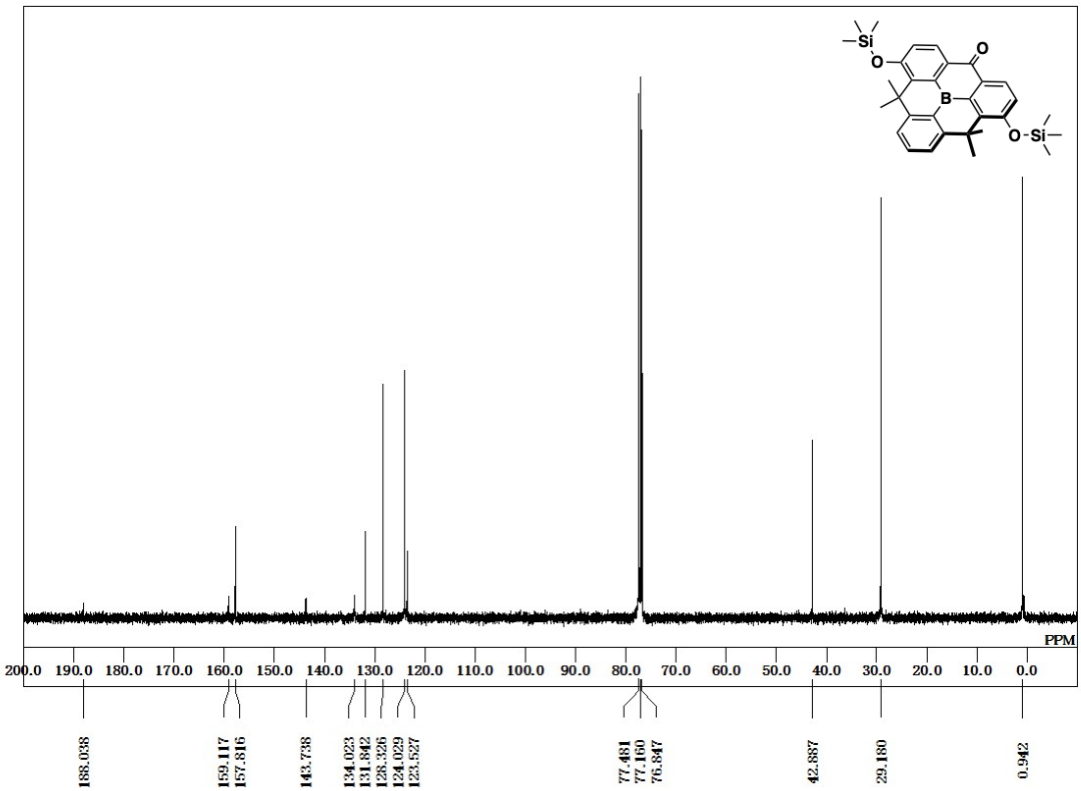

Fig. S57 $^{13}C\{^{1}H\}$ NMR spectrum of **7** (100 MHz, $CDCl_3$).

