Organometallic Chemistry in *Aqua Regia*: Metal and Ligand Based Oxidations of (NHC)AuCl Complexes

Volodymyr Levchenko, Cristiano Glessi, Sigurd Øien-Ødegaard and Mats Tilset*

Contents

1. General procedures

All chemicals and solvents were sourced commercially and used as received. (Me$_2$S)AuCl was prepared accordingly to the reported procedure.[1] The imidazolium salts 1,3-dimethyl-4,5-dichloroimidazolium iodide, 1,3-diethyl-4,5-dichloroimidazolium iodide, and 1,3-dimethylethyl-4,5-dichloroimidazolium iodide were prepared following the reported procedure for 1,3-dimethyl-4,5-dichloroimidazolium iodide[2] or by introducing minor modifications. **1g** was purchased from Sigma-Aldrich. Dichloromethane was used from solvent purifier MB SPS-800 from MBraun. NMR spectra were recorded on Bruker Advance DPX300, AVII400, AVIII400 and AVII600 instruments at ambient temperature. ^{1}H and ^{13}C spectra have been referenced relative to the residual solvent systems. Mass spectra were obtained on Micromass QTOF II spectrometer and a Bruker Daltronics maXis II spectrometer.

Reactions were carried out in a tall vial (30 mL) equipped with a plastic cap. *Aqua regia* was prepared by slow addition of 2 mL of concentrated nitric acid (HNO_3, 65%) to 6 mL of hydrochloric acid (HCl, 37%) and used immediately after preparation. The filtration of the suspension was performed through a glass frit (pore size 4) under reduced pressure into a vacuum filtering flask equipped with a NaOH solution in for immediate neutralization of the *aqua regia*.

Aqua regia handling protocol: Wear lab protection (gloves, protective googles, lab coat). Do not handle outside of a fume hood (toxic gaseous species are produced in *aqua regia*). Do not store in a closed vessel. All safety protocols for the handling of strong acid apply. Disposal: neutralize *aqua regia* with a NaOH solution.

2. Procedures for synthesis of (NHC)AuCl complexes

*General procedure for the synthesis of complexes **1a-1f**.*[3,4] 1 equiv. of the pertinent imidazolium salt (**1a**, **1c** chloride; **1b** bromide; **1d**, **1e**, **1f** iodide) was dissolved in CH_2Cl_2 under vigorous stirring. After the disappearance of all the solid, Ag_2O (0.5 equiv.) was added and the reaction mixture was left stirring in the dark for 20 h. To the resulting colorless solution, $(Me_2S)AuCl$ (1 equiv.) was added. The immediate appearance of a white to yellow precipitate in the reaction mixture was observed. The reaction mixture was left while stirring in the dark for 4 h. The suspension was filtered and the resulting colorless to yellow solution was concentrated to dryness, furnishing an off-white yellowish solid. The solid was dissolved in a small quantity of CH_2Cl_2 and purified through flash chromatography (stationary phase silica, eluent CH_2Cl_2). In the case of yellow discoloration, the product was further recrystallized from CH_2Cl_2:pentane, and colorless crystals were obtained.

(IMe$_2$)AuCl (1a): Yield: 89-96%. ^{1}H NMR (600 MHz, CD_2Cl_2): δ 6.95 (s, 2H, =C*H*-), 3.81 (s, 6H, -C*H*$_3$). ^{13}C NMR (150 MHz, CD_2Cl_2): δ 172.1 (NHC-*C*), 122.3 (=*C*H-), 38.6 (-*C*H$_3$). MS (ESI$^+$,MeOH): *m/z* 350.993 ([M(^{35}Cl)+Na]$^+$, 100%), 352.990 ([M(^{37}Cl)+Na]$^+$, 32.3%), 389.104 ([(NHC)$_2$Au]$^+$, 34.8%). HRMS (MeOH): *m/z* meas. 350.9933, calcd. 350.9934 for $[C_5H_8Au^{35}ClN_2Na]^+$ (Δ= 0.2 ppm). Characterization data are in accordance with the reported ones.[5]

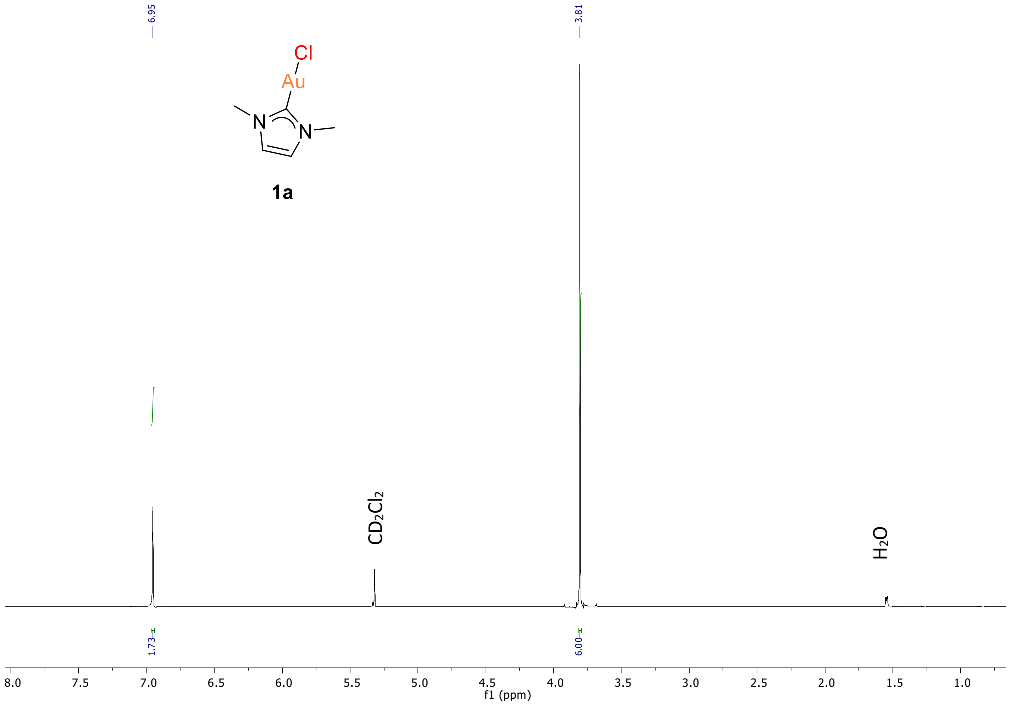


Figure S1. ^{1}H NMR spectrum of **1a** (600 MHz, CD_2Cl_2).

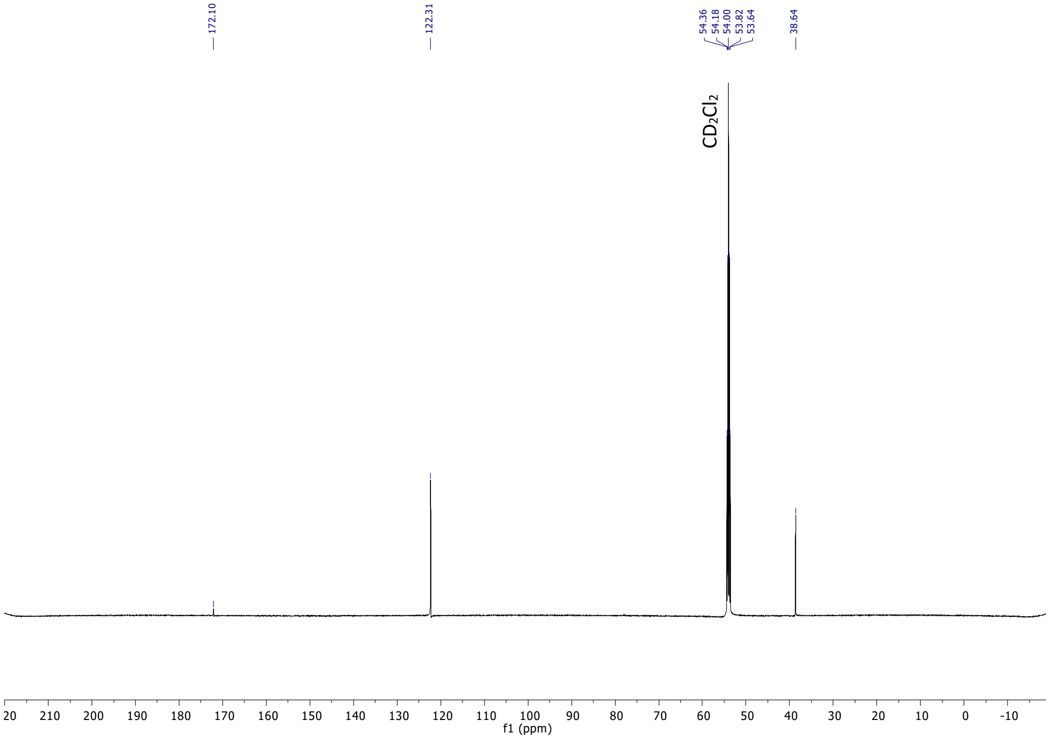


Figure S2. ^{13}C NMR spectrum of **1a** (150 MHz, CD_2Cl_2).

(IEt$_2$)AuCl (1b): Yield: 58-68%. ^{1}H NMR (600 MHz, CD_2Cl_2): δ 6.98 (s, 2H, =C*H*-), 4.21 (q, *J* = 7.3 Hz, 4H, -C*H*$_2$-), 1.46 (t, *J* = 7.3 Hz, 6H, -C*H*$_3$). ^{13}C NMR (150 MHz, CD_2Cl_2): δ 170.1 (NHC-*C*), 120.5 (=*C*H-), 47.1 (-*C*H$_2$-), 16.8 (-*C*H$_3$). MS (ESI$^+$,MeOH): *m/z* 379.125 ([M(^{35}Cl)+Na]$^+$, 100%), 381.022 ([M(^{37}Cl)+Na]$^+$, 30.9%). HRMS (MeOH): *m/z* meas. 379.0247, calcd. 379.0247 for [$C_7H_{12}Au^{35}ClN_2Na$]$^+$ (Δ= 0.0 ppm). Characterization data are in accordance with the reported ones.[4]

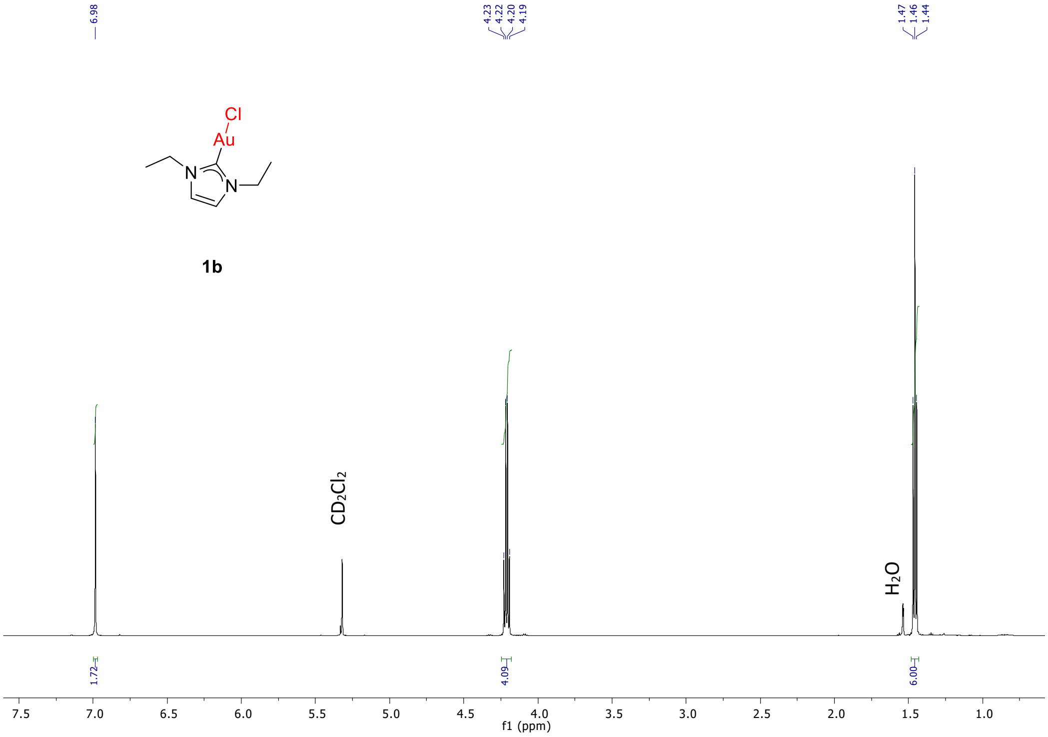


Figure S3. ^{1}H NMR spectrum of **1b** (600 MHz, CD_2Cl_2).

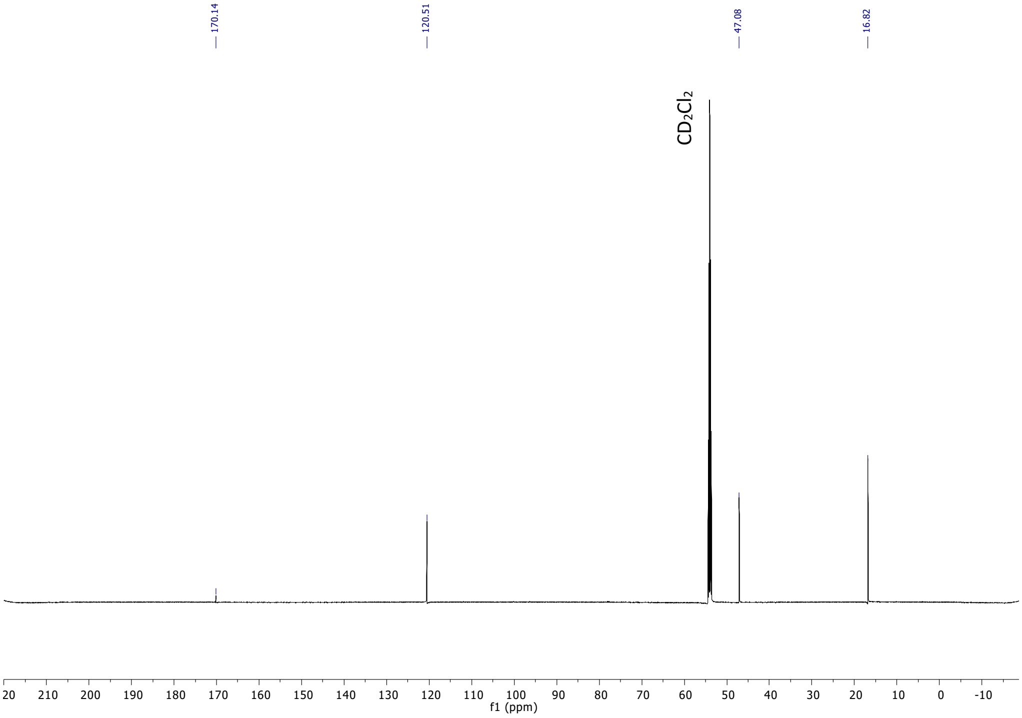


Figure S4. ^{13}C NMR spectrum of **1b** (150 MHz, CD_2Cl_2).

(IiPr$_2$)AuCl (1c): Yield: 83-91%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 6.98 (s, 2H, =C*H*-), 5.04 (hept., *J* = 6.8 Hz, 2H C*H*Me$_2$), 1.46 (d, *J* = 6.8 Hz, 12H, -C*H*$_3$). ^{13}C NMR (101 MHz, CDCl$_3$): δ 168.7 (NHC-*C*), 116.9 (=*C*H-), 53.8 (-*C*HMe$_2$), 23.5 (-*C*H$_3$). MS (ESI$^+$,MeOH): *m/z* 407.056 ([M(^{35}Cl)+Na]$^+$, 100%), 409.053 ([M(^{37}Cl)+Na]$^+$, 32.5%). HRMS (MeOH): *m/z* meas. 407.0559, calcd. 407.0560 for [$C_9H_{16}Au^{35}ClN_2Na$]$^+$ (Δ= 0.1 ppm). Characterization data are in accordance with the reported ones.[6]

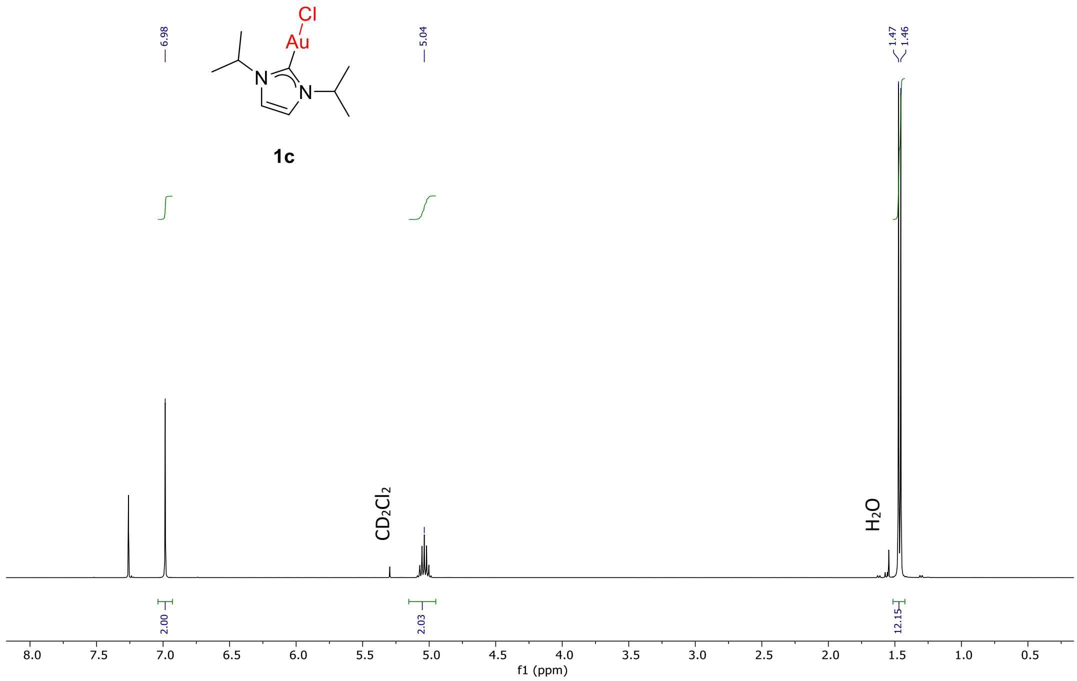


Figure S5. ^{1}H NMR spectrum of **1c** (400 MHz, CDCl$_3$).

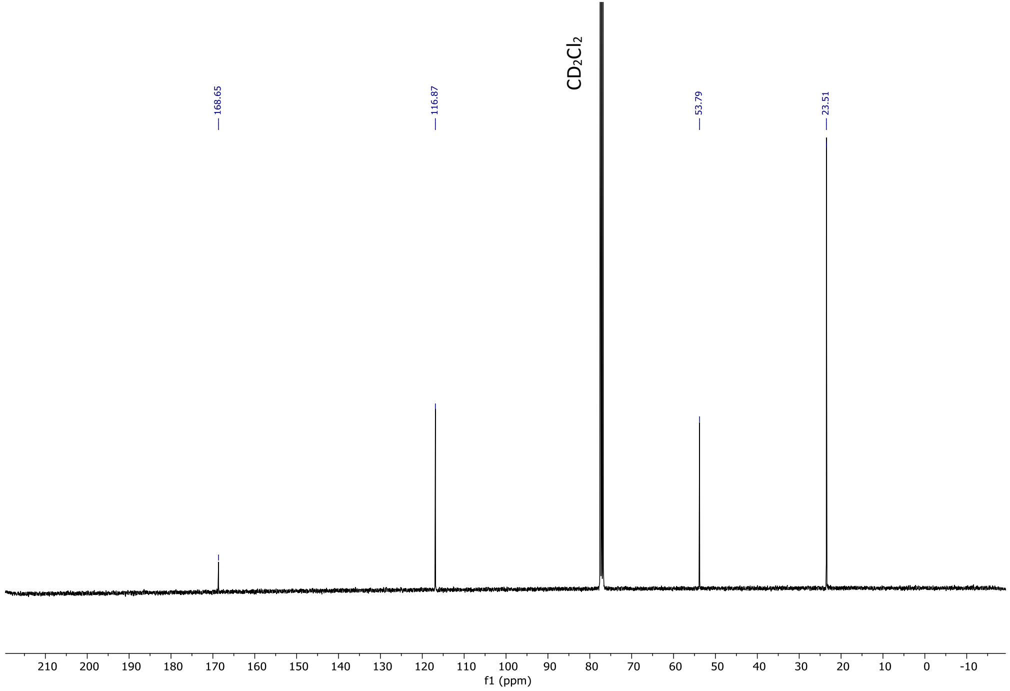


Figure S6. ^{13}C NMR spectrum of **1c** (101 MHz, CDCl$_3$).

