Electronic Supplementary Material (ESI) for RSC Advances.

ESI to accompany

[Cu(POP)(N^S)][PF_6] and [Cu(xantphos)(N^S)][PF_6] compounds with 2-(thiophen-2-yl)pyridines

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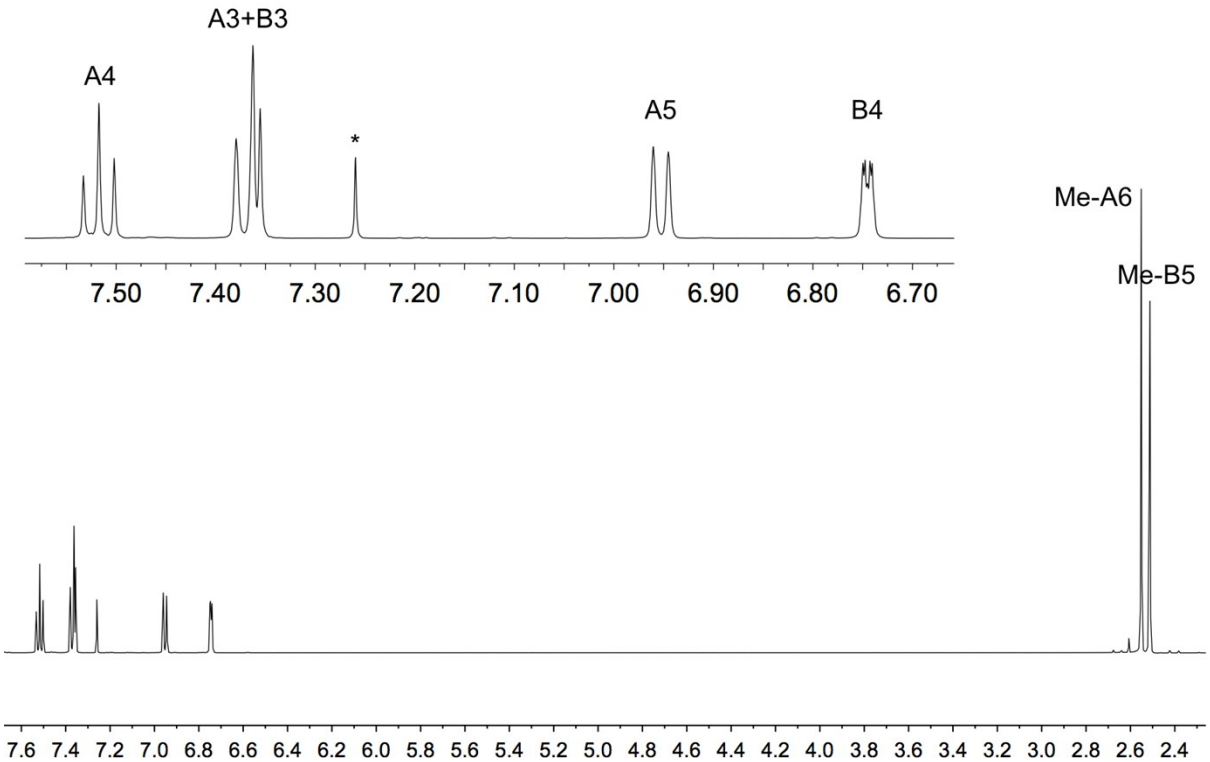

Fig. S1. ^{1}H NMR (500 MHz, 298 K, $CDCl_3$) spectrum of **4**. * = residual $CHCl_3$.

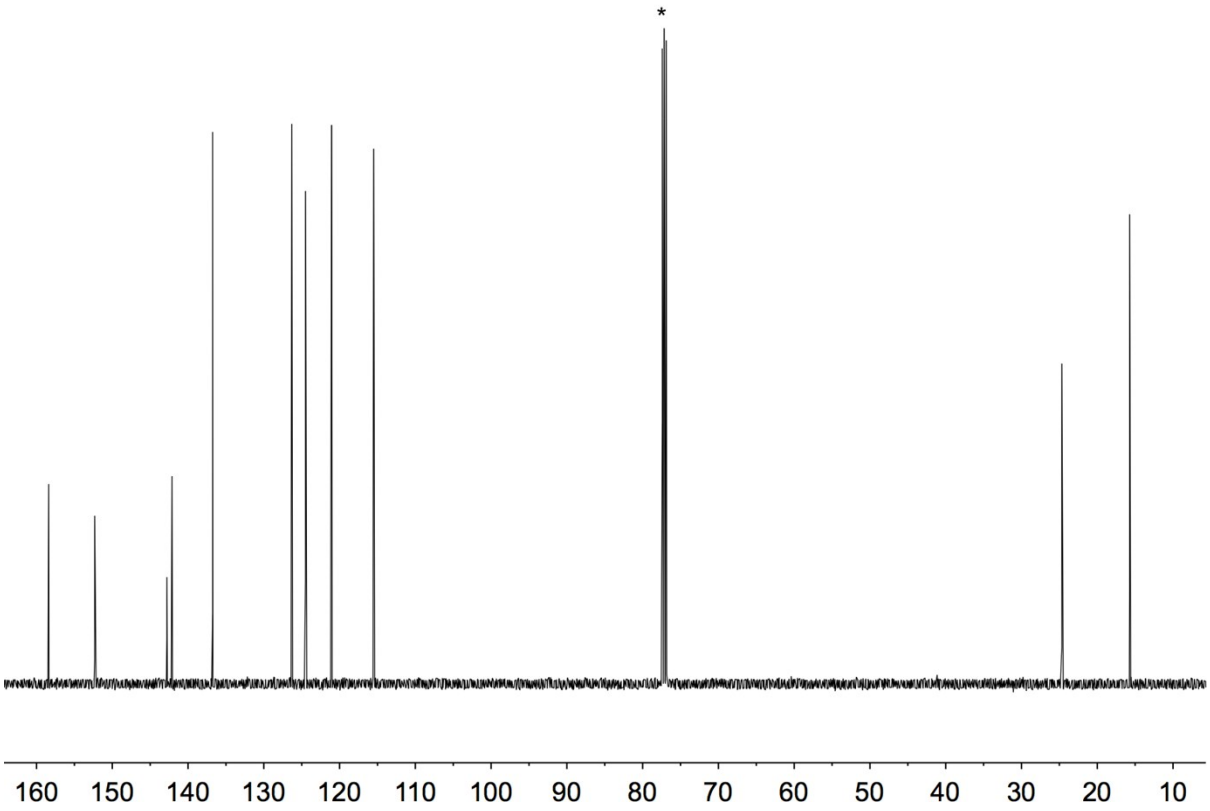

Fig. S2. $^{13}C\{^{1}H\}$ NMR (126 MHz, 298 K, $CDCl_3$) spectrum of **4**. * = $CDCl_3$.

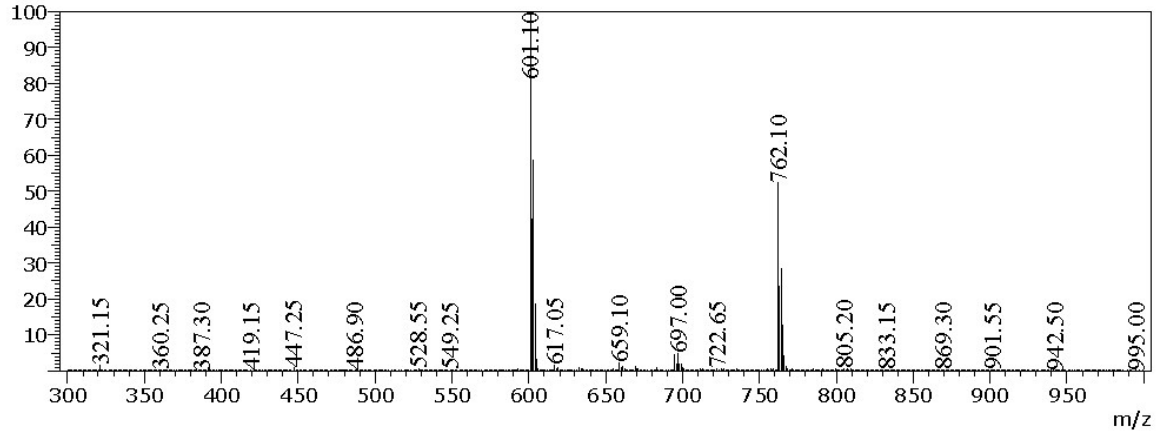

Fig. S3. ESI-MS (positive mode) of [Cu(POP)(**1**)][PF_6].

