

Supporting Information:

Introducing sterically demanding substituents and π - π -interactions into $[\text{Cu}(\text{P}^{\wedge}\text{P})(\text{N}^{\wedge}\text{N})]^+$ complexes†

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Experimental and analytical data

General procedure for the preparation of the $\text{N}^{\wedge}\text{N}$ ligands (refer to Schemes 3 and 4 in the main article)

Procedure shown in Scheme 3. The following procedure was adapted from a literature method.¹ The reaction was carried out in flame-dried glassware on a Schlenk line under an N_2 atmosphere. Diisopropylamine (1.0 eq.) was dissolved in dry THF (5 mL) and the mixture was cooled to -78°C . *n*-Butyllithium in hexanes (1.0 eq.) was added and the reaction mixture was stirred for 1 h at -78°C . For the preparation of the 6-substituted ligands, a solution of 6-methyl-2,2'-bipyridine (1.0 eq.) in dry THF (10 mL) was added; to obtain the 6,6'-disubstituted ligands, a solution of 6,6'-dimethyl-2,2'-bipyridine (1.0 eq.) in dry THF (10 mL) was added. Upon the addition of the bipyridine derivative, the mixture turned dark blue. After the reaction mixture was stirred at -78°C for another 3 h, a solution of the desired bromoalkane (alkylating reagent; 0.85 eq. for singly substituted ligands/1.7 eq. for doubly substituted ligands) in dry THF (10 mL) was added and the mixture was allowed to warm up to room temperature overnight keeping the vessel submerged in the cooling bath. Then, saturated aqueous NH_4Cl (15 mL) was added and the mixture was extracted with CH_2Cl_2 (3×35 mL). The combined organic fractions were dried over MgSO_4 and filtered. The solvent was removed under reduced pressure, and the obtained material was purified by flash column chromatography.

Procedure shown in Scheme 4. The following procedure was adapted from a literature method.² The reaction was carried out in flame-dried glassware on a Schlenk line under an Ar atmosphere. 4,4'-Di-*tert*-butyl-2,2'-bipyridine or 6-methyl-2,2'-bipyridine (1.0 eq.) was dissolved in MeCN (1.5 mL) and trifluoroacetic acid (2.0 eq.), di-*tert*-butyl peroxide (8.0 eq.), butane-2,3-dione (23 eq.) and cyclohexane (9.2 eq. or 5.0 eq., respectively) were added to the solution. The mixture was sealed with a septum and evacuated via three freeze-pump-thaw cycles using a liquid N_2 bath and backfilling with Ar. The reaction mixture was stirred for three days irradiating with two 45 W compact fluorescent lamps (Philips Tornado High Lumen 45W CDL E27 1CT/6). Aqueous NaHCO_3 (saturated) was added to the mixture until it was slightly basic and the reaction mixture was extracted with EtOAc (3×50 mL). The extract was dried over MgSO_4 and filtered. The solvent was removed under reduced pressure, and the obtained material was purified by flash column chromatography and/or preparative thin layer chromatography as stated in the respective procedures. The irradiation time while stirring could be shortened to 24 h but the yield was found to be lower. An alternative light source is the Thorlabs 4-Wavelength High-Power LED Source LED4D019 powered by a DC4104 driver with the 470 nm LED (blue). Both irradiation conditions employed for the reaction are illustrated in Fig. S1.

Ligand atom labelling: See Scheme 2 in the main article for atom labels used in NMR spectroscopic assignments.

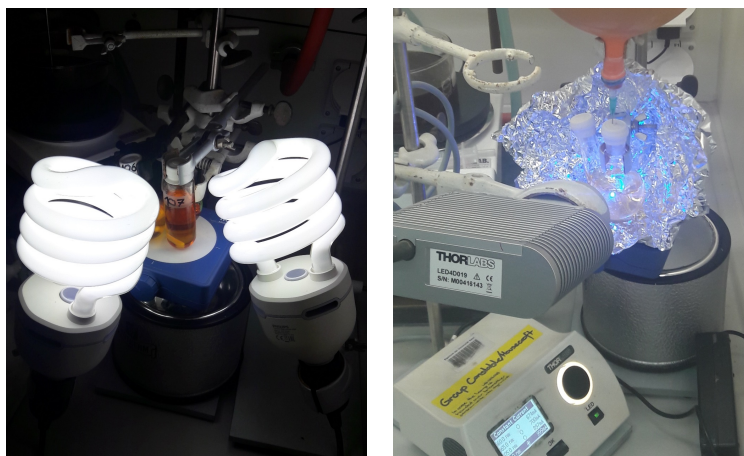


Fig. S1 Irradiation setups of the reactions carried out after general procedure B: Two 45 W compact fluorescent lamps (left), 470 nm blue LED (right).

6-(2-Cyclohexyl-ethyl)-2,2'-bipyridine (2-CyEtbpy)

General procedure A was followed. The reagents were diisopropylamine (178 mg, 0.249 mL, 1.76 mmol, 1.0 eq.), *n*-butyllithium in hexanes (479 mg, 0.704 mL, 2.5 M, 1.76 mmol, 1.0 eq.), 6-methyl-2,2'-bipyridine (300 mg, 1.76 mmol, 1.0 eq.) and (bromomethyl)-cyclohexane (265 mg, 0.209 mL, 1.50 mmol, 0.85 eq.). 6-(2-Cyclohexyl-ethyl)-2,2'-bipyridine (**2-CyEtbpy**, 215 mg, 0.808 mmol, 46%) was obtained as a colourless oil. For the purification by chromatography, two columns were run: first column: cyclohexane/ethyl acetate, gradient from 0 to 15% ethyl acetate in cyclohexane over 94 column volumes, basic alumina; second column: cyclohexane/ethyl acetate, gradient from 0 to 20% ethyl acetate in cyclohexane over 65 column volumes, basic alumina.

^1H NMR (500 MHz, CDCl_3 , 298 K) δ /ppm: 8.65 (ddd, $^3J_{\text{HH}} = 4.7$ Hz, $^4J_{\text{HH}} = 1.8$, 1.0 Hz, 1H, H^{A6}), 8.52 (ddd, $^3J_{\text{HH}} = 8.0$ Hz, $^4J_{\text{HH}} = 1.1$, 1.1 Hz, 1H, H^{A3}), 8.28 (dd, $^3J_{\text{HH}} = 7.8$ Hz, $^4J_{\text{HH}} = 1.0$ Hz, 1H, H^{B3}), 7.90 (ddd, $^3J_{\text{HH}} = 8.0$, 7.5 Hz, $^4J_{\text{HH}} = 1.8$ Hz, 1H, H^{A4}), 7.80 (dd, $^3J_{\text{HH}} = 7.7$, 7.7 Hz, 1H, H^{B4}), 7.38 (ddd, $^3J_{\text{HH}} = 7.5$, 4.8 Hz, $^4J_{\text{HH}} = 1.8$ Hz, 1H, H^{A5}), 7.28 (dd, $^3J_{\text{HH}} = 7.6$ Hz, $^4J_{\text{HH}} = 1.0$ Hz, 1H, H^{B5}), 2.87 (m, 2H, H^{a}), 1.84 (m, 2H, H^{F2}), 1.71 (m, 2H, H^{b}), 1.71 (m, 2H, H^{F3}), 1.64 (m, 1H, H^{F4}), 1.34 (m, 1H, H^{F1}), 1.24 (m, 2H, $\text{H}^{\text{F3'}}$), 1.18 (m, 1H, $\text{H}^{\text{F4'}}$), 0.99 (m, 2H, $\text{H}^{\text{F2'}}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3 , 298 K) δ /ppm: 162.9 (C^{B6}), 157.2 (C^{A2}), 156.1 (C^{B2}), 150.0 (C^{A6}), 138.0 (C^{B4}), 137.6 (C^{A4}), 124.6 (C^{A5}), 123.6 (C^{B5}), 121.4 (C^{A3}), 118.6 (C^{B3}), 38.2 (C^{b}), 38.2 (C^{F1}), 36.2 (C^{a}), 34.0 ($\text{C}^{\text{F2+F2'}}$), 27.4 ($\text{C}^{\text{F4+F4'}}$), 27.1 ($\text{C}^{\text{F3+F3'}}$). MALDI(+)-MS (m/z): 267.45 [$\text{M}+\text{H}$] $^+$ (base peak, calc. 267.18). UV-Vis (CH_2Cl_2 , 2.5×10^{-5} mol dm^{-3}): λ/nm ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) 241 (14,500), 246 (13,900), 293 (22,700), 302 sh (10,00). FTIR: 3060 (w), 2920 (s), 2849 (s), 1581 (m), 1563 (m), 1458 (m), 1447 (m), 1428 (s), 1348 (w), 1258 (w), 1147 (w), 1082 (w), 1043 (w), 992 (w), 843 (w), 760 (s), 638 (m), 620 (m), 547 (w), 402 (w) cm^{-1} . Found: C 80.59, H 8.33, N 10.40; $\text{C}_{18}\text{H}_{22}\text{N}_2$ requires C 81.16, H 8.32, N 10.52.

6,6'-Bis(2-cyclohexyl-ethyl)-2,2'-bipyridine ((2-CyEt) $_2$ bpy)

General procedure A was followed. The reagents were diisopropylamine (658 mg, 0.919 mL, 6.50 mmol, 2.0 eq.), *n*-butyllithium in hexanes (1768 mg, 2.60 mL, 2.5 M, 6.50 mmol, 2.0 eq.), 6,6'-dimethyl-2,2'-bipyridine (600 mg, 3.26 mmol, 1.0 eq.) and (bromomethyl)-cyclohexane (978 mg, 0.771 mL, 5.53 mmol, 1.7 eq.). 6,6'-Bis(2-cyclohexyl-ethyl)-2,2'-bipyridine (**((2-CyEt) $_2$ bpy**, 417 mg, 1.11 mmol, 34%) was obtained as a colourless oil. For the purification by chromatography, two columns were run: first column: cyclohexane/ethyl acetate, gradient from 1 to 20% ethyl acetate in cyclohexane over 45 column volumes, basic alumina; second column: cyclohexane/ethyl acetate, gradient from 1 to 10% ethyl acetate in cyclohexane over 37 column volumes, basic alumina.

^1H NMR (500 MHz, CDCl_3 , 298 K) δ /ppm: 8.31 (dd, $^3J_{\text{HH}} = 7.8$ Hz, $^4J_{\text{HH}} = 1.0$ Hz, 2H, H^{B3}), 7.79 (dd, $^3J_{\text{HH}} = 7.7$, 7.7 Hz, 2H, H^{B4}), 7.26 (dd, $^3J_{\text{HH}} = 7.6$ Hz, $^4J_{\text{HH}} = 1.0$ Hz, 2H, H^{B5}), 2.86 (m, 4H, H^{a}), 1.83 (m, 4H, H^{F2}), 1.71 (m, 4H, H^{b}), 1.71 (m, 4H, H^{F3}), 1.65 (m, 2H, H^{F4}), 1.65 (m, 2H, $\text{H}^{\text{F4'}}$), 1.34 (m, 2H, H^{F1}), 1.23 (m, 4H, $\text{H}^{\text{F3'}}$), 0.98 (m, 4H, $\text{H}^{\text{F2'}}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3 , 298 K) δ /ppm: 162.7 (C^{B6}), 156.5 (C^{B2}), 137.9 (C^{B4}), 123.4 (C^{B5}), 118.5 (C^{B3}), 38.2 (C^{b}), 38.2 (C^{F1}), 36.5 (C^{a}), 34.0 ($\text{C}^{\text{F2+F2'}}$), 27.4 ($\text{C}^{\text{F4+F4'}}$), 27.1 ($\text{C}^{\text{F3+F3'}}$). MALDI(+)-MS (m/z): 377.23 [$\text{M}+\text{H}$] $^+$ (base peak, calc. 377.29). UV-Vis (CH_2Cl_2 , 2.5×10^{-5} mol dm^{-3}): λ/nm ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) 241 (9,810), 247 (9,330), 294 (16,500), 303 sh (10,600). FTIR: 3062 (w), 2917 (m), 2847 (m), 1569 (s), 1436 (s), 1259 (w), 1150 (w), 1082 (m), 992 (w), 889 (w), 797 (s), 747 (m), 636 (m) cm^{-1} . Found: C 82.78, H 9.72, N 7.29; $\text{C}_{26}\text{H}_{36}\text{N}_2$ requires C 82.93, H 9.64, N 7.44.

6-(3-Ethylpentyl)-2,2'-bipyridine (3-EtPentbpy)

General procedure A was followed. The reagents were diisopropylamine (178 mg, 0.249 mL, 1.76 mmol, 1.0 eq.), *n*-butyllithium in hexanes (479 mg, 0.704 mL, 2.5 M, 1.76 mmol, 1.0 eq.), 6-methyl-2,2'-bipyridine (300 mg, 1.76 mmol, 1.0 eq.) and 1-bromo-2-ethylbutane (247 mg, 0.211 mL, 1.50 mmol, 0.85 eq.). 6-(3-Ethylpentyl)-2,2'-bipyridine (**3-EtPentbpy**, 251 mg, 0.985 mmol, 56%) was obtained as a colourless oil. Purification conditions for column chromatography: cyclohexane/ethyl acetate, gradient from 0 to 7% ethyl acetate in cyclohexane over 34 column volumes.

^1H NMR (500 MHz, CDCl_3 , 298 K) δ /ppm: 8.66 (ddd, $^3J_{\text{HH}} = 4.7$ Hz, $^4J_{\text{HH}} = 1.8$ Hz, $^5J_{\text{HH}} = 1.0$ Hz, 1H, H^{A6}), 8.52 (ddd, $^3J_{\text{HH}} = 7.9$ Hz, $^4J_{\text{HH}} = 1.1$ Hz, $^5J_{\text{HH}} = 1.1$ Hz, 1H, H^{A3}), 8.28 (dd, $^3J_{\text{HH}} = 8.0$ Hz, $^4J_{\text{HH}} = 1.0$ Hz, 1H, H^{B3}), 7.90 (ddd, $^3J_{\text{HH}} = 7.9$, 7.5 Hz, $^4J_{\text{HH}} = 1.8$ Hz, 1H, H^{A4}), 7.80 (dd, $^3J_{\text{HH}} = 7.7$, 7.7 Hz, 1H, H^{B4}), 7.39 (ddd, $^3J_{\text{HH}} = 7.5$, 4.8 Hz, $^4J_{\text{HH}} = 1.2$ Hz, 1H, H^{A5}), 7.29 (dd, $^3J_{\text{HH}} = 7.6$ Hz, $^4J_{\text{HH}} = 1.0$ Hz, 1H, H^{B5}), 2.85 (m, 2H, H^{a}), 1.78 (m, 2H, H^{b}), 1.41 (m, 4H, H^{d}), 1.30 (m, 1H, H^{c}), 0.89 (t, $^3J_{\text{HH}} = 7.6$ Hz, 6H, H^{e}). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3 , 298 K) δ /ppm: 162.9 (C^{B6}), 157.2 (C^{A2}), 156.2 (C^{B2}), 150.0 (C^{A6}), 138.0 (C^{B4}), 137.6 (C^{A4}), 124.6 (C^{A5}), 123.7 (C^{B5}), 121.4 (C^{A3}), 118.6 (C^{B3}), 40.9 (C^{c}), 36.1 (C^{a}), 33.6 (C^{b}), 26.0 (C^{d}), 11.1 (C^{e}). MALDI(+)-MS (m/z): 255.22 [$\text{M}+\text{H}$] $^+$ (base peak, calc. 255.18). UV-Vis (CH_2Cl_2 , 2.5×10^{-5} mol dm^{-3}): λ/nm ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) 240 (16,100), 246 (15,000), 290 (23,500), 300 sh (13,700). FTIR: 3060 (w), 2959 (m), 2921 (m), 2872 (m), 1563 (s), 1582 (s), 1458 (s), 1428 (s), 1379 (w), 1258 (w), 1148 (w), 1090 (w), 992 (w), 895 (w), 824 (w), 772 (s), 637 (m), 620 (m), 402 (w) cm^{-1} . Found: C 80.18, H 8.93, N 10.50; $\text{C}_{17}\text{H}_{22}\text{N}_2$ requires C 80.27, H 8.72, N 11.01.

6,6'-Bis(3-ethylpentyl)-2,2'-bipyridine ((3-EtPent) $_2$ bpy)

General procedure A was followed. The reagents were diisopropylamine (658 mg, 0.919 mL, 6.50 mmol, 2.0 eq.), *n*-butyllithium in hexanes (1768 mg, 2.60 mL, 2.5 M, 6.50 mmol, 2.0 eq.), 6,6'-dimethyl-2,2'-bipyridine (600 mg, 3.26 mmol, 1.0 eq.) and 1-bromo-2-ethylbutane (912 mg, 0.780 mL, 5.53 mmol, 1.7 eq.). 6,6'-Bis(3-ethylpentyl)-2,2'-bipyridine ((3-EtPent) $_2$ bpy, 321.8 mg, 0.913 mmol, 28%) was obtained as a colourless oil. For the purification by chromatography, three columns were run: first column: cyclohexane/ethyl acetate, gradient from 0 to 7% ethyl acetate in cyclohexane over 35 column volumes, basic alumina; second column: cyclohexane/ethyl acetate, gradient from 0 to 10% ethyl acetate in cyclohexane over 40 column volumes, basic alumina; third column: cyclohexane/ethyl acetate, gradient from 0 to 10% ethyl acetate in cyclohexane over 35 column volumes, silica.

^1H NMR (500 MHz, CDCl_3 , 298 K) δ /ppm: 8.32 (dd, $^3J_{\text{HH}} = 7.9$ Hz, $^4J_{\text{HH}} = 1.1$ Hz, 2H, H^{B3}), 7.79 (dd, $^3J_{\text{HH}} = 7.8$, 7.8 Hz, 2H, H^{B4}), 7.27 (dd, $^3J_{\text{HH}} = 7.6$ Hz, $^4J_{\text{HH}} = 1.0$ Hz, 2H, H^{B5}), 2.84 (m, 4H, H^{a}), 1.78 (m, 4H, H^{b}), 1.40 (m, 8H, H^{d}), 1.30 (m, 2H, H^{c}), 0.89 (t, $^3J_{\text{HH}} = 7.4$ Hz, 12H, H^{e}). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3 , 298 K) δ /ppm: 162.8 (C^{B6}), 156.5 (C^{B2}), 137.9 (C^{B4}), 123.4 (C^{B5}), 118.6 (C^{B3}), 40.9 (C^{c}), 36.1 (C^{a}), 33.6 (C^{b}), 26.0 (C^{d}), 11.1 (C^{e}). MALDI(+)-MS (m/z): 353.14 [$\text{M}+\text{H}$] $^+$ (base peak, calc. 353.29). UV-Vis (CH_2Cl_2 , 2.5×10^{-5} mol dm^{-3}): λ/nm ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) 241 (14,600), 247 (13,800), 293 (24,400), 303 sh (15,600). FTIR: 3058 (w), 2959 (m), 2919 (m), 2872 (m), 1571 (s), 1437 (s), 1379 (w), 1149 (w), 1085 (w), 897 (w), 792 (m), 750 (m), 635 (m), 421 (w) cm^{-1} . Found: C 81.71, H 10.31, N 7.80; $\text{C}_{24}\text{H}_{36}\text{N}_2$ requires C 81.76, H 10.29, N 7.95.

6-Phenethyl-2,2'-bipyridine (2-PhEtbp)

General procedure A was followed. The reagents were diisopropylamine (178 mg, 0.249 mL, 1.76 mmol, 1.0 eq.), *n*-butyllithium in hexanes (479 mg, 0.704 mL, 2.5 M, 1.76 mmol, 1.0 eq.), 6-methyl-2,2'-bipyridine (300 mg, 1.76 mmol, 1.0 eq.) and benzyl bromide (258 mg, 0.181 mL, 1.50 mmol, 0.85 eq.). 6-Phenethyl-2,2'-bipyridine (2-PhEtbp, 183 mg, 0.704 mmol, 40%) was obtained as a colourless oil. For the purification by chromatography, two columns were run: first column: cyclohexane/ethyl acetate, gradient from 0 to 5% ethyl acetate in cyclohexane over 17 column volumes, basic alumina; second column: cyclohexane/ethyl acetate (10:1), silica. ^1H NMR (500 MHz, CDCl_3 , 298 K) δ /ppm: 8.66 (ddd, $^3J_{\text{HH}} = 4.8$ Hz, $^4J_{\text{HH}} = 1.8$ Hz, $^5J_{\text{HH}} = 0.9$ Hz, 1H, H^{A6}), 8.54 (ddd, $^3J_{\text{HH}} = 8.0$ Hz, $^4J_{\text{HH}} = 1.1$ Hz, $^5J_{\text{HH}} = 1.1$ Hz, 1H, H^{A3}), 8.30 (dd, $^3J_{\text{HH}} = 7.8$ Hz, $^4J_{\text{HH}} = 1.0$ Hz, 1H, H^{B3}), 7.92 (ddd, $^3J_{\text{HH}} = 7.9$, 7.5 Hz, $^4J_{\text{HH}} = 1.8$ Hz, 1H, H^{A4}), 7.79 (dd, $^3J_{\text{HH}} = 7.7$, 7.7 Hz, 1H, H^{B4}), 7.40 (ddd, $^3J_{\text{HH}} = 7.5$, 4.8 Hz, $^4J_{\text{HH}} = 1.2$ Hz, 1H, H^{A5}), 7.27 (m, 2H, H^{F2}), 7.27 (m, 2H, H^{F3}), 7.24 (ov. dd, 1H, H^{B5}), 7.17 (m, 1H, H^{F4}), 3.17 (m, 2H, H^{a}), 3.17 (m, 2H, H^{b}). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3 , 298 K) δ /ppm: 161.5 (C^{B6}), 157.1 (C^{A2}), 156.3 (C^{B2}), 150.0 (C^{A6}), 142.8 (C^{F1}), 138.0 (C^{B4}), 137.7 (C^{A4}), 129.3 ($\text{C}^{\text{F2/F3}}$), 129.1 ($\text{C}^{\text{F2/F3}}$), 126.7 (C^{F4}), 124.6 (C^{A5}), 123.9 (C^{B5}), 121.5 (C^{A3}), 118.9 (C^{B3}), 40.6 (C^{a}), 36.2 (C^{b}). MALDI(+)-MS (m/z): 261.41 [$\text{M}+\text{H}$] $^+$ (base peak, calc. 261.13). UV-Vis (CH_2Cl_2 , 2.5×10^{-5} mol dm^{-3}): λ/nm ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) 240 sh (20,800), 246 (17,400), 282 (26,000), 289 (26,800), 299 sh (16,500). FTIR: 3060 (w), 3025 (s), 2924 (s), 2856 (m), 1580 (s), 1562 (s), 1495 (m), 1474 (m), 1454 (s), 1428 (s), 1083 (m), 1044 (w), 991 (m), 775 (s), 745 (s), 697 (s), 637 (m), 402 (w) cm^{-1} . Found: C 82.94, H 6.37, N 10.50; $\text{C}_{18}\text{H}_{16}\text{N}_2$ requires C 83.04, H 6.19, N 10.76.

6,6'-Diphenethyl-2,2'-bipyridine ((2-PhEt) $_2$ bpy)

General procedure A was followed. The reagents were diisopropylamine (658 mg, 0.919 mL, 6.50 mmol, 2.0 eq.), *n*-butyllithium in hexanes (1768 mg, 2.60 mL, 2.5 M, 6.50 mmol, 2.0 eq.), 6,6'-dimethyl-2,2'-bipyridine (600 mg, 3.26 mmol, 1.0 eq.) and benzyl bromide (955 mg, 0.667 mL, 5.53 mmol, 1.7 eq.). 6,6'-Diphenethyl-2,2'-bipyridine ((2-PhEt) $_2$ bpy, 285 mg, 0.783 mmol, 24%) was obtained as a colourless oil. For the purification by chromatography, two columns were run: first column: cyclohexane/ethyl acetate, gradient from 0 to 10% ethyl acetate in cyclohexane over 36 column volumes, basic alumina; second column: cyclohexane/ethyl acetate, gradient from 0 to 15% ethyl acetate in cyclohexane over 40 column volumes, silica. ^1H NMR (500 MHz, CDCl_3 , 298 K) δ /ppm: 8.36 (dd, $^3J_{\text{HH}} = 7.8$ Hz, $^4J_{\text{HH}} = 1.0$ Hz, 2H, H^{B3}), 7.79 (dd, $^3J_{\text{HH}} = 7.7$, 7.7 Hz, 2H, H^{B4}), 7.27 (m, 4H, $\text{H}^{\text{F2/F3}}$), 7.26 (m, 4H, $\text{H}^{\text{F2/F3}}$), 7.21 (dd, $^3J_{\text{HH}} = 7.5$ Hz, $^4J_{\text{HH}} = 1.0$ Hz, 2H, H^{B5}), 7.17 (m, 2H, H^{F4}), 3.17 (m, 4H, H^{a}), 3.17 (m, 4H, H^{b}). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3 , 298 K) δ /ppm: 161.4 (C^{B6}), 156.5 (C^{B2}), 142.8 (C^{F1}), 137.9 (C^{B4}), 129.3 ($\text{C}^{\text{F2/F3}}$), 129.1 ($\text{C}^{\text{F2/F3}}$), 126.7 (C^{F4}), 123.8 (C^{B5}), 119.0 (C^{B3}), 40.6 (C^{a}), 36.2 (C^{b}). MALDI(+)-MS (m/z): 365.02 [$\text{M}+\text{H}$] $^+$ (base peak, calc. 365.19). UV-Vis (CH_2Cl_2 , 2.5×10^{-5} mol dm^{-3}): λ/nm ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) 240 sh (20,800), 248 (19,900), 276 (34,100), 285 (37,000), 301 sh (22,800). FTIR: 3055 (w), 3030 (w), 2917 (w), 2854 (m), 1567 (s), 1435 (s), 1495 (m), 1390 (m), 1146 (w), 1098 (w), 1027 (w), 992 (w), 908 (w), 790 (s), 796 (s), 739 (s), 631 (m), 554 (m), 477 (m), 419 (w) cm^{-1} . Found: C 85.55, H 6.56, N 7.59; $\text{C}_{26}\text{H}_{24}\text{N}_2$ requires C 85.68, H 6.64, N 7.69.

6-(3-Phenylpropyl)-2,2'-bipyridine (3-PhPrbpy)

General procedure A was followed. The reagents were diisopropylamine (178 mg, 0.249 mL, 1.76 mmol, 1.0 eq.), *n*-butyllithium in hexanes (479 mg, 0.704 mL, 2.5 M, 1.76 mmol, 1.0 eq.), 6-methyl-2,2'-bipyridine (300 mg, 1.76 mmol, 1.0 eq.) and (2-bromoethyl)-benzene (283 mg, 0.209 mL, 1.50 mmol, 0.85 eq.). 6-(3-Phenylpropyl)-2,2'-bipyridine (**3-PhPrbpy**, 275 mg, 1.00 mmol, 57%) was obtained as a colourless oil. For the purification by chromatography, two columns were run: first column: cyclohexane/ethyl acetate, gradient from 0 to 20% ethyl acetate in cyclohexane over 65 column volumes, basic alumina; second column: cyclohexane/ethyl acetate, gradient from 0 to 15% ethyl acetate in cyclohexane over 40 column volumes, silica. ¹H NMR (500 MHz, CDCl₃, 298 K) δ /ppm: 8.66 (ddd, ³J_{HH} = 4.8 Hz, ⁴J_{HH} = 1.8 Hz, ⁵J_{HH} = 0.9 Hz, 1H, H^{A6}), 8.52 (ddd, ³J_{HH} = 8.0 Hz, ⁴J_{HH} = 1.1 Hz, ⁵J_{HH} = 1.1 Hz, 1H, H^{A3}), 8.30 (dd, ³J_{HH} = 8.0 Hz, ⁴J_{HH} = 1.0 Hz, 1H, H^{B3}), 7.91 (ddd, ³J_{HH} = 8.0, 7.5 Hz, ⁴J_{HH} = 1.8 Hz, 1H, H^{A4}), 7.82 (dd, ³J_{HH} = 7.7, 7.7 Hz, 1H, H^{B4}), 7.39 (ddd, ³J_{HH} = 7.5, 4.7 Hz, ⁴J_{HH} = 1.2 Hz, 1H, H^{A5}), 7.29 (ov. dd, 1H, H^{B5}), 7.28 (m, 2H, H^{F2}), 7.28 (m, 2H, H^{F3}), 7.18 (m, 1H, H^{F4}), 2.89 (t, ³J_{HH} = 7.6 Hz, 2H, H^a), 2.73 (t, ³J_{HH} = 7.6 Hz, 2H, H^c), 2.17 (m, 2H, H^b). ¹³C{¹H} NMR (126 MHz, CDCl₃, 298 K) δ /ppm: 129.3/129.2 (C^{F2}), 129.3/129.2 (C^{F3}), 162.2 (C^{B6}), 157.2 (C^{A2}), 156.2 (C^{B2}), 150.0 (C^{A6}), 143.3 (C^{F1}), 138.0 (C^{B4}), 137.6 (C^{A4}), 126.6 (C^{F4}), 124.6 (C^{A5}), 123.8 (C^{B5}), 121.4 (C^{A3}), 118.8 (C^{B3}), 38.2 (C^a), 36.1 (C^c), 32.1 (C^b). MALDI(+)-MS (m/z): 275.05 [M+H]⁺ (base peak, calc. 275.15). UV-Vis (CH₂Cl₂, 2.5 × 10⁻⁵ mol dm⁻³): λ /nm (ϵ /dm³ mol⁻¹ cm⁻¹) 240 (11,100), 248 (19,900), 276 (34,100), 287 (36,900), 302 sh (21,700). FTIR: 3060 (w), 3024 (w), 2925 (w), 2856 (m), 1580 (s), 1563 (s), 1495 (m), 1473 (m), 1428 (s), 1146 (w), 1083 (w), 1044 (w), 1029 (w), 908 (w), 823 (w), 774 (s), 743 (s), 697 (s), 637 (m), 619 (m), 491 (m), 402 (m) cm⁻¹. Satisfactory elemental analysis was not obtained. HR-ESI(+)-MS (CH₂Cl₂/MeOH, m/z): 275.1547 [M+H]⁺ (base peak, calc. 275.1543).

6,6'-Bis(3-phenylpropyl)-2,2'-bipyridine ((3-PhPr)₂bpy)

General procedure A was followed. The reagents were diisopropylamine (658 mg, 0.919 mL, 6.50 mmol, 2.0 eq.), *n*-butyllithium in hexanes (1768 mg, 2.60 mL, 2.5 M, 6.50 mmol, 2.0 eq.), 6,6'-dimethyl-2,2'-bipyridine (600 mg, 3.26 mmol, 1.0 eq.) and (2-bromoethyl)-benzene (1.04 g, 0.773 mL, 5.53 mmol, 1.7 eq.). 6,6'-Bis(3-phenylpropyl)-2,2'-bipyridine (**((3-PhPr)₂bpy**), 397 mg, 1.01 mmol, 31%) was obtained as a colourless oil. For the purification by chromatography, three columns were run: cyclohexane/ethyl acetate, gradient from 0 to 15% ethyl acetate in cyclohexane over 50 column volumes, basic alumina; second column: cyclohexane/ethyl acetate, gradient from 0 to 15% ethyl acetate in cyclohexane over 40 column volumes, silica. ¹H NMR (500 MHz, CDCl₃, 298 K) δ /ppm: 8.34 (dd, ³J_{HH} = 7.8 Hz, ⁴J_{HH} = 1.1 Hz, 2H, H^{B3}), 7.80 (dd, ³J_{HH} = 7.7, 7.7 Hz, 2H, H^{B4}), 7.27 (ov. dd, 2H, H^{B5}), 7.27 (m, 4H, H^{F2/F3}), 7.26 (m, 4H, H^{F2/F3}), 7.17 (m, 2H, H^{F4}), 2.89 (t, ³J_{HH} = 7.6 Hz, 4H, H^a), 2.73 (t, ³J_{HH} = 7.8 Hz, 4H, H^c), 2.16 (m, 4H, H^b). ¹³C{¹H} NMR (126 MHz, CDCl₃, 298 K) δ /ppm: 162.0 (C^{B6}), 156.5 (C^{B2}), 143.3 (C^{F1}), 137.9 (C^{B4}), 129.3 (C^{F2/F3}), 129.1 (C^{F2/F3}), 126.6 (C^{F4}), 123.6 (C^{B5}), 118.8 (C^{B3}), 38.2 (C^a), 36.1 (C^c), 32.1 (C^b). MALDI(+)-MS (m/z): 393.06 [M+H]⁺ (base peak, calc. 393.23). UV-Vis (CH₂Cl₂, 2.5 × 10⁻⁵ mol dm⁻³): λ /nm (ϵ /dm³ mol⁻¹ cm⁻¹) 241 (9,000), 247 (8,400), 294 (14,700), 302 sh (10,100). FTIR: 3057 (w), 3021 (w), 2921 (w), 2856 (m), 1572 (s), 1393 (w), 1444 (s), 1494 (w), 1458 (w), 1393 (w), 1352 (w), 1268 (w), 1246 (w), 1162 (w), 1082 (w), 991 (w), 804 (w), 791 (s), 756 (s), 746 (s), 760 (s), 636 (m), 591 (m), 426 (w) cm⁻¹. Found: C 85.85, H 7.19, N 7.04; C₂₈H₂₈N₂ requires C 85.67, H 7.19, N 7.14.

4,4'-Di-tert-butyl-6,6'-dicyclohexyl-2,2'-bipyridine (4,4'-tBu₂-6,6'-Cy₂bpy)

General procedure B was followed. The preparation of this compound has been previously reported and was adapted of a literature procedure.² The reagents were 4,4'-di-tert-butyl-2,2'-bipyridine (322 mg, 1.20 mmol, 1.0 eq.), trifluoroacetic acid (274 mg, 0.178 mL, 2.40 mmol, 2.0 eq.), di-tert-butyl peroxide (1.40 g, 1.77 mL, 9.60 mmol, 8.0 eq.), 2,3-butanedione (2.38 g, 2.41 mL, 27.6 mmol, 23 eq.), and cyclohexane (924 mg, 1.20 mL, 11.0 mmol, 9.2 eq.). 4,4'-Di-tert-butyl-6,6'-dicyclohexyl-2,2'-bipyridine (**4,4'-tBu₂-6,6'-Cy₂bpy**), 62.3 mg, 0.144 mmol, 12%) was obtained as a colourless oil. The purification was done by column chromatography: cyclohexane/ethyl acetate, gradient from 0 to 2% ethyl acetate in cyclohexane over 30 column volumes, basic alumina; followed by preparative thin layer chromatography: cyclohexane/ethyl acetate (30:1, *R_F* = 0.30, asymmetric singly substituted by-product *R_F* = 0.27), silica. ¹H NMR (500 MHz, CDCl₃, 298 K) δ /ppm: 8.20 (d, ⁴J_{HH} = 1.8 Hz, 2H, H^{B3}), 7.11 (d, ⁴J_{HH} = 1.8 Hz, 2H, H^{B5}), 2.76 (m, 2H, H^{F1}), 2.02 (m, 4H, H^{F2}), 1.88 (m, 4H, H^{F3}), 1.77 (m, 2H, H^{F4}), 1.62 (m, 4H, H^{F2'}), 1.45 (m, 4H, H^{F3'}), 1.37 (m, 18H, H^{tBu-Me}), 1.34 (m, 2H, H^{F4'}). ¹H NMR (500 MHz, acetone-d₆, 298 K) δ /ppm: 8.40 (d, ⁴J_{HH} = 1.8 Hz, 2H, H^{B3}), 7.29 (d, ⁴J_{HH} = 1.8 Hz, 2H, H^{B5}), 2.79 (m, 2H, H^{F1}), 1.97 (m, 4H, H^{F2}), 1.87 (m, 4H, H^{F3}), 1.76 (m, 2H, H^{F4}), 1.70 (m, 4H, H^{F2'}), 1.47 (m, 4H, H^{F3'}), 1.38 (m, 18H, H^{tBu-Me}), 1.33 (m, 2H, H^{F4'}). ¹³C{¹H} NMR (126 MHz, acetone-d₆, 298 K) δ /ppm: 166.2 (C^{B6}), 161.5 (C^{B4}), 156.8 (C^{B2}), 118.8 (C^{B5}), 116.0 (C^{B3}), 47.3 (C^{F1}), 35.5 (C^{tBu-Cq}), 33.8 (C^{F2}), 33.8 (C^{F2'}), 31.0 (C^{tBu-Me}), 27.3 (C^{F3}), 27.3 (C^{F3'}), 26.9 (C^{F4}), 26.9 (C^{F4'}). MALDI(+)-MS (m/z): 433.31 [M+H]⁺ (base peak, calc. 433.36). ESI(+)-MS (CH₂Cl₂/MeOH, m/z): 433.32 [M+H]⁺ (base peak, calc. 433.36). UV-Vis (CH₂Cl₂, 2.5 × 10⁻⁵ mol dm⁻³): λ /nm (ϵ /dm³ mol⁻¹ cm⁻¹) 244 (5,100), 251 (4,900), 292 (9,300), 302 sh (5,600). FTIR: 3045 (w), 2962 (s), 2949 (s), 2849 (s), 1567 (s), 1494 (m), 1452 (m), 1435 (s), 1390 (m), 1146 (w), 1098 (w), 1083 (w), 1027 (w), 908 (w), 790 (s), 739 (s), 696 (s), 631 (m), 554 (m), 477 (m), 539 (m), 419 (w) cm⁻¹. Satisfactory elemental analysis was not obtained. HR-ESI(+)-MS (CH₂Cl₂/MeOH, m/z): 433.3578 [M+H]⁺ (base peak, calc. 433.3577).

6-Cyclohexyl-6'-methyl-2,2'-bipyridine (6-Cy-6'-Mebpy)

General procedure B was followed. The reagents were 6-methyl-2,2'-bipyridine (409 mg, 2.40 mmol, 1.0 eq.), trifluoroacetic acid (547 mg, 0.355 mL, 4.80 mmol, 2.0 eq.), di-*tert*-butyl peroxide (2.80 g, 3.53 mL, 19.2 mmol, 8.0 eq.), 2,3-butanedione (4.75 g, 4.83 mL, 55.2 mmol, 23 eq.), and cyclohexane (1.01 g, 1.31 mL, 12.0 mmol, 5.0 eq.). 6-Cyclohexyl-6'-methyl-2,2'-bipyridine (6-Cy-6'-Mebpy, 109 mg, 0.432 mmol, 18%) was obtained as a colourless oil. For the purification by chromatography, two columns were run: first column: cyclohexane/ethyl acetate, gradient from 0 to 2% ethyl acetate in cyclohexane over 30 column volumes, basic alumina; second column: cyclohexane/ethyl acetate, gradient from 0 to 15% ethyl acetate in cyclohexane over 80 column volumes, silica. ^1H NMR (500 MHz, acetone- d_6 , 298 K) δ /ppm: 8.33 (d, $^3J_{\text{HH}} = 7.7$ Hz, 1H, H^{A3}), 8.28 (dd, $^3J_{\text{HH}} = 7.8$ Hz, $^4J_{\text{HH}} = 1.0$ Hz, 1H, H^{B3}), 7.79 (dd, $^3J_{\text{HH}} = 7.8$, 7.8 Hz, 1H, H^{B4}), 7.78 (dd, $^3J_{\text{HH}} = 7.7$, 7.7 Hz, 1H, H^{A4}), 7.26 (dd, $^3J_{\text{HH}} = 7.7$ Hz, $^4J_{\text{HH}} = 1.0$ Hz, 1H, H^{B5}), 7.25 (d, $^3J_{\text{HH}} = 7.7$ Hz, 1H, H^{A5}), 2.76 (m, 1H, H^{F1}), 2.57 (m, 3H, $\text{H}^{\text{B6-Me}}$), 1.98 (m, 2H, H^{F2}), 1.87 (m, 2H, H^{F3}), 1.76 (m, 1H, H^{F4}), 1.66 (m, 2H, $\text{H}^{\text{F2'}}$), 1.46 (m, 2H, $\text{H}^{\text{F3'}}$), 1.33 (m, 1H, $\text{H}^{\text{F4'}}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, acetone- d_6 , 298 K) δ /ppm: 166.4 (C^{B6}), 158.4 (C^{A6}), 156.6 (C^{A2}), 156.2 (C^{B2}), 138.0 (C^{B4}), 137.8 (C^{A4}), 123.8 (C^{A5}), 122.0 (C^{B5}), 118.7 (C^{B3}), 118.5 (C^{A3}), 47.1 (C^{F1}), 33.6 (C^{F2}), 33.6 ($\text{C}^{\text{F2'}}$), 27.3 (C^{F3}), 27.3 ($\text{C}^{\text{F3'}}$), 26.9 (C^{F4}), 26.9 ($\text{C}^{\text{F4'}}$), 24.6 ($\text{C}^{\text{B6-Me}}$). MALDI(+)-MS (m/z): 253.12 [$\text{M}+\text{H}$] $^+$ (calc. 253.17). ESI(+)-MS ($\text{CH}_2\text{Cl}_2/\text{MeOH}$, m/z): 253.25 [$\text{M}+\text{H}$] $^+$ (base peak, calc. 253.17). UV-Vis (CH_2Cl_2 , 2.5×10^{-5} mol dm^{-3}): λ/nm ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) 241 (9,300), 247 (8,700), 293 (15,900), 302 sh (10,200). FTIR: 3051 (w), 2922 (s), 2850 (s), 1572 (s), 1437 (s), 1416 (m), 1373 (w), 1258 (w), 1151 (m), 1081 (m), 992 (w), 891 (w), 863 (w), 707 (w), 790 (s), 745 (s), 631 (m), 420 (w) cm^{-1} . Satisfactory elemental analysis was not obtained. HR-ESI(+)-MS ($\text{CH}_2\text{Cl}_2/\text{MeOH}$, m/z): 253.1702 [$\text{M}+\text{H}$] $^+$ (base peak, calc. 253.1699).

General procedure for the preparation of the copper(I) complexes

POP-containing compounds were synthesized by the following procedure: POP (1.1 eq.) and $[\text{Cu}(\text{MeCN})_4][\text{PF}_6]$ (1.0 eq.) were dissolved in CH_2Cl_2 (20 mL) and the reaction mixture was stirred for 2 h. The desired N^*N ligand (1.0 eq.) was added and the mixture turned red, then yellow while it was stirred for 2 h. The mixture was then filtered and the solvent was removed under reduced pressure. The crude complex material was purified by crystallization from CH_2Cl_2 with diethyl ether (Et_2O), followed by decantation of the supernatant. The product was washed with Et_2O (60 mL) and dried under high vacuum.

Xantphos-containing compounds were prepared according to the following procedure: A solution of the appropriate N^*N ligand (1.0 eq.) and xantphos (1.1 eq.) in CH_2Cl_2 (10 mL) was added dropwise to a CH_2Cl_2 solution (10 mL) of $[\text{Cu}(\text{MeCN})_4][\text{PF}_6]$ (1.0 eq.). The mixture turned red, then yellow while it was stirred for 2 h. The mixture was filtered and the solvent was removed under reduced pressure. The crude complex material was purified by crystallization from CH_2Cl_2 with diethyl ether (Et_2O), followed by decantation of the supernatant. The product was washed with Et_2O (60 mL) and dried under high vacuum.

$[\text{Cu}(\text{POP})(2\text{-CyEtbp})][\text{PF}_6]$

The reagents were POP (93.7 mg, 0.174 mmol, 1.0 eq.), 2-CyEtbp (46.4 mg, 0.174 mmol, 1.0 eq.) and $[\text{Cu}(\text{MeCN})_4][\text{PF}_6]$ (64.9 mg, 0.174 mmol, 1.0 eq.). $[\text{Cu}(\text{POP})(2\text{-CyEtbp})][\text{PF}_6]$ was isolated as a yellow solid (136 mg, 0.134 mmol, 77%). ^1H NMR (500 MHz, acetone- d_6 , 298 K) δ /ppm: 8.59 (d, $^3J_{\text{HH}} = 5.2$ Hz, 1H, H^{A6}), 8.49 (d, $^3J_{\text{HH}} = 8.2$ Hz, 1H, H^{A3}), 8.40 (d, $^3J_{\text{HH}} = 8.0$ Hz, 1H, H^{B3}), 8.14 (dd, $^3J_{\text{HH}} = 7.9$, 7.9 Hz, 1H, H^{B4}), 8.07 (ddd, $^3J_{\text{HH}} = 7.9$, 7.9 Hz, $^4J_{\text{HH}} = 1.6$ Hz, 1H, H^{A4}), 7.53 (d, $^3J_{\text{HH}} = 7.9$ Hz, 1H, H^{B5}), 7.44 (m, 2H, H^{C5}), 7.38 (m, 2H, H^{D4}), 7.38 (m, 2H, $\text{H}^{\text{D4'}}$), 7.36 (ov. d, 1H, H^{A5}), 7.27 (m, 4H, H^{D3}), 7.27 (m, 4H, $\text{H}^{\text{D3'}}$), 7.20 (m, 2H, H^{C6}), 7.17 (m, 2H, H^{C4}), 7.11 (m, 4H, H^{D2}), 7.11 (m, 4H, $\text{H}^{\text{D2'}}$), 6.93 (m, 2H, H^{C3}), 2.87 (m, 2H, H^{A}), 1.58 (m, 2H, H^{F3}), 1.58 (m, 1H, H^{F4}), 1.34 (m, 2H, H^{F2}), 1.18 (m, 2H, H^{B}), 1.09 (m, 2H, $\text{H}^{\text{F3'}}$), 1.09 (m, 1H, $\text{H}^{\text{F4'}}$), 0.71 (m, 1H, H^{F1}), 0.62 (m, 2H, $\text{H}^{\text{F2'}}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, acetone- d_6 , 298 K) δ /ppm: 164.2 (C^{B6}), 158.8 (t, $^2J_{\text{CP}} = 6.0$ Hz, C^{C1}), 153.6 (t, $^3J_{\text{CP}} = 2.2$ Hz, C^{A2}), 152.4 (t, $^3J_{\text{CP}} = 1.9$ Hz, C^{B2}), 150.2 (C^{A6}), 140.0 (C^{B4}), 139.7 (C^{A4}), 134.9 (C^{C3}), 134.0 (t, $^2J_{\text{CP}} = 8.3$ Hz, C^{D2}), 133.9 (t, $^2J_{\text{CP}} = 8.2$ Hz, $\text{C}^{\text{D2'}}$), 133.2 (C^{C5}), 132.2 (t, $^1J_{\text{CP}} = 17.3$ Hz, C^{D1}), 132.2 (t, $^1J_{\text{CP}} = 17.3$ Hz, $\text{C}^{\text{D1'}}$), 131.1 (C^{D4}), 131.0 ($\text{C}^{\text{D4'}}$), 129.7 (ov. t, C^{D3}), 129.7 (ov. t, $\text{C}^{\text{D3'}}$), 126.6 (C^{A5}), 126.1 (t, $^3J_{\text{CP}} = 2.0$ Hz, C^{C4}), 125.3 (C^{B5}), 125.1 (t, $^1J_{\text{CP}} = 14.5$ Hz, C^{C2}), 123.6 (C^{A3}), 121.2 (t, $^3J_{\text{CP}} = 2.0$ Hz, C^{C6}), 121.1 (C^{B3}), 38.6 (C^{A}), 37.7 (C^{F1}), 36.7 (C^{B}), 33.7 (C^{F2}), 27.1 (C^{F4}), 26.9 (C^{F3}). $^{19}\text{F}\{^1\text{H}\}$ NMR (471 MHz, 298 K, acetone- d_6 , 298 K) δ /ppm: -72.7 (d, $^1J_{\text{FP}} = 707$ Hz, F^{PF6}). $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, 298 K, acetone- d_6 , 298 K) δ /ppm: -13.0 (broad, FWHM ≈ 200 Hz, P^{POP}), -144.2 (hept, $^1J_{\text{PF}} = 707$ Hz, P^{PF6}). ESI(+)-MS ($\text{CH}_2\text{Cl}_2/\text{MeOH}$, m/z): 601.06 [$\text{M}-\text{PF}_6-(2\text{-CyEtbp})$] $^+$ (calc. 601.09), 867.26 [$\text{M}-\text{PF}_6$] $^+$ (base peak, calc. 867.27). ESI(-)-MS ($\text{CH}_2\text{Cl}_2/\text{MeOH}$, m/z): 145.08 [PF_6] $^-$ (calc. 144.96), 312.88 [$2\text{PF}_6+\text{Na}$] $^-$ (base peak, calc. 312.91). HR-ESI(+)-MS ($\text{CH}_2\text{Cl}_2/\text{MeOH}$, m/z): 867.2688 [$\text{M}-\text{PF}_6$] $^+$ (calc. 867.2689). UV-Vis (CH_2Cl_2 , 2.5×10^{-5} mol dm^{-3}): λ/nm ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) 250 (25,500), 290 (21,900), 300 (20,700), 305 sh (18,400), 314 sh (14,000), 380 br (2,780). FTIR: 3062 (w), 3029 (w), 2923 (w), 2857 (w), 1597 (w), 1563 (w), 1435 (m), 1258 (w), 1215 (m), 1094 (w), 833 (s), 746 (s), 695 (s), 556 (s), 511 (s), 477 (m), 422 (m) cm^{-1} . Found: C 62.65, H 4.94, N 2.85; $\text{C}_{54}\text{H}_{50}\text{CuF}_6\text{N}_2\text{OP}_3 \cdot 0.3\text{CH}_2\text{Cl}_2$ requires C 62.78, H 4.91, N 2.70.

[Cu(xantphos)(2-CyEtbp)]⁺[PF₆][−]]

The reagents were xantphos (98.9 mg, 0.171 mmol, 1.0 eq.), 2-CyEtbp (45.6 mg, 0.171 mmol, 1.0 eq.) and [Cu(MeCN)₄][PF₆]₂ (63.7 mg, 0.171 mmol, 1.0 eq.). [Cu(xantphos)(2-CyEtbp)]⁺[PF₆][−] was isolated as a yellow solid (112 mg, 0.106 mmol, 62%). ¹H NMR (500 MHz, acetone-d₆, 298 K) δ/ppm: 8.50 (d, ³J_{HH} = 8.2 Hz, 1H, H^{A3}), 8.41 (d, ³J_{HH} = 7.7 Hz, 1H, H^{B3}), 8.36 (broad, 1H, H^{A6}), 8.18 (dd, ³J_{HH} = 7.9, 7.9 Hz, 1H, H^{B4}), 8.08 (ddd, ³J_{HH} = 7.9, 7.9 Hz, ⁴J_{HH} = 1.6 Hz, 1H, H^{A4}), 7.87 (dd, ³J_{HH} = 7.8 Hz, ⁴J_{HH} = 1.4 Hz, 2H, H^{C5}), 7.59 (dd, ³J_{HH} = 7.9 Hz, ⁴J_{HH} = 0.9 Hz, 1H, H^{B5}), 7.46 (dd, ³J_{HH} = 7.6, 5.1 Hz, 1H, H^{A5}), 7.39 (m, 2H, H^{D4}), 7.36 (m, 2H, H^{D4'}), 7.31 (dd, ³J_{HH} = 7.7, 7.7 Hz, 2H, H^{C4}), 7.25 (m, 4H, H^{D3}), 7.18 (m, 4H, H^{D3'}), 7.13 (m, 4H, H^{D2}), 6.98 (m, 4H, H^{D2'}), 6.73 (m, 2H, H^{C3}), 2.66 (m, 2H, H^a), 1.91 (s, 3H, H^{xantphos-Me}), 1.70 (s, 3H, H^{xantphos-Me'}), 1.52 (m, 1H, H^{F4}), 1.47 (m, 2H, H^{F3}), 1.18 (m, 2H, H^{F2}), 1.10 (m, 2H, H^b), 1.00 (m, 2H, H^{F3'}), 1.00 (m, 1H, H^{F4'}), 0.54 (m, 2H, H^{F2'}), 0.50 (m, 1H, H^{F1}). ¹³C{¹H} NMR (126 MHz, acetone-d₆, 298 K) δ/ppm: 163.7 (C^{B6}), 155.8 (t, ²J_{CP} = 6.3 Hz, C^{C1}), 153.6 (t, ³J_{CP} = 2.3 Hz, C^{A2}), 152.3 (t, ³J_{CP} = 1.8 Hz, C^{B2}), 149.8 (C^{A6}), 140.2 (C^{B4}), 139.9 (C^{A4}), 135.1 (t, ³J_{CP} = 1.7 Hz, C^{C6}), 134.0 (t, ²J_{CP} = 8.0 Hz, C^{D2'}), 133.5 (t, ²J_{CP} = 7.8 Hz, C^{D2}), 132.8 (t, ¹J_{CP} = 16.4 Hz, C^{D1}), 132.3 (t, ¹J_{CP} = 17.4 Hz, C^{D1'}), 131.5 (C^{C3}), 131.1 (C^{D4'}), 131.0 (C^{D4}), 129.8 (t, ³J_{CP} = 4.7 Hz, C^{D3}), 129.7 (t, ³J_{CP} = 4.7 Hz, C^{D3'}), 128.5 (C^{C5}), 126.8 (C^{A5}), 126.3 (t, ³J_{CP} = 2.4 Hz, C^{C4}), 125.8 (C^{B5}), 123.8 (C^{A3}), 121.4 (C^{B3}), 121.4 (t, ¹J_{CP} = 13.5 Hz, C^{C2}), 38.8 (C^a), 37.0 (C^{F1}), 36.9 (C^{xantphos-bridge}), 36.8 (C^b), 33.6 (C^{F2}), 30.1 (C^{xantphos-Me'}), 26.9 (C^{F4}), 26.6 (C^{xantphos-Me}), 26.6 (C^{F3}). ¹⁹F{¹H} NMR (471 MHz, 298 K, acetone-d₆, 298 K) δ/ppm −72.6 (d, ¹J_{FP} = 708 Hz, F^{PF6}). ³¹P{¹H} NMR (202 MHz, 298 K, acetone-d₆, 298 K) δ/ppm: −13.1 (broad, FWHM ≈ 240 Hz, P^{xantphos}), −144.2 (hept, ¹J_{PF} = 708 Hz, P^{PF6}). ESI(+)-MS (CH₂Cl₂/MeOH, m/z): 641.06 [M−PF₆−(2-CyEtbp)]⁺ (calc. 641.12), 907.26 [M−PF₆]⁺ (base peak, calc. 907.30). ESI(−)-MS (CH₂Cl₂/MeOH, m/z): 145.06 [PF₆][−] (calc. 144.96), 312.90 [2PF₆+Na][−] (base peak, calc. 312.91). UV-Vis (CH₂Cl₂, 2.5 × 10^{−5} mol dm^{−3}): λ/nm (ε/dm³ mol^{−1} cm^{−1}) 247 (36,900), 284 (34,100), 300 sh (24,400), 313 sh (14,700), 380 br (3,950). FTIR: 3055 (w), 2923 (w), 2853 (w), 1596 (w), 1449 (m), 1435 (m), 1406 (s), 1235 (m), 1097 (w), 836 (s), 776 (s), 739 (s), 694 (s), 557 (s), 508 (s) cm^{−1}. Found: C 64.26, H 5.33, N 2.75; C₅₇H₅₄CuF₆N₂O₃ requires C 64.98, H 5.17, N 2.66.

[Cu(POP)(3-EtPentbp)]⁺[PF₆][−]]

The reagents were POP (86.2 mg, 0.160 mmol, 1.0 eq.), 3-EtPentbp (40.7 mg, 0.160 mmol, 1.0 eq.) and [Cu(MeCN)₄][PF₆]₂ (59.6 mg, 0.160 mmol, 1.0 eq.). [Cu(POP)(3-EtPentbp)]⁺[PF₆][−] was isolated as a yellow solid (107 mg, 0.107 mmol, 67%). ¹H NMR 500 MHz, acetone-d₆, 298 K) δ/ppm: 8.53 (d, ³J_{HH} = 5.2 Hz, ⁴J_{HH} = 1.7 Hz, ⁵J_{HH} = 0.8 Hz, 1H, H^{A6}), 8.51 (d, ³J_{HH} = 8.2 Hz, 1H, H^{A3}), 8.42 (d, ³J_{HH} = 7.8 Hz, 1H, H^{B3}), 8.15 (dd, ³J_{HH} = 7.9, 7.9 Hz, 1H, H^{B4}), 8.06 (ddd, ³J_{HH} = 7.8, 7.8 Hz, ⁴J_{HH} = 1.6 Hz, 1H, H^{A4}), 7.54 (d, ³J_{HH} = 7.7 Hz, 1H, H^{B5}), 7.44 (m, 2H, H^{C5}), 7.42 (m, 2H, H^{D4}), 7.36 (m, 2H, H^{D4'}), 7.34 (ov. d, 1H, H^{A5}), 7.29 (m, 4H, H^{D3'}), 7.24 (m, 4H, H^{D3}), 7.20 (m, 2H, H^{C6}), 7.16 (m, 2H, H^{C4}), 7.15 (m, 4H, H^{D2}), 7.07 (m, 4H, H^{D2'}), 6.91 (m, 2H, H^{C3}), 2.86 (m, 2H, H^a), 1.28 (m, 2H, H^b), 1.03 (m, 4H, H^d), 0.78 (m, 1H, H^c), 0.66 (t, ³J_{HH} = 7.5 Hz, 6H, H^e). ¹³C{¹H} NMR (126 MHz, acetone-d₆, 298 K) δ/ppm: 164.0 (C^{B6}), 158.8 (t, ²J_{CP} = 6.0 Hz, C^{C1}), 153.6 (t, ³J_{CP} = 2.2 Hz, C^{A2}), 152.5 (t, ³J_{CP} = 1.9 Hz, C^{B2}), 150.1 (C^{A6}), 140.1 (C^{B4}), 139.7 (C^{A4}), 134.9 (C^{C3}), 134.0 (t, ²J_{CP} = 8.4 Hz, C^{D2}), 133.9 (t, ²J_{CP} = 8.7 Hz, C^{D2'}), 133.2 (C^{C5}), 132.2 (t, ¹J_{CP} = 17.0 Hz, C^{D1}), 132.0 (t, ¹J_{CP} = 16.1 Hz, C^{D1'}), 131.2 (C^{D4}), 131.0 (C^{D4'}), 129.7 (ov. t, C^{D3}), 129.7 (ov. t, C^{D3'}), 126.6 (C^{A5}), 126.1 (t, ³J_{CP} = 2.2 Hz, C^{C4}), 125.4 (C^{B5}), 125.0 (t, ¹J_{CP} = 14.4 Hz, C^{C2}), 123.6 (C^{A3}), 121.2 (C^{B3}), 121.2 (t, ³J_{CP} = NM, C^{C6}), 40.0 (C^c), 38.8 (C^a), 32.3 (C^b), 25.2 (C^d), 10.6 (C^e). ¹⁹F{¹H} NMR (471 MHz, 298 K, acetone-d₆, 298 K) δ/ppm −72.6 (d, ¹J_{FP} = 707 Hz, F^{PF6}). ³¹P{¹H} NMR (202 MHz, 298 K, acetone-d₆, 298 K) δ/ppm: −12.9 (broad, FWHM ≈ 250 Hz, P^{POP}), −144.2 (hept, ¹J_{PF} = 708 Hz, P^{PF6}). ESI(+)-MS (CH₂Cl₂/MeOH, m/z): 601.07 [M−PF₆−(3-EtPentbp)]⁺ (calc. 601.09), 855.26 [M−PF₆]⁺ (base peak, calc. 855.27). ESI(−)-MS (CH₂Cl₂/MeOH, m/z): 145.06 [PF₆][−] (calc. 144.96), 312.90 [2PF₆+Na][−] (base peak, calc. 312.91). UV-Vis (CH₂Cl₂, 2.5 × 10^{−5} mol dm^{−3}): λ/nm (ε/dm³ mol^{−1} cm^{−1}) 251 (29'400), 293 (25'100), 312 sh (17'500), 381 br (3'300). FTIR: 3061 (w), 2958 (w), 2928 (w), 2872 (w), 1597 (w), 1564 (w), 1435 (m), 1217 (m), 1093 (w), 876 (w), 834 (s), 746 (s), 695 (s), 557 (s), 510 (s), 479 (m), 423 (m) cm^{−1}. Found: C 63.03, H 5.17, N 2.74; C₅₃H₅₀CuF₆N₂O₃ requires C 63.57, H 5.03, N 2.80.