(IMe$_2$Cl$_2$)AuCl (1d): Yield: 48%. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 3.82 (s, 6H, -C*H*$_3$). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 172.4 (NHC-*C*), 117.9 (=*C*-Cl), 37.6 (-*C*H$_3$). MS (ESI$^+$,MeOH): *m/z* 418.915 ([M(^{35}Cl$_3$)+Na]$^+$, 100%), 420.913 ([M(^{35}Cl$_2$^{37}Cl$_1$)+Na]$^+$, 98.4%), 422.910 ([M(^{35}Cl$_1$^{37}Cl$_2$)+Na]$^+$, 31.5%). HRMS (MeOH): *m/z* meas. 418.9154, calcd. 418.9154 for [$C_5H_6Au^{35}Cl_3N_2Na$]$^+$ (Δ= 0.1 ppm). Characterization data are in accordance with the reported ones.[7]

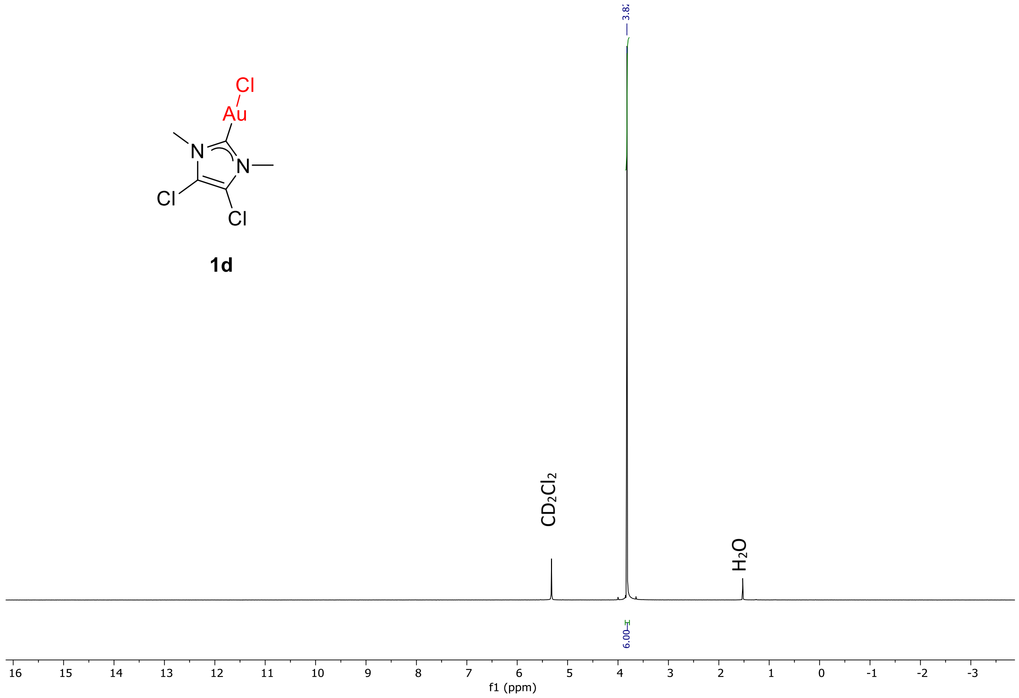


Figure S7. ^{1}H NMR spectrum of **1d** (400 MHz, CD_2Cl_2).

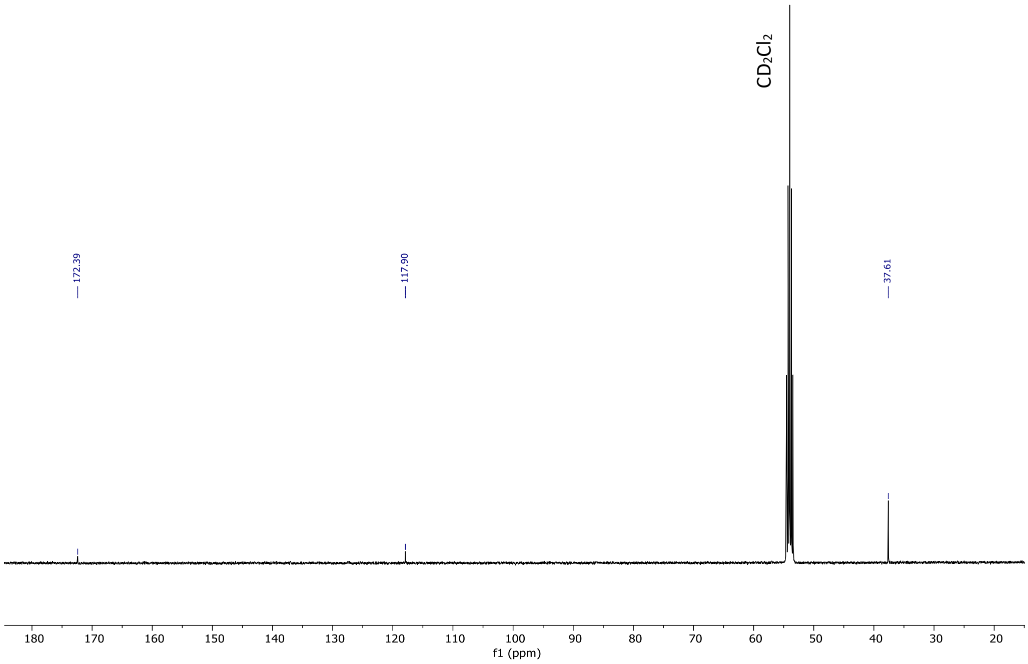


Figure S8. ^{13}C NMR spectrum of **1d** (101 MHz, CD_2Cl_2).

(IEt_2Cl_2)AuCl (1e): Yield: 84-89%. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 4.29 (q, *J* = 7.3 Hz, 4H, -C*H*$_2$-), 1.44 (t, *J* = 7.3 Hz, 6H, -C*H*$_3$). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 170.8 (NHC-*C*), 117.0 (=*C*-Cl), 46.5 (-*C*H$_2$-), 16.2 (-*C*H$_3$-). MS (ESI$^+$,MeOH): *m/z* 446.947 ([M($^{35}Cl_3$)+Na]$^+$, 100%), 448.944 (M($^{35}Cl_2{}^{37}Cl_1$)+Na]$^+$, 98.7%), 450.941 (M($^{35}Cl_1{}^{37}Cl_2$)+Na]$^+$, 32.2%), 870.904 ([2M($^{35}Cl_6$)+Na]$^+$, 19.1%), 872.901 ([2M($^{35}Cl_5{}^{37}Cl_1$)+Na]$^+$, 37.2%), 874.899 ([2M($^{35}Cl_4{}^{37}Cl_2$))+Na$^+$]$^+$, 29.4%). HRMS (MeOH): *m/z* meas. 446.9468, calcd. 446.9467 for $[C_7H_{10}Au^{35}Cl_3N_2Na]^+$ (Δ= 0.0 ppm).

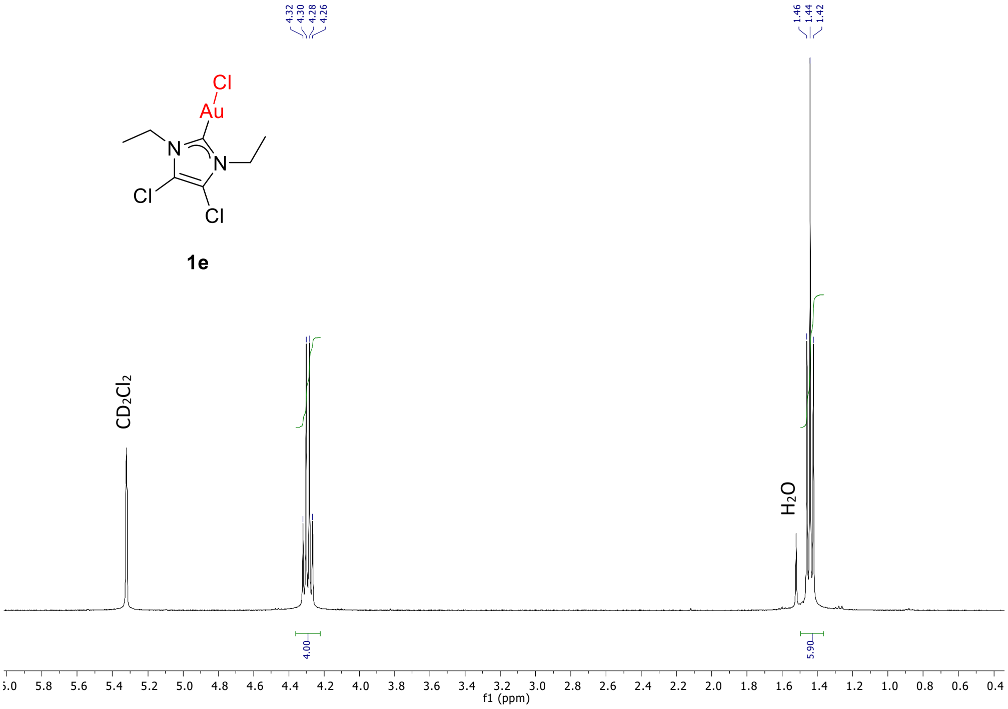


Figure S9. ^{1}H NMR spectrum of **1e** (400 MHz, CD_2Cl_2).

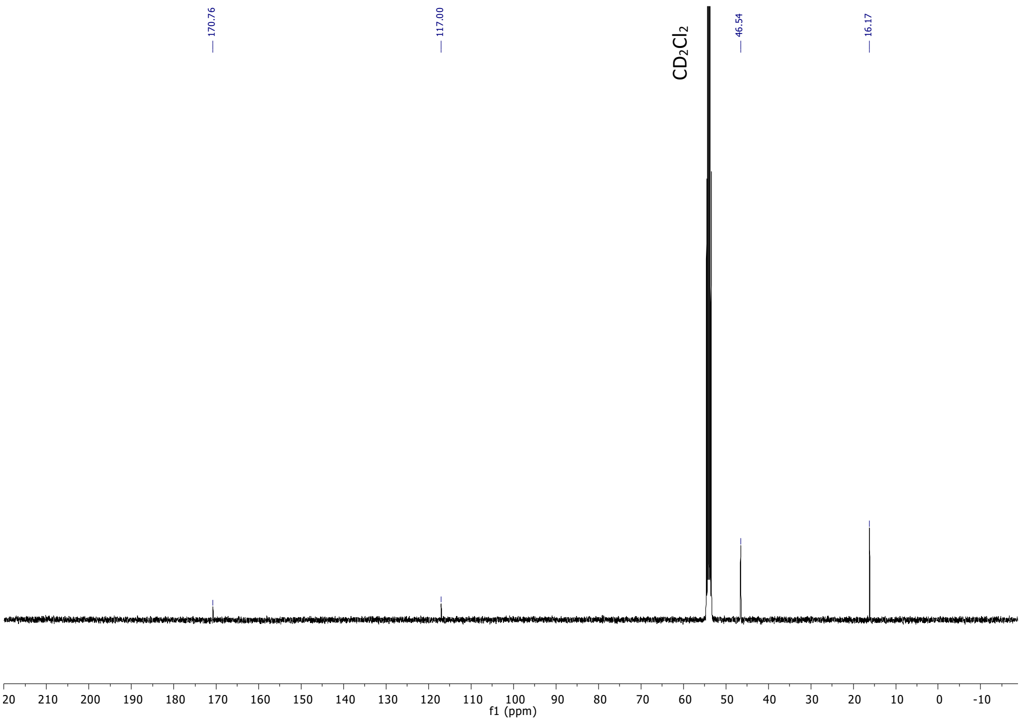


Figure S10. ^{13}C NMR spectrum of **1e** (101 MHz, CD_2Cl_2).

(IiPr$_2$Cl$_2$)AuCl (1f): Yield: 84-95%. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ 5.20 (hept., *J* = 7.0 Hz, 2H, C*H*Me$_2$), 1.67 (d, *J* = 7.0 Hz, 12H, -C*H*$_3$). ^{13}C NMR (101 MHz, CD$_2$Cl$_2$): δ 170.0 (NHC-*C*), 116.99 (=*C*-Cl), 56.9 (-*C*HMe$_2$), 22.2 (-*C*H$_3$). MS (ESI$^+$,MeOH): *m/z* 474.978 ([M(^{35}Cl$_3$)+Na]$^+$, 100%), 476.975 ([M(^{35}Cl$_2$^{37}Cl$_1$)+Na]$^+$, 96.4%), 478.972 ([M(^{35}Cl$_1$^{37}Cl$_2$)+Na]$^+$, 30.0%). HRMS (MeOH): *m/z* meas. 474.9780, calcd. 474.9780 for [C$_9$H$_{14}$Au^{35}Cl$_3$N$_2$Na]$^+$ (Δ= 0.1 ppm).

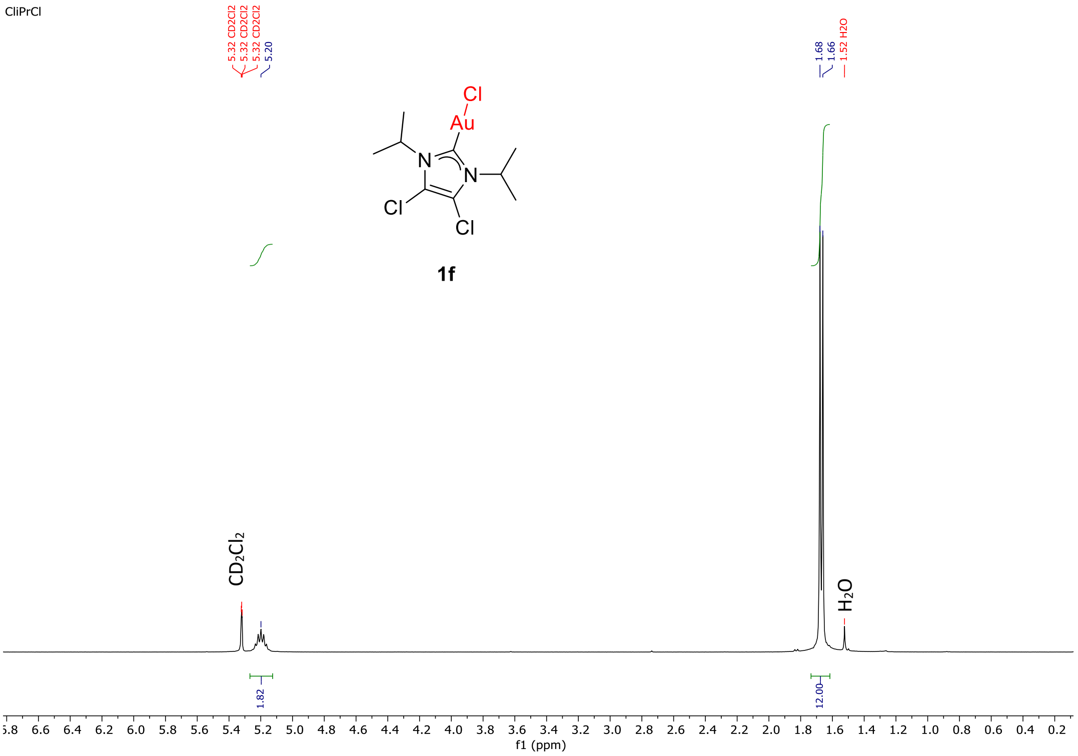


Figure S11. ^{1}H NMR spectrum of **1f** (400 MHz, CD$_2$Cl$_2$).

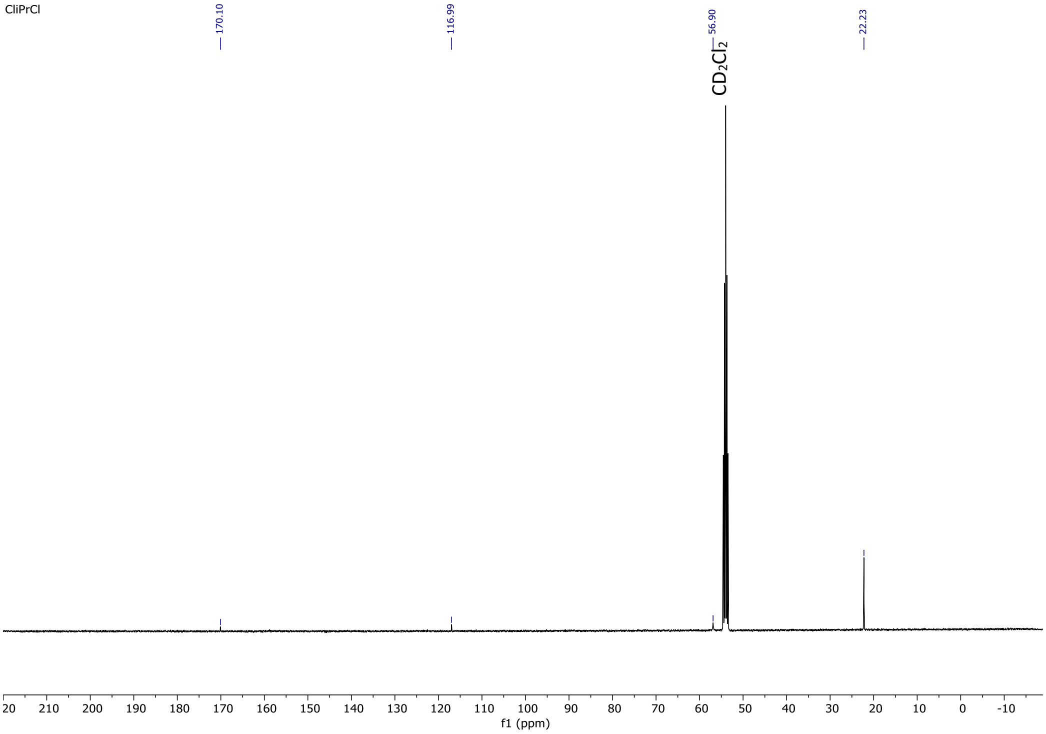


Figure S12. ^{13}C NMR spectrum of **1f** (101 MHz, CD$_2$Cl$_2$).

(SIPr)AuCl (1h): 1h was prepared following the reported procedure.[7] A white powder was obtained (320 mg, 73% yield). NMR spectra are in agreement with reported data. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.47 (t, *J* = 7.8 Hz, 2H, *p*-C*H*), 7.29 (d, *J* = 7.8 Hz, 4H, *m*-C*H*), 4.06 (s, 4H, -C*H*$_2$-), 3.07 (hept., *J* = 6.9 Hz, 4H, -C*H*Me$_2$), 1.40 (d, *J* = 6.8 Hz, 12H, -C*H*$_3$), 1.34 (d, *J* = 6.9 Hz, 12H, C*H*$_3$). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 147.3, 134.7, 130.5, 125.2, 29.5, 25.4, 24.4. MS (ESI$^+$,MeOH): *m/z* 645.228 ([M(^{35}Cl)+Na]$^+$, 100%), 647.226 ([M(^{37}Cl)+Na]$^+$, 33.0%). HRMS (MeOH): *m/z* meas. 645.2281, calcd. 645.2281 for $[C_{27}H_{38}Au^{35}ClN_2Na]^+$ (Δ= 0.1 ppm).

