Supporting Information:

The effects of introducing terminal alkenyl substituents into the 2,2'-bipyridine domain in $[Cu(N^N)(P^P)]^+$ coordination compounds

Jannika Wöhler,[a] Marco Meyer, [a] Alessandro Prescimone,[a] Catherine E. Housecroft [a]* and Edwin C. Constable [a]

Contents

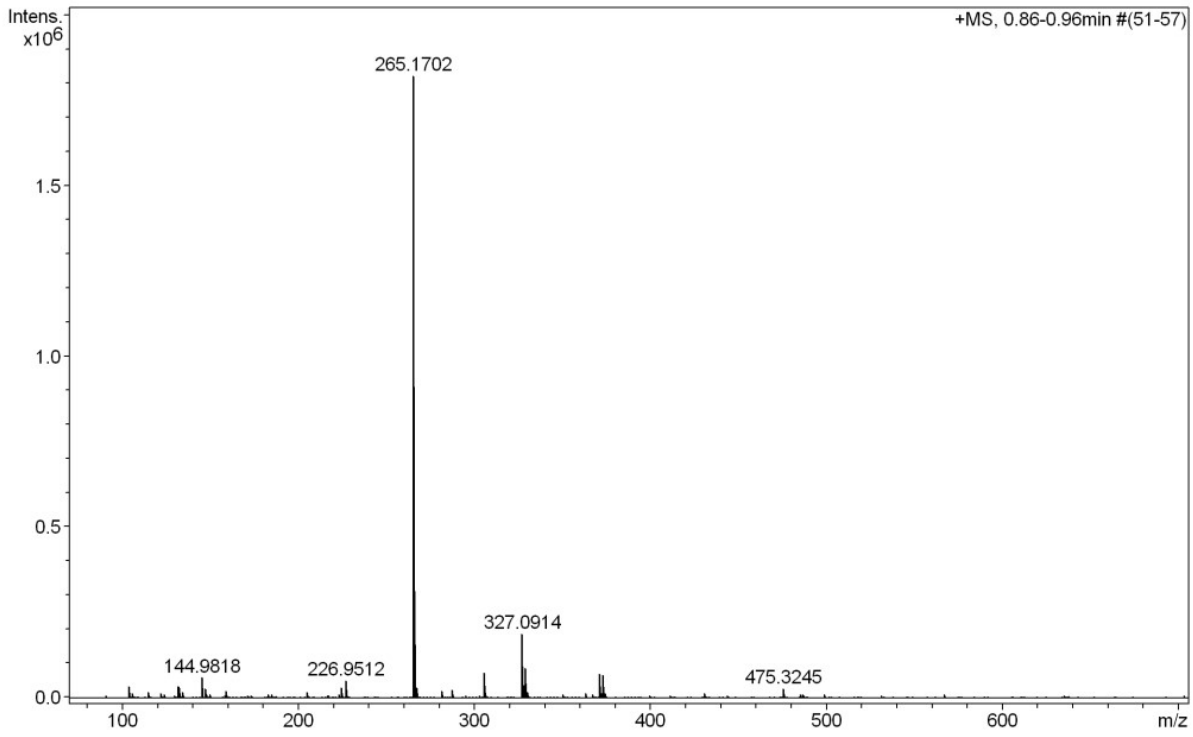


Fig. S1: HR-ESI-MS mass spectrum of ligand **1**.

1. G.J. Kubas, B. Monzyk and A.L. Crumbliss, *Inorg. Synth.* **2007**, 19, 90.

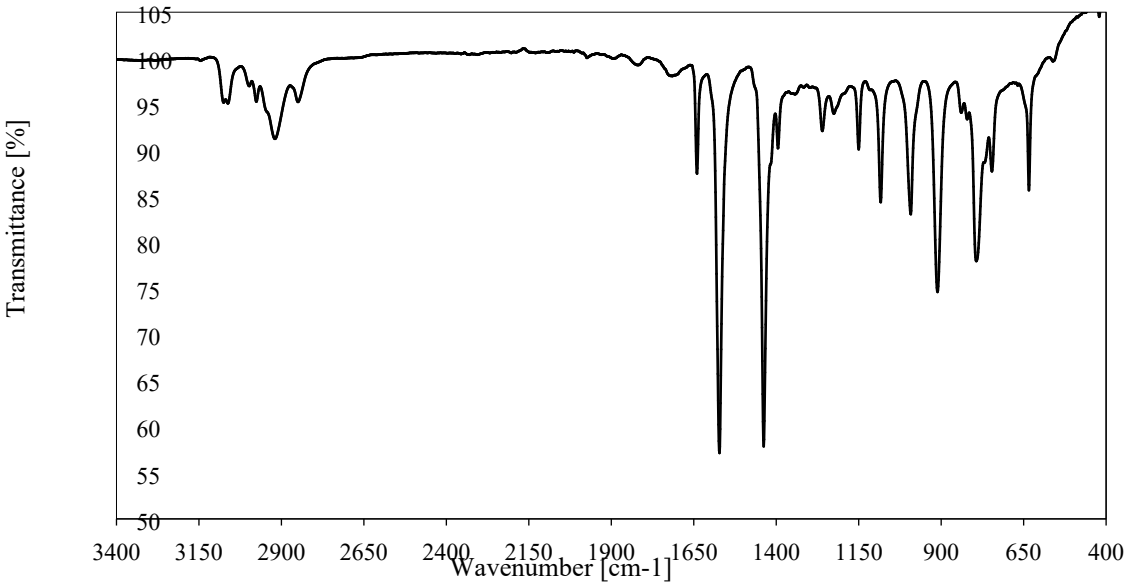


Fig. S2**:** IR spectrum of ligand **1**.

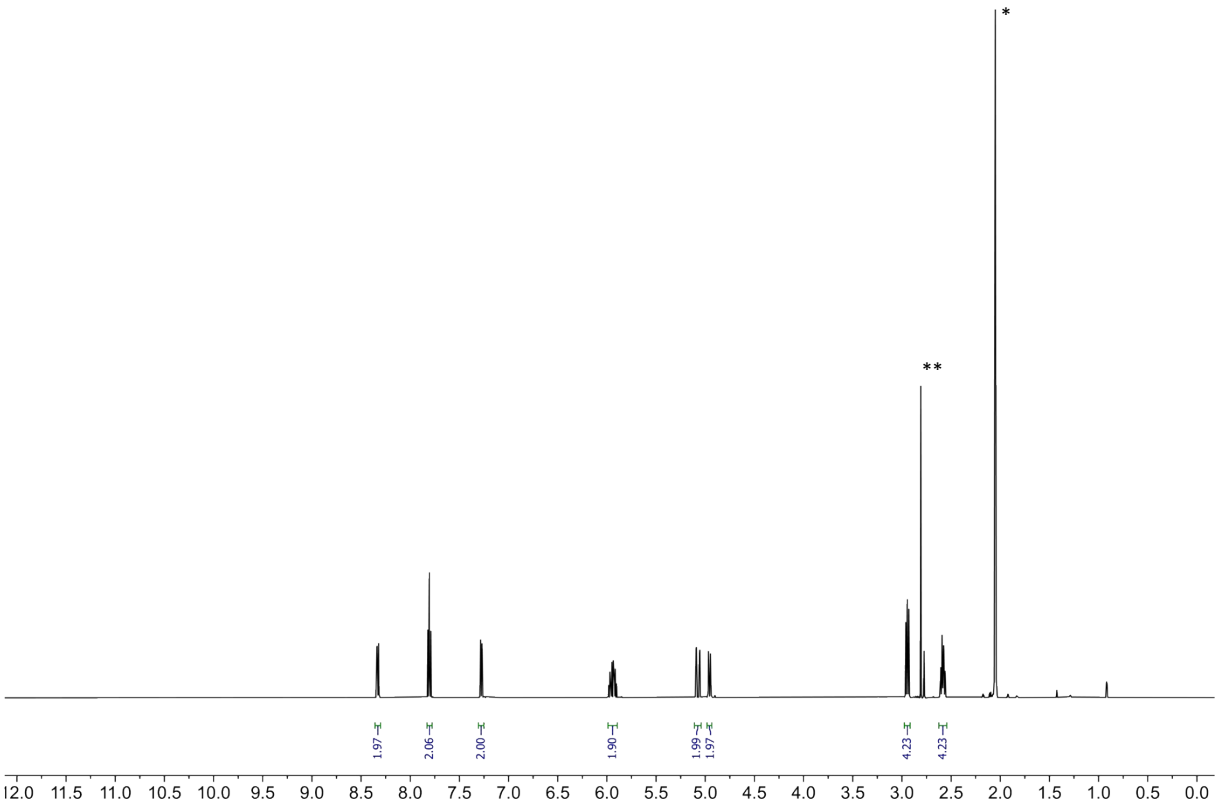


Fig. S3**:** ^{1}H-NMR spectrum (500 MHz, 298 K, acetone-d_6) of ligand **1**. Scale: δ / ppm. * = residual acetone; ** = residual H_2O and HDO.

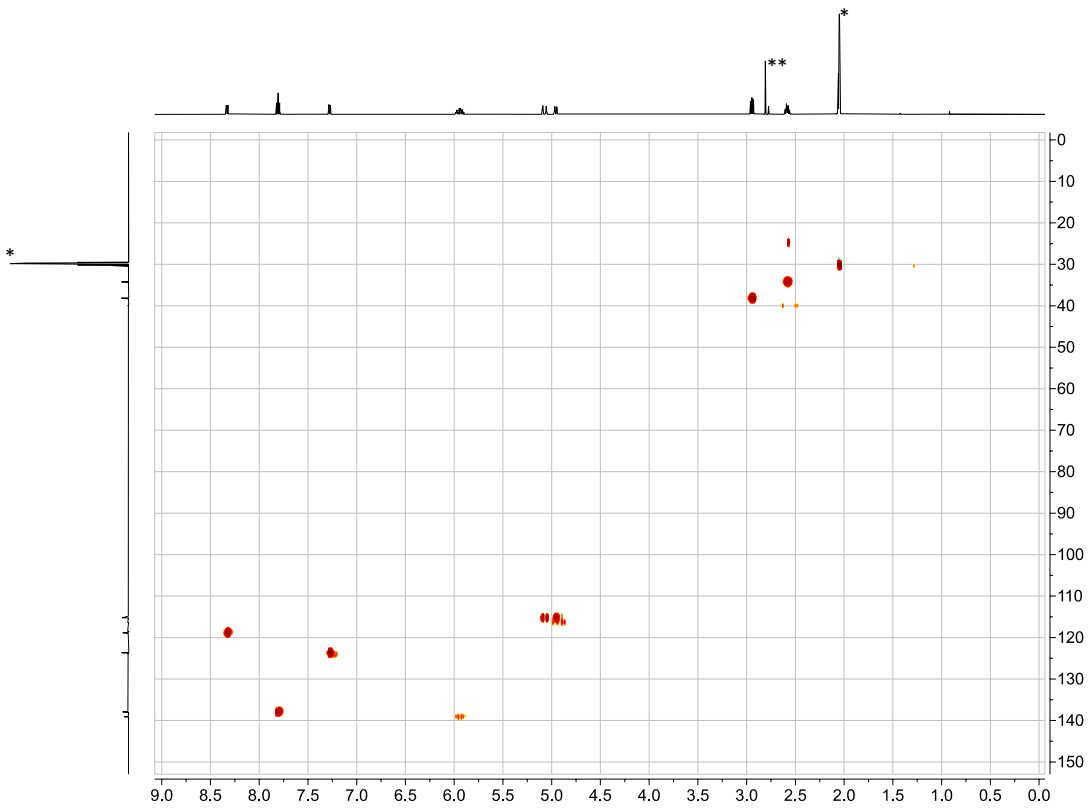


Fig. S4: HMQC spectrum (500 MHz ^{1}H, 126 MHz ^{13}C{^{1}H}, acetone-d_6, 298 K) of ligand **1**. Scale: δ / ppm. * = residual acetone; ** = residual H_2O and HDO.

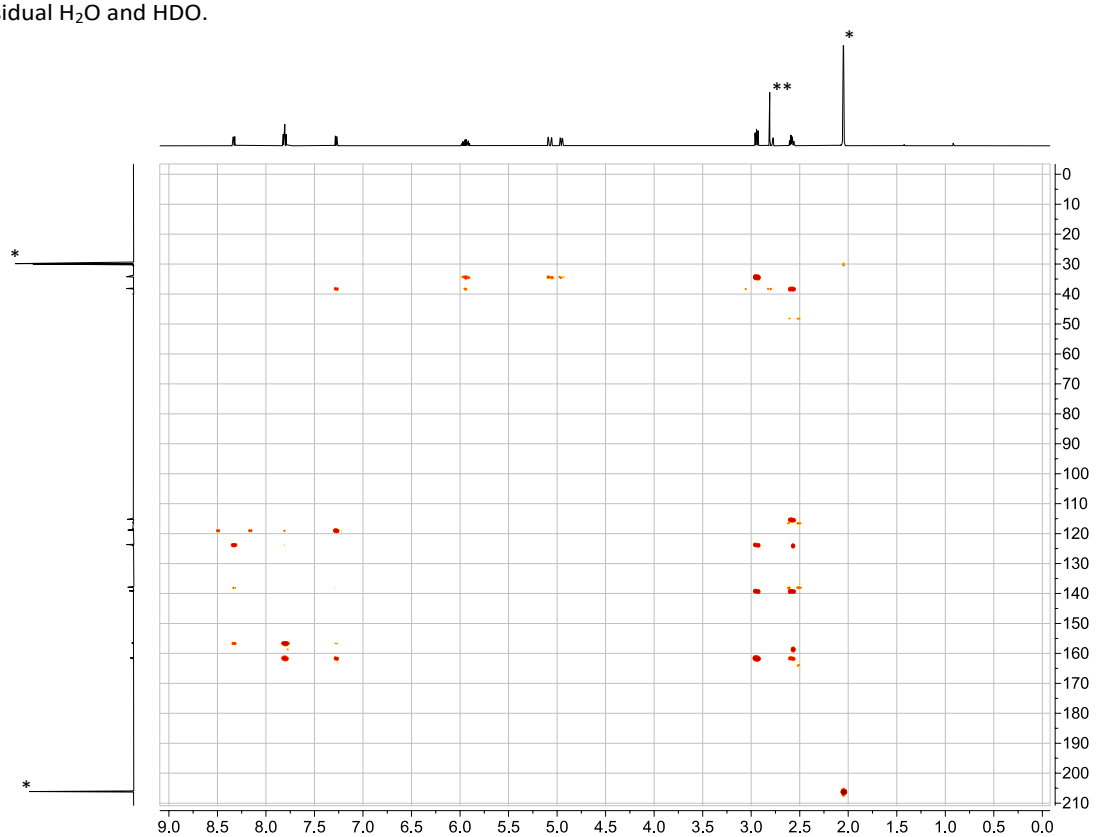


Fig. S5: HMBC spectrum (500 MHz ^{1}H, 126 MHz ^{13}C{^{1}H}, acetone-d_6, 298 K) of ligand **1**. Scale: δ / ppm. * = residual acetone; ** = residual H_2O and HDO.

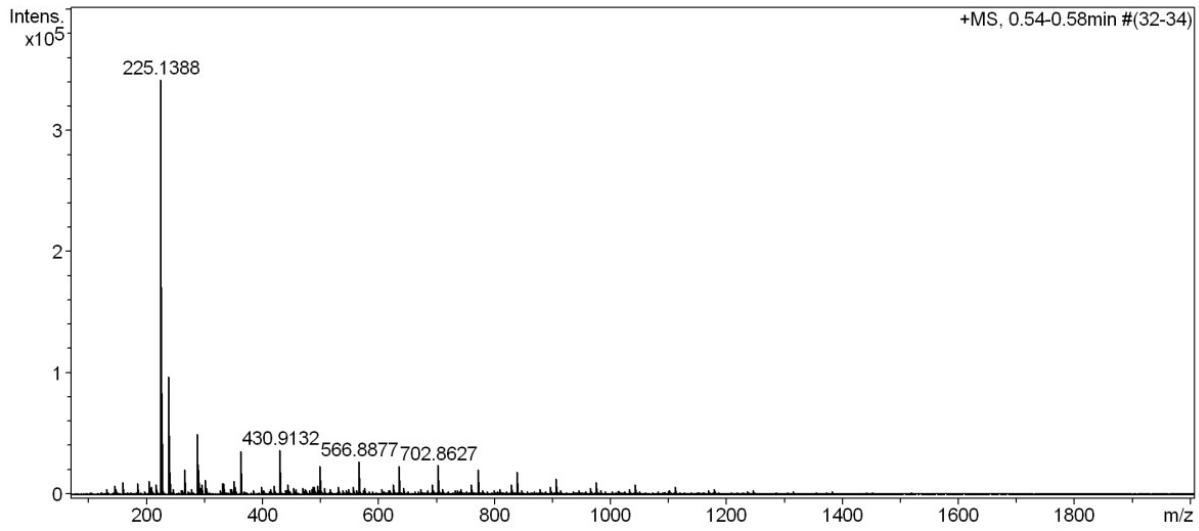


Fig. S6: HR-ESI-MS mass spectrum of ligand **2**.

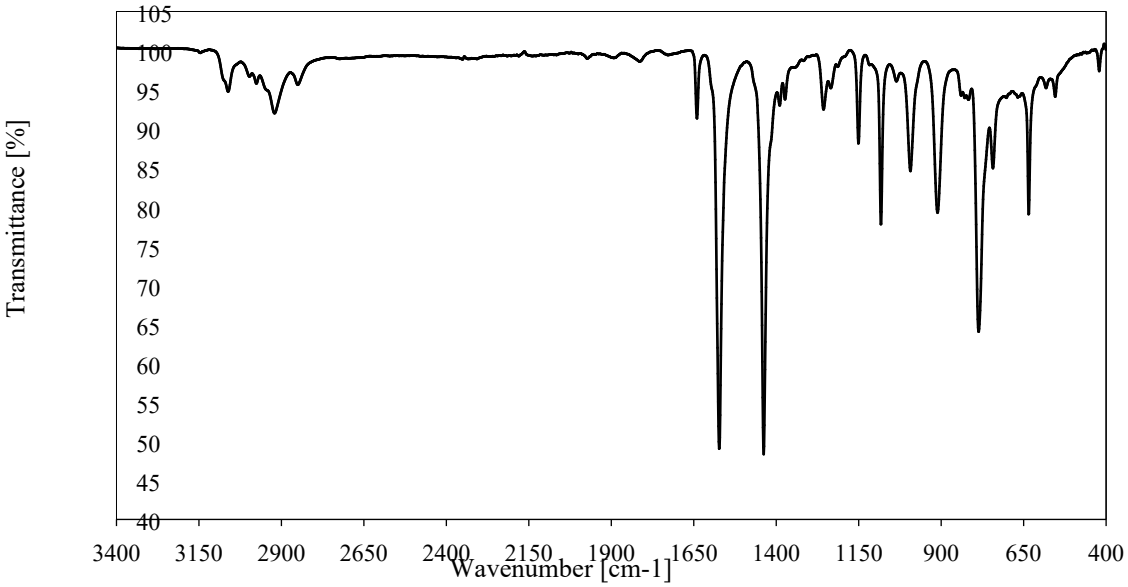


Fig. S7: IR spectrum of ligand **2**.

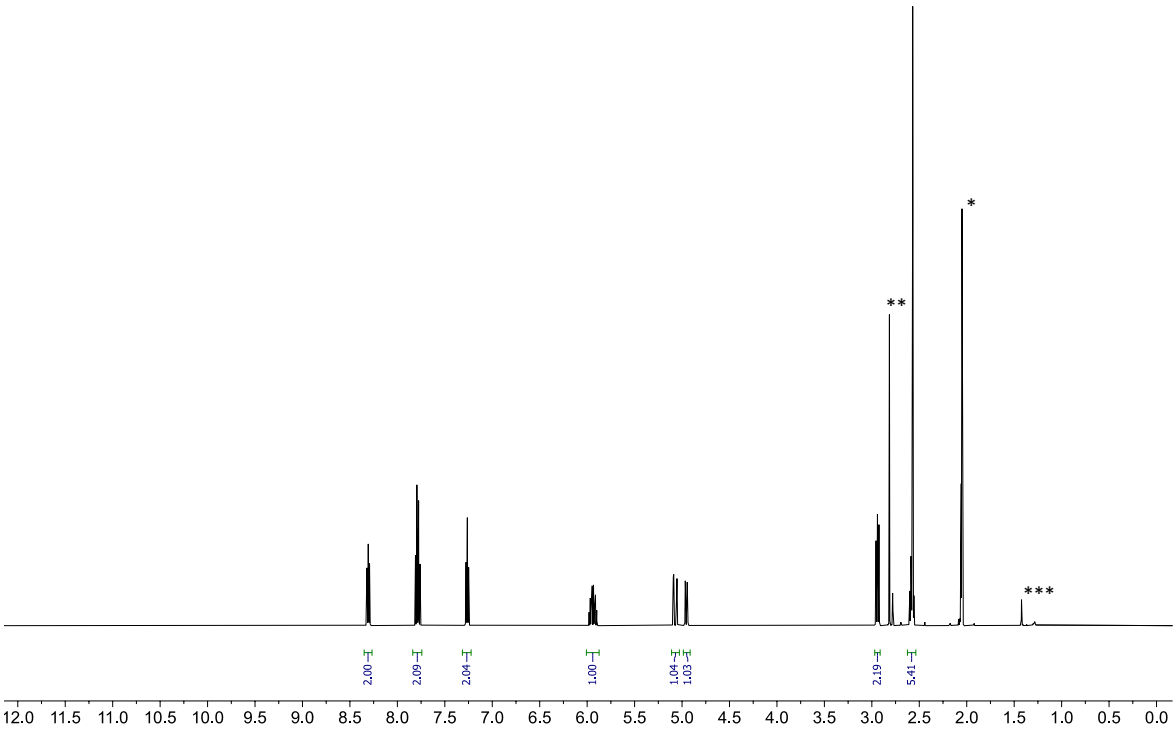


Fig. S8**:** ^{1}H-NMR spectrum (500 MHz, 298 K, acetone-d_6) of ligand **2**. Scale: δ / ppm. * = residual acetone; ** = residual H_2O and HDO; *** = residual cyclohexane.

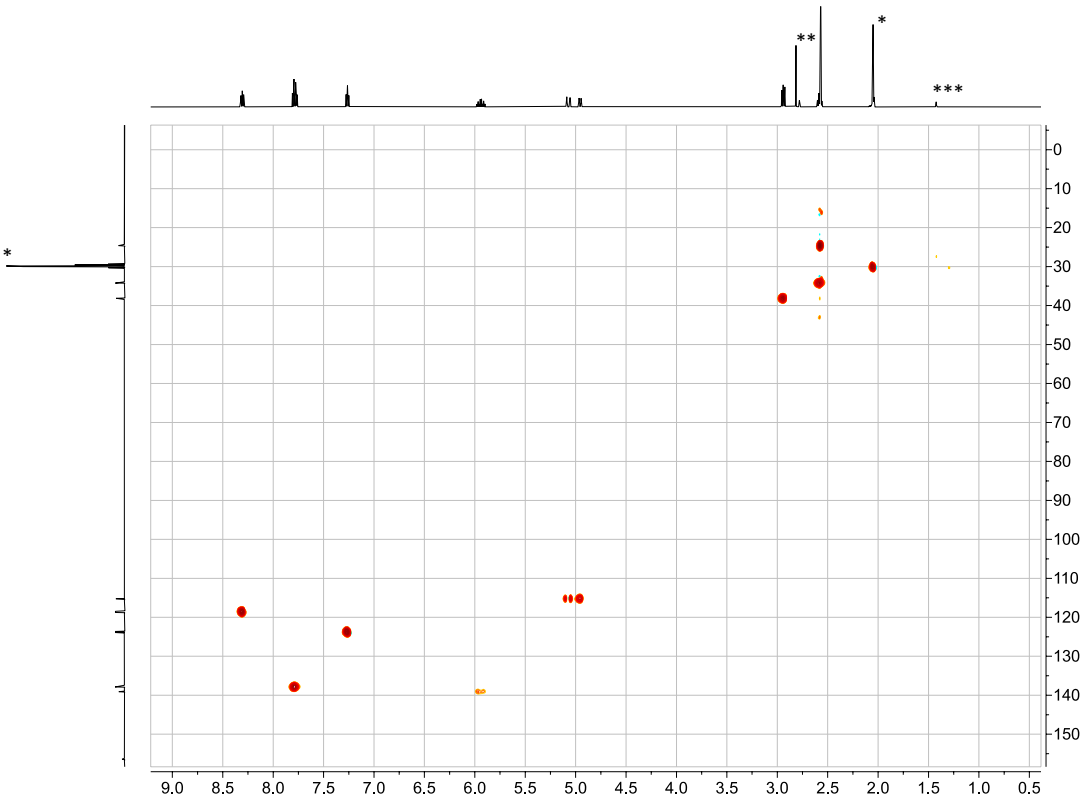


Fig. S9**:** HMQC spectrum (500 MHz ^{1}H, 126 MHz ^{13}C{^{1}H}, acetone-d_6, 298 K) of ligand **2**. Scale: δ / ppm. * = residual acetone; ** = residual H_2O and HDO; *** = residual cyclohexane.

