

# ADVANCED ENERGY MATERIALS

## Supporting Information

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Cyclopropenium Salts as Cyclable, High-Potential Catholytes  
in Nonaqueous Media

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**General Remarks**

All operations were conducted under an oxygen-free atmosphere in either a nitrogen filled glovebox or using standard Schlenk line techniques unless stated otherwise. NMR spectra were obtained on Varian VNMRs 700, Varian VNMRs 500, Varian Inova 500, or Varian MR400 spectrometers.  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts are reported in parts per million (ppm) relative to TMS, with the residual solvent peak used as an internal reference. NMR multiplicities are reported as follows: singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), broad signal (br). Coupling constants ( $J$ ) are reported in hertz (Hz). Infrared (IR) spectroscopy was performed on a Perkin-Elmer Spectrum BX FT-IR spectrometer using an ATR attachment. Melting points were determined with a Mel-Temp 3.0, Laboratory Devices Inc, USA instrument and are uncorrected. EPR spectroscopy was performed with a Bruker EMX electron spin resonance spectrometer equipped with dual microwave bridges for X-band and Q-band ranges.

All electrochemical analyses were carried out in a nitrogen-filled glovebox. The supporting electrolyte was battery-grade lithium hexafluorophosphate (Oakwood), which was dried under vacuum at 120 °C for 24 h prior to use. The solvent was acetonitrile (Sigma, anhydrous 99.8%). Cyclic voltammetry was performed with a Biologic VSP multichannel potentiostat/galvanostat. Cyclic voltammetry was carried out in a three-electrode electrochemical cell, consisting of a glassy carbon disk working electrode (0.07 cm<sup>2</sup>, BASi), a Ag/Ag<sup>+</sup> quasi-reference electrode (BASi) with 0.01 M AgBF<sub>4</sub> (Sigma) in acetonitrile, and a platinum wire counter electrode (23 cm, ALS). The glassy carbon disk electrode was polished in a nitrogen-filled glovebox using aluminum oxide polishing paper (9 micron and 0.3 micron, Fiber Instrument) and anhydrous acetonitrile. All experiments were run at a scan rate of 100 mV/s in an acetonitrile electrolyte containing 1-10 mM active species and 0.1-0.5 M LiPF<sub>6</sub> with added ferrocene (1-10 mM) as an internal voltage reference. Charge/discharge measurements were carried out with a BioLogic VSP galvanostat in a custom glass H-cell and reticulated vitreous carbon electrodes (100 ppi). A porous glass frit (P5, Adams and Chittenden) was used as the separator. The electrolyte contained 10 mM active species and 0.5 M LiPF<sub>6</sub>.

*Synthesis of 1:* Under atmospheric conditions, a 100 mL round-bottom flask was charged with pentachlorocyclopropane (1.90 g, 8.87 mmol), 1,2-dichloroethane (5.0 mL), and a magnetic stirbar. Separately, *N*-methylaniline (14.0 mL, 131 mmol) was dissolved in 1,2-dichloroethane (5.0 mL). The resulting solution was added dropwise to the solution of pentachlorocyclopropane. The mixture was allowed to reflux (130 °C) for 14 h. After this time, the resulting solution was allowed to cool to room temperature. Dichloromethane (100 mL) was added, and this solution was transferred to a separatory funnel and was washed with a HCl (1M aqueous solution; 3 x 100 mL). The organic layer was then washed with an aqueous solution of NH<sub>4</sub>PF<sub>6</sub> (2.18 g, 13.4 mmol in 50 mL water). The organic layer was collected, dried over MgSO<sub>4</sub>, and concentrated via rotary evaporation. The resulting crude solid was dissolved in a minimal amount of refluxing methanol. Once a homogeneous solution had formed, the solution was allowed cool to room temperature while stirring, yielding a white solid. The resulting white solid was collected via filtration and washed with Et<sub>2</sub>O. Residual solvent impurities were removed under vacuum overnight to yield **1** as a white solid (2.83 g, 64% yield). mp 156-158 °C; <sup>1</sup>H NMR (401 MHz, CD<sub>3</sub>CN) δ 7.38-7.16 (m, 12H), 7.12 (br s, 3H), 3.35 (s, 9H); <sup>13</sup>C NMR (101 MHz, CD<sub>3</sub>CN) δ 143.6, 129.4, 126.5, 121.8, 118.3, 41.5; IR (neat): ν = 3065 (w), 1590 (w), 1515 (s), 1492 (s), 1411 (s), 1286 (m), 1185 (m), 1047 (s) cm<sup>-1</sup>; Anal. calcd for C<sub>24</sub>H<sub>24</sub>F<sub>6</sub>N<sub>3</sub>P: C 57.72, H 4.84, N 8.41; found: C 57.80, H 4.86, N 8.27.

