Expedient Synthesis of Highly Functionalized Abnormal Carbene Gold(I) Complexes

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Supporting information

Contents:

Experimental section

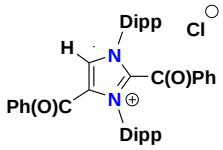
General methods

Commercially available reagents and solvents were used as received. NHCs **1** and **2** were synthesized according to the methods reported in the literature.[1] Imidazoliums **3** and **4** were synthesized with a slightly modified literature procedure, and their characterization is consistent with the reported data.[1] All manipulations related to the synthesis of imidazolium salts **7a-e** and gold complexes **8a-e** were performed under an atmosphere of dry nitrogen using standard Schlenk techniques. Elemental analyses were obtained with a Thermo Finnegan CHNSO-1112 apparatus and a Perkin Elmer Series II CHNS/O 2400 instruments. X-ray diffraction analyses were collected in an Agilent Gemini diffractometer using Cu Kα radiation (λ = 1.54184 Å). Data were integrated, scaled, sorted, and averaged using the CrysAlisPro software package. The structures we solved using direct methods, using SHELX 2014 and refined by full matrix least squares against F^2.[5] All non hydrogen atoms were refined anisotropically. The position of the hydrogen atoms were kept fixed with common isotropic display parameters. The crystallographic data and some details of the data collection and refinement are given in Table S1.

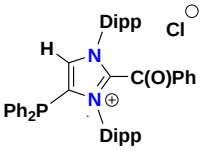
Table S1. Crystallographic Data and Summary of data Collection and Structure Refinement

	5
Formula	$C_{41}H_{44}AuClN_2O_2$
Fw	829.20
cryst syst	Monoclinic
Space group	P 21/c
T, K	293(2)
a, Å	20.6312(2)
b, Å	16.2870(1)
c, Å	11.5582(1)
α, deg	90
β, deg	104.311(1)
γ, deg	90
V, Å^3	3763.27(6)
Z	4
d_{calc} g.cm^{-3}	1.464
μ, mm^{-1}	8.270
refl collected	26638
T_{min}/T_{max}	0.815
N_{measd}	6520
[R_{int}]	0.0746
R [*I* > 2sigma(*I*)]	0.0373
R (all data)	0.0516
R_w[*I* > 2sigma(*I*)]	0.0876
R_w (all data)	0.0989
GOF	1.077

*Synthesis of imidazolium salts **3** and **4***

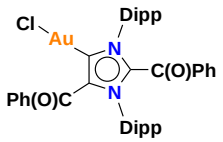


*Imidazolium salt **3**.* A solution of NHC **1** (0.202 g, 0.410 mmol) in 15 mL of THF was added slowly to a solution of benzolyl chloride (0.057 g, 0.408 mmol) in 5 mL of THF, and the resulting mixture was allowed stirring for 12 h at room temperature. The resulting suspension was evaporated under reduced pressure and the residue was washed with diethyl ether (3 x 30 mL) to give the title product as a white solid in 75% yield (194 mg, 0.306 mmol). ^{1}H NMR (CD_3CN, 400 MHz) δ = 1.09 (d, *J* = 7.2 Hz, 6H, CH(CH_3)$_2$), 1.13 (d, *J* = 7.2 Hz, 6H, CH(CH_3)$_2$), 1.26 (two doublets overlapping, 12H, CH(CH_3)$_2$), 2.69 (sept, *J* = 6.8 Hz, 2H, CH(CH_3)$_2$), 2.82 (sept, *J* = 6.8 Hz, 2H, CH(CH_3)$_2$), 7.31 (d, *J* = 7.8 Hz, 2H, CH_{ar}), 7.35 (d, *J* = 7.8 Hz, 2H, CH_{ar}), 7.52 (t, *J* = 7.8 Hz, 2H, CH_{ar}), 7.58-7.66 (m, 3H, CH_{ar}), 7.72-7.77 (m, 3H, CH_{ar}), 8.03 (d, *J* = 7.6 Hz, 2H, CH_{ar}), 8.18 (d, *J* = 7.6 Hz, 2H, CH_{ar}), 8.70 (s, 1H, CH_{imid}). ^{13}C NMR (CD_3CN, 100 MHz) δ = 22.6, 23.7, 25.2, 26.3, 30.3, 30.4, 126.4, 126.5, 129.4, 130.2, 130.3, 130.5, 130.9, 131.3, 131.5, 132.4, 132.8, 133.3, 134.1, 135.9, 136.3, 136.9, 138.7, 146.4, 146.5, 180.2, 182.9. Anal. Calcd. for $C_{41}H_{45}ClN_2O_2$: C, 77.76; H, 7.16; N, 4.42; Found: C, 78.01, H, 7.22, N, 4.17.



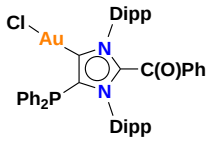
*Imidazolium salt **4**.* A solution of NHC **2** (0.235 g, 0.410 mmol) in 15 mL of THF was added slowly to a solution of benzolyl chloride (0.057 g, 0.408 mmol) in 5 mL of THF, and the resulting mixture was allowed stirring for 12 h at room temperature. The resulting suspension was evaporated under reduced pressure and the residue was washed with diethyl ether (3 x 30 mL) to give the title product as a white solid in 85% yield (248 mg, 0.347 mmol). ^{1}H NMR (CD_3CN, 400 MHz) δ 1.01 (d, *J* = 6.6 Hz, 6H, CH(CH_3)$_2$), 1.03 (d, *J* = 6.6 Hz, 6H, CH(CH_3)$_2$), 1.16 (d, *J* = 6.6 Hz, 6H, CH(CH_3)$_2$), 1.27 (d, *J* = 6.6 Hz, 6H, CH(CH_3)$_2$), 3.03 (sept, *J* = 6.4 Hz, 2H, CH(CH_3)$_2$), 3.31 (sept, *J* = 6.4 Hz, 2H, CH(CH_3)$_2$), 6.82 (d, *J* = 7.6 Hz, 2H, CH_{ar}), 6.89 (d, *J* = 7.6 Hz, 2H, CH_{ar}), 6.96-7.03 (m, 4H CH_{ar}), 7.08 (t, *J* = 7.6 Hz, 2H, CH_{ar}), 7.29-7.33 (m, 4H, CH_{ar}), 7.67 (t, *J* = 7.6 Hz, 3H, CH_{ar}), 7.74 (d, *J* = 7.6 Hz, 1H, C*H*ar), 7.88 (d, *J* = 7.6 Hz, 1H, C*H*ar), 8.29 (d, *J* = 7.4 Hz, 2H, C*H*ar), 8.62 (s, 1H, CH_{imid}). ^{13}C NMR (CD_3CN, 100 MHz) δ = 23.2, 25.1, 25.5, 27.0, 29.8, 30.0, 125.8, 129.5, 130.0, 130.5, 130.8, 131.0, 131.8, 132.9, 132.5, 133.0, 133.9, 134.8, 135.0, 135.9, 136.9, 141.4, 141.6, 146.3, 147.8, 181.6. ^{31}P NMR (CD_3CN, 121 MHz) δ = -36.8 ppm. Anal. Calcd. for $C_{46}H_{50}ClN_2OP$: C, 77.45; H, 7.07; N, 3.93; Found: C, 77.76, H, 6.85, N, 4.17.

*Synthesis of aNHC-Au complexes **5** and **6***



*Complex **5**. Method A: In strict absence of light*, silver(I) oxide (18 mg, 0.079 mmol) and triazolium **3** (100 mg, 0.158 mmol) were charged in a Schlenk flask and dry dichloromethane (10 mL) was added. The resulting suspension was stirred for 24 h at room temperature. The final dark brown suspension was filtered and transferred via cannula to a second Schlenk containing a solution of choloro(dimethylsulfide)gold (46.5 mg, 0.158 mmol) in 5 mL of dichlorometane. The resulting dark grey suspension was stirred for 6 h. After cannula filtration and removal of the solvent, the crude product is dissolved in 1 mL of DCM and purified by column chromatography using dichloromethane yielding the title product in 54 % yield (71 mg, 0.085 mmol) as white solid.

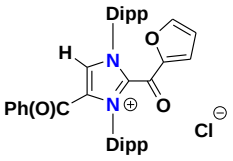
Method B: In strict absence of light, choloro(dimethylsulfide)gold (46.5 mg, 0.158 mmol) potassium hexamethyl disylazide (38 mg, 0.189 mmol) and triazolium **3** (100 mg, 0.158 mmol), were combined in a Schlenk flask and dissolved in THF (7 mL) at -78°C. The resulting mixture was stirred for 16 h. The final clear suspension was dried under vacuum and the residue was dissolved in 1 mL of dichloromethane and precipitated with hexane (10 mL). The solid is filtered and dried under vacuum yielding the title product in 87 % yield (114 mg, 0.137 mmol) as white solid. Single crystals were obtained by vapor diffusion of hexanes into a concentrated dichloromethane solution. ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 1.21 (d, *J* = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 1.24 (d, *J* = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 1.37 (d, *J* = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 1.41 (d, *J* = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 2.59 (sept, *J* = 6.8 Hz, 2H, CH(C*H*$_3$)$_2$), 2.66 (sept, *J* = 6.8 Hz, 2H, CH(C*H*$_3$)$_2$), 7.16-7.19 (m, 2H, C*H*$_{ar}$), 7.28-7.31 (m, 4H, C*H*$_{ar}$), 7.32-7.38 (m, 3H, C*H*$_{ar}$), 7.49-7.56 (m, 3H, C*H*$_{ar}$), 7.66 (t, *J* = 7.6 Hz, 2H, C*H*$_{ar}$), 7.80 (d, *J* = 7.6 Hz, 2H, C*H*$_{ar}$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 24.0, 24.3, 24.5, 24.6, 28.8, 29.4, 123.1, 124.0, 124.3, 124.5, 127.4, 128.3, 129.0, 129.6, 130.6, 130.7, 131.2, 133.0, 133.9, 137.0, 146.2, 146.3, 146.6, 155.1 (Au=C), 180.1, 181.2. Anal. Calcd. for $C_{41}H_{44}AuClN_2O_2$: C, 59.39; H, 5.35; N, 3.38; Found: C, 59.07, H, 5.22, N, 3.56.



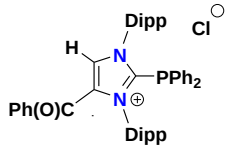
*Complex **6**. Method A: In strict absence of light*, silver(I) oxide (18 mg, 0.079 mmol) and triazolium **4** (113 mg, 0.158 mmol) were charged in a Schlenk flask and dry dichloromethane (10 mL) was added. The resulting suspension was stirred for 24 h at room temperature. The final dark brown suspension was filtered and transferred via cannula to a second Schlenk containing a solution of choloro(dimethylsulfide)gold (46.5 mg, 0.158 mmol) in 5 mL of dichlorometane. The resulting dark grey suspension was stirred for 6 h. After cannula filtration and removal of the solvent, the crude product is dissolved in 1 mL of DCM and purified by column chromatography using dichloromethane yielding the title product in 51 % yield (72 mg, 0.079 mmol) as white solid.

Method B: In strict absence of light, choloro(dimethylsulfide)gold (46.5 mg, 0.158 mmol) potassium hexamethyl disylazide (38 mg, 0.189 mmol) and triazolium **4** (113 mg, 0.158 mmol), were combined in a Schlenk flask and dissolved in THF (7 mL) at -78°C. The resulting mixture was stirred for 16 h. The final clear suspension was dried under vacuum and the residue was dissolved in 1 mL of dichloromethane and precipitated with hexane (10 mL). The solid is filtered and dried under vacuum yielding the title product in 93 % yield (134 mg, 0.147 mmol) as white solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 1.27 (d, *J* = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 1.40 (d, *J* = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 1.45 (d, *J* = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 1.48 (d, *J* = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 2.37 (sept, *J* = 6.4 Hz, 2H, CH(C*H*$_3$)$_2$), 2.65 (sept, *J* = 6.4 Hz, 2H, CH(C*H*$_3$)$_2$), 7.22-7.24 (m, 4H, C*H*$_{ar}$), 7.31-7.35 (m, 8H, C*H*$_{ar}$), 7.46-7.48 (m, 3H C*H*$_{ar}$), 7.54 (d, *J* = 7.6 Hz, 2H, C*H*$_{ar}$), 7.62 (t, *J* = 7.6 Hz, 2H, C*H*$_{ar}$), 7.71 (d, *J* = 7.6 Hz, 1H, C*H*$_{ar}$), 7.71 (t, *J* = 7.6 Hz, 1H, C*H*$_{ar}$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 22.4, 23.7, 24.7, 26.3, 29.1, 29.6, 118.2, 125.4, 126.6, 126.8, 127.8, 128.8, 130.5, 132.3, 133.0, 139.9, 140.8, 145.2, 145.4, 145.6, 147.4, 147.6, 148.5, 149.7, 157.3 (Au=C), 179.2. ^{31}P NMR ($CDCl_3$, 121 MHz) δ = -37.4 ppm. Anal. Calcd. for $C_{46}H_{49}AuClN_2OP$: C, 60.76; H, 5.43; N, 3.08; Found: C, 60.56, H, 5.67, N, 3.33.

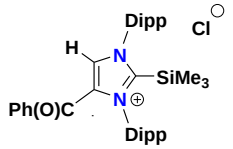
*Synthesis of imidazolium salts **7a-e***



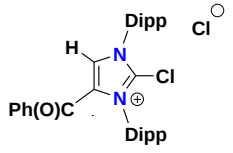
*Imidazolium salt **7a.*** A solution of NHC **1** (0.202 g, 0.410 mmol) in 15 mL of THF was added slowly to a solution of 2-furoyl chloride (0.053 g, 0.410 mmol) in 5 mL of THF, and the resulting mixture was allowed stirring for 12 h at room temperature. The resulting suspension was evaporated under reduced pressure and the residue was washed with diethyl ether (3 x 30 mL) to give the title product as a white solid in 83% yield (211 mg, 0.336 mmol). ^{1}H NMR (CD_3CN, 400 MHz) δ = 1.22 (d, *J* = 7.2 Hz, 6H, CH(C*H*$_3$)$_2$), 1.25 (two doublets overlapping, 12H, CH(C*H*$_3$)$_2$), 1.28 (d, *J* = 7.2 Hz, 6H, CH(C*H*$_3$)$_2$), 2.45 (sept, *J* = 6.8 Hz, 2H, CH(C*H*$_3$)$_2$), 2.65 (sept, *J* = 6.8 Hz, 2H, CH(C*H*$_3$)$_2$), 6.65 (dd, *J* = 2.8 Hz, 1H, C*H*), 7.02-7.06 (m, 3H, C*H*$_{ar}$), 7.11-7.13 (m, 4H, C*H*$_{ar}$, C*H*), 7.26-7.28 (m, 3H, C*H*$_{ar}$) 7.42 (t, *J* = 7.8 Hz, 2H, C*H*$_{ar}$), 7.55 (t, *J* = 7.8 Hz, 1H, C*H*$_{ar}$), 8.16 (dd, *J* = 2.8 Hz, 1H, C*H*$_{ar}$), 8.64 (s, 1H, C*H*$_{imid}$). ^{13}C NMR (CD_3CN, 100 MHz) δ = 22.5, 23.6, 24.5, 25.9, 29.1, 29.3, 112.2, 114.1, 116.1, 118.2, 125.1, 126.4, 126.7, 126.8, 127.8, 127.9, 130.5, 132.3, 133.0, 139.8, 139.9, 140.8, 146.6, 165.3, 180.2. Anal. Calcd. for $C_{39}H_{43}ClN_2O_3$: C, 75.16; H, 6.95; N, 4.49; Found: C, 75.01, H, 7.09, N, 4.23.



