

Supporting Information:

A counterion study of a series of [Cu(P[^]P)(N[^]N)][A] compounds with bis(phosphane) and 6-methyl and 6,6'-dimethyl-substituted 2,2'-bipyridine ligands for light-emitting electrochemical cells

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Experimental and analytical data

General Procedures for [PF₆][−] and [BF₄][−] salts of the copper(I) complexes

POP-containing compounds were synthesized by the following procedure: POP (1.1 eq.) and [Cu(MeCN)₄][PF₆] or [Cu(MeCN)₄][BF₄] (1.0 eq.) were dissolved in CH₂Cl₂ (20 mL) and the reaction mixture was stirred for 1.5 h. The respective N[^]N ligand (1.0 eq.) was added, followed by stirring the mixture for 2 h. The solvent was then removed under reduced pressure. The residue was purified by precipitation from CH₂Cl₂ with Et₂O, followed by centrifugation and the decantation of the supernatant. This step was repeated four times. Then the product was washed with cyclohexane (100 mL).

Compounds containing xantphos were prepared according to the following procedure: A solution of the respective N[^]N-ligand (1.0 eq.) and xantphos (1.1 eq.) in CH₂Cl₂ (10 mL) was added dropwise to a CH₂Cl₂ solution (10 mL) of [Cu(MeCN)₄][PF₆] or [Cu(MeCN)₄][BF₄] (1.0 eq.). The reaction mixture was then stirred for 2 h before the solvent was removed under reduced pressure. The residue was purified by precipitation from CH₂Cl₂ with Et₂O, followed by centrifugation and the decantation of the supernatant. This step was repeated four times. Then the product was washed with cyclohexane (100 mL) and dried under high vacuum.

General Procedures for [BPh₄][−] and [BAr^F₄][−] salts of the copper(I) complexes

The following procedure was adapted from a literature method¹. To synthesise the [BPh₄][−] and [BAr^F₄][−] salts, an ion exchange was carried out starting with the respective [PF₆][−] salt.

The [PF₆][−] salt (1.0 eq.) of the desired complex was dissolved in a minimal amount of MeOH at 45 °C while sonicating. Then, NaBPh₄ (1.3 eq.) or NaBAr^F₄ (1.3 eq.), respectively, was added into the warm solution. The mixture was sonicated and H₂O (60 mL) was added to precipitate the product. The product was then washed with H₂O and dried under vacuum. For the [BPh₄][−] salts, the crude product was dissolved in a minimal amount of MeOH/CH₂Cl₂ (3:1) while sonicating, followed by another addition of NaBPh₄ (1.3 eq.). The mixture was sonicated and H₂O (60 mL) was added to precipitate the product. The product was then washed with H₂O and dried under vacuum. The products were purified as follows. The crude product was dissolved in CH₂Cl₂ (20 mL) and water was added (15 mL). The mixture was vigorously shaken, centrifuged and the aqueous phase was removed. The organic phase was dried with MgSO₄. The product was precipitated from CH₂Cl₂ with Et₂O, followed by centrifugation and the decantation of the

supernatant. This step was repeated three times. Then the product was washed with cyclohexane (100 mL) and dried under high vacuum.

[Cu(POP)(Mebpy)][PF₆]

The reagents were POP (137 mg, 0.252 mmol), Mebpy (42.6 mg, 0.250 mmol) and [Cu(MeCN)₄][PF₆] (93.3 mg, 0.250 mmol). [Cu(POP)(Mebpy)][PF₆] was isolated as a yellow solid (165 mg, 0.180 mmol, 72%).

¹H NMR (500 MHz, acetone-d₆) δ/ppm 8.68 (d, ²J_{HH} = 4.7 Hz, 1H, H^{A6}), 8.50 (d, ²J_{HH} = 8.1 Hz, 1H, H^{A3}), 8.41 (d, ²J_{HH} = 7.9 Hz, 1H, H^{B3}), 8.10 (m, 1H, H^{B4}), 8.08 (m, 1H, H^{A4}), 7.47 (d, ²J_{HH} = 7.7 Hz, 1H, H^{B5}), 7.43 (m, 2H, H^{D4}), 7.41 (m, 1H, H^{A5}), 7.41 (m, 2H, H^{C5}), 7.38 (m, 2H, H^{D4'}), 7.27 (m, 4H, H^{D3}), 7.27 (m, 4H, H^{D3'}), 7.19 (m, 2H, H^{C6}), 7.15 (m, 2H, H^{C4}), 7.14 (m, 4H, H^{D2}), 7.10 (m, 4H, H^{D2'}), 6.90 (m, 2H, H^{C3}), 2.35 (s, 3H, H^{B6-Me}).

¹³C{¹H} NMR (126 MHz, acetone-d₆) δ/ppm 160.0 (s, C^{B6}), 158.9 (pseudo-t, ²J_{CP} = 6.0 Hz, C^{C1}), 153.5 (s, C^{A2}), 152.6 (s, C^{B2}), 150.3 (s, C^{A6}), 140.1 (s, C^{B4}), 139.7 (s, C^{A4}), 135.0 (s, C^{C3}), 134.0 (pseudo-t, ²J_{CP} = 7.5 Hz, C^{D2}), 133.8 (pseudo-t, ²J_{CP} = 7.2 Hz, C^{D2'}), 133.2 (s, C^{D4}), 132.1 (pseudo-t, ¹J_{CP} = 15.7 Hz, C^{D1+CD1'}), 131.0 (s, C^{D4'}), 131.0 (s, C^{C5}), 129.7 (pseudo-t, ³J_{CP} = 4.7 Hz, C^{D3+CD3'}), 127.1 (s, C^{B5}), 126.6 (s, C^{A5}), 126.1 (pseudo-t, ³J_{CP} = 2.3 Hz, C^{C4}), 125.1 (pseudo-t, ¹J_{CP} = 14.3 Hz, C^{C2}), 123.6 (s, C^{A3}), 121.2 (pseudo-t, ³J_{CP} = 2.3 Hz, C^{C6}), 120.9 (s, C^{B3}), 26.4 (s, C^{B6-Me}).

¹⁹F{¹H} NMR (202 MHz, 298 K, acetone-d₆) δ/ppm −72.7 (d, ¹J_{FP} = 707 Hz).

³¹P{¹H} NMR (202 MHz, 298 K, acetone-d₆) δ/ppm −12.9 (broad, FWHM ≈ 320 Hz, P^{POP}), −144.2 (hept., ¹J_{PF} = 707 Hz, P^{PF6}).

ESI(+)-MS (DCM/MeOH, m/z): 600.88 [M−PF₆−(bpy)]⁺ (calc. 601.09), 770.88 [M−PF₆]⁺ (base peak, calc. 717.17).

ESI(−)-MS (DCM/MeOH, m/z): 144.96 [PF₆][−] (calc. 144.96).

Found: C 61.53, H 4.24, N 3.33; C₄₇H₃₈CuF₆N₂OP₃ requires C 61.54, H 4.18, N 3.05.

[Cu(POP)(Me₂bpy)][PF₆]

The reagents were POP (136 mg, 0.252 mmol), Me₂bpy (46.2 mg, 0.251 mmol) and [Cu(MeCN)₄][PF₆] (93.2 mg, 0.250 mmol). [Cu(POP)(Me₂bpy)][PF₆] was isolated as a yellow solid (191 mg, 0.205 mmol, 82%).

¹H NMR (500 MHz, acetone-d₆) δ/ppm 8.23 (d, ²J_{HH} = 8.0 Hz, 2H, H^{B3}), 8.02 (m, 2H, H^{B4}), 7.45 (m, 2H, H^{C5}), 7.44 (m, 2H, H^{B5}), 7.35 (m, 4H, H^{D4}), 7.30 (m, 2H, H^{C4}), 7.29 (m, 2H, H^{C3}), 7.21 (m, 8H, H^{D3}), 7.11 (m, 8H, H^{D2}), 7.06 (m, 2H, H^{C6}), 2.32 (s, H^{B6-Me}).

¹³C{¹H} NMR (126 MHz, acetone-d₆) δ/ppm 159.6 (s, C^{B6}), 159.1 (pseudo-t, ²J_{CP} = 6.0 Hz, C^{C1}), 153.3 (s, C^{B2}), 139.9 (s, C^{B4}), 134.5 (s, C^{C3}), 133.9 (pseudo-t, ²J_{CP} = 7.8 Hz, C^{D2}), 133.3 (s, C^{C5}), 132.8 (pseudo-t, ¹J_{CP} = 16.2 Hz, C^{C2}), 130.8 (s, C^{D4}), 129.6 (pseudo-t, ³J_{CP} = 4.6 Hz, C^{D3}), 127.1 (s, C^{B5}), 126.2 (pseudo-t, ¹J_{CP} = 13.9 Hz, C^{D1}), 126.2 (pseudo-t, ³J_{CP} = 2.2 Hz, C^{C4}), 121.1 (pseudo-t, ³J_{CP} = 2.0 Hz, C^{C6}), 120.9 (s, C^{B3}), 26.9 (s, C^{B6-Me}).

¹⁹F{¹H} NMR (202 MHz, 298 K, acetone-d₆) δ/ppm −72.7 (d, ¹J_{FP} = 707 Hz).

³¹P{¹H} NMR (202 MHz, 298 K, acetone-d₆) δ/ppm −13.6 (broad, FWHM ≈ 300 Hz, P^{POP}), −144.2 (hept., ¹J_{PF} = 707 Hz, P^{PF6}).

ESI(+)-MS (DCM/MeOH, m/z): 600.88 [M−PF₆−(Me₂bpy)]⁺ (calc. 601.09), 784.88 [M−PF₆]⁺ (base peak, calc. 785.19).

ESI(−)-MS (DCM/MeOH, m/z): 144.96 [PF₆][−] (calc. 144.96).

Found: C 62.03, H 4.51, N 2.94; C₄₈H₄₀CuF₆N₂OP₃ requires C 61.90, H 4.33, N 3.01.

[Cu(xantphos)(Mebpy)][PF₆]

The reagents were xantphos (175 mg, 0.302 mmol), Mebpy (50.1 mg, 0.294 mmol) and [Cu(MeCN)₄][PF₆] (111 mg, 0.298 mmol). [Cu(xantphos)(Mebpy)][PF₆] was isolated as a yellow solid (264 mg, 0.276 mmol, 94%).

¹H NMR (500 MHz, acetone-d₆) δ/ppm 8.54 (m, 1H, H^{A3}), 8.54 (m, 1H, H^{A6}), 8.45 (d, ²J_{HH} = 8.0 Hz, 1H, H^{B3}), 8.15 (m, 1H, H^{B4}), 8.10 (m, 1H, H^{A4}), 7.85 (dd, ²J_{HH} = 7.8 Hz, ³J_{HH} = 1.4 Hz, 2H, H^{C5}), 7.52 (d, ²J_{HH} = 7.4 Hz, 1H, H^{A5}), 7.49 (m, 1H, H^{B5}), 7.39 (m, 2H, H^{D4}), 7.34 (m, 2H, H^{D4'}), 7.30 (d, ²J_{HH} = 7.7 Hz, 2H, H^{C4}), 7.26 (m, 4H, H^{D3}), 7.19 (m, 4H, H^{D3}), 7.17 (m, 4H, H^{D2'}), 6.92 (m, 4H, H^{D2}), 6.66 (m, 2H, H^{C3}), 2.03 (m, 3H, H^{B6-Me}), 1.89 (m, 3H, H^{xantphos-Me'}), 1.69 (m, 3H, H^{xantphos-Me}).

¹³C{¹H} NMR (126 MHz, acetone-d₆) δ/ppm 159.4 (s, C^{B6}), 155.8 (pseudo-t, ²J_{CP} = 6.1 Hz, C^{C1}), 153.3 (s, C^{A2}), 152.4 (s, C^{B2}), 149.9 (s, C^{A6}), 140.3 (s, C^{B4}), 139.9 (s, C^{A4}), 135.0 (s, C^{C6}), 133.9 (pseudo-t, ²J_{CP} = 8.0 Hz, C^{D2}), 133.5 (pseudo-t, ²J_{CP} = 7.8 Hz, C^{D2'}), 132.6 (pseudo-t, ¹J_{CP} = 16.5 Hz, C^{D1}), 132.5 (pseudo-t, ¹J_{CP} = 17.6 Hz, C^{D1}), 131.5 (s, C^{C3}), 131.1 (s, C^{D4'}), 131.0 (s, C^{D4}), 129.9 (pseudo-t, ³J_{CP} = 4.8 Hz, C^{D3}), 129.7 (pseudo-t, ³J_{CP} = 4.7 Hz, C^{D3}), 128.5 (s, C^{C5}), 127.1 (s, C^{A5}), 127.0 (s, C^{B5}), 126.3 (pseudo-t, ³J_{CP} = 2.6 Hz, C^{C4}), 123.8 (s, C^{A3}), 121.5 (pseudo-t, ¹J_{CP} = 13.5 Hz, C^{C2}), 121.1 (s, C^{B3}), 36.9 (s, C^{xantphos-bridge}), 30.3 (s, C^{xantphos-Me}), 26.4 (s, C^{xantphos-Me'}), 26.3 (s, C^{B6-Me}).

¹⁹F{¹H} NMR (202 MHz, 298 K, acetone-d₆) δ/ppm −72.6 (d, ¹J_{FP} = 707 Hz).

³¹P{¹H} NMR (202 MHz, 298 K, acetone-d₆) δ/ppm −12.8 (broad, FWHM ≈ 280 Hz, P^{xantphos}), −144.2 (hept., ¹J_{PF} = 707 Hz, P^{PF6}).

ESI(+)-MS (DCM/MeOH, m/z): 641.04 [M−PF₆−(Mebpy)]⁺ (calc. 641.12), 811.14 [M−PF₆]⁺ (base peak, calc. 811.21).

ESI(−)-MS (DCM/MeOH, m/z): 144.94 [PF₆][−] (calc. 144.96).

Found: C 62.68, H 4.87, N 3.00; C₅₀H₄₂CuF₆N₂OP₃ requires C 62.73, H 4.42, N 2.93.

[Cu(xantphos)(Me₂bpy)][PF₆]

The reagents were xantphos (145 mg, 0.250 mmol), Me₂bpy (0.45.8 mg, 0.248 mmol) and [Cu(MeCN)₄][PF₆] (94.3 mg, 0.253 mmol). [Cu(xantphos)(Me₂bpy)][PF₆] was isolated as a yellow solid (214 mg, 0.221 mmol, 89%).

¹H NMR (500 MHz, acetone-d₆) δ/ppm 8.19 (d, ²J_{HH} = 8.0 Hz, 2H, H^{B3}), 7.98 (m, 2H, H^{B4}), 7.83 (dd, ²J_{HH} = 7.9, ³J_{HH} = 1.4 Hz, 2H, H^{C5}), 7.42 (m, 4H, H^{D4}), 7.39 (m, 2H, H^{B5}), 7.31 (m, 2H, H^{C4}), 7.23 (m, 8H, H^{D3}), 7.17 (m, 8H, H^{D2}), 6.95 (m, 2H, H^{C3}), 2.14 (s, 6H, H^{B6-Me}), 1.76 (s, 6H, H^{xantphos-Me}).

¹³C{¹H} NMR (126 MHz, acetone-d₆) δ/ppm 159.2 (s, C^{B6}), 155.9 (pseudo-t, ²J_{CP} = 6.5 Hz, C^{C1}), 153.1 (s, C^{B2}), 139.9 (s, C^{B4}), 134.9 (s, C^{C6}), 134.0 (pseudo-t, ²J_{CP} = 7.6 Hz, C^{D2}), 132.5 (pseudo-t, ¹J_{CP} = 16.0 Hz, C^{D1}), 131.1 (s, C^{C3}), 131.0 (s, C^{D4}), 129.7 (pseudo-t, ³J_{CP} = 4.5 Hz, C^{D3}), 128.6 (s, C^{C5}), 126.7 (s, C^{B5}), 126.3 (pseudo-t, ³J_{CP} = 2.3 Hz, C^{C4}), 122.7 (pseudo-t, ¹J_{CP} = 12.2 Hz, C^{C2}), 121.0 (s, C^{B3}), 36.9 (s, C^{xantphos-bridge}), 28.6 (s, C^{B6-Me}), 27.0 (s, C^{xantphos-Me}).

¹⁹F{¹H} NMR (202 MHz, 298 K, acetone-d₆) δ/ppm −72.6 (d, ¹J_{FP} = 707 Hz).

³¹P{¹H} NMR (202 MHz, 298 K, acetone-d₆) δ/ppm −13.7 (broad, FWHM ≈ 285 Hz, P^{xantphos}), −144.2 (hept., ¹J_{PF} = 707 Hz, P^{PF6}).

ESI(+)-MS (DCM/MeOH, m/z): 641.05 [M−PF₆−(Me₂bpy)]⁺ (calc. 641.12), 825.14 [M−PF₆]⁺ (base peak, calc. 825.22).

ESI(−)-MS (DCM/MeOH, m/z): 144.94 [PF₆][−] (calc. 144.96).

Found: C 62.96, H 4.87, N 3.11; C₅₁H₄₄CuF₆N₂OP₃ requires C 63.06, H 4.57, N 2.88.

[Cu(POP)(Mebpy)][BF₄]

The reagents were POP (136 mg, 0.252 mmol), Mebpy (42.6 mg, 0.250 mmol) and [Cu(MeCN)₄][BF₄] (78.7 mg, 0.250 mmol). [Cu(POP)(Mebpy)][BF₄] was isolated as a yellow solid (182 mg, 0.213 mmol, 85%).

¹H NMR (500 MHz, acetone-d₆) δ/ppm 8.68 (d, ²J_{HH} = 5.1 Hz, 1H, H^{A6}), 8.50 (d, ²J_{HH} = 8.2 Hz, 1H, H^{A3}), 8.42 (d, ²J_{HH} = 7.9 Hz, 1H, H^{B3}), 8.10 (m, 1H, H^{B4}), 8.08 (m, 1H, H^{A4}), 7.47 (d, ²J_{HH} = 7.7 Hz, 1H, H^{B5}), 7.43 (m, 2H, H^{D4}), 7.41 (m, 1H, H^{A5}), 7.41 (m, 2H, H^{C5}), 7.38 (m, 2H, H^{D4'}), 7.27 (m, 4H, H^{D3}), 7.27 (m, 4H, H^{D3'}), 7.19 (m, 2H, H^{C6}), 7.15 (m, 2H, H^{C4}), 7.14 (m, 4H, H^{D2}), 7.10 (m, 4H, H^{D2'}), 6.90 (m, 2H, H^{C3}), 2.35 (s, 3H, H^{B6-Me}).

¹³C{¹H} NMR (126 MHz, acetone-d₆) δ/ppm 159.9 (s, C^{B6}), 158.9 (pseudo-t, ²J_{CP} = 6.0 Hz, C^{C1}), 153.4 (s, C^{A2}), 152.6 (s, C^{B2}), 150.3 (s, C^{A6}), 140.1 (s, C^{B4}), 139.7 (s, C^{A4}), 135.0 (s, C^{C3}), 134.1 (pseudo-t, ²J_{CP} = 7.5 Hz, C^{D2}), 133.8 (pseudo-t, ²J_{CP} = 7.2 Hz, C^{D2'}), 133.2 (s, C^{D4}), 132.1 (pseudo-t, ¹J_{CP} = 15.7 Hz, C^{D1+D1'}), 131.0 (s, C^{D4'}), 131.0 (s, C^{C5}), 129.7 (pseudo-t, ³J_{CP} = 4.7 Hz, C^{D3+D3'}), 127.1 (s, C^{B5}), 126.6 (s, C^{A5}), 126.1 (pseudo-t, ³J_{CP} = 2.3 Hz, C^{C4}), 125.1 (pseudo-t, ¹J_{CP} = 14.3 Hz, C^{C2}), 123.6 (s, C^{A3}), 121.2 (pseudo-t, ³J_{CP} = 2.3 Hz, C^{C6}), 120.9 (s, C^{B3}), 26.4 (s, C^{B6-Me}).

¹¹B{¹H} NMR (160 MHz, 298 K, acetone-d₆) δ/ppm −0.9 (s).

¹⁹F{¹H} NMR (202 MHz, 298 K, acetone-d₆) δ/ppm −151.8 (s).

³¹P{¹H} NMR (202 MHz, 298 K, acetone-d₆) δ/ppm −13.0 (broad, FWHM ≈ 310 Hz).

ESI(+)-MS (DCM/MeOH, m/z): 600.88 [M−BF₄−(Mebpy)]⁺ (calc. 601.09), 770.88 [M−BF₄]⁺ (base peak, calc. 771.17).

ESI(−)-MS (DCM/MeOH, m/z): 86.96 [BF₄][−] (calc. 87.00).

Found: C 65.50, H 4.37, N 3.28; C₄₇H₃₈BCuF₄N₂OP₂ requires C 65.71, H 4.46, N 3.26.

[Cu(POP)(Me₂bpy)][BF₄]

The reagents were POP (136 mg, 0.252 mmol), Me₂bpy (46.1 mg, 0.250 mmol) and [Cu(MeCN)₄][BF₄] (78.7 mg, 0.250 mmol). [Cu(POP)(Me₂bpy)][BF₄] was isolated as a yellow solid (192 mg, 0.220 mmol, 88%).

¹H NMR (500 MHz, acetone-d₆) δ/ppm 8.24 (d, ²J_{HH} = 8.0, 2H, H^{B3}), 8.02 (m, 2H, H^{B4}), 7.45 (m, 2H, H^{C5}), 7.44 (m, 2H, H^{B5}), 7.35 (m, 4H, H^{D4}), 7.30 (m, 2H, H^{C4}), 7.28 (m, 2H, H^{C3}), 7.21 (m, 8H, H^{D3}), 7.11 (m, 8H, H^{D2}), 7.06 (m, 2H, H^{C6}), 2.32 (s, H^{B6-Me}).

¹³C{¹H} NMR (126 MHz, acetone-d₆) δ/ppm 159.6 (s, C^{B6}), 159.1 (pseudo-t, ²J_{CP} = 6.0 Hz, C^{C1}), 153.3 (s, C^{B2}), 139.9 (s, C^{B4}), 134.5 (s, C^{C3}), 133.9 (pseudo-t, ²J_{CP} = 7.8 Hz, C^{D2}), 133.3 (s, C^{C5}), 132.8 (pseudo-t, ¹J_{CP} = 16.3 Hz, C^{C2}), 130.8 (s, C^{D4}), 129.6 (pseudo-t, ³J_{CP} = 4.6 Hz, C^{D3}), 127.1 (s, C^{B5}), 126.2 (pseudo-t, ¹J_{CP} = 14.0 Hz, C^{D1}), 126.2 (pseudo-t, ³J_{CP} = 2.2 Hz, C^{C4}), 121.0 (pseudo-t, ³J_{CP} = 2.0 Hz, C^{C6}), 120.9 (s, C^{B3}), 26.9 (s, C^{B6-Me}).

¹¹B{¹H} NMR (160 MHz, 298 K, acetone-d₆) δ/ppm −0.9 (s).

¹⁹F{¹H} NMR (202 MHz, 298 K, acetone-d₆) δ/ppm −151.8 (s).

³¹P{¹H} NMR (202 MHz, 298 K, acetone-d₆) δ/ppm −13.7 (broad, FWHM ≈ 310 Hz).

ESI(+)-MS (DCM/MeOH, m/z): 600.88 [M−BF₄−(Me₂bpy)]⁺ (calc. 601.09), 784.88 [M−BF₄]⁺ (base peak, calc. 785.19).

ESI(−)-MS (DCM/MeOH, m/z): 86.96 [BF₄][−] (calc. 87.00).

Found: C 65.70, H 4.51, N 3.26; C₄₈H₄₀BCuF₄N₂OP₂ requires C 66.03, H 4.62, N 3.21.

[Cu(xantphos)(Mebpy)][BF₄]

The reagents were xantphos (147 mg, 0.253 mmol), Mebpy (42.5 mg, 0.254 mmol) and [Cu(MeCN)₄][BF₄] (78.6 mg, 0.250 mmol). [Cu(xantphos)(Mebpy)][BF₄] was isolated as a yellow solid (205 mg, 0.228 mmol, 91%).

^1H NMR (500 MHz, acetone- d_6) δ /ppm 8.54 (m, 1H, H^{A3}), 8.54 (m, 1H, H^{A6}), 8.46 (d, $^2J_{\text{HH}} = 8.0$ Hz, 1H, H^{B3}), 8.15 (m, 1H, H^{B4}), 8.10 (m, 1H, H^{A4}), 7.85 (dd, $^2J_{\text{HH}} = 7.8$ Hz, $^3J_{\text{HH}} = 1.4$ Hz, 2H, H^{C5}), 7.52 (d, $^2J_{\text{HH}} = 7.6$ Hz, 1H, H^{A5}), 7.49 (m, 1H, H^{B5}), 7.39 (m, 2H, H^{D4}), 7.34 (m, 2H, H^{D4}), 7.30 (d, $^2J_{\text{HH}} = 7.7$ Hz, 2H, H^{C4}), 7.26 (m, 4H, H^{D3}), 7.19 (m, 4H, H^{D3}), 7.17 (m, 4H, D^2), 6.92 (m, 4H, H^{D2}), 6.66 (m, 2H, H^{C3}), 2.03 (m, 3H, $\text{H}^{\text{B6-Me}}$), 1.89 (m, 3H, $\text{H}^{\text{xantphos-Me}}$), 1.69 (m, 3H, $\text{H}^{\text{xantphos-Me}}$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, acetone- d_6) δ /ppm 159.3 (s, C^{B6}), 155.9 (pseudo-t, $^2J_{\text{CP}} = 6.3$ Hz, C^{C1}), 153.3 (s, C^{A2}), 152.4 (s, C^{B2}), 149.9 (s, C^{A6}), 140.3 (s, C^{B4}), 139.9 (s, C^{A4}), 135.0 (s, C^{C6}), 133.9 (pseudo-t, $^2J_{\text{CP}} = 8.0$ Hz, C^{D2}), 133.5 (pseudo-t, $^2J_{\text{CP}} = 7.8$ Hz, C^{D2}), 132.6 (pseudo-t, $^1J_{\text{CP}} = 16.6$ Hz, C^{D1}), 132.5 (pseudo-t, $^1J_{\text{CP}} = 17.6$ Hz, C^{D1}), 131.5 (s, C^{C3}), 131.1 (s, C^{D4}), 130.9 (s, C^{D4}), 129.9 (pseudo-t, $^3J_{\text{CP}} = 4.7$ Hz, C^{D3}), 129.7 (pseudo-t, $^3J_{\text{CP}} = 4.7$ Hz, C^{D3}), 128.5 (s, C^{C5}), 127.1 (s, C^{A5}), 127.0 (s, C^{B5}), 126.3 (pseudo-t, $^3J_{\text{CP}} = 2.5$ Hz, C^{C4}), 123.8 (s, C^{A3}), 121.5 (pseudo-t, $^1J_{\text{CP}} = 13.7$ Hz, C^{C2}), 121.1 (s, C^{B3}), 36.9 (s, $\text{C}^{\text{xantphos-bridge}}$), 30.3 (s, $\text{C}^{\text{xantphos-Me}}$), 26.4 (s, $\text{C}^{\text{xantphos-Me}}$), 26.3 (s, $\text{C}^{\text{B6-Me}}$).

$^{11}\text{B}\{^1\text{H}\}$ NMR (160 MHz, 298 K, acetone- d_6) δ /ppm -0.9 (s).

$^{19}\text{F}\{^1\text{H}\}$ NMR (202 MHz, 298 K, acetone- d_6) δ /ppm -151.9 (s).

$^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, 298 K, acetone- d_6) δ /ppm -12.9 (broad, FWHM ≈ 320 Hz).

ESI(+)-MS (DCM/MeOH, m/z): 640.88 [$\text{M-BF}_4\text{-(Mebpy)}$] $^+$ (calc. 641.12), 810.88 [M-BF_4] $^+$ (base peak, calc. 811.21).

ESI(-)-MS (DCM/MeOH, m/z): 86.96 [BF_4] $^-$ (calc. 87.00).

Found: C 66.48, H 5.06, N 3.31; $\text{C}_{50}\text{H}_{42}\text{BCuF}_4\text{N}_2\text{OP}_2$ requires C 66.79, H 4.71, N 3.12.

[Cu(xantphos)(Me₂bpy)][BF₄]

The reagents were xantphos (145 mg, 0.250 mmol), Me₂bpy (46.1 mg, 0.250 mmol) and $[\text{Cu}(\text{MeCN})_4][\text{BF}_4]$ (78.7 mg, 0.250 mmol). $[\text{Cu}(\text{xantphos})(\text{Me}_2\text{bpy})][\text{BF}_4]$ was isolated as a yellow solid (189 mg, 0.208 mmol, 83%).

^1H NMR (500 MHz, acetone- d_6) δ /ppm

8.20 (d, $^2J_{\text{HH}} = 8.0$ Hz, 2H, H^{B3}), 7.98 (m, 2H, H^{B4}), 7.83 (dd, $^2J_{\text{HH}} = 7.9$, $^3J_{\text{HH}} = 1.4$ Hz, 2H, H^{C5}), 7.41 (m, 4H, H^{D4}), 7.39 (m, 2H, H^{B5}), 7.31 (m, 2H, H^{C4}), 7.23 (m, 8H, H^{D3}), 7.17 (m, 8H, H^{D2}), 6.94 (m, 2H, H^{C3}), 2.14 (s, 6H, $\text{H}^{\text{B6-Me}}$), 1.76 (s, 6H, $\text{H}^{\text{xantphos-Me}}$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, acetone- d_6) δ /ppm 159.2 (s, C^{B6}), 155.9 (pseudo-t, $^2J_{\text{CP}} = 6.5$ Hz, C^{C1}), 153.1 (s, C^{B2}), 139.9 (s, C^{B4}), 134.9 (s, C^{C6}), 134.0 (pseudo-t, $^2J_{\text{CP}} = 7.7$ Hz, C^{D2}), 132.5 (pseudo-t, $^1J_{\text{CP}} = 16.0$ Hz, C^{D1}), 131.1 (s, C^{C3}), 131.0 (s, C^{D4}), 129.7 (pseudo-t, $^3J_{\text{CP}} = 4.6$ Hz, C^{D3}), 128.6 (s, C^{C5}), 126.7 (s, C^{B5}), 126.3 (pseudo-t, $^3J_{\text{CP}} = 2.3$ Hz, C^{C4}), 122.7 (pseudo-t, $^1J_{\text{CP}} = 12.2$ Hz, C^{C2}), 121.1 (s, C^{B3}), 36.9 (s, $\text{C}^{\text{xantphos-bridge}}$), 28.6 (s, $\text{C}^{\text{B6-Me}}$), 27.0 (s, $\text{C}^{\text{xantphos-Me}}$).

$^{11}\text{B}\{^1\text{H}\}$ NMR (160 MHz, 298 K, acetone- d_6) δ /ppm -0.9 (s).

$^{19}\text{F}\{^1\text{H}\}$ NMR (202 MHz, 298 K, acetone- d_6) δ /ppm -151.9 (s).

$^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, 298 K, acetone- d_6) δ /ppm -12.9 (broad, FWHM ≈ 270 Hz, $\text{P}^{\text{xantphos}}$).

ESI(+)-MS (DCM/MeOH, m/z): 640.88 [$\text{M-BF}_4\text{-(Me}_2\text{bpy)}$] $^+$ (calc. 641.12), 824.88 [M-BF_4] $^+$ (base peak, calc. 825.22).

ESI(-)-MS (DCM/MeOH, m/z): 86.96 [BF_4] $^-$ (calc. 87.00).

Found: C 50.79, H 3.40, N 2.56; $\text{C}_{48}\text{H}_{34}\text{Br}_2\text{CuF}_6\text{N}_2\text{OP}_3\cdot\text{CH}_2\text{Cl}_2$ requires C 50.26, H 3.18, N 2.39.

[Cu(POP)(Mebpy)][BPh₄]

The reagents were $[\text{Cu}(\text{POP})(\text{Mebpy})][\text{PF}_6]$ (153 mg, 0.167 mmol) and NaBPh₄ (149.4 mg, 0.436 mmol); two ion exchange steps executed, half amount of NaBPh₄ added per ion exchange step. $[\text{Cu}(\text{POP})(\text{Mebpy})][\text{BPh}_4]$ was isolated as a yellow solid (131 mg, 0.120 mmol, 72%).

^1H NMR (500 MHz, acetone- d_6) δ /ppm 8.65 (d, $^2J_{\text{HH}} = 5.1$ Hz, 1H, H^{A6}), 8.42 (d, $^2J_{\text{HH}} = 8.2$ Hz, 1H, H^{A3}), 8.34 (d, $^2J_{\text{HH}} = 7.9$ Hz, 1H, H^{B3}), 8.05 (m, 1H, H^{B4}), 8.02 (m, 1H, H^{A4}), 7.42 (d, $^2J_{\text{HH}} = 7.7$ Hz, 1H, H^{B5}), 7.41 (m, 2H, H^{D4}), 7.37 (m, 1H, H^{A5}), 7.36 (m, 2H, H^{C5}), 7.35 (m, 2H, H^{D4}), 7.34 (m, 8H, H^{E3}), 7.26 (m, 4H, H^{D3}), 7.26 (m, 4H, H^{D3}), 7.16 (m, 2H, H^{C6}), 7.13 (m, 2H, H^{C4}), 7.12 (m, 4H, H^{D2}), 7.10 (m, 4H, H^{D2}), 6.91 (m, 2H, H^{C3}), 6.91 (m, 8H, H^{E2}), 6.76 (m, 4H, H^{E4}), 2.32 (s, 3H, $\text{H}^{\text{B6-Me}}$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, acetone- d_6) δ /ppm 164.7 (q, $^1J_{\text{CB}} = 49.1$ Hz, C^{E1}), 159.8 (s, C^{B6}), 158.6 (pseudo-t, $^2J_{\text{CP}} = 6.0$ Hz, C^{C1}), 153.2 (s, C^{A2}), 152.3 (s, C^{B2}), 150.0 (s, C^{A6}), 139.7 (s, C^{B4}), 139.4 (s, C^{A4}), 136.8 (pseudo-q, $^2J_{\text{CP}} = 1.4$ Hz, C^{E3}), 134.7 (s, C^{C3}), 133.7 (pseudo-t, $^2J_{\text{CP}} = 7.5$ Hz, C^{D2}), 133.5 (pseudo-t, $^2J_{\text{CP}} = 7.2$ Hz, C^{D2}), 132.9 (s, C^{D4}), 131.9 (pseudo-t, $^1J_{\text{CP}} = 15.7$ Hz, $\text{C}^{\text{D1+C1}}$), 130.7 (s, C^{D4}), 130.7 (s, C^{C5}), 129.5 (pseudo-t, $^3J_{\text{CP}} = 4.7$ Hz, $\text{C}^{\text{D3+C3}}$), 126.8 (s, C^{B5}), 126.4 (s, C^{A5}), 125.8 (pseudo-t, $^3J_{\text{CP}} = 2.3$ Hz, C^{C4}), 125.8 (pseudo-q, $^2J_{\text{CP}} = 3.6$ Hz, C^{E2}), 124.8 (pseudo-t, $^1J_{\text{CP}} = 14.3$ Hz, C^{C2}), 123.3 (s, C^{A3}), 122.0 (m, C^{E4}), 121.0 (pseudo-t, $^3J_{\text{CP}} = 2.3$ Hz, C^{C6}), 120.6 (s, C^{B3}), 26.2 (s, $\text{C}^{\text{B6-Me}}$).

$^{11}\text{B}\{^1\text{H}\}$ NMR (160 MHz, 298 K, acetone- d_6) δ /ppm -6.9 (s).

$^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, 298 K, acetone- d_6) δ /ppm -12.9 (broad, FWHM ≈ 310 Hz).

ESI(+)-MS (DCM/MeOH, m/z): 601.66 [$\text{M-BPh}_4\text{-(Mebpy)}$] $^+$ (calc. 601.09), 771.66 [M-BPh_4] $^+$ (base peak, calc. 771.17).

ESI(-)-MS (DCM/MeOH, m/z): 318.88 [BPh_4] $^-$ (calc. 319.23).

Found: C 77.82, H 5.80, N 2.52; $\text{C}_{71}\text{H}_{58}\text{BCuN}_2\text{OP}_2$ requires C 78.12, H 5.36, N 2.57.

[Cu(POP)(Me₂bpy)][BPh₄]

The reagents were [Cu(POP)(Me₂bpy)][PF₆] (238 mg, 0.255 mmol) and NaBPh₄ (237 mg, 0.687 mmol); two ion exchange steps executed, half amount of NaBPh₄ added per ion exchange step. [Cu(POP)(Me₂bpy)][BPh₄] was isolated as a yellow solid (218 mg, 0.197 mmol, 77%).

¹H NMR (500 MHz, acetone-d₆) δ/ppm 8.15 (d, ²J_{HH} = 8.0, 2H, H^{B3}), 7.96 (m, 2H, H^{B4}), 7.43 (m, 2H, H^{C5}), 7.39 (m, 2H, H^{B5}), 7.34 (m, 4H, H^{D4}), 7.34 (m, 8H, H^{E3}), 7.29 (m, 2H, H^{C4}), 7.28 (m, 2H, H^{C3}), 7.19 (m, 8H, H^{D3}), 7.10 (m, 8H, H^{D2}), 7.05 (m, 2H, H^{C6}), 6.91 (m, 8H, H^{E2}), 6.76 (m, 4H, H^{E4}), 2.31 (s, H^{B6-Me}).

¹³C{¹H} NMR (126 MHz, acetone-d₆) δ/ppm 164.7 (q, ¹J_{CB} = 49.1 Hz, C^{E1}), 159.4 (s, C^{B6}), 158.9 (pseudo-t, ²J_{CP} = 6.0 Hz, C^{C1}), 153.1 (s, C^{B2}), 139.6 (s, C^{B4}), 136.8 (pseudo-q, ²J_{CP} = 1.4 Hz, C^{E3}), 134.2 (s, C^{C3}), 133.6 (pseudo-t, ²J_{CP} = 7.8 Hz, C^{D2}), 133.0 (s, C^{C5}), 132.5 (pseudo-t, ¹J_{CP} = 16.3 Hz, C^{C2}), 130.5 (s, C^{D4}), 129.3 (pseudo-t, ³J_{CP} = 4.6 Hz, C^{D3}), 126.8 (s, C^{B5}), 125.9 (pseudo-t, ¹J_{CP} = 14.0 Hz, C^{D1}), 125.9 (pseudo-t, ³J_{CP} = 2.2 Hz, C^{C4}), 125.8 (pseudo-q, ²J_{CP} = 3.6 Hz, C^{E2}), 122.0 (m, C^{E4}), 120.8 (pseudo-t, ³J_{CP} = 2.0 Hz, C^{C6}), 120.7 (s, C^{B3}), 26.7 (s, C^{B6-Me}).

