

Supporting Information for:

Dicopper Alkyl Complexes: Synthesis, Structure, and Unexpected Persistence

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1) Additional experimental details, synthetic procedures, and characterization

Table S1: X-ray Crystallography Experimental Details

Compound	Detector Distance (mm)	Image Width (°)	Exposure Time (seconds)
1	50	1 or 4 depending on angle	1
2	40	0.5	30
3	60	0.5	40
4	50	1 or 4 depending on angle	1
5	65	0.4	30
6	40	0.6	30

Synthesis of $[\text{Cu}_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-C}\equiv\text{C}(\text{C}_6\text{H}_4)\text{CF}_3)\text{DPFN}]\text{NTf}_2$. A solution of $[\text{Cu}_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-Ph})\text{DPFN}](\text{NTf}_2)$ (0.089 g, 0.090 mmol) and 1-ethynyl-4-(trifluoromethyl)benzene (0.153 g, 0.899 mmol, 10 equiv.) in *ortho*-difluorobenzene (6 mL) was sealed in a PTFE-valved tube and stirred at 100 °C for 2.5 h. Then the reaction mixture was filtered, and the dark filtrate concentrated *in vacuo* to an oily residue. The oil was triturated by stirring with diethyl ether (4 mL) for 1 h, resulting in a green powder. The powder was allowed to settle, and the supernatant was carefully decanted. The solid was similarly rinsed again with diethyl ether (4 mL, 1 h) and then rinsed briefly with diethyl ether (4 mL). The green powder was then dissolved in *ortho*-difluorobenzene (4.5 mL) and filtered, and the filtrate was cooled to –35 °C. Pentane (ca. 15 mL) was layered over the cold filtrate. After 2 d at –35 °C, dark crystalline solid formed, and the supernatant was carefully decanted. The solid was briefly rinsed with diethyl ether (3 x 2 mL), and residual volatile compounds were removed *in vacuo*. The solids were again triturated by stirring with diethyl ether (5 mL, 3 h, 3 times), each time carefully decanting the supernatant from the settled powder. Finally, the green powder was rinsed briefly with diethyl ether (2 x 2 mL) and residual volatile compounds were removed *in vacuo* to yield $[\text{Cu}_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-C}\equiv\text{C}(\text{C}_6\text{H}_4)\text{CF}_3)\text{DPFN}]\text{NTf}_2$ as a green powder (0.0658 g, 0.061 mmol, 69%). ^1H NMR (600.13 MHz, $\text{C}_6\text{D}_5\text{NO}_2$) δ 9.35 (d, J = 5.0 Hz, 4H, 6-pyridyl-C–H), 8.73 (d, J = 8.5 Hz, 2H, 4-naphth-C–H), 8.37 (dd, J = 8.5, 2.9 Hz, 2H, 3-naphth-C–H), 8.22 (dd, J = 8.2, 3.3 Hz, 4H, 3-pyridyl-C–H), 8.14 (td, J = 7.9, 1.7 Hz, 4H, 4-pyridyl-C–H), 8.00 (d, J = 8.0 Hz, 2H, *ortho*-C $\equiv$ C(C_6H_4)CF₃), 7.65 (ddd, J = 7.7, 5.0, 1.1 Hz, 4H, 5-pyridyl-C–H), 7.60 (d, J = 8.1 Hz, 2H, *meta*-C $\equiv$ C(C_6H_4)CF₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (150.92 MHz, $\text{C}_6\text{D}_5\text{NO}_2$) δ 159.65 (d, J = 30.4 Hz, 2-naphth-C), 153.36 (d, J = 29.3 Hz, 2-pyridyl-C), 150.77 (d, J = 2.1 Hz, 6-pyridyl-C–H), 149.5 (8a-naphth-C),^a 141.13 (d, J = 2.8 Hz, 4-naphth-C–H), 139.85 (d, J = 2.7 Hz, 4-pyridyl-C–H), 133.01 (–C $\equiv$ C(C_6H_4)CF₃), 132.24 (*ortho*-C $\equiv$ C(C_6H_4)CF₃), 125.99 (q, J = 3.2 Hz, *meta*-C $\equiv$ C(C_6H_4)CF₃), 125.61 (5-pyridyl-C–H), 122.92 (4a-naphth-C), 121.54 (q, J = 321.9 Hz, –SO₂–CF₃), 121.11 (d, J = 13.6 Hz, 3-pyridyl-C–H), 120.26 (d, J = 14.5 Hz, 3-naphth-C–H), 94.01 (d, J = 187.7 Hz, (pyridyl)₂(naphth)C–F). Carbon resonances assignable to the bridging phenylalkynyl's –CF₃ group, one of its aromatic resonances, as well as the internal and terminal bridging alkynyl carbon atoms were not observed. ^{19}F NMR (564.63 MHz, $\text{C}_6\text{D}_5\text{NO}_2$) δ –61.61 (s, 3F, –C $\equiv$ C(C_6H_4)CF₃), –78.17 (s, 6F, –SO₂–CF₃), –175.68 (s, 2F, (pyridyl)₂(naphth)C–F). ^{19}F NMR (564.63 MHz, *o*-C₆H₄F₂) δ –62.37 (s, 3F, –C $\equiv$ C(C_6H_4)CF₃), –78.52 (s, 6F, –SO₂–CF₃), –176.15 (s, 2F, (pyridyl)₂(naphth)C–F). IR (ATR, $\tilde{\nu}$ (cm^{–1})): 3069 (vw), 2037 (w), 2017 (w), 1605 (m), 1594 (m), 1575 (w), 1499 (w), 1461 (w), 1438 (w), 1353 (m), 1337 (m), 1323 (vs), 1300 (w), 1293 (w), 1227 (m), 1193 (s), 1176 (vs), 1152 (m), 1137 (m), 1119 (s), 1101 (m), 1075 (m), 1063 (vs), 1016 (w), 994 (vw), 929 (vw), 892 (vw), 859 (m), 848 (m), 808 (w), 773 (m), 754 (m), 739 (w), 711 (vw), 698 (w), 686 (m), 647 (w), 635 (w), 613 (s), 599 (m), 570 (m), 561 (m), 513 (m), 481 (vw), 453 (vw), 417 (m). Anal. Calcd for: C₄₁H₂₄Cu₂F₁₁N₇O₄S₂: C, 45.64; H, 2.24; N, 9.09. Found: C, 45.45; H, 1.99; N, 8.98.

2,7-bis(fluoro-di(2-pyridyl)methyl)-1,8-naphthyridine (DPFN). As mentioned in the Experimental Details section, DPFN was synthesized using previously published procedures.¹ ^1H NMR (600.13 MHz, THF-*d*₈) δ 8.43 (dd, J = 5.0, 1.7 Hz, 4H), 8.19 (d, J = 8.5 Hz, 2H), 7.77 (d, J = 8.5 Hz, 2H), 7.71 (td, J = 7.7, 1.9 Hz, 4H), 7.58 (d, J = 7.9 Hz, 4H), 7.21 (dd, J = 7.6, 4.8 Hz, 4H). ^{19}F NMR (564.61 MHz, THF-*d*₈) δ –143.65 (2F, (pyridyl)₂(naphth)C–F). ^1H NMR (600.13 MHz, *o*-C₆H₄F₂) δ 8.40 (d, J = 4.8 Hz, 4H), 7.89 (d, J = 8.5 Hz, 2H), 7.86 (d, J = 8.5 Hz, 2H), 7.58 (d, J = 8.0 Hz, 4H), 7.47 (td, J = 7.8, 1.8 Hz, 4H). The sixth expected ^1H resonance is likely obscured by the solvent resonance. ^{19}F NMR (564.61 MHz, *o*-C₆H₄F₂) δ –142.22 (2F, (pyridyl)₂(naphth)C–F). IR (ATR, $\tilde{\nu}$ (cm^{–1})): 3083 (vw), 3056 (w), 3003 (w), 1604 (m), 1586 (s), 1571 (m),

^a These proton and carbon resonances overlapped with or were obscured by solvent resonances, other complex resonances, or otherwise not observed directly and instead observed and assigned via ^1H – ^1H COSY and ^1H – ^{13}C HSQC and HMBC experiments.

1543 (w), 1500 (m), 1466 (s), 1435 (s), 1419 (m), 1378 (vw), 1303 (w), 1271 (w), 1230 (w), 1210 (w), 1152 (w), 1140 (w), 1126 (w), 1105 (w), 1092 (w, sh), 1063 (w, sh), 1053 (m), 1042 (m), 1021 (m), 993 (s), 966 (w), 955 (w), 945 (w), 927 (m), 896 (w), 859 (s), 817 (m), 790 (s), 775 (vs), 751 (s), 740 (s), 711 (m), 706 (m, sh), 689 (s), 673 (w), 656 (vw), 634 (w), 621 (m), 609 (m), 597 (m), 587 (m), 565 (m), 519 (m), 481 (w), 463 (vw).

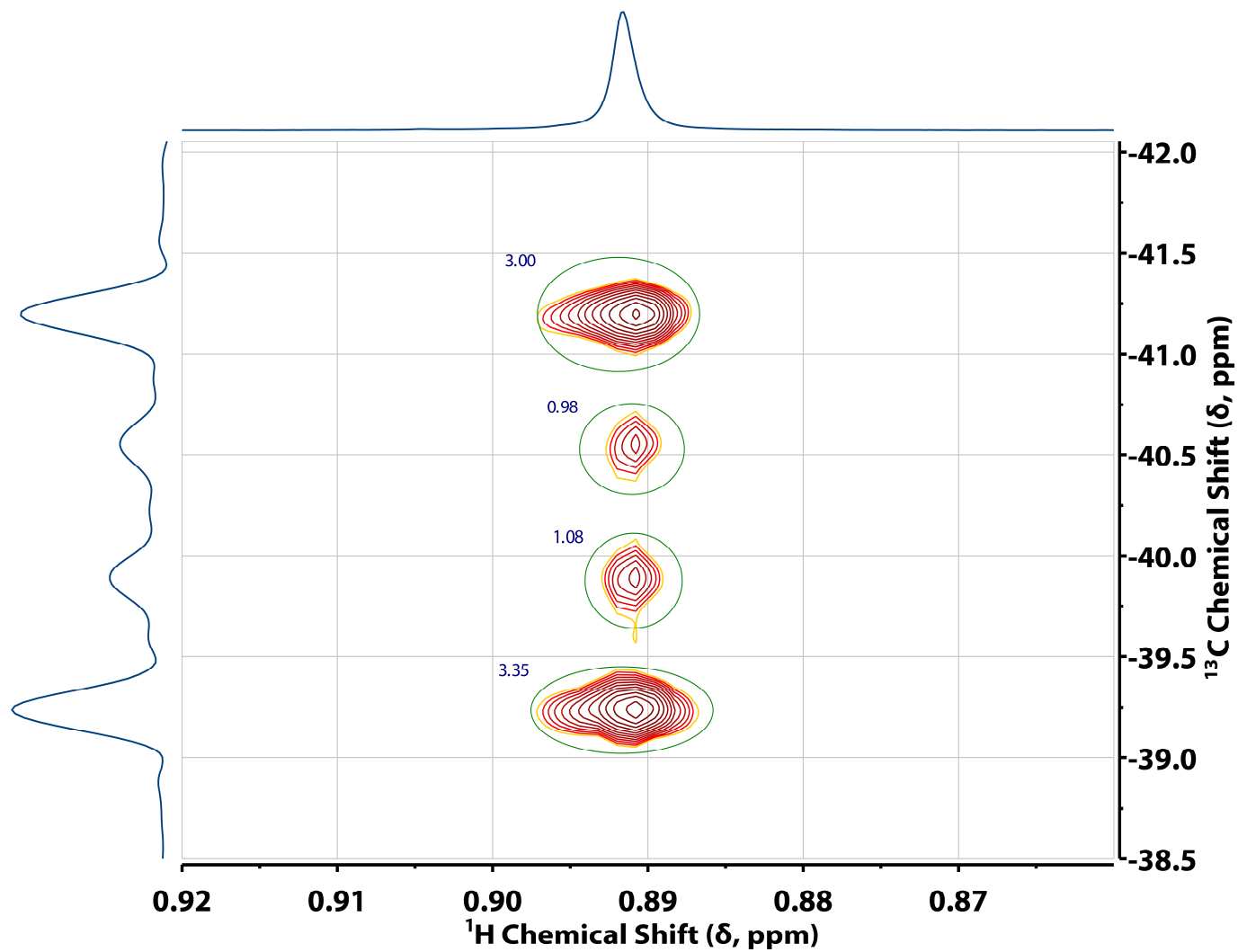
[Cu₂(μ-η¹:η¹-NCCH₃)DPFN](NTf₂)₂. As mentioned in the Experimental Details section, [Cu₂(μ-η¹:η¹-NCCH₃)DPFN](NTf₂)₂ was synthesized using previously published procedures.¹ ¹H NMR (600.13 MHz, THF-*H*₈) δ 9.26 (d, *J* = 5.1 Hz, 4H), 8.90 (d, *J* = 8.6 Hz, 2H), 8.46 (dd, *J* = 8.6, 3.0 Hz, 2H), 8.19 (dd, *J* = 8.1, 3.3 Hz, 4H), 8.12 (td, *J* = 7.9, 1.7 Hz, 4H), 7.70 (dd, *J* = 7.6, 5.1 Hz, 4H), 2.88 (s, 3H). ¹⁹F NMR (564.61 MHz, THF-*H*₈) δ -78.95 (s, 12F, -SO₂-CF₃), -174.50 (q, *J* = 3.3 Hz, 2F, (pyridyl)₂(naphth)C-F). ¹H NMR (600.13 MHz, *o*-C₆H₄F₂) δ 9.25 (d, *J* = 5.0 Hz, 4H), 8.50 (d, *J* = 8.5 Hz, 2H), 8.25 (dd, *J* = 8.6, 2.8 Hz, 2H), 8.03 (dd, *J* = 8.2, 3.3 Hz, 4H), 7.82 (td, *J* = 8.0, 1.7 Hz, 4H), 7.56 (dd, *J* = 7.7, 5.1 Hz, 4H), 2.91 (s, 3H). ¹⁹F NMR (564.61 MHz, *o*-C₆H₄F₂) δ -78.68 (s, 12F, -SO₂-CF₃), -175.07 (s, 2F, (pyridyl)₂(naphth)C-F).

[Cu₂(μ-η¹:η¹-Ph)DPFN]NTf₂. As mentioned in the Experimental Details section, [Cu₂(μ-η¹:η¹-Ph)DPFN]NTf₂ was synthesized using previously published procedures.¹ ¹H NMR (600.13 MHz, THF-*d*₈) δ 8.98 (dd, *J* = 5.2, 1.7 Hz, 4H, 6-pyridyl-C-H), 8.86 (d, *J* = 8.6 Hz, 2H, 4-naphth-C-H), 8.49 (dd, *J* = 7.5, 1.3 Hz, 2H, *o*-phenyl-C-H), 8.44 (dd, *J* = 8.6, 3.2 Hz, 2H, 3-naphth-C-H), 8.11 (ddt, *J* = 8.2, 3.4, 1.1 Hz, 4H, 3-pyridyl-C-H), 7.99 (td, *J* = 7.9, 1.8 Hz, 4H, 4-pyridyl-C-H), 7.48 (ddd, *J* = 7.6, 5.1, 1.2 Hz, 4H, 5-pyridyl-C-H), 7.37 (t, *J* = 7.5 Hz, 2H, *m*-phenyl-C-H), 7.17 (tt, *J* = 7.2, 1.4 Hz, 1H, *p*-phenyl-C-H). ¹³C{¹H} NMR (176.07 MHz, THF-*d*₈) δ 160.36 (d, *J* = 31.2 Hz, 2-naphth-C), 154.25 (d, *J* = 29.3 Hz, 2-pyridyl-C), 151.42 (8a-naphth-C),^a 150.31 (d, *J* = 2.9 Hz, 6-pyridyl-C-H), 145.13 (*o*-phenyl-C-H), 143.06 (*ipso*-phenyl-C-Cu₂),^a 141.69 (4-naphth-C-H), 139.46 (d, *J* = 3.5 Hz, 4-pyridyl-C-H), 126.74 (*m*-phenyl-C-H), 125.85 (*p*-phenyl-C-H), 125.10 (5-pyridyl-C-H), 123.89 (4a-naphth-C), 120.79 (d, *J* = 14.7 Hz, 3-pyridyl-C-H), 121.06 (d^b, *J* = 322.0 Hz, -SO₂-CF₃), 119.93 (d, *J* = 15.5 Hz, 3-naphth-C-H), 94.27 (d, *J* = 188.2 Hz, (pyridyl)₂(naphth)C-F). ¹⁹F NMR (564.61 MHz, THF-*d*₈) δ -79.06 (s, 6F, -SO₂-CF₃), -172.82 (q, *J* = 3.5 Hz, 2F, (pyridyl)₂(naphth)C-F). ¹H NMR (600.13 MHz, *o*-C₆H₄F₂) δ 9.00 (d, *J* = 5.1 Hz, 4H), 8.65 (d, *J* = 7.0 Hz, 2H), 8.33 (d, *J* = 8.6 Hz, 2H), 8.20 (dd, *J* = 8.6, 3.0 Hz, 2H), 7.95 (dd, *J* = 8.2, 3.3 Hz, 4H), 7.71 (td, *J* = 7.9, 1.7 Hz, 4H), 7.61 (t, *J* = 7.3 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 1H). The sixth expected DPFN ¹H resonance is likely obscured by the solvent resonance. ¹⁹F NMR (564.61 MHz, *o*-C₆H₄F₂) δ -78.54 (s, 6F, -SO₂-CF₃), -173.42 (q, *J* = 3.5 Hz, 2F, (pyridyl)₂(naphth)C-F). ¹H NMR (600.13 MHz, THF-*H*₈) δ 8.98 (d, *J* = 5.1 Hz, 4H), 8.85 (d, *J* = 8.6 Hz, 2H), 8.49 (d, *J* = 7.0 Hz, 2H), 8.44 (dd, *J* = 8.6, 3.2 Hz, 2H), 8.10 (dd, *J* = 8.2, 3.4 Hz, 4H), 7.98 (td, *J* = 7.9, 1.7 Hz, 4H), 7.48 (dd, *J* = 7.5, 5.2 Hz, 4H), 7.36 (t, *J* = 7.3 Hz, 2H), 7.17 (t, *J* = 7.1 Hz, 1H).

^b This doublet is presumably the central two resonances of a quartet assignable to the triflimide anion -SO₂-CF₃ resonance.

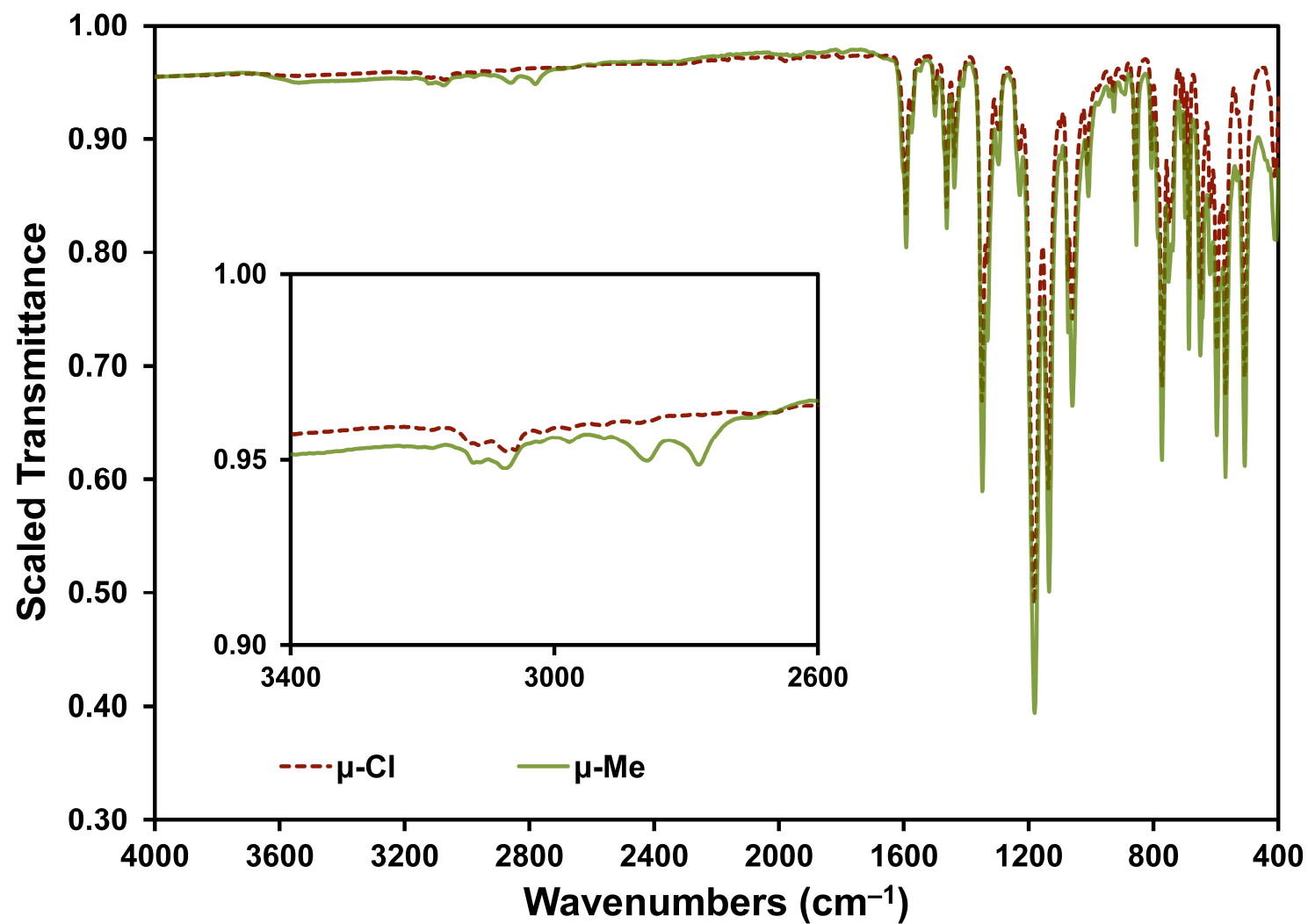
2) Supplementary figures

Figure S1: Excerpt from a spectrum obtained from a coupled ^1H – ^{13}C HSQC experiment of a solution of **1** in $\text{THF-}d_8$ at 16.4 T and 25 °C



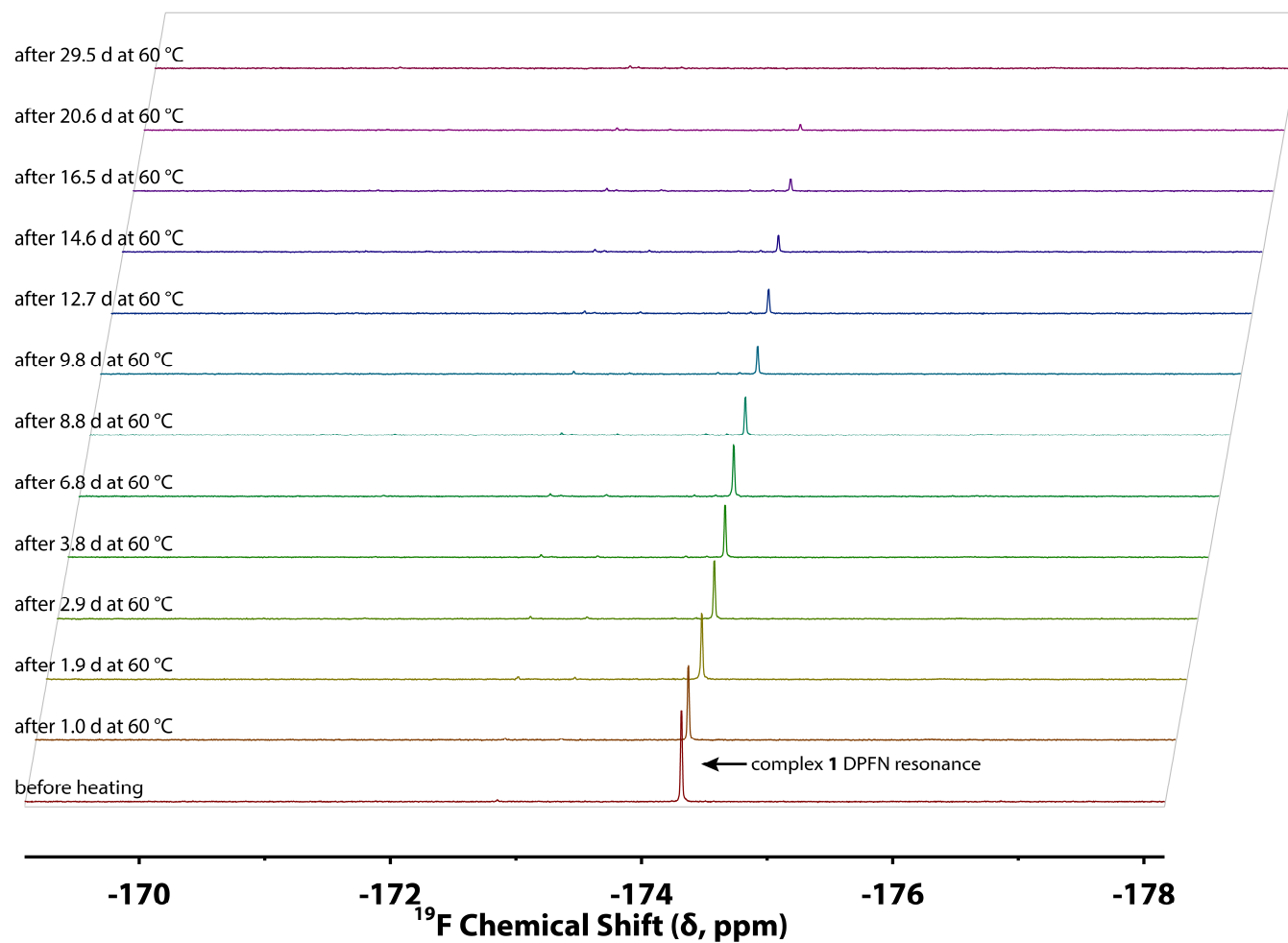
Details: The horizontal trace is a 1D ^1H NMR spectrum obtained at 16.4 T at 25 °C. The vertical trace is the maximum trace extracted from the HSQC experiment.

Figure S2: FTIR Spectra of Complexes **1** and **2**



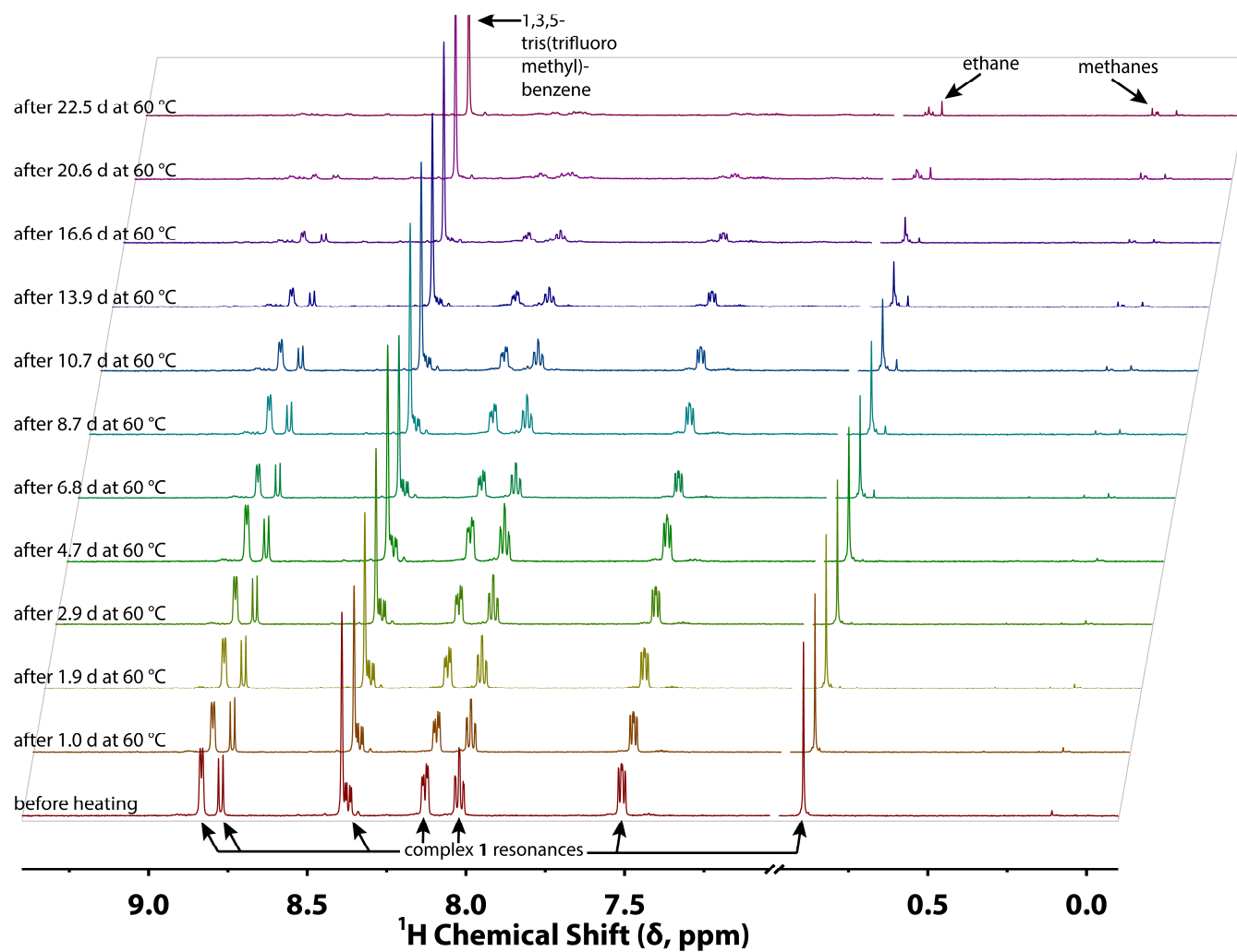
Details: The spectrum of complex **1** is scaled by a factor of 1.01 to align slightly better with that of complex **2**.