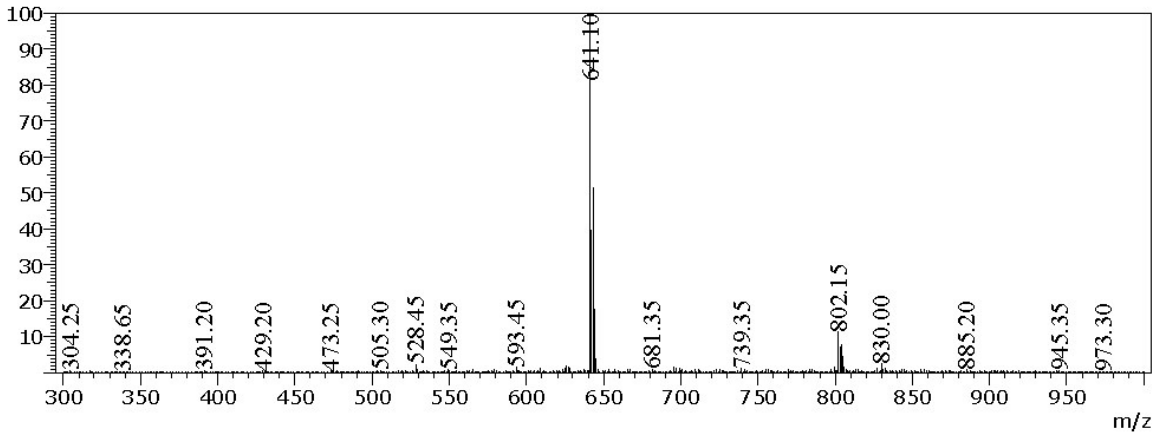

Fig. S4. ESI-MS (positive mode) of [Cu(xantphos)(**1**)][PF_6].

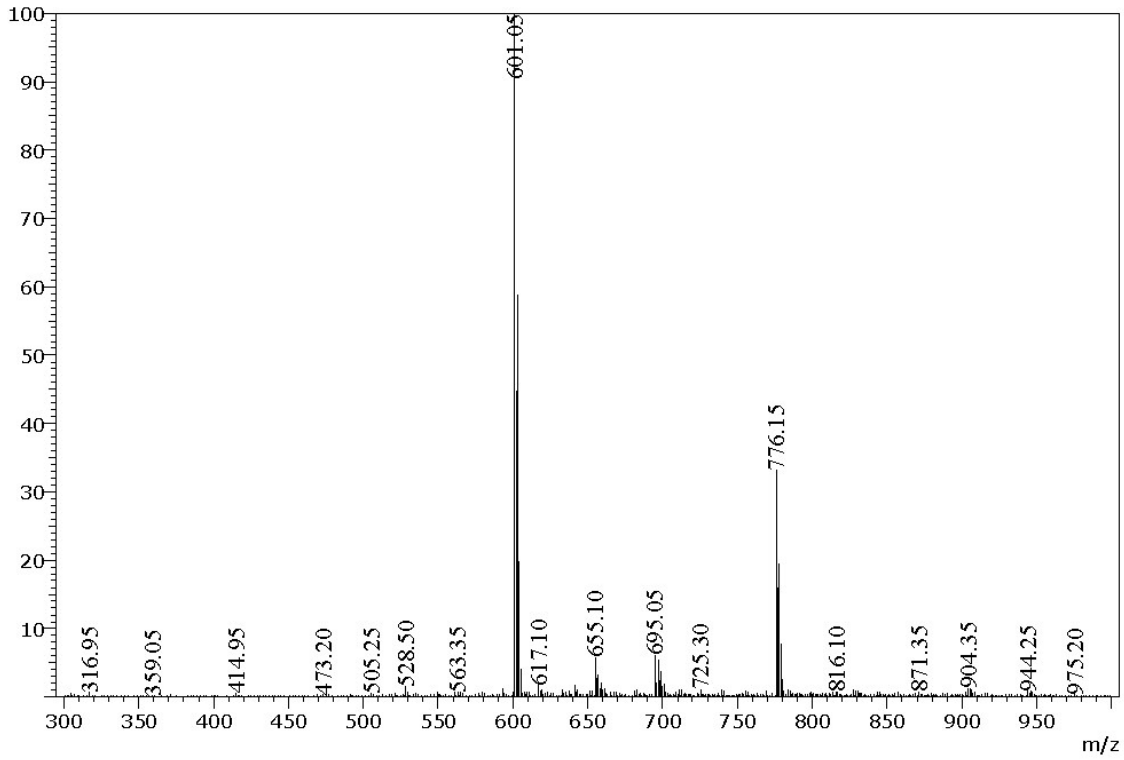

Fig. S5. ESI-MS (positive mode) of [Cu(POP)(**2**)][PF_6].

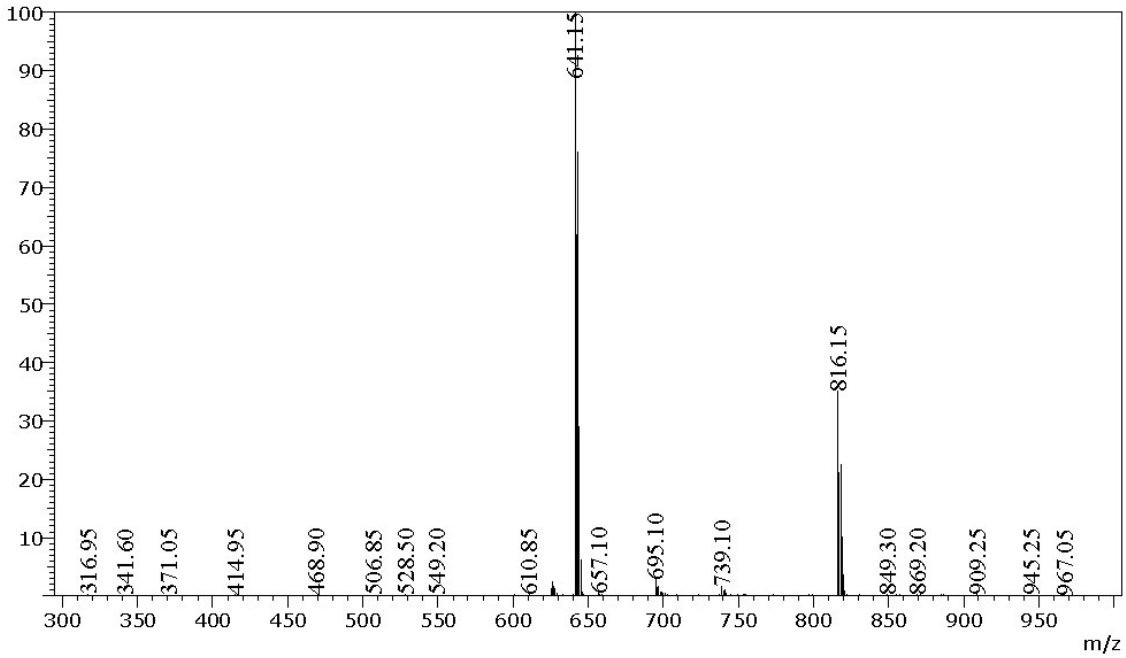

Fig. S6. ESI-MS (positive mode) of [Cu(xantphos)(**2**)][PF_6].

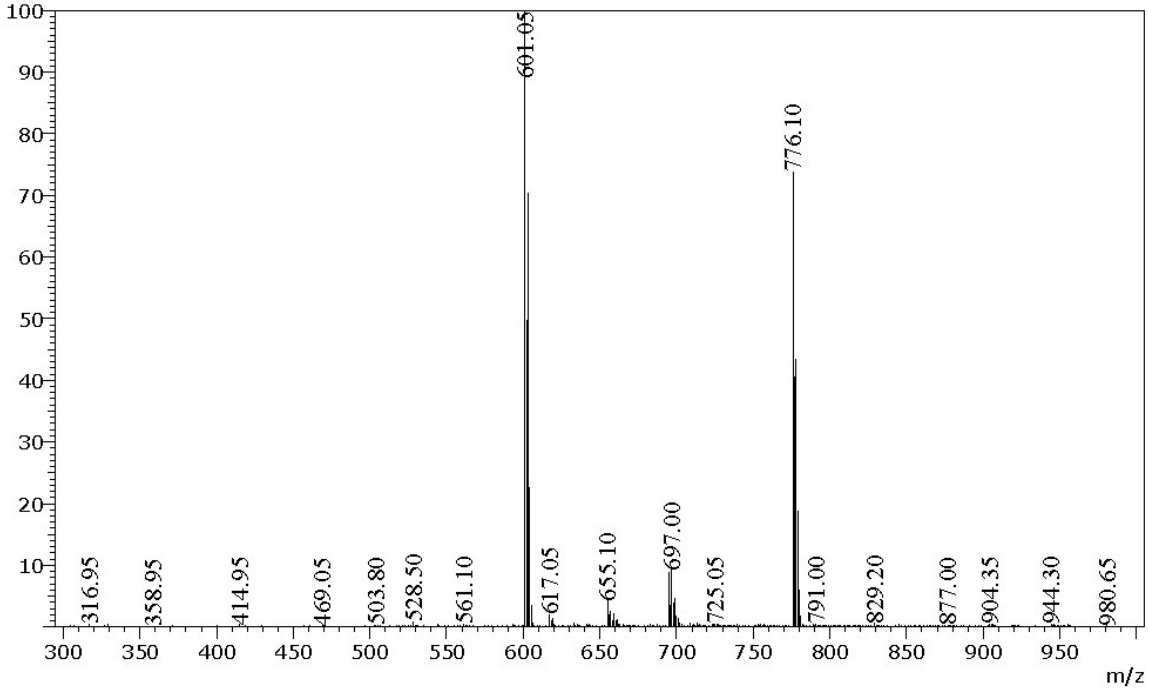

Fig. S7. ESI-MS (positive mode) of [Cu(POP)(**3**)][PF_6].