¹¹B{¹H} NMR (160 MHz, 298 K, acetone-d₆) δ/ppm –6.5 (s).

³¹P{¹H} NMR (202 MHz, 298 K, acetone-d₆) δ/ppm –13.6 (broad, FWHM ≈ 250 Hz).

ESI(+)-MS (DCM/MeOH, m/z): 601.66 [M–BPh₄–(Me₂bpy)]⁺ (calc. 601.09), 785.66 [M–BPh₄]⁺ (base peak, calc. 785.19).

ESI(–)-MS (DCM/MeOH, m/z): 318.88 [BPh₄][–] (calc. 319.23).

Found: C 78.17, H 6.23, N 2.34; C₇₂H₆₀BCuN₂OP₂ requires C 78.22, H 5.47, N 2.53.

[Cu(xantphos)(Mebpy)][BPh₄]

The reagents were [Cu(xantphos)(Mebpy)][PF₆] (149 mg, 0.156 mmol) and NaBPh₄ (143 mg, 0.418 mmol); two ion exchange steps executed, half amount of NaBPh₄ added per ion exchange step. [Cu(xantphos)(Mebpy)][BPh₄] was isolated as a yellow solid (141 mg, 0.125 mmol, 80%).

¹H NMR (500 MHz, acetone-d₆) δ/ppm 8.53 (m, 1H, H^{A3}), 8.52 (m, 1H, H^{A6}), 8.43 (d, ²J_{HH} = 8.0 Hz, 1H, H^{B3}), 8.12 (m, 1H, H^{B4}), 8.08 (m, 1H, H^{A4}), 7.85 (dd, ²J_{HH} = 7.8 Hz, ³J_{HH} = 1.4 Hz, 2H, H^{C5}), 7.50 (d, ²J_{HH} = 7.6 Hz, 1H, H^{A5}), 7.48 (m, 1H, H^{B5}), 7.38 (m, 2H, H^{D4}), 7.35 (m, 2H, H^{D4}), 7.34 (m, 8H, H^{E3}), 7.29 (d, ²J_{HH} = 7.7 Hz, 2H, H^{C4}), 7.26 (m, 4H, H^{D3}), 7.19 (m, 4H, H^{D3}), 7.17 (m, 4H, H^{D2}), 6.92 (m, 4H, H^{D2}), 6.91 (m, 8H, H^{E2}), 6.76 (m, 4H, H^{E4}), 6.66 (m, 2H, H^{C3}), 2.03 (m, 3H, H^{B6-Me}), 1.89 (m, 3H, H^{xantphos-Me}), 1.68 (m, 3H, H^{xantphos-Me}).

¹³C{¹H} NMR (126 MHz, acetone-d₆) δ/ppm 164.7 (q, ¹J_{CB} = 49.1 Hz, C^{E1}), 158.5 (s, C^{B6}), 153.1 (m, C^{C1}), 152.1 (s, C^{A2}), 149.7 (s, C^{B2}), 149.1 (s, C^{A6}), 140.1 (s, C^{B4}), 139.6 (s, C^{A4}), 136.8 (pseudo-q, ²J_{CP} = 1.4 Hz, C^{E3}), 134.8 (s, C^{C6}), 133.6 (pseudo-t, ²J_{CP} = 8.0 Hz, C^{D2}), 133.3 (pseudo-t, ²J_{CP} = 7.8 Hz, C^{D2}), 132.3 (pseudo-t, ¹J_{CP} = 16.6 Hz, C^{D1}), 132.2 (pseudo-t, ¹J_{CP} = 17.6 Hz, C^{D1}), 131.3 (s, C^{C3}), 131.2 (s, C^{D4}), 130.8 (s, C^{D4}), 129.6 (pseudo-t, ³J_{CP} = 4.7 Hz, C^{D3}), 129.5 (pseudo-t, ³J_{CP} = 4.7 Hz, C^{D3}), 128.3 (s, C^{C5}), 126.8 (s, C^{A5}), 126.8 (s, C^{B5}), 126.1 (pseudo-t, ³J_{CP} = 2.5 Hz, C^{C4}), 125.8 (pseudo-q, ²J_{CP} = 3.6 Hz, C^{E2}), 123.5 (s, C^{A3}), 122.0 (m, C^{E4}), 121.3 (pseudo-t, ¹J_{CP} = 13.7 Hz, C^{C2}), 120.8 (s, C^{B3}), 36.6 (s, C^{xantphos-bridge}), 30.1 (s, C^{xantphos-Me}), 26.2 (s, C^{xantphos-Me}), 26.0 (s, C^{B6-Me}).

¹¹B{¹H} NMR (160 MHz, 298 K, acetone-d₆) δ/ppm –6.5 (s).

³¹P{¹H} NMR (202 MHz, 298 K, acetone-d₆) δ/ppm –12.9 (broad, FWHM ≈ 270 Hz).

ESI(+)-MS (DCM/MeOH, m/z): 640.88 [M–BPh₄–(Mebpy)]⁺ (calc. 641.12), 810.66 [M–BPh₄]⁺ (base peak, calc. 811.21).

ESI(–)-MS (DCM/MeOH, m/z): 318.88 [BPh₄][–] (calc. 319.23).

Found: C 50.79, H 3.40, N 2.56; C₄₈H₃₄Br₂CuF₆N₂OP₃·CH₂Cl₂ requires C 50.26, H 3.18, N 2.39.

[Cu(xantphos)(Me₂bpy)][BPh₄]

The reagents were [Cu(xantphos)(Mebpy)][PF₆] (195 mg, 0.201 mmol) and NaBPh₄ (184 mg, 0.535 mmol); two ion exchange steps executed, half amount of NaBPh₄ added per ion exchange step. [Cu(xantphos)(Me₂bpy)][BPh₄] was isolated as a yellow solid (153 mg, 0.176 mmol, 78%).

¹H NMR (500 MHz, acetone-d₆) δ/ppm 8.15 (d, ²J_{HH} = 8.0 Hz, 2H, H^{B3}), 7.95 (m, 2H, H^{B4}), 7.83 (dd, ²J_{HH} = 7.9, ³J_{HH} = 1.4 Hz, 2H, H^{C5}), 7.40 (m, 4H, H^{D4}), 7.39 (m, 2H, H^{B5}), 7.34 (m, 8H, H^{E3}), 7.30 (m, 2H, H^{C4}), 7.22 (m, 8H, H^{D3}), 7.17 (m, 8H, H^{D2}), 6.95 (m, 2H, H^{C3}), 6.91 (m, 8H, H^{E2}), 6.76 (m, 4H, H^{E4}), 2.13 (s, 6H, H^{B6-Me}), 1.75 (s, 6H, H^{xantphos-Me}).

¹³C{¹H} NMR (126 MHz, acetone-d₆) δ/ppm 164.7 (q, ¹J_{CB} = 49.1 Hz, C^{E1}), 159.1 (s, C^{B6}), 155.8 (pseudo-t, ²J_{CP} = 6.5 Hz, C^{C1}), 153.1 (s, C^{B2}), 139.7 (s, C^{B4}), 136.8 (pseudo-q, ²J_{CP} = 1.4 Hz, C^{E3}), 134.9 (s, C^{C6}), 133.8 (pseudo-t, ²J_{CP} = 7.7 Hz, C^{D2}), 132.4 (pseudo-t, ²J_{CP} = 16.0 Hz, C^{D1}), 131.0 (s, C^{C3}), 130.9 (s, C^{D4}), 129.6 (pseudo-t, ³J_{CP} = 4.6 Hz, C^{D3}), 128.5 (s, C^{C5}), 126.6 (s, C^{B5}), 126.2 (pseudo-t, ³J_{CP} = 2.3 Hz, C^{C4}), 125.8 (pseudo-q, ²J_{CP} = 3.6 Hz, C^{E2}), 122.2 (pseudo-t, ¹J_{CP} = 12.2 Hz, C^{C2}), 122.0 (m, C^{E4}), 120.8 (s, C^{B3}), 36.8 (s, C^{xantphos-bridge}), 28.4 (s, C^{B6-Me}), 26.8 (s, C^{xantphos-Me}).

¹¹B{¹H} NMR (160 MHz, 298 K, acetone-d₆) δ/ppm –6.5 (s).

³¹P{¹H} NMR (202 MHz, 298 K, acetone-d₆) δ/ppm –13.3 (broad, FWHM ≈ 240 Hz).

ESI(+)-MS (DCM/MeOH, m/z): 641.66 [M–BPh₄–(Me₂bpy)]⁺ (calc. 641.12), 825.66 [M–BPh₄]⁺ (base peak, calc. 826.42).

ESI(–)-MS (DCM/MeOH, m/z): 318.88 [BPh₄][–] (calc. 319.23).

Found: C 78.10, H 5.72, N 2.69; C₇₅H₆₄BCuN₂OP₂ requires C 78.63, H 5.63, N 2.45.

[Cu(POP)(Mebpy)][BARF₄]

The reagents were [Cu(POP)(Mebpy)][PF₆] (257 mg, 0.280 mmol) and NaBARF₄ (332 mg, 0.375 mmol). [Cu(POP)(Mebpy)][BARF₄] was isolated as a yellow solid (381 mg, 0.232 mmol, 83%).

¹H NMR (500 MHz, acetone-d₆) δ/ppm 8.68 (d, ²J_{HH} = 5.1 Hz, 1H, H^{A6}), 8.50 (d, ²J_{HH} = 8.1 Hz, 1H, H^{A3}), 8.41 (d, ²J_{HH} = 7.9 Hz, 1H, H^{B3}), 8.11 (m, 1H, H^{B4}), 8.07 (m, 1H, H^{A4}), 7.79 (m, 8H, H^{E2}), 7.67 (s, 4H, H^{E4}), 7.47 (d, ²J_{HH} = 7.7 Hz, 1H, H^{B5}), 7.43 (m, 2H, H^{D4}), 7.26 (m, 1H, H^{A5}), 7.24 (m, 2H, H^{C5}), 7.35 (m, 2H, H^{D4}'), 7.27 (m, 4H, H^{D3}), 7.27 (m, 4H, H^{D3}'), 7.18 (m, 2H, H^{C6}), 7.15 (m, 2H, H^{C4}), 7.14 (m, 4H, H^{D2}), 7.09 (m, 4H, H^{D2}'), 6.90 (m, 2H, H^{C3}), 2.35 (s, 3H, H^{B6-Me}).

¹³C{¹H} NMR (126 MHz, acetone-d₆) δ/ppm 162.2 (m, C^{E1}), 159.1 (s, C^{B6}), 158.0 (m, C^{C1}), 152.6 (s, C^{A2}), 152.5 (s, C^{A6}), 151.9 (s, C^{B2}), 139.0 (s, C^{B4}), 138.8 (s, C^{A4}), 134.6 (m, C^{E2}), 134.1 (s, C^{C3}), 133.1 (m, C^{D2}), 132.9 (m, C^{D2}'), 132.3 (s, C^{D4}), 130.1 (s, C^{D4}'), 130.1 (s, C^{C5}), 129.8 (m, C^{D1+C1}'), 128.9 (pseudo-t, ³J_{CP} = 4.6 Hz, C^{D3+C3}'), 128.0 (m, C^{E3}), 126.2 (s, C^{B5}), 125.8 (s, C^{A5}), 125.2 (m, C^{C4}), 124.7 (q, ¹J_{CF} = 271.3 Hz, C^{E3-CF3}), 124.2 (m, C^{C2}), 122.7 (s, C^{A3}), 120.3 (m, C^{C6}), 120.0 (s, C^{B3}), 117.5 (m, C^{E4}), 25.5 (s, C^{B6-Me}).

¹¹B{¹H} NMR (160 MHz, 298 K, acetone-d₆) δ/ppm -6.6 (s).

¹⁹F{¹H} NMR (202 MHz, 298 K, acetone-d₆) δ/ppm -63.3 (s).

³¹P{¹H} NMR (202 MHz, 298 K, acetone-d₆) δ/ppm -12.9 (broad, FWHM ≈ 280 Hz).

ESI(+)-MS (DCM/MeOH, m/z): 601.03 [M-BARF₄-(Mebpy)]⁺ (calc. 601.09), 771.12 [M-BARF₄]⁺ (base peak, calc. 771.17).

ESI(-)-MS (DCM/MeOH, m/z): 862.00 [BARF₄]⁻ (calc. 862.06).

Found: C 58.55, H 4.33, N 1.88; C₇₉H₄₉BCuF₂₄N₂OP₂ requires C 58.05, H 3.02, N 1.71.

[Cu(POP)(Me₂bpy)][BARF₄]

The reagents were [Cu(POP)(Me₂bpy)][PF₆] (259 mg, 0.277 mmol) and NaBARF₄ (331 mg, 0.374 mmol). [Cu(POP)(Me₂bpy)][BARF₄] was isolated as a yellow solid (385 mg, 0.234 mmol, 84%).

¹H NMR (500 MHz, acetone-d₆) δ/ppm 8.23 (d, ²J_{HH} = 8.0, 2H, H^{B3}), 8.02 (m, 2H, H^{B4}), 7.79 (m, 8H, H^{E2}), 7.67 (s, 4H, H^{E4}), 7.44 (m, 2H, H^{C5}), 7.44 (m, 2H, H^{B5}), 7.35 (m, 4H, H^{D4}), 7.31 (m, 2H, H^{C4}), 7.29 (m, 2H, H^{C3}), 7.20 (m, 8H, H^{D3}), 7.11 (m, 8H, H^{D2}), 7.06 (m, 2H, H^{C6}), 2.32 (s, H^{B6-Me}).

¹³C{¹H} NMR (126 MHz, acetone-d₆) δ/ppm 162.2 (m, C^{E1}), 158.7 (s, C^{B6}), 158.2 (pseudo-t, ²J_{CP} = 6.0 Hz, C^{C1}), 152.5 (s, C^{B2}), 139.0 (s, C^{B4}), 134.6 (m, C^{E2}), 133.7 (s, C^{C3}), 133.0 (pseudo-t, ²J_{CP} = 7.8 Hz, C^{D2}), 132.5 (s, C^{C5}), 131.9 (pseudo-t, ¹J_{CP} = 16.3 Hz, C^{C2}), 129.9 (s, C^{D4}), 129.1 (qq, ²J_{CF} = 31.6 Hz, ⁴J_{CF} = 5.8 Hz, C^{E3}), 128.7 (pseudo-t, ³J_{CP} = 4.6 Hz, C^{D3}), 126.2 (s, C^{B5}), 125.4 (m, C^{D1}), 125.3 (pseudo-t, ³J_{CP} = 2.2 Hz, C^{C4}), 124.5 (q, ¹J_{CF} = 272.3 Hz, C^{E3-CF3}), 120.2 (pseudo-t, ³J_{CP} = 1.9 Hz, C^{C6}), 120.0 (s, C^{B3}), 117.6 (m, C^{E4}), 26.6 (s, C^{B6-Me}).

¹¹B{¹H} NMR (160 MHz, 298 K, acetone-d₆) δ/ppm -6.5 (s).

¹⁹F{¹H} NMR (202 MHz, 298 K, acetone-d₆) δ/ppm -63.3 (s).

³¹P{¹H} NMR (202 MHz, 298 K, acetone-d₆) δ/ppm -13.5 (broad, FWHM ≈ 280 Hz).

ESI(+)-MS (DCM/MeOH, m/z): 601.00 [M-BARF₄-(Me₂bpy)]⁺ (calc. 601.09), 785.11 [M-BARF₄]⁺ (base peak, calc. 785.19).

ESI(-)-MS (DCM/MeOH, m/z): 861.00 [BARF₄]⁻ (calc. 862.06).

Found: C 58.23, H 4.13, N 1.82; C₈₀H₅₁BCuF₂₄N₂OP₂ requires C 58.29, H 3.12, N 1.70.

[Cu(xantphos)(Mebpy)][BARF₄]

The reagents were [Cu(xantphos)(Mebpy)][PF₆] (271 mg, 0.283 mmol) and NaBARF₄ (332 mg, 0.375 mmol). [Cu(xantphos)(Mebpy)][BARF₄] was isolated as a yellow solid (385 mg, 0.229 mmol, 81%).

¹H NMR (500 MHz, acetone-d₆) δ/ppm 8.54 (m, 1H, H^{A3}), 8.53 (m, 1H, H^{A6}), 8.45 (d, ²J_{HH} = 7.9 Hz, 1H, H^{B3}), 8.15 (m, 1H, H^{B4}), 8.10 (m, 1H, H^{A4}), 7.85 (dd, ²J_{HH} = 7.8 Hz, ³J_{HH} = 1.4 Hz, 2H, H^{C5}), 7.79 (m, 8H, H^{E2}), 7.67 (s, 4H, H^{E4}), 7.52 (d, ²J_{HH} = 8.0 Hz, 1H, H^{A5}), 7.49 (m, 1H, H^{B5}), 7.38 (m, 2H, H^{D4}), 7.34 (m, 2H, H^{D4}'), 7.30 (d, ²J_{HH} = 7.7 Hz, 2H, H^{C4}), 7.26 (m, 4H, H^{D3}'), 7.19 (m, 4H, H^{D3}'), 7.16 (m, 4H, H^{D2}'), 6.92 (m, 4H, H^{D2}'), 6.66 (m, 2H, H^{C3}), 2.03 (m, 3H, H^{B6-Me}), 1.89 (m, 3H, H^{xantphos-Me}), 1.69 (m, 3H, H^{xantphos-Me}).

¹³C{¹H} NMR (126 MHz, acetone-d₆) δ/ppm 161.7 (q, ¹J_{CB} = 49.7 Hz, C^{E1}), 158.6 (s, C^{B6}), 154.9 (pseudo-t, ²J_{CP} = 6.2 Hz, C^{C1}), 152.5 (s, C^{A2}), 151.5 (s, C^{B2}), 149.1 (s, C^{A6}), 139.4 (s, C^{B4}), 138.9 (s, C^{A4}), 134.6 (m, C^{E2}), 134.1 (s, C^{C6}), 133.0 (pseudo-t, ²J_{CP} = 8.0 Hz, C^{D2}), 132.6 (pseudo-t, ²J_{CP} = 7.9 Hz, C^{D2}'), 131.7 (pseudo-t, ¹J_{CP} = 16.5 Hz, C^{D1}'), 131.6 (pseudo-t, ¹J_{CP} = 17.7 Hz, C^{D1}), 130.6 (s, C^{C3}), 130.2 (s, C^{D4}'), 130.1 (s, C^{D4}), 129.0 (pseudo-t, ³J_{CP} = 4.7 Hz, C^{D3}'), 128.8 (pseudo-t, ³J_{CP} = 4.7 Hz, C^{D3}), 127.7 (m, C^{E3}), 127.6 (s, C^{C5}), 126.2 (s, C^{B5}), 126.1 (s, C^{A5}), 125.4 (pseudo-t, ³J_{CP} = 2.5 Hz, C^{C4}), 124.5 (q, ¹J_{CF} = 271.8 Hz, C^{E3-CF3}), 122.9 (s, C^{A3}), 120.7 (pseudo-t, ¹J_{CP} = 12.9 Hz, C^{C2}), 120.2 (s, C^{B3}), 117.6 (m, C^{E4}), 36.0 (s, C^{xantphos-bridge}), 29.4 (s, C^{xantphos-Me}), 25.5 (s, C^{xantphos-Me}), 25.3 (s, C^{B6-Me}).

¹¹B{¹H} NMR (160 MHz, 298 K, acetone-d₆) δ/ppm -6.6 (s).

¹⁹F{¹H} NMR (202 MHz, 298 K, acetone-d₆) δ/ppm -63.3 (s).

³¹P{¹H} NMR (202 MHz, 298 K, acetone-d₆) δ/ppm -13.0 (broad, FWHM ≈ 270 Hz).

ESI(+)-MS (DCM/MeOH, m/z): 641.06 [M-BARF₄-(Mebpy)]⁺ (calc. 641.12), 811.11 [M-BARF₄]⁺ (base peak, calc. 811.21).

ESI(-)-MS (DCM/MeOH, m/z): 862.0 [BARF₄]⁻ (calc. 862.06).

Found: C 58.66, H 3.21, N 1.73; C₈₂H₅₃BCuF₂₄N₂OP₂ requires C 58.81, H 3.19, N 1.67.

[Cu(xantphos)(Me₂bpy)][BAR₄^F]

The reagents were [Cu(xantphos)(Mebpy)][PF₆] (272 mg, 0.280 mmol) and NaBAR₄^F (333 mg, 0.376 mmol). [Cu(xantphos)(Me₂bpy)][BAR₄^F] was isolated as a yellow solid (360 mg, 0.213 mmol, 76%).

¹H NMR (500 MHz, acetone-d₆) δ/ppm 8.19 (d, ²J_{HH} = 8.0 Hz, 2H, H^{B3}), 7.95 (m, 2H, H^{B4}), 7.83 (dd, ²J_{HH} = 7.8, ³J_{HH} = 1.4 Hz, 2H, H^{C5}), 7.79 (m, 8H, H^{E2}), 7.67 (s, 4H, H^{E4}), 7.40 (m, 4H, H^{D4}), 7.39 (m, 2H, H^{B5}), 7.31 (m, 2H, H^{C4}), 7.23 (m, 8H, H^{D3}), 7.17 (m, 8H, H^{D2}), 6.95 (m, 2H, H^{C3}), 2.14 (s, 6H, H^{6-Me}), 1.76 (s, 6H, H^{xantphos-Me}).

¹³C{¹H} NMR (126 MHz, acetone-d₆) δ/ppm 161.9 (m, C^{E1}), 158.3 (s, C^{B6}), 154.9 (m, C^{C1}), 152.2 (s, C^{B2}), 139.0 (s, C^{B4}), 133.9 (s, C^{C6}), 134.6 (m, C^{E2}), 133.1 (pseudo-t, ²J_{CP} = 7.6 Hz, C^{D2}), 131.50 (pseudo-t, ²J_{CP} = 16.4 Hz, C^{D1}), 130.2 (s, C^{C3}), 130.1 (s, C^{D4}), 128.2 (pseudo-t, ³J_{CP} = 4.5 Hz, C^{D3}), 127.8 (s, C^{C5}), 127.7 (m, C^{E3}), 125.8 (s, C^{B5}), 125.5 (pseudo-t, ³J_{CP} = 2.3 Hz, C^{C4}), 124.5 (q, ¹J_{CF} = 271.8 Hz, C^{E3-CF3}), 121.8 (m, C^{C2}), 120.1 (s, C^{B3}), 117.5 (m, C^{E4}), 27.72 (s, C^{xantphos-bridge}), 26.8 (s, C^{xantphos-Me}), 26.13 (s, C^{B6-Me}).

¹¹B{¹H} NMR (160 MHz, 298 K, acetone-d₆) δ/ppm −6.6 (s).

¹⁹F{¹H} NMR (202 MHz, 298 K, acetone-d₆) δ/ppm −63.3 (s).

³¹P{¹H} NMR (202 MHz, 298 K, acetone-d₆) δ/ppm −13.7 (broad, FWHM ≈ 280 Hz).

ESI(+)-MS (DCM/MeOH, m/z): 641.07 [M−BAR₄^F−(Me₂bpy)]⁺ (calc. 641.12), 825.16 [M−BAR₄^F]⁺ (base peak, calc. 826.42).

ESI(−)-MS (DCM/MeOH, m/z): 862.00 [BAR₄^F][−] (calc. 862.06).

Found: C 59.12, H 3.56, N 1.75; C₈₃H₅₅BCuF₂₄N₂OP₂ requires C 59.04, H 3.28, N 1.66.

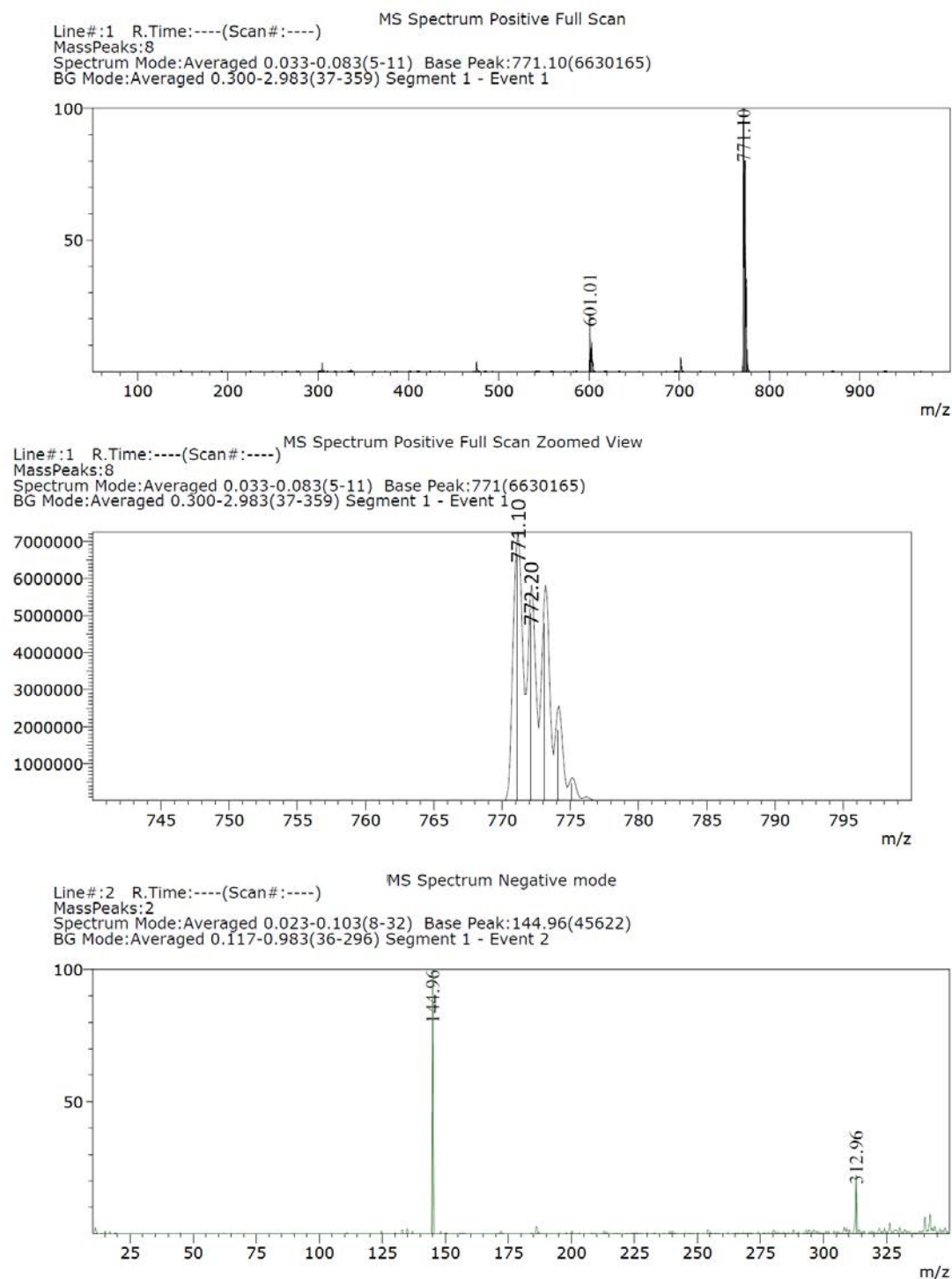


Fig. S1 The ESI mass spectrum (positive and negative mode) of $[\text{Cu}(\text{POP})(\text{Mebpy})][\text{PF}_6]$.

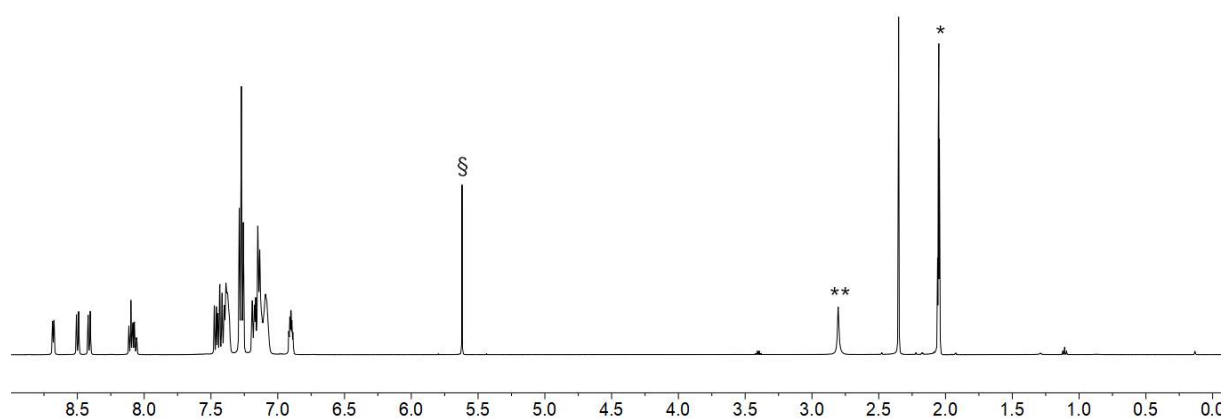


Fig. S2 ^1H NMR spectrum of $[\text{Cu}(\text{POP})(\text{Mebpy})][\text{PF}_6]$ (500 MHz, 298 K, acetone- d_6). * = residual acetone- d_5 ; ** = H_2O and HDO ; § = CH_2Cl_2 .

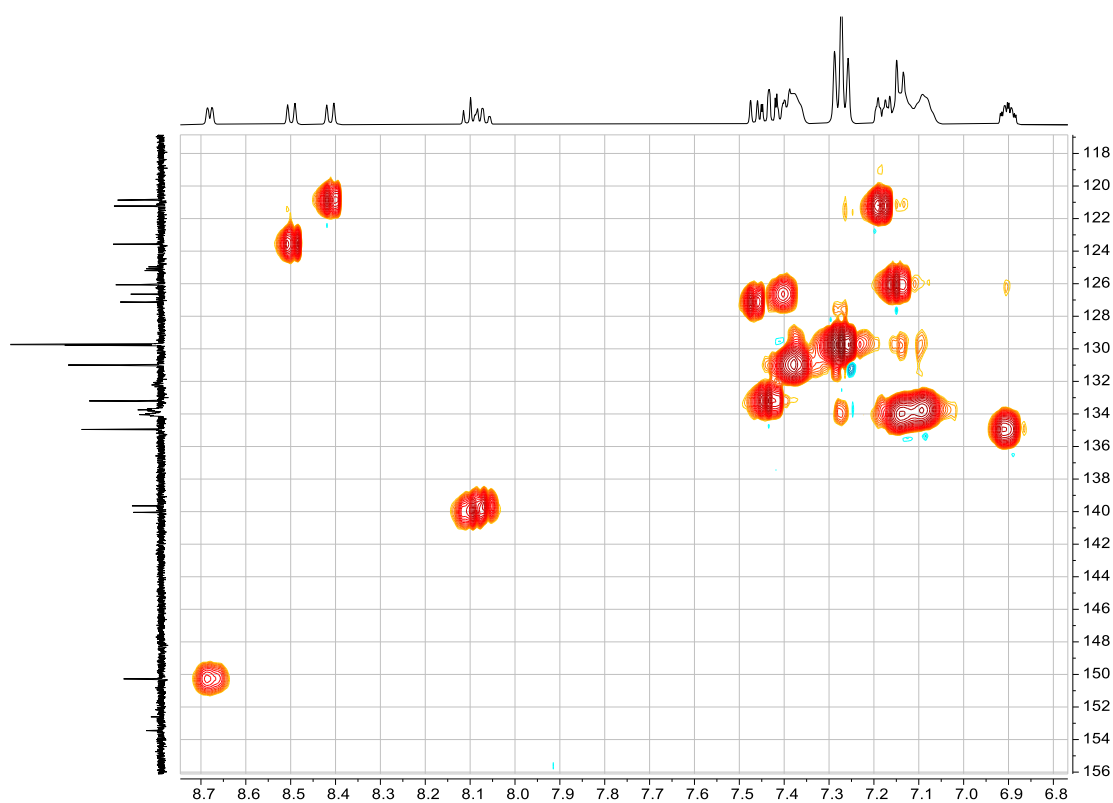


Fig. S3 The aromatic region of the HMQC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K) of $[\text{Cu}(\text{POP})(\text{Mebpy})][\text{PF}_6]$. Scale: δ / ppm.

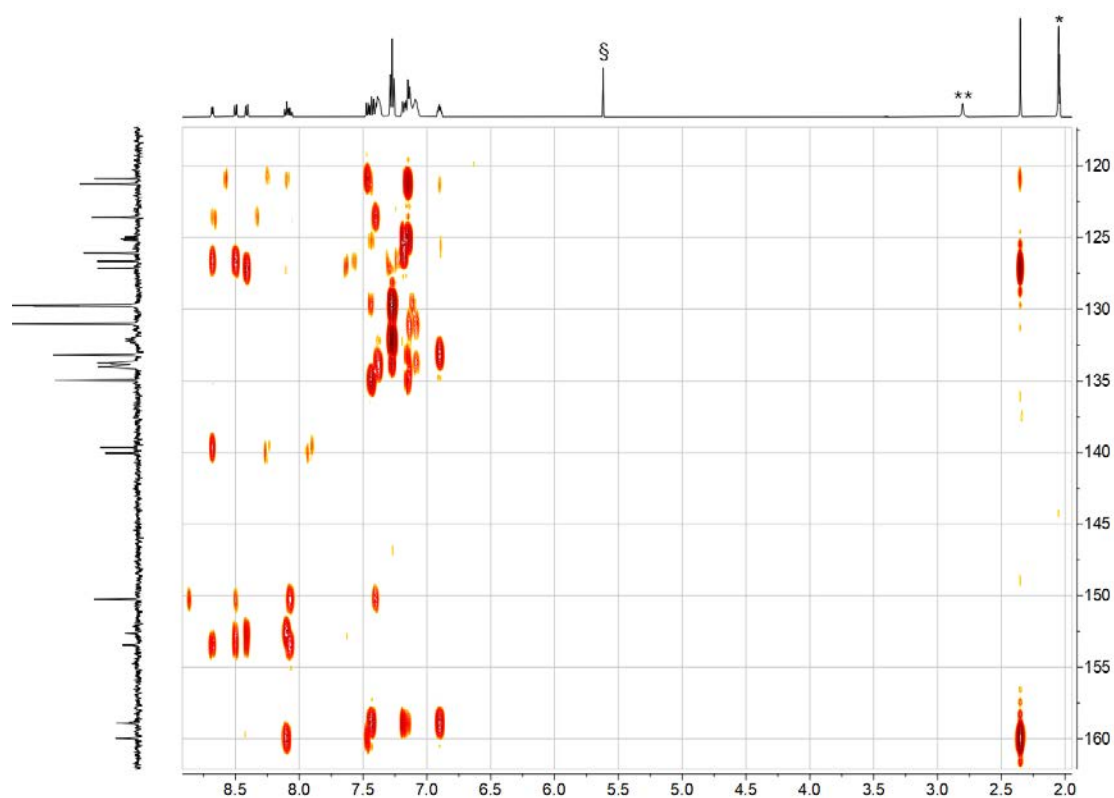


Fig. S4 Part of the HMBC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K) of $[\text{Cu}(\text{POP})(\text{Mebpy})][\text{PF}_6]$. Scale: δ / ppm. ** = H_2O and HDO ; § = CH_2Cl_2 .

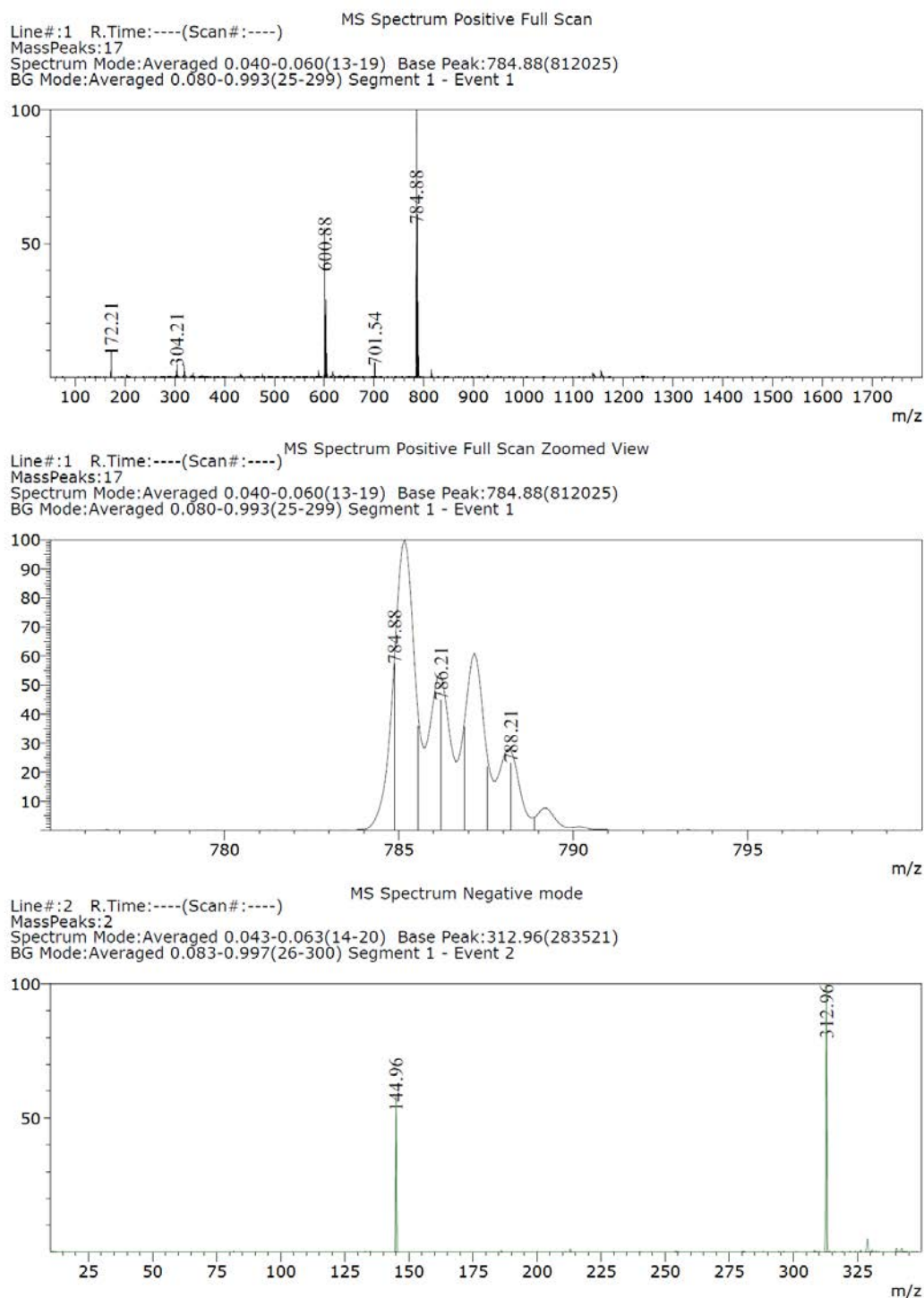


Fig. S5 The ESI mass spectrum (positive and negative mode) of $[\text{Cu}(\text{POP})(\text{Me}_2\text{bpy})][\text{PF}_6]$.

