Remote steric control of the tetrahedral coordination geometry around heteroleptic copper(I) bis(diimine) complexes

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Supporting information

Materials and Methods

All reagents and solvents were purchased from commercial sources and were used as received. The diaryl phenanthroline ligand was prepared following a previously published procedure [1]. The MnO_2 was from Honeywell Fluka (G1890). Dichloromethane was distilled from calcium hydride, THF and toluene from sodium/benzophenone ketyl. Most of the experiments were carried out under inert atmosphere by using standard Schlenk techniques. Chromatographic separations were performed using Merck silica gel (40-63 μm).

^{1}H and ^{13}C were performed on Bruker Avance 400, 500 or 600 MHz spectrometers equipped with a cryoprobe. $CDCl_3$ was used as a solvent and the spectra were recorded at 25 °C. Chemical shifts (δ (ppm)) are shown relative to TMS. UV-visible spectra were recorded on a Cary 5000 UV/vis/NIR double-beam spectrometer in dichloromethane. Emission and lifetime studies were carried out on a HORIBA scientific fluoromax spectrofluorometer in distilled dichloromethane. Lifetime studies were studies were carried out using a nanoLED at 456 nm and a colloidal silica suspension in water as a prompt. ESI MS were collected on a Bruker Daltonics MicroTOF and MALDI MS were collected on a Bruker Autoflex II TOF-TOF instrument in positive ionisation mode with dithranol as a matrix. Measurements were carried out by Stéphanie Coutin (Service de Spectrométrie de Masse, Institut de Chimie, Université de Strasbourg). Elemental analysis was performed on a ThermoFischer Scientific Flash2000 by the Service d'Analyses de l'Institut de Chimie de Strasbourg (Martine Heinrich, Noémie Bourgeois). Electrochemical measurements were carried out using a glassy carbon working electrode in distilled dichloromethane with NBu_4PF_6 (0.1 M) as the electrolyte and ferrocenium/ferrocene (Fc^+/Fc) couple as an internal reference. The three electrodes were connected to a computerised electrochemical device (Biologic SP-150). X-ray analysis was performed by Dr Lydia Karmazin and Corinne Bailly (Service de radiocristallographie, Institut de Chimie, Strasbourg) using a Bruker APEX II DUO Kappa-CCD diffractometer.

DFT Calculations

The calculations were performed with the ADF 2019 package at DFT level of theory using the B3LYP functional [2]. Scalar relativistic effects were included using zero order regular approximated (ZORA) Hamiltonian [3]. All atoms were described by the TZP basis set. Solvent corrections (dichloromethane) were introduced through a PCM (Polarisable Continuum Model). Van der Waals forces were described through Grimme's corrections [4]. All structures were fully optimized. Absorption spectra were computed by mean of TD-DFT on these optimized structures and spin-orbit coupling added by perturbation of the TD-DFT results. Excited state geometries were optimized in the same conditions. The nature of the computed electronic transitions was determined by mean of THEOdore analysis [5] of the TD-DFT results.

A second set of calculations were performed with GAUSSIAN 09 (version D.01) at DFT level of theory (B3LYP functional). All atoms were described by 6-31+G** basis set. Solvent corrections (dichloromethane) were introduced through a PCM (Polarisable Continuum Model). Van der Waals forces were described through Grimme's corrections. The structures were fully optimised. Non-covalent interactions were studied by mean of NCIPlot [6] performed on the wavefunction of the optimized structures.

References

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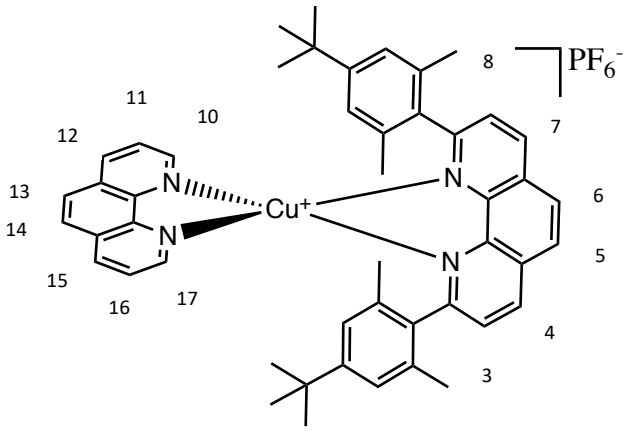
3. ADF, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands. Available online: https://www.scm.com/doc/ADF/index.html (accessed on 1 June 2019).
4. Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*, 154104.
5. Plasser,F. *J. Chem. Phys*. **2020**, *152*, 08418.
6. Contreras-Garcia, J.; Johnson, E. R.; Keinan, S.; Chaudret, R.; Piquemal, J.-P.; Beratan, D. N.; Yang, W. *J. Chem. Theory Comput.* **2011**, *7*, 625-632.

[Cu(2,9-(4-(*tert*-butyl)-2,6-dimethylphenyl)-1,10-phenanthroline)(1,10-phenanthroline)]PF_6 (**C1**)



Chemical formula: $C_{48}H_{48}CuF_6N_4P$

Exact mass: 888.28

Molecular weight: 889.45

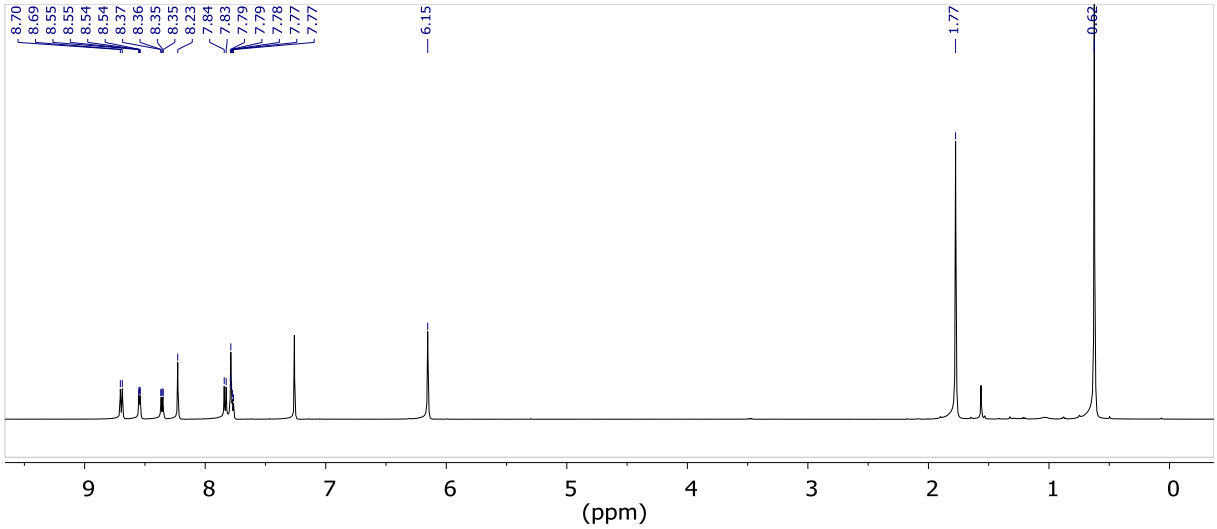
Under argon and at rt, to a solution of $[Cu(CH_3CN)_4]PF_6$ (58 mg, 0.16 mmol) in dichloromethane (20 mL) was added *via* cannula transfer a degassed solution of ligand **L1** (86 mg, 0.17 mmol) in dichloromethane (10 mL). The solution turned yellow and was stirred for 1 h. A solution of 1,10-phenanthroline (28 mg, 0.16 mmol) in degassed dichloromethane (10 mL) was then added *via* cannula transfer, rendering the solution red. The solution was once again stirred for 1 h. Solvent was then evaporated and the solid was dissolved in the minimum amount of dichloromethane and precipitated by addition of diethyl ether/pentane (1:1) to afford complex **C1** (98 mg, 0.11 mmol, 69%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 (d, J = 8.0 Hz, 2H, H_4 and H_7), 8.55 (dd, J = 4.7, 1.5 Hz, 2H, H_{10} and H_{17}), 8.36 (dd, J = 8.1, 1.5 Hz, 2H, H_{12} and H_{15}), 8.23 (s, 2H, H_5 and H_6), 7.83 (d, J = 8.0 Hz, 2H, H_3 and H_8), 7.78 (dd, J = 4.7, 8.1, 2H, H_{11} and H_{16}), 7.79 (s, 2H, H_{13} and H_{14}), 6.15 (s, 4H, H_{Ar}), 1.77 (s, 12H, H_{Me}), 0.62 (s, 18H, H_{tBu}).

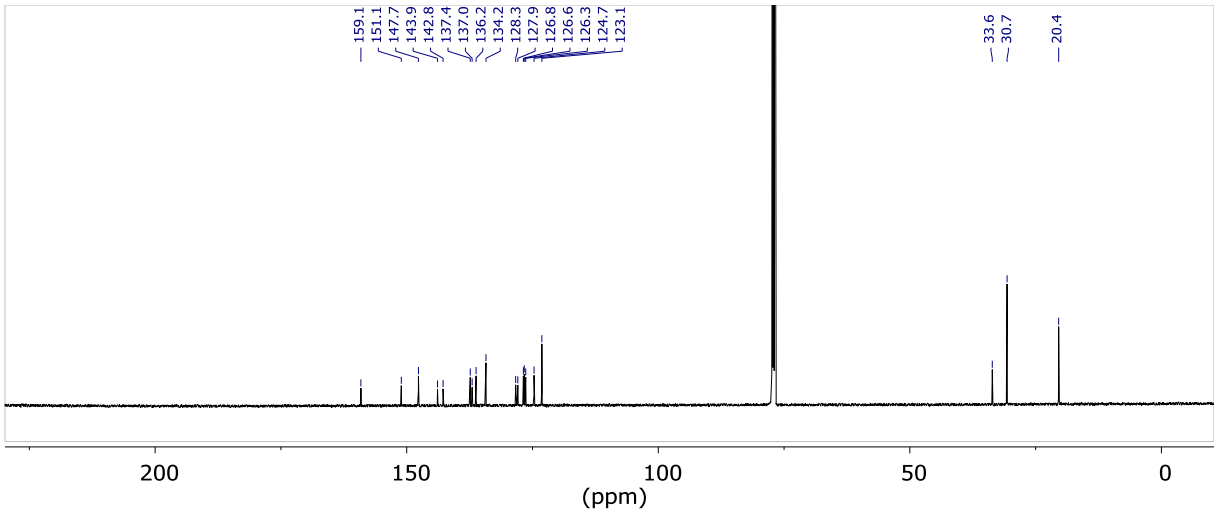
^{13}C NMR (125 MHz, $CDCl_3$) δ 159.1, 151.1, 147.7 (CH), 143.9, 142.8, 137.4 (CH), 137.0, 136.2 (CH), 134.2, 128.3, 127.9, 126.8 (CH), 126.6 (CH), 126.3 (CH), 124.7 (CH), 123.1 (CH), 33.6, 30.7 (CH_3), 20.4 (CH_3).

