Supplementary Materials: Heteroleptic [Cu(P^P)(N^N)][PF_6] Compounds with Isomeric Dibromo-1,10-Phenanthroline Ligands

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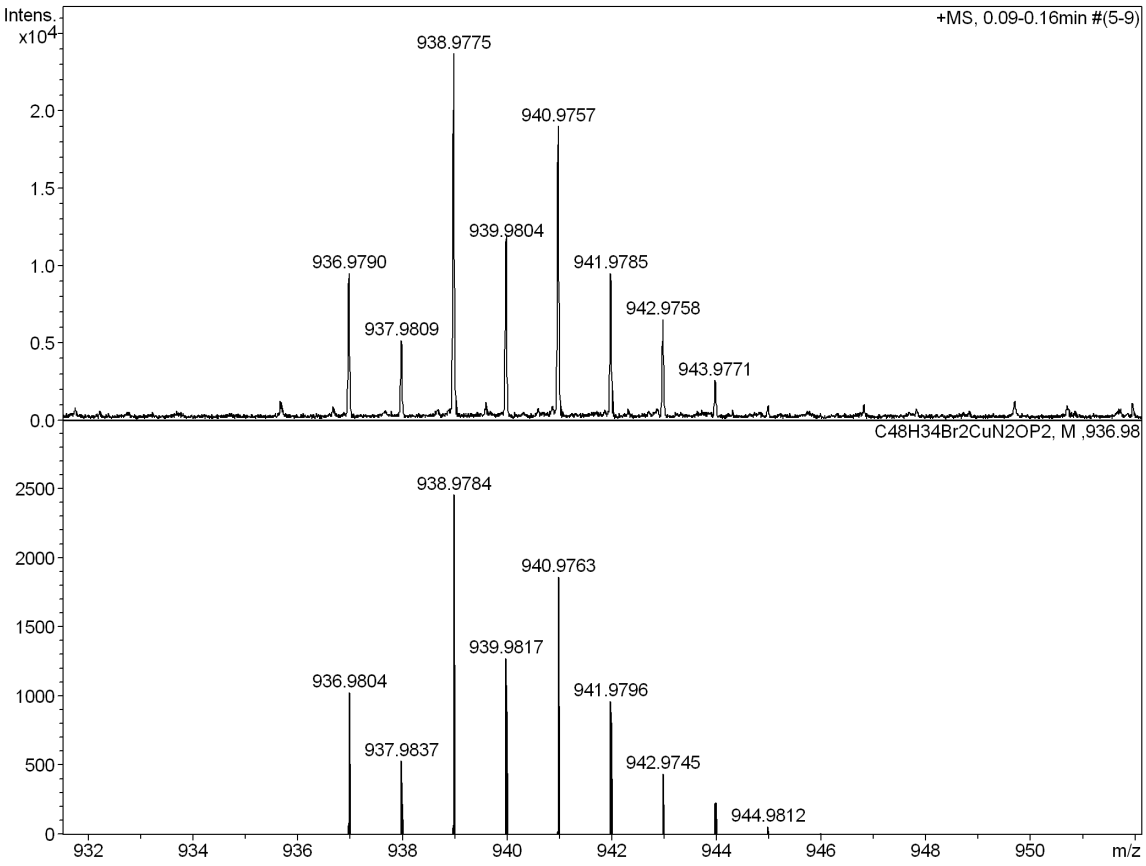


Fig. S1. The [M–PF_6]$^+$ peak in the high-resolution electrospray mass spectrum of [Cu(POP)(2,9-Br_2phen)][PF_6]: top, observed and bottom, calculated.

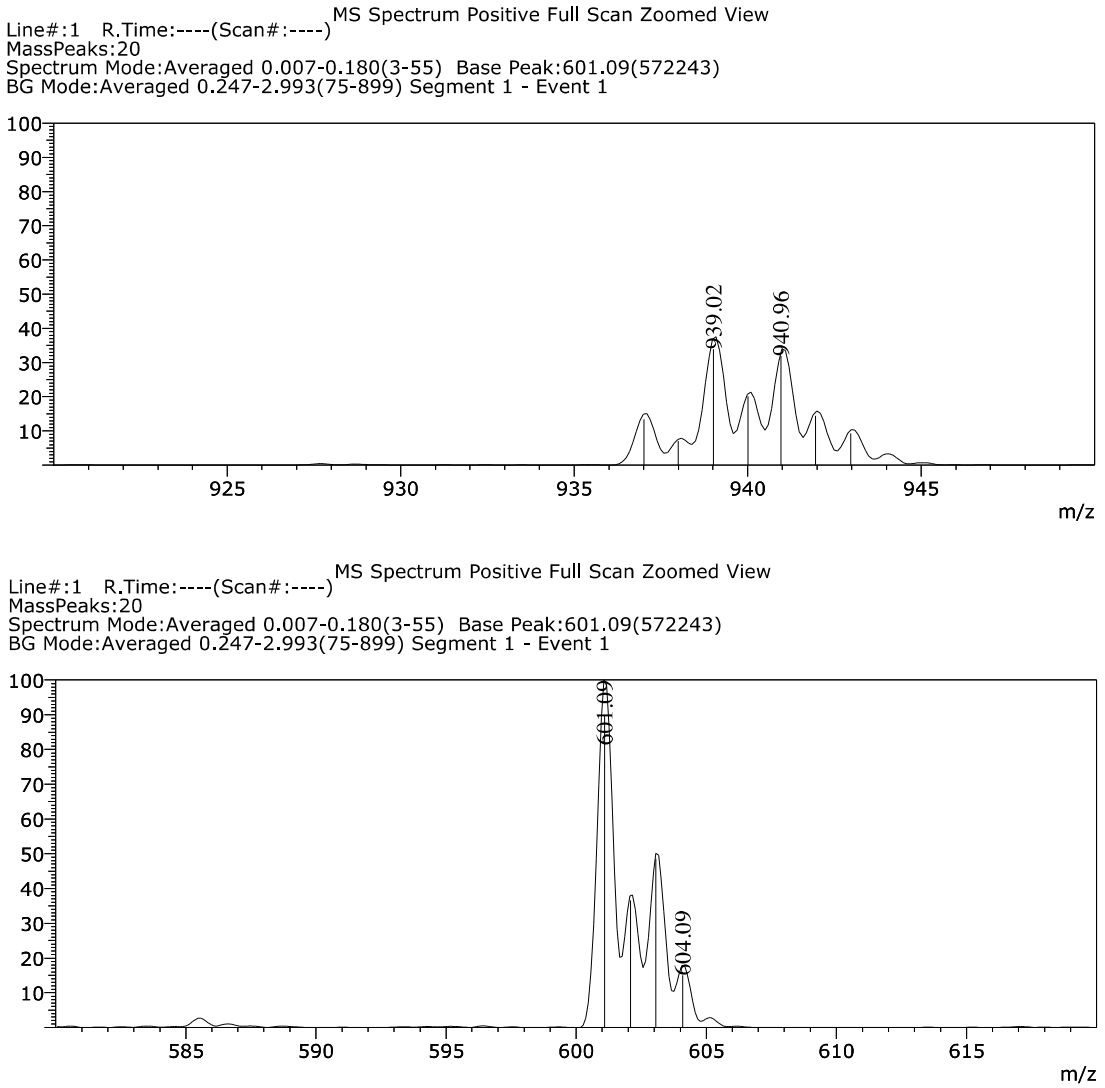


Fig. S2. Expansions of the peaks for the $[M–PF_6]^+$ and $[Cu(POP)]^+$ ions in the ESI mass spectrum of $[Cu(POP)(2,9\text{-}Br_2phen)][PF_6]$.

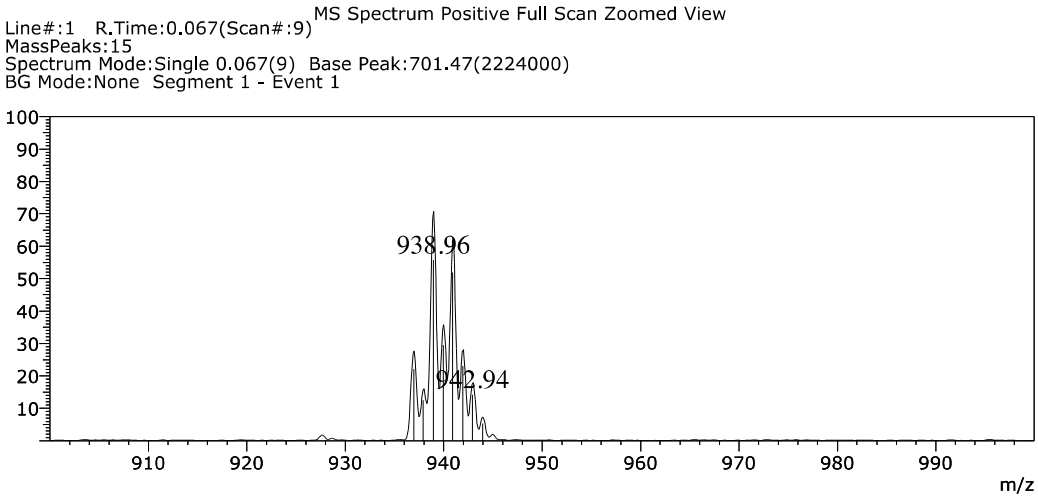


Fig. S3. Expansion of the peak for the $[M–PF_6]^+$ ion in the ESI mass spectrum of $[Cu(POP)(3,8\text{-}Br_2phen)][PF_6]$.

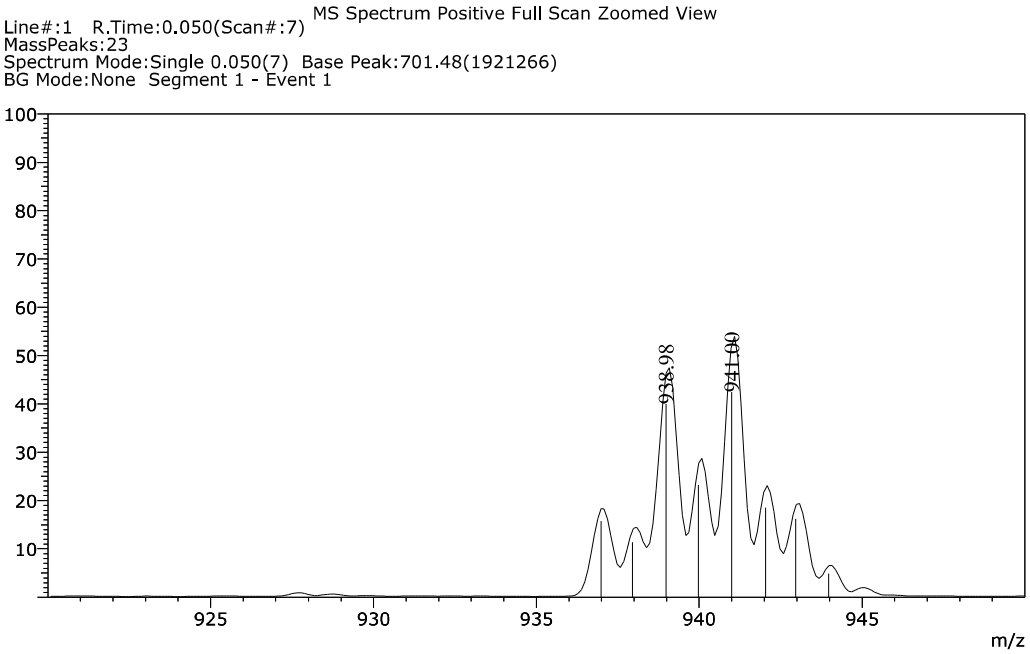


Fig. S4. Expansion of the peak for the $[M–PF_6]^+$ ion in the ESI mass spectrum of [Cu(POP)(4,7-Br_2phen)][PF_6].