[Cu(xantphos)(3-EtPentbp)]⁺[PF₆][−]]

The reagents were xantphos (92.6 mg, 0.160 mmol, 1.0 eq.), 3-EtPentbp (40.7 mg, 0.160 mmol, 1.0 eq.) and [Cu(MeCN)₄][PF₆]₂ (59.6 mg, 0.160 mmol, 1.0 eq.). [Cu(xantphos)(3-EtPentbp)]⁺[PF₆][−] was isolated as a yellow solid (126 mg, 0.121 mmol, 75%). ¹H NMR (500 MHz, acetone-d₆, 298 K) δ/ppm: 8.50 (d, ³J_{HH} = 8.3 Hz, 1H, H^{A3}), 8.40 (d, ³J_{HH} = 7.8 Hz, 1H, H^{B3}), 8.36 (broad, 1H, H^{A6}), 8.19 (dd, ³J_{HH} = 7.9, 7.9 Hz, 1H, H^{B4}), 8.09 (ddd, ³J_{HH} = 7.9, 7.9 Hz, ⁴J_{HH} = 1.6 Hz, 1H, H^{A4}), 7.86 (dd, ³J_{HH} = 7.8 Hz, ⁴J_{HH} = 1.4 Hz, 2H, H^{C5}), 7.60 (dd, ³J_{HH} = 7.8 Hz, ⁴J_{HH} = 0.9 Hz, 1H, H^{B5}), 7.46 (dd, ³J_{HH} = 7.5, 5.1 Hz, ⁴J_{HH} = 1.1 Hz, 1H, H^{A5}), 7.4 (m, 2H, H^{D4}), 7.36 (m, 2H, H^{D4'}), 7.3 (dd, ³J_{HH} = 7.7, 7.7 Hz, 2H, H^{C4}), 7.26 (m, 4H, H^{D3}), 7.17 (m, 4H, H^{D3'}), 7.15 (m, 4H, H^{D2}), 6.97 (m, 4H, H^{D2'}), 6.74 (m, 2H, H^{C3}), 2.66 (m, 2H, H^a), 1.89 (s, 3H, H^{xantphos-Me}), 1.69 (s, 3H, H^{xantphos-Me'}), 1.18 (m, 2H, H^b), 0.86 (m, 4H, H^d), 0.55 (t, ³J_{HH} = 7.4 Hz, 6H, H^e), 0.54 (m, 1H, H^c). ¹³C{¹H} NMR (126 MHz, acetone-d₆, 298 K) δ/ppm: 163.6 (C^{B6}), 155.8 (t, ²J_{CP} = 6.3 Hz, C^{C1}), 153.6 (t, ³J_{CP} = 2.2 Hz, C^{A2}), 152.3 (t, ³J_{CP} = 1.9 Hz, C^{B2}), 149.8 (C^{A6}), 140.2 (C^{B4}), 139.9 (C^{A4}), 135.1 (t, ³J_{CP} = 1.7 Hz, C^{C6}), 133.9 (t, ²J_{CP} = 8.0 Hz, C^{D2}), 133.5 (t, ²J_{CP} = 7.8 Hz, C^{D2'}), 132.8 (t, ¹J_{CP} = 16.3 Hz, C^{D1}), 132.3 (t, ¹J_{CP} = 17.6 Hz, C^{D1'}), 131.5 (C^{C3}), 131.1 (C^{D4'}), 131.0 (C^{D4}), 129.9 (t, ³J_{CP} = 4.7 Hz, C^{D3}), 129.7 (t, ³J_{CP} = 4.7 Hz, C^{D3'}), 128.6 (C^{C5}), 126.8 (C^{A5}), 126.3 (t, ³J_{CP} = 2.4 Hz, C^{C4}), 125.7 (C^{B5}), 123.8 (C^{A3}), 121.5 (C^{B3}), 121.4 (t, ¹J_{CP} = 13.4 Hz, C^{C2}), 39.2 (C^c), 38.8 (C^a), 37.0 (C^{xantphos-bridge}), 32.3 (C^b), 30.1 (C^{xantphos-Me'}), 26.4 (C^{xantphos-Me}), 25.1 (C^d), 10.4 (C^e). ¹⁹F{¹H} NMR (471 MHz, 298 K, acetone-d₆, 298 K) δ/ppm −72.6 (d, ¹J_{FP} = 708 Hz, F^{PF6}). ³¹P{¹H} NMR (202 MHz, 298 K, acetone-d₆, 298 K) δ/ppm: −13.1 (broad, FWHM ≈ 240 Hz, P^{xantphos}), −144.2 (hept, ¹J_{PF} = 708 Hz, P^{PF6}). ESI(+)-MS (CH₂Cl₂/MeOH, m/z): 641.08 [M−PF₆−(3-EtPentbp)]⁺ (calc. 641.12), 895.27 [M−PF₆]⁺ (base peak, calc. 895.30). ESI(−)-MS (CH₂Cl₂/MeOH, m/z): 145.06 [PF₆][−]

(calc. 144.96), 312.89 [2PF₆+Na][−] (base peak, calc. 312.91). UV-Vis (CH₂Cl₂, 2.5 × 10^{−5} mol dm^{−3}): λ/nm (ε/dm³ mol^{−1} cm^{−1}) 248 (31,300), 284 (29,000), 301 sh (19,900), 313 sh (12,300), 380 br (3,290). FTIR: 3054 (w), 2955 (w), 2930 (w), 2873 (w), 1596 (w), 1573 (w), 1482 (w), 1435 (m), 1406 (s), 1238 (m), 1097 (w), 836 (s), 777 (m), 740 (s), 694 (s), 557 (s), 508 (s), 468 (m) cm^{−1}. Found: C 63.7, H 5.40, N 2.75; C₅₆H₅₄CuF₆N₂OP₃ requires C 64.58, H 5.23, N 2.69.

[Cu(POP)(2-PhEtbp)] [PF₆]

The reagents were POP (92.1 mg, 0.171 mmol, 1.0 eq.), 2-PhEtbp (44.4 mg, 0.171 mmol, 1.0 eq.) and [Cu(MeCN)₄][PF₆] (63.7 mg, 0.171 mmol, 1.0 eq.). [Cu(POP)(2-PhEtbp)][PF₆] was isolated as a yellow solid (138 mg, 0.134 mmol, 80%). ¹H NMR (500 MHz, acetone-d₆, 298 K) δ/ppm: 8.55 (ddd, ³J_{HH} = 5.1 Hz, ⁴J_{HH} = 1.6 Hz, ⁵J_{HH} = 0.8 Hz, 1H, H^{A6}), 8.52 (d, ³J_{HH} = 8.2 Hz, 1H, H^{A3}), 8.46 (d, ³J_{HH} = 7.8 Hz, 1H, H^{B3}), 8.16 (dd, ³J_{HH} = 7.9, 7.9 Hz, 1H, H^{B4}), 8.07 (ddd, ³J_{HH} = 7.9, 7.9 Hz, ⁴J_{HH} = 1.6 Hz, 1H, H^{A4}), 7.54 (d, ³J_{HH} = 7.7 Hz, 1H, H^{B5}), 7.38 (m, 2H, H^{D4}), 7.38 (m, 2H, H^{D4'}), 7.34 (ov. d, 1H, H^{A5}), 7.34 (m, 2H, H^{C4}), 7.25 (m, 2H, H^{C5}), 7.25 (m, 4H, H^{D3}), 7.25 (m, 4H, H^{D3'}), 7.20 (m, 1H, H^{F4}), 7.06 (m, 4H, H^{D2}), 7.06 (m, 4H, H^{D2'}), 7.05 (m, 2H, H^{F3}), 6.93 (m, 2H, H^{C6}), 6.84 (m, 2H, H^{C3}), 6.71 (m, 2H, H^{F2}), 3.22 (m, 2H, H^a), 2.64 (m, 2H, H^b). ¹³C{¹H} NMR (126 MHz, acetone-d₆, 298 K) δ/ppm: 162.4 (C^{B6}), 158.7 (t, ²J_{CP} = 7.2 Hz, C^{C1}), 153.5 (t, ³J_{CP} = 2.0 Hz, C^{A2}), 152.7 (t, ³J_{CP} = 2.0 Hz, C^{B2}), 150.2 (C^{A6}), 141.0 (C^{F1}), 140.1 (C^{B4}), 139.7 (C^{A4}), 134.9 (C^{C3}), 133.9 (C^{C5}), 133.9 (ov. t, C^{D2}), 133.9 (ov. t, C^{D2'}), 132.2 (ov. t, C^{D1}), 132.1 (ov. t, C^{D1'}), 131.1 (C^{D4}), 131.0 (C^{D4'}), 129.8 (ov. t, C^{D3}), 129.8 (ov. t, C^{D3'}), 129.8 (C^{F3}), 129.3 (C^{F2}), 127.0 (C^{F4}), 126.6 (C^{A5}), 126.6 (t, ³J_{CP} = NM, C^{C4}), 125.4 (C^{B5}), 124.7 (t, ¹J_{CP} = 14.4 Hz, C^{C2}), 123.7 (C^{A3}), 121.5 (C^{B3}), 121.2 (t, ³J_{CP} = 2.0 Hz, C^{C6}), 41.9 (C^a), 34.2 (C^b). ¹⁹F{¹H} NMR (471 MHz, 298 K, acetone-d₆, 298 K) δ/ppm −72.7 (d, ¹J_{FP} = 707 Hz, F^{PF6}). ³¹P{¹H} NMR (202 MHz, 298 K, acetone-d₆, 298 K) δ/ppm: −13.3 (broad, FWHM ≈ 250 Hz, P^{POP}), −144.2 (hept, ¹J_{PF} = 707 Hz, P^{PF6}). ESI(+)-MS (CH₂Cl₂/MeOH, m/z): 601.08 [M−PF₆−(2-PhEtbp)]⁺ (calc. 601.09), 861.22 [M−PF₆]⁺ (base peak, calc. 861.22). ESI(−)-MS (CH₂Cl₂/MeOH, m/z): 145.07 [PF₆][−] (calc. 144.96), 312.89 [2PF₆+Na][−] (base peak, calc. 312.91). UV-Vis (CH₂Cl₂, 2.5 × 10^{−5} mol dm^{−3}): λ/nm (ε/dm³ mol^{−1} cm^{−1}) 250 (24,500), 292 (20,900), 300 (19,800), 314 sh (13,100), 382 br (2,680). FTIR: 3058 (w), 3029 (w), 2962 (w), 1598 (w), 1573 (w), 1453 (w), 1435 (m), 1216 (m), 1094 (w), 836 (s), 778 (m), 745 (m), 695 (s), 557 (s), 510 (m), 468 (m) cm^{−1}. Found: C 63.95, H 4.50, N 3.07; C₅₄H₄₄CuF₆N₂OP₃ requires C 64.38, H 4.40, N 2.78.

[Cu(xantphos)(2-PhEtbp)] [PF₆]

The reagents were xantphos (44.6 mg, 0.171 mmol, 1.0 eq.), 2-PhEtbp (44.6 mg, 0.171 mmol, 1.0 eq.) and [Cu(MeCN)₄][PF₆] (63.7 mg, 0.171 mmol, 1.0 eq.). [Cu(xantphos)(2-PhEtbp)][PF₆] was isolated as a yellow solid (124 mg, 0.118 mmol, 69%). ¹H NMR (500 MHz, acetone-d₆, 298 K) δ/ppm: 8.53 (d, ³J_{HH} = 8.1 Hz, 1H, H^{A3}), 8.43 (d, ³J_{HH} = 7.9 Hz, 1H, H^{B3}), 8.09 (dd, ³J_{HH} = 8.0, 8.0 Hz, 1H, H^{B4}), 8.08 (dd, ³J_{HH} = 7.9, 7.9 Hz, 1H, H^{A4}), 8.08 (ov. d, 1H, H^{A6}), 7.85 (dd, ³J_{HH} = 7.9 Hz, ⁴J_{HH} = 1.4 Hz, 2H, H^{C5}), 7.41 (ov. d, 1H, H^{B5}), 7.40 (m, 2H, H^{D4}), 7.36 (ov. d, 1H, H^{A5}), 7.31 (m, 2H, H^{D4'}), 7.29 (ov. dd, 2H, H^{C4}), 7.25 (m, 4H, H^{D3}), 7.13 (m, 1H, H^{F4}), 7.09 (m, 2H, H^{F3}), 7.07 (m, 4H, H^{D2}), 7.07 (m, 4H, H^{D2'}), 6.95 (m, 4H, H^{D2'}), 6.69 (m, 2H, H^{F2}), 6.68 (m, 2H, H^{C3}), 3.13 (m, 2H, H^a), 2.55 (m, 2H, H^b), 1.80 (s, 3H, H^{xantphos-Me}), 1.77 (s, 3H, H^{xantphos-Me'}). ¹³C{¹H} NMR (126 MHz, acetone-d₆, 298 K) δ/ppm: 162.0 (C^{B6}), 155.7 (t, ²J_{CP} = 6.2 Hz, C^{C1}), 153.5 (t, ³J_{CP} = 2.1 Hz, C^{A2}), 152.5 (t, ³J_{CP} = 1.9 Hz, C^{B2}), 149.5 (C^{A6}), 140.3 (C^{F1}), 140.0 (C^{A4}), 140.0 (C^{B4}), 135.0 (t, ³J_{CP} = 1.7 Hz, C^{C6}), 133.8 (t, ²J_{CP} = 7.9 Hz, C^{D2'}), 133.7 (t, ²J_{CP} = 7.9 Hz, C^{D2}), 132.6 (t, ¹J_{CP} = 16.9 Hz, C^{D1}), 132.1 (t, ¹J_{CP} = 17.1 Hz, C^{D1'}), 131.6 (C^{C3}), 131.1 (C^{D4}), 131.0 (C^{D4'}), 129.9 (t, ³J_{CP} = 4.7 Hz, C^{D3}), 129.7 (t, ³J_{CP} = 4.7 Hz, C^{D3'}), 129.3 (C^{F3}), 129.0 (C^{F2}), 128.7 (C^{C5}), 127.0 (C^{F4}), 126.8 (C^{A5}), 126.4 (t, ³J_{CP} = 2.5 Hz, C^{C4}), 125.8 (C^{B5}), 123.9 (C^{A3}), 121.6 (C^{B3}), 121.3 (t, ¹J_{CP} = 13.7 Hz, C^{C2}), 41.5 (C^a), 37.0 (C^{xantphos-bridge}), 33.9 (C^b), 28.8 (C^{xantphos-Me}), 28.0 (C^{xantphos-Me'}). ¹⁹F{¹H} NMR (471 MHz, 298 K, acetone-d₆, 298 K) δ/ppm −72.6 (d, ¹J_{FP} = 708 Hz, F^{PF6}). ³¹P{¹H} NMR (202 MHz, 298 K, acetone-d₆, 298 K) δ/ppm: −12.7 (broad, FWHM ≈ 240 Hz, P^{xantphos}), −144.2 (hept, ¹J_{PF} = 707 Hz, P^{PF6}). ESI(+)-MS (CH₂Cl₂/MeOH, m/z): 641.07 [M−PF₆−(2-PhEtbp)]⁺ (calc. 641.12), 901.25 [M−PF₆]⁺ (base peak, calc. 901.25). ESI(−)-MS (CH₂Cl₂/MeOH, m/z): 145.07 [PF₆][−] (calc. 144.96), 312.91 [2PF₆+Na][−] (base peak, calc. 312.91). UV-Vis (CH₂Cl₂, 2.5 × 10^{−5} mol dm^{−3}): λ/nm (ε/dm³ mol^{−1} cm^{−1}) 249 (30,200), 275 (26,800), 299 (21,200), 313 sh (12,100), 382 br (3,140). FTIR: 3059 (w), 3022 (w), 2969 (w), 1596 (w), 1565 (w), 1453 (w), 1434 (m), 1403 (m), 1227 (m), 1096 (w), 835 (s), 738 (s), 694 (s), 556 (s), 505 (s) cm^{−1}. Found: C 64.60, H 4.77, N 2.75; C₅₇H₄₈CuF₆N₂OP₃ requires C 65.36, H 4.62, N 2.67.

[Cu(POP)((2-PhEt)₂bpy)] [PF₆]

The reagents were POP (148 mg, 0.275 mmol, 1.1 eq.), (2-PhEt)₂bpy (91.1 mg, 0.250 mmol, 1.0 eq.) and [Cu(MeCN)₄][PF₆] (93.2 mg, 0.250 mmol, 1.0 eq.). [Cu(POP)((2-PhEt)₂bpy)][PF₆] was isolated as a yellow solid (188 mg, 0.169 mmol, 68%). ¹H NMR (500 MHz, CDCl₃, 298 K) δ/ppm: 8.08 (d, ³J_{HH} = 8.1 Hz, 2H, H^{B3}), 7.99 (dd, ³J_{HH} = 8.1, 7.8 Hz, 2H, H^{B4}), 7.30 (d, ³J_{HH} = 7.8 Hz, 2H, H^{B5}), 7.25 (dd, ³J_{HH} = 7.2, 7.2 Hz, 4H, H^{D4}), 7.19 (m, 2H, H^{C5}), 7.19 (m, 2H, H^{F4}), 7.12 (m, 4H, H^{F3}), 7.06 (m, 2H, H^{C3}), 7.03 (dd, ³J_{HH} = 7.3, 7.3 Hz, 8H, H^{D3}), 7 (m, 2H, H^{C4}), 6.89 (m, 8H, H^{D2}), 6.46 (m, 2H, H^{C6}), 6.44 (m, 4H, H^{F2}), 2.94 (m, 4H, H^a), 2.55 (m, 4H, H^b). ¹³C{¹H} NMR (126 MHz, CDCl₃, 298 K) δ/ppm: 160.8 (C^{B6}), 158.6 (t, ²J_{CP} = 6.1 Hz, C^{C1}), 158.5 (C^{F1}), 152.5 (t, ³J_{CP} = 2.0 Hz, C^{B2}), 139.6 (C^{B4}), 133.6 (C^{C5}), 133.6 (C^{F4}), 132.9 (t, ²J_{CP} = 7.8 Hz, C^{D2}), 132.3 (t, ¹J_{CP} = 16.2 Hz, C^{D1}), 132.1 (C^{C3}), 130.2 (C^{D4}), 128.9 (t, ²J_{CP} = 4.6 Hz, C^{D3}), 128.4 (C^{F3}), 128.3 (C^{F2}), 125.0 (t, ¹J_{CP} = 13.7 Hz, C^{C2}), 124.9 (t, ³J_{CP} = 1.9 Hz, C^{C4}), 123.9 (C^{B5}), 121.3 (C^{B3}), 120.4 (C^{C6}), 41.2 (C^a), 33.6 (C^b). ¹⁹F{¹H} NMR (471 MHz, 298 K, CDCl₃, 298 K) δ/ppm −72.2 (d, ¹J_{FP} = 712 Hz, F^{PF6}). ³¹P{¹H} NMR (202 MHz, 298 K, CDCl₃, 298 K) δ/ppm: −14.7 (broad, FWHM ≈ 120 Hz, P^{POP}), −144.2 (hept, ¹J_{PF} = 712 Hz, P^{PF6}). ESI(+)-MS (CH₂Cl₂/MeOH, m/z): 601.08 [M−PF₆−((2-PhEt)₂bpy)]⁺ (base peak, calc. 601.09), 965.27 [M−PF₆]⁺ (calc. 965.29), 1139.22 [M−((2-PhPr)₂bpy)+2POP]⁺ (calc. 1139.25). ESI(−)-MS

(CH₂Cl₂/MeOH, m/z): 145.00 [PF₆][−] (calc. 144.96), 312.87 [2PF₆+Na][−] (base peak, calc. 312.91). HR-ESI(+)-MS (CH₂Cl₂/MeOH, m/z): 965.2853 [M−PF₆]⁺ (calc. 965.2845). UV-Vis (CH₂Cl₂, 2.5 × 10^{−5} mol dm^{−3}): λ/nm (ε/dm³ mol^{−1} cm^{−1}) 260 sh (31,300), 282 (18,900), 290 (18,500), 305 (16,900), 313 sh (12,700), 369 br (2,460). FTIR: 3062 (w), 2933 (w), 2857 (w), 1597 (w), 1563 (w), 1435 (m), 1258 (w), 1215 (m), 1094 (m), 1000 (w), 833 (s), 746 (s), 695 (s), 556 (s), 511 (s), 477 (m), 412 (m) cm^{−1}. Found: C 63.62, H 4.46, N 2.37; C₆₂H₅₂CuF₆N₂OP₃·CH₂Cl₂ requires C 63.24, H 4.55, N 2.34.

[Cu(xantphos)((2-PhEt)₂bpy)][PF₆]

The reagents were xantphos (145 mg, 0.250 mmol, 1.0 eq.), (2-PhEt)₂bpy (91.1 mg, 0.250 mmol, 1.0 eq.) and [Cu(MeCN)₄][PF₆] (93.2 mg, 0.250 mmol, 1.0 eq.). [Cu(xantphos)((2-PhEt)₂bpy)][PF₆] was isolated as a yellow solid (207 mg, 0.180 mmol, 72%). ¹H NMR (500 MHz, acetone-d₆, 298 K) δ/ppm: 8.04 (d, ³J_{HH} = 8.1 Hz, 2H, H^{B3}), 7.89 (dd, ³J_{HH} = 7.9, 7.9 Hz, 2H, H^{B4}), 7.83 (dd, ³J_{HH} = 7.8 Hz, ⁴J_{HH} = 1.4 Hz, 2H, H^{C5}), 7.40 (dd, ³J_{HH} = 7.3, 7.3 Hz, 2H, H^{D4}), 7.31 (dd, ³J_{HH} = 7.7, 7.7 Hz, 2H, H^{C4}), 7.26 (d, ³J_{HH} = 7.9 Hz, 2H, H^{B5}), 7.15 (m, 4H, H^{D3}), 7.11 (m, 4H, H^{D2}), 7.09 (m, 2H, H^{F4}), 7.07 (m, 4H, H^{F3}), 7.00 (m, 2H, H^{C3}), 6.64 (m, 4H, H^{F2}), 2.99 (m, 4H, H^a), 2.48 (m, 4H, H^b), 1.72 (s, 3H, H^{xantphos-Me}). ¹³C{¹H} NMR (126 MHz, acetone-d₆, 298 K) δ/ppm: 161.9 (C^{B6}), 155.5 (t, ²J_{CP} = 6.5 Hz, C^{C1}), 153.6 (t, ³J_{CP} = 1.8 Hz, C^{B2}), 140.1 (C^{F1}), 139.7 (C^{B4}), 134.7 (t, ³J_{CP} = 1.7 Hz, C^{C6}), 134.1 (t, ²J_{CP} = 7.7 Hz, C^{D2}), 132.1 (t, ¹J_{CP} = 16.1 Hz, C^{D1}), 131.4 (C^{C3}), 131.1 (C^{D4}), 129.8 (t, ³J_{CP} = 4.6 Hz, C^{D3}), 129.2 (C^{F3}), 129.1 (C^{F2}), 128.9 (C^{C5}), 126.9 (C^{F4}), 126.4 (t, ³J_{CP} = 2.2 Hz, C^{C4}), 125.3 (C^{B5}), 122.8 (t, ¹J_{CP} = 12.2 Hz, C^{C2}), 121.6 (C^{B3}), 40.8 (C^a), 36.8 (C^{xantphos-bridge}), 34.1 (C^b), 28.9 (C^{xantphos-Me}). ¹⁹F{¹H} NMR (471 MHz, 298 K, acetone-d₆, 298 K) δ/ppm: −72.6 (d, ¹J_{FP} = 707 Hz, F^{PF6}). ³¹P{¹H} NMR (202 MHz, 298 K, acetone-d₆, 298 K) δ/ppm: −13.5 (broad, FWHM ≈ 150 Hz, P^{xantphos}), −144.2 (hept, ¹J_{PF} = 707 Hz, P^{PF6}). ESI(+)-MS (CH₂Cl₂/MeOH, m/z): 641.15 [M−PF₆−((2-PhEt)₂bpy)]⁺ (base peak, calc. 641.12), 1005.32 [M−PF₆]⁺ (calc. 1005.32), 1219.32 [M−((3-PhPr)₂bpy)+2xantphos]⁺ (calc. 1219.31). ESI(−)-MS (CH₂Cl₂/MeOH, m/z): 145.02 [PF₆][−] (calc. 144.96), 312.88 [2PF₆+Na][−] (base peak, calc. 312.91). UV-Vis (CH₂Cl₂, 2.5 × 10^{−5} mol dm^{−3}): λ/nm (ε/dm³ mol^{−1} cm^{−1}) 246 sh (32,900), 283 (30,200), 289 (29,400), 299 (22,500), 312 sh (13,400), 380 br (3,440). FTIR: 3061 (w), 3033 (w), 2964 (w), 2924 (w), 1599 (w), 1571 (w), 1456 (w), 1437 (m), 1402 (m), 1227 (m), 833 (s), 791 (m), 737 (s), 692 (s), 556 (s), 516 (s), 501 (s), 464 (m) cm^{−1}. Found: C 67.76, H 4.77, N 2.78; C₆₅H₅₆CuF₆N₂OP₃ requires C 67.79, H 4.90, N 2.43.

[Cu(POP)(3-PhPrbpy)][PF₆]

The reagents were xantphos (135 mg, 0.250 mmol, 1.0 eq.), 3-PhPrbpy (68.6 mg, 0.250 mmol, 1.0 eq.) and [Cu(MeCN)₄][PF₆] (93.2 mg, 0.250 mmol, 1.0 eq.). [Cu(POP)(3-PhPrbpy)][PF₆] was isolated as a yellow solid (144 mg, 0.141 mmol, 56%). ¹H NMR (500 MHz, acetone-d₆, 298 K) δ/ppm: 8.70 (ddd, ³J_{HH} = 5.1 Hz, ⁴J_{HH} = 1.5 Hz, ⁵J_{HH} = 0.8 Hz, 1H, H^{A6}), 8.51 (d, ³J_{HH} = 8.2 Hz, 1H, H^{A3}), 8.44 (d, ³J_{HH} = 7.8 Hz, 1H, H^{B3}), 8.16 (dd, ³J_{HH} = 7.9, 7.9 Hz, 1H, H^{B4}), 8.08 (ddd, ³J_{HH} = 7.7, 7.7 Hz, ⁴J_{HH} = 1.6 Hz, 1H, H^{A4}), 7.56 (d, ³J_{HH} = 7.9 Hz, 1H, H^{B5}), 7.41 (ov. d, 1H, H^{A5}), 7.39 (m, 2H, H^{D4}), 7.39 (m, 2H, H^{D4'}), 7.28 (m, 4H, H^{D3}), 7.28 (m, 4H, H^{D3'}), 7.27 (m, 2H, H^{C5}), 7.24 (m, 2H, H^{C6}), 7.22 (m, 2H, H^{F3}), 7.16 (m, 2H, H^{C4}), 7.16 (m, 1H, H^{F4}), 7.14 (m, 4H, H^{D2}), 7.13 (m, 4H, H^{D2}), 6.94 (m, 2H, H^{F2}), 6.90 (m, 2H, H^{C3}), 2.93 (m, 2H, H^a), 2.07 (m, 2H, H^c), 1.54 (m, 2H, H^b). ¹³C{¹H} NMR (126 MHz, acetone-d₆, 298 K) δ/ppm: 163.4 (C^{B6}), 158.8 (t, ²J_{CP} = 6.0 Hz, C^{C1}), 153.5 (t, ³J_{CP} = 2.1 Hz, C^{A2}), 152.5 (t, ³J_{CP} = 1.7 Hz, C^{B2}), 150.3 (C^{A6}), 142.5 (C^{F1}), 140.2 (C^{B4}), 139.7 (C^{A4}), 135.0 (C^{C3}), 134.3 (C^{C5}), 134.1 (t, ²J_{CP} = 7.8 Hz, C^{D2}), 133.8 (t, ²J_{CP} = 8.0 Hz, C^{D2}), 132.1 (t, ¹J_{CP} = 16.9 Hz, C^{D1}), 132.1 (t, ¹J_{CP} = 16.9 Hz, C^{D1}), 131.1 (C^{D4}), 131.1 (C^{D4}), 129.8 (ov. t, C^{D3}), 129.8 (ov. t, C^{D3'}), 129.1 (C^{F3}), 129.0 (C^{F2}), 126.7 (C^{A5}), 126.2 (C^{F4}), 126.1 (t, ³J_{CP} = 2.3 Hz, C^{C4}), 125.4 (C^{B5}), 125.1 (t, ¹J_{CP} = 14.6 Hz, C^{C2}), 123.6 (C^{A3}), 121.4 (t, ³J_{CP} = 2.0 Hz, C^{C6}), 121.3 (C^{B3}), 40.8 (C^a), 35.9 (C^c), 31.0 (C^b). ¹⁹F{¹H} NMR (471 MHz, 298 K, acetone-d₆, 298 K) δ/ppm: −72.6 (d, ¹J_{FP} = 707 Hz, F^{PF6}). ³¹P{¹H} NMR (202 MHz, 298 K, acetone-d₆, 298 K) δ/ppm: −12.0 (broad, FWHM ≈ 240 Hz, P^{POP}), −143.8 (hept, ¹J_{PF} = 708 Hz, P^{PF6}). ESI(+)-MS (CH₂Cl₂/MeOH, m/z): 601.06 [M−PF₆−(3-PhPrbpy)]⁺ (calc. 601.09), 875.24 [M−PF₆]⁺ (base peak, calc. 875.24). ESI(−)-MS (CH₂Cl₂/MeOH, m/z): 145.07 [PF₆][−] (calc. 144.96), 312.89 [2PF₆+Na][−] (base peak, calc. 312.91). UV-Vis (CH₂Cl₂, 2.5 × 10^{−5} mol dm^{−3}): λ/nm (ε/dm³ mol^{−1} cm^{−1}) 249 (27,400), 284 (22,500), 290 (23,200), 298 (22,300), 305 sh (19,400), 312 sh (16,100), 382 br (3,080). FTIR: 3059 (w), 3034 (w), 2944 (w), 1598 (w), 1563 (w), 1452 (m), 1435 (m), 1259 (w), 1219 (m), 1094 (w), 832 (s), 775 (m), 748 (s), 695 (s), 556 (s), 496 (m), 508 (s) cm^{−1}. Found: C 64.28, H 4.64, N 2.77; C₅₅H₄₆CuF₆N₂OP₃ requires C 64.67, H 4.54, N 2.74.

[Cu(xantphos)(3-PhPrbpy)][PF₆]

The reagents were xantphos (145 mg, 0.250 mmol, 1.0 eq.), 3-PhPrbpy (68.6 mg, 0.250 mmol, 1.0 eq.) and [Cu(MeCN)₄][PF₆] (93.2 mg, 0.250 mmol, 1.0 eq.). [Cu(xantphos)(3-PhPrbpy)][PF₆] was isolated as a yellow solid (188 mg, 0.178 mmol, 71%). ¹H NMR (500 MHz, acetone-d₆, 298 K) δ/ppm: 8.57 (broad, 1H, H^{A6}), 8.52 (d, ³J_{HH} = 8.2 Hz, 1H, H^{A3}), 8.45 (d, ³J_{HH} = 8.0 Hz, 1H, H^{B3}), 8.20 (dd, ³J_{HH} = 7.9, 7.9 Hz, 1H, H^{B4}), 8.11 (dd, ³J_{HH} = 8.0, 8.0 Hz, 1H, H^{A4}), 7.87 (dd, ³J_{HH} = 7.8 Hz, ⁴J_{HH} = 1.4 Hz, 2H, H^{C5}), 7.60 (dd, ³J_{HH} = 7.9 Hz, ⁴J_{HH} = 0.9 Hz, 1H, H^{B5}), 7.56 (ddd, ³J_{HH} = 7.6, 5.1 Hz, ⁴J_{HH} = 1.1 Hz, 1H, H^{A5}), 7.41 (m, 2H, H^{D4}), 7.35 (m, 2H, H^{D4'}), 7.32 (m, 2H, H^{C4}), 7.28 (m, 4H, H^{D3}), 7.23 (m, 4H, H^{D2}), 7.17 (m, 4H, H^{D3'}), 7.17 (m, 2H, H^{F3}), 7.11 (m, 1H, H^{F4}), 6.92 (m, 4H, H^{D2}), 6.82 (m, 2H, H^{F2}), 6.75 (m, 2H, H^{C3}), 2.57 (m, 2H, H^a), 2.47 (m, 2H, H^b), 1.91 (s, 3H, H^{xantphos-Me}), 1.70 (m, 2H, H^c), 1.64 (s, 3H, H^{xantphos-Me}). ¹³C{¹H} NMR (126 MHz, acetone-d₆, 298 K) δ/ppm: 162.7 (C^{B6}), 155.9 (t, ²J_{CP} = 6.2 Hz, C^{C1}), 153.5 (t, ³J_{CP} = 2.2 Hz, C^{A2}), 152.4 (t, ³J_{CP} = 1.9 Hz, C^{B2}), 150.1 (C^{A6}), 142.2 (C^{F1}), 140.4 (C^{B4}), 139.9 (C^{A4}), 135.2 (t, ³J_{CP} = 1.7 Hz, C^{C6}), 134.1 (t, ²J_{CP} = 8.1 Hz, C^{D2}), 133.4 (t, ²J_{CP} = 7.7 Hz, C^{D2}), 132.8 (t, ¹J_{CP} = 16.0 Hz, C^{D1}), 132.3 (t, ¹J_{CP} = 18.0 Hz, C^{D1}), 131.6 (C^{C3}), 131.2 (C^{D4}), 131.1 (C^{D4}), 129.9 (t, ³J_{CP} = 4.7 Hz, C^{D3}), 129.8 (t, ³J_{CP} = 4.7 Hz, C^{D3'}), 129.1 (C^{F3}), 128.9 (C^{F2}), 128.6 (C^{C5}), 127.1 (C^{A5}), 126.7 (C^{F4}), 126.4 (t, ³J_{CP} = 2.4 Hz, C^{C4}), 125.5 (C^{B5}), 123.8 (C^{A3}), 121.6

(t, $^1J_{CP}$ = 13.4 Hz, C^{C2}), 121.5 (C^{B3}), 41.2 (C^a), 37.0 (C^{xantphos-bridge}), 35.4 (C^c), 31.1 (C^{xantphos-Me'}), 30.7 (C^b), 25.4 (C^{xantphos-Me}). $^{19}F\{^1H\}$ NMR (471 MHz, 298 K, acetone- d_6 , 298 K) δ /ppm: -72.6 (d, $^1J_{FP}$ = 708 Hz, F^{PF6}). $^{31}P\{^1H\}$ NMR (202 MHz, 298 K, acetone- d_6 , 298 K) δ /ppm: -13.1 (broad, FWHM $\approx$ 260 Hz, P^{xantphos}), -144.2 (hept, $^1J_{PF}$ = 707 Hz, P^{PF6}). ESI(+)-MS (CH₂Cl₂/MeOH, m/z): 641.06 [M-PF₆-(3-PhPrbpy)]⁺ (calc. 641.12), 915.24 [M-PF₆]⁺ (base peak, calc. 915.27). ESI(-)-MS (CH₂Cl₂/MeOH, m/z): 145.06 [PF₆]⁻ (calc. 144.96), 312.81 [2PF₆+Na]⁻ (base peak, calc. 312.91). HR-ESI(+)-MS (CH₂Cl₂/MeOH, m/z): 915.2692 [M-PF₆]⁺ (calc. 915.2689). UV-Vis (CH₂Cl₂, 2.5×10^{-5} mol dm⁻³): λ /nm (ϵ /dm³ mol⁻¹ cm⁻¹) 248 (27,100), 277 (24,700), 282 (25,300), 288 (24,900), 298 sh (19,300), 311 sh (11,400), 379 br (3,820). FTIR: 3058 (w), 3024 (w), 2955 (w), 1596 (w), 1565 (w), 1452 (m), 1435 (m), 1405 (m), 1232 (m), 1095 (w), 836 (s), 778 (m), 740 (m), 694 (s), 557 (s), 508 (s), 467 (m) cm⁻¹. Found: C 63.72, H 4.70, N 2.72; C₅₈H₅₀CuF₆N₂OP₃·0.5CH₂Cl₂ requires C 63.65, H 4.66, N 2.54.

[Cu(POP)((3-PhPr)₂bpy)][PF₆]

The reagents were POP (148 mg, 0.275 mmol, 1.1 eq.), (3-PhPr)₂bpy (98.1 mg, 0.250 mmol, 1.0 eq.) and [Cu(MeCN)₄][PF₆] (93.2 mg, 0.250 mmol, 1.0 eq.). [Cu(POP)((3-PhPr)₂bpy)][PF₆] was isolated as a yellow solid (168 mg, 0.148 mmol, 59%). 1H NMR (500 MHz, CDCl₃, 298 K) δ /ppm: 8.10 (d, $^3J_{HH}$ = 8.1 Hz, 2H, H^{B3}), 7.97 (dd, $^3J_{HH}$ = 8.1, 7.7 Hz, 2H, H^{B4}), 7.29 (m, 4H, H^{D4}), 7.26 (d, $^3J_{HH}$ = 7.7 Hz, 2H, H^{B5}), 7.22 (m, 4H, H^{F3}), 7.19 (m, 2H, H^{C4}), 7.19 (m, 2H, H^{C5}), 7.16 (m, 2H, H^{F4}), 7.12 (m, 8H, H^{D3}), 7.01 (m, 2H, H^{C3}), 7.01 (m, 8H, H^{D2}), 6.94 (m, 2H, H^{C6}), 6.85 (m, 4H, H^{F2}), 2.74 (m, 4H, H^a), 1.89 (m, 4H, H^c), 1.49 (m, 4H, H^b). $^{13}C\{^1H\}$ NMR (126 MHz, CDCl₃, 298 K) δ /ppm: 161.7 (C^{B6}), 158.0 (t, $^2J_{CP}$ = 5.9 Hz, C^{C1}), 152.6 (t, $^3J_{CP}$ = 1.9 Hz, C^{B2}), 141.4 (C^{F1}), 139.6 (C^{B4}), 133.7 (C^{C5}), 133.2 (t, $^2J_{CP}$ = 7.9 Hz, C^{D2}), 131.6 (t, $^1J_{CP}$ = 16.1 Hz, C^{D1}), 130.3 (C^{D4}), 129.0 (C^{C3}), 129.0 (t, $^2J_{CP}$ = 4.7 Hz, C^{D3}), 128.5 (C^{F3}), 128.2 (C^{F2}), 126.2 (C^{F4}), 125.8 (t, $^1J_{CP}$ = 13.5 Hz, C^{C2}), 125.4 (t, $^3J_{CP}$ = 2.1 Hz, C^{C4}), 124.0 (C^{B5}), 121.1 (C^{B3}), 120.3 (t, $^3J_{CP}$ = 1.8 Hz, C^{C6}), 40.0 (C^a), 35.2 (C^c), 30.1 (C^b). $^{19}F\{^1H\}$ NMR (471 MHz, 298 K, CDCl₃, 298 K) δ /ppm: -72.2 (d, $^1J_{FP}$ = 712 Hz, F^{PF6}). $^{31}P\{^1H\}$ NMR (202 MHz, 298 K, CDCl₃, 298 K) δ /ppm: -13.7 (broad, FWHM $\approx$ 90 Hz, P^{POP}), -144.2 (hept, $^1J_{PF}$ = 712 Hz, P^{PF6}). ESI(+)-MS (CH₂Cl₂/MeOH, m/z): 601.06 [M-PF₆-(3-PhPr)₂bpy]⁺ (base peak, calc. 601.09), 993.33 [M-PF₆]⁺ (calc. 993.32), 1139.23 [M-((3-PhPr)₂bpy)+2POP]⁺ (calc. 1139.25). ESI(-)-MS (CH₂Cl₂/MeOH, m/z): 145.00 [PF₆]⁻ (calc. 144.96), 312.88 [2PF₆+Na]⁻ (base peak, calc. 312.91). UV-Vis (CH₂Cl₂, 2.5×10^{-5} mol dm⁻³): λ /nm (ϵ /dm³ mol⁻¹ cm⁻¹) 255 sh (24,500), 287 (20,600), 305 (19,400), 318 sh (14,600), 369 br (2,480). FTIR: 3061 (w), 3027 (w), 2949 (w), 1597 (w), 1565 (w), 1461 (m), 1435 (m), 1256 (w), 1211 (m), 834 (s), 776 (m), 740 (m), 696 (s), 556 (s), 505 (m), 485 (m), 419 (m) cm⁻¹. Found: C 67.60, H 4.92, N 2.66; C₆₄H₅₆CuF₆N₂OP₃ requires C 67.45, H 4.95, N 2.46.

[Cu(xantphos)((3-PhPr)₂bpy)][PF₆]

The reagents were xantphos (159 mg, 0.275 mmol, 1.1 eq.), (3-PhPr)₂bpy (98.1 mg, 0.250 mmol, 1.0 eq.) and [Cu(MeCN)₄][PF₆] (93.2 mg, 0.250 mmol, 1.0 eq.). [Cu(xantphos)((3-PhPr)₂bpy)][PF₆] was isolated as a yellow solid (209 mg, 0.178 mmol, 71%). 1H NMR (500 MHz, acetone- d_6 , 298 K) δ /ppm: 8.17 (d, $^3J_{HH}$ = 7.9 Hz, 2H, H^{B3}), 8.05 (dd, $^3J_{HH}$ = 7.9, 7.9 Hz, 2H, H^{B4}), 7.86 (dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.4 Hz, 2H, H^{C5}), 7.54 (d, $^3J_{HH}$ = 7.8 Hz, 2H, H^{B5}), 7.44 (dd, $^3J_{HH}$ = 7.2, 7.2 Hz, 2H, H^{D4}), 7.35 (dd, $^3J_{HH}$ = 7.8, 7.8 Hz, 2H, H^{C4}), 7.27 (m, 4H, H^{D3}), 7.24 (m, 4H, H^{D2}), 7.19 (m, 4H, H^{F3}), 7.12 (m, 2H, H^{F4}), 7.04 (m, 2H, H^{C3}), 6.88 (m, 4H, H^{F2}), 2.72 (m, 4H, H^a), 1.73 (s, 3H, H^{xantphos-Me}), 1.68 (m, 4H, H^c), 1.52 (m, 4H, H^b). $^{13}C\{^1H\}$ NMR (126 MHz, acetone- d_6 , 298 K) δ /ppm: 162.6 (C^{B6}), 155.9 (t, $^2J_{CP}$ = 6.5 Hz, C^{C1}), 153.5 (t, $^3J_{CP}$ = 1.8 Hz, C^{B2}), 142.4 (C^{F1}), 140.1 (C^{B4}), 135.2 (t, $^3J_{CP}$ = 1.8 Hz, C^{C6}), 134.2 (t, $^2J_{CP}$ = 7.6 Hz, C^{D2}), 132.3 (t, $^1J_{CP}$ = 16.1 Hz, C^{D1}), 131.2 (C^{C3}), 131.1 (C^{D4}), 129.9 (t, $^3J_{CP}$ = 4.5 Hz, C^{D3}), 129.1 (C^{F3}), 128.9 (C^{F2}), 128.7 (C^{C5}), 126.7 (C^{F4}), 126.5 (t, $^3J_{CP}$ = 2.2 Hz, C^{C4}), 124.9 (C^{B5}), 123.1 (t, $^1J_{CP}$ = 12.1 Hz, C^{C2}), 121.6 (C^{B3}), 41.0 (C^a), 37.0 (C^{xantphos-bridge}), 35.1 (C^c), 30.8 (C^b), 28.4 (C^{xantphos-Me}). $^{19}F\{^1H\}$ NMR (471 MHz, 298 K, acetone- d_6 , 298 K) δ /ppm: -72.6 (d, $^1J_{FP}$ = 708 Hz, F^{PF6}). $^{31}P\{^1H\}$ NMR (202 MHz, 298 K, acetone- d_6 , 298 K) δ /ppm: -14.4 (broad, FWHM $\approx$ 160 Hz, P^{xantphos}), -144.2 (hept, $^1J_{PF}$ = 707 Hz, P^{PF6}). ESI(+)-MS (CH₂Cl₂/MeOH, m/z): 641.07 [M-PF₆-(3-PhPr)₂bpy]⁺ (base peak, calc. 641.12), 1033.26 [M-PF₆]⁺ (calc. 1033.35), 1219.21 [M-((3-PhPr)₂bpy)+2xantphos]⁺ (calc. 1219.31). ESI(-)-MS (CH₂Cl₂/MeOH, m/z): 145.06 [PF₆]⁻ (calc. 144.96), 312.91 [2PF₆+Na]⁻ (base peak, calc. 312.91). UV-Vis (CH₂Cl₂, 2.5×10^{-5} mol dm⁻³): λ /nm (ϵ /dm³ mol⁻¹ cm⁻¹) 246 sh (32,900), 275 (27,400), 280 (27,800), 290 (26,600), 307 sh (17,800), 320 sh (11,200), 371 br (2,540). FTIR: 3057 (w), 3025 (w), 2923 (w), 2859 (w), 1598 (w), 1572 (w), 1461 (w), 1435 (m), 1403 (m), 1225 (m), 1094 (w), 835 (s), 742 (s), 695 (s), 556 (s), 513 (s), 501 (m), 458 (m) cm⁻¹. Found: C 67.89, H 5.14, N 2.43; C₆₇H₆₀CuF₆N₂OP₃ requires C 68.22, H 5.13, N 2.37.

[Cu(xantphos)(6-Cy-6'-Mebpy)][PF₆]

The reagents were xantphos (65.4 mg, 0.113 mmol, 1.0 eq.), 6-Cy-6'-Mebpy (28.4 mg, 0.113 mmol, 1.0 eq.) and [Cu(MeCN)₄][PF₆] (42.1 mg, 0.113 mmol, 1.0 eq.). [Cu(xantphos)(6-Cy-6'-Mebpy)][PF₆] was isolated as a yellow solid (89.3 mg, 0.0859 mmol, 76%). 1H NMR (500 MHz, acetone- d_6 , 298 K) δ /ppm: 8.19 (d, $^3J_{HH}$ = 7.9 Hz, 1H, H^{B3}), 8.14 (d, $^3J_{HH}$ = 7.6 Hz, 1H, H^{A3}), 8.11 (dd, $^3J_{HH}$ = 7.9, 7.9 Hz, 1H, H^{B4}), 7.96 (dd, $^3J_{HH}$ = 7.8, 7.8 Hz, 1H, H^{A4}), 7.82 (dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.4 Hz, 2H, H^{C5}), 7.65 (d, $^3J_{HH}$ = 7.9 Hz, 1H, H^{B5}), 7.43 (m, 2H, H^{D4}), 7.43 (m, 2H, H^{D4'}), 7.39 (d, $^3J_{HH}$ = 7.7 Hz, 1H, H^{A5}), 7.32 (dd, $^3J_{HH}$ = 7.8, 7.8 Hz, 2H, H^{C4}), 7.27 (m, 4H, H^{D2}), 7.24 (m, 4H, H^{D3}), 7.23 (m, 4H, H^{D3'}), 7.18 (m, 4H, H^{D2'}), 7.00 (m, 2H, H^{C3}), 2.84 (m, 1H, H^{F1}), 2.08 (s, 3H, H^{B6-Me}), 1.81 (s, 3H, H^{xantphos-Me}), 1.66 (s, 3H, H^{xantphos-Me'}), 1.21 (m, 2H, H^{F2}), 1.21 (m, 2H, H^{F2'}), 1.21 (m, 2H, H^{F3}), 0.95 (m, 1H, H^{F4}), 0.11 (m, 2H, H^{F3'}), 0.11 (m, 1H, H^{F4'}). $^{13}C\{^1H\}$ NMR (126 MHz, acetone- d_6 , 298 K) δ /ppm: 168.5 (C^{B6}), 159.4 (C^{A6}), 155.7 (t, $^2J_{CP}$ = 6.5 Hz, C^{C1}), 153.6 (t, $^3J_{CP}$ = NM, C^{A2}), 153.2 (t, $^3J_{CP}$ = NM, C^{B2}), 140.3 (C^{B4}), 139.8 (C^{A4}), 135.4 (t, $^3J_{CP}$ = 1.9 Hz, C^{C6}), 134.6 (t, $^2J_{CP}$ = 7.9 Hz, C^{D2}), 133.9 (t, $^2J_{CP}$ = 7.3 Hz, C^{D2}), 133.4 (t,

$^1J_{CP} = \text{NM}$, $C^{D1'}$, 133.3 (t, $^1J_{CP} = \text{NM}$, C^{D1}), 131.3 ($C^{D4'}$), 131.1 (C^{C3}), 130.9 (C^{D4}), 129.7 (t, $^3J_{CP} = 4.4$ Hz, C^{D3}), 129.7 (t, $^3J_{CP} = 4.6$ Hz, $C^{D3'}$), 128.6 (C^{C5}), 126.8 (C^{A5}), 126.5 (t, $^3J_{CP} = 2.4$ Hz, C^{C4}), 124.6 (C^{B5}), 122.1 (C^{B3}), 121.4 (t, $^1J_{CP} = \text{NM}$, C^{C2}), 121.1 (C^{A3}), 49.1 (C^{F1}), 36.9 ($C^{\text{xantphos-bridge}}$), 34.0 (C^{F2}), 30.1 ($C^{\text{xantphos-Me'}}$), 27.6 (C^{B6-Me}), 26.4 ($C^{\text{xantphos-Me}}$), 25.5 (C^{F3}), 25.5 (C^{F4}). $^{19}\text{F}\{^1\text{H}\}$ NMR (471 MHz, 298 K, acetone- d_6 , 298 K) δ/ppm -72.7 (d, $^1J_{FP} = 707$ Hz, F^{PF6}). $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, 298 K, acetone- d_6 , 298 K) δ/ppm : -14.4 (broad, FWHM ≈ 300 Hz, P^{xantphos}), -144.3 (hept, $^1J_{PF} = 707$ Hz, P^{PF6}). ESI(+)-MS ($\text{CH}_2\text{Cl}_2/\text{MeOH}$, m/z): 641.13 [$\text{M-PF}_6-(6\text{-Cy-6'-Mebpy})$] $^+$ (base peak, calc. 641.12), 893.29 [M-PF_6] $^+$ (calc. 893.28), 1219.27 [$\text{M}-(6\text{-Cy-6'-Mebpy})+2\text{xantphos}$] $^+$ (calc. 1219.31). ESI(-)-MS ($\text{CH}_2\text{Cl}_2/\text{MeOH}$, m/z): 145.06 [PF_6] $^-$ (calc. 144.96), 312.89 [$2\text{PF}_6+\text{Na}$] $^-$ (base peak, calc. 312.91). HR-ESI(+)-MS ($\text{CH}_2\text{Cl}_2/\text{MeOH}$, m/z): 641.1220 [$\text{M-PF}_6-(6\text{-Cy-6'-Mebpy})$] $^+$ (base peak, calc. 641.1219), 893.2832 [M-PF_6] $^+$ (calc. 893.2845). UV-Vis (CH_2Cl_2 , 2.5×10^{-5} mol dm^{-3}): λ/nm ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) 247 sh (31,800), 281 (37,500), 291 (25,200), 305 sh (18,200), 320 sh (11,000), 370 (2,200). FTIR: 3047 (w), 2918 (w), 2858 (w), 1600 (w), 1572 (w), 1435 (m), 1403 (m), 1225 (m), 1095 (w), 833 (s), 787 (m), 737 (s), 693 (s), 556 (s), 508 (s), 497 (m), 467 (m), 428 (m) cm^{-1} . Found: C 64.68, H 4.98, N 2.53; $\text{C}_{56}\text{H}_{52}\text{CuF}_6\text{N}_2\text{OP}_3$ requires C 64.71, H 5.04, N 2.69.

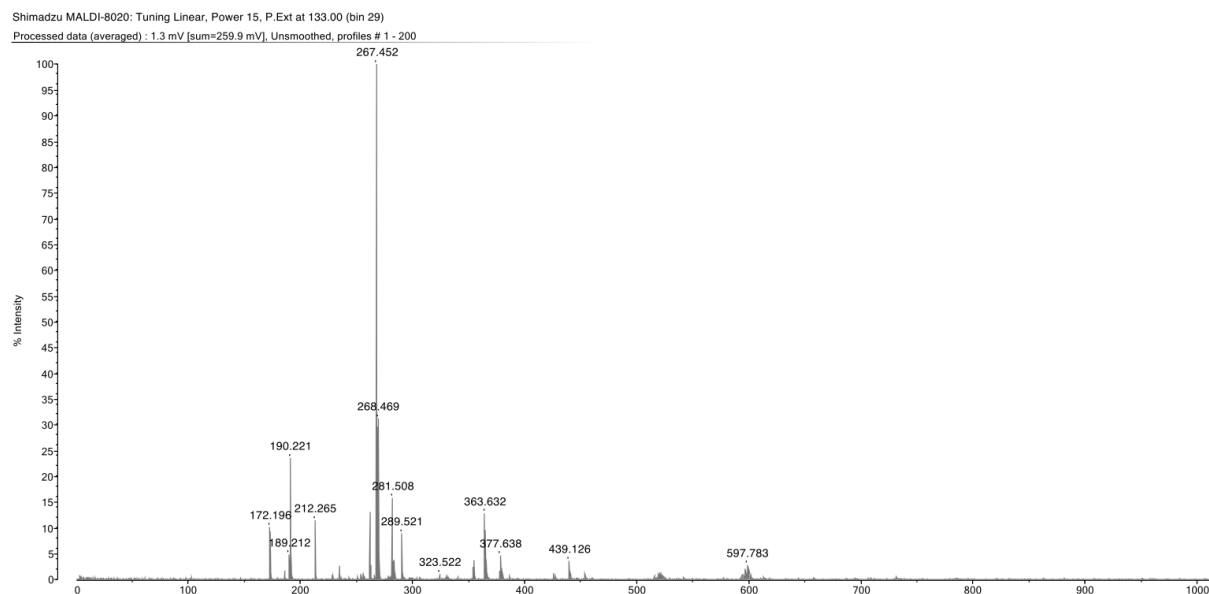


Fig. S2 MALDI mass spectrum (positive mode) of 2-CyEtbpY.

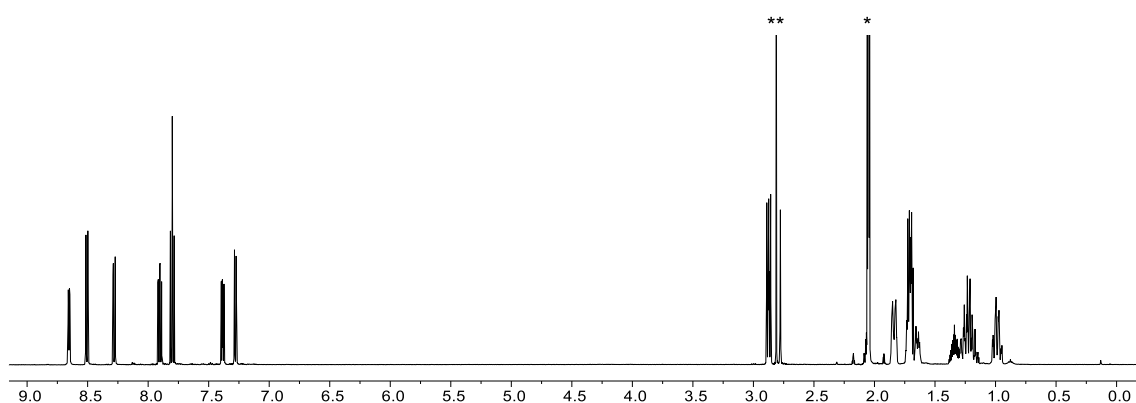


Fig. S3 1H NMR spectrum (500 MHz, acetone- d_6 , 298 K, δ /ppm) of 2-CyEtbpY. * = residual acetone- d_6 ; ** = H_2O and HDO .

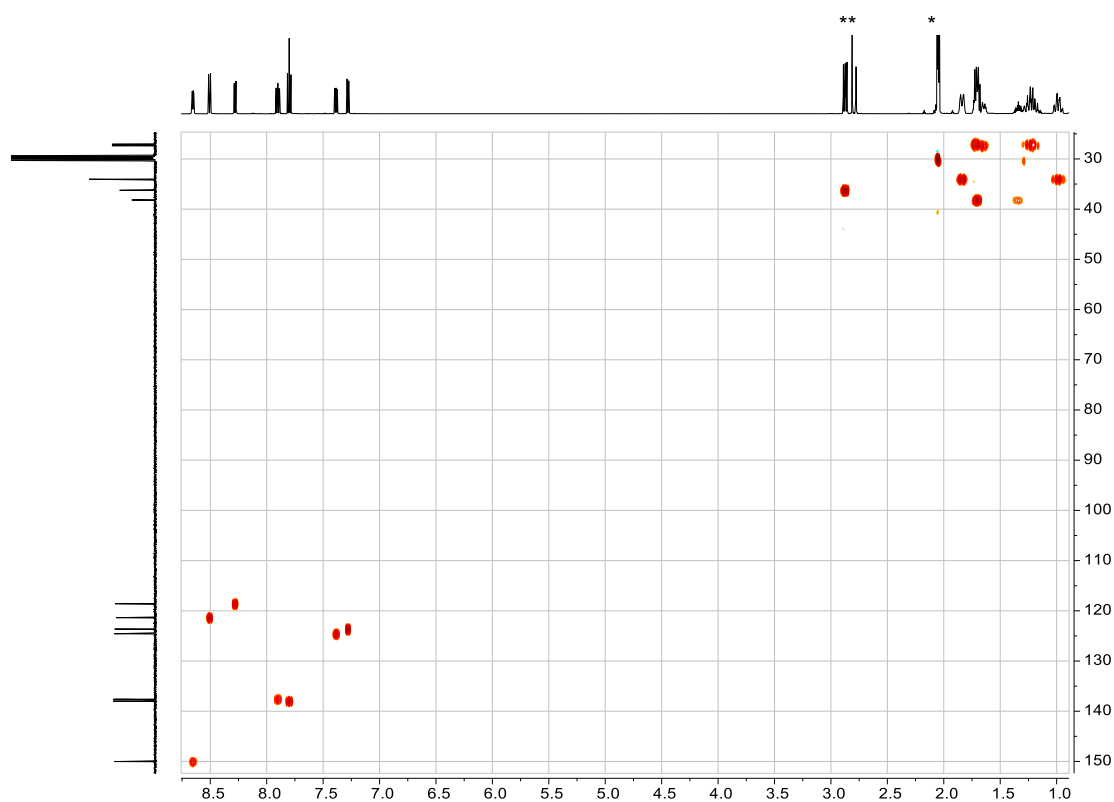


Fig. S4 Part of the HMQC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K, δ/ppm) of 2-CyEtbp. * = residual acetone- d_5 ; ** = H₂O and HDO.

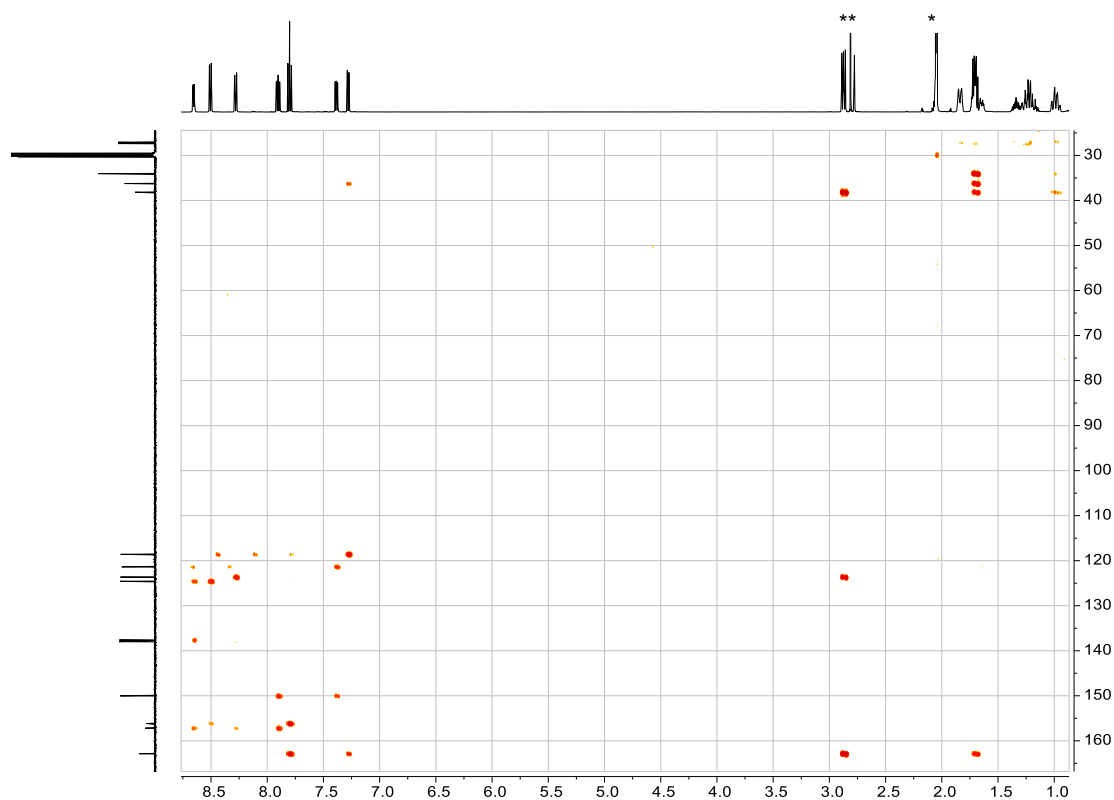


Fig. S5 Part of the HMBC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K, δ/ppm) of 2-CyEtbp. * = residual acetone- d_5 ; ** = H₂O and HDO.