Anal. calcd for $C_{48}H_{48}CuF_6N_4P$: C, 64.82; H, 5.44; N, 6.30. Found: C, 64.59; H, 5.47; N, 6.22.

C1: ^{1}H NMR



C1: ^{13}C NMR



C1: DEPT 135

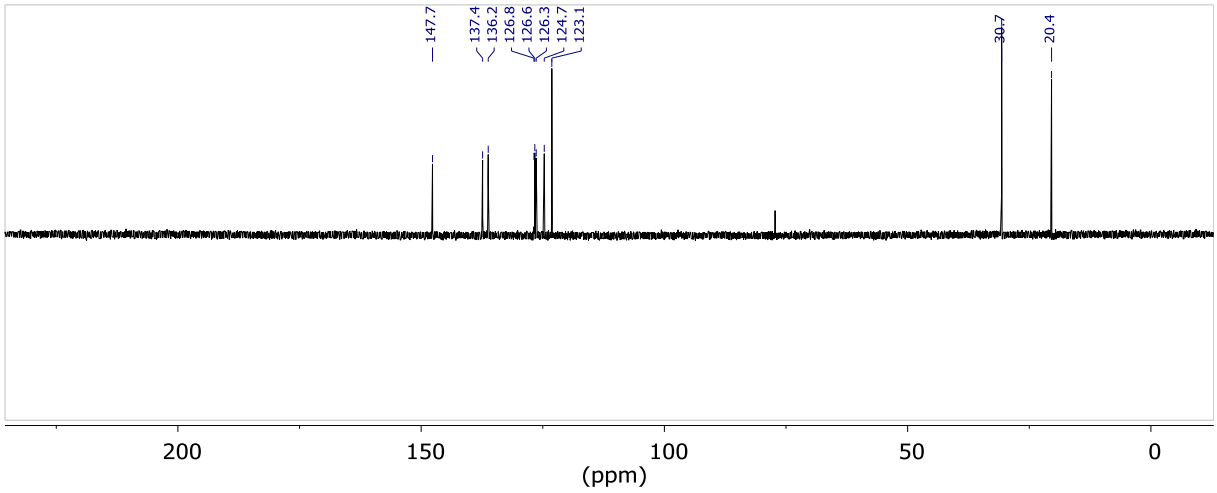
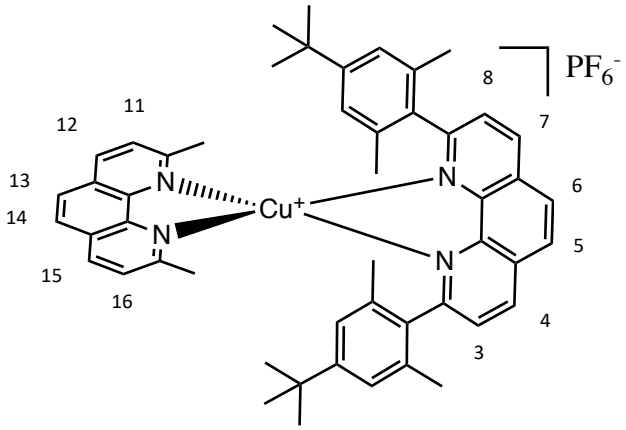


Figure S1: ^{1}H, ^{13}C and DEPT NMR spectra of complex **C1**.

[Cu(2,9-(4-(*tert*-butyl)-2,6-dimethylphenyl)-1,10-phenanthroline)(2,9-dimethyl-1,10-phenanthroline)]PF_6 (**C2**)



Chemical formula: $C_{50}H_{52}CuF_6N_4P$

Exact mass: 916.31

Molecular weight: 917.50

Complex **C2** was synthesised using the same method as for **C1**, with the addition of 2,9-dimethyl-1,10-phenanthroline (29 mg, 0.14 mmol) as opposed to 1,10-phenanthroline to yield **C2** (90 mg, 0.098 mmol, 61%).

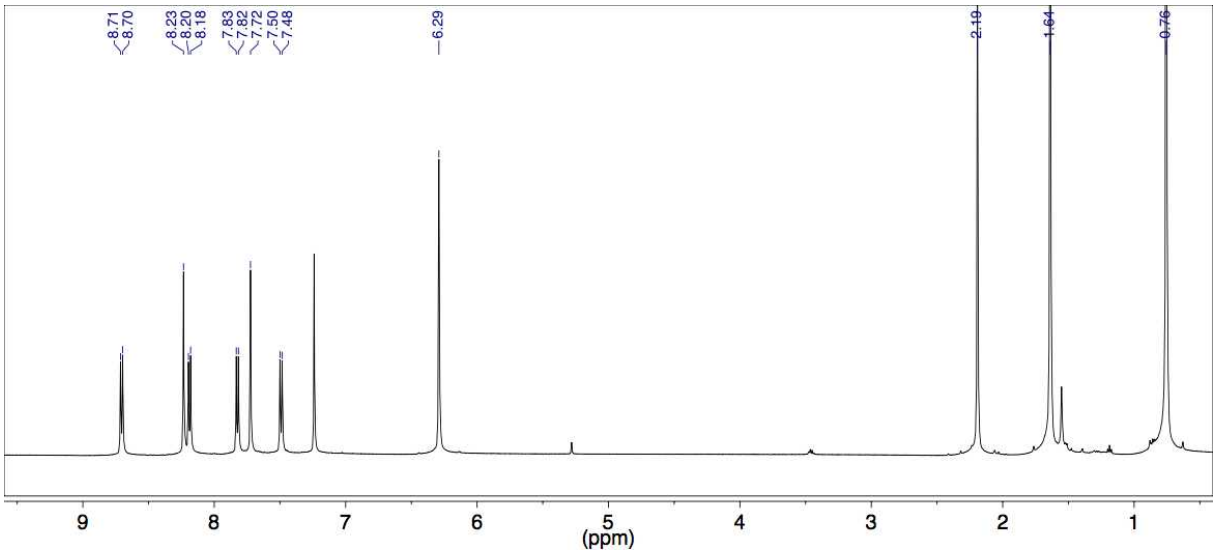
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.71 (d, J = 8.2 Hz, 2H, H_4 and H_7), 8.23 (s, 2H, H_5 and H_6), 8.19 (d, J = 8.2 Hz, 2H, H_{12} and H_{15}), 7.82 (d, J = 8.2 Hz, 2H, H_{11} and H_{16}), 7.72 (s, 2H, H_{13} and H_{14}), 7.49 (d, J = 8.2 Hz, 2H, H_3 and H_8), 6.29 (s, 4H, H_{Ar}), 2.19 (s, 6H, H_{Me}), 1.64 (s, 12H, H_{Me}), 0.76 (s, 18H, H_{tBu}).

^{13}C NMR (500 MHz, $CDCl_3$) δ 159.5, 156.8, 151.3, 143.8, 142.4, 137.6 (CH), 136.6, 136.6 (CH), 134.3, 128.2, 127.1 (CH), 126.9 (CH), 126.7, 125.6 (CH), 124.8 (CH), 123.3 (CH), 33.8, 30.8 (CH_3), 26.5 (CH_3), 20.2 (CH_3).

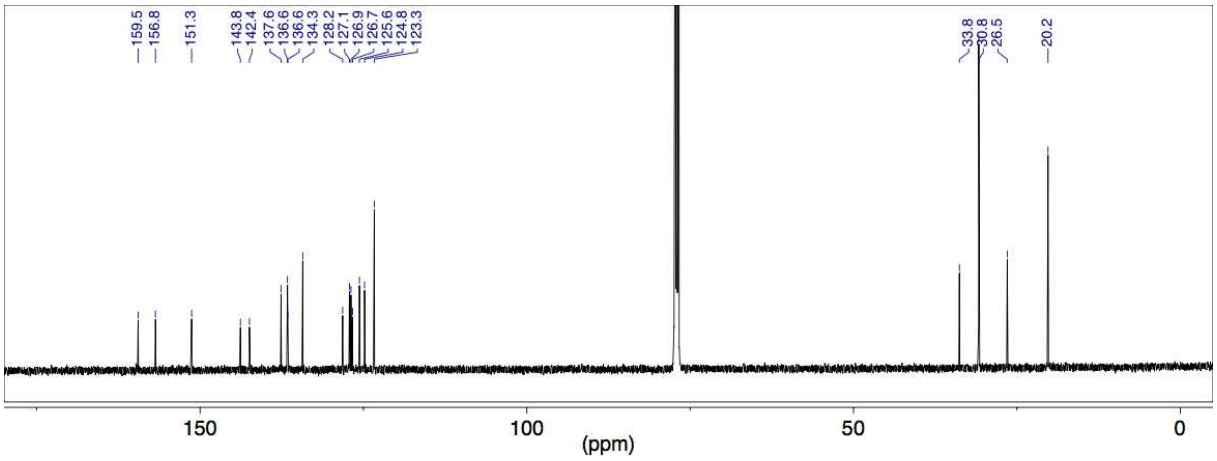
Anal. calcd for $C_{50}H_{52}CuF_6N_4P$: C, 65.45; H, 5.21; N, 6.11. Found: C, 65.34; H, 5.75; N, 6.08.

Crystal data from Et_2O/CH_2Cl_2 for **C2**. $C_{54}H_{62}CuF_6N_4P$, M = 991.58 g.mol^{-1} monoclinic, space group P21/c, a = 13.4772(6) Å, b = 19.4894 (8) Å, c = 19.6875(9) Å, α = 90°, β = 105.2060(10)°, γ = 103.534(2)°, V = 5027.6(4) Å^3, Z = 4, ρ_{calc} = 1.310 Mg/m^3, T = 173(2) K, MoK$_\alpha$ = 0.71073 Å, 1.873670 < θ < 29.204, transmission factors: T_{min}/T_{max} = 0.6888/0.7458, 99929 reflections measured, 13604 unique reflections, R_1 = 0.0731, wR_2 = 0.1854, GoF = 1.038.