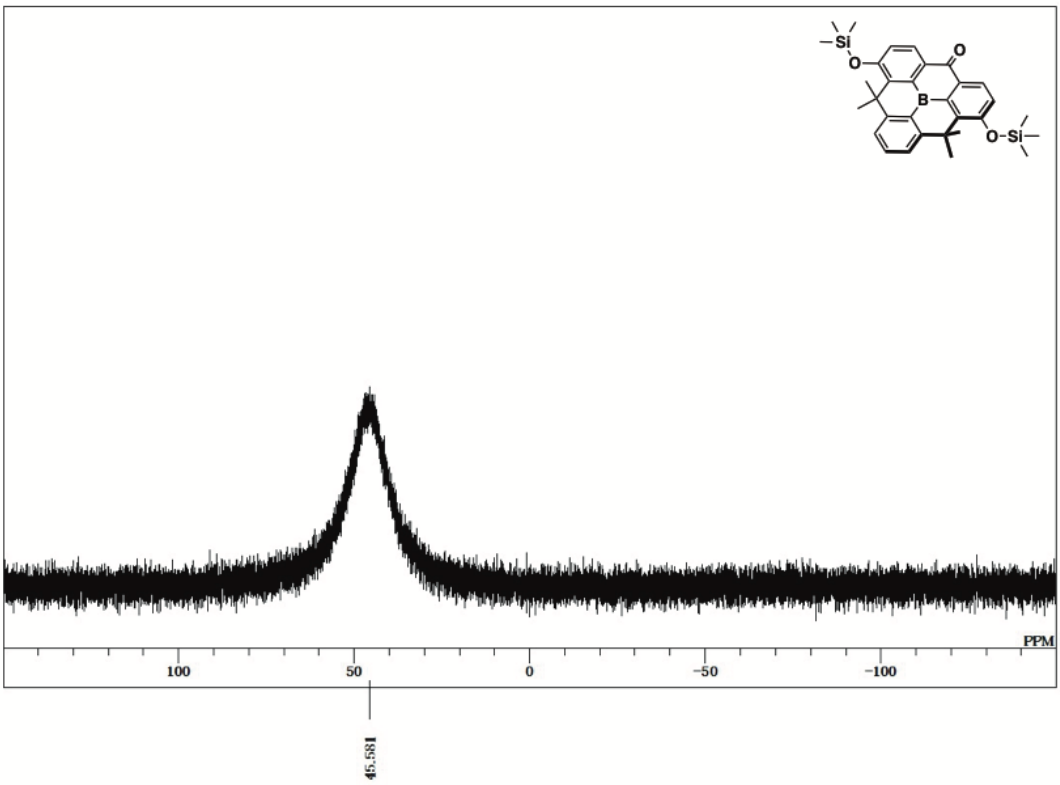

Fig. S58 $^{11}B\{^{1}H\}$ NMR spectrum of **7** (128 MHz, $CDCl_3$).

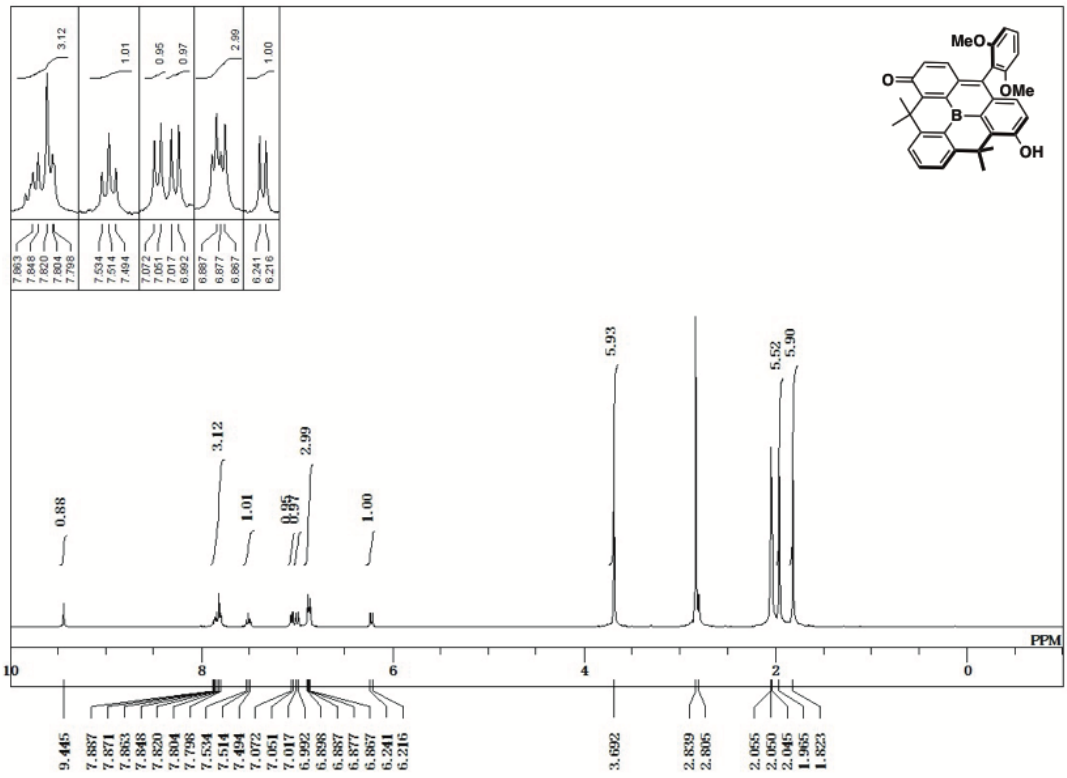

Fig. S59 ^{1}H NMR spectrum of **BF3** (400 MHz, acetone-d_6).

