Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Storage and release of two electrons from an electron-rich carbon–carbon bond: boron mediated reversible coupling of DMAP and 9-azajulolidine

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Contents

Experimental procedures

General considerations. All manipulations were conducted either under an atmosphere of dry argon or in *vacuo* using standard Schlenk line or glovebox techniques. Solvents were purified by distillation from Na/K under dry argon prior to use. [(dpp-bian)BBr] (**1**) were prepared according to published procedures[1]. NMR spectra were acquired on a Bruker *Avance 400* (^{1}H: 400.1 MHz, ^{11}B: 128.4 MHz, ^{13}C: 100.6 MHz) NMR spectrometer at 298 K. ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced to external TMS via the residual protons of the solvent (^{1}H) or the solvent itself (^{13}C). ^{11}B NMR spectra were referenced to external $BF_3{\cdot}OEt_2$. GC−MS analyses were performed using an Agilent 7820A gas chromatograph [(column) HP-5MS 5% phenyl methyl siloxane, 25 m, ⌀ 0.25 mm, film 0.25 µm; (injector) 250 °C; (oven) 80 °C (2 min), 80−280 °C (50 °C min^{-1}); (carrier gas) He (1.2 mL min^{-1})] equipped with an Agilent 5977B inert MSD with a triple-axis detector, operating in EI mode, and an Agilent G4567A series auto sampler/injector. High resolution mass spectrometry (HRMS) was performed with a Thermo Fisher Scientific Exactive Plus Orbitrap MS System with a Liquid Injection Field Desorption/Ionization (LIFDI) probe. The EPR spectrum was recorded with a Bruker ELEXYS E500 spectrometer.

Synthesis of 2

In an argon-filled glovebox, 10 mL of Et_2O was added to a vial containing [(dpp-bian)BBr] (**1**) (591 mg, 1 mmol) and a piece of lithium metal (100 mg, 14.4 mmol). The mixture was then allowed to stir for 8 h, while the color of the mixture turned dark green. The *in situ* generated Li_2[BIAN–BBr] (1 mmol) was separated from the excessive lithium metal by filtration and transferred into a vial containing **1** (591 mg, 1 mmol). A brown solution was formed after stirring for 3 h. Then DME (1 mL, 12.8 mmol) was added to the solution and a dark brown precipitate was formed after stirring for 0.5 h. The solids were then collected by filtration, washed with Et_2O (2x3 mL), and dried *in vacuo* to give [(dpp-bian)BBr]Li(DME)$_3$ (**2**) as a dark brown crystalline solid. Yield 71% (1.23 g, 1.42 mmol). Single crystals suitable for X-ray diffraction were obtained from diffusion of hexane into a concentrated DME solution of **2** at −30°C.

HRMS(toluene)**:** [(dpp-bian) BBr)$^{+}$]: 590.2452 (calc.: 590.2462).

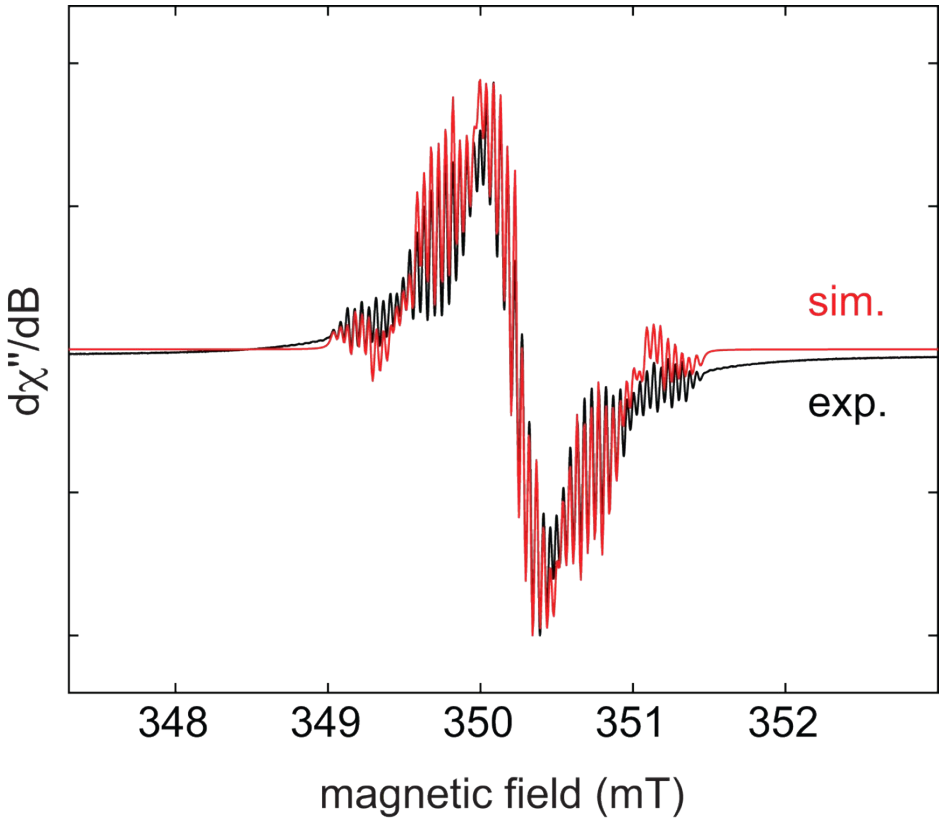

Figure S1. Experimental X-band (9.6 GHz) EPR spectrum of **2** in hexane solution at 298 K. In the simulation (red), the ^{1}H, ^{14}N hyperfine interactions are considered.

Simulation parameters:

g = 2.003
a(N) = 2.6 MHz (0.9 G, 2N)
a(H) = 15.4 MHz (5.5 G, 2H)
a(H) = 12.8 MHz (4.6 G, 2H)
a(H) = 1.3 MHz (0.5 G, 2H)

Synthesis of 3

Method 1 (Salt elimination promoted by introduction of a strong Lewis base)

In an argon-filled glovebox, hexane (5 mL) was added to a vial containing **2** (260 mg, 0.30 mmol) and DMAP (37 mg, 0.30 mmol). The color of the mixture turned from brown to purple within 1 min. The mixture was stirred for another 30 min. Then LiBr and minor insoluble impurities were removed by filtration. The filtrate was dried *in vacuo.* Then 5 mL of pentane were added and the resulting mixture was dried *in vacuo* again. The residue was washed with 2x3 mL of cold (−30°C) pentane and dried *in vacuo* to give $[(dpp\text{-}bian)B(DMAP)]_2$ (**3**) as a purple crystalline solid. Yield 69% (131 mg, 0.10 mmol). Single crystals suitable for X-ray diffraction were obtained by storing a concentrated pentane solution at −30°C for 72 h.

^{1}H NMR (400 MHz, 25 °C, toluene-d8): δ 1.08 (d, $^{3}J_{H\text{-}H}$=6.8 Hz, 24H, Dipp-CH(CH_3)$_2$), 1.27 (d, $^{3}J_{H\text{-}H}$=6.8 Hz, 24H, Dipp-CH(CH_3)$_2$), 1.96 (s, 12H, N(CH_3)$_2$), 3.48 (sept, $^{3}J_{H\text{-}H}$=6.8 Hz, 8H, Dipp-CH(CH$_3$)$_2$), 4.33 (d, $^{3}J_{H\text{-}H}$=8.6 Hz, 4H, NCH=CHR), 6.23 (d, $^{3}J_{H\text{-}H}$=8.6 Hz, 4H, NCH=CHR), 6.39 (d, $^{3}J_{H\text{-}H}$=6.8 Hz, 2H, Ar-*H*), 6.79-6.85 (m, 4H, Ar-*H*), 7.07-7.11 (m, 4H, Ar-*H*), 7.22-7.27 (m, 8H, Dipp-Ar-*H*), 7.30-7.37 (m, 4H, Dipp-Ar-*H*).

^{11}B NMR (128 MHz, 25 °C, toluene-d8): δ 26.8 (br).

^{13}C NMR: Clean spectrum could not be obtained due to the instability of **3** in toluene.

HRMS(CH_2Cl_2)**:** [M^+]: 1266.8223 (calc.: 1266.8252). (Attention: **3** decomposes quickly in DCM. Hence the sample must be freshly prepared and be measured immediately.)

Method 2 (Reduction of borenium cation)

In an argon-filled glovebox, toluene (3 mL) was added to a vial containing **5** (71.3 mg, 0.1 mmol) and KC_8 (13.5 mg, 0.1 mmol). A purple-red suspension was formed after stirring at room temperature for 8 h. Then all volatiles were removed *in vacuo* and the residue was extracted with 5 mL of hexane. The extraction was concentrated *in vacuo* to ca. 3 mL and stored at −30°C for 10 h to give **3** as purple crystals. Yield 16% (10 mg, 0.0079 mmol).