Figure S3: Excerpts of ^{19}F NMR spectra monitoring the decomposition of complex **1** in THF at 60 °C



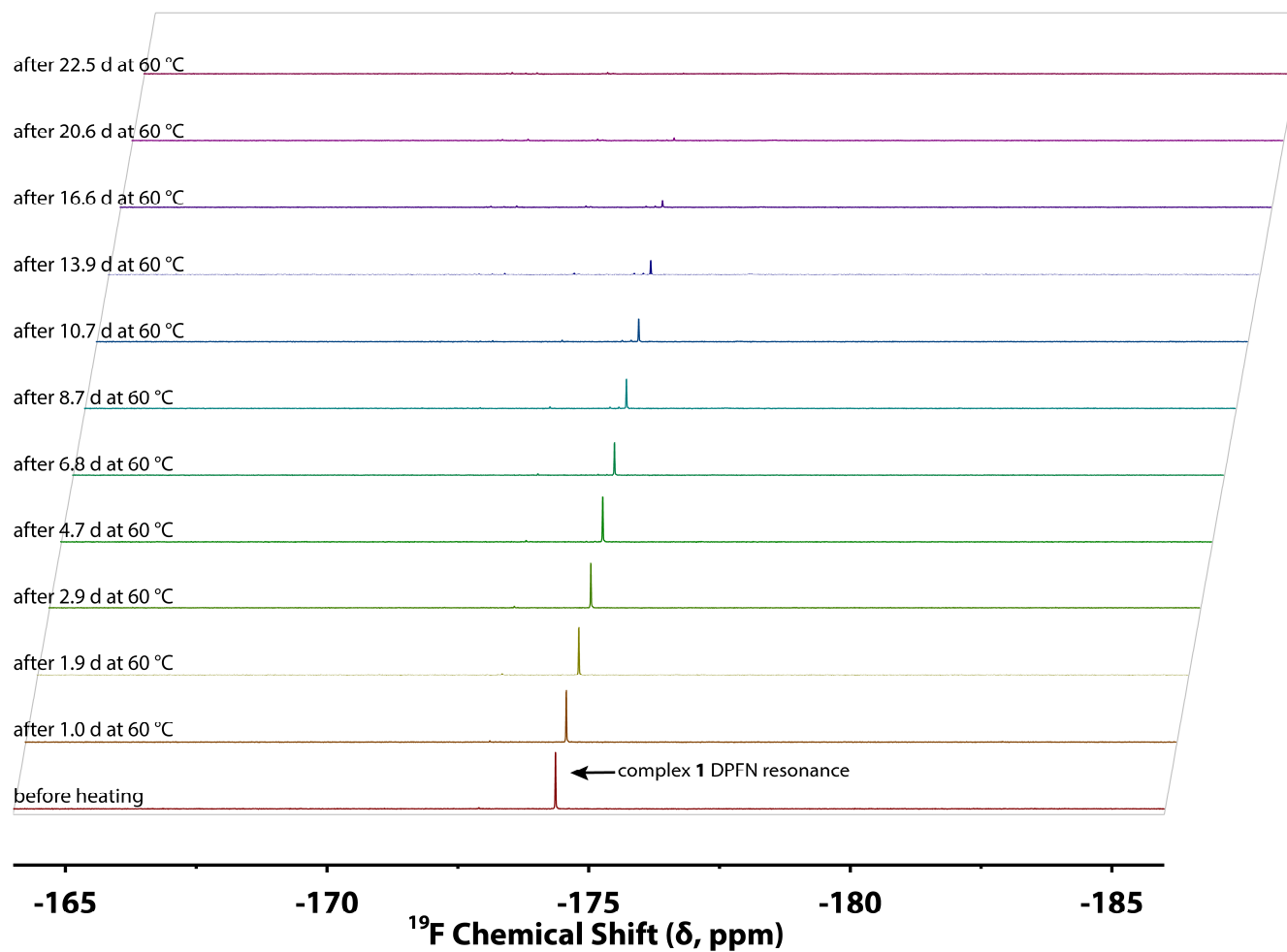
Details: ^{19}F NMR spectra acquired at 564.61 MHz. All spectra were recorded between 294.7 and 296.8 K and are normalized to an internal standard, 1,3,5-tris(trifluoromethyl)benzene (not shown).

Figure S4: Excerpts of ^1H NMR spectra monitoring the decomposition of complex **1** in $\text{THF-}d_8$ at 60°C



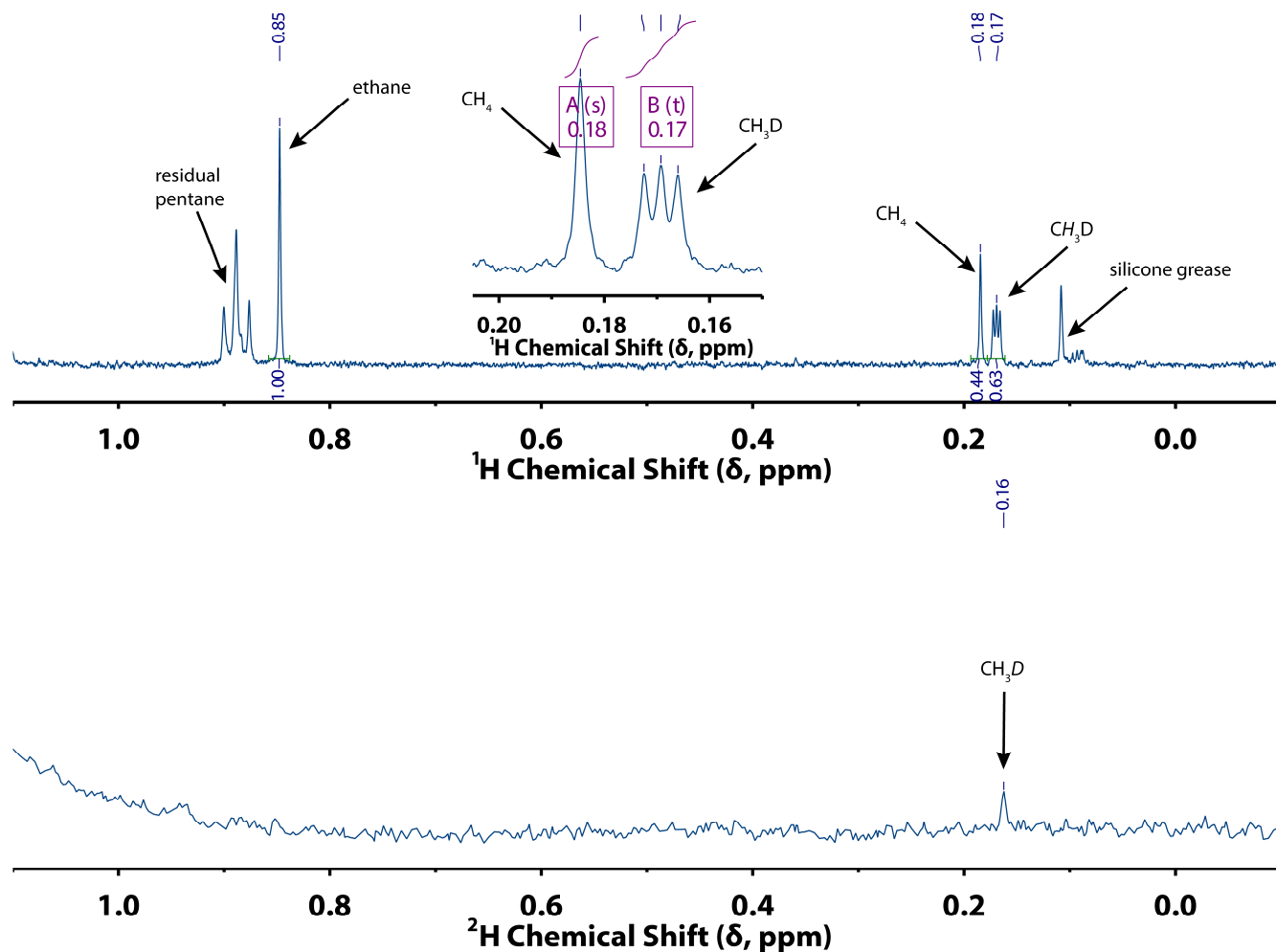
Details: ^1H NMR spectra acquired at 600.13 MHz. All spectra were recorded between 294.9 and 298.2 K and are normalized to an internal standard, 1,3,5-trimethoxybenzene (not shown).

Figure S5: Excerpts of ^{19}F NMR spectra monitoring the decomposition of complex **1** in $\text{THF-}d_8$ at 60°C



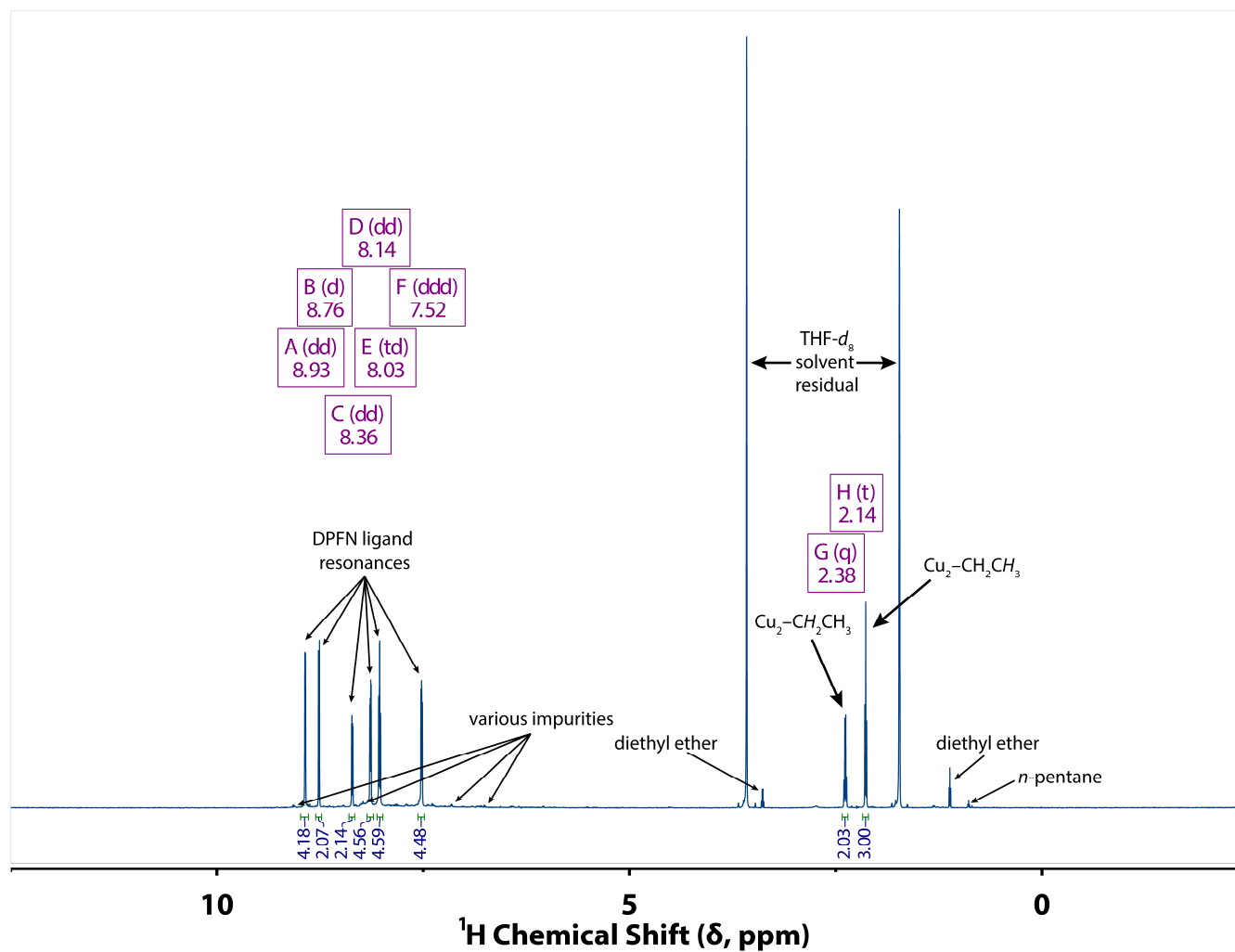
Details: ^{19}F NMR spectra acquired at 564.61 MHz. All spectra were recorded between 294.9 and 298.2 K and are normalized to an internal standard, 1,3,5-tris(trifluoromethyl)benzene (not shown).

Figure S6: Excerpts of ^1H and $^2\text{H}\{^1\text{H}\}$ NMR spectra acquired after the decomposition of complex **1** in $\text{THF-}d_8$ at 60°C



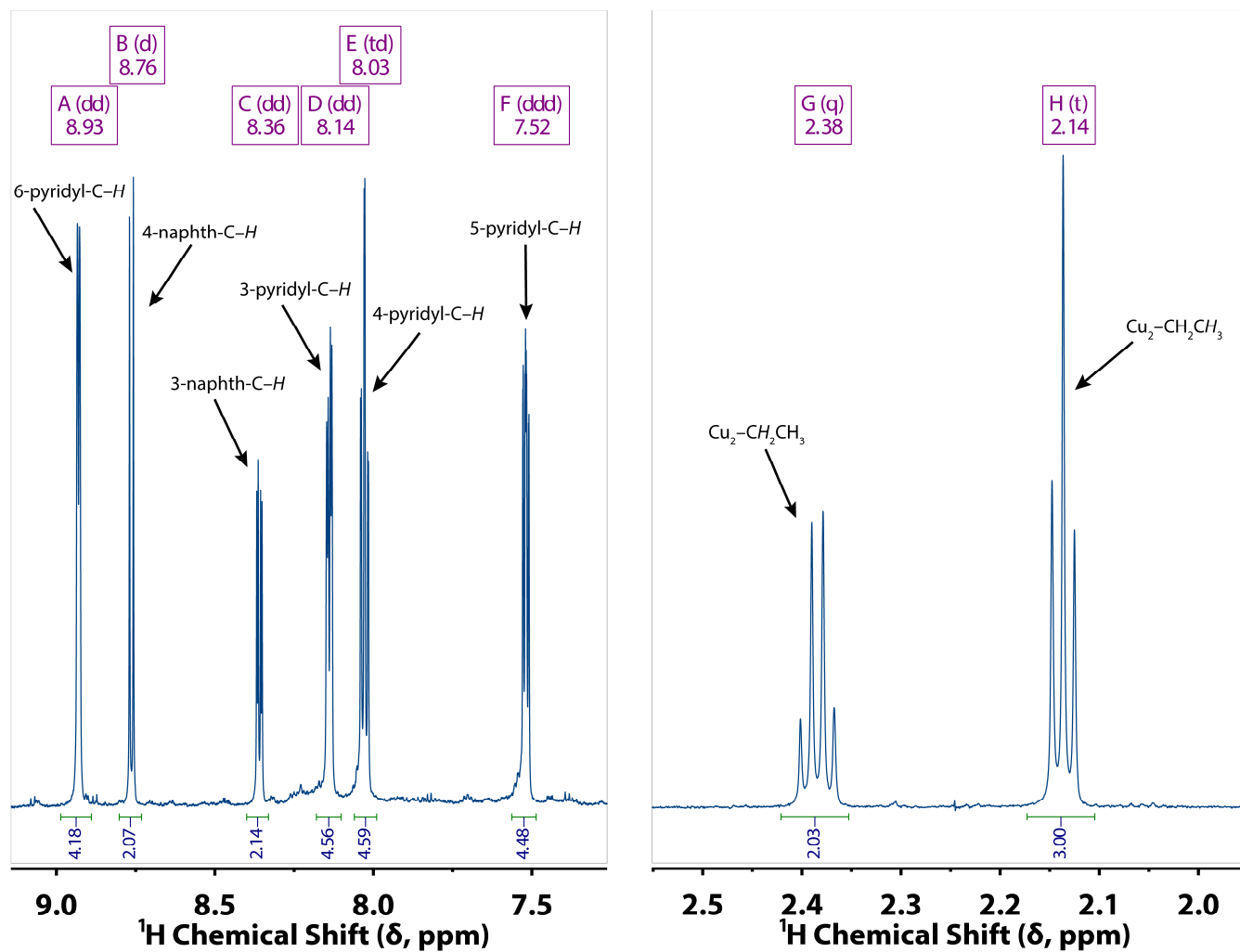
Details: ^1H NMR spectra acquired at 600.13 MHz; $^2\text{H}\{^1\text{H}\}$ at 92.12 MHz. All spectra were recorded between 298.1 and 299.3 K. Using the 1D ^1H spectrum, the $J_{\text{H-D}}$ coupling constant for the resonance assigned as CH_3D was determined to have an absolute value of 1.9 Hz, consistent with coupling values previously reported for CH_3D in a variety of solvents.²

Figure S7: ^1H NMR spectrum of a product mixture primarily containing complex **4** in $\text{THF-}d_8$ at 25 °C



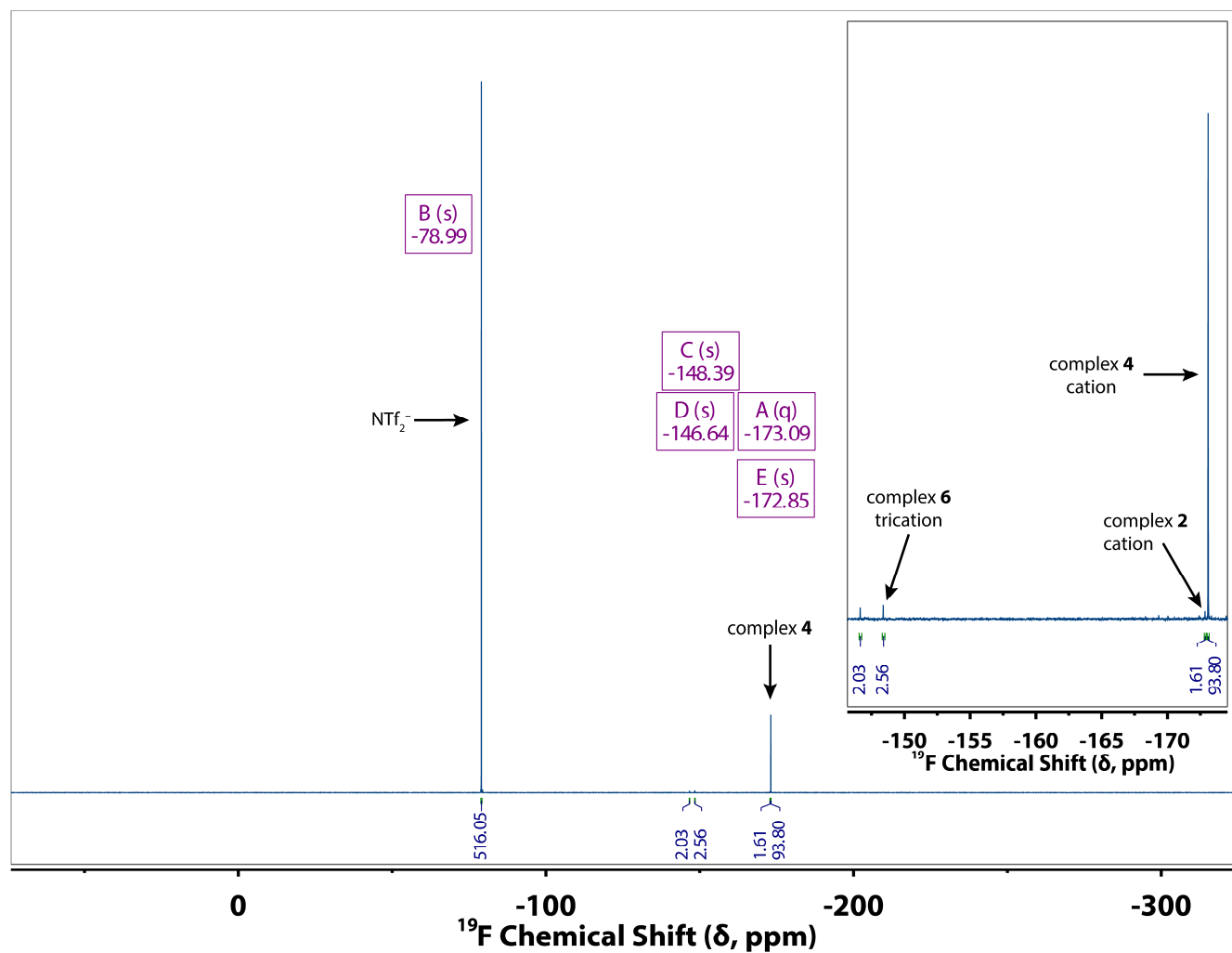
Details: ^1H NMR spectrum acquired at 700.13 MHz.

Figure S8: Excerpts of ^1H NMR spectrum of a product mixture primarily containing complex **4** in $\text{THF-}d_8$ at $25\text{ }^\circ\text{C}$



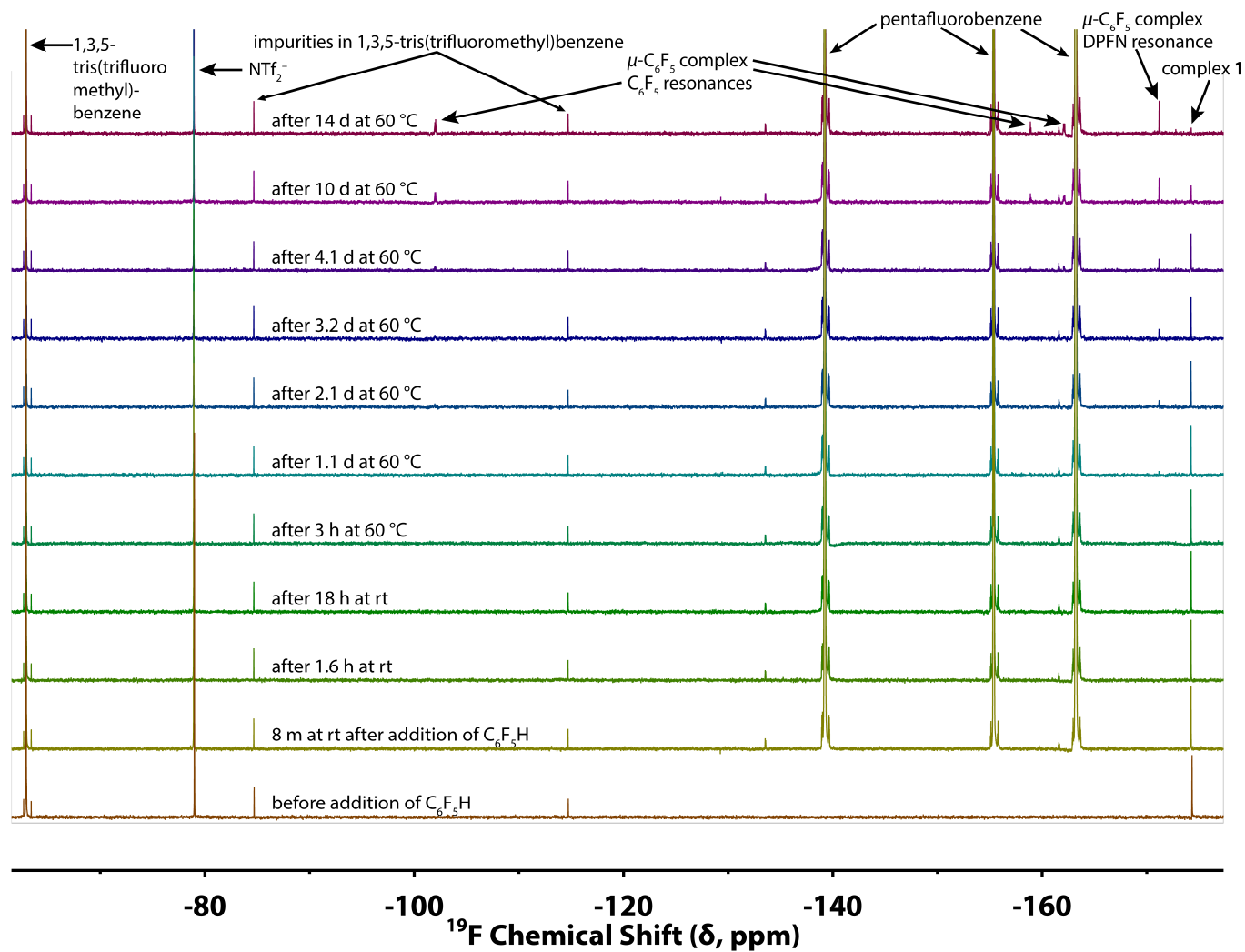
Details: ^1H NMR spectrum acquired at 700.13 MHz.

Figure S9: ^{19}F NMR spectrum of a product mixture primarily containing complex **4** in $\text{THF-}d_8$ at 25 °C



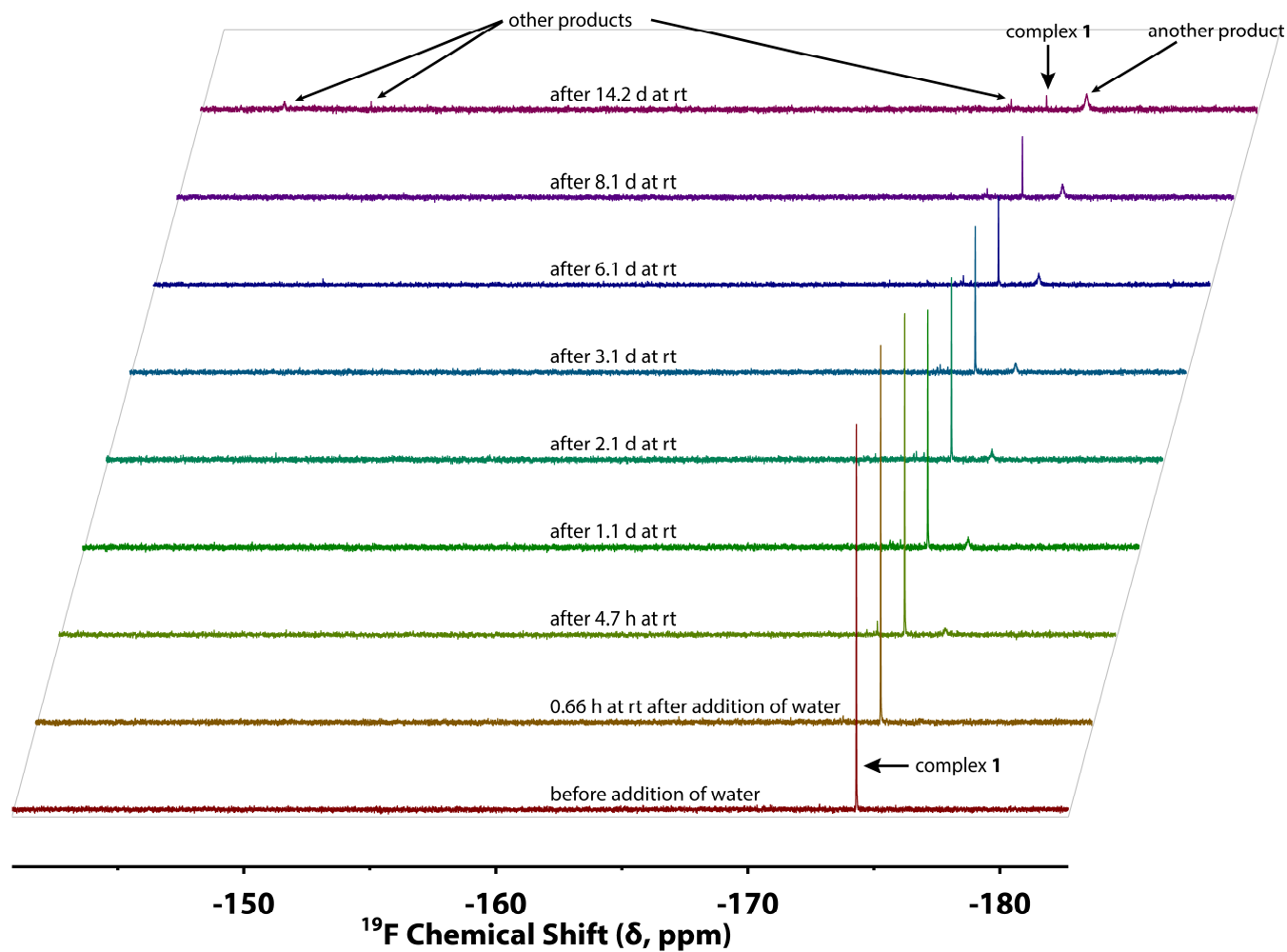
Details: ^{19}F NMR spectrum acquired at 564.61 MHz.