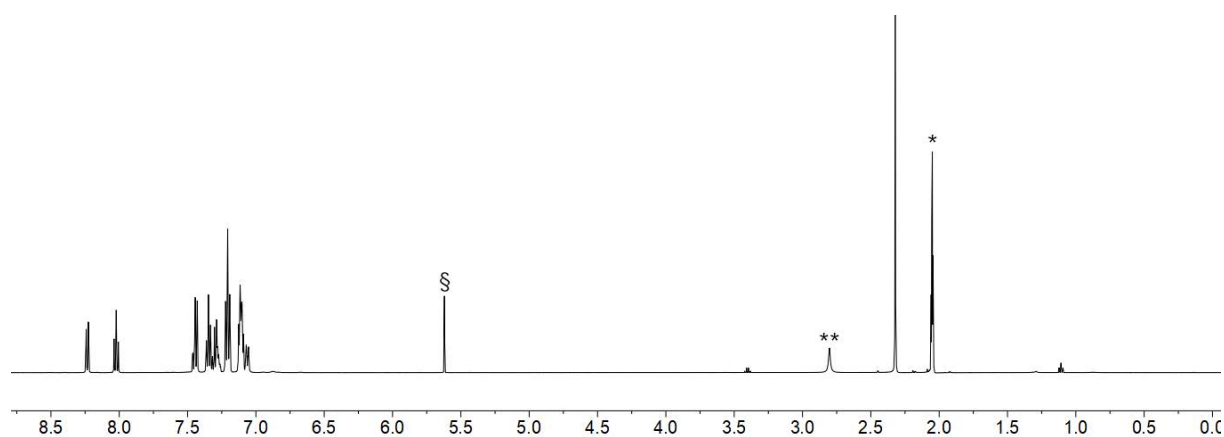


Fig. S6 ^1H NMR spectrum of $[\text{Cu}(\text{POP})(\text{Me}_2\text{bpy})][\text{PF}_6]$ (500 MHz, 298 K, acetone- d_6). * = residual acetone- d_5 ; ** = H_2O and HDO ; § = CH_2Cl_2 .

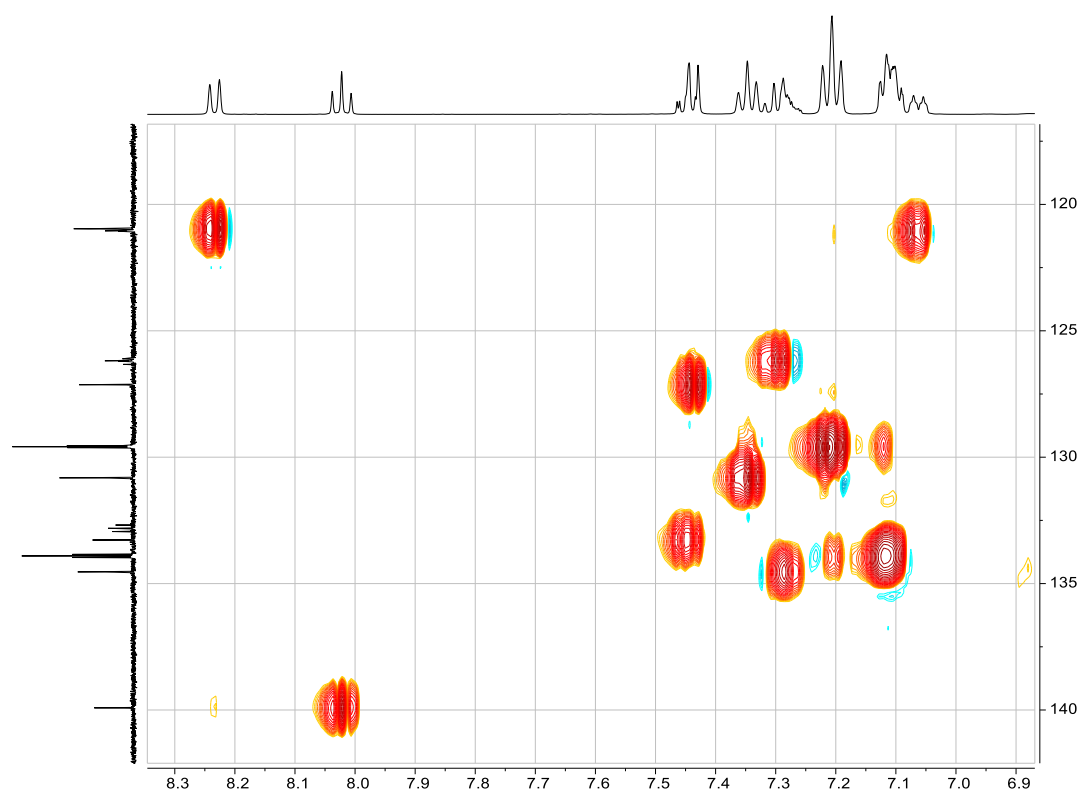


Fig. S7 The aromatic region of the HMQC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K) of $[\text{Cu}(\text{POP})(\text{Me}_2\text{bpy})][\text{PF}_6]$. Scale: δ / ppm.

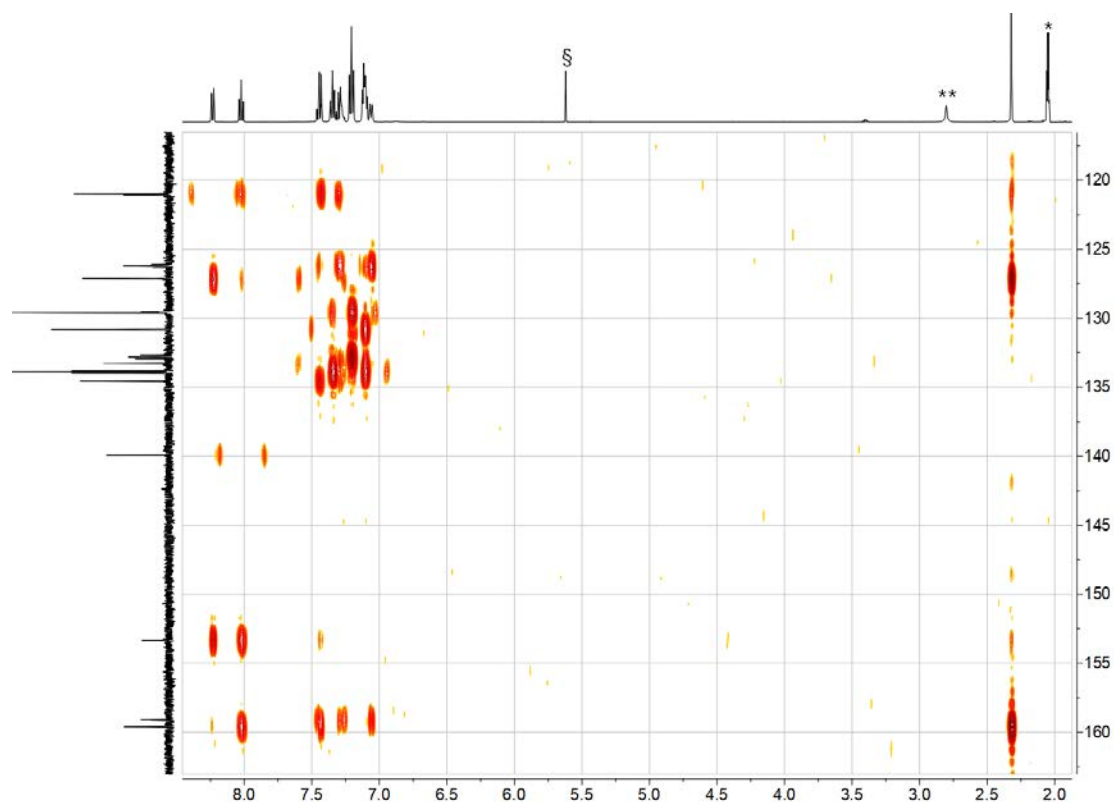


Fig. S8 Part of the HMBC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K) of $[\text{Cu}(\text{POP})(\text{Me}_2\text{bpy})][\text{PF}_6]$. Scale: δ / ppm. ** = H_2O and HDO ; § = CH_2Cl_2 .

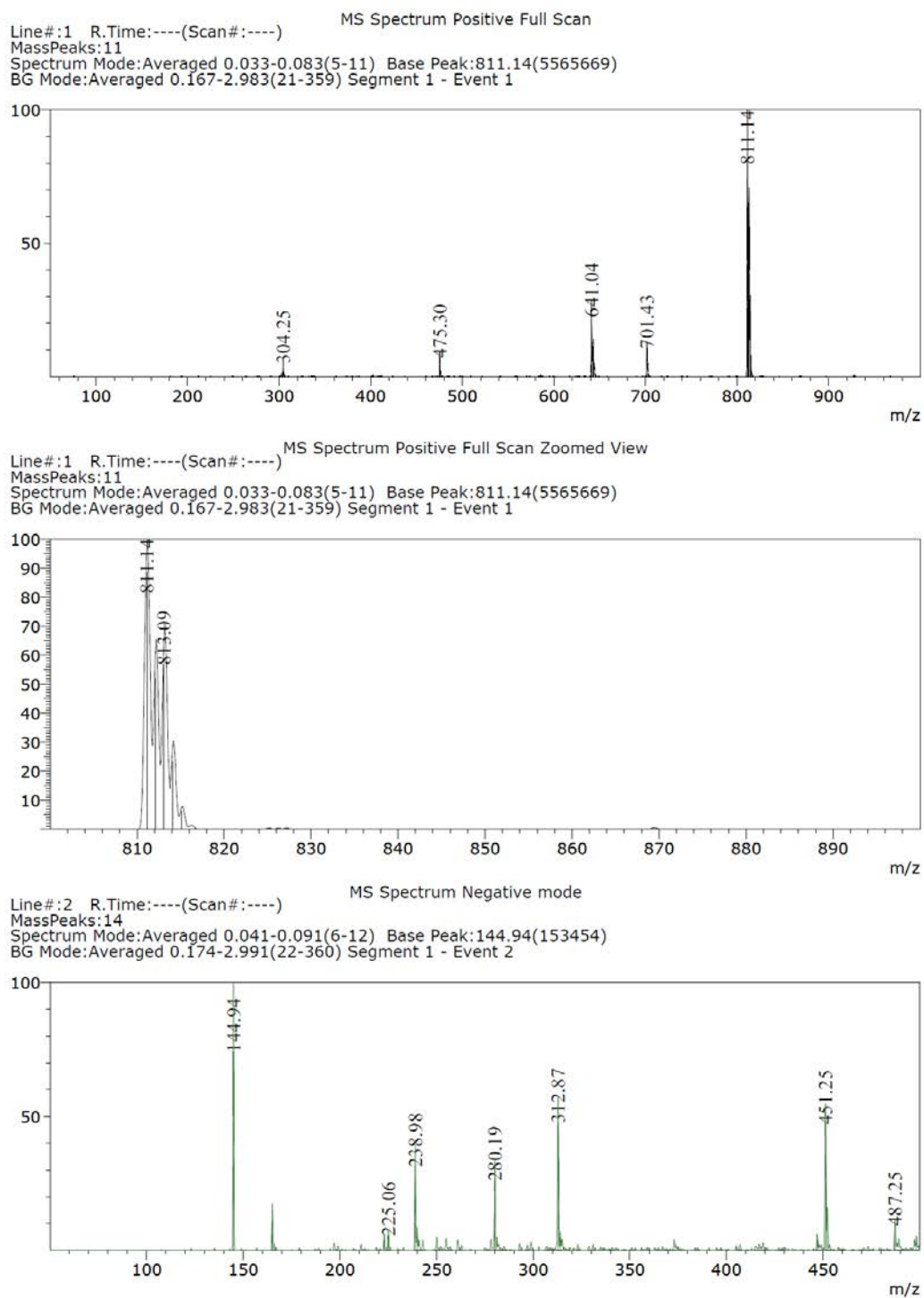


Fig. S9 The ESI mass spectrum (positive and negative mode) of $[\text{Cu}(\text{xantphos})(\text{Mebpy})][\text{PF}_6]$.

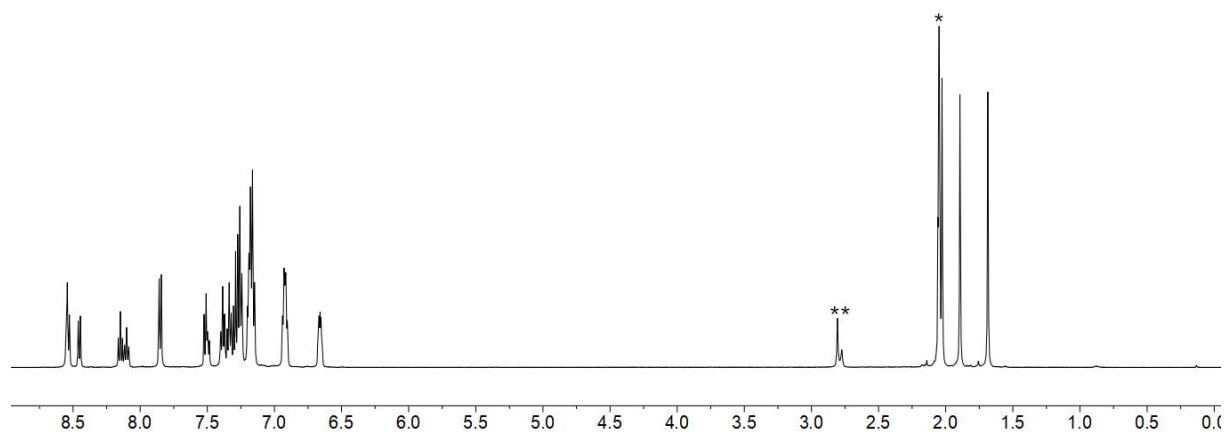


Fig. S10 ^1H NMR spectrum of $[\text{Cu}(\text{xantphos})(\text{Mebpy})][\text{PF}_6]$ (500 MHz, 298 K, acetone- d_6). * = residual acetone- d_5 ; ** = H_2O and HDO.

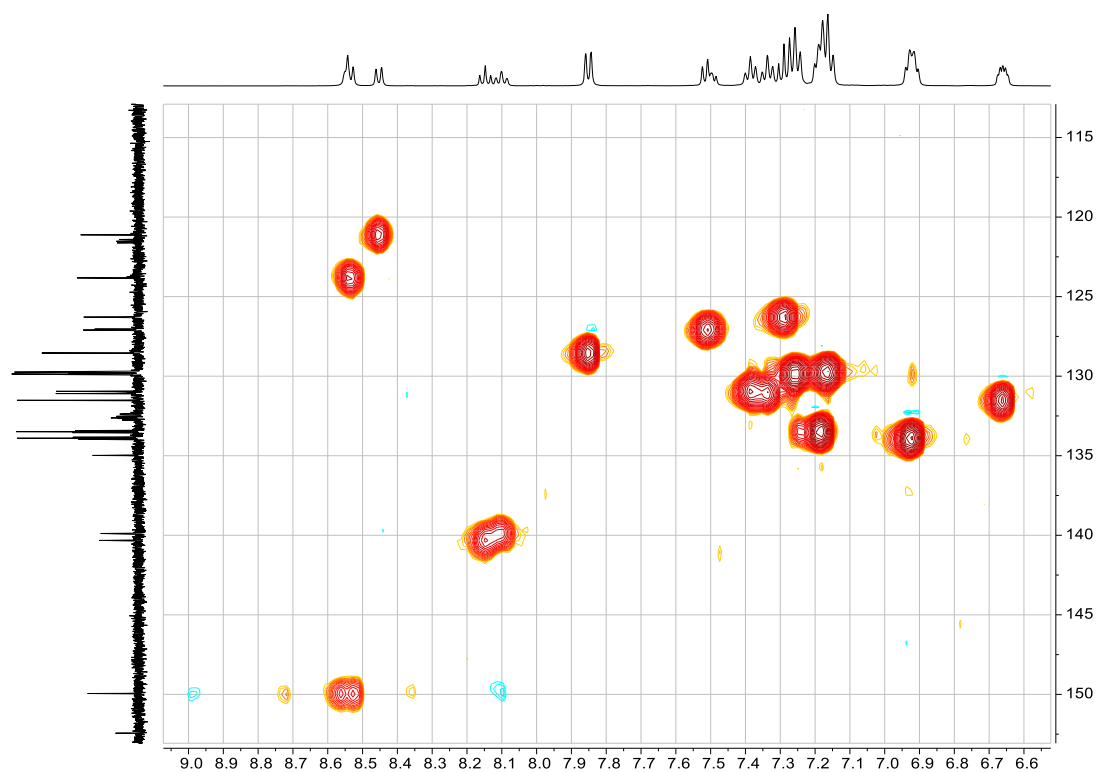


Fig. S11 The aromatic region of the HMQC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K) of $[\text{Cu}(\text{xantphos})(\text{Mebpy})][\text{PF}_6]$. Scale: δ / ppm.

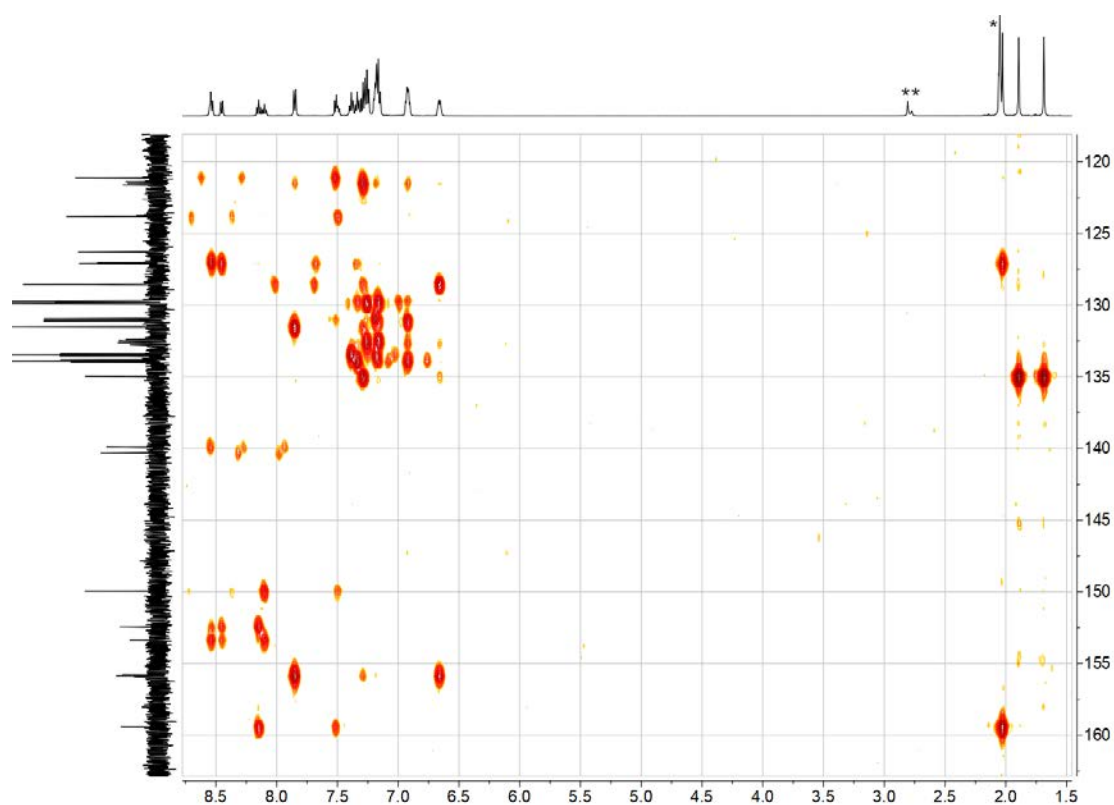


Fig. S12 Part of the HMBC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K) of $[\text{Cu}(\text{xantphos})(\text{Mebpy})][\text{PF}_6]$. Scale: δ / ppm. * = H_2O and HDO.

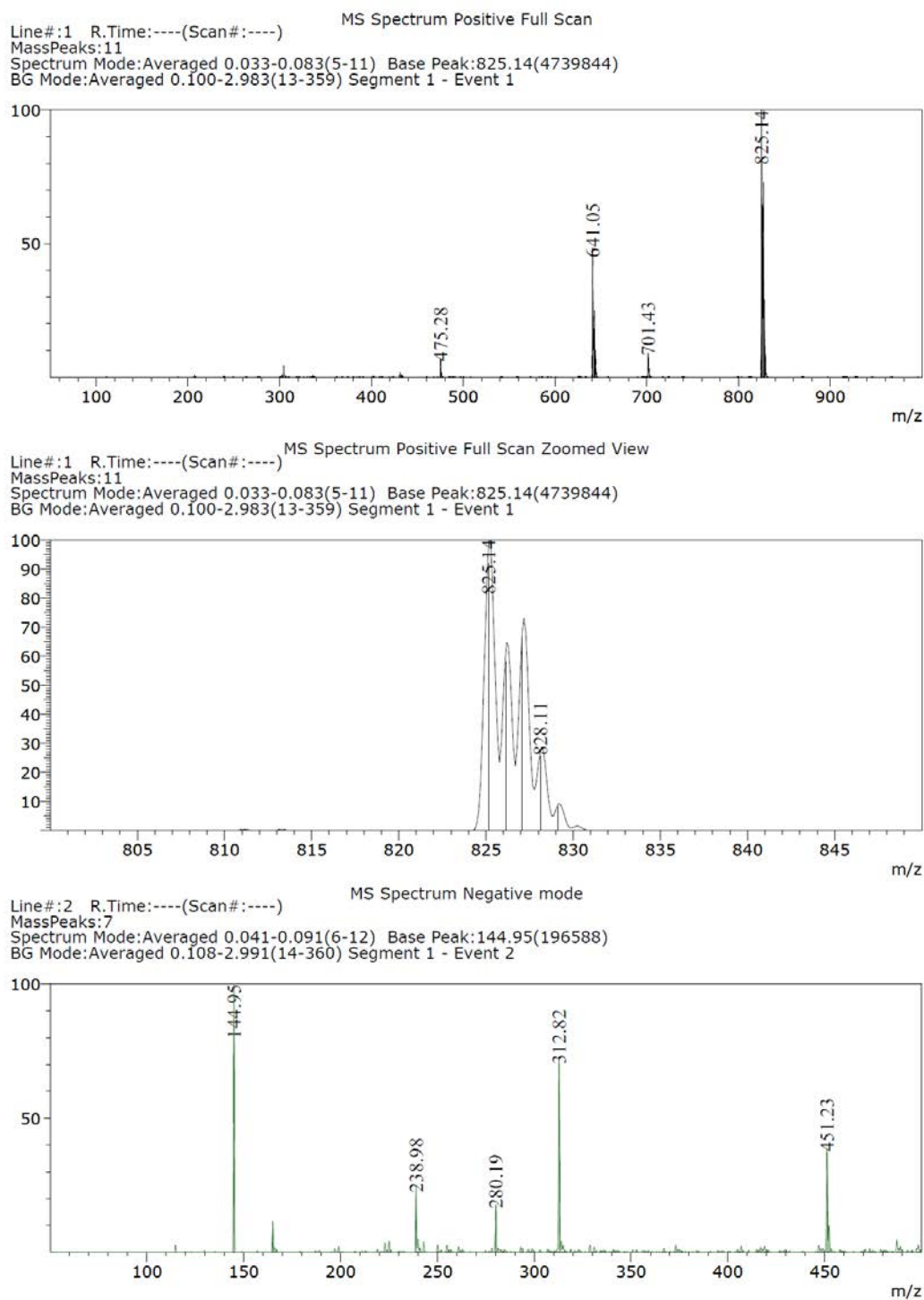


Fig. S13 The ESI mass spectrum (positive and negative mode) of $[\text{Cu}(\text{xantphos})(\text{Me}_2\text{bpy})][\text{PF}_6]$.

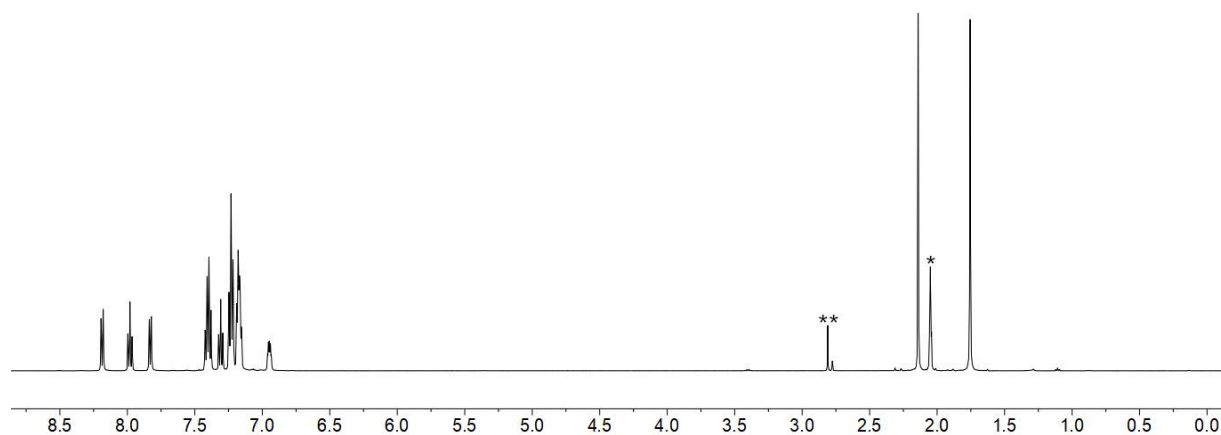


Fig. S14 ^1H NMR spectrum of $[\text{Cu}(\text{xantphos})(\text{Me}_2\text{bpy})][\text{PF}_6]$ (500 MHz, 298 K, acetone- d_6). * = residual acetone- d_5 ; ** = H_2O and HDO.

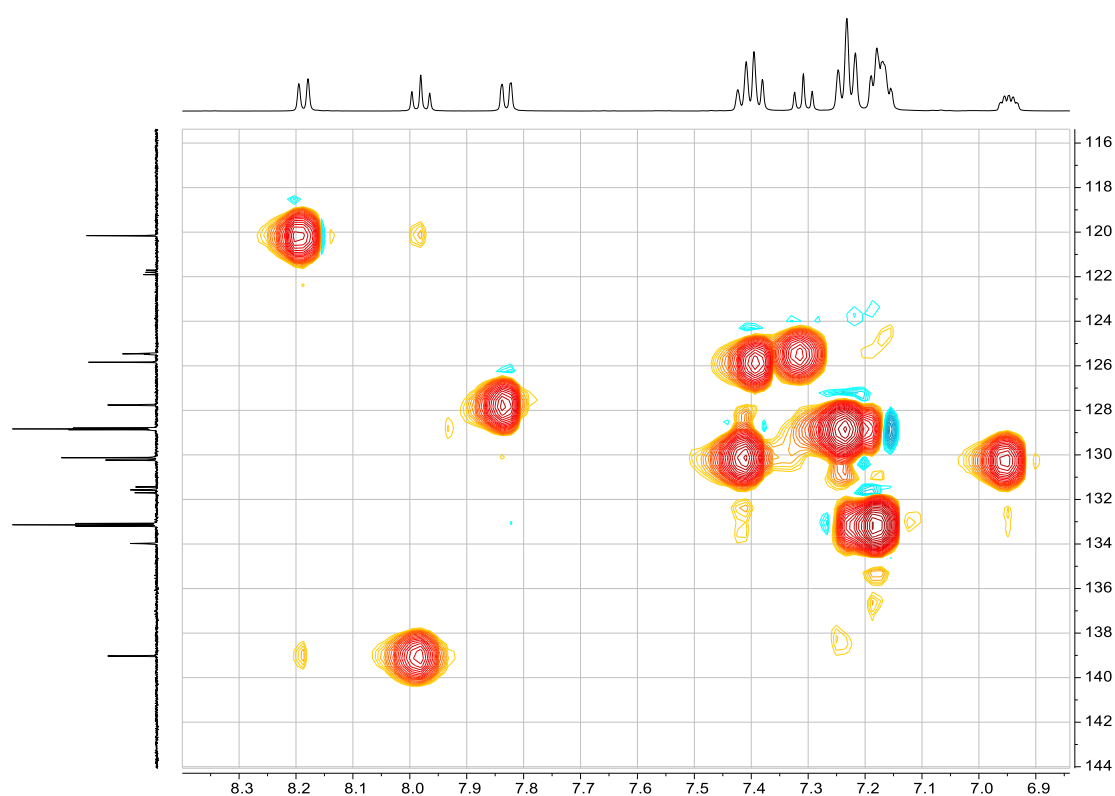


Fig. S15 The aromatic region of the HMQC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K) of $[\text{Cu}(\text{xantphos})(\text{Me}_2\text{bpy})][\text{PF}_6]$. Scale: δ / ppm.

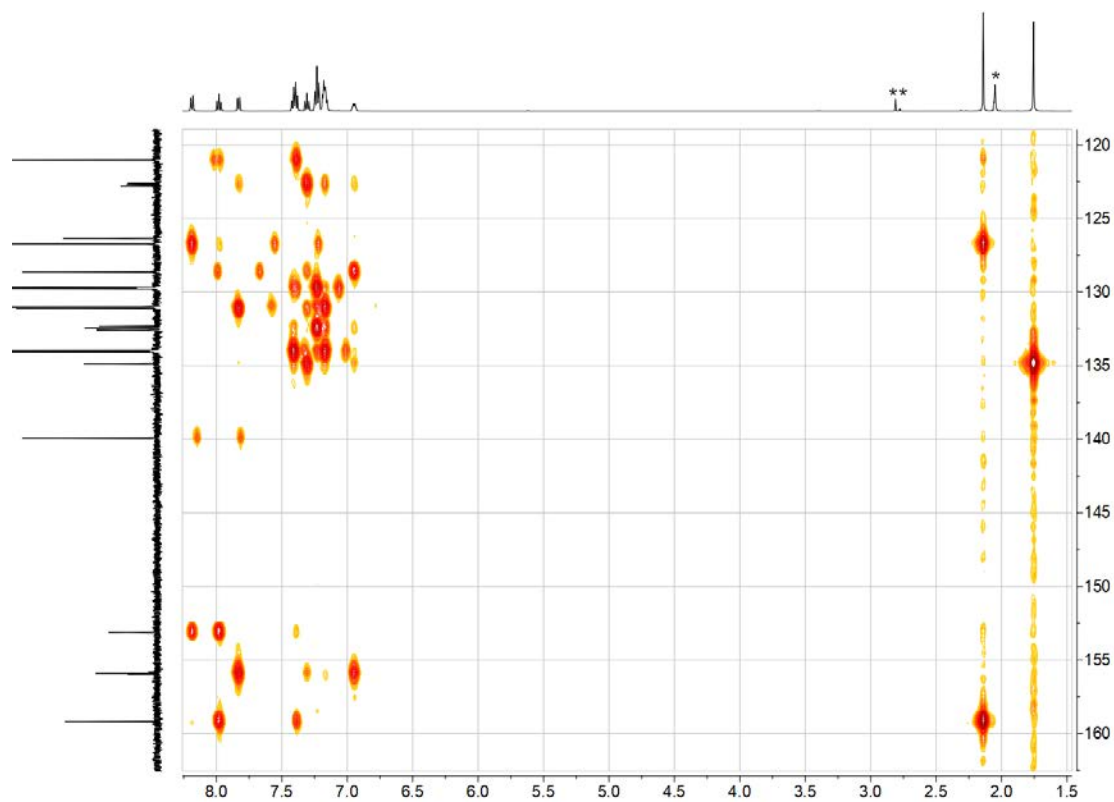


Fig. S16 Part of the HMBC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K) of $[\text{Cu}(\text{xantphos})(\text{Me}_2\text{bpy})][\text{PF}_6]$. Scale: δ / ppm. ** = H_2O and HDO .

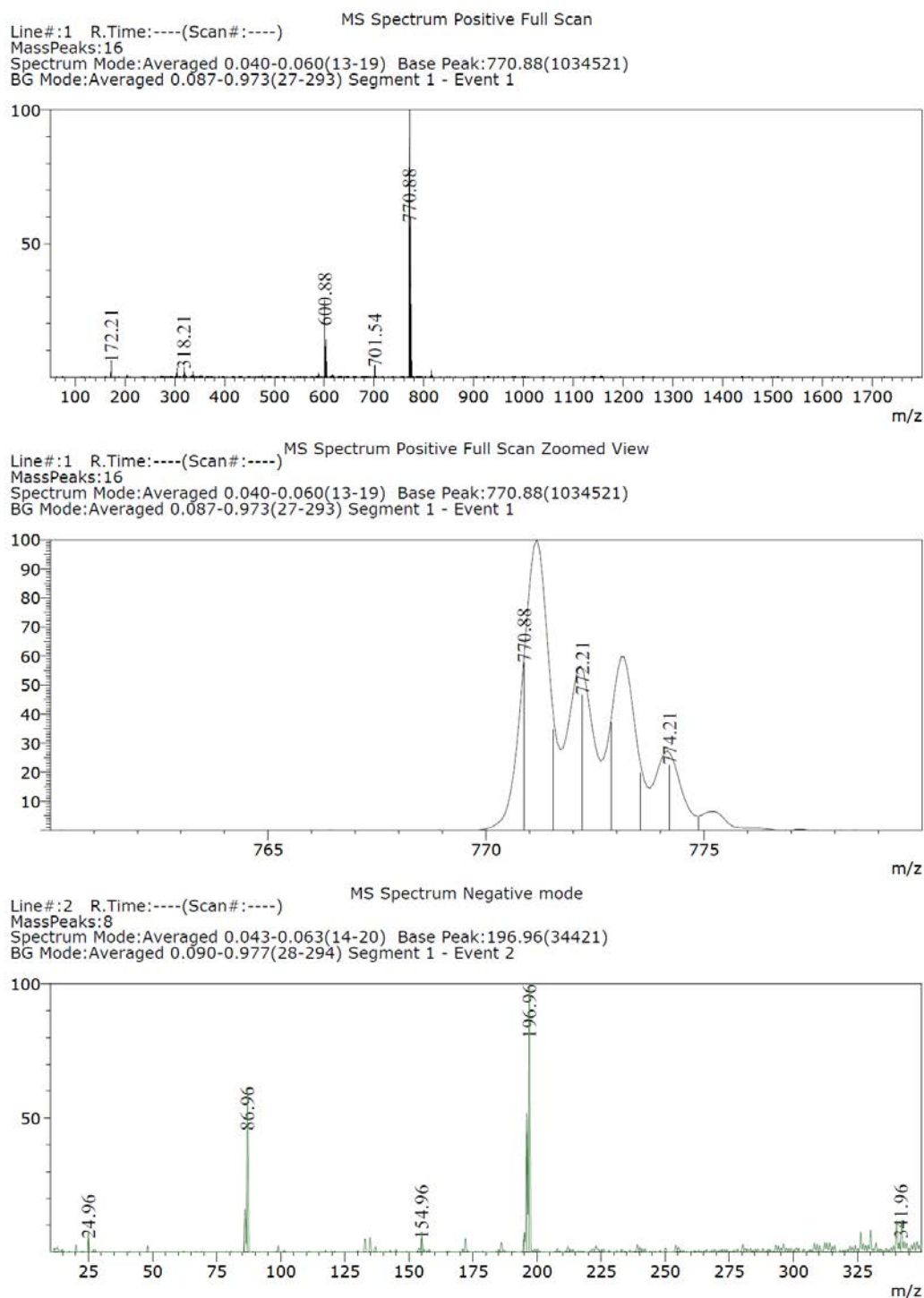


Fig. S17 The ESI mass spectrum (positive and negative mode) of $[\text{Cu}(\text{POP})(\text{Mebpy})][\text{BF}_4]$.

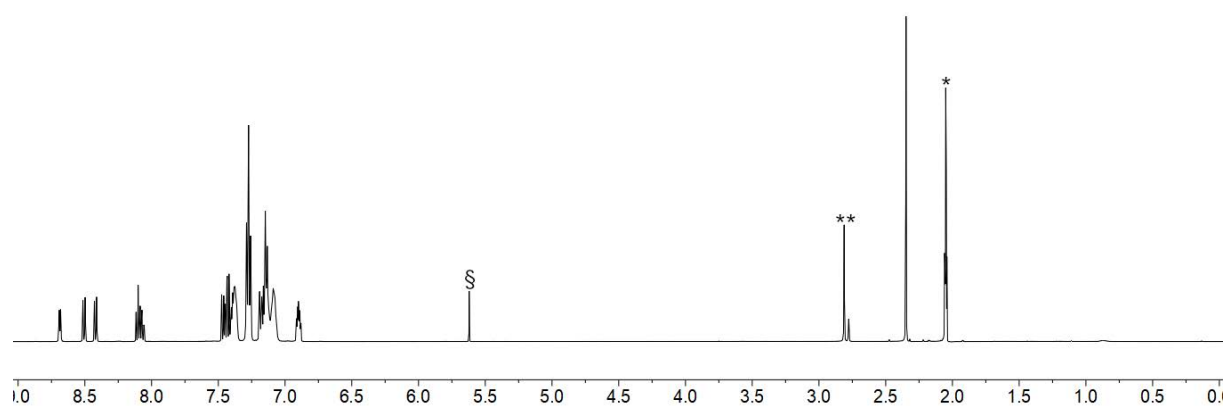


Fig. S18 ^1H NMR spectrum of $[\text{Cu}(\text{POP})(\text{Mebpy})][\text{BF}_4]$ (500 MHz, 298 K, acetone- d_6). * = residual acetone- d_5 ; ** = H_2O and HDO ; § = CH_2Cl_2 .

