Supporting Information

for

A Linear Di-coordinate Boron Radical Cation

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Content

1. General Consideration

All the manipulations were carried out under nitrogen atmosphere by using standard Schlenk-line techniques or in a glove-box. Toluene, hexane and dichloromethane were purified by with a molecular sieves packed solvent purification system. Pentane and diethyl ether were distilled from Na/K-benzophenone ketyl under nitrogen. Cobaltocene ($CoCp_2$), lithium diisopropylamide (LDA), tetrakis(dimethylamino)ethylene (TDAE), *4*-dimethylaminopyridine (DMAP) and 2,6-dimethylphenylisocyanide (CNXyl) were purchased and used without further purification. Cyclic (alkyl)(amino)carbene (CAAC), *2,2,6,6*-tetramethylpiperidine boron dichloride (TMP-BCl_2), potassium tetrakis(pentafluorophenyl) borate ($K[B(C_6F_5)_4]$) were synthesized according to literature procedures.[1-3] NMR spectrums were recorded using Bruker Avance Ⅲ-400 (^1H: 400.2 MHz, ^{11}B: 128.4 MHz, ^{13}C: 100.6 MHz, ^{19}F: 376 MHz). Chemical Shifts (δ) are given in ppm and are referenced to the signals of the residual solvents (1H, 13C) or external $BF_3{\cdot}OEt_2$ (^{11}B). Elemental analysis were performed on a Heraeus vario Ⅲ-NCH elemental analyzer.

2. Synthetic Methods

Synthesis of [1][OTf]

CAAC (4.00 g, 8.38 mmol) generated from the corresponding iminium salt was slowly added into a $TMPBCl_2$ (1.85 g, 8.38 mmol) hexane solution at -78 °C. The resulting solution was then slowly warmed to room temperature and stirred for another 16 hours. After the reaction, all volatiles were removed under vacuum and the solid residue was washed by 10 mL of pentane for two times before the addition of 20 mL of dichloromethane. The DCM solution was then filtered and the filtrate was dried to afford [**1**][OTf] as white powder (4.66 g, 84 %). X-ray quality crystals were obtained by layering a DCM solution of [**1**][OTf] with pentane. ^{1}H NMR (400.2 MHz, CD_2Cl_2, ppm): δ 7.53 (t, 1H, *para*-Dipp), 7.39 (d, 2H, *meta*-Dipp), 2.78 (sept, 2H, C*H*(CH_3)2), 2.46 (s, 2H, CH_2), 2.20-1.5 (m, 16H, $H_2C_{Cy,TMP}$), 1.63 (s, 6H, C(CH_3)$_2$), 1.54 (br. s, 6H, NC(CH_3)$_2$),1.40 (d, 6H, CH(CH_3)$_2$), 1.29 (d, 6H, CH(CH_3)$_2$), 1.12 (br. s, 6H, NC(CH_3)$_2$). ^{11}B NMR (128.4 MHz, CD_2Cl_2, ppm): δ 33.1. ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2, ppm): δ 145.7, 132.3, 131.9, 127.1, 85.3, 62.0, 59.6, 44.0, 40.0, 39.1, 33.3, 33.1, 32.0, 29.4, 28.9, 27.1, 25.8, 24.5, 22.6, 14.9. Anal. Calcd. for $C_{33}H_{53}BClF_3N_2O_3S$: C, 59.95; H, 8.08; N, 4.24. Found: C, 59.98; H, 8.02; N, 4.09.
$E_{1/2}$ = -1.18 V, peak different 502 mV.

Synthesis of 2$^\bullet$

In a solution $CoCp_2$ (1.00 g, 5.29mmol) in toluene (20 mL), [**1**][OTf] (3.61 g, 5.29 mmol) were added in one portion. After addition, the reaction mixture was stirred over-night, and the solvent was removed in *vacuo*. The product was extracted by 10 mL of pentane to give **2$^\bullet$** as reddish powder (1.98 g, 73%). Single crystals were obtained by slow evaporation of a benzene solution of **2$^\bullet$** at room temperature. Anal. Calcd for $C_{32}H_{53}BClN_2$: C, 75.06; H, 10.43; N, 5.47. Found: C 75.47; H 10.04; N 5.45.
$E_{1/2}$ = -1.15 V, peak different 430 mV.

Synthesis of [3][B(C_6F_5)$_4$]

An equimolar amount of **2$^\bullet$** (1.00 g, 1.95 mmol) and $KB(C_6F_5)_4$ was allowed to react in 30 mL of DCM at room temperature for 3 hours. Afterwards, all insoluble solids were removed by filtration and the filtrate was dried in *vacuo*. The solid residue was then washed with 10 mL of pentane to afford [**3**][$B(C_6F_5)_4$] as yellow powder (2.09 g, 93%). X-ray quality crystals were obtained from layering a DCM solution of [**3**][$B(C_6F_5)_4$] with pentane at – 40 °C. Anal. Calcd for $C_{56}H_{53}B_2F_{20}N_2$: C, 58.20; H, 4.62; N, 2.42. Found: C,58.49; H, 4.51; N, 2.31.
$E_{1/2}$ = -1.00 V, peak different 270 mV.

Synthesis of 4

An equimolar amount of [**3**][$B(C_6F_5)_4$] (50.0 mg, 0.043 mmol) and TDAE was mixed in 2 mL of *o*-difluorobenzene. The reaction mixture was stirred for 1 hour before the removal of solvent in *vacuo*. Compound **4** was extracted from the solid residue with 3 mL of hexane and obtained as yellow powder (18.4 mg, 88.5 %). ^{1}H NMR (400.2 MHz, C_6D_6, ppm): δ 7.15-7.10 (m, 3H, *Dipp*), 3.71 (sept, 2H, C*H*(CH_3)2), 2.33 (m, 2H, H_2C_{Cy}) 1.94 (s, 2H, CH_2), 1.80-1.40 (m, 10H, $H_2C_{Cy,TMP}$), 1.38 (s, 6H, C(CH_3)$_2$), 1.37 (d, 6H, CH(CH_3)$_2$), 1.31 (d, 6H, CH(CH_3)$_2$), 1.24 (br. s, 6H, NC(CH_3)$_2$), 1.15 (br. s, 6H, NC(CH_3)$_2$). ^{11}B NMR (128.4 MHz, C_6D_6, ppm): δ 71.8. ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, ppm): δ 151.7, 142.5, 126.5, 123.9, 63.8, 55.7, 53.2, 47.5, 44.4, 38.3, 35.3, 31.5, 27.8, 27.5, 26.9, 26.3, 25.9, 25.5, 17.2.

Synthesis of [6][B(C_6F_5)$_4$]

DCM (10 mL) was added to the mixture consisting of [**3**][B(C_6F_5)$_4$] (50 mg, 0.043 mmol) and DMAP (5.5 mg, 0.043 mmol) at ambient temperature. After stirring for 1 hour, solvent was removed with vacuum and the solid residue was washed by 10 mL of pentane to afford [**6**][B(C_6F_5)$_4$] as violet powder, which was further purified with re-crystallization from DCM/pentane solution (68% yield). Single crystals suitable for X-ray diffraction analysis were obtained from layering a DCM solution of [**6**][B(C_6F_5)$_4$] with pentane at – 40^{o}C. Anal. Calcd for $C_{63}H_{63}B_2F_{20}N_4$: C, 59.22; H, 4.97; N, 4.38. Found: C, 58.91; H, 4.95; N, 4.05.

Synthesis of 7

DCM (0.5 mL) was added to the J-Young's NMR tube consisting of **2$^\bullet$** (17.7 mg, 0.035 mmol) and [**3**][B(C_6F_5)$_4$] (40.0 mg, 0.035 mmol) at ambient temperature. The solution was de-gassed with three freeze-pump-thaw cycles. Then, the NMR tube was then connected though a tygon tubing to a CO-filled 100 mL Schlenk flask at ambient pressure. After the exposure to CO atmosphere to for 18 hours, all volatiles were removed in *vacuo*. **7** was obtained from the reaction mixture by hexane extraction and isolated as reddish powder. ^{1}H NMR (400.2 MHz, CD_2Cl_2, ppm): δ 7.36 (t, 1H, *para*-Dipp), 7.22 (d, 2H, *meta*-Dipp), 2.96 (sept, 2H, C*H*(CH_3)2), 2.71 (m, 2H, H_2C_{Cy}), 2.10 (s, 2H, CH_2), 1.90-1.60 (m, 8H, H_2C_{Cy}), 1.50-1.40 (m, 6H, H_2C_{TMP}), 1.31 (s, 6H, C(CH_3)$_2$), 1.30 (d, 6H, CH(CH_3)$_2$), 1.25 (d, 6H, CH(CH_3)$_2$), 1.21 (br. s, 6H, NC(CH_3)$_2$), 1.00 (br. s, 6H, NC(CH_3)$_2$). ^{11}B NMR (128.4 MHz, CD_2Cl_2, ppm): δ -5.6. ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, ppm): δ 229.4 (m, B*C*O), 202.5 (m, C_{CAAC}B),149.8, 134.3, 130.2, 126.0, 67.6, 55.4, 54.0, 48.2, 42.7, 37.7, 36.2, 32.21, 30.76, 28.2, 28.1, 27.2, 26.3, 25.2, 23.6, 19.0.

Synthesis of [9][B(C_6F_5)$_4$]

DCM (10 mL) was added to the mixture consisting of [**3**][B(C_6F_5)$_4$] (100 mg, 0.086 mmol) and CNXyl (12.5 mg, 0.095 mmol) at ambient temperature. After stirring for 1 hour, the reaction solution was concentrated to about 2 mL before the addition of 20 mL of pentane. The precipitates were collected and dried to afford [**9**][B(C_6F_5)$_4$] as violet powder (91 mg, 81%). X-ray quality crystals were obtained from layering a DCM solution of [**9**][B(C_6F_5)$_4$] with hexane at – 40 ^{o}C. Anal. Calcd for $C_{65}H_{62}B_2F_{20}N_3$•0.5CH_2Cl_2: C, 59.18; H, 4.78; N, 3.16. Found: C, 59.18; H, 4.80; N, 3.07.

3.Structural Determination

Diffraction datas were collected at T = 150 or 200 K with a Bruker AXS PEX CCD diffractometer equipped with a rotation anode using graphite-monochromated Mo K α radiation (λ = 0.71073 Å). The structures were solved by the direct method and refined by least-squares cycles. The non-hydrogen atoms were refined anisotropically. Crystallographic data of **2**$^{\bullet}$, [**3**][$B(C_6F_5)_4$], [**6**][$B(C_6F_5)_4$], and [**9**][$B(C_6F_5)_4$] were deposited at the Cambridge Crystallographic Data Center with deposition numbers CCDC 2167148, 2167149, 2167150, and 2167151.

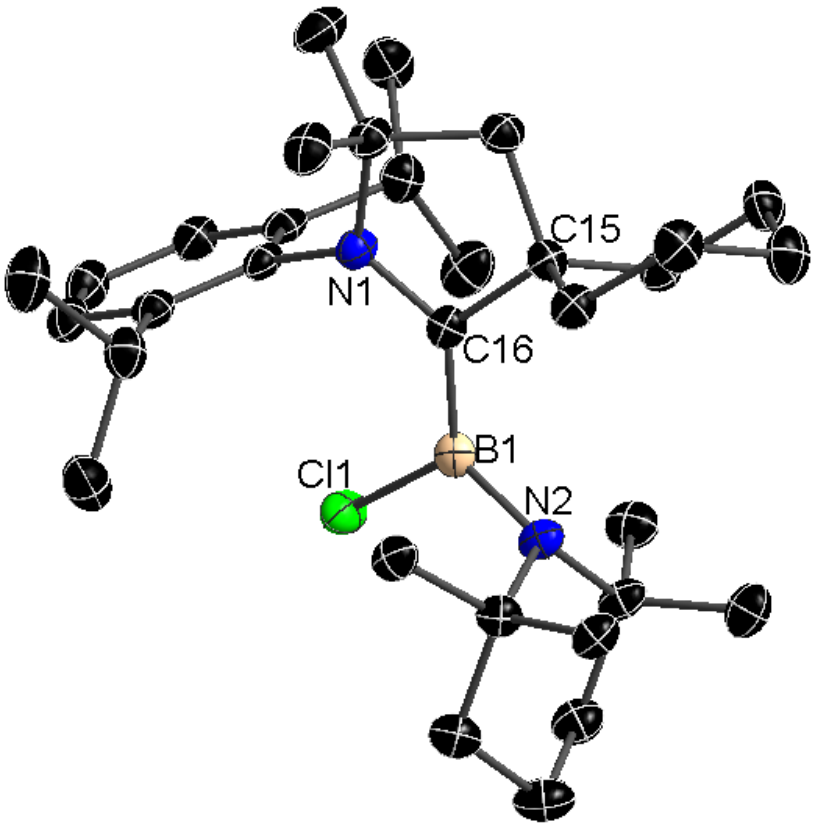


Figure S1. Crystal structure of **2˙**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at 50% probability. Selected bond distances [Å], bond angles [°]: N1-C16 1.376(4), C15-C16 1.550(5), C16-B1 1.522(6), B1-N2 1.463(5), B1-Cl1 1.856(4), N1-C16-C15 107.8(3), N1-C16-B1 128.3(3), C15-C16-B1 123.9(3), C16-B1-Cl1 118.7(3), C16-B1-N2 125.0(3), Cl1-B1-N2 116.2(3).

Table S1. Crystal data and experimental details for **2•**.

Empirical formula	C32 H53 B Cl N2	
Formula weight	512.02	
Crystal system	Monoclinic	
Space group	C2	
Unit cell dimensions	a = 32.6909(10) Å	α = 90°.
	b = 9.4007(2) Å	β = 108.913(3)°.
	c = 20.7052(6) Å	γ = 90°.
Volume	6019.5(3) $Å^3$	
Z	8	
F(000)	2248	
Density (calculated)	1.130 Mg/m^3	
Wavelength	0.71073 Å	
Cell parameters reflections used	5715	
Theta range for Cell parameters	3.6660 to 27.5430°.	
Absorption coefficient	0.149 mm^{-1}	
Temperature	150(2) K	
Crystal size	0.25 x 0.20 x 0.15 mm^3	
Diffractometer	Xcalibur, Atlas, Gemini	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.71808	
No. of measured reflections	16508	
No. of independent reflections	11547 [R(int) = 0.0357]	
No. of observed [I>2igma(I)]	9186	
Completeness to theta = 25.242°	99.7 %	
Theta range for data collection	3.120 to 27.500°.	
Final R indices [I>2sigma(I)]	R1 = 0.0529, wR2 = 0.1075	
R indices (all data)	R1 = 0.0752, wR2 = 0.1232	
Goodness-of-fit on F^2	1.007	
No. of reflections	11547	
No. of parameters	649	
No. of restraints	1	
Absolute structure parameter	0.00(4)	
Largest diff. peak and hole0.434 and -0.247 $e.Å^{-3}$		

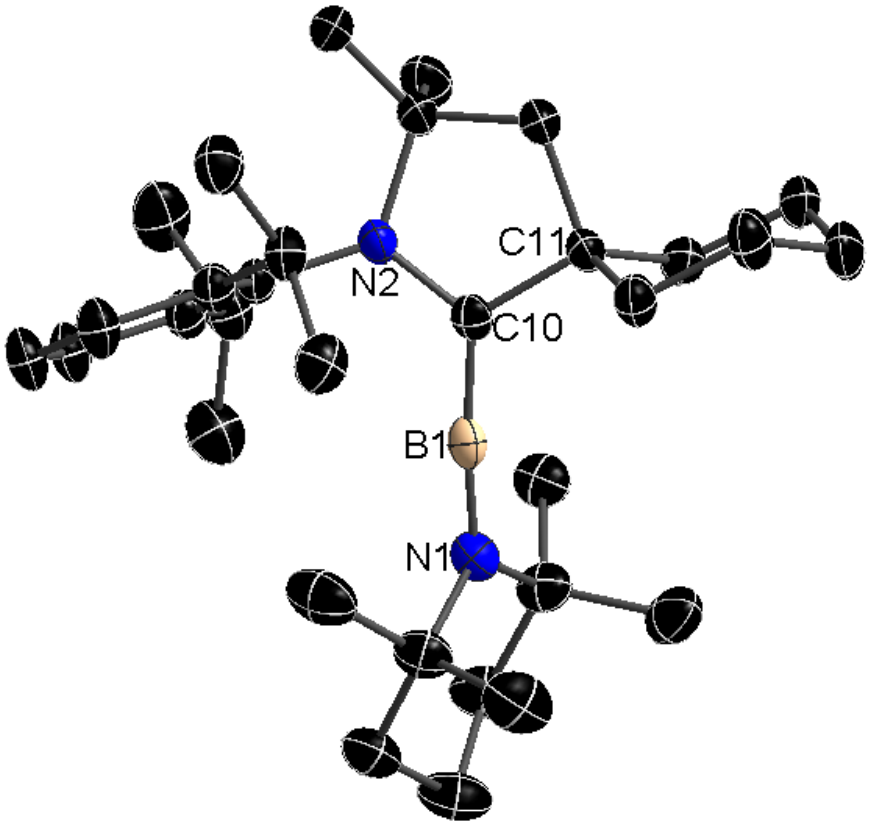


Figure S2. Crystal structure drawing of [**3**]$^{+\bullet}$. Hydrogen atoms and counter anion are omitted for clarity. Thermal ellipsoids are set at 50% probability. Selected bond distances [Å], bond angles [°]: N2-C10 1.358(2), C11-C10 1.527(3), C10-B1 1.462(3), C10-B1 1.462(3), B1-N1 1.340(3), C16-B1-N2 173.3(2), N2-C10-C11 110.6(4), N2-C10-B1 124.7(9), C11-C10-B1 124.4(7).

