Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Cationic ligands between σ-donation and hydrogen-bridge-bond-stabilisation of ancillary ligands in coinage metal complexes with protonated carbodiphosphoranes

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Contents

1 Experimental Procedures

1.1 Materials and Methods

All experiments were carried out under an atmosphere of purified argon or nitrogen in the MBraun glove boxes LABmaster 130 and UNIlab or using standard Schlenk techniques.
Diethylether was dried over Na/K alloy. *n*-Hexane was dried over $LiAlH_4$. Dichloromethane and MeCN were dried over CaH_2. After drying, solvents were stored over appropriate molecular sieves. Deuterated solvents were degassed with freeze-pump-thaw cycles and stored over appropriate molecular sieves under argon atmosphere.
^{1}H, ^{13}C, ^{11}B and ^{31}P NMR spectra were recorded using Bruker Avance HD 250, 300 A, DRX 400, DRX 500 and Avance 500 NMR spectrometers as well as Agilent Technologies 400 MHz VNMRS and 500 MHz DD2 NMR spectrometers at 300 K. ^{1}H and ^{13}C $\{^{1}H\}$, ^{13}C-APT (attached proton test) NMR chemical shifts are reported in ppm downfield from tetramethylsilane. The resonance of the residual protons in the deuterated solvent was used as internal standard for ^{1}H NMR spectra. The solvent peak of the deuterated solvent was used as internal standard for ^{13}C NMR spectra. The assignment of resonances in ^{1}H and ^{13}C NMR spectra was further supported by ^{1}H COSY and ^{1}H,^{13}C HMQC NMR spectra. ^{31}P NMR chemical shifts are reported in ppm downfield from H_3PO_4 and referenced to an external 85 % solution of phosphoric acid in D_2O. The following abbreviations are used for the description of NMR data: br (broad), s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet), m (multiplet).
FT-IR spectra were recorded by attenuated total reflection of the solid samples on a Bruker Tensor IF37 spectrometer. The intensity of the absorption band is indicated as w (weak), m (medium), s (strong), vs (very strong) and br (broad).
HR-ESI mass spectra were acquired with a LTQ-FT mass spectrometer (Thermo Fisher Scientific) or with Q-Exactive Plus mass spectrometer (Thermo Fisher Scientific). The resolution was set to 100.000. Elemental analyses were done by combustion analysis in a vario Micro cube (Elementar). In a glovebox, samples were weighed in Sn-crucibles of known mass and kept under exclusion of ambient air by cold pressure welding. Measurements were performed as double determinations, the values presented herein are the arithmetic mean.
Bis(diphenylphosphino)methane (dppm) was synthesized following the procedure published by K. Sommer.[1] [$HC(dppm)_2$]Cl (**1a**) was synthesized according to the literature by Peringer and coworkers.[2]

1.1 Synthesis of [({dppm}$_2$CH)CuCl](PF_6) (**2-Cl**)

121 mg [{dppm}$_2$CH](PF_6) (**1b**, 131 µmol, 1.0 eq.) and 13 mg CuCl (131 µmol, 1.0 eq.) were dissolved in 10 ml MeCN. *In vacuo* removal of all volatiles and recrystallization of the residue from CH_2Cl_2/*n*-hexane leads to the formation of single crystals of **2-Cl** (101 mg, 98.5 µmol, 75.4% yield). $^{31}P\{^{1}H\}$ NMR (202 MHz, CD_3CN) δ: -144.6 (sept, $^{1}J_{PF}$ = 706.2 Hz, *P*F_6), -27.2 (br, $W_{1/2}$ = 125.0 Hz, *P*-Cu-*P*), 22.1 (dd, J_{PP} = 39.1 Hz, J_{PP} = 27.3 Hz, *P*-CH-*P*) ppm. ^{19}F NMR (470 MHz, CD_3CN) δ: -72.9 (d, $^{1}J_{FP}$ = 706.4 Hz, P*F*$_6$) ppm. ^{1}H NMR (500 MHz, CD_3CN) δ: 2.93 (t, 1H, $^{2}J_{PH}$ = 10.6 Hz, P–C*H*–P), 3.87 (br d, 4H, *J* = 9.5 Hz, P–C*H*$_2$–P), 7.05 (t, 8H, *J* = 7.5 Hz, phenyl-*H*), 7.09-7.21 (m, 12H, phenyl-*H*), 7.33 (t, 4H, *J* = 7.4 Hz, phenyl-*H*), 7.44-7.55 (m, 16H, phenyl-*H*) ppm. ^{13}C APT NMR (126 MHz, CD_3CN) δ: -2.1 (m, P–C̲H–P), 29.8 (br, P–C̲H$_2$–P), 129.5 (t, J_{PC} = 5.2 Hz, phenyl-*C*), 129.9 (t, J_{PC} = 6.4 Hz, phenyl-*C*), 131.0 (s, phenyl-*C*), 133.5 (t, J_{PC} = 6.2 Hz, phenyl-*C*), 133.5 (t, J_{PC} = 3.1 Hz, phenyl-*C*), 133.6 (s, phenyl-*C*), 134.3 (br, phenyl-*C*), ppm. IR (ATR): $\tilde{\nu}$ / cm^{-1} = 3041 (w), 2972 (w), 2919 (w), 1587 (w), 1574 (w), 1486

(w), 1435 (m), 1375 (w), 1312 (w), 1262 (w), 1212 (w), 1178 (w), 1161 (w), 1145 (w), 1130 (w), 1108 (m), 1099 (m), 1026 (w), 999 (w), 962 (m), 840 (s), 825 (s), 788 (m), 774 (m), 755 (m), 732 (s), 686 (s), 616 (w), 555 (s), 522 (m), 499 (s), 481 (s), 467 (m), 451 (m), 423 (m), 414 (m), 403 (m). HR-ESI-MS (pos. mode, MeOH/HCOOH) m/z: 879.1451 (calculated for [({dppm}$_2$CH}CuCl]$^+$), 879.1487 (found, Δ = 4.1 ppm). Anal. Calcd for $C_{51}H_{45}Cl_1Cu_1P_5F_6 \cdot 1.5CH_2Cl_2$: C 54.68%, H 4.20%; Found: C 54.64%; H 4.10%.

1.2 Synthesis of [({dppm}$_2$CH)CuBr](PF$_6$) (**2-Br**)

115 mg [{dppm}$_2$CH](PF$_6$) (**1b**, 124 µmol, 1.0 eq.) and 17 mg CuBr (119 µmol, 1.0 eq.) were dissolved in 10 ml MeCN. *In vacuo* removal of all volatiles and recrystallization of the residue from CH_2Cl_2/*n*-hexane leads to the formation of single crystals of **2-Br** (93 mg, 86.9 µmol, 70.0 % yield). $^{31}P\{^1H\}$ NMR (202 MHz, CD_3CN) δ: -144.6 (sept, $^1J_{PF}$ = 706.4 Hz, *P*F$_6$), -28.5 (br, $W_{1/2}$ = 151.8 Hz, *P*-Cu-*P*), 23.1 (dd, J_{PP} = 40.6 Hz, J_{PP} = 27.7 Hz, *P*-CH-*P*) ppm. ^1H NMR (500 MHz, CD_3CN) δ: 2.90 (t, 1H, $^2J_{PH}$ = 11.6 Hz, P–C*H*–P), 3.91 (br m, 4H, P–C*H*$_2$–P), 7.03 (t, 8H, *J* = 7.5 Hz, phenyl-*H*), 7.09-7.20 (m, 12H, phenyl-*H*), 7.33 (t, 4H, *J* = 7.4 Hz, phenyl-*H*), 7.44-7.58 (m, 16H, phenyl-*H*) ppm. ^{13}C APT NMR (126 MHz, CD_3CN) δ: 29.1 (br, P–CH_2–P), 29.6 (br, P–CH_2–P),129.5 (t, J_{PC} = 4.9 Hz, phenyl-*C*), 129.9 (t, J_{PC} = 6.4 Hz, phenyl-*C*), 130.9 (s, phenyl-*C*), 131.9 (t, J_{PC} = 8.2 Hz, phenyl-*C*), 133.6 (t, J_{PC} = 5.4 Hz, phenyl-*C*), 134.3 (br, phenyl-*C*), ppm. IR (ATR): $\tilde{\nu}$ / cm^{-1} = 3056 (w), 3043 (w), 2972 (w), 2954 (w), 2918 (w), 1800 (w), 1588 (w), 1576 (w), 1559 (w), 1486 (w), 1435 (m), 1375 (w), 1313 (w),1270 (w), 1262 (w), 1211 (w), 1187 (w), 1177 (w), 1160 (w), 1145 (w), 1129 (w), 1107 (m), 1099 (m), 1073 (w), 1048 (w), 1026 (w), 999 (w), 959 (m), 868 (w), 840 (s), 826 (s), 809 (m), 788 (m), 773 (m), 755 (m), 731 (s), 696 (m), 686 (s), 616 (w), 569 (s), 527 (m), 521 (m), 499 (m), 481 (m), 467 (m), 452 (m), 429 (m), 429 (m), 424 (m), 414 (m), 402 (m). HR-ESI-MS (pos. mode, MeOH/HCOOH) m/z: 925.0957 (calculated for [({dppm}$_2$CH}CuBr]$^+$), 925.0925 (found, Δ = 3.5 ppm). Anal. Calcd for $C_{51}H_{45}Br_1Cu_1P_5F_6 \cdot 1.4CH_2Cl_2$: C 52.93%, H 4.05%; Found: C 52.77%; H 3.66%.

1.3 Synthesis of [({dppm}$_2$CH)CuI](PF$_6$) (**2-I**)

111 mg [{dppm}$_2$CH](PF$_6$) (**1b**, 120 µmol, 1.0 eq.) and 17 mg CuI (121 µmol, 1.0 eq.) were dissolved in 10 ml MeCN. *In vacuo* removal of all volatiles and recrystallization of the residue from CH_2Cl_2/*n*-hexane leads to the formation of single crystals of **2-Cl** (91 mg, 81.5 µmol, 68.0 % yield). $^{31}P\{^1H\}$ NMR (202 MHz, CD_3CN) δ: -144.6 (sept, $^1J_{PF}$ = 706.4 Hz, *P*F$_6$), -30.6 (br, $W_{1/2}$ = 201.4 Hz, *P*-Cu-*P*), 24.4 (dd, J_{PP} = 42.3 Hz, J_{PP} = 27.5 Hz, *P*-CH-*P*) ppm. ^{19}F NMR (470 MHz, CD_3CN) δ: -72.9 (d, $^1J_{FP}$ = 706.4 Hz, P*F*$_6$) ppm. ^1H NMR (500 MHz, CD_3CN) δ: 2.87 (t, 1H, $^2J_{PH}$ = 12.2 Hz, P–C*H*–P), 3.93 (br m, 4H, P–C*H*$_2$–P), 7.02 (t, 8H, *J* = 7.5 Hz, phenyl-*H*), 7.10-7.18 (m, 12H, phenyl-*H*), 7.34 (t, 4H, *J* = 7.4 Hz, phenyl-*H*), 7.44-7.57 (m, 16H, phenyl-*H*) ppm. ^{13}C APT NMR (126 MHz, CD_3CN) δ: -0.8 (m, P–C*H*–P), 29.0 (br, P–CH_2–P), 129.5 (t, J_{PC} = 4.9 Hz, phenyl-*C*), 129.9 (t, J_{PC} = 6.4 Hz, phenyl-*C*), 130.9 (s, phenyl-*C*), 133.3 (t, J_{PC} = 8.0 Hz, phenyl-*C*), 133.7 (t, J_{PC} = 5.4 Hz, phenyl-*C*), 134.4 (t, J_{PC} = 1.3 Hz, phenyl-*C*), ppm. IR (ATR): $\tilde{\nu}$ / cm^{-1} = 3055 (w), 2968 (w), 2918 (w), 1588 (w), 1573 (w), 1485 (w), 1435 (m), 1375 (w), 1336 (w), 1312 (w), 1268 (w), 1212 (w), 1176 (w), 1159 (w), 1144 (w), 1129 (w), 1107 (m), 1026 (w), 999 (w), 957 (m), 839 (s), 826 (s), 787 (m), 773 (m), 753 (m), 732 (s), 696 (m), 686 (s), 616 (w), 556 (s), 521 (m), 499 (s), 480 (s), 467 (m), 423 (m), 400 (m). Anal. Calcd for $C_{51}H_{45}I_1Cu_1P_5F_6 \cdot 1.43CH_2Cl_2$: C 51.30%, H 3.91%; Found: C 51.32%, H 3.75%.

1.4 Synthesis of [({dppm}$_2$CH)Cu(NCMe)](PF$_6$)(BF$_4$) (**2-NCMe**)

103 mg [{dppm}$_2$CH](PF$_6$) (**1b**, 111 µmol, 1.0 eq.) and 35.5 mg [Cu(NCMe)$_4$](BF$_4$) (113 µmol, 1.0 eq.) were dissolved in 4ml MeCN. After stirring for 16 h at ambient temperature the mixture is filtered and layered with 10 mL of diethylether and 2 mL of *n*-hexane. 59 mg of single crystals suitable for single crystal X-Ray diffraction of **2-NCMe** (50.2 µmol, 45.1 % yield) were isolated after 10 days. ^{31}P{^{1}H} NMR (202 MHz, CD$_3$CN) δ: -144.6 (sept, $^1J_{PF}$ = 706.6 Hz, *P*F$_6$), -20.1 (br, $W_{1/2}$ = 458.3 Hz, *P*-Cu-*P*), 26.5 (dd, J_{PP} = 43.1 Hz, J_{PP} = 26.7 Hz, *P*-CH-*P*) ppm. ^{19}F NMR (470 MHz, CD$_3$CN) δ: -151.6 (s, B*F*$_4$), -72.9 (d, $^1J_{FP}$ = 706.7 Hz, P*F*$_6$) ppm. ^{1}H NMR (500 MHz, CD$_3$CN) δ: 3.03 (t, 1H, $^2J_{PH}$ = 12.8 Hz, P–C*H*–P), 3.84 (m, 4H, P–C*H*$_2$–P), 7.14-7.23 (m, 16H, phenyl-*H*), 7.29 (br t, 4H, *J* = 7.4 Hz, phenyl-*H*), 7.33-7.47 (m, 20H, phenyl-*H*) ppm. ^{13}C APT NMR (126 MHz, CD$_3$CN) δ: -1.8 (m, P–CH–P), 28.8 (br d, J_{PC} = 65.4 Hz, P–CH$_2$–P), 130.0 (t, J_{PC} = 5.4 Hz, phenyl-*C*), 130.2 (t, J_{PC} = 6.2 Hz, phenyl-*C*), 131.6 (s, phenyl-*C*), 133.2 (t, J_{PC} = 8.5 Hz, phenyl-*C*), 133.3 (t, J_{PC} = 5.4 Hz, phenyl-*C*), 134.9 (t, J_{PC} = 1.5 Hz, phenyl-*C*), ppm. IR (ATR): $\tilde{\nu}$ / cm^{-1} = 3054 (w), 2962 (w), 2950 (w), 2910 (w), 2312 (w), 2272 (w), 2115 (w), 1810 (w), 1589 (w), 1574 (w), 1486 (w), 1437 (m), 1377 (w), 1337 (w), 1314 (w), 1283 (w), 1223 (w), 1181 (w), 1156 (w), 1106 (m), 1091 (m), 1047 (m), 1034 (m), 1025 (m), 996 (m), 961 (m), 835 (s), 812 (m), 791 (w), 777 (w), 767 (w), 749 (m), 735 (s), 687 (s), 615 (w), 556 (s), 522 (m), 500 (s), 484 (s), 472 (s), 447 (m), 429 (m), 415 (m). HR-ESI-MS (pos. mode, MeCN) m/z: 422.0878 (calculated for [({dppm}$_2$CH}Cu]$^{2+}$), 422.0889 (found, Δ = 2.6 ppm). Anal. Calcd for $C_{53}H_{48}B_1Cu_1F_{10}NP_5$: C 56.93%, H 4.33%, N 1.25; Found: C 57.27%, H 3.99%, N 1.52%.

1.5 Synthesis of [({dppm}$_2$CH)Ag](PF$_6$)$_2$ (**3**)

102 mg [{dppm}$_2$CH](PF$_6$) (**1b**, 110 µmol, 1.0 eq.) and 27 mg AgPF$_6$ (107 µmol, 1.0 eq.) were dissolved in 10 ml MeCN and stirred at ambient temperature for 16 hours. All volatiles of the mixture were removed *in vacuo* and 10 ml of dichloromethane were added to residue. After filtration of the resulting mixture the filtrate was layered with 20 ml of *n*-hexane. After the completed diffusion, isolation and subsequent drying of the formed crystalline solid under high vacuum 92 mg (75.4 µmol, 69 %) of **3** were isolated. ^{31}P{^{1}H} NMR (202 MHz, CD$_2$Cl$_2$) δ: -144.1 (sept, $^1J_{PF}$ = 713.7 Hz, *P*F$_6$), -8.9 (dm, $^1J_{PAg}$ = 519.9 Hz, *P*-Ag-*P*), 22.2 (t, J_{PP} = 14.5 Hz, *P*-CH-*P*) ppm. ^{19}F NMR (470 MHz, CD$_2$Cl$_2$) δ: -71.5 (d, $^1J_{FP}$ = 713.6 Hz, P*F*$_6$) ppm. ^{1}H NMR (500 MHz, CD$_2$Cl$_2$) δ: 2.66 (t, 1H, $^2J_{PH}$ = 7.9 Hz, P–C*H*–P), 3.53 (m, 4H, P–C*H*$_2$–P), 7.18-7.24 (m, 8H, phenyl-*H*), 7.27-7.33 (m, 8H, phenyl-*H*), 7.39-7.53 (m, 16H, phenyl-*H*), 7.56-7.64 (m, 8H, phenyl-*H*) ppm. ^{13}C-APT NMR (126 MHz, CD$_2$Cl$_2$) δ: 123.1 (s, phenyl-*C*), 123.8 (m, phenyl-*C*), 128.5 (m, phenyl-*C*), 130.1 (t, J_{PC} = 6.4 Hz, phenyl-*C*), 130.3 (t, J_{PC} = 5.2 Hz, phenyl-*C*), 132.5 (t, J_{PC} = 5.2 Hz, phenyl-*C*),132.6 (s, phenyl-*C*), 133.6 (t, J_{PC} = 5.2 Hz, phenyl-*C*), 134.5 (s, phenyl-*C*) ppm. The CH$_2$- and (R$_3$P)CH-resonances of the PCP-ligand could not directly be detected by ^{13}C-APT NMR spectroscopy, but were located in the ^{1}H,^{13}C-HSQC NMR spectrum: δ = -2.7 (P–CH–P), 30.7 (P–CH$_2$–P) ppm. IR (ATR): $\tilde{\nu}$ / cm^{-1} = 3063 (w), 2963 (w), 2915 (w), 2052 (w), 1587 (m), 1483 (m), 1436 (s), 1378 (m), 1334 (m), 1308 (m), 1218 (m), 1191 (m), 1165 (m), 1154 (m), 1106 (s), 1028 (m), 999 (m), 988 (s), 924 (m), 851 (s), 824 (vs), 782 (s), 766 (s), 746 (s), 731 (vs), 688 (vs), 617 (m), 555 (vs), 527 (s), 522 (s), 499 (s), 470 (s), 452 (s), 429 (s), 413 (s). Anal. Calcd for $C_{51}H_{45}Ag_1F_{12}P_6$: C 51.93%, H 3.85%; Found: C 51.88%, H 3.47%.

1.6 Synthesis of [({dppm}$_2$CH)AgCl](NO$_3$) (**3-Cl**)

303 mg [{dppm}$_2$CH]Cl (**1a**, 371 µmol, 1.0 eq.) and 63 mg AgNO$_3$ (371 µmol, 1.0 eq.) were dissolved in 10 ml MeCN. After stirring at ambient temperature for ten minutes a colorless

precipitate is formed. All volatiles of the mixture were removed *in vacuo* and 10 ml of dichloromethane were added to residue. After filtration of the resulting mixture into a light protected Schlenk tube, the filtrate is layered with 20 ml of *n*-hexane. After the completed diffusion, isolation and subsequent drying of the formed crystalline solid under high vacuum 333 mg (337 µmol, 91 %) of **3-Cl** were isolated. $^{31}P\{^{1}H\}$ NMR (202 MHz, CD_2Cl_2) δ: 18.6 (m, *P*–CH–*P*), -16.2 (br, *P*–Ag–*P*) ppm. ^{1}H NMR (500 MHz, CD_2Cl_2) δ: 2.54 (t, 1H, $^{2}J_{PH}$ = 8.1 Hz, P–C*H*–P), 4.73 (m, 4H, P–CH_2–P), 7.07 (m, 16H, phenyl-*H*), 7.17 (t, 4H, J_{HH} = 7.5 Hz, phenyl-*H*), 7.24 (t, 4H, J_{HH} = 7.3 Hz, phenyl-*H*), 7.54 (m, 8H, phenyl-*H*), 7.67 (dd, 8H, *J* = 8.1 Hz, *J* = 11.7 Hz, phenyl-*H*) ppm. ^{13}C-APT NMR (126 MHz, CD_2Cl_2) δ: -3.8 (tt, $^{1}J_{PC}$ = 158.1 Hz, $^{3}J_{PC}$ = 8.7 Hz, P–CH–P), 29.5 (br m, P–CH_2–P), 124.6 (m, phenyl-*C*), 129.0 (t, J_{PC} = 5.2 Hz, phenyl-*C*), 129.2 (t, J_{PC} = 12.9 Hz, phenyl-*C*), 130.2 (s, phenyl-*C*), 132.9 (m, phenyl-*C*), 133.1 (s, phenyl-*C*), 133.2 (t, J_{PC} = 5.2 Hz, phenyl-*C*), 133.6 (t, J_{PC} = 9.3 Hz, phenyl-*C*) ppm. IR (ATR): $\tilde{\nu}$ / cm^{-1} = 3050 (w), 3962 (w), 2884 (w), 2786 (w), 2711 (w), 1762 (w), 1653 (w), 1588 (w), 1575 (w), 1485 (m), 1435 (s), 1379 (m), 1338 (w), 1260 (m), 1217 (m), 1182 (m), 1160 (m), 1105 (s), 1026 (m), 999 (m), 981 (s), 803 (m), 784 (m), 735 (s), 685 (s), 615 (w), 530 (m), 522 (m), 499 (s), 482 (s), 473 (s), 451 (m), 442 (m), 415 (m), 405 (m), 376 (m), 351 (m), 319 (w), 279 (w), 259 (w), 225 (m), 215 (w). HR-ESI-MS (pos. mode, MeCN) m/z: 887.1436 (calculated for $[(\{dppm\}_2C\}Ag]^+$), 887.1447 (found, Δ = 1.2 ppm).

1.7 Synthesis of [({dppm}$_2$CH)AgBr](PF_6) (**3-Br**)

211 mg [{dppm}$_2$CH](PF_6) (**1b**, 228 µmol, 1.0 eq.) and 42.6 mg AgBr (227 µmol, 1.0 eq.) were suspended in a mixture of 5 ml CH_2Cl_2 and 2 ml MeCN. Stirring of the mixture at ambient temperature for 16 hours results in the formation of clear solution. Layering of the solution with diethylether yields 134 mg of a single crystalline solid of complex **3-Br** (120 µmol, 52.6 %). $^{31}P\{^{1}H\}$ NMR (162 MHz, CD_3CN) δ: -144.6 (sept, $^{1}J_{PF}$ = 706.4 Hz, *P*F_6), -19.6 (br, *P*-Ag-*P*), 18.3 (m, *P*-CH-*P*) ppm. ^{1}H NMR (500 MHz, CD_3CN) δ: 2.58 (t, 1H, $^{2}J_{PH}$ = 7.2 Hz, P–C*H*–P), 3.67 (m, 4H, P–CH_2–P), 7.08-7.21 (m, 16H, phenyl-*H*), 7.25-7.32 (m, 4H, phenyl-*H*), 7.32-7.44 (m, 12H, phenyl-*H*), 7.67 (m, 8H, phenyl-*H*) ppm. $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_3CN) δ: -3.9 (t, $^{2}J_{PC}$ = 8.2 Hz, P–CH–P), 29.1 (m, P–CH_2–P), 124.8 (s, phenyl-*C*), 125.8 (s, phenyl-*C*), 129.8 (t, J_{PC} = 5.3 Hz, phenyl-*C*), 130.0 (t, J_{PC} = 6.5 Hz, phenyl-*C*), 131.7 (s, phenyl-*C*), 133.4 (t, J_{PC} = 5.3 Hz, phenyl-*C*), 134.2 (t, J_{PC} = 5.5 Hz, phenyl-*C*), 134.2 (s superimposed, phenyl-*C*) ppm. IR (ATR): $\tilde{\nu}$ / cm^{-1} = 3058 (w), 1588 (w), 1484 (w), 1435 (m), 1374 (w), 1313 (w), 1270 (w), 1216 (w), 1179 (w), 1149 (w), 1106 (m), 1026 (w), 982 (m), 838 (s), 824 (s), 788 (m), 731 (s), 687 (s), 529 (s), 498 (s), 481 (s), 444 (m), 416 (m), 376 (m), 351 (m), 279 (m), 251 (m), 225 (m), 212 (m) ppm.