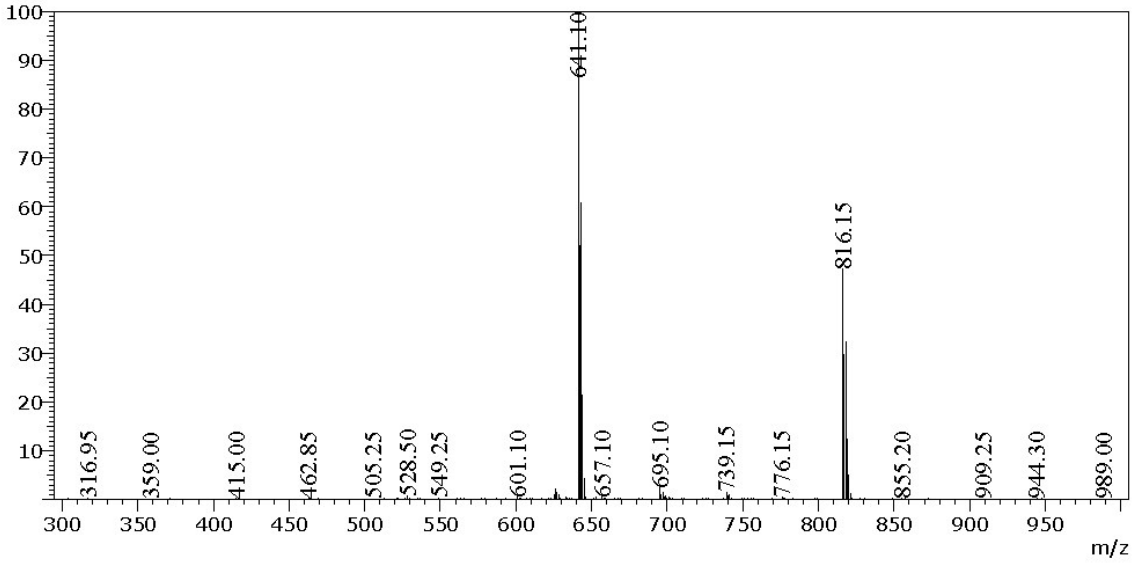

Fig. S8. ESI-MS (positive mode) of [Cu(xantphos)(**3**)][PF_6].

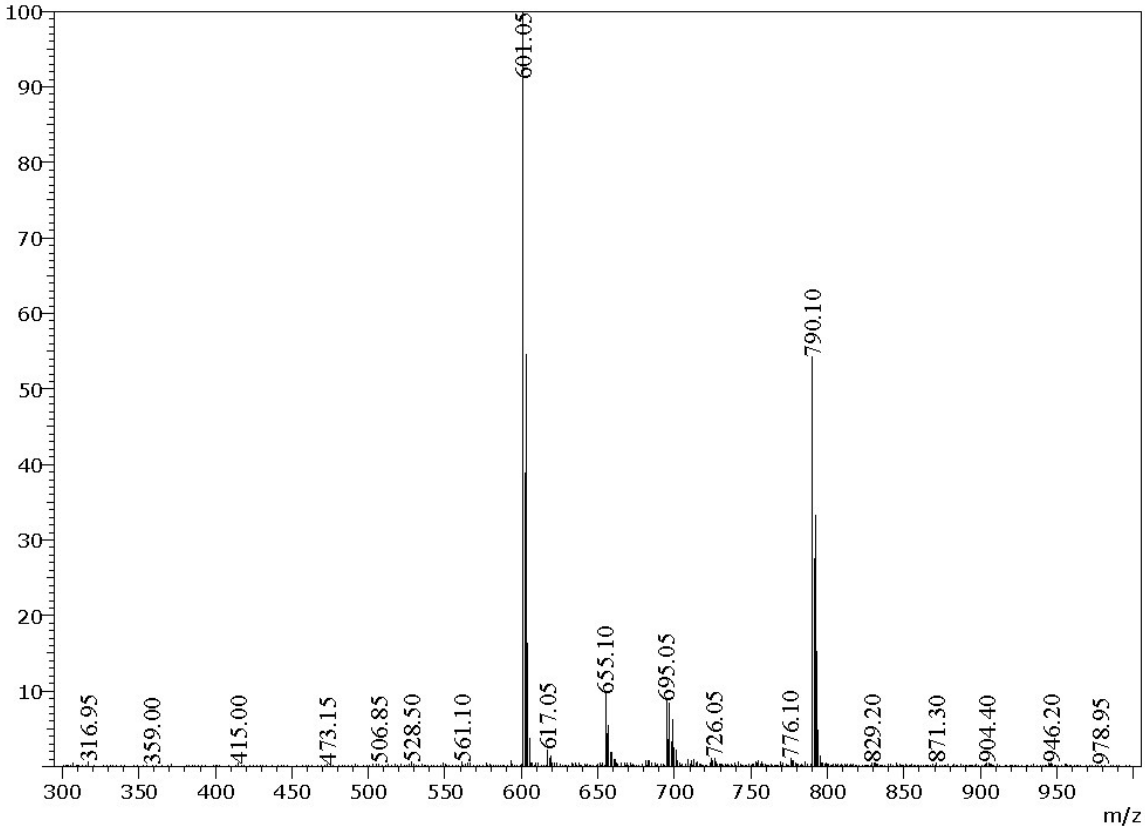

Fig. S9. ESI-MS (positive mode) of [Cu(POP)(**4**)][PF_6].

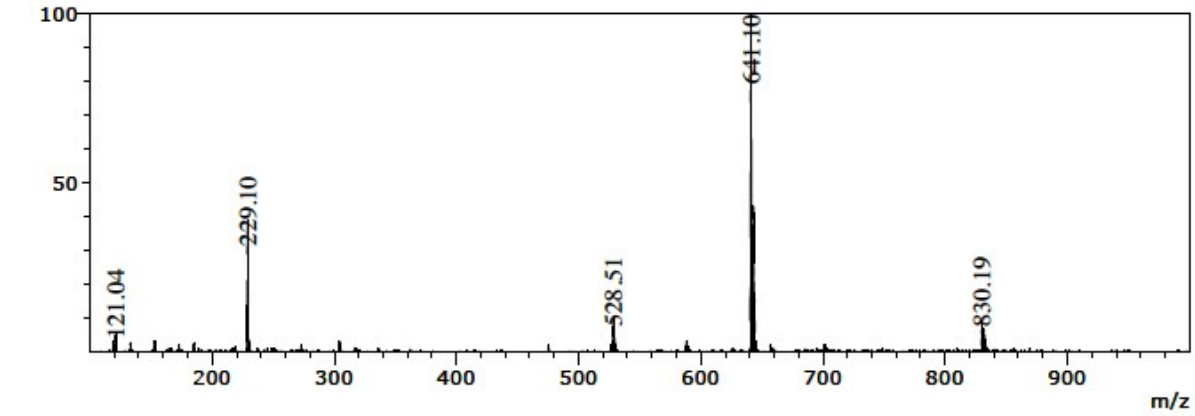

Fig. S10. ESI-MS (positive mode) of [Cu(xantphos)(**4**)][PF_6].