Table S2. Crystal data and experimental details for [**3**][$B(C_6F_5)_4$].

Empirical formula	C56 H53 B2 F20 N2	
Formula weight	1155.62	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 16.8466(4) Å	α = 90°.
	b = 20.3163(5) Å	β = 112.548(3)°.
	c = 16.5216(4) Å	γ = 90°.
Volume	5222.4(2) $Å^3$	
Z	4	
F(000)	2372	
Density (calculated)	1.470 Mg/m^3	
Wavelength	0.71073 Å	
Cell parameters reflections used	5548	
Theta range for Cell parameters	3.0580 to 27.0090°.	
Absorption coefficient	0.135 mm^{-1}	
Temperature	150(2) K	
Crystal size	0.25 x 0.20 x 0.15 mm^3	
Diffractometer	Xcalibur, Atlas, Gemini	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.82028	
No. of measured reflections	35224	
No. of independent reflections	11636 [R(int) = 0.0425]	
No. of observed [I>2igma(I)]	7313	
Completeness to theta = 25.242°	99.8 %	
Theta range for data collection	2.852 to 27.500°.	
Final R indices [I>2sigma(I)]	R1 = 0.0481, wR2 = 0.0929	
R indices (all data)	R1 = 0.0950, wR2 = 0.1130	
Goodness-of-fit on F^2	1.010	
No. of reflections	11636	
No. of parameters	721	
No. of restraints	1	
Largest diff. peak and hole	0.316 and -0.260 e.$Å^{-3}$	

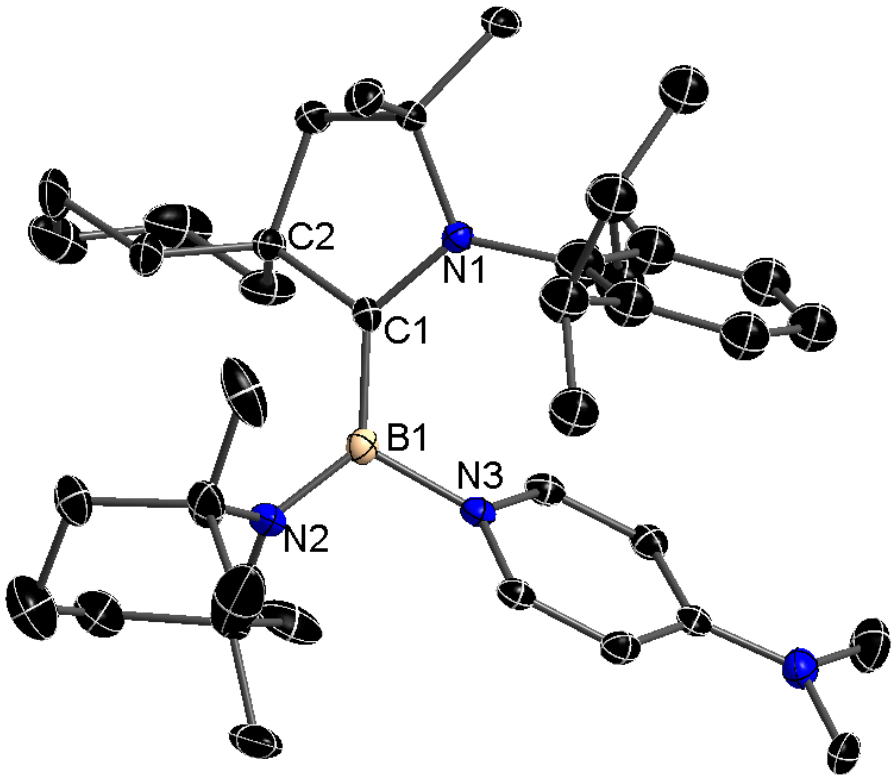


Figure S3. Crystal structure of [**6**]$^{+\bullet}$. Hydrogen atoms and counter anion are omitted for clarity. Thermal ellipsoids are set at 50% probability. Selected bond distances [Å], bond angles [°]: C2-C1 1.559(5), N1-C1 1.389(4), C1-B1 1.545(5), B1-N2 1.447(5), B1-N3 1.551(5), C2-C1-N1 106.1(3), C2-C1-B1 124.6(3), N1-C1-B1 129.1(3), C1-B1-N2 130.9(3), C1-B1-N3 114.9(3), N2-B1-N3 114.2(3).

Table S3. Crystal data and structure refinement for [**6**][$B(C_6F_5)_4$].

Empirical formula	C63 H63 B2 F20 N4	
Formula weight	1277.79	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 18.7850(6) Å	α = 90°.
	b = 16.7762(5) Å	β = 112.0207(7)°.
	c = 20.2902(7) Å	γ = 90°.
Volume	5927.8(3) $Å^3$	
Z	4	
Density (calculated)	1.432 Mg/m^3	
Absorption coefficient	0.127 mm^{-1}	
F(000)	2636	
Crystal size	0.234 x 0.222 x 0.025 mm^3	
Theta range for data collection	2.228 to 27.499°.	
Index ranges	-24<=h<=22, 0<=k<=21, 0<=l<=26	
Reflections collected	15785	
Independent reflections	15785 [R(int) = ?]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9590 and 0.7277	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15785 / 2 / 815	
Goodness-of-fit on F^2	1.117	
Final R indices [I>2sigma(I)]	R1 = 0.0892, wR2 = 0.1942	
R indices (all data)	R1 = 0.1194, wR2 = 0.2119	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.687 and -0.768 e.$Å^{-3}$	

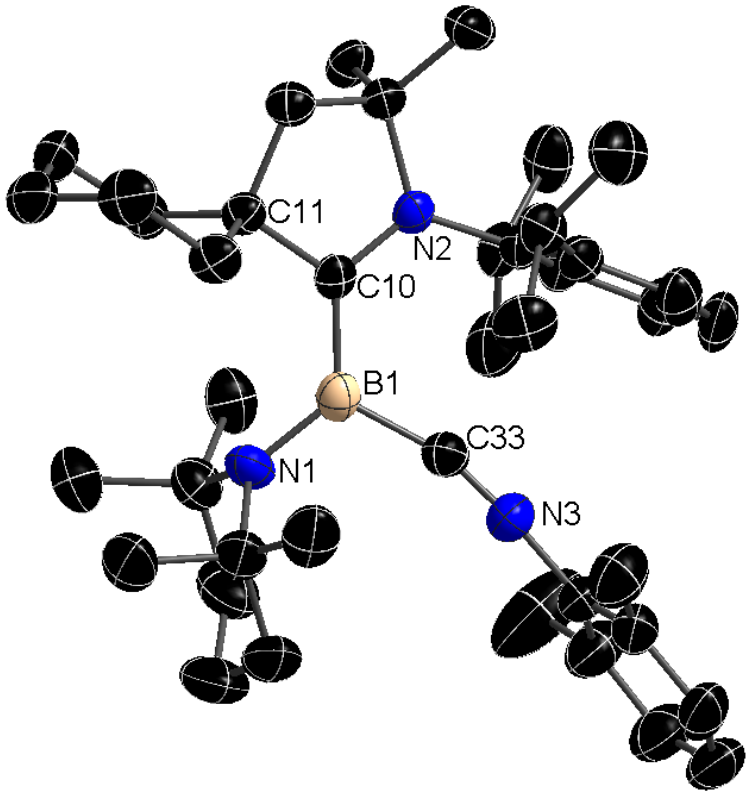


Figure S4. Crystal structure of [**9**]$^{+\bullet}$. Hydrogen atoms, solvents, and counter anion are omitted for clarity. Thermal ellipsoids are set at 50% probability. Selected bond distances [Å], bond angles [°]: C11-C10 1.538(4), N2-C10 1.332(4), C10-B1 1.560(5), B1-N1 1.458(5), B1-C33 1.578(5), C33-N3 1.172(5), C11-C10-N2 108.9(3), C11-C10-B1 125.5(3), N2-C10-B1 125.5(3), C10-B1-N1 127.1(3), C10-B1-C33 120.1(3), N1-B1-C33 112.8(3), B1-C33-N3 164.2(4).

Table S4. Crystal data and structure refinement for [**9**][$B(C_6F_5)_4$].

Empirical formula	C68 H67 B2 Cl1.50 F20 N3	
Formula weight	1381.04	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.6594(4) Å	α = 76.3140(10)°.
	b = 15.0335(5) Å	β = 79.8800(10)°.
	c = 19.7069(7) Å	γ = 89.9970(10)°.
Volume	3300.9(2) $Å^3$	
Z	2	
Density (calculated)	1.390 Mg/m^3	
Absorption coefficient	0.178 mm^{-1}	
F(000)	1423	
Crystal size	0.137 x 0.118 x 0.035 mm^3	
Theta range for data collection	1.960 to 25.000°.	
Index ranges	-13<=h<=13, -16<=k<=17, -23<=l<=23	
Reflections collected	46884	
Independent reflections	11596 [R(int) = 0.0627]	
Completeness to theta = 25.000°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9590 and 0.8753	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11596 / 3 / 875	
Goodness-of-fit on F^2	1.070	
Final R indices [I>2sigma(I)]	R1 = 0.0800, wR2 = 0.2370	
R indices (all data)	R1 = 0.1031, wR2 = 0.2595	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.137 and -0.521 $e.Å^{-3}$	

4. NMR spectra

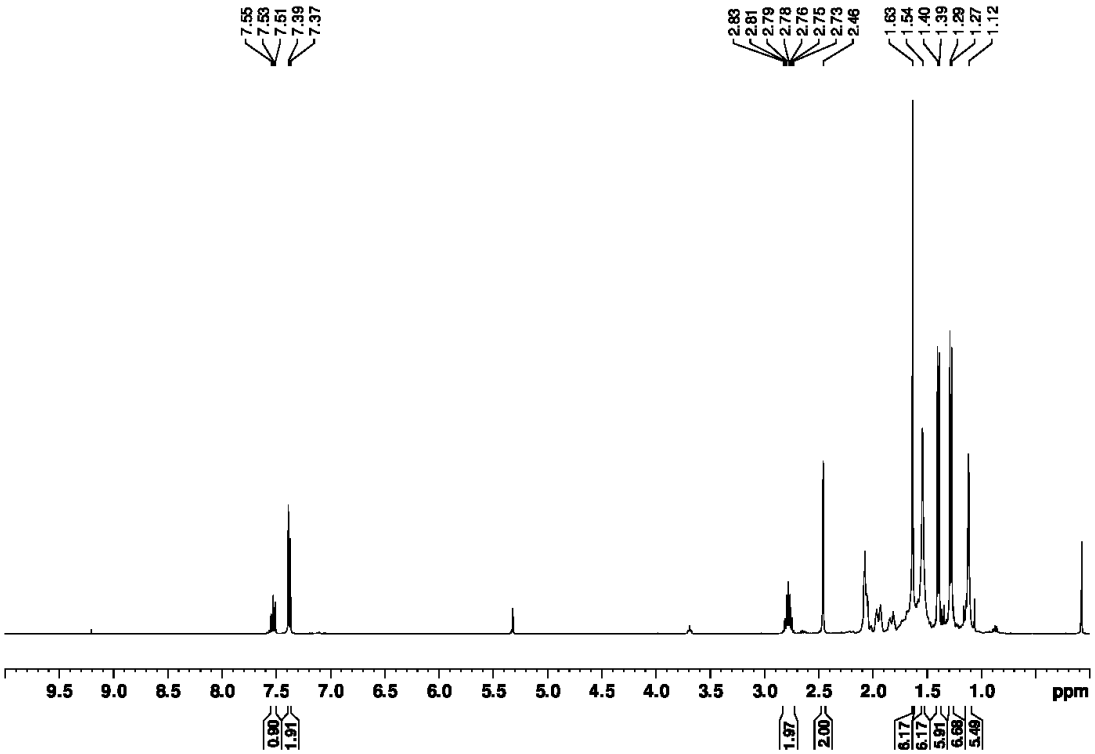


Figure S5. ^{1}H NMR spectrum of [**1**][OTf] in CD_2Cl_2.

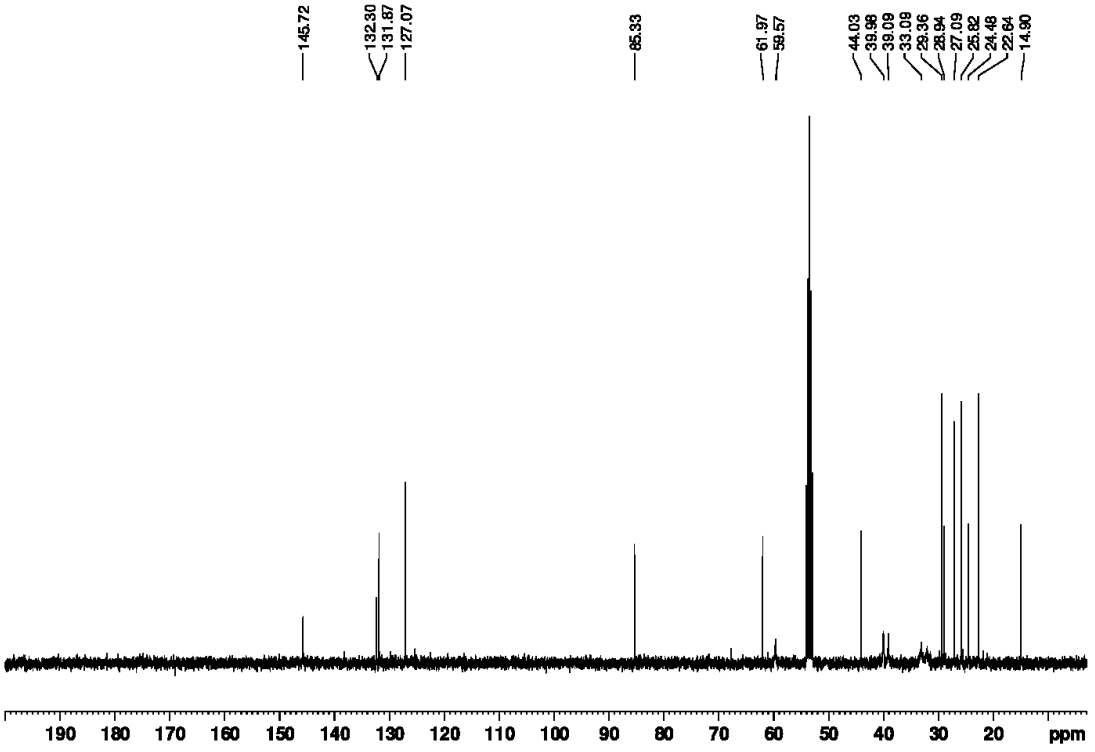


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of [**1**][OTf] in CD_2Cl_2.

