Multiple stable redox states and tunable ground states via the marriage of Viologens and Chichibabin's hydrocarbon

Yuyang Dai,[‡a] Zhuofeng Xie,[‡ a] Manling Bao,[a] Chunmeng Liu[a] and Yuanting Su[*a,b]

[a] College of Chemistry, Chemical Engineering and Materials Science, School of Radiation Medicine and Protection, Soochow University, Suzhou 215123, China.

[b.] State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210023, China.

E-mail: ytsu@suda.edu.cn

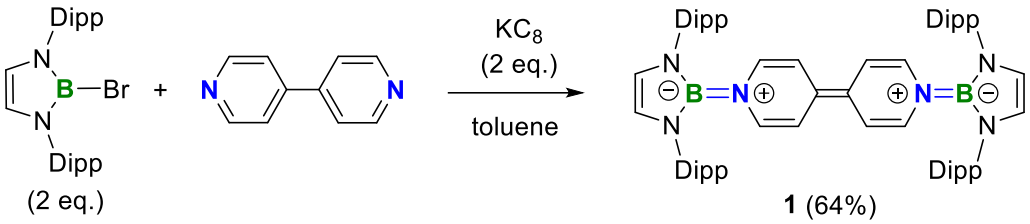
[‡] Y. Dai and Z. Xie contributed equally.

Contents

1. Synthesis and spectra data of new compounds

General considerations: All experiments were carried out under nitrogen atmosphere using standard Schlenk or dry glovebox techniques. Solvents were dried by standard methods and stored in activated 4 Å molecule sieve in the glovebox. ^{1}H, ^{13}C{^{1}H}, ^{11}B{^{1}H}, ^{19}F and ^{27}Al NMR spectra were obtained with a Bruker AVIII 400 MHz spectrometer. Chemical shifts (δ) are given in p.p.m. Coupling constants *J* are given in Hz. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, s = septet, m = multiplet, br = broad signal. UV-vis spectra were recorded on the Lambda 750 spectrometer at room temperature. EPR spectra were obtained using JEOL JES-X320 X-band apparatus. Element analyses were performed on an ElementarVario EL III instrument. Commercially available reagents were purchased from Energy Chemical and used as received. Bromoborane $(HCNDipp)_2BBr$[S1] (Dipp = 2,6-diisopropyl) and 3,3',5,5'-tetramethyl-4,4'-bipyridine[S2] were synthesized according to the literature procedures.

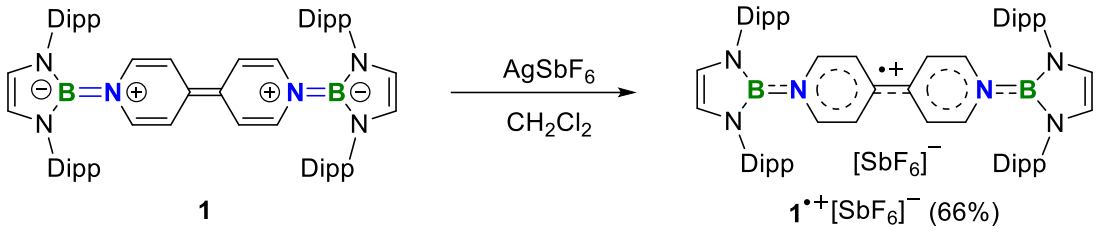
Synthesis of 1



Potassium graphite (0.70 g, 5.2 mmol) was added to the toluene (50 mL) solution of $(HCNDipp)_2BBr$ (2.34 g, 5.0 mmol) and 4, 4′-bipyridine (0.39 g, 2.5 mmol) at room temperature. After stirring for about twenty minutes, The color of the solution changed from yellow to brown and the mixture was stirred for 24 h. After filtration, the precipitation was extracted with THF (25 mL×2). The solvent was removed under vacuum and the residue was washed with hexane (20 mL) to afford **1** as an orange powder (1.48 g, 64%). Single crystals of **1** suitable for X-ray diffraction studies were grown from the THF/hexane solution at room temperature. ^{1}H NMR (THF-d_8, 300 MHz, 298 K): δ 7.26–7.23 (m, 4H, Ar-*H*), 7.18–7.16 (m, 8H, Ar-*H*), 5.99 (s, 4H, C*H*

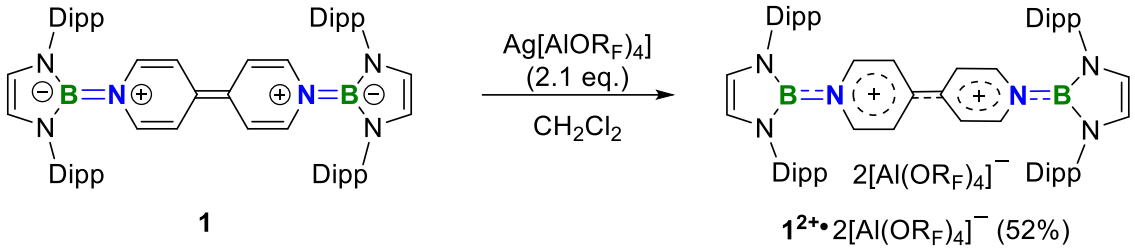
=C*H*), 5.35 (d, *J* = 6.0 Hz, 4H, C*H*=C*H*), 4.89 (d, *J* = 6.0 Hz, 4H, C*H*=C*H*), 3.08 (sep, 8H, $(CH_3)_2CH$), 1.17 (d, *J* = 6.0 Hz, 24H, CH $(CH_3)_2$), 1.16 (d, *J* = 6.0 Hz, 24H, CH $(CH_3)_2$); $^{13}C\{^1H\}$ NMR (THF-d_8, 400 MHz, 298 K): δ 146.64 (Ar-*C*), 139.52 (Ar-*C*), 128.21 (Ar-*C*H), 126.38 (*C*H=*C*H), 124.16 (Ar-*C*H), 118.98 (*C*H=*C*H), 110.05 (*C*=*C*), 108.97 (*C*H=*C*H), 29.05 ($(CH_3)_2CH$), 24.50 ($(CH_3)_2CH$), 23.50 ($(CH_3)_2CH$); $^{11}B\{^1H\}$ NMR (THF-d_8, 128 MHz, 298 K): δ 22.63 ppm; UV-vis (toluene): λ_{max} = 411 nm; Elemental analysis for $C_{62}H_{80}B_2N_6$ (%): Calculated: C 79.99, H 8.66, N 9.03; Found: C 80.13, H 8.71, N 8.88.

Synthesis of 1 $^+$[SbF$_6$]$^-$



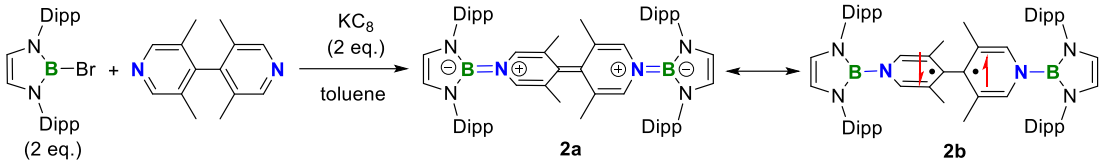
A 10 mL dichloromethane solution of $AgSbF_6$ (0.16 g, 0.48 mmol) was added dropwise into a dichloromethane (10 mL) solution of **1** (0.44 g, 0.48 mmol) at –30 °C. The color of the solution changed immediately from orange to purple. After slowly warm up to room temperature and stirring overnight, the solvent was removed under vacuum and the resulting residue was washed with hexane (10 ml). After filtration and removal of the solvent, **1 $^+$[SbF$_6$]$^-$** was obtained as an indigo powder (0.36 g, 66%). Single crystals of **1 $^+$[SbF$_6$]$^-$** suitable for X-ray diffraction studies were grown from the DCM/hexane solution at room temperature. UV-vis (DCM): λ_{max} = 564, 620, and 687 nm; Elemental analysis for $C_{62}H_{80}B_2F_6N_6Sb$ (%): Calculated: C 63.83, H 6.91, N 7.20; Found: C 63.61, H 6.79, N 7.32.

Synthesis of 1^{2+} ·2[Al(OC(CF$_3$)$_3$)$_4$]$^-$



A 10 mL dichloromethane solution of Ag[Al(OR$_F$)$_4$](RF= C(CF$_3$)$_3$) (0.49 g, 0.45 mmol) was added dropwise into a dichloromethane (10 mL) solution of **1** (0.20 g, 0.22 mmol) at –78 ºC. After slowly warm up to room temperature and stirring overnight, the solvent was removed under vacuum and the resulting residue was extracted with toluene (15 ml). After filtration and removal of the solvent, **1^{2+} ·2[Al(OC(CF$_3$)$_3$)$_4$]$^-$** was obtained as an indigo powder (0.32 g, 52%). Single crystals of **1^{2+} ·2[Al(OC(CF$_3$)$_3$)$_4$]$^-$** suitable for X-ray diffraction studies were grown from mixture DCM/hexane solution at room temperature. ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz, 298 K): δ 8.23 (d, *J* = 8.0 Hz, 4H, C*H*=C*H*), 7.80 (d, *J* = 4.0 Hz, 4H, C*H*=C*H*), 7.55 (t, *J* = 8.0 Hz, 4H, Ar-C*H*), 7.40 (d, *J* = 8.0 Hz, 8H, Ar-C*H*), 6.68 (s, 4H, C*H*=C*H*), 2.79 (sep, 8H, (CH$_3$)$_2$C*H*), 1.26 (d, *J* = 8.0 Hz, 24H, (C*H*$_3$)$_2$CH), 0.96 (d, *J* = 8.0 Hz, 24H, (C*H*$_3$)$_2$CH); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 100 MHz, 298 K): δ 148.98 (Ar-*C*), 145.16 (Ar-*C*), 144.73 (Ar-*C*H), 133.91 (*C*=*C*), 131.18 (Ar-*C*H), 126.54 (*C*H=*C*H), 126.15 (*C*H=*C*H), 123.15 (*C*H=*C*H), 120.19 (*C*F$_3$), 117.23 (*C*(CF$_3$)$_3$), 29.30 ((CH$_3$)$_2$*C*H), 24.65 ((*C*H$_3$)$_2$CH), 23.40 ((*C*H$_3$)$_2$CH); ^{11}B{^{1}H} NMR (CD$_2$Cl$_2$, 128 MHz, 298 K): δ 19.55 ppm; ^{19}F NMR (CD$_2$Cl$_2$, 377 MHz, 298 K): δ -75.62 ppm; ^{27}Al NMR (CD$_2$Cl$_2$, 104 MHz, 298 K): δ 34.63 ppm; UV-vis (DCM): λ_{max} = 580 nm; Elemental analysis for C$_{94}$H$_{80}$Al$_2$B$_2$F$_{72}$N$_6$O$_8$ (%): Calculated: C 39.41, H 2.81, N 2.93, O 4.47; Found: C 39.70, H 2.99, N 2.79, O 4.35.

Synthesis of 2



Potassium graphite (0.33 g, 2.43 mmol) was added to the toluene (20 mL) solution of $(HCNDipp)_2BBr$ (0.57 g, 1.21 mmol) and 3,3',5,5'-tetramethyl-4,4'-bipyridine (0.13 g, 0.61 mmol) at room temperature. After stirring for about twenty minutes, the color of the solution changed from yellow to purple and stirred for 24 h. After filtration, the precipitation was extracted with toluene (10 mL ×2). The solvent was removed under vacuum and the residue was recrystallization with hexane to afford **2** as a purple powder (0.30 g, 49%). Single crystals of **2** suitable for X-ray diffraction studies were grown from its saturated hexane solution at room temperature. ^{1}H NMR (C_6D_6, 300 MHz, 298 K): δ 7.20–7.16 (m, 4H, Ar-*H*), 7.10–7.08 (m, 8H, Ar-*H*), 5.95 (s, 4H, C*H*=C), 5.67 (s, 4H, C*H*=C*H*), 3.29 (sep, 8H, $(CH_3)_2CH$), 1.32 (s, 12H, CCH_3), 1.23 (d, J = 6.0 Hz, 24H, $CH(CH_3)_2$), 1.19 (d, J = 6.0 Hz, 24H, $CH(CH_3)_2$); $^{13}C\{^1H\}$ NMR (C_6D_6, 400 MHz, 298 K): δ 146.38 (Ar-*C*), 139.39 (Ar-*C*), 127.98 (Ar-*C*H), 124.85 (*C*H=C), 124.01 (*C*=*C*), 123.91 (Ar-*C*H), 118.71 (*C*H=*C*H), 119.60 (CH=*C*), 28.76 ($(CH_3)_2CH$), 24.75 ($(CH_3)_2CH$), 23.53 ($(CH_3)_2CH$), 19.24 (CCH_3); $^{11}B\{^1H\}$ NMR (C_6D_6, 128 MHz, 298 K): δ 21.53 ppm; UV-vis (toluene): λ_{max} = 527 nm; Elemental analysis for $C_{66}H_{88}B_2N_6$ (%): Calculated: C 80.31, H 8.99, N 8.51; Found: C 80.50, H 9.06, N 8.32.

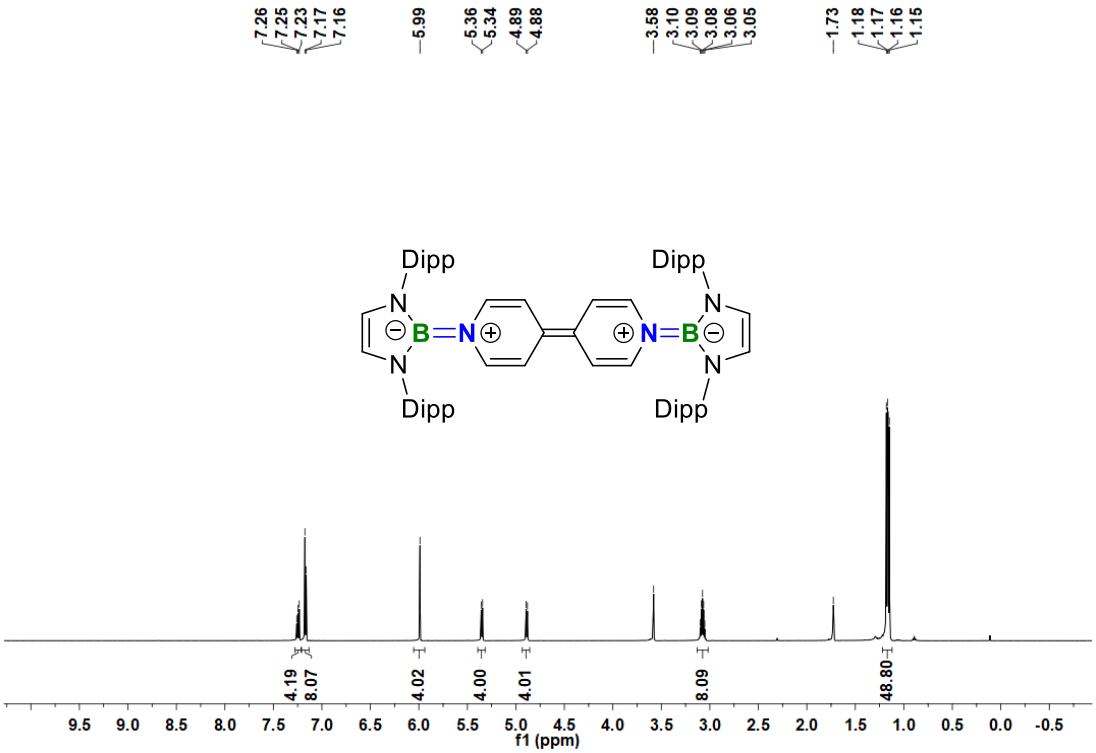


Fig. S1 ^{1}H NMR spectrum of **1** in THF-D_8 at 298 K.

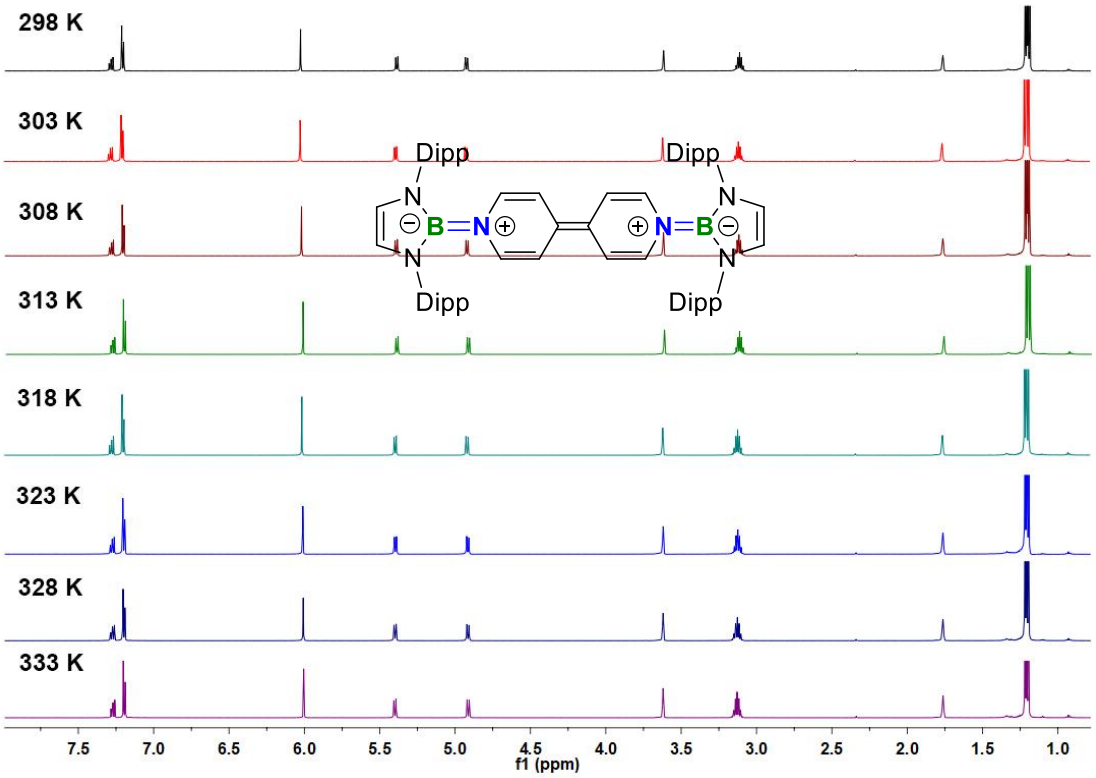


Fig. S2 ^{1}H VT-NMR spectrum of **1** in THF-D_8.