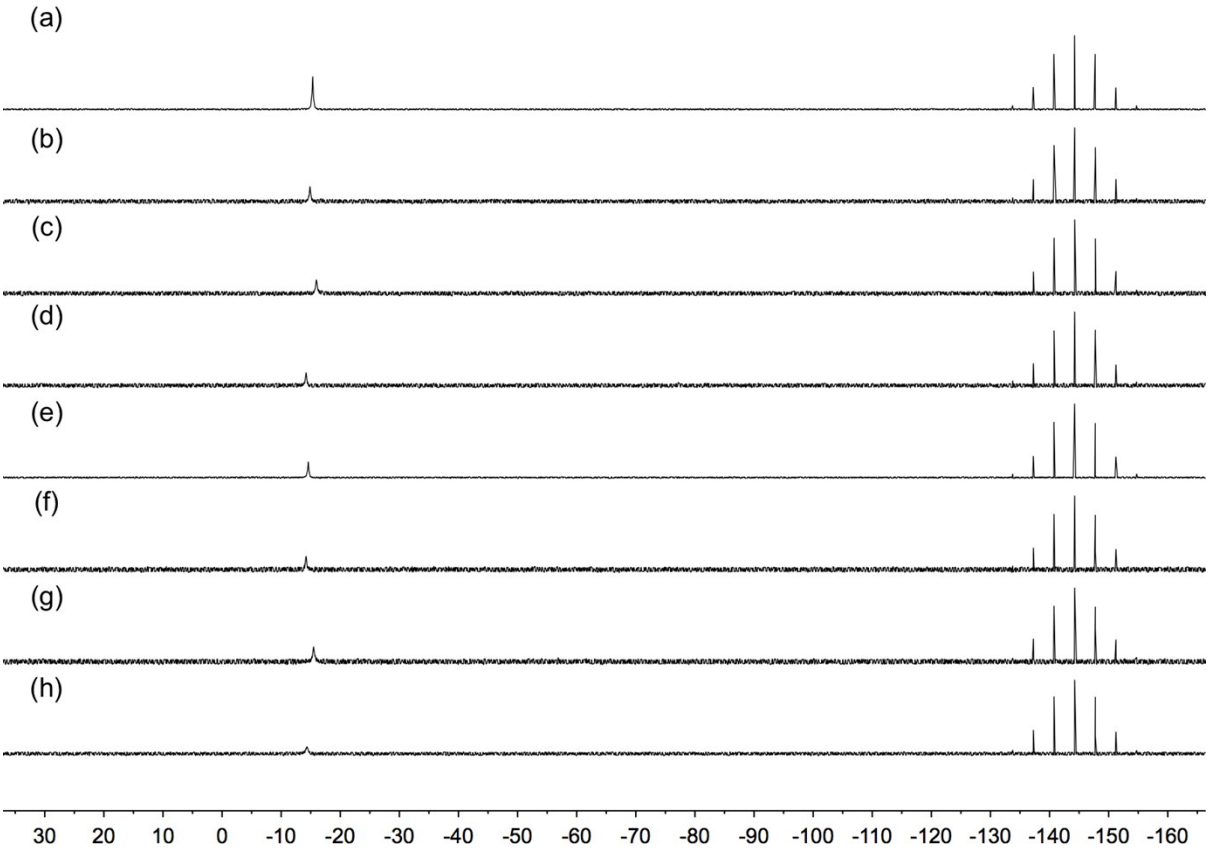

Fig. S11. $^{31}P\{^1H\}$ NMR (202 Hz, acetone-d_6, 298 K) of (a) [Cu(POP)(**1**)][PF_6], (b) [Cu(xantphos)(**1**)][PF_6], (c) [Cu(POP)(**2**)][PF_6], (d) [Cu(xantphos)(**2**)][PF_6], (e) [Cu(POP)(**3**)][PF_6], (f) [Cu(xantphos)(**3**)][PF_6], (g) [Cu(POP)(**4**)][PF_6] and (h) [Cu(xantphos)(**4**)][PF_6].

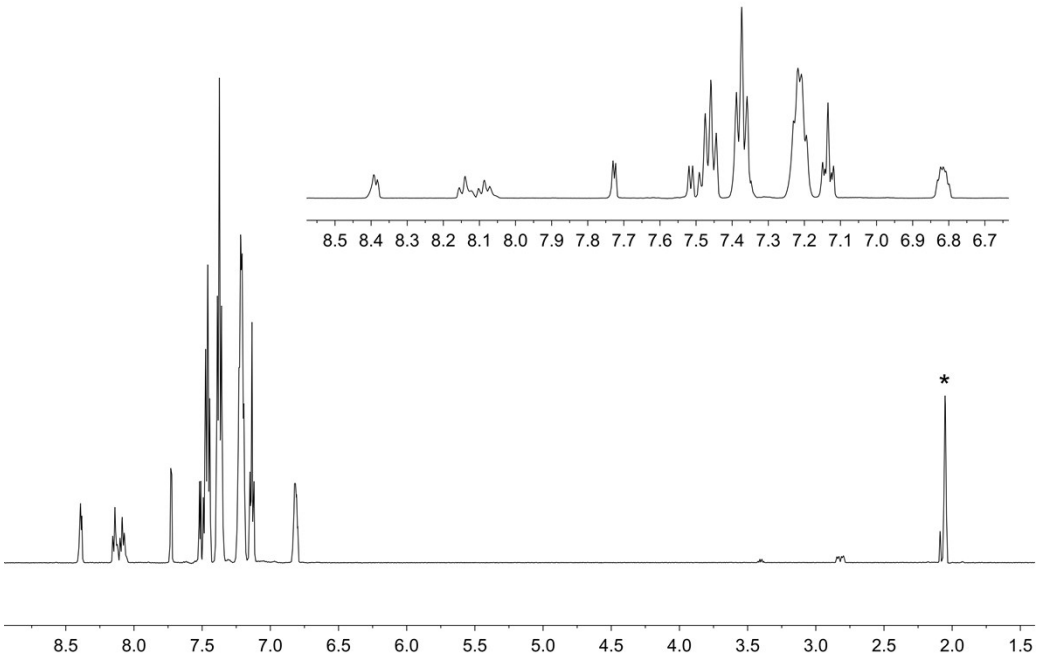

Fig. S12. ^{1}H NMR spectrum (500 MHz, 298 K, acetone-d_6) of [Cu(POP)(**1**)][PF_6]. * = residual $CD_3C(O)CHCD_2$.

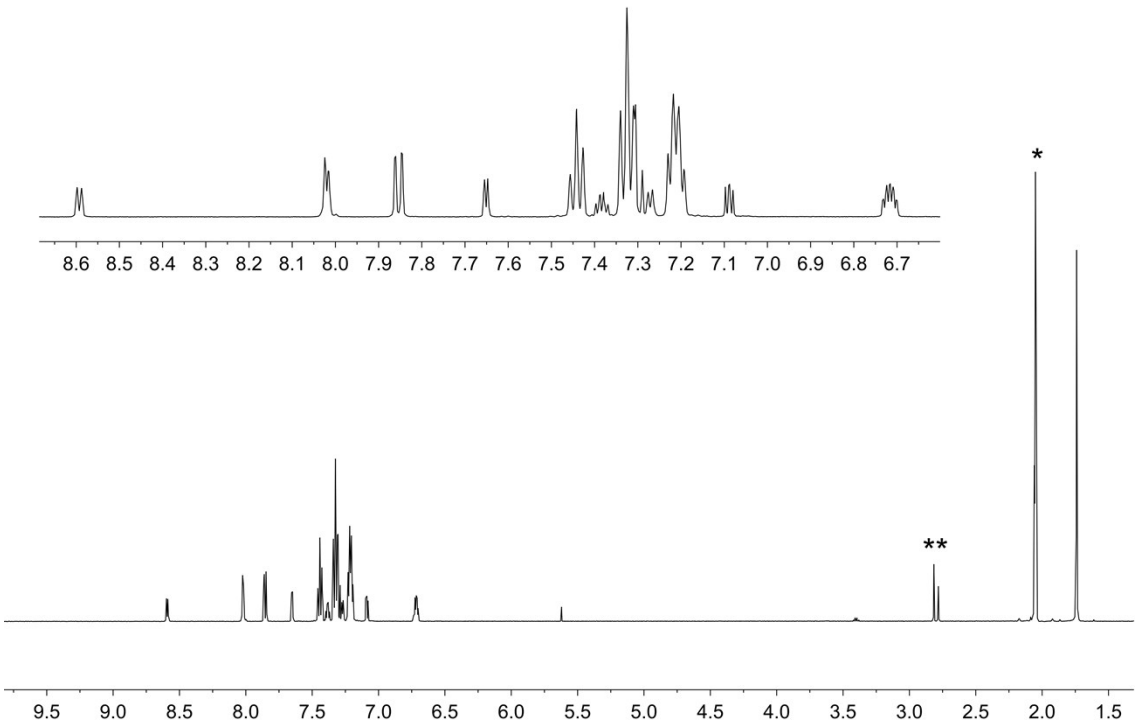

Fig. S13. ^{1}H NMR spectrum (500 MHz, 298 K, acetone-d_6) of [Cu(xantphos)(**1**)][PF_6] and expansion of the aromatic region. * = residual $CD_3C(O)CHCD_2$; ** = H_2O and HOD.

