
Supporting Information

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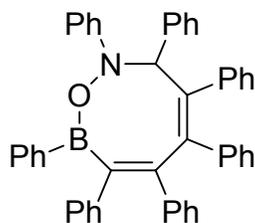
Experimental Section

General considerations

All syntheses were carried out with standard Schlenk and glovebox techniques under an argon atmosphere. Solvents were dried by distillation from suitable desiccants (toluene (Na), dichloromethane (P_2O_5), hexane and pentane (Na/K alloy)) under argon and were stored over molecular sieves. 1,2,3,4,5-pentaphenylborole^[1] and 1-mesityl-2,3,4,5-tetraphenylborole^[2] were synthesized according to published procedures. *N*, α -diphenylnitron and *N*-*tert*-butyl- α -phenylnitron were purchased from Acros Organics.

NMR spectra were recorded on a Bruker Avance 400 (1H : 400 MHz, ^{11}B : 128 MHz, $^{13}C\{^1H\}$: 101 MHz) and/or a Bruker Avance 500 FT-NMR spectrometer (1H : 500 MHz, ^{11}B : 160 MHz, $^{13}C\{^1H\}$: 126 MHz) at 296 K. Chemical shifts (δ) are given in ppm, and are referenced against external Me_4Si (1H , $^{13}C\{^1H\}$) and $BF_3 \cdot Et_2O$ (^{11}B). GC/MS analyses were performed on an Agilent Technologies GC/MS system (GC 7890A, EI-MS 5975C). Elemental analyses were obtained from an Elementar Vario MICRO cube instrument. UV/Vis absorption spectra were recorded on a JASCO V-660 UV/Vis spectrometer and the extinction coefficients were determined by serial dilution. Cyclic voltammetry experiments were performed using a Gamry Instruments Reference 600 potentiostat. EPR measurements at X-band (9.4 GHz) were carried out using a Bruker ELEXSYS E580 EPR spectrometer.

Synthesis of (4Z,6E)-2,3,4,5,6,7,8-heptaphenyl-3,8-dihydro-1,2,8-oxazaborocine (**5**)



To a solution of 1,2,3,4,5-pentaphenylborole (50.0 mg, 113.0 μmol) in toluene (1.0 mL) a solution of N, α -diphenylnitrone (22.2 mg, 113.0 μmol) was added dropwise at $-70\text{ }^{\circ}\text{C}$. Upon addition the colour changed from dark blue to dark red and gradually discoloured until the reaction reached $-40\text{ }^{\circ}\text{C}$. The reaction was slowly warmed to rt (3 h) and stirred overnight. Afterwards the solvent was removed *in vacuo*. The colourless residue was washed with hexane (2 mL) and **5** obtained as a colourless solid in good yields (43.6 mg, 68.0 μmol , 60%). Single crystals suitable for X-ray crystallography were obtained from a saturated solution of **5** in pentane.

$^1\text{H NMR}$ (500 MHz, CD_2Cl_2): δ = 8.28 – 8.24 (m, 2H, C_6H_5), 7.70 – 7.67 (m, 2H, C_6H_5), 7.66 – 7.62 (m, 1H, C_6H_5), 7.59 – 7.54 (m, 2H, C_6H_5), 7.39 – 7.32 (m, 3H, C_6H_5), 7.29 – 7.26 (m, 2H, C_6H_5), 7.16 – 7.11 (m, 5H, C_6H_5), 7.05 – 7.01 (m, 5H, C_6H_5), 7.01 – 6.97 (m, 2H, C_6H_5), 6.97 – 6.90 (m, 2H, C_6H_5), 6.90 – 6.85 (m, 2H, C_6H_5), 6.79 – 6.72 (m, 5H, C_6H_5), 6.46 – 6.42 (m, 2H, C_6H_5), 5.56 (s, 1H, ONBC₄CH) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CD_2Cl_2): δ = 151.36 (C, 1C, N- C_6H_5), 149.66 (C, 1C, ONBC₅), 145.12 (C, br, 1C, B-C ONBC₅), 145.04 (C, 1C, C_6H_5), 144.52 (C, 1C, C_6H_5), 144.24 (C, 1C, ONBC₅), 141.57 (C, 1C, C_6H_5), 140.37 (C, 1C, C_6H_5), 139.09 (C, 1C, ONBC₅), 138.98 (C, 1C, C_6H_5), 137.04 (CH, 2C, C_6H_5), 135.90 (C, br, 1C, B-C C_6H_5), 132.76 (CH, 1C, C_6H_5), 131.25 (CH, 2C, C_6H_5), 131.00 (CH, 2C, C_6H_5), 130.83 (CH, 2C, C_6H_5), 130.73 (CH, 2C, C_6H_5), 128.87 (CH, 2C, C_6H_5), 128.85 (CH, 2C, C_6H_6), 128.81 (CH, 2C, C_6H_5), 128.57 (CH, 2C, C_6H_5), 128.43 (CH, 2C, C_6H_5), 128.22 (CH, 2C, C_6H_6), 127.80 (CH, 1C, C_6H_5), 127.78 (CH, 2C, C_6H_5), 127.34 (CH, 2C, C_6H_5), 127.15 (CH, 1C, C_6H_5), 127.06 (CH, 1C,

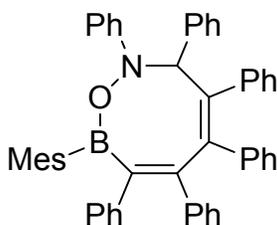
C₆H₅), 126.99 (CH, 1C, C₆H₅), 126.65 (CH, 1C, C₆H₅), 123.25 (CH, 1C, C₆H₅), 117.96 (CH, 2C, C₆H₅), 80.02 (CH, 1C, ONBC₄CH) ppm.

