

Supplementary Information

Metal-free electrocatalytic hydrogen oxidation using frustrated Lewis pairs and carbon-based Lewis acids

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S1. Experimental details

All synthetic reactions and manipulations were performed under a rigorously dry N₂ atmosphere using standard Schlenk-line techniques on a dual manifold vacuum/inert gas line or an MBraun glovebox. Anhydrous solvents were dried by reflux over appropriate drying agents and were collected by distillation. All solvents were sparged with nitrogen gas to remove any trace of dissolved oxygen and stored in ampoules over activated 4 Å molecular sieves. H₂ gas (99.995 %) was purchased from BOC gases and was used without further purification. **1-H**, **1**[BArCl];^{S1} BArF₁₈,^{S2} [tmpH][(μ -H)(BArF₁₈)₂];^{S3,S4} [ⁿBu₄N][HB(C₆F₅)₃],^{S5} and [ⁿBu₄N][B(C₆F₅)₄]^{S6,S7} were prepared according to the cited literature methods.

NMR spectra were recorded using a Bruker Avance DPX-500 MHz spectrometer. Chemical shifts are reported in ppm and are referenced relative to appropriate standards: ¹⁹F (CFCl₃); ¹¹B (Et₂O·BF₃).

All electrochemical experiments were performed in an MBraun glovebox using either an Autolab PGSTAT 30 or PGSTAT 302N computer-controlled potentiostat (Utrecht, The Netherlands). All electrochemical samples were prepared in CH₂Cl₂ containing 0.1 M [ⁿBu₄N][B(C₆F₅)₄] as a weakly coordinating electrolyte salt.

Cyclic voltammetry (CV) was performed using a three-electrode configuration consisting of a glassy carbon macrodisk working electrode (GCE) (diameter of 3 mm; BASi, Indiana, USA) combined with a Pt wire counter electrode (99.99%; GoodFellow, Cambridge, UK) and a Ag wire *pseudo*-reference electrode (99.99%; GoodFellow, Cambridge, UK).

Controlled-potential bulk electrolysis was performed using a three-electrode configuration consisting of a wet-proofed Toray carbon paper 060 (20 wt% PTFE treatment; Fuel Cell Store, Texas, USA) working electrode combined with a Ag wire *pseudo*-reference electrode (99.99%, GoodFellow, Cambridge, UK) and a Pt gauze counter electrode (52 mesh woven from 0.1 mm diameter wire, 99.9%; Alfa Aesar, Massachusetts, USA). The working and *pseudo*-reference electrodes were separated from the counter electrode compartment by a microporous ceramic frit (4 Å pore size).

The Ag wire *pseudo*-reference electrodes were calibrated to the Cp₂Fe^{0/+} couple in CH₂Cl₂ at the end of each run to allow for any drift in potential, following IUPAC recommendations.^{S8}

S2. NMR spectra

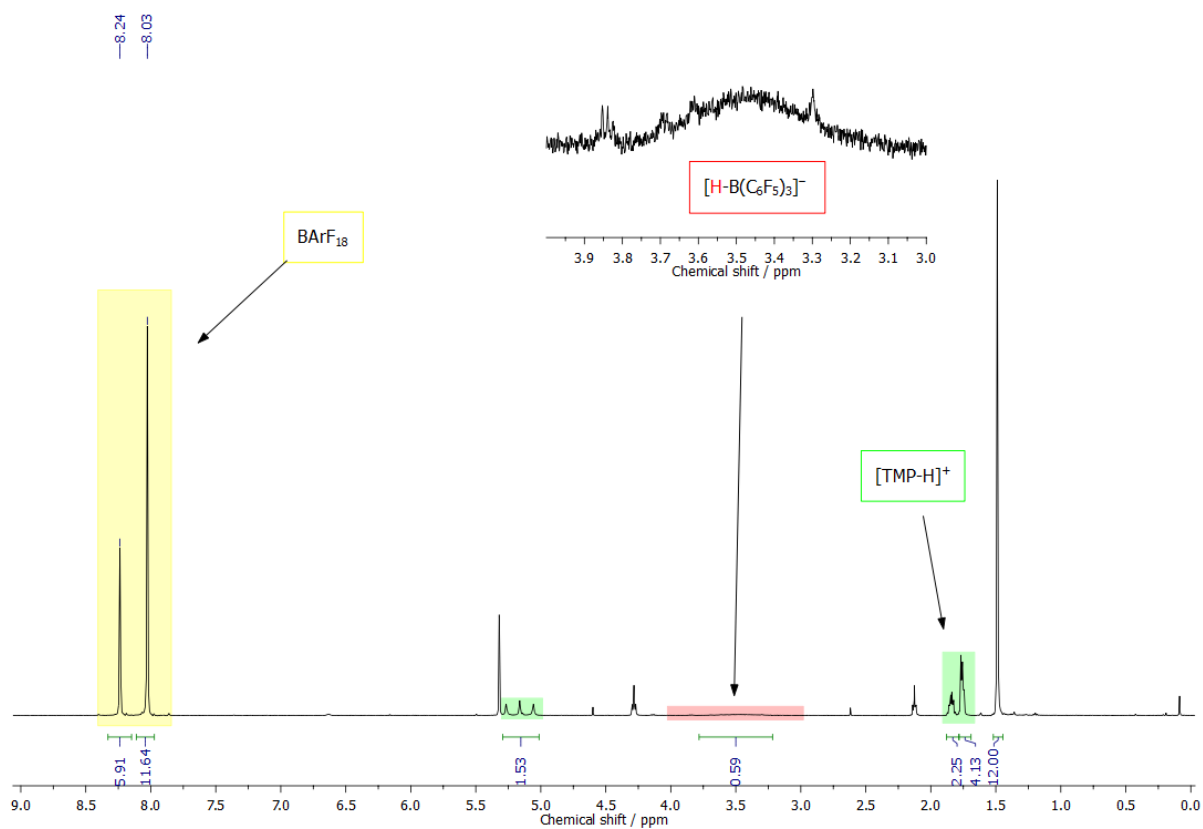


Fig. S1 ^1H NMR spectrum of a mixture of $[\text{tmpH}][\mu\text{-H}(\text{BArF}_{18})_2]$ and $\text{B}(\text{C}_6\text{F}_5)_3$ in CD_2Cl_2 ; the ability of $[\text{tmpH}][\mu\text{-H}(\text{BArF}_{18})_2]$ as a hydride donor is demonstrated by the generation of $[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ when treated with excess $\text{B}(\text{C}_6\text{F}_5)_3$.

