Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for

Heteroleptic copper(I) complexes with coumarin-substituted aminodiphosphine and diimine ligands: Synthesis and photophysical studies

Vanitha R. Naina,[a] Akhil Kumar Singh,[a] Shubham[a], Frederic Krätschmer[a], Sergei Lebedkin,[b] Manfred M. Kappes,[b,c] and Peter W. Roesky*[a]

a. Institute of Inorganic Chemistry, Karlsruhe Institute of Technology (KIT), Engesserstraße 15, 76131 Karlsruhe, Germany.
b. Institute of Nanotechnology, Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany.
c. Institute of Physical Chemistry, Karlsruhe Institute of Technology (KIT), Fritz-Haber-Weg 2, 76131 Karlsruhe, Germany.

Table of Contents

I. Synthesis and characterization

I.1 General procedures

All air- and moisture-sensitive manipulations were performed under dry N_2 or Ar atmosphere using standard Schlenk techniques or in an argon-filled MBraun glovebox, unless otherwise stated. All solvents (Et_2O and *n*-pentane) were dried using an MBraun solvent purification system (SPS-800) and degassed. CH_3CN and DCM were distilled under CaH_2 and P_2O_5, respectively. $CDCl_3$ and CD_2Cl_2 were dried over CaH_2 and degassed by freeze-pump-thaw cycles. $\mathbf{L^1}$,[1] Cu($\mathbf{L^1}$)$_2$,[1] bis(4-(tert-butyl)phenyl)chlorophosphine,[2] 2-(2′-pyridine)benzthiazol,[3] and 2-(2′-quinoline)benzthiazol,[3] were synthesized according to the reported procedure. All other chemicals were obtained from commercial sources and used without further purification.

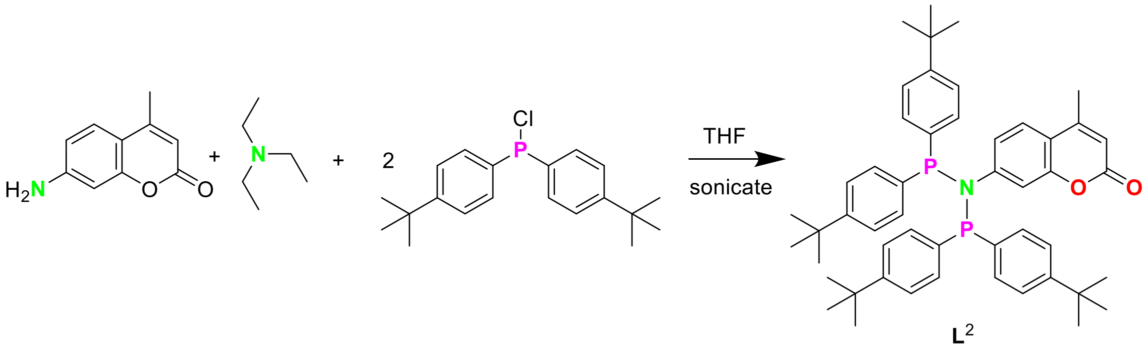
Elemental analyses were carried out with an Elementar vario MICRO cube.

NMR spectra were recorded on Bruker spectrometers (Avance III 300 MHz, Avance Neo 400 MHz or Avance III 400 MHz). Chemical shifts are referenced internally using signals of the residual protio solvent (^{1}H) or the solvent (^{13}C{^{1}H}) and are reported relative to tetramethylsilane (^{1}H, ^{13}C{^{1}H}), H_3PO_4 (^{31}P). All NMR spectra were measured at 298 K, unless otherwise specified. The multiplicity of the signals is indicated as s = singlet, d = doublet, dd = doublet of doublets, t = triplet, m = multiplet and br = broad. Assignments were determined based on unambiguous chemical shifts, coupling patterns and ^{13}C-DEPT experiments.

Infrared (IR) spectra were recorded in the region 3500-400 cm^{-1} on a Bruker Tensor 37 FTIR spectrometer equipped with a room temperature DLaTGS detector, a diamond attenuated total reflection (ATR) unit and a nitrogen-flushed chamber. In terms of their intensity, the signals were classified into different categories (s = strong, m = medium, w = weak, and sh = shoulder).

<u>Synthesis of di-substituted coumarin aminophosphines (L^2):</u>

7-Amino-4-methylcoumarin (5.6 mmol, 1.0 g) was suspended in THF and triethylamine was added in excess. It was followed by drop-wise addition of bis(4-(*tert*-butyl)phenyl)chlorophosphine (11.9 mmol, 3.7 g) dissolved in 20 mL of THF at 0 °C. The reaction mixture was sonicated for 10 min and left for stirring for 3 days at room temperature. The volatiles were evaporated under vacuum and the remaining solid was dissolved in THF. The resulting colorless precipitate of $HNEt_3Cl$ was filtered off. The volume of the reaction mixture was reduced to one-third and an equal volume of pentane was added. On storing the mixture at -30 °C, white colored solid was formed. The solid was washed with pentane thrice, dried under reduced pressure.



L^2

Analytical data for L^2**:**

Yield: 3.25 g (75%). Anal. calcd for $C_{50}H_{59}NO_2P_2$ (767.97 g/mol): C, 78.20; H, 7.74; N, 1.82. Found: C, 78.51; H, 7.43; N, 1.68.

^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ(ppm) = 7.36 - 7.19 (m, 16H, C*H*$_{Ph}$), 7.13 (d, *J* = 8.6 Hz, 1H, Coum-C*H*), 6.78 (s, 1H, Coum-C*H*), 6.76 (s, 1H, Coum-C*H*), 6.06 (s, 1H, Coum-C*H*), 2.26 (s, 3H, Coum-C*H*$_3$), 1.27 (s, 36H, -C(C*H*$_3$)$_3$).

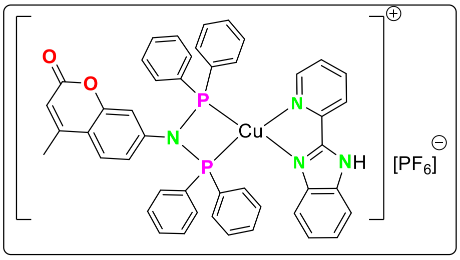
^{31}P{^{1}H} NMR (162 MHz, 298 K, $CDCl_3$): δ(ppm) = 65.6 (s).

^{13}C{^{1}H} NMR (100 MHz, 298 K, $CDCl_3$): δ (ppm) = 161.4 (Coum-*C*O), 153.4 (Coum-*C*), 152.4 (Coum-*C*), 152.3 (Coum-*C*), 134.7 (Ph-*C*), 132.7 (Ph-*C*), 132.1 (Ph-*C*H), 125.6 (Coum-*C*H), 125.2 (Ph-*C*H), 123.8 (Coum-*C*H), 116.1 (Coum-*C*(CH$_3$)), 115.4 (Coum-*C*H), 113.2 (Coum-*C*H), 34.8 (*C*(CH$_3$)$_3$), 31.1 (C(*C*H$_3$)$_3$), 18.7 (Coum-*C*H$_3$).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3073 (sh), 3057 (w), 3025 (w), 2959 (s), 2903 (m), 2865 (m), 1796 (w), 1726 (s), 1715 (s), 1608 (m), 1551 (w), 1491 (w), 1461 (w), 1386 (m), 1362 (w), 1308 (w), 1264 (s), 1238 (m), 1198 (w), 1140 (m), 1080 (m), 1064 (m), 1012 (m), 984 (m), 949 (m), 914 (w), 870 (s), 845 (m), 823 (m), 743 (w), 707 (w), 637 (m), 593 (w), 567 (m), 555 (sh), 485 (m), 451 (w), 432 (w).

Synthesis of the metal complexes:

Synthesis of Cu complex 1:



To a flask containing **L^1** (160.0 mg, 0.27 mmol, 1.0 eq) and $[Cu(CH_3CN)_4]PF_6$ (99.8 mg, 0.27 mmol, 1.0 eq), 10 mL of DCM was added. After stirring for 3 h, 2-(2-pyridyl)benzimidazole (52.3 mg, 0.27 mmol, 1.0 eq) dissolved in 5 mL of DCM was added to the flask and left for stirring overnight at room temperature. Yellow-colored single crystals were isolated from a mixture of DCM, acetonitrile and diethylether solution at room temperature.

Analytical data for 1:

Yield: 185 mg (73%).

^{1}H NMR (400 MHz, 298 K, $CDCl_3$): δ(ppm) = 11.57 (br (s), 1H, N-*H*), 8.45 (s, 1H, Ar-*C*H), 8.35 (s, 1H, Ar-*C*H), 8.01 (s, 1H, Ar-*C*H), 7.83 (s, 1H, Ar-*C*H), 7.60 - 7.41 (m, 20H, Ar-*C*H), 7.39 - 7.29 (m, 2H, Ar-*C*H), 7.25 - 7.12 (m, 2H, Ar-*C*H), 6.62 (s, 1H, Coum-C*H*), 6.53 (d, J = 8.4 Hz, 1H, Coum-C*H*), 6.31 (d, J = 8.4 Hz, 1H, Coum-C*H*), 6.19 (s, 1H, Coum-C*H*), 2.31 (s, 3H, Coum-CH_3).

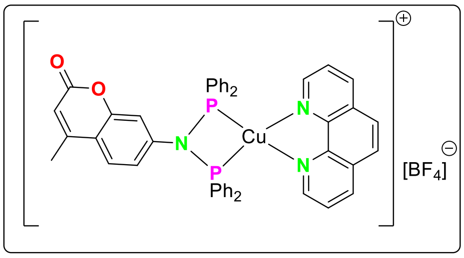
^{31}P{^{1}H} NMR (162 MHz, 298 K, $CDCl_3$): δ(ppm) = 87.4 (s), -143.8 (sept, PF_6).

^{13}C{^{1}H} NMR (100 MHz, 298 K, $CDCl_3$): δ (ppm) = 160.6 (Coum-*C*O), 160.4 (Ar-*C*), 153.3 (Coum-*C*), 153.2 (Ar-*C*), 152.1 (Coum-*C*), 150.0 (Ar-*C*H), 149.3 (Ar-*C*), 145.5 (Ar-*C*), 143.8 (Ar-*C*), 139.7 (Ar-*C*H), 132.7 (Ar-*C*H), 131.8 (Ar-*C*H), 129.7 (Ar-*C*), 129.5 (Ar-*C*H), 128.6 (Ar-*C*), 126.5 (Ar-*C*H), 125.3 (Ar-*C*H), 124.7 (Ar-*C*H), 124.1 (Coum-*C*H), 119.2 (Ar-*C*), 118.2 (Coum-*C*), 117.1 (Coum-*C*H), 116.0 (Coum-*C*H), 115.3 (Coum-*C*(CH_3)), 114.9 (Coum-*C*H), 18.6 (Coum-*C*H_3).

HRMS (ESI): m/z = 801.1599 $[M\text{-}PF_6]^+$.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3420 (m), 3055 (w), 2973 (w), 2865 (w), 2004 (w), 1724 (s), 1624 (m), 1603 (s), 1552 (w), 1480 (m), 1454 (s), 1437 (m), 1402 (m), 1387 (m), 1366 (m), 1317 (m), 1300 (m), 1264 (w), 1183 (s), 1150 (m), 1119 (s), 1098 (m), 1069 (m), 1015 (m), 990 (m), 917 (s), 833 (s), 789 (m), 763 (s), 742 (s), 698 (s), 642 (sh), 631 (m), 606 (w), 570 (w), 556 (m), 536 (m), 509 (m), 496 (m), 483 (m),467 (m), 441 (w), 431 (w), 416 (w).

Synthesis of Cu complex 2:



To a flask containing **L**^{1} (197.0 mg, 0.36 mmol, 1.0 eq) and $[\mathrm{Cu(CH_3CN)_4}]\mathrm{BF_4}$ (114.2 mg, 0.36 mmol, 1.0 eq), 10 mL of DCM was added. After stirring for 3 h, 1,10-phenanthroline (65.4 mg, 0.36 mmol, 1.0 eq) dissolved in 5 mL of DCM was added to the flask and left for stirring overnight at room temperature. Slow evaporation of diethylether into a concentrated solution of the reaction mixture led to the isolation of yellow-colored single crystals.

Analytical data for 2:

Yield: 248 mg (79 %), Anal. calcd for $\mathrm{C_{46}H_{35}CuN_3O_2P_2BF_4}$ (874.10 g/mol): C, 63.21; H, 4.81; N, 4.04. Found: C, 63.17; H, 4.95; N, 3.77.

^{1}H NMR (400 MHz, 298 K, $\mathrm{CDCl_3}$): δ (ppm) = 8.91 (s, 2H, C*H*$_{\mathrm{Phen}}$), 8.54 (d, *J* = 8.2 Hz, 2H, C*H*$_{\mathrm{Phen}}$), 8.01 - 7.95 (m, 4H, C*H*$_{\mathrm{Ph}}$ (2H) and C*H*$_{\mathrm{Phen}}$ (2H)), 7.59 - 7.52 (m, 18H, C*H*$_{\mathrm{Ph}}$), 7.33 (t, *J* = 8.2 Hz, 2H, C*H*$_{\mathrm{Phen}}$), 7.17 (d, *J* = 8.6 Hz, 1H, Coum-C*H*), 6.67 (s, 1H, Coum-C*H*), 6.44 (d, *J* = 8.6 Hz, 1H, Coum-C*H*), 6.18 (s, 1H, Coum-C*H*), 2.30 (s, 3H, Coum-C*H*$_3$).

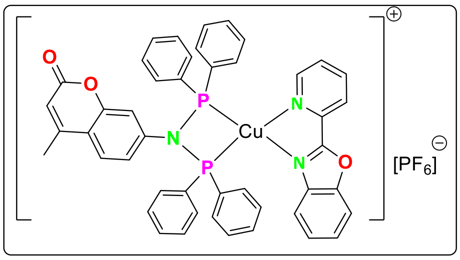
^{31}P{^{1}H} NMR (162 MHz, 298 K, $\mathrm{CDCl_3}$): δ(ppm) = 88.1 (s).

^{13}C{^{1}H} NMR (100 MHz, 298 K, $\mathrm{CDCl_3}$): δ (ppm) = 160.6 (Coum-*C*O), 153.3 (Coum-*C*), 152.1 (Coum-*C*), 150.3 (Phen-*C*H), 143.6 (Phen-*C*), 138.4 (Phen-*C*H), 132.7 (Ph-*C*), 132.6 (Ph-*C*H), 132.1 (Ph-*C*H), 129.8 (Ph-*C*H), 129.7 (Phen-*C*H), 127.4 (Phen-*C*H), 126.1 (Coum-*C*H), 124.9 (Coum-*C*H), 124.5 (Coum-*C*), 118.4 (Coum- *C*(CH$_3$)), 116.2 (Coum-*C*H), 114.9 (Coum-*C*H), 18.7 (Coum-*C*H$_3$).

HRMS (ESI): m/z = 786.1484 [M-BF$_4$]$^+$.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3056 (m), 2988 (w), 2360 (w), 2336 (w), 2183 (w), 2163 (w), 2150 (w), 2054 (w), 1980 (w), 1903 (w), 1743 (s), 1622 (m), 1604 (s), 1509 (m), 1479 (m), 1436 (s), 1421 (m), 1387 (m), 1365 (m), 1308 (w), 1289 (m), 1265 (w), 1220 (w), 1191 (m), 1152 (s), 1094 (m), 1054 (s), 1015 (sh), 993 (m), 911 (m), 844 (s), 809 (w), 777 (w), 741 (m), 726 (m), 693 (s), 632 (m), 604 (m), 569 (m), 533 (m), 507 (m), 494 (m), 484 (m), 465 (m), 453 (m), 440 (w), 421 (w).

Synthesis of Cu complex 3:



To a flask containing **L**^{1} (182.0 mg, 0.33 mmol, 1.0 eq) and [Cu(CH$_3$CN)$_4$]PF$_6$ (124.8 mg, 0.33 mmol, 1.0 eq), 10 mL of DCM was added. After stirring for 3 h, 2-(2-pyridyl)benzoxazole (65.7 mg, 0.33 mmol, 1.0 eq) dissolved in 5 mL of DCM was added to the flask and left for stirring overnight at room temperature. Yellow-colored single crystals were grown by layering a concentrated solution of the reaction mixture with diethylether.

Analytical data for 3:

Yield: 243 mg (85 %), Anal. calcd for $C_{46}H_{37}N_3O_3P_3CuF_6$ (950.28 g/mol): C, 58.14; H, 3.92; N, 4.42. Found: C, 57.82 H, 3.74; N, 4.80.

^{1}H NMR (400 MHz, 298 K, CD$_2$Cl$_2$): δ(ppm) = 8.62 (d, J = 5.0 Hz, 1H, Ar-C*H*), 8.44 (d, J = 8.2 Hz, 1H, Ar-C*H*), 8.25 (t, J = 7.8 Hz, 1H, Ar-C*H*), 7.84 (d, J = 8.3 Hz, 1H, Ar-C*H*), 7.66 - 7.56 (m, 4H, Ar-C*H*), 7.59 - 7.47 (m, 16H, Ar-C*H*), 7.40 - 7.21 (m, 5H, Ar-C*H* + Coum-C*H*), 6.53 (s, 1H, Coum-C*H*), 6.47 (d, J = 8.6 Hz, 1H, Coum-C*H*), 6.17 (s, 1H, Coum-C*H*), 2.30 (s, 3H, Coum-C*H*$_3$).

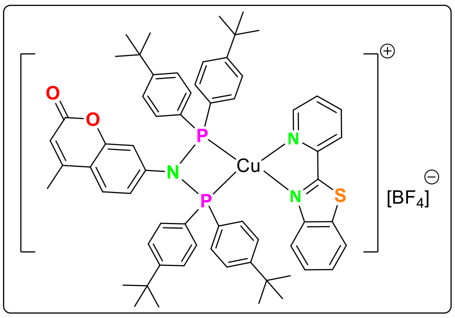
^{31}P{^{1}H} NMR (162 MHz, 298 K, CD$_2$Cl$_2$): δ(ppm) = -140.1 (sept, PF$_6$), 88.9 (s).

^{13}C{^{1}H} NMR (100 MHz, 298 K, CD$_2$Cl$_2$): δ(ppm) = 160.3 (Coum-*C*O), 160.2 (Ar-*C*), 155.8 (Ar-*C*), 154.0 (Ar-*C*), 153.7 (Ar-*C*H), 152.6 (Coum-*C*), 152.3 (Coum-*C*), 140.3 (Ar-*C*H), 133.0 (Ar-*C*H), 132.8 (Ar-*C*H), 132.7 (Ar-*C*H), 132.6 (Ar-*C*H), 132.4 (Ar-*C*H), 129.8 (Ar-*C*H), 128.6 (Ar-*C*H), 127.2 (Ar-*C*), 125.3 (Ar-*C*H), 124.8 (Ar-*C*H), 124.1 (Coum-*C*H), 119.6 (Coum-*C*), 119.1 (Ar-*C*), 116.9 (Coum-*C*H), 115.6 (Coum-*C*(CH$_3$)), 115.4 (Coum-*C*H), 112.8 (Coum-*C*H), 18.6 (Coum-*C*H$_3$).

HRMS (ESI): m/z = 802.1416 [M-PF$_6$]$^+$.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3080 (w), 3056 (w), 1722 (s), 1624 (sh), 1603 (m), 1570 (w), 1540 (w), 1499 (m), 1475 (m), 1451 (w), 1437 (m), 1403 (w), 1380 (m), 1366 (m), 1310 (w), 1264 (w), 1190 (m), 1150 (m), 1100 (w), 1069 (w), 1014 (m), 990 (m), 921 (m), 875 (s), 834 (sh), 795 (m), 761 (m), 744 (m), 697 (m), 632 (w), 606 (w), 570 (m), 556 (w), 537 (w), 509 (w), 495 (w), 484 (w), 467 (w), 442 (w), 418 (w).

***Synthesis of copper complex 4*:**



To a flask containing $\mathbf{L}^2$ (181.8 mg, 0.24 mmol, 1.0 eq) and [Cu(CH$_3$CN)$_4$]BF$_4$ (75.5 mg, 0.24 mmol, 1.0 eq), 10 mL of DCM was added. After stirring for 3 h, 2-(2′-pyridine)benzthiazol (50.9 mg, 0.24 mmol, 1.0 eq) dissolved in 5 mL of DCM was added to the flask and left for stirring overnight at room temperature. Orange colored single crystals were grown from a mixture of DCM solution of complex **5** and *n*-pentane. The same experiment with $\mathbf{L}^1$ instead of $\mathbf{L}^2$ led to the isolation of orange colored insoluble solid during the crystallization process.

Analytical data for 4:

Yield: 188 mg (69 %). Anal. calcd for $C_{62}H_{67}N_3O_2P_2CuSBF_4$ (1130.59 g/mol): C, 65.87; H, 5.97; N, 3.72; S, 2.84. Found: C, 65.67; H, 5.81; N, 3.82; S, 2.69.

^{1}H NMR (400 MHz, 298 K, CD$_2$Cl$_2$): δ (ppm) = 8.22 - 8.14 (m, 2H, Ar-C*H*), 7.58 - 7.49 (m, 16H, Ar-C*H*), 7.42 - 7.36 (m, 2H, Ar-C*H*), 7.31 (s, 2H, Ar-C*H*), 7.22 - 7.17 (m, 3H, Ar-C*H* and Coum-C*H*), 6.73 (s, 1H, Coum-C*H*), 6.32 (s, 1H, Coum-C*H*), 6.13 (s, 1H, Coum-C*H*), 2.29 (s, 3H, Coum-C*H$_3$*), 1.39 (s, 36H, C(C*H$_3$*)$_3$).

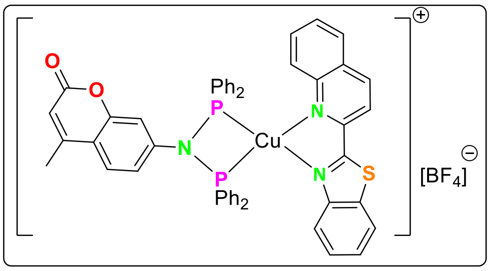
^{31}P{^{1}H} NMR (162 MHz, 298 K, CD$_2$Cl$_2$): δ (ppm) = 85.4 (s)

^{13}C{^{1}H} NMR (100 MHz, 298 K, CD$_2$Cl$_2$): δ (ppm) = 160.5 (Coum-*C*O), 160.3 (Ar-*C*), 156.1 (Ar-*C*), 156.0 (Ar-*C*), 152.3 (Coum-*C*), 152.2 (Coum-*C*), 150.3 (Ar-*C*H), 140.2 (Ar-*C*H), 134.9 (Ar-*C*), 133.2 (Ar-*C*H), 132.8 (Ar-*CH)*, 129.3 (Ar-*C*), 129.1 (Ar-*C*), 128.1 (Ar-*C*H), 126.9 (Ar-*C*H), 126.8 (Ar-*C*H), 126.8 (Ar-*C*H), 126.6 (Ar-*C*H), 125.0 (Coum-*C*H), 124.8 (Ar-*C*H), 123.5 (Coum-*C*), 122.9 (Coum-*C*H), 117.9 (Coum- *C*(CH$_3$)), 115.0 (Coum-*C*H), 114.8 (Coum-*C*H), 35.5 (*C*(CH$_3$)$_3$), 31.3 (C(*C*H$_3$)$_3$), 18.6 (Coum-*C*H$_3$).

HRMS (ESI): m/z = 1042.3712 [M-BF$_4$]$^+$.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3061 (w), 2957 (s), 2904 (m), 2867 (m), 2187 (w), 2051 (w), 1740 (s), 1624 (sh), 1606 (s), 1553 (w), 1493 (m), 1461 (m), 1387 (w), 1364 (m), 1322 (m), 1264 (w), 1201 (m), 1150 (w), 1119 (s), 1084 (s), 1049 (s), 1012 (m), 989 (w), 945 (m), 913 (w), 883 (w), 866 (m), 849 (m), 826 (m), 786 (m), 757 (m), 746 (m), 728 (m), 706 (m), 687 (m), 631 (m), 597 (m), 584 (m), 569 (m), 558 (m), 520 (w), 494 (m), 455 (m), 429 (m).

Synthesis of copper complex 5:



To a flask containing **L**^{1} (197.0 mg, 0.36 mmol, 1.0 eq) and [Cu(CH$_3$CN)$_4$]BF$_4$ (114.2 mg, 0.36 mmol, 1.0 eq), 10 mL of DCM was added. After stirring for 3 h, 2-(2’-quinoline)benzthiazol (95.2 mg, 0.36 mmol, 1.0 eq) dissolved in 5 mL of DCM was added to the flask and left for stirring overnight at room temperature. Red colored single crystals were grown by slow diffusion of diethylether into the concentrated reaction mixture.

Analytical data for 5:

Yield: 252 mg (73 %). Anal. calcd for $C_{50}H_{37}N_3O_2P_2CuSBF_4$ 0.5 CH_2Cl_2 (956.22 g/mol): C, 60.74; H, 3.84; N, 4.21; S, 3.21. Found: C, 60.43; H, 3.64; N, 4.15; S, 3.08.

^{1}H NMR (400 MHz, 298 K, CD_2Cl_2): Homoleptic complex is the major compound formed on dissolving the crystals due to which all the peaks could not be assigned unambigiuosly.

^{31}P{^{1}H} NMR (162 MHz, 298 K, CD_2Cl_2): δ (ppm) = 86.0 (s).

^{13}C{^{1}H} NMR (100 MHz, 298 K, CD_2Cl_2): Homoleptic complex is the major compound formed on dissolving the crystals due to which peaks could not be assigned unambigiuosly.

