SUPPORTING INFORMATION

FOR

Exploiting Synergy Between Ligand Design Effects and Counterion Interactions to Boost Room Temperature Phosphorescence from Luminescent Cu(I) Compounds

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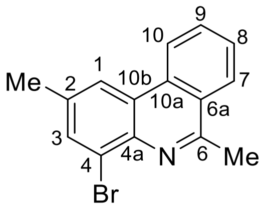
GENERAL EXPERIMENTAL DETAILS

Unless otherwise stated, all air sensitive experiments were carried out inside an inert-atmosphere glove box (N_2) or using standard Schlenk techniques (Ar). 2,6-Dibromoaniline (AK Scientific), *N*-iodosuccinimide (AK Scientific), *p*-toluidine (Alfa Aesar), *N*-bromosuccinimide (Alpha Aesar), 2-formylphenyl boronic acid (Combi Blocks), 2-acetylphenyl boronic acid (Combi blocks), $Pd(PPh_3)_4$ (Alfa Aesar), Na_2CO_3 (Alfa Aesar), chlorodiphenylphosphine (VWR), CuBr (Aldrich), sodium hexafluorophosphate (Alfa Aesar) and sodium tetraphenylborate (Aldrich) were purchased from commercial suppliers and used as received. 2-Bromo-4-methylaniline,[1] 6-bromo-2-iodo-4-methylaniline,[2] 4-bromo-2-methylphenanthridine,[2] 8-bromo-6-methylquinoline,[1] (4-diphenylphosphino)phenanthridine[3] (**L1**) and (4-diphenylphosphino)-2-methylphenanthridine[4] (**L2**) were synthesized following published procedures. Organic solvents were dried over appropriate reagents and deoxygenated prior to use, with the exception of 1,2-dimethoxyethane (1,2-DME) and water, which were simply degassed. NMR spectra were recorded on a Bruker Avance 300 MHz or Bruker Avance-III 500 MHz spectrometer as noted. Electronic absorption spectra (750–190 nm) were recorded on a Thermo Scientific Helios Zeta UV-VIS spectrophotometer at room temperature and concentrations on the order of 1.0×10^{-4} mol L^{-1}. Elemental analyses were performed by Canadian Microanalytical Service Ltd., Delta, BC and at the University of Manitoba on a Perkin Elmer EA2400 CHN Analyzer.

Synthesis of 2,6-dimethyl-4-bromophenanthridine



2-Bromo-6-iodo-*p*-toluidine (1.78 g, 5.70 mmol), 2-acetylphenylboronic acid (0.98 g, 6.00 mmol) and Pd(PPh$_3$)$_4$ (0.20 g, 0.17 mmol) were combined in a thick-walled, 500 mL Teflon-stoppered flask under N$_2$ atmosphere, followed by addition of degassed 1,2-DME (100 mL) and a solution of Na$_2$CO$_3$ (1.8 g, 17.10 mmol) in 40 mL of degassed water. The flask was then sealed and vigorously stirred overnight in an oil bath (130 °C). The flask was allowed to cool to room temperature and the mixture pumped dry. The crude was extracted with CH$_2$Cl$_2$ and excess MgCl$_2$ (0.5 g) was added and stirred overnight. The mixture was filtered through celite, concentrated nearly to dryness and passed through a plug of neutral Al$_2$O$_3$. Drying *in vacuo* gave a pale yellow solid. Isolated yield = 1.42 g (87%). ^{1}H NMR (CD$_2$Cl$_2$, 500 MHz, 22 °C): δ 8.52 (d, J_{HH} = 5 Hz, 1H, C$_7$-*H*), 8.23 (s, 1H, C$_3$-*H*), 8.17 (d, J_{HH} = 5 Hz, 1H, C$_{10}$-*H*), 7.83 (br, 1H, C$_1$-*H*), 7.82-7.79 (overlapped m, 1H, C$_9$-*H*), 7.70-7.67 (overlapped m, 1H, C$_8$-*H*), 3.01 (s, 3H, $^{\text{phen}}C^{6}_{\text{Me}}$-*H*), 2.55 ppm (s, 3H, $^{\text{phen}}C^{2}_{\text{Me}}$-*H*). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 126 MHz, 22 °C): δ 159.4 (C$_6$=N), 139.4 (C$_{4a}$), 137.3 (C$_3$), 134.2 (C$_1$-*H*), 132.4 (C$_{10a}$), 131.0 (C$_9$-*H*), 128.2 (C$_8$-*H*), 127.0 (C$_{10}$-*H*), 126.4 (C$_{6a}$), 125.5 (C$_4$-Br), 125.2 (C$_{10b}$), 122.9 (C$_7$-*H*), 122.0 (C$_3$-*H*), 23.8 (s, $^{\text{phen}}C^{6}_{\text{Me}}$-*H*), 21.8 ppm (s, $^{\text{phen}}C^{2}_{\text{Me}}$-*H*).

Synthesis of (2,6-dimethyl)(4-diphenylphosphino)phenanthridine (L3)

2,6-Dimethyl-4-bromophenanthridine (0.268 g, 1.00 mmol) was dissolved in dry diethylether (5 mL) and cooled to -78 °C. A solution of *sec*-butyllithium in cyclohexane (1.6 M; 0.80 mL, 1.00 mmol) was added drop-wise over a period of 10 min. The reaction mixture was stirred for 6 h at -78 °C. A solution of chlorodiphenylphosphine (0.220 g, 1.00 mmol) in dry diethylether (6 mL) was added drop-wise to the reaction mixture and the mixture allowed to warm to room temperature overnight, at which point an off-white suspension was observed. The volatiles were removed under reduced pressure and the solid residue was dissolved in dichloromethane (10 mL) and filtered through a small plug of celite. The filtrate was concentrated to ~2 mL under vacuum and 3 mL of pentane added. A precipitate formed overnight upon standing at -35° C. Isolated yield = 0.241 g (61%). ^{1}H NMR (CD_2Cl_2, 500 MHz, 22 °C): δ 8.63 (d, J_{HH} = 10 Hz, 1H, $^{phen}C_{Ar}\text{-}H$), 8.35 (s, 1H, $^{phen}C_{Ar}\text{-}H$), 8.16 (d, 1H, J_{HH} = 5, 10 Hz, $^{phen}C_{Ar}\text{-}H$), 7.83 (t, 1H, J_{HH} =5, 10 Hz, $^{phen}C_{Ar}\text{-}H$), 7.68 (t, 1H, J_{HH} =5, 10 Hz, $^{phen}C_{Ar}\text{-}H$), 7.37-7.32 (overlapped m, 10H, $PC_{Ar}\text{-}H$), 6.98 (br, 1H, $^{phen}C_{Ar}\text{-}H$), 2.83 (s, 3H, $^{phen}C^{6}_{Me}\text{-}H$), 2.46 ppm (s, 3H, $^{phen}C^{2}_{Me}\text{-}H$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 126 MHz, 22 °C): δ 157.3 ($^{phen}C_{Ar}\text{-}H$), 143.8 (d, J_{CP} = 12 Hz, $^{phen}C_{Ar}$), 139.1 (d, J_{CP} = 12 Hz, PC_{Ar}), 138.6 (d, J_{CP} = 11 Hz, PC_{Ar}), 136.5 ($^{phen}C_{Ar\text{-}}{}^{2}$Me), 134.9 ($^{phen}C_{Ar}$), 134.7 (d, J_{CP} = 20 Hz, $PC_{12}\text{–}H$), 132.8 (br, J_{CP} = 2 Hz, $^{phen}C_{Ar}$), 130.7 ($^{phen}C_{Ar}\text{-}H$), 128.8 ($^{phen}C_{Ar}\text{-}H$), 128.7 (d, J_{CP} = 12 Hz, PC_{Ar}), 127.8 (PC_{Ar}), 127.0 ($^{phen}C_{Ar}\text{-}H$), 126.4 (br, PC_{Ar}), 123.6 (br, J_{CP} = 2 Hz, $^{phen}C_{Ar}$) 123.0 ($^{phen}C_{Ar}\text{-}H$), 23.36 (C^{6}_{Me}), 22.32 ppm (C^{2}_{Me}). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202 MHz, 22 °C): δ -12.97 ppm (s).

Synthesis of 1BPh$_4$

A solution of (4-diphenylphosphino)phenanthridine (0.023 g, 0.063 mmol) in CH_2Cl_2 (3 mL) was added drop-wise to a suspension of CuBr (0.009 g, 0.063 mmol) in CH_2Cl_2 (3 mL) with constant stirring. The reaction mixture was stirred overnight at room temperature. An orange suspension formed, which was filtered through celite and drop-wise added to a solution of one more equivalent of (4-diphenylphosphino)phenanthridine (0.023 g, 0.063 mmol) in CH_2Cl_2 (2 mL). After one hour, a solution of sodium tetraphenylborate (0.021 g, 0.063 mmol) in THF (3 mL) was added. The color changed to yellowish green. Stirring was continued overnight and the reaction mixture then filtered through small plug of celite and dried under vacuum to give a greenish solid, which was washed with Et_2O (50 mL) and dried in vacuum to give an off-white product. X-ray quality single crystals were grown by slow diffusion of hexane into a DCM solution of the product. Yield = 0.044 g (64%). ^{1}H NMR ($CDCl_3$, 500 MHz, 22 °C): δ 8.77 (m, J_{HH} = 10 Hz, 2H, $^{phen}C_{Ar}$-H), 8.61 (m, J_{HH} = 10 Hz, 2H, $^{phen}C_{Ar}$-H), 8.31 (s, 2H, $^{phen}C_{Ar}$-H), 7.95-7.89 (m, 4H, $^{phen}C_{Ar}$-H), 7.84 (m, J_{HH} = 10, 5 Hz, 4H, $^{phen}C_{Ar}$-H), 7.62 (m, J_{HH} = 10, 5 Hz, 2H, PC_{Ar}-H), 7.46-7.36 ppm (overlapped m, 21H, PC_{Ar}-H), 7.33-7.30 (overlapped m, 8H, PC_{Ar}-H, PC_{BPh4}-H), 6.96-6.39 (br, 8H, PC_{BPh4}-H), 6.80-6.77 ppm (br, 4H, PC_{BPh4}-H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz, 22 °C): δ 164.4 (q, J_{CB} = 49 Hz, $^{phen}C_{Ar}$), 156.5 ($^{phen}C_{Ar}$), 145.5 (br, $^{phen}C_{Ar}$-H), 136.4 (br, PC_{Ar}-H), 136.3 (s, $^{phen}C_{Ar}$), 133.8 ($^{phen}C_{Ar}$-H), 133.2 (v br, J_{CP} = 31 Hz, PC_{Ar}), 132.7 (s, PC_{Ar}-H), 130.7 (t, $^{phen}C_{Ar}$-H), 129.6 (PC_{Ar}-H), 129.4 (br, $^{phen}C_{Ar}$-H), 129.3 ($^{phen}C_{Ar}$-H), 128.9 ($^{phen}C_{Ar}$), 126.4 ($^{phen}C_{Ar}$-H), 126.2 ($^{phen}C_{Ar}$), 125.7 (br, $^{phen}C_{Ar}$), 125.5 (br, J_{CB} = 4, PC_{BPh4}), 122.5($^{phen}C_{Ar}$-H), 121.5 ppm ($^{phen}C_{Ar}$-H). ^{31}P{^{1}H} NMR ($CDCl_3$, 121 MHz, 22 °C): δ -13.3 ppm (br, s). Anal. Calc. for $C_{74}H_{56}N_2P_2BCu$: C, 80.10; H, 5.09 %. Found: C, 80.26, H, 5.35 %.

Synthesis of $1PF_6$

$1PF_6$ was prepared by a similar procedure to **$1BPh_4$** using (4-diphenylphosphino)phenanthridine (0.023 g, 0.063 mmol) in CH_2Cl_2 (3 mL) and CuBr (0.009 g, 0.063 mmol) in CH_2Cl_2 (3 mL) and followed by addition of one more equivalent (4-diphenylphosphino)phenanthridine (0.023 g, 0.063 mmol) and sodium hexafluorophosphate (0.021 g, 0.063 mmol) in THF (3 mL); solid off white product. X-ray quality single crystals were grown by slow diffusion of Et_2O in DCM solution of the product. Yield = 0.046 g (78%). ^{1}H NMR ($CDCl_3$, 300 MHz, 22 °C): δ 8.93 (br m, J = 5 Hz, 2H, $^{phen}C_{Ar}$-H), 8.75 (m, J = 5 Hz, 2H, $^{phen}C_{Ar}$-H), 8.36 (v br, 2H, $^{phen}C_{Ar}$-H), 8.04-8.01 (br, 2H, $^{phen}C_{Ar}$-H), 7.97-7.93 (overlapped m, 4H, $^{phen}C_{Ar}$-H), 7.74-7.71 (m, 2H, PC_{Ar}-H), 7.53-7.33 ppm (overlapped m, 22H, PC_{Ar}-H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz, 22 °C): δ 156.5 ($^{phen}C_{Ar}$H), 145.6 (br, J_{CP} = 16 Hz, $^{phen}C_{Ar}$), 136.3 ($^{phen}C_{Ar}$-H), 133.8 (s, PC_{Ar}-H), 133.2 (v br, $^{phen}C_{Ar}$), 133.0 (br, PC_{Ar}), 132.8 ($^{phen}C_{Ar}$H), 131.1 (v br, PC_{Ar}), 130.6 (PC_{Ar}H), 129.7 ($^{phen}C_{Ar}$H), 129.4 (br, PC_{Ar}H), 129.3 ($^{phen}C_{Ar}$H), 128.8 ($^{phen}C_{Ar}$), 126.4 ($^{phen}C_{Ar}$), 126.3 ($^{phen}C_{Ar}$H), 125.8 ($^{phen}C_{Ar}$), 122.5 ppm ($^{phen}C_{Ar}$H). ^{31}P{^{1}H} NMR ($CDCl_3$, 121 MHz, 22 °C): δ -13.1 (br, s), 144.3 (sep) ppm. ^{19}F NMR ($CDCl_3$, 121 MHz, 25 °C): -73.89 ppm (d, J_{PF} = 755 Hz). Anal. Calc'd for: $C_{50}H_{36}N_2P_3F_6Cu•0.5CH_2Cl_2$: C, 62.14, H, 3.99 %. Found: C, 60.20; H, 4.00 %.

Synthesis of $2BPh_4$

Following the similar procedure of **$1BPh_4$,** (2-methyl,4-diphenylphosphino)phenanthridine (0.024 g, 0.063 mmol) was added drop-wise to CuBr (0.009 g, 0.063 mmol) in CH_2Cl_2 (6 mL). Then one more equivalent (2-methyl,4-diphenylphosphino)phenanthridine (0.024 g, 0.063 mmol) was added before sodium tetraphenylborate (0.021 g, 0.063 mmol) in THF (3 mL) was added to give an orange solid. X-ray quality single crystals were grown by slow diffusion of Et_2O into a DCM solution of the product. Yield = 0.065 g (91%). ^{1}H NMR ($CDCl_3$, 500 MHz, 22 °C): δ 8.60 (br, 4H, $^{phen}C_{Ar}$-H), 8.25 (s, 2H, $^{phen}C_{Ar}$-H), 7.91 (m, J_{HH} = 15, 10 Hz, 2H, $^{phen}C_{Ar}$-H), 7.70 (br, J_{HH}= 10 Hz, 2H, $^{phen}C_{Ar}$-H), 7.61 (m, J_{HH} = 10, 15 Hz, 4H, $^{phen}C_{Ar}$-H), 7.46-7.32 (overlapped m, 30H, PC_{Ar}-H, PC_{BPh4}-H), 6.96 (overlapped m, 8H, PC_{BPh4}-H), 6.79 (overlapped m, 4H, PC_{BPh4}-H), 2.65 ppm (s, 3H, $^{phen}C_{Me}$-H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz, 22 °C): δ 164.4 (q, J_{CB} = 49 Hz, PC_{BPh4}), 155.5 (br, $^{phen}C_{Ar}$-H), 144.0 (t, J_{CP} = 10, 11 Hz, $^{phen}C_{Ar}$), 139.2 (s, PC_{Ar}), 137.5 (s, $^{phen}C_{Ar}$-H), 133.5 ($^{phen}C_{Ar}$-H), 133.2 (v br, PC_{Ar}), 132.9 (t, J_{CP} = 16, 17 Hz, PC_{Ar}), 132.4 ($^{phen}C_{Ar}$), 131.1 (v br, PC_{Ar}), 130.6 (PC_{Ar}-H), 129.5 (PC_{Ar}-H), 129.4 (br, $^{phen}C_{Ar}$-H), 129.1 (PC_{Ar}H), 126.3 ($^{phen}C_{Ar}$H), 126.1 (s, $^{phen}C_{Ar}$), 125.6(t, $^{phen}C_{Ar}$), 125.5 (br, J_{CB} = 3 Hz, PC_{BPh4}-H), 122.4 (s, $^{phen}C_{Ar}$), 121.5 (s, PC_{BPh4}-H), 22.15 ppm ($^{phen}C_{Me}$-H). ^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz, 22 °C): δ -13.1 ppm (br, s). Anal. Calc'd for: $C_{78}H_{60}BCuN_2P_2$: C, 80.24; H, 5.32 %. Found: C: 80.41, H: 5.32 %.

Synthesis of 2PF$_6$

Complex **2PF$_6$** was synthesized in a similar way to **1BPh$_4$** using **L2** (0.024 g, 0.063 mmol) and CuBr (0.089 g, 0.063 mmol). Then one more equivalent (2-methyl,4-diphenylphosphino)phenanthridine (0.024 g, 0.063 mmol) was added to the reaction mixture, before adding a solution of sodium hexafluorophosphate (0.021 g, 0.063 mmol) in THF (3 mL); solid yellowish-green product. X-ray quality single crystals were grown by slow diffusion of hexane into a DCM solution of the product. Yield = 0.49 g (80%). ^{1}H NMR ($CDCl_3$, 300 MHz, 22 °C): δ 8.71 (m, J = 5 Hz, 2H, $^{phen}C_{Ar}$-H), 8.68 (br, 2H, $^{phen}C_{Ar}$-H), 8.27 (br, 2H, $^{phen}C_{Ar}$-H), 8.00 (m, 2H, $^{phen}C_{Ar}$-H), 7.72-7.69 (overlapped m, 4H, $^{phen}C_{Ar}$-H), 7.51-7.34 (overlapped m, 22H, $^{phen}C_{Ar}$-H, PC_{Ar}-H), 2.68 ppm (s, 6H, $^{phen}C_{Me}$-H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75 MHz, 22 °C): δ 155.6 ($^{phen}C_{Ar}$-H), 144.0 (br, J_{CP} = 9,11 Hz, $^{phen}C_{Ar}$), 139.2 ($^{phen}C_{Ar}$-H), 137.4 (PC_{Ar}-H), 133.5 ($^{phen}C_{Ar}$), 133.2 (v br, $^{phen}C_{Ar}$-H), 132.8 (PC_{Ar}), 132.5 (PC_{Ar}), 131.1 (v br, PC_{Ar}), 130.6 (PC_{Ar}-H), 129.7 ($^{phen}C_{Ar}$), 129.4 (br, PC_{Ar}-H), 129.1 ($^{phen}C_{Ar}$-H), 126.4 ($^{phen}C_{Ar}$), 126.1 ($^{phen}C_{Ar}$), 125.6 ($^{phen}C_{Ar}$), 122.4 ($^{phen}C_{Ar}$-H), 22.14 ppm ($^{phen}C_{Me}$-H). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121 MHz, 22 °C): δ -13.06 (br, s), 144.3 ppm (sep). ^{19}F NMR ($CDCl_3$, 282 MHz, 22 °C): -73.9 ppm (d, J_{PF} = 755 Hz). Anal. Calc'd for: $C_{52}H_{40}N_2P_3F_6Cu$: C, 60.73, H, 4.04 %. Found: C, 60.16; H, 4.14 %.

Synthesis of ((2,6-dimethyl)(4-diphenylphosphino)phenanthridine)$_2$Cu$_2$Br$_2$

This complex was synthesized via a procedure analogous to that described previously.[4] **L3** (0.024 g, 0.063 mmol) in CH_2Cl_2 (3 mL) was drop-wise added to a stirring suspension of CuBr (0.009 g, 0.063 mmol) in CH_2Cl_2 (3 mL). The reaction mixture was stirred overnight at room temperature, giving a yellow suspension, which was filtered through a small plug of Celite and recrystallized following slow diffusion of hexane into a dichloromethane solution. Orange-yellow crystals. Yield = 0.026 g (81%). ^{1}H NMR ($CDCl_3$, 300 MHz, 22 °C): δ 8.71 (br, J_{HH} = 15 Hz, 1H, $^{phen}C_{Ar}$-H), 8.58 (s, 1H, $^{phen}C_{Ar}$-H), 8.07 (br, 1H, $^{phen}C_{Ar}$-H), 7.97 (m, J_{HH} = 10, 15 Hz, 1H, $^{phen}C_{Ar}$-H), 7.74 (m, J_{HH} = 10, 15 Hz, 1H, $^{phen}C_{Ar}$-H), 7.50 (s, 1H, $^{phen}C_{Ar}$-H), 7.37 – 7.28 (overlapped m, 5H, PC_{Ar}-H), 7.23 – 7.18 (overlapped m, 5H, PC_{Ar}-H), 2.59 ppm (s, 6H, $^{phen}C^{2}_{Me}$-H, $^{phen}C^{6}_{Me}$-H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz, 22 °C): δ 162.1 (s, $^{phen}C_{Ar}$-H), 143.6 (s, $^{phen}C_{Ar}$), 137.7 (br, $^{phen}C_{Ar}$-H), 133.2 ($^{phen}C_{Ar}$), 132.5 (d, PC_{Ar}-H), 132.3 (d, $^{phen}C_{Ar}$-H), 129.9 ($^{phen}C_{Ar}$-H), 128.9 ($^{phen}C_{Ar}$-H), 127.8 ($^{phen}C_{Ar}$-H), 126.4 ($^{phen}C_{Ar}$), 125.7 (br, $^{phen}C_{Ar}$), 125.2 (d, $^{phen}C_{Ar}$), 122.8 ($^{phen}C_{Ar}$-H), 25.7 (C^{2}_{Me}), 21.9 ppm (C^{6}_{Me}). ^{31}P{^{1}H} NMR (CDCl$_3$, 121 MHz, 22 °C): δ -28.6 ppm (br, s).

