Supporting Material

Desymmetrizing heteroleptic [Cu(P^P)(N^N)][PF_6] compounds: effects on structural, dynamic and photophysical properties

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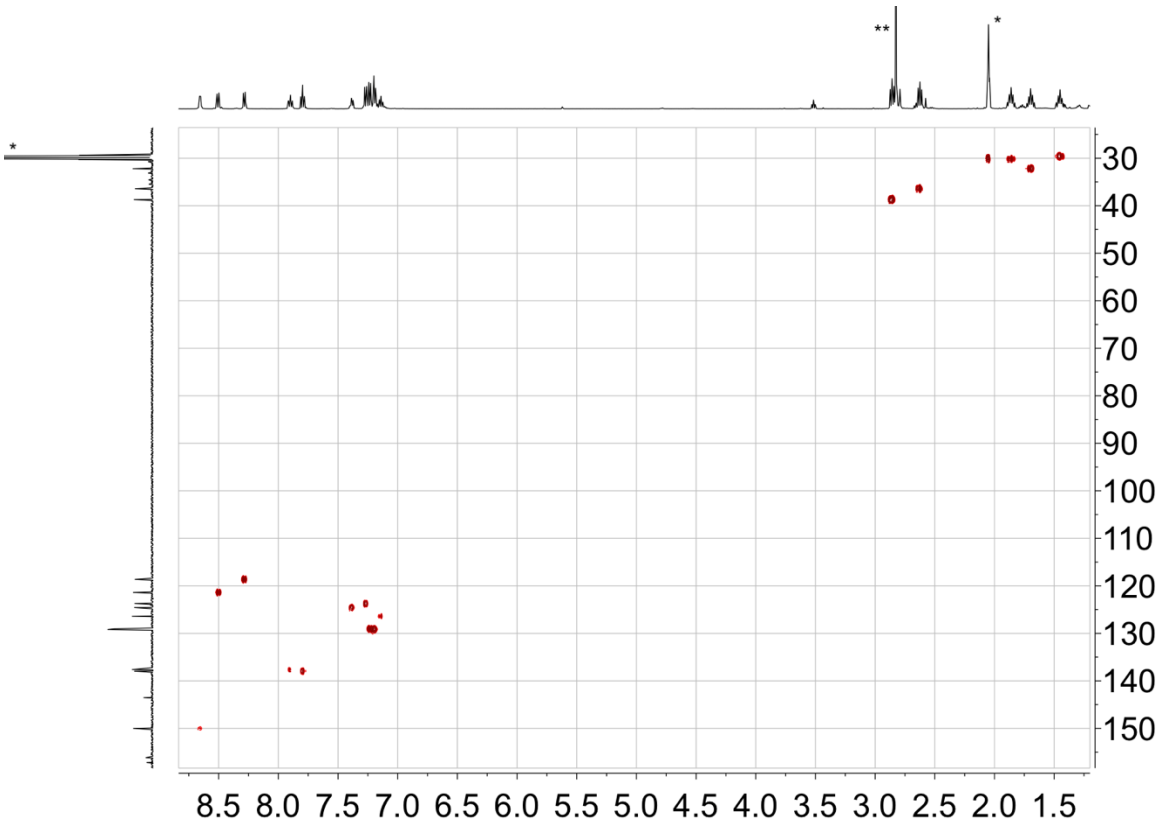

Figure S1. HMQC spectrum of **2** (^{1}H 500 MHz, ^{13}C 126 MHz, acetone-d_6, 298 K). * = acetone-d_6 (in $^{13}C\{^{1}H\}$ or residual acetone-d_5 (in ^{1}H); ** = H_2O.

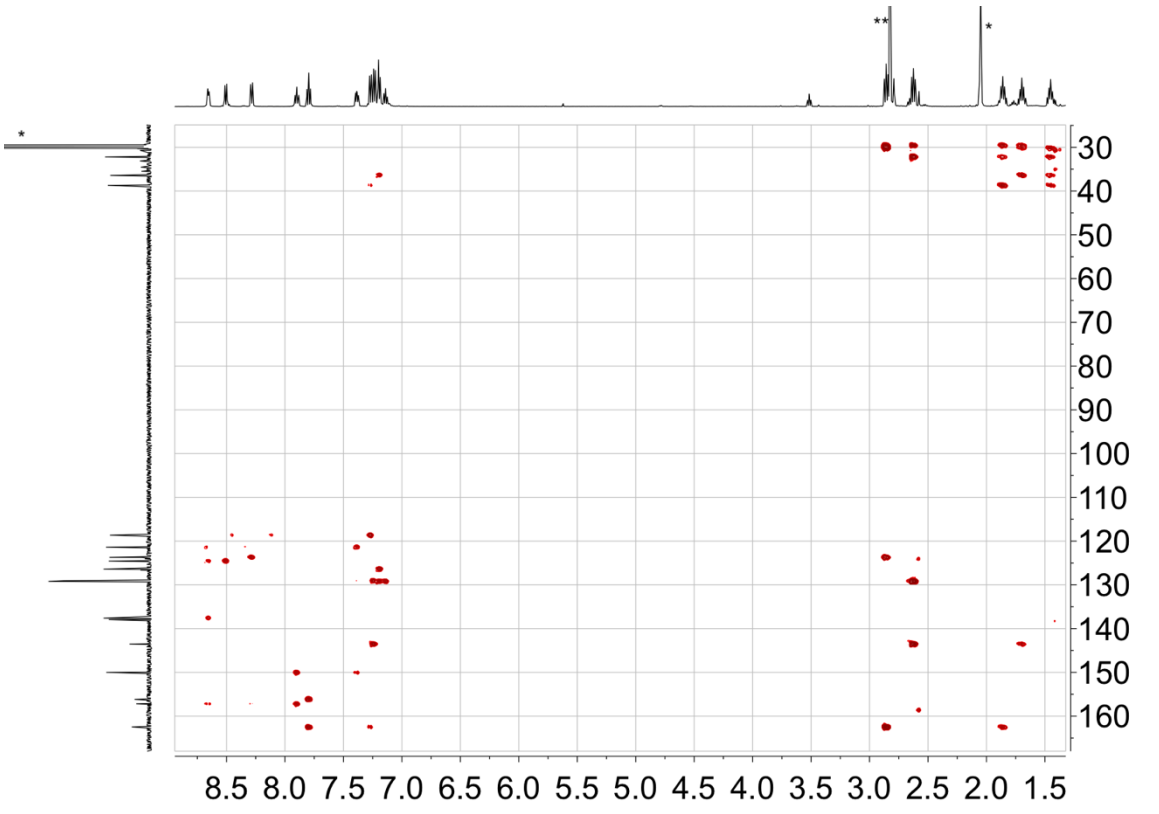

Figure S2. HMBC spectrum of **2** (^{1}H 500 MHz, ^{13}C 126 MHz, acetone-d_6, 298 K). * = acetone-d_6 (in $^{13}C\{^{1}H\}$ or residual acetone-d_5 (in ^{1}H); ** = H_2O.