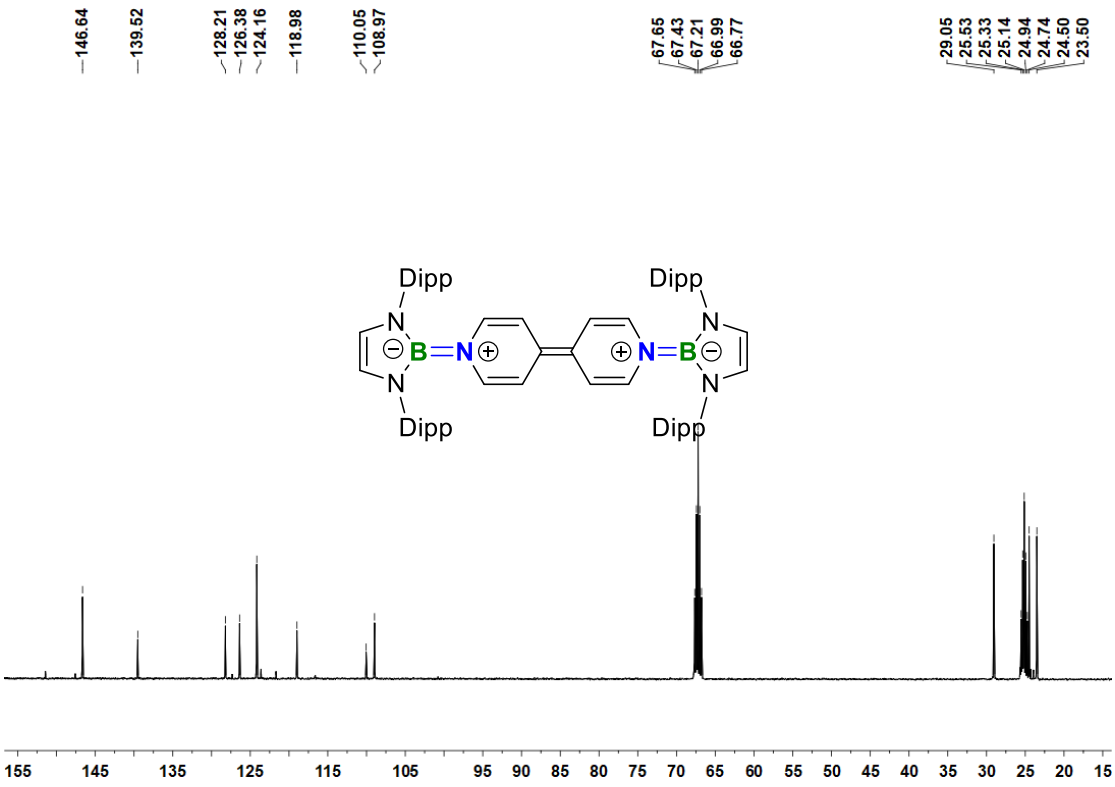


Fig. S3 $^{13}C\{^{1}H\}$ NMR spectrum of **1** in THF-D_8 at 298 K.

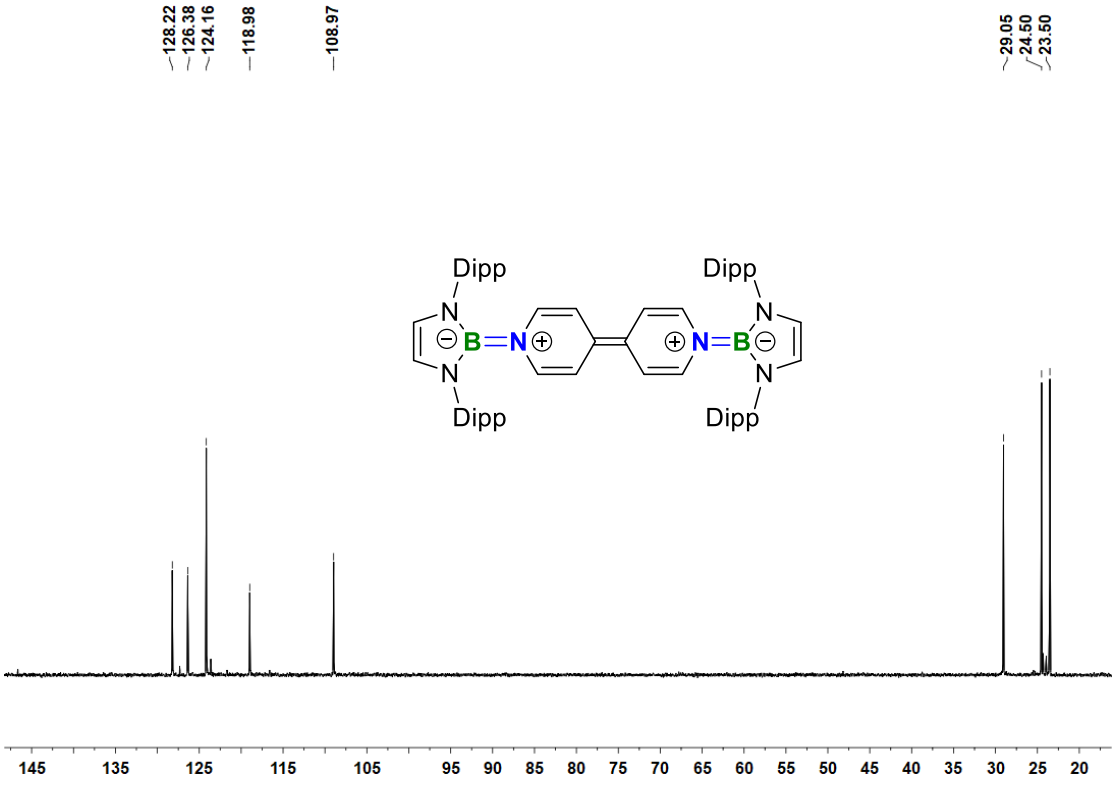


Fig. S4 $^{13}C\{DEPT135\}$ NMR spectrum of **1** in THF-D_8 at 298 K.

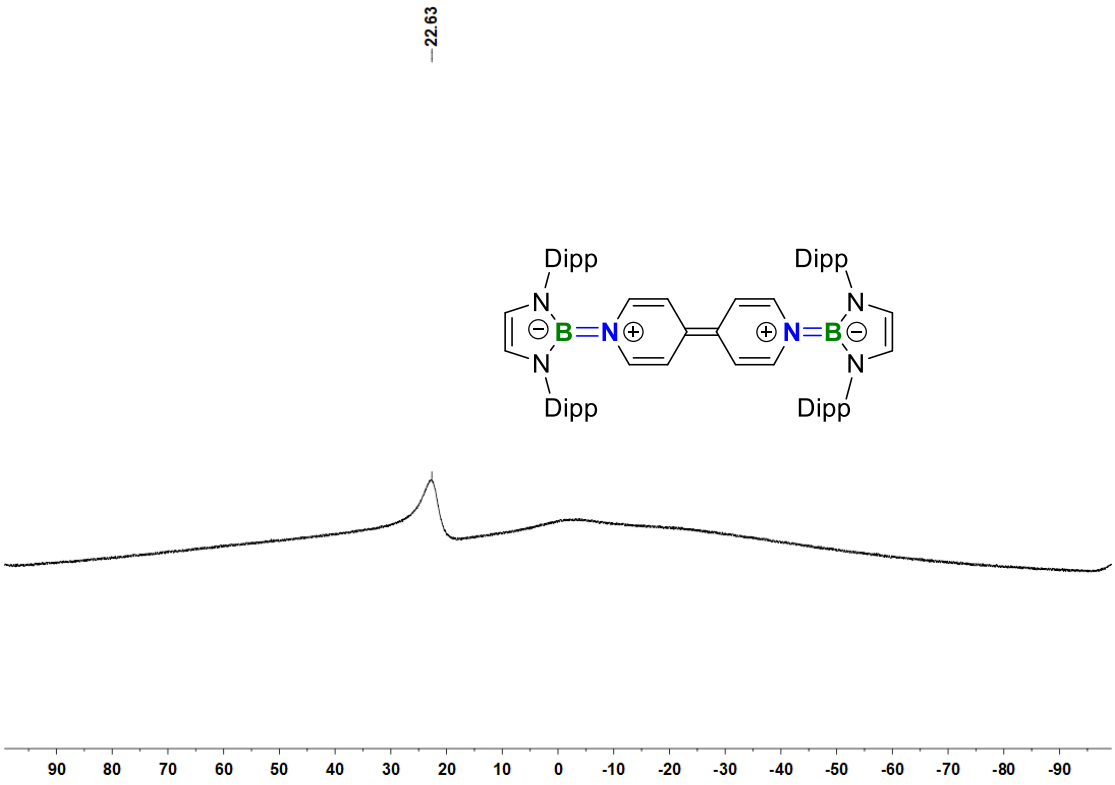


Fig. S5 $^{11}B\{^{1}H\}$ NMR spectrum of **1** in THF-D_8 at 298 K.

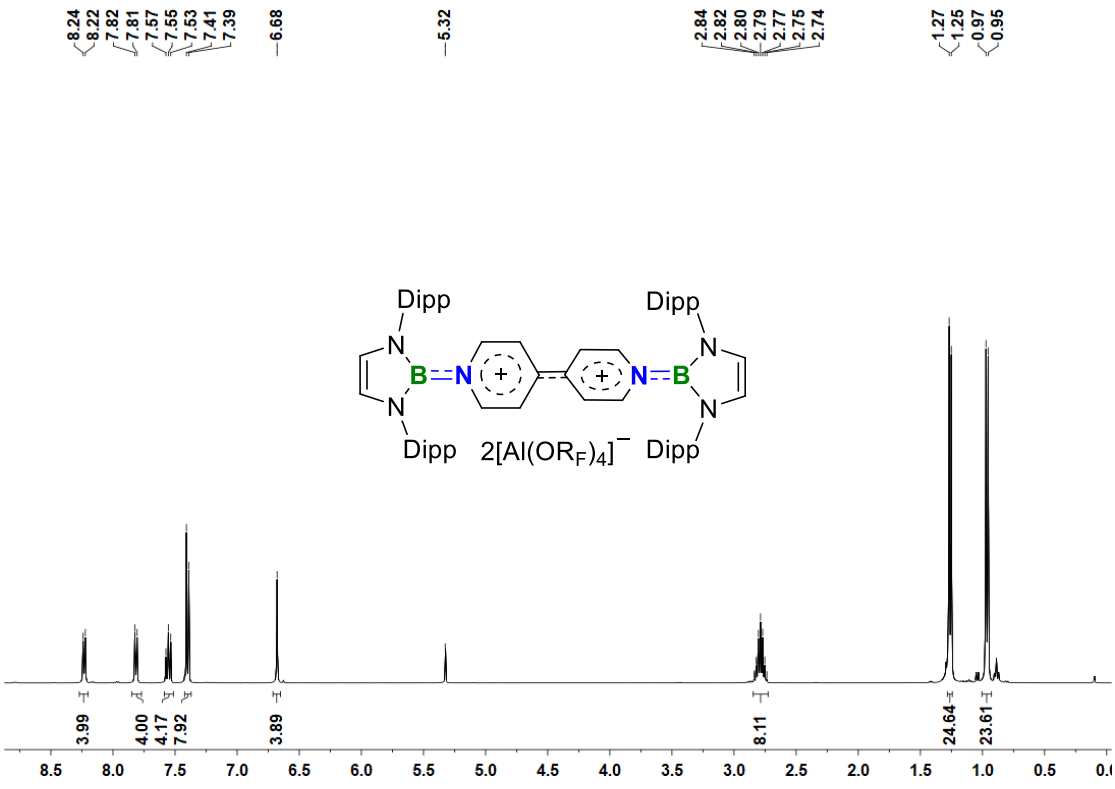


Fig. S6 ^{1}H NMR spectrum of $\mathbf{1}^{2+}$ **2[Al(OC(CF$_3$)$_3$)$_4$]**$^-$ in CD_2Cl_2 at 298 K.

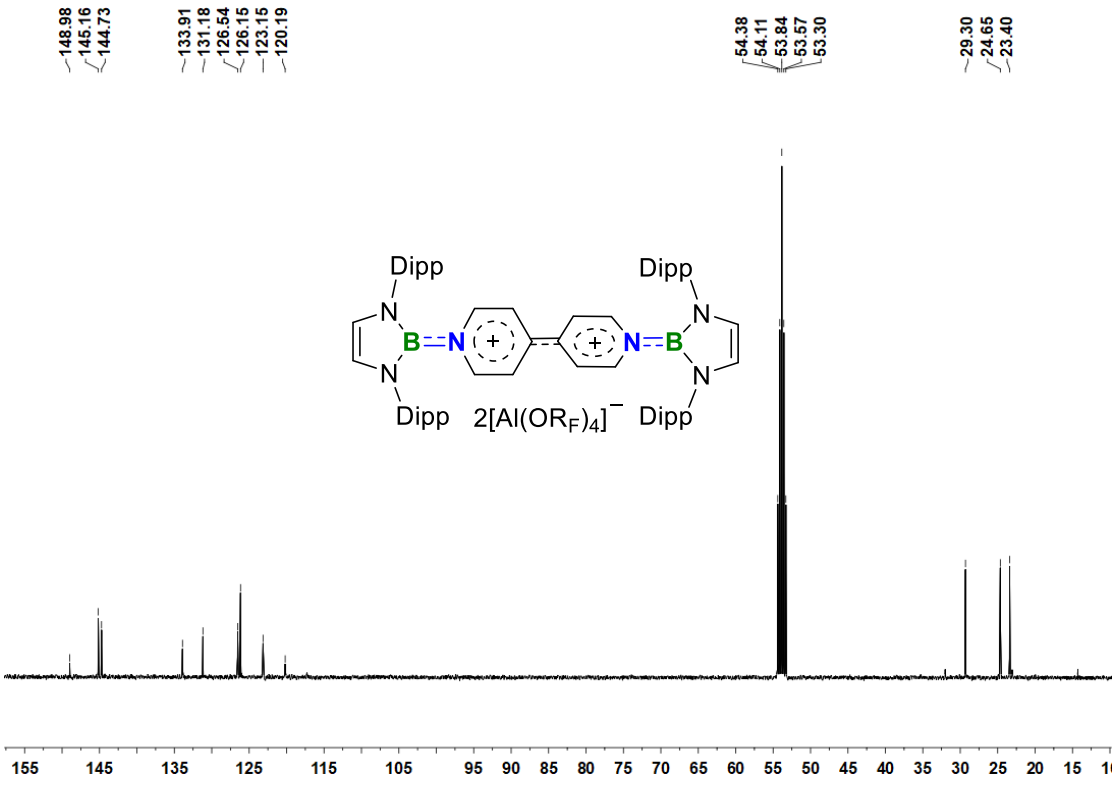


Fig. S7 $^{13}C\{^{1}H\}$ NMR spectrum of $\mathbf{1^{2+}}$ **2[Al(OC(CF$_3$)$_3$)$_4$]**$^-$ in CD_2Cl_2 at 298 K.