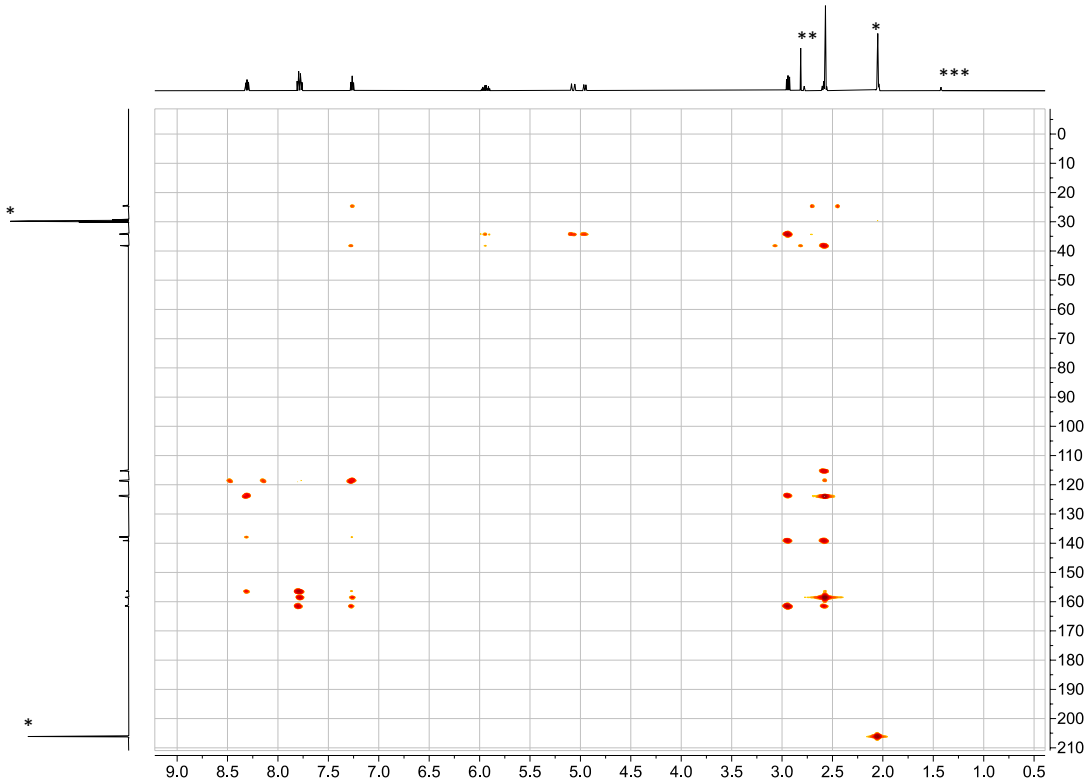


Fig. S10: HMBC spectrum (500 MHz ^{1}H, 126 MHz ^{13}C{^{1}H}, acetone-d_6, 298 K) of ligand **2**. Scale: δ / ppm. * = residual acetone; ** = residual H_2O and HDO; *** = residual cyclohexane.

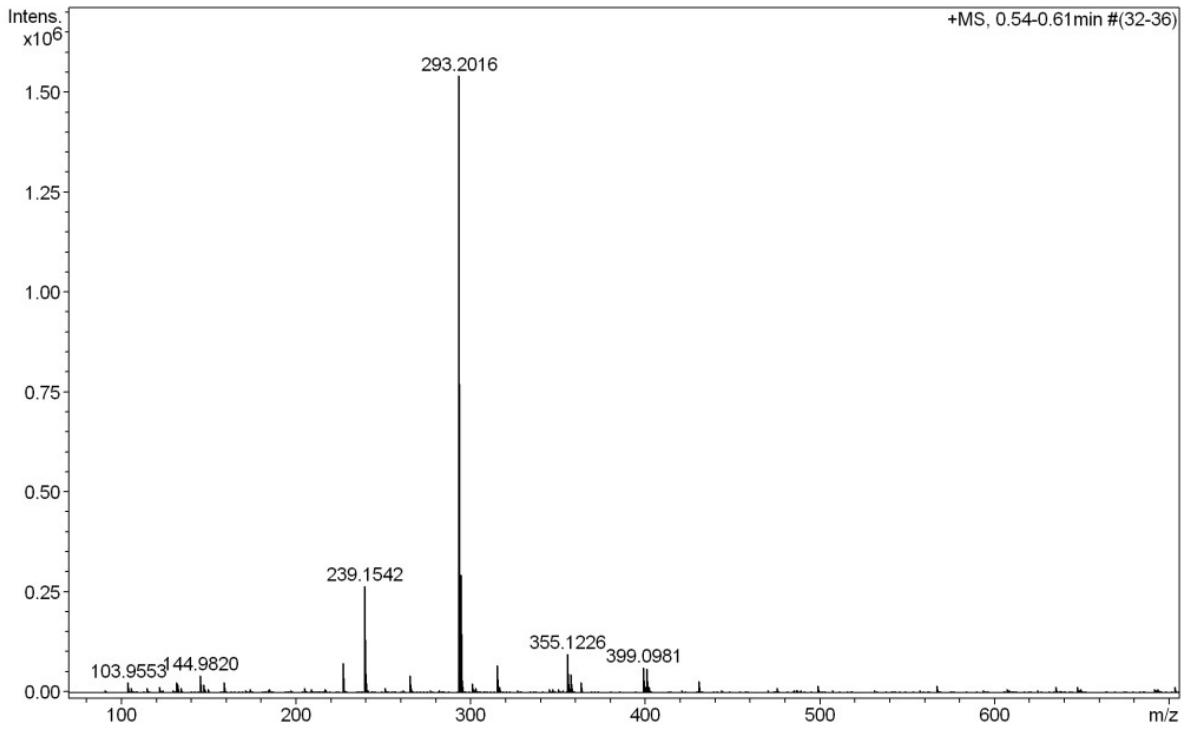


Fig. S11**:** HR-ESI-MS mass spectrum of ligand **3**.

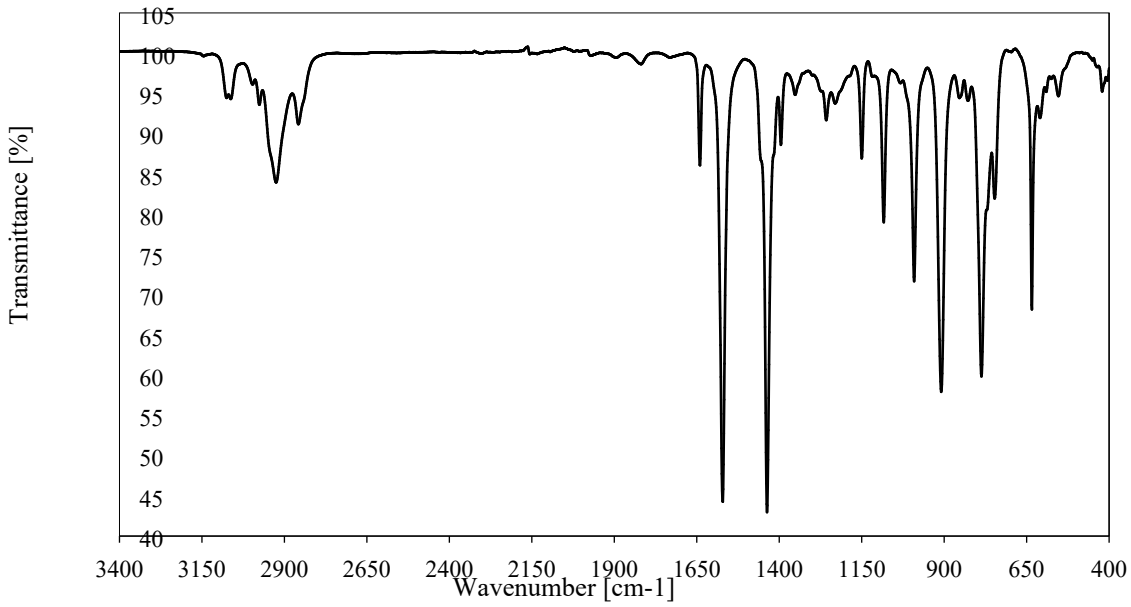


Fig. S12**:** IR spectrum of ligand **3**.

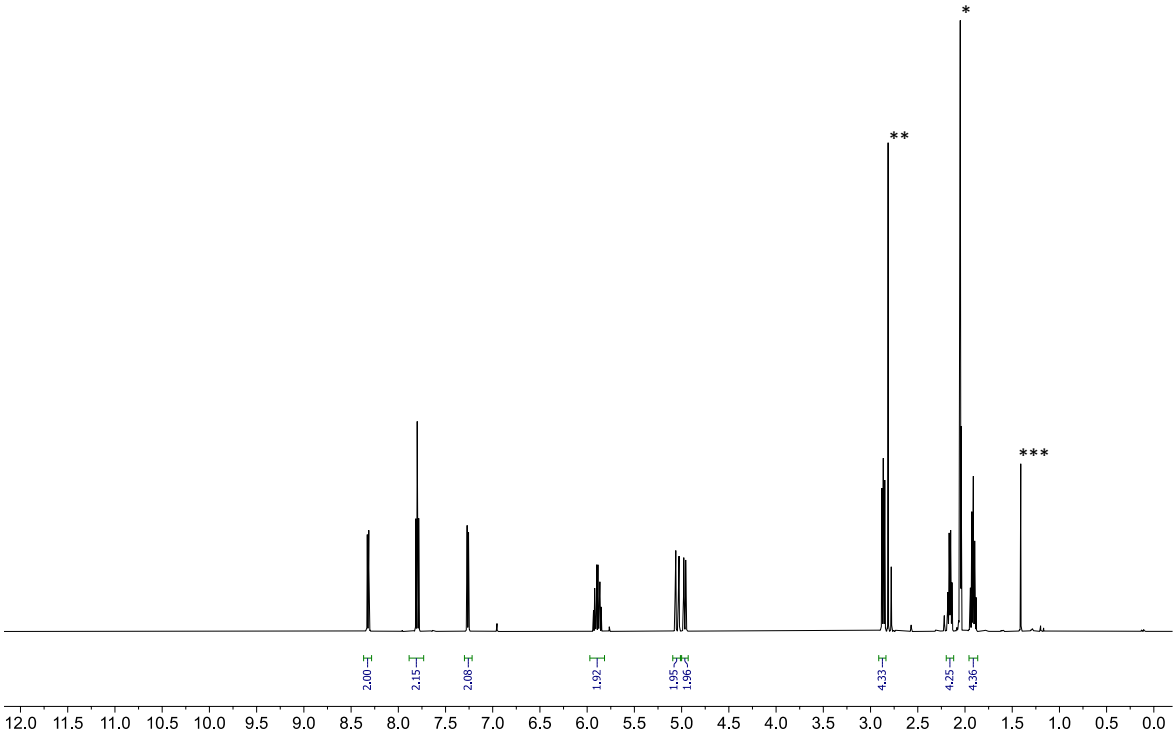


Fig. S13: ^{1}H-NMR spectrum (500 MHz, 298 K, acetone-d_6) of ligand **3**. Scale: δ / ppm. * = residual acetone; ** = residual H_2O and HDO; *** = residual cyclohexane.

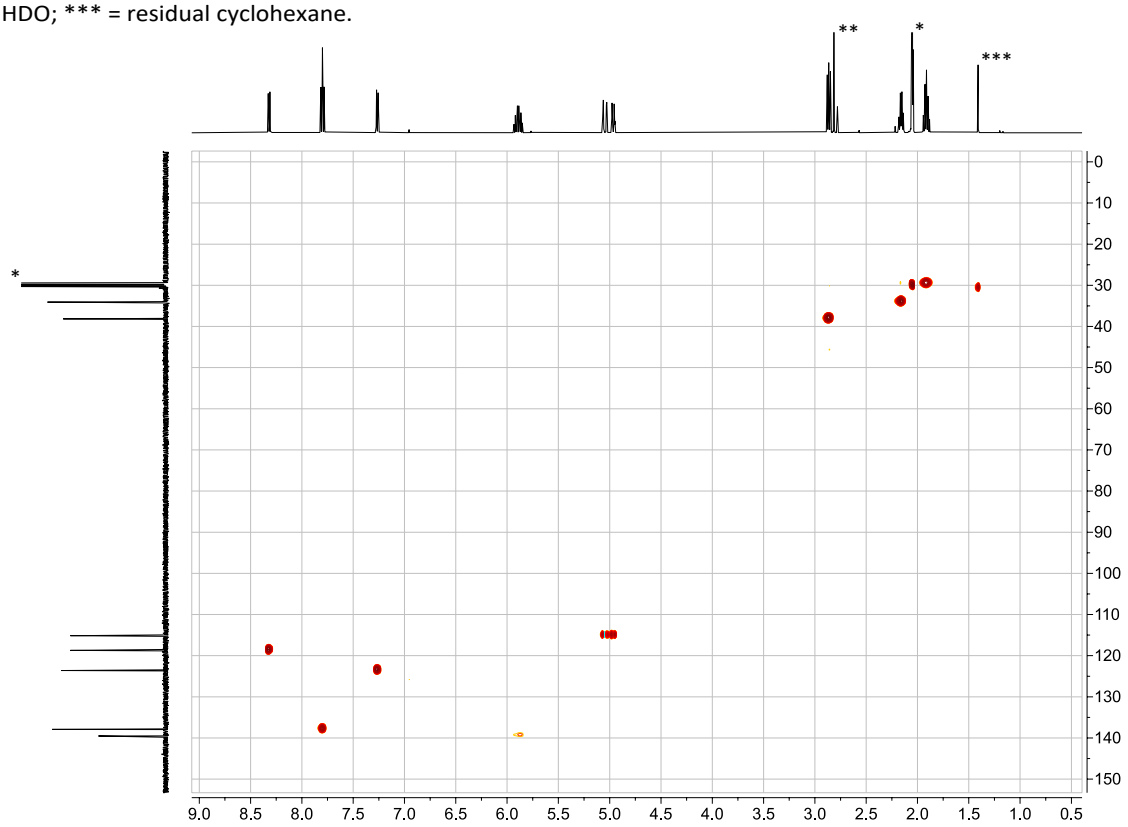


Fig. S14: HMQC spectrum (500 MHz ^{1}H, 126 MHz ^{13}C{^{1}H}, acetone-d_6, 298 K) of ligand **3**. Scale: δ / ppm. * = residual acetone; ** = residual H_2O and HDO; *** = cyclohexane.

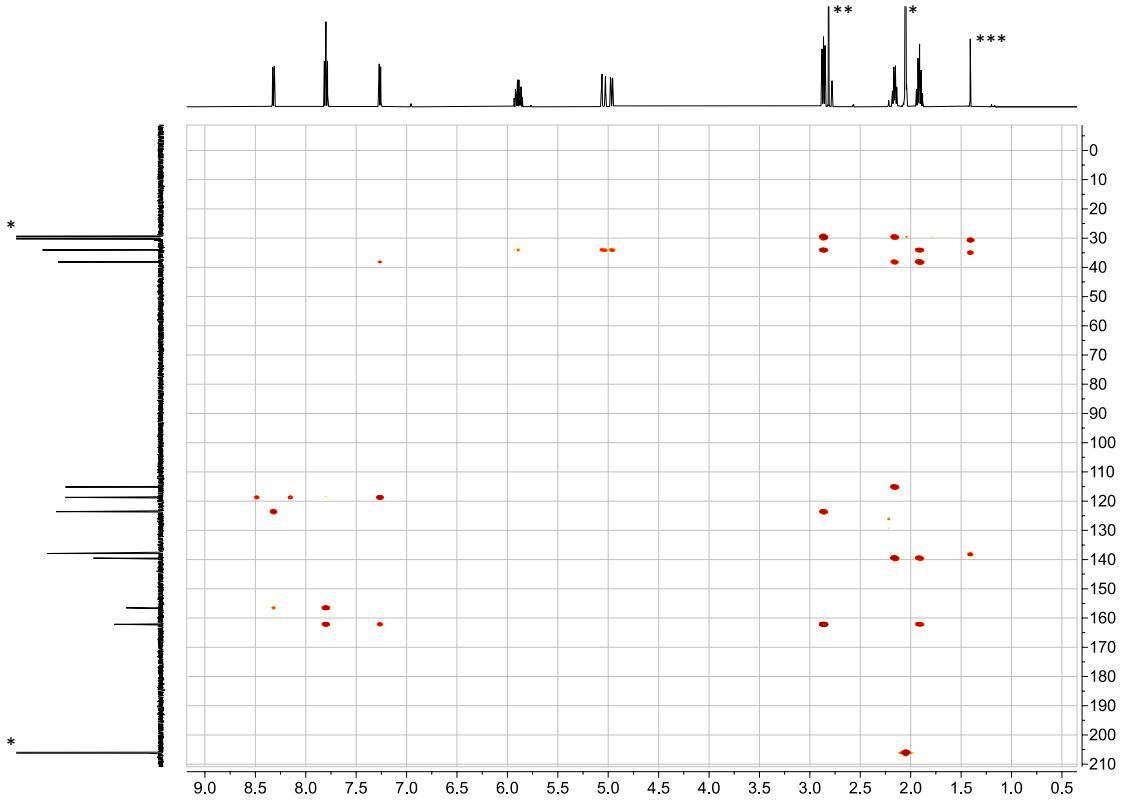


Fig. S15: HMBC spectrum (500 MHz ^{1}H, 126 MHz ^{13}C{^{1}H}, acetone-d_6, 298 K) of ligand **3**. Scale: δ / ppm. * = residual acetone-d_5; ** = residual H_2O and HDO; *** = residual cyclohexane.

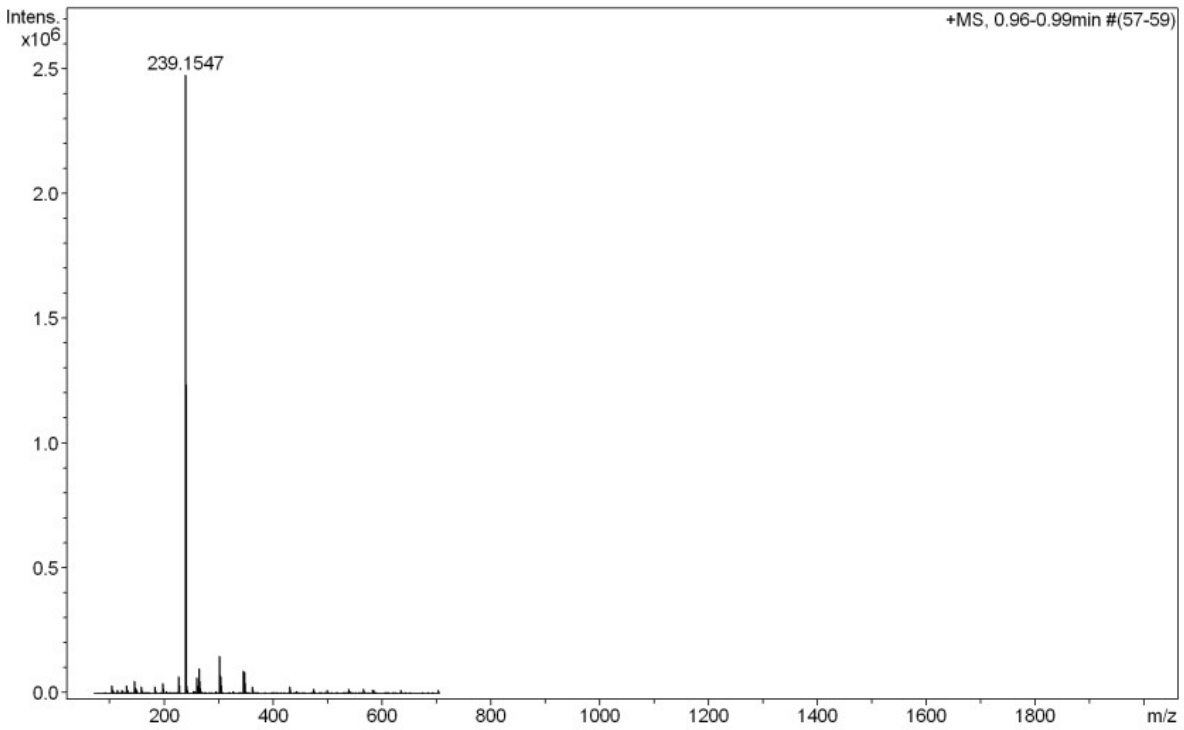


Fig. S16**:** HR-ESI-MS mass spectrum of ligand **4**.

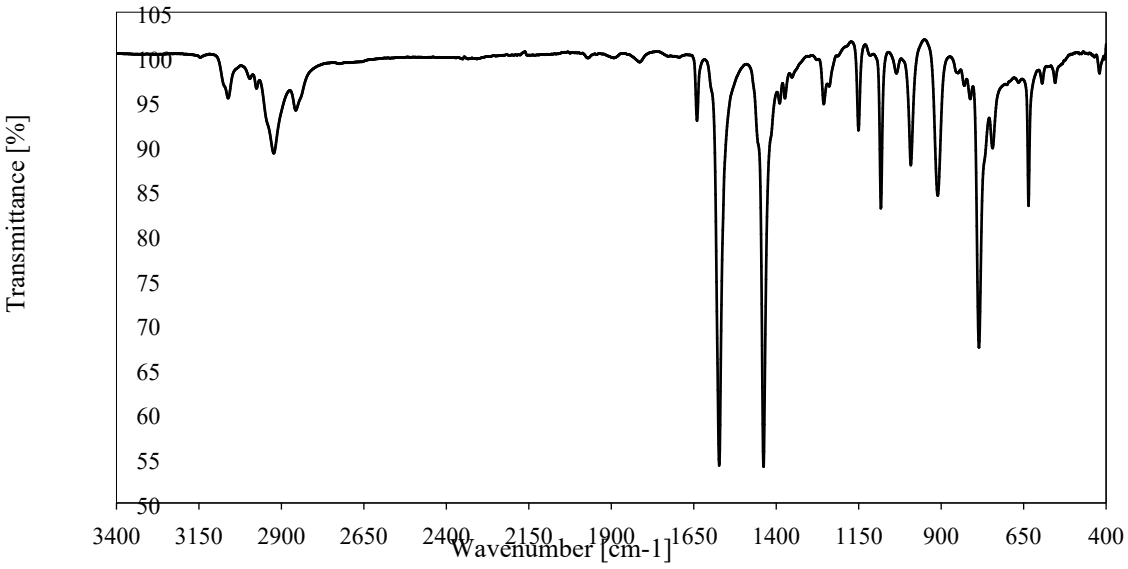


Fig. S17**:** IR spectrum of ligand **4**.

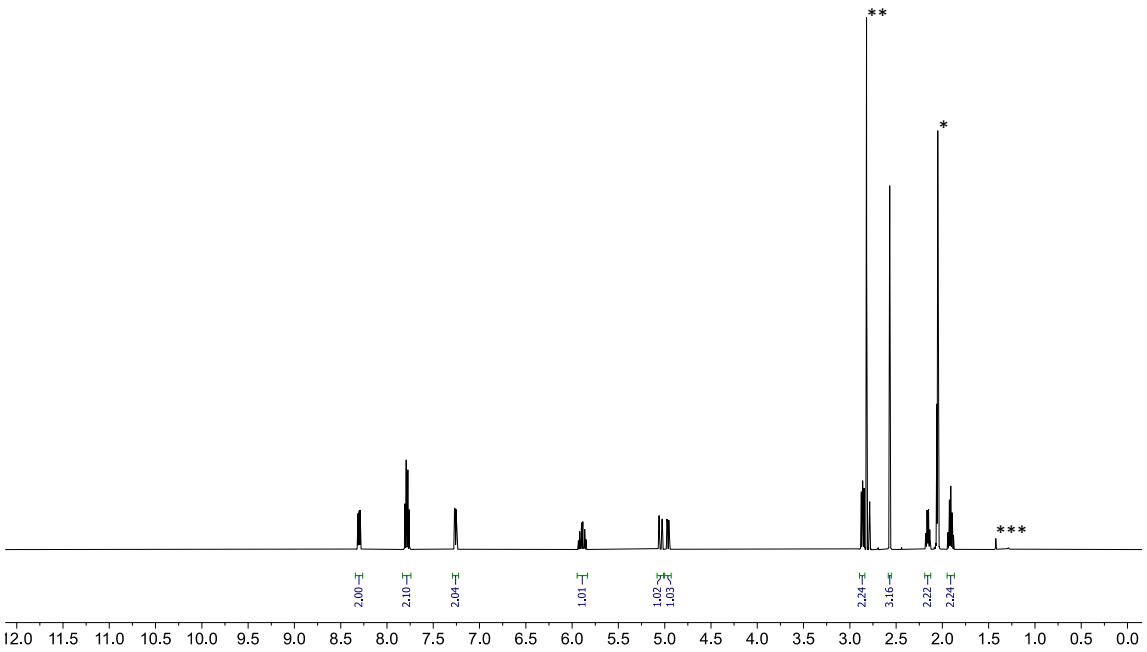


Fig. S18: ^{1}H-NMR spectrum (500 MHz, 298 K, acetone-d_6) of ligand **4**. Scale: δ / ppm. * = residual acetone; ** = residual H_2O and HDO; *** = residual cyclohexane.

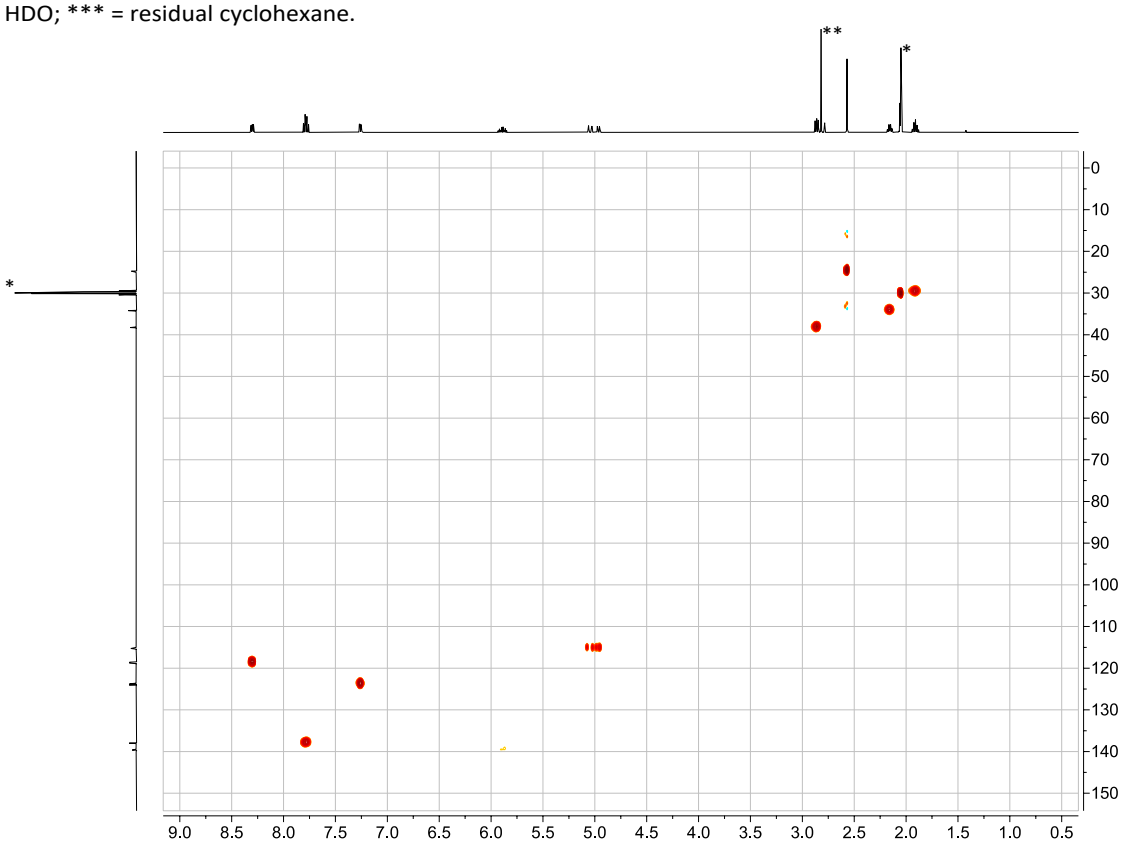


Fig. S19: HMQC spectrum (500 MHz ^{1}H, 126 MHz ^{13}C{^{1}H}, acetone-d_6, 298 K) of ligand **4**. Scale: δ / ppm. * = residual acetone; ** = residual H_2O and HDO.

