Supplementary Information

Kinetically Stabilized Dibenzoborole as an Electron-Accepting Building Unit

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General. Melting points (mp) were measured on a Yanaco MP-S3 instrument. ^{1}H and ^{13}C NMR spectra were recorded with a JEOL A-400 spectrometer or a JEOL GSX-270 spectrometer in $CDCl_3$ or C_6D_6 (400 MHz or 270 MHz for ^{1}H, 100 MHz or 67.5 MHz for ^{13}C). UV-vis absorption spectra and fluorescence spectra measurement were performed with a Shimadzu UV-3150 spectrometer and a Hitachi F-4500 spectrometer, respectively, in degassed spectral grade solvents. Quantum yields were determined with a Hamamatsu C9920-01 calibrated integrating sphere system. Cyclic Voltammetry (CV) was performed on an ALS/chi-617A electrochemical analyzer. The CV cell consisted of a glassy carbon electrode, a Pt wire counter electrode, and an $Ag/AgNO_3$ reference electrode. The measurement was carried out under argon atmosphere using THF solutions of samples with a concentration of 1 mM and 0.1M tetrabutylammonium perchlorate ($Bu_4N^+ClO_4^-$) as a supporting electrolyte. The redox potentials were calibrated with ferrocene as an internal standard. Thin layer chromatography (TLC) was performed on plates coated with 0.25 mm thick silica gel 60F-254 (Merck). Column chromatography was performed using PSQ 60B (Fuji Silysia) or ODS-SM (Yamazen). Preparative gel permeation chromatography (GPC) was performed with a JAI LC–918 chromatograph equipped with JAIGEL 1H and 2H column. All reactions were carried out under argon atmosphere. 2,4,6-tri-*tert*-butylphenyllithium (Mes*Li) was prepared by the reaction of 1-bromo-2,4,6-tri-*tert*-butylbenzene (1.30 g, 4.0 mmol) with *n*-BuLi (1.6 M hexane solution, 2.5 mL, 4.0 mmol) in hexane at 80 °C for 12 h and isolated as white crystals by recrystallization from hexane. $ZnCl_2$(tmen) (tmen: *N,N,N',N'*-tetraethylenediamine) was purchased from Aldrich and directly used as received.

Computation Method. All calculations were conducted using the Gaussian 03 program.[1]

5-(2,4,6-Tri-*t*-butylphenyl)dibenzo[*b,d*]borole (3). The mixture of 5,5-dimethyldibenzosilole (**1**) (5.26 g, 25.0 mmol) and BBr_3 (4.70 mL, 12.5 g, 50.0 mmol) were heated at 50 °C for 48 h. After removal of excess amounts of BBr_3 and the produced dimethyldibromosilane under reduced pressure, distillation (212-218 °C, 1.5 mmHg) gave 5.58 g (23.0 mmol) of 5-bromodibenzo[*b,d*]borole (**2**) in 92% yield as yellow solids: ^{1}H NMR ($CDCl_3$) δ 7.57 (d, J_{HH} = 6.9 Hz, 2H), 7.38 (dd, J_{HH} = 6.9, 1.3 Hz, 2H), 7.31 (d, J_{HH} = 6.9 Hz, 2H), 7.15 (dd, J_{HH} = 6.9 Hz, 1.3 Hz, 2H).[2] This compound was very unstable in the air, but could be stored under Ar. The obtained compound **2** (0.485 g, 2.00 mmol) and 2,4,6-tri-*tert*-butylphenyl lithium (1.00 g, 4.00 mmol) were dissolved into 10 mL of toluene at room temperature. The mixture was stirred at room temperature for 22 h. After addition of water (10 mL), the mixture was extracted with 10 mL of ether three times. The combined organic layer was dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The obtained crude product was purified by a silica gel column chromatography (hexane/toluene, 7/1; $R_f = 0.46$) to give 0.52 g (1.27 mmol) of **3** in 64% yield as pale green solids: mp 135.5-136.8 °C; ^{1}H NMR ($CDCl_3$) δ 7.49 (d, $J_{HH} = 7.5$ Hz, 2H), 7.44 (d, $J_{HH} = 7.2$ Hz, 2H), 7.43 (s, 2H), 7.32 (dd, $J_{HH} = 7.5$, 7.2 Hz, 2H), 7.11 (dd, $J_{HH} = 7.5$, 7.2 Hz, 2H), 1.40 (s, 9H), 1.25 (s, 18H); ^{13}C NMR ($CDCl_3$) δ 153.0, 150.7, 149.0, 146.9 (br), 134.3, 132.5, 130.5, 128.3, 121.5, 120.0, 38.0, 35.0, 34.1, 31.6; EI MS *m*/*z* 408 (M^+); HRMS cald for $C_{30}H_{37}B$, 408.2988; found, 408.2994.

4,4'-Bis(*N,N*-diethyltriazenyl)-2,2'-dibromobiphenyl (5). To a solution of 4,4'-diamino-2,2'-dibromobiphenyl (34.2 g, 100 mmol) and $BF_3 \cdot OEt_2$ (96 mL, 750 mmol) in THF (350 mL), a solution of *tert*-butyl nitrite (88 mL, 650 mmol) in THF (100 mL) was added dropwise at –10 °C.[3] The mixture was stirred for 0.5 h at the same temperature and then allowed to warm to 0 °C. The resulting pale brown precipitate was collected by filtration and washed with cold ether (0 °C, 20 mL) three times. After addition of 600 mL of CH_2Cl_2 to the precipitate at 0 °C, K_2CO_3 (55.3 g, 400 mmol) was added. The resulting suspension was stirred for 0.5 h at 0 °C. Diethylamine (41.5 mL, 400 mmol) was slowly added to the reaction mixture, followed by stirring for an additional hour at the same temperature. The produced salts were removed by filtration and the filtrate was concentrated under reduced pressure. After addition of 300 mL of ether, the solution was washed with water (100 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give 46.7 g (91.6 mmol) of **5** in 92% yield as red solids: mp 95.3-96.4 °C; ^{1}H NMR ($CDCl_3$) δ 7.74 (d, $J_{HH} = 2.2$ Hz, 2H), 7.40 (dd, $J_{HH} = 7.8$, 2.2 Hz, 2H), 7.20 (d, $J_{HH} = 7.8$ Hz, 2H), 3.79 (q, $J_{HH} = 7.0$ Hz, 8H), 1.29 (t, $J_{HH} = 7.0$ Hz, 12H); ^{13}C NMR ($CDCl_3$) δ 151.6, 138.2, 131.3, 124.0, 123.6, 119.5, 31.7, 22.8. Anal. Calcd for $C_{20}H_{26}Br_2N_6$: C, 47.08; H, 5.14; N, 16.47. Found: C, 47.18; H, 5.09; N, 16.36.

3,7-Bis(*N,N*-diethyltriazenyl)-5,5-di(*n*-butyl)dibenzo[*b,d*]stannole (6). To a solution of **5** (5.10 g, 10.0 mmol) in THF (100 mL) cooled at –78 °C was added *n*-BuLi (1.6 M in hexane, 12.5 mL, 20.0 mmol) dropwise. After the mixture was stirred at –78 °C for 1.5 h, a solution of dibutylstannyl dichloride (3.04 g, 10.0 mmol) in THF (10 mL) was added to the mixture at –78 °C. The reaction mixture was gradually warmed to room temperature and stirred for 12 h. After addition of a saturated $NaHCO_3$ aqueous solution (50 mL), the mixture was extracted with ether (50 mL) three times. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The mixture was purified by a silica gel column chromatography (hexane/Et_3N, 14/1, $R_f = 0.41$) to give 4.95 g (8.48 mmol) of **6** in 85% yield as yellow oil, which spontaneously solidified upon standing in refrigerator: mp 41.5-42.3 °C; ^{1}H NMR (C_6D_6) δ 8.19 (td, J_{HSn} = 18.8 Hz, J_{HH} = 2.2 Hz, 2H), 7.96 (d, J_{HH} = 7.8 Hz, 2H), 7.82 (dd, J_{HH} = 7.8 Hz, J_{HH} = 2.2 Hz, 2H), 3.45 (br, 8H), 1.59-1.51 (m, 4 H), 1.32-1.16 (m, 8H), 0.98 (t, J_{HH} = 7.0 Hz, 12H), 0.76 (t, J_{HH} = 7.0 Hz, 6H); ^{13}C NMR (C_6D_6) δ 150.5 (t, J_{CSn} = 22.3), 146.7 (t, J_{CSn} = 28.5), 142.0 (t, J_{CSn} = 201.4), 129.0 (t, J_{CSn} = 22.7), 123.5 (t, J_{CSn} = 19.9), 122.3, 48.5 (br), 41.0 (br), 29.4 (t, J_{CSn} = 12.0), 27.5 (t, J_{CSn} = 28.5), 13.8, 12.0 (t, J_{CSn} = 174.4). Anal. Calcd for $C_{28}H_{44}BN_6Sn$: C, 57.64; H, 7.60; N, 14.41. Found: C, 57.65; H, 7.71; N, 14.52.