1.8 Synthesis of [({dppm}$_2$CH)AgI](PF_6) (**3-I**)

106 mg [{dppm}$_2$CH](PF_6) (**1b**, 114 µmol, 1.0 eq.) and 27 mg AgI (115 µmol, 1.0 eq.) were suspended in 10 ml CH_2Cl_2. Stirring of the mixture at ambient temperature for 16 hours results in the formation of clear solution. Layering of the solution with *n*-hexane yields 118 mg of a single crystalline solid of complex **3-I** (102 µmol, 88.8 %). $^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2) δ: -144.1 (sept, $^{1}J_{PF}$ = 711.4 Hz, *P*F_6), -22.5 (br, *P*-Ag-*P*), 18.4 (m, *P*-CH-*P*) ppm. ^{1}H NMR (500 MHz, CD_2Cl_2) δ: 2.40 (br, 1H, P–C*H*–P), 3.58 (br, 4H, P–CH_2–P), 7.10-7.19 (br m, 16H, phenyl-*H*), 7.25 (br, 4H, phenyl-*H*), 7.35 (br t, 4H, J_{PH} = 7.5 Hz, phenyl-*H*), 7.67 (m superimposed, 16H, phenyl-*H*) ppm. ^{13}C-APT NMR (126 MHz, CD_2Cl_2) δ: 30.0 (m, P–CH_2–P), 129.4 (t, J_{PC} = 5.0 Hz, phenyl-*C*), 129.7 (t, J_{PC} = 6.4 Hz, phenyl-*C*), 130.9 (s, phenyl-*C*), 132.7 (superimposed, phenyl-*C*), 133.2 (m, phenyl-*C*), 133.7 (s, phenyl-*C*) ppm. IR (ATR): $\tilde{\nu}$ / cm^{-1} = 3055 (w), 2966 (w), 2911 (w), 2325 (w), 2114 (w), 1981 (w), 1802 (w), 1620 (w), 1588 (w), 1484 (m), 1435 (s), 1374 (w), 1336 (w), 1312 (w), 1267 (w), 1217 (w), 1178 (m), 1149 (m), 1136 (w), 1107 (s), 1069 (w), 1026 (m), 982 (s), 837 (w), 824 (vs), 789 (m), 776 (m), 729 (vs), 697 (s), 685 (vs), 615 (w), 555 (vs), 528 (s), 521 (s), 499 (s), 481 (s), 467 (s), 428 (m), 416 (m), 402 (m), 376 (m), 352 (m), 305 (w), 286 (w), 253 (w), 221 (w), 214 (w), 205 (w). HR-ESI-

MS (+) m/z: 1015.0562 (calculated for [({dppm}$_2$CH}AgI]$^+$), 1015.0581 (found, Δ = 1.9 ppm). Anal. Calcd for $C_{53}H_{48}Ag_1F_6I_1P_5$: C 48.92%, H 3.75%; Found: C 48.31%, H 3.41%.

1.9 Synthesis of [({dppm}$_2$CH)Ag(NCMe)](PF$_6$)$_2$ (**3-NCMe**)

146 mg [{dppm}$_2$CH](PF$_6$) (**1b**, 158 µmol, 1.0 eq.) and 40 mg AgPF$_6$ (158 µmol, 1.0 eq.) were dissolved in 2 ml MeCN and stirred at ambient temperature for 16 hours. Layering of the reaction mixture with 8 ml of diethylether results in the formation of 139 mg **3-NCMe** (114 µmol, 72.1 %) as a crystalline solid.
^{1}H NMR (500 MHz, CD_3CN) δ: 2.29 (t, 1H, $^2J_{PH}$ = 7.2 Hz, P–C*H*–P), 3.53 (m, 4H, P–C*H*$_2$–P), 7.18 (m, 8H, phenyl-*H*), 7.31 (m, 8H, phenyl-*H*), 7.37 (m, 8H, phenyl-*H*), 7.46 (m, 8H, phenyl-*H*), 7.60 (m, 8H, phenyl-*H*) ppm. ^{13}C-APT NMR (126 MHz, CD_3CN) δ: 124.8 (s, phenyl-*C*), 125.6 (s, phenyl-*C*), 130.2 (t, J_{PC} = 6.5 Hz, phenyl-*C*), 130.2 (t, J_{PC} = 6.5 Hz, phenyl-*C*), 130.4 (t, J_{PC} = 5.5 Hz, phenyl-*C*), 132.5 (s, phenyl-*C*), 133.2 (t, J_{PC} = 5.5 Hz, phenyl-*C*), 134.0 (t, J_{PC} = 9.5 Hz, phenyl-*C*), 134.7 (s, phenyl-*C*) ppm.The CH_2- and (R_3P)CH-resonances of the PCP-ligand could not directly be detected by ^{13}C-APT NMR spectroscopy, but were located in the ^{1}H,^{13}C-HSQC NMR spectrum: δ = -4.3 (P–C<u>H</u>–P), The CH_2- and (R_3P)CH-resonances of the PCP-ligand could not directly be detected by ^{13}C-APT NMR spectroscopy, but were located in the ^{1}H,^{13}C-HSQC NMR spectrum: δ = -2.7 (P–C<u>H</u>–P), 30.7 (P–C<u>H</u>$_2$–P) ppm. 28.6 (P–C<u>H</u>$_2$–P) ppm. ^{31}P{^{1}H} NMR (122 MHz, CD_3CN) δ: -144.3 (sept, $^1J_{PF}$ = 708.8 Hz, *P*F$_6$), -13.7 (br d, $^1J_{PAg}$ = 439.2 Hz, *P*-Ag-*P*), 20.6 (dd, J_{PP} = 24.3 Hz, J_{PP} = 14.4 Hz, *P*-CH-*P*) ppm. IR (ATR): $\tilde{\nu}$ / cm^{-1} = 3057 (w), 2960 (w), 2912 (w), 2312 (w), 2275 (w), 1588 (w), 1574 (w), 1485 (w), 1436 (m), 1376 (w), 1335 (w), 1314 (w),1219 (w), 1180 (w), 1158 (w), 1144 (w), 1105 (m), 1073 (w), 1026 (w), 999 (w), 971 (m), 933 (w), 832 (s), 820 (s), 762 (m), 749 (s), 741 (s), 731 (s), 687 (s), 616 (w), 555 (s), 526 (m), 521 (s), 499 (s), 484 (s), 472 (s), 445 (m), 423 (m). HR-ESI-MS (+) m/z: 887.1439 (calculated for [({dppm}$_2$C}Ag]$^+$), 887.1447 (found, Δ = 0.9 ppm). Anal. Calcd for $C_{53}H_{48}Ag_1F_{12}N_1P_6$: C 52.15%, H 3.96%, N 1.15; Found: C 51.87%, H 3.55%, N 1.49%.

1.10 Synthesis of [({dppm}$_2$CH)Ag(H$_2$O)](PF$_6$)$_2$ (**3-H$_2$O**)

211 mg [{dppm}$_2$CH](PF$_6$) (**1b**, 220 µmol, 1.0 eq.) and 55.6 mg AgPF$_6$ (220 µmol, 1.0 eq.) were dissolved in 10 ml CH_2Cl_2 and 2 mL of water-containing MeOH. After stirring at ambient temperature for 16 hour the mixture is filtered through syringe filter and the resulting filtrate is layered with Et_2O. Within five days single crystals of **3-H$_2$O** are formed, which were separated and dried in a stream of air, yielding 139 mg of **3-H$_2$O** (123 µmol, 72.1 %). Complex **3** is formed, when **3-H$_2$O** is dried under vacuum. ^{1}H NMR (500 MHz, CD_2Cl_2) δ: 1.72 (br, 2H, Ag–O*H*$_2$), 2.66 (t, 1H, $^2J_{PH}$ = 7.9 Hz, P–C*H*–P), 3.87 (br m, 4H, P–C*H*$_2$–P), 7.15-7.24 (br m, 8H, phenyl-*H*), 7.26-7.34 (br m, 8H, phenyl-*H*), 7.38-7.53 (br m, 16H, phenyl-*H*), 7.56-7.65 (br m, 8H, phenyl-*H*) ppm. ^{13}C-APT NMR (126 MHz, CD_2Cl_2) δ: -2.8 (m, P–C<u>H</u>–P), 30.6 (m, P–C<u>H</u>$_2$–P), 120.9 (s, phenyl-*C*), 123.2 (s, phenyl-*C*), 123.9 (s, phenyl-*C*),128.4 (s, phenyl-*C*), 128.7 (t, J_{PC} = 17.3 Hz, phenyl-*C*), 130.1 (t, J_{PC} = 6.4 Hz, phenyl-*C*), 130.2 (t, J_{PC} = 5.7 Hz, phenyl-*C*), 132.5 (t, J_{PC} = 5.5 Hz, phenyl-*C*), 132.5 (s, phenyl-*C*), 133.6 (t, J_{PC} = 9.2 Hz, phenyl-*C*), 134.6 (s, phenyl-*C*), 148.9 (s, phenyl-*C*), 149.4 (s, phenyl-*C*), 152.7 (s, phenyl-*C*) ppm. ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2) δ: -144.1 (sept, $^1J_{PF}$ = 714.1 Hz, *P*F$_6$), -22.5 (br, *P*-Ag-*P*), 18.4 (m, *P*-CH-*P*) ppm. IR (ATR): $\tilde{\nu}$ / cm^{-1} = 3620 (w), 3541 (w), 3062 (w), 2971 (w), 2894 (w), 1767 (w), 1609 (w), 1589 (w), 1576 (w), 1506 (w), 1483 (m), 1437 (w), 1409 (w), 1384 (w), 1365 (w), 1351 (w), 1312 (w), 1187 (w), 1176 (w), 1162 (w), 1143 (w), 1108 (m), 1081 (w), 1027 (w), 1015 (w), 999 (w), 948 (w), 832 (s), 784 (m), 776 (m), 755 (m), 738 (s), 724 (m), 687 (s), 655 (m), 617 (w), 555 (s), 520 (m), 499 (s), 470 (m), 441 (m), 418 (m), 406 (m). %. HR-ESI-MS (+) m/z: 887.1439 (calculated for [({dppm}$_2$C}Ag]$^+$), 887.1444 (found, Δ = 0.6 ppm); 445.0759 (calculated for [({dppm}$_2$CH}Ag]$^{2+}$), 445.0760 (found, Δ = 0.2 ppm). Anal. Calcd for $C_{51}H_{47}Ag_1F_{12}O_1P_6$: C 51.94%, H 4.52%; Found: C 52.34%, H 4.06%.

1.11 Synthesis of [({dppm}$_2$CH)Ag(NO_3)](PF_6) (**3-NO_3**)

120 mg [{dppm}$_2$CH](PF_6) (**1b**, 130 µmol, 1.0 eq.) and 22 mg $AgNO_3$ (115 µmol, 1.0 eq.) were dissolved in 2 ml dichloromethane. After stirring for 72 h at ambient temperature the mixture is layered with 10 mL of *n*-hexane. After three days cuboid single crystals are formed, which were separated and dried in vacuo to give 59 mg of complex **3-NO_3** (54 µmol, 41.6 %). $^{31}P\{^1H\}$ NMR (101 MHz, CD_2Cl_2) δ: -144.4 (sept, $^1J_{PF}$ = 711.2 Hz, *P*F_6), -14.8 (d br, $^1J_{PAg}$ = 429.6 Hz, *P*-Ag-*P*), 19.7 (dd, J_{PP} = 24.8 Hz, J_{PP} = 16.6 Hz, *P*-CH-*P*) ppm. ^1H NMR (300 MHz, CD_2Cl_2) δ: 3.36 (br m, 4H, P–C*H*$_2$–P), 3.58 (br, 1H, P–C*H*–P), 7.15 (br m, 8H, phenyl-*H*), 7.30 (br m, 16H, phenyl-*H*), 7.41 (br m, 8H, phenyl-*H*), 7.56 (br m, 8H, phenyl-*H*) ppm. ^{19}F NMR (470 MHz, CD_2Cl_2) δ: -72.8 (d, $^1J_{FP}$ = 711.2 Hz, P*F*$_6$) ppm. ^{13}C-APT NMR (126 MHz, CD_2Cl_2) δ: 124.5 (s, phenyl-*C*), 125.3 (s, phenyl-*C*), 129.7 (s, phenyl-*C*), 131.5 (s, phenyl-*C*), 132.6 (t, J_{PC} = 5.0 Hz, phenyl-*C*), 133.4 (t, J_{PC} = 9.5 Hz, phenyl-*C*), 133.9 (s, phenyl-*C* ppm. The CH_2- and (R_3P)CH-resonances of the PCP-ligand could not directly be detected by ^{13}C-APT NMR spectroscopy, but were in part located in the ^1H,^{13}C-HSQC NMR spectrum: δ = 30.0 (P–CH_2–P) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2) δ: -3.8 (m, P–C<u>H</u>–P), 29.6 (br d, J_{PC} = 65.5 Hz, P–C<u>H</u>$_2$–P), 123.3 (br, phenyl-*C*), 124.5 (br, phenyl-*C*), 130.0 (br, phenyl-*C*), 132.1 (s, phenyl-*C*), 132.5 (br, phenyl-*C*), 133.4 (t, J_{PC} = 9.1 Hz, phenyl-*C*), 134.4 (br, phenyl-*C*) ppm.
IR (ATR): $\tilde{\nu}$ / cm^{-1} = 3061 (w), 2891 (w), 2814 (w), 1589 (w), 1575 (m), 1554 (m), 1484 (m), 1436 (s), 1404 (m), 1336 (w), 1316 (w), 1227 (m), 1185 (m), 1154 (w), 1141 (w), 1107 (m), 1072 (m), 1029 (m), 1009 (m), 989 (m), 924 (w), 823 (vs), 778 (m), 756 (s), 742 (s), 732 (vs), 687 (vs), 659 (m), 617 (w), 556 (s), 529 (m), 519 (m), 499 (s), 484 (s), 472 (s), 445 (m), 418 (m). HR-ESI-MS (+, MeOH) m/z: 887.1439 (calculated for [({dppm}$_2$C}Ag]$^+$), 887.1441 found, Δ = 0.23 ppm). Anal. Calcd for $C_{51}H_{45}Ag_1F_6NO_3P_5$: C 55.86%, H 4.14%; Found: C 55.65%; H 4.09%.

2 Spectra

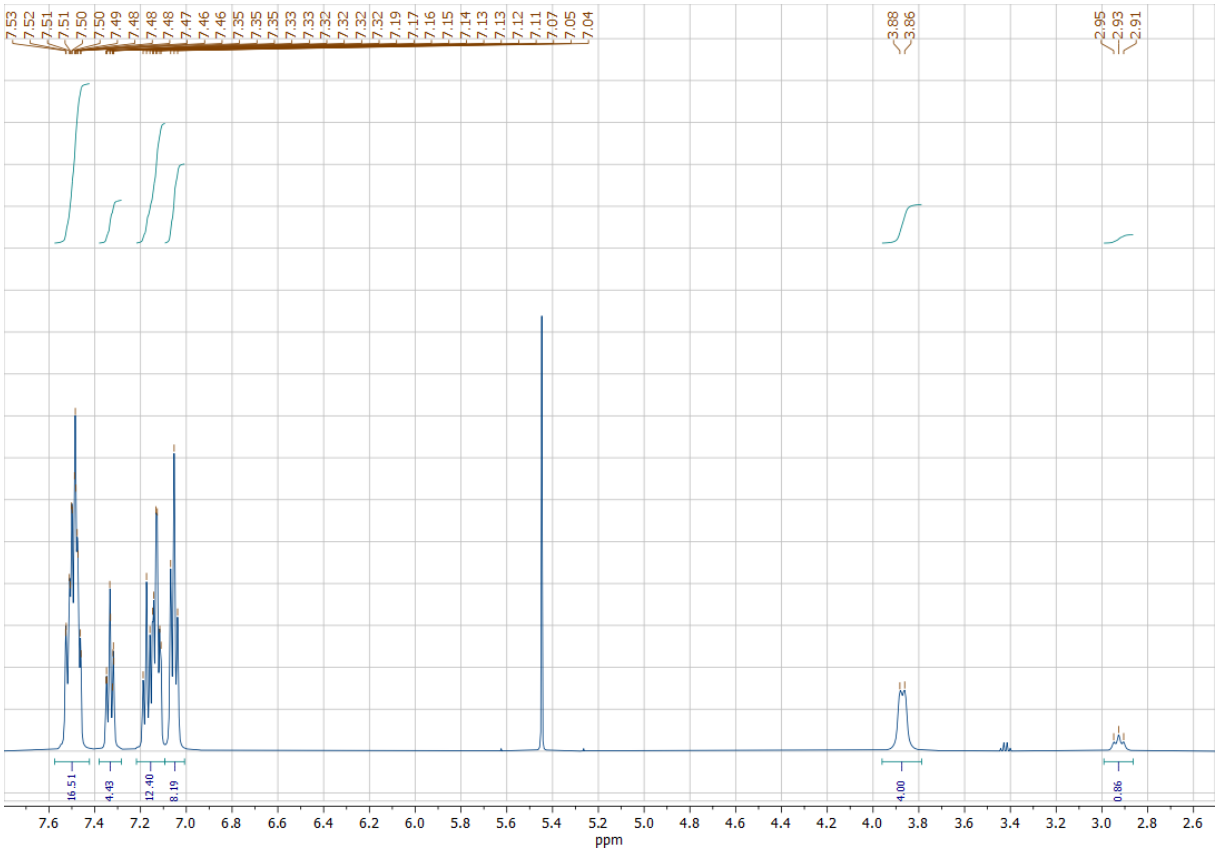

Figure 1 ^{1}H NMR spectrum of [({dppm}$_2$CH)CuCl](PF$_6$) (**2-Cl**) in CD_3CN.

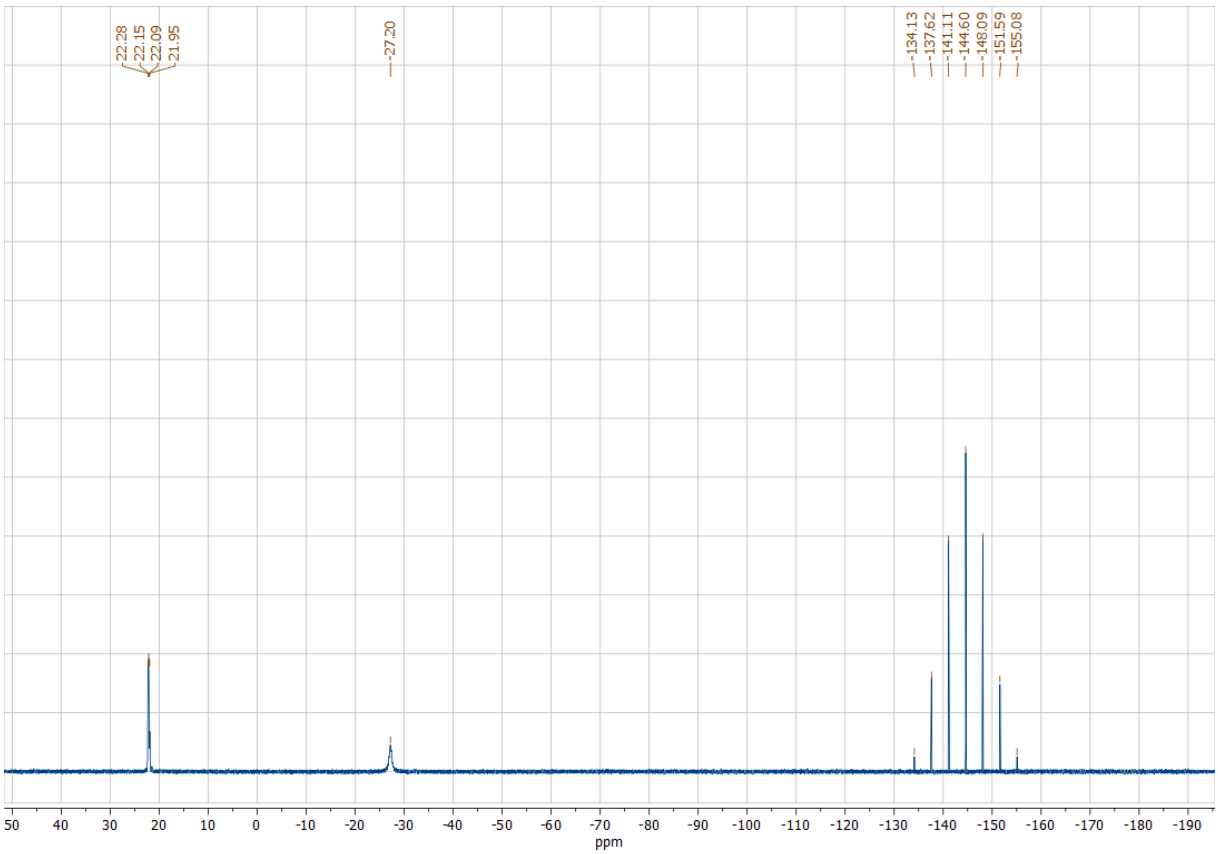

Figure 2 $^{31}P\{^{1}H\}$ NMR spectrum of [({dppm}$_2$CH)CuCl](PF$_6$) (**2-Cl**) in CD_3CN.

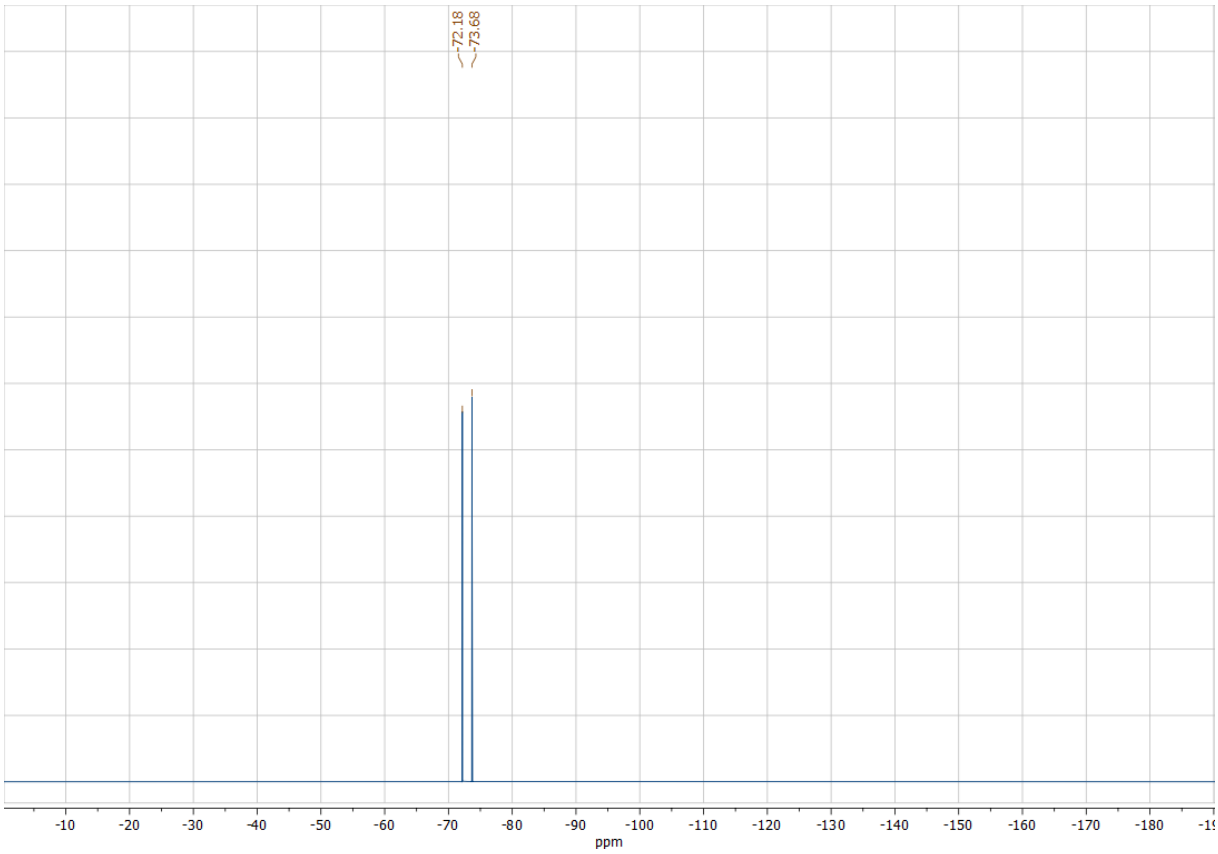

Figure 3 ^{19}F NMR spectrum of [({dppm}$_2$CH)CuCl](PF$_6$) (**2-Cl**) in CD_3CN.

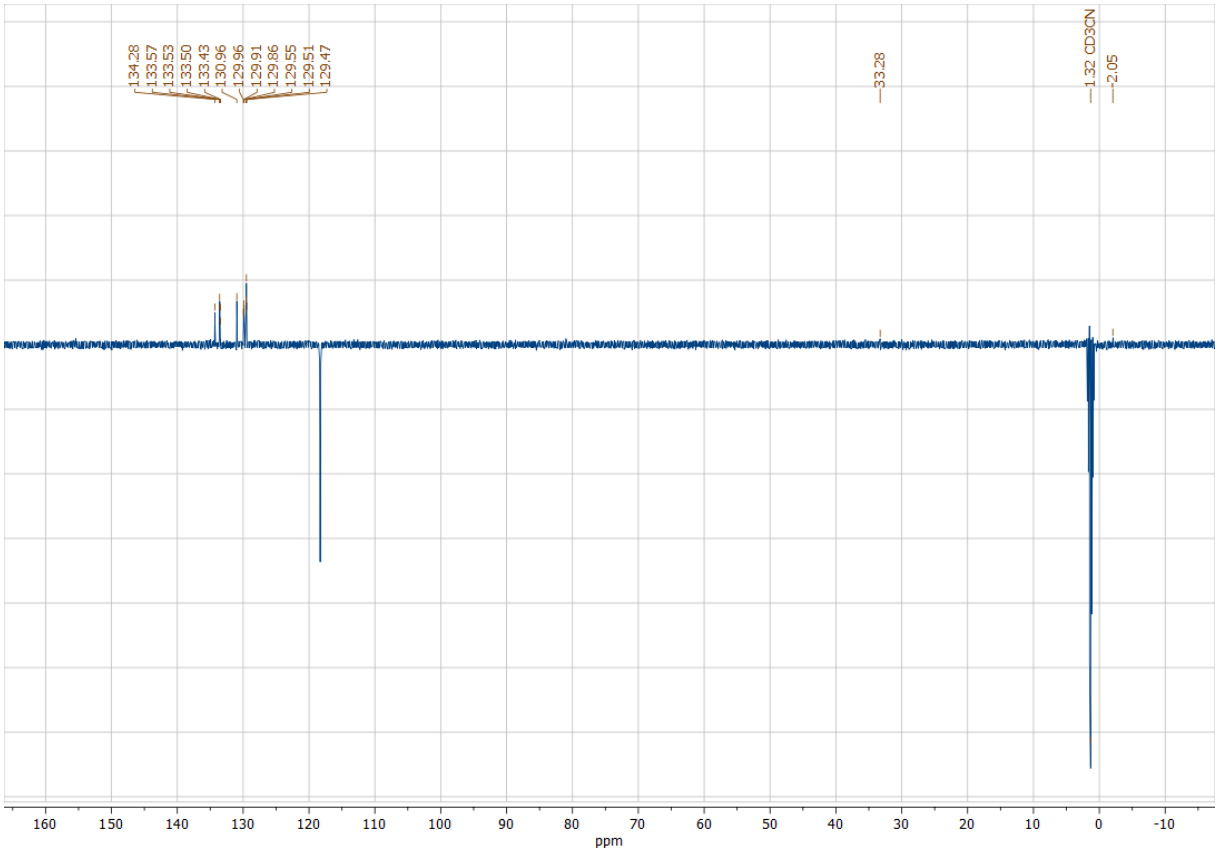

Figure 4 ^{13}C-APT NMR spectrum of [({dppm}$_2$CH)CuCl](PF$_6$) (**2-Cl**) in CD_3CN.

