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Synthesis and characterization of oxygen-functionalised-NHC silver(I) complexes and NHC transmetallation to nickel(II)

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Contents:

1) Experimental details

All reactions were carried out under inert atmosphere using standard Schlenk techniques unless stated otherwise. The compounds 1-(2,6-diisopropylphenyl)-1*H*-imidazol, 1-mesityl-1*H*-imidazole, 1-mesityl-1*H*-imidazole and 3-(2-hydroxyethyl)-1-methyl-1*H*-imidazol-3-ium chloride ([ImMe(C_2OH)]Cl, **3**) and [NiCl_2(dme)] were synthesized according to published procedures.[1] All reagents were used as received from commercial suppliers. TMSCl was distilled over Na prior to use. Solvents were purified and dried under argon by conventional methods. ^{1}H NMR and ^{13}C{^{1}H} NMR spectra were recorded on the following instruments: Bruker AVANCE I – 300 MHz spectrometer, Bruker AVANCE III – 400 MHz spectrometer, Bruker AVANCE I – 500 MHz spectrometer and Bruker AVANCE III – 600 MHz spectrometer. The chemical shifts are given in parts per million (ppm). Data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad), coupling constants (*J*/Hz) and integration. Assignments were determined either on the basis of unambiguous chemical shifts, coupling patterns or 2D correlations. The residual solvent proton (^{1}H) or carbon (^{13}C) resonances were used as references. For ^{1}H NMR: $CDCl_3$ = 7.26 ppm, $CHDCl_2$ = 5.32 ppm, C_6D_6 = 7.16 ppm. For ^{13}C{^{1}H} NMR: $CDCl_3$ = 77.1 ppm, CD_2Cl_2 = 53.8 ppm, C_6D_6 = 128.06 ppm. IR spectra were recorded in the region 4000-200 cm^{-1} on a Nicolet 6700 FT-IR spectrometer (ATR mode, diamond crystal). Elemental analyses were performed by the “Service de Microanalyses”, Université de Strasbourg. Mass spectrometry analyses were performed by the “Service de spectrométrie de masse”, Université de Strasbourg. For the X-ray diffraction studies, the intensity data were collected at 173(2) or 293(2) K on a Kappa CCD diffractometer 88 (graphite-monochromated Mo-K_α radiation, λ = 0.71073 Å). Crystallographic and experimental details for all the structures are summarized below (page S30). The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (based on F^2, SHELXL-97) with anisotropic thermal parameters for all the non-hydrogen atoms.[2] The hydrogen atoms were introduced into the geometrically calculated positions (SHELXL-97 procedures) and refined riding on the corresponding parent atoms, exception made for the hydroxyl-groups.

Synthesis of [ImDiPP(C_2OH)]Cl (1). A mixture of 1-(2,6-diisopropylphenyl)-1H-imidazole (5.567 g, 24.81 mmol) and 1-chloroethanol (20.0 mL, 256 mmol) was refluxed for 1.5 days.

The unreacted 1-chloroethanol was removed under reduced pressure. The resulting sticky solid was dissolved in the minimum amount of CH_2Cl_2 and precipitated with Et_2O. The beige solid was then stirred in Et_2O for 2 h and then collected by filtration to give **1**. The same procedure was used with THF to afford **1** as a white solid that was dried using a toluene Dean-Stark when needed (5.926 g, 19.19 mmol). Yield: 77%. ^{1}H NMR (CD_2Cl_2, 500 MHz): 9.97 (t, J = 1.4 Hz, 1H, $CH^{imidazole}$), 8.10 (t, J = 1.7 Hz, 1H, $CH^{imidazole}$), 7.55 (t, J = 7.8 Hz, 1H, $CH^{p\text{-}Ar}$), 7.33 (d, J = 7.9 Hz, 2H, $CH^{m\text{-}Ar}$), 7.23 (t, J = 1.8 Hz, 1H, $CH^{imidazole}$), 5.73 (t, J = 5.5 Hz, 1H, OH), 4.78 (t, J = 5.2 Hz, 2H, CH_2), 3.92 (td, J = 5.2 Hz, J = 5.5 Hz, 2H, CH_2OH), 2.32 (septet, J = 6.8 Hz, 2H, CH^{iPr}), 1.17 (d, J = 6.8 Hz, 6H, CH_3^{iPr}), 1.15 (d, J = 6.8 Hz, 6H, CH_3^{iPr}). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 126 MHz): 145.9 (C^{Ar}), 139.0 ($CH^{imidazole}$), 132.0 (CH^{Ar}), 130.6 (C^{Ar}), 124.9 (CH^{Ar}), 124.1 ($CH^{imidazole}$), 60.4 (CH_2OH), 52.5 (CH_2), 28.9 (CH^{iPr}), 24.5 (CH_3^{iPr}), 24.1 (CH_3^{iPr}). MS (ESI): *m/z* 273.18 $[M\text{-}Cl]^+$. FTIR: ν_{max}(solid)/cm^{-1}: 3202m br, 3036m, 2963s, 2868m, 1561w, 1543m, 1462m, 1443m, 1387w, 1365m, 1313w, 1278vw, 1258w, 1190s, 1112w, 1078s, 1061s, 939w, 877m, 816s, 781m, 766s, 718w, 673s.

Synthesis of [ImMes(C_2OH)]Cl (2). A mixture of 1-mesityl-1*H*-imidazole (4.000 g, 21.48 mmol) and 1-chloroethanol (17.0 mL, 205 mmol) was refluxed for 20 h. The unreacted 1-chloroethanol was removed under reduced pressure. The resulting sticky solid was triturated with Et_2O (3 times). The beige solid was then stirred in THF for 16 h and then collected by filtration to afford **2** as a white solid. The resulting powder was dried if needed using a toluene Dean-Stark (5.315 g, 19.92 mmol). Yield: 93%. ^{1}H NMR (CD_2Cl_2, 500 MHz): 9.75 (bt, J = 1.5 Hz, 1H, $CH^{imidazole}$), 7.90 (bt, J = 1.5 Hz, 1H, $CH^{imidazole}$), 7.23 (bt, J = 1.5 Hz, 1H), 7.03 (s, 2H, $CH^{m\text{-}Ar}$), 5.68 (s br, 1H, OH), 4.68 (t, J = 5.0 Hz, 2H, CH_2), 3.95 (t, J = 5.0 Hz, 2H, CH_2OH), 2.34 (s, 3H, *p*-CH_3), 2.07 (s, 6H, *o*-CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 126 MHz): 141.5 (C^{Ar}), 138.5 ($CH^{imidazole}$), 134.9 (C^{Ar}), 131.2 (C^{Ar}), 130.0 (CH^{Ar}), 123.9 ($CH^{imidazole}$), 123.3 ($CH^{imidazole}$), 60.2 (CH_2OH), 52.7 (CH_2), 21.2 (*p*-CH_3), 17.7 (*o*-CH_3). MS (ESI): *m/z* 231.15 $[M\text{-}Cl]^+$. FTIR: ν_{max}(solid)/cm^{-1}: 3259w br, 3111vw, 3042w, 2911vw, 1564m, 1546m, 1468m, 1465m, 1446m, 1382w, 1370w, 1315w, 1271w, 1258vw, 1235w, 1201s, 1158m, 1101vw, 1080s, 1065s, 1043m, 968vw, 934vw, 867s, 759s, 730w, 678m.

Synthesis of [Ag{ImDiPP(C_2OH)}$_2$]Cl (4). A mixture of the imidazolium salt [ImDiPP(C_2OH)]Cl (0.487 g, 1.58 mmol), Ag_2O (0.201 g, 0.867 mmol) and molecular sieves in MeOH (25 mL) was stirred in the absence of light for 16 h. It was then filtered through Celite and the filtrate was evaporated under reduced pressure. The resulting solid was dissolved in the minimum amount of CH_2Cl_2 and precipitated by addition of pentane. The white precipitate was filtered, washed with pentane (3x10 mL) and dried under vacuum to afford **4** as a white powder (0.515 g, 0.748 mmol). Yield: 95%. ^{1}H NMR (CD_2Cl_2, 300 MHz): 7.36 (t, J = 7.5 Hz, 1H, $CH^{p\text{-}Ar}$), 7.27 (t, ^3J(H-H) = 1.5 Hz, ^4J(H-Ag) = 1.5 Hz, 1H, $CH^{imidazole}$), 7.12 (d, J = 7.5 Hz, 2H, $CH^{m\text{-}Ar}$), 6.92 (t, ^3J(H-H) = 1.5 Hz, ^4J(H-Ag) = 1.5 Hz, 1H, $CH^{imidazole}$), 4.28 (t, J = 5.8 Hz, 2H, CH_2), 3.92 (t, J = 5.8 Hz, 2H, CH_2OH), 2.27 (septet, J = 6.5 Hz, 2H, CH^{iPr}), 1.04 (d, J = 6.5 Hz, 6H, CH_3^{iPr}), 0.84 (d, J = 6.5 Hz, 6H, CH_3^{iPr}). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 150.9 MHz): 182.6 (d, $^1J(^{13}C\text{-}^{107}Ag)$ = 184 Hz, $^1J(^{13}C\text{-}^{109}Ag)$ = 212 Hz, $C^{carbene}$), 146.4 (C^{Ar}), 135.4 (C^{Ar}), 130.6 (CH^{Ar}), 124.3 (CH^{Ar}), 123.7 (d, ^3J(C-Ag) = 5.5 Hz, $CH^{imidazole}$), 122.7 (d, ^3J(C-Ag) = 5.5 Hz, $CH^{imidazole}$), 61.9 (CH_2OH), 54.7 (CH_2), 28.5 (CH^{iPr}), 24.8 (CH_3^{iPr}), 24.2 (CH_3^{iPr}). MS (ESI): m/z 651.29 $[M\text{-}Cl]^+$. FTIR: ν_{max}(solid)/cm^{-1} : 3162m, 3131m, 2961m, 2869m, 1619vw, 1594vw, 1553w, 1470m, 1459m, 1443m, 1415m, 1387w, 1360m, 1313w, 1277vw, 1256m, 1218w, 1199w, 1182w, 1123w, 1091s, 1077s, 1057m, 1024w, 967, w, 939w, 885m, 810m, 757s, 729s, 693m, 678m, 638m, 570w, 505w, 468w, 419w, 397w, 375w, 351w, 335vw, 328w, 303w, 289w, 280w, 266vw, 254w, 247w, 227w, 208w, 202w, 195w, 188vw, 171w, 151w, 140w, 133w, 127vw, 121w, 106vw. Anal. calcd for $C_{34}H_{48}AgClN_4O_2$ (%): C 59.17, H 7.30, N 8.20; found: C 58.08, H 6.98, N 7.92. Despite several attempts, better results could not be obtained.

Synthesis of [Ag{ImMes(C_2OH)}$_2$]Cl (5). A mixture of the imidazolium salt [ImMes(C_2OH)]Cl (1.939 g, 7.268 mmol), Ag_2O (0.926 g, 4.00 mmol) and molecular sieves in MeOH (40 mL) was stirred under exclusion of light for 16 h. The reaction mixture was then filtered through Celite and the filtrate was evaporated under reduced pressure. The resulting solid was dissolved in the minimum amount of CH_2Cl_2 and precipitated by addition of pentane. The white precipitate was filtered, washed with pentane (3x10 mL) and dried under reduced pressure to afford **5** as a white powder (2.048 g, 3.391 mmol). Yield: 92%. ^{1}H NMR (CD_2Cl_2, 300 MHz): 7.24 (bs, 1H, $CH^{imidazole}$), 6.88 (bs, 3H, $CH^{m\text{-}Ar}$ and $CH^{imidazole}$), 4.31 (t, J = 5.5 Hz, 2H, CH_2), 3.91 (t, J = 5.5 Hz, 2H, CH_2OH), 2.39 (s, 3H, p-CH_3), 1.75 (s, 6H, o-CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125.7 MHz): 182.6 (d, $^1J(^{13}C\text{-}^{107}Ag)$ = 182 Hz, $^1J(^{13}C\text{-}^{109}Ag)$ = 210 Hz, $C^{carbene}$) 139.1 (C^{Ar}), 136.1 (C^{Ar}), 135.3 (C^{Ar}), 129.2 (CH^{Ar}), 122.4 (d, ^3J(C-Ag) = 5.0 Hz, $CH^{imidazole}$), 122.3 (d, ^3J(C-Ag) = 5.0 Hz, $CH^{imidazole}$), 61.8 (CH_2OH), 54.6 (CH_2), 21.2 (p-CH_3), 17.6 (o-CH_3). MS (ESI): m/z 567.20 $[M\text{-}Cl]^+$. FTIR: ν_{max}(solid)/cm^{-1} : 3152vw, 3079vw, 2913vw, 1488m, 1449m, 1410m, 1378m, 1351m, 1310w, 1283w, 1262w, 1232m, 1186m, 1163m, 1114w, 1071s, 1014m, 970m, 936m, 857s, 754s, 738m, 688m, 642m, 584m, 507m, 463m, 397vw, 357m, 341m, 280m, 246w. Anal. calcd for $C_{28}H_{36}AgClN_4O_2$ (%): C 55.68, H 6.01,N 9.28; found: C 54.59, H 6.50, N 9.03. Despite several attempts, better results could not be obtained.

Synthesis of [Ag{ImMe(C_2OH)}$_2$]Cl (6). A mixture of the imidazolium salt [ImMe(C_2OH)]Cl (0.600 g, 3.69 mmol), Ag_2O (0.470 g, 2.03 mmol) and molecular sieves in MeOH (25 mL) was stirred under exclusion of light for 16 h. The reaction mixture was then filtered through Celite and the filtrate was evaporated under reduced pressure. The resulting solid was dissolved in the minimum amount of MeOH and precipitated by addition of Et_2O. The white precipitate was filtered, washed with Et_2O (3x10 mL) and dried under reduced pressure to afford **6** as a white powder (0.622 g, 1.57 mmol). Yield: 85%. ^{1}H NMR ($CDCl_3$, 300 MHz): 7.14 (d, J = 1.8 Hz, 1H, CH^{imidazole}), 6.98 (d, J = 1.8 Hz, 1H, CH^{imidazole}), 4.27 (t, J = 5.2 Hz, 2H, CH_2), 3.91 (t, J = 5.2 Hz, 2H, CH_2OH), 3.84 (s, 3H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz): 181.2 (C^{carbene}), 122.2 (CH^{imidazole}), 122.1 (CH^{imidazole}), 62.0 (CH_2OH), 54.3 (CH_2), 38.9 (CH_3). MS (ESI): m/z 359.06 [M-Cl]$^+$. FTIR: ν_{max}(solid)/cm^{-1}: 3259w, 2941vw, 2853w, 1456m, 1429w, 1403m, 1341w, 1278w, 1223m, 1165m, 115vw, 1058s, 870w, 753s, 623s, 454m, 383w, 314s, 247s, 198w, 178vw, 150w, 119s. Anal. calcd for $C_{12}H_{20}AgClN_4O_2$ (%): C 36.43, H 5.10, N 14.16; found: C 34.84, H 5.36, N 14.20. Despite several attempts, better results could not be obtained.

Synthesis of [ImHDiPP(C_2OH)]$_3$Cl[$NiCl_4$] (8). A mixture of the silver complex **4** (0.213 g, 0.310 mmol) and [$NiCl_2$(dme)] (0.136 g, 0.619 mmol) in CH_2Cl_2 was stirred overnight. A green solution and a white suspension were obtained. The solution was filtered through Celite and the filtrate was dried under reduced pressure. The resulting green solid was precipitated from CH_2Cl_2 and Et_2O and blue crystals are obtained by vapour diffusion of pentane into a CH_2Cl_2 solution of the product.

Synthesis of [Ag{ImDiPP(C_2OH)}$_2$]BF_4 (9). A mixture of the silver complex **4** (0.354 g, 0.514 mmol) and $NaBF_4$ (0.132 g, 1.20 mmol) in acetone (20 mL) was stirred for 12 h. The solution was filtered through Celite and the filtrate was dried under reduced pressure. The resulting powder was precipitated from CH_2Cl_2 and pentane to afford **9** as a white solid (0.217 g, 0.293 mmol). Yield: 57%. ^{1}H NMR (CD_2Cl_2, 500 MHz): 7.43 (t, J = 7.8, 1H, CH$^{p\text{-}Ar}$),7.34 (t, ^3J(H-H) = 1.7 Hz, ^4J(H-Ag) = 1.7 Hz 1H, CH^{imidazole}), 7.20 (d, J = 7.8, 2H, CH$^{m\text{-}Ar}$), 6.98 (t, ^3J(H-H) = 1.7 Hz, ^4J(H-Ag) = 1.7 Hz 1H, CH^{imidazole}), 4.10 (t, J = 5.2, 2H, CH_2), 3.82 (t, J =

5.2, 2H, CH_2OH), 2.95 (s br, 1H, OH), 2.25 (septet, *J* = 6.9, 2H, CH^{iPr}), 1.08 (d, *J* = 6.9, 6H, $CH_3{}^{iPr}$), 0.92 (d, *J* = 6.9, 6H, $CH_3{}^{iPr}$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 126 MHz) 182.6 (d, $^1J(^{13}C\text{-}^{107}Ag)$ = 184 Hz, $^1J(^{13}C\text{-}^{109}Ag)$ = 213 Hz, $C^{carbene}$), 146.5 (C^{Ar}), 135.3 (C^{Ar}), 130.7 (CH^{Ar}), 124.4 (CH^{Ar}), 124.2 (d, ^3J(C-Ag) = 5.9 Hz, $CH^{imidazole}$), 122.5 (d, ^3J(C-Ag) = 5.7 Hz), 62.5 (CH_2OH), 54.2 (d, ^3J(C-Ag) = 2.2 Hz, CH_2), 28.5 (CH^{iPr}), 24.8 ($CH_3{}^{iPr}$), 24.2 ($CH_3{}^{iPr}$). MS (ESI): *m/z* 651.28 $[M\text{-}BF_4]^+$. FTIR: ν_{max}(solid)/cm^{-1} : 3455w, 3164vw, 2965m, 2870w, 1470m, 1419w, 1384w, 1363m, 1307vw, 1248vw, 1224vw, 1183w, 1066vs, 938m, 869m, 846vw, 811m, 768m, 741m, 689w, 674vw, 647vw, 567m, 540m, 513s, 467s, 408w, 352w, 372vw, 303w, 279m, 254vw, 247vw, 227m, 203m, 171m, 150m, 140m, 133vw, 121w. Anal. calcd for $C_{34}H_{48}AgBF_4N_4O_2$ (%): C 55.23, H 6.53, N 7.58; found: C 55.25, H 6.81, N 6.95. Despite several attempts, better results could not be obtained.

Synthesis of [ImDiPP(C_2OTMS)]Cl (10). A mixture of the imidazolium salt **1** (0.221 g, 0.716 mmol), HMDS (0.15 mL, 0.72 mmol) and TMSCl (0.20 mL, 1.6 mmol) in dioxane (10 mL) was refluxed for 16 h. The solvent was removed under reduced pressure. The white solid was dissolved in CH_2Cl_2 and the ammonium salts were removed by filtration. The filtrate was evaporated under reduced pressure and the powder was washed with pentane to afford **10** as a white powder (0.223 g, 0.585 mmol). Yield: 81%. ^1H NMR (CD_2Cl_2, 500 MHz): 10.56 (t, *J* = 1.6 Hz, 1H, $CH^{imidazole}$), 8.08 (t, *J* = 1.6 Hz, 1H, $CH^{imidazole}$), 7.56 (t, *J* = 7.8 Hz, 1H, $CH^{p\text{-}Ar}$), 7.34 (d, *J* = 7.9 Hz, 2H, $CH^{m\text{-}Ar}$), 7.17 (t t, *J* = 1.7 Hz, 1H, $CH^{imidazole}$), 4.92 (t, *J* = 4.7 Hz, 2H, CH_2), 4.05 (t, *J* = 4.7 Hz, 2H, CH_2OSiMe_3), 2.30 (sept., *J* = 6.8 Hz, 2H, CH^{iPr}), 1.21 (d, *J* = 6.8 Hz, 6H, $CH_3{}^{iPr}$), 1.15 (d, *J* = 6.8 Hz, 6H, $CH_3{}^{iPr}$), 0.11 (s, 9H, $CH_3{}^{TMS}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): 145.8 (C^{Ar}), 139.2 ($CH^{imidazole}$), 132.1 (CH^{Ar}), 130.7 (C^{Ar}), 125.0 (CH^{Ar}), 124.5 ($CH^{imidazole}$), 123.7 ($CH^{imidazole}$), 61.9 (CH_2OTMS), 52.7 (CH_2), 29.0 (CH^{iPr}), 24.4 ($CH_3{}^{iPr}$), 24.3 ($CH_3{}^{iPr}$), -0.7 ($CH_3{}^{TMS}$). MS (ESI): *m/z* 345.23 $[M\text{-}Cl]^+$. FTIR: ν_{max}(solid)/cm^{-1} : 2960m, 2870w, 1565w, 1543m, 1461m, 1442m, 1411vw, 1384w, 1367m, 1313vw, 1248m, 1193m, 1104m, 1081m, 940m, 839s, 816s, 767m, 757m, 672m, 645w.

Synthesis of [ImDiPP(C_2OMe)]Cl (12). A mixture of 1-(2,6-diisopropylphenyl)-1*H*-imidazole (2.066 g, 9.209 mmol) and 2-chloroethyl methyl ether (8.4 mL, 92 mmol) was refluxed for 1.5 days. The unreacted 2-chloroethyl methyl ether was removed under reduced pressure. The resulting sticky solid was dissolved and precipitated from CH_2Cl_2 and Et_2O. The beige solid was then stirred in Et_2O for 2 h and collected by filtration. The same procedure was used with THF to afford **12** as a white solid. If needed, the resulting white powder was dried using a toluene Dean-Stark (2.415 g, 7.480 mmol). Yield: 81%. ^{1}H NMR (CD_2Cl_2, 500 MHz): 10.45 (t, *J* = 1.7 Hz, 1H, $CH^{imidazole}$), 8.32 (t, *J* = 1.7 Hz, 1H, $CH^{imidazole}$), 7.54 (t, *J* = 7.8 Hz, 1H, $CH^{p\text{-}Ar}$), 7.31 (d, *J* = 7.9 Hz, 2H, $CH^{m\text{-}Ar}$), 7.22 (t, *J* = 1.7 Hz, 1H, $CH^{imidazole}$), 4.91 (t, *J* = 4.9 Hz, 2H, CH_2), 3.82 (t, *J* = 4.9 Hz, 2H, CH_2^{OMe}), 3.36 (s, 3H, CH_3^{OMe}), 2.28 (septet, *J* = 6.8 Hz, 2H, CH^{iPr}), 1.16 (d, *J* = 6.8 Hz, 6H, CH_3^{iPr}), 1.14 (d, *J* = 6.8 Hz, 6H, CH_3^{iPr}). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 126 MHz): 145.72 (C^{Ar}), 139.29 ($CH^{imidazole}$), 131.91 (CH^{Ar}), 130.67 (C^{Ar}), 124.81 (CH^{Ar}), 124.45 ($CH^{imidazole}$), 123.84 ($CH^{imidazole}$), 70.78 (CH_2^{OMe}), 59.02 (CH_3^{OMe}), 50.01 (CH_2), 28.89 (CH^{iPr}), 24.42 (CH_3^{iPr}), 23.97 (CH_3^{iPr}). MS (ESI): *m/z* 287.20 $[M\text{-}Cl]^+$. FTIR: ν_{max}(solid)/cm^{-1} : 3357w, 3062m, 3013vw, 2962m, 2921m, 2873m, 2820w, 1565m, 1541m, 1459m, 1411vw, 1388w, 1363m, 1341m, 1316vw, 1294vw, 1272vw, 1247vw, 1224vw, 1191s, 1107s, 1089vw, 1076m, 1061vw, 1027vw, 1015m, 974vw, 957vw, 912w, 832m, 810s, 788m, 766s, 739vw, 673m, 651m, 637w, 613vw.