MS-ESI: m/z = 868.1365 [M-BF$_4$]$^+$.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3078 (sh) 3059 (m), 2952 (w), 2919 (w), 2325 (w), 2162 (w), 2115 (w), 1982 (w), 1724 (s), 1623 (m), 1604 (m), 1554 (w), 1513 (m), 1480 (m), 1458 (w), 1436 (m), 1403 (m), 1386 (m), 1366 (w), 1347 (w), 1314 (m), 1296 (m), 1263 (s), 1249 (sh), 1184 (w), 1148 (m), 1092 (s), 1049 (s), 1014 (m), 988 (m), 953 (w), 916 (s), 876 (m), 850 (m), 820 (m), 784 (m), 766 (m), 740 (s), 701 (s), 632 (m), 619 (m), 606 (m), 569 (m), 536 (m), 510 (m), 497 (m), 478 (m), 465 (m), 441 (m), 415 (w).

II. NMR spectra

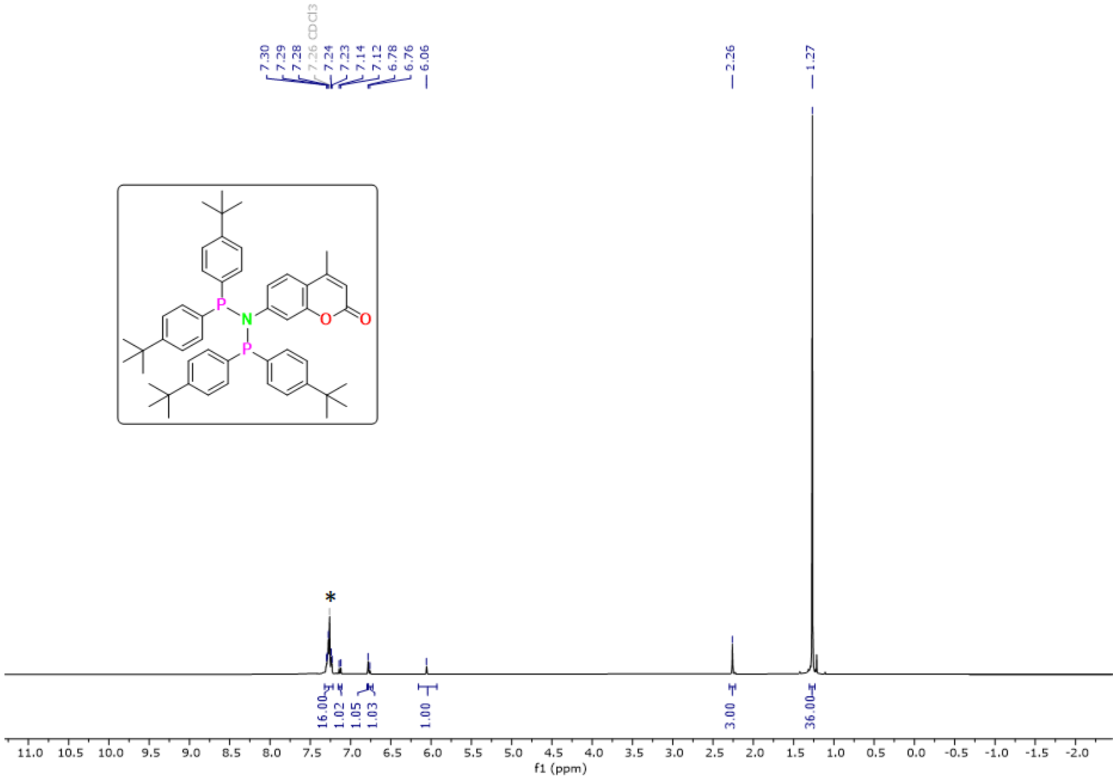


Figure S1. ^{1}H NMR spectrum of **L**^{2} in $CDCl_3$. *, residual protio solvent signal.

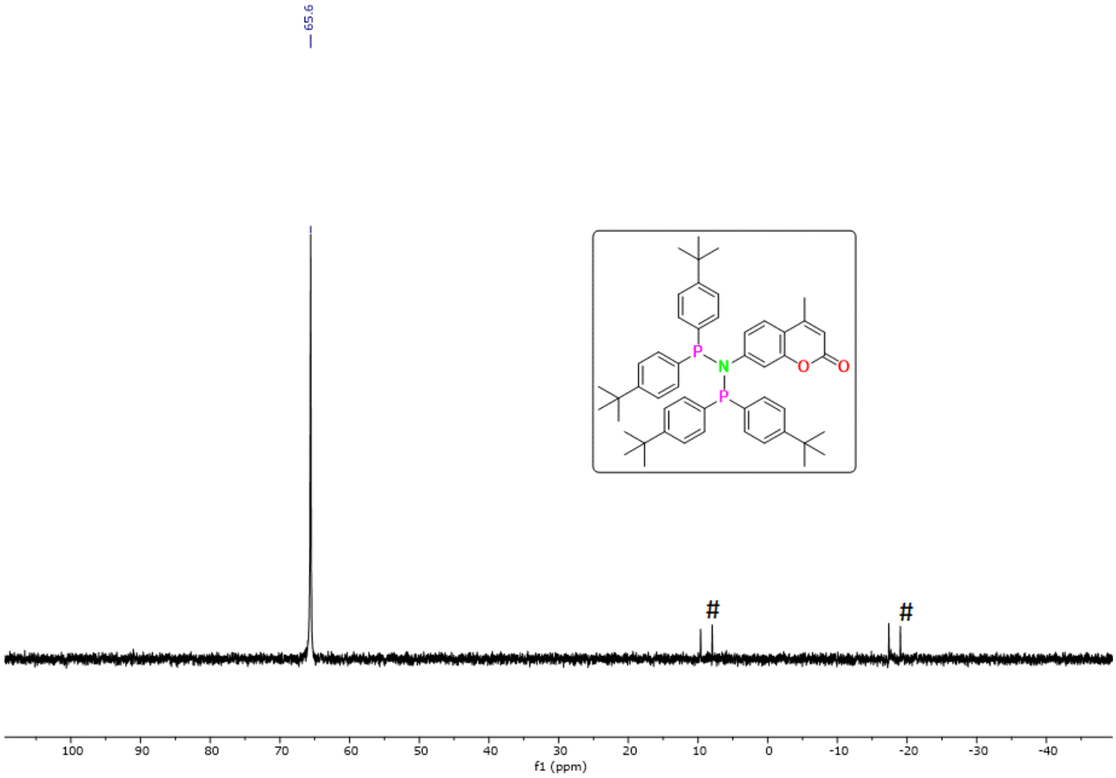


Figure S2. ^{31}P{^{1}H} NMR spectrum of **L**^{2} in $CDCl_3$. #- unidentified minor products, which were not observed for the metal complexes.

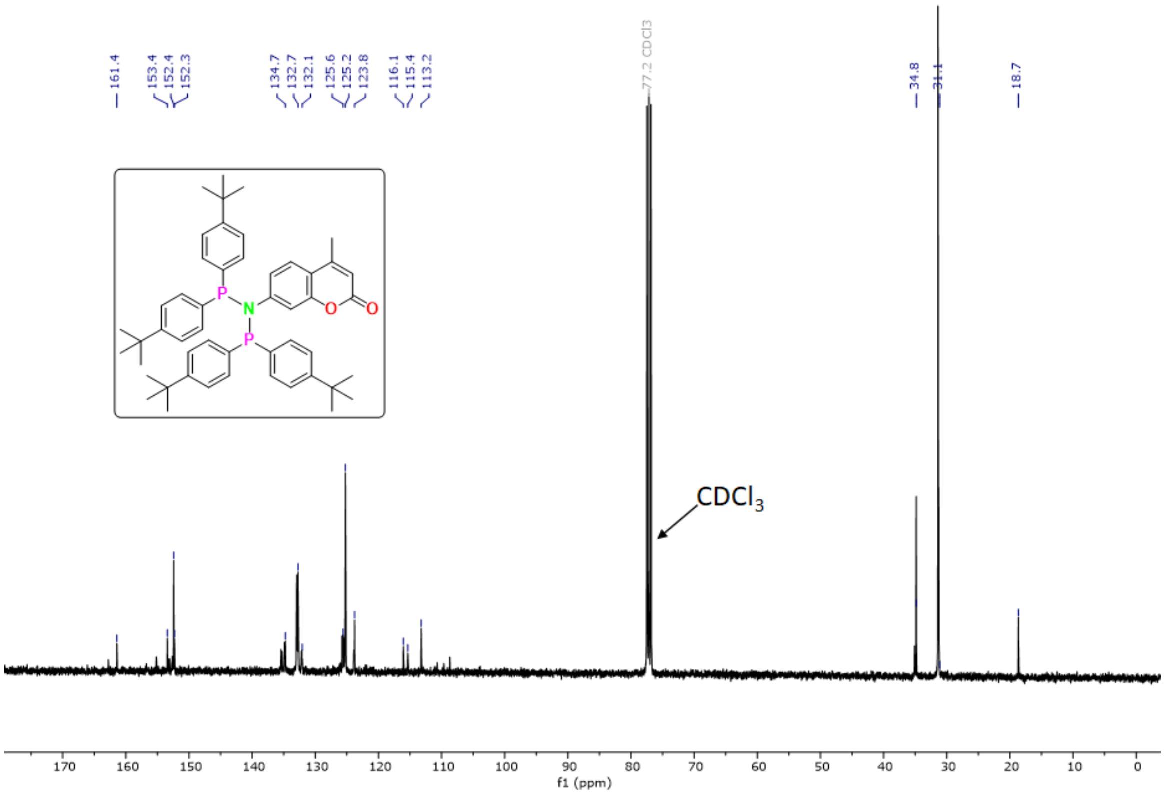


Figure S3. $^{13}C\{^1H\}$ NMR spectrum of **L**^{2} in $CDCl_3$.

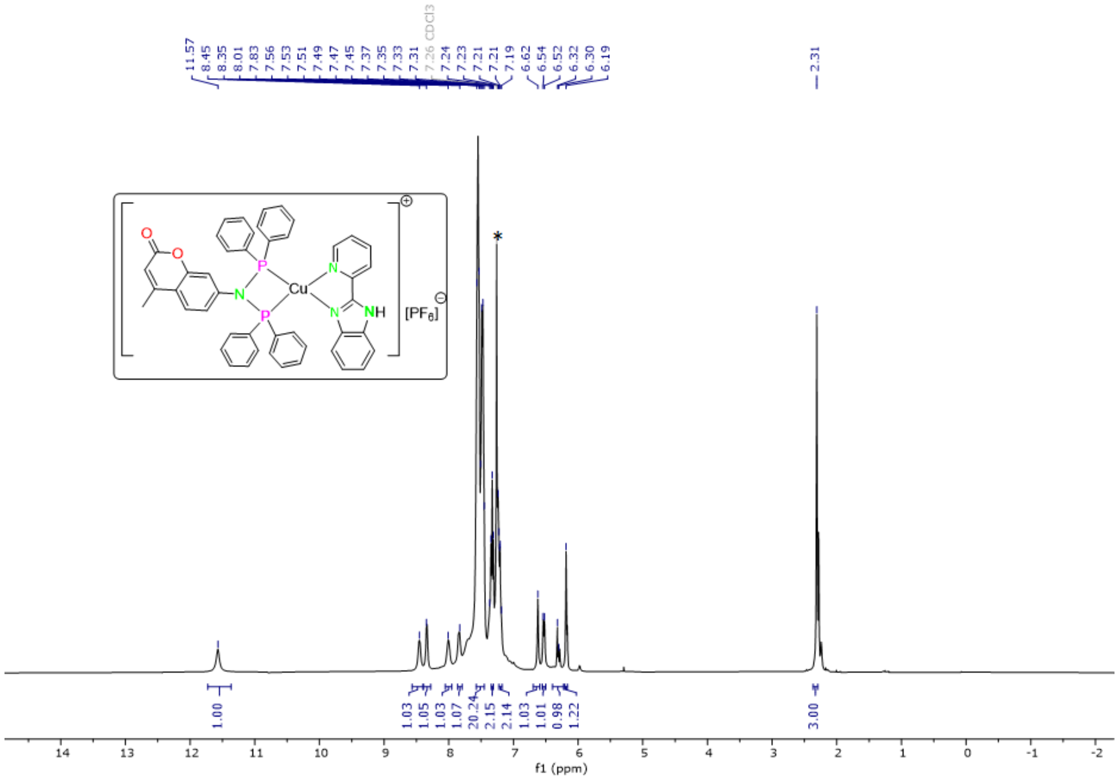


Figure S4. ^1H NMR spectrum of **1** in $CDCl_3$. *, residual protio solvent signal. Integration was performed for all compounds in the solution.

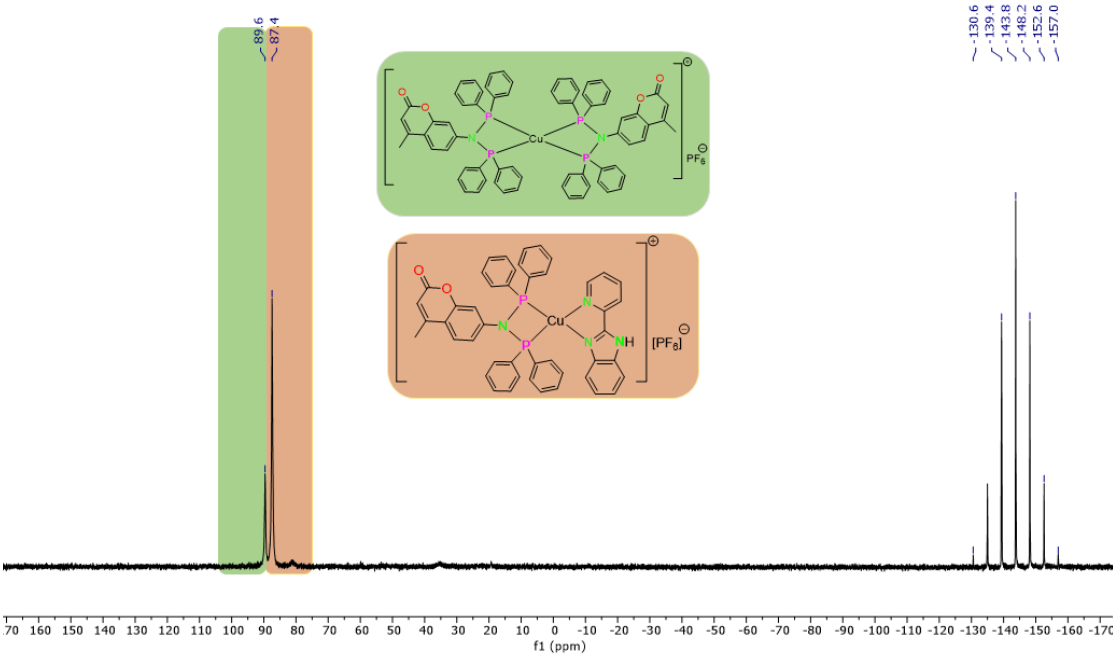


Figure S5. $^{31}P\{^1H\}$ NMR spectrum of **1** in $CDCl_3$.

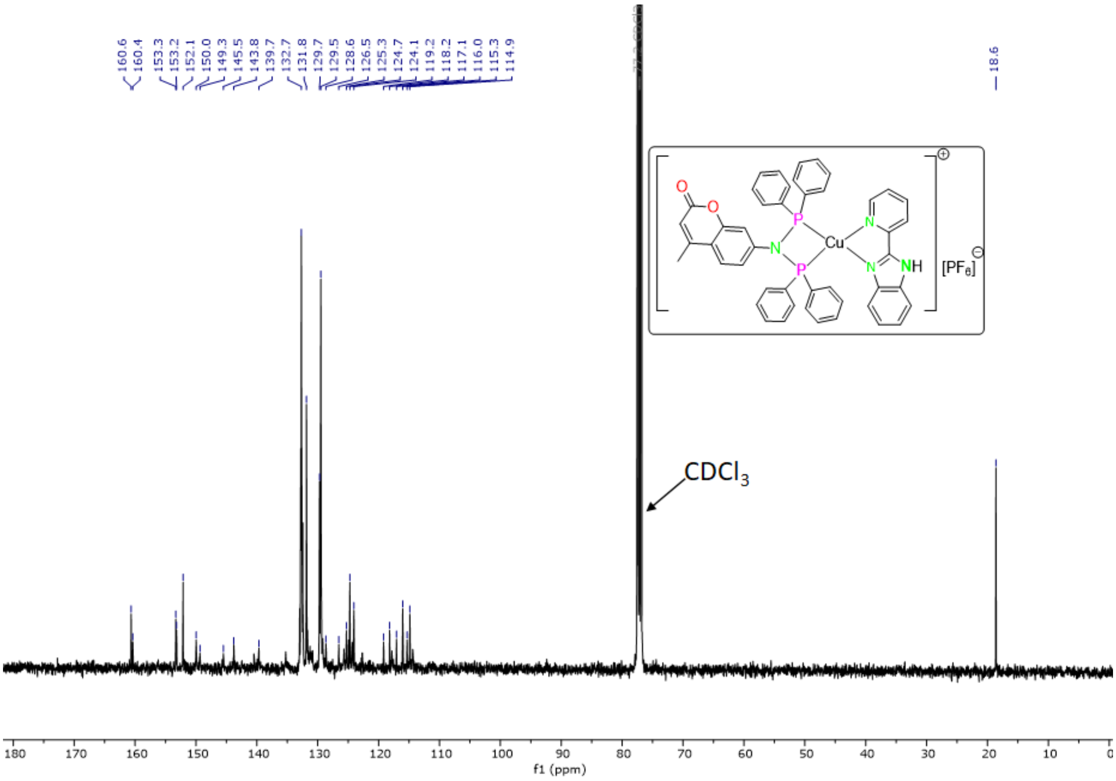


Figure S6. $^{13}C\{^1H\}$ NMR spectrum of **1** in $CDCl_3$.

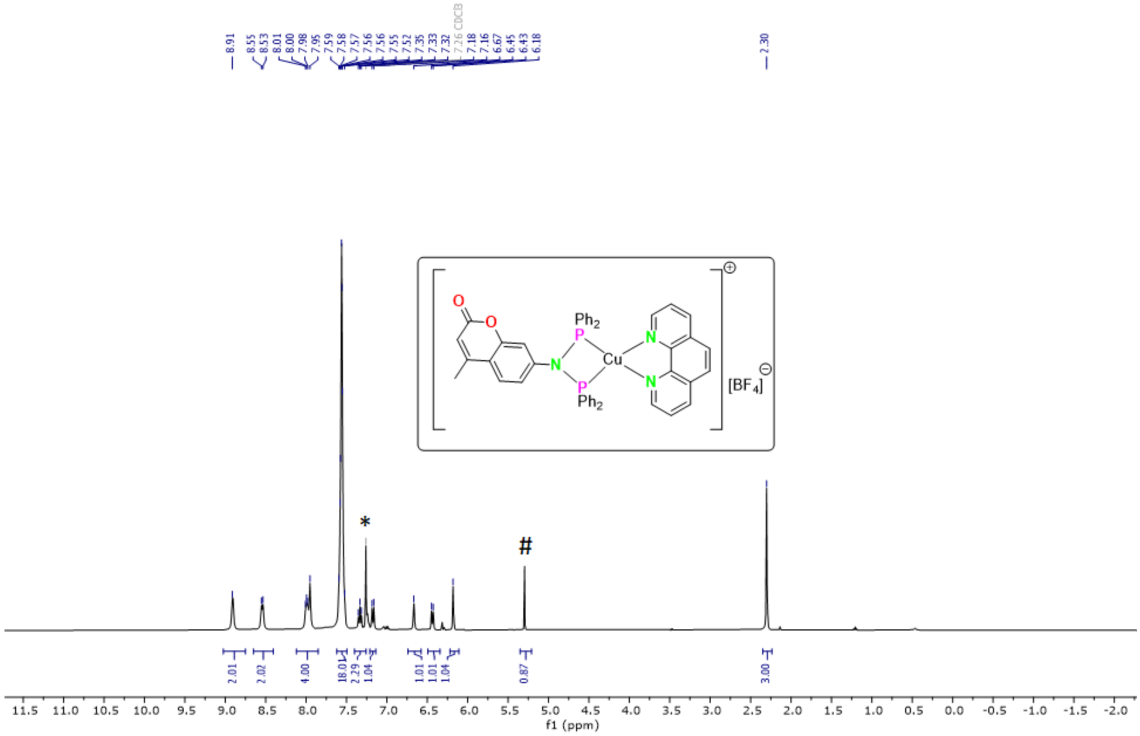


Figure S7. ^{1}H NMR spectrum of **2** in CDCl$_3$. *, residual protio solvent signal. # - DCM

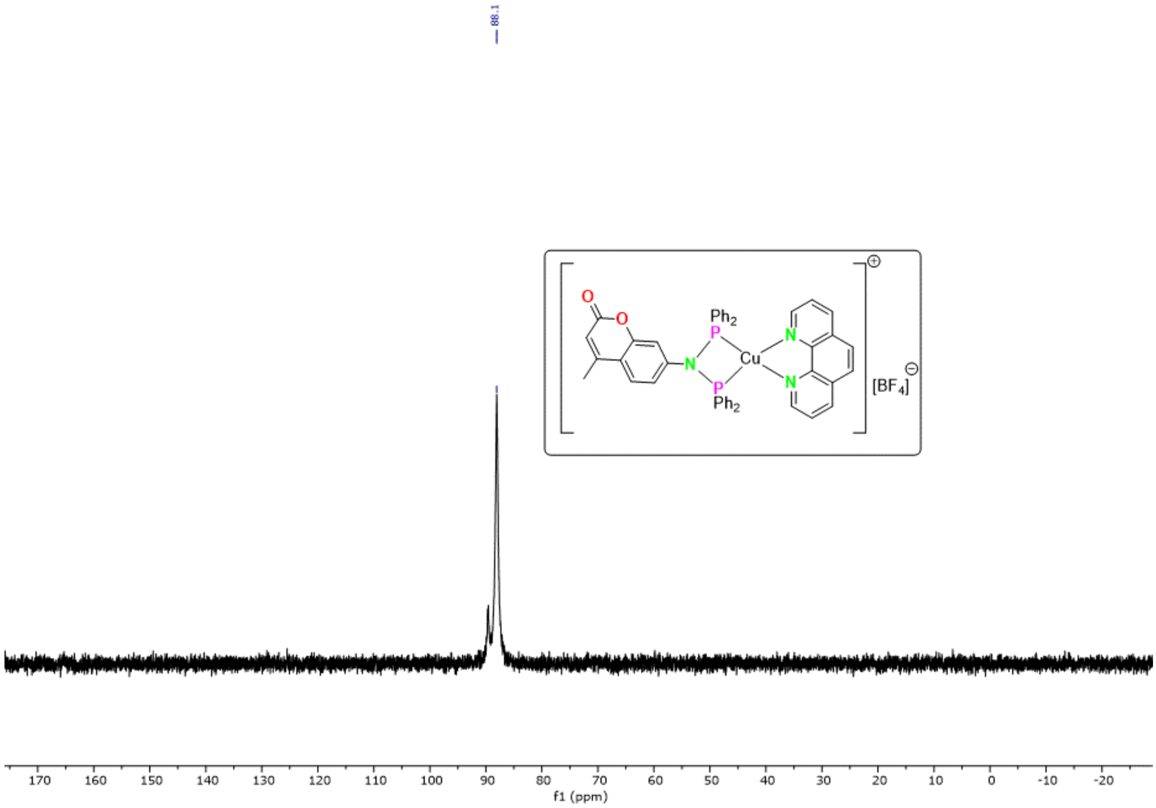


Figure S8. ^{31}P{^{1}H} NMR spectrum of **2** in CDCl$_3$.

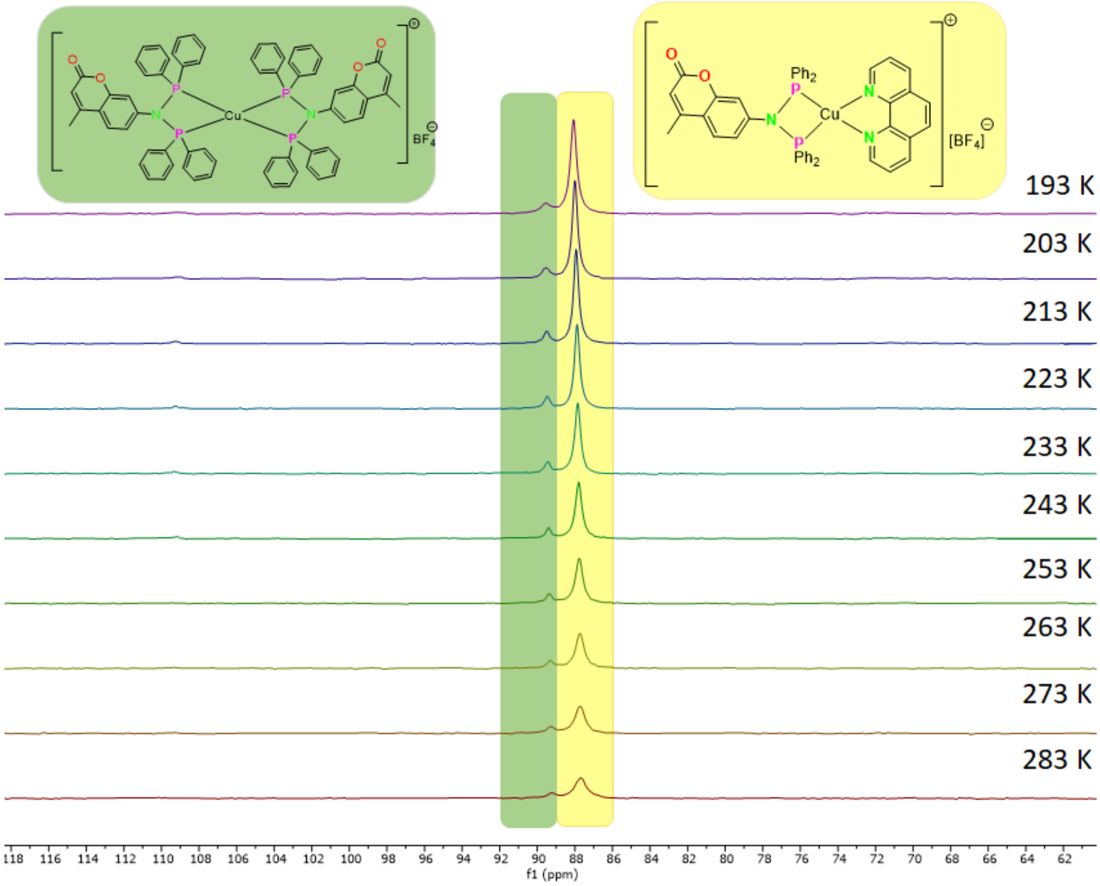


Figure S9. Variable temperature $^{31}P\{^{1}H\}$ NMR spectrum of **2** in CD_2Cl_2.