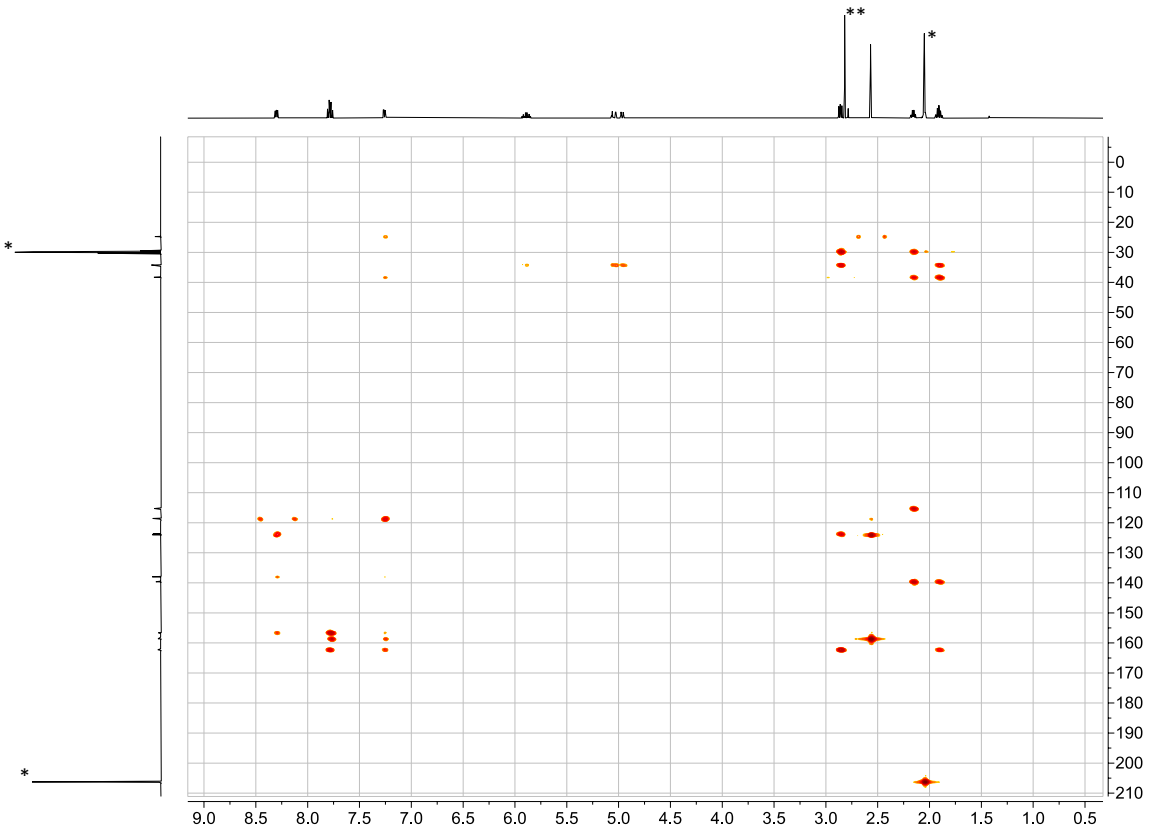
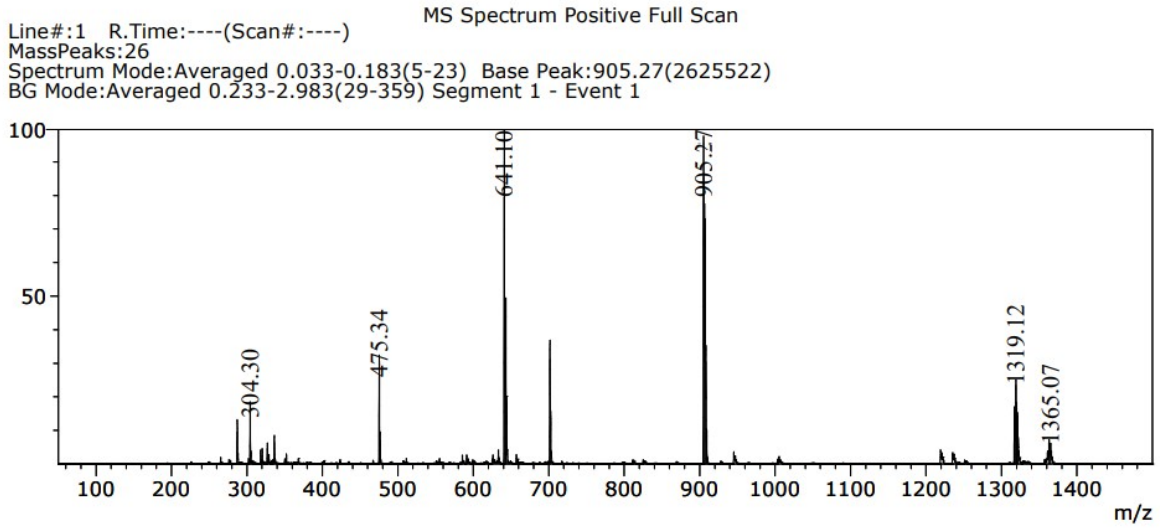
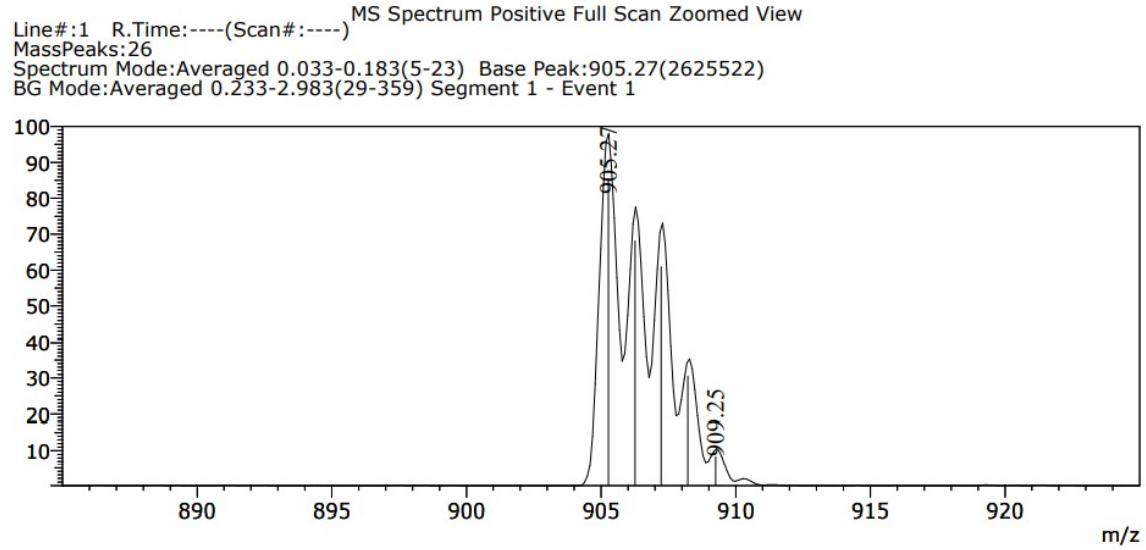


Fig. S20**:** HMBC spectrum (500 MHz ^{1}H, 126 MHz ^{13}C{^{1}H}, acetone-d_6, 298 K) of ligand **4**. Scale: δ / ppm. * = residual acetone; ** = residual H_2O and HDO.





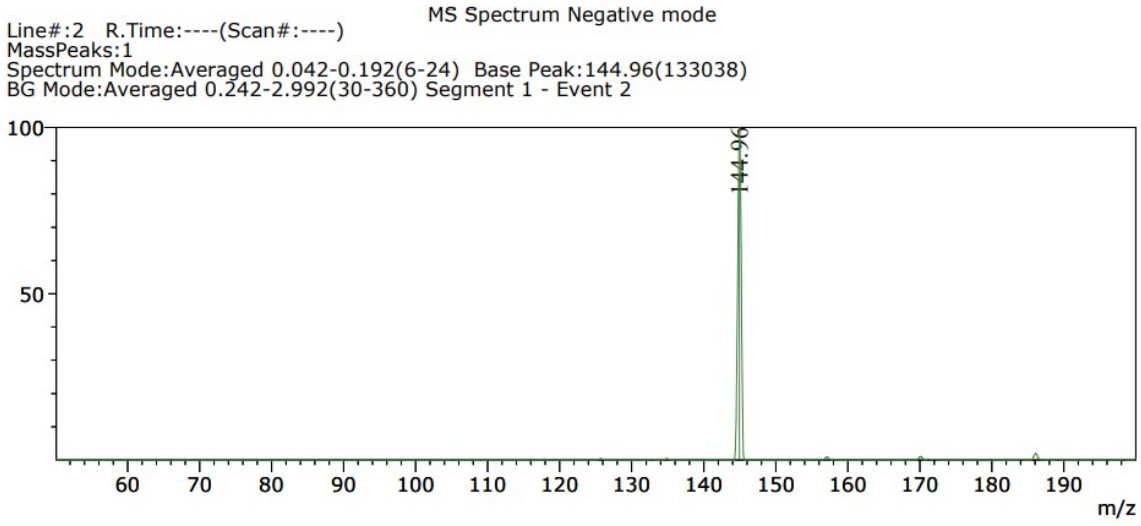


Fig. S21: The ESI mass spectrum (positive and negative mode) of [Cu(**1**)(xantphos)][PF_6].

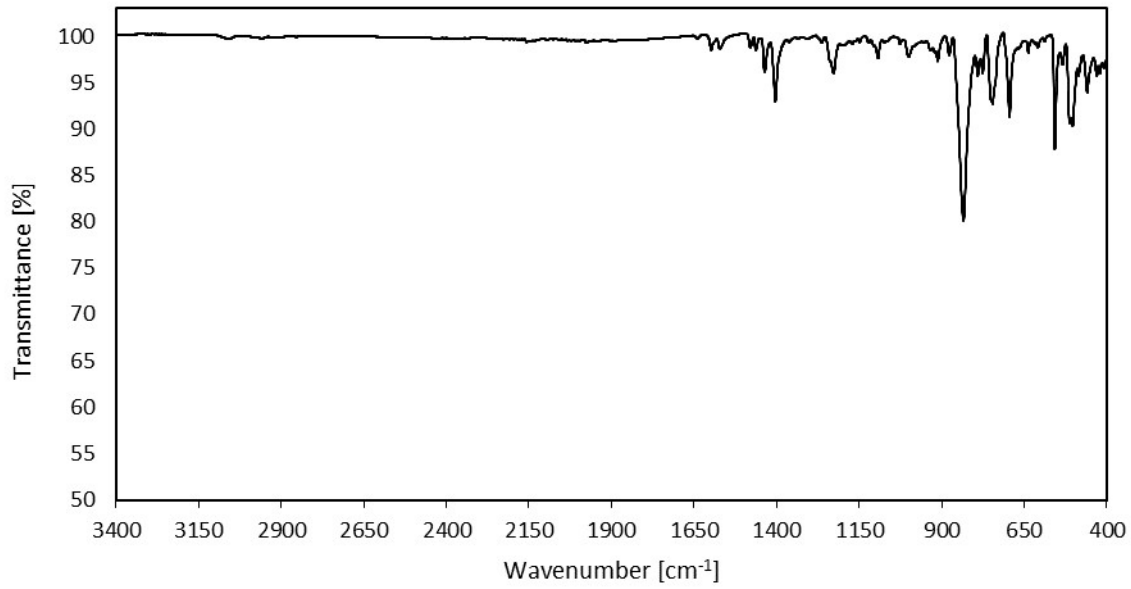


Fig. S22: IR spectrum of [Cu(**1**)(xantphos)][PF_6].

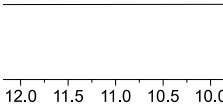


Fig. S23**:** ^{1}H-NMR spectrum (500 MHz, 298 K, acetone-d_6) of [Cu(**1**)(xantphos)][PF_6]. Scale: δ / ppm. * = residual acetone; ** = residual H_2O and HDO; *** = residual diethyl ether.

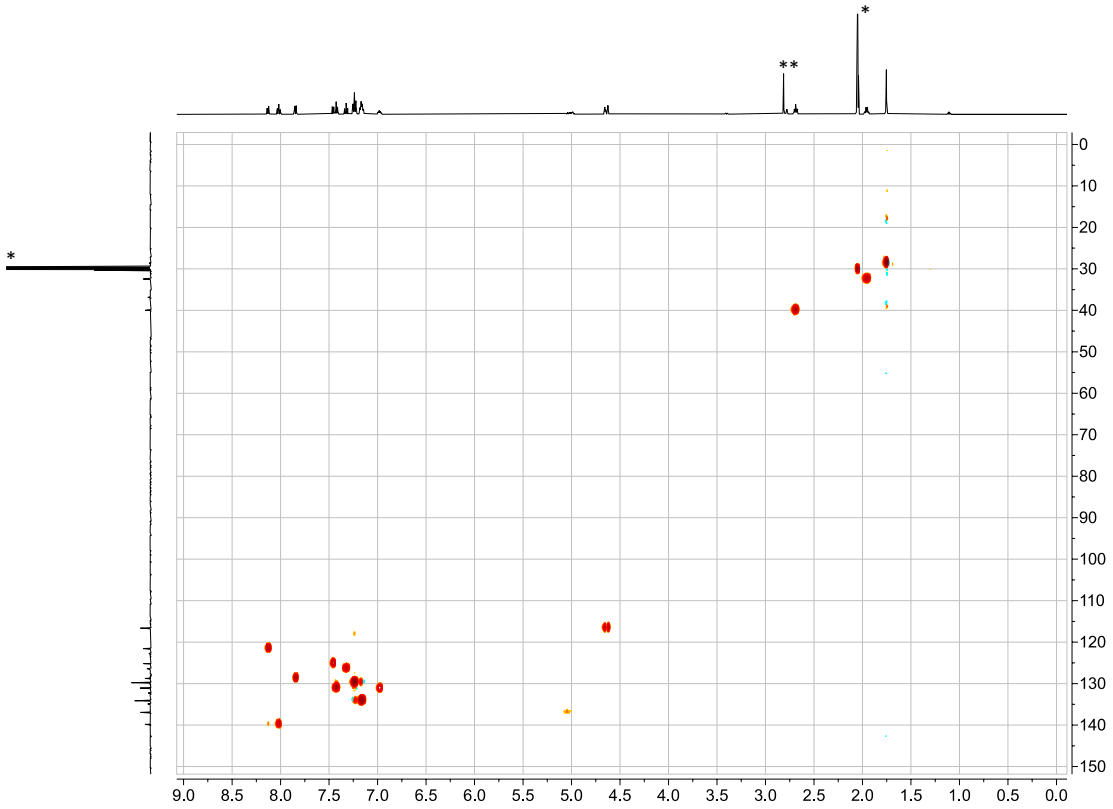


Fig. S24: HMQC spectrum (500 MHz ^{1}H, 126 MHz ^{13}C{^{1}H}, acetone-d_6, 298 K) of [Cu(**1**)(xantphos)][PF_6]. Scale: δ / ppm. * = residual acetone; ** = residual H_2O and HDO.

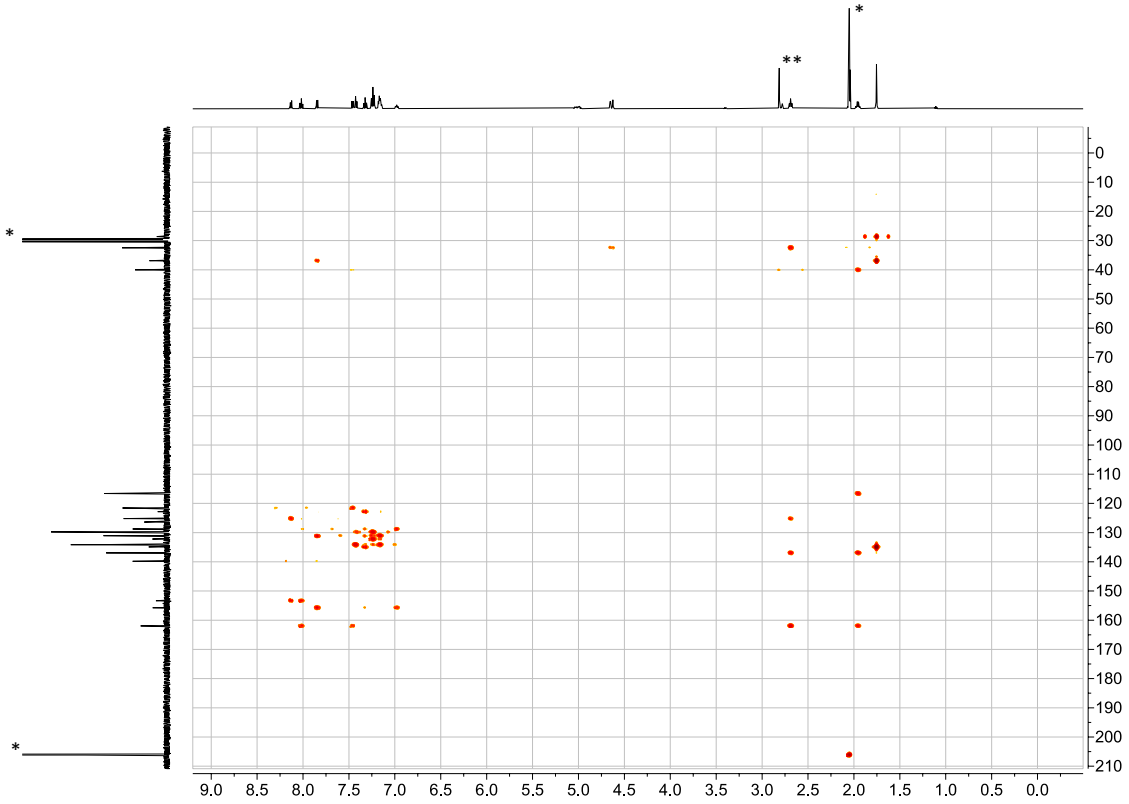


Fig. S25: HMBC spectrum (500 MHz ^{1}H, 126 MHz ^{13}C{^{1}H}, acetone-d_6, 298 K) of [Cu(**1**)(xantphos)][PF_6]. Scale: δ / ppm. * = residual acetone; ** = residual H_2O and HDO.

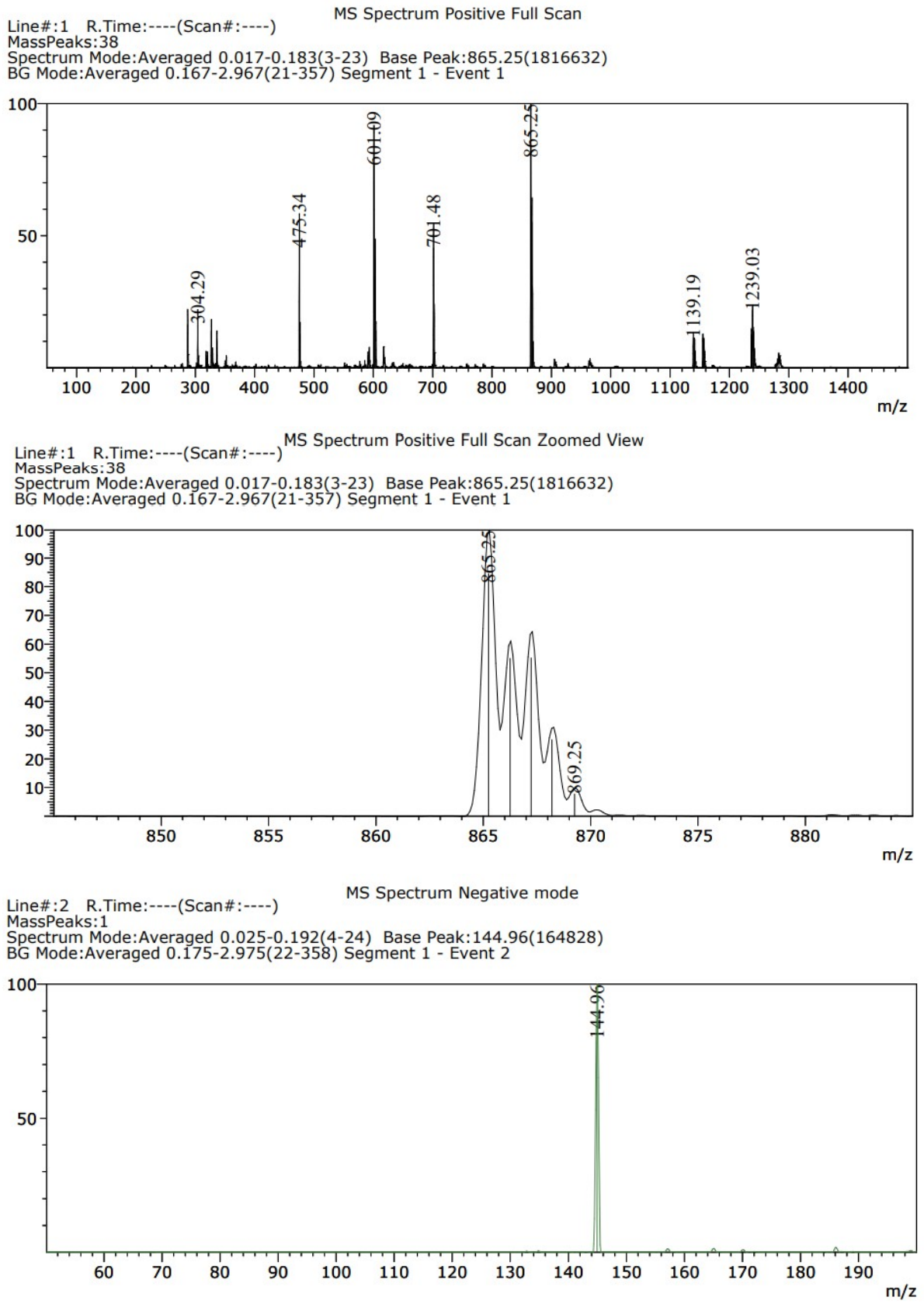


Fig. S26: ESI mass spectrum (positive and negative mode) of [Cu(**1**)(POP)][PF_6].

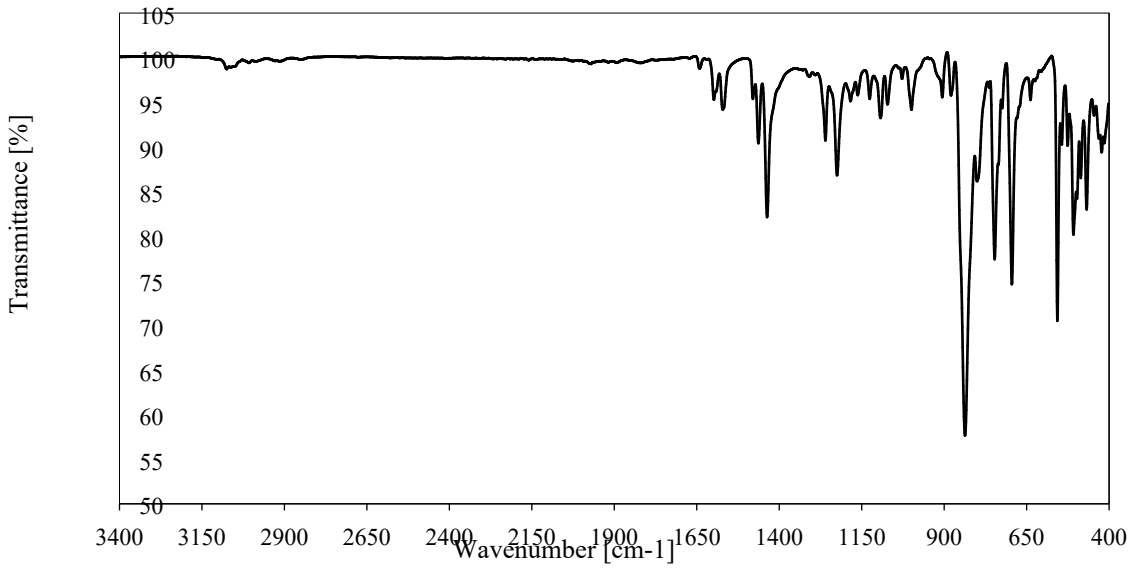


Fig. S27: IR spectrum of [Cu(**1**)(POP)][PF_6].

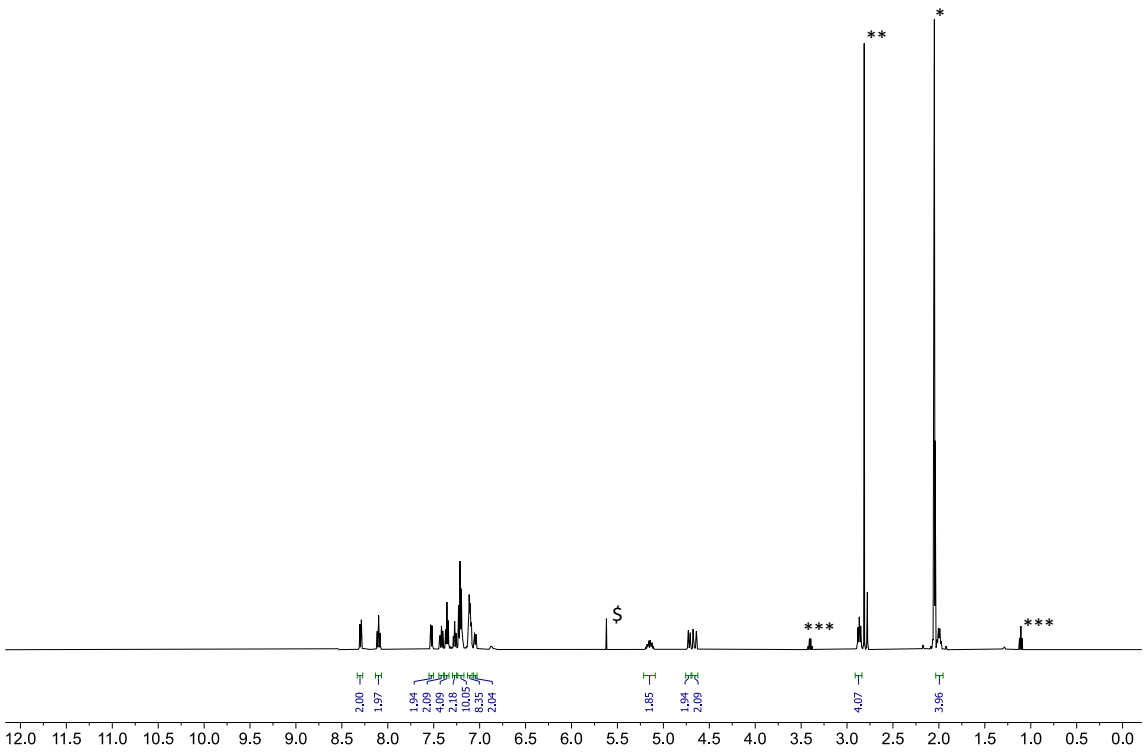


Fig. S28**:** ^{1}H-NMR spectrum (500 MHz, 298 K, acetone-d_6) of [Cu(**1**)(POP)][PF_6]. Scale: δ / ppm. * = residual acetone; ** = residual H_2O and HDO; *** = residual diethyl ether; $ = residual dichloromethane.