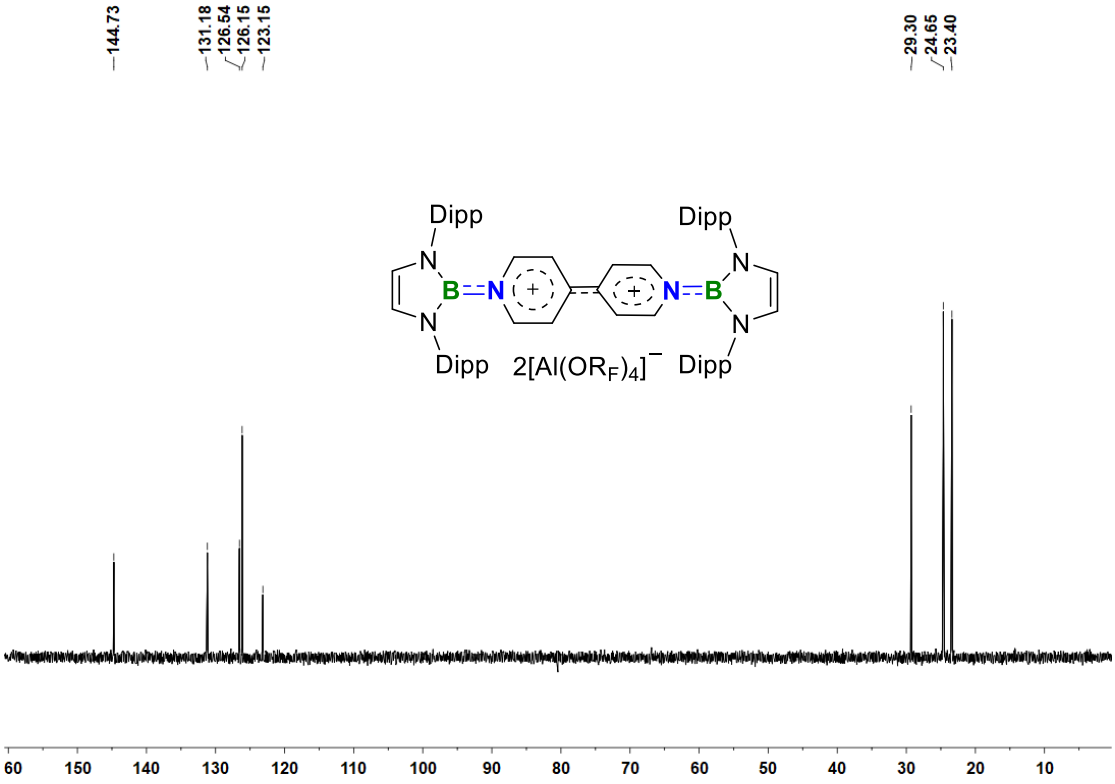


Fig. S8 $^{13}C\{DEPT135\}$ NMR spectrum of $\mathbf{1^{2+}}$ **2[Al(OC(CF$_3$)$_3$)$_4$]**$^-$ in CD_2Cl_2 at 298 K.

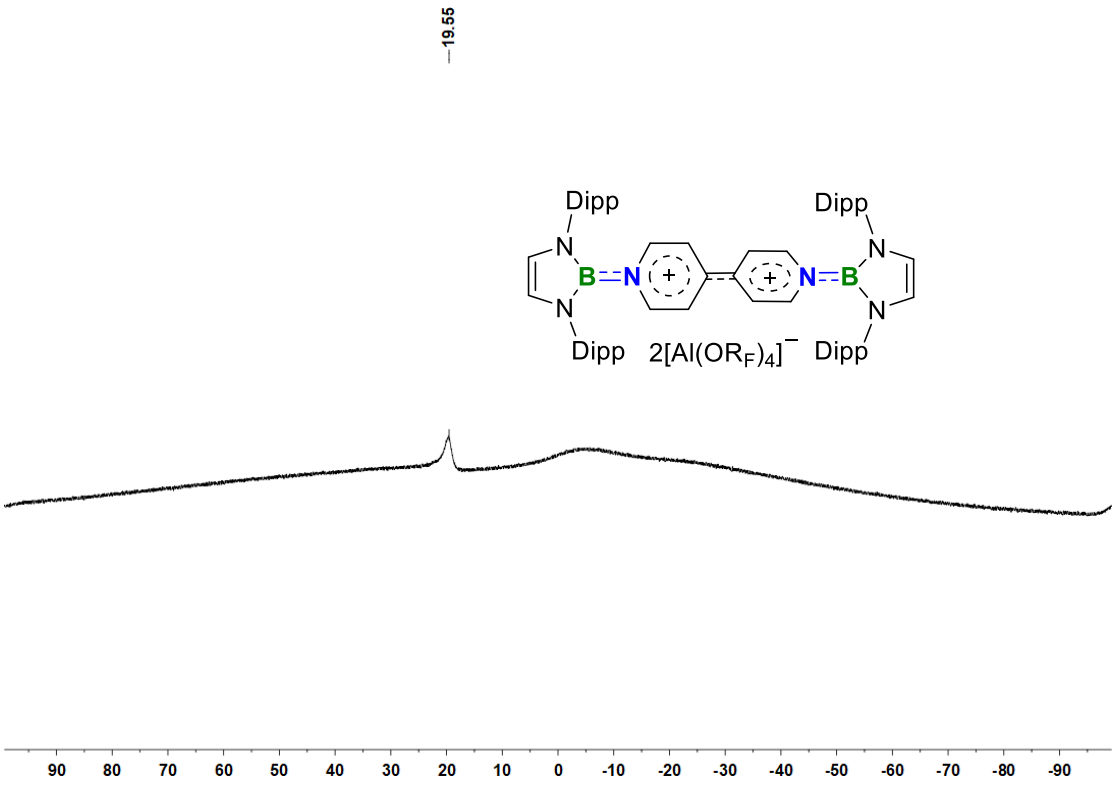


Fig. S9 $^{11}B\{^1H\}$ NMR spectrum of $\mathbf{1^{2+}\cdot 2[Al(OC(CF_3)_3)_4]^-}$ in CD_2Cl_2 at 298 K.

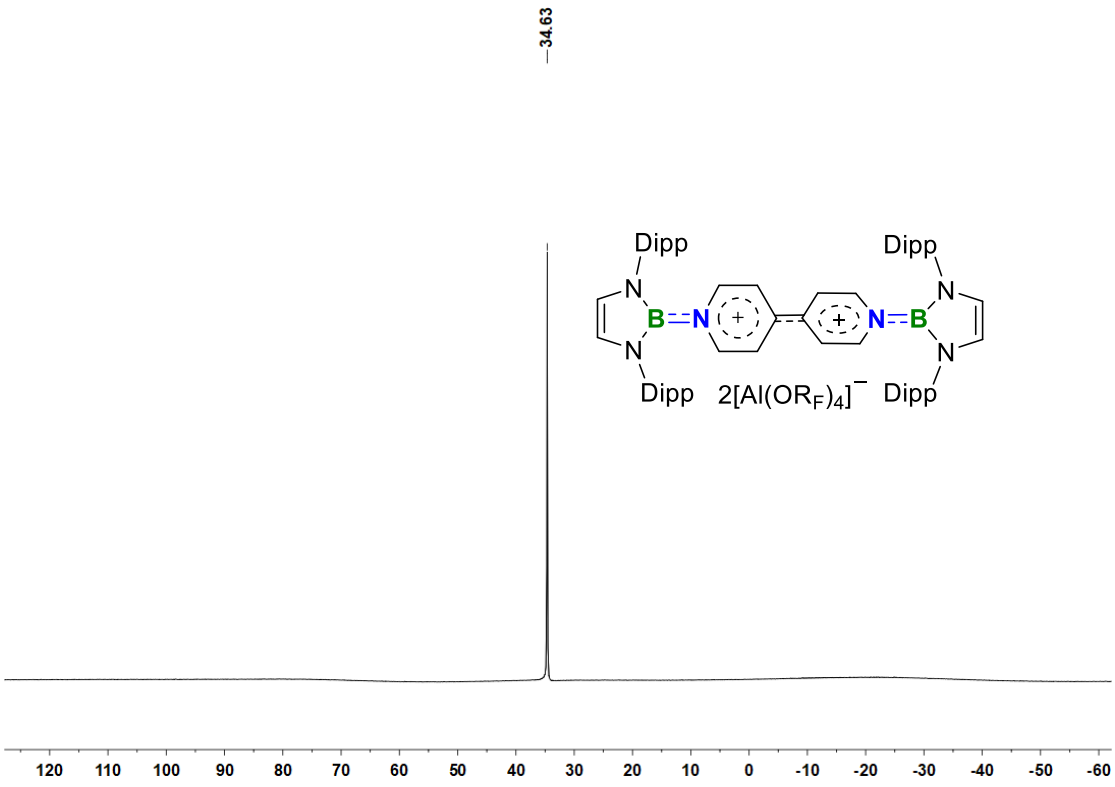


Fig. S10 ^{27}Al NMR spectrum of $\mathbf{1^{2+}\cdot 2[Al(OC(CF_3)_3)_4]^-}$ in CD_2Cl_2 at 298 K.

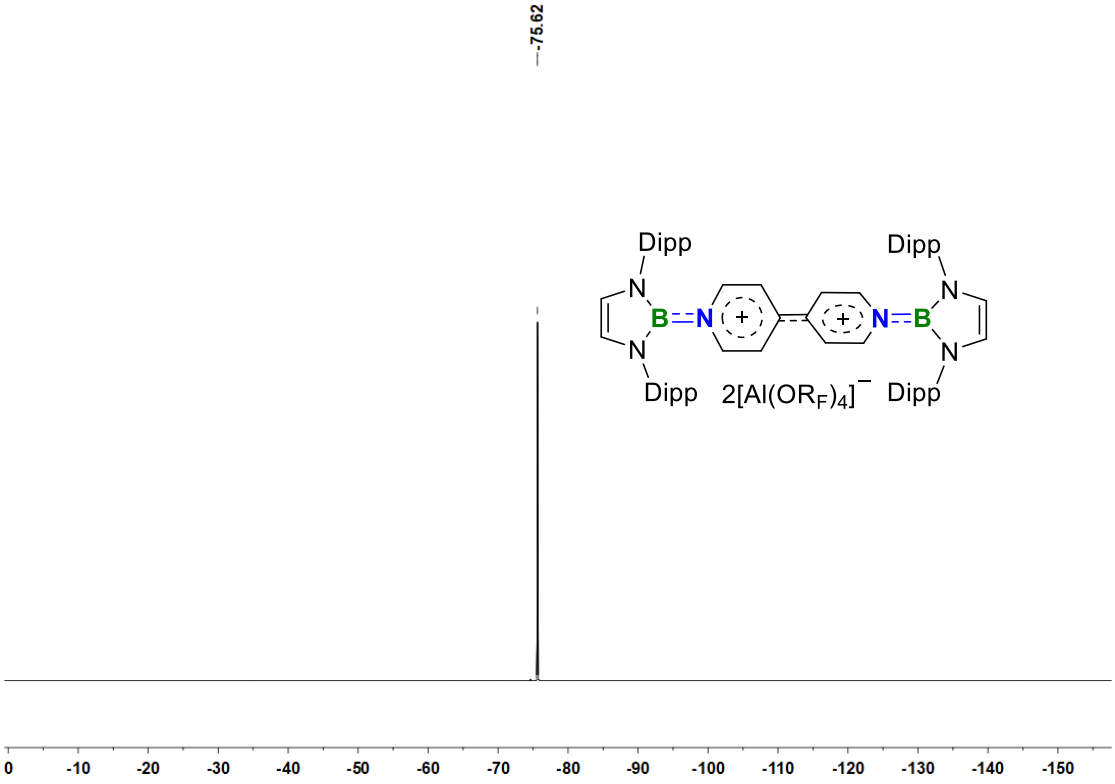


Fig. S11 ^{19}F NMR spectrum of $\mathbf{1}^{2+}$ $\mathbf{2[Al(OC(CF_3)_3)_4]^-}$ in CD_2Cl_2 at 298 K.

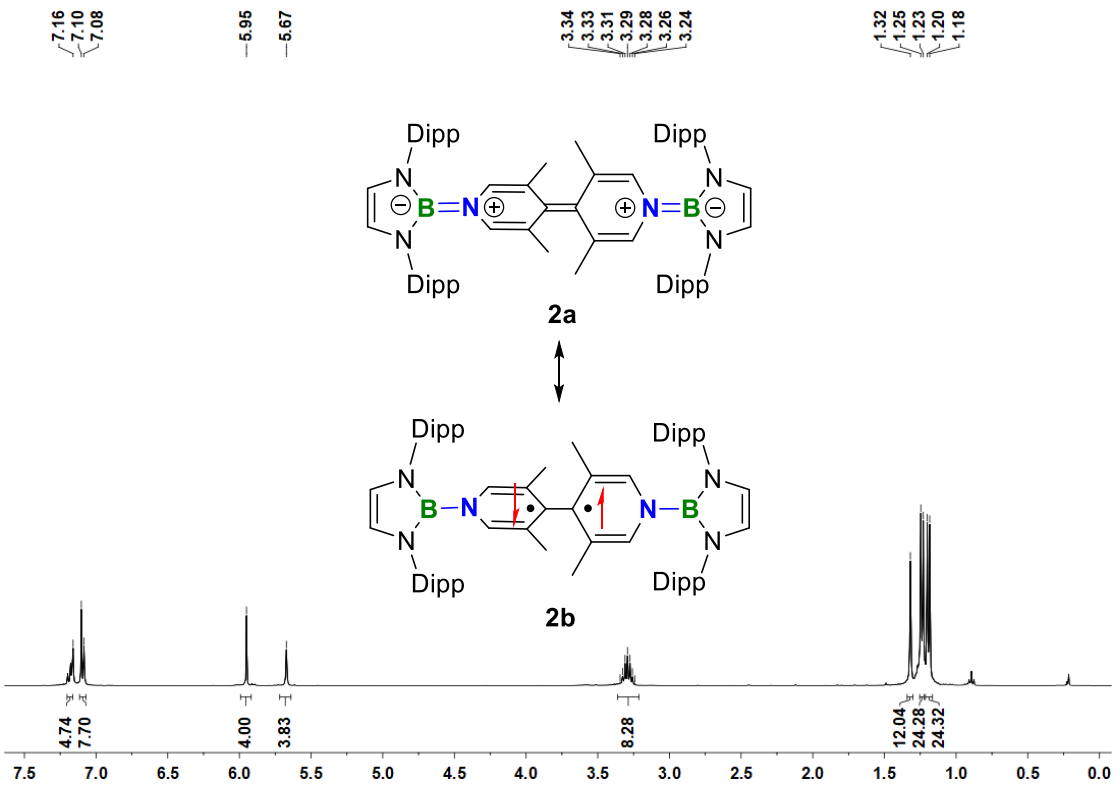


Fig. S12 ^{1}H NMR spectrum of **2** in C_6D_6 at 298 K.

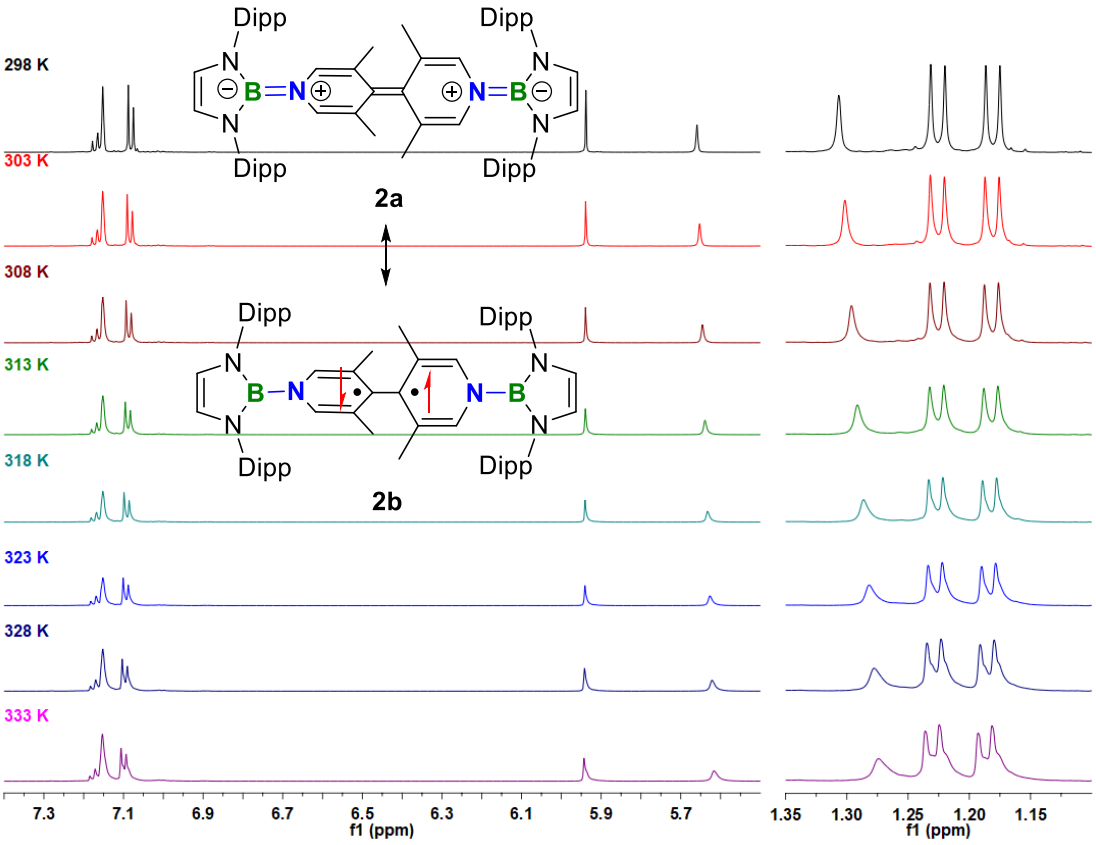


Fig. S13 ^{1}H VT-NMR spectrum of **2** in THF-D_8.