3,7-Diiodo-5,5-dibutyldibenzo[*b,d*]stannole (7). Compound **6** (16.6 g, 28.5 mmol) was dissolved in hexane (10 mL) and transferred into a glass tube. The solvent was removed under vacuum and methyl iodide (57 mL, 853 mmol) was added. The mixture was stirred at 90 °C for 1.5 h under dark.[4] The remaining methyl iodide was removed under reduced pressure and the mixture was dissolved with CH_2Cl_2 (30 mL) and poured into hexane (600 mL). The produced black precipitates were removed by filtration and the filtrate was evaporated under reduced pressure. The mixture was purified by a reversed phase chromatography (CH_3CN/THF, 3/1, $R_f = 0.46$) to give 8.13 g (12.7 mmol) of **7** in 45% yield as a colorless oil: ^{1}H NMR (C_6D_6) δ 7.98 (t, J_{SnH} = 17.0 Hz, 2H), 7.55 (d, J_{HH} = 8.4 Hz, 2H), 7.18 (d, J_{HH} = 8.4 Hz, 2H), 1.42-1.30 (m, 4H), 1.19-1.02 (m, 8H), 0.72 (t, J_{HH} = 7.3 Hz, 6H); ^{13}C NMR (C_6D_6) δ 147.5 (t, J_{CSn} = 22.3 Hz), 145.2 (t, J_{CSn} = 21.4 Hz), 144.8 (t, J_{CSn} = 190.8 Hz), 138.3, 125.1, (t, J_{CSn} = 17.2 Hz), 95.9 (t, J_{CSn} = 22.2 Hz), 29.1 (t, J_{CSn} = 12.4 Hz), 27.3, (t, J_{CSn} = 28.0 Hz), 14.0, 12.3 (t, J_{CSn} = 181.9 Hz); EI MS *m/z* 637 (M^+). HRMS cald for $C_{20}H_{24}I_2Sn$, 637.8993; found, 637.9006.

3,7-Diiodo-5-(2,4,6-tri-*t*-butylphenyl)dibenzo[*b,d*]borole (8). To a toluene solution (3 mL) of **7** (230 mg, 0.36 mmol) was added 1 M BCl_3/hexane solution (0.36 mL, 0.36

mmol) at –78 °C. The mixture was stirred at –78 °C for 1 h and then allowed to warm to room temperature. A solution of 2,4,6-tri-*tert*-butylphenyllithium (513 mg, 2.0 mmol) in toluene (10 mL) was added to the reaction mixture via cannula and the mixture was stirred at room temperature for 12 h. After addition of water (10 mL), the mixture was extracted with ether (20 mL) three times. The combined organic layer was washed with brine (20 mL), dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The mixture was purified by a silica gel column chromatography (hexane/CH_2Cl_2, 9/1, R_f = 0.55) followed by the recrystallization from hexane to give 147 mg (0.22 mmol) of **8** in 62% yield as yellow crystalls: mp 135.5-136.8 °C; ^{1}H NMR (C_6D_6) δ 7.93 (d, J_{HH} = 1.6 Hz, 2H), 7.59 (s, 2H), 7.42 (dd, J_{HH} = 7.8 Hz, 1.6 Hz, 2H), 6.71 (d, J_{HH} = 7.8 Hz, 2H), 1.35 (s, 3H), 1.12 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 153.0, 149.5, 148.4, 142.4, 140.9, 121.9, 121.5, 94.8, 94.8, 37.8, 34.8, 34.1, 31.4 (one peak for the carbon atoms bonding to the boron atoms is not observed due to quadrupolar relaxation); EI MS *m*/*z* 660 (M^+). HRMS calcd for $C_{30}H_{35}BI_2$, 660.0921; found, 660.0934. Anal. Calcd for $C_{30}H_{35}BI_2$: C, 54.58; H, 5.34. Found: C, 54.58; H, 5.33.

3,7-Bis(bithienyl)-5-(2,4,6-tri-*t*-butylphenyl)dibenzo[*b*,*d*]borole (9). To a solution of 5-bromo-2,2'-bithiophene (0.307 g, 1.25 mmol) in THF (12.5 mL) was added *t*-BuLi in pentane (1.68 M, 1.50 mL, 2.52 mmol) dropwise at –78 °C. After the mixture was stirred at –78 °C for 1.5 h, $ZnCl_2$(tmen) (0.316 g, 1.25 mmol) (tmen: *N,N,N',N'*-tetraethylethlenediamine) was added to the stirred mixture at –78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 1.5 h. The reaction mixture was added to a solution of 3,7-diiodo-5-tri-*t*-butylphenyldibenzoborole **8** (0.331 g, 0.500 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (0.0276 g, 0.03 mmol), and trifurylphosphine (0.0256 g, 0.110 mmol) in THF (2.5 mL). The mixture was stirred at 40 °C for 12 h. After the solvent was removed under reduced pressure, the mixture was purified by a silica gel column chromatography (hexane/CH_2Cl_2, 4/1, R_f = 0.33) followed by a recycling GPC ($CHCl_3$) to give 0.220 g (0.299 mmol) of **9** in 60% yield as red solids: mp 134.7-135.4 °C; ^{1}H NMR (C_6D_6) δ 7.98 (d, J_{HH} = 1.6 Hz, 2H), 7.71 (s, 2H), 7.48 (dd, J_{HH} = 7.8, 1.6 Hz, 2H), 7.28 (d, J_{HH} = 7.6 Hz, 2H), 6.94 (d, J_{HH} = 3.8 Hz, 2H), 6.93 (d, J_{HH} = 3.8 Hz, 2H), 6.70 (d, J_{HH} = 3.8 Hz, 2H), 6.66 (t, J_{HH} = 3.8 Hz, 2H), 6.64 (d, J_{HH} = 3.8 Hz, 2H), 1.42 (s, 18H), 1.31 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 153.2, 149. 3, 147.6, 143.2, 137.4, 136.4, 133.9, 131.1, 129.6, 127.8, 124.6, 124.3, 123.6, 123.6, 121.6, 120.4,37.8, 34.8, 34.0, 31.4 (two peaks for the carbon atoms bonding to the boron atoms is not observed due to quadrupolar relaxation). Anal. Calcd for $C_{46}H_{45}BS_4$: C, 74.97; H, 6.15. Found: C, 74.86; H, 6.12.