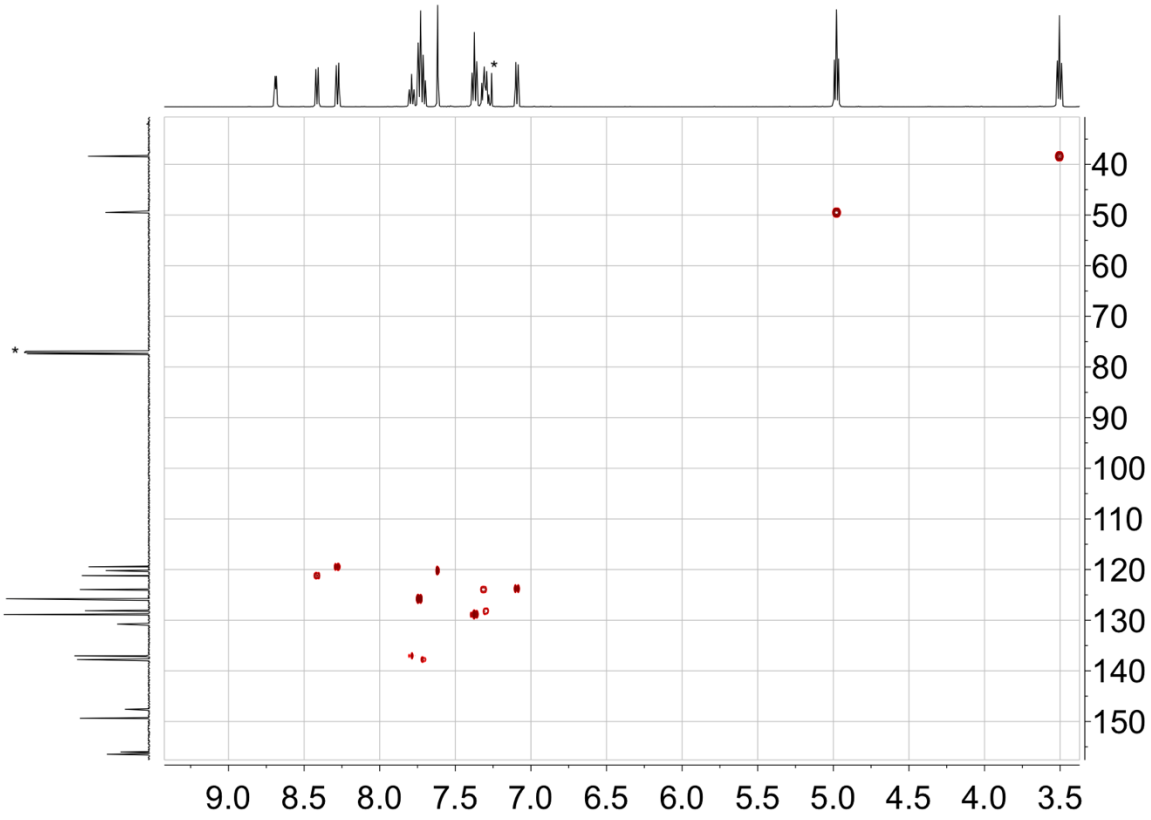

Figure S3. HMQC spectrum of **3** (^{1}H 500 MHz, ^{13}C 126 MHz,$CDCl_3$, 298 K). * = $CDCl_3$ (in $^{13}C\{^{1}H\}$ or residual $CHCl_3$ (in ^{1}H); ** = H_2O.

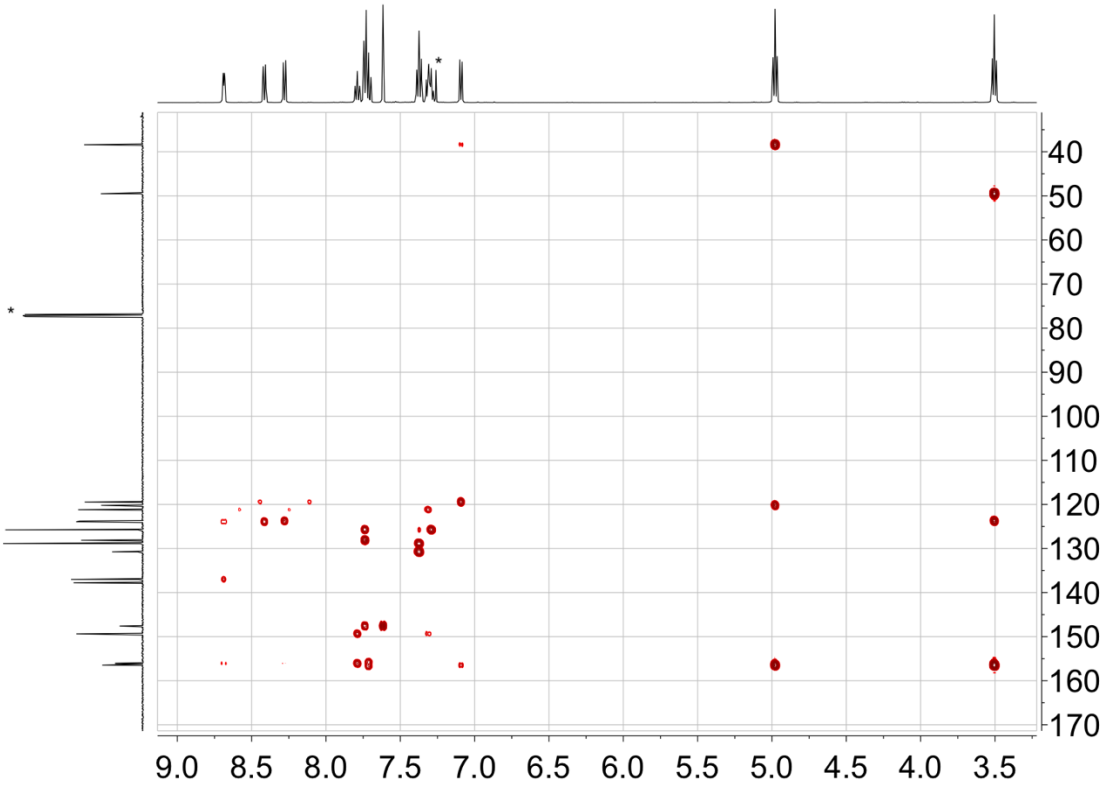

Figure S4. HMBC spectrum of **3** (^{1}H 500 MHz, ^{13}C 126 MHz, $CDCl_3$, 298 K). * = $CDCl_3$ (in $^{13}C\{^{1}H\}$ or residual $CHCl_3$ (in ^{1}H); ** = H_2O.

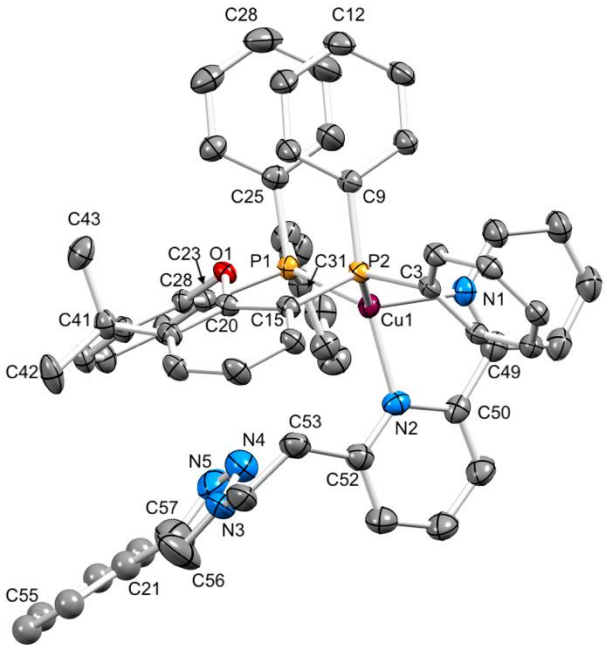

Figure S5. ORTEP representation of the structure of the [Cu(xantphos)(**3**)]$^{+}$ cation in [Cu(xantphos)(**3**)][PF_6]·0.5Et_2O. Ellipsoids are drawn at a 40% probability level and H atoms are omitted; the phenyl ring in ligand **3** was orientationally disordered and the rings were refined isotropically.