Synthesis of [Ag{ImDiPP(C_2OMe)}$_2$]Cl (13). A mixture of the imidazolium salt **12** (0.404 g, 1.25 mmol), Ag_2O (0.159 g, 0.686 mmol) and molecular sieves in MeOH (25 mL) was stirred overnight under exclusion of light for 12 h. The solution was filtered through Celite and the solvent was evaporated under reduced pressure. The resulting power was redissolved in CH_2Cl_2 and precipitated from pentane to afford **13** as a white solid (0.329 g, 0.459 mmol). Yield: 74%. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 7.52 (t, ^3J(H-H) = 1.5 Hz, ^4J(H-Ag) = 1.5 Hz, 1H, $CH^{imidazole}$), 7.46 (t, *J* = 7.8 Hz, 1H, $CH^{p\text{-}Ar}$), 7.22 (d, *J* = 7.8 Hz, 2H, $CH^{m\text{-}Ar}$), 7.00 (t, ^3J(H-H) = 1.5 Hz, ^4J(H-Ag) = 1.5 Hz, 1H, $CH^{imidazole}$), 4.07 (t, *J* = 4.9 Hz, 2H, CH_2), 3.50 (t, *J* = 4.9 Hz, 2H, CH_2^{OMe}), 3.26 (s, 3H, CH_3^{OMe}), 2.26 (septet, *J* = 6.9 Hz, 2H, CH^{iPr}), 1.08 (d, *J* = 6.9 Hz, 6H, CH_3^{iPr}), 0.98 (d, *J* = 6.9 Hz, 6H, CH_3^{iPr}). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 126 MHz): 182.4 (d, $^1J(^{13}C\text{-}^{107}Ag)$ = 183 Hz, $^1J(^{13}C\text{-}^{109}Ag)$ = 212 Hz, $C^{carbene}$), 146.4 (C^{Ar}), 135.3 (C^{Ar}), 130.8 (CH^{Ar}), 124.4 (CH^{Ar}), 124.1 (d, ^3J(C-Ag) = 5.8 Hz, $CH^{imidazole}$), 122.9 (d, ^3J(C-Ag) = 5.7 Hz, $CH^{imidazole}$), 72.2 (CH_2^{OMe}), 59.3 (CH_3^{OMe}), 52.0 (d, ^3J(C-Ag) = 2.2 Hz, CH_2), 28.6 (CH^{iPr}), 24.7 (CH_3^{iPr}), 24.2 (CH_3^{iPr}). MS (ESI): *m/z* 681.31 $[M\text{-}Cl]^+$. FTIR: ν_{max}(solid)/cm^{-1} : 2959w, 1471m, 1460m, 1413m, 1381m, 1360m, 1302w, 1251w, 1231vw, 1205w, 1178w, 1095s, 1075m, 1058m, 1037w, 1007m, 966vw, 937w, 895vw, 838m, 805m, 763s, 742s, 690m, 676m, 646w567m, 529w, 466m, 417w, 368vw, 278w , 247vw, 151vw. Anal. calcd for $C_{36}H_{52}AgClN_4O_2$ (%): C 60.38, H 7.32, N 8.82; found: C 59.46, H 7.52, N 7.61. Despite several attempts, better results could not be obtained.

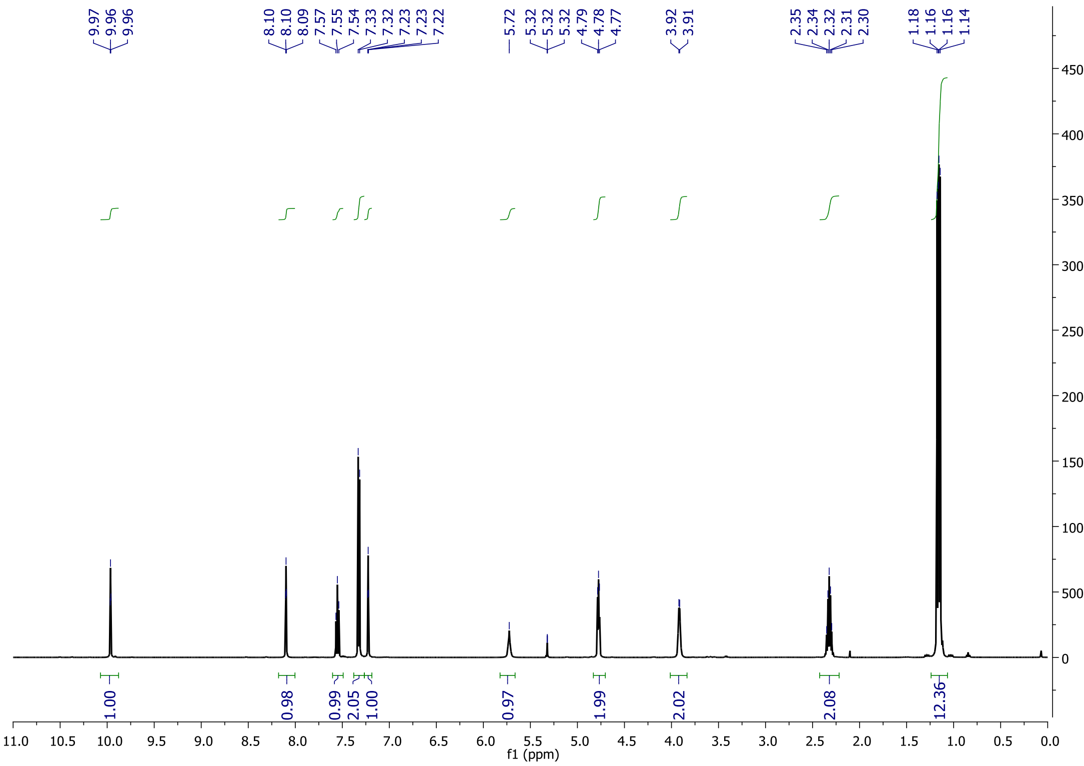
Synthesis of [$\mathbf{NiCl_2\{ImDiPP(C_2OMe)\}_2}$] (15). A mixture of the silver complex **13** (0.197 g, 0.275 mmol) in THF and [$NiCl_2$(dme)] (0.061 g, 0.28 mmol) was stirred overnight at room temperature to afford an orange solution and a white precipitate. The precipitate was removed by filtration through Celite and the solvent was evaporated under reduced pressure. The resulting orange solid was washed with H_2O, dissolved in THF and the solution was dried with Na_2SO_4. The solvent was removed under reduced pressure to afford **15** as an orange solid (0.100 g, 0.142 mmol). Yield: 50%. *Major product*: ^{1}H NMR (C_6D_6, 500 MHz): 7.39-7.31 (m, 3H, $\mathrm{CH}^{\mathrm{Ar}}$), 6.66 (d, J = 1.7 Hz, 1H, $\mathrm{CH}^{\mathrm{imidazole}}$), 6.33 (d, J = 1.7 Hz, 1H, $\mathrm{CH}^{\mathrm{imidazole}}$), 4.96 (t, J = 4.7 Hz, 2H, CH_2), 3.85 (t, J = 4.7 Hz, 2H, CH_2OMe), 3.13 (septet, J = 6.9 Hz, 2H, $\mathrm{CH}^{i\mathrm{Pr}}$), 3.01 (s, 3H, $\mathrm{CH_3}^{\mathrm{OMe}}$), 1.53 (d, J = 6.6 Hz, 6H, $\mathrm{CH_3}^{i\mathrm{Pr}}$), 0.92 (d, J = 6.9 Hz, 6H, $\mathrm{CH_3}^{i\mathrm{Pr}}$). ^{13}C{^{1}H} NMR ($C_6D_6$, 126 MHz): 171.5 ($\mathrm{C}^{\mathrm{carbene}}$), 148.4 ($\mathrm{C}^{\mathrm{Ar}}$), 136.7 ($\mathrm{C}^{\mathrm{Ar}}$), 129.9 ($\mathrm{CH}^{\mathrm{Ar}}$), 123.9 ($\mathrm{CH}^{\mathrm{Ar}}$), 123.6 ($\mathrm{CH}^{\mathrm{imidazole}}$), 121.7 ($\mathrm{CH}^{\mathrm{imidazole}}$), 72.3 ($CH_2OMe$), 58.7 ($\mathrm{CH_3}^{\mathrm{OMe}}$), 51.5 ($CH_2$), 28.7 ($\mathrm{CH}^{\mathrm{iPr}}$), 26.8 ($\mathrm{CH_3}^{i\mathrm{Pr}}$), 23.0 ($\mathrm{CH_3}^{i\mathrm{Pr}}$). *Minor product*: ^{1}H NMR (500 MHz, C_6D_6): δ 7.39-7.31 (m, 1H, $\mathrm{CH}^{p\text{-}\mathrm{Ar}}$), 7.19 (d, J = 7.8 Hz, 2H, $\mathrm{CH}^{m\text{-}\mathrm{Ar}}$), 6.68-6.66 (m sh, 1H, $\mathrm{CH}^{\mathrm{imidazole}}$), 6.25 (d, J = 1.6 Hz, 1H, $\mathrm{CH}^{\mathrm{imidazole}}$), 5.65 (t, J = 5.3 Hz, 2H, CH_2), 4.18 (t, J = 5.4 Hz, 2H, CH_2OMe), 3.08 (s, 3H, $\mathrm{CH_3}^{\mathrm{OMe}}$), 2.91 (septet, J = 6.7 Hz, 2H, $\mathrm{CH}^{i\mathrm{Pr}}$), 1.21 (d, J = 6.7 Hz, 6H, $\mathrm{CH_3}^{\mathrm{iPr}}$), 0.91-0.88 (m sh, 6H, $\mathrm{CH_3}^{i\mathrm{Pr}}$). ^{13}C{^{1}H} NMR ($C_6D_6$, 126 MHz): 170.2 ($\mathrm{C}^{\mathrm{carbene}}$), 147.3 ($\mathrm{C}^{\mathrm{Ar}}$), 136.3 ($\mathrm{C}^{\mathrm{Ar}}$), 129.7($\mathrm{CH}^{\mathrm{Ar}}$), 124.1 ($\mathrm{CH}^{\mathrm{Ar}}$), 124.0 ($\mathrm{CH}^{\mathrm{imidazole}}$), 121.4 ($\mathrm{CH}^{\mathrm{imidazole}}$), 72.8 ($CH_2OMe$), 58.8 ($\mathrm{CH_3}^{\mathrm{OMe}}$), 51.4 ($CH_2$), 28.4 ($\mathrm{CH}^{i\mathrm{Pr}}$), 26.5 ($\mathrm{CH_3}^{i\mathrm{Pr}}$), 23.3 ($\mathrm{CH_3}^{i\mathrm{Pr}}$). MS (ESI): *m/z* 665.31 [M-Cl]$^+$. FTIR: ν_{max}(solid)/cm^{-1} : 3133vw, 2964m, 2865m, 1466m, 1446m, 1413m, 1380m, 1356m, 1321w, 1292m, 1269m, 1181m, 1162vw, 1120s, 1089vw, 1059w, 1040w, 1011m, 957m, 933w, 897vw, 843w, 822w, 803m, 762s, 735m, 706s, 641w, 614w, 567m, 536s, 474m, 427m, 392vs, 350m, 316w, 275w, 225m, 128vs. Anal. calcd for $C_{36}H_{52}Cl_2N_4NiO_2$ (%): C 61.56, H 7.64, N 7.98; found: C 61.57, H 7.46, N 7.94.

Catalytic oligomerization of ethylene

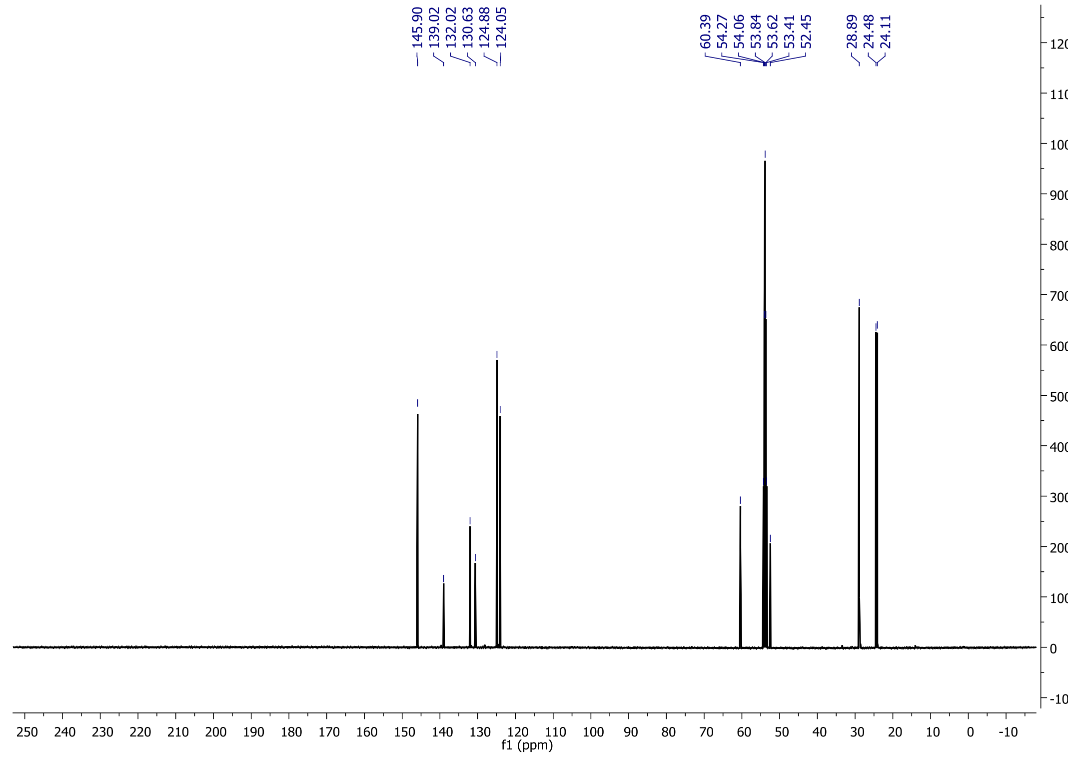
The catalytic reactions were performed in a magnetically stirred (1200 rpm) 145 mL stainless steel autoclave. A 125 mL glass container was used to avoid corrosion of the autoclave walls. The precatalyst solution was prepared by dissolving 28.1 mg (4 x 10^{-5} mol) of a powder of **15** in toluene (10 mL). $AlEtCl_2$ was used as cocatalyst (8 x 10^{-5} mol in toluene). The precatalyst solution was injected into the reactor under an ethylene flux, followed by 5 mL of the cocatalyst solution (10 equiv.) (total volume of the solution: 15 mL). The catalytic reaction was started at 20 °C. No cooling of the reactor was done during the reaction. After injection of the catalyst and cocatalyst solutions under a constant low flow of ethylene, which is considered as the t_0 time, the reactor was immediately pressurized to 10 bar of ethylene. The temperature increased to 32 °C, owing solely to the exothermicity of the reaction. The 10 bar working pressure was maintained through a continuous feed of ethylene from a bottle placed on a balance to allow continuous monitoring of the ethylene uptake. At the end of each test (35 min), a dry ice bath was used to rapidly cool the reactor. When the inner temperature reached 0 °C, the ice bath was removed, allowing the temperature to slowly rise to 18 °C. The gaseous phase was then transferred into a 10 L polyethylene tank filled with water. An aliquot of this gaseous phase was transferred into a Schlenk flask, previously evacuated, for GC analysis. The amount of ethylene consumed was thus determined by differential weighting of the bottle (accuracy of the scale: 0.1 g). To this amount of ethylene, the remaining ethylene (calculated using the GC analysis) in the gaseous phase was subtracted. Although this method is of limited accuracy, it was used throughout and gave satisfactory reproducibility. The reaction mixture in the reactor was quenched in situ by the addition of ethanol (1 mL), transferred into a Schlenk flask, and separated from the metal complexes by trap- to-trap evaporation (20 °C, 0.8 mbar) into a second Schlenk flask previously immersed in liquid nitrogen in order to avoid loss of product.

2) ^{1}H and ^{13}C NMR spectra for 1, 2, 4, 5, 6, 9, 10, 12, 13 and 15

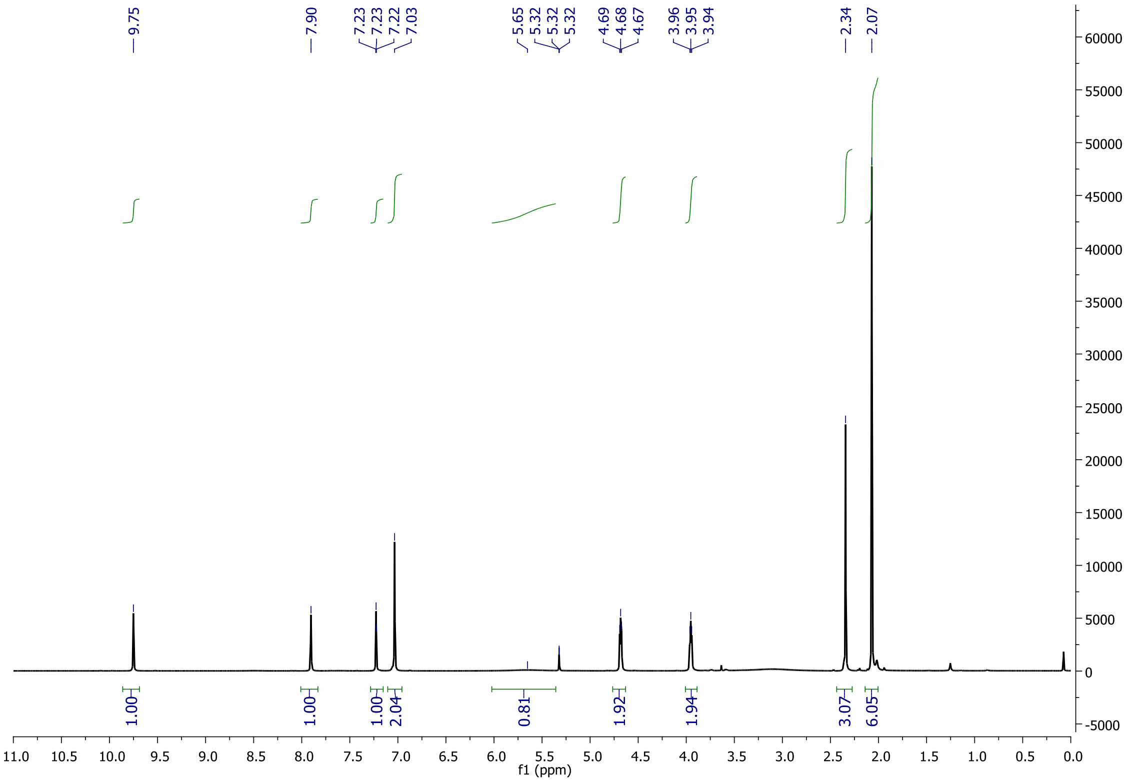
^{1}H NMR (CD_2Cl_2, 500 MHz) of [ImDiPP(C_2OH)]Cl **(1).**



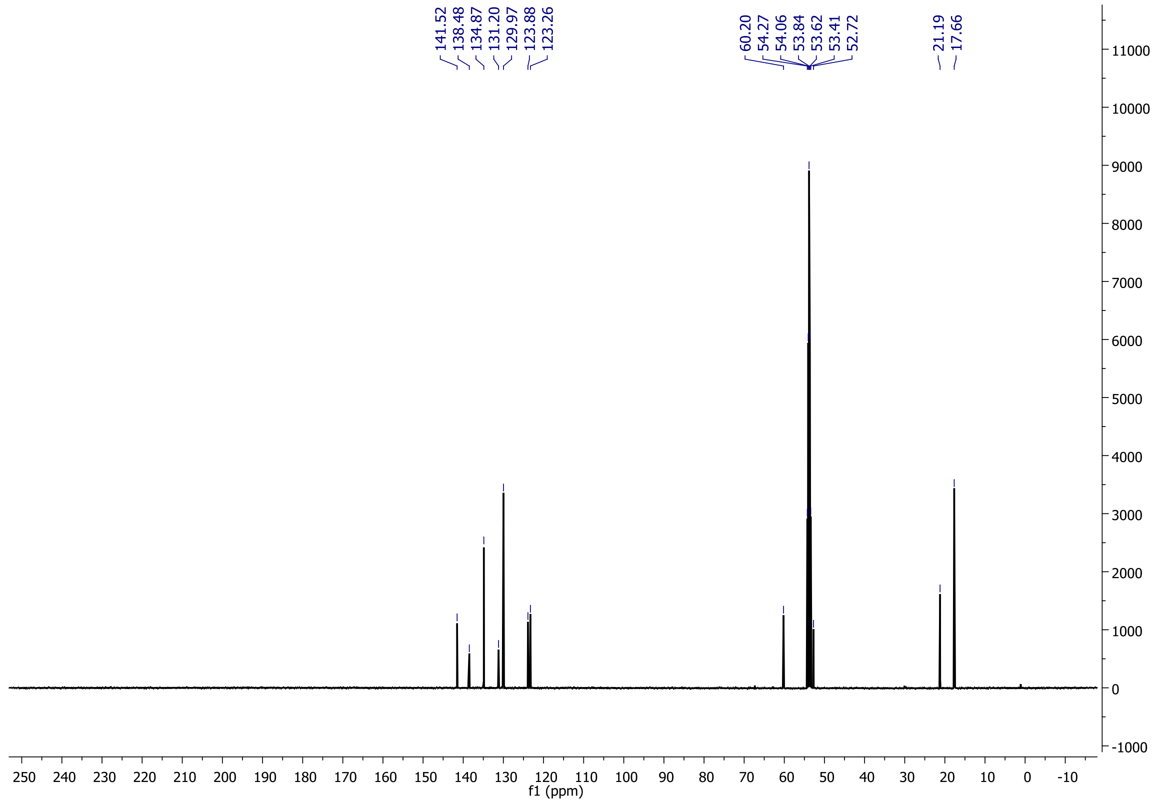
^{13}C NMR (CD_2Cl_2, 500 MHz) of [ImDiPP(C_2OH)]Cl **(1).**



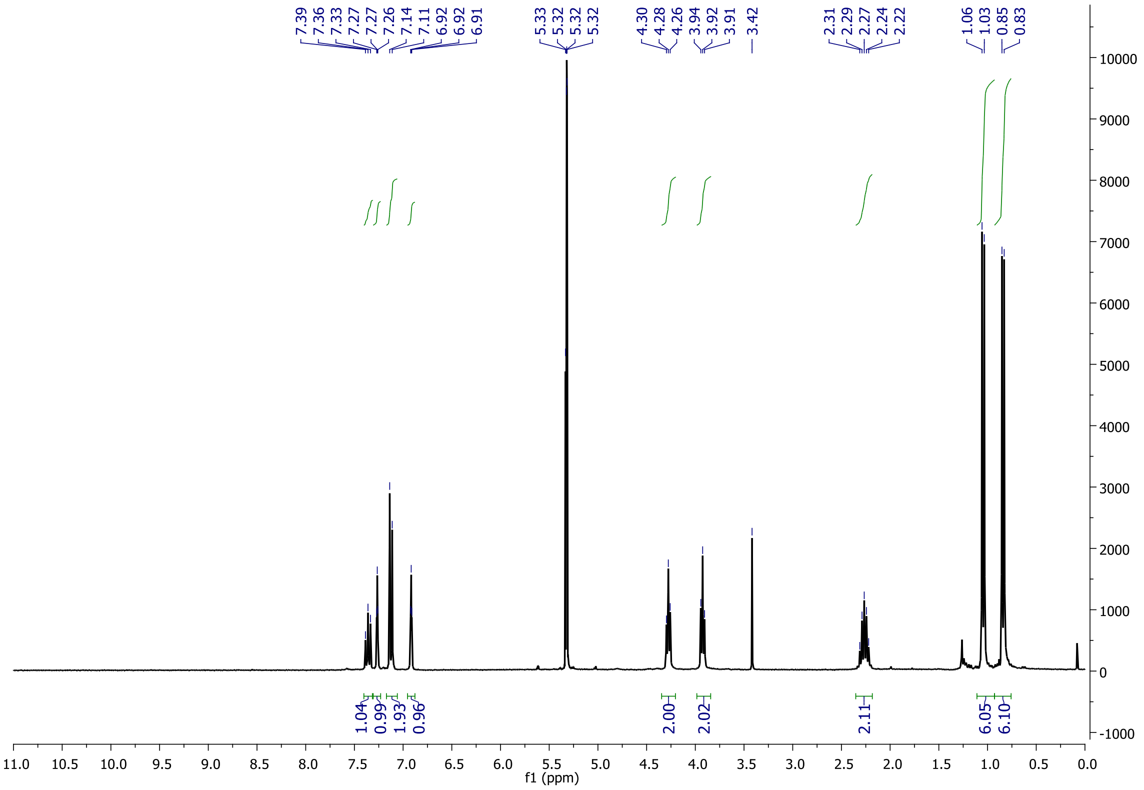
^{1}H NMR (CD_2Cl_2, 500 MHz) of [ImMes(C_2OH)]Cl **(2)**