*Imidazolium salt **7b.*** Following the general procedure but using chlorodiphenylphosphine (0.090 g, 0.410 mmol) the title product is isolated as a white solid in 71% yield (208 mg, 0.291 mmol) after recrystallization from acetonitrile/diethylether. ^{1}H NMR (CD_3CN, 400 MHz) δ = 1.11 (d, *J* = 7.2 Hz, 6H, CH(C*H*$_3$)$_2$), 1.19 (d, *J* = 7.2 Hz, 6H, CH(C*H*$_3$)$_2$), 1.27 (d, *J* = 7.2 Hz, 6H, CH(C*H*$_3$)$_2$), 1.45 (d, *J* = 7.2 Hz, 6H, CH(C*H*$_3$)$_2$), 2.57 (sept, *J* = 6.8 Hz, 2H, CH(C*H*$_3$)$_2$), 2.67 (sept, *J* = 6.8 Hz, 2H, CH(C*H*$_3$)$_2$), 7.41-7.47 (m, 6H, C*H*$_{ar}$), 7.51-7.58 (m, 4H, C*H*$_{ar}$), 7.59-7.63 (m, 3H, C*H*$_{ar}$), 7.69-7.74 (m, 3H, C*H*$_{ar}$), 7.57-7.81 (m, 4H, C*H*ar), 8.73 (s, 1H, C*H*$_{imid}$). ^{13}C NMR (CD_3CN, 100 MHz) δ = 22.5, 23.7, 24.7, 26.4, 29.1, 29.6, 123.1, 124.1, 124.3, 124.6, 127.1, 127.7, 128.5, 129.0, 129.1, 129.8, 129.9, 130.0, 130.7, 131.2, 132.0, 132.9, 133.1, 134.0, 145.6, 179.2. ^{31}P NMR (CD_3CN, 121 MHz) δ = -38.7 ppm. Anal. Calcd. for $C_{46}H_{50}ClN_2OP$: C, 77.45; H, 7.07; N, 3.93; Found: C, 77.76, H, 6.85, N, 4.17.

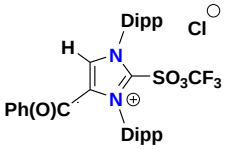


*Imidazolium salt **7c.*** Following the general procedure but using chlorotrimethylsilane (0.045 g, 0.410 mmol) the title product is isolated as a white solid in 68% yield (168 mg, 0.279 mmol) after recrystallization from acetonitrile/diethylether. ^{1}H NMR (CD_3CN, 400 MHz) δ = -0.28 (s, 9H, C*H*$_3$), 1.07 (d, *J* = 7.2 Hz, 6H, CH(C*H*$_3$)$_2$), 1.20 (d, *J* = 7.2 Hz, 6H, CH(C*H*$_3$)$_2$), 1.25 (d, *J* = 7.2 Hz, 6H, CH(C*H*$_3$)$_2$), 1.29 (d, *J* = 7.2 Hz, 6H, CH(C*H*$_3$)$_2$), 2.17 (sept, *J* = 6.8 Hz, 2H, CH(C*H*$_3$)$_2$), 2.45 (sept, *J* = 6.8 Hz, 2H, CH(C*H*$_3$)$_2$), 7.02-7.06 (m, 2H C*H*$_{ar}$), 7.11-7.15 (m, 4H, C*H*$_{ar}$), 7.26-7.28 (m, 2H, C*H*$_{ar}$), 7.29.7.33 (m, 1H, CHar), 7.42-7.45 (m, 1H, C*H*$_{ar}$), 7.57 (t, *J* = 7.8 Hz, 1H, C*H*$_{ar}$), 8.26 (s, 1H, C*H*$_{imid}$). ^{13}C NMR (CD_3CN, 100 MHz) δ = -1.72, 22.5, 22.9, 24.0, 24.5, 28.9, 29.3, 112.2, 114.1, 116.1, 125.4, 126.8, 127.8, 128.7, 129.3, 129.7, 133.0, 131.4, 131.7, 140.8, 146.5, 149.7, 180.3. Anal. Calcd. for $C_{37}H_{49}ClN_2OSi$: C, 73.90; H, 8.21; N, 4.66; Found: C, 73.27, H, 8.22, N, 4.81.



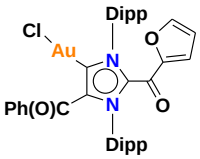
*Imidazolium salt **7d.*** NHC **1** (0.202 g, 0.410 mmol) and hexacholorethane (0.107 g, 0.450 mmol) were combined in a Schlenk flask and dissolved in acetonitrile (15 mL). The resulting solution was sonicated for 24 h at room temperature. Removal of the volatiles under vacuum gave a light yellow solid

that was washed with toluene (10 mL) and recrystallized from acetonitrile/diethylether to give the title product as a white solid in 57% yield (132 mg, 0.234 mmol). ^{1}H NMR (CD_3CN, 400 MHz) δ = 1.07 (d, *J* = 7.2 Hz, 6H, CH(C*H*$_3$)$_2$), 1.24 (two doublets overlapping, 12H, CH(C*H*$_3$)$_2$), 1.34 (d, *J* = 7.2 Hz, 6H, CH(C*H*$_3$)$_2$), 2.23 (sept, *J* = 6.8 Hz, 2H, CH(C*H*$_3$)$_2$), 2.61 (sept, *J* = 6.8 Hz, 2H, CH(C*H*$_3$)$_2$), 7.13 (d, *J* = 7.8 Hz, 2H, C*H*$_{ar}$), 7.22-7.28 (m, 3H C*H*$_{ar}$), 7.32 (d, *J* = 7.8 Hz, 2H, C*H*$_{ar}$), 7.50 (t, *J* = 7.8 Hz, 1H, C*H*$_{ar}$), 7.58 (t, *J* = 7.8 Hz, 1H, C*H*$_{ar}$), 7.92 (d, *J* = 7.6 Hz, 2H, C*H*$_{ar}$), 8.53 (s, 1H, C*H*$_{imid}$). ^{13}C NMR (CD_3CN, 100 MHz) δ = 23.9, 24.1, 24.5, 24.7, 28.5, 28.7, 123.6, 123.7, 124.3, 127.3, 128.5, 128.9, 129.7, 130.1, 130.6, 130.8, 133.7, 134.5, 134.7, 136.4, 146.6, 180.4. Anal. Calcd. for $C_{34}H_{40}Cl_2N_2O$: C, 72.46; H, 7.15; N, 4.97; Found: C, 72.01, H, 7.22, N, 4.58.

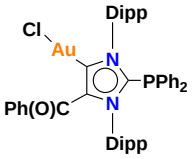


Imidazolium salt ***7e.*** Following the general procedure but using trifluoromethanesulfonyl chloride (0.069 g, 0.410 mmol) the title product is isolated as a white solid in 63% yield (171 mg, 0.258 mmol) after recrystallization from acetonitrile/diethylether. ^{1}H NMR (CD_3CN, 400 MHz) δ = 1.21 (d, *J* = 7.2 Hz, 6H, CH(C*H*$_3$)$_2$), 1.25 (two doublets overlapping, 12H, CH(C*H*$_3$)$_2$), 1.28 (d, *J* = 7.2 Hz, 6H, CH(C*H*$_3$)$_2$), 2.45 (sept, *J* = 6.8 Hz, 2H, CH(C*H*$_3$)$_2$), 2.64 (sept, *J* = 6.8 Hz, 2H, CH(C*H*$_3$)$_2$), 7.38 (d, *J* = 7.6 Hz, 2H, C*H*$_{ar}$), 7.47-7.51 (m, 3H C*H*$_{ar}$), 7.54 (t, *J* = 7.8 Hz, 1H, C*H*$_{ar}$), 7.64-7.69 (m, 3H, C*H*$_{ar}$), 7.90 (d, *J* = 7.6 Hz, 2H, C*H*$_{ar}$), 8.97 (s, 1H, C*H*$_{imid}$). ^{13}C NMR (CD_3CN, 100 MHz) δ = 21.7, 22.8, 23.6, 25.0, 28.9, 29.2, 124.6, 125.2, 125.9, 127.2, 128.3, 128.8, 129.4, 132.1, 132.6, 133.2, 137.2, 138.9, 146.3, 146.4, 179.7. ^{19}F NMR ($CDCl_3$, 282 MHz) δ = -79.2. Anal. Calcd. for $C_{34}H_{40}ClF_3N_2O_4S$: C, 61.39; H, 6.06; N, 4.21; Found: C, 61.78, H, 6.22, N, 4.17.

Synthesis of aNHC-Au(I) complexes ***8a-e***

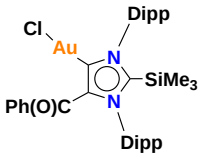


Complex ***8a.*** *In strict absence of light*, choloro(dimethylsulfide)gold (46.5 mg, 0.158 mmol) potassium hexamethyl disylazide (38 mg, 0.189 mmol) and triazolium **7a** (98 mg, 0.158 mmol), were combined in a Schlenk flask and dissolved in THF (7 mL) at -78°C. The resulting mixture was stirred for 16 h. The final clear suspension was dried under vacuum and the residue was dissolved in 1 mL of dichloromethane and precipitated with hexane (10 mL). The solid is filtered and dried under vacuum yielding the title product as a white solid in 91% yield (93 mg, 0.114 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 1.14 (d, *J* = 7.2 Hz, 6H, CH(C*H*$_3$)$_2$), 1.16 (d, *J* = 7.2 Hz, 6H, CH(C*H*$_3$)$_2$), 1.21 (d, *J* = 7.2 Hz, 6H, CH(C*H*$_3$)$_2$), 1.26 (d, *J* = 7.2 Hz, 6H, CH(C*H*$_3$)$_2$), 2.51 (sept, *J* = 6.8 Hz, 2H, CH(C*H*$_3$)$_2$), 2.55 (sept, *J* = 6.8 Hz, 2H, CH(C*H*$_3$)$_2$), 6.69-6.60 (dd, *J* = 2.6 Hz, 1H C*H*), 6.91-6.92 (m, 1H C*H*), 7.01-7.06 (m, 2H, C*H*$_{ar}$), 7.11-7.15 (m, 4H, C*H*$_{ar}$), 7.26-7.30 (m, 2H, C*H*$_{ar}$), 7.42 (t, *J* = 7.6 Hz, 2H, C*H*$_{ar}$), 7.56 (t, *J* = 7.6 Hz, 1H, C*H*$_{ar}$), 8.33 (m, 1H, C*H*). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 23.4, 23.6, 24.5, 24.6, 29.0, 29.1, 112.3, 115.5, 118.2, 121.2, 125.1, 126.7, 129.0, 129.7, 130.5, 132.3, 137.6, 139.7, 141.1, 142.1, 145.3, 145.4, 147.5, 157.6, 163.5, 179.9. Anal. Calcd. for $C_{39}H_{42}AuClN_2O_3$: C, 57.18; H, 5.17; N, 3.42; Found: C, 57.01, H, 5.09, N, 3.23.

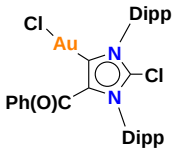


Complex ***8b.*** Following the general procedure but using imidazolium salt **7b** (113 mg, 0.158 mmol), the title product is isolated as a white solid in 84% yield (121 mg, 0.133 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 1.20 (d, *J* = 7.2 Hz, 6H, CH(C*H*$_3$)$_2$), 1.27 (d, *J* = 7.2 Hz, 6H, CH(C*H*$_3$)$_2$), 1.47 (d, *J* = 7.2 Hz, 6H, CH(C*H*$_3$)$_2$), 1.56 (d, *J* = 7.2 Hz, 6H, CH(C*H*$_3$)$_2$), 2.43 (sept, *J* = 6.8 Hz, 2H, CH(C*H*$_3$)$_2$), 2.84 (sept, *J* = 6.8 Hz, 2H, CH(C*H*$_3$)$_2$), 7.33 (d, *J* = 7.8 Hz, 2H, C*H*$_{ar}$), 7.39-7.53 (m,

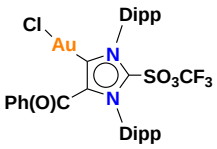
3H, CH_{ar}), 7.48-7.51 (m, 5H, CH_{ar}), 7.55-7.57 (m, 4H, CH_{ar}), 7.64-7.68 (m, 5H, CH_{ar}), 7.69-7.72 (m, 2H, CH_{ar}). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 20.8, 21.1, 22.8, 24.9, 29.3, 29.7, 109.4, 116.4, 117.8, 121.5, 122.8, 132.3, 123.9, 124.3, 126.4, 127.1, 130.3, 131.0, 131.6, 134.1, 134.5, 153.4, 177.6. ^{31}P NMR ($CDCl_3$, 121 MHz) δ = -35.2 ppm. Anal. Calcd. for $C_{46}H_{49}AuClN_2OP$: C, 60.76; H, 5.43; N, 3.08; Found: C, 60.79, H, 5.67, N, 3.17.