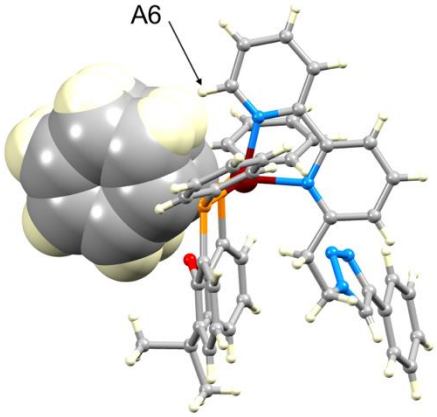

Figure S6. π-Stacking interaction in the [Cu(xantphos)(**3**)]$^{+}$ cation and the proximity of proton H^{A6} to these phenyl rings.

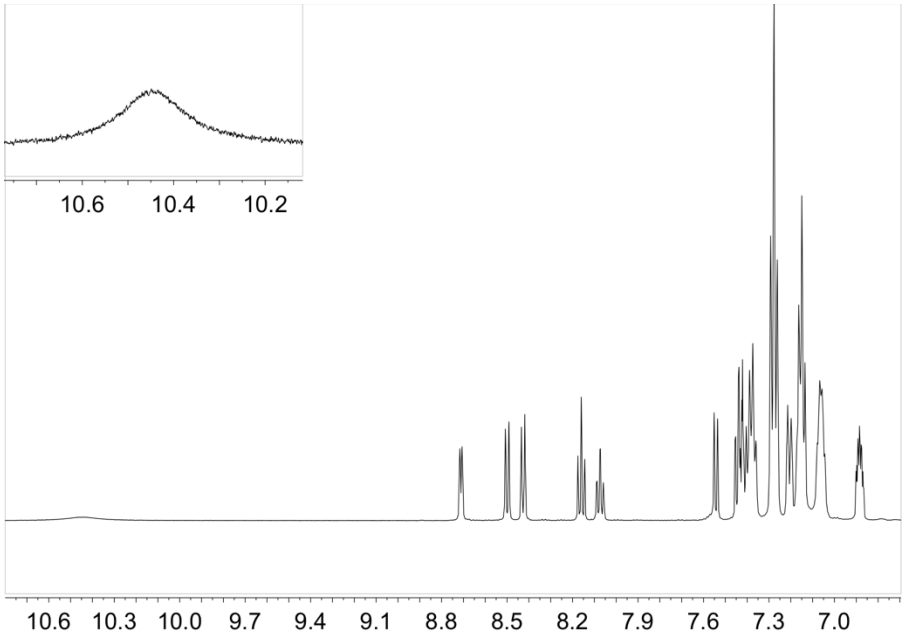

Figure S7. ^{1}H NMR spectrum of [Cu(POP)(**1**)][PF_6] (500 MHz, acetone-d_6, 298 K) with the CO_2H signal inset.

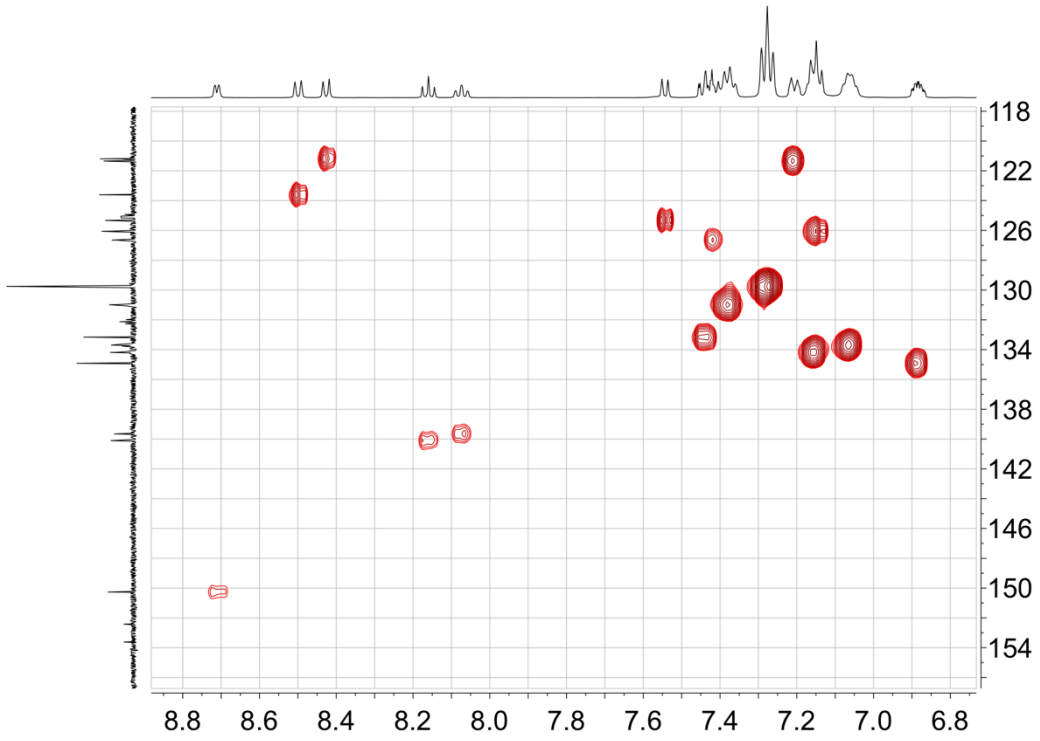

Figure S8. HMQC spectrum of [Cu(POP)(**1**)][PF_6] (^{1}H 500 MHz, ^{13}C 126 MHz, acetone-d_6, 298 K).