Synthesis of 3BPh$_4$

L3 (0.025 g, 0.063 mmol) and CuBr (0.009 g, 0.063 mmol) were first combined in THF (3 mL) to give a yellow suspension. A second equivalent of **L3** (0.025 g, 0.063 mmol) and sodium tetraphenylborate (0.011 g, 0.063 mmol) in THF (3 mL) were then added. The resulting yellow-green solution was filtered through Celite and dried, and X-ray quality single crystals were grown by slow diffusion of hexane into a CH$_2$Cl$_2$ solution of the product. Yield = 0.041 (56%). ^{1}H NMR (CD$_2$Cl$_2$, 500 MHz, 22 °C): δ 8.77 (m, J_{HH}= 15 Hz , 2H, $^{phen}C_{Ar}$-H), 8.71 (s, 2H, $^{phen}C_{Ar}$-H), 8.02 (m, J_{HH} = 15, 10 Hz, 2H, $^{phen}C_{Ar}$-H), 7.97 (br, J_{HH}= 10 Hz, 2H, $^{phen}C_{Ar}$-H), 7.75 (m, J_{HH} = 10, 15 Hz, 4H, $^{phen}C_{Ar}$-H), 7.65 (v br, 2H, PC_{Ar}-H), 7.39-7.37 (overlapped m, 4H, $^{phen}C_{Ar}$-H, PC_{Ar}-H), 7.33 (overlapped m, 8H, PC_{Ar}-H), 7.23-7.16 (overlapped m, 16H, PC_{Ar}-H, PC$_{BPh4}$-H), 7.02-7.00 (overlapped m, 8H, PC$_{BPh4}$-H), 6.87-6.84 (overlapped m, 4H, PC$_{BPh4}$-H), 2.64 (s, 3H, $^{phen}C^{6}_{Me}$-H), 2.43 ppm (s, 3H, $^{phen}C^{2}_{Me}$-H). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 126 MHz, 22 °C): δ 164.6 (q, J_{CB} = 49 Hz, PC$_{BPh4}$), 162.8 (br, $^{phen}C_{Ar}$), 144.2 (t, J_{CP} = 8,10 Hz, $^{phen}C_{Ar}$), 138.9 (PC_{Ar}-H), 138.6 ($^{phen}C_{Ar}$-H), 136.4 ($^{phen}C_{Ar}$-H), 133.3 (br, PC_{Ar}-H), 132.8 (PC_{Ar}), 132.6 (t, J_{CP} = 16,16 Hz, $^{phen}C_{Ar}$), 132.2 (br, PC_{Ar}), 130.6 ($^{phen}C_{Ar}$-H), 129.4 (br, $^{phen}C_{Ar}$-H), 129.2 (PC_{Ar}),128.8 ($^{phen}C_{Ar}$), 128.1 ($^{phen}C_{Ar}$H), 126.7 ($^{phen}C_{Ar}$), 126.4 ($^{phen}C_{Ar}$-H), 126.1 (br, J_{CB} = 3 Hz, PC$_{BPh4}$-H), 125.9 (br, $^{phen}C_{Ar}$), 123.2 ($^{phen}C_{Ar}$), 122.2 ($^{phen}C_{Ar}$-H), 26.10 ($^{phen}C^{2}_{Me}$-H), 22.04 ppm ($^{phen}C^{6}_{Me}$-H). ^{31}P{^{1}H} NMR (CDCl$_3$, 121 MHz, 22 °C): δ -17.7 ppm (br, s). Anal. Calc'd for: $C_{78}H_{64}BCuN_2P_2$. CH_2Cl_2: C, 75.87; H, 5.32 %. Found: C, 75.57; H, 5.43 %.

Synthesis of 3PF$_6$

This complex was prepared by a similar procedure using **L3** (0.025 g, 0.063 mmol) and CuBr (0.089 g, 0.063 mmol) in CH_2Cl_2 (6 mL). A yellow suspension formed. Addition of one more equivalent of **L3** (0.025 g, 0.063 mmol) and sodium hexafluorophosphate (0.021 g, 0.063 mmol) in THF (3 mL) gave the product; yellow solid. X-ray quality single crystals were grown by slow diffusion of diethylether into a CH_2Cl_2 solution. Yield = 0.041 g (66%). ^{1}H NMR ($CDCl_3$, 500 MHz, 22 °C): δ 8.78 (d, J = 10 Hz, $^{phen}C_{Ar}$-H), 8.69 (br, 1H, $^{phen}C_{Ar}$-H), 8.03 (m, J = 5, 10 Hz, 1H, $^{phen}C_{Ar}$-H), 7.98 (d, J = 5 Hz, 2H, $^{phen}C_{Ar}$-H), 7.77 (t, J = 10, 15 Hz, 2H, $^{phen}C_{Ar}$-H), 7.54 (v br, 2H, PC_{Ar}-H), 7.39-7.36 (overlapped m, 4H, PC_{Ar}-H), 7.16 (overlapped m, 16H, PC_{Ar}-H), 2.63 (s, 3H, $^{phen}C^2_{Me}$-H), 2.40 ppm (s, 3H, $^{phen}C^6_{Me}$-H). ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz, 22 °C): δ 162.5 ($^{phen}C_{Ar}$-H), 143.7 (t, J_{CP} = 16 Hz, $^{phen}C_{Ar}$), 138.4 ($^{phen}C_{Ar}$-H), 138.1 (br, J_{CP} = 15 Hz, PC_{Ar}H), 133.1 ($^{phen}C_{Ar}$), 132.8 (v br, $^{phen}C_{Ar}$-H), 132.4 (br, PC_{Ar}), 132.0 (t, J_{CP} = 31 Hz, PC_{Ar}-H), 130.5 ($^{phen}C_{Ar}$-H), 129.9 (br, PC_{Ar}), 129.2 (PC_{Ar}-H), 129.0 (br, $^{phen}C_{Ar}$), 127.8 ($^{phen}C_{Ar}$-H), 126.2 ($^{phen}C_{Ar}$), 125.5 (br, $^{phen}C_{Ar}$-H), 122.9 ($^{phen}C_{Ar}$), 25.70 ($^{phen}C^2_{Me}$), 21.93 ppm ($^{phen}C^6_{Me}$). ^{31}P{^{1}H} NMR ($CDCl_3$, 121 MHz, 22 °C): δ -17.7 (br, s), -144.3 ppm (sep, J_{PF} = 755 Hz). ^{19}F NMR ($CDCl_3$, 500 MHz, 22 °C): -73.9 ppm (d, J_{PF} = 755 Hz). Anal. Calc'd for $C_{54}H_{44}CuF_6N_2P_3$•CH_2Cl_2: C, 61.37; H, 4.34 %. Found: C, 61.61; H, 4.46 %.

X-RAY CRYSTALLOGRAPHY EXPERIMENTAL DETAILS

X-ray crystal structure data was collected from multi-faceted crystals of suitable size and quality selected from a representative sample of crystals of the same habit using an optical microscope. In each case, crystals were mounted on MiTiGen loops with data collection carried out in a cold stream of nitrogen (150 K; Bruker D8 QUEST ECO). All diffractometer manipulations were carried out using Bruker APEX3 software.[5] Structure solution and refinement was carried out using XS, XT and XL software, embedded within the Bruker SHELXTL suite.[6] For each structure, the absence of additional symmetry was confirmed using ADDSYM incorporated in the PLATON program.[7] CCDC 1872863-1872869 contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Crystal structure data for **$\mathbf{1PF_6}$**: X-ray quality crystals were grown following diffusion of diethylether vapor into CH_2Cl_2 at room temperature. Crystal structure parameters: $C_{51}H_{38}Cl_2$ $CuF_6N_2P_3$ 1020.18 g/mol, triclinic, space group *P*-1; a = 9.1636(17) Å, b = 10.448(2) Å, c = 12.101(2) Å, α = 96.098(14)°, β = 99.601(13)°, γ = 109.077(17)°, V = 1063.4(4) Å^3; Z = 1, ρ_{calcd} = 1.488 g cm^{-3}; crystal dimensions 0.310 x 0.270 x 0.100 mm; diffractometer Bruker D8 QUEST ECO CMOS; Mo K_α radiation, 150(2) K, θ_{max} = 34.463°; 78831 reflections, 8169 independent (R_{int} = 0.0288), direct methods; absorption coeff (μ = 1.241 mm^{-1}), absorption correction semi-empirical from equivalents (SADABS); refinement (against F_o^2) with SHELXTL V6.1, 272 parameters, 0 restraints, R_1 = 0.0297 ($I > 2\sigma$) and wR_2 = 0.0759 (all data), Goof = 1.024, residual electron density 0.592/−0.404 e Å^{-3}.

Crystal structure data for **$\mathbf{1BPh_4}$**: X-ray quality crystals were grown following diffusion of hexanes vapor into CH_2Cl_2 at room temperature. Crystal structure parameters: $C_{74}H_{56}B$ CuN_2P_2 1109.49 g/mol, Monoclinic, space group C2/c; a = 18.204(7) Å, b = 18.807(7) Å, c = 18.109(6) Å, α = 90°, β = 116.99(13)°, γ = 90°, V = 5524.5(4) Å^3; Z = 4, ρ_{calcd} = 1.334 Mg/m^3; crystal dimensions 0.250 x 0.120 x 0.120 mm;

diffractometer Bruker D8 QUEST ECO CMOS; Mo K_{α} radiation, 150(2) K, θ_{max} = 30.622°; 91982 reflections, 8513 independent (R_{int} = 0.0722), direct methods; absorption coeff (μ = 0.502 mm^{-1}), absorption correction semi-empirical from equivalents (SADABS); refinement (against F_o^2) with SHELXTL V6.1, 362 parameters, 0 restraints, $R_1 = 0.0490$ ($I > 2\sigma$) and $wR_2 = 0.1559$ (all data), Goof = 1.005, residual electron density 0.556/−0.477 e $Å^{-3}$.

Crystal structure data for **$2PF_6$**: X-ray quality crystals were grown following diffusion of hexanes vapor into CH_2Cl_2 at room temperature. Crystal structure parameters: $C_{104}H_{80}Cu_2$ $F_{12}N_4P_6$ 1926.62 g/mol, Monoclinic, space group C2/c; a = 24.047(7) Å, b = 9.432(3) Å, c = 20.640(6) Å, α = 90°, β = 93.49(16)°, γ = 90°, V = 4672.9(2) $Å^3$; Z = 2, ρ_{calcd} = 1.369 Mg/m^3; crystal dimensions 0.280 x 0.090 x 0.080 mm; diffractometer Bruker D8 QUEST ECO CMOS; Mo K_{α} radiation, 150(2) K, θ_{max} = 30.614°; 87059 reflections, 7202 independent (R_{int} = 0.0836), direct methods; absorption coeff (μ = 0.632 mm^{-1}), absorption correction semi-empirical from equivalents (SADABS); refinement (against F_o^2) with SHELXTL V6.1, 292 parameters, 0 restraints, $R_1 = 0.0540$ ($I > 2\sigma$) and $wR_2 = 0.1144$ (all data), Goof = 1.012, residual electron density 0.606/−0.683 e $Å^{-3}$.

Crystal structure data for **$2BPh_4$**: X-ray quality crystals were grown following diffusion of diethylether vapor into CH_2Cl_2 at room temperature. Crystal structure parameters: $C_{76.50}H_{61}B$ $ClCuN_2P_2$ 1180.01 g/mol, Triclinic, space group P-1; a = 13.929(6) Å, b = 18.462(8) Å, c = 25.833(12) Å, α = 107.47(3)°, β = 95.17(3)°, γ = 107.16(3)°, V = 5937.2(5) $Å^3$; Z = 4, ρ_{calcd} = 1.320 Mg/m^3; crystal dimensions 0.100 x 0.100 x 0.050 mm; diffractometer Bruker D8 QUEST ECO CMOS; Mo K_{α} radiation, 150(2) K, θ_{max} = 27.603°; 134866 reflections, 27407 independent (R_{int} = 0.1484), direct methods; absorption coeff (μ = 0.515 mm^{-1}), absorption correction semi-empirical from equivalents (SADABS); refinement (against F_o^2) with SHELXTL V6.1, 1508 parameters, 0 restraints, R_1 = 0.0596 ($I > 2\sigma$) and wR_2 = 0.1528 (all data), Goof = 1.005, residual electron density 0.411/−0.629 e Å^{-3}.

Crystal structure data for **$3PF_6$**: X-ray quality crystals were grown following diffusion of diethylether vapor into CH_2Cl_2 at room temperature. Crystal structure parameters: $C_{109}H_{88Cl2}Cu_2$ $F_{12}N_4P_6$ 2065.63 g/mol, Monoclinic, space group C2/c; a = 27.339(7) Å, b = 25.087(11) Å, c = 17.994(9) Å, α = 90°, β = 128.56(10)°, γ = 90°, V = 9651.0(8) Å^3; Z = 4, ρ_{calcd} = 1.422 Mg/m^3; crystal dimensions 0.320 x 0.200 x 0.090 mm; diffractometer Bruker D8 QUEST ECO CMOS; Mo K_α radiation, 150(2) K, θ_{max} = 34.390°; 158133 reflections, 18551 independent (R_{int} = 0.0602), direct methods; absorption coeff (μ = 0.671 mm^{-1}), absorption correction semi-empirical from equivalents (SADABS); refinement (against F_o^2) with SHELXTL V6.1, 645 parameters, 0 restraints, R_1 = 0.0580 ($I > 2\sigma$) and wR_2 = 0.1706 (all data), Goof = 1.000, residual electron density 1.075/−1.409 e Å^{-3}.

Crystal structure data for **$3BPh_4$**: X-ray quality crystals were grown following diffusion of hexanes vapor into CH_2Cl_2 at room temperature. Crystal structure parameters: $C_{39}H_{32}B_{0.50}Cu_{0.50}NP$ 582.80 g/mol, Triclinic, space group P-1; a = 11.749(4) Å, b = 16.295(6) Å, c = 17.841(6) Å, α = 66.52(19)°, β = 87.83(2)°, γ = 88.68(2)°, V = 3130.62(19) Å^3; Z = 4, ρ_{calcd} = 1.237 Mg/m^3; crystal dimensions 0.200 x 0.100 x 0.050 mm; diffractometer Bruker D8 QUEST ECO CMOS; Mo K_α radiation, 150(2) K, θ_{max} = 29.718°; 144753 reflections, 17714 independent (R_{int} = 0.0814), direct methods;

absorption coeff (μ = 0.446 mm^{-1}), absorption correction semi-empirical from equivalents (SADABS); refinement (against F_o^2) with SHELXTL V6.1, 761 parameters, 0 restraints, $R_1 = 0.0501$ ($I > 2\sigma$) and $wR_2 = 0.1400$ (all data), Goof = 1.062, residual electron density 0.489/−0.795 e $Å^{-3}$.

Crystal structure data for $[(\mathbf{L3})Cu]_2(\mu\text{-}Br)_2$: X-ray quality crystals were grown following diffusion of diethylether vapor into CH_2Cl_2 at room temperature. Crystal structure parameters: $C_{55}H_{46}Br_2Cl_2Cu_2N_2P_2$ 1154.68 g/mol, triclinic, space group *P*-1; a = 12.3597(8) Å, b = 13.5264(9) Å, c = 14.5021(9) Å, α = 80.780(3)°, β = 89.069(3)°, γ = 88.363(3)°, V = 2392.0(3) $Å^3$; Z = 2, ρ_{calcd} = 1.603 g cm^{-3}; crystal dimensions 0.587 x 0.208 x 0.205 mm; diffractometer Bruker D8 QUEST ECO CMOS; Mo K_α radiation, 150(2) K, θ_{max} = 27.565°; 79926 reflections, 11013 independent (R_{int} = 0.0325), direct methods; absorption coeff (μ = 2.779 mm^{-1}), absorption correction semi-empirical from equivalents (SADABS); refinement (against F_o^2) with SHELXTL V6.1, 272 parameters, 0 restraints, $R_1 = 0.0291$ ($I > 2\sigma$) and $wR_2 = 0.0650$ (all data), Goof = 1.033, residual electron density 0.700/−0.691 e $Å^{-3}$.

OPTICAL SPECTROSCOPY MEASUREMENTS

The absorption spectra of the complexes were measured in solution in CH_2Cl_2 in 1 cm quartz cuvettes using a Thermo Scientific Genesys UV−vis spectrometer at room temperature. Emission spectra at 77 K were recorded in 4 mm diameter tubes held within a liquid-nitrogen-cooled quartz dewar, using a Jobin Yvon Fluoromax-2 spectrometer equipped with a Hamamatsu R928 photomultiplier tube (PMT). The spectra in the solid state were recorded by means of an integrating sphere attached to a Jobin Yvon Fluorolog instrument through optical fibers. Finely powdered samples were contained within

Spectralon sample holders of 10 mm diameter. Quantum yields were determined using a sample of finely powdered $BaSO_4$ as a non-emissive blank. Scattered light at λ_{ex} = 425 nm for sample and blank was measured using a neutral density filter of O.D. = 2, while the emission region was monitored in the absence of the filter. The detector for this set-up was also a Hamamatsu R928 PMT. Luminescence lifetimes at ambient temperature were measured by time-correlated single-photon counting (TCSPC) following excitation using a pulsed laser diode at 405 nm and using an R928 PMT for detection. The same detector operating in multichannel scaling (MCS) mode was used to measure the longer lifetimes at 77 K, following excitation with a microsecond-pulsed xenon lamp.

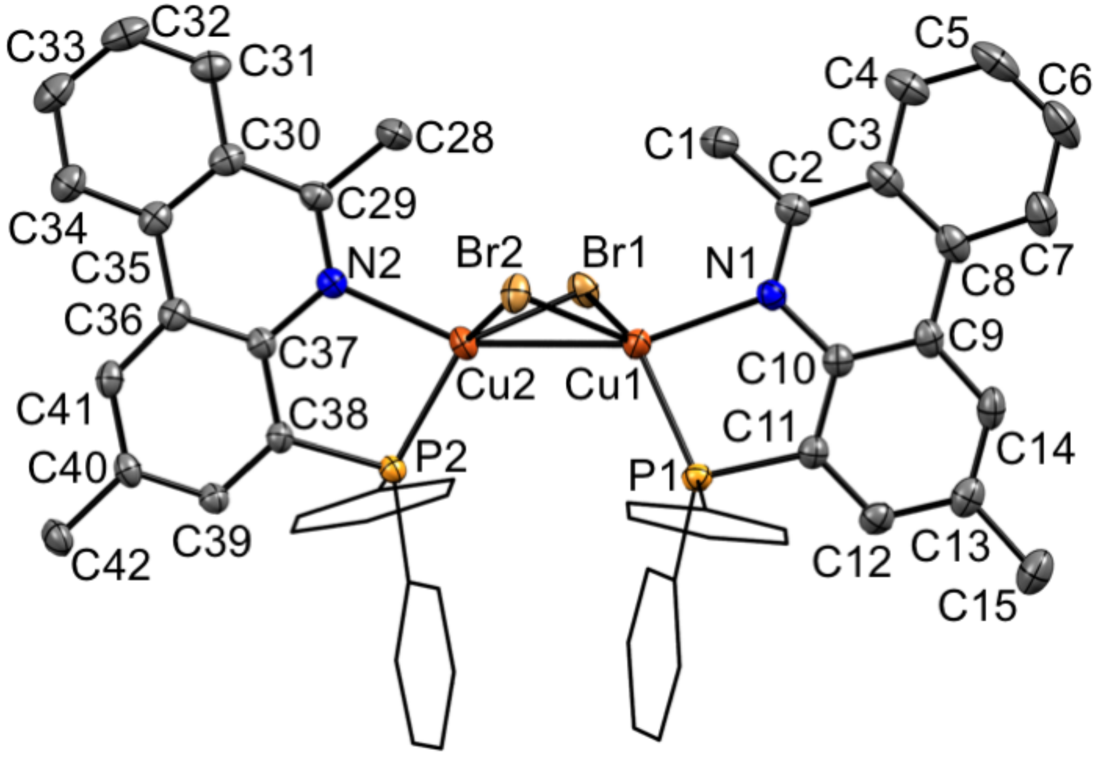
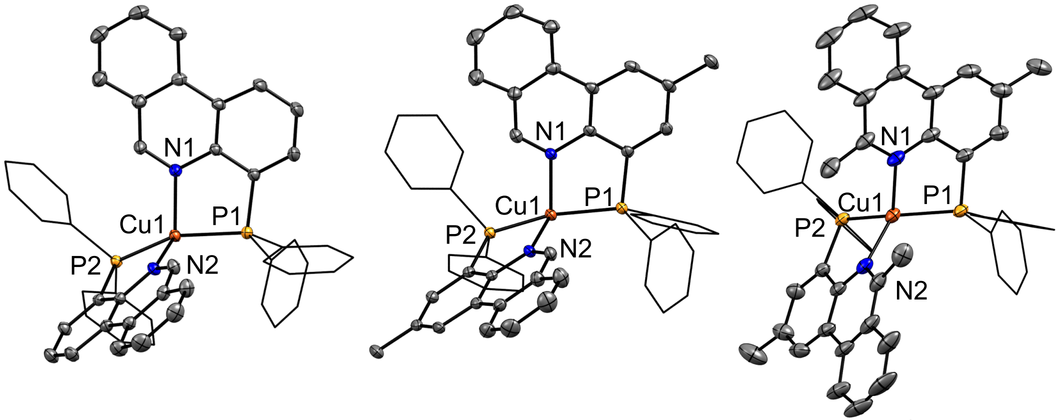


Figure S1. Solid-state X-ray structure of (**L3**)$_2$Cu$_2$Br$_2$ with thermal ellipsoids (where shown at 50% probability levels). Hydrogen atoms and a molecule of the solvent of crystallization (CH_2Cl_2) are omitted for clarity.



[1]$^+$ **[2]**$^+$ **[3]**$^+$

Figure S2. Solid-state X-ray structures of the cationic fragments of **1PF$_6$**, **2PF$_6$** and **3PF$_6$** with thermal ellipsoids (where shown at 50% probability levels). Hydrogen atoms, counterions and lattice-confined solvent molecules are omitted for clarity.

Table S1. Dihedral angles (°) from X-ray structures (**1X**, **2X** and **3X**; X = PF$_6$, BPh$_4$).

	θ_{Cu}[a]	θ_{Phen}[b]	α_P[c]	α_N[d]	P-Cu-P	N-Cu-N	β_N[e]	β_P[f]
1-BPh$_4$	86.9	88.3	144.27(6)	106.41(7)	136.73(3)	105.46(9)	5.71(6)	6.56(3)
1-PF$_6$	83.3	79.3	156.77(5), 151.05(5)	117.82(6), 122.49(6)	145.49(2)	109.20(6)	2.53(5), 5.94(5)	1.34(7), 2.92(6)
2-BPh$_4$[g]	79.6	70.45	142.23(9), 155.53(9)	132.95(12), 119.91(12)	131.49(4)	101.40(11)	0.21(10), 3.91(10)	3.05(14), 7.52(11)
	87.4	89.6	146.74(9), 153.00(10)	126.57(12), 120.98(13)	137.17(4)	105.94(11)	11.90(10), 8.12(10)	0.15(14), 3.31(14)
2-PF$_6$	88.4	84.1	154.16(6)	100.27(8)	146.99(4)	100.19(10)	5.58(6)	--
3-BPh$_4$	81.5	89.4	148.14(6), 129.44(6)	128.05(7), 143.88(6)	126.15(2)	123.78(7)	20.29(6), 15.22(6)	4.99(7), 5.37(7)
3-PF$_6$	83.4	83.6	140.96(8), 146.71(6)	133.11(9), 128.41(8)	133.23(2)	118.93(7)	21.09(6), 17.45(7)	8.92(10), 1.10(11)

[a] dihedral angle between planes formed by P1-Cu1-N1/P2-Cu1-N2

[b] dihedral angle between planes formed by C/N atoms of the two phenanthridine moieties

[c] angle formed by (P-Cu) bond vector with P-Cu-N plane of second ligand calculated as (180 – β). β is the acute angle between a line through the bond and the perpendicular projection of that bond on the plane.

[d] angle formed by (N-Cu) bond vector with P-Cu-N plane of second ligand.

[e] dihedral angle between (N-Cu) bond vector and phenanthridine plane of same ligand.

[f] dihedral angle between (P-Cu) bond vector and phenanthridine plane of same ligand.

[g] two crystallographically distinct molecules in the asymmetric unit

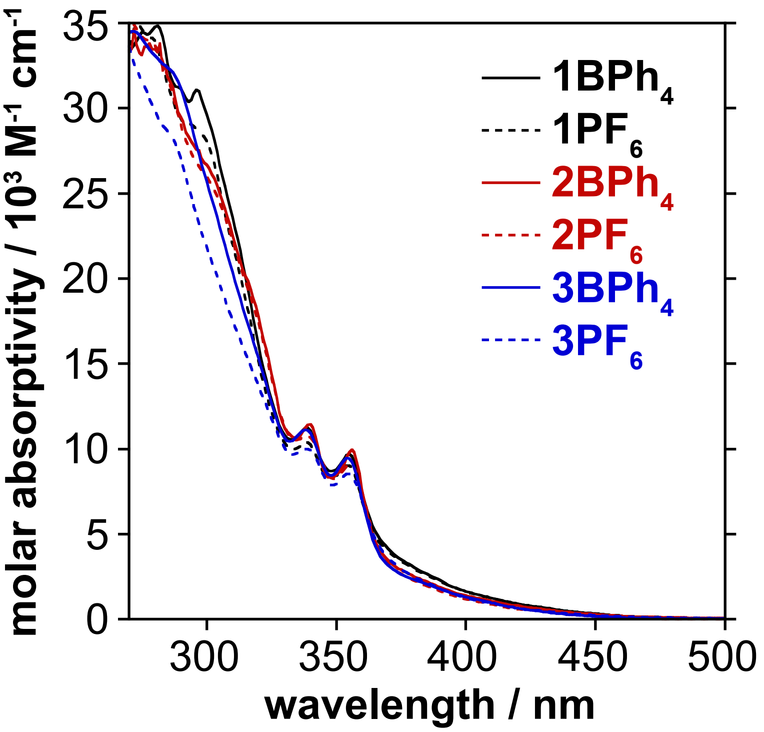


Figure S3. UV-Vis absorption spectra of **1X**, **2X** and **3X** recorded in CH_2Cl_2 at room temperature.