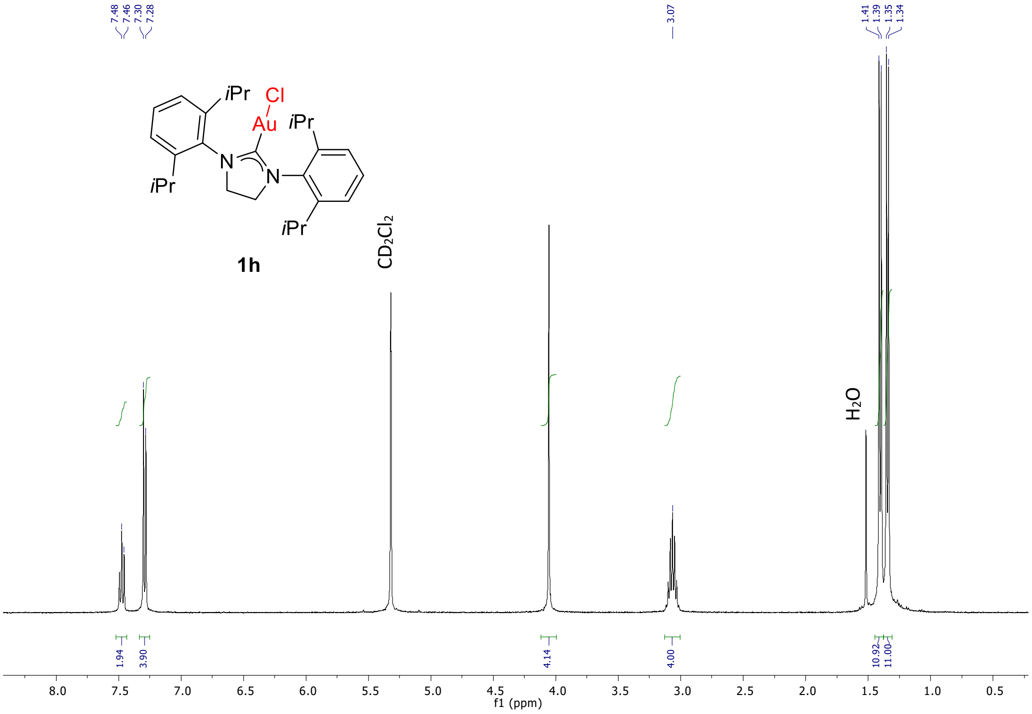


Figure S13. ^{1}H NMR spectrum of **1h** (400 MHz, CD_2Cl_2)

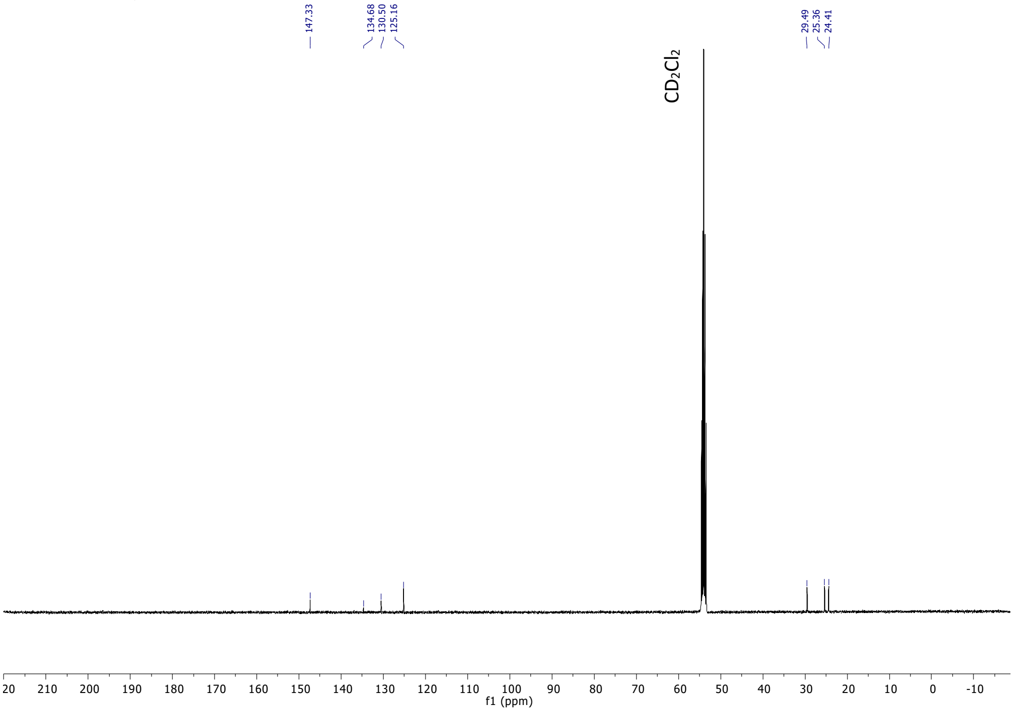


Figure S14. ^{13}C NMR spectrum of **1h** (101 MHz, CD_2Cl_2).

(BzIMe$_2$)AuCl (1i): 1i was prepared following a modification of the reported procedure.[8] Dimethylbenzimidazolium iodide (1 mmol) was dissolved in a 1:1 mixture of ethanol and CH_2Cl_2 (90 mL). Solid Ag_2O (0.5 equiv.) was added to the solution under stirring. The resulting suspension was stirred in the dark under inert atmosphere at room temperature for 5 h, until the appearance of a white suspension. Solid (Me_2S)AuCl (1 equiv.) was added to the suspension which turned grayish purple. The resulting suspension was stirred for 15 h in the dark under inert atmosphere. The suspension was filtered through a celite pad under reduced pressure. After the removal of CH_2Cl_2 under reduced pressure, a white solid precipitated from the yellow solution. The solvent was removed and the residual white solid was washed with ethanol to give the product (218 mg, yield: 58%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.49 (m, 4H, =C*H*^{Ar}), 4.04 (s, 6H, -C*H*$_3$). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 179.6 (NHC-*C*), 134.3 (*C*$_{quat}$), 125.0 (*C*H^{Ar}), 111.8 (C*H*^{Ar}), 35.7 (-*C*H$_3$). MS (ESI$^+$,MeOH): *m/z* 401.009 ([M(^{35}Cl)+Na]$^+$, 100%), 403.006 ([M(^{37}Cl)+Na]$^+$, 32.4%). HRMS (MeOH): *m/z* meas. 401.0090, calcd. 401.0090 for [$C_9H_{10}Au^{35}ClN_2Na$]$^+$ (Δ= 0.0 ppm).

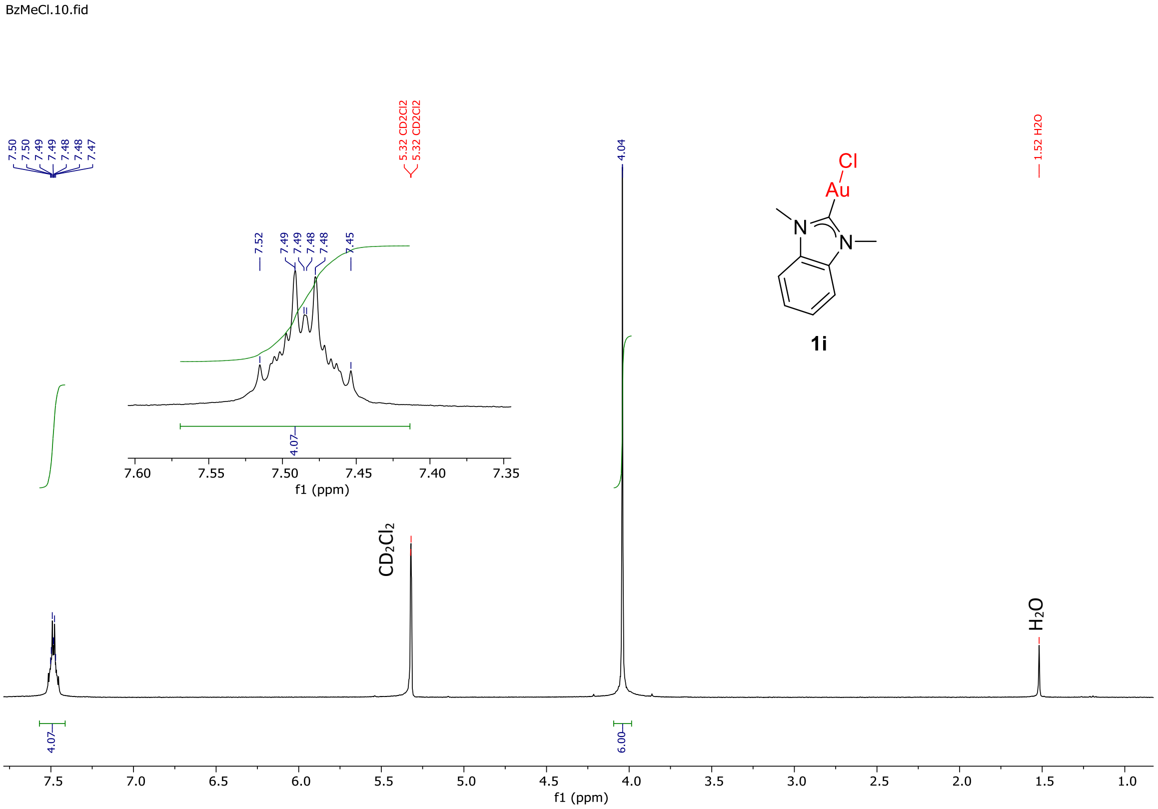


Figure S15. ^{1}H NMR spectrum of **1i** (400 MHz, CD_2Cl_2).

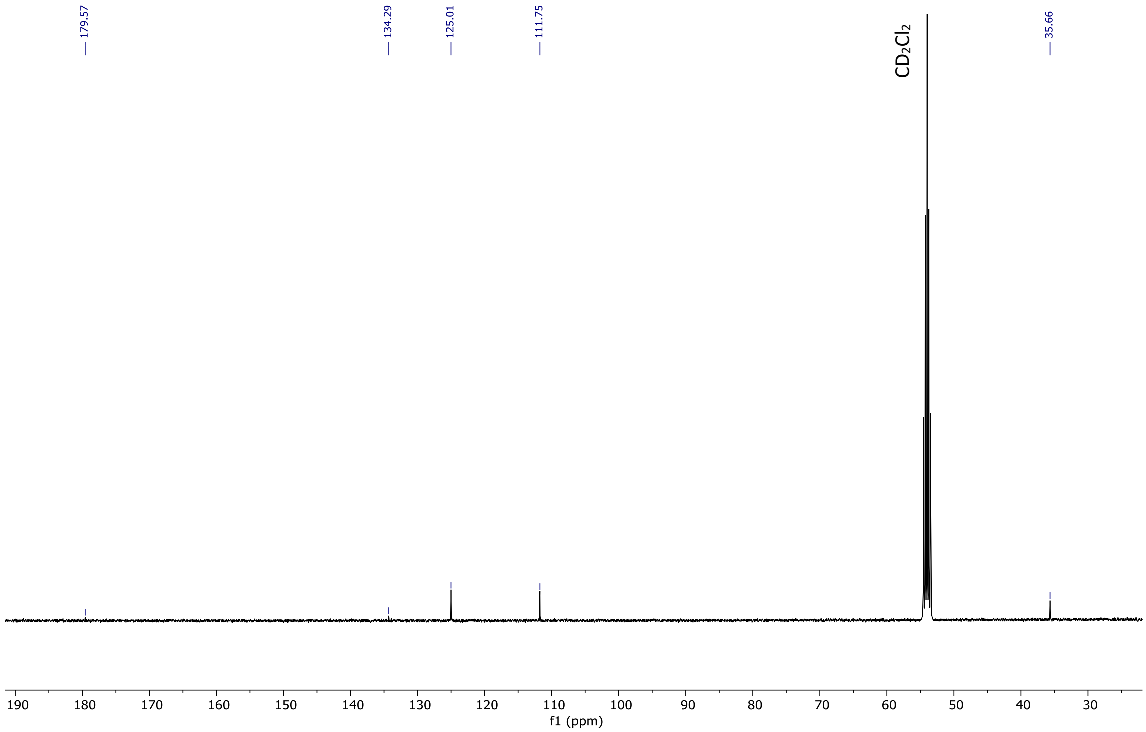


Figure S16. ^{13}C NMR spectrum of **1i** (101 MHz, CD_2Cl_2).

3. Procedures for the synthesis of NHC-$AuCl_3$ complexes

$(IMe_2)AuCl_3$ (2a)

*Via reaction of **1a** and $PhICl_2$.*

A solution of $PhICl_2$ (57 mg, 0.21 mmol) in CH_2Cl_2 (8 mL) was added dropwise to a solution of **1a** (57 mg, 0.17 mmol) in CH_2Cl_2 (5 mL). The reaction mixture was stirred at room temperature overnight before it was concentrated. The addition of pentane resulted in pale-yellow product, which was filtered, washed with pentane and dried under a flow of air. Yield: 45 mg, 65%.

^1H NMR (300 MHz, $CDCl_3$): δ 7.15 (s, 2H, =C*H*-), 3.99 (s, 6H, -CH_3). HRMS (MeCN): *m*/*z* meas. 420.9304, calcd. 420.9311 for $[C_5H_8AuCl_3N_2Na]^+$ (Δ -1.64 ppm).

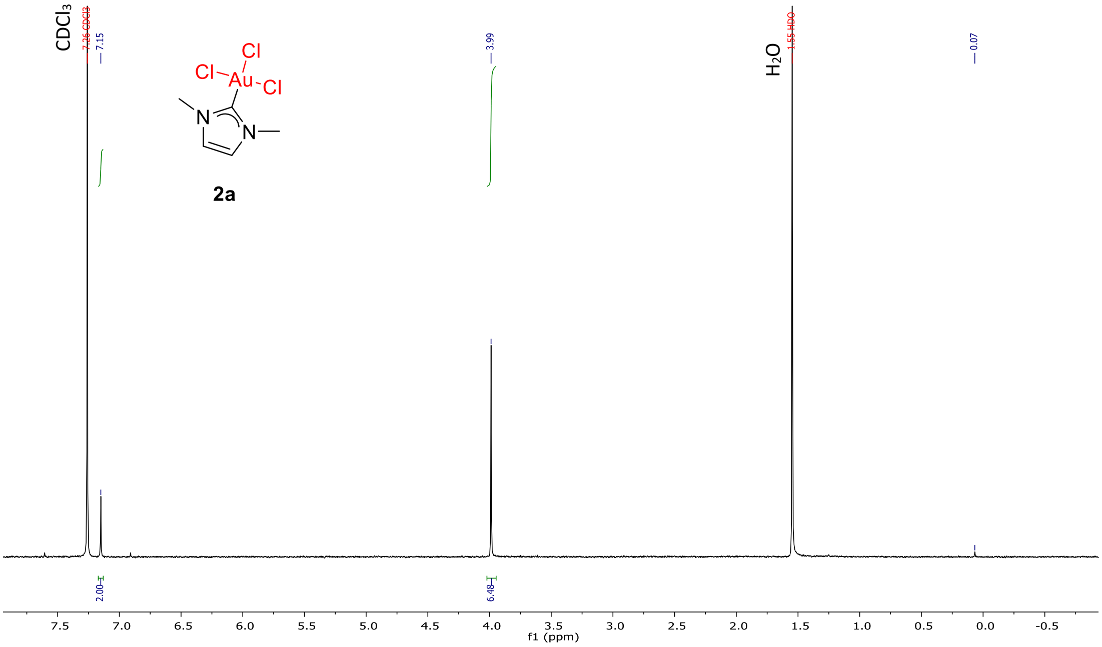


Figure S17. ^1H NMR spectrum of **2a** (300 MHz, $CDCl_3$).

*Attempted synthesis of **2a** in aqua regia.*

Stirring of **1a** (45 mg, 0.14 mmol) in *aqua regia* (8 mL) for 24 h resulted in a mixture of products (28 mg of material isolated). The product ratio was determined by ^{1}H NMR:

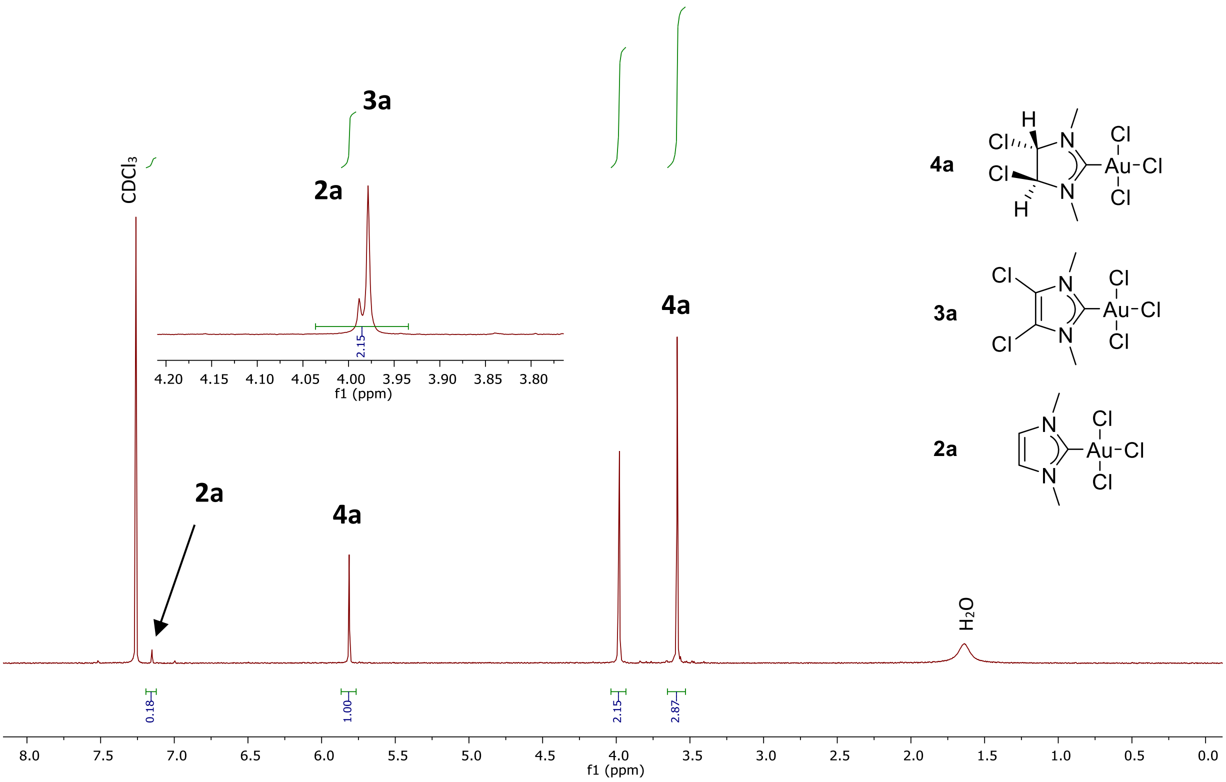
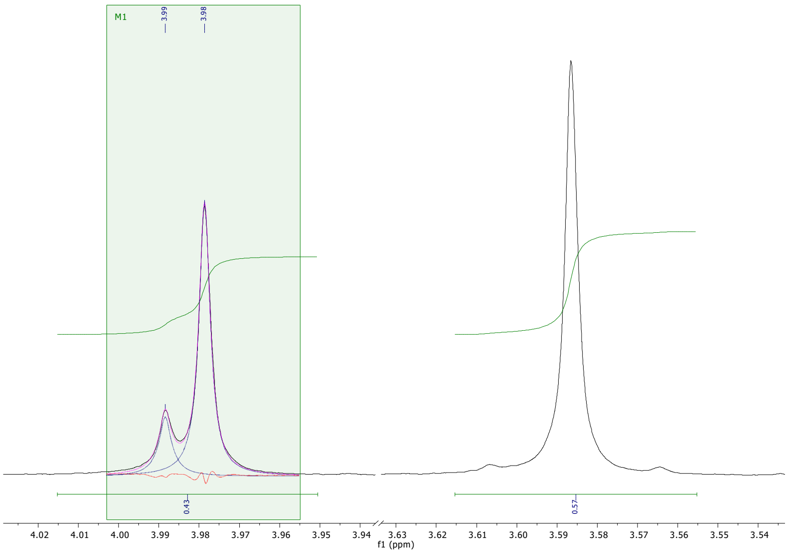


Figure S18. ^{1}H NMR spectrum of the crude mixture from the reaction between **1a** and *aqua regia* (400 MHz, $CDCl_3$).

The quantification of the three species present in the mixture was done using the integration of the NMR signals of the protons of the methyl groups.



2a: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (s, 2H, =C*H*-), 3.99 (s, 6H, -C*H*$_3$).

3a: ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.98 (s, 3H, -C*H*$_3$).

4a: ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.81 (s, 2H, -C*H*(Cl)-), 3.59 (s, 6H, -C*H*$_3$).