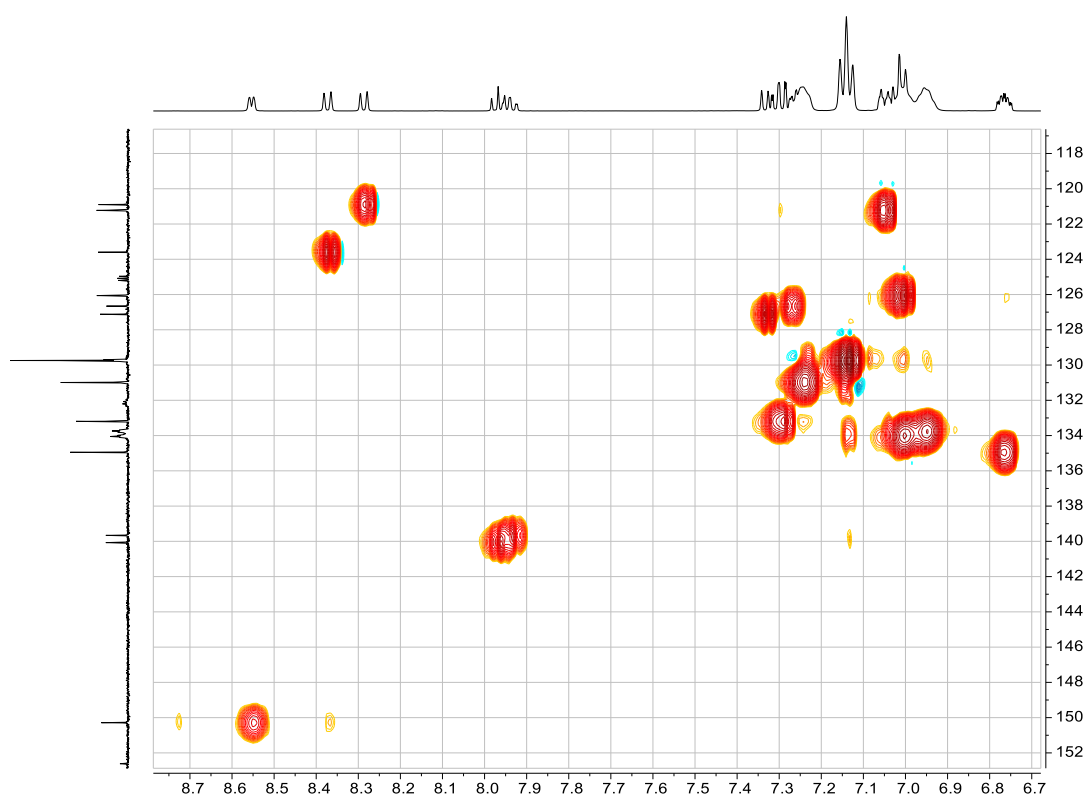


Fig. S19 The aromatic region of the HMQC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K) of $[\text{Cu}(\text{POP})(\text{Mebpy})][\text{BF}_4]$. Scale: δ / ppm.

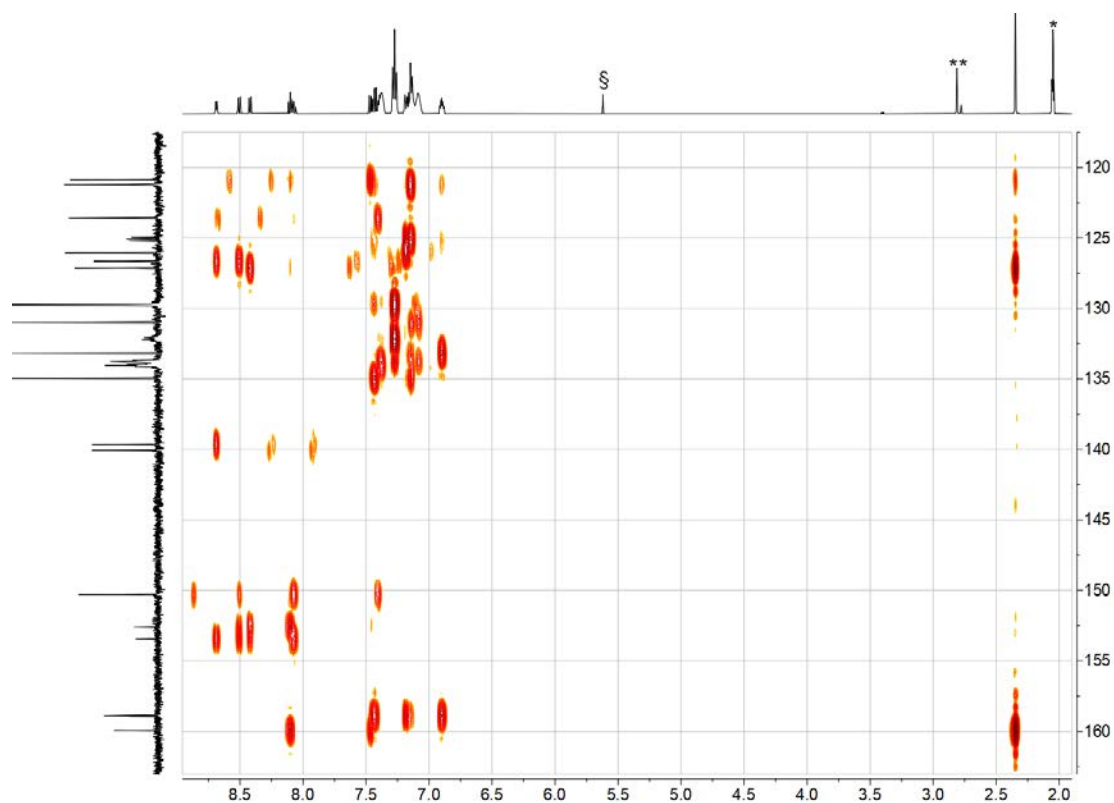


Fig. S20 Part of the HMBC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K) of $[\text{Cu}(\text{POP})(\text{Mebpy})][\text{BF}_4]$. Scale: δ / ppm. $\text{**} = \text{H}_2\text{O}$ and HDO ; $\text{§} = \text{CH}_2\text{Cl}_2$.

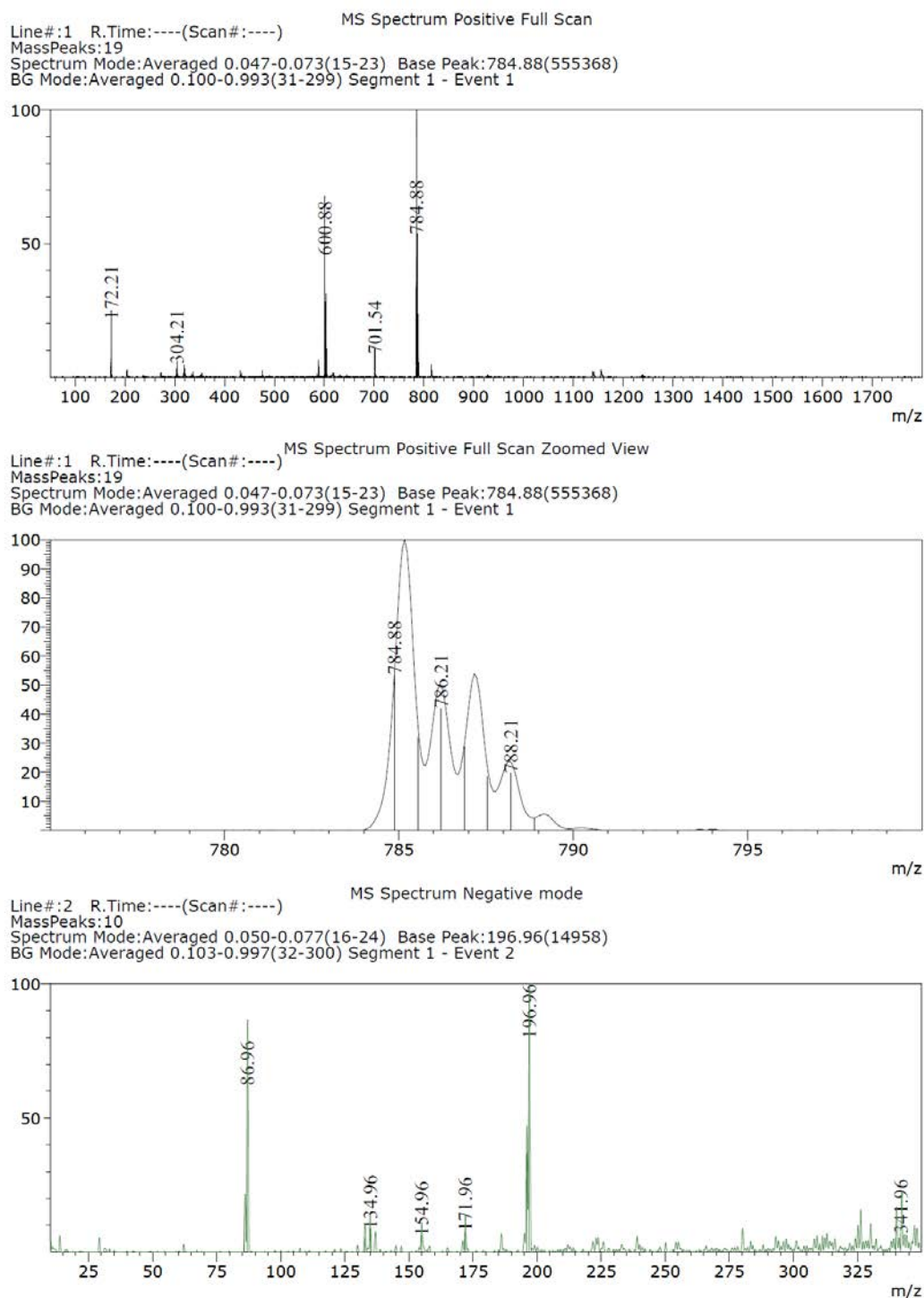


Fig. S21 The ESI mass spectrum (positive and negative mode) of $[\text{Cu}(\text{POP})(\text{Me}_2\text{bpy})][\text{BF}_4]$.

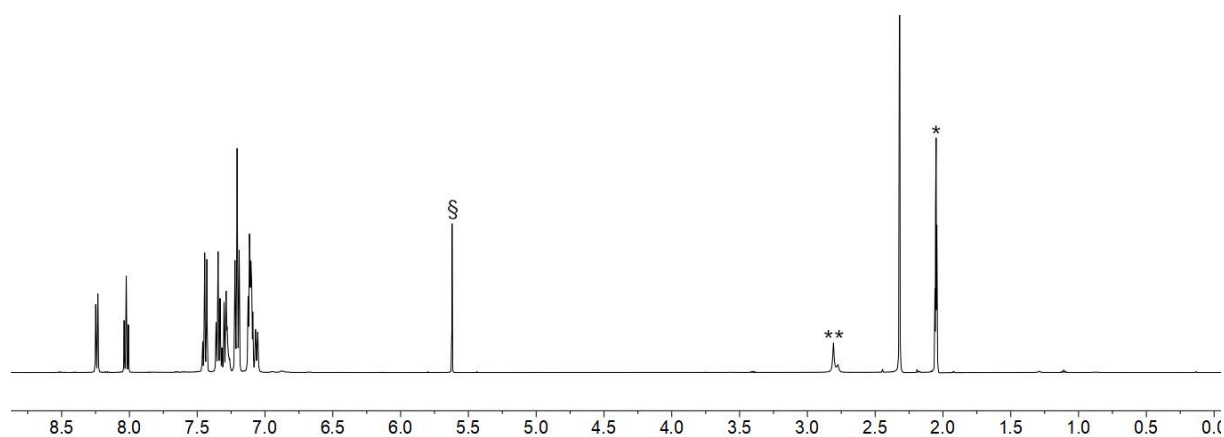


Fig. S22 ^1H NMR spectrum of $[\text{Cu}(\text{POP})(\text{Me}_2\text{bpy})][\text{BF}_4]$ (500 MHz, 298 K, acetone- d_6). * = residual acetone- d_5 ; ** = H_2O and HDO ; § = CH_2Cl_2 .

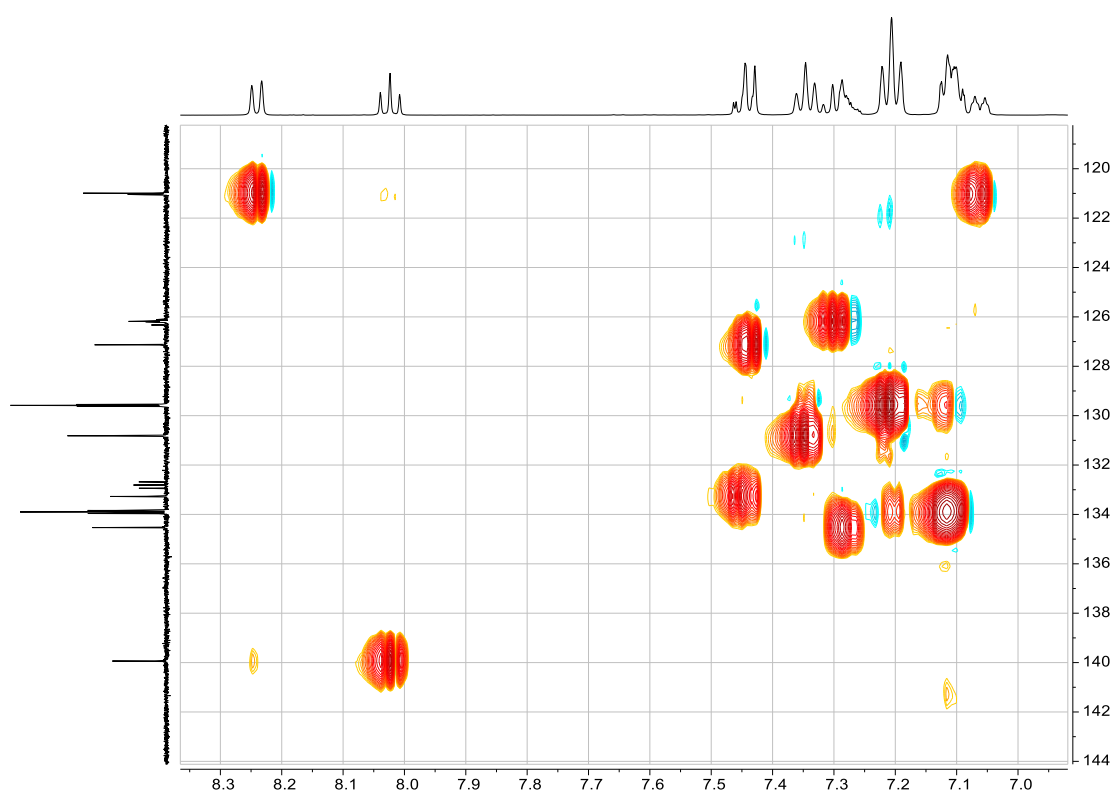


Fig. S23 The aromatic region of the HMQC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K) of $[\text{Cu}(\text{POP})(\text{Me}_2\text{bpy})][\text{BF}_4]$. Scale: δ / ppm.

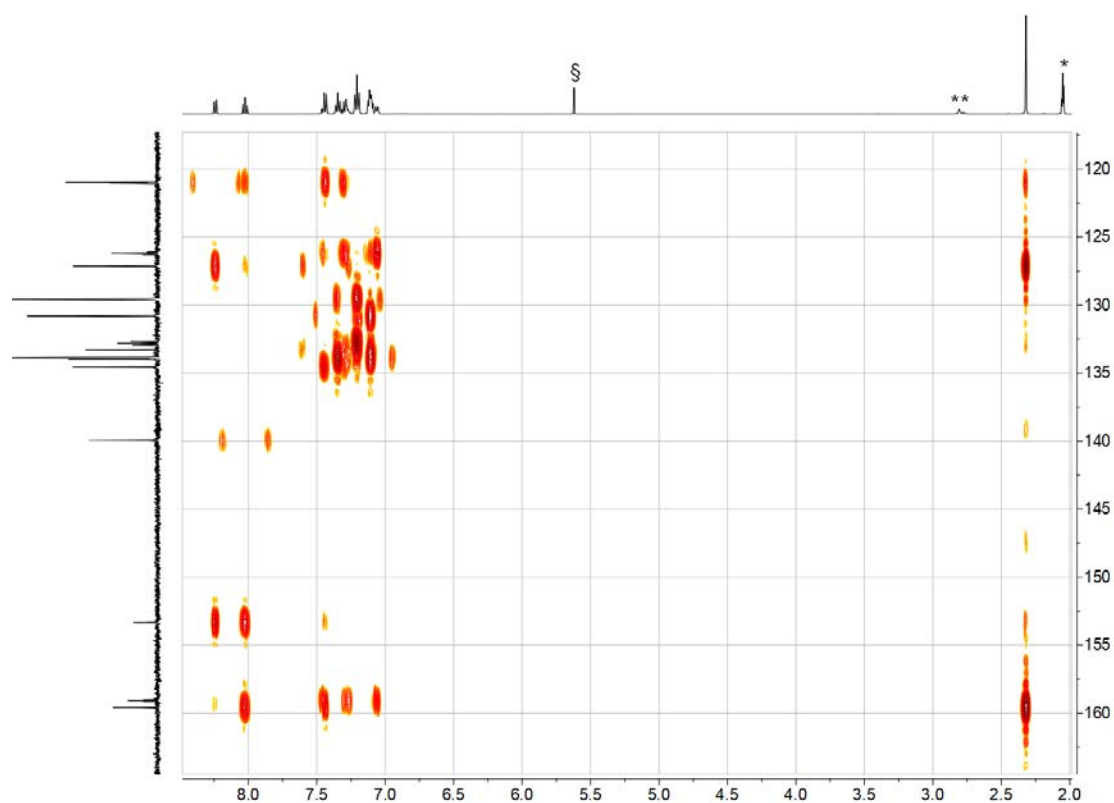


Fig. S24 Part of the HMBC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K) of $[\text{Cu}(\text{POP})(\text{Me}_2\text{bpy})][\text{BF}_4]$. Scale: δ / ppm. ** = H_2O and HDO ; § = CH_2Cl_2 .

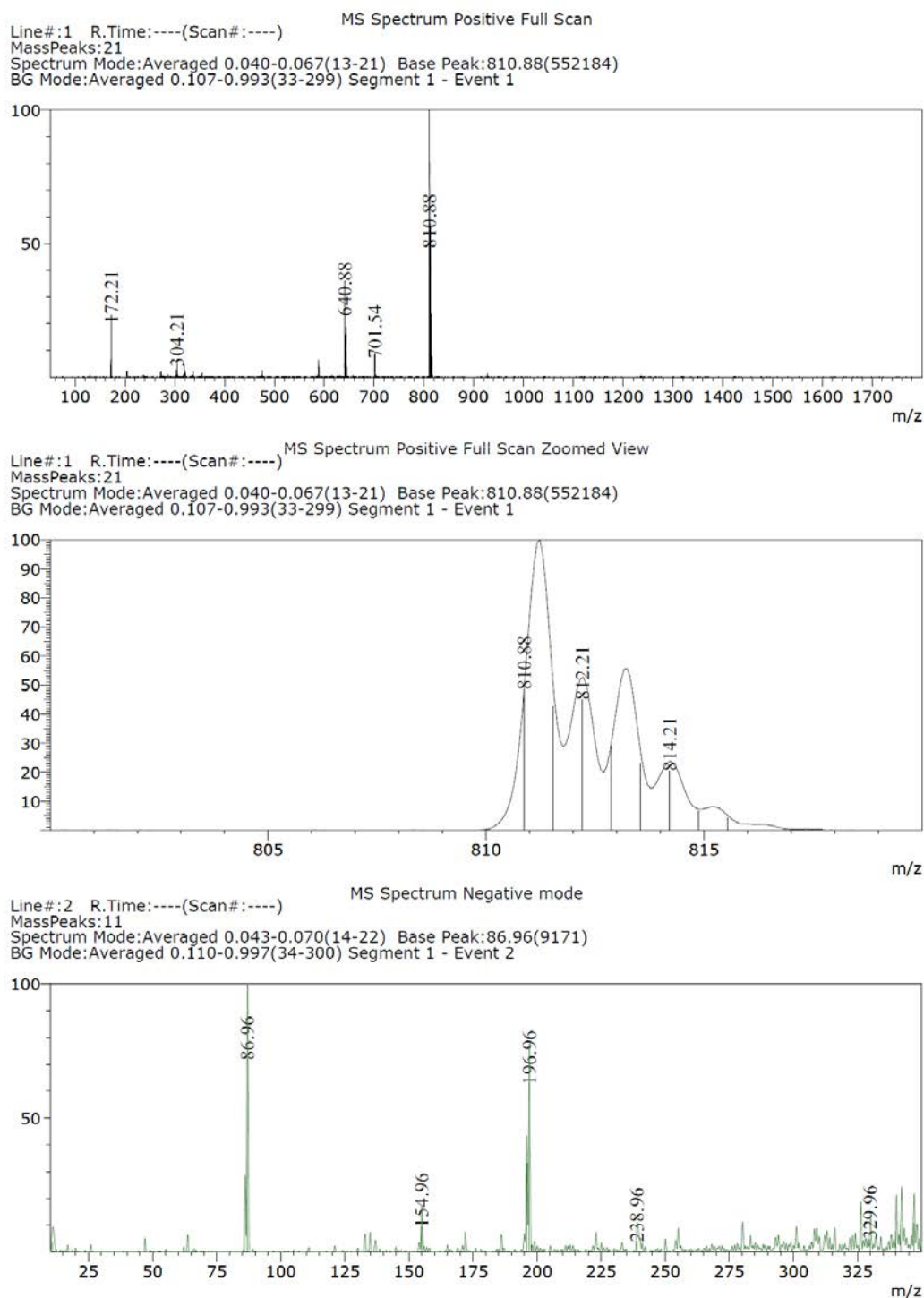


Fig. S25 The ESI mass spectrum (positive and negative mode) of $[\text{Cu}(\text{xantphos})(\text{Mebpy})][\text{BF}_4]$.

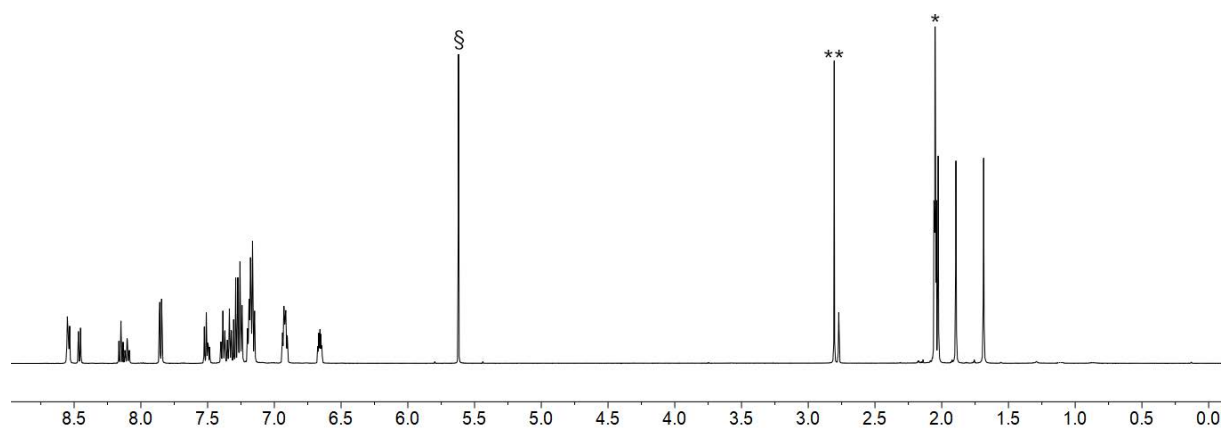


Fig. S26 ^1H NMR spectrum of $[\text{Cu}(\text{xantphos})(\text{Mebpy})][\text{BF}_4]$ (500 MHz, 298 K, acetone- d_6). * = residual acetone- d_5 ; ** = H_2O and HDO; § = CH_2Cl_2 .

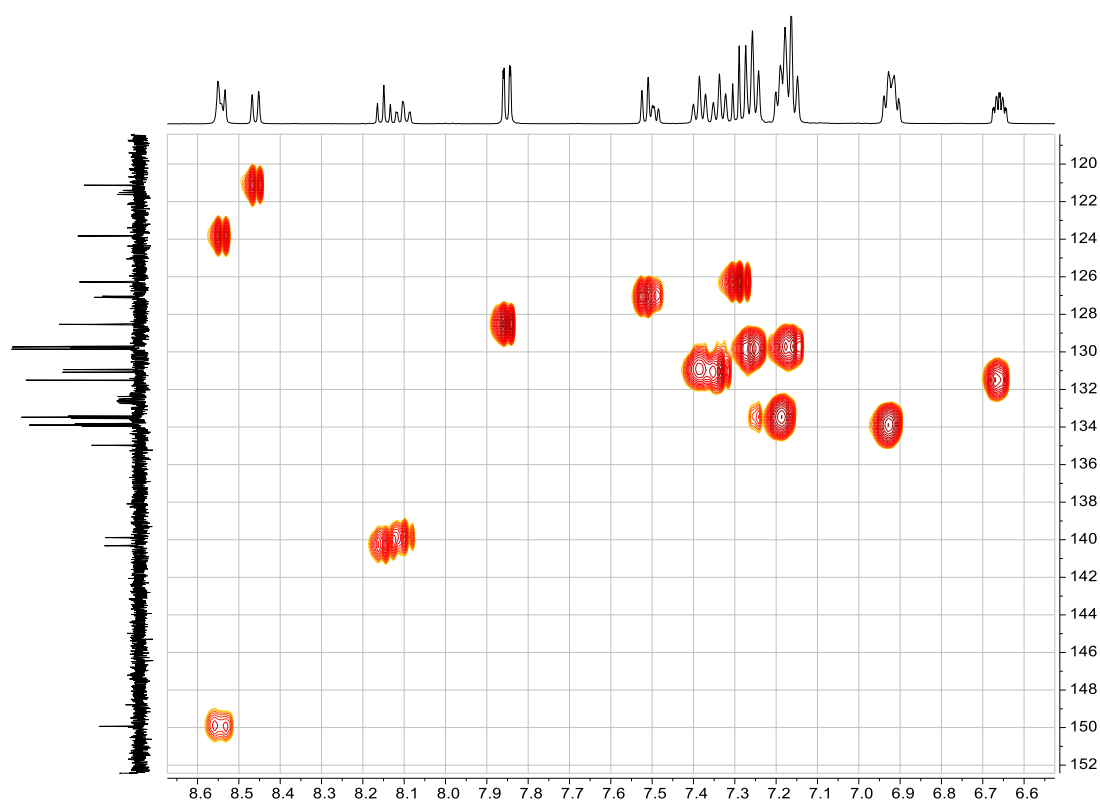


Fig. S27 The aromatic region of the HMQC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K) of $[\text{Cu}(\text{xantphos})(\text{Mebpy})][\text{BF}_4]$. Scale: δ / ppm.

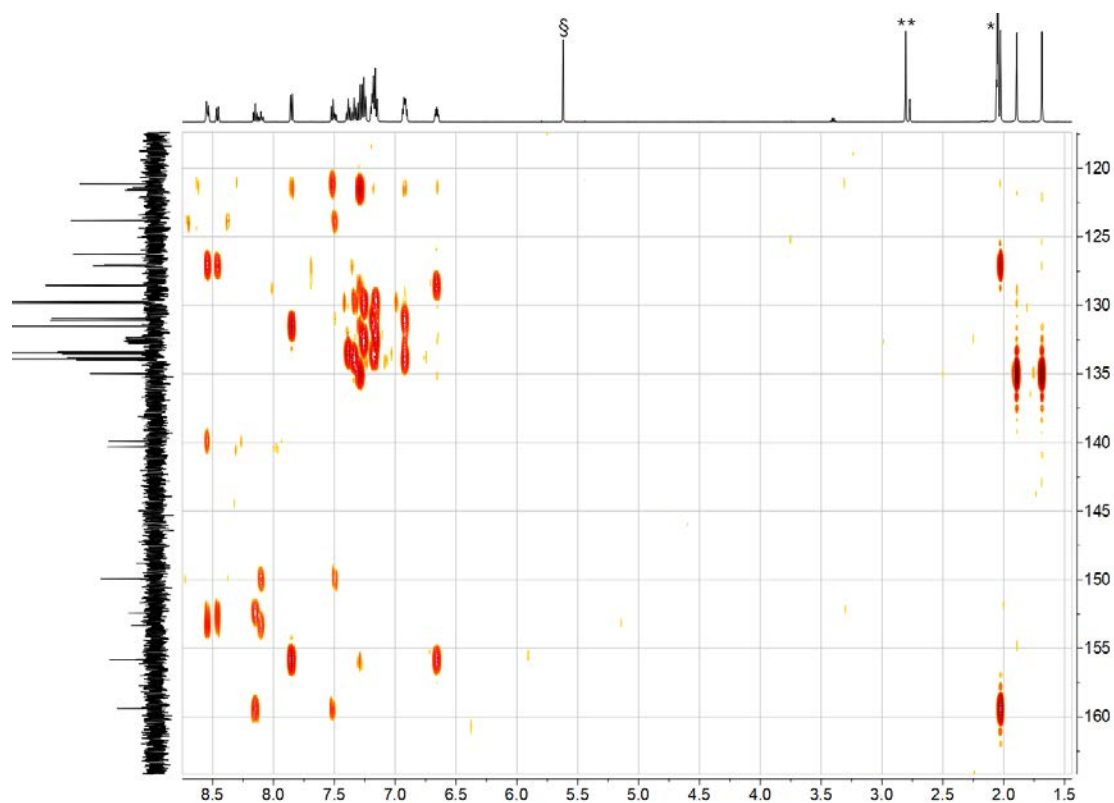


Fig. S28 Part of the HMBC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K) of $[\text{Cu}(\text{xantphos})(\text{Mebpy})][\text{BF}_4]$. Scale: δ / ppm. ** = H_2O and HDO ; § = CH_2Cl_2 .

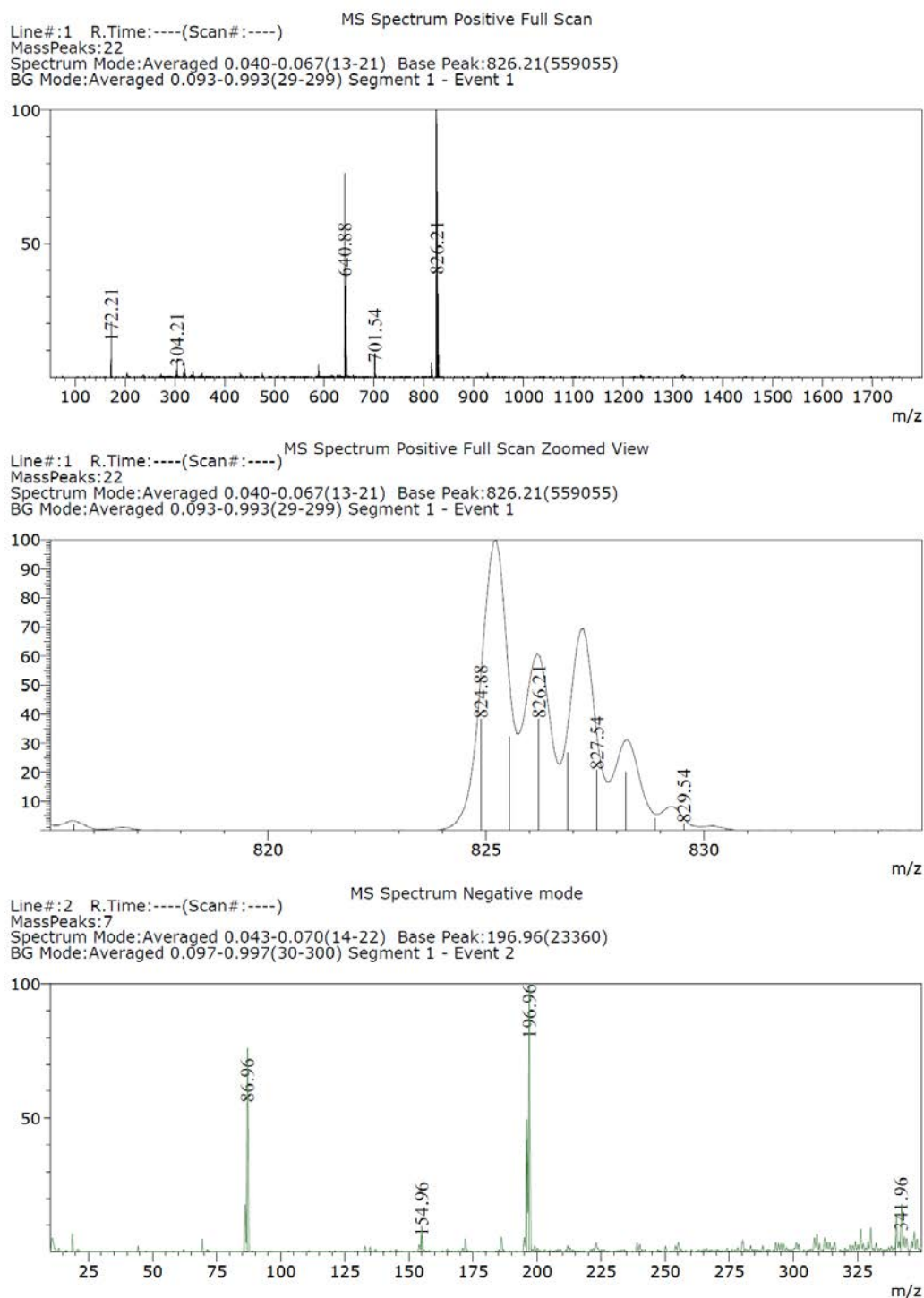


Fig. S29 The ESI mass spectrum (positive and negative mode) of $[\text{Cu}(\text{xantphos})(\text{Me}_2\text{bpy})][\text{BF}_4]$.

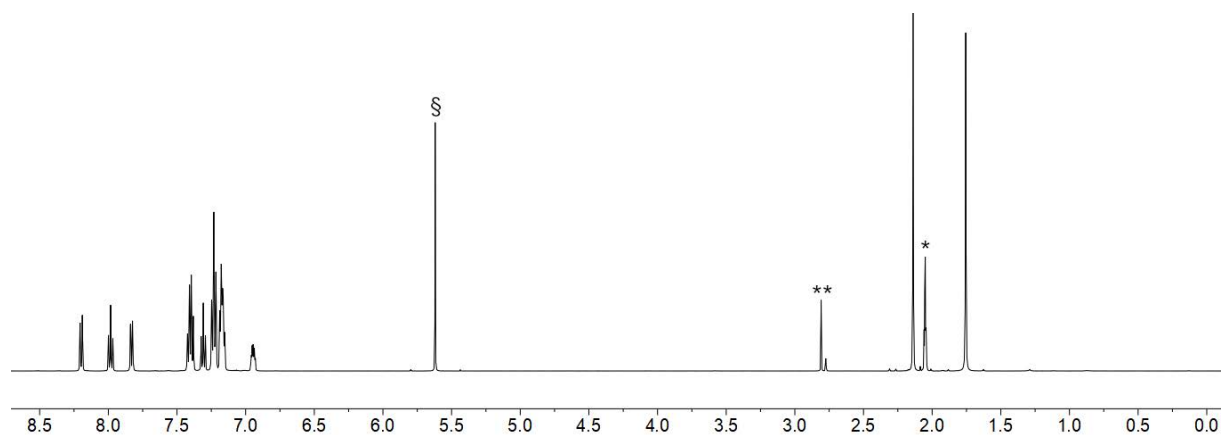


Fig. S30 ^1H NMR spectrum of $[\text{Cu}(\text{xantphos})(\text{Me}_2\text{bpy})][\text{BF}_4]$ (500 MHz, 298 K, acetone- d_6). * = residual acetone- d_5 ; ** = H_2O and HDO; § = CH_2Cl_2 .

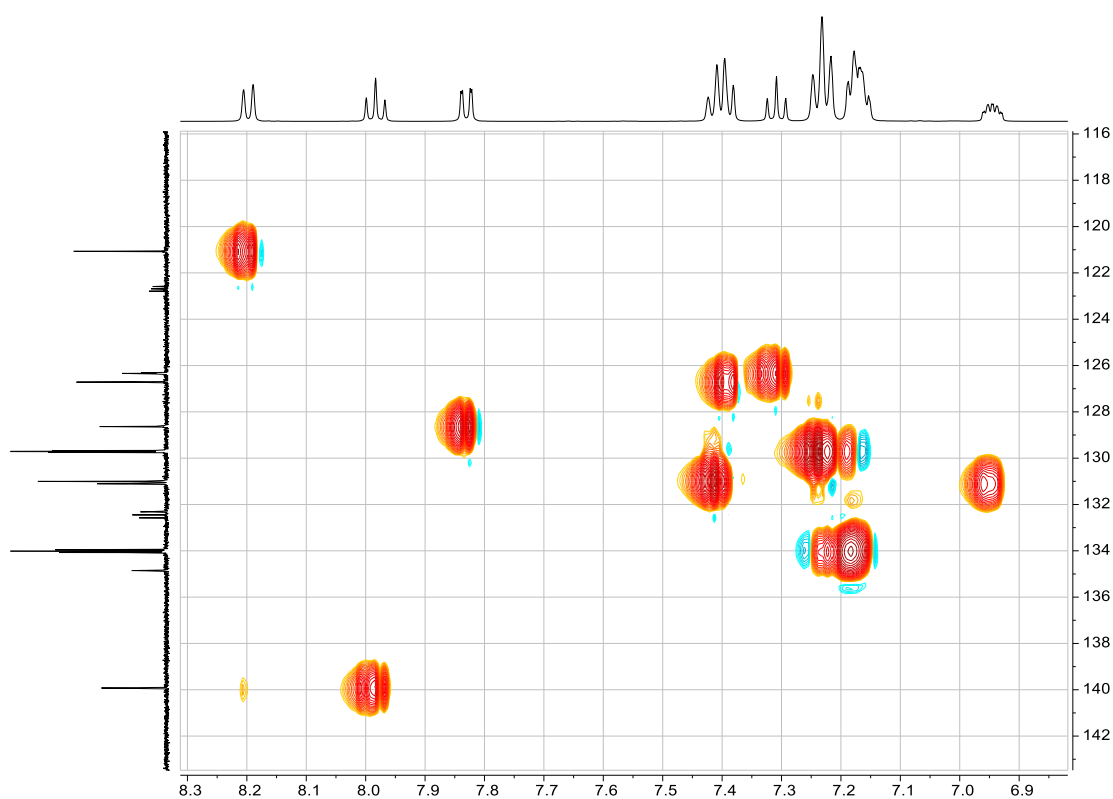


Fig. S31 The aromatic region of the HMQC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K) of $[\text{Cu}(\text{xantphos})(\text{Me}_2\text{bpy})][\text{BF}_4]$. Scale: δ / ppm.