*Complex **8c.*** Following the general procedure but using imidazolium salt **7c** (116 mg, 0.158 mmol), the title product is isolated as a white solid in 88% yield (111 mg, 0.139 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = -0.32, 1.16 (d, *J* = 7.2 Hz, 6H, CH(CH_3)$_2$), 1.19 (d, *J* = 7.2 Hz, 6H, CH(CH_3)$_2$), 1.25 (d, *J* = 7.2 Hz, 6H, CH(CH_3)$_2$), 1.27 (d, *J* = 7.2 Hz, 6H, CH(CH_3)$_2$), 2.46 (sept, *J* = 6.8 Hz, 2H, CH(CH_3)$_2$), 2.87 (sept, *J* = 6.8 Hz, 2H, CH(CH_3)$_2$), 7.21-7.24 (m, 4H, CH_{ar}), 7.36-7.40 (m, 2H, CH_{ar}), 7.43-7.46 (m, 2H, CH_{ar}), 7.51 (d, *J* = 7.6 Hz, 2H, CH_{ar}), 7.61 (t, *J* = 7.6 Hz, 1H, CH_{ar}). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = -2.42, 23.7, 24.9, 25.9, 27.6, 30.3, 30.7, 125.8, 126.2, 127.8, 130.0, 130.3, 130.7, 131.2, 133.6, 134.6, 137.8, 139.8, 140.6, 142.2, 146.4, 150.7, 180.5. Anal. Calcd. for $C_{37}H_{48}AuClN_2OSi$: C, 55.74; H, 6.07; N, 3.51; Found: C, 55.41, H, 6.22, N, 3.81.



*Complex **8d.*** Following the general procedure but using imidazolium salt **7d** (89 mg, 0.158 mmol), the title product is isolated as a white solid in 75% yield (90 mg, 0.119 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 1.17 (d, *J* = 7.2 Hz, 6H, CH(CH_3)$_2$), 1.20 (d, *J* = 7.2 Hz, 6H, CH(CH_3)$_2$), 1.25 (d, *J* = 7.2 Hz, 6H, CH(CH_3)$_2$), 1.27 (d, *J* = 7.2 Hz, 6H, CH(CH_3)$_2$), 2.44 (sept, *J* = 6.8 Hz, 2H, CH(CH_3)$_2$), 2.93 (sept, *J* = 6.8 Hz, 2H, CH(CH_3)$_2$), 7.02-7.06 (m, 2H, CH_{ar}), 7.11-7.15 (m, 3H, CH_{ar}), 7.26-7.29 (m, 2H, CH_{ar}), 7.34 (d, *J* = 7.8 Hz, 1H, CH_{ar}), 7.42 (t, *J* = 7.6 Hz, 2H, CH_{ar}), 7.55 (t, *J* = 7.6 Hz, 1H, CH_{ar}). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 23.7, 24.0, 24.5, 25.6, 28.8, 29.1, 123.1, 124.1, 124.3, 124.6, 127.1, 127.7, 129.1, 129.9, 130.7, 131.2, 132.0, 132.9, 133.1, 146.0, 152.2, 175.3. Anal. Calcd. for $C_{34}H_{39}AuCl_2N_2O$: C, 53.76; H, 5.18; N, 3.69; Found: C, 53.91, H, 5.40, N, 3.71.



*Complex **8e.*** Following the general procedure but using imidazolium salt **7e** (107 mg, 0.158 mmol), the title product is isolated as a white solid in 81% yield (112 mg, 0.128 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 1.07 (d, *J* = 7.2 Hz, 6H, CH(CH_3)$_2$), 1.20 (d, *J* = 7.2 Hz, 6H, CH(CH_3)$_2$), 1.25 (d, *J* = 7.2 Hz, 6H, CH(CH_3)$_2$), 1.29 (d, *J* = 7.2 Hz, 6H, CH(CH_3)$_2$), 2.16 (sept, *J* = 6.8 Hz, 2H, CH(CH_3)$_2$), 2.45 (sept, *J* = 6.8 Hz, 2H, CH(CH_3)$_2$), 7.02-7.06 (m, 2H, CH_{ar}), 7.12 (d, *J* = 7.6 Hz, 3H, CH_{ar}), 7.26-7.30 (m, 2H, CH_{ar}), 7.34 (d, *J* = 7.6 Hz, 1H, CH_{ar}), 7.44 (t, *J* = 7.6 Hz, 2H, CH_{ar}), 7.55 (t, *J* = 7.8 Hz, 1H, CH_{ar}). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 22.5, 23.8, 24.7, 26.4, 29.1, 29.6, 120.1, 121.5 (q, *J* (C,F) = 328 Hz), 122.0, 124.6, 127.3, 128.8, 128.9, 129.1, 129.6, 132.4, 136.6, 141.0, 145.2, 161.8, 181.7. ^{19}F NMR ($CDCl_3$, 282 MHz) δ = -76.8. Anal. Calcd. for $C_{35}H_{39}AuClF_3N_2O_4S$: C, 48.14; H, 4.50; N, 3.21; Found: C, 47.96, H, 4.09, N, 3.58.

References:

1) D. Mendoza-Espinosa, B. Donnadieu and G. Bertrand, *J. Am. Chem. Soc.*, 2010, **132**, 7264.
2) G. M. Sheldrick, G. M. *SHELXS-2014, Program for Crystal Structure Solution and Refinement*; Institut Für Anorganishe Chemie, Göttingen, Germany, 2013.

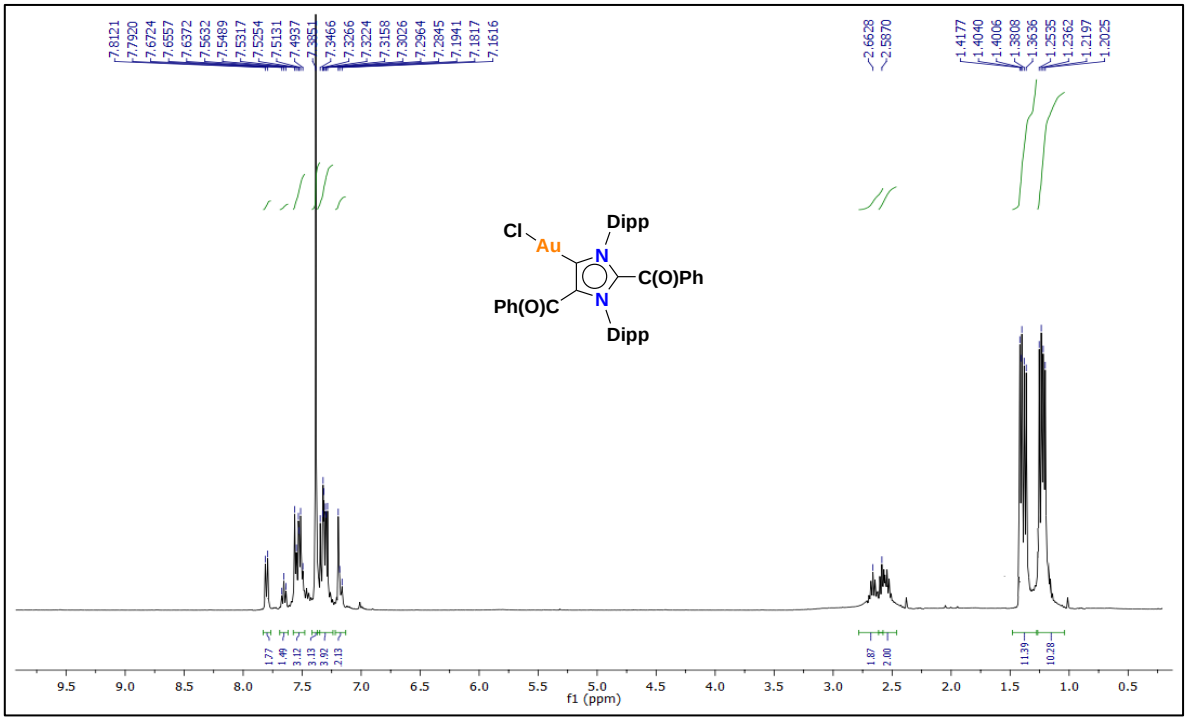


Figure S1. ^{1}H NMR (400 MHz) spectrum of complex **5** in $CDCl_3$.