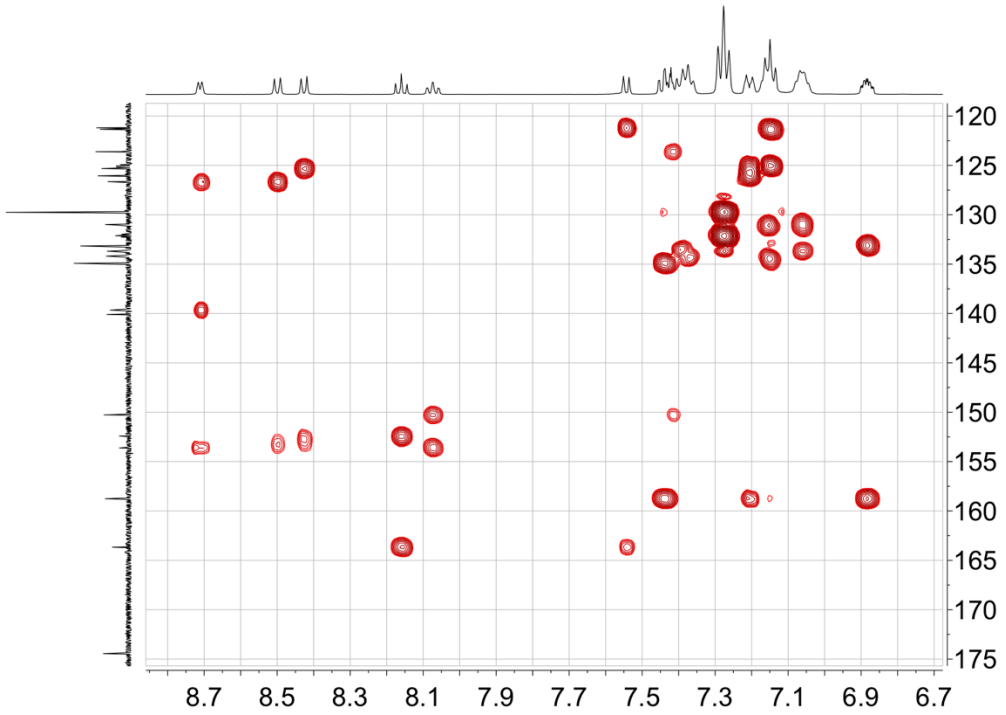

Figure S9. HMBC spectrum of [Cu(POP)(**1**)][PF_6] (^{1}H 500 MHz, ^{13}C 126 MHz, acetone-d_6, 298 K).

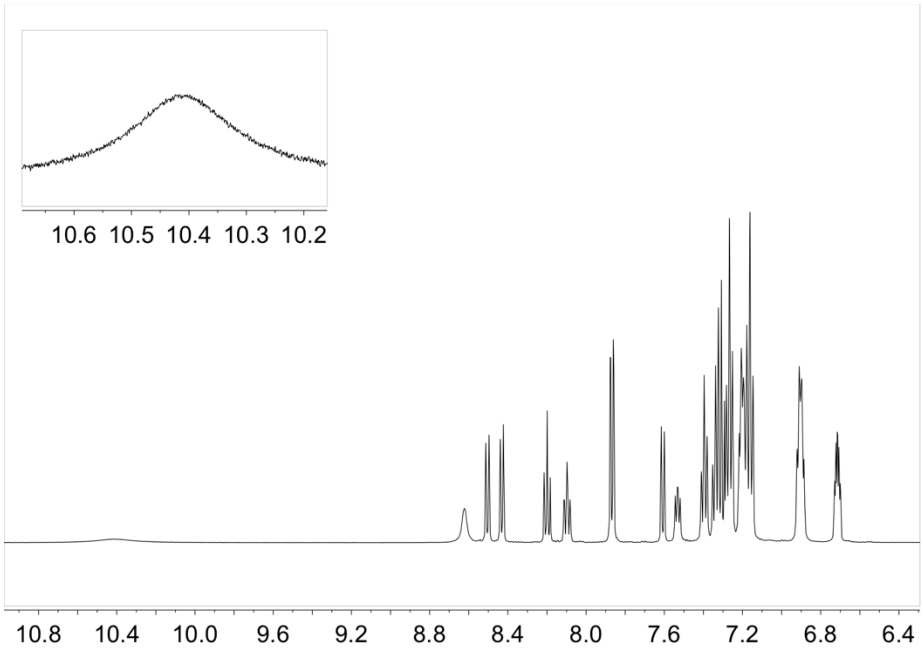

Figure S10. Part of the ^{1}H NMR spectrum of [Cu(xantphos)(**1**)][PF_6] (500 MHz, acetone-d_6, 298 K) with the CO_2H signal inset.

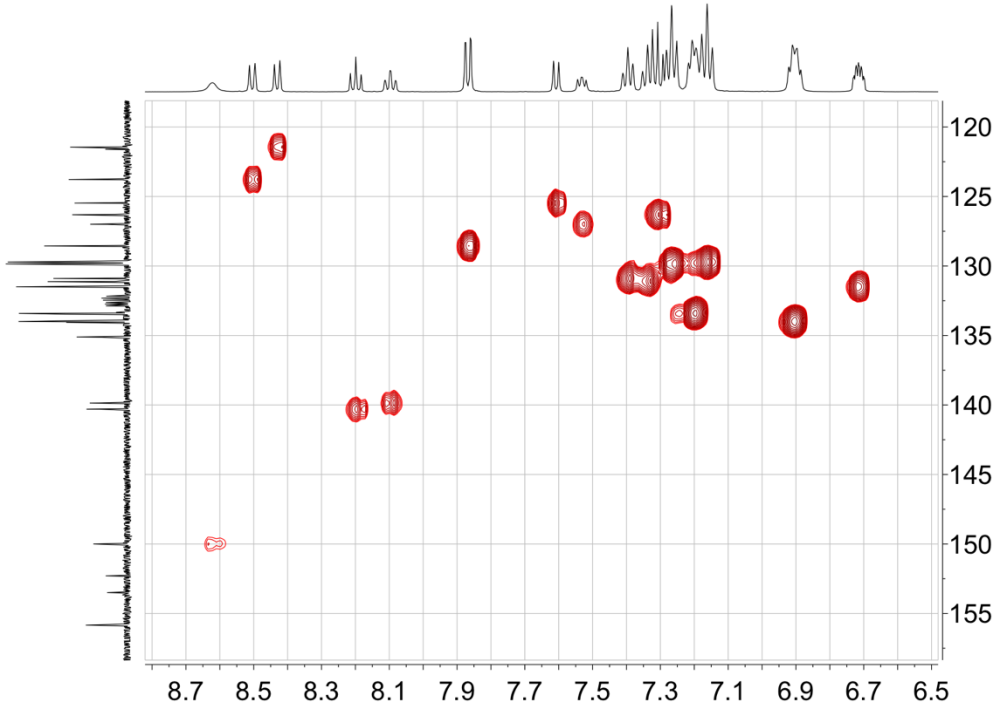

Figure S11. Part of the HMQC spectrum of [Cu(xantphos)(**1**)][PF_6] (^{1}H 500 MHz, ^{13}C 126 MHz, acetone-d_6, 298 K).