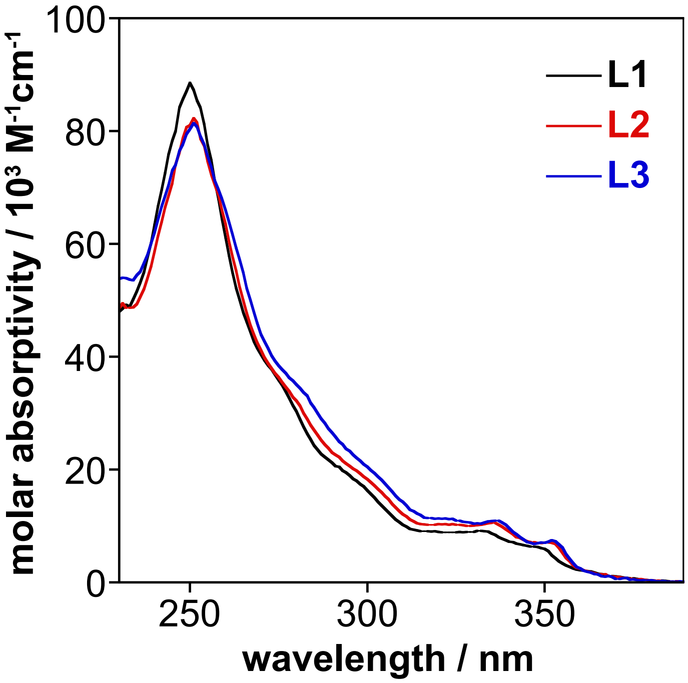


Figure S4. Absorption spectra of **L1, L2,** and **L3** in CH_2Cl_2 at 298 ± 3 K.

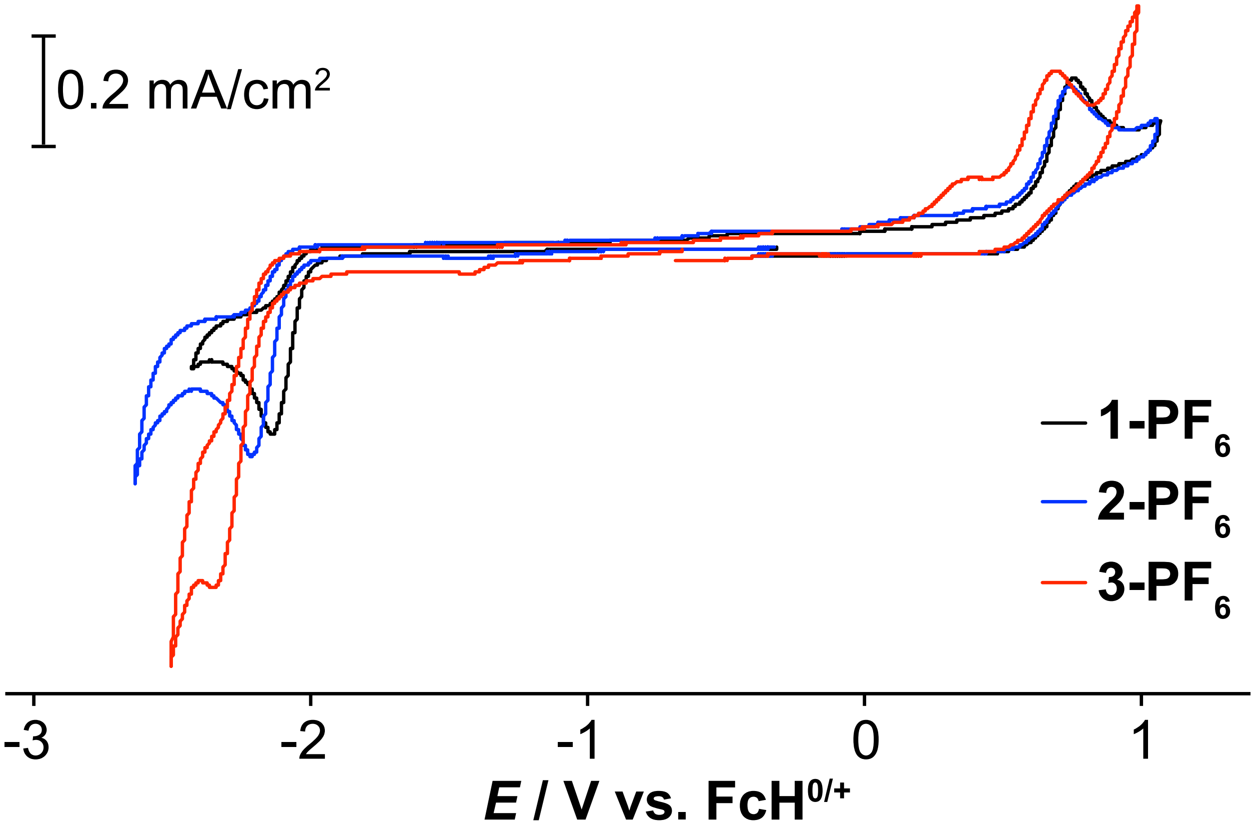


Figure S5. Cyclic voltammograms of **1-PF$_6$**, **2-PF$_6$** and **3-PF$_6$** ([analyte] = 1.1 mM; 0.1 M [*n*Bu$_4$N][PF$_6$], 100 mV/s scan rate).

Table S2. Tabulated potentials vs. FcH$^{0/+}$ of irreversible redox events for **1PF$_6$**, **2PF$_6$** and **3PF$_6$** ([analyte] = 1.1 mM; 0.1 mM [*n*Bu$_4$N][PF$_6$], 100 mV/s scan rate)

	$E_{\text{peak, cathodic}}$	$E_{\text{peak, anodic}}$	$\Delta E_{\text{cathodic-anodic}}$
1PF$_6$	-2.142	0.755	2.897
2PF$_6$	-2.216	0.741	2.957
3PF$_6$	-2.355	0.690, 0.335[a]	3.045

[a] Minor anodic peak observable in Figure S1.

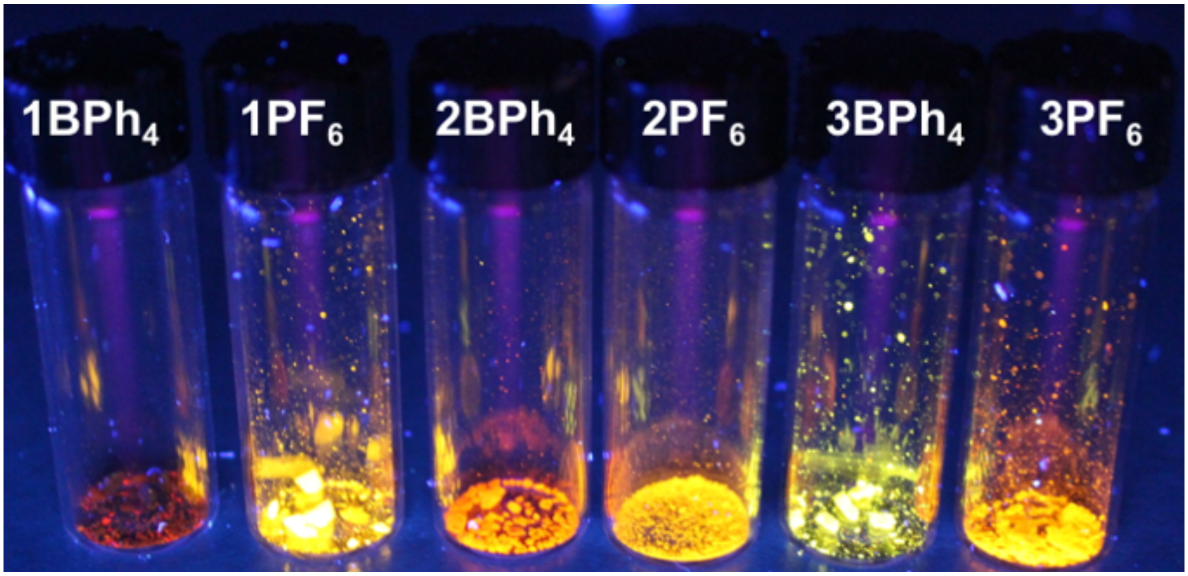


Figure S6. Optical photographs of **1X-3X** under UV light (λ = 365 nm).

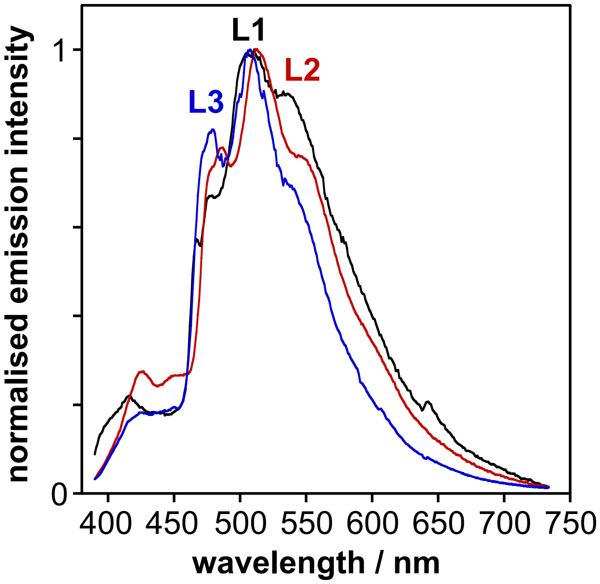


Figure S7. Emission spectra of ligands **L1**, **L2**, and **L3** in EPA at 77 K (EPA = diethyl ether / isopentane / ethanol, 2:2:1 v/v); λ_{ex} = 370 nm.

NMR SPECTRA

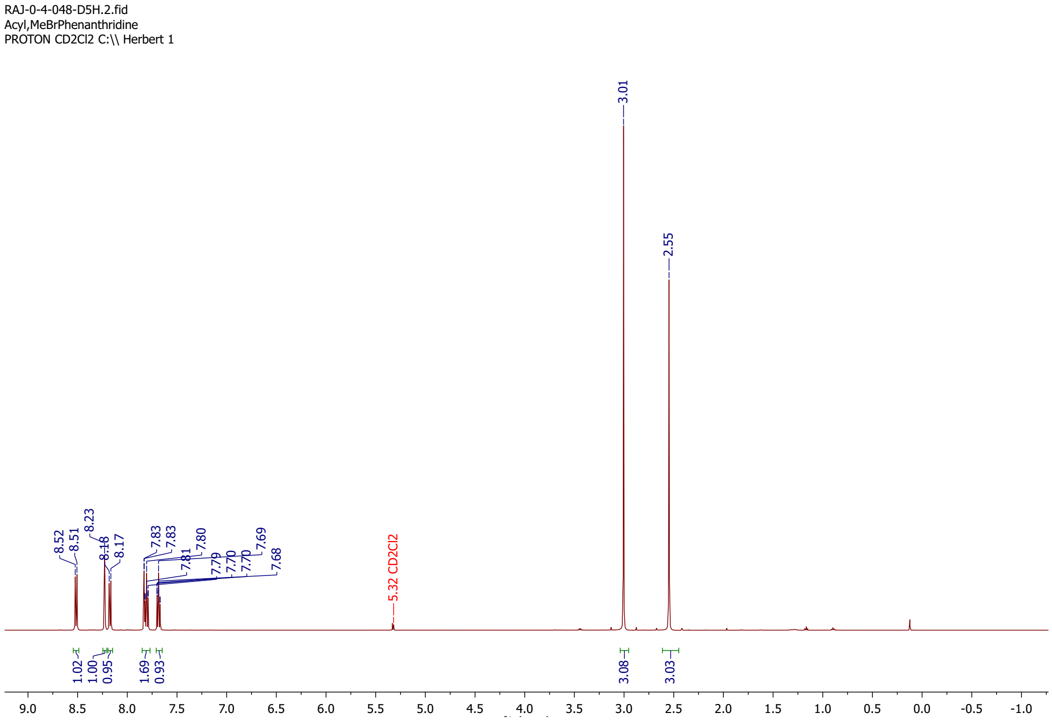


Figure S8. ^{1}H NMR (500 MHz, 22°C, CD_2Cl_2) of 4-bromo-2,6-dimethylphenanthridine.

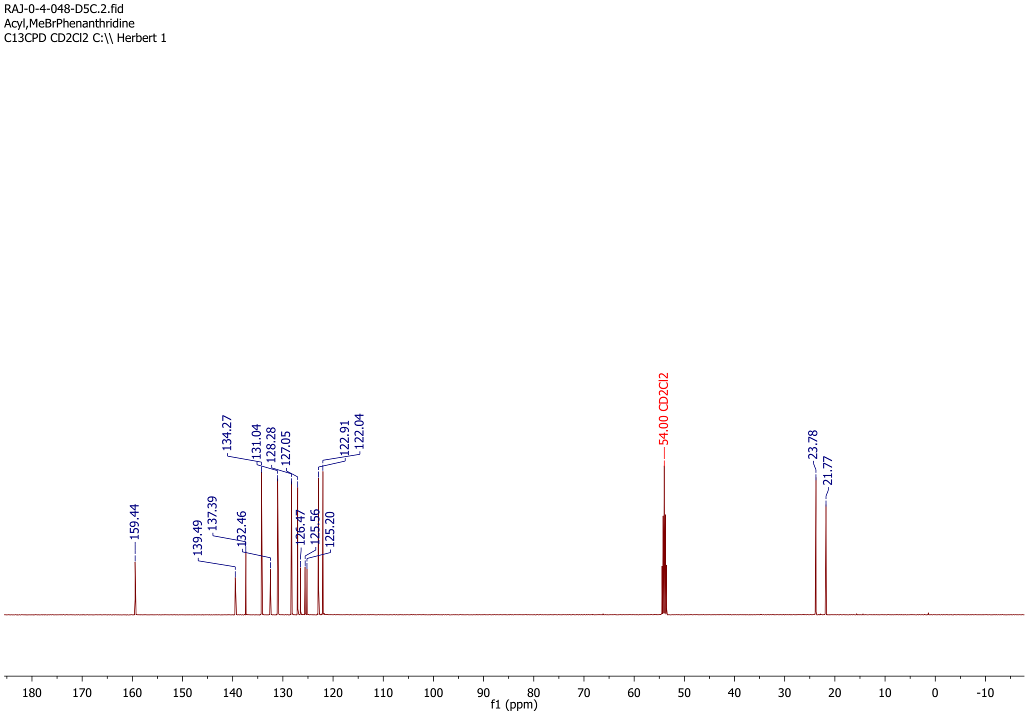


Figure S9. $^{13}C\{^1H\}$ (126 MHz, 22°C, CD_2Cl_2) of 4-bromo-2,6-dimethylphenanthridine.

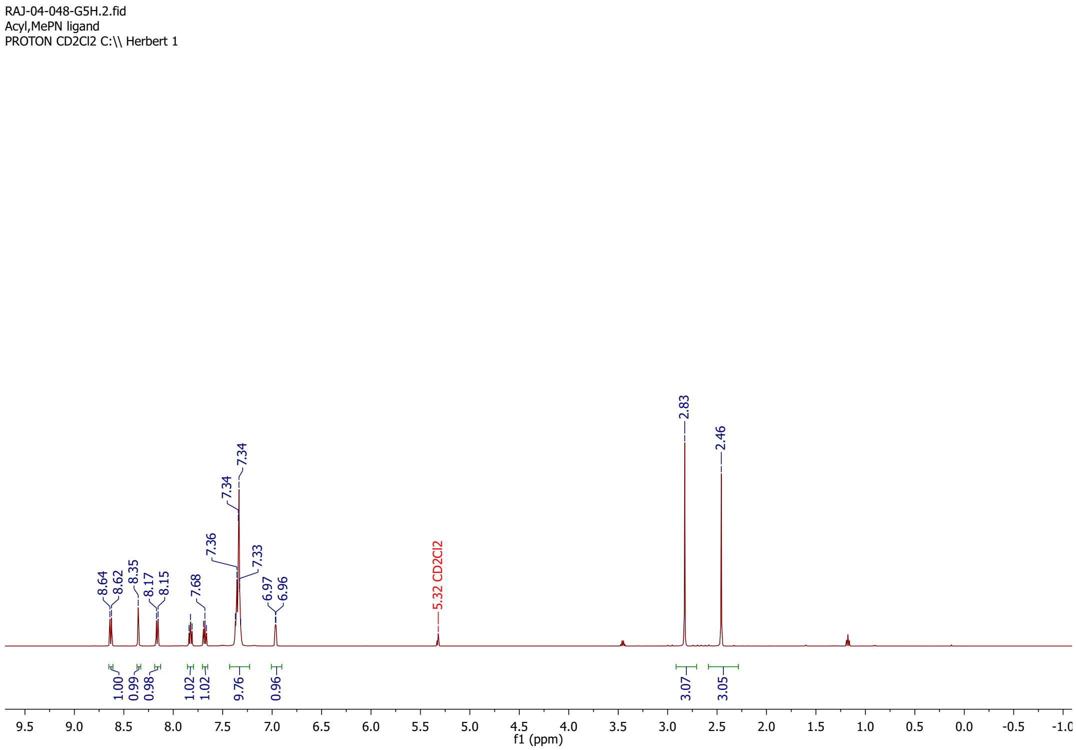


Figure S10. ^{1}H NMR (500 MHz, 22°C, CD_2Cl_2) spectrum of **L3**.

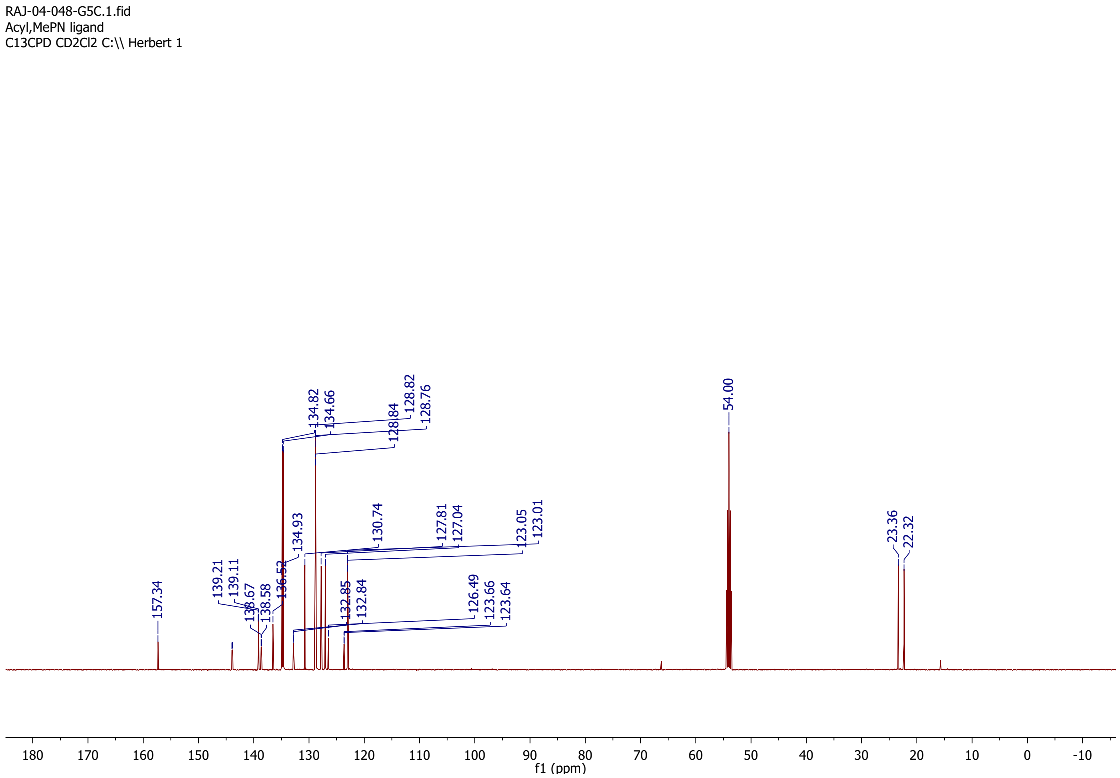


Figure S11. $^{13}C\{^1H\}$ (126 MHz, 22°C, CD_2Cl_2) NMR spectrum of **L3**.

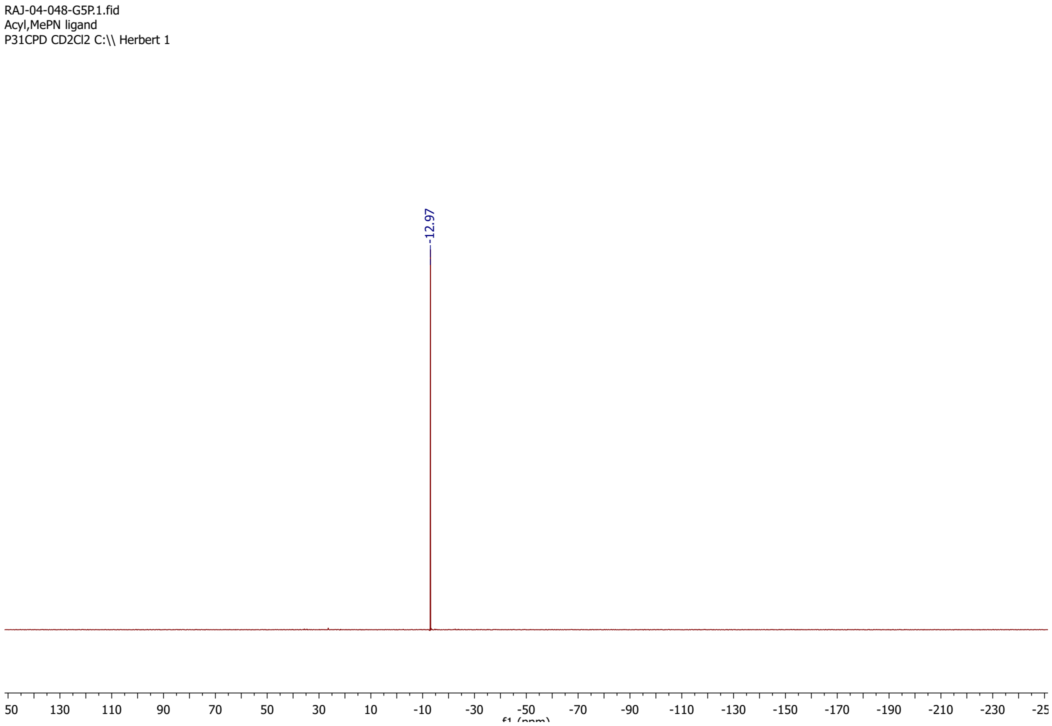


Figure S12. $^{31}P\{^{1}H\}$ (202 MHz, 22°C, CD_2Cl_2) NMR spectrum of **L3** in CD_2Cl_2.

