A Crystalline Radical Cation Derived from Thiele's Hydrocarbon with Redox Range Beyond 1 V

Ying Kai Loh,[a] Petra Vasko,[b] Caitilín McManus,[a] Andreas Heilmann,[a] William K Myers,[a] Simon Aldridge*[a]

[a] Inorganic Chemistry Laboratory, Dept of Chemistry, University of Oxford, South Parks Road, Oxford OX1 3QR, UK.
[b] Department of Chemistry, Nanoscience Center, University of Jyväskylä, P. O. Box 35, Jyväskylä, Finland FI-40014.
* simon.aldridge@chem.ox.ac.uk

Supplementary Information

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1. General considerations and starting material preparation

All manipulations were carried out using standard Schlenk line or dry-box techniques under an atmosphere of argon or dinitrogen. Solvents were degassed by sparging with argon and dried by passing through a column of the appropriate drying agent. NMR spectra were measured in benzene-d_6 (which was dried over potassium), with the solvent then being distilled under reduced pressure and stored under argon in Teflon valve ampoules. NMR samples were prepared under argon in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. ^{1}H, ^{13}C{^{1}H}, ^{11}B{^{1}H}, ^{19}F{^{1}H} NMR spectra were recorded on Bruker Avance III HD nanobay 400 MHz or Bruker Avance 500 MHz spectrometer at ambient temperature and referenced internally to residual protio-solvent (^{1}H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane (δ = 0 ppm). ^{19}F resonances are referenced externally to $CFCl_3$. Assignments were confirmed using two-dimensional ^{1}H-^{1}H and ^{13}C-^{1}H NMR correlation experiments. Chemical shifts are quoted in δ (ppm) and coupling constants in Hz. Elemental analyses were carried out by London Metropolitan University. $(HCDippN)_2BBr$ was prepared by the literature method (see below).[s1] All other reagents were used as received.

literature synthesis of $(HCDippN)_2BBr$: A mixture of *N*,*N*'-bis(diisopropylphenyl)-1,4-diazabutadiene (4.00 g, 10.6 mmol) and $Ph_3P{\cdot}BBr_3$ (5.45 g, 10.6 mmol) in diethyl (60 mL) was refluxed for 18 h. Solvents were removed in vacuo and the residue extracted with pentane (80 mL). After filtration, concentration of the filtrate in vacuo (to ca. 15 mL), and storage at –30 °C, $(HCDippN)_2BBr$ was obtained as yellow-orange crystals (70-75 %).

2. Synthetic, spectroscopic and analytical data

Preparation of (HCDippN)$_2$BOTf. To a mixture of (HCDippN)$_2$BBr (2.00 g, 4.28 mmol) and AgOTf (1.65 g, 6.42 mmol) was added $CHCl_3$ (3 mL) and stirred for 3 days at 60 ºC in an ampoule. To the suspension was added benzene (20 mL) and filtered. The filtrate was dried under vacuum to yield a solid covered in a tar-like substance. To this was added *n*-hexane (250 mL) and benzene (10 mL) to dislodge the tar-like substance and filtered. The filtrate was dried under vacuum to yield (HCDippN)$_2$BOTf (1.08 g, 47% yield) as a greyish-green powder. **^{1}H NMR** (400 MHz, C_6D_6, 297 K): δ = 1.16 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$), 1.33 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$), 3.16 (sept, $^3J_{HH}$ = 6.9 Hz, 4H, C*H*(CH$_3$)$_2$), 6.01 (s, 2H, NC*H*), 7.10−7.12 (m, 4H, Dipp-*m*-C*H*), 7.18−7.22 (m, 2H, Dipp-*p*-C*H*); **^{11}B{^{1}H} NMR** (128 MHz, C_6D_6): δ = 19.0; **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): δ = 22.5 (CH(*C*H$_3$)$_2$), 24.6 (CH(*C*H$_3$)$_2$), 29.1 (*C*H(CH$_3$)$_2$), 116.7 (N*C*H), 123.2 (Dipp-*m*-*C*H), 128.4 (Dipp-*p*-*C*H), 139.1 (Dipp-*i*-*C*), 148.1 (Dipp-*o*-*C*); **^{19}F{^{1}H} NMR** (377 MHz, C_6D_6): δ = −76.68. **Elemental analysis** calculated for $C_{27}H_{36}BF_3N_2O_3S$: C 60.45%, H 6.76%, N 5.22%, found: C 60.11%, H 6.55%, N 4.98%.

Preparation of (HCDippN)$_2$B(NC$_4$H$_4$C)C(NDippCH)$_2$ [1]. To a mixture of (HCDippN)$_2$BOTf (200 mg, 0.37 mmol) and (HCDippN)$_2$C (145 mg, 0.37 mmol) in benzene (1 mL) was added pyridine (0.1 mL, 1.24 mmol) and stirred for 5 min at room temperature to form a red solution. To the solution was added K[N(SiMe$_3$)$_2$] (75 mg, 0.38 mmol) at room temperature and stirred for 5 min at room temperature to form a deep red solution. Volatiles were removed under vacuum. To the residue was added benzene (5 mL) and the mixture filtered. The filtrate was dried under vacuum to yield **1** (264 mg, 83% yield) as an orange-red powder. **^{1}H NMR** (500 MHz, C_6D_6, 297 K): δ = 1.18 (t, $^3J_{HH}$ = 6.6 Hz, 24H, CH(C*H*$_3$)$_2$), 1.30 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$), 1.35 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$), 3.27 (sept, $^3J_{HH}$ = 6.9 Hz, 4H, C*H*(CH$_3$)$_2$), 3.38 (sept, $^3J_{HH}$ = 6.9 Hz, 4H, C*H*(CH$_3$)$_2$), 4.14 (d, $^3J_{HH}$ = 8.6 Hz, 2H, Py-C*H*), 4.81 (d, $^3J_{HH}$ = 8.6 Hz, 2H, Py-C*H*), 5.61 (s, 2H, NC*H*), 5.80 (s, 2H, NC*H*), 6.95 (d, $^3J_{HH}$ = 7.6 Hz, 4H, Dipp-*m*-C*H*), 7.01−7.08 (m, 8H, Dipp-C*H*); **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): δ = 23.3 (CH(*C*H$_3$)$_2$), 23.7 (CH(*C*H$_3$)$_2$), 24.5 (CH(*C*H$_3$)$_2$), 24.7 (CH(*C*H$_3$)$_2$), 28.7 (*C*H(CH$_3$)$_2$), 81.5 (Py-*p*-*C*), 107.6 (Py-*C*H), 117.3 (N*C*H), 118.5 (N*C*H), 121.1 (Py-*C*H), 123.6 (Dipp-*m*-*C*H), 123.9 (Dipp-*m*-*C*H), 127.6 (Dipp-*p*-*C*H), 128.7 (Dipp-*p*-*C*H), 132.4 (N*C*N), 137.7 (Dipp-*i*-*C*), 139.8 (Dipp-*i*-*C*), 146.3 (Dipp-*o*-*C*), 147.7 (Dipp-*o*-*C*); **^{11}B{^{1}H} NMR** (128 MHz, C_6D_6): δ = 19.9; **UV-vis** (CH_2Cl_2, λ_{max}): 342 nm (ε = 16284 $M^{-1}cm^{-1}$).

Preparation of (HCDippN)$_2$B(NC$_4$H$_4$C)C(NMesCH)$_2$ [2]. To a mixture of (HCDippN)$_2$BOTf (200 mg, 0.37 mmol) and (HCMesN)$_2$C (114 mg, 0.37 mmol) in benzene (1 mL) was added pyridine (0.1 mL, 1.24 mmol) and stirred for 5 min at room temperature to form a red solution. To the solution was added K[N(SiMe$_3$)$_2$] (75 mg, 0.38 mmol) at room temperature and stirred for 5 min at room temperature to form a deep red solution. Volatiles were removed under vacuum. To the residue was added *n*-hexane (25 mL) and the mixture filtered. The filtrate was dried under vacuum to yield **2** (159 mg, 56% yield) as an orange-red powder. Single crystals (yellow plates) suitable for X-ray crystallography were obtained by slow evaporation of a concentrated solution of **2** in *n*-pentane at room temperature. **^{1}H NMR** (500 MHz, C_6D_6, 297 K): δ = 1.20 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$), 1.29 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$), 2.07 (s, 6H, Mes-*p*-CC*H*$_3$), 2.21 (s, 12H, Mes-*o*-CC*H*$_3$), 3.32 (sept, $^3J_{HH}$ = 6.9 Hz, 4H, C*H*(CH$_3$)$_2$), 4.28 (d, $^3J_{HH}$ = 8.4 Hz, 2H, Py-C*H*), 4.92 (d, $^3J_{HH}$ = 8.4 Hz, 2H, Py-C*H*), 5.47 (s, 2H, NC*H*), 5.83 (s, 2H, NC*H*), 6.57 (s, 4H, Mes-*m*-C*H*), 6.99−7.01 (m, 4H, Dipp-C*H*), 7.05−7.08 (m, 2H, Dipp-C*H*); **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): δ = 18.4 (Mes-*o*-C*C*H$_3$), 21.0 (Mes-*p*-C*C*H$_3$), 23.6 (CH(*C*H$_3$)$_2$), 24.7 (CH(*C*H$_3$)$_2$), 28.7 (*C*H(CH$_3$)$_2$), 81.5 (Py-*p*-*C*), 107.6 (Py-*C*H), 116.3 (N*C*H), 118.4 (N*C*H), 121.4 (Py-*C*H), 123.6 (Dipp-*m*-*C*H), 127.6 (Dipp-*p*-*C*H), 129.3 (Mes-*m*-*C*H), 131.2 (N*C*N), 136.5 (Mes-*p*-*C*), 136.6 (Mes-*o*-*C*), 136.9 (Mes-*i*-*C*), 140.0 (Dipp-*i*-*C*), 146.3 (Dipp-*o*-*C*); **^{11}B{^{1}H} NMR** (128 MHz, C_6D_6): δ = 20.5; **Elemental analysis** calculated for $C_{52}H_{64}BN_5$: C 81.12%, H 8.38%, N 9.10%, found: C 80.91%, H 8.20%, N 8.89%.

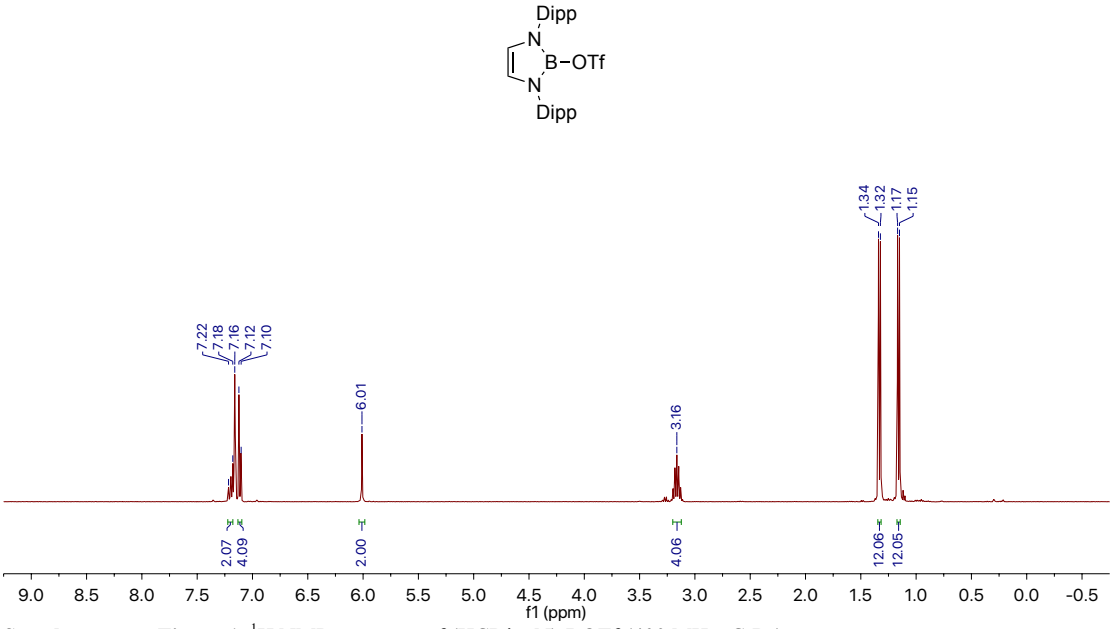
Preparation of [(HCDippN)$_2$B(NC$_4$H$_4$C)C(NDippCH)$_2$][SbF$_6$] [1][SbF$_6$]. To a mixture of **1** (300 mg, 0.35 mmol) and $AgSbF_6$ (121 mg, 0.35 mmol) was added CH_2Cl_2 (3 mL) and stirred for 5 min at room temperature to form a dark brown solution. The mixture was filtered and the filtrate was dried under vacuum to yield **[1][SbF$_6$]** (325 mg, 85% yield) as a

dark brown powder. Single crystals (brown rods and plates) suitable for X-ray crystallography were obtained by slow evaporation of a concentrated solution of **[1][SbF$_6$]** in fluorobenzene at room temperature. **X-band EPR** g = 2.0021 (1xB: −9.3 MHz; 1xN_{Py}: 8.8 MHz; 2xN_{IDipp}: 6.3 MHz; 2x$H_{Py\text{-}o\text{-}CH}$: −8.9 MHz); **UV-vis** (CH_2Cl_2, λ_{max}): 364 nm (ε = 13983 $M^{-1}cm^{-1}$), 442 nm (ε = 13682 $M^{-1}cm^{-1}$); **Elemental analysis** calculated for $C_{58}H_{76}BF_6N_5Sb$: C 63.92%, H 7.03%, N 6.43%, found: C 63.77%, H 7.13%, N 6.29%.