¹¹B NMR (160 MHz, CD₂Cl₂): δ = 47.4 ppm.

EI-MS: m/z = 641.3 [M⁺].

Anal. calcd. for C₄₇H₃₆BNO: C 87.98, H 5.66, N 2.18; found: C 88.04, H 5.56, N 2.18.

Synthesis of (4Z,6E)-8-mesityl-2,3,4,5,6,7-hexaphenyl-3,8-dihydro-1,2,8-oxazaborocine (**6**)



To a solution of 1-mesityl-2,3,4,5-tetraphenylborole-C₆H₆ (20.0 mg, 35.4 μmol) in toluene (0.5 mL) a solution of N,α-diphenylnitrone (6.99 mg, 35.4 μmol) in toluene (0.5 mL) was added dropwise at -60 °C. Upon addition a colour change from green to dark red and gradual discolouration until the reaction reached -45 °C was observed. Within 3 h, the reaction was slowly warmed to rt and stirred overnight. All volatile substances were removed in *vacuo*, the crude product was washed with hexane (0.5 mL) and dried under vacuum. **6** was isolated as a colourless solid (21.0 mg, 30.7 μmol, 87%). Single crystals suitable for X-ray crystallography were obtained from a saturated pentane solution of **6**.

¹H NMR (500 MHz, C₆D₆): δ = 7.72 – 7.69 (m, 2H, C₆H₅), 7.45 – 7.42 (m, 2H, C₆H₅), 7.41 – 7.38 (m, 2H, C₆H₅), 7.31 – 7.27 (m, 2H, C₆H₅), 7.20 – 7.16 (m, 2H, C₆H₅), 7.15 – 7.10 (m, 4H, C₆H₅), 7.05 – 7.00 (m, 1H, C₆H₅), 6.96 – 6.88 (m, 6H, C₆H₅), 6.87 – 6.82 (m, 4H, C₆H₅), 6.82– 6.77 (m, 3H,

$C_6H_2(CH_3)_3$, C_6H_5), 6.75 – 6.70 (m, 3H, C_6H_5), 6.30 – 6.59 (m, 1H, C_6H_5), 5.78 (s, 1H, ONBC₄CH), 2.45 (s, 6H, $C_6H_2(CH_3)_3$), 2.15 (s, 3H, $C_6H_2(CH_3)_3$) ppm.

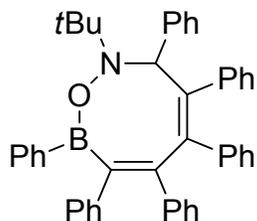
¹³C{¹H} NMR (126 MHz, C₆D₆): δ = 150.61 (C, 1C, N-C₆H₅), 145.73 (C, br, 1C, B-C ONBC₅), 144.80 (C, 1C, C₆H₅), 144.51 (C, 1C, ONBC₅), 143.45 (C, 1C, C₆H₅), 142.98 (C, 1C, ONBC₅), 142.52 (C, 2C C₆H₂(CH₃)₃), 141.88 (C, 1C, ONBC₅), 141.18 (C, 1C, C₆H₅), 141.00 (C, 1C, C₆H₅), 139.62 (C, 1C, C₆H₅), 139.27 (C, 1C, C₆₂(CH₃)₃), 134.33 (C, br, 1C, B-C C₆₂(CH₃)₃), 132.06 (CH, 2C, C₆H₅), 132.01 (CH, 2C, C₆H₅), 130.89 (CH, 2C, C₆H₅), 130.87 (CH, 2C, C₆H₅), 130.26 (CH, 2C, C₆H₅), 128.64 (CH, 2C, C₆H₅), 128.61 (CH, 4C, C₆H₂(CH₃)₃, C₆H₅), 128.40 (CH, 2C, C₆H₅), 128.35 (CH, 2C, C₆H₅), 128.05 (CH, 2C, C₆H₅), 127.64 (CH, 2C, C₆H₅), 127.16 (CH, 2C, C₆H₅), 126.80 (CH, 1C, C₆H₅), 126.69 (CH, 2C, C₆H₅), 126.32 (CH, 1C, C₆H₅), 125.05 (CH, 2C, C₆H₅), 82.35 (CH, 1C, ONBC₄CH), 24.07 (CH₃, 2C, C₆H₂(CH₃)₃), 21.34 (CH₃, 1C, C₆H₂(CH₃)₃) ppm.