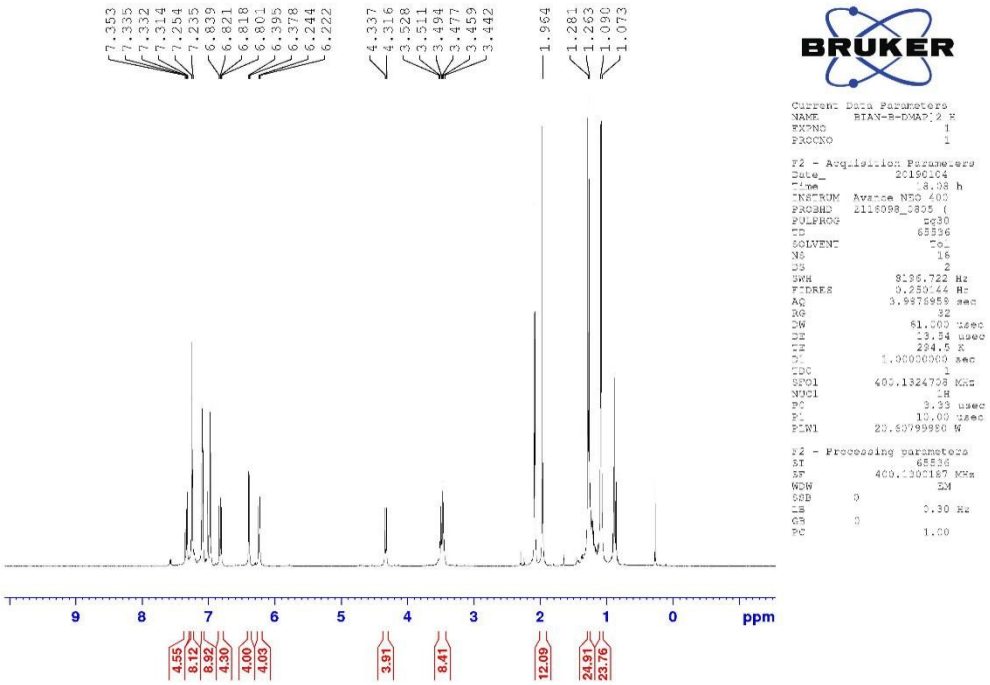

Figure S2. ^{1}H NMR spectrum of **3** in toluene-d8.

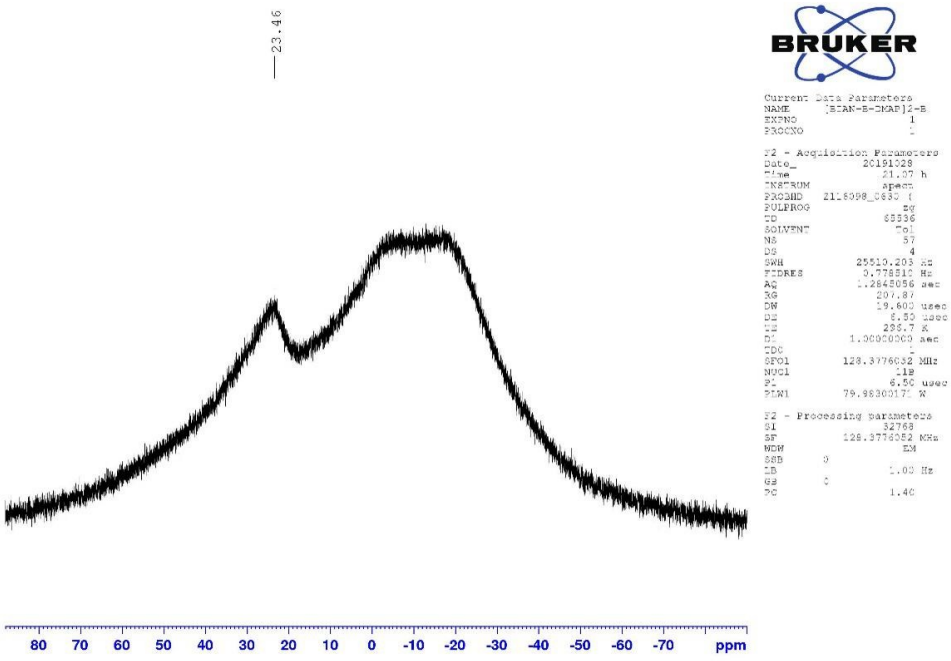

Figure S3. ^{11}B NMR spectrum of **3** in toluene-d8.

Synthesis of 4

Method 1 (Salt elimination promoted by introduction of a base)

In an argon-filled glovebox, toluene (5 mL) was added to a vial containing **2** (260 mg, 0.30 mmol) and 9-AJ (52 mg, 0.30 mmol). The mixture was stored for 8 h before the color of the mixture turned from brown to purple. Then LiBr and minor insoluble impurities were removed by filtration. All volatiles were removed *in vacuo.* Then 5 mL of hexane was added, and the resulting mixture was dried *in vacuo* again. The residue was washed with 2*3 mL of cold (−30°C) pentane and dried *in vacuo* to give [(dpp-bian)B(9-AJ)]$_2$ (**4**) as a purple crystalline solid. Yield 85% (174 mg, 0.13 mmol). Single crystals suitable for X-ray diffraction were obtained from the procedure as follows: Remove most of the volatiles of a toluene solution containing 50 mg **4** *in vacuo* to obtain a purple oily substance. Then ca. 3 mL hexane were added to the mixture. The resulting suspension was filtered. The filtrate was left standing at room temperature for 3 h to give single crystals.

^{1}H NMR (400 MHz, 25 °C, toluene-d8): δ 0.32 (dd, $^{3}J_{H-H}$=5.7 Hz, $^{3}J_{B-H}$=17.1 Hz, 2H, NC*H*-C*H*N), 0.80 (d, $^{3}J_{H-H}$=6.7 Hz, 6H, Dipp-CH(C*H*$_3$)$_2$), 1.22 (d, $^{3}J_{H-H}$=7.1 Hz, 6H, Dipp-CH(C*H*$_3$)$_2$), 1.30-1.46 (m, 32H: 24H for Dipp-CH(C*H*$_3$)$_2$ and 8H for CCH$_2$C*H*$_2$CH$_2$N), 1.60 (d, $^{3}J_{H-H}$=6.4 Hz, 6H, Dipp-CH(C*H*$_3$)$_2$), 1.62-1.86 (m, 8H, CC*H*$_2$CH$_2$CH$_2$N), 2.20-2.55 (m, 8H, CCH$_2$CH$_2$C*H*$_2$N), 3.01 (sept, $^{3}J_{H-H}$=6.7 Hz, 1H, Dipp-C*H*(CH$_3$)$_2$), 3.16 (sept, $^{3}J_{H-H}$=6.8 Hz, 1H, Dipp-C*H*(CH$_3$)$_2$), 3.68 (sept, $^{3}J_{H-H}$=6.8 Hz, 1H, Dipp-C*H*(CH$_3$)$_2$), 4.04 (sept, $^{3}J_{H-H}$=6.7 Hz, 1H, Dipp-C*H*(CH$_3$)$_2$), 5.47 (s, 2H, NC*H*=C), 6.30 (d, $^{3}J_{H-H}$=6.9 Hz, 2H, Ar-*H*), 6.39 (d, $^{3}J_{H-H}$=6.9 Hz, 2H, Ar-*H*), 6.79-6.89 (m, 4H, Ar-*H*), 7.03-7.07 (m, 2H, Ar-*H*), 7.17-7.44 (m, 14H, Ar-*H*).

^{11}B NMR (128 MHz, 25 °C, toluene-d8): δ 26.8 (br).

^{13}C NMR (101 MHz, 25 °C, toluene-d8): δ 23.3, 23.6, 24.9, 25.2, 25.5, 26.1, 26.5, 26.8, 27.7, 28.3, 28.5, 29.0, 29.4, 49.4, 52.1, 64.7, 96.7, 113.8, 119.2, 119.4, 123.5, 124.8, 125.2, 125.3, 126.3, 126.8, 127.0, 128.2, 131.5, 131.8, 134.0, 134.5, 135.2, 139.0, 139.5, 146.6, 147.0, 147.3, 148.0.

HRMS(CH$_2$Cl$_2$)**:** [M$^+$]: 1370.8866 (calc.: 1370.8878).

Method 2 (Reduction of borenium cation)

In an argon-filled glovebox, toluene (3 mL) was added to a vial containing [(dpp-bian) B(9-AJ)]Br (**6**) (71.3 mg, 0.1 mmol) and KC$_8$ (13.5 mg, 0.1 mmol). A purple suspension was formed after stirring at room temperature for 16 h. Then all volatiles were removed *in vacuo* and the residue

was extracted with 5 mL of hexane. The extraction was concentrated *in vacuo* to ca. 3 mL and stored at −30°C for 10 h to give **4** as a purple crystalline solid. Yield 12% (8 mg, 0.0058 mmol)

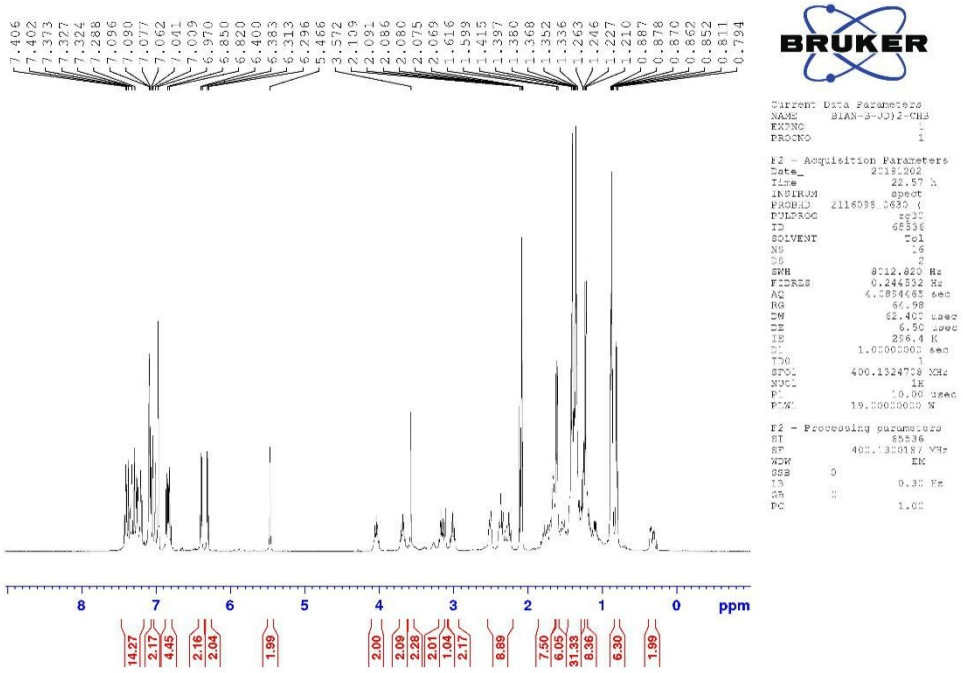

Figure S4. ^{1}H NMR spectrum of **4** in toluene-d8.