*Synthesis of 2:* Compound **2** was prepared in analogy to compound **1** but with pentachlorocyclopropane (1.5 g, 7.0 mmol) and *N*-ethylaniline (13.2 mL, 105 mmol). Compound **2** was isolated as a white solid (2.34 g, 74% yield). mp 149-151 °C; <sup>1</sup>H NMR (700 MHz, CDCl<sub>3</sub>) δ 7.33 (br s, 6H), 7.25 (br s, 6H), 7.14 (br s, 3H), 3.35 (br s, 6H), 0.94 (br s, 9H); <sup>13</sup>C NMR (176 MHz, CDCl<sub>3</sub>) δ 141.6, 129.7, 127.7, 125.2, 116.4, 50.2, 13.6; IR (neat): ν = 2983 (w), 1589 (w), 1491 (s), 1444 (s), 1247 (m), 1056 (s) cm<sup>-1</sup>; Anal. calcd for C<sub>27</sub>H<sub>30</sub>F<sub>6</sub>N<sub>3</sub>P: C 59.89, H 5.58, N 7.76; found: C 59.97, H 5.69, N 7.74.

*Cyclic Voltammetry.* Cyclic voltammetry was performed using a three-electrode cell setup. A glassy carbon disk was used as the working electrode, a platinum wire was used as the counter electrode, and a silver wire with 10 mM AgBF<sub>4</sub> in 0.5 M LiPF<sub>6</sub>/acetonitrile was used as a pseudo-reference electrode. CVs were performed with one equivalent of ferrocene, which served as an internal reference. Redox potentials reported for the CP derivatives are in reference to the Fc/Fc<sup>+</sup> redox couple. CV was performed at a scan rate of 100 mV/s unless otherwise noted.

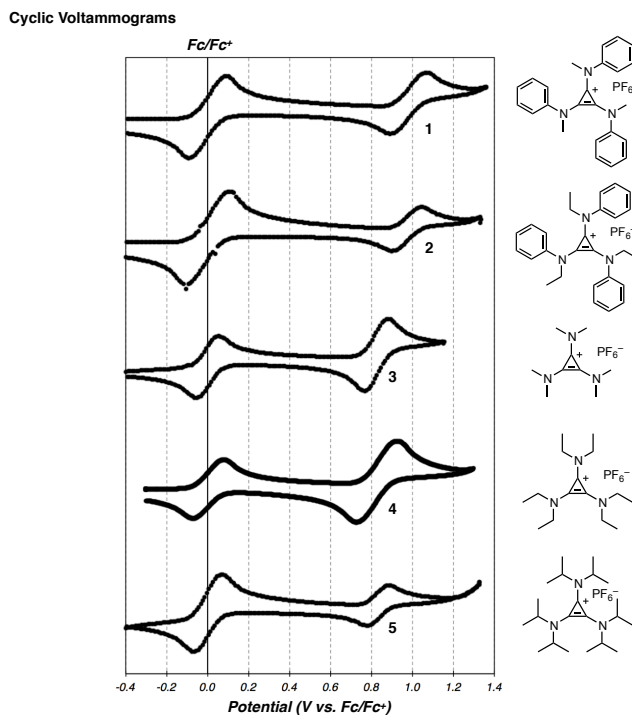


Figure S1. CV of compounds 1-5 referenced against an internal standard of ferrocene (Fc).