3,7-Bis[*p*-(*N*,*N*-diphenylamino)phenyl]-5-(2,4,6-tri-*t*-butylphenyl)dibenzo[*b*,*d*]borole (10). To a solution of (4-iodophenyl)diphenylamine (0.463 g, 1.25 mmol) in THF (5 mL) was added a pentane solution of *t*-BuLi (1.49 M, 1.67 mL, 2.48 mmol) dropwise at –78 °C. After the mixture was stirred at –78 °C for 1 h, $ZnCl_2$(tmen) (0.316 g, 1.25 mmol) was added to the stirred mixture at –78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 1 h. The reaction mixture was added to a solution of 3,7-diiodo-5-tri-*t*-butylphenyldibenzoborole **8** (0.331 g, 0.500 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (0.0279 g, 0.03 mmol), and tri(2-furyl)phosphine (0.0240 g, 0.103 mmol) in THF (5 mL). The mixture was stirred at 40 °C for 12 h. After the solvent was removed under reduced pressure, the mixture was purified by a silica gel column chromatography (hexane/toluene, 3/2, R_f = 0.43) to give 0.344 g (0.384 mmol) of **10** in a 77% yield as orange solids: mp 134.5-136.3 °C; ^{1}H NMR (C_6D_6) δ 7.98 (d, J_{HH} = 1.9 Hz, 2H), 7.71 (s, 2H), 7.50 (dd, J_{HH} = 7.8, 1.9 Hz, 2H), 7.44 (d, J_{HH} = 7.8 Hz, 2H), 7.27 (d, J_{HH} = 8.6 Hz, 4H), 7.08 (d, J_{HH} = 8.6 Hz, 4H), 7.06 (t, J_{HH} = 8.6 Hz, 4H), 6.98 (d, J_{HH} = 8.6 Hz, 4H), 6.86 (d, J_{HH} = 8.6 Hz, 2H), 1.42 (s, 18H), 1.34 (s, 9H); ^{13}C NMR (C_6D_6) δ 153.8, 149.9, 149.6, 148.4 (br), 148.3, 147.5, 141.0, 135.2, 132.7, 131.3, 129.6, 128.6, 124.8, 124.6, 123.2, 122.2, 120.9, 38.3, 35.0, 34.4, 31.6 (one peak for the carbon atoms bonding to the boron atoms is not observed due to quadrupolar relaxation). HRMS cald for $C_{66}H_{63}BN_2$, 894.5084; found, 894.5100.

Preparation of Radical Anion $3^{\bullet-}$. In a ESR tube connected as a sidearm of a Pyrex tube connectable to a vacuum line were placed **3** (6.9 mg, 1.7×10^{-3} mmol) and potassium (13 mg, 3.3×10^{-1} mmol). The tube was connected to a vacuum line and evacuated with cooling by liquid nitrogen. THF (0.75 mL) was dried over Na/K alloy, degassed by three freeze-pump-thaw cycles, and vapor transferred directly into the cooled tube containing **9** and potassium. The whole apparatus was sealed under vacuum. The color of the solution turned to deep green by mixing at room temperature. The ESR spectrum was taken on the resulting solution (2.3×10^{-3} M) at room temperature to give an eleven-line signal (*g* = 2.002).

Preparation of Radical Anion $9^{\bullet-}$. In a ESR tube connected as a sidearm of a Pyrex tube connectable to a vacuum line were placed **9** (1.5 mg, 2.0×10^{-3} mmol) and potassium (1.4 mg, 3.6×10^{-2} mmol). The tube was connected to a vacuum line and evacuated with cooling by liquid nitrogen. THF (0.75 mL) was dried over Na/K alloy, degassed by three freeze-pump-thaw cycles, and vapor transferred directly into the cooled tube containing **9** and potassium. The whole apparatus was sealed under vacuum. The color of the solution turned to deep green by mixing at room temperature. The ESR spectrum was taken on the resulting solution (2.7×10^{-3} M) at room temperature to give a six-line signal ($g = 2.002$).

X-Ray Crystal Structure Analysis of 9. Single crystals of **9** suitable for X-ray crystal analysis were obtained by slow diffusion of CH_3CN into a CH_2Cl_2 solution of **9**. Intensity data were collected at 100 K on a Rigaku Single Crystal CCD X-ray Diffractometer (Saturn 70 with MicroMax-007) with Mo Kα radiation (λ = 0.71070 Å) and graphite monochromator. A total of 13893 reflections were measured at a maximum 2θ angle of 50.0°, of which 7146 were independent reflections ($R_{\mathrm{int}} = 0.0231$). The structure was solved by direct methods (SHELXS-97[5]) and refined by the full-matrix least-squares on F^2 (SHELXL-97[3]). The disordered solvent molecules of CH_2Cl_2 and CH_3CN are included in a lattice. As an appropriate disordered model, these molecules were placed to occupy the same volume element with a half-occupancy. The bond distances in CH_3CN (C47B, C48B, N1) were restrained by DFIX instructions during refinement. One thiophene ring (S4, C25, C26, C27, and C28) is disordered and solved using an appropriate disordered model. Thus, two sets of thiophene rings, *i.e.*, (S4A, C25, C26A, C27, C28) and (S4B, C25, C26B, C27, C8), were placed and their occupancies were refined to be 0.73 and 0.27, respectively. The two sets of disordered thiophene rings (S4A, C25, C26A, C27, C28) and (S4B, C25, C26B, C27, C8) were restrained by DFIX instructions during refinement. All non-hydrogen atoms except for disordered solvent molecules (C47A, Cl1, Cl2) and (C47B, C48B, N1) were refined anisotropically and all hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: $C_{46}H_{45}BS_4{\cdot}0.5(CH_2Cl_2){\cdot}0.5(CH_3CN){\cdot}$; FW = 799.86, crystal size $0.20 \times 0.10 \times 0.05$ mm^3, Triclinic, P–1, a = 9.353(2) Å, b = 13.047(2) Å, c = 18.255(4) Å, α = 69.849(6)°, β = 87.420(8)°, γ = 81.615(7)°, V = 2068.9(7) Å^3, Z = 2, D_c = 1.284 g cm^{-3}. The refinement converged to $R_1 = 0.0613$, w$R_2 = 0.1479$ ($I > 2\sigma(I)$), GOF = 1.065.

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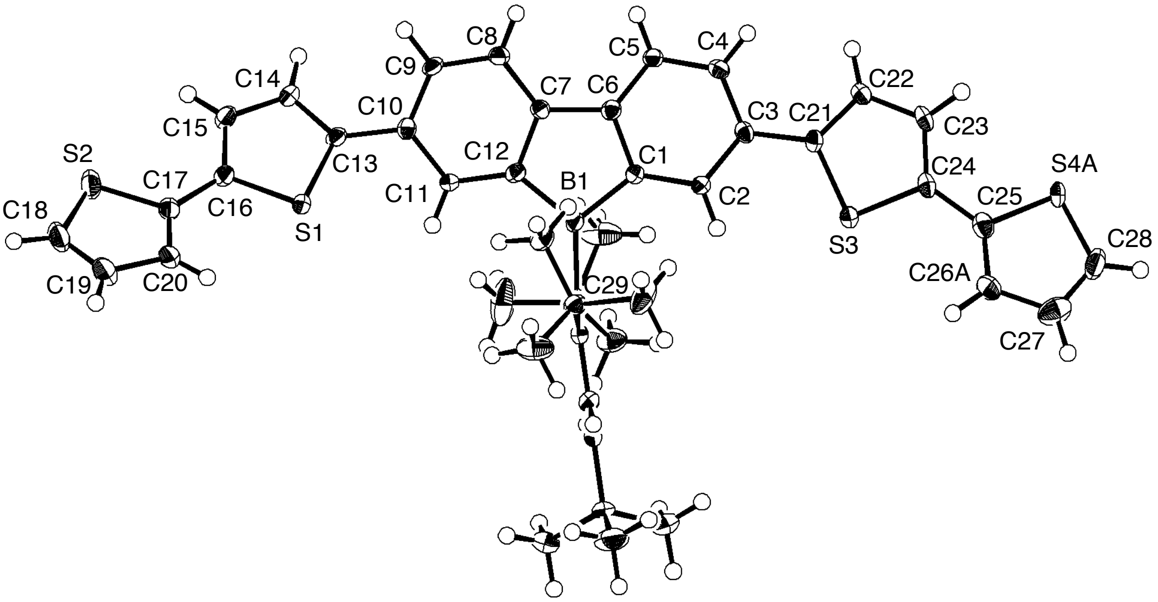


Figure S1. ORTEP drawing of **9**. Thermal ellipsoids are drawn at the 50% probability level. Solvent molecules (CH_2Cl_2 and CH_3CN) are omitted for clarity. Selected bond length (Å) and angles (deg) are as follows: B1–C1, 1.585(4); B1–C29, 1.585(4); C1–C2, 1.392(4);C2–C3, 1.410(4); C3–C4, 1.400(4); C4–C5, 1.383(4); C5–C6, 1.382(4); C6–C7, 1.481(4); C6–C1, 1.410(4); C29–B1–C1, 126.7(3); C29–B1–C12, 130.5(3); C1–B1–C12, 102.8(2); B1–C1–C6, 108.0(2); C1–C6–C7, 110.9(3); C1–C6–C5, 120.9(3); C6–C5–C4, 119.2(3); C5–C4–C3, 122.0(3); C4–C3–C2, 118.1(3); C3–C2–C1, 120.7(3); C2–C1–C6, 119.2(3).