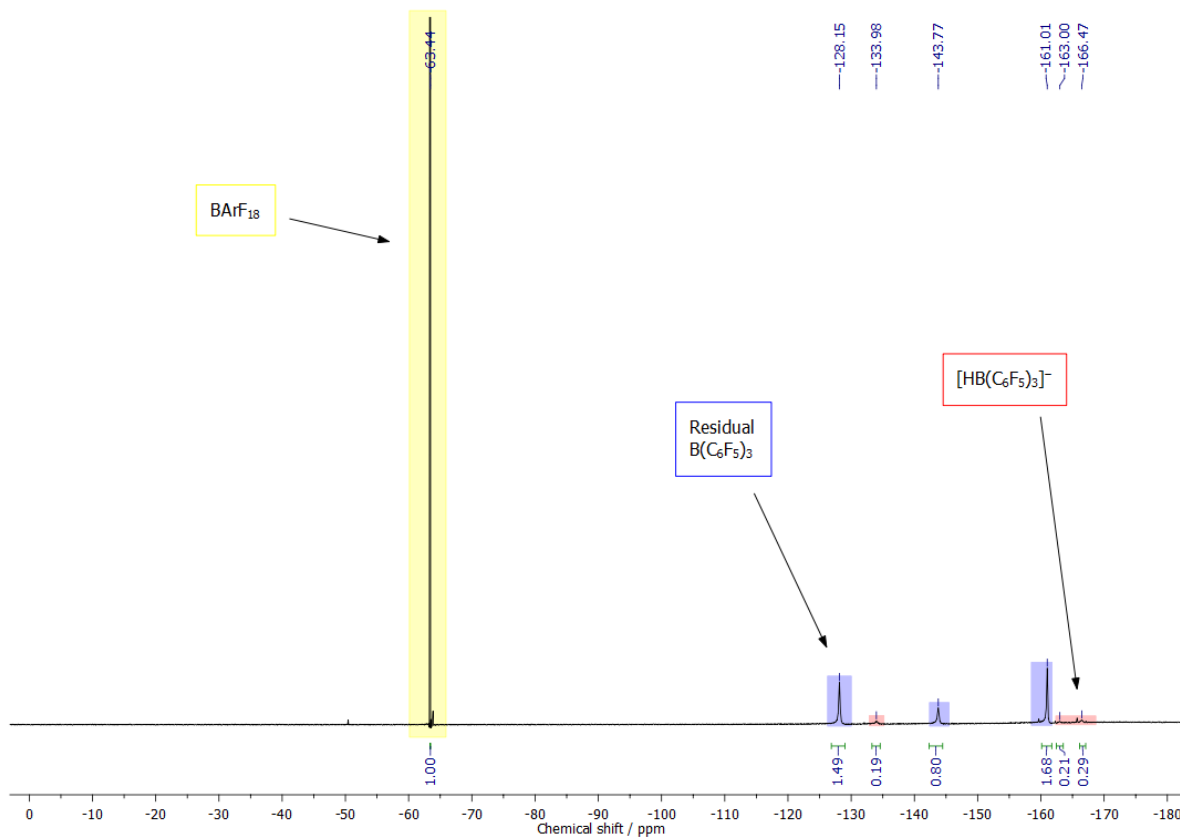


Fig. S2 $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of a mixture of $[\text{tmpH}][\mu\text{-H}(\text{BArF}_{18})_2]$ and $\text{B}(\text{C}_6\text{F}_5)_3$ in CD_2Cl_2 ; the ability of $[\text{tmpH}][\mu\text{-H}(\text{BArF}_{18})_2]$ as a hydride donor is demonstrated by the generation of $[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ when treated with excess $\text{B}(\text{C}_6\text{F}_5)_3$.