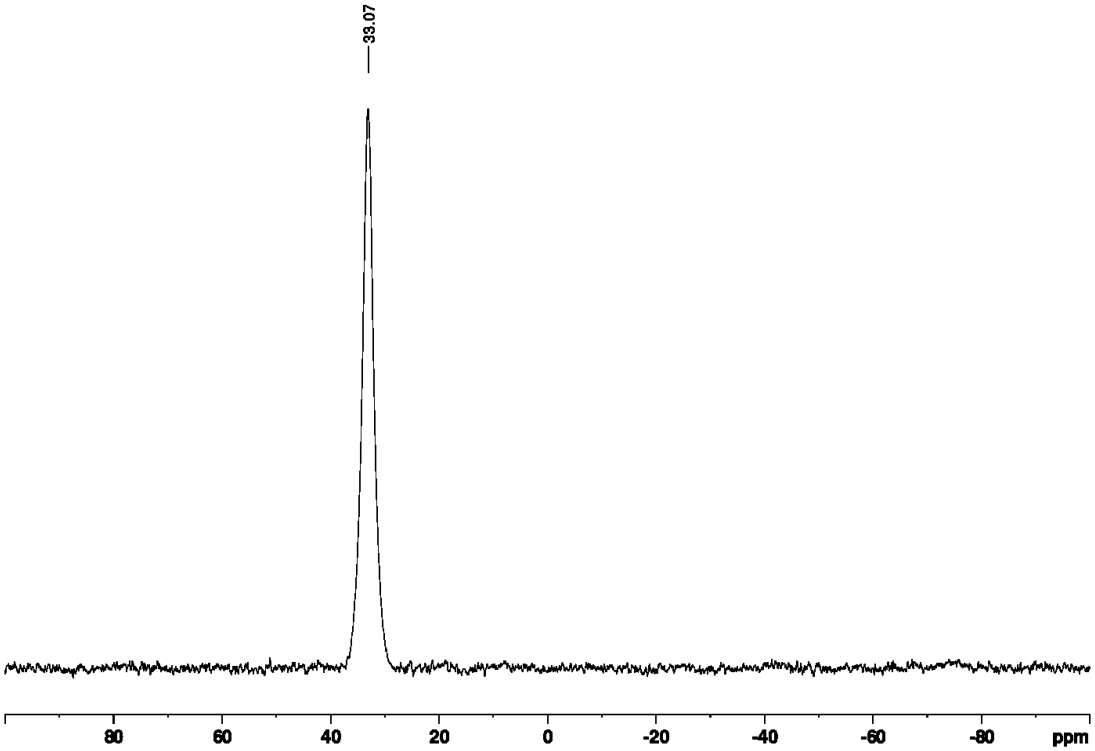


Figure S7. ^{11}B NMR spectrum of [**1**][OTf] in CD_2Cl_2.

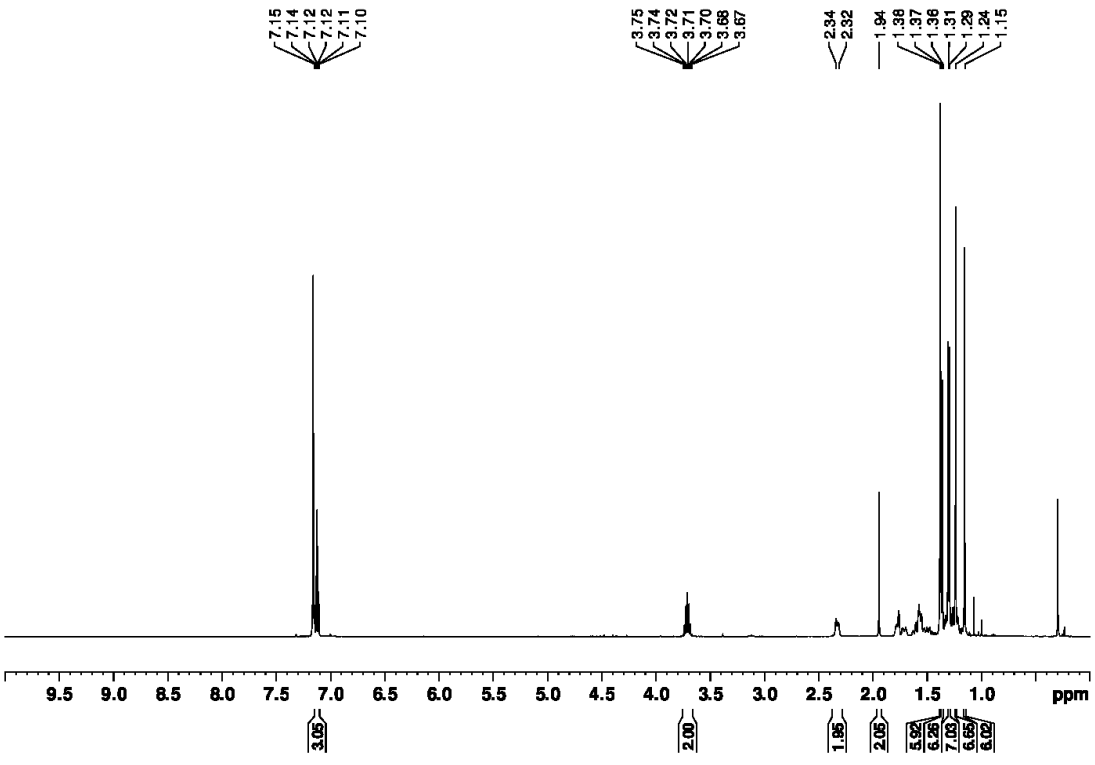


Figure S8. ^{1}H NMR spectrum of **4** in C_6D_6.

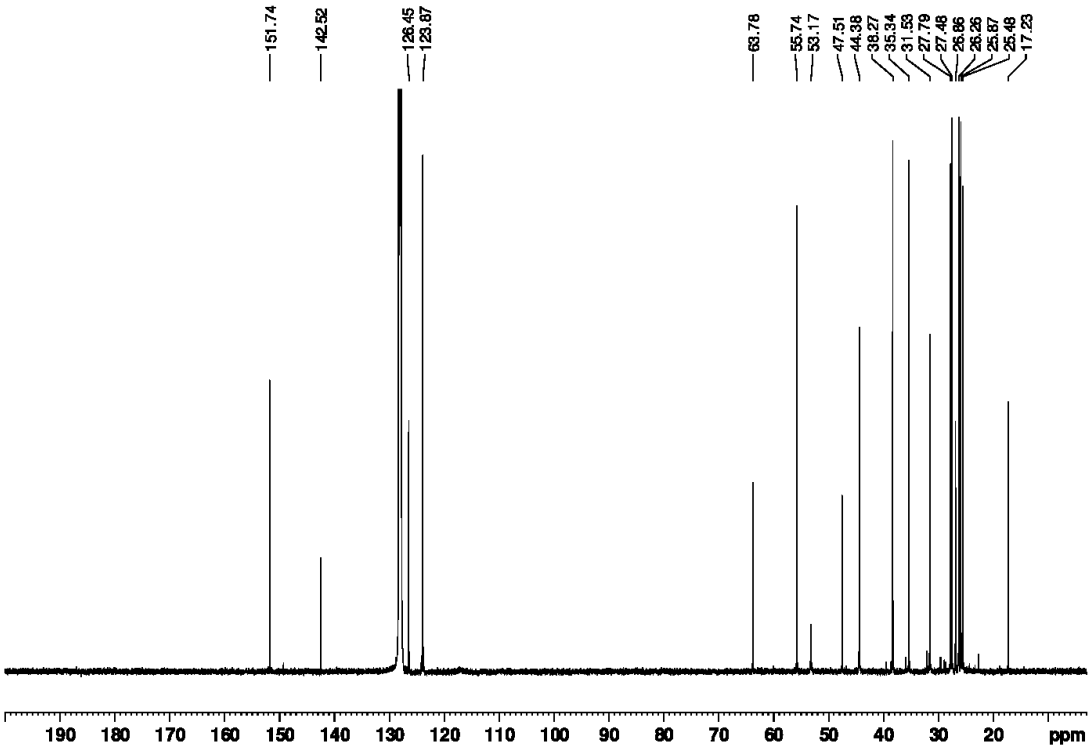


Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum of **4** in C_6D_6.

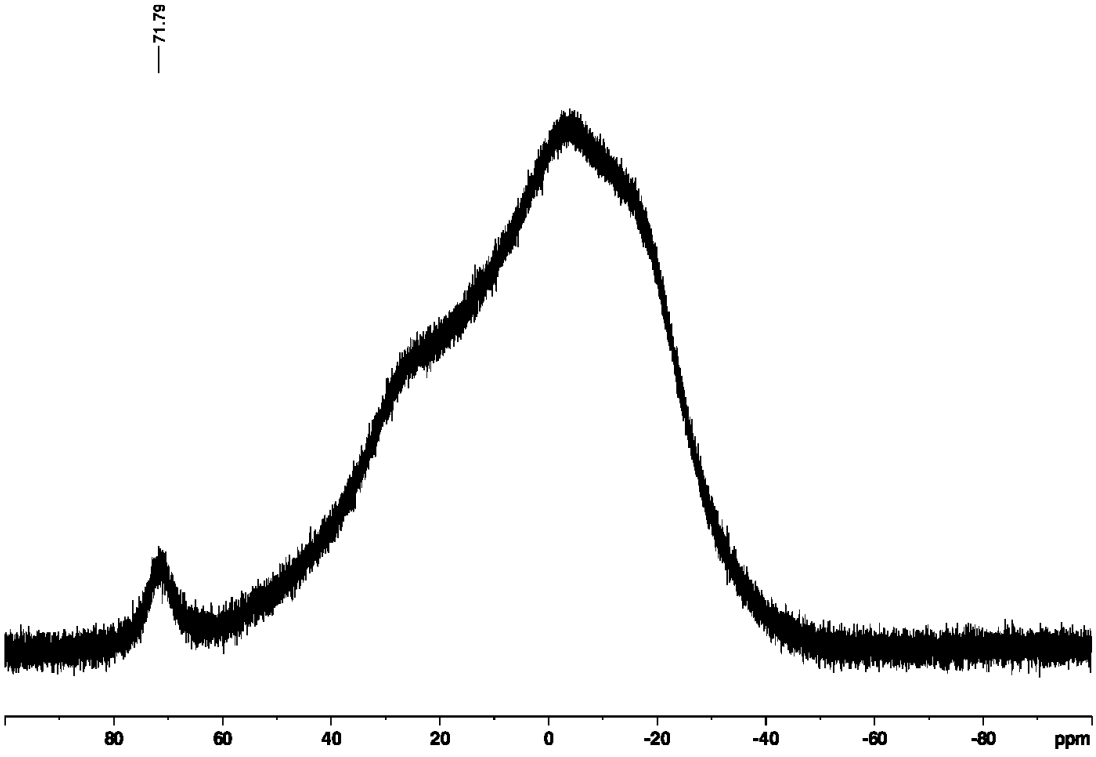


Figure S10. ^{11}B NMR spectrum of **4** in C_6D_6.

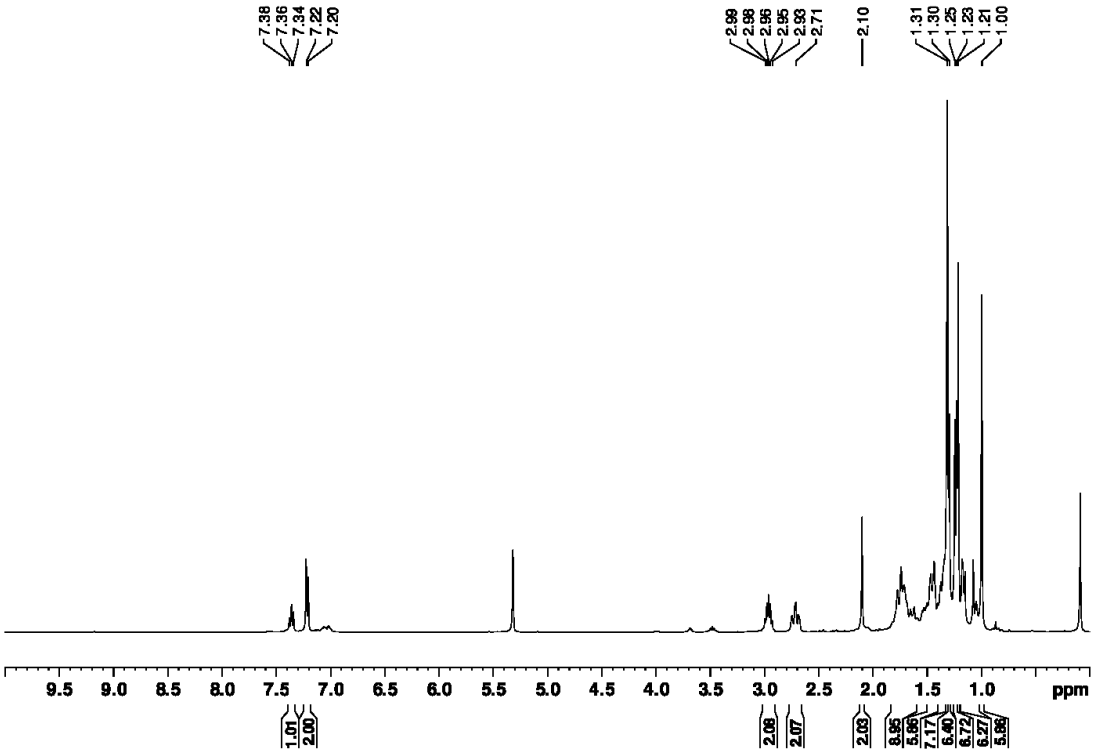


Figure S11. ^{1}H NMR spectrum of **7** in CD_2Cl_2.