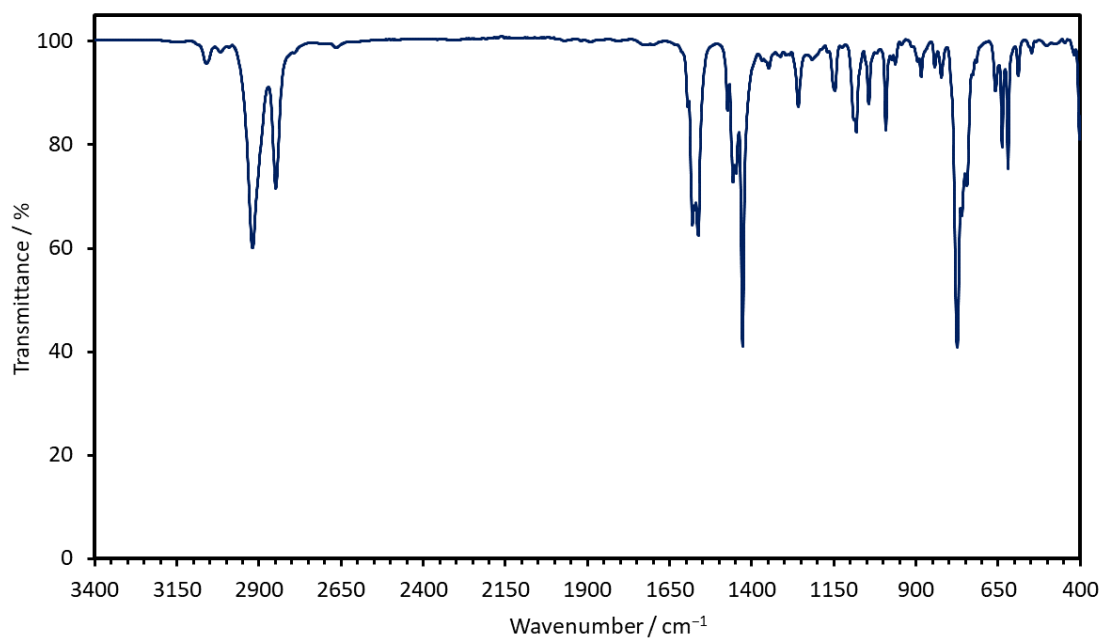


Fig. S6 FTIR spectrum of 2-CyEtbpy.

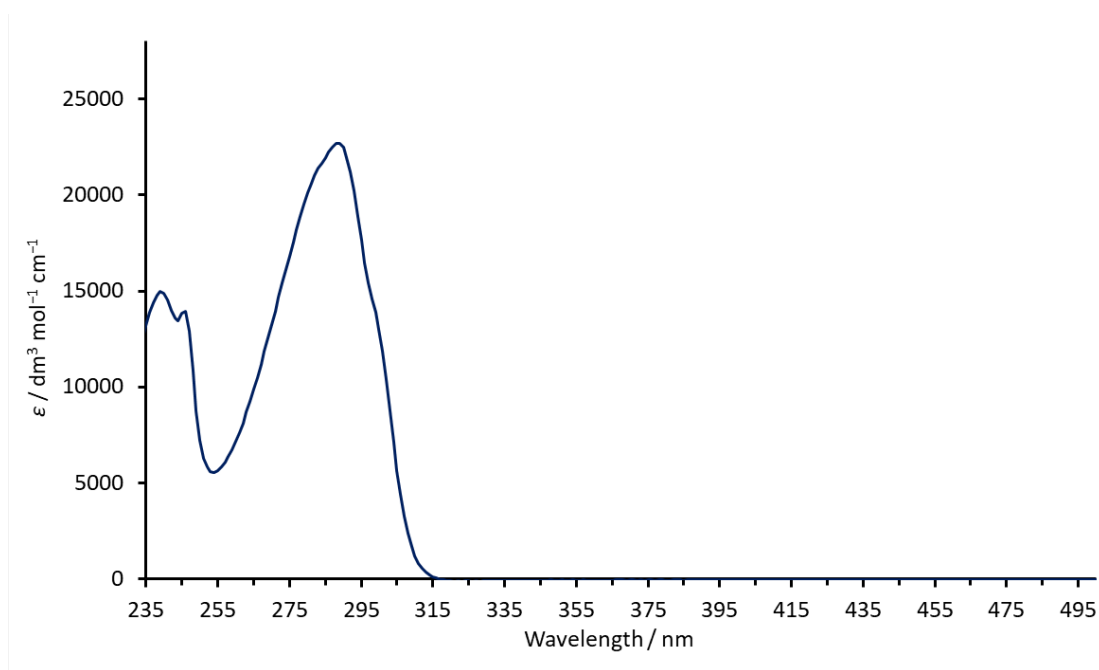


Fig. S7 Solution absorption spectrum (CH₂Cl₂, 2.5×10^{-5} mol dm⁻³) of 2-CyEtbpy.

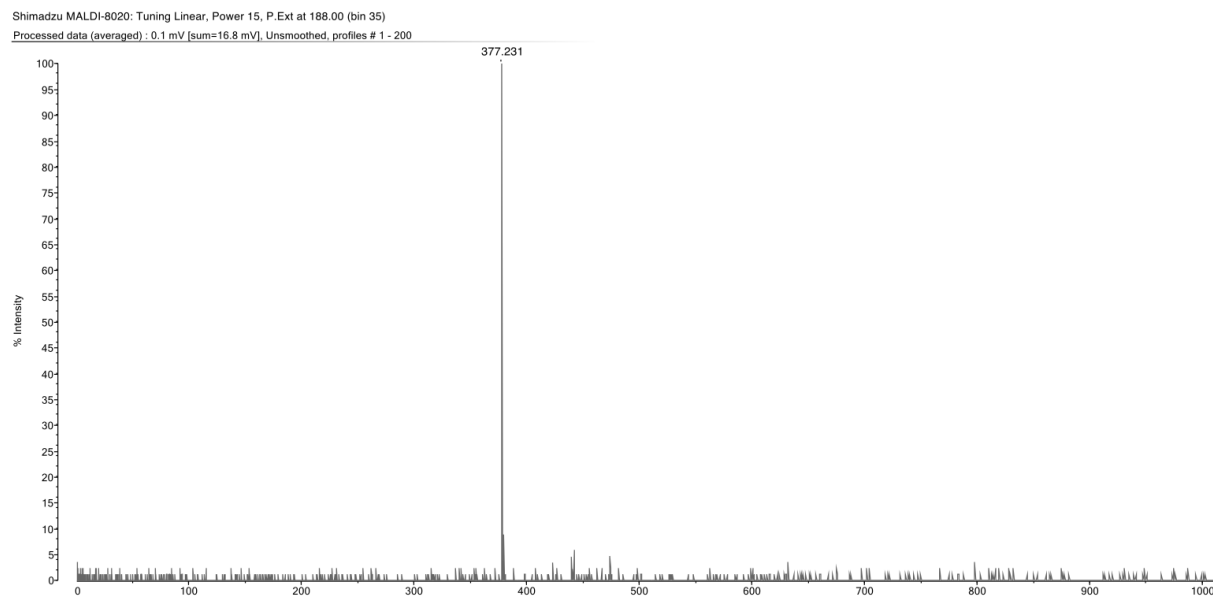


Fig. S8 MALDI mass spectrum (positive mode) of (2-CyEt)₂bpy.

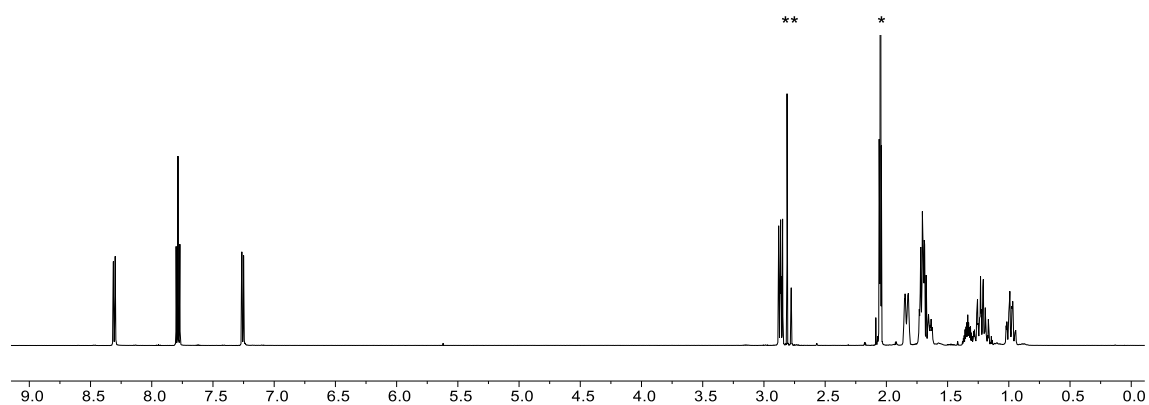


Fig. S9 ¹H NMR spectrum (500 MHz, acetone-*d*₆, 298 K, δ/ppm) of (2-CyEt)₂bpy. * = residual acetone-*d*₅; ** = H₂O and HDO.

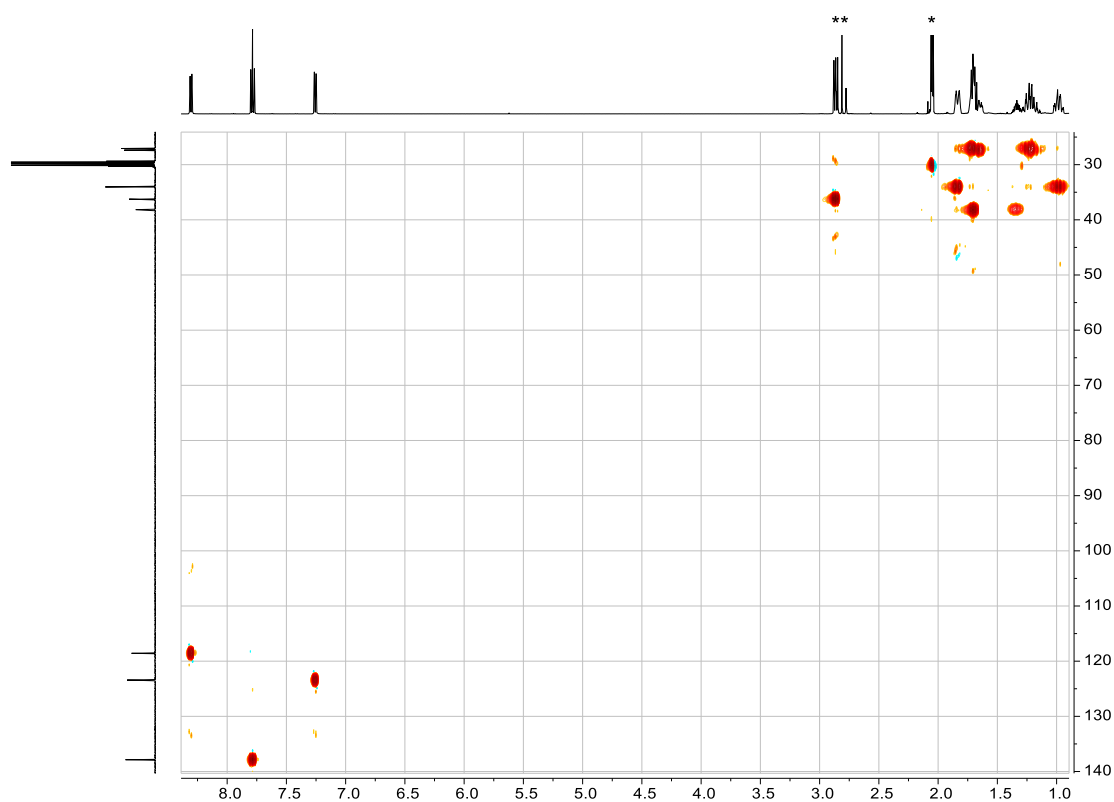


Fig. S10 Part of the HMBC spectrum (500 MHz ¹H, 126 MHz ¹³C{¹H}, acetone-*d*₆, 298 K, δ /ppm) of (2-CyEt)₂bpy. * = residual acetone-*d*₅; ** = H₂O and HDO.

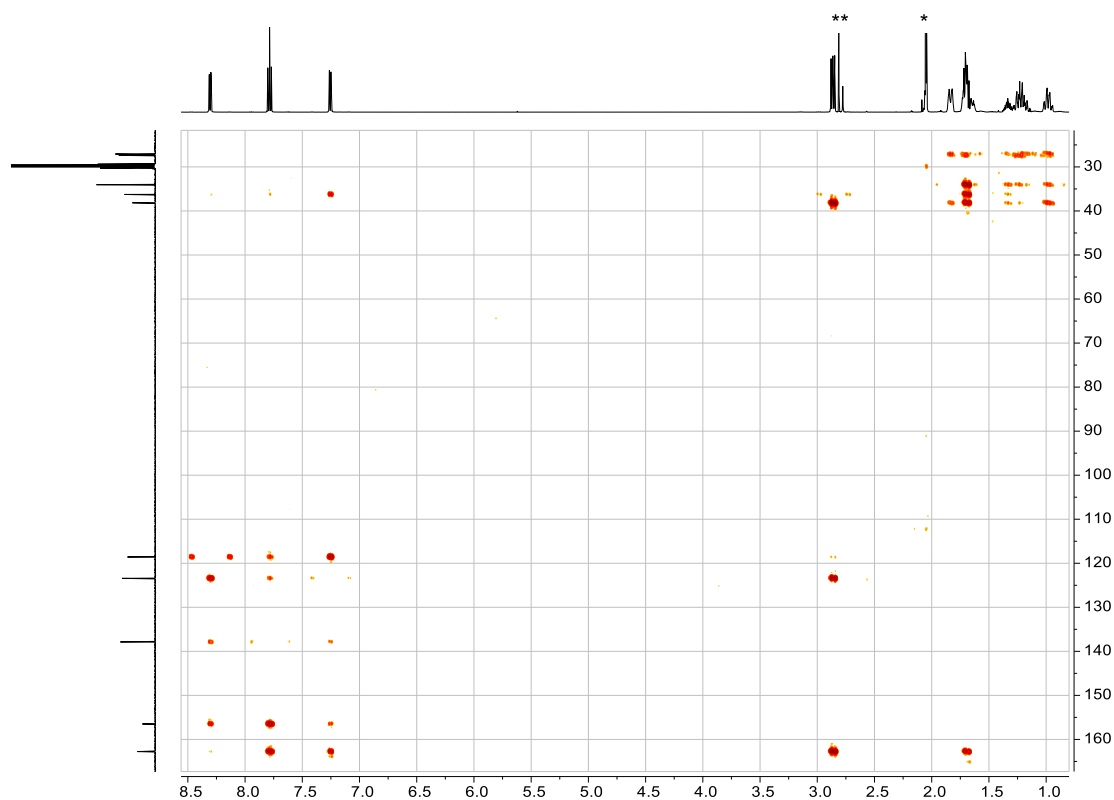


Fig. S11 Part of the HMBC spectrum (500 MHz ¹H, 126 MHz ¹³C{¹H}, acetone-*d*₆, 298 K, δ /ppm) of (2-CyEt)₂bpy. * = residual acetone-*d*₅; ** = H₂O and HDO.

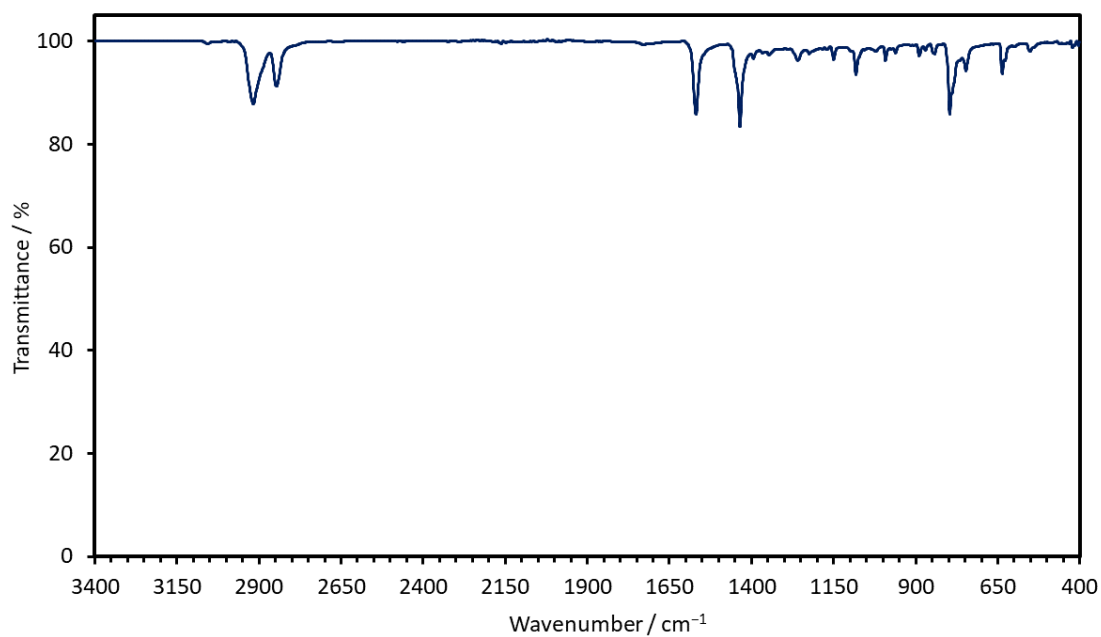


Fig. S12 FTIR spectrum of (2-CyEt)₂bpy.

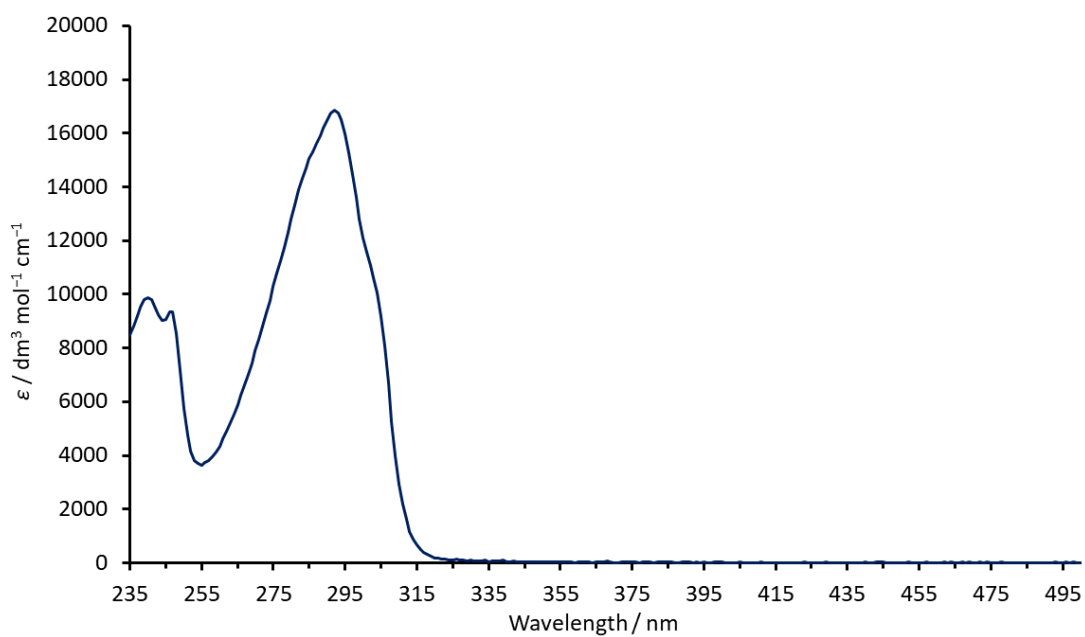


Fig. S13 Solution absorption spectrum (CH_2Cl_2 , $2.5 \times 10^{-5} \text{ mol dm}^{-3}$) of (2-CyEt)₂bpy.

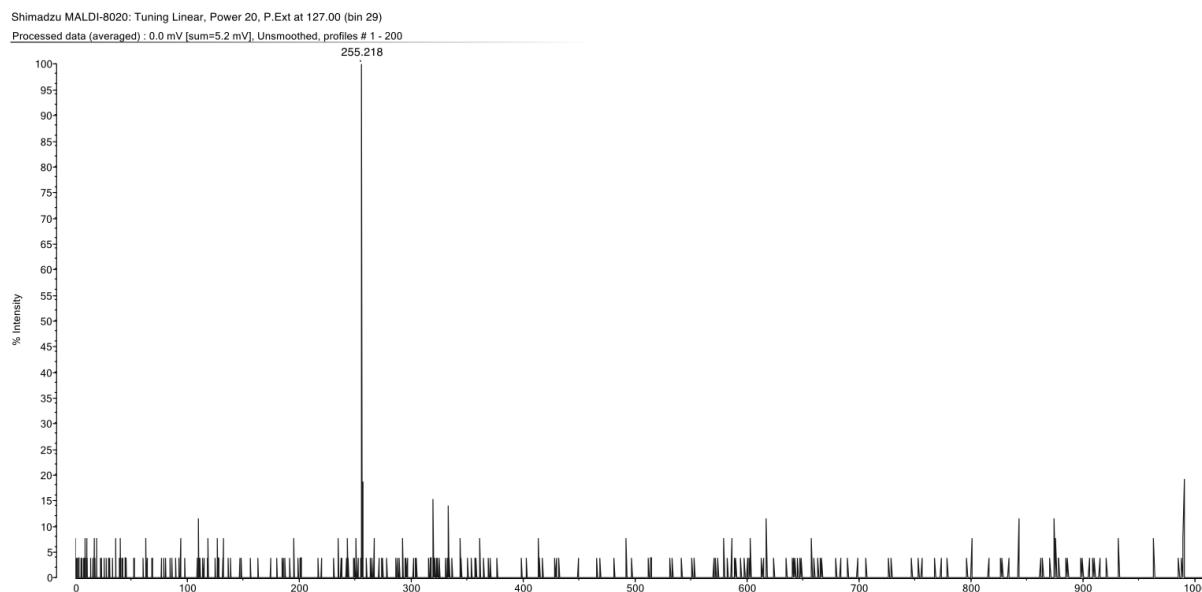


Fig. S14 MALDI mass spectrum (positive mode) of 3-EtPentbp.

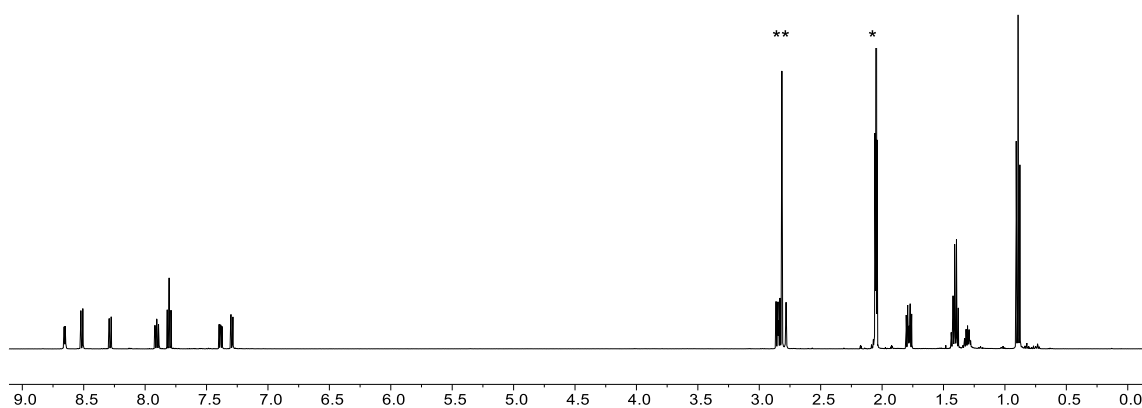


Fig. S15 ^1H NMR spectrum (500 MHz, acetone- d_6 , 298 K, δ /ppm) of 3-EtPentbp. * = residual acetone- d_6 ; ** = H_2O and HDO.

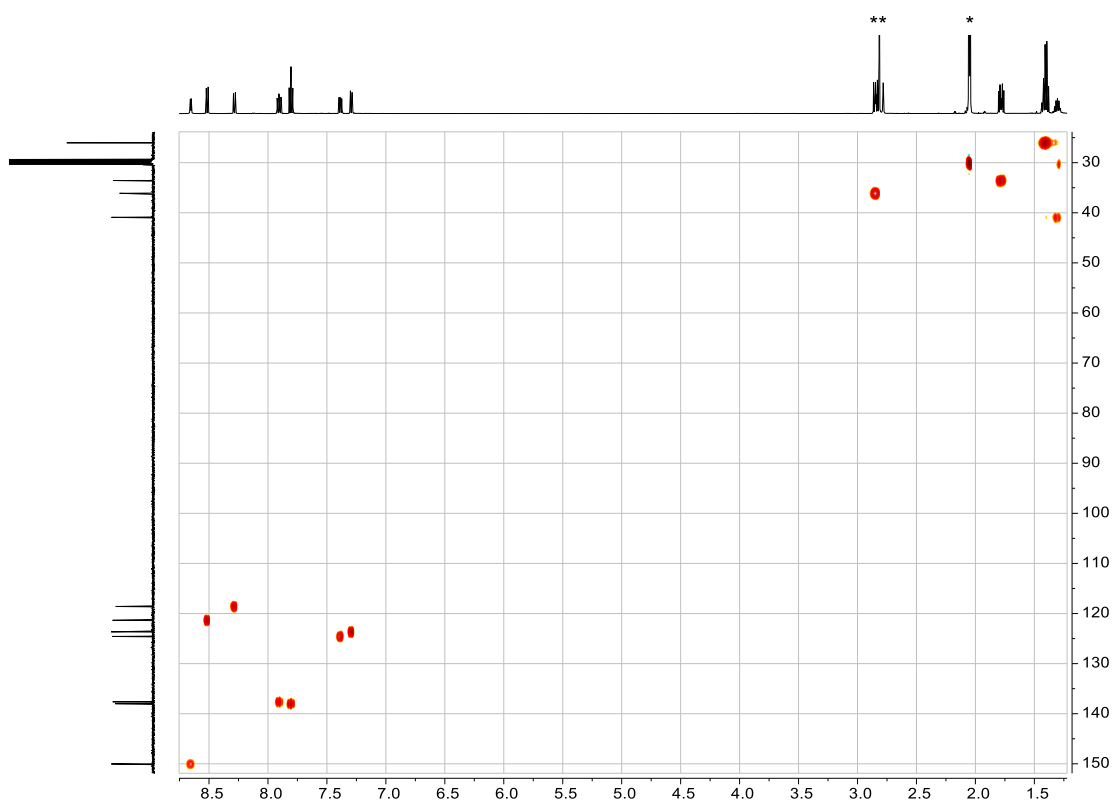


Fig. S16 Part of the HMBC spectrum (500 MHz ^1H , 126 MHz ^{13}C { ^1H }, acetone- d_6 , 298 K, δ /ppm) of 3-EtPentbpy. * = residual acetone- d_5 ; ** = H_2O and HDO.

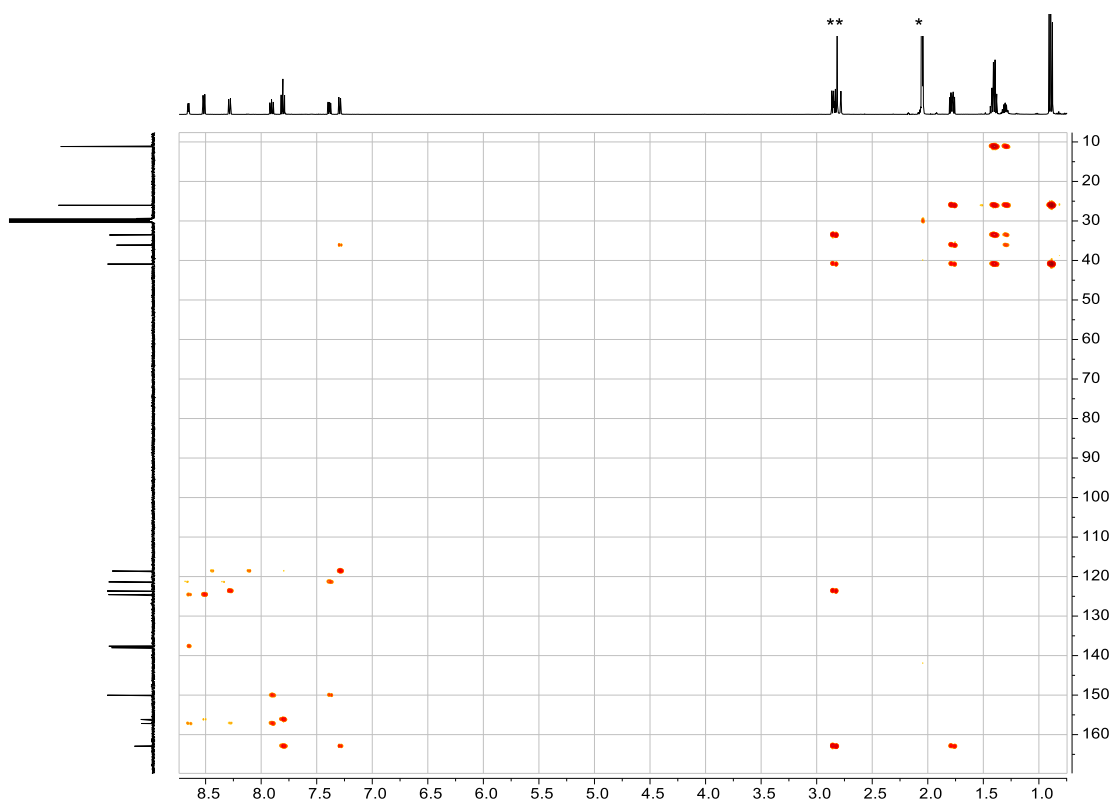


Fig. S17 Part of the HMBC spectrum (500 MHz ^1H , 126 MHz ^{13}C { ^1H }, acetone- d_6 , 298 K, δ /ppm) of 3-EtPentbpy. * = residual acetone- d_5 ; ** = H_2O and HDO.

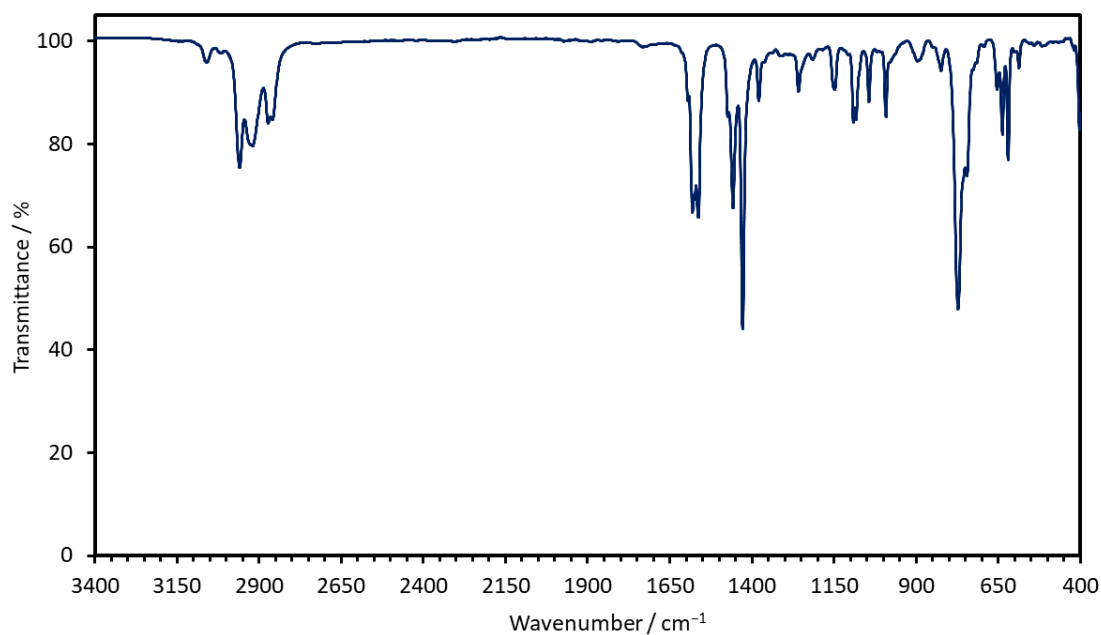


Fig. S18 FTIR spectrum of 3-EtPentbpy.

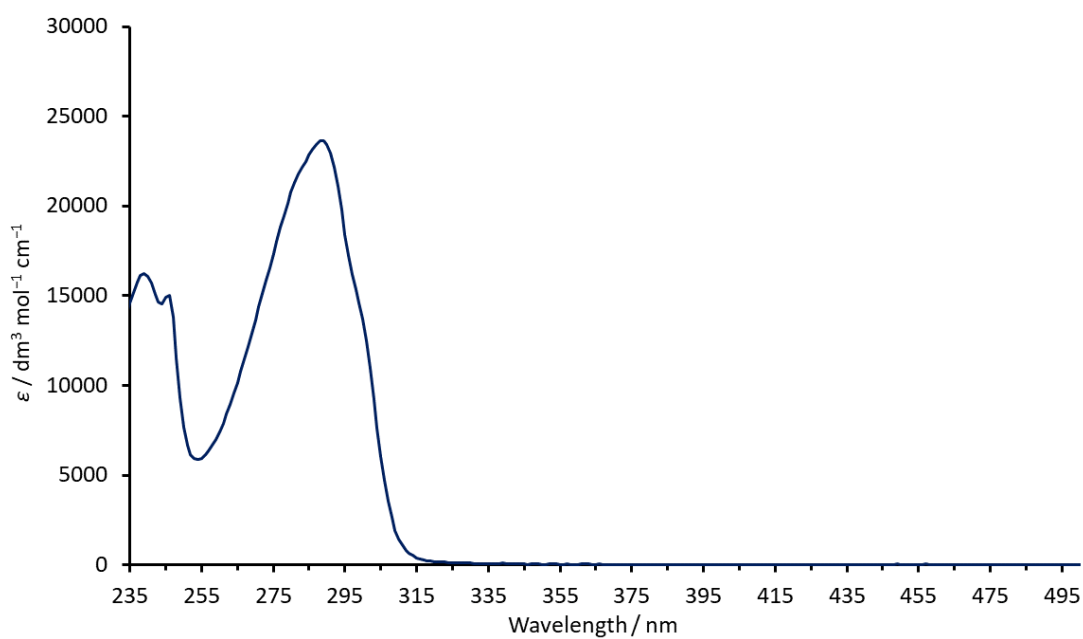


Fig. S19 Solution absorption spectrum (CH_2Cl_2 , $2.5 \times 10^{-5} \text{ mol dm}^{-3}$) of 3-EtPentbpy.

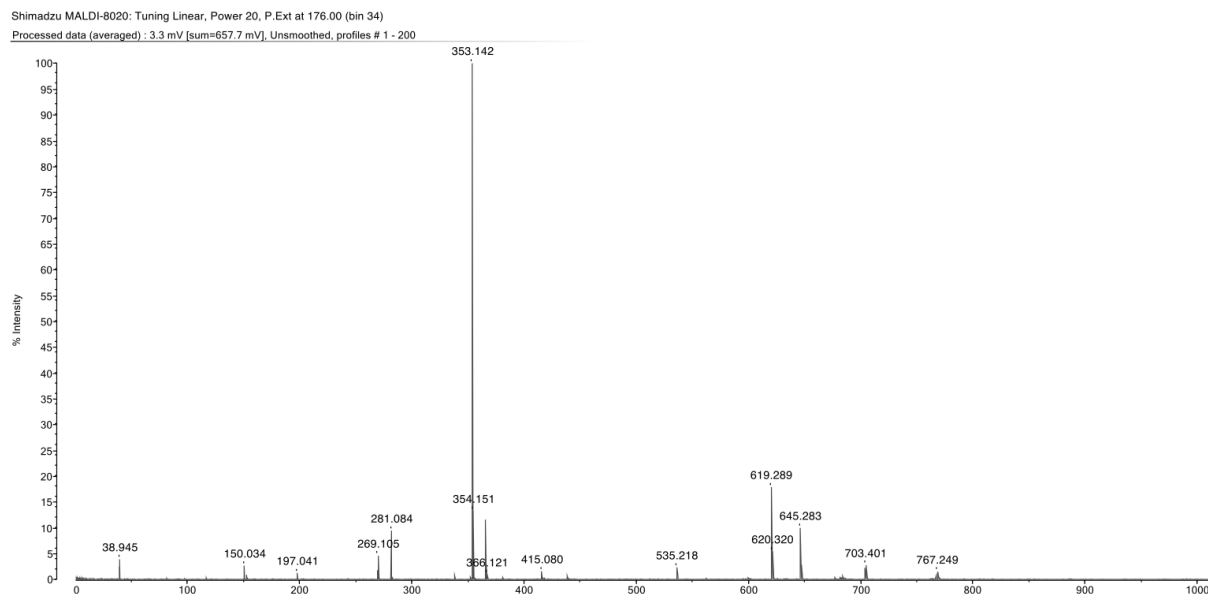


Fig. S20 MALDI mass spectrum (positive mode) of (3-EtPent)₂bpy.

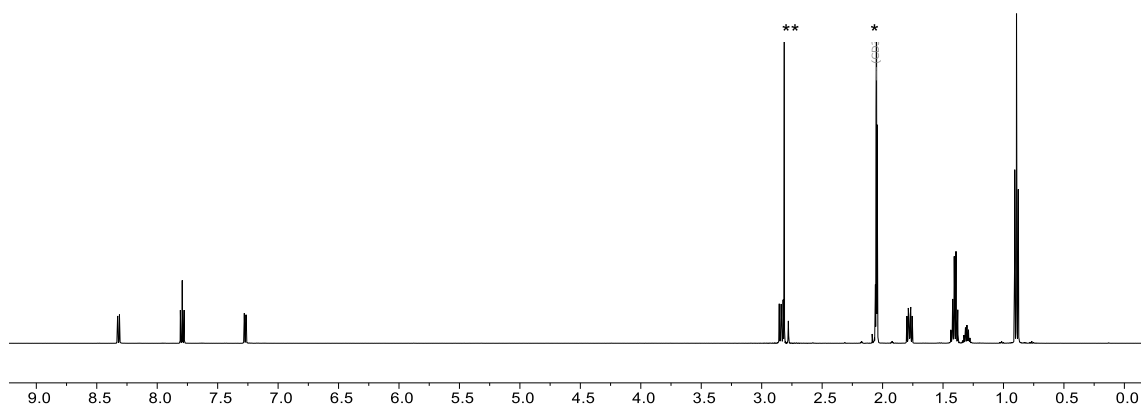


Fig. S21 ¹H NMR spectrum (500 MHz, acetone-*d*₆, 298 K, δ /ppm) of (3-EtPent)₂bpy. * = residual acetone-*d*₅; ** = H₂O and HDO.

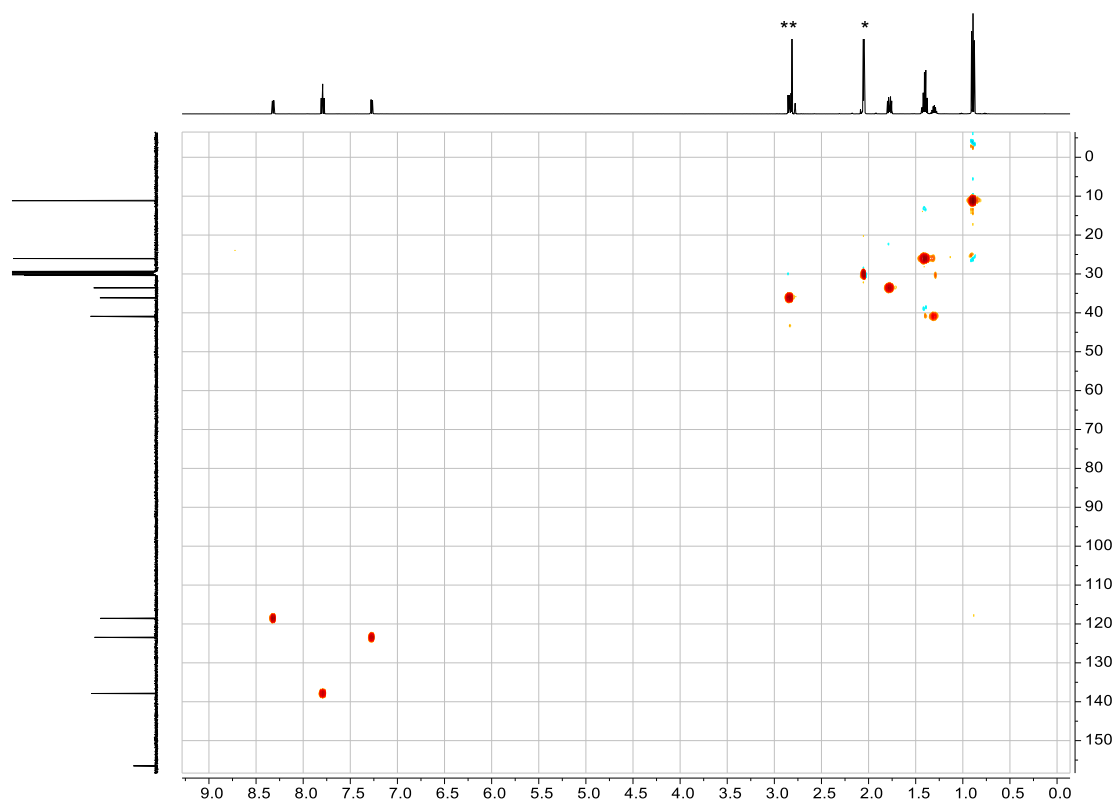


Fig. S22 Part of the HMBC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K, δ/ppm) of (3-EtPent) $_2$ bpy. * = residual acetone- d_5 ; ** = H_2O and HDO.

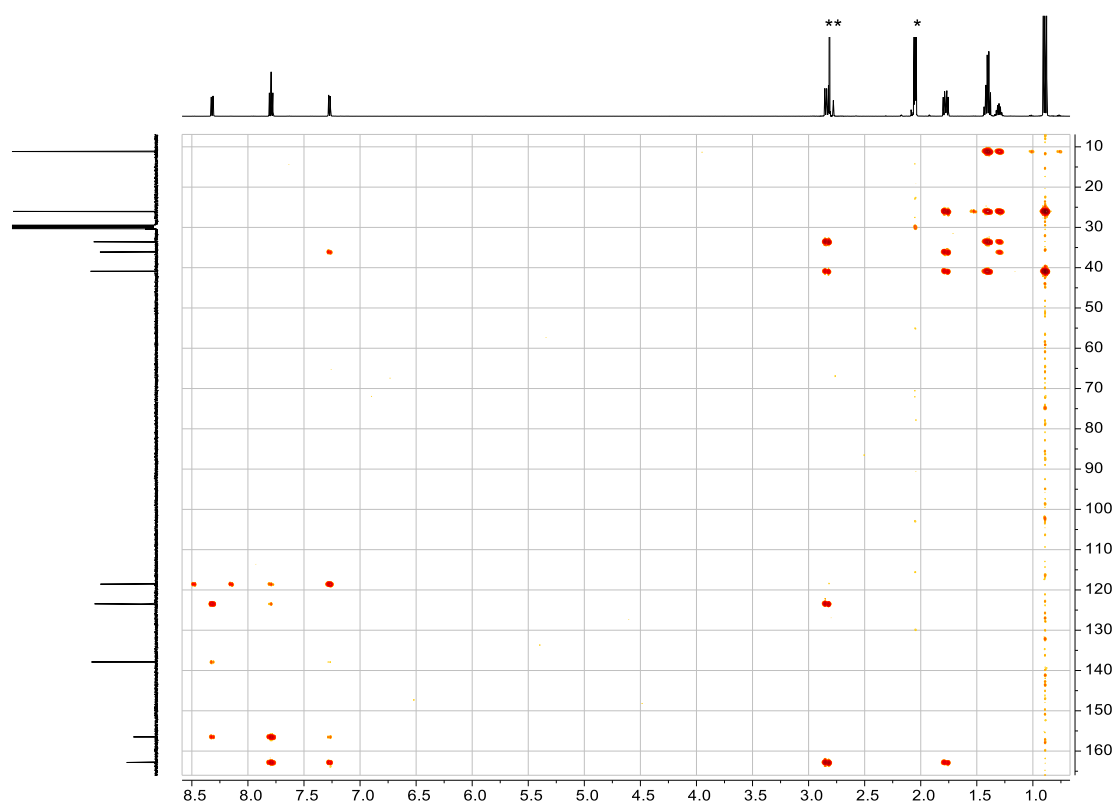


Fig. S23 Part of the HMBC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K, δ/ppm) of (3-EtPent) $_2$ bpy. * = residual acetone- d_5 ; ** = H_2O and HDO.

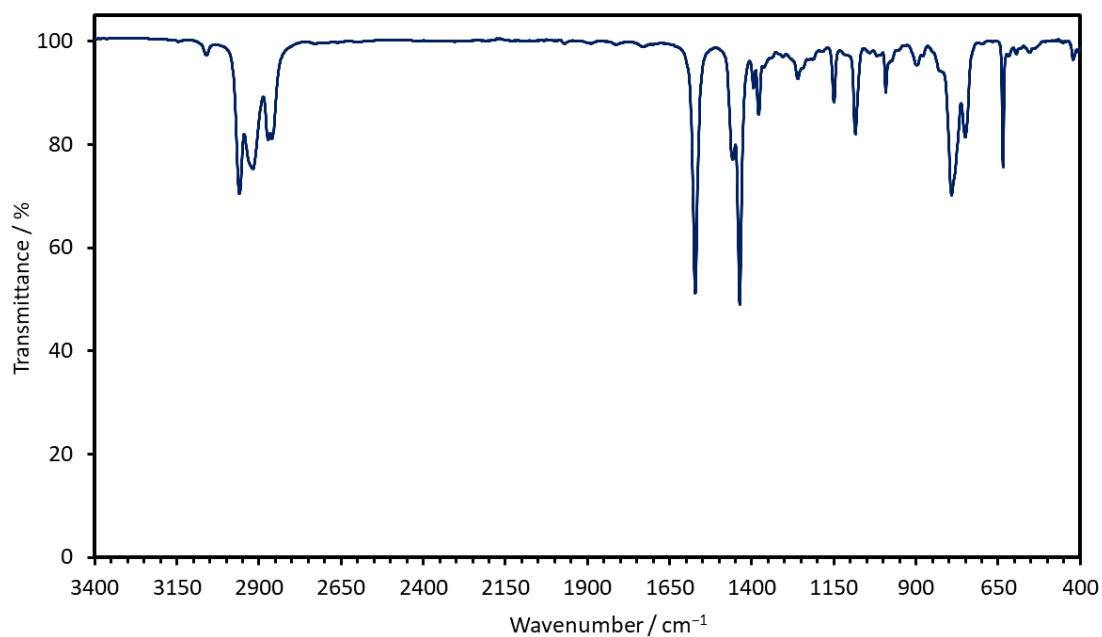


Fig. S24 FTIR spectrum of (3-EtPent)₂bpy.

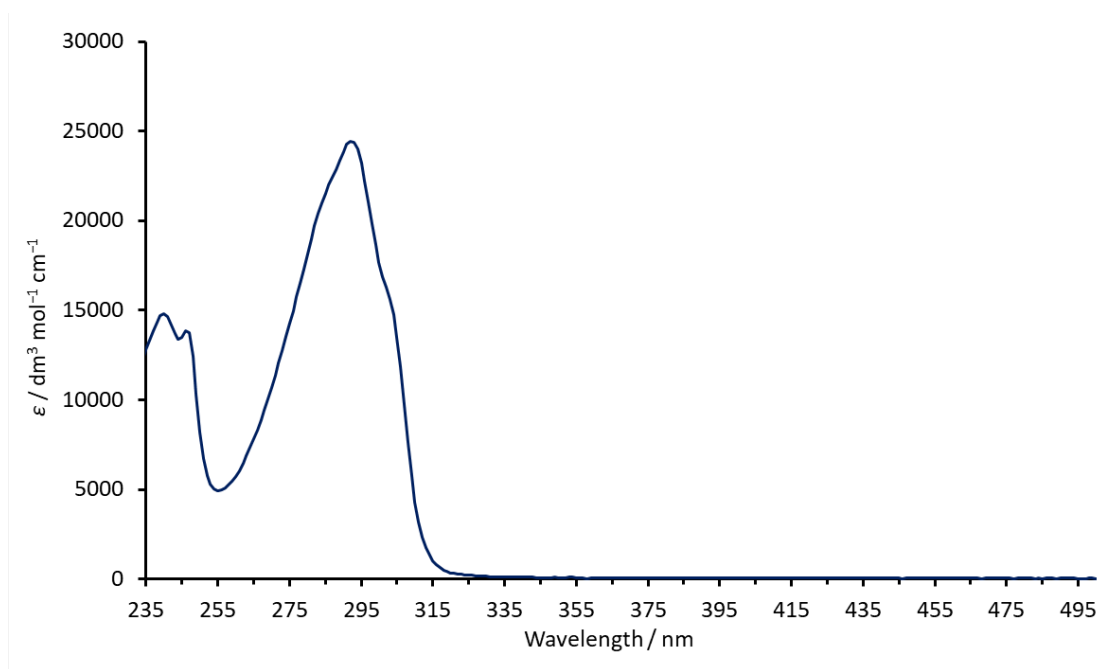


Fig. S25 Solution absorption spectrum (CH_2Cl_2 , $2.5 \times 10^{-5} \text{ mol dm}^{-3}$) of (3-EtPent)₂bpy.

Shimadzu MALDI-8020: Tuning Linear, Power 15, P.Ext at 130.00 (bin 29)
Processed data (averaged) : 0.2 mV (sum=47.8 mV), Unsmoothed, profiles # 1 - 200

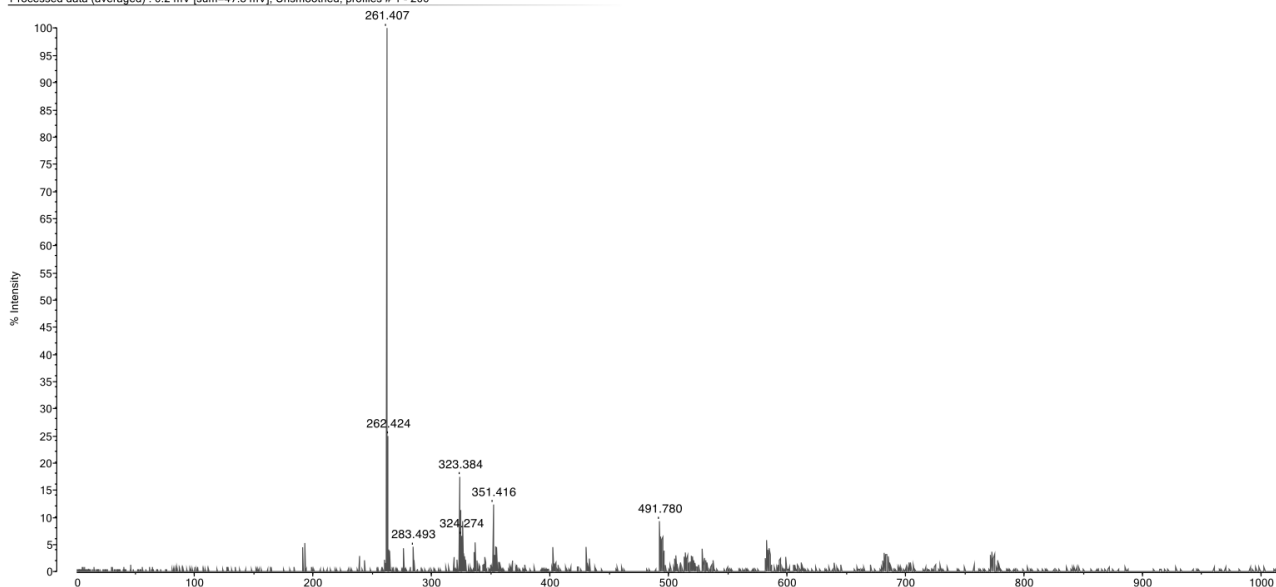


Fig. S26 MALDI mass spectrum (positive mode) of 2-PhEtbpv.

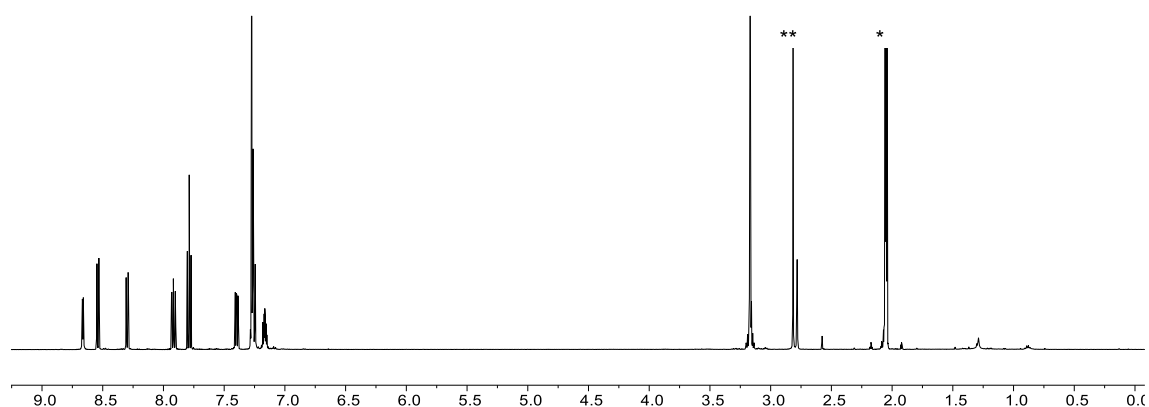


Fig. S27 ^1H NMR spectrum (500 MHz, acetone- d_6 , 298 K, δ/ppm) of 2-PhEtbpv. * = residual acetone- d_5 ; ** = H_2O and HDO.

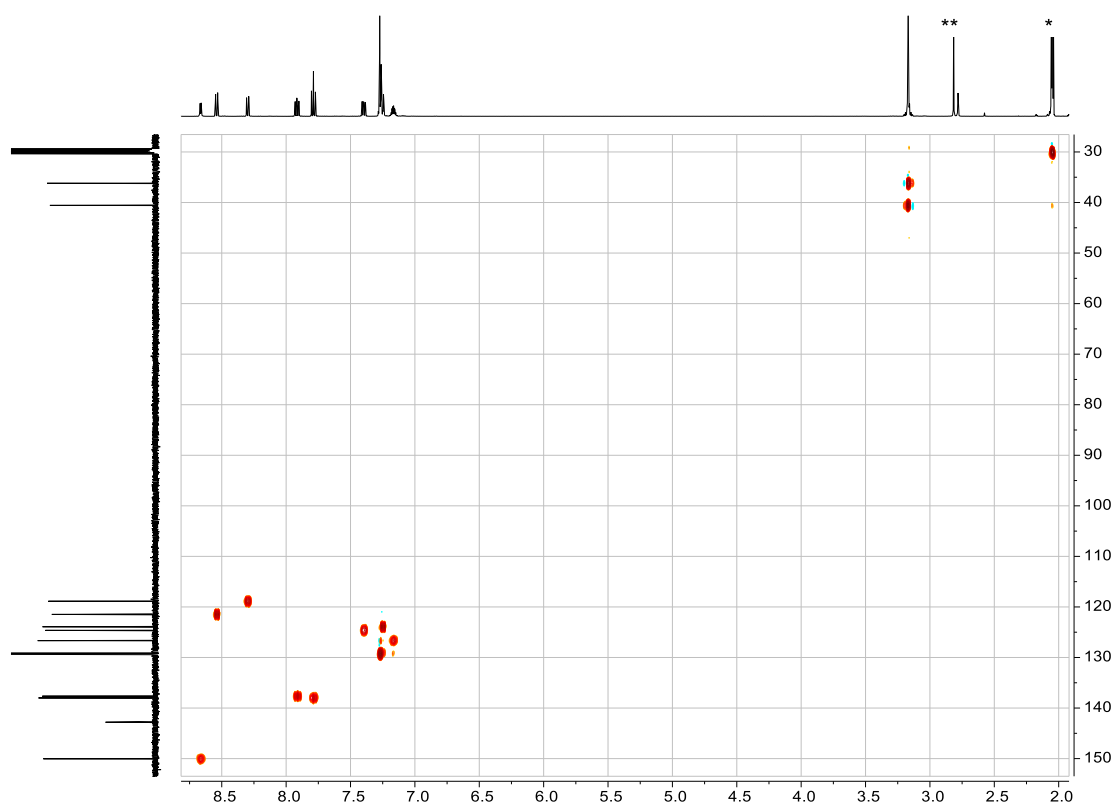


Fig. S28 Part of the HMBC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K, δ/ppm) of 2-PhEtbp. * = residual acetone- d_5 ; ** = H_2O and HDO.

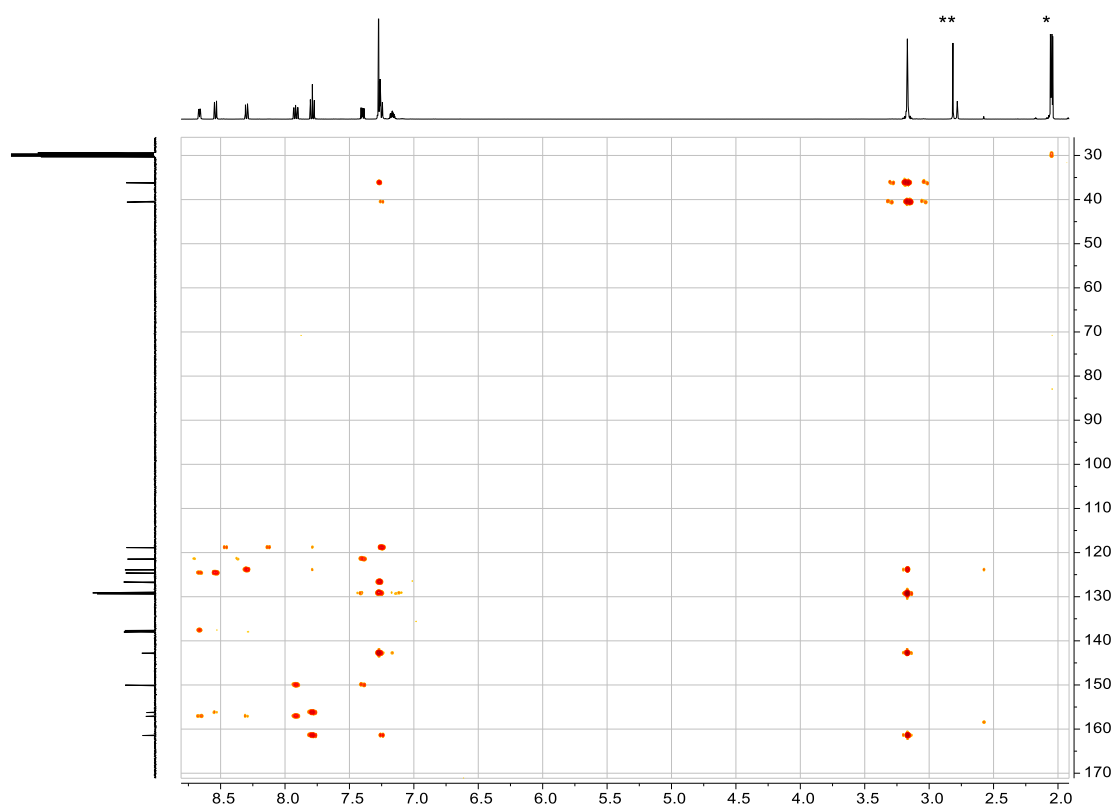


Fig. S29 Part of the HMBC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K, δ/ppm) of 2-PhEtbp. * = residual acetone- d_5 ; ** = H_2O and HDO.

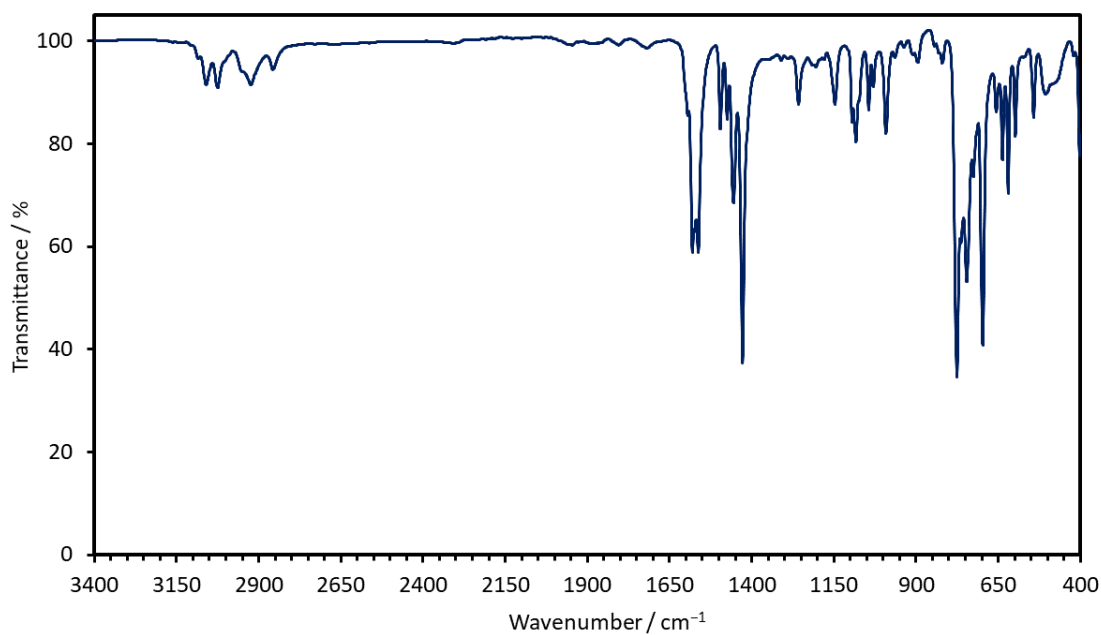


Fig. S30 FTIR spectrum of 2-PhEtbpY.