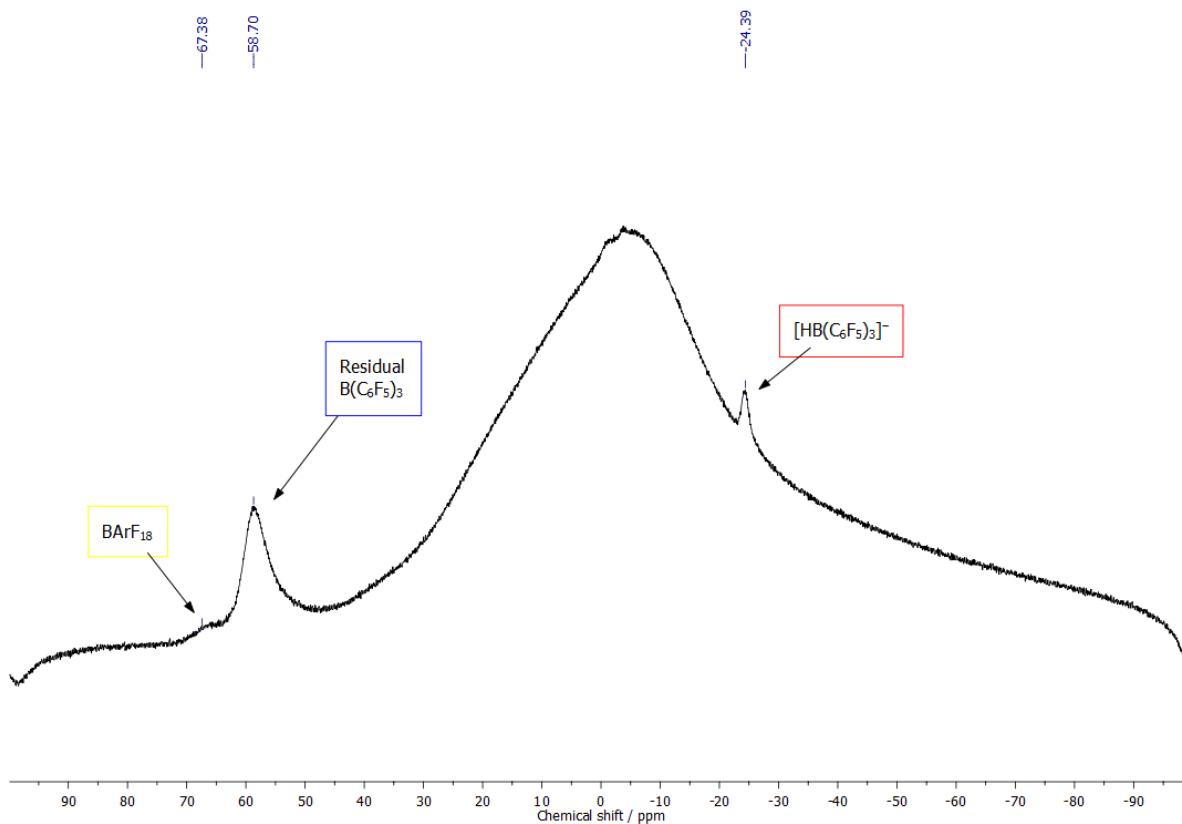


Fig. S3 ^{11}B NMR spectrum of a mixture of $[\text{tmpH}][\mu\text{-H}(\text{BArF}_{18})_2]$ and $\text{B}(\text{C}_6\text{F}_5)_3$ in CD_2Cl_2 ; the ability of $[\text{tmpH}][\mu\text{-H}(\text{BArF}_{18})_2]$ as a hydride donor is demonstrated by the generation of $[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ when treated with excess $\text{B}(\text{C}_6\text{F}_5)_3$.

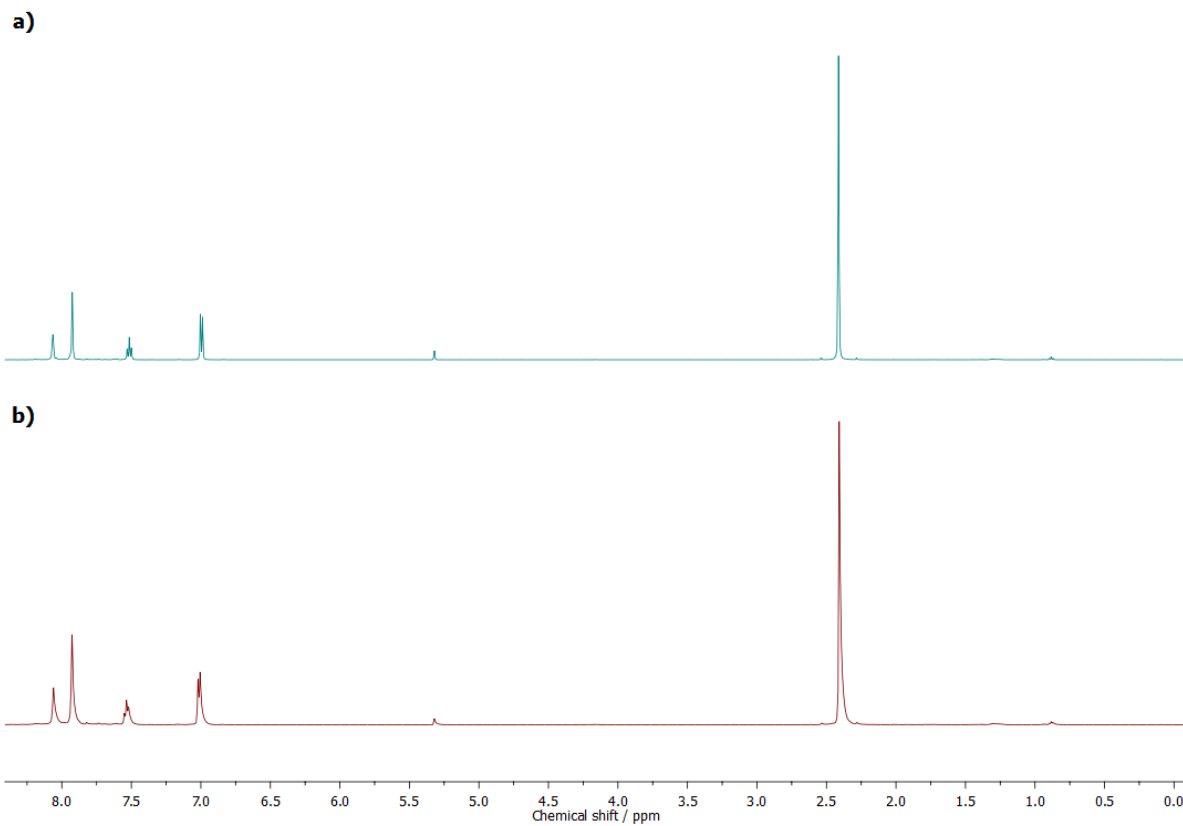


Fig. S4 ^1H NMR spectroscopy demonstrates that BArF₁₈ (0.08 mmol) and 2,6-lutidine (0.08 mmol) remain as individual components after 2 days in CD₂Cl₂ solution. (a) Freshly prepared sample. (b) Sample after 2 days.