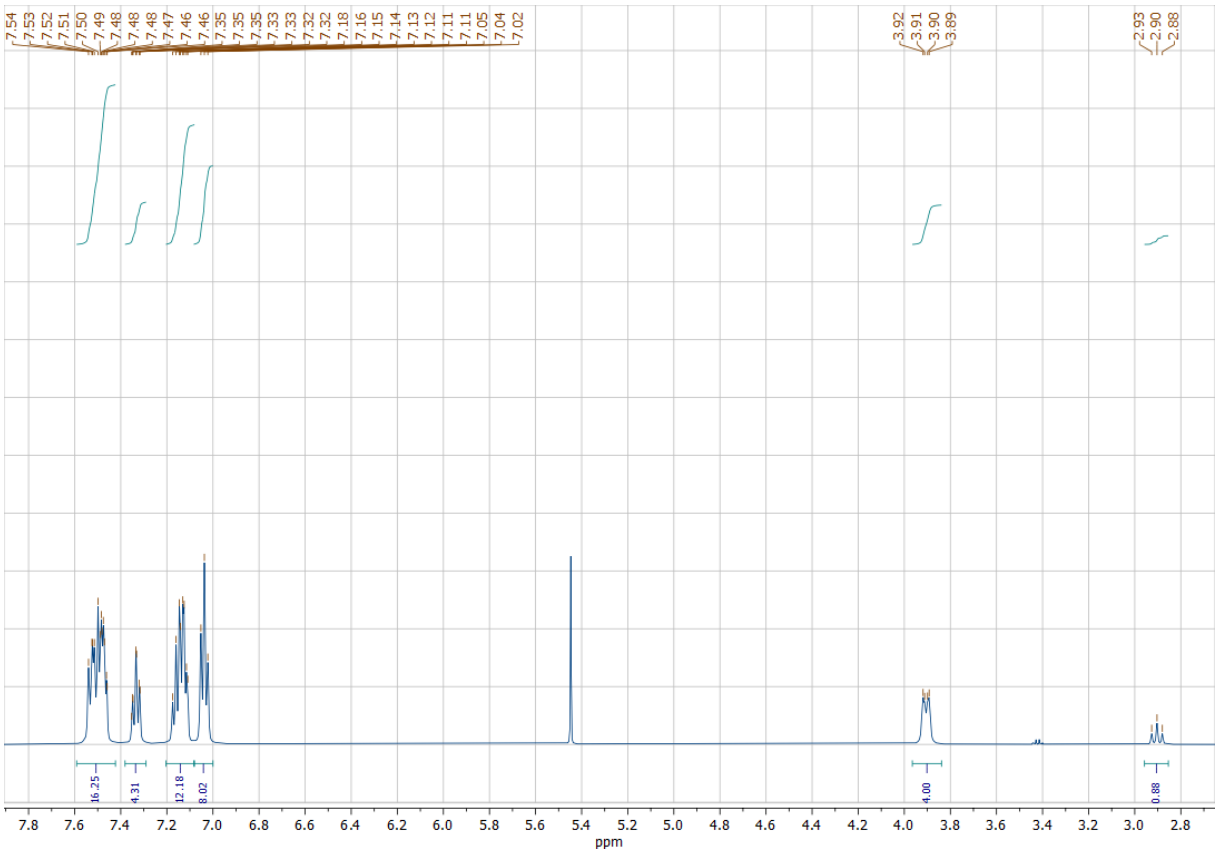

Figure 5 ^{1}H NMR spectrum of [({dppm}$_2$CH)CuBr](PF$_6$) (**2-Br**) in CD_3CN.

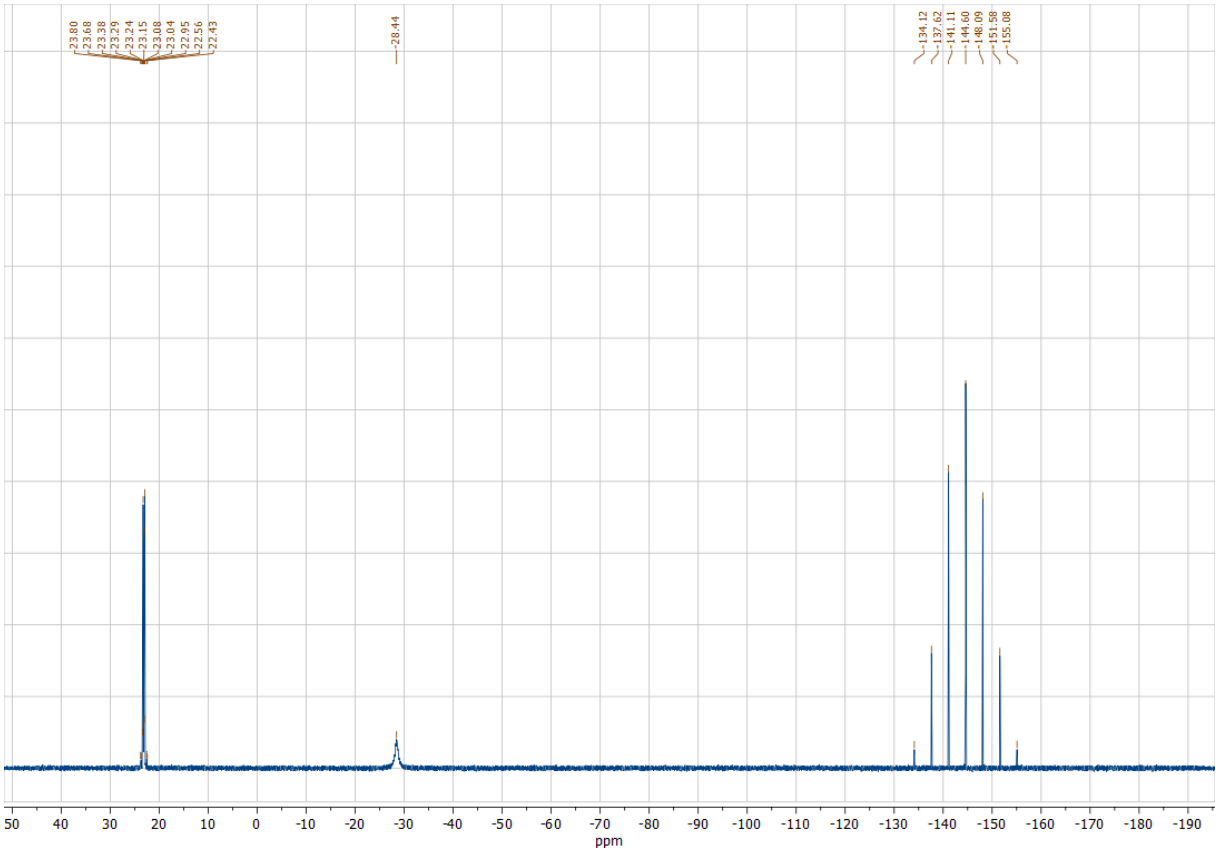

Figure 6 $^{31}P\{^{1}H\}$ NMR spectrum of [({dppm}$_2$CH)CuBr](PF$_6$) (**2-Br**) in CD_3CN.

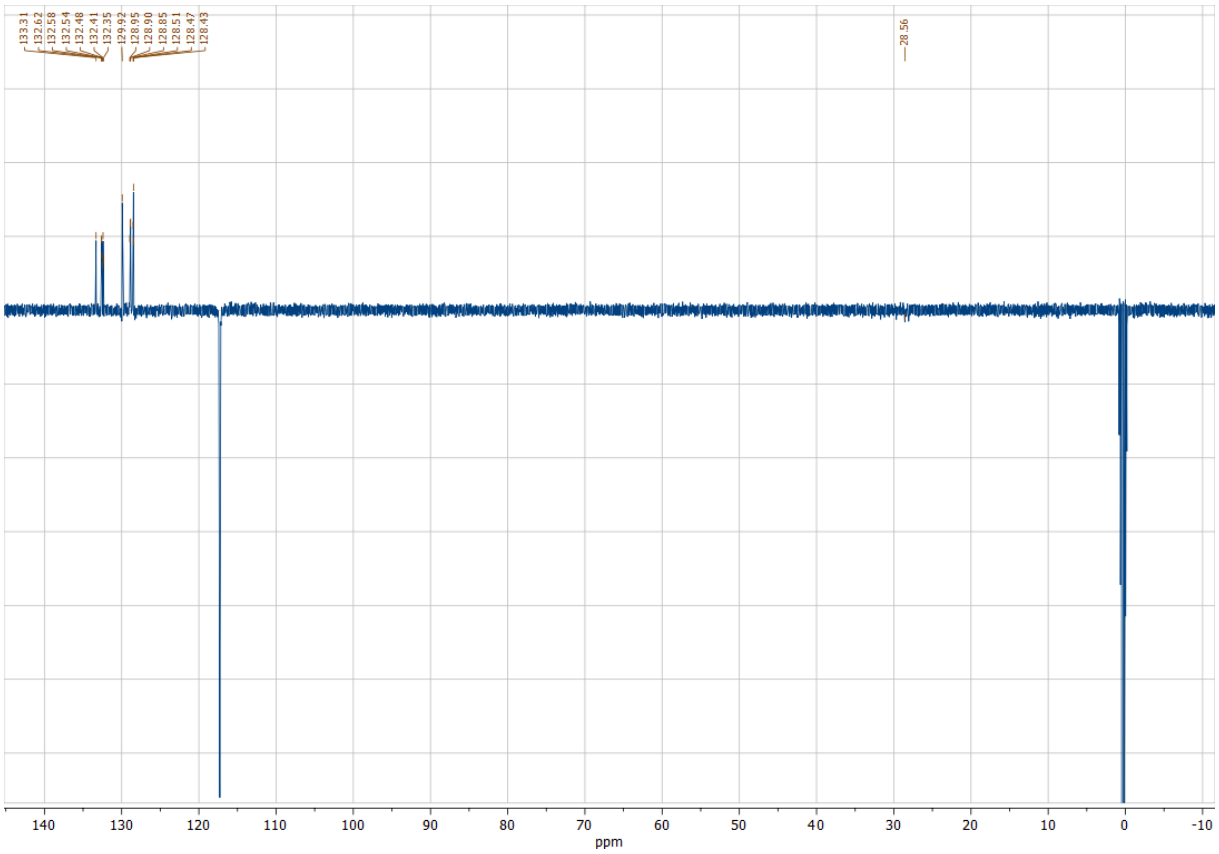

Figure 7 ^{13}C-APT NMR spectrum of [({dppm}$_2$CH)CuBr](PF$_6$) (**2-Br**) in CD$_3$CN.

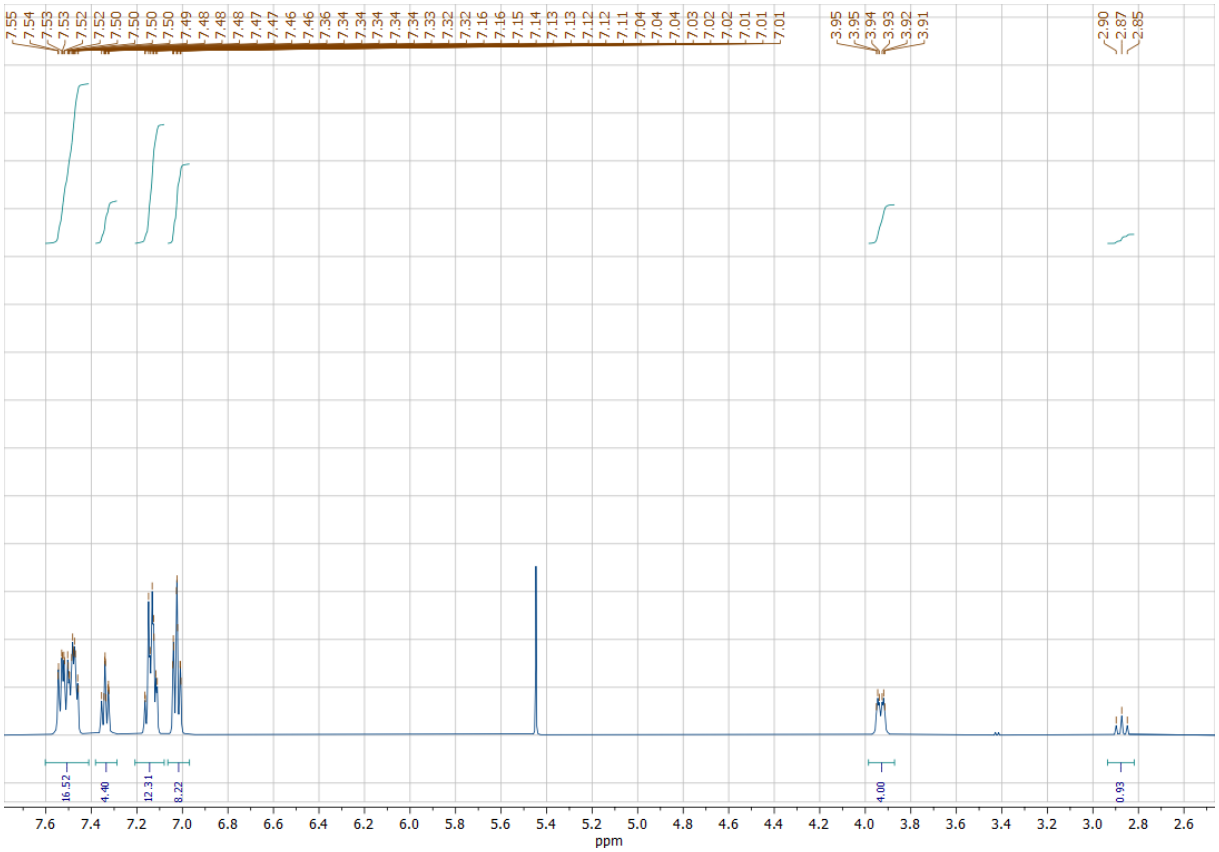

Figure 8 ^{1}H NMR spectrum of [({dppm}$_2$CH)CuI](PF$_6$) (**2-I**) in CD$_3$CN.

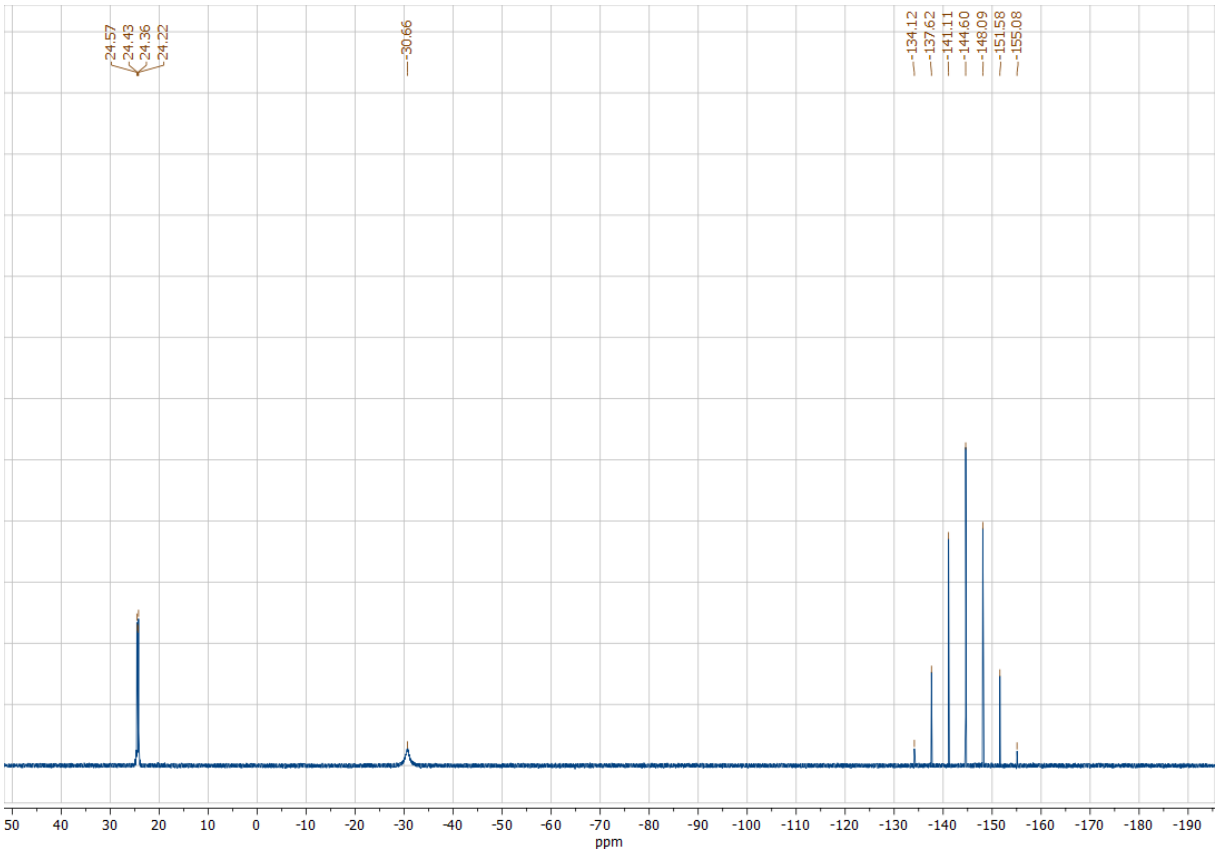

Figure 9 $^{31}P\{^{1}H\}$ NMR spectrum of [({dppm}$_2$CH)CuI](PF$_6$) (**2-I**) in CD_3CN.

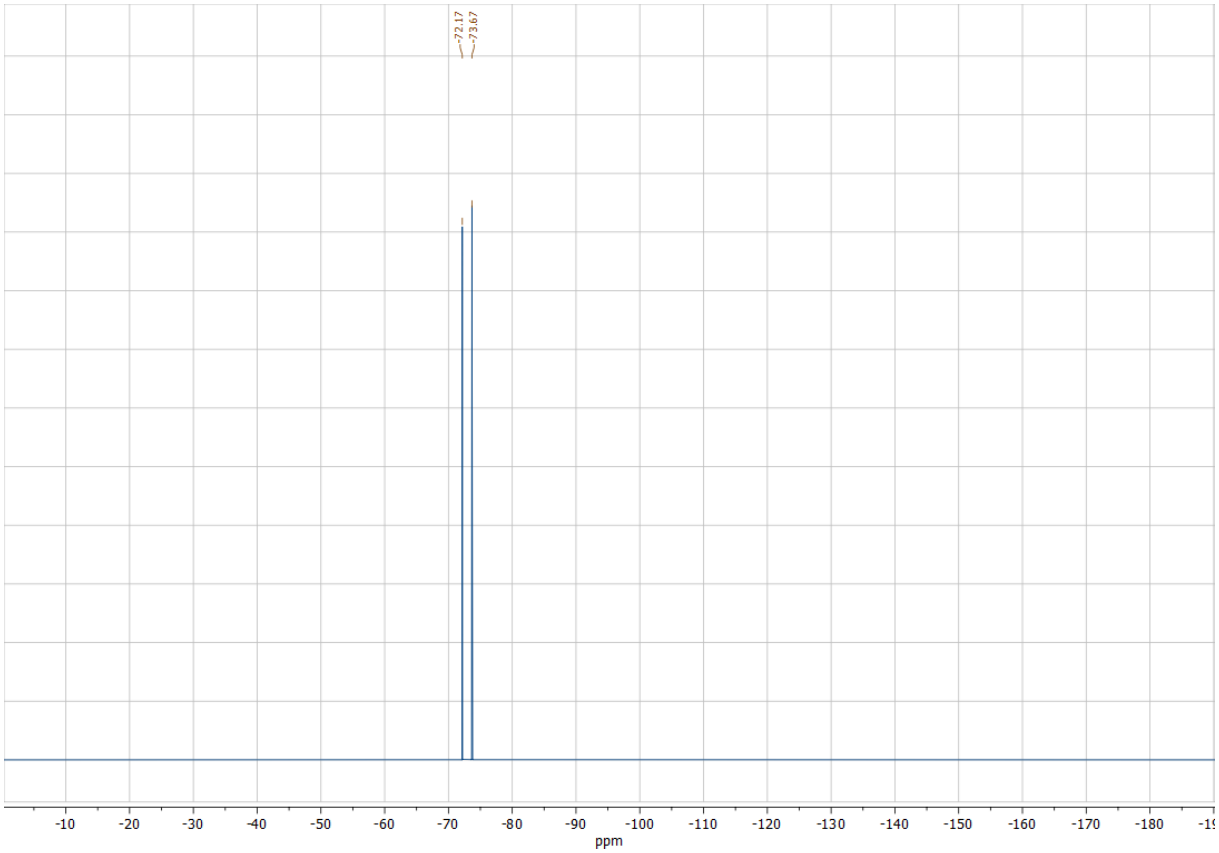

Figure 10 ^{19}F NMR spectrum of [({dppm}$_2$CH)CuI](PF$_6$) (**2-I**) in CD_3CN.

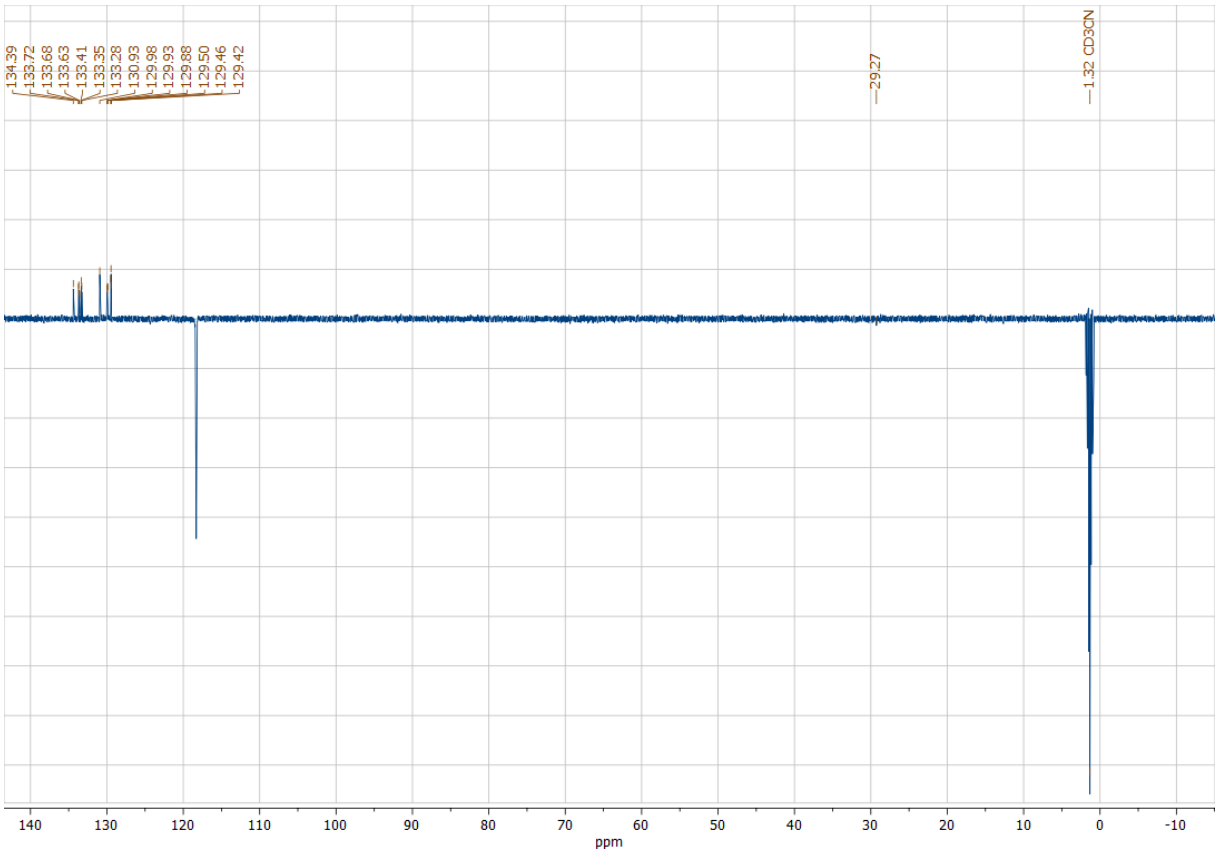

Figure 11 ^{13}C-APT NMR spectrum of [({dppm}$_2$CH)CuBr](PF$_6$) (**2-I**) in CD$_3$CN.