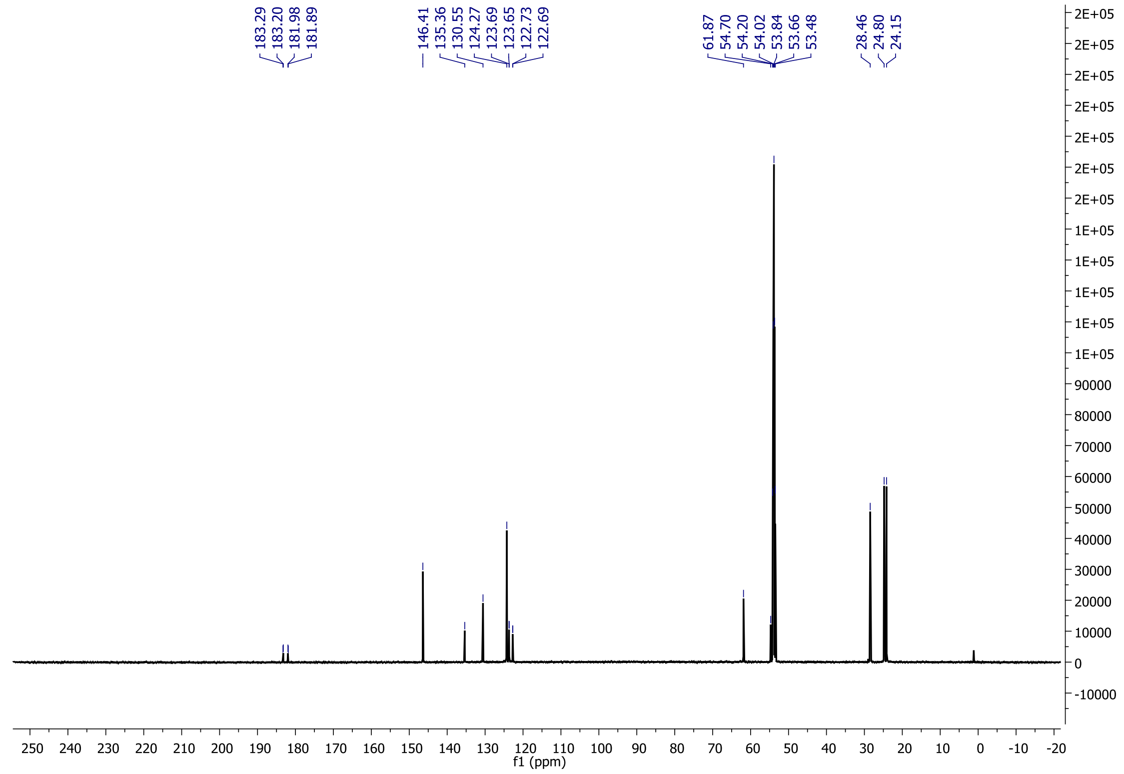
^{13}C NMR (CD_2Cl_2, 500 MHz) of [ImMes(C_2OH)]Cl **(2)**



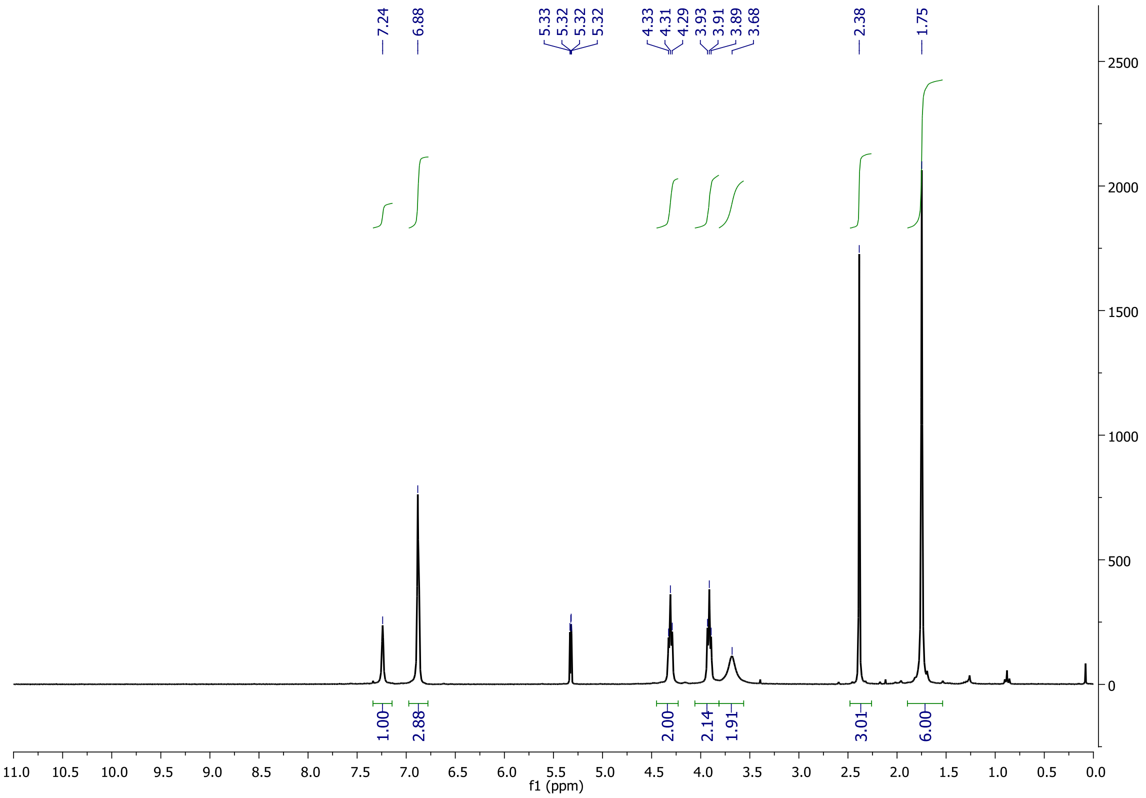
^{1}H NMR (CD_2Cl_2, 300 MHz) of [Ag{ImDiPP(C_2OH)}$_2$]Cl **(4)**



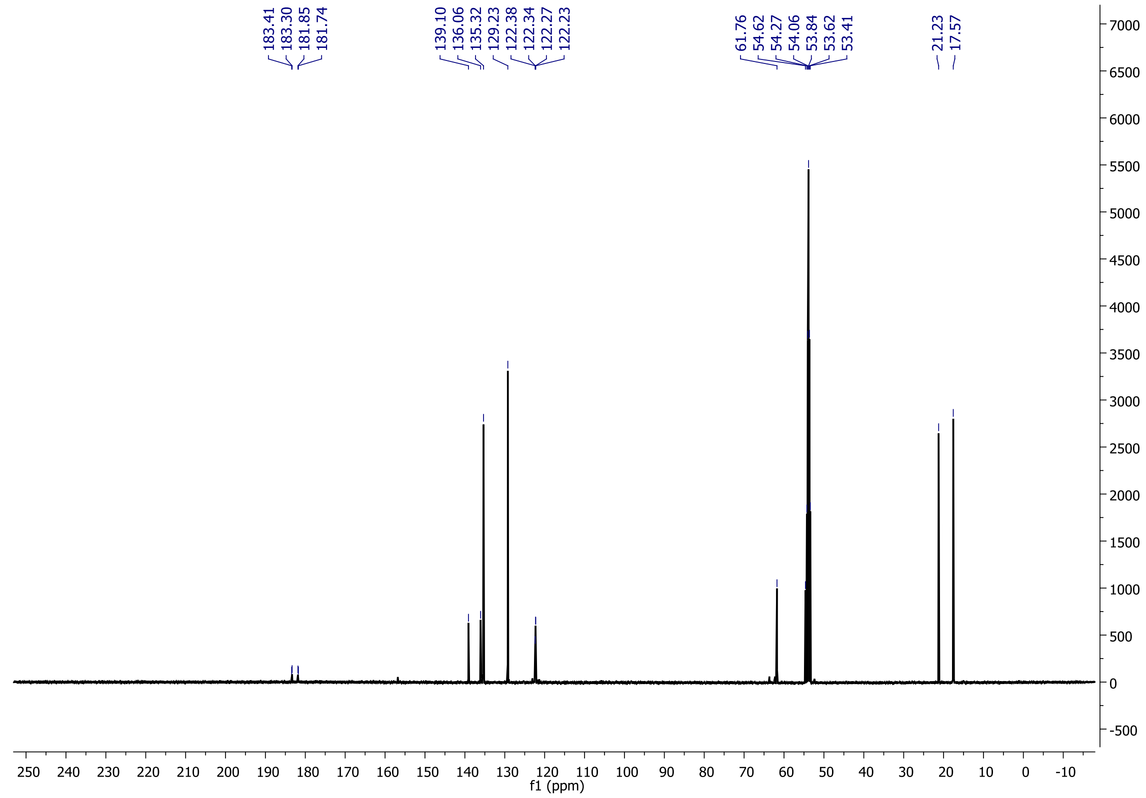
^{13}C NMR (CD_2Cl_2, 150.9 MHz) of [Ag{ImDiPP(C_2OH)}$_2$]Cl **(4)**



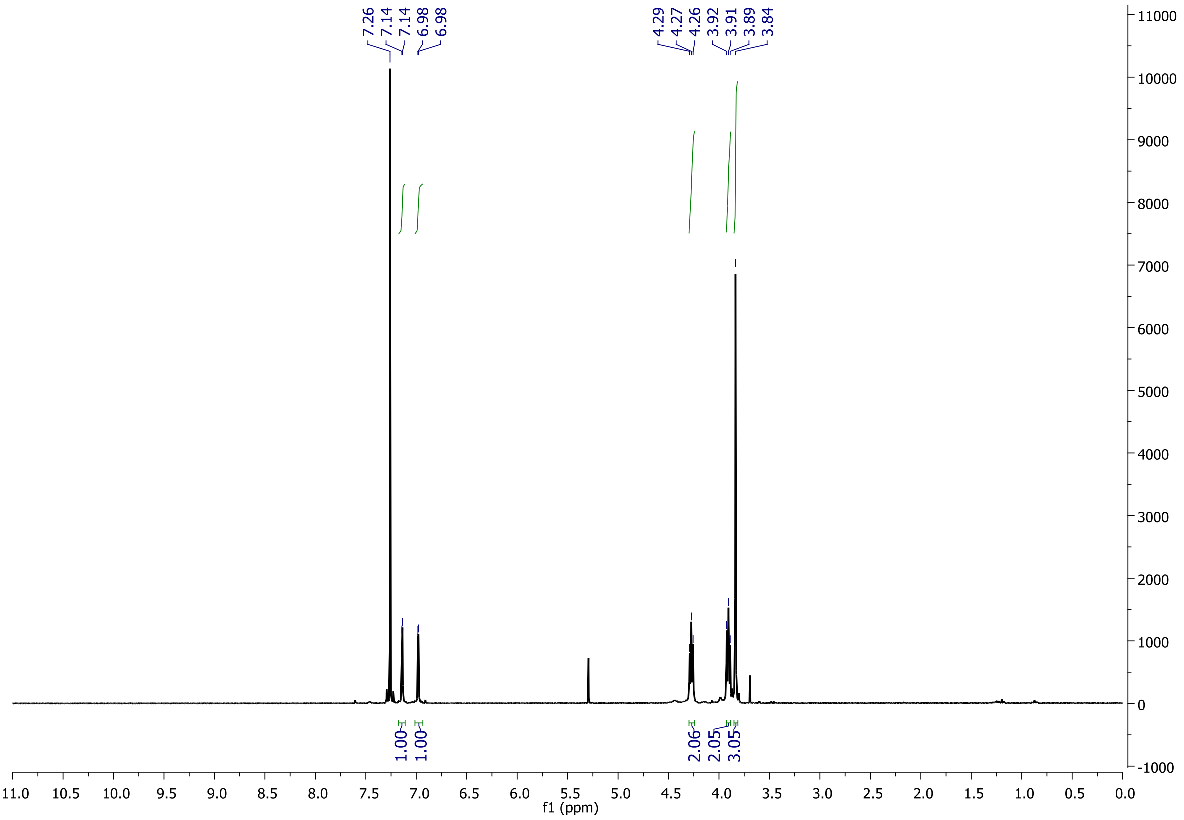
^{1}H NMR (CD_2Cl_2, 500 MHz) of [Ag{ImMes(C_2OH)}$_2$]Cl **(5)**



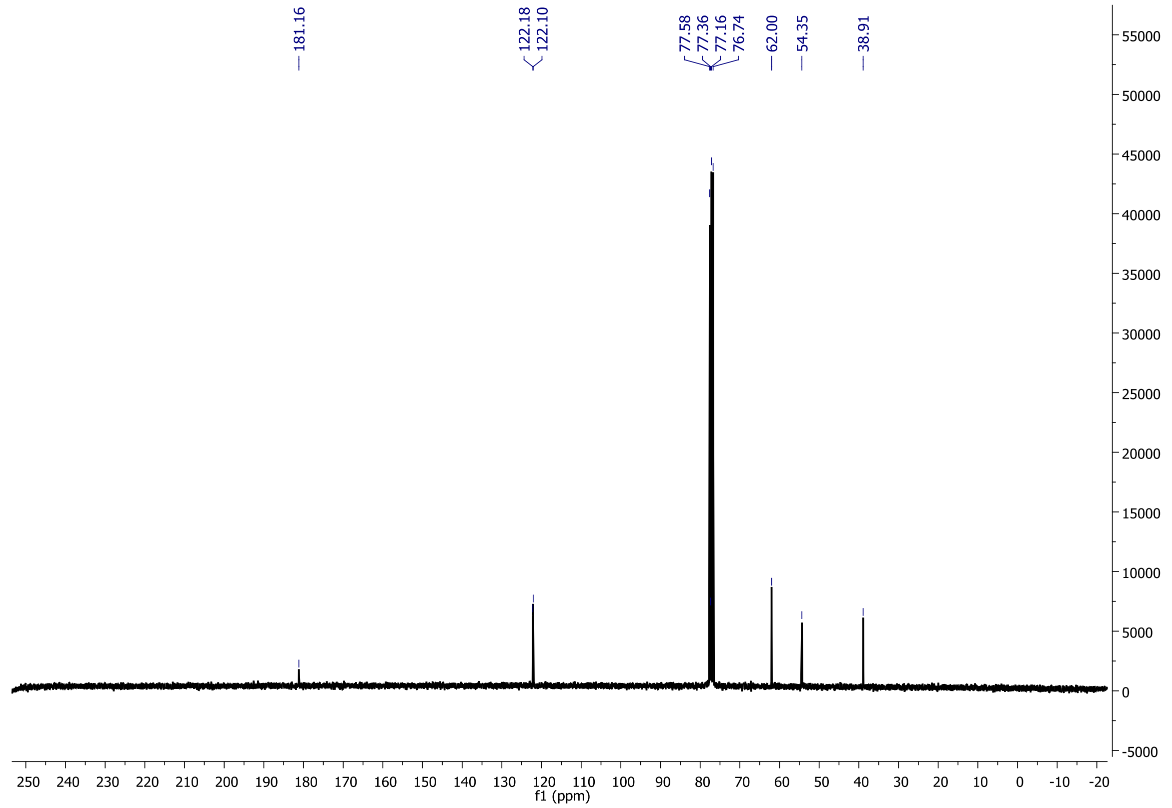
^{13}C NMR (CD_2Cl_2, 500 MHz) of [Ag{ImMes(C_2OH)}$_2$]Cl **(5)**



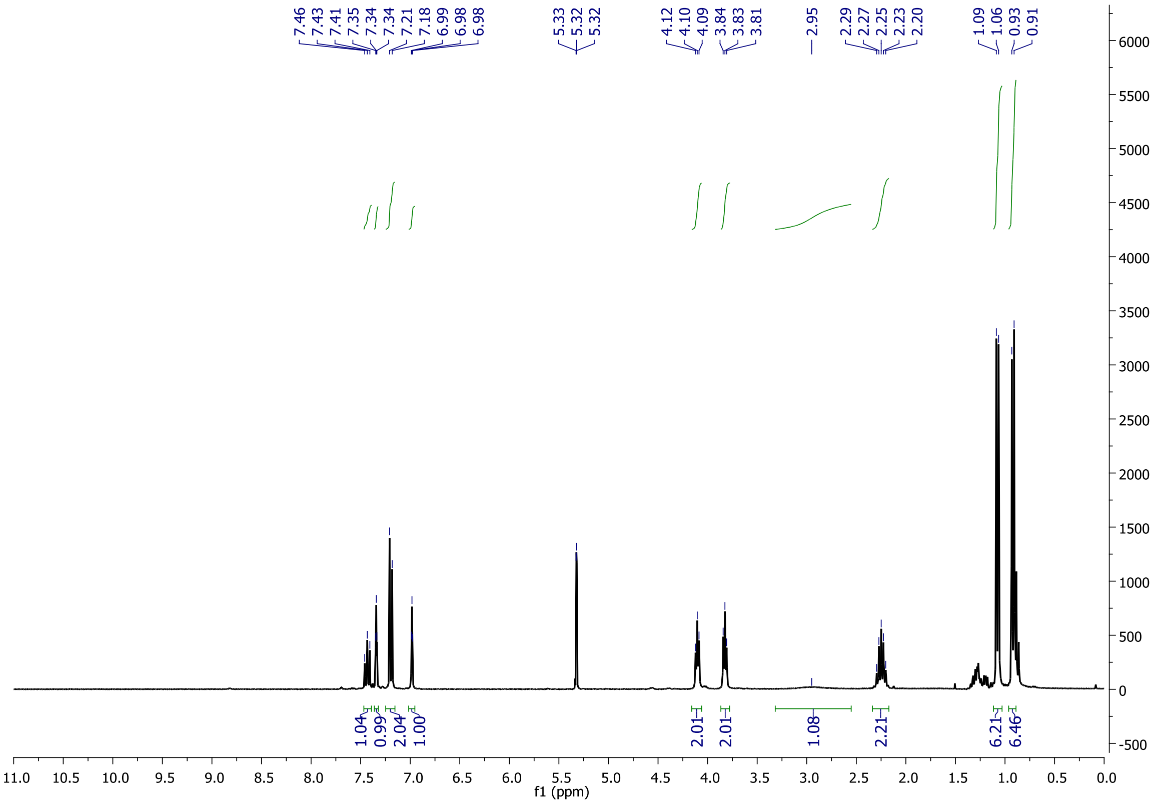
^{1}H NMR ($CDCl_3$, 500 MHz) of [Ag{ImMe(C_2OH)}$_2$]Cl **(6)**



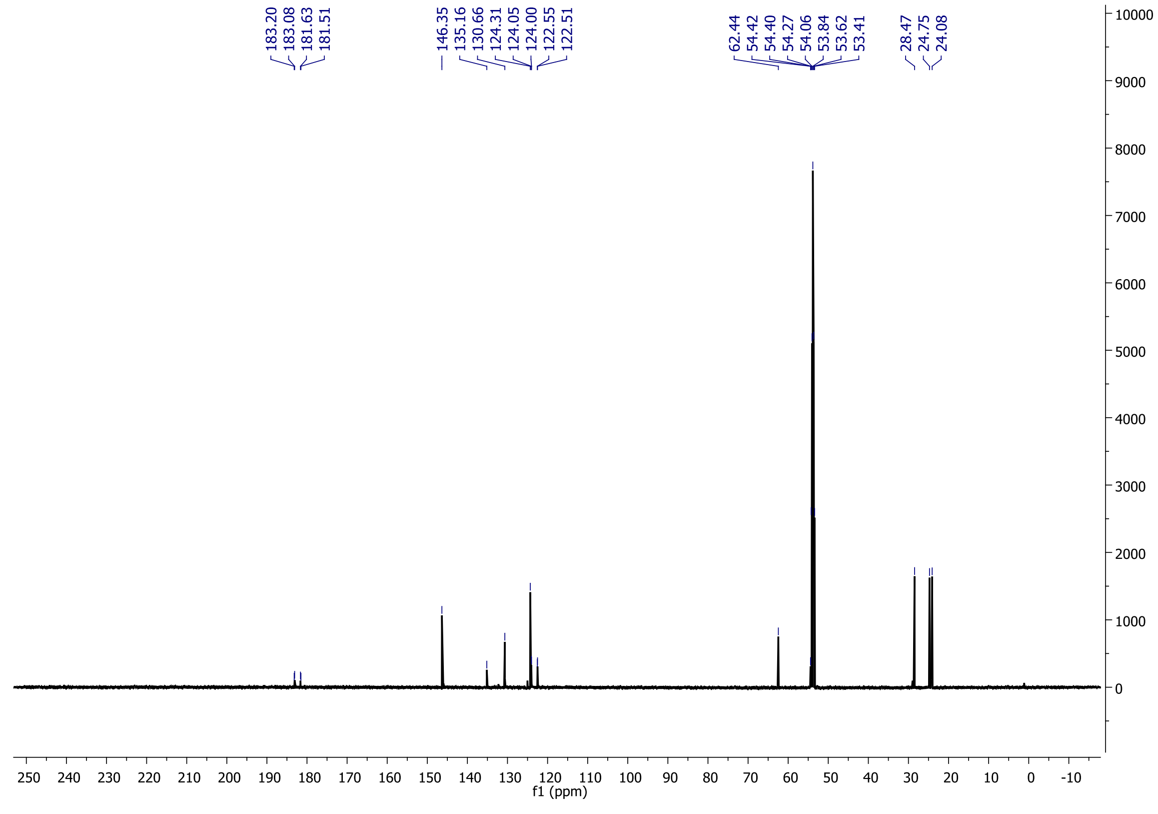
^{13}C NMR ($CDCl_3$, 500 MHz) of [Ag{ImMe(C_2OH)}$_2$]Cl **(6)**



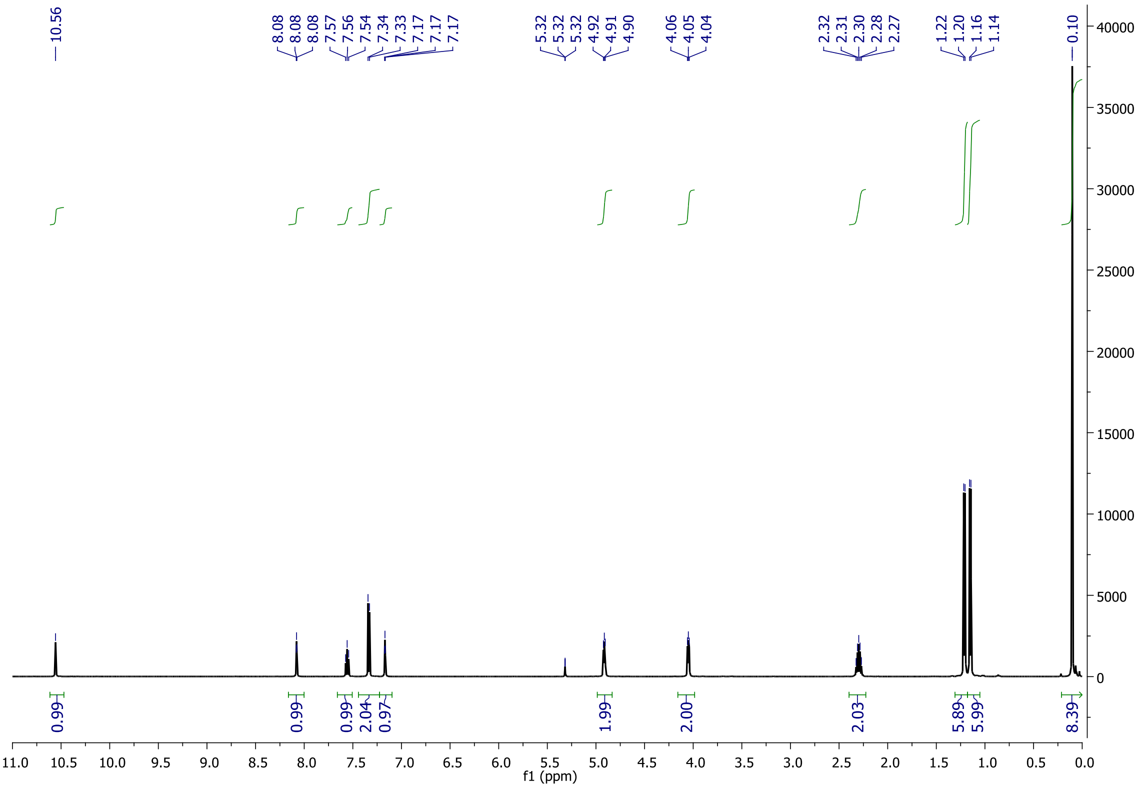
^{1}H NMR (CD_2Cl_2, 500 MHz) of [Ag{ImDiPP(C_2OH)}$_2$]BF_4 **(9)**