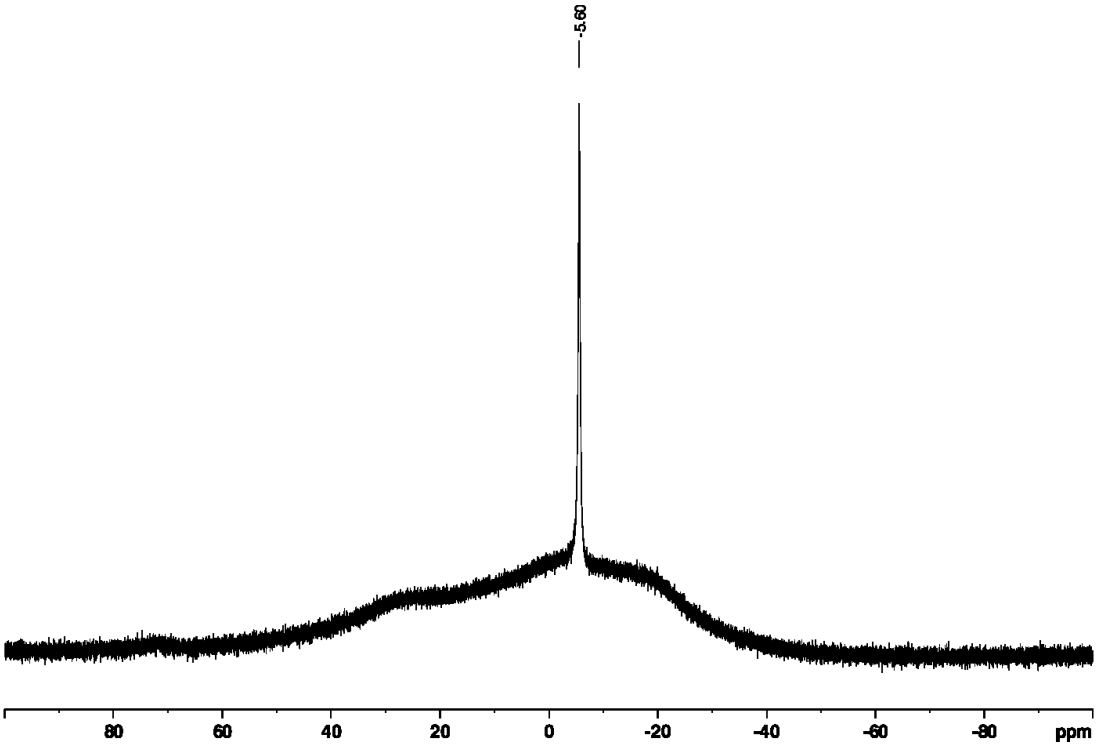


Figure S12. ^{11}B NMR spectrum of **7** in CD_2Cl_2.

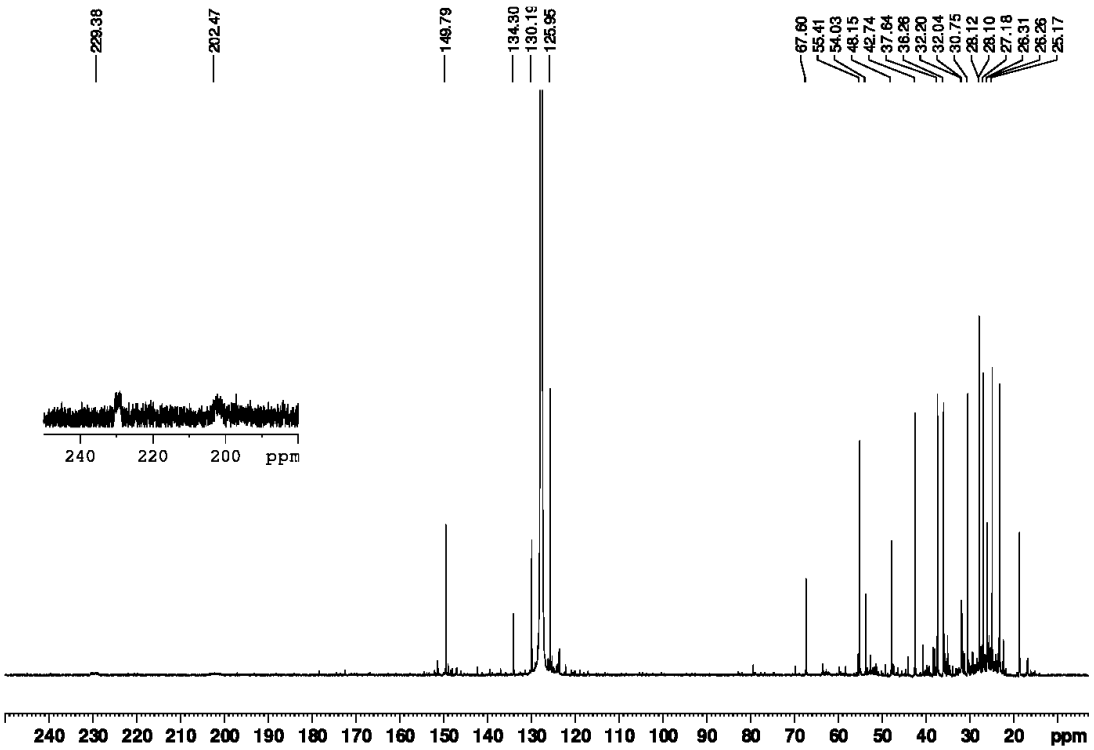


Figure S13. $^{13}C\{^{1}H\}$ NMR spectrum of **7** in C_6D_6.

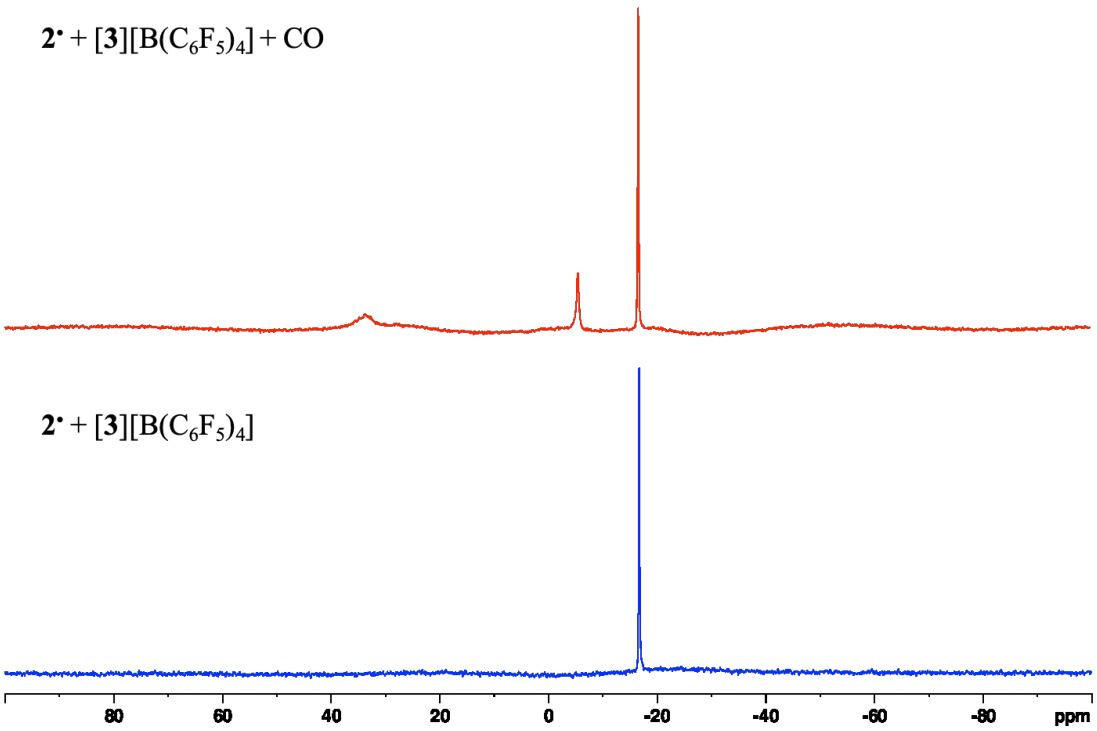


Figure S14. ^{11}B NMR spectrum of an equimolar mixture of **2**• and [**3**][B(C$_6$F$_5$)$_4$] in CD_2Cl_2 before and after CO exposure.

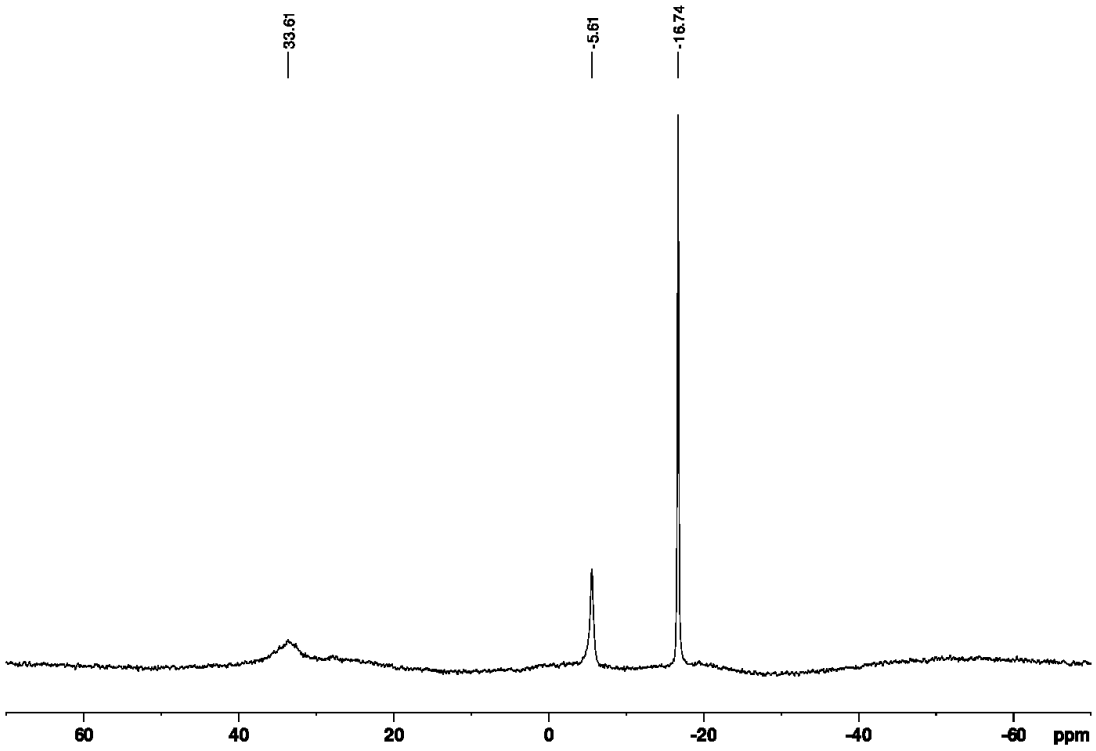


Figure S15. ^{11}B NMR spectrum (in CD_2Cl_2) of [**1**][B(C$_6$F$_5$)$_4$] and **7** obtained from the reaction of **2**• and [**3**][B(C$_6$F$_5$)$_4$] with CO.

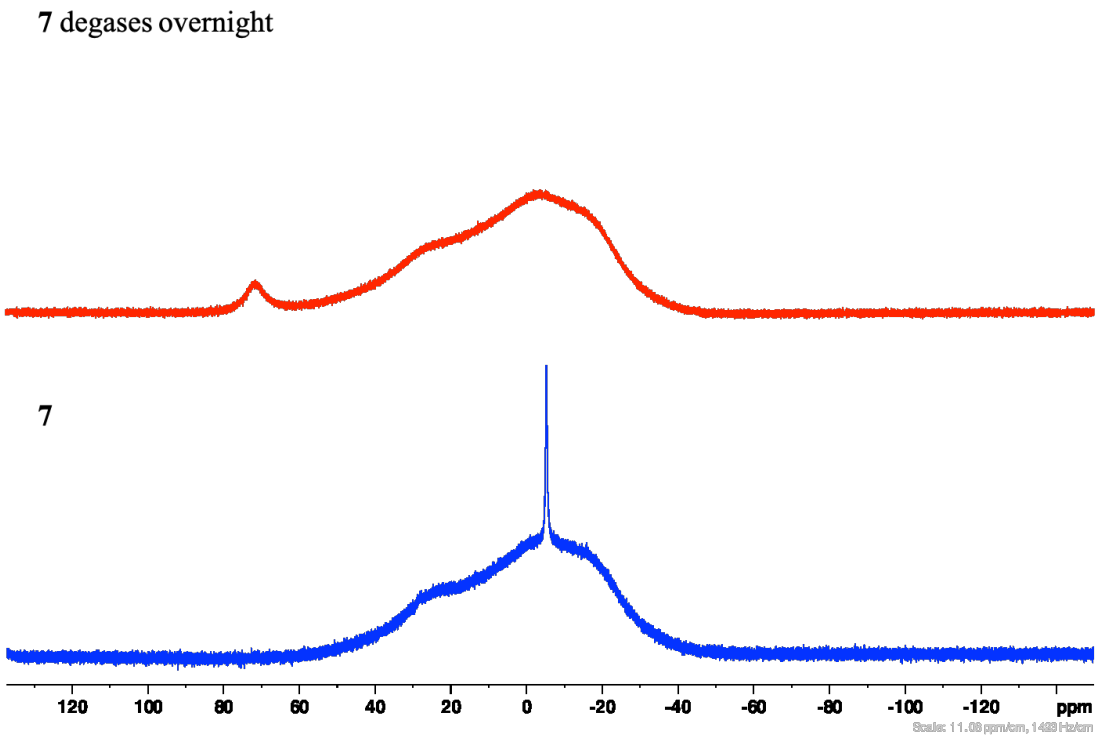


Figure S16. ^{11}B NMR spectrum (in C_6D_6) of **4** obtained from the removal of CO from **7** under vacuum.

5. Electrochemical Measurement

All electrochemical experiments were performed with an electrochemical analyzer from CH Instruments (Model 660 D) at a scan rate of 100 mV/s with a standard 3-electrode system: an $Ag/AgNO_3$ reference electrode, a glassy carbon working electrode, and a platinum wire auxiliary electrode. Electrode was immersed in a solution (10 mL) containing $^{n}Bu_4NPF_6$ (0.1 M) and analyte (0.001 M in CH_2Cl_2). The supporting electrolyte, *n*-Bu_4NPF_6, was dried at 80 °C under vacuum for overnight, and was stored inside a glove box. In all cases, ferrocene was used as an internal standard, and all reduction potentials are reported with respect to the $E_{1/2}$ of the Fc/Fc^+ redox couple.

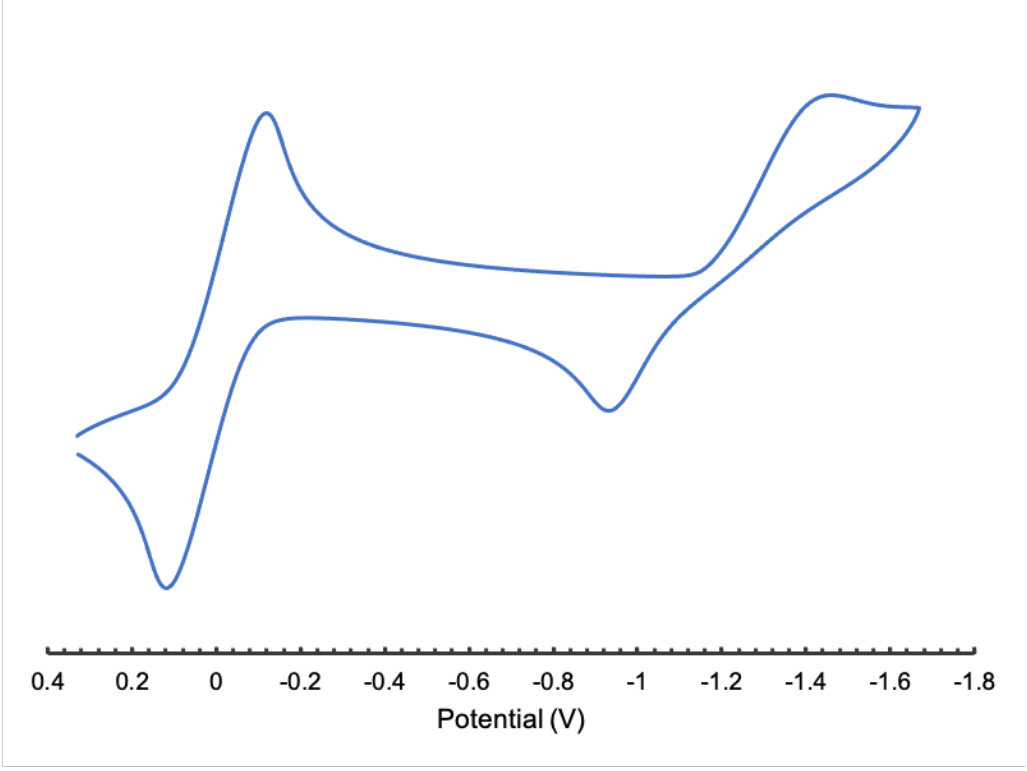


Figure S17. Cyclic voltammogram of [**1**][OTf] with ferrocene as internal reference.