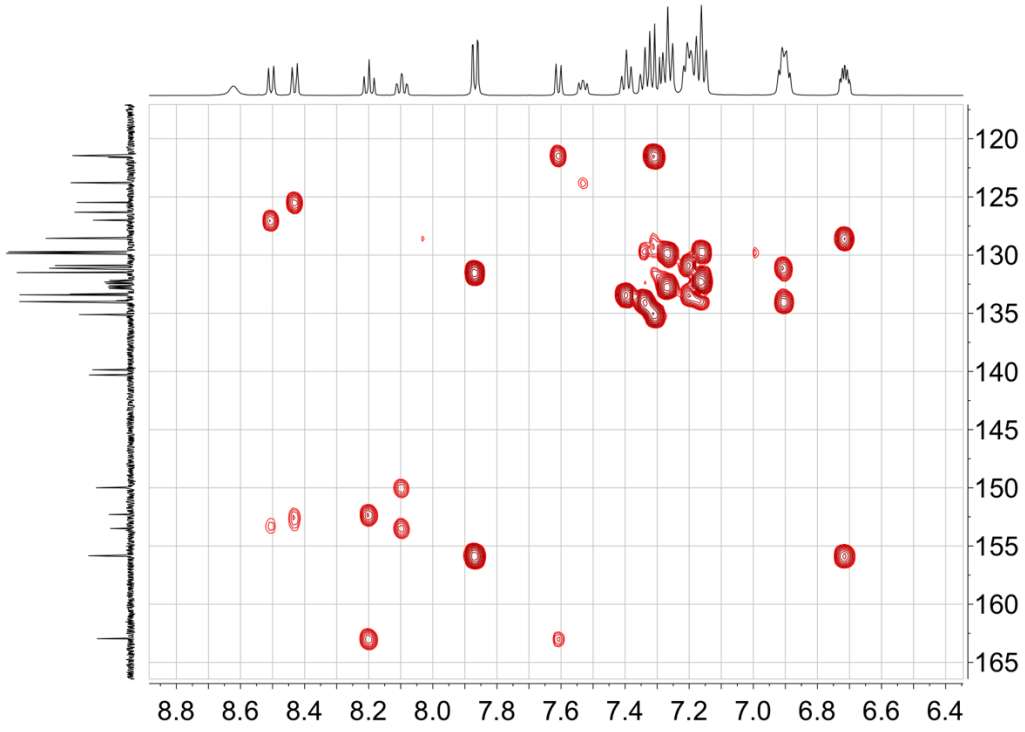

Figure S12. Part of the HMBC spectrum of [Cu(xantphos)(**1**)][PF_6] (^{1}H 500 MHz, ^{13}C 126 MHz, acetone-d_6, 298 K).

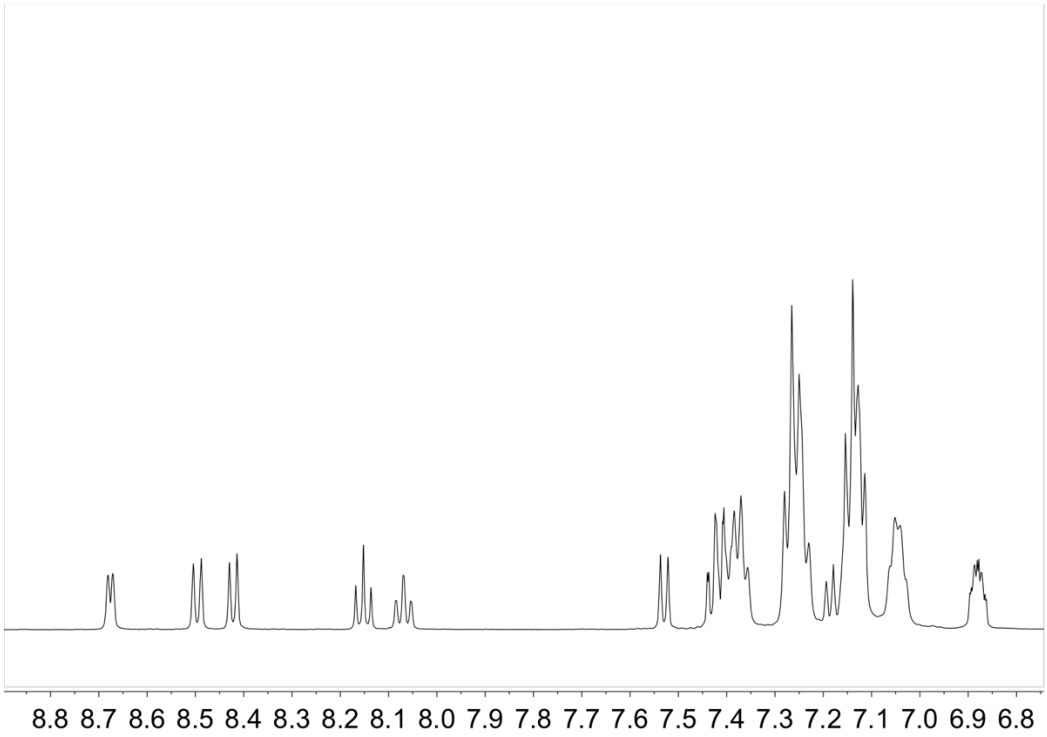

Figure S13. Aromatic region of the ^{1}H NMR spectrum of [Cu(POP)(**2**)][PF_6] (500 MHz, acetone-d_6, 298 K).

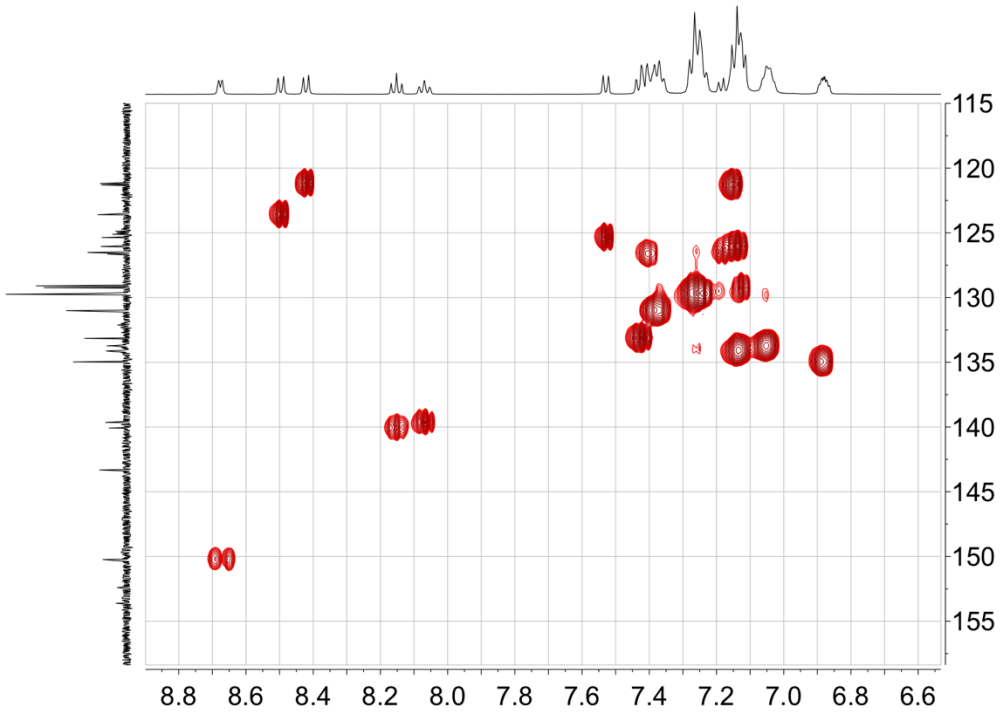

Figure S14. Aromatic region of the HMQC spectrum of [Cu(POP)(**2**)][PF_6] (^{1}H 500 MHz, ^{13}C 126 MHz, acetone-d_6, 298 K).