Figure S10: Excerpts of ^{19}F NMR spectra monitoring the reaction of complex **1** with pentafluorobenzene (220 equiv) in THF at 60 °C



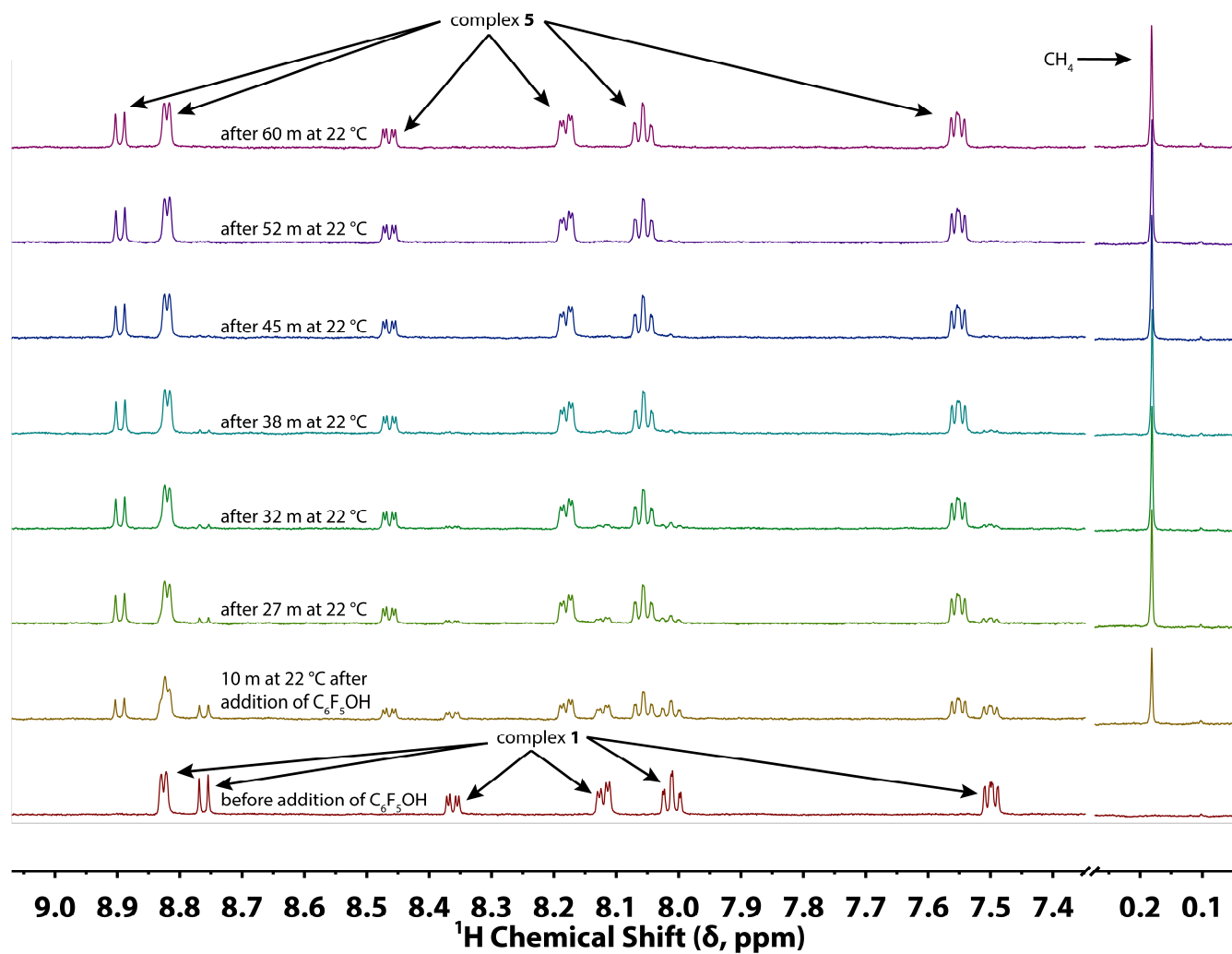
Details: ^{19}F NMR spectra acquired at 376.45 MHz. All spectra were recorded between 293.5 and 294.0 K and are normalized to an internal standard, 1,3,5-tris(trifluoromethyl)benzene (shown at left).

Figure S11: Excerpts of ^{19}F NMR spectra monitoring the reaction of complex **1** with water (170 equiv) in THF at room temp.



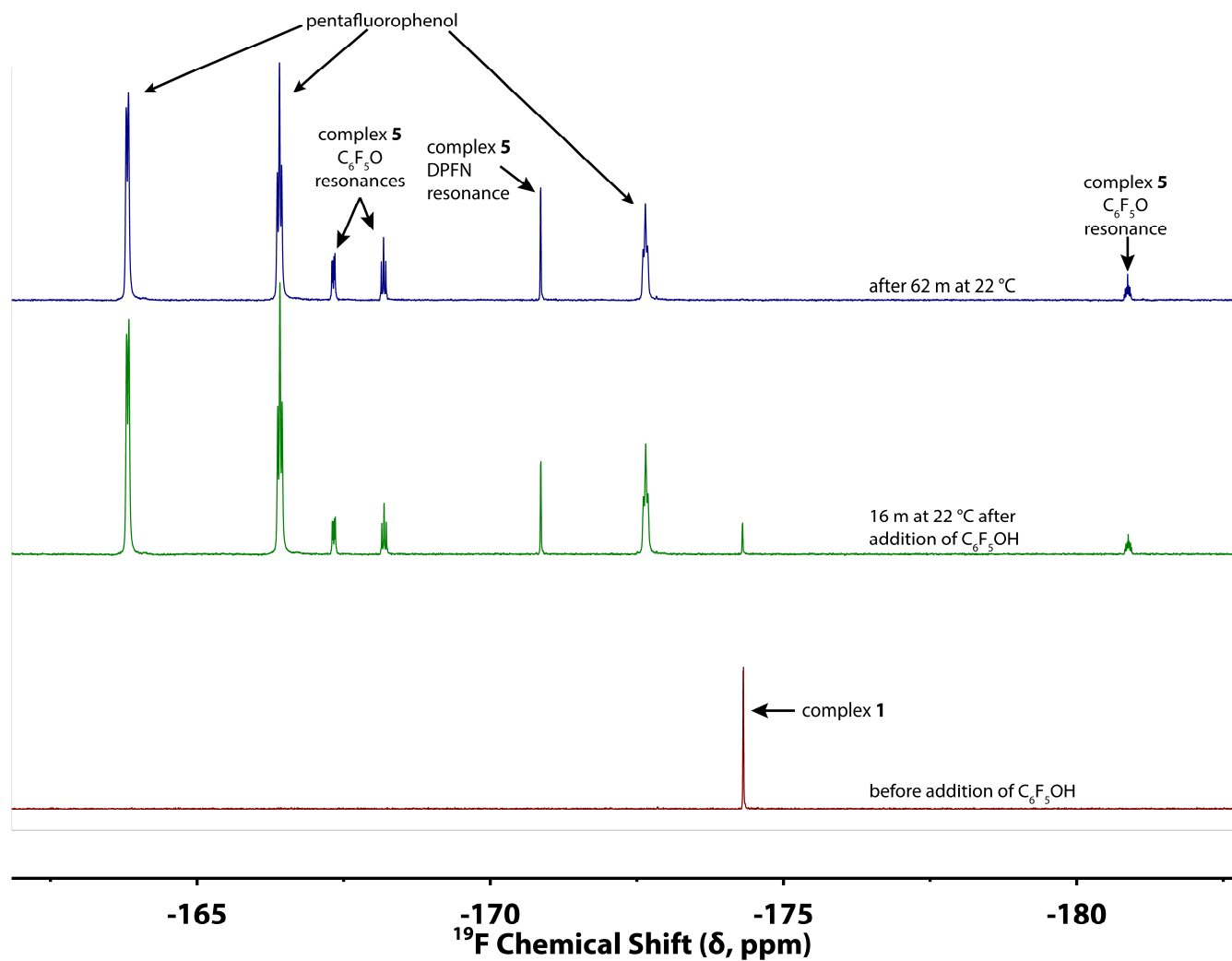
Details: ^{19}F NMR spectra acquired at 564.61 MHz. All spectra were recorded between 293.9 and 295.8 K and are normalized to an internal standard, 1,3,5-tris(trifluoromethyl)benzene (not shown).

Figure S12: Excerpts of ^1H NMR spectra monitoring the reaction of complex **1** with pentafluorophenol (10 equiv) in THF at 22 °C



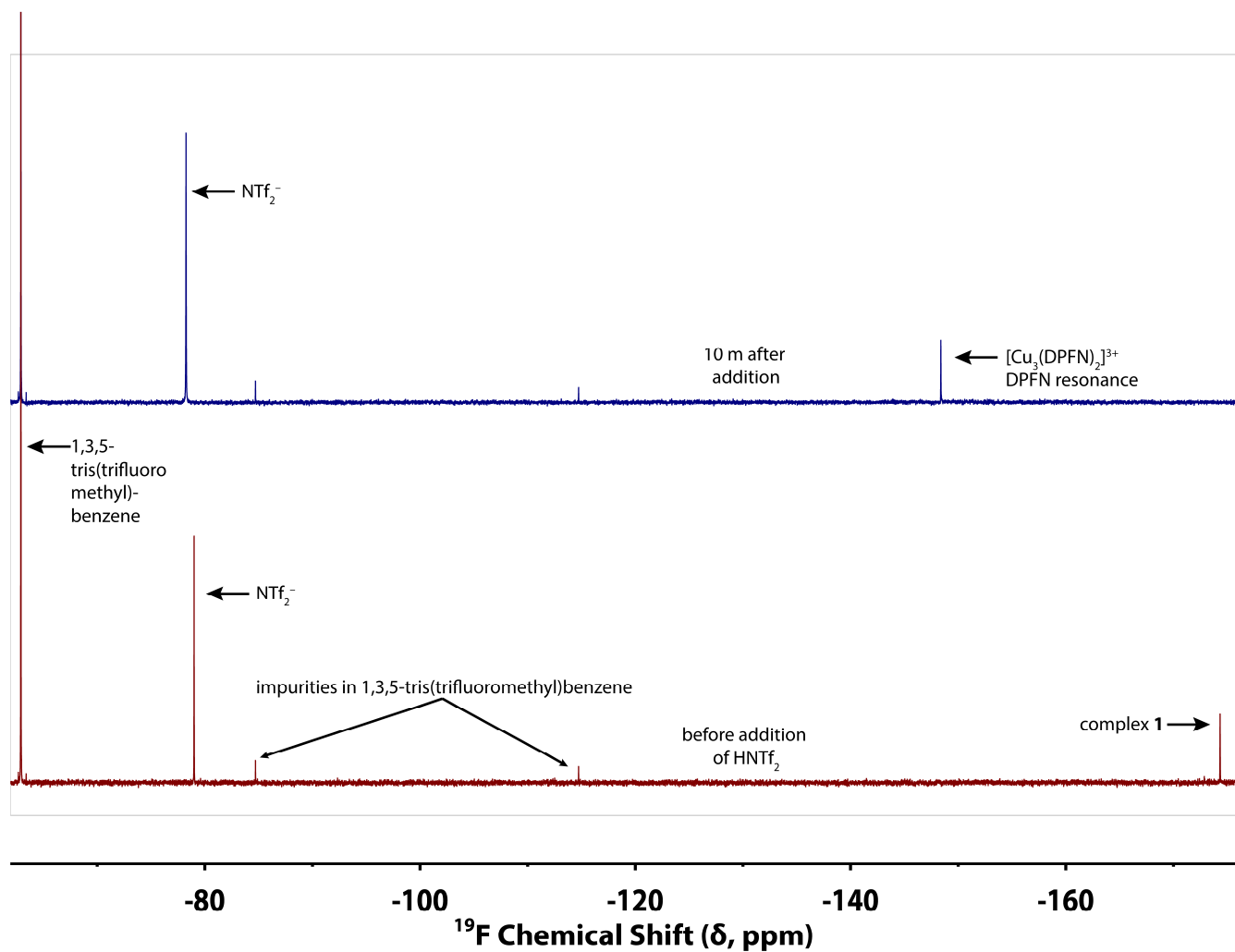
Details: ^1H NMR spectra acquired at 600.13 MHz. All spectra were recorded between 295.0 and 296.2 K and are normalized to an internal standard, 1,3,5-trimethoxybenzene (not shown).

Figure S13: Excerpts of ^{19}F NMR spectra monitoring the reaction of complex **1** with pentafluorophenol (10 equiv) in THF at 22 °C



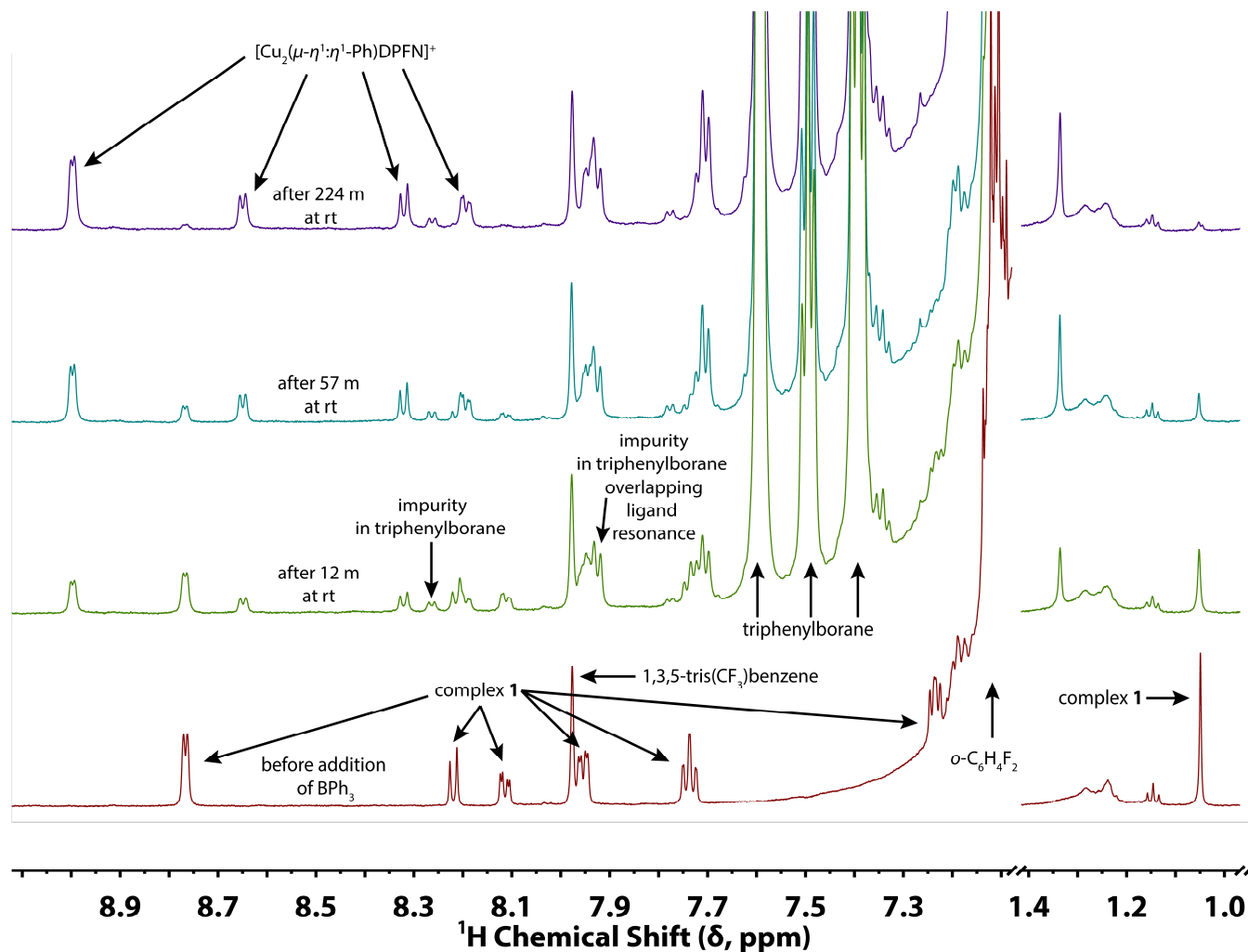
Details: ^{19}F NMR spectra acquired at 564.61 MHz. All spectra were recorded between 295.0 and 296.2 K and for display purposes are normalized to the anion (triflimide) resonance (not shown).

Figure S14: Excerpts of ^{19}F NMR spectra monitoring the reaction of complex **1** with triflimidic acid (1 equiv) in THF at room temperature



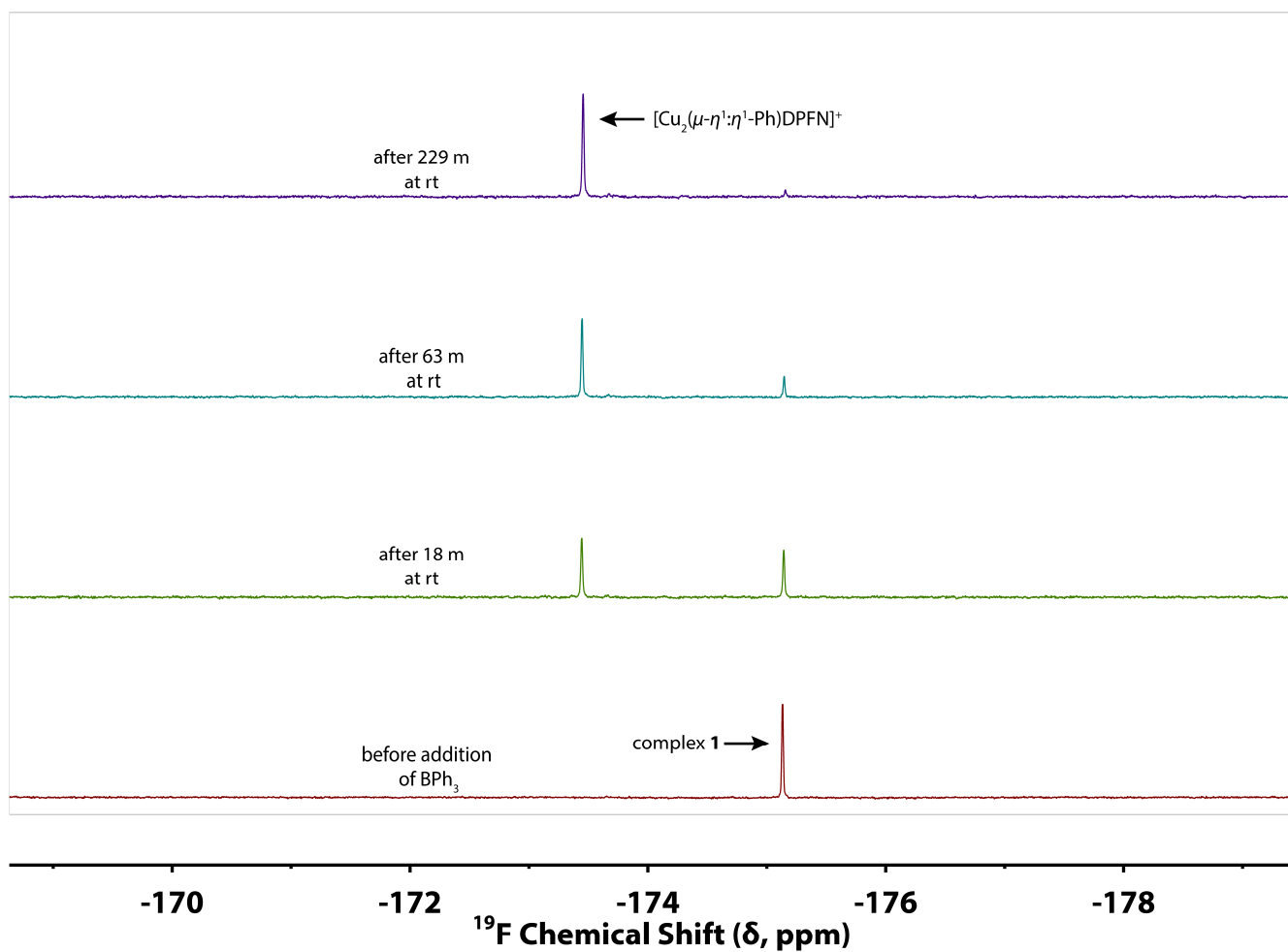
Details: ^{19}F NMR spectra acquired at 376.44 MHz. All spectra were recorded at ca. 293.0 K and are normalized to an internal standard, 1,3,5-tris(trifluoromethyl)benzene (shown at far left).

Figure S15: Excerpts of ^1H NMR spectra monitoring the reaction of complex **1** with triphenylborane (10 equiv) in $o\text{-C}_6\text{H}_4\text{F}_2$ at room temp.



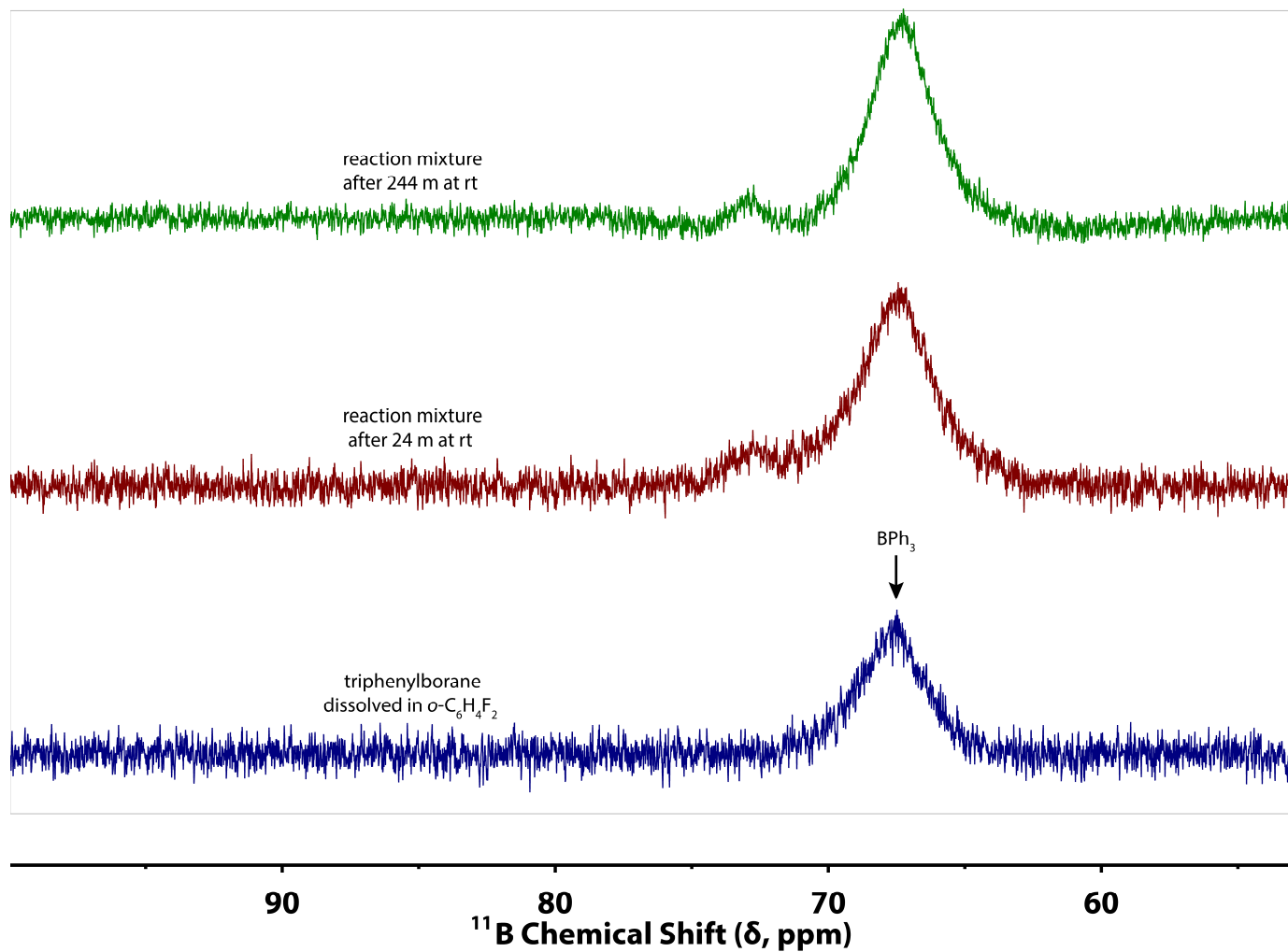
Details: ^1H NMR spectra acquired at 600.13 MHz. All spectra were recorded between 294.3 and 295.6 K and are normalized to an internal standard, 1,3,5-tris(trifluoromethyl)benzene.

Figure S16: Excerpts of ^{19}F NMR spectra monitoring the reaction of complex **1** with triphenylborane (10 equiv) in $o\text{-C}_6\text{H}_4\text{F}_2$ at room temp.



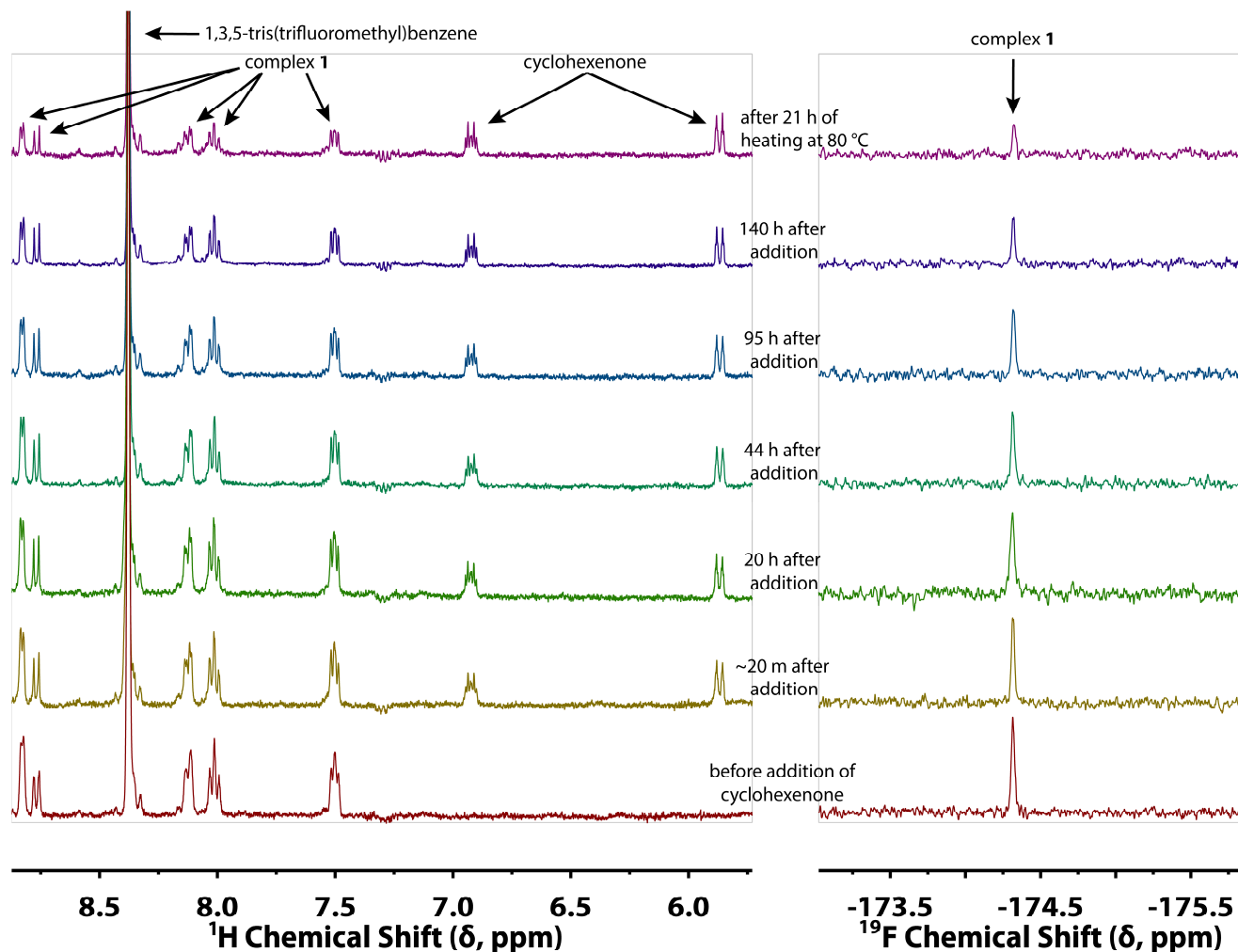
Details: ^{19}F NMR spectra acquired at 564.61 MHz. All spectra were recorded between 294.3 and 295.6 K and are normalized to an internal standard, 1,3,5-tris(trifluoromethyl)benzene (not shown).

Figure S17: Excerpts of $^{11}\text{B}\{^1\text{H}\}$ NMR spectra monitoring the reaction of complex **1** with triphenylborane (10 equiv) in *o*-C₆H₄F₂ at room temp.