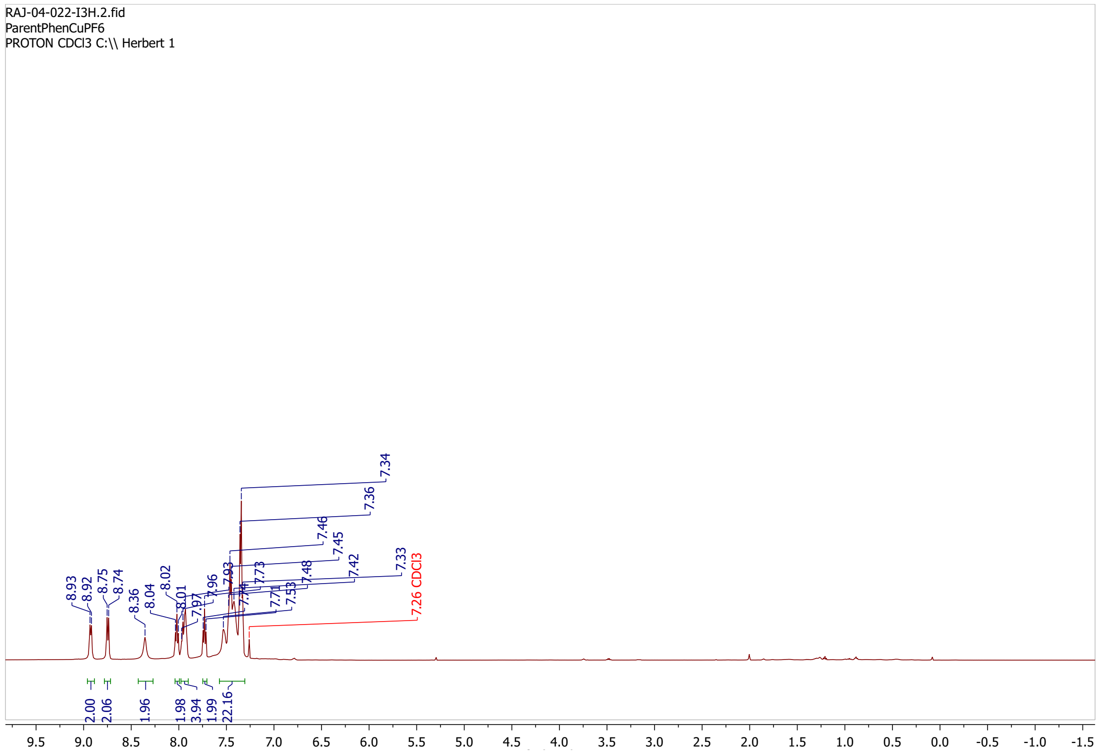


Figure S13. ^{1}H NMR (300 MHz, 22°C) spectrum of $\mathbf{1PF_6}$ in $CDCl_3$.

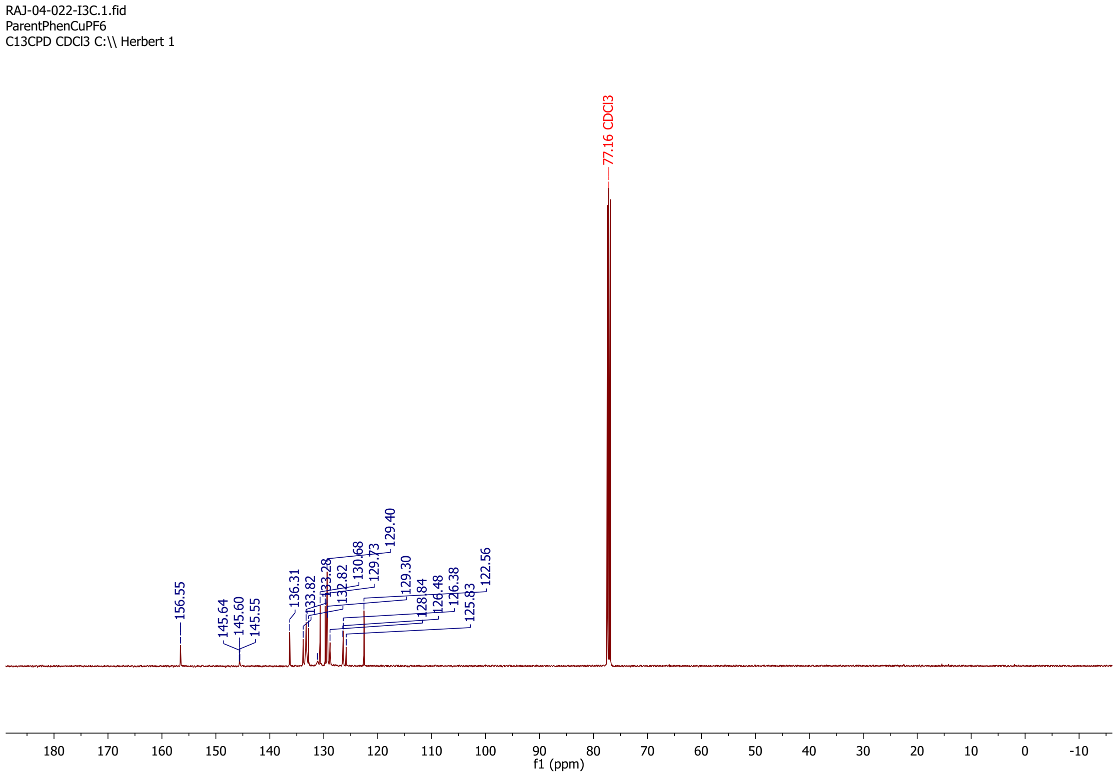


Figure S14. $^{13}C\{^{1}H\}$ NMR (75 MHz, 22°C) spectrum of $\mathbf{1PF_6}$ in $CDCl_3$.

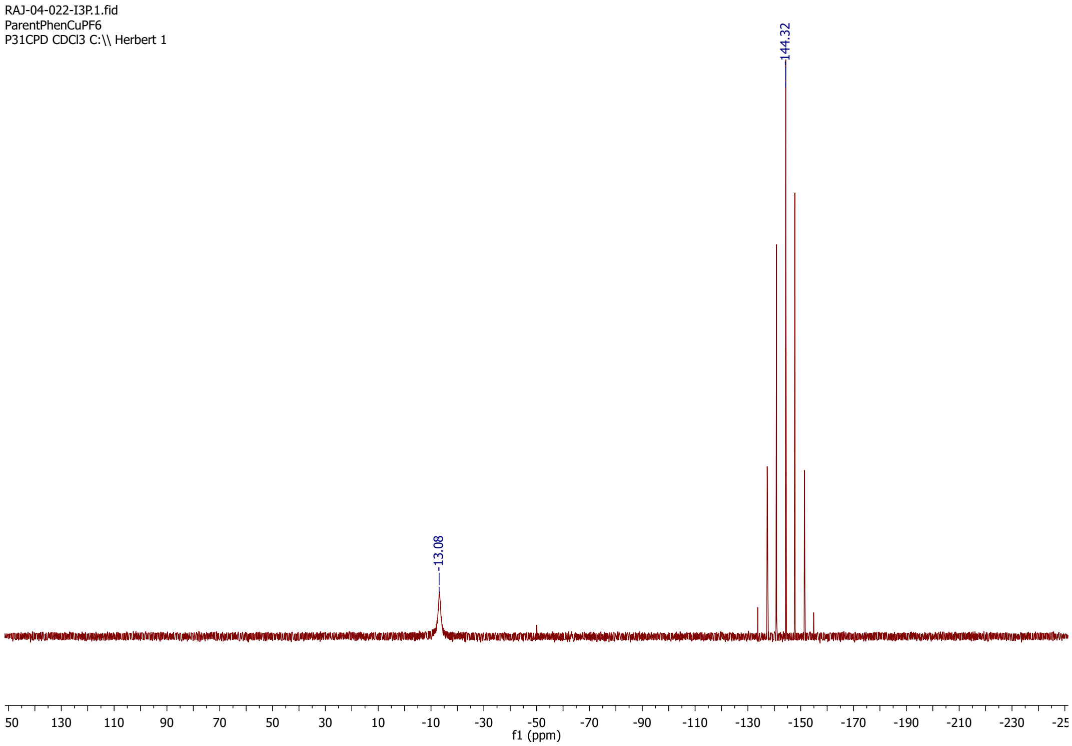


Figure S15. $^{31}P\{^{1}H\}$ (121 MHz, 22°C) NMR spectrum of $\mathbf{1PF_6}$ in $CDCl_3$.

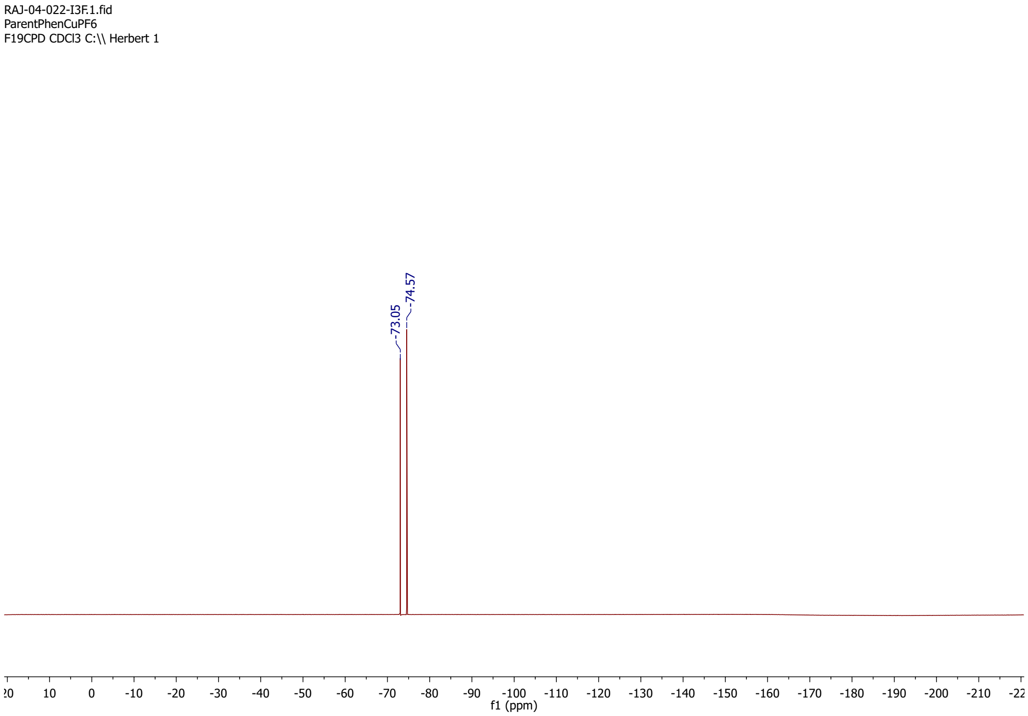


Figure S16. ^{19}F NMR (282 MHz, 22°C) spectrum of **1PF$_6$** in CDCl$_3$.

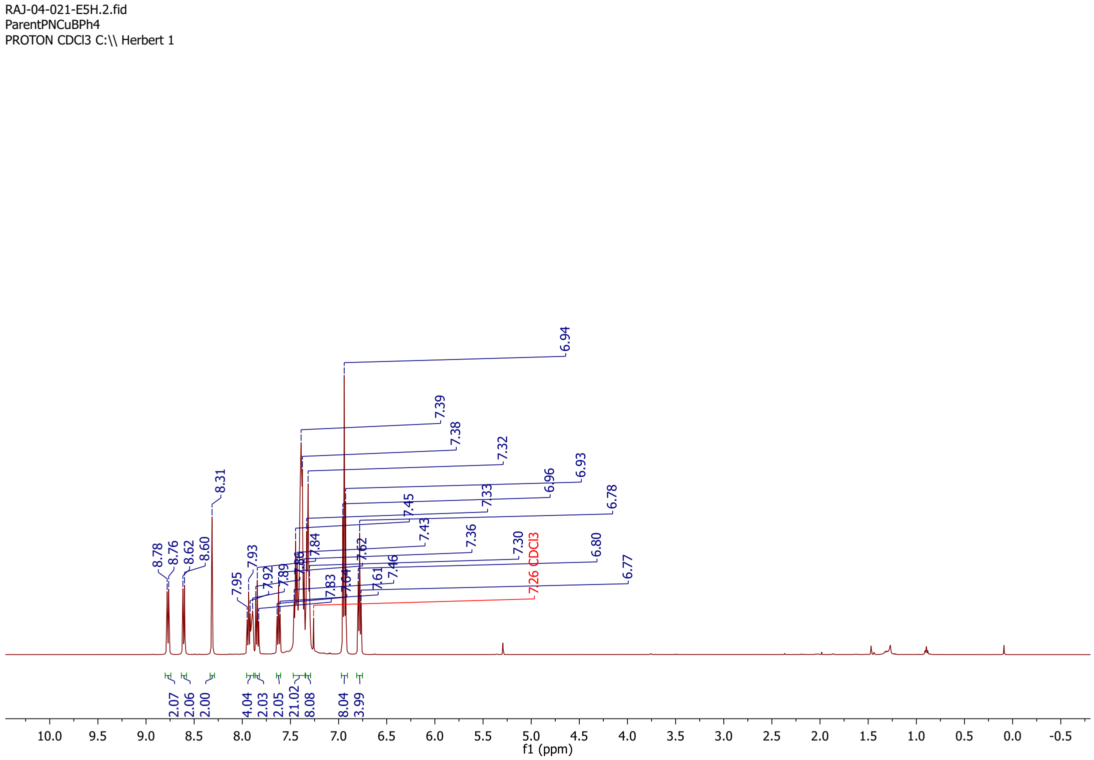


Figure S17. ^{1}H NMR (500 MHz, 22°C) spectrum of **1BPh$_4$** in CDCl$_3$.

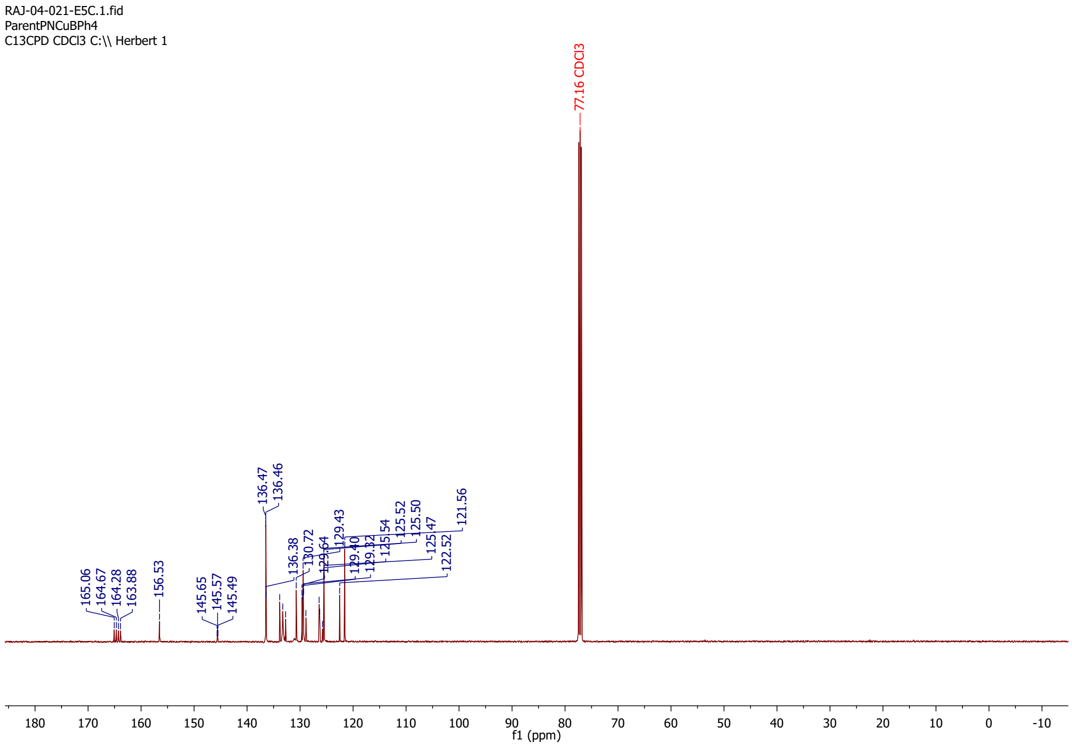


Figure S18. $^{13}C\{^1H\}$ NMR (126 MHz, 22°C) spectrum of **$1BPh_4$** in $CDCl_3$.

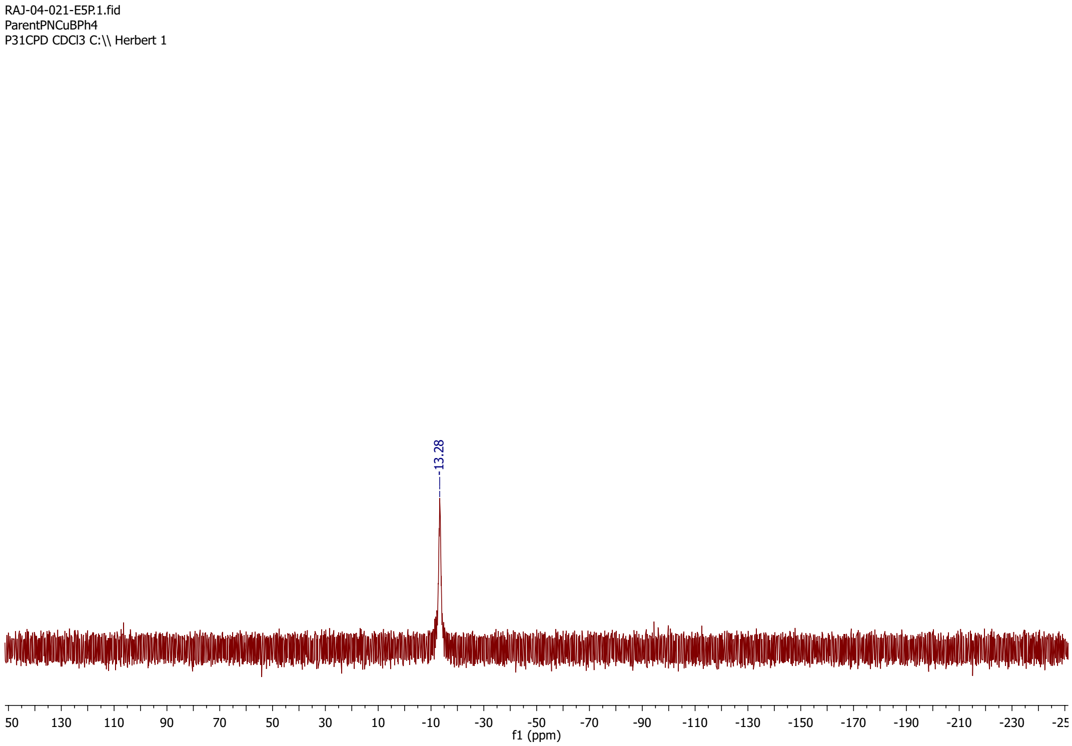


Figure S19. $^{31}P\{^1H\}$ (202 MHz, 22°C) NMR spectrum of **$1BPh_4$** in $CDCl_3$.

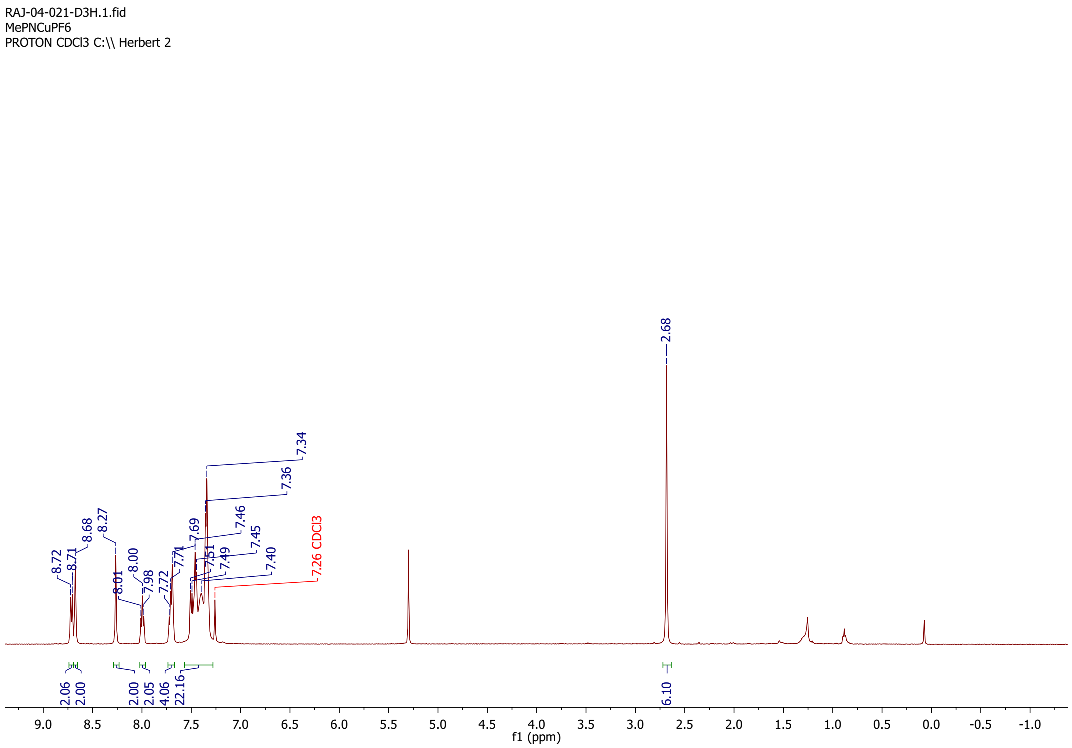


Figure S20. ^{1}H NMR (300 MHz, 22°C) spectrum of **$2PF_6$** in $CDCl_3$.

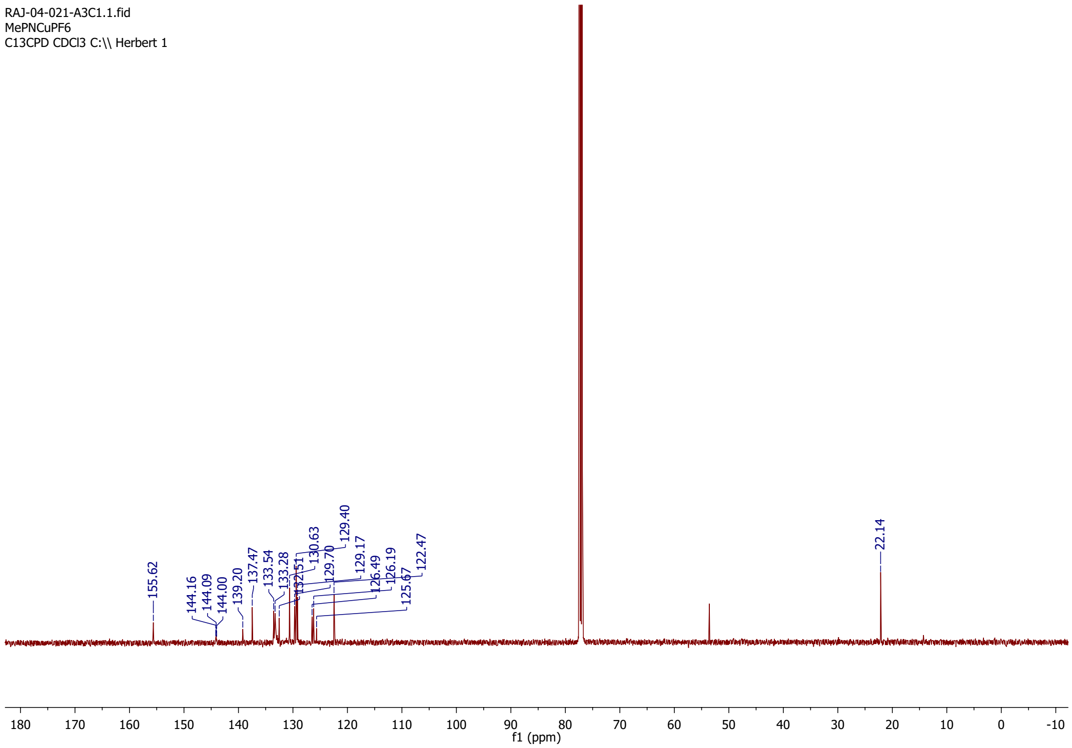


Figure S21. $^{13}C\{^{1}H\}$ NMR (75 MHz, 22°C) spectrum of **$2PF_6$** in $CDCl_3$.