(IEt_2)$AuCl_3$ (2b)

*Via reaction of **2b** with $PhICl_2$.*

A solution of $PhICl_2$ (44.4 mg, 0.16 mmol) in CH_2Cl_2 (8 mL) was added dropwise to a solution of **1b** (48 mg, 0.13 mmol) in CH_2Cl_2 (5 mL). The reaction mixture was stirred at room temperature overnight before it was concentrated. The addition of pentane resulted in pale-yellow product, which was filtered, washed with pentane and dried under a flow of air (yield 32 mg, 56%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.19 (s, 2H, =CH-), 4.36 (q, J = 7.4 Hz, 4H, -CH_2-), 1.60 (t, J = 7.4 Hz, 6H, -CH_3).

HRMS (CH_3CN): meas. 448.9606, calcd. 448.9624 for $[C_7H_{12}Au^{35}Cl_3N_2Na]^+$ (Δ = -4.03 ppm).

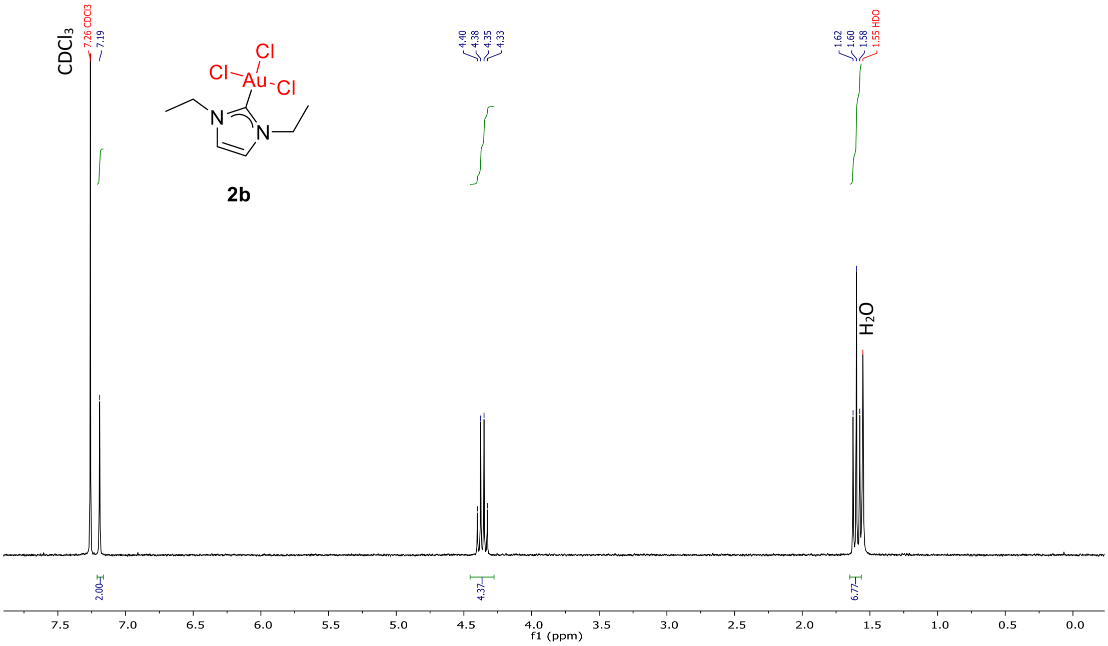


Figure S19. ^{1}H NMR spectrum of **2b** (300 MHz, $CDCl_3$).

*Attempted synthesis of **2b** in aqua regia.*

Stirring of **1b** (68 mg, 0.19 mmol) in *aqua regia* (8 mL) for 24 h resulted in mixture of products (30 mg of material isolated). The product ratio was determined by ^{1}H NMR:

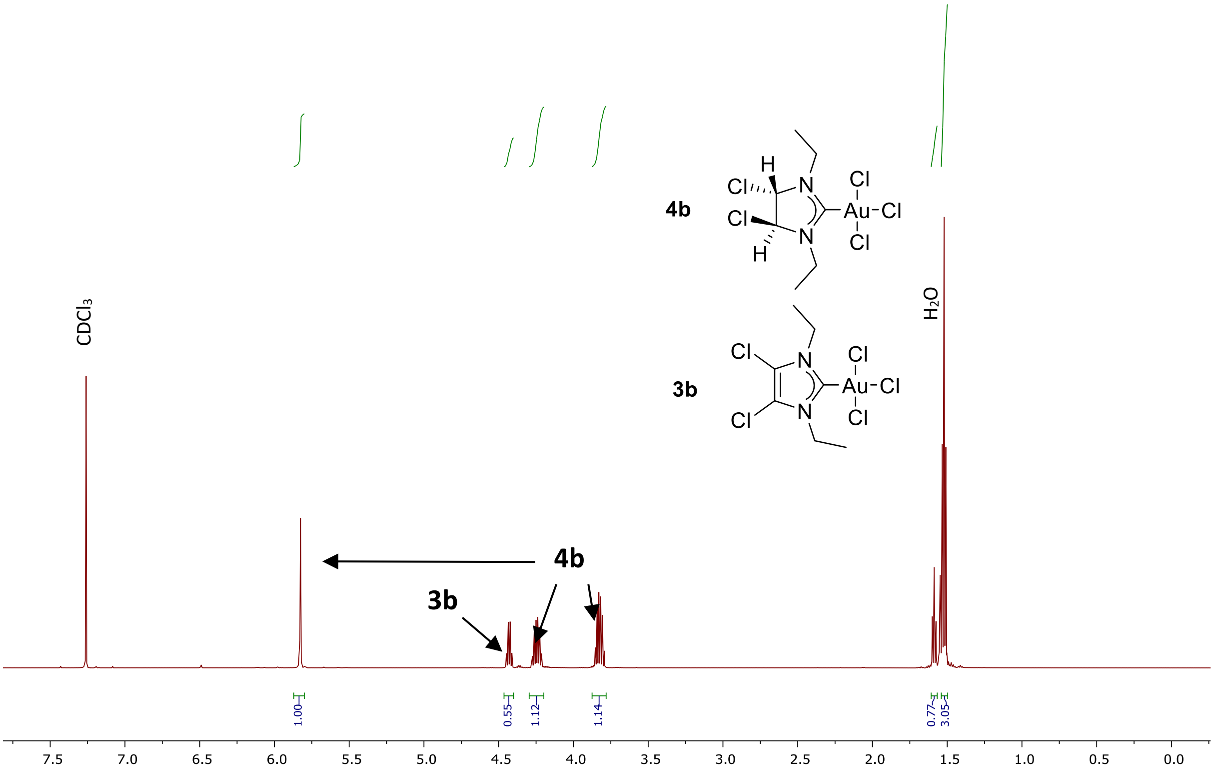
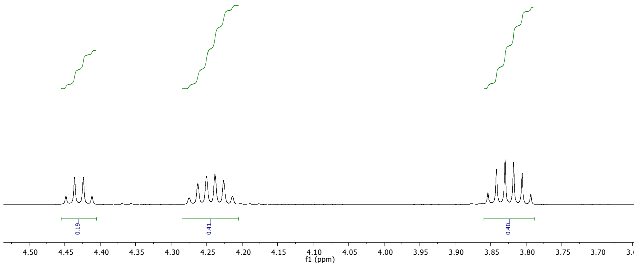


Figure S20. ^{1}H NMR spectrum of the crude mixture from the reaction of **1b** in *aqua regia* (400 MHz, $CDCl_3$).

The quantification of the three species present in the mixture was performed using the integration of the NMR signals of the CH_2 protons of the ethyl groups.



3b: ^{1}H NMR (600 MHz, $CDCl_3$): δ 4.43 (q, *J* = 7.4 Hz, 4H, -CH_2-), 1.59 (t, *J* = 7.3 Hz, 6H, -CH_3).

4b: ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.83 (s, 2H, -C*H*(Cl)-), 4.24 (m, 2H, -CH_2-), 3.82 (m, 2H, -CH_2-), 1.52 (t, *J* = 7.3 Hz, 6H, -CH_3).

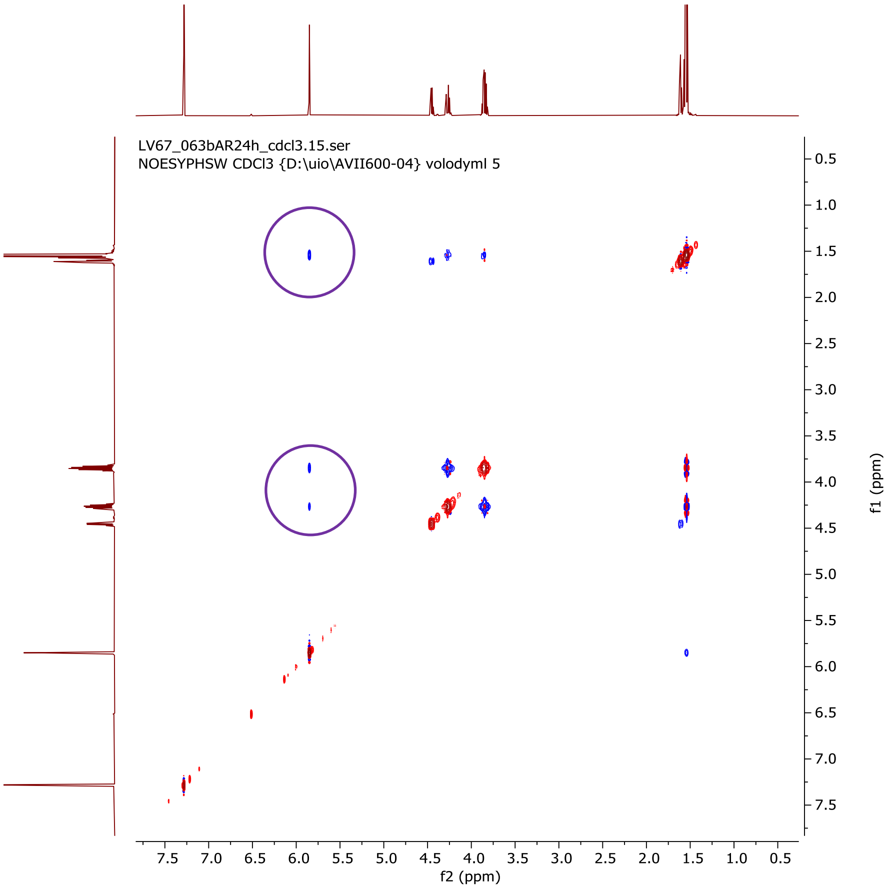
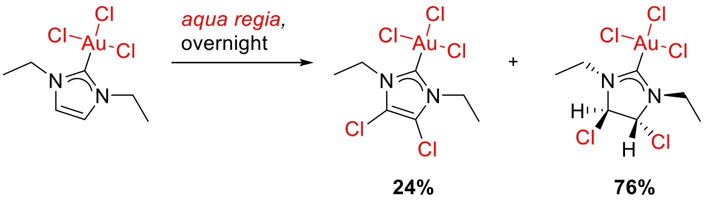


Figure S21. ^{1}H NOESY spectrum of the crude mixture from the reaction of **1b** in *aqua regia* (600 MHz, $CDCl_3$). Through-space correlations between the >C(Cl)-*H* singlet and the diastereotopic CH_2 protons in the ethyl group are circled.

Control experiment – oxidation of ***2b*** *with aqua regia.*



Stirring of **2b** in *aqua regia* (8 mL) for 24 h resulted in a mixture of two products. The product ratio was determined by ^{1}H NMR:

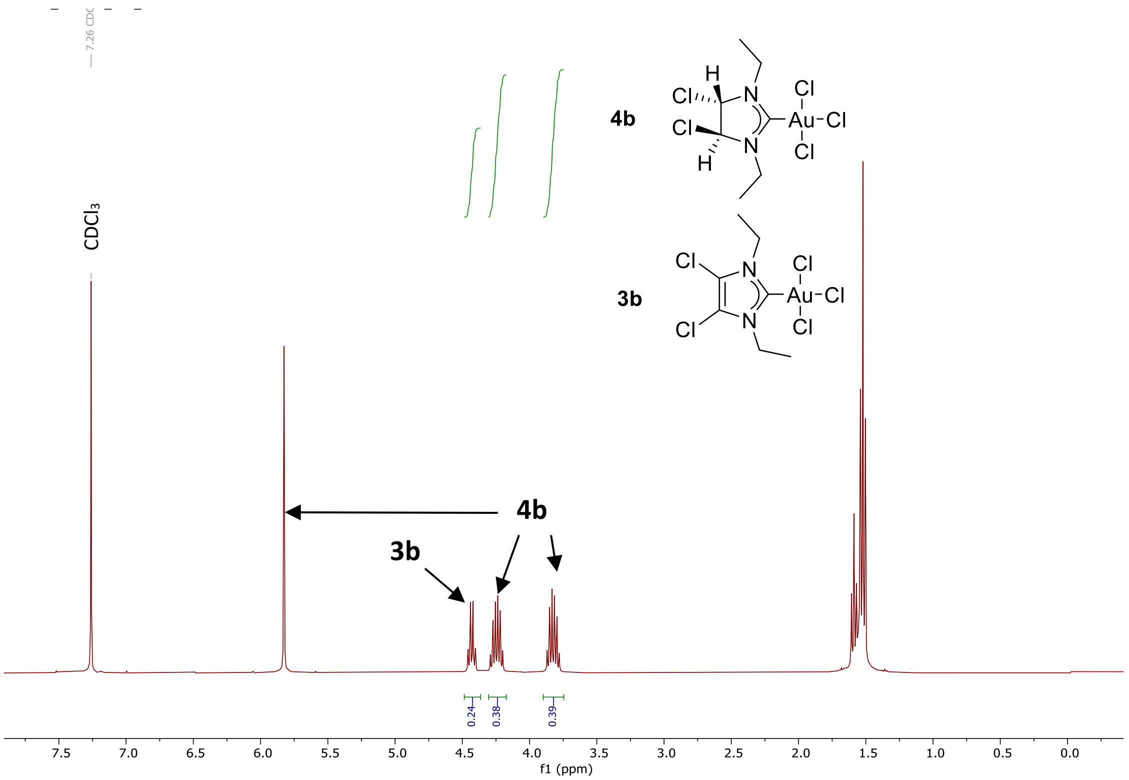


Figure S22. ^{1}H NMR spectrum of the crude mixture from the reaction between **2b** and *aqua regia*.

(IiPr$_2$)AuCl$_3$ (2c)

*Via the reaction of **1c** with PhICl$_2$.*

A solution of PhICl$_2$ (42 mg, 0.15 mmol) in CH$_2$Cl$_2$ (8 mL) was added dropwise to a solution of **1c** (49 mg, 0.13 mmol) in CH$_2$Cl$_2$ (5 mL). The reaction mixture was stirred at room temperature overnight before it was concentrated. The addition of diethyl ether resulted in the pale-yellow product, which was filtered, washed with diethyl ether and dried under a flow of air (yield 30 mg, 52%).

^{1}H NMR (300 MHz, CDCl$_3$): δ 7.23 (s, 2H, =C*H*-), 5.08 (hept., *J* = 6.7 Hz, 2H, -C*H*Me$_2$), 1.57 (d, *J* = 6.8 Hz, 12H, -C*H*$_3$). HRMS (CH$_3$CN): *m/z* meas. 476.9923, calcd. 476.9937 for [C$_9$H$_{16}$Au^{35}Cl$_3$N$_2$Na]$^+$ (Δ = -2.89 ppm).

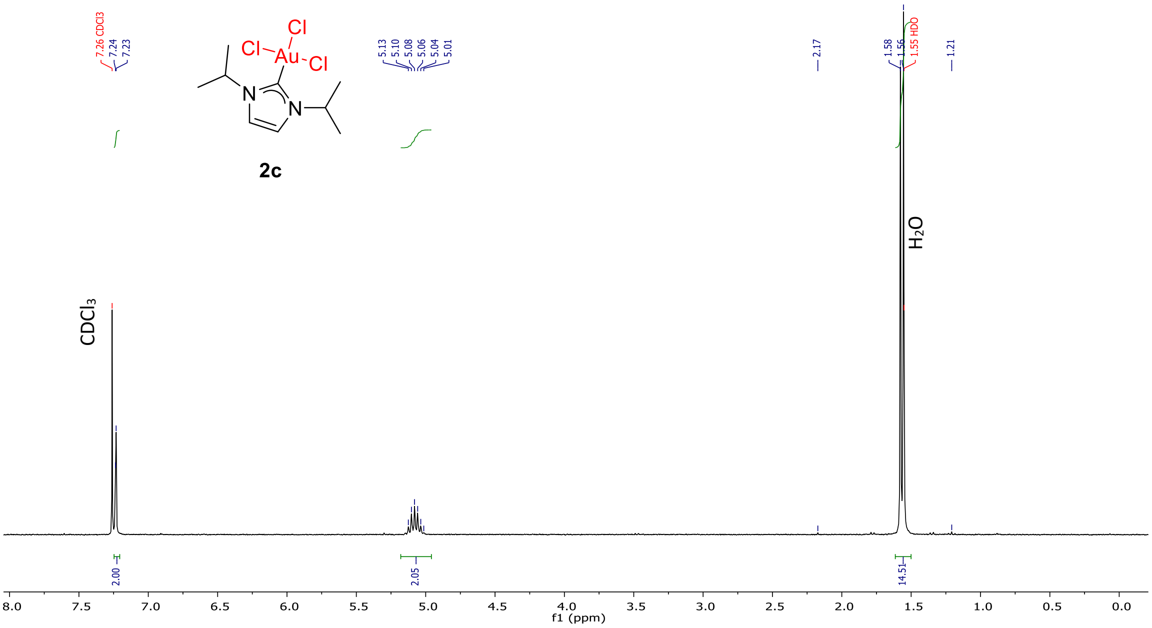


Figure S23. ^{1}H NMR spectrum of **2c** (300 MHz, CDCl$_3$).

*Attempted synthesis of **2c** in aqua regia.*

Stirring of **1c** (45 mg, 0.12 mmol) in *aqua regia* (8 mL) for 24 h resulted in a mixture of **2c** and **4c** as well as traces of unreacted **1c**. The product ratio was determined by ^{1}H NMR:

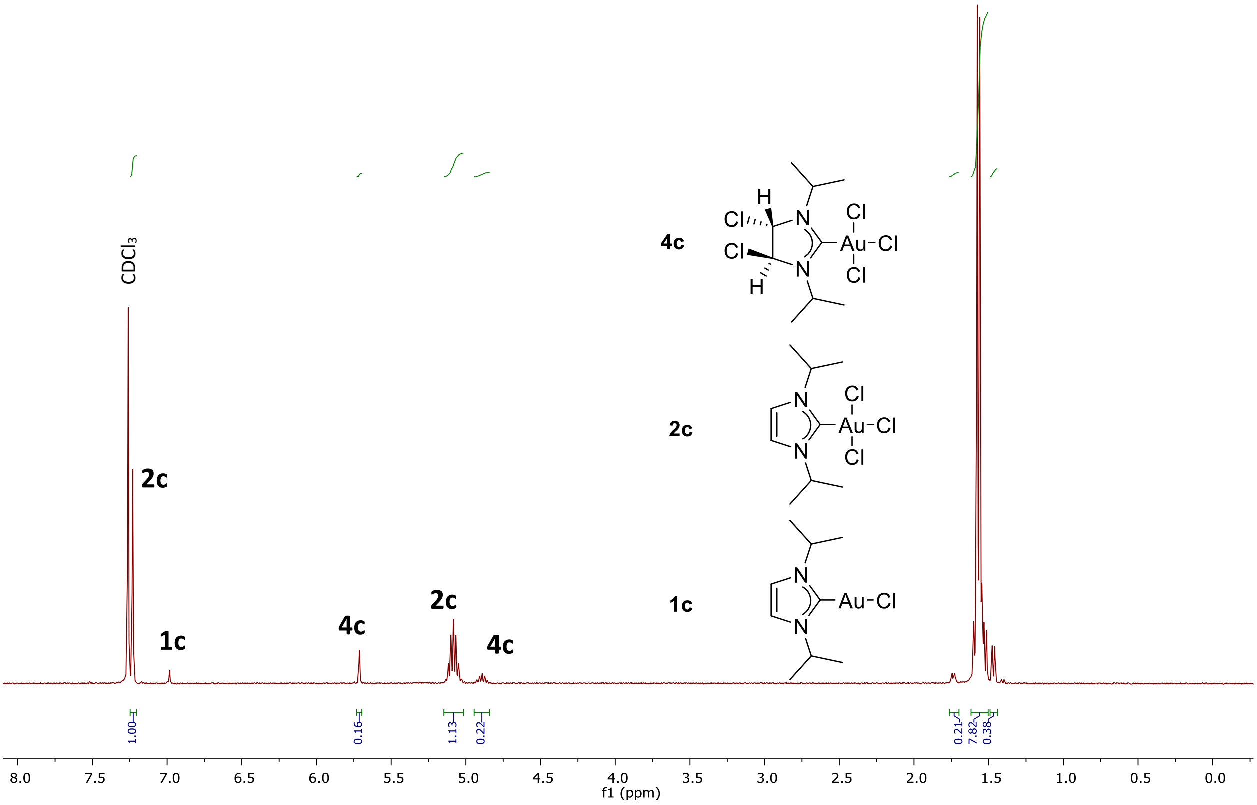
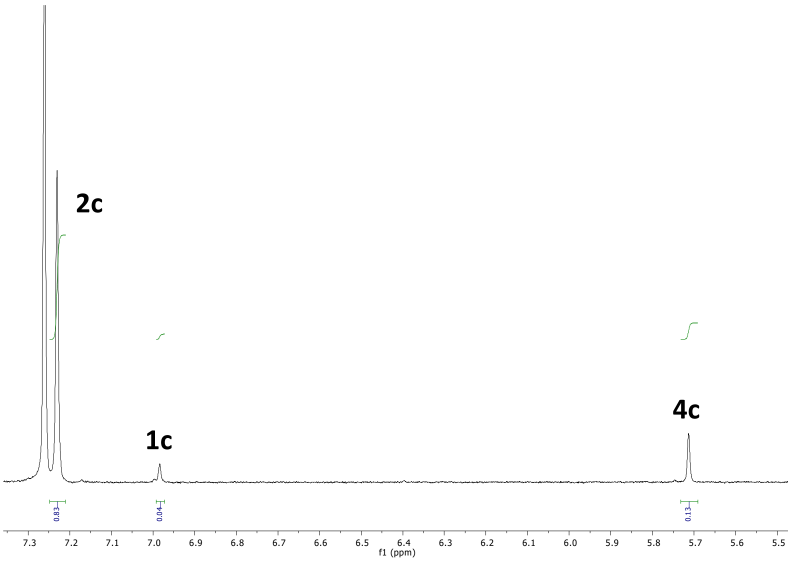


Figure S24. ^{1}H NMR spectrum of the crude mixture from the reaction between **1c** and *aqua regia* (400 MHz, $CDCl_3$).