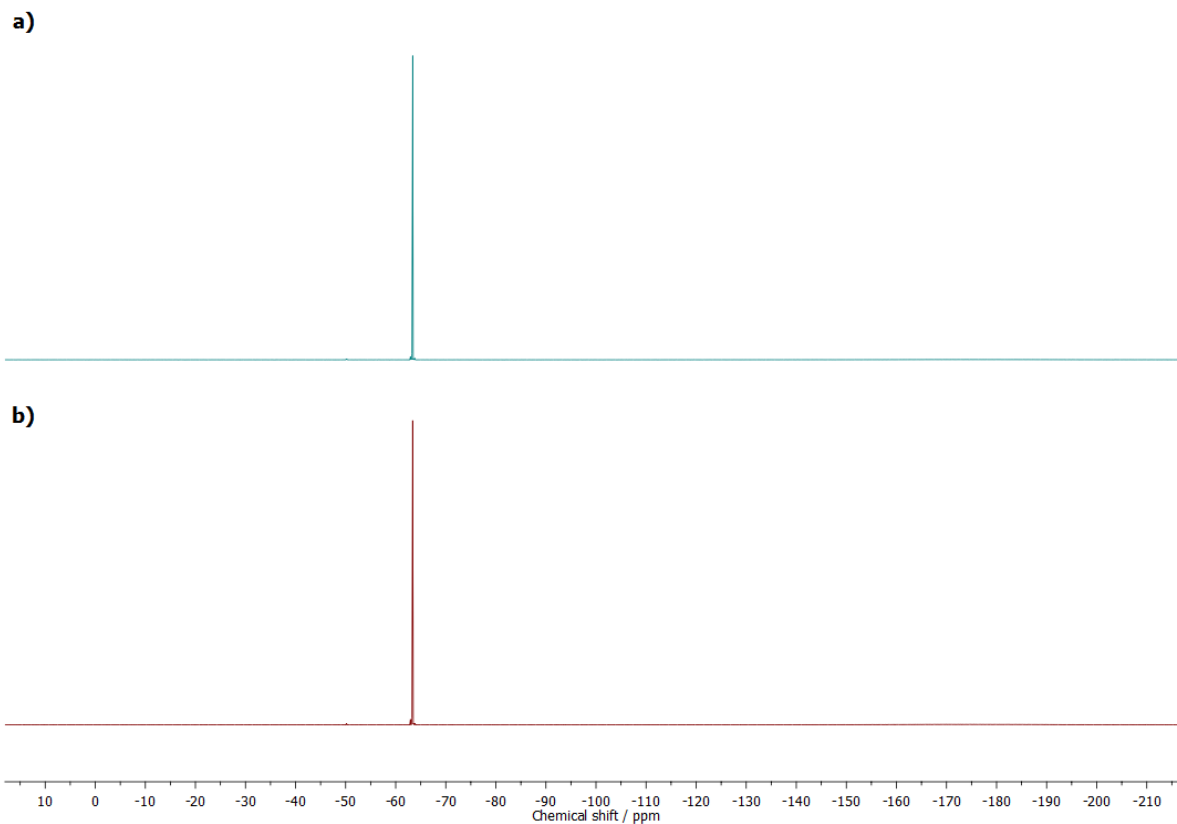


Fig. S5 $^{19}\text{F}\{^1\text{H}\}$ NMR spectroscopy demonstrates that BARF_{18} (0.08 mmol) and 2,6-lutidine (0.08 mmol) remain as individual components after 2 days in CD_2Cl_2 solution. (a) Freshly prepared sample. (b) Sample after 2 days.

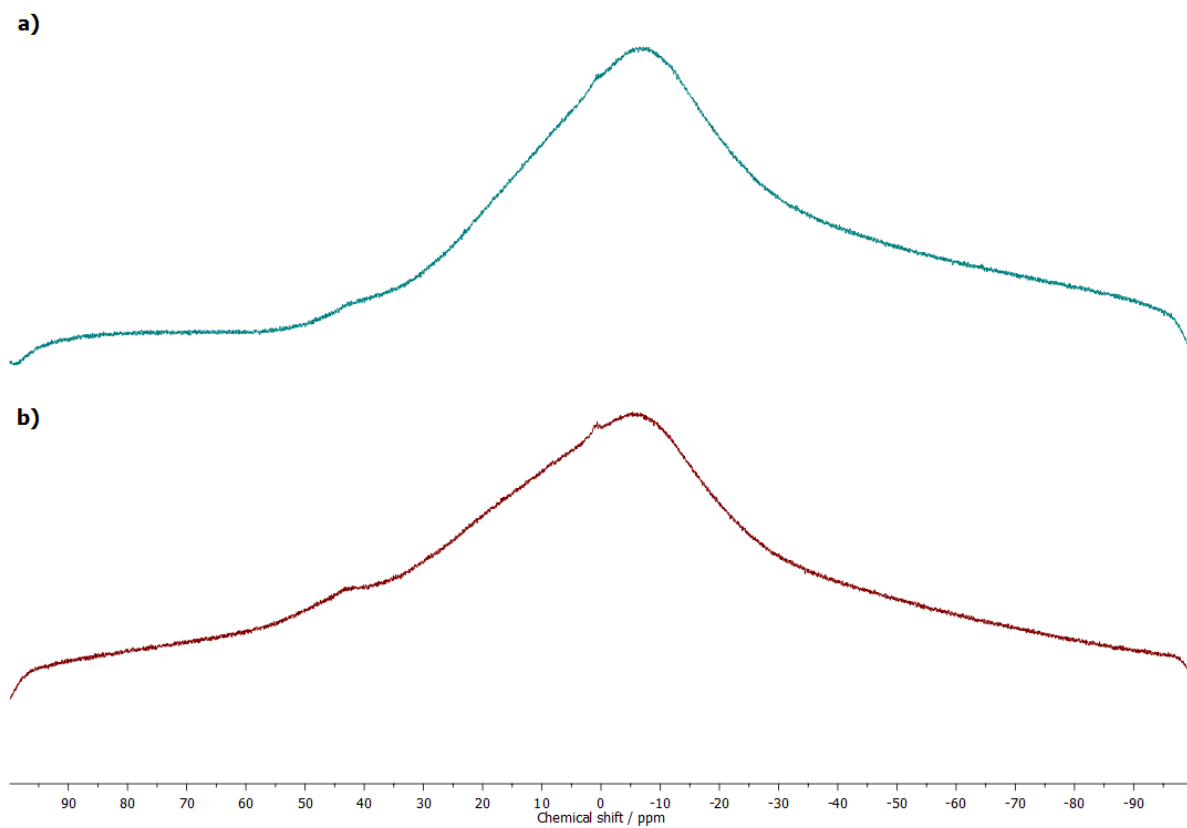


Fig. S6 ^{11}B NMR spectroscopy demonstrates that BARF_{18} (0.08 mmol) and 2,6-lutidine (0.08 mmol) remain as individual components after 2 days in CD_2Cl_2 solution. (a) Freshly prepared sample. (b) Sample after 2 days.