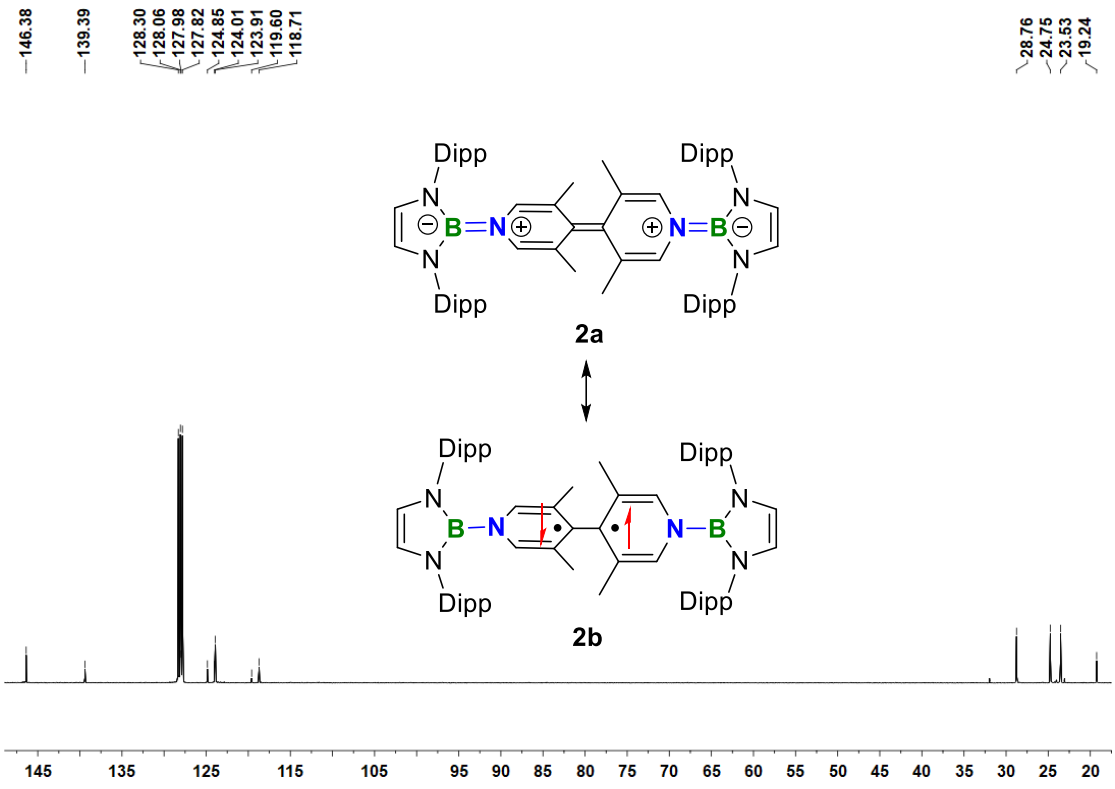


Fig. S14 $^{13}C\{^{1}H\}$ NMR spectrum of **2** in C_6D_6 at 298 K.

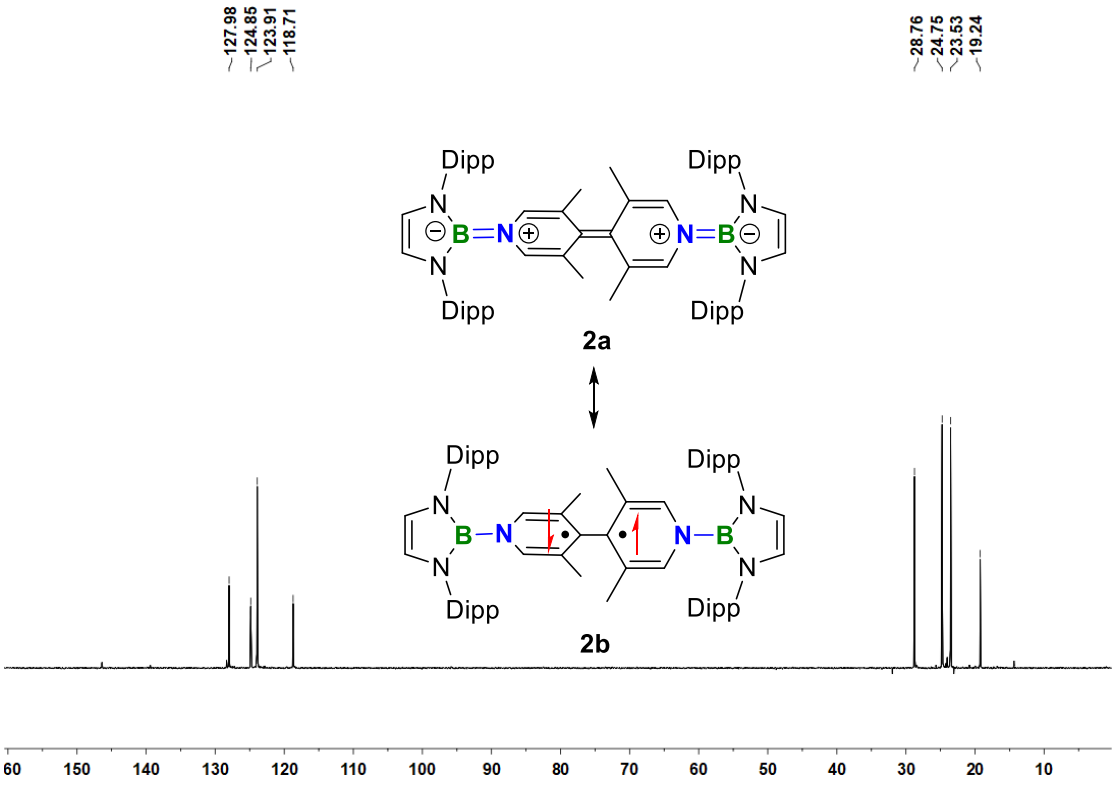


Fig. S15 $^{13}C\{DEPT135\}$ NMR spectrum of **2** in C_6D_6 at 298 K.

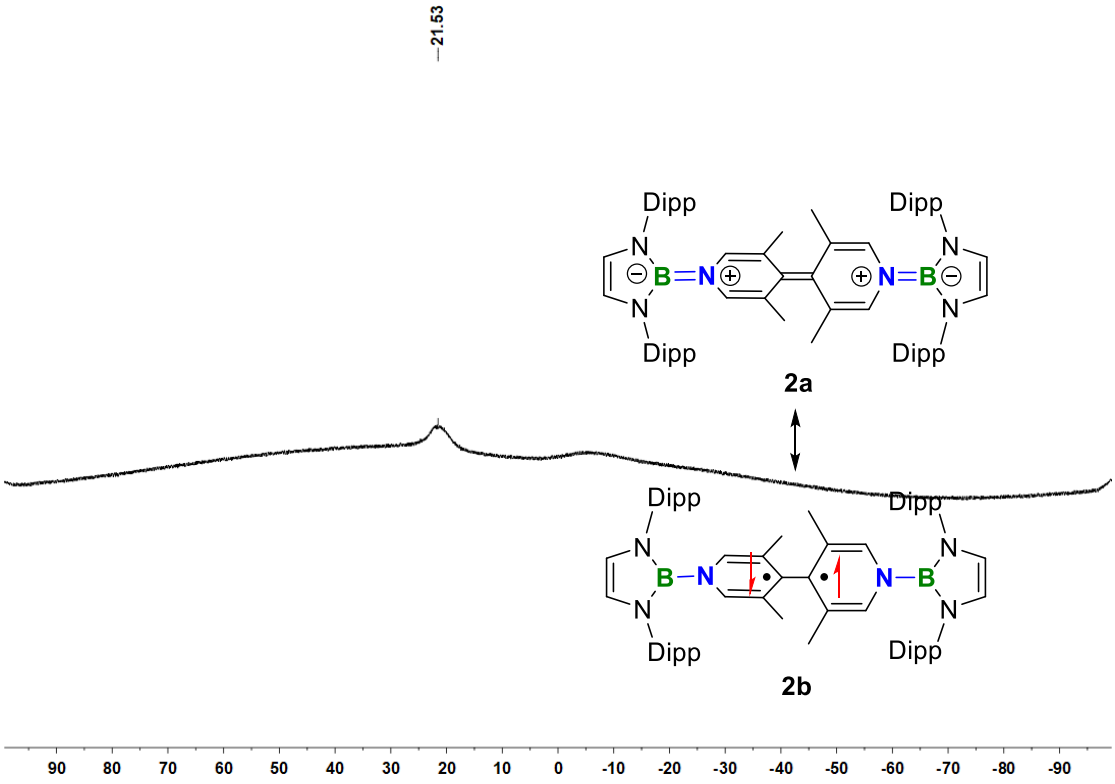


Fig. S16 $^{11}B\{^1H\}$ NMR spectrum of **2** in C_6D_6 at 298 K.

2. Crystal structural parameters

For the single crystal X-ray structure analyses the crystals were each mounted on a glass capillary in perfluorinated oil and measured in a cold N_2 flow. The data for all compounds were collected on the Bruker D8 CMOS detector at low temperatures. Using Olex2,[S3] the structures were solved with the SHELXT[S4] structure solution program and refined with the SHELXLS4 refinement package. The positions of the H atoms were calculated and considered isotropically according to a riding model. CCDC: 2205846–2205849 contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from the Cambridge Crystallography Data Center via www.ccdc.cam.ac.uk/data_request/cif

Table S1. Summary of data collection and structure refinement.

Compounds	**1•C_6H_6**	**$1^{+}[SbF_6]^{-}$**	**1^{2+}•2[$Al(OC(CF_3)_3)_4$]$^{-}$•2C_7H_8**	**2**
CCDC	2205846	2205848	2205849	2205847
Formula	$C_{68}H_{86}B_2N_6$	$C_{62}H_{80}B_2F_6N_6Sb$	$C_{108}H_{96}Al_2B_2F_{72}N_6O_8$	$C_{66}H_{88}B_2N_6$
F_w	1009.04	1166.69	3049.48	987.04
Crystal syst	triclinic	triclinic	monoclinic	monoclinic
Space group	P-1	P-1	P21/c	C2/c
Size, mm^3	0.1 ×0.12 ×0.15	0.1 ×0.11 ×0.16	0.2 ×0.22 ×0.24	0.13 ×0.16 ×0.18
T, K	131.0	138.0	120.0	135.0
a, Å	9.3498(8)	9.7065(10)	24.7100(12)	32.041(3)
b, Å	11.4321(10)	10.4206(11)	21.2756(10)	12.9784(11)
c, Å	15.5813(14)	16.6116(17)	24.7191(12)	16.7286(14)
α, deg	69.242(2)	73.769(4)	90	90
β, deg	84.549(2)	73.502(4)	98.219(2)	117.642(2)
γ, deg	77.162(2)	79.487(4)	90	90
V, $Å^3$	1518.2(2)	1537.1(3)	12861.8(11)	6162.5(9)
Z	1	1	4	4
dcalcd, g•cm^{-1}	1.104	1.260	1.575	1.064
μ, mm^{-1}	0.310	2.715	1.067	0.298
Reflections collected	22537	20897	204947	33194
Independent reflections	5342	5571	203898	5595
[R_{int}]	0.0466	0.0750	0.0815	0.0665
R_1[I>2sigma(I)]	0.0550	0.0637	0.1444	0.0644
wR_2[I>2sigma(I)]	0.1395	0.1782	0.3288	0.1693
R_1[all data]	0.0567	0.0690	0.1491[a]	0.0674
wR_2[all data]	0.1410	0.1815	0.3316[a]	0.1724
GOF	1.043	1.089	1.028	1.063
Largest diff. Peak/hole, e•$Å^{-3}$	0.45/-0.38	2.46/-1.27	1.48/-0.90	0.58/-0.50

[a] This is attributed to highly disordered solvent (toluene) molecules and two [$Al(OC(CF_3)_3)_4$]$^{-}$ anions in the structure. But such a disorder does not affect the structral identification of this dicationic salt, which has been also fully characterized by ^{1}H, ^{13}C, ^{11}B, ^{19}F, and ^{27}Al NMR spectra. Additionally, the geometry has been well reproduced by DFT calculations. We believe the key findings of the structural feature of this dicationic salt are unambiguous.

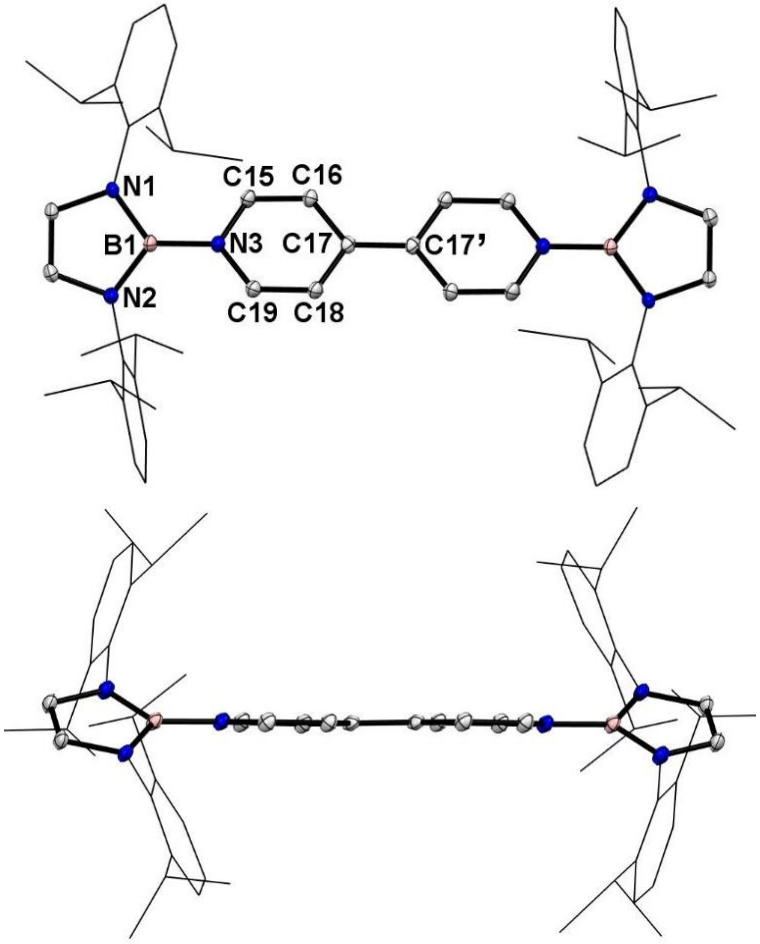


Fig. S17 Solid-state structures of **1** (top) with side view (bottom). Hydrogen atoms are omitted and Dipp groups are simplified as wireframes for clarity. Thermal ellipsoids are set at the 30% probability level. Selected bond lengths (Å) and angles (°): B1−N1 1.4340(18), B1−N2 1.4326(18), B1−N3 1.4340(18), N3−C15 1.4004(17), N3−C19 1.4028(17), C15−C16 1.3396(19), C18−C19 1.3444(19), C16−C17 1.4579(18), C17−C18 1.4536(18), C17−C17′ 1.374(2), N1–B1–N2 105.86(11), N1–B1–N3 128.26(12), N2–B1–N3 125.87(12).

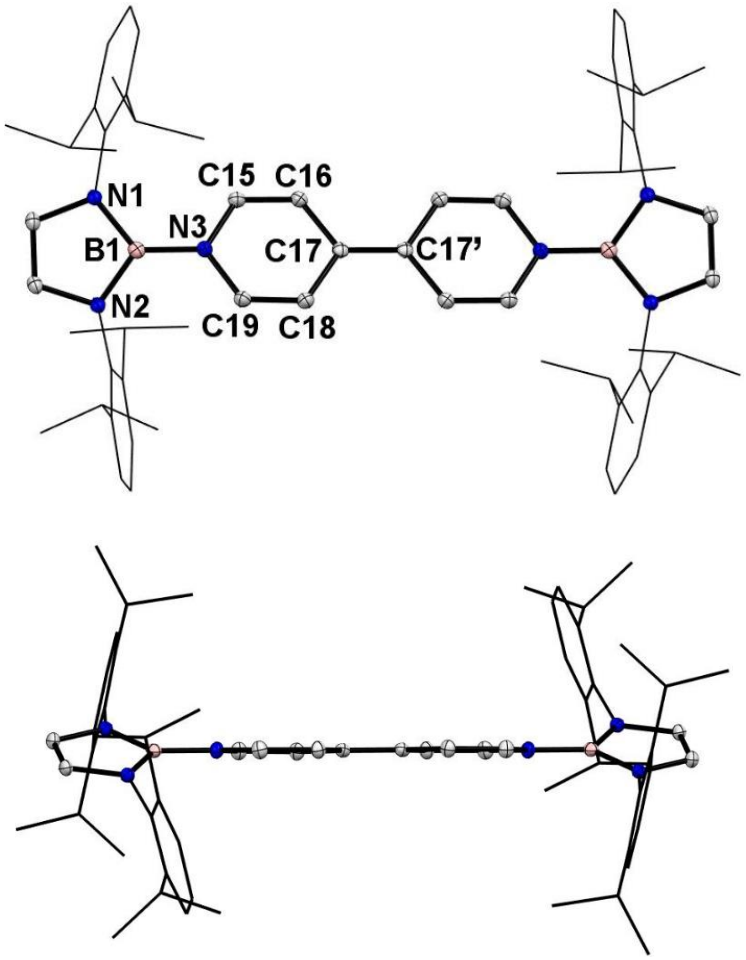


Fig. S18 Solid-state structures of $\mathbf{1}^{\bullet+}$ (top) with side view (bottom). Hydrogen atoms are omitted and Dipp groups are simplified as wireframes for clarity. Thermal ellipsoids are set at the 30% probability level. Selected bond lengths (Å) and angles (°): B1−N1 1.424(5), B1−N2 1.423(5), B1−N3 1.476(5), N3−C15 1.380(5), N3−C19 1.377(4), C15−C16 1.350(5), C18−C19 1.359(5), C16−C17 1.426(5), C17−C18 1.427(5), C17−C17′ 1.424(7), N1–B1–N2 107.0(3), N1–B1–N3 126.5(3), N2–B1–N3 126.5(3).