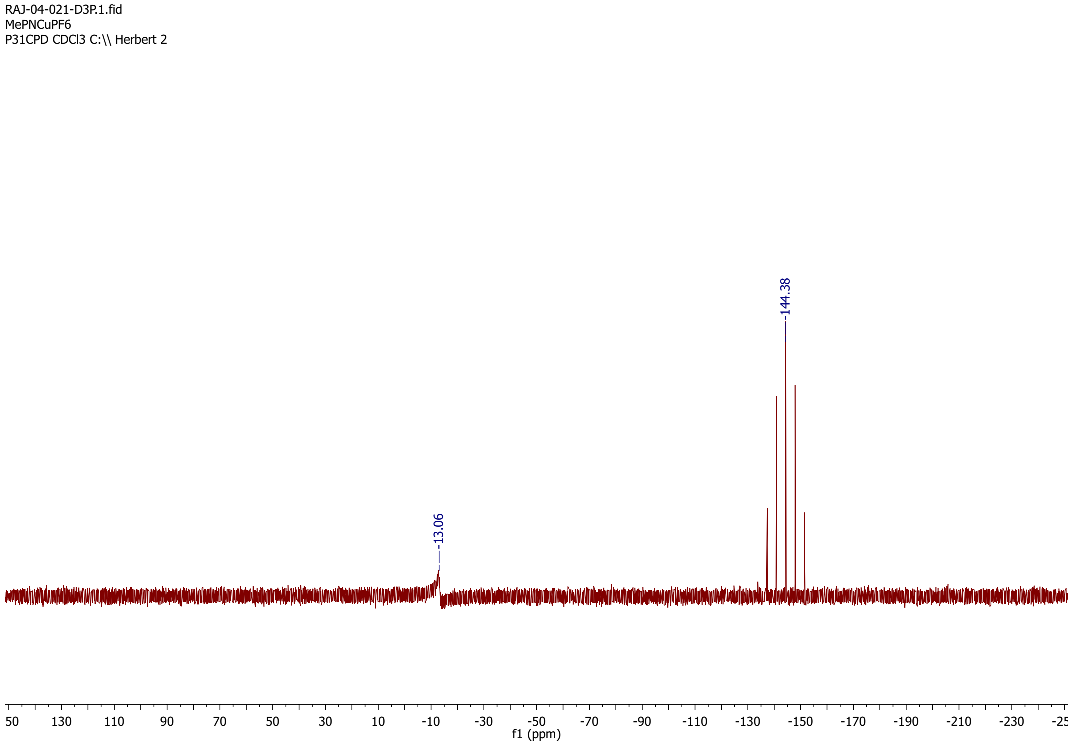


Figure S22. $^{31}P\{^1H\}$ (121 MHz, 22°C) NMR spectrum of **$2PF_6$** in CDCl$_3$.

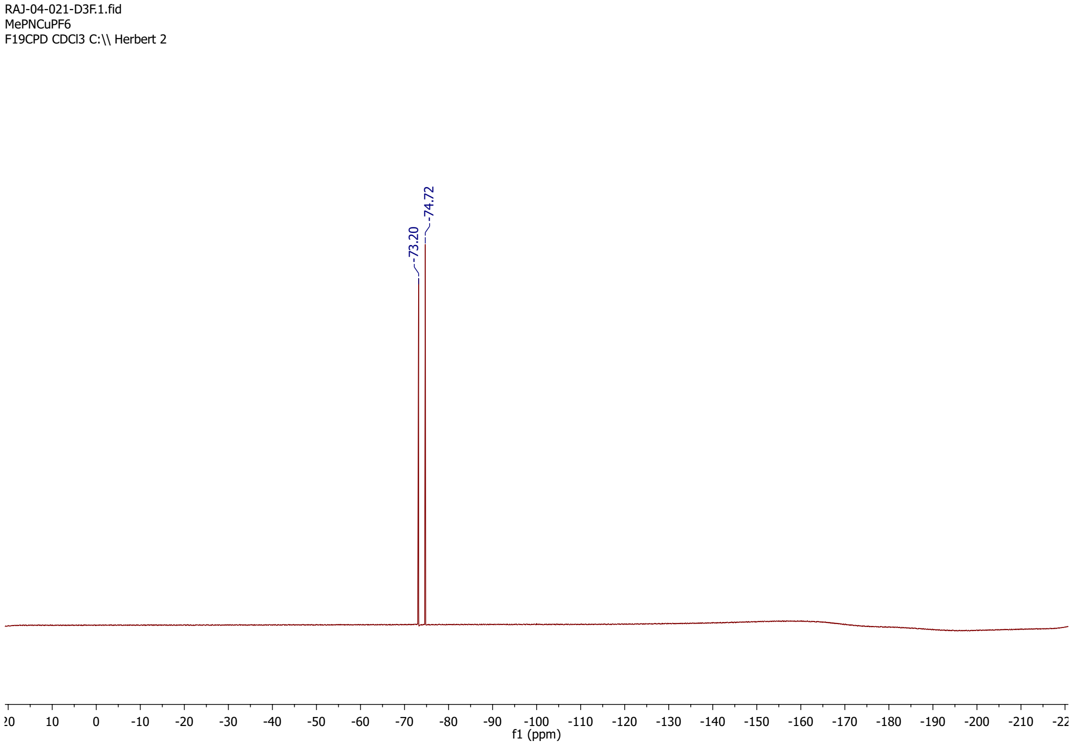


Figure S23. ^{19}F NMR (282 MHz, 22°C) spectrum of **$2PF_6$** in CDCl$_3$.

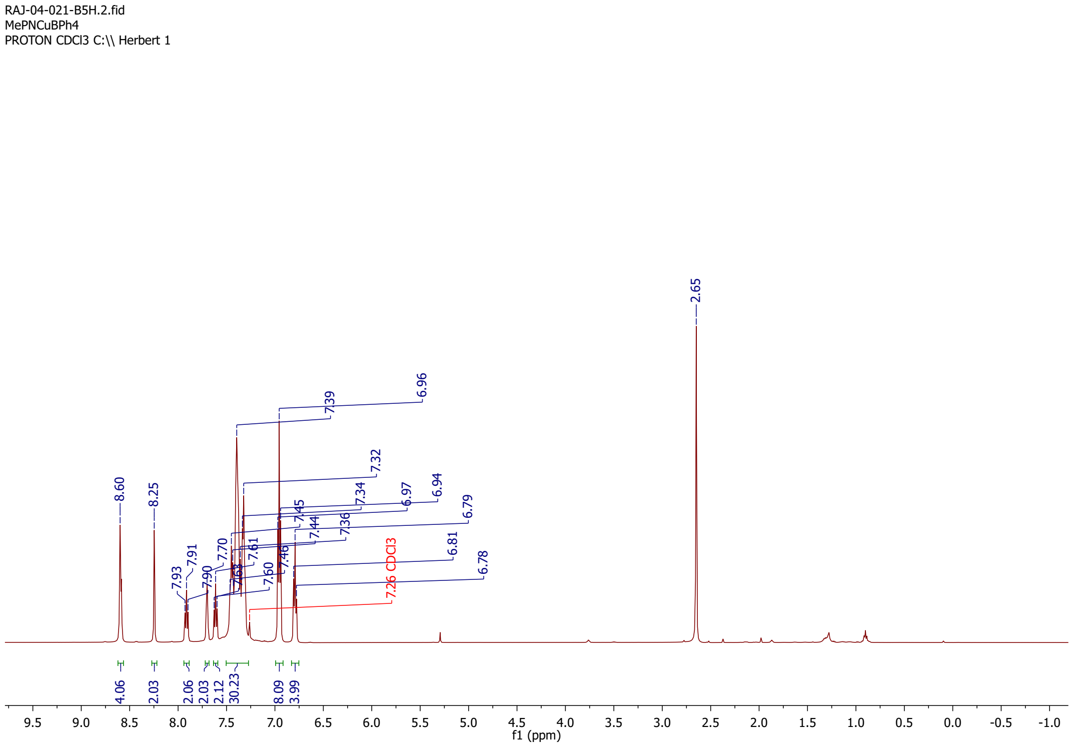


Figure S24. ^{1}H NMR (500 MHz, 22°C) spectrum of **$2BPh_4$** in $CDCl_3$.

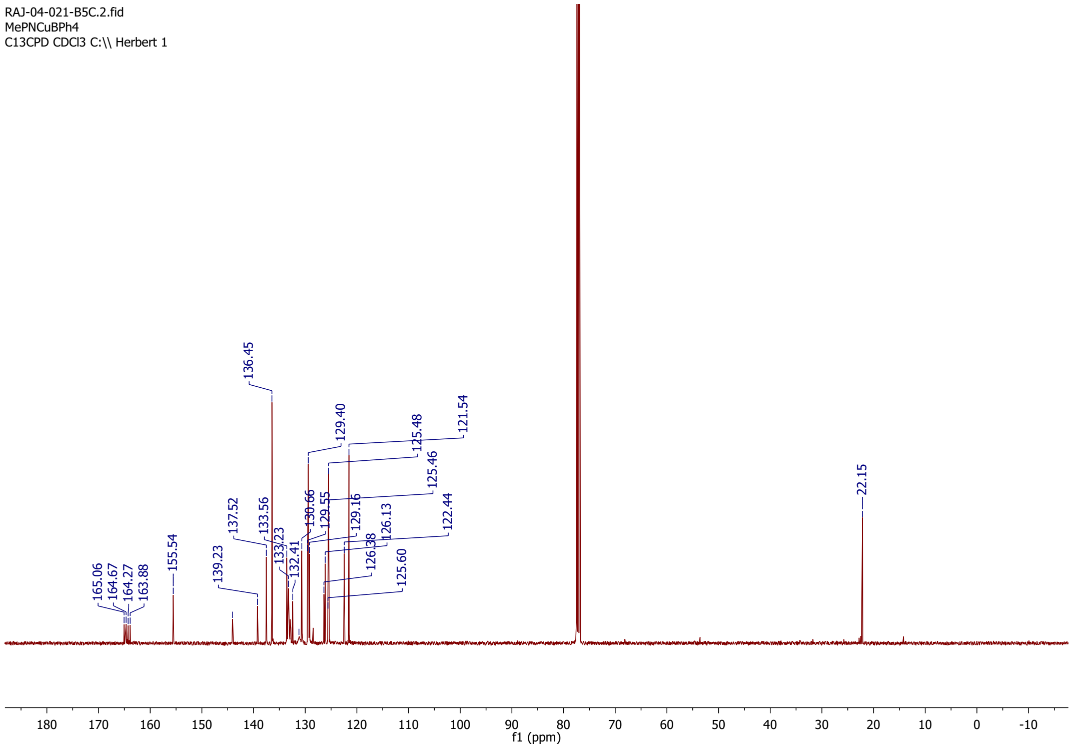


Figure S25. $^{13}C\{^1H\}$ NMR (126 MHz, 22°C) spectrum of **$2BPh_4$** in $CDCl_3$.

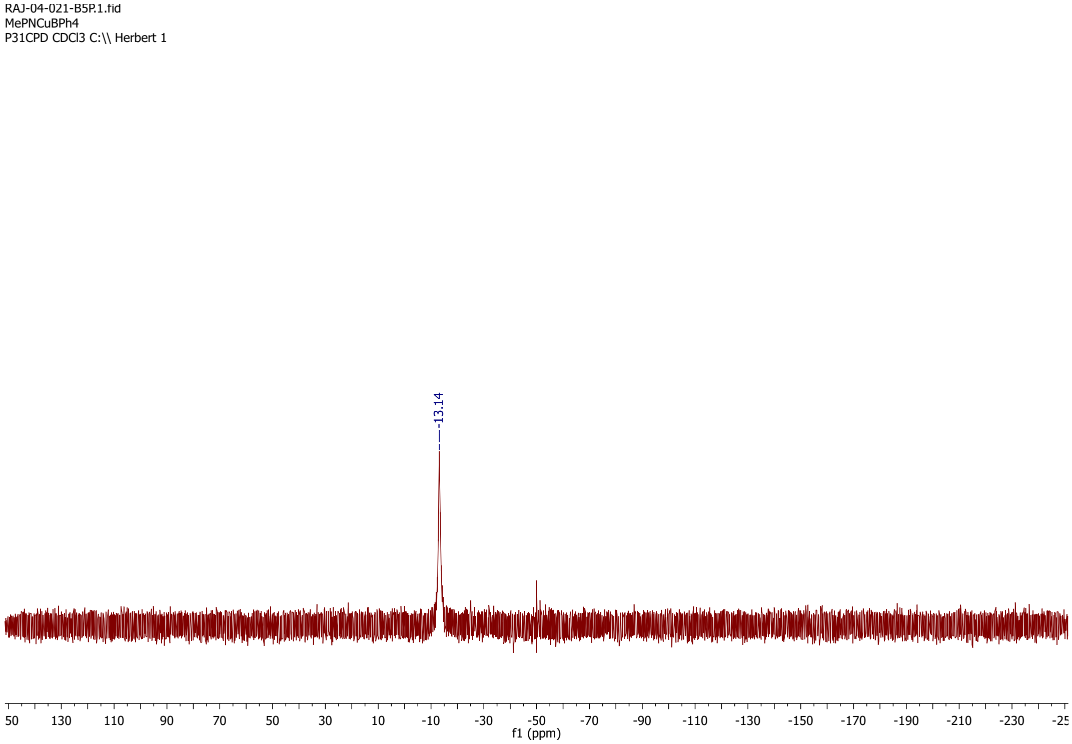


Figure S26. $^{31}P\{^{1}H\}$ (202 MHz, 22°C) NMR spectrum of **$2BPh_4$** in $CDCl_3$.

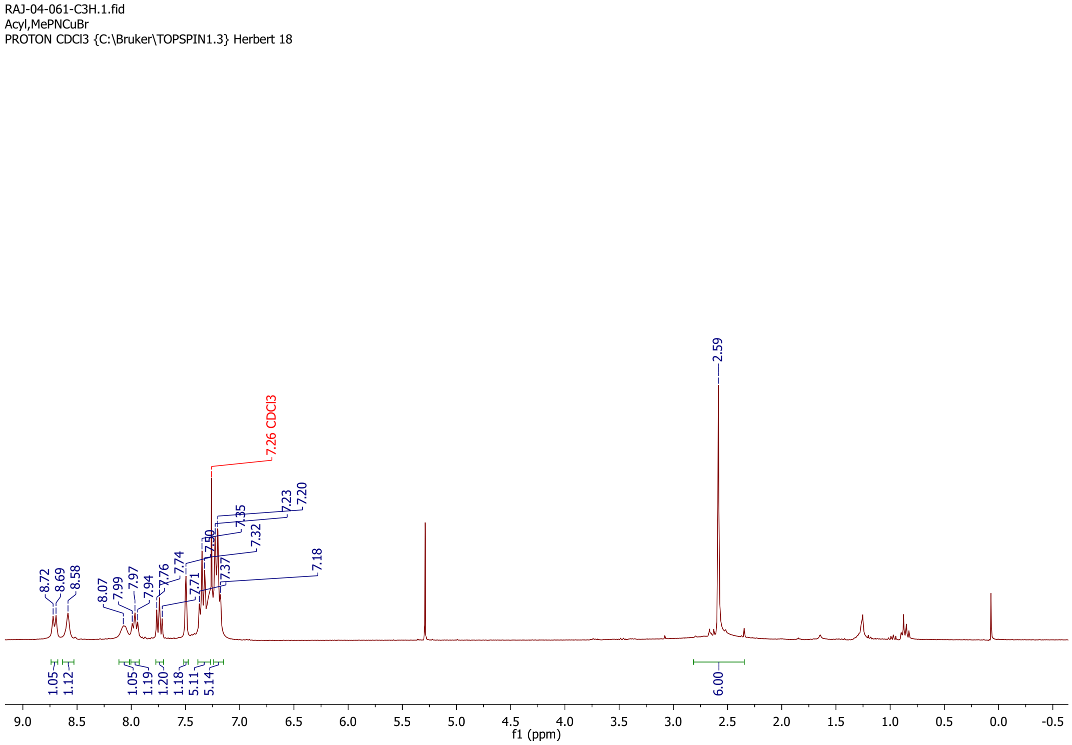


Figure S27. ^{1}H NMR (300 MHz, 22°C) spectrum of $(\mathbf{L3})_2Cu_2(\mu\text{-}Br)_2$ in $CDCl_3$.

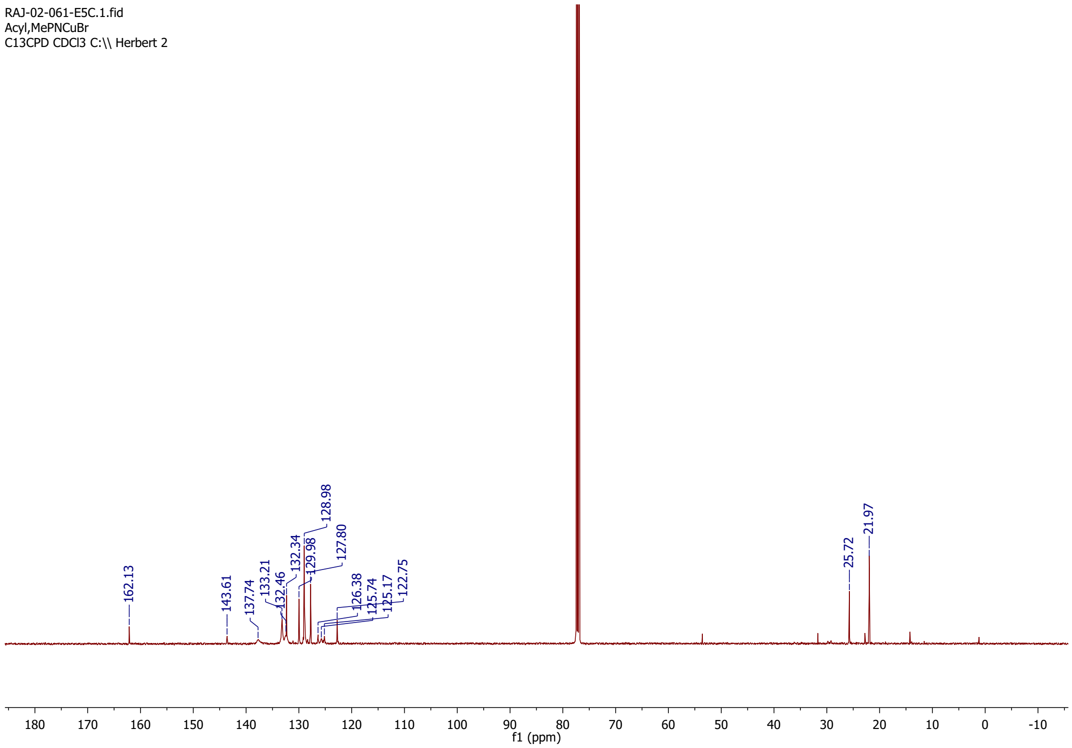


Figure S28. $^{13}C\{^{1}H\}$ NMR (75 MHz, 22°C) spectrum of $(\mathbf{L3})_2Cu_2(\mu\text{-Br})_2$ in $CDCl_3$.

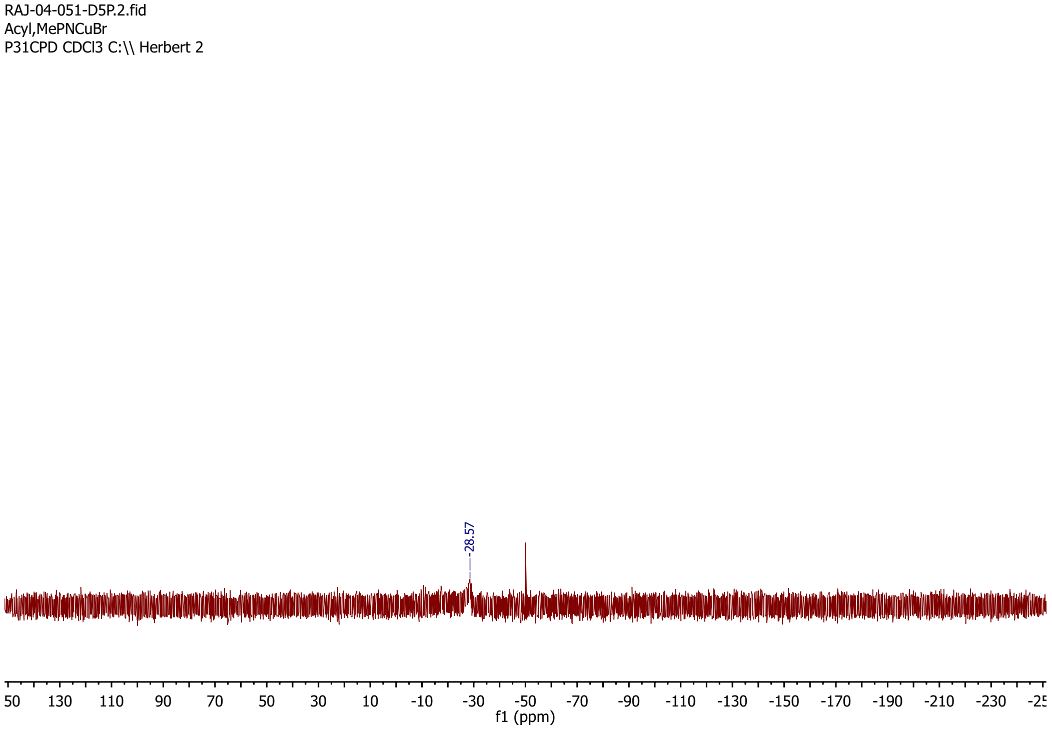


Figure S29. $^{31}P\{^{1}H\}$ (121 MHz, 22°C) NMR spectrum of $(\mathbf{L3})_2Cu_2(\mu\text{-Br})_2$ in $CDCl_3$.

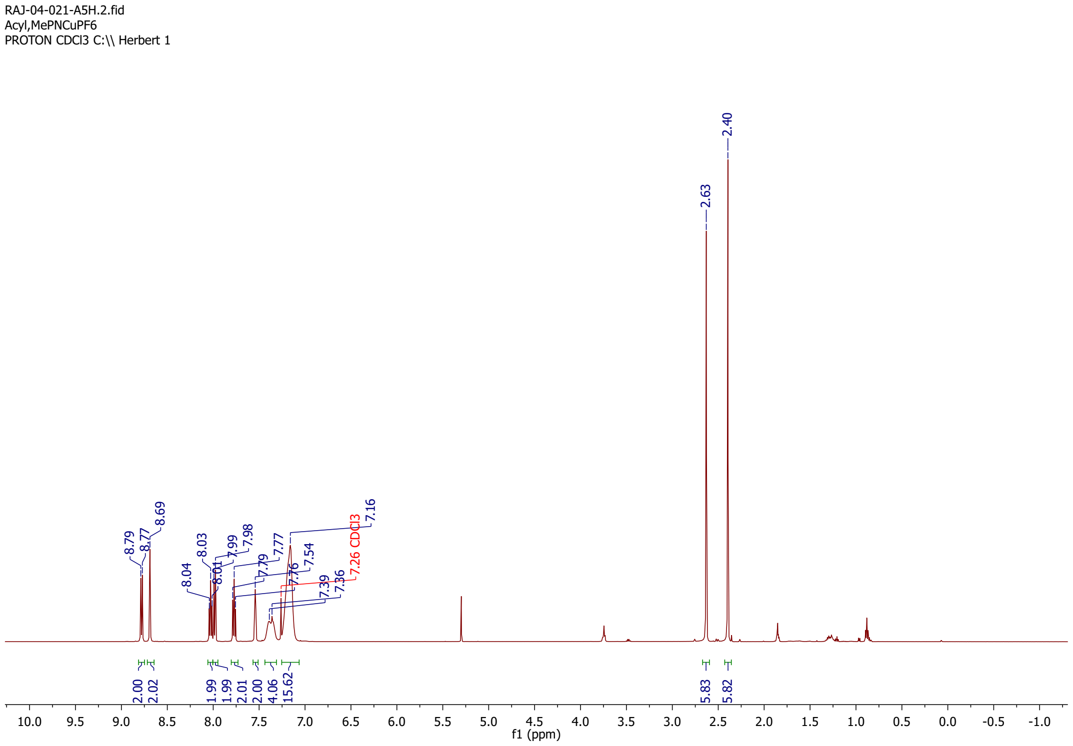


Figure S30. ^{1}H NMR (500 MHz, 22°C) spectrum of **$3PF_6$** in $CDCl_3$.

