

Supplementary Materials: Softening the Donor-Set: From $[\text{Cu}(\text{P}^{\wedge}\text{P})(\text{N}^{\wedge}\text{N})][\text{PF}_6]$ to $[\text{Cu}(\text{P}^{\wedge}\text{P})(\text{N}^{\wedge}\text{S})][\text{PF}_6]$

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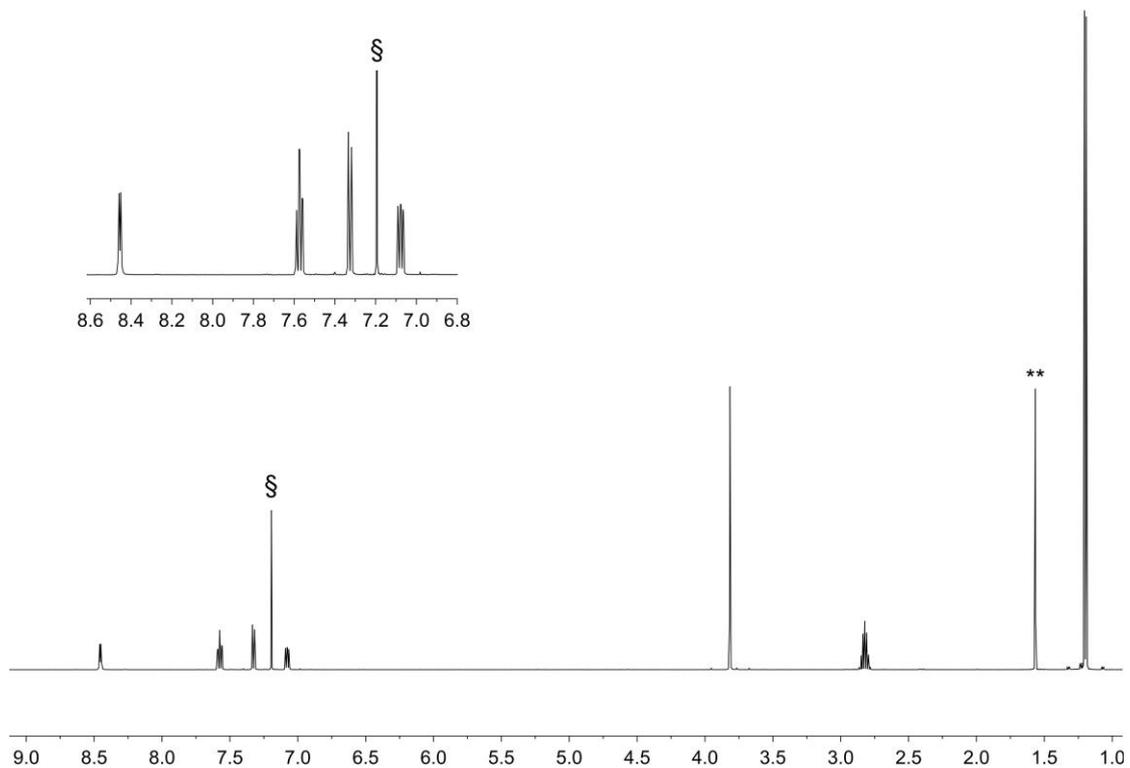


Figure S1. ^1H NMR spectrum of *iPrSPy* (500 MHz, CDCl_3 , 298 K). Inset: expansion of the aromatic region. § = residual CHCl_3 ; ** = H_2O .

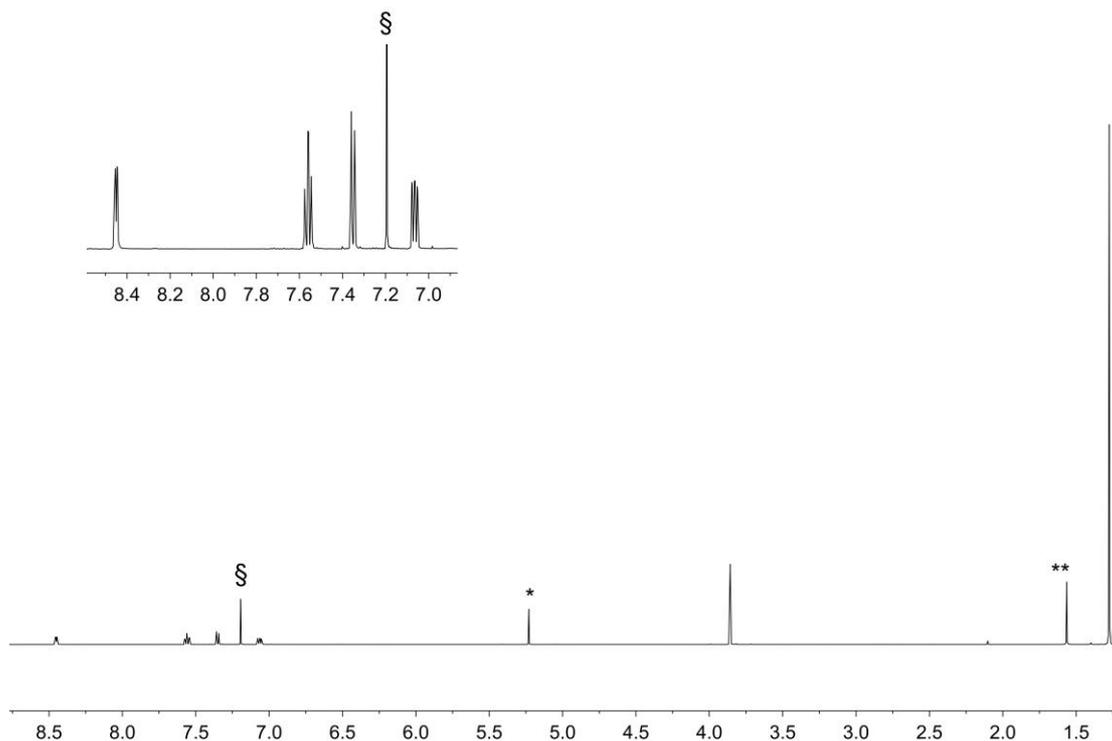


Figure S2. ¹H NMR spectrum of *t*BuSPy (500 MHz, CDCl₃, 298 K). Inset: expansion of the aromatic region. § = residual CHCl₃; * = CH₂Cl₂; ** = H₂O.

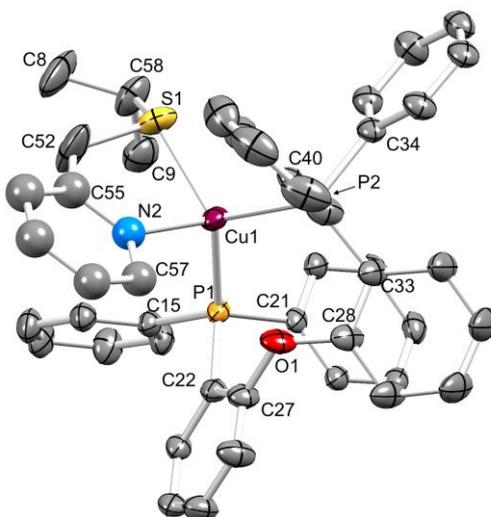


Figure S3. ORTEP-style plot of the [Cu(POP)(*i*PrSPy)]⁺ cation in [Cu(POP)(*i*PrSPy)][PF₆] with only one of each of the disordered sites (see manuscript) shown. Ellipsoids are plotted at 40% probability level and H atoms are omitted. The pyridine ring was refined isotropically. Selected bond parameters: Cu1–N2 = 2.114(5), Cu–S1 = 2.3229(12), Cu1–P1 = 2.2550(10), Cu1–P2 = 2.2722(11), C27–O1 = 1.393(4), C28–O1 = 1.385(5) Å; S1–Cu1–P1 = 123.57(5), S1–Cu1–P2 = 114.22(5), P1–Cu1–P2 = 111.84(4), C27–O1–C28 = 116.2(3)°.