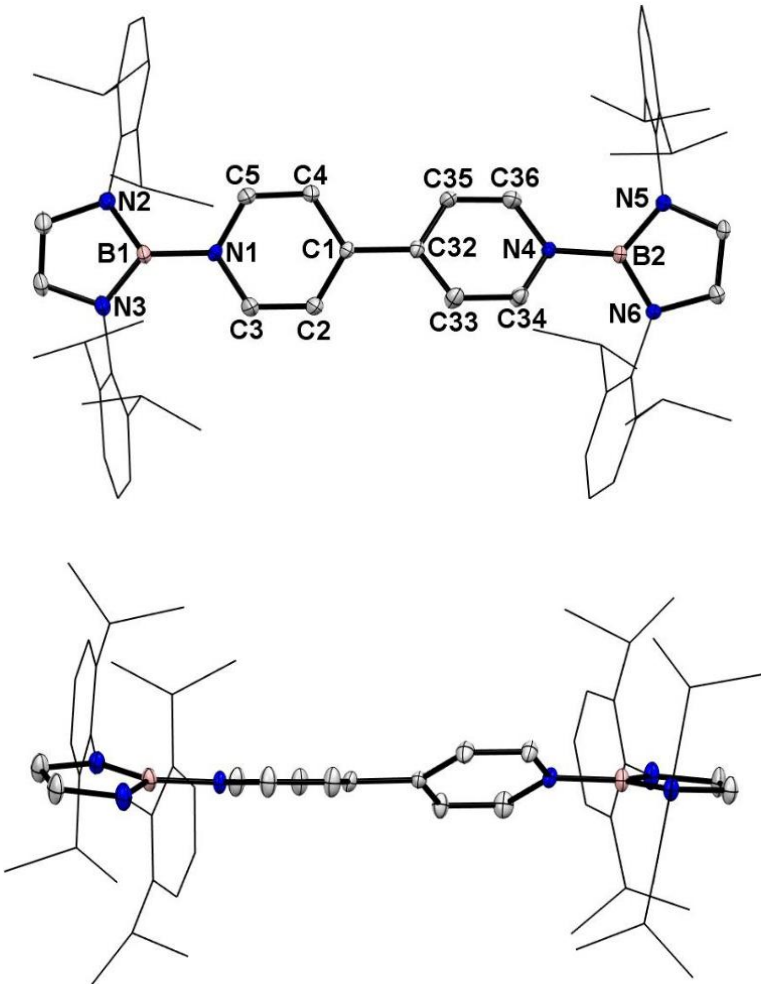


Fig. S19 Solid-state structures of $\mathbf{1}^{2+}$ (top) with side view (bottom). Hydrogen atoms are omitted and Dipp groups are simplified as wireframes for clarity. Thermal ellipsoids are set at the 30% probability level. Selected bond lengths (Å) and angles (°): B1−N1 1.514(9), B1−N2 1.406(10), B1−N3 1.398(9), B2−N3 1.398(9), B2−N4 1.508 (8), B2−N6 1.411(9), N1−C3 1.349(9), N1−C5 1.358(9), N4−C34 1.343(9), N4−C36 1.402(9), C1−C2 1.360(9), C1−C4 1.403(9), C2−C3 1.363(10), C4−C5 1.357(10), C32C33 1.386(9), C32C35 1.408(9), C33−C34 1.371(10), C35−C36 1.338(10), C1−C32 1.479(8), N1–B1–N2 125.1(6), N1–B1–N3 127.1(7), N2–B1–N3 107.7(6), N4–B2–N5 127.2(6), N4–B2–N6 124.7(6), N5–B2–N6 108.1(5).

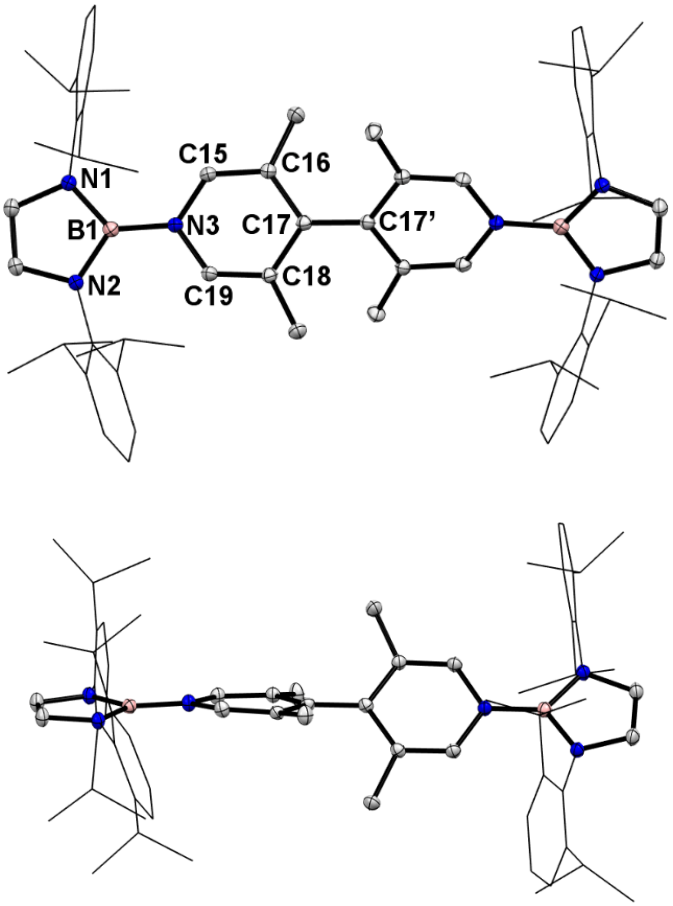


Fig. S20 Solid-state structures of **2** (top) with side view (bottom). Hydrogen atoms are omitted and Dipp groups are simplified as wireframes for clarity. Thermal ellipsoids are set at the 30% probability level. Selected bond lengths (Å) and angles (°): B1−N1 1.434(2), B1−N2 1.439(2), B1−N3 1.451(2), N3−C15 1.3989(19), N3−C19 1.4008(19), C15−C16 1.353(2), C18−C19 1.347(2), C16−C17 1.460(2), C17−C18 1.455(2), C17−C17′ 1.417(3), N1–B1–N2 105.25(13), N1–B1–N3 128.58(14), N2–B1–N3 126.17(14).

3.

3. VT-EPR spectra of 2 in toluene

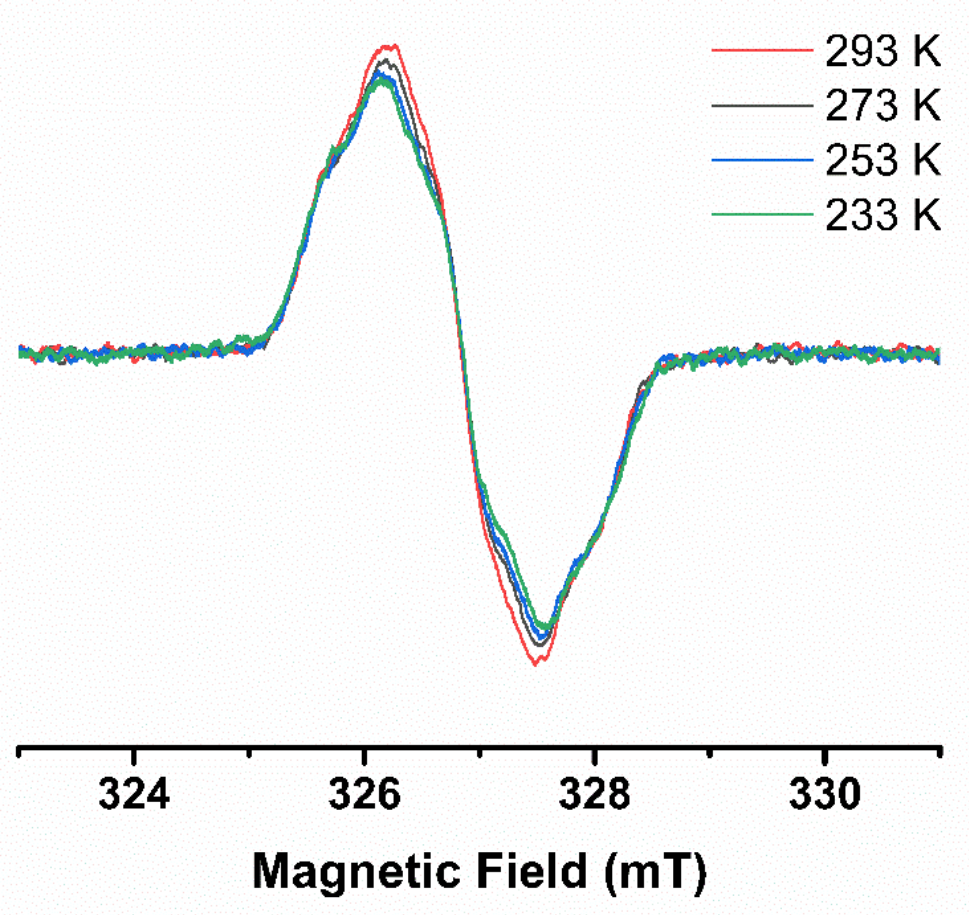


Fig. S21 VT-EPR spectra of **2** in toluene.

4. Theoretical calculations

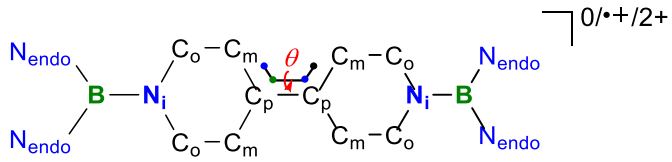
The calculations were performed with the Gaussian 16 program.[S5] For gometry optimizations and frequency calculations on the simplified model **1′** and **2′**, in which the Dipp groups were replaced with the phenyls, three electronic states (closed-shell singlet (CS), open-shell singlet (OS), and triplet (T) state) with the (U)B3LYP, (U)BH&HLYP, and (U)PBE0 functional and Def2SVP and 6-311G(d) basis-sets were considered. The diradical character for **2′** was calculated at the UBH&HLYP/def2-SVP level. Gometry optimizations and frequency calculations for $\mathbf{1}^{+}$ and $\mathbf{1}^{2+}$ were performed at the (U)B3LYP/6-311G(d) level. TD-DFT, NICS, and natural bond orbital (NBO) calculations were conducted under the UB3LYP/6-311G(d) level of theory. The calculated Kohn-Sham orbitals related to the

observed transitions are shown in Tables S8-S11. To gain further insight into the electronic structures, Multiwfn[S6] and VMD[S7] were also used.

Table S2. Electronic energies (E in Hartrees) and relative electronic energies ($\Delta E_{CS\text{-}T}$ in kcal/mol) of **1′** in closed-shell singlet (CS) and triplet (T) states.

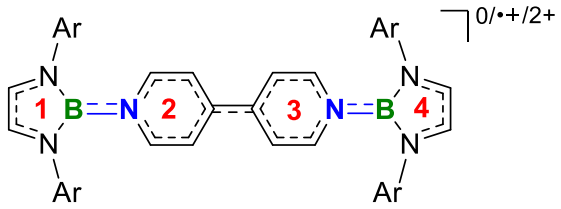
Methods	E_{CS}	E_T	$\Delta E_{CS\text{-}T}$
B3LYP/6-311G(d)	-1845.438394	-1845.392669	-28.69
BH&HLYP/6-311G(d)	-1844.272981	-1844.233030	-25.07
BH&HLYP/def2-SVP	-1842.596472	-1842.556486	-25.09
PBE0/def2-SVP	-1841.596450	-1841.551817	-28.01

Table S3. Experimental and calculated bond lengths (avg., Å) and angles of **1**, **1**$^{+}$, and **1**$^{2+}$ at the (U)B3LYP/6-311G(d) level**.**



	1$_{exp}$	**1′**$_{CS}$	**1′**$_{T}$	**1**$^{+}_{exp}$	**1**$^{+}_{cal}$	**1**$^{2+}_{exp}$	**1**$^{2+}_{cal}$
$B–N_{endo}$	1.4340(18)	1.4481	1.4500	1.424(5)	1.4331	1.407(9)	1.4295
$B–N_i$	1.4033(18)	1.4543	1.4542	1.476(5)	1.4890	1.511(8)	1.5045
$N_i–C_o$	1.4016(18)	1.4027	1.4100	1.378(4)	1.3791	1.363(9)	1.3647
$C_o–C_m$	1.3420(19)	1.3476	1.3634	1.354(5)	1.3619	1.357(10)	1.3765
$C_m–C_p$	1.4558(18)	1.4561	1.4221	1.426(5)	1.4294	1.389(9)	1.4050
$C_p–C_p$	1.374(2)	1.3829	1.4808	1.424(7)	1.4279	1.479(8)	1.4729
BLA	0.0867(18)	0.0818	0.0527	0.048(5)	0.0423	0.019(9)	0.0084
θ	0	0	67.5	0	0	27.5	30.4

Table S4. NICS values for **1′** and **1**$^{+}$and **1**$^{2+}$ calculated at the (U)B3LYP/6-311G(d) level.



	1′	**1**$^{+}$	**1**$^{2+}$
Ring 1 NICS (0)	-8.1933	-8.8637	-12.9781
Ring 1 NICS (1)	-4.2853	-5.1200	-5.3309
Ring 1 NICS (1)$_{zz}$	-15.0098	-17.2694	-17.3682
Ring 2 NICS (0)	1.7625	-4.7459	-5.5317
Ring 2 NICS (1)	1.3514	-3.5568	-8.0522
Ring 2 NICS (1)$_{zz}$	9.9999	-4.2387	-17.8129
Ring 3 NICS (0)	1.7625	-4.7459	-5.3786
Ring 3 NICS (1)	1.3514	-3.5568	-7.9972
Ring 3 NICS (1)$_{zz}$	9.9999	-4.2387	-17.9567
Ring 4 NICS (0)	-8.1933	-8.8637	-11.4110
Ring 4 NICS (1)	-4.2853	-5.1200	-5.3679
Ring 4 NICS (1)$_{zz}$	-15.0098	-17.2694	-17.3583

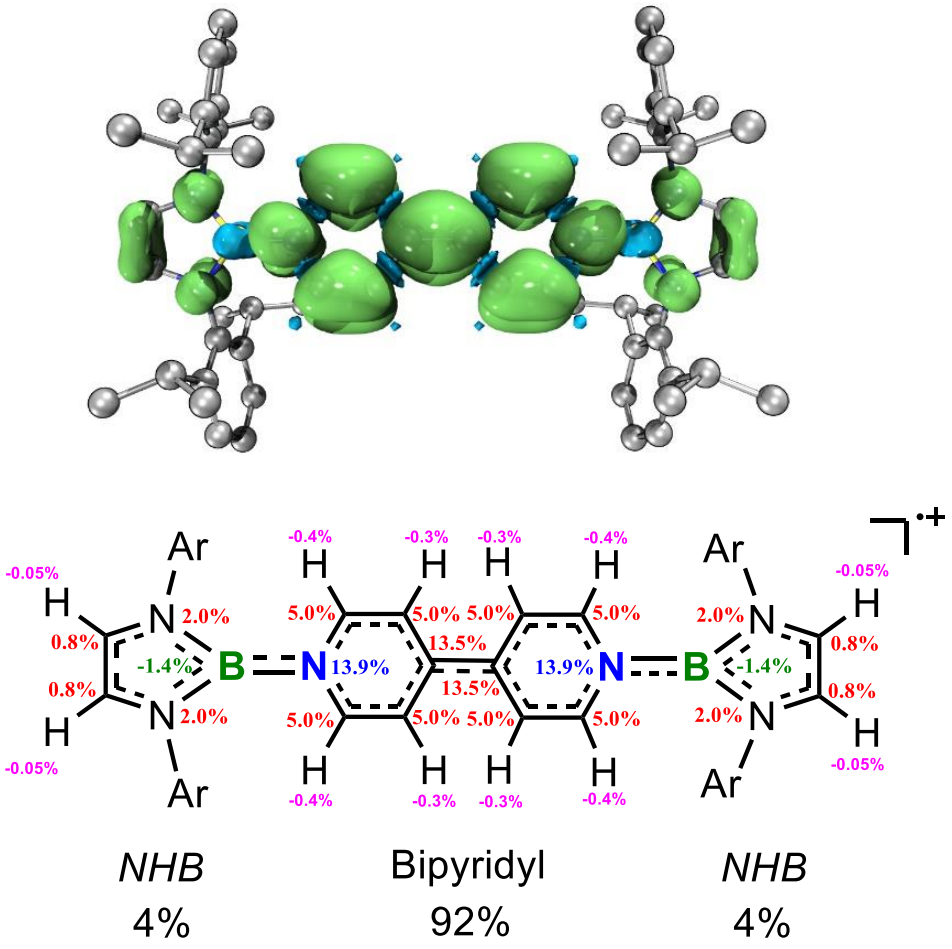
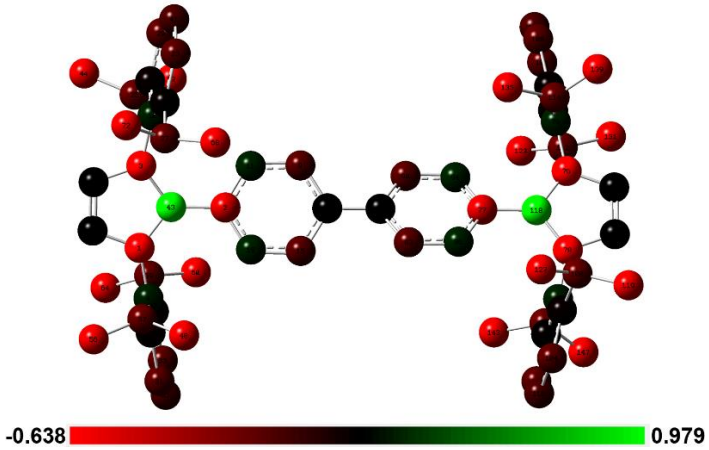


Fig S22. The calculated spin density map of $\mathbf{1}^{\cdot+}$.