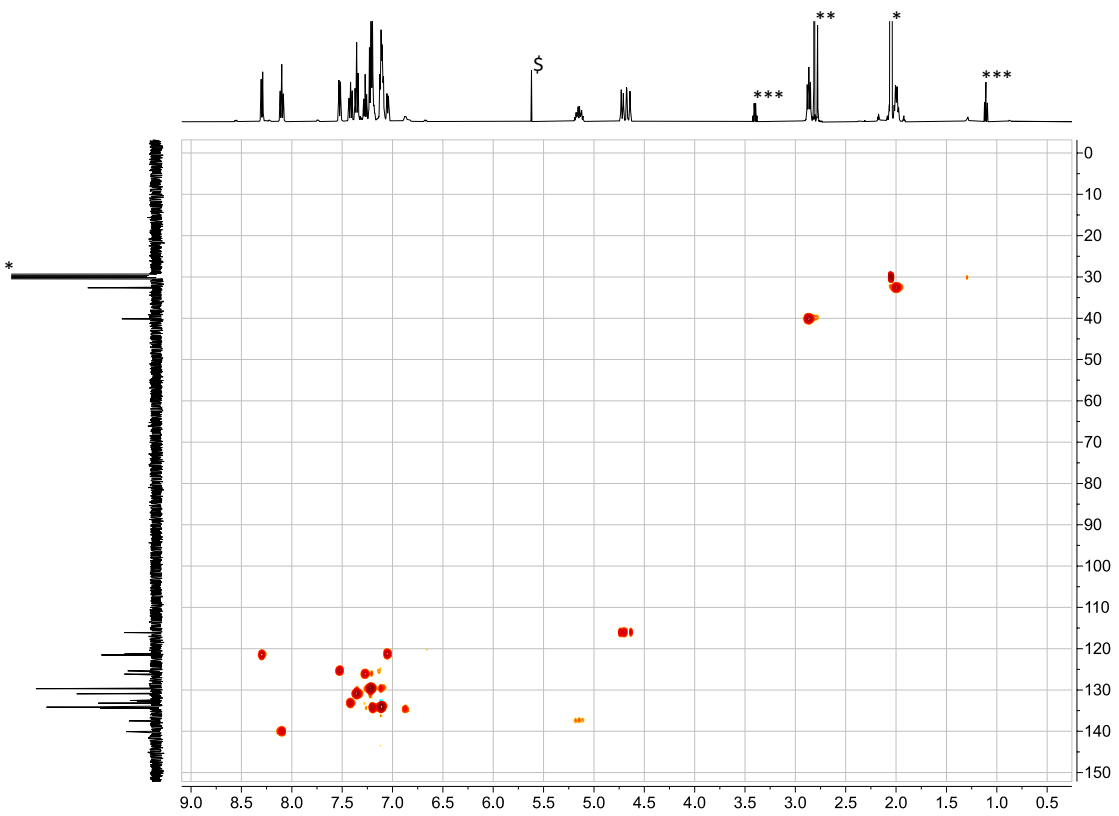


Fig. S29: HMQC spectrum (500 MHz ^{1}H, 126 MHz ^{13}C{^{1}H}, acetone-d_6, 298 K) of [Cu(**1**)(POP)][PF_6]. Scale: δ / ppm. * = residual acetone; ** = residual H_2O and HDO; *** = residual diethyl ether; $ = residual dichloromethane.

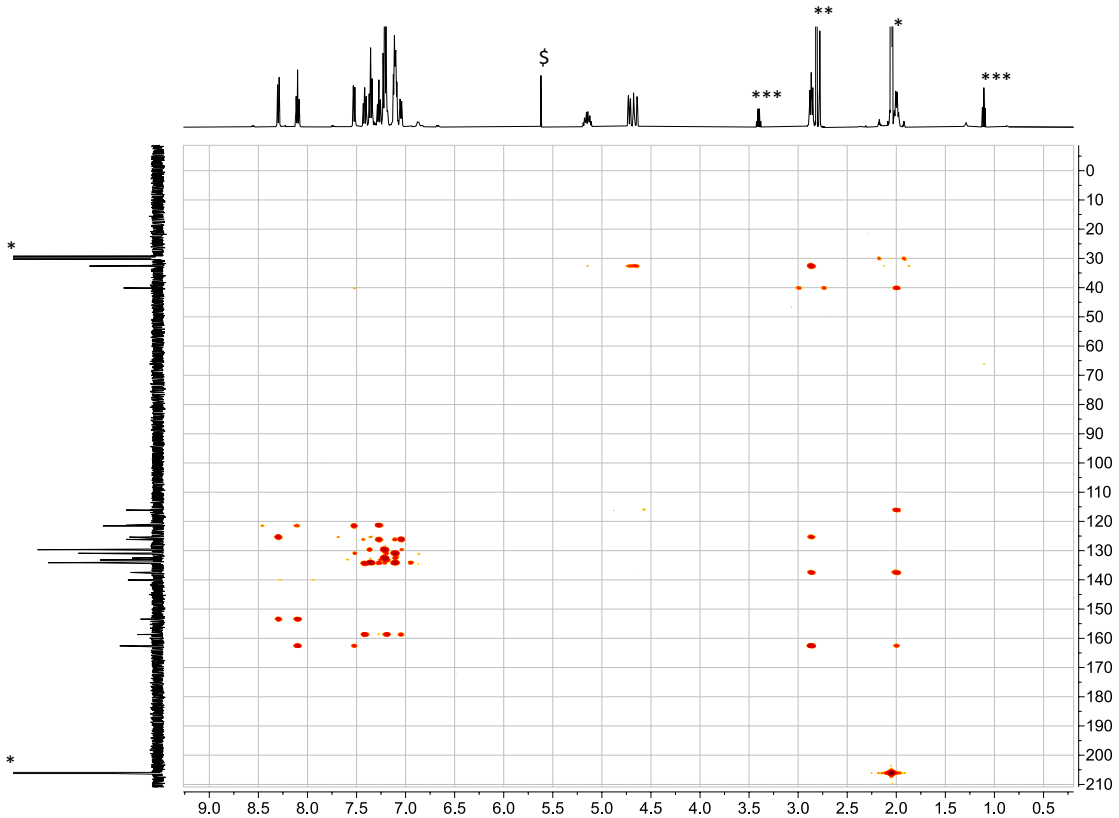


Fig. S30: HMBC spectrum (500 MHz ^{1}H, 126 MHz ^{13}C{^{1}H}, acetone-d_6, 298 K) of [Cu(**1**)(POP)][PF_6]. Scale: δ / ppm. * = residual acetone; ** = residual H_2O and HDO; *** = residual diethyl ether; $ = residual dichloromethane.

MS Spectrum Positive Full Scan

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MassPeaks:20
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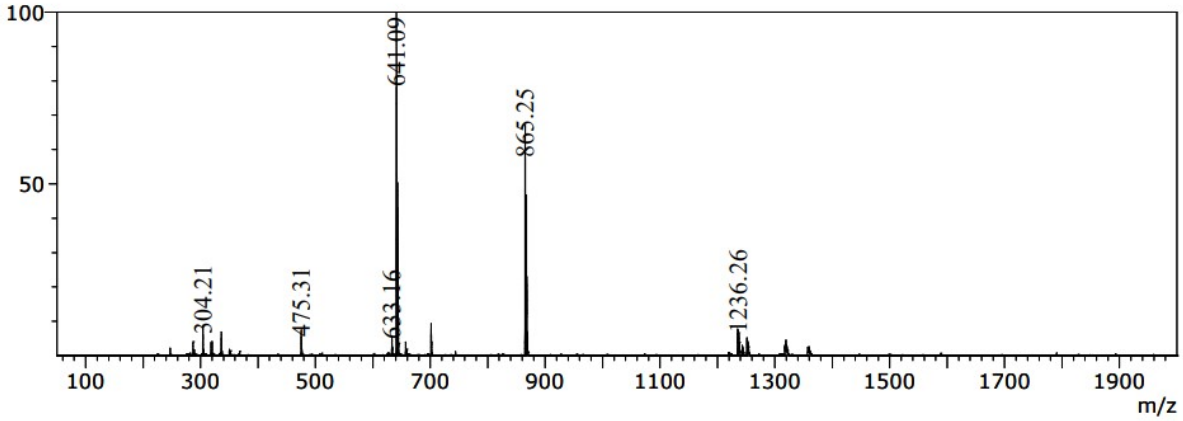
BG Mode:Averaged 0.200-2.983(25-359) Segment 1 - Event 1



MS Spectrum Positive Full Scan Zoomed View

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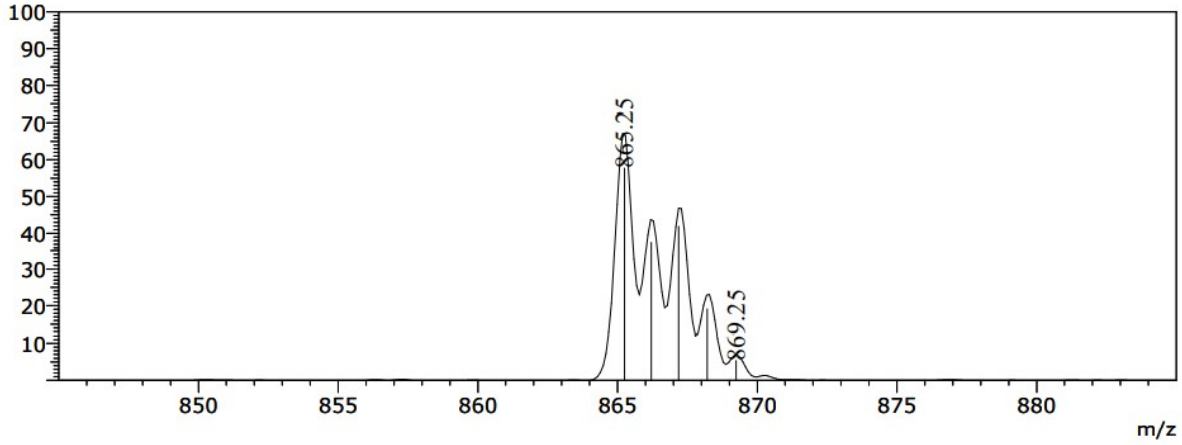
BG Mode:Averaged 0.200-2.983(25-359) Segment 1 - Event 1



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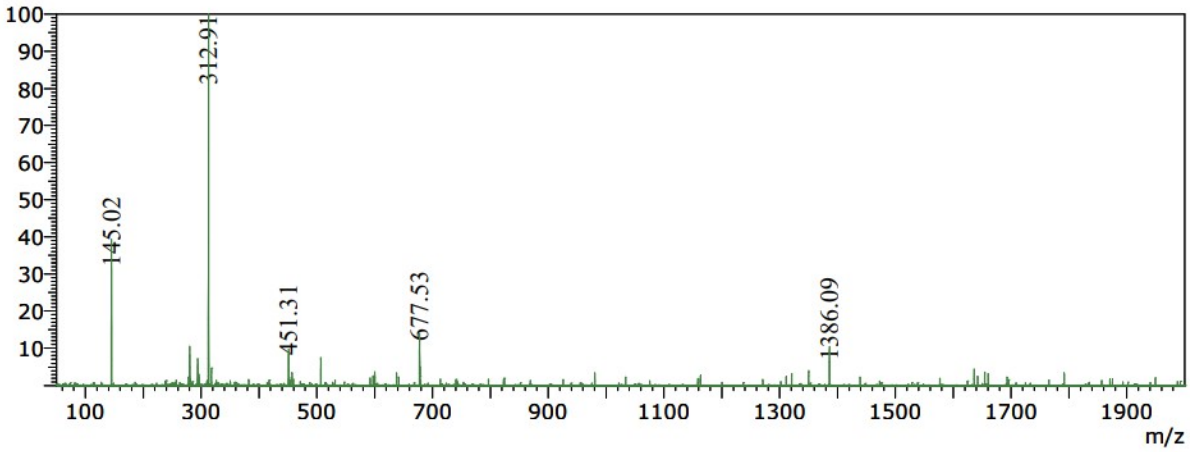


Fig. S31**:** ESI mass spectrum (positive and negative mode) of [Cu(**2**)(xantphos)][PF_6].

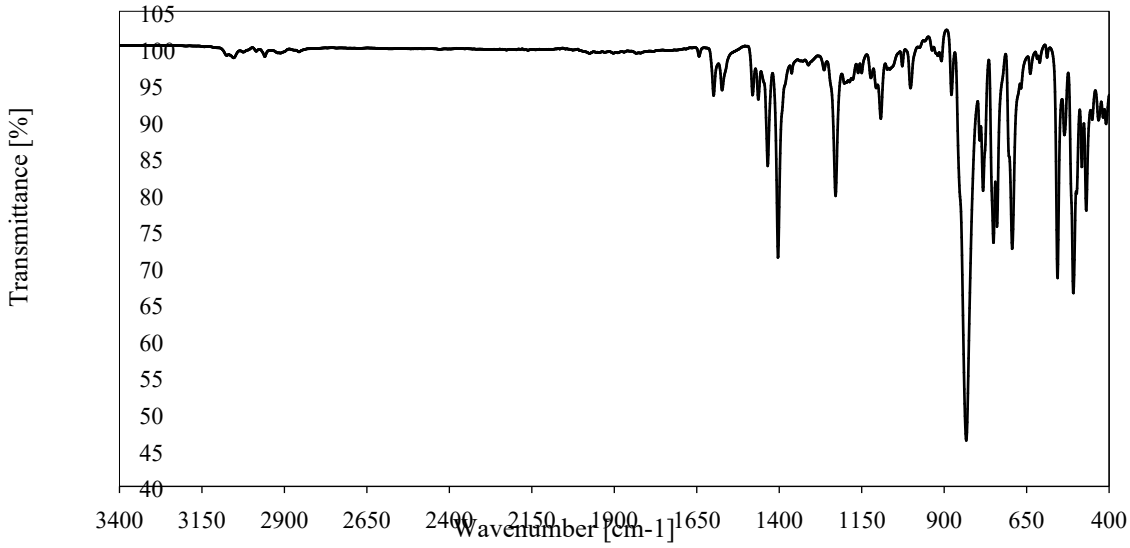


Fig. S32: IR spectrum of [Cu(**2**)(xantphos)][PF_6].

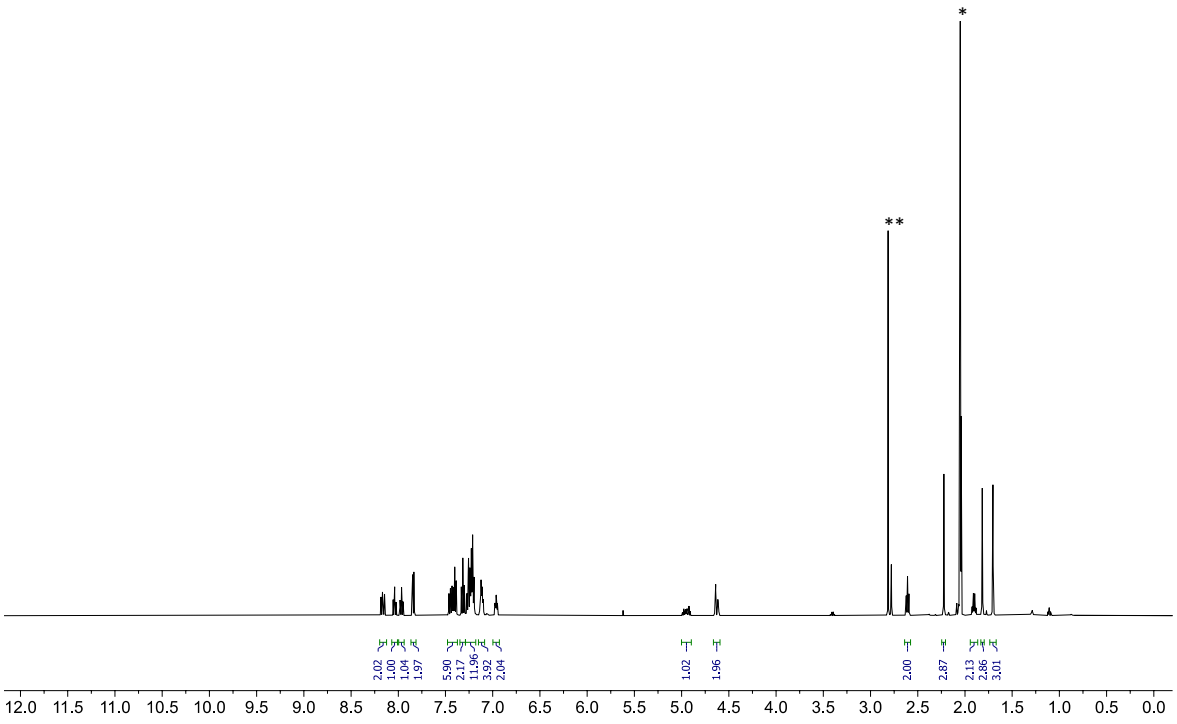


Fig. S33**:** ^{1}H-NMR spectrum (500 MHz, 298 K, acetone-d_6) of [Cu(**2**)(xantphos)][PF_6]. Scale: δ / ppm. * = residual acetone; ** = residual H_2O and HDO.

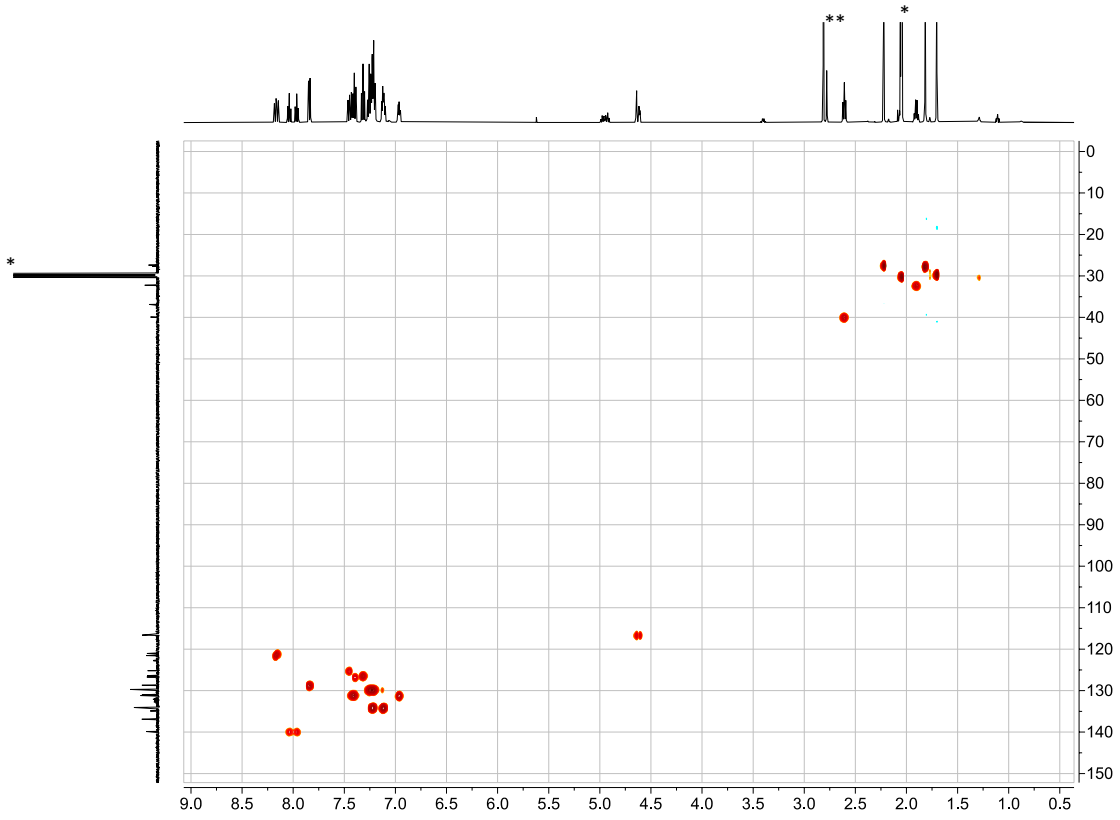


Fig. S34: HMQC spectrum (500 MHz ^{1}H, 126 MHz ^{13}C{^{1}H}, acetone-d_6, 298 K) of [Cu(**2**)(xantphos)][PF_6]. Scale: δ / ppm. * = residual acetone; ** = residual H_2O and HDO.

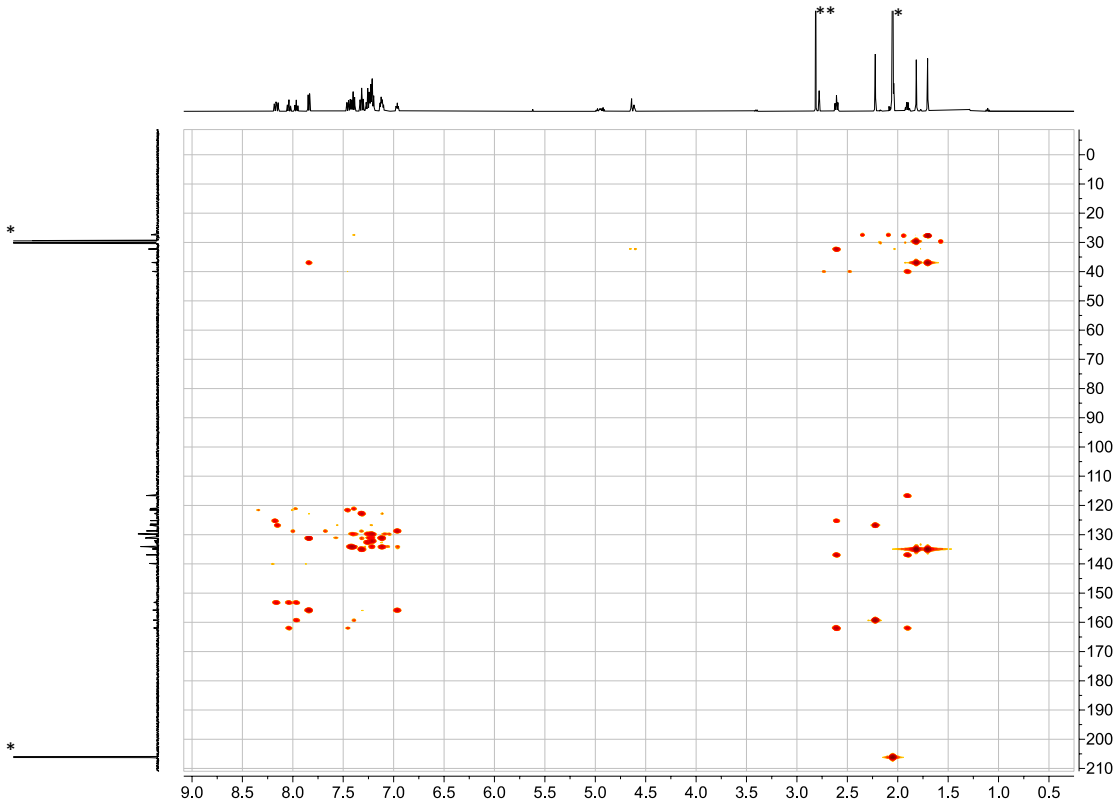


Fig. S35: HMBC spectrum (500 MHz ^{1}H, 126 MHz ^{13}C{^{1}H}, acetone-d_6, 298 K) of [Cu(**2**)(xantphos)][PF_6]. Scale: δ / ppm. * = residual acetone; ** = residual H_2O and HDO.