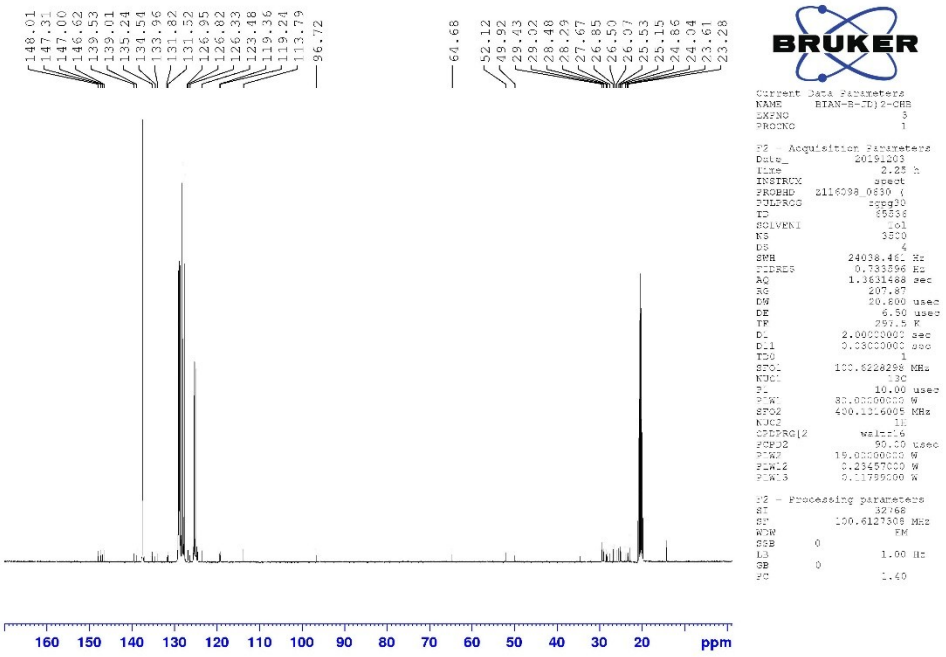

Figure S5. ^{13}C NMR spectrum of **4** in toluene-d8.

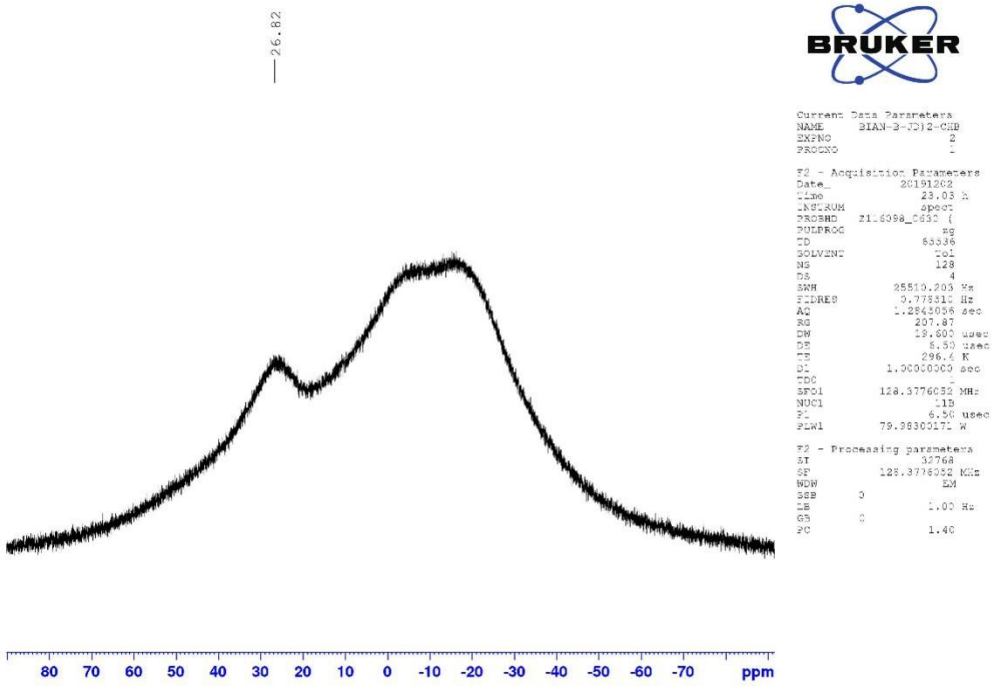

Figure S6. ^{11}B NMR spectrum of **4** in toluene-d8.

Synthesis of 5

In an argon-filled glovebox, 1 mL of hexane was added to a vial containing **1** (59.1 mg, 0.1 mmol) and DMAP (12.2 mg, 0.1 mmol). The mixture was stirred for 30 min. Then DCM was added dropwise until the orange solid was completely dissolved. Then the solution was layered with *ca.* 8 mL of hexane and the mixture was stored at −30°C for 48 h. The mother liquor was decanted and the crystals were dried *in vacuo* to give [(dpp-bian)B(DMAP)]Br (**5**) as orange blocks. Yield 88% (63 mg, 0.088 mmol).

^{1}H NMR (400 MHz, 25 °C, CD_2Cl_2): δ 1.00–1.08 (m, 24H, Dipp-CH(C*H*$_3$)$_2$), 3.03(sept, $^{3}J_{H\text{-}H}$=6.9 Hz, 4H, Dipp-C*H*(CH$_3$)$_2$), 3.19(s, 6H, N(C*H*$_3$)$_2$), 7.14-7.20 (m, 2H, Ar-*H*), 7.38-7.47 (m, 6H, Ar-*H*), 7.49-7.59 (m, 6H, Ar-*H*).

^{11}B NMR (128 MHz, 25 °C, CD_2Cl_2): δ 22.0 (br)

^{13}C NMR (101 MHz, 25 °C, CD_2Cl_2): δ 28.4, 28.8, 33.9, 46.0, 113.5, 124.6, 128.7, 130.4, 131.6, 132.4, 133.0, 133.5, 133.8, 135.0, 138.0, 139.0, 144.8, 150.3, 161.0.

HRMS(CH_2Cl_2)**:** [(dpp-bian)B(DMAP)]$^{+}$: 633.4111 (calc.: 633.4123).

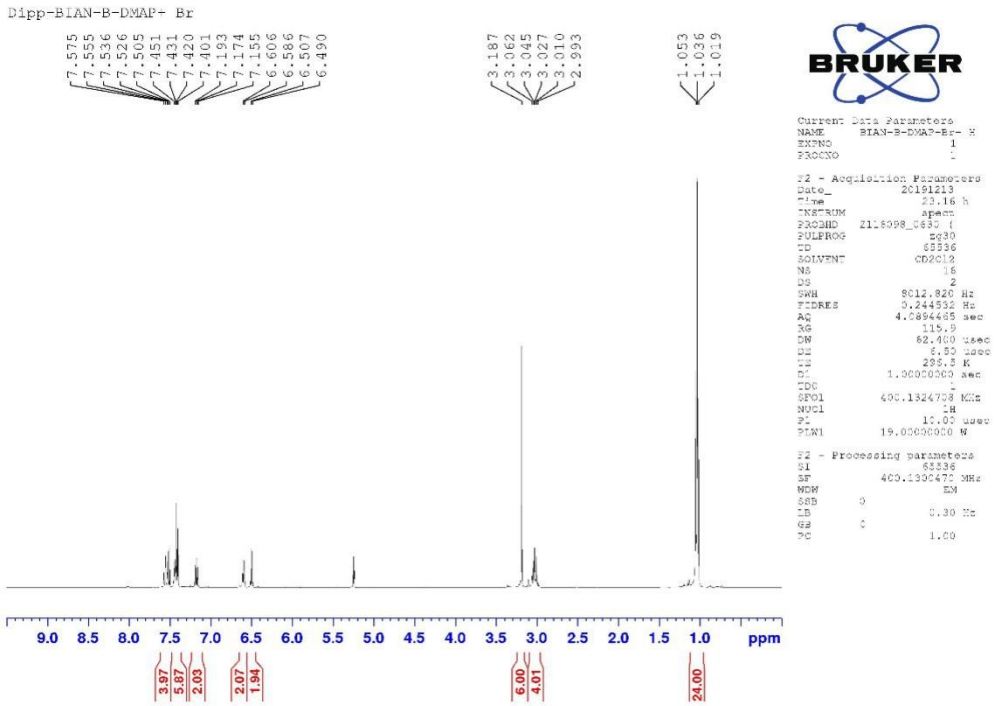

Figure S7. ^{1}H NMR spectrum of **5** in CD_2Cl_2.

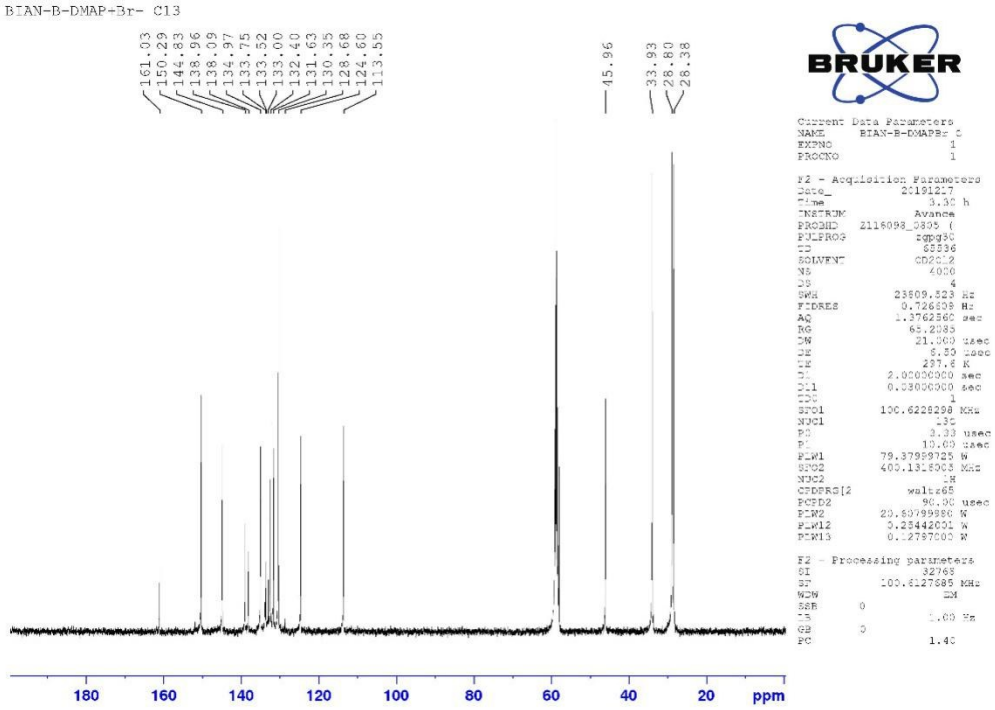

Figure S8. ^{13}C NMR spectrum of **5** in CD_2Cl_2.