¹¹B NMR (128 MHz, C₆D₆): δ = 48.5 ppm.

EI-MS: m/z = 683.4 [M⁺].

Anal. calcd. for C₅₀H₄₂BNO: C 87.84, H 6.19, N 2.05; found: C 88.43, H 6.23, N 1.95.

Synthesis of (4Z,6E)-2-(*tert*-butyl)-3,4,5,6,7,8-hexaphenyl-3,8-dihydro-1,2,8-oxazaborocine (**7**)



A solution of 1,2,3,4,5-pentaphenylborole (50.0 mg, 112.6 μmol) in toluene (1 mL) was cooled to –70 °C. A solution of *N-tert*-butyl- α -phenylnitron (19.9 mg, 112.6 μmol) in toluene (3 mL) was added dropwise while stirring. Upon addition the colour changed from blue to dark red and

gradually discoloured until the reaction reached $-40\text{ }^{\circ}\text{C}$. The reaction was warmed to rt within 3 h and stirred for additional 72 h. All volatile substances were removed in *vacuo*. The crude product was recrystallised from hexane to yield **7** as colourless crystals (58.0 mg, 93.3 μmol , 83%). Single crystals suitable for X-ray crystallography of **7** were obtained from a saturated hexane solution.

$^1\text{H NMR}$ (500 MHz, C_6D_6): $\delta = 8.46 - 8.45$ (m, 2H, C_6H_5), 8.29 – 8.26 (m, 1H, C_6H_5), 7.77 – 7.74 (m, 1H, C_6H_5), 7.61 – 7.58 (m, 2H, C_6H_5), 7.43 – 7.35 (m, 4H, C_6H_5), 7.29 – 7.23 (m, 3H, C_6H_5), 7.23 – 7.19 (m, 1H, C_6H_5), 7.02 – 6.89 (m, 7H, C_6H_5), 6.85 – 6.78 (m, 3H, C_6H_5), 6.75 – 6.71 (m, 1H, C_6H_5), 6.61 – 6.56 (m, 2H, C_6H_5), 6.55 – 6.52 (m, 2H, C_6H_5), 6.48 – 6.44 (m, 1H, C_6H_5), 5.66 (s, 1H, ONBC₄CH), 1.00 (s, 9H, *t*Bu) ppm.

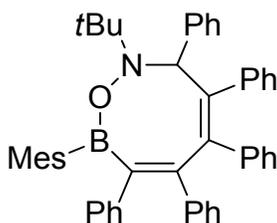
$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6): $\delta = 150.43$ (C, 1C, C_6H_5), 147.11 (C, 1C, ONBC₅), 145.88 (C, br, 1C, B-C ONBC₅), 145.69 (C, 1C, C_6H_5), 145.39 (C, 1C, ONBC₅), 145.25 (C, 1C, ONBC₅), 140.36 (C, 1C, C_6H_5), 139.44 (C, 1C, C_6H_5), 139.21 (C, 1C, C_6H_5), 137.87 (C, br, 1C, B-C C_6H_5), 136.72 (CH, 2C, C_6H_5), 132.11 (CH, 1C, C_6H_5), 131.42 (CH, 2C, C_6H_5), 131.24 (C, 4C, C_6H_5), 130.87 (CH, 2C, C_6H_5), 130.67 (CH, 1C, C_6H_5), 128.48 (CH, 2C, C_6H_5), 128.35 (CH, 1C, C_6H_5), 128.29 (CH, 2C, C_6H_5), 128.23 (CH, 2C, C_6H_5), 128.20 (CH, 1C, C_6H_5), 127.85 (CH, 2C, C_6H_5), 127.58 (CH, 1C, C_6H_5), 127.41 (CH, 2C, C_6H_5), 127.27 (CH, 1C, C_6H_5), 127.14 (CH, 1C, C_6H_5), 126.83 (CH, 2C, C_6H_5), 126.55 (CH, 1C, C_6H_5), 72.95 (CH, 1C, ONBC₄CH), 61.32 (C, 1C, *t*Bu), 26.15 (CH₃, 3C, *t*Bu) ppm.

$^{11}\text{B NMR}$ (128 MHz, C_6D_6): $\delta = 44.9$ ppm.

EI-MS: $m/z = 621.3$ [$\text{M}^+ - t\text{Bu}$].

Anal. calcd. for $\text{C}_{45}\text{H}_{40}\text{BNO}$: C 86.95, H 6.49, N 2.25; found: C 86.42, H 6.70, N 1.98.

Synthesis of (4Z,6E)-2-(*tert*-butyl)-8-mesityl-3,4,5,6,7-pentaphenyl-3,8-dihydro-1,2,8-oxazaborocine (**8**)



A solution of *N-tert*-butyl- α -phenylnitrone (15.7 mg, 88.6 μ mol) in toluene (3 mL) was added to a green solution of 1-mesityl-2,3,4,5-tetraphenylborole (50.0 mg, 88.6 μ mol) in toluene (1 mL) at rt and the mixture was stirred for 11 d. All volatile substances were removed *in vacuo*. The off-white solid was recrystallised from a benzene/hexane solution and **8** was isolated as colourless crystals (45.0 mg, 67.8 μ mol, 76%). Single crystals of **8** suitable for X-ray crystallography were obtained from a saturated hexane solution.