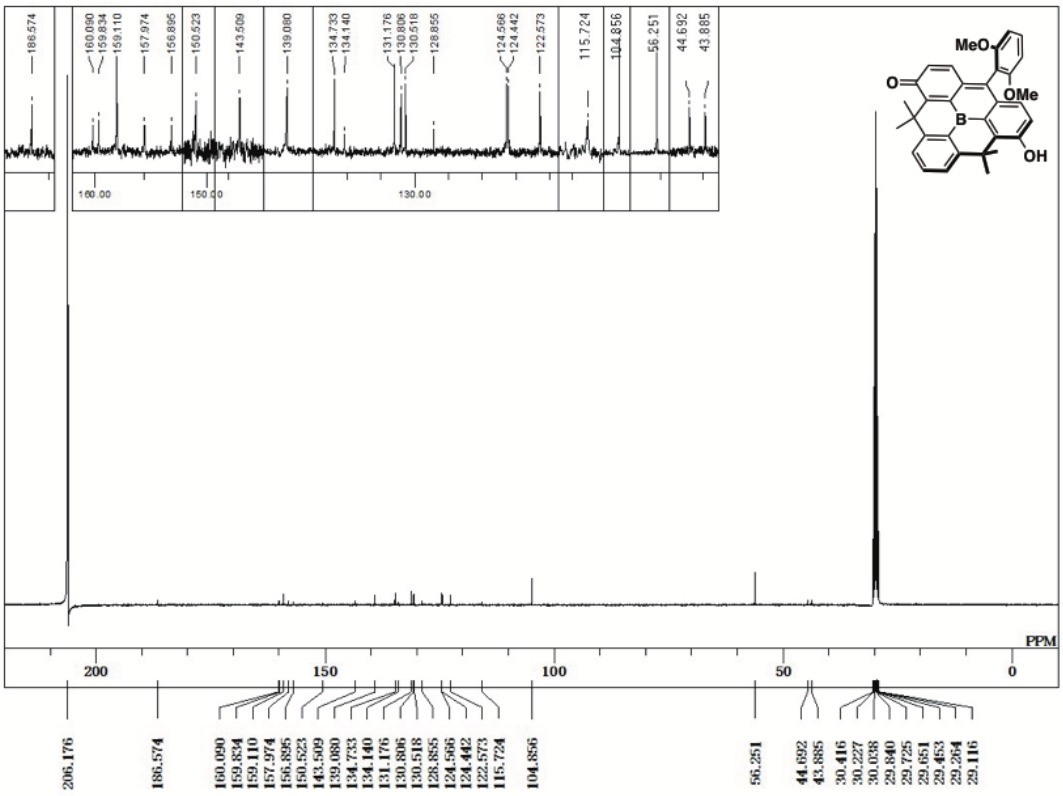

Fig. S60 ^{13}C{^{1}H} NMR spectrum of **BF3** (100 MHz, acetone-d_6).