C2: ^{1}H NMR



C2: ^{13}C NMR



C2: DEPT 135

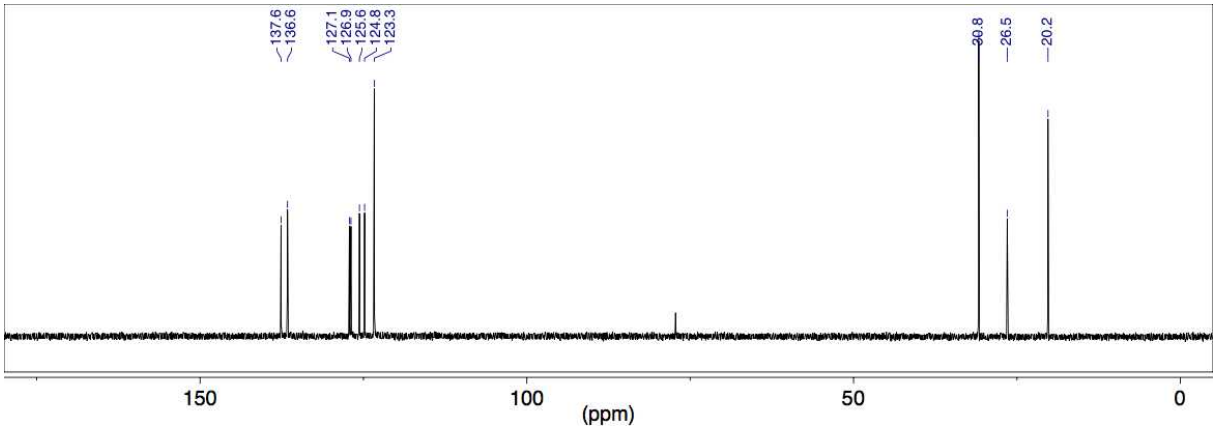
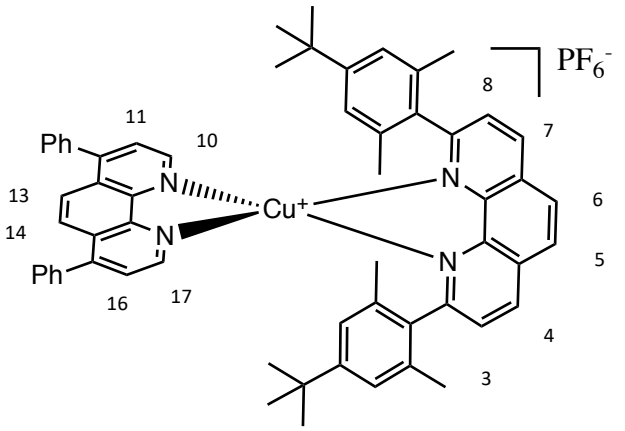


Figure S2: ^{1}H, ^{13}C and DEPT NMR spectra of complex **C2**.

[Cu(2,9-(4-(*tert*-butyl)-2,6-dimethylphenyl)-1,10-phenanthroline)(bathophenanthroline)]PF_6 (**C3**)



Chemical formula: $C_{60}H_{56}CuF_6N_4P$

Exact mass: 1040.34

Molecular weight: 1041.65

Complex **C3** was synthesised using the same method as for **C1**, with the addition of bathophenanthroline (57 mg, 0.17 mmol) as opposed to 1,10-phenanthroline. Complex **C3** was isolated as orange-red plates (120 mg, 0.12 mmol, 75%).

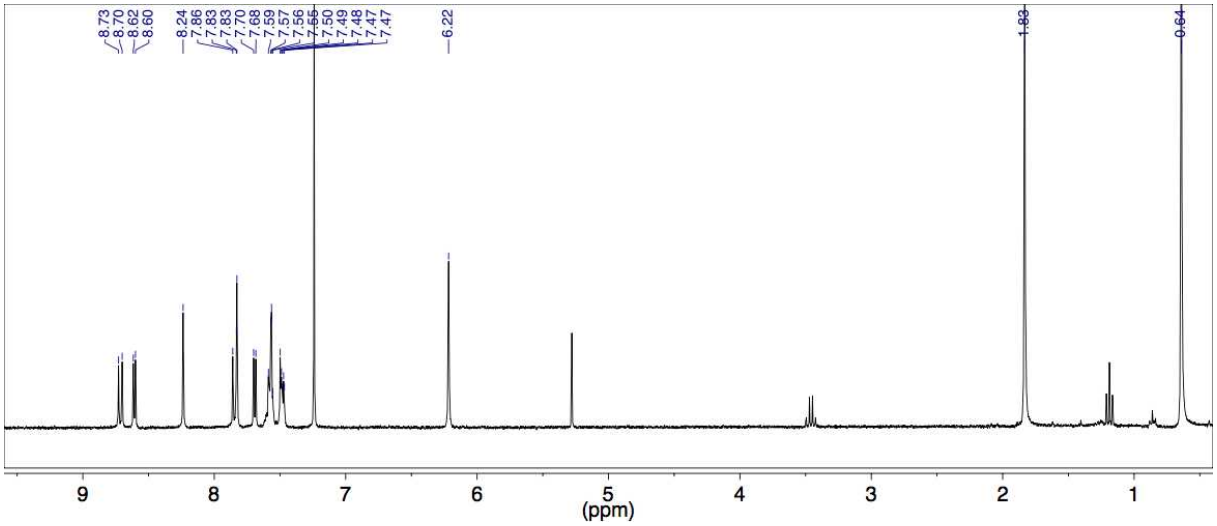
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.72 (d, J = 8.3 Hz, 2H, H_4 and H_7), 8.62 (d, J = 4.9 Hz, 2H, H_{10} and H_{17}), 8.24 (s, 2H, H_5 and H_6), 7.84 (d, J = 8.3 Hz, 2H, H_3 and H_8), 7.83 (s, 2H, H_{13} and H_{14}), 7.69 (d, J = 4.9 Hz, 2H, H_{11} and H_{16}), 7.60 – 7.55 (m, 6H, H_{meta} and H_{para}), 7.51 – 7.45 (m, 4H, H_{ortho}), 6.22 (s, 4H, H_{Ar}), 1.83 (s, 12H, H_{Me}), 0.64 (s, 18H, H_{tBu}).

^{13}C NMR (125 MHz, $CDCl_3$) δ 158.9, 150.9, 148.7, 147.4 (CH), 143.9, 143.4, 137.5 (CH), 137.4, 136.3, 134.5 (CH), 129.5 (CH), 129.4, 129.1 (CH), 128.0, 126.9 (CH), 126.3 (CH), 126.0, 124.9 (CH), 124.3 (CH), 123.1 (CH), 33.7, 30.8 (CH_3), 20.6 (CH_3).

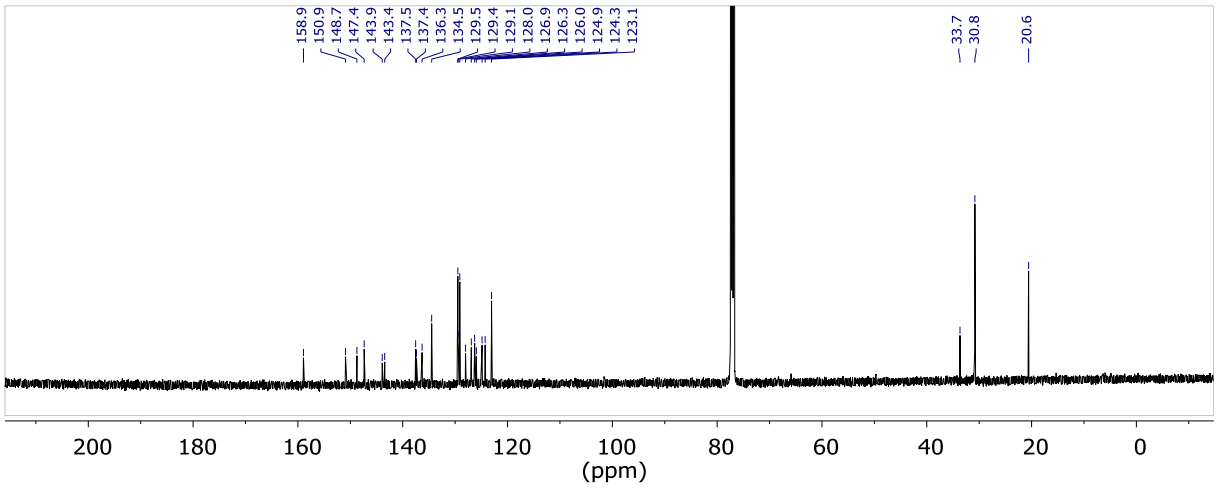
Anal. calcd for $C_{60}H_{56}CuF_6N_4P.H_2O$: C, 67.68; H, 5.52; N, 5.29. Found: C, 67.68; H, 5.33; N, 5.27.

Crystal data from Et_2O/CH_2Cl_2 for **C3**. $C_{60}H_{56}CuF_6N_4P$, M = 1041.59 g.mol^{-1} monoclinic, space group P21/c, a = 10.9274(3) Å, b = 22.7485(6) Å, c = 21.5054(6) Å, α = 90°, β = 107.212(2) °, γ = 90°, V = 5106.4(2) Å^3, Z = 4, ρ_{calc} = 1.355 Mg/m^3, T = 173(2) K, MoK$_\alpha$ = 1.54178 Å, 2.898 < θ < 66.688, transmission factors: T_{min}/T_{max} = 0.6010/0.7528, 65968 reflections measured, 8989 unique reflections, R_1 = 0.0658, wR_2 = 0.1478, GoF = 1.028.

C3: ^{1}H NMR



C3: ^{13}C NMR



C3: DEPT 135

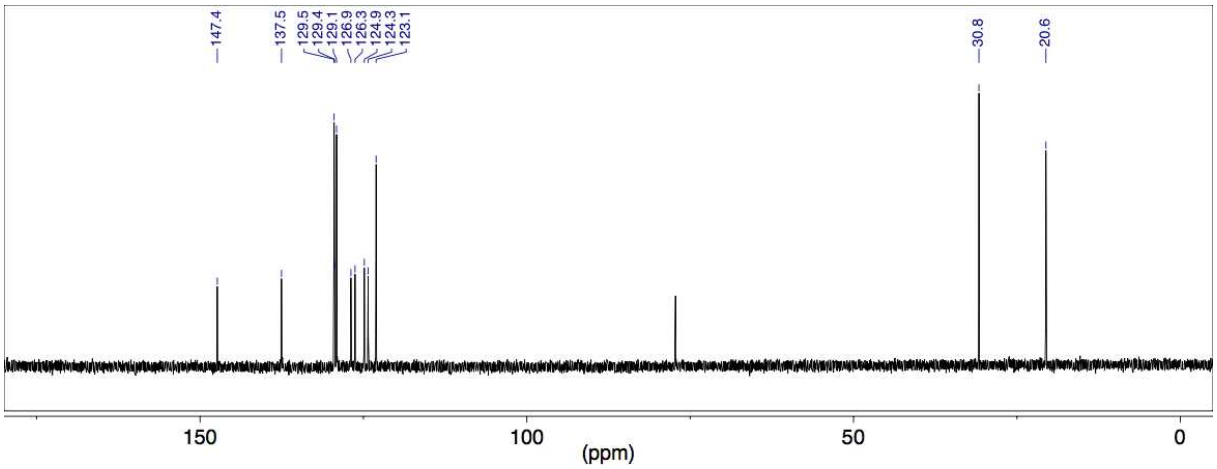
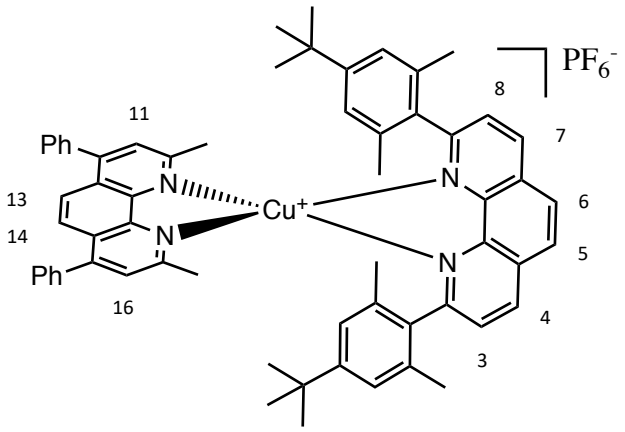


Figure S3: ^{1}H, ^{13}C and DEPT NMR spectra of complex **C3**.