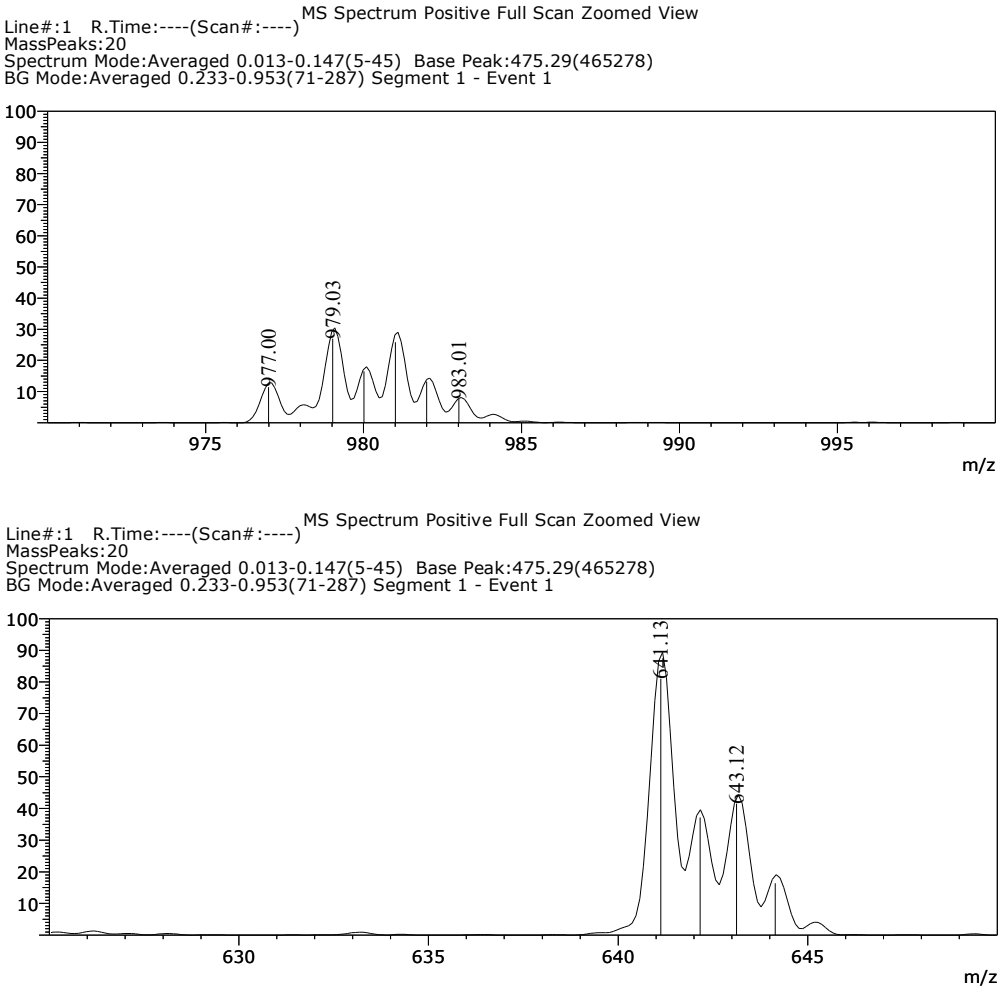


Fig. S5. Expansions of the peaks for the $[M–PF_6]^+$ and $[Cu(xantphos)]^+$ ions in the ESI mass spectrum of [Cu(xantphos)(2,9-Br_2phen)][PF_6].

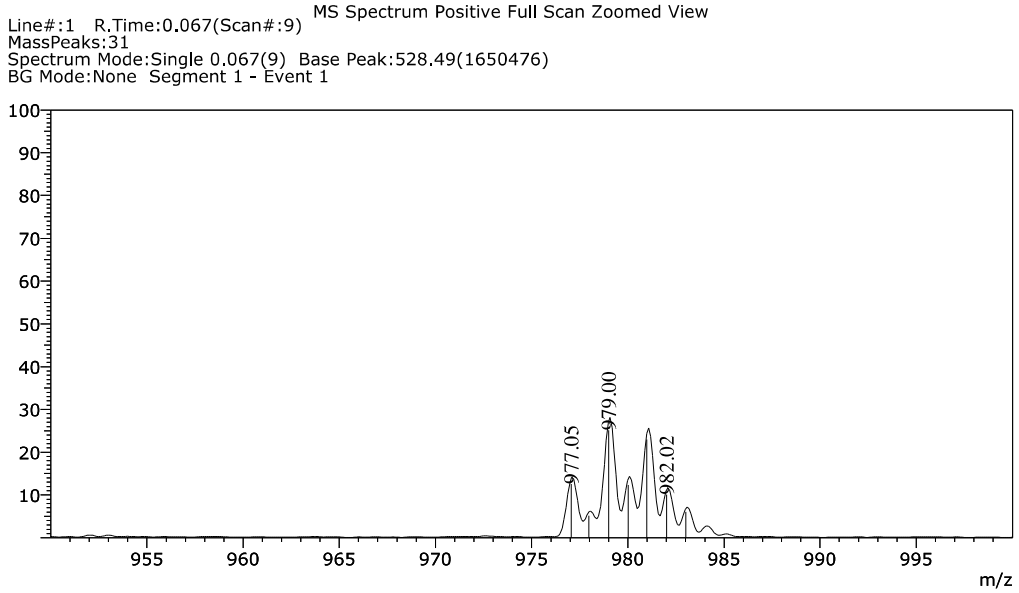


Fig. S6. Expansion of the peak for the $[M–PF_6]^+$ ion in the ESI mass spectrum of [Cu(xantphos)(3,8-Br_2phen)][PF_6].

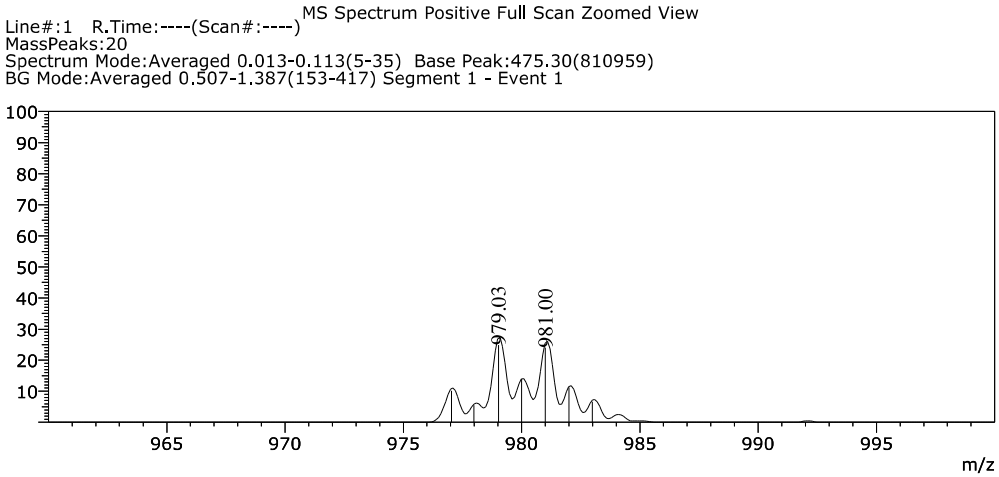


Fig. S7. Expansion of the peak for the $[M–PF_6]^+$ ion in the ESI mass spectrum of [Cu(xantphos)(4,7-Br_2phen)][PF_6].

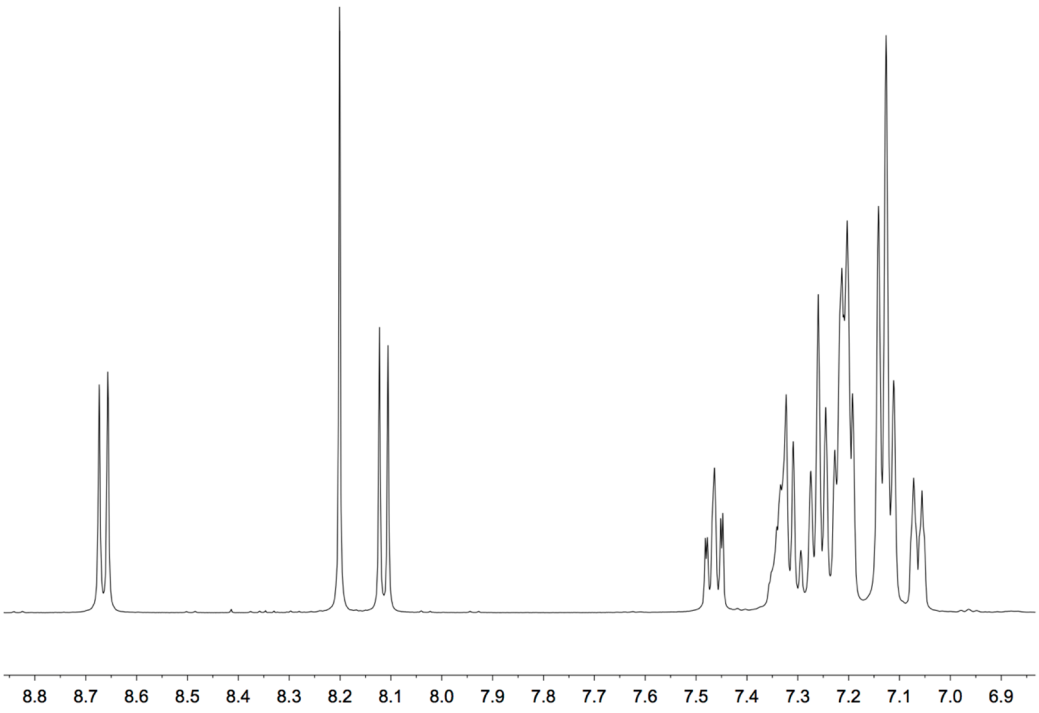


Fig. S8. Aromatic region of the ^{1}H NMR spectrum (500 MHz, acetone-d_6, 298 K) of [Cu(POP)(2,9-Br_2phen)][PF_6].

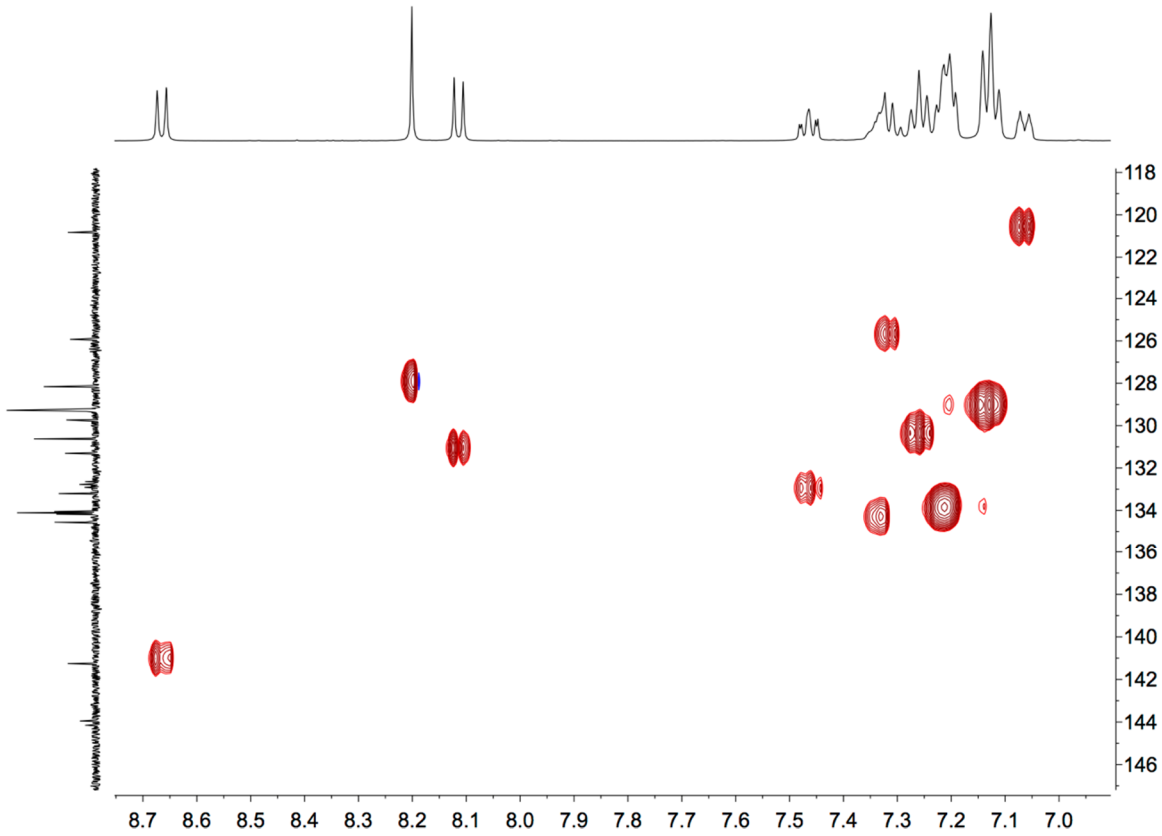


Fig. S9. HMQC spectrum (500 MHz ^{1}H, 126 MHz ^{13}C{^{1}H}, acetone-d_6, 298 K) of [Cu(POP)(2,9-Br_2phen)][PF_6].