The quantification of the three species present in the mixture was performed using the integration of the NMR signals of the protons of the backbone CH groups.



1c: ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.98 (s, 2H, =C*H*-). (other peaks are not recognizable from the mixture).

2c: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (s, 2H, =C*H*-), 5.08 (hept., *J* = 6.7 Hz, 2H, -C*H*Me_2), 1.57 (d, *J* = 6.8 Hz, 12H, -CH_3).

4c: ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.71 (s, 2H, -C*H*(Cl)-), 4.89 (m, 2H, -C*H*Me_2). (other peaks are not recognizable from the mixture).

(IMe$_2$Cl$_2$)AuCl$_3$ (3a): Stirring of **1d** (44 mg, 0.11 mmol) in *aqua regia* (8 mL) for 3 h resulted in a yellow powder (40 mg, 77%). The NMR spectra were in agreement with the reported ones.[9]

^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ 3.96 (s, 3H, -C*H*$_3$).

Elemental analysis: Calcd. for C$_5$H$_6$AuCl$_5$N$_2$: C, 12.82; H, 1.29; N, 5.98. Found: C, 12.78; H, 1.31; N, 5.91%.

(IEt$_2$Cl$_2$)AuCl$_3$ (3b): Stirring of **1e** (44 mg, 0.103 mmol) in *aqua regia* (8 mL) for 3 h resulted in a yellow powder (39 mg, 76%).

^{1}H NMR (600 MHz, CDCl$_3$): δ 4.43 (q, *J* = 7.4 Hz, 4H, -C*H*$_2$-), 1.59 (t, *J* = 7.3 Hz, 6H, -C*H*$_3$). ^{13}C NMR (151 MHz, CDCl$_3$): δ 142.6 (NHC-*C*), 119.9 (=*C*-Cl), 46.1 (-*C*H$_2$-), 15.0 (-*C*H$_3$). MS (ESI$^+$, CH$_3$CN): *m/z* 518.881 ([M(^{35}Cl$_4$^{37}Cl)+Na$^+$], 58%), 534.855 ([M(^{35}Cl$_4$^{37}Cl)+K$^+$], 100%). HRMS (CH$_3$CN): *m/z* meas. 518.8815, calcd. 518.8815 for [C$_7$H$_{10}$AuN$_2$^{35}Cl$_4$^{37}ClNa]$^+$ (Δ = -0.1 ppm).

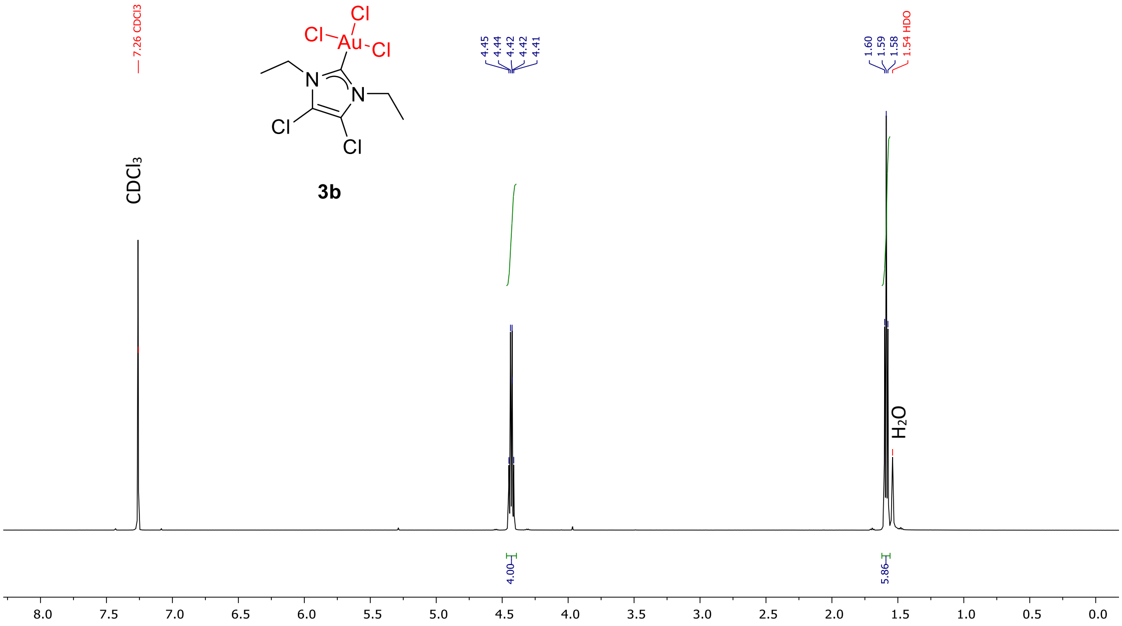


Figure S25. ^{1}H NMR spectrum of **3b** (600 MHz, CDCl$_3$).

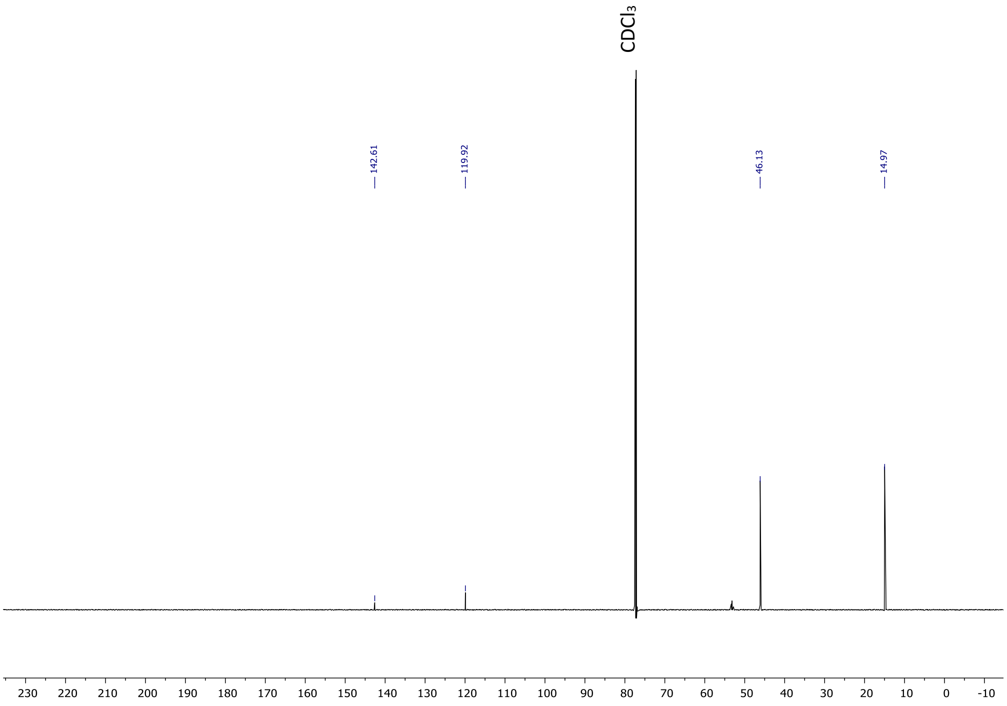


Figure S26. ^{13}C NMR spectrum of **3b** (150 MHz, CDCl$_3$).

(IiPr$_2$Cl$_2$)AuCl$_3$ (3c): Stirring of **1f** (55.6 mg, 0.123 mmol) in *aqua regia* (8 mL) for 5 h resulted in a yellow powder (54 mg, 84%). ^{1}H NMR (600 MHz, CD$_2$Cl$_2$): δ 5.28 (hept., *J* = 7.0 Hz, 2H, -C*H*Me$_2$), 1.71 (d, *J* = 7.0 Hz, 12H, -C*H*$_3$). ^{13}C NMR (151 MHz, CD$_2$Cl$_2$): δ 141.4 (NHC-*C*), 120.4 (=*C*-Cl), 59.1 (-*C*H-), 21.1 (-*C*H$_3$).

MS (ESI$^+$, MeCN): *m/z* 529.980 ([M-Cl+MeCN], 20%). HRMS (MeCN): *m/z* meas. 544.9159, calcd. 544.9158 for [C$_9$H$_{14}$Au^{35}Cl$_5$N$_2$Na]$^+$ (Δ = -0.3 ppm).

Elemental analysis: Calcd. for C$_9$H$_{14}$AuCl$_5$N$_2$: C, 20.61; H, 2.69; N, 5.34. Found: C, 20.27; H, 2.67; N, 5.24%.

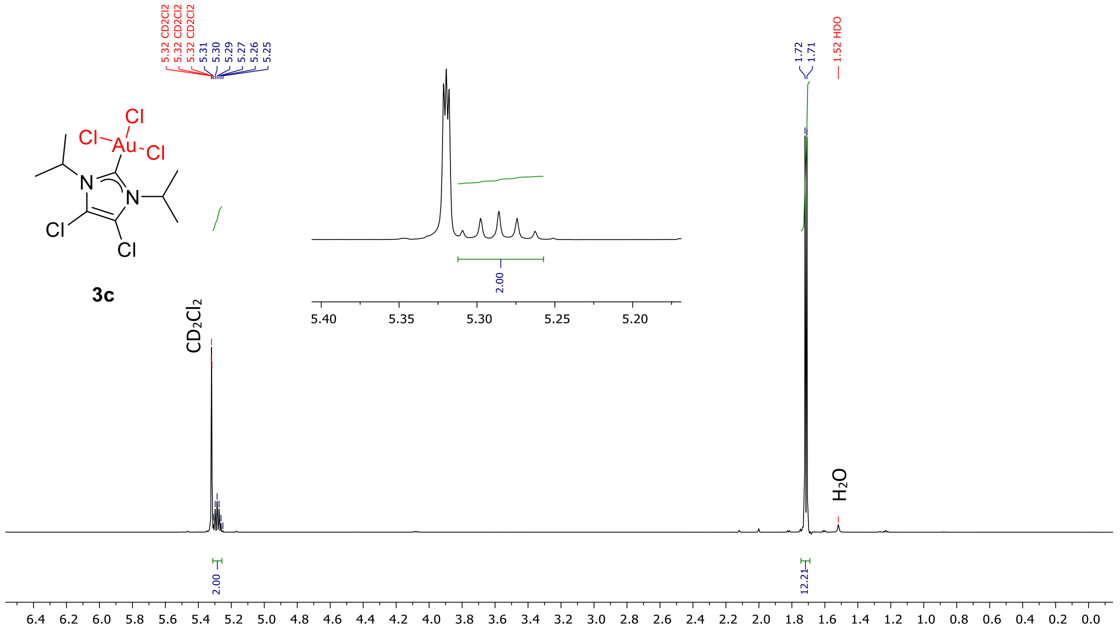


Figure S27. ^{1}H NMR spectrum of **3c** (600 MHz, CD$_2$Cl$_2$).

CD$_2$Cl$_2$

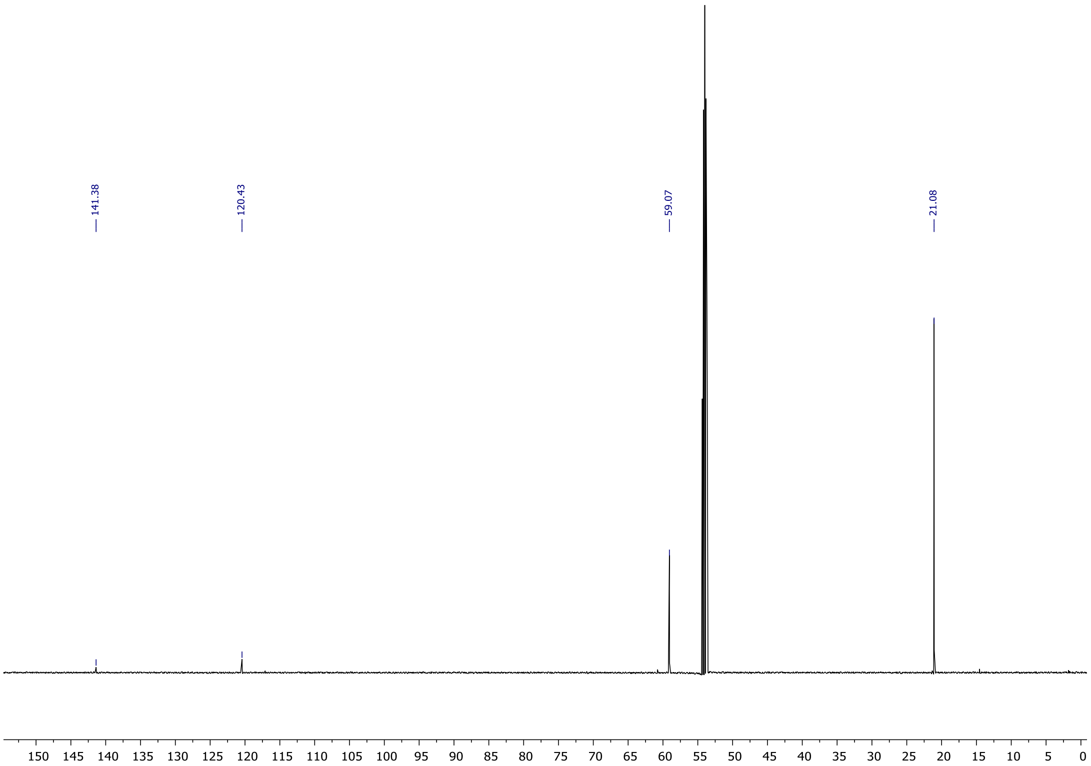


Figure S28. ^{13}C NMR spectrum of **3c** (150 MHz, CD_2Cl_2).

(IPr)AuCl$_3$ (2g): Stirring of **1g** (50 mg, 0.081 mmol) in *aqua regia* (8 mL) for 5 h resulted in a yellow powder (40 mg, 72%). Spectroscopic data were in agreement with those previously reported.[10]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (t, *J* = 7.8 Hz, 2H, *p*-C*H*), 7.40-7.31 (m, 6H, *m*-C*H* and =C*H*-), 2.85 (hept., *J* = 6.8 Hz, 4H, -C*H*Me$_2$), 1.40 (d, *J* = 6.6 Hz, 12H, -C*H*$_3$), 1.13 (d, *J* = 6.8 Hz, 12H, -C*H*$_3$).

Elemental analysis: Calcd. for $C_{27}H_{36}AuCl_3N_2$: C, 46.87; H, 5.24; N, 4.05. Found: C, 44.41; H, 5.05; N, 3.81%.

(SIPr)AuCl$_3$ (2h): Stirring of **1h** (50 mg, 0.080 mmol) in *aqua regia* (8 mL) for 20 h resulted in a yellow powder (25.1 mg, 45%). In addition to the general procedure the product was washed with two fractions of diethyl ether. Spectroscopic data were in agreement with those previously reported.[10]

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.53-7.41 (m, 2H, *p*-C*H*), 7.34-7.28 (m, 4H, *m*-C*H*), 4.28 (s, 4H, -C*H*$_2$-), 3.43-3.25 (hept., *J* = 6.8 Hz, 4H, -C*H*Me$_2$), 1.47 (d, *J* = 6.5 Hz, 12H, -C*H*$_3$), 1.27 (d, *J* = 6.8 Hz, 12H, -C*H*$_3$).

NHC(BIm)-AuCl$_3$ (2i): Stirring of **1i** (49 mg, 0.13 mmol) in *aqua regia* (8 mL) for 7 h resulted in a yellow powder (49 mg, 85%).

^{1}H NMR (600 MHz, CD$_2$Cl$_2$): δ 7.66-7.62 (m, 2H, =C*H*^{Ar}), 7.59-7.55 (m, 2H, C*H*^{Ar}), 4.16 (s, 6H, -C*H*$_3$). ^{13}C NMR (151 MHz, CD$_2$Cl$_2$): δ 151.7 (NHC-*C*), 134.8 (*C*$_{quat.}$), 126.5 (*C*H^{Ar}), 112.4 (*C*H^{Ar}), 35.3 (-*C*H$_3$). MS (ESI$^+$, MeCN): *m/z* 181.053 ([M-AuCl$_2$]$^+$, 100%), 470.947 ([M+Na]$^+$, 29%), 486.921 ([M+K]$^+$, 29%). HRMS (MeCN): *m/z* meas. 470.9468, calcd. 470.9467 for $C_9H_{10}AuN_2{}^{35}Cl_3Na^+$, (Δ -0.1 ppm). Also observed 472.9439 ($C_9H_{10}AuN_2{}^{35}Cl_2{}^{37}ClNa^+$), 474.9410 ($C_9H_{10}AuN_2{}^{35}Cl^{37}Cl_2Na^+$), 476.9377 ($C_9H_{10}AuN_2{}^{37}Cl_3Na^+$).

Elemental analysis: Calcd. for $C_9H_{10}AuCl_3N_2$: C, 24.05; H, 2.24; N, 6.23. Found: C, 23.90; H, 2.27; N, 6.16%.