[Cu(2,9-(4-(*tert*-butyl)-2,6-dimethylphenyl)-1,10-phenanthroline)(bathocuproine)]PF_6 (**C4**)



Chemical formula: $C_{62}H_{60}CuF_6N_4P$

Exact mass: 1068.38

Molecular weight: 1069.70

Complex **C4** was synthesised using the same method as for **C1**, with the addition of bathocuproine (50 mg, 0.14 mmol) as opposed to 1,10-phenanthroline to yield **C4** (86 mg, 0.080 mmol, 50%).

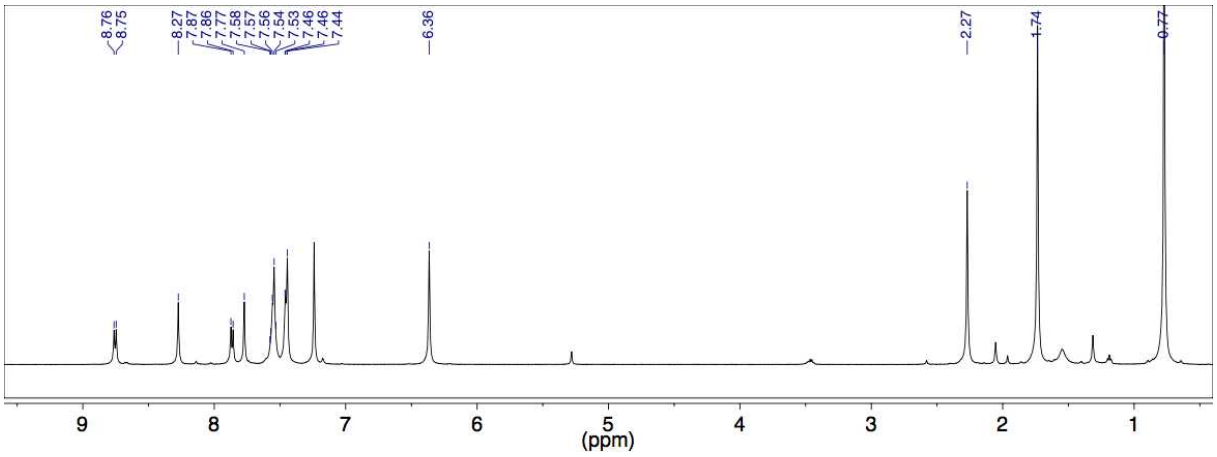
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.75 (d, *J* = 8.2 Hz, 2H, H_4 and H_7), 8.27 (s, 2H, H_5 and H_6), 7.86 (d, *J* = 8.2 Hz, 2H, H_3 and H_8), 7.77 (s, 2H, H_{11} and H_{16}), 7.56 - 7.44 (m, 12H, H_{ph}, H_{13} and H_{14}), 6.36 (s, 4H, H_{Ar}), 2.27 (s, 6H, H_{Me}), 1.74 (s, 12H, H_{Me}), 0.77 (s, 18H, H_{tBu}).

^{13}C NMR (125 MHz, $CDCl_3$) δ 159.3, 156.3, 151.2, 148.9, 143.8, 143.2, 137.8 (CH), 136.8, 136.5, 134.5, 129.5 (CH), 129.3 (CH), 129.0 (CH), 128.3, 127.3 (CH), 126.9 (CH), 125.1 (CH), 124.5, 123.3 (CH), 123.3 (CH), 33.8, 31.0 (CH_3), 26.8 (CH_3), 20.4 (CH_3).

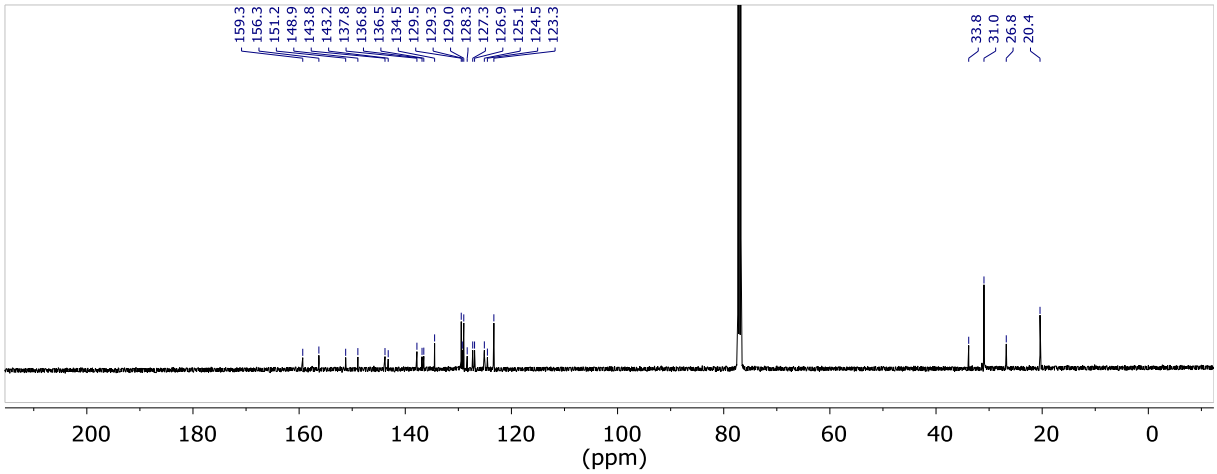
MS ESI: calcd for $C_{62}H_{60}CuN_4$ $(M - PF_6)^+$ 923.41; obsd 923.42.

Crystal data from Et_2O/CH_2Cl_2 for **C4**. $C_{62}H_{60}CuF_6N_4P$, M = 1069.65 g.mol^{-1}, monoclinic, space group P21/c, *a* = 11.1445(5) Å, *b* = 21.9682(9) Å, *c* = 22.5256(9) Å, α = 90°, β = 108.285(3)°, γ = 90°, V = 5236(4) Å^3, Z = 4, ρ_{calc} = 1.357 Mg/m^3, T = 173(2) K, MoK_α = 0.71073, 2.4390 < θ < 24.30, transmission factors: T_{min}/T_{max} = 0.6331/0.7456, 12676 reflections measured, 7892 unique reflections, R_1 = 0.0564, wR_2 = 0.1135, GoF = 1.050.

C4: ^{1}H NMR



C4: ^{13}C NMR



C4: DEPT 135

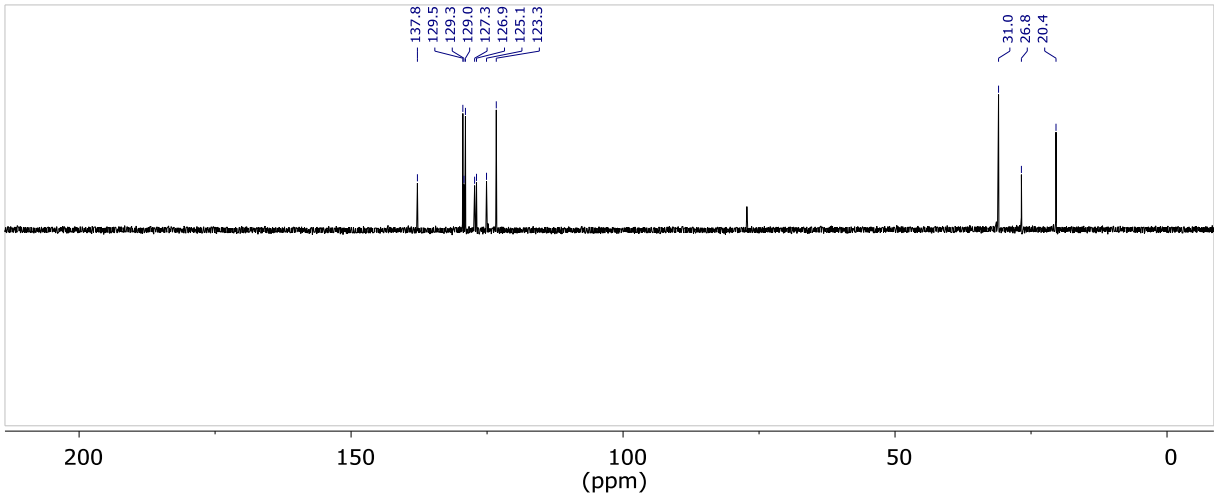
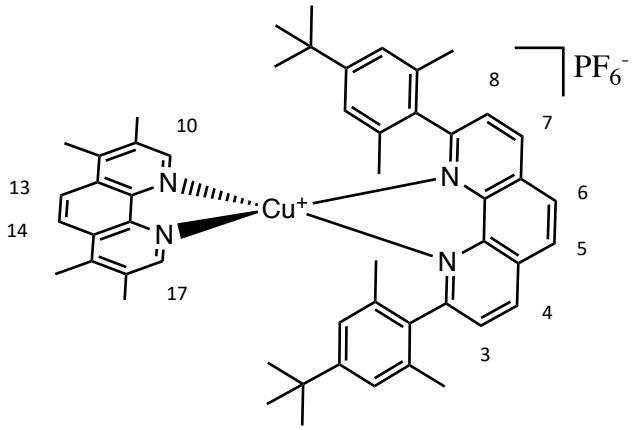


Figure S4: ^{1}H, ^{13}C and DEPT NMR spectra of complex **C4**.