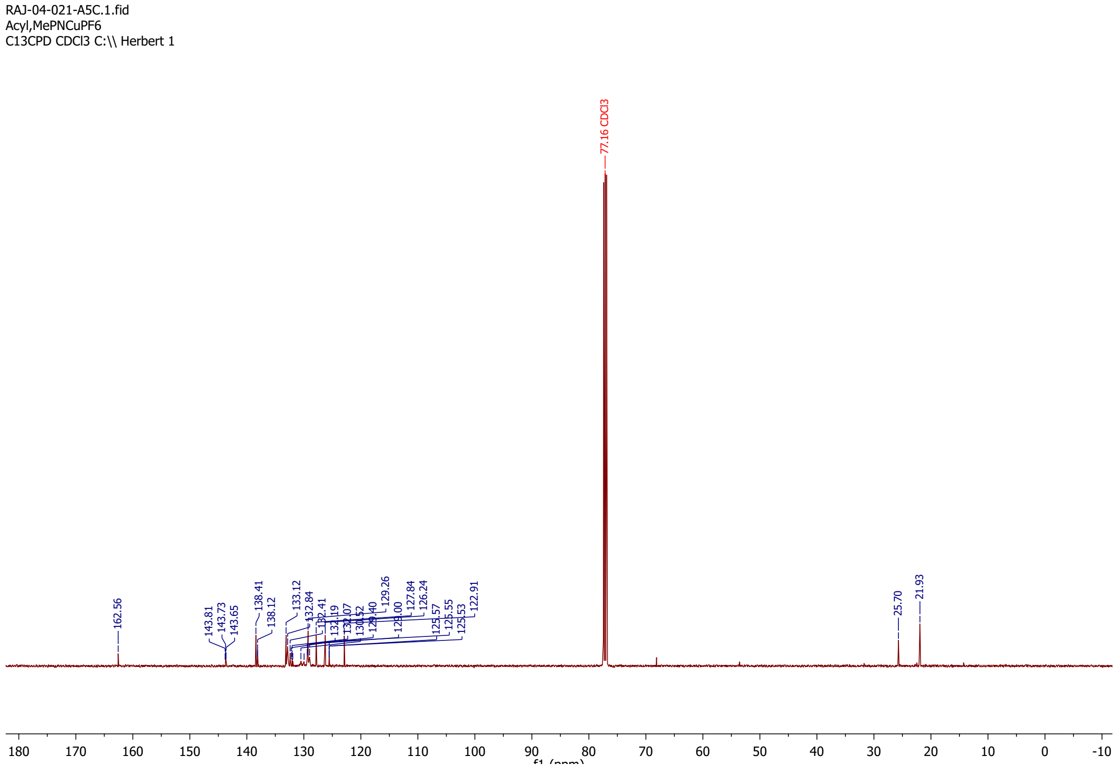


Figure S31. $^{13}C\{^1H\}$ NMR (126 MHz, 22°C) spectrum of **$3PF_6$** in $CDCl_3$.

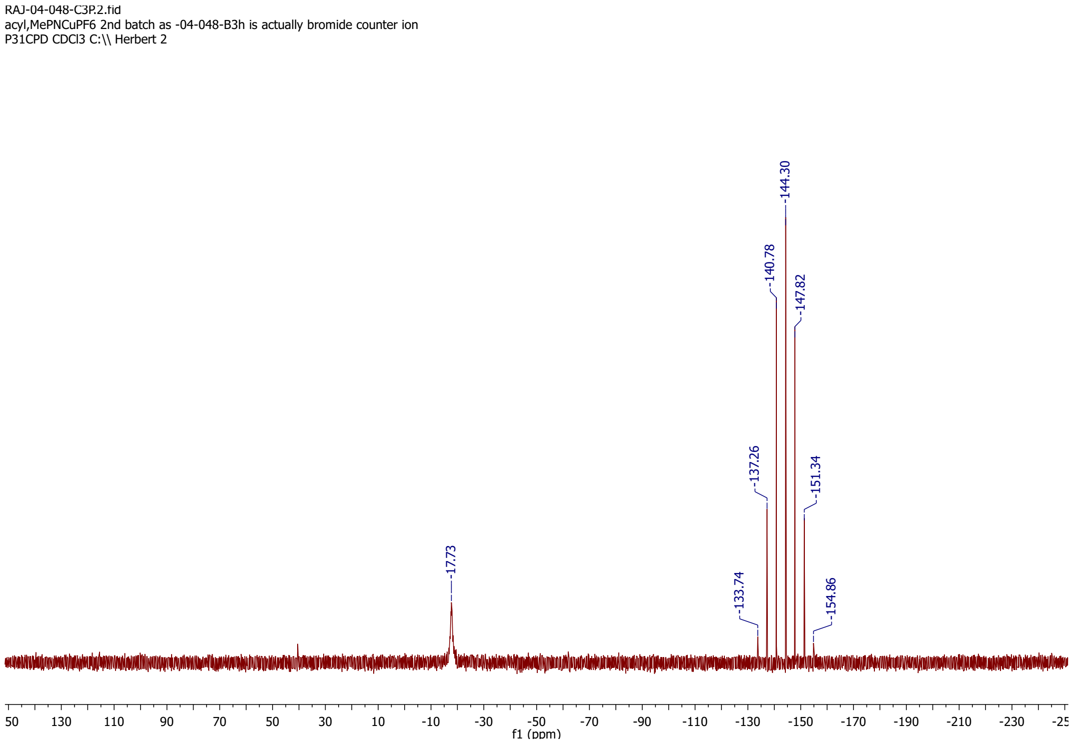


Figure S32. $^{31}P\{^{1}H\}$ (121 MHz, 22°C) NMR spectrum of $\mathbf{3PF_6}$ in $CDCl_3$.

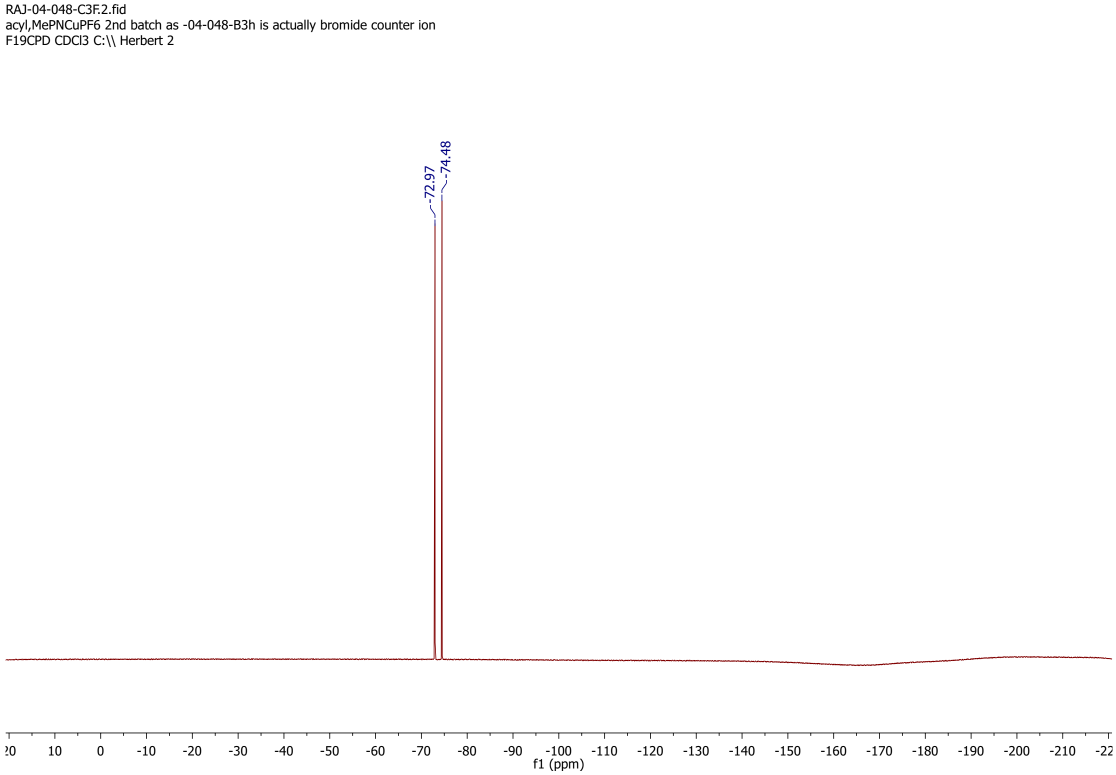


Figure S33. ^{19}F NMR(282 MHz, 22°C) NMR spectrum of $\mathbf{3PF_6}$ in $CDCl_3$.

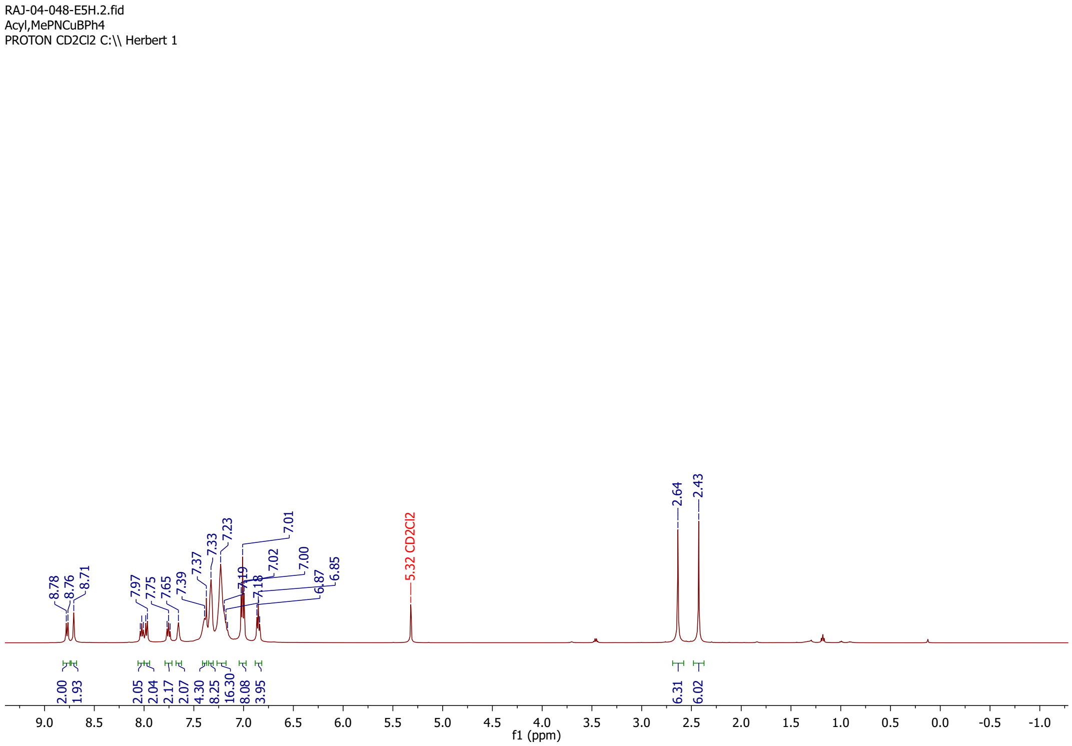


Figure S34. ^{1}H NMR (500 MHz, 22°C) spectrum of **3BPh$_4$** in CDCl$_3$.

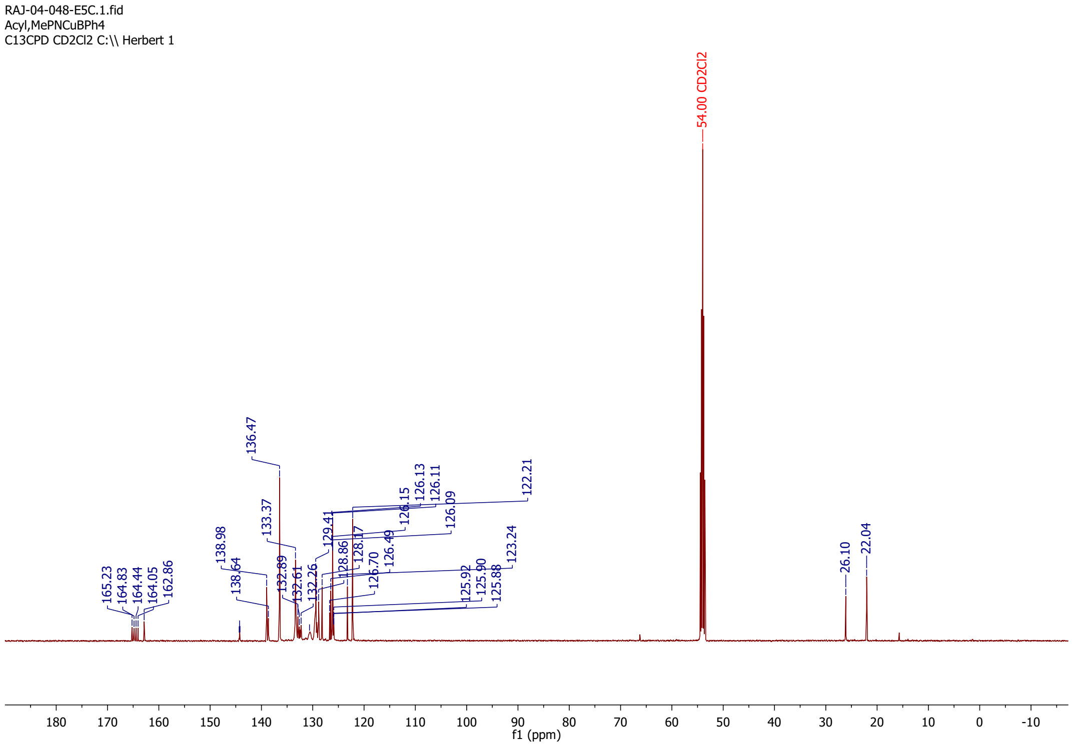


Figure S35. ^{13}C{^{1}H} NMR (126 MHz, 22°C) spectrum of **3BPh$_4$** in CDCl$_3$.

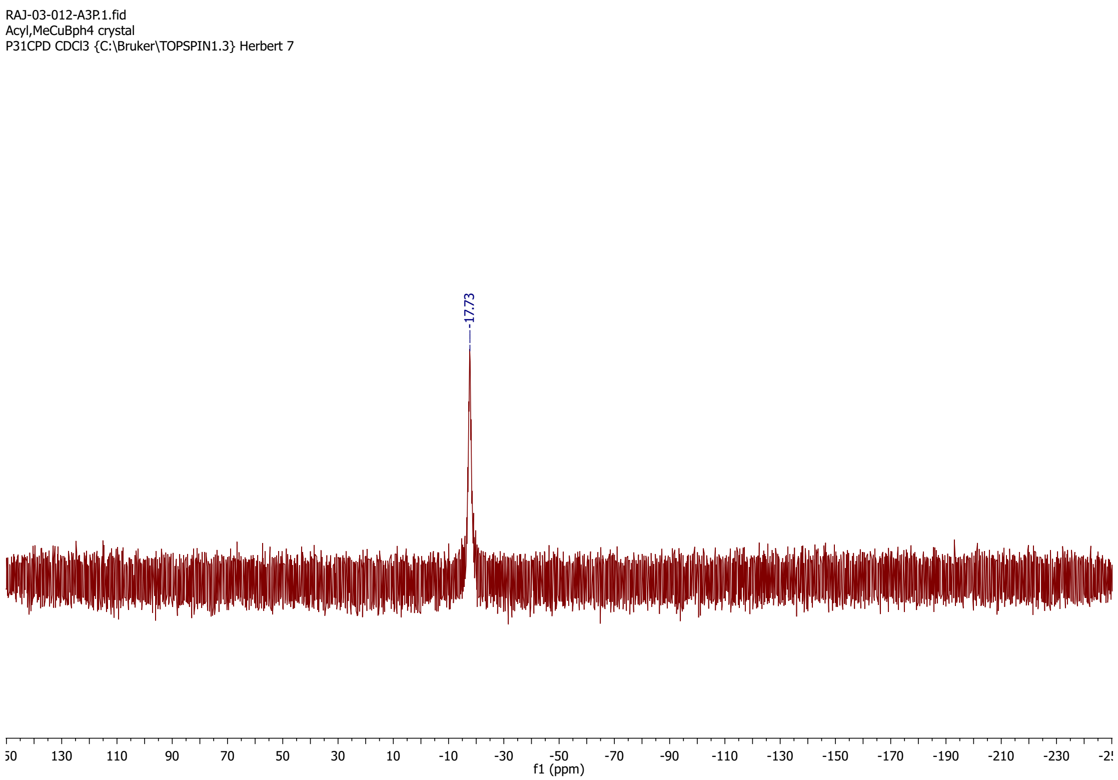
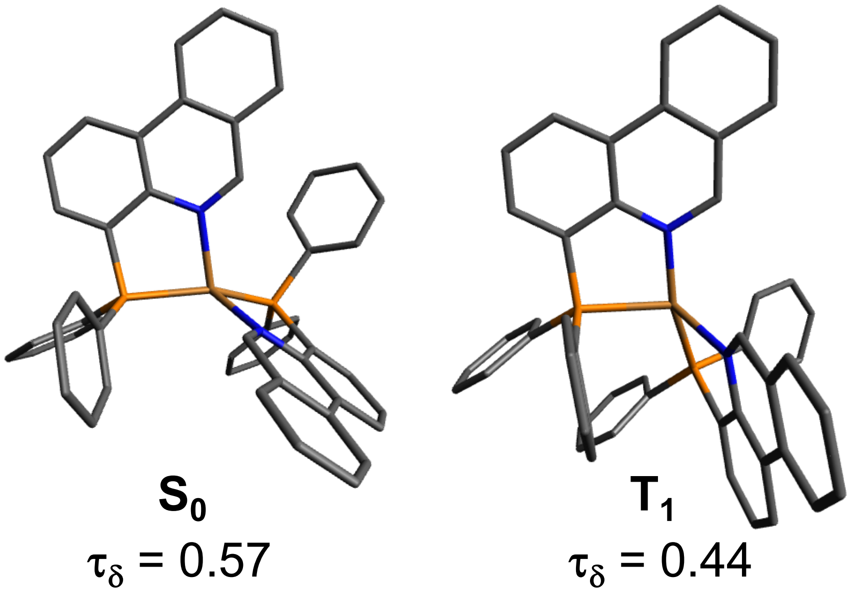


Figure S36. $^{31}P\{^{1}H\}$ (121 MHz, 22°C) NMR spectrum of **$3BPh_4$** in $CDCl_3$.

COMPUTATIONAL DETAILS

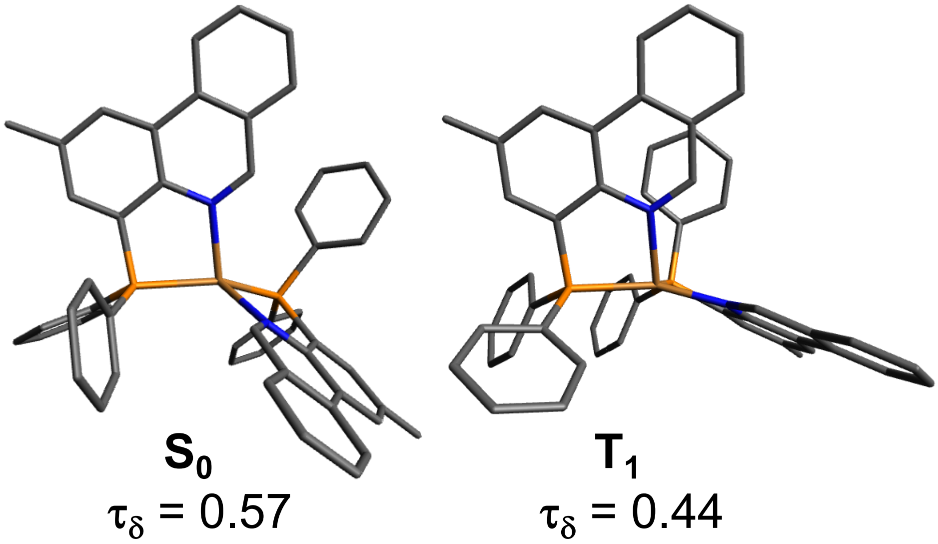
All calculations were carried out using the Gaussian 16, Revision B.01 software package.[9] Optimization of the ground state geometries (S_0) was carried out in the gas phase with the dispersion-corrected CAM-B3LYP functional[10]using Grimme's D3 dispersion and Becke-Johnson damping,[11] and the def2-svp basis set[12] on all atoms. Crystal structure coordinates obtained for the [Cu(*P^N*)$_2$][PF$_6$] analogues were used as starting input. Subsequently, the T_1 state geometries were optimized at the same level of theory with CAM-B3LYP-D3(BJ)/def2-svp, using the optimized S_0 geometries as starting input. Frequency analyses on all optimized structures were performed at the same level of theory to confirm that these are at a minimum on the potential energy surface. All single point calculations, including time-dependent DFT (TDDFT), were carried out with the M06 functional[13] and def2-svp basis set on all atoms. TDDFT analyses on **1X**, **2X**, and **3X** were carried out with the GaussSum software.[14] All structures presented and MOs were generated using the Avogadro molecular editing software,[15] and the fragment contributions to the MOs were analyzed with the QMForge software.[16] The electron-hole density maps for the $S_1 \leftarrow S_0$ transition of the three complexes were extracted from the TDDFT output files and generated using the Multiwfn program.[17] The electron or 'to' and hole or 'from' orbitals are shown in green and blue, respectively. The photophysical parameters: adiabatic energy, $\Delta E(\text{adiab})$; phosphorescence energy, $\Delta E(\text{phos})$; and reorganization energy, λ_T, were calculated as previously reported.[4] The $\Delta E(S_1\text{-}T_1)$ gap is estimated from the difference between the TDDFT energy of the S_1 state, $\Delta E(S_1\text{-TD})$; and the single point energy obtained for the optimized T_1 geometry.



S_0
$\tau_\delta = 0.57$

T_1
$\tau_\delta = 0.44$

Figure S37. Alternate view of DFT optimized structures of (a) S_0 and (b) T_1 states for **1**$^+$.



S_0
$\tau_\delta = 0.57$

T_1
$\tau_\delta = 0.44$

Figure S38. Alternate view of DFT optimized structures of (a) S_0 and (b) T_1 states for **2**$^+$.

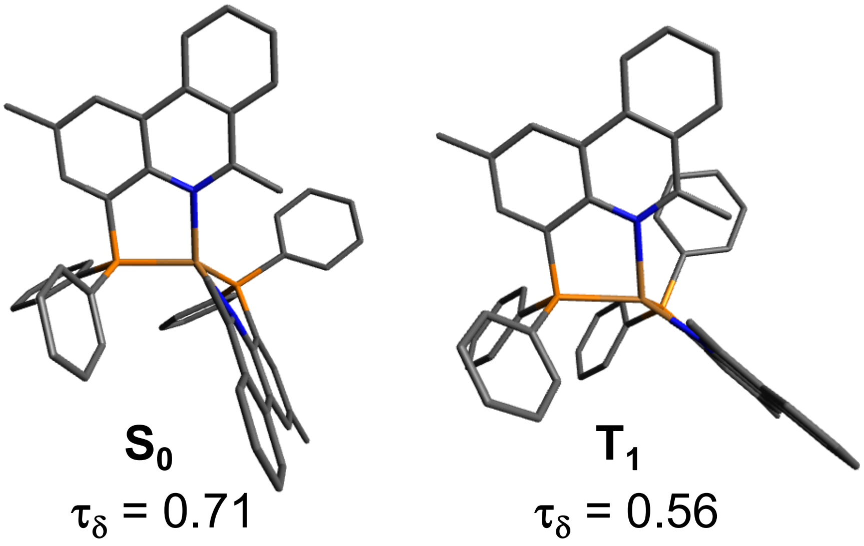


Figure S39. Alternate view of DFT optimized structures of (a) S_0 and (b) T_1 states for **3**$^+$.