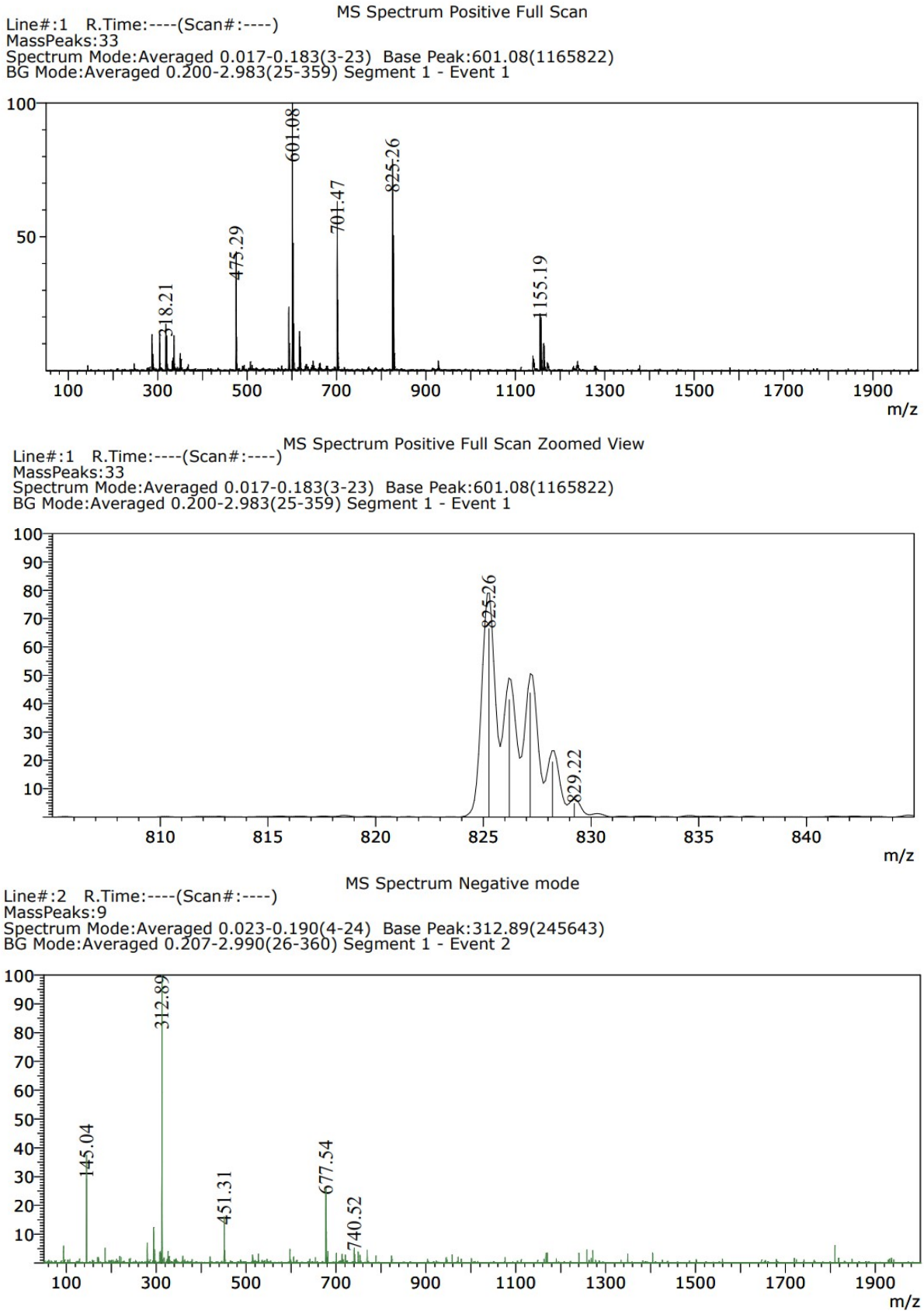


Fig. S36: ESI mass spectrum (positive and negative mode) of [Cu(**2**)(POP)][PF_6].

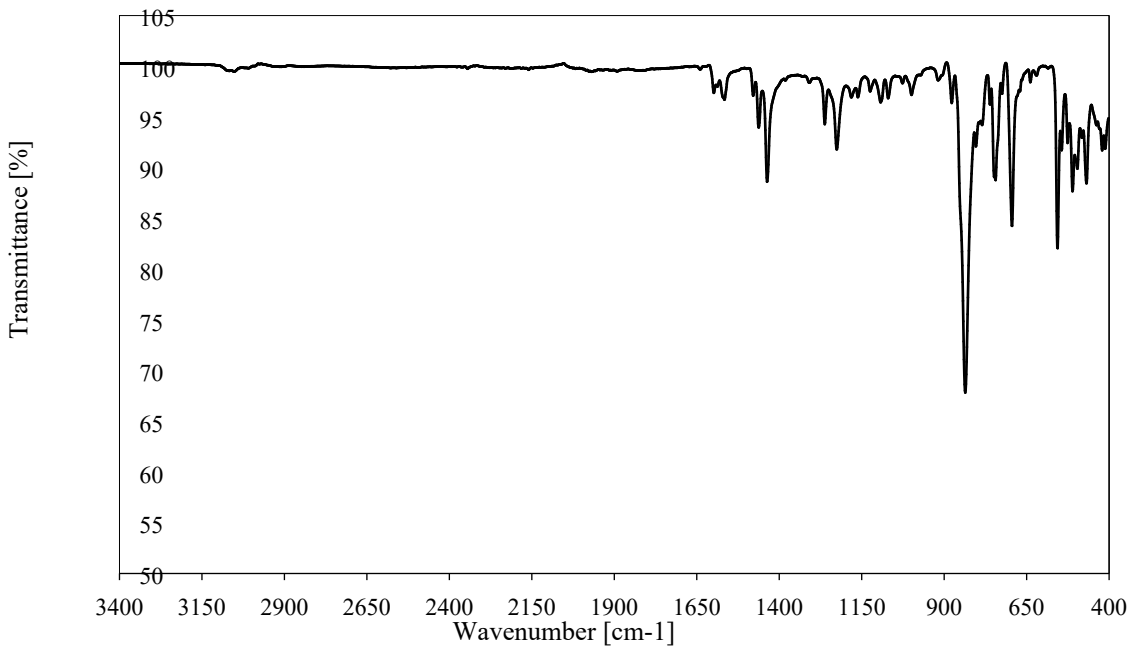


Fig. S37: IR spectrum of [Cu(**2**)(POP)][PF_6].

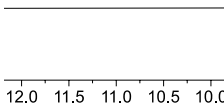


Fig. S38**:** ^{1}H-NMR spectrum (500 MHz, 298 K, acetone-d_6) of [Cu(**2**)(POP)][PF_6]. Scale: δ / ppm. * = residual acetone; ** = residual H_2O and HDO.

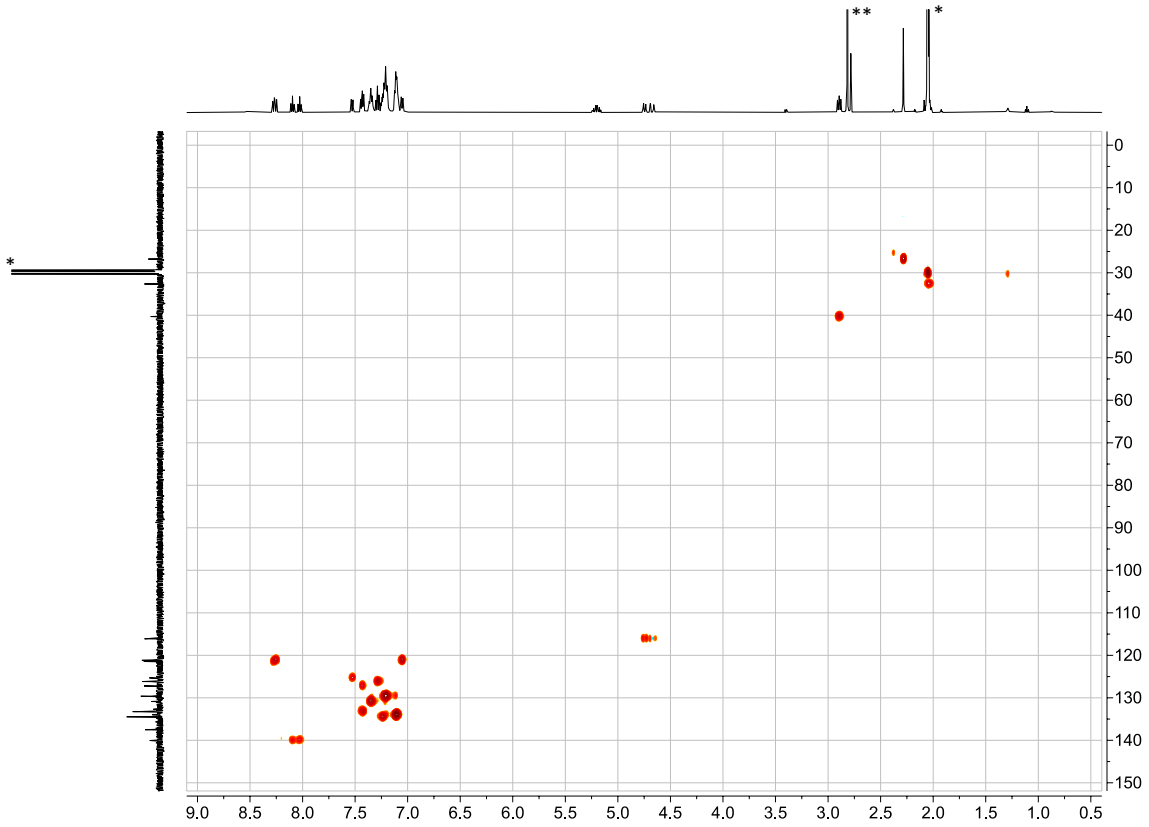


Fig. S39: HMQC spectrum (500 MHz ^{1}H, 126 MHz ^{13}C{^{1}H}, acetone-d_6, 298 K) of [Cu(**2**)(POP)][PF_6]. Scale: δ / ppm. * = residual acetone; ** = residual H_2O and HDO.

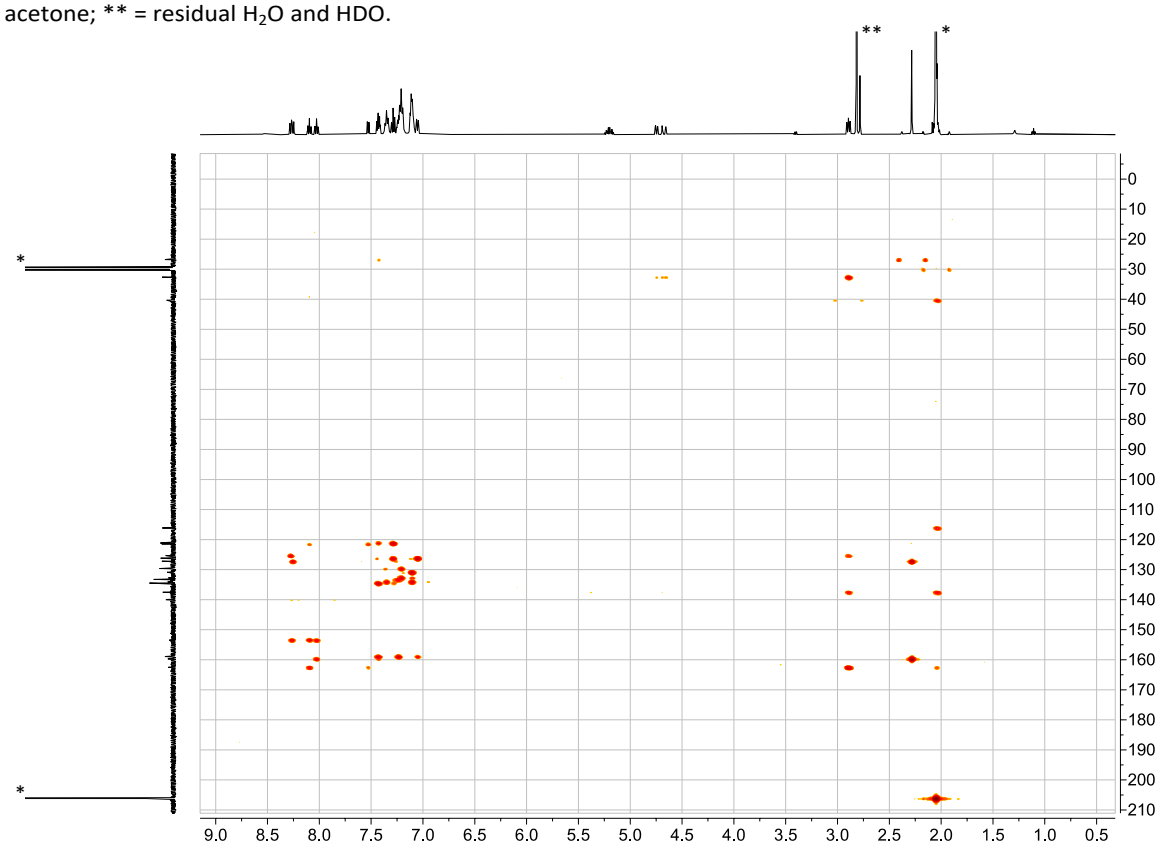


Fig. S40: HMBC spectrum (500 MHz ^{1}H, 126 MHz ^{13}C{^{1}H}, acetone-d_6, 298 K) of [Cu(**2**)(POP)][PF_6]. Scale: δ / ppm. * = residual acetone; ** = residual H_2O and HDO.

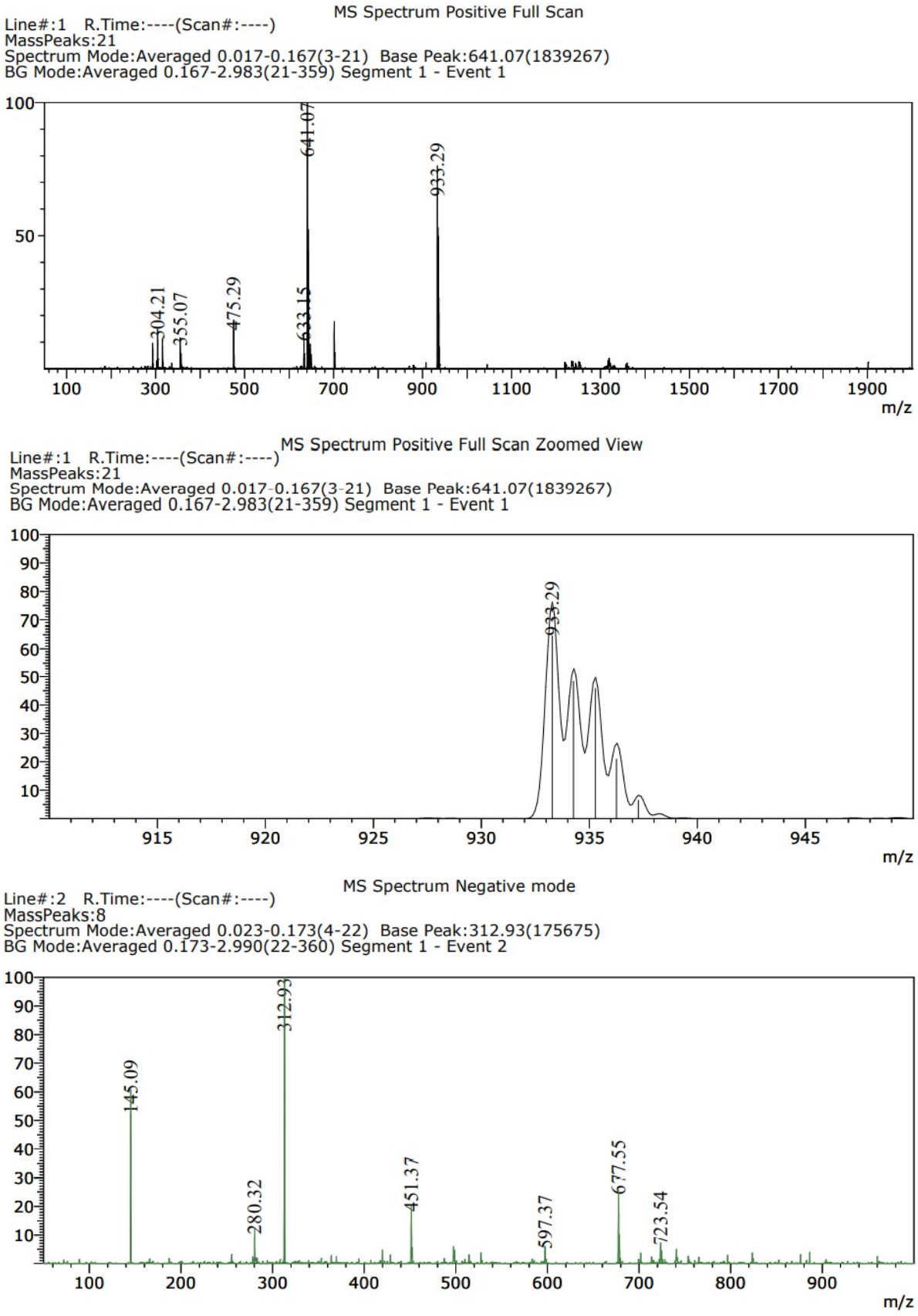


Fig. S41**:** ESI mass spectrum (positive and negative mode) of [Cu(**3**)(xantphos)][PF_6].

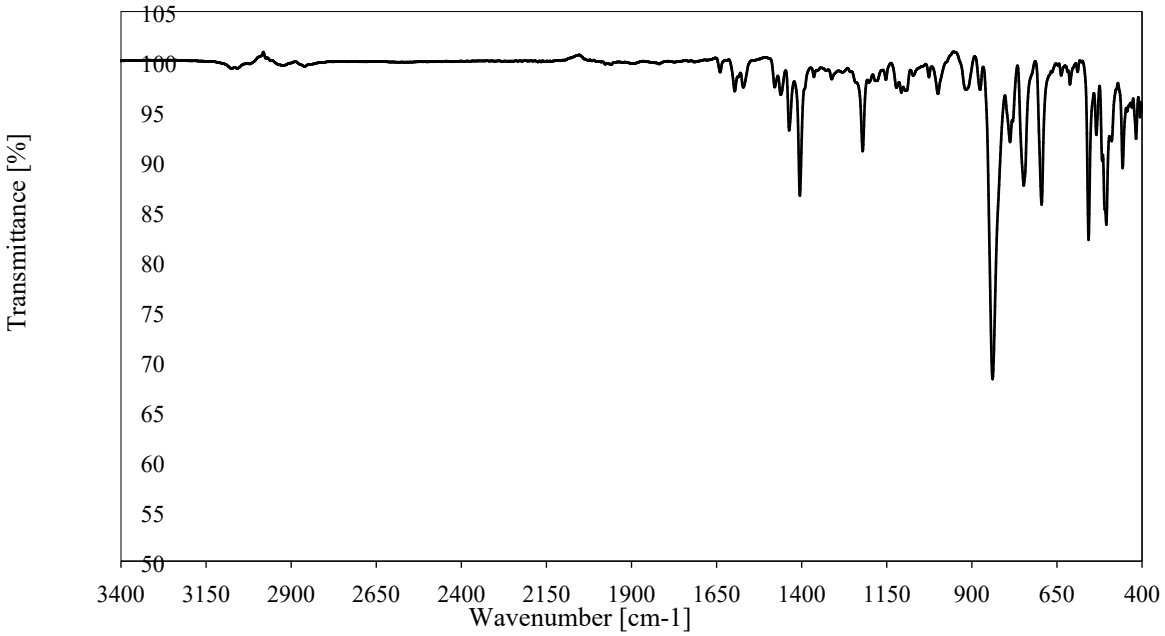


Fig. S42: IR spectrum of [Cu(**3**)(xantphos)][PF_6].

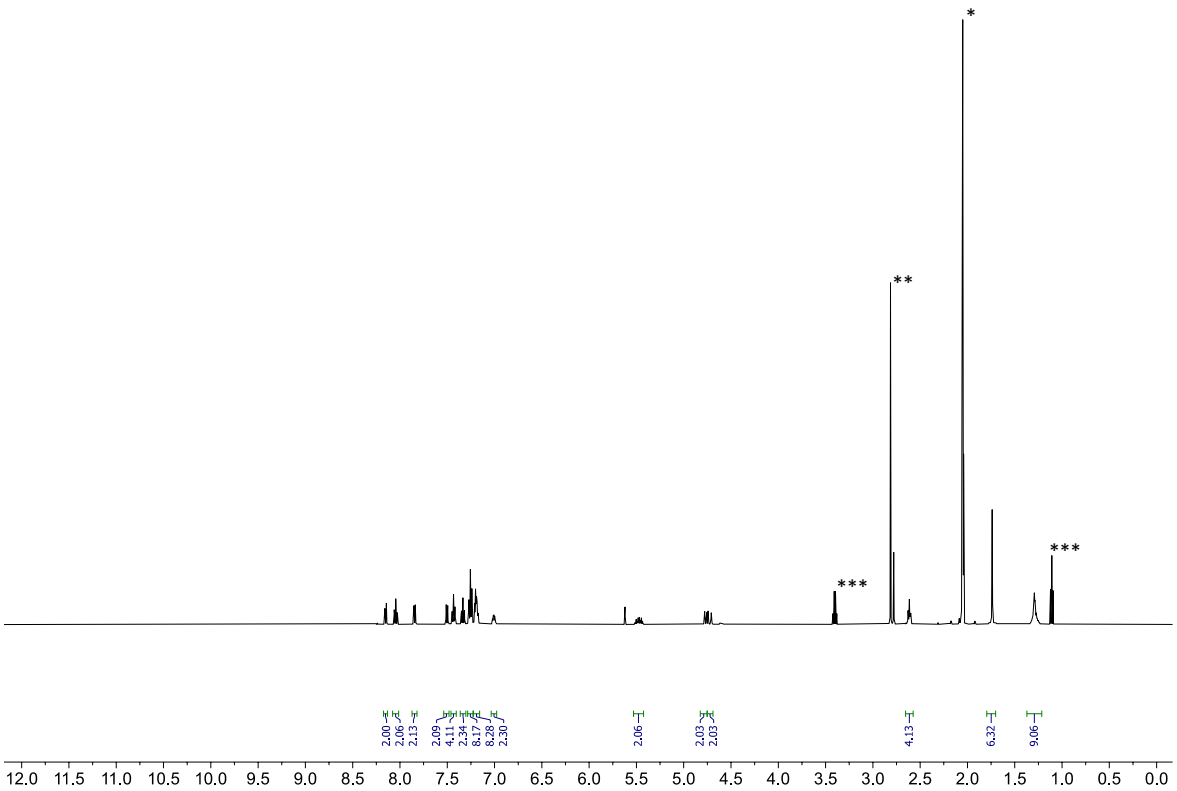


Fig. S43: ^{1}H-NMR spectrum (500 MHz, 298 K, acetone-d_6) of [Cu(**3**)(xantphos)][PF_6]. Scale: δ / ppm. * = residual acetone; ** = residual H_2O and HDO; *** = residual diethyl ether.

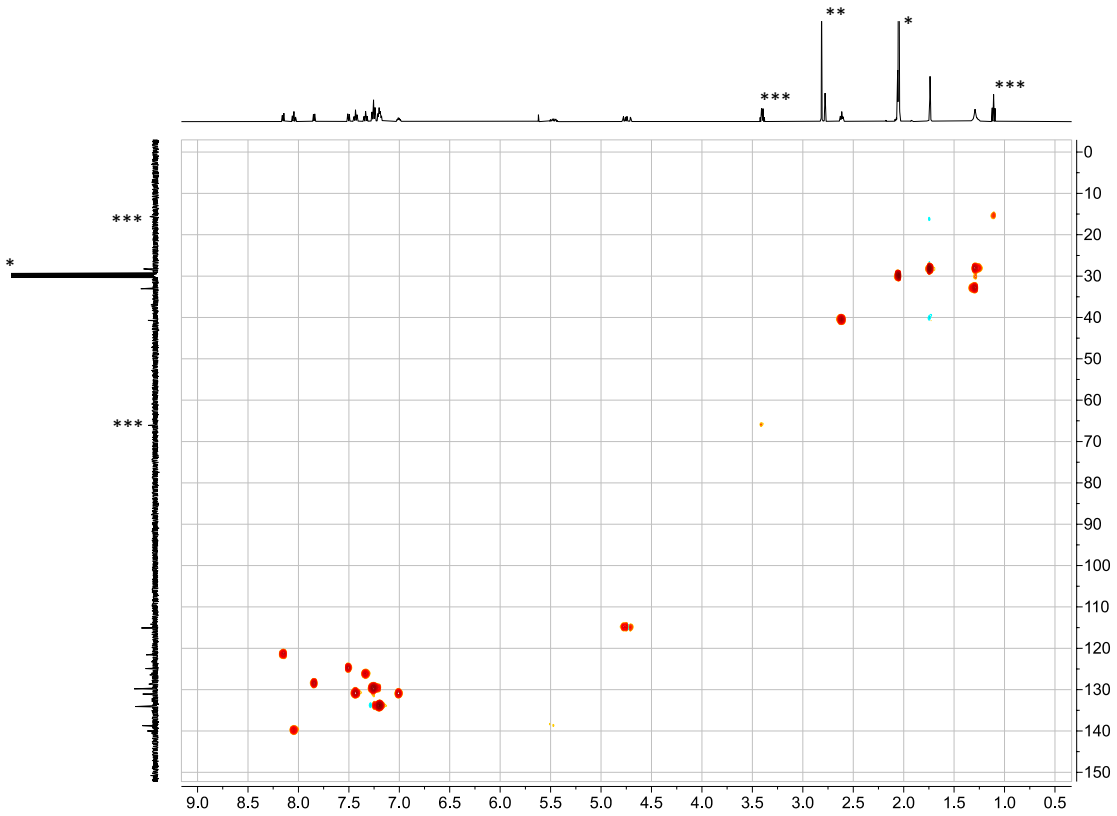


Fig. S44: HMQC spectrum (500 MHz ^{1}H, 126 MHz ^{13}C{^{1}H}, acetone-d_6, 298 K) of [Cu(**3**)(xantphos)][PF_6]. Scale: δ / ppm. * = residual acetone; ** = residual H_2O and HDO; *** = residual diethyl ether.

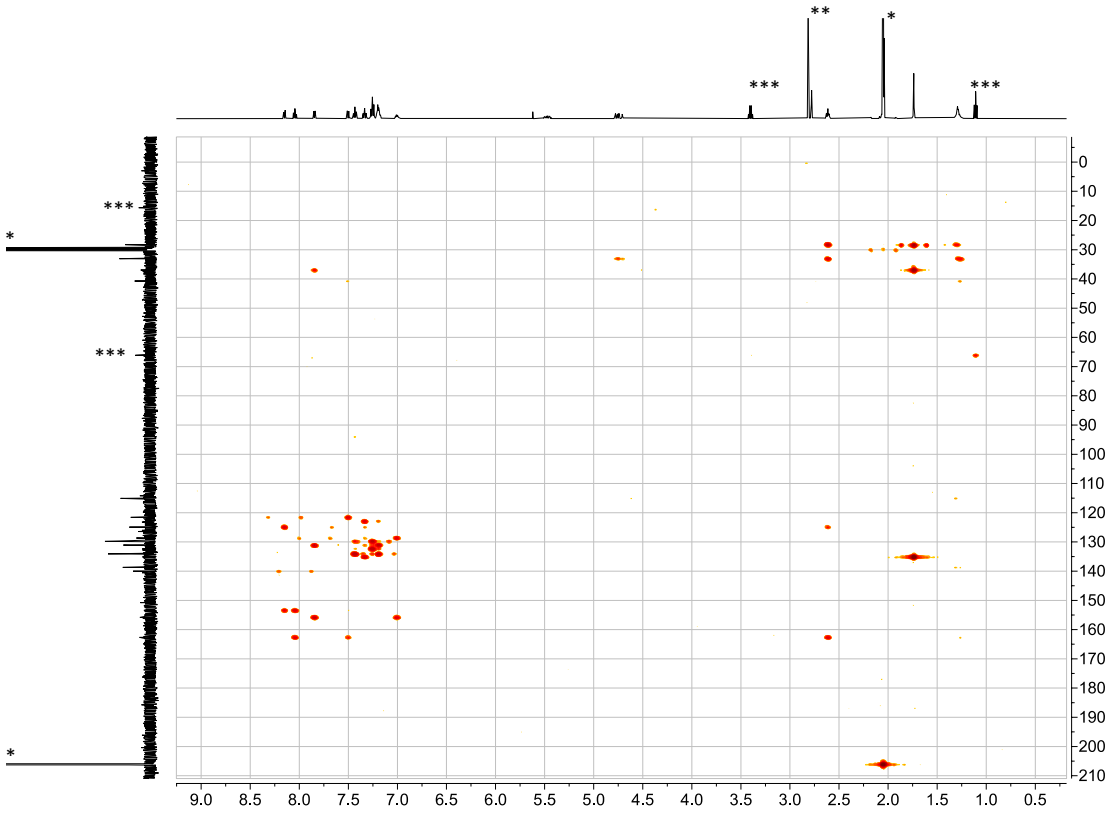


Fig. S45: HMBC spectrum (500 MHz ^{1}H, 126 MHz ^{13}C{^{1}H}, acetone-d_6, 298 K) of [Cu(**3**)(xantphos)][PF_6]. Scale: δ / ppm. * = residual acetone; ** = residual H_2O and HDO; *** = residual diethyl ether.