Comment: By increasing the reaction temperature to 100 °C, the reaction time can be reduced to 3 h, but also leads to the formation of an unknown byproduct.

$^1\text{H NMR}$ (500 MHz, C_6D_6): δ = 7.71 – 7.68 (m, 2H, C_6H_5), 7.43 – 7.31 (m, 2H, C_6H_5), 7.29 – 7.25 (m, 2H, C_6H_5), 7.21 – 7.15 (m, 3H, C_6H_5), 7.04 – 7.00 (m, 2H, C_6H_5), 6.97 – 6.93 (m, 3H, C_6H_5), 6.91 (s, 2H, $\text{C}_6\text{H}_2(\text{CH}_3)_3$), 6.89 – 6.82 (m, 4H, C_6H_5), 6.79 – 6.75 (m, 4H, C_6H_5), 6.58 – 6.54 (m, 2H, C_6H_5), 6.52 – 6.48 (m, 1H, C_6H_5), 5.71 (s, 1H, ONBC₄CH), 2.90 (s, 6H, $\text{C}_6\text{H}_2(\text{CH}_3)_3$), 2.16 (s, 3H, $\text{C}_6\text{H}_2(\text{CH}_3)_3$), 1.01 (s, 9H, tBu) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6): δ = 148.51 (C, br, 1C, B-C ONBC₅), 148.02 (C, 1C, ONBC₅), 147.47 (C, 2C, $\text{C}_6\text{H}_2(\text{CH}_3)_3$), 147.45 (C, 1C, C_6H_5), 145.37 (C, 1C, ONBC₅), 144.59 (C, 1C, C_6H_5), 140.91 (C, 1C, $\text{C}_6\text{H}_2(\text{CH}_3)_3$), 140.82 (C, 1C, C_6H_5), 139.76 (C, 1C, ONBC₅), 139.74 (C, 1C, C_6H_5), 139.47 (C, 1C, C_6H_5), 131.89 (C, br, 1C, B-C $\text{C}_6\text{H}_2(\text{CH}_3)_3$), 131.10 (CH, 2C, C_6H_5), 131.01 (CH, 2C, C_6H_5), 130.96 (CH, 2C, $\text{C}_6\text{H}_2(\text{CH}_3)_3$), 130.86 (CH, 2C, C_6H_5), 130.38 (CH, 2C, C_6H_5), 128.40 (CH, 2C, C_6H_5), 128.35 (CH, 4C, C_6H_5), 128.21 (CH, 2C, C_6H_5), 127.82 (CH, 2C, C_6H_5), 127.29 (CH, 1C, C_6H_5), 127.26 (CH,

2C, C₆H₅), 127.06 (CH, 2C, C₆H₅), 126.64 (CH, 1C, C₆H₅), 126.28 (CH, 1C, C₆H₅), 73.63 (CH, 1C, ONBC₄CH), 61.40 (C, 1C, tBu), 27.17 (CH₃, 3C, tBu), 26.87 (CH₃, 2C, C₆H₂(CH₃)₃), 21.21 (CH₃, 1C, C₆H₂(CH₃)₃) ppm.

¹¹B NMR (128 MHz, C₆D₆): δ = 48.5 ppm.

EI-MS: m/z = 664.4 [M⁺-tBu].

Anal. calcd. for C₄₈H₄₆BNO: C 86.86, H 6.99, N 2.11; found: C 87.02, H 7.02, N 1.89.

Crystal structure determination

The crystal data of **5**, **6**, **7**, and **8** were collected on a BRUKER D8 QUEST diffractometer with a CMOS area detector and multi-layer mirror monochromated Mo_{Kα} radiation. The structures were solved using intrinsic phasing method (SHELXT), refined with the SHELXL program^[5] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factors calculations. All hydrogen atoms were assigned to idealized geometric positions.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-1408403 (**5**), CCDC-1408404 (**6**), CCDC-1408405 (**7**) and CCDC-1408406 (**8**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

Crystal data for **5**: C₄₇H₃₆BNO, $M_r = 641.58$, colourless plate, 0.161×0.142×0.058 mm³, monoclinic space group *C2/c*, $a = 19.192(4)$ Å, $b = 10.2930(17)$ Å, $c = 35.255(15)$ Å, $\beta = 96.30(3)^\circ$, $V = 6922(4)$ Å³, $Z = 8$, $\rho_{calcd} = 1.231$ g·cm⁻³, $\mu = 0.072$ mm⁻¹, $F(000) = 2704$, $T = 100(2)$ K, $R_1 = 0.0522$, $wR^2 = 0.1062$, 6962 independent reflections [$2\theta \leq 52.732^\circ$] and 451 parameters. One reflection with error/esd > 10 was omitted. The disagreement was caused by beamstop.