<sup>1</sup>H NMR Spectrum

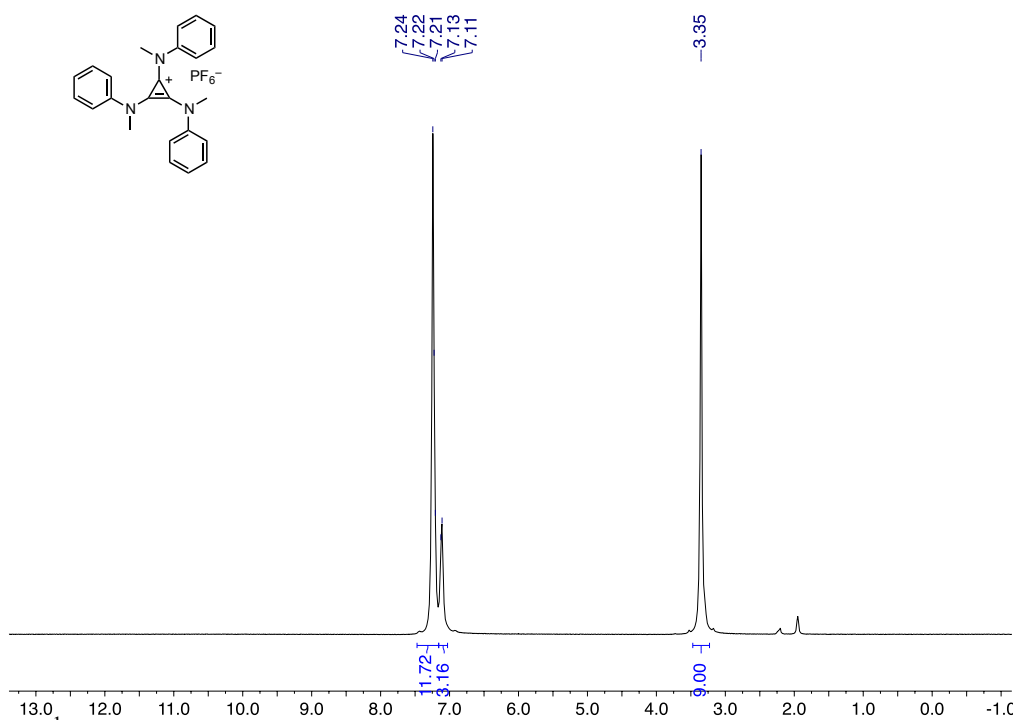
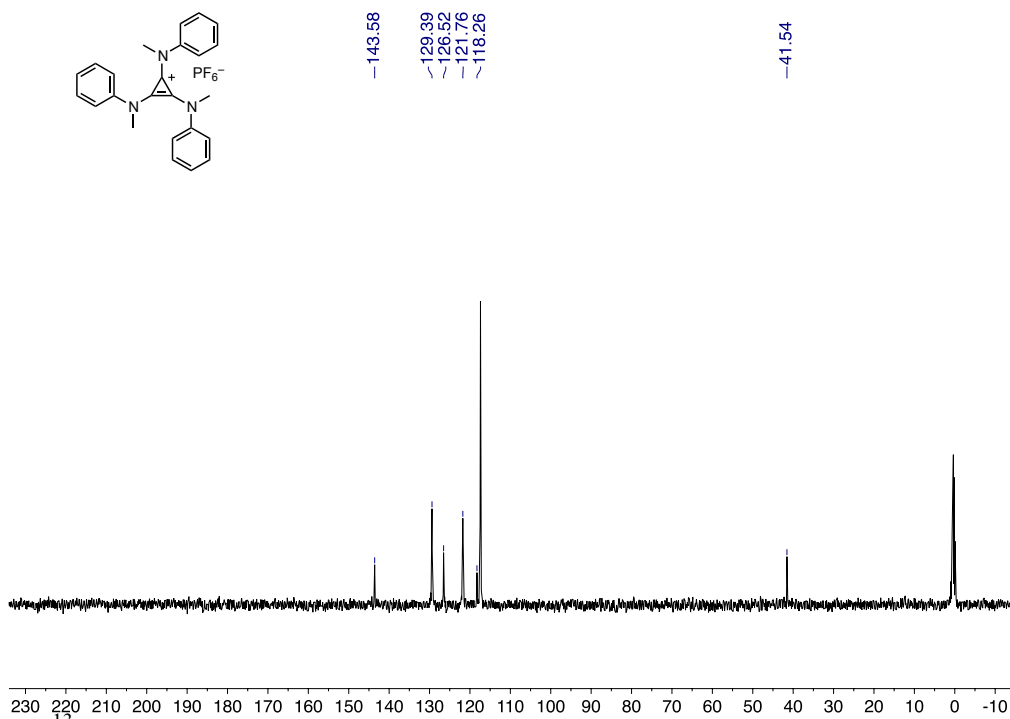