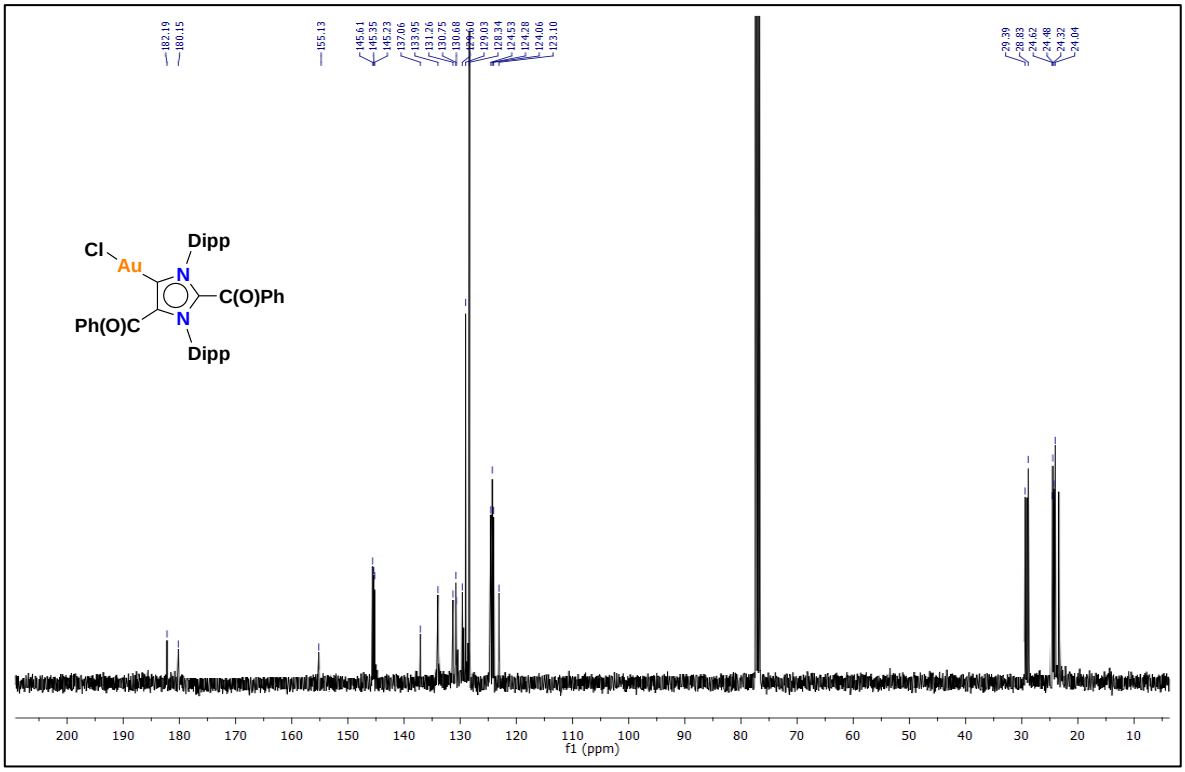


Figure S2. ^{13}C-NMR (100 MHz) spectrum of complex **5** in $CDCl_3$

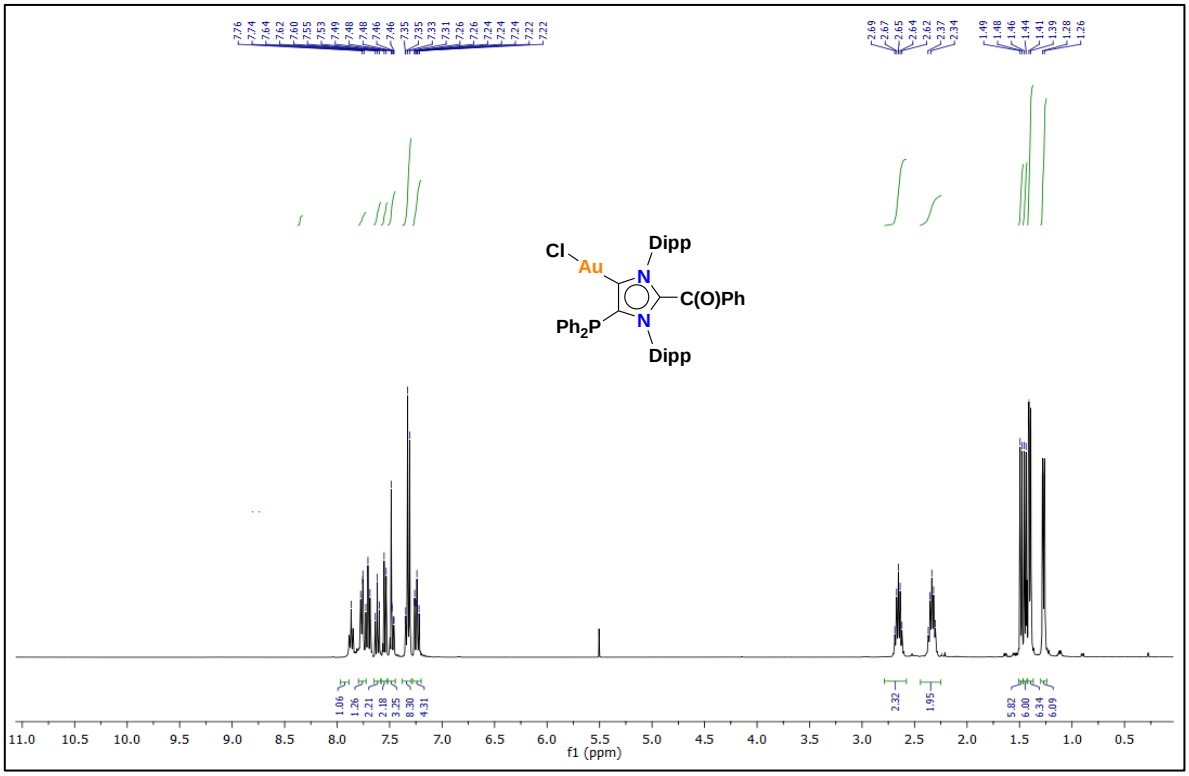


Figure S3. ^{1}H NMR (400 MHz) spectrum of complex **6** in $CDCl_3$

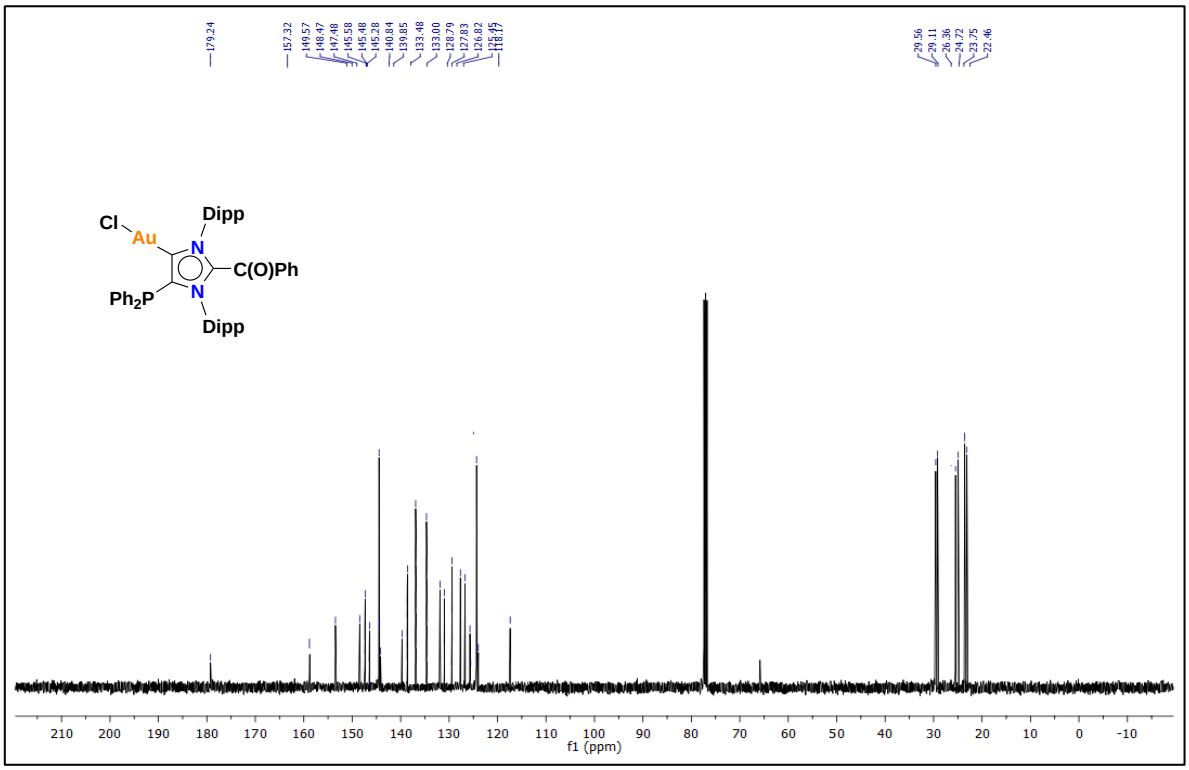


Figure S4. ^{13}C-NMR (100 MHz) spectrum of complex **6** in $CDCl_3$

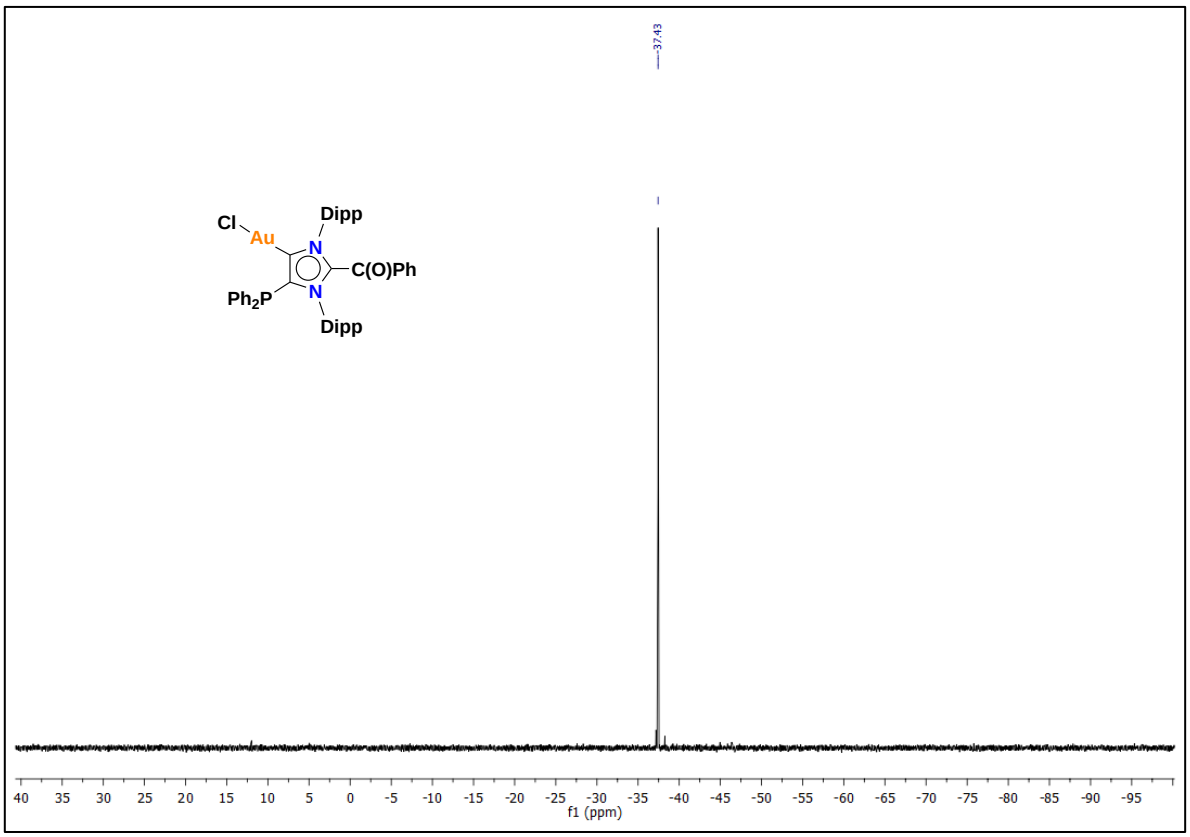


Figure S5. ^{31}P-NMR (126 MHz) spectrum of complex **6** in $CDCl_3$

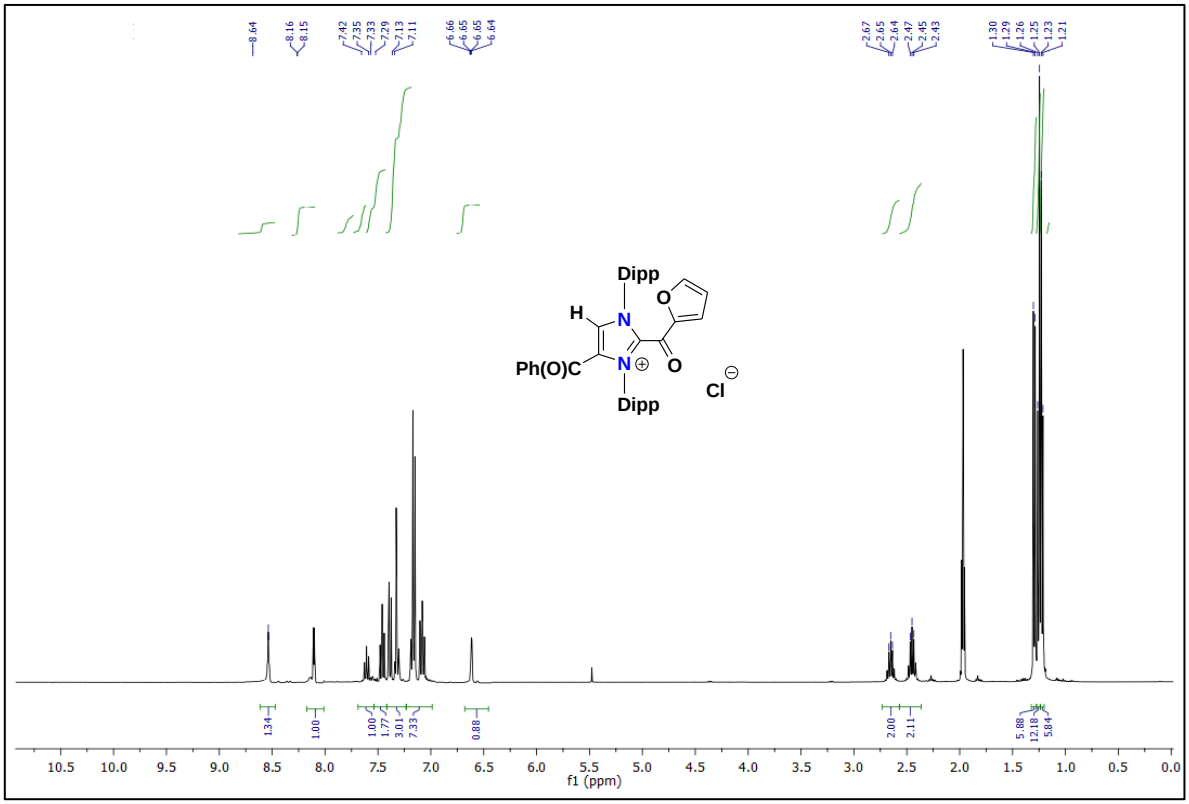


Figure S6. ^{1}H NMR (400 MHz) spectrum of salt **7a** in CD_3CN

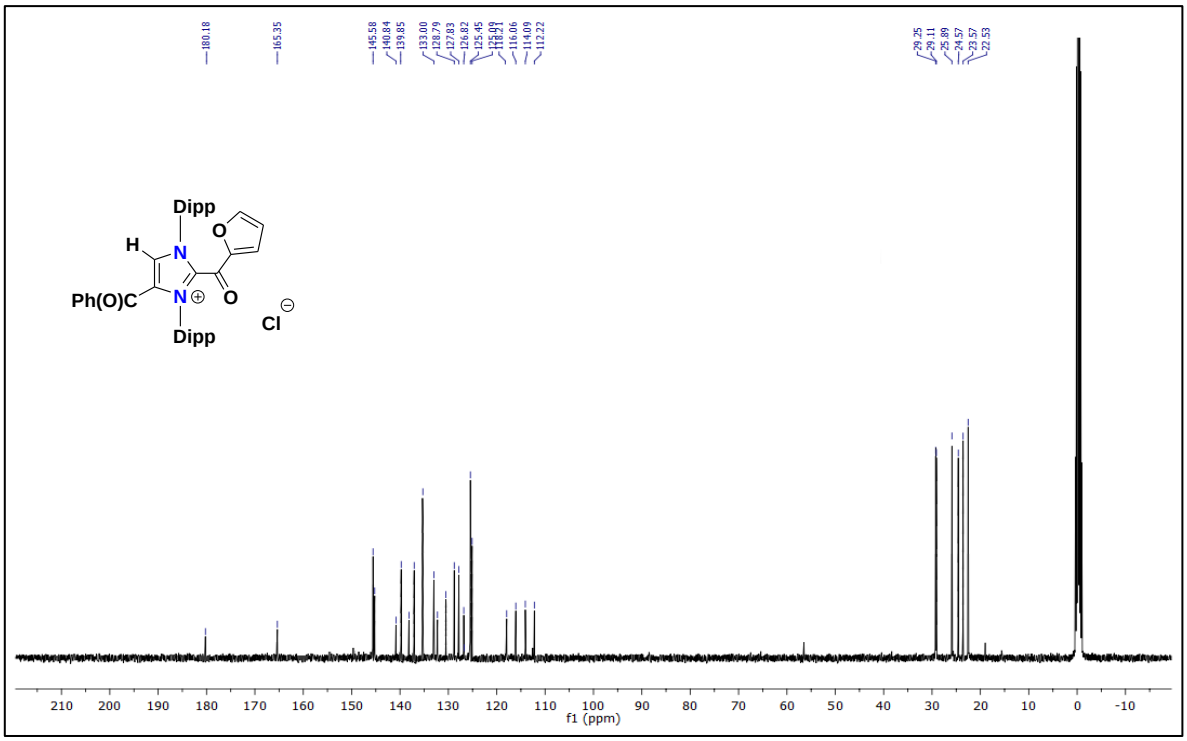