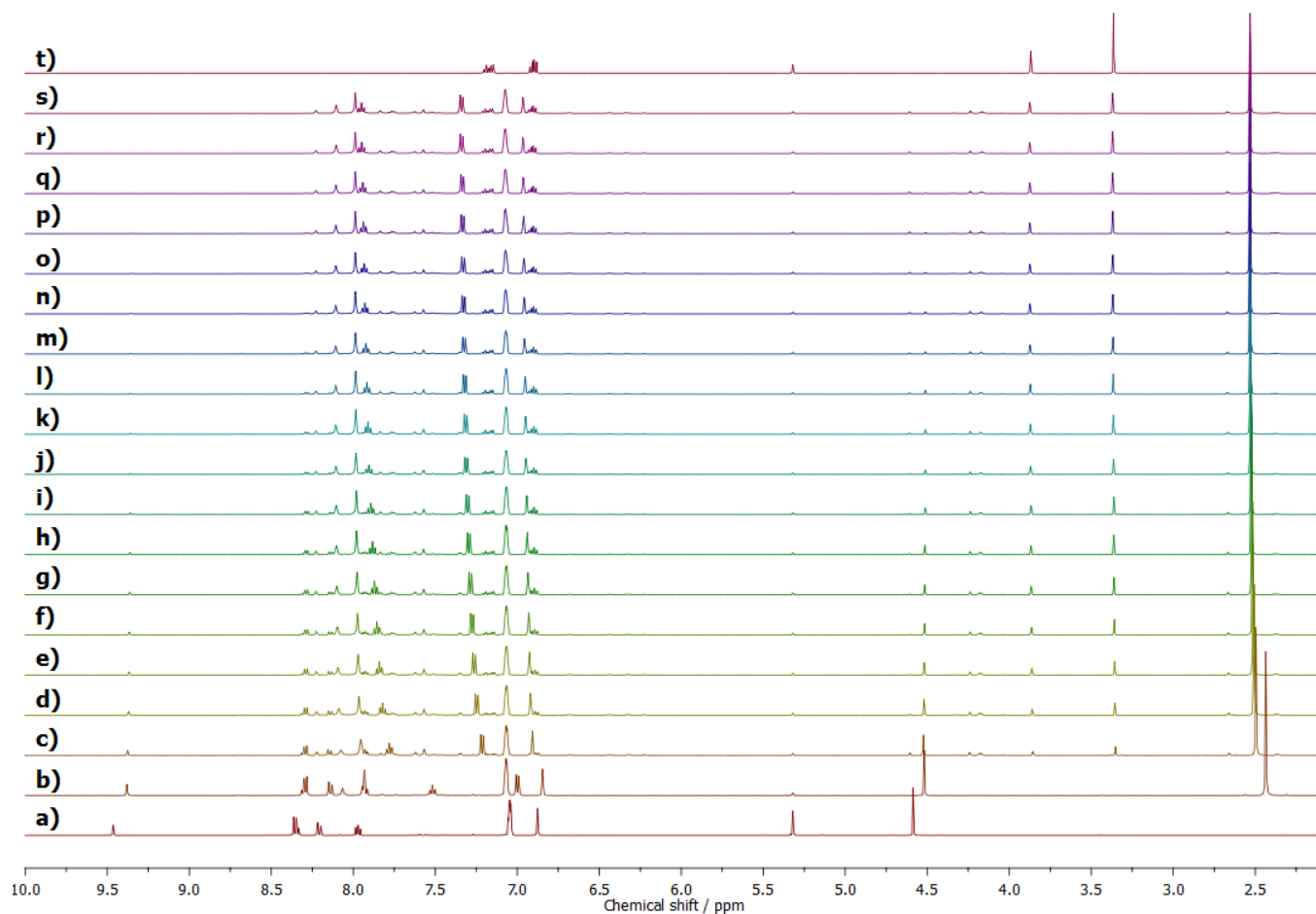


Fig. S7 ^1H NMR spectra showing the progress of H_2 activation by the $\mathbf{1}[\text{BArCl}]/2,6\text{-lutidine}$ system (in CD_2Cl_2) in the presence of BArF_{18} . (a) Authentic $\mathbf{1}[\text{BArCl}]$. (b) Sample of $\mathbf{1}[\text{BArCl}]$ (1.0 eq.), BArF_{18} (2.3 eq.), and 2,6-lutidine (1.7 eq.) under N_2 . (c-s) Monitoring the progress of $\mathbf{1}\text{-H}$ formation following the admission of H_2 (4 bar) to the sample in b (after 0.5-17 h). (t) Authentic $\mathbf{1}\text{-H}$.