Crystal data for **6**: C₅₀H₄₂BNO, $M_r = 683.65$, colourless plate, 0.131×0.083×0.04 mm³, triclinic space group *P-1*, $a = 12.5924(9)$ Å, $b = 15.3654(11)$ Å, $c = 20.1748(12)$ Å, $\alpha = 103.700(2)^\circ$, $\beta = 92.293(2)^\circ$, $\gamma = 94.425(3)^\circ$, $V = 3774.4(4)$ Å³, $Z = 4$, $\rho_{calcd} = 1.203$ g·cm⁻³, $\mu = 0.070$ mm⁻¹, $F(000) = 1448$, $T = 100(2)$ K, $R_1 = 0.0819$, $wR^2 = 0.1184$, 15432 independent reflections [$2\theta \leq 52.744^\circ$] and 961 parameters. Two reflections with error/esd > 10 were omitted. The disagreement was caused by beamstop.

Crystal data for **7**: C₅₁H₄₆BNO, $M_r = 699.70$, colourless block, 0.197×0.151×0.117 mm³, monoclinic space group *P21/n*, $a = 13.873(6)$ Å, $b = 17.556(4)$ Å, $c = 16.244(10)$ Å, $\beta = 102.03(4)^\circ$, $V = 3869(3)$ Å³, $Z = 4$, $\rho_{calcd} = 1.201$ g·cm⁻³, $\mu = 0.070$ mm⁻¹, $F(000) = 1488$, $T = 100(2)$ K,

$R_1 = 0.0460$, $wR^2 = 0.0964$, 7856 independent reflections [$2\theta \leq 52.744^\circ$] and 490 parameters. Five reflections with error/esd > 10 were omitted. The disagreement was caused by beamstop.

Crystal data for **8**: $C_{48}H_{46}BNO$, $M_r = 663.67$, colourless plate, $0.20 \times 0.195 \times 0.055$ mm³, monoclinic space group $P21/c$, $a = 10.604(6)$ Å, $b = 32.490(8)$ Å, $c = 11.704(5)$ Å, $\beta = 114.40(4)^\circ$, $V = 3672(3)$ Å³, $Z = 4$, $\rho_{calcd} = 1.200$ g·cm⁻³, $\mu = 0.070$ mm⁻¹, $F(000) = 1416$, $T = 100(2)$ K, $R_1 = 0.0685$, $wR^2 = 0.1394$, 7460 independent reflections [$2\theta \leq 52.742^\circ$] and 466 parameters.

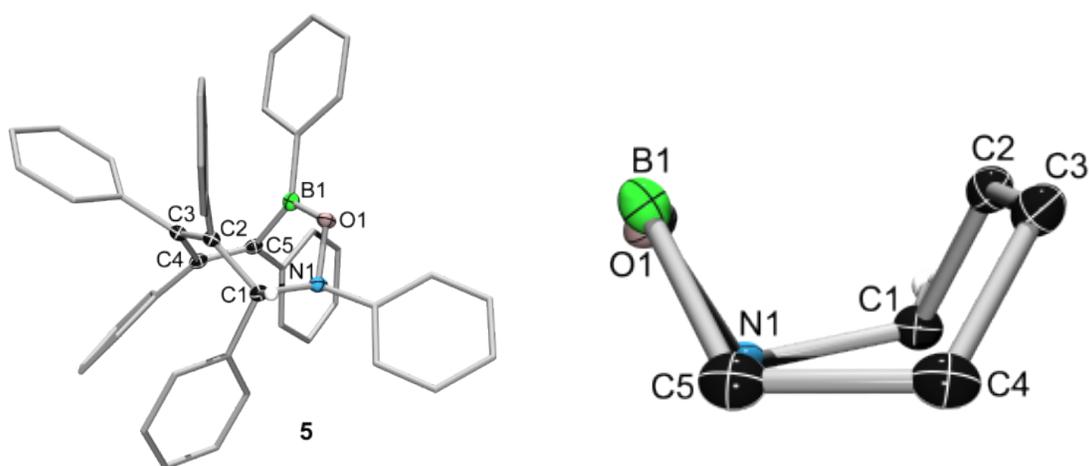


Figure S1: Molecular structures of **5** in the solid state. Hydrogen atoms are omitted for clarity (except for the hydrogen atom at C1). Ellipsoids are set at 50% probability. Selected bond lengths [Å] and angles [°] of **5**: O1–N1 1.444(1), N1–C1 1.503(2), C1–C2 1.537(2), C2–C3 1.359(2), C3–C4 1.501(2), C4–C5 1.356(2), C5–B1 1.578(2), B1–O1 1.371(2); B1–O1–N1 114.3(1), O1–N1–C1 109.4(1), N1–C1–C2 114.1(1), C1–C2–C3 122.8(1), C2–C3–C4 122.1(1), C3–C4–C5 115.0(1), C4–C5–B1 117.3(1), C5–B1–O1 121.5(1). Right side: Side view on the 8-membered ring adopting a boat-like structure.