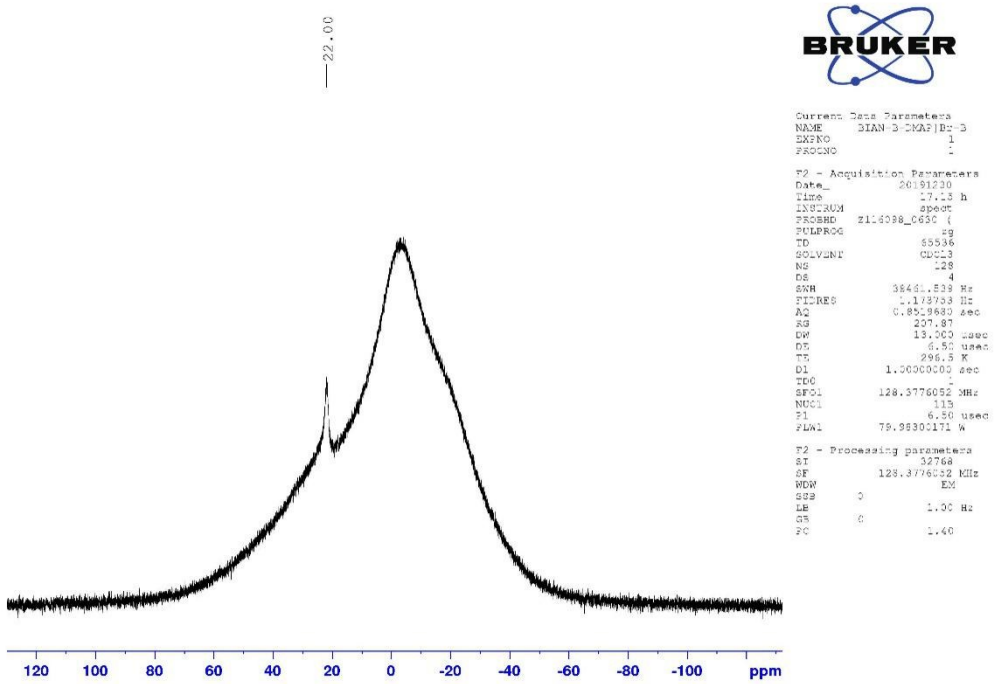

Figure S9. ^{11}B NMR spectrum of **5** in CD_2Cl_2.

Synthesis of 6

In an argon-filled glovebox, hexane (1 mL) was added to a vial containing **1** (59.1 mg, 0.1 mmol) and 9-AJ (17.4 mg, 0.1 mmol). The mixture was stirred for 30 min. Then DCM was added dropwise until the orange solid was completely dissolved. Then the solution was layered with ca. 8 mL of hexane and the mixture was stored at −30°C for 48 h. The mother liquor was decanted and the crystals were dried *in vacuo* to give [(dpp-bian)B(9-AJ)]Br (**6**) as orange blocks. Yield 78% (60 mg, 0.078 mmol).

^{1}H NMR (400 MHz, 25 °C, CD_2Cl_2): δ 1.08 (d, $^{3}J_{H-H}$=6.9 Hz, 12H, Dipp-CH(C*H*$_3$)$_2$), 1.12 (d, $^{3}J_{H-H}$=6.9 Hz, 12H, Dipp-CH(C*H*$_3$)$_2$, 1.88 (d, $^{3}J_{H-H}$=6.1 Hz, 4H, CCH$_2$C*H*$_2$CH$_2$N), 2.27 (t, $^{3}J_{H-H}$=6.3 Hz, 4H, CC*H*$_2$CH$_2$CH$_2$N), 3.13 (sept, $^{3}J_{H-H}$=6.8 Hz, 4H, Dipp-C*H*(CH$_3$)$_2$), 3.53 (t, $^{3}J_{H-H}$=5.7 Hz, 4H, CCH$_2$CH$_2$C*H*$_2$N), 6.06 (d, $^{3}J_{H-H}$=6.8 Hz, 2H, Ar-*H*), 6.06 (d, $^{3}J_{H-H}$=6.8 Hz, 2H, Ar-*H*), 7.07 (s, 2H, Ar-*H*), 7.22-7.28 (m, 2H, Ar-*H*), 7.45-7.50 (m, 4H, Ar-*H*), 7.56-7.66 (m, 4H, Ar-*H*).

^{11}B NMR (128 MHz, 25 °C, CD_2Cl_2): δ 24.1 (br).

^{13}C NMR (101 MHz, 25 °C, CD_2Cl_2): δ 21.0, 22.0, 25.1, 25.5, 25.6, 30.7, 52.3, 119.1, 121.3, 127.0, 128.4, 129.2, 129.8, 130.3, 130.7, 131.7, 134.8, 136.1, 137.6, 147.2, 153.8.

HRMS(CH_2Cl_2)**:** [(dpp-bian)B(9-AJ)$^{+}$]: 685.4414 (calc.: 685.4436).

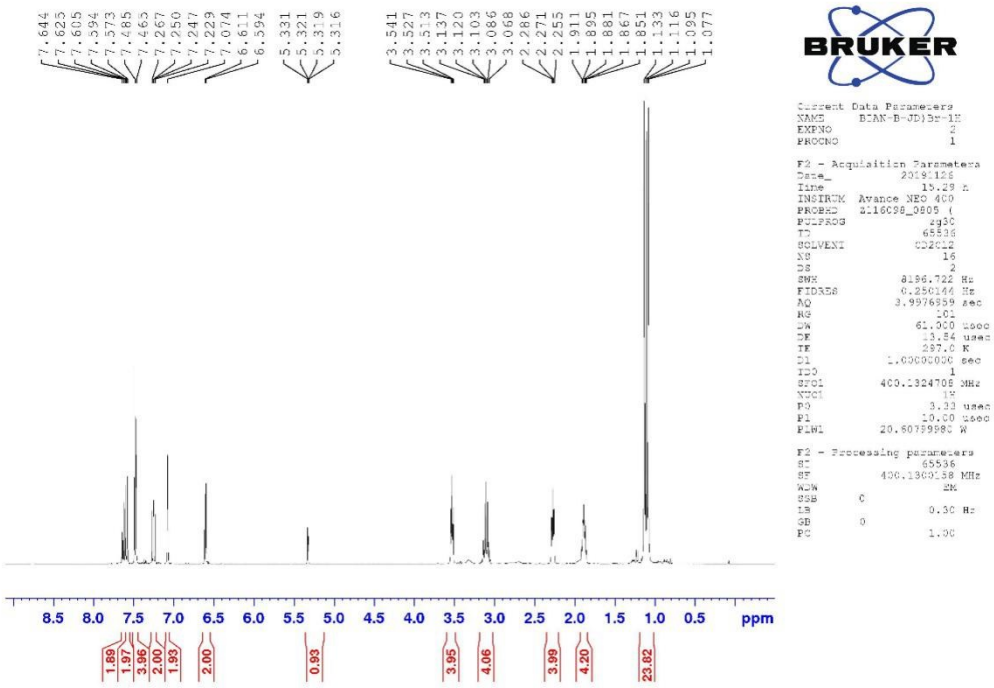

Figure S10. ^{1}H NMR spectrum of **6** in CD_2Cl_2.

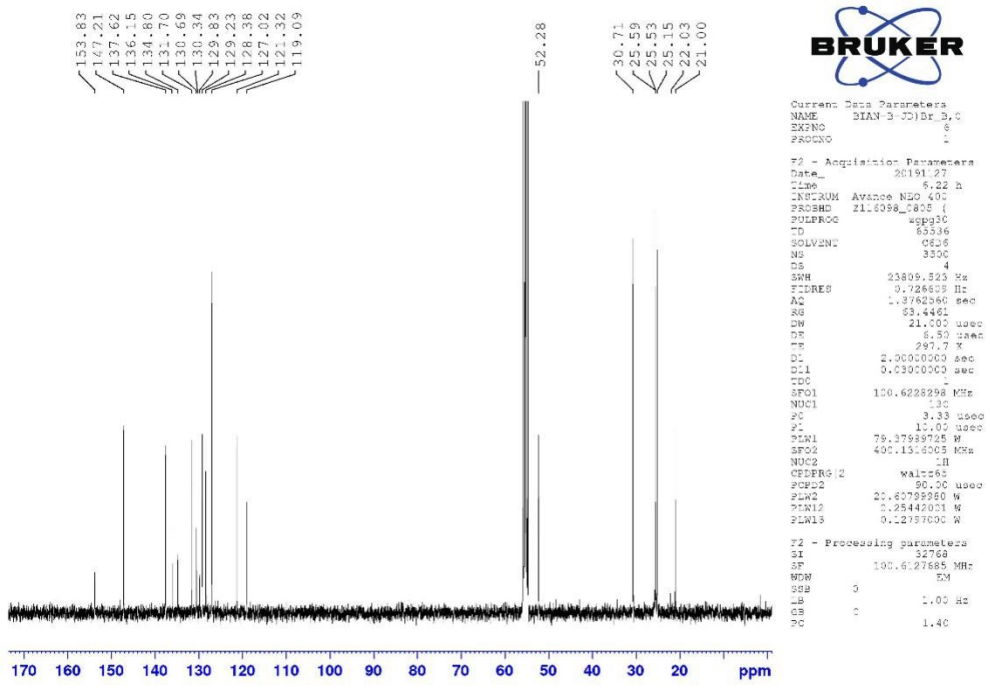

Figure S11. ^{13}C NMR spectrum of **6** in CD_2Cl_2.