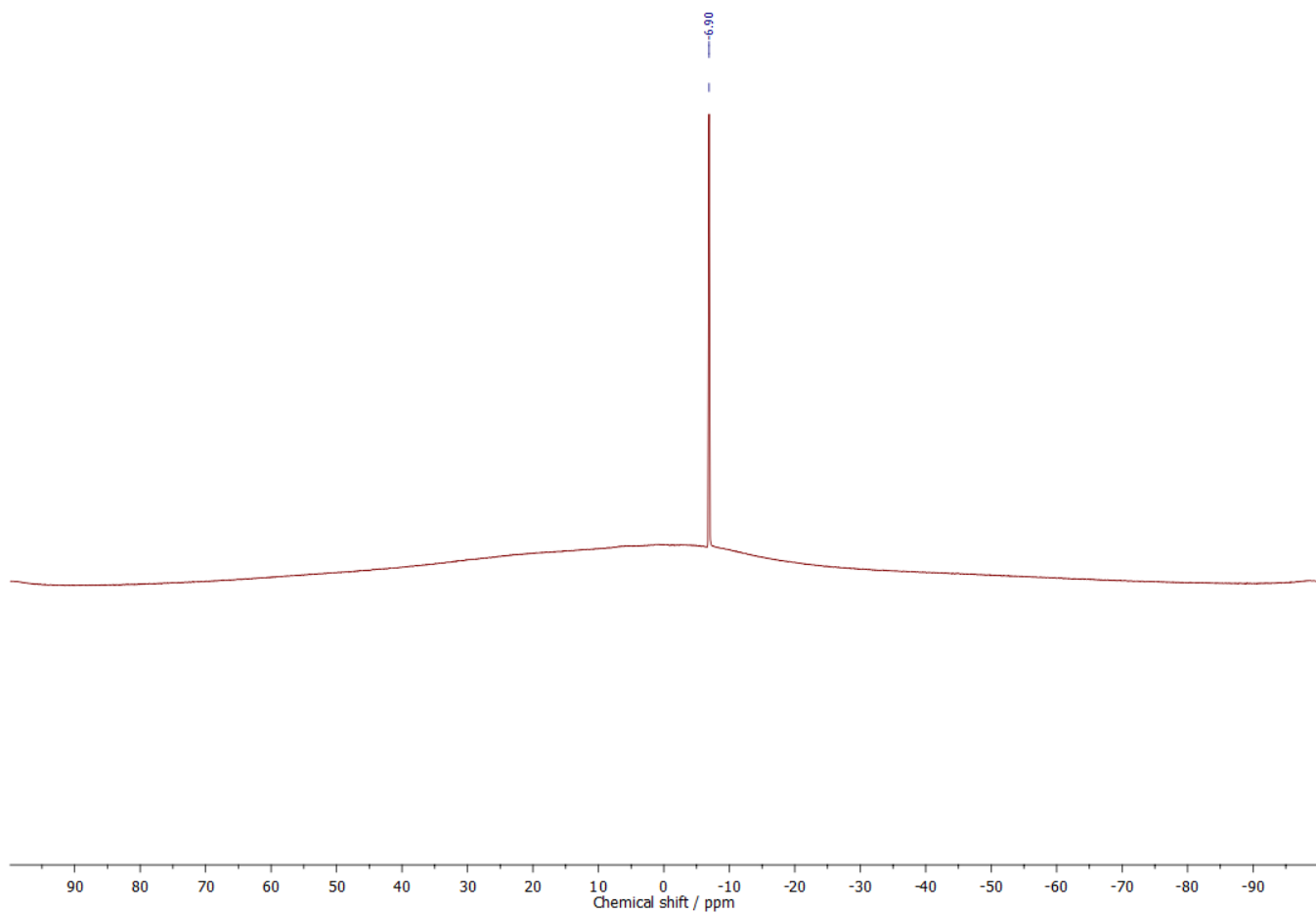


Fig. S8 ^{11}B NMR spectra of the **1**[BArCl] (1.0 eq.)/BArF₁₈ (2.3 eq.)/2,6-lutidine (2.0 eq.) system (in CD₂Cl₂) after a 30 second sparge with pure CO gas demonstrates that the system is tolerant towards CO.

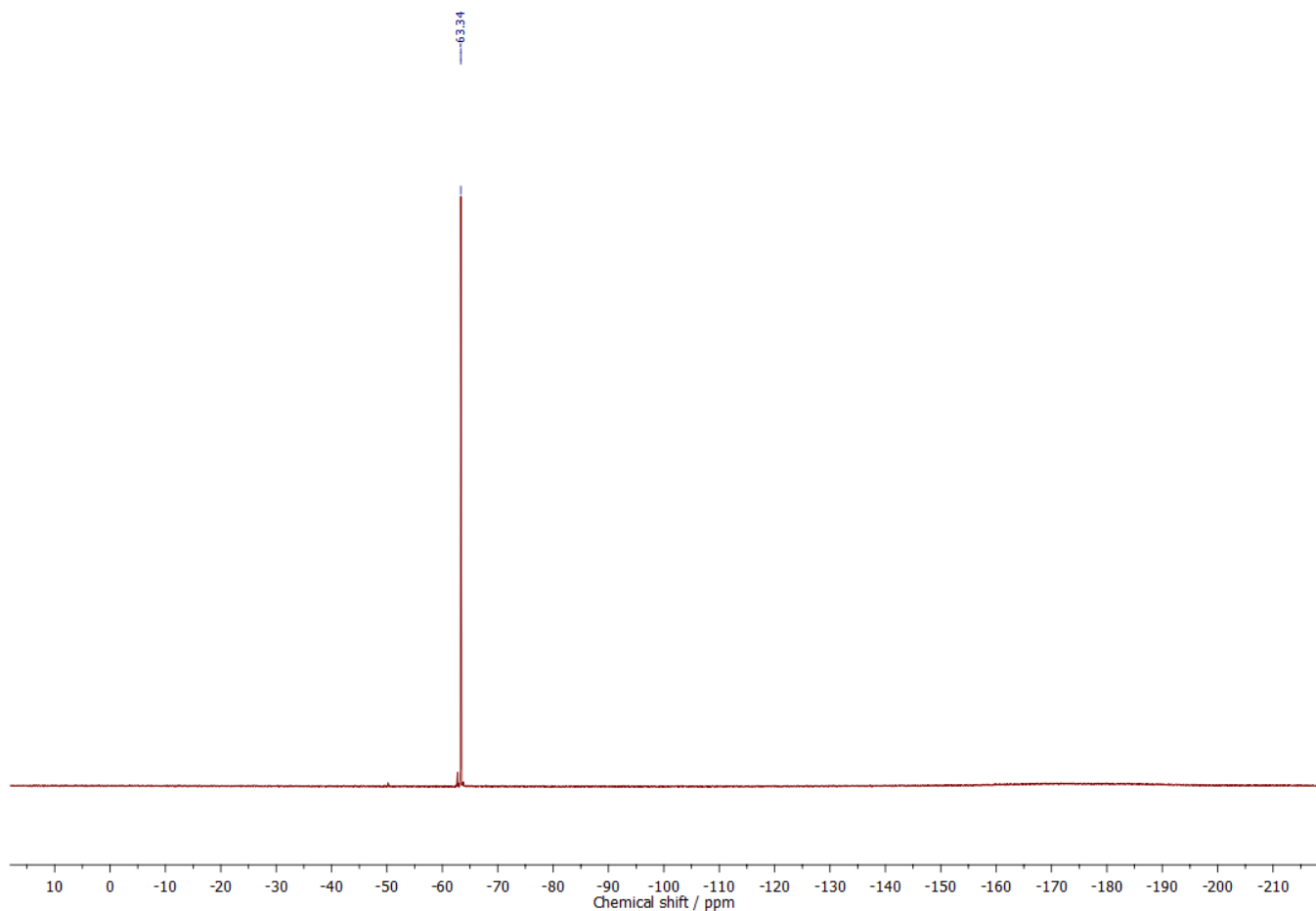


Fig. S9 $^{19}\text{F}\{^1\text{H}\}$ NMR spectra of the **1**[BArCl] (1.0 eq.)/BArF₁₈ (2.3 eq.)/2,6-lutidine (2.0 eq.) system (in CD₂Cl₂) after a 30 second sparge with pure CO gas demonstrates that the system is tolerant towards CO.