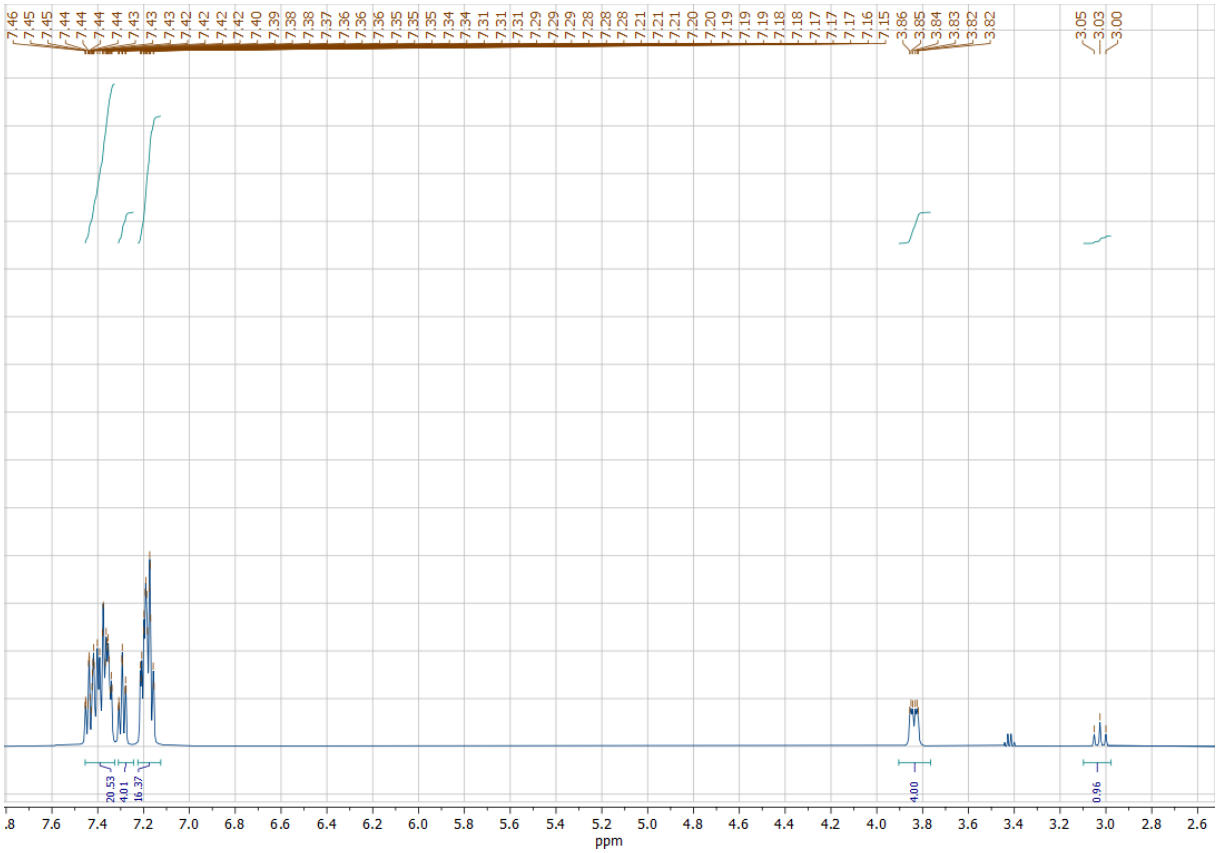

Figure 12 ^{1}H NMR spectrum of [({dppm}$_2$CH)Cu(NCMe)](PF$_6$)(BF$_4$) (**2-MeCN**) in CD$_3$CN.

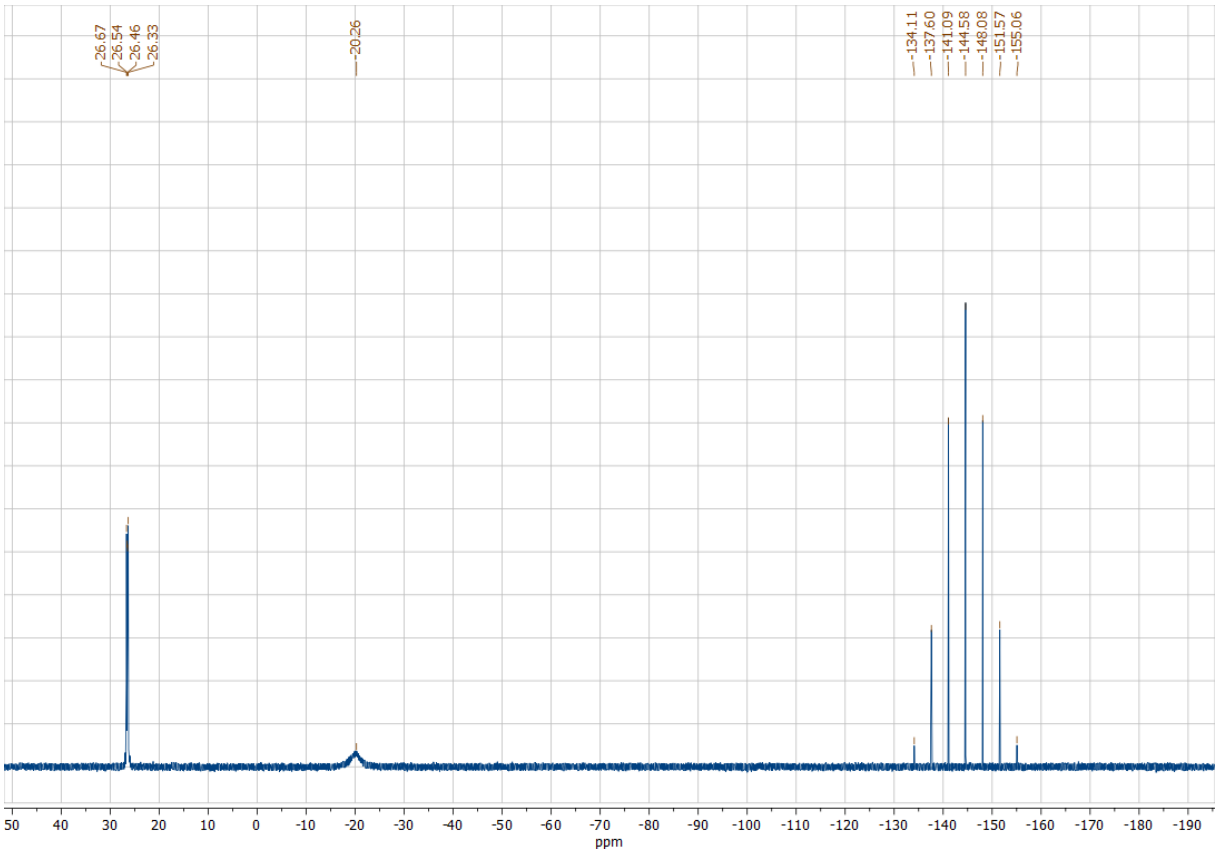

Figure 13 $^{31}P\{^{1}H\}$ NMR spectrum [({dppm}$_2$CH)Cu(NCMe)](PF$_6$)(BF$_4$) (**2-MeCN**) in CD_3CN.

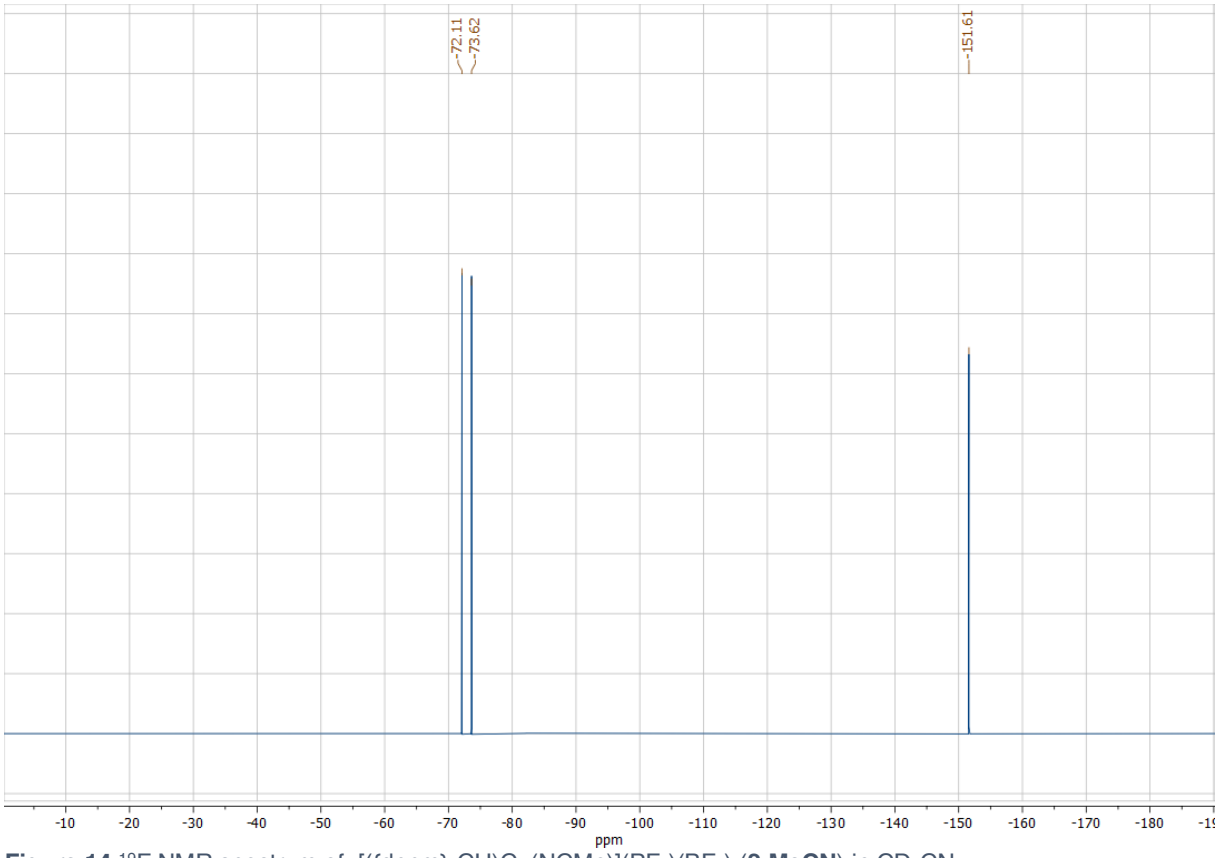

Figure 14 ^{19}F NMR spectrum of [({dppm}$_2$CH)Cu(NCMe)](PF$_6$)(BF$_4$) (**2-MeCN**) in CD_3CN.

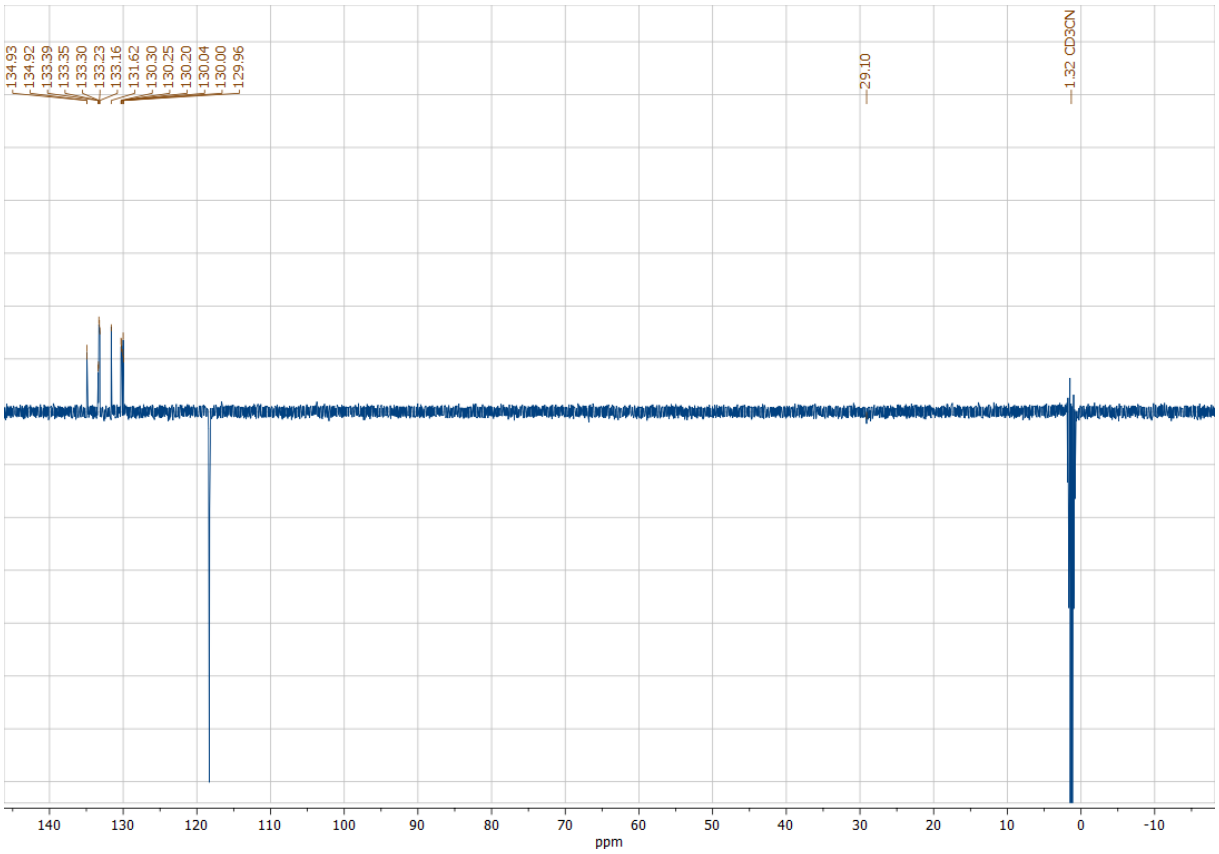

Figure 15 ^{13}C-APT NMR spectrum of [({dppm}$_2$CH)Cu(NCMe)](PF$_6$)(BF$_4$) (**2-MeCN**) in CD_3CN.

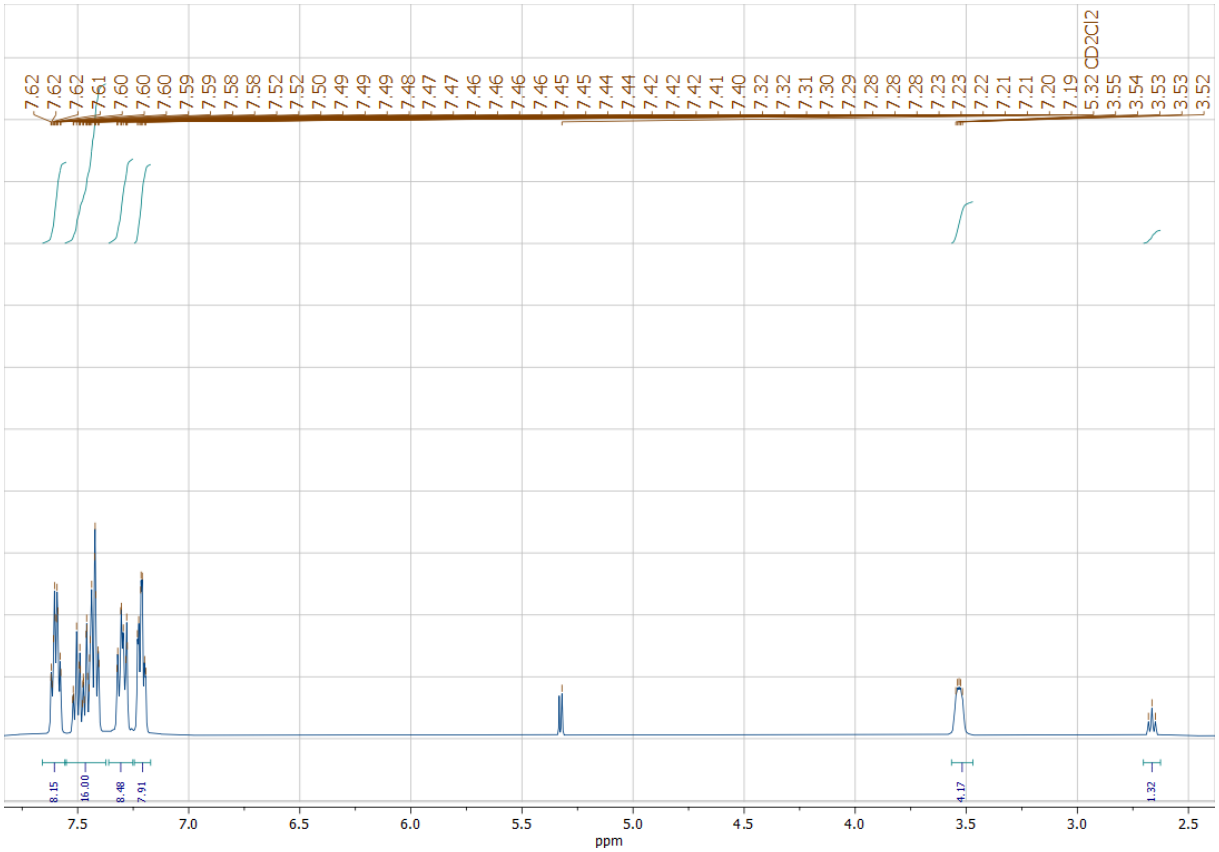

Figure 16 ^{1}H NMR spectrum of [({dppm}$_2$CH)Ag](PF$_6$)$_2$ (**3**) in CD_2Cl_2.

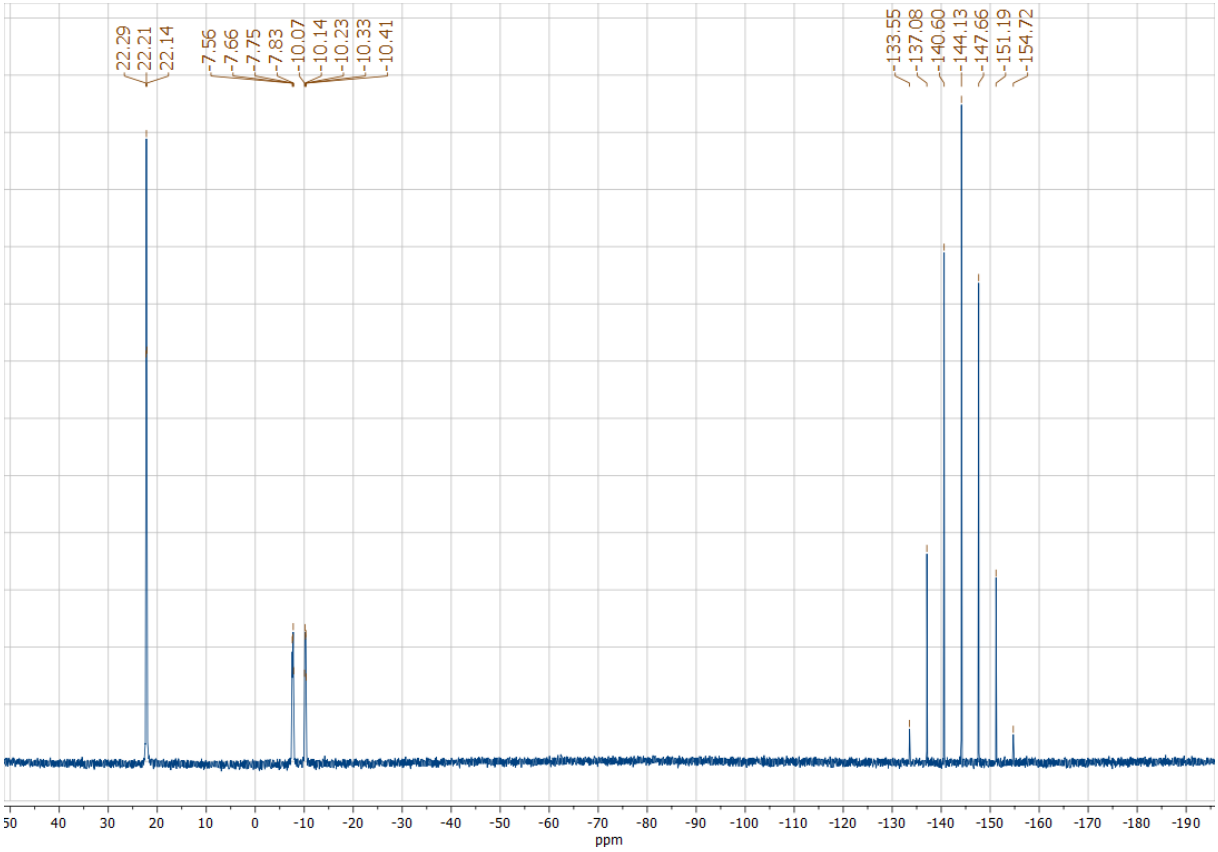

Figure 17 $^{31}P\{^{1}H\}$ NMR spectrum of $[(\{dppm\}_2CH)Ag](PF_6)_2$ (**3**) in CD_2Cl_2.

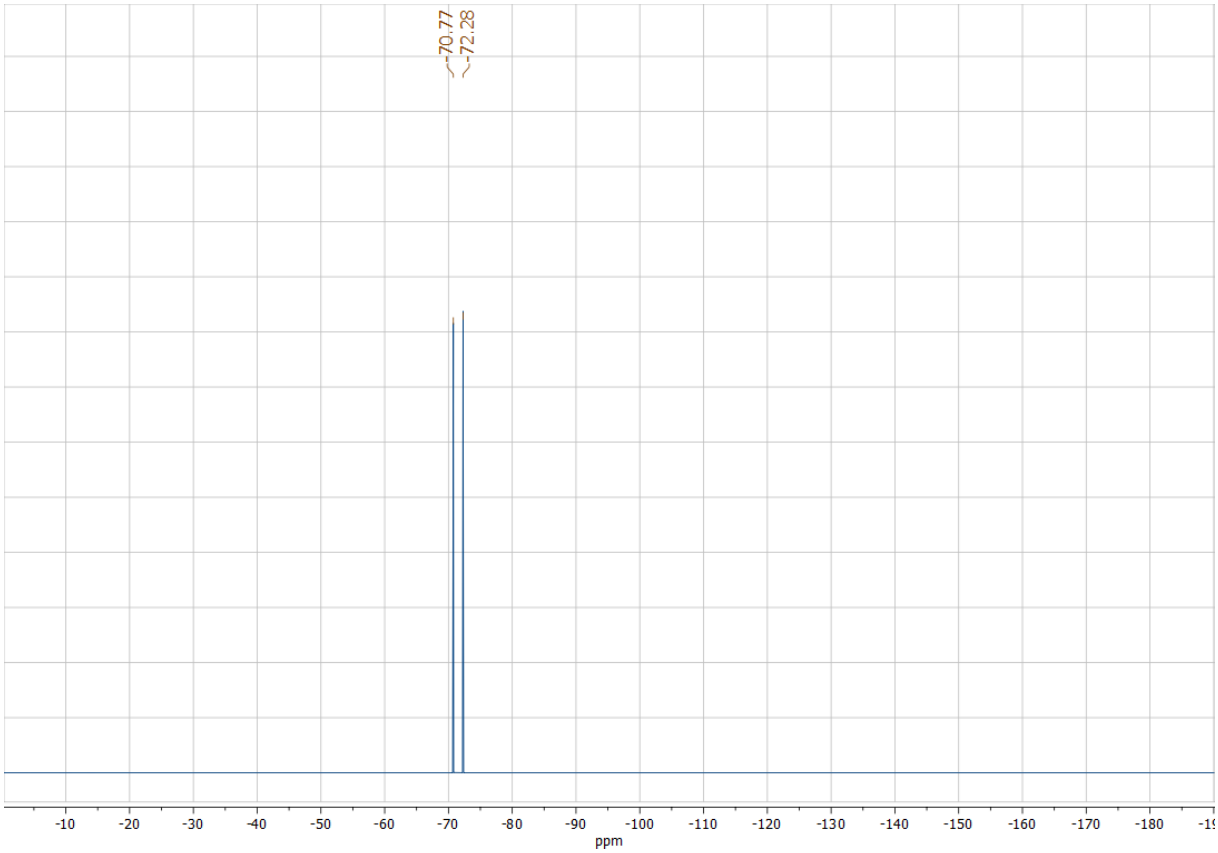

Figure 18 ^{19}F NMR spectrum of $[(\{dppm\}_2CH)Ag](PF_6)_2$ (**3**) in CD_2Cl_2.

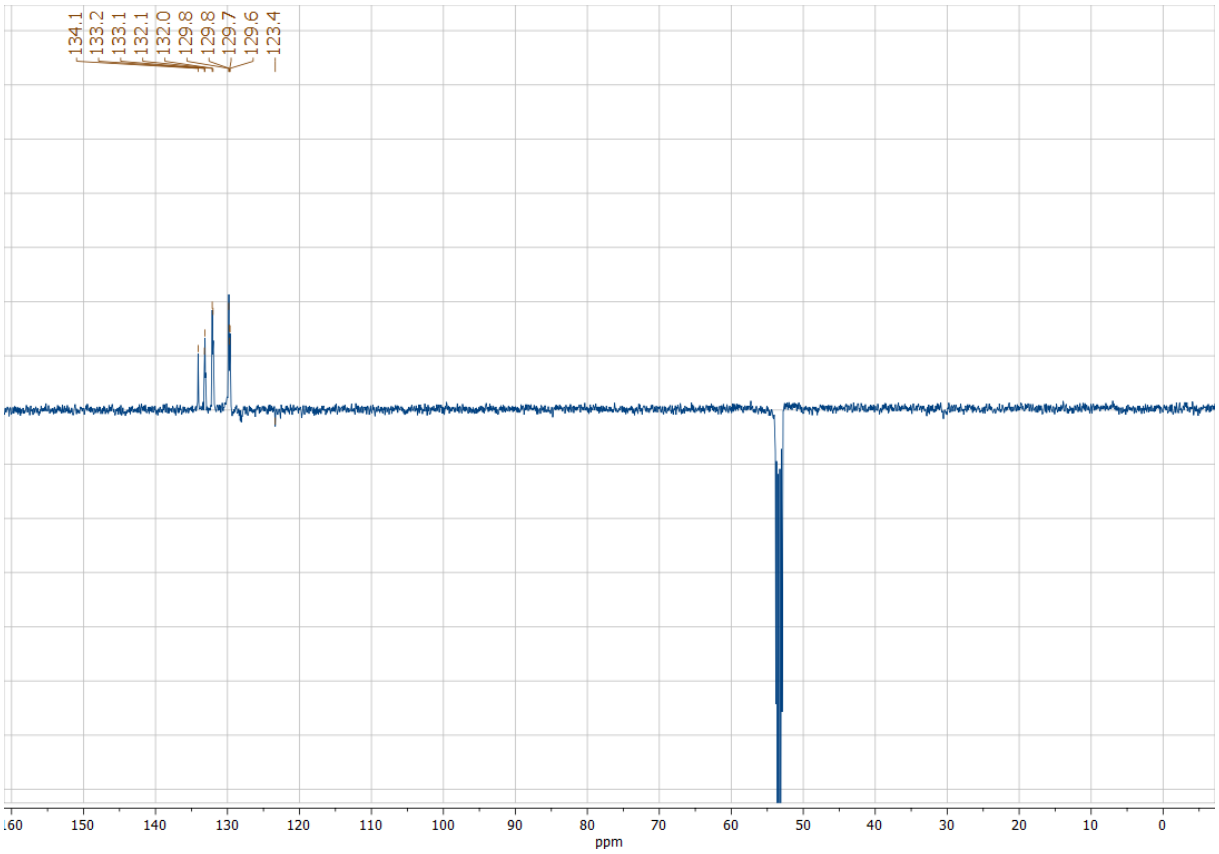

Figure 19 ^{13}C-APT NMR spectrum of [({dppm}$_2$CH)Ag](PF$_6$)$_2$ (**3**) in CD_2Cl_2.