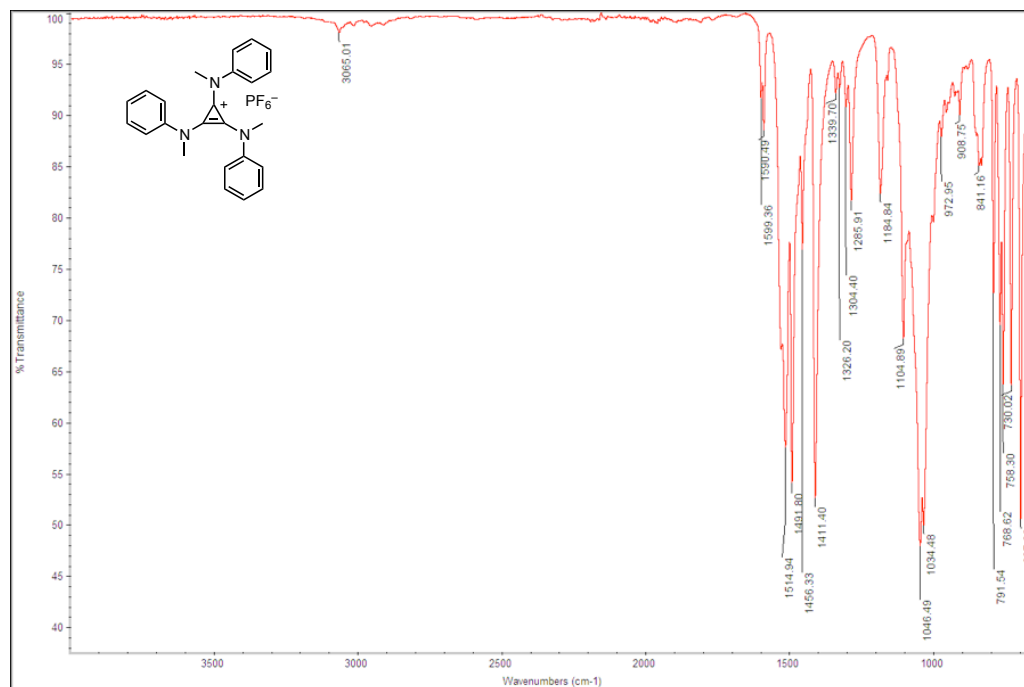
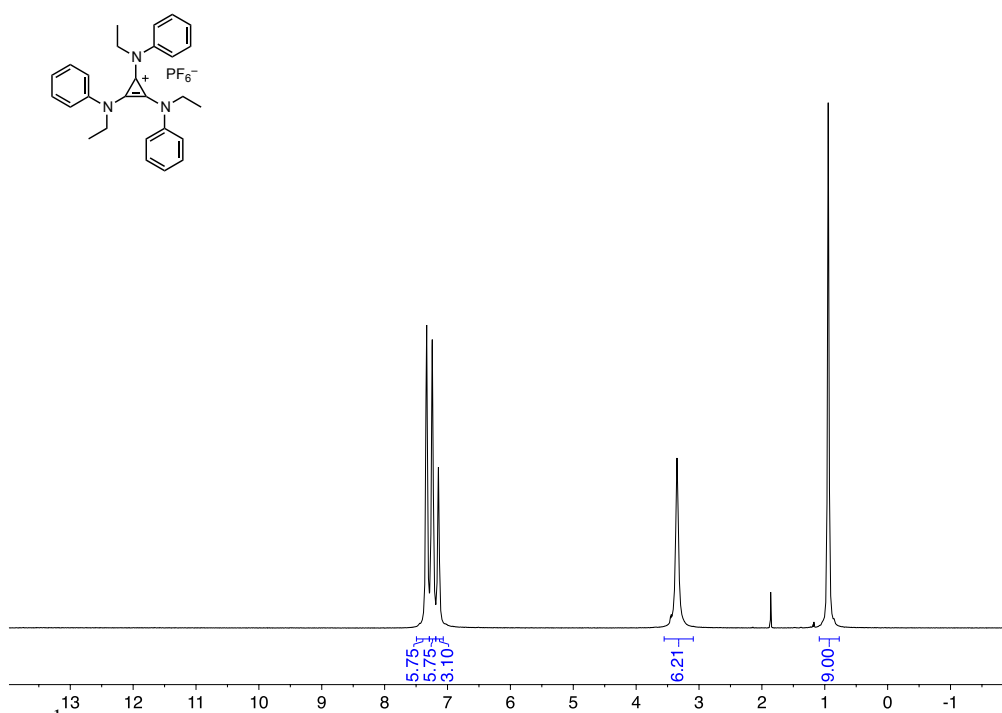
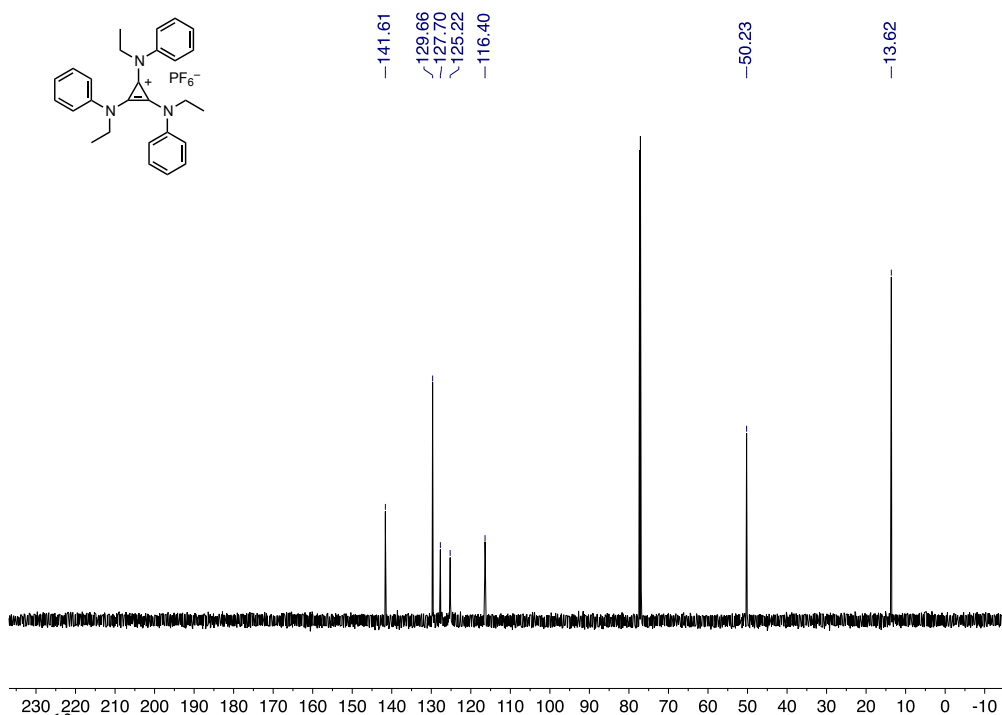