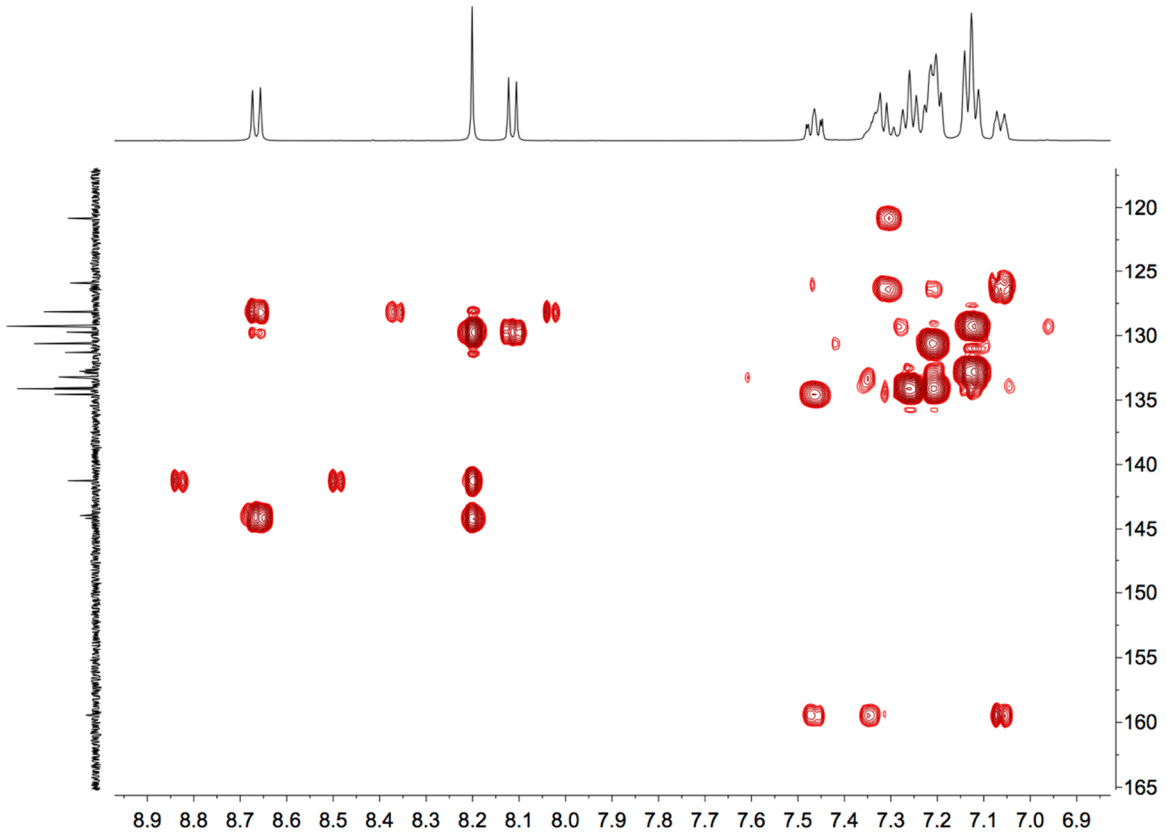


Fig. S10. HMBC spectrum (500 MHz ^{1}H, 126 MHz ^{13}C{^{1}H}, acetone-d_6, 298 K) of [Cu(POP)(2,9-Br_2phen)][PF_6].

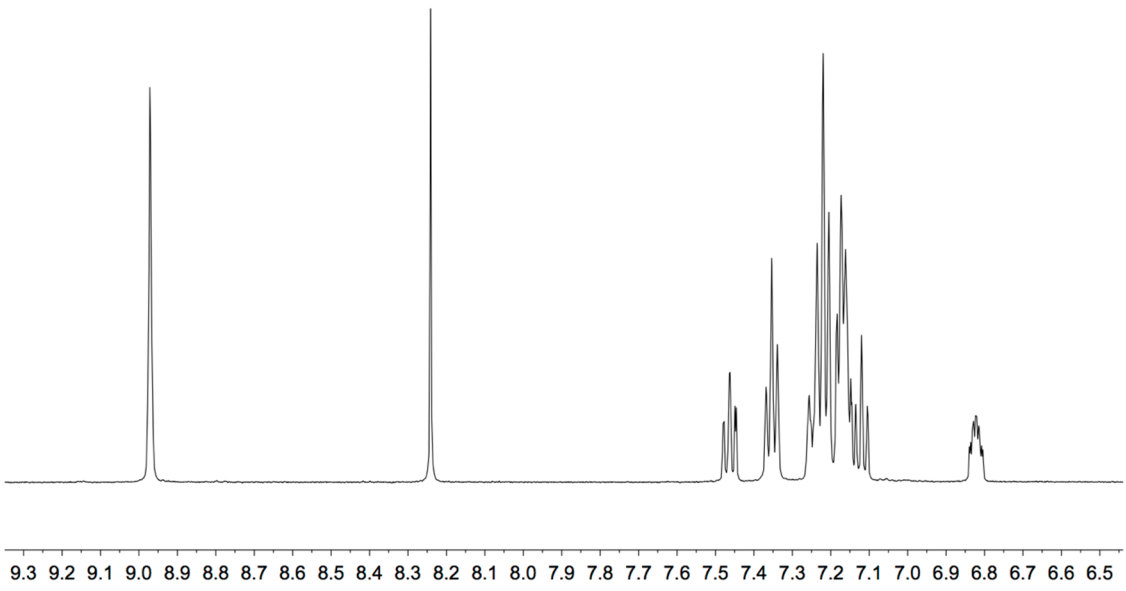


Fig. S11. Aromatic region of the ^{1}H NMR spectrum (500 MHz, acetone-d_6, 298 K) of [Cu(POP)(3,8-Br_2phen)][PF_6].

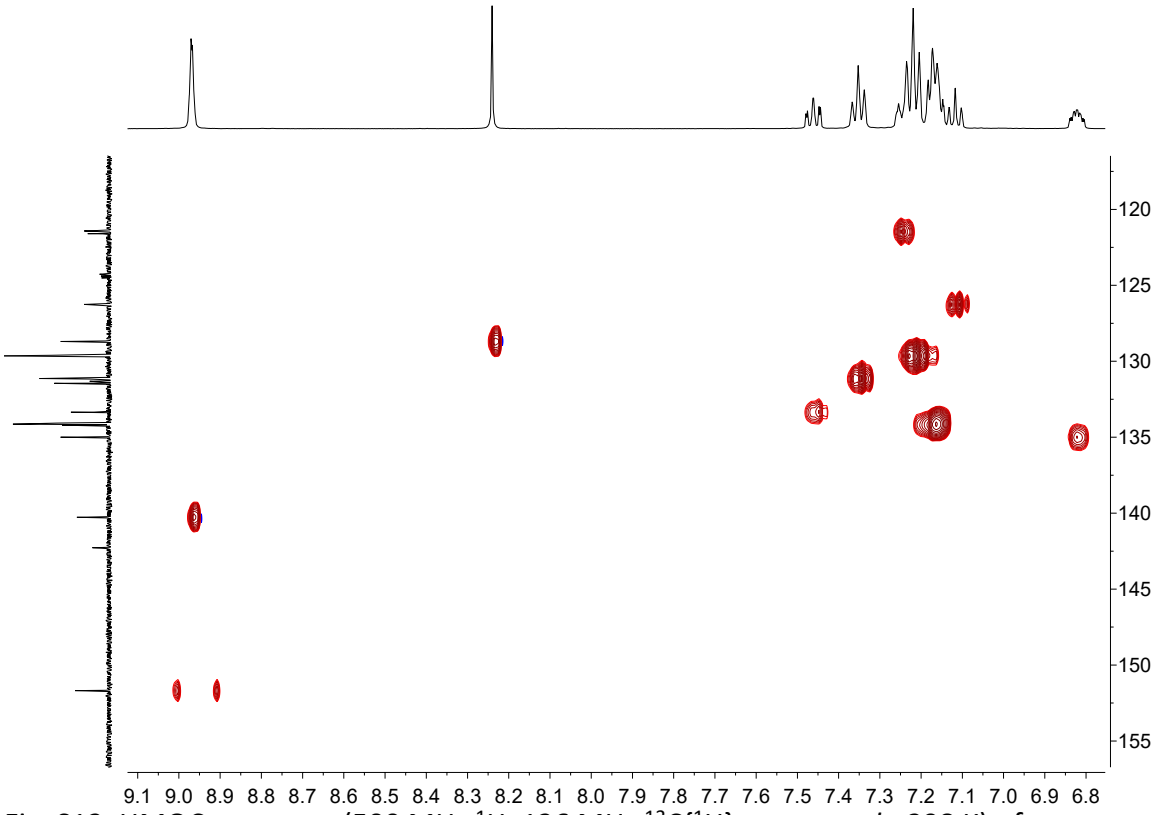


Fig. S12. HMQC spectrum (500 MHz ^{1}H, 126 MHz ^{13}C{^{1}H}, acetone-d_6, 298 K) of [Cu(POP)(3,8-Br_2phen)][PF_6].

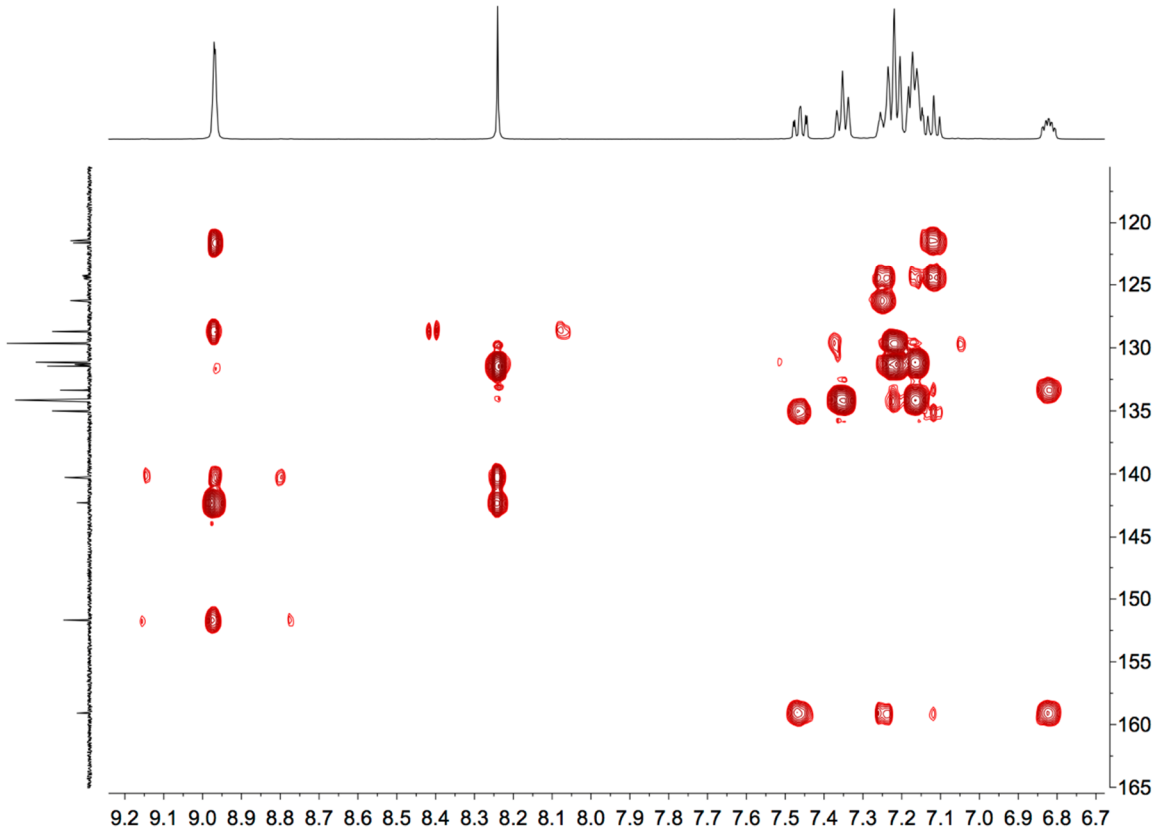


Fig. S13. HMBC spectrum (500 MHz ^{1}H, 126 MHz ^{13}C{^{1}H}, acetone-d_6, 298 K) of [Cu(POP)(3,8-Br_2phen)][PF_6].

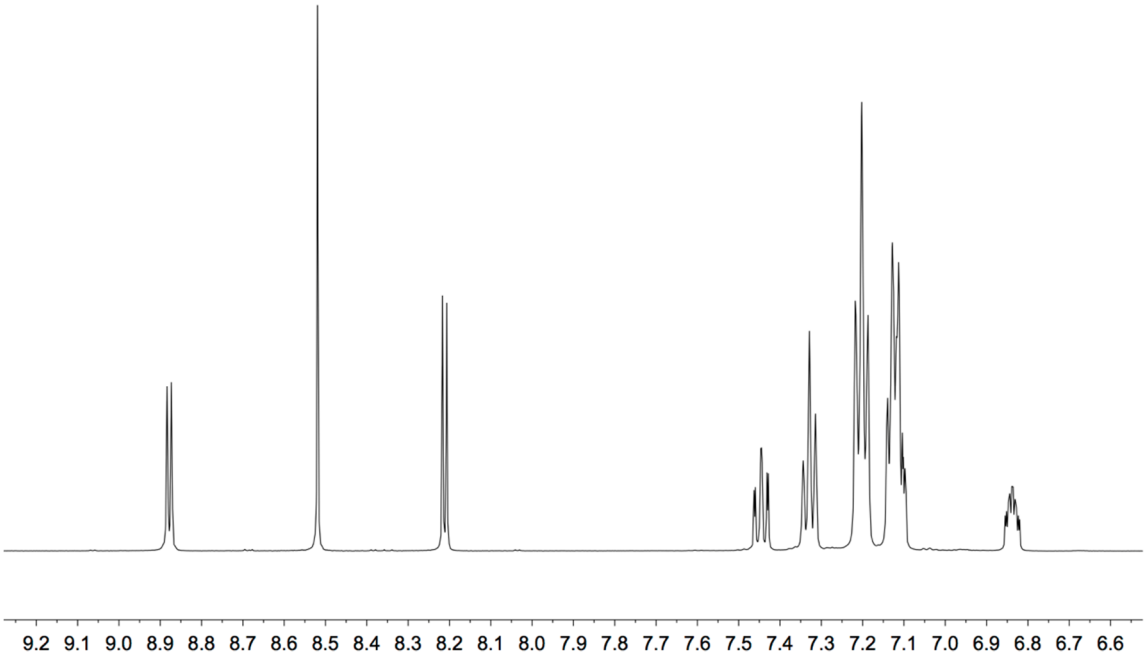


Fig. S14. Aromatic region of the ^{1}H NMR spectrum (500 MHz, acetone-d_6, 298 K) of [Cu(POP)(4,7-Br_2phen)][PF_6].