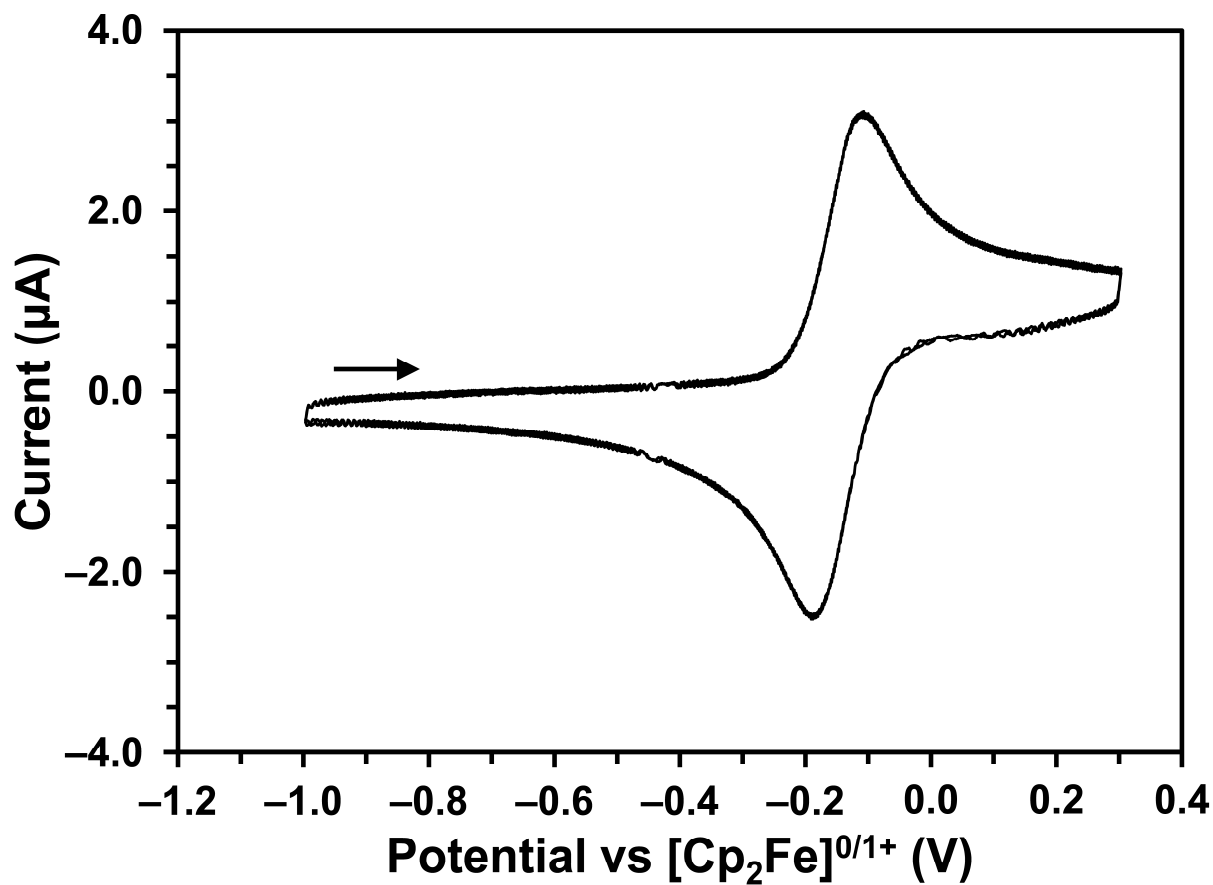
Details: $^{11}\text{B}\{^1\text{H}\}$ NMR spectra acquired at 192.55 MHz. All spectra were recorded between 294.4 and 295.2 K.

Figure S18: Excerpts of ^1H and ^{19}F NMR spectra monitoring the treatment of complex **1** with cyclohexenone (2.1 equiv) in THF at room temp. and upon heating to 80 °C



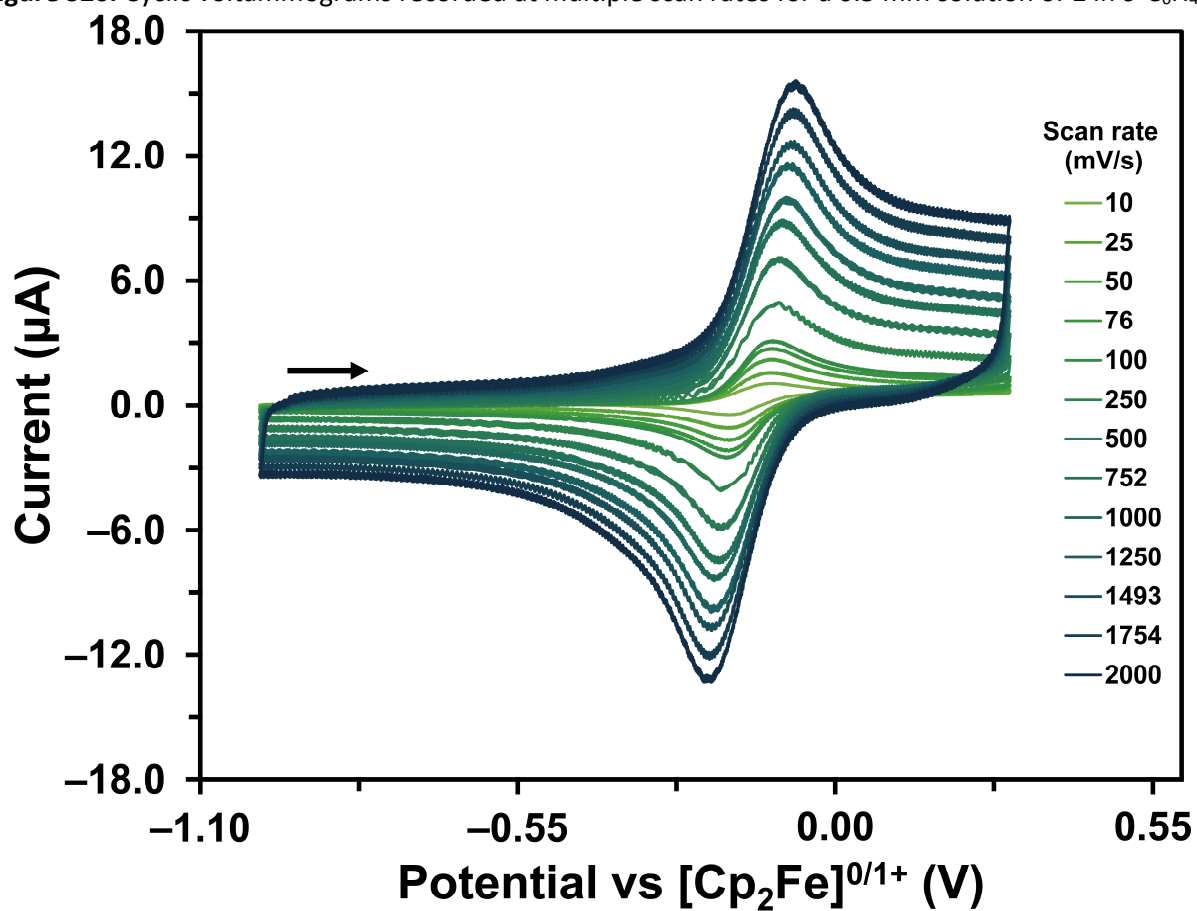
Details: ^1H NMR spectra were acquired at 400.13 MHz, ^{19}F NMR at 376.46 MHz. All spectra were recorded between 293.2 and 293.5 K and are normalized to an internal standard, 1,3,5-tris(trifluoromethyl)benzene, which is shown in the ^1H NMR spectra but not in the ^{19}F NMR spectra.

Figure S19. Cyclic voltammogram recorded for a 0.5 mM solution of **1** in *o*-C₆H₄F₂



Notes: Solution contained 0.1 M [ⁿBu₄N][PF₆] supporting electrolyte. The arrow indicates the initial potential and scanning direction. The voltammogram displays two complete cycles (5 segments) and was recorded at 100 mV/s.

Figure S20. Cyclic voltammograms recorded at multiple scan rates for a 0.5 mM solution of **1** in *o*-C₆H₄F₂



Notes: Solution contained 0.1 M [^{*n*}Bu₄N][PF₆] supporting electrolyte. The arrow indicates the initial potential and scanning direction for all scans. Each voltammogram displays two complete cycles (5 segments).

Figure S21. Scan rate dependence of cyclic voltammograms' peak currents of a 0.5 mM solution of **1** in *o*-C₆H₄F₂ with 0.1 M [ⁿBu₄N][PF₆] supporting electrolyte

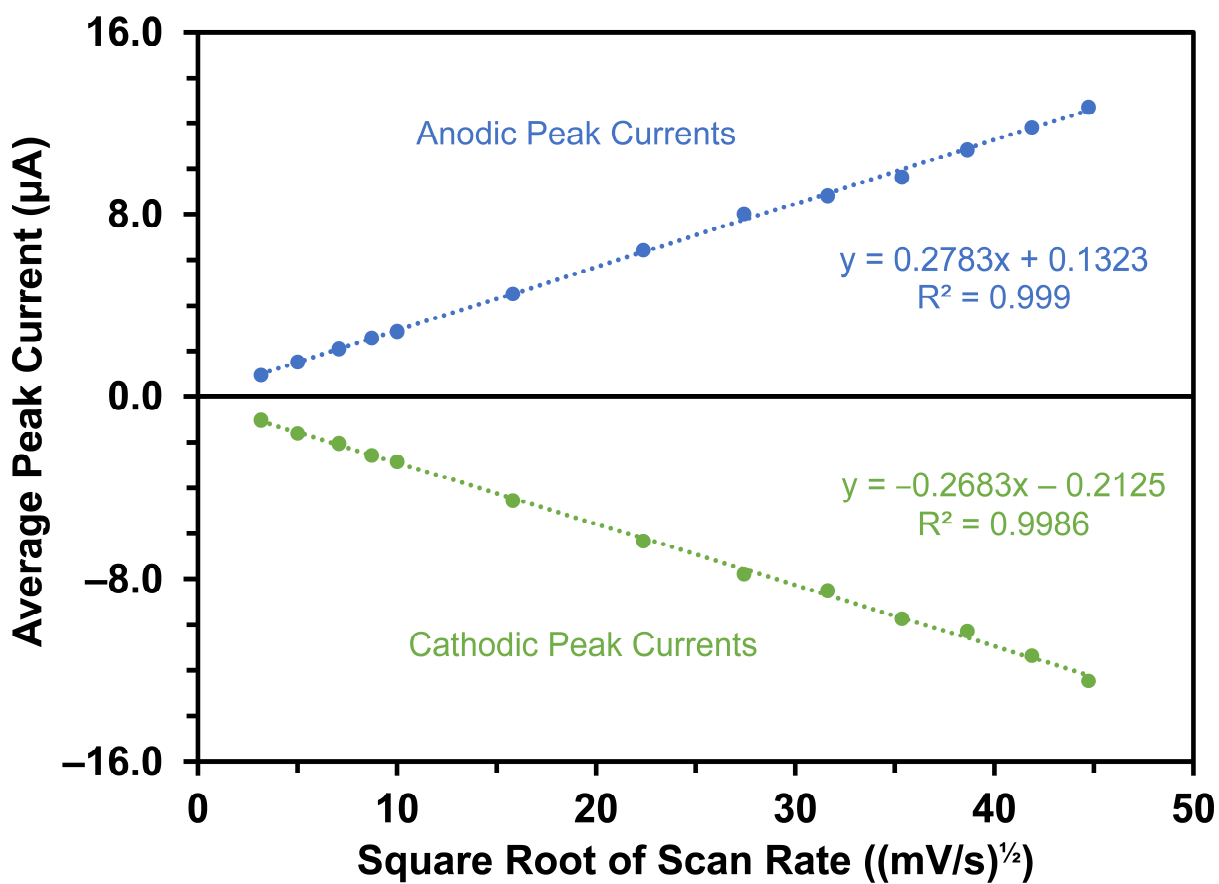
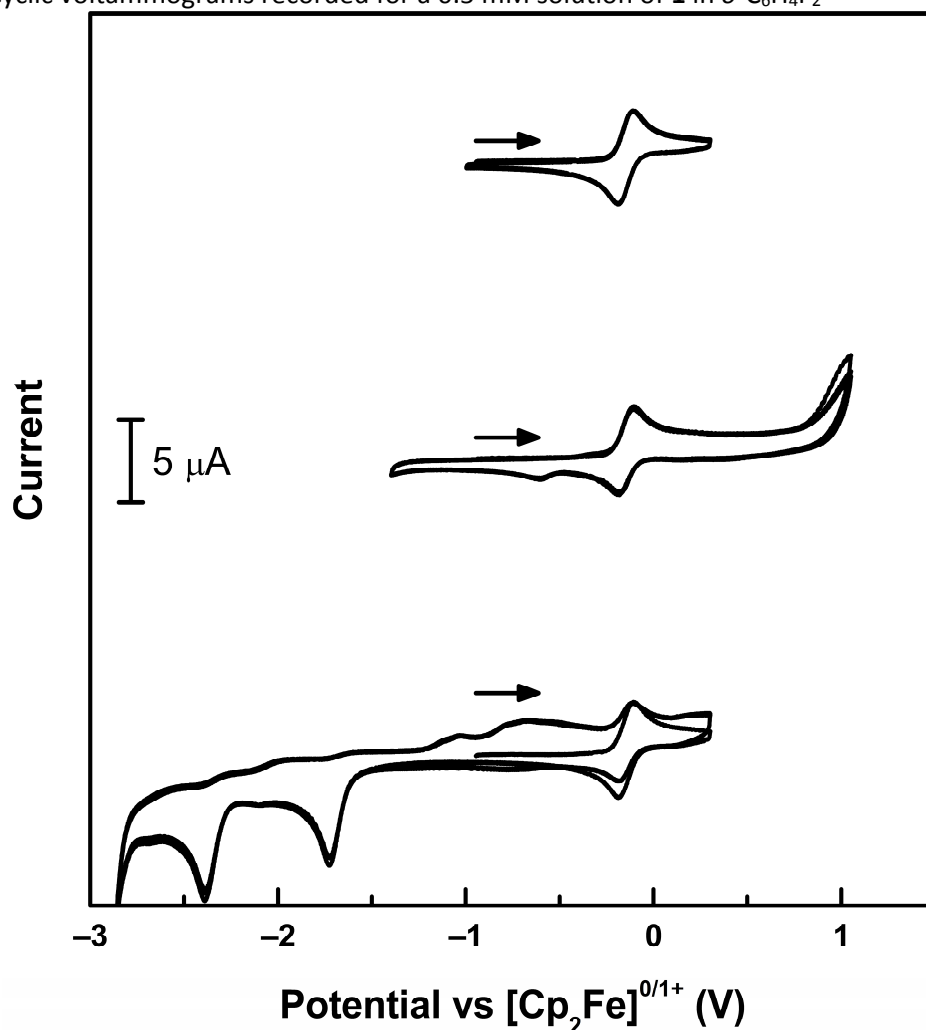
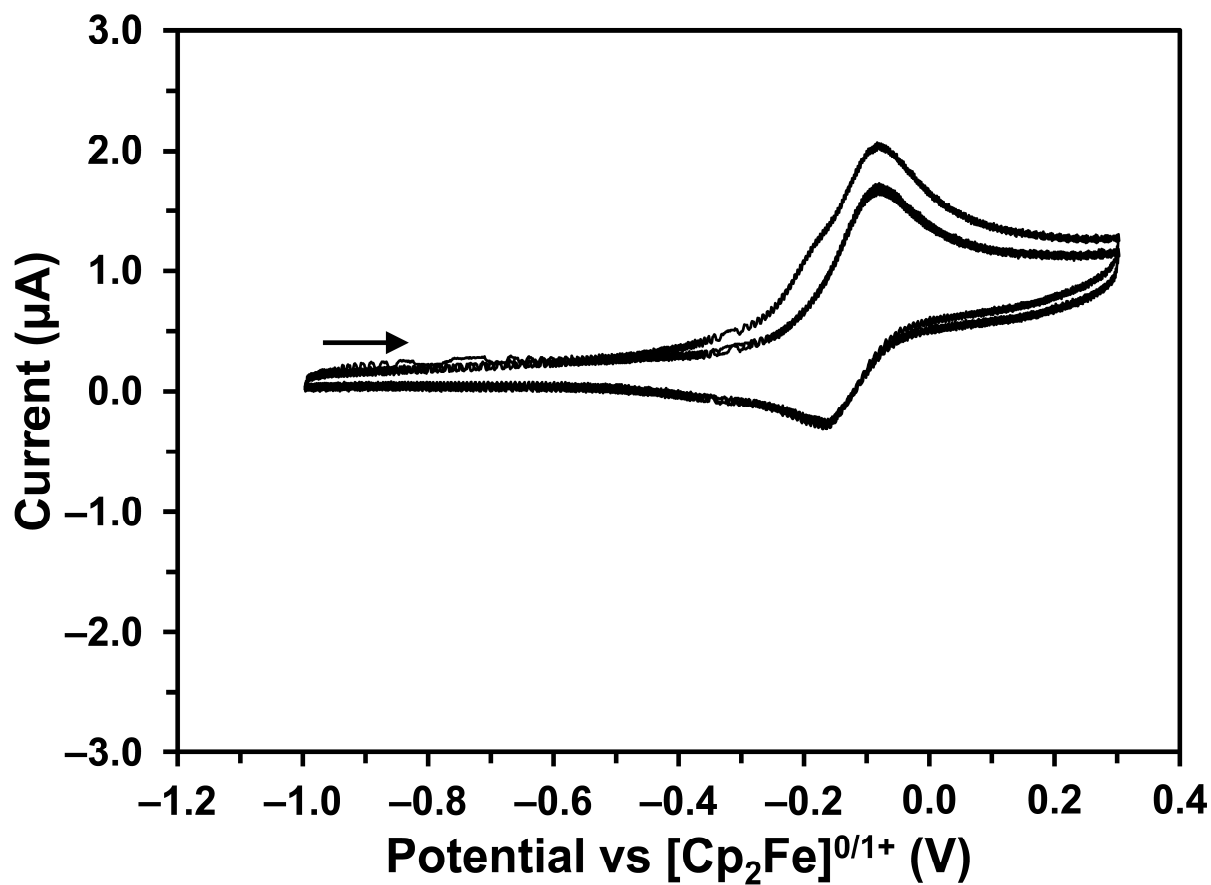


Figure S22. Cyclic voltammograms recorded for a 0.5 mM solution of **1** in *o*-C₆H₄F₂



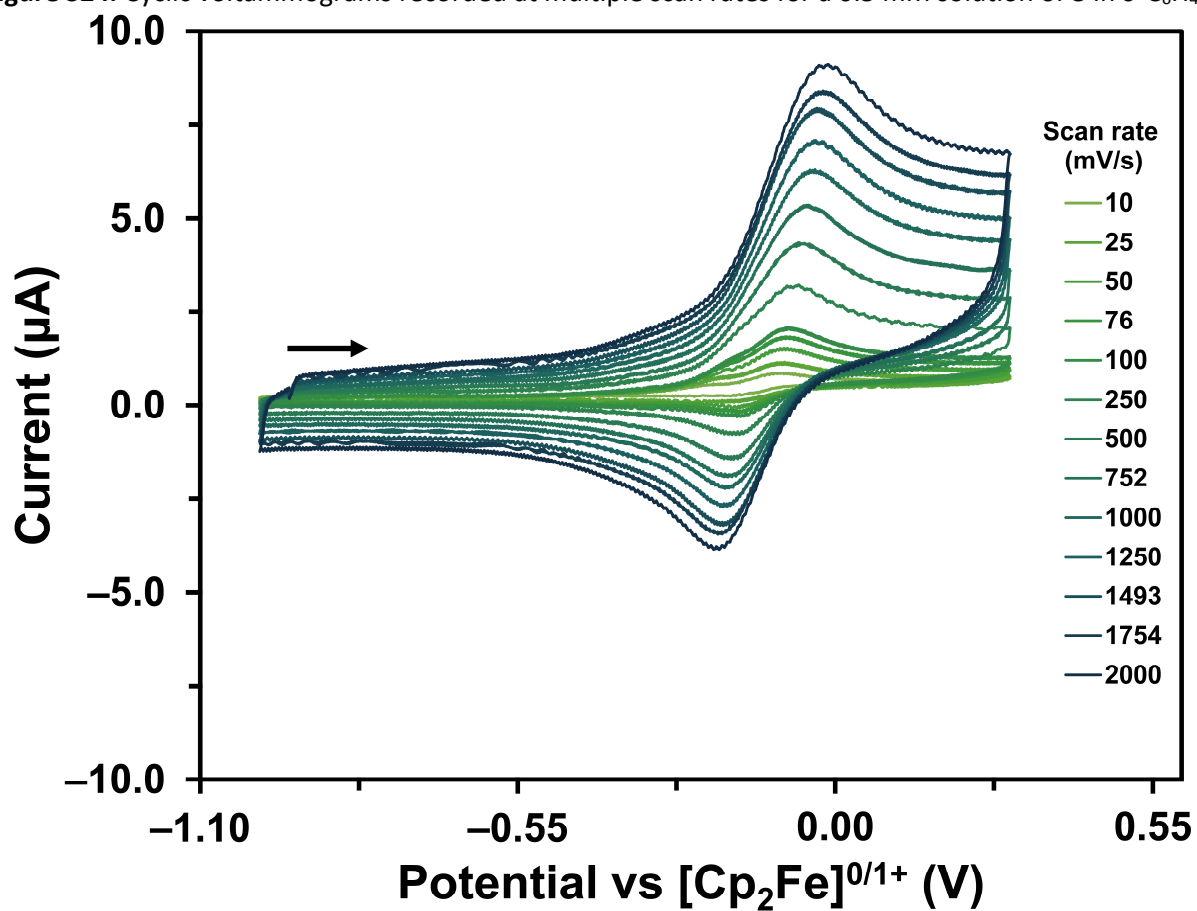
Details: Solution contained 0.1 M [ⁿBu₄N][PF₆] as supporting electrolyte. The arrows indicate the initial potentials and scanning directions. Scan rate was 100 mV/s for all voltammograms shown. Three complete cycles (7 segments) are displayed for each voltammogram. The first voltammogram highlights the reversible feature assigned to the one-electron oxidation of **1**. Upon extending the scan range almost to the positive edge of the accessible potential range (second voltammogram), an increase in current is observed close to the edge of the range, while the current of the reversible wave's reduction (at -0.183 V vs [Cp₂Fe]^{0/1+}) is diminished. In addition, a second reduction feature appears (at ca. -0.606 V vs [Cp₂Fe]^{0/1+}). Upon extending the range to the negative edge (the third voltammogram), two electrochemically irreversible (up to 1000 mV/s) reduction features are observed (at E° = -1.725 V and -2.389 V vs [Cp₂Fe]^{0/1+}) and give rise to similarly electrochemically irreversible oxidation features (at ca. -1.033 V and -0.677 V vs [Cp₂Fe]^{0/1+}). In addition, the cathodic wave of the originally reversible feature (at -0.184 V vs [Cp₂Fe]^{0/1}) is diminished in the second and third cycles.

Figure S23. Cyclic voltammogram recorded for a 0.5 mM solution of **3** in *o*-C₆H₄F₂



Notes: Solution contained 0.1 M [ⁿBu₄N][PF₆] supporting electrolyte. The arrow indicates the initial potential and scanning direction. The voltammogram displays the first three complete cycles (7 segments) and was recorded at 100 mV/s.

Figure S24. Cyclic voltammograms recorded at multiple scan rates for a 0.5 mM solution of **3** in *o*-C₆H₄F₂



Notes: Solution contained 0.1 M [^{*n*}Bu₄N][PF₆] supporting electrolyte. The arrow indicates the initial potential and scanning direction for all scans. Each voltammogram displays one complete cycle (3 segments).

Figure S25. Scan rate dependence of cyclic voltammograms' peak currents of a 0.5 mM solution of **3** in *o*-C₆H₄F₂ with 0.1 M [ⁿBu₄N][PF₆] supporting electrolyte

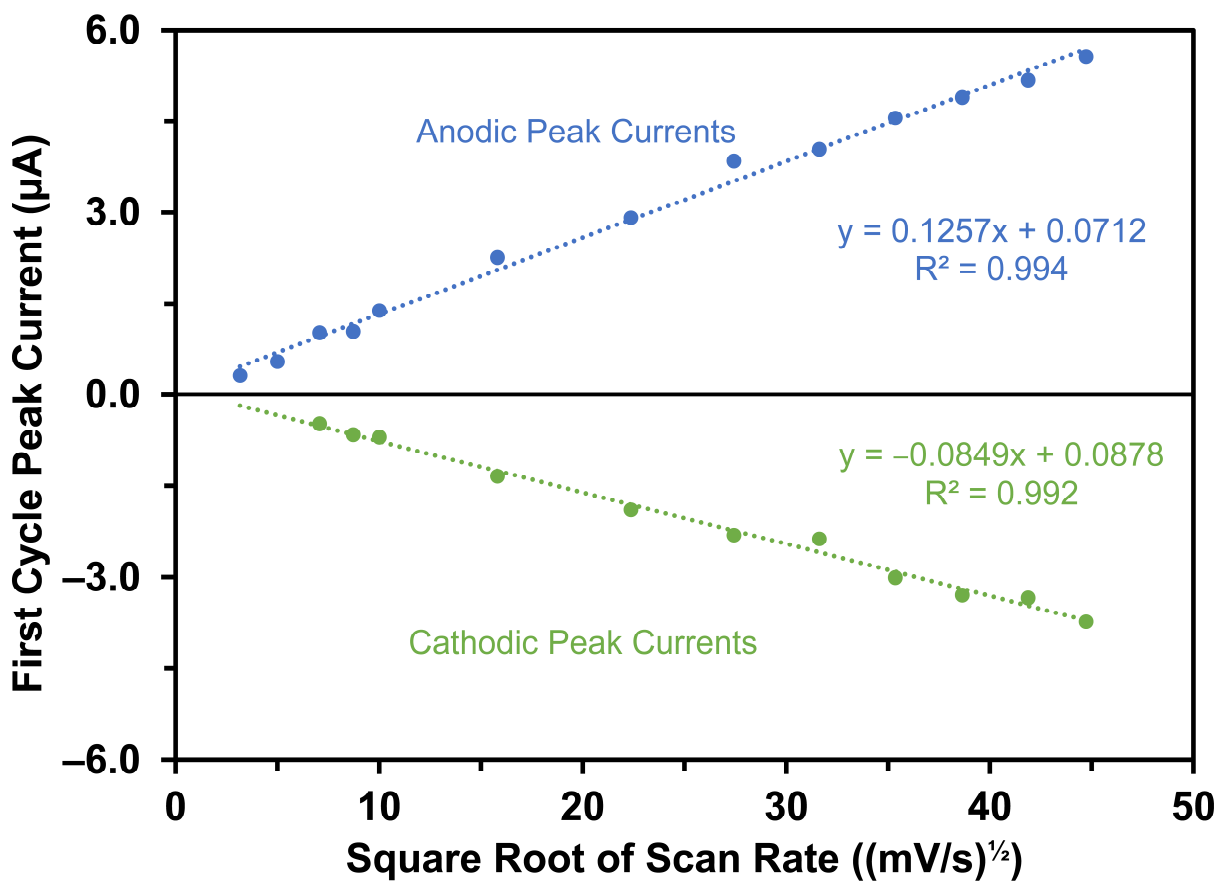
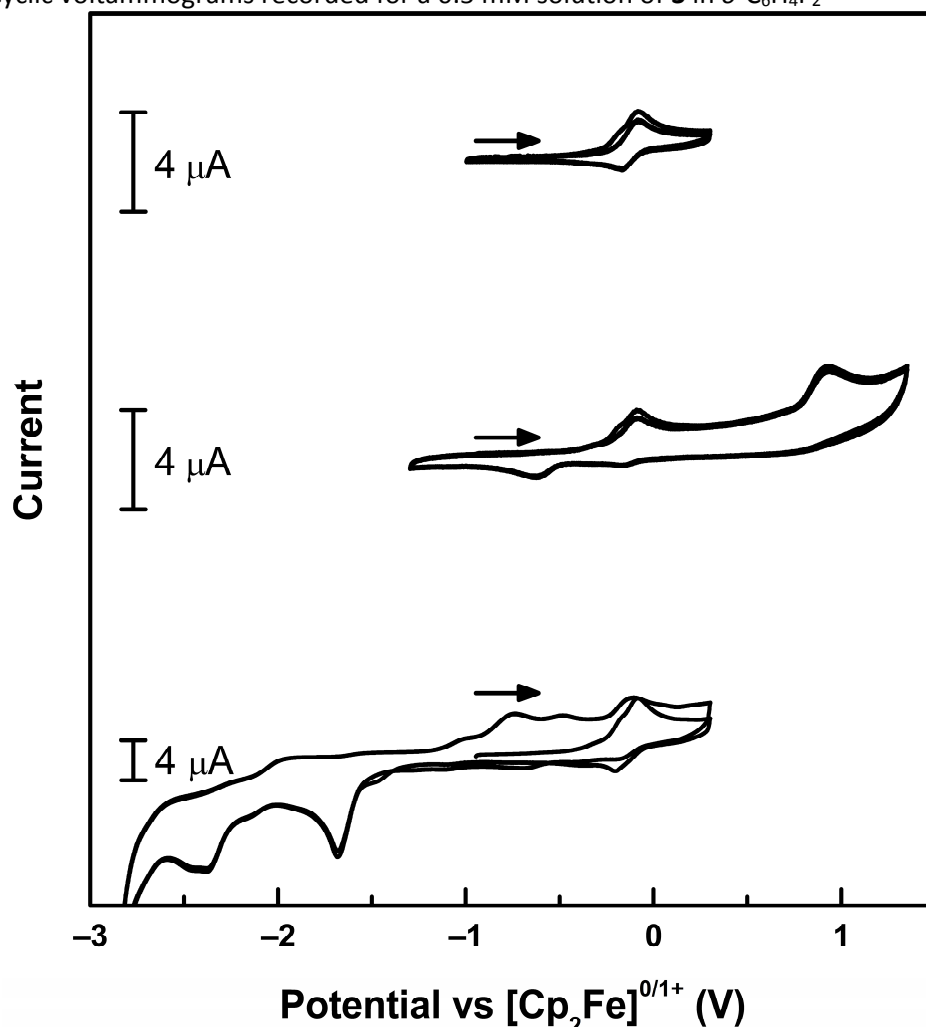
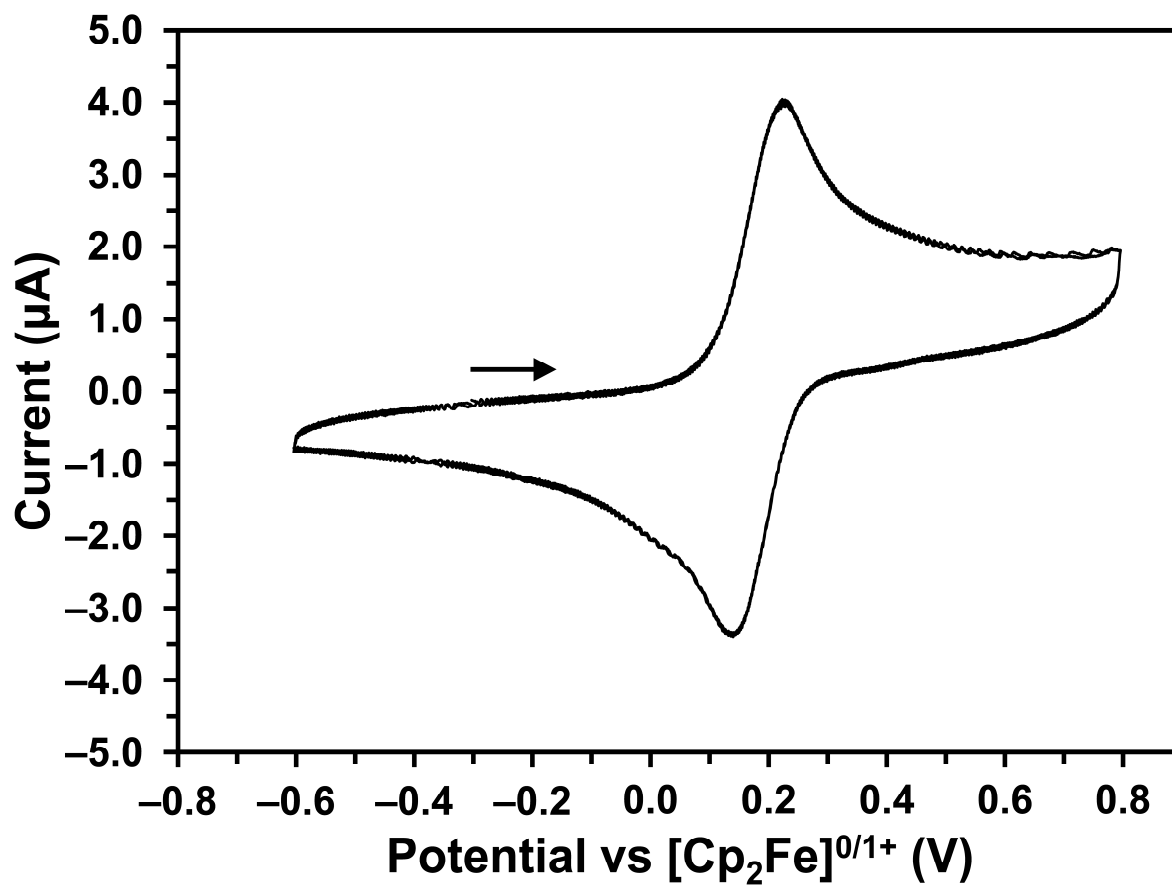