Figure S2. <sup>1</sup>H NMR spectrum of 1.

<sup>13</sup>C NMR SpectrumFigure S3. <sup>13</sup>C NMR spectrum of **1**.

## IR Spectrum

Figure S4. IR spectrum of **1**.

<sup>1</sup>H NMR SpectrumFigure S5. <sup>1</sup>H NMR spectrum of 2.<sup>13</sup>C NMR SpectrumFigure S6. <sup>13</sup>C NMR spectrum of 2.

## IR Spectrum

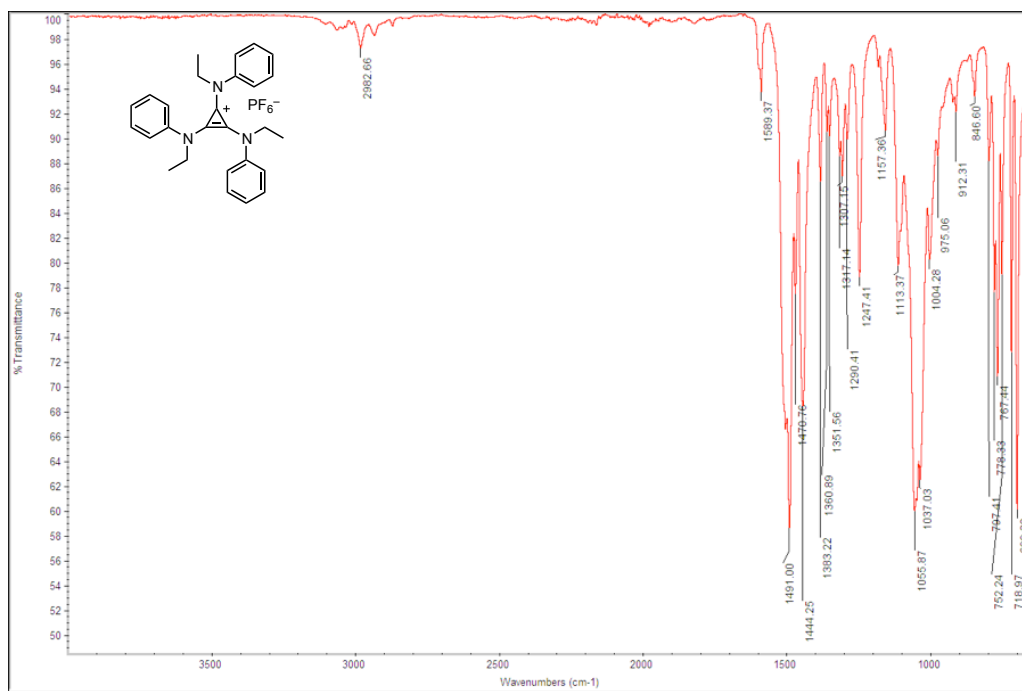
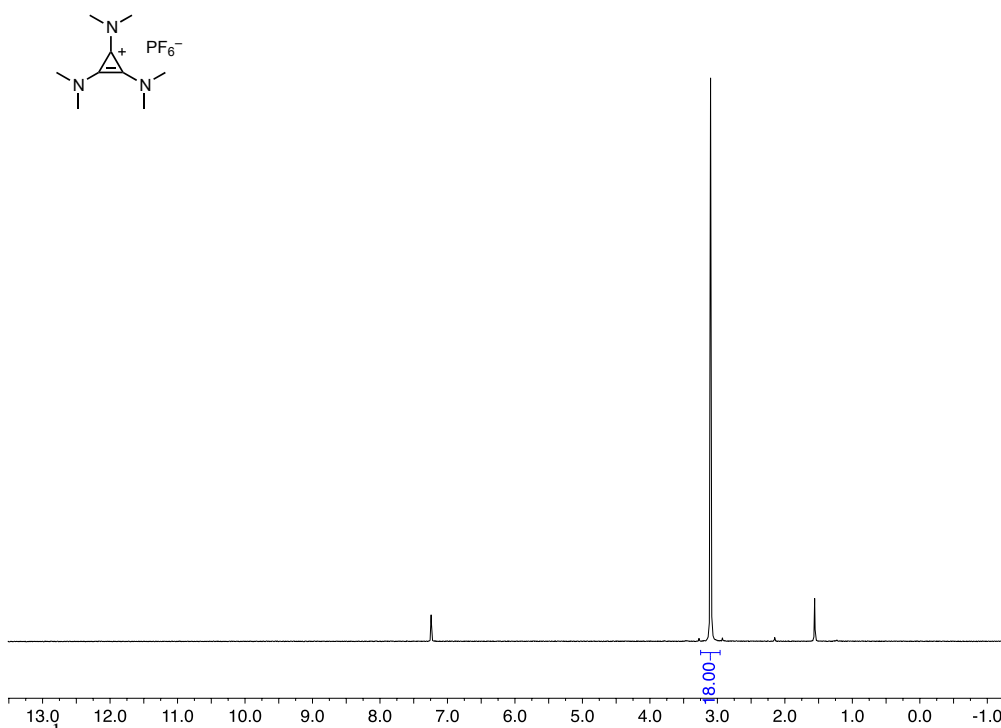
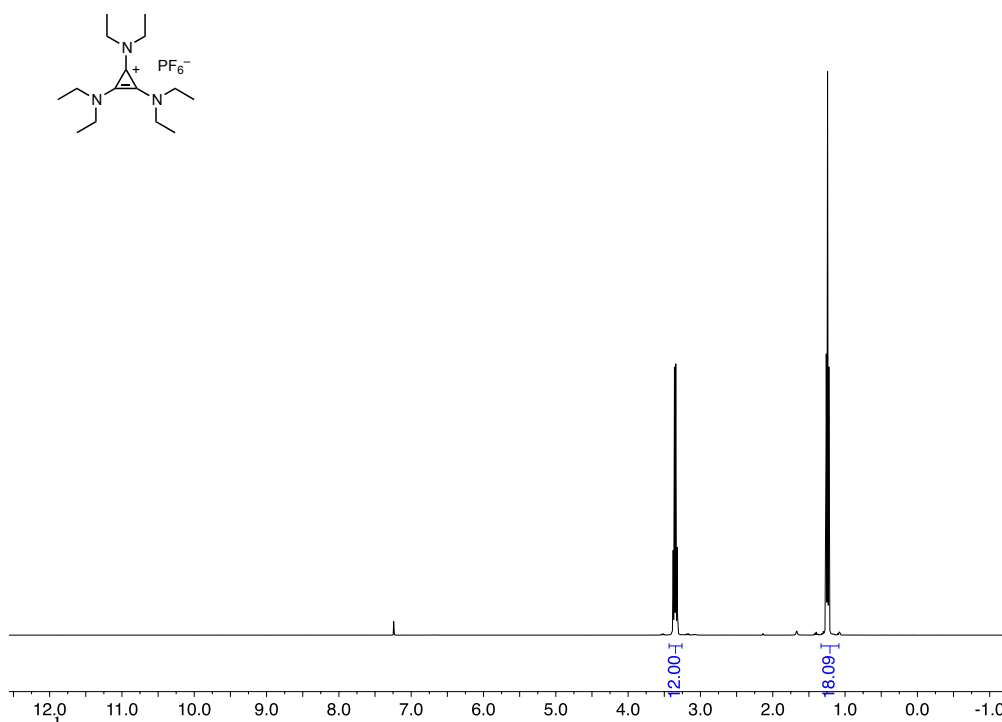
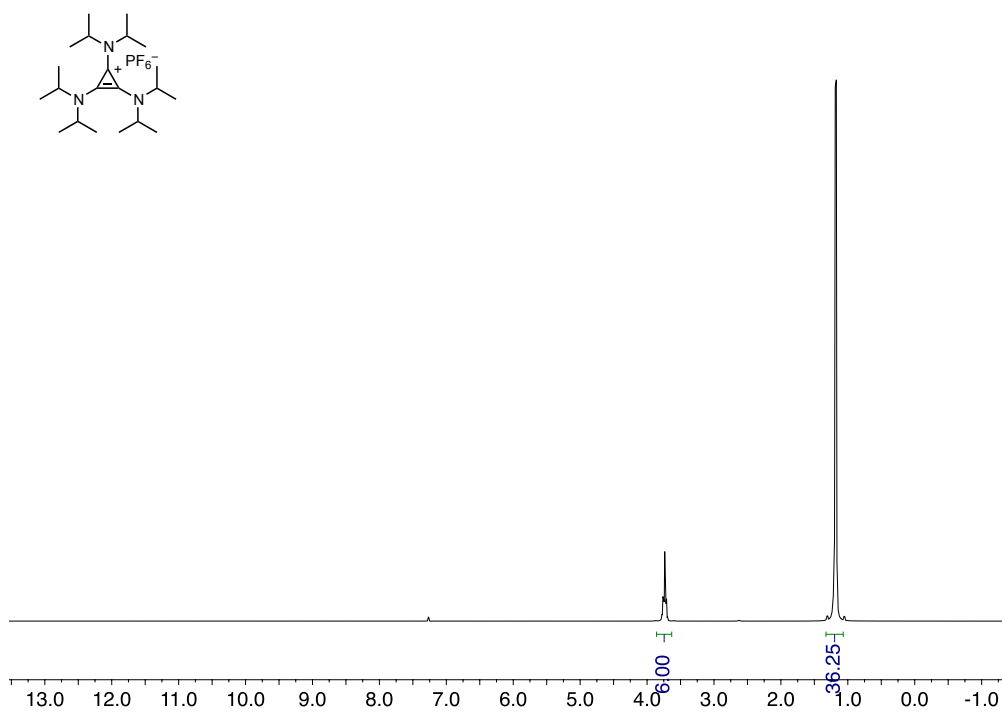
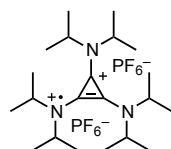