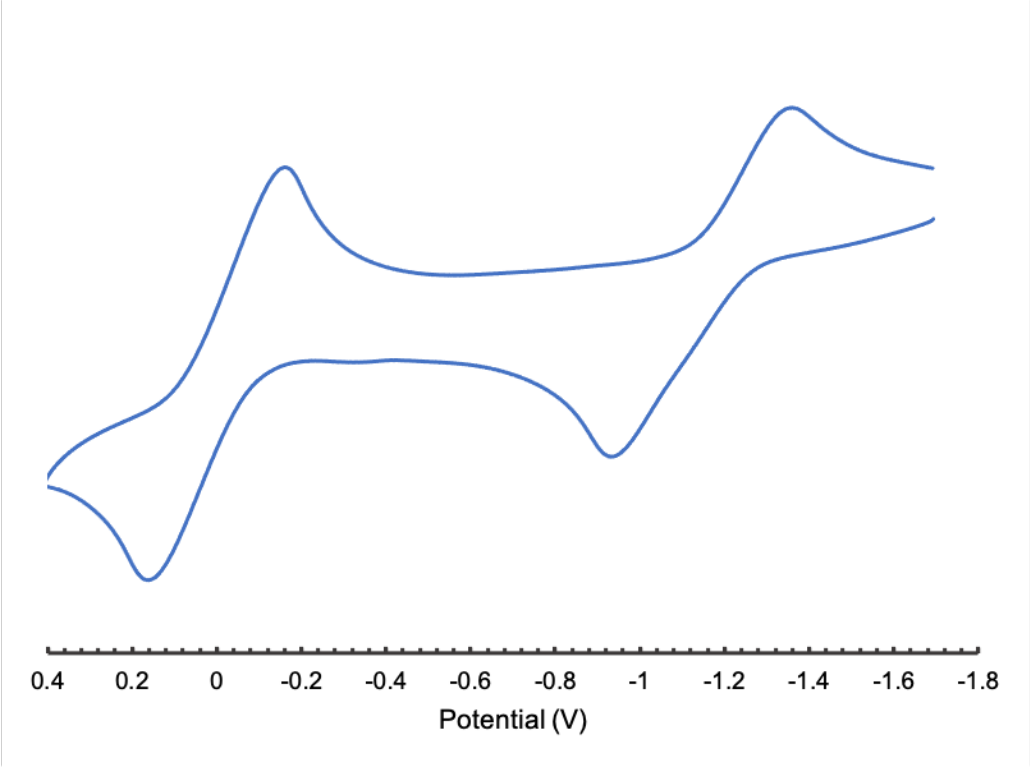


Figure S18. Cyclic voltammogram of **2**$^{\bullet}$ with ferrocene as internal reference.

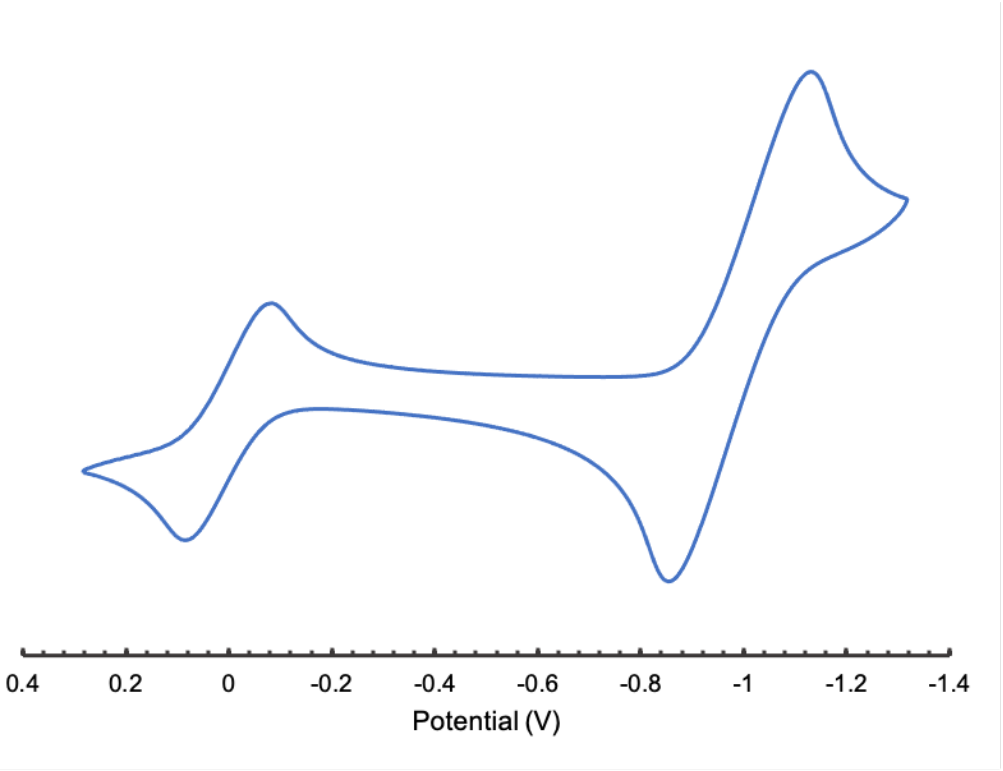


Figure S19. Cyclic voltammogram of [**3**][$B(C_6F_5)_4$] with ferrocene as internal reference.

6. EPR spectra and simulation

Solution EPR measurement was carried out on a Bruker EMX nano spectrometer. Samples containing around 0.002 M of radical species were transferred to a quartz J-Young's tube under nitrogen atmosphere. EPR spectra were obtained with a microwave power of 0.3162 mW, modulation amplitude of 1 G, time constant of 1.28 ms, and sweep time of 10 s. The EPR spectra were simulated using Easyspin5.2.30[4] with hyperfine coupling constants listed in the figure caption.

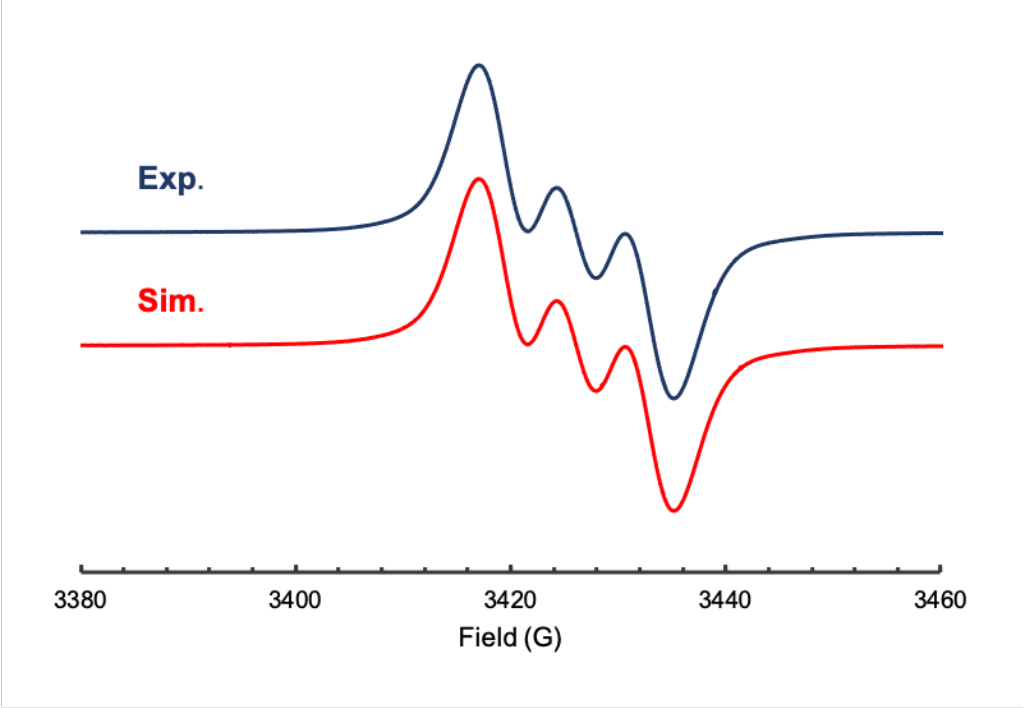


Figure S20. EPR spectrum of **2•** in DCM at room temperature. The simulation parameters are g_{iso} = 2.0047, a($^{14}N_{CAAC}$) = 6.62 G, and a($^{11,10}B$) = 0.77/0.26 G.

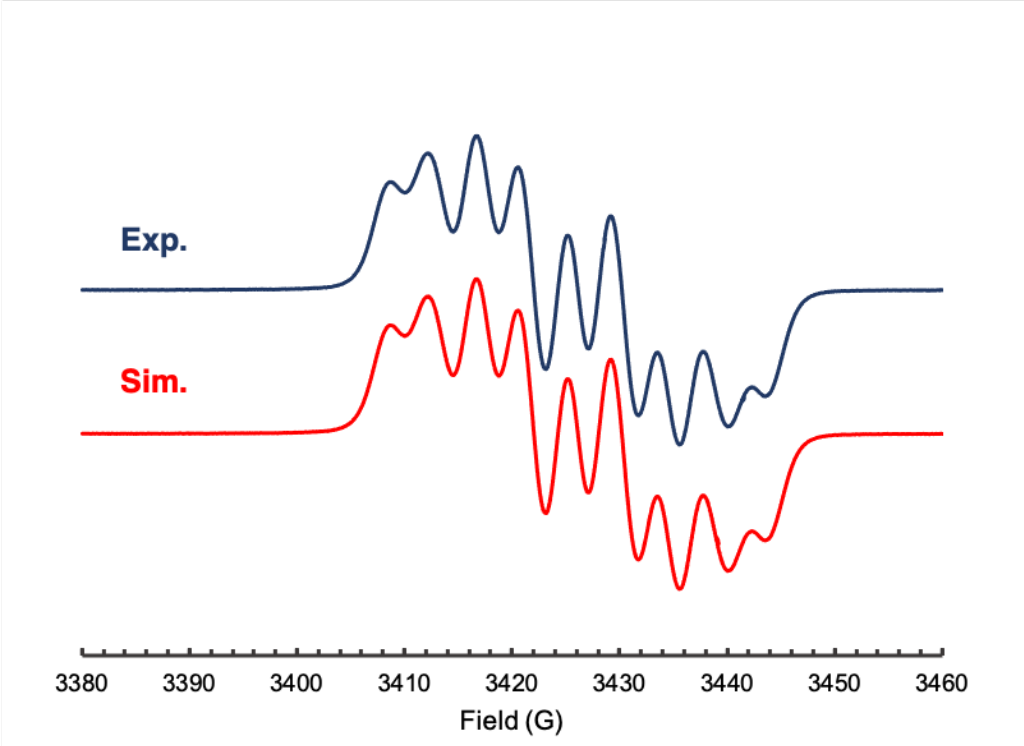


Figure S21. EPR spectrum of [**3**][$B(C_6F_5)_4$] in DCM at room temperature. The simulation parameters are g_{iso} = 2.0047, a($^{11,10}B$) = 3.82/1.27 G, a($^{14}N_{CAAC}$) = 8.32 G, and a($^{14}N_{TMP}$) = 2.42 G.

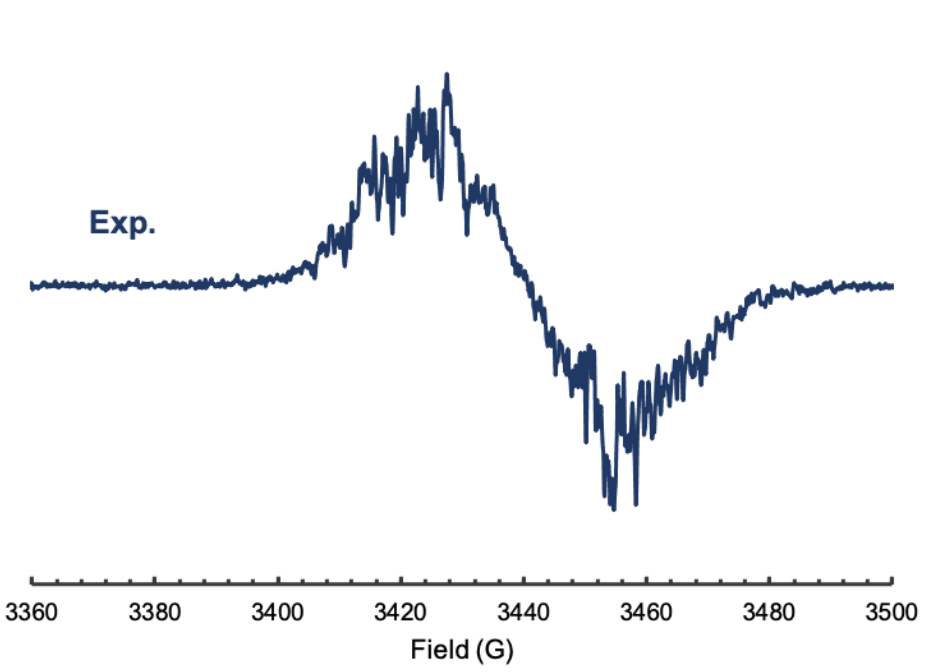


Figure S22. EPR spectrum of [**6**][$B(C_6F_5)_4$] in DCM at 77 K.

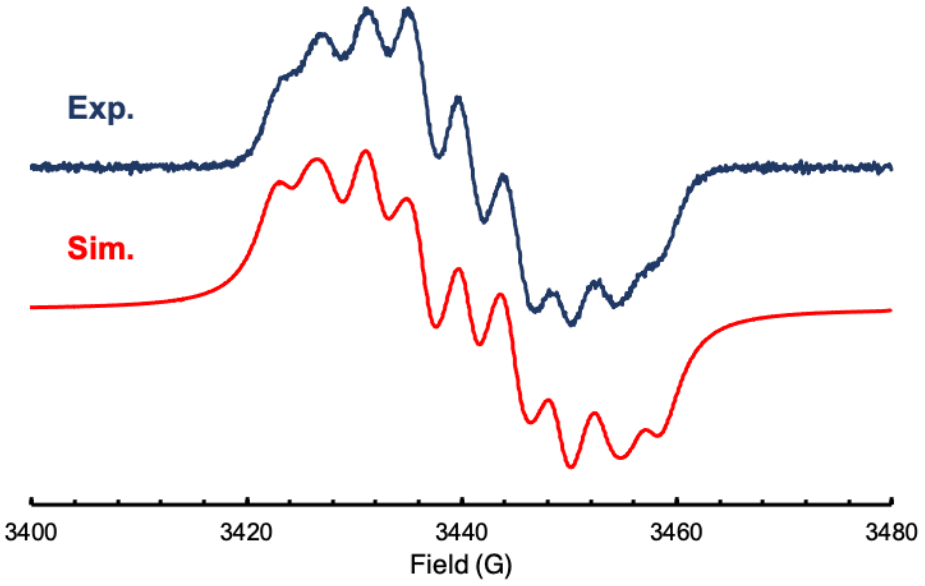
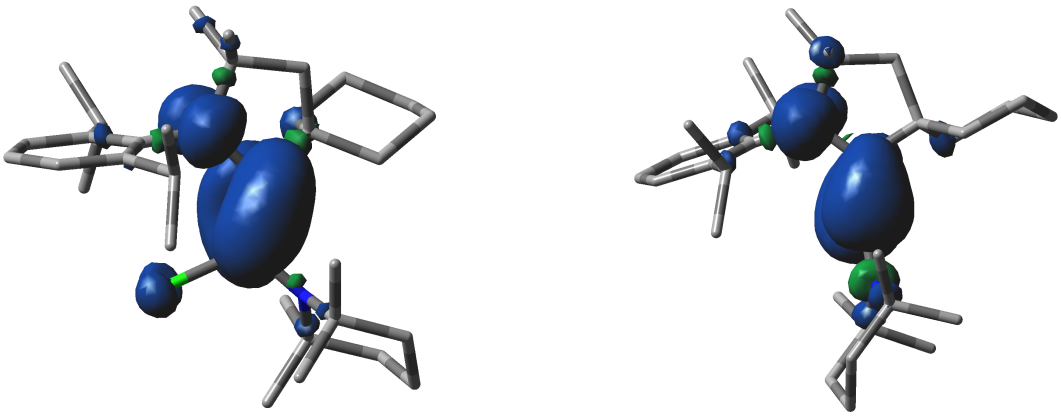


Figure S23. EPR spectrum of [**9**][$B(C_6F_5)_4$] in DCM at room temperature. The simulation parameters are g_{iso} = 2.0032, a(^{11,10}B) = 4.09 G, a($^{14}N_{cAAC}$) = 8.38 G, and a($^{14}N_{CNXyl}$) = 2.39 G.