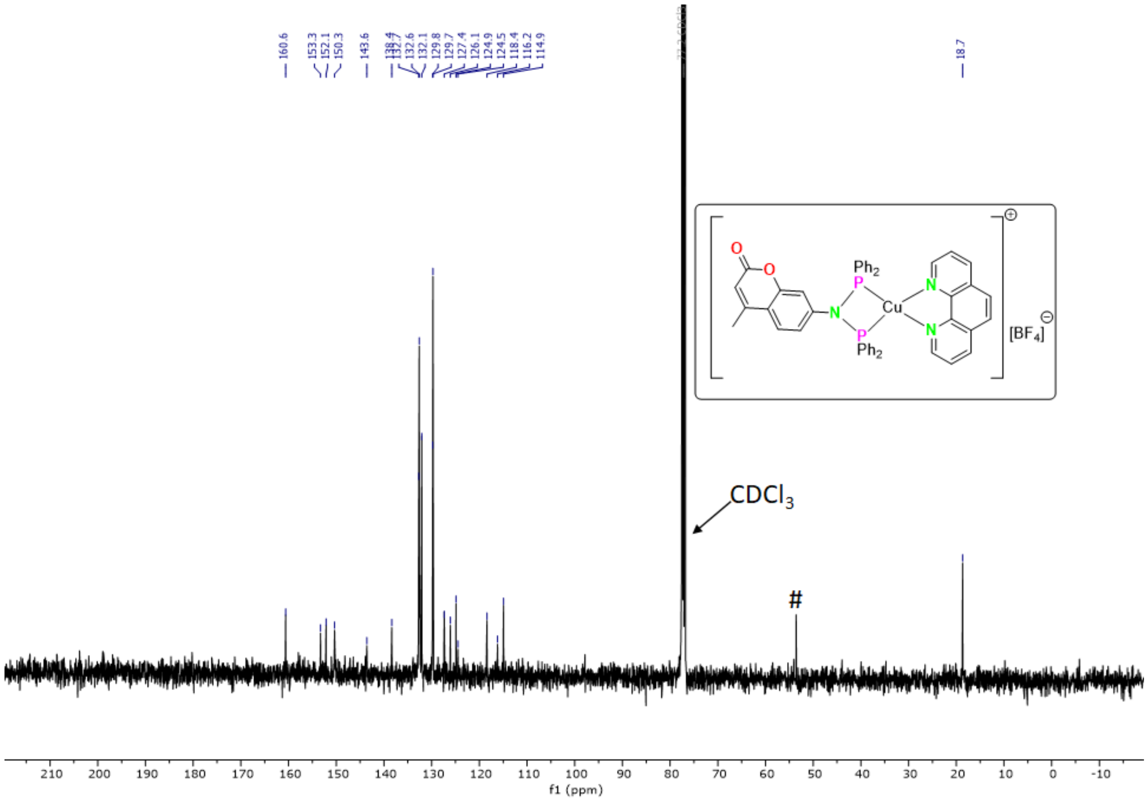


Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum of **2** in $CDCl_3$. # - DCM

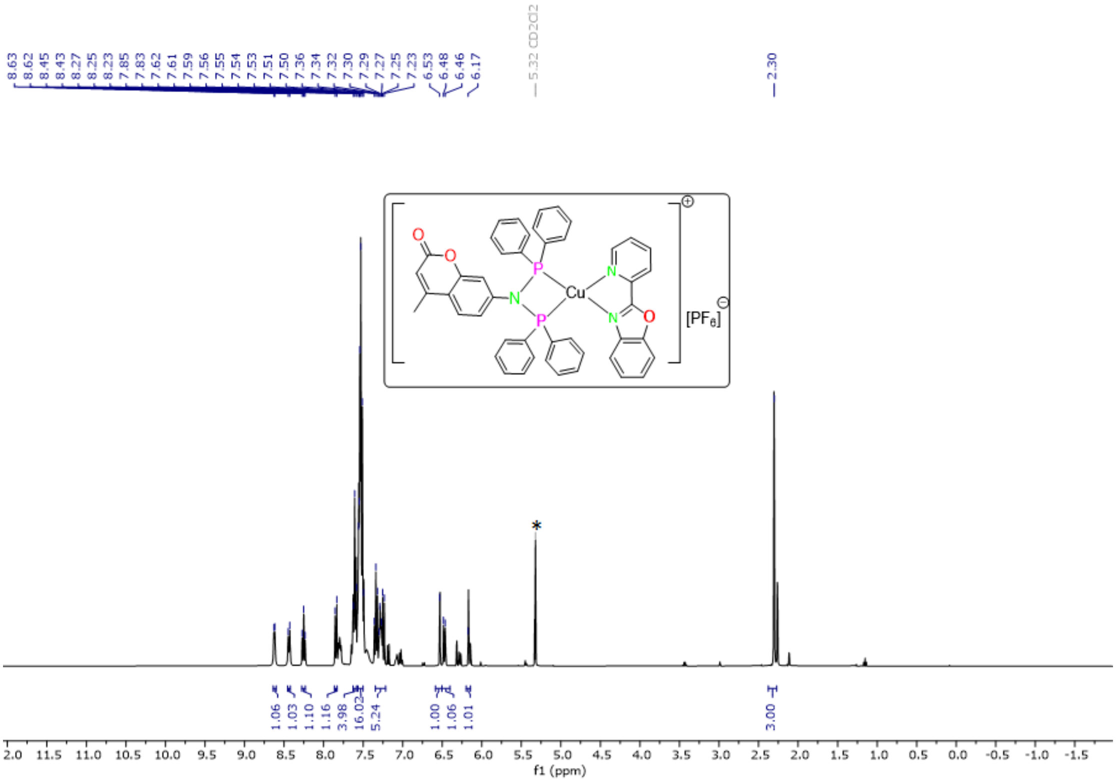


Figure S11. ^{1}H NMR spectrum of **3** in CD_2Cl_2. *, residual protio solvent signal. Integration was performed for all compounds in the solution.

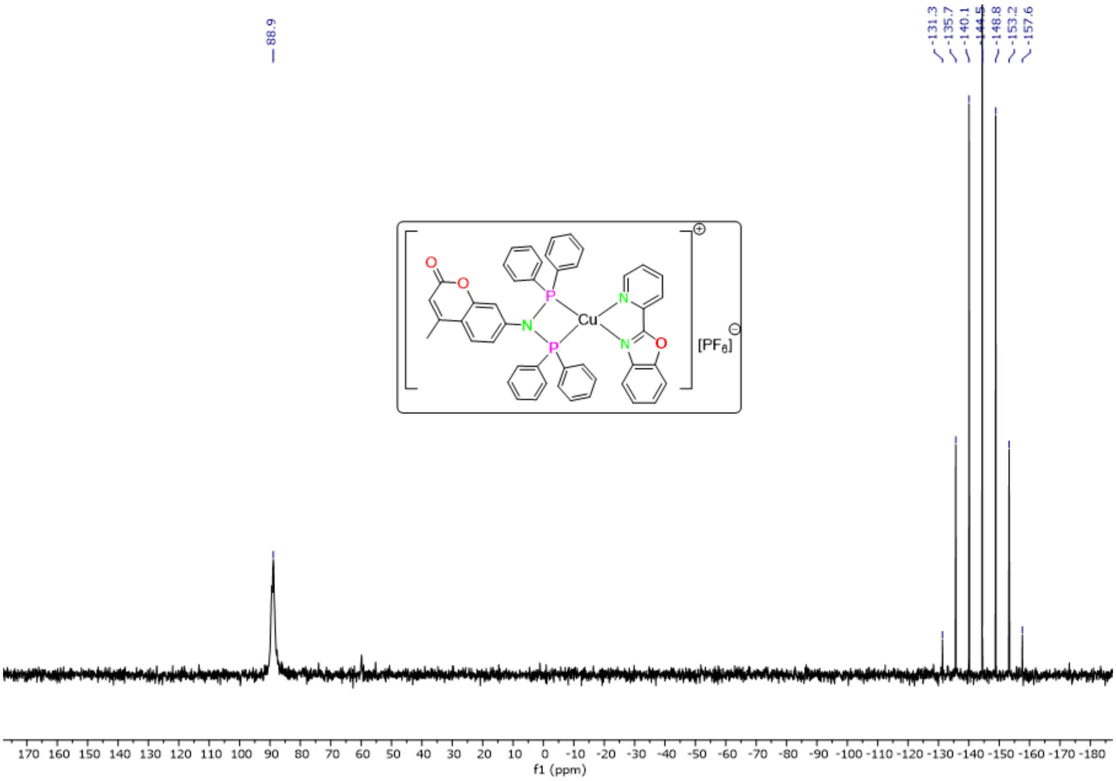


Figure S12. $^{31}P\{^1H\}$ NMR spectrum of **3** in CD_2Cl_2.

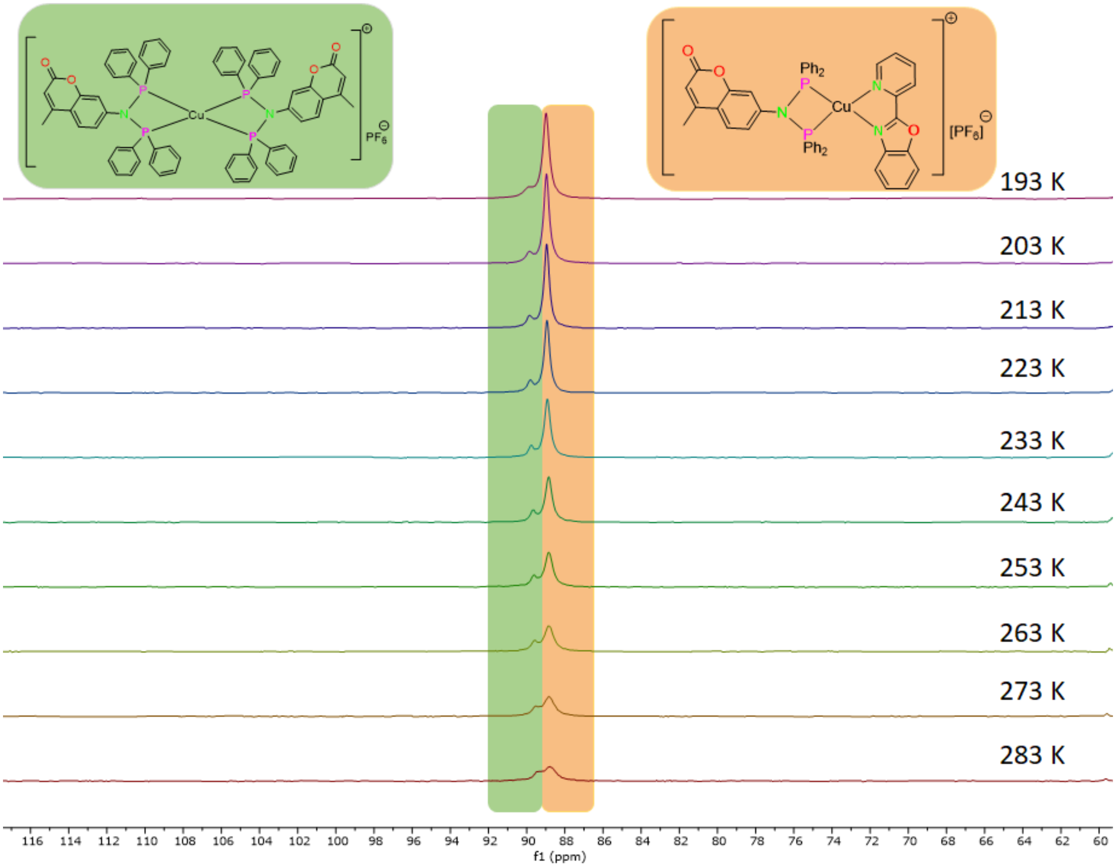


Figure S13. Variable temperature $^{31}P\{^1H\}$ NMR spectrum of **3** in CD_2Cl_2.

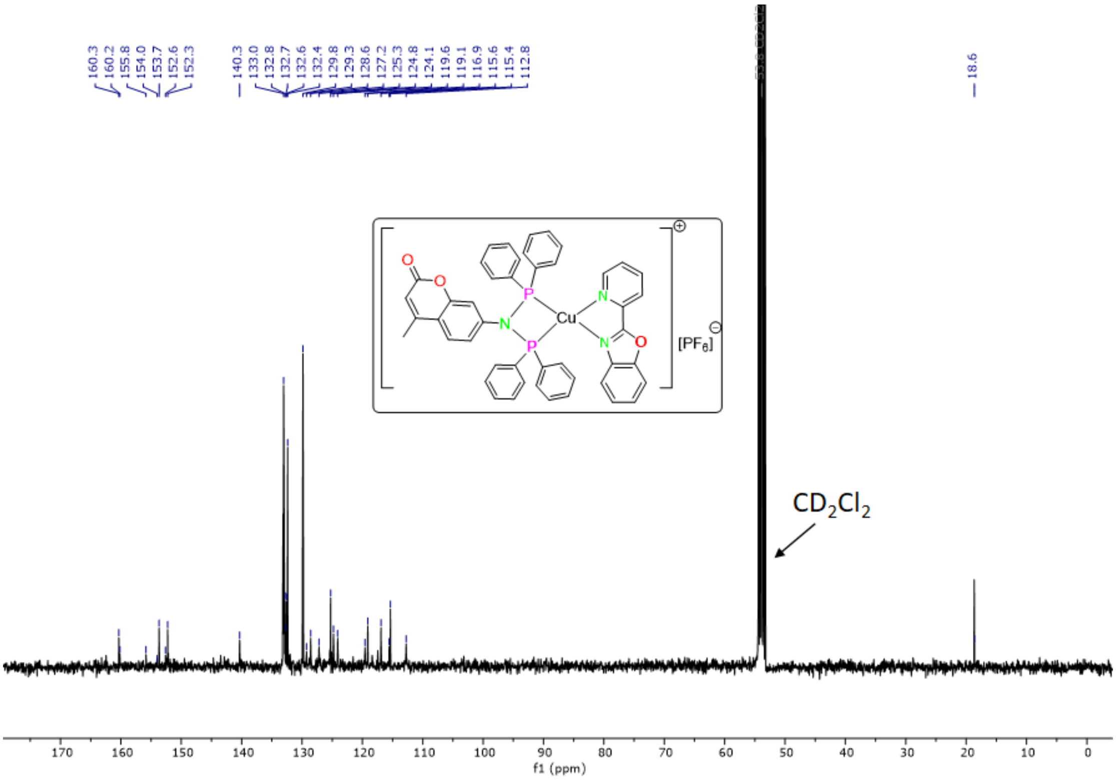


Figure S14. $^{13}C\{^1H\}$ NMR spectrum of **3** in CD_2Cl_2.

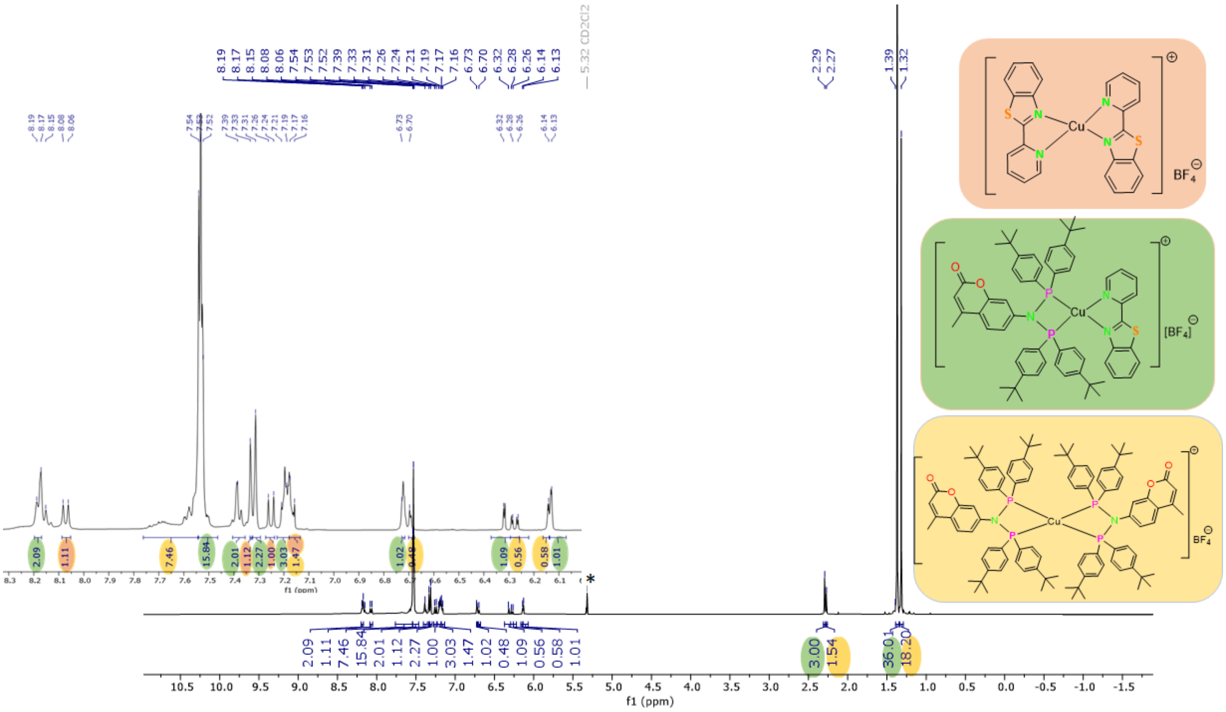


Figure S15. ^{1}H NMR spectrum of **4** in CD_2Cl_2. *, residual protio solvent signal. Integration was performed for all compounds in the solution.

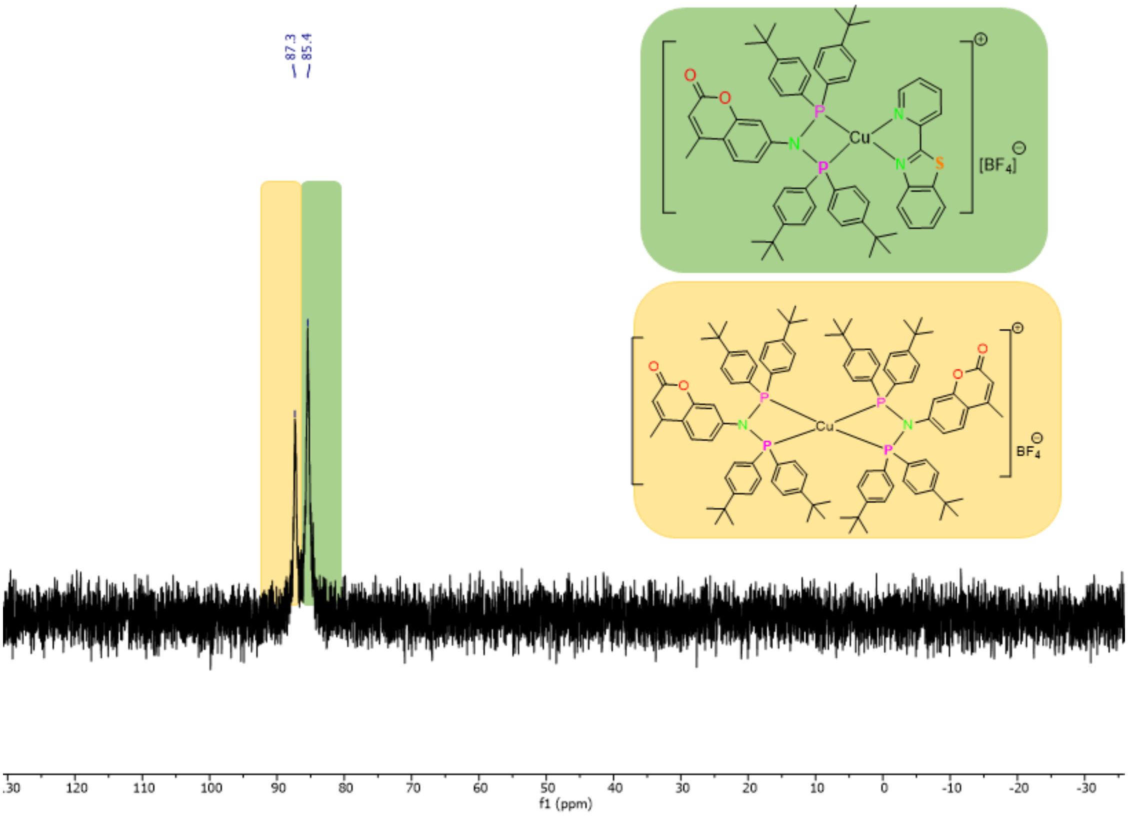


Figure S16. $^{31}P\{^1H\}$ NMR spectrum of **4** in CD_2Cl_2.

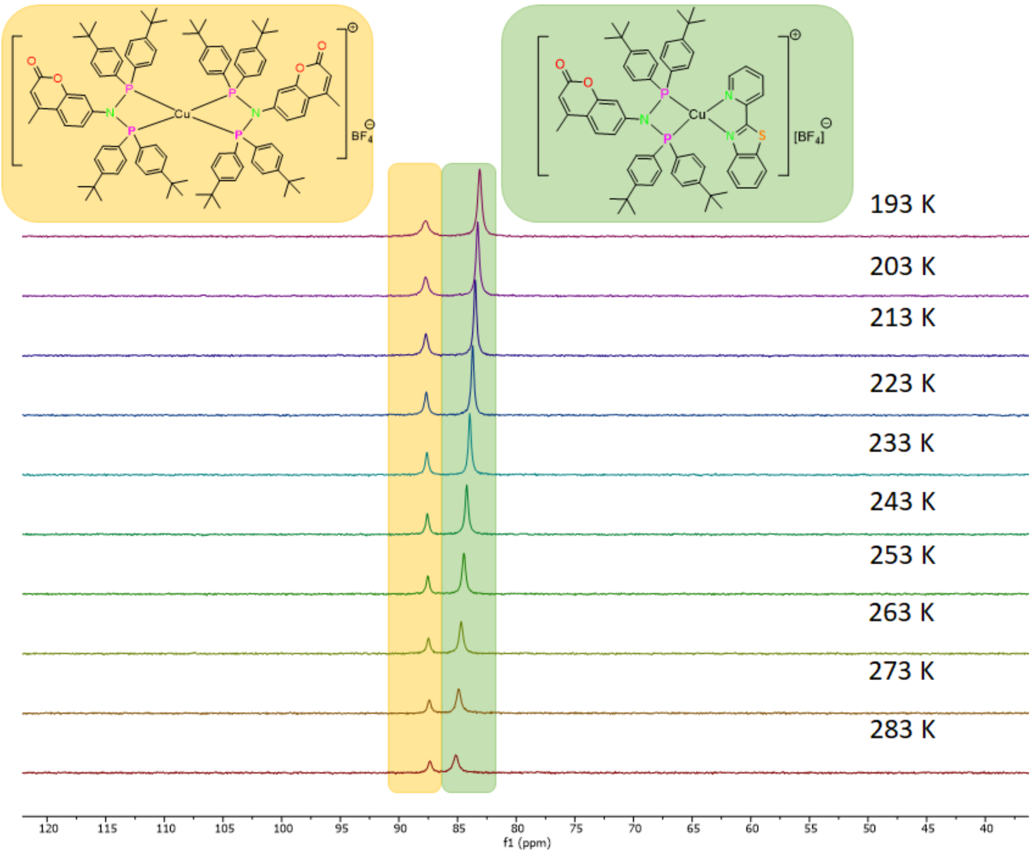


Figure S17. Variable temperature $^{31}P\{^{1}H\}$ NMR spectrum of **4** in CD_2Cl_2.

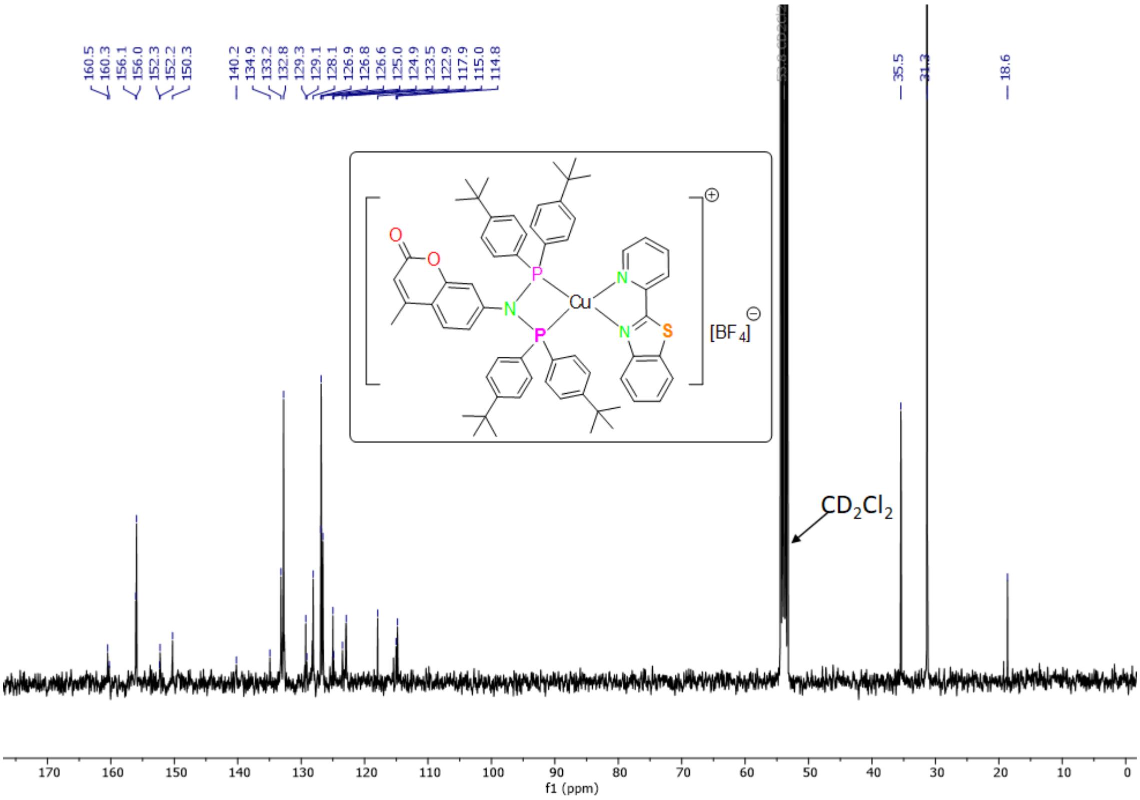


Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum of **4** in CD_2Cl_2.