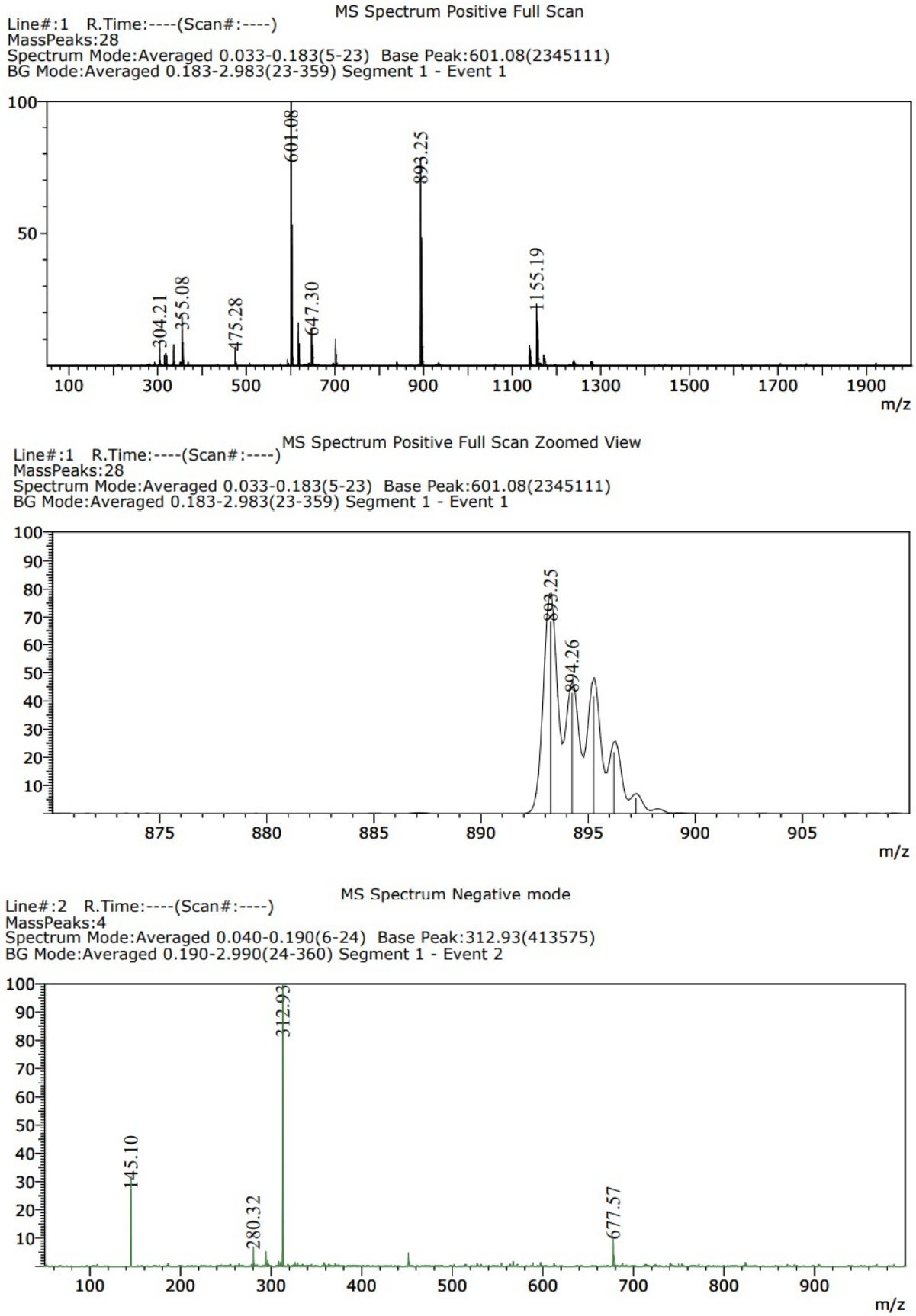


Fig. S46**:** ESI mass spectrum (positive and negative mode) of [Cu(**3**)(POP)][PF_6].

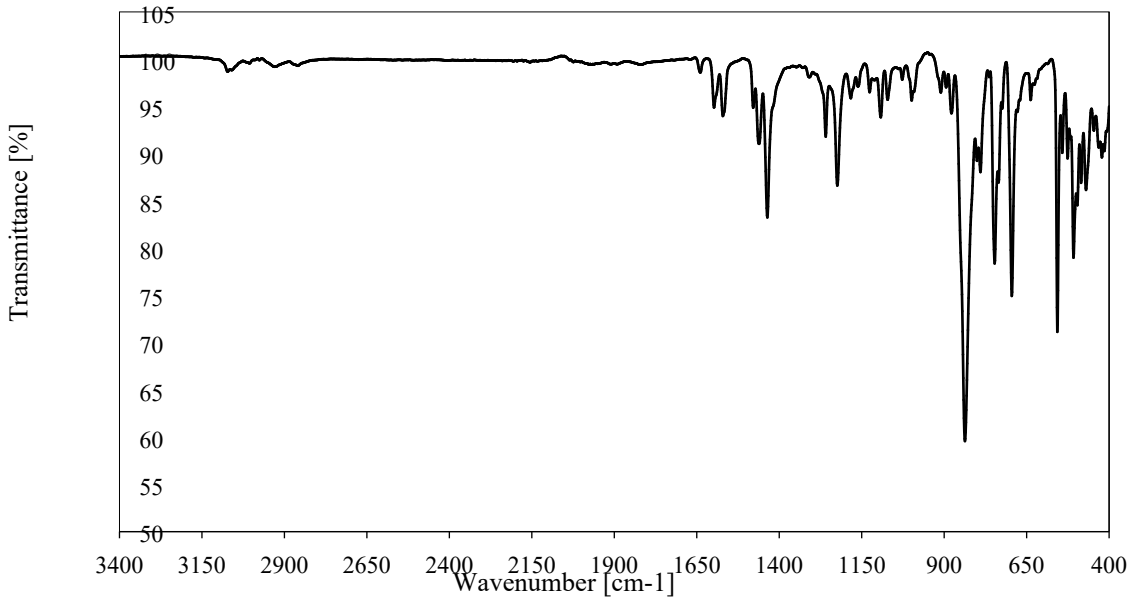


Fig. S47: IR spectrum of [Cu(**3**)(POP)][PF_6].

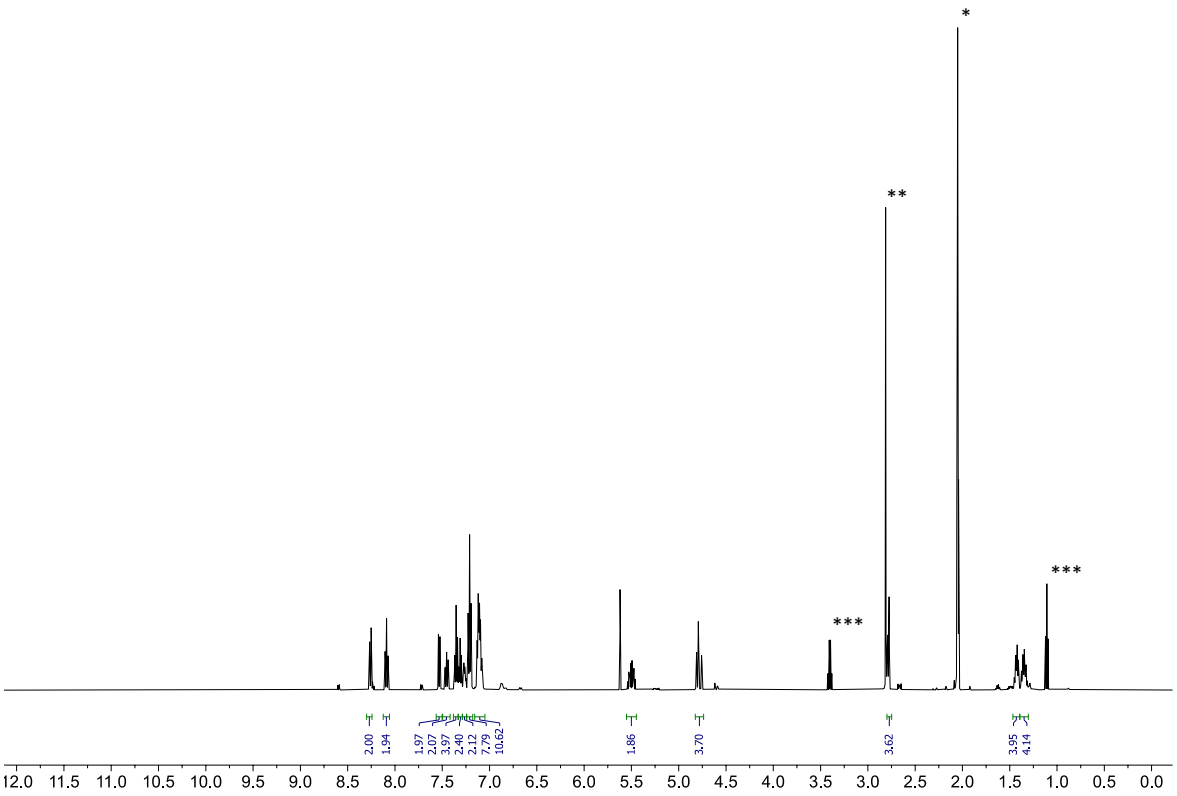


Fig. S48: ^{1}H-NMR spectrum (500 MHz, 298 K, acetone-d_6) of [Cu(**3**)(POP)][PF_6]. Scale: δ / ppm. * = residual acetone; ** = residual H_2O and HDO; *** = residual diethyl ether.

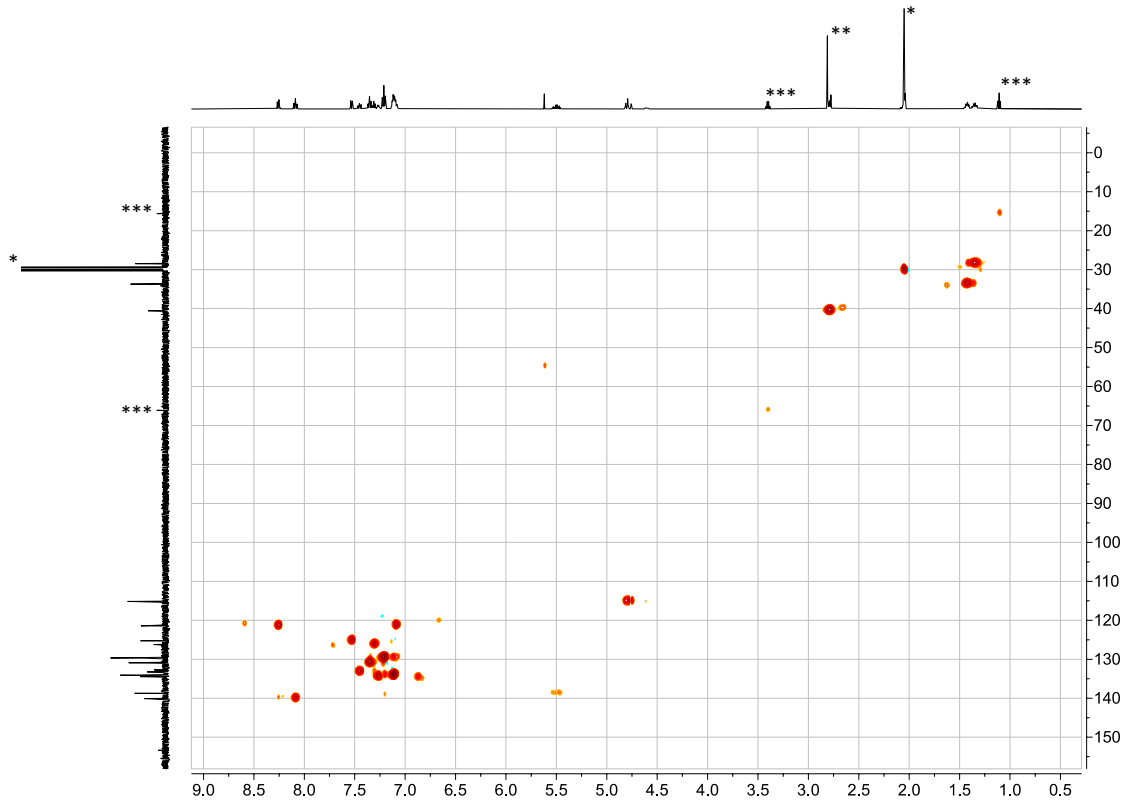


Fig. S49: HMQC spectrum (500 MHz ^{1}H, 126 MHz ^{13}C{^{1}H}, acetone-d_6, 298 K) of [Cu(**3**)(POP)][PF_6]. Scale: δ / ppm. * = residual acetone; ** = residual H_2O and HDO; *** = residual diethyl ether.

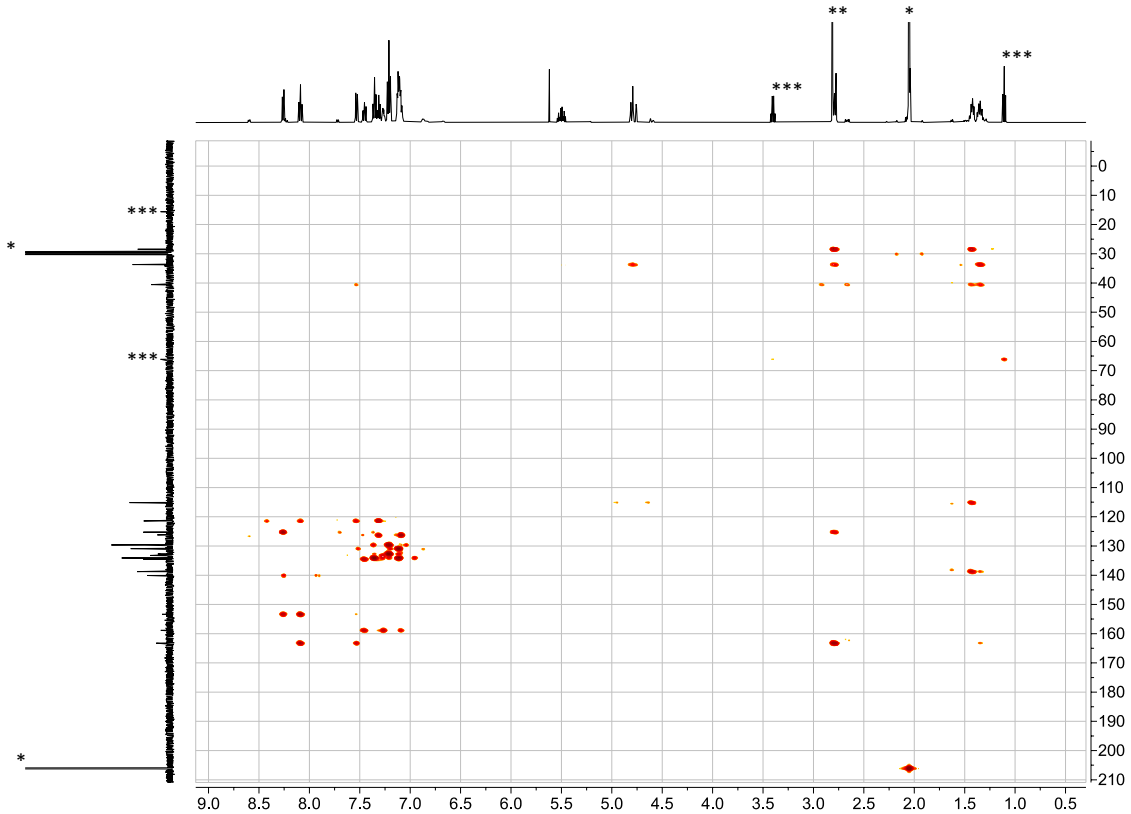


Fig. S50: HMBC spectrum (500 MHz ^{1}H, 126 MHz ^{13}C{^{1}H}, acetone-d_6, 298 K) of [Cu(**3**)(POP)][PF_6]. Scale: δ / ppm. * = residual acetone; ** = residual H_2O and HDO; *** = residual diethyl ether.

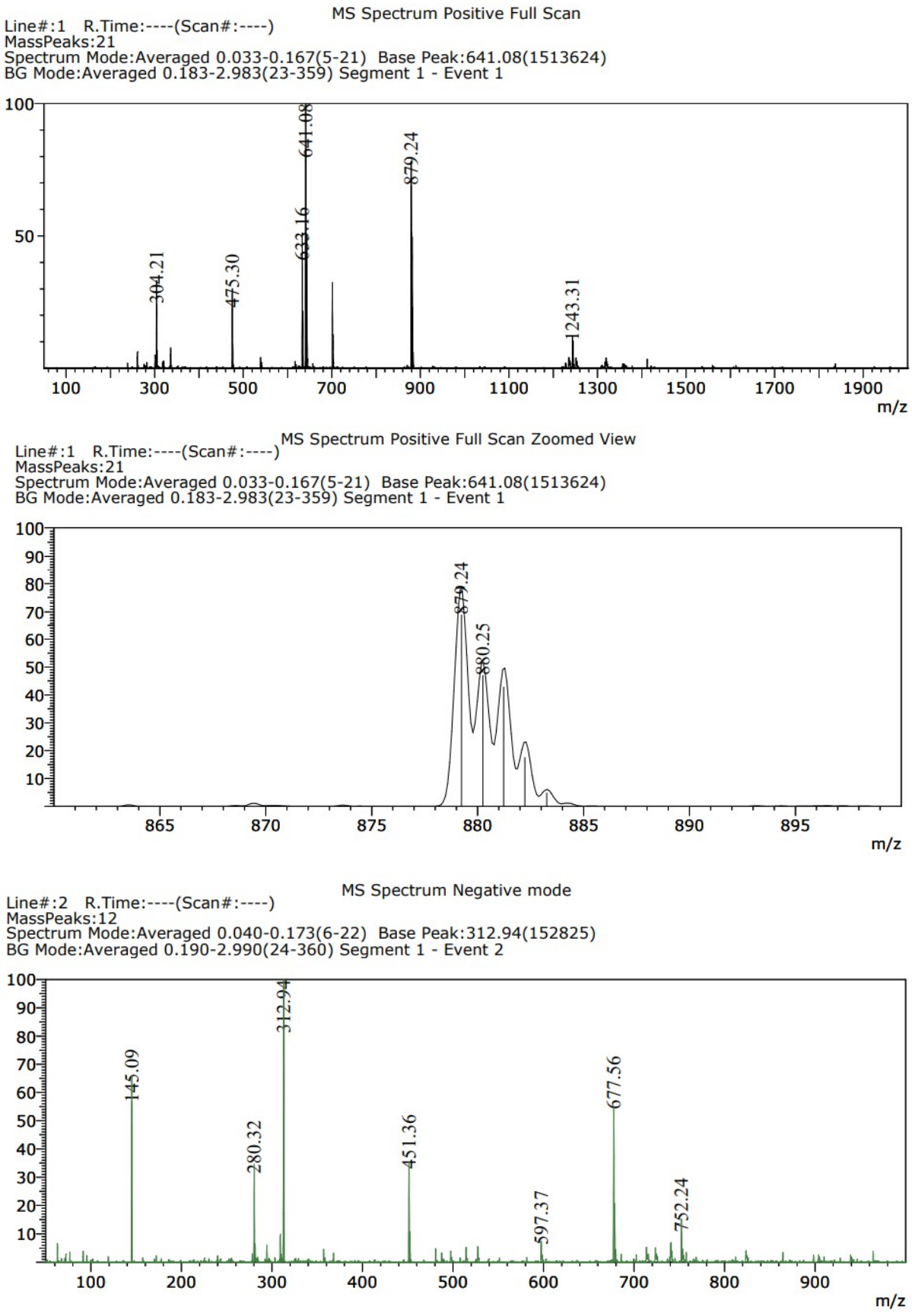


Fig. S51: ESI mass spectrum (positive and negative mode) of [Cu(**4**)(xantphos)][PF_6].

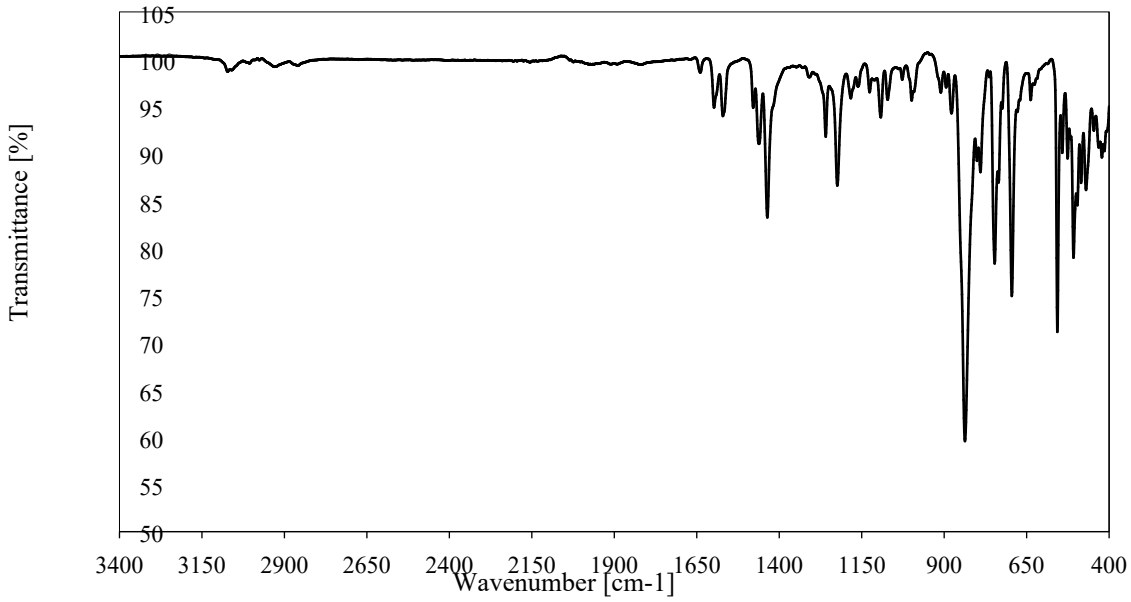


Fig. S52: IR spectrum of [Cu(**4**)(xantphos)][PF_6].

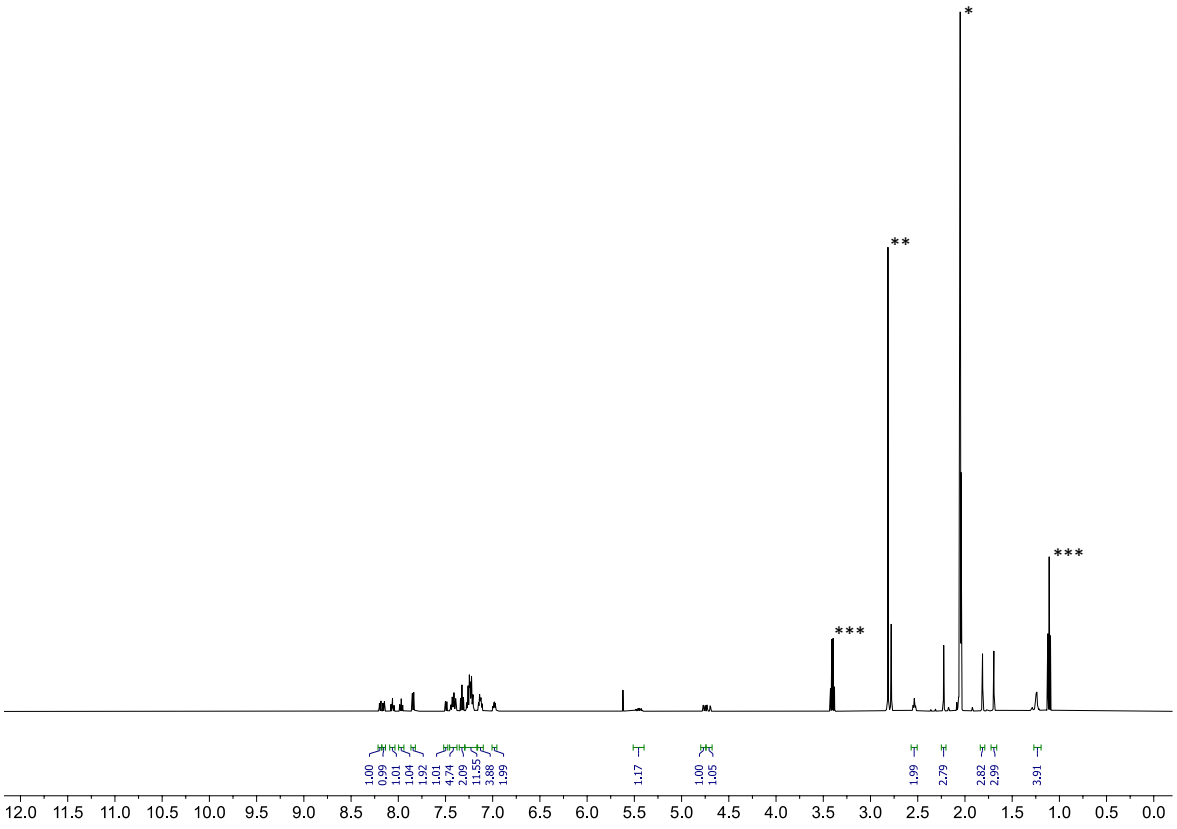


Fig. S53: ^{1}H-NMR spectrum (500 MHz, 298 K, acetone-d_6) of [Cu(**4**)(xantphos)][PF_6]. Scale: δ / ppm. * = residual acetone; ** = residual H_2O and HDO; *** = residual diethyl ether.