7. Computational Details

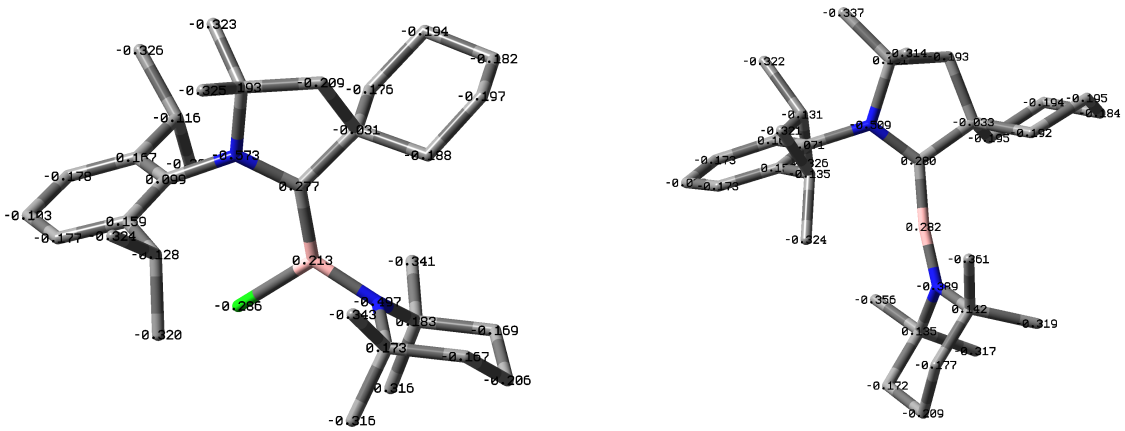
Density functional theory (DFT) calculations (full geometry optimization) were carried out with Gaussian 16 program package[5] at the theory level of UCAM-B3LYP/6-31G(d,p)/SMD(CH_2Cl_2). Frequency calculations were performed to verify the optimized structures as minima. The molecular orbital surface was generated by GaussView 6.[6] The redox potentials are calculated in terms of Gibbs free energy change of the corresponding solvated redox reaction.[7]



2$^{\bullet}$ | **[3]**$^{+\bullet}$

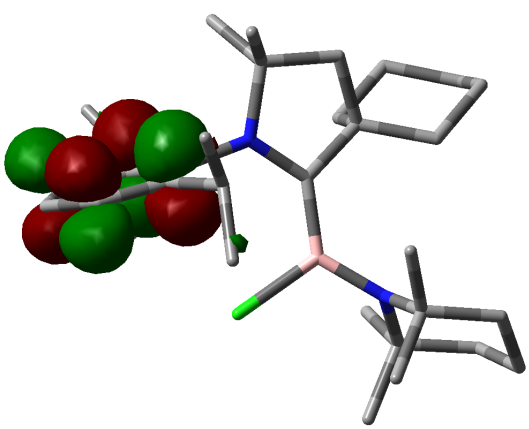
N_{cAAC}: 19.8%, C_{cAAC}: 48.4%, B: 30.8%, Cl: 0.1%, N_{TMP}: 0.1% | N_{cAAC}: 33.6%, C_{cAAC}: 18.8%, B: 46.4%, N_{TMP}: 0.3%

Figure S24. Spin density plots of **2**$^{\bullet}$ and **[3]**$^{+\bullet}$ (isovalue = 0.002). Hydrogen atoms are omitted for clarity.

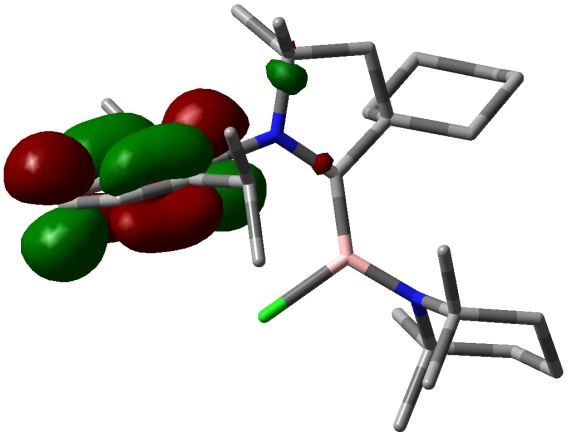


2$^{\bullet}$ | **[3]**$^{+\bullet}$

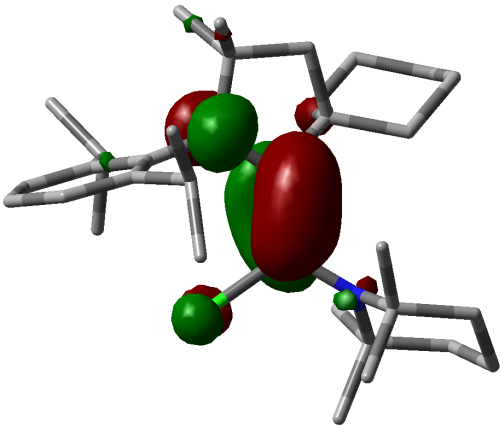
Figure S25. Mulliken charges of **2**$^{\bullet}$ and **[3]**$^{+\bullet}$. Hydrogen atoms are omitted for clarity.



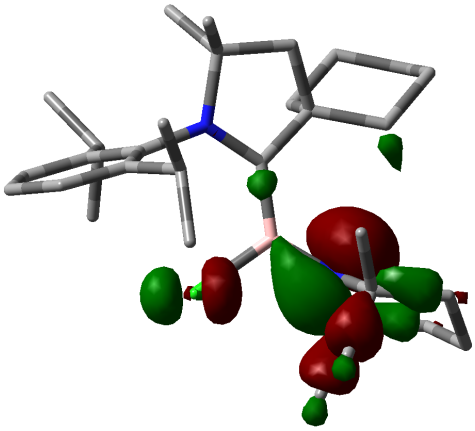
LUMO+1 (1.46)



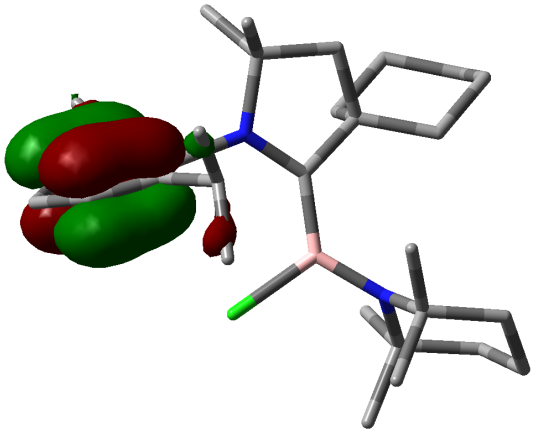
LUMO (1.35)



SOMO (-5.56)

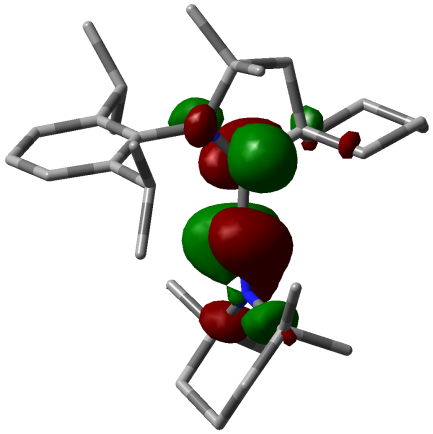


SOMO-1 (-6.72)

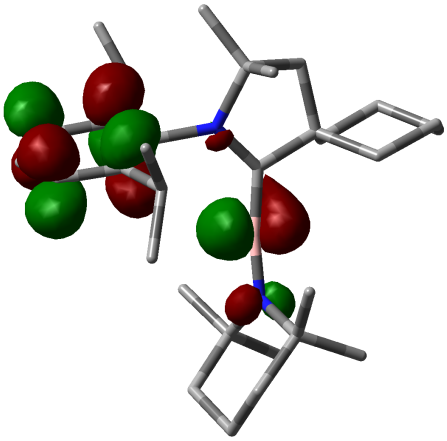


SOMO-2 (-7.64)

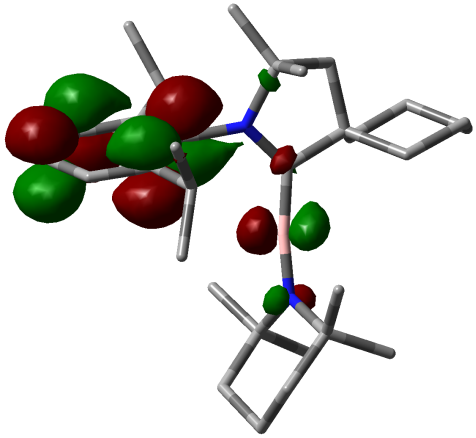
Figure S26. Selected molecular orbitals of **2˙** (isovalue = 0.05). Hydrogen atoms are omitted for clarity.



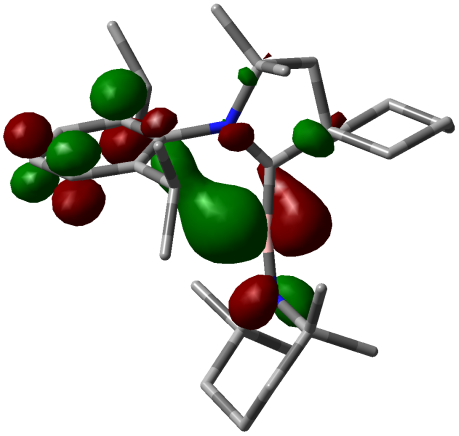
LUMO+3 (1.50)



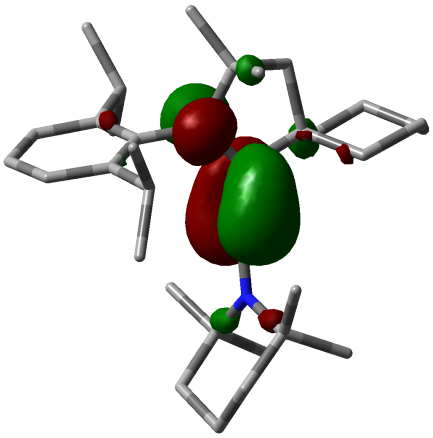
LUMO+2 (1.02)



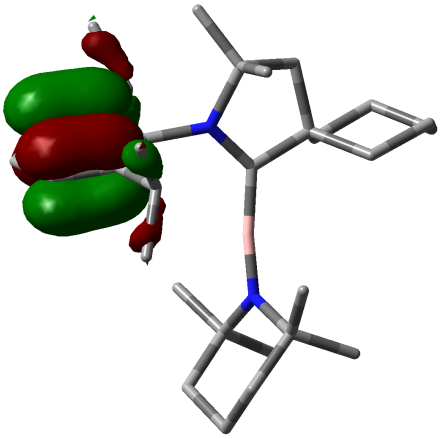
LUMO+1 (0.87)



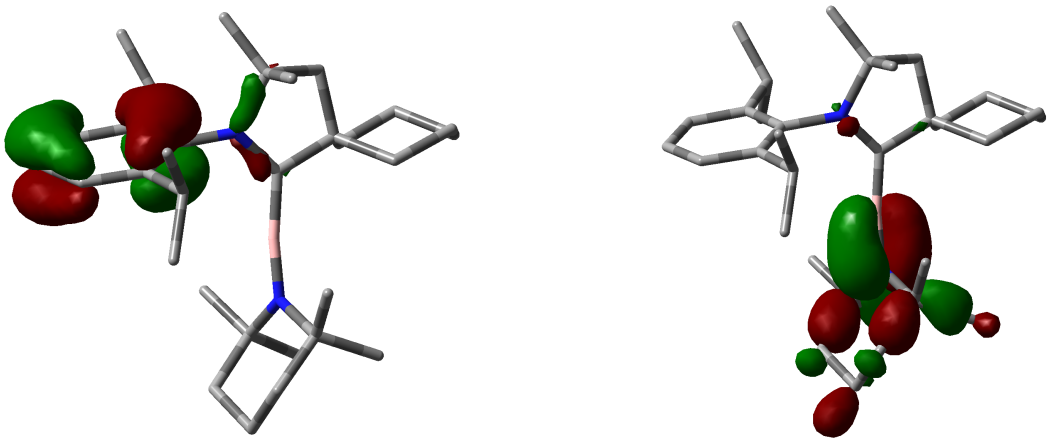
LUMO (0.66)



SOMO (-7.01)



SOMO-1 (-8.15)



SOMO-2 (-8.51) SOMO-3 (-9.36)

Figure S27. Selected molecular orbitals of [**3**]$^{+\bullet}$ (isovalue = 0.05). Hydrogen atoms are omitted for clarity.

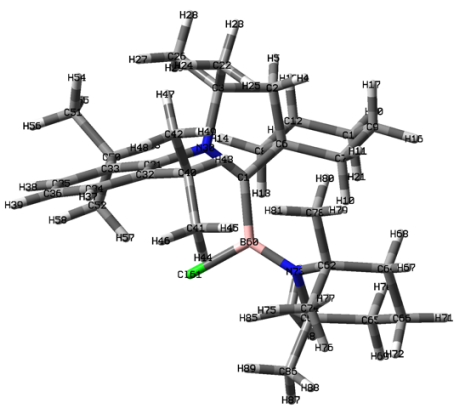
Table S5. Calculated Gibbs free energy (Hartree) at UCAM-B3LYP/6-31G**/SMD(CH_2Cl_2) level.

	Gibbs free energy (Hartree)
$[\mathbf{1}]^+$	-1844.324352
$\mathbf{2}^{\bullet}$	-1844.460150
$[\mathbf{3}]^{+\bullet}$	-1384.088845
4	-1384.217597
$[\mathbf{8}]^{+\bullet}$	-1497.345888
7	-1497.495492

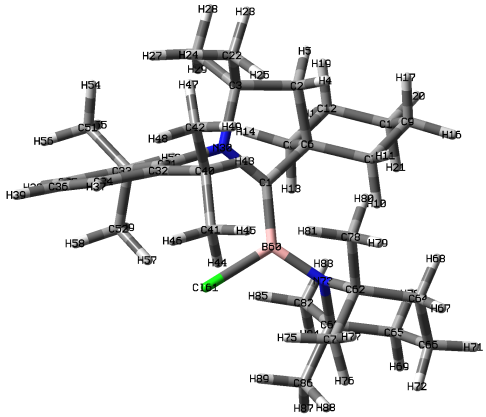
Table S6. Calculated redox potential (eV) at UCAM-B3LYP/6-31G**/SMD(CH_2Cl_2) level.