Preparation of [(HCDippN)$_2$B(NC$_4$H$_4$C)C(NDippCH)$_2$][SbF$_6$]$_2$ [1][SbF$_6$]$_2$. To a mixture of **1** (50 mg, 0.06 mmol) and $AgSbF_6$ (40 mg, 0.12 mmol) was added CH_2Cl_2 (2 mL) and stirred for 5 min at room temperature to form a deep purple solution. The mixture was filtered and the filtrate was dried under vacuum to yield **[1][SbF$_6$]$_2$** (43 mg, 56% yield) as a purple powder. Single crystals (purple rods) suitable for X-ray crystallography were obtained by slow evaporation of a concentrated solution of **[1][SbF$_6$]$_2$** in CH_2Cl_2at room temperature. **^{1}H NMR** (400 MHz, CD_2Cl_2, 297 K): δ = 0.85 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH(CH_3)$_2$), 0.91 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH(CH_3)$_2$), 1.17 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH(CH_3)$_2$), 1.22 (d, $^3J_{HH}$ = 6.7 Hz, 12H, CH(CH_3)$_2$), 2.21 (sept, $^3J_{HH}$ = 6.8 Hz, 4H, C*H*(CH$_3$)$_2$), 2.66 (sept, $^3J_{HH}$ = 6.8 Hz, 4H, C*H*(CH$_3$)$_2$), 6.56 (s, 2H, NC*H*), 7.14 (d, $^3J_{HH}$ = 7.2 Hz, 2H, Py-C*H*), 7.27 (d, $^3J_{HH}$ = 7.8 Hz, 4H, Dipp-*m*-C*H*), 7.38 (d, $^3J_{HH}$ = 7.9 Hz, 4H, Dipp-*m*-C*H*), 7.47 (t, $^3J_{HH}$ = 7.8 Hz, 2H, Dipp-*p*-C*H*), 7.69 (t, $^3J_{HH}$ = 7.9 Hz, 2H, Dipp-*p*-C*H*), 7.97 (d, $^3J_{HH}$ = 7.2 Hz, 2H, Py-C*H*), 8.03 (s, 2H, NC*H*); **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2): δ = 22.7 (CH(*C*H$_3$)$_2$), 23.4 (CH(*C*H$_3$)$_2$), 25.2 (CH(*C*H$_3$)$_2$), 25.5 (CH(*C*H$_3$)$_2$), 29.1 (*C*H(CH$_3$)$_2$), 29.9 (*C*H(CH$_3$)$_2$), 122.7 (N*C*H), 125.6 (Dipp-*m*-*C*H), 126.8 (Dipp-*m*-*C*H), 127.3 (Py-*C*H), 128.8 (Dipp-*i*-*C*), 130.1 (N*C*H), 130.6 (Dipp-*p*-*C*H), 133.4 (Dipp-*i*-*C*), 134.4 (Dipp-*p*-*C*H), 137.3 (Py-*p*-*C*), 137.4 (N*C*N), 144.7 (Dipp-*o*-*C*), 145.3 (Py-*C*H), 145.4 (Dipp-*o*-*C*); **^{11}B{^{1}H} NMR** (128 MHz, CD_2Cl_2): δ = 20.1; **UV-vis** (CH_2Cl_2, λ_{max}): 313 nm (ε = 8294 $M^{-1}cm^{-1}$), 537 nm (ε = 5756 $M^{-1}cm^{-1}$); **Elemental analysis** for $C_{58}H_{76}BF_{12}N_5Sb_2$: C 52.55%, H 5.78%, N 5.28%, found: C 52.63%, H 5.51%, N 5.30%.

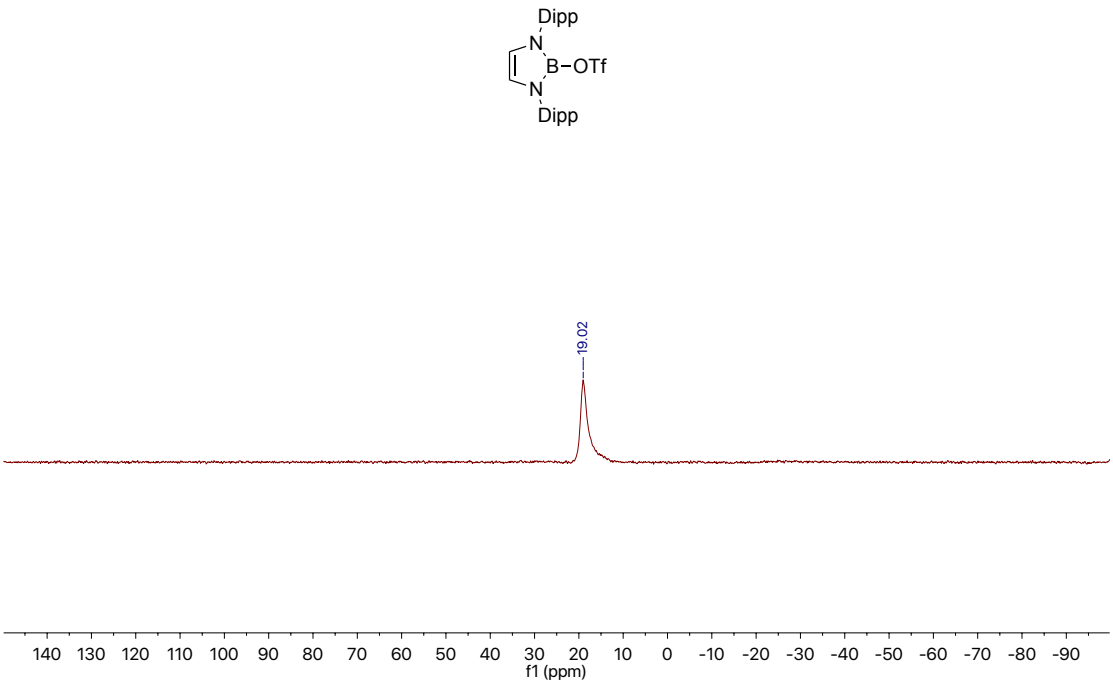
3. NMR spectra

(HCDippN)2BOTf



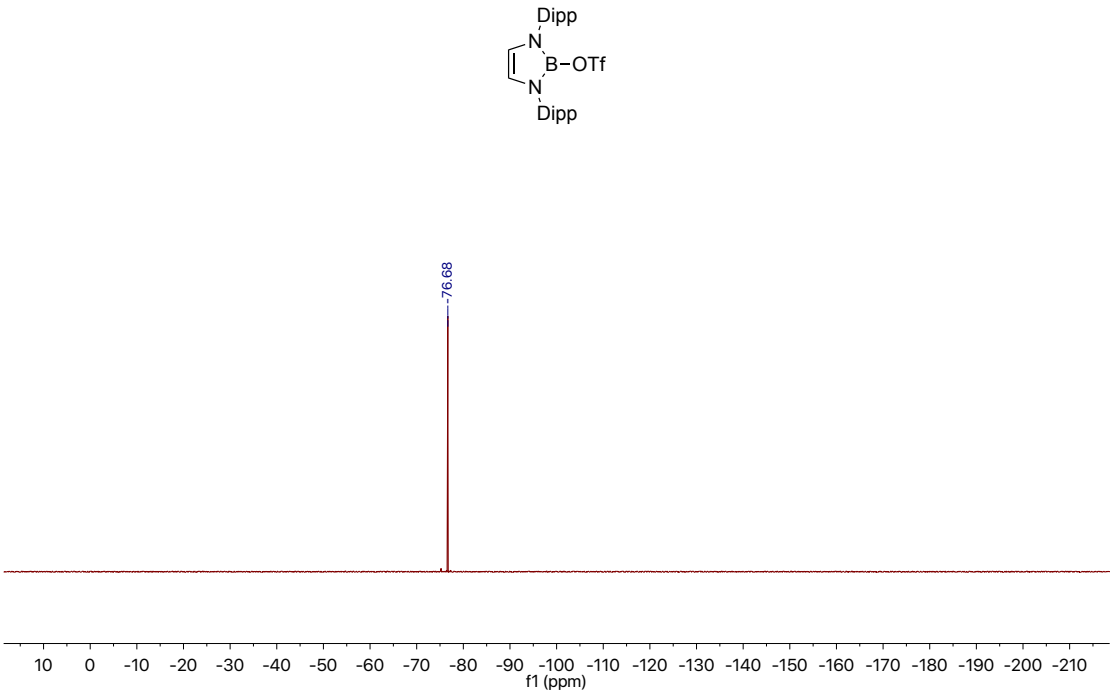
Supplementary Figure 1. ^{1}H NMR spectrum of $(HCDippN)_2BOTf$ (400 MHz, C_6D_6).

(HCDippN)2BOTf

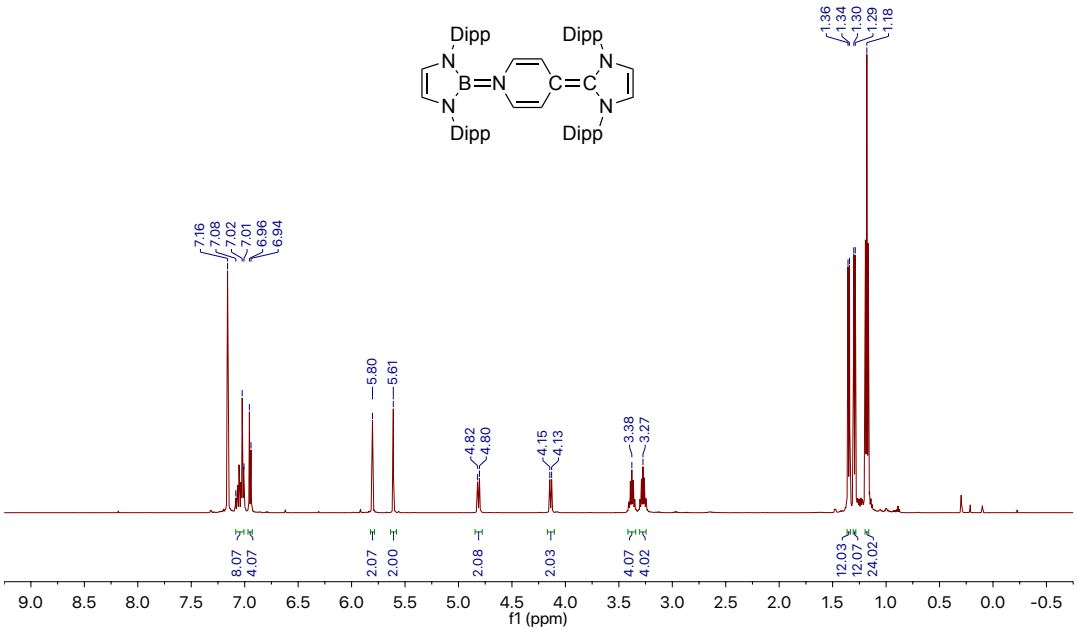


Supplementary Figure 2. $^{11}B\{^{1}H\}$ NMR spectrum of $(HCDippN)_2BOTf$ (128 MHz, C_6D_6).

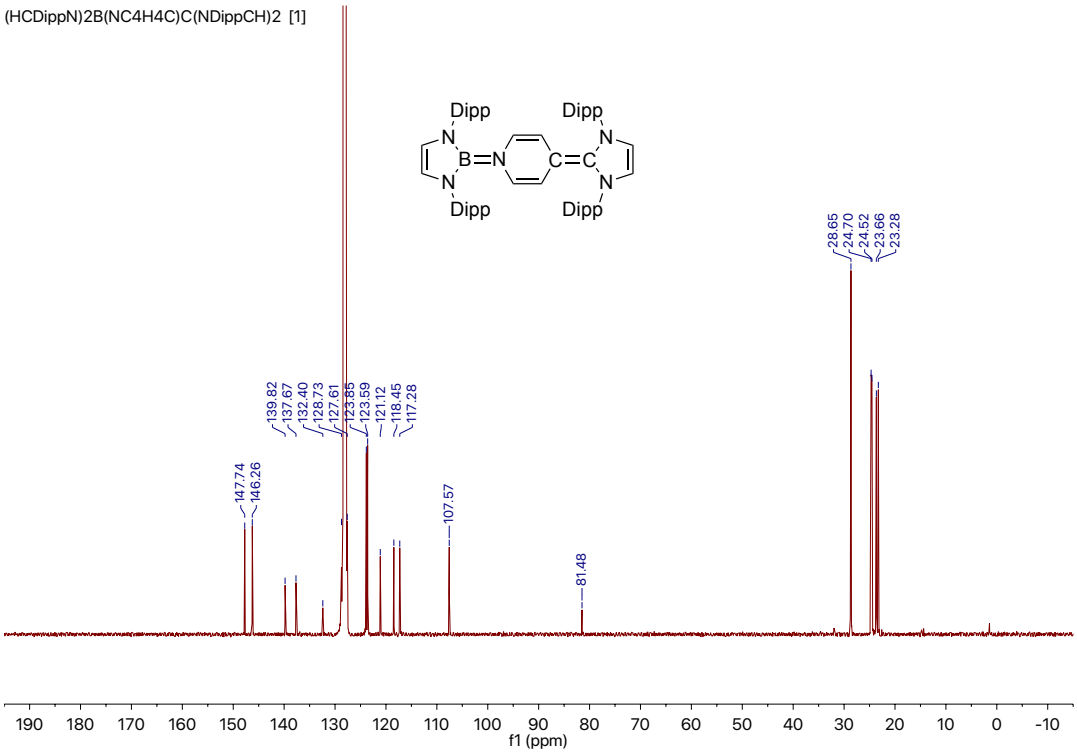
(HCDippN)2BOTf



Supplementary Figure 3. $^{19}F\{^{1}H\}$ NMR spectrum of $(HCDippN)_2BOTf$ (377 MHz, C_6D_6).