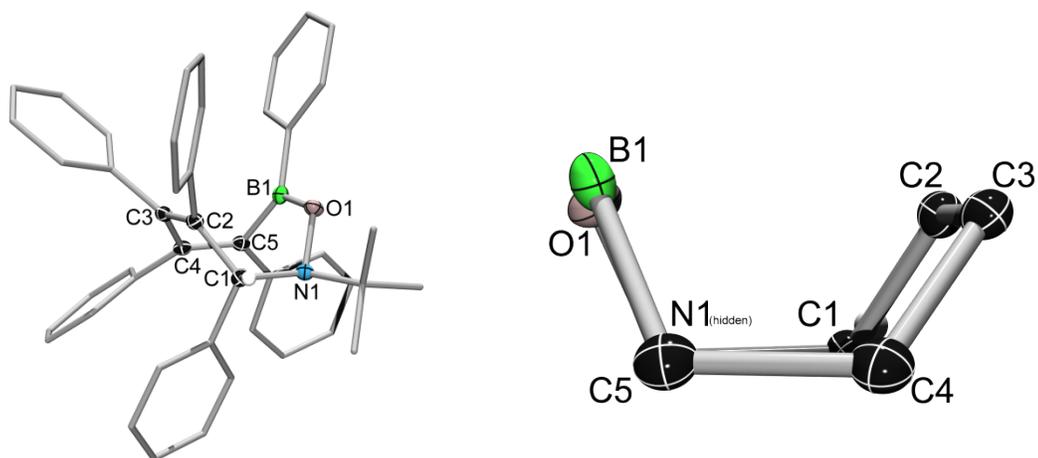


Figure S2: Solid-state structure of **7** as determined by single-crystal X-ray diffraction. Hydrogen atoms are omitted for clarity (except for the hydrogen atom at C1) and thermal ellipsoids are set at 50% probability. Selected bond lengths [\AA] and angles [$^\circ$] of **7**: O1–N1 1.458(1), N1–C1 1.508(2), C1–C2 1.538(2), C2–C3 1.359(2), C3–C4 1.496(2), C4–C5 1.360(2), C5–B1 1.583(2), B1–O1 1.359(2); B1–O1–N1 114.8(1), O1–N1–C1 109.7(1), N1–C1–C2 115.0(1), C1–C2–C3 124.6(1), C2–C3–C4 121.4(1), C3–C4–C5 115.8(1), C4–C5–B1 115.2(1), C5–B1–O1 122.9(1). Right side: Side view on the 8-membered ring adopting a boat-like structure.

Cyclic voltammetry

Cyclic voltammetry experiments were performed using a Gamry Instruments Reference 600 potentiostat. 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. All potentials are referenced to the ferrocene/ferrocenium redox couple ($\text{Fc}^{+/0}$) by either using ferrocene or decamethylferrocene ($E_{1/2} = -0.532$ V in CH_2Cl_2) as an internal standard. Tetra-*n*-butylammonium hexafluorophosphate ($[\text{n-Bu}_4\text{N}][\text{PF}_6]$) was employed as the supporting electrolyte. Compensation for resistive losses (iR drop) was employed for all measurements.

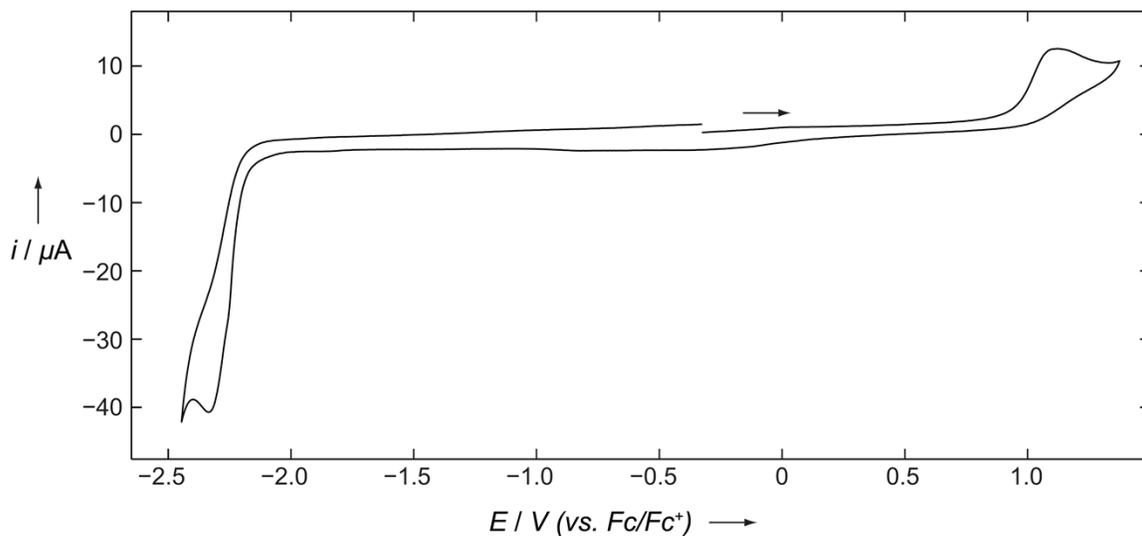


Figure S3. Experimental cyclic voltammetry curve of **3** in $\text{CH}_2\text{Cl}_2/0.1$ M $[\text{n-Bu}_4\text{N}][\text{PF}_6]$, scan rate 250 mV/s. Formal potentials: $E_{\text{pa}} = +1.13$ V and $E_{\text{pc}} = -2.33$ V.