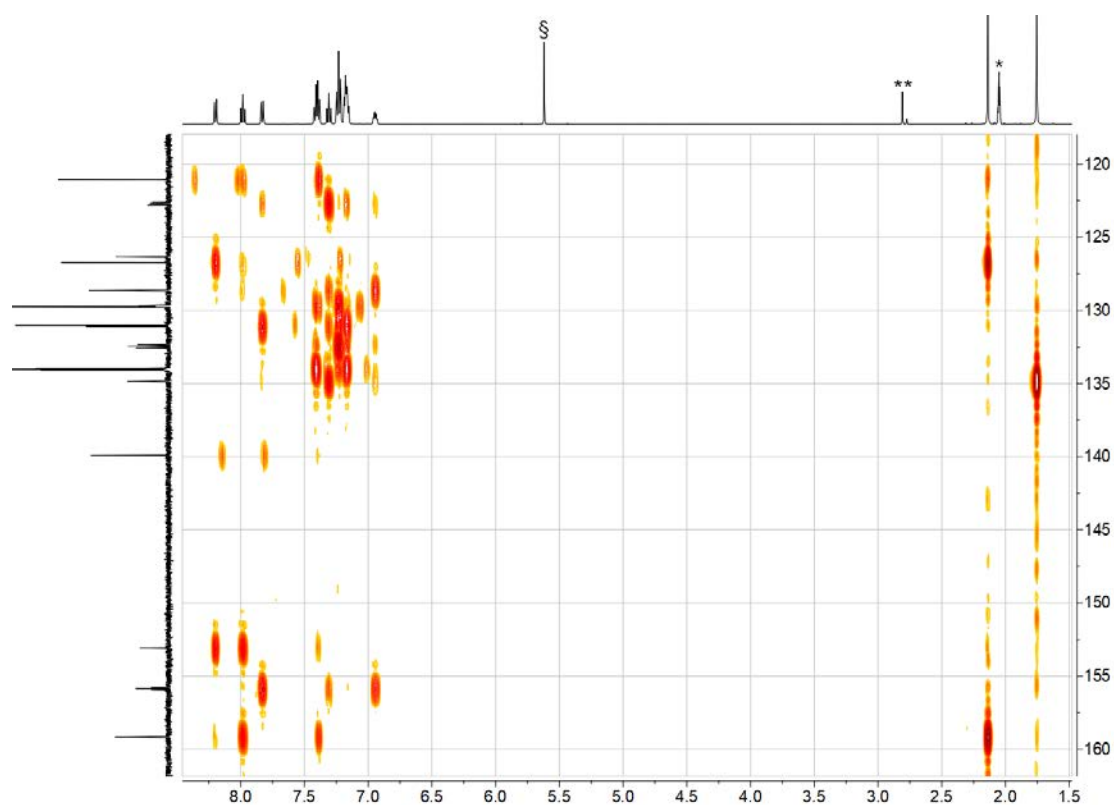


Fig. S32 Part of the HMBC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K) of $[\text{Cu}(\text{xantphos})(\text{Me}_2\text{bpy})][\text{BF}_4]$. Scale: δ / ppm. ** = H_2O and HDO ; § = CH_2Cl_2 .

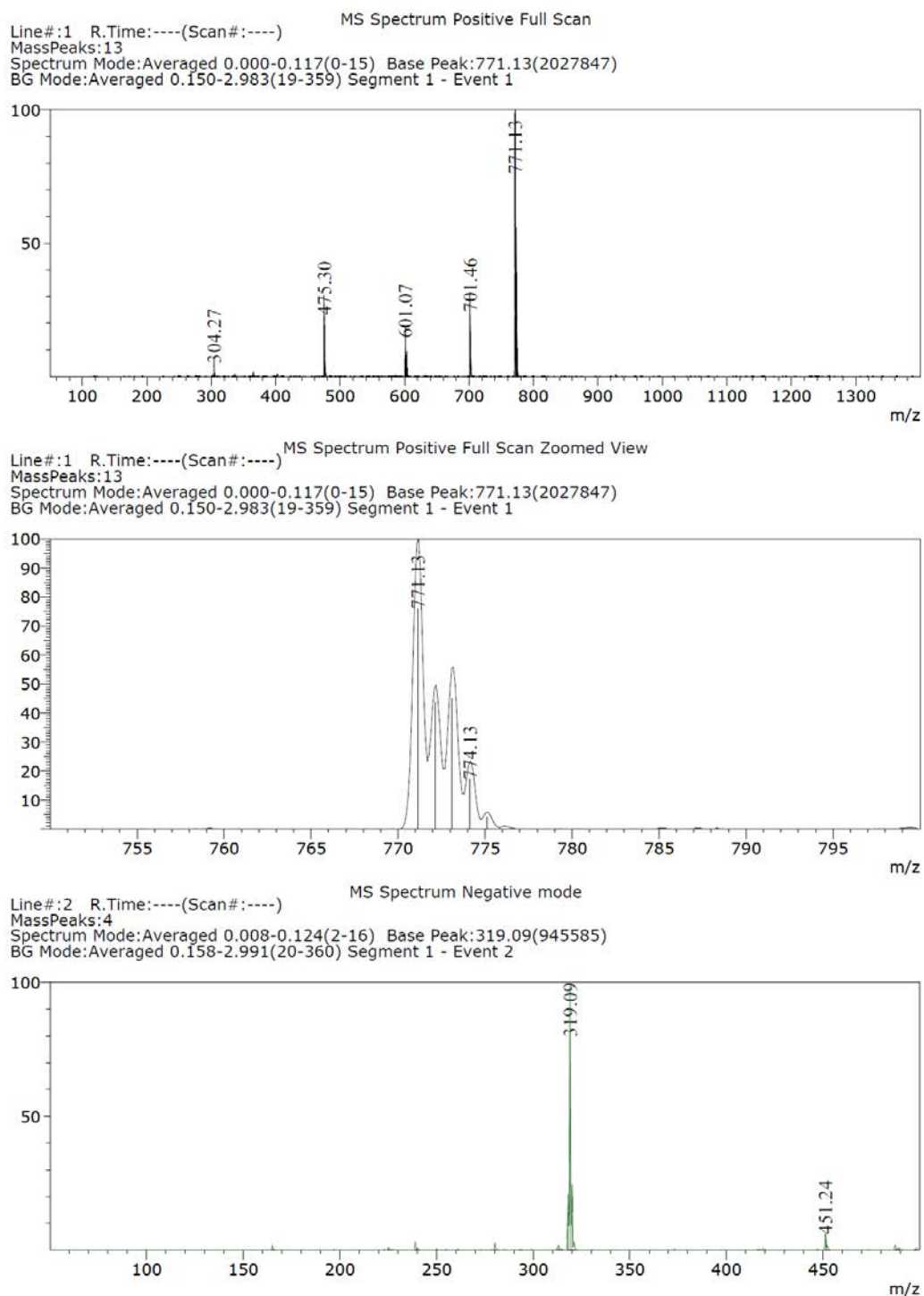


Fig. S33 The ESI mass spectrum (positive and negative mode) of $[\text{Cu}(\text{POP})(\text{Mebpy})][\text{BPh}_4]$.

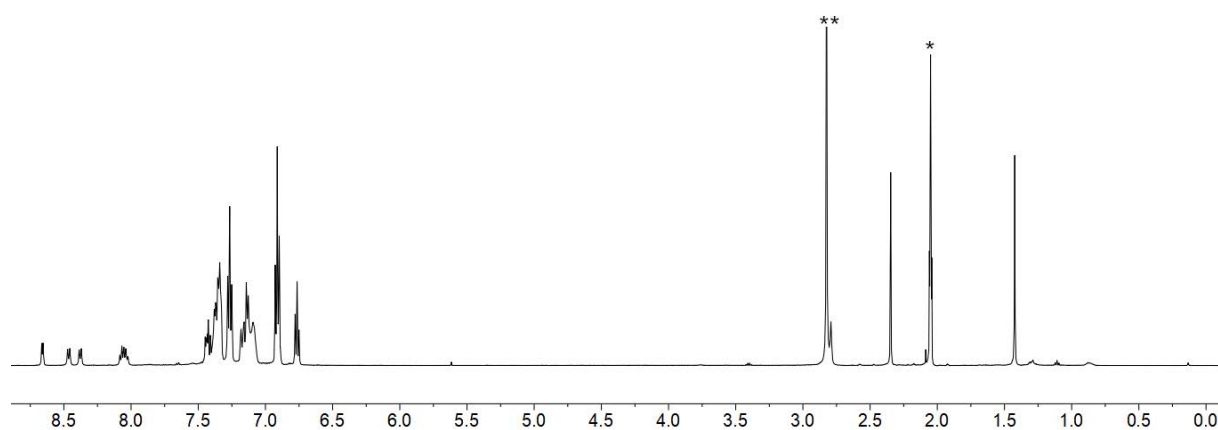


Fig. S34 ^1H NMR spectrum of $[\text{Cu}(\text{POP})(\text{Mebpy})][\text{BPh}_4]$ (500 MHz, 298 K, acetone- d_6). * = residual acetone- d_5 ; ** = H_2O and HDO.

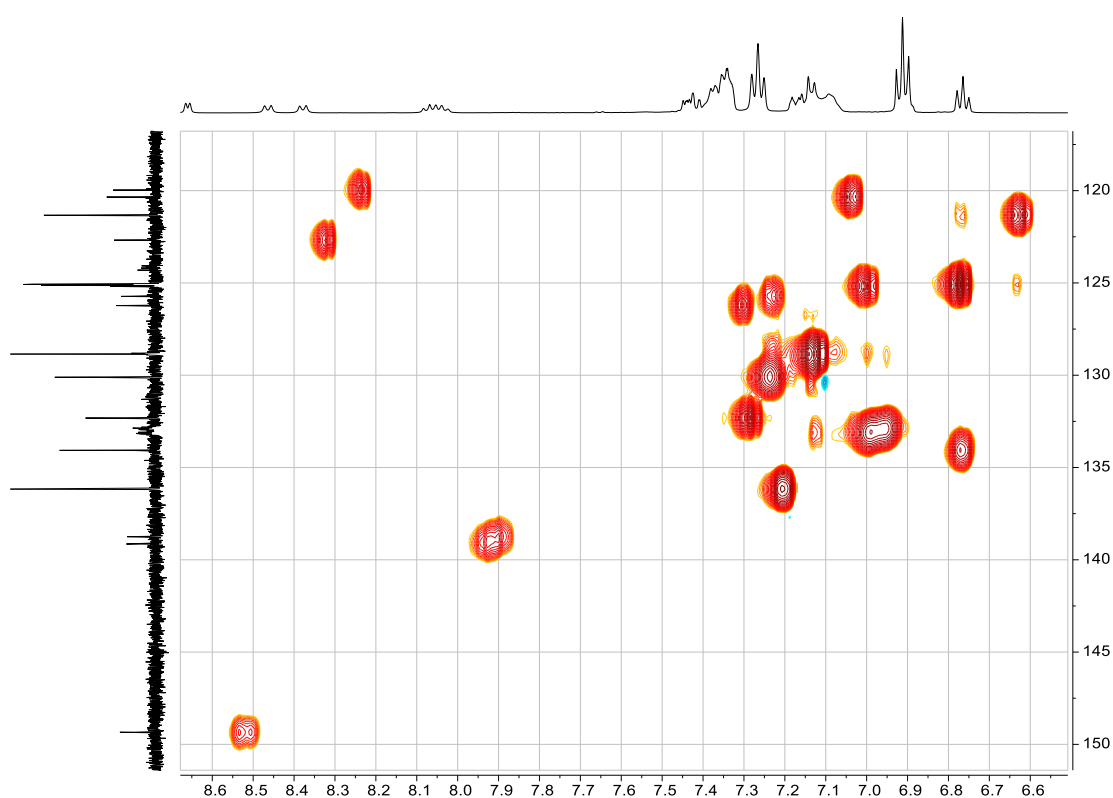


Fig. S35 The aromatic region of the HMQC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K) of $[\text{Cu}(\text{POP})(\text{Mebpy})][\text{BPh}_4]$. Scale: δ / ppm.

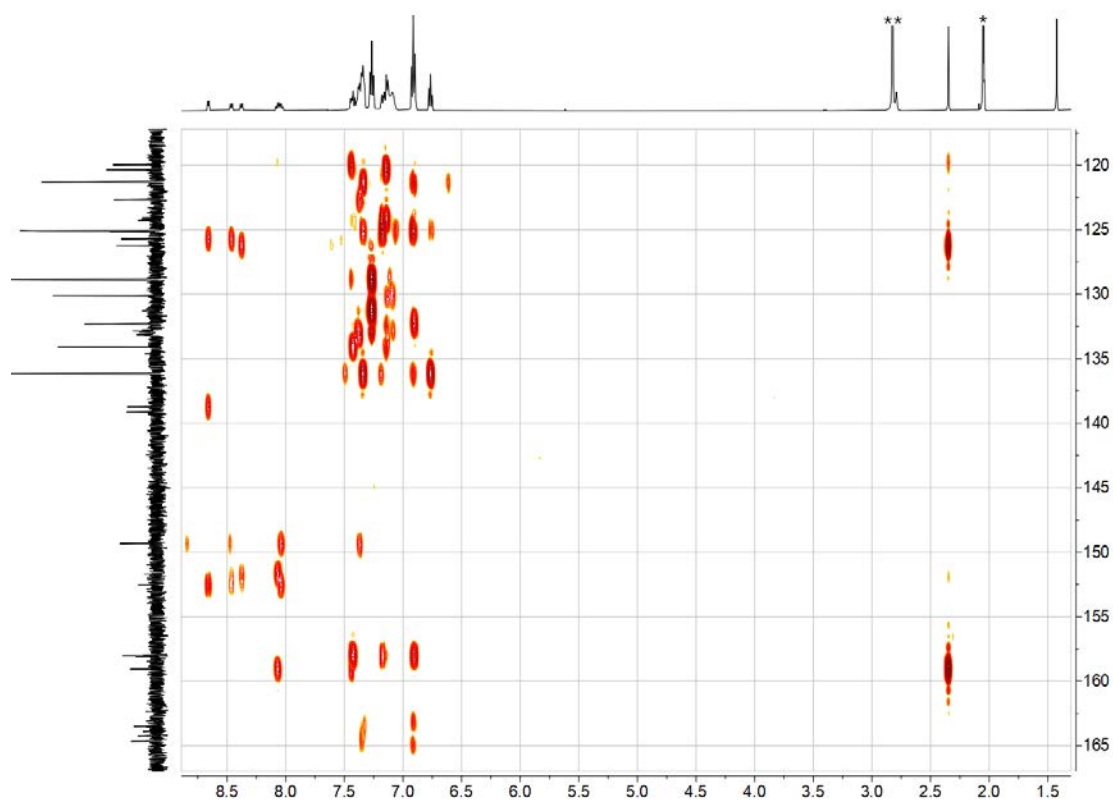


Fig. S36 Part of the HMBC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K) of $[\text{Cu}(\text{POP})(\text{Mebpy})][\text{BPh}_4]$. Scale: δ / ppm. ** = H_2O and HDO.

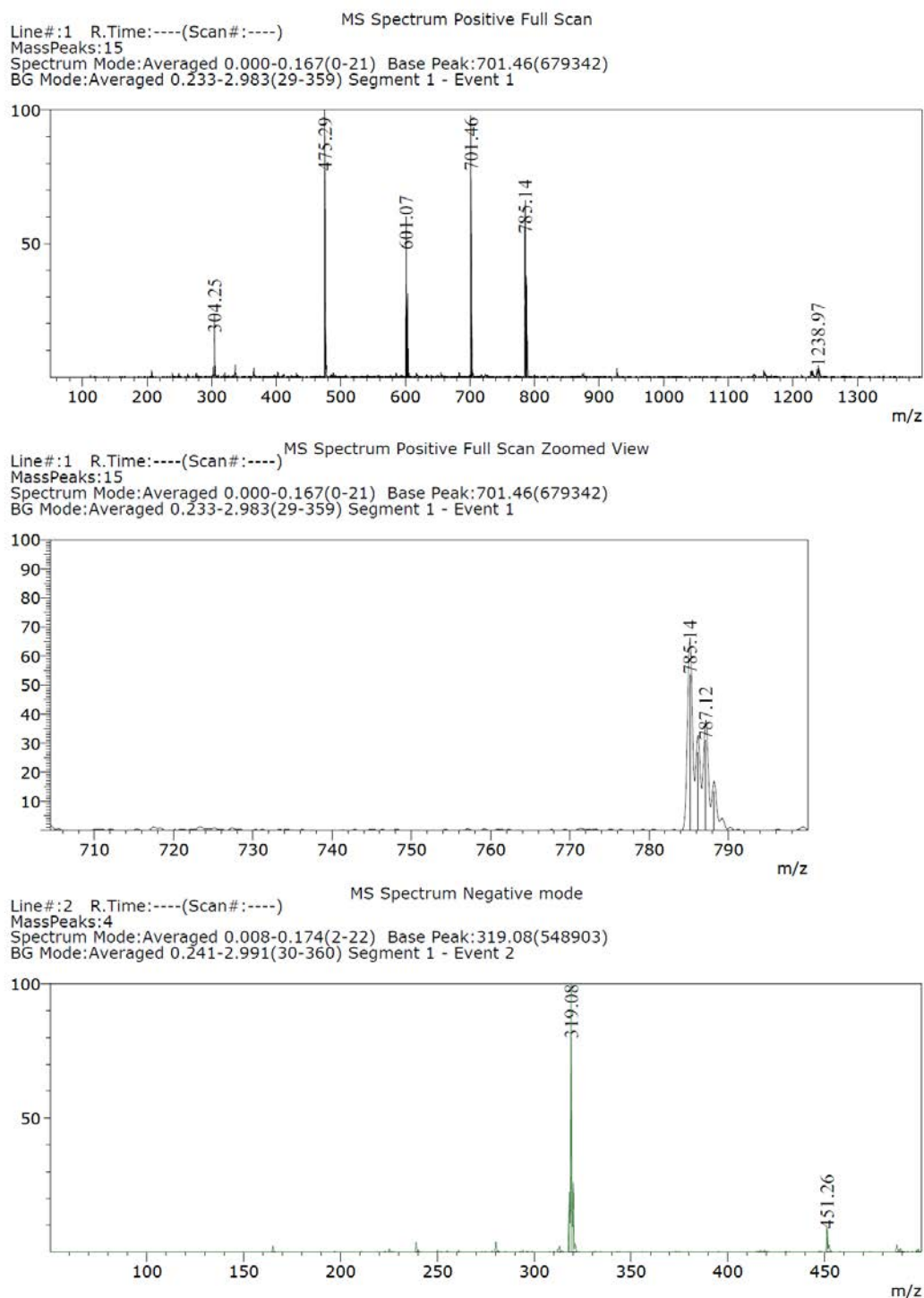


Fig. S37 The ESI mass spectrum (positive and negative mode) of $[\text{Cu}(\text{POP})(\text{Me}_2\text{bpy})][\text{BPh}_4]$.

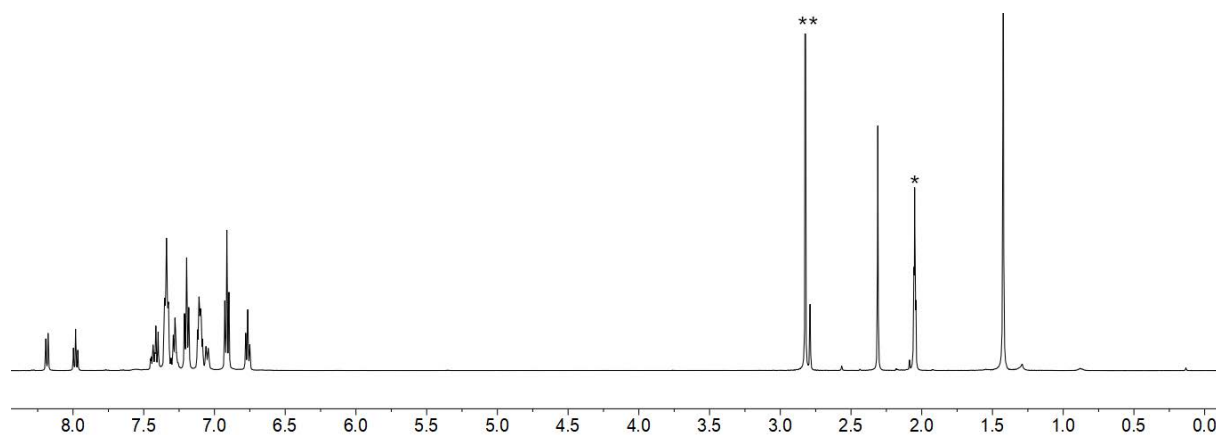


Fig. S38 ^1H NMR spectrum of $[\text{Cu}(\text{POP})(\text{Me}_2\text{bpy})][\text{BPh}_4]$ (500 MHz, 298 K, acetone- d_6). * = residual acetone- d_5 ; ** = H_2O and HDO; $\delta = \text{CH}_2\text{Cl}_2$.

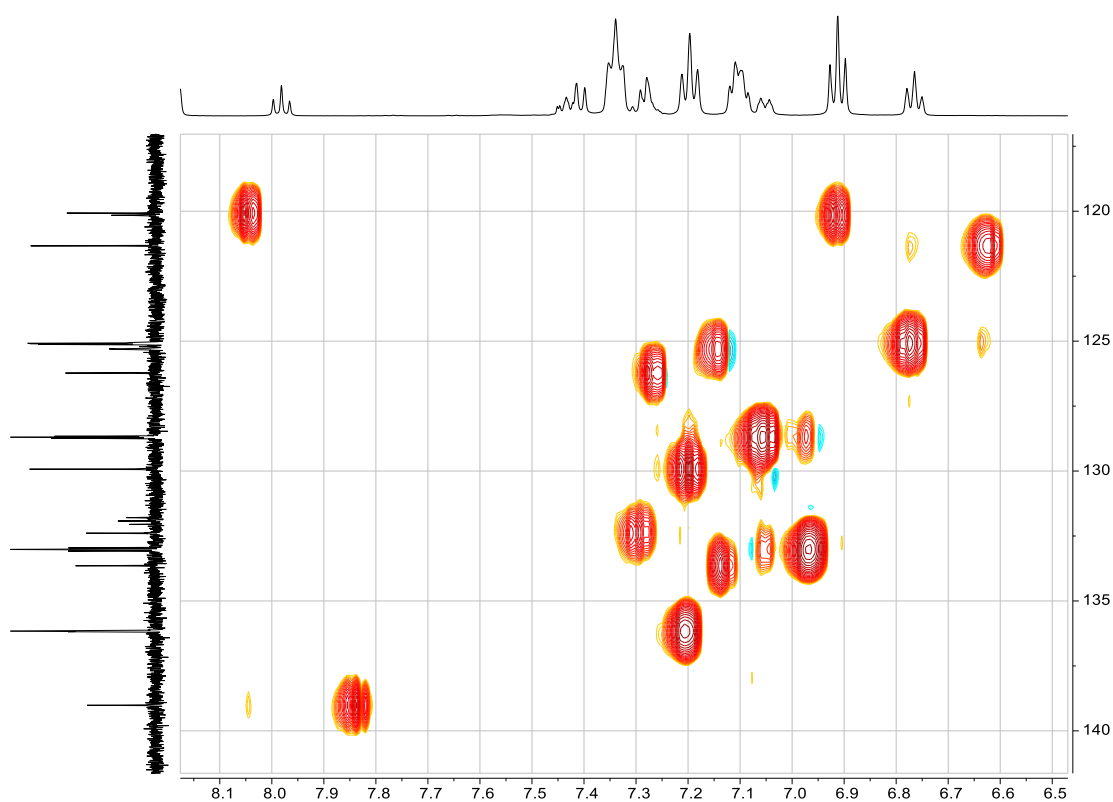


Fig. S39 The aromatic region of the HMQC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K) of $[\text{Cu}(\text{POP})(\text{Me}_2\text{bpy})][\text{BPh}_4]$. Scale: δ / ppm.

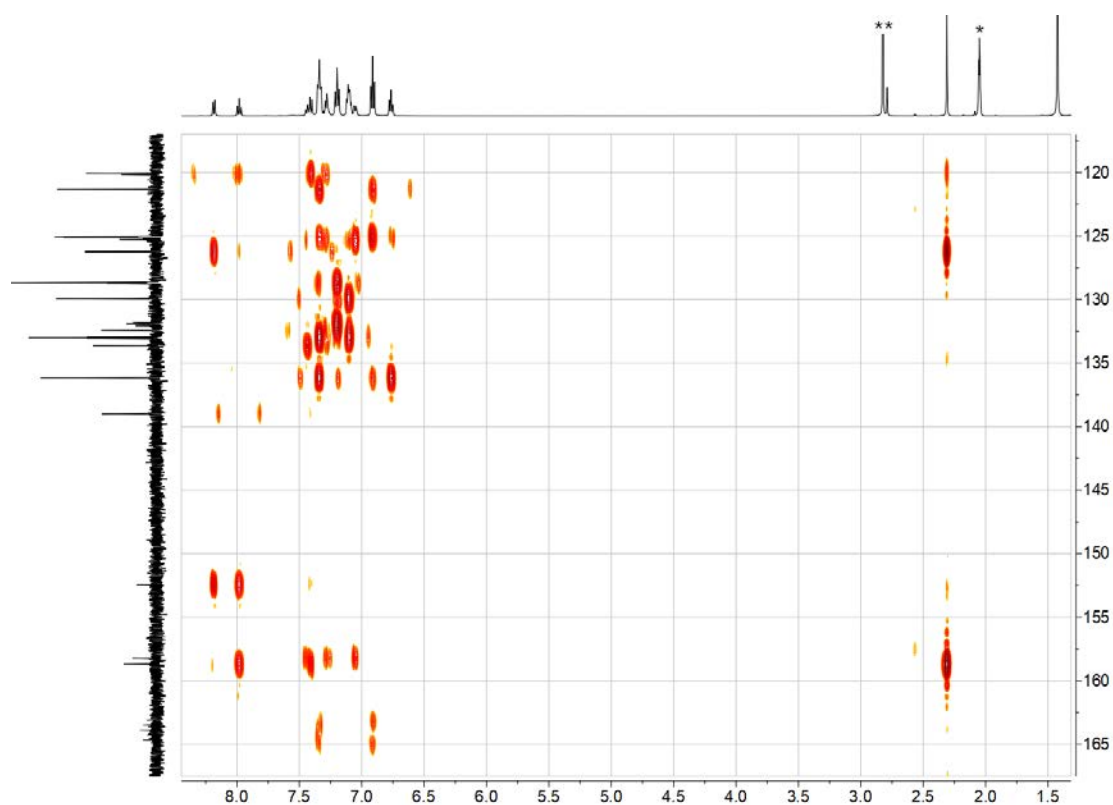


Fig. S40 Part of the HMBC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K) of $[\text{Cu}(\text{POP})(\text{Me}_2\text{bpy})][\text{BPh}_4]$. Scale: δ / ppm. ** = H_2O and HDO.

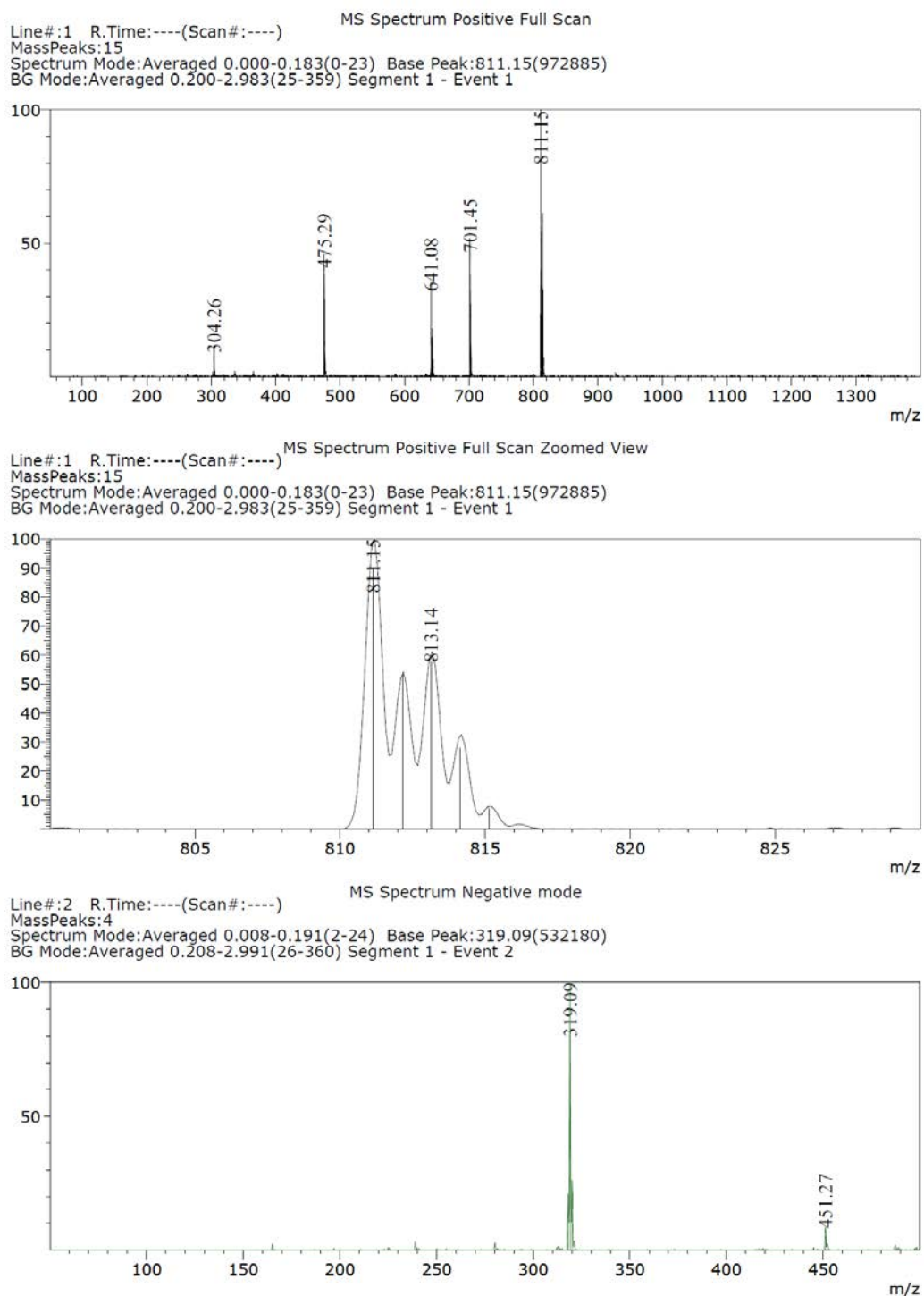


Fig. S41 The ESI mass spectrum (positive and negative mode) of $[\text{Cu}(\text{xantphos})(\text{Mebpy})][\text{BPh}_4]$.

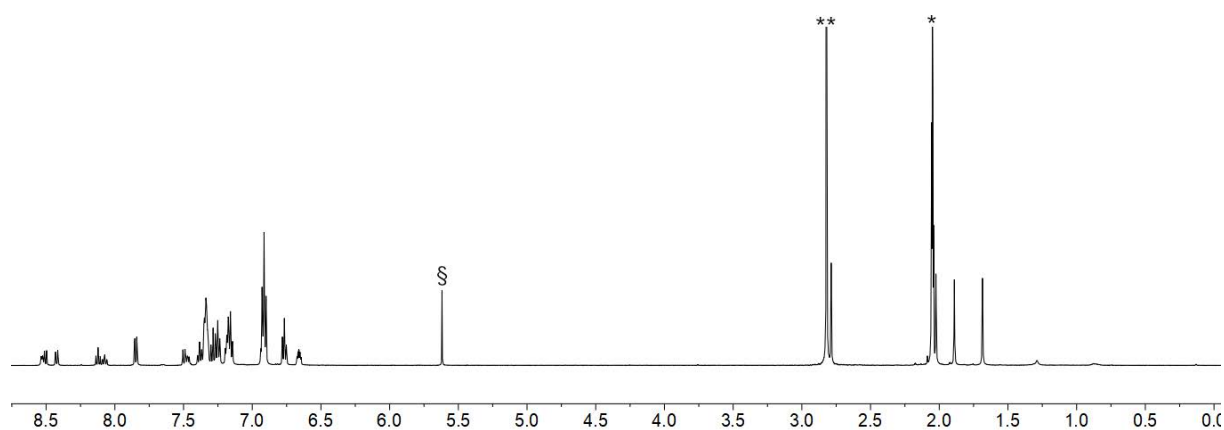


Fig. S42 ^1H NMR spectrum of $[\text{Cu}(\text{xantphos})(\text{Mebpy})][\text{BPh}_4]$ (500 MHz, 298 K, acetone- d_6). * = residual acetone- d_5 ; ** = H_2O and HDO; § = CH_2Cl_2 .

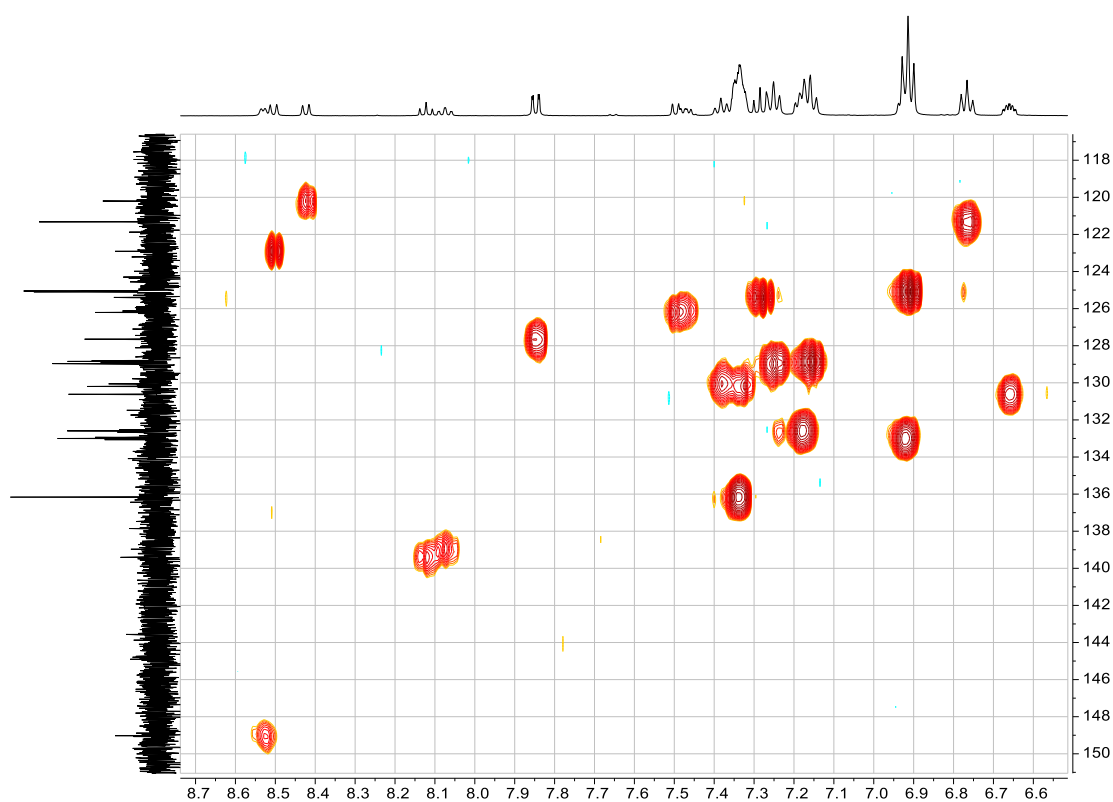


Fig. S43 The aromatic region of the HMQC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K) of $[\text{Cu}(\text{xantphos})(\text{Mebpy})][\text{BPh}_4]$. Scale: δ / ppm.