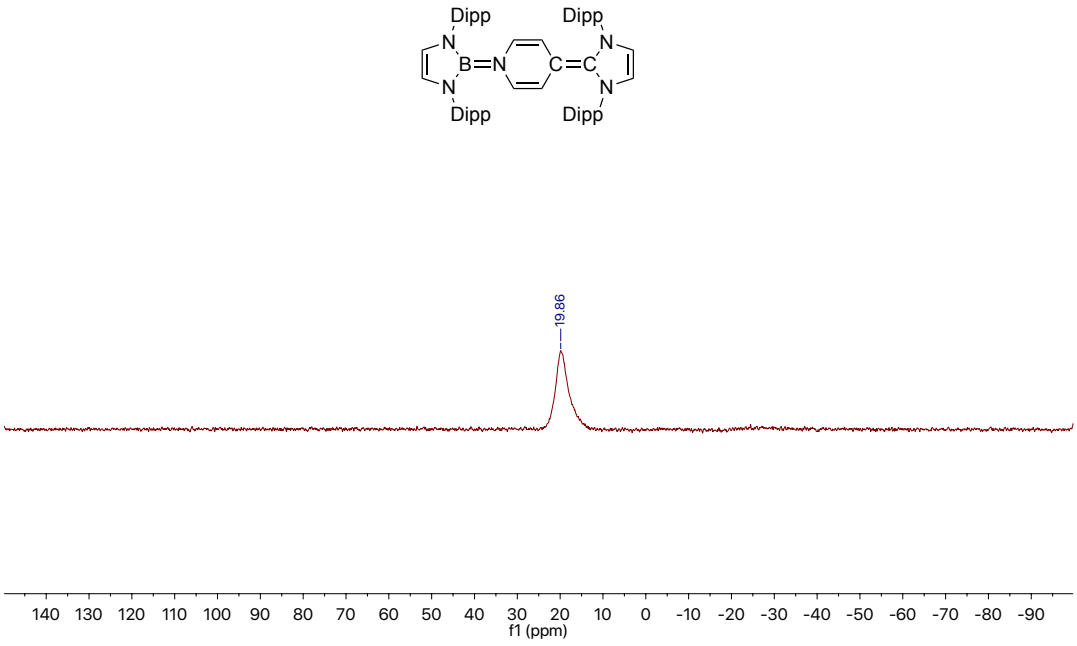


Supplementary Figure 4. ^{1}H NMR spectrum of **1** (500 MHz, C_6D_6).

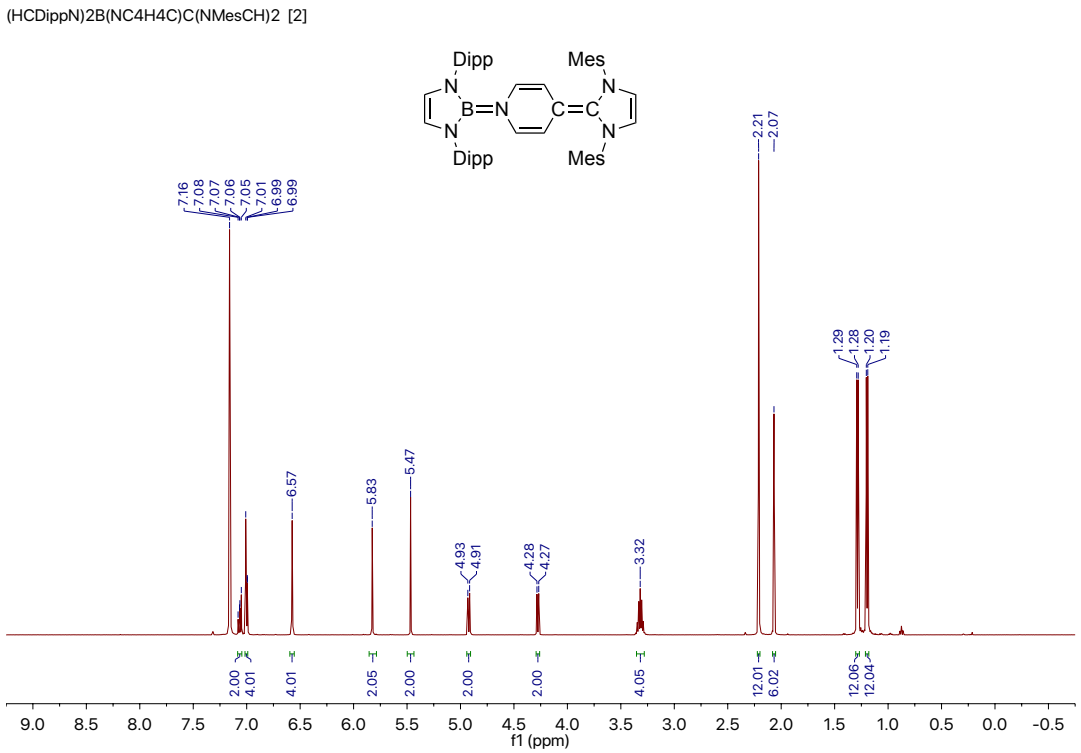


Supplementary Figure 5. ^{13}C{^{1}H} NMR spectrum of **1** (126 MHz, C_6D_6).

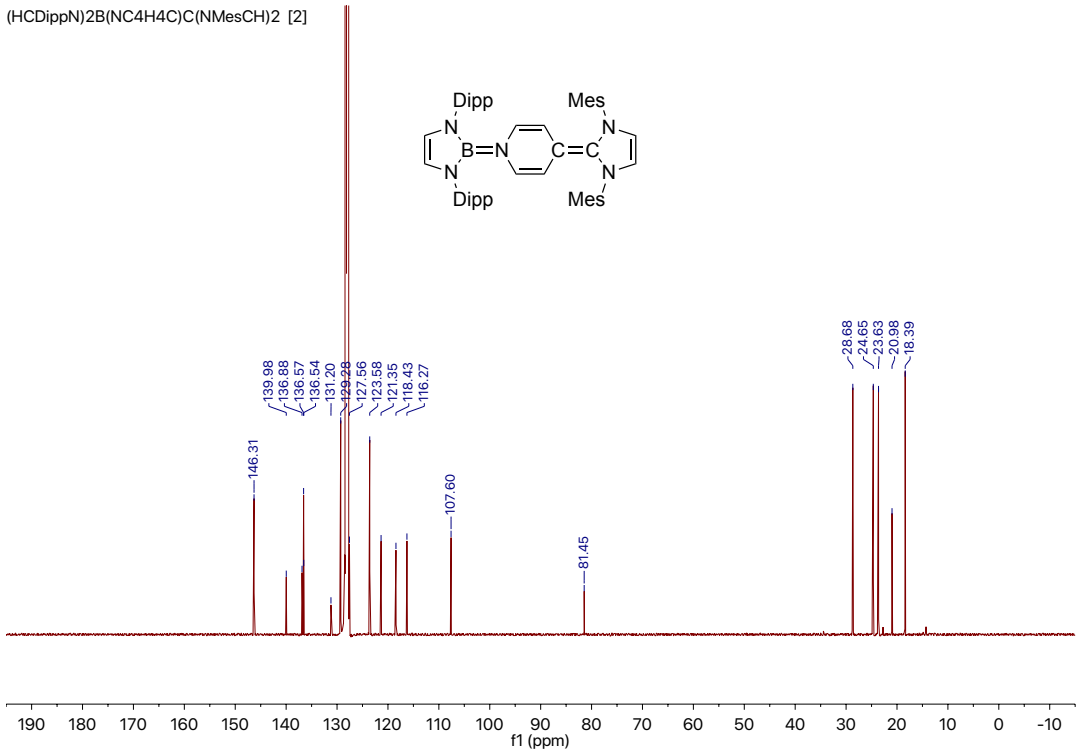
(HCDippN)2B(NC4H4C)C(NDippCH)2 [1]



Supplementary Figure 6. $^{11}B\{^{1}H\}$ NMR spectrum of **1** (128 MHz, C_6D_6).

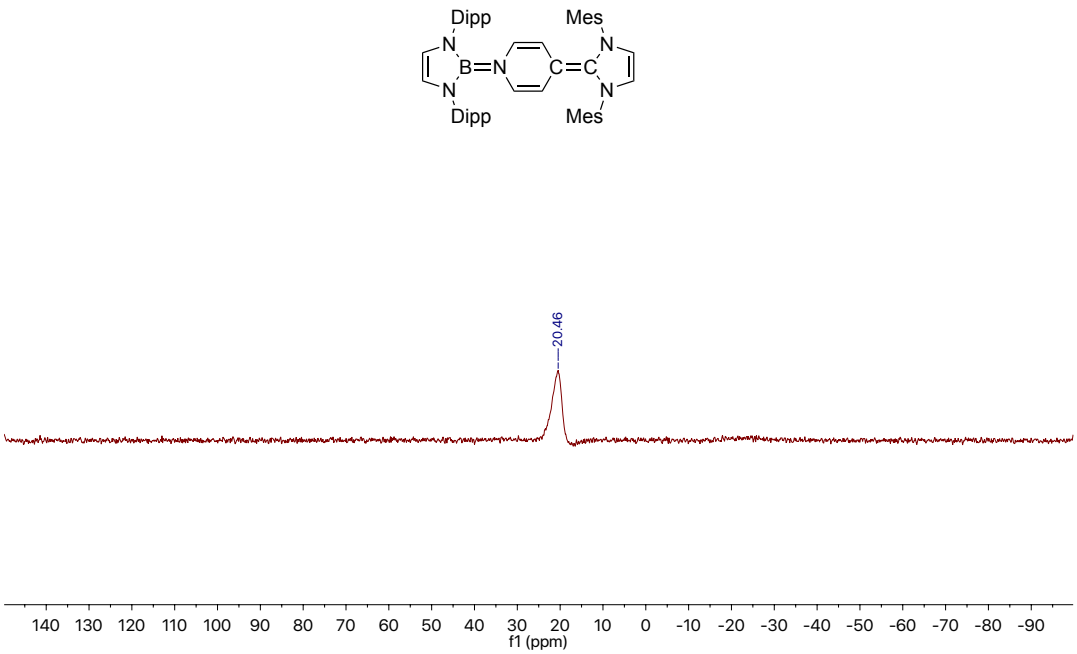


Supplementary Figure 7. ^{1}H NMR spectrum of **2** (500 MHz, C_6D_6).

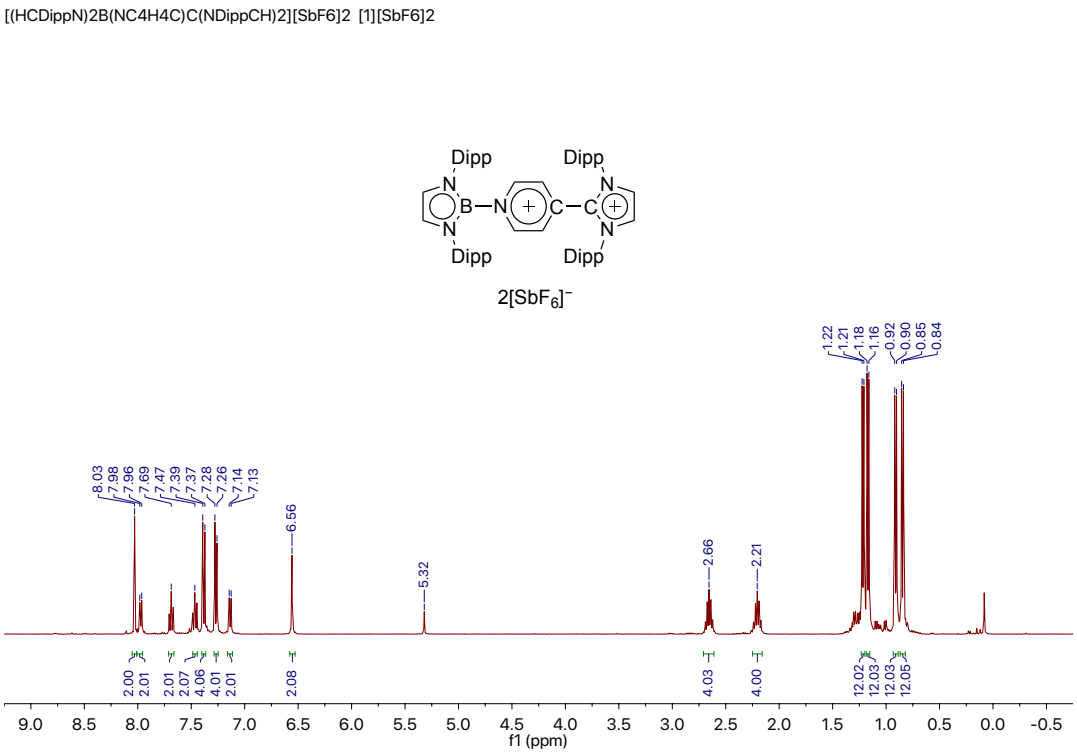


Supplementary Figure 8. ^{13}C{^{1}H} NMR spectrum of **2** (126 MHz, C_6D_6).