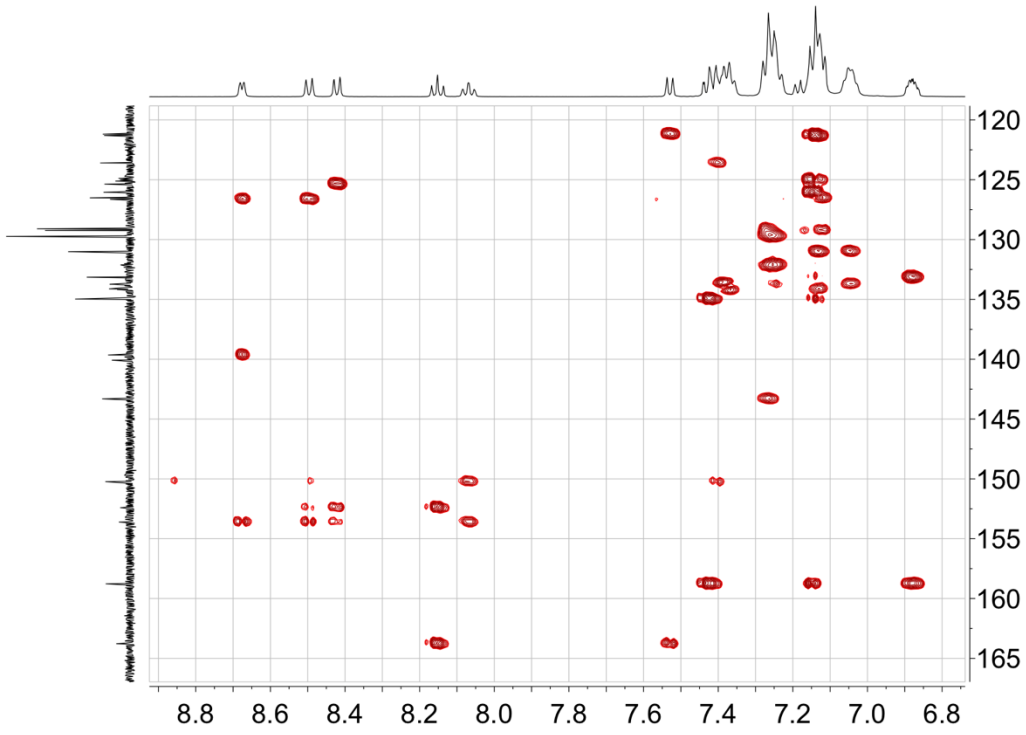

Figure S15. Aromatic region of the HMBC spectrum of [Cu(POP)(**2**)][PF_6] (^{1}H 500 MHz, ^{13}C 126 MHz, acetone-d_6, 298 K).

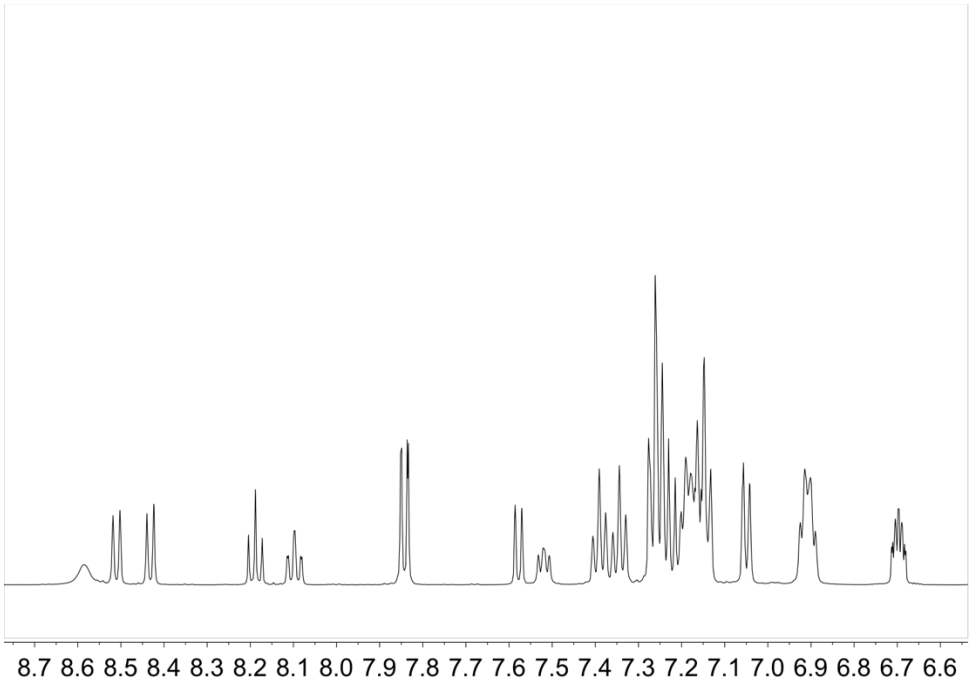

Figure S16. Aromatic region of the ^{1}H NMR spectrum of [Cu(xantphos)(**2**)][PF_6] (500 MHz, acetone-d_6, 298 K).

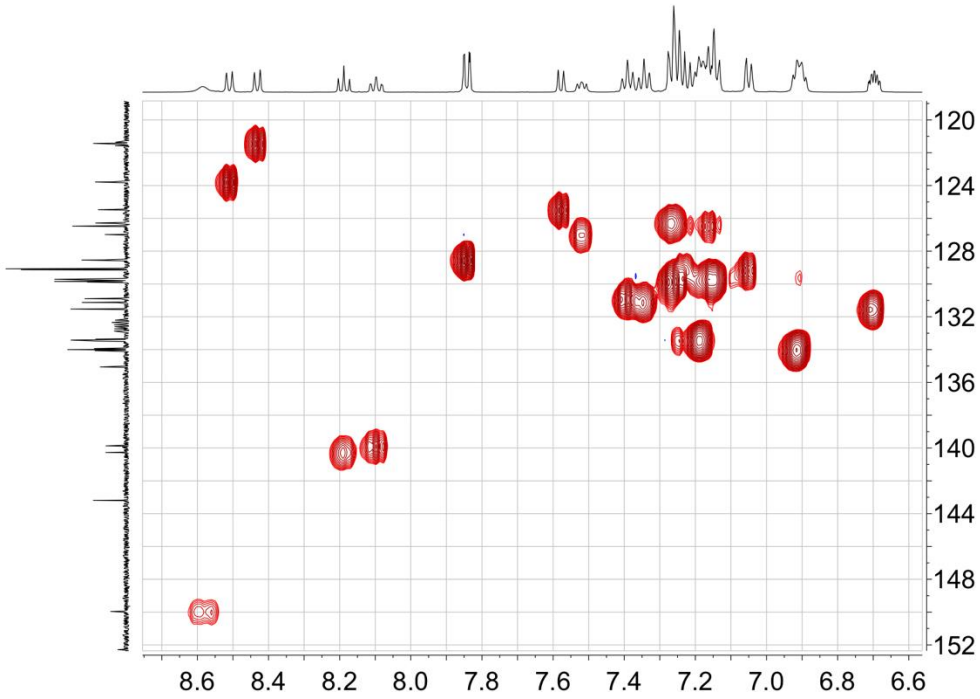

Figure S17. Aromatic region of the HMQC spectrum of [Cu(xantphos)(**2**)][PF_6] (^{1}H 500 MHz, ^{13}C 126 MHz, acetone-d_6, 298 K).