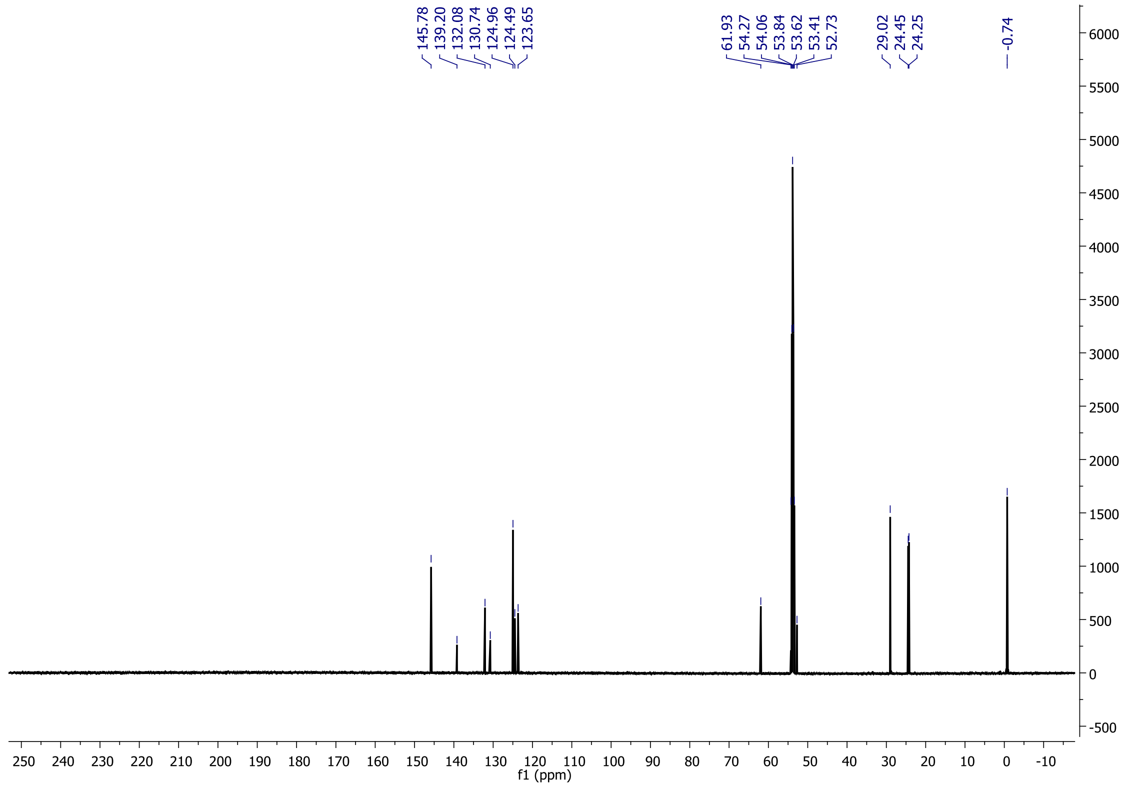
^{13}C NMR (CD_2Cl_2, 500 MHz) of [Ag{ImDiPP(C_2OH)}$_2$]BF_4 **(9)**



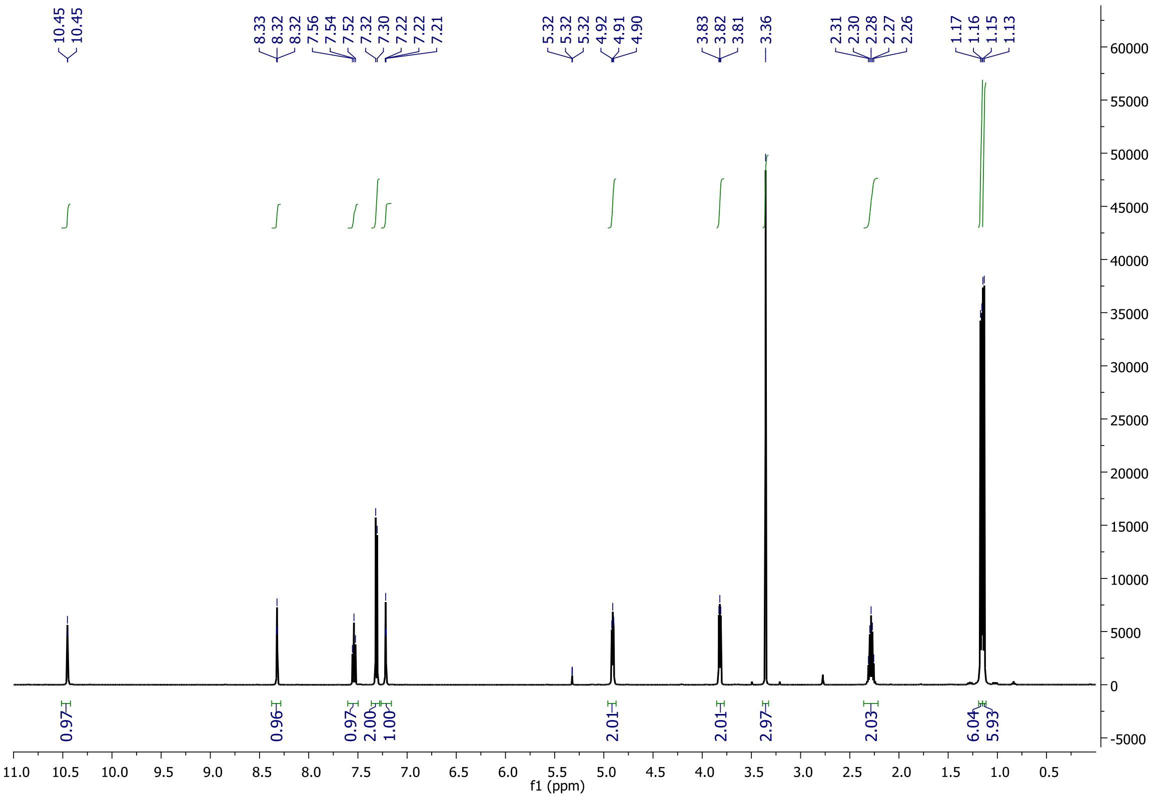
^{1}H NMR (CD$_2$Cl$_2$, 500 MHz) of [ImDiPP(C$_2$OTMS)]Cl **(10)**



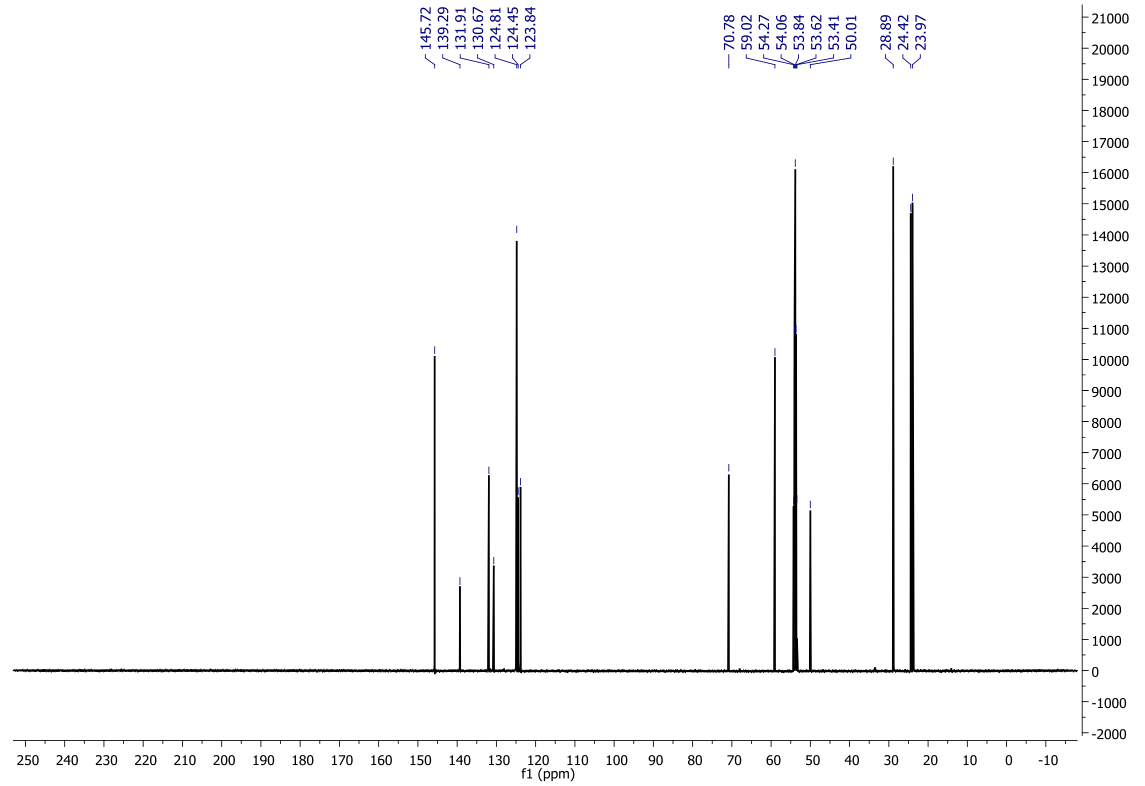
^{13}C NMR (CD$_2$Cl$_2$, 500 MHz) of [ImDiPP(C$_2$OTMS)]Cl **(10)**



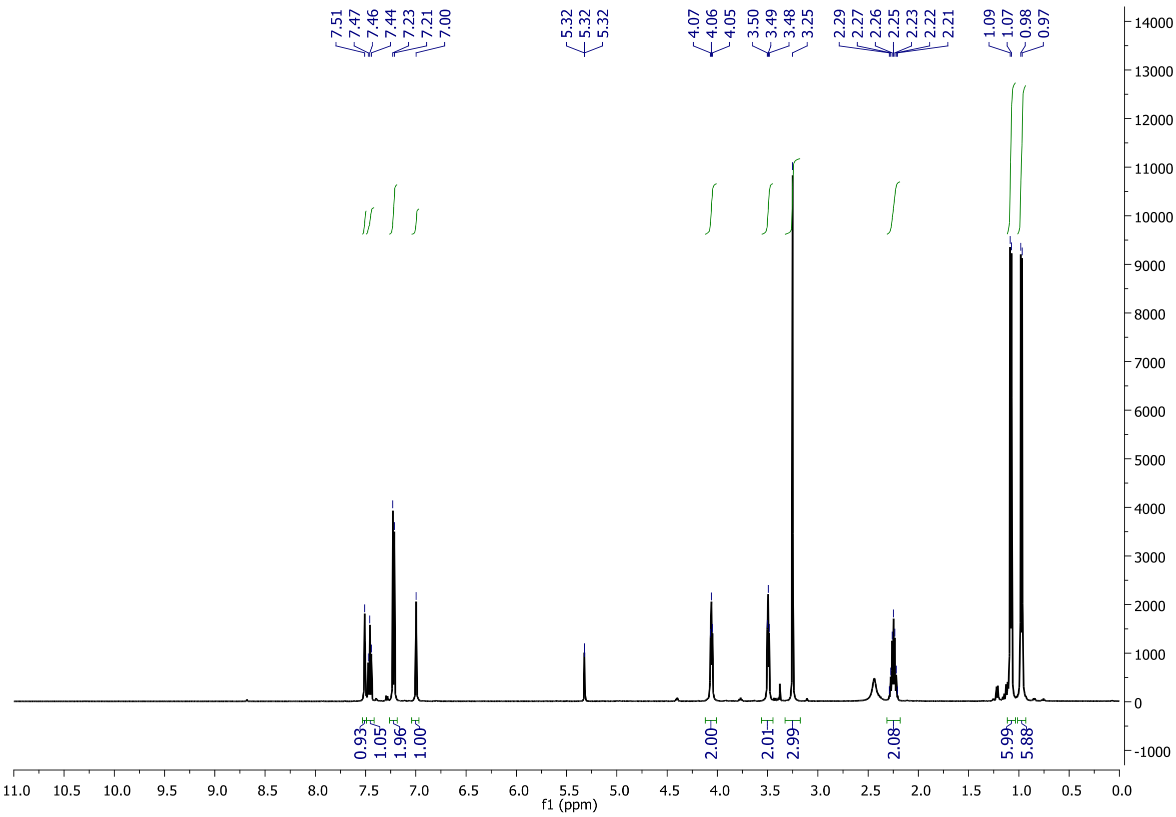
^{1}H NMR (CD_2Cl_2, 500 MHz) of [ImDiPP(C_2OMe)]Cl **(12)**



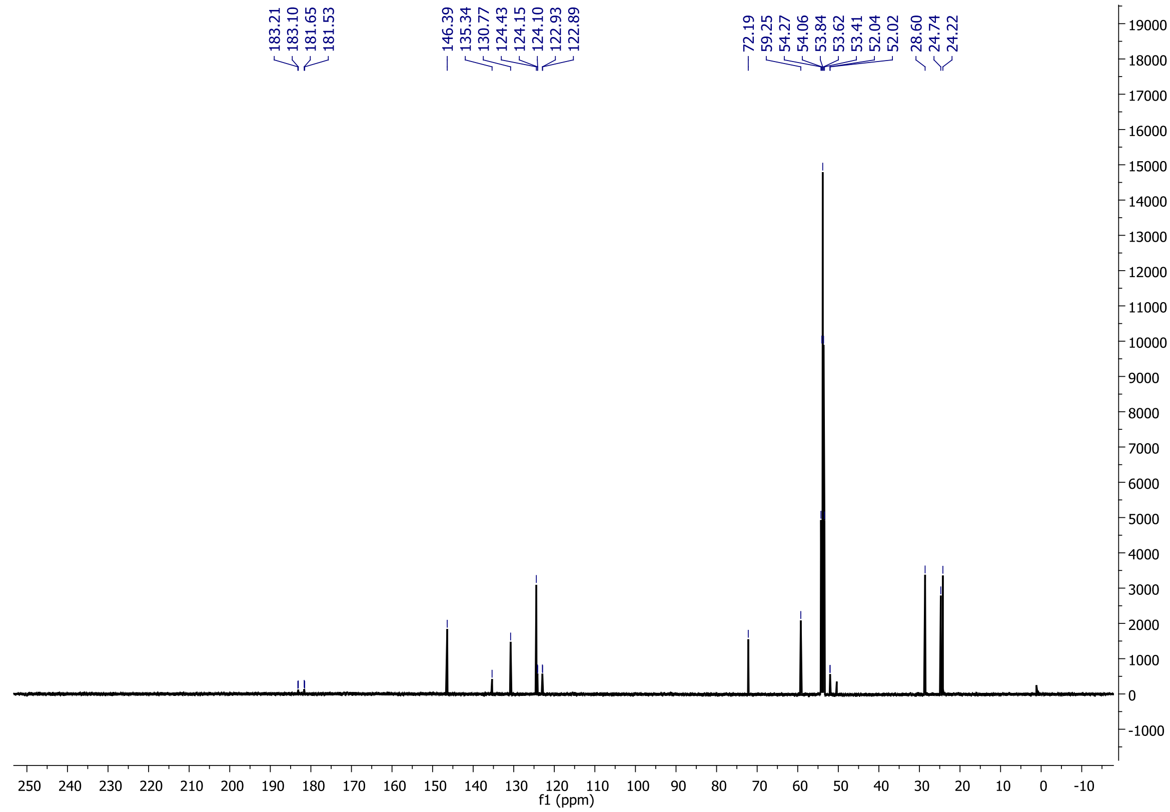
^{13}C NMR (CD_2Cl_2, 500 MHz) of [ImDiPP(C_2OMe)]Cl **(12)**



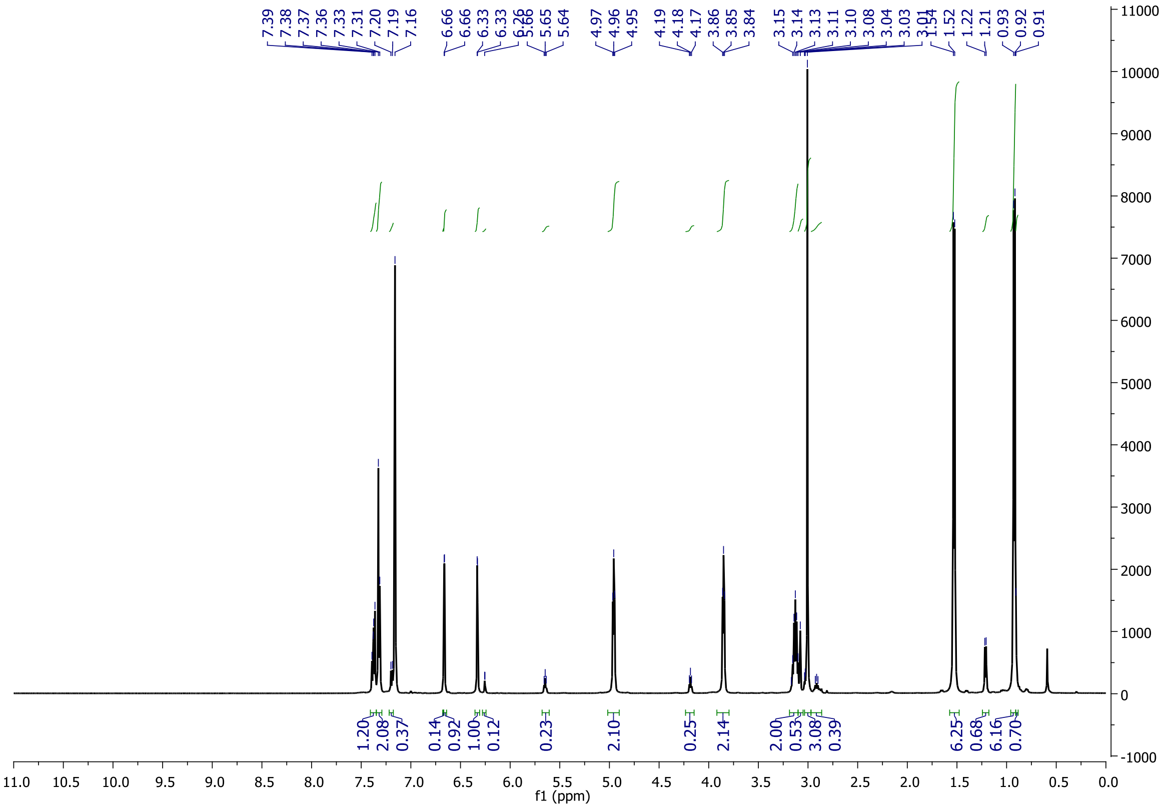
^{1}H NMR (CD_2Cl_2, 500 MHz) of [Ag{ImDiPP(C_2OMe)}$_2$]Cl **(13)**



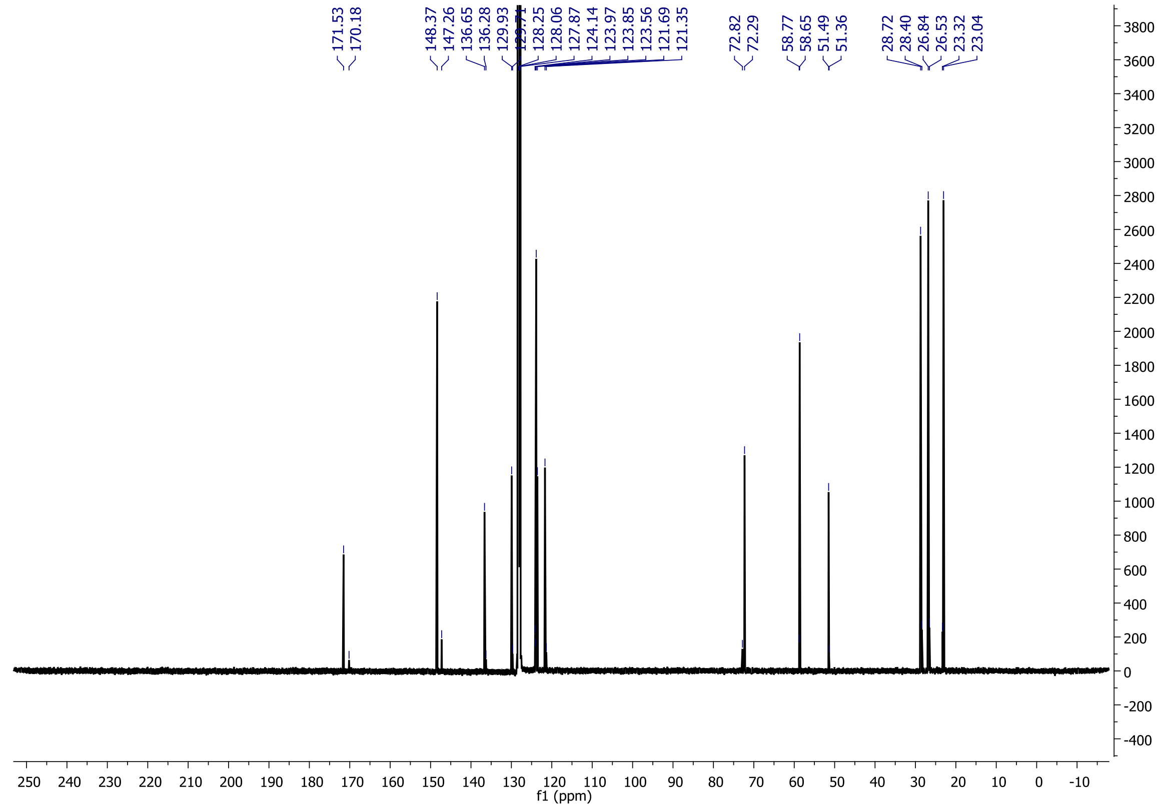
^{13}C NMR (CD_2Cl_2, 500 MHz) of [Ag{ImDiPP(C_2OMe)}$_2$]Cl **(13)**