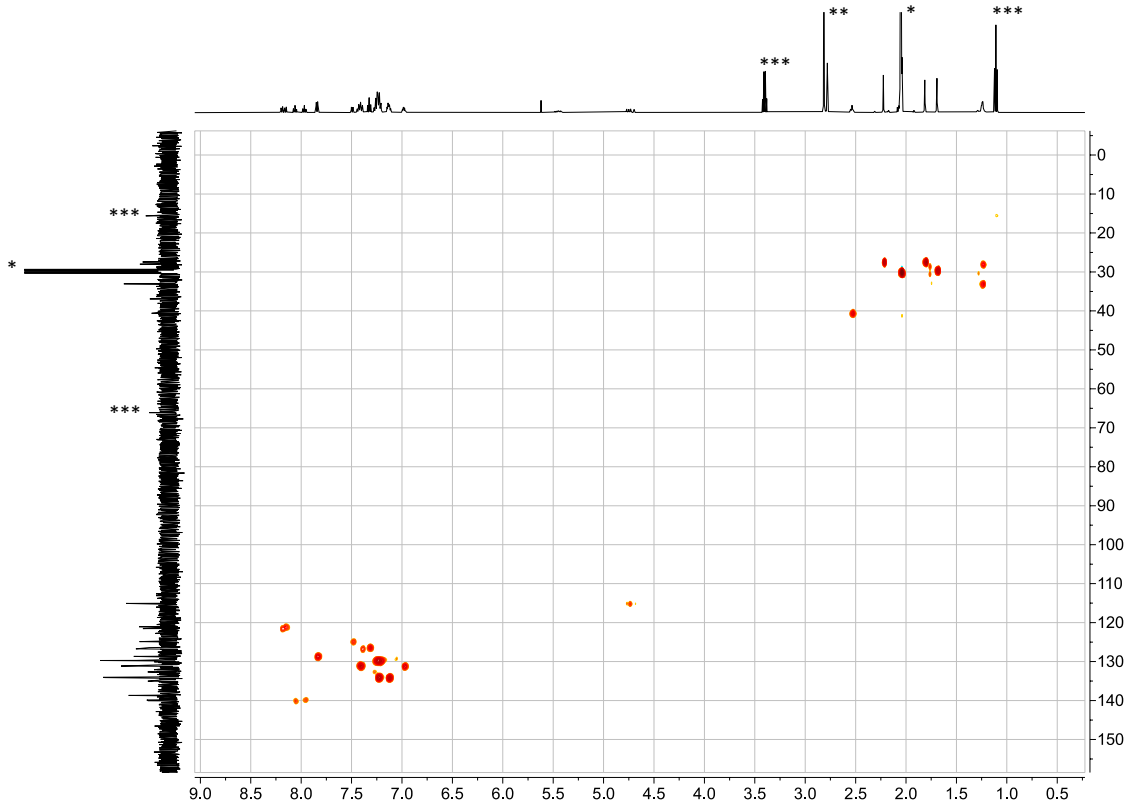


Fig. S54: HMQC spectrum (500 MHz ^{1}H, 126 MHz ^{13}C{^{1}H}, acetone-d_6, 298 K) of [Cu(**4**)(xantphos)][PF_6]. Scale: δ / ppm. * = residual acetone; ** = residual H_2O and HDO; *** = residual diethyl ether.

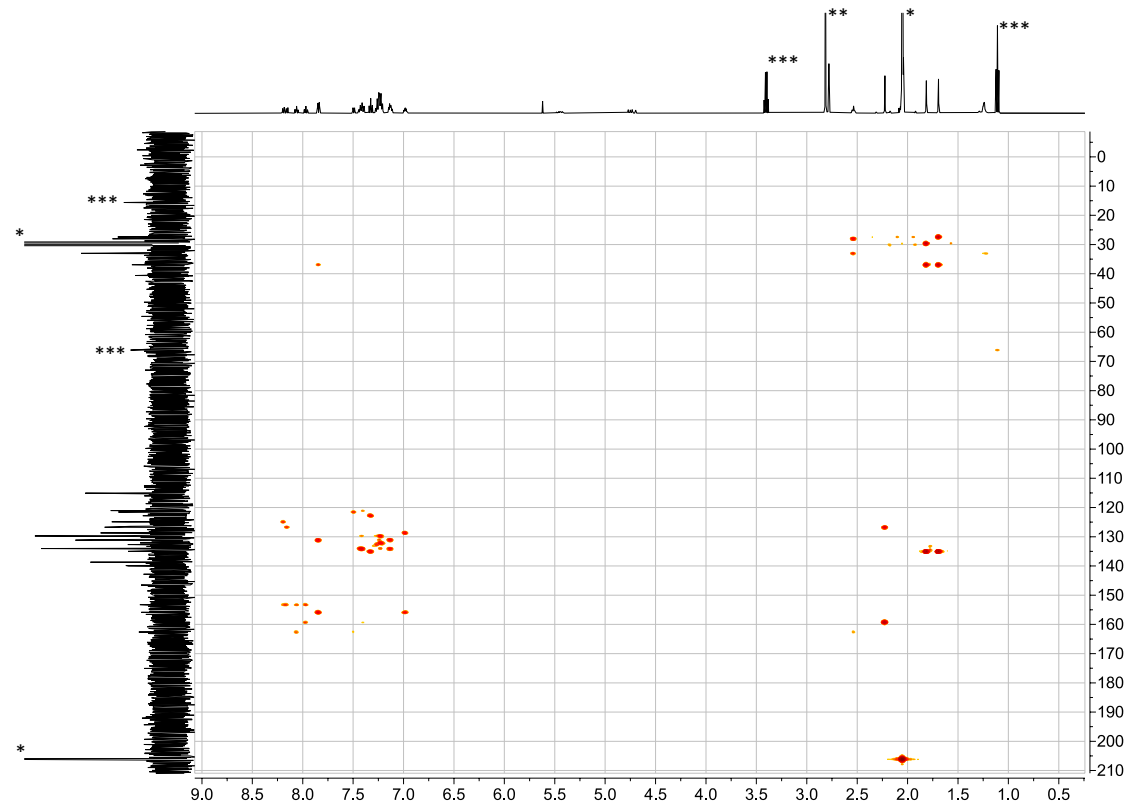


Fig. S55: HMBC spectrum (500 MHz ^{1}H, 126 MHz ^{13}C{^{1}H}, acetone-d_6, 298 K) of [Cu(**4**)(xantphos)][PF_6]. Scale: δ / ppm. * = residual acetone; ** = residual H_2O and HDO; *** = residual diethyl ether.

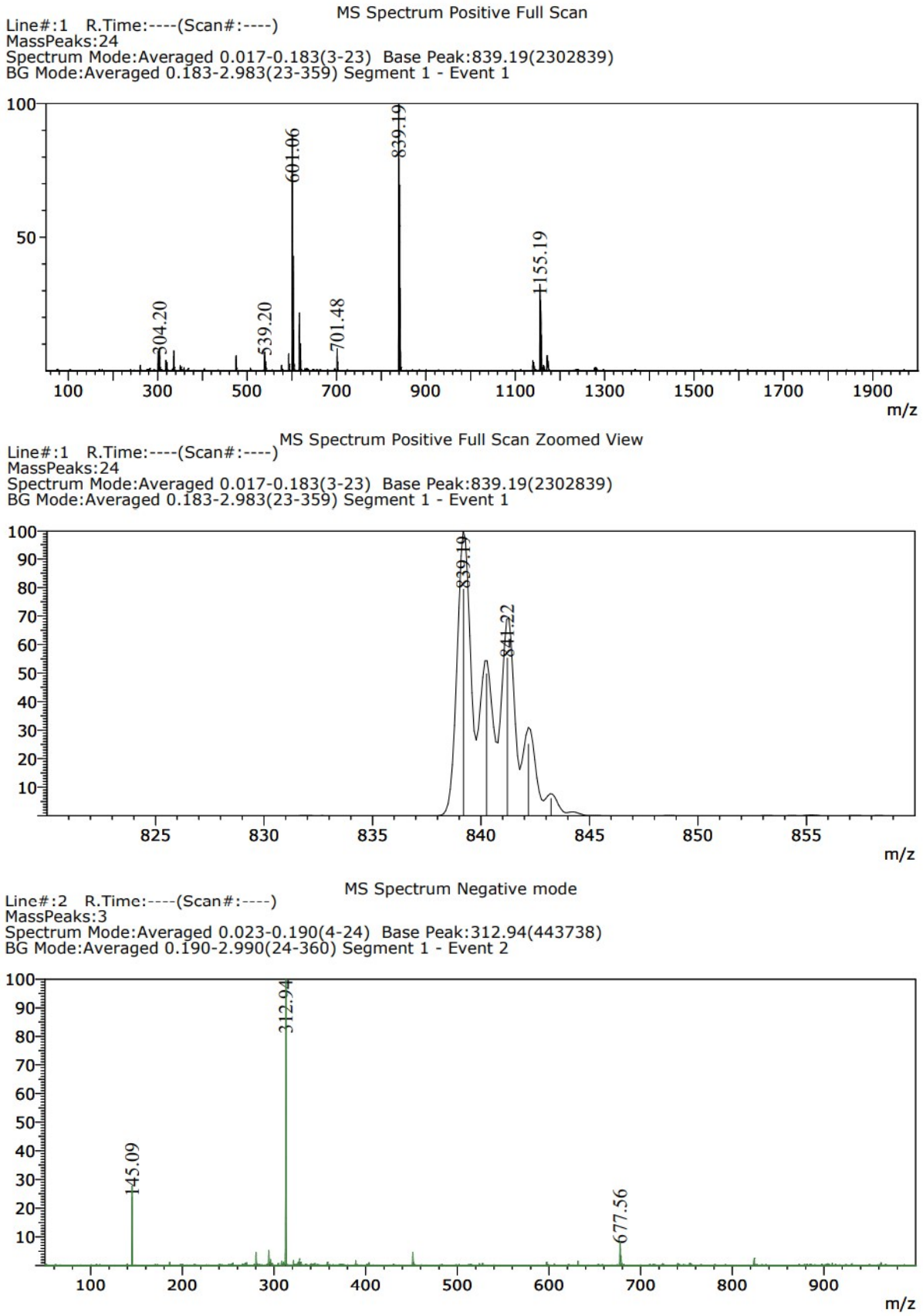


Fig. S56: ESI mass spectrum (positive and negative mode) of [Cu(**4**)(POP)][PF_6].

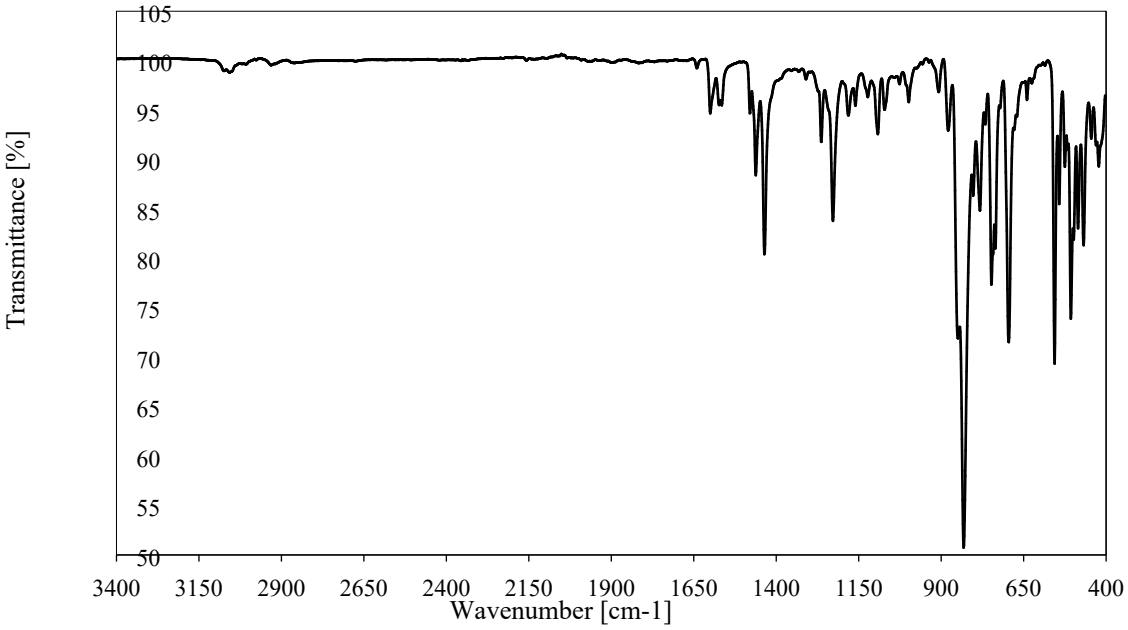


Fig. S57: IR spectrum of [Cu(**4**)(POP)][PF_6].

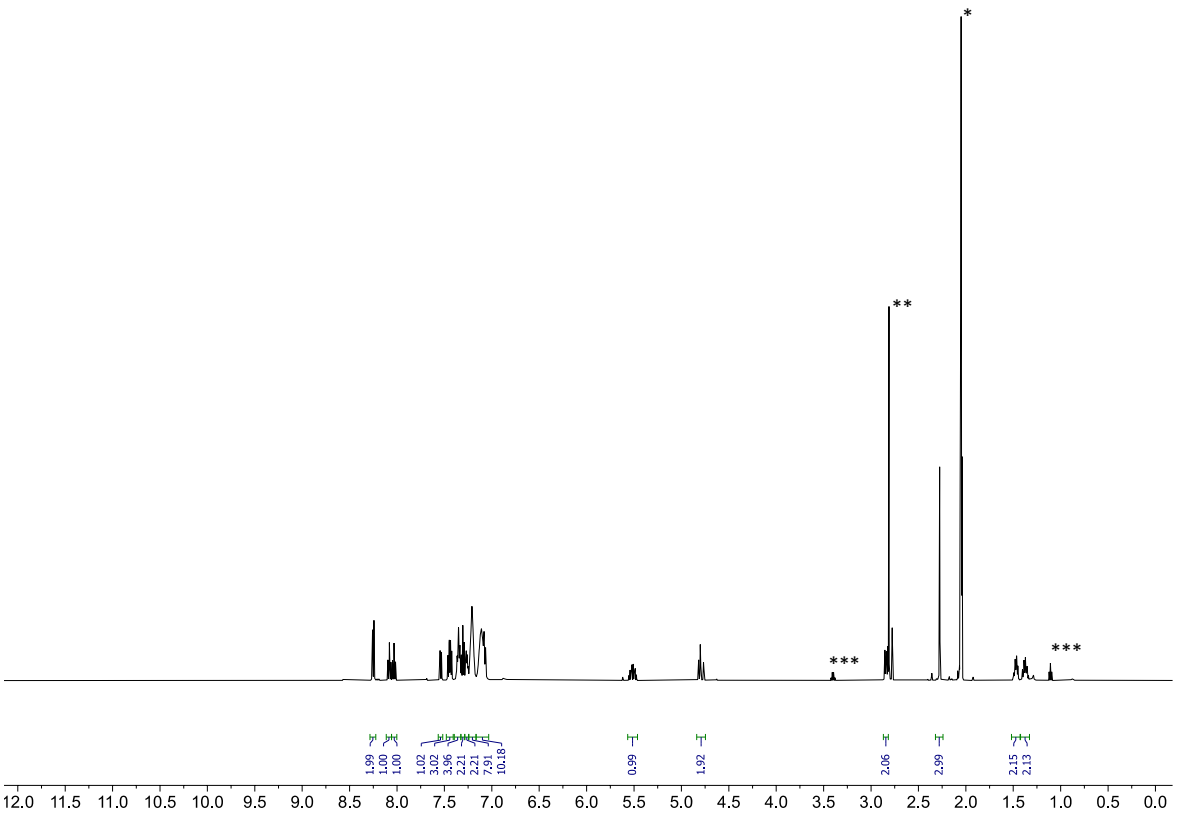


Fig. S58: ^{1}H-NMR spectrum (500 MHz, 298 K, acetone-d_6) of [Cu(**4**)(POP)][PF_6]. Scale: δ / ppm. * = residual acetone; ** = residual H_2O and HDO; *** = residual diethyl ether.

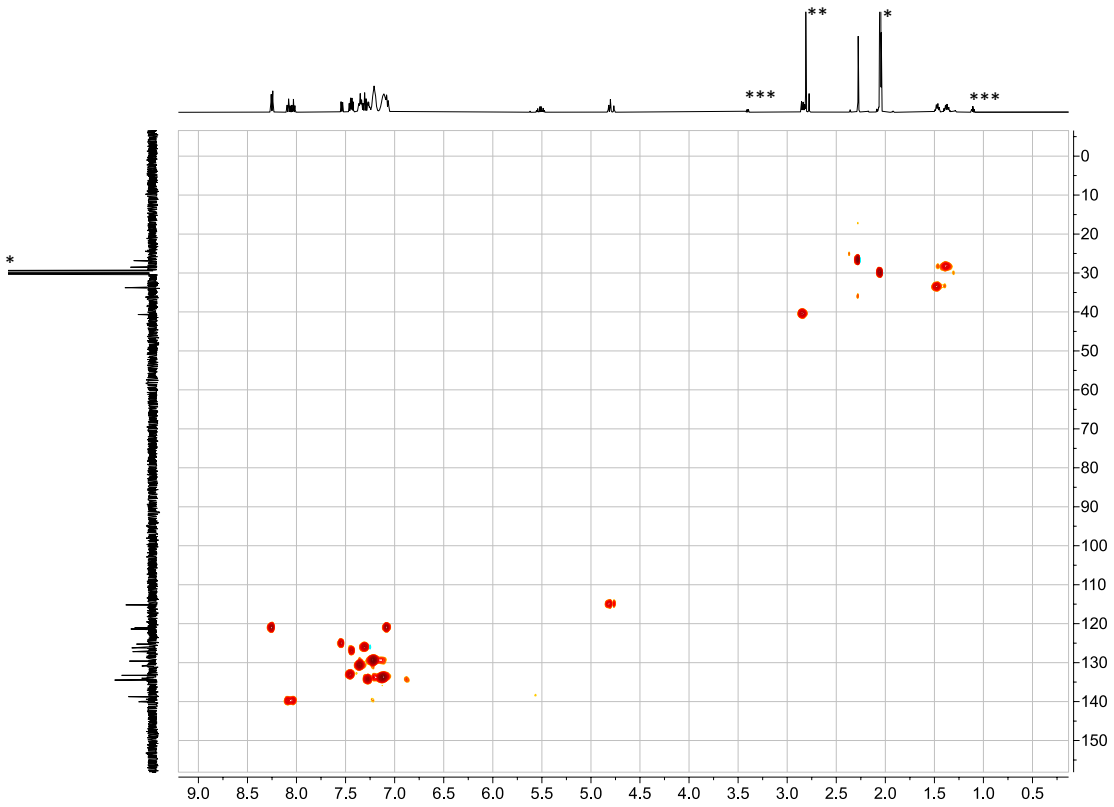


Fig. S59: HMQC spectrum (500 MHz ^{1}H, 126 MHz ^{13}C{^{1}H}, acetone-d_6, 298 K) of [Cu(**4**)(POP)][PF_6]. Scale: δ / ppm. * = residual acetone; ** = residual H_2O and HDO; *** = residual diethyl ether.

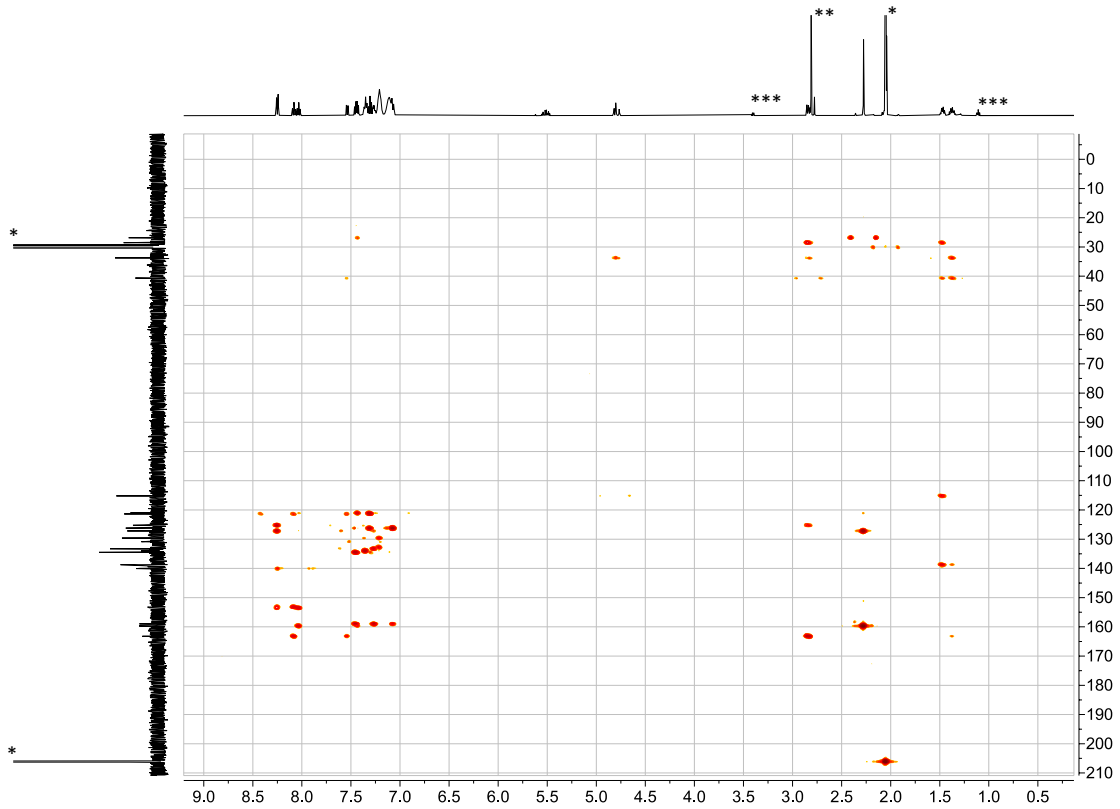


Fig. S60: HMBC spectrum (500 MHz ^{1}H, 126 MHz ^{13}C{^{1}H}, acetone-d_6, 298 K) of [Cu(**4**)(POP)][PF_6]. Scale: δ / ppm. * = residual acetone; ** = residual H_2O and HDO; *** = residual diethyl ether.

Table S1 Crystallographic data for the Cu(I) complexes

Compound	**[Cu(1)(xantphos)][PF_6]**	**[Cu(1)(POP)][PF_6]·CH_2Cl_2**	**[Cu(2)(xantphos)][PF_6]**
Formula	$C_{57}H_{56}CuF_6N_2OP_3$	$C_{55}Cl_2CuF_6H_{50}N_2OP_3$	$C_{54}H_{48}CuF_6N_2OP_3$
Formula weight	1055.48	1096.32	1011.39
Crystal colour and habit	Colourless block	Yellow plate	Yellow block
Crystal system	monoclinic	Triclinic	monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a, b, c / Å	17.4311(3), 15.1404(3), 20.4627(4)	11.9227(5), 13.4650(6), 18.5972(8)	10.9358(2), 20.1224(2), 21.6456(4)
α, β, γ / °	90, 110.268(2), 90	104.521(3), 98.067(4), 110.792(3)	90, 95.5430(10), 90
U / Å^3	5066.01(18)	2613.8(2)	4740.94(13)
Dc / Mg m^{-3}	1.384	1.393	1.417
Z	4	2	4
Radiation type	Cu K_α	Cu K_α	Cu K_α
μ / mm^{-1}	2.046	2.923	2.163
T / K	150	150	150
Refln. collected (R_{int})	43735 (0.0196)	40293 (0.0691)	48448 (0.0201)
Unique refln.	9442	9708	9239
Refln. for refinement	9355	8577	8304
Parameters	633	620	619
Threshold	I≥2 σ(I)	I≥2 σ(I)	I≥2 σ(I)
*R*1 (*R*1 all data)	0.0488 (0.0491)	0.0750 (0.0811)	0.0453 (0.0494)
*wR*2 (*wR*2 all data)	0.1327 (0.1331)	0.2202 (0.2330)	0.1214 (0.1242)
Goodness of fit	1.036	1.147	1.033
CCDC deposition number	2171124	2171125	2171127

Compound	**[Cu(2)(POP)][PF_6]**	**[Cu(3)(POP)][PF_6]·0.5 $C_4H_{10}O$**
Formula	$C_{51}H_{44}CuF_6N_2OP_3$	$C_{58}CuF_6H_{57}N_2O_{1.5}P_3$
Formula weight	971.33	1076.50
Crystal colour and habit	Yellow block	Yellow block
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
a, b, c / Å	14.0520(6), 20.4008(11), 15.9262(6)	11.7231(3), 14.5309(4), 17.2049(4)
α, β, γ / °	90, 93.489(3), 90	88.374(2), 73.464(2), 67.052(2)
U / Å^3	4557.1(4)	2575.89(12)
Dc / Mg m^{-3}	1.416	1.388
Z	4	2
Radiation type	Cu K_α	Cu K_α
μ / mm^{-1}	2.226	2.030
T / K	150	150
Refln. collected (R_{int})	39183 (0.0627)	44238 (0.0232)
Unique refln.	8875	9903
Refln. for refinement	8015	9076
Parameters	597	634
Threshold	I≥2 σ(I)	I≥2 σ(I)
*R*1 (*R*1 all data)	0.0844 (0.0902)	0.0688 (0.0717)
*wR*2 (*wR*2 all data)	0.2064 (0.2139)	0.2012 (0.2053)
Goodness of fit	1.016	1.110
CCDC deposition number	2171126	2171128

Table S2: Selected bond parameters for [Cu(N^N)(P^P)][PF_6] complexes.