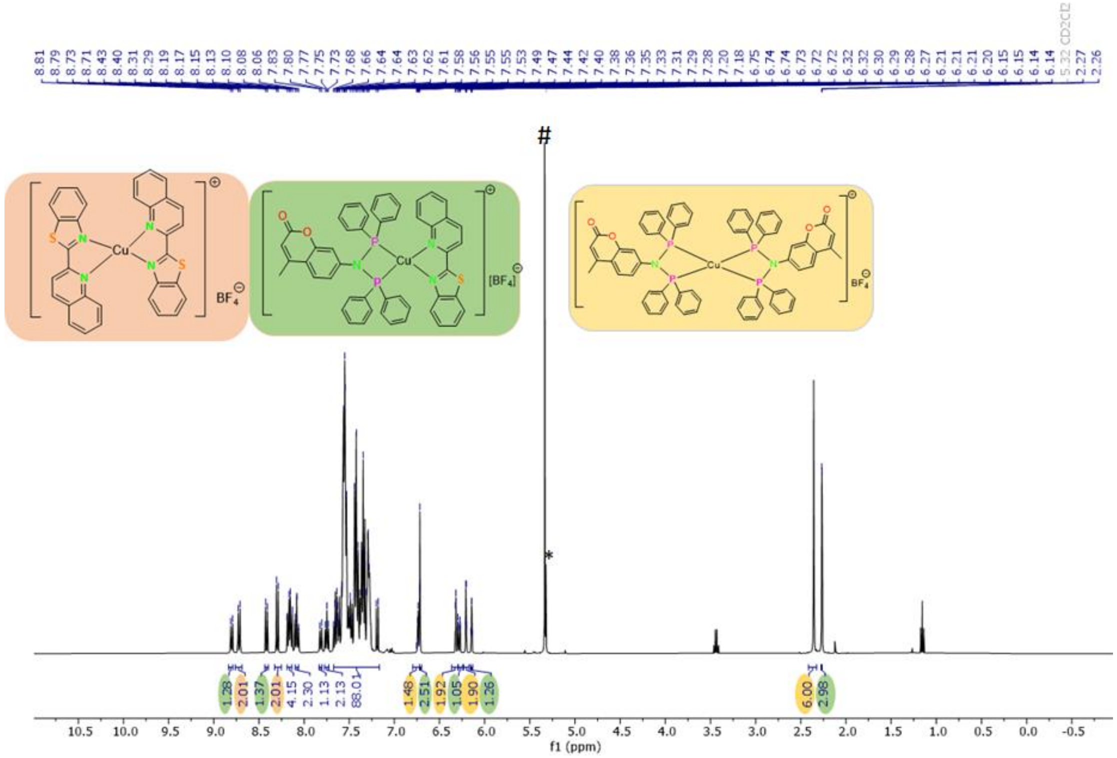


Figure S19. ^{1}H NMR spectrum of **5** in CD_2Cl_2. *, residual protio solvent signal. #- DCM. Integration was performed for all compounds in the solution.

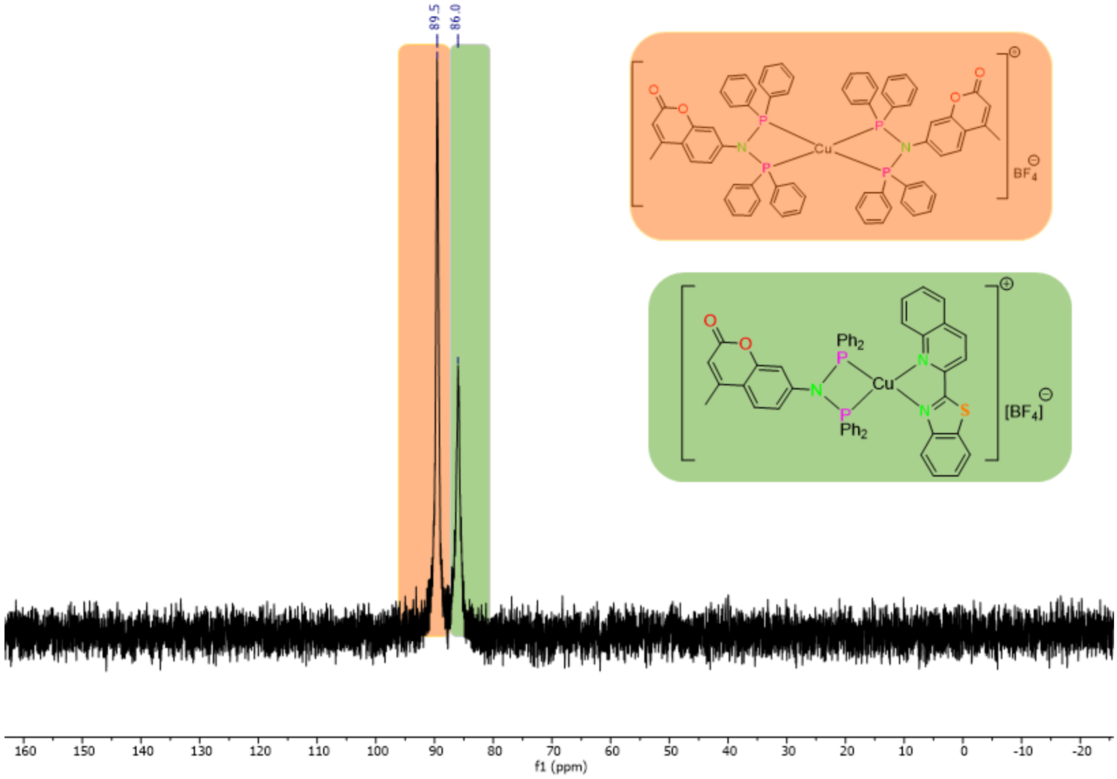


Figure S20. $^{31}P\{^1H\}$ NMR spectrum of **5** in CD_2Cl_2.

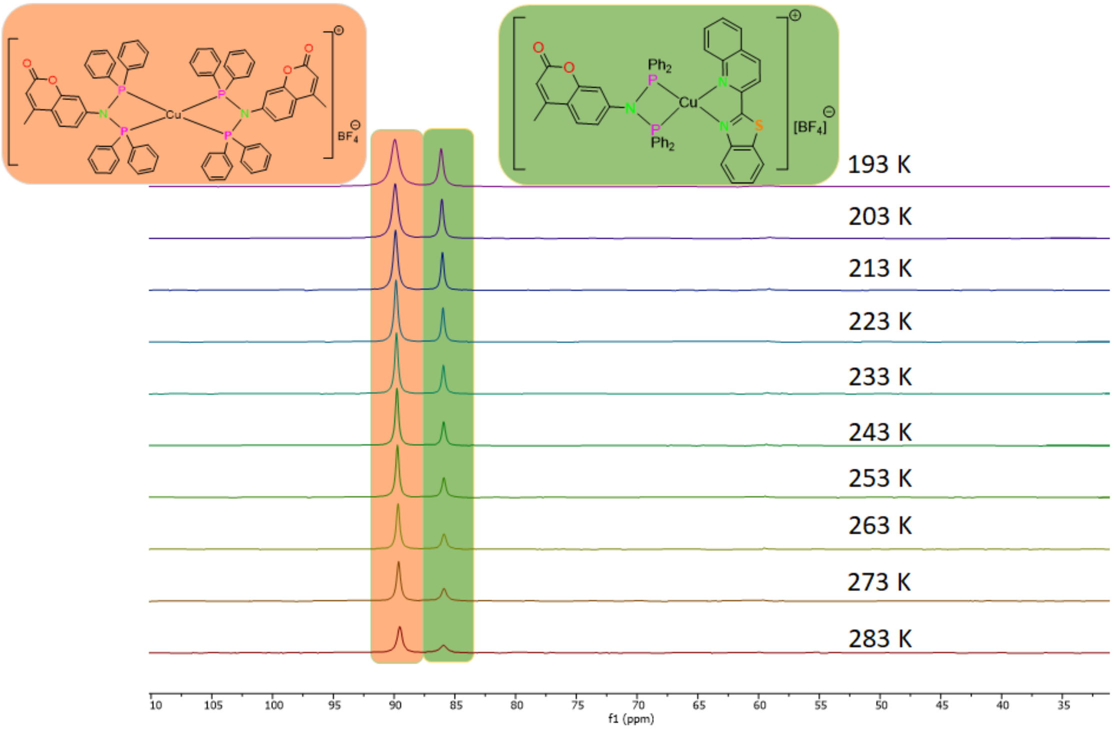


Figure S21. Variable temperature$^{31}P\{^{1}H\}$ NMR spectrum of **5** in CD_2Cl_2.

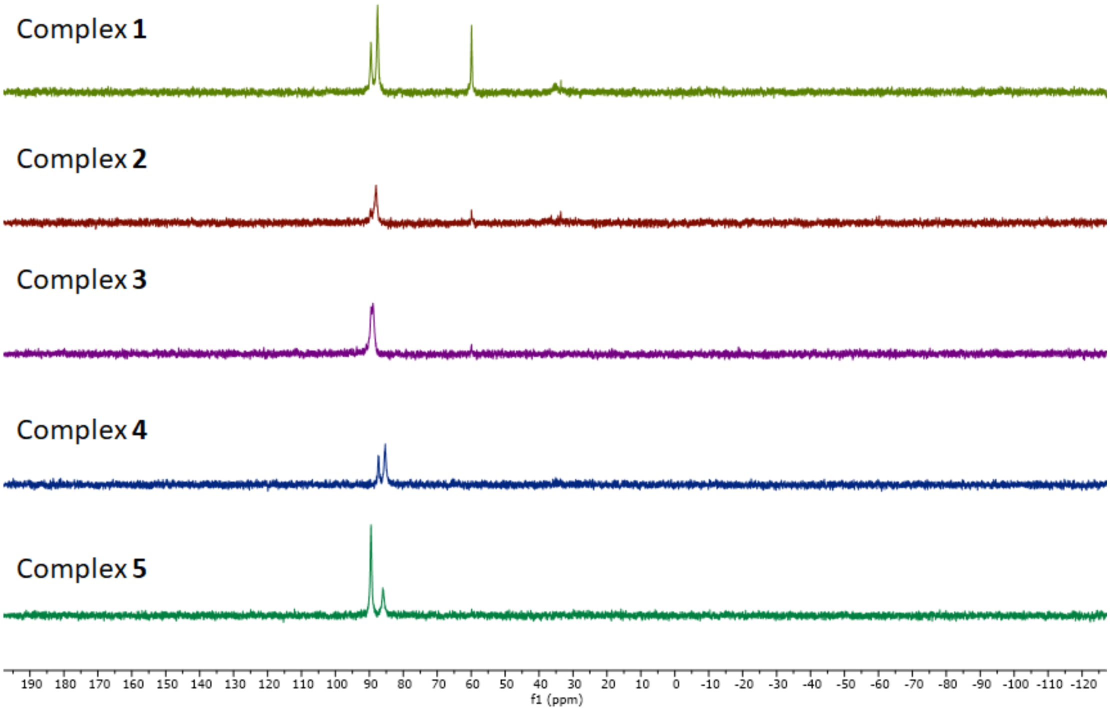


Figure S22. Changes in $^{31}P\{^{1}H\}$ NMR spectra of **1**-**5** in CD_2Cl_2 after nearly 3 months (~ 80-85 days) storage (at ambient temperature, in sealed NMR tubes, in dark). Practically no decomposition of the sample solutions is observed for **3** and **4**, moderate decomposition for **5**, and a more significant decrease of the NMR signals for **1** and **2**. Green crystalline precipitate is observed in the NMR tube of complex **1**.

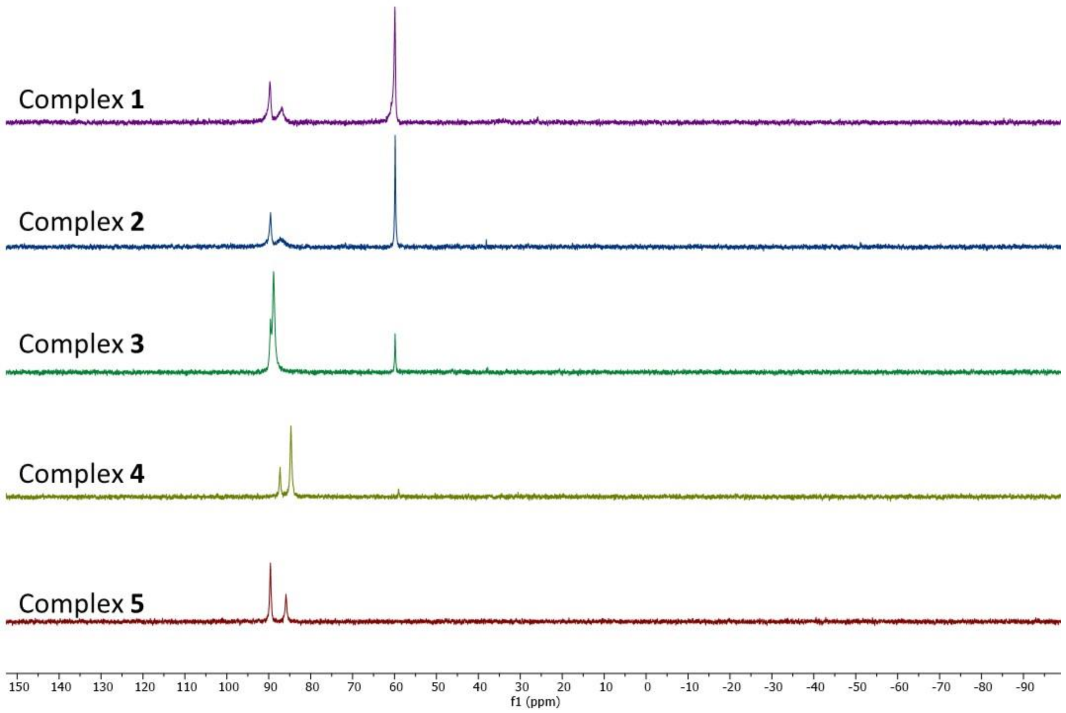


Figure S23. Changes in the $^{31}P\{^{1}H\}$ NMR spectra of **1**-**5** in $CDCl_3$ after heating the freshly prepared samples at 50 °C for 5 h. Rapid decomposition into ligand was observed for complexes **1** and **2** followed by complexes **3** and **4**. Practically no decomposition was observed for complex **5**.

III. IR spectra

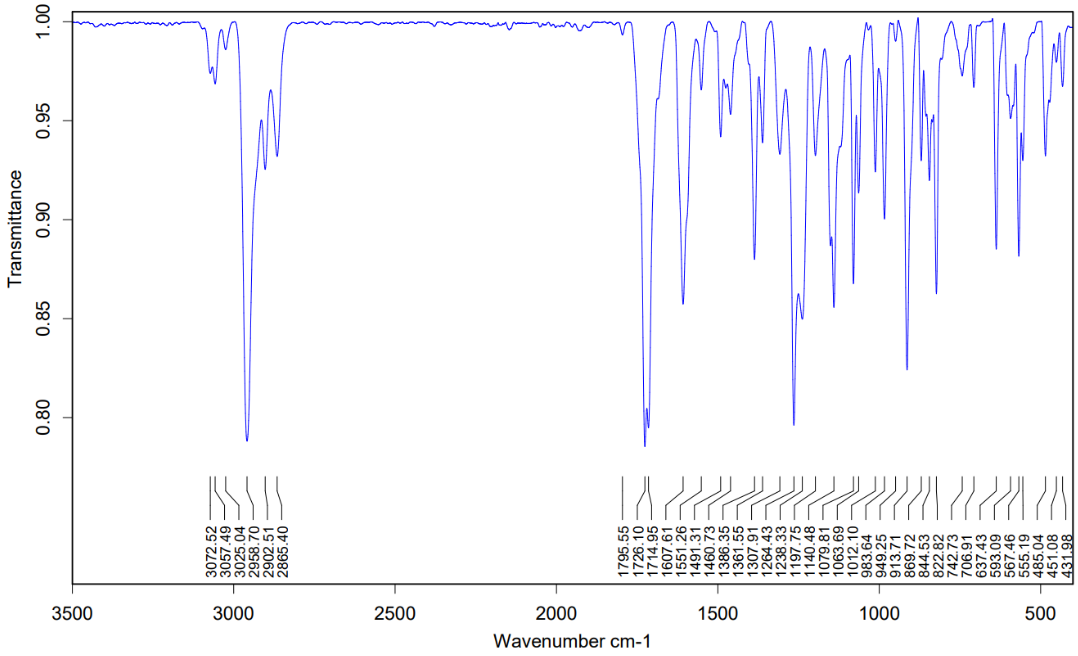


Figure S24. IR spectrum of ligand **L**^{2}.

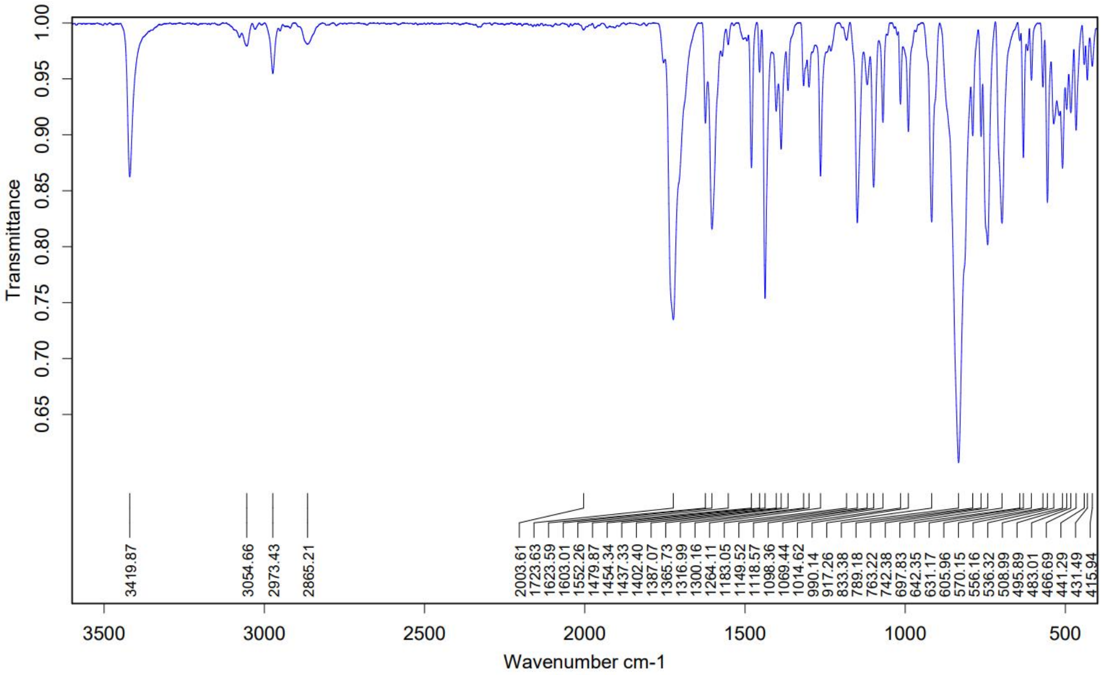


Figure S25. IR spectrum of complex **1**.

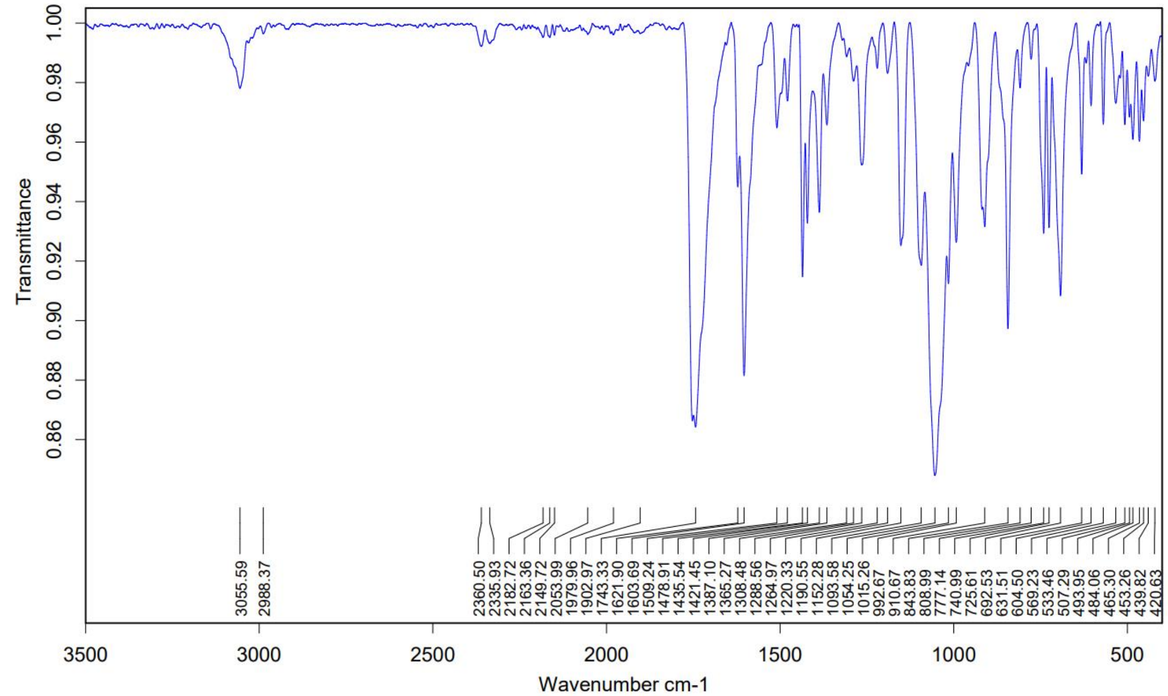


Figure S26. IR spectrum of complex **2**.

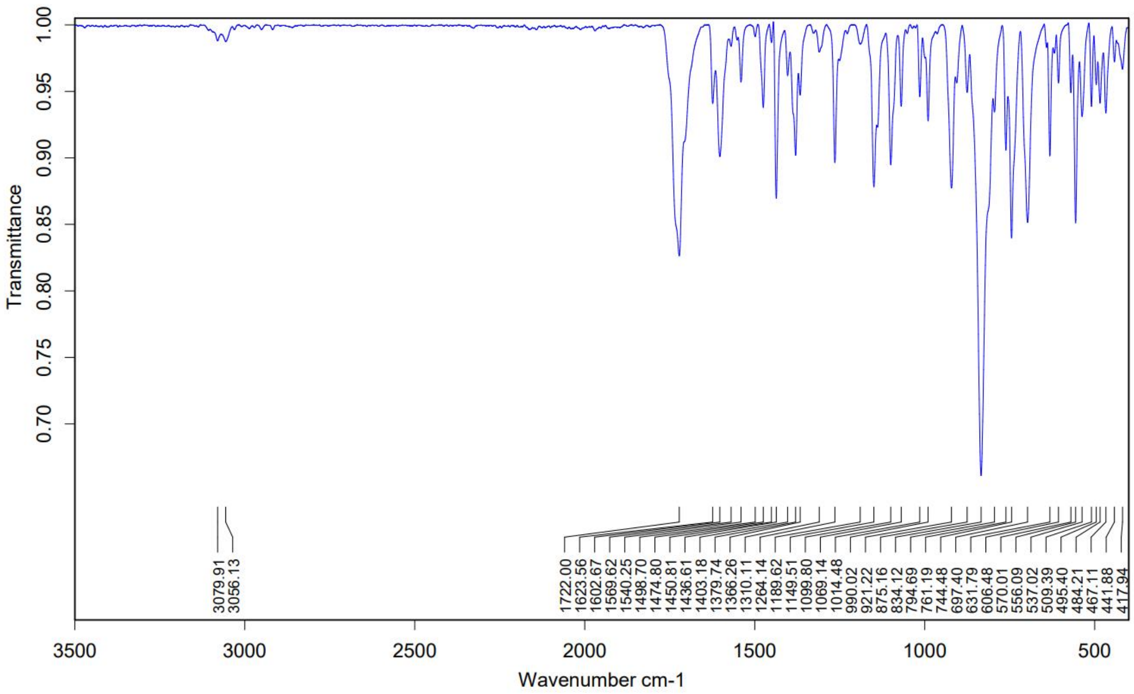


Figure S27. IR spectrum of complex **3**.