^{1}H NMR (C_6D_6, 500 MHz) of $[NiCl_2\{ImDiPP(C_2OMe)\}_2]$ **(15)**

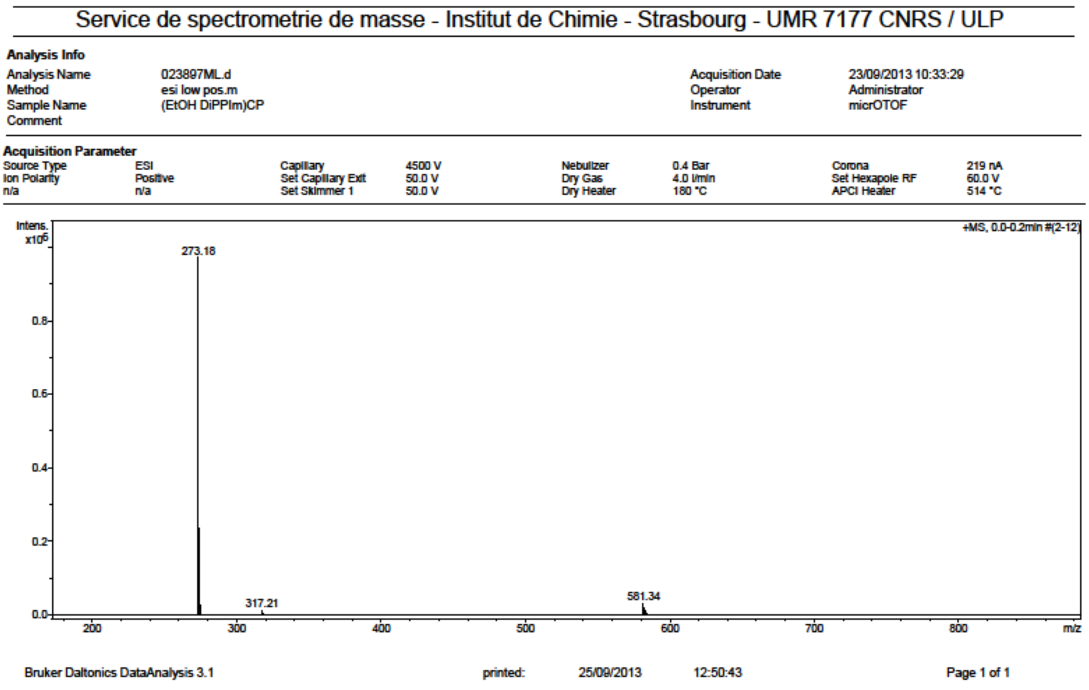


^{13}C NMR (C_6D_6, 500 MHz) of $[NiCl_2\{ImDiPP(C_2OMe)\}_2]$ **(15)**



3) Mass spectrometry analyses of 1, 2, 4, 5, 6, 9, 10, 12, 13 and 15

MS (ESI) of [ImDiPP(C_2OH)]Cl **(1)**



Service de spectrometrie de masse - Institut de Chimie - Strasbourg - UMR 7177 CNRS / ULP

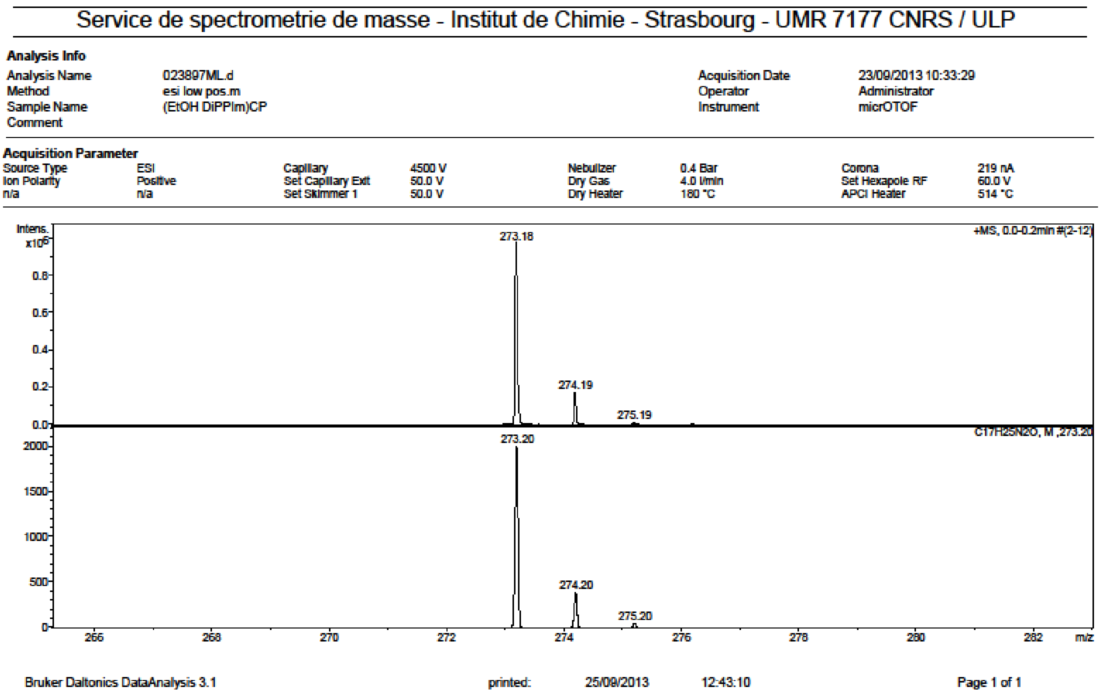
Analysis Info

Analysis Name	023897ML.d	Acquisition Date	23/09/2013 10:33:29
Method	esi low pos.m	Operator	Administrator
Sample Name	(EtOH DiPPIm)CP	Instrument	micrOTOF
Comment			

Acquisition Parameter

Source Type	ESI	Capillary	4500 V	Nebulizer	0.4 Bar	Corona	219 nA
Ion Polarity	Positive	Set Capillary Exit	50.0 V	Dry Gas	4.0 l/min	Set Hexapole RF	60.0 V
n/a	n/a	Set Skimmer 1	50.0 V	Dry Heater	180 °C	APCI Heater	514 °C

Bruker Daltonics DataAnalysis 3.1 printed: 25/09/2013 12:50:43 Page 1 of 1



Service de spectrometrie de masse - Institut de Chimie - Strasbourg - UMR 7177 CNRS / ULP

Analysis Info

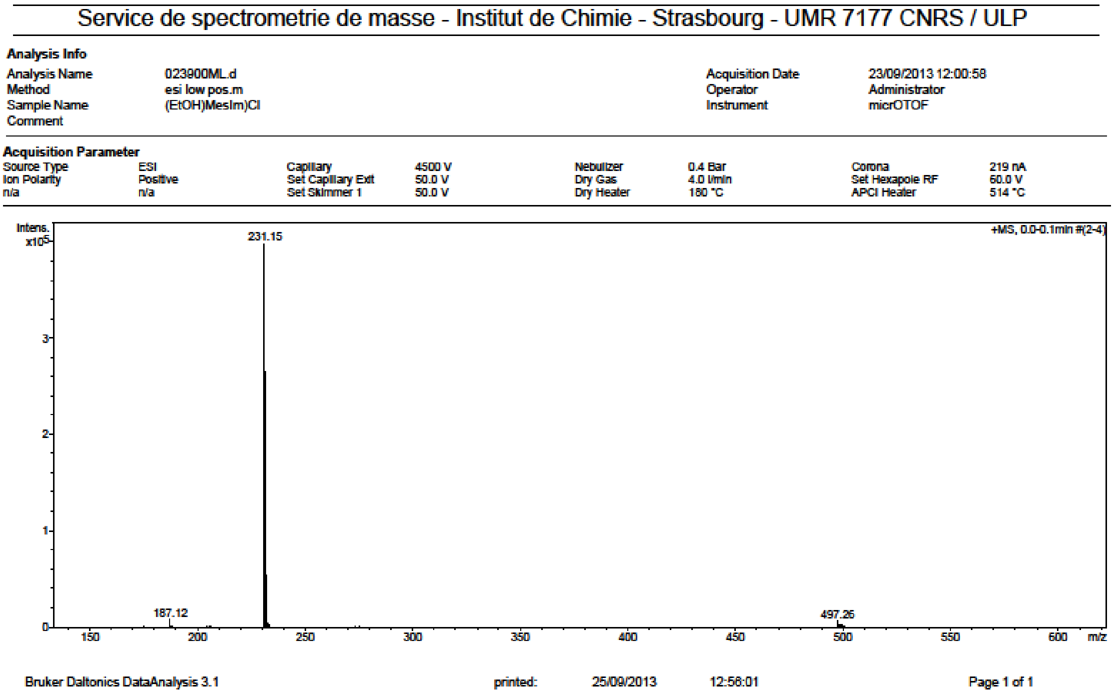
Analysis Name	023897ML.d	Acquisition Date	23/09/2013 10:33:29
Method	esi low pos.m	Operator	Administrator
Sample Name	(EtOH DiPPIm)CP	Instrument	micrOTOF
Comment			

Acquisition Parameter

Source Type	ESI	Capillary	4500 V	Nebulizer	0.4 Bar	Corona	219 nA
Ion Polarity	Positive	Set Capillary Exit	50.0 V	Dry Gas	4.0 l/min	Set Hexapole RF	60.0 V
n/a	n/a	Set Skimmer 1	50.0 V	Dry Heater	180 °C	APCI Heater	514 °C

Bruker Daltonics DataAnalysis 3.1 printed: 25/09/2013 12:43:10 Page 1 of 1

MS (ESI) of [ImMes(C_2OH)]Cl **(2)**



Service de spectrometrie de masse - Institut de Chimie - Strasbourg - UMR 7177 CNRS / ULP

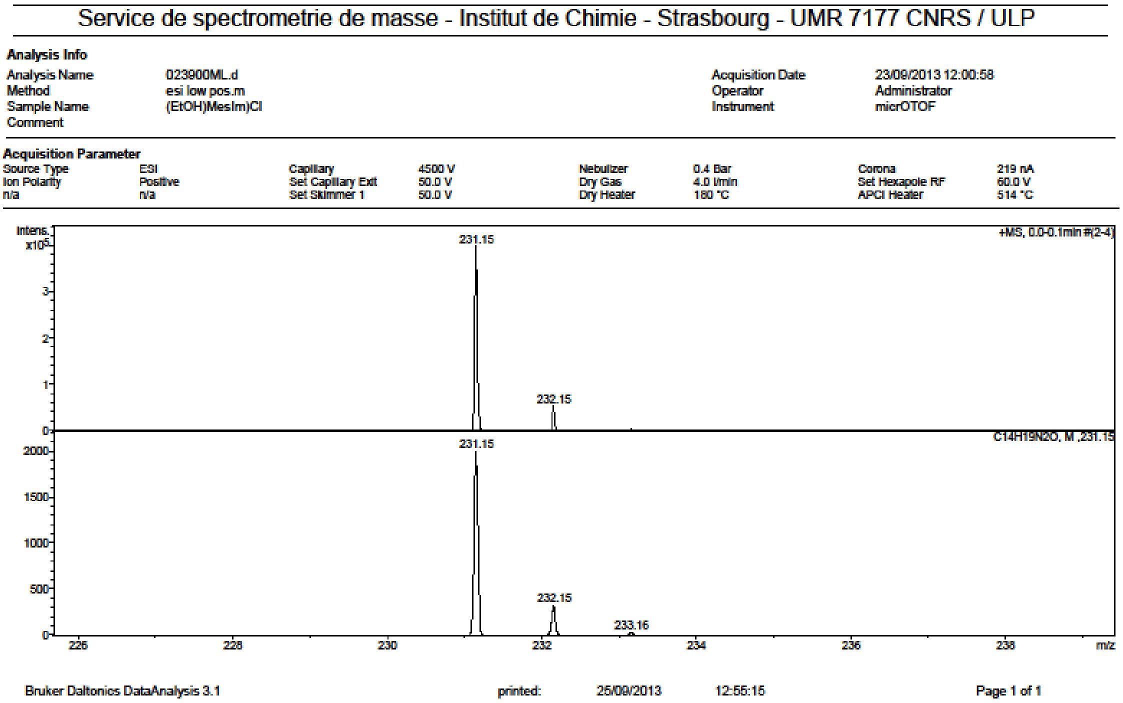
Analysis Info

Analysis Name	023900ML.d	Acquisition Date	23/09/2013 12:00:58
Method	esi low pos.m	Operator	Administrator
Sample Name	(EtOH)MesIm)Cl	Instrument	micrOTOF
Comment			

Acquisition Parameter

Source Type	ESI	Capillary	4500 V	Nebulizer	0.4 Bar	Corona	219 nA
Ion Polarity	Positive	Set Capillary Exit	50.0 V	Dry Gas	4.0 l/min	Set Hexapole RF	60.0 V
n/a	n/a	Set Skimmer 1	50.0 V	Dry Heater	180 °C	APCI Heater	514 °C

Bruker Daltonics DataAnalysis 3.1 printed: 25/09/2013 12:56:01 Page 1 of 1



Service de spectrometrie de masse - Institut de Chimie - Strasbourg - UMR 7177 CNRS / ULP

Analysis Info

Analysis Name	023900ML.d	Acquisition Date	23/09/2013 12:00:58
Method	esi low pos.m	Operator	Administrator
Sample Name	(EtOH)MesIm)Cl	Instrument	micrOTOF
Comment			

Acquisition Parameter

Source Type	ESI	Capillary	4500 V	Nebulizer	0.4 Bar	Corona	219 nA
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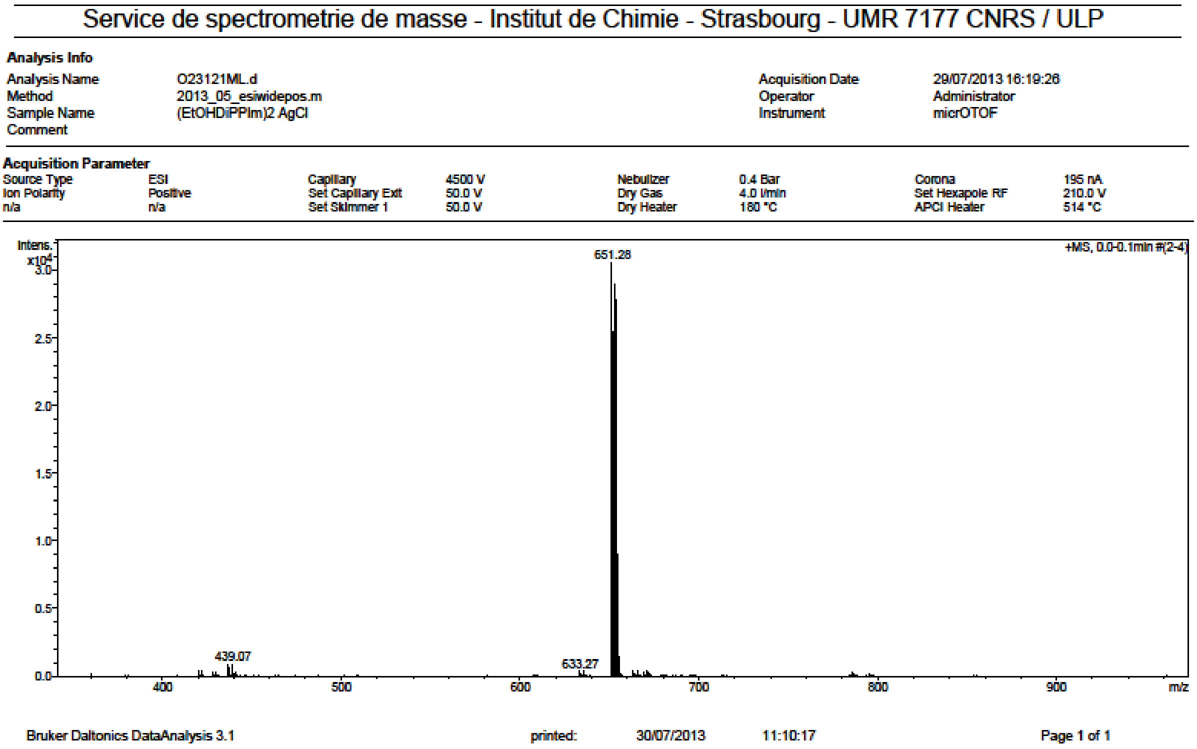
n/a	n/a	Set Skimmer 1	50.0 V	Dry Heater	180 °C	APCI Heater	514 °C

Bruker Daltonics DataAnalysis 3.1 printed: 25/09/2013 12:55:15 Page 1 of 1

MS (ESI) of [Ag{ImDiPP(C$_2$OH)}$_2$]Cl **(4)**



Service de spectrometrie de masse - Institut de Chimie - Strasbourg - UMR 7177 CNRS / ULP

Analysis Info

Analysis Name O23121ML.d
Method 2013_05_esiwidepos.m
Sample Name (EtOHDiPPIm)2 AgCl
Comment
Acquisition Date 29/07/2013 16:19:26
Operator Administrator
Instrument micrOTOF

Acquisition Parameter

Source Type ESI
Ion Polarity Positive
n/a n/a
Capillary 4500 V
Set Capillary Exit 50.0 V
Set Skimmer 1 50.0 V
Nebulizer 0.4 Bar
Dry Gas 4.0 l/min
Dry Heater 180 °C
Corona 195 nA
Set Hexapole RF 210.0 V
APCI Heater 514 °C

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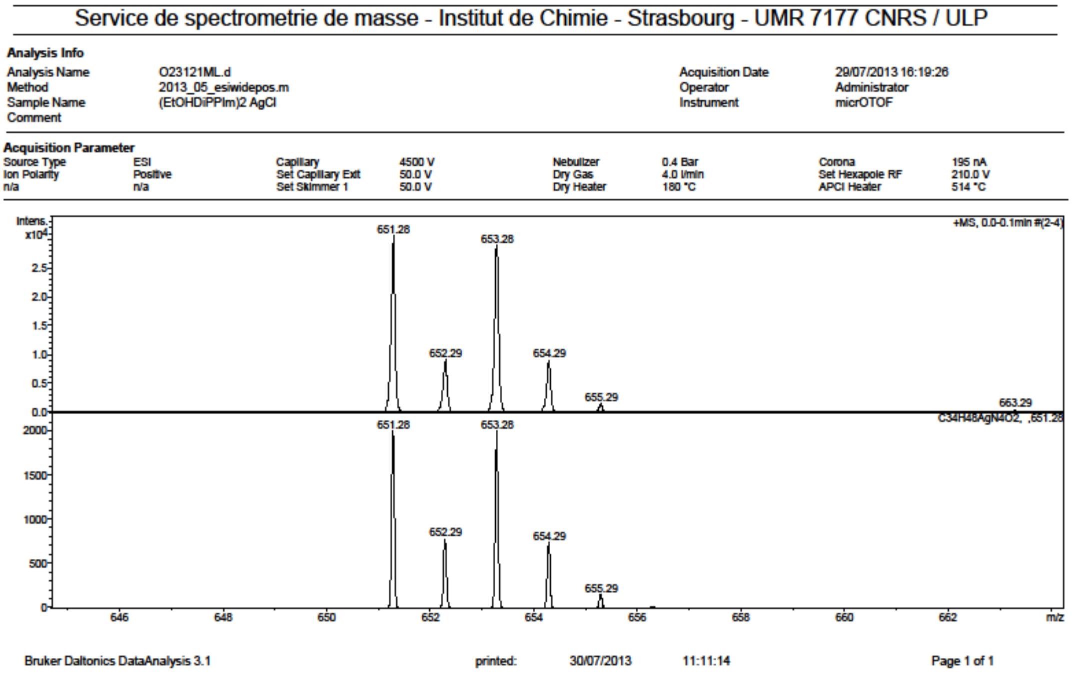

Service de spectrometrie de masse - Institut de Chimie - Strasbourg - UMR 7177 CNRS / ULP

Analysis Info

Analysis Name O23121ML.d
Method 2013_05_esiwidepos.m
Sample Name (EtOHDiPPIm)2 AgCl
Comment
Acquisition Date 29/07/2013 16:19:26
Operator Administrator
Instrument micrOTOF

Acquisition Parameter

Source Type ESI
Ion Polarity Positive
n/a n/a
Capillary 4500 V
Set Capillary Exit 50.0 V
Set Skimmer 1 50.0 V
Nebulizer 0.4 Bar
Dry Gas 4.0 l/min
Dry Heater 180 °C
Corona 195 nA
Set Hexapole RF 210.0 V
APCI Heater 514 °C

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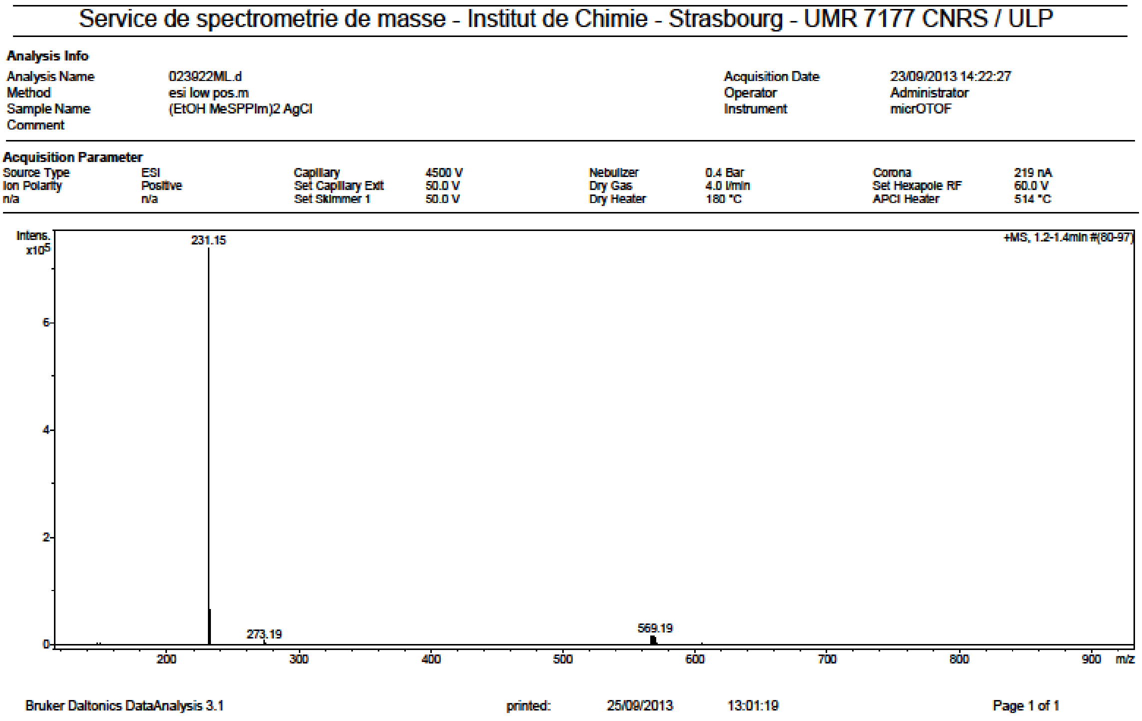
MS (ESI) of $[Ag\{ImMes(C_2OH)\}_2]Cl$ **(5)**



Service de spectrometrie de masse - Institut de Chimie - Strasbourg - UMR 7177 CNRS / ULP

Analysis Info

Analysis Name	023922ML.d	Acquisition Date	23/09/2013 14:22:27
Method	esi low pos.m	Operator	Administrator
Sample Name	(EtOH MeSPPIm)2 AgCl	Instrument	micrOTOF
Comment			

Acquisition Parameter

Source Type	ESI	Capillary	4500 V	Nebulizer	0.4 Bar	Corona	219 nA
Ion Polarity	Positive	Set Capillary Exit	50.0 V	Dry Gas	4.0 l/min	Set Hexapole RF	60.0 V
n/a	n/a	Set Skimmer 1	50.0 V	Dry Heater	180 °C	APCI Heater	514 °C

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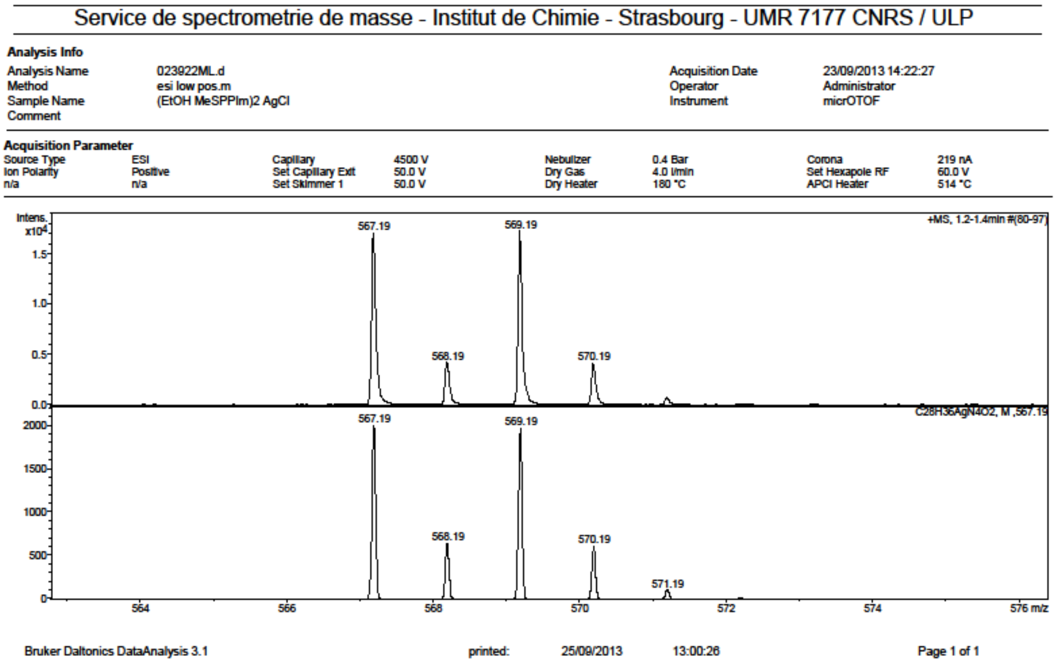