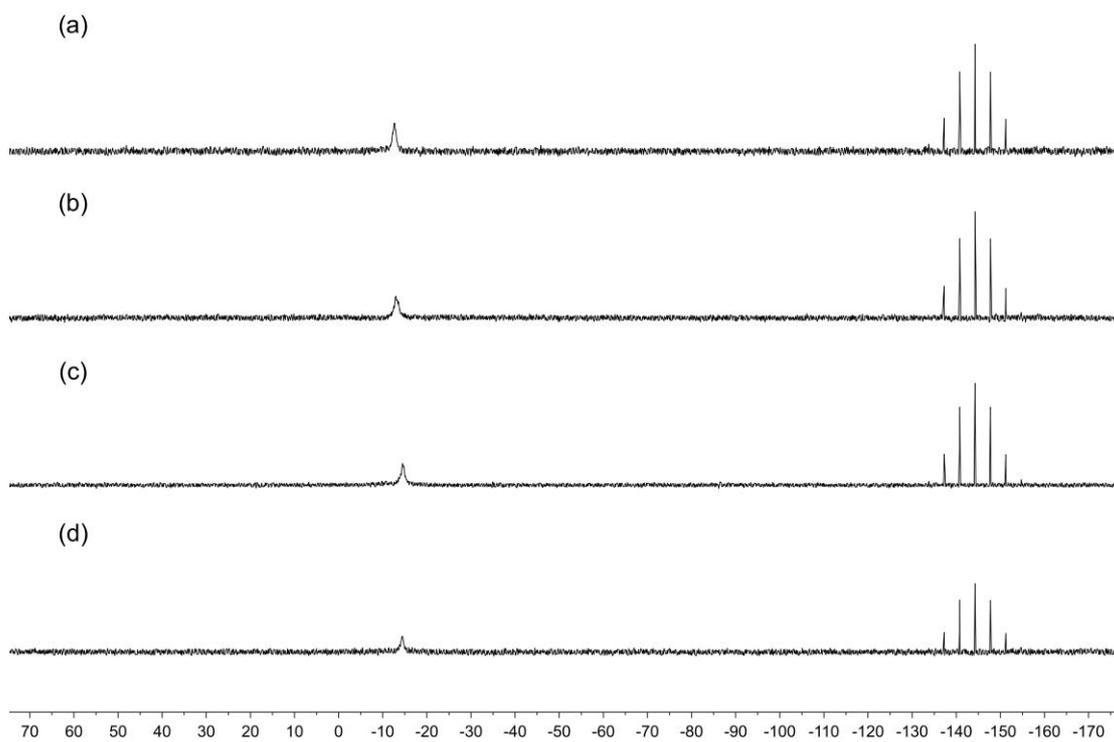


Figure S4. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (202 MHz, acetone- d_6 , 298 K) of (a) $[\text{Cu}(\text{POP})(i\text{PrSPy})][\text{PF}_6]$, (b) $[\text{Cu}(\text{POP})(t\text{BuSPy})][\text{PF}_6]$, (c) $[\text{Cu}(\text{xantphos})(i\text{PrSPy})][\text{PF}_6]$ and (d) $[\text{Cu}(\text{xantphos})(t\text{BuSPy})][\text{PF}_6]$.

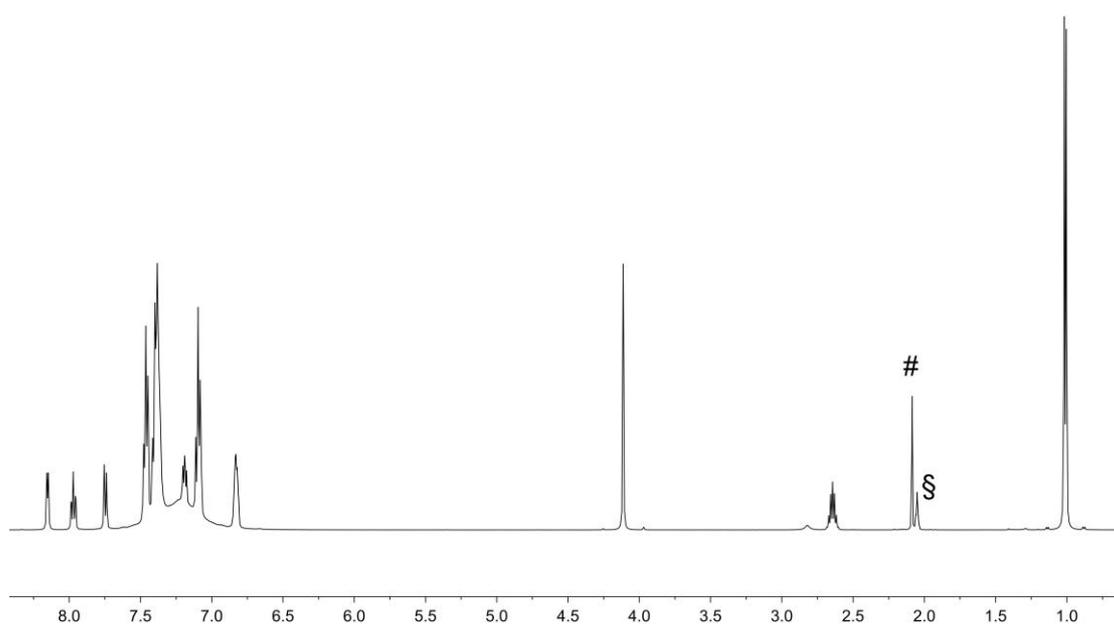


Figure S5. ^1H NMR spectrum of $[\text{Cu}(\text{POP})(i\text{PrSPy})][\text{PF}_6]$ (500 MHz, acetone- d_6 , 298 K). § = residual acetone- d_5 ; # = Me_2CO