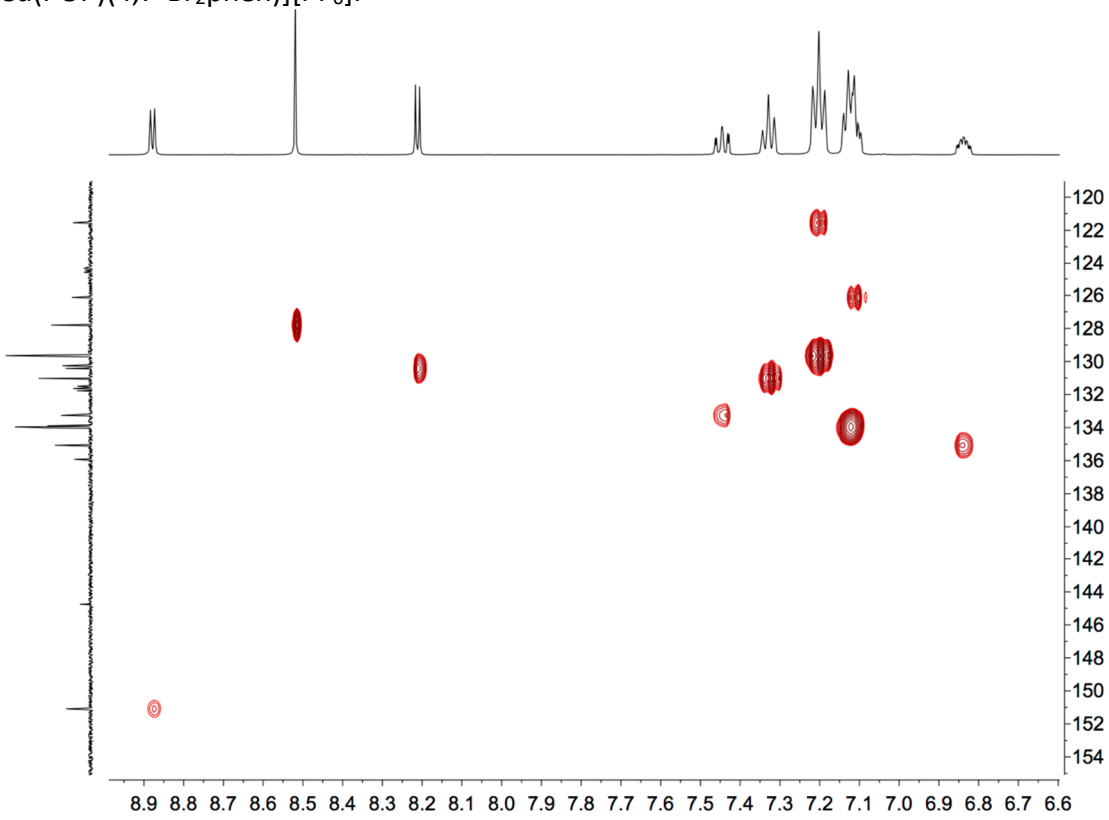


Fig. S15. HMQC spectrum (500 MHz ^{1}H, 126 MHz ^{13}C{^{1}H}, acetone-d_6, 298 K) of [Cu(POP)(4,7-Br_2phen)][PF_6].

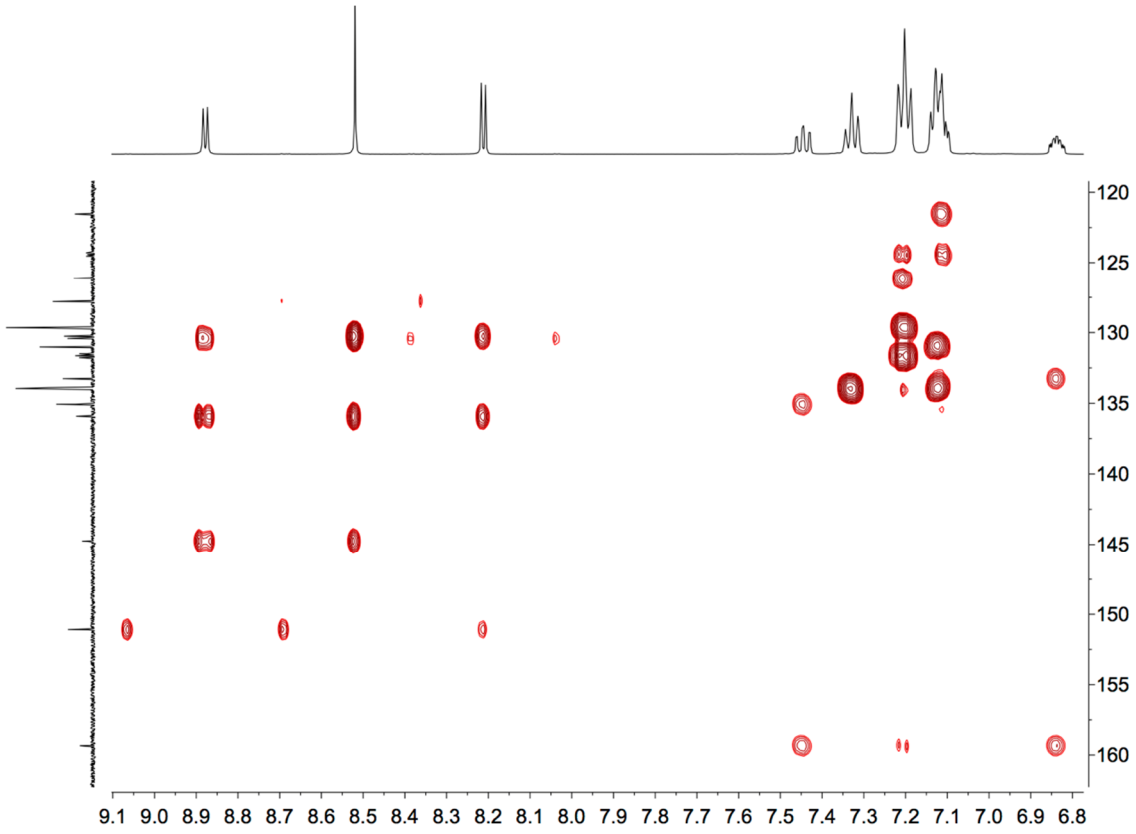


Fig. S16. HMBC spectrum (500 MHz ^{1}H, 126 MHz ^{13}C{^{1}H}, acetone-d_6, 298 K) of [Cu(POP)(4,7-Br_2phen)][PF_6].

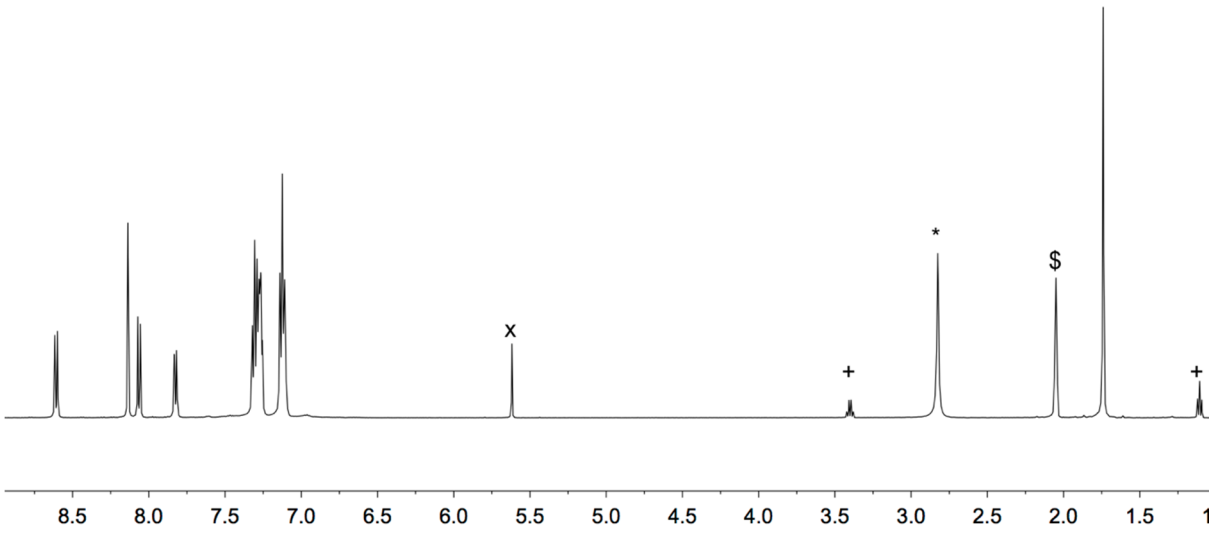


Fig. S17. ^{1}H NMR spectrum (500 MHz, acetone-d_6, 298 K) of [Cu(xantphos)(2,9-Br_2phen)][PF_6]. $ = acetone-d_5; * = H_2O; + = Et_2O; x = CH_2Cl_2.

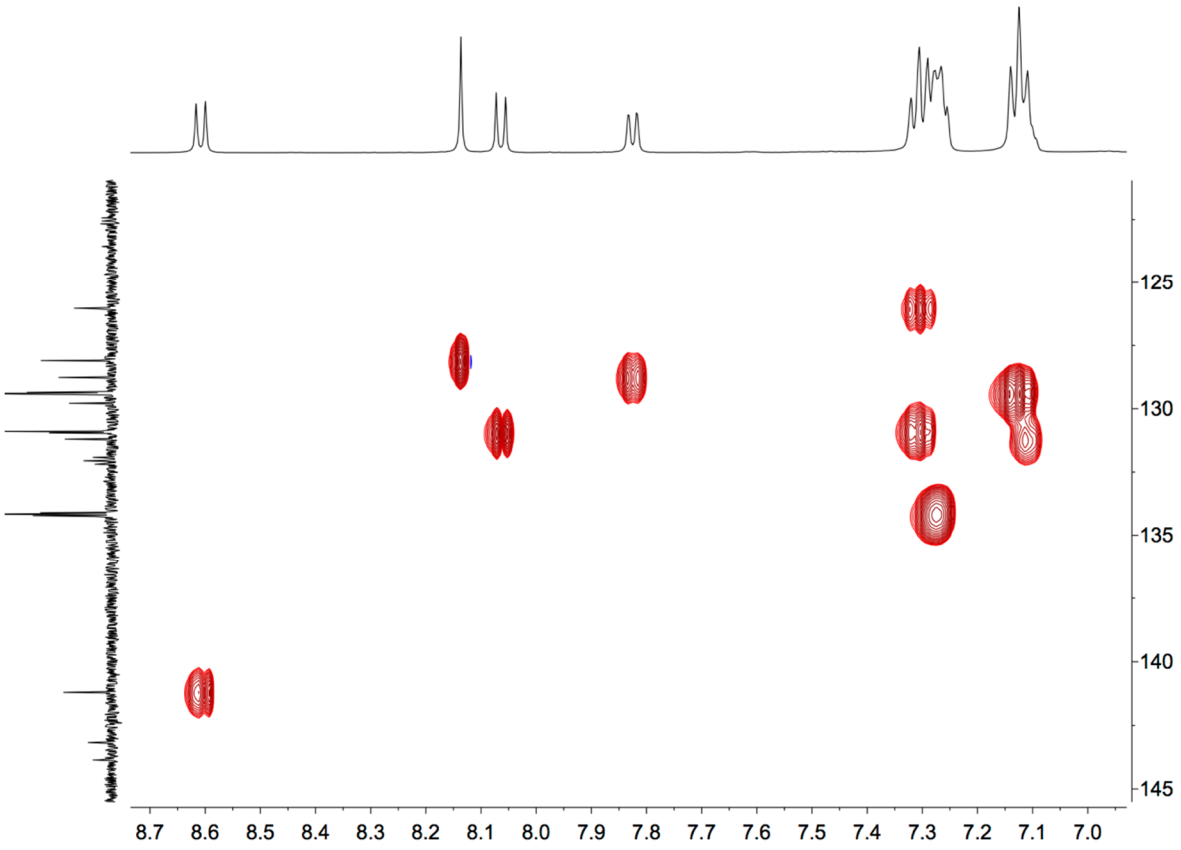


Fig. S18. HMQC spectrum (aromatic region, 500 MHz ^{1}H, 126 MHz ^{13}C{^{1}H}, acetone-d_6, 298 K) of [Cu(xantphos)(2,9-Br_2phen)][PF_6].