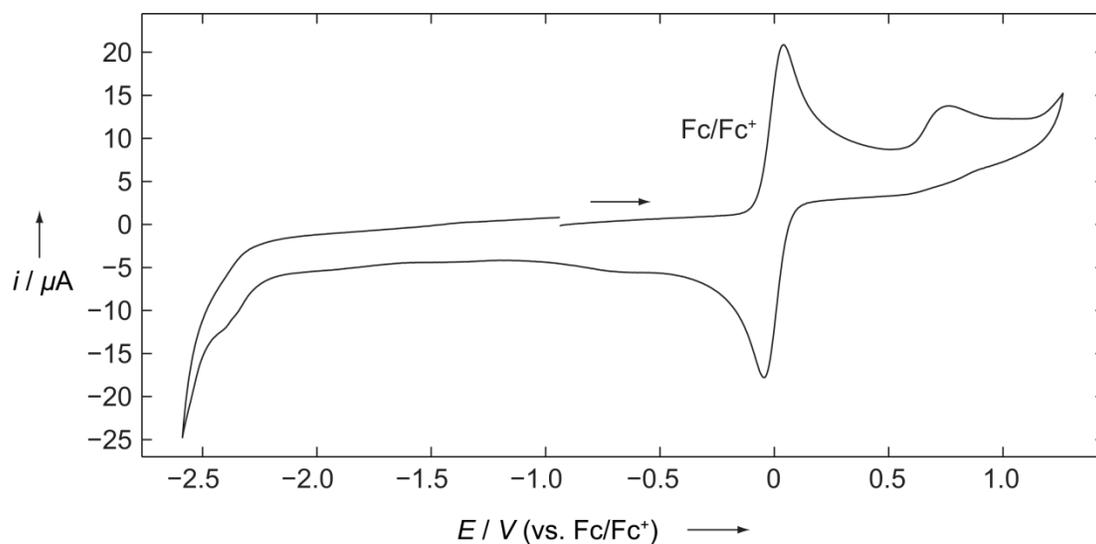


Figure S4. Experimental cyclic voltammetry curve of **5** in $\text{CH}_2\text{Cl}_2/0.1 \text{ M } [n\text{-Bu}_4\text{N}][\text{PF}_6]$ with ferrocene as internal standard, scan rate 250 mV/s. Formal potential: $E_{\text{pa}}(1) = +0.77 \text{ V}$ (in CH_2Cl_2), $E_{\text{pc}}(1) = -2.32 \text{ V}$, $E_{\text{pc}}(2) = -2.48 \text{ V}$ (in THF, not shown).

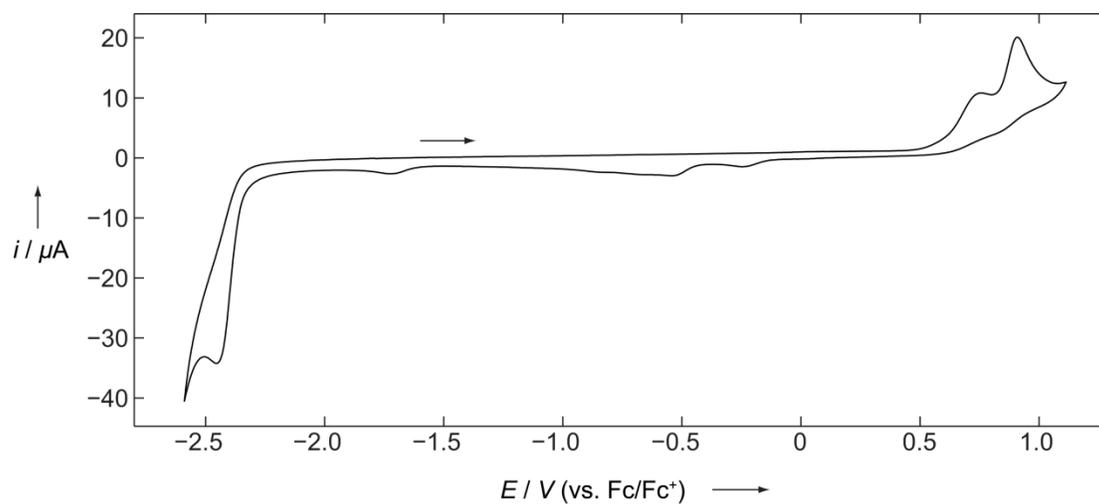


Figure S5. Cyclic voltammogram of **6** in $\text{CH}_2\text{Cl}_2/0.1 \text{ M } [n\text{-Bu}_4\text{N}][\text{PF}_6]$, scan rate 250 mV/s. Formal potentials: $E_{\text{pa}}(1) = +0.74 \text{ V}$, $E_{\text{pa}}(2) = +0.91 \text{ V}$, $E_{\text{pc}} = -2.45 \text{ V}$.