Figure S7. IR spectrum of 2.

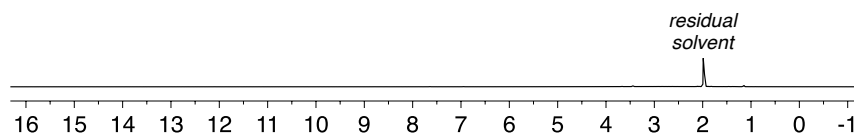
<sup>1</sup>H NMR SpectrumFigure S8. <sup>1</sup>H NMR spectrum of 3.

<sup>1</sup>H NMR SpectrumFigure S9. <sup>1</sup>H NMR spectrum of 4.<sup>1</sup>H NMR SpectrumFigure S10. <sup>1</sup>H NMR spectrum of 5.

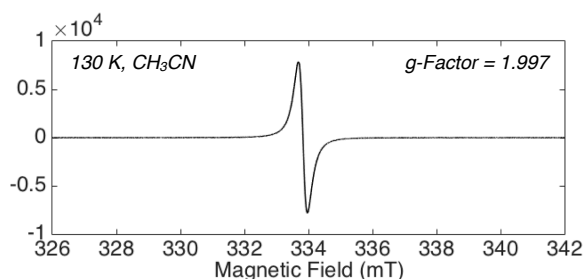




$^1\text{H}$  NMR Spectrum - no observed resonances from paramagnetic compound



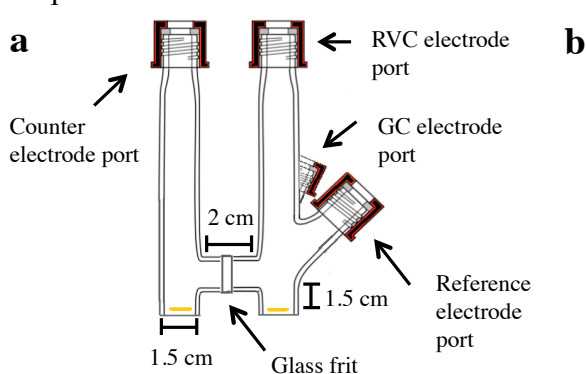
EPR Spectrum



**Figure S11.** (top)  $^1\text{H}$  NMR spectrum of  $5^+$ . No resonances are detected, which is consistent with a radical species. (bottom) EPR spectrum of  $5^+$ .

### General procedure for bulk electrolysis studies

Bulk electrolysis studies were carried out in an nitrogen-filled glovebox using a BioLogic VSP potentiostat-galvanostat. These experiments were performed in a custom glass H-cell (**Figure S12**) comprised of two 5 mL chambers separated by an ultra-fine glass frit (P5, Adams and Chittenden). Both chambers were stirred continuously during cycling. Reticulated vitreous carbon (100 PPI, Duocell) was used as the working and counter electrodes ( $0.50\text{ cm}^3$  in solution) in addition to a  $\text{Ag}/\text{Ag}^+$  quasi-reference electrode containing  $0.01\text{ M AgBF}_4$  in acetonitrile with  $0.5\text{ M LiPF}_6$ . Bulk electrolysis of compounds **1-5** was conducted galvanostatically at a current of  $4\text{ mA}$ . Potential cutoffs of  $1.4\text{ V}$  and  $0\text{ V}$  were used for charge and discharge, respectively. Solutions of  $10\text{ mM}$  catholyte in  $0.5\text{ M LiPF}_6$  in acetonitrile were used for all experiments.



**Figure S12.** **a** Schematic of the custom bulk electrolysis cell including relevant ports and dimensions. **b** Photograph of the bulk electrolysis cell.