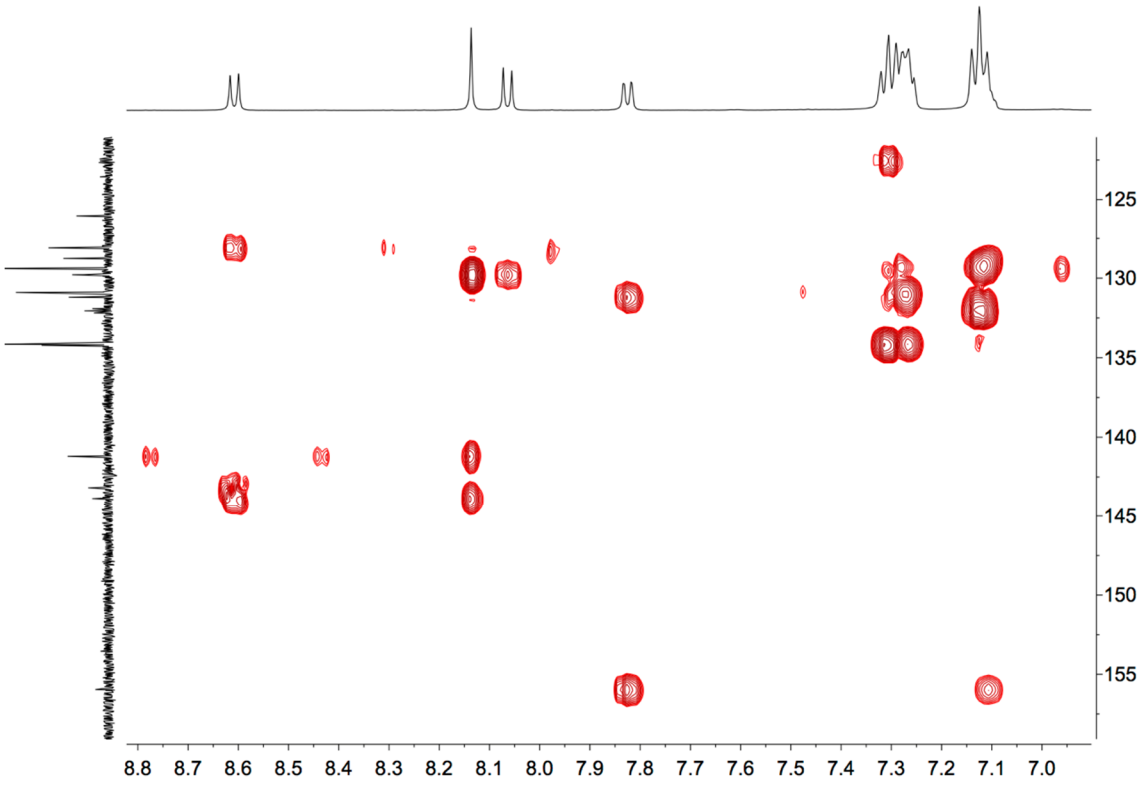


Fig. S19. HMBC spectrum (aromatic region, 500 MHz ^{1}H, 126 MHz ^{13}C{^{1}H}, acetone-d_6, 298 K) of [Cu(xantphos)(2,9-Br_2phen)][PF_6].

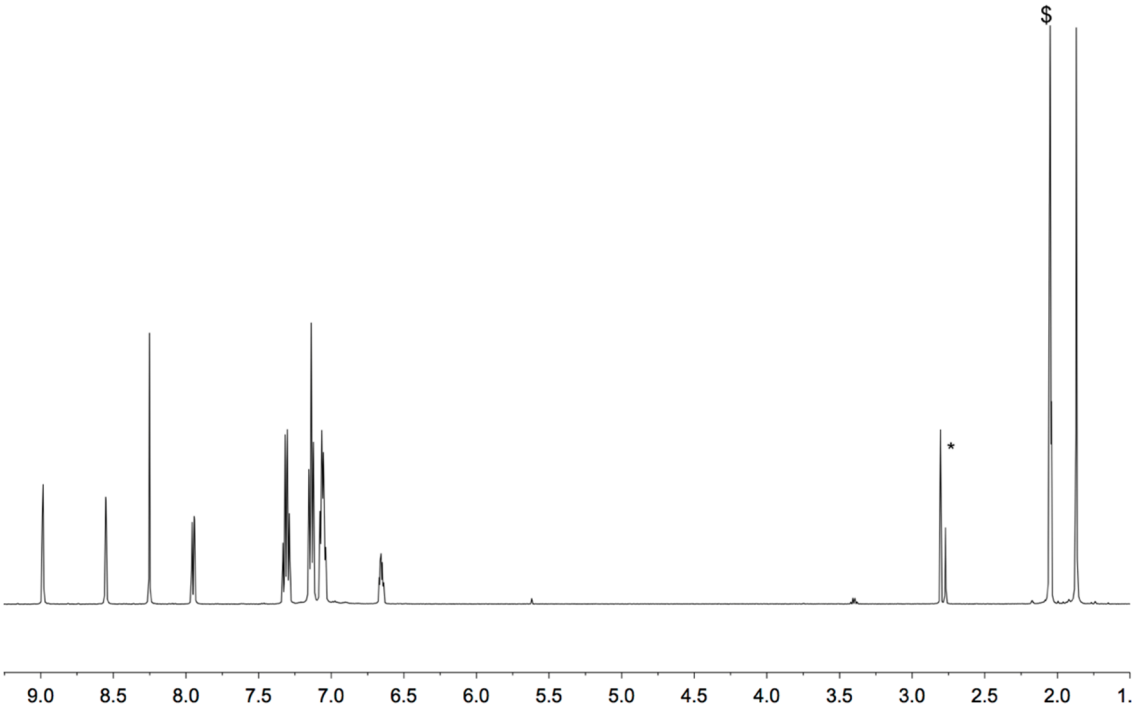


Fig. S20. ^{1}H NMR spectrum (500 MHz, acetone-d_6, 298 K) of [Cu(xantphos)(3,8-Br_2phen)][PF_6]. $ = acetone-d_5; * = H_2O and HOD.

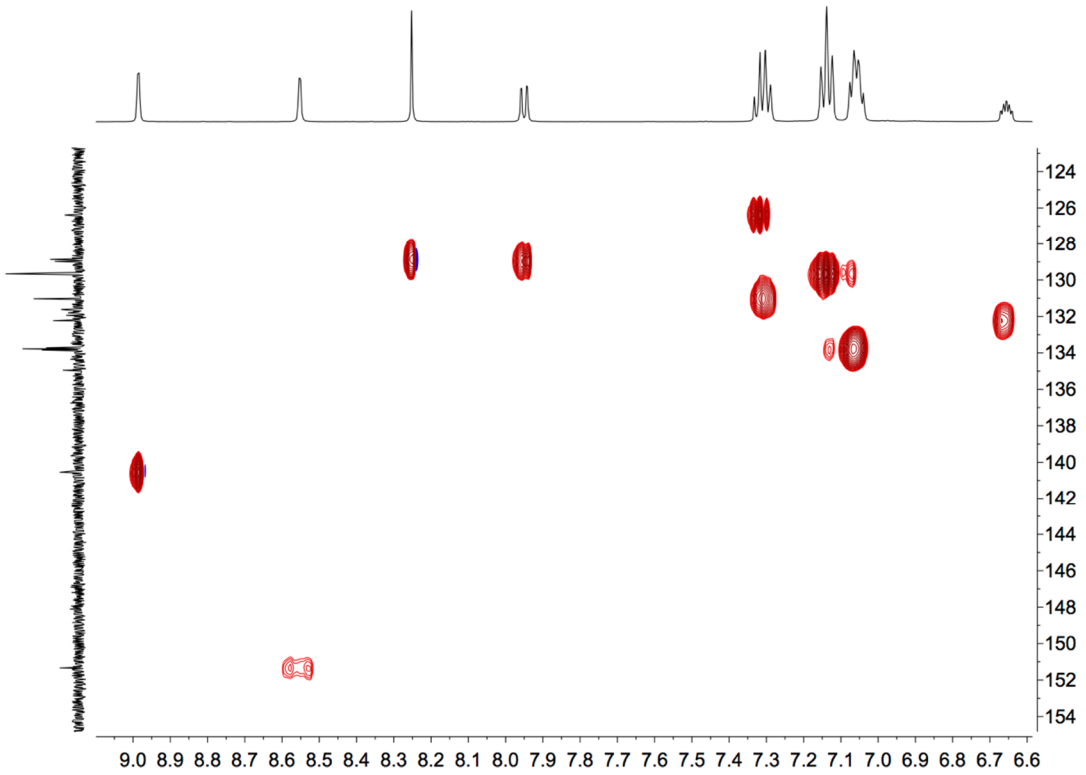


Fig. S21. HMQC spectrum (aromatic region, 500 MHz ^{1}H, 126 MHz ^{13}C{^{1}H}, acetone-d_6, 298 K) of [Cu(xantphos)(3,8-Br$_2$phen)][PF$_6$].

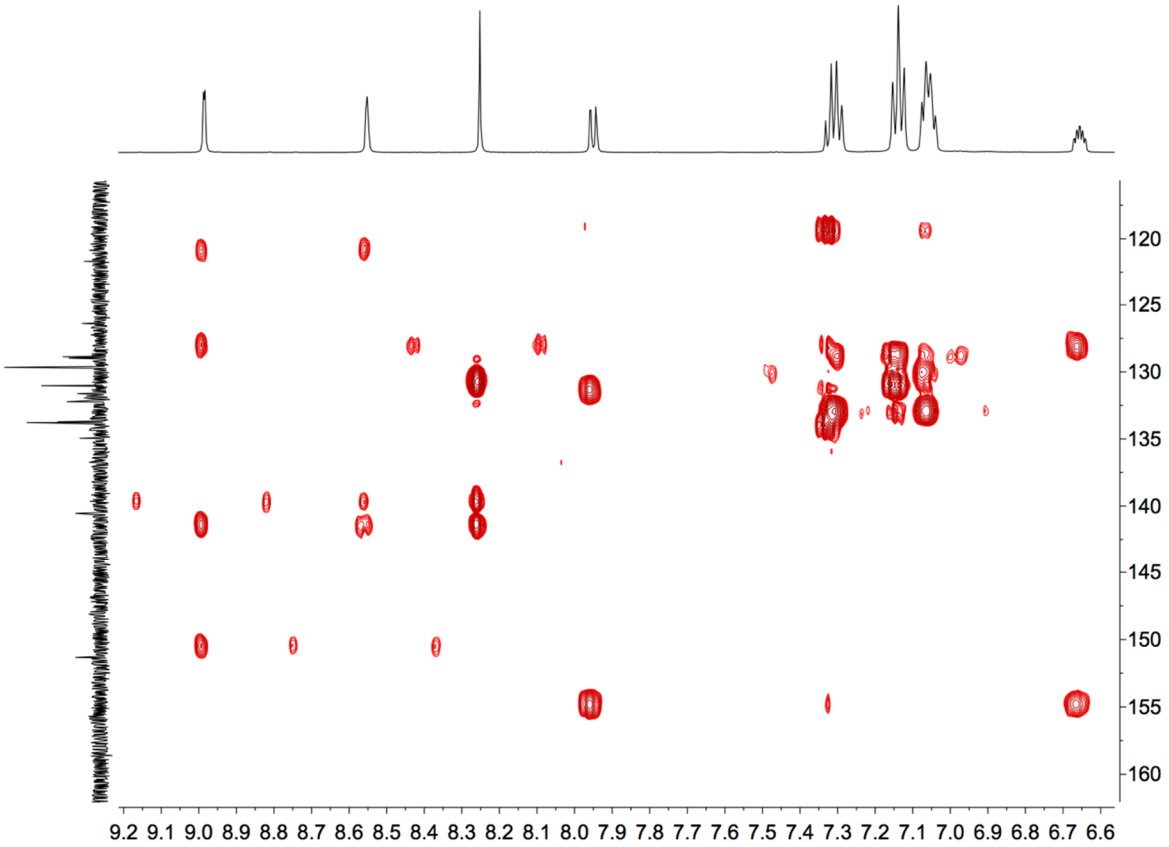


Fig. S22. HMBC spectrum (aromatic region, 500 MHz ^{1}H, 126 MHz ^{13}C{^{1}H}, acetone-d_6, 298 K) of [Cu(xantphos)(3,8-Br$_2$phen)][PF$_6$].

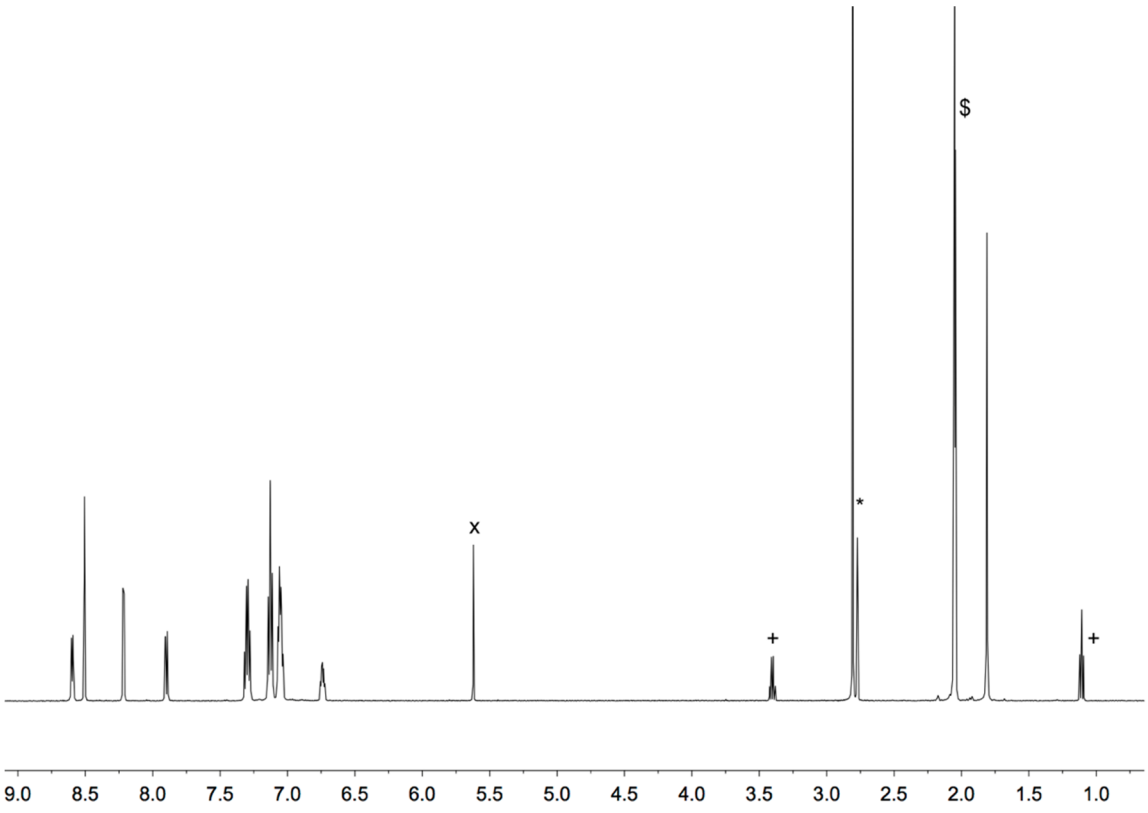


Fig. S23. ^{1}H NMR spectrum (500 MHz, acetone-d_6, 298 K) of [Cu(xantphos)(4,7-Br_2phen)][PF_6]. $ = acetone-d_5; * = H_2O and HOD; x = CH_2Cl_2; + = Et_2O.