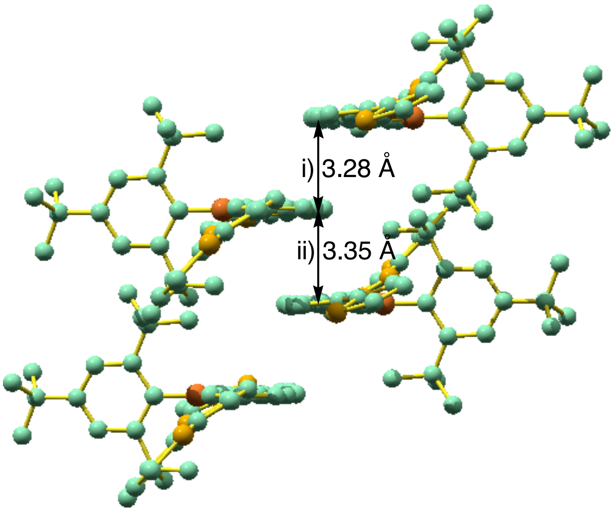


Figure S2. Packing structure of compound **9** including the distances i) between C5 and C5* (symmetry operation at (1–x, –y, 1–z)) and ii) between C5 and C24* (symmetry operation at (2–x, –y, 1–z)).

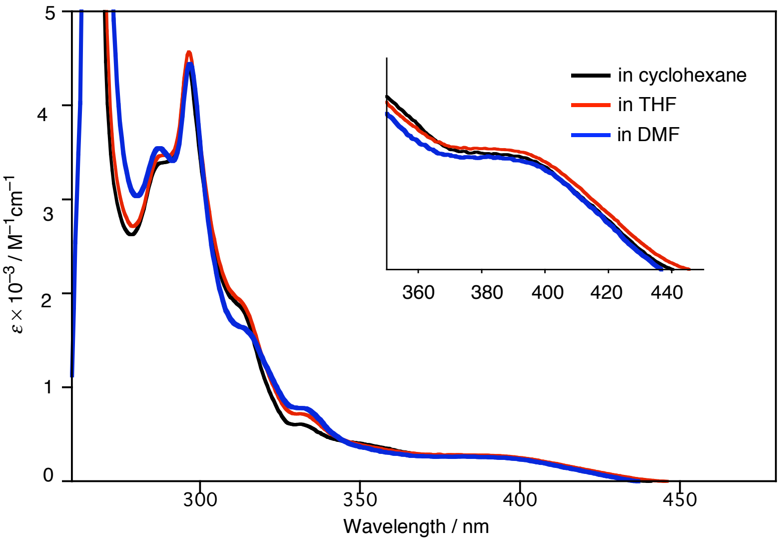


Figure S3. UV-vis absorption spectra of **3**: black line in cyclohexane; red line in THF; blue line in DMF.

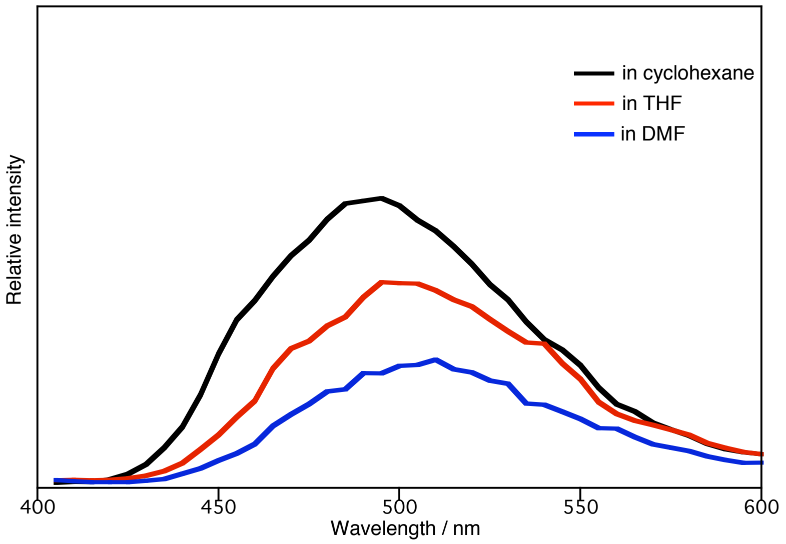


Figure S4. Fluorescence spectra of **3**: black line in cyclohexane; red line in THF; blue line in DMF.

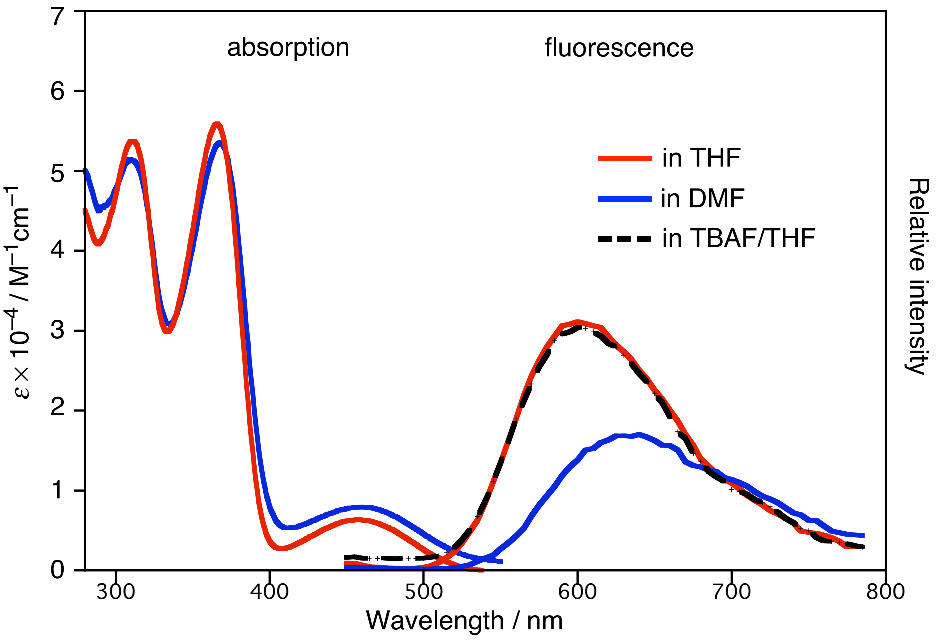


Figure S5. UV-vis absorption and fluorescence spectra of **10**: red line in THF; blue line in DMF; dashed line in THF (5.7×10^{-6} M) with TBAF (0.01 M).

Cyclic Voltammetry

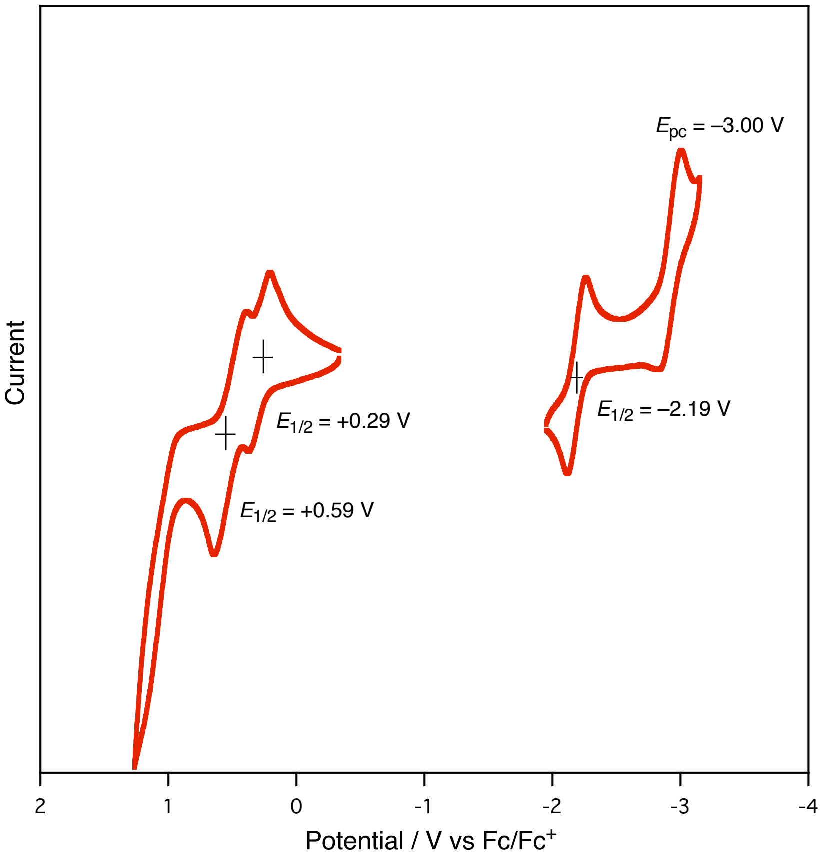


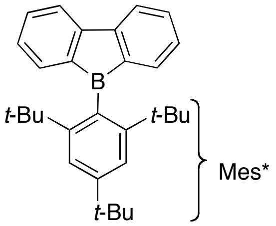
Figure S6. Cyclic voltammogram of **10** in THF, measured with *n*-$Bu_4N^+ClO_4^-$ (0.1 M) as a supporting electrode at a scan rate of 100 mV s^{-1}.