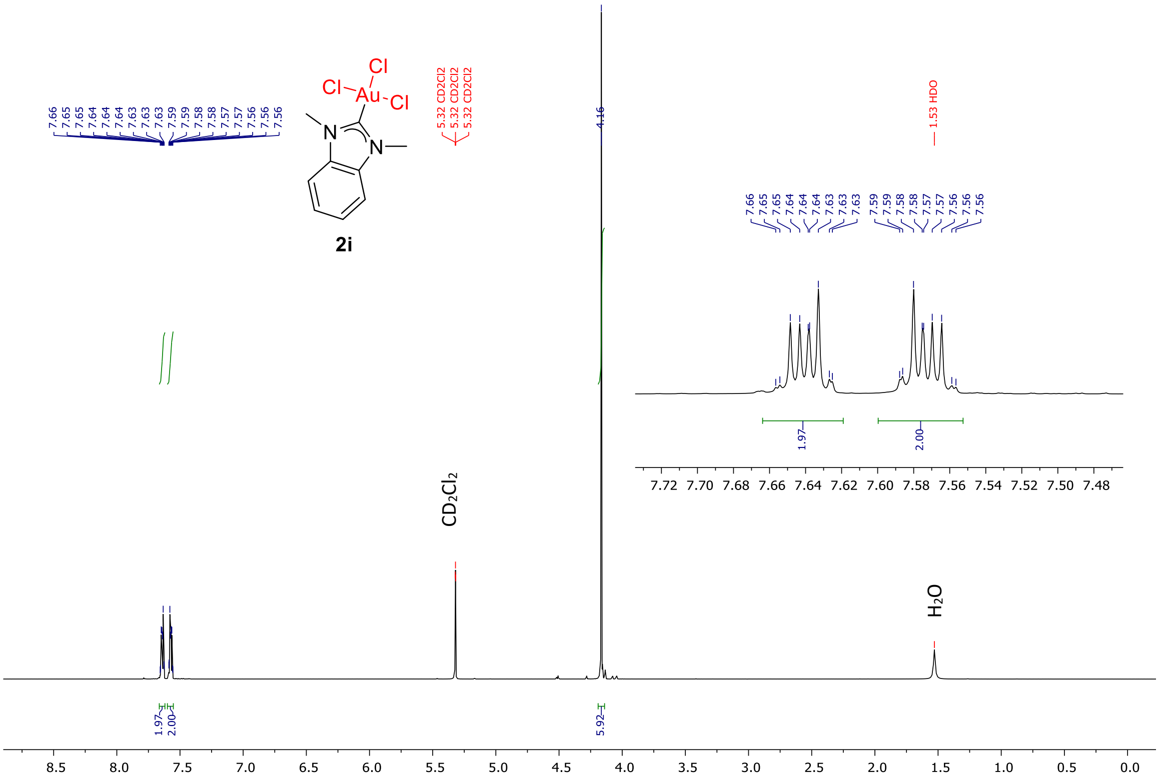


Figure S29. ^{1}H NMR spectrum of **2i** (600 MHz, CD$_2$Cl$_2$).

CD$_2$Cl$_2$

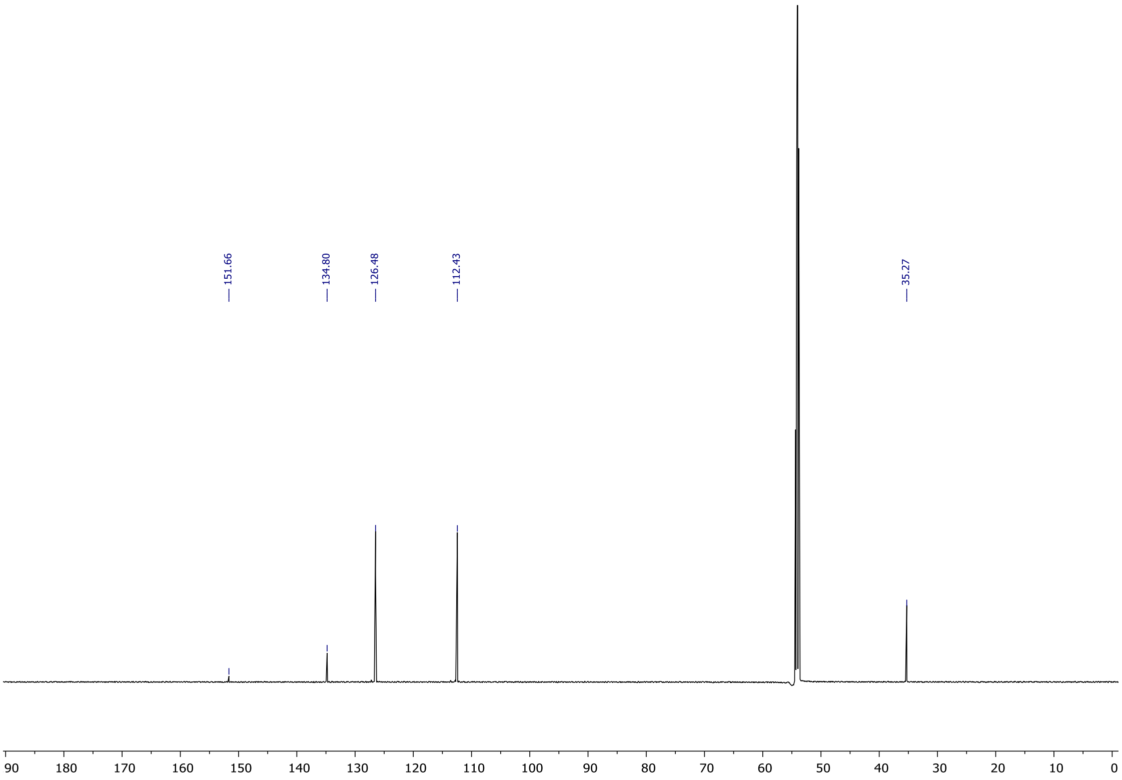


Figure S30. ^{13}C NMR spectrum of **2i** (150 MHz, CD_2Cl_2).

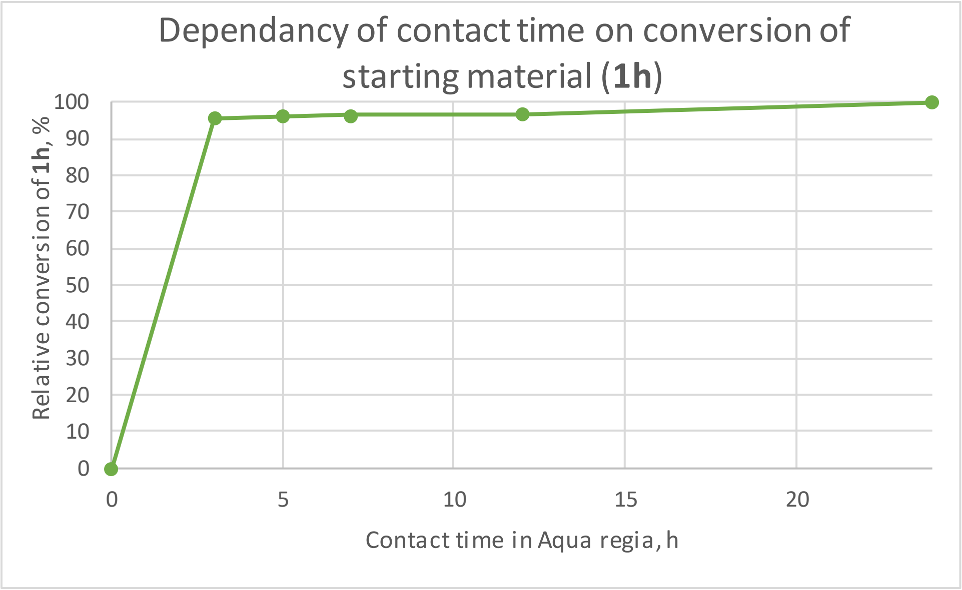
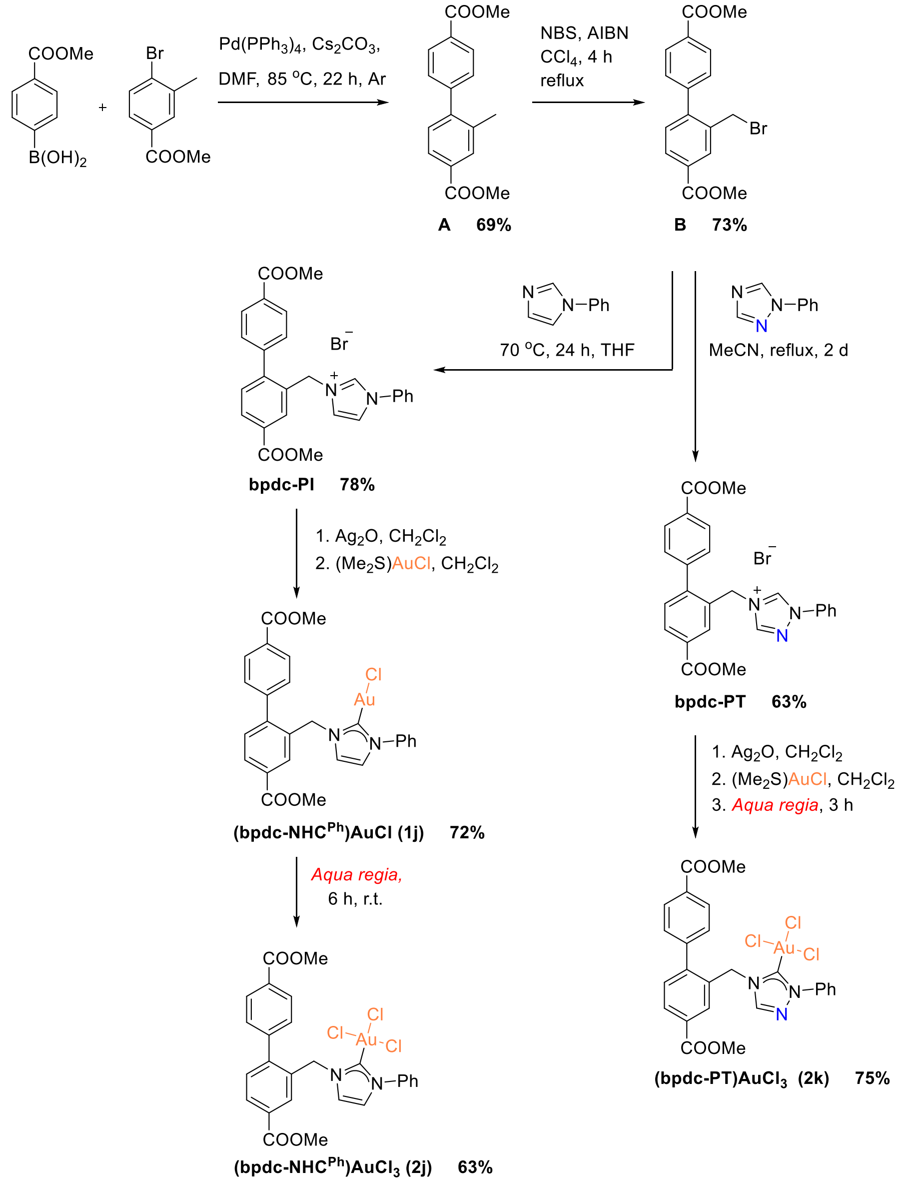


Figure S31. Oxidation of **1h** into **2h** in *aqua regia* over time.

4. Syntheses of (bpdc^{Ph})AuCl$_3$ (2j) and (abpdc^{Ph})AuCl$_3$ (2k)



Intermediate A: The procedure was slightly modified from the reported one.[11] A stirred solution of methyl-4-bromo-3-methylbenzoate (2.06 g, 9 mmol), 4-methoxycarbonyl-phenylboronic acid (1.62 g, 9 mmol), Pd(PPh$_3$)$_4$ (312 mg, 0.27 mmol, 3 mmol%) and Cs$_2$CO$_3$ (4.40 g, 13.5 mmol) in DMF (40 mL) was heated to 85°C under argon for 22 h. The mixture was cooled to room temperature followed by addition of water and filtration. The solids were dissolved in CH$_2$Cl$_2$, filtered through a silica plug, and the solvent was removed in vacuo. The obtained residue was recrystallized from EtOH (ca 30 mL) to give intermediate **A** as a white-pinkish powder (1.77 g, 69% yield). The NMR spectra matched those of the known compound.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17-8.07 (m, 2H), 7.97 (d, *J* = 1.7 Hz, 1H), 7.94-7.87 (m, 1H), 7.44-7.36 (m, 2H), 7.29 (d, *J* = 7.9 Hz, 1H), 3.95 (s, 3H), 3.94 (s, 3H), 2.30 (s, 3H).

Intermediate B: The procedure was modified from the reported one and resulted in a higher yield.[11] A stirred solution of intermediate **A** (1.50 g, 5.28 mmol), NBS (1.083 g, 6.08 mmol), and AIBN (90 mg, 0.55 mmol) in CCl_4 (30 mL) was heated at reflux for 4 h. After cooling to room temperature, the solvent was removed under reduced pressure and the solid crude product was recrystallized from iPrOH (20 mL), yielding **B** as a white powder (1.4 g, 73%). The NMR spectra matched those previously described.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.22 (d, *J* = 1.7 Hz, 1H), 8.20-8.10 (m, 2H), 8.02 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.58-7.48 (m, 2H), 7.34 (d, *J* = 8.0 Hz, 1H), 4.42 (s, 2H), 3.96 (s, 6H).

bpdc-PI: A solution of intermediate **B** (733 mg, 2 mmol) and 1-phenylimidazole (320 mg, 2.22 mmol) in dry THF (25 mL) was stirred and heated at reflux overnight. After cooling to room temperature, the white solid was collected by filtration. The obtained white solids were rinsed with THF and dried under a flow of air to give **bpdc-PI** as white powder (799 mg, 78%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 10.70 (s, 1H, *H*-imid.), 8.20 (d, *J* = 1.6 Hz, 1H), 8.13 (dd, *J* = 8.0, 1.7 Hz, 1H), 8.11-8.05 (m, 2H), 7.58-7.48 (m, 5H), 7.48-7.36 (m, 4H), 6.88 (t, *J* = 1.8 Hz, 1H), 6.03 (s, 2H, $-CH_2-$), 3.94 (s, 3H), 3.87 (s, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 166.3, 166.0, 145.7, 143.0, 137.2, 134.1, 131.5, 131.2, 131.0, 131.0, 131.0, 130.8, 130.6, 130.4, 130.4, 128.9, 122.0, 121.9, 120.4, 52.7, 52.5, 52.0. MS (ESI$^+$, CH_3CN) *m/z* : 427.165 ($[M-Br]^+$, 100%), 413.266 ($[M-Br-CH_3+H]^+$, 29%). HRMS (MeCN): *m/z* meas. 427.1652, calcd. 427.1652 for $[C_{26}H_{23}N_2O_4]^+$ ($[M-Br]^+$), (Δ = 0.1 ppm).

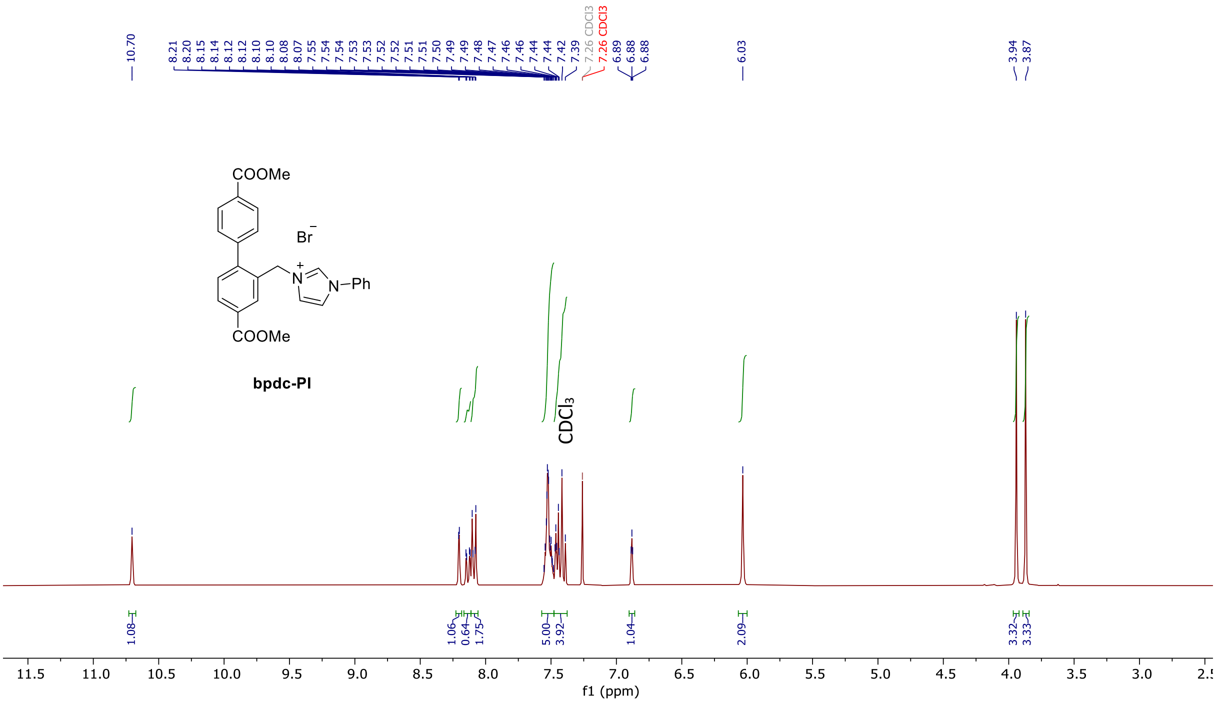


Figure S32. ^{1}H NMR spectrum of **bpdc-PI** (400 MHz, CDCl$_3$).

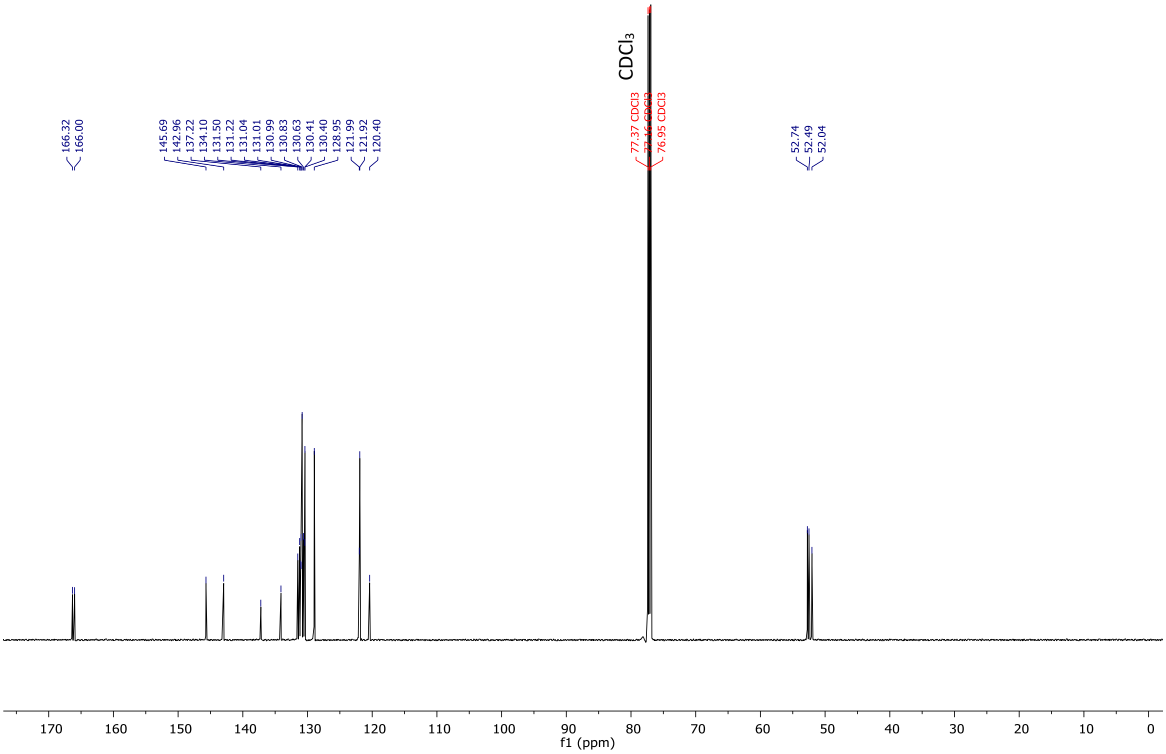


Figure S33. ^{13}C NMR spectrum of **bpdc-PI** (150 MHz, CDCl$_3$).