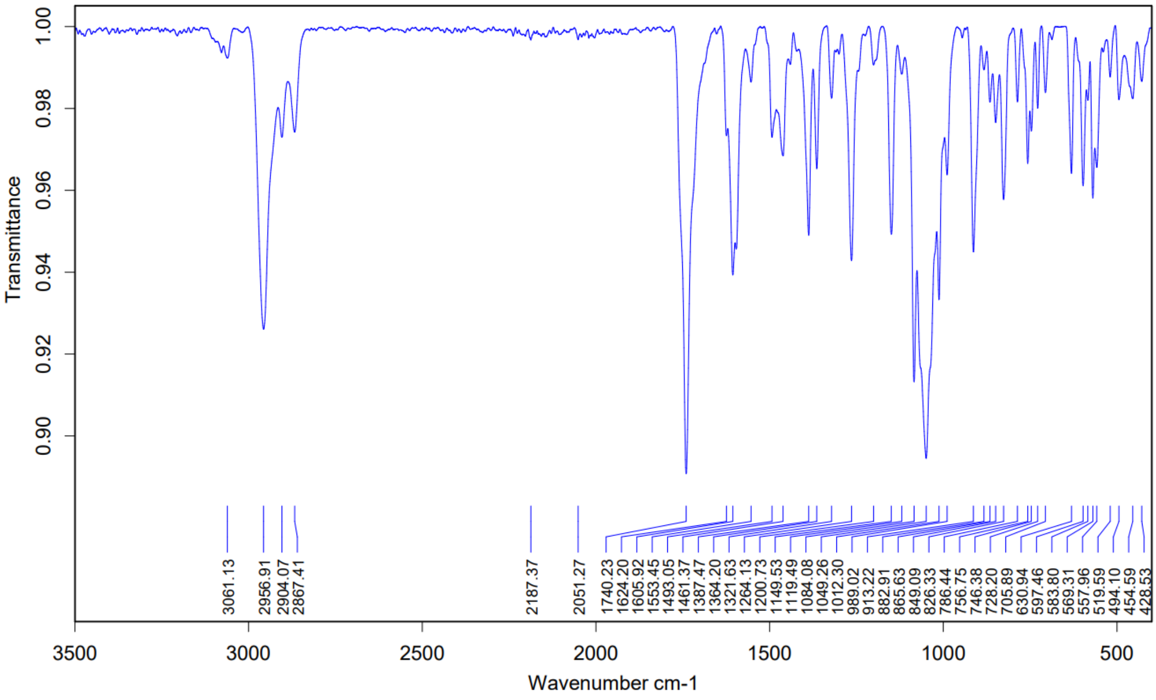


Figure S28. IR spectrum of complex **4**.

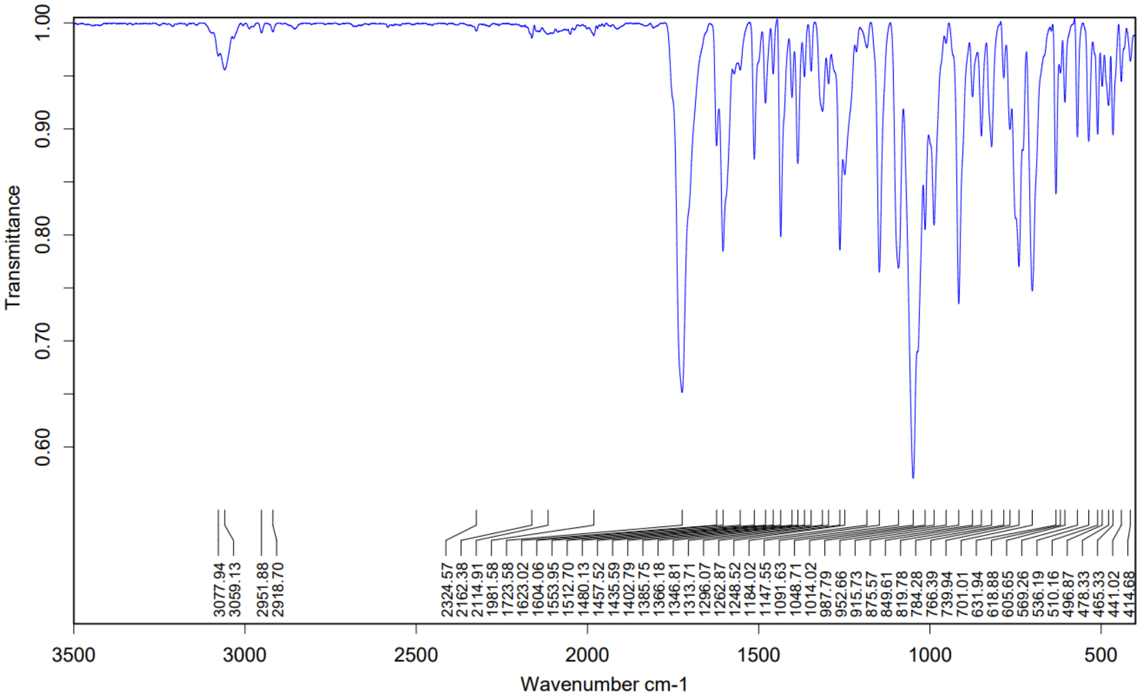


Figure S29. IR spectrum of complex **5**.

IV. Mass spectra

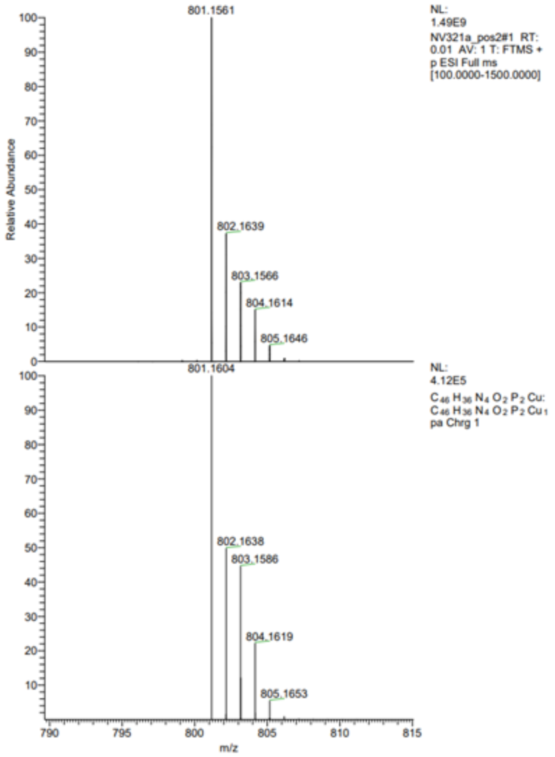


Figure S30. MS-ESI spectra of complex **1**. Shown is the molecular ion peak [M-PF$_6$]$^+$. Top: experimental spectrum, bottom: simulated signals.

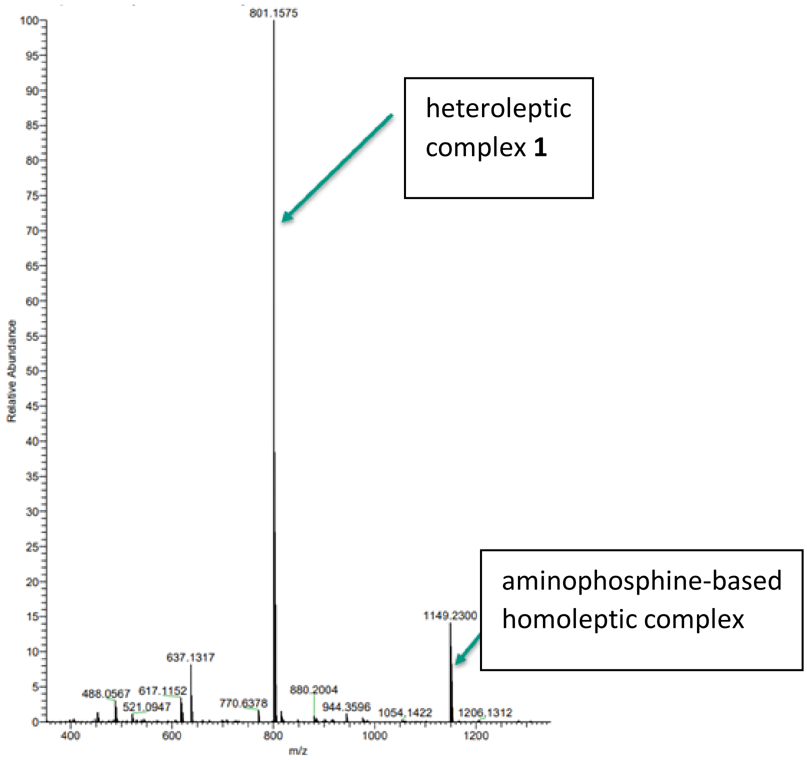


Figure S31. MS-ESI spectra of complex **1**. Indicated are the molecular ion peak [M-PF$_6$]$^+$ of **1** and the peak of the related homoleptic complex**.**

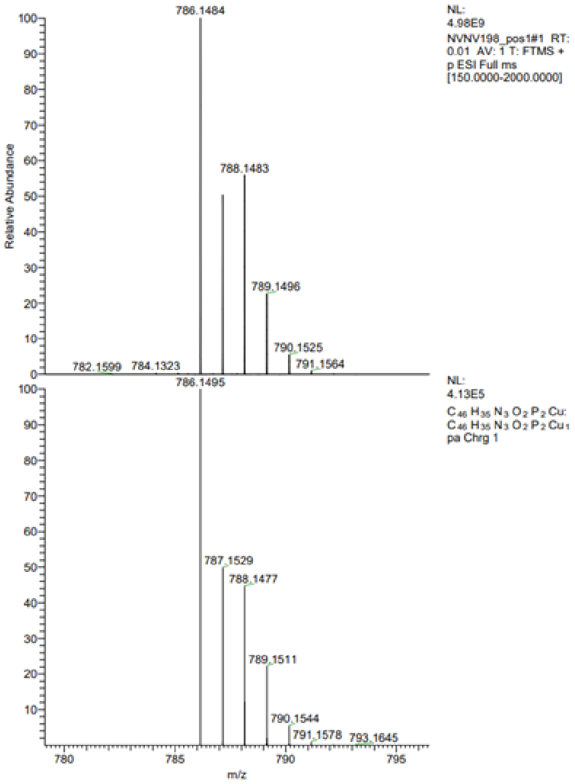


Figure S32. MS-ESI spectra of complex **2**. Shown is the molecular ion peak [M-BF_4]$^+$. Top: experimental spectrum, bottom: simulated signals.

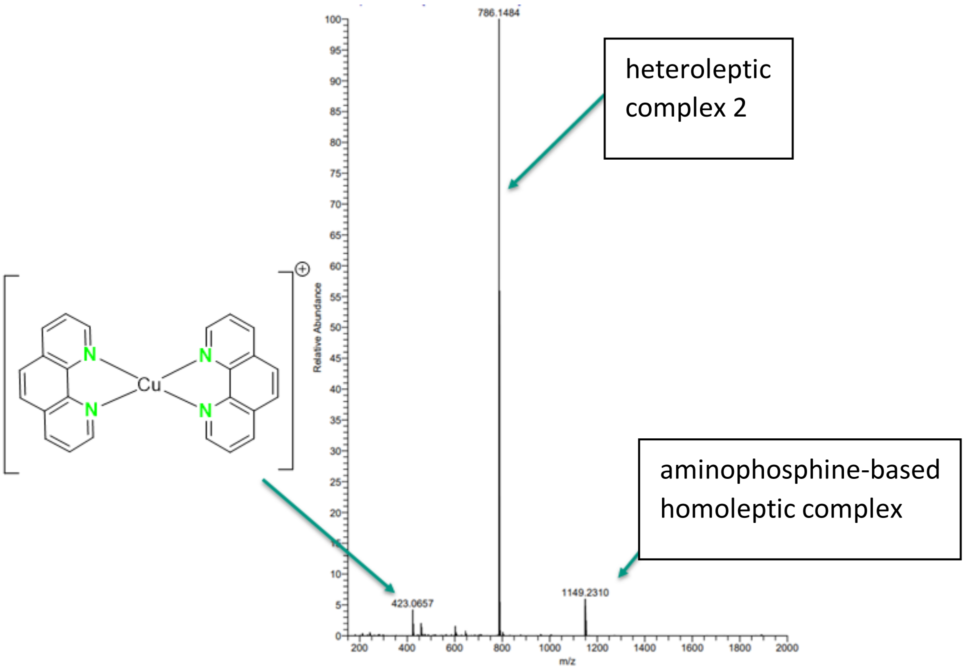


Figure S33. MS-ESI spectra of complex **2**. Indicated are the molecular ion peak [M-BF_4]$^+$ of **2** and molecular ion peaks of two related homoleptic complexes**.**

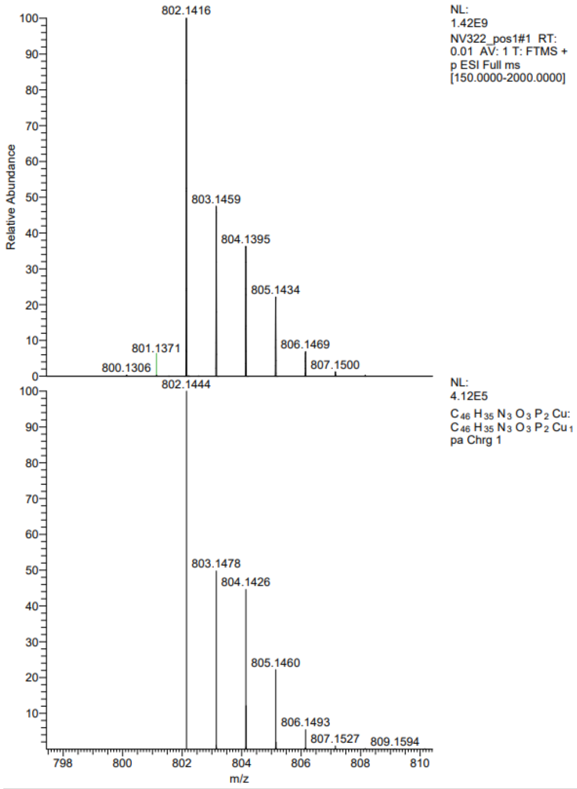


Figure S34. MS-ESI spectra of complex **3**. Indicated are the molecular ion peak $[M\text{-}PF_6]^+$. Top: experimental spectrum, bottom: simulated signals.

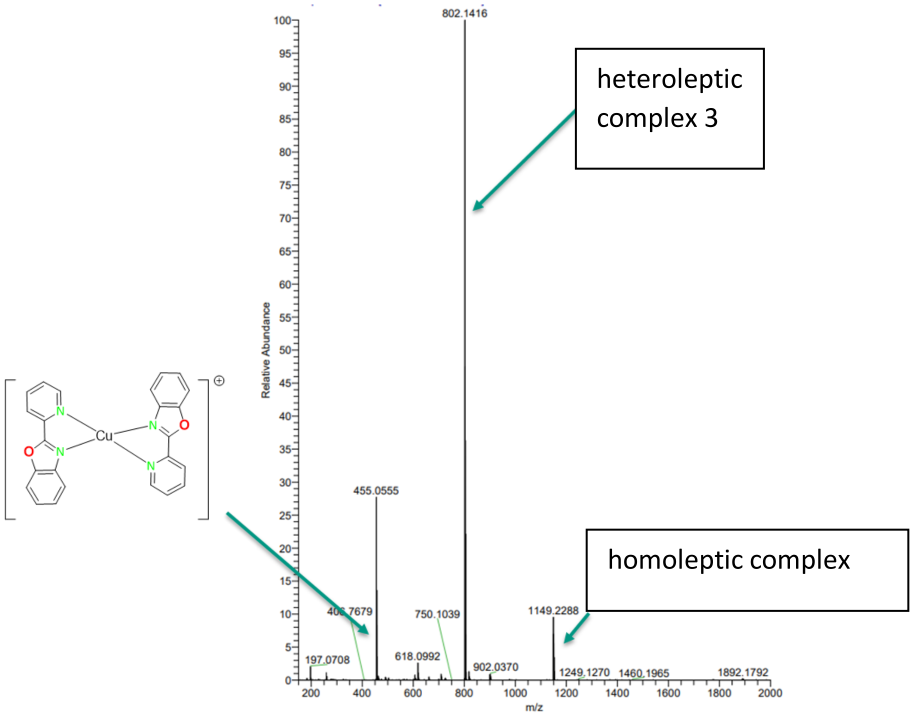


Figure S35. MS-ESI spectra of complex **3**. Indicated are the molecular ion peak $[M\text{-}PF_6]^+$ of **3** and the peaks of two related homoleptic complexes**.**

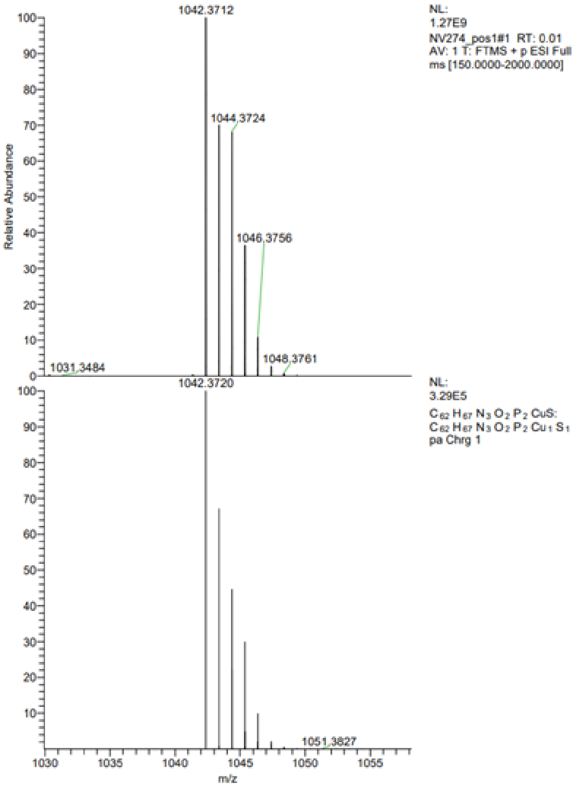
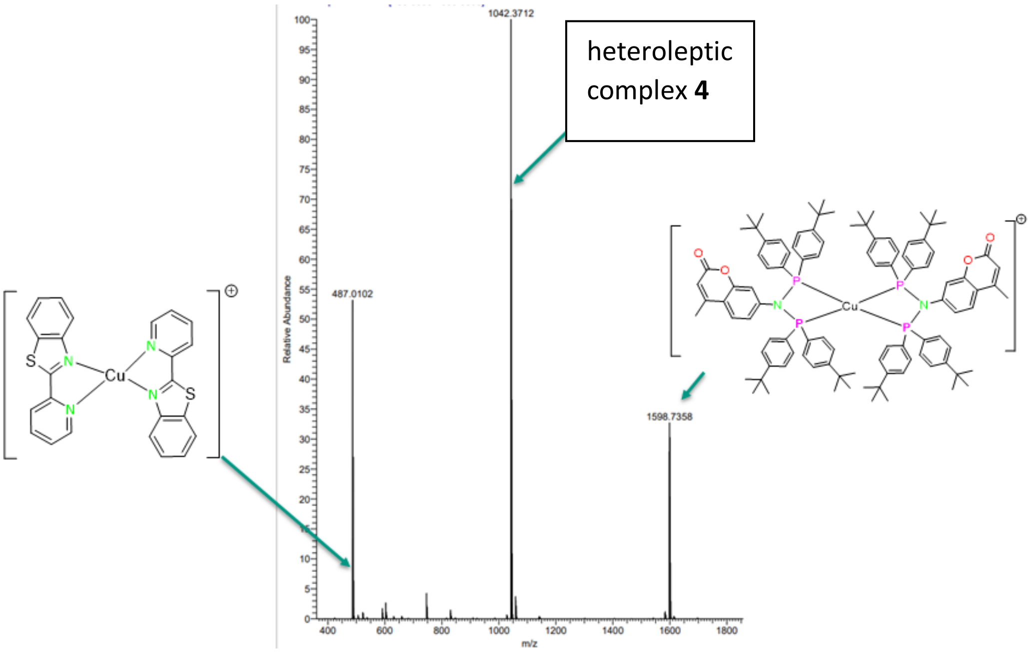


Figure S36. MS-ESI spectra of complex **4**. Shown is the molecular ion peak [M-BF_4]$^+$. Top: experimental spectrum, bottom: simulated signals.



heteroleptic complex **4**

Figure S37. MS-ESI spectra of complex **4**. Indicated are the molecular ion peak [M-PF_6]$^+$ of **4** and the peaks of two related homoleptic complexes**.**

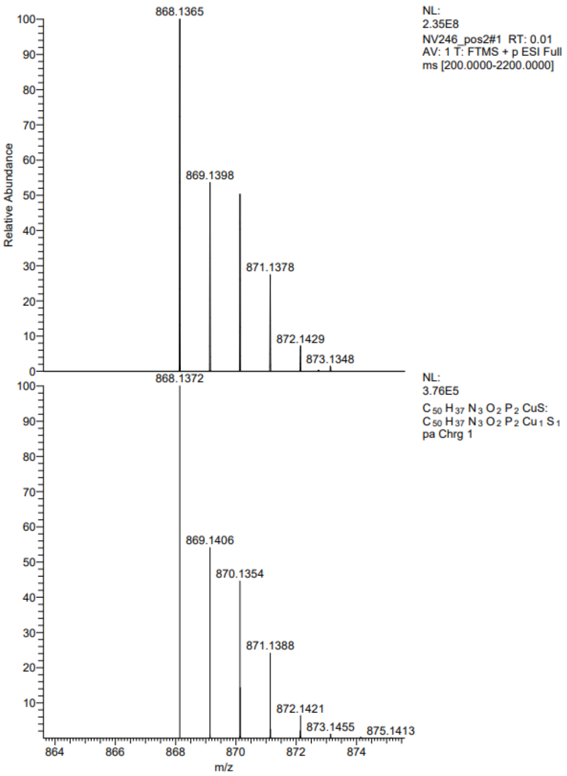


Figure S38. MS-ESI spectra of complex **5**. Shown is the molecular ion peak [M-BF_4]$^+$. Top: experimental spectrum, bottom: simulated signals.

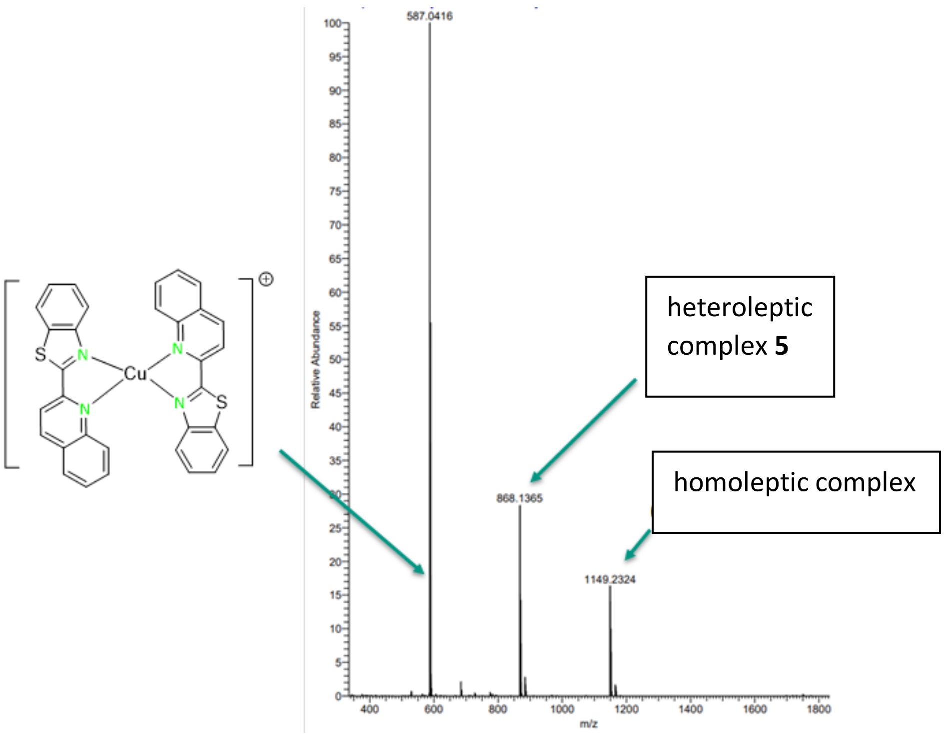


Figure S39. MS-ESI spectra of complex **5**. Indicated are the molecular ion peak [M-PF_6]$^+$ of **5** and the peaks of two related homoleptic complexes**.**

V. X-ray crystallography

V.1 General methods

Suitable crystals for the X-ray analysis of all compounds were obtained as described above. A suitable crystal was covered in mineral oil (Aldrich) and mounted on a glass fibre. The crystal was transferred directly to the cold stream of a STOE StadiVari (100 K or 150 K) diffractometer. All structures were solved by using the program SHELXS/T[4,5] and Olex2.[6] The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F^2 by using the program SHELXL.[5,6] The H-atoms were introduced into the geometrically calculated positions (SHELXL procedures) unless otherwise stated and refined riding on the corresponding parent atoms. In each case, the locations of the largest peaks in the final difference Fourier map calculations, as well as the magnitude of the residual electron densities, were of no chemical significance. Summary of the crystal data, data collection and refinement for compounds are given in Table S1.

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication no. 2266992-2266996. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+(44)1223-336-033; email: deposit@ccdc.cam.ac.uk).