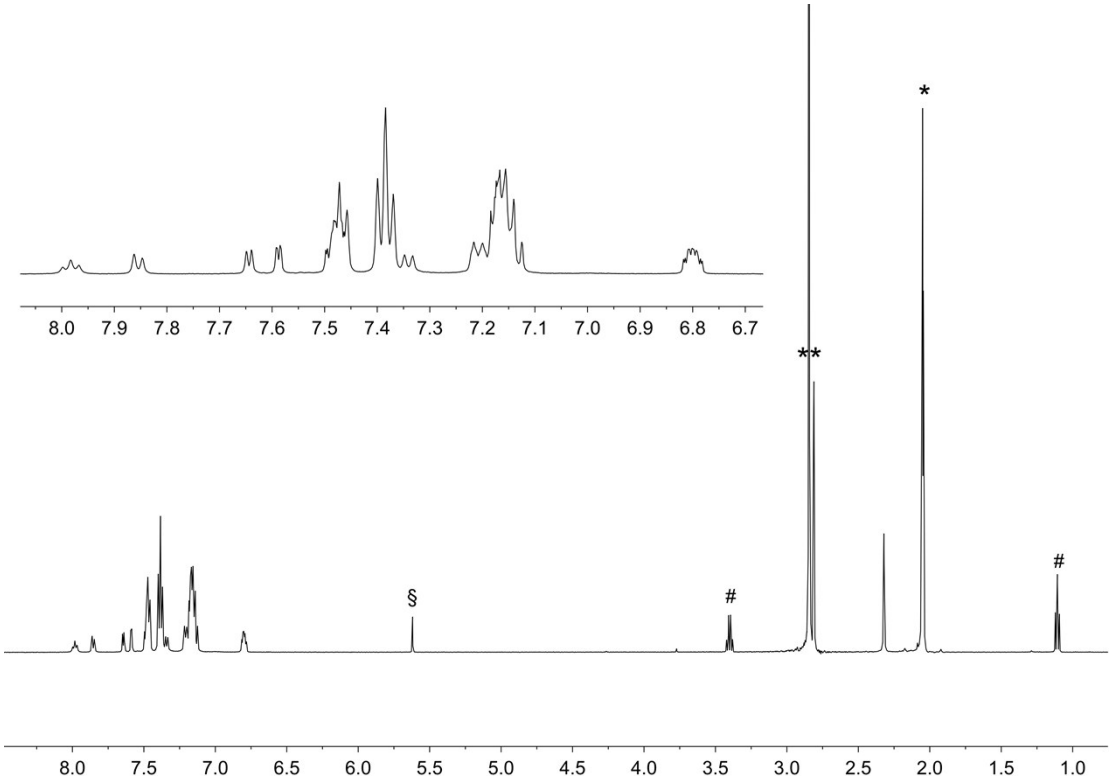

Fig. S14. ^{1}H NMR spectrum (500 MHz, 298 K, acetone-d_6) of [Cu(POP)(**2**)][PF_6] and expansion of the aromatic region. * = residual $CD_3C(O)CHCD_2$; ** = H_2O and HOD; § = CH_2Cl_2; # = Et_2O.

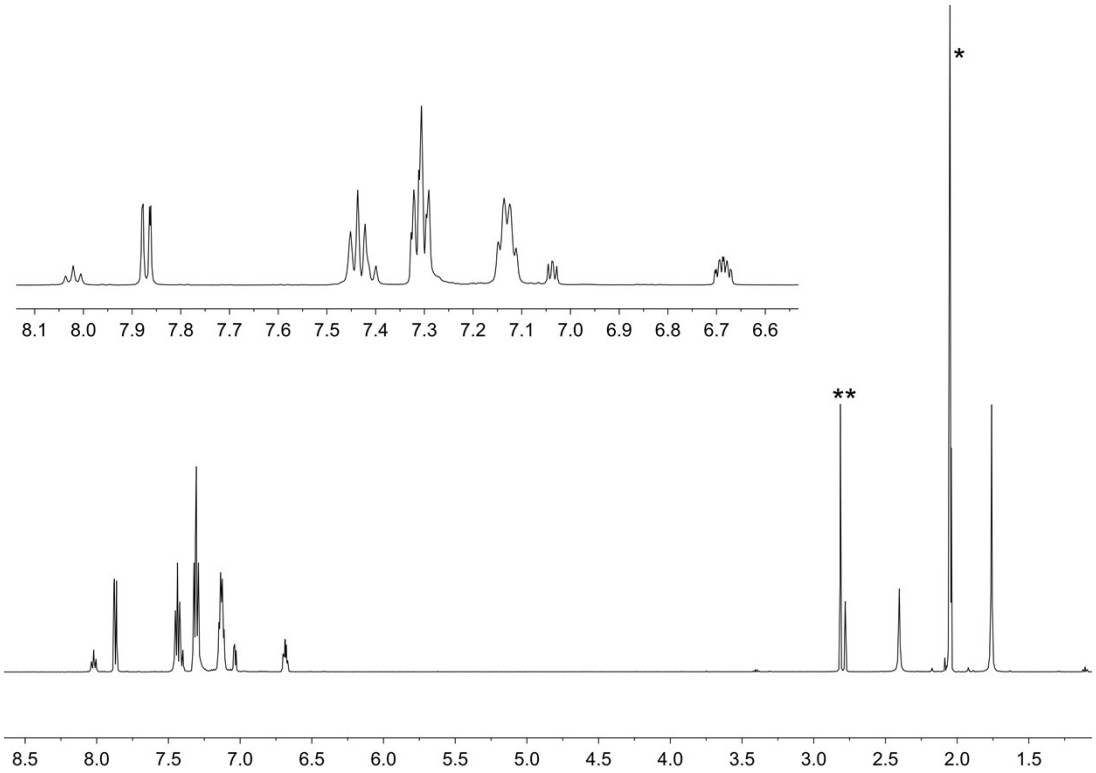

Fig. S15. ^{1}H NMR spectrum (500 MHz, 298 K, acetone-d_6) of [Cu(xantphos)(**2**)][PF_6] and expansion of the aromatic region. * = residual $CD_3C(O)CHCD_2$; ** = H_2O and HOD.

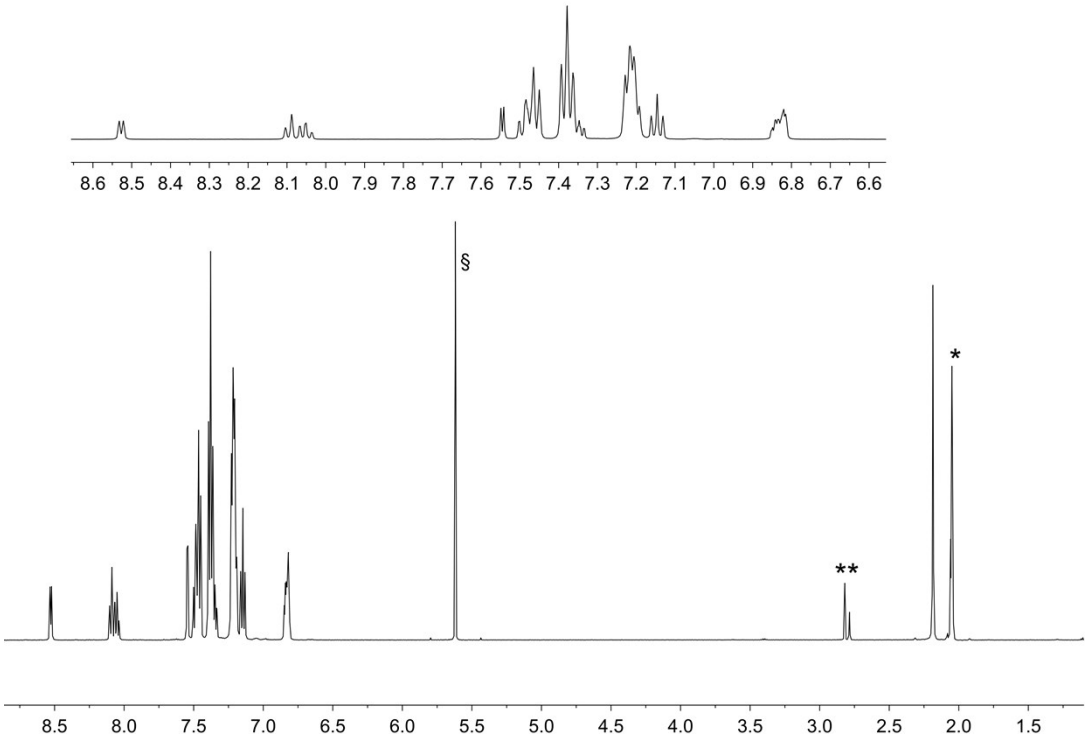

Fig. S16. ^{1}H NMR spectrum (500 MHz, 298 K, acetone-d_6) of [Cu(POP)(**3**)][PF_6] and expansion of the aromatic region. * = residual $CD_3C(O)CHCD_2$; ** = H_2O and HOD; § = CH_2Cl_2.