Theoretical Calculations

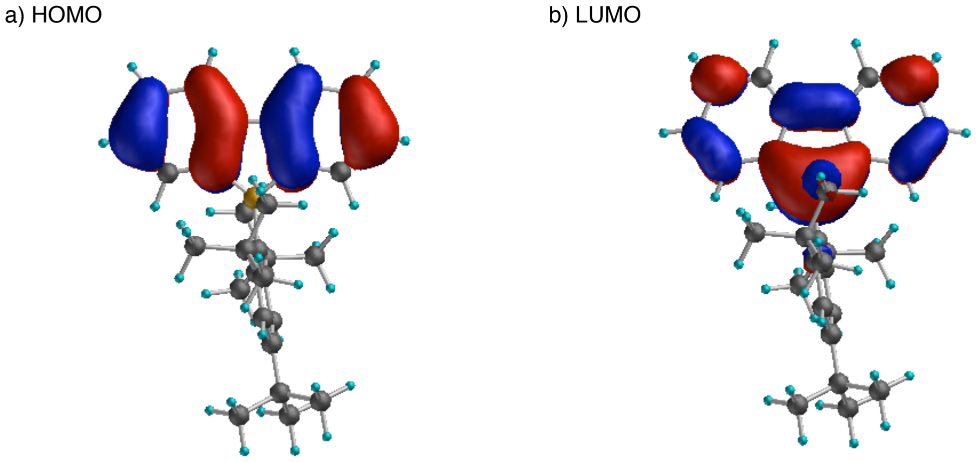
Table S1. Calculated HOMO,^{a} LUMO,^{a} and Excitation Energies^b

Compd	HOMO /eV^a	LUMO /eV^a	Transition /eV^b	Main CI coefficient ^{b}	Oscillator Strength f^b
3	–5.81	–1.92	3.07 (403 nm)	0.68(HOMO→LUMO)	0.0027
			3.23 (384 nm)	0.70(HOMO–1→LUMO)	0.0022
9	–5.01	–2.16	2.33 (532 nm)	0.66(HOMO→LUMO)	0.3698
			2.96 (419 nm)	0.65(HOMO→LUMO+1)	1.2233
10	–4.80	–1.93	2.40 (517 nm)	0.68(HOMO→LUMO)	0.2465
			3.23 (384 nm)	0.59(HOMO→LUMO+1)	0.8872

^{a}Calculated at the B3LYP/6-31G(d) level. ^{b}Calculated at the B3LYP/6-31+G(d) level using the TD-DFT method.



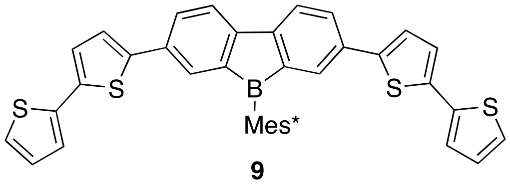
3



a) HOMO

b) LUMO

Figure S7. Pictorial presentation of (a) HOMO and (b) LUMO of **3** calculated at the B3LYP/6-31G(d) level of theory.



9

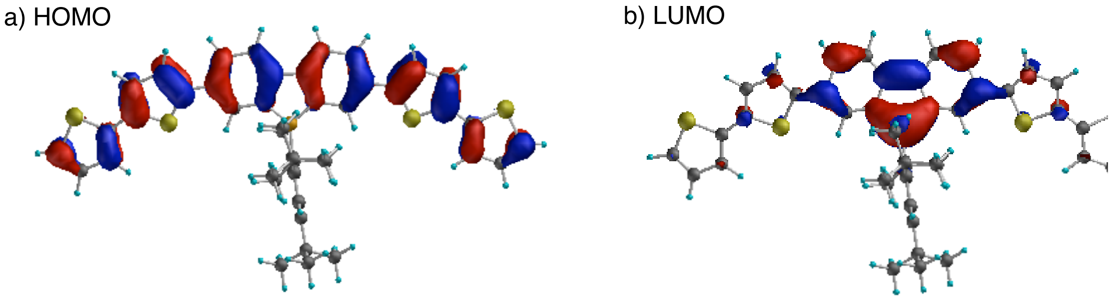
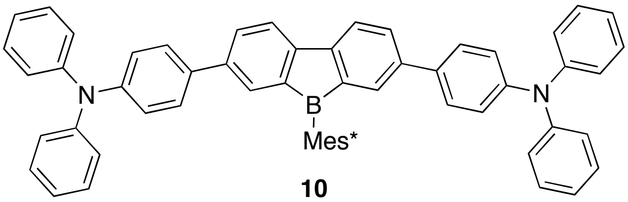


Figure S8. Pictorial presentation of (a) HOMO and (b) LUMO of **9** calculated at the B3LYP/6-31G(d) level of theory.



10

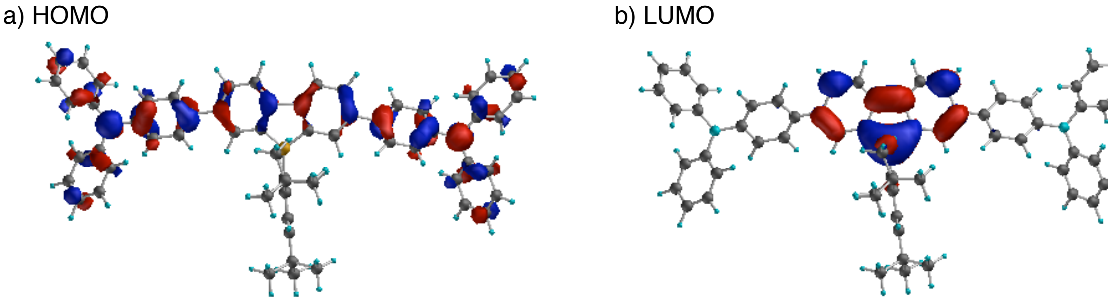


Figure S9. Pictorial presentation of (a) HOMO and (b) LUMO of **10** calculated at the B3LYP/6-31G(d) level of theory.