Table S3. Selected bond distances [Å] and angles [°] for the DFT-optimized S_0 and T_1 state structures of **1^+**, **2^+**, and **3^+.**

	1^+		**2^+**		**3^+**	
Bond (Å)	**S_0**	**T_1**	**S_0**	**T_1**	**S_0**	**T_1**
Cu-N1	2.104	1.921	2.102	2.097	2.146	2.185
Cu-N2	2.104	2.098	2.102	1.920	2.121	1.945
Cu-P1	2.238	2.297	2.238	2.299	2.244	2.262
Cu-P2	2.237	2.271	2.238	2.272	2.257	2.290
Angle (°)	**S_0**	**T_1**	**S_0**	**T_1**	**S_0**	**T_1**
N1-Cu-N2	109.2	105.6	109.2	105.8	118.5	120.9
N1-Cu-P1	85.7	84.4	115.5	114.7	86.0	84.1
N1-Cu-P2	115.5	159.0	85.8	84.2	114.5	113.2
N2-Cu-P1	115.4	115.0	85.8	84.4	124.2	144.9
N2-Cu-P2	85.7	84.1	115.5	159.0	86.4	85.9
P1-Cu-P2	144.3	108.7	144.1	108.6	130.6	107.7
$\angle(PCuN)_{plane} - (CuP)_{bond}$	154.0°, 153.3°	120.9°, 160.4°	149.2°, 151.8°	123.5°, 161.4°	135.5°, 143.5°	146.2°, 115.4°
$\angle(C_{6b} - N - Cu)$	170.2°, 170.2°	171.4°, 164.1°	170.2°, 170.2°	163.7°, 171.6°	174.2°, 169.8°	174.2°, 169.8°
$\angle(C_1 - C_4 - P)$	177.4°, 177.4°	173.8°, 176.7°	177.6°, 177.6°	176.9°, 174.0°	178.7°, 178.3°	178.7°, 178.3°
θ_{Cu}[a]	85.3	73.0	85.3	72.1	85.5	**80.3**
θ_{Phen}[b]	82.3	71.9	82.6	73.6	86.2	**79.0**

[a] dihedral angle between planes formed by P1-Cu1-N1/P2-Cu1-N2

[b] dihedral angle between planes formed by carbon/nitrogen atoms of the two phenanthridine moieties

Table S4. Geometric indices (τ_δ)[18] of 1X, 2X, and 3X (X = PF_6 or BPh_4) crystal structures, and DFT optimized S_0 and T_1 structures of **1**$^+$, **2**$^+$ and **3**$^+$.

$\boldsymbol{\tau_\delta}$	**PF_6**	**BPh_4**	**S_0**	**T_1**
1X	0.56	0.64	0.57	0.44
2X	0.54	0.64	0.57	0.44
3X	0.70	0.72	0.71	0.56

Table S5. Calculated photophysical parameters for **1**$^+$, **2**$^+$ and **3**$^+$ complexes.

***E* (eV)**	**1**$^+$	**2**$^+$	**3**$^+$
Δ*E* (S_1-TD)[a]	3.110	3.172	3.158
Δ*E* (S_1-T_1)	0.863	0.901	0.721
Δ*E*(adiab)	2.247	2.272	2.436
Δ*E*(phos)	1.444	1.477	1.691
$\boldsymbol{\lambda_T}$	0.803	0.795	0.745

[a] Energy of the S_1 state estimated by TDDFT

Table S6. First four TD-DFT calculated electronic transitions for **1**$^{+}$, **2**$^{+}$ and **3**$^{+}$ with the corresponding oscillators strengths and MO characters (>10% contribution).

Complex	State	Calc. $\lambda_{abs.}$ (nm)	Oscillator strength	MO character	% Contribution
1^{+}	S_1	398.70	0.0046	HOMO → LUMO	49%
				HOMO-1 → LUMO+1	47%
	S_2	398.13	0.0011	HOMO-1 → LUMO	54%
				HOMO → LUMO+1	41%
	S_3	376.85	0.0494	HOMO-1 → LUMO+1	50%
				HOMO → LUMO	48%
	S_4	375.85	0.0142	HOMO → LUMO+1	55%
				HOMO-1 → LUMO	42%
2^{+}	S_1	390.87	0.0049	HOMO → LUMO	49%
				HOMO-1 → LUMO+1	47%
	S_2	390.30	0.0013	HOMO-1 → LUMO	55%
				HOMO → LUMO+1	41%
	S_3	369.80	0.528	HOMO-1 → LUMO+1	51%
				HOMO → LUMO	47%
	S_4	368.87	0.0132	HOMO → LUMO+1	55%
				HOMO-1 → LUMO	42%
3^{+}	S_1	392.65	0.0180	HOMO → LUMO	85%
	S_2	387.03	0.0148	HOMO → LUMO+1	84%
				HOMO-1 → LUMO+1	10%
	S_3	358.16	0.0299	HOMO-1 → LUMO+1	58%
				HOMO-1 → LUMO	29%
	S_4	357.43	0.0100	HOMO-1 → LUMO	58%
				HOMO-1 → LUMO+1	27%

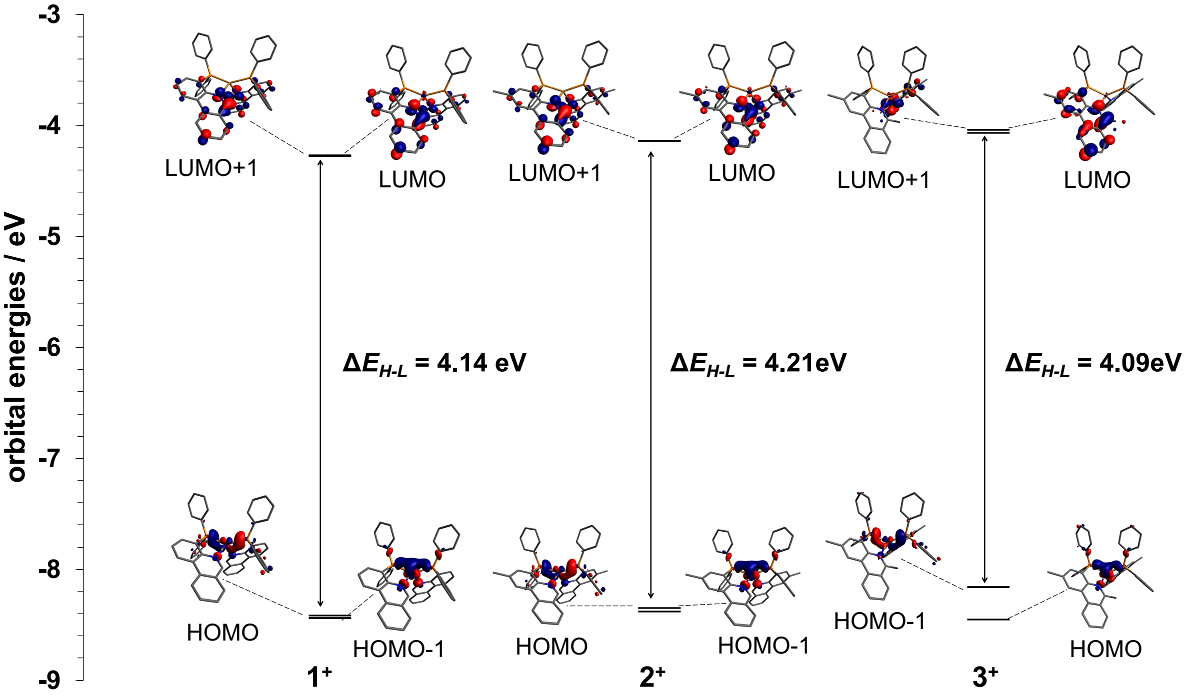


Figure S40. TD-DFT orbital energies, HOMO-LUMO gap ($\Delta E_{H\text{-}L}$), and frontier molecular orbital (MO; isosurface value = 0.05) diagrams of **1**$^+$, **2**$^+$, and **3**$^+$.

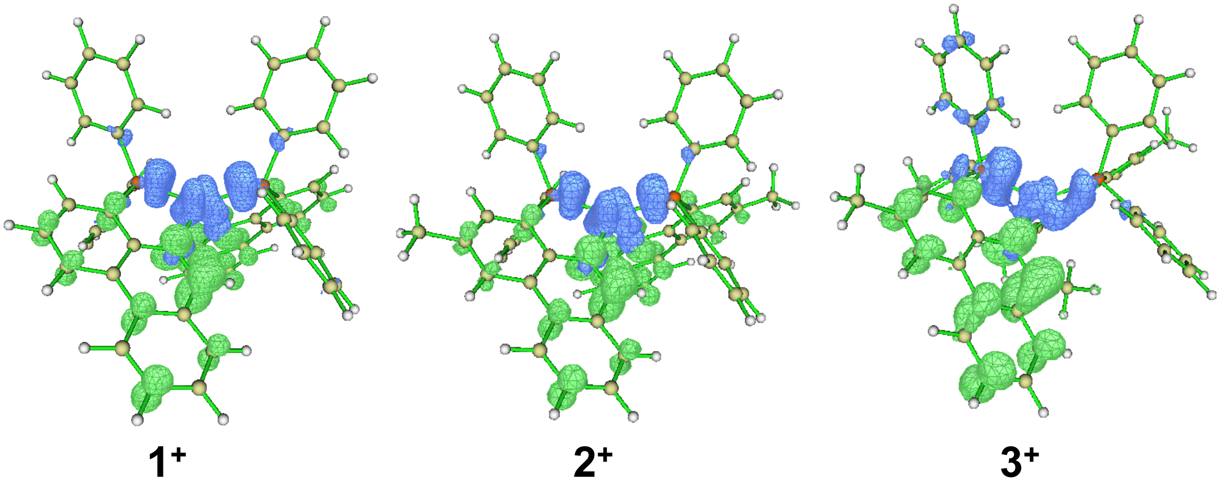


Figure S41. Electron-hole density maps (green = electron, blue = hole; isosurface value = 0.002) for the $S_1 \leftarrow S_0$ transition of **1**$^+$, **2**$^+$ and **3**$^+$.

Table S7. Fragment contributions to the two highest occupied MOs and two lowest unoccupied MOs of **1**$^+$. Fragment contributions >10% are in bold.

Fragment	HOMO-1	HOMO	LUMO	LUMO+1
Cu	**36.2**	**26.6**	0.9	0.5
P_1	9.0	**13.5**	0.4	0.5
Ph_{1a}	7.8	5.6	0.7	0.4
Ph_{1b}	2.0	8.4	2.0	1.3
$(HC{=}N)_1$ [a]	5.2	3.2	**19.8**	**15.7**
$(Ar_{phenan})_1$ [b]	7.8	6.2	**33.7**	**24.8**
P_2	9.1	**13.4**	0.4	0.5
Ph_{2a}	7.8	5.5	0.6	0.5
Ph_{2b}	2.0	8.3	2.2	1.2
$(HC{=}N)_2$ [a]	5.3	3.2	**14.5**	**20.9**
$(Ar_{phenan})_2$ [b]	7.9	6.1	**24.8**	**33.6**

[a] $(HC{=}N)_n$ refers to the imine-bridge fragment of phenanthridine.

[b] $(Ar_{phenan})_n$ refers to the biphenyl fragment of phenanthridine.

Table S8. Fragment contributions to the two highest occupied MOs and two lowest unoccupied MOs of **2**$^+$. Fragment contributions >10% are in bold.

Fragment	HOMO-1	HOMO	LUMO	LUMO+1
Cu	**36.2**	**26.7**	0.9	0.5
P_1	9.0	**13.4**	0.4	0.6
Ph_{1a}	7.7	5.4	0.7	0.5
Ph_{1b}	1.9	8.2	2.2	1.2
$(HC{=}N)_1$[a]	5.3	3.3	**17.1**	**18.3**
$(Ar_{phenan})_1$[b]	8.0	6.2	**28.9**	**28.8**
Me_1[c]	0.1	0.1	0.3	0.4
P_2	9.0	**13.4**	0.4	0.6
Ph_{2a}	7.7	5.4	0.7	0.5
Ph_{2b}	1.9	8.2	2.2	1.2
$(HC{=}N)_2$[a]	5.3	3.3	**17.1**	**18.3**
$(Ar_{phenan})_2$[b]	8.0	6.2	**28.9**	**28.9**
Me_2[c]	0.1	0.1	0.3	0.45

[a] $(HC{=}N)_n$ refers to the imine-bridge fragment of phenanthridine.

[b] $(Ar_{phenan})_n$ refers to the biphenyl fragment of phenanthridine.

[c] Me_{na} refers to the methyl substituent at the C_2-position of phenanthridine.

Table S9. Fragment contributions to the two highest occupied MOs and two lowest unoccupied MOs of **3**$^+$. Fragment contributions >10% are in bold.

Fragment	HOMO-1	HOMO	LUMO	LUMO+1
Cu	**36.4**	**25.2**	0.9	0.8
P_1	7.9	**13.9**	0.3	0.4
$(C{=}N)_1$ [a]	5.7	2.2	0.5	**32.5**
$(Ar_{phenan})_1$ [b]	7.8	5.3	0.5	**54.5**
Ph_{1a}	8.0	5.6	0.1	0.9
Ph_{1b}	2.1	8.6	0.5	1.0
Me_{1a} [c]	0.1	0.1	0.0	0.7
Me_{1b} [d]	1.5	0.3	1.4	3.9
P_2	8.4	**15.3**	0.4	0.4
$(C{=}N)_2$ [a]	4.5	2.8	**33.2**	0.3
$(Ar_{phenan})_2$ [b]	6.0	6.7	**55.2**	1.0
Ph_{2a}	8.2	5.9	1.1	0.4
Ph_{2b}	1.5	7.5	1.2	1.6
Me_{2a} [c]	0.1	0.1	0.7	0.0
Me_{2b} [d]	1.9	0.5	4.2	1.5

[a] $(C{=}N)_n$ refers to the imine-bridge fragment of phenanthridine.

[b] $(Ar_{phenan})_n$ refers to the biphenyl fragment of phenanthridine.

[c] Me_{na} refers to the methyl substituent at the C_2-position of phenanthridine.

[d] Me_{nb} refers to the methyl substituent at the C_6-position of phenanthridine.

Energies and Reaction Coordinates

1$^+$ (S_0)

```
HF = -4356.9073317 hartrees
Zero-point correction=                           0.726635
(Hartree/Particle)
Thermal correction to Gibbs Free Energy=         0.643816
Sum of electronic and zero-point Energies=          -4356.180696
Sum of electronic and thermal Free Energies=        -4356.263515
```

```
                        Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1         29           0       -0.000323   -0.001770    0.293419
      2         15           0       -1.424963    1.580375    0.981777
      3          6           0       -1.703381    1.100502    3.680063
      4          1           0       -1.300317    0.117489    3.423255
      5          6           0       -1.866131    2.064262    2.678354
      6          6           0       -2.045838    1.392564    4.995802
      7          1           0       -1.919225    0.634959    5.771636
      8          6           0       -2.691484    3.621264    4.332030
      9          1           0       -3.072313    4.611703    4.588600
     10          6           0       -2.539580    2.654010    5.322518
     11          1           0       -2.801947    2.886585    6.356439
     12          6           0       -2.357669    3.329636    3.012114
     13          1           0       -2.472536    4.094051    2.240865
     14          7           0       -1.579286   -0.672258   -0.924114
     15          6           0       -2.848194   -0.185388   -0.644317
     16          6           0       -1.434762   -1.646843   -1.767167
     17          1           0       -0.417031   -2.003523   -1.953867
     18          6           0       -2.519097   -2.286778   -2.442835
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     20          6           0       -3.833474   -1.840780   -2.181472
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     28          1           0       -5.926278   -2.172715   -2.666416
     29          6           0       -3.340659   -3.969482   -3.964511
     30          1           0       -3.167649   -4.795993   -4.655595
     31          6           0       -4.652785   -3.527765   -3.713200
     32          1           0       -5.490284   -4.016509   -4.214730
     33          6           0       -1.150038    3.141794    0.074088
     34          6           0       -0.014227    3.890526    0.414090
     35          1           0        0.610238    3.579953    1.255880
     36          6           0        0.330834    5.020269   -0.316641
     37          1           0        1.214894    5.597429   -0.039149
     38          6           0       -1.922790    3.537606   -1.019889
     39          1           0       -2.806837    2.964487   -1.302933
     40          6           0       -1.568217    4.666610   -1.758644
     41          1           0       -2.181641    4.968804   -2.609856
     42          6           0       -0.444701    5.408961   -1.409270
     43          1           0       -0.171315    6.294438   -1.986449
     44          6           0       -2.971813    0.895130    0.271172
     45          6           0       -4.227189    1.373854    0.594894
     46          1           0       -4.328690    2.189557    1.313268
     47         15           0        1.428066   -1.581852    0.978015
     48          6           0        1.708787   -1.105715    3.676705
     49          1           0        1.303227   -0.123184    3.422002
     50          6           0        1.872350   -2.067496    2.673239
     51          6           0        2.053589   -1.399150    4.991533
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    54          1           0        3.086677   -4.615341    4.577792
    55          6           0        2.550549   -2.660017    5.315560
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    57          6           0        2.367139   -3.332324    3.004313
    58          1           0        2.482683   -4.095239    2.231679
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    61          6           0        1.428114    1.644862   -1.770967
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    63          6           0        2.510339    2.287182   -2.447773
    64          6           0        3.996771    0.747591   -1.250288
    65          6           0        3.825967    1.844108   -2.187734
    66          6           0        5.258166    0.221524   -0.903442
    67          1           0        6.159186    0.639242   -1.351422
    68          6           0        2.271680    3.354205   -3.338541
    69          1           0        1.243999    3.681769   -3.508612
    70          6           0        5.374989   -0.811054    0.001593
    71          1           0        6.361295   -1.197312    0.263666
    72          6           0        4.888458    2.493329   -2.847812
    73          1           0        5.917546    2.180694   -2.674742
    74          6           0        3.326661    3.971767   -3.970196
    75          1           0        3.151123    4.797917   -4.661076
    76          6           0        4.640015    3.532967   -3.720203
    77          1           0        5.475929    4.023591   -4.222542
    78          6           0        1.153696   -3.142321    0.068484
    79          6           0        0.020738   -3.894382    0.410637
    80          1           0       -0.601485   -3.587242    1.255340
    81          6           0       -0.324338   -5.023159   -0.321588
    82          1           0       -1.206123   -5.602967   -0.042380
    83          6           0        1.923566   -3.533855   -1.029062
    84          1           0        2.805394   -2.958129   -1.313748
    85          6           0        1.568954   -4.661893   -1.769270
    86          1           0        2.180132   -4.960731   -2.623278
    87          6           0        0.448275   -5.407548   -1.417811
    88          1           0        0.174892   -6.292296   -1.996111
    89          6           0        2.972789   -0.893656    0.265760
    90          6           0        4.229485   -1.369890    0.587982
    91          1           0        4.333477   -2.185473    1.306128
```

1^+ (T_1)

```
HF = -4356.8225394 hartrees
Zero-point correction=                           0.723727
(Hartree/Particle)
Thermal correction to Gibbs Free Energy=         0.640649
Sum of electronic and zero-point Energies=          -4356.098813
Sum of electronic and thermal Free Energies=        -4356.181890

                         Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1         29           0       -0.212856    0.260850    0.586020
```

2	15	0	-0.101624	1.462900	-1.368231
3	6	0	1.729102	3.488725	-1.080677
4	1	0	1.337808	3.553310	-0.062660
5	6	0	1.213019	2.538138	-1.971114
6	6	0	2.739328	4.348179	-1.489943
7	1	0	3.137644	5.087815	-0.793552
8	6	0	2.742372	3.311777	-3.671077
9	1	0	3.135659	3.246918	-4.687312
10	6	0	3.248331	4.258645	-2.784910
11	1	0	4.044321	4.933760	-3.105181
12	6	0	1.724534	2.450913	-3.269240
13	1	0	1.324888	1.715973	-3.969872
14	7	0	-2.048276	0.826179	0.608131
15	6	0	-2.492918	1.842692	-0.188983
16	6	0	-2.881197	0.283973	1.562799
17	1	0	-2.486035	-0.549578	2.147297
18	6	0	-4.173898	0.780106	1.799107
19	6	0	-3.791946	2.409349	-0.035012
20	6	0	-4.672685	1.859783	1.006398
21	6	0	-4.145850	3.466375	-0.872070
22	1	0	-5.128157	3.924896	-0.757908
23	6	0	-5.010544	0.227049	2.805466
24	1	0	-4.628964	-0.597606	3.412215
25	6	0	-3.284999	3.978034	-1.851025
26	1	0	-3.606789	4.811970	-2.475844
27	6	0	-5.964887	2.334017	1.249132
28	1	0	-6.362614	3.156250	0.653504
29	6	0	-6.279701	0.718991	3.017849
30	1	0	-6.908813	0.282505	3.796487
31	6	0	-6.767307	1.780299	2.238669
32	1	0	-7.771954	2.170288	2.408062
33	6	0	-0.339601	0.080545	-2.526400
34	6	0	0.719044	-0.804461	-2.772251
35	1	0	1.713911	-0.590583	-2.377331
36	6	0	0.508724	-1.964319	-3.507334
37	1	0	1.339508	-2.647892	-3.691786
38	6	0	-1.611703	-0.216097	-3.024150
39	1	0	-2.442478	0.464901	-2.830751
40	6	0	-1.818261	-1.381868	-3.758007
41	1	0	-2.814008	-1.605741	-4.145329
42	6	0	-0.763536	-2.258276	-3.996464
43	1	0	-0.931846	-3.175373	-4.564039
44	6	0	-1.640853	2.351002	-1.203837
45	6	0	-2.030662	3.419166	-2.020015
46	1	0	-1.347734	3.800904	-2.781978
47	15	0	1.898632	-0.113991	1.332131
48	6	0	3.862645	0.654676	-0.500487
49	1	0	3.458545	-0.120647	-1.153169
50	6	0	3.347951	0.830271	0.789592
51	6	0	4.900643	1.457820	-0.956060
52	1	0	5.294370	1.313569	-1.963450
53	6	0	4.919411	2.631384	1.150034
54	1	0	5.333914	3.403926	1.800330
55	6	0	5.431174	2.446960	-0.130979
56	1	0	6.247376	3.076892	-0.489450
57	6	0	3.878891	1.829827	1.611108
58	1	0	3.485253	1.981309	2.617831

```
     59          7           0       -0.266206   -1.822039    0.342917
     60          6           0        0.944941   -2.493683    0.280701
     61          6           0       -1.348361   -2.389438   -0.097251
     62          1           0       -2.271612   -1.803273   -0.048235
     63          6           0       -1.383864   -3.705926   -0.645649
     64          6           0        1.032475   -3.805526   -0.235766
     65          6           0       -0.178624   -4.438891   -0.726226
     66          6           0        2.298550   -4.424329   -0.276212
     67          1           0        2.390797   -5.438822   -0.662587
     68          6           0       -2.593348   -4.251223   -1.123321
     69          1           0       -3.508592   -3.660103   -1.049705
     70          6           0        3.430069   -3.766863    0.157194
     71          1           0        4.400391   -4.263644    0.112026
     72          6           0       -0.221022   -5.727052   -1.294063
     73          1           0        0.685861   -6.325348   -1.373515
     74          6           0       -2.607920   -5.510994   -1.676254
     75          1           0       -3.539137   -5.941043   -2.048162
     76          6           0       -1.411847   -6.247622   -1.758603
     77          1           0       -1.425751   -7.247819   -2.195901
     78          6           0        1.942011   -0.190040    3.145775
     79          6           0        0.817378    0.245813    3.852812
     80          1           0       -0.050381    0.643604    3.319020
     81          6           0        0.797193    0.180899    5.243811
     82          1           0       -0.083105    0.524127    5.789985
     83          6           0        3.047956   -0.692028    3.842034
     84          1           0        3.933369   -1.032459    3.301510
     85          6           0        3.024282   -0.754113    5.229384
     86          1           0        3.888032   -1.144973    5.770255
     87          6           0        1.898996   -0.318901    5.930210
     88          1           0        1.884533   -0.369898    7.020632
     89          6           0        2.115936   -1.819038    0.717147
     90          6           0        3.341059   -2.456346    0.648596
     91          1           0        4.247967   -1.935629    0.961496
```