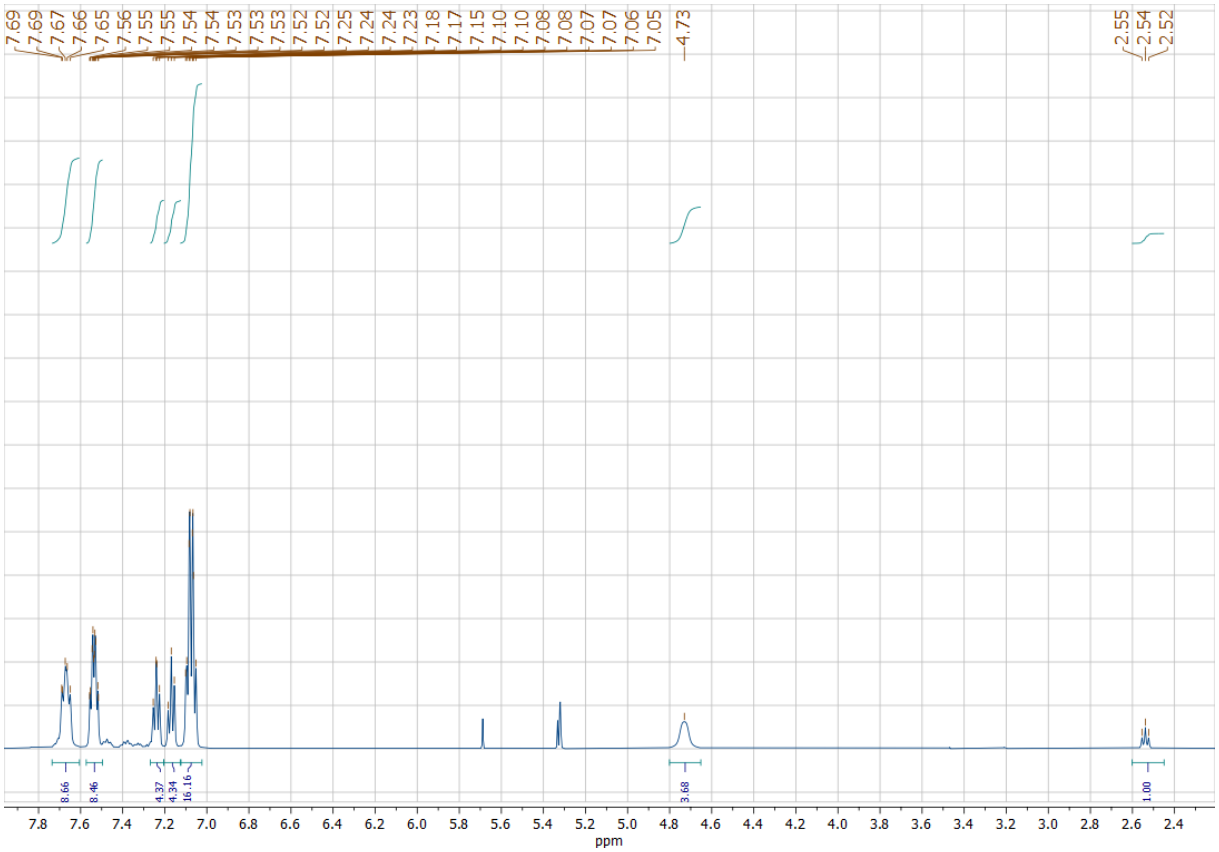

Figure 20 ^{1}H NMR spectrum of [({dppm}$_2$CH)AgCl](NO$_3$) (**3-Cl**) in CD_2Cl_2.

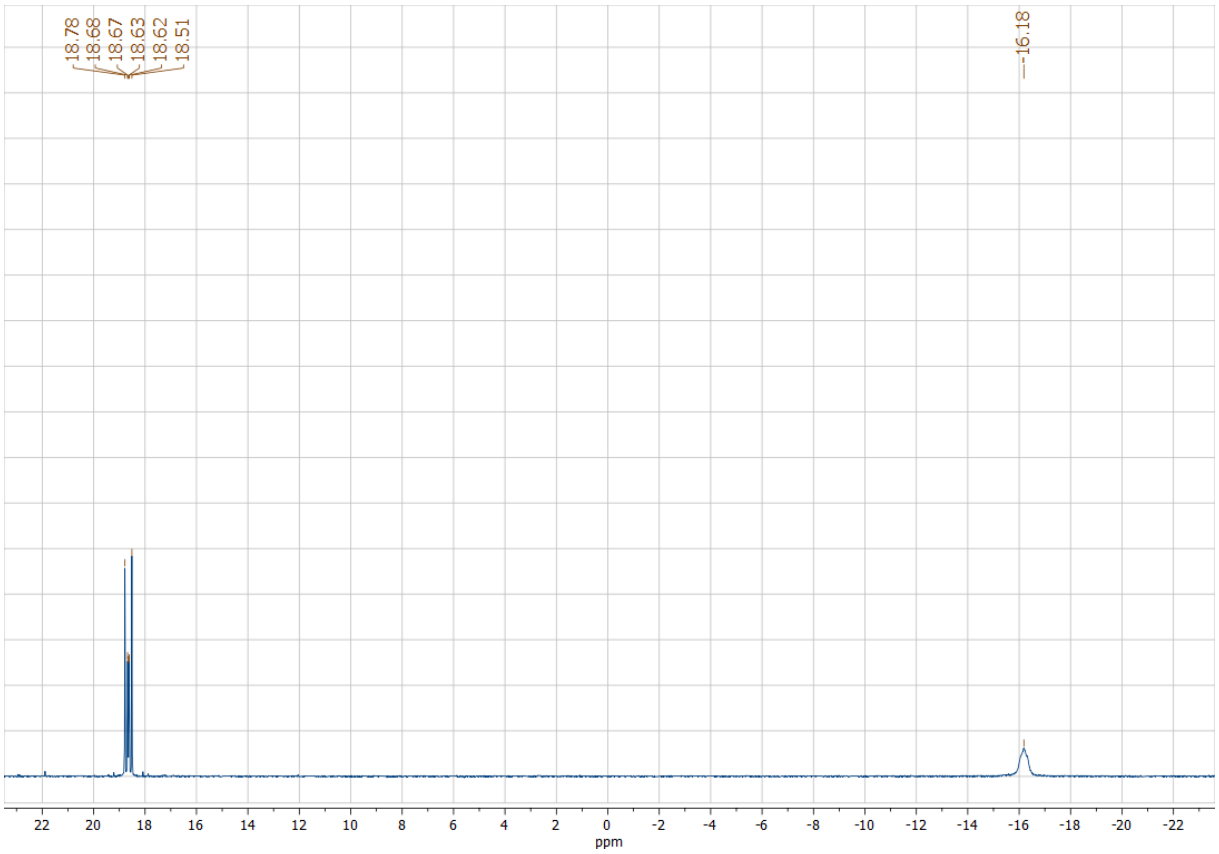

Figure 21 $^{31}P\{^{1}H\}$ NMR spectrum of [({dppm}$_2$CH)AgCl](NO$_3$) (**3-Cl**) in CD_2Cl_2.

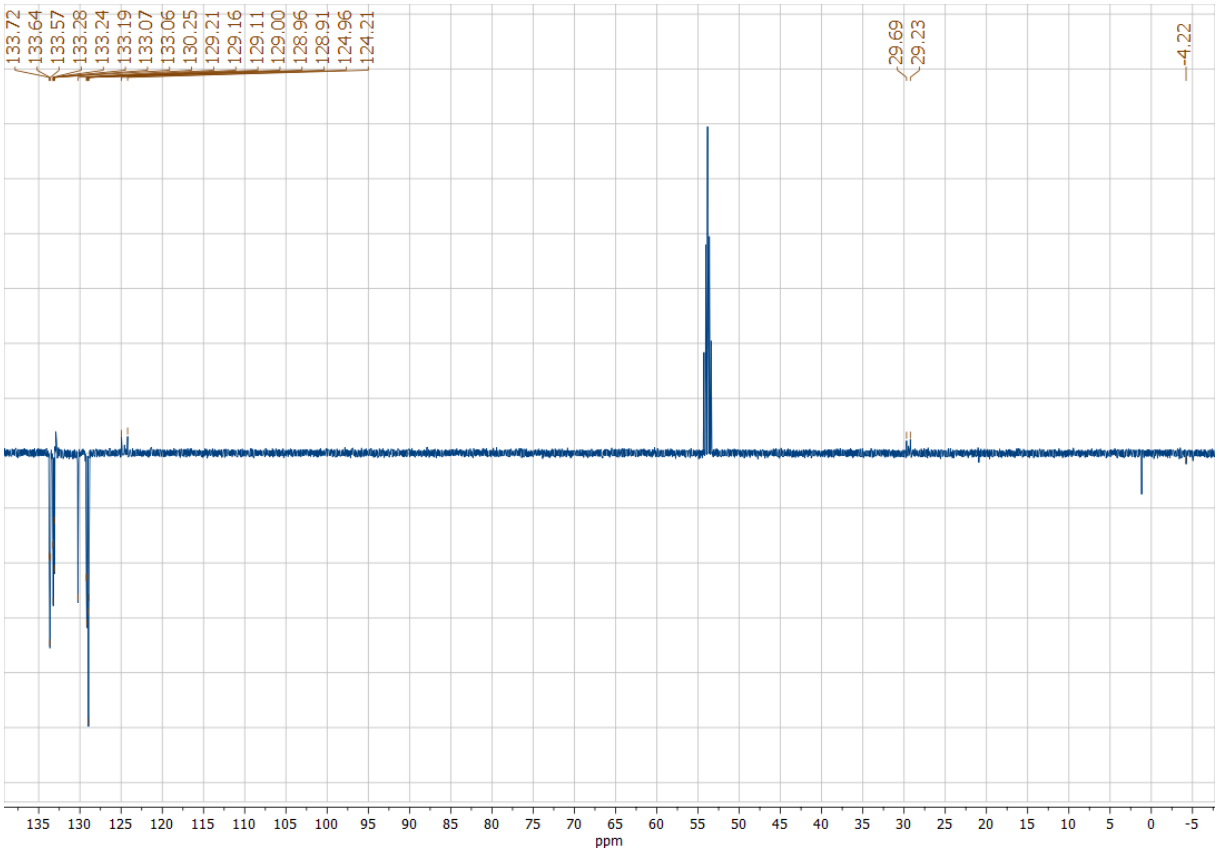

Figure 22 ^{13}C-APT NMR spectrum of [({dppm}$_2$CH)AgCl](NO$_3$) (**3-Cl**) in CD_2Cl_2.

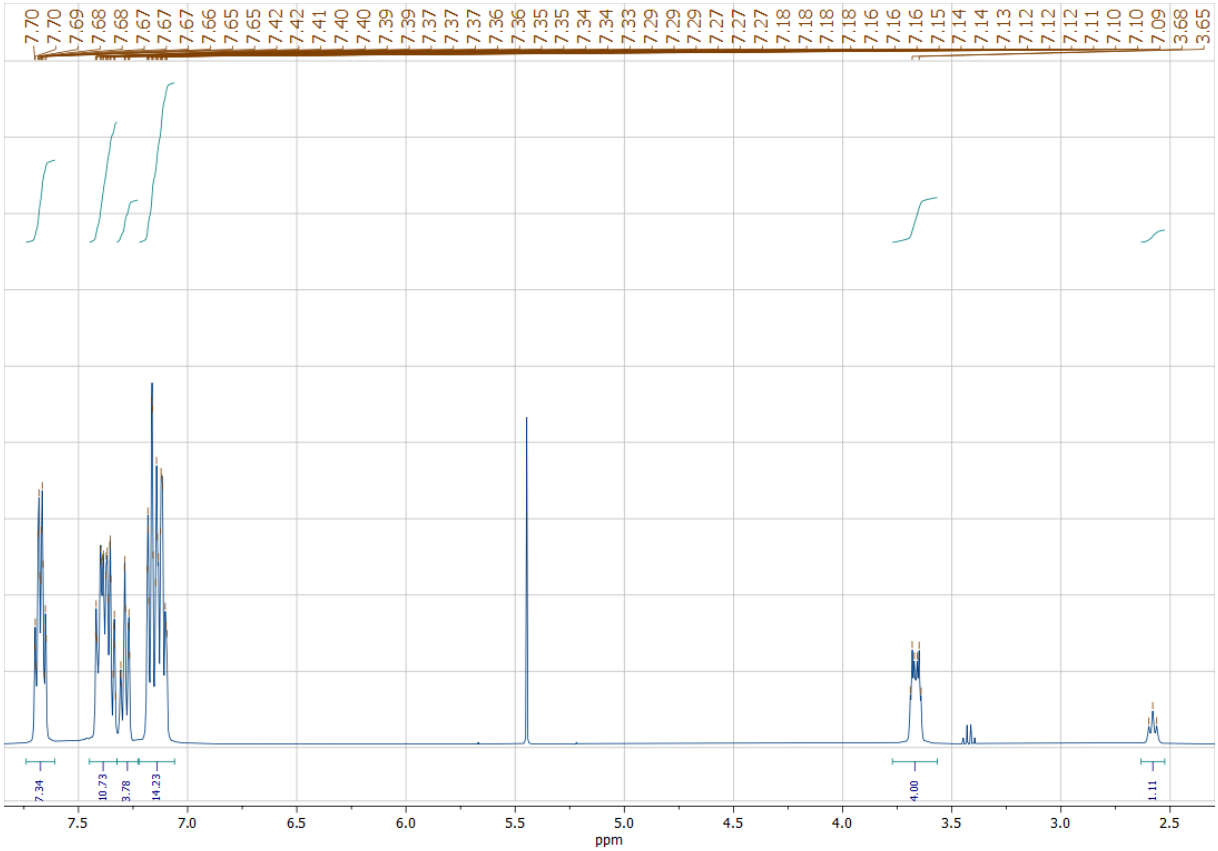

Figure 23 ^{1}H NMR spectrum of [({dppm}$_2$CH)AgBr](PF$_6$) (**3-Br**) in CD_3CN.

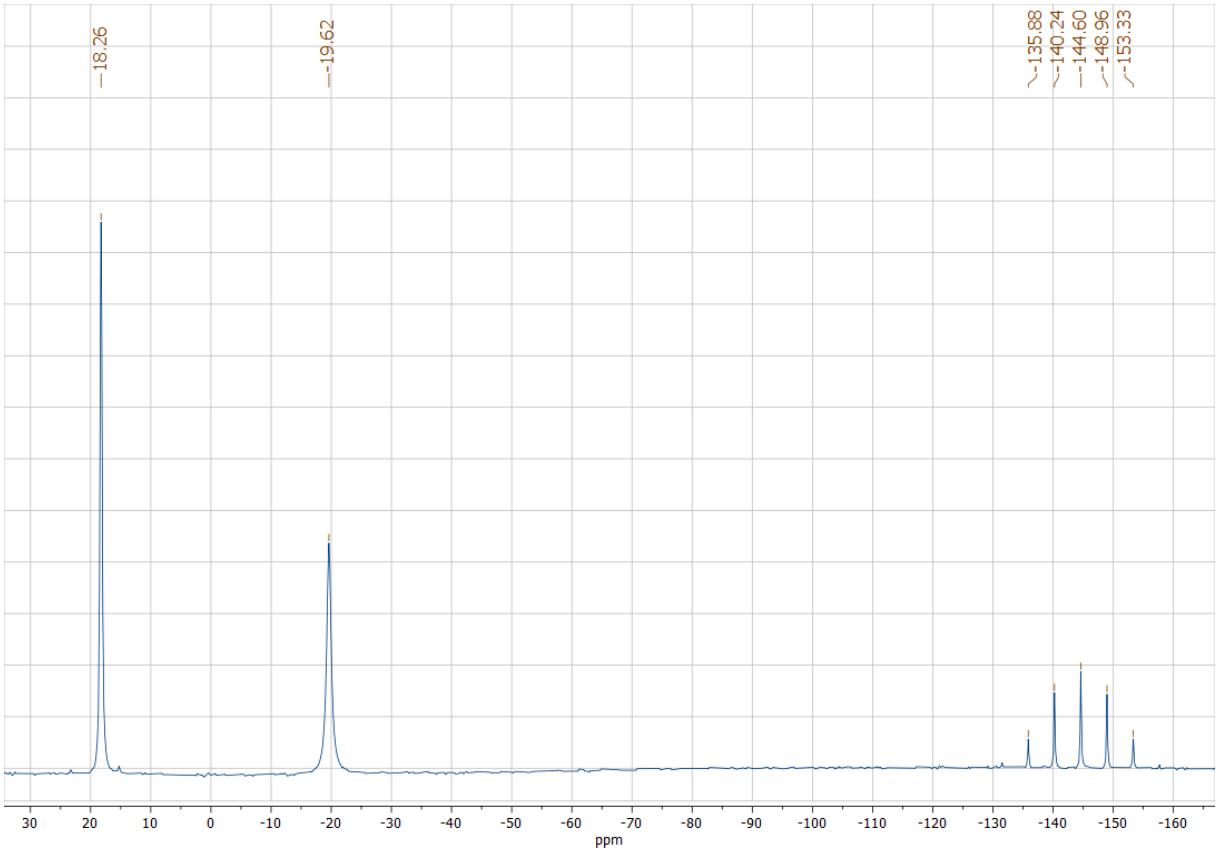

Figure 24 $^{31}P\{^{1}H\}$ NMR spectrum of [({dppm}$_2$CH)AgBr](PF$_6$) (**3-Br**) in CD_3CN.

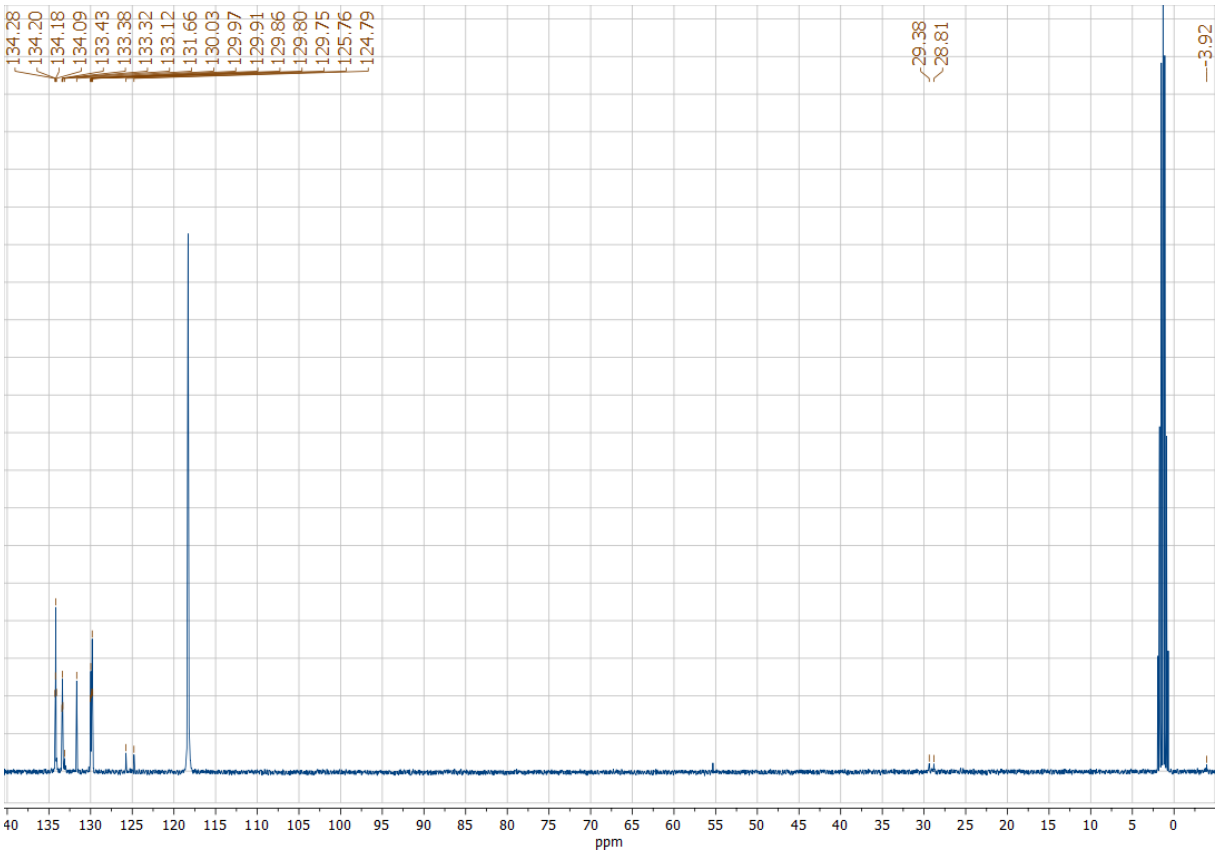

Figure 25 ^{13}C-APT NMR spectrum of [({dppm}$_2$CH)AgBr](PF$_6$) (**3-Br**) in CD_3CN.

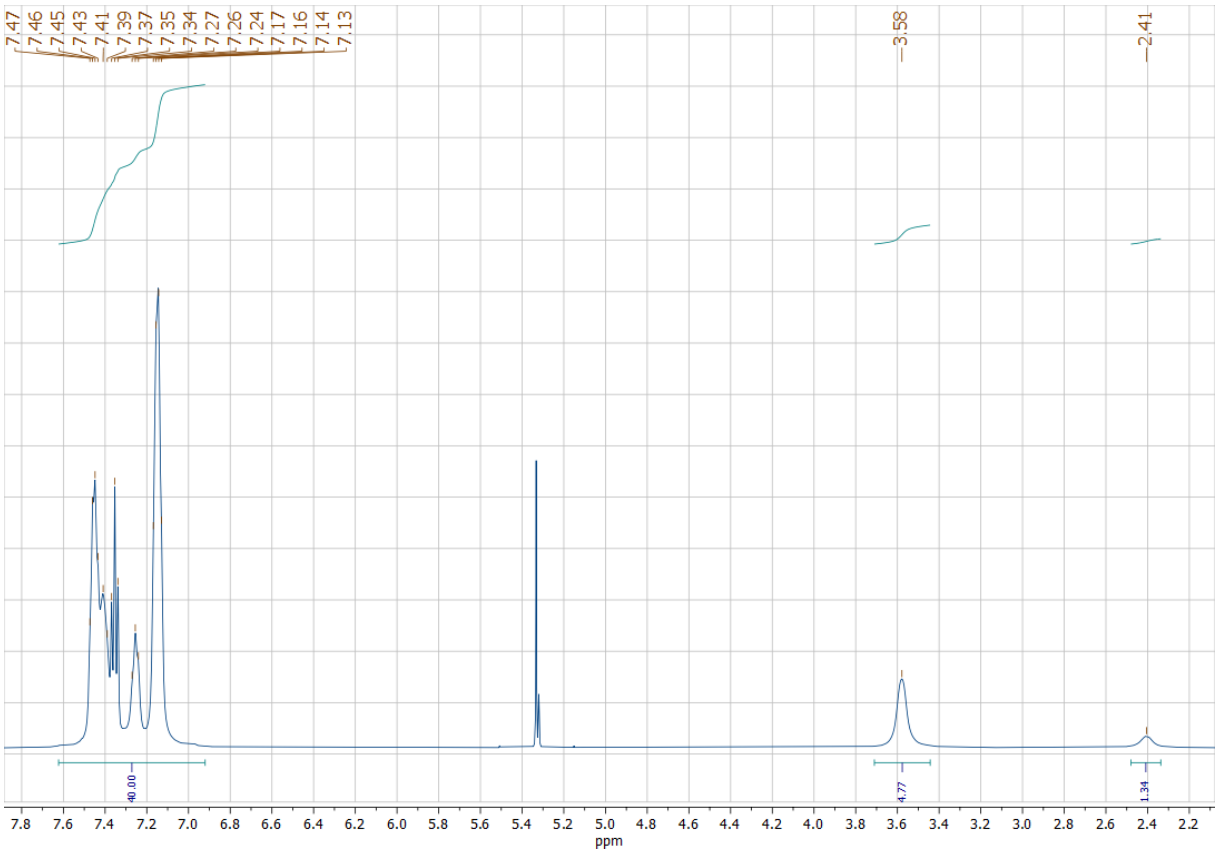

Figure 26 ^{1}H NMR spectrum of [({dppm}$_2$CH)AgI](PF$_6$) (**3-I**) in CD_2Cl_2.

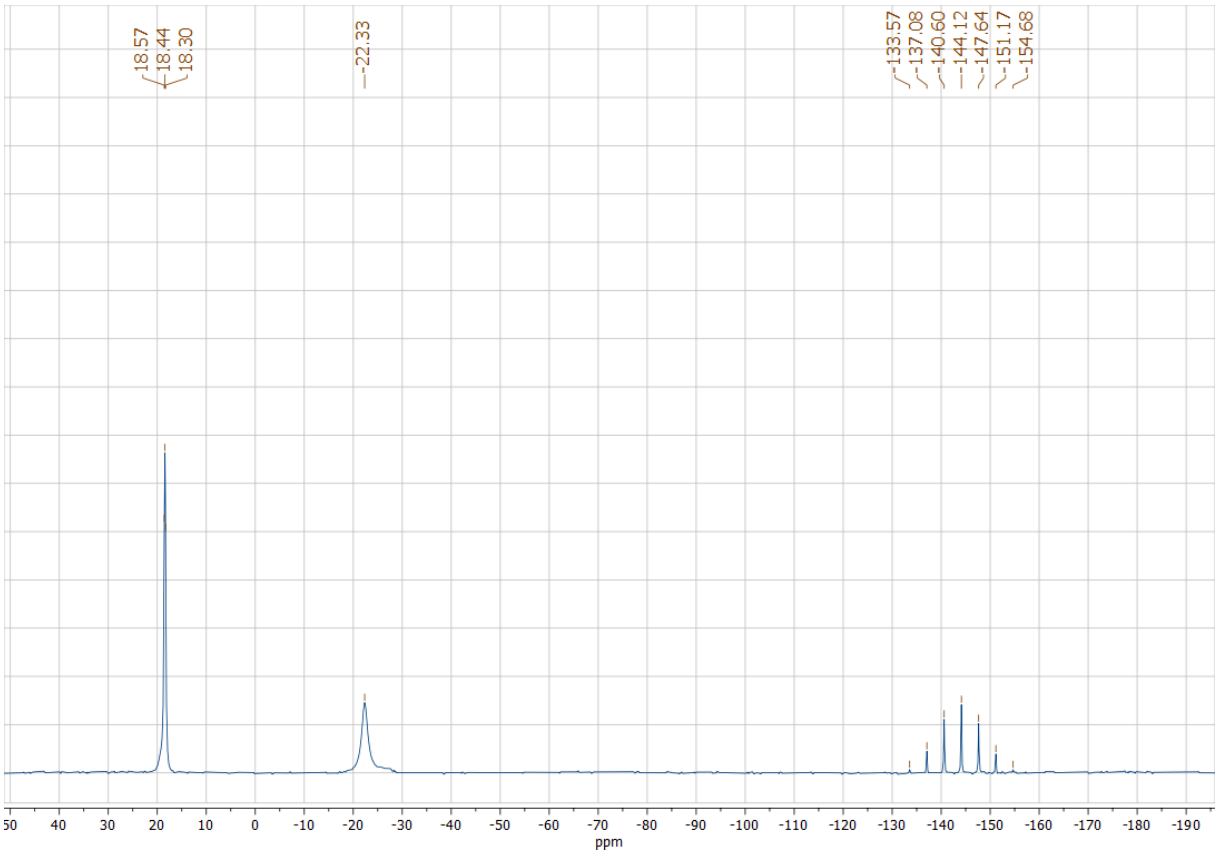

Figure 27 $^{31}P\{^{1}H\}$ NMR spectrum of [({dppm}$_2$CH)AgI](PF$_6$) (**3-I**) in CD_2Cl_2.