Figure S26. Cyclic voltammograms recorded for a 0.5 mM solution of **3** in *o*-C₆H₄F₂



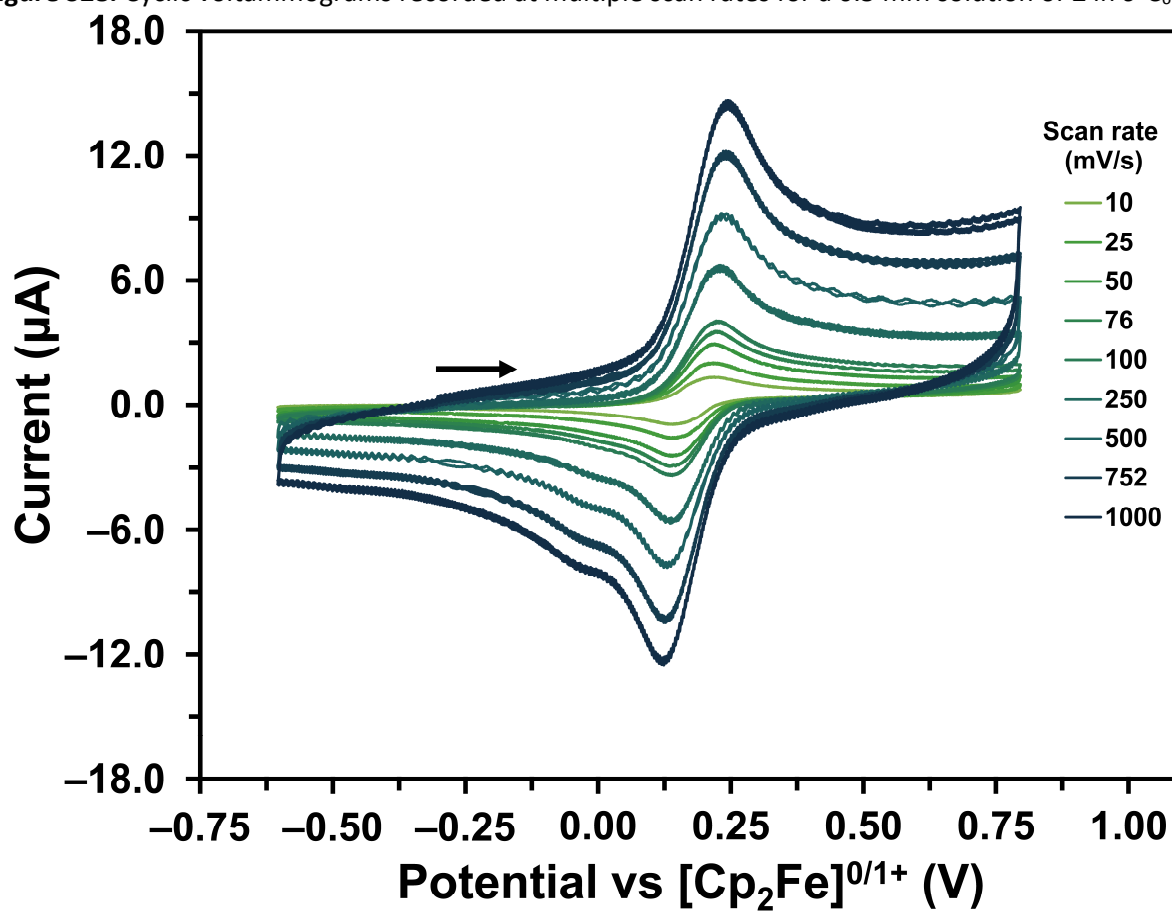
Details: Solution contained 0.1 M [ⁿBu₄N][PF₆] as supporting electrolyte. The arrows indicate the initial potentials and scanning directions. Scan rate was 100 mV/s for all voltammograms shown. Three complete cycles (7 segments) are displayed for each voltammogram. The first voltammogram displays the quasireversible (nearly irreversible at 100 mV/s) feature assigned to the one-electron oxidation of **3**. Upon extending the scan range almost to the positive edge of the accessible potential range (second voltammogram), a second oxidation event is observed (at ca. 0.928 V vs [Cp₂Fe]^{0/1+}). Upon sweeping back in the cathodic direction, the current of the quasireversible wave's reduction (at -0.160 V vs [Cp₂Fe]^{0/1+}) is significantly diminished while a second reduction feature appears at ca. -0.624 V vs [Cp₂Fe]^{0/1+}. Upon extending the range to the negative edge (the third voltammogram), two electrochemically irreversible (up to 2000 mV/s) reduction features are observed (at E° = -1.681 V and -2.371 V vs [Cp₂Fe]^{0/1+}) and give rise to three similarly electrochemically irreversible oxidation features (at ca. -1.006 V, -0.765 V, and -0.490 V vs [Cp₂Fe]^{0/1+}). In addition, the cathodic wave of the originally quasireversible feature (at ca. -0.200 V vs [Cp₂Fe]^{0/1}) is diminished in the second and third cycles.

Figure S27. Cyclic voltammogram recorded for a 0.5 mM solution of **2** in *o*-C₆H₄F₂



Notes: Solution contained 0.1 M [ⁿBu₄N][PF₆] supporting electrolyte. The arrow indicates the initial potential and scanning direction. The voltammogram displays the two complete cycles (5 segments) and was recorded at 100 mV/s. The peak-to-peak separation (ΔE_p) is 0.085 V and the i_{pa}/i_{pc} ratio is 1.15.

Figure S28. Cyclic voltammograms recorded at multiple scan rates for a 0.5 mM solution of **2** in *o*-C₆H₄F₂



Notes: Solution contained 0.1 M [^{*n*}Bu₄N][PF₆] supporting electrolyte. The arrow indicates the initial potential and scanning direction for all scans. Each voltammogram displays two complete cycles (5 segments).

Figure S29. Scan rate dependence of cyclic voltammograms' peak currents of a 0.5 mM solution of **2** in *o*-C₆H₄F₂ with 0.1 M [ⁿBu₄N][PF₆] supporting electrolyte

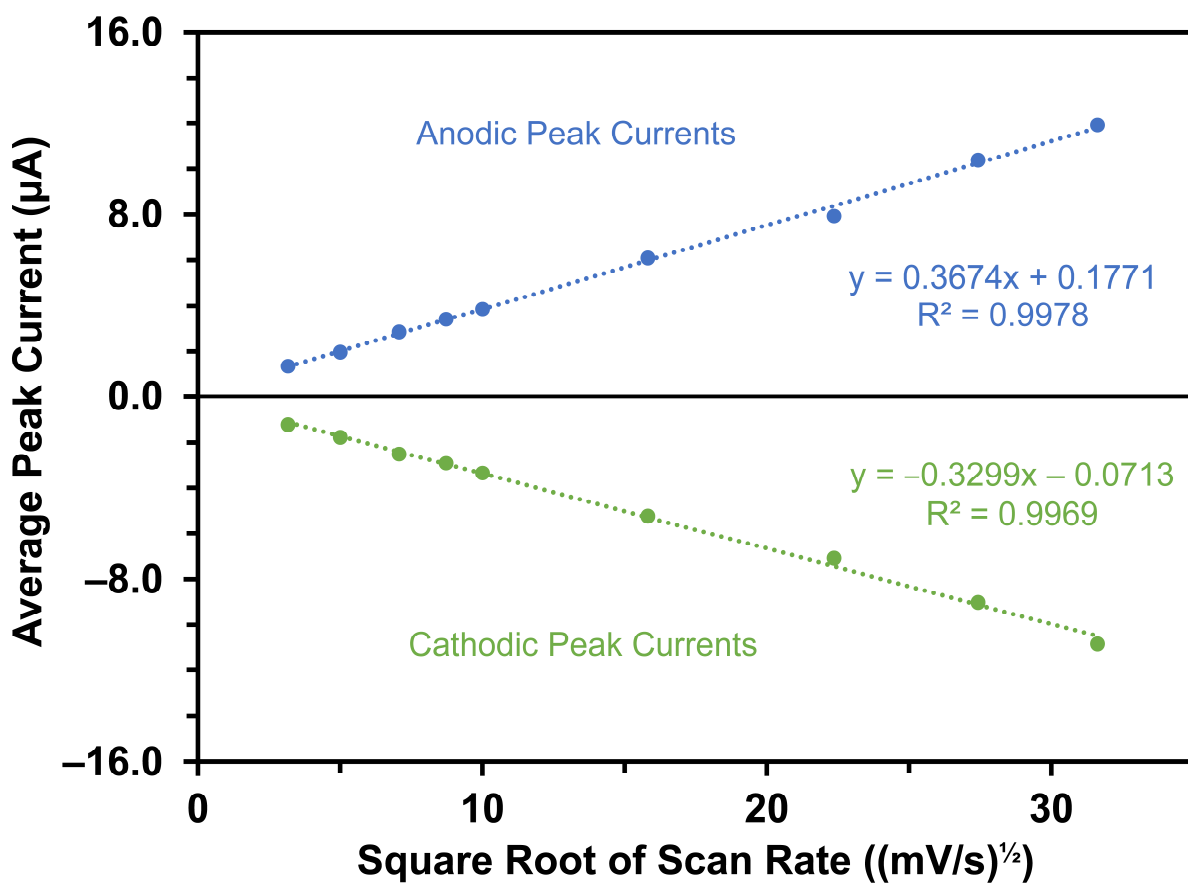
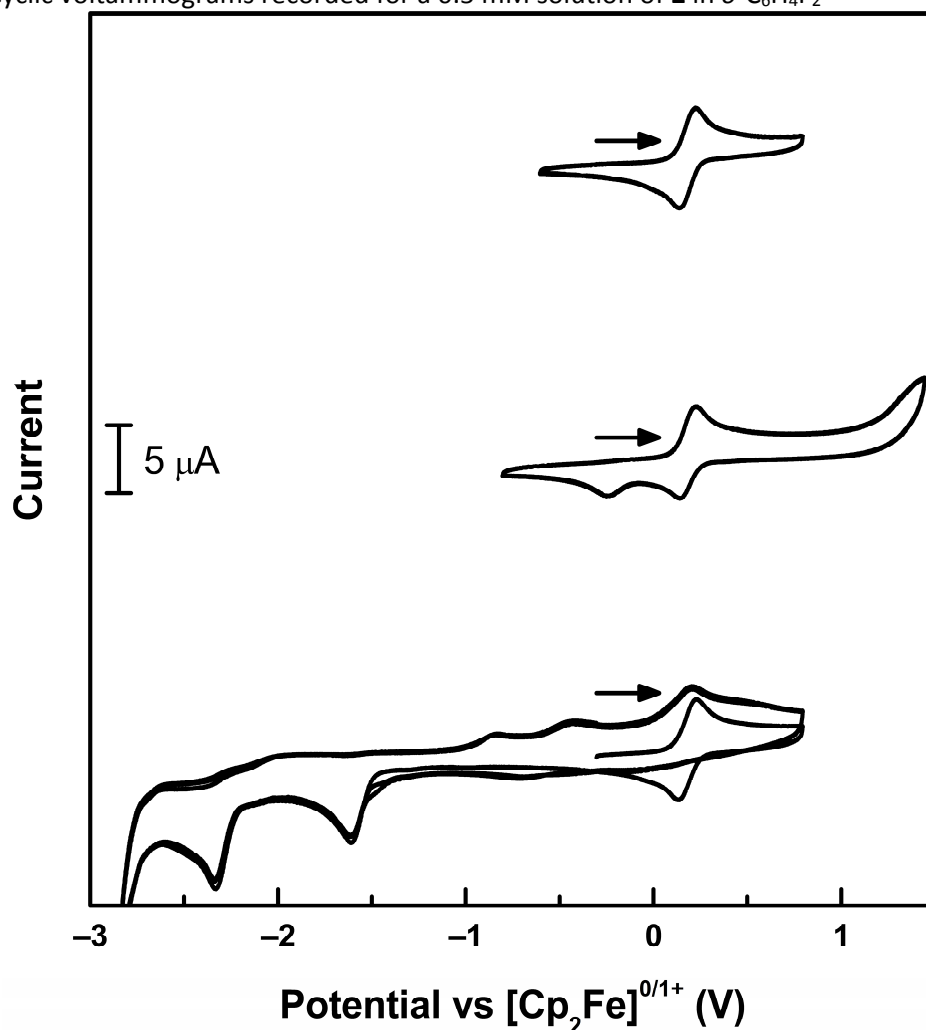
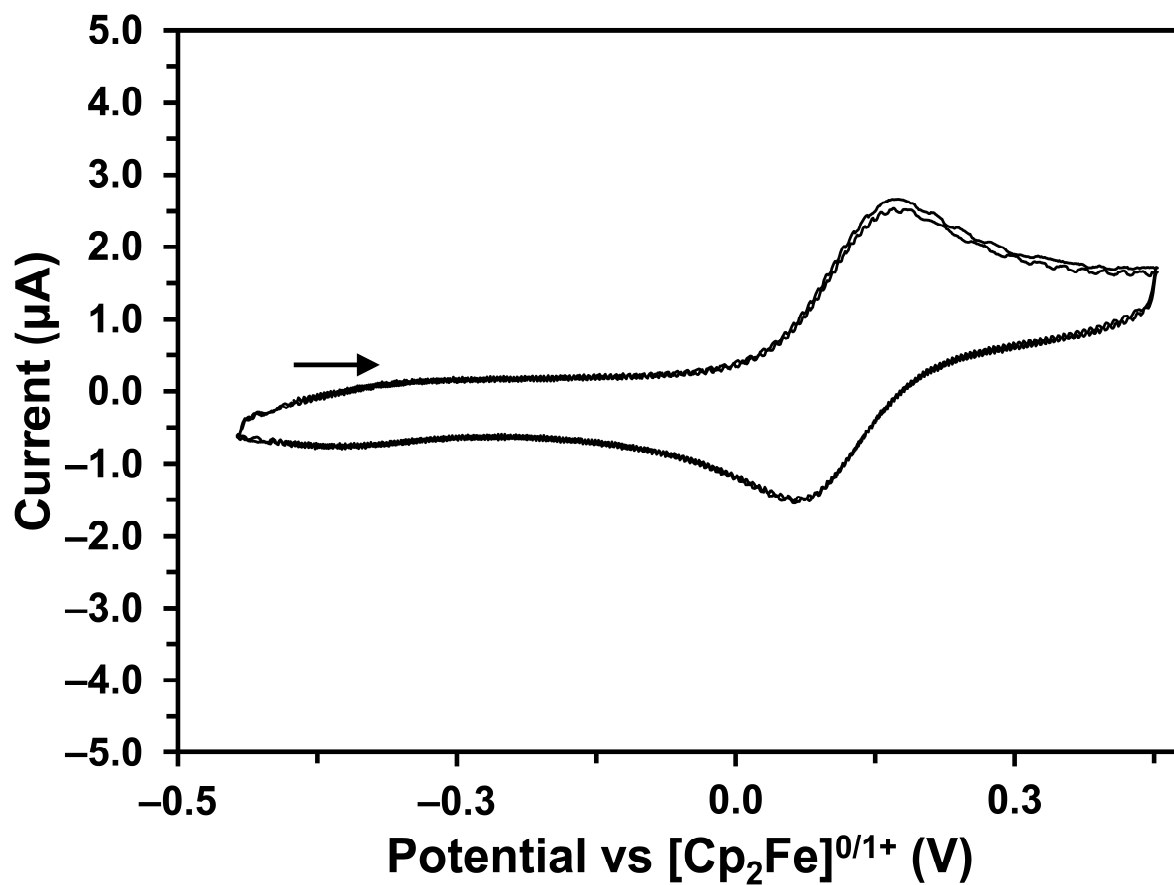


Figure S30. Cyclic voltammograms recorded for a 0.5 mM solution of **2** in *o*-C₆H₄F₂



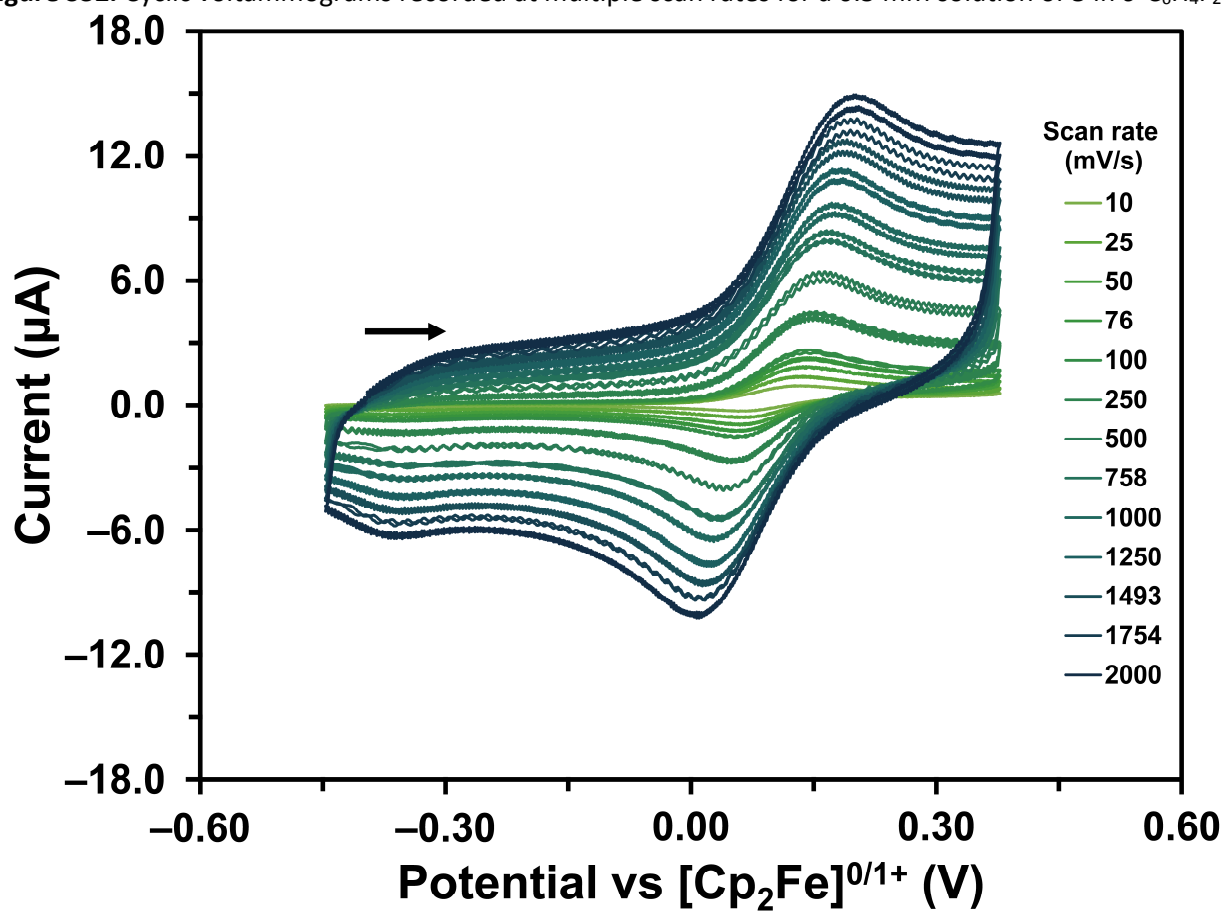
Details: Solution contained 0.1 M [ⁿBu₄N][PF₆] as supporting electrolyte. The arrows indicate the initial potentials and scanning directions. Scan rate was 100 mV/s for all voltammograms shown. Two complete cycles (5 segments) are displayed the top two voltammograms. Three complete cycles (7 segments) are displayed for the third voltammogram. The first voltammogram displays the feature assigned to the one-electron oxidation of **2**. Upon extending the scan range almost to the positive edge of the accessible potential range (second voltammogram), an increase in current is observed at the edge of the range. Upon sweeping back in the cathodic direction, the current of the original wave's reduction (at 0.142 V vs [Cp₂Fe]^{0/1+}) is significantly diminished while a second reduction feature appears at ca. -0.236 V vs [Cp₂Fe]^{0/1+}. Upon extending the range to the negative edge (the third voltammogram), two electrochemically irreversible (up to 1000 mV/s) reduction features are observed (at E° = -1.611 V and -2.335 V vs [Cp₂Fe]^{0/1+}) and give rise to two similarly electrochemically irreversible oxidation features (at ca. -0.853 V and -0.455 V vs [Cp₂Fe]^{0/1+}). In addition, the cathodic wave of the original one-electron feature is significantly diminished in the second and third cycles.

Figure S31. Cyclic voltammogram recorded for a 0.5 mM solution of **5** in *o*-C₆H₄F₂



Notes: Solution contained 0.1 M [ⁿBu₄N][PF₆] supporting electrolyte. The arrow indicates the initial potential and scanning direction. The voltammogram displays two complete cycles (5 segments) and was recorded at 100 mV/s. The peak-to-peak separation (ΔE_p) is 0.075 V and the *i*_{pa}/*i*_{pc} ratio is 1.40.

Figure S32. Cyclic voltammograms recorded at multiple scan rates for a 0.5 mM solution of **5** in *o*-C₆H₄F₂



Notes: Solution contained 0.1 M [^{*n*}Bu₄N][PF₆] supporting electrolyte. The arrow indicates the initial potential and scanning direction for all scans. Each voltammogram displays two complete cycles (5 segments).