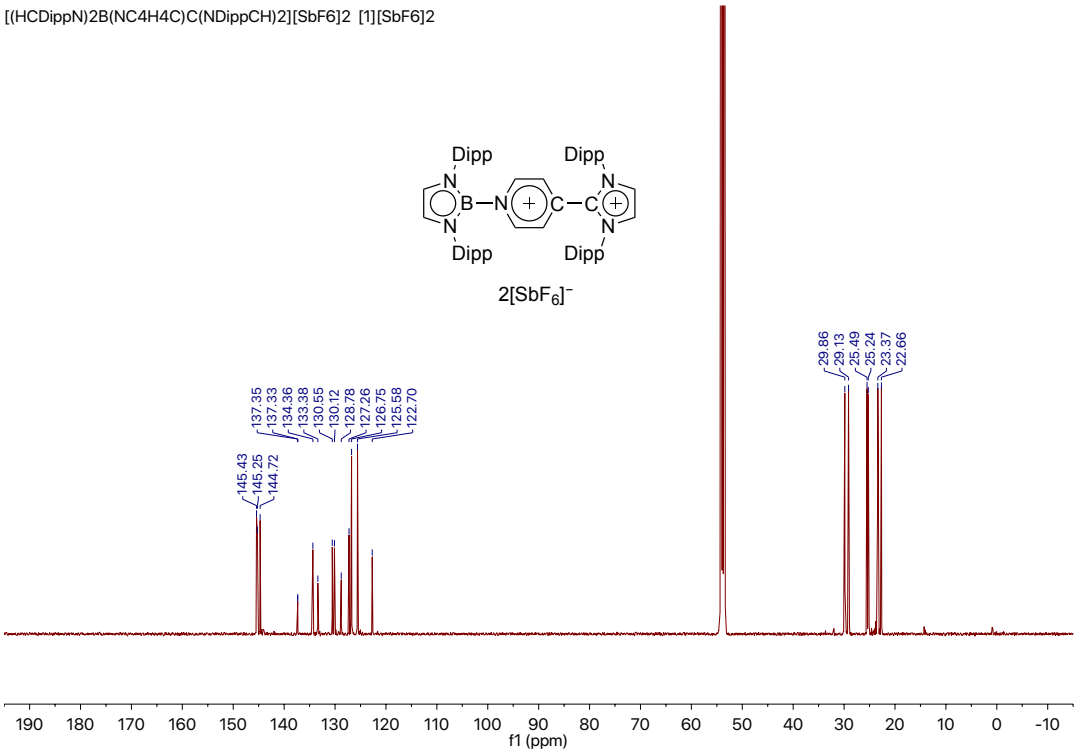
(HCDippN)2B(NC4H4C)C(NMesCH)2 [1]



Supplementary Figure 9. $^{11}B\{^{1}H\}$ NMR spectrum of **2** (128 MHz, C_6D_6).

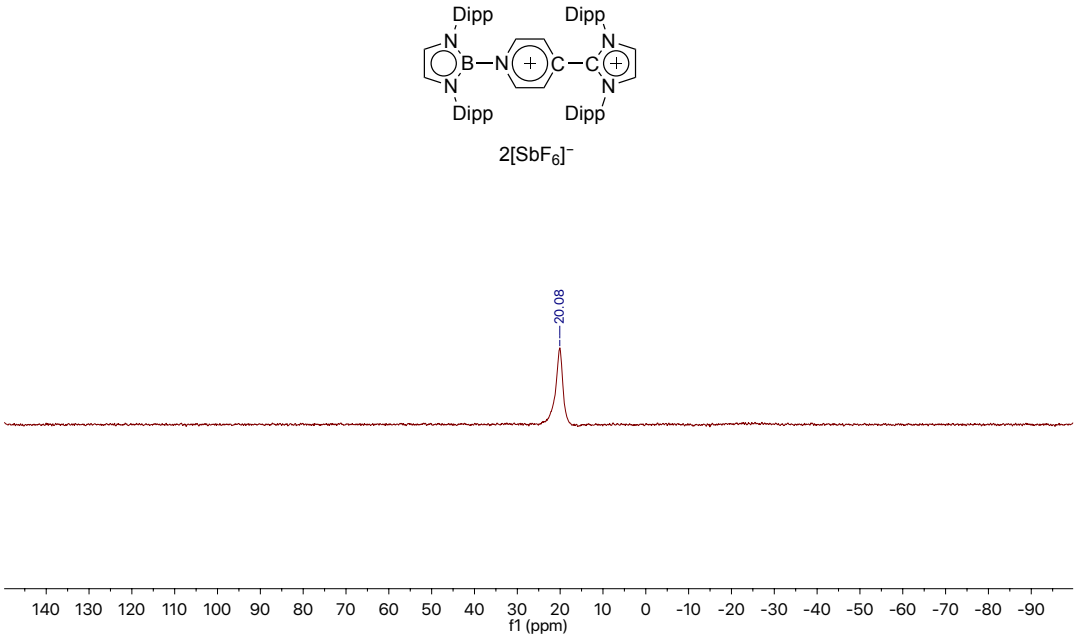


Supplementary Figure 10. ^{1}H NMR spectrum of **1[SbF$_6$]$_2$** (400 MHz, CD_2Cl_2).



Supplementary Figure 11. $^{13}C\{^{1}H\}$ NMR spectrum of **1[SbF$_6$]$_2$** (126 MHz, CD_2Cl_2).

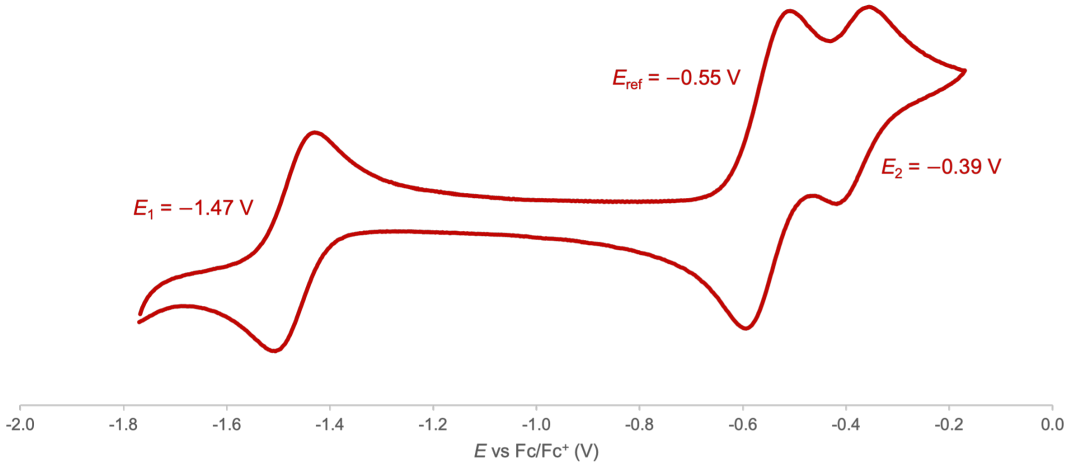
[(HCDippN)2B(NC4H4C)C(NDippCH)2][SbF6]2 [1][SbF6]2



Supplementary Figure 12. $^{11}B\{^{1}H\}$ NMR spectrum of **1[SbF$_6$]$_2$** (126 MHz, CD_2Cl_2).

4. Cyclic voltammetry studies

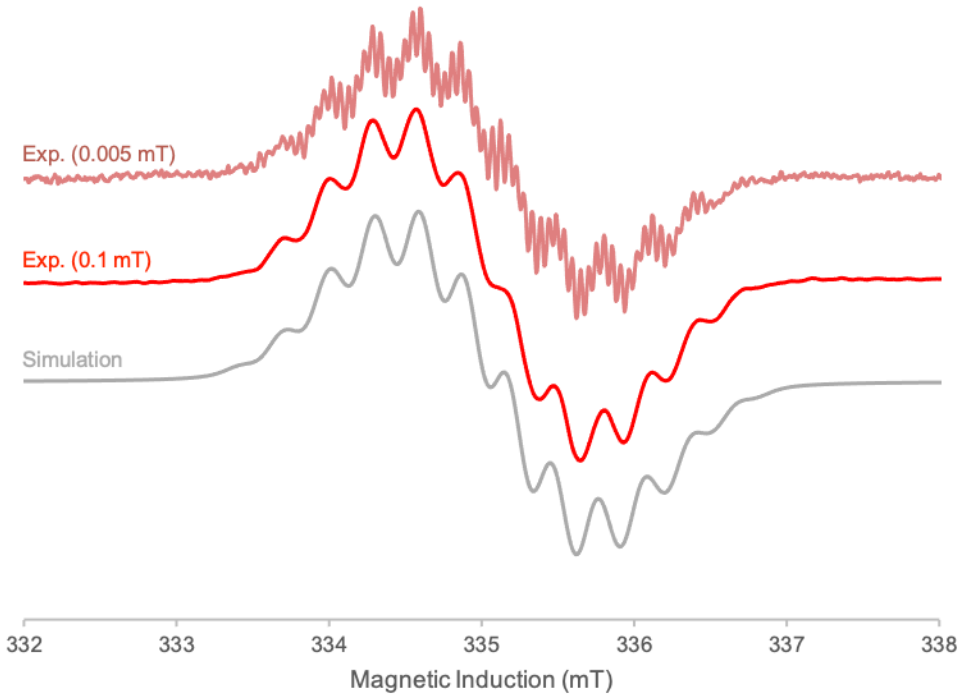
All electrochemical experiments were measured as freshly distilled dichloromethane solutions in the argon atmosphere glove box using the Gamry Instruments Reference 600 potentiostat. As the electrolyte 0.1 M $^{n}Bu_4N^{+}$ PF_6^{-} was used, the working, counter and reference electrodes were platinum and the voltammograms were internally referenced to decamethylferrocene. The scan rate is 100 mV s^{-1} and the voltammogram shown is from the second cycle of the measurements.



Supplementary Figure 13. Cyclic voltammagram of **1** in CH_2Cl_2, referenced internally with decamethylferrocene against Fc/Fc^{+}.

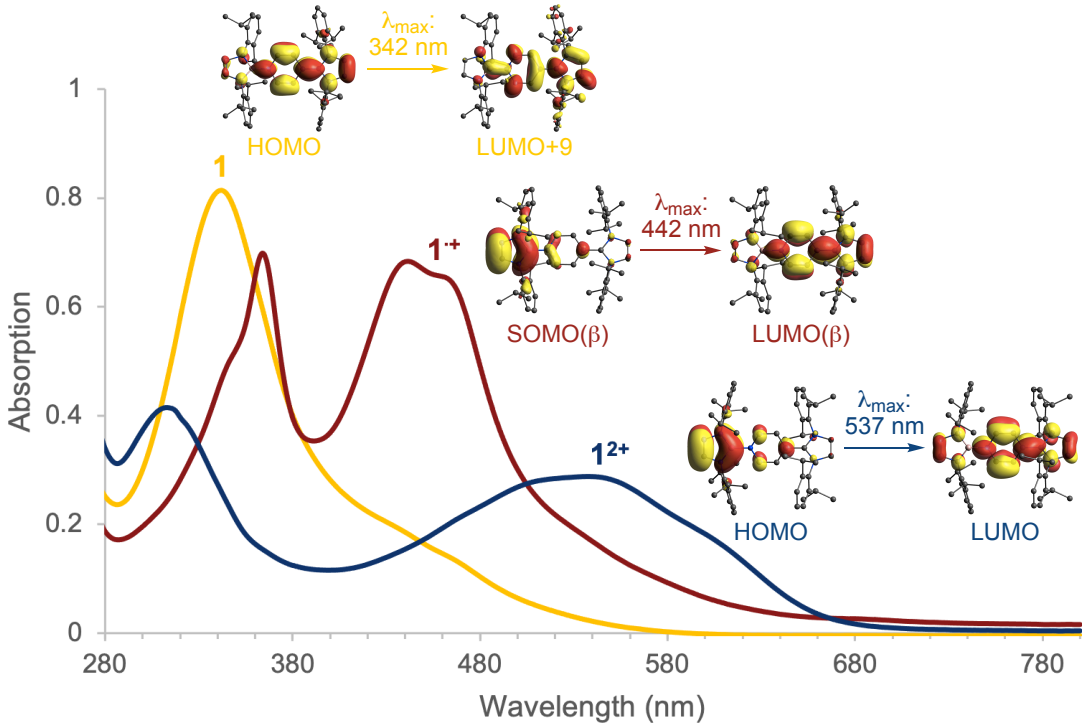
5. EPR studies

Continuous wave electron paramagnetic resonance (CW-EPR) was collected in the Centre for Advanced Electron Spin Resonance (CAESR) in the Department of Chemistry of the University of Oxford. The spectrometer was a Bruker BioSpin EMXmicro with a 6-inch magnet and ER4123-SHQE-W1 resonator at room temperature. Samples were held in 3.8 mm OD x 2.8 mm ID clear fused quartz tubes filled to 4 cm height with J. Young stable more than one day from glovebox transfer to measurement. Alternatively, samples were in filled in 1.6 mm OD x 1.2 mm ID x 10 cm tubes to 4 cm height and these were dropped into the J. Young tubes. EPR Spin quantitation used manufacturer hardware calibration that was previously found to be accurate within 10% of sample preparation. EPR simulations used the EasySpin package of routines written in MatLAB (The MathWorks, Natick, N.J.) program development environment.[2] DFT calculations were performed with the ORCA ab initio, DFT, and semi-empirical SCF-MO package[3,4] with geometry optimization starting from single crystal coordinates and subsequent EPR-NMR properties calculations. The functional was B3LYP and the basis set was EPR-II including a Def2 auxiliary basis.[5,6]



Supplementary Figure 14. X-band field-modulated CW-EPR absorption spectra (dχ''/dB) of **1[SbF$_6$]** (modulations 0.005 mT in salmon and 0.1 mT in red) in CH_2Cl_2 collected at 295 K and simulated EPR spectrum in grey**.** For the experiment, top spectrum of 0.005 mT modulation amplitude, the microwave frequency was 9.3903 GHz, a microwave power of 10 microWatts, a sweep rate was 7 mT per 600 seconds as the average of 20 sweeps with a time constant of 10.24 msec for 14000 points. For the experiment, middle spectrum of 0.1 mT modulation amplitude, the microwave frequency was 9.3903 GHz, the microwave power of 10 microWatts, the sweep rate was 7 mT per 120 seconds for one sweep with a time constant of 81.92 msec for 700 points. The simulation of $\mathbf{1}^{\cdot+}$, at bottom in grey, involves instrument parameter values and the largest isotropic values from DFT results (in MHz): H(C3) −8.8197, N(2) 6.2299, N(3) 6.514, H(C4) −8.9517, N(1) 8.8132, B(1) −9.2702, according to Scheme 3 labeling. Following the field correction of 0.085 mT, the calculated isotropic g-value was shifted by −0.001 to 2.0021 with a pseudo-Voigt lineshape of 0.175 mT used.