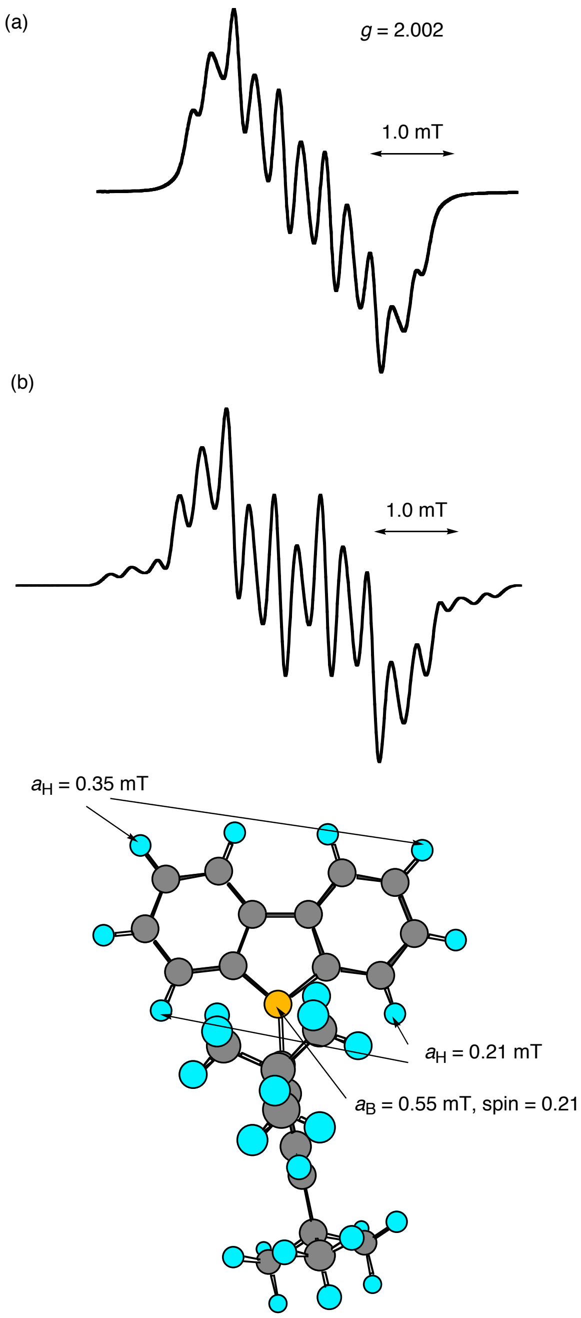


Figure S10. ESR spectra of **3**$^{\bullet-}\cdot K^+$ (a) obtained in THF and (b) simulated using the coupling constant for boron (0.55 mT) and two sets of two equivalent protons (0.35 mT, 0.21 mT).

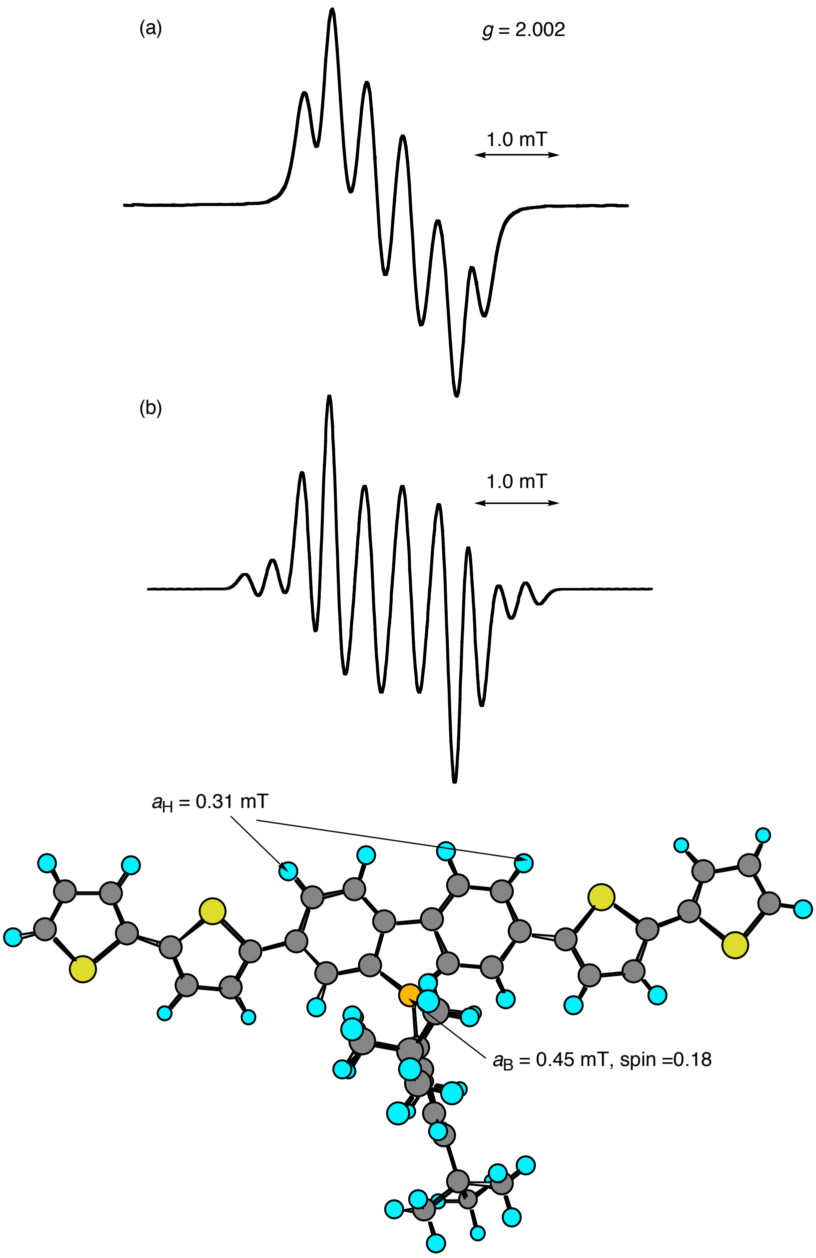
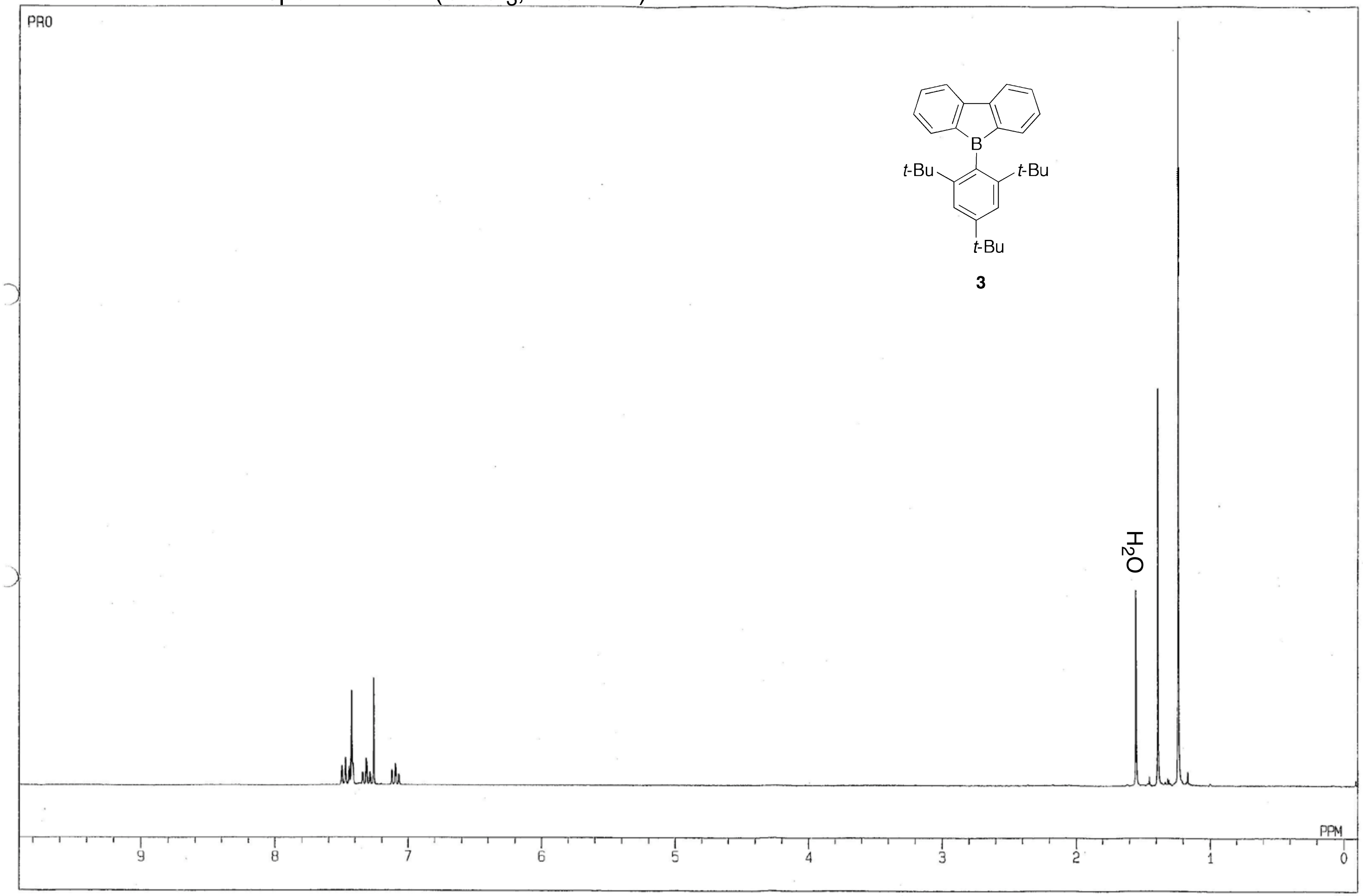
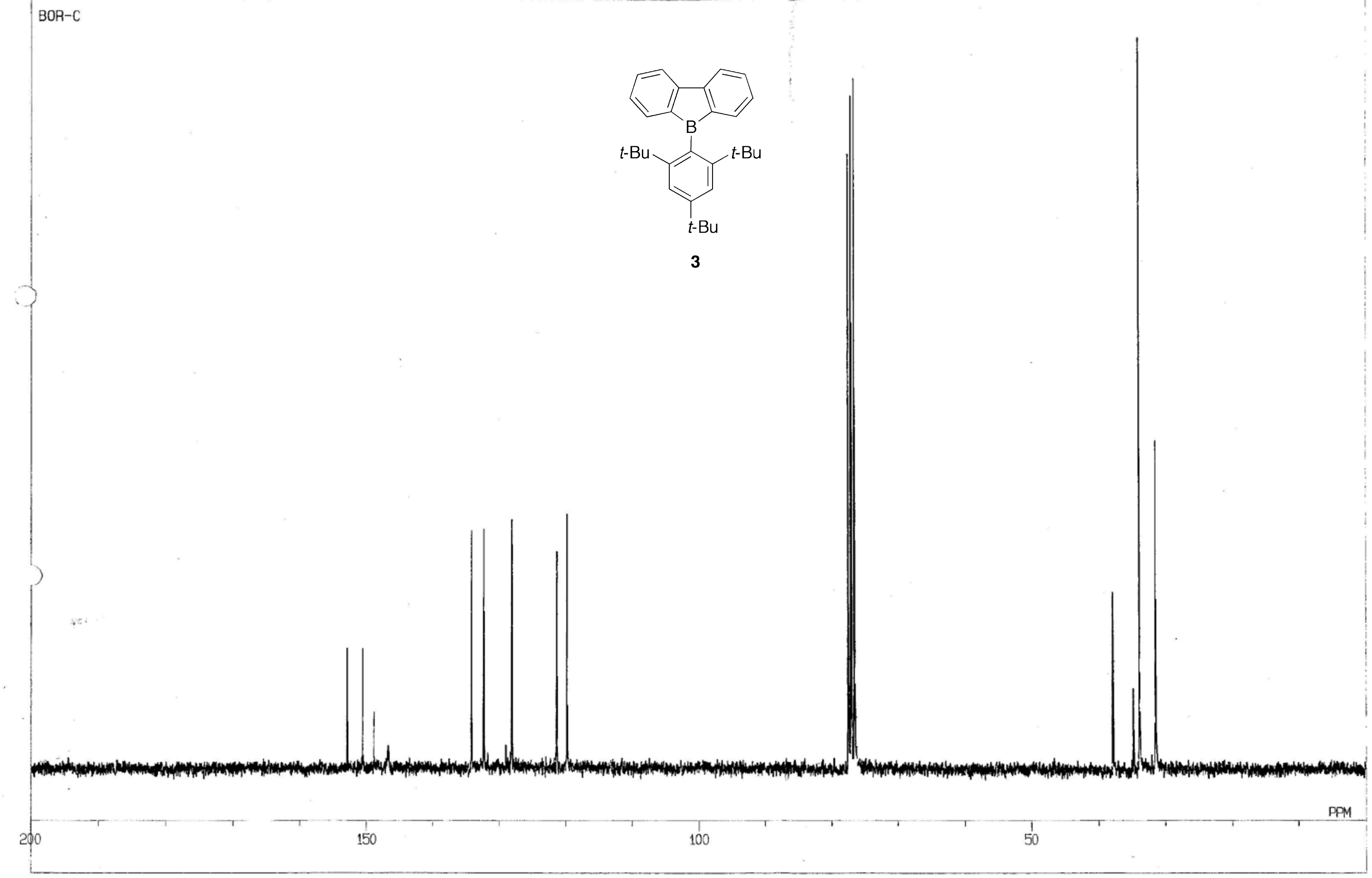