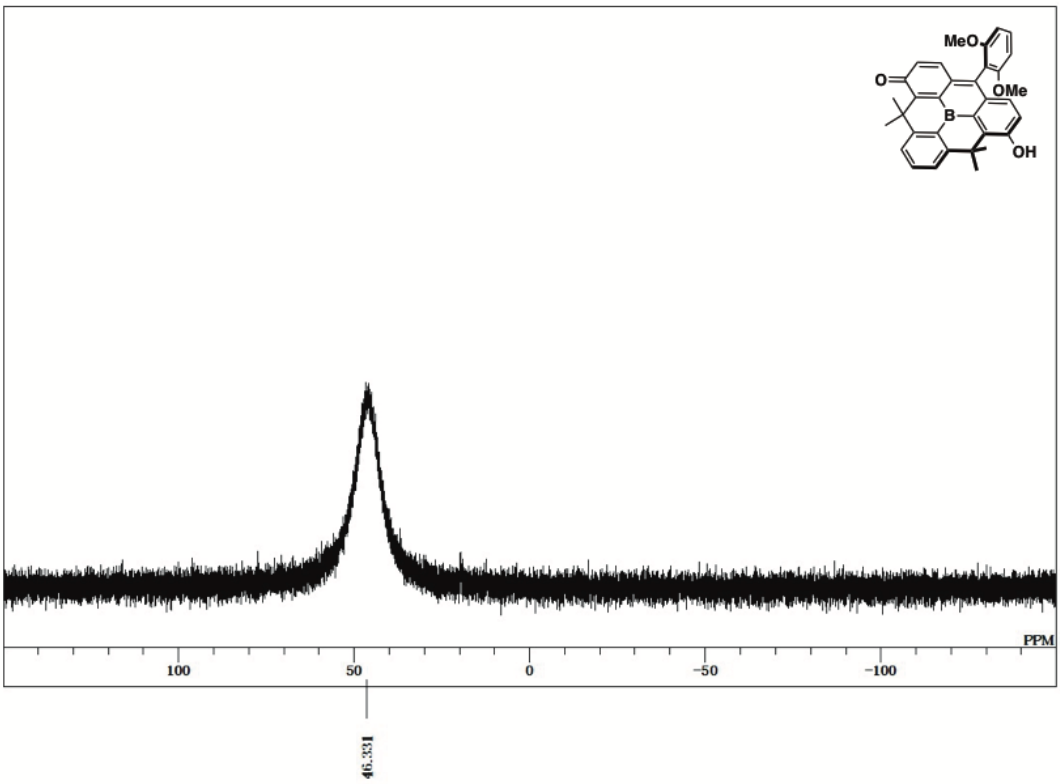

Fig. S61 $^{11}B\{^{1}H\}$ NMR spectrum of **BF3** (128 MHz, acetone-d_6).

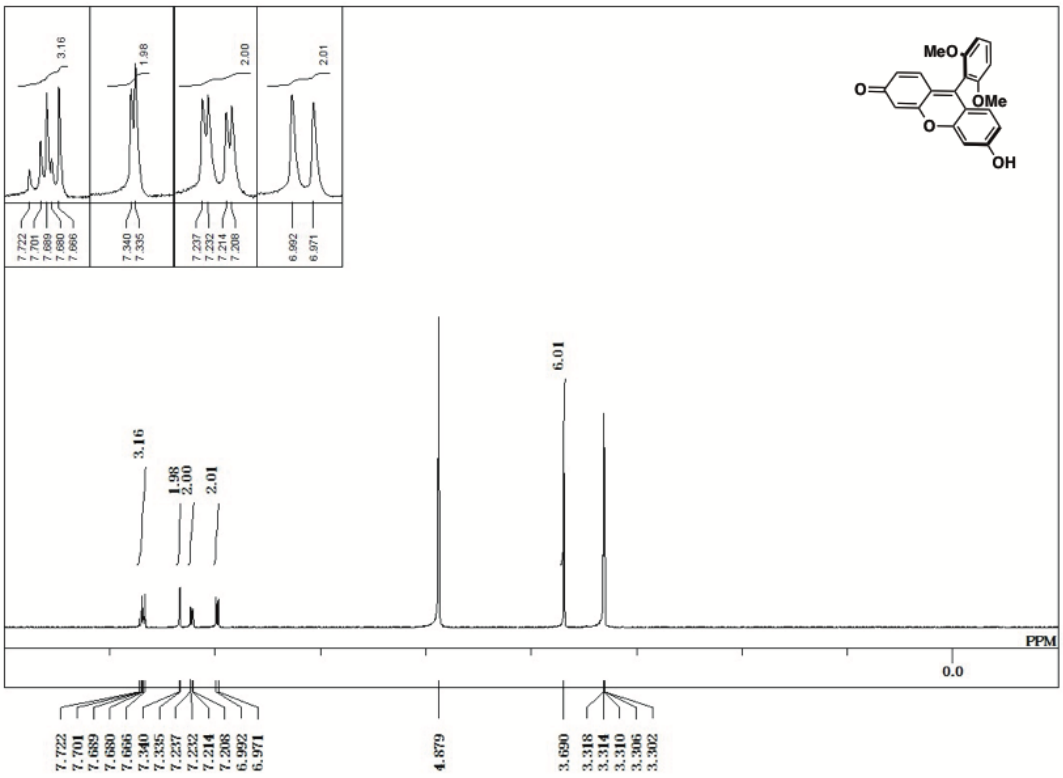

Fig. S62 ^{1}H NMR spectrum of **OF** (400 MHz, CD_3OD).