Reaction	$\Delta G°$	$E_{1/2}$ (vs. SHE[a])	$E_{1/2}$ (vs. Fc/Fc^{+}[b])
$[\mathbf{1}]^+ + e^- \rightarrow \mathbf{2}^{\bullet}$	-3.69525	-0.58	-0.98
$[\mathbf{3}]^{+\bullet} + e^- \rightarrow \mathbf{4}$	-3.50352	-0.78	-1.18
$[\mathbf{8}]^{+\bullet} + e^- \rightarrow \mathbf{7}$	-4.07093	-0.21	-0.61

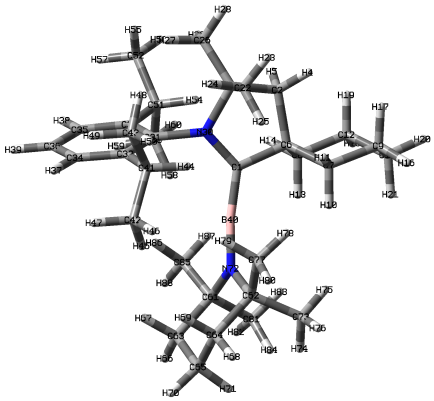
a. $\Delta G°_{SHE}$ = -4.28 eV.[8] *b*. Fc/Fc$^+$, $E_{1/2}$ = 0.4 V (vs. SHE).



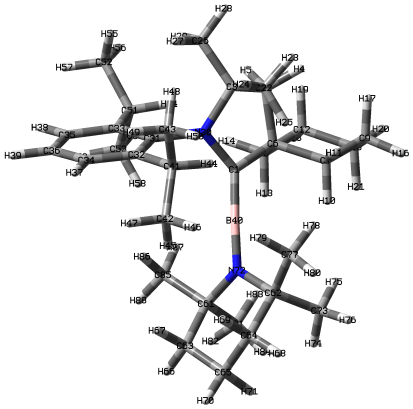
$[\mathbf{1}]^{+}$



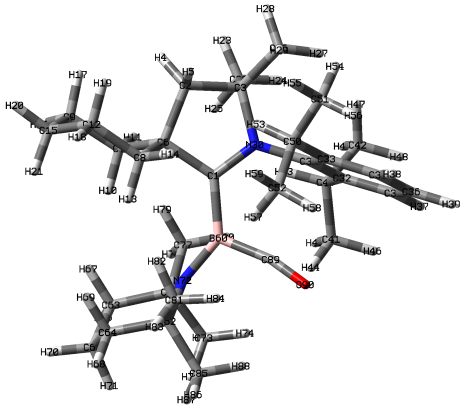
$\mathbf{2}^{\bullet}$



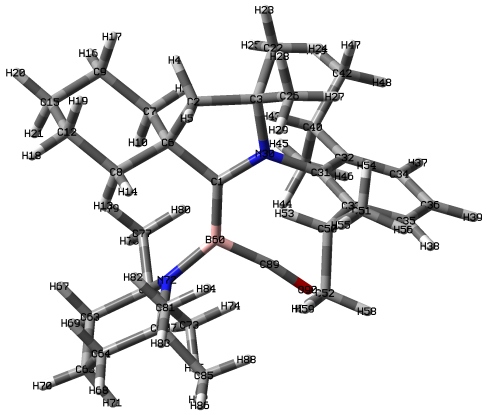
$[\mathbf{3}]^{+\bullet}$



$\mathbf{4}$



$[\mathbf{8}]^{+\bullet}$



$\mathbf{7}$

Figure S28. Optimized structure at UCAM-B3LYP/6-31G**/SMD(CH_2Cl_2) level. Hydrogen atoms are omitted for clarity.

Table S5. Cartesian coordinates for the optimized geometry of [**1**]$^{+}$.

Label	Element	X	Y	Z
1	C	-1.10065	0.62481	-0.09404
2	C	0.93221	1.82242	0.30615
3	C	-0.24174	2.80732	0.32441
4	H	1.28153	1.64218	1.32599
5	H	1.76989	2.23387	-0.25674
6	C	0.42031	0.50612	-0.29167
7	C	1.14555	-0.71486	0.30244
8	C	0.59184	0.4511	-1.84678
9	C	2.61073	-0.79834	-0.1361
10	H	0.63059	-1.62892	-0.00008
11	H	1.11775	-0.67274	1.3918
12	C	2.05066	0.32746	-2.29295
13	H	0.0344	-0.40928	-2.23267
14	H	0.15306	1.33927	-2.30122
15	C	2.74524	-0.86848	-1.6528
16	H	3.06173	-1.67908	0.33181
17	H	3.1639	0.07062	0.2411
18	H	2.06665	0.24914	-3.38461
19	H	2.59708	1.24364	-2.04087
20	H	3.79959	-0.89776	-1.94521
21	H	2.28831	-1.79744	-2.01743
22	C	-0.42094	3.42554	1.70552
23	H	0.48545	3.99472	1.92768
24	H	-1.26209	4.11845	1.73147
25	H	-0.53807	2.67166	2.48497
26	C	-0.07879	3.93457	-0.68278
27	H	-0.95738	4.57868	-0.70535
28	H	0.76509	4.5434	-0.34971
29	H	0.14701	3.57974	-1.68677
30	N	-1.44266	1.88232	0.01168
31	C	-2.78345	2.47989	-0.19256
32	C	-3.65955	2.66148	0.89779
33	C	-3.1435	2.92514	-1.49352
34	C	-4.89514	3.26885	0.66275
35	C	-4.39704	3.51491	-1.65243
36	C	-5.27143	3.69055	-0.59583

37	H	-5.57472	3.4053	1.49609
38	H	-4.68963	3.85226	-2.6402
39	H	-6.23812	4.15725	-0.75453
40	C	-3.40911	2.20945	2.32843
41	C	-4.41322	1.11689	2.72221
42	C	-3.49686	3.35973	3.34035
43	H	-2.40448	1.79651	2.38976
44	H	-4.43545	0.29953	1.99835
45	H	-4.16321	0.70056	3.70254
46	H	-5.4253	1.52638	2.78431
47	H	-2.83859	4.19274	3.08735
48	H	-4.51585	3.74958	3.41118
49	H	-3.2164	2.99771	4.33413
50	C	-2.29284	2.86253	-2.76443
51	C	-2.03893	4.2689	-3.33728
52	C	-2.92285	2.01964	-3.8833
53	H	-1.33314	2.41315	-2.52382
54	H	-1.69247	4.98389	-2.59111
55	H	-1.28677	4.21421	-4.13004
56	H	-2.95157	4.67403	-3.7834
57	H	-3.04167	0.97424	-3.60721
58	H	-3.90325	2.40941	-4.17161
59	H	-2.2817	2.06321	-4.7691
60	B	-2.05449	-0.69755	-0.27856
61	Cl	-3.32207	-0.45948	-1.52325
62	C	-1.82352	-2.11694	1.83395
63	C	-2.01038	-3.23384	-0.49615
64	C	-0.80404	-3.18197	2.25456
65	C	-0.9968	-4.26903	0.04446
66	C	-1.01828	-4.50614	1.54296
67	H	-0.8795	-3.30283	3.33983
68	H	0.20543	-2.81413	2.04291
69	H	-1.18365	-5.20187	-0.49634
70	H	0.00896	-3.9369	-0.24026
71	H	-0.22659	-5.21195	1.8128
72	H	-1.96108	-4.96774	1.85273
73	N	-1.88581	-1.95533	0.32923
74	C	-3.22216	-2.49153	2.36578
75	H	-3.98515	-1.82687	1.95591

76	H	-3.51225	-3.5156	2.14423
77	H	-3.22715	-2.38226	3.45403
78	C	-1.46186	-0.80181	2.51441
79	H	-1.42893	-0.9691	3.59366
80	H	-0.48884	-0.41424	2.22356
81	H	-2.22307	-0.04869	2.33343
82	C	-1.56742	-3.00599	-1.95291
83	H	-0.6436	-2.42395	-2.003
84	H	-1.36198	-3.98318	-2.39705
85	H	-2.32153	-2.52692	-2.57269
86	C	-3.4296	-3.82231	-0.51895
87	H	-3.49202	-4.55667	-1.32723
88	H	-3.6946	-4.3373	0.40328
89	H	-4.17629	-3.05037	-0.71178

Table S6. Cartesian coordinates for the optimized geometry of **2˙.**

Label	Element	X	Y	Z
1	C	-1.1329	0.60701	-0.05849
2	C	0.86772	1.85008	0.40724
3	C	-0.2668	2.85841	0.21751
4	H	1.03775	1.69328	1.47739
5	H	1.80033	2.22693	-0.01526
6	C	0.40789	0.52637	-0.22016
7	C	1.12712	-0.65889	0.44806
8	C	0.73462	0.48302	-1.7424
9	C	2.62886	-0.69793	0.14659
10	H	0.66658	-1.59159	0.11892
11	H	0.98975	-0.60739	1.53042
12	C	2.23025	0.41163	-2.06302
13	H	0.24524	-0.39277	-2.1733
14	H	0.30066	1.34732	-2.24617
15	C	2.903	-0.76002	-1.35335
16	H	3.07021	-1.56473	0.65084
17	H	3.12135	0.18719	0.56907
18	H	2.35669	0.3278	-3.14813
19	H	2.72608	1.34474	-1.769
20	H	3.98082	-0.76061	-1.54963
21	H	2.50849	-1.70329	-1.75406
22	C	-0.42525	3.71172	1.47547
23	H	0.50035	4.27468	1.6276
24	H	-1.23807	4.43347	1.37658
25	H	-0.59134	3.10084	2.36291
26	C	-0.01387	3.82509	-0.94343
27	H	-0.86248	4.49732	-1.08219
28	H	0.85525	4.44112	-0.69696
29	H	0.19412	3.32362	-1.88735
30	N	-1.45319	1.95334	-0.01237
31	C	-2.75634	2.56972	-0.17438
32	C	-3.56365	2.85572	0.94947
33	C	-3.19169	2.93777	-1.4696
34	C	-4.75546	3.55656	0.75642
35	C	-4.39509	3.63008	-1.60215
36	C	-5.16984	3.95529	-0.50195

37	H	-5.37758	3.78092	1.61664
38	H	-4.73324	3.91196	-2.59392
39	H	-6.10041	4.50044	-0.62679
40	C	-3.27528	2.37383	2.36702
41	C	-4.33654	1.35897	2.81928
42	C	-3.22523	3.51494	3.39254
43	H	-2.30915	1.86679	2.36342
44	H	-4.42326	0.5237	2.12314
45	H	-4.08422	0.96154	3.80766
46	H	-5.32006	1.83265	2.89685
47	H	-2.52544	4.30418	3.11432
48	H	-4.21079	3.97345	3.51777
49	H	-2.92317	3.12552	4.37004
50	C	-2.46135	2.56915	-2.75584
51	C	-2.16698	3.78518	-3.64448
52	C	-3.25237	1.53663	-3.57138
53	H	-1.51461	2.10796	-2.48356
54	H	-1.64589	4.58098	-3.10905
55	H	-1.54328	3.48528	-4.4927
56	H	-3.08831	4.20897	-4.05552
57	H	-3.45349	0.63409	-2.99319
58	H	-4.2131	1.94673	-3.89949
59	H	-2.68948	1.25556	-4.46761
60	B	-2.08791	-0.5881	-0.02167
61	Cl	-3.88013	-0.27346	-0.48036
62	C	-1.94199	-2.34663	1.80032
63	C	-1.90528	-3.06783	-0.65034
64	C	-0.97694	-3.49907	2.13087
65	C	-0.93106	-4.19759	-0.26195
66	C	-1.09778	-4.67771	1.17339
67	H	-1.15832	-3.82165	3.16248
68	H	0.04854	-3.11258	2.09269
69	H	-1.0627	-5.02841	-0.96447
70	H	0.09367	-3.82904	-0.39314
71	H	-0.33601	-5.42948	1.40682
72	H	-2.06554	-5.17498	1.30015
73	N	-1.7922	-1.96834	0.35838
74	C	-3.38522	-2.74604	2.18815
75	H	-4.10455	-2.02151	1.80101

76	H	-3.67371	-3.73235	1.82858
77	H	-3.47735	-2.76448	3.27893
78	C	-1.587	-1.16515	2.70931
79	H	-1.61122	-1.50163	3.75
80	H	-0.59375	-0.76925	2.50811
81	H	-2.30799	-0.35232	2.61342
82	C	-1.45514	-2.53983	-2.01569
83	H	-0.42327	-2.19027	-1.97731
84	H	-1.50624	-3.34406	-2.75509
85	H	-2.09012	-1.72494	-2.37512
86	C	-3.31954	-3.6597	-0.84769
87	H	-3.31806	-4.29678	-1.73803
88	H	-3.64646	-4.28065	-0.01505
89	H	-4.05892	-2.87297	-0.99722

Table S7. Cartesian coordinates for the optimized geometry of **[3]**$^{+\bullet}$.

Label	Element	X	Y	Z
1	C	-0.97684	0.70971	-0.0427
2	C	0.8148	2.27465	-0.33028
3	C	-0.41829	2.98316	0.24864
4	H	1.71446	2.56286	0.21503
5	H	0.95007	2.58021	-1.37149
6	C	0.54371	0.75271	-0.25953
7	C	1.33749	0.04792	0.86119
8	C	0.87363	0.05544	-1.6008
9	C	2.84143	-0.00564	0.57991
10	H	0.9643	-0.9792	0.9545
11	H	1.15276	0.54015	1.82045
12	C	2.37469	0.03191	-1.89234
13	H	0.50834	-0.97881	-1.55749
14	H	0.33117	0.55278	-2.41157
15	C	3.14282	-0.65989	-0.76759
16	H	3.33761	-0.55127	1.38908
17	H	3.25788	1.0088	0.59099
18	H	2.5501	-0.47584	-2.84636
19	H	2.74491	1.0577	-2.01272
20	H	4.21874	-0.63662	-0.96872
21	H	2.85109	-1.7178	-0.73041
22	C	-0.28721	3.17448	1.76439
23	H	0.60128	3.77777	1.96859
24	H	-1.14824	3.70238	2.17518
25	H	-0.17895	2.22262	2.28792
26	C	-0.67657	4.33441	-0.39767
27	H	-1.62868	4.76328	-0.07624
28	H	0.11623	5.01863	-0.08452
29	H	-0.65607	4.28252	-1.4844
30	N	-1.49575	1.96269	-0.03655
31	C	-2.87543	2.28156	-0.34734
32	C	-3.85208	2.35346	0.66515
33	C	-3.21188	2.52944	-1.69963
34	C	-5.1622	2.67047	0.29964
35	C	-4.53971	2.82643	-2.00409
36	C	-5.51054	2.90087	-1.01893

37	H	-5.92175	2.73545	1.07125
38	H	-4.81317	3.01245	-3.03718
39	H	-6.53624	3.14177	-1.27944
40	B	-1.67188	-0.55546	0.18195
41	C	-3.57525	2.10902	2.13956
42	C	-4.48462	1.00949	2.70376
43	C	-3.75601	3.39339	2.95961
44	H	-2.53997	1.77827	2.24365
45	H	-4.43404	0.09442	2.10839
46	H	-4.19546	0.76621	3.73048
47	H	-5.52912	1.33231	2.72722
48	H	-3.15806	4.22099	2.57028
49	H	-4.80251	3.71289	2.95266
50	H	-3.4667	3.22462	4.00138
51	C	-2.21692	2.51419	-2.85487
52	C	-2.21601	3.84801	-3.61721
53	C	-2.50249	1.37853	-3.84403
54	H	-1.21689	2.35374	-2.44874
55	H	-2.11454	4.71	-2.95459
56	H	-1.38918	3.86904	-4.33358
57	H	-3.1423	3.97608	-4.18457
58	H	-2.46346	0.39972	-3.36679
59	H	-3.49243	1.49141	-4.29657
60	H	-1.76571	1.39108	-4.65322
61	C	-2.80675	-2.59889	-0.647
62	C	-2.00167	-2.37804	1.84011
63	C	-4.12961	-3.15364	-0.10301
64	C	-3.35794	-2.96127	2.26243
65	C	-3.98365	-3.88452	1.22488
66	H	-4.55194	-3.81318	-0.86745
67	H	-4.82878	-2.318	0.02133
68	H	-3.20845	-3.48695	3.21062
69	H	-4.04407	-2.13068	2.46281
70	H	-4.96746	-4.21206	1.57353
71	H	-3.3828	-4.79133	1.10139
72	N	-2.13578	-1.78895	0.44487
73	C	-0.89591	-3.44089	1.88098
74	H	-1.17734	-4.37809	1.40482
75	H	0.01929	-3.07369	1.41009

76	H	-0.66974	-3.66307	2.92719
77	C	-1.61616	-1.2707	2.81993
78	H	-0.60575	-0.89824	2.63997
79	H	-2.31567	-0.43534	2.78221
80	H	-1.64027	-1.68068	3.83266
81	C	-1.88786	-3.7153	-1.15885
82	H	-2.31188	-4.11607	-2.08333
83	H	-0.89255	-3.32525	-1.38705
84	H	-1.78281	-4.54593	-0.46374
85	C	-3.10026	-1.66891	-1.8196
86	H	-3.68622	-0.79795	-1.51238
87	H	-2.17508	-1.33383	-2.29533
88	H	-3.67705	-2.21216	-2.57214

Table S8. Cartesian coordinates for the optimized geometry of **4**.