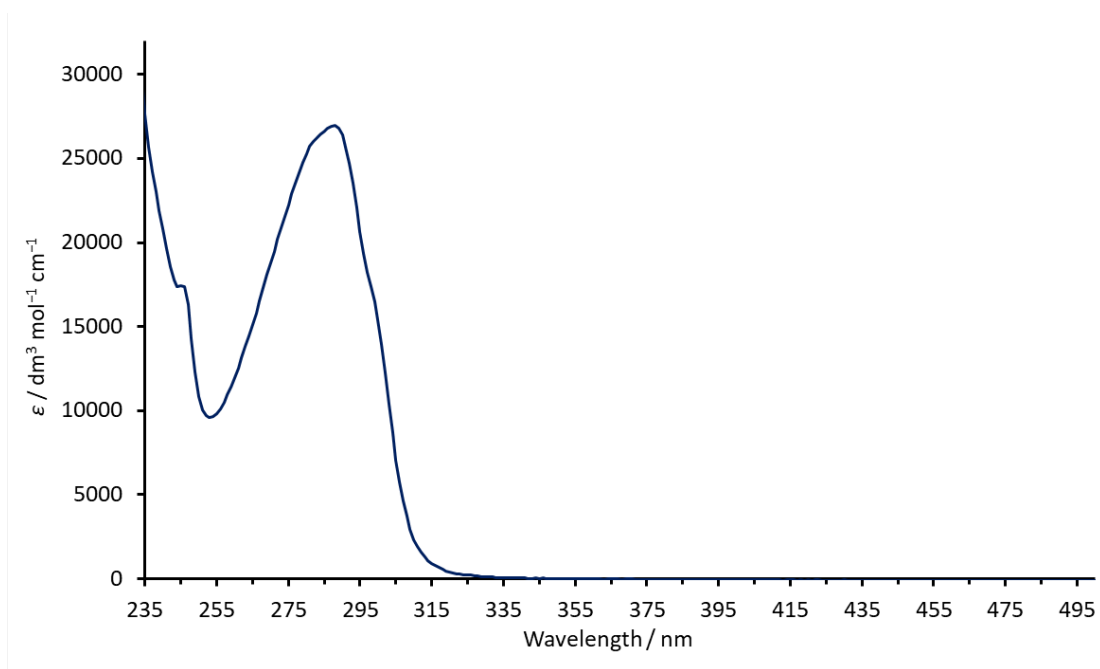


Fig. S31 Solution absorption spectrum (CH₂Cl₂, 2.5 × 10⁻⁵ mol dm⁻³) of 2-PhEtbpY.

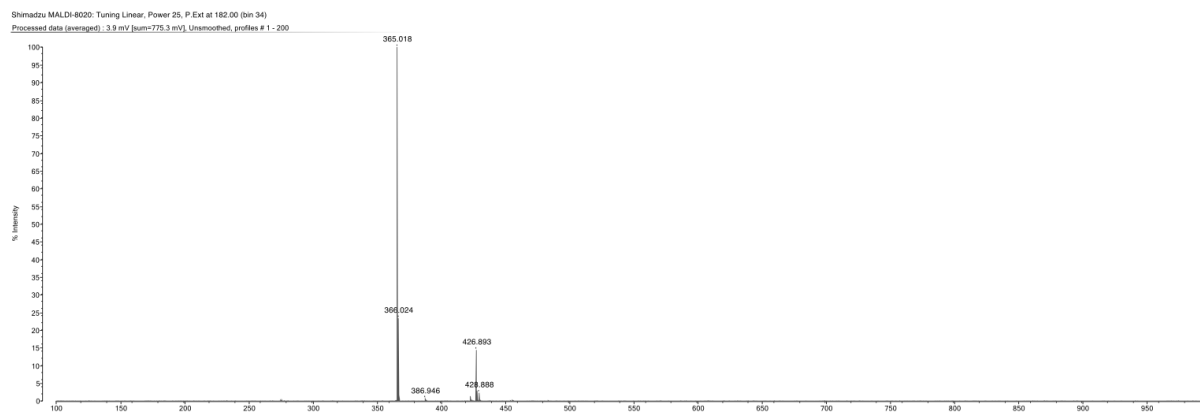


Fig. S32 MALDI mass spectrum (positive mode) of (2-PhEt)₂bpy.

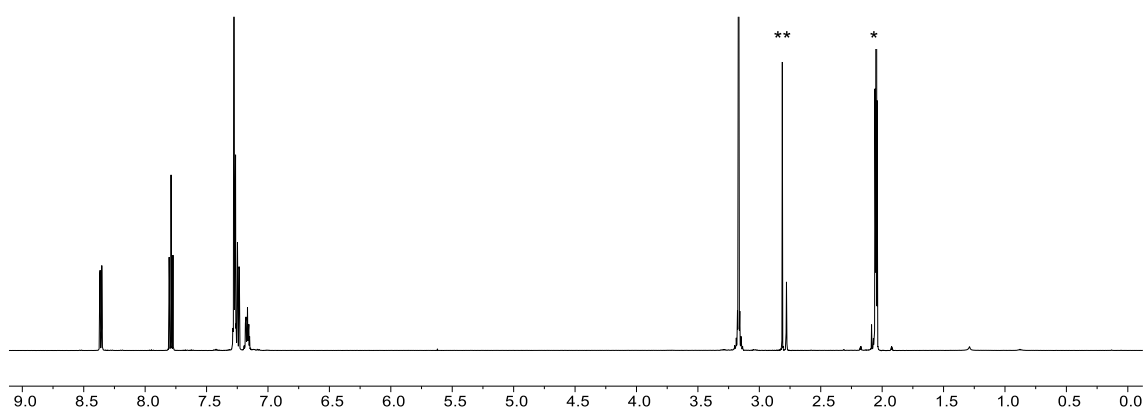


Fig. S33 ¹H NMR spectrum (500 MHz, acetone-*d*₆, 298 K, δ /ppm) of (2-PhEt)₂bpy. * = residual acetone-*d*₅; ** = H₂O and HDO.

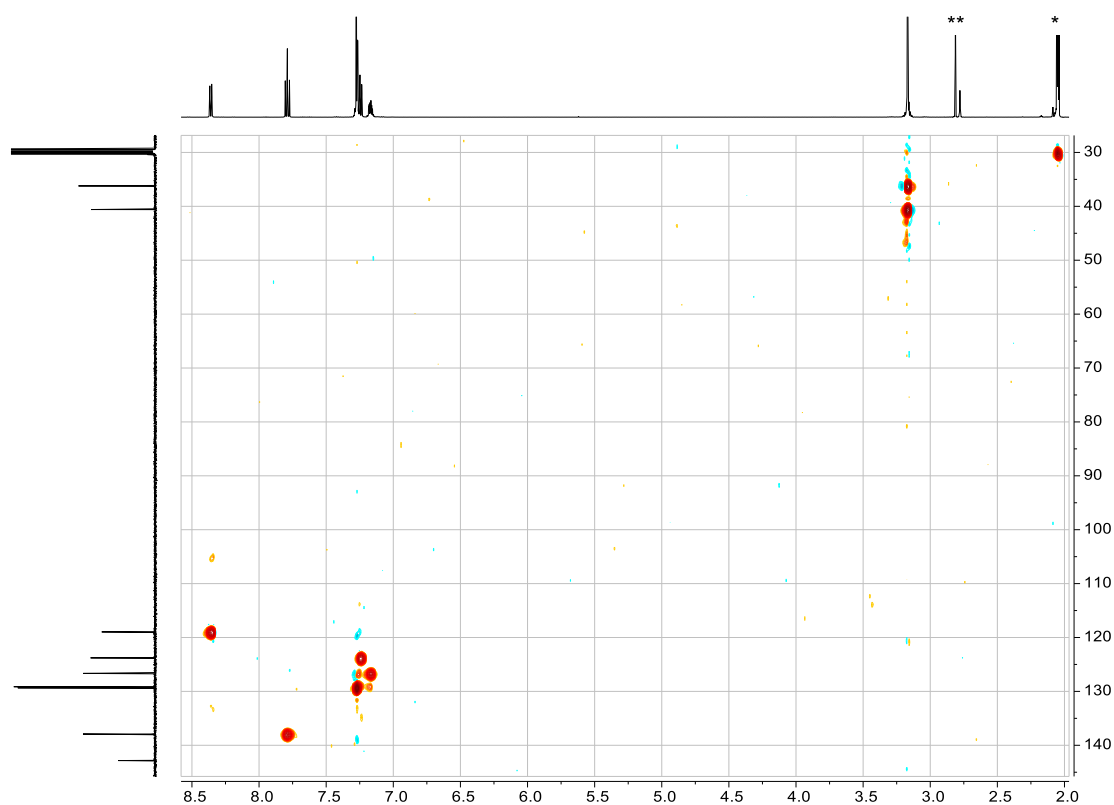


Fig. S34 Part of the HMBC spectrum (500 MHz ^1H , 126 MHz ^{13}C), acetone- d_6 , 298 K, δ /ppm) of (2-PhEt) $_2$ bpy. * = residual acetone- d_5 ; ** = H_2O and HDO.

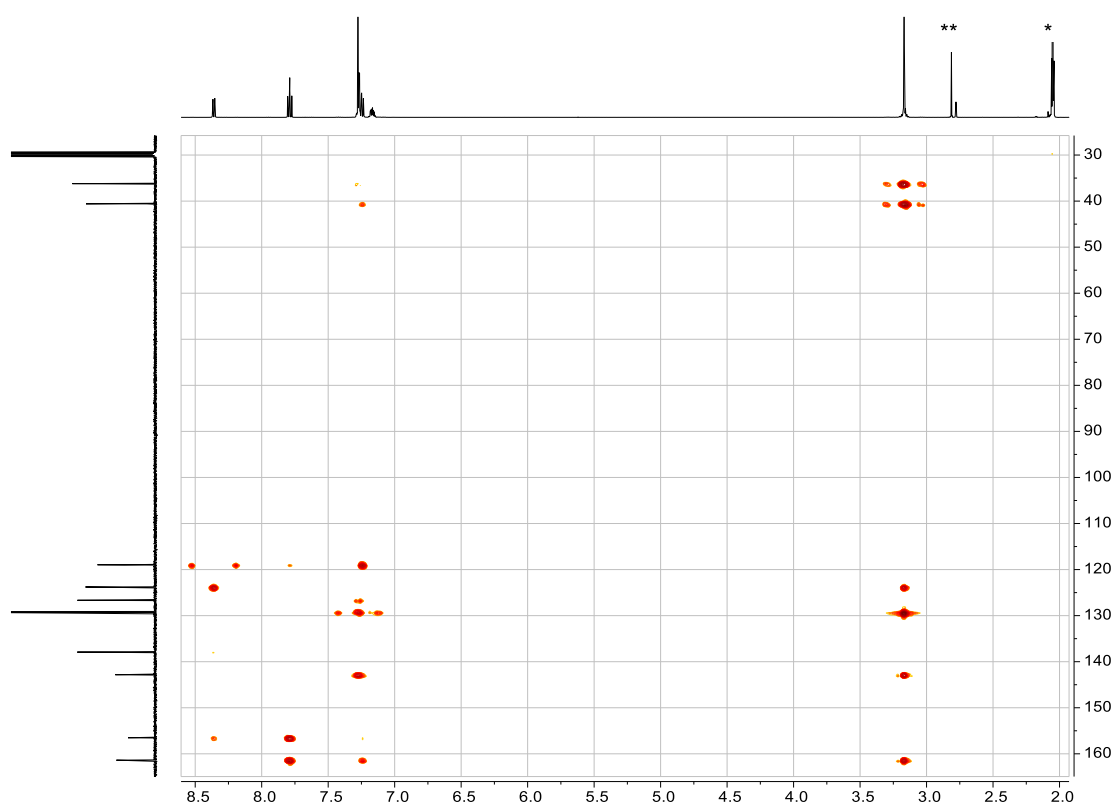


Fig. S35 Part of the HMBC spectrum (500 MHz ^1H , 126 MHz ^{13}C), acetone- d_6 , 298 K, δ /ppm) of (2-PhEt) $_2$ bpy. * = residual acetone- d_5 ; ** = H_2O and HDO.

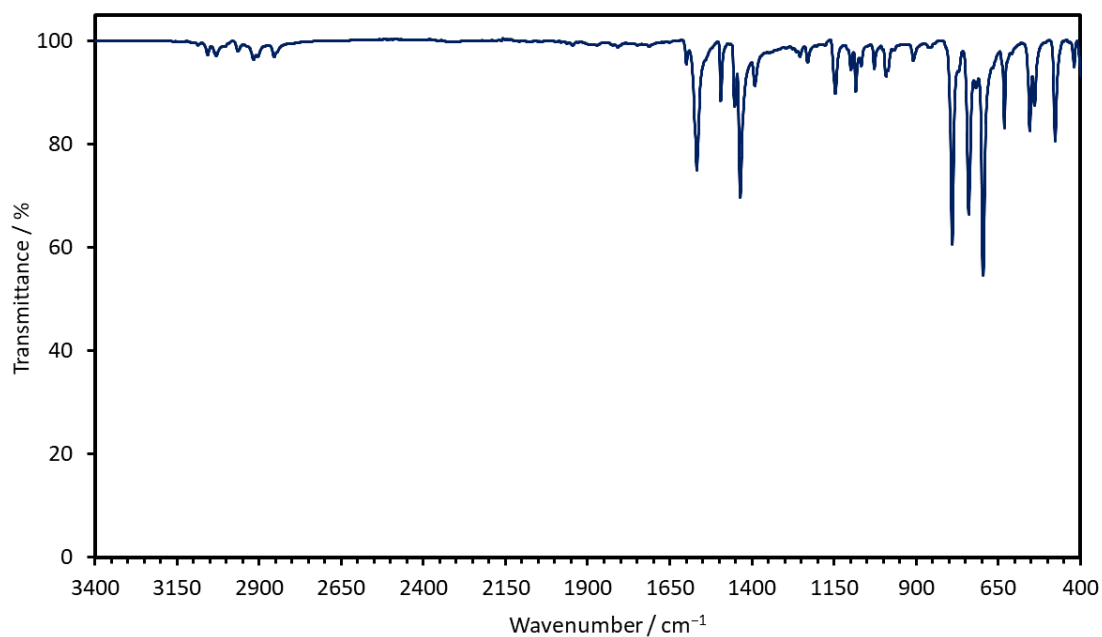


Fig. S36 FTIR spectrum of (2-PhEt)₂bpy.

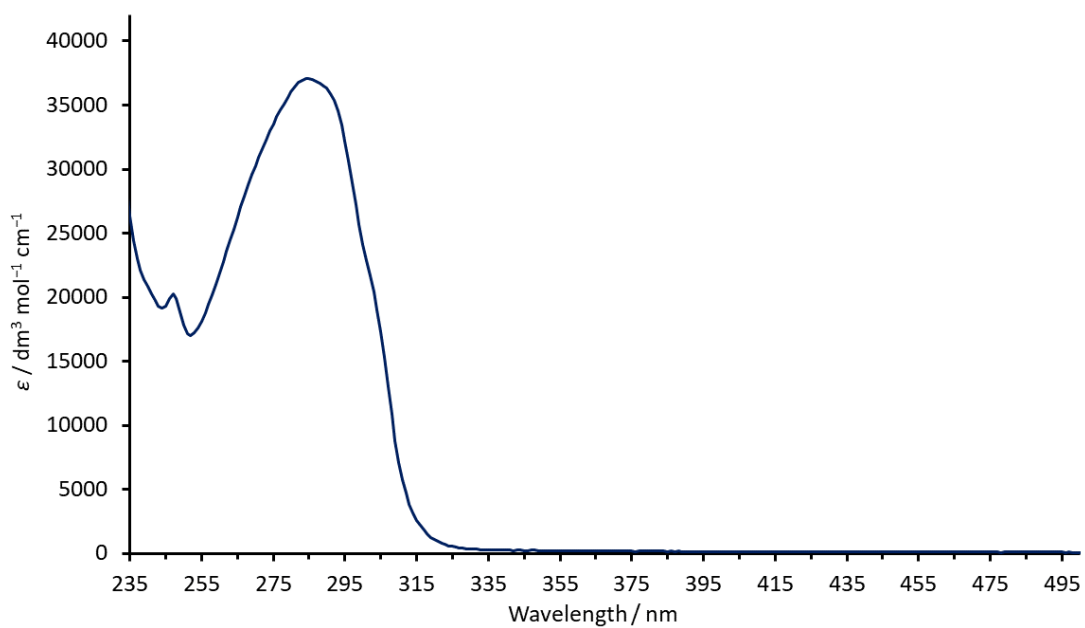


Fig. S37 Solution absorption spectrum (CH_2Cl_2 , $2.5 \times 10^{-5} \text{ mol dm}^{-3}$) of (2-PhEt)₂bpy.

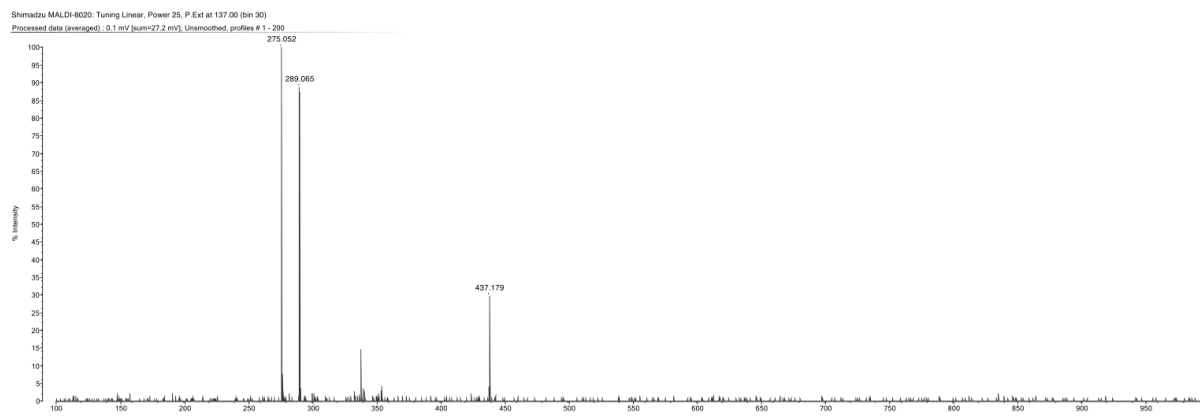


Fig. S38 MALDI mass spectrum (positive mode) of 3-PhPrbpy.

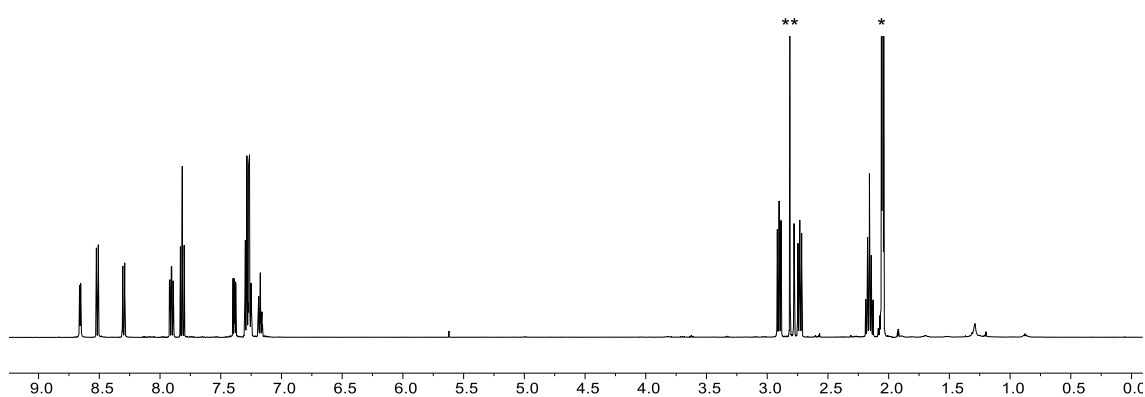


Fig. S39 ¹H NMR spectrum (500 MHz, acetone-*d*₆, 298 K, δ /ppm) of 3-PhPrbpy. * = residual acetone-*d*₆; ** = H₂O and HDO.

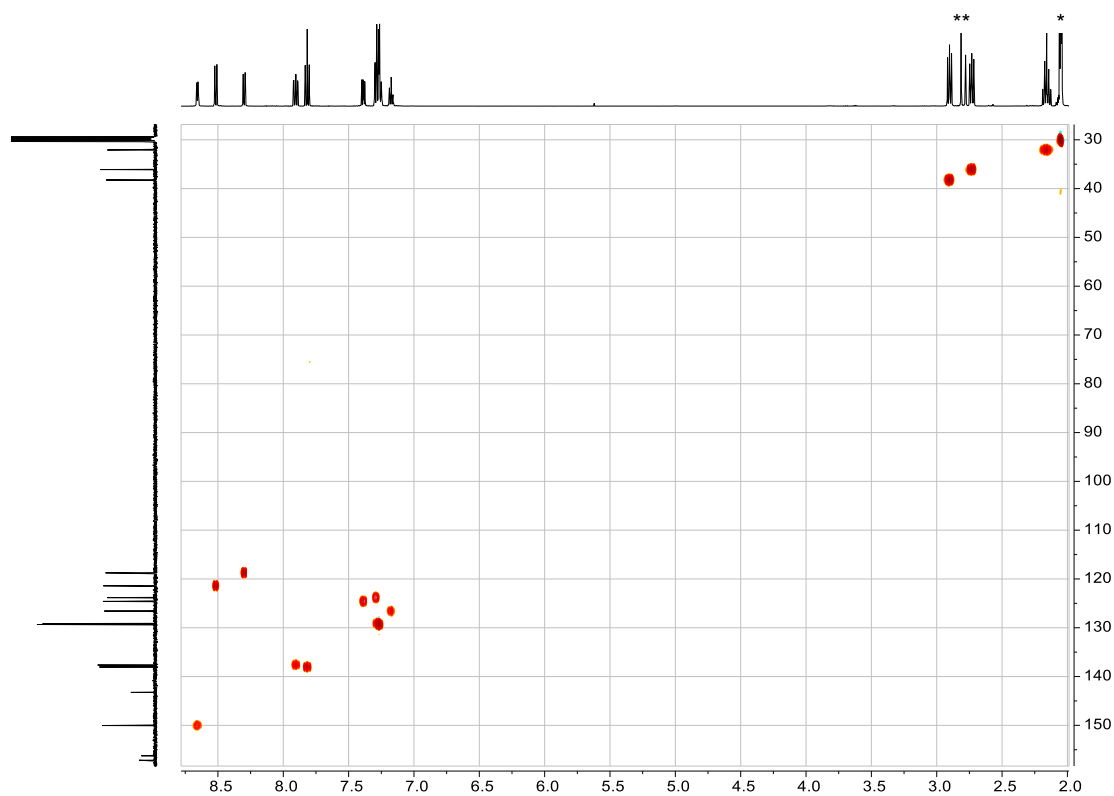


Fig. S40 Part of the HMBC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K, δ/ppm) of 3-PhPrbpy. * = residual acetone- d_6 ; ** = H_2O and HDO .

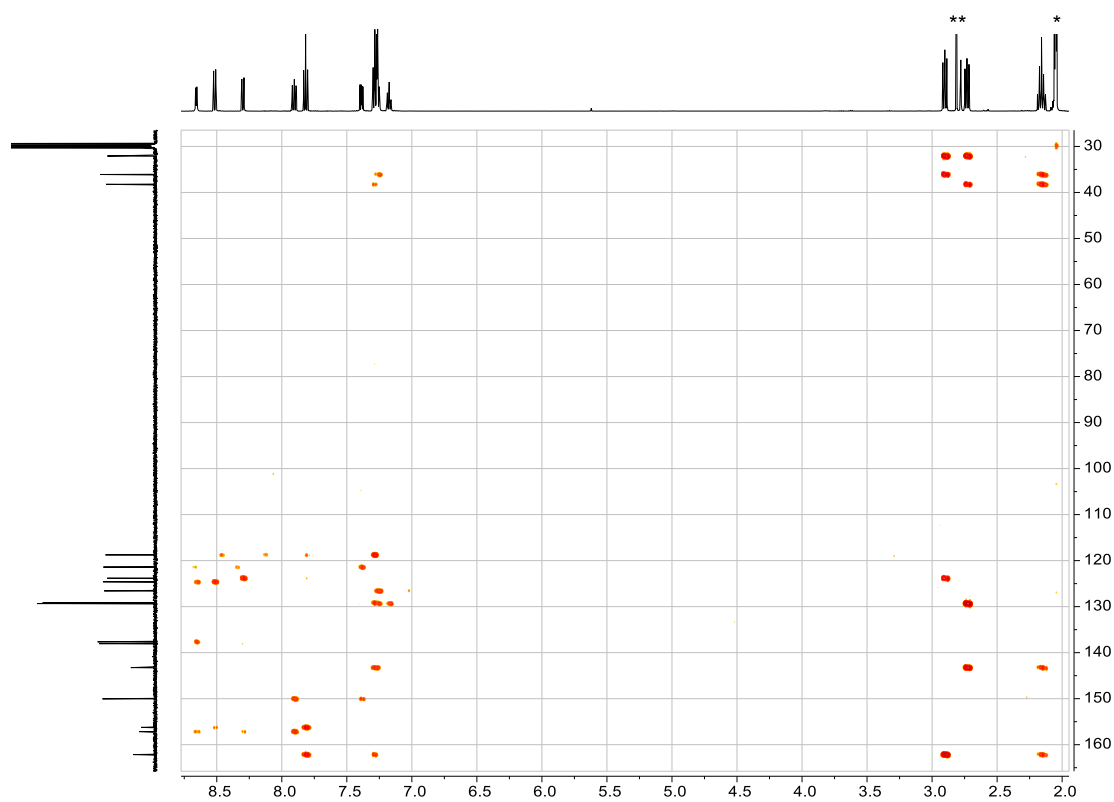


Fig. S41 Part of the HMBC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K, δ/ppm) of 3-PhPrbpy. * = residual acetone- d_6 ; ** = H_2O and HDO .

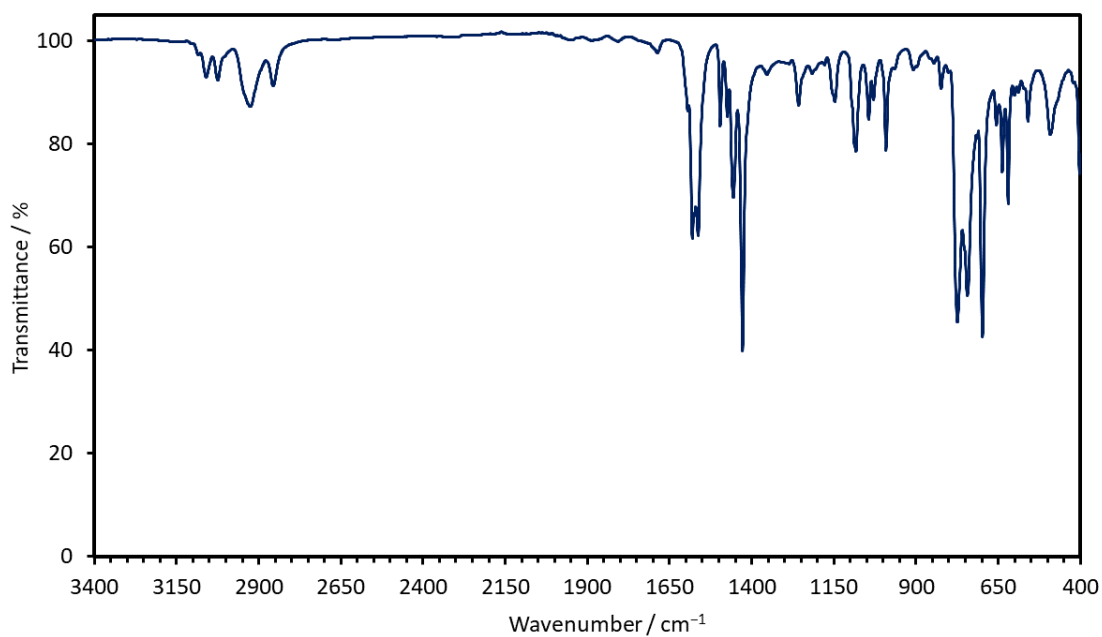


Fig. S42 FTIR spectrum of 3-PhPrbpy.

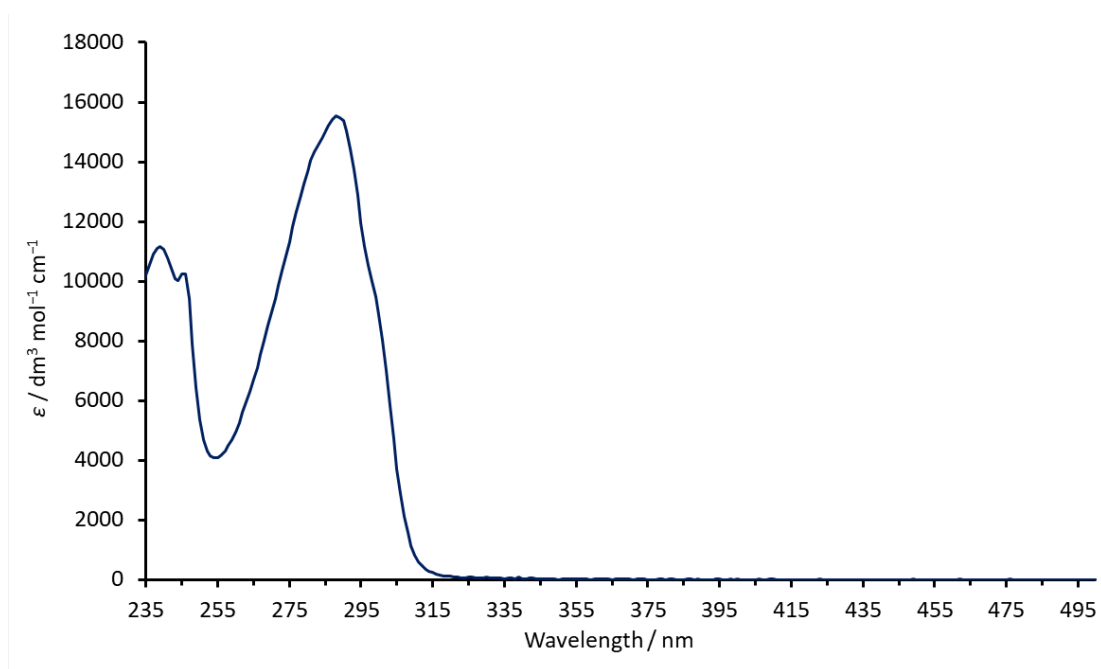


Fig. S43 Solution absorption spectrum (CH_2Cl_2 , $2.5 \times 10^{-5} \text{ mol dm}^{-3}$) of 3-PhPrbpy.

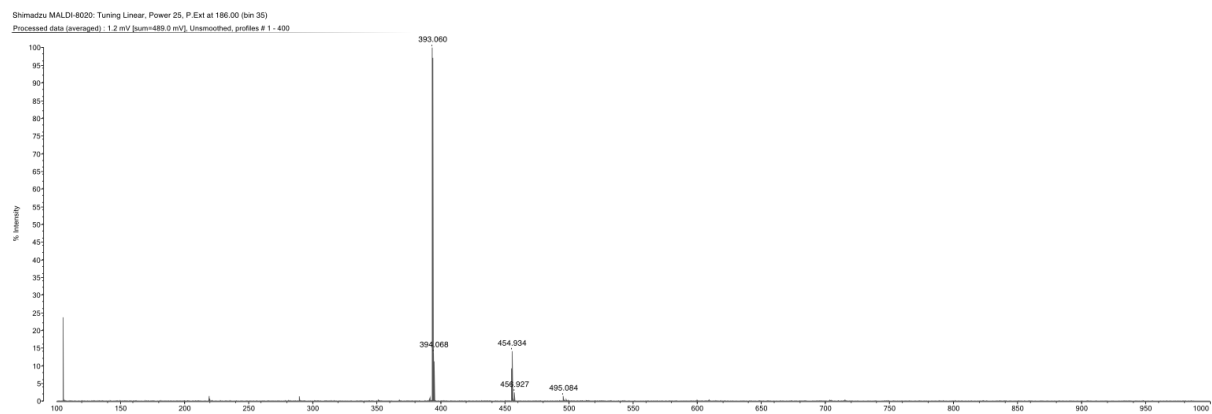


Fig. S44 MALDI mass spectrum (positive mode) of (3-PhPr)₂bpy.

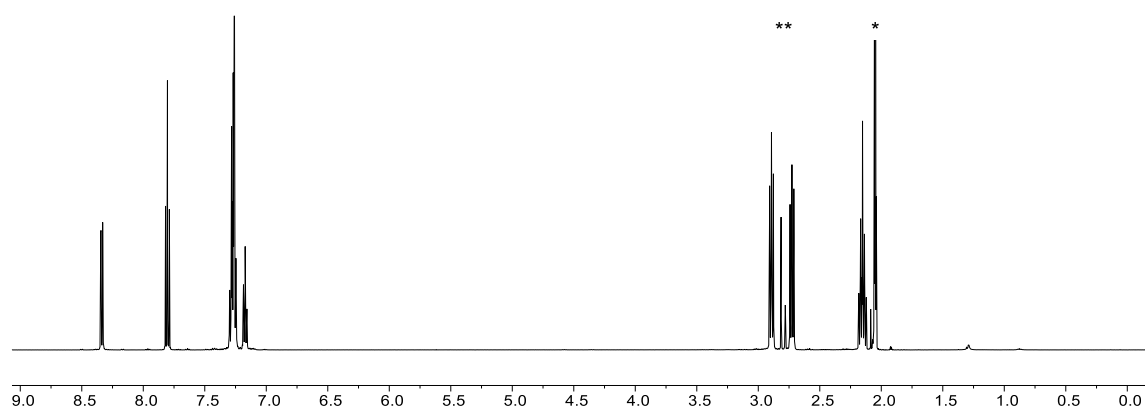


Fig. S45 ¹H NMR spectrum (500 MHz, acetone-*d*₆, 298 K, δ/ppm) of (3-PhPr)₂bpy. * = residual acetone-*d*₆; ** = H₂O and HDO.

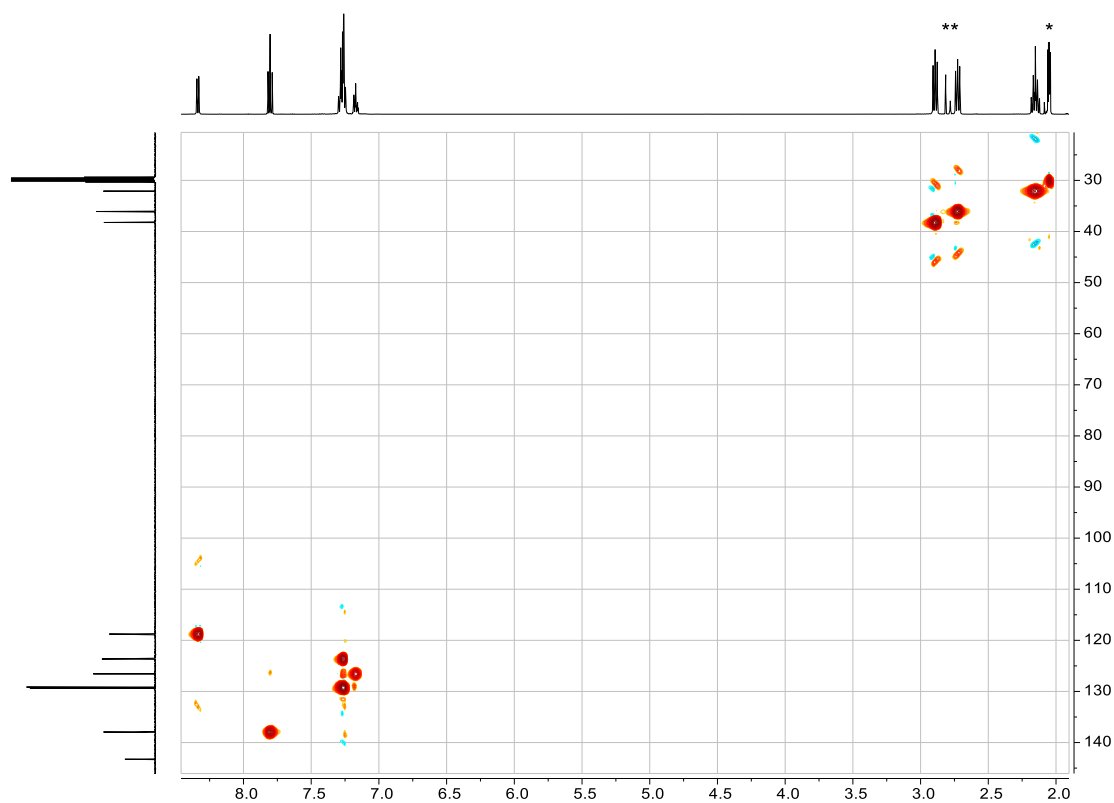


Fig. S46 Part of the HMBC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K, δ/ppm) of (3-PhPr) $_2$ bpy. * = residual acetone- d_6 ; ** = H $_2$ O and HDO.

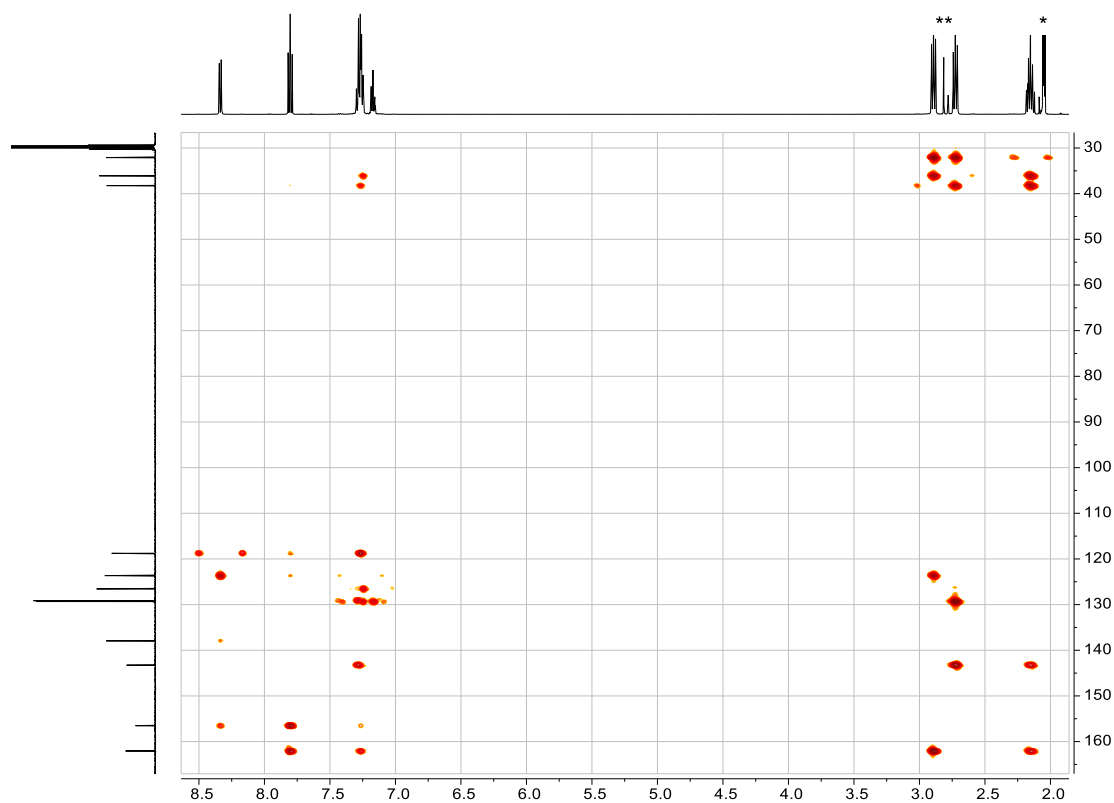


Fig. S47 Part of the HMBC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K, δ/ppm) of (3-PhPr) $_2$ bpy. * = residual acetone- d_6 ; ** = H $_2$ O and HDO.

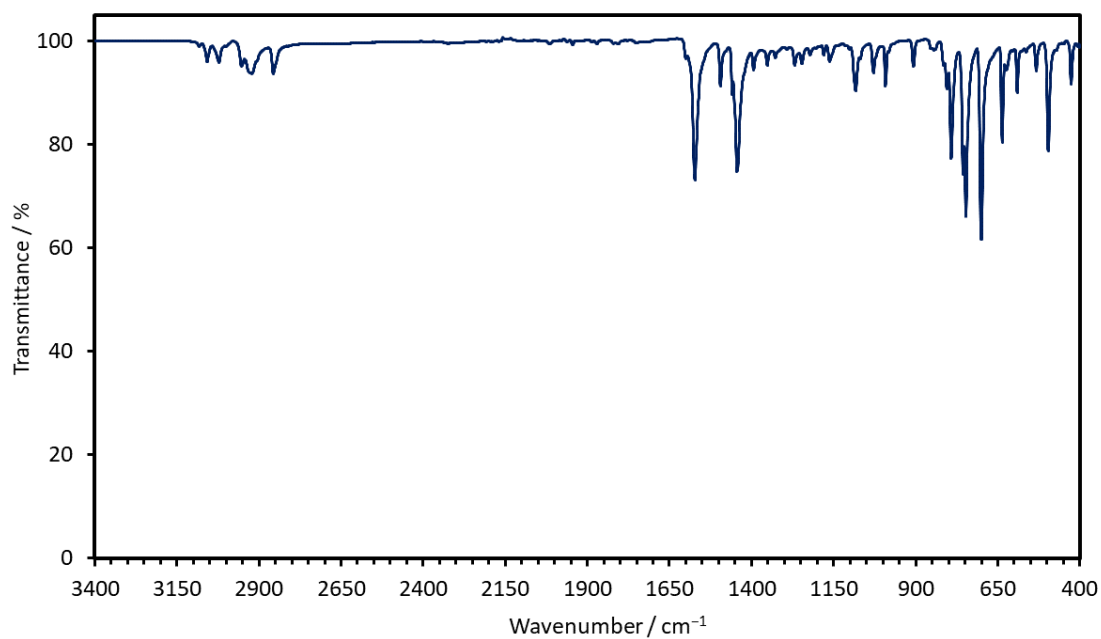


Fig. S48 FTIR spectrum of (3-PhPr)₂bpy.

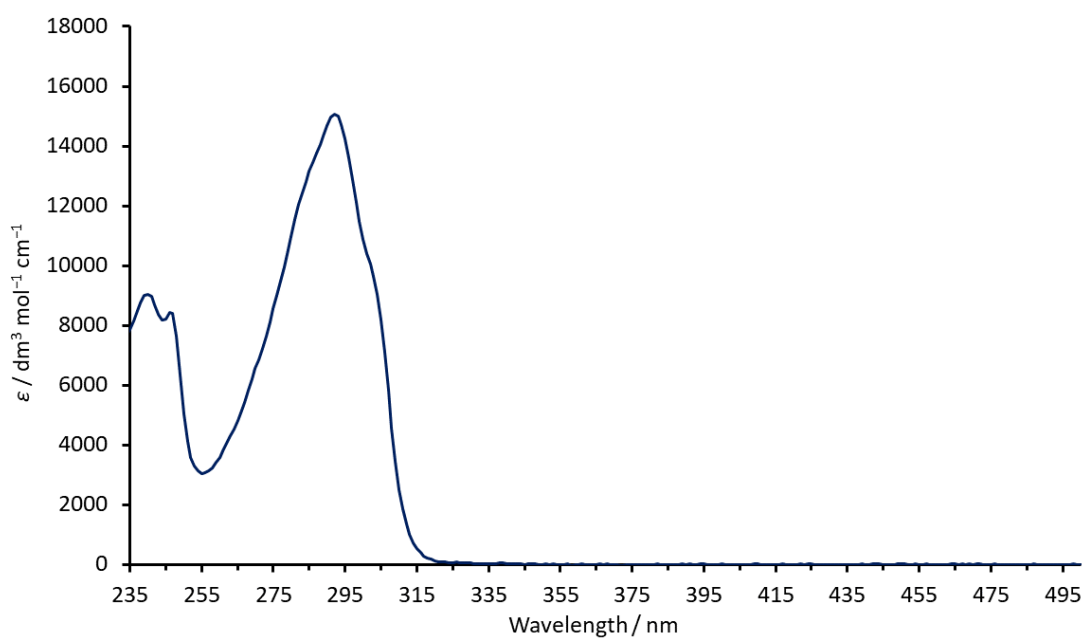


Fig. S49 Solution absorption spectrum (CH_2Cl_2 , $2.5 \times 10^{-5} \text{ mol dm}^{-3}$) of (3-PhPr)₂bpy.

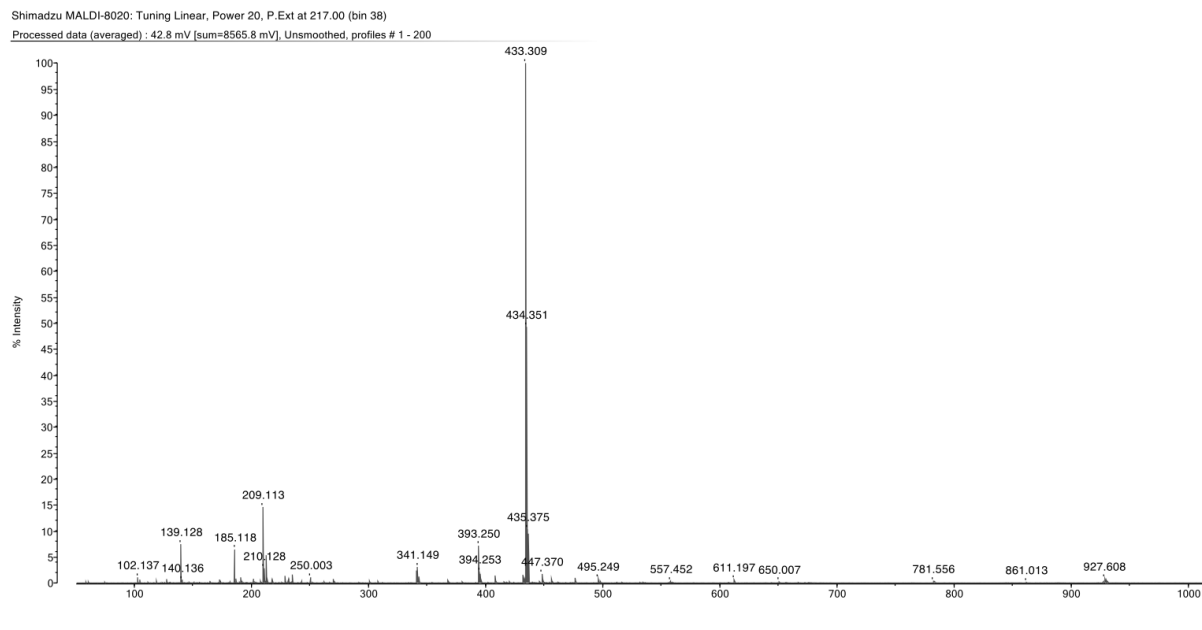


Fig. S50 MALDI mass spectrum (positive mode) of 4,4'-tBu₂-6,6'-Cy₂bpy.

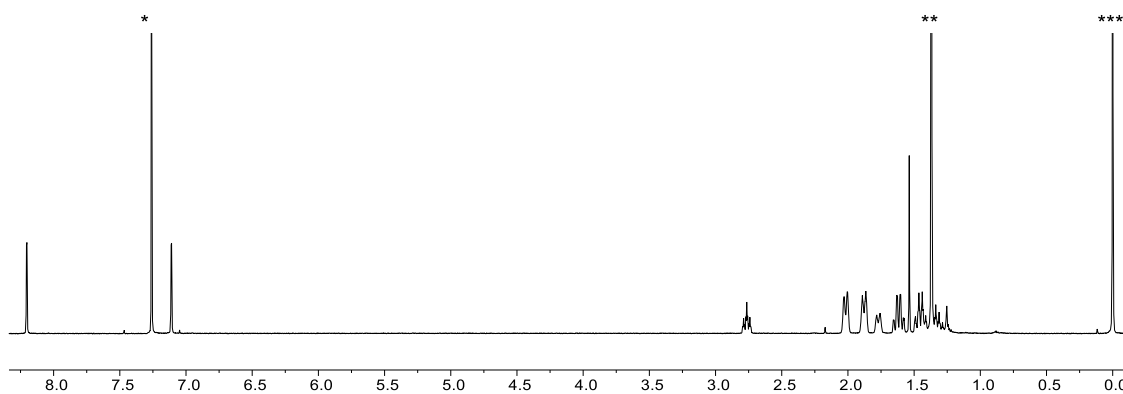


Fig. S51 ¹H NMR spectrum (500 MHz, CDCl₃, 298 K, δ /ppm) of 4,4'-tBu₂-6,6'-Cy₂bpy. * = residual CHCl₃; ** = H₂O and HDO; *** = TMS.

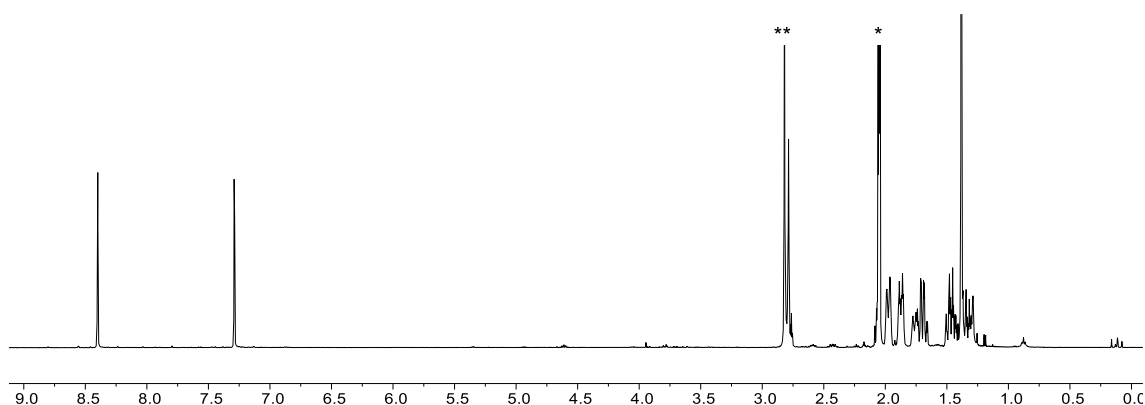


Fig. S52 ¹H NMR spectrum (500 MHz, acetone-*d*₆, 298 K, δ /ppm) of 4,4'-tBu₂-6,6'-Cy₂bpy. * = residual acetone-*d*₅; ** = H₂O and HDO.

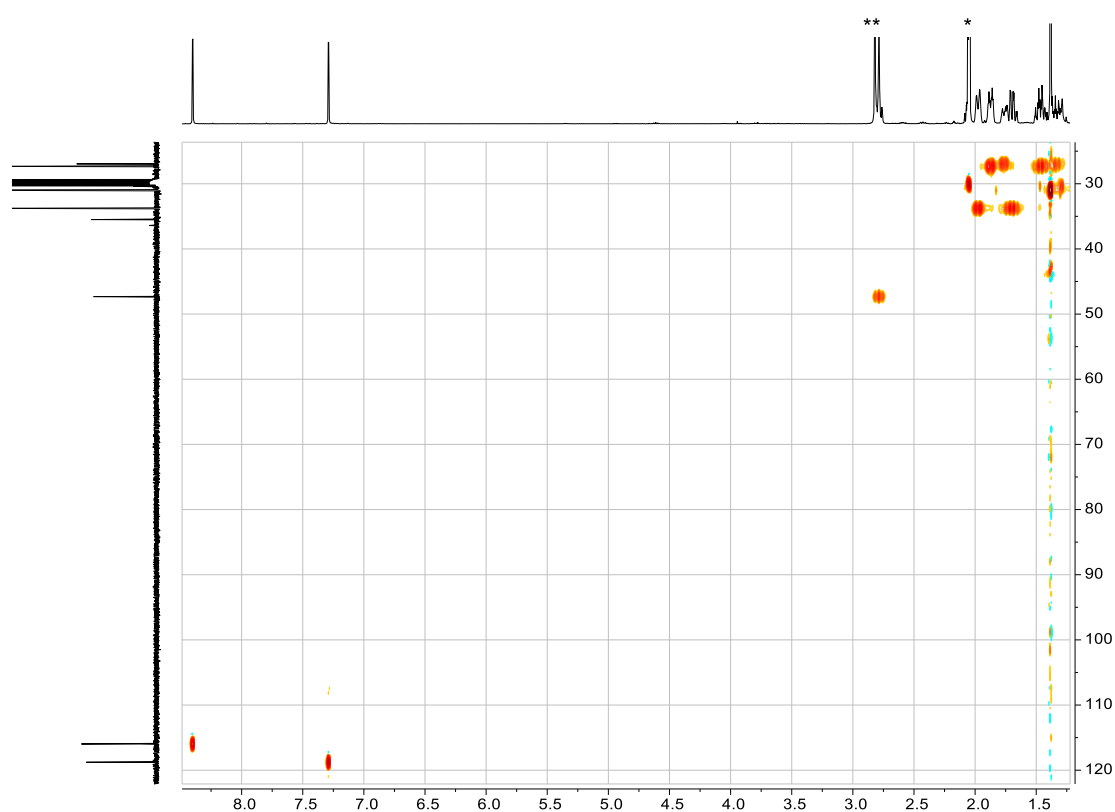


Fig. S53 Part of the HMBC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K, δ/ppm) of 4,4'- $t\text{Bu}_2$ -6,6'- Cy_2bpy . * = residual acetone- d_5 ; ** = H_2O and HDO .

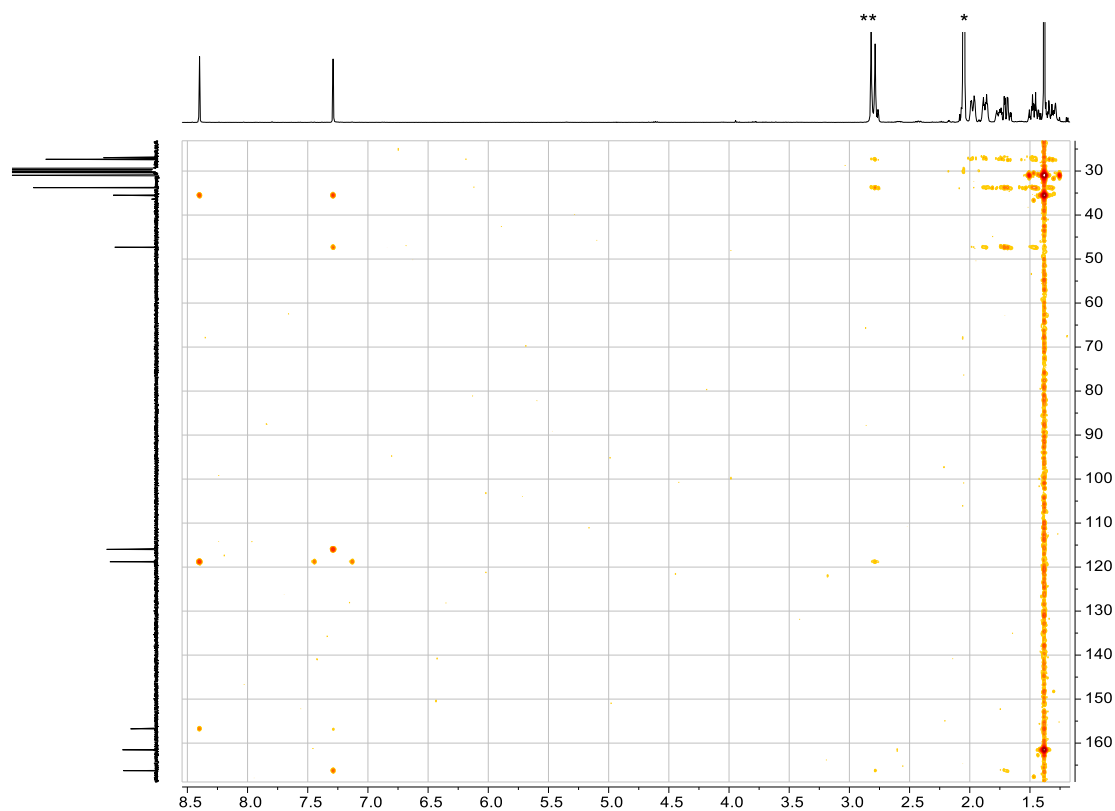


Fig. S54 Part of the HMBC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K, δ/ppm) of 4,4'- $t\text{Bu}_2$ -6,6'- Cy_2bpy . * = residual acetone- d_5 ; ** = H_2O and HDO .

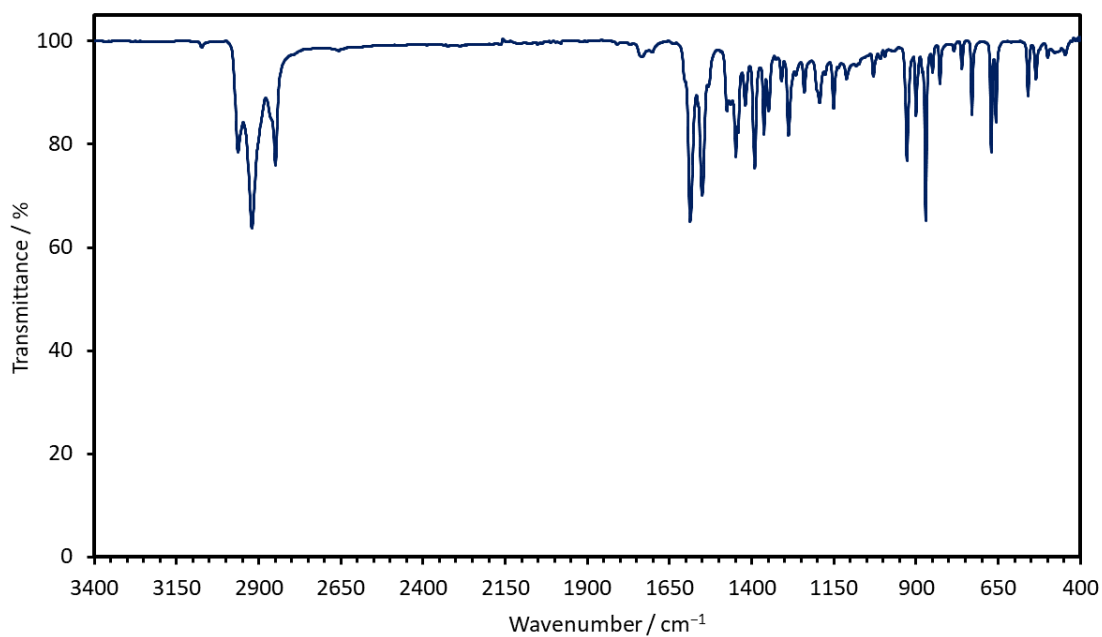


Fig. S55 FTIR spectrum of 4,4'-tBu₂-6,6'-Cy₂bpy.