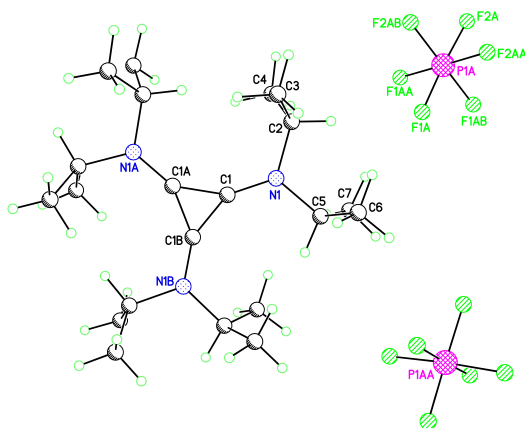
### Solubility measurements

CP **5** was added to a 1 mL vial containing acetonitrile (0.3 mL) until a solid persisted. The suspension was filtered through an ultrafine glass filter to remove the solids, and the saturated solution of **5** was collected. The masses of aliquots (2 x 25  $\mu\text{L}$ , 2 x 50  $\mu\text{L}$ ) of this saturated solution were measured (see the **Table S1**). The increase in mass from aliquots of pure acetonitrile represents the mass of **5** that is dissolved in the dispensed volume. Solubilities of compounds **1-5**, **4**<sup>+</sup>, and **5**<sup>+</sup> were measured according the procedure described above.

**Table S1.** Determination of the solubility of **5**.

Entry	Volume Saturated Soln ( $\mu\text{L}$ )	Mass (mg)	mmol <b>5</b>	Concentration <b>5</b> (M)
1	25	18	0.037	1.5
2	25	18	0.037	1.5
3	50	37	0.077	1.5
4	50	36	0.075	1.5

### X-ray crystallographic data for **5**<sup>+</sup>



**Figure S13.** PLUTO representation of **5**<sup>+</sup>.

Red polyhedral crystals of **5**<sup>+</sup> were grown from an acetonitrile solution of the compound at  $-30\text{ }^{\circ}\text{C}$ . A crystal of dimensions 0.16 x 0.12 x 0.12 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode ( $\lambda = 1.54184\text{ \AA}$ ) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 2028 images were collected with an oscillation width of  $1.0^{\circ}$  in  $\omega$ . The exposure times were 1 sec. for the low angle images, 4 sec. for high angle. Rigaku d\*trek images were exported to CrysAlisPro for processing and corrected for absorption. The integration of the data yielded a total of 45517 reflections to a maximum  $2\theta$  value of  $138.58^{\circ}$  of which 967 were independent and 949 were greater than  $2\sigma(I)$ . The final cell constants (Table 1) were based on the xyz centroids 21213 reflections above  $10\sigma(I)$ . Analysis of the data showed negligible decay during data collection; the data were processed with CrystalClear 2.0 and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 2014/6) software package, using the space group Pa3bar (#205) with  $Z = 4$  for the formula  $\text{C}_{21}\text{H}_{42}\text{N}_3(\text{PF}_6)_2(\text{C}_2\text{H}_3\text{N})$ . All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. Full matrix least-squares refinement based on  $F^2$  converged at  $R1 = 0.0473$  and  $wR2 = 0.1166$  [based on  $I > 2\sigma(I)$ ],  $R1 = 0.0477$  and  $wR2 = 0.1168$  for all data. Additional details are presented in **Table S2** and CIF file.

**Table S2.** Crystal data and structure refinement for **5<sup>+</sup>**

Empirical formula	C <sub>23</sub> H <sub>45</sub> F <sub>12</sub> N <sub>4</sub> P <sub>2</sub>
Formula weight	667.57
Temperature	85(2) K
Wavelength	1.54178 Å
Crystal system, space group	Cubic, Pa-3
Unit cell dimensions	a = 14.58040(10) Å    alpha = 90 deg.
b = 14.58040(10) Å	beta = 90 deg.
c = 14.58040(10) Å	gamma = 90 deg.
Volume	3099.62(6) Å <sup>3</sup>
Z, Calculated density	4, 1.431 Mg/m <sup>3</sup>
Absorption coefficient	2.133 mm <sup>-1</sup>
F(000)	1396
Crystal size	0.160 x 0.120 x 0.120 mm
Theta range for data collection	6.070 to 69.292 deg.
Limiting indices	-17<=h<=17, -17<=k<=17, -15<=l<=16
Reflections collected / unique	45517 / 967 [R(int) = 0.0786]
Completeness to theta = 67.679	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.78916
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	967 / 103 / 177
Goodness-of-fit on F <sup>2</sup>	1.071
Final R indices [I>2sigma(I)]	R1 = 0.0473, wR2 = 0.1166
R indices (all data)	R1 = 0.0477, wR2 = 0.1168
Extinction coefficient	0.0010(3)
Largest diff. peak and hole	0.251 and -0.303 e.Å <sup>-3</sup>