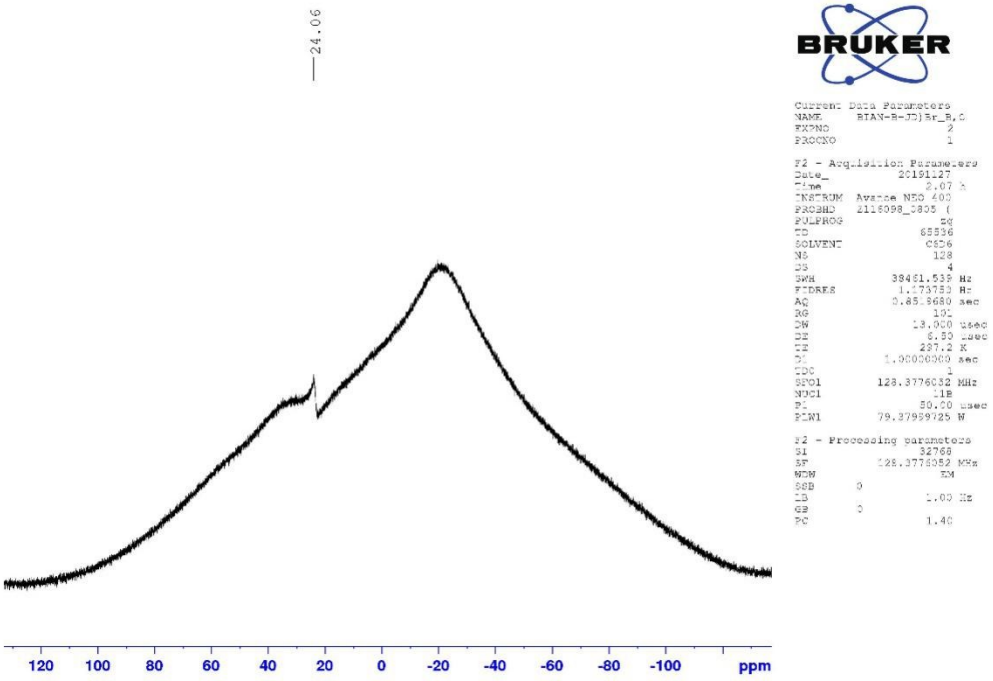

Figure S12. ^{11}B NMR spectrum of **6** in CD_2Cl_2.

Reaction of 3 with PhI and B_2pin_2

In an argon-filled glovebox, PhI (20 mg, 0.1 mmol) was dissolved in C_6D_6 (0.5 mL), then added to a solution of **3** (61 mg, 0.05 mmol) and B_2pin_2 (25 mg,0.1 mmol) in C_6D_6 (1 mL) at room temperature. The mixture was left for 1 h at room temperature. A dark brown precipitate was formed. The suspension was exposed to air, filtered through a short plug of dry celite (2 cm) to obtain a clear solution for the GC-MS analysis, which revealed ca. 89% conversion of PhI, and PhBpin as the borylation product (Fig. S13). GC yield: 32%.

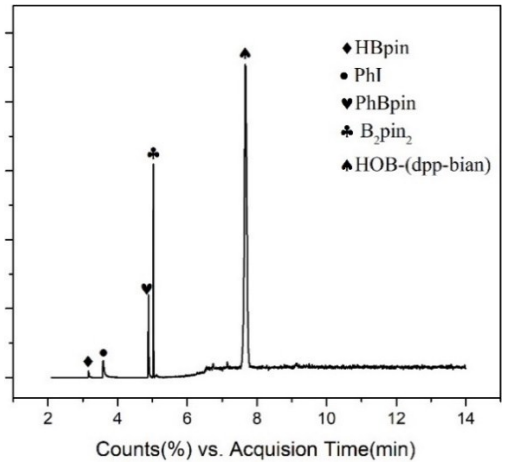

Figure S13. GC-MS analysis of the reaction mixture.

Reaction of 4 with PhI and B_2pin_2

In an argon-filled glovebox, PhI (20 mg, 0.1 mmol) was dissolved in C_6D_6 (0.5 mL), then added to a solution of **4** (69 mg, 0.05 mmol) and B_2pin_2 (25 mg,0.1 mmol) in C_6D_6 (1 mL) at room temperature. The reaction mixture was left for 16 h. A dark brown precipitate was formed. The suspension was exposed to air, filtered through a short plug of dry celite (2 cm) to obtain a clear solution for GC-MS analysis, which revealed ca. 45% conversion of PhI, and PhBpin as the expected borylation product (Fig. S14). GC yield: 15%.

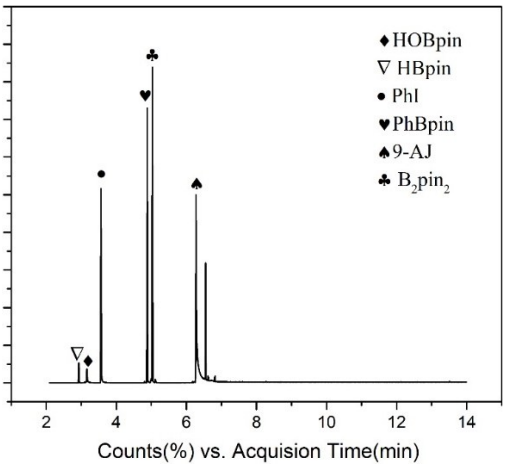

Figure S14. GC-MS analysis of the reaction mixture.

Crystallographic Details

Crystal data were collected on a Bruker D8 VENTURE diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Data reduction, scaling and absorption corrections were performed using SAINT (Bruker, V8.38A, 2013). The structure was solved with the XT structure solution program using the Intrinsic Phasing solution method[2] and by using Olex2 as the graphical interface. The model was refined with the ShelXL program using Least Squares minimization[3]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms were assigned to idealized geometric positions.

Crystal data for **2**: $C_{48}H_{70}BBrLiN_2O_6$, M_r = 868.769, brown block, 0.201 × 0.198 × 0.094 mm^3, orthorhombic space group $P2_12_12_1$, a = 12.9156(7) Å, b = 19.1434(11) Å, c = 19.3790(12) Å, α = 90°, β = 90°, γ = 90°, V = 4791.4(5) Å^3, Z = 4, r_{calcd} = 1.204 g·cm^{-3}, m = 0.905 mm^{-1}, F(000) = 1852.0, T = 99.99 K, R_1 = 0.0397, wR^2 = 0.0662, 9812/ independent reflections [2θ≤52.82°] and 546 parameters.

Crystal data for **3**: $C_{86}H_{100}B_2N_8$, M_r = 1267.37, violet prism, 0.2 × 0.168 × 0.154 mm^3, monoclinic space group $P2_1/n$, a = 17.282(2) Å, b = 30.185(4) Å, c = 18.933(2) Å, a = 90°, b = 111.157(3)°, g = 90°, V = 9211(2) Å^3, Z = 4, r_{calcd} = 0.914 g·cm^{-3}, m = 0.053 mm^{-1}, F(000) = 2728.0, T = 99.92 K, R_1 = 0.1345, wR^2 = 0.2243, 15742 independent reflections [2θ≤49.548°] and 885 parameters.

Crystal data for **4**: $C_{94}H_{108}B_2N_8$, M_r = 1478.71, violet block, 0.257 × 0.182 × 0.182 mm^3, triclinic space group $P\text{-}1$, a = 16.5767(16) Å, b = 22.881(2) Å, c = 24.197(2) Å, α = 78.233(3)°, β = 71.810(3)°, γ = 85.539(3)°, V = 8535.0(14) Å^3, Z = 4, r_{calcd} = 1.151 g·cm^{-3}, m = 0.066 mm^{-1}, F(000) = 3200.0, T = 100.03 K, R_1 = 0.0974, wR^2 = 0.1599, 29305 independent reflections [2θ≤49.646°] and 1905 parameters.

Crystal data for **5**: $C_{46}H_{56}BBrCl_6N_4$, M_r = 968.427, orange block, 0.176×0.153×0.082 mm^3, triclinic space group $P\text{-}1$, a = 11.7554(14) Å, b = 13.4782(16) Å, c = 16.2117(19) Å, α = 80.556(4)°, β = 126.076(4)°, γ = 79.442(4)°, V = 2444.4(5) Å^3, Z = 2, r_{calcd} = 1.316 g·cm^{-3}, m = 1.204 mm^{-1}, F(000) = 1633.0, T = 100.04 K, R_1 = 0.0927, wR^2 = 0.1698, 9941 independent reflections [2θ≤52.92°] and 533 parameters.