V.2. Table S1. Summary of crystal data

Compound	**1**	**2**	**3**	**4**
CCDC Number	2266992	2266993	2266994	2266995
Formula	$C_{50}H_{46}CuF_6N_4O_3P_3$ (**1** (THF))	$C_{95}H_{76}B_2Cl_6Cu_2F_8N_6O_4P_4$ (2 **2** (CH_2Cl_2))	$C_{47}H_{37}Cl_2CuF_6N_3O_3P_3$ (**3** (CH_2Cl_2))	$C_{65}H_{73}BCl_6CuF_4N_3O_2P_2S$ (**4** (3 CH_2Cl_2))
$D_{calc.}$/ g cm^{-3}	1.462	1.478	1.495	1.412
μ /mm^{-1}	0.647	0.795	0.767	0.720
Formula Weight	1021.36	2002.89	1033.14	1385.31
Colour	Yellow	Yellow	Yellow	Orange
Shape	Fragment	Fragment	Prism	Fragment
Size/mm^3	0.41×0.40×0.38	0.25×0.40×0.63	0.49×0.40×0.31	0.39 × 0.28 × 0.17
T/K	100	150	100	110
Crystal System	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space Group	$P2_1/c$	$C2/c$	$P2_1/c$	P-1
a/Å	17.8014(8)	40.1317(18)	17.9964(7)	14.757(2)
b/Å	14.6604(6)	14.1718(4)	14.6953(3)	15.000(4)
c/Å	17.7919(7)	17.4639(8)	17.3565(6)	16.552(5)
α/°				77.69(2)
β/°	92.318(3)	115.037(3)	90.960(3)	65.656(19)
γ/°				87.432(18)
V/Å^3	4639.5(3)	8999.1(7)	4589.5(3)	3257.7(15)
Z	4	4	4	2
Z'	1	0.5	1	1
Wavelength/Å	0.71073	0.71073	0.71073	0.71073
Radiation type	Mo K$_\alpha$	Mo K$_\alpha$	Mo K$_\alpha$	Mo K$_\alpha$
Measured Reflections	30397	27976	28411	45610
Independent Reflections	12721	9958	12587	18077
R_{int}	0.0395	0.0278	0.0345	0.0484
GooF	1.081	1.057	1.047	1.083
wR_2 (all data)	0.1915	0.1208	0.1553	0.2256
wR_2	0.1685	0.1079	0.1387	0.1857
R_1 (all data)	0.1046	0.0725	0.0793	0.0995
R_1	0.0635	0.0485	0.0545	0.0716

Compound	**5**
CCDC Number	2266996
Formula	$C_{51}H_{39}BCl_2CuF_4N_3O_2P_2S$ (**3** (CH_2Cl_2))
$D_{calc.}$/ g cm^{-3}	1.520
μ /mm^{-1}	0.777
Formula Weight	1041.10
Colour	Red
Shape	Block
Size/mm^3	0.48×0.47×0.45
T/K	100
Crystal System	Monoclinic
Space Group	$P2_1/c$
a/Å	17.8322(5)
b/Å	14.3406(3)
c/Å	17.8408(6)
α/°	
β/°	94.179(2)
γ/°	
V/Å^3	4550.2(2)
Z	4
Z'	1
Wavelength/Å	0.71073
Radiation type	Mo K_{α}
Measured Reflections	62922
Independent Reflections	11721
R_{int}	0.0471
GooF	1.055
wR_2 (all data)	0.1199
wR_2	0.1133
R_1 (all data)	0.0718
R_1	0.0429

V.3 Crystal structures

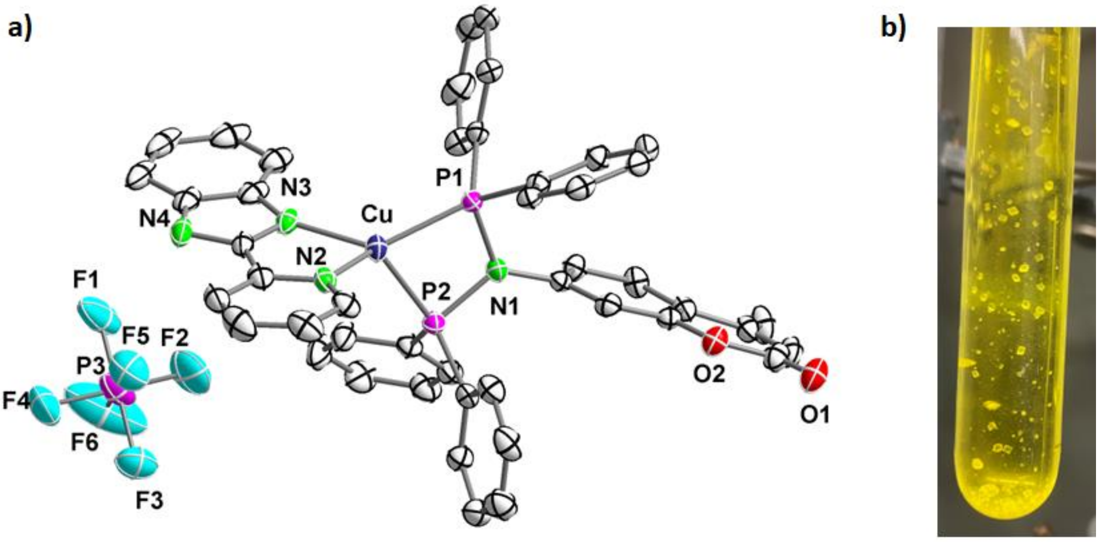


Figure S40. a) Molecular structure of complex **1** in the solid-state. Hydrogen atoms and the non-coordinating solvent molecules are omitted for clarity. Selected bond distances (Å) and angles (°): Cu-P1 2.2503(9), Cu-P2 2.3011(9), Cu-N2 2.057(3), Cu-N3 2.015(3), N1-P1 1.737(3), N1-P2 1.701(3); P1-Cu-P2 74.24(3), P2-Cu-N2 118.42(8), N2-Cu-N3 82.21(11), N3-Cu-P1 128.79(9), P1-N1-P2 106.07(11). b) Photographs of the crystals of complex **1.**

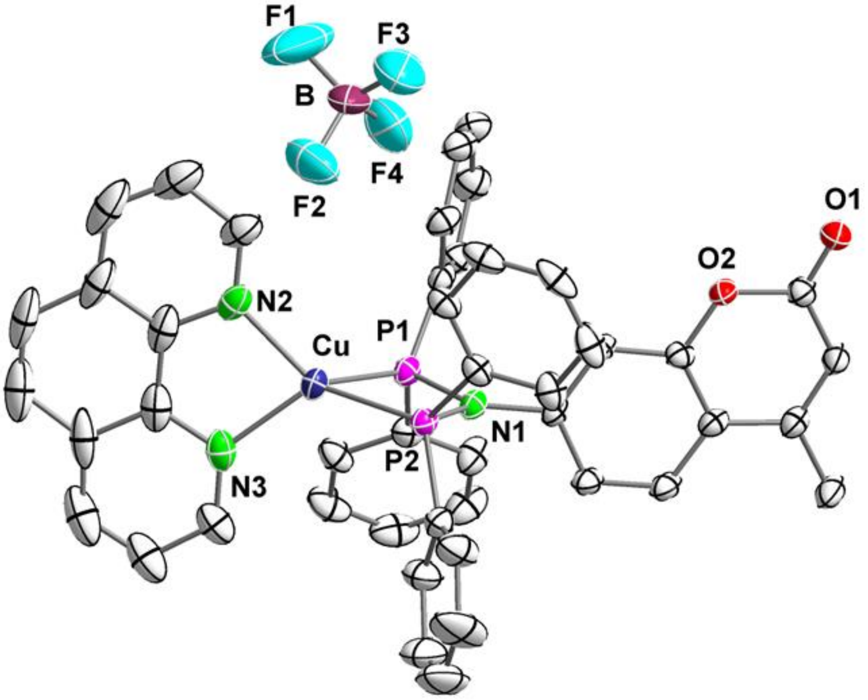


Figure S41. Molecular structure of complex **2** in the solid state. Hydrogen atoms and the non-coordinating solvent molecules are ommited for clarity. Selected bond distances (Å) and angles (°): Cu-P1 2.2548(7), Cu-P2 2.2879(8), Cu-N2 2.045(3), Cu-N3 2.017(2), N1-P1 1.721(2), N1-P2 1.715(2); P1-Cu-P2 74.69(3), P2-Cu-N3 121.75(7), N3-Cu-N2 83.09(11), N2-Cu-P1 126.63(8), P1-N1-P2 106.27(13).

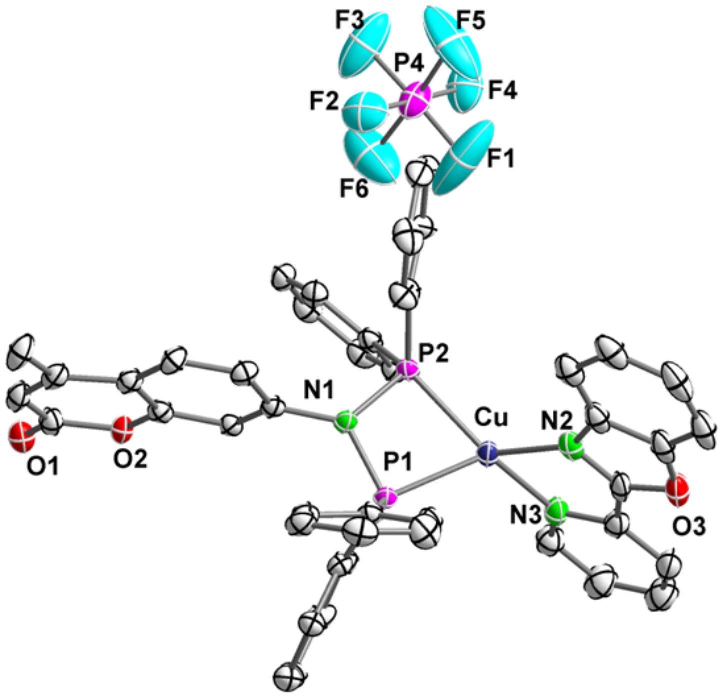


Figure S42: Molecular structure of complex **3** in the solid state**.** Hydrogen atoms and non-coordinationg solvents are removed for clarity. Selected bond distances (Å) and angles (°): Cu-P1 2.2705(7), Cu-P2 2.2953(7), Cu-N2 2.051(2), Cu-N3 2.055(2), N1-P1 1.722(2), N1-P2 1.718(2); P1-Cu-P2 74.44(2), P2-Cu-N2 120.00(7), N2-Cu-N3 81.84(9), N3-Cu-P1 138.44(7), P1-N1-P2 106.79(11).

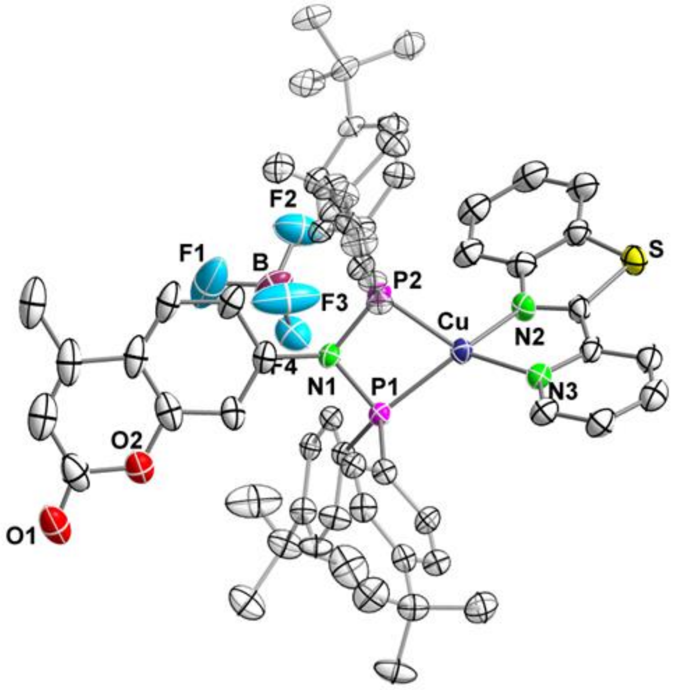


Figure S43: Molecular structure of complex **4** in the solid state. Hydrogen atoms and the non-coordinating solvent molecules were removed for clarity. Selected bond distances (Å) and angles (°): Cu-P1 2.1940(10), Cu-P2 2.2368(11), Cu-N2 2.013(3), Cu-N3 1.993(3), N1-P1 1.716(3), N1-P2 1.708(3); P1-Cu-P2 74.42(4), P2-Cu-N2 128.53(8), N2-Cu-N3 82.85(12), N3-Cu-P1 141.68(9), P1-N1-P2 102.99(14).

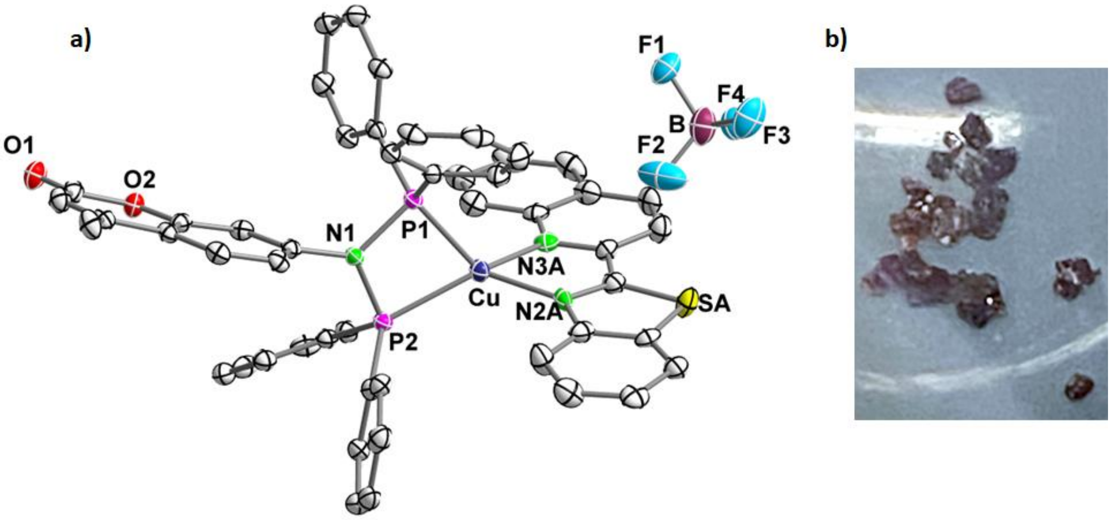


Figure S44: a) Molecular structure of complex **5** in the solid state. Hydrogen atoms and the non-coordinating solvent molecules are removed for clarity. Please note that N-N co-ligand is disordered. Only the main part (66%) is displayed. Selected bond distances (Å) and bond angles (°): Cu-P1 2.3080(6), Cu-P2 2.3006(6), Cu-N2A 2.065(5), Cu-N3A 2.100(3), N1-P1 1.718(2), N1-P2 1.719(2); P1-Cu-P2 73.59(2), P2-Cu-N2A 119.80(3), N2A-Cu-N3A 79.76(2), N3A-Cu-P1 142.99(14), P1-N1-P2 106.85(9). b) Photograph of crystals of complex **5**.

VI. Photoluminescence data

Photoluminescence measurements were carried out on a PTI QuantaMaster™ 8075-22 fluorometer with double excitation and emission monochromators (HORIBA Jobin Yvon). The samples (polycrystalline solids) were sealed under inert atmosphere in a Young-type NMR tube (material: Suprasil® quartz). The tube was placed in a glass dewar vessel (equipped with a quartz finger on the bottom where spectroscopy takes place) which was filled with liquid nitrogen for measurements at 77 K. For emission detection a R928 photomultiplier (250-800 nm) or a liquid nitrogen cooled DSS IGA020L/CUS detector (800-1550 nm) was used. The PL spectra at temperatures down to 3.2 K were measured on a Fluorolog-322 spectrometer (HORIBA Jobin Yvon) equipped with an optical cryostat based on a PT403 pulse tube cryocooler (Cryomech). All spectra were corrected for the wavelength dependent response of the detector and the spectrometer (in relative photon flux units). For detection of the emission decay traces, the samples were excited with either a Delta Diode™ (HORIBA Jobin Yvon, Model DD-370, λ_{exc} = 371 nm, pulse < 2 ns, 2 µW) for fluorescence lifetimes or a PTI XenonFLash™ pulsed lamp (set before the excitation monochromator) for phosphorescence decay times. In case of using the Delta Diode, signal was recorded until a satisfying signal-to-noise ratio was obtained. When using the Xenon Flash lamp, 10000 traces were recorded and averaged. For determination of the lifetimes the obtained traces were fit with an exponential decay curve (one or two exponentials) using Origin(Pro), Version 2019 (OriginLab Corp.). The absolute PL efficiency of polycrystalline samples at ambient temperature was determined using an integrating sphere made of optical PTFE, which was installed into the sample chamber of the spectrometer. The uncertainty of these measurements was estimated to be ±10 %.

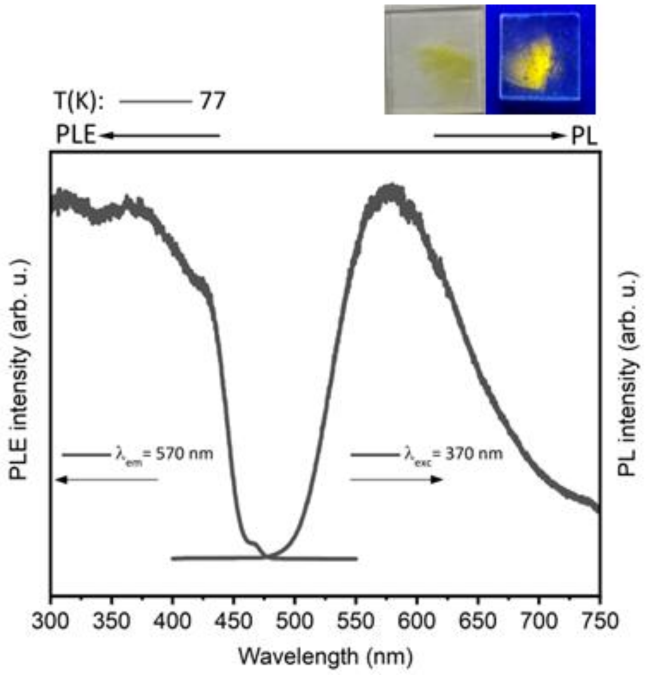


Figure S45: PL and PLE spectra of complex **1** recorded at 77 K at the given emission (PLE spectra λ_{em}) and excitation wavelengths (PL spectra λ_{exc}).

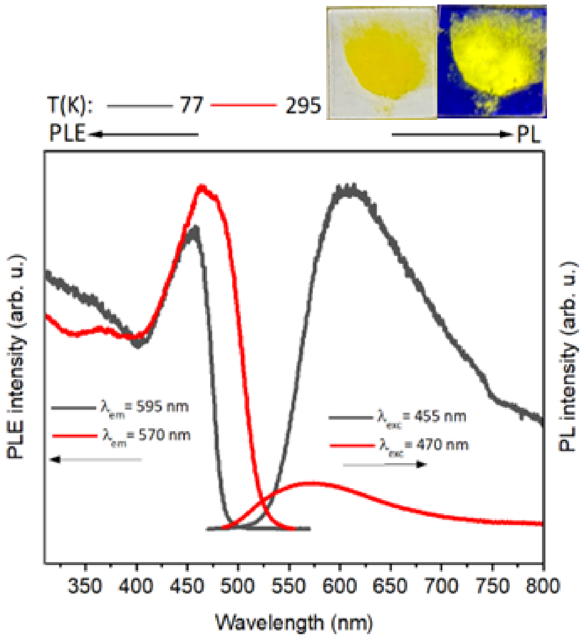


Figure S46: PL and PLE spectra of complex **2** recorded at 77 K and room temperature at the given emission (PLE spectra: λ_{em}) and excitation wavelengths (PL spectra: λ_{exc}).

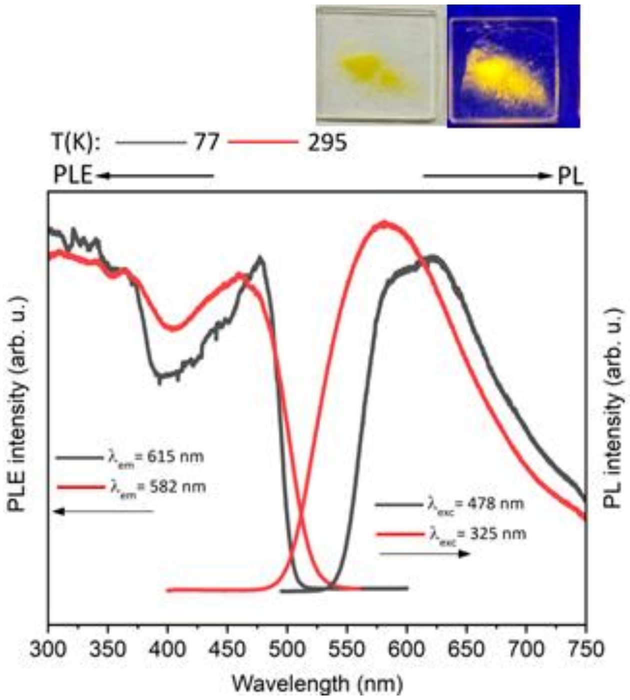


Figure S47: PL and PLE spectra of complex **3** recorded at 77 K and room temperature at the given emission (PLE spectra: λ_{em}) and excitation wavelengths (PL spectra: λ_{exc}).

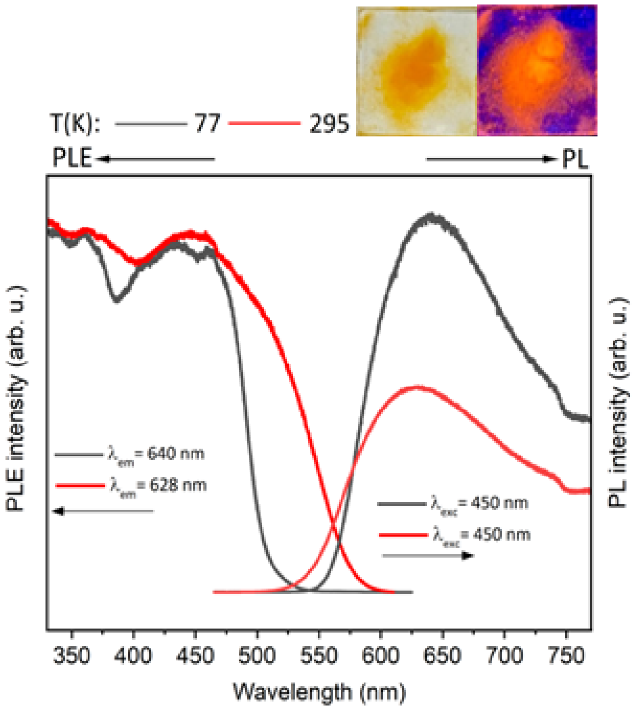


Figure S48: PL and PLE spectra of complex **4** recorded at 77 K and room temperature at the given emission (PLE spectra: λ_{em}) and excitation wavelengths (PL spectra: λ_{exc}).

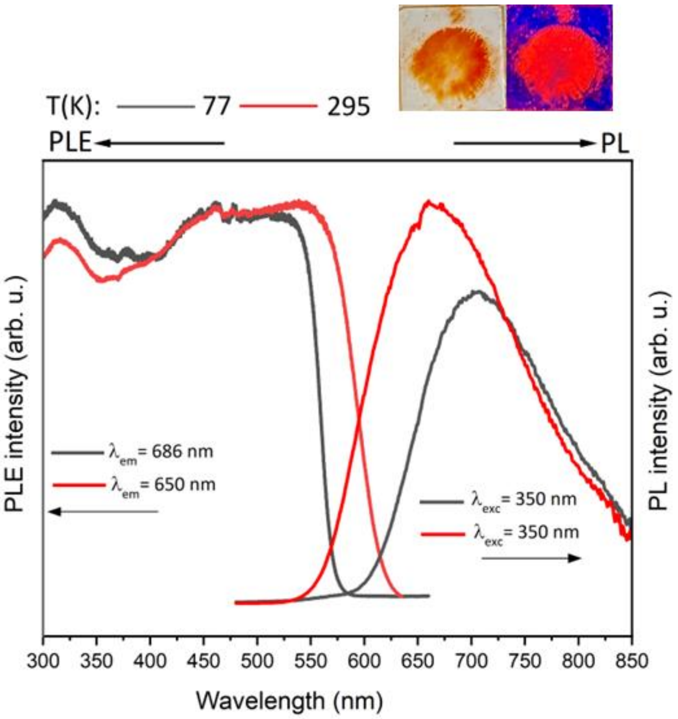
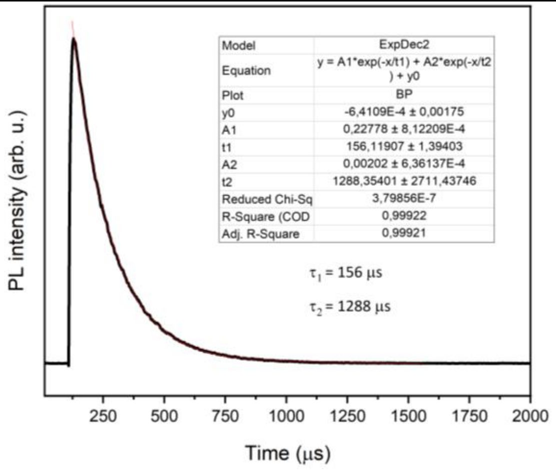
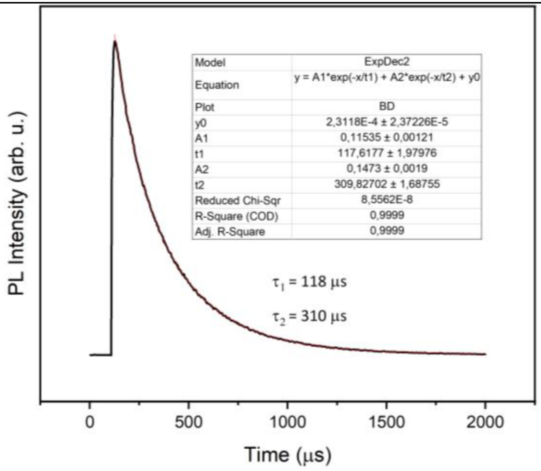
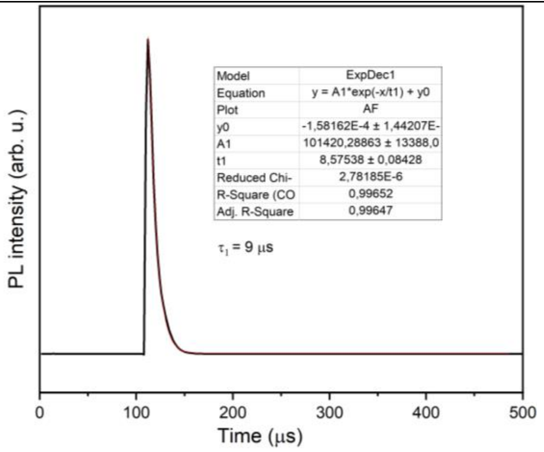
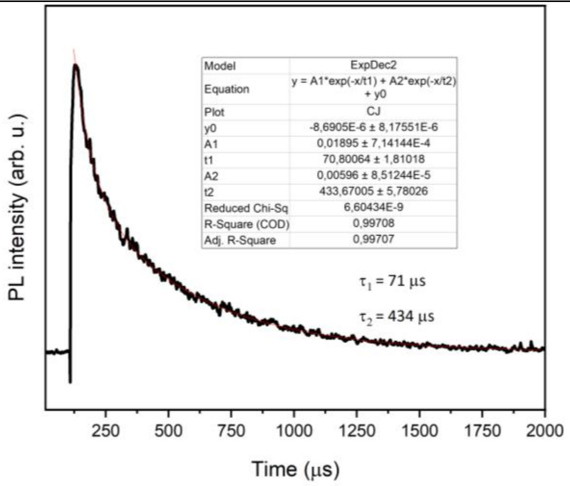
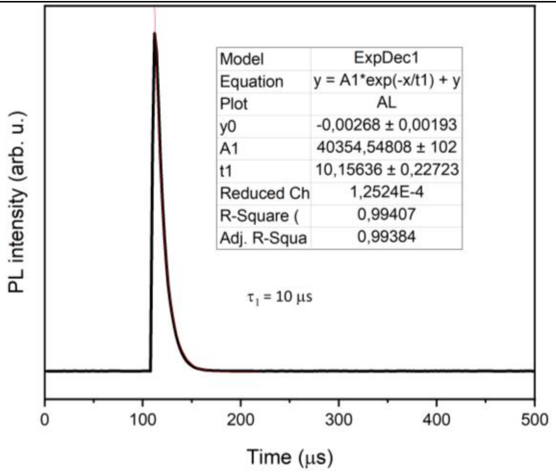
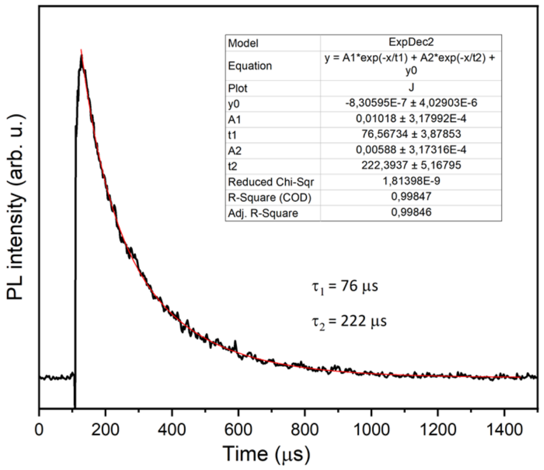


Figure S49: PL and PLE spectra of complex **5** recorded at 77 K and room temperature at the given emission (PLE spectra: λ_{em}) and excitation wavelengths (PL spectra: λ_{exc}).