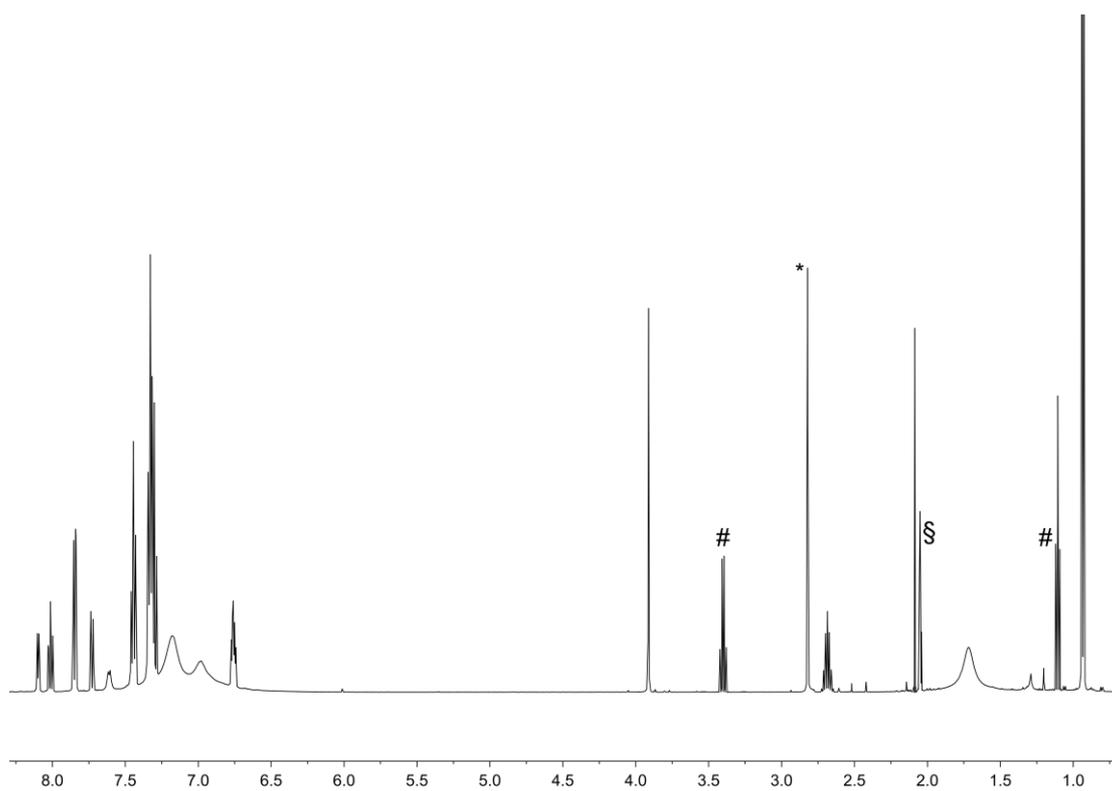


Figure S6. ^1H NMR spectrum of $[\text{Cu}(\text{xantphos})(i\text{PrSPy})][\text{PF}_6]$ (500 MHz, acetone- d_6 , 298 K). * = H_2O , § = residual acetone- d_5 , # = Et_2O .

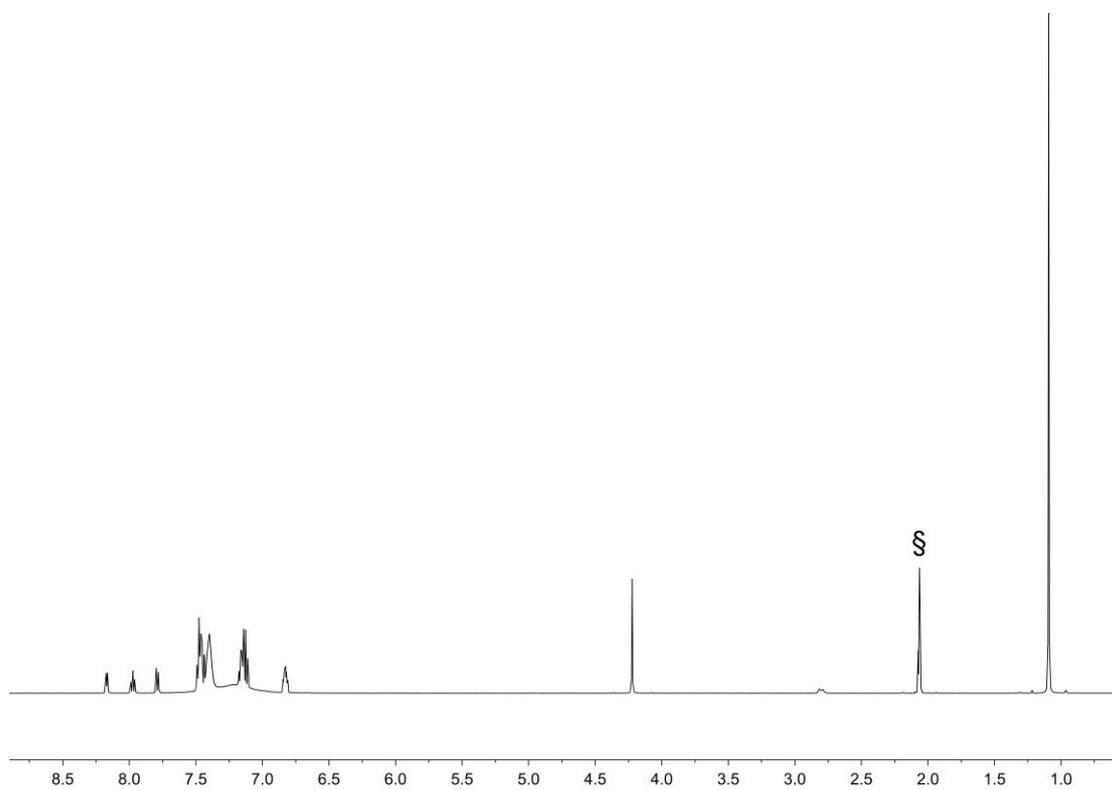


Figure S7. ^1H NMR spectrum of $[\text{Cu}(\text{POP})(t\text{BuSPy})][\text{PF}_6]$ (500 MHz, acetone- d_6 , 298 K). § = residual acetone- d_5 .