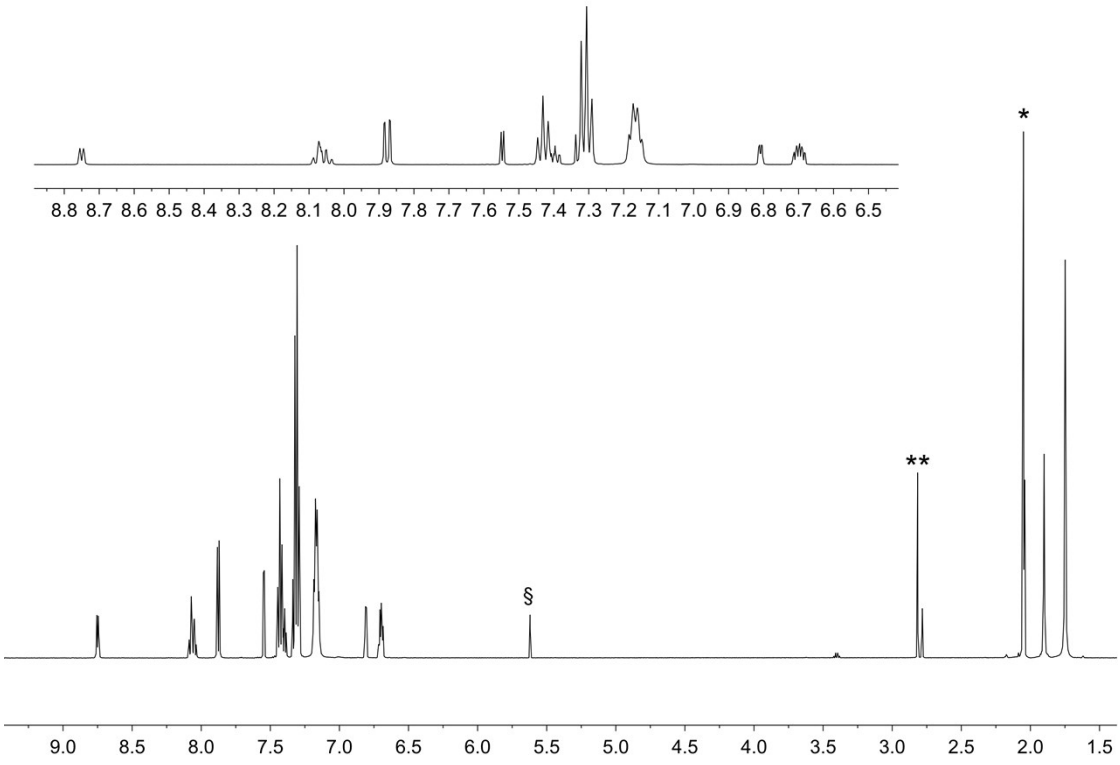

Fig. S17. ^{1}H NMR spectrum (500 MHz, 298 K, acetone-d_6) of [Cu(xantphos)(**3**)][PF_6] and expansion of the aromatic region. * = residual $CD_3C(O)CHCD_2$; ** = H_2O and HOD; § = CH_2Cl_2.

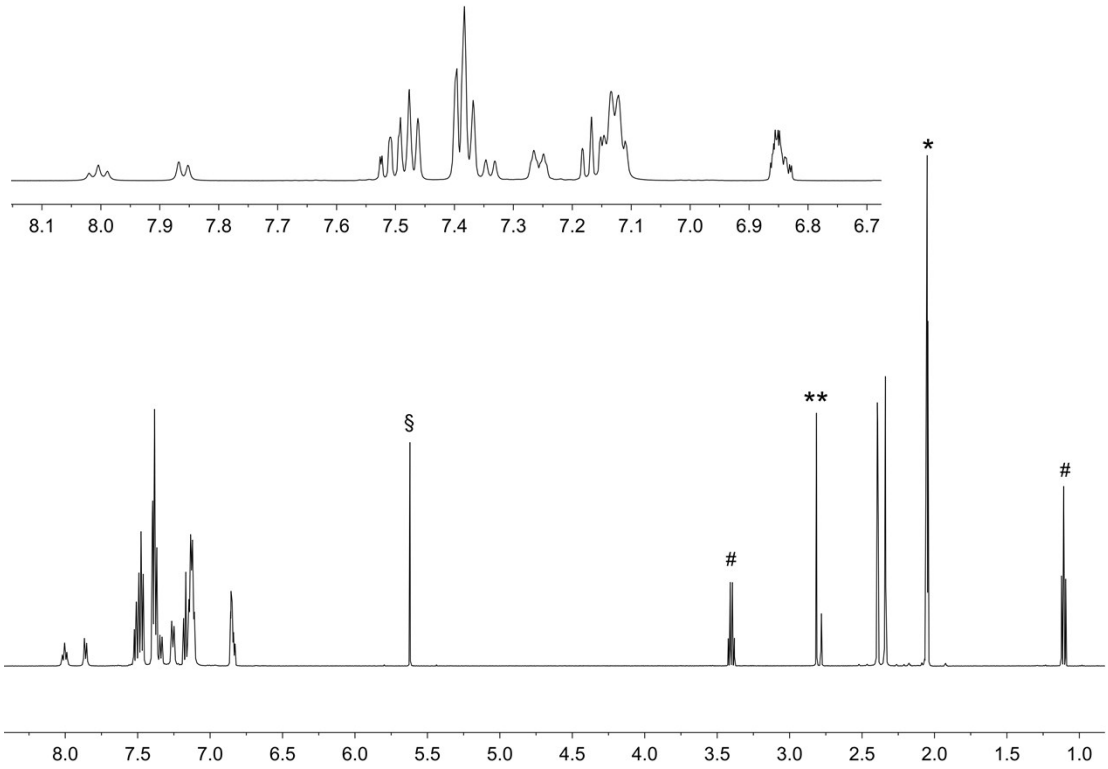

Fig. S18. ^{1}H NMR spectrum (500 MHz, 298 K, acetone-d_6) of [Cu(POP)(**4**)][PF_6] and expansion of the aromatic region. * = residual $CD_3C(O)CHCD_2$; ** = H_2O and HOD; § = CH_2Cl_2; # = Et_2O.

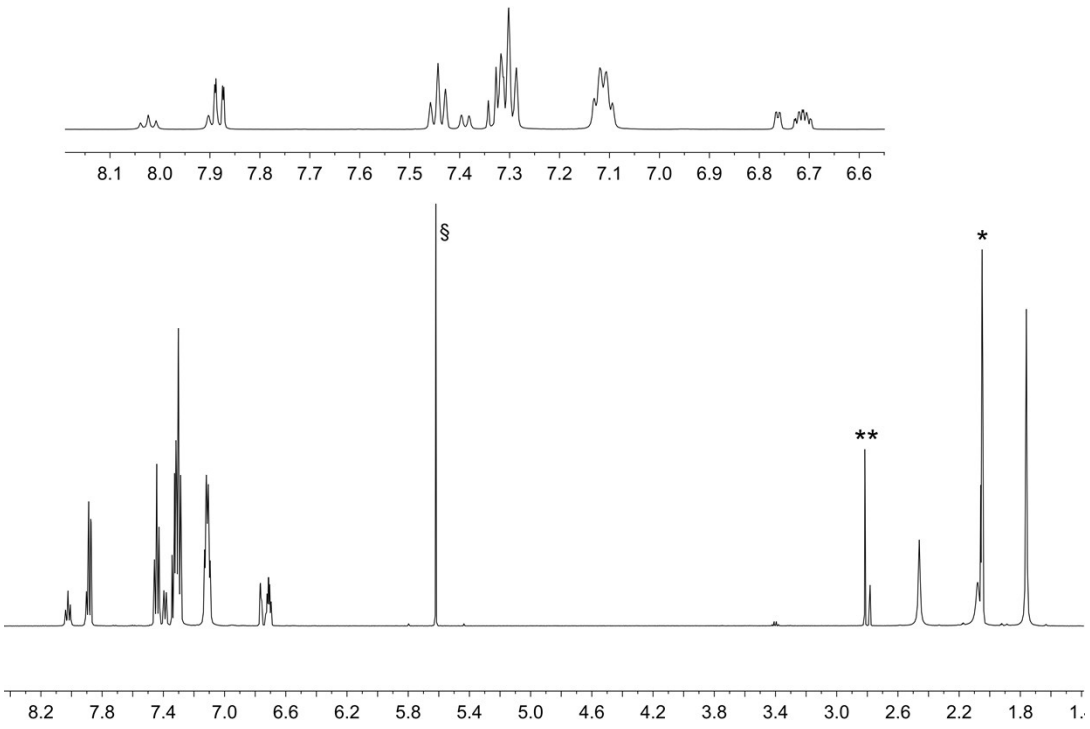

Fig. S19. ^{1}H NMR spectrum (500 MHz, 298 K, acetone-d_6) of [Cu(xantphos)(**4**)][PF_6] and expansion of the aromatic region. * = residual $CD_3C(O)CHCD_2$; ** = H_2O and HOD; § = CH_2Cl_2.