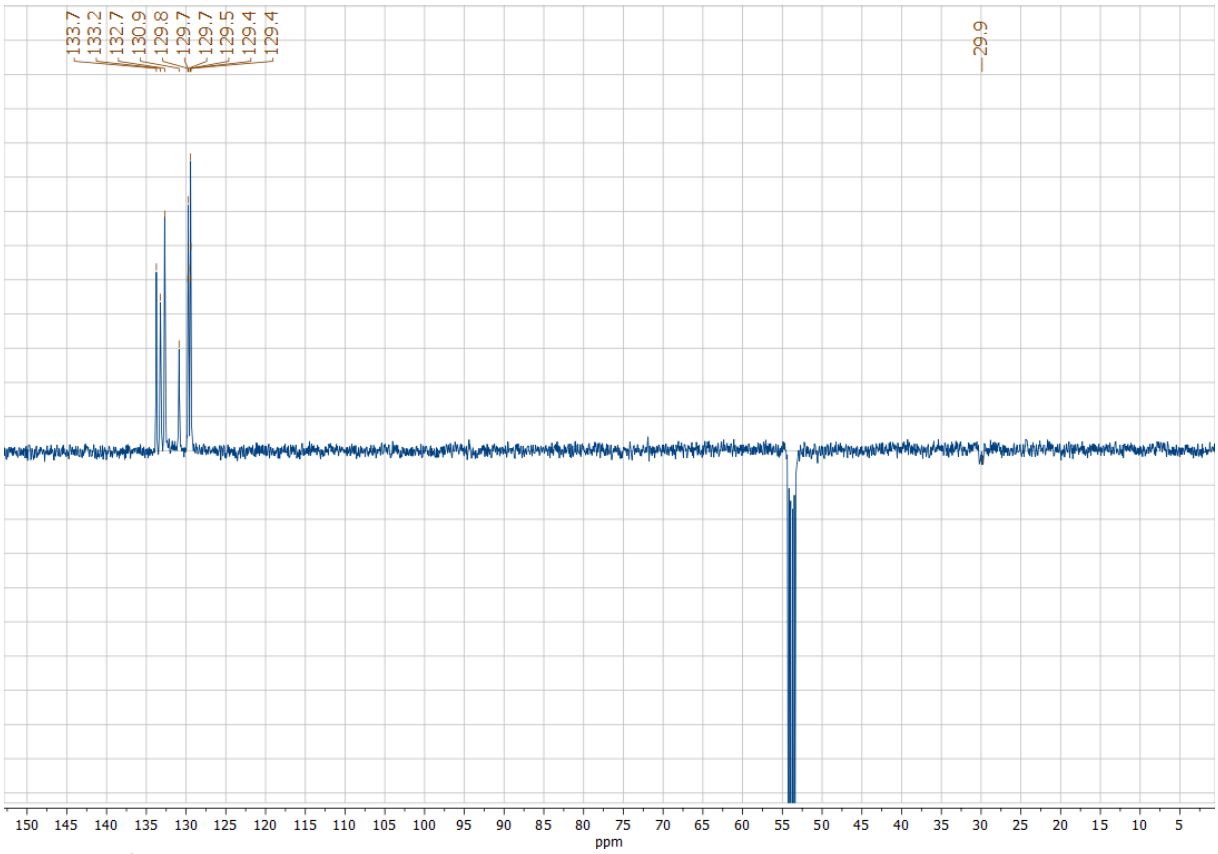

Figure 28 ^{13}C-APT NMR spectrum of [({dppm}$_2$CH)AgI](PF$_6$) (**3-I**) in CD_2Cl_2.

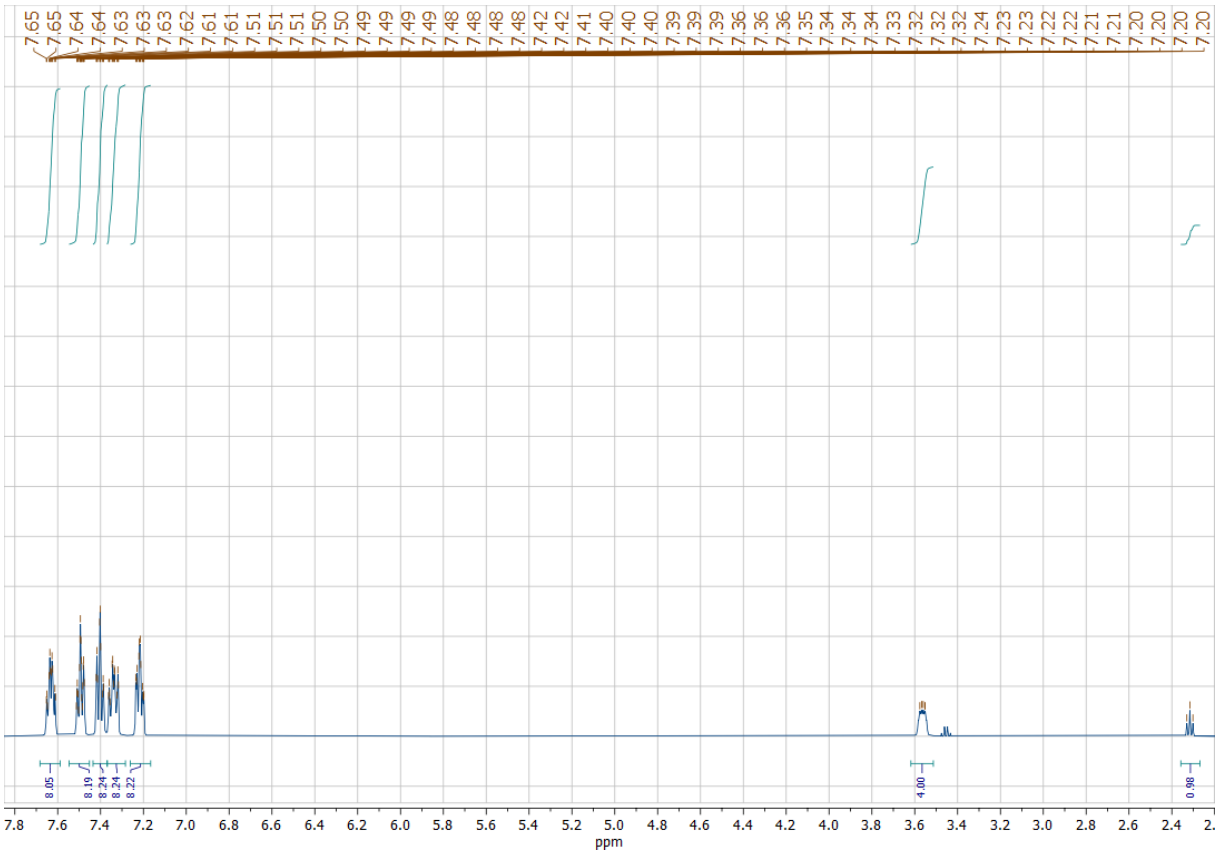

Figure 29 ^{1}H NMR spectrum of [({dppm}$_2$CH)Ag(NCMe)](PF$_6$)$_2$ (**3-NCMe**) in CD_3CN.

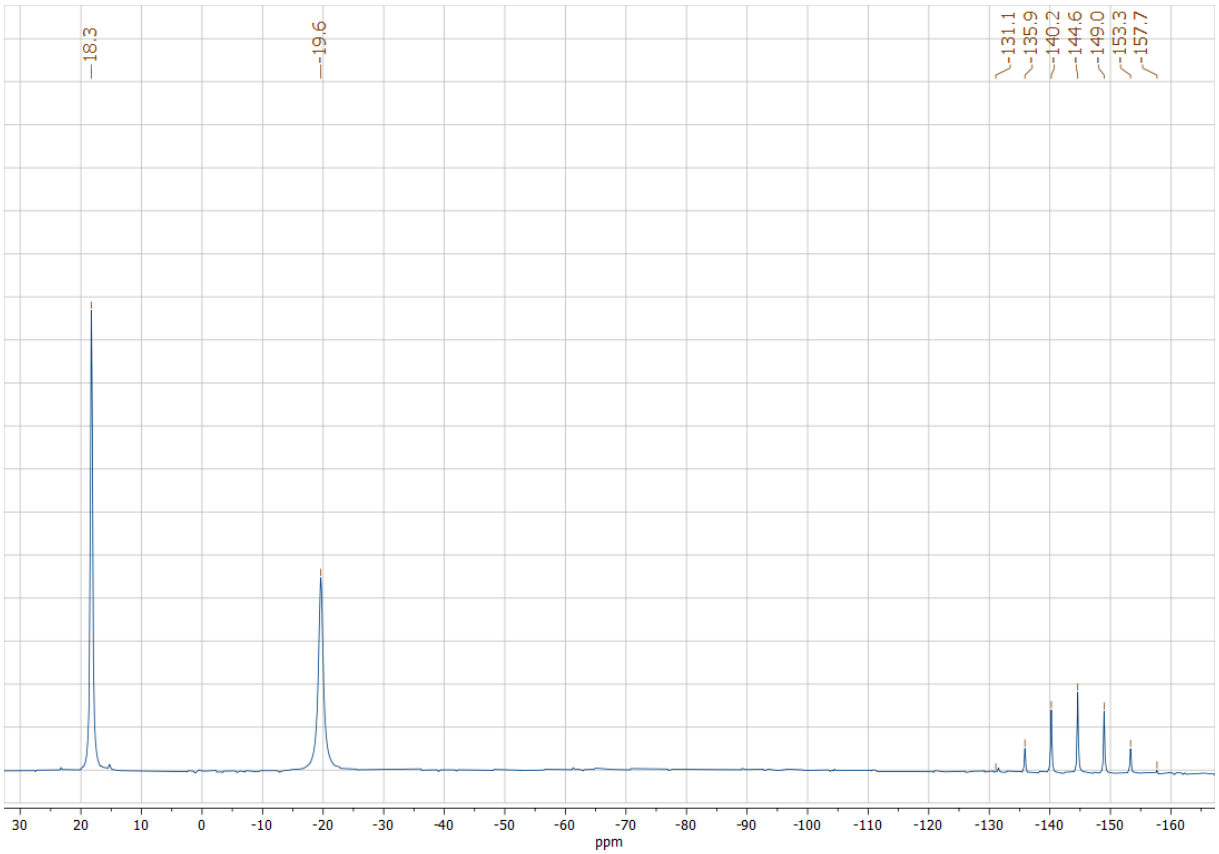

Figure 30 $^{31}P\{^{1}H\}$ NMR spectrum of [({dppm}$_2$CH)Ag(NCMe)](PF$_6$)$_2$ (**3-NCMe**) in CD_3CN.

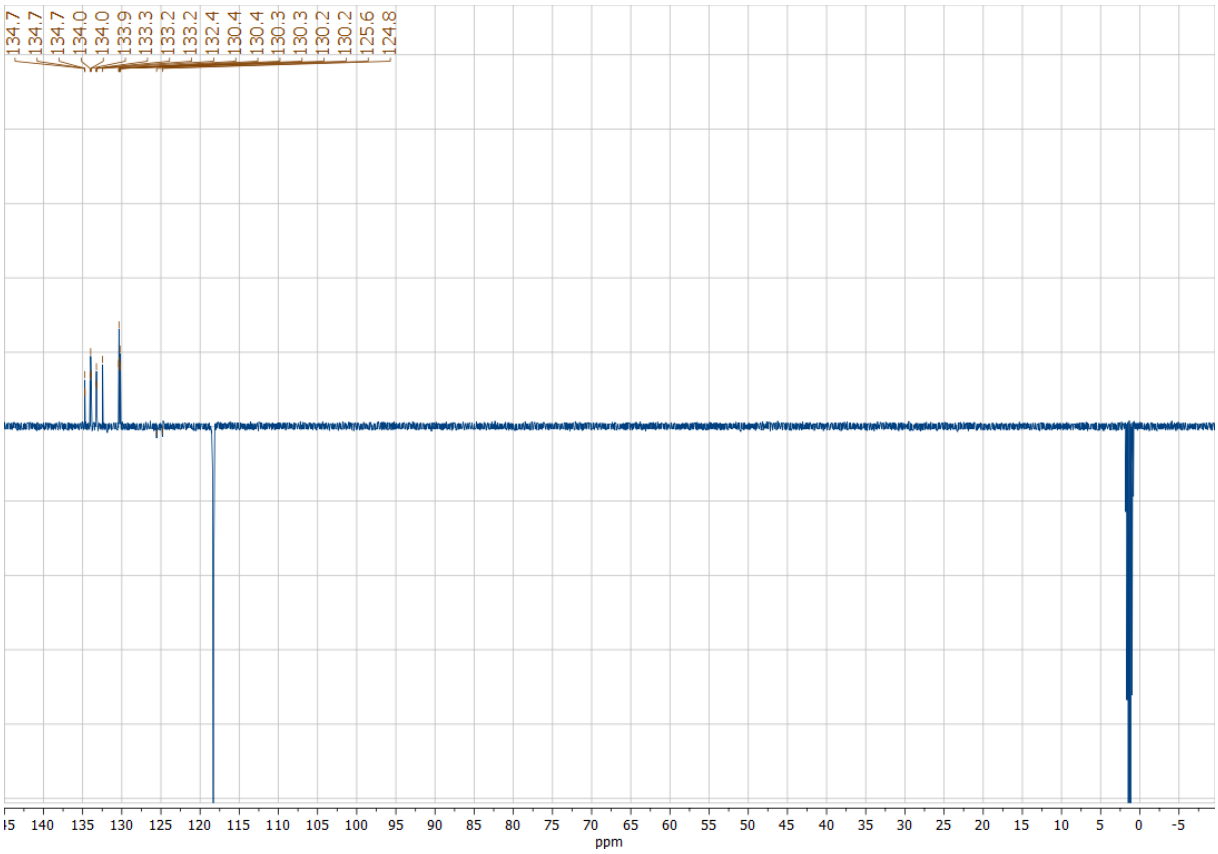

Figure 31 ^{13}C-APT NMR spectrum of [({dppm}$_2$CH)Ag(NCMe)](PF$_6$)$_2$ (**3-NCMe**) in CD$_3$CN.

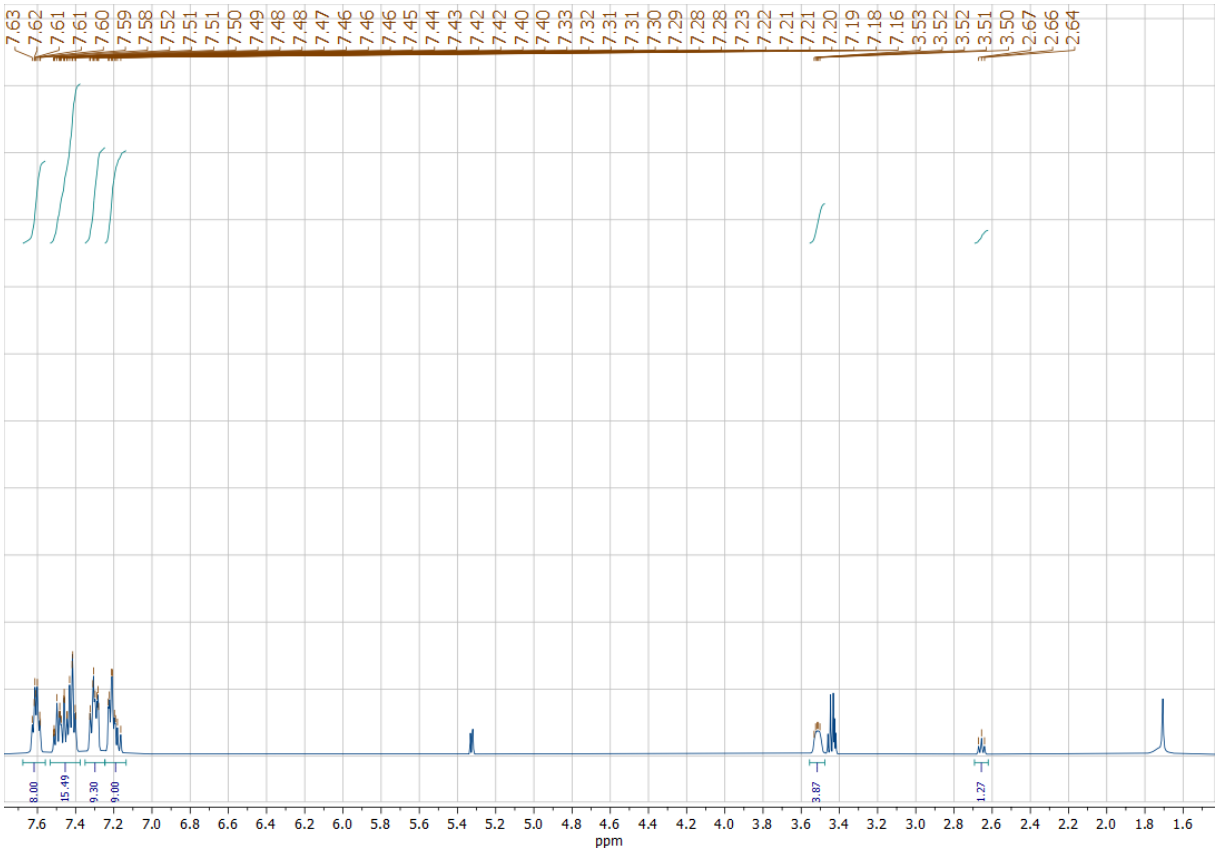

Figure 32 ^{1}H NMR spectrum of [({dppm}$_2$CH)Ag(H$_2$O)](PF$_6$)$_2$ (**3-H$_2$O**) in CD$_2$Cl$_2$.

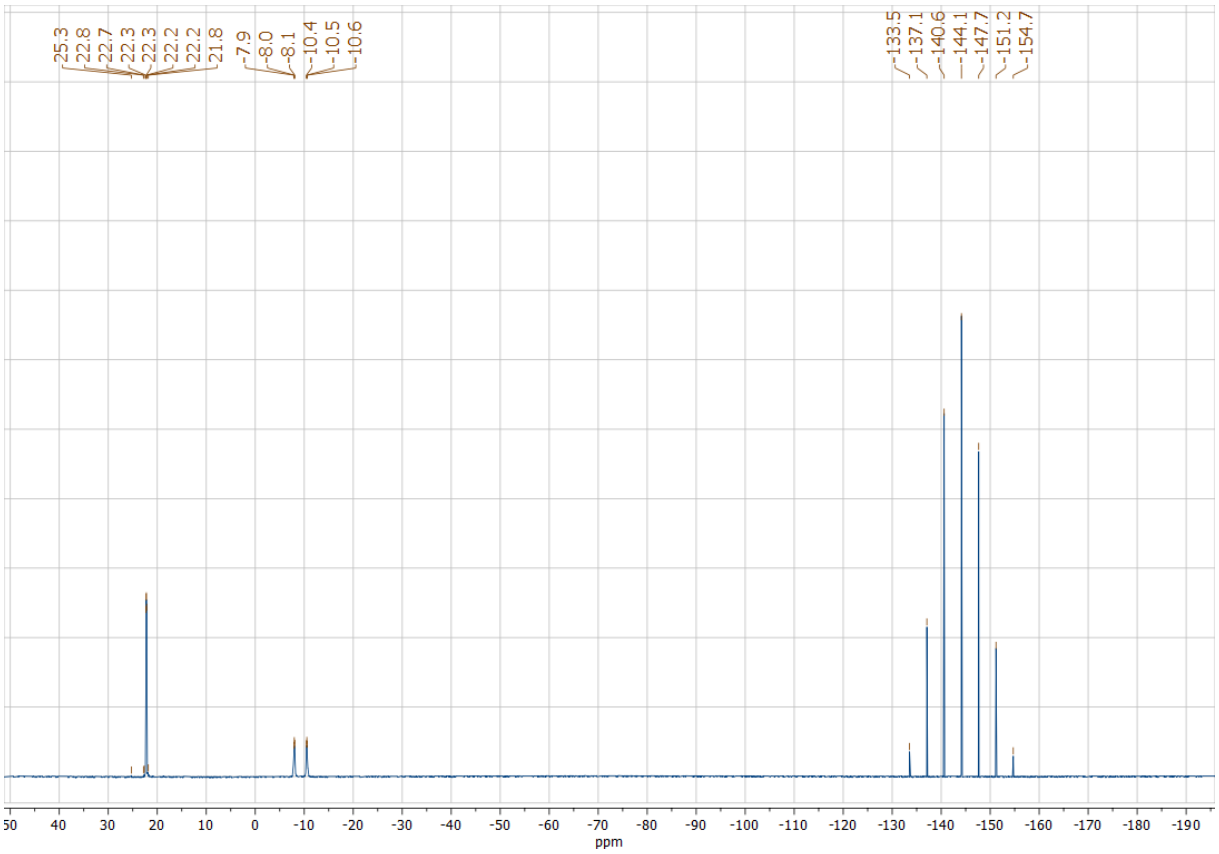

Figure 33 $^{31}P\{^{1}H\}$ NMR spectrum of [({dppm}$_2$CH)Ag(H_2O)](PF_6)$_2$ (**3-H_2O**) in CD_2Cl_2.

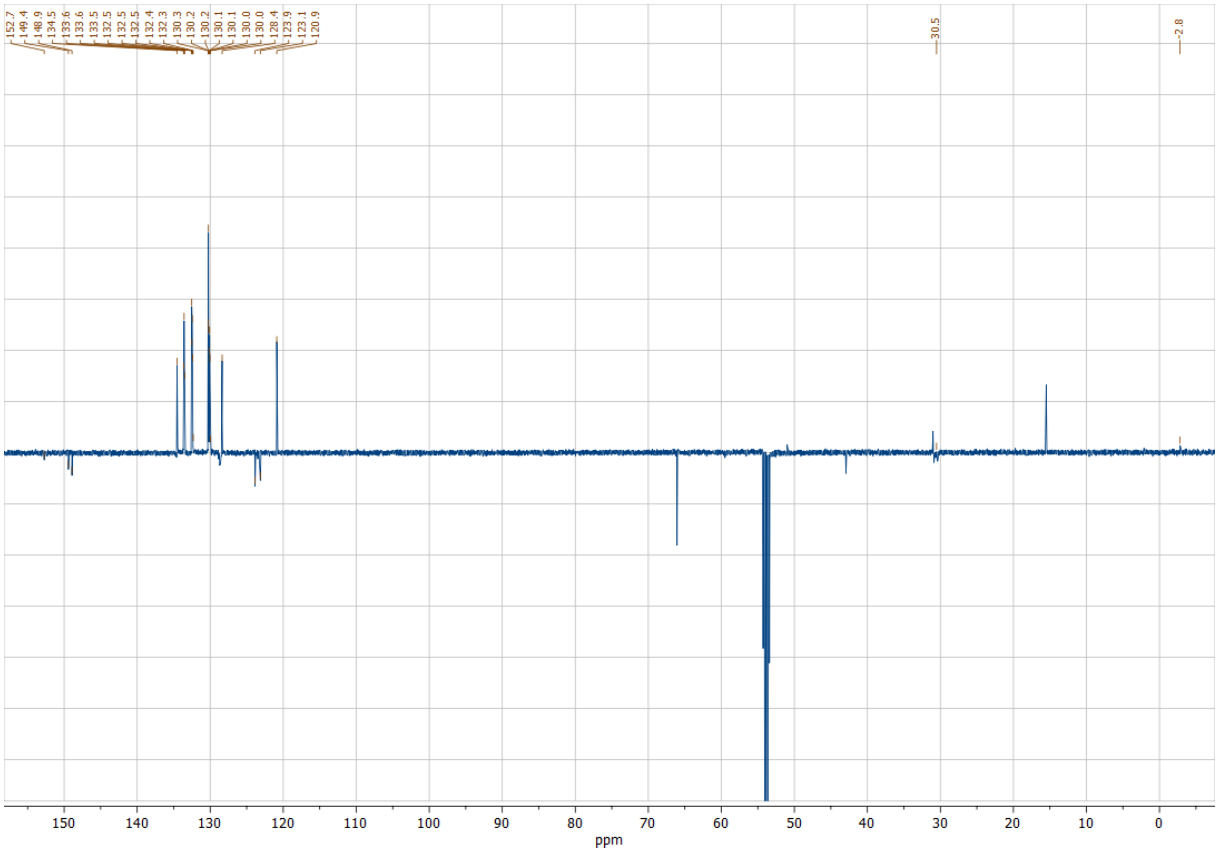

Figure 34 ^{13}C-APT NMR spectrum of [({dppm}$_2$CH)Ag(H_2O)](PF_6)$_2$ (**3-H_2O**) in CD_2Cl_2.