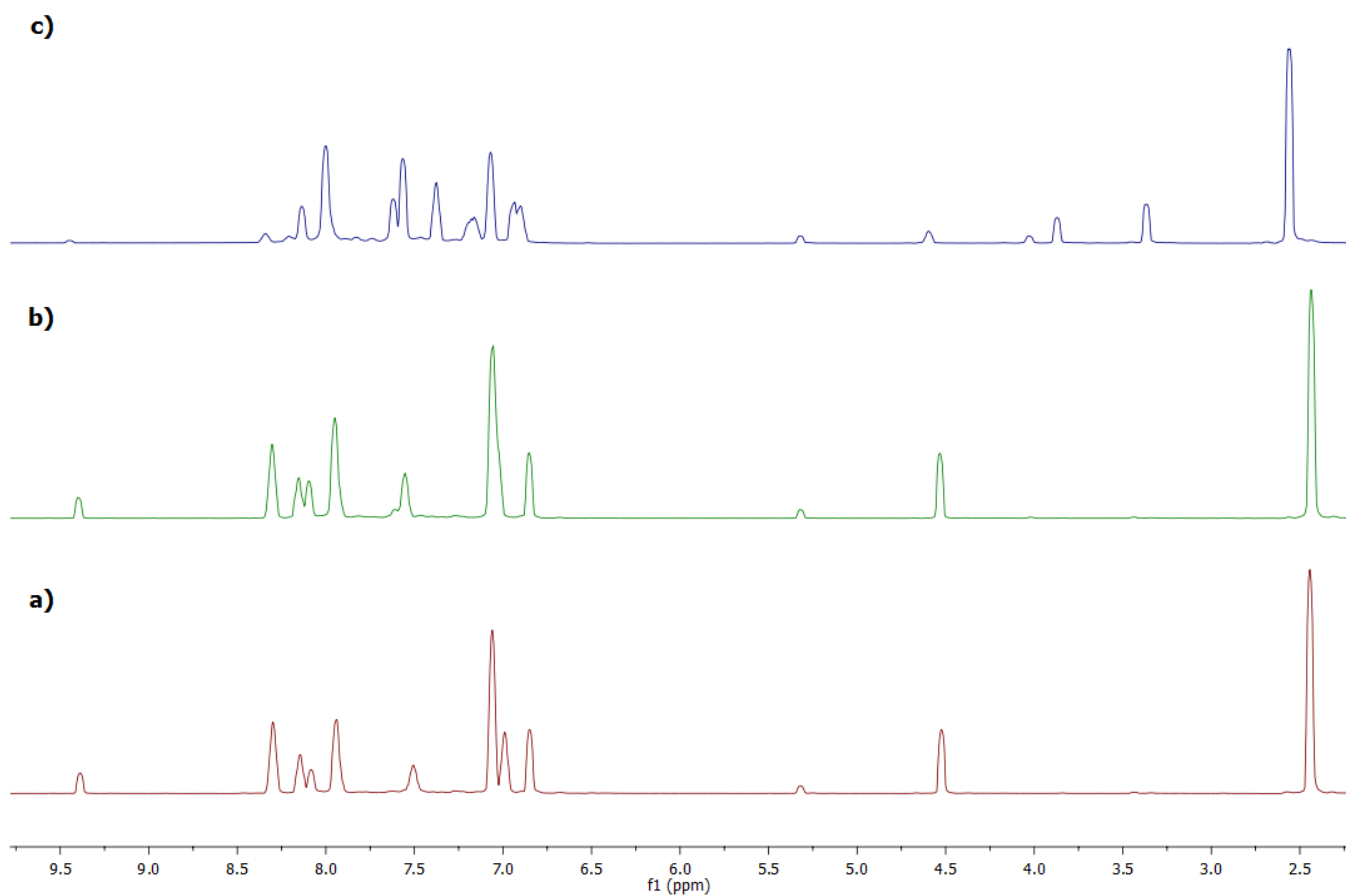
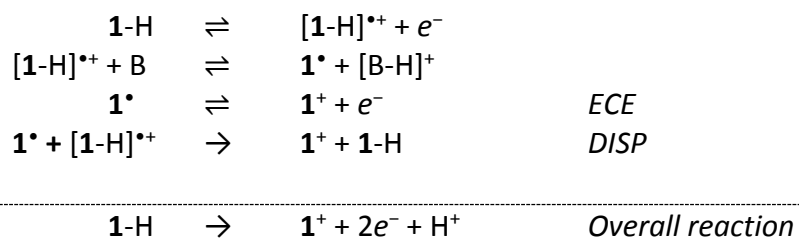


Fig. S10 ^1H NMR spectra of a sample of **1**[BArCl] (1.0 eq.), BArF₁₈ (2.3 eq.), and 2,6-lutidine (2.0 eq.) in CD₂Cl₂ (a) under N₂, (b) after a 30 second sparge with pure CO gas, and (c) after a 30 second sparge with pure CO gas and exposure to excess H₂ over 24 hours.

S3. Electrochemical data



Scheme S1. ECE-DISP1 mechanism of **1-H** oxidation in the presence of Brønsted base (B). Single-electron oxidation of **1-H** is followed by the deprotonation of the resulting radical cation, $[\mathbf{1-H}]^{\bullet+}$, by the Brønsted base. This homogeneous deprotonation reaction is the rate-determining step and generates the neutral radical $\mathbf{1}^{\bullet}$, which is then oxidized either immediately at the electrode surface (ECE) or homogeneously in solution *via* a disproportionation reaction with $[\mathbf{1-H}]^{\bullet+}$ (DISP).^{S9}