Table S5. Selected data of NPA charges of $\mathbf{1}^{2+}$



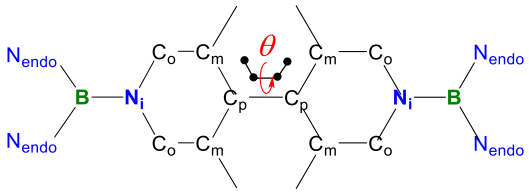
Natural Population

Atom	No	Natural Charge	Core	Valence	Rydberg	Total
N	1	-0.63788	1.99913	5.62807	0.01069	7.63788
N	2	-0.51390	1.99916	5.50352	0.01122	7.51390
N	3	-0.63788	1.99913	5.62807	0.01069	7.63788
C	5	-0.00033	1.99894	3.98451	0.01688	6.00033
C	6	-0.00266	1.99909	3.98344	0.02013	6.00266
C	8	-0.19320	1.99902	4.17954	0.01464	6.19320
C	11	0.12245	1.99909	3.85802	0.02043	5.87755
C	13	-0.00266	1.99909	3.98344	0.02013	6.00266
C	15	-0.19320	1.99902	4.17954	0.01464	6.19320
C	19	0.12245	1.99909	3.85802	0.02043	5.87755
B	43	0.97831	1.99854	1.99962	0.02353	4.02169
N	76	-0.63828	1.99912	5.62847	0.01068	7.63828
N	77	-0.51405	1.99916	5.50368	0.01121	7.51405
N	78	-0.63828	1.99912	5.62847	0.01068	7.63828
C	80	-0.00008	1.99894	3.98426	0.01688	6.00008
C	81	-0.00334	1.99909	3.98413	0.02012	6.00334
C	83	-0.19345	1.99902	4.17984	0.01460	6.19345
C	86	0.12314	1.99909	3.85749	0.02028	5.87686
C	88	-0.00334	1.99909	3.98413	0.02012	6.00334
C	90	-0.19345	1.99902	4.17984	0.01460	6.19345
C	94	0.12314	1.99909	3.85749	0.02028	5.87686

Table S6. Electronic energies (E in Hartrees) and relative electronic energies ($\Delta E_{CS\text{-}T}$ in kcal/mol) of **2′** in closed-shell singlet (CS) and open-shell singlet (OS) and triplet (T) states at BH&HLYP/def2-SVP.

State	E	$<S^2>$	$\Delta E_{X\text{-}OS}$
CS	-1999.483034	0	6.82
OS	-1999.492838	1.0248	0
T	-1999.491710	2.1131	1.37

Table S7. Experimental and calculated bond lengths (avg., Å) of **2′** at the (U)BH&HLYP/def2-SVP level.



	2-exp	**2′-CS**	**2′-OS**	**2′-T**
$B–N_{endo}$	1.436(2)	1.4392	1.4402	1.4404
$B–N_i$	1.451(2)	1.4481	1.4473	1.4476
$N_i–C_o$	1.400(2)	1.3835	1.3942	1.3955
$C_o–C_m$	1.350(2)	1.3460	1.3590	1.3609
$C_m–C_p$	1.458(2)	1.4741	1.4353	1.4293
$C_p–C_p$	1.417(3)	1.3981	1.4712	1.4836
BLA	0.079(2)	0.0828	0.0558	0.0515
θ	53.2	44.6	72.7	89.53

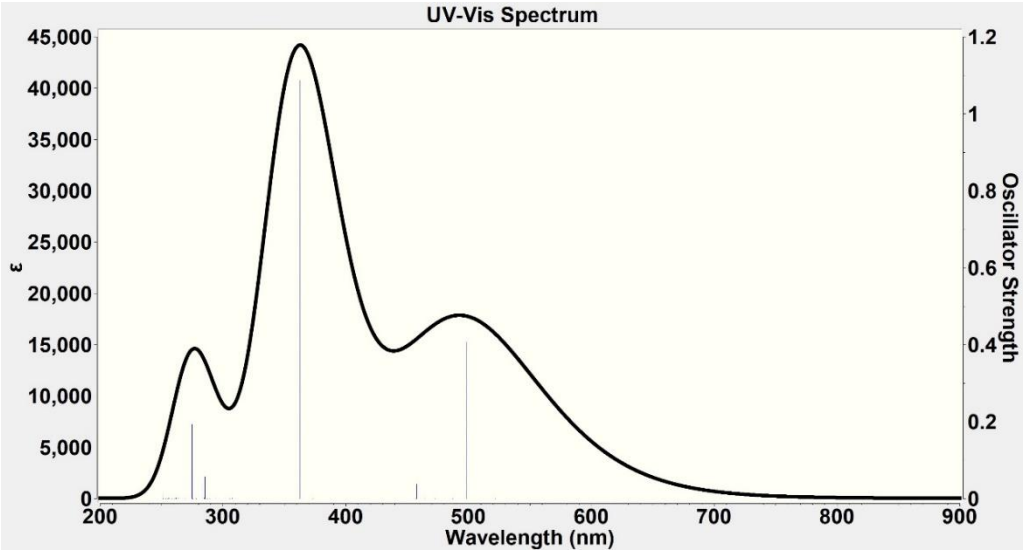


Fig S23. Calculated UV-vis spectrum of **1′** at the TD-DFT//B3LYP/6-311G(d) level.

Table S8. Calculated absorption properties of **1′** including wavelength (nm), oscillator strength (f) and the related transition nature.

Energy/ ev	Wavelength/ nm	Oscillator strength/ f	Transition nature
2.4870	498.52	0.4061	HOMO→LUMO (0.67138) HOMO→LUMO+8 (0.20438)
3.4178	362.76	1.0683	HOMO→LUMO (-0.19715) HOMO→LUMO+8 (0.66115)

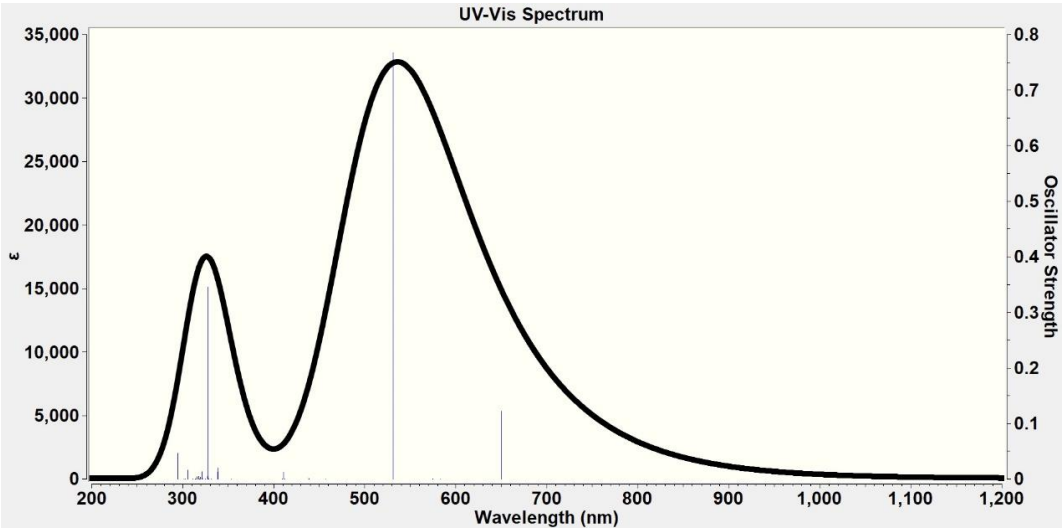


Figure S24. Calculated UV-vis spectrum of $\mathbf{1}^{+}$ at the TD-DFT//UB3LYP/6-311G(d) level.

Table S9. Calculated absorption properties of $\mathbf{1}^{+}$ including wavelength (nm), oscillator strength (f) and the related transition nature.

Energy/ ev	Wavelength /nm	Oscillator strength/ f	Transition nature
1.9073	650.06	0.1224	SOMO-1 (β)→SOMO (β) (0.95814) SOMO (α)→LUMO (α) (0.25532)
2.3344	531.11	0.7675	SOMO (α)→LUMO (α) (0.93472) SOMO−1 (β)→SOMO (β) (-0.25217)
3.7800	328.00	0.3460	SOMO−13 (β)→SOMO (β) (0.86836) SOMO−2 (β)→LUMO+1 (β) (0.25715)

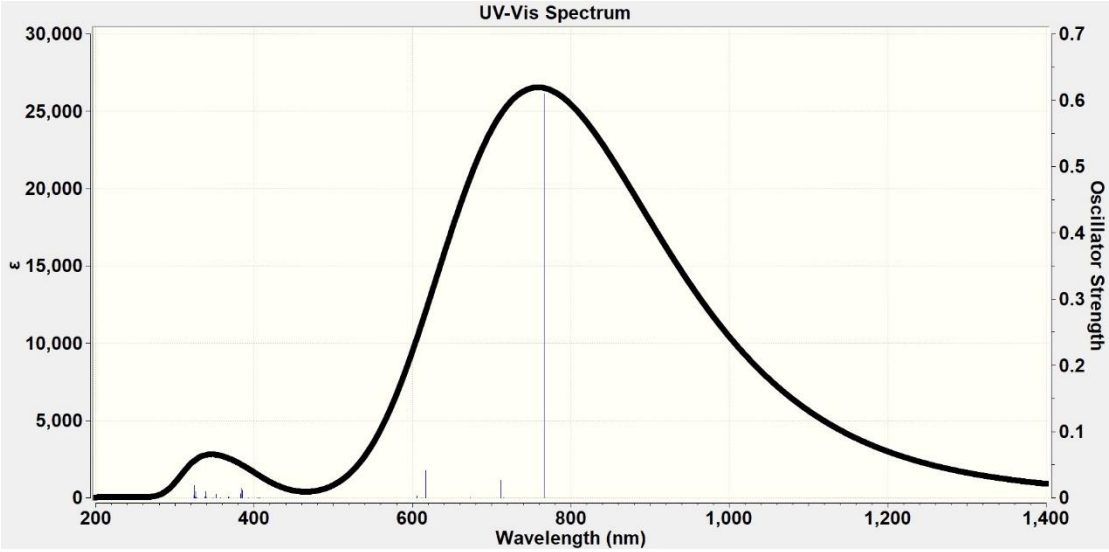


Figure S25. Calculated UV-vis spectrum of $\mathbf{1}^{2+}$ at the TD-DFT//UB3LYP/6-311G(d) level.

Table S10. Calculated absorption properties of $\mathbf{1}^{2+}$ including wavelength (nm), oscillator strength (f) and the related transition nature

Energy/ ev	Wavelength /nm	Oscillator strength/ f	Transition nature
1.6180	766.29	0.6100	HOMO→LUMO (0.69804)
2.0107	616.62	0.0412	HOMO−6→LUMO (0.69906)

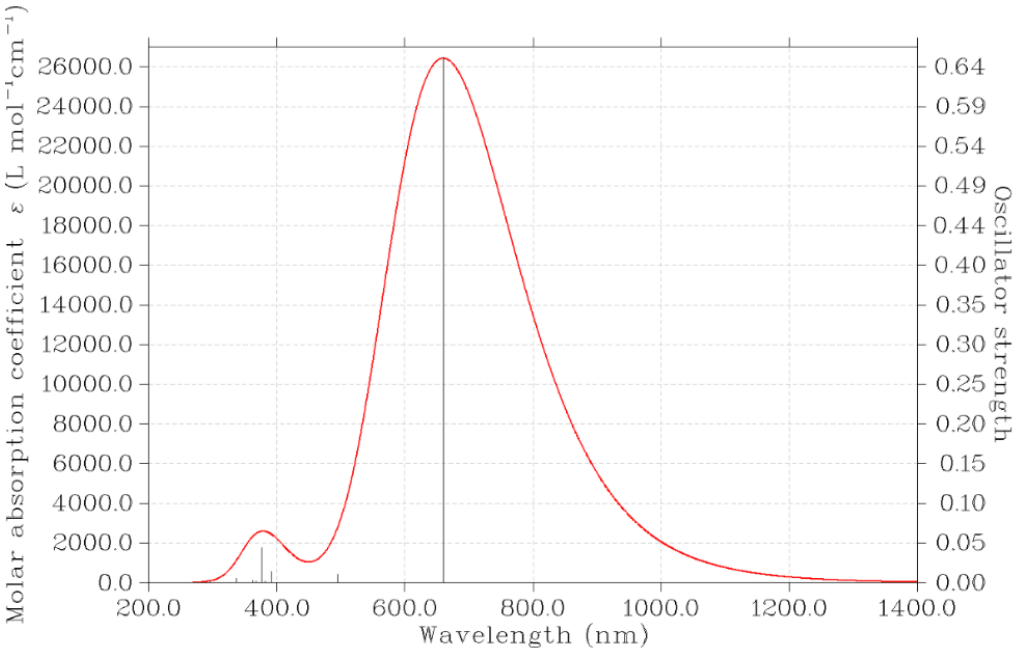


Figure S26. Calculated UV-vis spectrum of **2** at the TD-DFT//UBH&HLYP/6-311G(d) level.

Table S11. Calculated absorption properties of **2′** including wavelength (nm), oscillator strength (f) and the related transition nature.

Energy/ ev	Wavelength /nm	Oscillator strength/ f	Transition nature
1.8788	659.90	0.6528	HOMO (α)→LUMO (α) (0.70967) HOMO (β)→LUMO (β) (0.70967) LUMO (α)→HOMO (α) (-0.13725) LUMO (β)→HOMO (β) (-0.13725)
3.2874	377.15	0.0431	HOMO (β)→LUMO+8 (β) (0.65733) HOMO (α)→LUMO+2 (α) (0.22067) HOMO (β)→LUMO+2 (β) (0.22067)

5. Coordinates of the studied molecules

1′-CS calculated at the B3LYP/6-311G(d) level.

B	-5.05221300	0.00000000	-0.00000100
C	-7.25581700	-0.67245300	-0.02022600
H	-8.09585100	-1.34812500	-0.01268300
C	-7.25581700	0.67245300	0.02022400
H	-8.09585000	1.34812500	0.01268000
C	-5.64618900	-2.54030000	0.04159100
C	-6.34800300	-3.43894200	-0.77055900
C	-6.08440800	-4.80407600	-0.69948200
H	-6.63671200	-5.48840900	-1.33571400
C	-5.10881700	-5.28893700	0.16891000
H	-4.90026200	-6.35245300	0.21914600
C	-4.40233500	-4.39491300	0.97124500
H	-3.64140500	-4.75966700	1.65360300
C	-4.67130900	-3.03058200	0.91734500
C	-5.64618800	2.54030000	-0.04159100
C	-6.34800200	3.43894100	0.77056000
C	-6.08440500	4.80407500	0.69948400
H	-6.63671000	5.48840800	1.33571600
C	-5.10881400	5.28893500	-0.16890700
H	-4.90025800	6.35245100	-0.21914200
C	-4.40233100	4.39491200	-0.97124200
H	-3.64140000	4.75966500	-1.65359900
C	-4.67130700	3.03058100	-0.91734300
C	-2.85004400	0.89991100	0.77360600
H	-3.43106200	1.58180600	1.37965800
C	-1.50264900	0.91531600	0.79011800
H	-1.03335700	1.64709700	1.43564900
C	-0.69146800	0.00000000	-0.00000100
C	-1.50264800	-0.91531700	-0.79012000
H	-1.03335700	-1.64709700	-1.43565100
C	-2.85004400	-0.89991100	-0.77360800
H	-3.43106200	-1.58180600	-1.37966100
N	-5.93157600	-1.15039900	-0.01649400
N	-5.93157600	1.15039800	0.01649300
N	-3.59792300	0.00000000	-0.00000100
B	5.05221200	0.00000000	-0.00000100
C	7.25581600	0.67245500	0.02022200
H	8.09584900	1.34812800	0.01267800
C	7.25581700	-0.67245100	-0.02022600
H	8.09585100	-1.34812300	-0.01268300

C	5.64618600	2.54030100	-0.04159400
C	6.34800100	3.43894300	0.77055500
C	6.08440400	4.80407800	0.69947700
H	6.63670800	5.48841100	1.33570800
C	5.10881200	5.28893600	-0.16891500
H	4.90025600	6.35245200	-0.21915100
C	4.40233000	4.39491200	-0.97124800
H	3.64139900	4.75966400	-1.65360600
C	4.67130500	3.03058100	-0.91734700
C	5.64619000	-2.54029900	0.04159400
C	6.34800500	-3.43894100	-0.77055500
C	6.08441100	-4.80407600	-0.69947600
H	6.63671500	-5.48840900	-1.33570700
C	5.10882200	-5.28893600	0.16891800
H	4.90026700	-6.35245200	0.21915500
C	4.40233900	-4.39491200	0.97125200
H	3.64141000	-4.75966500	1.65361100
C	4.67131100	-3.03058100	0.91734900
C	2.85004400	-0.89991100	-0.77360700
H	3.43106100	-1.58180600	-1.37966100
C	1.50264800	-0.91531700	-0.79012000
H	1.03335600	-1.64709700	-1.43565100
C	0.69146700	0.00000000	0.00000000
C	1.50264800	0.91531600	0.79011900
H	1.03335600	1.64709600	1.43565000
C	2.85004400	0.89991100	0.77360700
H	3.43106100	1.58180500	1.37966000
N	5.93157500	1.15039900	0.01649200
N	5.93157600	-1.15039700	-0.01649300
N	3.59792200	0.00000000	0.00000000
H	7.08639100	-3.06262700	-1.47064300
H	4.13162500	-2.34142400	1.55574300
H	7.08638900	3.06263000	1.47064100
H	4.13161800	2.34142400	-1.55574000
H	-4.13162000	2.34142500	-1.55573700
H	-7.08639000	3.06262600	1.47064500
H	-4.13162200	-2.34142600	1.55573800
H	-7.08639000	-3.06262700	-1.47064600

1′-T calculated at the UB3LYP/6-311G(d) level.