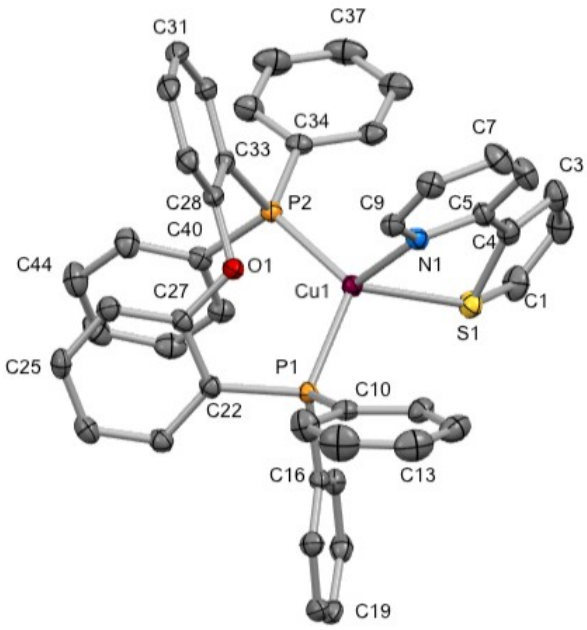

Fig. S20. ORTEP-style plot of the [Cu(POP)(**1**)]$^{+}$ cation in [Cu(POP)(**1**)][PF_6] with ellipsoids plotted at 50% probability level and H atoms omitted. Selected bond parameters: Cu1–S1 = 2.4770(5), Cu1–N1 = 2.0640(15), Cu1–P1 = 2.2655(5), Cu1–P2 = 2.2406(5), C4–S1 = 1.736(2), C1–S1 = 1.721(2), C27–O1 = 1.396(2), C28–O1 = 1.404(2) Å. S1–Cu1–N1 = 81.34(5), S1–Cu1–P1 = 110.02(2), N1–Cu1–P1= 110.83(5), S1–Cu1–P2 = 119.44(2), N1–Cu1–P2 = 115.14(5), P1–Cu1–P2 = 115.38(2), C4–S1–C1 = 91.95(10), C28–O1–C27 = 117.40(13)°.

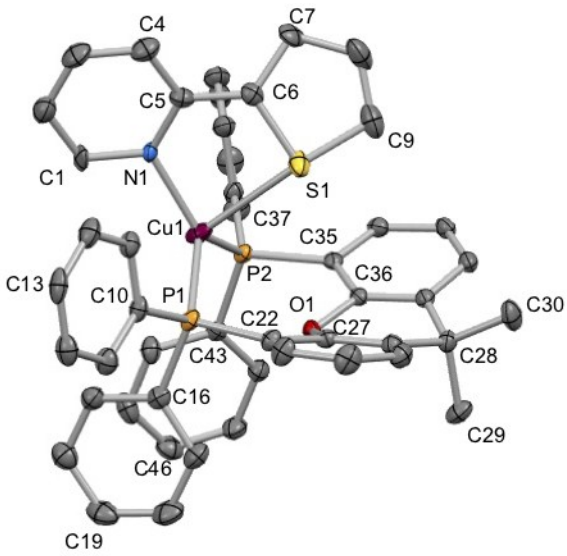

Fig. S21. ORTEP-style plot of the [Cu(xantphos)(**1**)]$^{+}$ cation in [Cu(xantphos)(**1**)][PF_6] with ellipsoids plotted at 50% probability level and H atoms omitted. Ligand **1** is disordered over two sites (0.75 : 0.25) and only the major occupancy site is shown. Selected bond parameters for major occupancy site of **1**: Cu1–S1 = 2.6403(9), Cu1–N1 = 2.013(2), Cu1–P1 = 2.2897(7), Cu1–P2 = 2.2534(6), S1–C6 = 1.69530(16), S1–C9 = 1.70896(14), C27–O1 = 1.384(2), C36–O1 = 1.388(2) Å; N1–Cu1–S1 = 80.52(5), P1–Cu1–S1 = 103.47(2), P2–Cu1–S1 = 96.66(2), P1–Cu1–N1 = 112.83(5), P2–Cu1–N1 = 128.30(5), P1–Cu1–P2 = 117.89(2), C36–O1–C27 = 116.25(16), C6–S1–C9 = 93.687(12)°.

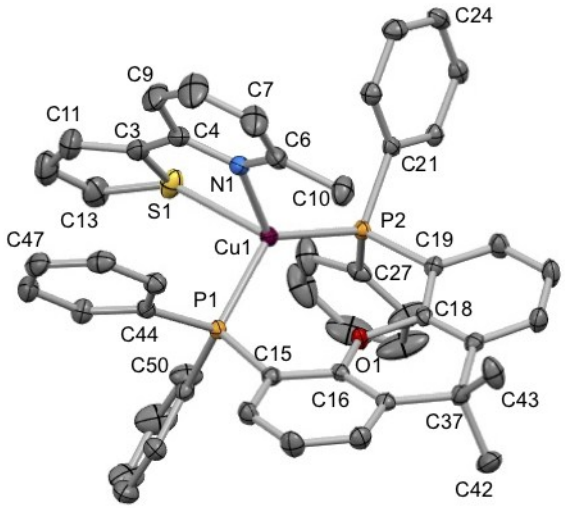

Fig. S22. ORTEP-style plot of the [Cu(xantphos)(**2**)]$^{+}$ cation in [Cu(xantphos)(**2**)][PF_6] with ellipsoids plotted at 50% probability level and H atoms omitted. Selected bond parameters: Cu1–S1 = 2.5789(6), Cu1–N1 = 2.0558(16), Cu1–P1 = 2.2874(5), Cu1–P2 = 2.2660(5), C16–O1–1.379(2), O1–C18 = 1.379(2), S1–C3 = 1.727(2), S1–C13 = 1.720(2) Å; S1–Cu1–N1 = 80.34(5), S1–Cu1–P1 = 99.701(19), N1–Cu1–P1 = 102.04(4), S1–Cu1–P2 = 109.172(19), N1–Cu1–P2 = 124.62(4), P1–Cu1–P2 = 127.804(19), C3–S1–C13 = 92.78(11), C16–O1–C18 = 119.18(14)^{o}.

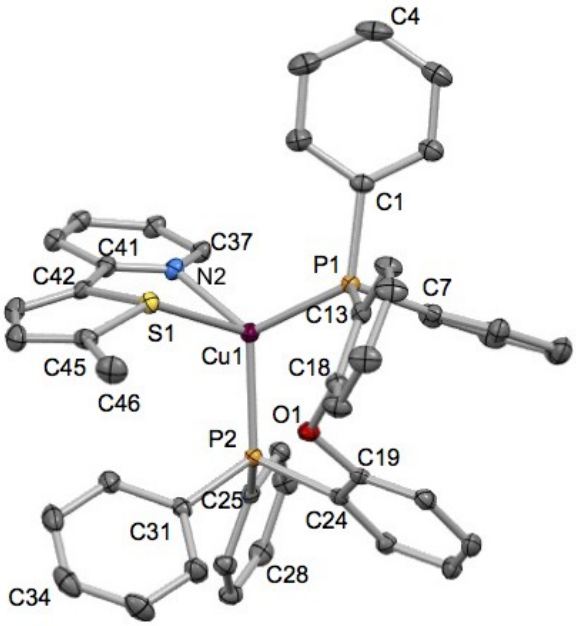

Fig. S23. ORTEP-style plot of the [Cu(POP)(**3**)]$^{+}$ cation in [Cu(POP)(**3**)][PF_6]·CH_2Cl_2 with ellipsoids plotted at 40% probability level. H atoms and the solvent molecule are omitted. Ligand **3** is disordered over two sites (0.80 : 0.20) and only the major occupancy site is shown. Selected bond parameters for major occupancy site of **3**: Cu1–P2 = 2.2770(6), Cu1–P1 = 2.2649(6), Cu1–S1 = 2.5567(16), Cu1–N2 = 2.151(9), O1–C19 = 1.394(3), O1–C18 = 1.394(3 Å; P2–Cu1–S1 = 110.40(5), P1–Cu1–P2 = 116.02(2), P1–Cu1–S1 = 100.95(4), N2–Cu1–P2 = 116.9(3), N2–Cu1–P1 = 123.4(3), N2–Cu1–S1 = 78.2(3), C19–O1–C18 = 116.76(16), C45–S1–C42 = 92.5(2)^{o}.