Cu(2,9-(4-(*tert*-butyl)-2,6-dimethylphenyl)-1,10-phenanthroline)(3,4,7,8-tetramethyl-1,10-phenanthroline)]PF_6 (**C5**)



Chemical formula: $C_{52}H_{56}CuF_6N_4P$

Exact mass: 944.34

Molecular weight: 945.56

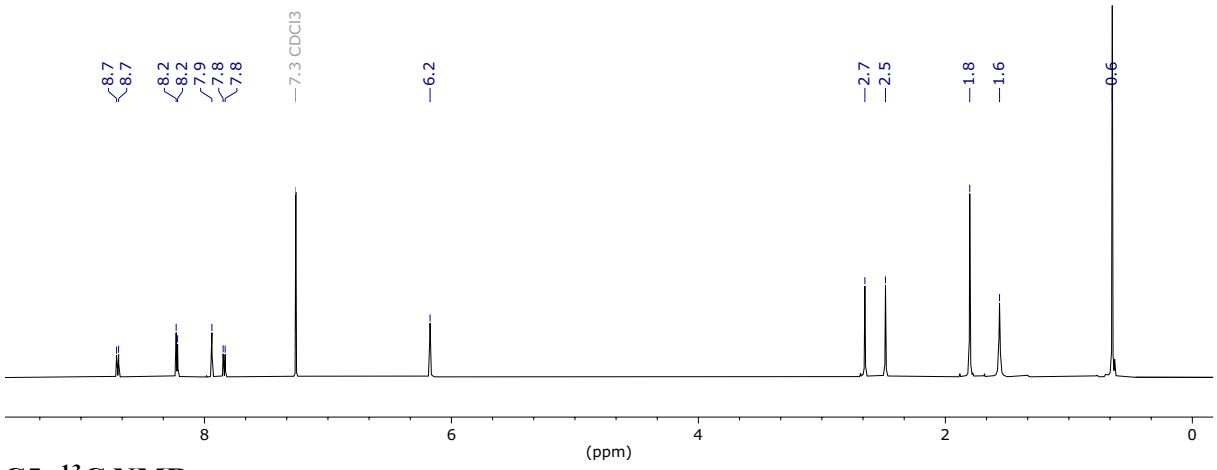
Complex **C5** was synthesised using the same method as for **C1**, with the addition of 3,4,5,6-tetramethyl-1,10-phenanthroline (40 mg, 0.17 mmol) as opposed to 1,10-phenanthroline to yield **C5** (127 mg, 0.13 mmol, 83%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 (d, J = 8.2 Hz, 2H, H_4 and H_7), 8.23 (s, 2H, H_{10} and H_{17}), 8.22 (s, 2H, H_5 and H_6), 7.94 (s, 2H, H_{13} and H_{14}), 7.84 (d, J = 8.2 Hz, 2H, H_3 and H_8), 6.17 (s, 4H, H_{Ar}), 2.65 (s, 6H, H_{Me} of phenanthroline), 2.49 (s, 6H, H_{Me} of phenanthroline), 1.80 (s, 12H, H_{Me} of aryl), 0.65 (s, 18H H_{tBu}).

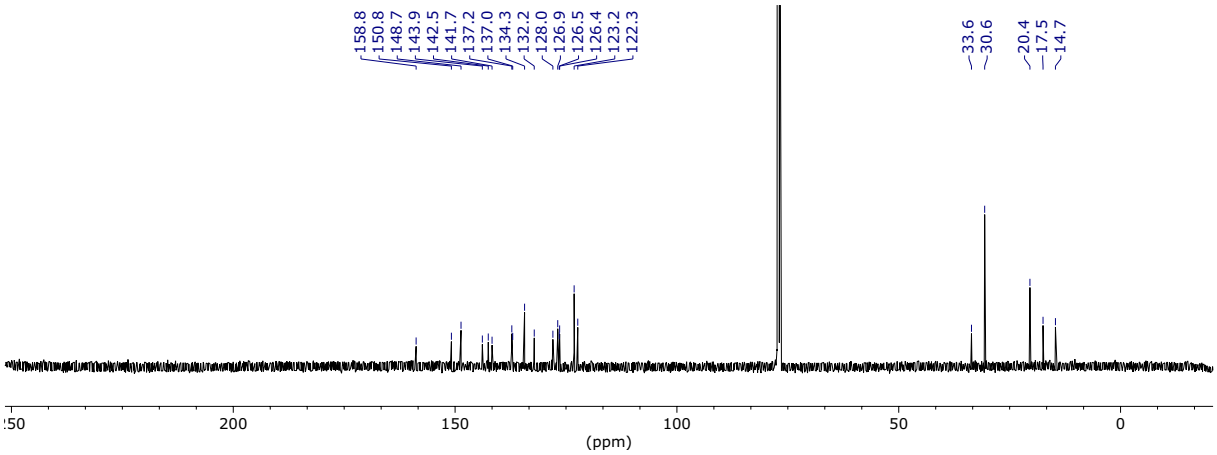
^{13}C NMR (125 MHz, $CDCl_3$) δ 158.8, 150.8, 148.7 (CH), 143.9, 142.5, 141.7, 137.2 (CH), 137.0, 134.3, 132.2, 128.0, 126.9 (CH), 126.5, 126.4 (CH), 123.2 (CH), 122.3 (CH), 33.6, 30.6 (CH_3), 20.4 (CH_3), 17.5 (CH_3), 14.7 (CH_3).

MS ESI: calcd for $C_{52}H_{56}CuN_4$ $(M - PF_6)^+$ 799.38; obsd 799.38.

C5: ^{1}H NMR



C5: ^{13}C NMR



C5: DEPT

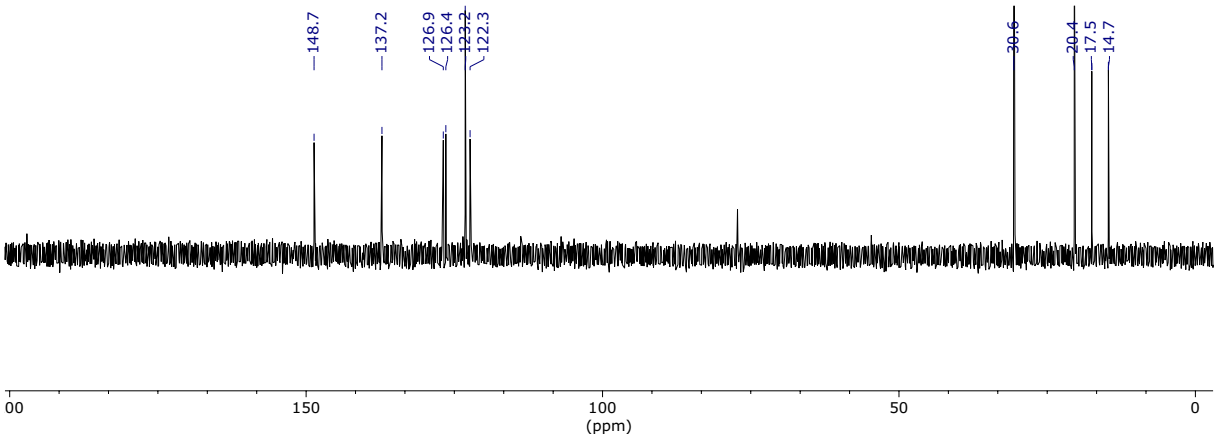
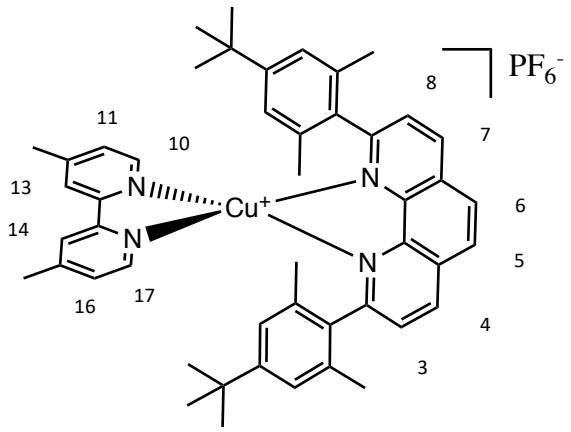


Figure S5: ^{1}H, ^{13}C and DEPT NMR spectra of complex **C5**.

[Cu(2,9-(4-(*tert*-butyl)-2,6-dimethylphenyl)-1,10-phenanthroline)(4,4'-dimethyl-2,2'-bipyridine)]PF_6 (**C6**)



Chemical formula: $C_{48}H_{52}CuF_6N_4P$

Exact mass: 892.31

Molecular weight: 893.48

Complex **C6** was obtained by using the procedure followed for **C1**, replacing 1,10-phenanthroline by 4,4'-dimethyl-2,2'-bipyridine (35 mg 0.17 mmol). Complex **C6** was isolated as an orange-red solid (96 mg, 0.13 mmol, 83%).

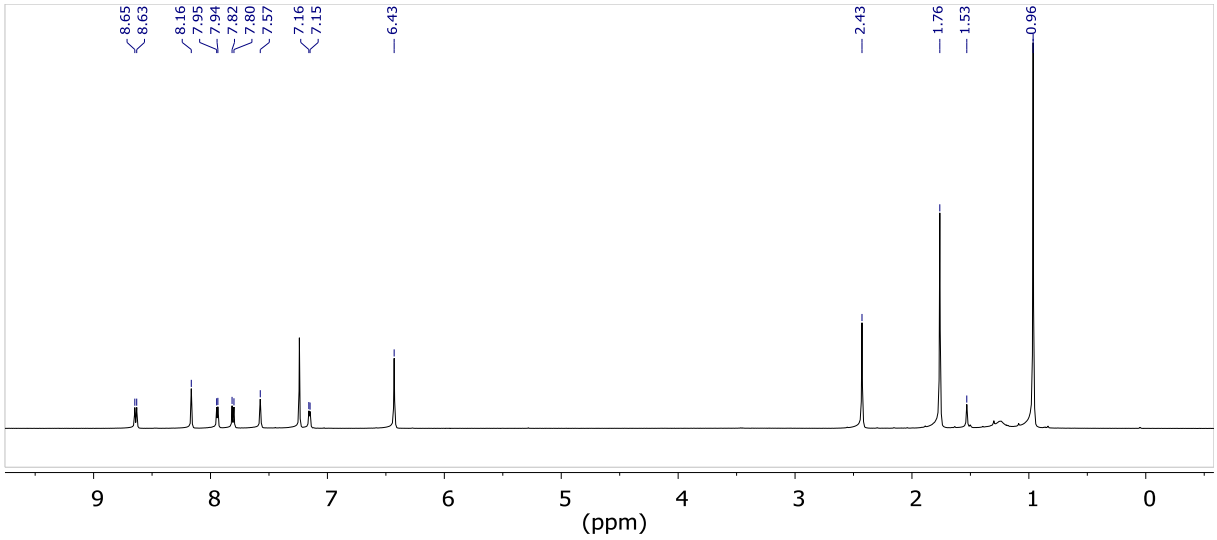
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.64 (d, *J* = 8.1 Hz, 2H, H_4 and H_7), 8.16 (s, 2H, H_5 and H_6), 7.94 (d, *J* = 5.2 Hz, 2H, H_{10} and H_{17}), 7.81 (d, *J* = 8.1 Hz, 2H, H_3 and H_8), 7.57 (s, 2H, H_{13} and H_{14}), 7.15 (d, *J* = 5.2 Hz, 2H, H_{11} and H_{16}), 6.43 (s, 4H, H_{Ar}), 2.43 (s, 6H, H_{Me}), 1.76 (s, 12H, H_{Me}), 0.96 (s, 18H, H_{tBu}).