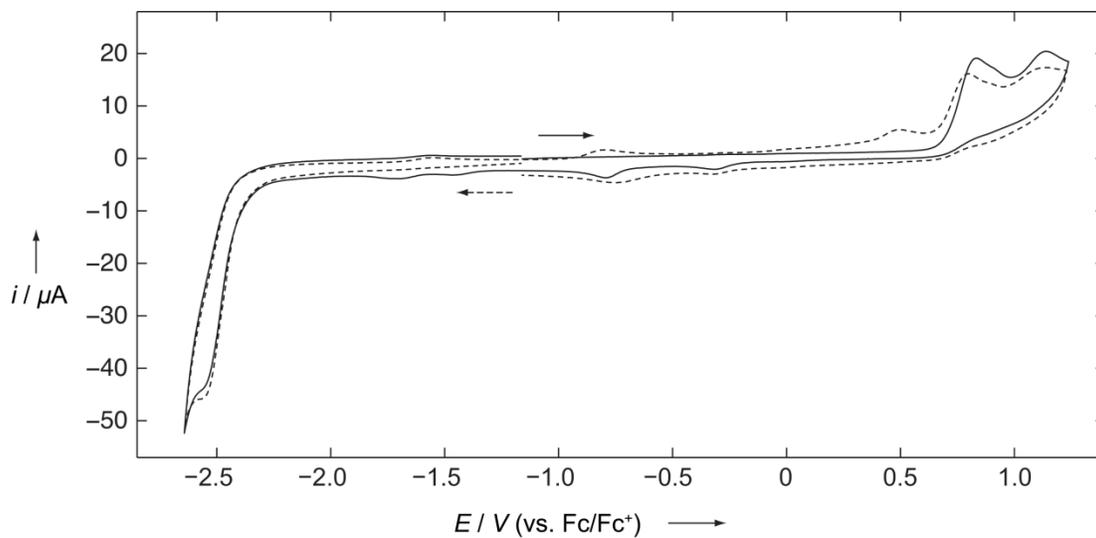


Figure S6. Experimental cyclic voltammetry curve of **7** in $\text{CH}_2\text{Cl}_2/0.1 \text{ M } [n\text{-Bu}_4\text{N}][\text{PF}_6]$, scan rate 250 mV/s. Formal potentials: $E_{pa}(1) = +0.83 \text{ V}$, $E_{pa}(2) = +1.12 \text{ V}$, $E_{pc} = -2.55 \text{ V}$.

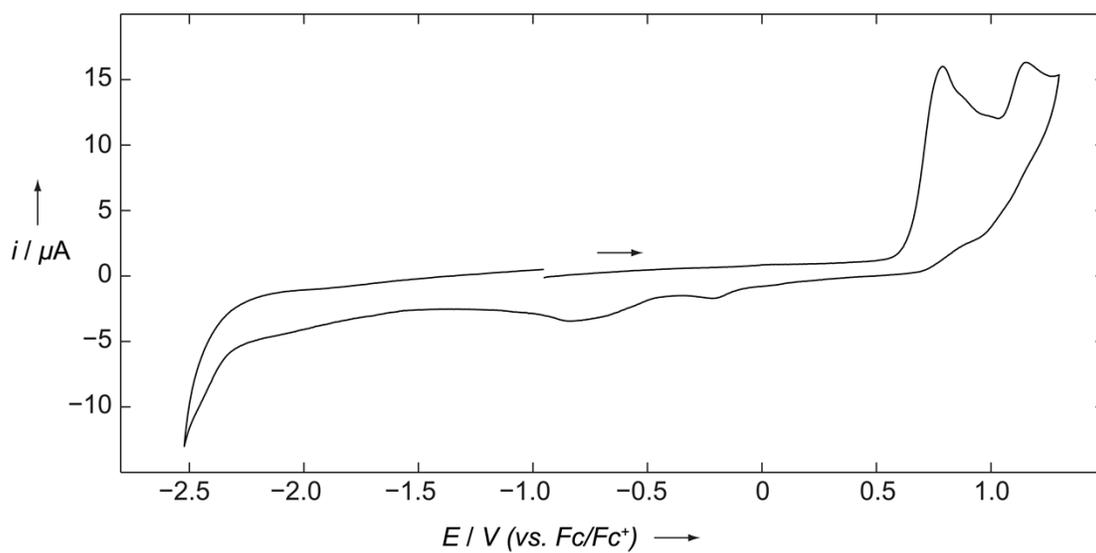


Figure S7. Experimental cyclic voltammetry curve of **8** in $\text{CH}_2\text{Cl}_2/0.1 \text{ M } [n\text{-Bu}_4\text{N}][\text{PF}_6]$, scan rate 250 mV/s. Formal potentials: $E_{pa}(1) = +0.75 \text{ V}$, $E_{pa}(2) = +0.92 \text{ V}$, $E_{pa}(3) = +1.15 \text{ V}$.

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