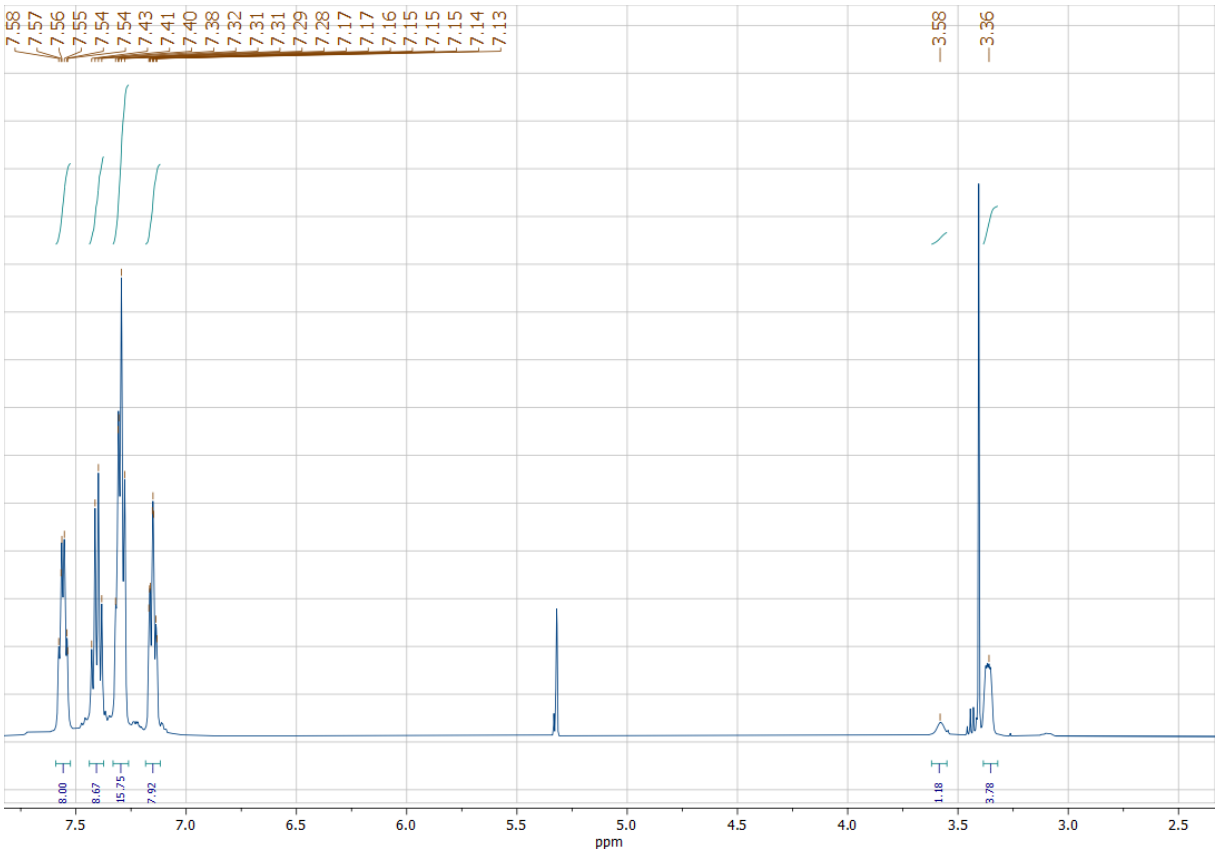

Figure 35 ^{1}H NMR spectrum of [({dppm}$_2$CH)Ag(NO_3)](PF_6) (**3-NO_3**) in CD_2Cl_2.

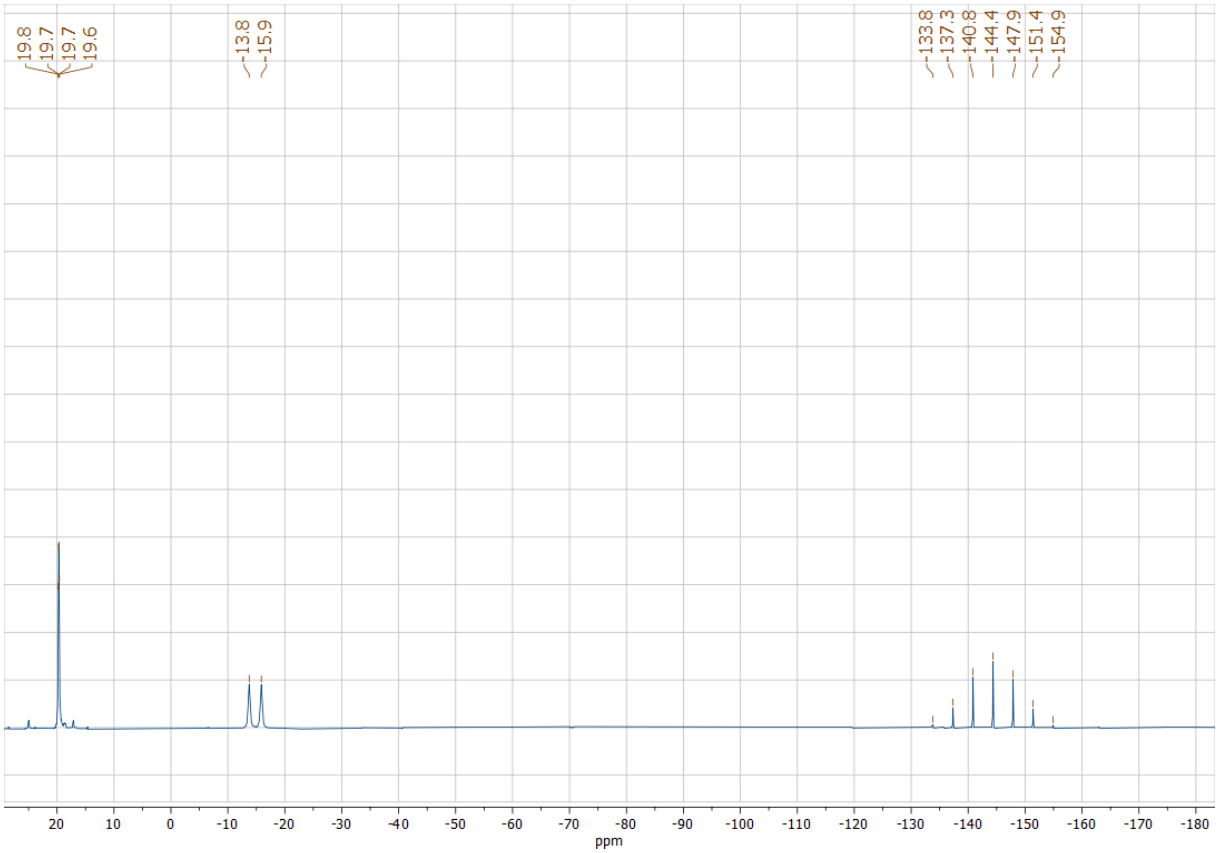

Figure 36 $^{31}P\{^{1}H\}$ NMR spectrum of [({dppm}$_2$CH)Ag(NO_3)](PF_6) (**3-NO_3**) in CD_2Cl_2.

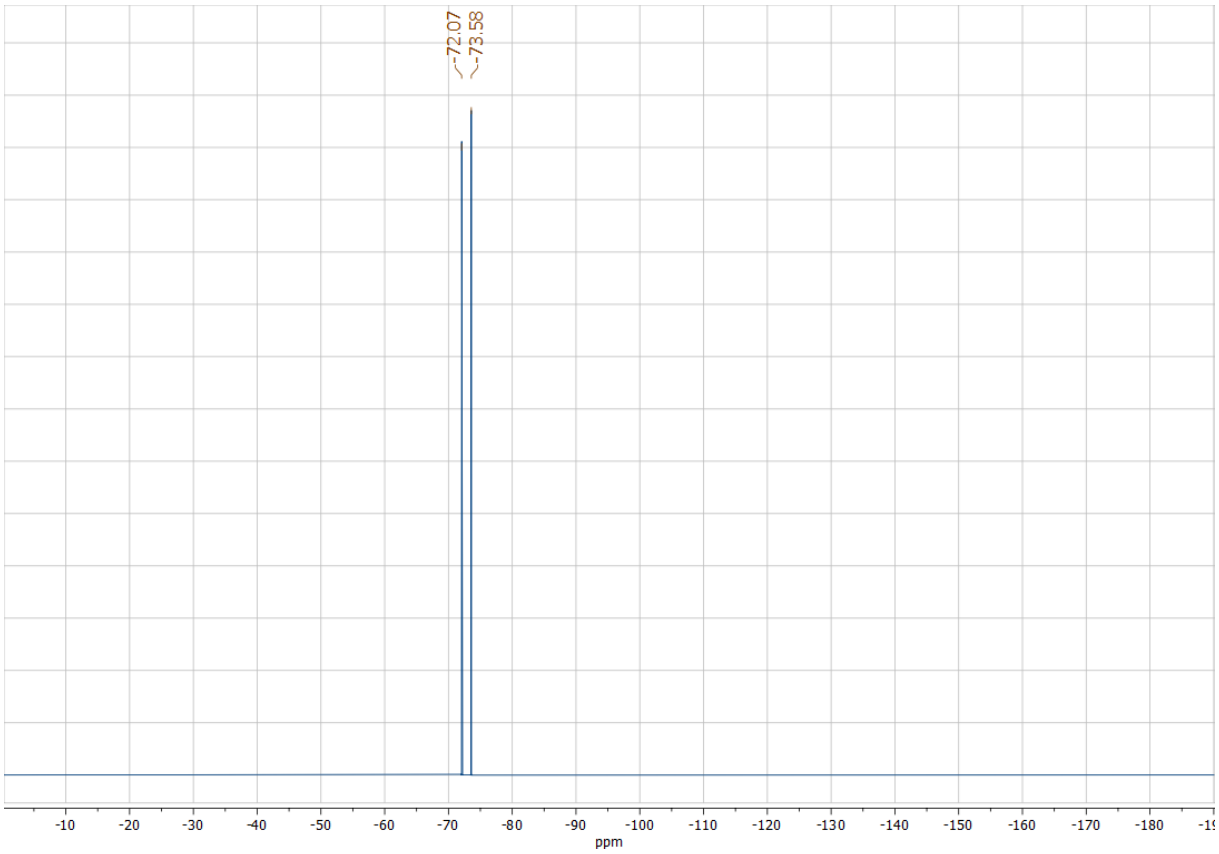

Figure 37 ^{19}F NMR spectrum of [({dppm}$_2$CH)Ag(NO_3)](PF_6) (**3-NO_3**) in CD_2Cl_2.

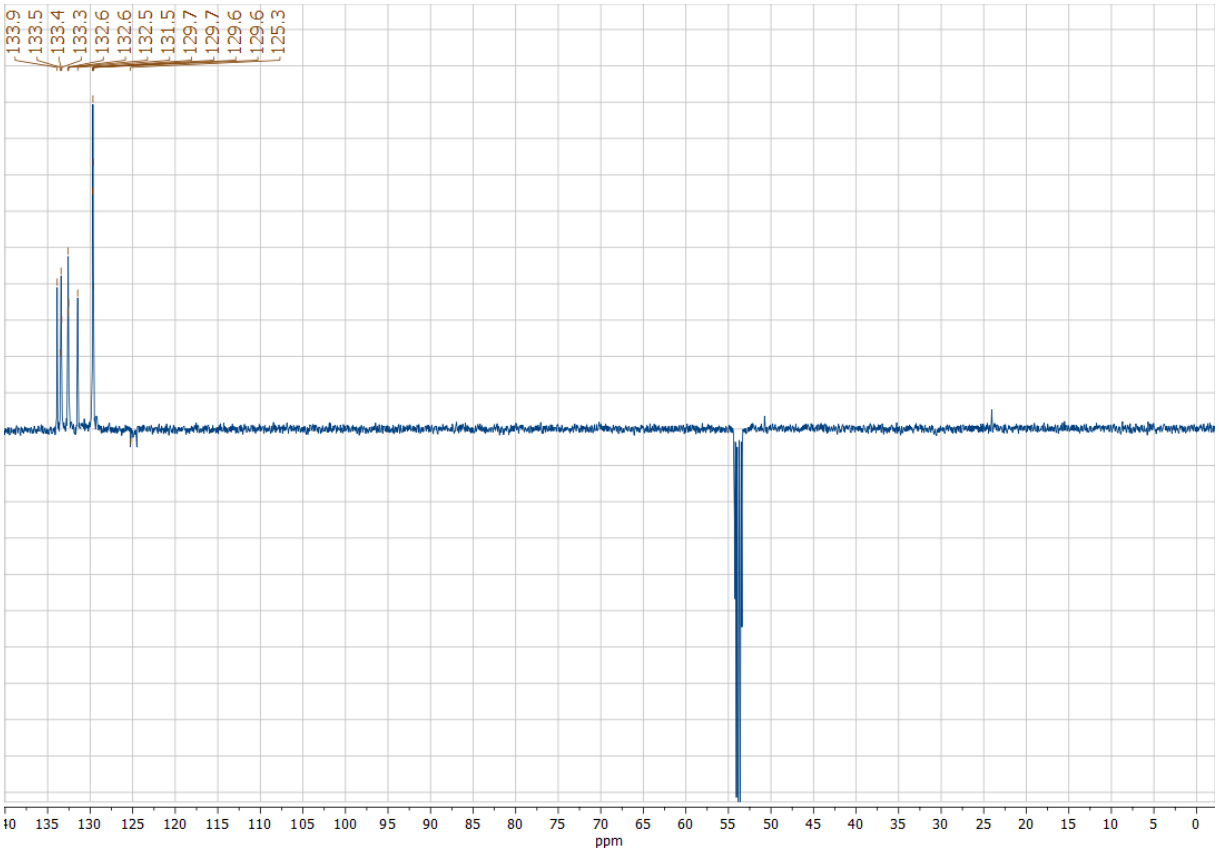

Figure 38 ^{13}C-APT NMR spectrum of [({dppm}$_2$CH)Ag(NO_3)](PF_6) (**3-NO_3**) in CD_2Cl_2.

3 X-Ray Crystallography

The single crystal X-ray diffraction data for the structural analysis were collected using graphite-monochromated Mo-Kα-radiation (λMoKα= 0.71073) on the pixel detector system Bruker Quest D8 or an imaging plate system STOE IPDS2T. The structures were solved with the Olex2 software by direct methods with SHELXT and refined against F^2 by full-matrix-least- square techniques using SHELXL.[3–6] Crystallographic data for **2-X** and **3-X** was deposited at Cambridge Crystallographic Data Centre (CCDC 2172292 - 2172302) and can be obtained free of charge via www.ccdc.cam.ac.uk/. Selected Crystallographic data is summarized in Table S1 and S2.

Table S1. Crystallographic data of complexes **2-Cl**, **2-Br**, **2-I**, **2-NCMe** and **3**.

Complex	**2-Cl**	**2-Br**	**2-I**	**2-NCMe**	**3**
Formula	$C_{51}H_{45}ClCuP_5F_6 \cdot 1.5(CH_2Cl_2)$	$C_{51}H_{45}BrCuP_5F_6 \cdot CH_2Cl_2$	$C_{51}H_{45}CuF_6IP_5$	$C_{53}H_{48}CuNP_6F_{12}$	$C_{51}H_{45}AgF_{12}P_6$
M / g·mol^{-1}	1153.10	1155.09	1117.16	1176.28	1179.56
T/K	100	170	170	170	170
Crystal System	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space Group	*C*2/*c*	*C*2/*c*	*C*2/*c*	$P2_1$	$P\bar{1}$
a / Å	23.711(1)	23.897(2)	24.032(1)	11.749(1)	12.3098(7)
b / Å	11.715(1)	11.821(1)	11.905(1)	18.185(1)	13.7462(8)
c / Å	38.189(2)	39.320(3)	39.489(2)	13.280(1)	16.8265(10)
α / °	90	90	90	90	87.104(5)
β / °	105.715(1)	109.930(6)	110.076(4)	115.779(2)	79.167(5)
γ / °	90	90	90	90	64.063(4)
V / Å^3	10211.5(8)	10442.3(14)	10611.4(10)	2554.97(13)	2513.2(3)
Z	8	8	8	2	2
$\rho_{calc.}$ / g·cm^{-3}	1.500	1.469	1.399	1.529	1.559
μ / mm^{-1}	0.853	1.496	1.197	0.698	0.673
F(000)	4712	4688	4496	1200	1192
Θ_{min}/°	2.124	2.422	2.331	2.812	1.648
Θ_{max}/°	26.427	26.500	25.999	25.998	29.251
Measured Refl.	62444	31960	41551	43743	53058
Independent Refl.	10472 (R_{Int} = 0.0989)	10459 (R_{Int} = 0.1461)	10434 (R_{Int} = 0.0792)	9055 (R_{Int} = 0.0327)	13478 (R_{Int} = 0.0582)
Ind. Refl. (I>2σ(I))	7472	7373	8948	8471	11682
Parameters / Restraints	631/0	604/0	606 /47	651/159	664/0
R_1	0.0491	0.0839	0.0555	0.0667	0.0345
R_1 (all data)	0.0862	0.1211	0.0625	0.0705	0.0411
wR_2	0.0899	0.2078	0.1652	0.1803	0.0915
wR_2 (all data)	0.1004	0.2601	0.1754	0.1864	0.0958
GooF	1.038	1.157	1.041	1.091	1.040
Flack parameter				0.006(7)	
Max. peak + hole / e·Å^{-3}	0.651/-0.852	1.589 / -0.968	0.707 / -1.077	1.082 / -0.909	0.751 / -0.795
CCDC	2172298	2172295	2172293	2172294	2172299

Table S2. Crystallographic data of complexes **3-Cl**, **3-Br**, **3-I**, **3-H_2O**, **3-NCMe**, **3-NO_3**.

Complex	**3-Cl**	**3-Br**	**3-I**	**3-H_2O**	**3-NCMe**	**3-OAc**
Formula	$C_{51}H_{45}AgClP_4 \cdot C_2H_3O_2 \cdot CH_2Cl_2 \cdot CH_4O$	$C_{51}H_{45}AgBrP_5F_6 \cdot 0.75(C_4H_{10}O)$	$C_{51}H_{45}AgIP_5F_6 \cdot 1.5(CH_2Cl_2)$	$C_{51}H_{47}AgOP_6F_{12} \cdot C_4H_{10}O$	$C_{53}H_{48}AgF_{12}NP_6$	$C_{53}H_{48}AgF_6O_2P_5 \cdot 0.5(CH_2Cl_2)$
M / g·mol^{-1}	1101.08	1170.09	1288.88	1271.69	1220.61	1136.09
T/K	100	170	170	100(2)	100(2)	100(2)
Crystal System	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space Group	$P2_1$	$P2_1$	$C2/c$	$P2_1/c$	$P2_1$	$P2_1$
a / Å	11.571(2)	11.695(2)	24.0437(14)	18.913(4)	11.6318(5)	11.818(1)
b / Å	18.782(4)	18.914(4)	11.8271(5)	14.607(3)	18.2132(7)	18.871(1)
c / Å	13.122(3)	13.280(3)	40.075(2)	20.359(4)	13.3823(6)	13.321(1)
α / °	90	90	90	90	90	90
β / °	114.91(3)	115.34(3)	109.918(4)	95.42(3)	115.4520(10)	115.01(1)
γ / °	90	90	90	90	90	90
V / Å^3	2586.4(11)	2654.9(11)	10714.3(10)	5599(2)	2559.91(19)	2692.2(3)
Z	2	2	8	4	2	2
$\rho_{calc.}$ / g·cm^{-3}	1.414	1.464	1.493	1.509	1.584	1.401
μ / mm^{-1}	0.711	1.341	1.206	0.612	0.664	0.632
F(000)	1132	1187	4808	2592	1236	1158
Θ_{min}/°	1.711	2.742	2.368	1.718	2.236	2.877
Θ_{max}/°	26.716	29.173	29.200	26.793	27.876	26.733
Measured Refl.	36829	19821	47682	74348	86131	23646
Independent Refl.	10914 (R_{Int} = 0.0877)	11400 (R_{Int} = 0.0547)	14163 (R_{Int} =0.0665)	11818 (R_{Int} = 0.0751)	11912 (R_{Int} = 0.0393)	10100 (R_{Int} = 0.0641)
Ind. Refl. (I>2σ(I))	9198	10115	11661	7808	11283	9816
Parameters / Restraints	599/1	627/3	624/0	759/0	659/1	620/3
R_1	0.0354	0.0416	0.0432	0.0400	0.0235	0.0472
R_1 (all data)	0.0430	0.0493	0.0553	0.0621	0.0273	0.0499
wR_2	0.0732	0.1085	0.1084	0.0931	0.0507	0.1358
wR_2 (all data)	0.0748	0.1141	0.1183	0.0974	0.0517	0.1337
GooF	0.923	1.015	1.058	0.927	1.037	1.122
Flack parameter	-0.036(12)	0.020(10)			-0.014(4)	-0.04(2)
Max. peak + hole / e·Å^{-3}	1.083/-0.681	1.113/-0.622	1.074 / -1.465	0.736/-0.919	0.577/-0.367	1.739/-0.534
CCDC	2172300	2172292	2172297	2172296	2172301	2172302

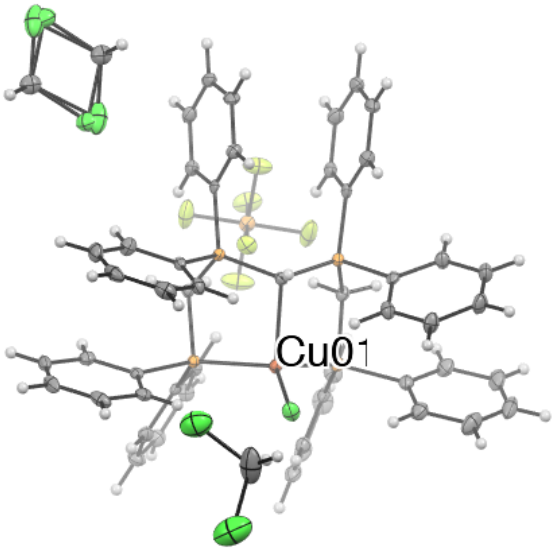

Figure 39 ORTEP plot of **2-Cl** (thermal ellipsoids are drawn at 50% probability level).

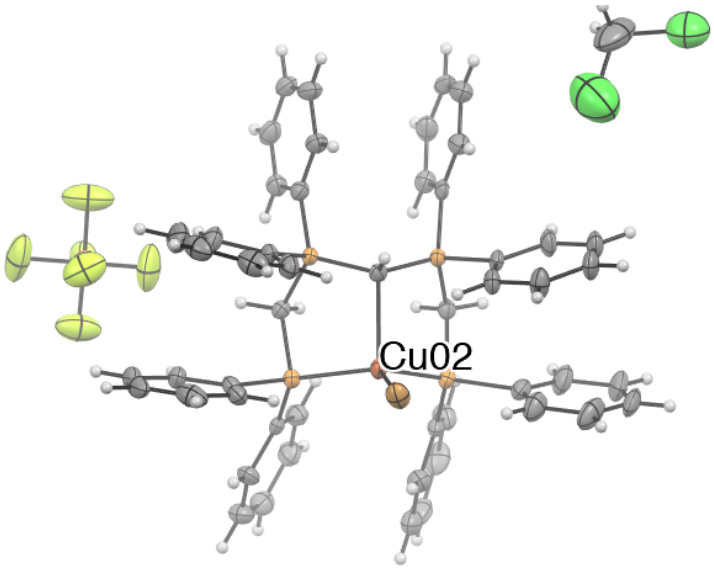

Figure 40 ORTEP plot of **2-Br** (thermal ellipsoids are drawn at 50% probability level).

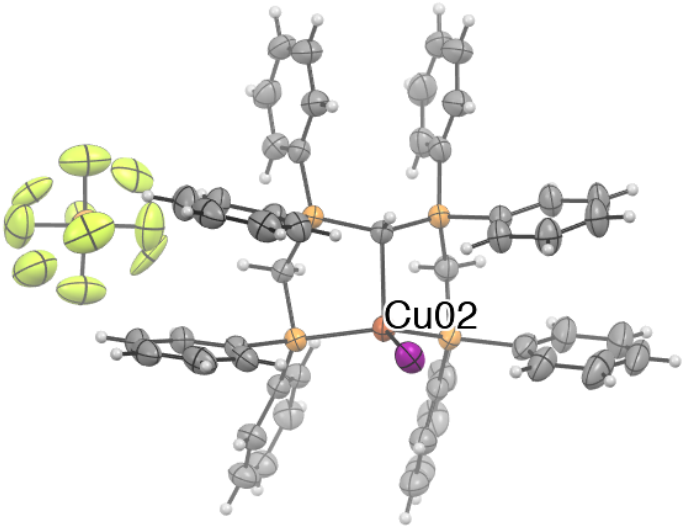

Figure 41 ORTEP plot of **2-I** (thermal ellipsoids are drawn at 50% probability level).

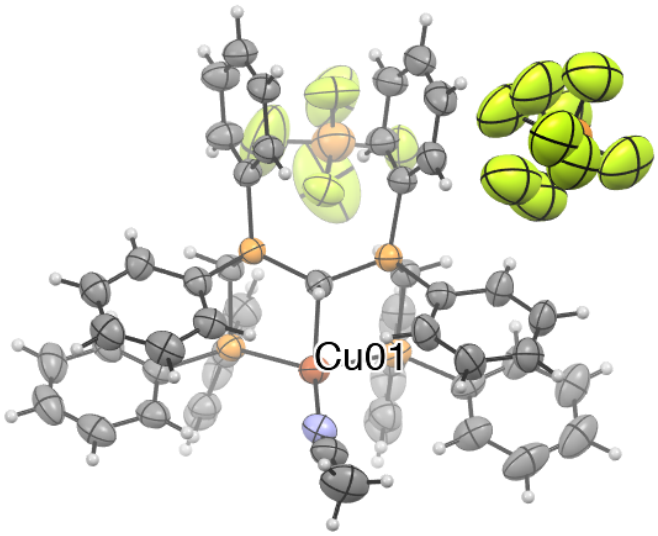

Figure 42 ORTEP plot of **2-NCMe** (thermal ellipsoids are drawn at 50% probability level).