Figure S11. ESR spectra of $\mathbf{9}^{\bullet-}\cdot K^+$ (a) obtained in THF and (b) simulated using the coupling constant for boron (0.45 mT) and two equivalent protons (0.31 mT).

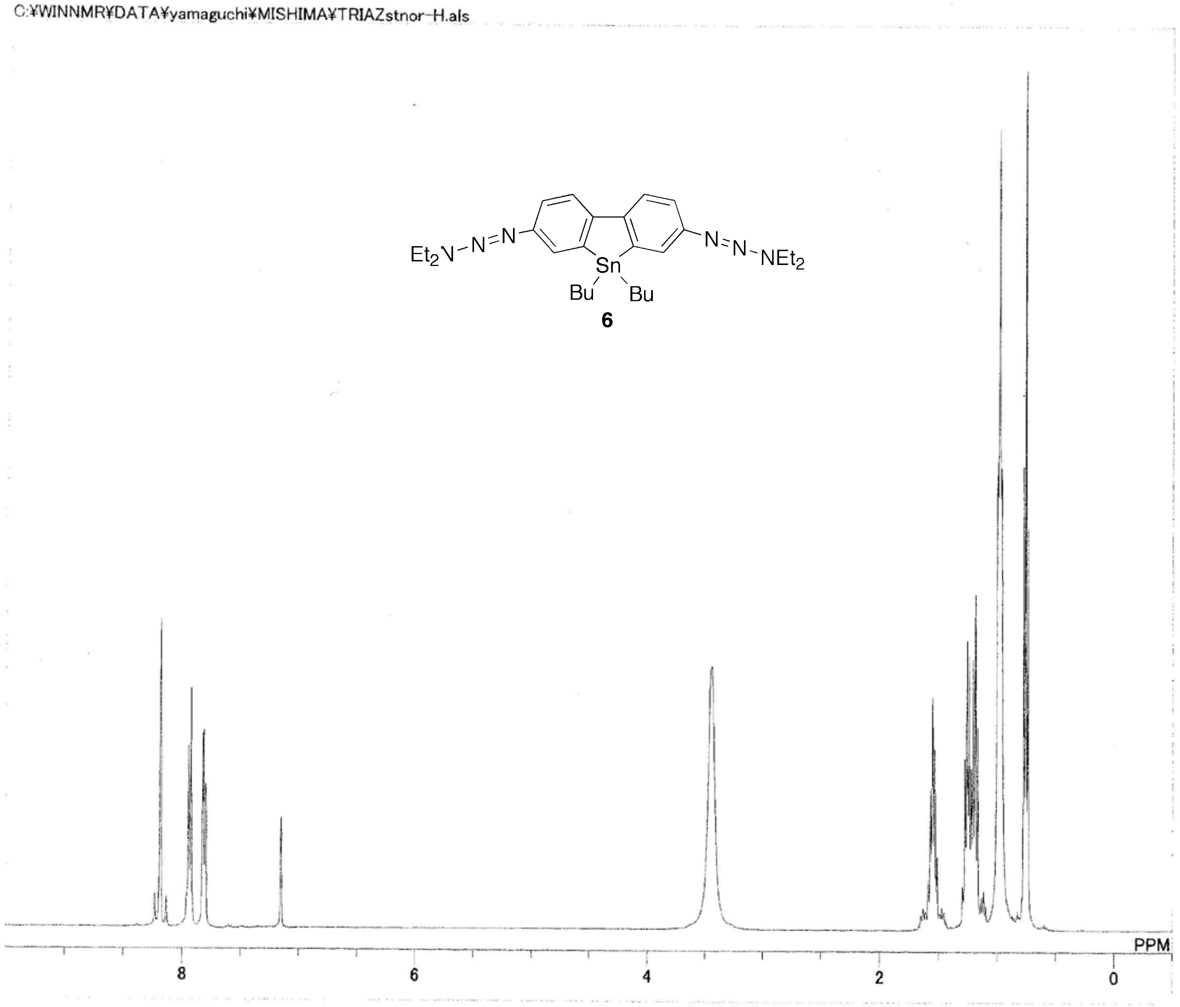
^{1}H NMR spectrum of **3** ($CDCl_3$, 270 MHz)