Figure S33. Scan rate dependence of cyclic voltammograms' peak currents of a 0.5 mM solution of **5** in *o*-C₆H₄F₂ with 0.1 M [ⁿBu₄N][PF₆] supporting electrolyte

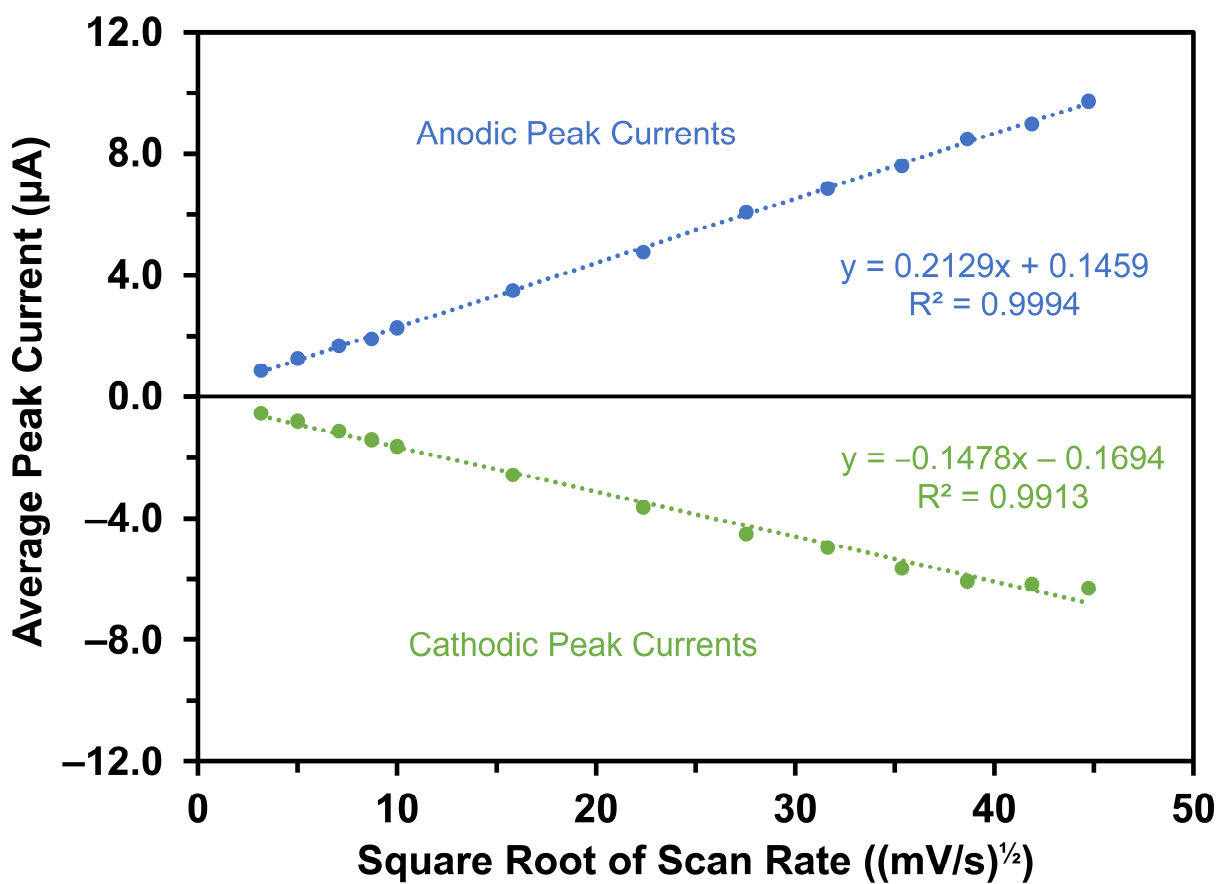
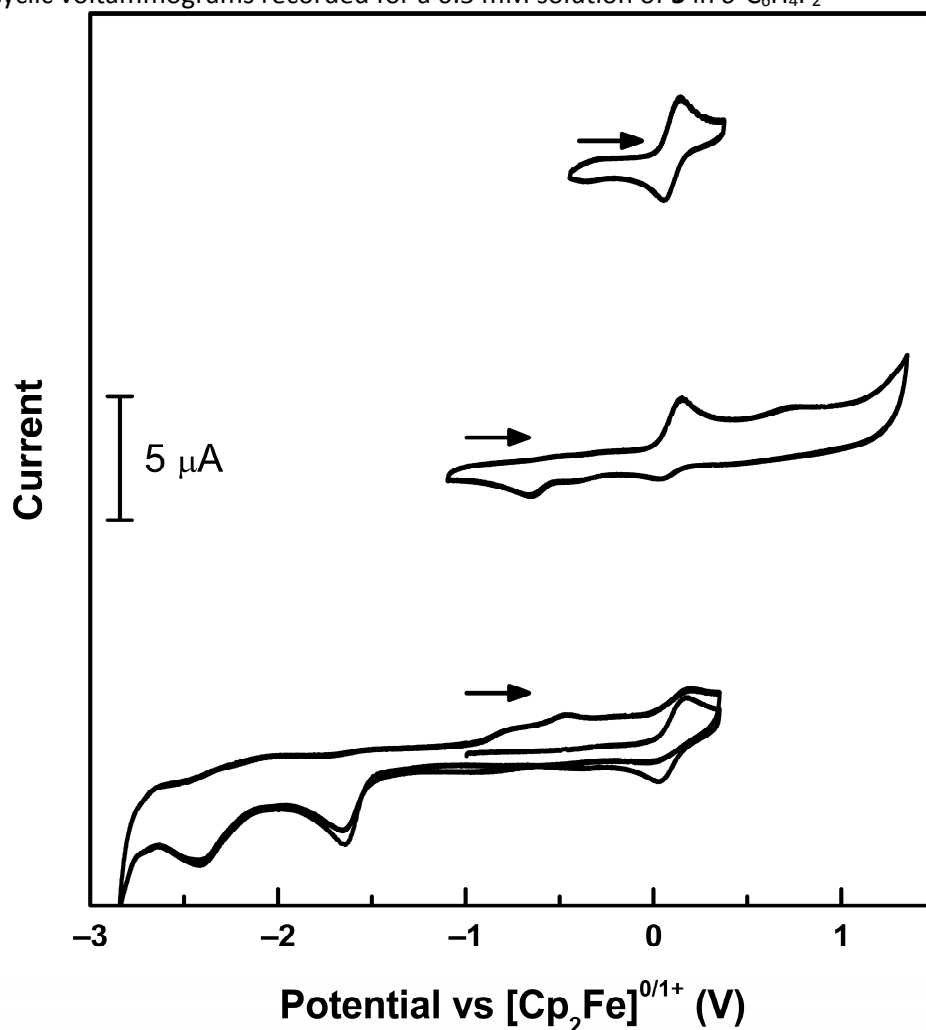
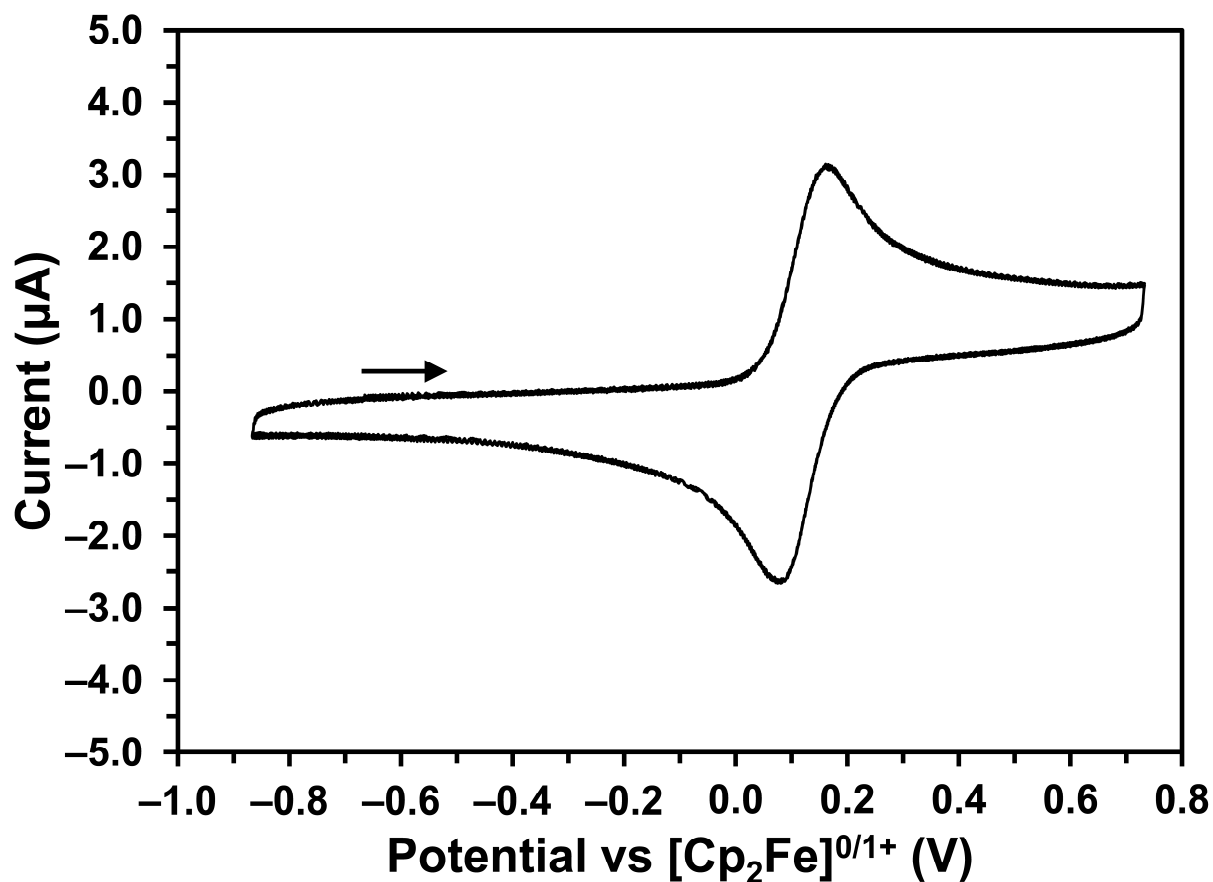


Figure S34. Cyclic voltammograms recorded for a 0.5 mM solution of **5** in *o*-C₆H₄F₂



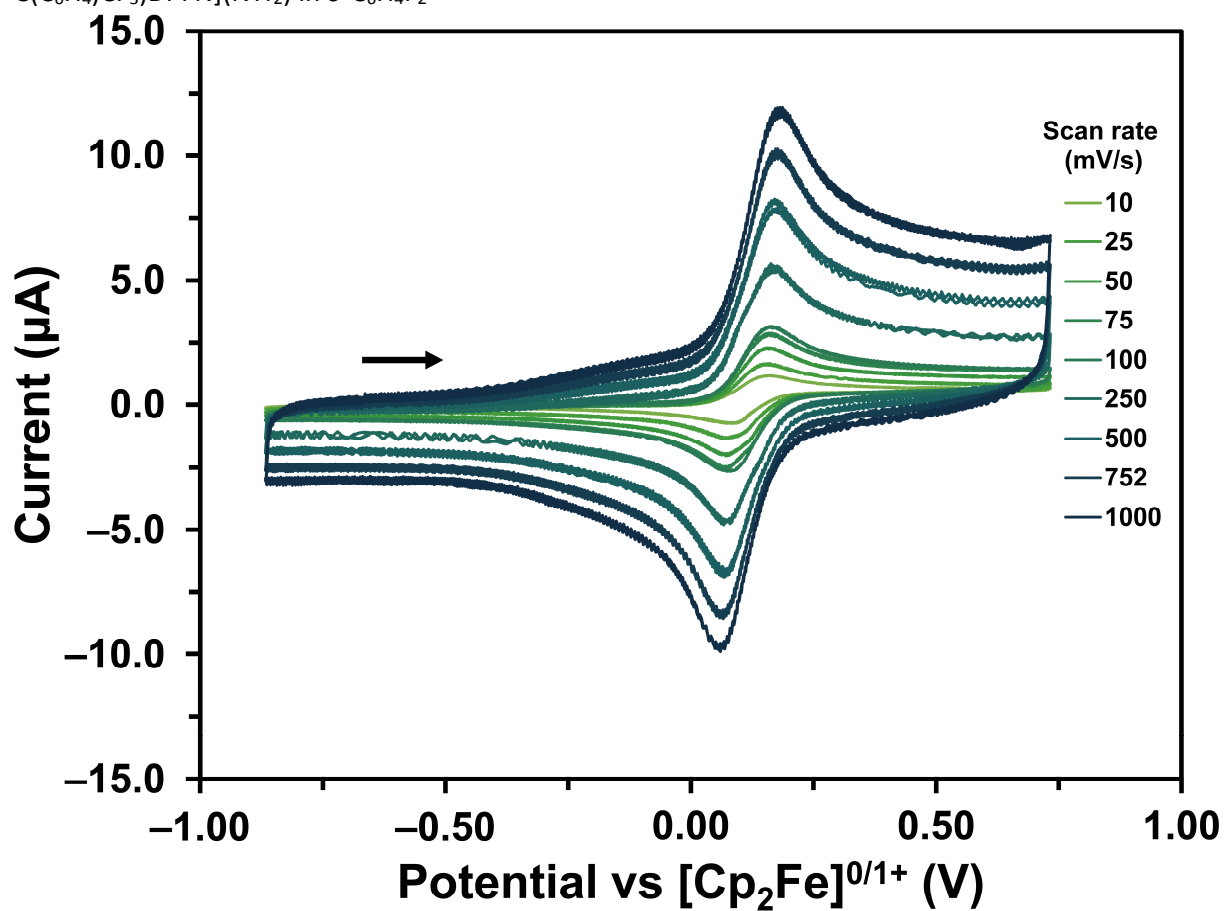
Details: Solution contained 0.1 M [ⁿBu₄N][PF₆] as supporting electrolyte. The arrows indicate the initial potentials and scanning directions. Scan rate was 100 mV/s for all voltammograms shown. Two complete cycles (5 segments) are displayed for the top two voltammograms while three complete cycles (7 segments) are displayed for the third voltammogram. The first voltammogram displays the feature assigned to the one-electron oxidation of **5**. Upon extending the scan range almost to the positive edge of the accessible potential range (second voltammogram), a broad second oxidation event is observed (at ca. 0.743 V vs [Cp₂Fe]^{0/1+}). Upon sweeping back in the cathodic direction, the current of the original wave's reduction event (at 0.033 V vs [Cp₂Fe]^{0/1+}) is partially diminished while a second reduction feature appears at ca. -0.652 V vs [Cp₂Fe]^{0/1+}. Upon extending the range to the negative edge (the third voltammogram), two electrochemically irreversible (up to 2000 mV/s) reduction features are observed (at E° = -1.646 V and -2.408 V vs [Cp₂Fe]^{0/1+}) and give rise to two similarly electrochemically irreversible oxidation features (at ca. -0.763 V and -0.473 V vs [Cp₂Fe]^{0/1+}). In addition, the cathodic wave of the original one-electron feature is diminished in the second and third cycles.

Figure S35. Cyclic voltammogram recorded for a 0.5 mM solution of $[\text{Cu}_2(\mu-\eta^1:\eta^1-\text{C}\equiv\text{C}(\text{C}_6\text{H}_4)\text{CF}_3)\text{DPPFN}](\text{NTf}_2)$ in $o\text{-C}_6\text{H}_4\text{F}_2$



Notes: Solution contained 0.1 M $[\text{nBu}_4\text{N}][\text{PF}_6]$ supporting electrolyte. The arrow indicates the initial potential and scanning direction. The voltammogram displays two complete cycles (5 segments) and was recorded at 100 mV/s. The peak-to-peak separation (ΔE_p) is 0.079 V and the i_{pa}/i_{pc} ratio is 1.02.

Figure S36. Cyclic voltammograms recorded at multiple scan rates for a 0.5 mM solution of $[\text{Cu}_2(\mu-\eta^1:\eta^1\text{-C}\equiv\text{C}(\text{C}_6\text{H}_4)\text{CF}_3)\text{DPFN}](\text{NTf}_2)$ in $o\text{-C}_6\text{H}_4\text{F}_2$



Notes: Solution contained 0.1 M $[\text{nBu}_4\text{N}][\text{PF}_6]$ supporting electrolyte. The arrow indicates the initial potential and scanning direction for all scans. Each voltammogram displays two complete cycles (5 segments).

Figure S37. Scan rate dependence of cyclic voltammograms' peak currents of a 0.5 mM solution of $[\text{Cu}_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-C}\equiv\text{C}(\text{C}_6\text{H}_4)\text{CF}_3)\text{DPPFN}](\text{NTf}_2)$ in $o\text{-C}_6\text{H}_4\text{F}_2$ with 0.1 M $[\text{nBu}_4\text{N}][\text{PF}_6]$ supporting electrolyte

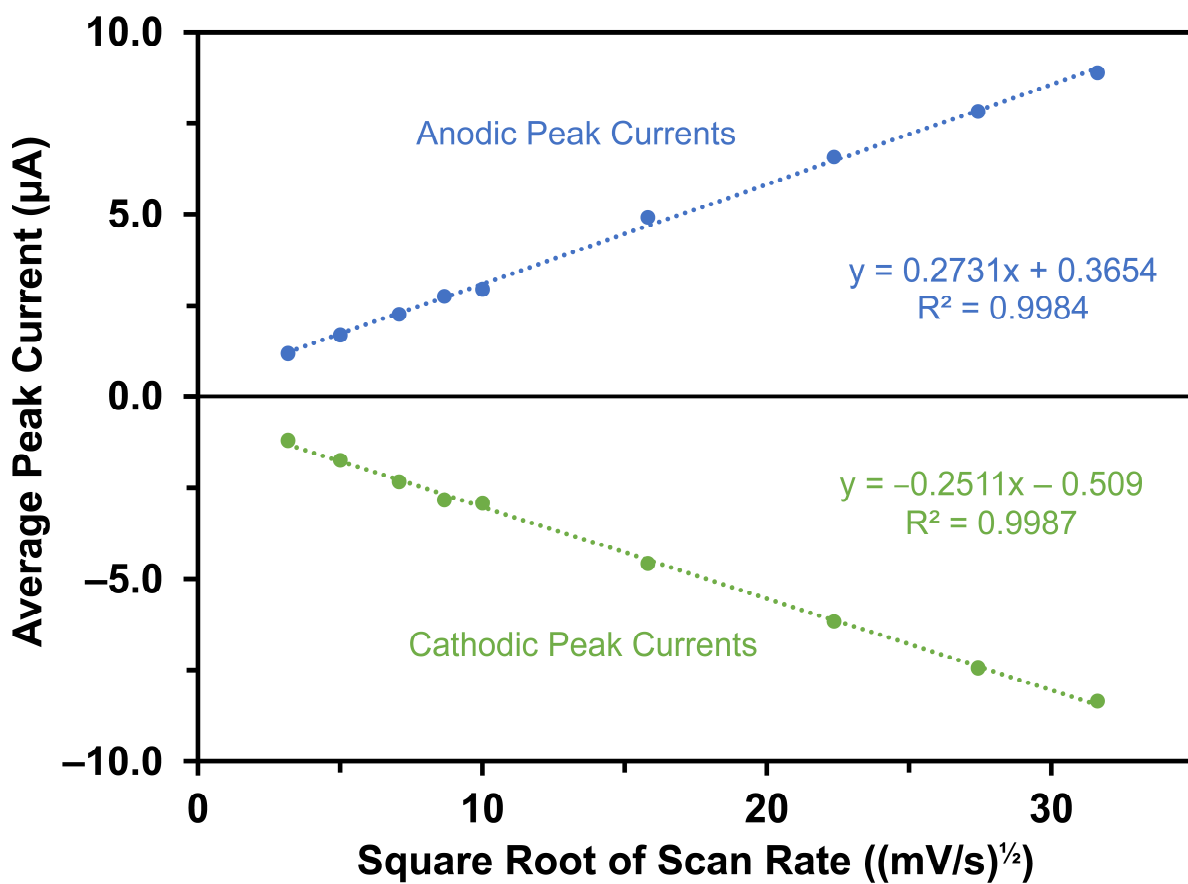
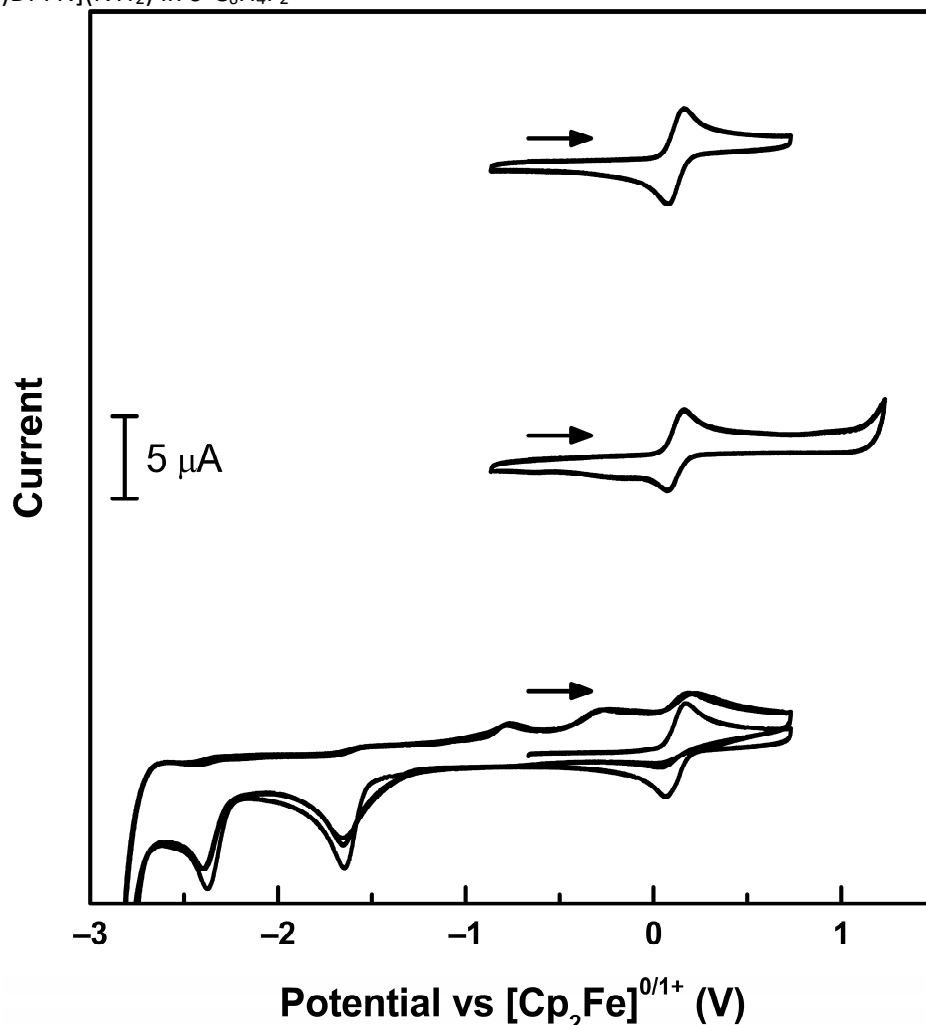


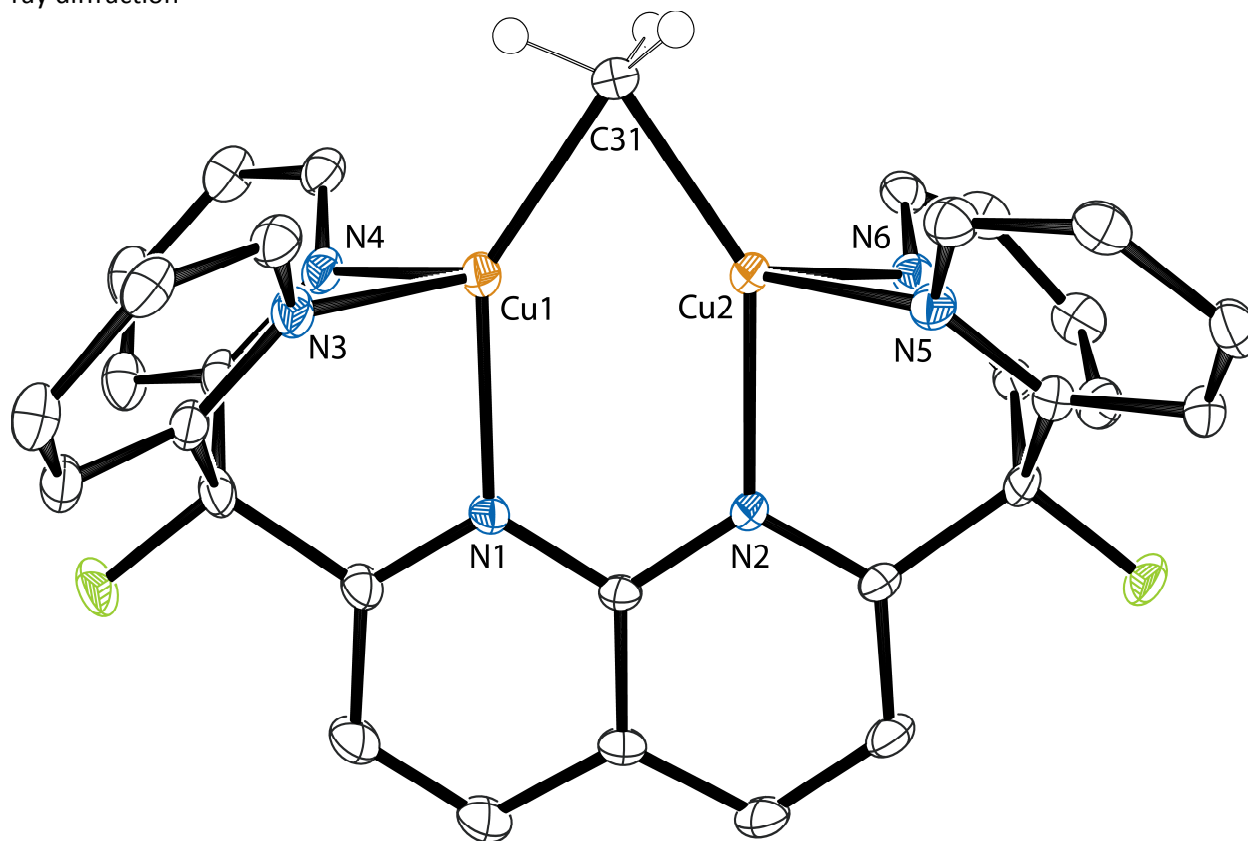
Figure S38. Cyclic voltammograms recorded for a 0.5 mM solution of $[\text{Cu}_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-C}\equiv\text{C}(\text{C}_6\text{H}_4)\text{CF}_3)\text{DPFN}](\text{NTf}_2)$ in $o\text{-C}_6\text{H}_4\text{F}_2$



Details: Solution contained 0.1 M $[\text{nBu}_4\text{N}][\text{PF}_6]$ as supporting electrolyte. The arrows indicate the initial potentials and scanning directions. Scan rate was 100 mV/s for all voltammograms shown. Two complete cycles (5 segments) are displayed for the top two voltammograms while three complete cycles (7 segments) are displayed for the third voltammogram. The first voltammogram displays the reversible feature assigned to the one-electron oxidation of $[\text{Cu}_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-C}\equiv\text{C}(\text{C}_6\text{H}_4)\text{CF}_3)\text{DPFN}](\text{NTf}_2)$. Upon extending the scan range almost to the positive edge of the accessible potential range (second voltammogram), a small second oxidation event is observed (at ca. 0.944 V vs $[\text{Cp}_2\text{Fe}]^{0/1+}$). Upon sweeping back in the cathodic direction, the current of the reversible wave's reduction event (at 0.075 V vs $[\text{Cp}_2\text{Fe}]^{0/1+}$) is partially diminished while a very small second reduction feature appears at ca. -0.218 V vs $[\text{Cp}_2\text{Fe}]^{0/1+}$. Upon extending the range to the negative edge (the third voltammogram), two electrochemically irreversible (up to 1000 mV/s) reduction features are observed (at $E^\circ = -1.647$ V and -2.390 V vs $[\text{Cp}_2\text{Fe}]^{0/1+}$) and give rise to two similarly electrochemically irreversible oxidation features (at ca. -0.787 V and -0.285 V vs $[\text{Cp}_2\text{Fe}]^{0/1+}$). In addition, the cathodic wave of the originally reversible feature is diminished in the second and third cycles.

3) Single-crystal x-ray diffraction crystal structure figures and data tables

Figure S39. Solid state structure of $[\text{Cu}_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-CH}_3)\text{DPFN}](\text{NTf}_2)$ (**1**) as determined by single-crystal X-ray diffraction

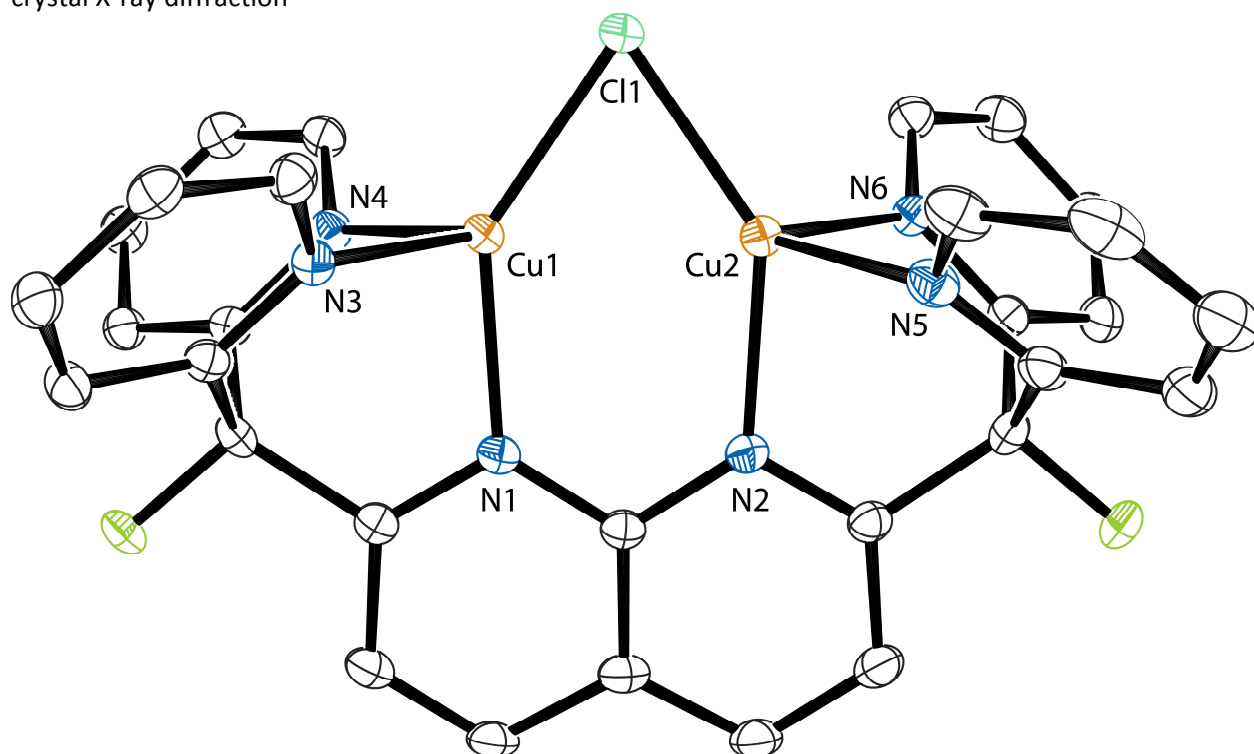


Details: Only one dicopper cation in the asymmetric unit is shown; the other cation, two NTf_2^- anions, and hydrogen atoms on the DFPN ligand are omitted for clarity. Displayed hydrogen atoms were located in the difference electron density map and refined isotopically. Thermal ellipsoids are set at the 50% probability level. Selected bond lengths [Å] and angles [°] for the cation shown: Cu1...Cu2: 2.3527(3), Cu1–N1: 2.125(2), Cu1–N3: 2.099(2), Cu1–N4: 2.078(2), Cu2–N2: 2.108(2), Cu2–N5: 2.086(2), Cu2–N6: 2.142(2), Cu1–C31: 2.075(2), Cu2–C31: 2.067(3), Cu1–C31–Cu2: 69.22(9), C31–Cu1–Cu2: 55.23(8), C31–Cu2–Cu1: 55.54(8), H31A–C31–H31B: 101(4), H31B–C31–H31C: 103(4), H31C–C31–H31A: 108(4).