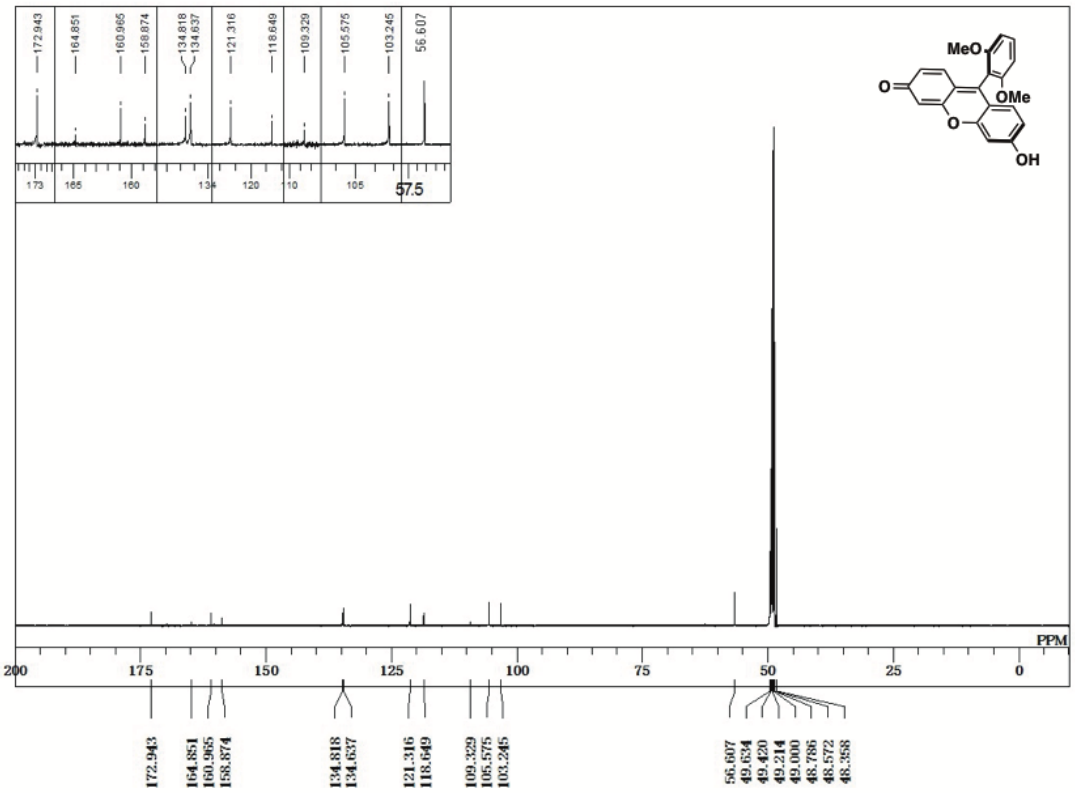

Fig. S63 $^{13}C\{^{1}H\}$ NMR spectrum of **OF** (100 MHz, CD_3OD).