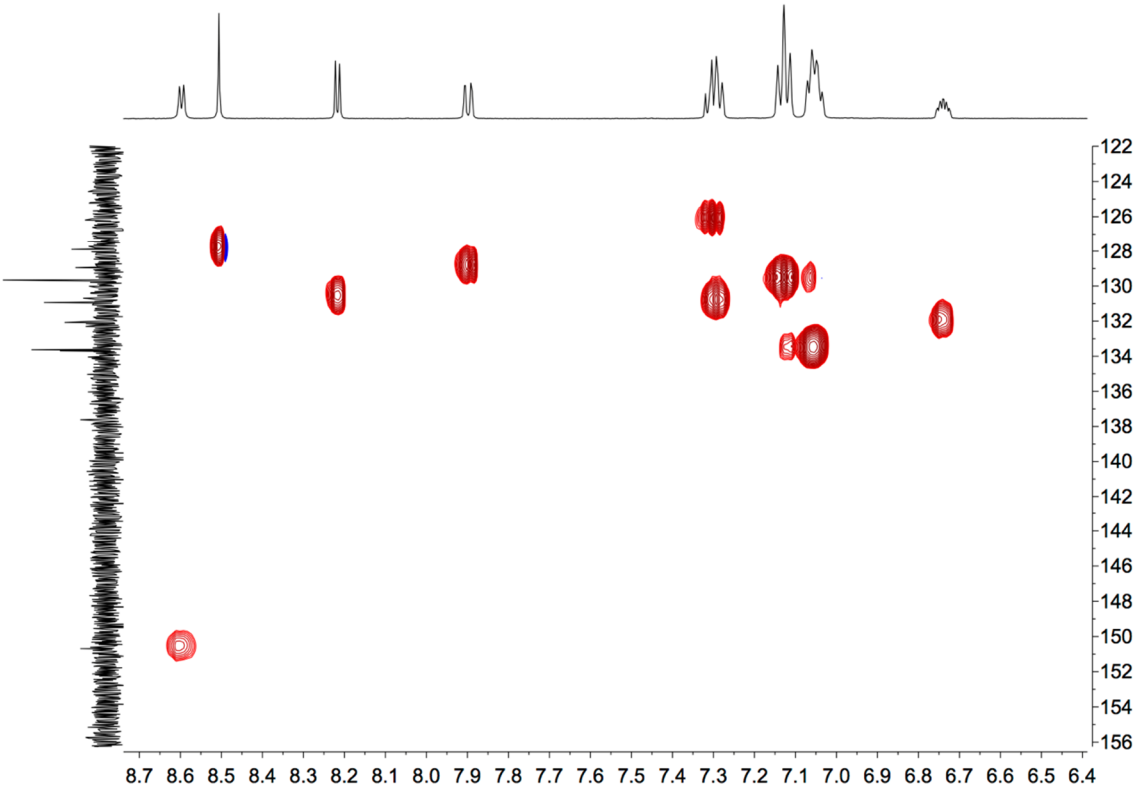


Fig. S24. HMQC spectrum (aromatic region, 500 MHz ^{1}H, 126 MHz ^{13}C{^{1}H}, acetone-d_6, 298 K) of [Cu(xantphos)(4,7-Br_2phen)][PF_6].

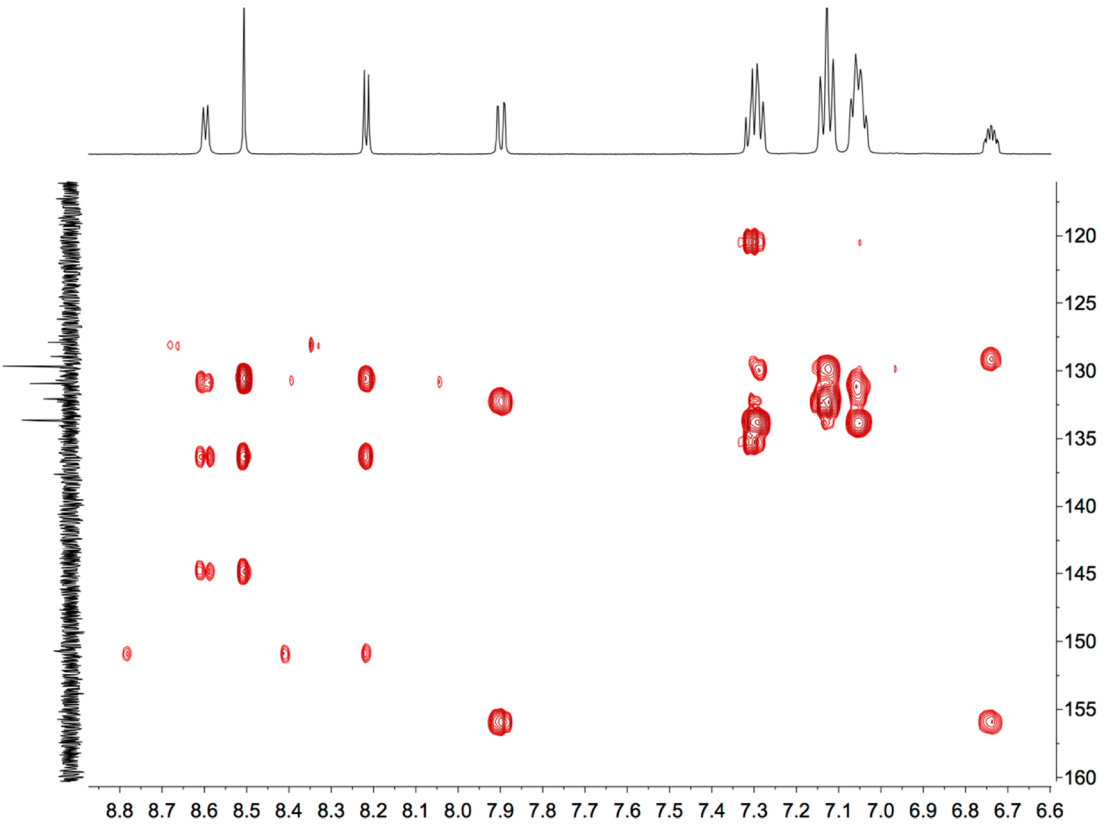
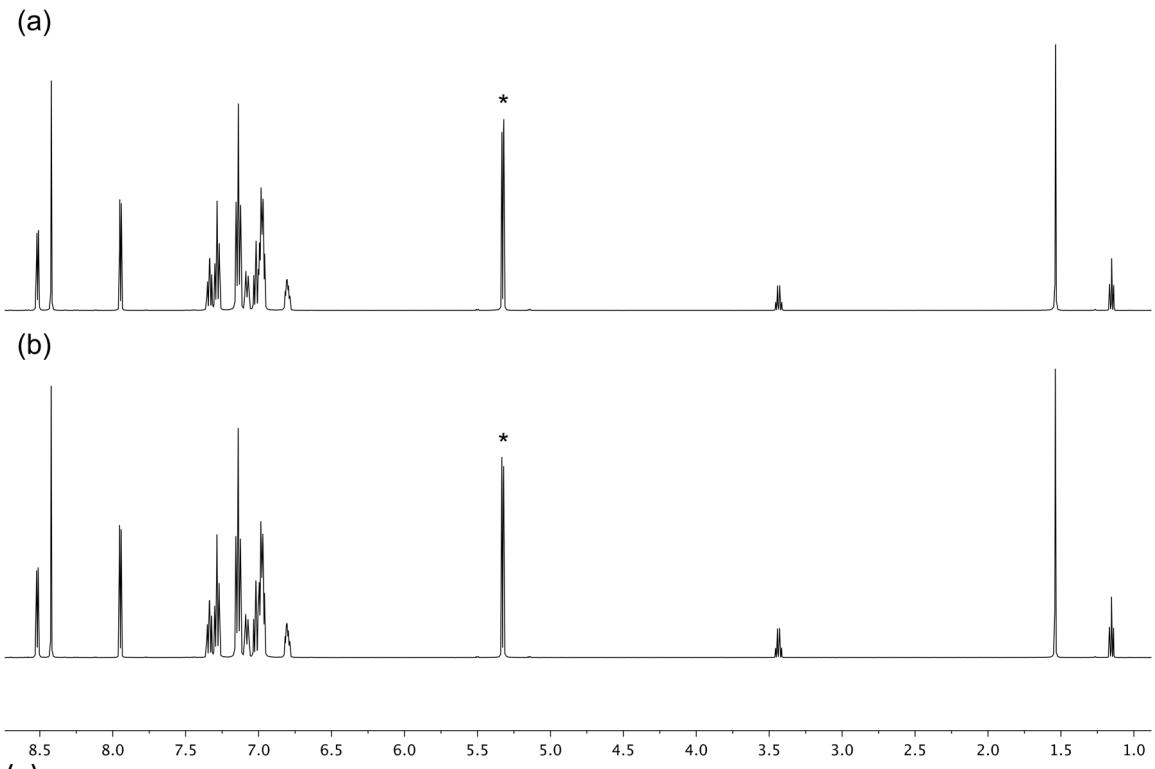
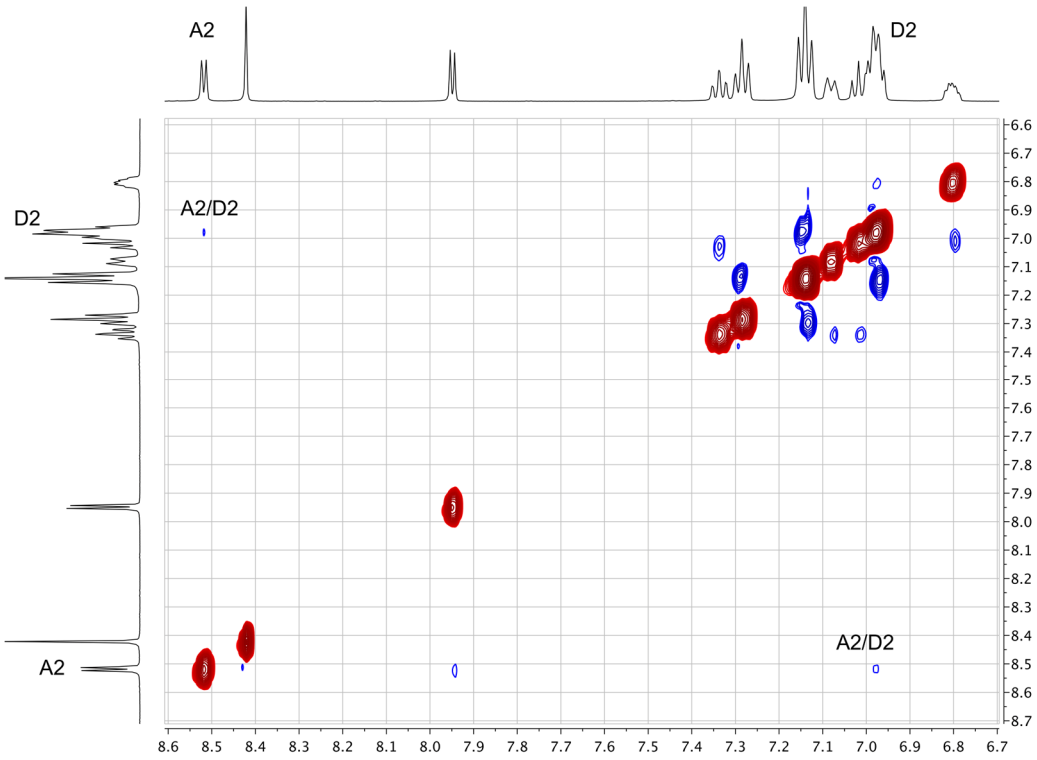


Fig. S25. HMBC spectrum (aromatic region, 500 MHz ^{1}H, 126 MHz ^{13}C{^{1}H}, acetone-d_6, 298 K) of [Cu(xantphos)(4,7-Br_2phen)][PF_6].