B	-5.06629300	0.00000100	0.00000000
C	-7.27041600	-0.54738200	-0.39089900
H	-8.11097400	-1.11379000	-0.75814700

C	-7.27041500	0.54738500	0.39090200
H	-8.11097300	1.11379300	0.75815200
C	-5.66748100	-2.14098400	-1.37094800
C	-6.37836000	-2.44694200	-2.53779900
C	-6.12054600	-3.62700900	-3.22961200
H	-6.67954500	-3.84930400	-4.13308200
C	-5.14205400	-4.50985800	-2.77703400
H	-4.93825800	-5.42671500	-3.32009800
C	-4.42681300	-4.20294300	-1.62119900
H	-3.66415300	-4.88340200	-1.25629300
C	-4.68898000	-3.03208500	-0.91590700
C	-5.66747900	2.14098600	1.37094900
C	-6.37835600	2.44694500	2.53780100
C	-6.12054000	3.62701100	3.22961400
H	-6.67953800	3.84930600	4.13308500
C	-5.14205000	4.50986100	2.77703400
H	-4.93825300	5.42671700	3.32009800
C	-4.42681100	4.20294600	1.62119700
H	-3.66415100	4.88340500	1.25629100
C	-4.68897900	3.03208800	0.91590600
C	-2.86745100	0.35649000	1.14301700
H	-3.44679400	0.60574800	2.02004500
C	-1.50404900	0.35419500	1.14643000
H	-0.99844200	0.62230700	2.06860500
C	-0.74070000	0.00000100	-0.00000300
C	-1.50405100	-0.35419300	-1.14643600
H	-0.99844500	-0.62230500	-2.06861100
C	-2.86745200	-0.35648800	-1.14302000
H	-3.44679700	-0.60574500	-2.02004800
N	-5.94685900	-0.94719800	-0.65571700
N	-5.94685800	0.94720100	0.65571800
N	-3.61213400	0.00000100	-0.00000100
B	5.06575500	-0.00000100	0.00000100
C	7.26975700	0.57455500	-0.34975900
H	8.11024000	1.13487400	-0.72640800
C	7.26975500	-0.57455900	0.34976900
H	8.11023600	-1.13487800	0.72642100
C	5.66718400	2.10162600	-1.43084600
C	6.37658900	3.29549500	-1.25238700
C	6.11958400	4.39486700	-2.06662800
H	6.67741400	5.31357700	-1.91511100
C	5.14330400	4.32437200	-3.05839600
H	4.94000900	5.18367800	-3.68874700
C	4.42952000	3.14021000	-3.23166200

H	3.66823400	3.07121800	-4.00202300
C	4.69113700	2.03202200	-2.43134200
C	5.66717700	-2.10162900	1.43085000
C	6.37658300	-3.29549800	1.25239400
C	6.11957400	-4.39487000	2.06663300
H	6.67740500	-5.31358000	1.91511800
C	5.14328900	-4.32437600	3.05839600
H	4.93999200	-5.18368200	3.68874600
C	4.42950400	-3.14021400	3.23165900
H	3.66821500	-3.07122200	4.00201600
C	4.69112500	-2.03202600	2.43134100
C	2.86688900	-1.19201800	-0.11353100
H	3.44618200	-2.09701900	-0.22438400
C	1.50359000	-1.19472200	-0.11170400
H	0.99783400	-2.15048400	-0.20430100
C	0.74013000	0.00000100	-0.00000400
C	1.50359100	1.19472300	0.11169600
H	0.99783600	2.15048500	0.20429200
C	2.86689000	1.19201800	0.11352500
H	3.44618300	2.09701800	0.22437800
N	5.94618900	0.97513300	-0.61327700
N	5.94618600	-0.97513500	0.61328200
N	3.61166400	-0.00000100	-0.00000200
H	7.11528400	-3.36530700	0.46094300
H	4.14665200	-1.10773000	2.58254300
H	7.11528600	3.36530400	-0.46093300
H	4.14666400	1.10772600	-2.58254700
H	-4.14366700	2.80743200	0.00717400
H	-7.11887700	1.74776400	2.91157900
H	-4.14366600	-2.80743000	-0.00717600
H	-7.11888200	-1.74776200	-2.91157500

1^{+} calculated at the UB3LYP/6-311G(d) level.

N	-5.92536900	1.14734800	0.03239700
N	-3.57824300	-0.00000900	0.00007000
N	-5.92521600	-1.14760300	-0.03196600
C	-0.71397800	-0.00000100	0.00000900
C	-7.24689000	0.67444500	0.02070900
H	-8.08143400	1.35632600	0.05172800
C	-2.85445200	-1.06905000	0.48509400
H	-3.43218500	-1.90043800	0.85894800
C	-7.24679700	-0.67488800	-0.02006900
H	-8.08125800	-1.35688300	-0.05082800

C	-1.49276300	1.09210900	-0.49410200
H	-1.02442400	1.97935000	-0.89789900
C	-5.64948800	2.55906400	0.12892300
C	-2.85448000	1.06902300	-0.48500500
H	-3.43222300	1.90040200	-0.85887200
C	-5.34691900	3.11654000	1.38826300
C	-1.49273600	-1.09212300	0.49414300
H	-1.02437000	-1.97935400	0.89793000
C	-5.64911200	-2.55923700	-0.12893600
C	-5.71367900	3.35045600	-1.03876700
C	-5.34620500	-3.11630300	-1.38838100
C	-5.71340100	-3.35098300	1.03850700
C	-5.07807800	4.48759400	1.44808800
H	-4.84212200	4.94330300	2.40378700
C	-3.94693900	2.30574600	3.34707900
H	-3.16516600	1.94999100	2.67051700
H	-3.94655000	1.66065900	4.23026400
H	-3.66543000	3.30955200	3.67671500
B	-5.06728200	-0.00006200	0.00010600
C	-5.33061100	2.29430700	2.67279300
H	-5.55885300	1.25835700	2.41249300
C	-5.32993300	-2.29372700	-2.67271900
H	-5.55800400	-1.25781000	-2.41207800
C	-6.08693300	-2.77616000	2.40262700
H	-6.15357000	-1.69027400	2.30428500
C	-5.44336000	4.71679600	-0.91797100
H	-5.49085900	5.35036000	-1.79711500
C	-6.08687300	2.77519300	-2.40278300
H	-6.15285300	1.68927800	-2.30428400
C	-5.12235000	5.28169800	0.30993200
H	-4.91726500	6.34489900	0.38120800
C	-5.12149100	-5.28173700	-0.31061800
H	-4.91618200	-6.34487700	-0.38216500
C	-5.07712000	-4.48729300	-1.44853000
H	-4.84096400	-4.94271100	-2.40431600
C	-5.44285300	-4.71724500	0.91738100
H	-5.49041600	-5.35105800	1.79634200
C	-6.42436200	2.76247800	3.65040800
H	-6.25501700	3.78894000	3.98677800
H	-6.44232600	2.12420800	4.53829900
H	-7.41450700	2.72441200	3.18987800
C	-7.47121600	-3.27790500	2.85535900
H	-8.24602900	-3.03578700	2.12404700
H	-7.75416200	-2.81893200	3.80670300

H	-7.47783700	-4.36240800	2.99520100
C	-7.47146100	3.27605700	-2.85555600
H	-8.24612600	3.03350200	-2.12423500
H	-7.75411400	2.81685600	-3.80687800
H	-7.47872400	4.36054900	-2.99543900
C	-5.02520000	-3.07277800	3.47713600
H	-4.92937700	-4.14342800	3.67503800
H	-5.29624300	-2.59179000	4.42087000
H	-4.03771100	-2.70100800	3.18874600
C	-5.02534900	3.07227700	-3.47736500
H	-4.93032900	4.14293200	-3.67563200
H	-5.29601600	2.59077700	-4.42094300
H	-4.03759100	2.70135400	-3.18882200
C	-3.94639000	-2.30512600	-3.34726500
H	-3.16445400	-1.94960300	-2.67079800
H	-3.66499900	-3.30887100	-3.67724000
C	-6.42393500	-2.76155400	-3.65024000
H	-6.25482000	-3.78801900	-3.98673900
H	-6.44193200	-2.12318100	-4.53806000
H	-7.41400700	-2.72338000	-3.18955700
N	5.92536900	-1.14734600	-0.03233800
N	3.57823900	0.00000600	-0.00007800
N	5.92521200	1.14760700	0.03192400
C	0.71397300	-0.00000400	-0.00002500
C	7.24688900	-0.67444200	-0.02066700
H	8.08143400	-1.35632300	-0.05165200
C	2.85444800	1.06904100	-0.48511600
H	3.43218000	1.90042600	-0.85897700
C	7.24679400	0.67489300	0.02005700
H	8.08125200	1.35689100	0.05079800
C	1.49275800	-1.09211000	0.49409400
H	1.02441900	-1.97934800	0.89789800
C	5.64949300	-2.55906800	-0.12880100
C	2.85447600	-1.06902300	0.48500200
H	3.43221700	-1.90039900	0.85887600
C	5.34692200	-3.11659700	-1.38811600
C	1.49273300	1.09211400	-0.49416700
H	1.02436700	1.97934100	-0.89796400
C	5.64911500	2.55924800	0.12882000
C	5.71369800	-3.35041200	1.03892100
C	5.34627300	3.11638100	1.38824900
C	5.71336100	3.35093200	-1.03866500
C	5.07808800	-4.48765500	-1.44788400
H	4.84212800	-4.94340400	-2.40356300

C	3.94692000	-2.30588300	-3.34694700
H	3.16515400	-1.95010100	-2.67039200
H	3.94651900	-1.66083000	-4.23015900
H	3.66540800	-3.30970200	-3.67654000
B	5.06727900	0.00006400	-0.00010300
C	5.33059900	-2.29441400	-2.67267800
H	5.55884100	-1.25845400	-2.41241900
C	5.32999400	2.29386600	2.67262000
H	5.55823100	1.25796800	2.41205500
C	6.08686800	2.77603800	-2.40276100
H	6.15344200	1.69015100	-2.30437700
C	5.44338700	-4.71675900	0.91818200
H	5.49089700	-5.35028700	1.79735100
C	6.08690900	-2.77509500	2.40291000
H	6.15286900	-1.68918200	2.30437200
C	5.12237000	-5.28171200	-0.30969600
H	4.91729100	-6.34491800	-0.38092700
C	5.12151600	5.28176000	0.31038400
H	4.91621000	6.34490400	0.38188400
C	5.07719800	4.48737600	1.44834200
H	4.84107500	4.94284300	2.40411400
C	5.44282200	4.71720200	-0.91759900
H	5.49035800	5.35096800	-1.79659400
C	6.42434100	-2.76262000	-3.65028700
H	6.25499300	-3.78909400	-3.98661800
H	6.44229400	-2.12438200	-4.53820100
H	7.41449000	-2.72453500	-3.18976900
C	7.47118600	3.27768800	-2.85549200
H	8.24597700	3.03554000	-2.12416700
H	7.75411400	2.81867800	-3.80682300
H	7.47787000	4.36218800	-2.99535600
C	7.47151500	-3.27592000	2.85567100
H	8.24616000	-3.03337500	2.12432500
H	7.75417900	-2.81668300	3.80697200
H	7.47879900	-4.36040700	2.99558900
C	5.02516800	3.07267500	-3.47729700
H	4.92942500	4.14332000	-3.67526100
H	5.29619100	2.59161700	-4.42100200
H	4.03765000	2.70099100	-3.18890100
C	5.02541300	-3.07216100	3.47752400
H	4.93042000	-4.14281000	3.67583400
H	5.29608900	-2.59062000	4.42107900
H	4.03764000	-2.70127100	3.18898800
C	3.94636500	2.30513400	3.34701700

H	3.16453000	1.94955500	2.67044200
H	3.94605400	1.65983400	4.23004900
H	3.66487100	3.30885700	3.67693700
C	6.42382100	2.76185500	3.65025600
H	6.25456200	3.78831100	3.98671100
H	6.44178000	2.12351600	4.53810200
H	7.41395300	2.72377000	3.18969600
H	-3.94613000	-1.65977400	-4.23034400

1 $^{2+}$ calculated at the B3LYP/6-311G(d) level.

N	5.90646100	1.10677100	-0.31286500
N	3.55220400	0.00000000	0.00000000
N	5.90646000	-1.10677100	0.31286600
C	5.62725100	2.45816400	-0.75208900
C	0.73326100	0.00000000	-0.00000100
C	7.21668700	0.65264200	-0.18908200
H	8.05383800	1.30180200	-0.39017900
C	1.47332900	-1.19103200	-0.08835100
H	0.98754800	-2.15750500	-0.13270500
C	5.62724900	-2.45816500	0.75209100
C	2.84969600	-1.16679600	-0.08821600
H	3.43255600	-2.07412500	-0.14755500
C	7.21668600	-0.65264300	0.18908500
H	8.05383700	-1.30180300	0.39018200
C	1.47332900	1.19103300	0.08834900
H	0.98754900	2.15750600	0.13270300
C	5.63168900	-3.49681900	-0.20437700
C	5.38483300	-2.69318200	2.12110800
C	2.84969600	1.16679700	0.08821500
H	3.43255600	2.07412500	0.14755500
C	5.63168700	3.49681900	0.20437900
C	5.38484000	2.69318200	-2.12110700
C	5.10824900	-4.00769600	2.51081200
H	4.92321700	-4.22586500	3.55677900
C	5.96160400	-3.26698000	-1.67747900
H	6.03339900	-2.18937200	-1.84755000
C	5.44526300	-1.59456500	3.17817400
H	5.66708600	-0.64906200	2.67641000
C	5.35380000	-4.79073800	0.24761400
H	5.36028300	-5.61495800	-0.45683300
C	5.35379900	4.79073700	-0.24761200
H	5.36027900	5.61495700	0.45683500

C	5.10825700	4.00769700	-2.51081200
H	4.92322900	4.22586600	-3.55678000
C	5.08864400	5.04512800	-1.58769700
H	4.88347900	6.05847100	-1.91594000
C	5.96159700	3.26697900	1.67748200
H	6.03338500	2.18937000	1.84755400
C	5.44527300	1.59456600	-3.17817300
H	5.66709400	0.64906200	-2.67640900
C	5.08864000	-5.04512800	1.58769700
H	4.88347400	-6.05847100	1.91594000
B	5.05693700	0.00000000	0.00000000
C	7.33154100	-3.87513000	-2.03539600
H	8.12926200	-3.47394300	-1.40591000
H	7.58653400	-3.65995100	-3.07615900
H	7.33109300	-4.96111300	-1.91208400
C	4.86792200	3.80427000	2.61833900
H	4.76816400	4.89026800	2.55458800
H	5.10966600	3.56329200	3.65645100
H	3.88693000	3.37033100	2.39864000
C	4.86792700	-3.80426400	-2.61833700
H	4.76815800	-4.89026100	-2.55458400
H	5.10967400	-3.56329000	-3.65645000
H	3.88693700	-3.37031600	-2.39864200
C	7.33153800	3.87512000	2.03540100
H	8.12925700	3.47392600	1.40591700
H	7.58652700	3.65994200	3.07616400
H	7.33109700	4.96110200	1.91208600
C	4.10093800	1.42238200	-3.90864900
H	3.28303100	1.21291700	-3.21144000
H	4.15547000	0.59410600	-4.61993400
H	3.82805100	2.31749500	-4.47294900
C	6.58678700	1.84725900	-4.18102000
H	6.42570700	2.76250500	-4.75598600
H	6.65965600	1.02083300	-4.89270000
H	7.55092700	1.94056500	-3.67599100
C	4.10092500	-1.42238100	3.90864500
H	3.28302000	-1.21291600	3.21143400
H	4.15545500	-0.59410500	4.61993100
H	3.82803600	-2.31749400	4.47294400
C	6.58677300	-1.84725900	4.18102500
H	6.42569200	-2.76250500	4.75599000
H	6.65964000	-1.02083300	4.89270500
H	7.55091500	-1.94056500	3.67599800
N	-5.91116500	-1.11784700	-0.27013900