Service de spectrometrie de masse - Institut de Chimie - Strasbourg - UMR 7177 CNRS / ULP

Analysis Info

Analysis Name	023922ML.d	Acquisition Date	23/09/2013 14:22:27
Method	esi low pos.m	Operator	Administrator
Sample Name	(EtOH MeSPPIm)2 AgCl	Instrument	micrOTOF
Comment			

Acquisition Parameter

Source Type	ESI	Capillary	4500 V	Nebulizer	0.4 Bar	Corona	219 nA
Ion Polarity	Positive	Set Capillary Exit	50.0 V	Dry Gas	4.0 l/min	Set Hexapole RF	60.0 V
n/a	n/a	Set Skimmer 1	50.0 V	Dry Heater	180 °C	APCI Heater	514 °C

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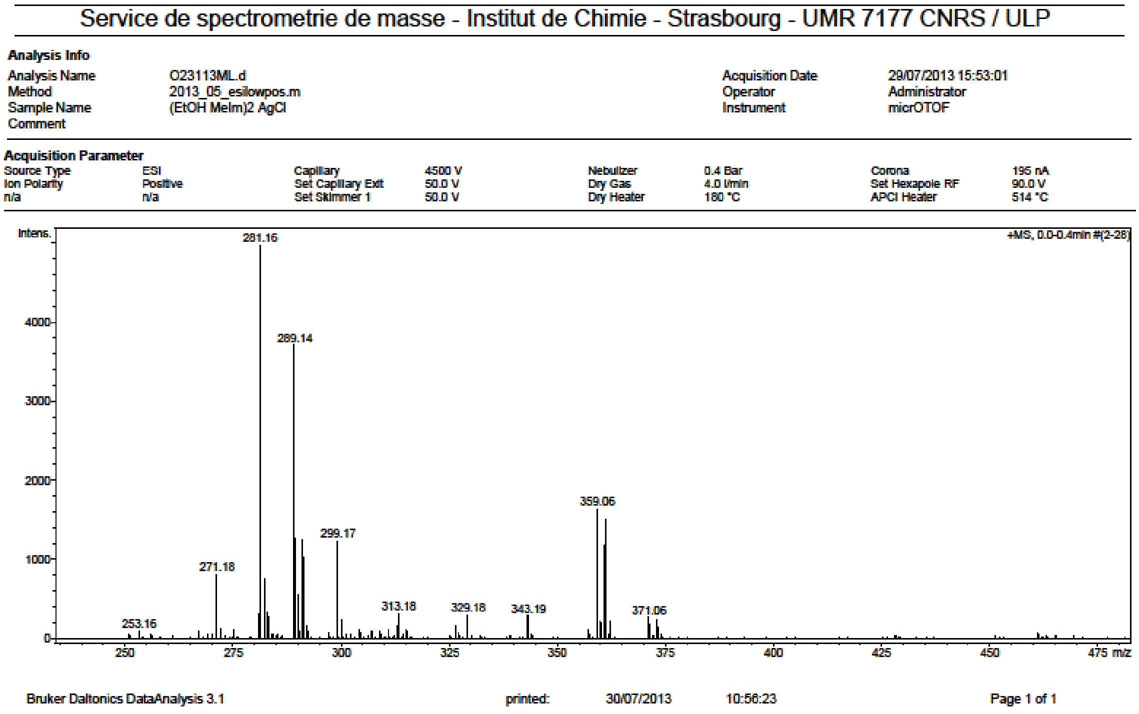
MS (ESI) of [Ag{ImMe(C_2OH)}$_2$]Cl **(6)**



Service de spectrometrie de masse - Institut de Chimie - Strasbourg - UMR 7177 CNRS / ULP

Analysis Info

Analysis Name: O23113ML.d
Method: 2013_05_esilowpos.m
Sample Name: (EtOH MeIm)2 AgCl
Comment:
Acquisition Date: 29/07/2013 15:53:01
Operator: Administrator
Instrument: micrOTOF

Acquisition Parameter

Source Type	ESI	Capillary	4500 V	Nebulizer	0.4 Bar	Corona	195 nA
Ion Polarity	Positive	Set Capillary Exit	50.0 V	Dry Gas	4.0 l/min	Set Hexapole RF	90.0 V
n/a	n/a	Set Skimmer 1	50.0 V	Dry Heater	180 °C	APCI Heater	514 °C

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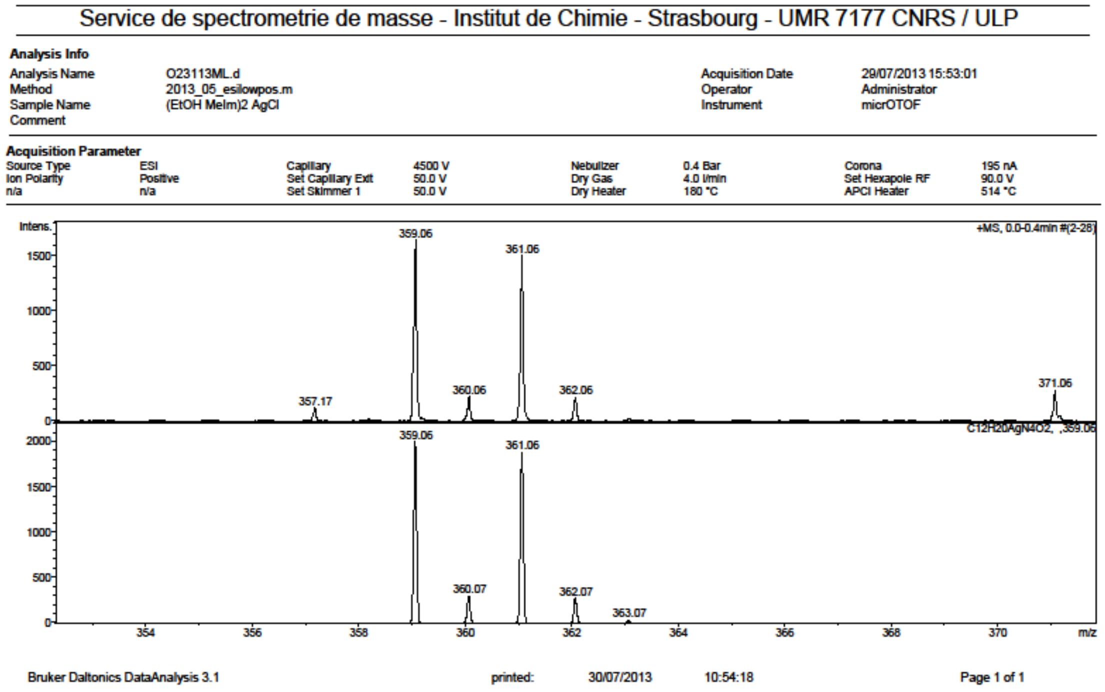


Service de spectrometrie de masse - Institut de Chimie - Strasbourg - UMR 7177 CNRS / ULP

Analysis Info

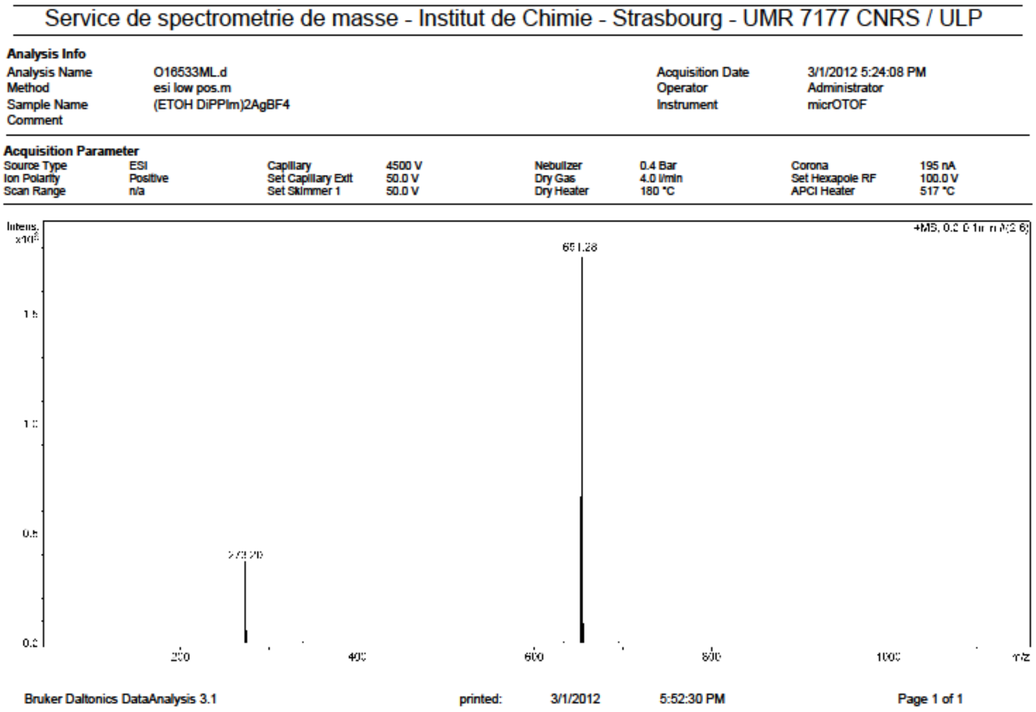
Analysis Name: O23113ML.d
Method: 2013_05_esilowpos.m
Sample Name: (EtOH MeIm)2 AgCl
Comment:
Acquisition Date: 29/07/2013 15:53:01
Operator: Administrator
Instrument: micrOTOF

Acquisition Parameter

Source Type	ESI	Capillary	4500 V	Nebulizer	0.4 Bar	Corona	195 nA
Ion Polarity	Positive	Set Capillary Exit	50.0 V	Dry Gas	4.0 l/min	Set Hexapole RF	90.0 V
n/a	n/a	Set Skimmer 1	50.0 V	Dry Heater	180 °C	APCI Heater	514 °C

Bruker Daltonics DataAnalysis 3.1 printed: 30/07/2013 10:54:18 Page 1 of 1

MS (ESI) of [Ag{ImDiPP(C_2OH)}$_2$]BF_4 **(9)**



Service de spectrometrie de masse - Institut de Chimie - Strasbourg - UMR 7177 CNRS / ULP

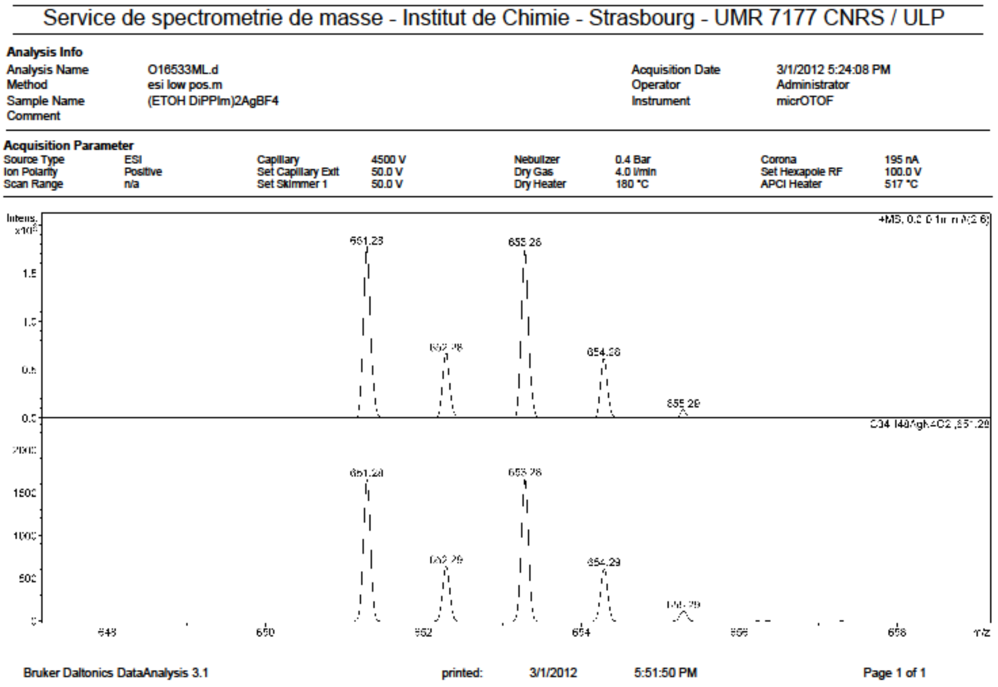
Analysis Info

Analysis Name	O16533ML.d	Acquisition Date	3/1/2012 5:24:08 PM
Method	esi low pos.m	Operator	Administrator
Sample Name	(ETOH DiPPIm)2AgBF4	Instrument	micrOTOF
Comment			

Acquisition Parameter

Source Type	ESI	Capillary	4500 V	Nebulizer	0.4 Bar	Corona	195 nA
Ion Polarity	Positive	Set Capillary Exit	50.0 V	Dry Gas	4.0 l/min	Set Hexapole RF	100.0 V
Scan Range	n/a	Set Skimmer 1	50.0 V	Dry Heater	180 °C	APCI Heater	517 °C

Bruker Daltonics DataAnalysis 3.1 printed: 3/1/2012 5:52:30 PM Page 1 of 1



Service de spectrometrie de masse - Institut de Chimie - Strasbourg - UMR 7177 CNRS / ULP

Analysis Info

Analysis Name	O16533ML.d	Acquisition Date	3/1/2012 5:24:08 PM
Method	esi low pos.m	Operator	Administrator
Sample Name	(ETOH DiPPIm)2AgBF4	Instrument	micrOTOF
Comment			

Acquisition Parameter

Source Type	ESI	Capillary	4500 V	Nebulizer	0.4 Bar	Corona	195 nA
Ion Polarity	Positive	Set Capillary Exit	50.0 V	Dry Gas	4.0 l/min	Set Hexapole RF	100.0 V
Scan Range	n/a	Set Skimmer 1	50.0 V	Dry Heater	180 °C	APCI Heater	517 °C

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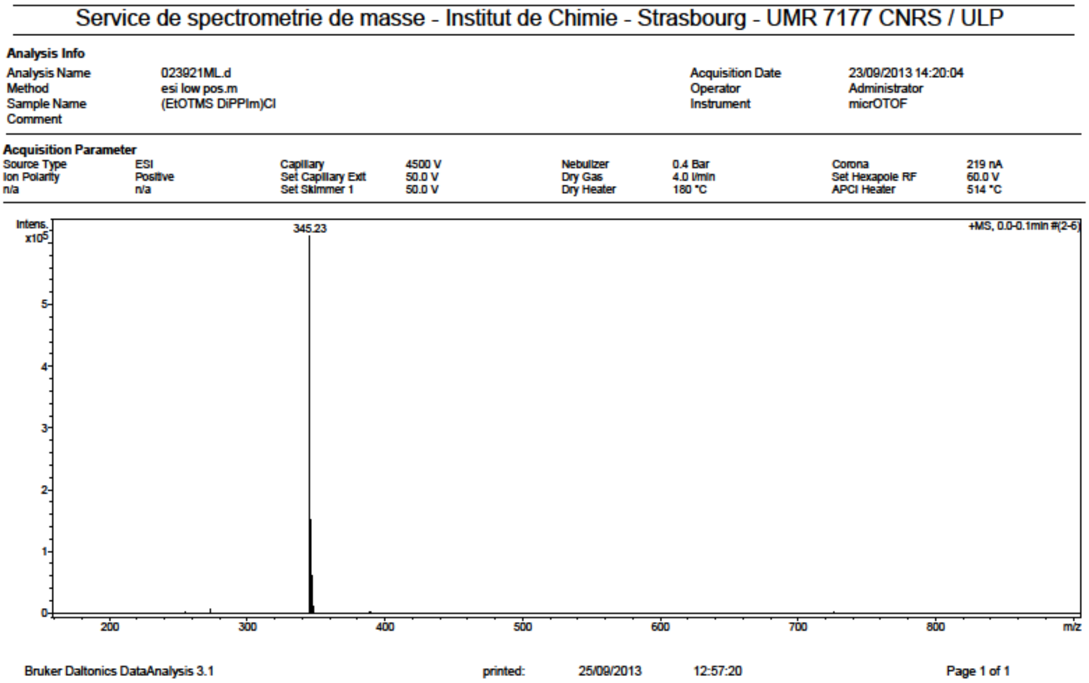
MS (ESI) of [ImDiPP(C_2OTMS)]Cl **(10)**



Service de spectrometrie de masse - Institut de Chimie - Strasbourg - UMR 7177 CNRS / ULP

Analysis Info

Analysis Name	023921ML.d	Acquisition Date	23/09/2013 14:20:04
Method	esi low pos.m	Operator	Administrator
Sample Name	(EtOTMS DiPPIm)Cl	Instrument	micrOTOF
Comment			

Acquisition Parameter

Source Type	ESI	Capillary	4500 V	Nebulizer	0.4 Bar	Corona	219 nA
Ion Polarity	Positive	Set Capillary Exit	50.0 V	Dry Gas	4.0 l/min	Set Hexapole RF	60.0 V
n/a	n/a	Set Skimmer 1	50.0 V	Dry Heater	180 °C	APCI Heater	514 °C

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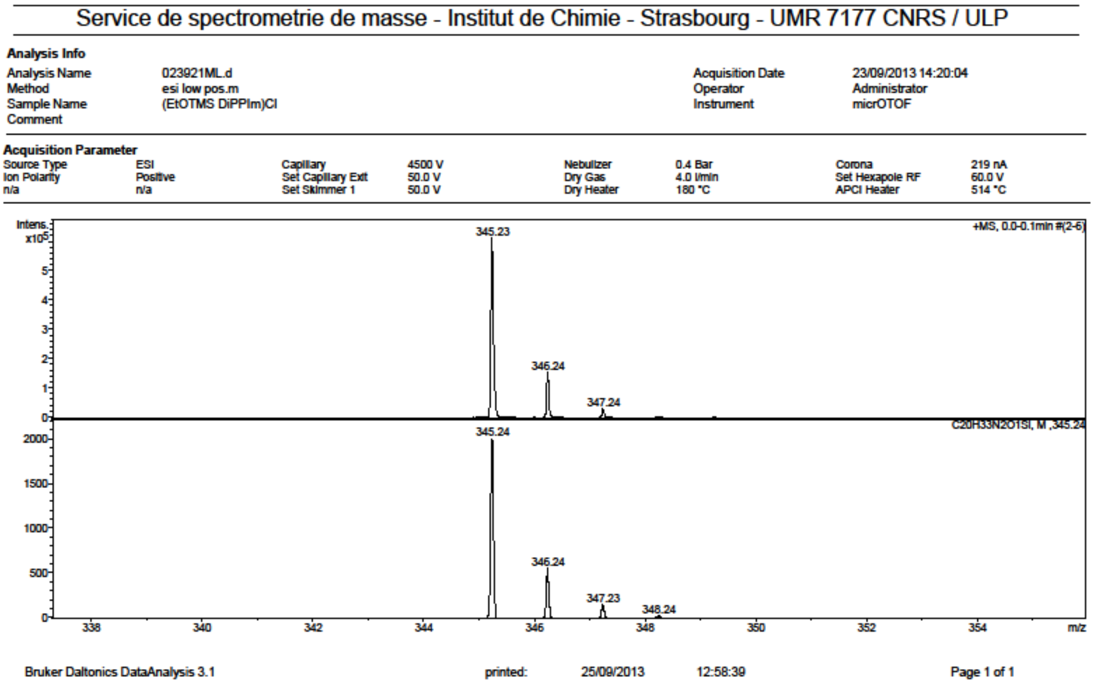

Service de spectrometrie de masse - Institut de Chimie - Strasbourg - UMR 7177 CNRS / ULP

Analysis Info

Analysis Name	023921ML.d	Acquisition Date	23/09/2013 14:20:04
Method	esi low pos.m	Operator	Administrator
Sample Name	(EtOTMS DiPPIm)Cl	Instrument	micrOTOF
Comment			

Acquisition Parameter

Source Type	ESI	Capillary	4500 V	Nebulizer	0.4 Bar	Corona	219 nA
Ion Polarity	Positive	Set Capillary Exit	50.0 V	Dry Gas	4.0 l/min	Set Hexapole RF	60.0 V
n/a	n/a	Set Skimmer 1	50.0 V	Dry Heater	180 °C	APCI Heater	514 °C

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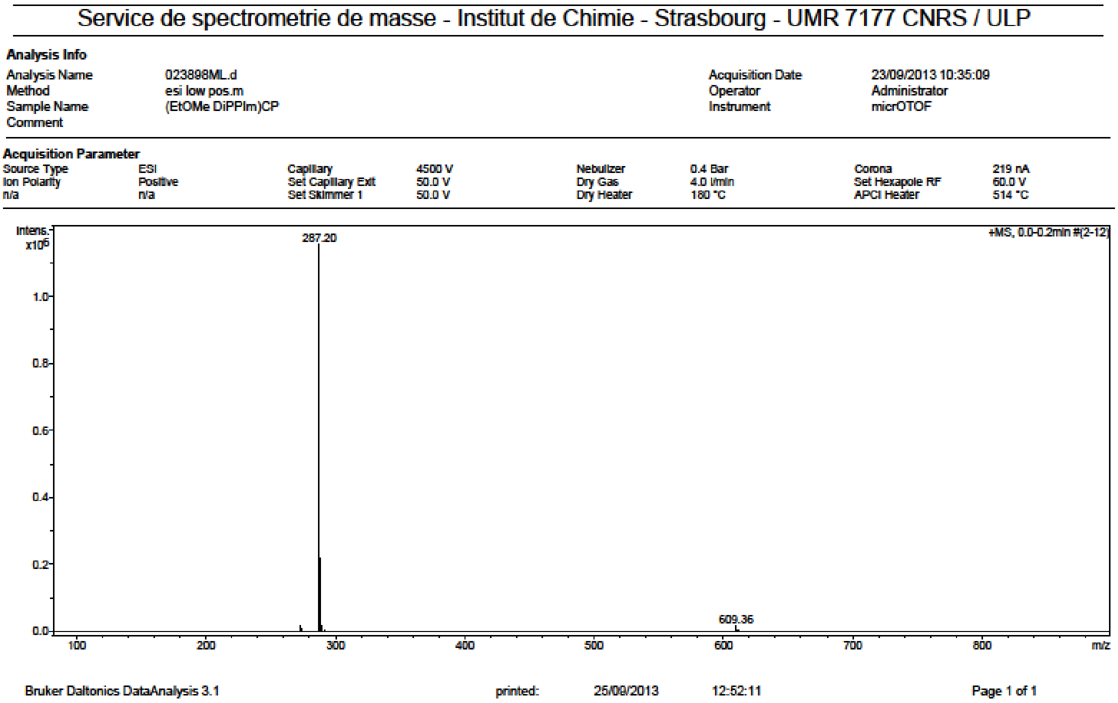
MS (ESI) of [ImDiPP(C_2OMe)]Cl **(12)**



Service de spectrometrie de masse - Institut de Chimie - Strasbourg - UMR 7177 CNRS / ULP