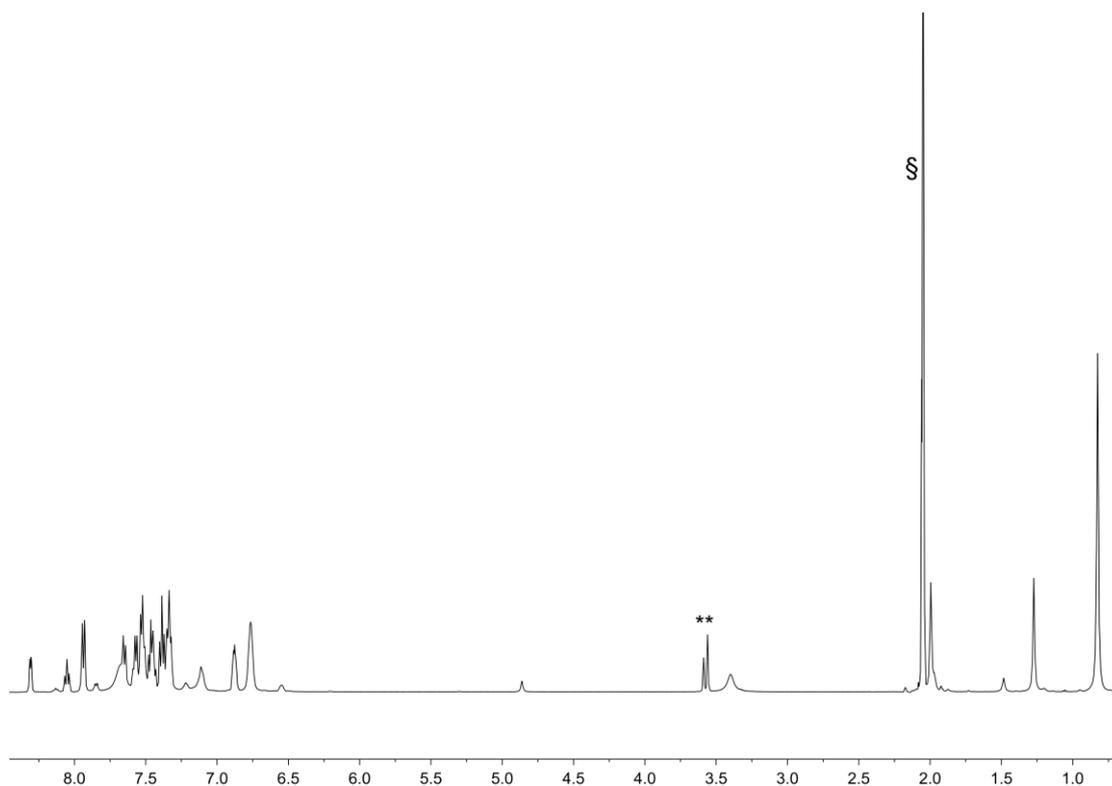


Figure S8. ^1H NMR spectrum of $[\text{Cu}(\text{xantphos})(t\text{BuSPy})][\text{PF}_6]$ (500 MHz, acetone- d_6 , 298 K). § = residual acetone- d_5 , ** = unidentified impurities.

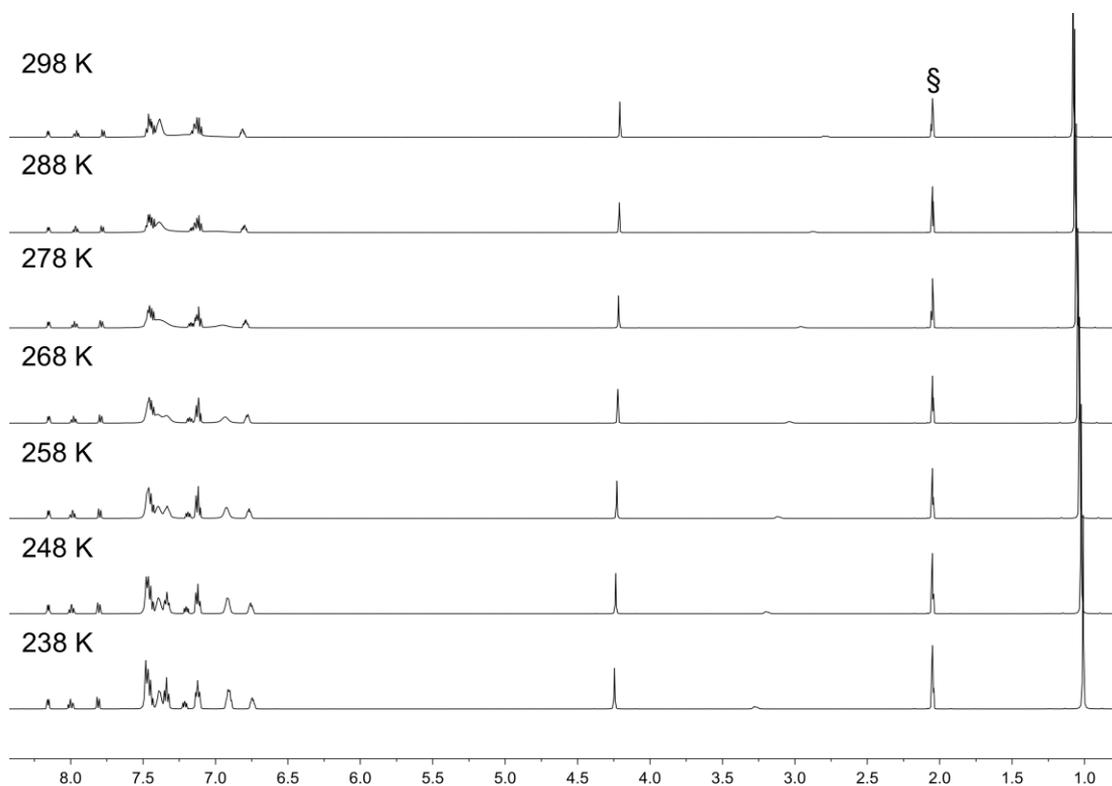


Figure S9. Variable temperature ^1H NMR spectra of $[\text{Cu}(\text{POP})(t\text{BuSPy})][\text{PF}_6]$ (500 MHz, acetone- d_6). § = residual acetone- d_5 . The signals at δ 4.25 and 1.01 ppm arise from the CH_2 and $t\text{Bu}$ groups of the $t\text{BuSPy}$ ligand.

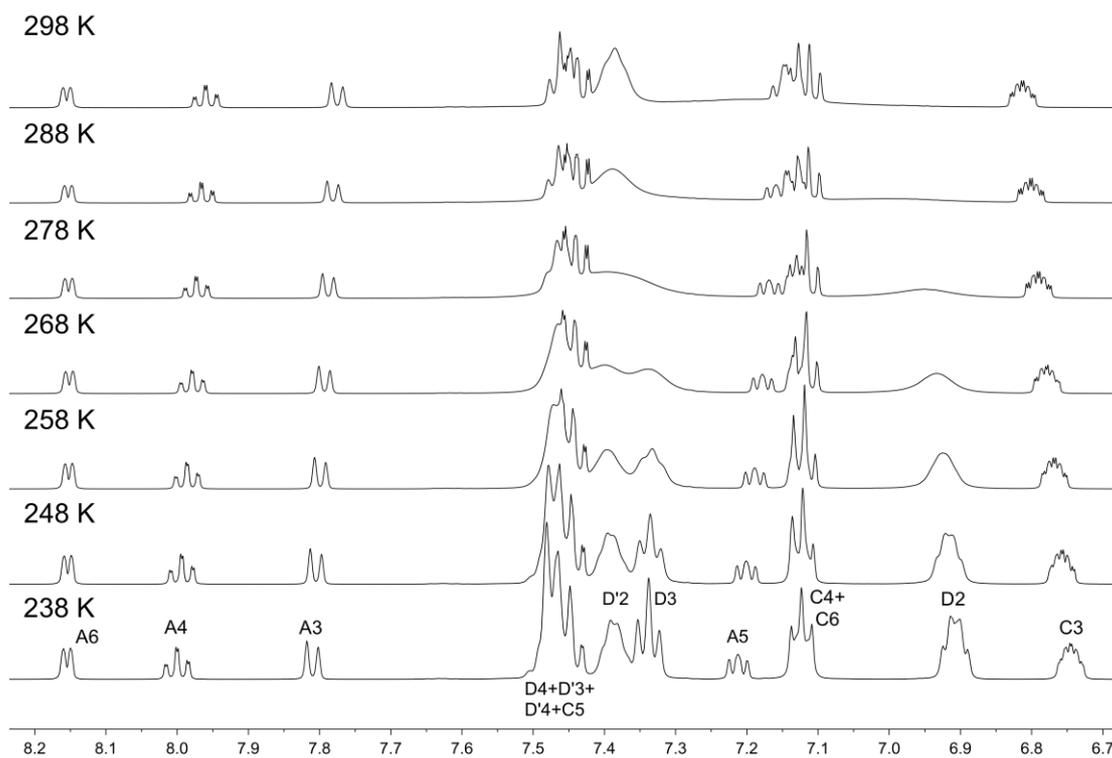


Figure S10. Aromatic region of the variable temperature ^1H NMR spectra of $[\text{Cu}(\text{POP})(t\text{BuSPy})][\text{PF}_6]$ (500 MHz, acetone- d_6). (An expansion of Fig. S9).