Table S2. Crystal data and structure refinement for [Cu₂(μ-η¹:η¹-CH₃)DPFN](NTf₂) (**1**)

Empirical formula	C ₃₃ H ₂₃ Cu ₂ F ₈ N ₇ O ₄ S ₂	
Formula weight	924.78	
Temperature	100(2) K	
Wavelength	0.7749 Å	
Crystal system	Triclinic	
Space group	<i>P</i> $\bar{1}$	
Unit cell dimensions	a = 13.3097(7) Å	α = 76.428(2)°
	b = 14.4543(7) Å	β = 77.660(3)°
	c = 20.0509(10) Å	γ = 69.092(2)°
Volume	3466.8(3) Å ³	
Z	4	
Density (calculated)	1.772 Mg/m ³	
Absorption coefficient	1.822 mm ⁻¹	
F(000)	1856	
Crystal size	0.690 x 0.240 x 0.180 mm ³	
Theta range for data collection	2.040 to 37.331°	
Index ranges	-20 ≤ h ≤ 20, -22 ≤ k ≤ 22, -31 ≤ l ≤ 31	
Reflections collected	54384	
Independent reflections	27199 [R(int) = 0.0400]	
Completeness to theta = 35.000°	99.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7473 and 0.4597	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	27199 / 0 / 1070	
Goodness-of-fit on F ²	1.075	
Final R indices [I > 2σ(I)]	R1 = 0.0496, wR2 = 0.1076	
R indices (all data)	R1 = 0.0773, wR2 = 0.1209	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.252 and -1.165 e/Å ³	

Figure S40. Solid state structure of $[\text{Cu}_2(\mu\text{-Cl})\text{DPFN}](\text{NTf}_2) \cdot (\text{C}_4\text{H}_8\text{O})$ ($2 \cdot (\text{C}_4\text{H}_8\text{O})$) as determined by single-crystal X-ray diffraction

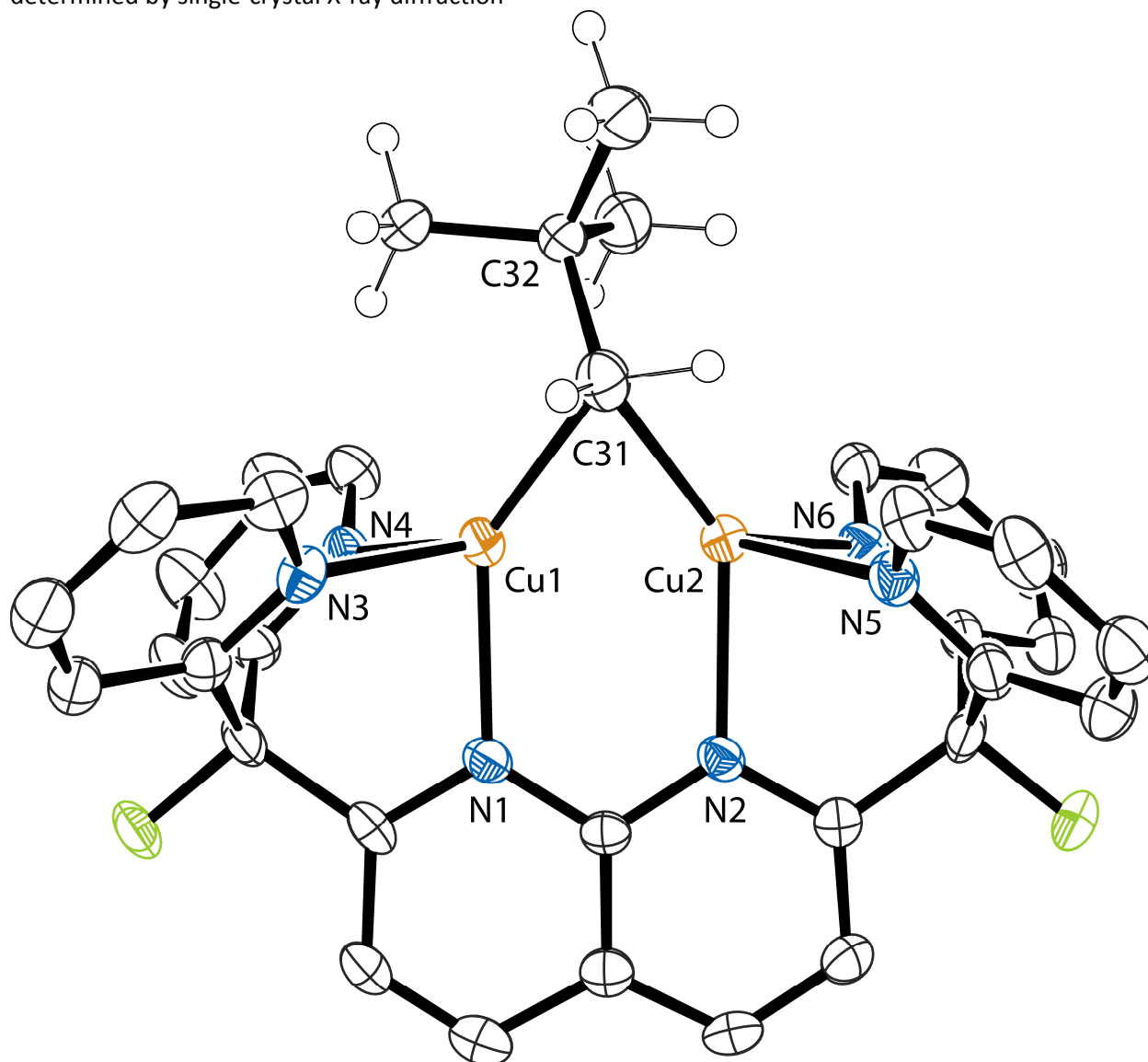


Details: The NTf_2^- anion, cocrystallizing molecule of THF, and hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at the 50% probability level. Selected bond lengths [Å] and angles [°]: Cu1...Cu2: 2.5704(5), Cu1–N1: 2.053(2), Cu1–N3: 2.083(2), Cu1–N4: 2.088(2), Cu2–N2: 2.051(2), Cu2–N5: 2.086(2), Cu2–N6: 2.093(2), Cu1–Cl1: 2.2438(6), Cu2–Cl1: 2.2469(6), Cu1–Cl1–Cu2: 69.83(2), Cl1–Cu1–Cu2: 55.14(2), Cl1–Cu2–Cu1: 55.03(2).

Table S3. Crystal data and structure refinement for [Cu₂(μ-Cl)DPFN](NTf₂)·(C₄H₈O) (**2**·(C₄H₈O))

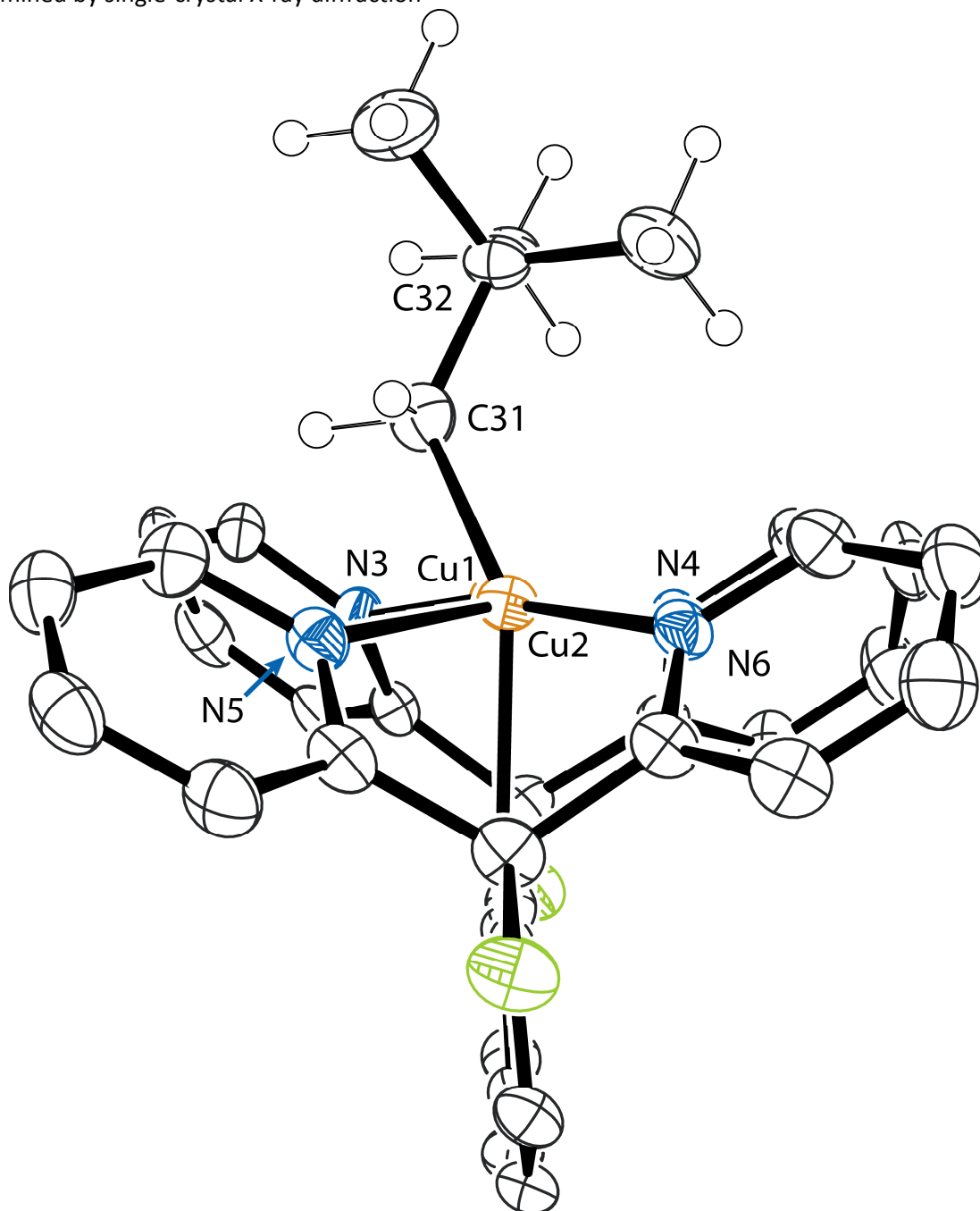
Empirical formula	C ₃₆ H ₂₈ ClCu ₂ F ₈ N ₇ O ₅ S ₂	
Formula weight	1017.30	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	<i>P</i> 2 ₁ / <i>c</i>	
Unit cell dimensions	<i>a</i> = 14.7626(5) Å	$\alpha = 90^\circ$
	<i>b</i> = 17.4755(5) Å	$\beta = 95.267(2)^\circ$
	<i>c</i> = 14.7269(5) Å	$\gamma = 90^\circ$
Volume	3783.3(2) Å ³	
<i>Z</i>	4	
Density (calculated)	1.786 Mg/m ³	
Absorption coefficient	1.400 mm ⁻¹	
<i>F</i> (000)	2048	
Crystal size	0.100 x 0.080 x 0.010 mm ³	
Theta range for data collection	1.385 to 29.129°	
Index ranges	-20 ≤ <i>h</i> ≤ 20, -23 ≤ <i>k</i> ≤ 21, -20 ≤ <i>l</i> ≤ 20	
Reflections collected	63161	
Independent reflections	10070 [<i>R</i> (int) = 0.0289]	
Completeness to theta = 29.000°	99.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6297 and 0.5658	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	10070 / 0 / 578	
Goodness-of-fit on <i>F</i> ²	1.053	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0375, <i>wR</i> 2 = 0.0970	
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0466, <i>wR</i> 2 = 0.1027	
Extinction coefficient	<i>n/a</i>	
Largest diff. peak and hole	1.096 and -1.115 e/Å ³	

Figure S41. Solid state structure of $[\text{Cu}_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-CH}_2\text{C}(\text{CH}_3)_3)\text{DPFN}](\text{NTf}_2)\cdot(\text{C}_4\text{H}_8\text{O})$ (**3** $\cdot(\text{C}_4\text{H}_8\text{O})$) as determined by single-crystal X-ray diffraction



Details: Only one dicopper cation in the asymmetric unit is shown; the three other cations, four NTf_2^- anions, four cocrystallizing THF molecules, and hydrogen atoms on DPFN are omitted for clarity. Displayed hydrogen atoms bound to C31 were located in the difference electron density map and refined isotopically. Thermal ellipsoids are set at the 50% probability level. Selected bond lengths [Å] and angles [°] for the cation shown: Cu1...Cu2: 2.374(1), Cu1–N1: 2.156(4), Cu1–N3: 2.141(4), Cu1–N4: 2.157(4), Cu2–N2: 2.163(4), Cu2–N5: 2.199(4), Cu2–N6: 2.054(4), Cu1–C31: 2.099(5), Cu2–C31: 2.112(5), C31–C32: 1.547(7), Cu1–C31–Cu2: 68.6(2), C31–Cu1–Cu2: 55.9(1), C31–Cu2–Cu1: 55.4(1), H31A–C31–C32: 112(3), H31B–C31–C32: 103(3), H31A–C31–H31B: 100(4).

Figure S42. Solid state structure of $[\text{Cu}_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-CH}_2\text{C}(\text{CH}_3)_3)\text{DPFN}](\text{NTf}_2)\cdot(\text{C}_4\text{H}_8\text{O})$ (**3** $\cdot(\text{C}_4\text{H}_8\text{O})$) as determined by single-crystal X-ray diffraction

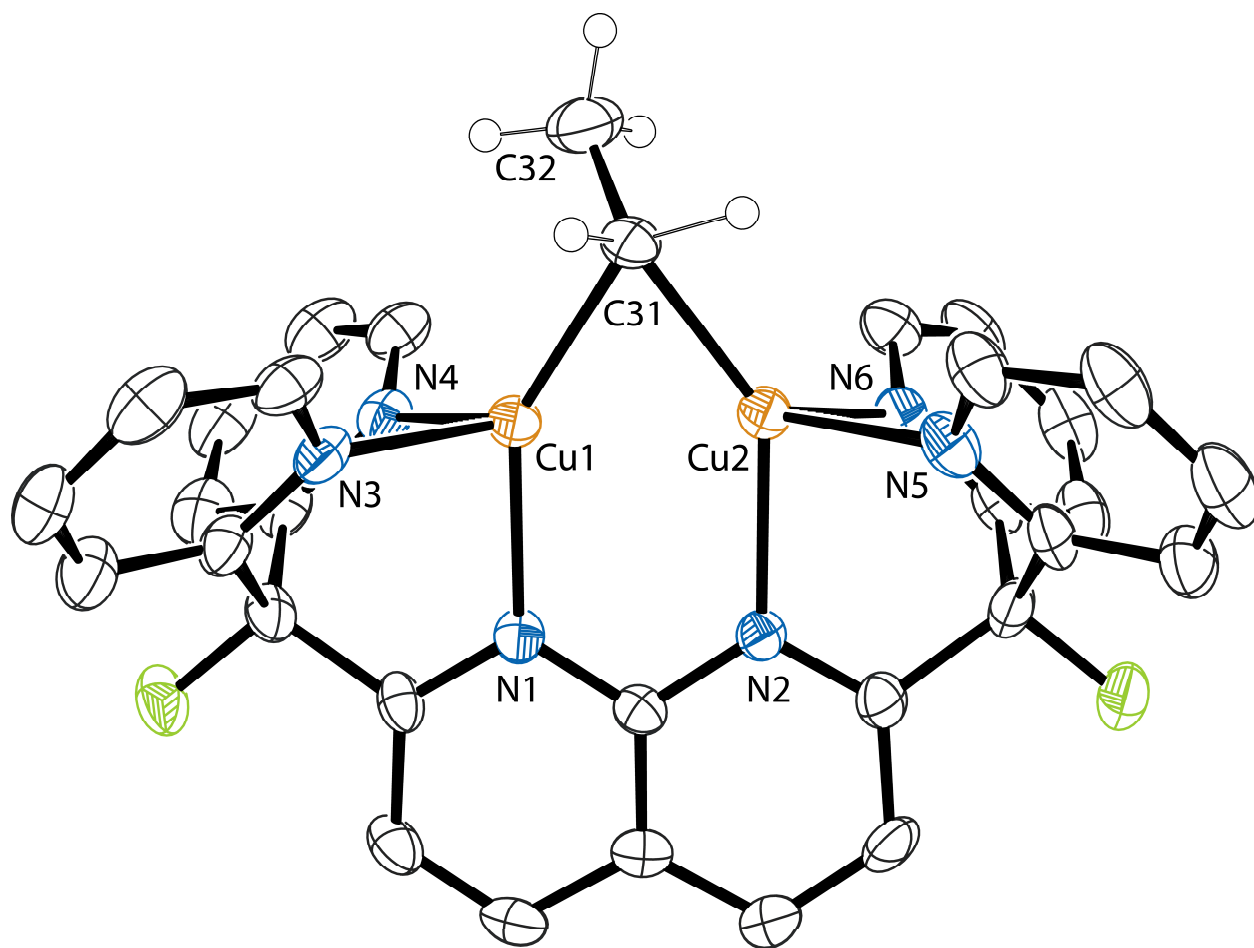


Details: Only one dicopper cation in the asymmetric unit is shown, the same as in Figure S41. The three other cations, four NTf_2^- anions, four cocrystallizing THF molecules, and hydrogen atoms on DPFN are omitted for clarity. Displayed hydrogen atoms bound to C31 were located in the difference electron density map and refined isotopically. Thermal ellipsoids are set at the 50% probability level. Selected angle [$^\circ$] for the cation shown: C32–C31–centroid between Cu1 and Cu2: 129.5.

Table S4. Crystal data and structure refinement for $[\text{Cu}_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-CH}_2\text{C}(\text{CH}_3)_3)\text{DPFN}](\text{NTf}_2)\cdot(\text{C}_4\text{H}_8\text{O})$ (**3**·($\text{C}_4\text{H}_8\text{O}$))

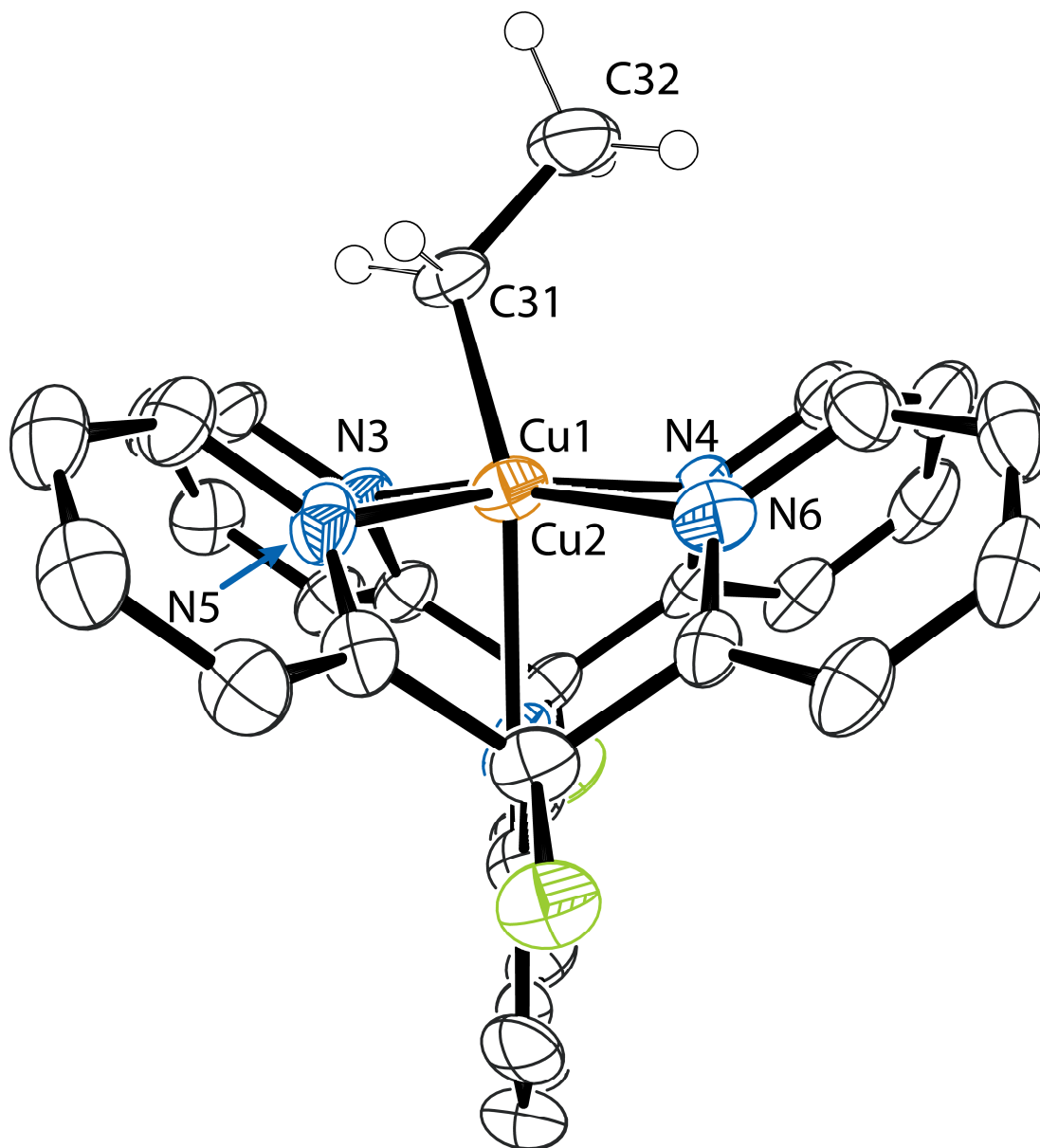
Empirical formula	$\text{C}_{41}\text{H}_{39}\text{Cu}_2\text{F}_8\text{N}_7\text{O}_5\text{S}_2$	
Formula weight	1052.99	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	$a = 15.8674(5)$ Å	$\alpha = 90^\circ$
	$b = 23.5913(8)$ Å	$\beta = 97.698(2)^\circ$
	$c = 45.9462(15)$ Å	$\gamma = 90^\circ$
Volume	$17044.2(10)$ Å ³	
Z	16	
Density (calculated)	1.641 Mg/m ³	
Absorption coefficient	1.186 mm ⁻¹	
F(000)	8576	
Crystal size	$0.050 \times 0.050 \times 0.030$ mm ³	
Theta range for data collection	0.972 to 26.373°	
Index ranges	$-19 \leq h \leq 19$, $-28 \leq k \leq 29$, $-57 \leq l \leq 57$	
Reflections collected	133840	
Independent reflections	34708 [R(int) = 0.0666]	
Completeness to theta = 26.000°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6745 and 0.6215	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	34708 / 12 / 2646	
Goodness-of-fit on F^2	1.040	
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0657$, $wR2 = 0.1705$	
R indices (all data)	$R1 = 0.1134$, $wR2 = 0.1982$	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.211 and -1.206 e/Å ³	

Figure S43. Solid state structure of $[\text{Cu}_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-CH}_2\text{CH}_3)\text{DPFN}](\text{NTf}_2) \cdot 1.5(\text{C}_4\text{H}_8\text{O}) \cdot n(\text{C}_4\text{H}_{10}\text{O})$ ($4 \cdot 1.5(\text{C}_4\text{H}_8\text{O}) \cdot n(\text{C}_4\text{H}_{10}\text{O})$) as determined by single-crystal X-ray diffraction



Details: Disordered NTf_2^- counterions, THF molecules of solvation, and hydrogen atoms on DPFN are omitted for clarity. Displayed hydrogen atoms bound to C31 were located in the difference electron density map and refined isotopically. Thermal ellipsoids are set at the 50% probability level. Selected bond lengths [Å] and angles [°]: Cu1...Cu2: 2.362(1), Cu1–N1: 2.077(5), Cu1–N3: 2.132(5), Cu1–N4: 2.122(4), Cu2–N2: 2.139(5), Cu2–N5: 2.149(4), Cu2–N6: 2.073(5), Cu1–C31: 2.082(6), Cu2–C31: 2.116(8), C31–C32: 1.528(9), Cu1–C31–Cu2: 68.5(2), C31–Cu1–Cu2: 56.4(2), C31–Cu2–Cu1: 55.1(2), H31A–C31–C32: 107(4), H31B–C31–C32: 106(4), H31A–C31–H31B: 103(6).

Figure S44. Solid state structure of $[\text{Cu}_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-CH}_2\text{CH}_3)\text{DPFN}](\text{NTf}_2) \cdot 1.5(\text{C}_4\text{H}_8\text{O}) \cdot n(\text{C}_4\text{H}_{10}\text{O})$ ($4 \cdot 1.5(\text{C}_4\text{H}_8\text{O}) \cdot n(\text{C}_4\text{H}_{10}\text{O})$) as determined by single-crystal X-ray diffraction

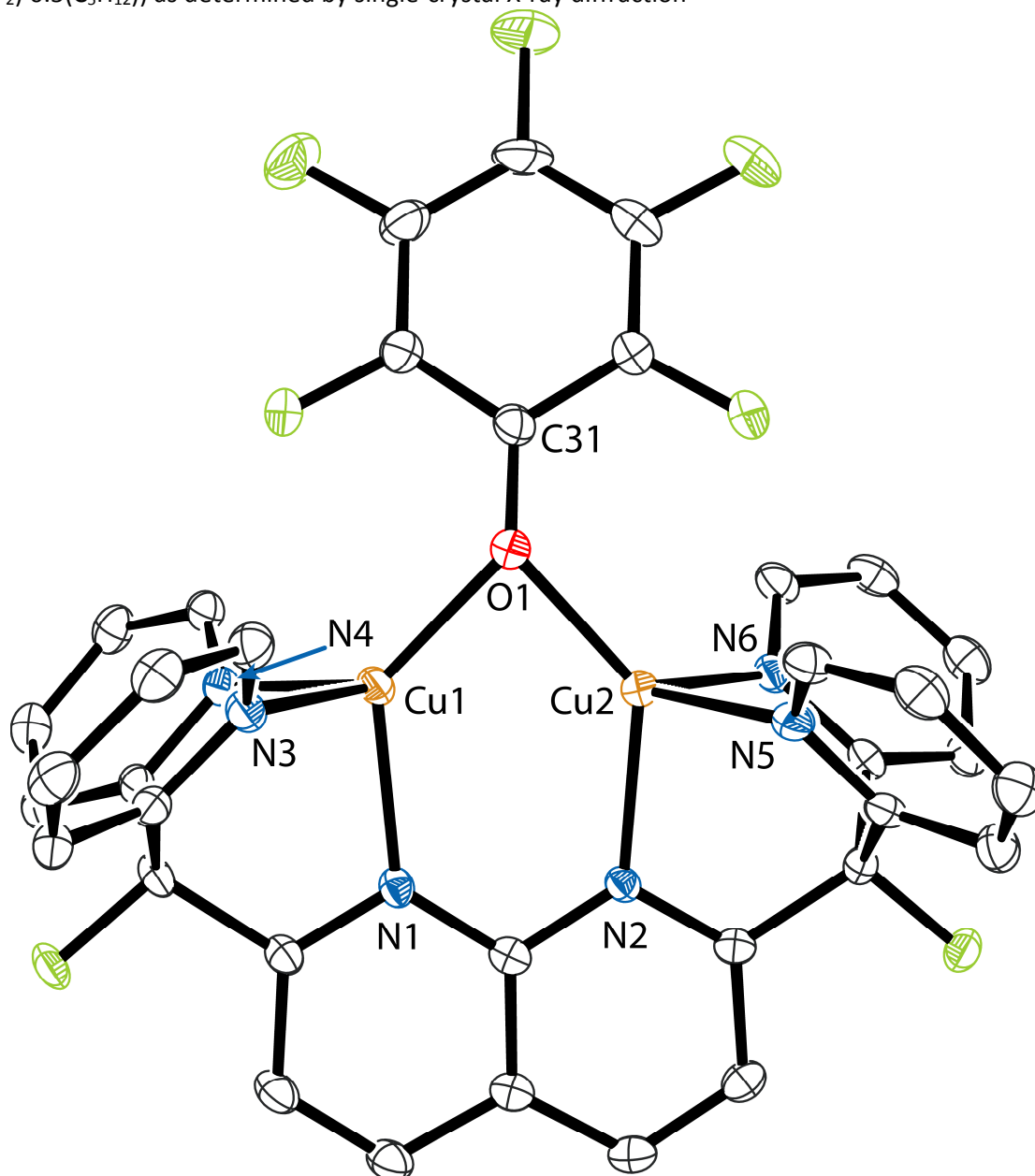


Details: As in S43, Disordered NTf_2^- counterions, THF molecules of solvation, and hydrogen atoms on DPFN are omitted for clarity. Displayed hydrogen atoms bound to C31 were located in the difference electron density map and refined isotopically. Thermal ellipsoids are set at the 50% probability level. Selected angle [°]: C32–C31–centroid between Cu1 and Cu2: 122.1 .