^{13}C NMR (125 MHz, $CDCl_3$) δ 158.9, 151.1, 150.8, 148.9, 147.6 (CH), 143.8, 137.1 (CH), 137.0, 134.4, 127.8, 126.7 (CH), 126.4 (CH), 126.0 (CH), 123.6 (CH), 121.4 (CH), 34.0, 31.0 (CH_3), 21.3 (CH_3), 20.5 (CH_3).

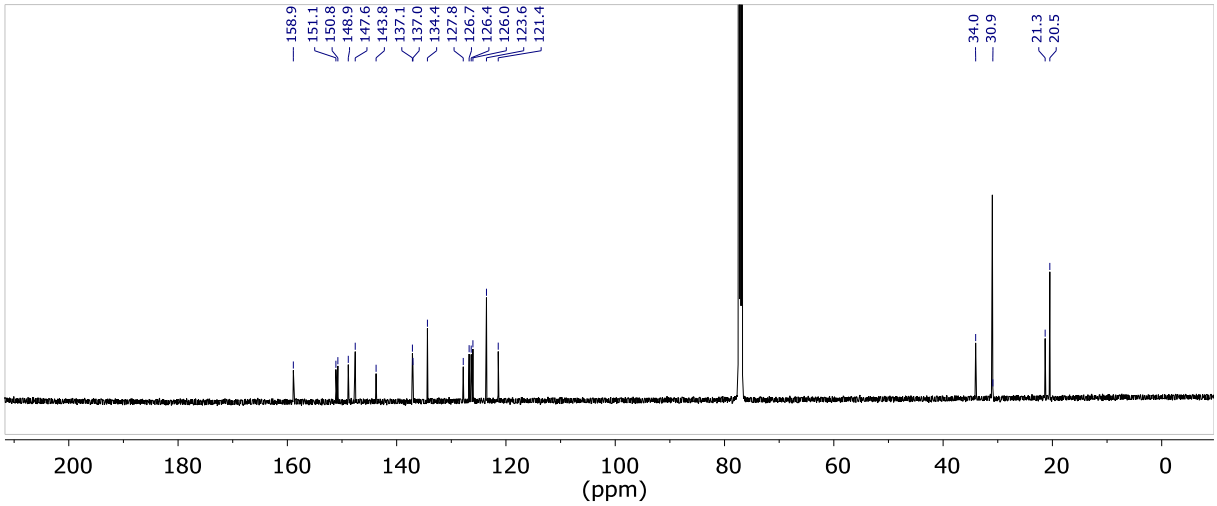
Anal. calcd for $C_{48}H_{52}CuF_6N_4P.H_2O$: C, 64.53; H, 5.87; N, 6.27. Found: C, 64.24; H, 5.87; N, 6.23.

Crystal data from Et_2O/CH_2Cl_2 for **C6**. $C_{48}H_{52}CuF_6N_4P$, M = 893.44 g.mol^{-1}, orthorhombic, space group Pbca, *a* = 20.1400(4) Å, *b* = 19.3338(4) Å, *c* = 23.5931(4) Å, α = 90°, β = 90°, γ = 90°, V = 9186.7(3) Å^3, Z = 8, ρ_{calc} = 1.292 Mg/m^3, T = 173(2) K, MoK_α = 0.71073, 3.68 < θ < 63.84, transmission factors: T_{min}/T_{max} = 0.5553/0.7528, 8127 reflections measured, 5749 unique reflections, R_1 = 0.0606, wR_2 = 0.1595, GoF = 1.048

C6: ^{1}H NMR



C6: ^{13}C NMR



C6: DEPT 135

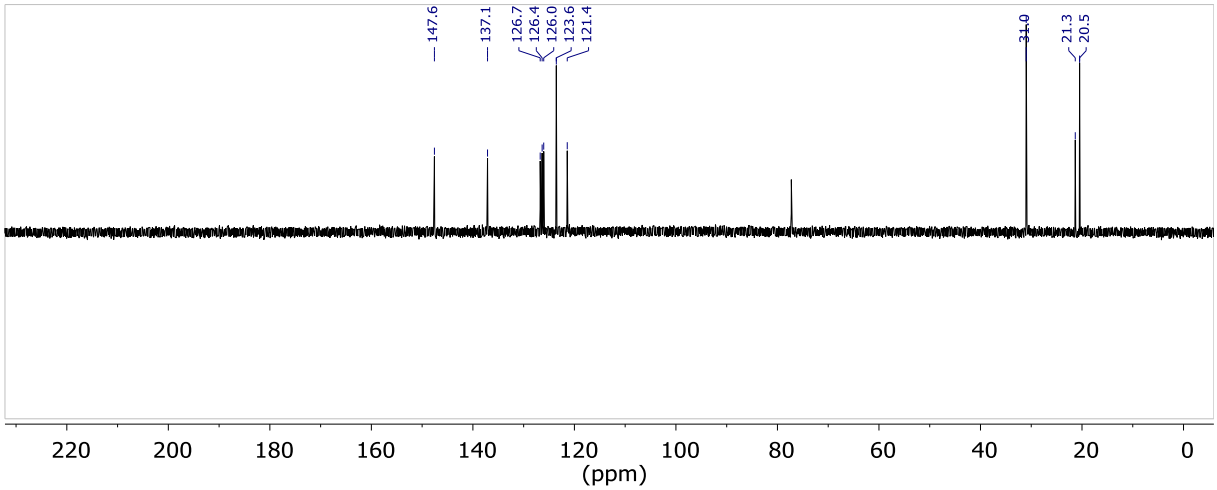
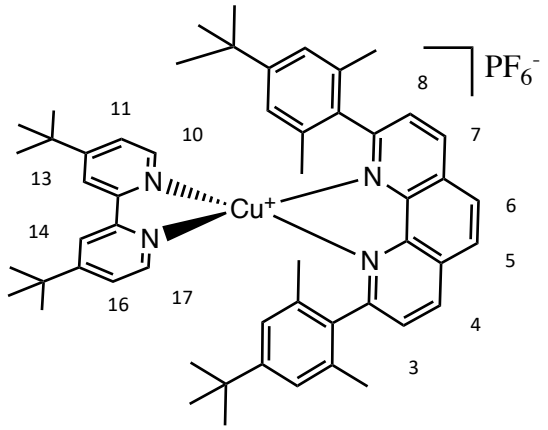


Figure S6: ^{1}H, ^{13}C and DEPT NMR spectra of complex **C6**.

[Cu(2,9-(4-(*tert*-butyl)-2,6-dimethylphenyl)-1,10-phenanthroline)(4,4'-(tert-butyl)-2,2'-bipyridine)]PF_6 (**C7**)



Chemical formula: $C_{54}H_{64}CuF_6N_4P$

Exact mass: 976.41

Molecular weight: 977.64

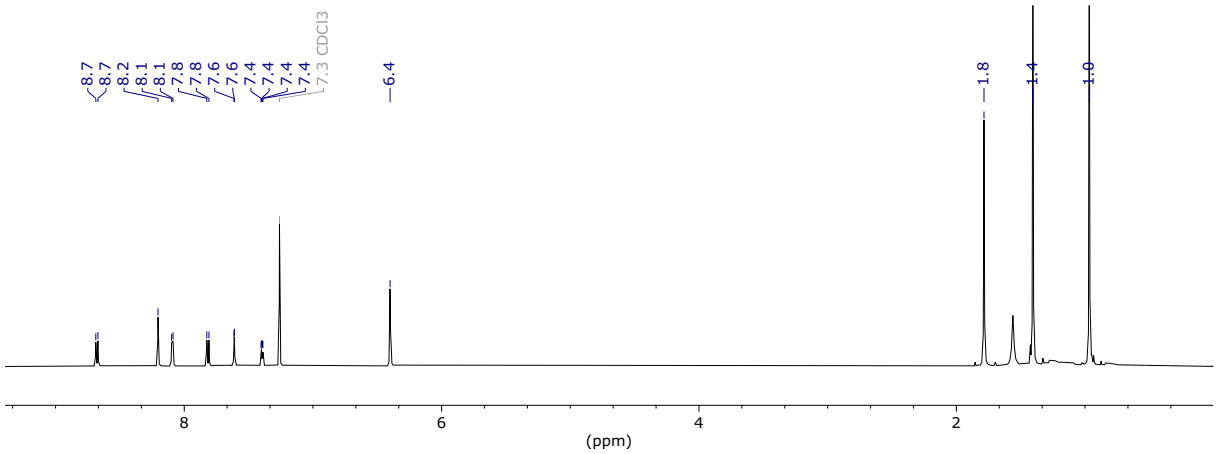
Complex **C7** was obtained by using the procedure followed for **C1**, replacing 1,10-phenanthroline by 4,4'-ditert-butyl-2,2'-bipyridine (46 mg, 0.17 mmol). Complex **C7** was isolated as an orange-red solid in 83% yield (85 mg, 0.087 mmol, 54%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 (d, J = 8.2 Hz, 2H, H_4 and H_7), 8.23 (s, 2H, H_5 and H_6), 8.12 (d, J = 5.5 Hz, 2H, H_{10} and H_{17}), 7.84 (d, J = 8.2 Hz, 2H, H_3 and H_8), 7.64 (d, J = 1.8 Hz, 2H, H_{13} and H_{14}), 7.42 (dd, J = 5.6, 1.8 Hz, 2H, H_{11} and H_{16}), 6.42 (s, 4H, H_{Ar}), 1.81 (s, 12H, H_{Me}), 1.43 (s, 18H, H_{tBu}), 0.99 (s, 18H, H_{tBu}).