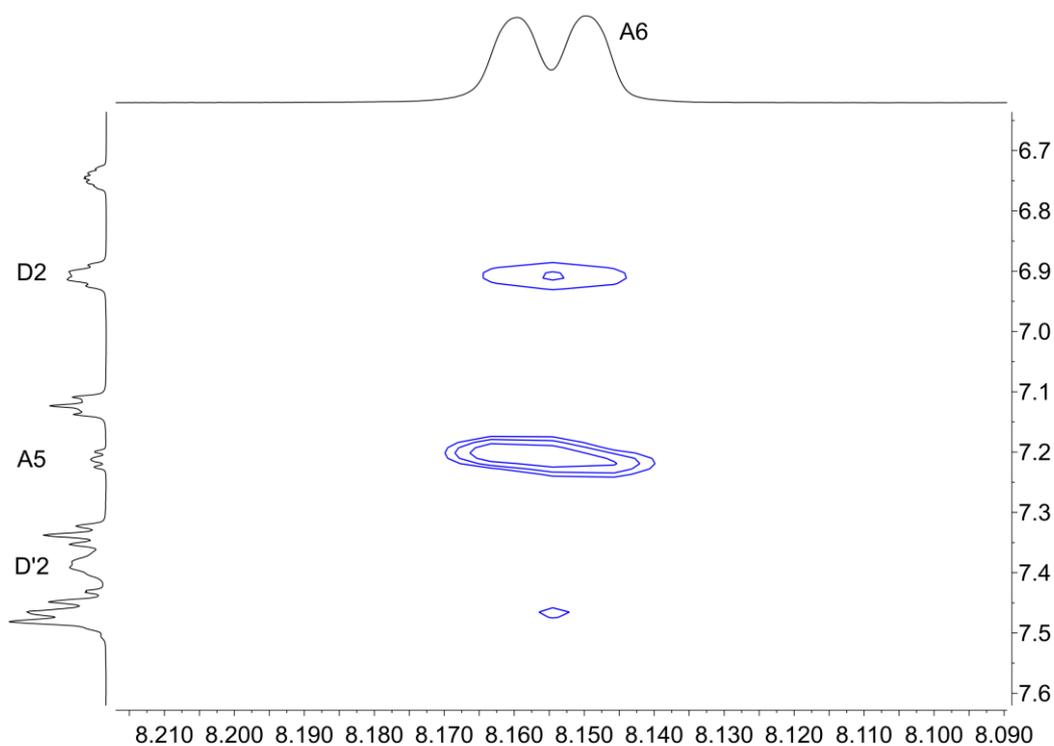


Figure S11. $\text{H}^{\text{A6}}/\text{H}^{\text{D2}}$ NOESY cross-peak in the the ROESY spectrum of $[\text{Cu}(\text{POP})(t\text{BuSPy})][\text{PF}_6]$ (500 MHz ^1H , acetone- d_6 , 238 K). The figure also shows an $\text{H}^{\text{A6}}/\text{H}^{\text{A5}}$ COSY cross-peak.

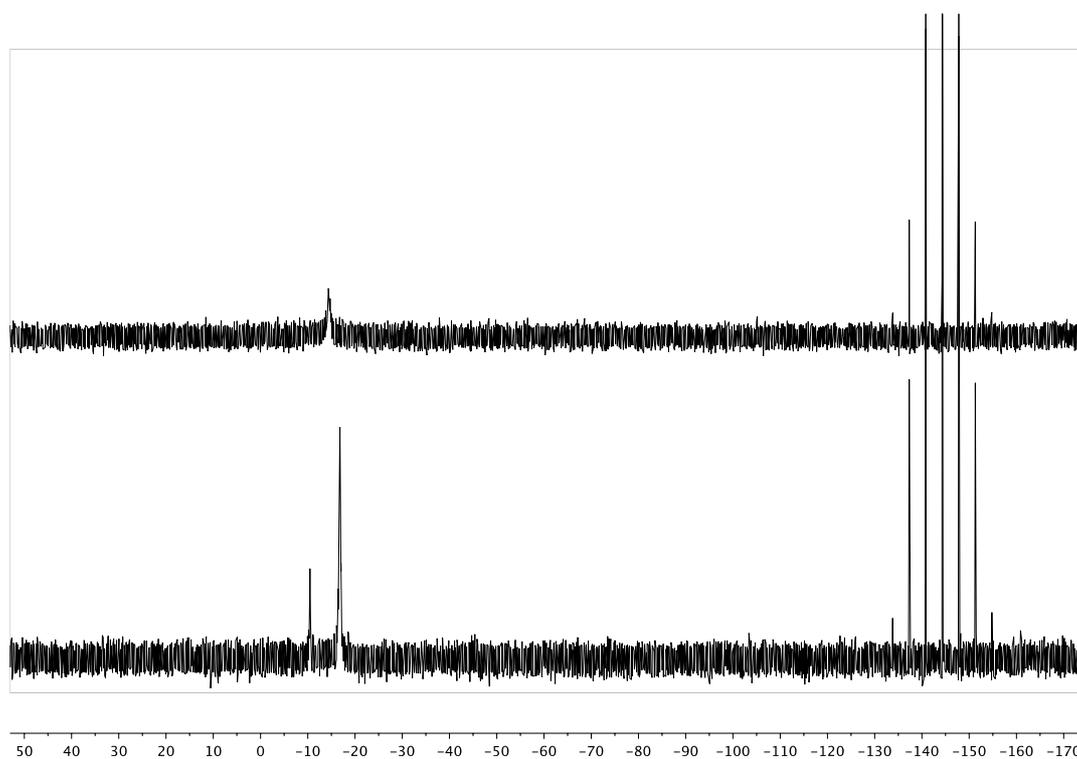


Figure S12. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of $[\text{Cu}(\text{xantphos})(\text{tBuSPy})][\text{PF}_6]$ (202 MHz, $\text{acetone-}d_6$) at 298 K (top) and 198 K.