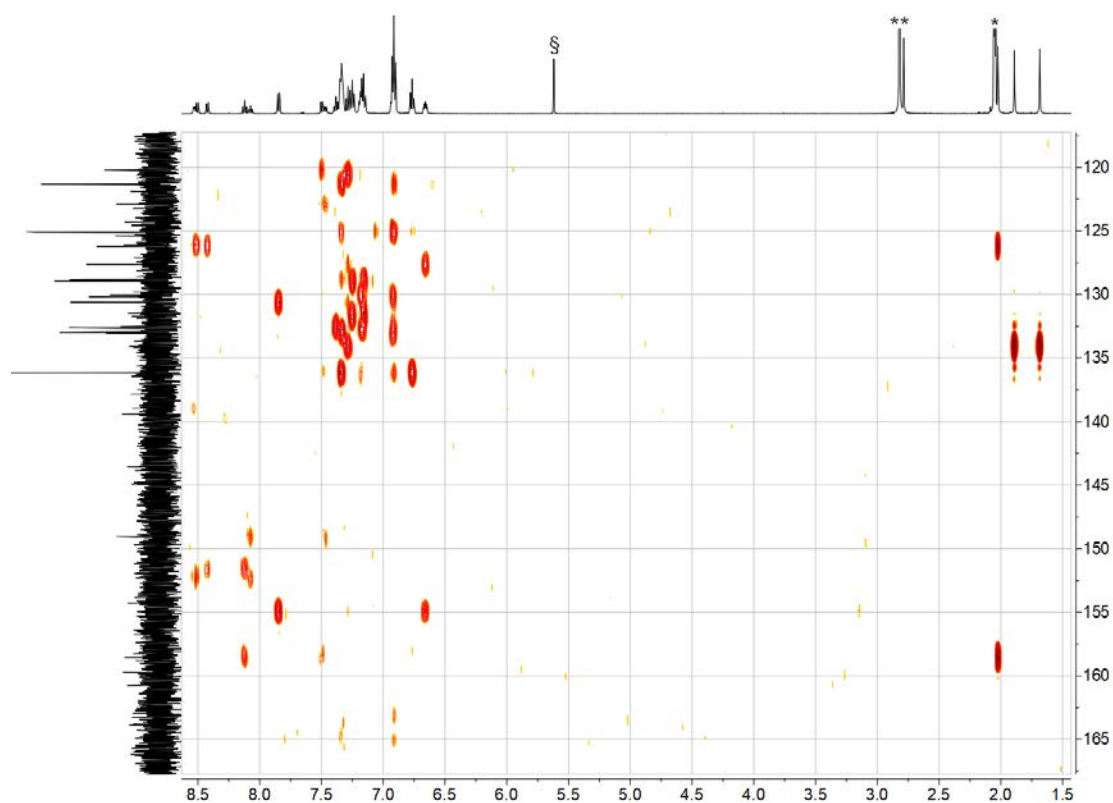


Fig. S44 Part of the HMBC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K) of $[\text{Cu}(\text{xantphos})(\text{Mebpy})][\text{BPh}_4]$. Scale: δ / ppm. ** = H_2O and HDO ; § = CH_2Cl_2 .

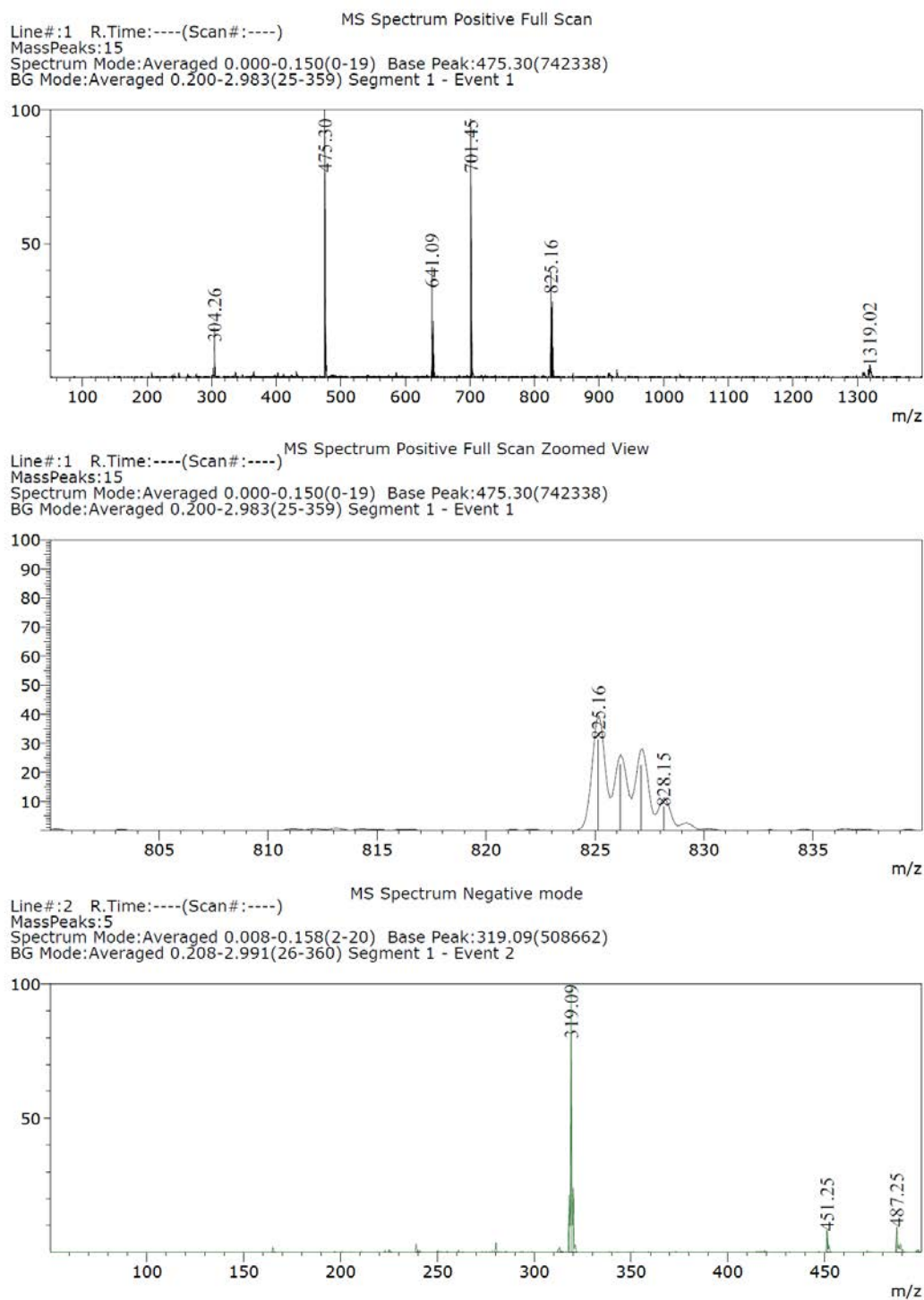


Fig. S45 The ESI mass spectrum (positive and negative mode) of $[\text{Cu}(\text{xantphos})(\text{Me}_2\text{bpy})][\text{BPh}_4]$.

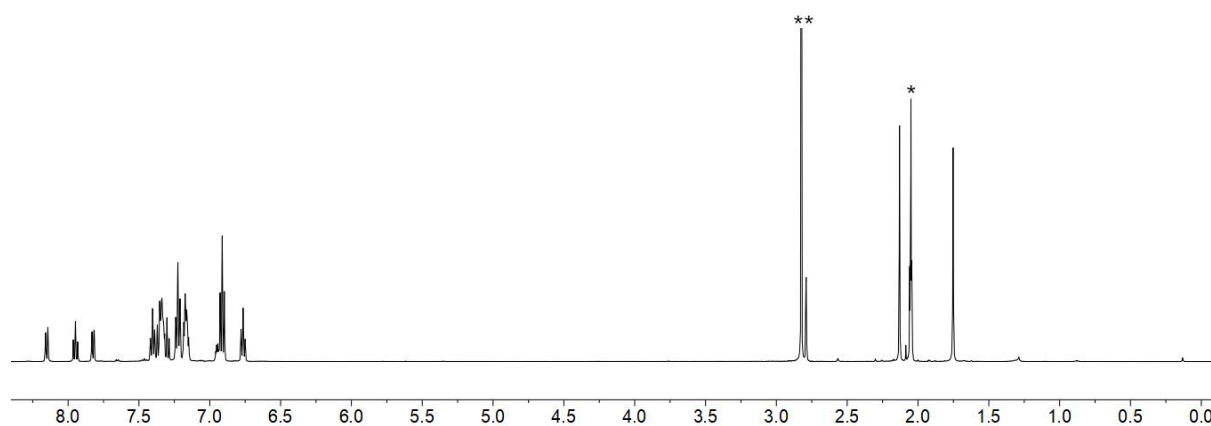


Fig. S46 ^1H NMR spectrum of $[\text{Cu}(\text{xantphos})(\text{Me}_2\text{bpy})][\text{BPh}_4]$ (500 MHz, 298 K, acetone- d_6). * = residual acetone- d_5 ; ** = H_2O and HDO; δ = CH_2Cl_2 .

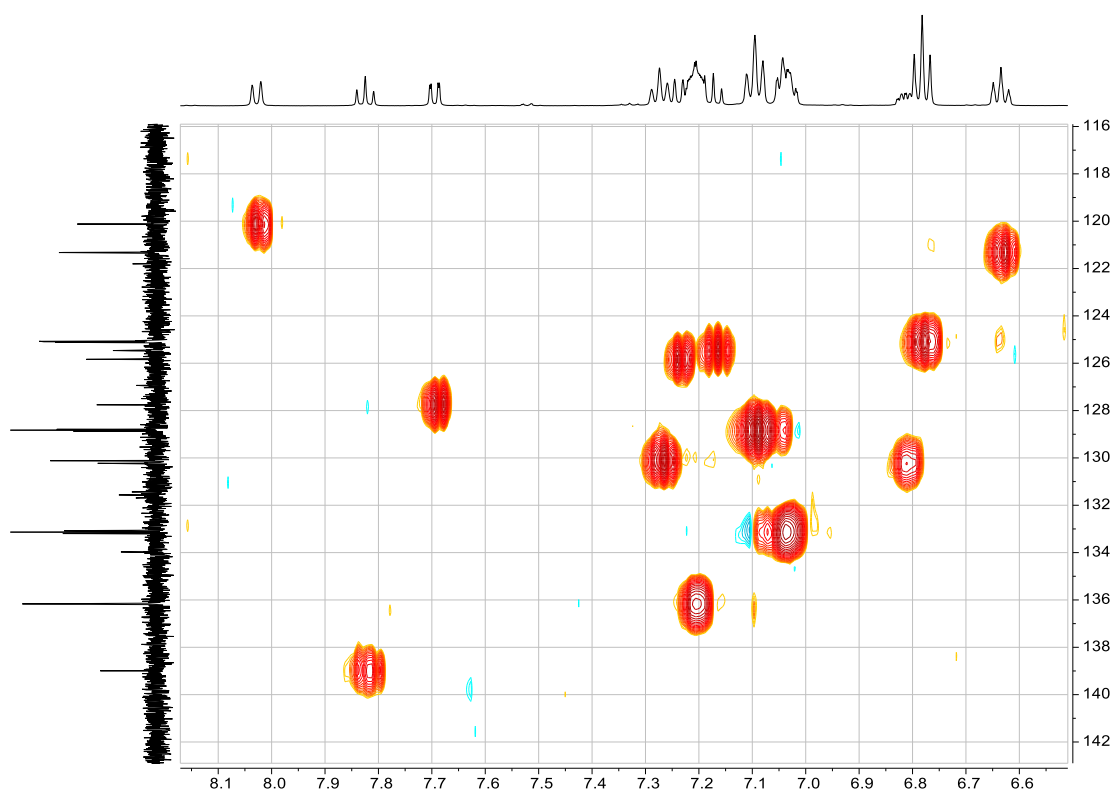


Fig. S47 The aromatic region of the HMQC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K) of $[\text{Cu}(\text{xantphos})(\text{Me}_2\text{bpy})][\text{BPh}_4]$. Scale: δ / ppm.

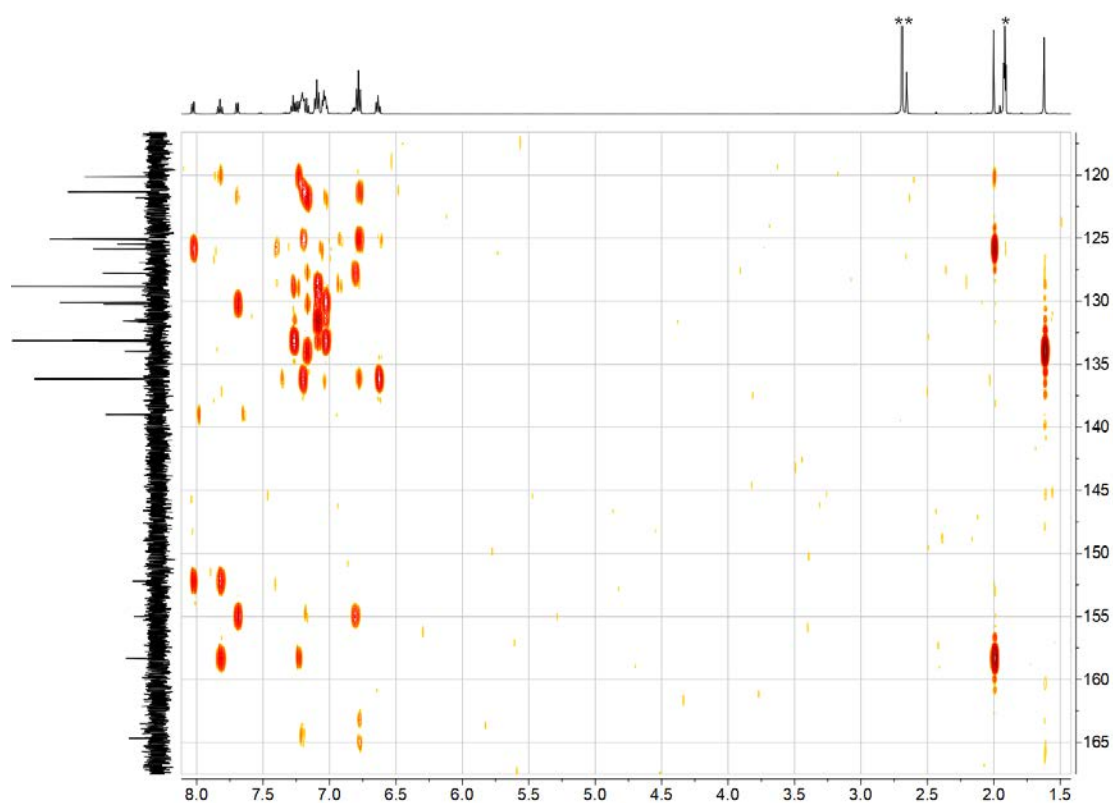


Fig. S48 Part of the HMBC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K) of $[\text{Cu}(\text{xantphos})(\text{Me}_2\text{bpy})][\text{BPh}_4]$. Scale: δ / ppm. ** = H_2O and HDO .

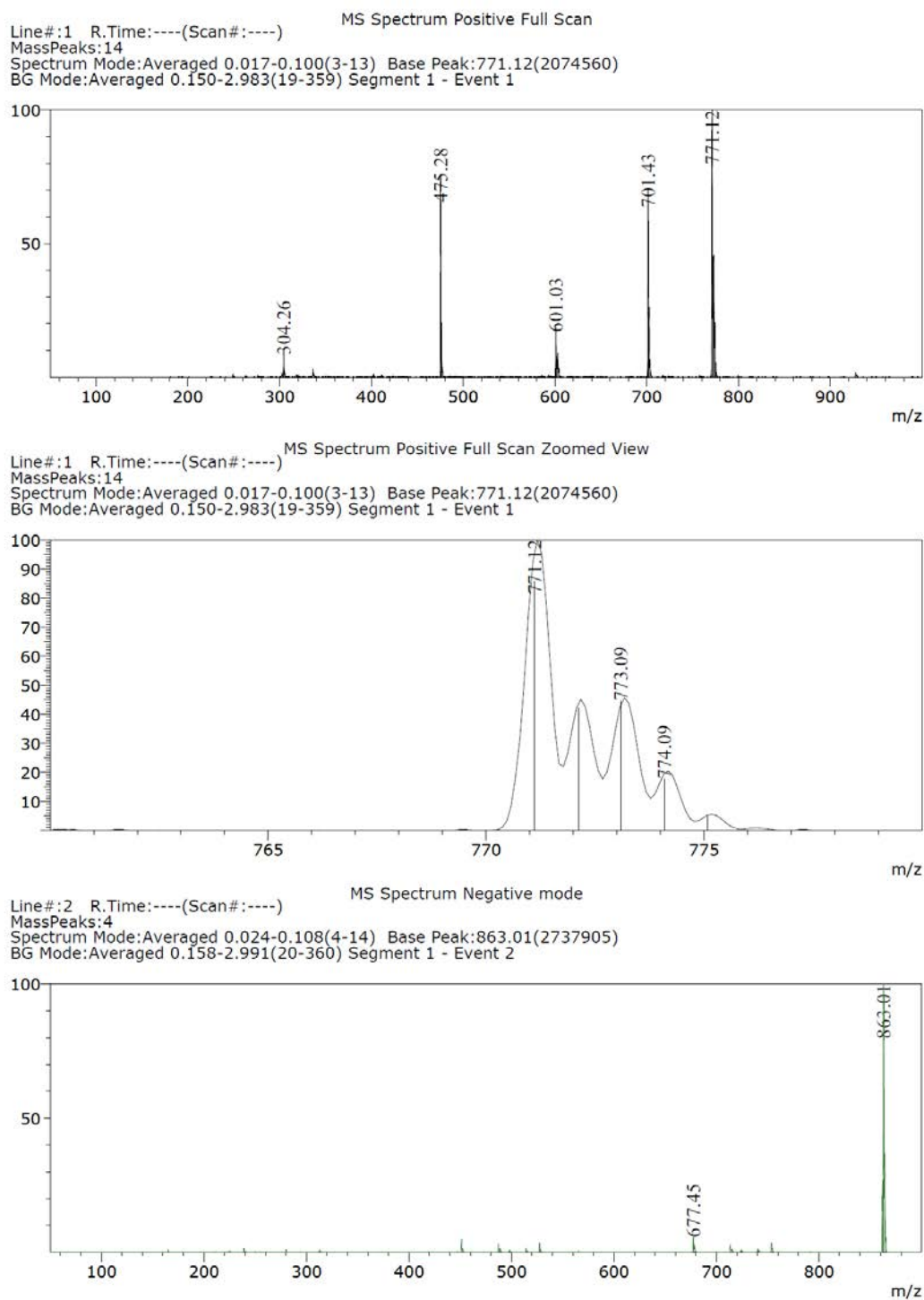


Fig. S49 The ESI mass spectrum (positive and negative mode) of $[\text{Cu}(\text{POP})(\text{Mebpy})][\text{BARF}_4]$.

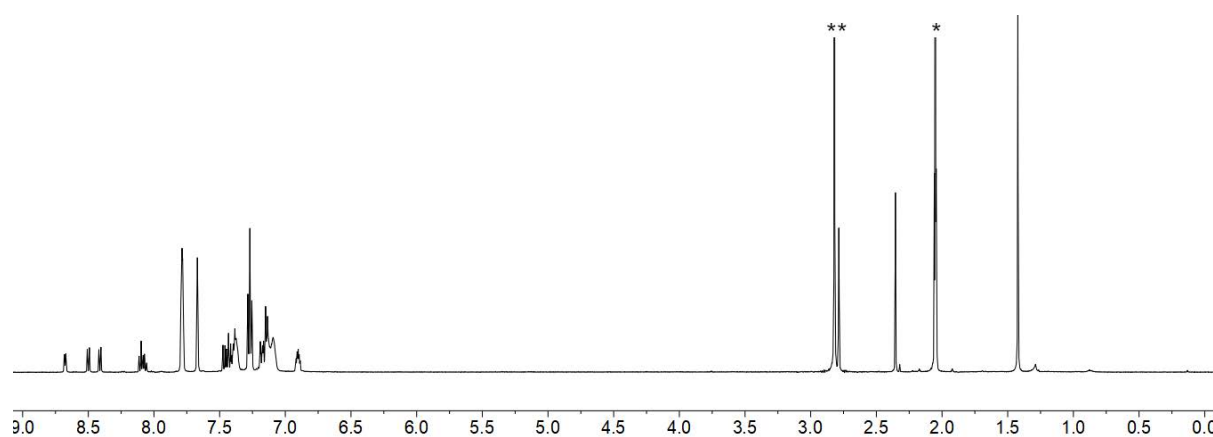


Fig. S50 ^1H NMR spectrum of $[\text{Cu}(\text{POP})(\text{Mebpy})][\text{BARF}_4]$ (500 MHz, 298 K, acetone- d_6). * = residual acetone- d_5 ; ** = H_2O and HDO.

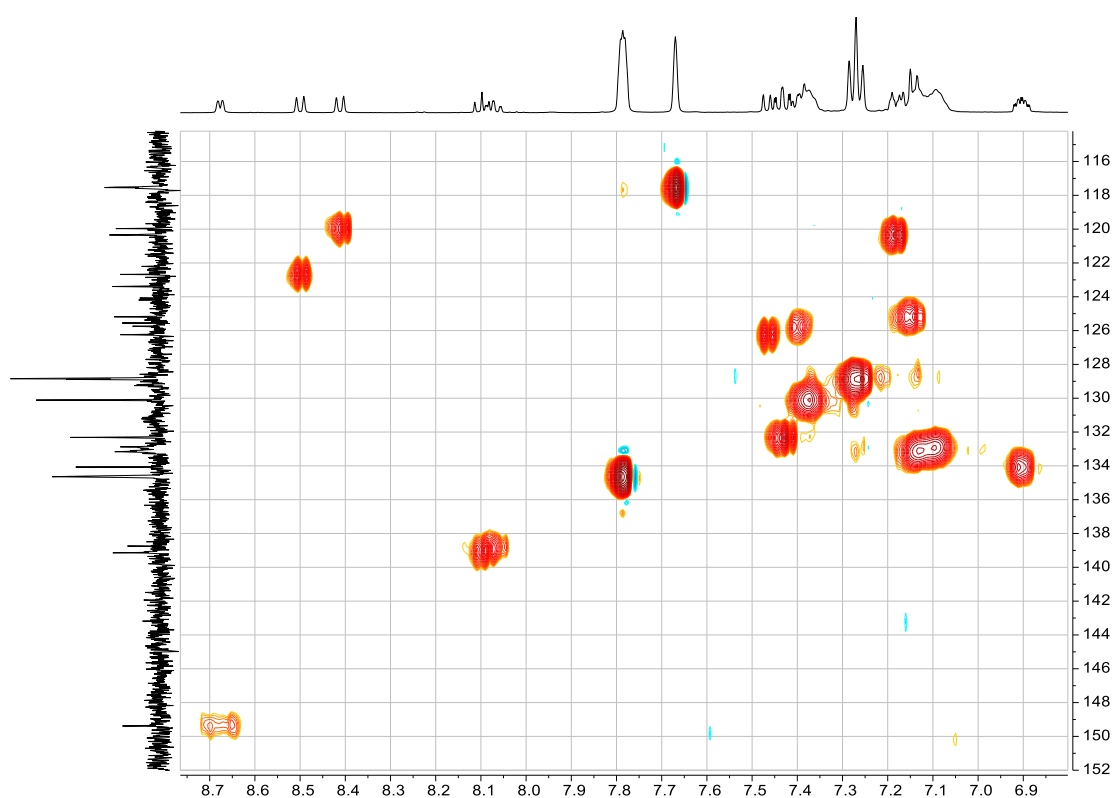


Fig. S51 The aromatic region of the HMQC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K) of $[\text{Cu}(\text{POP})(\text{Mebpy})][\text{BARF}_4]$. Scale: δ / ppm.

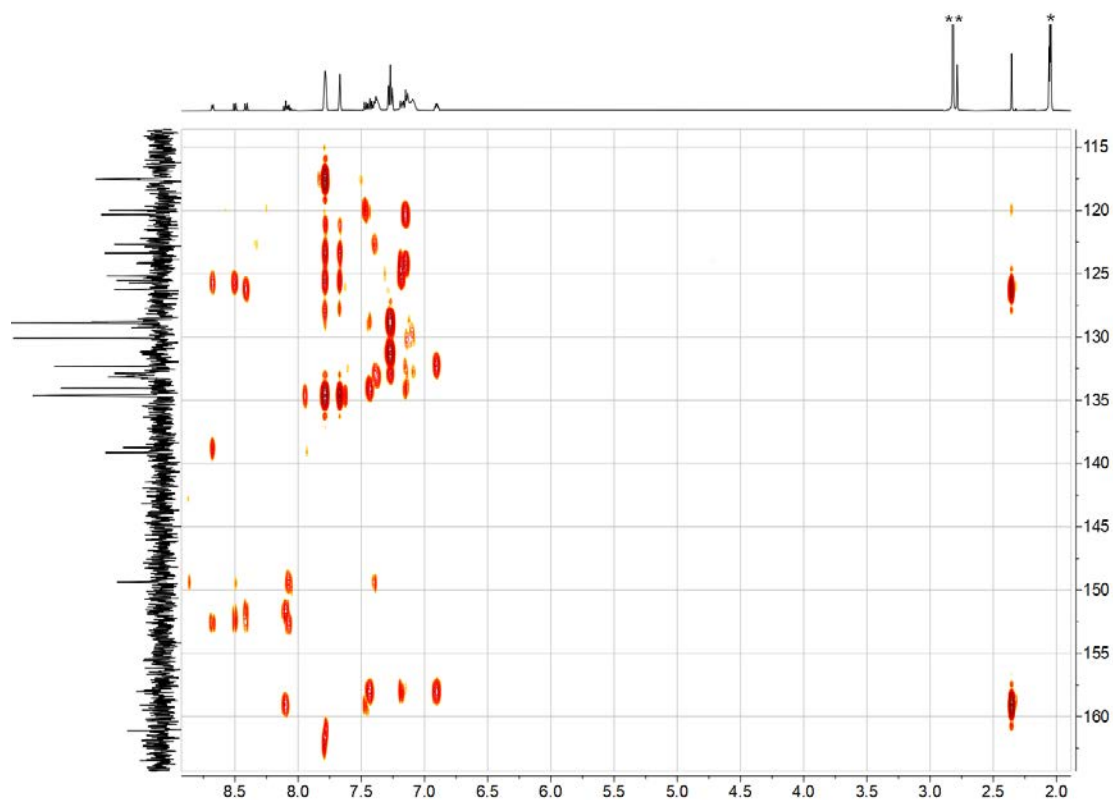


Fig. S52 Part of the HMBC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K) of $[\text{Cu}(\text{POP})(\text{Mebpy})][\text{BARF}_4]$. Scale: δ / ppm. ** = H_2O and HDO.

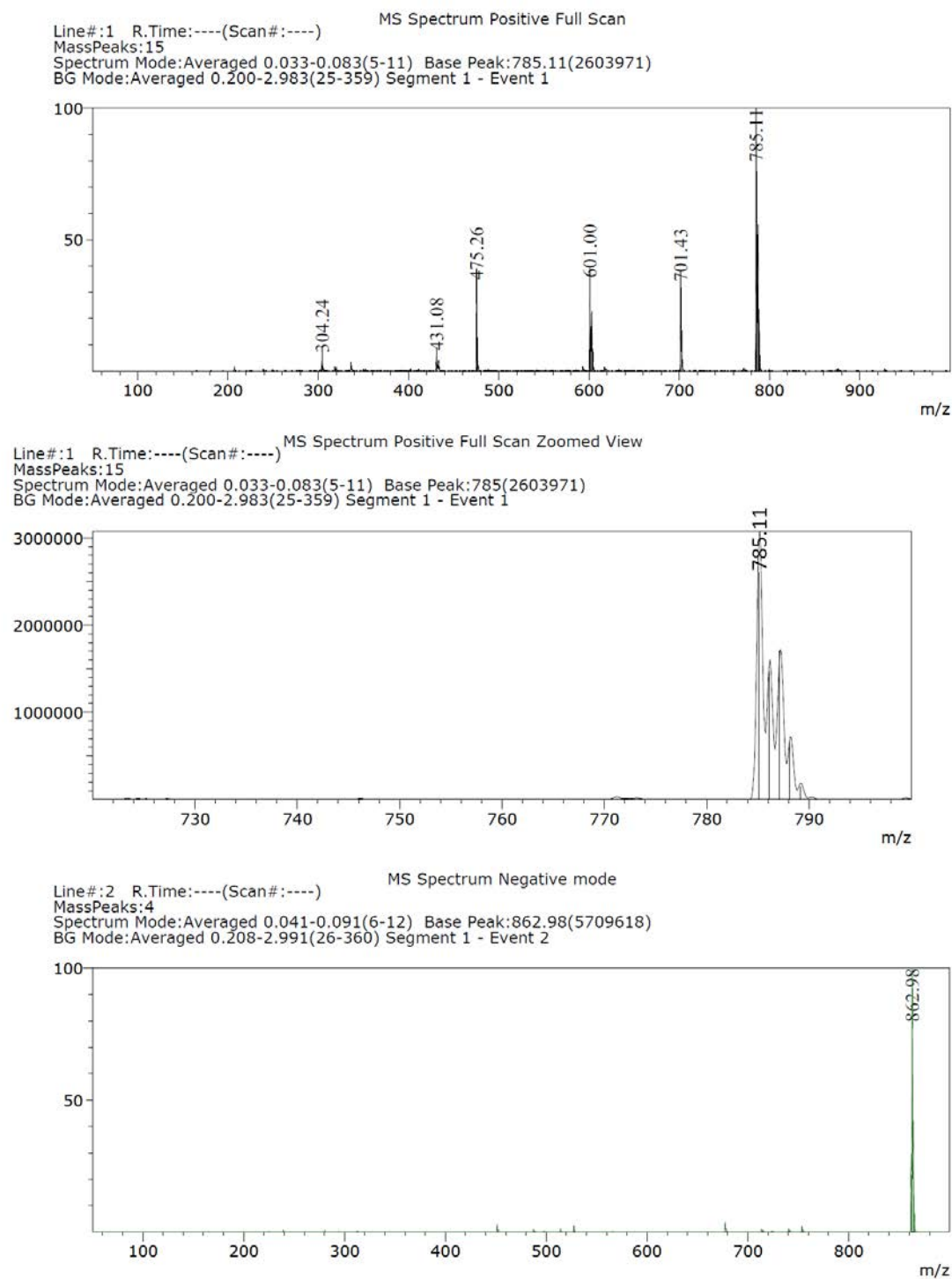


Fig. S53 The ESI mass spectrum (positive and negative mode) of $[\text{Cu}(\text{POP})(\text{Me}_2\text{bpy})][\text{BAr}^{\text{F}}_4]$.

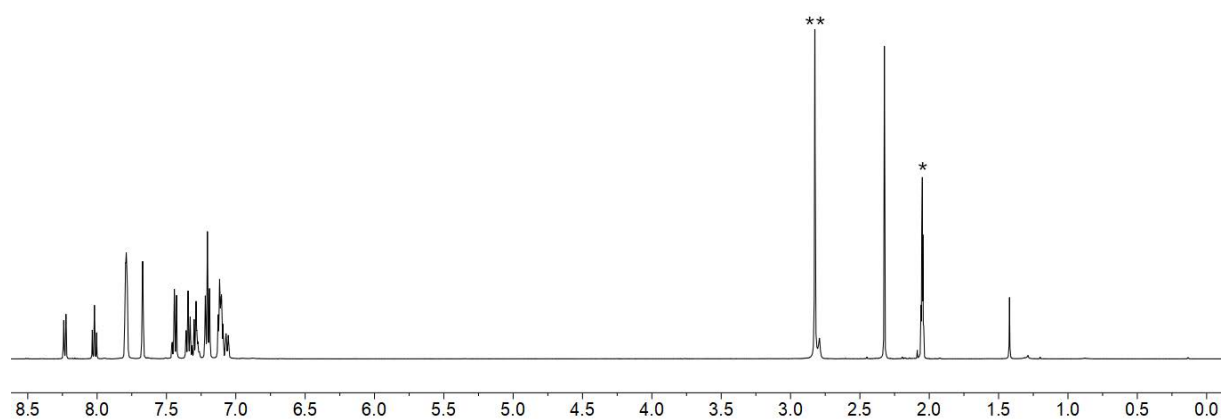


Fig. S54 ^1H NMR spectrum of $[\text{Cu}(\text{POP})(\text{Me}_2\text{bpy})][\text{BArF}_4]$ (500 MHz, 298 K, acetone- d_6). * = residual acetone- d_5 ; ** = H_2O and HDO.

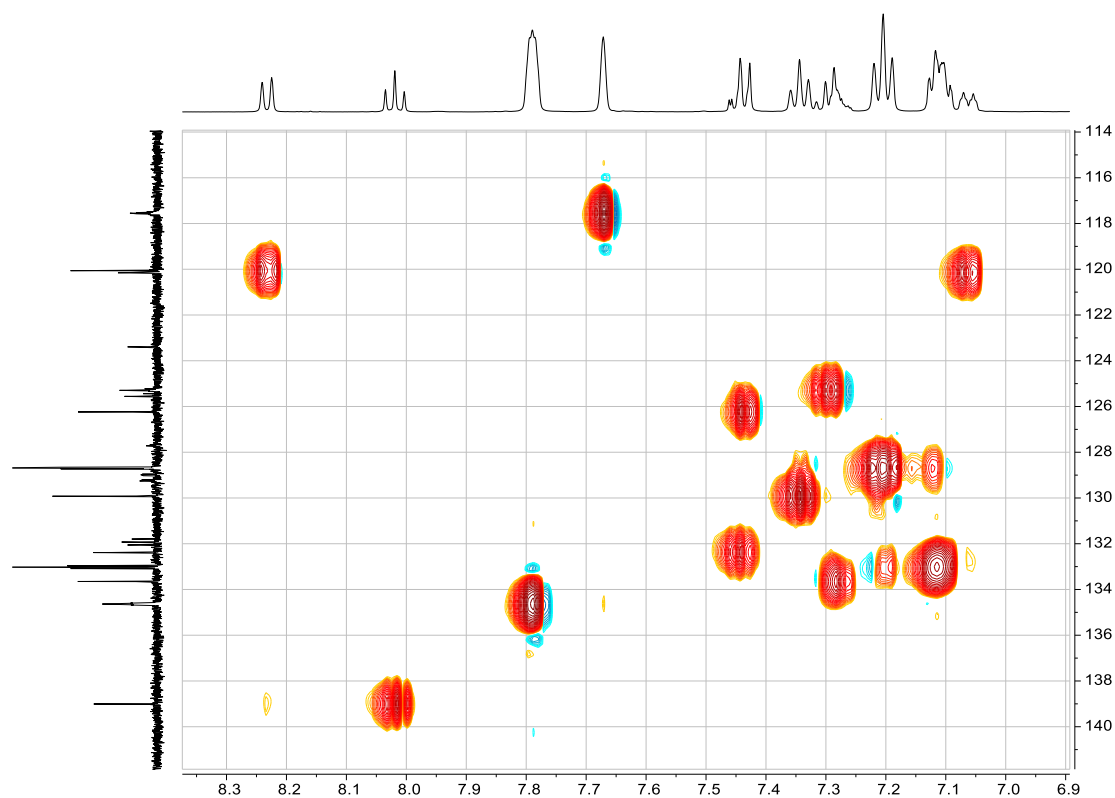


Fig. S55 The aromatic region of the HMQC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K) of $[\text{Cu}(\text{POP})(\text{Me}_2\text{bpy})][\text{BArF}_4]$. Scale: δ / ppm.

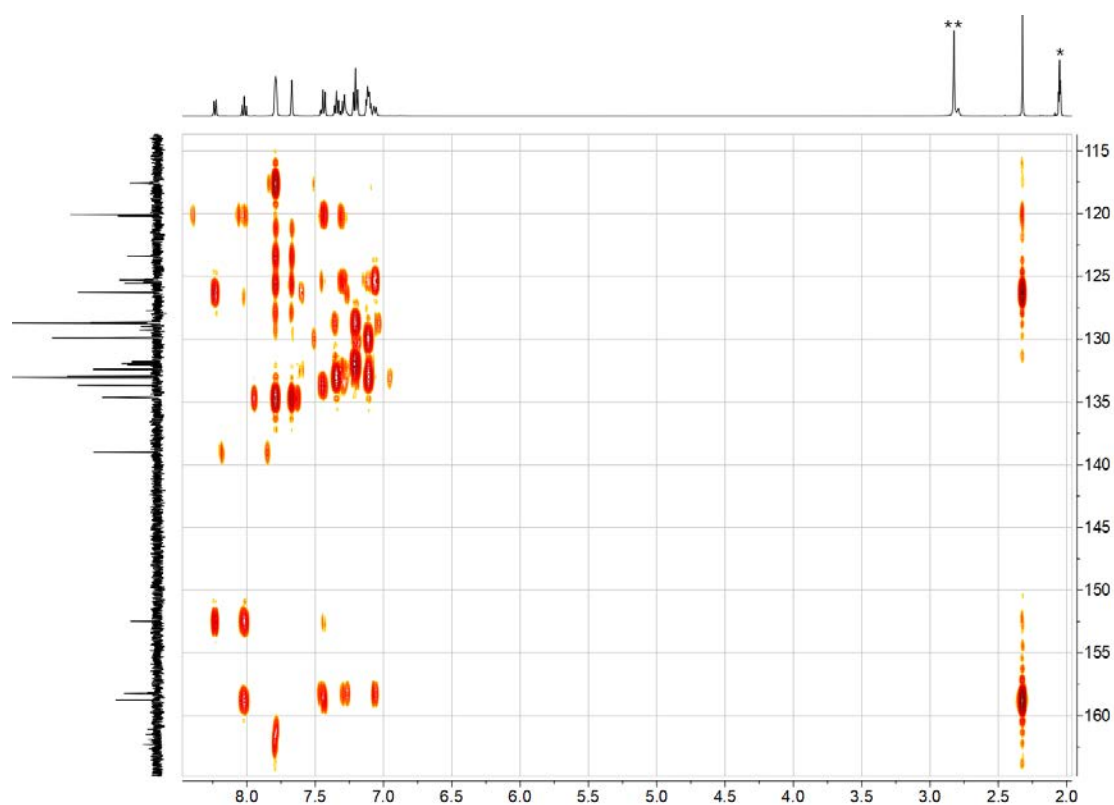


Fig. S56 Part of the HMBC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K) of $[\text{Cu}(\text{POP})(\text{Me}_2\text{bpy})][\text{BARF}_4]$. Scale: δ / ppm. ** = H_2O and HDO.