Figure S7. ^{13}C NMR (100 MHz) spectrum of salt **7a** in CD_3CN

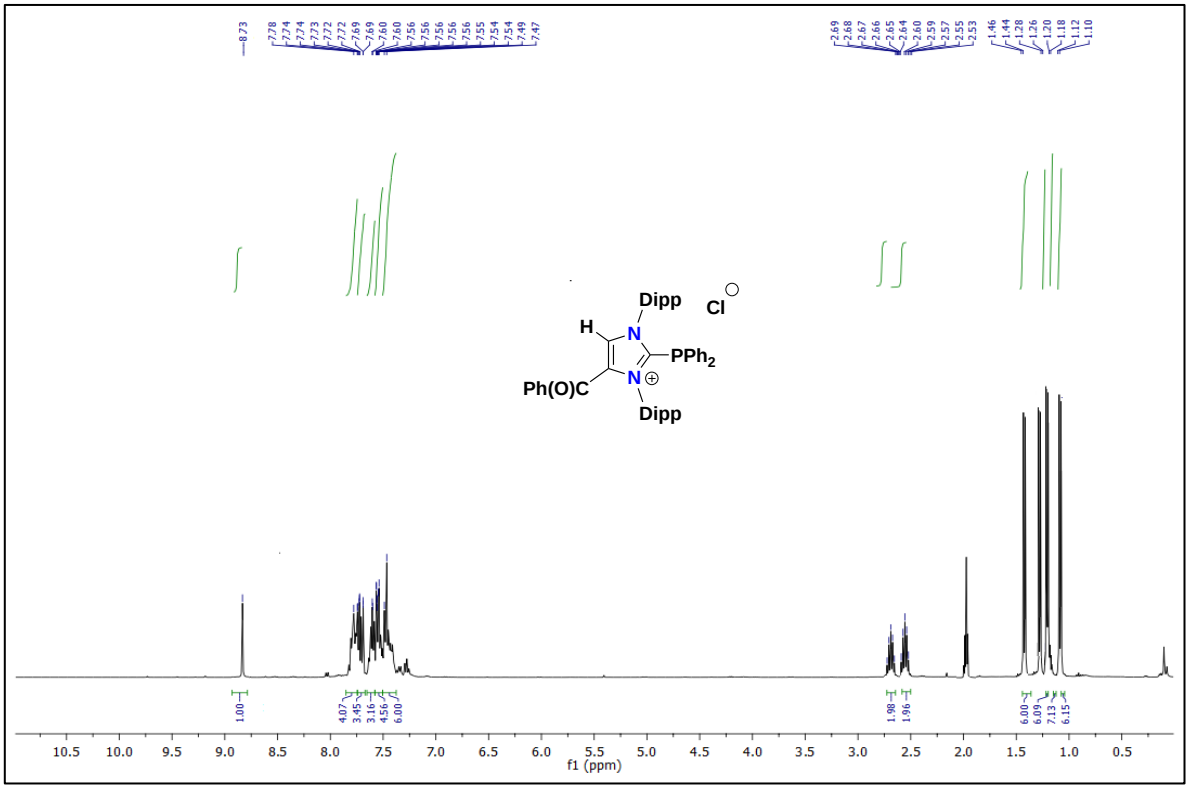


Figure S8. ^{1}H NMR (400 MHz) spectrum of salt **7b** in CD_3CN

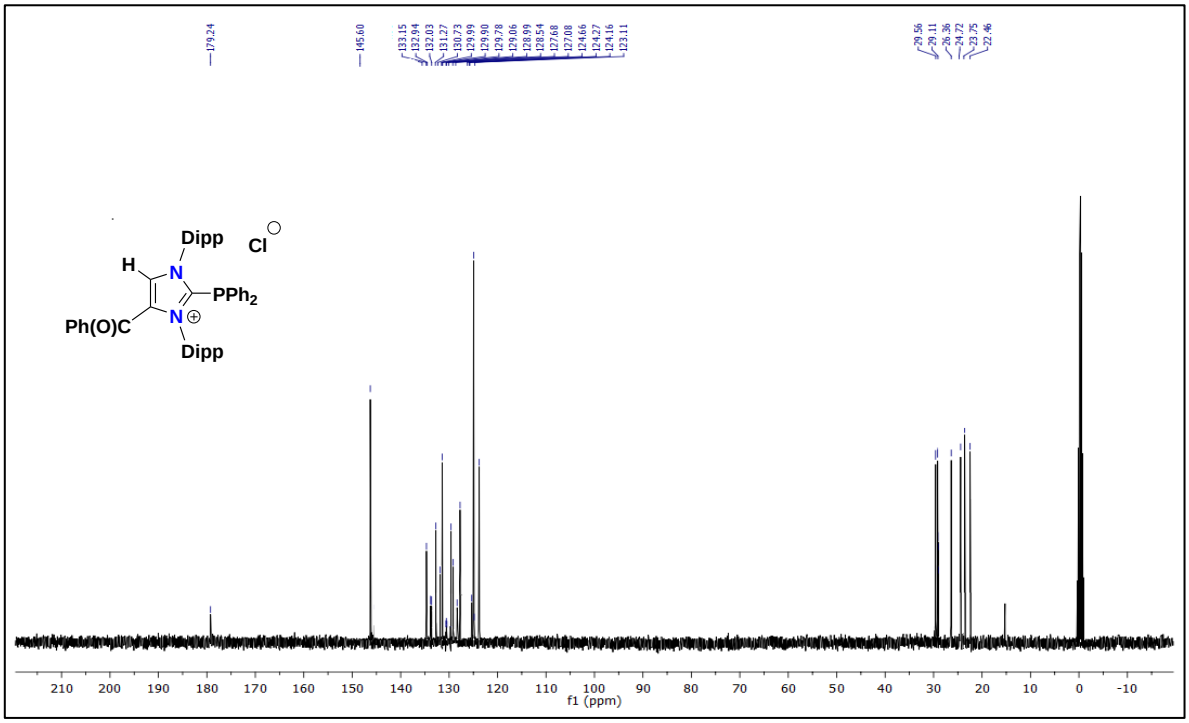


Figure S9. ^{13}C NMR (100 MHz) spectrum of salt **7b** in CD_3CN

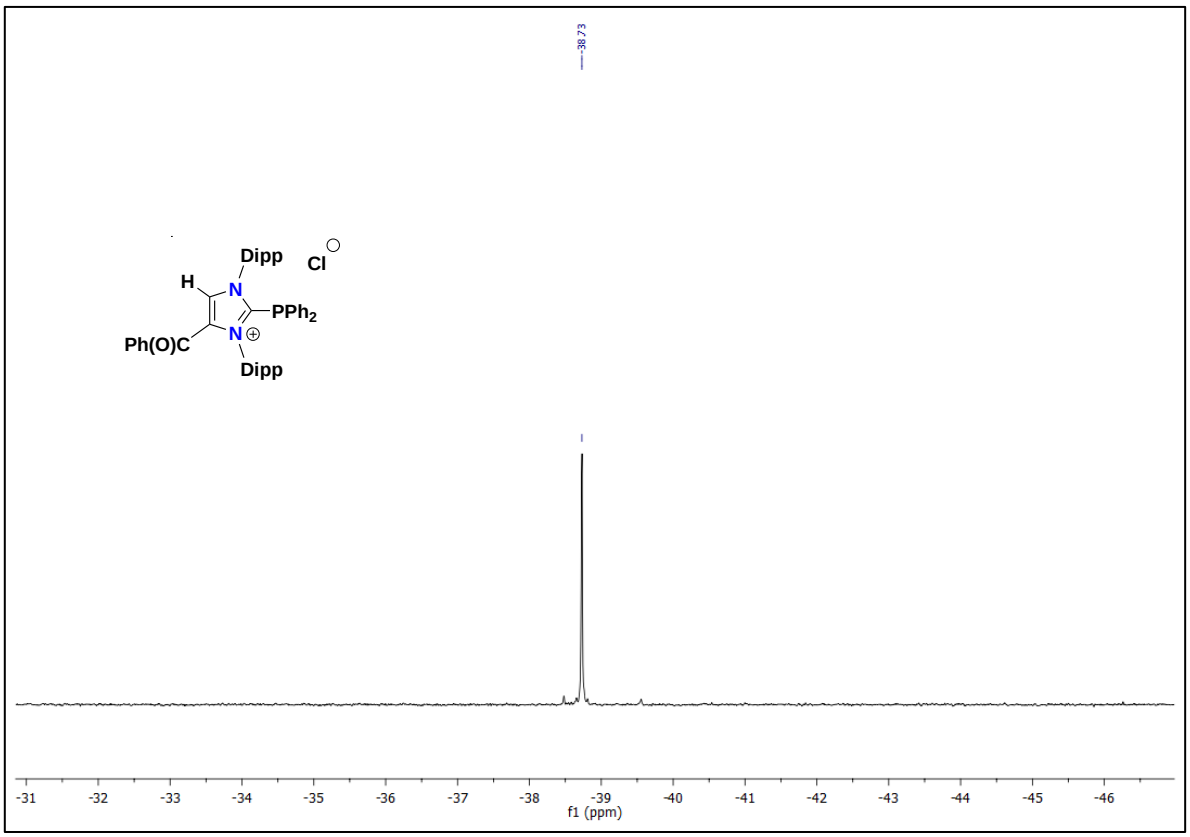


Figure S10. ^{31}P-NMR (126 MHz) spectrum of salt **7b** in CD_3CN

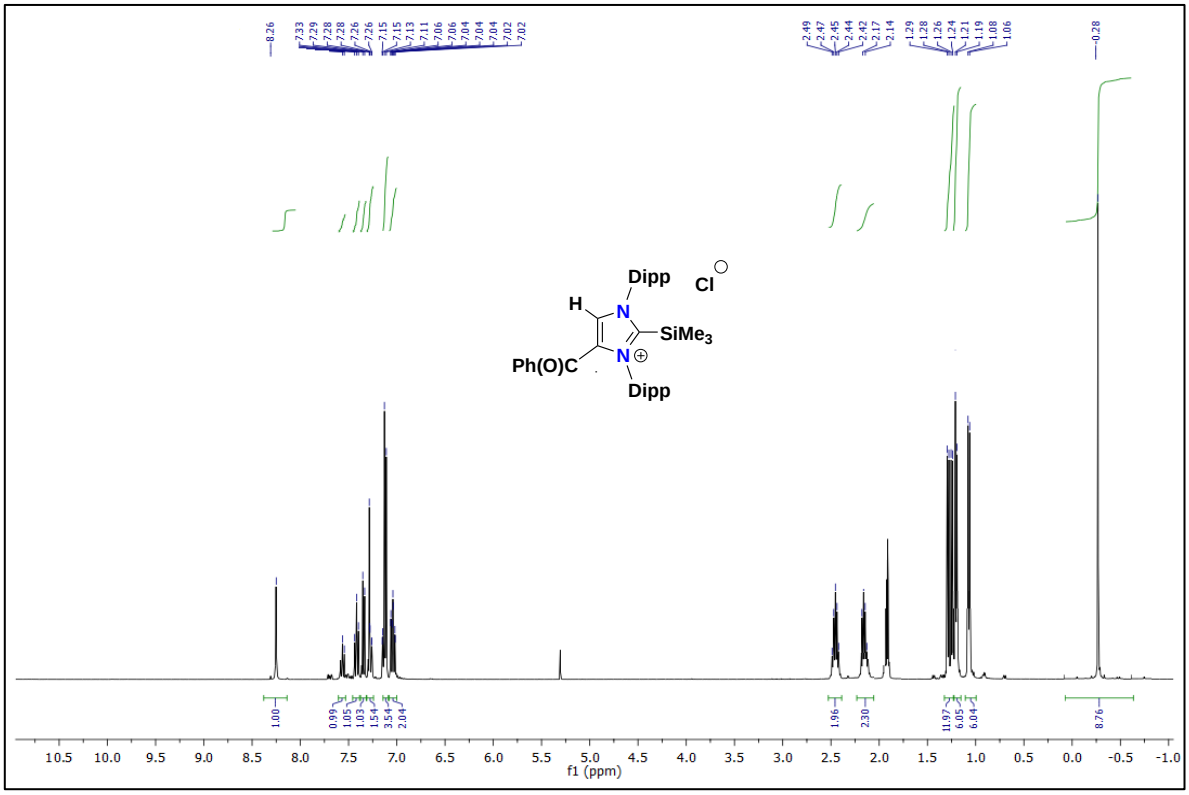


Figure S11. ^{1}H NMR (400 MHz) spectrum of salt **7c** in CD_3CN

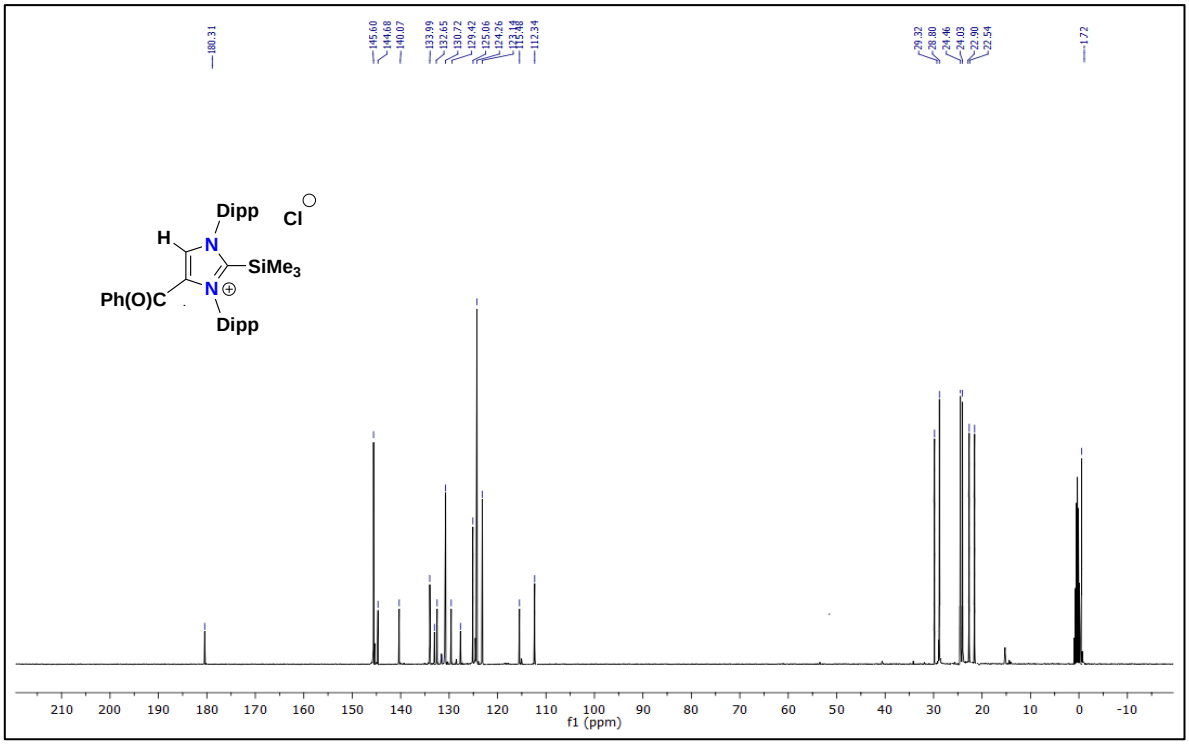