Crystal data for **6**: $C_{51}H_{58}BBrCl_8N_4$, M_r = 1101.404, orange block, 0.258 × 0.208 × 0.083 mm^3, monoclinic space group $P2_1/c$, a = 18.7601(16) Å, b = 13.8832(11) Å, c = 22.628(2) Å, α = 90°, β = 112.512(2)°, γ = 90°, V = 5444.3(8) $Å^3$, Z = 4, r_{calcd} = 1.344 $g \cdot cm^{-3}$, m = 1.185 mm^{-1}, $F(000)$ = 2272.0, T = 99.98 K, R_1 = 0.0877, wR^2 = 0.1732, 11207 independent reflections [$2\theta \leq 52.92°$] and 604 parameters.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC- 1986779 (**2**), 1986780 (**3**), 1986781 (**4**), 1986782 (**5**) and 1986783 (**6**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Cyclic Voltammetry

Cyclic voltammetry experiments were performed using a Metrohm Autolab PGSTAT204. A standard three-electrode cell configuration was employed using a platinum disk working electrode, a platinum wire counter electrode, and a silver wire, separated by a Vycor tip, serving as the reference electrode. Formal redox potentials are referenced to the ferrocene/ferrocenium (Fc/Fc+) redox couple. Tetra-*n*-butylammonium hexafluorophosphate ([^{n}Bu$_4$N][PF$_6$]) was employed as the supporting electrolyte. Compensation for resistive losses (*iR* drop) was employed for all measurements. For all measured cyclic voltammograms, the scan rate was 100 mV/s.

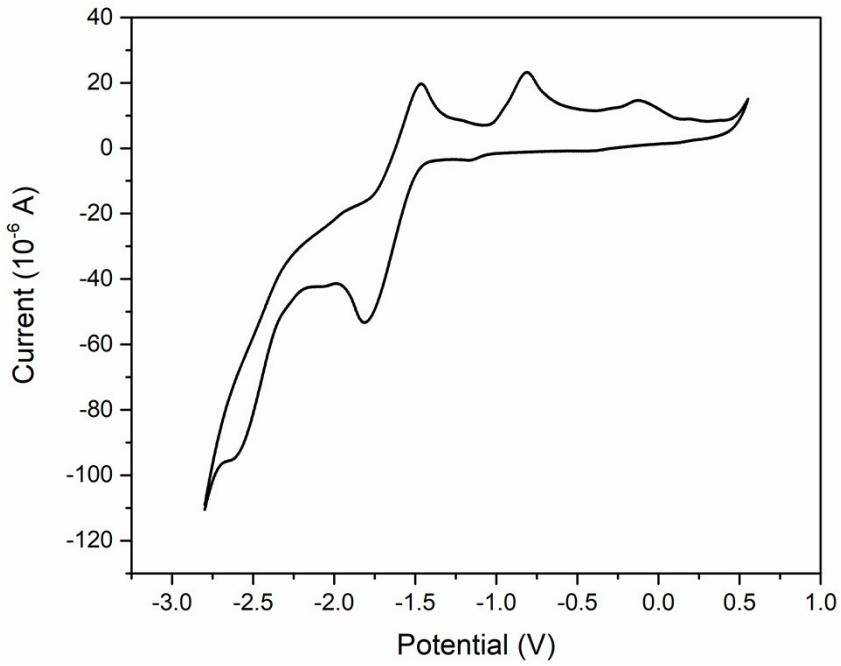

Figure S15. Wide-range cyclic voltammogram of 2 mM **3** measured in THF with 0.1 M [*n*Bu$_4$N][PF$_6$] as the supporting electrolyte. Formal potentials for reduction: E_{red} = −1.82 V; for oxidation: E_{ox} = −1.46, −0.82, −0.13 V. The irreversible oxidation wave at −0.82 V disappeared on the narrow-range scan (−2.2 to −0.5 V), which only displayed one clear oxidation wave at −1.52 V (Fig. 4). Very likely, the peak at −0.82 V is the corresponding oxidation for the irreversible second reduction at ca. −2.5 V.

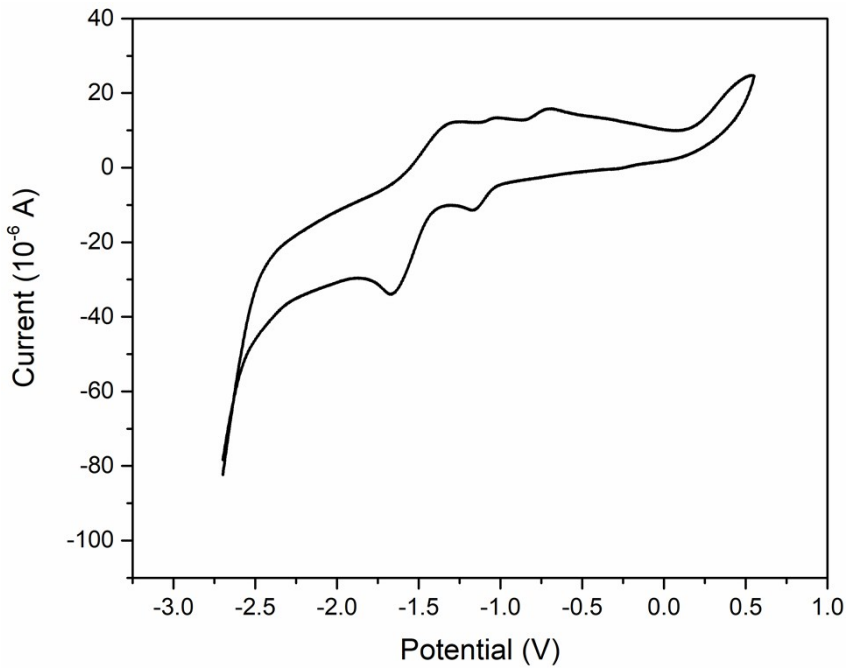

Figure S16. Wide-range cyclic voltammogram of 2 mM **4** measured in THF with 0.1 M [nBu$_4$N][PF$_6$] as the supporting electrolyte. Formal potentials for reduction: E_{red} = −1.68, −1.16 V; for oxidation: E_{ox} = −1.30, −1.02, −0.72 V.

Computational details

All calculations were performed using the Gaussian 09 software package.[4] All structures were optimized using the B3LYP hybrid functional[5]. The 6-311G** basis set was used for all atoms.[6] The optimized structures have been verified as minima on the potential energy surface by calculation of the vibrational frequencies at the same level.

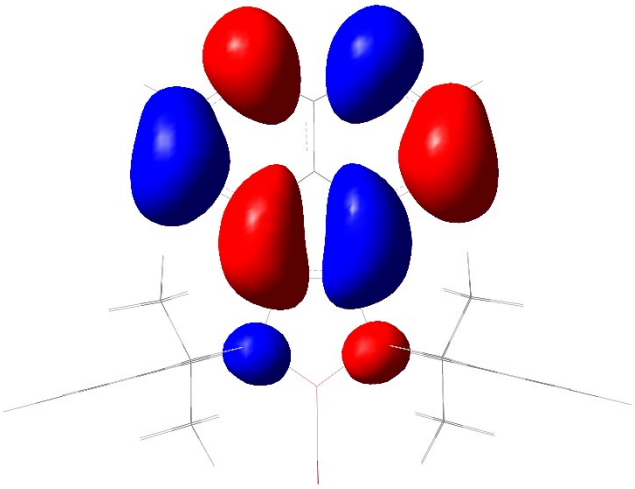

Figure S17. Plot of SOMO of **[(dpp-bian)BBr]$^{\bullet-}$** at an isovalue of 0.02.

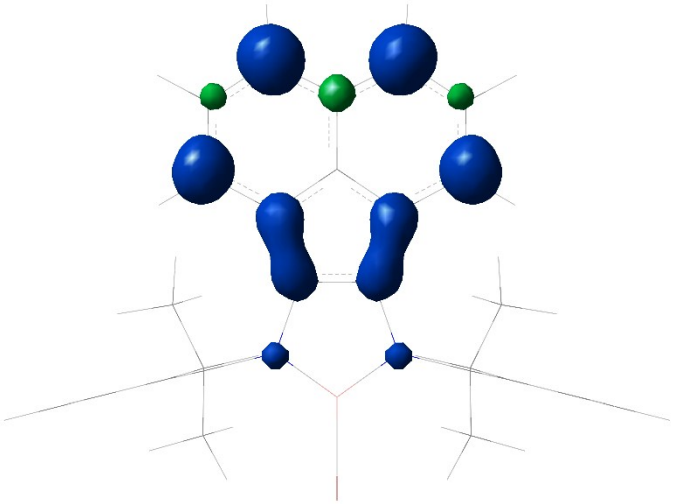

Figure S18. Plot of total spin density of **[(dpp-bian)BBr]$^{\bullet-}$** at an isovalue of 0.004.

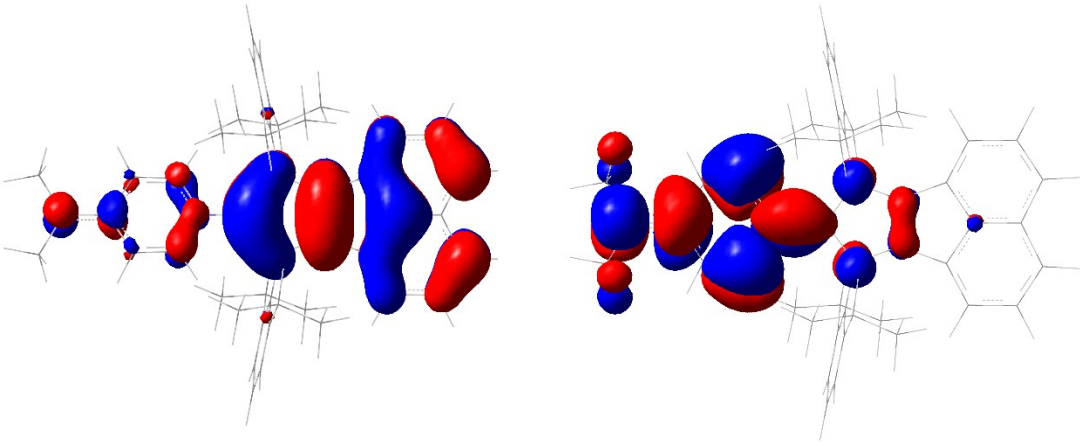

Figure S19. Plot of HOMO (left) and LUMO (right) of **5** at an isovalue of 0.02.