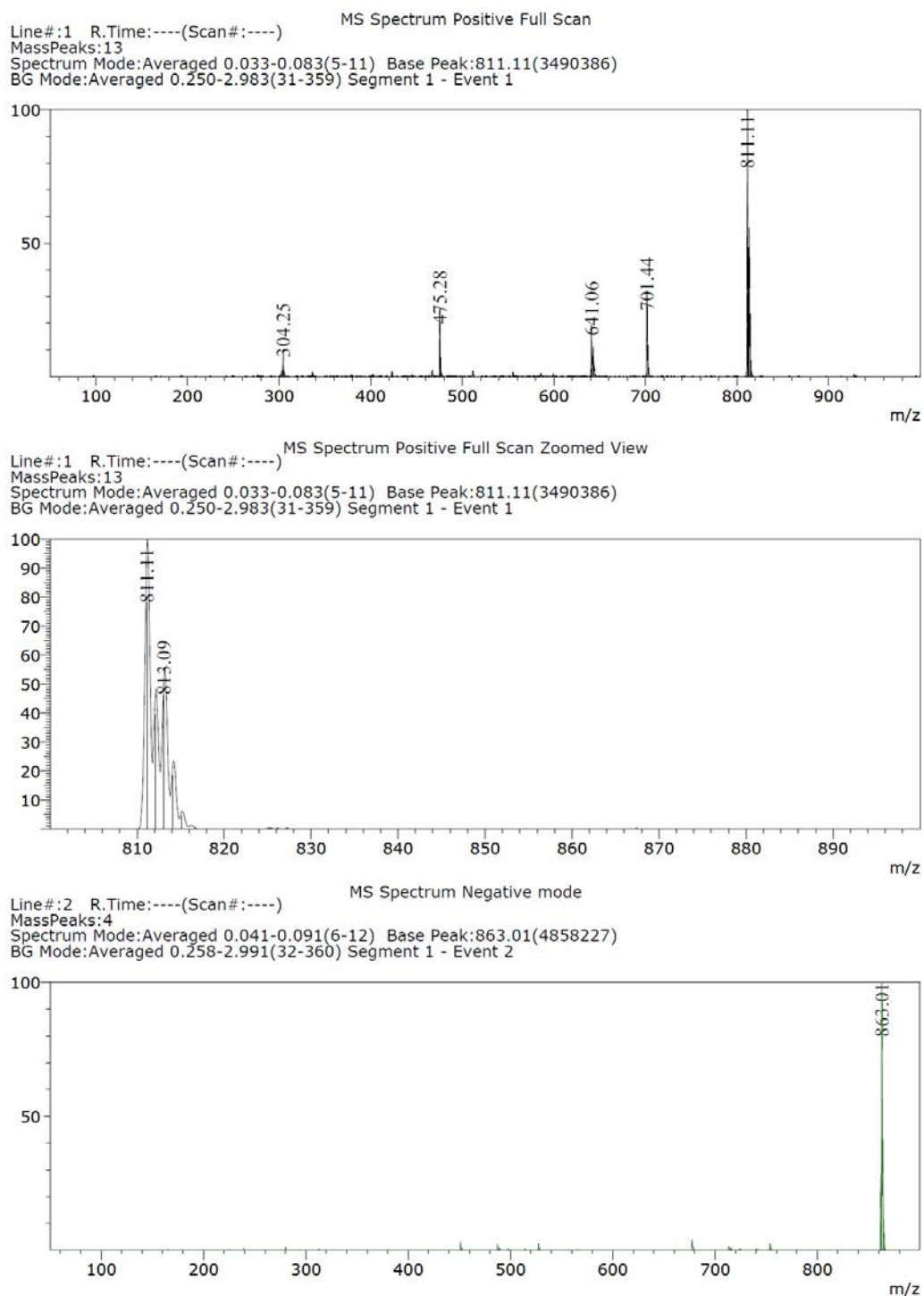


Fig. S57 The ESI mass spectrum (positive and negative mode) of $[\text{Cu}(\text{xantphos})(\text{Mebpy})][\text{BAR}^{\text{F}}_4]$.

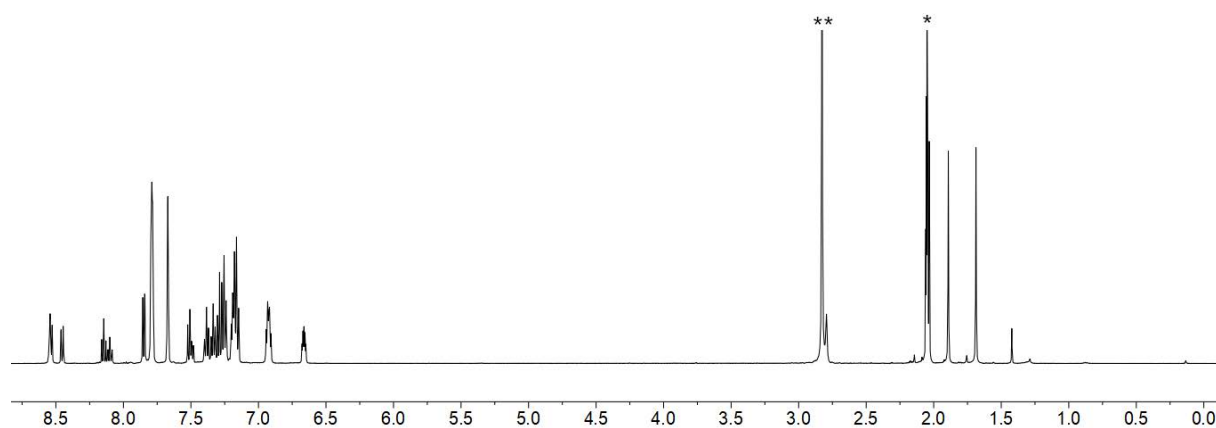


Fig. S58 ^1H NMR spectrum of $[\text{Cu}(\text{xantphos})(\text{Mebpy})][\text{BArF}_4]$ (500 MHz, 298 K, acetone- d_6). * = residual acetone- d_5 ; ** = H_2O and HDO.

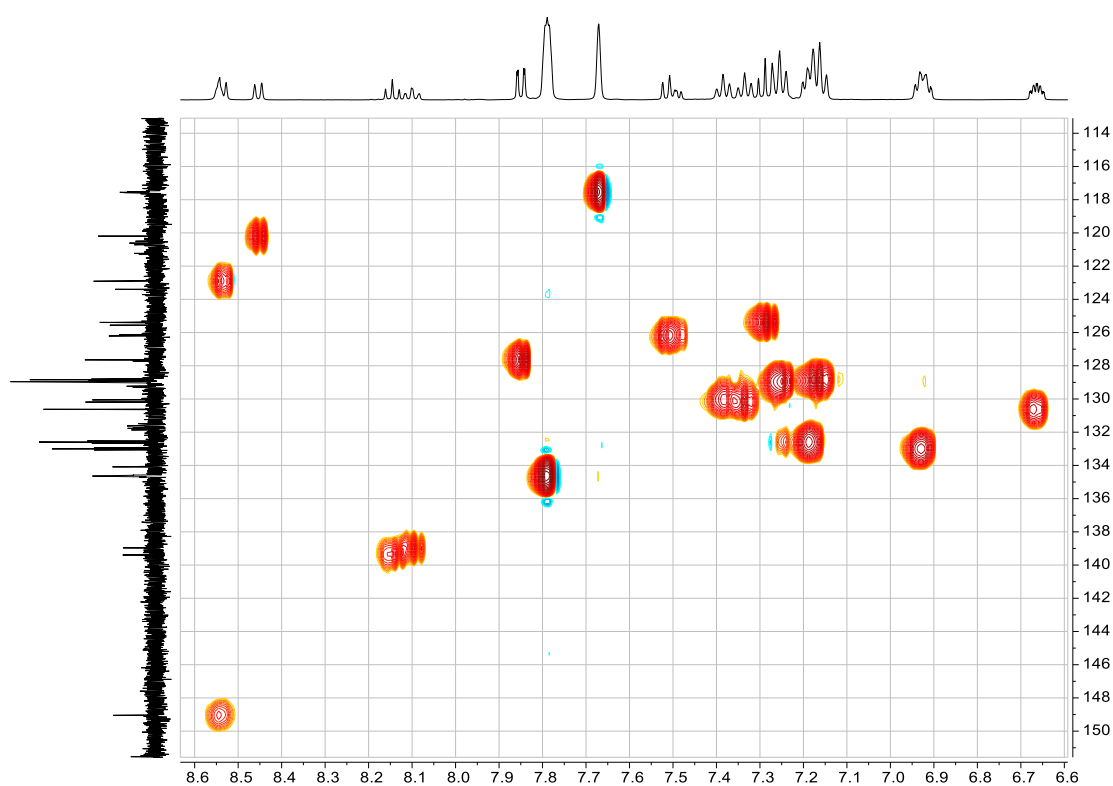


Fig. S59 The aromatic region of the HMQC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K) of $[\text{Cu}(\text{xantphos})(\text{Mebpy})][\text{BArF}_4]$. Scale: δ / ppm.

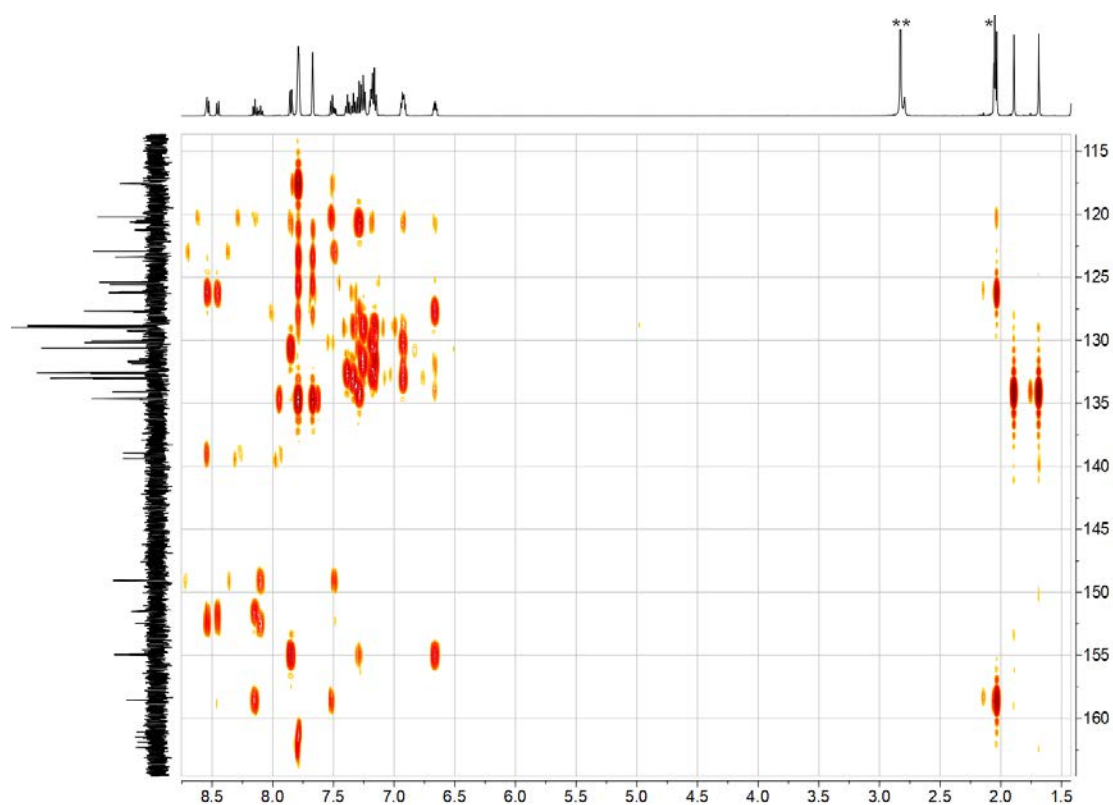


Fig. S60 Part of the HMBC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K) of $[\text{Cu}(\text{xantphos})(\text{Mebpy})][\text{BAr}^{\text{F}}_4]$. Scale: δ / ppm. ** = H_2O and HDO.

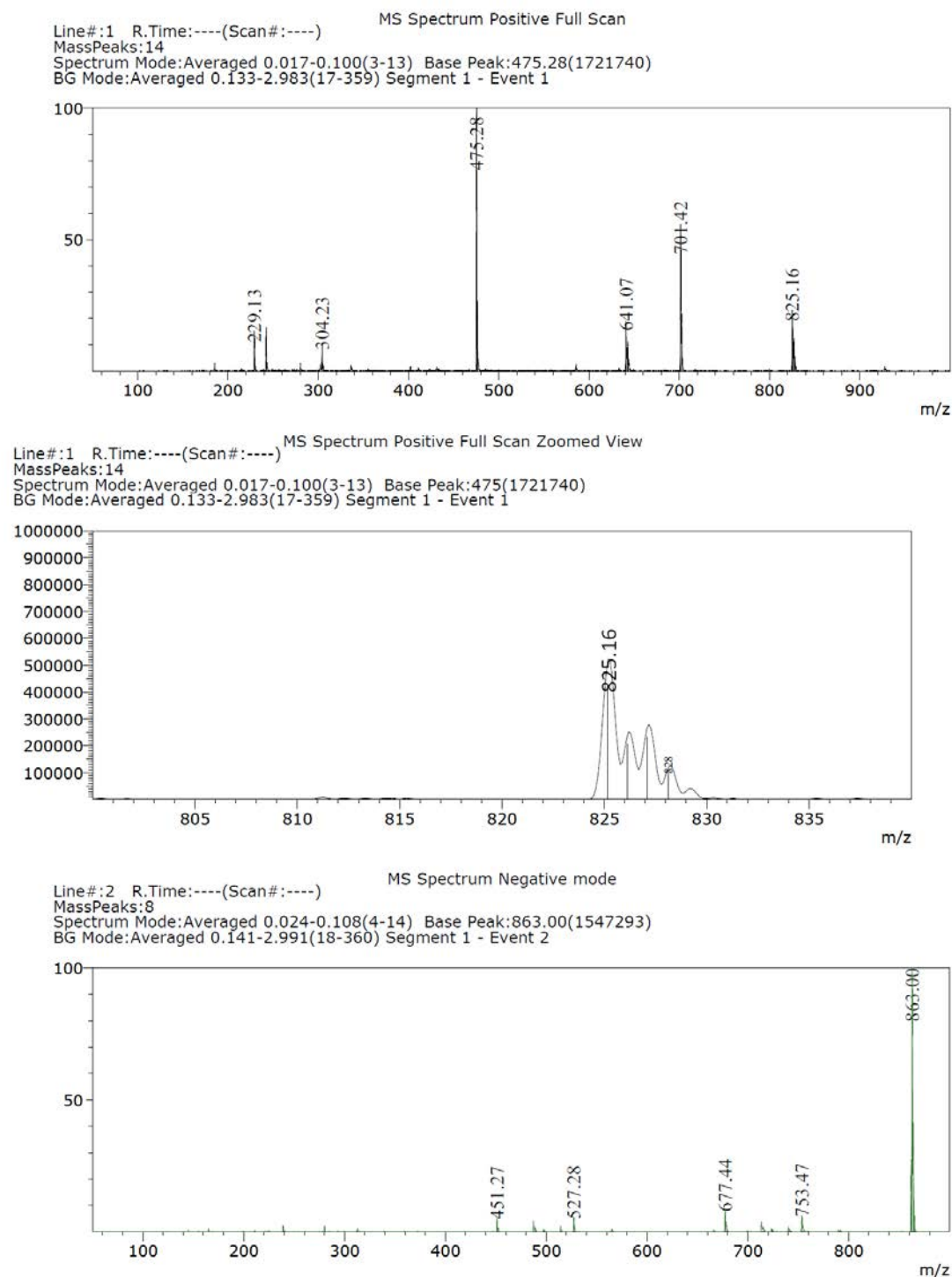


Fig. S61 The ESI mass spectrum (positive and negative mode) of $[\text{Cu}(\text{xantphos})(\text{Me}_2\text{bpy})][\text{BAr}^{\text{F}}_4]$.

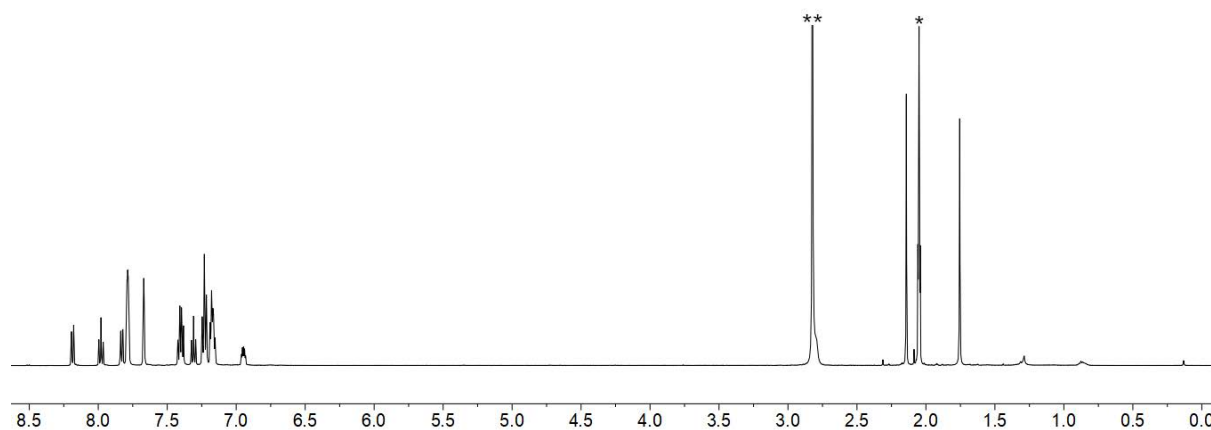


Fig. S62 ^1H NMR spectrum of $[\text{Cu}(\text{xantphos})(\text{Me}_2\text{bpy})][\text{BARF}_4]$ (500 MHz, 298 K, acetone- d_6). * = residual acetone- d_6 ; ** = H_2O and HDO.

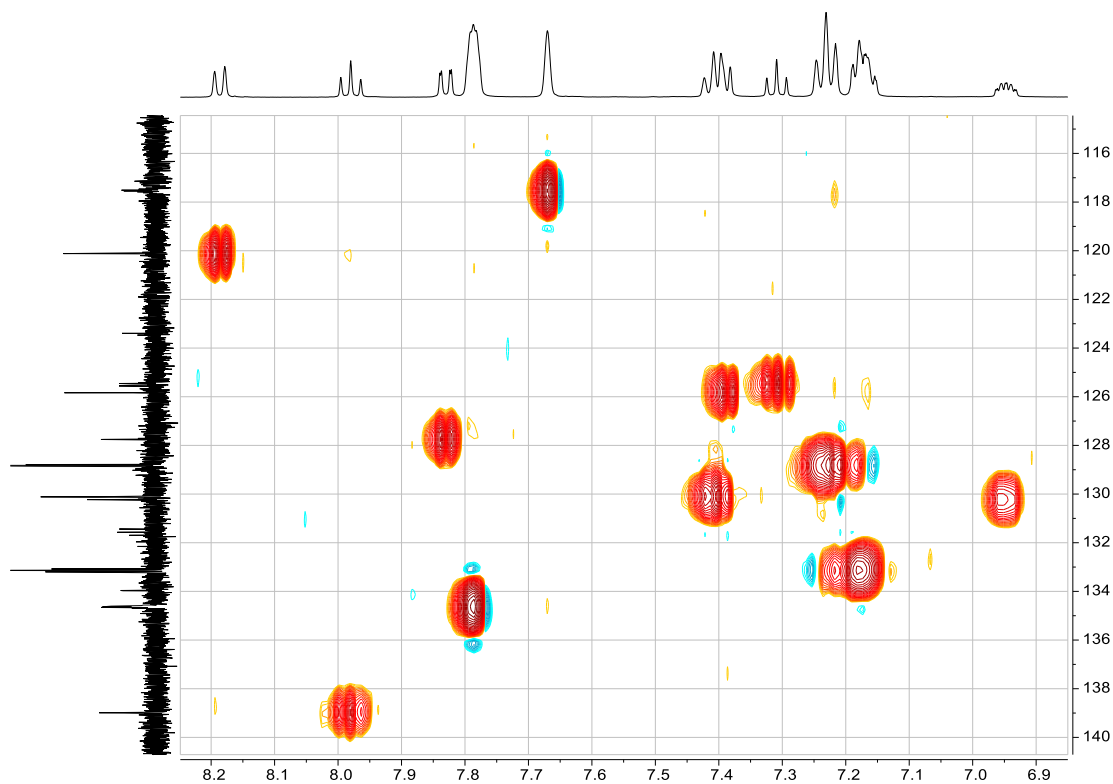


Fig. S63 The aromatic region of the HMQC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K) of $[\text{Cu}(\text{xantphos})(\text{Me}_2\text{bpy})][\text{BARF}_4]$. Scale: δ / ppm.

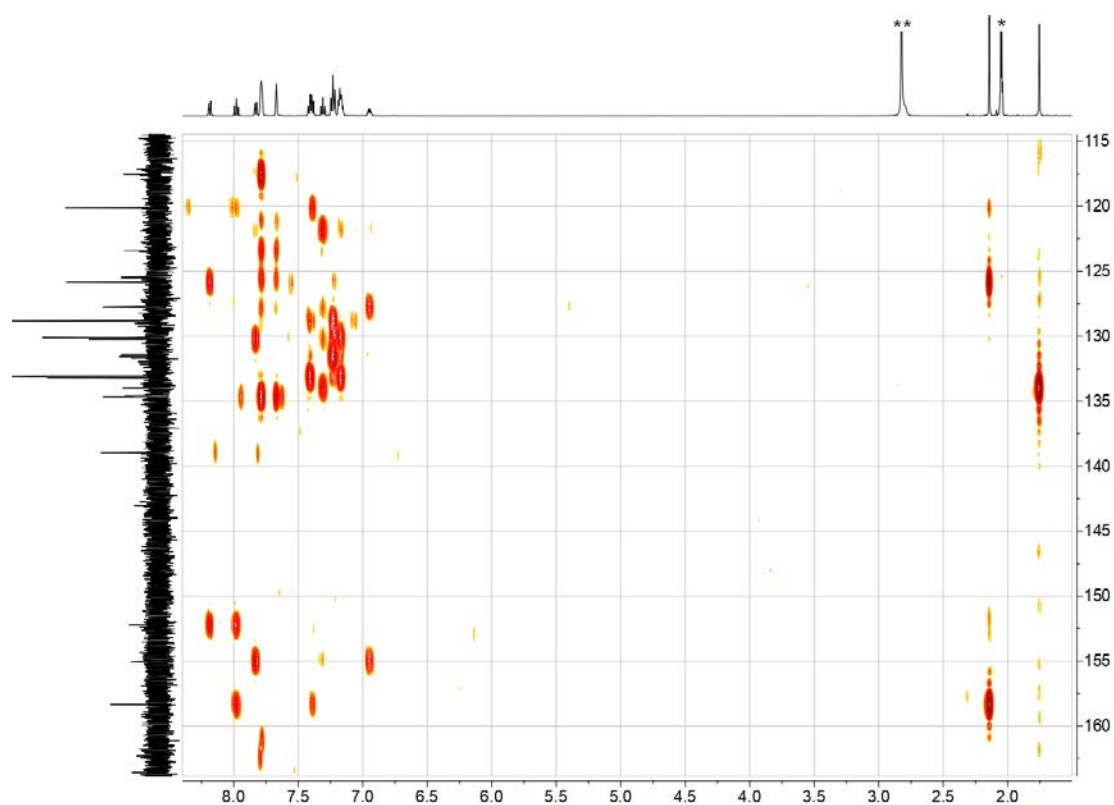


Fig. S64. Part of the HMBC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K) of $[\text{Cu}(\text{xantphos})(\text{Me}_2\text{bpy})][\text{BAr}^{\text{F}}_4]$. Scale: δ / ppm. ** = H_2O and HDO .

Table S1 Crystallographic data for the Cu(I) complexes

Compound	[Cu(POP)(Mebpy)][PF ₆]·0.5CH ₂ Cl ₂ ·0.3Et ₂ O	[Cu(xantphos)(Mebpy)][PF ₆]·0.5CH ₂ Cl ₂ ·Et ₂ O	[Cu(xantphos)(Mebpy)][BF ₄]·CH ₂ Cl ₂ ·Et ₂ O
Formula	C _{48.70} H _{41.70} ClCuF ₆ N ₂ O _{1.30} P ₃	C _{54.50} H ₅₃ ClCuF ₆ N ₂ O ₂ P ₃	C ₅₅ H ₅₄ BCl ₂ CuF ₄ N ₂ O ₂ P ₂
Formula weight	981.64	1073.89	1058.19
Crystal colour and habit	Yellow block	Yellow block	Yellow block
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 1̄	<i>P</i> 1̄
<i>a</i> , <i>b</i> , <i>c</i> / Å	9.7279(9), 16.4029(15), 29.365(3)	11.0667(8), 15.0405(11), 18.1887(14)	10.8320(5), 14.9163(6), 18.2441(8)
<i>α</i> , <i>β</i> , <i>γ</i> / °	90, 96.379(2), 90	109.125(2), 96.617(2), 109.348(2)	109.7369(15), 93.2992(17), 110.6852(16)
<i>U</i> / Å ³	4656.6(7)	2612.4(3)	2542.84(19)
<i>D</i> _c / Mg m ⁻³	1.400	1.365	1.382
<i>Z</i>	4	2	2
Radiation type	Cu-Kα	Cu-Kα	Cu-Kα
<i>μ</i> / mm ⁻¹	2.704	2.467	2.649
<i>T</i> / K	150	150	150
Refln. collected (<i>R</i> _{int})	27579 (0.0258)	33044(0.0307)	33057 (0.0267)
Unique refln.	8442	9401	9409
Refln. for refinement	8258	9314	8707
Parameters	615	645	547
Threshold	<i>I</i> > 2σ(<i>I</i>)	<i>I</i> > 2σ(<i>I</i>)	<i>I</i> > 2σ(<i>I</i>)
<i>R</i> 1 (<i>R</i> 1 all data)	0.0534 (0.0541)	0.0569 (0.0573)	0.0610 (0.0645)
<i>wR</i> 2 (<i>wR</i> 2 all data)	0.1426 (0.1431)	0.1806 (0.1813)	0.1758 (0.1805)
Goodness of fit	1.152	1.078	1.042
CCDC deposition number	2081386	2081394	2081392
Compound	[Cu(xantphos)(Me ₂ bpy)][PF ₆]	[Cu(xantphos)(Me ₂ bpy)][BF ₄]·0.5C ₆ H ₁₂ ·0.8Me ₂ CO	[Cu(xantphos)(Me ₂ bpy)][BPh ₄]·0.7Me ₂ CO
Formula	C ₅₁ H ₄₄ CuF ₆ N ₂ O ₃	C _{56.4} H _{54.8} BCuF ₄ N ₂ O _{1.8} P ₂	C _{77.10} H _{68.20} BCuN ₂ O _{1.70} P ₂
Formula weight	971.33	1001.71	1186.22
Crystal colour and habit	Yellow block	Yellow block	Yellow plate
Crystal system	Orthorhombic	Triclinic	Orthorhombic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 1̄	<i>P</i> na2 ₁
<i>a</i> , <i>b</i> , <i>c</i> / Å	19.7640(3), 19.7573(3), 22.6092(4)	11.0536(7), 14.3637(9), 18.0991(12)	28.7566(8), 14.3706(4), 30.3845(10)
<i>α</i> , <i>β</i> , <i>γ</i> / °	90, 90, 90	67.326(3), 77.613(3), 85.130(3)	90, 90, 90
<i>U</i> / Å ³	8828.5(2)	2589.8(3)	12556.4(6)
<i>D</i> _c / Mg m ⁻³	1.462	1.285	1.255
<i>Z</i>	8	2	8
Radiation type	Ga-Kα	Cu-Kα	Cu-Kα
<i>μ</i> / mm ⁻¹	3.715	1.642	1.345
<i>T</i> / K	150	150	150
Refln. collected (<i>R</i> _{int})	55800 (0.0882)	27941 (0.0277)	48359 (0.0895)
Unique refln.	17467	9439	18870
Refln. for refinement	13131	8700	15392
Parameters	1162	587	1507
Threshold	<i>I</i> > 2σ(<i>I</i>)	<i>I</i> > 2σ(<i>I</i>)	<i>I</i> > 2σ(<i>I</i>)
<i>R</i> 1 (<i>R</i> 1 all data)	0.0670 (0.1002)	0.0583 (0.0613)	0.0592 (0.0764)
<i>wR</i> 2 (<i>wR</i> 2 all data)	0.1495 (0.1668)	0.1805 (0.1842)	0.1389 (0.1509)
Goodness of fit	1.022	1.047	1.009
Flack parameter	0.370(6)		0.10(3)
CCDC deposition number	2081393	2081391	2081387

Compound	[Cu(xantphos)(Me ₂ bpy)][BAR ^F ₄]	[Cu(POP)(Me ₂ bpy)][BAR ^F ₄]	[Cu(POP)(Mebpy)][BAR ^F ₄].C ₆ H ₁₂
Formula	C ₈₃ H ₅₆ BCuF ₂₄ N ₂ OP ₂	C ₈₀ H ₅₂ BCuF ₂₄ N ₂ OP ₂	C ₈₅ H ₆₂ B Cu F ₂₄ N ₂ O P ₂
Formula weight	1689.58	1649.52	1719.65
Crystal colour and habit	Yellow block	Yellow block	Yellow plate
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , <i>b</i> , <i>c</i> / Å	10.7126(2), 18.8554(4), 19.4247(4)	13.4775(10), 13.7430(11), 20.8898(16)	14.2327(4), 30.8018(9), 18.4314(5)
α , β , γ / °	79.4640(10), 89.642(2), 74.7590(10)	89.276(3), 76.079(3), 85.590(3)	90, 94.048(2), 90
<i>U</i> / Å ³	3718.16(13)	3744.4(5)	8060.0(4)
<i>D</i> _c / Mg m ⁻³	1.509	1.463	1.417
<i>Z</i>	2	2	4
Radiation type	Ga-K α	Cu-K α	Cu-K α
μ / mm ⁻¹	2.475	1.768	1.665
<i>T</i> / K	150	150	150
Refln. collected (<i>R</i> _{int})	52347 (0.0686)	34371 (0.0266)	58689 (0.0377)
Unique refln.	14623	13675	12748
Refln. for refinement	13290	12292	14521
Parameters	1037	1002	962
Threshold	<i>I</i> > 2 σ (<i>I</i>)	<i>I</i> > 2 σ (<i>I</i>)	<i>I</i> > 2 σ (<i>I</i>)
<i>R</i> 1 (<i>R</i> 1 all data)	0.0644 (0.0693)	0.0633 (0.0689)	0.0865 (0.0953)
<i>wR</i> 2 (<i>wR</i> 2 all data)	0.1716 (0.1760)	0.1633 (0.1692)	0.2089 (0.2156)
Goodness of fit	1.039	1.051	1.057
CCDC deposition number	2081388	2081389	2081390

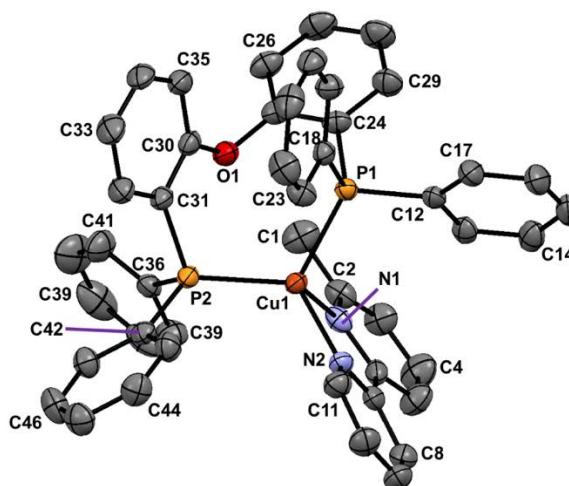


Fig. S65 Structure of the [Cu(POP)(Mebpy)]⁺ cation in [Cu(POP)(Mebpy)][PF₆].0.5CH₂Cl₂.0.5Et₂O. H atoms and solvent molecules are omitted and ellipsoids are plotted at 50% probability level. Selected bond parameters:

Cu1–P2 = 2.2528(8),
 Cu1–P1 = 2.2736(8),
 Cu1–N2 = 2.051(2),
 Cu1–N1 = 2.118(2),
 C25–O1 = 1.397(4),
 C30–O1 = 1.380(4) Å;
 P2–Cu1–P1 = 112.93(3),
 P2–Cu1–N2 = 118.39(7),
 P1–Cu1–N2 = 113.20(7),
 P2–Cu1–N1 = 119.44(7),
 P1–Cu1–N1 = 108.74(7),
 N2–Cu1–N1 = 80.11(9),
 C25–O1–C30 = 119.0(2) °.

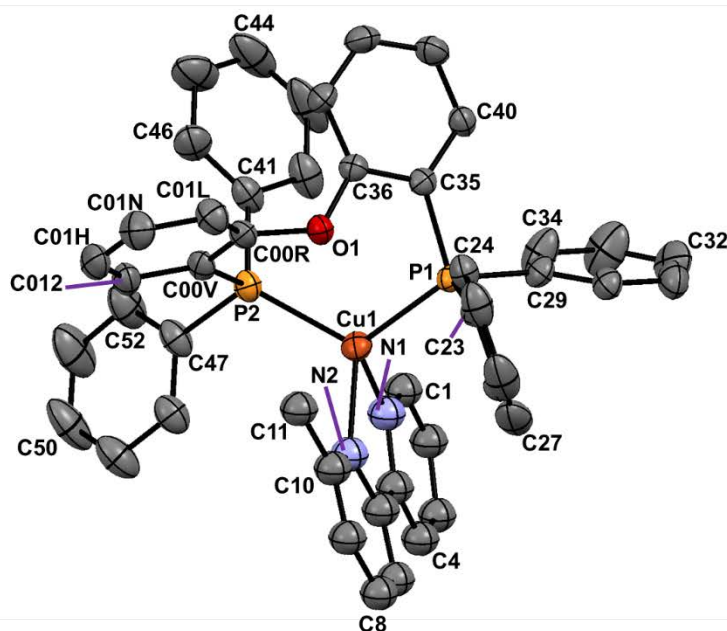


Fig. S66 Structure of the $[\text{Cu}(\text{POP})(\text{Mebpy})]^+$ cation in $[\text{Cu}(\text{POP})(\text{Mebpy})][\text{BAr}^f_4] \cdot \text{C}_6\text{H}_{12}$. H atoms and solvent molecules are omitted and ellipsoids are plotted at 50% probability level. Selected bond parameters:

Molecule 1

$\text{Cu1-P2} = 2.254(1)$,
 $\text{Cu1-P1} = 2.272(1)$,
 $\text{Cu1-N2} = 2.163(6)$,
 $\text{Cu1-N1} = 2.028(6)$,
 $\text{C36-O1} = 1.385(5)$;
 $\text{C00R-O1} = 1.397(5) \text{ \AA}$;
 $\text{P2-Cu1-P1} = 115.43(4)$,
 $\text{P2-Cu1-N2} = 115.2(2)$,
 $\text{P1-Cu1-N2} = 111.2(2)$,
 $\text{P2-Cu1-N1} = 115.9(2)$,
 $\text{P1-Cu1-N1} = 114.8(2)$,
 $\text{N2-Cu1-N1} = 79.1(2)$,
 $\text{C36-O1-C00R} = 121.5(3)^\circ$.

Molecule 2

$\text{Cu1-P2} = 2.254(1)$,
 $\text{Cu1-P1} = 2.272(1)$,
 $\text{Cu1-N4} = 1.983(6)$,
 $\text{Cu1-N3} = 2.049(6)$,
 $\text{C36-O2} = 1.385(5)$,
 $\text{C00R-O2} = 1.397(5) \text{ \AA}$;
 $\text{P2-Cu1-P1} = 115.43(4)$,
 $\text{P2-Cu1-N4} = 109.7(2)$,
 $\text{P1-Cu1-N4} = 106.6(2)$,
 $\text{P2-Cu1-N3} = 120.1(2)$,
 $\text{P1-Cu1-N3} = 116.7(2)$,
 $\text{N4-Cu1-N3} = 81.4(3)$,
 $\text{C36-O2-C00R} = 121.5(3)^\circ$.

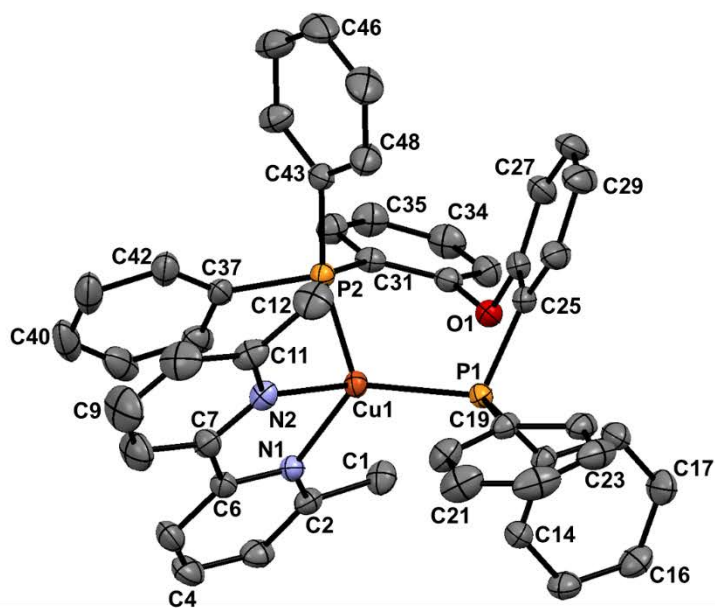


Fig. S67 Structure of the $[\text{Cu}(\text{POP})(\text{Me}_2\text{bpy})]^+$ cation in $[\text{Cu}(\text{POP})(\text{Me}_2\text{bpy})][\text{BAr}^{\text{F}}_4]$. H atoms and solvent molecules are omitted and ellipsoids are plotted at 50% probability level. Selected bond parameters:

$\text{Cu1-P2} = 2.3185(7)$,
 $\text{Cu1-P1} = 2.2296(8)$,
 $\text{Cu1-N2} = 2.089(3)$,
 $\text{Cu1-N1} = 2.068(3)$,
 $\text{C26-O1} = 1.387(4)$,
 $\text{C32-O1} = 1.395(3) \text{ \AA}$;
 $\text{P2-Cu1-P1} = 115.92(3)$,
 $\text{P2-Cu1-N2} = 103.13(7)$,
 $\text{P1-Cu1-N2} = 125.13(7)$,
 $\text{P2-Cu1-N1} = 100.75(7)$,
 $\text{P1-Cu1-N1} = 124.41(7)$,
 $\text{N2-Cu1-N1} = 80.5(1)$,
 $\text{C26-O1-C32} = 118.5(2)^\circ$.