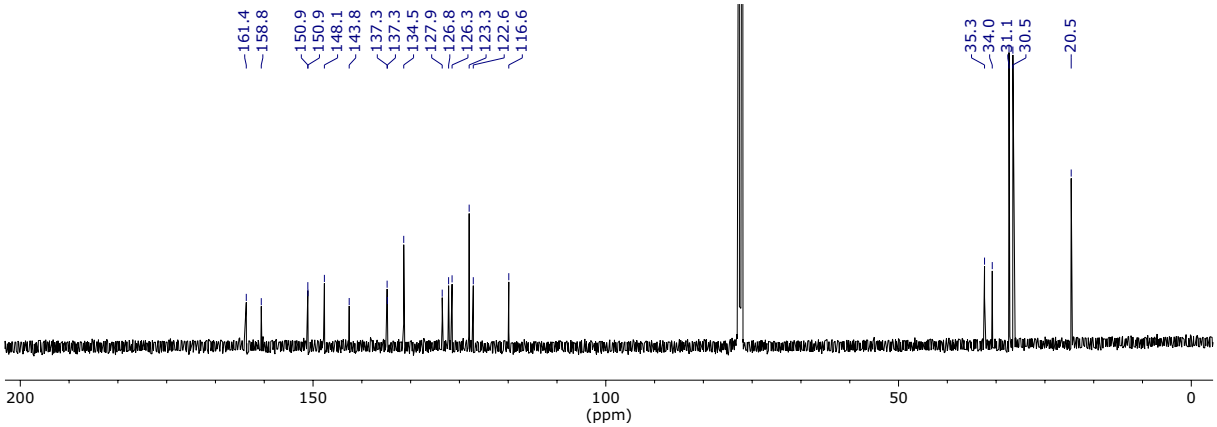
^{13}C NMR (125 MHz, $CDCl_3$) δ 161.4, 158.8, 150.9, 150.9, 148.1 (CH), 143.8, 137.3 (CH), 137.3 (CH), 134.5, 127.9, 126.8 (CH), 126.3 (CH), 123.3 (CH), 122.6 (CH), 116.6 (CH), 35.3, 34.0, 31.1 (CH), 30.5 (CH), 20.5 (CH).

MS ESI: calcd for $C_{54}H_{64}CuN_4$ $(M - PF_6)^{+\cdot}$ 831.44 obsd 831.44

C7: ^{1}H NMR



C7: ^{13}C NMR



C7: DEPT

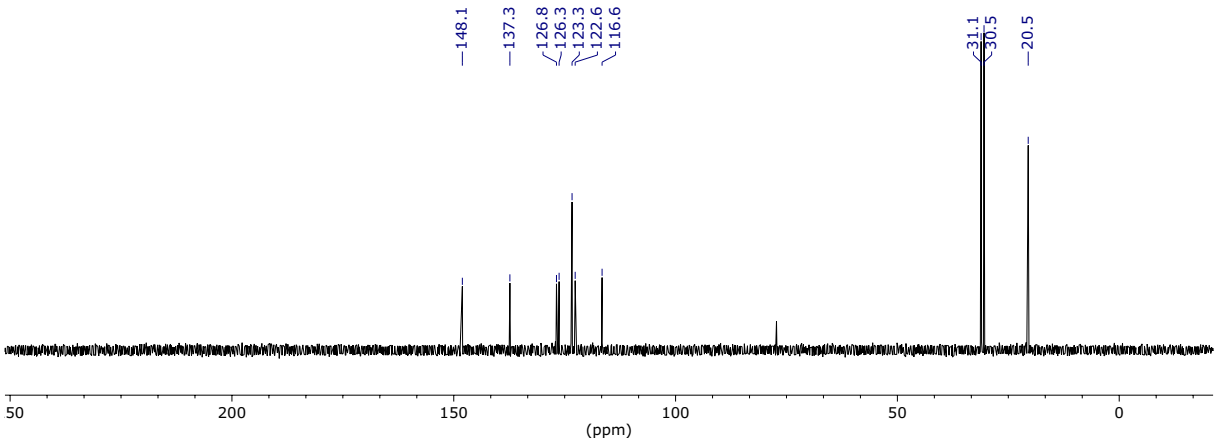
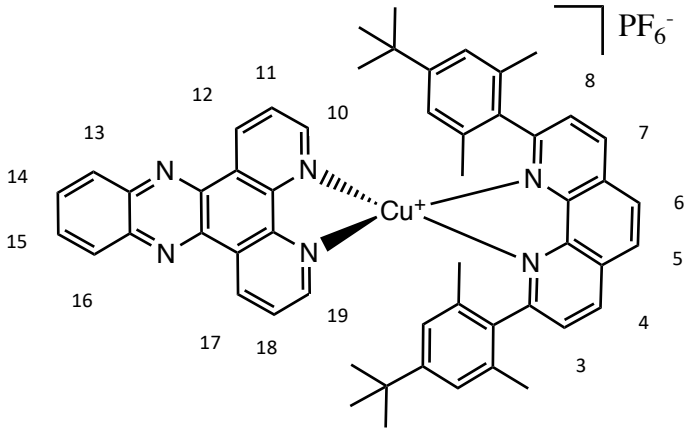


Figure S7: ^{1}H, ^{13}C and DEPT NMR spectra of complex **C7**.

[Cu(2,9-(4-(*tert*-butyl)-2,6-dimethylphenyl)-1,10-phenanthroline)(dipyridophenazine)]PF_6 (**C8**)



Chemical formula: $C_{54}H_{50}CuF_6N_4P$

Exact mass: 990.30

Molecular weight: 991.55

Complex **C8** was synthesised using the same method as for **C1**, with the addition of dipyridophenazine (44 mg, 0.16 mmol) as opposed to 1,10-phenanthroline to yield **C8** (100 mg, 0.10 mmol, 63%).

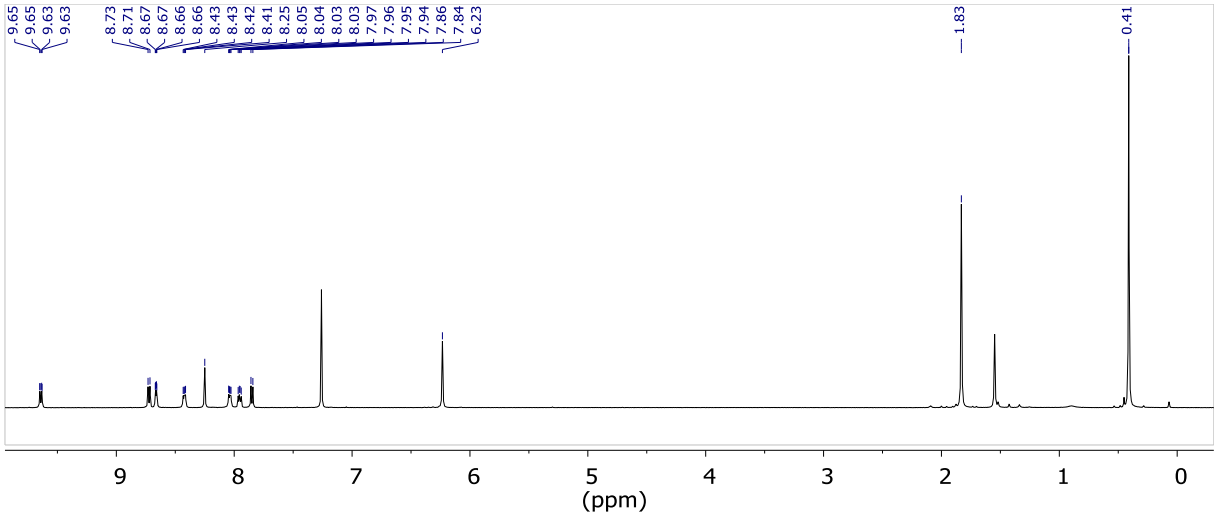
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.64 (dd, *J* = 8.1, 1.5 Hz, 2H, H_{10} and H_{19}), 8.72 (d, *J* = 8.2 Hz, 2H, H_4 and H_7), 8.66 (dd, *J* = 4.9, 1.5 Hz, 2H, H_{12} and H_{18}), 8.42 (dd, *J* = 6.5, 3.5 Hz, 2H, H_{13} and H_{16}), 8.25 (s, 2H, H_5 and H_6), 8.04 (dd, *J* = 6.5, 3.5 Hz, 2H, H_{14} and H_{15}), 7.95 (dd, *J* = 8.1, 4.9 Hz, 2H, H_{11} and H_{18}), 7.85 (d, *J* = 8.2 Hz, 2H, H_3 and H_7), 6.23 (s, 4H, H_{Ar}), 1.83 (s, 12H, H_{Me}), 0.41 (s, 18H, H_{tBu}).

^{13}C NMR (125 MHz, $CDCl_3$) δ 159.0, 151.1, 149.5 (CH), 144.7, 143.9, 142.6, 139.6, 137.6 (CH), 137.2, 134.5, 133.7 (CH), 131.7 (CH), 129.7 (CH), 128.0, 127.8, 126.9 (CH), 126.4 (CH), 125.9 (CH), 123.2 (CH), 33.5, 30.4 (CH), 20.5 (CH).

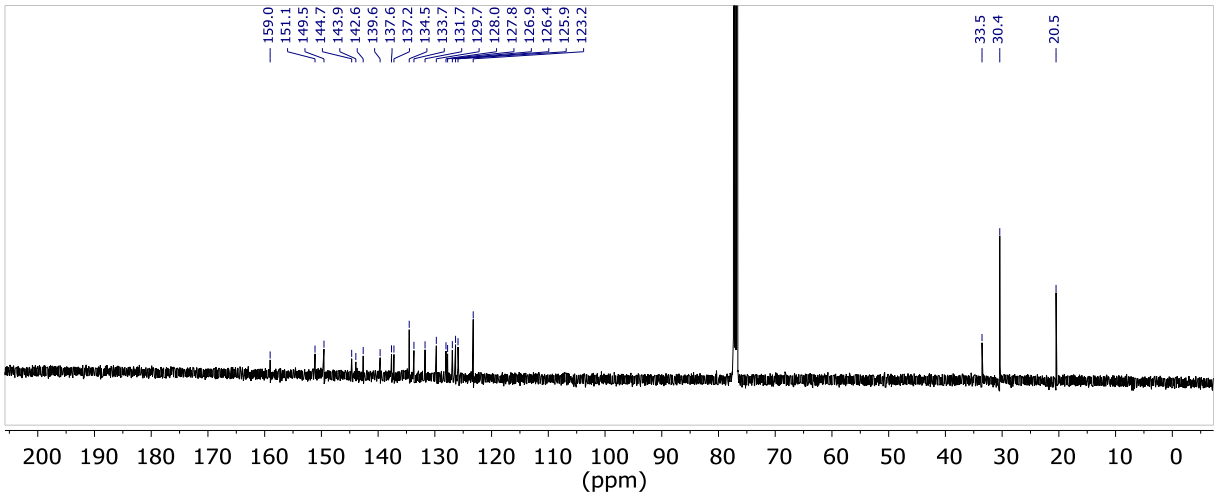
MS ESI: calcd for $C_{54}H_{50}CuN_6$ $(M - PF_6)^+$ 845.34; obsd 845.34.