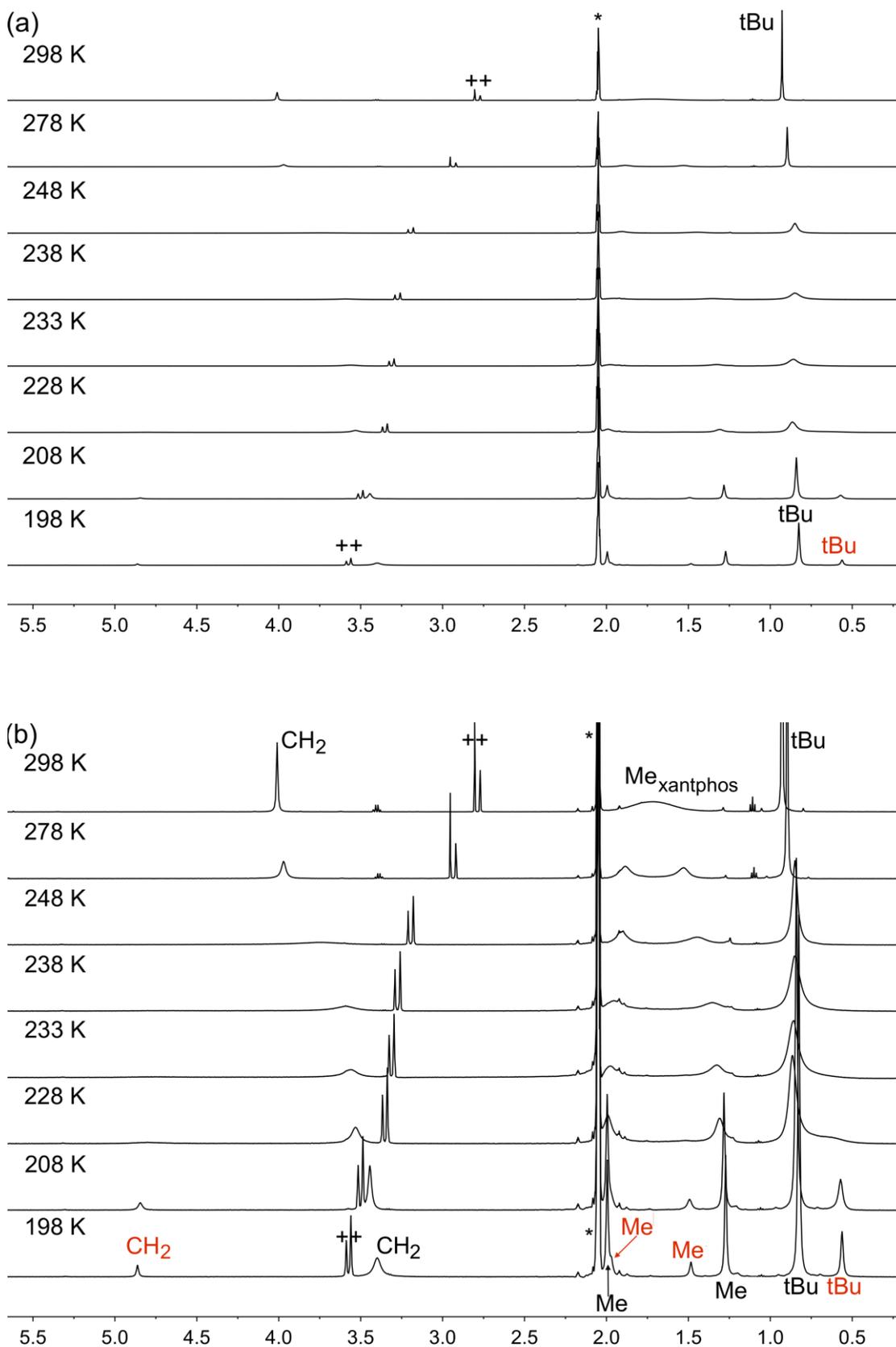
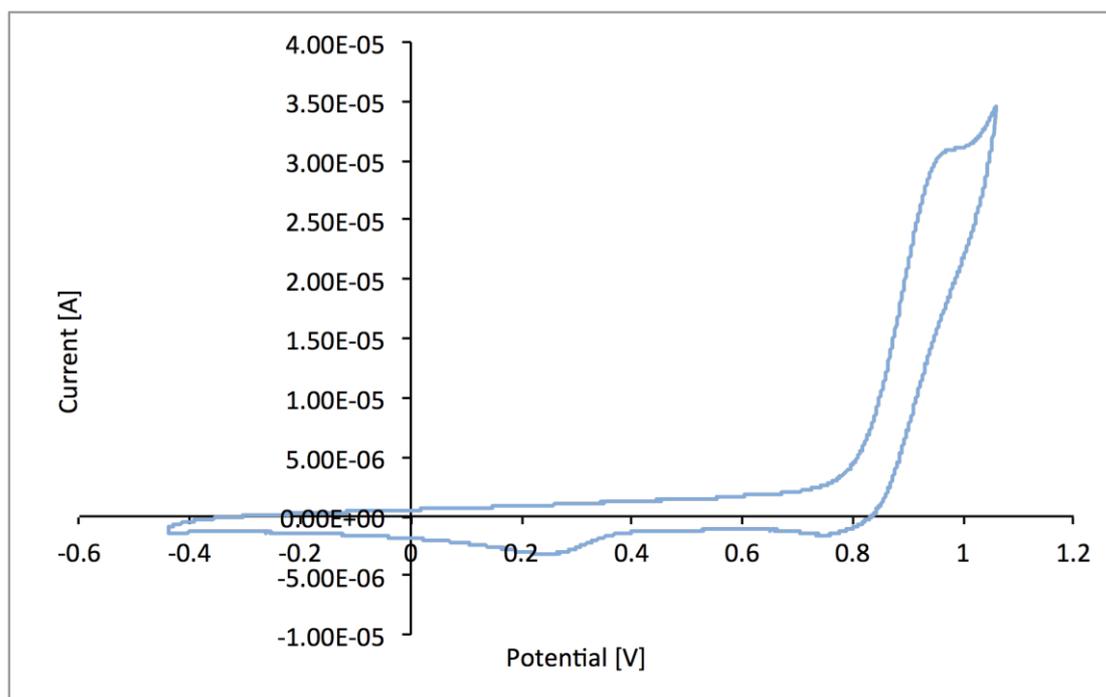
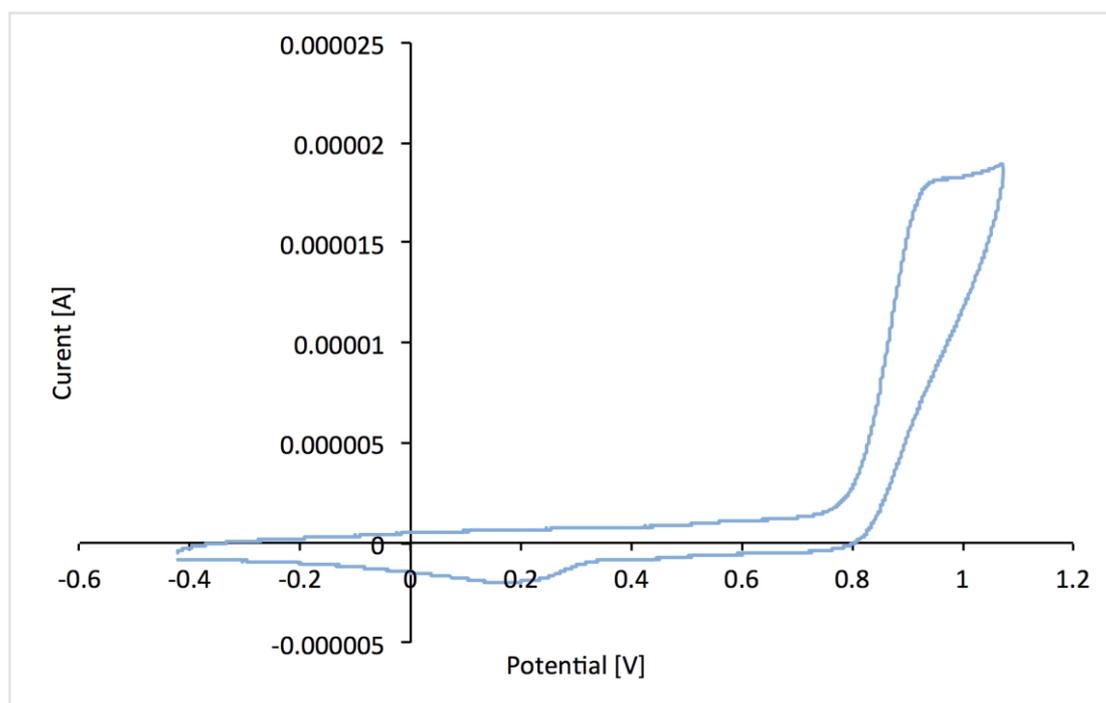