Figure S12. ^{13}C NMR (100 MHz) spectrum of salt **7c** in CD_3CN

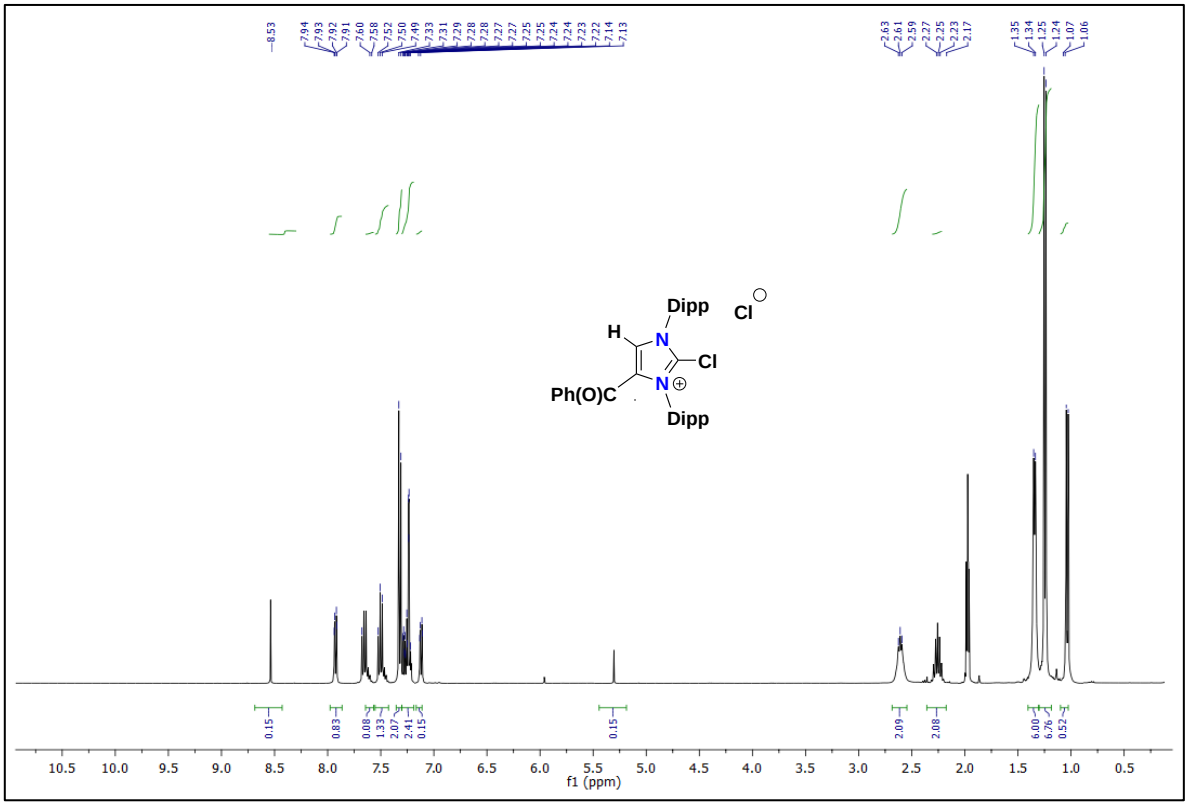


Figure S13. ^{1}H NMR (400 MHz) spectrum of salt **7d** in CD_3CN

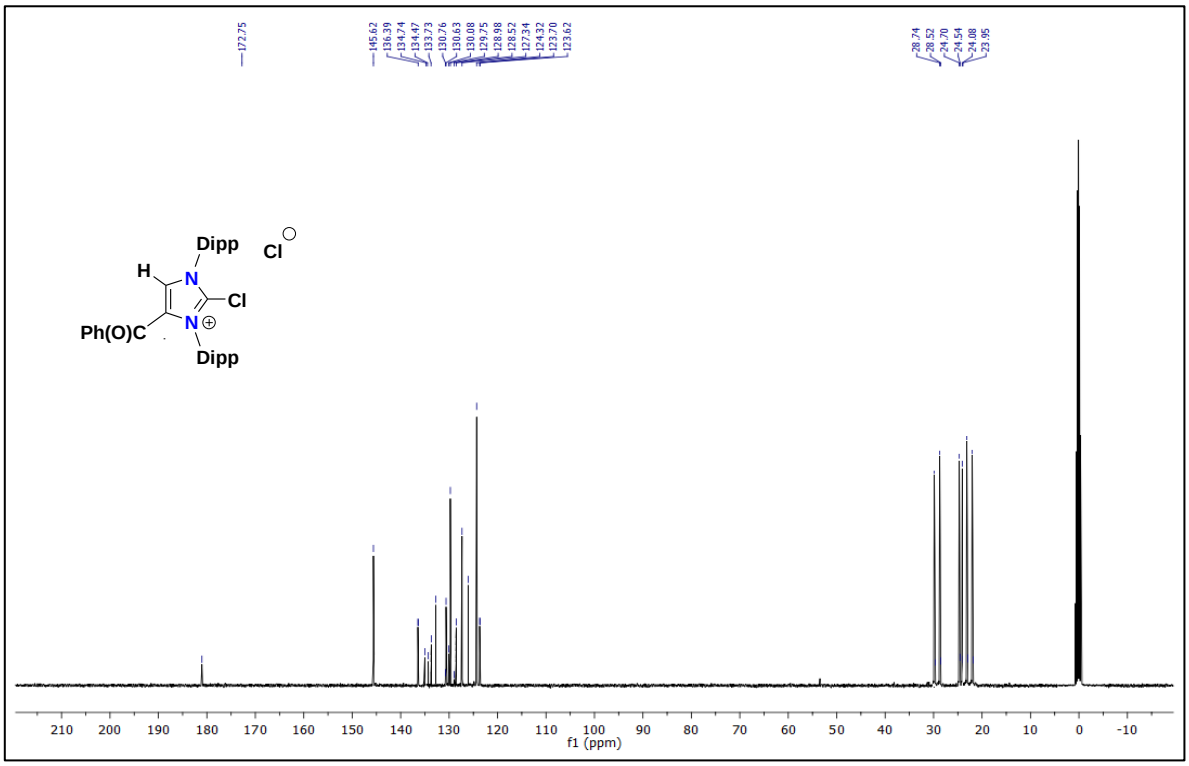


Figure S14. ^{13}C NMR (100 MHz) spectrum of salt **7d** in CD_3CN

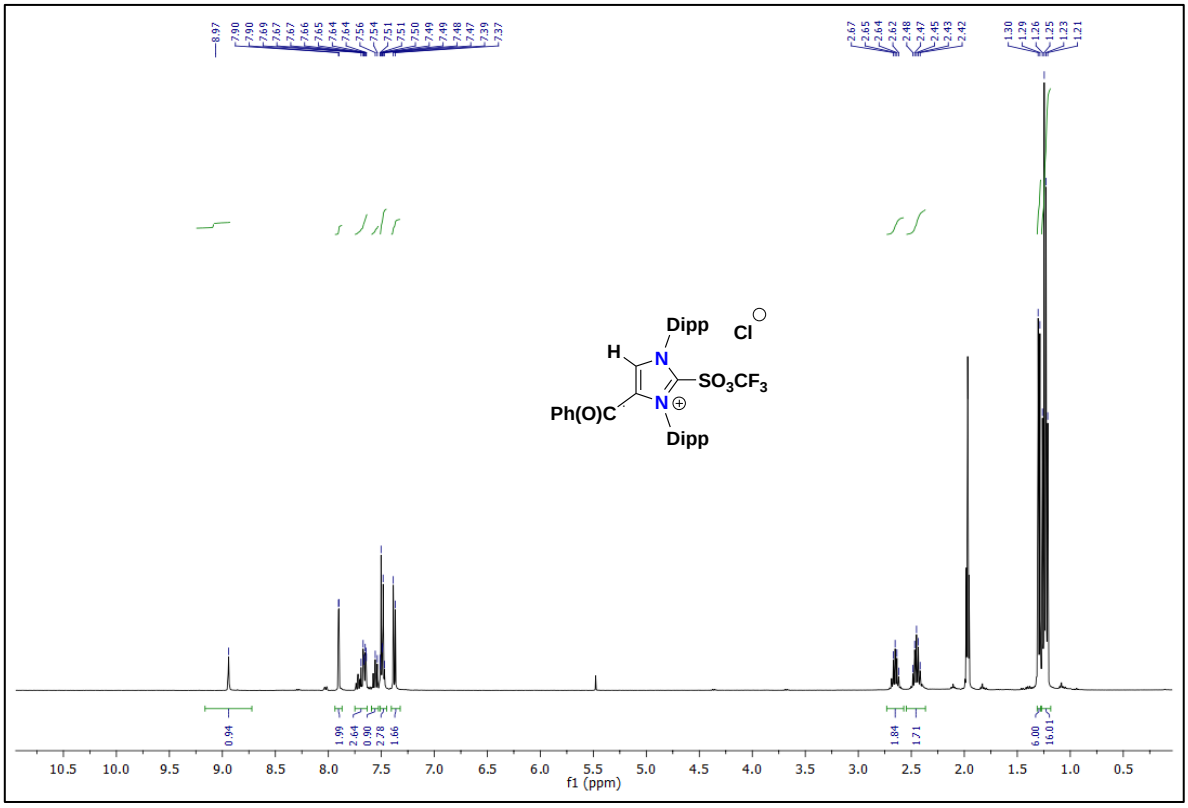


Figure S15. ^{1}H NMR (400 MHz) spectrum of salt **7e** in CD_3CN

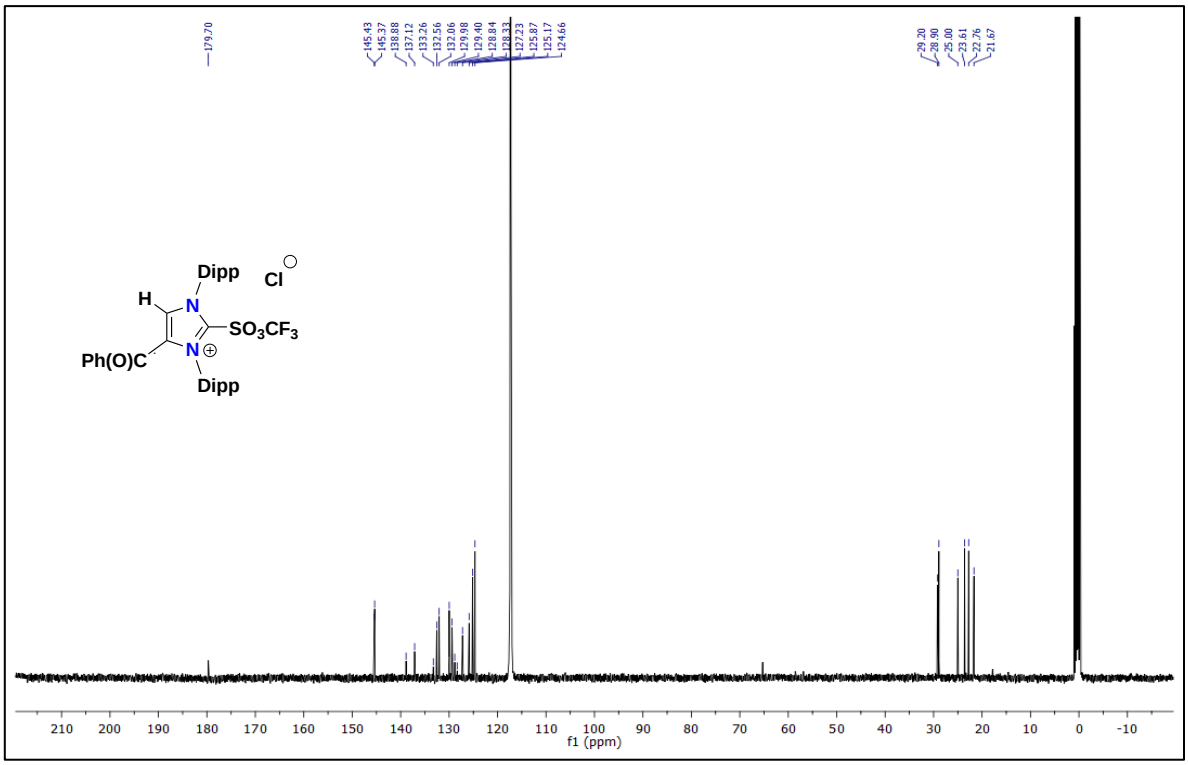


Figure S16. ^{13}C NMR (100 MHz) spectrum of salt **7e** in CD_3CN

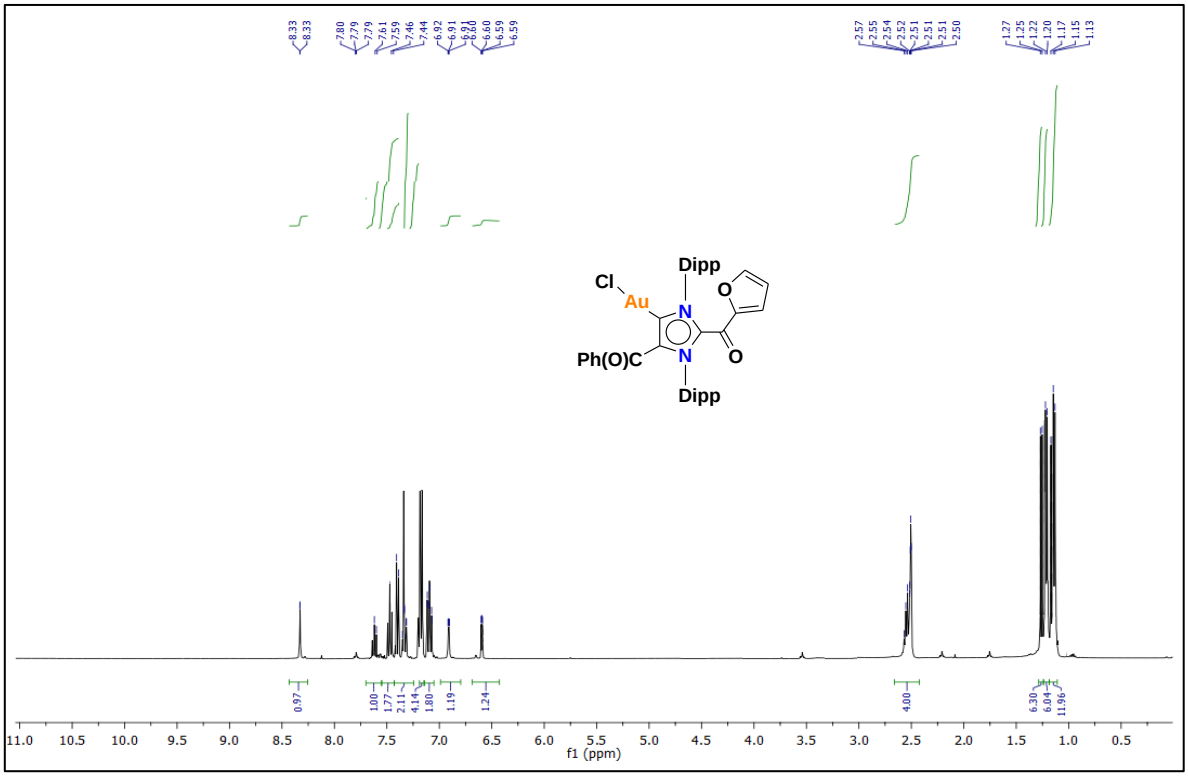


Figure S17. ^{1}H NMR (400 MHz) spectrum of complex **8a** in $CDCl_3$