(a)



(b)

Fig. S26. (a) ^{1}H NMR spectrum (500 MHz, CD_2Cl_2, 298 K, aromatic region) of [Cu(POP)(4,7-Br_2phen)][PF_6]: (a) after freshly preparing the NMR sample and (b) after 6 hours standing at room temperature. (b) NOESY spectrum (500 MHz, CD_2Cl_2, 298 K, aromatic region) of [Cu(POP)(4,7-Br_2phen)][PF_6].

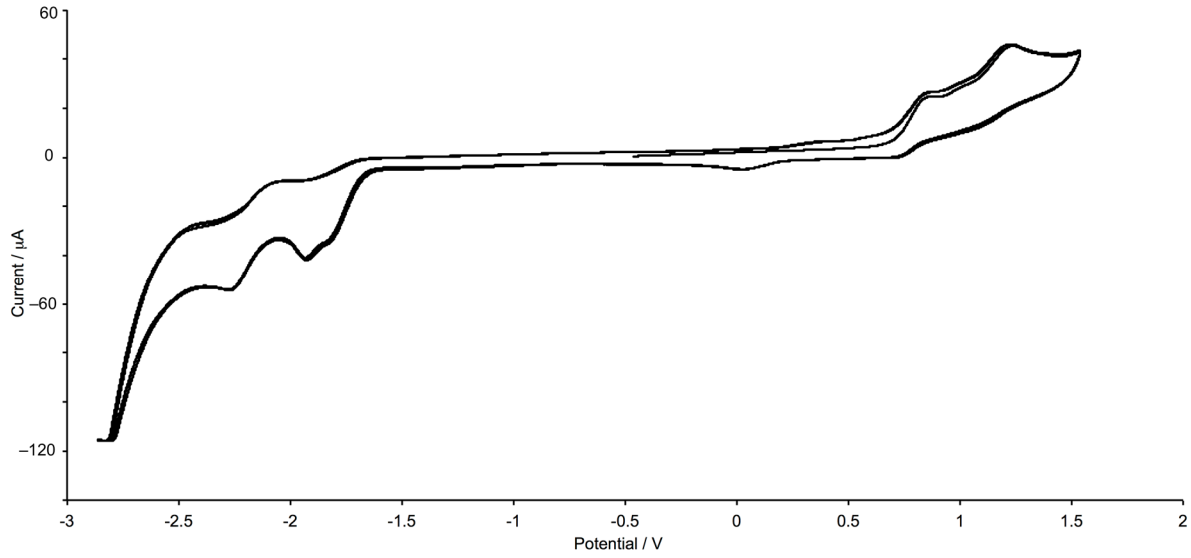
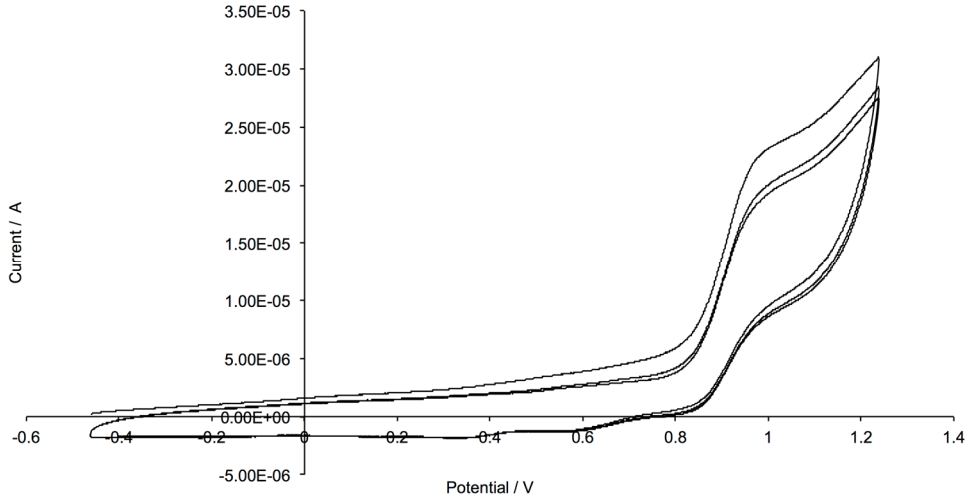
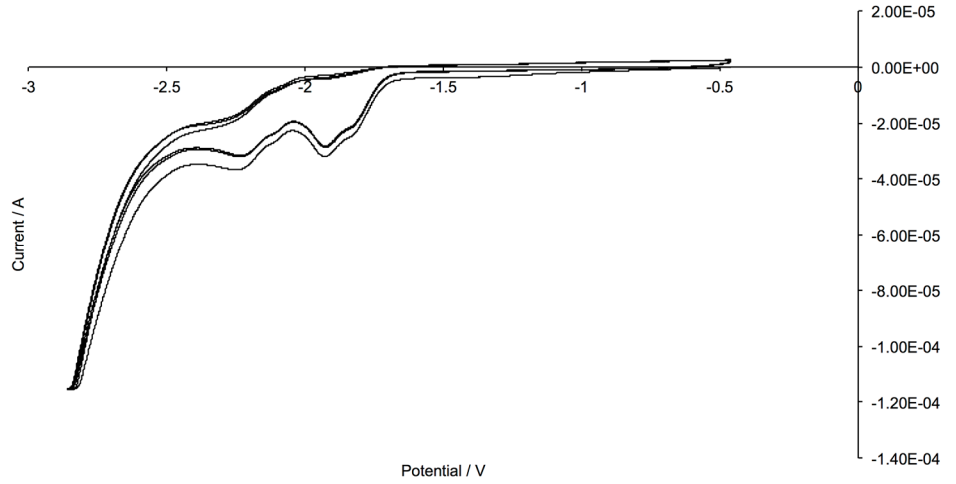


Fig. S27. Representative CV showing two successive cycles for [Cu(POP)(4,7-Br_2phen)][PF_6]. Referenced to internal Fc/Fc^+ = 0.0 V; CH_2Cl_2 solution with [^{n}Bu$_4$N][PF_6] as supporting electrolyte and scan rate of 0.1 V s^{-1}.

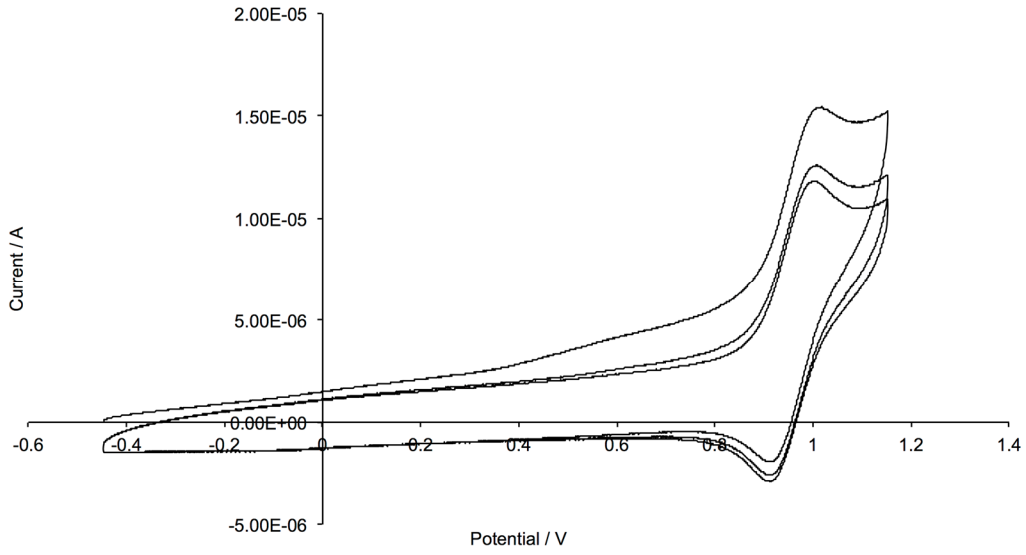


(a)

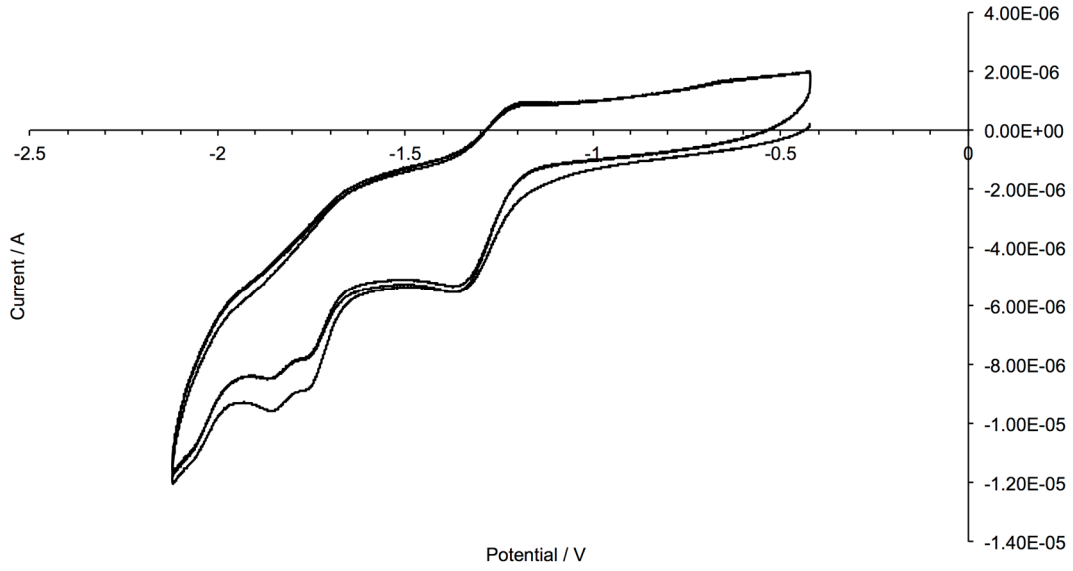


(b)

Fig. S28. Successive cycles in the (a) anodic and (b) cathodic scans for [Cu(POP)(2,9-Br_2phen)][PF_6]. Referenced to internal Fc/Fc^+ = 0.0 V; CH_2Cl_2 solution with [^{n}Bu$_4$N][PF_6] as supporting electrolyte and scan rate of 0.1 V s^{-1}.

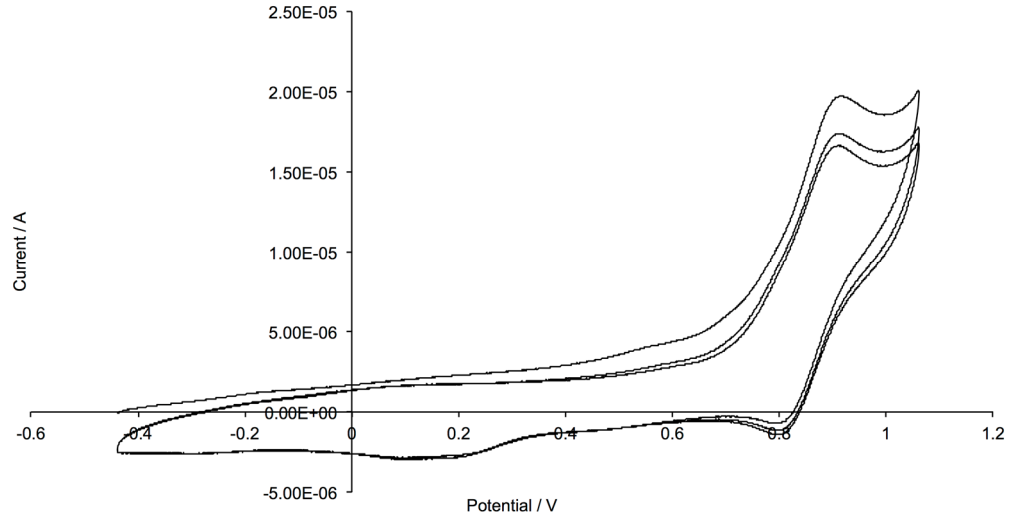


(a)

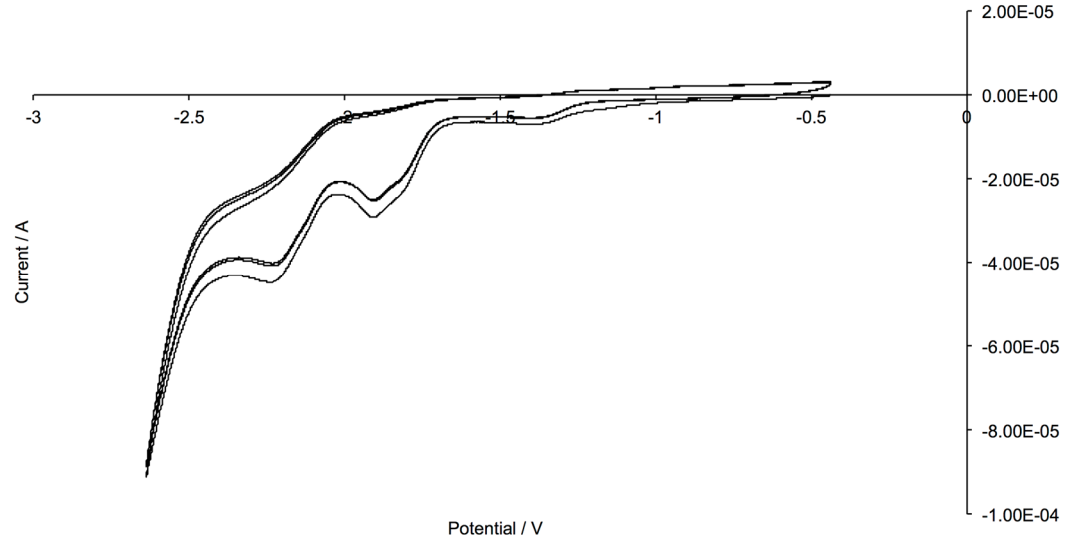


(b)

Fig. S29. Successive cycles in the (a) anodic and (b) cathodic scans for [Cu(xantphos)(2,9-Br_2phen)][PF_6]. Referenced to internal Fc/Fc^+ = 0.0 V; CH_2Cl_2 solution with [^{n}Bu$_4$N][PF_6] as supporting electrolyte and scan rate of 0.1 V s^{-1}.