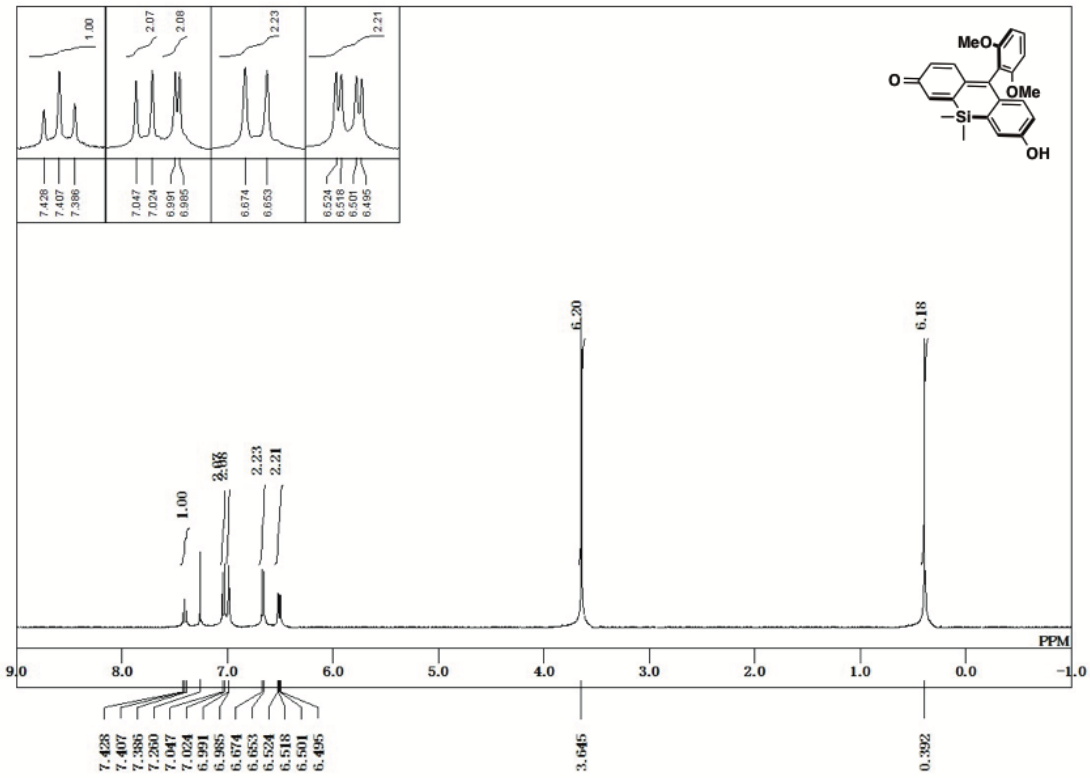

Fig. S64 ^{1}H NMR spectrum of **SiF** (400 MHz, $CDCl_3$).