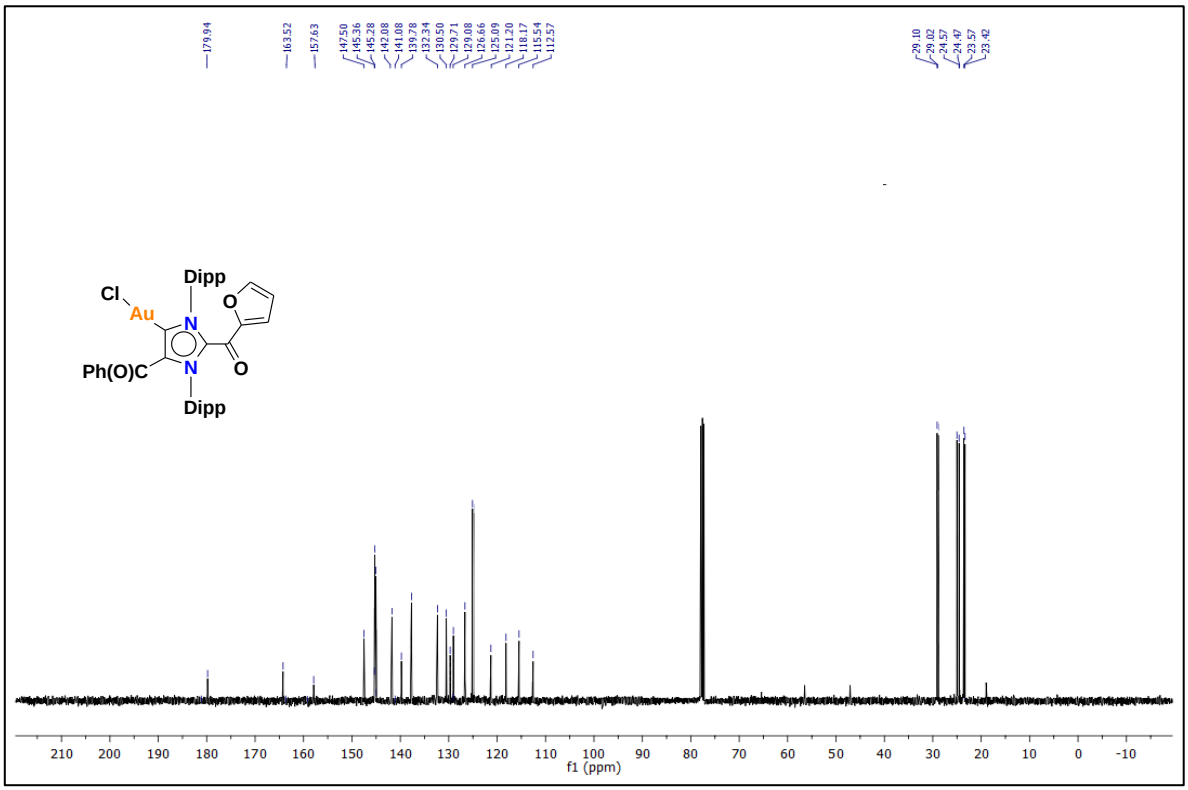


Figure S18. ^{13}C NMR (100 MHz) spectrum of complex **8a** in $CDCl_3$

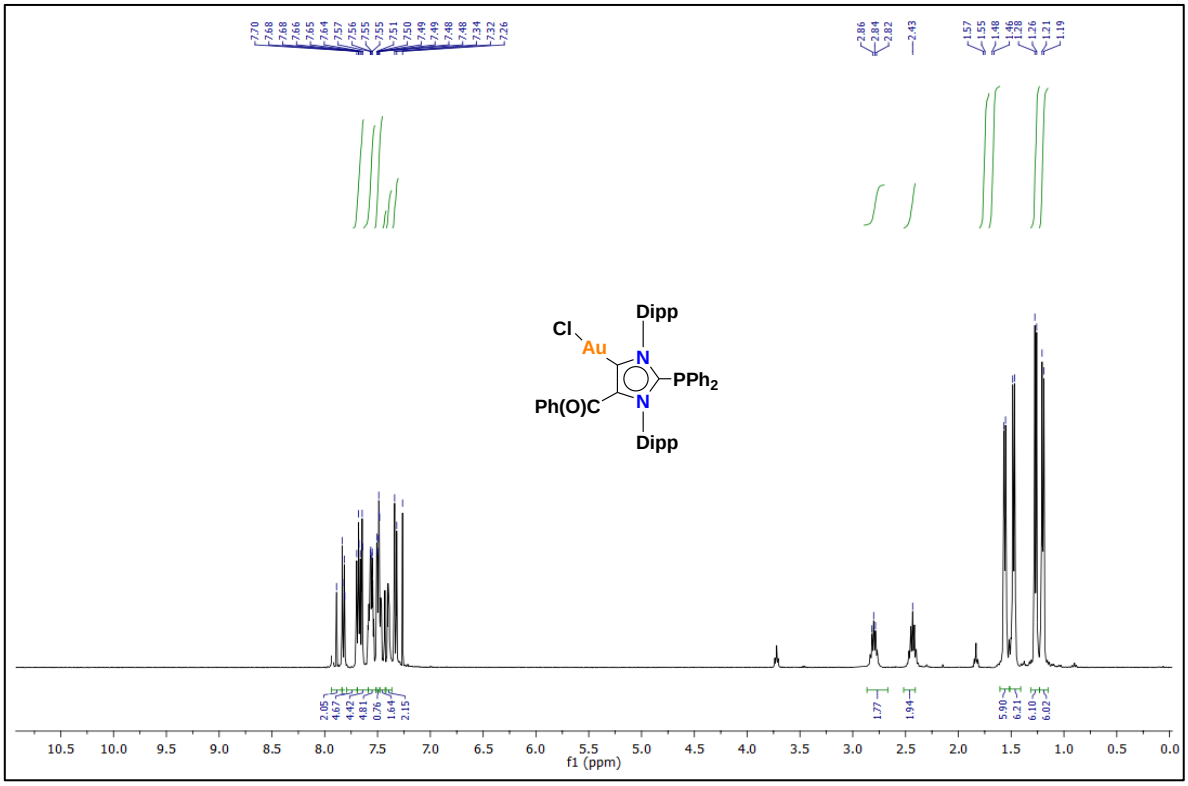


Figure S19. ^{1}H NMR (400 MHz) spectrum of complex **8b** in $CDCl_3$

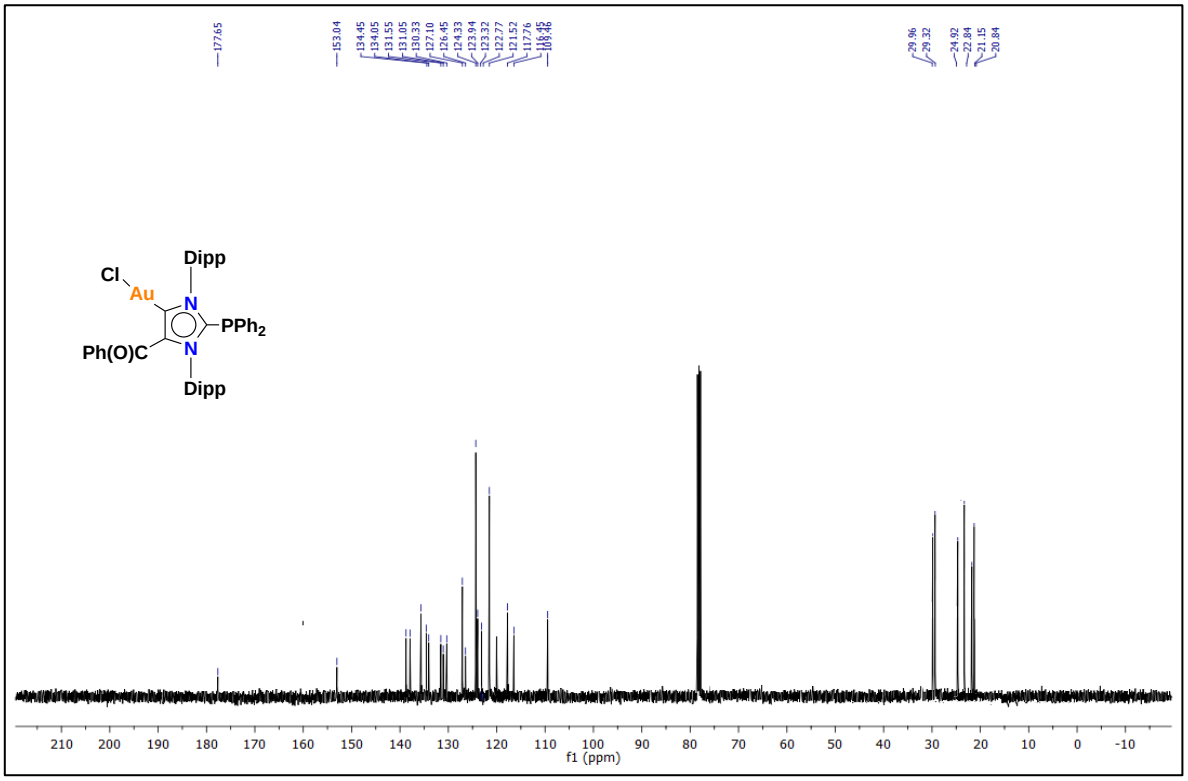


Figure S20. ^{13}C NMR (100 MHz) spectrum of complex **8b** in $CDCl_3$

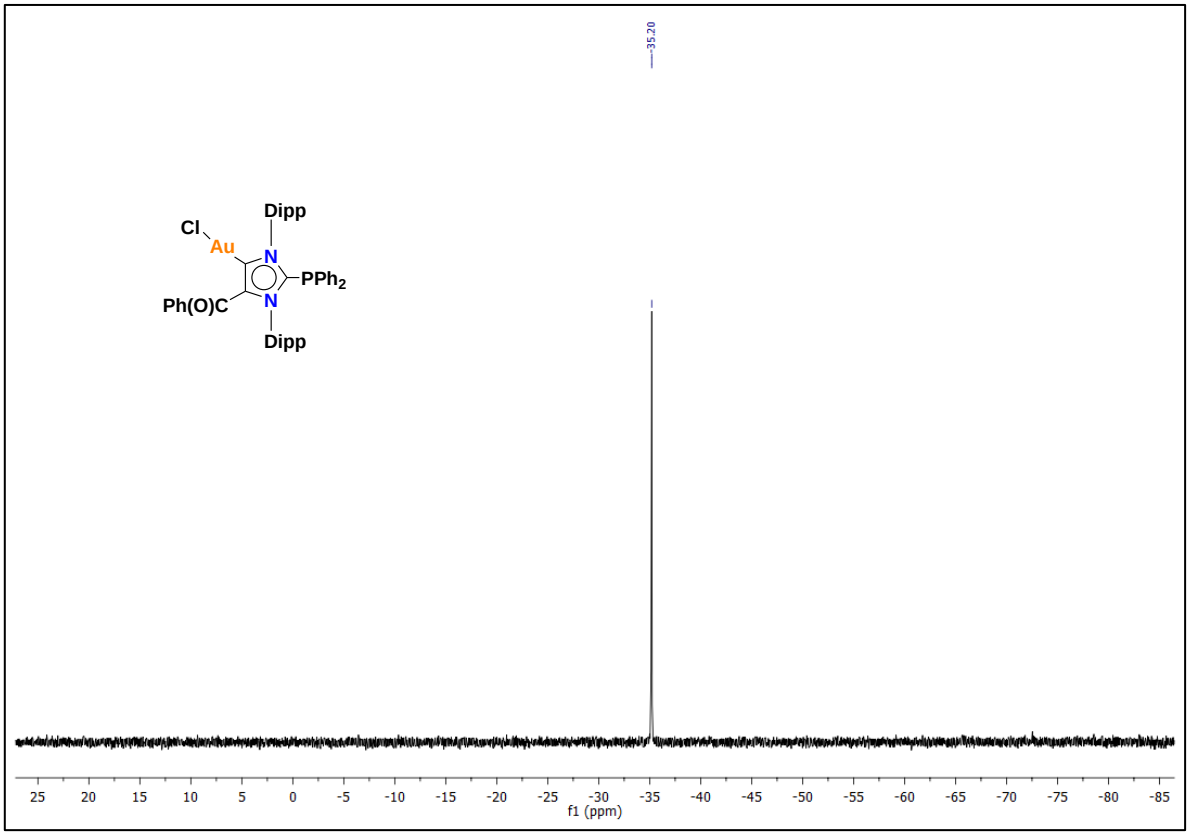


Figure S21. ^{31}P NMR (126 MHz) spectrum of complex **8b** in $CDCl_3$

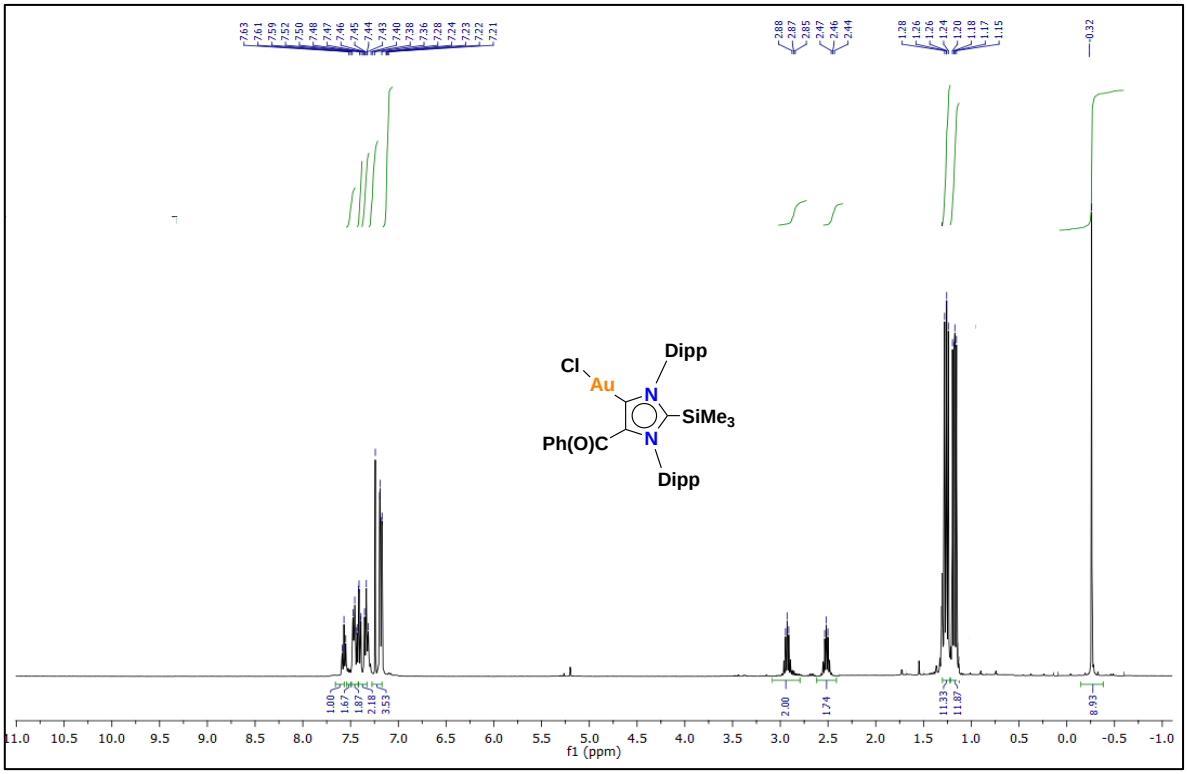


Figure S22. ^{1}H NMR (400 MHz) spectrum of complex **8c** in $CDCl_3$