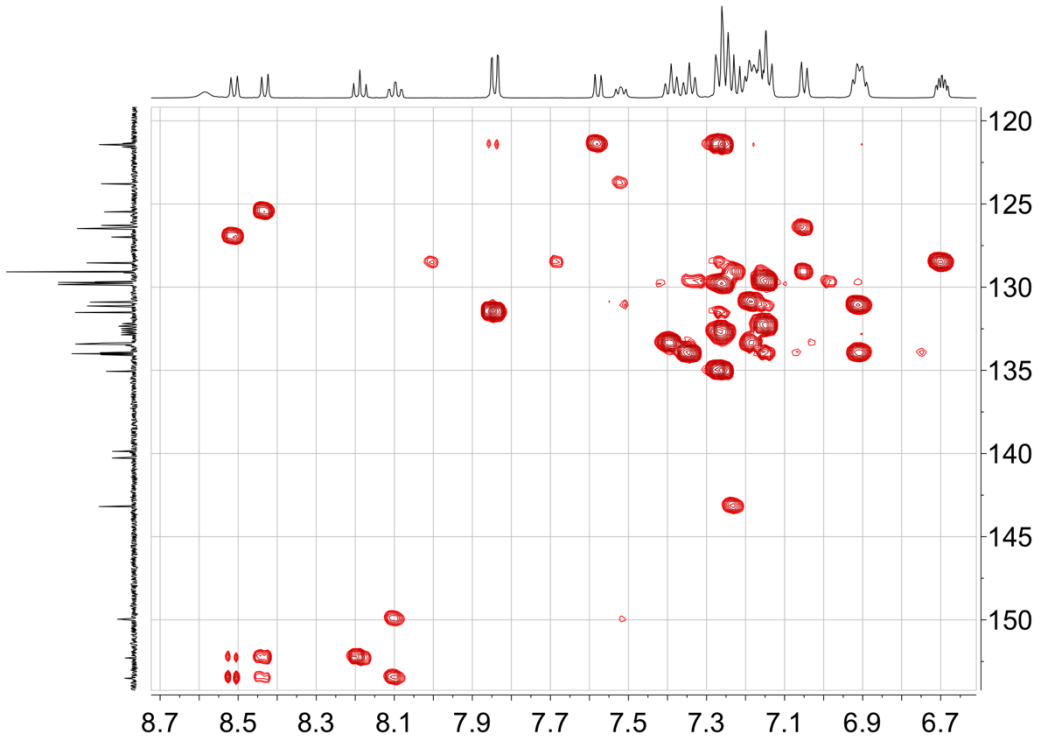

Figure S18. Aromatic region of the HMBC spectrum of [Cu(xantphos)(**2**)][PF_6] (^{1}H 500 MHz, ^{13}C 126 MHz, acetone-d_6, 298 K).

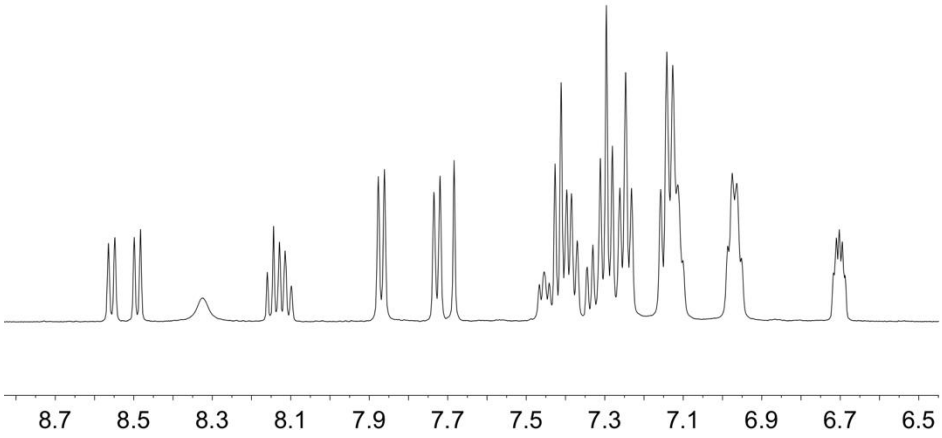

Figure S19. Aromatic region of the ^{1}H NMR spectrum of [Cu(xantphos)(**3**)][PF_6] (500 MHz, acetone-d_6, 298 K).

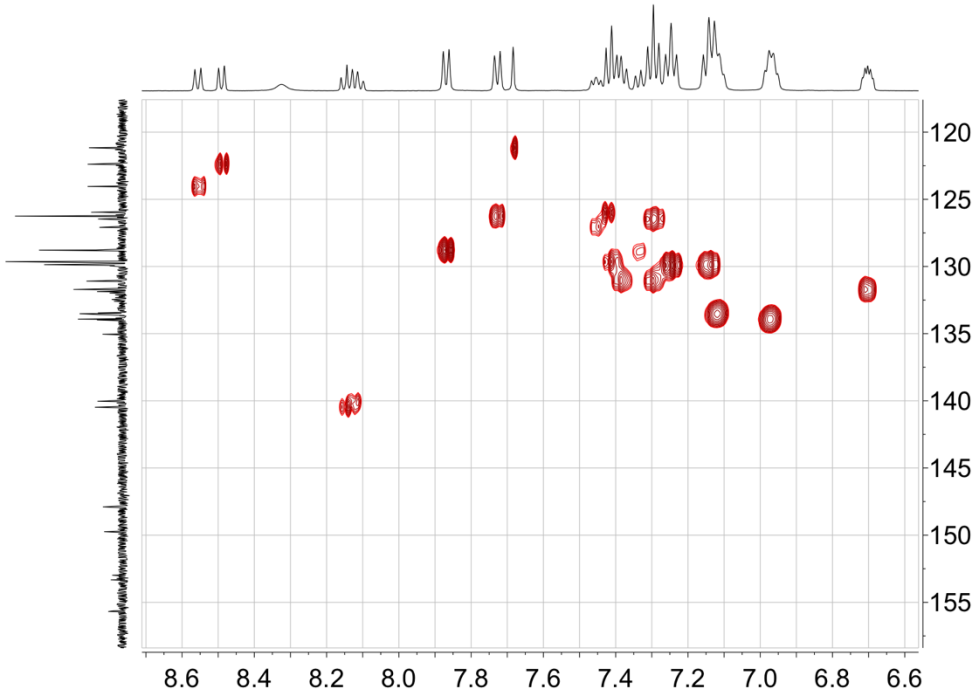

Figure S20. Aromatic region of the HMQC spectrum of [Cu(xantphos)(**3**)][PF_6] (^{1}H 500 MHz, ^{13}C 126 MHz, acetone-d_6, 298 K).

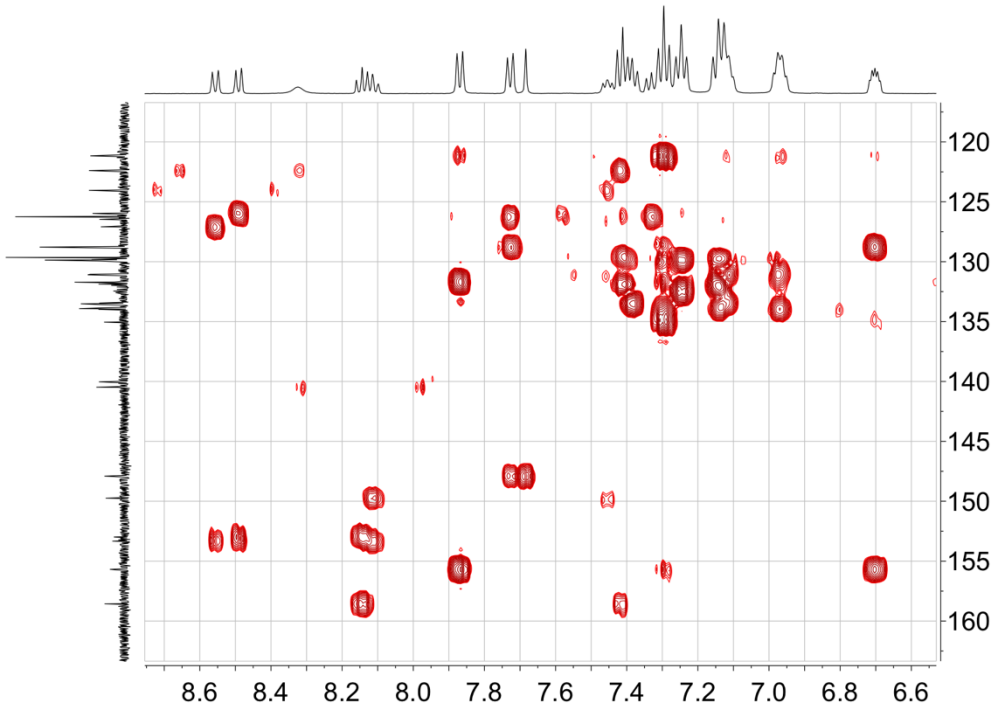

Figure S21. Aromatic region of the HMBC spectrum of [Cu(xantphos)(**3**)][PF_6] (^{1}H 500 MHz, ^{13}C 126 MHz, acetone-d_6, 298 K).