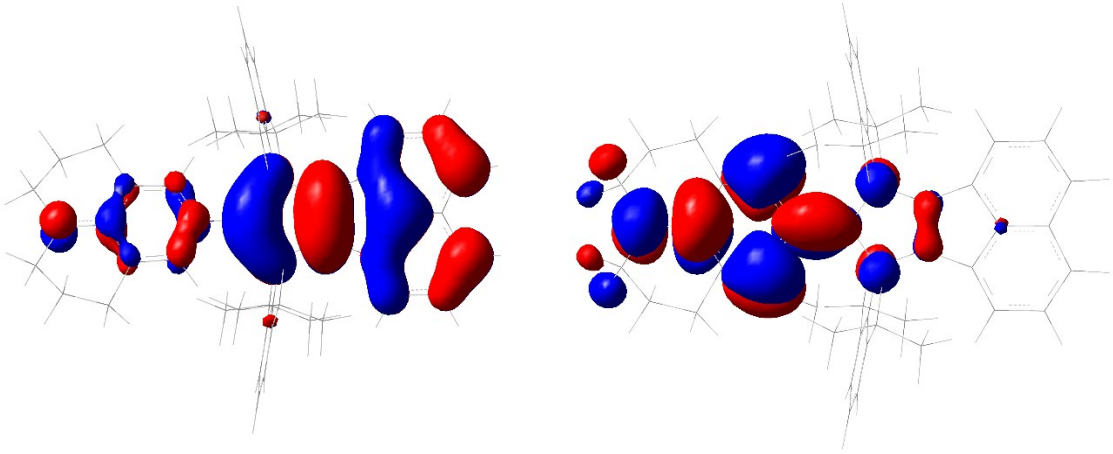

Figure S20. Plot of HOMO (left) and LUMO (right) of **6** at an isovalue of 0.02.

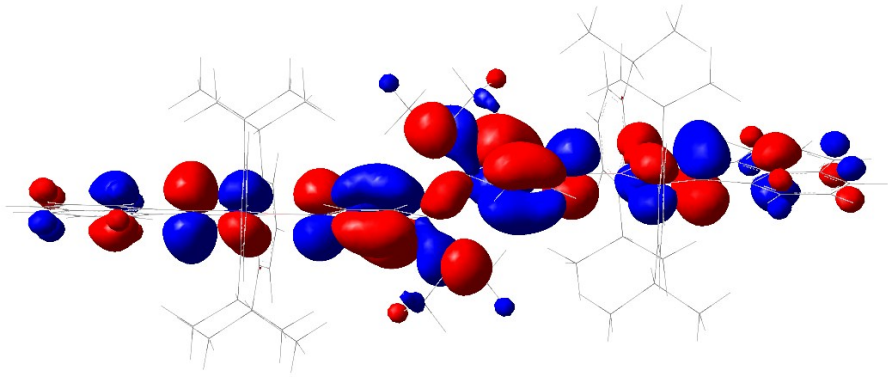

Figure S21. Plot of HOMO of **3** at an isovalue of 0.02.

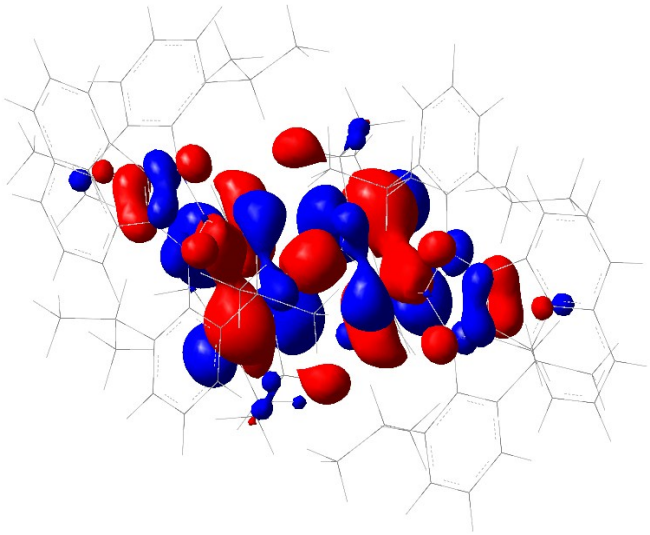

Figure S22. Plot of HOMO of **4** at an isovalue of 0.02.

Cartesian coordinates of all structures

[(dpp-bian)BBr]⁻: E = –4104.96863192

Br	0.00000	-3.12959	0.00021
N	-1.16454	-0.33795	0.00003
N	1.16454	-0.33795	0.00006
C	-2.54091	-1.89781	3.42428
H	-3.56060	-2.18530	3.70155
H	-1.97854	-1.73738	4.34983
H	-2.08652	-2.73654	2.89138
C	-2.52661	-0.62162	2.56298
H	-1.48509	-0.38222	2.34624
C	-3.22910	-0.83099	1.22709
C	-2.55190	-0.67836	-0.00004

C	2.55189	-0.67836	0.00000
C	3.22896	-0.83097	-1.22720
C	4.58490	-1.17047	-1.20167
H	5.11938	-1.29670	-2.13734
C	5.26025	-1.34412	-0.00015
H	6.31300	-1.60850	-0.00021
C	-2.54045	-1.89814	-3.42423
H	-2.08621	-2.73685	-2.89118
H	-1.97789	-1.73783	-4.34970
H	-3.56010	-2.18559	-3.70167
C	-2.52621	-0.62188	-2.56304
H	-1.48472	-0.38252	-2.34616
C	-3.22893	-0.83110	-1.22724
C	0.69811	1.00426	-0.00009
C	-0.69811	1.00427	-0.00011
C	-1.19265	2.34636	-0.00002
C	0.00000	3.14577	0.00002
C	0.00001	4.55050	0.00006
C	-1.27783	5.18485	0.00008
H	-1.34112	6.26938	0.00012
C	-2.44765	4.41470	0.00004
H	-3.40759	4.92578	0.00006
C	-2.43919	3.01374	-0.00001
H	-3.37577	2.46612	-0.00004
C	1.27784	5.18484	0.00011
H	1.34114	6.26938	0.00015
C	2.44766	4.41470	0.00010
H	3.40760	4.92577	0.00014
C	2.43920	3.01374	0.00005

H	3.37578	2.46611	0.00004
C	1.19265	2.34635	0.00001
C	2.52629	-0.62163	-2.56300
H	1.48480	-0.38222	-2.34613
C	2.54048	-1.89785	-3.42426
H	3.56013	-2.18534	-3.70168
H	1.97797	-1.73745	-4.34974
H	2.08617	-2.73656	-2.89127
C	3.11823	0.57691	-3.32771
H	3.06065	1.48844	-2.72908
H	2.56325	0.74609	-4.25614
H	4.16728	0.40488	-3.59176
C	4.58500	-1.17063	1.20145
H	5.11955	-1.29697	2.13705
C	3.22906	-0.83113	1.22713
C	2.52652	-0.62188	2.56301
H	1.48500	-0.38252	2.34627
C	3.11850	0.57667	3.32768
H	4.16759	0.40469	3.59158
H	2.56363	0.74579	4.25620
H	3.06078	1.48822	2.72910
C	2.54087	-1.89811	3.42425
H	2.08655	-2.73684	2.89129
H	1.97846	-1.73776	4.34980
H	3.56057	-2.18556	3.70154
C	-4.58504	-1.17049	1.20140
H	-5.11962	-1.29672	2.13700
C	-5.26025	-1.34411	-0.00020
H	-6.31300	-1.60849	-0.00026

C	-4.58487	-1.17060	-1.20172
H	-5.11931	-1.29693	-2.13739
C	-3.11866	0.57693	3.32757
H	-3.06097	1.48846	2.72894
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C	-3.11807	0.57665	-3.32782
H	-4.16713	0.40466	-3.59188
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H	-3.06045	1.48821	-2.72924
B	0.00000	-1.16902	0.00013

3: E = –3826.17585145

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N	3.55023	-0.26474	0.26271
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C	-9.29713	0.49096	0.28922
C	-8.63795	-0.77051	0.41987
C	-7.22691	-0.45823	0.20338
C	-5.01950	3.40821	0.52669
C	9.29711	0.49111	-0.28934
C	5.92626	-2.53082	-0.34034
C	8.63797	-0.77038	-0.42001

C	-7.07505	0.87802	-0.03770
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N	0.00217	-1.05285	1.88603
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H	-5.23388	1.88174	1.99156
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C	-9.40961	-1.87995	0.69097
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H	-6.16382	-5.41783	-1.43034
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C	0.60327	-0.66660	0.55288
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H	3.13453	1.74410	0.73225
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H	-4.43522	5.41473	1.02395
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H	0.77241	1.53820	0.89589
C	-2.67313	0.78098	-0.58069

H	-3.13451	1.74413	-0.73232
C	-6.26691	-2.82297	-2.19399
H	-6.26734	-1.73394	-2.12822
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C	-1.34088	0.64649	-0.66321
H	-0.77240	1.53821	-0.89598
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H	-10.66146	4.03509	-0.14171
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H	6.26749	-1.73369	2.12819
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H	1.57744	0.34774	-1.80253
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H	5.86931	-6.36870	-0.82380
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H	11.41686	-2.59816	-1.04357
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H	-1.39950	-0.50902	3.33213
H	-1.57749	0.34765	1.80237
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C	5.01868	2.95169	-1.98169
H	5.23395	1.88196	-1.99161

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H	5.58109	-1.13819	-2.52617
C	-3.64320	3.15100	2.64482
H	-2.85300	2.64610	2.08459
H	-3.65117	2.74480	3.66040
H	-3.37992	4.21042	2.71597
C	0.96617	-1.52378	2.87636
H	1.54095	-2.36605	2.49610
H	0.41184	-1.86315	3.75592
H	1.67503	-0.74227	3.20554
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C	5.00966	4.32225	2.12615
H	5.00395	4.68620	3.14743
C	-4.27286	-2.44353	3.60132
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H	-4.15876	-1.74908	4.43898
H	-3.41437	-2.31738	2.93785
C	5.10253	-3.22751	3.11715
H	4.14288	-2.89701	2.71345
H	5.22778	-2.77684	4.10610
H	5.05544	-4.31231	3.25079
C	5.01940	3.40827	-0.52659
C	-6.96661	2.55349	-3.77883
H	-7.81806	2.62500	-3.09852
H	-7.22968	1.85320	-4.57704
H	-6.81519	3.53604	-4.23586
C	5.70033	2.07381	3.04411
H	5.91736	1.08559	2.63587
C	4.68986	4.73217	-0.22094