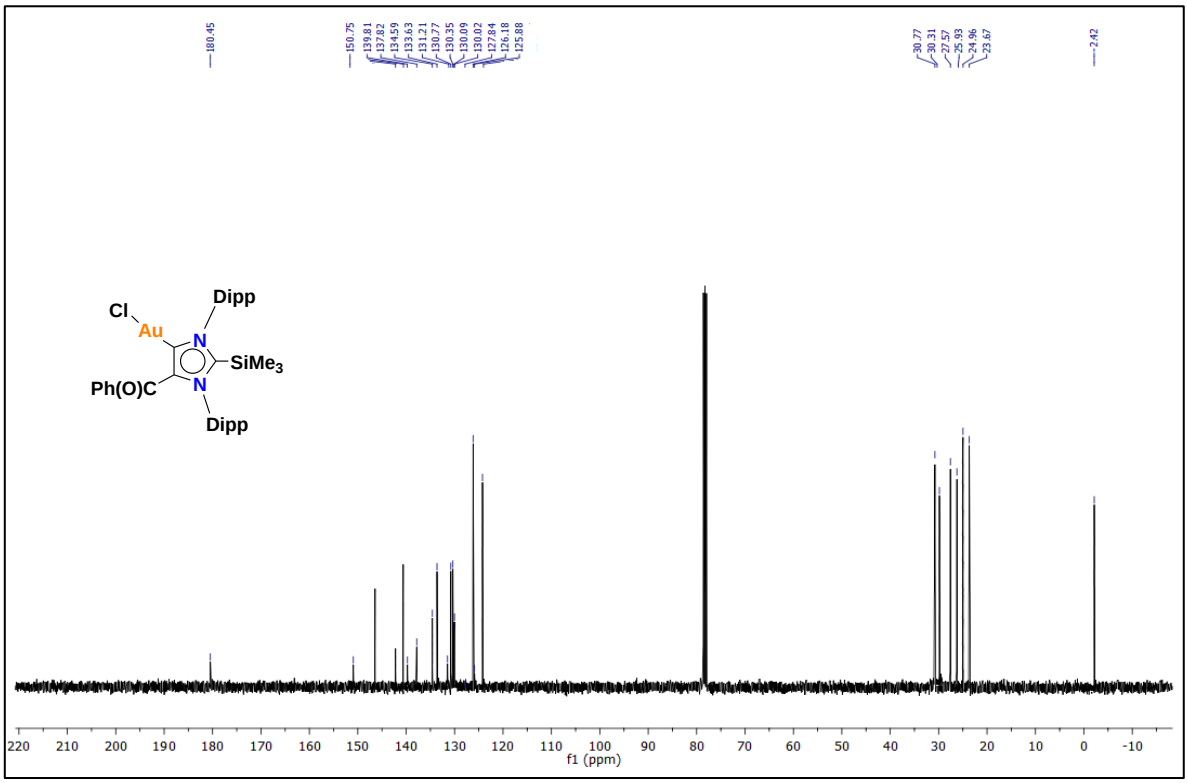


Figure S23. ^{13}C NMR (100 MHz) spectrum of complex **8c** in $CDCl_3$

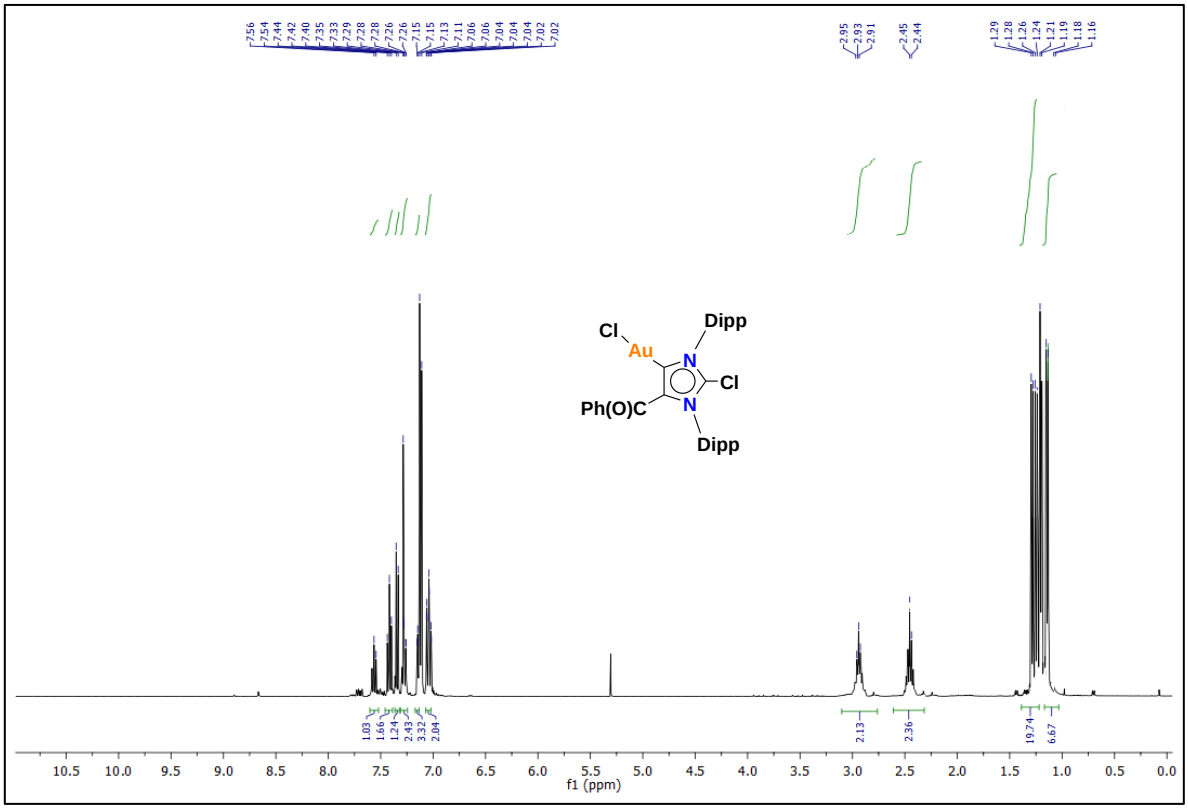


Figure S24. ^{1}H NMR (400 MHz) spectrum of complex **8d** in $CDCl_3$

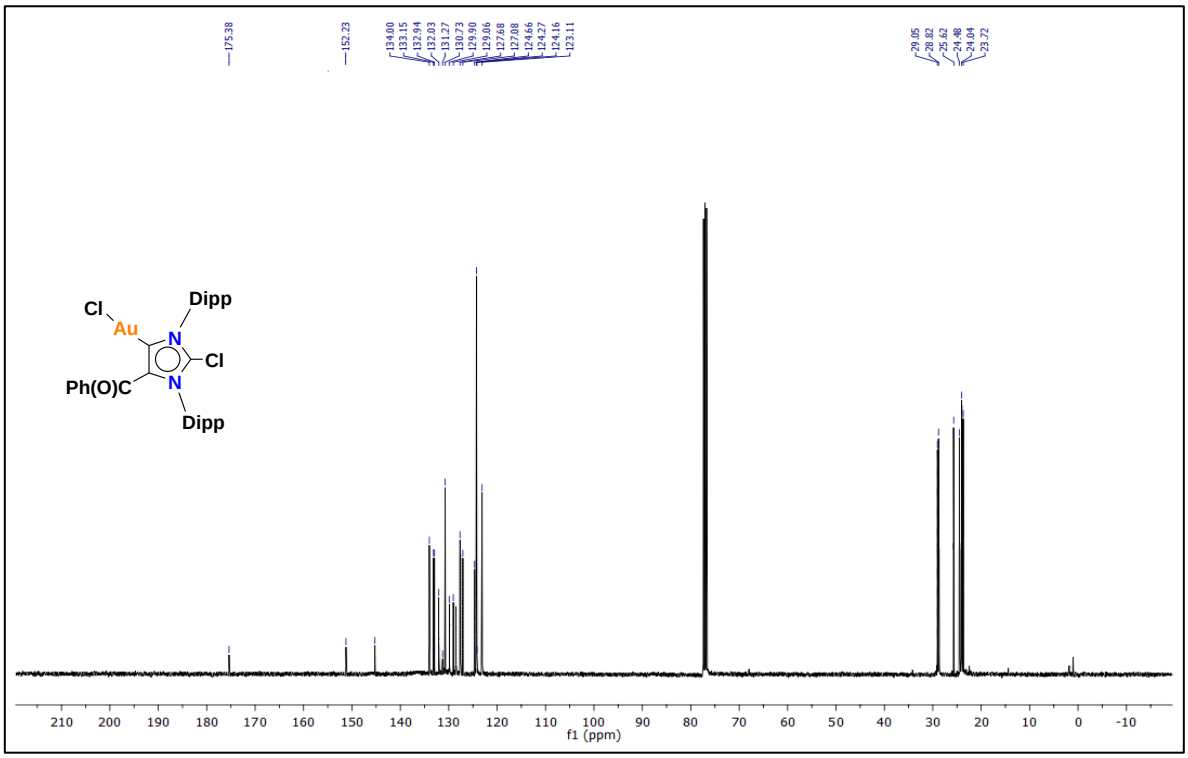


Figure S25. ^{13}C NMR (100 MHz) spectrum of complex **8d** in $CDCl_3$

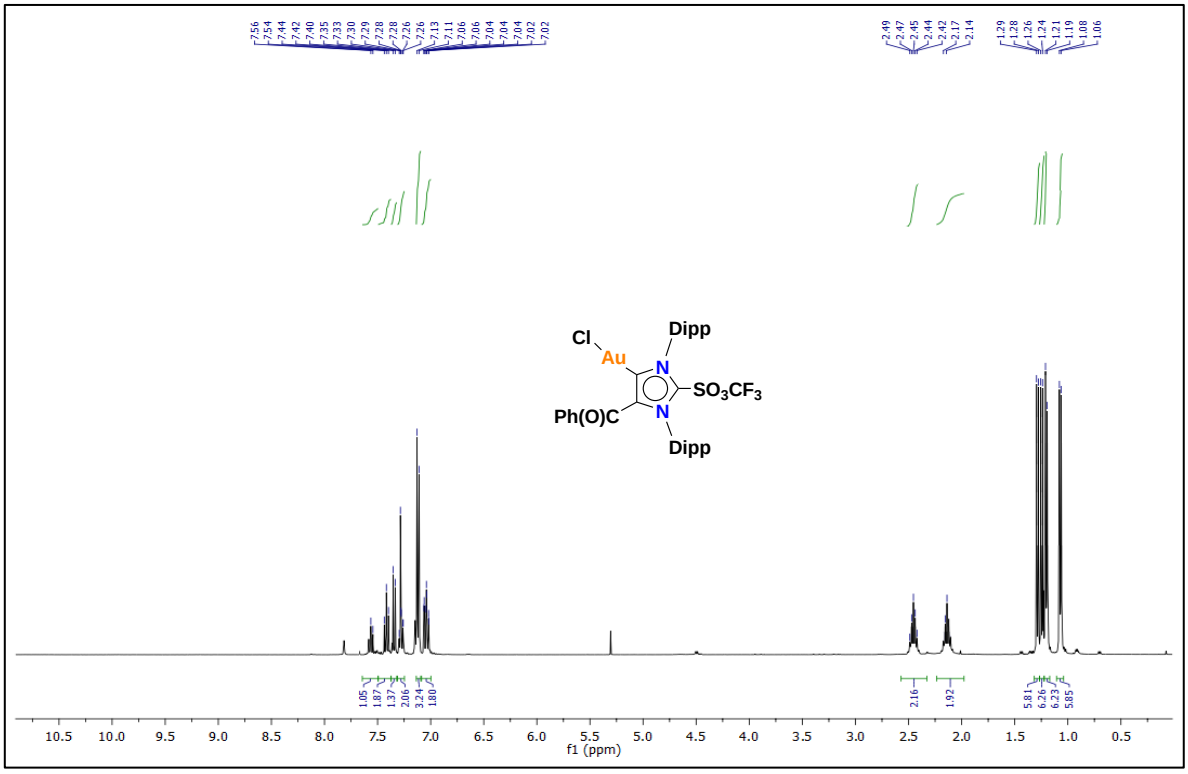


Figure S26. ^{1}H NMR (400 MHz) spectrum of complex **8e** in $CDCl_3$

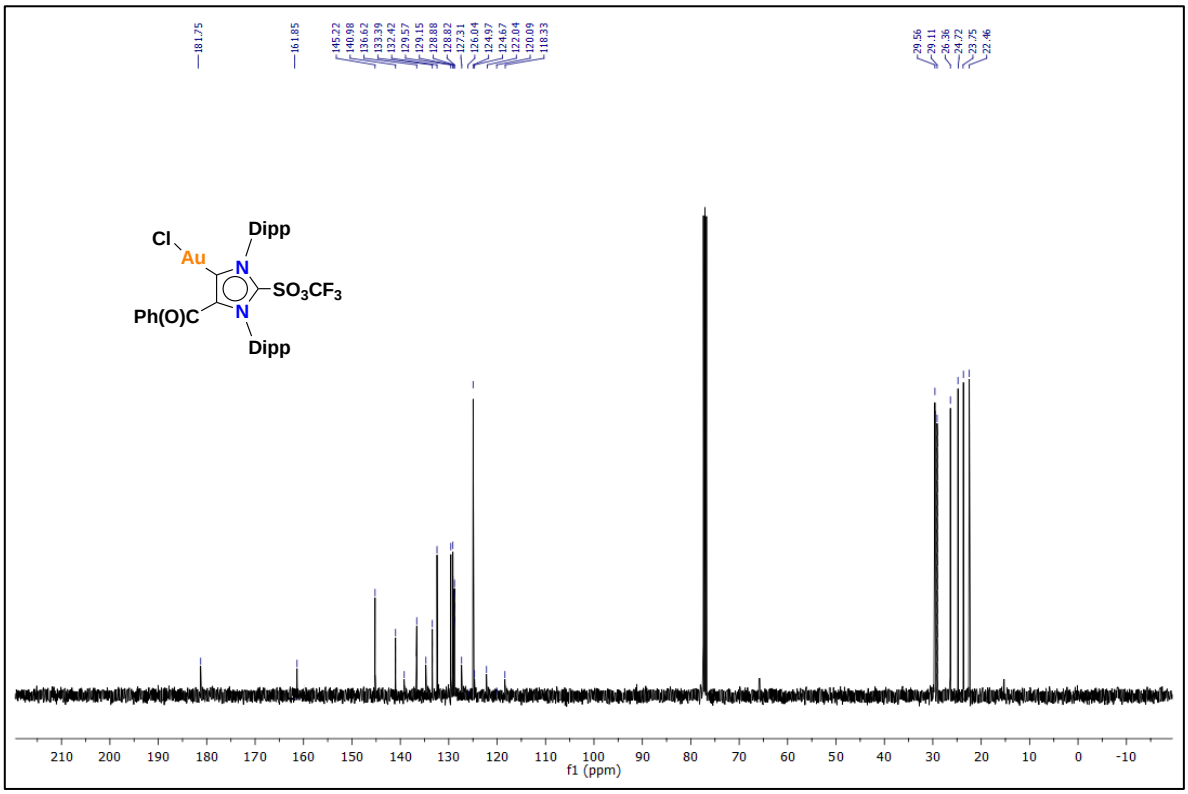


Figure S27. ^{13}C NMR (100 MHz) spectrum of complex **8e** in $CDCl_3$