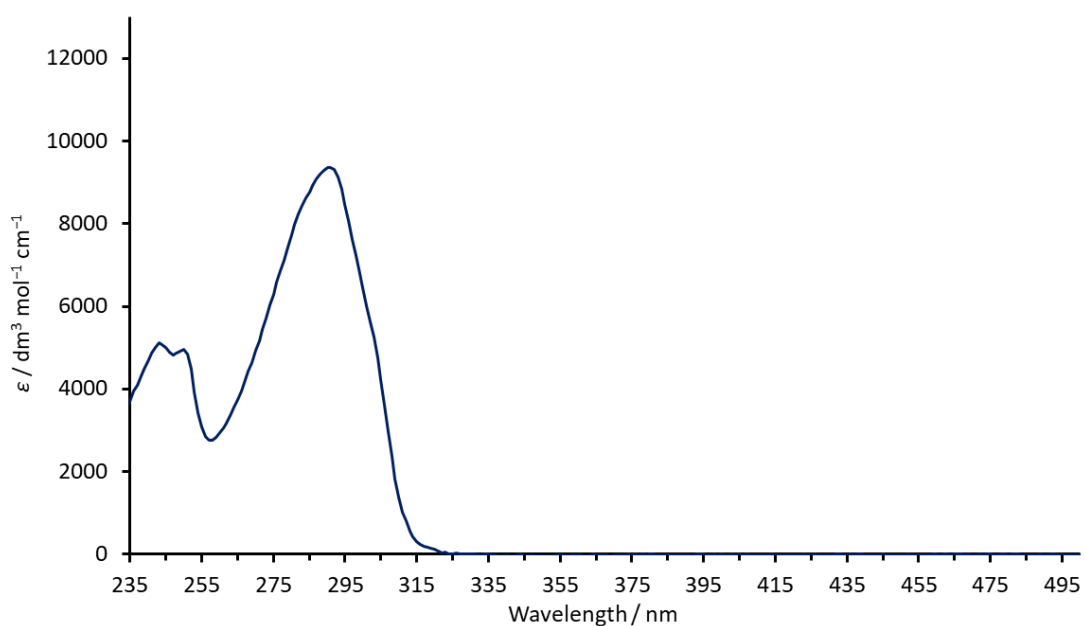


Fig. S56 Solution absorption spectrum (CH₂Cl₂, 2.5 × 10⁻⁵ mol dm⁻³) of 4,4'-tBu₂-6,6'-Cy₂bpy.

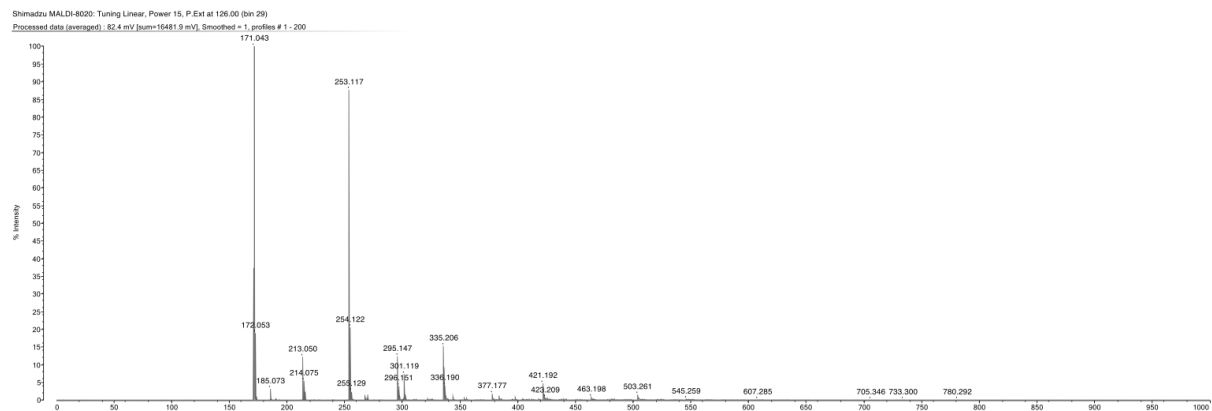


Fig. S57 MALDI mass spectrum (positive mode) of 6-Cy-6'-Mebpy.

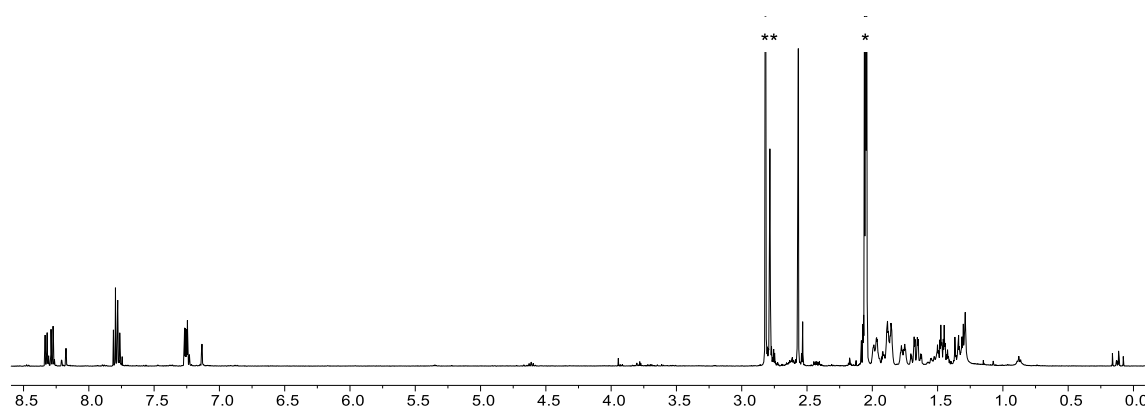


Fig. S58 ^1H NMR spectrum (500 MHz, acetone- d_6 , 298 K, δ/ppm) of 6-Cy-6'-Mebpy. * = residual acetone- d_5 ; ** = H_2O and HDO.

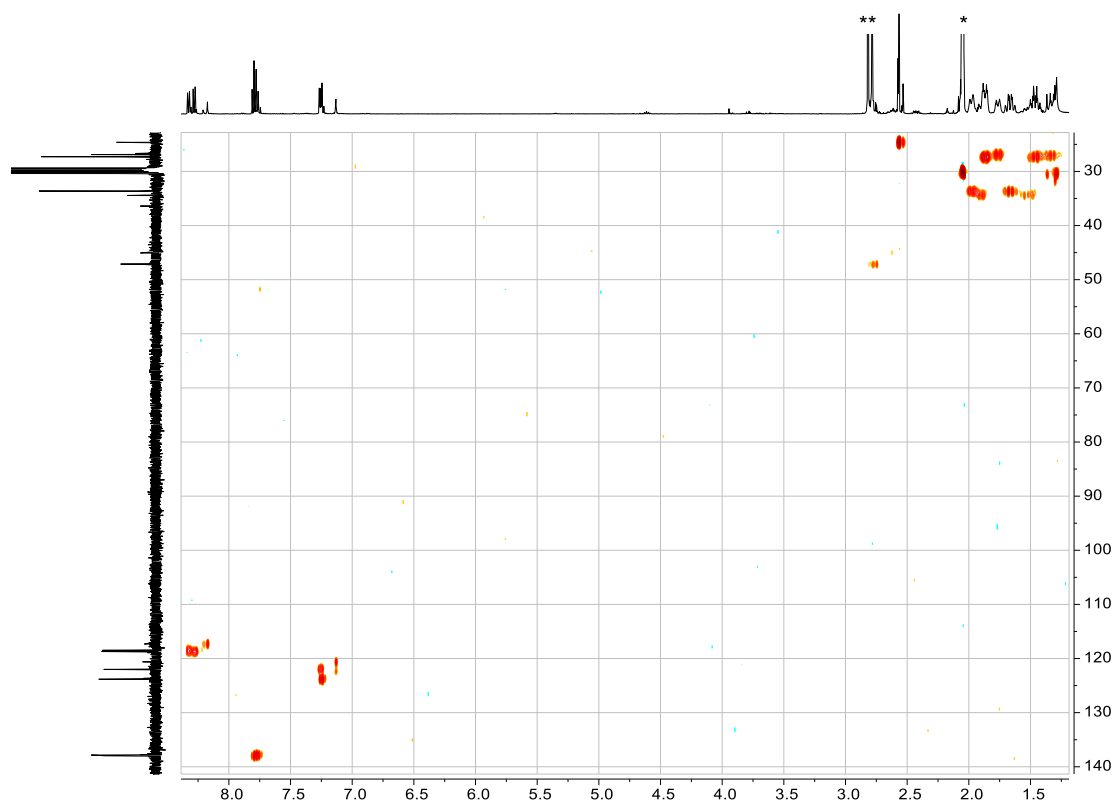


Fig. S59 Part of the HMQC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K, δ/ppm) of 6-Cy-6'-Mebpy. * = residual acetone- d_6 ; ** = H_2O and HDO.

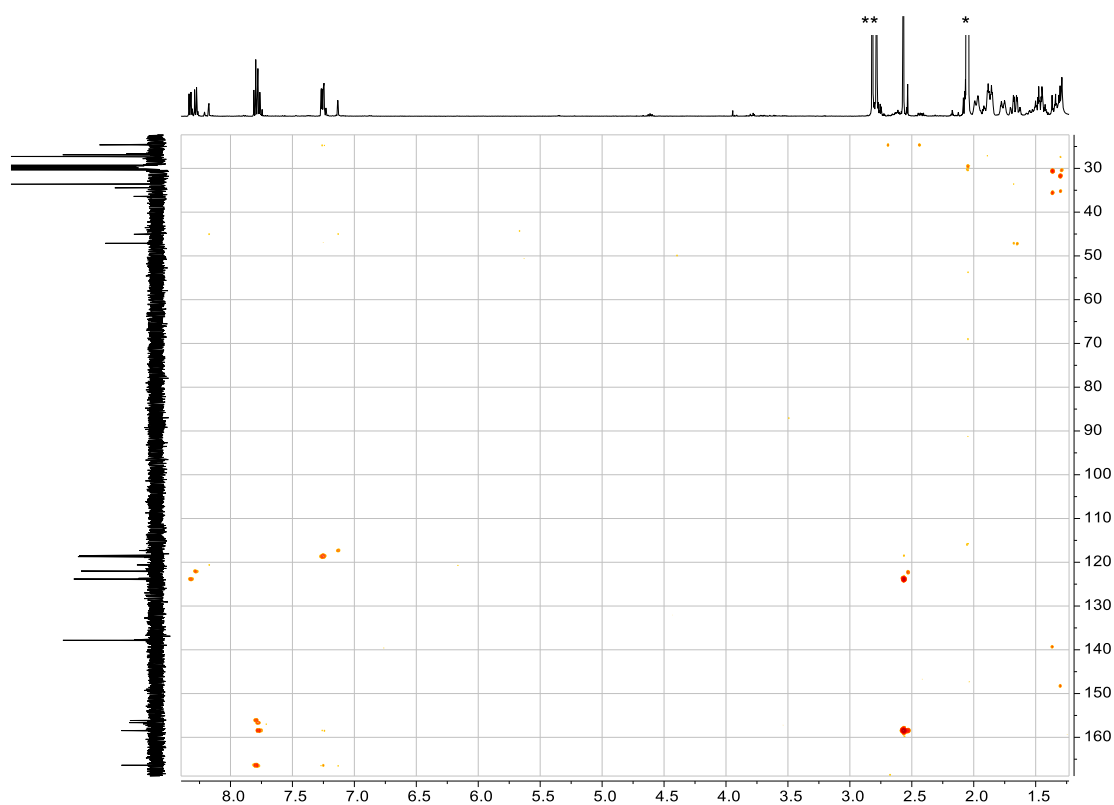


Fig. S60 ^1H NMR spectrum (500 MHz, acetone- d_6 , 298 K, δ/ppm) of 6-Cy-6'-Mebpy. * = residual acetone- d_6 ; ** = H_2O and HDO.

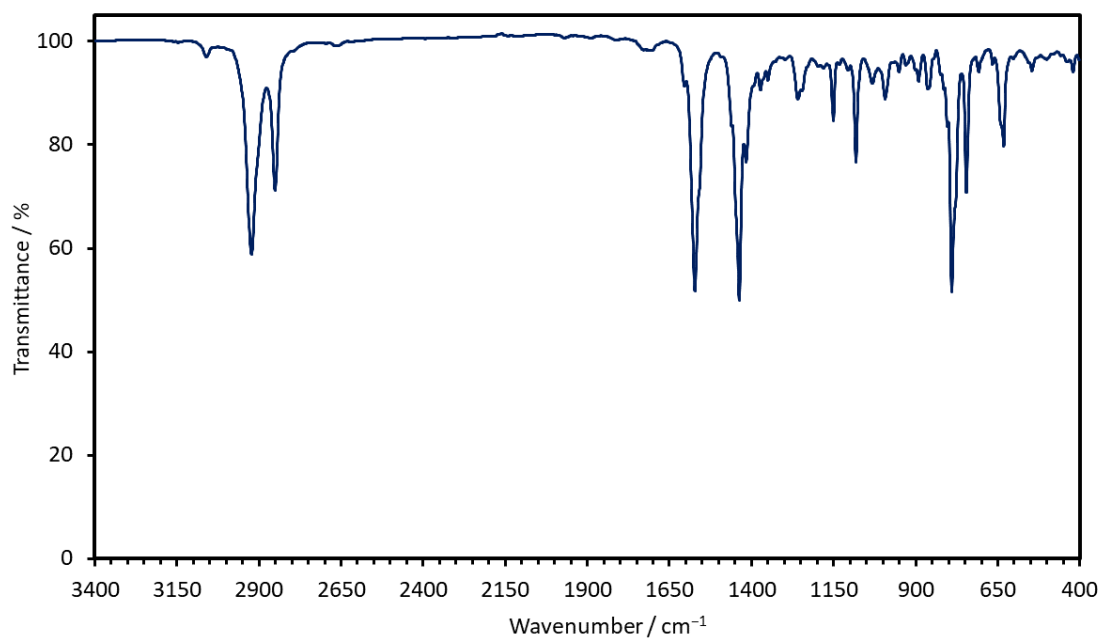


Fig. S61 FTIR spectrum of 6-Cy-6'-Mebpy.

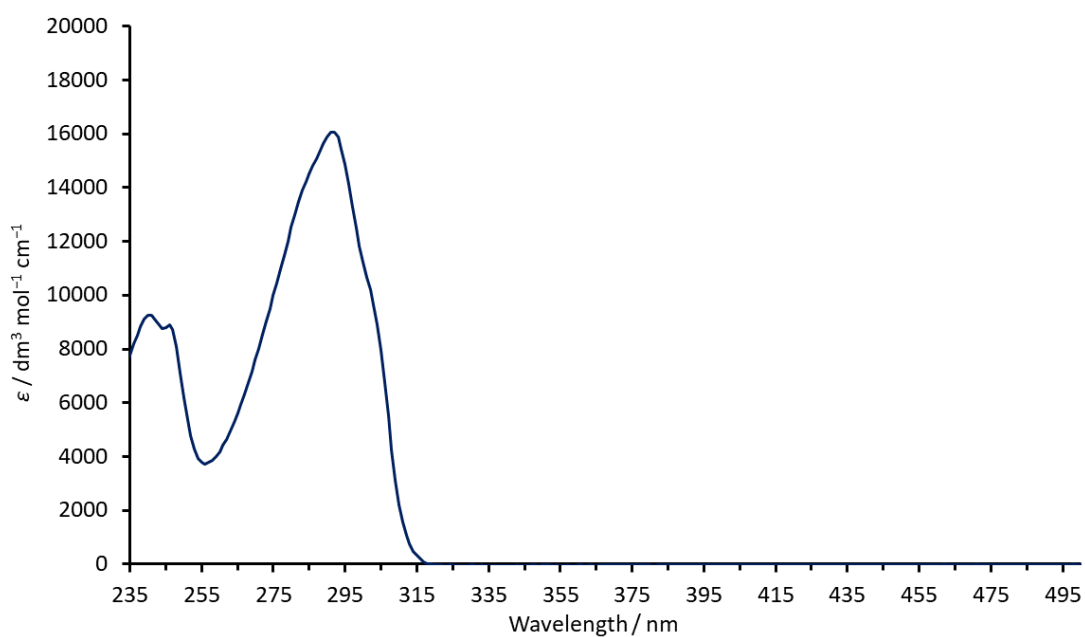
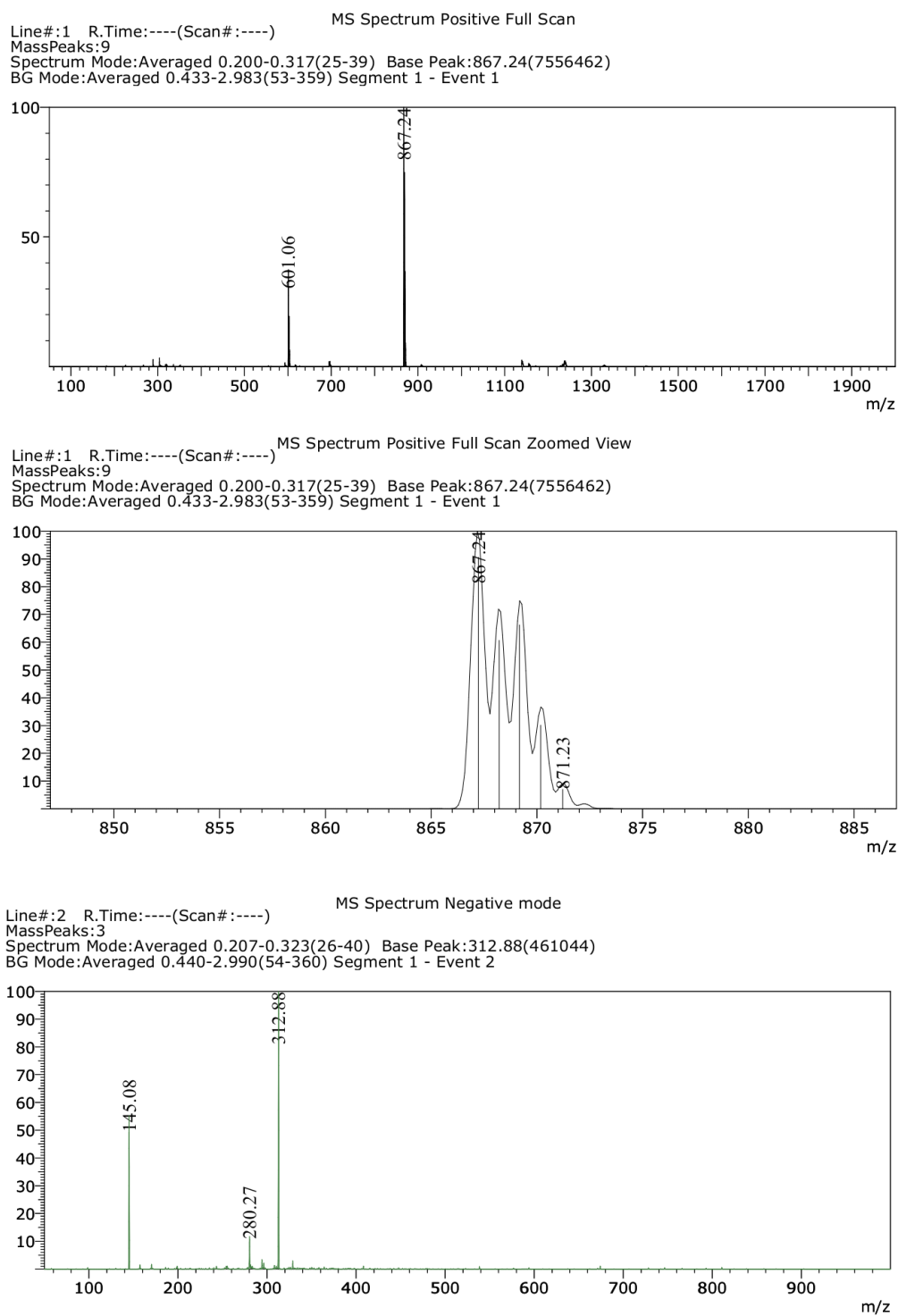


Fig. S62 Solution absorption spectrum (CH₂Cl₂, $2.5 \times 10^{-5} \text{ mol dm}^{-3}$) of 6-Cy-6'-Mebpy.

Fig. S63 ESI mass spectrum (positive and negative mode) of $[\text{Cu}(\text{POP})(2\text{-CyEtbp})](\text{PF}_6)$.

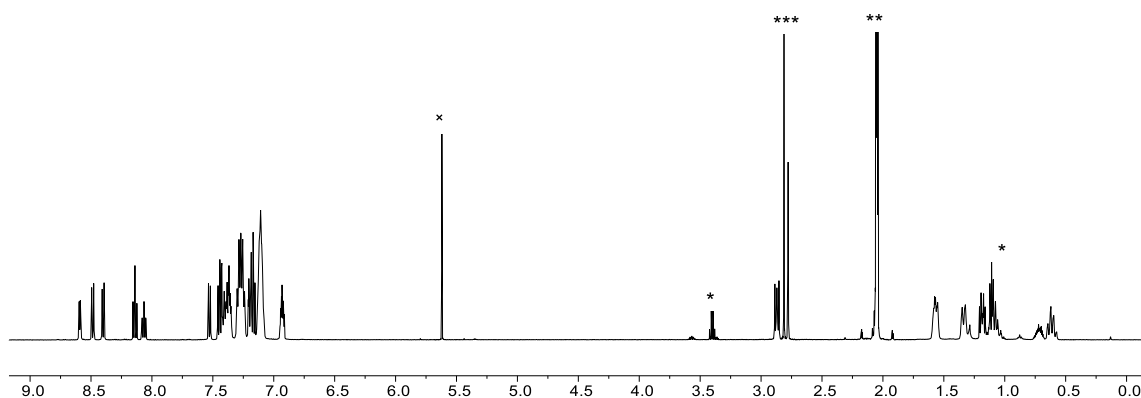


Fig. S64 ^1H NMR spectrum (500 MHz, acetone- d_6 , 298 K, δ/ppm) of $[\text{Cu}(\text{POP})(2\text{-CyEtbp})][\text{PF}_6]$. * = Et_2O ; ** = residual acetone- d_6 ; *** = H_2O and HDO ; * = CH_2Cl_2 .

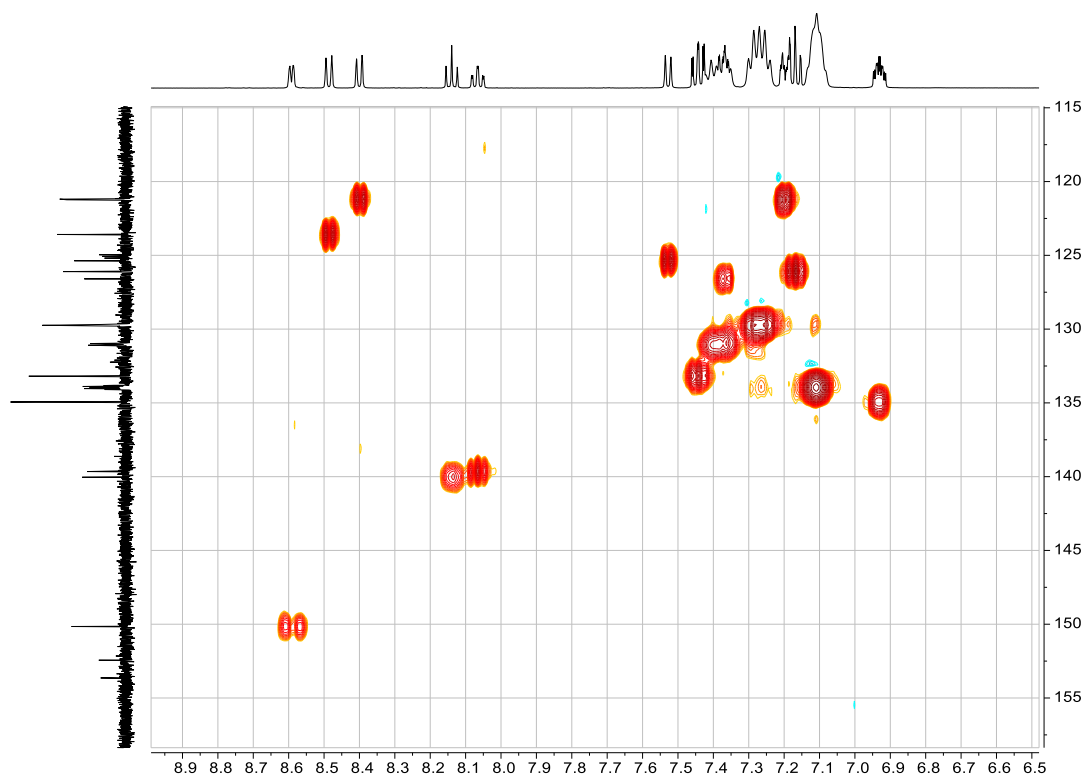


Fig. S65 The aromatic region of the HMQC spectrum (500 MHz ^1H , 126 MHz ^{13}C , acetone- d_6 , 298 K, δ/ppm) of $[\text{Cu}(\text{POP})(2\text{-CyEtbp})][\text{PF}_6]$.

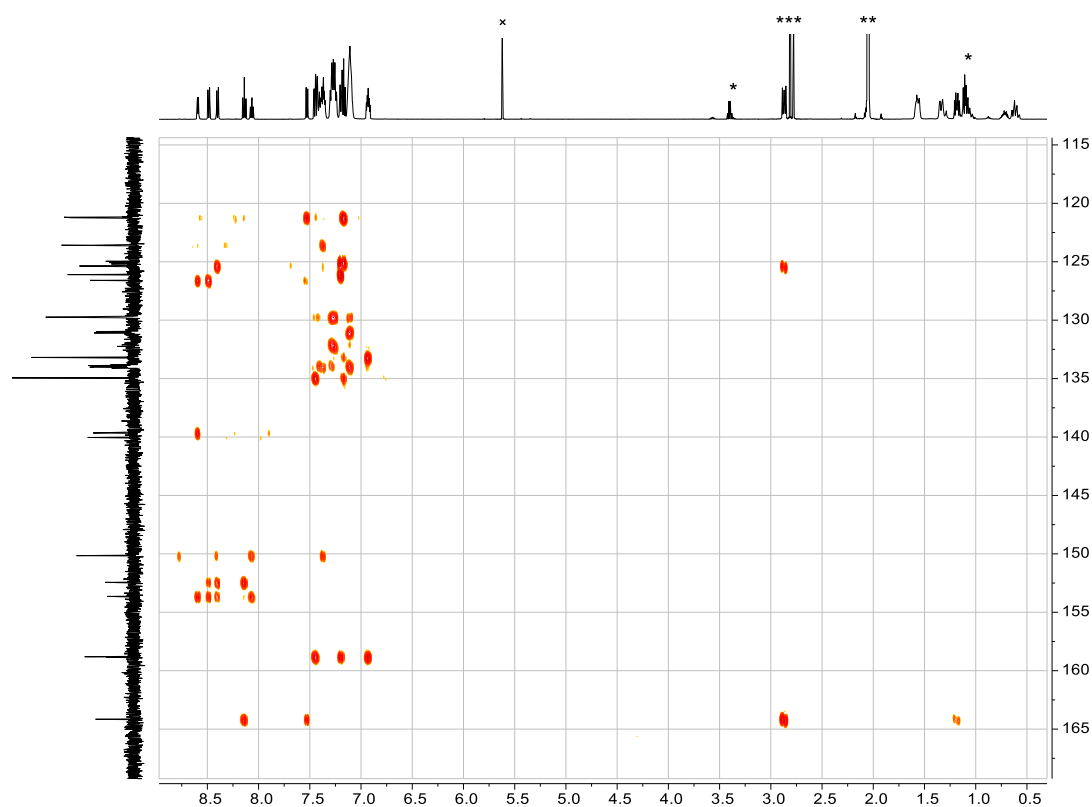


Fig. S66 Part of the HMBC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K, δ/ppm) of $[\text{Cu}(\text{POP})(2\text{-CyEtbpv})][\text{PF}_6]$. * = Et_2O ; ** = residual acetone- d_5 ; *** = H_2O and HDO ; x = CH_2Cl_2 .

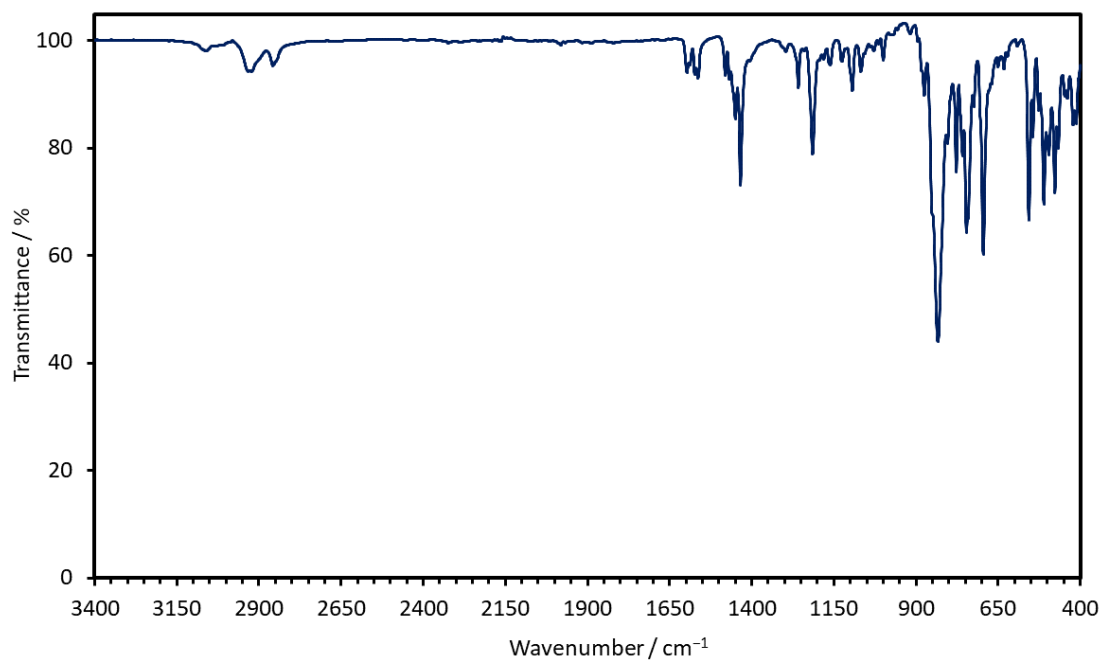
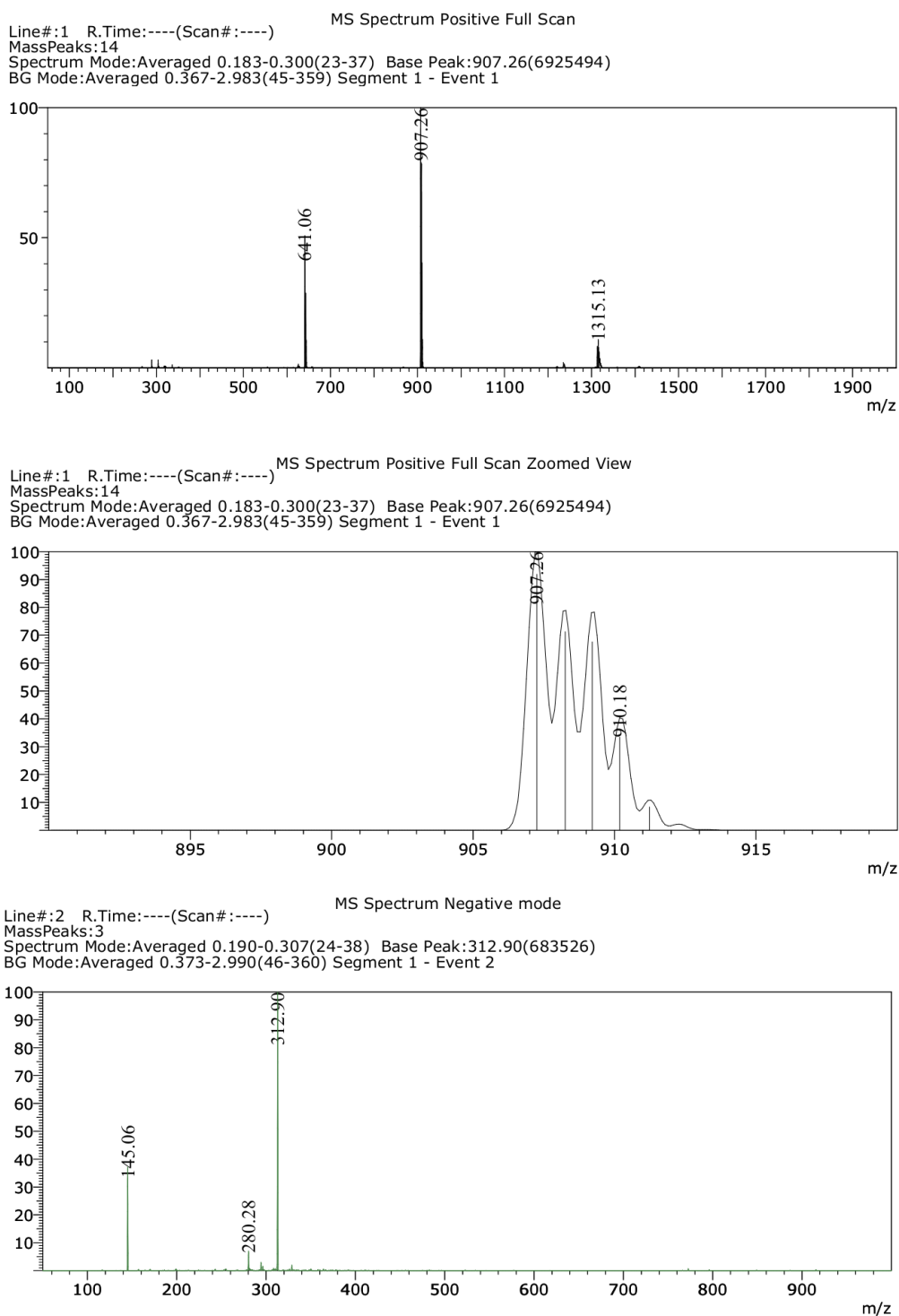


Fig. S67 FTIR spectrum of $[\text{Cu}(\text{POP})(2\text{-CyEtbpv})][\text{PF}_6]$.

Fig. S68 ESI mass spectrum (positive and negative mode) of $[\text{Cu}(\text{xantphos})(2\text{-CyEtbpy})][\text{PF}_6]$.

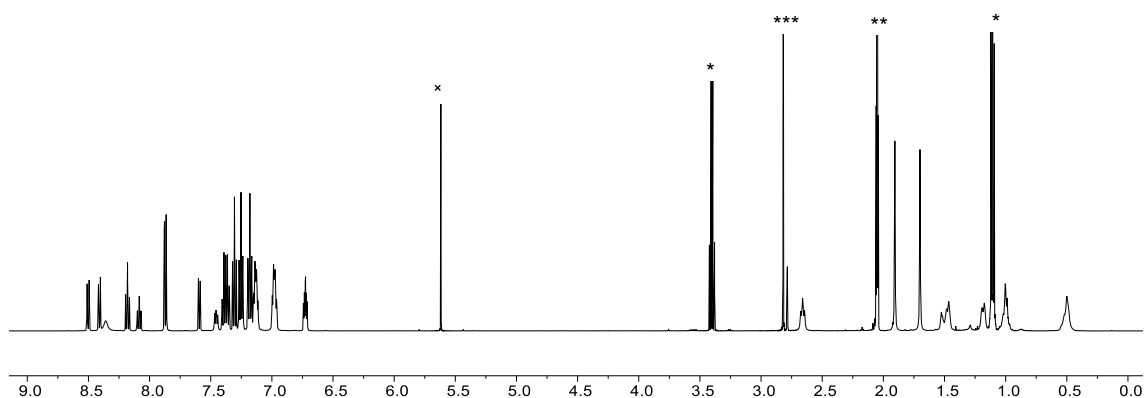


Fig. S69 ^1H NMR spectrum (500 MHz, acetone- d_6 , 298 K, δ/ppm) of $[\text{Cu}(\text{xantphos})(2\text{-CyEtbp})](\text{PF}_6)$. * = Et_2O ; ** = residual acetone- d_5 ; *** = H_2O and HDO ; * = CH_2Cl_2 .

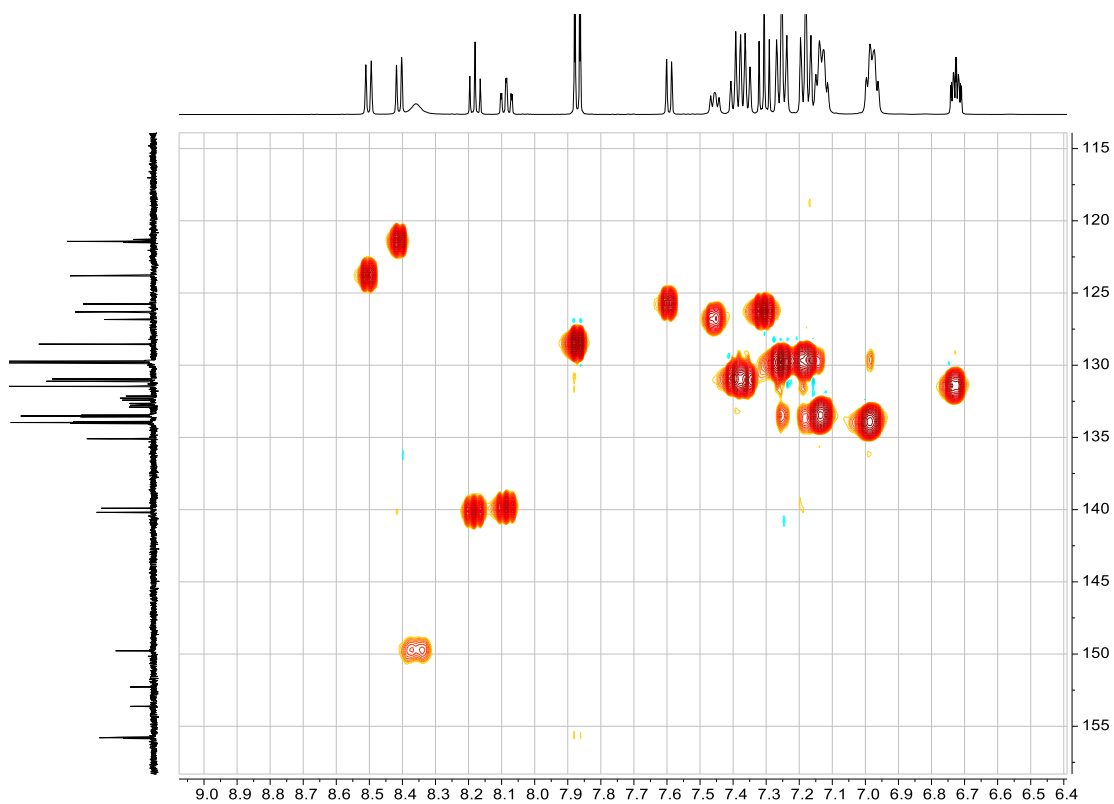


Fig. S70 The aromatic region of the HMQC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K, δ/ppm) of $[\text{Cu}(\text{xantphos})(2\text{-CyEtbp})](\text{PF}_6)$.

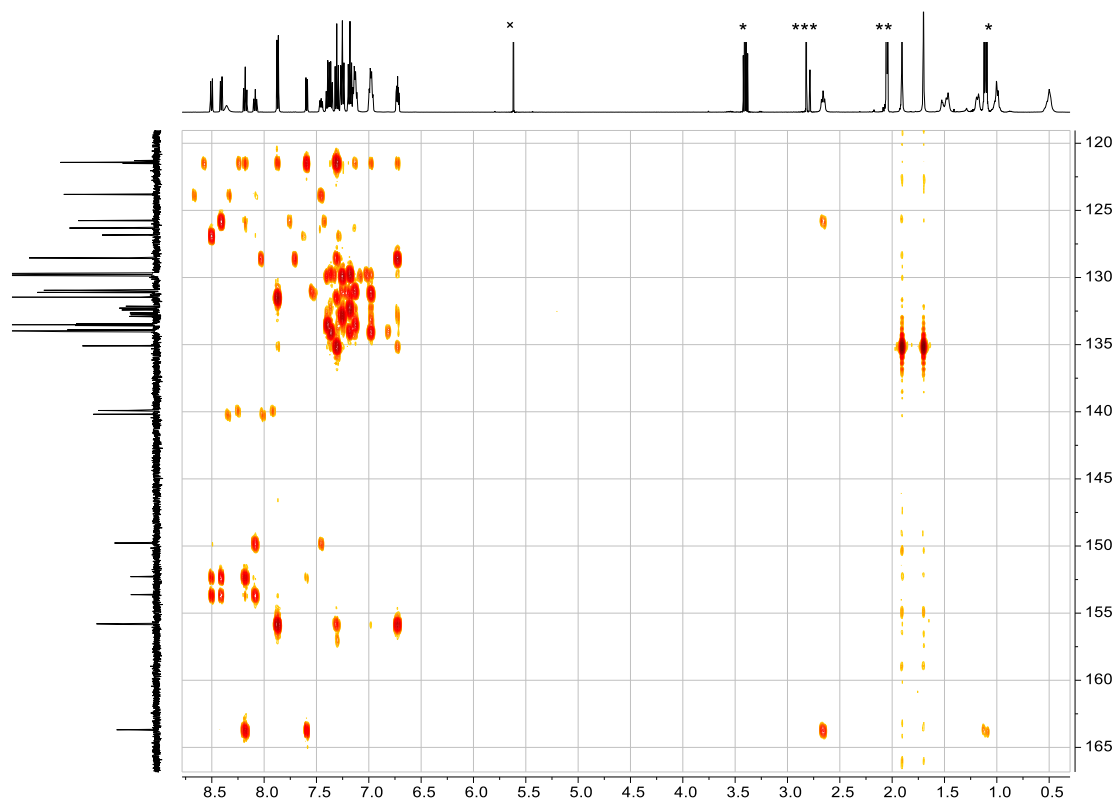


Fig. S71 Part of the HMBC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K, δ/ppm) of $[\text{Cu}(\text{xantphos})(2\text{-CyEtbpv})][\text{PF}_6]$. * = Et_2O ; ** = residual acetone- d_5 ; *** = H_2O and HDO ; x = CH_2Cl_2 .

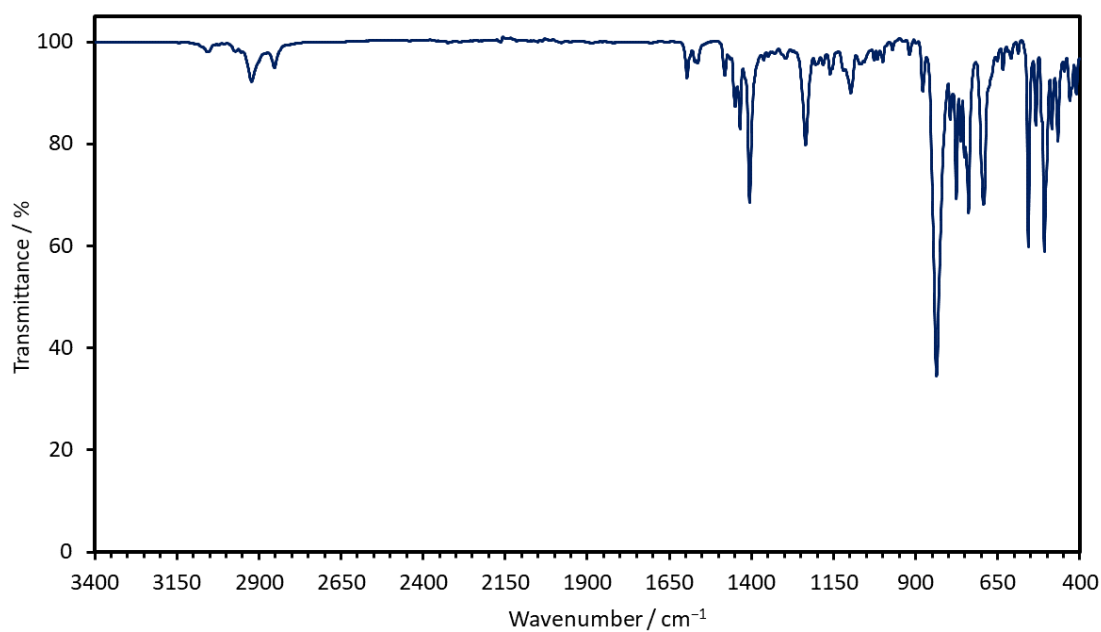
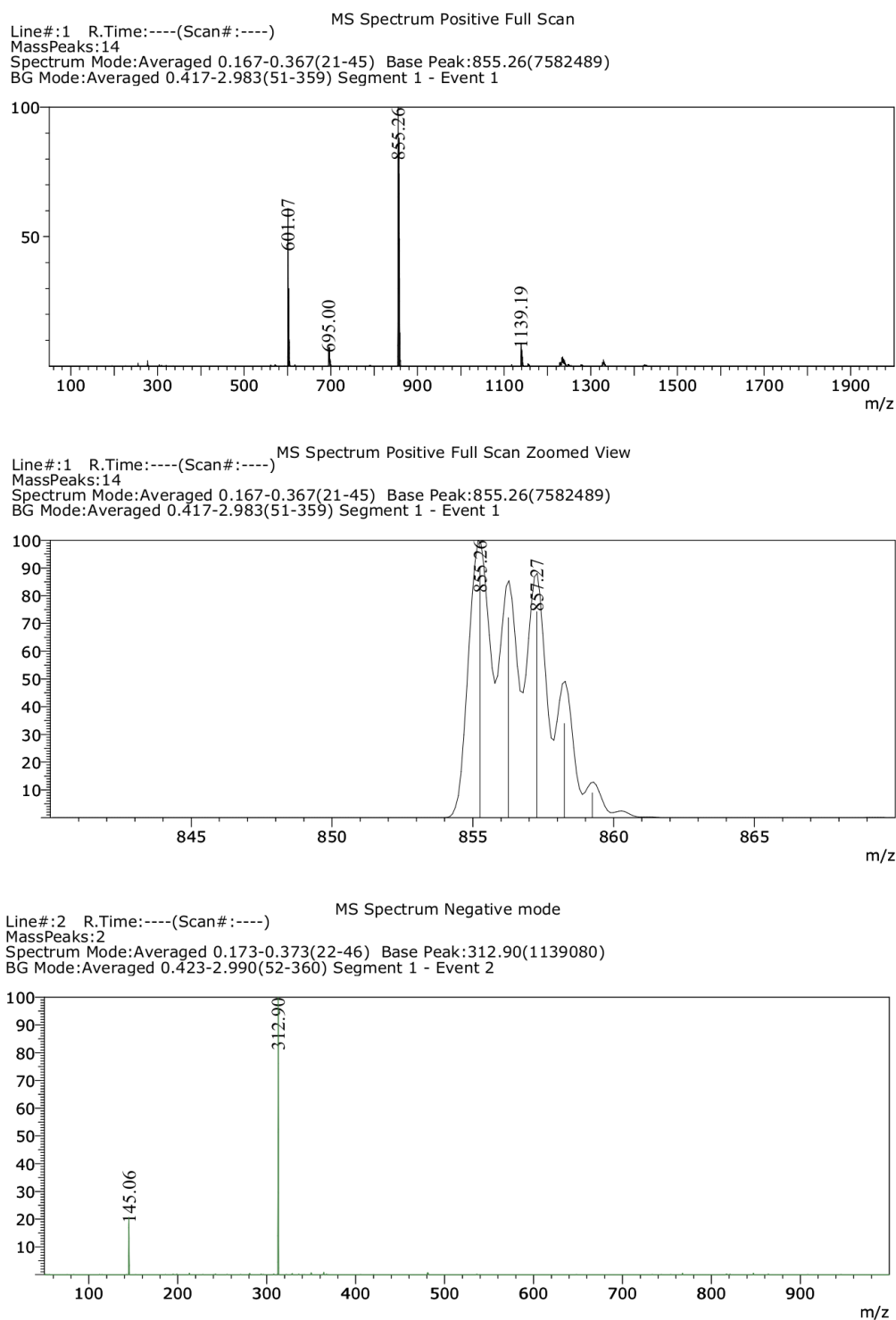


Fig. S72 FTIR spectrum of $[\text{Cu}(\text{xantphos})(2\text{-CyEtbpv})][\text{PF}_6]$.

Fig. S73 ESI mass spectrum (positive and negative mode) of $[\text{Cu}(\text{POP})(3\text{-EtPentbp})][\text{PF}_6]$.

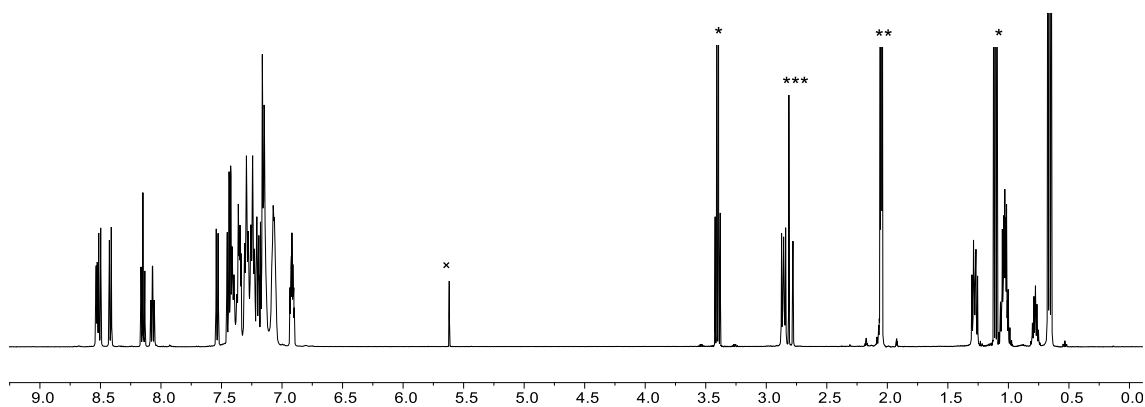


Fig. S74 ^1H NMR spectrum (500 MHz, acetone- d_6 , 298 K, δ/ppm) of $[\text{Cu}(\text{POP})(3\text{-EtPentbpy})][\text{PF}_6]$. * = Et_2O ; ** = residual acetone- d_5 ; *** = H_2O and HDO ; x = CH_2Cl_2 .

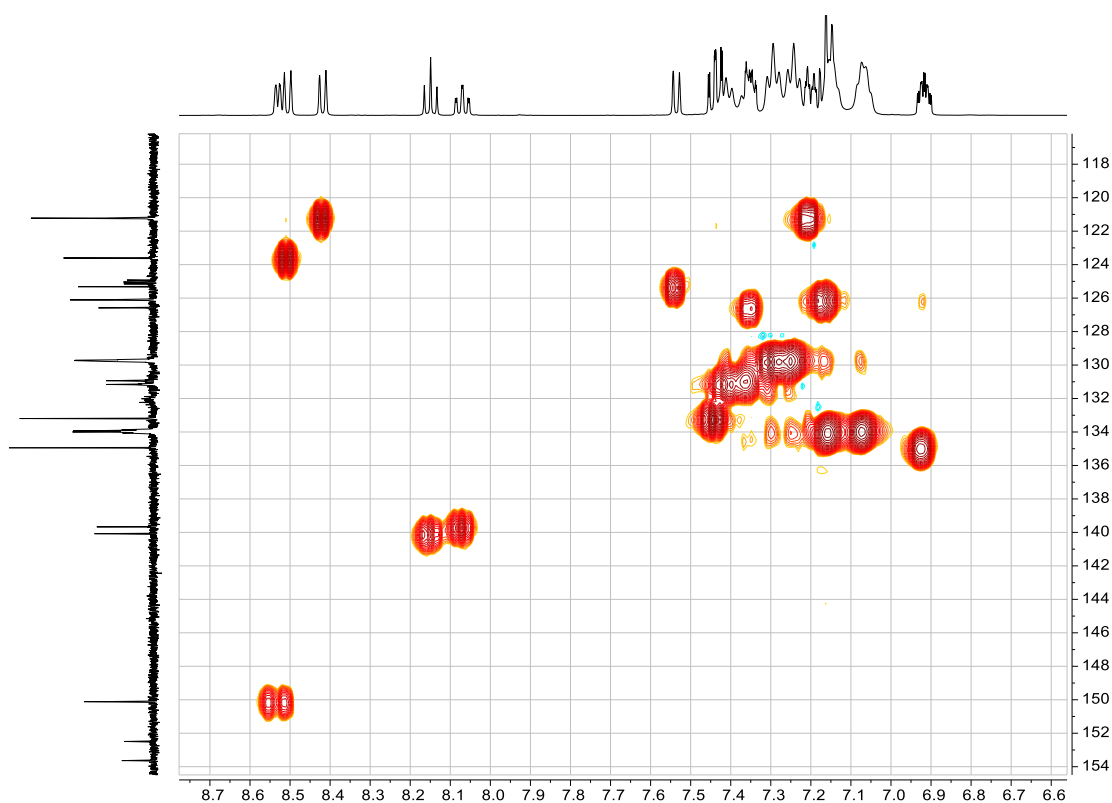


Fig. S75 The aromatic region of the HMQC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K, δ/ppm) of $[\text{Cu}(\text{POP})(3\text{-EtPentbpy})][\text{PF}_6]$.

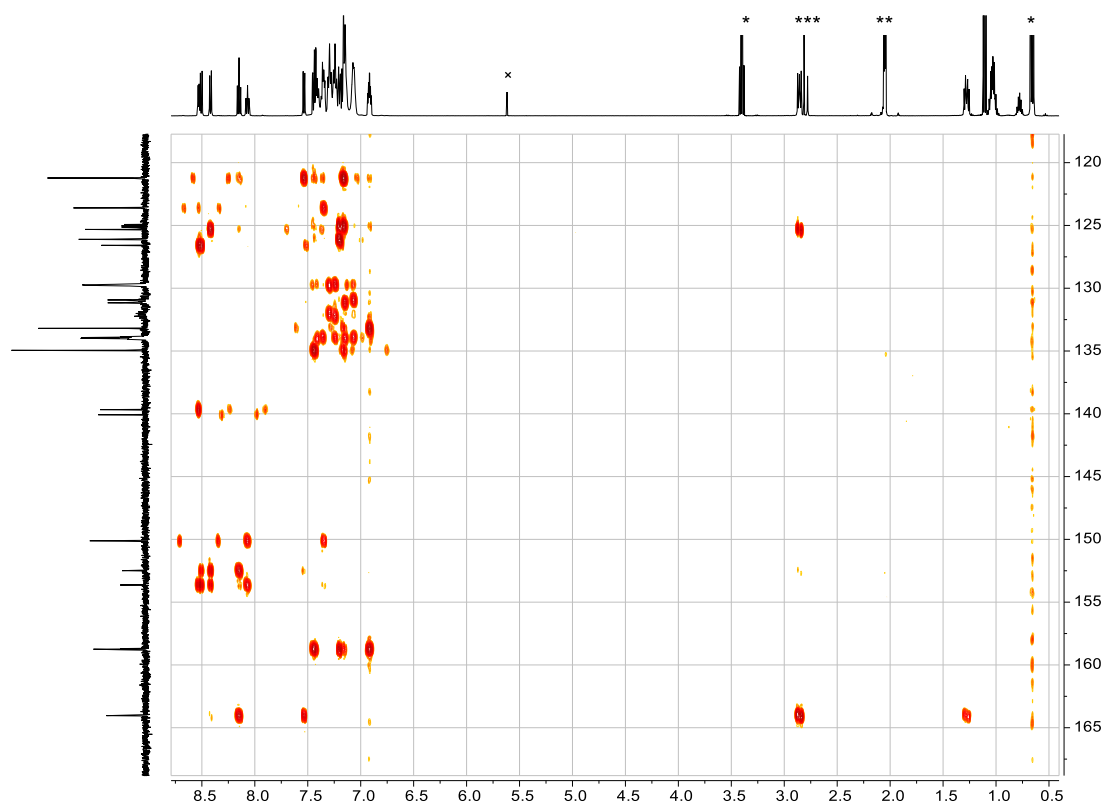


Fig. S76 Part of the HMBC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K, δ/ppm) of $[\text{Cu}(\text{POP})(3\text{-EtPentbpy})][\text{PF}_6]$. * = Et_2O ; ** = residual acetone- d_5 ; *** = H_2O and HDO ; x = CH_2Cl_2 .

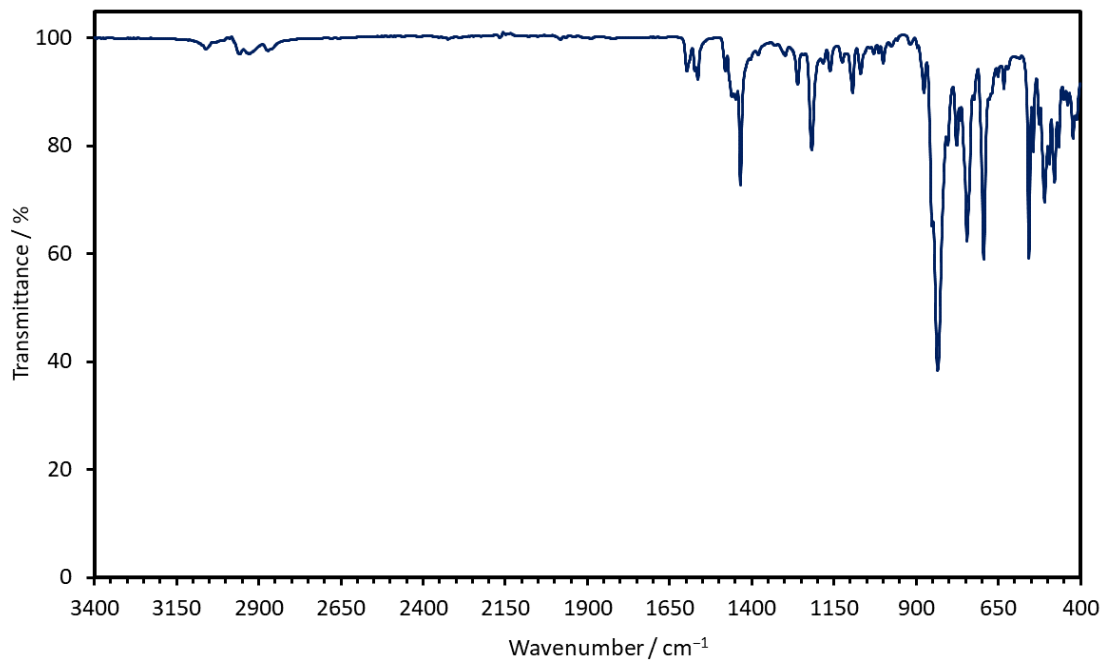
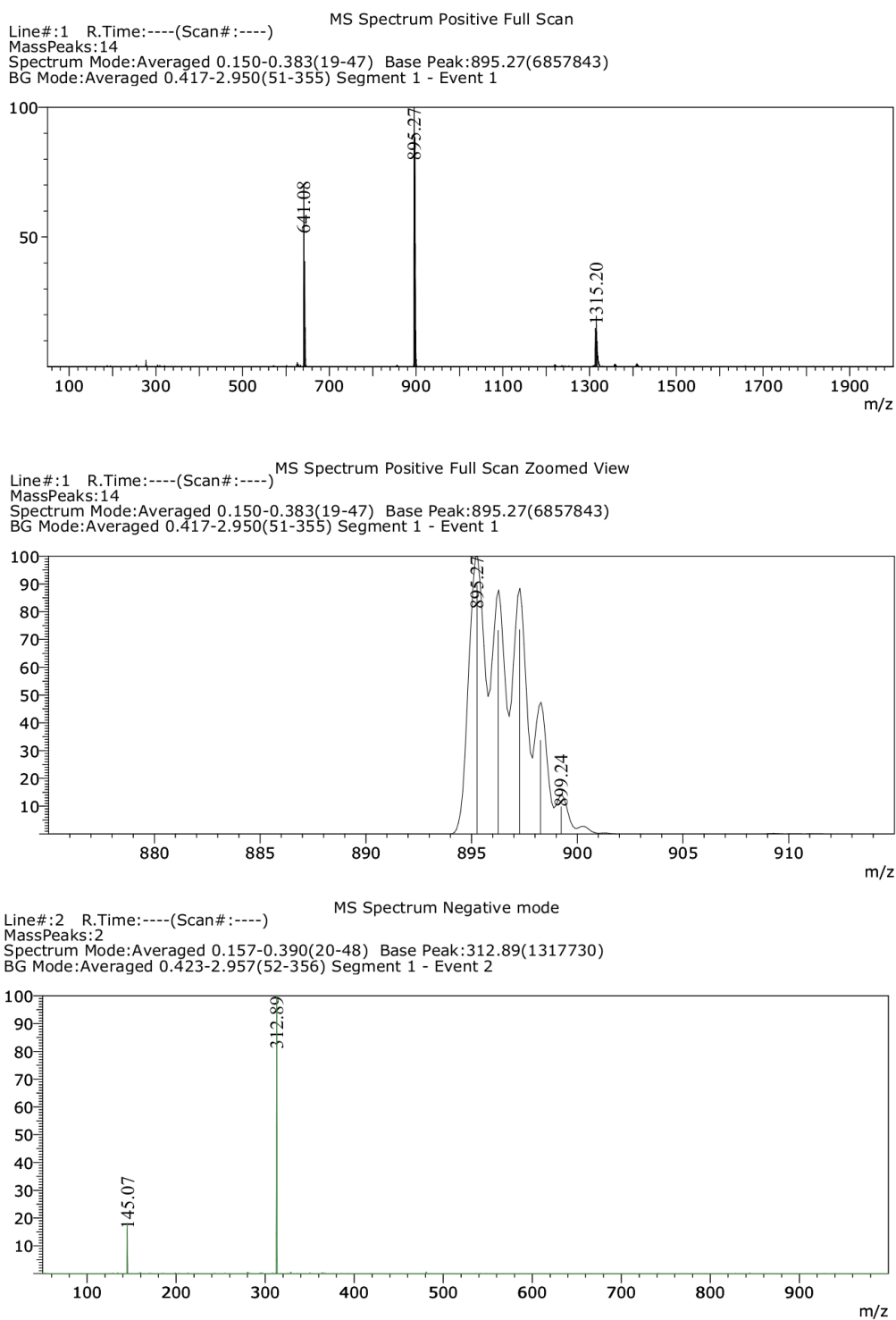


Fig. S77 FTIR spectrum of $[\text{Cu}(\text{POP})(3\text{-EtPentbpy})][\text{PF}_6]$.