Figure S13. (a) Alkyl region in the variable temperature ^1H NMR spectra of $[\text{Cu}(\text{xantphos})(\text{tBuSPy})][\text{PF}_6]$ (500 MHz, acetone- d_6) and (b) a vertical expansion of the same set of spectra. Major species represented by black labels, minor by red labels. * = residual acetone- d_5 . ++ = unidentified impurities.

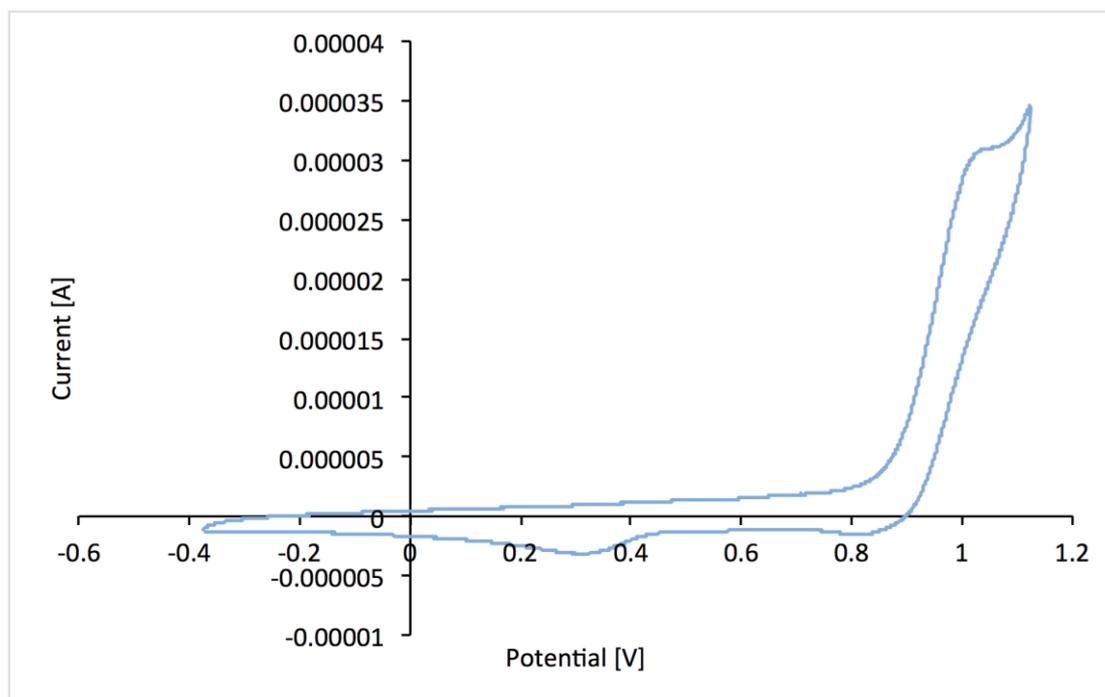


(a)

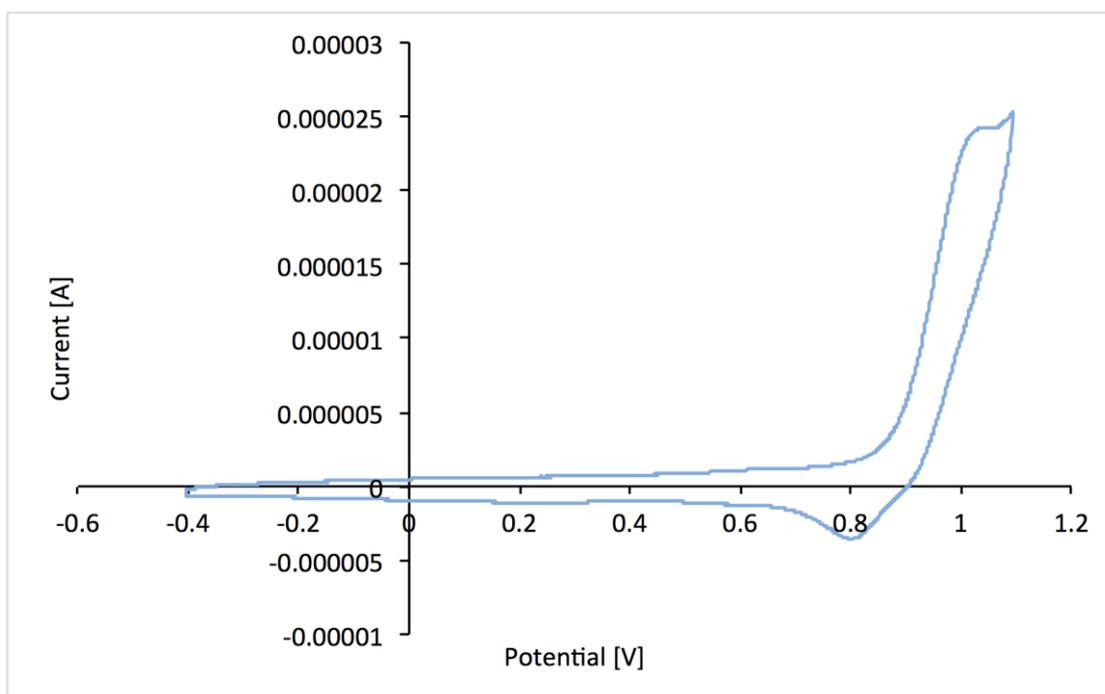


(b)

Figure S14. Cyclic voltammograms of (a) [Cu(POP)(iPrSPy)][PF₆] and (b) [Cu(POP)(tBuSPy)][PF₆] in CH₂Cl₂ ($1-5 \times 10^{-3}$ M, vs. Fc⁺/Fc, [nBu₄N][PF₆] as supporting electrolyte, scan rate = 0.1 V s⁻¹).