(bpdc-NHC^{Ph})AuCl (1j): To a solution of **bpdc-PI** (100 mg, 0.197 mmol, 1 equiv.) in CH_2Cl_2 (9 mL), Ag_2O (26 mg, 0.148 mmol, 0.76 equiv.) was added in the absence of light. The reaction was stirred at room temperature for 4 h and filtered through Celite. A solution of $(Me_2S)AuCl$ (64 mg, 0.217 mmol, 1.1 equiv.) in CH_2Cl_2 (8 mL) was added dropwise during 15 min and the reaction mixture was stirred at room temperature for a further 30 min. The suspension was filtered through Celite and the solution was concentrated under reduced pressure followed by addition of the pentane. The resulting cloudy suspension was placed in the freezer overnight followed by filtration of the white solid of product (93 mg, 72%). ^1H NMR (600 MHz, CD_2Cl_2): δ 8.14-8.08 (m, 3H), 8.08-8.06 (m, 1H), 7.59-7.53 (m, 2H), 7.53-7.47 (m, 3H), 7.43 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.42-7.38 (m, 2H), 7.13 (d, *J* = 2.0 Hz, 1H), 6.73 (d, *J* = 2.1 Hz, 1H), 5.52 (s, 2H), 3.94 (s, 3H), 3.93 (s, 3H). ^{13}C NMR (151 MHz, CD_2Cl_2): δ 172.2, 167.0, 166.6, 146.2, 144.1, 139.6, 133.5, 131.3, 131.2, 131.0, 130.7, 130.6, 130.3, 130.1, 129.7, 129.5, 125.5, 122.5, 121.4, 53.7, 52.9, 52.8. MS (ESI$^+$, MeOH) *m/z* 681.083 ([M+Na]$^+$, 100%), 623.124 ([M-Cl]$^+$, 9.9%). HRMS (MeOH): *m/z* meas. 681.0826, calcd. 681.0826 for $[C_{26}H_{22}AuN_2{}^{35}ClO_4Na]^+$ (Δ = 0.1 ppm). Also observed 683.0803 ($[C_{26}H_{22}AuN_2{}^{37}ClO_4Na]^+$.

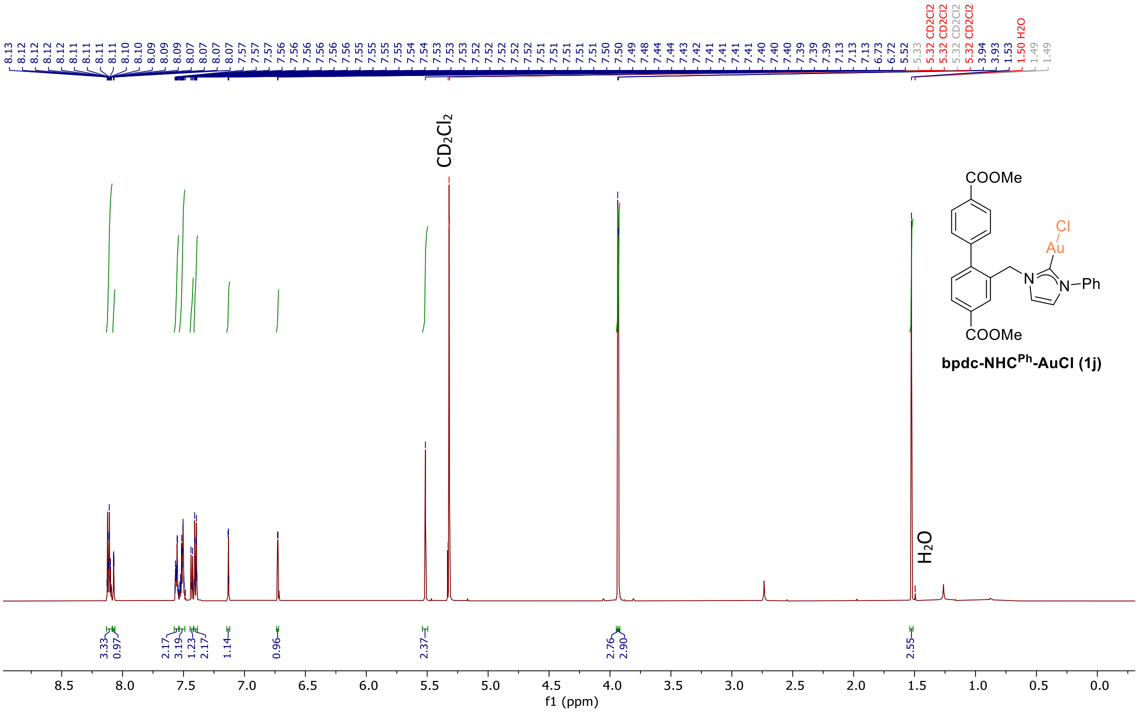


Figure S34. ^{1}H NMR spectrum of (bpdc-NHC^{Ph})AuCl (**1j**) (600 MHz, CD_2Cl_2).

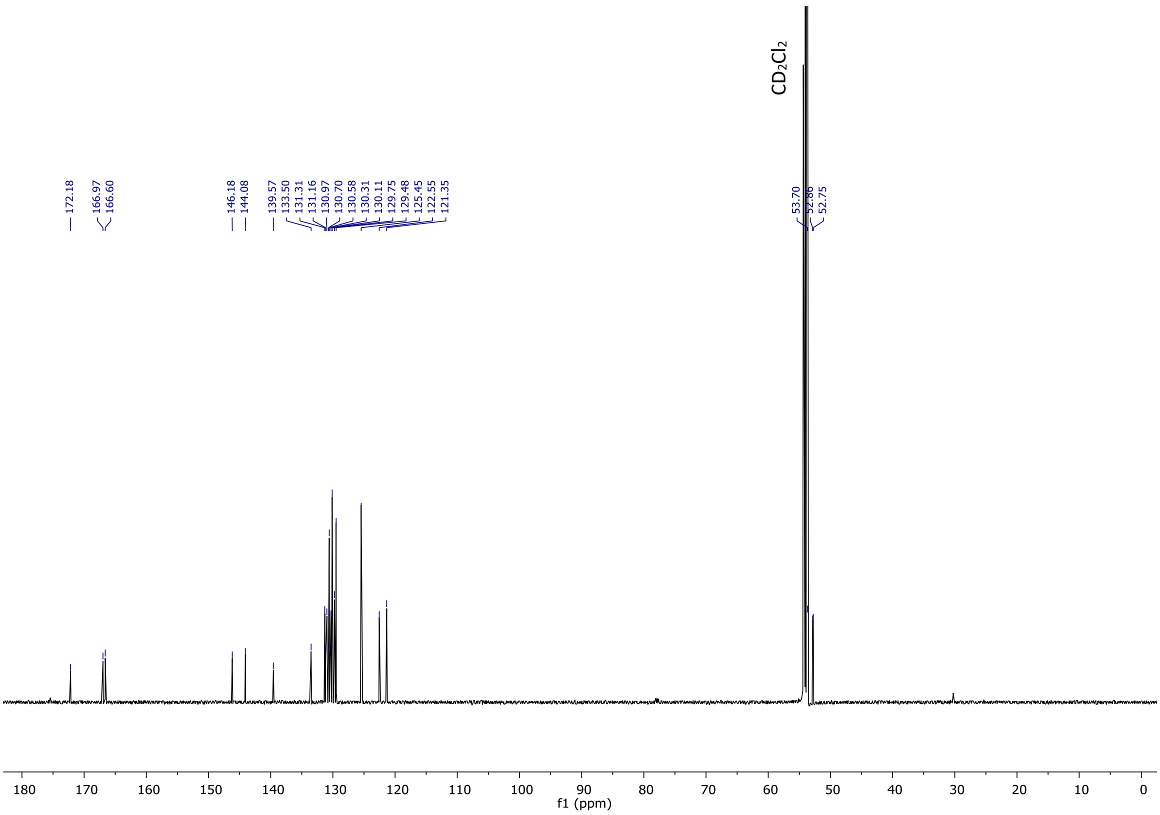


Figure S35. ^{13}C NMR spectrum of (bpdc-NHC^{Ph})AuCl (**1j**) (150 MHz, CD_2Cl_2).

(bpdc-NHC^{Ph})AuCl$_3$ (2j)

Method A (starting from imidazolium salt): To a solution of bpdc-PI (100 mg, 0.197 mmol, 1 equiv.) in CH_2Cl_2 (8 mL), Ag_2O (26 mg, 0.112 mmol, 0.76 equiv.) was added in the absence of light. The reaction was stirred at room temperature for 4 h. A solution of $(Me_2S)AuCl$ (64 mg, 0.217 mmol, 1.1 equiv.) in CH_2Cl_2 (8 mL) was added dropwise during 30 min and the reaction mixture was stirred at room temperature for a further 1 h. Filtration of the reaction mixture through Celite, followed by evaporation in vacuo, afforded (bpdc-NHC^{Ph})AuCl (**1j**) that was immediately stirred with freshly prepared *aqua regia* (8 mL) for 6 h. The pale yellow solid product was collected by filtration and washed with water (99 mg, 69%).

Method B (starting from (bpdc-NHC^{Ph})AuCl: (bpdc-NHC^{Ph})AuCl (**1j**; 44.5 mg, 0.068 mmol) was stirred with *aqua regia* (8 mL) for 6 h. The suspension was filtered, washed with water, and dried under a flow of air furnishing 41 mg of the product (bpdc-NHC^{Ph})AuCl$_3$ (**2j**; yield 82%).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.31 (d, *J* = 1.6 Hz, 1H), 8.20-8.13 (m, 3H), 7.58-7.52 (m, 5H), 7.49-7.40 (m, 3H), 7.16 (d, *J* = 2.1 Hz, 1H), 6.72 (d, *J* = 2.1 Hz, 1H), 5.55 (s, 2H), 3.97 (s, 3H), 3.95 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 166.6, 166.0, 146.0, 143.5, 136.9, 132.2, 131.3, 131.2, 131.1, 130.9, 130.6, 130.5, 130.4, 129.0, 129.0, 125.9, 125.8, 124.2, 123.8, 77.4, 77.2, 76.9, 52.8, 52.7, 52.6. MS (ESI$^+$, MeCN): *m/z* 751.209 ($[M+Na]^+$, 100%), 794.969 ($[M-Cl+Br+Na]^+$, 12%). HRMS (MeCN): *m/z* meas. 751.0197, calcd. 751.0203 for $[C_{26}H_{22}AuO_4N_2{}^{35}Cl_3Na]^+$), (Δ = 0.8 ppm). Also observed 753.0170 ($[C_{26}H_{22}AuO_4N_2{}^{37}Cl^{35}Cl_2Na]^+$), 755.0175 ($[C_{26}H_{22}AuO_4N_2{}^{37}Cl_2{}^{35}ClNa]^+$), 757.0131 ($[C_{26}H_{22}AuO_4N_2{}^{37}Cl_3Na]^+$).

Elemental analysis: Calcd. for $C_{26}H_{22}AuCl_3N_2O_4$: C, 42.79; H, 3.04; N, 3.84. Found: C, 41.82; H, 2.97; N, 3.71%.

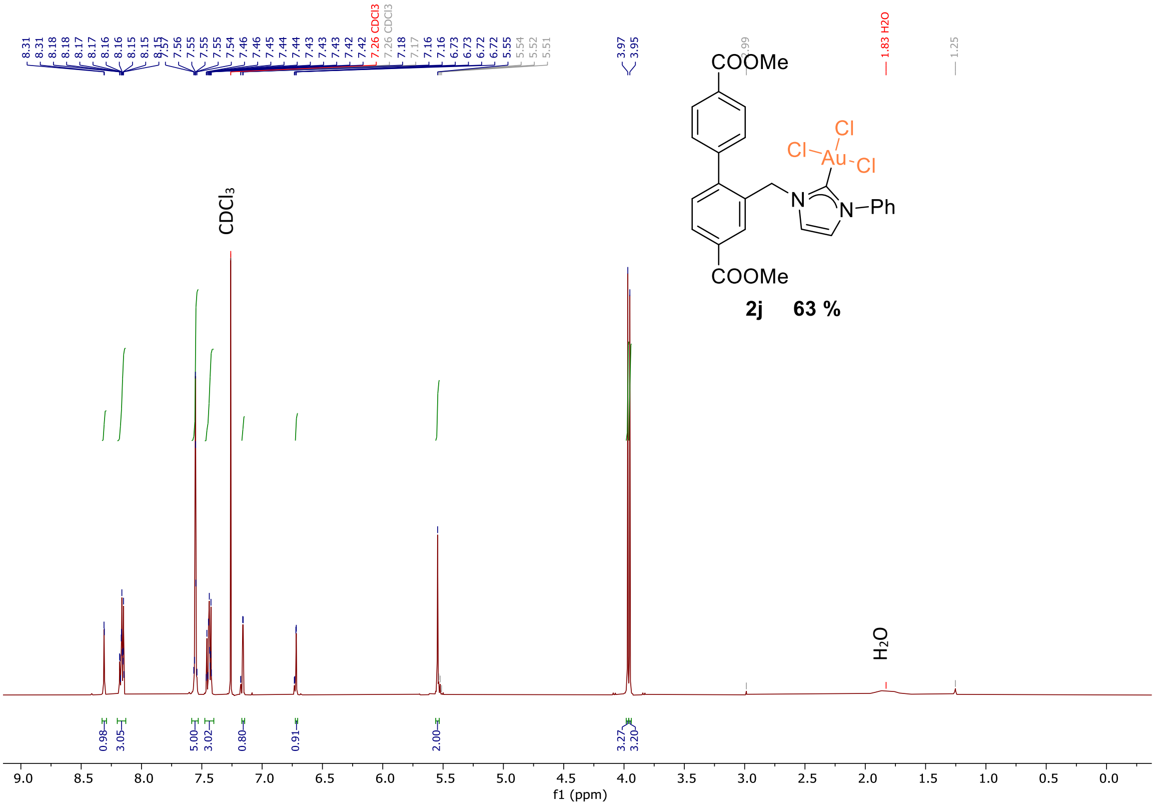


Figure S36. ^{1}H NMR spectrum of (bpdc-NHC^{Ph})AuCl$_3$ (**2j**) (600 MHz, CDCl$_3$).

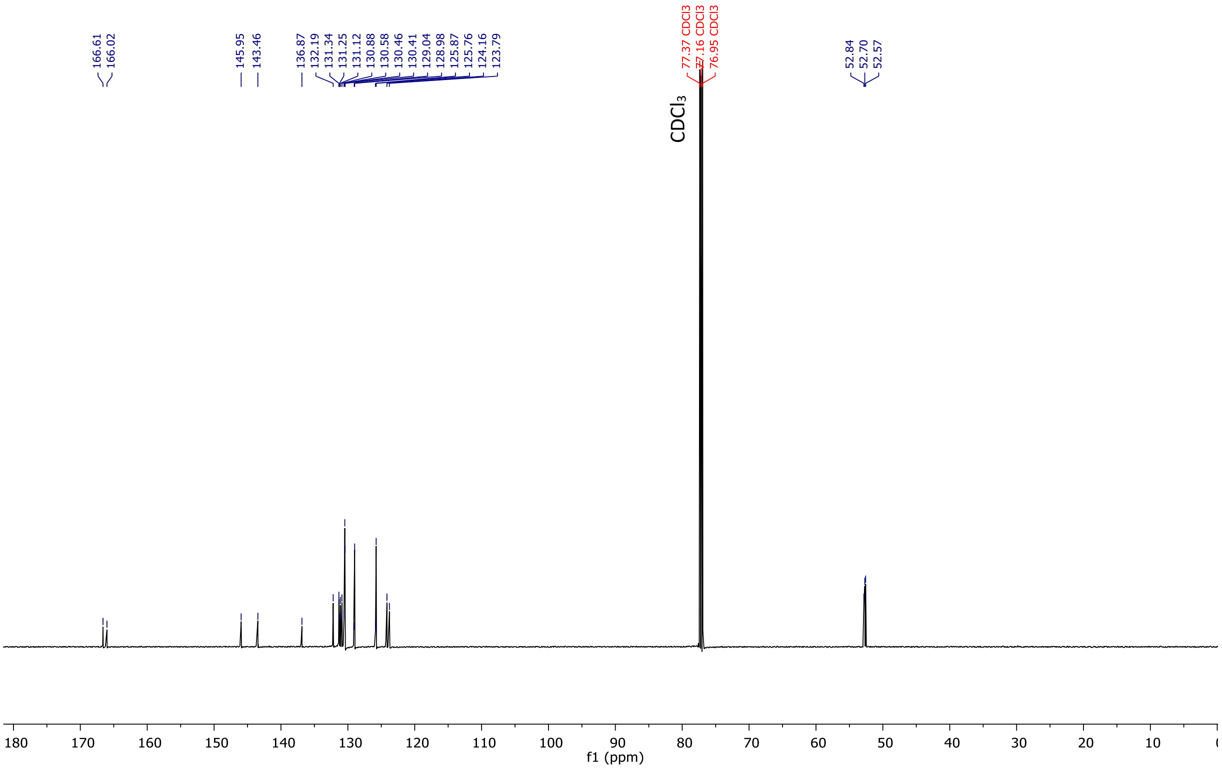


Figure S37. ^{13}C NMR spectrum of (bpdc-NHC^{Ph})AuCl$_3$ (**2j**) (150 MHz, CDCl$_3$).

bpdc-PT: A mixture of **B** (200 mg, 0.55 mmol) and phenyl-1,2,4-triazole (91 mg, 0.63 mmol) was heated at reflux in MeCN (3 mL) for 2 d. The reaction mixture was cooled and the product was recovered by filtration (185 mg, 63% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 12.30 (s, 1H), 8.37 (d, *J* = 1.7 Hz, 1H), 8.20 (dd, *J* = 8.0, 1.7 Hz, 1H), 8.16-8.11 (m, 2H), 7.86-7.81 (m, 3H), 7.58-7.50 (m, 3H), 7.45 (d, *J* = 7.9 Hz, 1H), 7.44-7.41 (m, 2H), 6.14 (s, 2H), 3.97 (s, 3H), 3.89 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 166.1, 165.8, 145.6, 142.7, 142.6, 141.5, 141.4, 134.4, 131.9, 131.6, 131.4, 131.4, 131.3, 130.7, 130.5, 129.9, 128.9, 120.5, 52.8, 52.6, 50.7. MS (ESI$^+$, MeCN) *m/z* 428.160 ([M-Br]$^+$, 100%), 413.266 ([M-Br-CH_3]$^+$, 28%). HRMS (MeCN): *m/z* meas. 428.1604, calcd. 428.1605 for [$C_{25}H_{22}N_3O_4$]$^+$ ([M-Br]$^+$) (Δ = 0.1 ppm).

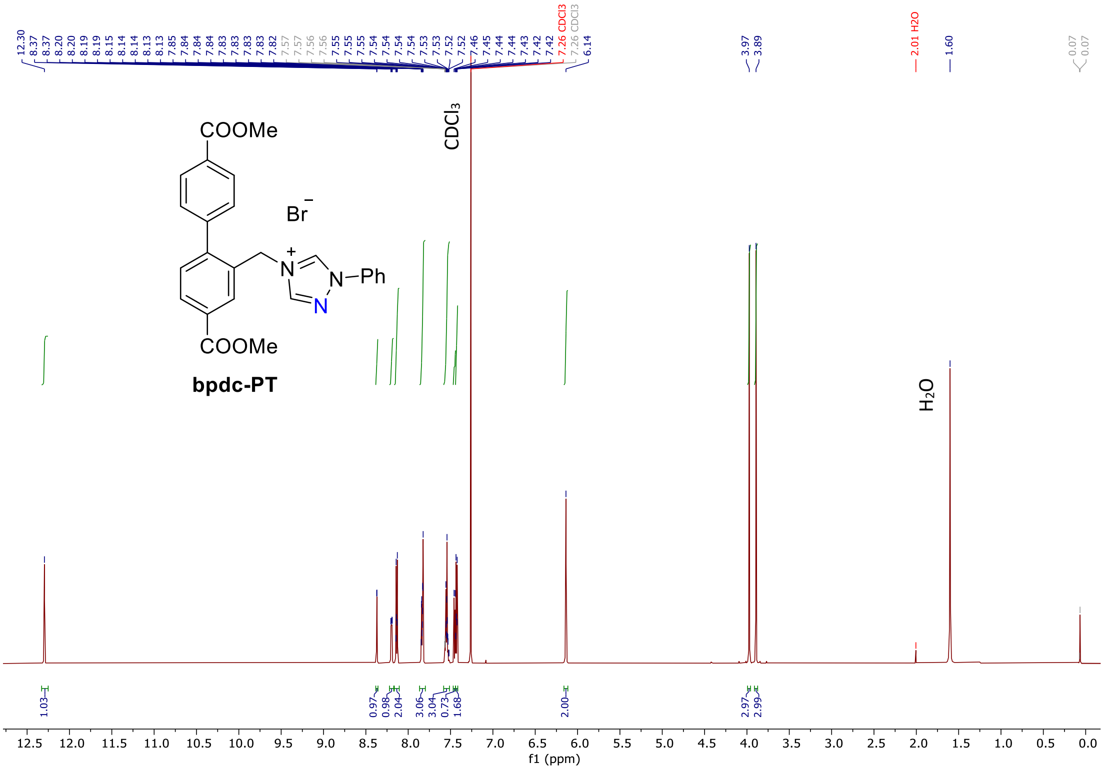


Figure S38. ^{1}H NMR spectrum of bpdc-PT (600 MHz, $CDCl_3$).