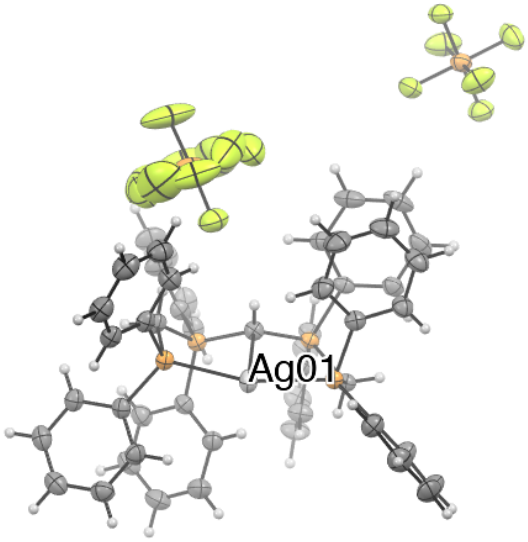

Figure 43 ORTEP plot of **3** (thermal ellipsoids are drawn at 50% probability level).

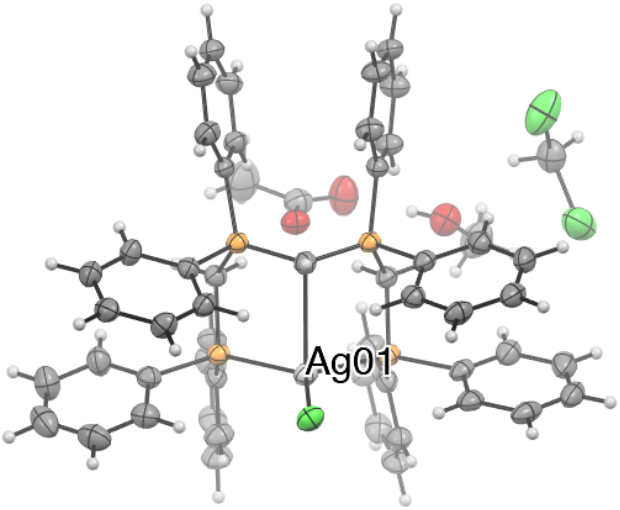

Figure 44 ORTEP plot of **3-Cl** (thermal ellipsoids are drawn at 50% probability level).

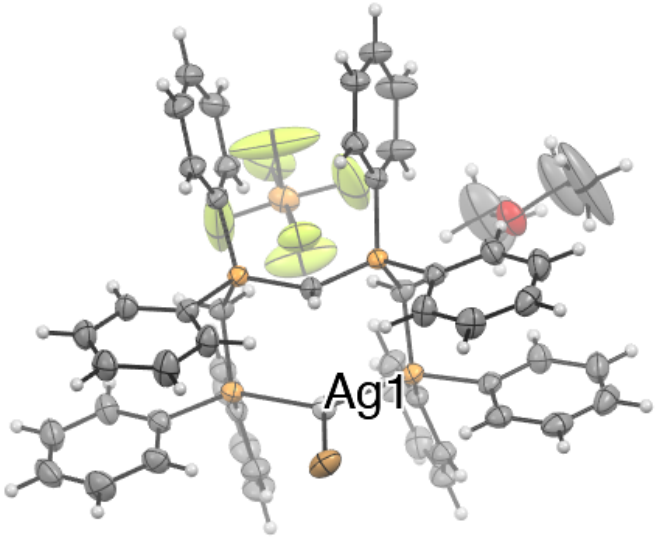

Figure 45 ORTEP plot of **3-Br** (thermal ellipsoids are drawn at 50% probability level).

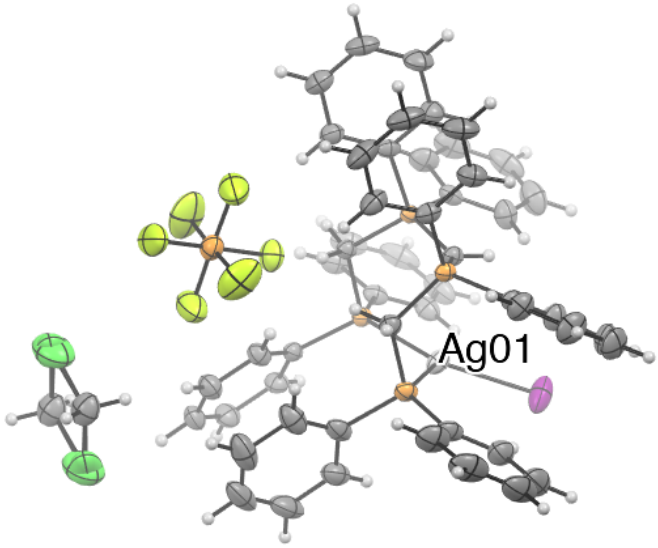

Figure 46 ORTEP plot of **3-I** (thermal ellipsoids are drawn at 50% probability level).

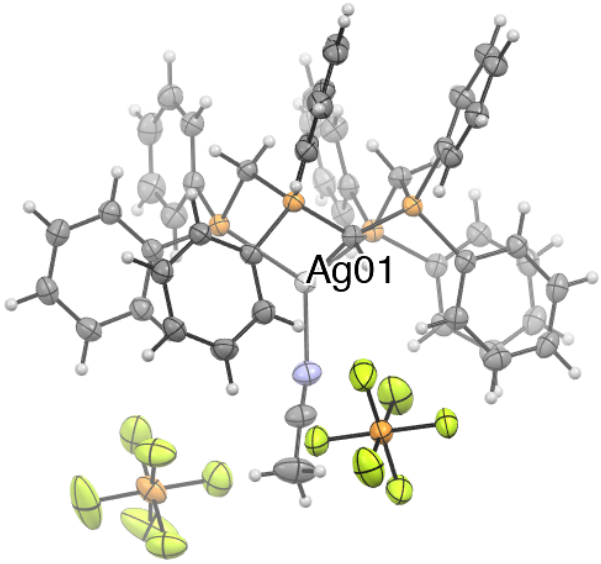

Figure 47 ORTEP plot of **3-NCMe** (thermal ellipsoids are drawn at 50% probability level).

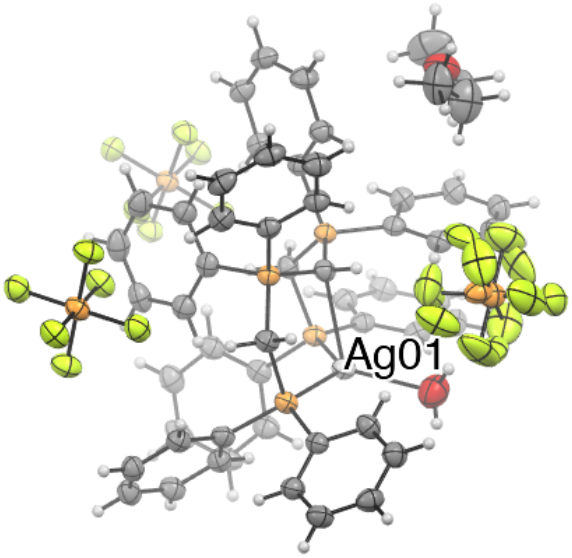

Figure 48 ORTEP plot of **3-H_2O** (thermal ellipsoids are drawn at 50% probability level).

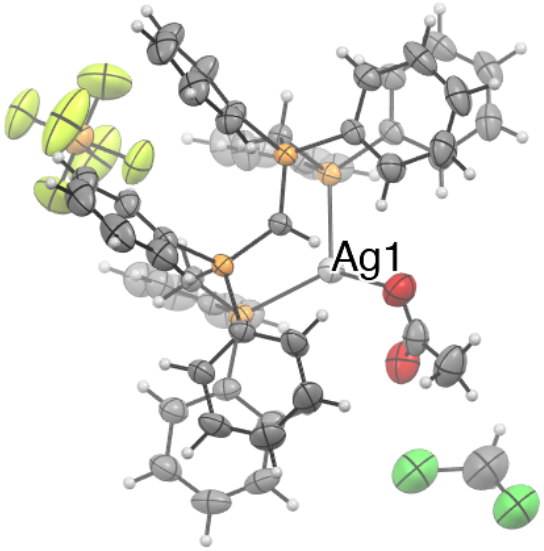

Figure 49 ORTEP plot of **3-OAc** (thermal ellipsoids are drawn at 50% probability level).

4 Computational Details

DFT calculations were performed with Grimme's B97D3 functional including Grimme's D3 dispersion correction[7] and the def2-TZVPP basis set after a pre-optimisation with the def2-SVP basis set[8,9] in Gaussian16.[10] Crystal structures were used as starting models, where possible. After optimization, a frequency calculation was run to ascertain that a ground state was found (no imaginary modes).
All natural bond orbital (NBO) analysis were performed using the NBO 3.0 package.[11] Laplacian contour line plots were created with the program Multiwfn.[12] Cartesian coordinates of the discussed structure are listed in the following:

2-Cl open form (with hydrogen bridge bond)

Cl	8.93850	8.25970	6.25560
Cu	8.41430	9.24420	4.31050
P	8.28990	8.16060	2.35660
P	7.84360	11.42190	4.23740
C	5.64400	8.67250	4.71940
C	8.98490	9.03890	0.91580
C	8.93180	6.46070	2.18490
C	6.48660	8.00050	1.93470
C	8.50300	12.49000	2.90440
C	8.08630	12.39580	5.75780
C	6.01710	11.51480	3.88670
P	5.50900	7.56210	3.42830
P	5.05440	10.27250	4.83070
H	6.29360	8.36620	5.53010
C	10.24070	9.63770	1.10100
C	8.35950	9.13480	-0.33400
C	9.49600	5.85370	3.31350
C	8.89140	5.77100	0.96480
H	6.14480	8.98590	1.60270
H	6.29700	7.28060	1.13380
C	9.48840	13.44650	3.18670
C	8.11060	12.29020	1.57230
C	7.39080	13.58260	6.02760
C	9.03830	11.92750	6.67380
H	5.62100	12.51780	4.06630
H	5.89370	11.28580	2.82430
C	3.81500	7.34910	2.81630
C	6.09380	5.94260	3.95700
C	3.35110	10.42690	4.24080
C	5.10790	10.82630	6.54470
H	10.72080	9.58660	2.07500
C	10.86500	10.30530	0.05160
C	8.98210	9.81590	-1.38110
H	7.38880	8.67850	-0.50370
C	10.00350	4.55730	3.22020
H	9.52510	6.39170	4.25740

C	9.39640	4.47640	0.87980
H	8.48300	6.24880	0.07830
H	9.80630	13.61120	4.21090
C	10.05700	14.19490	2.15550
H	7.38450	11.52470	1.31730
C	8.66870	13.04960	0.54830
H	6.66470	13.97020	5.31910
C	7.63200	14.28160	7.20690
H	9.54970	10.98810	6.48560
C	9.29140	12.64240	7.84440
C	3.30650	8.11850	1.76250
C	2.98190	6.42710	3.46670
C	6.58670	5.70640	5.24450
C	6.06080	4.89930	3.01640
C	2.95610	11.36790	3.28220
C	2.39630	9.56940	4.80910
C	4.19210	11.80200	6.96610
C	6.11070	10.37600	7.41380
C	10.23610	10.39710	-1.19150
H	11.83430	10.76850	0.20810
H	8.48960	9.88570	-2.34680
H	10.43780	4.08800	4.09790
C	9.95310	3.86850	2.00900
H	9.36760	3.94480	-0.06710
C	9.64560	14.00430	0.83640
H	10.81790	14.93420	2.38810
H	8.35240	12.88200	-0.47620
C	8.58560	13.81390	8.11540
H	7.08130	15.19400	7.41630
H	10.02990	12.27270	8.54960
H	3.93320	8.84220	1.25200
C	1.97890	7.96870	1.36530
C	1.66020	6.27240	3.05780
H	3.37250	5.82830	4.28370
H	6.65520	6.50240	5.97420
C	7.04300	4.43380	5.58590
C	6.51780	3.63440	3.36500
H	5.67850	5.07340	2.01510
H	3.67820	12.04330	2.83700
C	1.61890	11.44550	2.89080
C	1.06510	9.65390	4.41800
H	2.70740	8.83580	5.54610
H	3.41190	12.14810	6.29500
C	4.27900	12.32120	8.25540
H	6.85150	9.64670	7.09770
C	6.18910	10.90600	8.69970
H	10.71890	10.92610	-2.00770
H	10.35240	2.86070	1.93920
H	10.08510	14.59310	0.03690

H	8.77390	14.36350	9.03310
C	1.15690	7.04340	2.00790
H	1.58840	8.57510	0.55400
H	1.02340	5.54850	3.55730
C	7.00830	3.40030	4.65220
H	7.43850	4.26130	6.58170
H	6.50090	2.83470	2.63160
H	1.31740	12.17600	2.14610
C	0.67480	10.59110	3.45770
H	0.33170	8.98450	4.85610
H	3.56610	13.07190	8.58280
C	5.27890	11.87530	9.12150
H	6.97550	10.56480	9.36520
H	0.12520	6.92270	1.69140
H	7.37150	2.41280	4.92090
H	-0.36540	10.65290	3.15230
H	5.34880	12.28510	10.12470

2-Cl closed form (with Cu–C bond)

Cl	8.99790	8.27680	6.30640
Cu	8.27680	9.17950	4.38140
P	8.25400	8.16690	2.38350
P	7.84240	11.38870	4.22470
C	5.69440	8.69620	4.69950
C	8.97080	9.08900	0.98190
C	8.88510	6.47010	2.14650
C	6.45090	8.03550	1.93720
C	8.54610	12.43520	2.89670
C	8.06820	12.39200	5.72980
C	6.02430	11.50050	3.83800
P	5.49930	7.55860	3.42390
P	5.05280	10.29080	4.79760
H	5.82780	8.23860	5.67180
C	10.21470	9.69660	1.21340
C	8.38280	9.19360	-0.28520
C	9.52380	5.85610	3.23040
C	8.77970	5.79450	0.92230
H	6.11600	9.02790	1.61980
H	6.24660	7.32640	1.13060
C	9.63130	13.27550	3.18650
C	8.09940	12.33820	1.57070
C	7.39040	13.59720	5.95840
C	8.99250	11.92600	6.67490
H	5.62340	12.50500	3.99510
H	5.90890	11.25260	2.77930
C	3.79810	7.30110	2.84260
C	6.10890	5.95490	3.96810
C	3.34530	10.46150	4.21180

C	5.10080	10.82110	6.51620
H	10.66300	9.63970	2.20200
C	10.86540	10.37980	0.19040
C	9.03210	9.88970	-1.30540
H	7.42170	8.73070	-0.48930
C	10.04090	4.56750	3.09010
H	9.60320	6.38440	4.17690
C	9.29260	4.50720	0.79020
H	8.31460	6.27760	0.06720
H	9.99210	13.36150	4.20650
C	10.24280	14.01160	2.17210
H	7.29310	11.66300	1.30260
C	8.70200	13.08690	0.56350
H	6.68850	13.98370	5.22480
C	7.61940	14.31690	7.12780
H	9.48910	10.97260	6.51730
C	9.23520	12.66250	7.83450
C	3.26590	8.03890	1.77710
C	2.97410	6.40930	3.54590
C	6.75880	5.78020	5.19500
C	5.95730	4.86810	3.09050
C	2.95960	11.37170	3.22000
C	2.38350	9.62100	4.79400
C	4.18690	11.79350	6.95020
C	6.10260	10.35410	7.37900
C	10.27530	10.47780	-1.07080
H	11.82440	10.85100	0.38220
H	8.56930	9.96620	-2.28530
H	10.53370	4.09300	3.93350
C	9.92400	3.89260	1.87580
H	9.21180	3.98640	-0.15960
C	9.77640	13.92630	0.86020
H	11.07990	14.66060	2.41240
H	8.34110	13.00060	-0.45650
C	8.54540	13.85180	8.06580
H	7.08260	15.24430	7.30550
H	9.95290	12.29540	8.56220
H	3.88390	8.74060	1.22660
C	1.92860	7.88270	1.41690
C	1.64190	6.24920	3.17540
H	3.38030	5.83550	4.37350
H	6.96330	6.61790	5.85140
C	7.23340	4.51800	5.54810
C	6.44650	3.61680	3.44640
H	5.45790	4.99890	2.13500
H	3.68610	12.03300	2.76090
C	1.62550	11.43940	2.81510
C	1.05560	9.69640	4.39140
H	2.68360	8.90680	5.55500

H	3.40900	12.15180	6.28300
C	4.27500	12.29350	8.24660
H	6.84430	9.63160	7.04830
C	6.17840	10.86270	8.67370
H	10.77900	11.01870	-1.86630
H	10.32920	2.89040	1.76930
H	10.24880	14.50660	0.07340
H	8.72540	14.41820	8.97500
C	1.11720	6.98540	2.11090
H	1.52190	8.46210	0.59390
H	1.01340	5.54750	3.71560
C	7.07790	3.43910	4.68030
H	7.74810	4.39320	6.49550
H	6.33960	2.78210	2.76100
H	1.33180	12.14750	2.04610
C	0.67470	10.60520	3.40020
H	0.31760	9.04130	4.84310
H	3.56590	13.04330	8.58390
C	5.27160	11.82960	9.10770
H	6.96280	10.50860	9.33480
H	0.07760	6.85980	1.82360
H	7.46040	2.46070	4.95520
H	-0.36290	10.65960	3.08460
H	5.34160	12.22470	10.11680

3-Cl open form (with hydrogen bridge bond)

Ag	-0.01680	-1.51230	-1.10110
P	2.03530	-1.50870	0.15900
P	-2.14440	-1.46150	0.06990
Cl	-0.09620	-0.82490	-3.48040
C	-0.02670	1.53420	-0.51740
C	3.61520	-1.59060	-0.74520
C	2.10580	0.10280	1.09270
C	2.18280	-2.75390	1.48830
C	-2.11370	0.07460	1.13920
C	-3.64420	-1.32230	-0.94580
C	-2.48360	-2.72540	1.34960
P	-1.52550	1.62120	0.30970
P	1.57260	1.56850	0.09170
H	-0.11150	1.21770	-1.55320
C	3.57260	-1.54910	-2.14610
C	4.84540	-1.71220	-0.07900
H	1.40540	0.01600	1.93260
H	3.10630	0.29180	1.50060
C	2.54850	-2.46170	2.81110
C	1.88160	-4.08180	1.13800
H	-3.09970	0.26670	1.58050
H	-1.41740	-0.15640	1.95510

C	-4.85510	-0.79360	-0.47030
C	-3.55550	-1.77670	-2.27080
C	-3.71610	-3.38470	1.46730
C	-1.43320	-3.06270	2.22080
C	-1.50680	2.87290	1.62180
C	-2.82390	2.05080	-0.87240
C	2.74830	1.68680	-1.27390
C	1.89710	2.97290	1.20150
H	2.61680	-1.45750	-2.65950
C	4.76310	-1.61650	-2.87440
H	4.87530	-1.77420	1.00680
C	6.02930	-1.77930	-0.81290
C	2.60950	-3.48010	3.76780
H	2.79090	-1.44400	3.10510
C	1.95790	-5.09770	2.08980
H	1.57560	-4.31680	0.12040
C	-5.96490	-0.72280	-1.31110
H	-4.93570	-0.43470	0.55260
H	-2.60440	-2.13430	-2.65900
C	-4.67460	-1.71860	-3.10460
H	-4.52870	-3.14630	0.78760
C	-3.89610	-4.35790	2.45510
H	-0.45730	-2.59610	2.10800
C	-1.62180	-4.02420	3.21320
C	-1.15920	4.18350	1.25380
C	-1.84890	2.59050	2.95180
C	-2.77660	1.55390	-2.18430
C	-3.91660	2.82080	-0.44410
C	2.35160	1.69200	-2.61710
C	4.11270	1.76490	-0.94200
C	1.77560	2.86410	2.59380
C	2.23840	4.20780	0.62720
C	5.98740	-1.73130	-2.21180
H	4.72940	-1.58300	-3.96010
H	6.98170	-1.88050	-0.29830
C	2.31840	-4.79830	3.40830
H	2.89250	-3.24270	4.79030
H	1.72340	-6.12020	1.80620
C	-5.87670	-1.19150	-2.62720
H	-6.89750	-0.30410	-0.94190
H	-4.59870	-2.06980	-4.13020
C	-2.85540	-4.67420	3.33230
H	-4.85220	-4.86880	2.53650
H	-0.79950	-4.27740	3.87690
H	-0.88890	4.40090	0.22450
C	-1.15460	5.19670	2.20900
H	-2.12790	1.58520	3.25120
C	-1.83740	3.61030	3.90750
C	-3.82390	1.83730	-3.06090

H	-1.95300	0.93360	-2.53070
H	-3.95120	3.21050	0.56980
C	-4.95630	3.10110	-1.33180
H	1.31100	1.59530	-2.90140
C	3.31940	1.77910	-3.62060
C	5.07000	1.85220	-1.94830
H	4.42870	1.76310	0.09800
H	1.50850	1.91770	3.05430
C	1.99110	3.98050	3.40410
C	2.46380	5.31740	1.44110
H	2.33890	4.29500	-0.45140
H	6.91080	-1.79130	-2.78260
H	2.37010	-5.58940	4.15190
H	-6.74430	-1.13680	-3.28000
H	-3.00050	-5.43170	4.09820
C	-1.49290	4.91150	3.53660
H	-0.88280	6.20780	1.92000
H	-2.10310	3.38670	4.93720
H	-3.78790	1.44430	-4.07270
C	-4.91010	2.60920	-2.63930
H	-5.79760	3.70530	-1.00280
C	4.67250	1.86230	-3.29010
H	3.00620	1.76820	-4.66060
H	6.12310	1.90540	-1.68760
H	1.88830	3.89150	4.48200
C	2.33990	5.20510	2.82980
H	2.74040	6.26760	0.99210
H	-1.48790	5.70430	4.28000
H	-5.72120	2.82710	-3.32920
H	5.42110	1.92660	-4.07550
H	2.51690	6.07070	3.46290

3-Cl closed form (with Cu–C bond)

Ag	-0.05900	-1.08410	-1.35280
P	1.83920	-1.57940	0.09680
P	-2.07300	-1.29400	0.05830
Cl	-0.22040	-0.54560	-3.74130
C	0.12100	1.46080	-0.52620
C	3.53720	-1.81720	-0.53000
C	1.97820	-0.05970	1.16660
C	1.60490	-2.91320	1.31930
C	-1.94810	0.19420	1.16880
C	-3.72250	-1.12240	-0.69680
C	-2.29380	-2.65110	1.26350
P	-1.37930	1.69040	0.28730
P	1.69600	1.44720	0.16790
H	0.11230	1.85870	-1.53410
C	3.71120	-1.88050	-1.91770

C	4.64480	-1.95800	0.31820
H	1.19450	-0.11930	1.92790
H	2.94400	0.02230	1.67180
C	2.03860	-2.85150	2.65070
C	0.97810	-4.08020	0.85600
H	-2.90080	0.40170	1.66310
H	-1.20210	-0.02180	1.93860
C	-4.89030	-1.04920	0.07800
C	-3.80790	-1.08650	-2.09370
C	-2.96850	-3.80310	0.82620
C	-1.73500	-2.64280	2.54850
C	-1.37240	2.99920	1.54620
C	-2.62560	2.12960	-0.93530
C	2.91930	1.45820	-1.15230
C	2.09150	2.83660	1.26670
H	2.85140	-1.76910	-2.57280
C	4.98610	-2.07010	-2.45140
H	4.51630	-1.94120	1.39700
C	5.91570	-2.14270	-0.21920
C	1.85920	-3.94390	3.49920
H	2.52420	-1.95880	3.03370
C	0.81150	-5.17300	1.70190
H	0.61400	-4.12250	-0.16720
C	-6.13040	-0.92760	-0.54110
H	-4.83090	-1.10780	1.16180
H	-2.90180	-1.13600	-2.69310
C	-5.05540	-0.96960	-2.70890
H	-3.40380	-3.82950	-0.16850
C	-3.09840	-4.90680	1.66570
H	-1.17850	-1.78480	2.91100
C	-1.87290	-3.74680	3.38810
C	-0.96500	4.27610	1.12930
C	-1.73200	2.79110	2.88350
C	-2.42360	1.91150	-2.30400
C	-3.84340	2.65430	-0.47440
C	2.56300	1.30640	-2.49760
C	4.27260	1.56400	-0.78830
C	1.86910	2.76550	2.64810
C	2.52780	4.04250	0.69720
C	6.08700	-2.19820	-1.60570
H	5.11600	-2.11480	-3.52850
H	6.77170	-2.25410	0.44030
C	1.25280	-5.10720	3.02400
H	2.19920	-3.88830	4.52940
H	0.32060	-6.06850	1.33430
C	-6.21290	-0.88800	-1.93680
H	-7.03340	-0.87230	0.06010
H	-5.11730	-0.93980	-3.79250
C	-2.55720	-4.88030	2.95230

H	-3.63010	-5.78660	1.31520
H	-1.43560	-3.72120	4.38130
H	-0.67490	4.43710	0.09510
C	-0.92420	5.32720	2.03730
H	-2.05090	1.81340	3.22760
C	-1.68640	3.84950	3.79240
C	-3.43460	2.23950	-3.20510
H	-1.52320	1.43560	-2.68160
H	-4.00040	2.82830	0.58640
C	-4.85020	2.96440	-1.38310
H	1.53450	1.14320	-2.80280
C	3.55910	1.28430	-3.47300
C	5.25760	1.52860	-1.76830
H	4.55430	1.67590	0.25460
H	1.52140	1.84520	3.10610
C	2.08670	3.88450	3.45010
C	2.75380	5.15400	1.50430
H	2.69910	4.10500	-0.37310
H	7.07870	-2.34750	-2.02280
H	1.11430	-5.95660	3.68610
H	-7.18230	-0.79790	-2.41850
H	-2.66390	-5.73940	3.60770
C	-1.28460	5.11550	3.37100
H	-0.60460	6.31110	1.70860
H	-1.96830	3.68220	4.82760
H	-3.27510	2.05810	-4.26340
C	-4.64340	2.76400	-2.75010
H	-5.79310	3.36660	-1.02560
C	4.90050	1.39710	-3.11310
H	3.27410	1.15470	-4.51230
H	6.30260	1.59920	-1.48380
H	1.90650	3.82370	4.51880
C	2.53350	5.07690	2.88110
H	3.10400	6.08030	1.05890
H	-1.24970	5.93790	4.07920
H	-5.43000	3.00970	-3.45740
H	5.67250	1.36930	-3.87630
H	2.70880	5.94530	3.50890

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