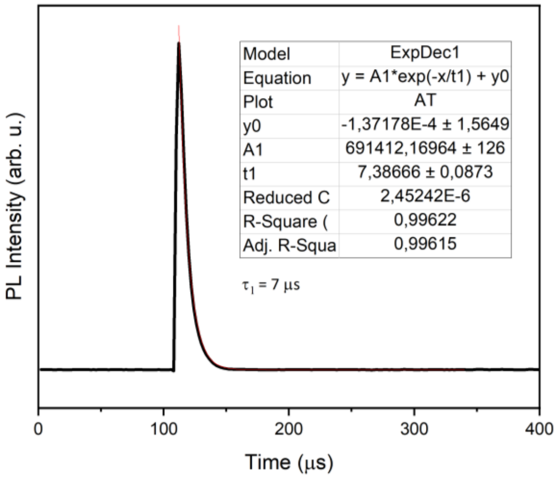
Lifetime Determination

	77 K	**295 K**
1	 Model: ExpDec2 Equation: y = A1*exp(-x/t1) + A2*exp(-x/t2) + y0 Plot: BP y0: -6,4109E-4 ± 0,00175 A1: 0,22778 ± 8,12209E-4 t1: 156,11907 ± 1,39403 A2: 0,00202 ± 6,36137E-4 t2: 1288,35401 ± 2711,43746 Reduced Chi-Sq: 3,79856E-7 R-Square (COD: 0,99922 Adj. R-Square: 0,99921 τ_1 = 156 µs τ_2 = 1288 µs λ_{exc} = 370 nm and λ_{em} = 570 nm	
2	 Model: ExpDec2 Equation: y = A1*exp(-x/t1) + A2*exp(-x/t2) + y0 Plot: BD y0: 2,3118E-4 ± 2,37226E-5 A1: 0,11535 ± 0,00121 t1: 117,6177 ± 1,97976 A2: 0,1473 ± 0,0019 t2: 309,82702 ± 1,68755 Reduced Chi-Sqr: 8,5562E-8 R-Square (COD): 0,9999 Adj. R-Square: 0,9999 τ_1 = 118 µs τ_2 = 310 µs λ_{exc} = 455 nm and λ_{em} = 595 nm	 Model: ExpDec1 Equation: y = A1*exp(-x/t1) + y0 Plot: AF y0: -1,58162E-4 ± 1,44207E- A1: 101420,28863 ± 13388,0 t1: 8,57538 ± 0,08428 Reduced Chi-: 2,78185E-6 R-Square (CO: 0,99652 Adj. R-Square: 0,99647 τ_1 = 9 µs λ_{exc} = 470 nm and λ_{em} = 571 nm
3	 Model: ExpDec2 Equation: y = A1*exp(-x/t1) + A2*exp(-x/t2) + y0 Plot: CJ y0: -8,6905E-6 ± 8,17551E-6 A1: 0,01895 ± 7,14144E-4 t1: 70,80064 ± 1,81018 A2: 0,00596 ± 8,51244E-5 t2: 433,67005 ± 5,78026 Reduced Chi-Sq: 6,60434E-9 R-Square (COD): 0,99708 Adj. R-Square: 0,99707 τ_1 = 71 µs τ_2 = 434 µs λ_{exc} = 478 nm and λ_{em} = 615 nm	 Model: ExpDec1 Equation: y = A1*exp(-x/t1) + y Plot: AL y0: -0,00268 ± 0,00193 A1: 40354,54808 ± 102 t1: 10,15636 ± 0,22723 Reduced Ch: 1,2524E-4 R-Square (: 0,99407 Adj. R-Squa: 0,99384 τ_1 = 10 µs λ_{exc} = 325 nm and λ_{em} = 582 nm

4

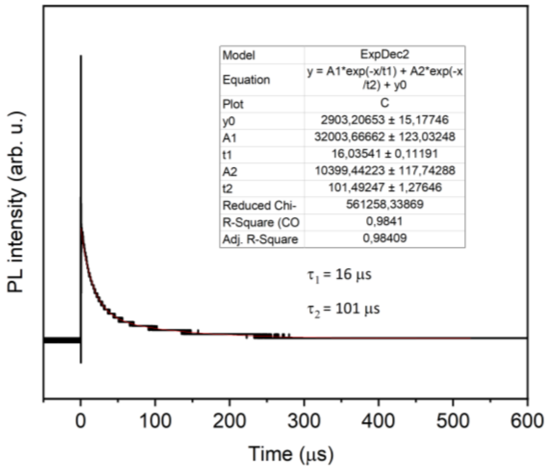


λ_{exc} = 450 nm and λ_{em} = 640 nm

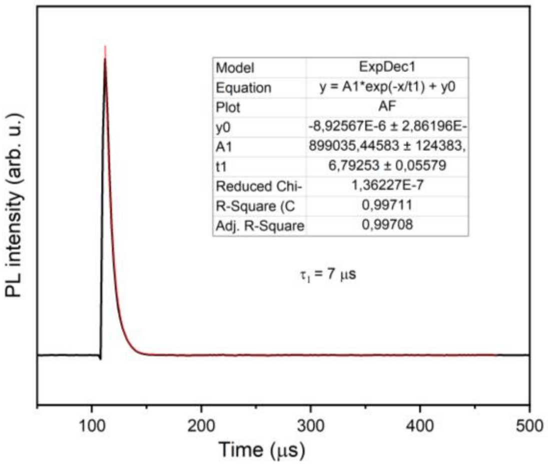


λ_{exc} = 450 nm and λ_{em} = 620 nm

5



λ_{exc} = 350 nm and λ_{em} = 700 nm



λ_{exc} = 450 nm and λ_{em} = 650 nm

Figure S50. Emission decay traces (black) of solid **1-5** at low (77 K) and ambient temperatures. The red lines indicate decay fits with biexponential curves.

Table S2. Photophysical parameters of heteroleptic Cu(I) complexes **1**-**5** in the solid state.

Complex	**Ex ($\lambda_{exc,}$ onset, nm)**	**Em (λ_{em} max, nm)**	**Ex ($\lambda_{exc,}$ onset, nm)**	**Em (λ_{em} max, nm)**	**Lifetime (µs)**		**QY (Φ_{PL}) %**
	77 K		**295 K**		**77 K**	**295 K**	**295 K**
1	460	570	-	-	156/	-	<0.05
2	500	595	550	570	118/	9	2.8
3	515	615	545	582	71/4	10	21
4	530	640	595	628	76/2	7	4.3
5	580	686	625	650	16/1	7	7.4

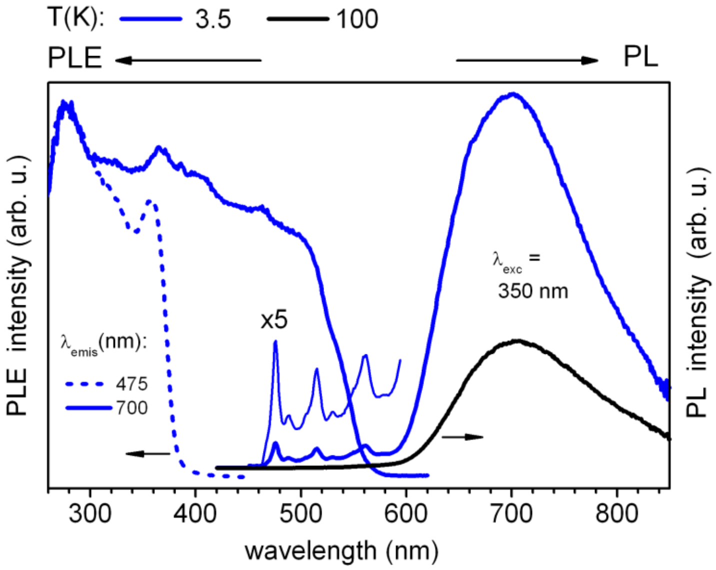


Figure S51: PL and PLE spectra of solid complex **5** recorded at 3.5 K at the given excitation (λ_{exc}) and emission (λ_{em}) wavelengths, respectively. The weak, vibronically structured emission within 460-590 nm is attributed to the coumarin groups (see the main text). It is only observed at temperatures below ~50 K.

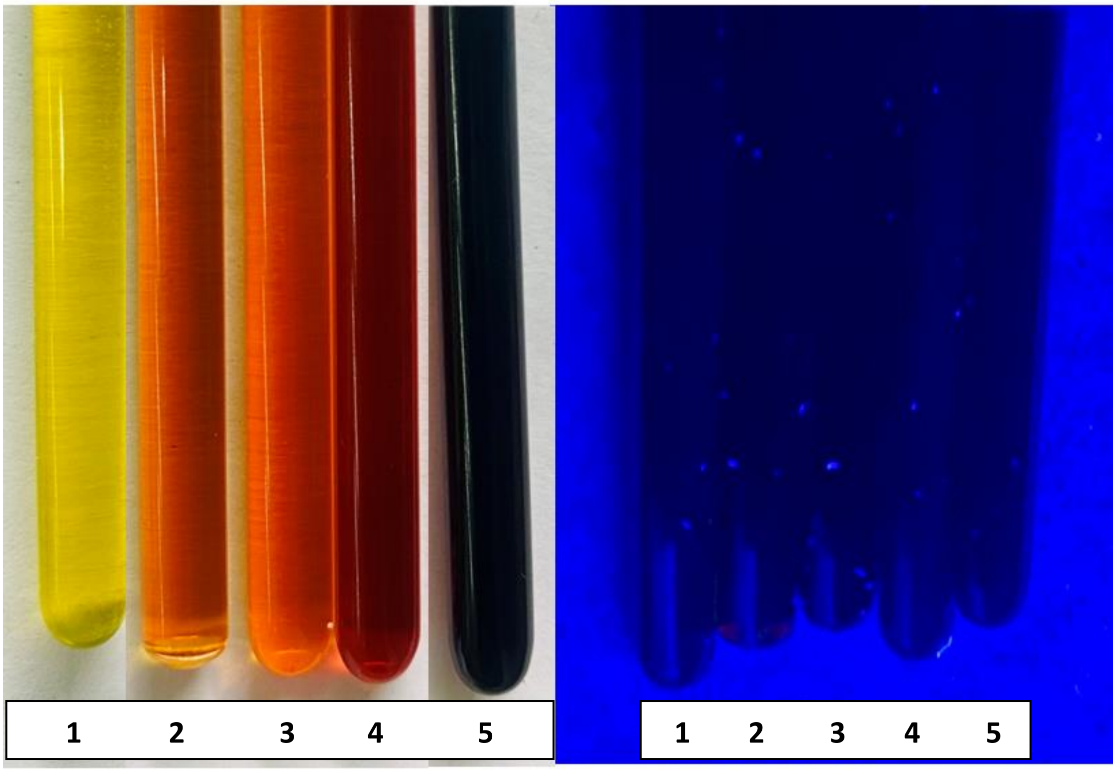


Figure S52. Photogaphs of DCM solutions of the copper complexes **1-5**. left: under day light; right: under UV illumination.

VI. Quantum chemical calculations

The geometry optimizations were initiated from the crystal structure coordinates. Counter anions were removed and not included in the calculations. All calculations were performed with the Gaussian 16, revision C.01, package.[7] The molecular geometries in the ground state

(S_0) and the lowest singlet and triplet excited states (S_1 and T_1) were optimized *via* density functional theory (DFT), time-dependent DFT (TD-DFT) and spin-unrestricted DFT (UDFT) calculations, respectively. Vibrational frequencies were obtained for all optimized geometries to ensure that the latter did not lead to any imaginary frequencies. Geometry optimizations were carried out using CAM-B3LYP functional,[8] which is considered suitable for long-range electronic interactions. The basis set was LANL2DZ for the copper and 6-31G** for C, N, O, P, S and H atoms. Figure **S53** and **S54** display the frontier molecular orbitals (visualized employing the Chemcraft software)[9] of the homoleptic copper complex Cu($\mathbf{L^1}$)$_2$ (A) and heteroleptic complexes **1-5**.

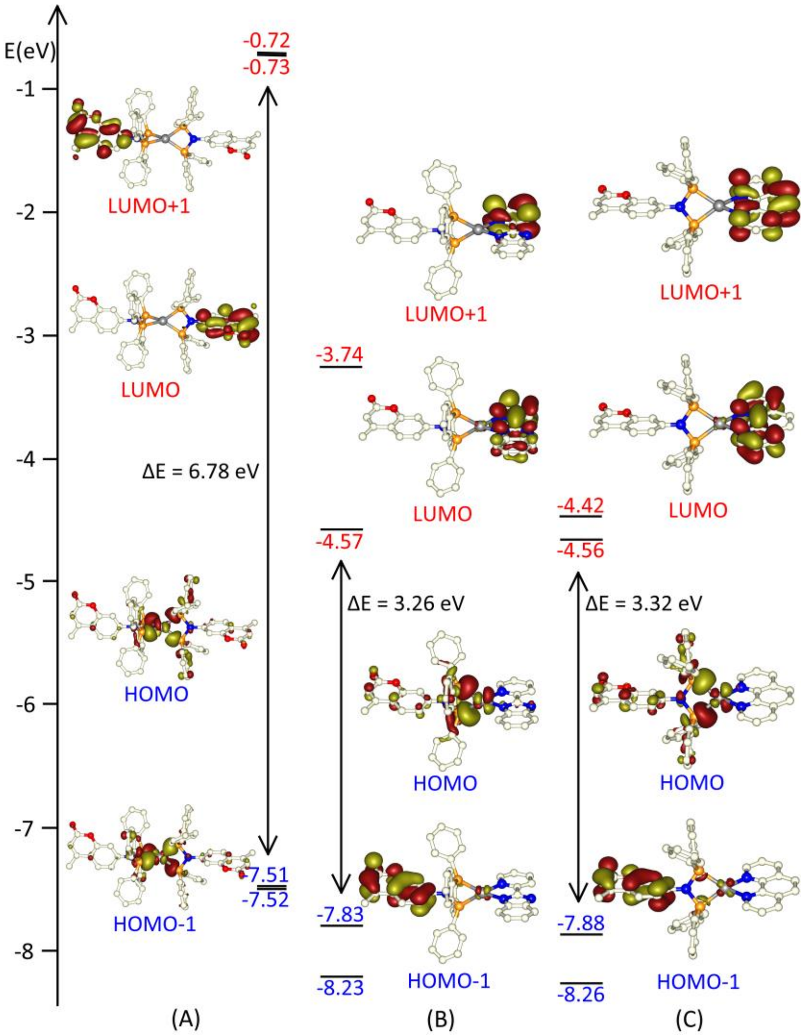


Figure S53. Energy diagrams and selected Kohn-Sham orbitals of CAM-B3LYP/6-31G**/ LANL2DZ optimized geometry of (A) homoleptic coumarin-aminodiphosphine Cu(I) complex (Cu($\mathbf{L^1}$)$_2$), (B) heteroleptic complex **1** and (C) heteroleptic complex **2.**

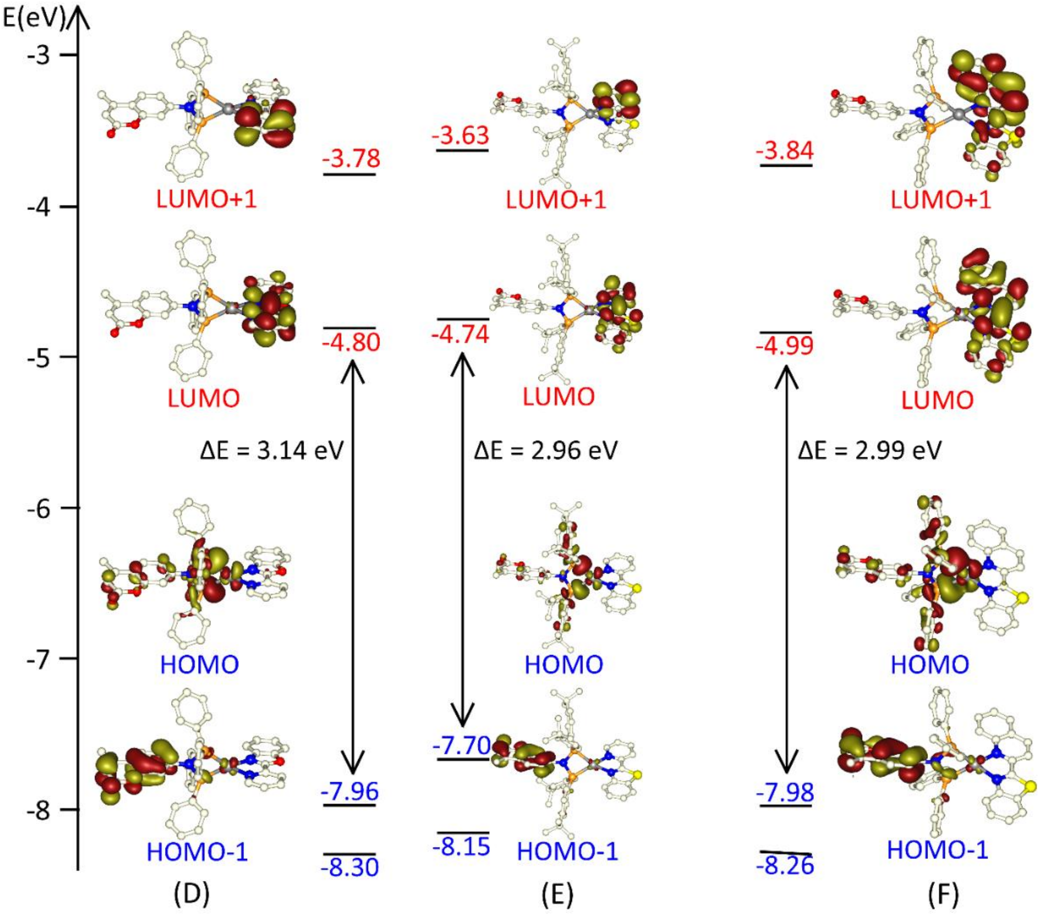


Figure S54. Energy diagrams and selected Kohn-Sham orbitals of CAM-B3LYP/6-31G**/ LANL2DZ optimized geometry of (D) complex **3**, (E) complex **4** and (F) complex **5.**

Table S3. TD-DFT calculated (CAM-B3LYP/LANL2DZ/ 6-31G**) Energy levels (eV) of S_1 (E_{S1}) and T_1 (E_{T1}) excited states and singlet-triplet energy gaps (ΔE_{ST}).

Complex		**E_{S1}**	**E_{T1}**	**E_{T2}**	**E_{T3}**	**E_{T4}**	**E_{T5}**	**E_{T6}**	**E_{T7}**	**E_{T8}**
$Cu(L^1)_2$		2.78	1.75	1.78	2.15	2.73	2.78	2.77	2.93	3.07
	$\Delta E=E_{S1}-E_{Tn}$		1.03	0.97	0.63	0.05	0.00	0.01	-0.15	-0.29
1		2.67	1.65	1.73	1.96	2.29	2.56	2.58	2.59	2.64
	$\Delta E=E_{S1}-E_{Tn}$		1.02	0.94	0.71	0.38	0.11	0.09	0.08	0.03
2		2.63	1.41	1.62	1.77	2.20	2.22	2.31	2.55	2.62
	$\Delta E=E_{S1}-E_{Tn}$		1.22	1.01	0.86	0.43	0.41	0.32	0.08	0.01
3		2.66	1.73	1.84	2.14	2.44	2.60	2.64	2.70	2.77
	$\Delta E=E_{S1}-E_{Tn}$		0.93	0.82	0.52	0.22	0.06	0.02	-0.04	-0.11
4		2.58	1.73	1.90	2.34	2.53	2.55	2.62	2.64	2.68
	$\Delta E=E_{S1}-E_{Tn}$		0.85	0.68	0.24	0.05	0.03	-0.04	-0.06	-0.10
5		2.58	1.65	1.90	2.22	2.47	2.52	2.56	2.64	2.66
	$\Delta E=E_{S1}-E_{Tn}$		0.93	0.68	0.36	0.11	0.06	0.02	-0.06	-0.08

Table S4. Correlation between the heteroatom in the diimine ligand and other parameters.