Fig. S78 ESI mass spectrum (positive and negative mode) of [Cu(xantphos)(3-EtPentbpy)][PF₆].

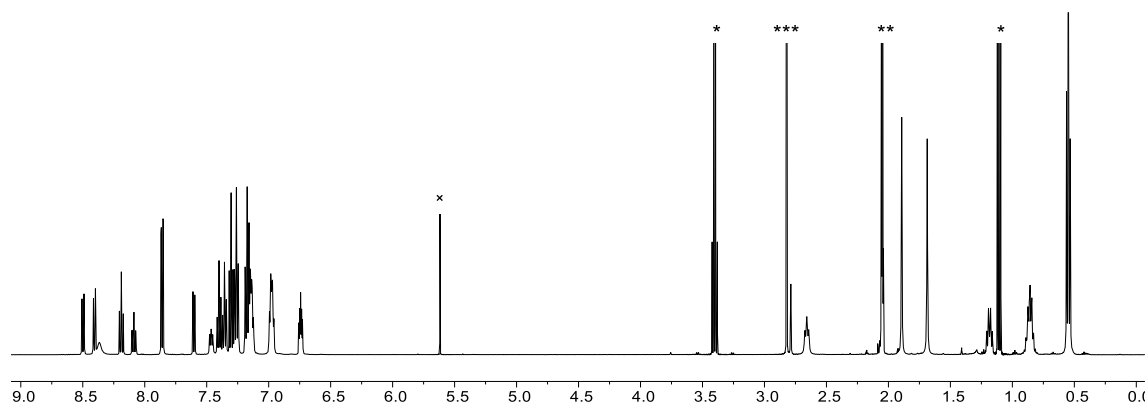


Fig. S79 ^1H NMR spectrum (500 MHz, acetone- d_6 , 298 K, δ/ppm) of $[\text{Cu}(\text{xantphos})(3\text{-EtPentbpy})][\text{PF}_6]$. * = Et_2O ; ** = residual acetone- d_5 ; *** = H_2O and HDO ; x = CH_2Cl_2 .

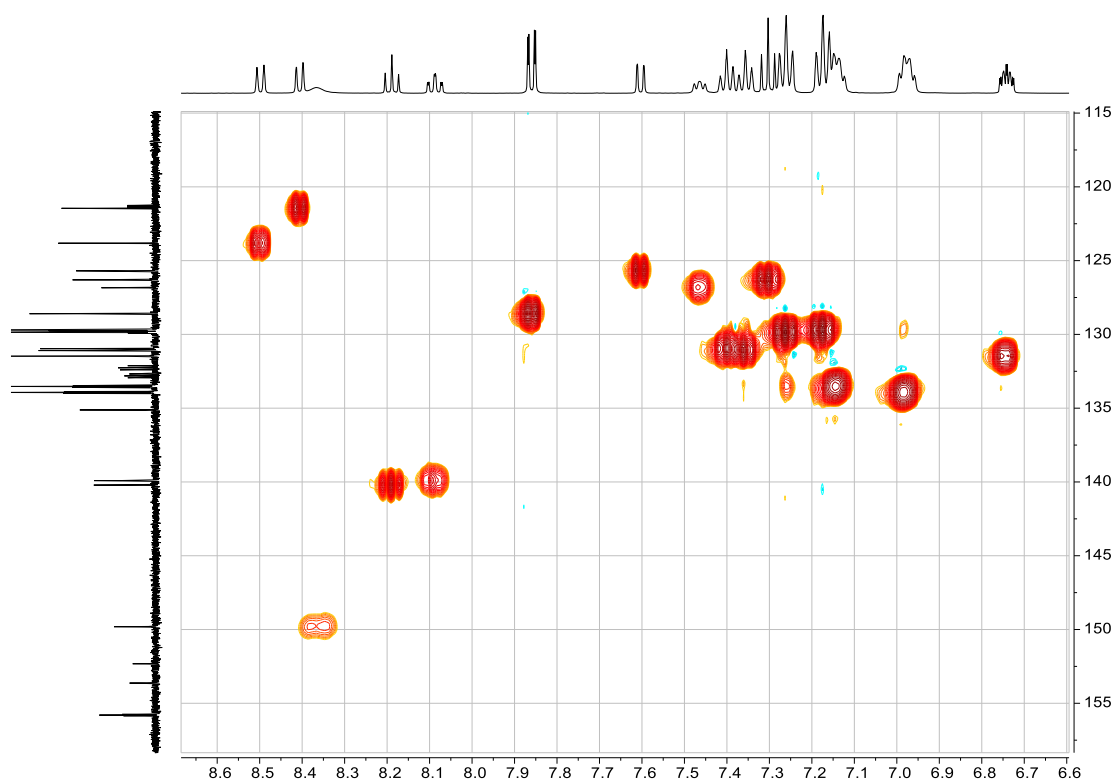


Fig. S80 The aromatic region of the HMQC spectrum (500 MHz ^1H , 126 MHz ^{13}C , acetone- d_6 , 298 K, δ/ppm) of $[\text{Cu}(\text{xantphos})(3\text{-EtPentbpy})][\text{PF}_6]$.

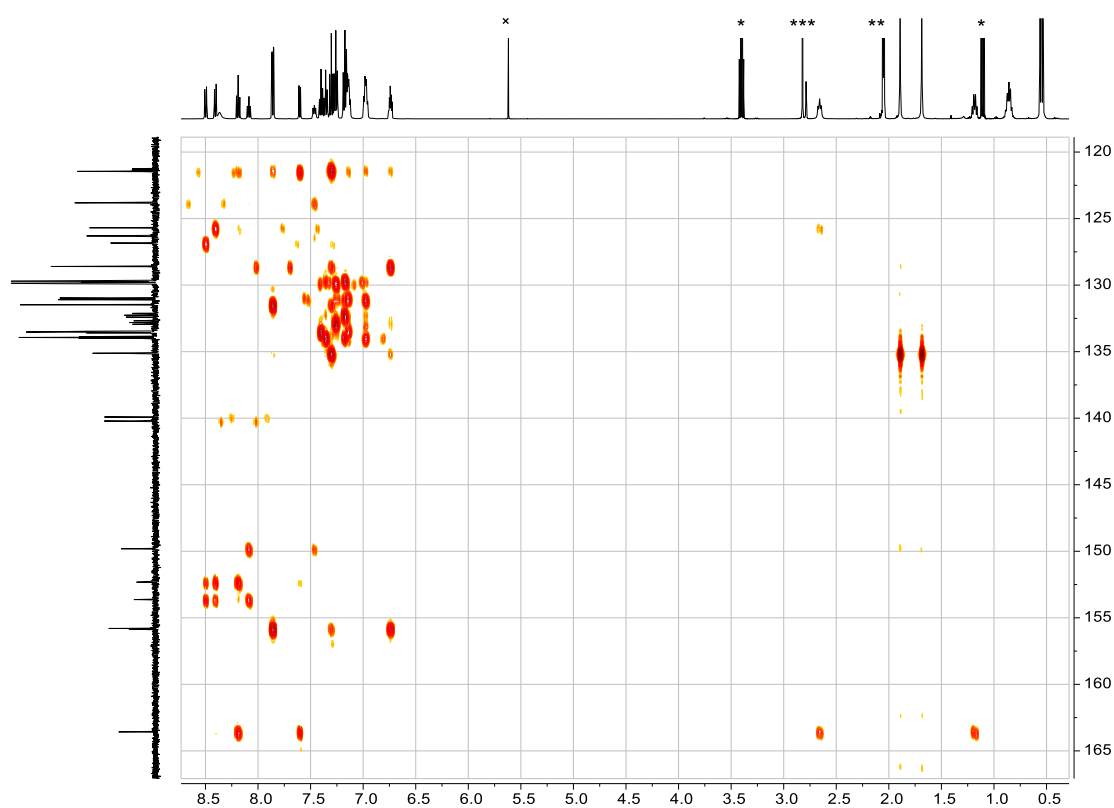


Fig. S81 Part of the HMBC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K, δ/ppm) of $[\text{Cu}(\text{xantphos})(3\text{-EtPentbpy})][\text{PF}_6]$. * = Et_2O ; ** = residual acetone- d_5 ; *** = H_2O and HDO ; * = CH_2Cl_2 .

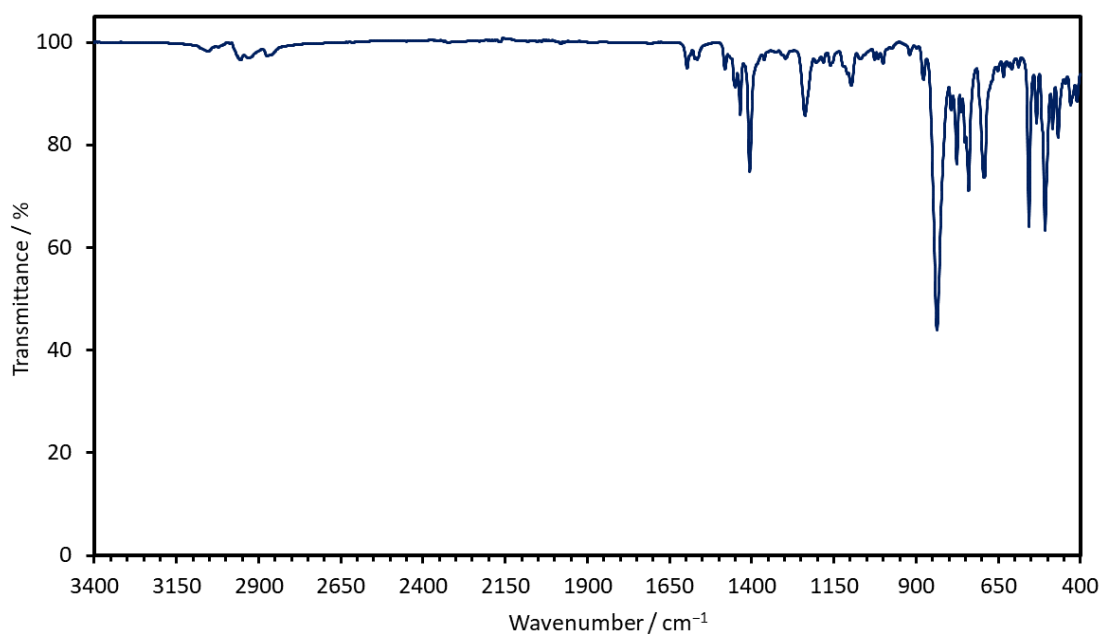
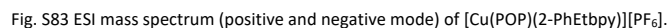


Fig. S82 FTIR spectrum of $[\text{Cu}(\text{xantphos})(3\text{-EtPentbpy})][\text{PF}_6]$.



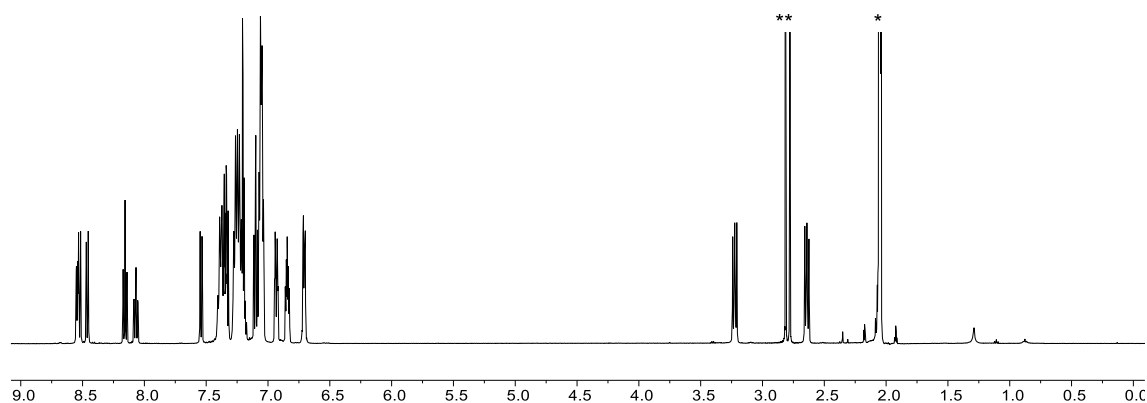


Fig. S84 ^1H NMR spectrum (500 MHz, acetone- d_6 , 298 K, δ/ppm) of $[\text{Cu}(\text{POP})(2\text{-PhEtbpv})][\text{PF}_6]$. * = residual acetone- d_5 ; ** = H_2O and HDO.

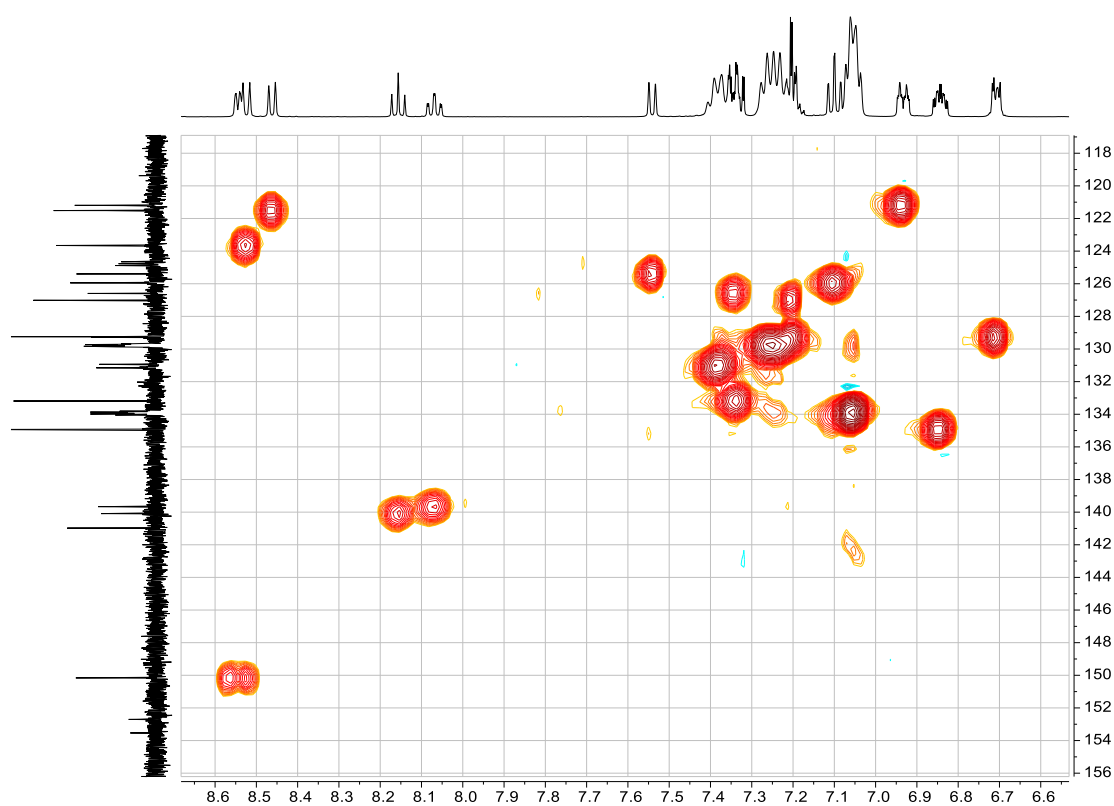


Fig. S85 The aromatic region of the HMQC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K, δ/ppm) of $[\text{Cu}(\text{POP})(2\text{-PhEtbpv})][\text{PF}_6]$.

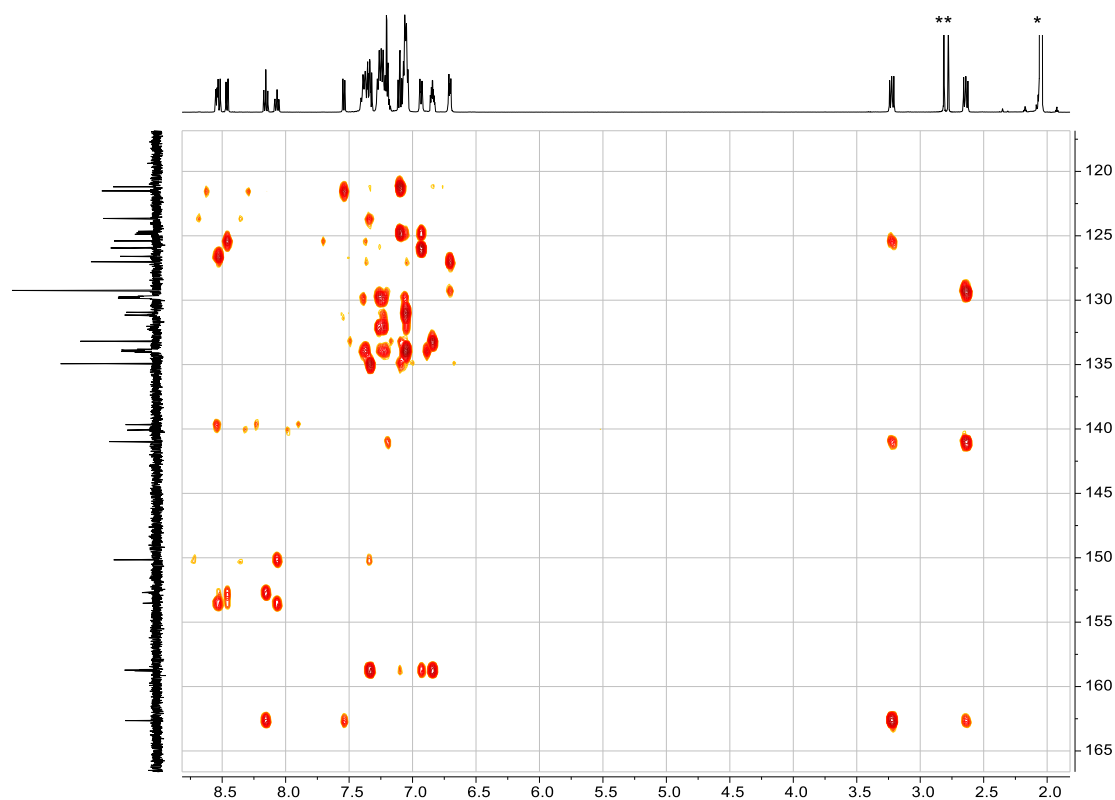


Fig. S86 Part of the HMBC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K, δ/ppm) of $[\text{Cu}(\text{POP})(2\text{-PhEtbp})][\text{PF}_6]_3$. * = residual acetone- d_5 ; ** = H_2O and HDO .

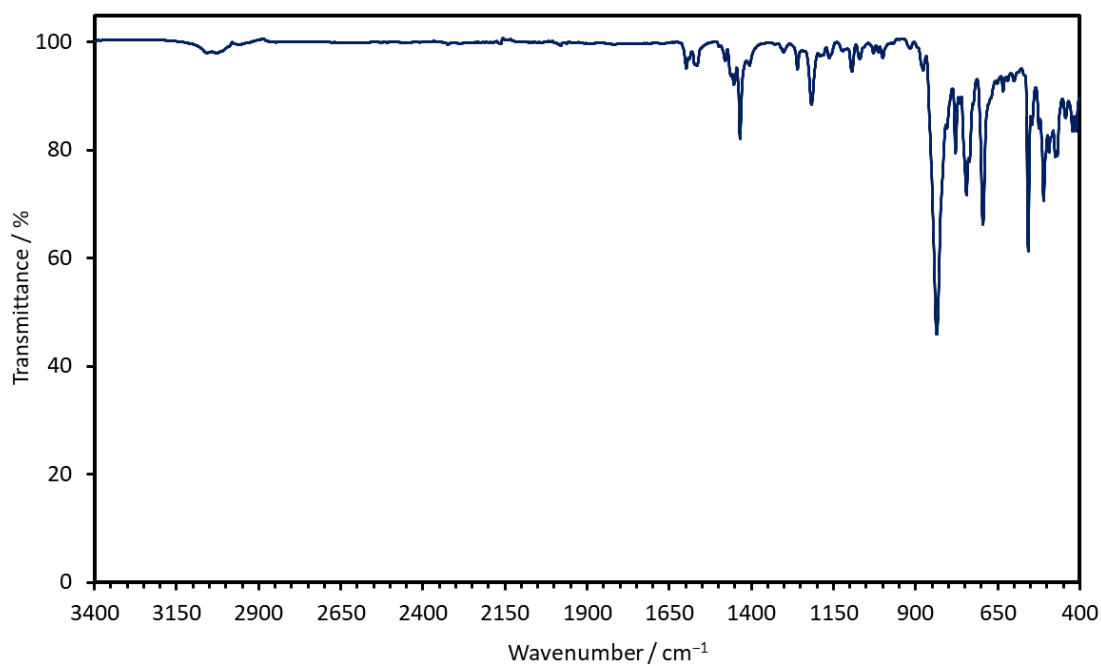
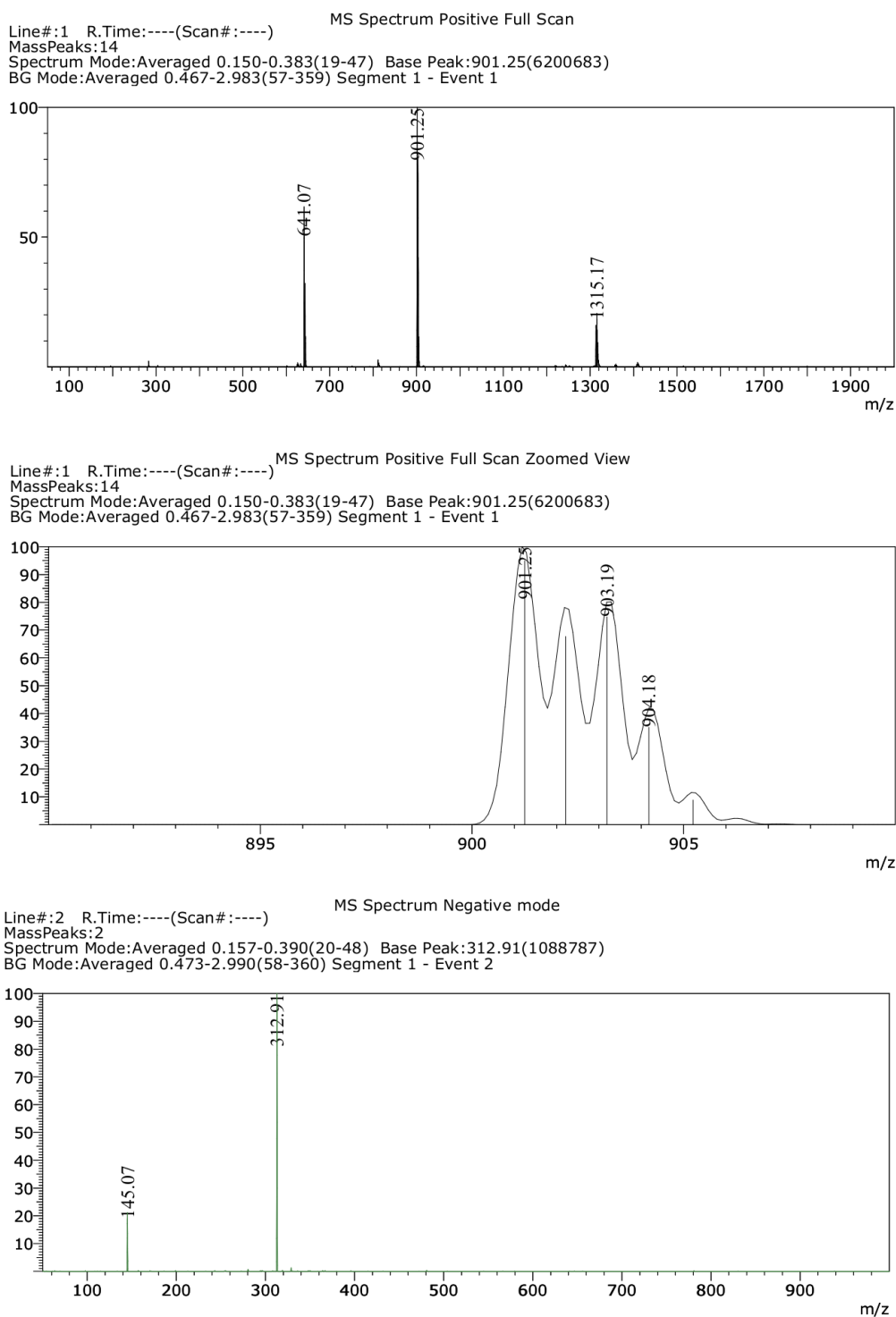


Fig. S87 FTIR spectrum of $[\text{Cu}(\text{POP})(2\text{-PhEtbp})][\text{PF}_6]_3$.

Fig. S88 ESI mass spectrum (positive and negative mode) of [Cu(xantphos)(2-PhEtbpv)][PF₆].

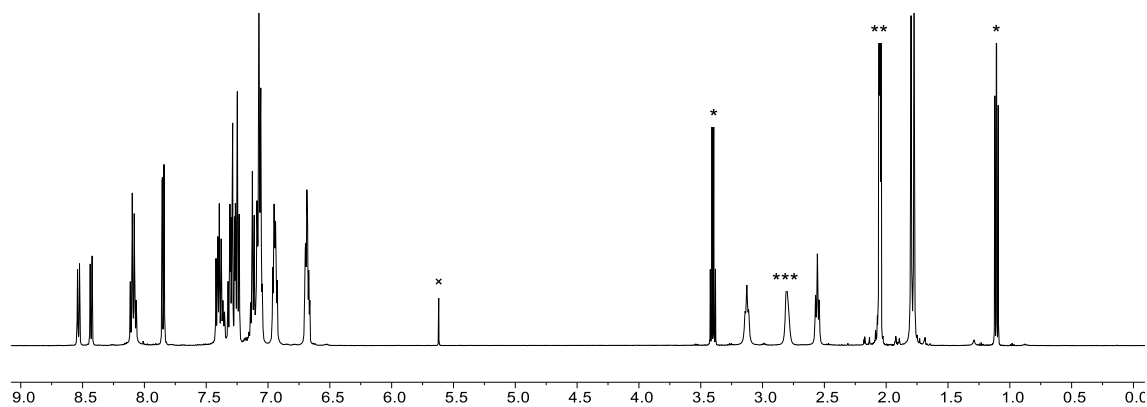


Fig. S89 ^1H NMR spectrum (500 MHz, acetone- d_6 , 298 K, δ/ppm) of $[\text{Cu}(\text{xantphos})(2\text{-PhEtbp})][\text{PF}_6]$. * = Et_2O ; ** = residual acetone- d_5 ; *** = H_2O and HDO ; x = CH_2Cl_2 .

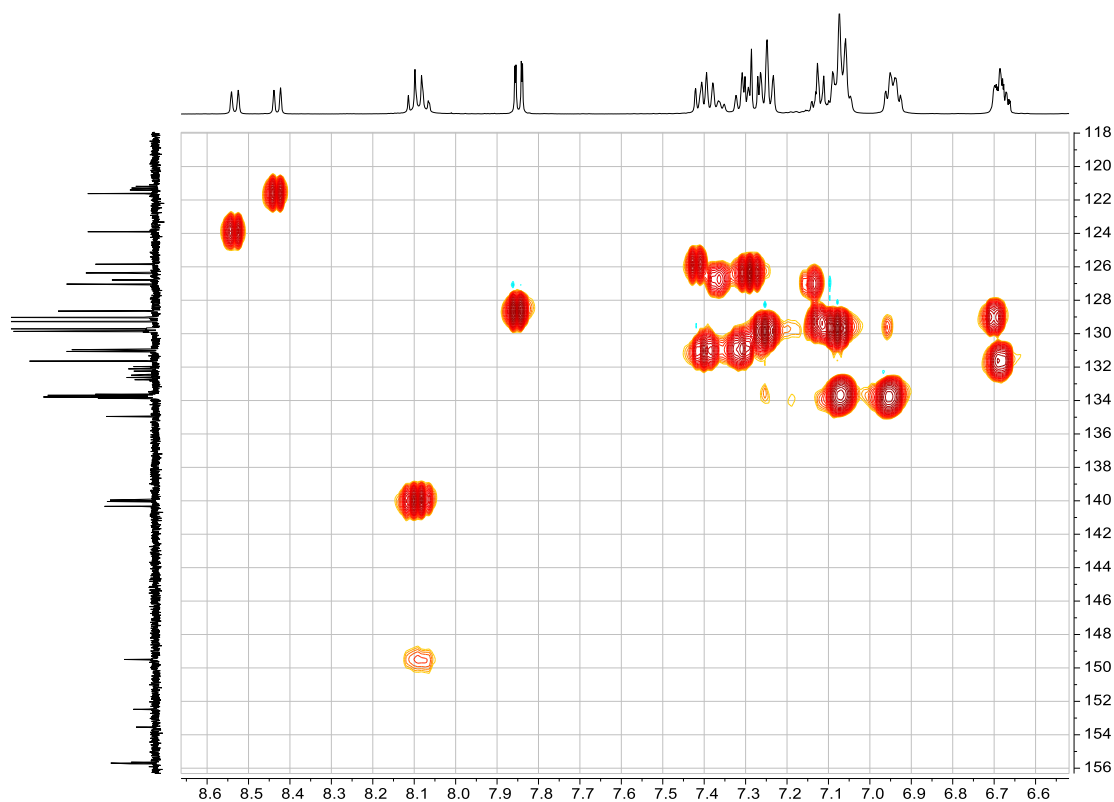


Fig. S90 The aromatic region of the HMQC spectrum (500 MHz ^1H , 126 MHz ^{13}C , acetone- d_6 , 298 K, δ/ppm) of $[\text{Cu}(\text{xantphos})(2\text{-PhEtbp})][\text{PF}_6]$.

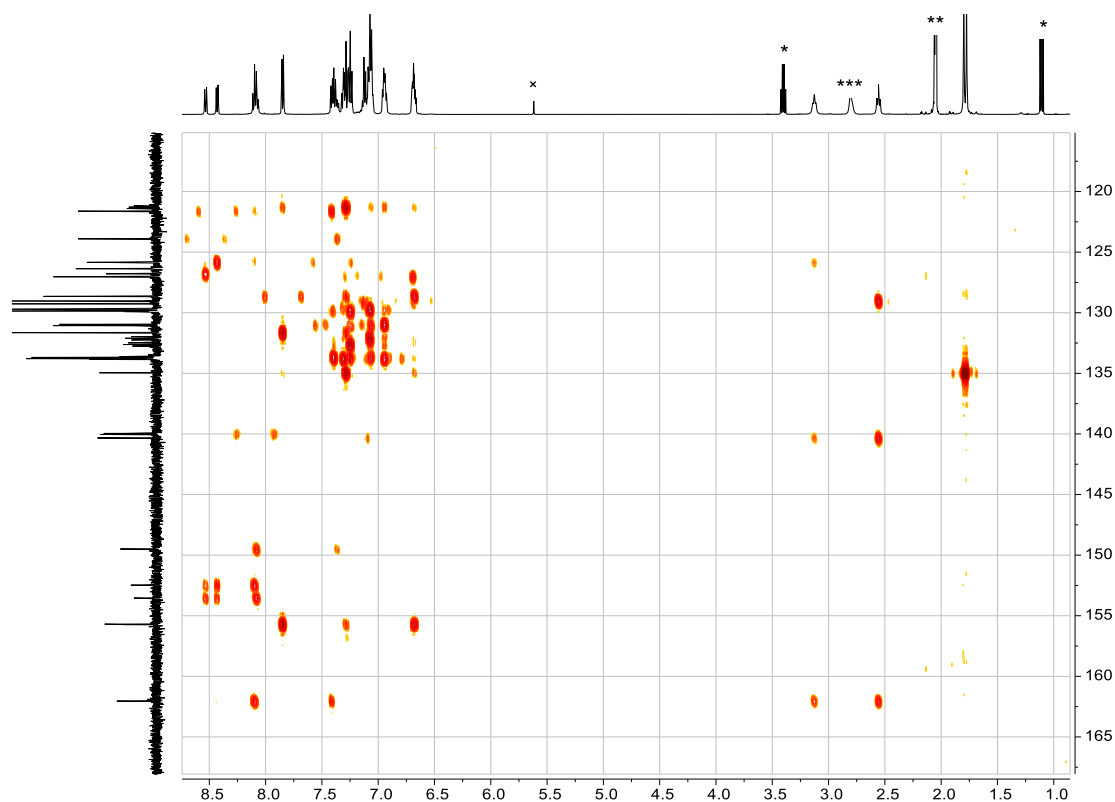


Fig. S91 Part of the HMBC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K, δ/ppm) of $[\text{Cu}(\text{xantphos})(2\text{-PhEtbp})][\text{PF}_6]$. * = Et_2O ; ** = residual acetone- d_5 ; *** = H_2O and HDO ; x = CH_2Cl_2 .

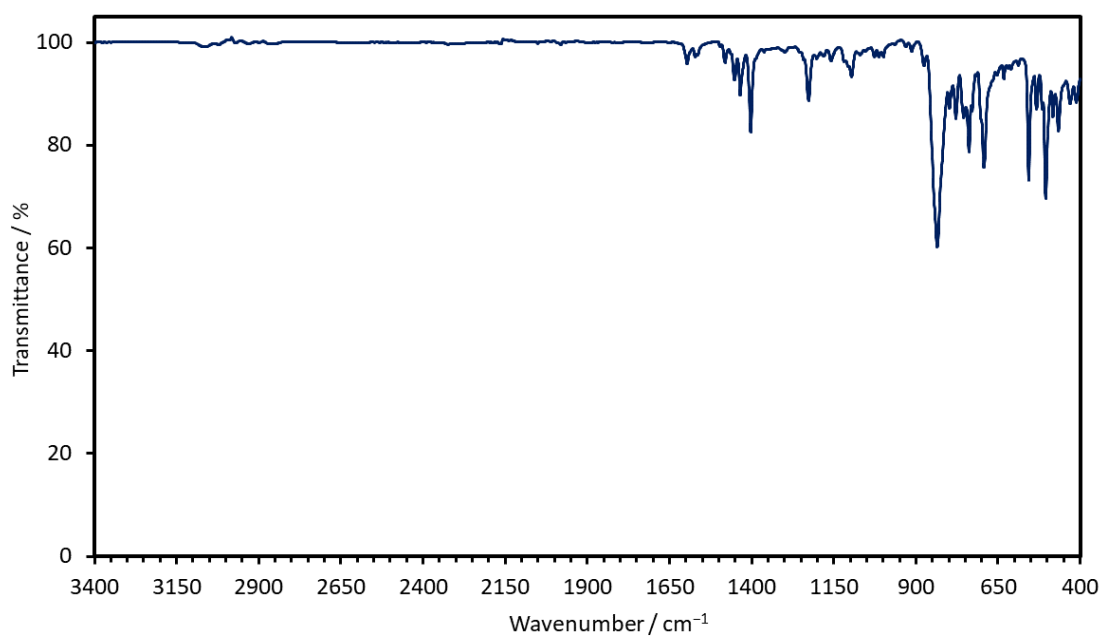


Fig. S92 FTIR spectrum of $[\text{Cu}(\text{xantphos})(2\text{-PhEtbp})][\text{PF}_6]$.

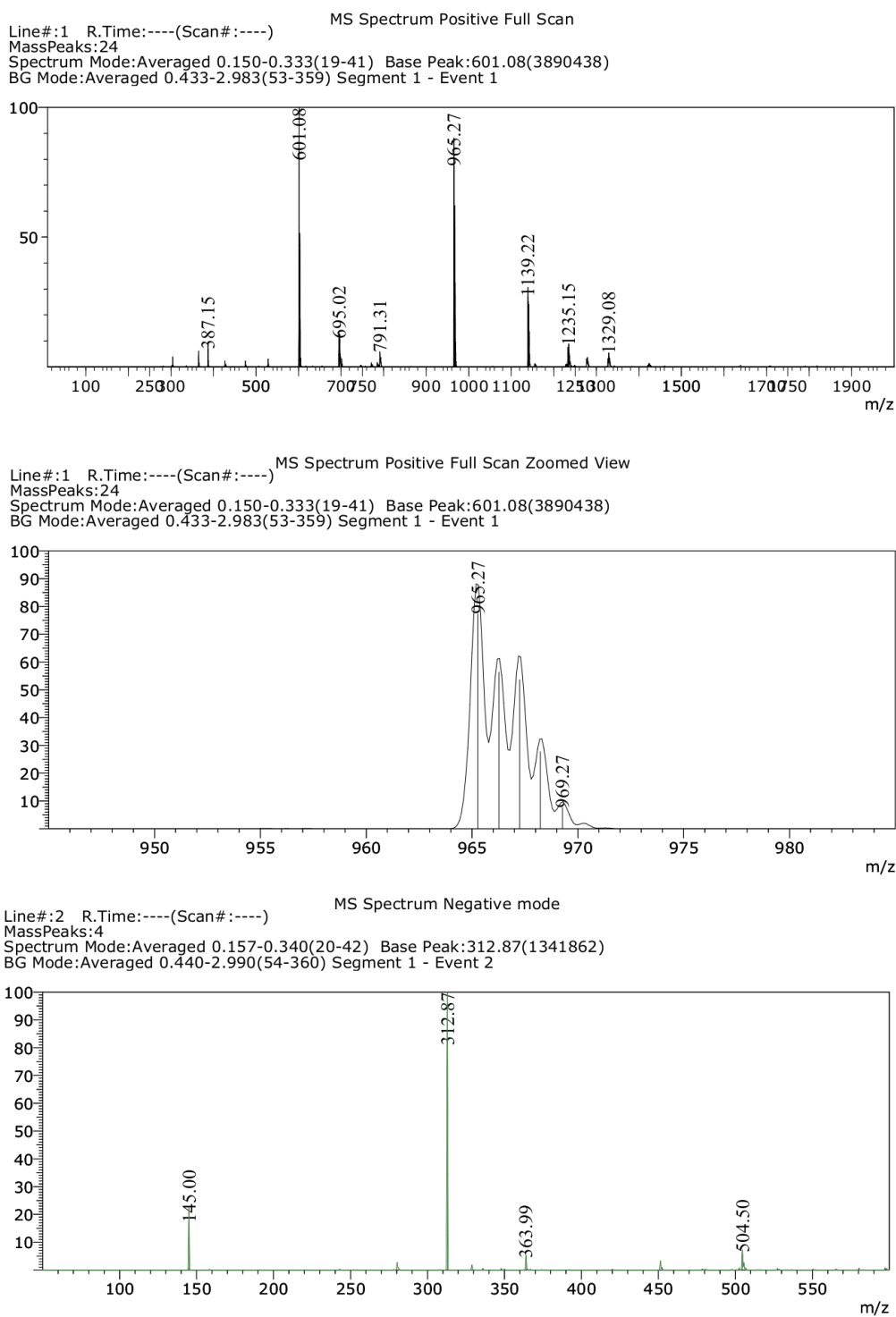


Fig. S93 ESI mass spectrum (positive and negative mode) of $[\text{Cu}(\text{POP})((2\text{-PhEt})_2\text{bpy})][\text{PF}_6]$.

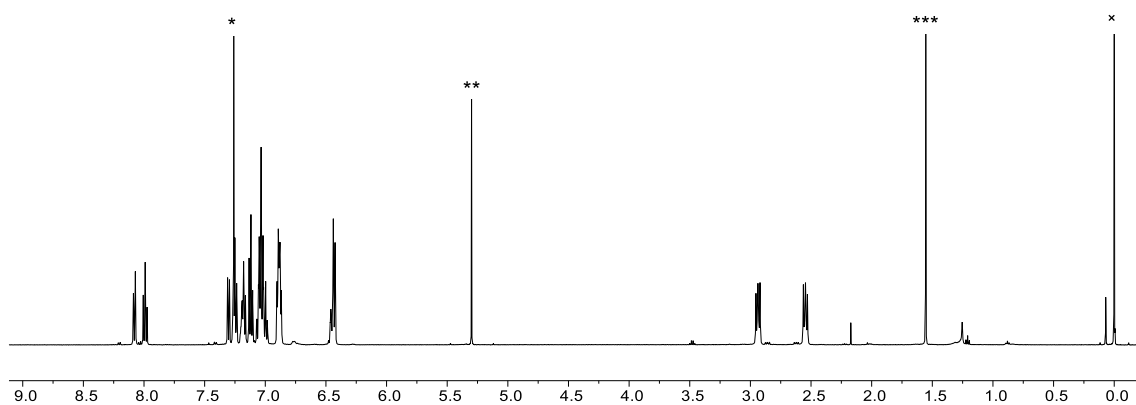


Fig. S94 ^1H NMR spectrum (500 MHz, CDCl_3 , 298 K, δ/ppm) of $[\text{Cu}(\text{POP})((2\text{-PhEt})_2\text{bpy})][\text{PF}_6]$. * = residual CHCl_3 ; ** = CH_2Cl_2 ; *** = H_2O ; x = TMS.

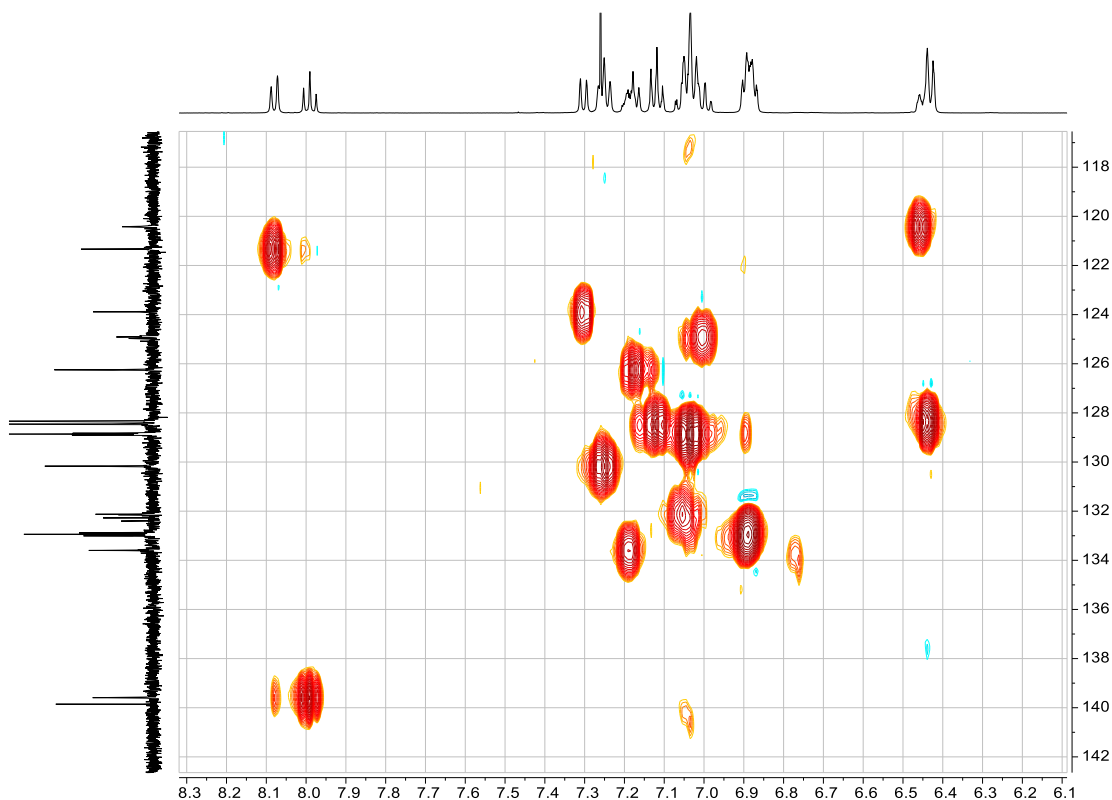


Fig. S95 The aromatic region of the HMQC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, CDCl_3 , 298 K, δ/ppm) of $[\text{Cu}(\text{POP})((2\text{-PhEt})_2\text{bpy})][\text{PF}_6]$.

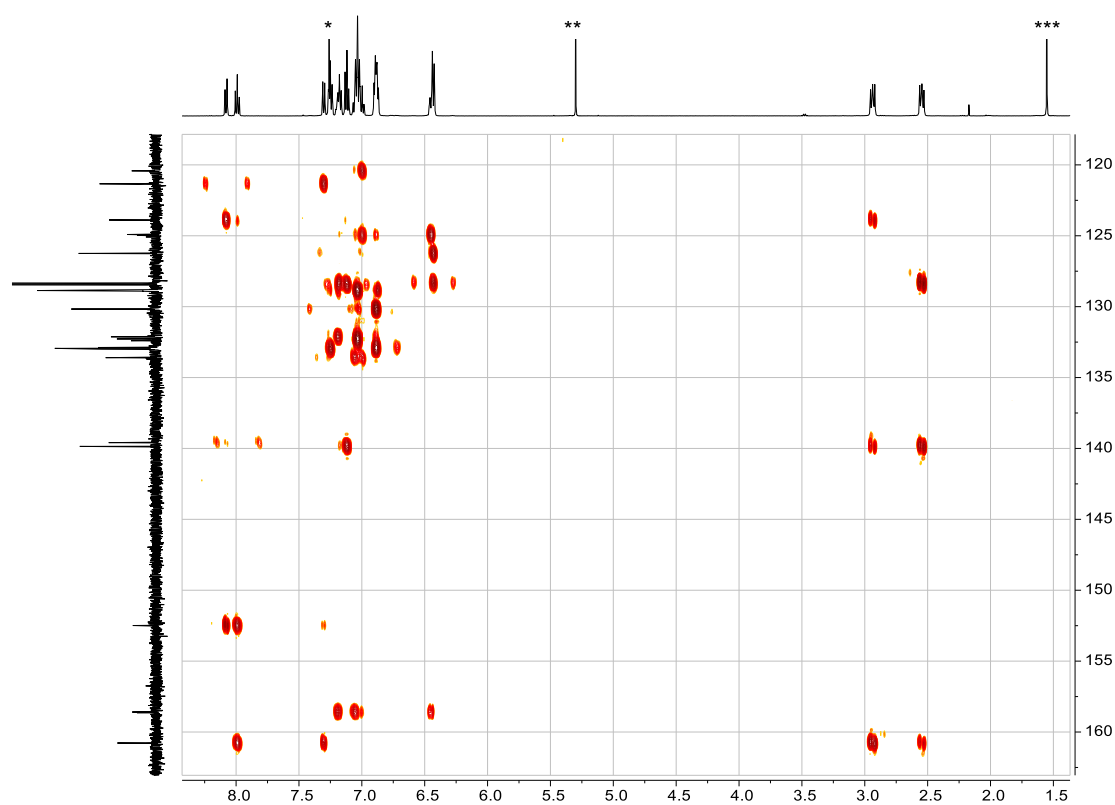


Fig. S96 Part of the HMBC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, CDCl_3 , 298 K, δ/ppm) of $[\text{Cu}(\text{POP})((2\text{-PhEt})_2\text{bpy})][\text{PF}_6]$. * = residual CHCl_3 ; ** = CH_2Cl_2 ; *** = H_2O .

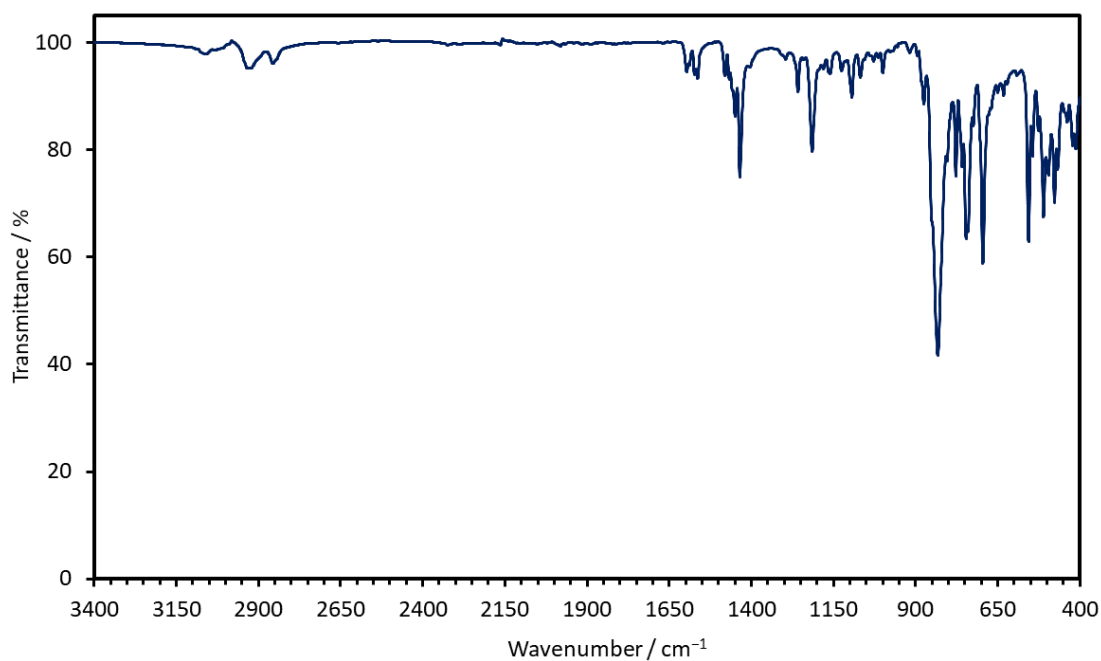


Fig. S97 FTIR spectrum of $[\text{Cu}(\text{POP})((2\text{-PhEt})_2\text{bpy})][\text{PF}_6]$.

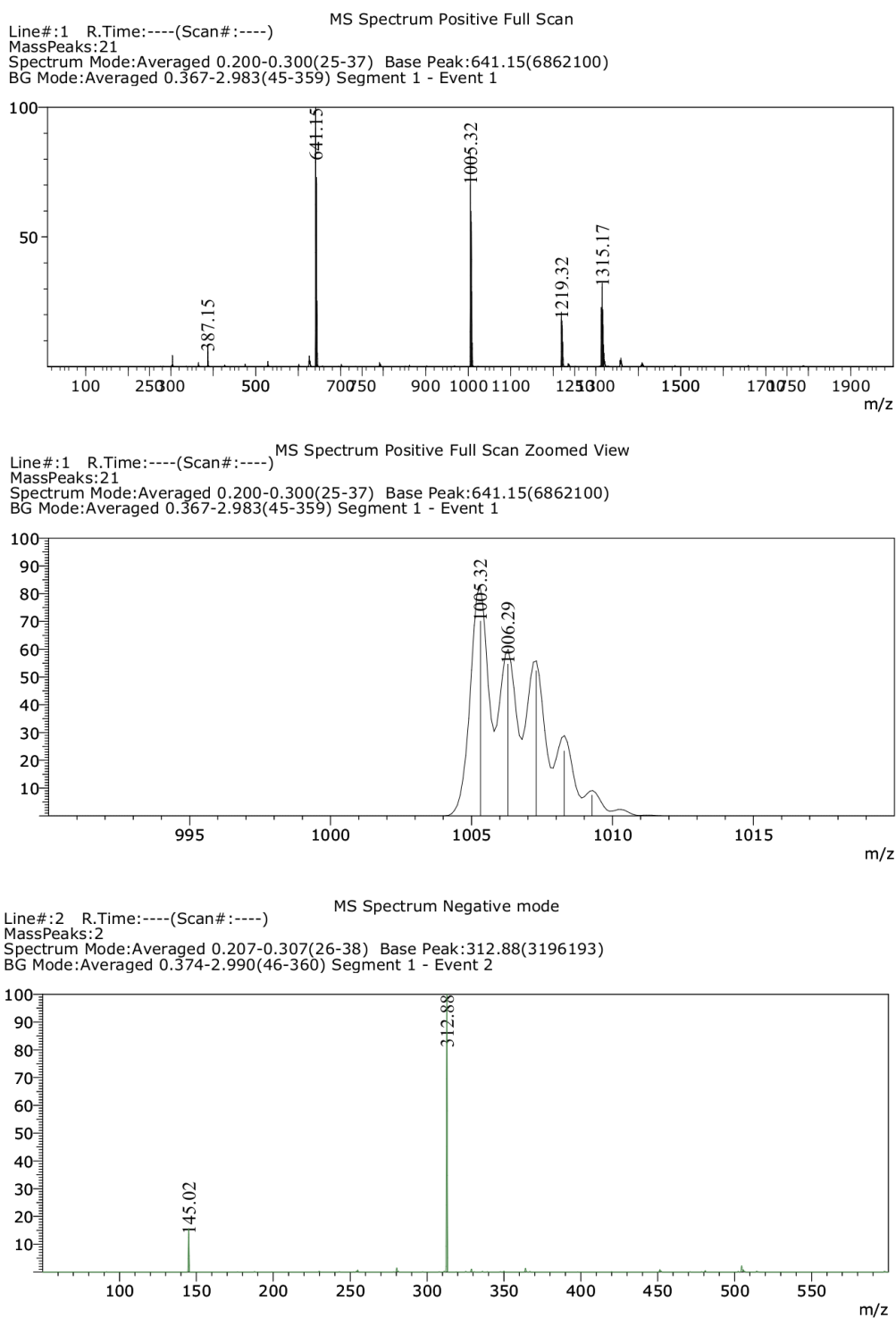


Fig. S98 ESI mass spectrum (positive and negative mode) of $[\text{Cu}(\text{xantphos})((2\text{-PhEt})_2\text{bpy})][\text{PF}_6]$.

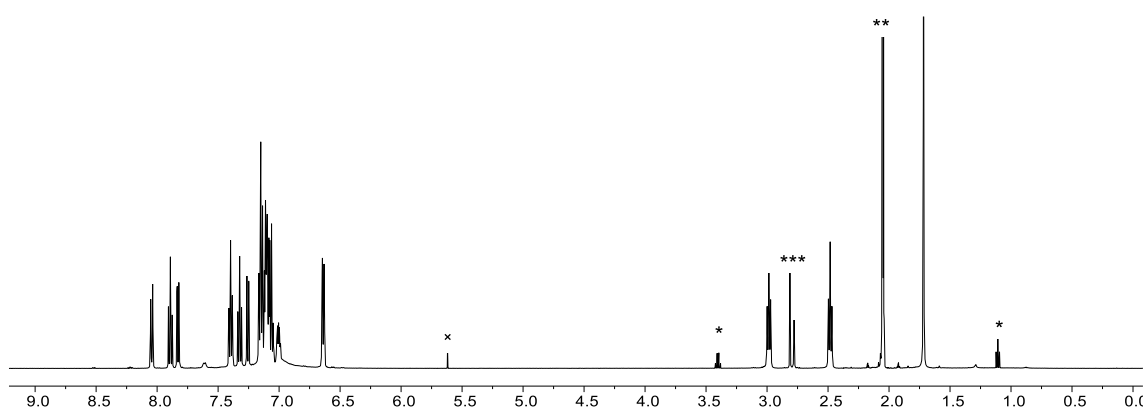


Fig. S99 ^1H NMR spectrum (500 MHz, acetone- d_6 , 298 K, δ/ppm) of $[\text{Cu}(\text{xantphos})((2\text{-PhEt})_2\text{bpy})](\text{PF}_6)$. * = Et_2O ; ** = residual acetone- d_5 ; *** = H_2O and HDO ; x = CH_2Cl_2 .

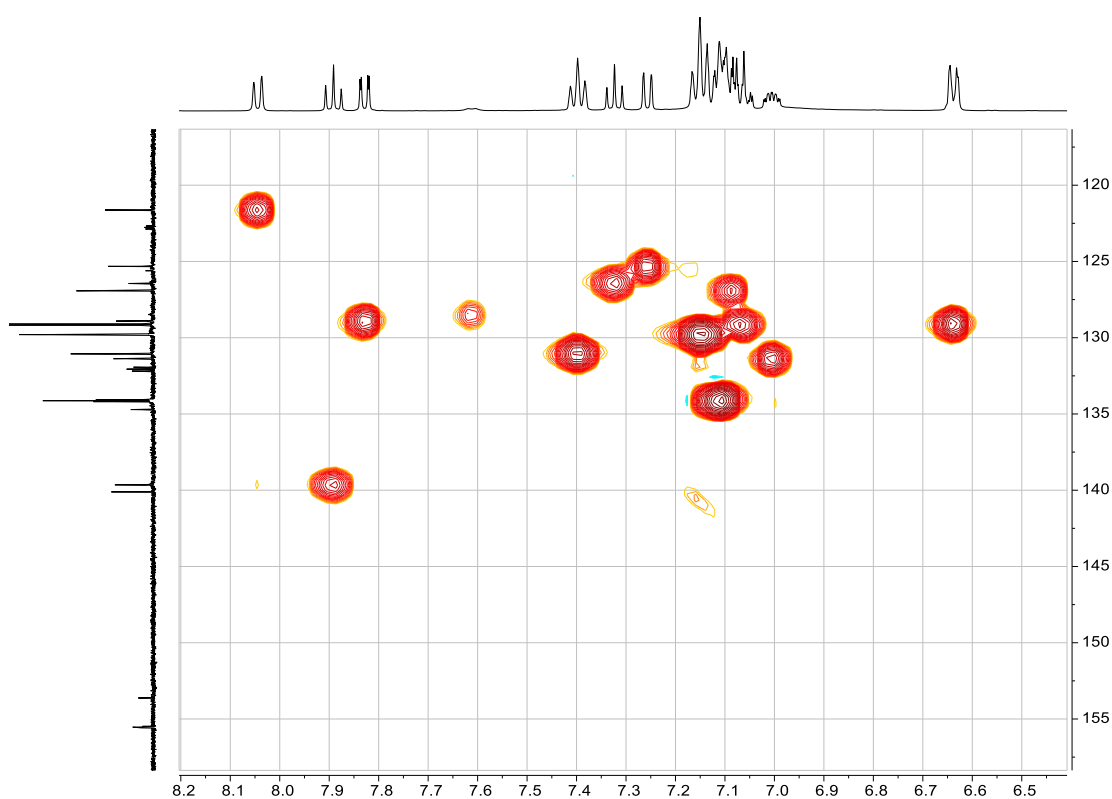


Fig. S100 The aromatic region of the HMQC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K, δ/ppm) of $[\text{Cu}(\text{xantphos})((2\text{-PhEt})_2\text{bpy})](\text{PF}_6)$.

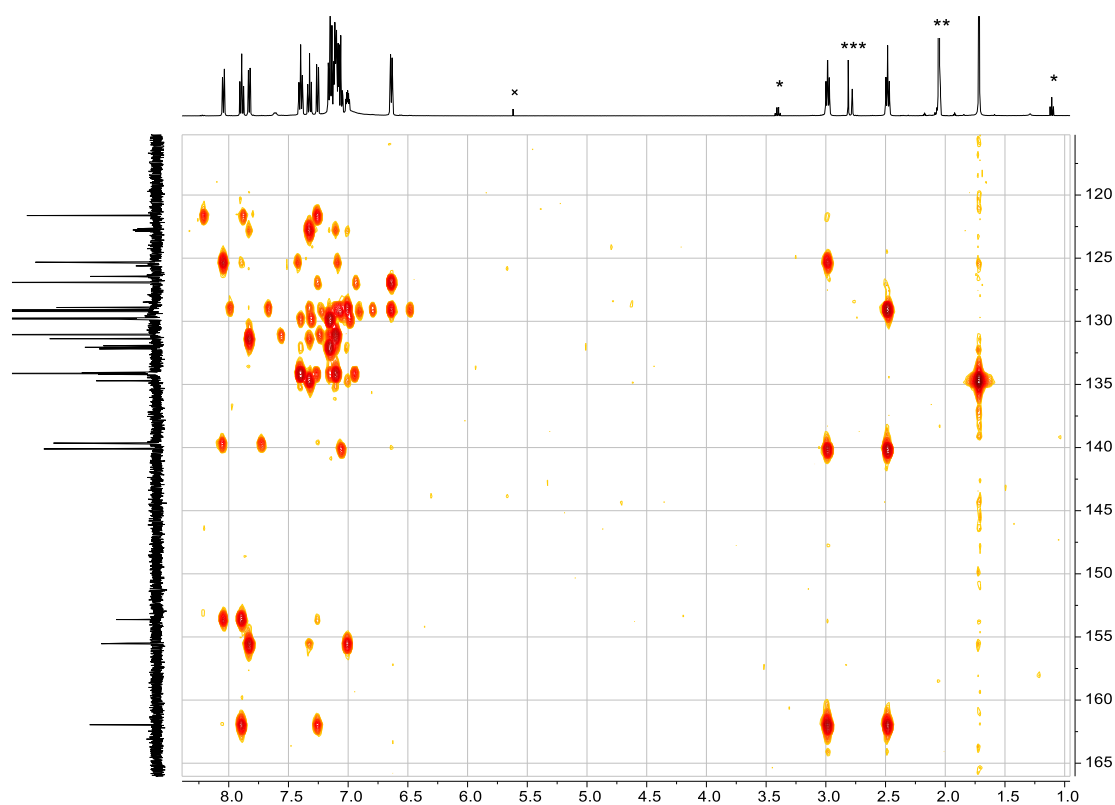


Fig. S101 Part of the HMBC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K, δ/ppm) of $[\text{Cu}(\text{xantphos})((2\text{-PhEt})_2\text{bpy})][\text{PF}_6]$. * = Et_2O ; ** = residual acetone- d_5 ; *** = H_2O and HDO ; x = CH_2Cl_2 .