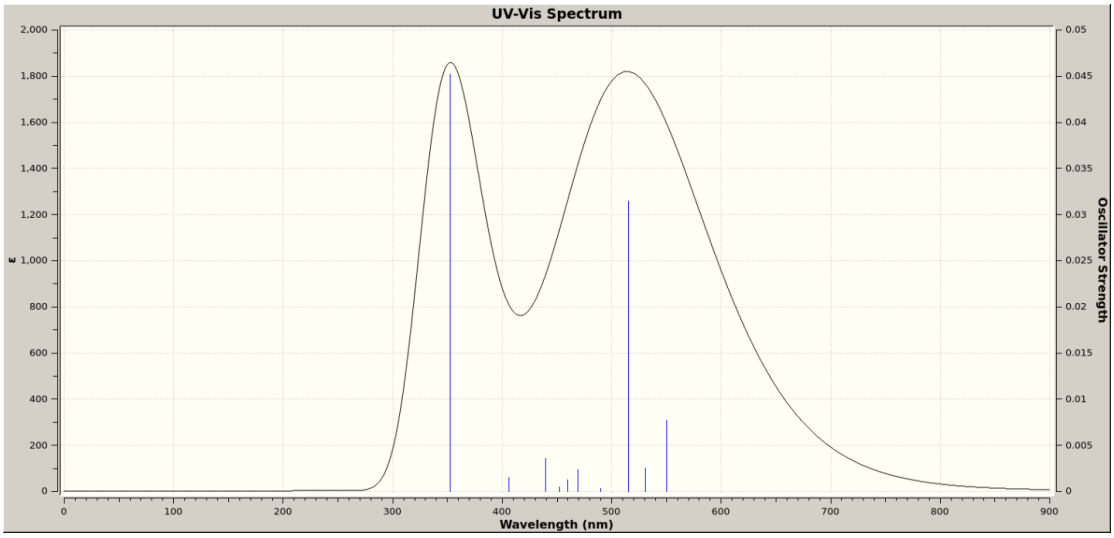
6. UV-vis studies



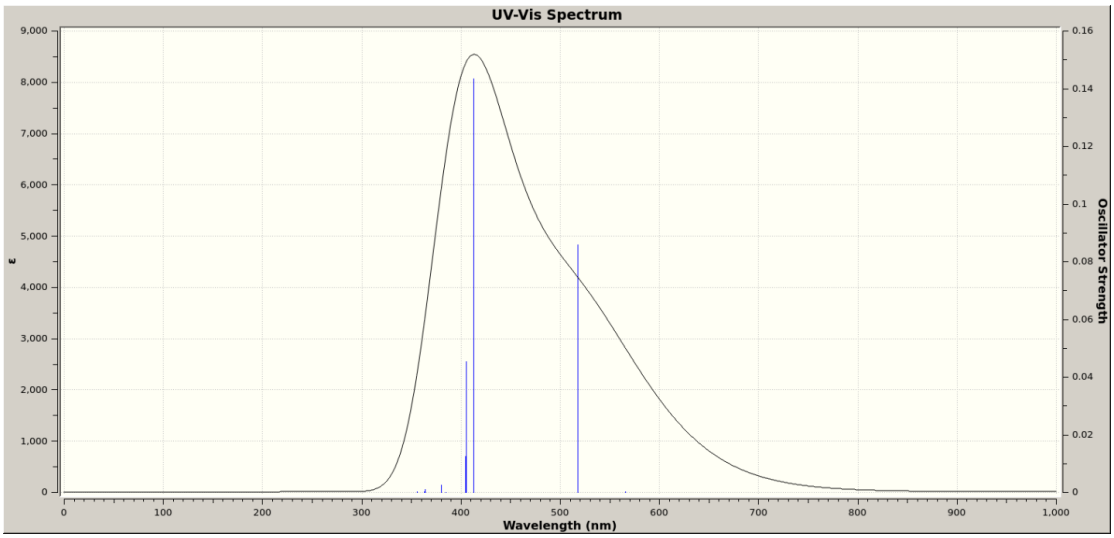
Supplementary Figure 15. UV-vis spectra of **1** (0.05 mM), **1[SbF$_6$]** (0.05 mM) and **1[SbF$_6$]$_2$** (0.05 mM) in CH_2Cl_2.

Supplementary Table 1. TD-DFT data for **1**, **1**$^{\cdot+}$ and **1**$^{2+}$.

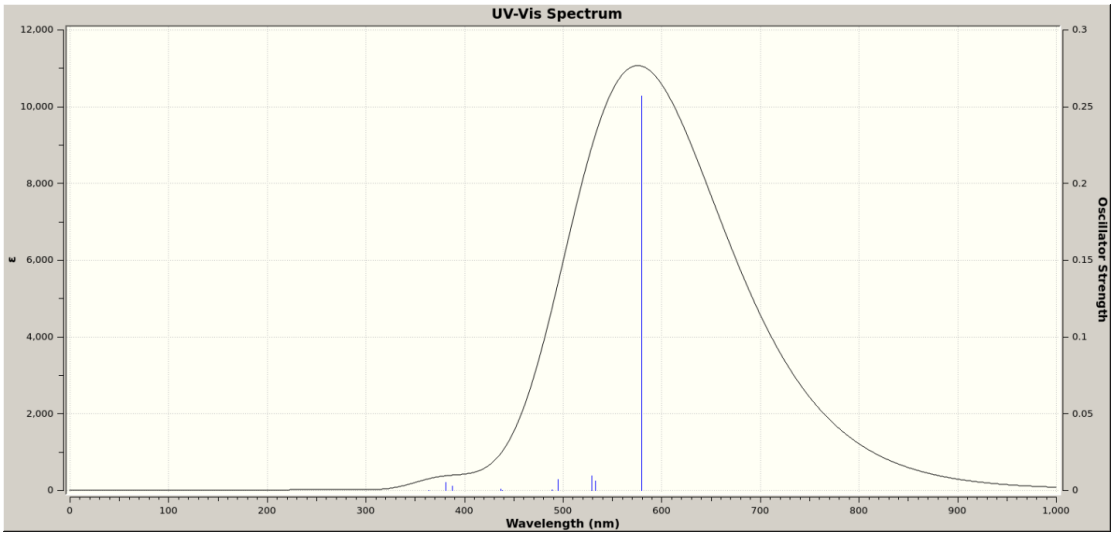
	λ (nm)	f (oscillator strength)	Assignment		
1	352	0.0452	232 -> 242	0.44348	contribution: 39.3%
			232 -> 243	-0.40356	contribution: 32.6%
			232 -> 244	0.36003	contribution: 25.9%
	515	0.0315	232 -> 234	0.14514	contribution: 4.2%
			232 -> 235	0.66635	contribution: 88.8%
			232 -> 236	0.13973	contribution: 3.9%
1$^{\cdot+}$	413	0.143	232A -> 234A	0.59616	contribution: 35.5%
			232A -> 235A	0.17130	contribution: 2.9%
			232A -> 238A	0.70345	contribution: 49.5%
			224B -> 232B	-0.25282	contribution: 6.4%
			231B -> 232B	-0.10225	contribution: 10.5%
	518	0.0858	232A -> 238A	0.11270	contribution: 1.3%
			231B -> 232B	0.98146	contribution: 96.3%
1^{2+}	381	0.0054	223 -> 232	0.69840	contribution: 97.6%
	580	0.257	231 -> 232	0.70179	contribution: 98.5%



Supplementary Figure 16. TD-DFT simulated spectrum of **1.**



Supplementary Figure 17. TD-DFT simulated spectrum of **1**$^{\bullet-}$.



Supplementary Figure 18. TD-DFT simulated spectrum of **1**$^{2-}$.

7. X-ray crystallographic studies

Single-crystal X-ray diffraction data for **2, 1[SbF_6]** and **1[SbF_6]$_2$** were collected at 150 K on Oxford Diffraction/Agilent SuperNova diffractometers with Cu-$K\alpha$ (λ = 1.54184 Å) radiation equipped with nitrogen gas Oxford Cryosystems Cryostream unit.[7] Raw frame data were reduced using CrysAlisPro.[8] The structures were solved using SHELXT[9] and refined to convergence on F^2 and against all independent reflections by full-matrix least-squares using SHELXL[10] in combination with the X-seed[11] or Olex2 programs.[12] Distances and angles were calculated using the full covariance matrix. Restraints were used to maintain sensible geometries for the disordered groups and approximate the displacement parameters to typical values. Selected crystallographic data are summarized in the Supplementary Table 2 and full details are given in the supplementary deposited CIF files (2063252-2063254). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

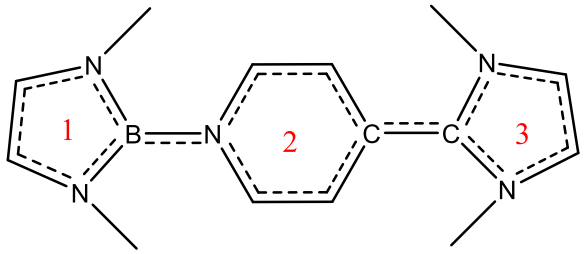
Supplementary Table 2. Selected crystallographic and refinement data for **2**, **1[SbF$_6$]** and **1[SbF$_6$]$_2$**.

	2	**1[SbF$_6$]**	**1[SbF$_6$]$_2$**
Formula	C_{52} H_{64} B N_5	C_{58} H_{76} B F_6 N_5 Sb	C_{60} H_{80} B Cl_4 F_{12} N_5 Sb_2
Fw	769.89	1089.79	1495.40
Cryst. System	Triclinic	Triclinic	Triclinic
Space Group	P –1	P –1	P –1
Wavelength/Å	1.54184	1.54184	1.54184
a/Å	12.0050(5)	10.5062(3)	11.7766(2)
b/Å	17.1016(7)	13.8854(3)	12.6941(2)
c/Å	22.3322(12)	22.0812(6)	13.0385(3)
α/°	93.809(4)	73.714(2)	72.300(2)
β/°	92.653(4)	76.539(2)	86.382(2)
γ/°	97.847(3)	70.779(2)	66.833(2)
Volume/Å^3	4524.8(4)	2884.38(14)	1703.61(6)
Z	4	2	1
Temp./K	150(2)	150(2)	150(2)
Refls. Collect.	16119	11931	6948
$2\theta_{max}$	133.996	152.63	152.362
Goodness of fit	0.989	1.037	1.051
$R[F^2>2\sigma]$, F	0.0598	0.0467	0.0343
R_w (all data), F^2	0.1601	0.1167	0.0918
CCDC ref	2063252	20632053	20632054

8. Computational studies

The geometry optimizations for **1**, $\mathbf{1}^{\cdot+}$, $\mathbf{1}^{2+}$ and **2** were performed with the Gaussian16 (Revision C.01) programme[13] using the PBE1PBE hybrid exchange functional[14-16] and Def-TZVP basis set.[17,18] In addition, Grimme's empirical dispersion correction with Becke-Johnson damping (GD3BJ)[19] was used as well as an ultrafine integration grid. Full analytical frequency calculations were performed for the optimized structures to ensure the nature of the stationary points found (minima, no imaginary frequencies). The NBO analyses were performed using the program NBO 7.0.5.[20] TD-DFT and NICS calculations were performed as single-point calculations in the gas phase for the optimized systems **1**, $\mathbf{1}^{\cdot+}$ and $\mathbf{1}^{2+}$ as implemented in Gaussian16.

NICS(0) and NICS(1) Calculations

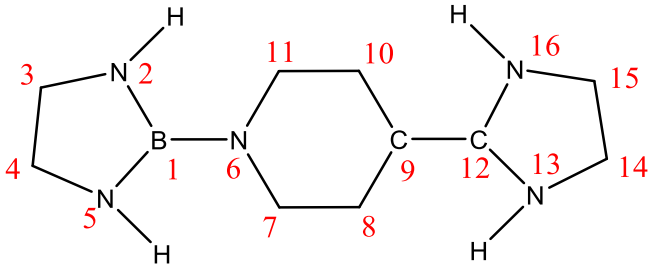


Supplementary Table 3. NICS(0) and NICS(1) data for **1**, $\mathbf{1}^{\cdot+}$ and $\mathbf{1}^{2+}$.

	1	$\mathbf{1}^{\cdot+}$	$\mathbf{1}^{2+}$
Ring 1 NICS(0)	-8.1382	-9.0253	-9.001
Ring 1 NICS(1)	-4.1778	-5.0367	-7.111
Ring 2 NICS(0)	6.7618	1.522	-7.5506
Ring 2 NICS(1)	4.137	-0.8654	-8.9863
Ring 3 NICS(0)	-7.0003	-10.135	-12.3617
Ring 3 NICS(1)	-2.4116	-5.3367	-10.3018

NRT calculations

In all three structures, the Dipp-substituents were replaced with protons for computational efficiency. The proton positions for the simplified model compounds were optimized by freezing all heavy atoms and the NRT analysis was then performed.



Supplementary Table 4. Natural Bond Orders for **1**, $\mathbf{1}^{\cdot+}$ and $\mathbf{1}^{2+}$.