Complex	**Heteroatom in the diimine ligand**	**Dipole moment S_1 (Debye)**	**Dipole moment T_1 (Debye)**	**λ_{max} (nm)**
1	N	11.47	4.95	570
3	O	9.37	4.93	615
4	S	9.28	4.90	640
5	S	8.32	4.69	686

VII Cartesian coordinates of the optimized geometries:

Complex 1 (UB3LYP/6-31G**/LANL2DZ)

29	-1.993403431	0.482948631	-0.099489568
15	-0.153352971	-0.556828919	-1.275546092
15	-0.039999298	0.630830055	1.313216448
8	5.472428893	1.051657850	-0.576269277
8	7.555751144	1.763903423	-0.946334321
7	-3.098338148	2.337472161	-0.437420354
7	0.887967293	-0.200233756	0.085774967
7	-3.954621371	-0.212743331	0.009941607
7	-6.123563559	0.283083929	-0.140853608
1	-6.964813248	0.822626984	-0.274986964
6	4.604117815	0.093710446	-0.153545769
6	2.289104847	-0.520280363	0.172521944
6	5.044036780	-1.151537209	0.336858796
6	0.076129383	1.192135761	-3.411548086
1	-0.866749698	1.580612538	-3.034752385
6	2.708196829	-1.769263454	0.669432805
1	1.970515404	-2.492059118	0.992199690
6	3.246512869	0.409088517	-0.239507805
1	2.963635238	1.377157258	-0.629500408
6	0.679245450	0.098070963	-2.768790286
6	4.060946209	-2.072668733	0.743870439
1	4.364715467	-3.040507933	1.127790226
6	-0.134156369	-2.383771466	-1.471313924
6	0.738613766	2.281920716	1.526648179
6	0.256318512	-0.251077111	2.889871295
6	0.671537481	1.773291234	-4.532448568
1	0.193282936	2.613932290	-5.026092030
6	6.479521832	-1.400720298	0.388414289
6	-4.839991769	0.756839107	-0.172717306
6	-0.099963368	-3.000220775	-2.731328495
1	0.030612065	-2.403756363	-3.627845842
6	1.877787071	1.268077623	-5.019443849
1	2.343602399	1.719087947	-5.890412191
6	-4.438112219	2.149836106	-0.377740889
6	-4.681681971	-1.382376168	0.158549720
6	6.860047689	0.862236578	-0.549745157
6	-0.326691150	-3.185181834	-0.331040976
1	-0.374284491	-2.725029280	0.652334115
6	0.869972319	2.887982916	2.785508212
6	0.548871141	-2.994065332	-0.259410103
1	0.442920288	-2.343291777	-1.123774422
6	0.564486500	-3.325179533	2.136522154
1	0.465336679	-2.943203376	3.146922091
6	2.915698368	1.481899930	0.794049592
1	2.288869284	2.253529435	1.221984755
6	0.393748137	-0.232185991	2.919525245
6	7.285257483	-0.362093841	-0.241122175
1	8.369128803	-0.377092902	-0.260164538
6	-0.558989936	0.445073959	3.698494328
1	-1.550086265	0.629470536	3.291668521
6	-4.775671354	-1.011469775	-0.409276706
6	0.038490014	2.793830895	-0.862878322
6	0.111525406	3.669247183	-1.956694093
1	0.184975360	3.277336269	-2.965512489
6	0.095519094	5.052613150	-1.758506699
1	0.160662289	5.716829564	-2.615088732
6	0.003418488	5.579011594	-0.470485137
1	-0.002899731	6.654175619	-0.319520265
6	-0.082319916	4.715819153	0.626081970
1	-0.151911682	5.118777198	1.632457255
6	-0.074638486	3.335320141	0.431436243
1	-0.141071407	2.673441769	1.291262683
6	0.965223800	-5.196198930	0.651193039
1	1.181567234	-6.249645330	0.502774958
6	1.843303808	1.071035469	-3.125234513
1	2.419246255	1.731601872	-2.485383695
6	0.823194389	-4.347436300	-0.450663691
1	0.933626224	-4.738839014	-1.457745338
6	7.301340926	1.836662406	0.940690931
1	7.021793731	2.773732526	0.445739948
1	8.384655445	1.724045226	0.869672889
1	7.036929682	1.939051038	1.999396057
6	1.613953583	-0.140950140	-5.207683547
1	2.013390096	-0.425076600	-6.176547008
6	2.351301737	0.700102813	-4.369361193
1	3.322916289	1.066851524	-4.686107586
6	-4.936628409	0.342541444	0.072313916
6	1.669308878	-0.478650477	3.459070156
1	2.414169725	-1.010935660	2.876634371
6	-6.241184104	0.877041994	0.227087593
6	0.829717721	-4.683268767	1.940725868
1	0.937595456	-5.336983225	2.801021107
6	-3.951722824	2.313084424	0.782527747
1	-3.033027156	2.855778961	0.984855181
6	0.364483485	-0.612061932	-4.802439822
1	-0.213029285	-1.258863573	-5.455952854
6	1.979410477	-0.049406095	4.748825425
1	2.966054647	-0.243756156	5.158521875
6	-0.246035615	0.870007414	4.990902558
1	-0.992513931	1.385275503	5.587811230
6	-5.925525853	-1.791579314	-0.693099252
6	1.023800076	0.624321964	5.514913836
1	1.268760384	0.951883908	6.520840098
6	-3.352180500	-2.740803223	-0.992635182
1	-2.328512507	-3.089474498	-1.092591530
6	-5.203078218	2.930472658	0.957241378
1	-5.251762779	3.956832406	1.303849947
6	-5.719528845	-3.114167575	-1.145424725
1	-6.576091600	-3.742519779	-1.372022889
6	-7.230690207	-1.220383396	-0.515759169
1	-8.098767542	-1.832641008	-0.740810021
6	-6.348795578	2.209424147	0.684531873
1	-7.331502812	2.653632871	0.814293352
6	-4.431901329	-3.591490788	-1.290063065
1	-4.240237721	-4.603509542	-1.629169593
6	-7.382041833	0.060984102	-0.078840928
1	0.616174756	2.338172416	3.685529342
6	1.497685033	-0.271793250	3.551161253
1	2.338457552	0.284405142	3.149744559
6	-6.062002782	-1.085789227	0.068916400
6	1.891602635	-0.407335261	-3.272791663
1	2.366648015	-1.259015881	-2.797204061
6	1.058450618	3.031243029	0.379172788
1	0.952024950	2.585134416	-0.606267267
6	-2.633694075	3.582819579	-0.597560380
1	-1.553616491	3.690435657	-0.616553800
6	-4.254077860	-2.701865948	0.359889076
1	-3.197370665	-2.942015537	0.406978460
6	1.531345554	4.338114816	0.491574130
1	1.797644870	4.894392100	-0.402482365
6	2.485746674	0.178260362	-4.389838035
1	3.423699070	-0.214892861	-4.769978565
6	7.317971856	-0.423980879	-0.039129705
1	8.394640120	-0.550313361	-0.025327070
6	1.651161618	-0.998394763	4.731182015
1	2.612209426	-1.008462180	5.236599480
6	1.672209748	4.926463120	1.751675545
1	2.043733072	5.942725913	1.840036112
6	1.334904137	4.201232765	2.894106137
1	1.439791174	4.652282327	3.876304080
6	-0.821574080	-0.967979173	3.435711526
1	-1.786088243	-0.949584062	2.934607728
6	7.001706269	-2.713243767	0.904786990
1	6.681431105	-2.885892538	1.938647138
1	8.092560346	-2.738156061	0.877542935
1	6.625394145	-3.550457543	0.305870318
6	-5.342115873	3.210522153	-0.491903732
1	-6.412466502	3.042341104	-0.433956101
6	-3.468021766	4.694119192	-0.722512824
1	-3.040823868	5.682071139	-0.853038065
6	0.572063139	-1.708667484	5.265180428
1	0.695497431	-2.269106075	6.187093193
6	-5.231862609	-3.681144807	0.472516808
1	-4.937224733	-4.714413033	0.625035337
6	-4.847209709	4.500467497	-0.671433111
1	-8.372629628	0.487119658	0.048424369

Complex 3 (UB3LYP/6-31G**/LANL2DZ)

29	-1.963034171	0.510928622	-0.107244143
15	-0.007867416	0.679440240	1.296822140
15	-0.149644525	-0.589841197	-1.253920772
8	5.490657991	1.038256198	-0.576782299
8	7.576462824	1.742990735	-0.947834226
8	-6.098900777	0.336412748	-0.137476501
7	0.902645421	-0.196956259	0.087998648
7	-3.936612575	-0.246480874	0.025048985
7	-3.104721015	2.327796165	-0.465313122
6	3.262718377	0.403692196	-0.239615956
1	2.982602596	1.373423304	-0.627785482
6	0.306793460	-0.146515361	2.899056775
6	2.302724578	-0.523003041	0.172061554
6	4.619251978	0.082865184	-0.155591185
6	6.877897208	0.843015670	-0.552957818
6	0.770112476	2.337832615	1.440826859
6	-0.172006648	-2.423149873	-1.374590515
6	7.331120588	-0.446651063	-0.046791547
1	8.407273169	-0.577536747	-0.034869602
6	0.687295697	-0.011282897	-2.774419943
6	5.054697346	-1.165821481	0.330384581
6	0.097171723	1.060350465	-3.465191176
1	-0.840056601	1.477858259	-3.105787181
6	0.929660427	2.983212822	2.676472896
1	0.699169159	2.461491697	3.599173431
6	1.892749976	-0.554477711	-3.255182924
1	2.357501250	-1.389500354	-2.741352239
6	1.059996678	3.050916770	0.262478654
1	0.933293203	2.572989893	-0.705605362
6	4.068485652	-2.084283311	0.735933182
1	4.369034733	-3.054264346	1.116975002
6	6.489306796	-1.421143979	0.379197397
6	1.561641359	-0.158390658	3.534782678
1	2.400743720	0.370607269	3.094937459
6	-0.768472497	-0.826786820	3.494502176
1	-1.743324990	-0.814197460	3.013652447
6	1.392754572	4.300506158	2.732290200
1	1.519798525	4.782664378	3.696898578
6	0.698582693	1.582467097	-4.611573356
1	0.230549160	2.406004986	-5.142339540
6	-0.383405776	-3.171868999	-0.202067841
1	-0.419752851	-2.670669087	0.761595929
6	2.716750683	-1.774996137	0.665295602
1	1.976321891	-2.495067009	0.988292790
6	-4.708189925	-1.396348532	0.196423128
6	1.730600420	-0.841128528	4.738596423
1	2.701891169	-0.844869621	5.224063621
6	2.492802855	-0.027475692	-4.397876788
1	3.425227773	-0.449233650	-4.760515119
6	1.531133766	4.361815522	0.322346582
1	1.774470844	4.890318388	-0.594786327
6	1.897740710	1.040268860	-5.075825156
1	2.368129902	1.445443057	-5.966621546
6	-4.439628349	2.108662200	-0.409541858
6	-4.361790767	-2.731950140	0.420405770
1	-3.324395287	-3.043127588	0.475852504
6	-6.056319365	-1.023787005	0.099172915
6	0.653879889	-1.515097415	5.322145624
1	0.789549532	-2.041035961	6.262455018
6	1.699878511	4.990043915	1.559747867
1	2.069828173	6.009596031	1.607023340
6	-0.149521971	-3.091749018	-2.607857652
1	-5.529437317	5.339445275	-0.762907310
6	-7.049454408	-2.067005092	0.182363531
1	-8.106401771	-1.831785016	0.112783438
6	-6.606715828	-3.368786469	0.387798328
1	-7.336429929	-4.166547795	0.481494652
6	-0.228872102	-4.386921665	-2.844763036
1	-0.193323808	-4.849195071	-3.826679558
6	-0.395710956	-5.174433690	-1.706128438
1	-0.489335959	-6.252293174	-1.797072915
6	-0.664473399	-1.692840417	4.618416110
1	-1.506075567	-2.237419105	5.035722537
6	-0.445857707	-4.569301699	-0.447028761
1	-0.576570094	-5.176099974	0.444420494

Complex 2 (UB3LYP/6-31G**/LANL2DZ)

29	-2.054758443	-0.052562083	-0.019069597
15	-0.142499737	0.976188146	-1.070150399
15	-0.097260081	-0.712219157	1.222896284
8	5.246106261	-1.524138636	-0.844857471
8	7.205814379	-2.455128187	-1.372065810
7	0.889667449	0.231878969	0.129843355
7	-3.512861177	-1.488312188	-0.572789233
7	-3.817054956	1.058015909	0.361312968
6	2.322093540	0.356854970	0.190466735
6	0.433524350	-2.461740606	1.038567074
6	4.524405068	-0.512708879	-0.292122542
6	3.134984736	-0.638986143	-0.354865693
1	2.714220586	-1.513975914	-0.831640962
6	5.139005823	0.607689573	0.301574047
6	0.587642492	0.596616026	-2.703977656
6	6.647107028	-1.518193229	-0.858334049
6	6.595694230	0.663721649	0.317451992
6	4.298397185	1.600023373	0.839586607
1	4.738555623	2.474256092	1.306942247
6	-0.145560714	-0.246591308	-3.555508418
1	-1.121047143	-0.608725385	-3.240756330
1	-0.004155948	-2.535944078	-3.527923911
6	-2.680599828	3.583371569	-0.654528078
1	-1.604892317	3.728259548	-0.672489862
6	-0.595909569	-1.507063954	4.701245992
1	-1.435508686	-2.022976137	5.157168959
6	-4.799632769	0.716222499	-0.169961256
6	-5.410780590	-3.639451726	0.546087124
1	-5.188142027	-4.687571401	0.717650611
6	-0.494445419	-5.214568154	-1.494069546
1	-0.611041409	-6.293022571	-1.540397035
6	-3.555469952	4.660640534	-0.811033970
1	-3.160253326	5.658832373	-0.963719058
6	7.006785788	-2.737276145	0.891153813
1	8.097448145	-2.766540219	0.862243743
1	6.626271468	-3.571249113	0.290436883
1	6.687350640	-2.911427431	1.924986629
6	-5.385579847	3.124683132	-0.557375549
1	-6.443271709	2.893535699	-0.505429296
6	-0.308848055	-4.478919643	-2.663988129
1	-0.281889644	-4.982260866	-3.625752618
6	-0.532449988	-4.556817116	-0.260951586
1	-0.675506739	-5.123515509	0.654716725
6	-4.928839957	4.425212084	-0.765760670
1	-5.635101737	5.240371207	-0.885345886
6	-6.758418616	-3.237536287	0.451796209
1	-7.540442999	-3.982406802	0.556580391
6	-7.116277376	-1.908085787	0.221614943
1	-8.148673878	-1.588603437	0.141579506

Complex 4 (UB3LYP/6-31G**/LANL2DZ)

29	1.291271541	-1.842668049	0.490078028
15	0.021317513	-0.795836179	-1.279348728
15	0.387586837	0.218073186	1.365355922
16	4.838853196	-4.569095357	1.347299722
7	-0.378464318	0.508278786	-0.182353000
7	3.250233694	-2.590262017	0.782726855
8	-4.756924863	2.469010416	-0.215553601
6	-3.437779323	2.624025594	-0.513133344
6	-2.933888851	3.809402227	-1.083113035
6	-3.871427251	4.891143820	-1.357443214
6	-5.179274127	4.703659146	-1.049747901
1	-5.923269547	5.471287775	-1.230280508
6	-5.697320916	3.477028887	-0.457193298
6	-1.570423669	-1.577434257	-1.747845989
8	-6.845289888	3.255137765	-0.159437277
6	2.027927818	-0.185206233	-3.090240339
1	2.653995479	-0.762904494	-2.414498524
6	-1.292937450	-0.879424853	3.276762984
1	-0.782341376	-1.806285970	3.026119154
6	-2.987660271	0.279696046	4.594615559
6	2.597179485	0.390877987	-4.228106651
1	3.656077734	0.244621919	-4.405419442
6	-1.239030608	1.620307451	-0.488682465
6	-0.912402682	0.312448245	2.644723748
6	2.279863894	2.155454423	0.633745838
1	2.180101949	1.749520973	-0.369514330
6	-2.310359188	-0.893102032	4.233280035
1	-2.567047884	-1.836270523	4.700964105
6	2.004935754	-4.644709372	1.103561544
6	1.968163354	-6.025235811	1.324542476
1	2.885615911	-6.583913422	1.477329124
6	0.734641815	-6.671738747	1.338587301
1	0.680542083	-7.742157058	1.508638875
6	-0.422101489	-5.924053470	1.124020542

1	-1.402006268	-6.388297390	1.119143528
6	-0.300197275	-4.551011666	0.910244671
1	-1.173951580	-3.934158637	0.725039259
7	0.880044954	-3.917447675	0.906935921
6	-2.505003021	-1.879417403	-0.745019150
1	-2.329952124	-1.551346003	0.276553078
6	0.661864269	-0.037793052	-2.813361822
6	3.390642161	3.726045185	2.139041197
6	-3.954948434	-3.032511097	-2.336554001
6	-3.674417361	-2.582275764	-1.037102131
1	-4.376368643	-2.769484741	-0.232704522
6	-0.715743387	2.796259702	-1.059952486
1	0.342971493	2.861805575	-1.273173944
6	1.826624416	1.135024201	-5.131847796
6	-2.999605887	-2.748598216	-3.326724349
1	-3.166960499	-3.079010970	-4.347273065
6	1.472531868	1.665163547	1.671112907
6	-1.832811895	-2.040029006	-3.046828500
1	-1.129463516	-1.844844576	-3.849514138
6	3.210713742	3.169585949	0.863518320
1	3.798728399	3.526629596	0.025746015
6	-0.121370118	0.706699330	-3.714571950
1	-1.184384754	0.834298067	-3.537327121
6	4.854506445	-0.708417579	0.566122230
1	4.069181239	0.013896332	0.372114897
6	6.189845549	-0.334419099	0.616862507
1	6.461071909	0.702469193	0.446566358
6	7.199398104	-1.276033343	0.892380694
1	8.235784761	-0.955487992	0.925180889
6	6.893376859	-2.612370312	1.130243185
1	7.673882186	-3.333402090	1.348053192
6	5.549196372	-2.989214867	1.081714811
6	4.527450351	-2.053233344	0.796814485
6	3.253441185	-3.872328938	1.054632154
6	-4.115374354	0.305705250	5.640029700
6	-5.237919349	-3.800179245	-2.698555225
6	2.592602927	3.211586884	3.174758571
1	2.696051211	3.605092141	4.181313708
6	-2.593663330	1.472489507	3.957595236
1	-3.089907296	2.404732182	4.208288402
6	4.405250121	4.845263644	2.429884972
6	0.455161017	1.276849525	-4.844047484
1	-0.180069747	1.843033324	-5.518226909
6	-2.606616763	1.542112776	-0.217498936
1	-3.044923150	0.657034251	0.222295215
6	2.414575900	1.779292009	-6.398945494
6	-5.411209594	0.834006364	4.978040518
1	-5.725012708	0.187714317	4.152030759
1	-5.287923202	1.845894262	4.581646822
1	-6.222932621	0.862756357	5.712373786
6	-1.580430897	1.497009591	3.006153730
1	-1.304896559	2.440513470	2.546185595
6	1.655520080	2.204607353	2.954277299
1	1.062688608	1.844087593	3.788463731
6	-4.860703449	-5.185542438	-3.276458866
1	-4.304857709	-5.780318134	-2.543794057
1	-4.244382021	-5.100940654	-4.176304833
1	-5.765350197	-5.740695564	-3.545778790
6	-1.552633947	3.865765034	-1.347743247
1	-1.131011508	4.763642430	-1.786522089
6	-4.404119597	-1.090146610	6.223801954
1	-5.211851406	-1.019274848	6.958258541
1	-3.531707438	-1.509131873	6.736256249
1	-4.725125063	-1.798086405	5.452368419
6	-3.711126064	1.244195542	6.802950469
1	-3.537175136	2.268886466	6.461721315
1	-2.797556975	0.893166057	7.293901753
1	-4.507830782	1.276295968	7.553404296
6	2.188700698	3.309729182	-6.345596702
1	1.126555105	3.566142431	-6.291259300
1	2.597448291	3.781806216	-7.245087586
1	2.686720303	3.751429648	-5.476082597
6	-6.153228018	-4.017437928	-1.478748828
1	-7.048632966	-4.566090096	-1.785743171
1	-6.484236802	-3.070090566	-1.040991325
1	-5.661372265	-4.605999876	-0.696713660
6	5.182260094	5.272249019	1.170275185
1	5.888263149	6.067770761	1.426737980
1	4.518258060	5.662132851	0.391671250
1	5.761710198	4.445190928	0.746076081
6	5.424407751	4.350469989	3.484525661
1	5.973015860	3.474941986	3.121606553
1	4.939275771	4.074749523	4.425356989
1	6.151953125	5.138637188	3.705288403
6	-6.028275088	-2.998194217	-3.760859020
1	-5.447436275	-2.848137858	-4.675724842
1	-6.313664876	-2.013124100	-3.378131802
1	-6.943662245	-3.533970629	-4.033322183
6	3.656875098	6.083250571	2.980478918
1	4.367196657	6.887779646	3.198299879
1	3.118126398	5.857769839	3.905401463
1	2.930987955	6.460220515	2.252630400
6	-3.385412594	6.177737709	-1.966263147
1	-2.633417199	6.656220783	-1.328476470
1	-4.209285943	6.879704295	-2.107156489
1	-2.916640689	6.000268382	-2.940926147
6	1.702306112	1.197472482	-7.644149621
1	1.848248810	0.114514893	-7.710942109
1	2.107469302	1.650383039	-8.555082958
1	0.625706667	1.390943658	-7.628857828
6	3.926089721	1.518768381	-6.540920575
1	4.493842923	1.932049663	-5.700579589
1	4.296022846	1.997417770	-7.452528877
1	4.152220934	0.450205114	-6.617757323

Complex 5 (UB3LYP/6-31G**/LANL2DZ)

29	-1.885140349	0.517410727	0.101795302
15	0.041357750	0.546606506	-1.363068982
15	-0.042244189	-0.497609032	1.289836116
16	-6.433715085	0.347686617	0.163911347
7	0.984044989	-0.210901483	-0.098681968
7	-3.887789311	-0.159908626	0.034051840
8	5.548180299	1.085425978	0.614979530
6	4.695117310	0.120359475	0.178258147
6	5.153483065	-1.116918846	-0.315084883
6	6.592179171	-1.350089111	-0.353824951
6	7.415370792	-0.366584332	0.087529565
1	8.493450689	-0.480965056	0.083686890
6	6.938300462	0.911557702	0.601014082
6	0.826108398	2.175030266	-1.690094135
8	7.619716396	1.818460269	1.009855689
6	-0.786674015	-1.182875562	-3.362393521
1	-1.739567339	-1.134155604	-2.841547654
6	0.183090468	1.388668847	3.306207047
1	-0.755739218	1.756004918	2.899389373
6	1.974330968	1.559958914	4.918372984
6	-0.656270199	-1.979835644	-4.501107733
1	-1.506491807	-2.549568434	-4.863711980
6	2.389905916	-0.516573609	-0.174316006
6	0.784100541	0.251208968	2.741254521
6	-0.128670324	-3.185245060	0.499086028
1	-0.146568346	-2.789818948	-0.512783911
6	0.774708730	2.039179475	4.390344669
1	0.298187201	2.913018349	4.824349030
6	-4.292627915	2.212607121	0.328153016
6	-5.172533224	3.296119209	0.415540469
1	-6.245494041	3.139591785	0.378222087
6	-4.648651626	4.580191913	0.544537047
1	-5.311620235	5.436448333	0.614428392
6	-3.264870477	4.745033547	0.574626801
1	-2.814599975	5.727195829	0.665974584
6	-2.455398977	3.612890552	0.481505050
1	-1.373408100	3.698058027	0.486940256
7	-2.948715371	2.372507399	0.368957345
6	1.175921829	2.988425986	-0.596471122
1	1.084973775	2.603529099	0.415803589
6	0.302243673	-0.432521325	-2.887864602
6	-0.214460370	-5.084259156	1.995524099
6	1.775011954	4.792749332	-2.092021417
6	1.656502947	4.281872731	-0.796441489
1	1.945763556	4.888089324	0.057065371
6	2.827766789	-1.758477890	-0.672653452
1	2.102164311	-2.488766117	-1.005367594
6	0.564417617	-2.034659227	-5.175266112
6	1.407280355	4.004088130	-3.181893251
1	1.493649559	4.395254730	-4.191160717
6	0.002822570	-2.309214429	1.591628357
6	0.934743132	2.703923786	-2.985531651
1	0.656648672	2.104484589	-3.845767431
6	-0.226776107	-4.561676064	0.699508721
1	-0.310033142	-5.226506165	-0.155497990
6	1.527324415	-0.492881826	-3.576737924
1	2.376107133	0.088042675	-3.231281978
6	-3.884534877	-2.629085518	-0.227651438
1	-2.801533985	-2.684435035	-0.233981814
6	-4.670931370	-3.767305791	-0.334718620
1	-4.196223049	-4.737490083	-0.439572420
6	-6.076051803	-3.686437204	-0.302473361
1	-6.666242025	-4.593096593	-0.388841077
6	-6.724692351	-2.464410088	-0.155287321
1	-7.807425674	-2.407372607	-0.124979969
6	-5.933436365	-1.318540108	-0.045010253
6	-4.521016810	-1.386773197	-0.084946323
6	-4.743884835	0.822964202	0.174813596
6	-0.107398118	-4.222381556	3.086950545
1	-0.101265324	-4.620477917	4.097160311
6	2.579271667	0.426831565	4.367109697
1	3.511700897	0.053779503	4.779607178
6	1.654161455	-1.291252782	-4.712714173
1	2.602627444	-1.331277876	-5.239911855
6	3.333435492	0.420935659	0.250789227
1	3.037188351	1.384475276	0.641637151
6	1.989163012	-0.227696423	3.286874514
1	2.461601977	-1.112124817	2.872463449
6	-0.000672843	-2.843615155	2.889538824
1	0.084460417	-2.188803602	3.750186478
6	4.184560930	-2.046100193	-0.737130080
1	4.502515355	-3.008717838	-1.122639442
6	7.133874372	-2.653781951	-0.872409328
1	6.760654178	-3.498530734	-0.282242051
1	8.224570966	-2.666998158	-0.834045121
1	6.826231093	-2.823640243	-1.910545646
1	2.152103228	5.798666455	-2.248638303
1	0.666980593	-2.650960912	-6.063442462
1	2.437003014	2.064738535	5.761023855
1	-0.290390823	-6.155932749	2.152153622

VII. References

1. V. R. Naina, A. K. Singh, P. Rauthe, S. Lebedkin, M. T. Gamer, M. M. Kappes, A.-N. Unterreiner and P. W. Roesky*, Chem. - Eur. J.,* 2023, e202300497.
2. D. Müller, L. Guénée and A. Alexakis, *Eur. J. Org. Chem.,* 2013, 6335-6343.
3. S. Meghdadi, M. Amirnasr and P. C. Ford, *Tetrahedron Lett.,* 2012, **53***,* 6950-6953.
4. .G. Sheldrick, *Acta Cryst. A,* 2008, **64**, 112-122.
5. G. Sheldrick, *Acta Cryst. C,* 2015, **71**, 3-8.
6. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr*., 2009, **42**, 339-341.
7. M. J. T. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. C. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. N. B. Mennucci, H. Petersson, M. Caricato, X. Li, H. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, Y. K. T. Nakajima, O. Honda, H. Nakai, T. Vreven, J. A. Montgomery, Jr. J. E. O. Peralta, F. Oligaro, M. Bearpark, J. J. Heyd, E. Brothers, V. N. Kudin, K. K. N. R. Staroverov, J. Normand, K. Raghavachari, A. B. Rendell, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Rega, M. Millam, J. E. Knox, J. B. Cross, V. Bakken, C. J. Adamo, J. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, J. W. Pomelli, J. W. Ochterski, R. L. Martin, K. Z. Morokuma, V. G. Zarkrzewski, A. G. Voth, P. Salvador, J. J. D. Dannenberg, S. Dapprich, A. D. Daniels, Ö, Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09, Revision B.01*, Gaussian, Inc., Wallingford, CT, 2010.
8. T. Yanai, D. P. Tew and N. C. Handy, *Chem. Phys. Lett*., 2004, **393**, 51-57.
9. http://www.chemcraftprog.com.