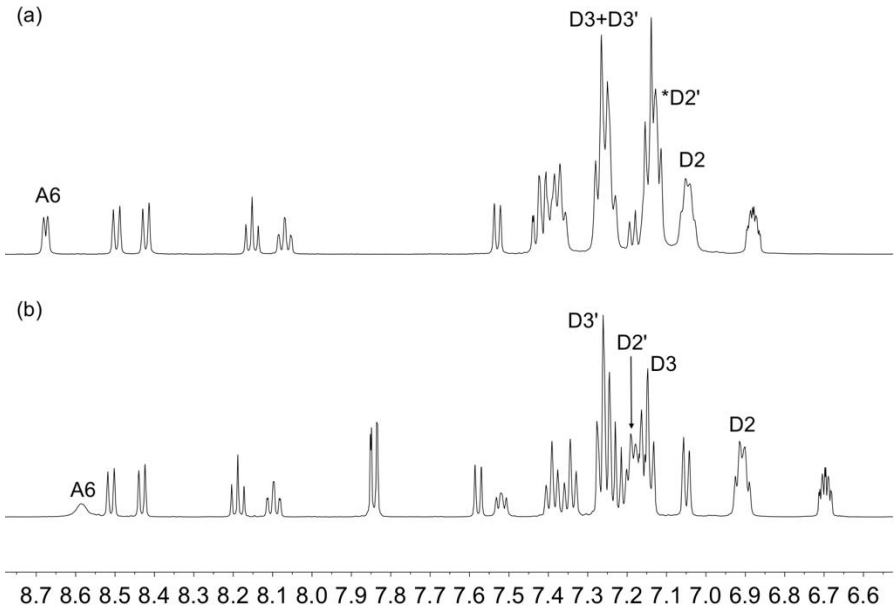

Figure S22. Aromatic regions of the ^{1}H NMR spectra (500 MHz, acetone-d_6, 298 K) of (a) [Cu(POP)(**2**)][PF_6] and (b) [Cu(xantphos)(**2**)][PF_6]. Compare with Figure 2 in the main article.

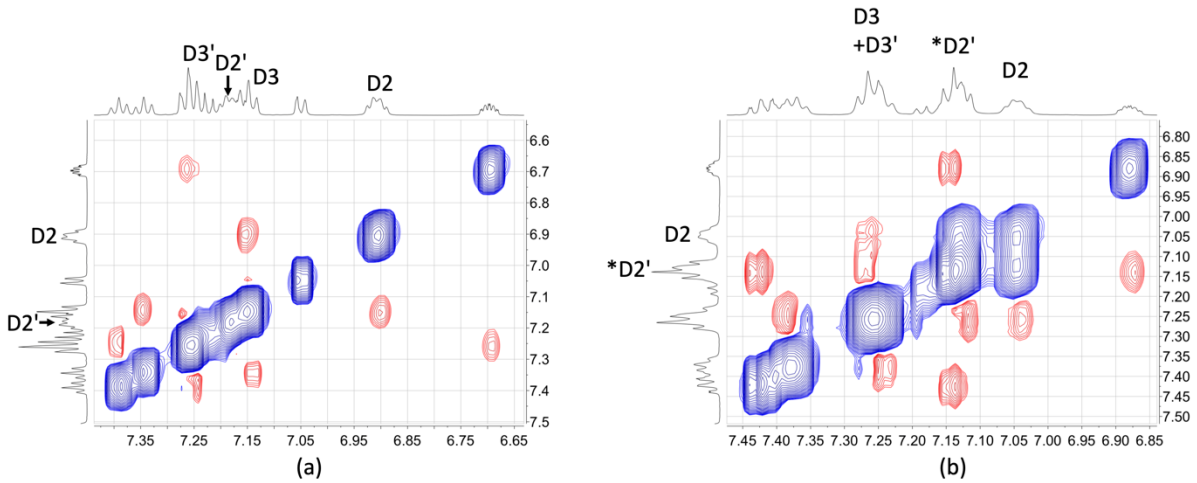

Figure S23. Part of the NOESY spectra (500 MHz, acetone-d_6, 298 K) of (a) [Cu(xantphos)(**2**)][PF_6] and (b) [Cu(POP)(**2**)][PF_6]. EXSY peaks appear in the opposite phase (blue) to NOESY crosspeaks (red), and are observed between H^{D2} and $H^{D2'}$ in [Cu(POP)(**2**)][PF_6] but not in [Cu(xantphos)(**2**)][PF_6]. * The signal for D2' overlaps with signals assigned to E2, C4 and C6.

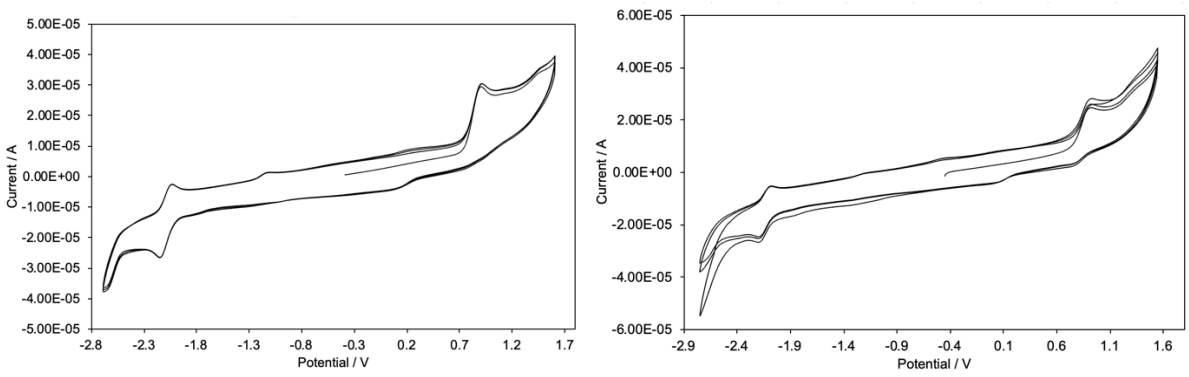

Figure S24. Three successive scans in the cyclic voltammograms of [Cu(POP)(**2**)][PF_6] (left) and [Cu(xantphos)(**2**)][PF_6] (right). Propylene carbonate solutions, and referenced internally to Fc/Fc^+ = 0.0 V; [^{n}Bu$_4$N][PF_6] as supporting electrolyte and scan rate of 0.1 V s^{-1}.