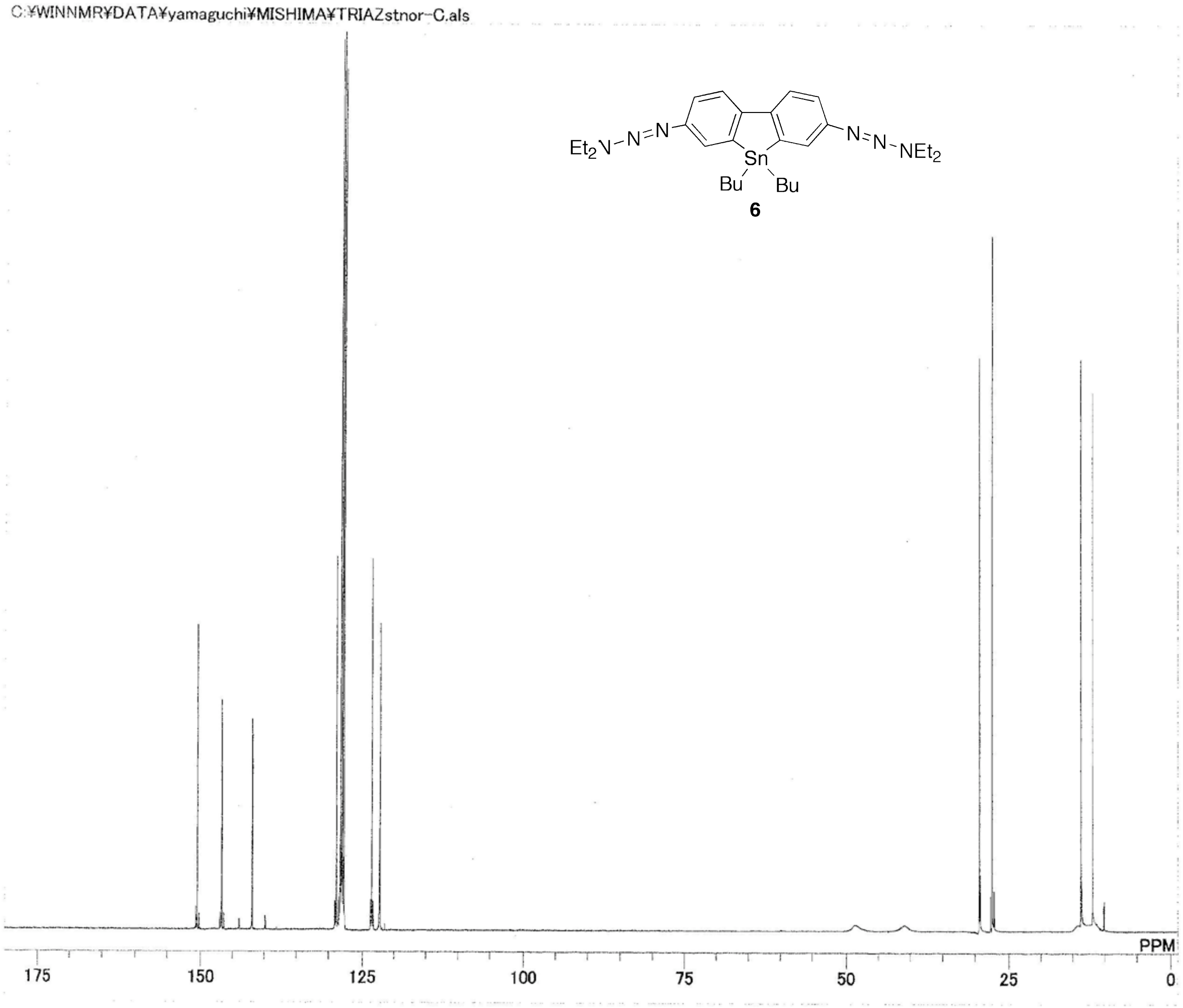
^{13}C NMR spectrum of **3** ($CDCl_3$, 67.5 MHz)



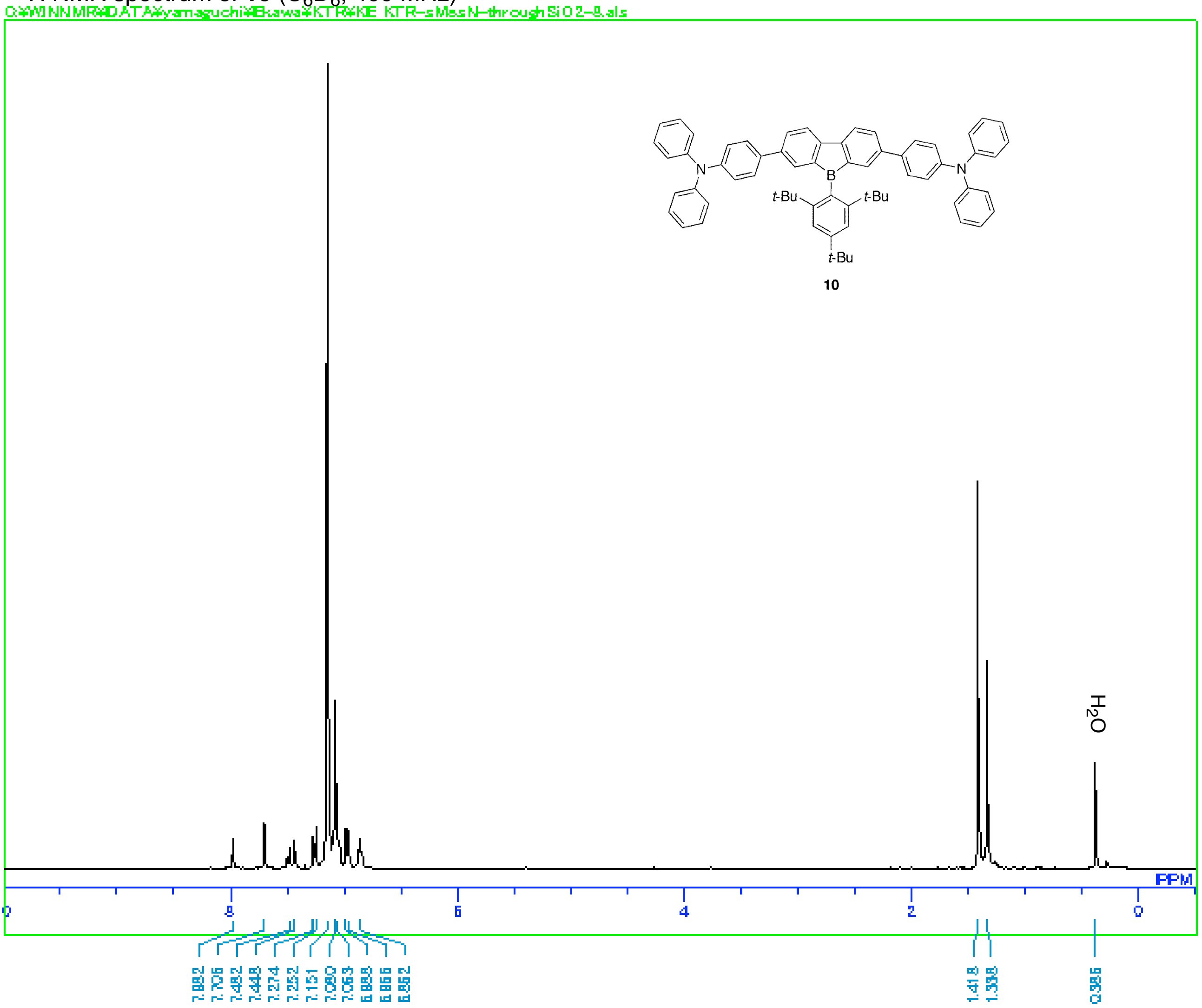
^{1}H NMR spectrum of **6** (C_6D_6, 400 MHz)



^{13}C NMR spectrum of **6** (C_6D_6, 100 MHz)



^{1}H NMR spectrum of **10** (C_6D_6, 400 MHz)



^{13}C NMR spectrum of **10** ((C_6D_6, 100 MHz)

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