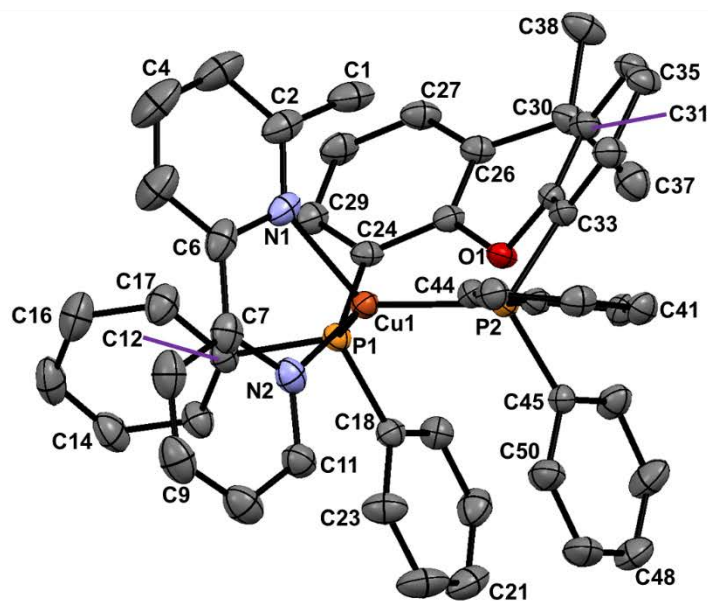


Fig. S68 Structure of the $[\text{Cu}(\text{xantphos})(\text{Mebpy})]^+$ cation in $[\text{Cu}(\text{xantphos})(\text{Mebpy})][\text{PF}_6] \cdot \text{CH}_2\text{Cl}_2 \cdot \text{Et}_2\text{O}$. H atoms and solvent molecules are omitted and ellipsoids are plotted at 50% probability level. Selected bond parameters:

$\text{Cu1-P2} = 2.2509(9)$,
 $\text{Cu1-P1} = 2.2677(8)$,
 $\text{Cu1-N2} = 2.040(3)$,
 $\text{Cu1-N1} = 2.074(4)$,
 $\text{C25-O1} = 1.388(4)$,
 $\text{C32-O1} = 1.397(4)$ Å;
 $\text{P2-Cu1-P1} = 113.44(3)$,
 $\text{P2-Cu1-N2} = 114.95(9)$,
 $\text{P1-Cu1-N2} = 111.21(9)$,
 $\text{P2-Cu1-N1} = 121.03(9)$,
 $\text{P1-Cu1-N1} = 111.30(9)$,
 $\text{N2-Cu1-N1} = 80.8(1)$,
 $\text{C25-O1-C32} = 114.2(2)^\circ$.

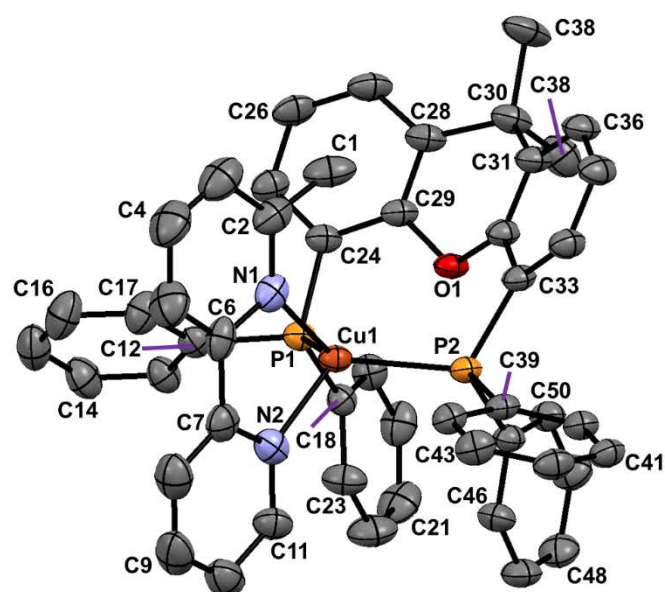


Fig. S69 Structure of the $[\text{Cu}(\text{xantphos})(\text{Mebpy})]^+$ cation in $[\text{Cu}(\text{xantphos})(\text{Mebpy})][\text{BF}_4]$. H atoms and solvent molecules are omitted and ellipsoids are plotted at 50% probability level. Selected bond parameters:

$\text{Cu1-P2} = 2.2559(9)$,
 $\text{Cu1-P1} = 2.2654(8)$,
 $\text{Cu1-N2} = 2.045(2)$,
 $\text{Cu1-N1} = 2.072(4)$,
 $\text{C29-O1} = 1.389(3)$,
 $\text{C32-O1} = 1.399(4)$ Å;
 $\text{P2-Cu1-P1} = 113.34(3)$,
 $\text{P2-Cu1-N2} = 114.83(9)$,
 $\text{P1-Cu1-N2} = 111.77(9)$,
 $\text{P2-Cu1-N1} = 119.20(9)$,
 $\text{P1-Cu1-N1} = 112.66(9)$,
 $\text{N2-Cu1-N1} = 81.1(1)$,
 $\text{C29-O1-C32} = 113.9(2)^\circ$.

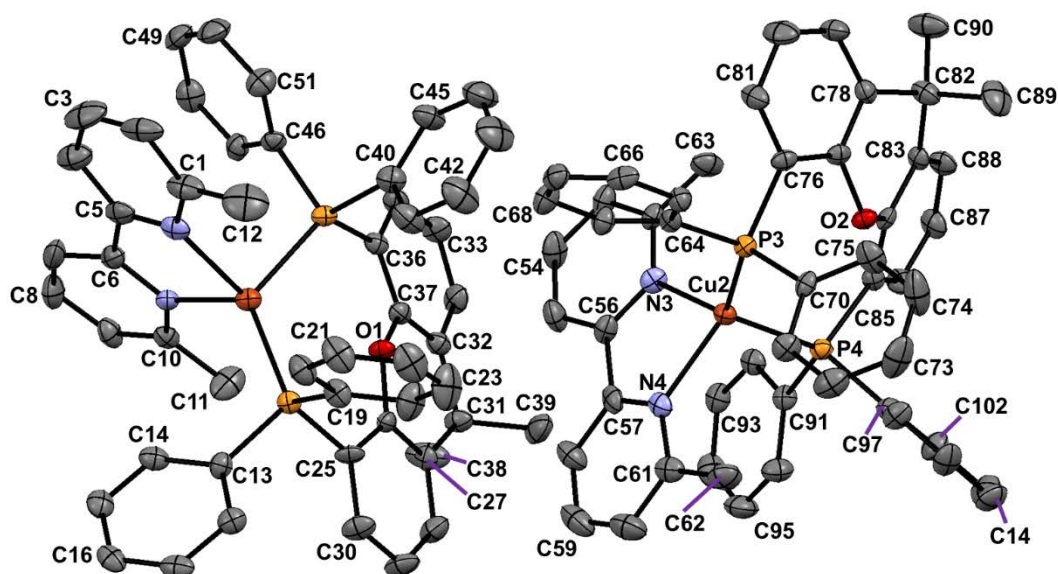


Fig. S70 Structure of the $[\text{Cu}(\text{xantphos})(\text{Me}_2\text{bpy})]^+$ cations in $[\text{Cu}(\text{xantphos})(\text{Me}_2\text{bpy})][\text{PF}_6]$. H atoms and solvent molecules are omitted and ellipsoids are plotted at 50% probability level. Selected bond parameters:

Molecule 1

Cu1–P2 = 2.323(2),
 Cu1–P1 = 2.280(2),
 Cu1–N2 = 2.087(6),
 Cu1–N1 = 2.142(7),
 C26–O1 = 1.369(8);
 C37–O1 = 1.392(9) Å;
 P2–Cu1–P1 = 121.53(8),
 P2–Cu1–N2 = 101.7(2),
 P1–Cu1–N2 = 120.5(2),
 P2–Cu1–N1 = 97.5(2),
 P1–Cu1–N1 = 126.9(2),
 N2–Cu1–N1 = 79.1(2),
 C26–O1–C37 = 118.7(6) °.

Molecule 2

Cu2–P4 = 2.320(2),
 Cu2–P3 = 2.266(2),
 Cu2–N4 = 2.127(7),
 Cu2–N3 = 2.096(6),
 C77–O2 = 1.401(8),
 C84–O2 = 1.40(1) Å;
 P4–Cu2–P3 = 117.77(8),
 P4–Cu2–N4 = 99.9(2),
 P3–Cu2–N4 = 129.3(2),
 P4–Cu2–N3 = 102.9(2),
 P3–Cu2–N3 = 119.8(2),
 N4–Cu2–N3 = 79.0(2),
 C77–O2–C84 = 115.0(6) °.

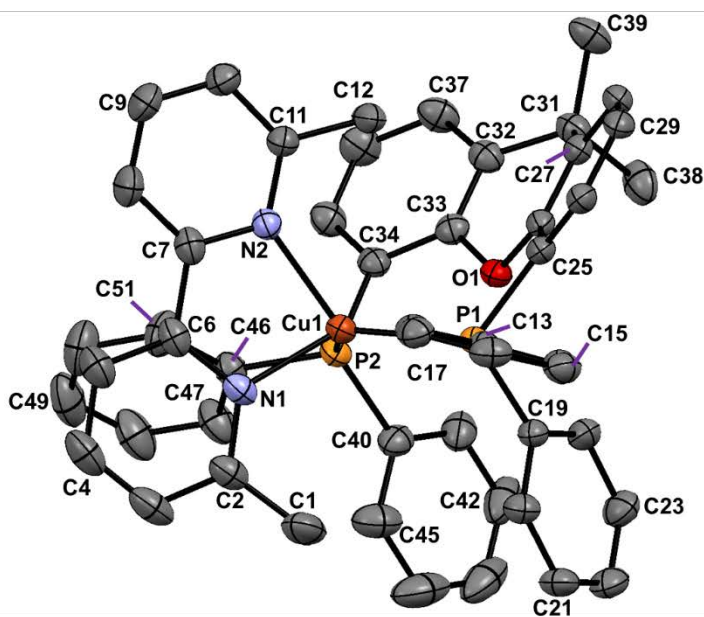


Fig. S71 Structure of the $[\text{Cu}(\text{xantphos})(\text{Me}_2\text{bpy})]^+$ cation in $[\text{Cu}(\text{xantphos})(\text{Me}_2\text{bpy})][\text{BF}_4] \cdot \text{C}_6\text{H}_{12}$. H atoms and solvent molecules are omitted and ellipsoids are plotted at 50% probability level. Selected bond parameters:

$\text{Cu1-P2} = 2.2988(7)$,
 $\text{Cu1-P1} = 2.2695(9)$,
 $\text{Cu1-N2} = 2.110(3)$,
 $\text{Cu1-N1} = 2.091(2)$,
 $\text{C26-O1} = 1.397(3)$,
 $\text{C33-O1} = 1.387(4)$ Å;
 $\text{P2-Cu1-P1} = 111.54(3)$,
 $\text{P2-Cu1-N2} = 110.18(7)$,
 $\text{P1-Cu1-N2} = 120.03(7)$,
 $\text{P2-Cu1-N1} = 109.75(7)$,
 $\text{P1-Cu1-N1} = 121.94(7)$,
 $\text{N2-Cu1-N1} = 79.60(9)$,
 $\text{C26-O1-C33} = 114.8(2)^\circ$.

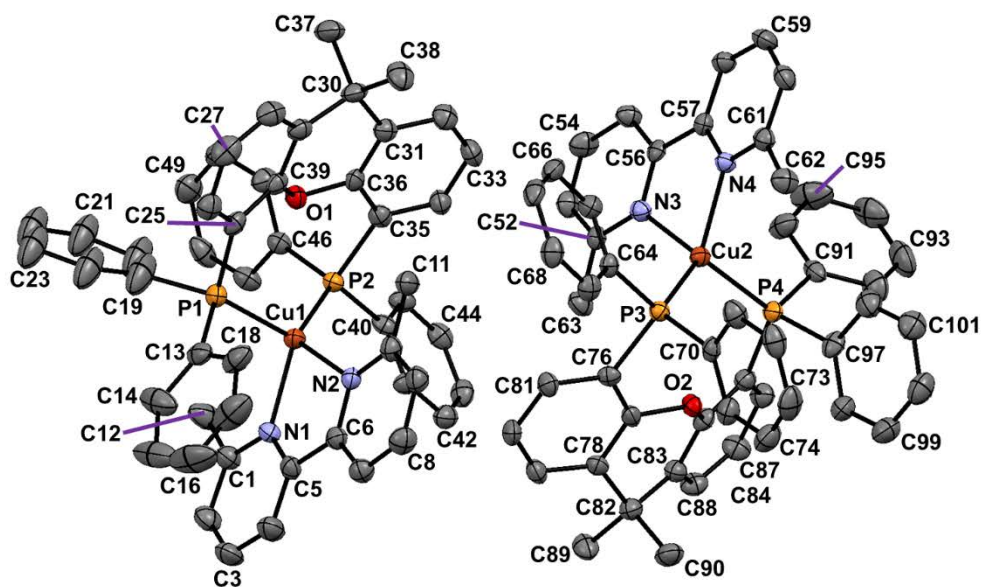


Fig. S72 Structure of the $[\text{Cu}(\text{xantphos})(\text{Me}_2\text{bpy})]^+$ cations in $[\text{Cu}(\text{xantphos})(\text{Me}_2\text{bpy})][\text{BPh}_4] \cdot 0.7\text{C}_3\text{H}_6\text{O}$. H atoms and solvent molecules are omitted and ellipsoids are plotted at 50% probability level. Selected bond parameters:

Molecule 1

Cu1–P2 = 2.255(2),
 Cu1–P1 = 2.310(2),
 Cu1–N2 = 2.129(5),
 Cu1–N1 = 2.093(5),
 C36–O1 = 1.377(7);
 C39–O1 = 1.376(7) Å;
 P2–Cu1–P1 = 117.99(7),
 P2–Cu1–N2 = 123.1(2),
 P1–Cu1–N2 = 100.7(2),
 P2–Cu1–N1 = 124.1(1),
 P1–Cu1–N1 = 103.8(1),
 N2–Cu1–N1 = 79.3(2),
 C36–O1–C39 = 118.5(5) °.

Molecule 2

Cu2–P4 = 2.306(2),
 Cu2–P3 = 2.287(2),
 Cu2–N4 = 2.122(5),
 Cu2–N3 = 2.102(5),
 C77–O2 = 1.397(7),
 C84–O2 = 1.387(7) Å;
 P4–Cu2–P3 = 113.48(7),
 P4–Cu2–N4 = 113.3(1),
 P3–Cu2–N4 = 118.1(1),
 P4–Cu2–N3 = 108.5(2),
 P3–Cu2–N3 = 120.1(2),
 N4–Cu2–N3 = 78.9(2),
 C77–O2–C84 = 115.9(4) °.

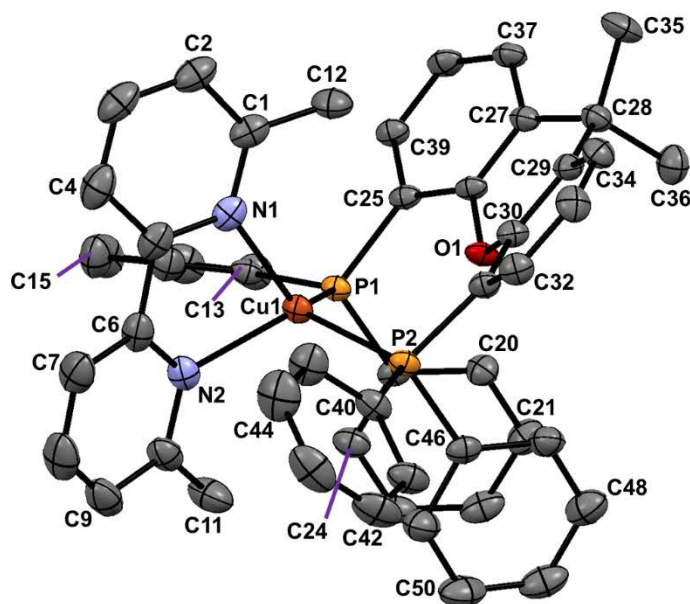


Fig. S73 Structure of the $[\text{Cu}(\text{xantphos})(\text{Me}_2\text{bpy})]^+$ cation in $[\text{Cu}(\text{xantphos})(\text{Me}_2\text{bpy})][\text{BAR}^{\text{F}}_4] \cdot \text{C}_6\text{H}_{12}$. H atoms and solvent molecules are omitted and ellipsoids are plotted at 50% probability level. Selected bond parameters:

$\text{Cu1-P2} = 2.2914(7)$,
 $\text{Cu1-P1} = 2.2871(8)$,
 $\text{Cu1-N2} = 2.116(2)$,
 $\text{Cu1-N1} = 2.122(2)$,
 $\text{C26-O1} = 1.387(3)$,
 $\text{C30-O1} = 1.386(3)$ Å;
 $\text{P2-Cu1-P1} = 113.12(3)$,
 $\text{P2-Cu1-N2} = 109.78(7)$,
 $\text{P1-Cu1-N2} = 119.10(7)$,
 $\text{P2-Cu1-N1} = 112.14(7)$,
 $\text{P1-Cu1-N1} = 119.31(7)$,
 $\text{N2-Cu1-N1} = 79.02(9)$,
 $\text{C26-O1-C30} = 116.6(2)^\circ$.

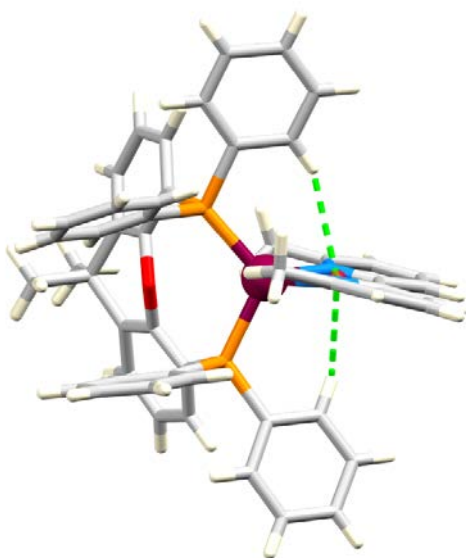


Fig. S74 One of the independent cations in $[\text{Cu}(\text{xantphos})(\text{Me}_2\text{bpy})][\text{BPh}_4]$ features $\text{C-H}\cdots\pi$ contacts between one phenyl ring of each PPh_2 group and the bpy domain; the centroid of the chelate ring is shown in red.

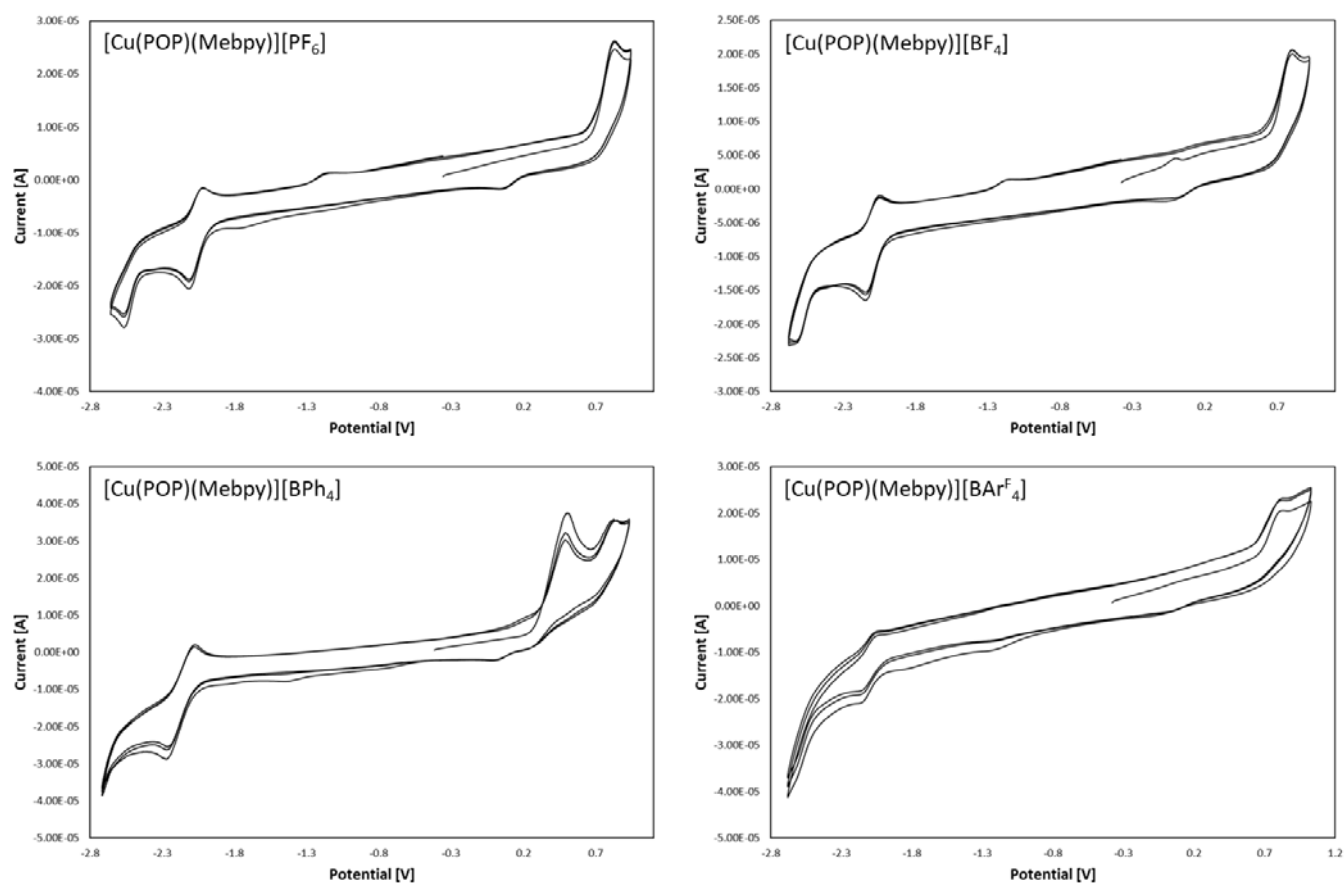


Fig. S75 Three consecutive scans in the cyclic voltammograms of $[\text{Cu}(\text{POP})(\text{Mebpy})][\text{A}]$ in CH_2Cl_2 solution (ca. $10^{-4} \text{ mol dm}^{-3}$) with $[\text{nBu}_4\text{N}][\text{PF}_6]$ as supporting electrolyte and a scan rate of 0.1 V s^{-1} (referenced to internal $\text{Fc}/\text{Fc}^+ = 0.0 \text{ V}$).

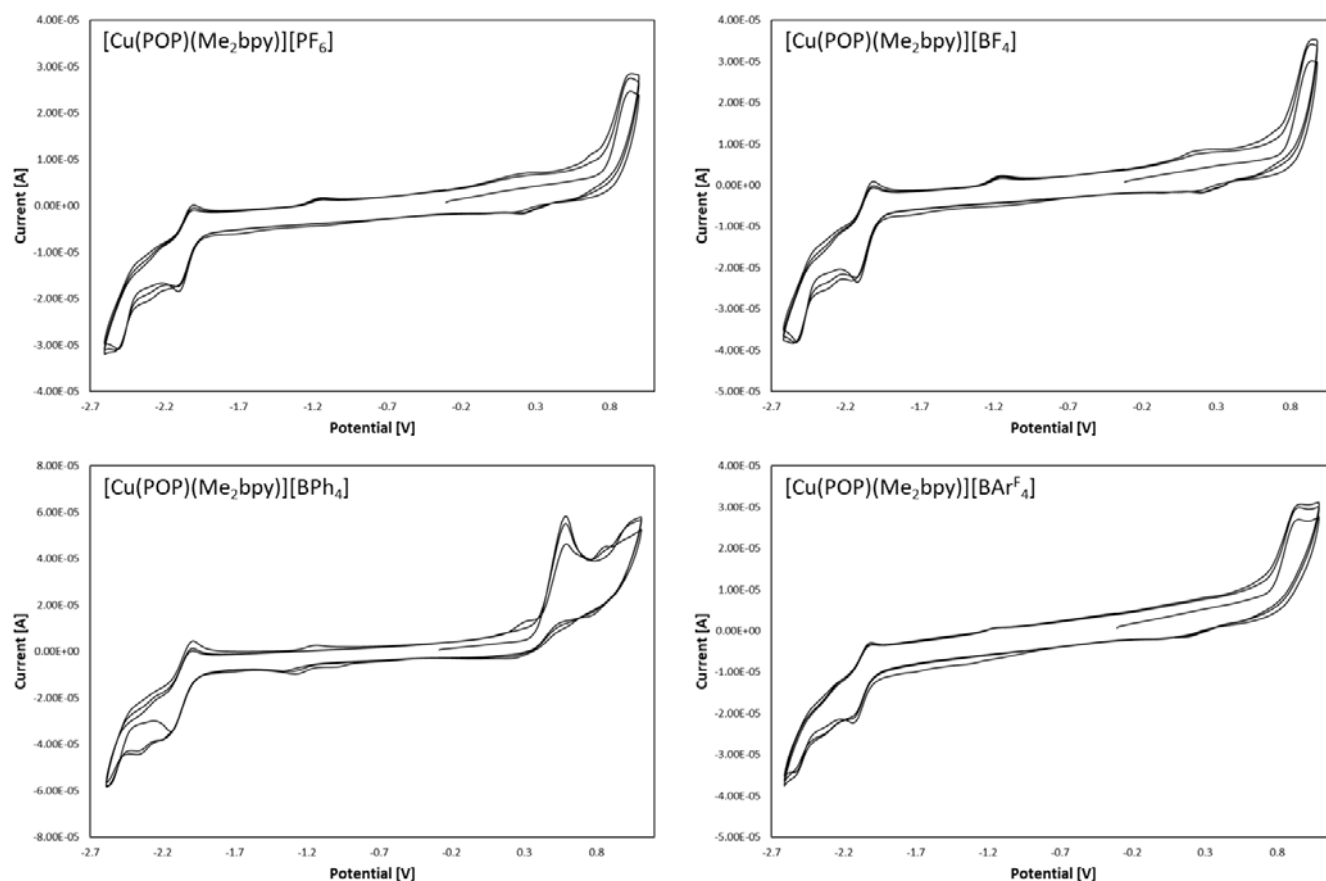


Fig. S76 Three consecutive scans in the cyclic voltammograms of $[\text{Cu}(\text{POP})(\text{Me}_2\text{bpy})][\text{A}]$ in CH_2Cl_2 solution (ca. $10^{-4} \text{ mol dm}^{-3}$) with $[\text{nBu}_4\text{N}][\text{PF}_6]$ as supporting electrolyte and a scan rate of 0.1 V s^{-1} (referenced to internal $\text{Fc}/\text{Fc}^+ = 0.0 \text{ V}$).

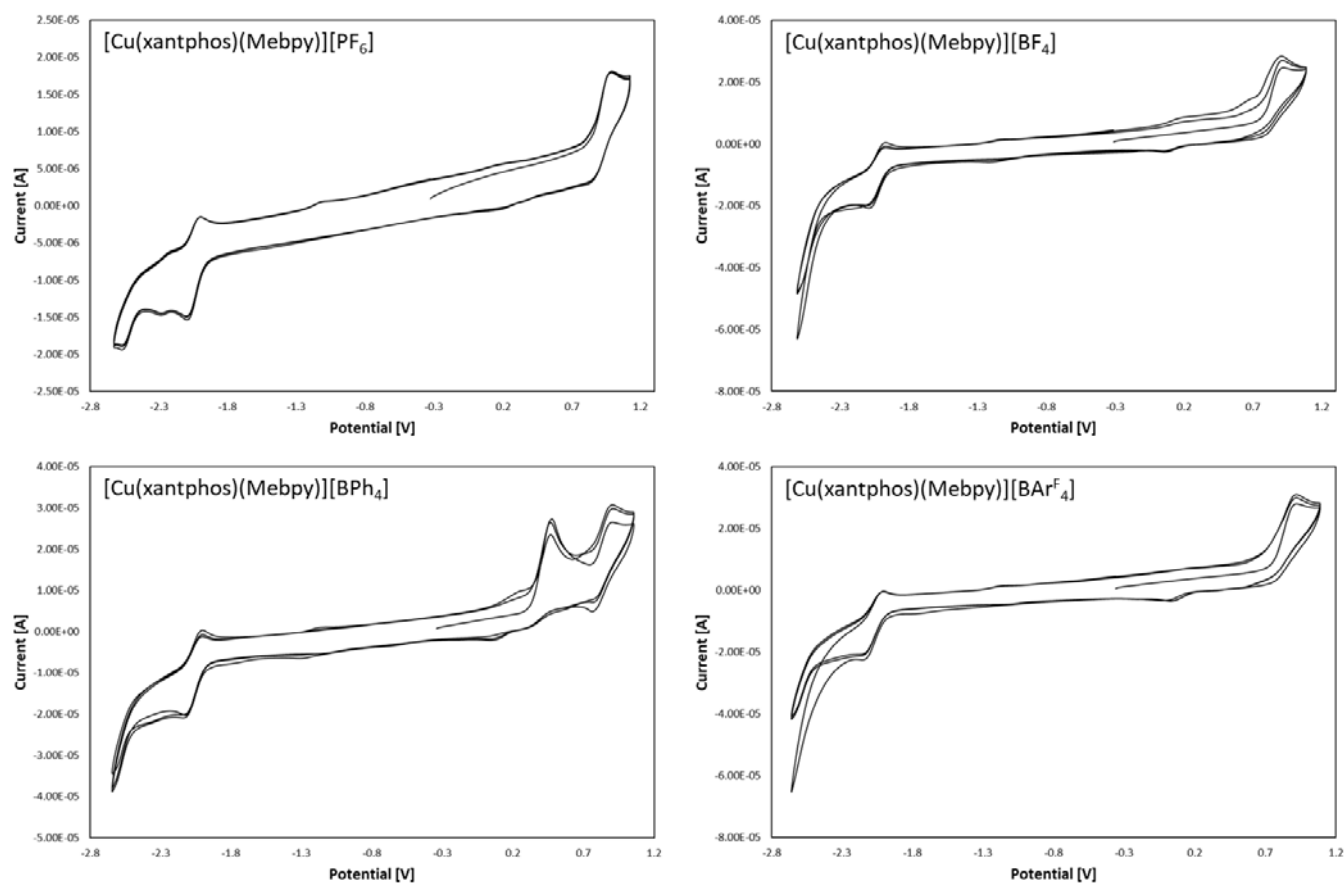


Fig. S77 Three consecutive scans in the cyclic voltammograms of $[\text{Cu}(\text{xantphos})(\text{Mebpy})][\text{A}]$ in CH_2Cl_2 solution (ca. $10^{-4} \text{ mol dm}^{-3}$) with $[\text{nBu}_4\text{N}][\text{PF}_6]$ as supporting electrolyte and a scan rate of 0.1 V s^{-1} (referenced to internal $\text{Fc}/\text{Fc}^+ = 0.0 \text{ V}$).

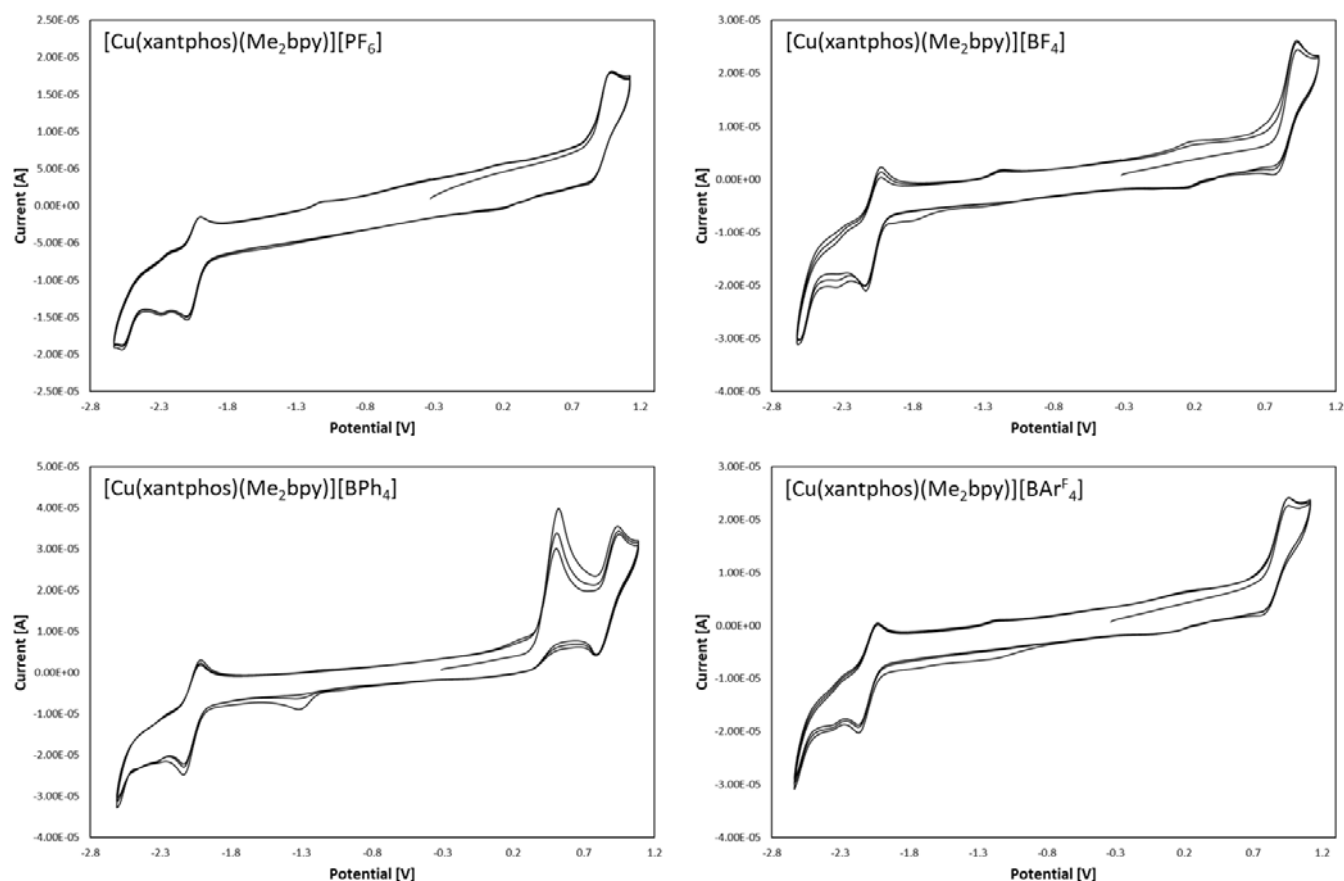


Fig. S78 Three consecutive scans in the cyclic voltammograms of $[\text{Cu}(\text{xantphos})(\text{Me}_2\text{bpy})][\text{A}]$ in CH_2Cl_2 solution (ca. $10^{-4} \text{ mol dm}^{-3}$) with $[\text{nBu}_4\text{N}][\text{PF}_6]$ as supporting electrolyte and a scan rate of 0.1 V s^{-1} (referenced to internal $\text{Fc}/\text{Fc}^+ = 0.0 \text{ V}$).

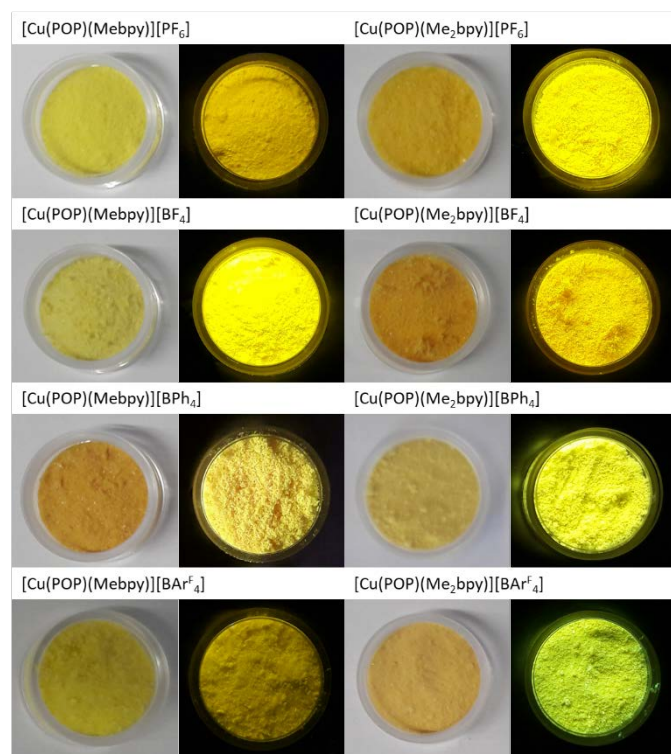


Fig. S79. Powder samples of $[\text{Cu}(\text{xantphos})(\text{N}^{\wedge}\text{N})][\text{A}]$ complexes under ambient light (left) and under UV light ($\lambda_{\text{exc}} = 366 \text{ nm}$, right).

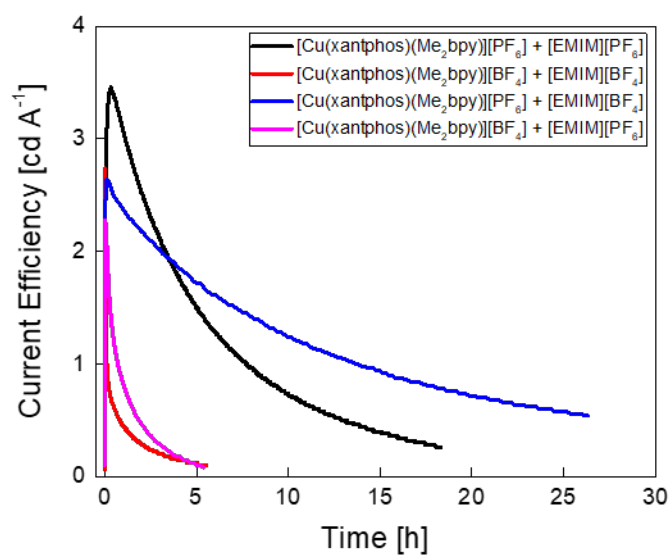


Fig. S80. Current efficiency of the best working LECs.

References

1. C. S. Smith, C. W. Branham, B. J. Marquardt and K. R. Mann, *J. Am. Chem. Soc.*, 2010, **132**, 14079-14085.