Table S5. Crystal data and structure refinement for[[Cu₂(μ-η¹:η¹-CH₂CH₃)DPPN](NTf₂)·1.5(C₄H₈O)·n(C₄H₁₀O) (**4**·1.5(C₄H₈O)·n(C₄H₁₀O))

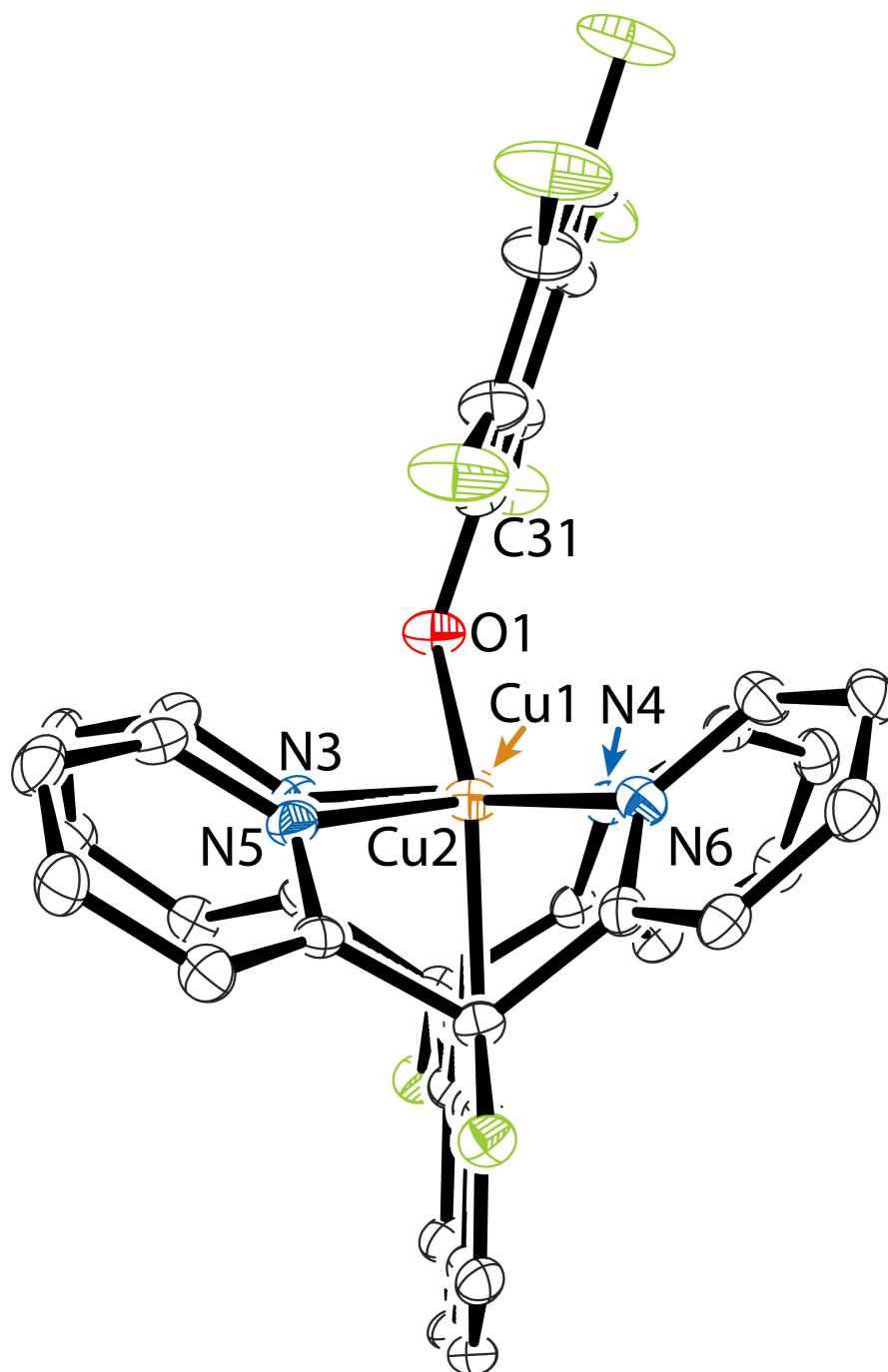
Empirical formula	C ₄₀ H ₃₇ Cu ₂ F ₈ N ₇ O _{5.50} S ₂	
Formula weight	1046.96	
Temperature	100(2) K	
Wavelength	0.7749 Å	
Crystal system	Triclinic	
Space group	<i>P</i> $\bar{1}$	
Unit cell dimensions	<i>a</i> = 13.0730(5) Å	α = 102.094(2)°
	<i>b</i> = 13.8279(6) Å	β = 111.002(2)°
	<i>c</i> = 14.0725(6) Å	γ = 94.763(2)°
Volume	2287.10(17) Å ³	
<i>Z</i>	2	
Density (calculated)	1.520 Mg/m ³	
Absorption coefficient	1.395 mm ⁻¹	
<i>F</i> (000)	1064	
Crystal size	0.170 x 0.140 x 0.030 mm ³	
Theta range for data collection	2.083 to 28.633°	
Index ranges	-16 ≤ <i>h</i> ≤ 16, -17 ≤ <i>k</i> ≤ 17, -17 ≤ <i>l</i> ≤ 17	
Reflections collected	26637	
Independent reflections	8525 [<i>R</i> (int) = 0.0771]	
Completeness to theta = 28.500°	94.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6751 and 0.4913	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	8525 / 16 / 694	
Goodness-of-fit on <i>F</i> ²	1.113	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0716, <i>wR</i> 2 = 0.1828	
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1150, <i>wR</i> 2 = 0.2076	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.468 and -0.896 e/Å ³	

Figure S45. Solid state structure of $[\text{Cu}_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-OC}_6\text{F}_5)\text{DPFN}](\text{NTf}_2) \cdot 2(o\text{-C}_6\text{H}_4\text{F}_2) \cdot 0.5(\text{C}_5\text{H}_{12})$ (**5**·2(*o*-C₆H₄F₂)·0.5(C₅H₁₂)) as determined by single-crystal X-ray diffraction



Details: The NTf_2^- anion, two cocrystallizing *ortho*-difluorobenzene molecules, one-half of a cocrystallizing pentane molecule, and hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at the 50% probability level. Selected bond lengths [Å] and angles [°]: Cu1···Cu2: 2.675(1), Cu1–N1: 2.071(3), Cu1–N3: 2.068(3), Cu1–N4: 2.054(3), Cu2–N2: 2.034(3), Cu2–N5: 2.103(3), Cu2–N6: 2.045(3), Cu1–O1: 2.002(2), Cu2–O2: 1.989(3), Cu1–O1–Cu2: 84.18(9), O1–Cu1–Cu2: 47.69(7), O1–Cu2–Cu1: 48.13(7).

Figure S46. Solid state structure of $[\text{Cu}_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-OC}_6\text{F}_5)\text{DPFN}](\text{NTf}_2)_2 \cdot 2(o\text{-C}_6\text{H}_4\text{F}_2) \cdot 0.5(\text{C}_5\text{H}_{12})$ (**5**·2(*o*-C₆H₄F₂)·0.5(C₅H₁₂)) as determined by single-crystal X-ray diffraction

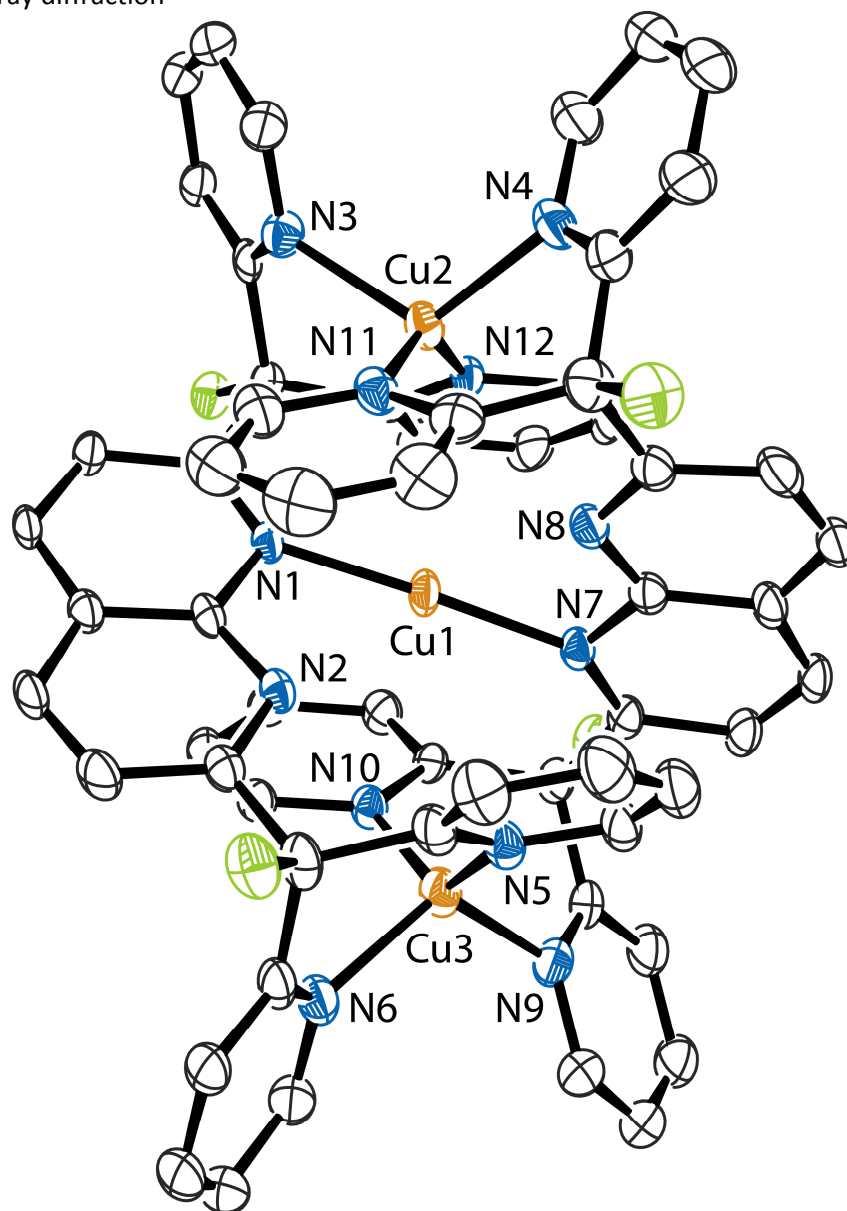


Details: As in Figure S45, the NTf_2^- anion, two cocrystallizing *ortho*-difluorobenzene molecules, one-half of a cocrystallizing pentane molecule, and hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at the 50% probability level. Selected angle [°]: C31–O1–centroid between Cu1 and Cu2: 148.18.

Table SC6. Crystal data and structure refinement for $[\text{Cu}_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-OC}_6\text{F}_5)\text{DPFN}](\text{NTf}_2)\cdot 2(o\text{-C}_6\text{H}_4\text{F}_2)\cdot 0.5(\text{C}_5\text{H}_{12})$ (**5**·2(*o*-C₆H₄F₂)·0.5(C₅H₁₂))

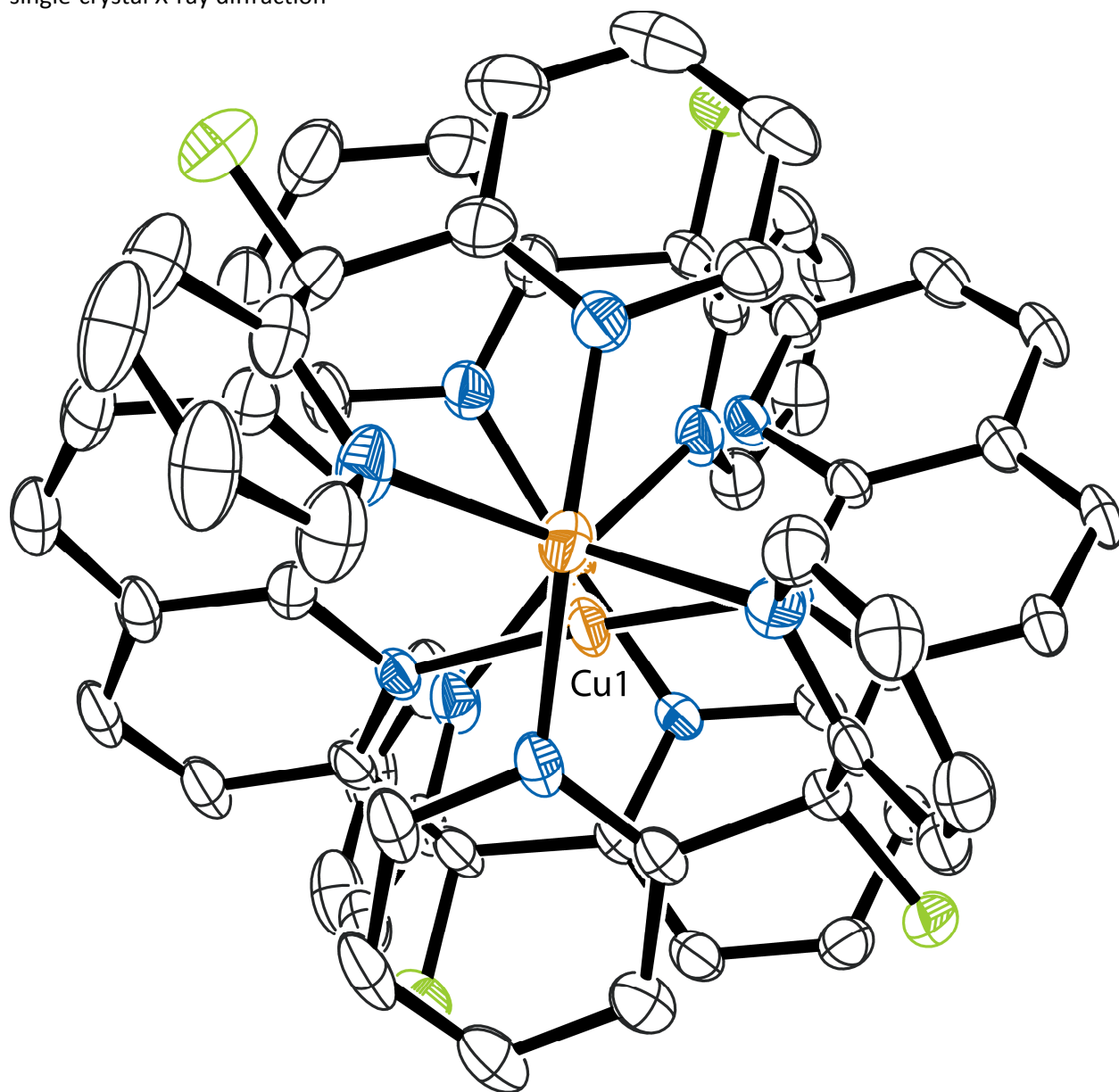
Empirical formula	$\text{C}_{52.50}\text{H}_{34}\text{Cu}_2\text{F}_{17}\text{N}_7\text{O}_5\text{S}_2$	
Formula weight	1357.06	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	$P4_32_12$	
Unit cell dimensions	$a = 14.5357(8)$ Å	$a = 90^\circ$
	$b = 14.5357(8)$ Å	$b = 90^\circ$
	$c = 49.499(3)$ Å	$g = 90^\circ$
Volume	$10458.5(13)$ Å ³	
Z	8	
Density (calculated)	1.724 Mg/m ³	
Absorption coefficient	1.012 mm ⁻¹	
F(000)	5448	
Crystal size	$0.120 \times 0.110 \times 0.100$ mm ³	
Theta range for data collection	1.460 to 27.510°	
Index ranges	$-17 \leq h \leq 17$, $-18 \leq k \leq 18$, $-61 \leq l \leq 64$	
Reflections collected	94805	
Independent reflections	11936 [$R(\text{int}) = 0.0340$]	
Completeness to $\theta = 27.500^\circ$	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6653 and 0.6274	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11936 / 6 / 888	
Goodness-of-fit on F^2	1.103	
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0302$, $wR2 = 0.0804$	
R indices (all data)	$R1 = 0.0328$, $wR2 = 0.0815$	
Absolute structure parameter	0.002(2)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.315 and -0.621 e/Å ³	

Figure S47. Solid state structure of $[\text{Cu}_3\text{DPFN}_2](\text{NTf}_2)_3 \cdot 2(o\text{-C}_6\text{H}_4\text{F}_2)$ (**6**·2(*o*-C₆H₄F₂)) as determined by single-crystal X-ray diffraction



Details: The three NTf_2^- anions, two cocrystallizing *ortho*-difluorobenzene molecules, and hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at the 50% probability level. Selected bond lengths [Å] and angles [°]: Cu1···Cu2: 3.2326(6), Cu1···Cu3: 3.5101(7), Cu2···Cu3: 6.5914(7), Cu1–N1: 1.924(3), Cu1–N7: 1.922(3), Cu1–N2: 2.562(3), Cu1–N8: 2.560(3), Cu2–N3: 2.098(3), Cu2–N4: 2.007(3), Cu2–N11: 2.011(3), Cu2–N12: 2.062(3), Cu3–N5: 2.000(3), Cu3–N6: 2.063(3), Cu3–N9: 2.061(4), Cu3–N10: 2.008(3); Cu2···Cu1···Cu3: 155.66(2), N1···Cu1···N7: 174.7(1).

Figure S48. Solid state structure of $[\text{Cu}_3\text{DPFN}_2](\text{NTf}_2)_3 \cdot 2(o\text{-C}_6\text{H}_4\text{F}_2)$ (**6**·2(*o*-C₆H₄F₂)) as determined by single-crystal X-ray diffraction



Details: As in S47, the three NTf₂⁻ anions, two cocrystallizing *ortho*-difluorobenzene molecules, and hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at the 50% probability level.

Table SC7. Crystal data and structure refinement for [Cu₃DPFN₂](NTf₂)₃·2(*o*-C₆H₄F₂) (**6**·2(*o*-C₆H₄F₂))

Empirical formula	C ₇₈ H ₄₈ Cu ₃ F ₂₆ N ₁₅ O ₁₂ S	
Formula weight	2264.29	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	<i>P</i> $\bar{1}$	
Unit cell dimensions	<i>a</i> = 13.2293(8) Å	<i>a</i> = 91.311(3)°
	<i>b</i> = 14.2590(8) Å	<i>b</i> = 100.758(3)°
	<i>c</i> = 23.4954(13) Å	<i>c</i> = 96.298(3)°
Volume	4323.6(4) Å ³	
<i>Z</i>	2	
Density (calculated)	1.739 Mg/m ³	
Absorption coefficient	1.003 mm ⁻¹	
<i>F</i> (000)	2268	
Crystal size	0.11 x 0.10 x 0.03 mm ³	
Theta range for data collection	1.438 to 27.547°	
Index ranges	-17 ≤ <i>h</i> ≤ 15, -18 ≤ <i>k</i> ≤ 18, -30 ≤ <i>l</i> ≤ 30	
Reflections collected	74315	
Independent reflections	19641 [<i>R</i> (int) = 0.0364]	
Completeness to theta = 27.500°	98.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7041 and 0.6318	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	19641 / 298 / 1602	
Goodness-of-fit on <i>F</i> ²	1.034	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0589, <i>wR</i> 2 = 0.1316	
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0851, <i>wR</i> 2 = 0.1460	
Extinction coefficient	<i>n/a</i>	
Largest diff. peak and hole	1.567 and -0.994 e/Å ³	

4) Additional computational figures

Figure S49. Excerpts of experimental and calculated IR spectra for complex **1**

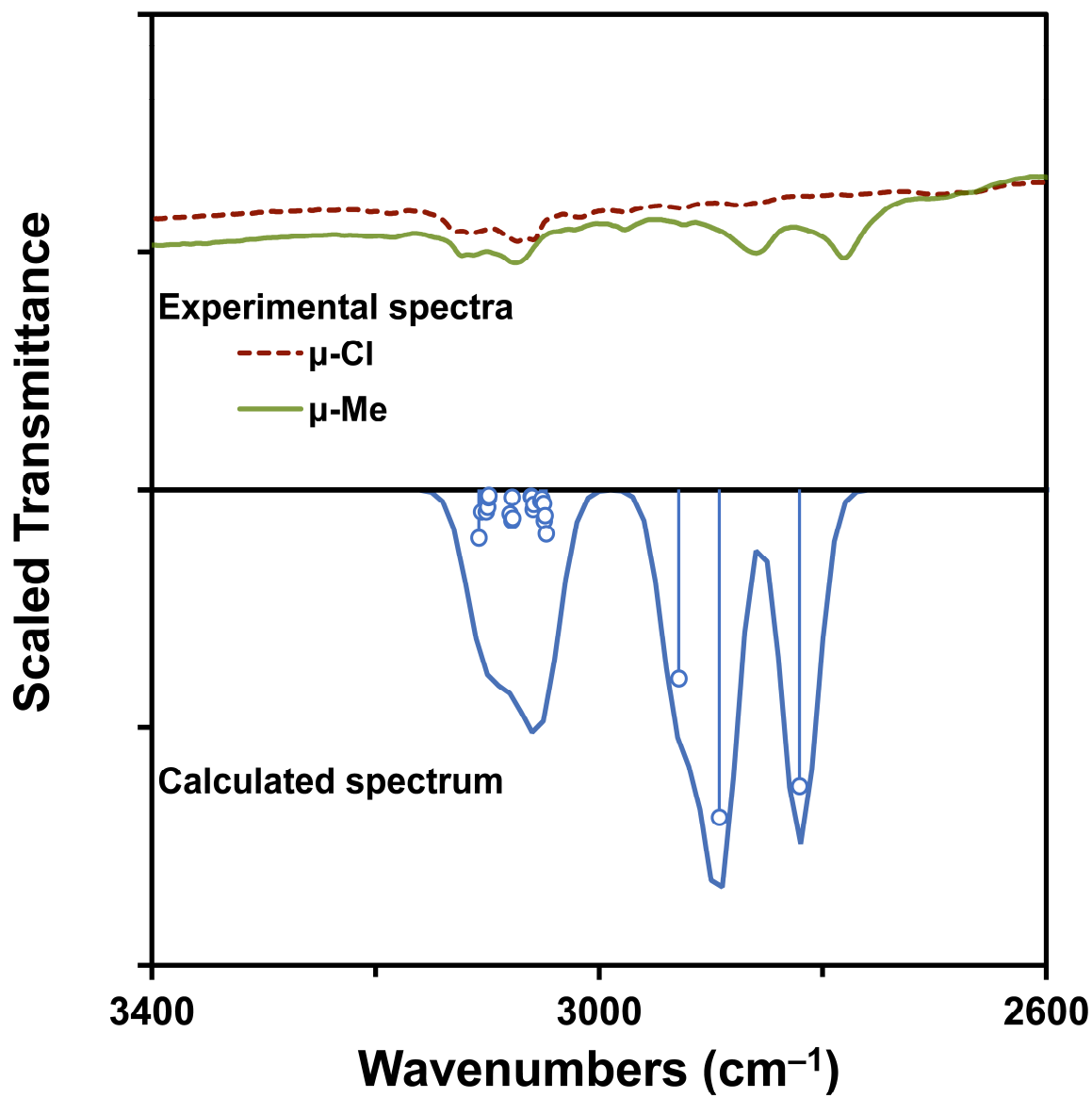
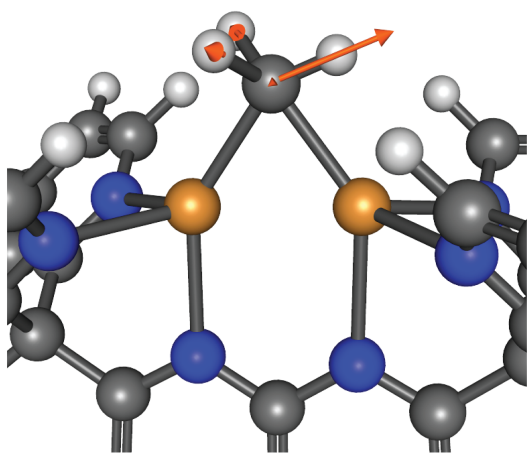
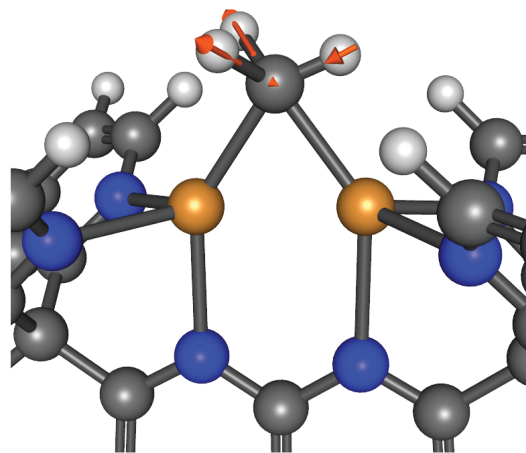


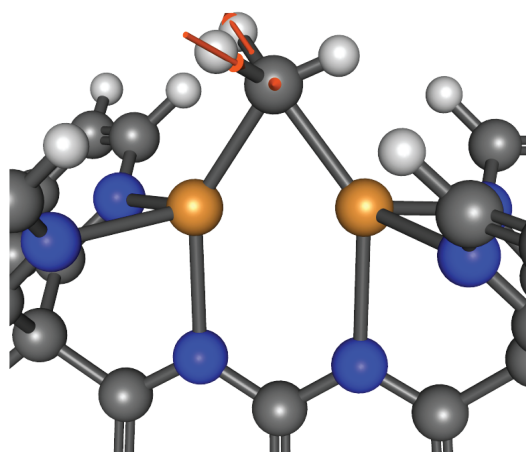
Figure S50. Selected vibrational modes and their frequencies calculated for the cation of complex **1**



2821 cm⁻¹



2892 cm⁻¹



2929 cm⁻¹

Figure S51. Primarily three-center two-electron canonical orbital of $[\text{Cu}_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-Ph})\text{DPFN}]^+$

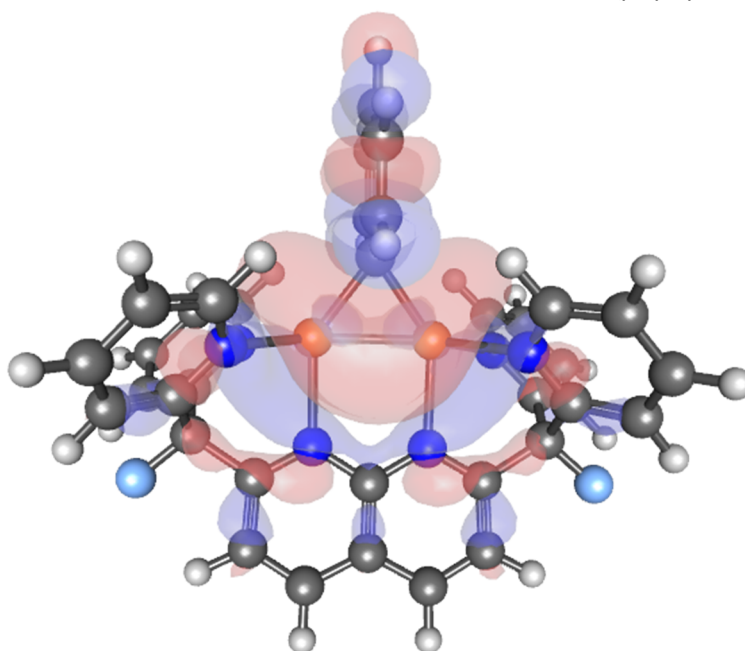


Figure S52. Primarily three-center two-electron canonical orbital of $[\text{Cu}_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-C}\equiv\text{C}(\text{C}_6\text{H}_5))\text{DPFN}]^+$

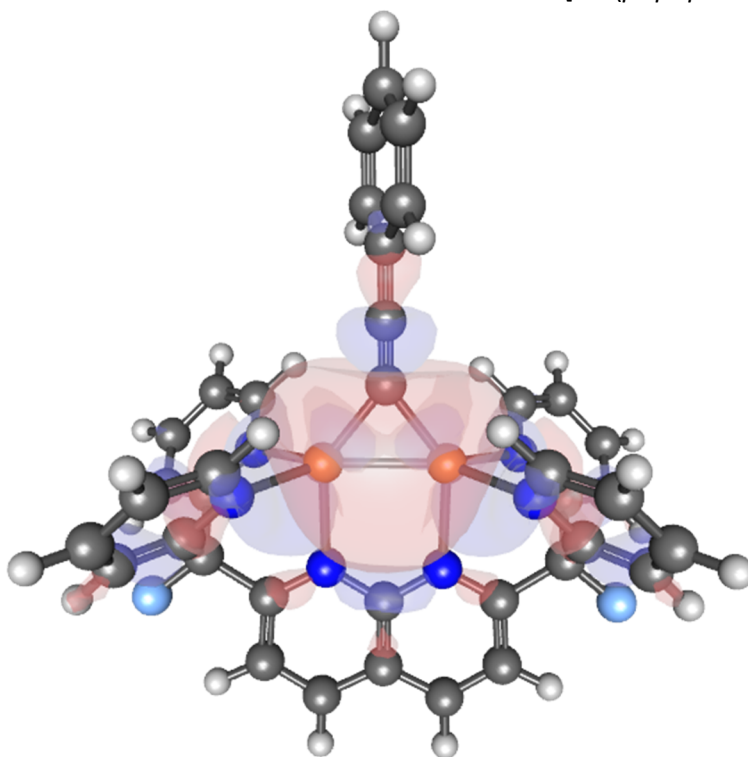


Table S8. Final energies of calculated structures

Cation	Final energy (Ha)
$[\text{Cu}_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-CH}_3)\text{DPFN}]^+$	−5002.1797672498
$[\text{Cu}_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-Ph})\text{DPFN}]^+$	−5193.7318356684
$[\text{Cu}_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-C}\equiv\text{C}(\text{C}_6\text{H}_5))\text{DPFN}]^+$	−5269.8276128894
$[\text{Cu}_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-OC}_6\text{F}_5)\text{DPFN}]^+$	−5764.49685906570

5) References

- (1) Ziegler, M. S.; Levine, D. S.; Lakshmi, K. V.; Tilley, T. D. Aryl Group Transfer from Tetraarylborato Anions to an Electrophilic Dicopper(I) Center and Mixed-Valence μ -Aryl Dicopper(I,II) Complexes. *J. Am. Chem. Soc.* **2016**, *138* (20), 6484–6491.
- (2) Anet, F. A. L.; O’Leary, D. J. H-D Coupling Constants and Deuterium Isotope Effects on the Proton Chemical Shifts in Partially Deuteriated Methanes. *Tetrahedron Lett.* **1989**, *30* (21), 2755–2758.