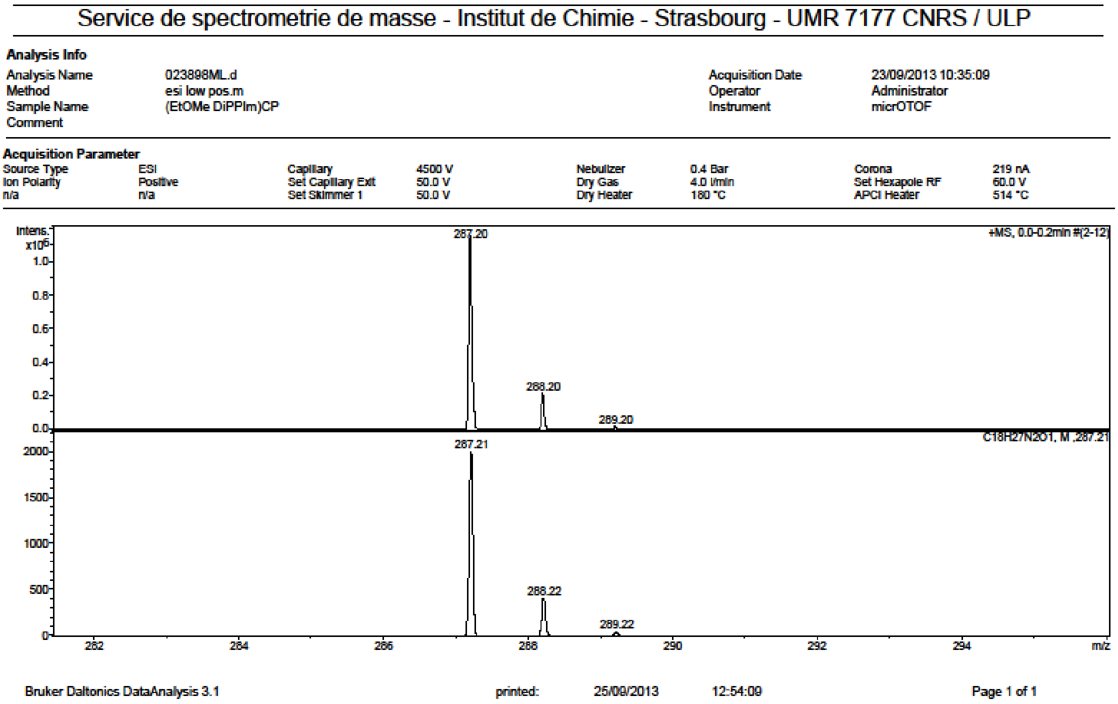
Analysis Info

Analysis Name	023898ML.d	Acquisition Date	23/09/2013 10:35:09
Method	esi low pos.m	Operator	Administrator
Sample Name	(EtOMe DiPPIm)CP	Instrument	micrOTOF
Comment			

Acquisition Parameter

Source Type	ESI	Capillary	4500 V	Nebulizer	0.4 Bar	Corona	219 nA
Ion Polarity	Positive	Set Capillary Exit	50.0 V	Dry Gas	4.0 l/min	Set Hexapole RF	60.0 V
n/a	n/a	Set Skimmer 1	50.0 V	Dry Heater	180 °C	APCI Heater	514 °C

Bruker Daltonics DataAnalysis 3.1 printed: 25/09/2013 12:52:11 Page 1 of 1



Service de spectrometrie de masse - Institut de Chimie - Strasbourg - UMR 7177 CNRS / ULP

Analysis Info

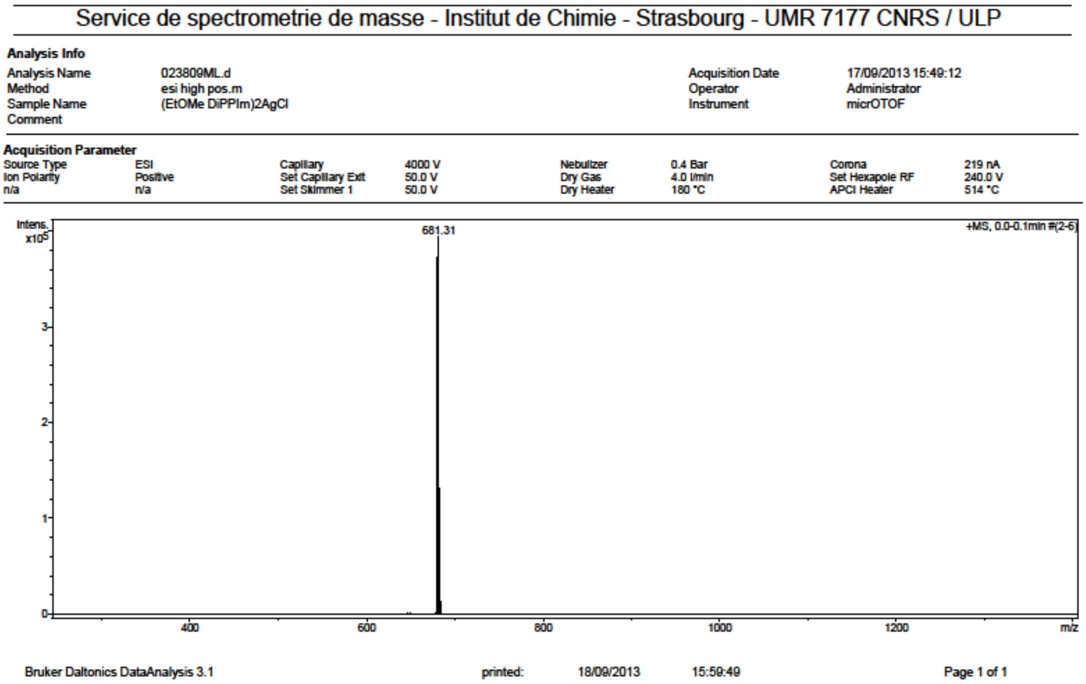
Analysis Name	023898ML.d	Acquisition Date	23/09/2013 10:35:09
Method	esi low pos.m	Operator	Administrator
Sample Name	(EtOMe DiPPIm)CP	Instrument	micrOTOF
Comment			

Acquisition Parameter

Source Type	ESI	Capillary	4500 V	Nebulizer	0.4 Bar	Corona	219 nA
Ion Polarity	Positive	Set Capillary Exit	50.0 V	Dry Gas	4.0 l/min	Set Hexapole RF	60.0 V
n/a	n/a	Set Skimmer 1	50.0 V	Dry Heater	180 °C	APCI Heater	514 °C

Bruker Daltonics DataAnalysis 3.1 printed: 25/09/2013 12:54:09 Page 1 of 1

MS (ESI) of [Ag{ImDiPP(C_2OMe)}$_2$]Cl **(13)**



Service de spectrometrie de masse - Institut de Chimie - Strasbourg - UMR 7177 CNRS / ULP

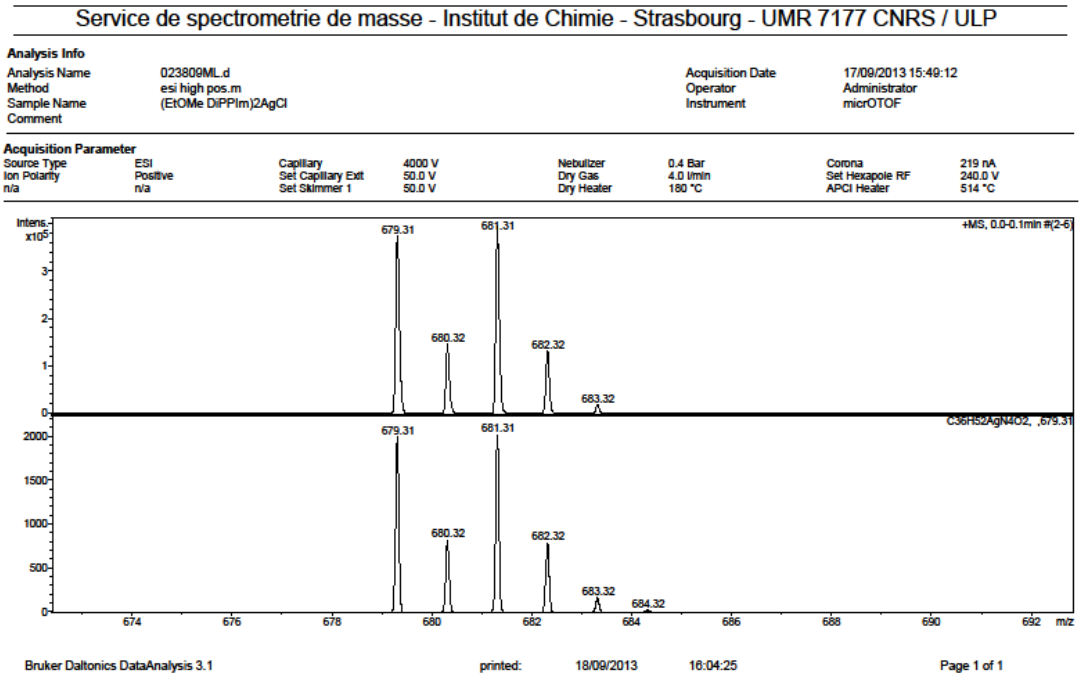
Analysis Info

Analysis Name	023809ML.d	Acquisition Date	17/09/2013 15:49:12
Method	esi high pos.m	Operator	Administrator
Sample Name	(EtOMe DiPPIm)2AgCl	Instrument	micrOTOF
Comment			

Acquisition Parameter

Source Type	ESI	Capillary	4000 V	Nebulizer	0.4 Bar	Corona	219 nA
Ion Polarity	Positive	Set Capillary Exit	50.0 V	Dry Gas	4.0 l/min	Set Hexapole RF	240.0 V
n/a	n/a	Set Skimmer 1	50.0 V	Dry Heater	180 °C	APCI Heater	514 °C

Bruker Daltonics DataAnalysis 3.1 printed: 18/09/2013 15:59:49 Page 1 of 1



Service de spectrometrie de masse - Institut de Chimie - Strasbourg - UMR 7177 CNRS / ULP

Analysis Info

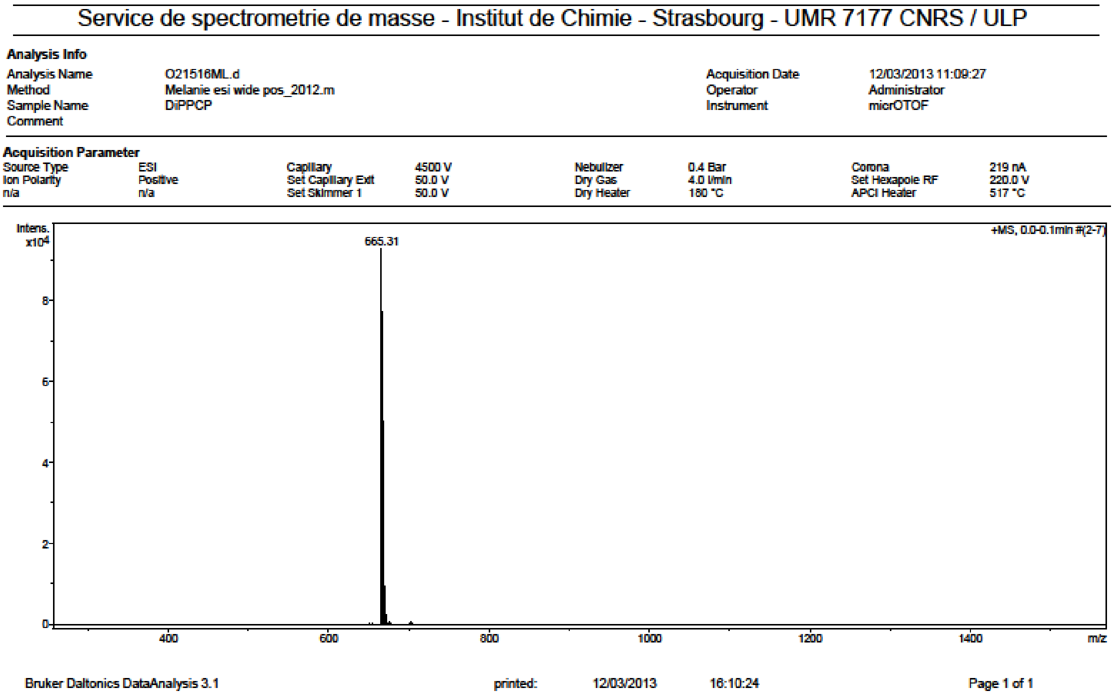
Analysis Name	023809ML.d	Acquisition Date	17/09/2013 15:49:12
Method	esi high pos.m	Operator	Administrator
Sample Name	(EtOMe DiPPIm)2AgCl	Instrument	micrOTOF
Comment			

Acquisition Parameter

Source Type	ESI	Capillary	4000 V	Nebulizer	0.4 Bar	Corona	219 nA
Ion Polarity	Positive	Set Capillary Exit	50.0 V	Dry Gas	4.0 l/min	Set Hexapole RF	240.0 V
n/a	n/a	Set Skimmer 1	50.0 V	Dry Heater	180 °C	APCI Heater	514 °C

Bruker Daltonics DataAnalysis 3.1 printed: 18/09/2013 16:04:25 Page 1 of 1

MS (ESI) of [$NiCl_2\{ImDiPP(C_2OMe)\}_2$] **(15)**



Service de spectrometrie de masse - Institut de Chimie - Strasbourg - UMR 7177 CNRS / ULP

Analysis Info
Analysis Name O21516ML.d
Method Melanie esi wide pos_2012.m
Sample Name DiPPCP
Comment
Acquisition Date 12/03/2013 11:09:27
Operator Administrator
Instrument micrOTOF

Acquisition Parameter
Source Type ESI
Ion Polarity Positive
n/a n/a
Capillary 4500 V
Set Capillary Exit 50.0 V
Set Skimmer 1 50.0 V
Nebulizer 0.4 Bar
Dry Gas 4.0 l/min
Dry Heater 180 °C
Corona 219 nA
Set Hexapole RF 220.0 V
APCI Heater 517 °C

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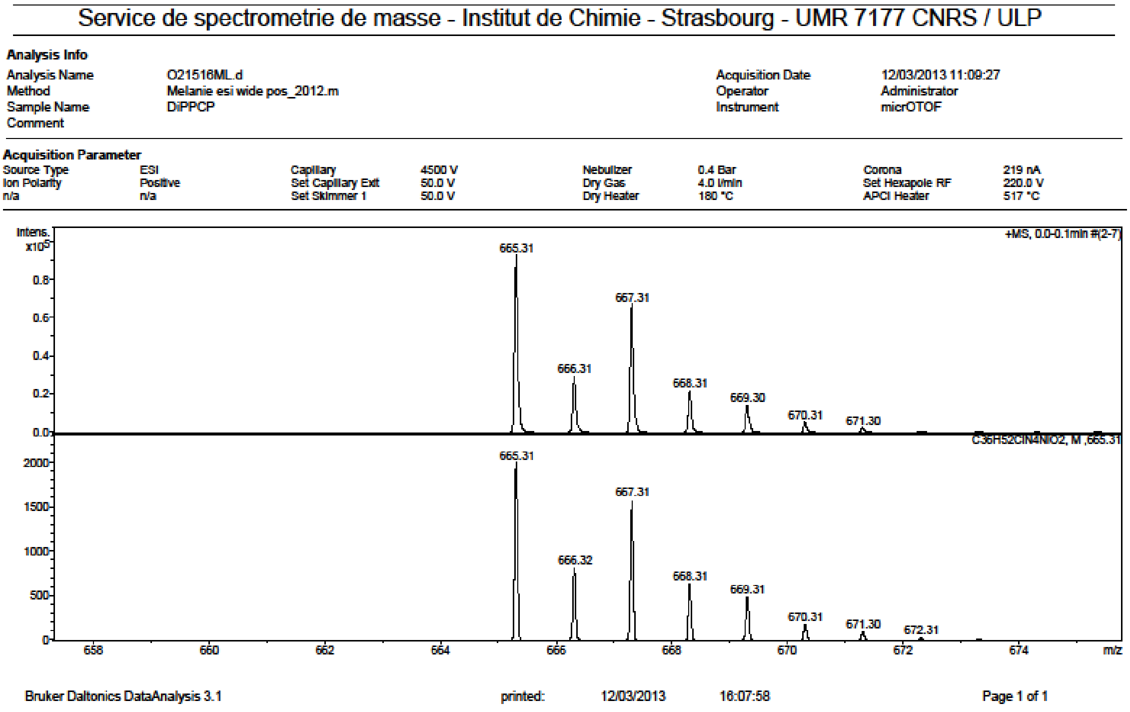

Service de spectrometrie de masse - Institut de Chimie - Strasbourg - UMR 7177 CNRS / ULP

Analysis Info
Analysis Name O21516ML.d
Method Melanie esi wide pos_2012.m
Sample Name DiPPCP
Comment
Acquisition Date 12/03/2013 11:09:27
Operator Administrator
Instrument micrOTOF

Acquisition Parameter
Source Type ESI
Ion Polarity Positive
n/a n/a
Capillary 4500 V
Set Capillary Exit 50.0 V
Set Skimmer 1 50.0 V
Nebulizer 0.4 Bar
Dry Gas 4.0 l/min
Dry Heater 180 °C
Corona 219 nA
Set Hexapole RF 220.0 V
APCI Heater 517 °C

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4) Crystallographic data for the compounds **4**•CH_2Cl_2, **5**, **6**, **8**, **9**•Et_2O, **13**•H_2O, **14** and **15**

Identification code	[Ag{ImDiPP(C_2OH)}$_2$]Cl (**4**)•CH_2Cl_2	
Empirical formula	$C_{34}H_{48}AgClN_4O_2$•CH_2Cl_2	
Formula weight	773.01 g·mol^{-1}	
Temperature	173(2) K	
Wavelength	0.71069 Å	
Crystal system	Monoclinic	
Space group	*C*2/c	
Unit cell dimensions	*a* = 19.5798(5) Å	α = 90°
	b = 19.7314(9) Å	β = 126.049(2)°
	c = 12.2390(5) Å	γ = 90°
Volume	3823.0(3) Å^3	
Z	4	
Density (calculated)	1.343 Mg/m^3	
Absorption coefficient	0.771 mm^{-1}	
F(000)	1608.0	
Theta range for data collection	1.65 to 25.99°	
Index ranges	-24<=h<=24, -24<=k<=22, -15<=l<=15	
Reflections collected	6562	
Independent reflections	3734 [R(int) = 0.0251]	
Completeness to theta = 26.00°	99.3%	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3734 / 0 / 214	
Goodness-of-fit on F^2	1.092	
Final R indices [$I>2\sigma(I)$]	R1 = 0.0416, wR2 = 0.1213	
R indices (all data)	R1 = 0.0634, wR2 = 0.1465	
Largest diff. peak and hole	-0.723 and 0.900 e·Å^{-3}	

Identification code	$[Ag\{ImMes(C_2OH)\}_2]Cl$ (**5**)	
Empirical formula	$C_{28}H_{36}AgClN_4O_2$	
Formula weight	603.93 $g \cdot mol^{-1}$	
Temperature	173(2) K	
Wavelength	0.71069 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	*a* = 10.7920(2) Å	α = 71.2680(10)°
	b = 11.4820(2) Å	β = 70.5740(10)°
	c = 13.1690(3) Å	γ = 84.4080(10)°
Volume	1457.33(5) $Å^3$	
Z	2	
Density (calculated)	1.376 Mg/m^3	
Absorption coefficient	0.813 mm^{-1}	
F(000)	624.0	
Theta range for data collection	1.72 to 26.00°	
Index ranges	-13<=h<=13, -14<=k<=14, -16<=l<=16	
Reflections collected	30258	
Independent reflections	5728 [R(int) = 0.0719]	
Completeness to theta = 26.00°	100%	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5728 / 503 / 399	
Goodness-of-fit on F^2	1.077	
Final R indices [$I>2\sigma(I)$]	R1 = 0.0476, wR2 = 0.1382	
R indices (all data)	R1 = 0.0657, wR2 = 0.1621	
Largest diff. peak and hole	-1.029 and 1.912 $e \cdot Å^{-3}$	

Identification code	[Ag{ImMe(C_2OH)}$_2$]Cl (**6**)	
Empirical formula	$C_{12}H_{20}AgClN_4O_2$	
Formula weight	395.64 g·mol^{-1}	
Temperature	173(2) K	
Wavelength	0.71069 Å	
Crystal system	Monoclinic	
Space group	*C*2/c	
Unit cell dimensions	*a* = 17.7643(9) Å	α = 90°
	b = 8.9962(7) Å	β = 130.261(3)°
	c = 13.1655(7)Å	γ = 90°
Volume	1605.57(17) Å^3	
Z	4	
Density (calculated)	1.637 Mg/m^3	
Absorption coefficient	1.428 mm^{-1}	
F(000)	800.0	
Theta range for data collection	2.72 to 27.45°	
Index ranges	-22<=h<=17, -10<=k<=11, -14<=l<=17	
Reflections collected	5165	
Independent reflections	1829 [R(int) = 0.0489]	
Completeness to theta = 26.00°	99.9%	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1829 / 0 / 97	
Goodness-of-fit on F^2	1.062	
Final R indices [$I>2\sigma(I)$]	R1 = 0.0361, wR2 = 0.0766	
R indices (all data)	R1 = 0.0520, wR2 = 0.0845	
Largest diff. peak and hole	-1.087 and 0.588 e·Å^{-3}	

Identification code	[ImHDiPP(C_2OH)]$_3$Cl[NiCl$_4$] (**8**)	
Empirical formula	$C_{68}H_{100}Cl_6N_8NiO_4$	
Formula weight	1364.95 g·mol^{-1}	
Temperature	173(2) K	
Wavelength	0.71069 Å	
Crystal system	Orthorhombic	
Space group	$P2_122_1$	
Unit cell dimensions	a = 14.9628(4) Å	α = 90°
	b = 15.0822(3) Å	β = 90°
	c = 16.1788(5) Å	γ = 90°
Volume	3651.10(17) Å^3	
Z	2	
Density (calculated)	1.242 Mg/m^3	
Absorption coefficient	0.535 mm^{-1}	
F(000)	1452.0	
Theta range for data collection	2.72 to 26.00°	
Index ranges	-18<=h<=18, -18<=k<=13, -19<=l<=17	
Reflections collected	29561	
Independent reflections	7164 [R(int) = 0.0748]	
Completeness to theta = 26.00°	179.0%	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7164 / 0 / 410	
Goodness-of-fit on F^2	1.142	
Final R indices [I>2σ(I)]	R1 = 0.0637, wR2 = 0.0986	
R indices (all data)	R1 = 0.0840, wR2 = 0.1029	
Largest diff. peak and hole	-0.309 and 0.608 e·Å^{-3}	

Identification code	$[\mathrm{Ag\{ImDiPP(C_2OH)\}_2]BF_4}$ (**9**)•$\mathrm{Et_2O}$	
Empirical formula	$\mathrm{C_{34}H_{48}AgN_4O_2BF_4}$•$\mathrm{C_4H_{10}O}$	
Formula weight	813.56 g·mol^{-1}	
Temperature	173(2) K	
Wavelength	0.71069 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	*a* = 12.1561(5) Å	α = 84.300(2)°
	b = 13.6336(6) Å	β = 66.395(2)°
	c = 14.9663(6) Å	γ = 66.881(2)°
Volume	2085.38(15) Å^3	
Z	2	
Density (calculated)	1.296 Mg/m^3	
Absorption coefficient	0.539 mm^{-1}	
F(000)	852.0	
Theta range for data collection	2.85 to 26.00°	
Index ranges	-14<=h<=14, -13<=k<=16, -18<=l<=18	
Reflections collected	18804	
Independent reflections	8182 [R(int) = 0.0640]	
Completeness to theta = 26.00°	99.8%	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8182 / 13 / 480	
Goodness-of-fit on F^2	1.026	
Final R indices [I>2σ(I)]	R1 = 0.0678, wR2 = 0.1553	
R indices (all data)	R1 = 0.1064, wR2 = 0.1706	
Largest diff. peak and hole	-1.639 and 1.573 e·Å^{-3}	