Compound	[Cu(1)(xantphos)][PF_6]	[Cu(1)(POP)][PF_6]·CH_2Cl_2	[Cu(2)(xantphos)][PF_6]	[Cu(2)(POP)][PF_6]	[Cu(3)(POP)][PF_6]·0.5 $C_4H_{10}O$
Cu–P1 distance/Å	2.2848(5)	2.288(1)	2.3174(7)	2.280(1)	2.2828(8)
Cu–P2 distance/Å	2.3078(8)	2.285(1)	2.2946(8)	2.292(1)	2.281(1)
Cu–N1 distance/Å	2.110(2)	2.117(3)	2.156(2)	2.104(3)	2.104(3)
Cu–N2 distance/Å	2.116(2)	2.121(2)	2.144(2)	2.119(3)	2.131(3)
N1–Cu–P1 angle/°	118.29(6)	113.89(9)	114.39(6)	120.76(9)	119.03(8)
N1–Cu–P2 angle/°	109.85(6)	121.08(9)	116.03(6)	107.10(9)	115.49(8)
N2–Cu–P1 angle/°	118.57(6)	120.21(9)	111.62(2)	112.30(9)	106.52(8)
N2–Cu–P2 angle/°	110.11(6)	107.24(9)	121.42(6)	122.32(9)	121.25(8)
C(P1)–O1 distance/Å	1.388(3)	1.400(5)	1.388(3)	1.391(5)	1.389(4)
C(P2)–O1 distance/Å	1.389(3)	1.390(4)	1.392(2)	1.386(5)	1.406(5)
C29–O1–C34 angle/°	115.0(2)	119.4(3)	115.5(2)	121.4(3)	121.7(2)
Angle between POP and PPh_2 ring planes/°	-	19.7	-	10.4	14.1
Distance between POP and PPh_2 ring centroids/Å	-	3.80	-	3.55	3.71

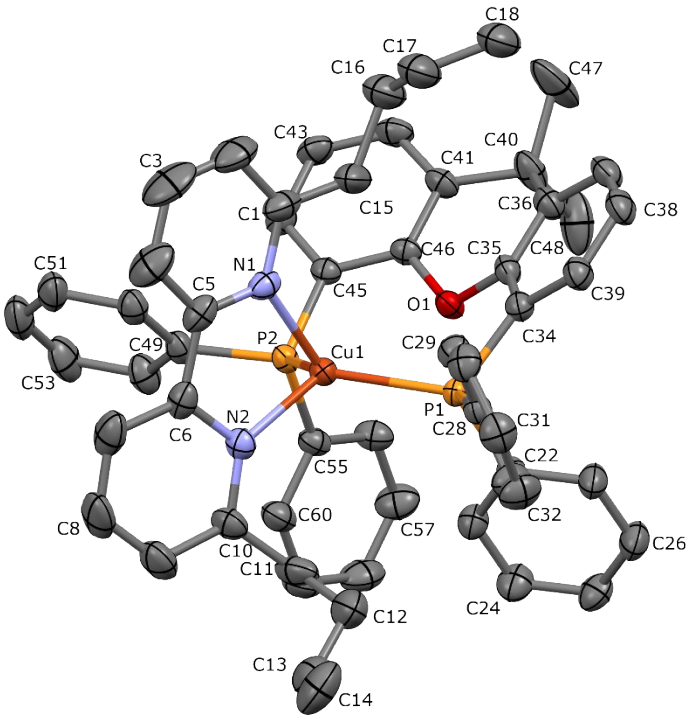


Fig. S61: Structure of the [Cu(**1**)(xantphos)]$^+$ cation in [Cu(**1**)(xantphos)][PF_6]. H atoms and solvent molecules are omitted and ellipsoids are plotted at 50% probability level. The plot shows only the cation with a fractional occupancy of 0.7.

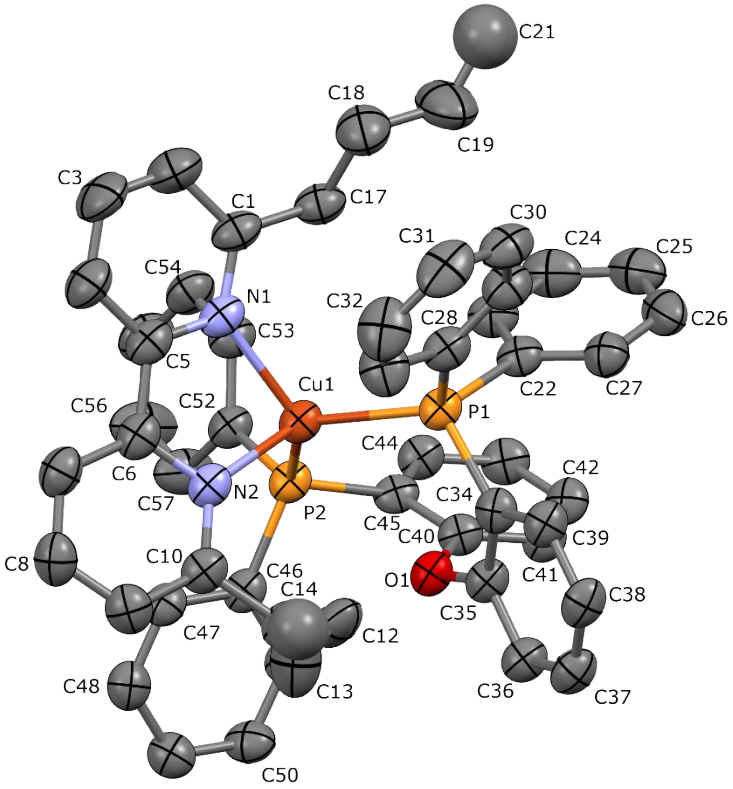


Fig. S62**:** Structure of the [Cu(**1**)(POP)]$^{+}$ cation in [Cu(**1**)(POP)][PF_6]·CH_2Cl_2. H atoms and solvent molecules are omitted and ellipsoids are plotted at 50% probability level. The plot shows only one of the cations with a fractional occupancy of 0.5.

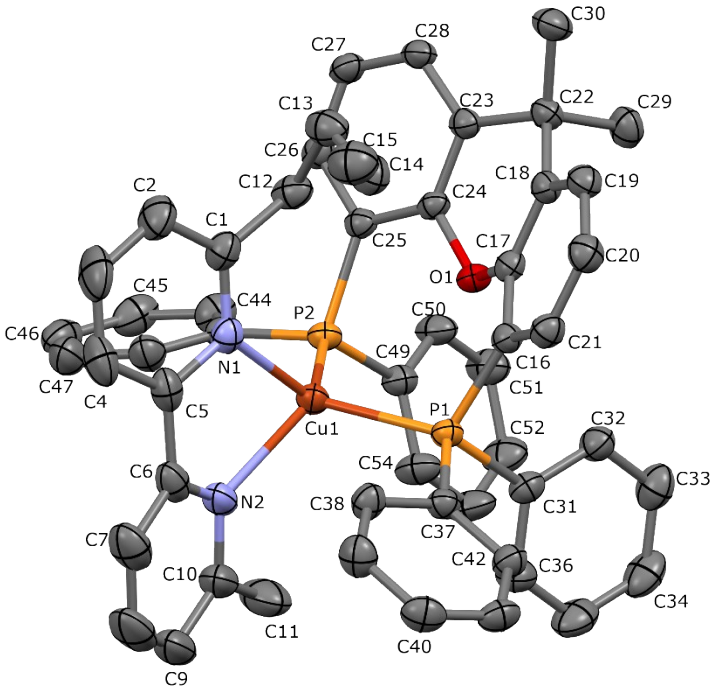


Fig. S63**:** Structure of the [Cu(**2**)(xantphos)]$^{+}$ cation in [Cu(**2**)(xantphos)][PF_6]. H atoms and solvent molecules are omitted and ellipsoids are plotted at 50% probability level.

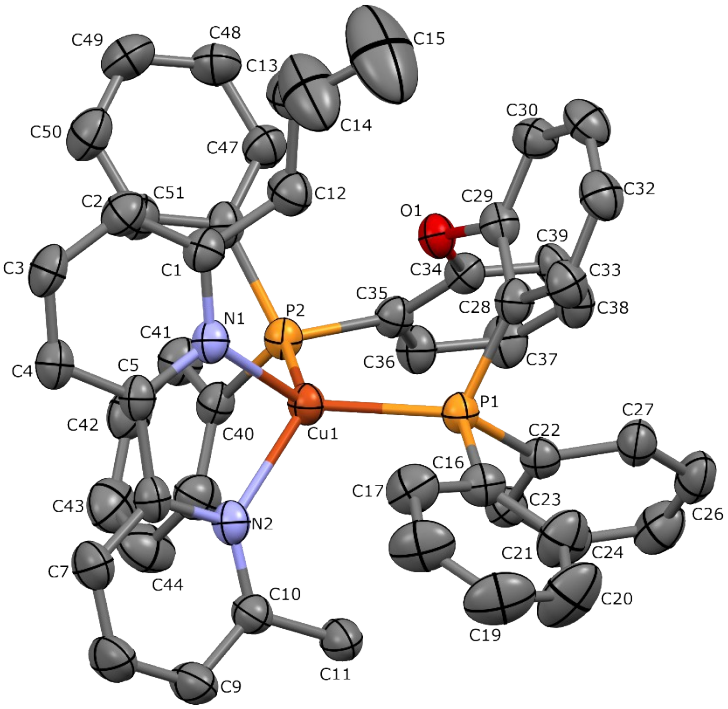


Fig. S64**:** Structure of the [Cu(**2**)(POP)]$^{+}$ cation in [Cu(**2**)(POP)][PF_6]. H atoms and solvent molecules are omitted and ellipsoids are plotted at 50% probability level.

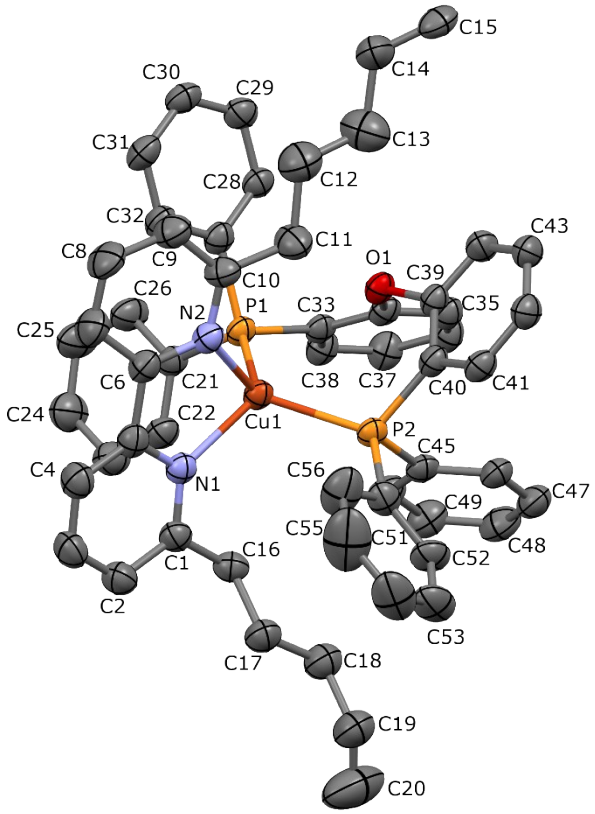
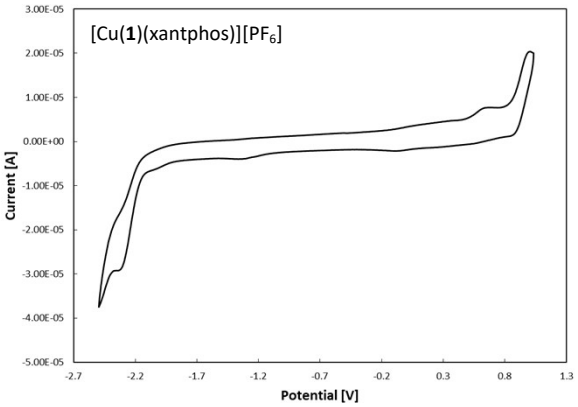
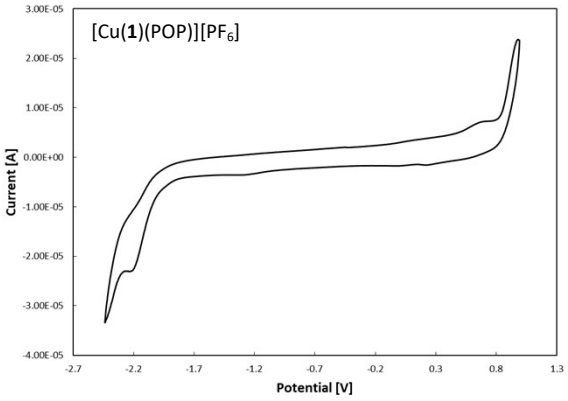
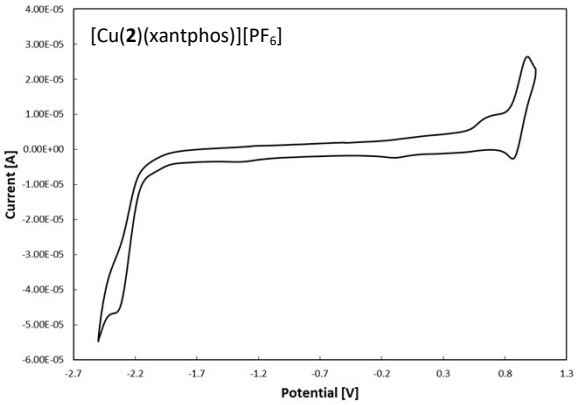
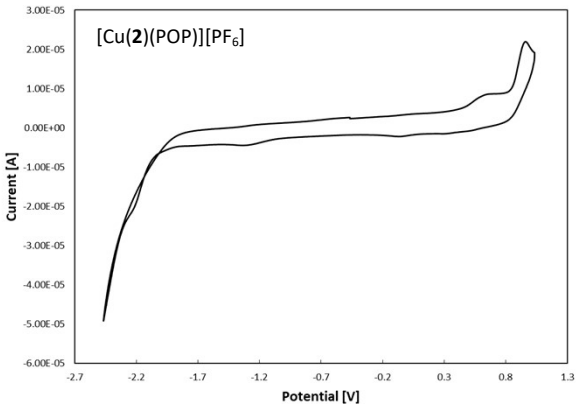


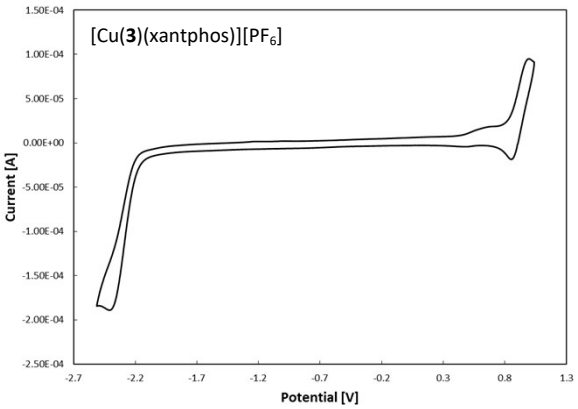
Fig. S65**:** Structure of the [Cu(**3**)(POP)]$^{+}$ cation in [Cu(**3**)(POP)][PF_6]·0.5 diethyl ether. H atoms and solvent molecules are omitted and ellipsoids are plotted at 50% probability level. The plot shows only the cation with a fractional occupancy of 0.75.

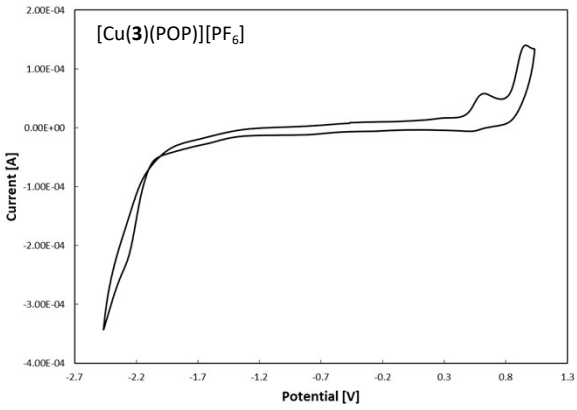


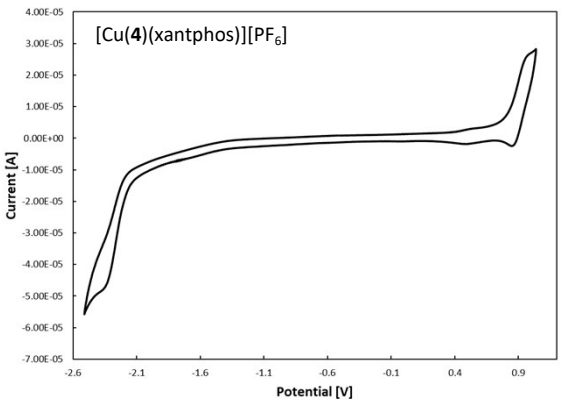












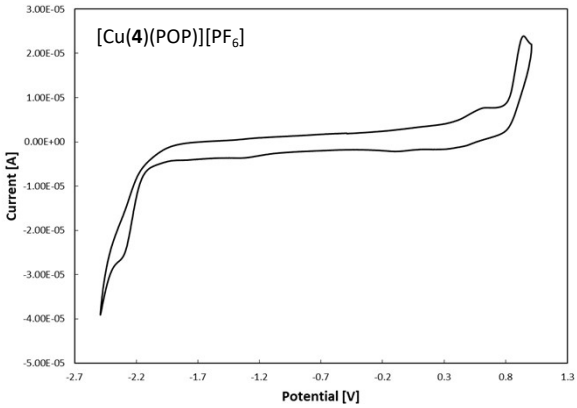


Fig. S66: Cyclic voltammograms (one scan, 2nd cycle) of [Cu(N^N)(P^P)][PF_6] complexes referenced internally Fc/Fc^+ = 0 V; deaerated CH_2Cl_2 solutions with [nBu$_4$N][PF_6] as supporting electrolyte at room temperature. All scans were taken only up to +1.0 V.

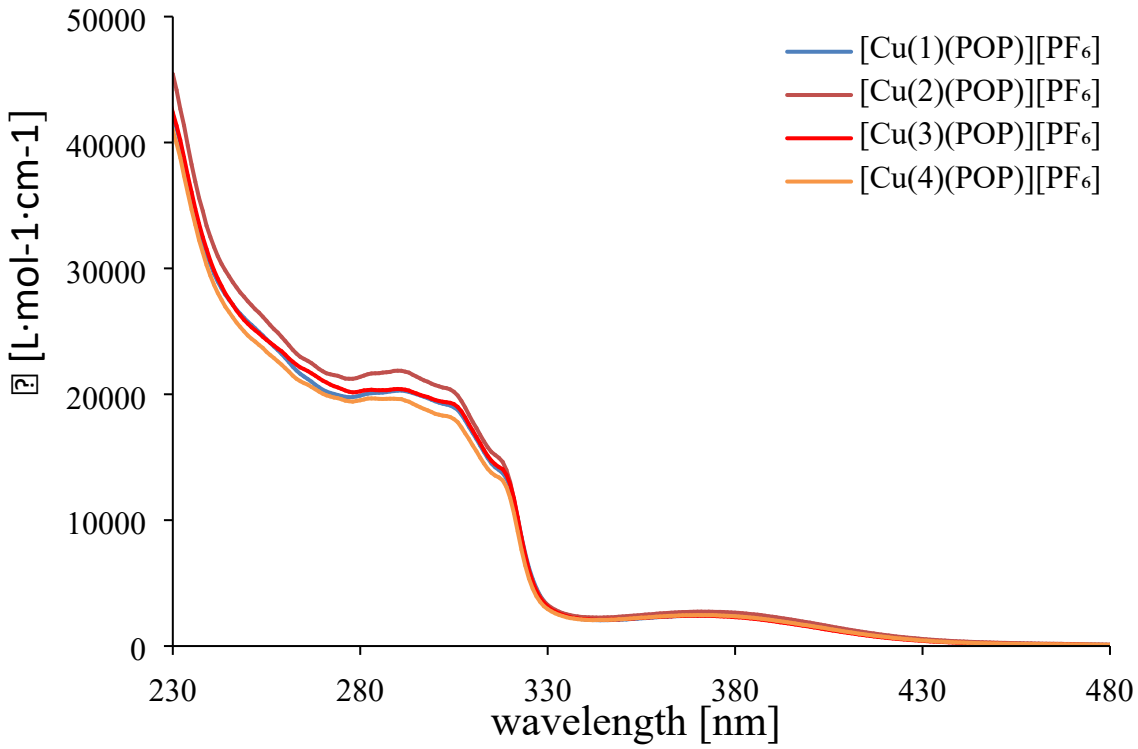


Fig. S67: Solution absorption spectra of the [Cu(N^N)(POP)][PF_6] complexes in dichloromethane (5.0 x 10^{-5} M).

Table S3. Excited state lifetime from a biexponential fit[a] of the [Cu(N^N)(P^P)][PF_6] complexes as powders.

Complex Cation	τ_1 / μs	A_1	τ_2 / μs	A_2	$<\tau>$ / μs
[Cu(**1**)(xantphos)]$^+$	13.7	0.868	1.75	0.0921	12.6
[Cu(**1**)(POP)]$^+$	15.7	0.918	1.31	0.0447	15.1
[Cu(**2**)(xantphos)]$^+$	13.1	0.864	1.58	0.0826	12.0
[Cu(**2**)(POP)]$^+$	12.9	0.904	1.71	0.0618	12.2
[Cu(**3**)(xantphos)]$^+$	12.5	0.895	1.99	0.0685	11.8
[Cu(**3**)(POP)]$^+$	16.6	0.928	0.864	0.0260	16.1
[Cu(**4**)(xantphos)]$^+$	12.4	0.782	2.57	0.154	10.8
[Cu(**4**)(POP)]$^+$	14.0	0.839	1.76	0.104	12.7

[a] The excited state lifetime $<\tau>$ is calculated from the equation $\sum A_i\tau_i / \sum (A_i)$ where A_i is the pre-exponential factor of the lifetime τ_i.

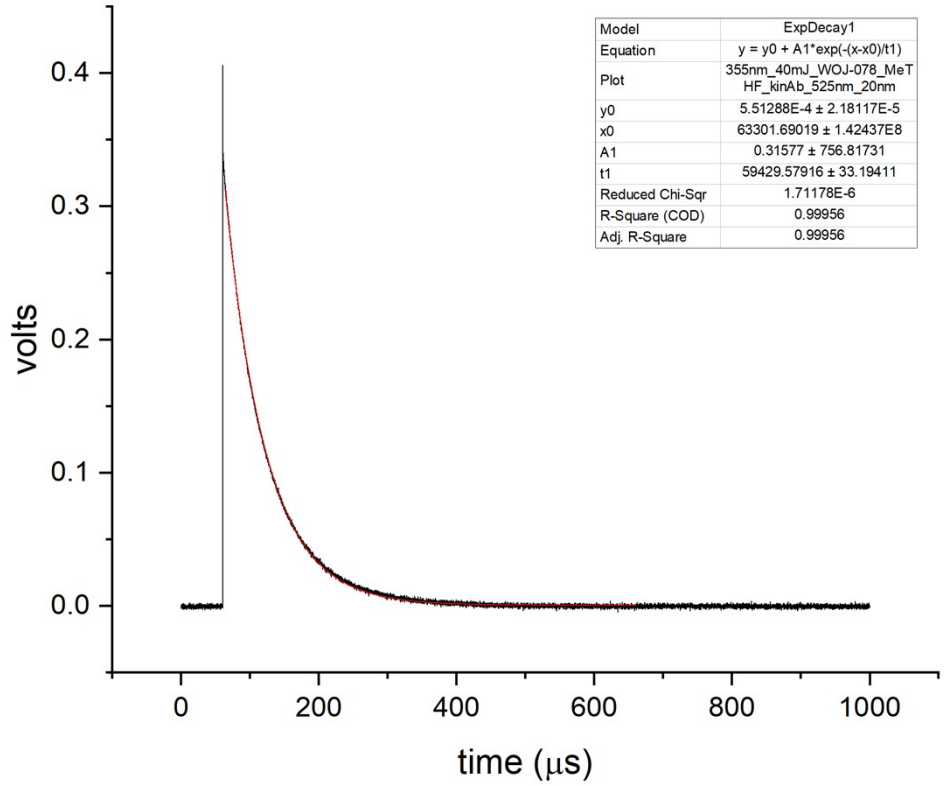


Fig. S68: Excited state lifetime plot fitted of [Cu(**3**)(POP)][PF_6] in deaerated MeTHF at 77 K. The lifetime was fitted monoexponentially. (= 355 nm)

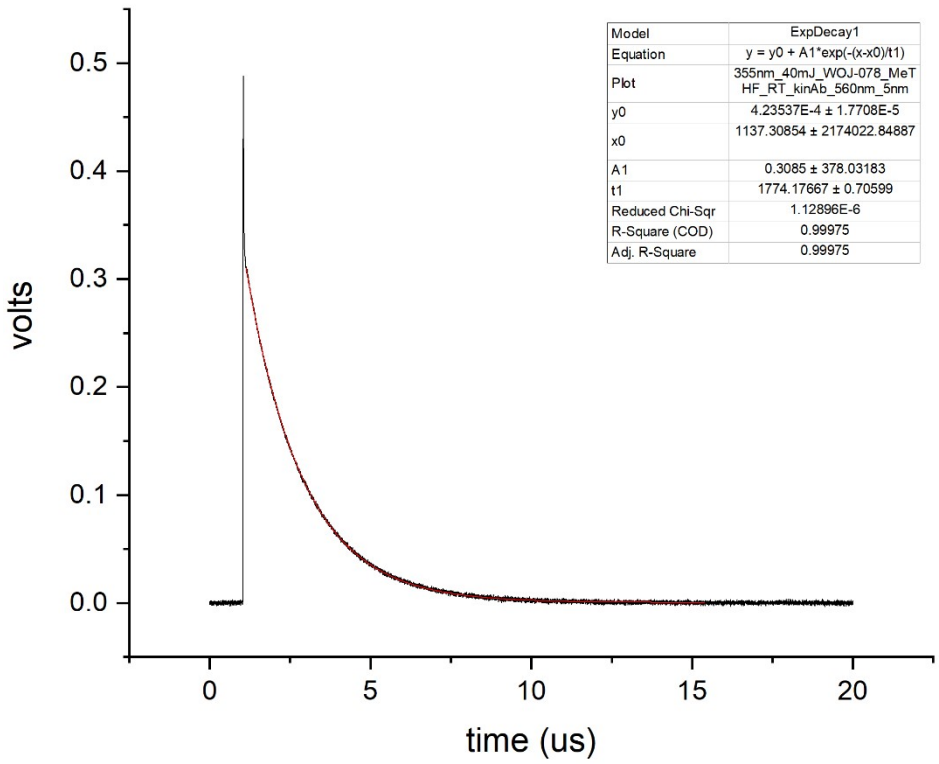


Fig. S69: Excited state lifetime plot fitted of [Cu(**3**)(POP)][PF_6] in deaerated MeTHF at room temperature (293 K). The lifetime was fitted monoexponentially. (= 355 nm)