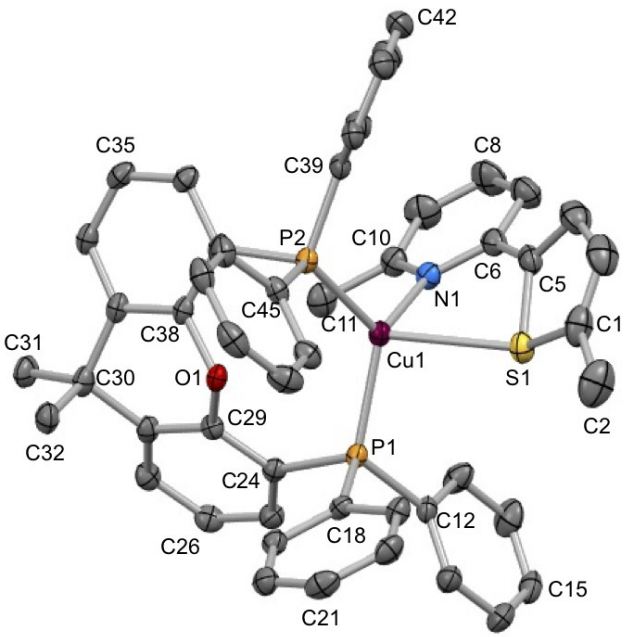

Fig. S24. ORTEP-style plot of the [Cu(xantphos)(**4**)]$^{+}$ cation in [Cu(xantphos)(**4**)][PF_6] with ellipsoids plotted at 40% probability level and H atoms omitted. Selected bond parameters: Cu1–P2 = 2.2621(11), Cu1–P1 = 2.2559(11), Cu1–S1 = 2.6780(12), Cu1–N1 = 2.044(3), S1–C5 = 1.735(5), S1–C1 = 1.732(5), O1–C29 = 1.396(5), O1–C38 = 1.387(5) Å; P2–Cu1–S1 = 118.75(4), P1–Cu1–P2 = 120.86(4), P1–Cu1–S1 = 96.23(4), N1–Cu1–P2 = 111.35(10), N1–Cu1–P1 = 121.48(10), N1–Cu1–S1 = 79.40(10), C38–O1–C29 = 114.1(3), C1–S1–C5 = 92.3(3)°.

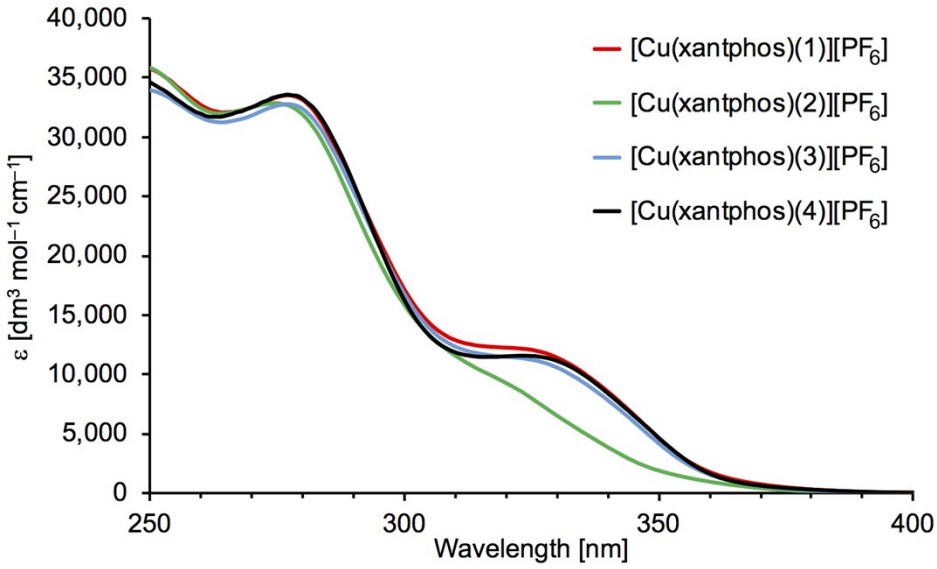

Fig. S25. Absorption spectra of 5 x 10^{-5} M solutions of the [Cu(xantphos)(N^S)][PF_6] complexes

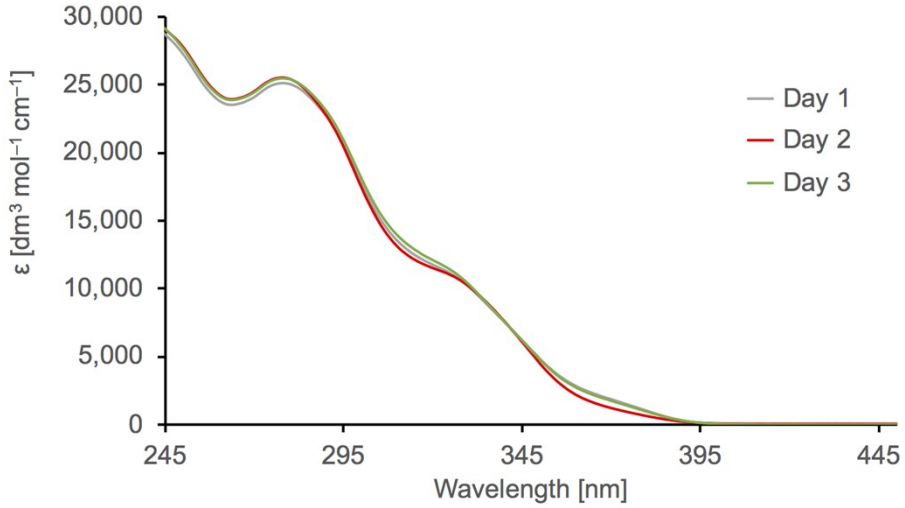

Fig. S26. Absorption spectra of a 5 x 10^{-5} M CH_2Cl_2 solution of [Cu(POP)(**3**)][PF_6] recorded over a period of 3 days.

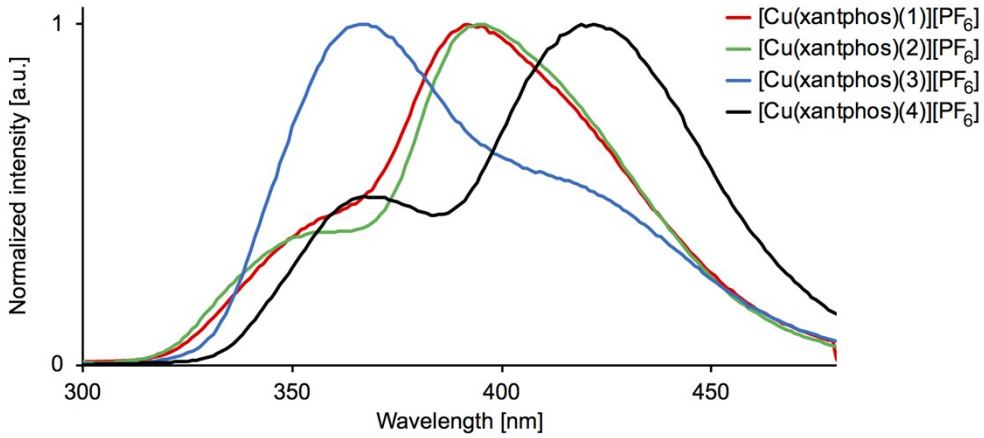

Fig. S27. Emission spectra for CH_2Cl_2 solutions of [Cu(xantphos)(N^S)][PF_6] (5.0 x 10^{-5} M). λ_{exc} = 250 nm for **1**, 275 nm for **2** and **3**, 270 nm for **4**.