Crystal data from Et_2O/CH_2Cl_2 for **C8**. $C_{56}H_{54}Cl_4CuF_6N_4P$, M = 1161.36 g.mol^{-1}, monoclinic, space group P 21/c, *a* = 10.5002(4) Å, *b* = 40.819(2) Å, *c* = 12.7406(6) Å, α = 90°, β = 96.385(2) °, γ = 90°, V = 5426.9(4) Å^3, Z = 4, ρ_{calc} = 1.421 Mg/m^3, T = 120(2) K, MoK_α = 0.71073, 2.20 < θ < 27.87, transmission factors: T_{min}/T_{max} = 0.7151/0.7456, 13008 reflections measured, 10771 unique reflections, R_1 = 0.0597606, wR_2 = 0.1628, GoF = 1.033.

C8: ^{1}H NMR



C8: ^{13}C NMR



C8: DEPT 135

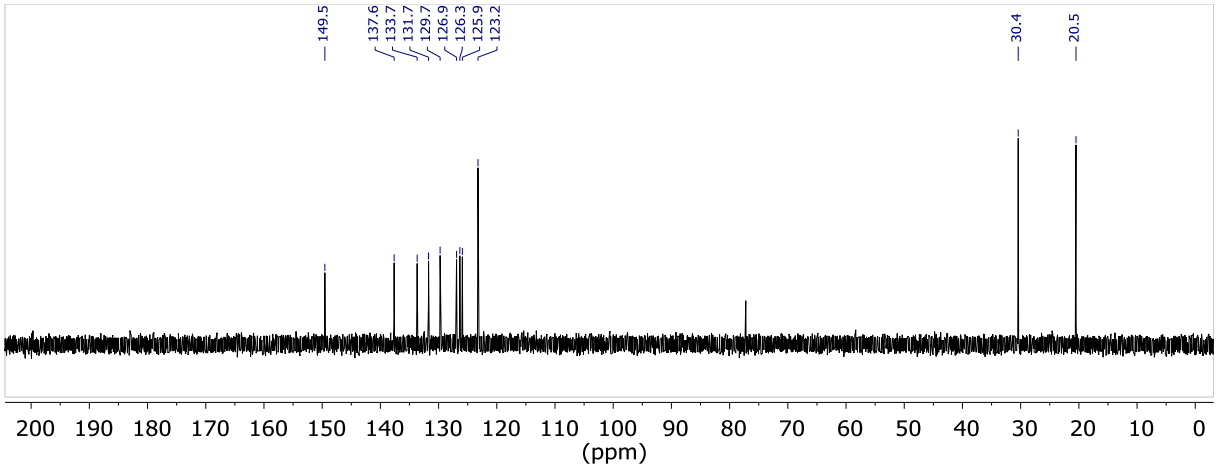


Figure S8: ^{1}H, ^{13}C and DEPT NMR spectra of complex **C8**.

X-ray structure informations.

Compound Cif file	**C2** jwja180321	**C3** jwja180313	**C4** jwja180417	**C6** jwja180716	**C8** jwja210204
CCDC Nr	2226783	2226772	2226784	2226785	2226786
Formula	$C_{50}H_{52}CuN_4,F_6P,C_4H_{10}O$	$C_{60}H_{56}CuN_4,F_6P$	$C_{62}H_{60}CuN_4,F_6P$	$C_{48}H_{52}CuN_4,F_6P$	$C_{54}H_{50}CuN_6,F_6P,2CH_2Cl_2$
Space group	P $2_1/c$	P $2_1/c$	P $2_1/c$	Pbca	P $2_1/c$
a	13.4772(6)	10.9274(3)	11.1445(5)	20.1400(4)	10.5002(4)
b	19.4894(8)	22.7485(6)	21.9682(9)	19.3338(4)	40.819(2)
c	19.6875(9)	21.5054(6)	22.5256(9)	23.5931(4)	12.7406(6)
α	90	90	90	90	90
β	103.534(2)	107.212(2)	108.285(3)	90	96.385(2)
γ	90	90	90	90	90
Cell volume	5027.57	5106.45	5236.36	9186.75	5426.85
Z	4	4	4	8	4
R-Factor (%)	7.31	6.58	5.64	6.06	5.97

Detailed X-ray experimental procedures

The crystals were placed in oil, and a single crystal was selected, mounted on a glass fibre and placed in a low-temperature N_2 stream.

For compounds **jwja180321, jwja180417**, X-ray diffraction data collection was carried out on a Bruker APEX II DUO Kappa-CCD diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using Mo-Kα radiation (λ = 0.71073 Å). The crystal-detector distance was 38mm. The cell parameters were determined (APEX3 software) [1] from reflections taken from three sets of 6 frames, each at 10s exposure. The structure was solved using the program SHELXT-2014 [2]. The refinement and all further calculations were carried out using SHELXL-2014 [3]. The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. A semi-empirical absorption correction was applied using SADABS in APEX3 [1]; transmission factors: T_{min}/T_{max} = 0.6888/0.7458; T_{min}/T_{max} = 0.6331/0.7456, respectively for jwja180321, jwja180417.
For jwja180321, the atoms F1, F2, F3, F4, F5, F6 of the hexafluorophosphate group are disordered over two positions with an occupancy ratio of 0.60/0.40.

For compounds **jwja180313, jwja180716**, X-Ray diffraction data collection was carried out on a Bruker APEX II DUO Kappa-CCD diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using Cu-Kα radiation (λ = 1,54178 Å). The crystal-detector distance was 40 mm. The cell parameters were determined (APEX3 software) [1] from reflections taken from three sets of 6 frames, each at 10s exposure. The structure was solved using the program SHELXT-2014 [2]. The refinement and all further calculations were carried out using SHELXL-2014 [3]. The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. A semi-empirical absorption correction was applied using SADABS in APEX3 [1]; transmission factors: T_{min}/T_{max} = 0.6010/0.7528; T_{min}/T_{max} = 0.5553/0.7528; respectively for jwja180313, jwja180716.
For jwja180716, the methyls C22, C23 are disordered over two positions with an occupancy ratio of 0.50/0.50 and the methyls C34, C35, C36 are disordered over two positions with an occupancy ratio of 0.65/0.35.

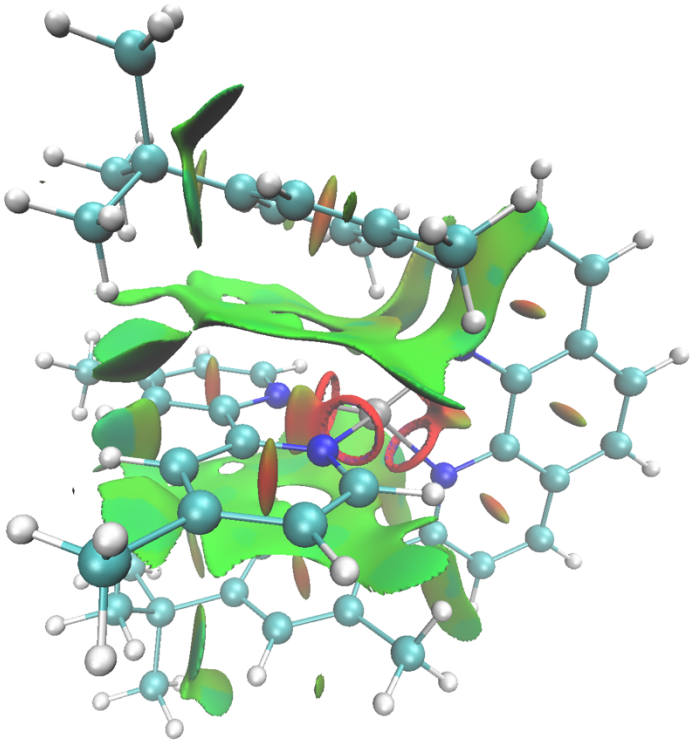
For compound **jwja210204**, X-Ray diffraction data collection was carried out on a Bruker PHOTON-III DUO CPAD diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using Mo-Kα radiation (λ = 0.71073 Å). The crystal-detector distance was 37 mm. The cell parameters were determined (APEX3 software) [1] from reflections taken from one set of 180 frames, each at 1s exposure. The structures were solved using the program SHELXT-2014 [2]. The refinement and all further calculations were carried out using SHELXL-2014 [3]. The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. A semi-empirical absorption correction was applied using SADABS in APEX3 [1]; transmission factors: T_{min}/T_{max} = 0.7151/0.7456.

The methyls C34, C35, C36 are disordered over two positions with an occupancy ratio of 0.50/0.50

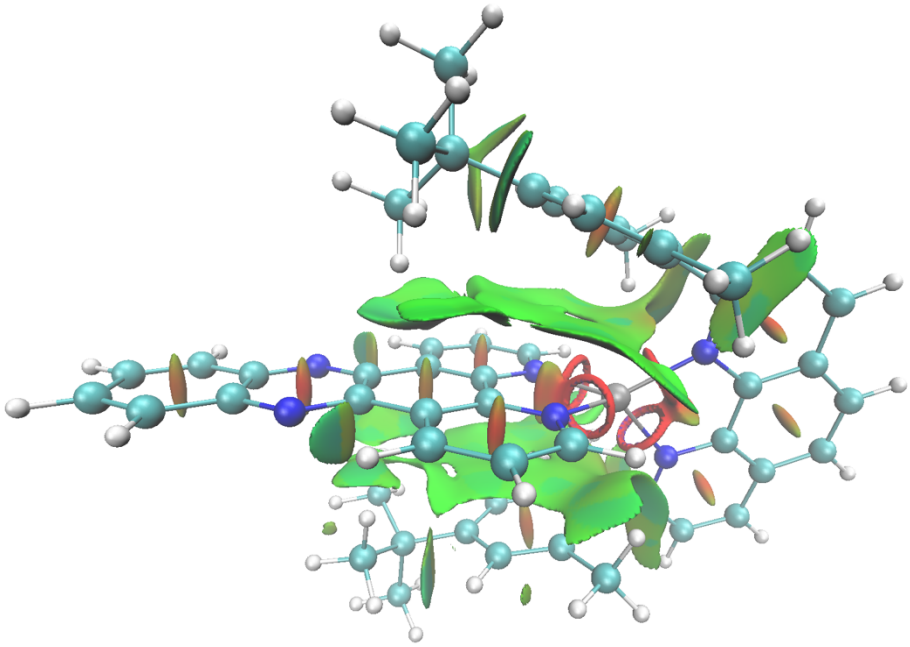
[1] "M86-EXX229V1 APEX3 User Manual", Bruker AXS Inc., Madison, USA, 2016.

[2] G. M. Sheldrick, *Acta Cryst.* **2015***,* A71, 3-8.

[3] G. M. Sheldrick, *Acta Cryst.* **2015**, C71, 3-8.



NCI for compound C6



NCI for compound 8