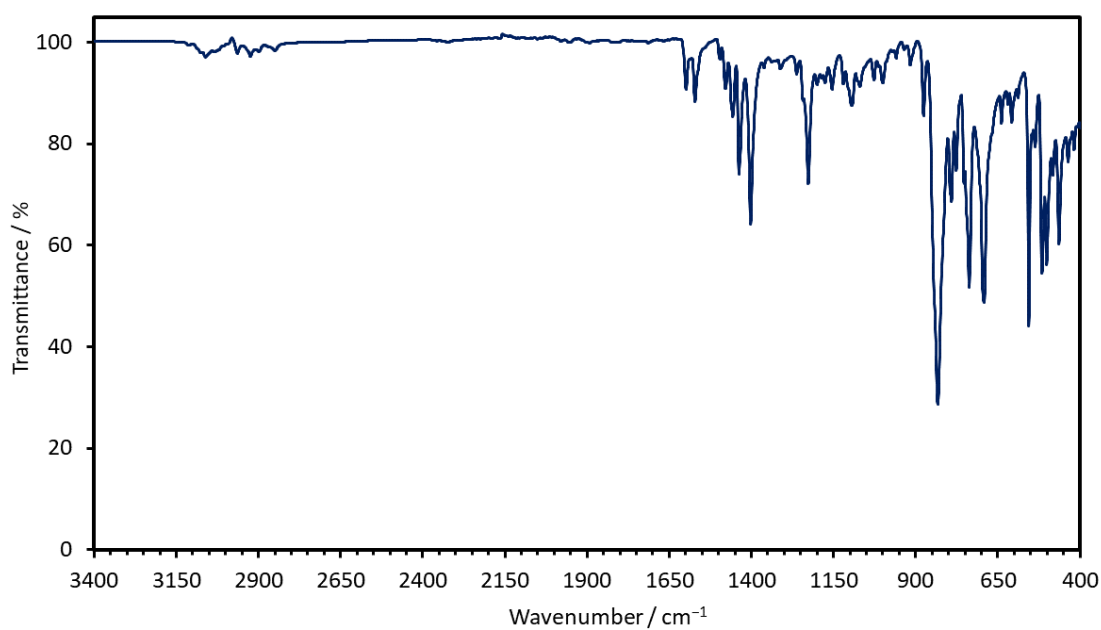


Fig. S102 FTIR spectrum of $[\text{Cu}(\text{xantphos})((2\text{-PhEt})_2\text{bpy})][\text{PF}_6]$.

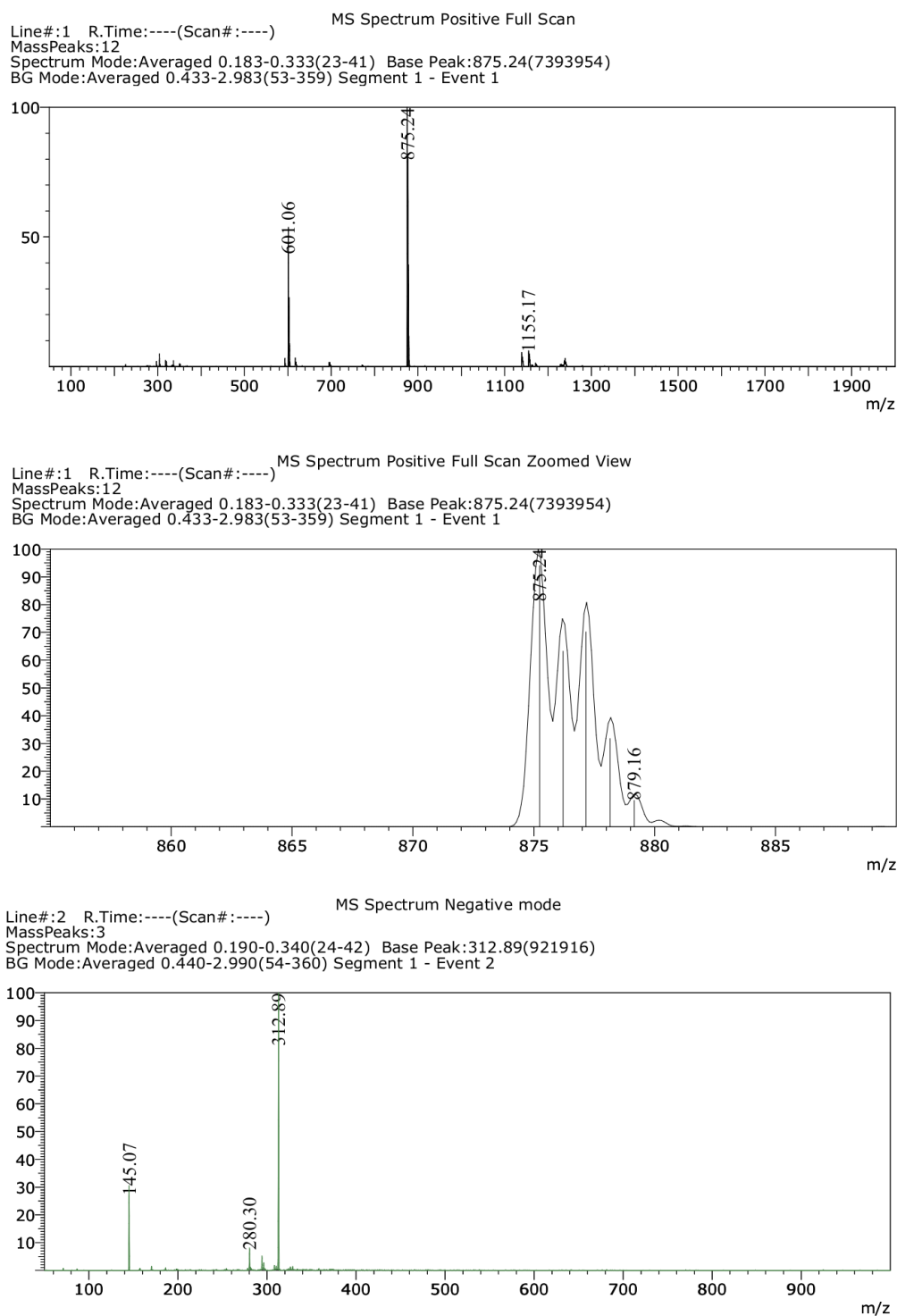


Fig. S103 ESI mass spectrum (positive and negative mode) of $[\text{Cu}(\text{POP})(3\text{-PhPrbpy})][\text{PF}_6]$.

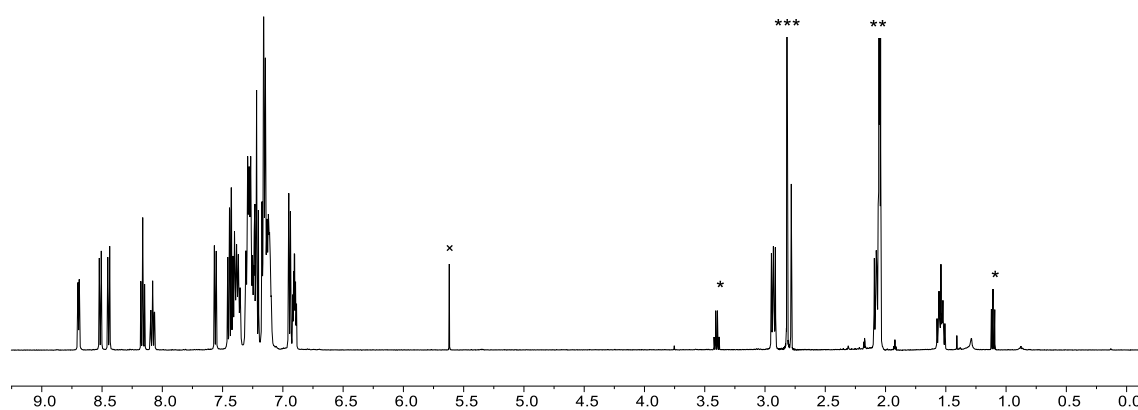


Fig. S104 ^1H NMR spectrum (500 MHz, acetone- d_6 , 298 K, δ/ppm) of $[\text{Cu}(\text{POP})(3\text{-PhPrbpy})][\text{PF}_6]$. * = Et_2O ; ** = residual acetone- d_5 ; *** = H_2O and HDO ; x = CH_2Cl_2 .

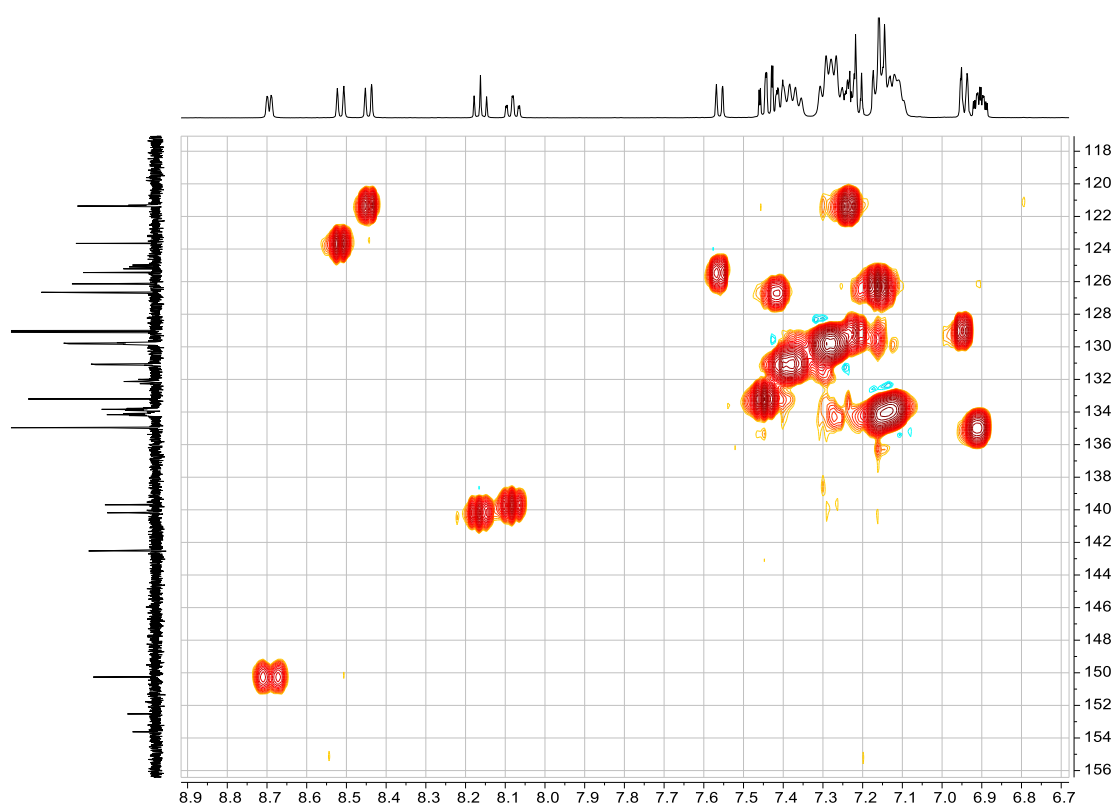


Fig. S105 The aromatic region of the HMQC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K, δ/ppm) of $[\text{Cu}(\text{POP})(3\text{-PhPrbpy})][\text{PF}_6]$.

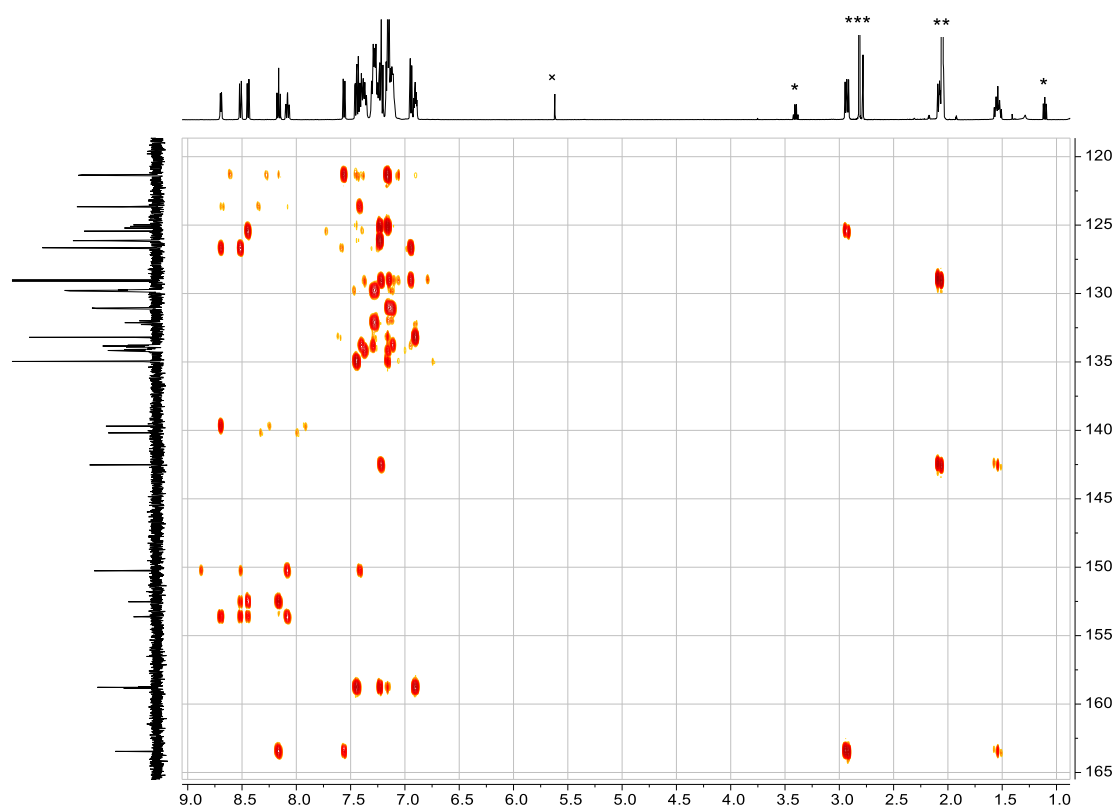


Fig. S106 Part of the HMBC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K, δ/ppm) of $[\text{Cu}(\text{POP})(3\text{-PhPrbpy})][\text{PF}_6]$. * = Et_2O ; ** = residual acetone- d_5 ; *** = H_2O and HDO ; x = CH_2Cl_2 .

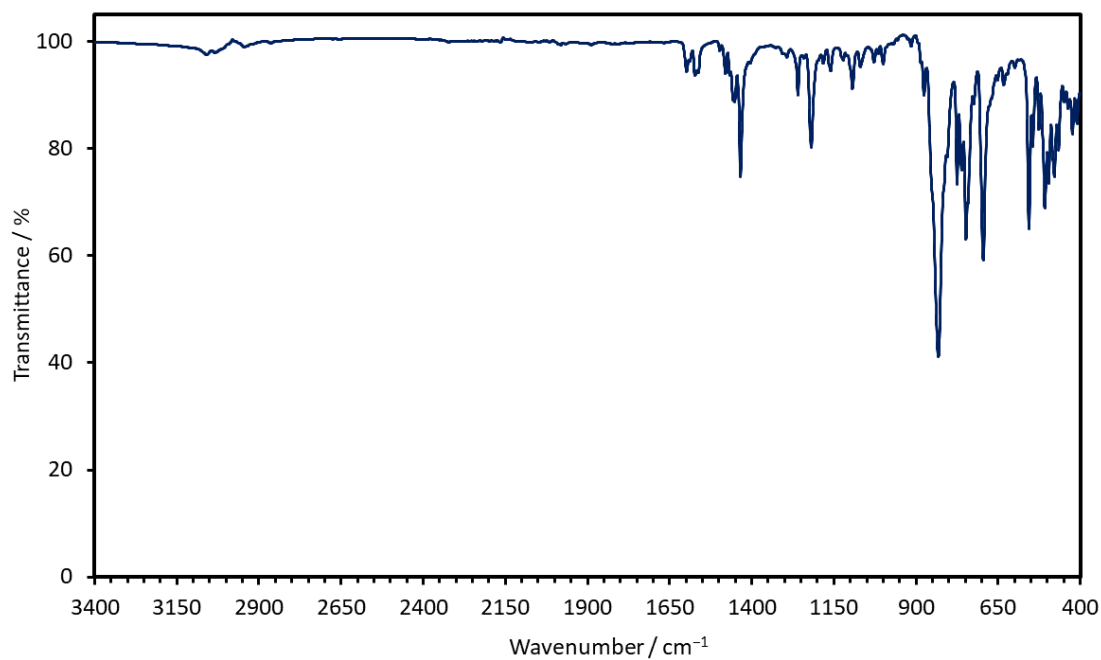


Fig. S107 FTIR spectrum of $[\text{Cu}(\text{POP})(3\text{-PhPrbpy})][\text{PF}_6]$.

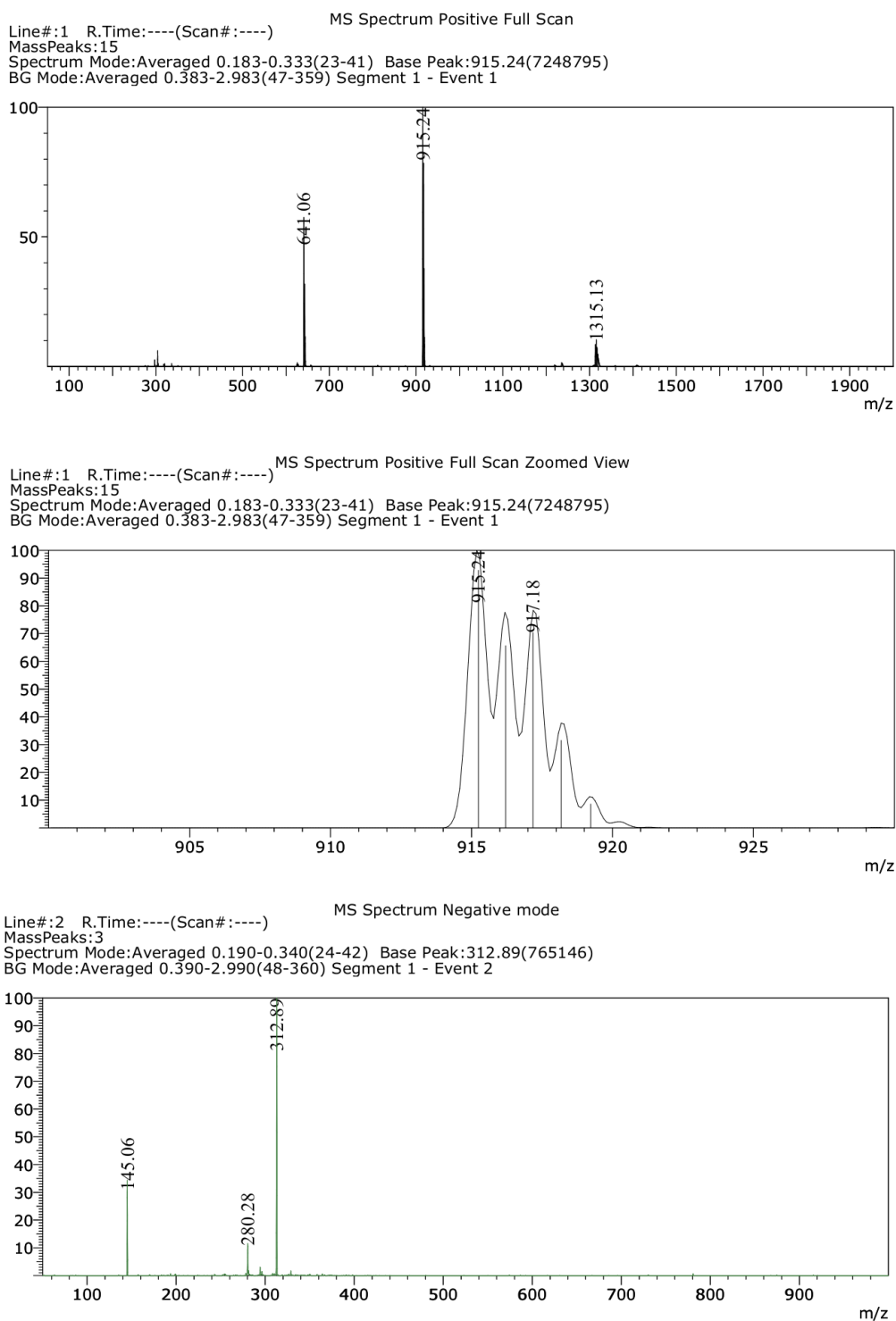


Fig. S108 ESI mass spectrum (positive and negative mode) of $[\text{Cu}(\text{xantphos})(3\text{-PhPrbpy})][\text{PF}_6]$.

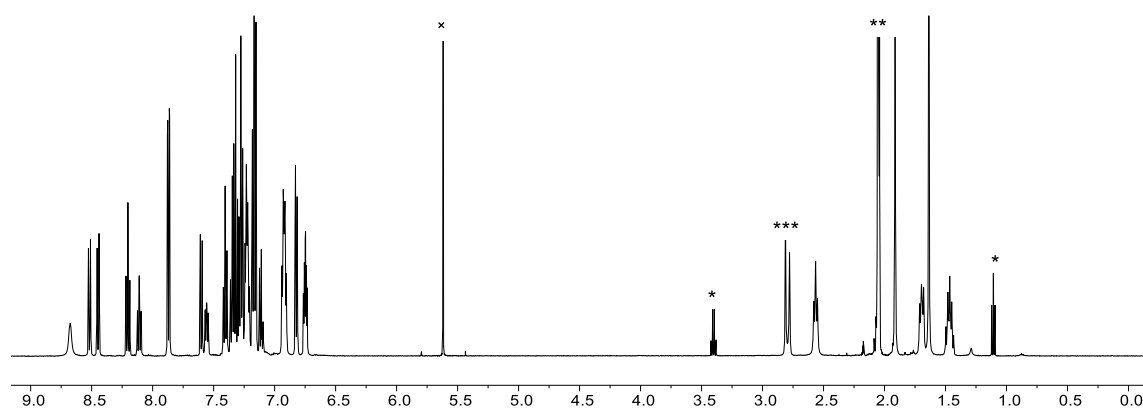


Fig. S109 ^1H NMR spectrum (500 MHz, acetone- d_6 , 298 K, δ/ppm) of $[\text{Cu}(\text{xantphos})(3\text{-PhPrbpy})](\text{PF}_6)$. * = Et_2O ; ** = residual acetone- d_5 ; *** = H_2O and HDO ; x = CH_2Cl_2 .

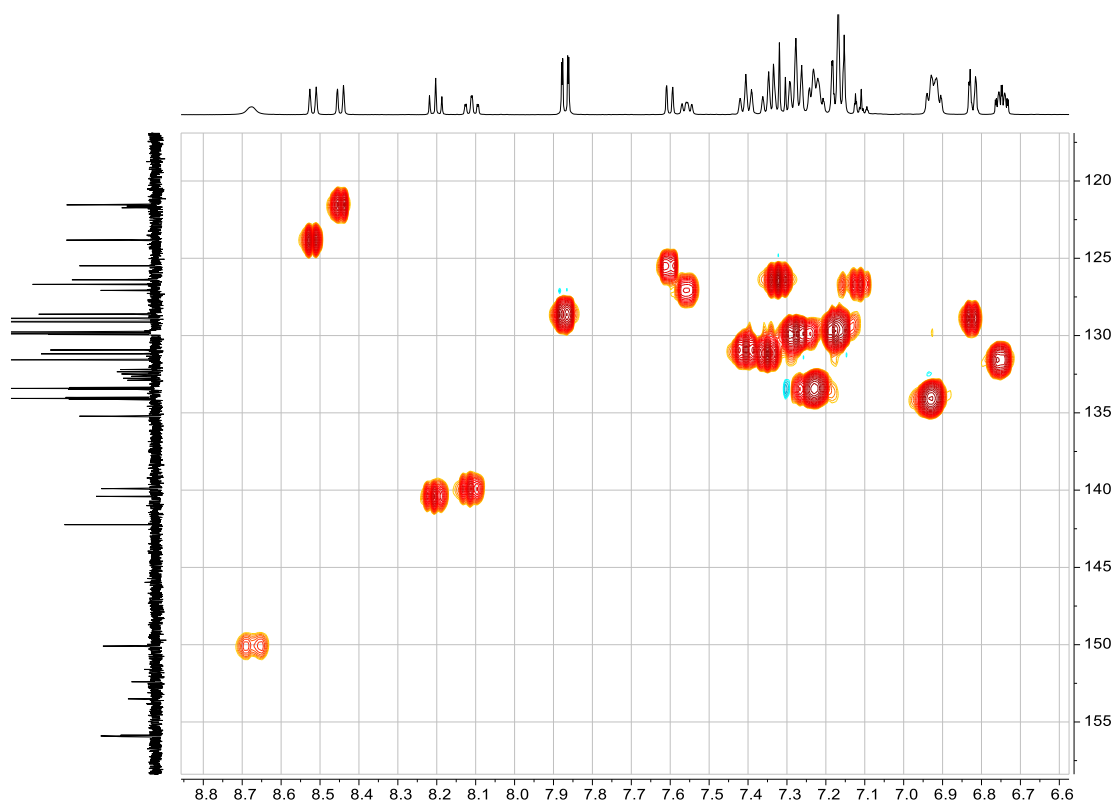


Fig. S110 The aromatic region of the HMQC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K, δ/ppm) of $[\text{Cu}(\text{xantphos})(3\text{-PhPrbpy})](\text{PF}_6)$.

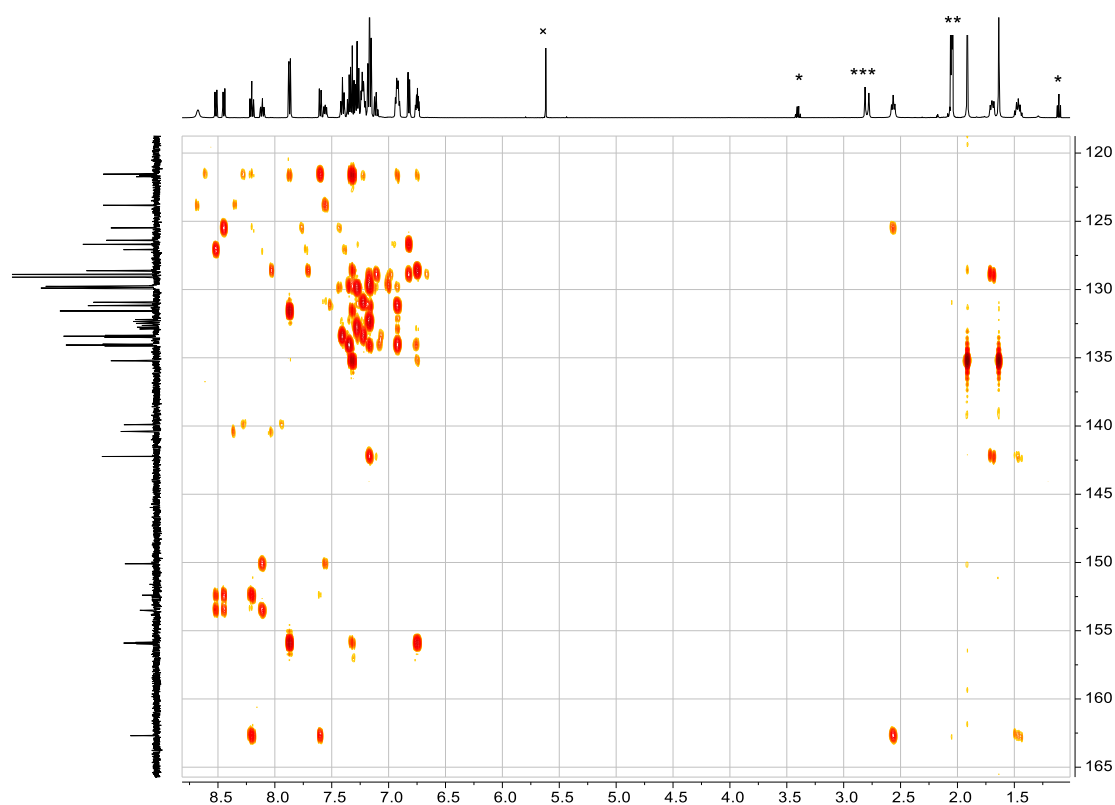


Fig. S111 Part of the HMBC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K, δ/ppm) of $[\text{Cu}(\text{xantphos})(3\text{-PhPrbpy})][\text{PF}_6]$. * = Et_2O ; ** = residual acetone- d_6 ; *** = H_2O and HDO; x = CH_2Cl_2 .

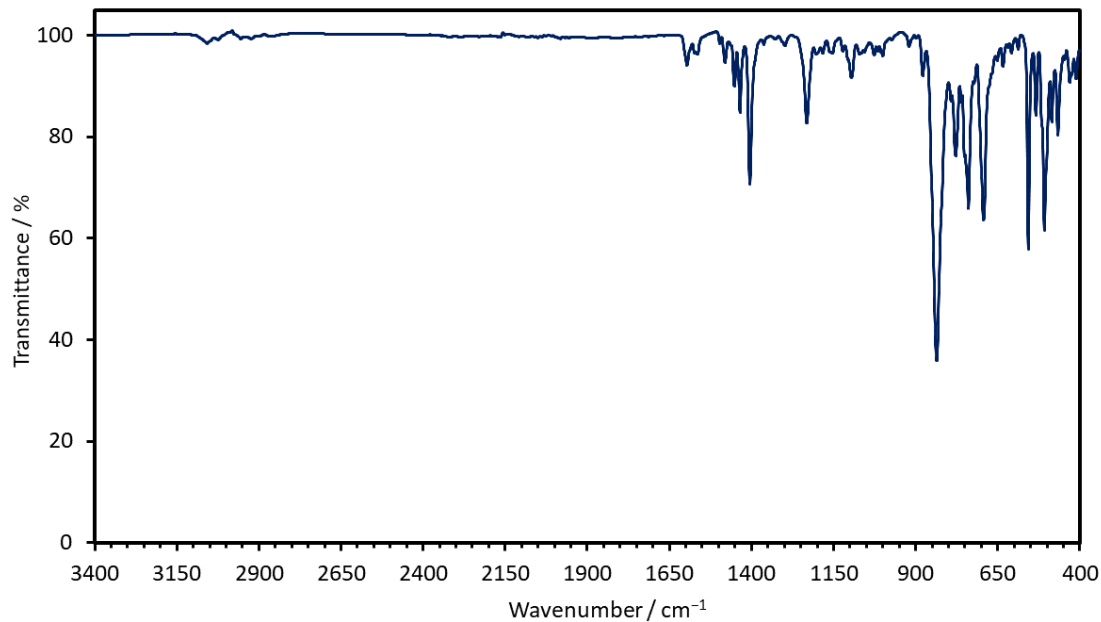


Fig. S112 FTIR spectrum of $[\text{Cu}(\text{xantphos})(3\text{-PhPrbpy})][\text{PF}_6]$.

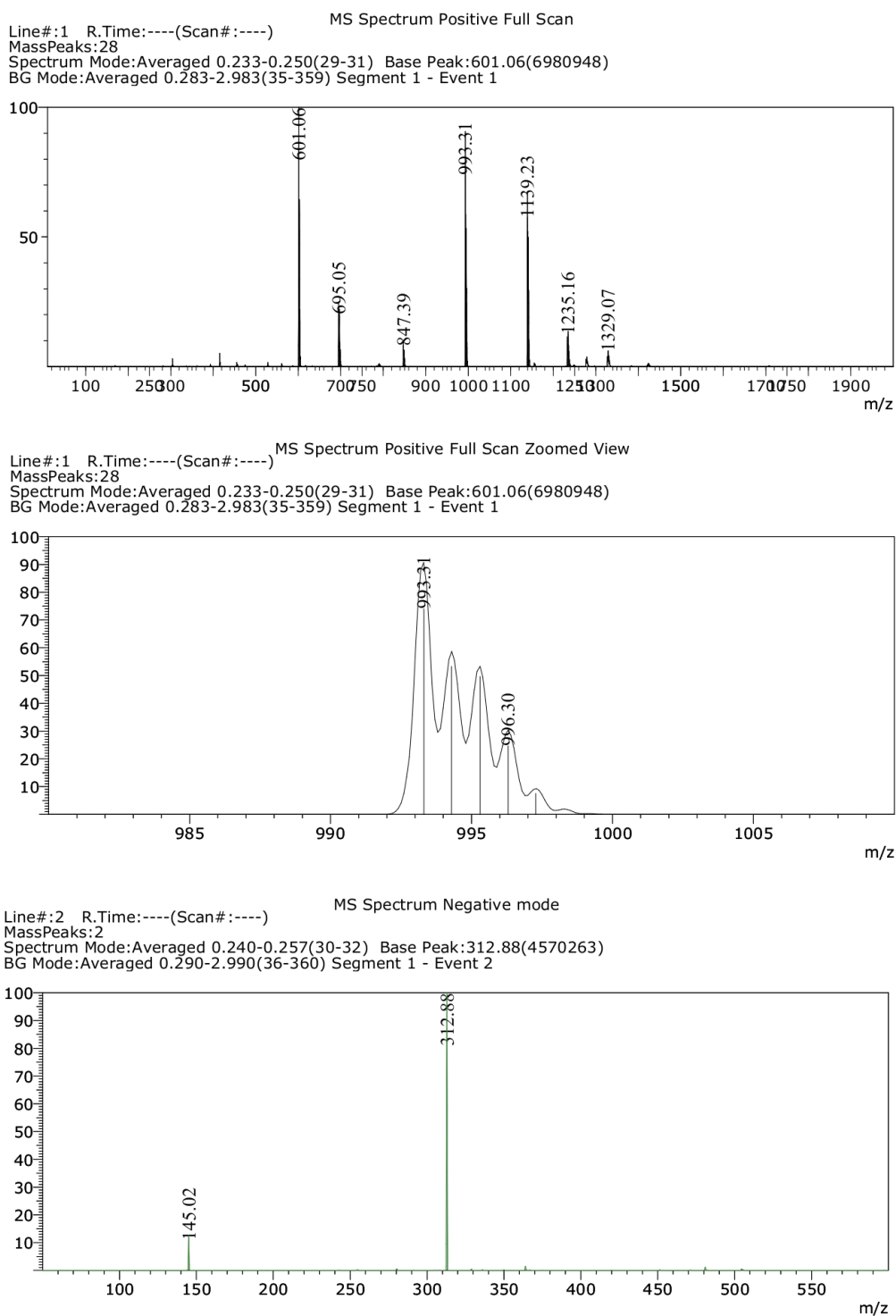


Fig. S113 ESI mass spectrum (positive and negative mode) of $[\text{Cu}(\text{POP})((3\text{-PhPr})_2\text{bpy})][\text{PF}_6]$.

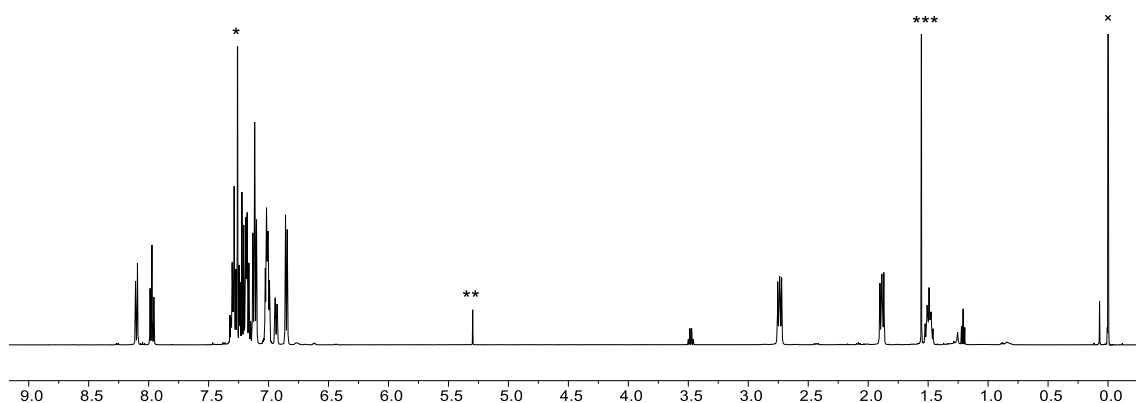


Fig. S114 ^1H NMR spectrum (500 MHz, CDCl_3 , 298 K, δ/ppm) of $[\text{Cu}(\text{POP})((3\text{-PhPr})_2\text{bpy})][\text{PF}_6]$. * = residual CHCl_3 ; ** = CH_2Cl_2 ; *** = H_2O ; x = TMS.

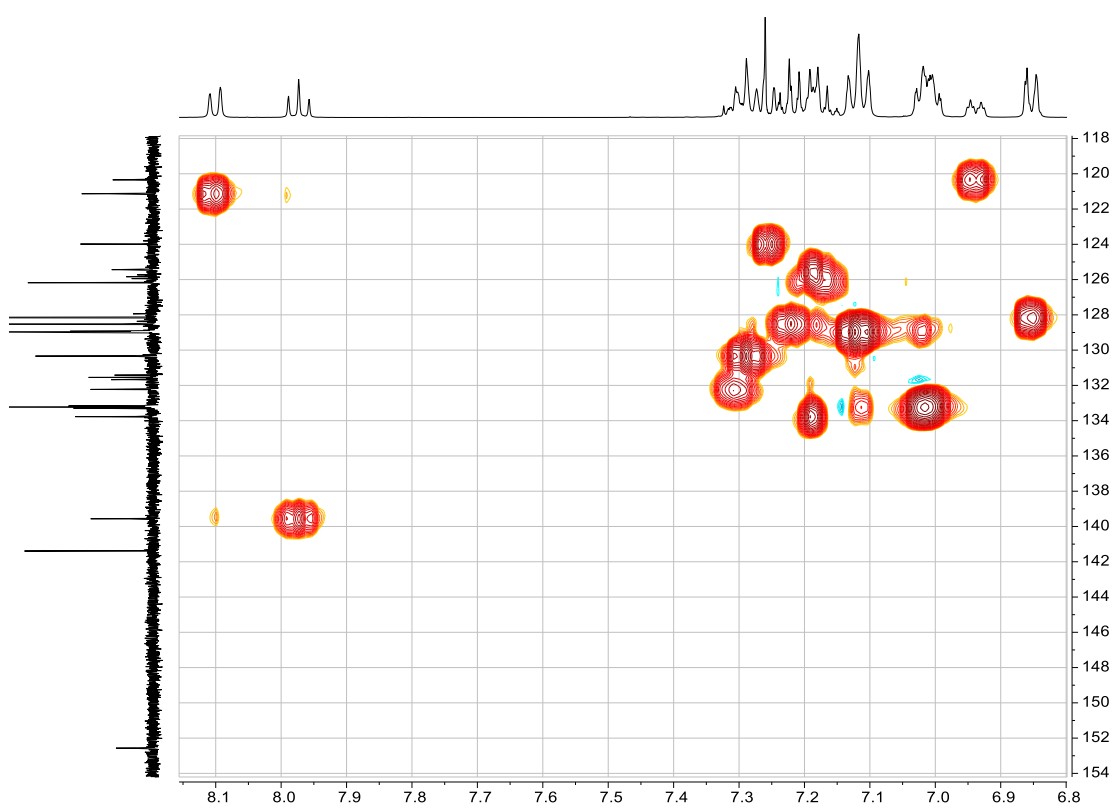


Fig. S115 The aromatic region of the HMQC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, CDCl_3 , 298 K, δ/ppm) of $[\text{Cu}(\text{POP})((3\text{-PhPr})_2\text{bpy})][\text{PF}_6]$.

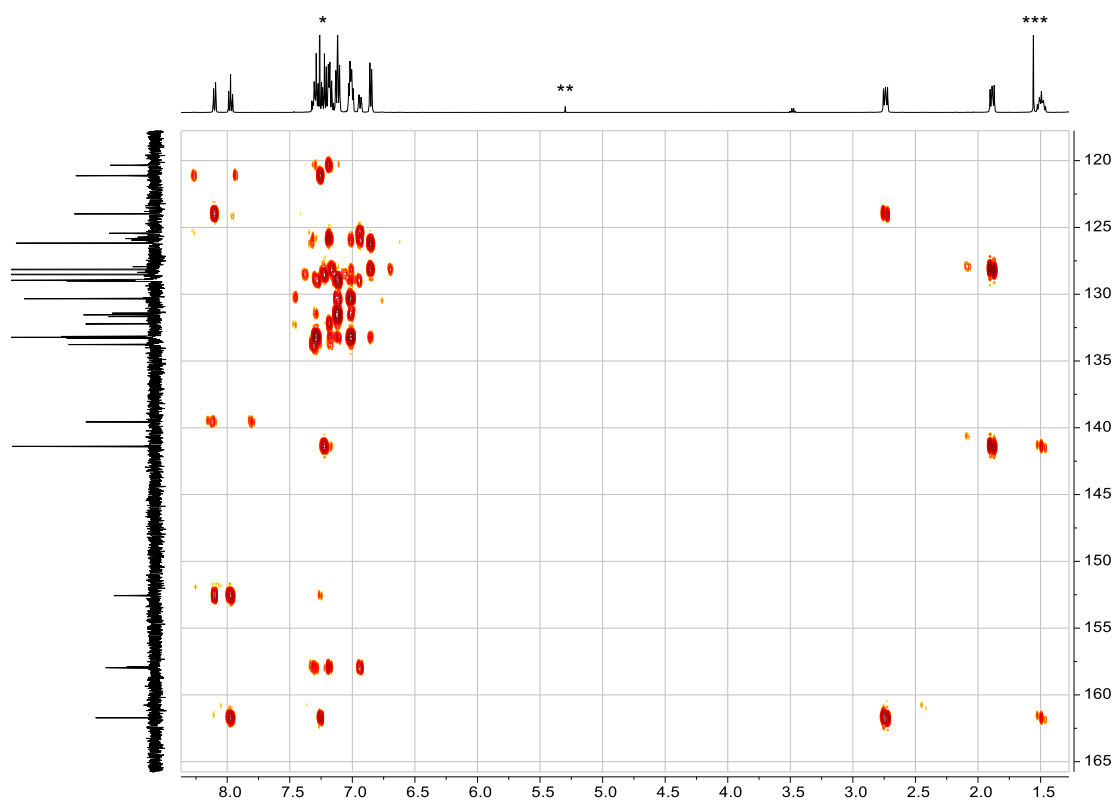


Fig. S116 Part of the HMBC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, CDCl_3 , 298 K, δ/ppm) of $[\text{Cu}(\text{POP})((3\text{-PhPr})_2\text{bpy})][\text{PF}_6]$. * = residual CHCl_3 ; ** = CH_2Cl_2 ; *** = H_2O .

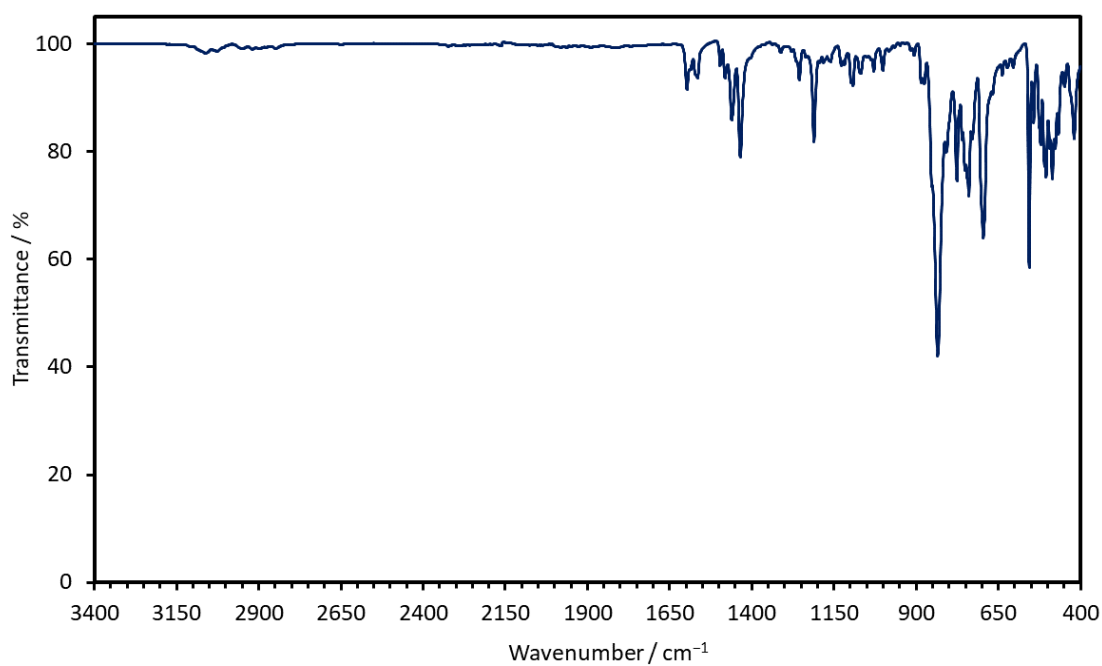
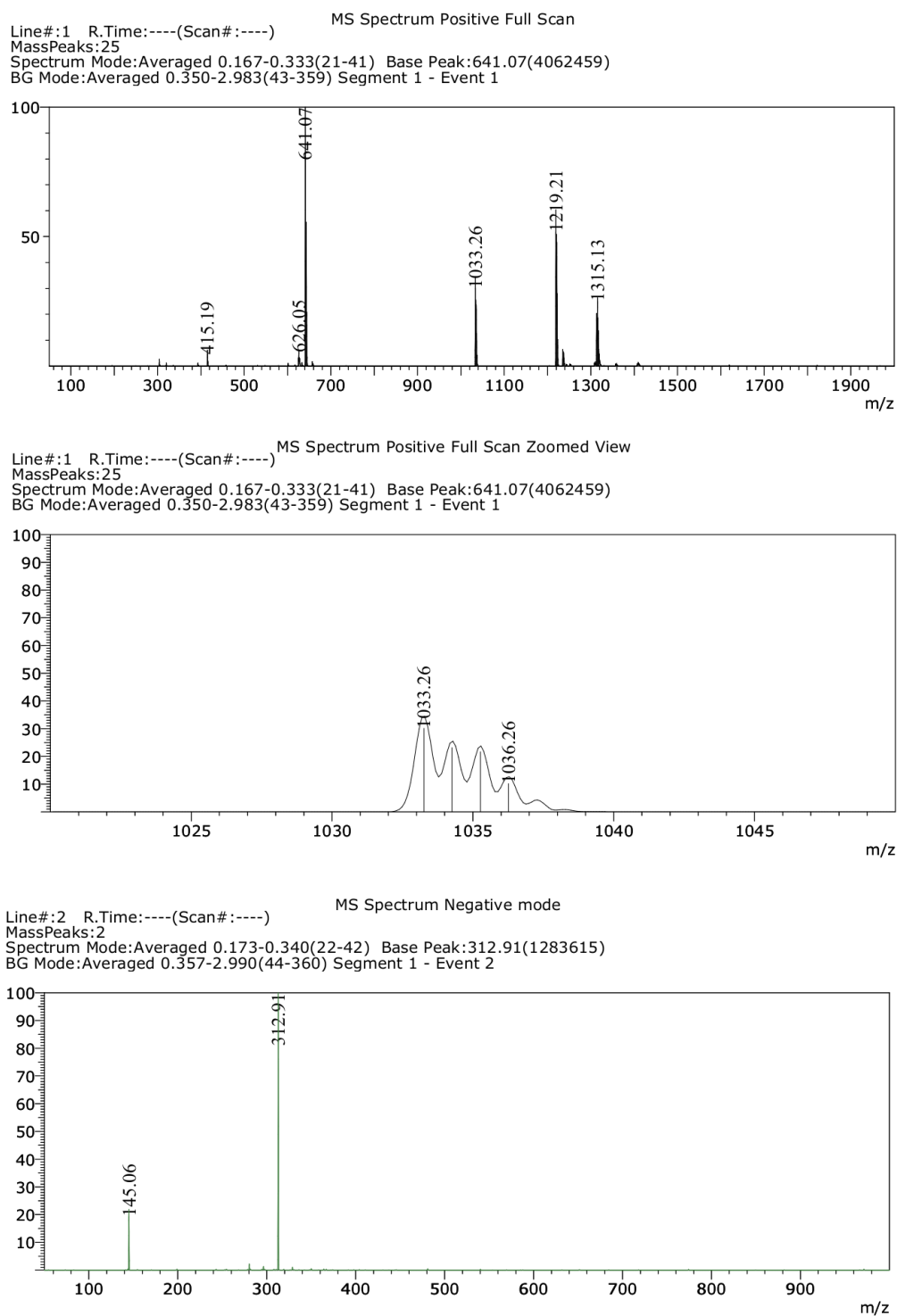


Fig. S117 FTIR spectrum of $[\text{Cu}(\text{POP})((3\text{-PhPr})_2\text{bpy})][\text{PF}_6]$.

Fig. S118 ESI mass spectrum (positive and negative mode) of $[\text{Cu}(\text{xantphos})((3\text{-PhPr})_2\text{bpy})][\text{PF}_6]$.

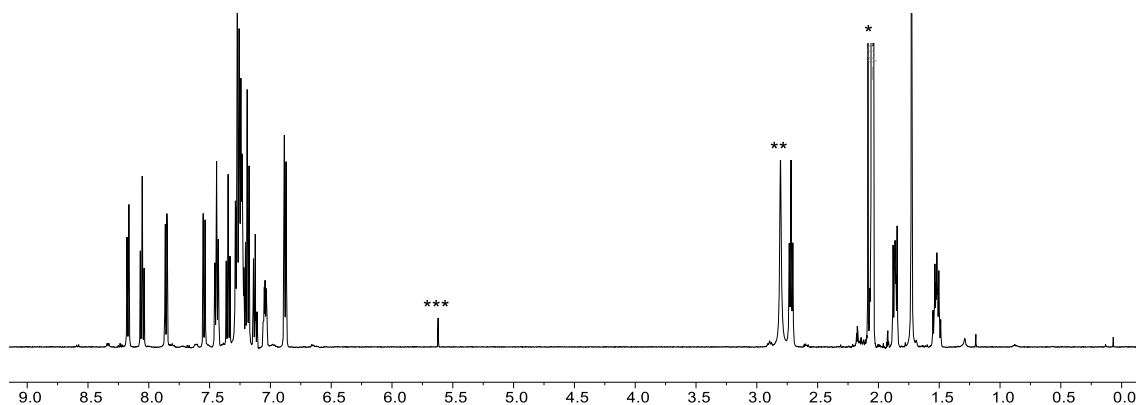


Fig. S119 ^1H NMR spectrum (500 MHz, acetone- d_6 , 298 K, δ/ppm) of $[\text{Cu}(\text{xantphos})((3\text{-PhPr})_2\text{bpy})][\text{PF}_6]$. * = residual acetone- d_5 ; ** = H_2O and HDO ; *** = CH_2Cl_2 .

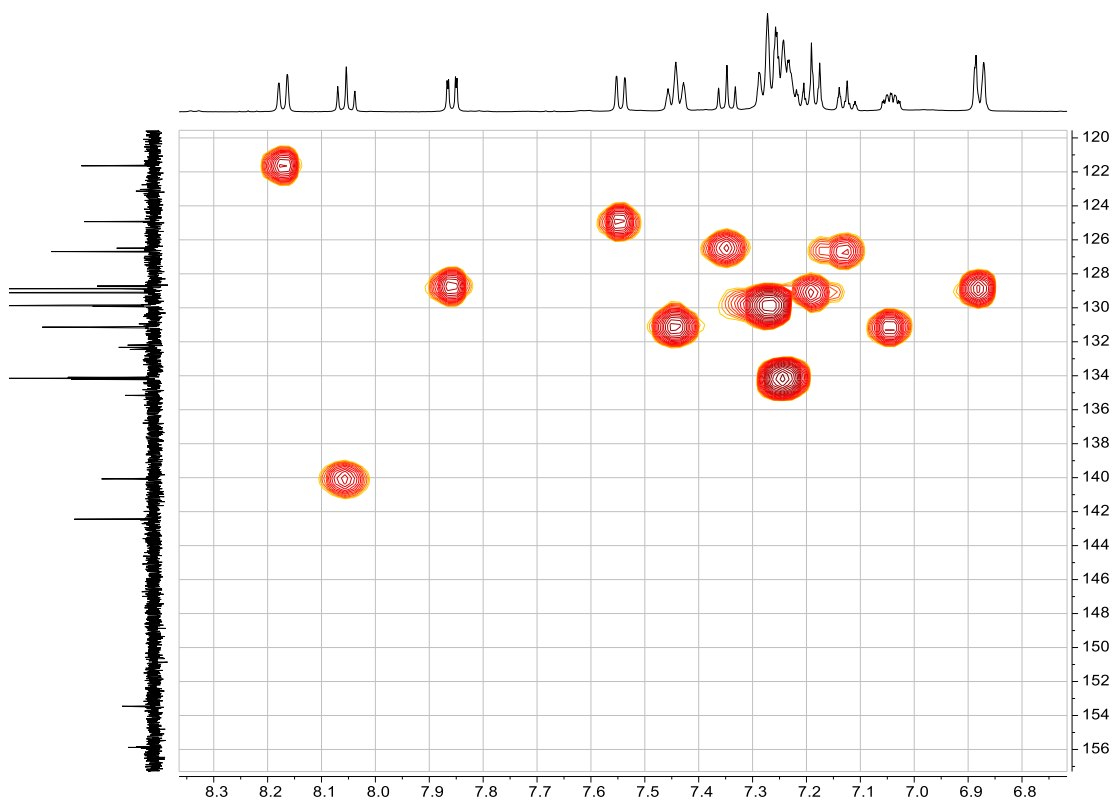


Fig. S120 The aromatic region of the HMQC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K, δ/ppm) of $[\text{Cu}(\text{xantphos})((3\text{-PhPr})_2\text{bpy})][\text{PF}_6]$.

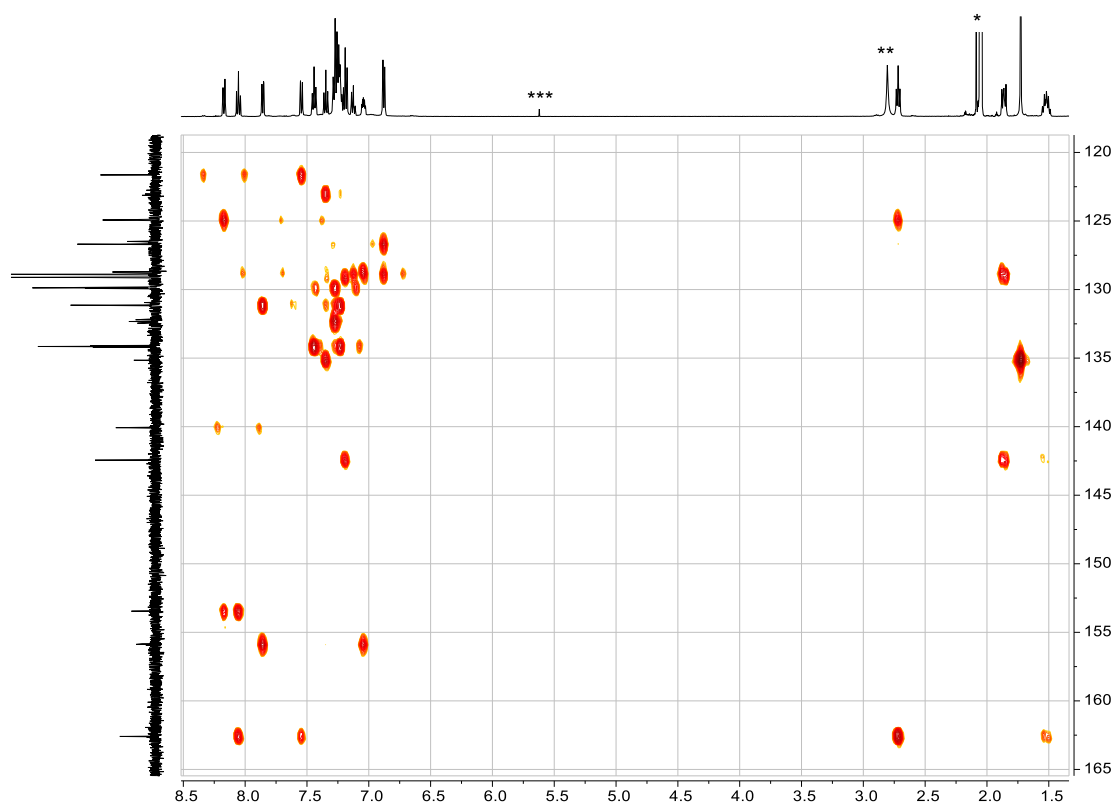


Fig. S121 Part of the HMBC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K, δ/ppm) of $[\text{Cu}(\text{xantphos})((3\text{-PhPr})_2\text{bpy})][\text{PF}_6]$. * = residual acetone- d_5 ; ** = H_2O and HDO ; *** = CH_2Cl_2 .

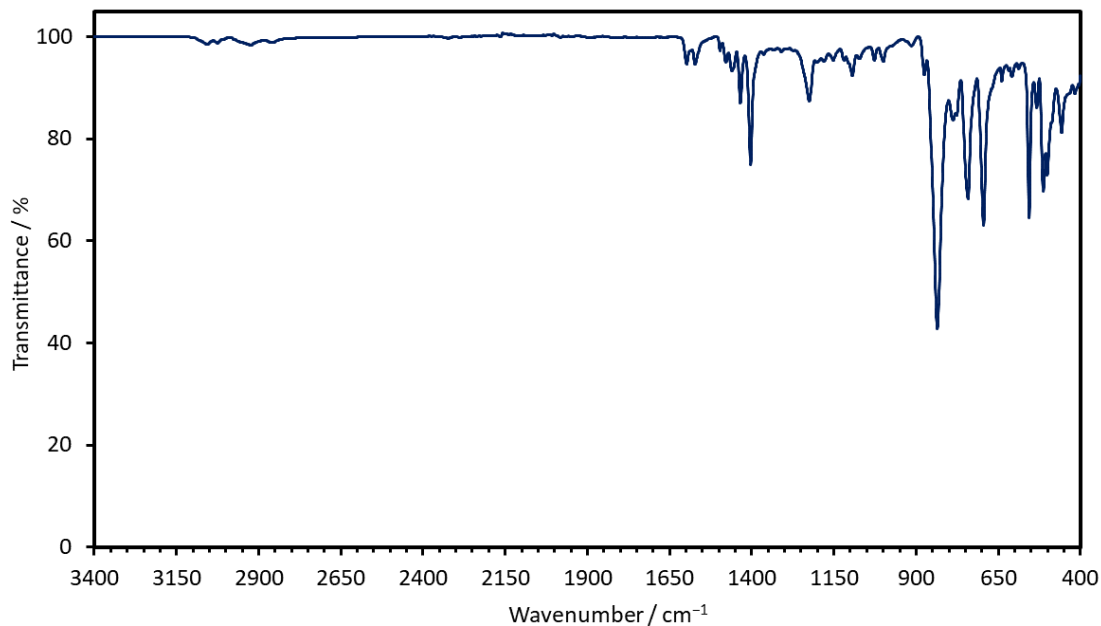


Fig. S122 FTIR spectrum of $[\text{Cu}(\text{xantphos})((3\text{-PhPr})_2\text{bpy})][\text{PF}_6]$.