Identification code	$[Ag\{ImDiPP(EtOMe)\}_2]Cl\bullet H_2O$ (**13**•H_2O)	
Empirical formula	$C_{36}H_{52}AgN_4O_2Cl\bullet H_2O$	
Formula weight	734.15 g·mol^{-1}	
Temperature	173(2) K	
Wavelength	0.71069 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	*a* = 8.8012(3) Å	α = 97.641(2)°
	b = 11.5154(5) Å	β = 102.770(3)°
	c = 19.3453(12) Å	γ = 92.692(3)°
Volume	1889.24(16) Å^3	
Z	2	
Density (calculated)	1.291 Mg/m^3	
Absorption coefficient	0.642 mm^{-1}	
F(000)	772.0	
Theta range for data collection	2.61 to 26.00°	
Index ranges	-10<=h<=10, -14<=k<=13, -23<=l<=23	
Reflections collected	17158	
Independent reflections	7271 [R(int) = 0.0403]	
Completeness to theta = 26.00°	97.9%	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7271 / 14 / 422	
Goodness-of-fit on F^2	1.079	
Final R indices [$I>2\sigma(I)$]	R1 = 0.0487, wR2 = 0.1059	
R indices (all data)	R1 = 0.0788, wR2 = 0.1159	
Largest diff. peak and hole	-0.680 and 0.694 e·Å^{-3}	

Identification code	[AgCl{ImDiPP(C_2OMe)}] (**14**)	
Empirical formula	$C_{18}H_{26}AgClN_2O$	
Formula weight	429.73 g·mol^{-1}	
Temperature	173(2) K	
Wavelength	0.71069 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 8.8411(3) Å	α = 90°
	b = 19.1464(10) Å	β = 125.638(3)°
	c = 14.1647(6) Å	γ = 90°
Volume	1948.67(15) Å^3	
Z	4	
Density (calculated)	1.465 Mg/m^3	
Absorption coefficient	1.177 mm^{-1}	
F(000)	880.0	
Theta range for data collection	2.77 to 26.00°	
Index ranges	-10<=h<=10, -23<=k<=23, -15<=l<=17	
Reflections collected	18032	
Independent reflections	3823 [R(int) = 0.0887]	
Completeness to theta = 26.00°	99.7%	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3823 / 0 / 213	
Goodness-of-fit on F^2	1.001	
Final R indices [$I>2\sigma(I)$]	R1 = 0.0460, wR2 = 0.0942	
R indices (all data)	R1 = 0.1057, wR2 = 0.1106	
Largest diff. peak and hole	-1.025 and 0.860 e·Å^{-3}	

Identification code	[$NiCl_2\{ImDiPP(C_2OMe)\}_2$] (**15**)	
Empirical formula	$C_{36}H_{52}Cl_2N_4NiO_2$	
Formula weight	702.41 g·mol^{-1}	
Temperature	173(2) K	
Wavelength	0.71069 Å	
Crystal system	Orthorhombic	
Space group	$Pca2_1$	
Unit cell dimensions	*a* = 28.655(3) Å	α = 90°
	b = 8.0546(8) Å	β = 90°
	c = 16.2099(17) Å	γ = 90°
Volume	3741.3(7) Å^3	
Z	4	
Density (calculated)	1.247 Mg/m^3	
Absorption coefficient	0.697 mm^{-1}	
F(000)	1496.0	
Theta range for data collection	2.51 to 25.18°	
Index ranges	-34<=h<=34, -9<=k<=9, -19<=l<=19	
Reflections collected	45690	
Independent reflections	6715 [R(int) = 0.0277]	
Completeness to theta = 26.00°	192.0%	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6715 / 1 / 417	
Goodness-of-fit on F^2	1.073	
Final R indices [$I>2\sigma(I)$]	R1 = 0.0331, wR2 = 0.0833	
R indices (all data)	R1 = 0.0401, wR2 = 0.0863	
Largest diff. peak and hole	-0.161 and 0.572 e·Å^{-3}	

5) Notable features in the crystal packing for 9 and 13

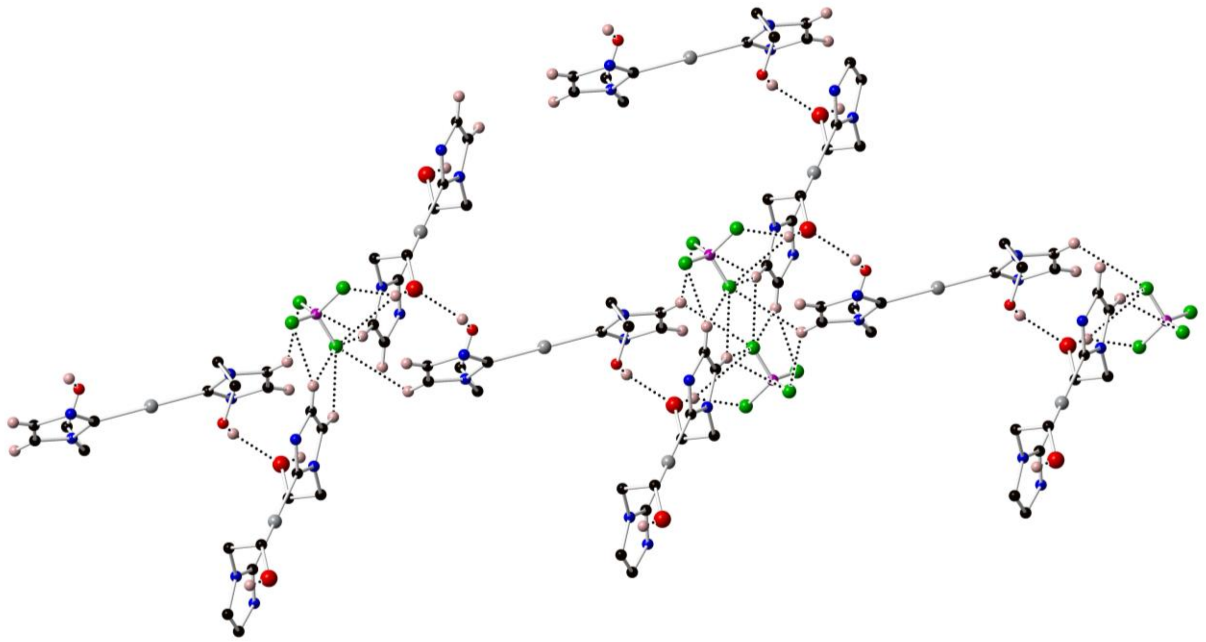

Figure S1. Ball and stick representation of the polymeric network of H-bonds in the packing of [Ag{ImDiPP(C_2OH)}$_2$]BF_4 (**9**). The DiPP groups and the hydrogen atoms have been omitted for clarity, except the OH protons.

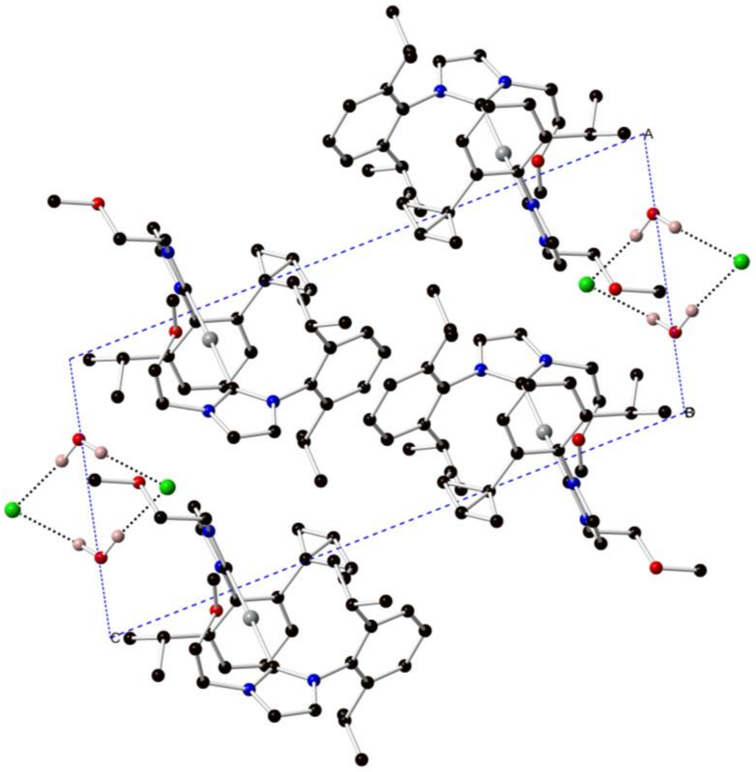

Figure S2. Ball and stick representation of [Ag{ImDiPP(C_2OMe)}$_2$]Cl in **13**·H_2O: view of the cell. Hydrogen atoms have been omitted for clarity, except the OH protons.

6) ORTEP views of the molecular structures of 4•CH_2Cl_2, 5, 6, 8, 9•Et_2O, 13•H_2O, 14 and 15

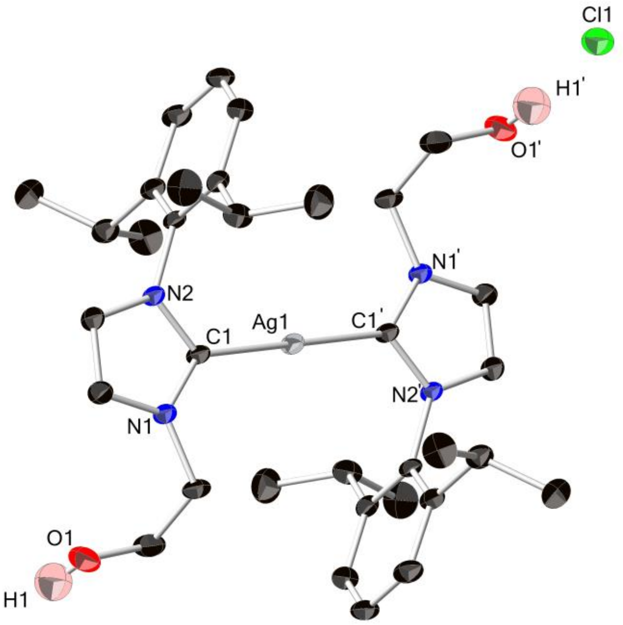

Figure S3. ORTEP of the molecular structure of **4.** Ellipsoids at 30% probability level. Hydrogen atoms have been omitted for clarity, except the OH protons.

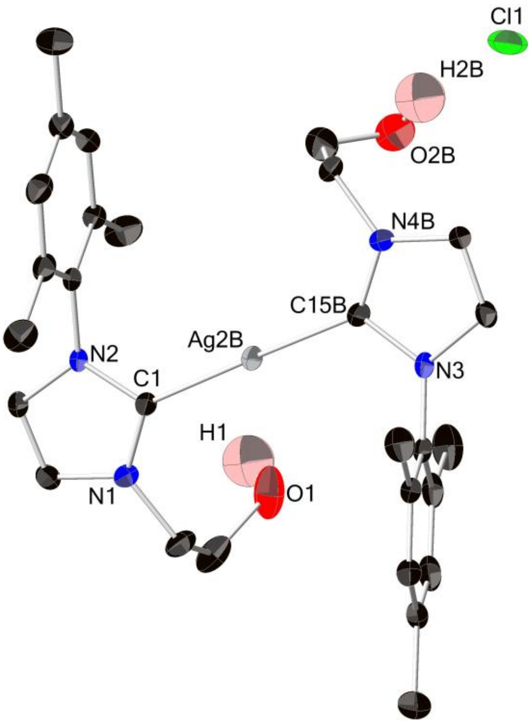

Figure S4. ORTEP of the molecular structure of **5.** Ellipsoids at 30% probability level. Hydrogen atoms have been omitted for clarity, except the OH protons.

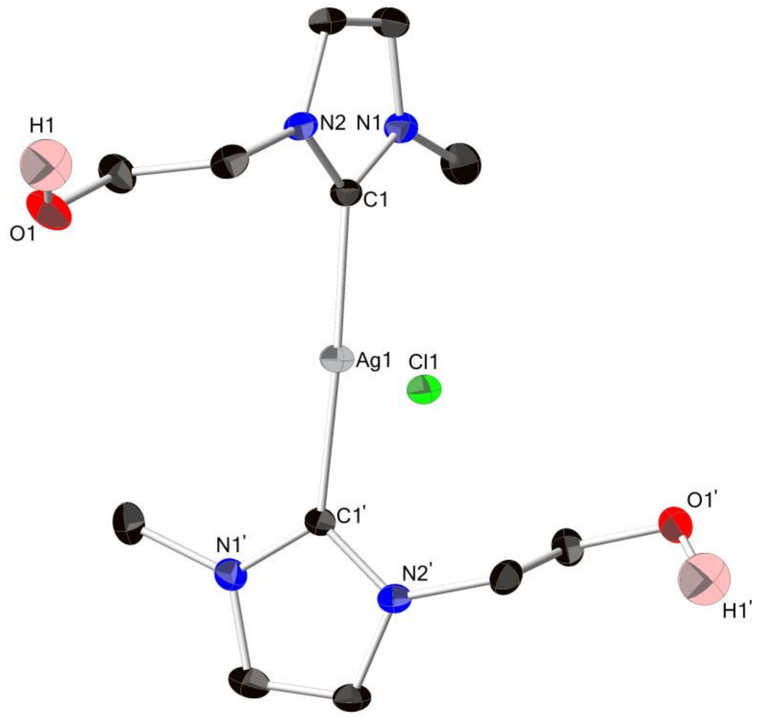

Figure S5. ORTEP of the molecular structure of **6.** Ellipsoids at 30% probability level. Hydrogen atoms have been omitted for clarity, except the OH protons.

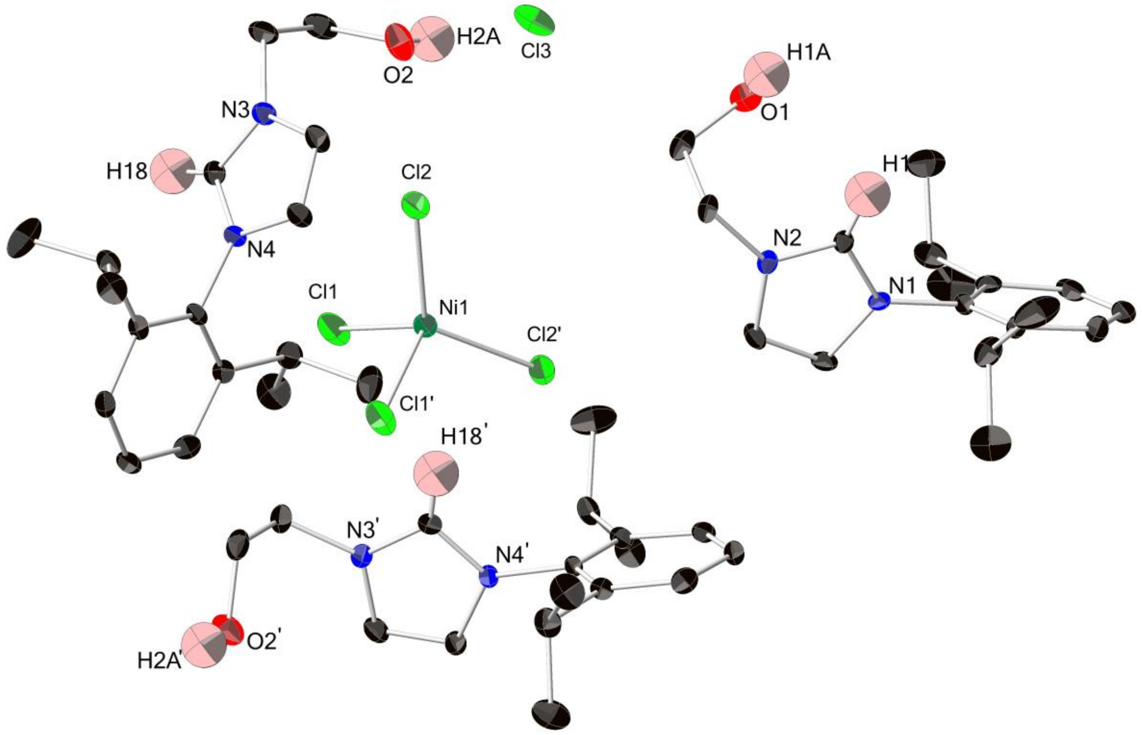

Figure S6. ORTEP of the molecular structure of **8.** Ellipsoids at 30% probability level. Hydrogen atoms have been omitted for clarity, except the NCHN and the OH protons.

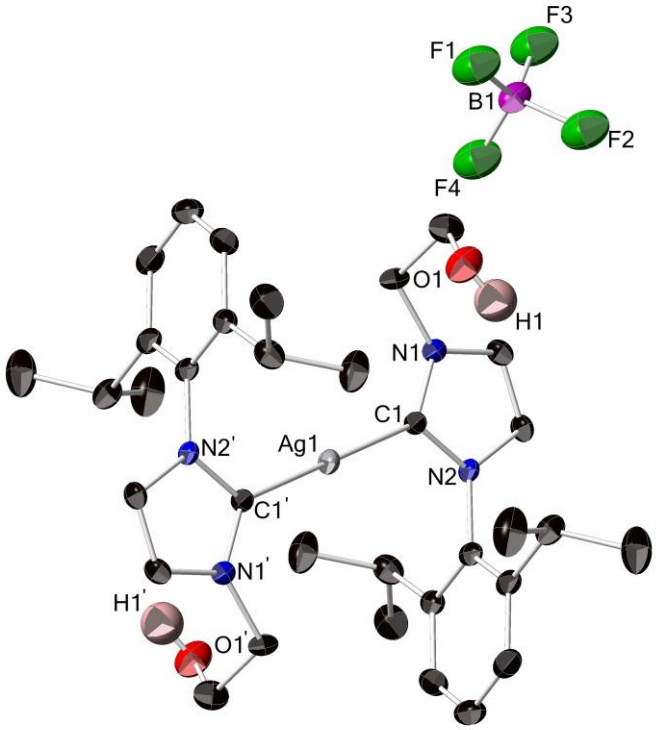

Figure S7. ORTEP of the molecular structure of **9.** Ellipsoids at 30% probability level. Hydrogen atoms have been omitted for clarity, except the OH protons.

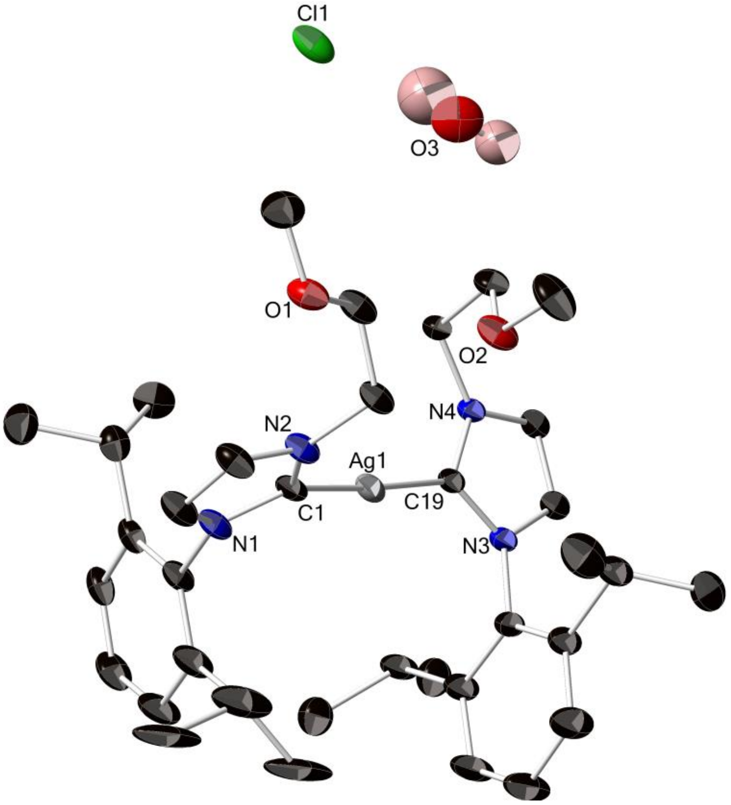

Figure S8. ORTEP of the molecular structure of **13.** Ellipsoids at 30% probability level. Hydrogen atoms have been omitted for clarity.

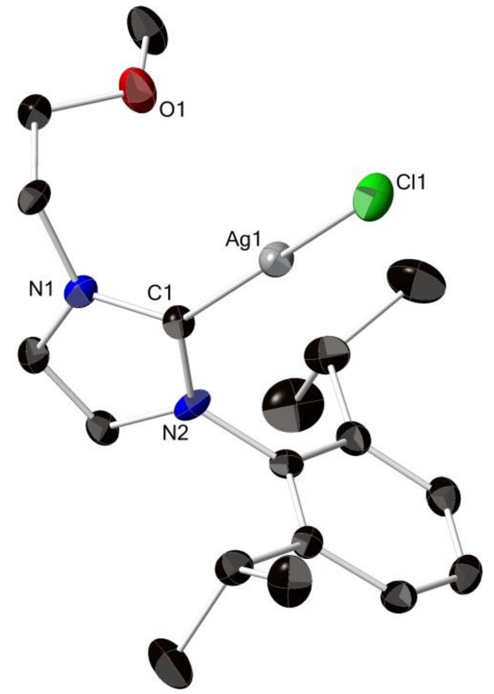

Figure S9. ORTEP of the molecular structure of **14.** Ellipsoids at 30% probability level. Hydrogen atoms have been omitted for clarity.

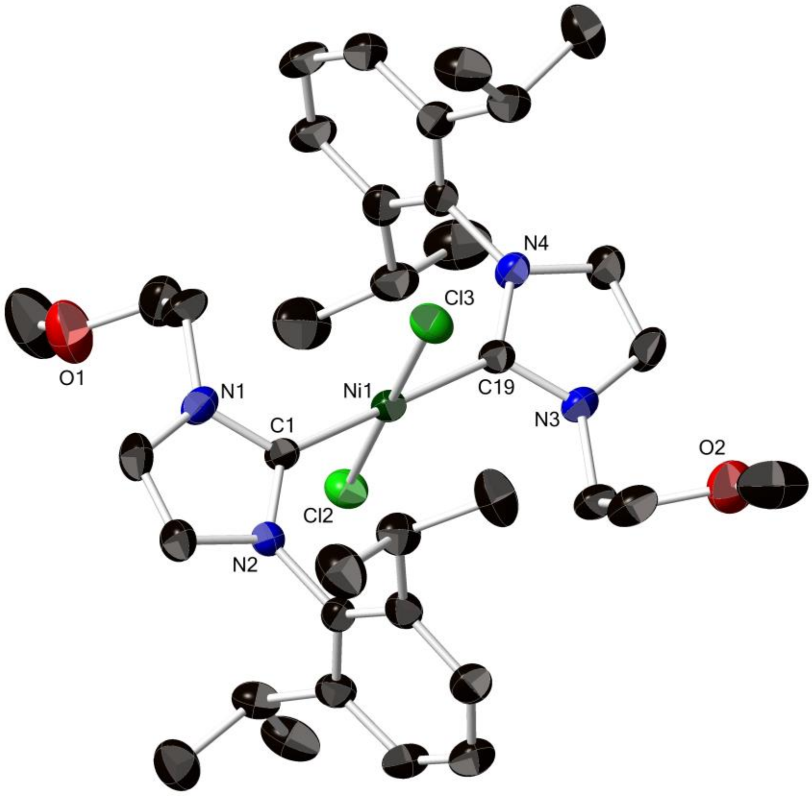

Figure S10. ORTEP of the molecular structure of **15.** Ellipsoids at 30% probability level. Hydrogen atoms have been omitted for clarity.

References

1 (a) A. L. Johnson, 1972, US3637731A; (b) J. Liu, J. Chen, J. Zhao, Y. Zhao, L. Li and H. Zhang, *Synthesis*, 2003, 2661-2666; (c) S. Zhang, X. Qi, X. Ma, L. Lu and Y. Deng, *J. Phys. Chem. B*, 2010, **114**, 3912-3920; (d) R. J. Errington *Advanced Practical Inorganic and Metalorganic Chemistry*; CRC Press, Boca Raton, FL, 1997.

2 G. M. Sheldrick, *Acta Cryst. A*, 2008, **64**, 112-122.