N	-3.55818700	0.00000100	-0.00000100
N	-5.91116500	1.11784700	0.27013600
C	-5.62662700	-2.51018900	-0.54695600
C	-0.73970400	0.00000100	-0.00000100
C	-7.22178700	-0.66153900	-0.15511300
H	-8.05900100	-1.32599300	-0.29734300
C	-1.47975200	0.98210000	0.67987000
H	-0.99385100	1.75821800	1.25737400
C	-5.62662700	2.51018900	0.54695500
C	-2.85601600	0.95671700	0.67387900
H	-3.43865600	1.69424500	1.20583100
C	-7.22178700	0.66154000	0.15510800
H	-8.05900100	1.32599400	0.29733700
C	-1.47975200	-0.98209800	-0.67987200
H	-0.99385100	-1.75821600	-1.25737600
C	-5.64048300	2.95232300	1.88788000
C	-5.36706300	3.37985900	-0.53214100
C	-2.85601600	-0.95671500	-0.67388100
H	-3.43865600	-1.69424400	-1.20583300
C	-5.64048300	-2.95232400	-1.88788000
C	-5.36706400	-3.37985800	0.53214100
C	-5.08138200	4.71536600	-0.23025300
H	-4.88409400	5.41358200	-1.03620900
C	-5.99191700	2.03827800	3.05959300
H	-6.06960700	1.01473200	2.68327800
C	-5.42189600	2.93634500	-1.99107900
H	-5.65204900	1.86803200	-2.01551900
C	-5.35248600	4.30008800	2.12543400
H	-5.36522500	4.67726900	3.14187400
C	-5.35248800	-4.30009000	-2.12543300
H	-5.36522700	-4.67727200	-3.14187300
C	-5.08138400	-4.71536500	0.23025500
H	-4.88409700	-5.41358000	1.03621100
C	-5.06935100	-5.17206500	-1.08128500
H	-4.85698000	-6.21520200	-1.28985800
C	-5.99191600	-2.03828100	-3.05959500
H	-6.06960800	-1.01473400	-2.68328100
C	-5.42189600	-2.93634100	1.99107800
H	-5.65205200	-1.86803000	2.01551800
C	-5.06934900	5.17206400	1.08128700
H	-4.85697700	6.21520100	1.28986100
B	-5.06255100	0.00000000	-0.00000100
C	-7.36512600	2.40916100	3.65253200
H	-8.15474500	2.37340400	2.89832400

H	-7.63626800	1.71712500	4.45381000
H	-7.35923500	3.41771400	4.07366400
C	-4.91073900	-2.03949000	-4.15553100
H	-4.80651400	-3.01834500	-4.62919100
H	-5.16890700	-1.32672200	-4.94258500
H	-3.92774000	-1.75701200	-3.76465900
C	-4.91074100	2.03948600	4.15553100
H	-4.80651700	3.01834100	4.62919300
H	-5.16890900	1.32671700	4.94258300
H	-3.92774100	1.75701100	3.76465900
C	-7.36512400	-2.40916500	-3.65253600
H	-8.15474500	-2.37340800	-2.89832800
H	-7.63626600	-1.71712900	-4.45381500
H	-7.35923300	-3.41771900	-4.07366700
C	-4.07194300	-3.13149600	2.70513200
H	-3.26141700	-2.60177600	2.19380100
H	-4.12331400	-2.75562000	3.73029200
H	-3.79043800	-4.18602100	2.75961600
C	-6.55356500	-3.65478600	2.74986000
H	-6.38422800	-4.73304300	2.80380900
H	-6.62323600	-3.28137300	3.77480200
H	-7.52163600	-3.49672900	2.26908200
C	-4.07194500	3.13150400	-2.70513500
H	-3.26141600	2.60178700	-2.19380500
H	-4.12331600	2.75562800	-3.73029400
H	-3.79044200	4.18603000	-2.75961900
C	-6.55356800	3.65478700	-2.74985800
H	-6.38423500	4.73304400	-2.80380400
H	-6.62323900	3.28137600	-3.77480000
H	-7.52163800	3.49672500	-2.26907900

2′-CS calculated at the BH&HLYP/def2-SVP level.

N	5.67409400	1.31376000	-0.39231800
N	3.55363400	-0.10269200	0.02412700
N	6.01907500	-0.88019400	0.17319100
C	5.17938200	2.57017600	-0.79646100
C	1.37650000	0.74117100	0.60900900
C	0.69640800	-0.44619000	0.06064800
C	2.71768300	0.85087900	0.57718100
H	3.21817500	1.67448900	1.07118900

C	2.94197600	-1.26704300	-0.41756900
H	3.60719200	-1.98663700	-0.87624400
C	5.75735800	3.74304300	-0.31220300
C	7.04459900	1.04468500	-0.34214000
H	7.77876200	1.80251600	-0.56861000
C	1.61339900	-1.50223000	-0.37264100
C	4.11716200	2.65978500	-1.69491700
C	5.94573900	-2.21576900	0.61759700
C	0.62828500	1.70224000	1.49401300
H	1.29821600	2.47354900	1.88107600
H	0.20757700	1.15564100	2.34557600
H	-0.21162000	2.20073600	1.00970000
C	7.24576700	-0.24122500	-0.02888800
H	8.18227900	-0.76192400	0.09946000
C	6.75904100	-3.19326900	0.04578500
C	1.14131800	-2.77467600	-1.02108300
H	0.99616200	-3.58449800	-0.30538900
H	1.87384100	-3.12212600	-1.75256200
H	0.19328100	-2.61750500	-1.54061800
C	5.07206400	-2.57625700	1.64231600
C	3.64076000	3.90009600	-2.09128300
H	2.81221700	3.95232000	-2.78922500
C	6.70340500	-4.50424000	0.49609700
H	7.34309600	-5.25257400	0.04067800
B	4.98579000	0.09426300	-0.06018300
C	5.28553100	4.98062100	-0.72486200
H	5.74672700	5.88328200	-0.33866300
C	4.22296900	5.06640400	-1.61322000
H	3.85102100	6.03408800	-1.93061400
C	5.01068500	-3.89130500	2.07718000
H	4.32427900	-4.15602900	2.87414700
C	5.82712000	-4.86125900	1.51116700
H	5.78035800	-5.88721800	1.85865300
N	-5.67409800	1.31375500	0.39231200
N	-3.55363400	-0.10269400	-0.02412100
N	-6.01907300	-0.88020000	-0.17319800
C	-5.17938900	2.57017200	0.79645600
C	-1.37650000	0.74117000	-0.60899900
C	-0.69640800	-0.44619000	-0.06063600
C	-2.71768300	0.85087700	-0.57717400
H	-3.21817400	1.67448600	-1.07118400
C	-2.94197600	-1.26704300	0.41757800
H	-3.60719300	-1.98663700	0.87625300
C	-5.75736100	3.74303800	0.31219300

C	-7.04460200	1.04467900	0.34212500
H	-7.77876700	1.80250900	0.56859100
C	-1.61339900	-1.50222900	0.37265300
C	-4.11717600	2.65978100	1.69492100
C	-5.94573300	-2.21577500	-0.61760300
C	-0.62828400	1.70224000	-1.49400200
H	0.21161900	2.20073700	-1.00968900
H	-1.29821500	2.47354700	-1.88106700
H	-0.20757400	1.15564000	-2.34556400
C	-7.24576700	-0.24123100	0.02887300
H	-8.18227700	-0.76193100	-0.09948200
C	-6.75903800	-3.19327500	-0.04579700
C	-1.14131800	-2.77467400	1.02109800
H	-0.99616100	-3.58449700	0.30540600
H	-1.87384200	-3.12212300	1.75257700
H	-0.19328200	-2.61750100	1.54063400
C	-5.07204900	-2.57626200	-1.64231500
C	-3.64077700	3.90009300	2.09128900
H	-2.81224000	3.95231800	2.78923800
C	-6.70339700	-4.50424600	-0.49610800
H	-7.34309200	-5.25258000	-0.04069400
B	-4.98579100	0.09425900	0.06018200
C	-5.28553700	4.98061700	0.72485500
H	-5.74673000	5.88327700	0.33865000
C	-4.22298200	5.06640000	1.61322100
H	-3.85103700	6.03408500	1.93061700
C	-5.01066600	-3.89131000	-2.07717800
H	-4.32425300	-4.15603400	-2.87413900
C	-5.82710500	-4.86126400	-1.51117100
H	-5.78033900	-5.88722400	-1.85865600
H	4.44476900	-1.82031900	2.09787600
H	6.57051100	3.68268000	0.40200900
H	7.42676700	-2.92511400	-0.76490900
H	3.66964700	1.75368500	-2.08350500
H	-3.66966400	1.75368200	2.08351300
H	-6.57050800	3.68267400	-0.40202500
H	-4.44475100	-1.82032400	-2.09787000
H	-7.42677100	-2.92511900	0.76489100

2′-OS calculated at the UBH&HLYP/def2-SVP level.

N	-5.89921500	1.06721600	0.13848200
N	-3.58099300	-0.07737100	0.03945200
N	-5.90170900	-1.22029800	-0.00769600

C	-5.60989000	2.43490700	0.31427000
C	-1.49940500	0.90419600	-0.70751900
C	-0.73557500	-0.07787500	0.00801400
C	-2.85785100	0.87537400	-0.67681700
H	-3.44839800	1.57486100	-1.25308300
C	-2.84253900	-1.03047400	0.73944300
H	-3.42043900	-1.72982900	1.32854400
C	-6.32822700	3.40262700	-0.38709700
C	-7.21356200	0.59238300	0.11398800
H	-8.05808200	1.26107300	0.17907700
C	-1.48374800	-1.05976500	0.74013100
C	-4.61310500	2.84184000	1.20003200
C	-5.61745700	-2.58822200	-0.18982800
C	-0.81870200	1.90721700	-1.59467600
H	-1.54521400	2.56349100	-2.07830200
H	-0.24171500	1.39975000	-2.37398900
H	-0.11108200	2.53325200	-1.04716100
C	-7.21482400	-0.74446600	0.04612200
H	-8.06109000	-1.41251800	-0.00010800
C	-6.32066000	-3.55533600	0.52753100
C	-0.78401200	-2.06312100	1.61196300
H	-0.08916300	-2.68962600	1.04885800
H	-1.49995400	-2.71894500	2.11169200
H	-0.18948600	-1.55597800	2.37819100
C	-4.64111100	-2.99598600	-1.09768900
C	-4.33923800	4.19007600	1.37157600
H	-3.55963200	4.49000100	2.06346100
C	-6.05673800	-4.90342500	0.33399500
H	-6.61327600	-5.64270100	0.90002700
B	-5.02823800	-0.07687200	0.05564900
C	-6.05891900	4.75049300	-0.19950000
H	-6.62741200	5.49024800	-0.75288500
C	-5.06137900	5.15178100	0.67775500
H	-4.84804800	6.20527600	0.81982400
C	-4.37227800	-4.34445400	-1.27529200
H	-3.60864900	-4.64504400	-1.98449000
C	-5.07947400	-5.30555000	-0.56541700
H	-4.87026100	-6.35922300	-0.71221000
N	5.89921800	1.06722100	-0.13845900
N	3.58099400	-0.07736300	-0.03945600
N	5.90170800	-1.22029300	0.00771800
C	5.60989600	2.43491300	-0.31424900
C	1.49940100	0.90420200	0.70750400
C	0.73557600	-0.07787100	-0.00803200

C	2.85784600	0.87538300	0.67680800
H	3.44838900	1.57487200	1.25307500
C	2.84254500	-1.03046500	-0.73945100
H	3.42044900	-1.72981900	-1.32855100
C	6.32822000	3.40263200	0.38713200
C	7.21356400	0.59238800	-0.11394900
H	8.05808500	1.26107800	-0.17902700
C	1.48375400	-1.05975900	-0.74014600
C	4.61312600	2.84184700	-1.20002600
C	5.61745400	-2.58821700	0.18984700
C	0.81869200	1.90722300	1.59465500
H	0.11107400	2.53325700	1.04713500
H	1.54520000	2.56350000	2.07828300
H	0.24170200	1.39975700	2.37396600
C	7.21482500	-0.74446100	-0.04608200
H	8.06109000	-1.41251300	0.00015800
C	6.32066900	-3.55533100	-0.52749900
C	0.78402400	-2.06311500	-1.61198300
H	0.08917300	-2.68962100	-1.04888200
H	1.49997000	-2.71893800	-2.11170900
H	0.18950200	-1.55597200	-2.37821300
C	4.64109100	-2.99598000	1.09769100
C	4.33926100	4.19008300	-1.37157300
H	3.55966700	4.49000900	-2.06347000
C	6.05674400	-4.90342100	-0.33396700
H	6.61329300	-5.64269700	-0.89998800
B	5.02823900	-0.07686600	-0.05563700
C	6.05891400	4.75049700	0.19953400
H	6.62739800	5.49025100	0.75293000
C	5.06138900	5.15178700	-0.67773700
H	4.84806100	6.20528200	-0.81980700
C	4.37225600	-4.34444800	1.27529000
H	3.60861400	-4.64503800	1.98447400
C	5.07946400	-5.30554500	0.56542800
H	4.87024900	-6.35921800	0.71221800
H	-4.09799800	-2.25100300	-1.66541000
H	-7.09095500	3.09466000	-1.09302200
H	-7.06710000	-3.24672300	1.25038000
H	-4.05800600	2.09640700	1.75543400
H	4.05803600	2.09641500	-1.75543900
H	7.09093600	3.09466300	1.09307000
H	4.09796800	-2.25099700	1.66540200
H	7.06712200	-3.24671900	-1.25033600

2′-T calculated at the UBH&HLYP/def2-SVP level.

N	5.90178800	1.14331600	0.07880900
N	3.58165800	0.00000600	-0.00000600
N	5.90177700	-1.14332700	-0.07880700
C	5.61489200	2.52264900	0.08253000
C	1.49069500	0.86439100	0.85727600
C	0.74182000	0.00000800	-0.00000200
C	2.85125400	0.84517000	0.83649000
H	3.43543700	1.48061100	1.48818100
C	2.85125100	-0.84515600	-0.83650200
H	3.43543100	-1.48059600	-1.48819600
C	6.32650200	3.38798400	0.91273500
C	7.21559200	0.66701800	0.05479000
H	8.06107100	1.33683800	0.08801500
C	1.49069100	-0.86437500	-0.85728400
C	4.62700600	3.04479100	-0.75129400
C	5.61486900	-2.52265700	-0.08252900
C	0.78471500	1.79835800	1.79688300
H	1.49470600	2.39351800	2.37483200
H	0.14707000	1.25007400	2.49627900
H	0.12827600	2.48354900	1.25307100
C	7.21558600	-0.66704200	-0.05477900
H	8.06105800	-1.33686900	-0.08799900
C	6.32647600	-3.38799900	-0.91272900
C	0.78470700	-1.79833800	-1.79689200
H	0.12825100	-2.48351500	-1.25308200
H	1.49469600	-2.39351400	-2.37482800
H	0.14707900	-1.25004900	-2.49629900
C	4.62697100	-3.04479000	0.75128700
C	4.35541900	4.40433500	-0.74579900
H	3.58291700	4.79443500	-1.39965200
C	6.05946100	-4.74927100	-0.90242000
H	6.62263800	-5.40840500	-1.55436300
B	5.02920400	-0.00000100	-0.00000200
C	6.05950000	4.74925800	0.90242400
H	6.62267800	5.40838700	1.55437100
C	5.07091900	5.26469100	0.07615100
H	4.85943500	6.32808700	0.07250300
C	4.35537000	-4.40433100	0.74578900
H	3.58286000	-4.79442400	1.39963600
C	5.07086900	-5.26469400	-0.07615500
H	4.85937400	-6.32808700	-0.07250900

N	-5.90178700	1.14331600	-0.07880800
N	-3.58165800	0.00000600	0.00000600
N	-5.90177700	-1.14332700	0.07880700
C	-5.61489200	2.52264900	-0.08252900
C	-1.49069500	0.86439100	-0.85727700
C	-0.74182000	0.00000800	0.00000100
C	-2.85125400	0.84517000	-0.83649000
H	-3.43543700	1.48061100	-1.48818100
C	-2.85125100	-0.84515600	0.83650100
H	-3.43543100	-1.48059600	1.48819600
C	-6.32650100	3.38798400	-0.91273400
C	-7.21559200	0.66701900	-0.05478900
H	-8.06107000	1.33683800	-0.08801400
C	-1.49069100	-0.86437500	0.85728300
C	-4.62700500	3.04479100	0.75129400
C	-5.61486900	-2.52265700	0.08253000
C	-0.78471500	1.79835800	-1.79688400
H	-0.12827600	2.48354900	-1.25307200
H	-1.49470700	2.39351800	-2.37483300
H	-0.14707000	1.25007400	-2.49627900
C	-7.21558600	-0.66704100	0.05478000
H	-8.06105900	-1.33686800	0.08800000
C	-6.32647700	-3.38799900	0.91272900
C	-0.78470700	-1.79833800	1.79689100
H	-0.12825100	-2.48351500	1.25308100
H	-1.49469600	-2.39351400	2.37482800
H	-0.14707800	-1.25004900	2.49629800
C	-4.62697200	-3.04478900	-0.75128700
C	-4.35541700	4.40433500	0.74579800
H	-3.58291500	4.79443500	1.39965100
C	-6.05946200	-4.74927100	0.90242000
H	-6.62263800	-5.40840500	1.55436400
B	-5.02920400	-0.00000100	0.00000200
C	-6.05949900	4.74925900	-0.90242400
H	-6.62267700	5.40838800	-1.55437100
C	-5.07091800	5.26469200	-0.07615100
H	-4.85943300	6.32808700	-0.07250300
C	-4.35537200	-4.40433100	-0.74578900
H	-3.58286100	-4.79442400	-1.39963700
C	-5.07087000	-5.26469400	0.07615500
H	-4.85937500	-6.32808700	0.07250800
H	4.07718900	-2.38021700	1.40580200
H	7.08201500	2.98812100	1.57924000
H	7.08199900	-2.98814400	-1.57922800

H	4.07722300	2.38022400	-1.40581300
H	-4.07722200	2.38022400	1.40581300
H	-7.08201500	2.98812200	-1.57923900
H	-4.07719100	-2.38021700	-1.40580200
H	-7.08199800	-2.98814300	1.57922900

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