H	4.43500	5.41480	-1.02369
C	-4.52108	1.92017	-4.02330
H	-4.26930	2.87194	-4.50047
H	-4.77714	1.21069	-4.81566
H	-3.62601	1.55192	-3.51660
C	7.62126	-3.24459	2.79434
H	7.68651	-4.33022	2.91361
H	7.75456	-2.79431	3.78245
H	8.45234	-2.92395	2.16227
C	6.12667	3.65079	-2.79227
H	5.96495	4.73218	-2.83646
H	6.14096	3.27417	-3.81931
H	7.11125	3.47444	-2.35385
C	4.27288	-2.44398	-3.60126
H	4.23748	-3.45861	-4.00870
H	4.15869	-1.74960	-4.43897
H	3.41440	-2.31788	-2.93778
C	4.68342	5.18889	1.09082
H	4.42393	6.21969	1.30608
C	6.79737	-2.31693	-3.82806
H	7.73871	-2.07768	-3.32863
H	6.68360	-1.63846	-4.67869
H	6.87294	-3.33485	-4.22249
C	3.64309	3.15108	-2.64471
H	2.85299	2.64599	-2.08454
H	3.65111	2.74503	-3.66035
H	3.37966	4.21048	-2.71570
C	6.96637	2.55332	3.77901
H	7.81787	2.62505	3.09879

H	7.22945	1.85293	4.57714
H	6.81479	3.53577	4.23619
C	4.52088	1.91968	4.02313
H	4.26893	2.87137	4.50039
H	4.77690	1.21013	4.81542
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N	-5.98864	-1.10360	0.16220

4: E = –4135.94183559

N	4.04768	-0.32032	-0.92320
N	3.13396	-1.05148	1.11356
N	-1.93524	0.97534	0.07430
N	1.93530	0.97536	-0.07431
N	-1.14777	4.25808	-2.35956
N	-4.04775	-0.32006	0.92326
N	1.14786	4.25877	2.35863
C	4.79243	-1.38336	-0.40422
C	4.26797	-1.80355	0.78535
C	5.09654	-2.87019	1.34727
C	4.58634	0.42333	-2.04005
C	1.71977	-2.10474	2.84391
C	6.12339	-3.06568	0.37243
C	2.64886	-1.10945	2.47251
C	-0.49519	2.03989	-1.61872
C	-5.63510	1.34556	1.80782

C	-4.26811	-1.80352	-0.78507
C	-2.64882	-1.11002	-2.47223
C	-4.12477	0.16796	3.35148
C	-1.71968	-2.10542	-2.84319
C	-5.98106	-2.17159	0.73300
C	-1.98387	3.37535	-0.21955
C	-4.79262	-1.38306	0.40438
C	-3.21659	-0.24885	-3.44070
C	1.13284	3.21911	1.40546
C	5.63503	1.34521	-1.80794
C	5.98087	-2.17195	-0.73271
C	-1.13276	3.21868	-1.40610
C	-5.09667	-2.87027	-1.34680
C	-4.58634	0.42379	2.04000
C	1.98393	3.37545	0.21885
C	3.21659	-0.24783	3.44060
C	7.15319	-3.99401	0.49748
C	0.49526	2.04038	1.61839
C	4.12485	0.16727	-3.35151
C	-7.15337	-3.99387	-0.49686
C	-6.12356	-3.06553	-0.37196
B	-2.94306	-0.07300	-0.03132
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B	2.94308	-0.07300	0.03140
C	0.40799	-3.05472	-1.84416
H	0.78564	-2.05974	-1.60078
H	0.80800	-3.75810	-1.11034
H	0.81608	-3.33771	-2.81746
C	-1.61177	-4.53611	-2.09775

H	-1.17884	-5.21360	-1.35554
H	-2.69679	-4.61862	-2.03198
H	-1.30285	-4.88963	-3.08642
C	-4.04927	2.16242	-3.64645
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H	-3.11658	2.56956	-3.25511
H	-4.00321	2.18253	-4.73951
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H	-1.47415	-2.79998	-0.85311
C	-2.41064	4.75147	0.21685
H	-1.61332	5.21423	0.81620
H	-3.28856	4.69213	0.86686
C	-2.67347	5.64559	-0.99888
H	-2.86662	6.67712	-0.68807
H	-3.55401	5.29199	-1.54470
C	-1.46173	5.61425	-1.92437
H	-0.60039	6.08208	-1.41038
H	-1.65414	6.21115	-2.82111
C	-0.13951	4.18194	-3.40995
H	0.85434	4.46902	-3.02494
H	-0.40703	4.90580	-4.18587
C	-0.08058	2.77377	-3.99510
H	0.67189	2.73955	-4.78885

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C	-0.58344	0.95818	-0.56020
H	-0.47769	-0.00796	-1.06008
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C	-6.08037	3.09138	0.00748
H	-5.03432	3.39830	-0.01242
H	-6.49285	3.23940	-0.99493
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C	-7.70449	1.18687	0.34744
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H	-7.83208	0.13485	0.60520
C	-6.22582	1.61659	0.42510
H	-5.67558	1.01566	-0.29857
C	-3.72161	-2.28996	3.78030
H	-4.45384	-2.29357	4.59387
H	-4.22954	-2.59729	2.86662
H	-2.96179	-3.04199	4.01182
C	-2.23460	-0.60064	4.89917
H	-1.38543	-1.28551	4.94694
H	-1.84100	0.41692	4.89886
H	-2.81505	-0.74080	5.81614
C	-3.07253	-0.89691	3.64528
H	-2.39536	-0.92821	2.79004
C	5.68342	0.23148	3.62962

H	5.91750	-0.75739	3.23160
H	6.48616	0.91498	3.33700
H	5.68472	0.16440	4.72203
C	4.04949	2.16348	3.64566
H	4.85976	2.83446	3.34538
H	3.11671	2.57065	3.25453
H	4.00382	2.18385	4.73873
C	4.32497	0.74797	3.11237
H	4.39242	0.82205	2.02686
C	-0.40807	-3.05438	1.84561
H	-0.78581	-2.05949	1.60201
H	-0.80822	-3.75799	1.11207
H	-0.81597	-3.33708	2.81908
C	1.61173	-4.53567	2.09923
H	2.69673	-4.61825	2.03329
H	1.30295	-4.88890	3.08805
H	1.17865	-5.21338	1.35730
C	1.12854	-3.09420	1.84540
H	1.47386	-2.79989	0.85408
C	0.13956	4.18295	3.40902
H	0.40706	4.90708	4.18469
H	-0.85428	4.46990	3.02390
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H	0.60049	6.08250	1.40895
C	2.67355	5.64589	0.99754
H	3.55410	5.29244	1.54344
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H	1.84091	0.41591	-4.89863
H	2.81488	-0.74179	-5.81602
C	3.07274	-0.89775	-3.64518
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C	3.72198	-2.29072	-3.78023
H	4.45418	-2.29425	-4.59385
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C	6.08053	3.09131	-0.00791
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H	6.49306	3.23944	0.99447
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C	7.70431	1.18642	-0.34744
H	8.32635	1.77975	-1.02440
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H	7.83171	0.13433	-0.60502
C	6.22572	1.61641	-0.42525
H	5.67534	1.01572	0.29851
C	-6.90969	-2.24693	1.74910

H	-6.86087	-1.59737	2.61464
C	-7.96245	-3.20198	1.65140
H	-8.68498	-3.25283	2.45856
C	-8.09592	-4.05005	0.57326
H	-8.91642	-4.75847	0.53316
C	-7.16597	-4.77838	-1.68919
H	-7.94488	-5.51789	-1.84110
C	-6.19514	-4.58489	-2.64747
H	-6.22057	-5.17754	-3.55537
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C	-5.71219	1.80765	4.19063
H	-6.14269	2.34896	5.02612
C	-4.70121	0.88086	4.40773
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H	-3.22852	0.26865	-5.52439
C	-1.88014	-1.34812	-5.14647
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H	-0.64806	-2.96986	-4.49249
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H	8.68472	-3.25358	-2.45813

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H	7.94473	-5.51775	1.84202
C	6.19503	-4.58456	2.64826
H	6.22049	-5.17702	3.55629
C	5.14940	-3.62773	2.49801
H	4.42237	-3.50933	3.29187
C	1.35226	-2.20201	4.19032
H	0.64828	-2.96858	4.49361
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C	5.71213	1.80702	-4.19081
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C	4.70127	0.88009	-4.40783
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H	-2.15877	-1.97257	0.66373
C	-4.86707	0.00004	-0.00011
C	0.04482	-2.58233	-0.08736
C	1.64015	-0.68685	-0.02105
C	-0.16900	-3.18330	-1.34779
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H	-1.83600	-2.45917	3.03766
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H	-0.69209	-6.37553	-0.25650
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C	3.01399	-1.18666	-0.04968
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C	-0.09547	2.40211	2.65694
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C	-0.48499	5.31072	0.20940
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C	1.57006	3.26782	-3.11609
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C	4.43157	0.00002	-0.00003
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C	-2.05706	-0.68441	0.05485
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C	3.68869	-1.18684	-0.29076
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C	0.01428	-4.48868	1.59455
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H	-3.52761	3.33014	-0.31901
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H	1.21532	-3.32269	3.93002
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C	6.56733	1.18063	0.39504
H	7.44642	0.81984	0.93907
H	6.93178	1.68408	-0.51127

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