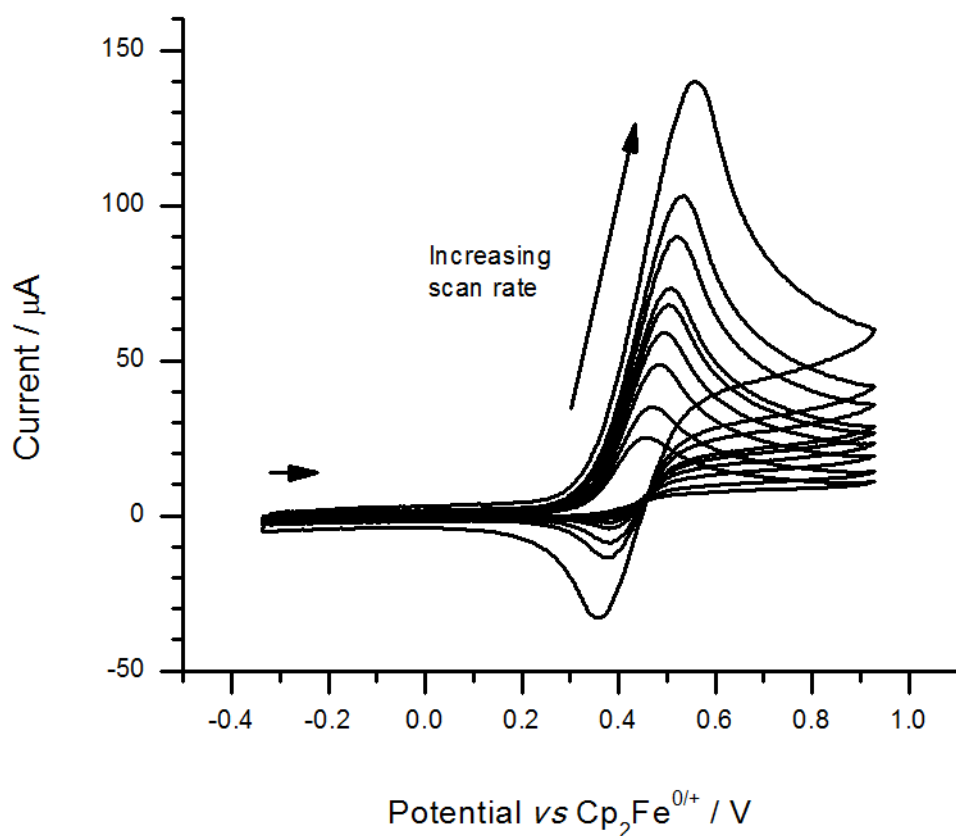


Fig. S11 CVs of **1-H** (1.8 mM) obtained in the absence of Brønsted base at scan rates of 50, 100, 200, 300, 400, 500, 750, 1000, and 2000 mV s^{-1} .

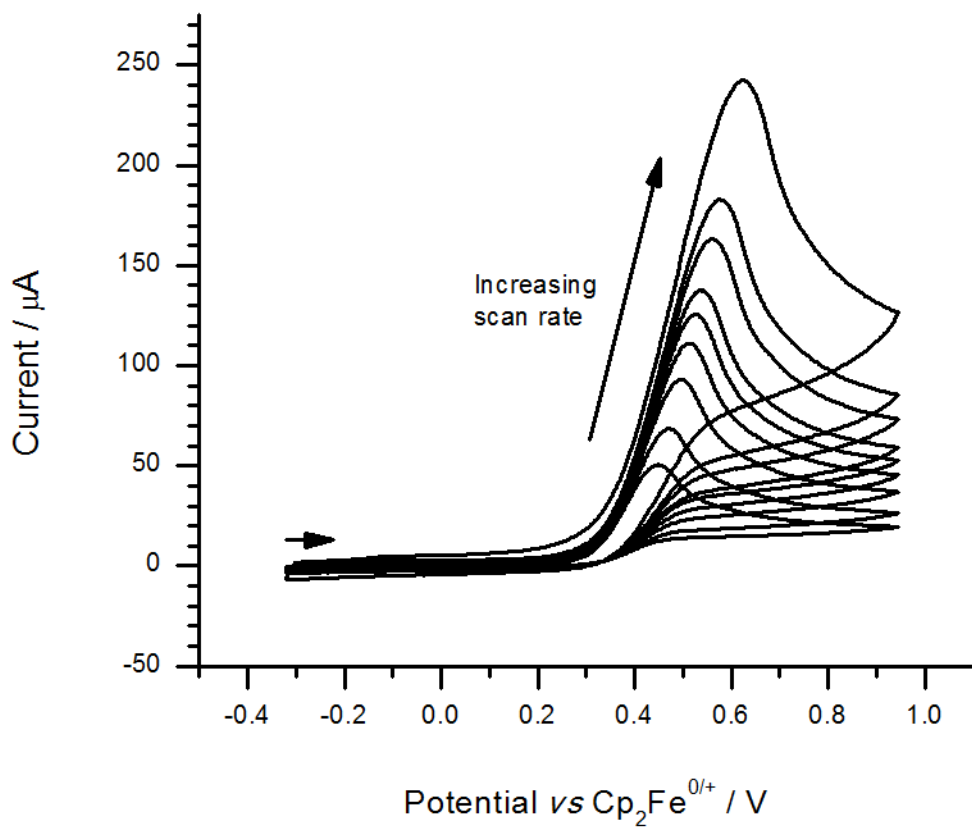


Fig. S12 CVs of 1-H (1.8 mM) obtained in the presence of excess 2,6-lutidine (6.7 mM) at scan rates of 50, 100, 200, 300, 400, 500, 750, 1000, and 2000 mV s⁻¹.

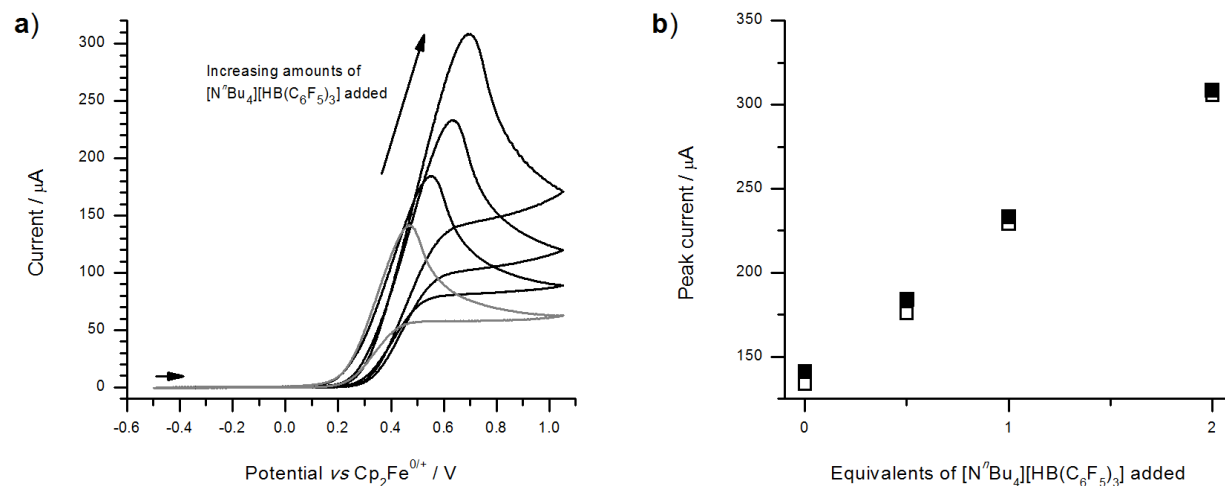


Fig. S13 (a) CVs showing the effect of adding increasing amounts of the hydride donor [$n\text{Bu}_4\text{N}][\text{HB}(\text{C}_6\text{F}_5)_3]$ (0.5, 1, and 2 equivalents, black lines) to a sample of **1-H** (4.1 mM, grey line) whilst in the presence of excess 2,6-lutidine (41 mM, 10 eq.). (b) Observed (closed squares) and simulated (open squares) peak current of the **1-H** signal with added [$n\text{Bu}_4\text{N}][\text{HB}(\text{C}_6\text{F}_5)_3]$.

S4. References

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