Bond	**1**	$\mathbf{1}^{\cdot+}$	$\mathbf{1}^{2+}$
B1-N6	1.0879	1.0029	1.0075
B1-N2	1.3596	1.3831	1.3439

N2-C3	1.2521	1.2526	1.3418
C3-C4	1.6148	1.6086	1.5482
C4-N5	1.2483	1.2565	1.3418
N5-B1	1.3566	1.4135	1.3439
N6-C7	1.1628	1.3040	1.3928
C7-C8	1.7517	1.6367	1.4788
C8-C9	1.1413	1.2922	1.4544
C9-C10	1.1444	1.2869	1.4544
C10-C11	1.7537	1.6527	1.4788
C11-N6	1.1610	1.2948	1.3928
C9-C12	1.4440	1.3029	1.0356
C12-N13	1.1320	1.2261	1.3777
N13-C14	1.2211	1.2927	1.3466
C14-C15	1.6285	1.5925	1.5678
C15-N16	1.2442	1.2901	1.3466
N16-C12	1.1267	1.2230	1.3777

Compound 1:

3-Center, 4-Electron A:-B-:C Hyperbonds (A-B :C <=> A: B-C)

Hyperbond A:-B-:C %A-B/%B-C

1. N6:- B1-: N5 45.7/54.3
2. N6:- B1-: N2 45.6/54.4

Resonance structures: Over 125 resonance structures were found in total, which is in agreement with highly delocalized system, parent structure has a weight of only 5.92%. The 20 highest contributions total to 44.46%, of which ca. 54% have C9-C12 double bond and either C7-C8 or C10-C11 double bond and ca. 39% feature structures that exhibit 3 C-C/C-N double bonds in ring 2.

Supplementary Table 5. Natural Atomic Valencies and Charges for **1**.

Atom	Valency	Covalent valency	Ionic valency	Formal charge
B1	3.8041	1.6819	2.1223	-1.1331
N2	3.6005	2.0539	1.5466	0.6867
C3	3.8063	3.2182	0.5882	-0.1937
C4	3.8066	3.2200	0.5866	-0.1850
N5	3.5939	2.0497	1.5442	0.6760
N6	3.4117	2.0892	1.3224	0.5867
C7	3.8642	3.2671	0.5971	-0.1358
C8	3.8478	3.5466	0.3012	-0.1276
C9	3.8152	3.5401	0.2751	-0.0620
C10	3.8545	3.5490	0.3055	-0.1386
C11	3.8627	3.2671	0.5956	-0.1304
C12	3.7215	3.0116	0.7099	-0.2677
N13	3.3881	2.2675	1.1206	0.4602
C14	3.7960	3.2218	0.5742	-0.1837
C15	3.8289	3.2307	0.5982	-0.1687
N16	3.3921	2.2755	1.1167	0.5190

Compound $\mathbf{1}^{\cdot+}$:

3-Center, 4-Electron A:-B-:C Hyperbonds (A-B :C <=> A: B-C)

α-spin

Hyperbond A:-B-:C %A-B/%B-C

1. N2:- B1-: N5 50.2/49.8

β-spin

Hyperbond A:-B-:C %A-B/%B-C

1. N13:-C14-: C15 27.0/73.0
2. C12:- N16-: C15 54.6/45.4

Resonance structures: (α-spin) Over 180 resonance structures were found in total, which is in agreement with highly delocalized system, parent structure has a weight of only 1.73%. The 20 highest contributions total 24.84% of the calculated resonance structures, of which: ca. 4% exhibit a C9-C12 single bond and C7-C8 and C10-C11 double bonds (resembling structure $\mathbf{1}^{\cdot+}\mathbf{a}$). Ca. 66% of structures have a C9-C12 double bond and two C-C double bonds in ring 2 (resembling structure $\mathbf{1}^{\cdot+}\mathbf{b}$). Ca. 30% of the structures feature 3 double bonds in the ring 2 with cationic charge localized on N6 (resembling structure $\mathbf{1}^{\cdot+}\mathbf{c}$). (β-spin) Over 162 resonance structures found in total, which is in agreement with highly delocalized system, parent structure has a weight of only 2.52%. The 20 highest contributions total 43.41% of the calculated resonance structures, of which all feature 3 double bonds in the ring 2 and C9-C12 single bond (resembling structure $\mathbf{1}^{\cdot+}\mathbf{c}$).

Supplementary Table 6. Natural Atomic Valencies and Charges for $\mathbf{1}^{\cdot+}$

Atom	Valency	Covalent valency	Ionic valency	Formal charge
B1	3.8147	1.7268	2.0879	-1.1439
N2	3.6462	2.0818	1.5644	0.7123
C3	3.8156	3.1924	0.6232	-0.1808
C4	3.8209	3.1961	0.6248	-0.1758
N5	3.6677	2.0688	1.5990	0.7443
N6	3.6343	2.3117	1.3225	0.7619
C7	3.9264	3.2764	0.6500	-0.0558
C8	3.8987	3.5310	0.3677	-0.0434
C9	3.9034	3.5710	0.3324	-0.0374
C10	3.8918	3.5197	0.3721	-0.0632
C11	3.9118	3.2494	0.6624	-0.0612
C12	3.7921	3.0052	0.7868	-0.1956
N13	3.5645	2.3921	1.1724	0.6075
C14	3.8372	3.1958	0.6413	-0.1552
C15	3.8304	3.1923	0.6381	-0.1572
N16	3.5565	2.3945	1.1621	0.5994

Compound $\mathbf{1}^{2+}$:

3-Center, 4-Electron A:-B-:C Hyperbonds (A-B :C <=> A: B-C)

Hyperbond A:-B-:C %A-B/%B-C

1. N13:- C14-: C15 24.4/75.6
2. C 12:- N16-: C15 54.4/45.6

Resonance structures: Over 128 resonance structures were found in total. Parent structure has a weight of only 2.48%. 24 biggest contributions total 45.02% of the overall structures, of which: ca 71% exhibit 3 C-C/C-N double bonds in the ring 2 (resembling structure $\mathbf{1}^{2+}\mathbf{a}$). Ca. 23% resemble structure $\mathbf{1}^{2+}\mathbf{b}$ and ca. 6% of resonance structures have C9-C12 double bond and either C7-C8 or C10-C11 double bond (resembling structure $\mathbf{1}^{2+}\mathbf{c}$).

Supplementary Table 7. Natural Atomic Valencies and Charges for $\mathbf{1}^{2+}$

Atom	Valency	Covalent valency	Ionic valency	Formal charge
B1	3.7751	1.7370	2.0381	-1.0661
N2	3.6791	2.1051	1.5740	0.7849
C3	3.8274	3.1369	0.6905	-0.1708
C4	3.8274	3.1369	0.6905	-0.1708
N5	3.6791	2.1051	1.5740	0.7849
N6	3.7931	2.3914	1.4017	0.8602
C7	3.9138	3.1961	0.7177	-0.0570
C8	3.9559	3.5856	0.3703	-0.0264
C9	3.9443	3.7775	0.1668	-0.0113
C10	3.9559	3.5856	0.3703	-0.0264
C11	3.9138	3.1961	0.7177	-0.0570
C12	3.7909	2.9989	0.7920	-0.1866
N13	3.7052	2.4466	1.2586	0.7701
C14	3.8757	3.1723	0.7034	-0.1146
C15	3.8757	3.1723	0.7034	-0.1146
N16	3.7052	2.4466	1.2586	0.7701

Frontier orbital energies

1

HOMO: -0.12611 au = -3.432 eV = -331.1 kJ/mol

LUMO: -0.01229 au = -0.3344 eV = -32.3 kJ/mol

HOMO-LUMO gap: 3.097 eV = 298.8 kJ/mol

$\mathbf{1}^{\cdot+}$

SOMO (alpha): -0.25129 au = -6.837 eV = -659.76 kJ/mol

LUMO (alpha): -0.12027 au = -3.273 eV = -315.77 kJ/mol

LUMO (beta): -0.18070 au = -4.9171 eV = -474.43 kJ/mol

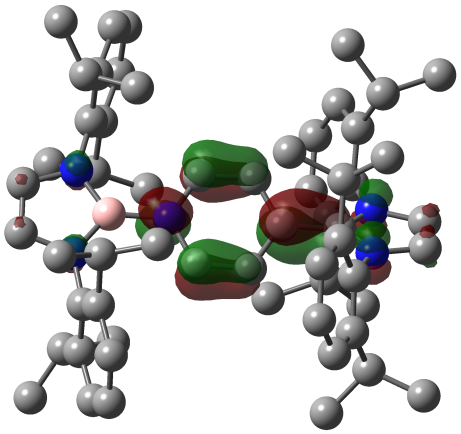
SOMO-LUMO (alpha) gap: 0.13102 au = 3.564 eV = 343.99 kJ/mol

$\mathbf{1}^{2+}$

HOMO: -0.40190 au = -10.936 eV = -1055.19 kJ/mol

LUMO: -0.30782 au = -8.376 eV = -808.18 kJ/mol

HOMO-LUMO gap: 0.09408 au = 2.56 eV = 247.0 kJ/mol



Supplementary Figure 19. DFT calculated LUMO for **1**$^{2-}$. Isovalue is set at 0.005 a.u.

Xyz-coordinates of optimized structures:

(HCDippN)$_2$B(NC$_4$H$_4$C)C(NDippCH)$_2$ [1]

140

C	2.380308	-5.329636	-0.674276
C	2.709901	-4.705896	0.514611
C	3.105465	-3.371589	0.534384
C	3.153111	-2.675536	-0.679504
C	2.829823	-3.287505	-1.899835
C	2.444995	-4.624784	-1.865561
N	3.561672	-1.311985	-0.665166
C	2.800163	-0.217012	-0.214210
N	3.753563	0.804148	-0.058743
C	5.031391	0.299449	-0.290779
C	4.916693	-0.983701	-0.641087
C	3.545205	2.175792	0.239343
C	3.927934	2.649281	1.501510
C	3.744112	4.001900	1.771610
C	3.182321	4.844313	0.827092
C	2.802987	4.352536	-0.411506
C	2.988159	3.013841	-0.737267
C	1.452747	-0.161440	0.029349
C	0.533552	-1.273312	-0.175150
C	-0.791484	-1.156105	-0.021229
N	-1.421755	0.041901	0.332640
C	-0.559037	1.092496	0.661754
C	0.772271	1.021552	0.542811
B	-2.848594	0.209430	0.341257
N	-3.569093	1.441452	0.143592
C	-3.081622	2.651107	-0.417491
C	-2.986331	3.797482	0.381661
C	-2.494225	4.964762	-0.193583
C	-2.098498	4.993046	-1.519852
C	-2.194117	3.849024	-2.293634
C	-2.688420	2.661588	-1.763849
C	-3.395659	3.777104	1.836890
C	-4.673153	4.584834	2.057574
C	-2.784579	1.431147	-2.638114
C	-3.720940	1.660518	-3.821566
C	4.429956	1.695587	2.565202
C	2.830070	-2.581528	-3.242504
C	3.434917	-2.705034	1.850849
C	2.597358	2.459833	-2.088751
H	3.034023	5.893230	1.059540
H	2.070009	-6.368766	-0.675948
C	-4.935259	1.157019	0.208590
C	-5.111260	-0.156889	0.439626
N	-3.868219	-0.787078	0.530179
C	-3.734377	-2.182698	0.740297
C	-3.943423	-3.055521	-0.337507
C	-3.756175	-4.417578	-0.127180
C	-3.366350	-4.900395	1.110980
C	-3.165648	-4.023602	2.163020
C	-3.349984	-2.653662	2.002435
C	-4.308992	-2.542579	-1.713574
C	-3.163816	-2.757608	-2.702193
C	-3.111836	-1.714637	3.162671
C	-1.631976	-1.668384	3.539060
C	-3.977302	-2.078144	4.366203
C	-5.603219	-3.167794	-2.225618
C	-2.277041	4.267781	2.752681
C	-1.406625	0.967125	-3.103858
H	-5.676285	1.929639	0.080460
H	0.894436	-2.250993	-0.451027
H	-6.028030	-0.708615	0.574082
H	-1.443529	-2.005301	-0.163518
H	-1.036270	1.979787	1.050934
H	1.327837	1.886984	0.867251
H	-3.403875	-0.714402	2.835554
H	-4.474791	-1.466900	-1.631910
H	-3.607887	2.737339	2.096699
H	-2.857354	-4.408748	3.129008
H	-3.905095	-5.109529	-0.949278
H	-2.412436	5.863098	0.408772
H	-3.216126	-5.964696	1.255427
H	-3.217057	0.629971	-2.035289
H	-1.878280	3.876828	-3.331059
H	5.896360	0.936272	-0.221829
H	4.028128	4.399224	2.738367
H	-5.036795	-2.098778	4.100671
H	-3.839523	-1.346330	5.166556
H	-3.713277	-3.060018	4.768596
H	5.015412	0.916716	2.069119
C	3.247832	1.004851	3.247485
C	5.335843	2.355651	3.596082
H	5.663910	-1.710677	-0.906357
H	2.655051	-5.258976	1.445929
H	-1.710773	5.909343	-1.951565
H	-0.945846	1.707923	-3.762581
H	-1.489617	0.030855	-3.662059
H	-0.735223	0.800993	-2.259655
H	2.353370	5.021395	-1.134358
H	2.182946	-5.116849	-2.796459
H	-1.284119	-2.646211	3.884937
H	-1.465407	-0.948929	4.345425
H	-1.015574	-1.375375	2.687637