(a)



(b)

Figure S15. Cyclic voltammograms of (a) $[\text{Cu}(\text{xantphos})(i\text{PrSPy})][\text{PF}_6]$ and (b) $[\text{Cu}(\text{xantphos})(t\text{BuSPy})][\text{PF}_6]$ in CH_2Cl_2 ($1\text{--}5 \times 10^{-3}$ M, vs. Fc^+/Fc , $[\text{nBu}_4\text{N}][\text{PF}_6]$ as supporting electrolyte, scan rate = 0.1 V s^{-1}).

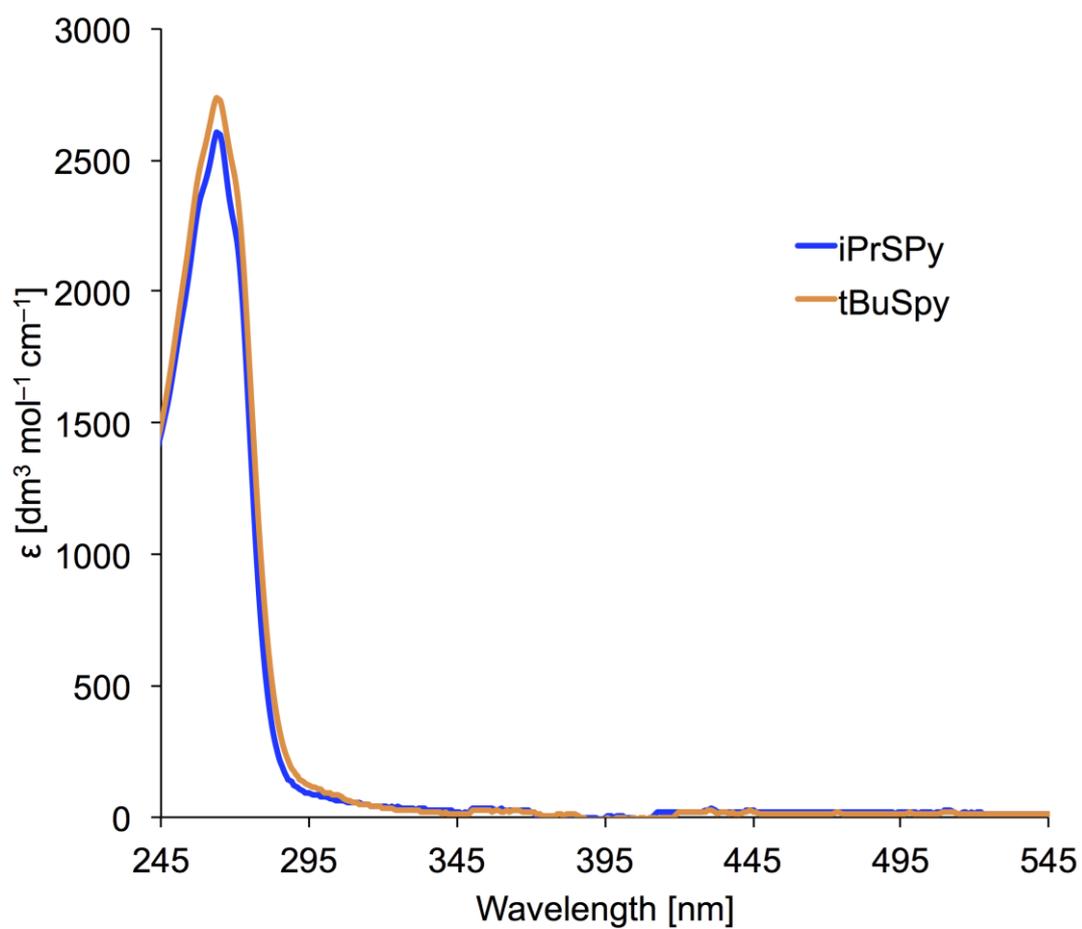


Figure S16. Absorption spectra of the ligands *iPrSPy* and *tBuSPy* (CH_2Cl_2 , $1 \times 10^{-4} \text{ mol dm}^{-3}$).

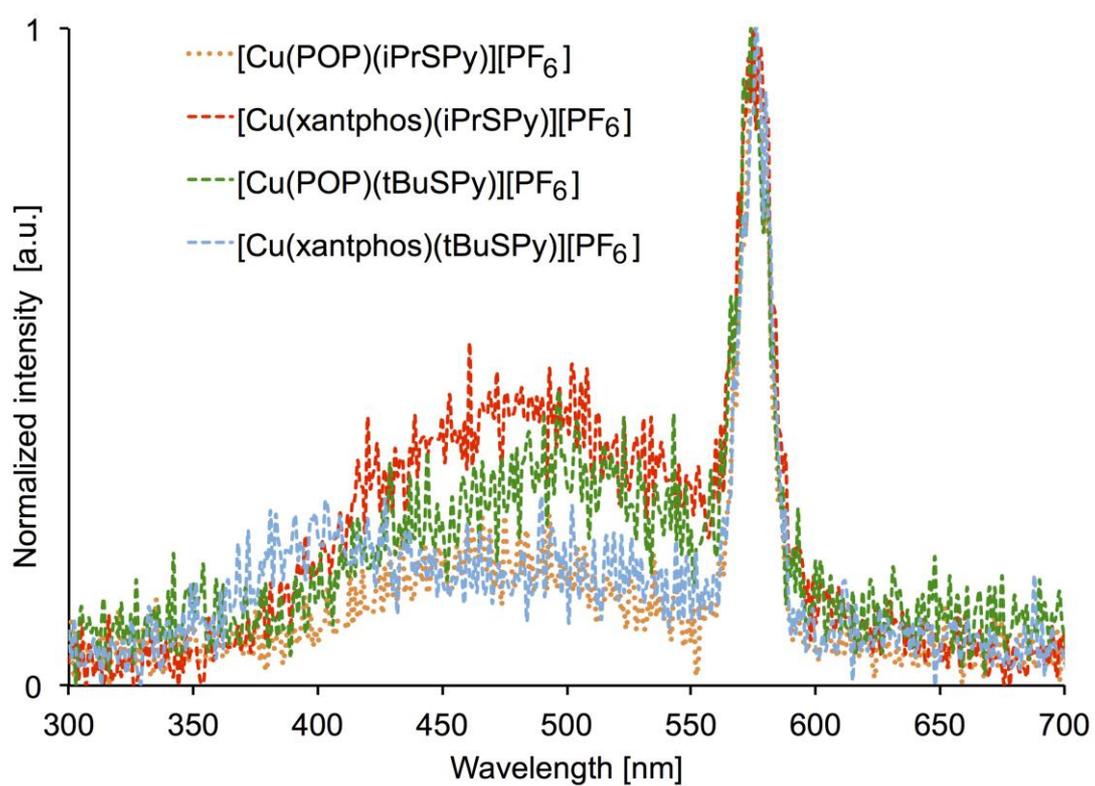


Figure S17. Solid-state emission spectra of the [Cu(P[^]P)(N[^]S)][PF₆] complexes, excited at 280 nm. The spectra are normalized to the harmonic of the excitation irradiation.