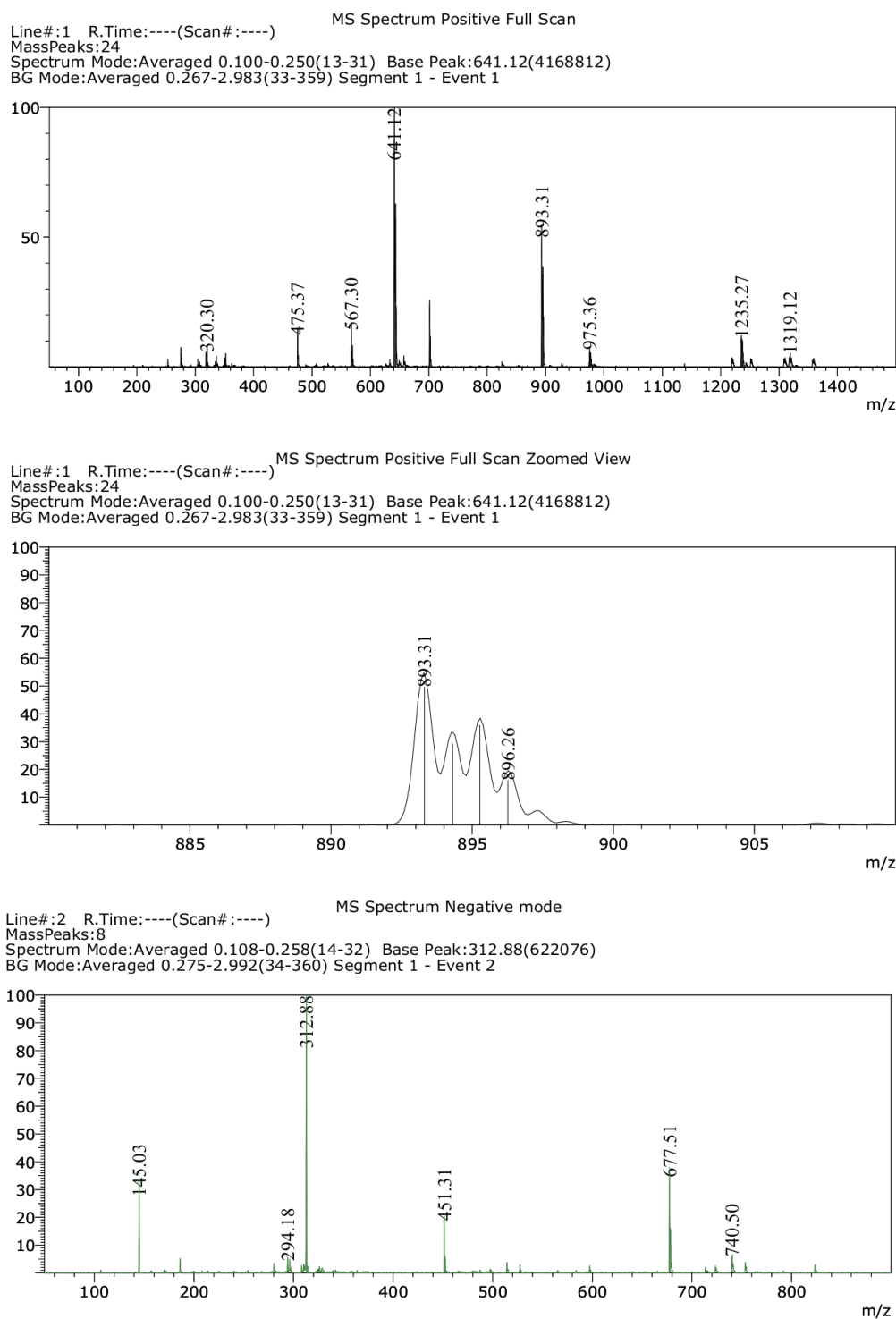


Fig. S123 ESI mass spectrum (positive and negative mode) of [Cu(xantphos)(6-Cy-6'-Mebpy)][PF₆].

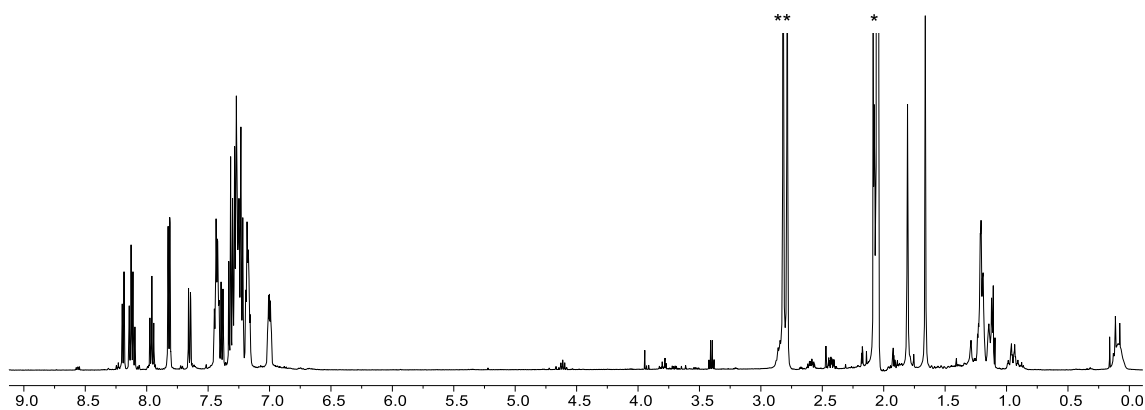


Fig. S124 ^1H NMR spectrum (500 MHz, acetone- d_6 , 298 K, δ/ppm) of $[\text{Cu}(\text{xantphos})(6\text{-Cy-6'-Mebpy})][\text{PF}_6]$. * = residual acetone- d_5 ; ** = H_2O and HDO .

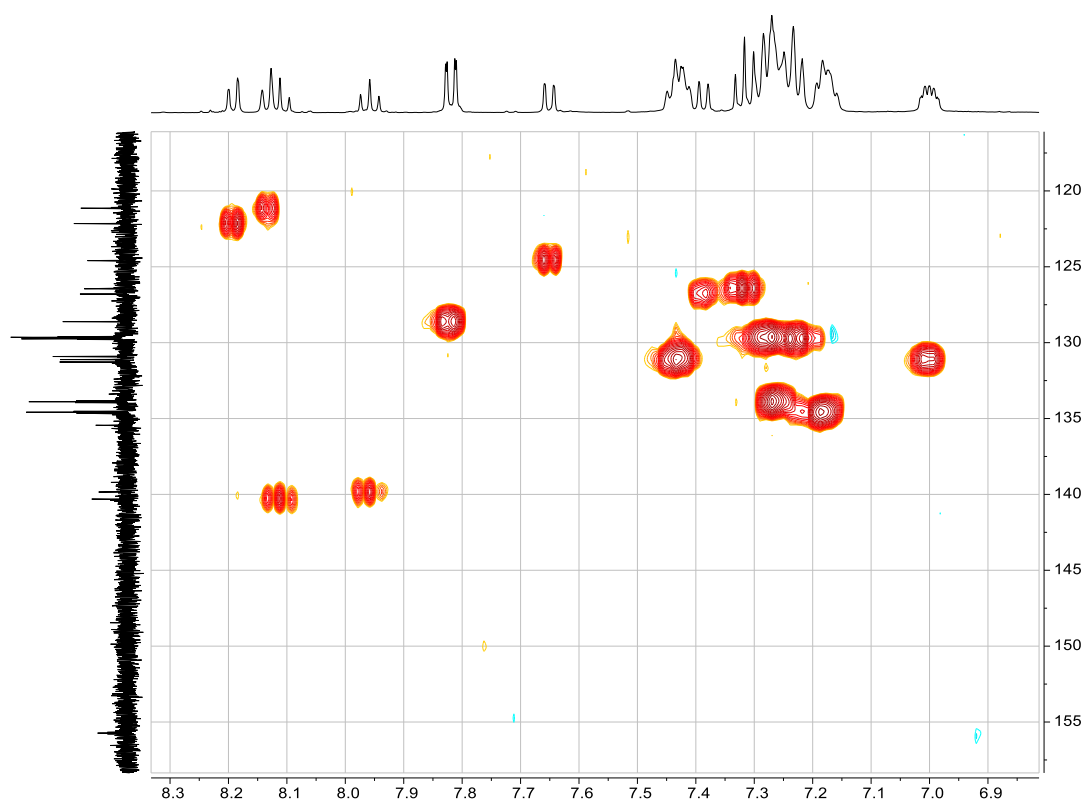


Fig. S125 The aromatic region of the HMQC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K, δ/ppm) of $[\text{Cu}(\text{xantphos})(6\text{-Cy-6'-Mebpy})][\text{PF}_6]$.

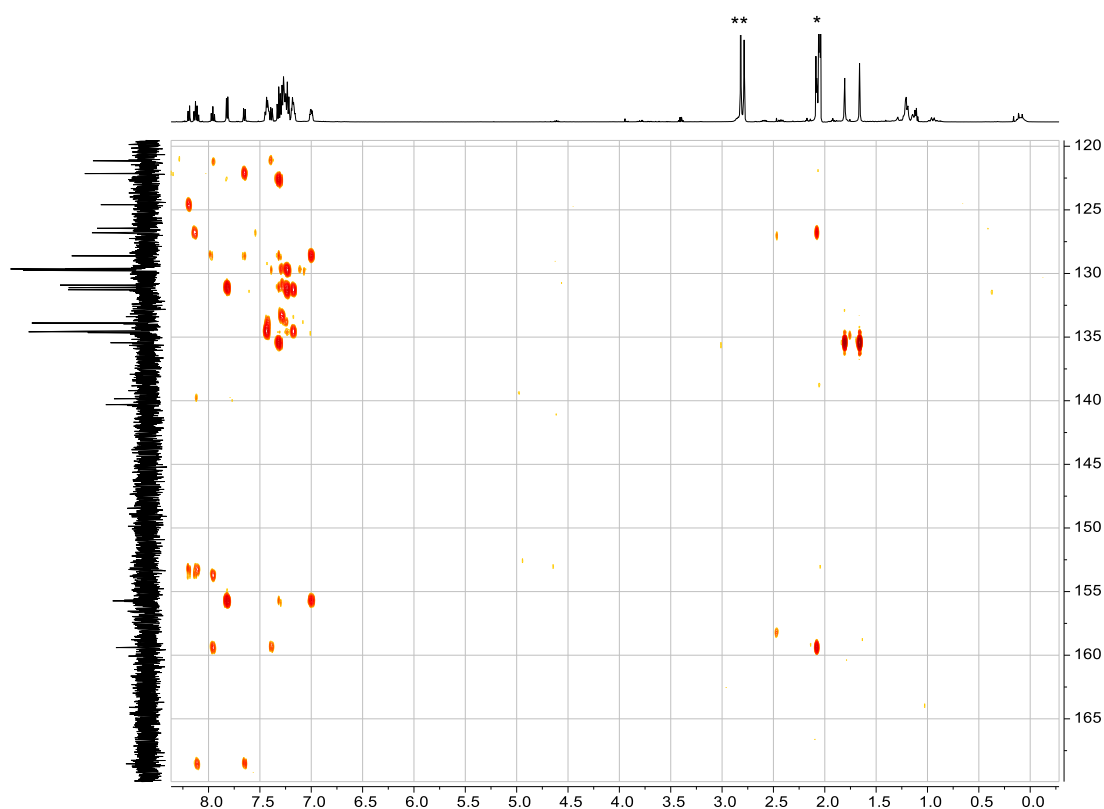


Fig. S126 Part of the HMBC spectrum (500 MHz ^1H , 126 MHz $^{13}\text{C}\{^1\text{H}\}$, acetone- d_6 , 298 K, δ/ppm) of $[\text{Cu}(\text{xantphos})(6\text{-Cy-6'-Mebpy})][\text{PF}_6]$. * = residual acetone- d_5 ; ** = H_2O and HDO.

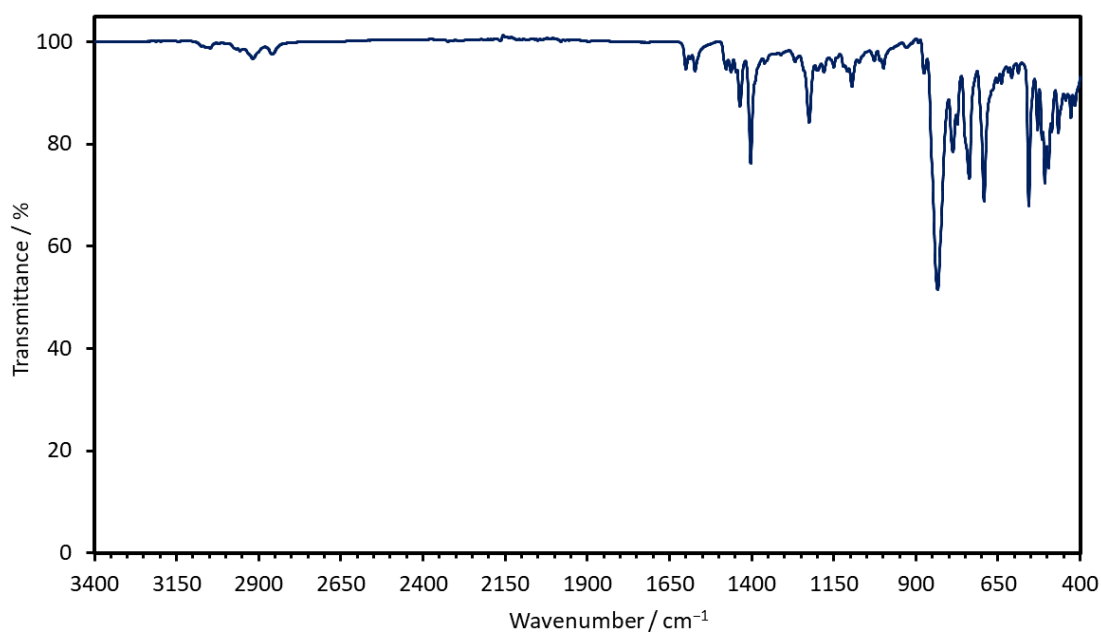


Fig. S127 FTIR spectrum of $[\text{Cu}(\text{xantphos})(6\text{-Cy-6'-Mebpy})][\text{PF}_6]$.

Table S1 Crystallographic data for the Cu(I) complexes

Compound	[Cu(xantphos)(2-CyEtbpv)][PF ₆] ·1.5Et ₂ O	[Cu(POP)(3-EtPentbpv)][PF ₆] Polymorph 1	[Cu(POP)(3-EtPentbpv)][PF ₆] Polymorph 2
Formula	C ₆₃ CuF ₆ H ₆₉ N ₂ O _{2.5} P ₃	C _{53.5} ClCuF ₆ H ₅₁ N ₂ OP ₃	C ₅₃ H ₅₀ CuF ₆ N ₂ OP ₃
Formula weight	1164.65	1186.22	1001.40
Crystal colour and habit	Yellow block	Yellow block	Yellow block
Crystal system	Triclinic	Monoclinic	Orthorhombic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>Pbca</i>
<i>a</i> , <i>b</i> , <i>c</i> / Å	11.1185(2), 15.4476(3), 18.7346(4)	9.6663(2), 18.8768(6), 27.6792(6)	19.4572(3), 24.5273(3), 20.2217(4)
α , β , γ / °	111.777(2), 92.067(2), 110.6690(10)	90, 94.976(2), 90	90, 90, 90
<i>U</i> / Å ³	2743.64(10)	5031.6(2)	9650.5(3)
<i>D_c</i> / Mg m ⁻³	1.410	1.378	1.378
<i>Z</i>	2	4	8
Radiation type	Cu-K α	Cu-K α	Cu-K α
μ / mm ⁻¹	1.962	2.531	2.118
<i>T</i> / K	150	150	150
Refln. collected (<i>R</i> _{int})	51953 (0.0526)	41811 (0.0197)	80876 (0.0354)
Unique refln.	10717	9294	9493
Refln. for refinement	9265	8987	8541
Parameters	634	597	598
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)	0.1261 (0.1369)	0.0468 (0.0477)	0.0574 (0.0643)
<i>wR</i> 2 (<i>wR</i> 2 all data)	0.2600 (0.2708)	0.1263 (0.1271)	0.1506 (0.1643)
Goodness of fit	0.912	1.029	1.085
CCDC	2324349	2324343	2324368

Compound	[Cu(xantphos)(3-EtPentbpv)][PF ₆] ·0.8Et ₂ O	[Cu(POP)(2-PhEtbpv)][PF ₆] ·0.4CH ₂ Cl ₂ ·0.75Et ₂ O	[Cu(xantphos)(2-PhEtbpv)][PF ₆] ·0.5Et ₂ O
Formula	C _{59.2} H _{61.6} CuF ₆ N ₂ O _{1.8} P ₃	C _{57.4} H _{50.3} Cl _{0.8} CuF ₆ N ₂ O _{1.75} P ₃	C ₅₉ H ₅₃ CuF ₆ N ₂ O _{1.5} P ₃
Formula weight	1073.89	1094.90	1084.48
Crystal colour and habit	Yellow block	Yellow block	Yellow block
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>
<i>a</i> , <i>b</i> , <i>c</i> / Å	11.1704(2), 15.2169(3), 18.9218(3)	9.9285(3), 14.8219(4), 19.2356(6)	47.5822(7), 10.7647(2), 23.4775(4)
α , β , γ / °	113.4400(10), 90.8650(10), 109.8700(10)	99.235(2), 93.135(2), 106.725(2)	90, 115.8860(10), 90
<i>U</i> / Å ³	2732.78(9)	2660.53(14)	10818.8(3)
<i>D_c</i> / Mg m ⁻³	1.337	1.367	1.332
<i>Z</i>	2	2	8
Radiation type	Cu-K α	Cu-K α	Ga-K α
μ / mm ⁻¹	1.929	2.342	1.940
<i>T</i> / K	150	150	150
Refln. collected (<i>R</i> _{int})	48998 (0.0223)	42511 (0.0202)	81904 (0.0323)
Unique refln.	10128	9771	10139
Refln. for refinement	9417	9342	9740
Parameters	715	645	672
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)	0.0732 (0.0759)	0.0763 (0.0777)	0.0728 (0.0756)
<i>wR</i> 2 (<i>wR</i> 2 all data)	0.1993 (0.2025)	0.2192 (0.2208)	0.2031 (0.2071)
Goodness of fit	1.071	1.044	1.052
CCDC	2324345	2324344	2324347

Compound	[Cu(POP)((2-PhEt) ₂ bpy)][PF ₆] ·1.125Et ₂ O	[Cu(xantphos)((2-PhEt) ₂ bpy)][PF ₆]	[Cu(POP)(3-PhPrbpy)][PF ₆]
Formula	C _{66.5} CuF ₆ H _{63.25} N ₂ O _{2.13} P ₃	C ₆₅ H ₅₆ CuF ₆ N ₂ OP ₃	C ₅₅ H ₄₆ CuF ₆ N ₂ OP ₃
Formula weight	1194.97	1151.56	1021.39
Crystal colour and habit	Yellow block	Yellow plate	Yellow block
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> , <i>b</i> , <i>c</i> / Å	18.1906(3), 18.7096(3), 18.9000(3)	11.9248(2), 12.5855(2), 18.3632(3)	9.6732(3), 16.9223(4), 29.1542(9)
α , β , γ / °	85.9700(10), 66.9620(10), 89.8750(10)	83.1420(10), 77.5710(10), 85.1960(10)	90, 95.071(3), 90
<i>U</i> / Å ³	5902.51(17)	2667.30(8)	4753.7(2)
<i>D</i> _c / Mg m ⁻³	1.345	1.434	1.427
<i>Z</i>	4	2	4
Radiation type	Cu-K α	Cu-K α	Ga-K α
μ / mm ⁻¹	1.837	1.997	3.469
<i>T</i> / K	150	150	150
Refln. collected (<i>R</i> _{int})	123971 (0.0675)	50581 (0.0239)	47843 (0.1478)
Unique refln.	22922	10383	9089
Refln. for refinement	15721	9499	5706
Parameters	1428	706	613
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)	0.1074 (0.1401)	0.0552 (0.0583)	0.0749 (0.1197)
<i>wR</i> 2 (<i>wR</i> 2 all data)	0.2457 (0.2775)	0.1571 (0.1637)	0.1853 (0.2099)
Goodness of fit	1.043	1.138	0.974
CCDC	2324369	2324365	2324366

Compound	[Cu(xantphos)(3-PhPrbpy)][PF ₆] ·0.8Et ₂ O	[Cu(POP)((3-PhPr) ₂ bpy)][PF ₆] ·0.5CH ₂ Cl ₂ ·0.5Et ₂ O	[Cu(xantphos)(6-Cy-6'-Mebpy)][PF ₆] ·0.75Et ₂ O·0.5H ₂ O
Formula	C _{61.2} CuF ₆ H ₅₈ N ₂ O _{1.8} P ₃	C ₆₄ H ₅₆ CuF ₆ N ₂ OP ₃	C ₅₉ H _{60.50} CuF ₆ N ₂ O _{2.25} P ₃
Formula weight	1120.74	1139.55	1104.04
Crystal colour and habit	Yellow block	Yellow plate	Yellow block
Crystal system	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> , <i>b</i> , <i>c</i> / Å	11.1103(4), 15.0046(5), 18.8034(6)	11.1961(2), 13.9132(3), 19.7956(4)	10.9048(2), 16.0127(4), 17.4940(4)
α , β , γ / °	112.692(2), 91.288(3), 110.119(3)	78.071(2), 80.439(2), 67.579(2)	76.289(2), 81.110(2), 70.345(2)
<i>U</i> / Å ³	2671.60(17)	2775.96(11)	2785.40(12)
<i>D</i> _c / Mg m ⁻³	1.393	1.363	1.316
<i>Z</i>	2	2	2
Radiation type	Ga-K α	Mo-K α	Ga-K α
μ / mm ⁻¹	3.125	0.545	2.995
<i>T</i> / K	150	150	150
Refln. collected (<i>R</i> _{int})	31586 (0.0473)	78218 (0.0322)	38847 (0.0414)
Unique refln.	10050	15998	10854
Refln. for refinement	7758	12256	10577
Parameters	612	697	676
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)	0.0772 (0.0992)	0.0383 (0.0578)	0.0548 (0.0558)
<i>wR</i> 2 (<i>wR</i> 2 all data)	0.2028 (0.2166)	0.0967 (0.1054)	0.1600 (0.1613)
Goodness of fit	1.046	1.018	1.040
CCDC	2324346	2324348	2324342

Compound	[Cu((2-CyEt) ₂ bpy) ₂][PF ₆]
Formula	C ₅₂ H ₇₂ CuF ₆ N ₄ P
Formula weight	961.64
Crystal colour and habit	Orange block
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , <i>b</i> , <i>c</i> / Å	15.0492(4), 12.3630(2), 27.1473(7)
α , β , γ / °	90, 90.068(2), 90
<i>U</i> / Å ³	5050.8(2)
<i>D</i> _c / Mg m ⁻³	1.265
<i>Z</i>	4
Radiation type	Cu-K α
μ / mm ⁻¹	1.406
<i>T</i> / K	150
Refln. collected (<i>R</i> _{int})	104207 (0.0488)
Unique refln.	9998
Refln. for refinement	8147
Parameters	632
Threshold	<i>I</i> > 2 σ (<i>I</i>)
<i>R</i> 1 (<i>R</i> 1 all data)	0.0882 (0.1058)
<i>wR</i> 2 (<i>wR</i> 2 all data)	0.1794 (0.1961)
Goodness of fit	0.992
CCDC	2324367

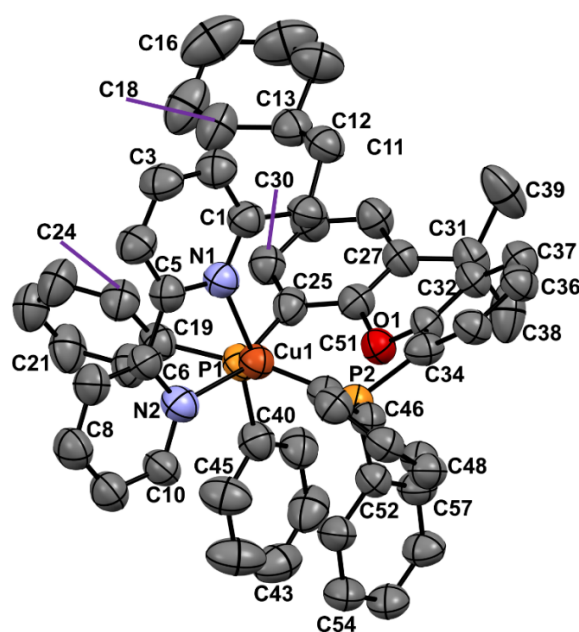


Fig. S128 Structure of the [Cu(xantphos)(2-CyEtbpy)]⁺ cation in [Cu(xantphos)(2-CyEtbpy)][PF₆].1.5Et₂O. H atoms and solvent molecules are omitted and ellipsoids are plotted at 50% probability level. Selected bond parameters: Cu1–P2 = 2.267(2), Cu1–P1 = 2.273(2), Cu1–N2 = 2.057(4), Cu1–N1 = 2.088(7), C26–O1 = 1.390(6), C33–O1 = 1.385(8) Å; P2–Cu1–P1 = 113.52(7), P2–Cu1–N2 = 112.9(2), P1–Cu1–N2 = 112.4(2), P2–Cu1–N1 = 116.9(2), P1–Cu1–N1 = 116.5(2), N2–Cu1–N1 = 80.2(2), C26–O1–C33 = 116.0(5)°.

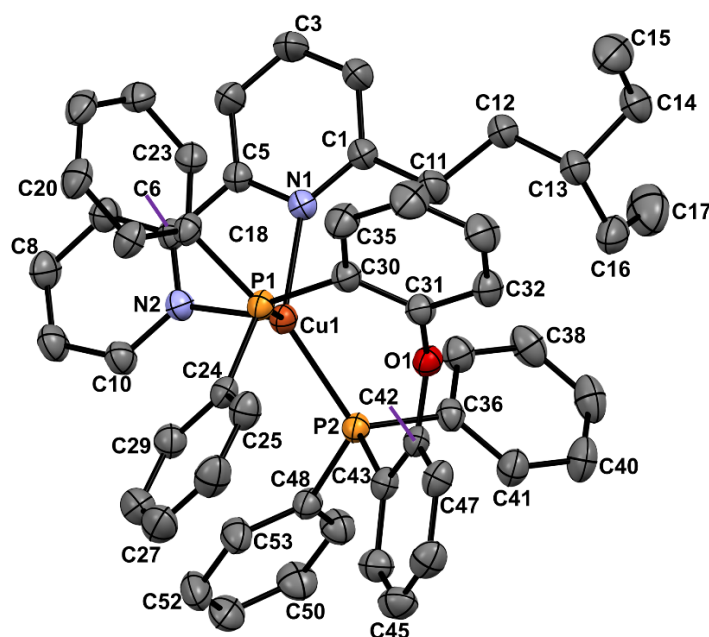


Fig. S129 Structure of the $[\text{Cu}(\text{POP})(3\text{-EtPentbpy})]^+$ cation in $[\text{Cu}(\text{POP})(3\text{-EtPentbpy})][\text{PF}_6] \cdot 0.5\text{CH}_2\text{Cl}_2$. H atoms and solvent molecules are omitted and ellipsoids are plotted at 50% probability level. Selected bond parameters: $\text{Cu1-P2} = 2.2576(7)$, $\text{Cu1-P1} = 2.2887(6)$, $\text{Cu1-N2} = 2.072(2)$, $\text{Cu1-N1} = 2.119(2)$, $\text{C31-O1} = 1.397(3)$, $\text{C42-O1} = 1.388(3)$ Å; $\text{P2-Cu1-P1} = 111.61(3)$, $\text{P2-Cu1-N2} = 116.41(5)$, $\text{P1-Cu1-N2} = 111.11(5)$, $\text{P2-Cu1-N1} = 125.51(5)$, $\text{P1-Cu1-N1} = 108.43(5)$, $\text{N2-Cu1-N1} = 79.90(7)$, $\text{C31-O1-C42} = 118.3(2)^\circ$.

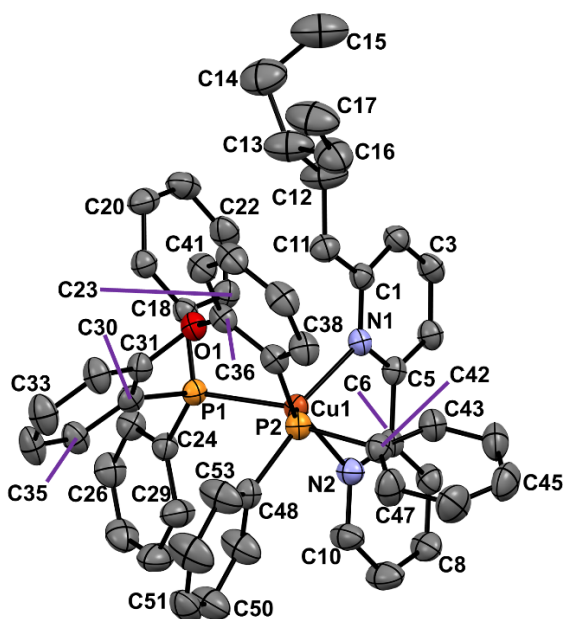


Fig. S130 Structure of the $[\text{Cu}(\text{POP})(3\text{-EtPentbpy})]^+$ cation in $[\text{Cu}(\text{POP})(3\text{-EtPentbpy})][\text{PF}_6]$. H atoms and solvent molecules are omitted and ellipsoids are plotted at 50% probability level. Selected bond parameters: $\text{Cu1-P2} = 2.2575(8)$, $\text{Cu1-P1} = 2.2665(8)$, $\text{Cu1-N2} = 2.069(2)$, $\text{Cu1-N1} = 2.110(2)$, $\text{C31-O1} = 1.389(3)$, $\text{C36-O1} = 1.398(3)$ Å; $\text{P2-Cu1-P1} = 113.21(3)$, $\text{P2-Cu1-N2} = 115.81(7)$, $\text{P1-Cu1-N2} = 112.53(7)$, $\text{P2-Cu1-N1} = 123.08(7)$, $\text{P1-Cu1-N1} = 108.48(6)$, $\text{N2-Cu1-N1} = 79.50(9)$, $\text{C31-O1-C36} = 117.2(2)^\circ$.

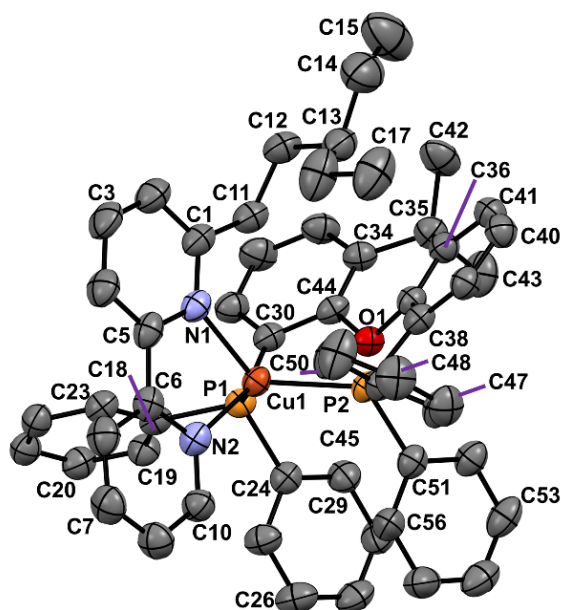


Fig. S131 Structure of the $[\text{Cu}(\text{xantphos})(3\text{-EtPentbpy})]^+$ cation in $[\text{Cu}(\text{xantphos})(3\text{-EtPentbpy})][\text{PF}_6] \cdot 0.8\text{Et}_2\text{O}$. H atoms and solvent molecules are omitted and ellipsoids are plotted at 50% probability level. Selected bond parameters: $\text{Cu1-P2} = 2.271(1)$, $\text{Cu1-P1} = 2.268(1)$, $\text{Cu1-N2} = 2.061(3)$, $\text{Cu1-N1} = 2.092(4)$, $\text{C37-O1} = 1.387(4)$, $\text{C44-O1} = 1.386(5)$ Å; $\text{P2-Cu1-P1} = 113.29(4)$, $\text{P2-Cu1-N2} = 112.2(1)$, $\text{P1-Cu1-N2} = 112.4(1)$, $\text{P2-Cu1-N1} = 118.65(9)$, $\text{P1-Cu1-N1} = 115.66(9)$, $\text{N2-Cu1-N1} = 80.3(1)$, $\text{C37-O1-C44} = 115.8(3)^\circ$.

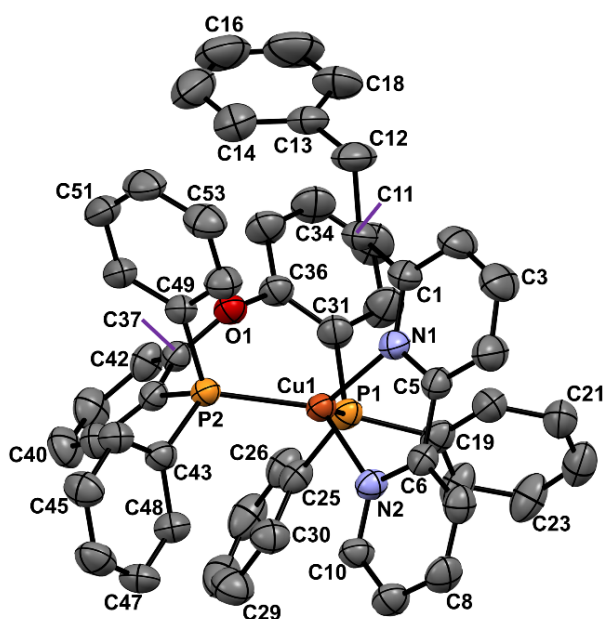


Fig. S132 Structure of the $[\text{Cu}(\text{POP})(2\text{-PhEtbpy})]^+$ cation in $[\text{Cu}(\text{POP})(2\text{-PhEtbpy})][\text{PF}_6] \cdot 0.4\text{CH}_2\text{Cl}_2 \cdot 0.75\text{Et}_2\text{O}$. H atoms and solvent molecules are omitted and ellipsoids are plotted at 50% probability level. Selected bond parameters: $\text{Cu1-P2} = 2.2623(8)$, $\text{Cu1-P1} = 2.274(1)$, $\text{Cu1-N2} = 2.075(3)$, $\text{Cu1-N1} = 2.109(3)$, $\text{C36-O1} = 1.387(4)$, $\text{C37-O1} = 1.388(5)$ Å; $\text{P2-Cu1-P1} = 113.34(4)$, $\text{P2-Cu1-N2} = 115.99(9)$, $\text{P1-Cu1-N2} = 112.68(9)$, $\text{P2-Cu1-N1} = 118.58(9)$, $\text{P1-Cu1-N1} = 111.93(9)$, $\text{N2-Cu1-N1} = 80.3(1)$, $\text{C36-O1-C37} = 119.0(3)^\circ$.



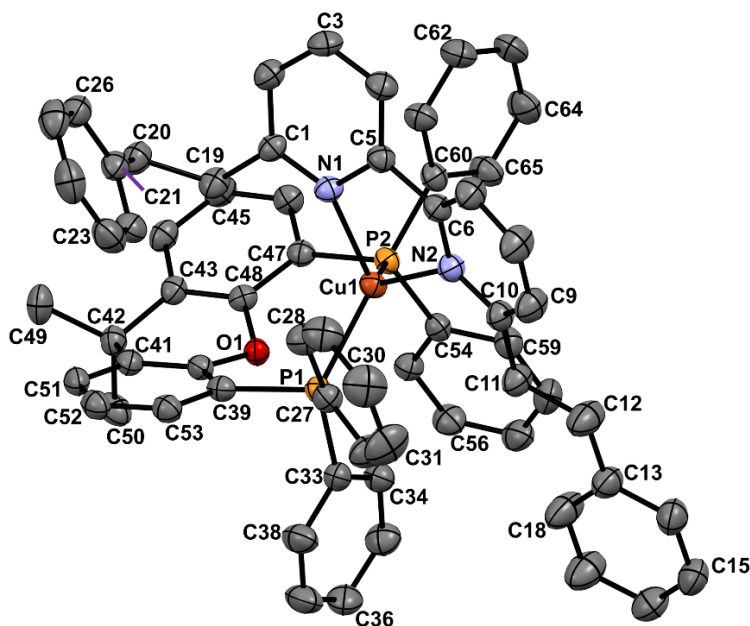


Fig. S135 Structure of the $[\text{Cu}(\text{xantphos})((2\text{-PhEt})_2\text{bpy})]^+$ cation in $[\text{Cu}(\text{xantphos})((2\text{-PhEt})_2\text{bpy})][\text{PF}_6]$. H atoms and solvent molecules are omitted and ellipsoids are plotted at 50% probability level. Selected bond parameters: $\text{Cu1-P2} = 2.2597(6)$, $\text{Cu1-P1} = 2.2836(6)$, $\text{Cu1-N2} = 2.097(2)$, $\text{Cu1-N1} = 2.162(2)$, $\text{C40-O1} = 1.394(3)$, $\text{C48-O1} = 1.385(2)$ Å; $\text{P2-Cu1-P1} = 119.53(2)$, $\text{P2-Cu1-N2} = 125.31(6)$, $\text{P1-Cu1-N2} = 103.79(5)$, $\text{P2-Cu1-N1} = 106.92(5)$, $\text{P1-Cu1-N1} = 114.43(5)$, $\text{N2-Cu1-N1} = 80.74(7)$, $\text{C40-O1-C48} = 115.6(2)^\circ$.

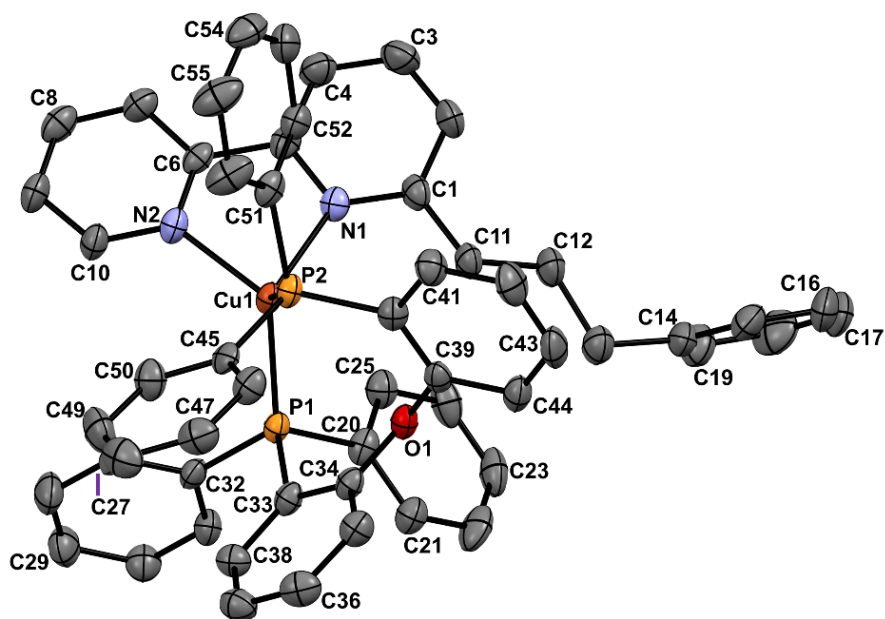


Fig. S136 Structure of the $[\text{Cu}(\text{POP})(3\text{-PhPrbpy})]^+$ cation in $[\text{Cu}(\text{POP})(3\text{-PhPrbpy})][\text{PF}_6]$. H atoms and solvent molecules are omitted and ellipsoids are plotted at 50% probability level. Selected bond parameters: $\text{Cu1-P2} = 2.285(1)$, $\text{Cu1-P1} = 2.255(1)$, $\text{Cu1-N2} = 2.071(4)$, $\text{Cu1-N1} = 2.104(4)$, $\text{C34-O1} = 1.394(6)$, $\text{C39-O1} = 1.395(5)$ Å; $\text{P2-Cu1-P1} = 111.82(5)$, $\text{P2-Cu1-N2} = 113.1(1)$, $\text{P1-Cu1-N2} = 118.5(1)$, $\text{P2-Cu1-N1} = 108.9(1)$, $\text{P1-Cu1-N1} = 120.9(1)$, $\text{N2-Cu1-N1} = 80.1(1)$, $\text{C34-O1-C39} = 117.3(3)^\circ$.

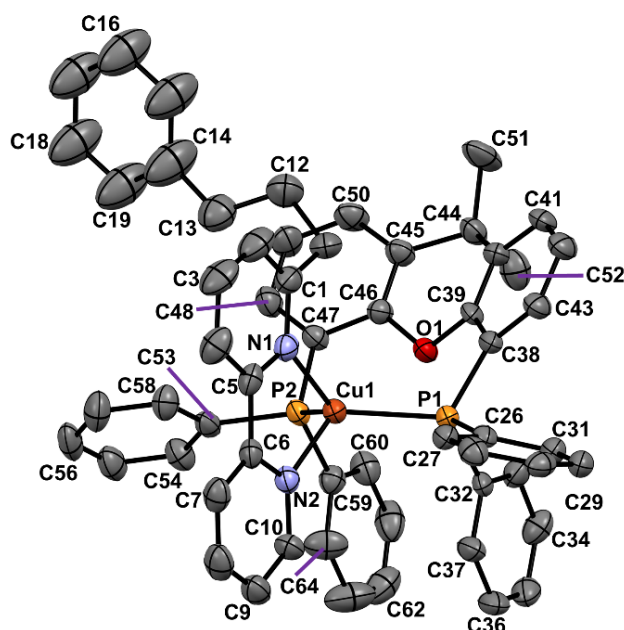


Fig. S137 Structure of the $[\text{Cu}(\text{xantphos})(3\text{-PhPrbpy})]^+$ cation in $[\text{Cu}(\text{xantphos})(3\text{-PhPrbpy})][\text{PF}_6] \cdot 0.8\text{Et}_2\text{O}$. H atoms and solvent molecules are omitted and ellipsoids are plotted at 50% probability level. Selected bond parameters: $\text{Cu1-P2} = 2.270(1)$, $\text{Cu1-P1} = 2.264(2)$, $\text{Cu1-N2} = 2.046(3)$, $\text{Cu1-N1} = 2.091(5)$, $\text{C39-O1} = 1.398(8)$, $\text{C46-O1} = 1.395(6)$ Å; $\text{P2-Cu1-P1} = 112.81(6)$, $\text{P2-Cu1-N2} = 112.9(1)$, $\text{P1-Cu1-N2} = 112.5(1)$, $\text{P2-Cu1-N1} = 117.9(1)$, $\text{P1-Cu1-N1} = 116.5(1)$, $\text{N2-Cu1-N1} = 79.9(2)$, $\text{C39-O1-C46} = 114.9(4)^\circ$.

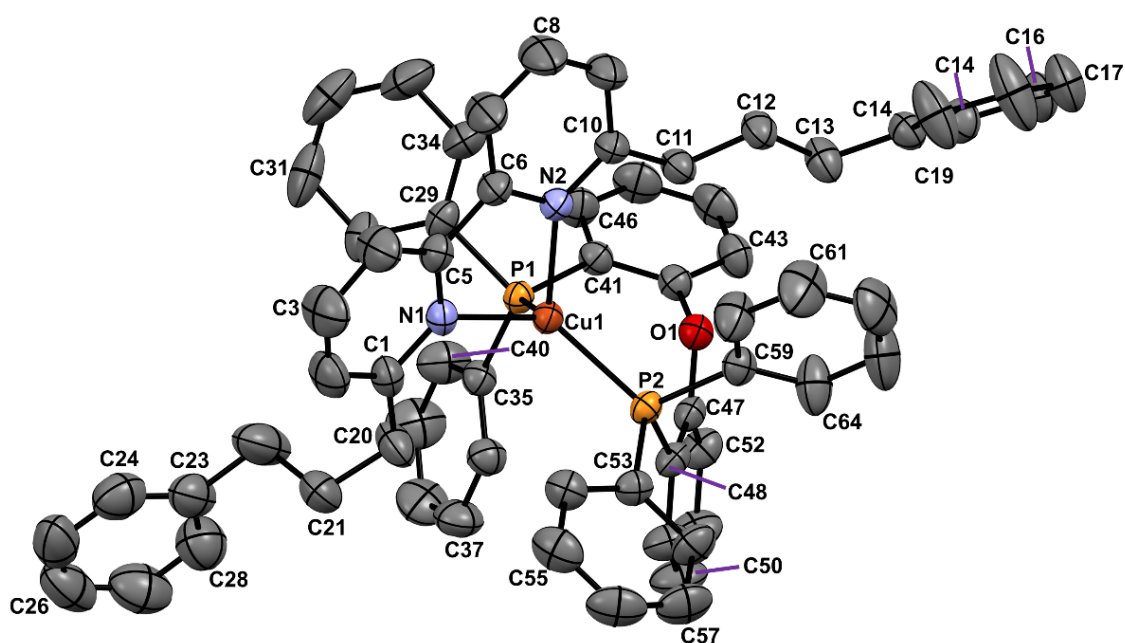


Fig. S138 Structure of the $[\text{Cu}(\text{POP})((3\text{-PhPr})_2\text{bpy})]^+$ cation in $[\text{Cu}(\text{POP})((3\text{-PhPr})_2\text{bpy})][\text{PF}_6] \cdot 0.5\text{CH}_2\text{Cl}_2 \cdot 0.5\text{Et}_2\text{O}$. H atoms and solvent molecules are omitted and ellipsoids are plotted at 50% probability level. Selected bond parameters: $\text{Cu1-P2} = 2.2619(5)$, $\text{Cu1-P1} = 2.2973(6)$, $\text{Cu1-N2} = 2.102(1)$, $\text{Cu1-N1} = 2.105(2)$, $\text{C42-O1} = 1.404(2)$, $\text{C47-O1} = 1.385(2)$ Å; $\text{P2-Cu1-P1} = 114.43(2)$, $\text{P2-Cu1-N2} = 118.38(4)$, $\text{P1-Cu1-N2} = 107.36(4)$, $\text{P2-Cu1-N1} = 121.83(4)$, $\text{P1-Cu1-N1} = 109.88(4)$, $\text{N2-Cu1-N1} = 79.81(6)$, $\text{C42-O1-C47} = 117.1(1)^\circ$.

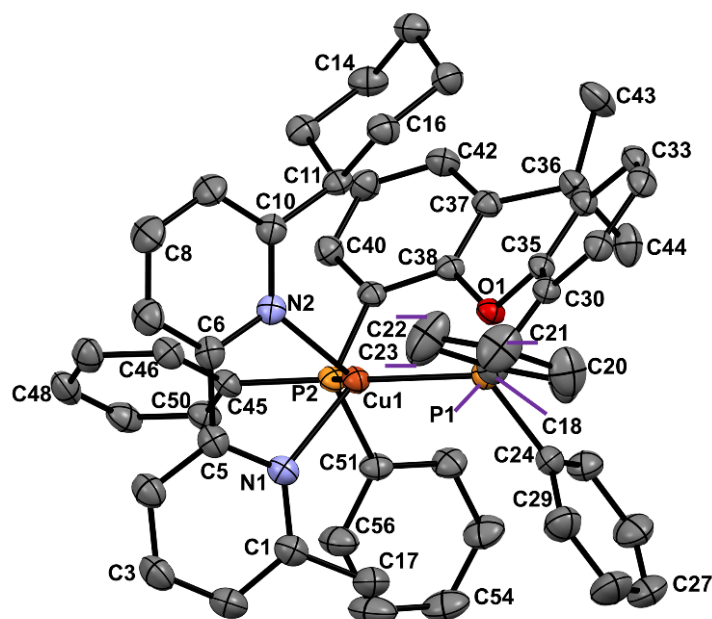


Fig. S139 Structure of the $[\text{Cu}(\text{xantphos})(6\text{-Cy-6'-Mebpy})]^+$ cation in $[\text{Cu}(\text{xantphos})(6\text{-Cy-6'-Mebpy})][\text{PF}_6] \cdot 0.75\text{Et}_2\text{O} \cdot 0.5\text{H}_2\text{O}$. H atoms and solvent molecules are omitted and ellipsoids are plotted at 50% probability level. Selected bond parameters: $\text{Cu1-P2} = 2.2988(7)$, $\text{Cu1-P1} = 2.2794(6)$, $\text{Cu1-N2} = 2.090(3)$, $\text{Cu1-N1} = 2.109(2)$, $\text{C35-O1} = 1.394(3)$, $\text{C38-O1} = 1.392(3)$ Å; $\text{P2-Cu1-P1} = 119.35(3)$, $\text{P2-Cu1-N2} = 111.21(6)$, $\text{P1-Cu1-N2} = 116.76(6)$, $\text{P2-Cu1-N1} = 107.35(6)$, $\text{P1-Cu1-N1} = 115.52(6)$, $\text{N2-Cu1-N1} = 79.79(9)$, $\text{C35-O1-C38} = 114.9(2)^\circ$.

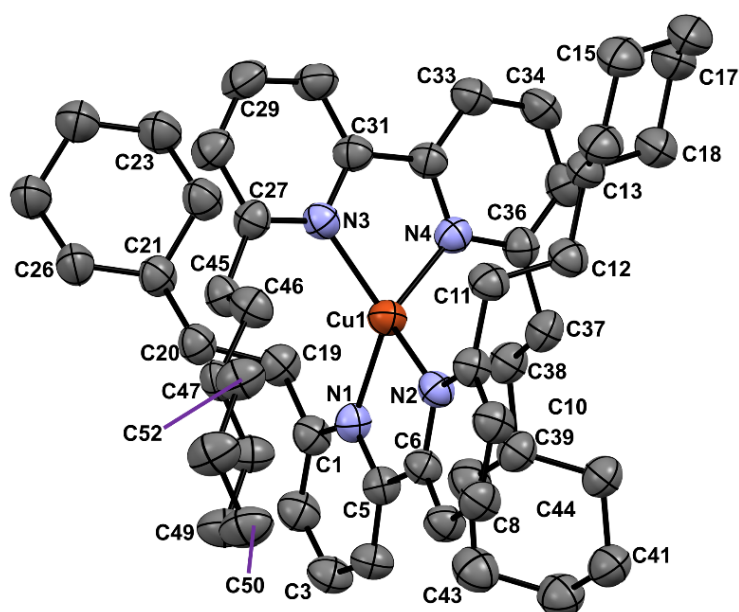


Fig. S140 Structure of the $[\text{Cu}((2\text{-CyEt})_2\text{bpy})_2]^+$ cation in $[\text{Cu}((2\text{-CyEt})_2\text{bpy})_2][\text{PF}_6]$. H atoms and solvent molecules are omitted and ellipsoids are plotted at 50% probability level. Selected bond parameters: $\text{Cu1-N4} = 2.041(4)$, $\text{Cu1-N3} = 2.040(3)$, $\text{Cu1-N2} = 2.046(3)$, $\text{Cu1-N1} = 2.028(4)$ Å; $\text{N4-Cu1-N3} = 81.5(1)$, $\text{N4-Cu1-N2} = 120.8(1)$, $\text{N3-Cu1-N2} = 123.1(1)$, $\text{N4-Cu1-N1} = 125.8(1)$, $\text{N3-Cu1-N1} = 129.7(1)$, $\text{N2-Cu1-N1} = 81.8(1)^\circ$.

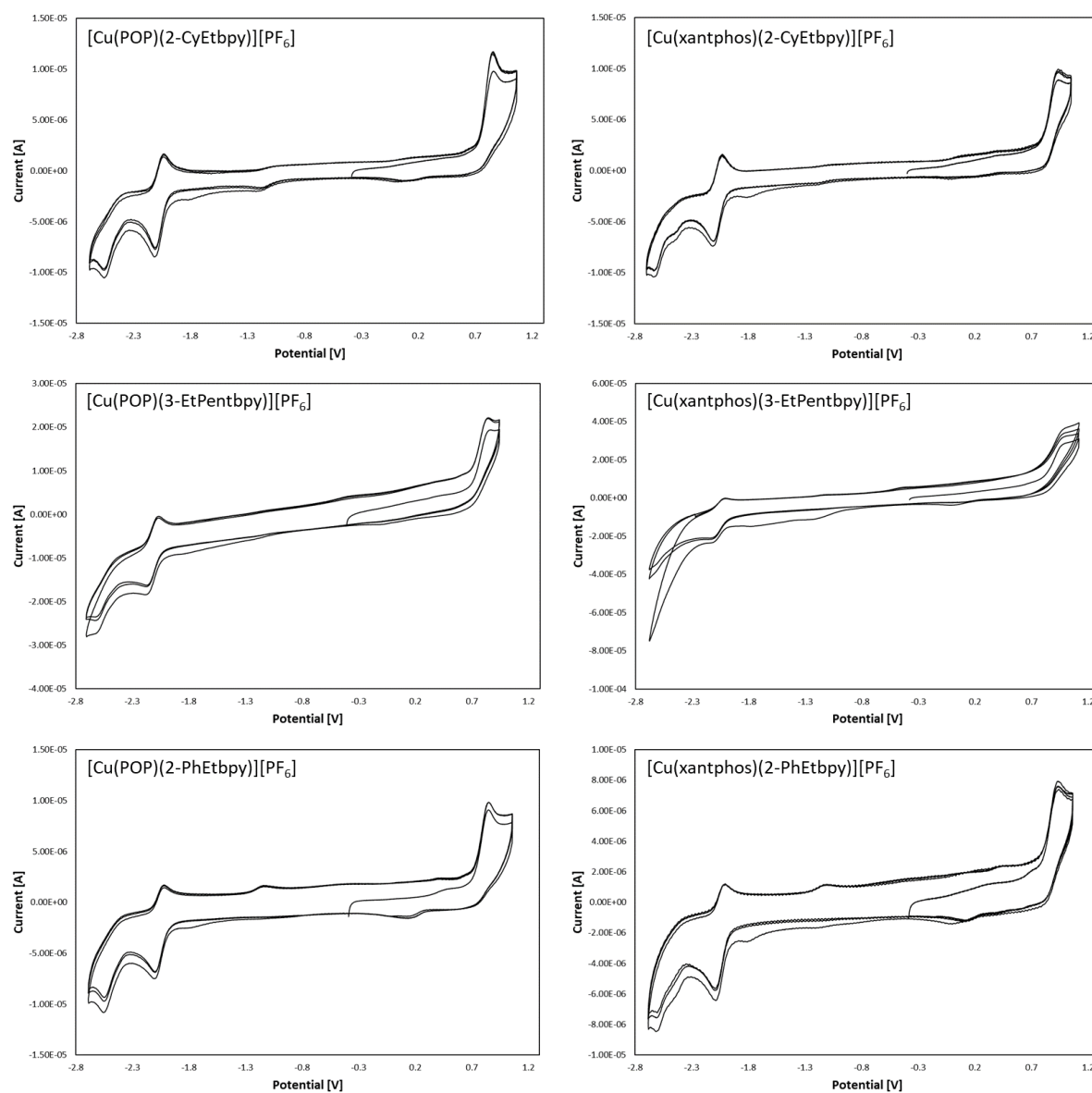


Fig. S141 Three consecutive scans in the cyclic voltammograms of $[\text{Cu}(\text{P}^*\text{P})(6\text{-CyEtbpy})][\text{PF}_6]$, $[\text{Cu}(\text{P}^*\text{P})(3\text{-EtPentbpy})][\text{PF}_6]$ and $[\text{Cu}(\text{P}^*\text{P})(2\text{-PhEtbpy})][\text{PF}_6]$ in propylene carbonate solution (ca. $10^{-4} \text{ mol dm}^{-3}$) 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 $\text{Fc}/\text{Fc}^+ = 0.0 \text{ V}$).

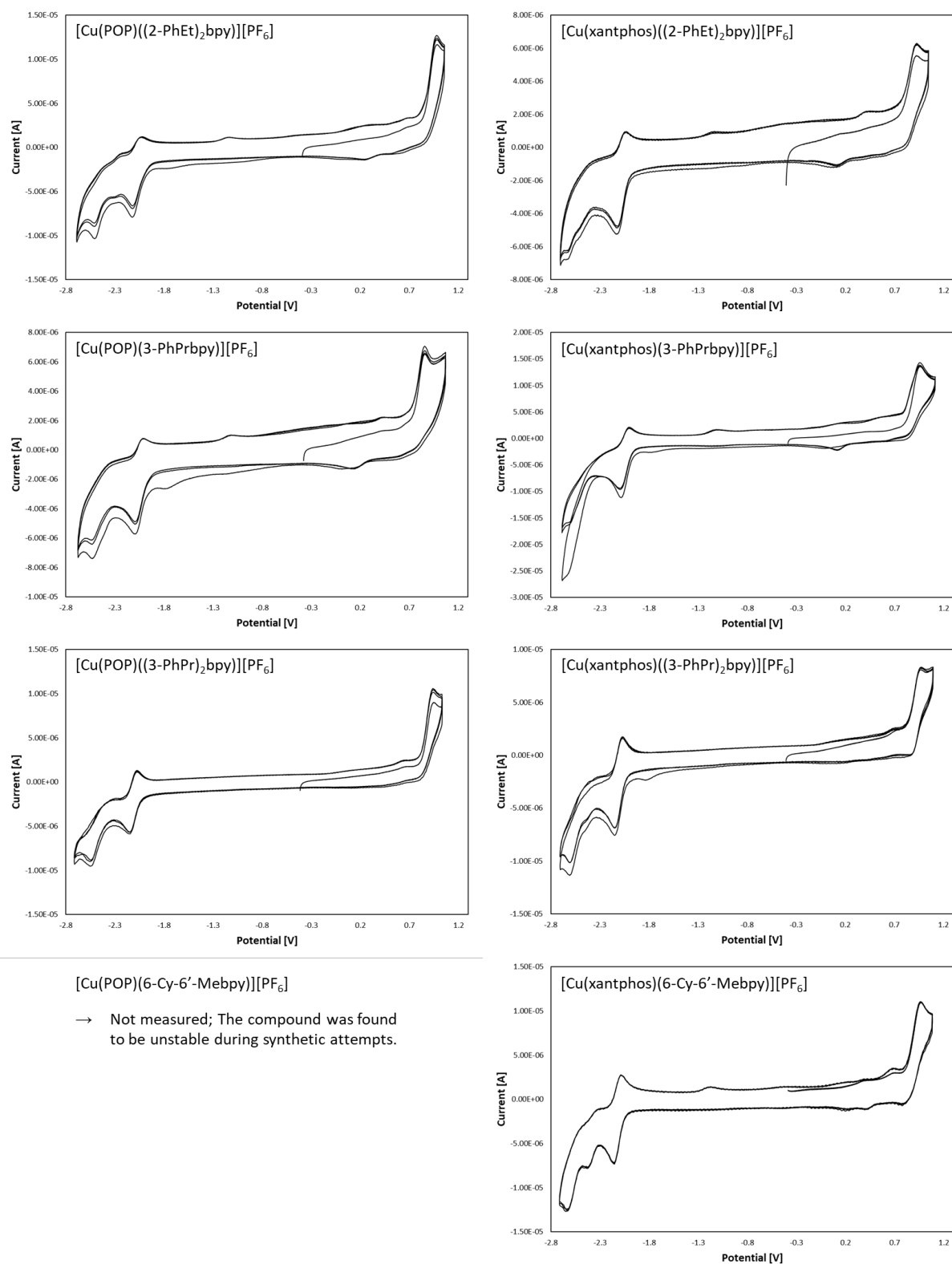


Fig. S142 Three consecutive scans in the cyclic voltammograms of [Cu(P⁺P)((2-PhEt)₂bpy)][PF₆], [Cu(P⁺P)(3-PhPrbpy)][PF₆], [Cu(P⁺P)((3-PhPr)₂bpy)][PF₆] and [Cu(P⁺P)(6-Cy-6'-Mebpy)][PF₆] in propylene carbonate solution (ca. 10⁻⁴ mol dm⁻³) with [nBu₄N][PF₆] as supporting electrolyte and a scan rate of 0.1 V s⁻¹ (referenced to internal Fc/Fc⁺ = 0.0 V).

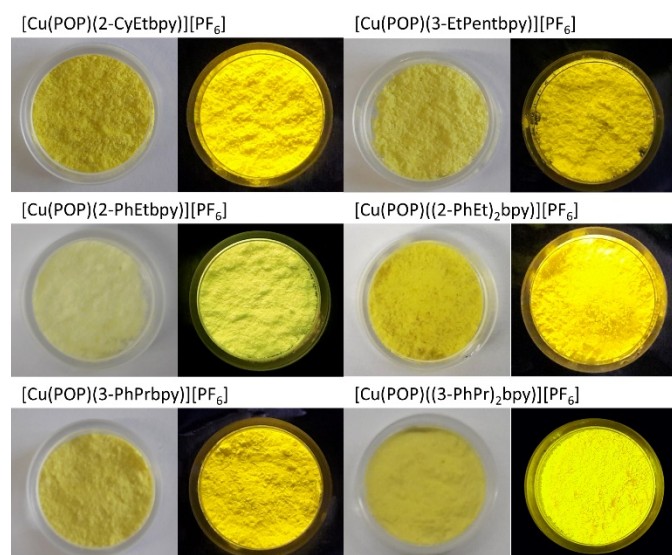


Fig. S143 Powder samples of $[\text{Cu}(\text{POP})(\text{N}^{\wedge}\text{N})][\text{PF}_6]$ complexes both under ambient light (left, white background) and under UV light ($\lambda_{\text{exc}} = 366 \text{ nm}$, right, dark background).

References

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- 2 C.-Y. Huang, J. Li, W. Liu and C.-J. Li, *Chem. Sci.*, 2019, **10**, 5018-5024.