H	-1.359066	3.693269	2.608577
H	-2.575313	4.171100	3.799899
H	-2.042273	5.320173	2.572574
H	-5.500357	-4.247483	-2.364607
H	-5.879077	-2.734540	-3.190616
H	-6.426669	-2.998389	-1.527979
H	-2.248069	-2.267685	-2.363652
H	-3.424585	-2.347287	-3.681866
H	-2.947059	-3.821809	-2.830688
C	1.777671	-1.479112	-3.337086
H	2.543452	-3.356048	-3.962857
C	4.201602	-2.069627	-3.677269
H	3.712747	-1.670721	1.643928
C	4.628357	-3.373508	2.528037
C	2.215187	-2.674590	2.768832
H	-4.715741	1.961245	-3.485208
H	-3.820983	0.743405	-4.408706
H	-3.340050	2.440750	-4.486453
H	-4.517681	5.638315	1.807789
H	-4.988996	4.529388	3.102851
H	-5.490176	4.213174	1.435133
C	3.828743	2.243333	-2.969325
C	1.567969	3.311480	-2.816160
H	2.137200	1.482797	-1.909552
H	4.882267	-2.847495	3.452224
H	4.410772	-4.413540	2.786348
H	5.507356	-3.365545	1.879201
H	2.450043	-2.143596	3.694789
H	1.377319	-2.167837	2.287045
H	1.893056	-3.685248	3.035235
H	4.169330	-1.781086	-4.731421
H	4.503728	-1.192844	-3.103958
H	4.969424	-2.839110	-3.562789
H	1.753428	-1.075342	-4.353207
H	0.781537	-1.854533	-3.095341
H	1.993484	-0.657966	-2.652584
H	3.535734	1.798448	-3.924257
H	4.324921	3.196020	-3.176290
H	4.552835	1.576635	-2.498644
H	1.250346	2.798576	-3.726722
H	0.682096	3.485090	-2.202079
H	1.979488	4.279300	-3.118065
H	5.764073	1.594596	4.252658
H	6.158276	2.898948	3.124415
H	4.786855	3.055461	4.232005
H	3.604865	0.293497	3.997675
H	2.613120	1.739609	3.751054
H	2.628069	0.462426	2.531549

[(HCDippN)$_2$B(NC$_4$H$_4$C)C(NDippCH)$_2$]$^{\cdot+}$ [1]$^{\cdot+}$

140

N	3.733378	-1.064209	0.394609
N	3.709422	1.110691	-0.274909
C	3.393586	-2.371266	0.841030
C	3.339868	2.393216	-0.766958
C	3.503602	-3.444341	-0.054143
C	5.043360	-0.605533	0.262109
H	5.885308	-1.243967	0.475633
C	2.901693	-2.537715	2.142488
C	3.417328	3.500188	0.089098
C	2.994176	4.732914	-0.397964
H	3.049287	5.605995	0.242828
C	0.674501	1.134557	0.321095
H	1.247459	2.021066	0.549692
C	5.029209	0.682738	-0.137395
H	5.857156	1.340636	-0.346299
C	3.926281	3.379852	1.508809
H	4.129227	2.324115	1.701735
C	3.109027	-4.703892	0.385776
H	3.188832	-5.551730	-0.285671
C	2.852929	2.501170	-2.076777
C	2.788537	-1.386433	3.117041
H	3.170631	-0.491356	2.620515
C	0.688491	-1.140426	-0.234133
H	1.272142	-2.029177	-0.424320
C	2.509564	-3.815062	2.531197
H	2.124928	-3.971222	3.533066
C	4.012262	-3.260085	-1.467397
H	4.222273	-2.198108	-1.611315
C	2.430362	3.753152	-2.512997
H	2.048226	3.863525	-3.521939
C	2.781060	1.315455	-3.013263
H	3.163313	0.443313	-2.477528
C	2.499946	4.860283	-1.685053
H	2.173131	5.828810	-2.046587
C	2.612123	-4.889704	1.664791
H	2.308286	-5.878522	1.989507
C	3.651005	-1.623128	4.354574
H	3.309518	-2.495496	4.917625
H	3.605119	-0.758735	5.021672
H	4.695306	-1.788989	4.082267
C	5.236979	4.143267	1.687186
H	5.997416	3.797579	0.983581
H	5.624075	4.009089	2.700106
H	5.095230	5.214509	1.521934

C	2.883059	3.841342	2.524648
H	2.647401	4.901601	2.404204
H	3.256730	3.699488	3.541600
H	1.949662	3.279946	2.429515
C	1.334440	-1.121234	3.503587
H	0.713561	-0.936949	2.624286
H	1.266239	-0.248522	4.158233
H	0.906746	-1.972786	4.039513
C	5.317326	-4.022161	-1.686109
H	6.080500	-3.717081	-0.966853
H	5.703964	-3.838721	-2.691444
H	5.170016	-5.099687	-1.576207
C	2.962483	-3.665100	-2.500784
H	2.712461	-4.726088	-2.422659
H	3.337731	-3.486687	-3.511475
H	2.037180	-3.094850	-2.382017
C	3.673067	1.524174	-4.234920
H	3.335313	2.374127	-4.833440
H	3.655815	0.638617	-4.875160
H	4.707553	1.712614	-3.940746
C	1.342603	1.013502	-3.428708
H	0.698942	0.856363	-2.560471
H	1.305839	0.113826	-4.048408
H	0.918663	1.835325	-4.011885
N	-3.704933	1.063144	0.176171
N	-3.695536	-1.028763	-0.416201
C	-1.448979	-0.001047	-0.015871
C	-3.369356	2.367602	0.661499
C	-3.341875	-2.372346	-0.760344
C	-3.294066	2.555528	2.044801
C	-5.016007	0.679993	-0.012849
H	-5.823345	1.374703	0.141251
C	-3.139630	3.385763	-0.267872
C	-3.128109	-2.677537	-2.107123
C	-2.775930	-3.988456	-2.411927
H	-2.595069	-4.265241	-3.444199
C	-0.663062	-1.168754	-0.274189
H	-1.116440	-2.115709	-0.512873
C	-5.010201	-0.614662	-0.379028
H	-5.810947	-1.292039	-0.620169
C	-3.226101	-1.635890	-3.198522
H	-3.559095	-0.699506	-2.743791
C	-2.863276	0.007779	-0.074314
C	-2.955373	3.828076	2.493332
H	-2.878253	4.014867	3.558156
C	-3.234051	-3.312268	0.269007
C	-3.201475	3.148622	-1.759669
H	-3.411761	2.088688	-1.924331
C	-0.676977	1.161556	0.300013
H	-1.141554	2.104395	0.532638
C	-2.811366	4.640632	0.234519
H	-2.621446	5.456663	-0.453111
C	-3.521119	1.428876	3.027991
H	-3.895594	0.565324	2.472416
C	-2.879842	-4.608294	-0.090864
H	-2.779284	-5.365817	0.677855
C	-3.448086	-2.951993	1.721883
H	-3.728270	-1.896797	1.771350
C	-2.650066	-4.942206	-1.415472
H	-2.372651	-5.957699	-1.674275
C	-2.715794	4.858469	1.599082
H	-2.454079	5.842876	1.970058
C	-4.337111	3.948503	-2.394149
H	-4.176125	5.022956	-2.276435
H	-4.400722	3.736637	-3.463946
H	-5.300635	3.705145	-1.940542
C	-4.260024	-2.026747	-4.251197
H	-5.241877	-2.196673	-3.803834
H	-4.357725	-1.235487	-4.997907
H	-3.969797	-2.940561	-4.775129
C	-1.859278	-1.376838	-3.830830
H	-1.479895	-2.272954	-4.328560
H	-1.932166	-0.585147	-4.580372
H	-1.124910	-1.070639	-3.083217
C	-1.863207	3.458324	-2.429037
H	-1.047868	2.881719	-1.987809
H	-1.911644	3.217861	-3.493821
H	-1.609590	4.517515	-2.340626
C	-4.577796	1.791064	4.067730
H	-5.517781	2.086499	3.596687
H	-4.775810	0.935364	4.717154
H	-4.248812	2.615770	4.704218
C	-2.208918	1.013170	3.692823
H	-1.790670	1.835323	4.279302
H	-2.376343	0.171391	4.369174
H	-1.462039	0.713269	2.955208
C	-4.593273	-3.758445	2.329132
H	-4.365137	-4.826969	2.339230
H	-4.769723	-3.448124	3.361587
H	-5.520529	-3.621073	1.768416
C	-2.160775	-3.121274	2.527776
H	-1.344898	-2.526568	2.112613
H	-2.319031	-2.806140	3.562018
H	-1.838694	-4.165472	2.543710
N	1.399411	-0.000335	0.051393
B	2.868075	0.012895	0.058488

$[(HCDippN)_2B(NC_4H_4C)C(NDippCH)_2]^{2+}$ $[1]^{2+}$

140

N	-3.713794	-1.018168	-0.370100
C	-3.294275	-3.397318	-0.074237
C	-5.024704	-0.636989	-0.237664
H	-5.832418	-1.298826	-0.500578
C	2.940049	4.124889	-2.280776
H	2.915651	4.448314	-3.314041
N	-3.714215	1.016679	0.371177
C	3.662996	-1.830436	3.072630
H	4.336911	-1.082644	2.646494
C	0.621809	1.094108	-0.404768
H	1.206534	1.944279	-0.727194
C	2.942423	-4.124837	2.279823
H	2.918553	-4.448772	3.312936
C	-2.337413	-3.516689	-2.709315
H	-1.971940	-3.583054	-3.727246
N	3.663424	-1.100730	0.291556
C	1.735139	3.084948	2.541861
H	1.400786	4.125104	2.560058
H	1.786721	2.734943	3.575575
H	0.965500	2.503239	2.026923
C	-2.358957	4.650132	1.914903
H	-2.007613	5.593863	2.315750
C	3.352320	-2.455704	0.624096
C	3.099855	2.951714	1.867696
H	3.395218	1.900636	1.921130
N	3.663053	1.102015	-0.291380
C	-5.024964	0.634877	0.238977
H	-5.832943	1.296333	0.502038
C	-2.799175	1.079136	3.130326
H	-3.132261	0.211897	2.551848
C	2.408592	-1.095713	3.550046
H	1.934422	-0.526770	2.745435
H	2.660150	-0.389371	4.344635
H	1.673053	-1.800746	3.947178
C	3.325979	-2.822206	1.977807
C	-0.748220	1.122876	-0.405730
H	-1.242698	2.024531	-0.736339
C	3.040469	3.348212	0.409088
C	3.351375	2.456733	-0.624410
C	-3.258494	-2.275606	-0.909234
C	3.041405	-3.346828	-0.409706
C	0.622262	-1.093786	0.405408
H	1.207342	-1.943731	0.727788
C	-2.357241	-4.650377	-1.915633
H	-2.005584	-5.593784	-2.316968
C	-3.259413	2.274540	0.909732
C	-3.295957	3.395900	0.074284
C	4.383607	2.472459	-4.251895
H	4.733537	1.698966	-4.938284
H	5.249551	3.051245	-3.925502
H	3.728078	3.134720	-4.822330
C	-2.338384	3.516777	2.709044
H	-1.972643	3.583723	3.726842
C	-3.797057	-1.263900	-4.272723
H	-3.510790	-2.101664	-4.912221
H	-3.832542	-0.367126	-4.894932
H	-4.803917	-1.460559	-3.898581
C	-3.813245	-3.345666	1.346837
H	-3.922943	-2.295341	1.636598
C	-2.794384	2.293322	2.227575
C	-3.796407	1.263950	4.273857
H	-3.510267	2.102097	4.912909
H	-3.831254	0.367412	4.896438
H	-4.803499	1.460010	3.900025
C	-2.793829	-2.293636	-2.227220
C	2.664719	-4.638888	-0.051506
H	2.425828	-5.358154	-0.826705
C	4.160741	-3.757955	-2.612583
H	5.143146	-3.643676	-2.150467
H	4.232568	-3.427496	-3.651213
H	3.917276	-4.823064	-2.618261
C	3.099997	-2.949604	-1.868149
H	3.394405	-1.898236	-1.921197
C	1.735223	-3.083742	-2.542005
H	1.401811	-4.124190	-2.560673
H	1.786213	-2.733155	-3.575552
H	0.965180	-2.503009	-2.026568
C	-5.196061	3.994699	-1.435769
H	-5.912434	3.529132	-0.755187
H	-5.590914	3.917086	-2.450738
H	-5.140789	5.054445	-1.176789
C	3.661446	1.830505	-3.072799
H	4.335378	1.082861	-2.646444
C	-1.402443	0.765288	3.662945
H	-0.678259	0.638422	2.855099
H	-1.420800	-0.153535	4.253052
H	-1.035862	1.563435	4.311611
C	4.967473	-0.655035	0.169335
H	5.802672	-1.316904	0.334655
C	2.606406	5.022738	-1.278232
H	2.318829	6.035374	-1.536971
C	-0.747752	-1.123078	0.406488
H	-1.241864	-2.024910	0.737168
C	-2.849303	-3.989185	2.341371

H	-2.749178	-5.062350	2.168911
H	-3.222249	-3.858504	3.359056
H	-1.848466	-3.551357	2.292919
C	4.385154	-2.472683	4.251569
H	4.735010	-1.699361	4.938186
H	5.251151	-3.051327	3.925061
H	3.729628	-3.135137	4.821790
C	-2.799459	-1.079108	-3.129506
H	-3.132674	-0.212215	-2.550581
C	2.407056	1.095617	-3.549990
H	1.671466	1.800522	-3.947256
H	1.932932	0.526878	-2.745199
H	2.658593	0.389074	-4.344407
C	3.324367	2.822590	-1.978279
C	-2.832265	-4.592102	-0.615452
H	-2.845559	-5.490787	-0.010718
C	2.662981	4.639904	0.050415
H	2.424035	5.359428	0.825360
C	-3.815296	3.343475	-1.346627
H	-3.924826	2.293001	-1.635901
C	4.967254	0.656712	-0.169393
H	5.802227	1.318830	-0.334850
C	2.608872	-5.022386	1.276973
H	2.321933	-6.035297	1.535347
C	-5.193831	-3.997262	1.436065
H	-5.910518	-3.531547	0.755918
H	-5.588410	-3.920237	2.451184
H	-5.138365	-5.056868	1.176555
C	-2.851752	3.986763	-2.341697
H	-2.751627	5.059985	-2.169595
H	-3.225054	3.855747	-3.359210
H	-1.850880	3.548992	-2.293470
C	-2.834344	4.591114	0.614887
H	-2.848240	5.489551	0.009799
C	4.160082	3.761355	2.611457
H	3.915653	4.826245	2.616783
H	5.142446	3.647784	2.149080
H	4.232539	3.431392	3.650201
C	-1.403067	-0.764455	-3.662536
H	-1.036412	-1.562150	-4.311714
H	-0.678616	-0.637656	-2.854922
H	-1.422039	0.154628	-4.252224
C	-2.920377	-0.000552	0.000466
C	-1.467061	-0.000243	0.000396
N	1.313467	0.000292	0.000277
B	2.812270	0.000522	0.000169