2^+ (S_0)

```
HF = -4435.4439075 hartrees
Zero-point correction=                           0.781268
(Hartree/Particle)
Thermal correction to Gibbs Free Energy=         0.693458
Sum of electronic and zero-point Energies=          -4434.662640
Sum of electronic and thermal Free Energies=        -4434.750450

                         Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1         29           0        0.000000    0.000005    0.274723
      2         15           0        1.672241   -1.318644    0.964243
      3         15           0       -1.672249    1.318655    0.964222
      4          7           0       -1.440128   -0.928098   -0.943276
      5          7           0        1.440141    0.928096   -0.943273
      6          6           0       -2.191360    1.727176    2.658853
      7          6           0        2.771433    0.663072   -0.661150
      8          6           0       -3.079772    0.378415    0.256009
```

9	6	0	3.079772	-0.378410	0.256036
10	6	0	3.816955	1.402369	-1.256022
11	6	0	-1.667104	2.900809	0.050649
12	6	0	1.135732	1.862882	-1.789018
13	1	0	0.073274	2.043946	-1.978902
14	6	0	-2.771423	-0.663073	-0.661166
15	6	0	2.100996	2.672912	-2.462910
16	6	0	3.471055	2.453423	-2.196971
17	6	0	-1.135710	-1.862896	-1.789004
18	1	0	-0.073249	-2.043966	-1.978870
19	6	0	-0.677969	3.835487	0.388369
20	1	0	-0.011608	3.641436	1.232935
21	6	0	2.191339	-1.727156	2.658880
22	6	0	5.454861	0.098894	0.005763
23	6	0	5.146814	1.093529	-0.902496
24	1	0	5.963433	1.658618	-1.351808
25	6	0	2.634993	4.466242	-3.987173
26	1	0	2.328273	5.250683	-4.680917
27	6	0	-2.891999	2.891393	2.987205
28	1	0	-3.133584	3.622252	2.212719
29	6	0	-2.100966	-2.672939	-2.462890
30	6	0	4.001923	4.250551	-3.731396
31	1	0	4.747474	4.871212	-4.232158
32	6	0	-2.961774	2.202735	5.299892
33	1	0	-3.262146	2.390848	6.332531
34	6	0	-4.395346	0.634864	0.579882
35	1	0	-4.628219	1.423036	1.299964
36	6	0	4.414456	3.268000	-2.855412
37	1	0	5.480177	3.129238	-2.677642
38	6	0	1.667097	-2.900801	0.050675
39	6	0	-3.816938	-1.402380	-1.256038
40	6	0	-6.873722	0.211076	0.389917
41	1	0	-7.117513	1.264421	0.184313
42	1	0	-7.032342	0.047247	1.466831
43	1	0	-7.588768	-0.416673	-0.157621
44	6	0	1.693946	3.684530	-3.357654
45	1	0	0.627012	3.837798	-3.532524
46	6	0	-1.869388	0.808751	3.664599
47	1	0	-1.304390	-0.092240	3.412139
48	6	0	-1.693906	-3.684575	-3.357610
49	1	0	-0.626969	-3.837847	-3.532466
50	6	0	-5.454858	-0.098898	0.005721
51	6	0	4.395343	-0.634859	0.579922
52	1	0	4.628208	-1.423027	1.300011
53	6	0	-2.259711	1.042673	4.978659
54	1	0	-2.007700	0.320345	5.757559
55	6	0	-4.001878	-4.250604	-3.731367
56	1	0	-4.747423	-4.871276	-4.232125
57	6	0	-3.273716	3.126565	4.305451
58	1	0	-3.817989	4.038734	4.557616
59	6	0	-2.634946	-4.466299	-3.987125
60	1	0	-2.328218	-5.250753	-4.680851
61	6	0	-3.471028	-2.453447	-2.196970
62	6	0	-2.492829	3.151768	-1.047497
63	1	0	-3.263673	2.433000	-1.329182
64	6	0	1.869360	-0.808724	3.664618
65	1	0	1.304365	0.092266	3.412148

```
     66          6           0       -0.529808    5.003553   -0.348569
     67          1           0        0.241326    5.725395   -0.072940
     68          6           0        6.873722   -0.211080    0.389971
     69          1           0        7.588774    0.416659   -0.157569
     70          1           0        7.117510   -1.264429    0.184382
     71          1           0        7.032335   -0.047239    1.466885
     72          6           0        2.259672   -1.042640    4.978683
     73          1           0        2.007655   -0.320306    5.757576
     74          6           0        2.891974   -2.891372    2.987244
     75          1           0        3.133564   -3.622235    2.212764
     76          6           0       -5.146801   -1.093541   -0.902526
     77          1           0       -5.963415   -1.658638   -1.351837
     78          6           0       -4.414421   -3.268038   -2.855405
     79          1           0       -5.480144   -3.129276   -2.677646
     80          6           0        0.677946   -3.835466    0.388381
     81          1           0        0.011576   -3.641408    1.232938
     82          6           0        2.961731   -2.202701    5.299928
     83          1           0        3.262095   -2.390809    6.332570
     84          6           0       -1.356935    5.246943   -1.445349
     85          1           0       -1.237486    6.162658   -2.027716
     86          6           0        3.273679   -3.126537    4.305495
     87          1           0        3.817949   -4.038705    4.557669
     88          6           0        2.335025   -4.320522   -1.792527
     89          1           0        2.987963   -4.507594   -2.647442
     90          6           0       -2.335028    4.320525   -1.792558
     91          1           0       -2.987959    4.507592   -2.647479
     92          6           0        1.356916   -5.246928   -1.445331
     93          1           0        1.237462   -6.162640   -2.027703
     94          6           0        2.492831   -3.151767   -1.047462
     95          1           0        3.263684   -2.433006   -1.329139
     96          6           0        0.529779   -5.003529   -0.348562
     97          1           0       -0.241368   -5.725362   -0.072943
```

2^+ (T_1)

```
HF = -4435.3578597 hartrees
Zero-point correction=                          0.778441
(Hartree/Particle)
Thermal correction to Gibbs Free Energy=        0.690788
Sum of electronic and zero-point Energies=         -4434.579419
Sum of electronic and thermal Energies=            -4434.531124
Sum of electronic and thermal Enthalpies=          -4434.530180
Sum of electronic and thermal Free Energies=       -4434.667072

                         Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1         29           0       -0.269426    0.067860    0.677863
      2         15           0       -0.807926    1.354251   -1.150476
      3         15           0        1.859994    0.553026    1.302636
      4          7           0        0.520516   -1.819518    0.220069
      5          7           0       -2.167004   -0.182424    0.825046
      6          6           0        2.742121    2.058298    0.808564
      7          6           0       -3.044770    0.616414    0.146077
```

8	6	0	2.711978	-0.848075	0.500226
9	6	0	-2.557962	1.506350	-0.840878
10	6	0	-4.447900	0.582923	0.396960
11	6	0	2.079184	0.356008	3.094559
12	6	0	-2.636378	-1.092608	1.745844
13	1	0	-1.895936	-1.734387	2.228083
14	6	0	1.891014	-1.911247	0.039609
15	6	0	-3.998115	-1.192826	2.073379
16	6	0	-4.949897	-0.357855	1.409195
17	6	0	-0.259009	-2.751083	-0.239545
18	1	0	-1.335389	-2.616185	-0.093273
19	6	0	0.937495	0.218495	3.889541
20	1	0	-0.057529	0.255137	3.437113
21	6	0	-0.102176	2.923635	-1.687900
22	6	0	-4.775340	2.362291	-1.282513
23	6	0	-5.259811	1.456245	-0.320436
24	1	0	-6.333245	1.452850	-0.125040
25	6	0	-5.802653	-2.211032	3.350965
26	1	0	-6.141397	-2.926677	4.103113
27	6	0	2.876239	3.118664	1.710441
28	1	0	2.535501	3.009963	2.741681
29	6	0	0.215265	-3.906953	-0.928532
30	6	0	-6.735667	-1.388450	2.698588
31	1	0	-7.796906	-1.461809	2.940478
32	6	0	3.893465	4.466777	-0.013820
33	1	0	4.345871	5.407074	-0.334266
34	6	0	4.078005	-0.904631	0.314452
35	1	0	4.705911	-0.075187	0.648443
36	6	0	-6.302178	-0.479251	1.742493
37	1	0	-7.042247	0.148814	1.245597
38	6	0	-0.543342	0.095549	-2.437210
39	6	0	2.478043	-3.010823	-0.620151
40	6	0	6.180339	-2.040187	-0.490663
41	1	0	6.684799	-2.073413	0.487250
42	1	0	6.540445	-1.139466	-1.010199
43	1	0	6.502887	-2.917770	-1.065689
44	6	0	-4.462561	-2.117769	3.047582
45	1	0	-3.735399	-2.755675	3.555655
46	6	0	3.179999	2.218961	-0.511489
47	1	0	3.080751	1.401349	-1.227019
48	6	0	-0.690286	-4.869444	-1.420911
49	1	0	-1.759591	-4.729468	-1.249083
50	6	0	4.688071	-2.005902	-0.321353
51	6	0	-3.412776	2.373672	-1.535029
52	1	0	-2.999577	3.058662	-2.279359
53	6	0	3.754846	3.416444	-0.918380
54	1	0	4.091487	3.532107	-1.949873
55	6	0	1.160830	-6.115891	-2.318022
56	1	0	1.530171	-6.986128	-2.864014
57	6	0	3.453621	4.316305	1.297936
58	1	0	3.561935	5.136288	2.010275
59	6	0	-0.222762	-5.964078	-2.110689
60	1	0	-0.916577	-6.713391	-2.494899
61	6	0	1.606015	-4.051831	-1.133850
62	6	0	3.346714	0.312106	3.687230
63	1	0	4.245534	0.421483	3.077161
64	6	0	0.029989	3.934413	-0.726851

```
     65          1           0       -0.284486    3.753054    0.303622
     66          6           0        1.060436    0.038607    5.265112
     67          1           0        0.165228   -0.066717    5.880378
     68          6           0       -5.723454    3.281379   -2.001995
     69          1           0       -6.502496    2.715498   -2.535918
     70          1           0       -5.197857    3.905797   -2.737183
     71          1           0       -6.238655    3.953504   -1.298077
     72          6           0        0.561436    5.166558   -1.081999
     73          1           0        0.661625    5.951216   -0.330328
     74          6           0        0.311183    3.156154   -3.002887
     75          1           0        0.207362    2.375458   -3.758166
     76          6           0        3.879152   -3.030483   -0.776340
     77          1           0        4.347279   -3.877142   -1.278343
     78          6           0        2.058792   -5.183092   -1.840805
     79          1           0        3.123033   -5.332196   -2.019027
     80          6           0        0.763351   -0.253269   -2.804941
     81          1           0        1.610978    0.315728   -2.418618
     82          6           0        0.973699    5.395619   -2.394119
     83          1           0        1.393361    6.364446   -2.672028
     84          6           0        2.322499   -0.004060    5.848374
     85          1           0        2.420104   -0.144498    6.926608
     86          6           0        0.849287    4.392278   -3.350978
     87          1           0        1.164811    4.574182   -4.380066
     88          6           0       -1.383183   -1.738176   -3.769239
     89          1           0       -2.226681   -2.318928   -4.147262
     90          6           0        3.465146    0.133786    5.059554
     91          1           0        4.454396    0.101047    5.519693
     92          6           0       -0.083021   -2.081266   -4.128625
     93          1           0        0.096327   -2.936935   -4.782227
     94          6           0       -1.616844   -0.655257   -2.924873
     95          1           0       -2.636533   -0.394135   -2.636019
     96          6           0        0.991136   -1.332284   -3.649679
     97          1           0        2.012884   -1.597681   -3.927283
```

3^+ (S_0)

```
HF = -4513.9891121 hartrees
Zero-point correction=                           0.837257
(Hartree/Particle)
Thermal correction to Gibbs Free Energy=         0.747345
Sum of electronic and zero-point Energies=          -4513.151856
Sum of electronic and thermal Free Energies=        -4513.241767

                         Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1         29           0        0.063161    0.159798   -0.055000
      2         15           0       -1.350116    1.713916    0.734603
      3         15           0        1.186358   -1.474578    1.011409
      4          7           0       -1.588033   -0.524066   -1.242595
      5          7           0        1.896672    0.600474   -1.026300
      6          6           0       -2.910801    0.935506    0.169101
      7          6           0       -2.832535   -0.133105   -0.765753
      8          6           0        3.031392    0.032123   -0.461144
```

9	6	0	2.882187	-0.982275	0.524941
10	6	0	0.900058	-3.120235	0.275631
11	6	0	-1.666755	2.044586	2.499334
12	6	0	4.328005	0.432589	-0.843001
13	6	0	-1.298937	3.351930	-0.066859
14	6	0	-4.021142	-0.761961	-1.189660
15	6	0	1.882806	-3.868755	-0.375169
16	6	0	1.334629	-1.763783	2.805480
17	6	0	-4.139085	1.330640	0.659716
18	6	0	-2.634890	-2.186025	-2.634541
19	6	0	1.993569	1.497775	-1.968885
20	6	0	-2.239116	3.775233	-1.007870
21	6	0	4.000973	-1.536416	1.114620
22	6	0	-1.481565	-1.463821	-2.141269
23	6	0	3.274970	1.984229	-2.432345
24	6	0	-2.042581	3.294919	2.996812
25	6	0	3.364480	2.982559	-3.427744
26	6	0	4.590165	3.448238	-3.846721
27	6	0	5.698798	1.951942	-2.307978
28	6	0	5.303495	-1.142669	0.750782
29	6	0	5.439927	-0.172317	-0.222923
30	6	0	-2.150242	2.381359	5.230017
31	6	0	1.548959	-5.066037	-1.005749
32	6	0	-3.916635	-1.847282	-2.148003
33	6	0	5.764784	2.925970	-3.280756
34	6	0	-5.252791	-0.317879	-0.667857
35	6	0	-5.335961	0.712443	0.248634
36	6	0	-5.030881	-2.574202	-2.614915
37	6	0	4.455678	1.459166	-1.861408
38	6	0	-2.281185	3.459919	4.359519
39	6	0	-1.530007	0.966105	3.380469
40	6	0	1.465901	-0.638130	3.628098
41	6	0	-6.651547	1.173929	0.808189
42	6	0	-0.184572	4.160113	0.197722
43	6	0	-0.420721	-3.589604	0.288264
44	6	0	-1.775423	1.132131	4.738246
45	6	0	-4.876502	-3.594622	-3.528343
46	6	0	-3.601291	-3.929958	-4.012399
47	6	0	0.732266	2.022281	-2.585505
48	6	0	1.305596	-3.035467	3.382176
49	6	0	-2.498302	-3.234408	-3.571251
50	6	0	-0.122487	-1.789970	-2.680136
51	6	0	-0.022939	5.374550	-0.457547
52	6	0	-2.067943	4.987807	-1.674220
53	6	0	6.493537	-1.770498	1.419052
54	6	0	-0.963746	5.788717	-1.400916
55	6	0	-0.750331	-4.788479	-0.332550
56	6	0	0.235263	-5.526668	-0.987065
57	6	0	1.578251	-0.783902	5.005159
58	6	0	1.409949	-3.177640	4.764700
59	6	0	1.548029	-2.055764	5.576291
60	1	0	-1.201948	-3.000428	0.775615
61	1	0	-1.783056	-5.141976	-0.318738
62	1	0	-0.022994	-6.463915	-1.483857
63	1	0	2.913059	-3.511733	-0.405473
64	1	0	2.323203	-5.642120	-1.516304
65	1	0	0.636425	-1.174923	-2.188769

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     66          1           0       -0.087632   -1.598297   -3.763436
     67          1           0        0.127124   -2.847642   -2.521644
     68          1           0       -3.486389   -4.739585   -4.734923
     69          1           0       -1.511144   -3.502047   -3.945170
     70          1           0       -6.029925   -2.335262   -2.253617
     71          1           0       -5.751905   -4.145844   -3.876838
     72          1           0       -6.175380   -0.798544   -0.992055
     73          1           0       -4.187203    2.140169    1.392139
     74          1           0       -6.817769    2.241289    0.597343
     75          1           0       -6.676397    1.053302    1.902008
     76          1           0       -7.492672    0.609287    0.385114
     77          1           0       -3.108214    3.154711   -1.230898
     78          1           0       -2.807451    5.308405   -2.410652
     79          1           0        0.844976    5.999381   -0.237718
     80          1           0       -0.834461    6.739542   -1.921579
     81          1           0        0.567402    3.831665    0.920322
     82          1           0       -2.147037    4.145889    2.321394
     83          1           0       -2.337567    2.515301    6.297244
     84          1           0       -2.572516    4.439907    4.742526
     85          1           0       -1.222491   -0.009455    2.998478
     86          1           0       -1.661842    0.283743    5.415930
     87          1           0       -0.135939    1.497609   -2.174788
     88          1           0        0.747172    1.880123   -3.675959
     89          1           0        0.611328    3.097856   -2.391577
     90          1           0        2.456335    3.393983   -3.866355
     91          1           0        4.650146    4.220815   -4.614957
     92          1           0        6.624375    1.565446   -1.884219
     93          1           0        6.737412    3.294286   -3.612308
     94          1           0        3.875383   -2.295795    1.890602
     95          1           0        6.445034    0.133550   -0.511740
     96          1           0        6.494740   -2.862339    1.280411
     97          1           0        6.478189   -1.582879    2.503572
     98          1           0        7.437326   -1.376584    1.019883
     99          1           0        1.473096    0.361074    3.185633
    100          1           0        1.680472    0.100314    5.637296
    101          1           0        1.200128   -3.920841    2.752961
    102          1           0        1.630920   -2.171101    6.658769
    103          1           0        1.385357   -4.174751    5.208596
```

3^+ (T_1)

```
HF = -4513.8961241 hartrees
Zero-point correction=                           0.834299
(Hartree/Particle)
Thermal correction to Gibbs Free Energy=         0.743587
Sum of electronic and zero-point Energies=          -4513.061825
Sum of electronic and thermal Free Energies=        -4513.152537
```

```
                         Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
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      1         29           0        0.293930    0.118028    0.446381
      2         15           0       -1.374506   -1.158246    1.286455
      3         15           0        0.944130   -0.809408   -1.543839
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4	7	0	-1.274557	1.623177	0.223877
5	7	0	2.156683	0.640063	0.651299
6	6	0	-2.816715	-0.120603	0.915680
7	6	0	-2.581559	1.186459	0.408623
8	6	0	3.096217	0.161155	-0.215311
9	6	0	2.699460	-0.611288	-1.336048
10	6	0	0.304013	0.385761	-2.752117
11	6	0	-1.830416	-2.837508	0.774103
12	6	0	4.492011	0.396316	-0.027353
13	6	0	-1.135807	-1.189455	3.088203
14	6	0	-3.691361	1.991024	0.078541
15	6	0	1.167475	1.220502	-3.466381
16	6	0	0.591147	-2.478102	-2.132375
17	6	0	-4.107797	-0.587407	1.075457
18	6	0	-2.100862	3.712989	-0.647844
19	6	0	2.526623	1.403423	1.747991
20	6	0	-2.187290	-1.054456	3.999950
21	6	0	3.639657	-1.166374	-2.222621
22	6	0	-1.033733	2.806087	-0.278987
23	6	0	3.885014	1.668596	2.018964
24	6	0	-1.587516	-3.937191	1.600346
25	6	0	4.284715	2.421780	3.159580
26	6	0	5.613622	2.694100	3.404695
27	6	0	6.241377	1.484116	1.417052
28	6	0	4.991328	-0.942075	-2.041379
29	6	0	5.383570	-0.157017	-0.938409
30	6	0	-2.444790	-5.413284	-0.106298
31	6	0	0.647245	2.206959	-4.301616
32	6	0	-3.441995	3.310779	-0.470348
33	6	0	6.606575	2.227981	2.531456
34	6	0	-4.990598	1.482285	0.276160
35	6	0	-5.223841	0.211940	0.767108
36	6	0	-4.471853	4.198810	-0.840938
37	6	0	4.904489	1.188090	1.137759
38	6	0	-1.895083	-5.221571	1.156972
39	6	0	-2.372963	-3.037116	-0.501747
40	6	0	0.974532	-3.544692	-1.307708
41	6	0	-6.613654	-0.321550	0.967775
42	6	0	0.173786	-1.348293	3.558914
43	6	0	-1.082331	0.553251	-2.877912
44	6	0	-2.683948	-4.318335	-0.935524
45	6	0	-4.178704	5.437912	-1.368440
46	6	0	-2.844361	5.837759	-1.546508
47	6	0	1.434304	1.909915	2.639621
48	6	0	-0.036250	-2.735527	-3.354335
49	6	0	-1.822388	4.986957	-1.191128
50	6	0	0.383395	3.231543	-0.499000
51	6	0	0.424727	-1.391694	4.926733
52	6	0	-1.930193	-1.090626	5.366243
53	6	0	6.026067	-1.511126	-2.971876
54	6	0	-0.627061	-1.262084	5.829965
55	6	0	-1.596332	1.538261	-3.710993
56	6	0	-0.730182	2.369786	-4.421547
57	6	0	0.741041	-4.852384	-1.708415
58	6	0	-0.269365	-4.050347	-3.749456
59	6	0	0.118361	-5.106472	-2.930195
60	1	0	-1.765985	-0.079643	-2.307134

61	1	0	-2.676636	1.667032	-3.799310
62	1	0	-1.133847	3.148368	-5.071646
63	1	0	2.247327	1.102048	-3.360654
64	1	0	1.325981	2.853770	-4.860760
65	1	0	1.083800	2.437815	-0.229014
66	1	0	0.618035	4.123626	0.100125
67	1	0	0.541017	3.488601	-1.555593
68	1	0	-2.619075	6.820618	-1.963359
69	1	0	-0.790594	5.304427	-1.331241
70	1	0	-5.514769	3.913858	-0.712120
71	1	0	-4.989921	6.112602	-1.648200
72	1	0	-5.849293	2.104337	0.026032
73	1	0	-4.269836	-1.606944	1.433827
74	1	0	-6.802575	-0.538045	2.030405
75	1	0	-6.758839	-1.262059	0.415240
76	1	0	-7.374560	0.393573	0.629280
77	1	0	-3.209244	-0.911942	3.645904
78	1	0	-2.752997	-0.981921	6.075182
79	1	0	1.447628	-1.516530	5.286476
80	1	0	-0.430201	-1.288372	6.903437
81	1	0	1.005704	-1.427700	2.853919
82	1	0	-1.165758	-3.794289	2.596576
83	1	0	-2.688547	-6.420678	-0.448949
84	1	0	-1.709170	-6.076373	1.809848
85	1	0	-2.561499	-2.186252	-1.159376
86	1	0	-3.107552	-4.465080	-1.930187
87	1	0	0.438325	1.681571	2.233426
88	1	0	1.483379	3.002727	2.775053
89	1	0	1.474902	1.461508	3.646896
90	1	0	3.528095	2.789381	3.852629
91	1	0	5.892664	3.275479	4.286076
92	1	0	7.025998	1.127421	0.749507
93	1	0	7.658249	2.444031	2.724841
94	1	0	3.294492	-1.776950	-3.060651
95	1	0	6.451904	0.007299	-0.791949
96	1	0	5.563749	-2.100542	-3.775395
97	1	0	6.727942	-2.167720	-2.434392
98	1	0	6.625285	-0.714693	-3.440095
99	1	0	1.463827	-3.346608	-0.351122
100	1	0	1.042215	-5.679551	-1.063604
101	1	0	-0.331268	-1.911690	-4.006006
102	1	0	-0.063468	-6.135878	-3.245108
103	1	0	-0.748883	-4.249078	-4.709807

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