Label	Element	X	Y	Z
1	C	-0.99834	0.65159	-0.01023
2	C	0.75752	2.29296	-0.26988
3	C	-0.49054	2.92868	0.3813
4	H	1.66713	2.54798	0.28027
5	H	0.87239	2.69653	-1.28107
6	C	0.51057	0.75988	-0.33483
7	C	1.38241	-0.00782	0.68274
8	C	0.83435	0.20223	-1.73994
9	C	2.87832	0.00393	0.35321
10	H	1.04008	-1.05062	0.70643
11	H	1.21847	0.39391	1.6877
12	C	2.32394	0.25385	-2.08737
13	H	0.50358	-0.84383	-1.77831
14	H	0.24924	0.74124	-2.49111
15	C	3.15238	-0.51383	-1.05831
16	H	3.42042	-0.59806	1.09135
17	H	3.27065	1.02471	0.44299
18	H	2.48638	-0.15612	-3.09075
19	H	2.66205	1.2978	-2.12112
20	H	4.22075	-0.44222	-1.29098
21	H	2.88945	-1.57909	-1.10992
22	C	-0.32252	2.97375	1.91113
23	H	0.58732	3.51938	2.18247
24	H	-1.16619	3.47908	2.38662
25	H	-0.24998	1.96623	2.32753
26	C	-0.73427	4.34713	-0.11987
27	H	-1.66391	4.76075	0.28176
28	H	0.08419	4.99447	0.20906
29	H	-0.77872	4.39276	-1.2084
30	N	-1.54049	1.97841	-0.02996
31	C	-2.86535	2.31029	-0.44245
32	C	-3.9249	2.35921	0.49323
33	C	-3.14119	2.59144	-1.80557
34	C	-5.21243	2.68694	0.06188
35	C	-4.44581	2.89956	-2.19177
36	C	-5.47966	2.95294	-1.27021

37	H	-6.01992	2.73153	0.78646
38	H	-4.65325	3.10828	-3.23702
39	H	-6.48746	3.20164	-1.58938
40	B	-1.62966	-0.55865	0.33616
41	C	-3.72149	2.07121	1.97122
42	C	-4.64942	0.95553	2.46653
43	C	-3.92419	3.33307	2.81949
44	H	-2.69144	1.73373	2.09645
45	H	-4.52961	0.0449	1.87379
46	H	-4.43199	0.71249	3.5116
47	H	-5.70129	1.25314	2.41429
48	H	-3.28722	4.15628	2.48456
49	H	-4.96215	3.67813	2.76764
50	H	-3.69373	3.13315	3.87113
51	C	-2.07054	2.57379	-2.88517
52	C	-1.99961	3.8998	-3.6542
53	C	-2.28076	1.42028	-3.87262
54	H	-1.11414	2.41807	-2.38597
55	H	-1.89994	4.75935	-2.98624
56	H	-1.14065	3.89813	-4.3331
57	H	-2.89542	4.05778	-4.26285
58	H	-2.29547	0.45404	-3.36523
59	H	-3.22778	1.53049	-4.41145
60	H	-1.47779	1.40063	-4.61704
61	C	-2.83842	-2.60353	-0.45516
62	C	-1.9875	-2.39765	1.99267
63	C	-4.10735	-3.26582	0.10648
64	C	-3.29633	-3.0673	2.44302
65	C	-3.88264	-4.01702	1.40953
66	H	-4.50952	-3.93179	-0.66409
67	H	-4.85818	-2.48383	0.27397
68	H	-3.10226	-3.58886	3.38606
69	H	-4.0303	-2.28149	2.65902
70	H	-4.8315	-4.42434	1.77317
71	H	-3.21901	-4.87395	1.25163
72	N	-2.16128	-1.78963	0.62047
73	C	-0.82836	-3.40738	2.01068
74	H	-1.04923	-4.33226	1.4796
75	H	0.07003	-2.96656	1.57103

76	H	-0.60002	-3.67435	3.0468
77	C	-1.64943	-1.30514	3.00873
78	H	-0.66402	-0.87176	2.83058
79	H	-2.38685	-0.50117	2.9939
80	H	-1.64803	-1.74882	4.00881
81	C	-1.88796	-3.65523	-1.04912
82	H	-2.32862	-4.0663	-1.96221
83	H	-0.93043	-3.19814	-1.31364
84	H	-1.69386	-4.49193	-0.37885
85	C	-3.26501	-1.6796	-1.59541
86	H	-3.87257	-0.84724	-1.23135
87	H	-2.40199	-1.27179	-2.12268
88	H	-3.86151	-2.252	-2.31167

Table S9. Cartesian coordinates for the optimized geometry of **7**.

Label	Element	X	Y	Z
1	C	-1.00708	0.72804	-0.05741
2	C	0.93582	2.0552	-0.58215
3	C	-0.24481	3.00972	-0.39547
4	H	1.85011	2.47214	-0.15807
5	H	1.11271	1.90731	-1.65237
6	C	0.53228	0.71234	0.05083
7	C	0.92707	0.66319	1.55268
8	C	1.22132	-0.45763	-0.67021
9	C	2.44011	0.62285	1.78527
10	H	0.48825	-0.23078	1.99222
11	H	0.49244	1.51103	2.08665
12	C	2.73693	-0.47707	-0.45331
13	H	0.78738	-1.39619	-0.31651
14	H	1.00831	-0.39041	-1.74058
15	C	3.09211	-0.53422	1.03077
16	H	2.63089	0.53345	2.8604
17	H	2.90139	1.56667	1.47037
18	H	3.16478	-1.33682	-0.98042
19	H	3.19081	0.4162	-0.90137
20	H	4.17891	-0.51593	1.16743
21	H	2.7373	-1.48534	1.44928
22	C	-0.07423	3.95444	0.79848
23	H	0.78486	4.60484	0.61217
24	H	-0.9513	4.59496	0.90993
25	H	0.09906	3.43435	1.73948
26	C	-0.42635	3.88636	-1.63292
27	H	-1.30364	4.53155	-1.54787
28	H	0.45048	4.53303	-1.73027
29	H	-0.50383	3.29326	-2.54367
30	N	-1.37366	2.03508	-0.21089
31	C	-2.73774	2.49262	-0.16298
32	C	-3.31724	2.8216	1.08614
33	C	-3.49078	2.61454	-1.35484
34	C	-4.61692	3.32604	1.10554
35	C	-4.78601	3.12568	-1.27225
36	C	-5.34571	3.4915	-0.06003

37	H	-5.06878	3.58398	2.05773
38	H	-5.37145	3.22683	-2.18014
39	H	-6.35529	3.889	-0.02195
40	C	-2.63452	2.59437	2.42974
41	C	-3.36366	1.51535	3.2437
42	C	-2.54258	3.87564	3.26871
43	H	-1.62373	2.23422	2.24081
44	H	-3.44135	0.5758	2.69438
45	H	-2.82335	1.31925	4.17545
46	H	-4.37559	1.83677	3.5096
47	H	-2.06416	4.69562	2.72983
48	H	-3.53466	4.21656	3.58006
49	H	-1.96365	3.68674	4.17824
50	C	-3.01055	2.15481	-2.72675
51	C	-3.02059	3.28662	-3.76387
52	C	-3.87594	1.00071	-3.25361
53	H	-1.98986	1.78231	-2.62236
54	H	-2.46038	4.16373	-3.43694
55	H	-2.58349	2.93714	-4.7046
56	H	-4.04374	3.60827	-3.98089
57	H	-3.91357	0.16665	-2.55238
58	H	-4.90242	1.33125	-3.43976
59	H	-3.47195	0.62959	-4.20085
60	B	-1.96295	-0.45325	0.02984
61	C	-1.94005	-2.74695	1.25857
62	C	-2.0111	-2.66663	-1.295
63	C	-1.27906	-4.13594	1.14568
64	C	-1.3377	-4.05342	-1.31124
65	C	-1.67825	-4.9051	-0.10073
66	H	-1.51274	-4.70498	2.05231
67	H	-0.19064	-3.99684	1.13046
68	H	-1.6159	-4.56212	-2.24103
69	H	-0.25024	-3.90945	-1.34084
70	H	-1.14439	-5.86088	-0.14499
71	H	-2.74644	-5.14817	-0.08271
72	N	-1.72997	-1.9592	0.00073
73	C	-3.41788	-2.92423	1.67553
74	H	-3.91048	-1.95978	1.81326
75	H	-4.00399	-3.49861	0.95935

76	H	-3.46829	-3.45301	2.63298
77	C	-1.24455	-2.05282	2.43156
78	H	-1.41881	-2.62086	3.35056
79	H	-0.16625	-2.01033	2.26954
80	H	-1.6178	-1.03871	2.58711
81	C	-1.40308	-1.88865	-2.46784
82	H	-0.32127	-1.80831	-2.3687
83	H	-1.61468	-2.41918	-3.40131
84	H	-1.81615	-0.88295	-2.55284
85	C	-3.51203	-2.84768	-1.62216
86	H	-3.62171	-3.22417	-2.64442
87	H	-4.01251	-3.55927	-0.96607
88	H	-4.05494	-1.90312	-1.56479
89	C	-3.40617	-0.12977	0.10015
90	O	-4.56672	-0.07385	0.19939

Table S10. Cartesian coordinates for the optimized geometry of $[8]^{+\bullet}$.

Label	Element	X	Y	Z
1	C	-1.02152	0.73507	-0.02988
2	C	0.9128	2.14524	-0.31706
3	C	-0.2254	2.94563	0.30973
4	H	1.85176	2.34567	0.19862
5	H	1.03867	2.45097	-1.35937
6	C	0.50293	0.65363	-0.24888
7	C	1.32609	-0.13552	0.7924
8	C	0.71723	-0.03321	-1.6236
9	C	2.80748	-0.24082	0.4143
10	H	0.91919	-1.14682	0.86308
11	H	1.23951	0.32716	1.77872
12	C	2.19421	-0.09742	-2.01609
13	H	0.33668	-1.05524	-1.56038
14	H	0.13879	0.48697	-2.39372
15	C	3.00369	-0.85726	-0.96856
16	H	3.31652	-0.84062	1.1755
17	H	3.27513	0.75012	0.44056
18	H	2.27782	-0.58332	-2.99342
19	H	2.5996	0.9143	-2.13629
20	H	4.06552	-0.8645	-1.2344
21	H	2.67382	-1.90411	-0.94952
22	C	-0.03754	3.10845	1.82059
23	H	0.89308	3.65516	1.99213
24	H	-0.84745	3.68526	2.26697
25	H	0.03409	2.14612	2.33197
26	C	-0.41801	4.3149	-0.32041
27	H	-1.30273	4.82285	0.06955
28	H	0.45289	4.9237	-0.06451
29	H	-0.47946	4.26892	-1.40625
30	N	-1.38957	1.99523	0.05544
31	C	-2.74421	2.47237	-0.18003
32	C	-3.65489	2.6518	0.8793
33	C	-3.09232	2.76703	-1.51976
34	C	-4.93115	3.11782	0.56427
35	C	-4.38622	3.2196	-1.76709
36	C	-5.29984	3.39527	-0.7407

37	H	-5.65074	3.25689	1.36339
38	H	-4.68239	3.43698	-2.78706
39	H	-6.30179	3.75009	-0.9592
40	C	-3.35554	2.33349	2.33468
41	C	-4.32221	1.27258	2.87788
42	C	-3.42405	3.59281	3.20812
43	H	-2.34454	1.92785	2.39846
44	H	-4.34316	0.38096	2.24627
45	H	-4.02448	0.97011	3.88614
46	H	-5.34275	1.66109	2.9379
47	H	-2.77979	4.39252	2.83396
48	H	-4.445	3.98387	3.24832
49	H	-3.11774	3.35966	4.23217
50	C	-2.15817	2.59406	-2.71336
51	C	-2.09327	3.86072	-3.57818
52	C	-2.56941	1.40225	-3.58743
53	H	-1.1514	2.39459	-2.3449
54	H	-1.8884	4.75694	-2.98776
55	H	-1.30162	3.7571	-4.32594
56	H	-3.03043	4.02435	-4.11736
57	H	-2.51446	0.45478	-3.04743
58	H	-3.59158	1.52088	-3.95933
59	H	-1.90522	1.32867	-4.45389
60	B	-2.06935	-0.45755	-0.08844
61	C	-1.87014	-2.26534	1.72566
62	C	-2.30002	-2.94174	-0.71565
63	C	-0.86408	-3.41974	1.85975
64	C	-1.25937	-4.06369	-0.52863
65	C	-1.14825	-4.57175	0.90331
66	H	-0.87383	-3.77053	2.89721
67	H	0.14193	-3.03115	1.66473
68	H	-1.51726	-4.88433	-1.20657
69	H	-0.28387	-3.67812	-0.8497
70	H	-0.34606	-5.31375	0.96892
71	H	-2.06676	-5.09164	1.19484
72	N	-1.97639	-1.8573	0.28146
73	C	-3.23835	-2.67628	2.31224
74	H	-4.0121	-1.95535	2.03615
75	H	-3.56997	-3.66561	2.00659

76	H	-3.16683	-2.68649	3.4036
77	C	-1.40183	-1.09275	2.58736
78	H	-1.27914	-1.44408	3.61515
79	H	-0.44762	-0.68766	2.26885
80	H	-2.1417	-0.29065	2.60572
81	C	-2.15076	-2.41876	-2.15099
82	H	-1.20923	-1.89283	-2.3043
83	H	-2.16752	-3.27383	-2.83188
84	H	-2.97191	-1.76397	-2.45116
85	C	-3.72996	-3.51511	-0.61835
86	H	-3.95756	-4.04817	-1.54581
87	H	-3.86253	-4.2259	0.19443
88	H	-4.47578	-2.72548	-0.50365
89	C	-3.4667	-0.11224	-0.57385
90	O	-4.55405	-0.10525	-0.9551

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