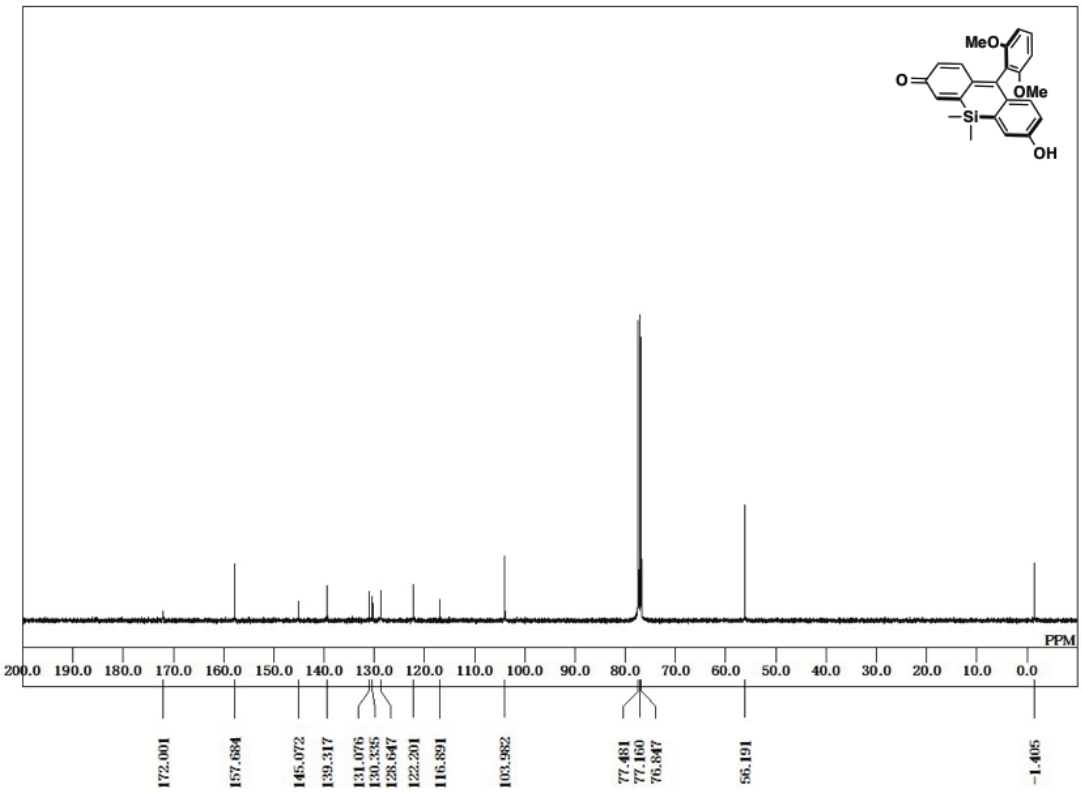

Fig. S65 $^{13}C\{^{1}H\}$ NMR spectrum of **SiF** (100 MHz, $CDCl_3$).

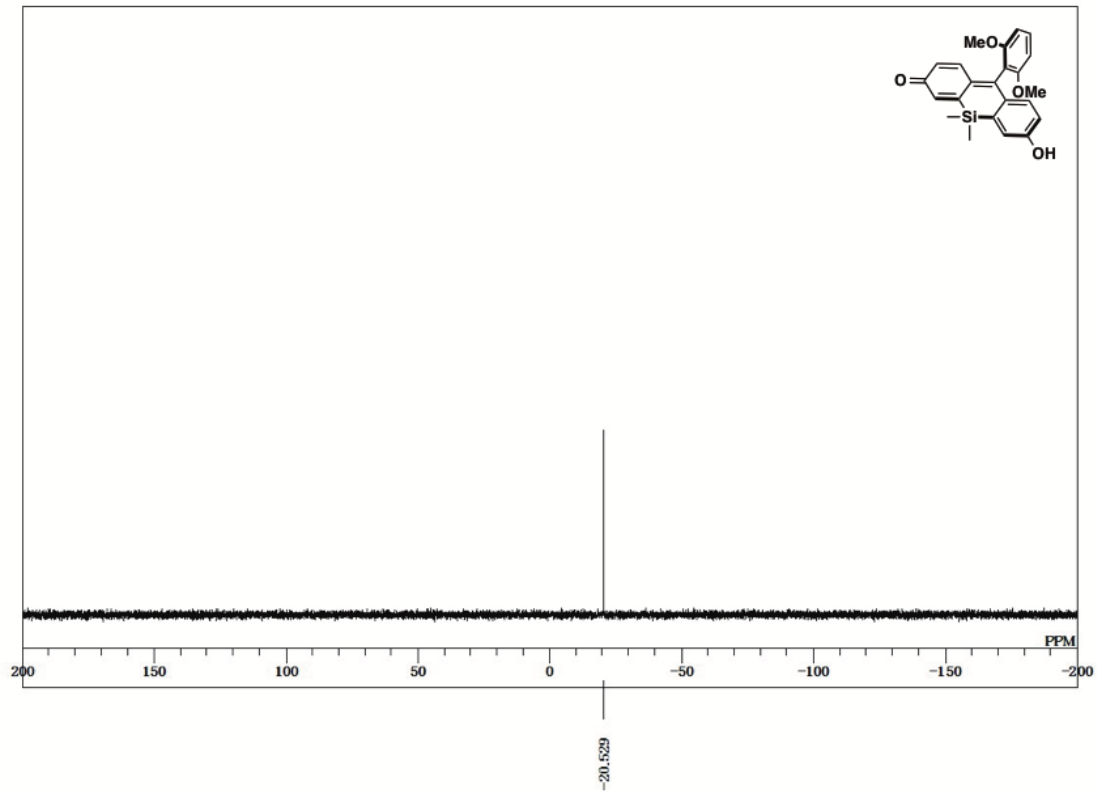

Fig. S66 $^{29}Si\{^{1}H\}$ NMR spectrum of **SiF** (79 MHz, $CDCl_3$).