$(HCDippN)_2B(NC_4H_4C)C(NMesCH)_2$ [2]

122

N	3.324829	-0.953395	0.327748
N	0.755272	-0.597594	0.423381
N	2.035609	-2.661744	-0.461553
N	-4.071863	1.434744	0.100083
N	-2.732914	3.196126	0.104286
C	3.884580	0.263215	0.796366
C	-1.647265	0.996558	0.468166
C	0.549462	-4.588649	-0.385507
C	0.768330	0.760566	0.785344
H	1.727193	1.166268	1.069176
C	-1.657424	-0.455221	0.372308
H	-2.583681	-1.008953	0.318822
C	4.119909	0.425452	2.167762
C	1.035657	-3.465945	-1.067745
C	-2.730701	1.801263	0.247577
C	-1.005380	3.729278	-1.530119
C	3.385407	-2.995747	-0.588988
H	3.688098	-3.941134	-1.009927
C	4.166268	1.281236	-0.124729
C	4.144874	-1.989440	-0.124146
H	5.218838	-1.916328	-0.061560
C	-0.333479	1.519436	0.807530
H	-0.213856	2.544656	1.128031
C	-0.525016	-1.170365	0.350259
H	-0.553739	-2.246449	0.273357
C	-1.608773	3.967836	-0.293471
C	-4.636154	0.189712	0.476632
C	1.055727	-4.955356	0.991060
H	1.802680	-4.209588	1.270399
C	-4.724924	-0.146039	1.828872
C	-0.441651	-5.352503	-0.994017
H	-0.834819	-6.223169	-0.479826
C	4.876916	2.674997	1.715660
H	5.256372	3.624255	2.078003
C	-5.086478	-0.673672	-0.523295
C	0.552536	-3.112588	-2.335378
C	3.799471	-0.677999	3.150281
H	3.641189	-1.589391	2.569433
C	0.121322	4.472026	-1.863314
H	0.605314	4.285008	-2.817224
C	4.659983	2.487912	0.360826
H	4.872622	3.294793	-0.332564
C	3.903810	1.102662	-1.603215
H	3.605421	0.063800	-1.757349
C	-5.633431	-1.893168	-0.143519
H	-5.980831	-2.575985	-0.913231
C	-1.128890	4.952114	0.573702

C	-5.726292	-2.266566	1.193272
C	4.613115	1.649550	2.608698
H	4.789835	1.804101	3.667393
C	-1.540903	2.688978	-2.460607
H	-1.319175	1.687662	-2.080814
H	-1.096934	2.791779	-3.451561
H	-2.627400	2.760926	-2.554259
C	0.645125	5.435876	-1.011312
C	-5.270754	-1.379807	2.162761
H	-5.341854	-1.654282	3.211188
C	-4.849537	2.574651	-0.103161
H	-5.919445	2.502301	-0.198593
C	-4.040517	3.638922	-0.110364
H	-4.252316	4.682028	-0.270317
C	-0.444151	-3.900440	-2.901743
H	-0.839122	-3.638138	-3.877523
C	-0.938815	-5.011935	-2.240561
H	-1.715661	-5.614677	-2.698279
C	-0.004195	5.674147	0.195946
H	0.386243	6.429379	0.871861
C	1.737271	-6.321257	0.986815
H	1.033097	-7.115496	0.723204
H	2.143465	-6.550104	1.975713
H	2.557844	-6.351272	0.266224
C	-0.063856	-4.901101	2.028403
H	-0.529766	-3.913451	2.058912
H	0.329090	-5.120984	3.024733
H	-0.845271	-5.634125	1.809230
C	1.072532	-1.901050	-3.075250
H	1.861866	-1.459150	-2.463794
C	-4.925910	-0.308902	-1.966806
H	-5.480906	0.597283	-2.222756
H	-5.275387	-1.116733	-2.610699
H	-3.875201	-0.111712	-2.197292
B	1.947705	-1.343425	0.127413
C	-4.217998	0.790243	2.879541
H	-3.126465	0.855429	2.836597
H	-4.508693	0.451385	3.874475
H	-4.603140	1.801841	2.727931
C	-6.271600	-3.609251	1.577926
H	-6.735173	-3.582091	2.565909
H	-5.472387	-4.356535	1.610964
H	-7.016326	-3.957595	0.859715
C	4.947481	-0.938923	4.119942
H	5.878944	-1.143960	3.587199
H	4.718302	-1.801398	4.751133
H	5.120322	-0.086899	4.783043
C	-1.786250	5.181822	1.899776
H	-2.783096	5.618258	1.789091
H	-1.190475	5.857552	2.514506
H	-1.915608	4.239391	2.438067
C	2.502673	-0.376410	3.900829
H	2.600375	0.538710	4.492356
H	2.257136	-1.194833	4.583313
H	1.664661	-0.242615	3.213873
C	5.161236	1.347101	-2.432301
H	5.501030	2.383312	-2.350343
H	4.963514	1.146777	-3.488716
H	5.980029	0.699714	-2.110055
C	1.901940	6.172452	-1.364951
H	2.061236	6.192239	-2.444633
H	2.772552	5.686148	-0.912241
H	1.878789	7.202444	-1.002984
C	1.693231	-2.287197	-4.414846
H	2.494347	-3.017938	-4.282641
H	2.113049	-1.405442	-4.906740
H	0.949970	-2.721396	-5.089439
C	2.752652	1.991912	-2.068324
H	1.840471	1.798280	-1.500247
H	2.541579	1.818323	-3.127642
H	2.999845	3.050213	-1.945155
C	-0.018909	-0.847857	-3.249983
H	-0.826372	-1.218330	-3.888641
H	0.390929	0.052113	-3.716229
H	-0.451725	-0.571231	-2.286877

For EPR simulation:

[(HCDippN)$_2$B(NC$_4$H$_4$C)C(NDippCH)$_2$]$^{\bullet-}$ [1]$^{\bullet-}$

140			
N	9.15434373543757	11.93682870877447	3.67109215471535
N	8.92347354699295	10.07446914915655	2.33044512253287
C	9.07880191352909	13.25351308052618	4.25813237488727
C	8.86646198932185	10.81128712792764	4.46640966012809
H	8.78007748740632	10.89126738272625	5.53979318486658
C	7.40290558392967	8.86298028634328	0.82218087372941
C	8.72433255419977	9.11073842050864	1.2780871891580
C	8.73207304973959	9.71237529370569	3.67649846219658
H	8.51955588554315	8.69155241435011	3.95912669687676
C	10.14923549834735	13.73169589571136	5.05638065355375
C	7.89249152562195	14.01438219154912	4.07024938365705
C	9.21959348520633	11.92047405561534	-0.19085449725546
H	8.69960557011855	10.97879015802980	-0.29315162998264
C	7.80556615605591	15.27130841902630	4.69302493470503
H	6.90800599000472	15.86897415839214	4.57031859122286
C	9.84260447928495	8.43268801837307	0.73255610505465
C	11.41757922113451	12.91514684095379	5.31570517440569

H	11.38144557141854	12.02434164305732	4.68201772429108
C	6.18001788679400	9.52770709649900	1.46036761717398
H	6.52747474844970	10.15988375392286	2.28044547453696
C	10.00897873428859	14.99684567494695	5.65987273106015
H	10.81096842295715	15.38289545740881	6.28239337035665
C	10.16598409704500	13.53787023265404	1.24388995004930
C	6.70233465025682	13.47533991310967	3.27463159987361
H	7.06977705509477	12.70609657519132	2.58988254872640
C	11.25743075524751	8.64625482798410	1.27291643685197
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H	8.76354190927690	16.73237249697046	5.96195298049013
C	8.32815156177101	7.31765502099464	-0.82917930898402
H	8.17424875875734	6.62678418207154	-1.65342804337180
C	7.23073006332031	7.95889018781152	-0.24210191269732
H	6.23036739389635	7.74938495179974	-0.61146886674332
C	9.61867123836884	7.54559054552430	-0.33695453676337
H	10.45874588206802	7.02069191587207	-0.78228560737884
C	12.70499692532415	13.69492173522545	4.95961541231037
H	12.70342158135640	14.03547436253100	3.91800654985366
H	13.58022609260033	13.05423149837666	5.11155019915098
H	12.83095134143355	14.57585801782252	5.59654232805035
C	11.48659583753890	12.43981556392996	6.78806564578010
H	11.63077228839283	13.28618180319443	7.46791688506213
H	12.32705092974317	11.75276501246213	6.93021889906109
H	10.57167606720731	11.92147097525261	7.09109445210204
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H	4.86108953083560	12.35562528154346	3.63450692320624
H	5.25135795840392	13.51819182422876	4.91516475534277
C	11.94401393462710	7.31398516360467	1.65078892564399
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H	12.90648552628594	7.50889000198045	2.13540958052896
H	12.13838649779288	6.69412948383777	0.76952688650475
C	6.00443431272320	14.54439778461728	2.41059440732991
H	5.47027023306711	15.27982887276168	3.02132310308475
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H	6.71671370688318	15.08339451205911	1.77777535157669
C	12.12572161639409	9.44565355302525	0.27383817569316
H	12.32313363076913	8.86016279746301	-0.63102228493016
H	13.09005830891748	9.70540361407486	0.72478477940162
H	11.63266092347002	10.37343048972730	-0.03359623411071
C	5.41847830490672	10.43270734843631	0.46652537245132
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H	4.99353247978306	9.85064794009769	-0.35829210190375
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H	5.75032891447884	7.82490025913913	2.77431185622781
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C	10.84722577551288	12.94846955435751	-4.14205518361776
C	11.09819832489861	15.38754719243308	-4.42524653415122
H	11.26462637929696	15.27355374736593	-5.48410782307400
C	11.80903247745449	17.41295897775279	-0.46036934483962
C	10.70059987573474	17.04717440963437	-1.26330147385111
C	11.19288880312560	16.47910242933947	-3.62215759101925
H	11.42466539939574	17.50651859154708	-3.85263055327940
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C	12.08178707196562	12.27330785958620	-3.97459451849111
C	10.50502982875665	14.32574060772914	0.17799293325419
H	11.00909003323565	15.25313558780867	0.40182719064934
C	12.19676977331402	10.98800712110674	-4.53293208905139
H	13.12745290355232	10.43976844878240	-4.42417340158398
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C	8.48073430299019	13.18388079692255	-5.16616999556709
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C	13.19961804837155	16.81357974200386	-0.68263069961730
H	13.07692479306953	15.87465763476435	-1.23298176046880
C	10.59900565782668	14.72204230322442	-2.31444882490973
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C	9.55346222484297	12.66026466871410	-1.29496977136866
H	9.26668251154950	12.26222310818635	-2.25858537428147
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H	12.96069058997360	13.82223152225446	-2.77906784158249
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H	8.58962640612875	16.53561269078462	-2.76626297850845
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H	11.25040440275581	9.42258235733175	-5.67668919039718
C	10.32286621958746	18.94451392535887	0.72745587713544
H	10.17334684219777	19.68250683182401	1.51017644467083
C	11.59026895160835	18.37774933281951	0.53728130174982
H	12.41196953516495	18.68791222368730	1.17453438592614
C	9.25252120332157	18.57358373086626	-0.09165655388859
H	8.28049339654225	19.03345543071941	0.05916314947515
C	7.20411965167821	12.37682974183837	-4.83663812324917
H	7.18857922184814	12.03534152425124	-3.79645737762197
H	6.32150507976200	13.00211925325707	-5.00708459784333
H	7.10536268521596	11.49626295989429	-5.47839627649539
C	8.43697843839399	13.65204051581321	-6.64244150510939
H	8.34430754571800	12.79740404236031	-7.32036241986418
H	7.57563923289120	14.30619357171438	-6.81092426146206
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C	14.32160889126537	13.36452765569241	-4.37489492622670

H	13.86515632176361	14.03056140606979	-5.11369043521481
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C	7.81794682083126	18.52754619364008	-2.86121320168728
H	8.66226215946767	18.97422349812781	-3.39577044419105
H	7.05893448960987	18.24535829938787	-3.59811089687778
H	7.38525819039497	19.29883165796675	-2.21633160950785
C	13.95411778000195	12.00993745671153	-2.24777336944383
H	14.40664266341259	11.12228172436328	-2.70132914152174
H	14.75155196979784	12.55613460259396	-1.73274444299593
H	13.22883807859947	11.67679397577790	-1.50021335509516
C	7.05475859577464	16.67866631238888	-1.28411484919366
H	6.64861704510486	17.37961241651994	-0.54790058851859
H	6.25060784790735	16.43094559496924	-1.98459737482602
H	7.34309842545286	15.76440996820160	-0.75705631613135
C	13.94401511552532	16.48200244441899	0.62991145267685
H	13.33694993226701	15.86661240317785	1.30103097282933
H	14.86250688303754	15.93030745561097	0.40620642754653
H	14.23573107479390	17.38648085840904	1.17284349734911
C	14.05892232287781	17.75308931965630	-1.56234843358039
H	14.29753352232387	18.67575749034100	-1.02297376887038
H	15.00158439812966	17.26706572140513	-1.83613974213436
H	13.54095157110205	18.03338157541627	-2.48498476446519
H	10.40983867434662	13.83920767449494	2.25310315705225
N	9.51824546807696	12.31550315283241	1.11029820269366
B	9.20492485124716	11.48565824550135	2.30118141774144

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