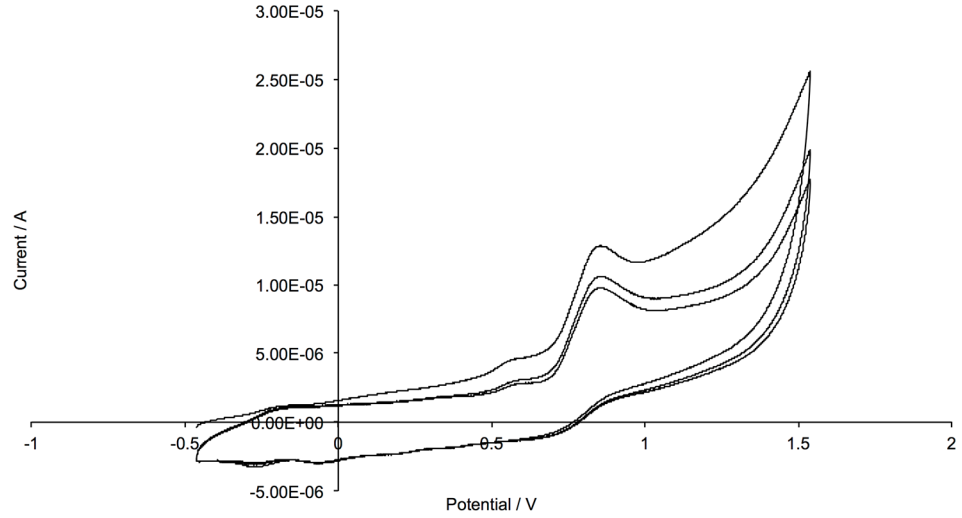


(a)

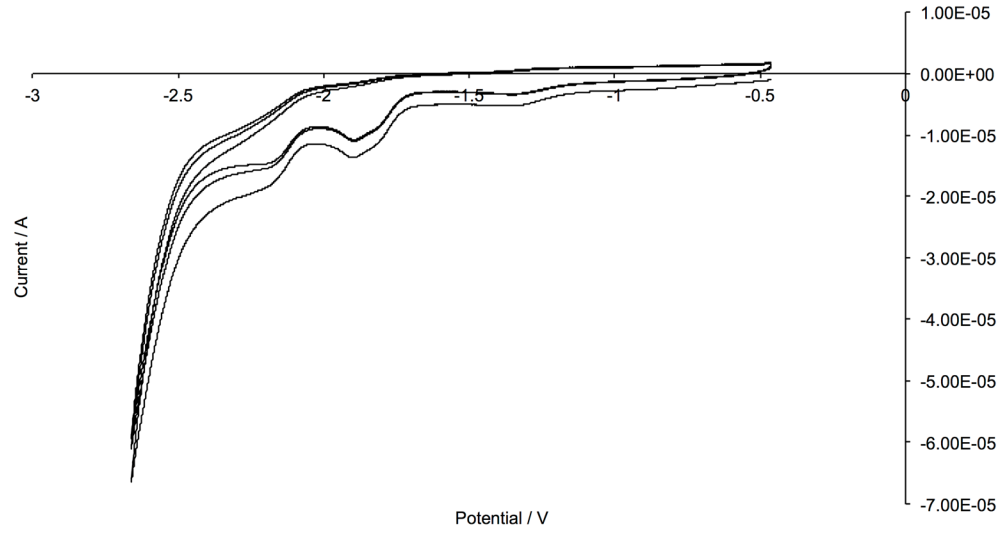


(b)

Fig. S30. Successive cycles in the (a) anodic and (b) cathodic scans for [Cu(POP)(3,8-Br_2phen)][PF_6]. Referenced to internal Fc/Fc^+ = 0.0 V; CH_2Cl_2 solution with [^{n}Bu$_4$N][PF_6] as supporting electrolyte and scan rate of 0.1 V s^{-1}.

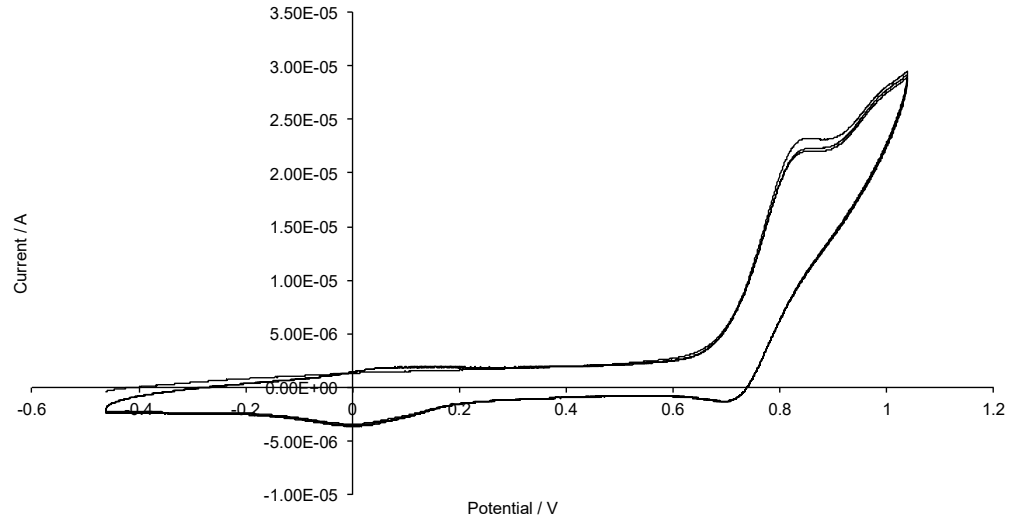


(a)

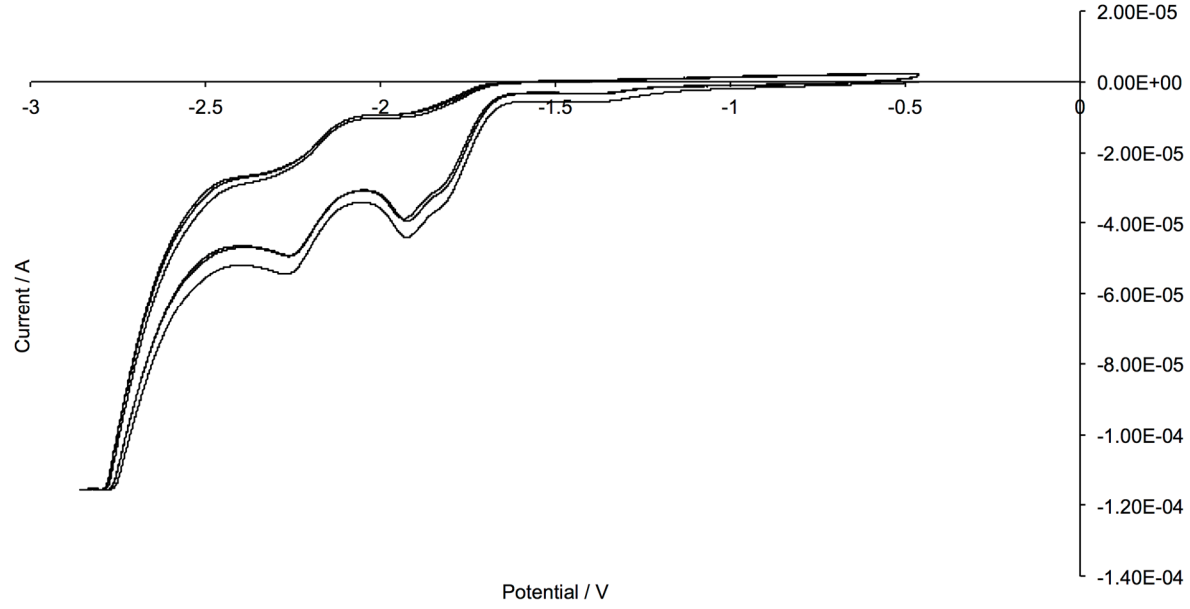


(b)

Fig. S31. Successive cycles in the (a) anodic and (b) cathodic scans for [Cu(xantphos)(3,8-Br_2phen)][PF_6]. Referenced to internal Fc/Fc^+ = 0.0 V; CH_2Cl_2 solution with [^{n}Bu$_4$N][PF_6] as supporting electrolyte and scan rate of 0.1 V s^{-1}.

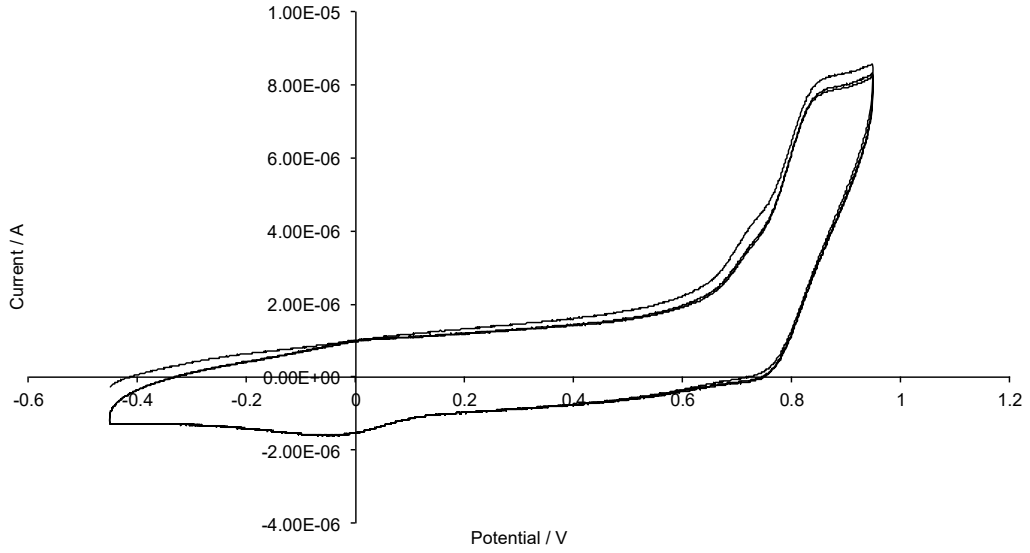


(a)

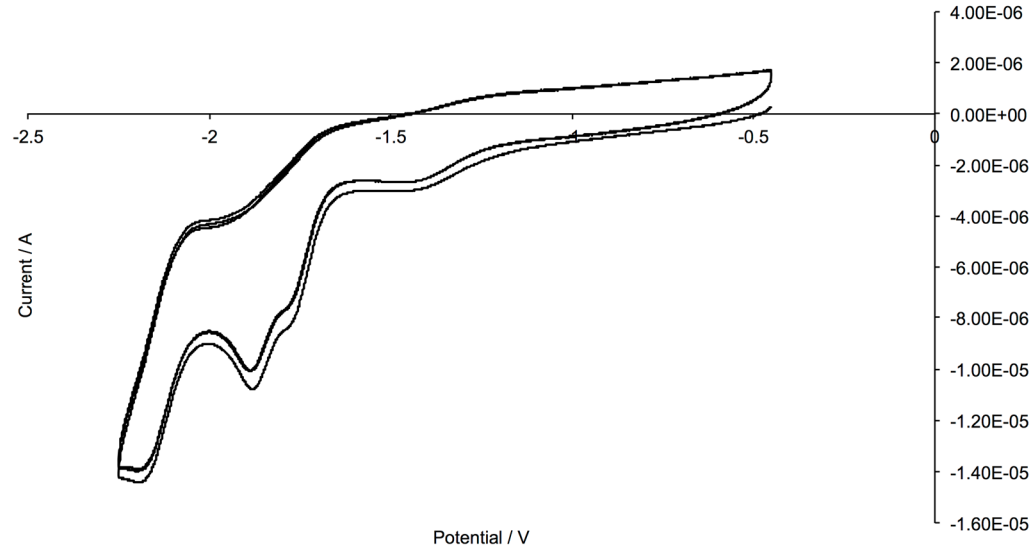


(b)

Fig. S32. Successive cycles in the (a) anodic and (b) cathodic scans for [Cu(POP)(4,7-Br_2phen)][PF_6]. Referenced to internal Fc/Fc^+ = 0.0 V; CH_2Cl_2 solution with [^{n}Bu_4N][PF_6] as supporting electrolyte and scan rate of 0.1 V s^{-1}.



(a)



(b)

Fig. S33. Successive cycles in the (a) anodic and (b) cathodic scans for [Cu(xantphos)(4,7-Br_2phen)][PF_6]. Referenced to internal Fc/Fc^+ = 0.0 V; CH_2Cl_2 solution with [^{n}Bu_4N][PF_6] as supporting electrolyte and scan rate of 0.1 V s^{-1}.