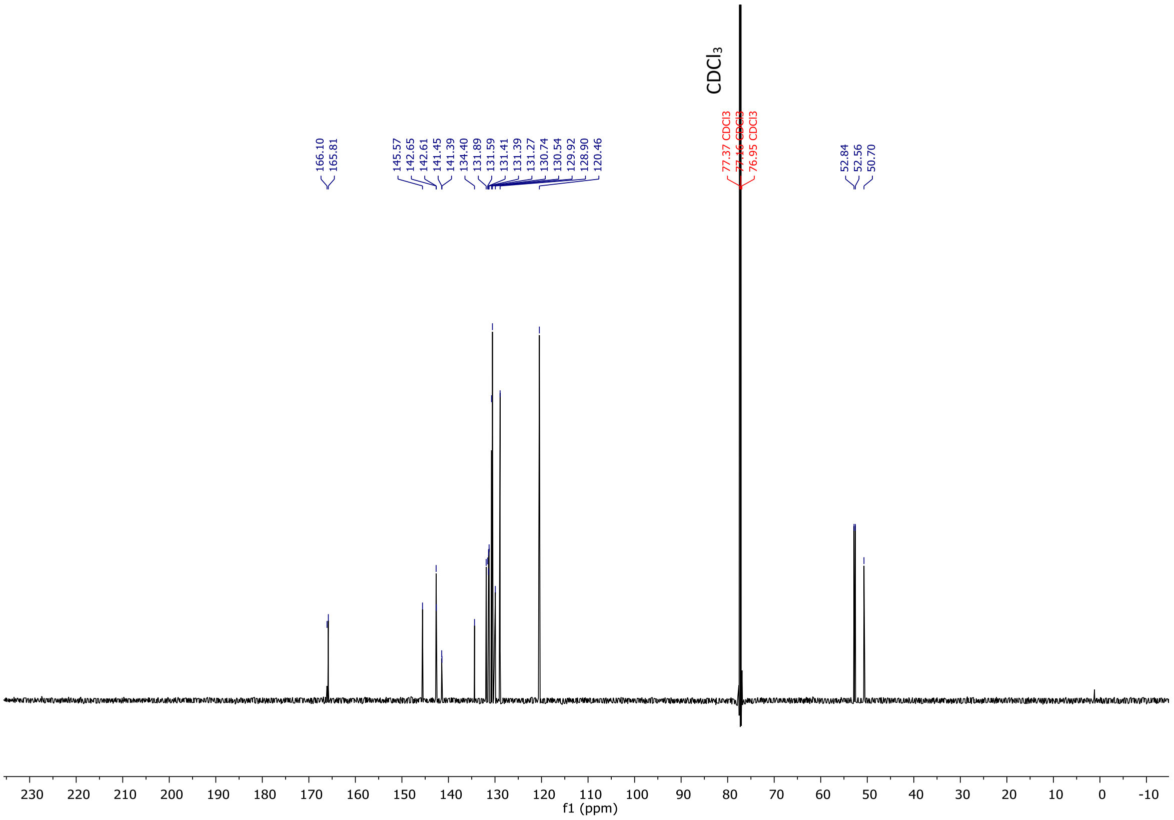


Figure S39. ^{13}C NMR spectrum of **bpdc-PT** (150 MHz, CDCl$_3$).

(abpdc-NHC^{Ph})AuCl$_3$ (2k): To a solution of bpdc-PT (50 mg, 0.098 mmol, 1 equiv.) in CH_2Cl_2 (8 mL), Ag_2O (13.7 mg, 0.059 mmol, 0.6 equiv.) was added in the absence of light. The reaction was stirred at room temperature for 3 h. A solution of (Me_2S)AuCl (31.8 mg, 0.108 mmol, 1.1 equiv.) in CH_2Cl_2 (8 mL) was added in one portion and the reaction mixture was stirred at room temperature for a further 30 min. Filtration of the reaction mixture through Celite, followed by evaporation in vacuo, afforded the corresponding (NHC)Au(I) complex that was immediately stirred with freshly prepared *aqua regia* for 3 h. The solid yellow product was collected by filtration (54 mg, 75% yield). ^{1}H NMR (600 MHz, CDCl$_3$): δ 8.43 (s, 1H), 8.23 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.17 (d, *J* = 7.9 Hz, 2H), 7.72-7.66 (m, 2H), 7.61-7.53 (m, 3H), 7.50 (s, 1H), 7.45 (d, *J* = 7.9 Hz, 1H), 7.40 (d, *J* = 7.9 Hz, 2H), 5.60 (s, 2H), 3.98 (s, 3H), 3.97 (s, 3H). ^{13}C NMR (151 MHz, CDCl$_3$): δ 166.4, 165.7, 151.3, 145.9, 144.2, 143.2, 136.9, 132.9, 131.9, 131.7, 131.6, 131.4, 130.8, 130.6, 130.2, 129.4, 128.7, 124.7, 52.8, 52.7, 51.8. MS (ESI$^+$, CH_3OH): *m/z* 748.065 ([M-Cl+OMe+Na]$^+$, 100%), 752.061 ([M+Na]$^+$, 11.4%), 694.057 ([M-Cl]$^+$, 8.4%). HRMS (MeCN): *m/z* meas. 752.0156, calcd. 752.0156 for $[C_{25}H_{21}AuN_3{}^{35}Cl_3O_4Na]^+$ [M+Na]$^+$), (Δ = -0.1 ppm). Also observed 754.0129 ($[C_{25}H_{21}AuN_3{}^{35}Cl_2{}^{37}ClO_4Na]^+$), 756.0105 ($[C_{25}H_{21}AuN_3{}^{35}Cl^{37}Cl_2O_4Na]^+$), 758.0081 ($[C_{25}H_{21}AuN_3{}^{37}Cl_3O_4Na]^+$).

Elemental analysis: Calcd. for $C_{25}H_{21}AuCl_3N_3O_4$: C, 41.09; H, 2.90; N, 5.75. Found: C, 40.78; H, 2.87; N, 5.71%.

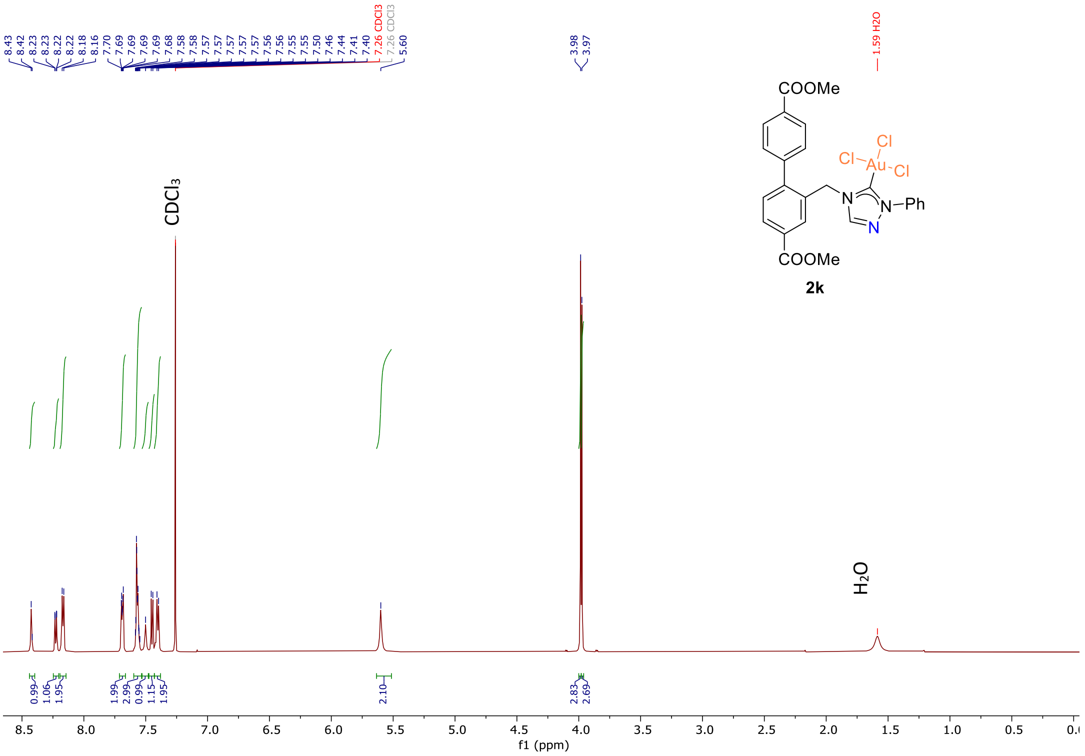


Figure S40. ^{1}H NMR spectrum of (abpdc-NHC^{Ph})AuCl$_3$ (**2k**) (600 MHz, CDCl$_3$).

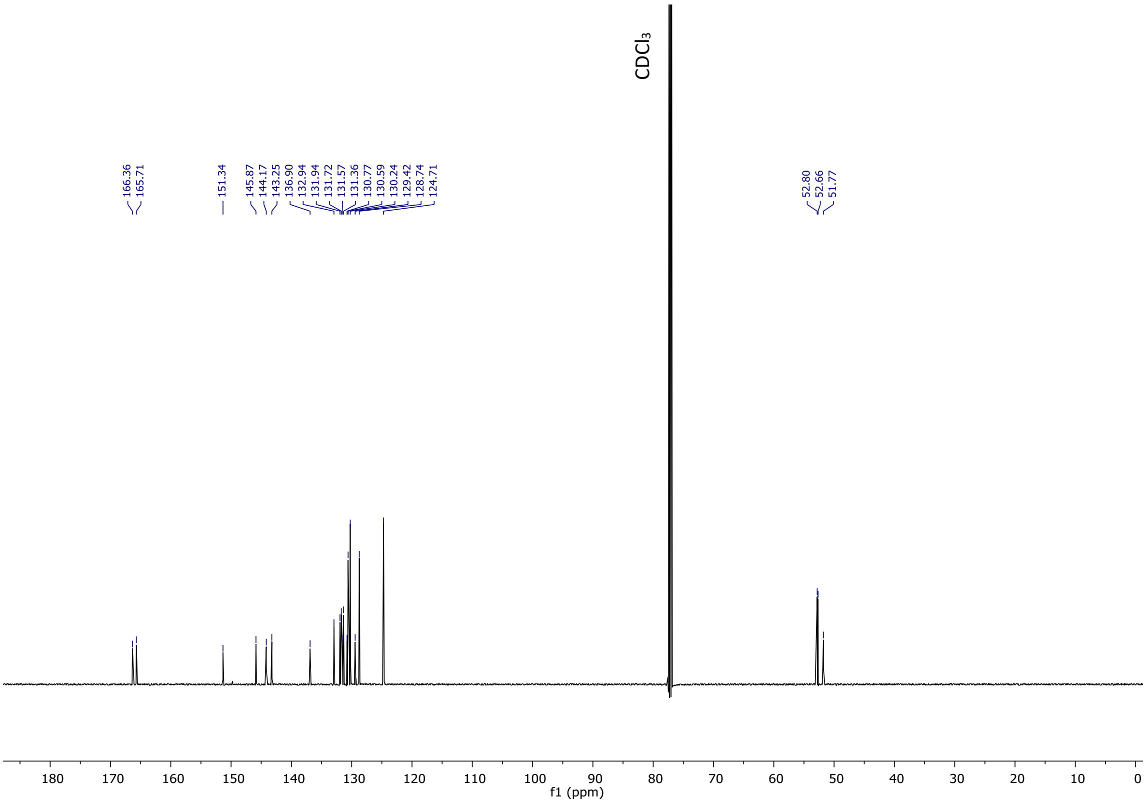


Figure S41. ^{13}C NMR spectrum of (abpdc-NHC^{Ph})AuCl$_3$ (**2k**) (150 MHz, CDCl$_3$).

5. Crystallographic data

Single crystal diffraction data was acquired on a Bruker D8 Venture equipped with a Photon 100 detector and using Mo Kα radiation (λ = 0.71073 Å) from an Incoatec iµS microsource. Data reduction was performed with the Bruker Apex3 Suite,[12] the structure was solved with ShelXT[13] and refined with ShelXL.[14] Olex2 was used as user interface.[15] The CIF files were edited with enCIFer v1.4,[16] and molecular graphics were produced with Mercury 4.2.0.[17]

Full details of the data collection, structure solution and refinement are contained in the CIF file, available as ESI and from https://www.ccdc.cam.uk/ (CCDC numbers: 1960925 for **4b**, 1960926 for **2k**, 1960927 for **2j**, 1960928 for **2i**, 1960929 for **3b** and 1960930 for **1j**) and are summarized in Table S1.

Table S1. Crystallographic data

Crystal data	**1j**	**2i**	**2j**	**2k**	**3b**	**4b**
Chemical formula	$C_{26}H_{22}AuClN_2O_4$	$C_9H_{10}AuCl_3N_2$	$C_{26}H_{22}AuCl_3N_2O_4{\cdot}CHCl_3$	$C_{25}H_{21}AuCl_3N_3O_4{\cdot}CH_2Cl_2$	$C_7H_{10}AuCl_5N_2$	$C_7H_{12}AuCl_5N_2$
M_r	658.88	449.51	849.14	815.69	496.39	498.41
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$	Tetragonal, $P4_2/n$
Temperature (K)	100	100	100	100	100	100
a, b, c (Å)	8.684 (2), 20.099 (5), 13.321 (3)	7.793 (5), 13.984 (9), 11.539 (7)	14.9973 (15), 12.2343 (12), 17.0500 (17)	19.4915 (14), 15.0501 (11), 21.4077 (16)	8.5971 (4), 14.5741 (7), 10.8547 (5)	19.5310 (11), 19.5310 (11), 7.6932 (4)
β (°)	91.35 (1)	100.78 (2)	103.282 (2)	113.209 (2)	99.788 (1)	
V (Å^3)	2324.4 (9)	1235.3 (14)	3044.7 (5)	5771.7 (7)	1340.24 (11)	2934.6 (4)
Z	4	4	4	8	4	8
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	6.48	12.53	5.40	5.60	11.94	10.91
Crystal size (mm)	0.41 × 0.20 × 0.18	0.21 × 0.20 × 0.15	0.33 × 0.17 × 0.12	0.27 × 0.10 × 0.08	0.26 × 0.22 × 0.17	0.26 × 0.16 × 0.12
Diffractometer	Bruker Photon100 area detector	Bruker D8 Venture	Bruker D8 Venture	Bruker D8 Venture	Bruker D8 Venture	Bruker D8 Venture
Absorption correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan	Multi-scan	Multi-scan
T_{min}, T_{max}	0.440, 0.746	0.554, 0.746	0.551, 0.746	0.538, 0.746	0.521, 0.746	0.330, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	23470, 7051, 6777	12193, 3761, 3276	36599, 7604, 6765	84147, 19243, 14959	21790, 4095, 4000	17021, 5342, 4292
R_{int}	0.019	0.029	0.035	0.045	0.020	0.041
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.716	0.716	0.669	0.736	0.716	0.758
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.022, 0.068, 1.14	0.022, 0.051, 1.02	0.022, 0.056, 1.03	0.035, 0.083, 1.03	0.019, 0.083, 1.49	0.028, 0.054, 1.03
No. of reflections	7051	3761	7604	19243	4095	5342
No. of parameters	309	138	363	722	138	138
CCDC no.	1960930	1960928	1960927	1960926	1960929	1960925

Crystallographic structure determination of 1j

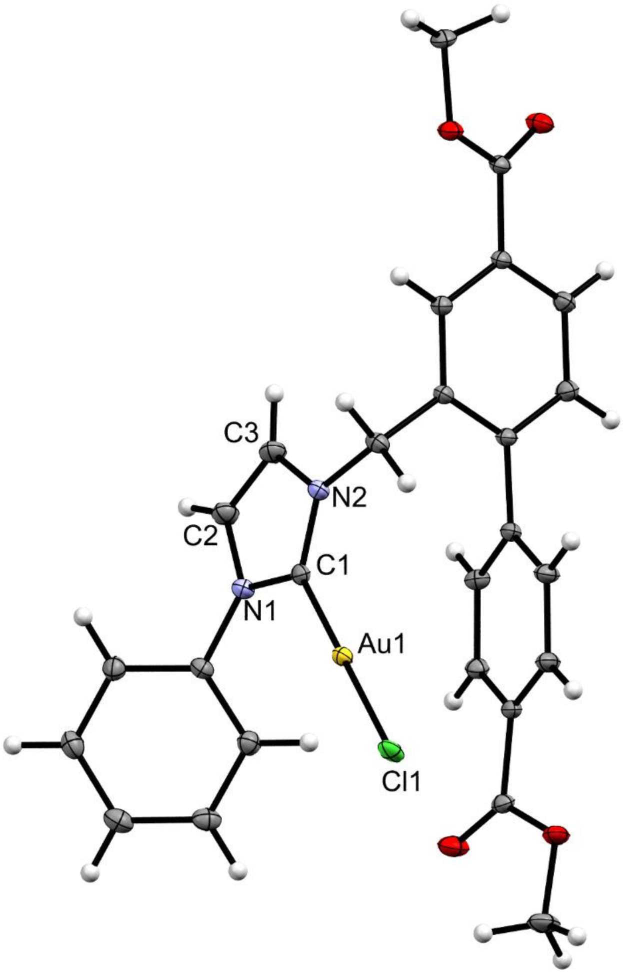


Figure S42. ORTEP plot of **1j** with 50% ellipsoids. Selected bond distances (Å) and angles (°): Cl1-Au1 2.3366(8), Au1-C1 1.986(3), C1-N2 1.359(3), C1-N1 1.365(4); C1-Au1-Cl1 178.91(7), N1-C1-Au1 128.0(2), Au1-C1-N2 127.7(2), N1-C1-N2 104.2(2).

Crystallographic structure determination of 2i

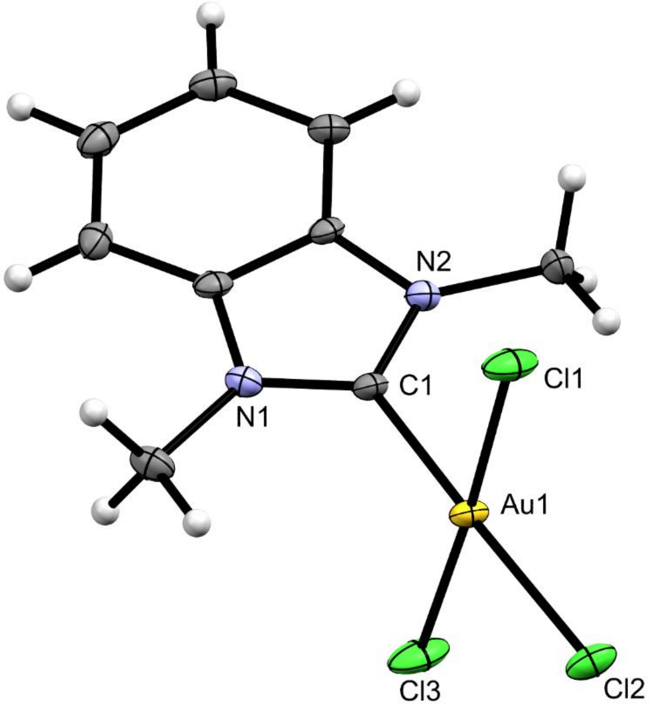


Figure S43. ORTEP plot of **2i** with 50% ellipsoids. Selected bond distances (Å) and angles (º): C1-Au1 2.008(3), Au1-Cl2 2.321(1), Cl3-Au1 2.276(2), Au1-Cl1 2.281(2); C1-Au1-Cl1 90.19(8), Cl1-Au1-Cl2 91.36(3), Cl2-Au1-Cl3 91.74(3), Cl3-Au1-C1 86.76(8).

Crystallographic structure determination of 2j

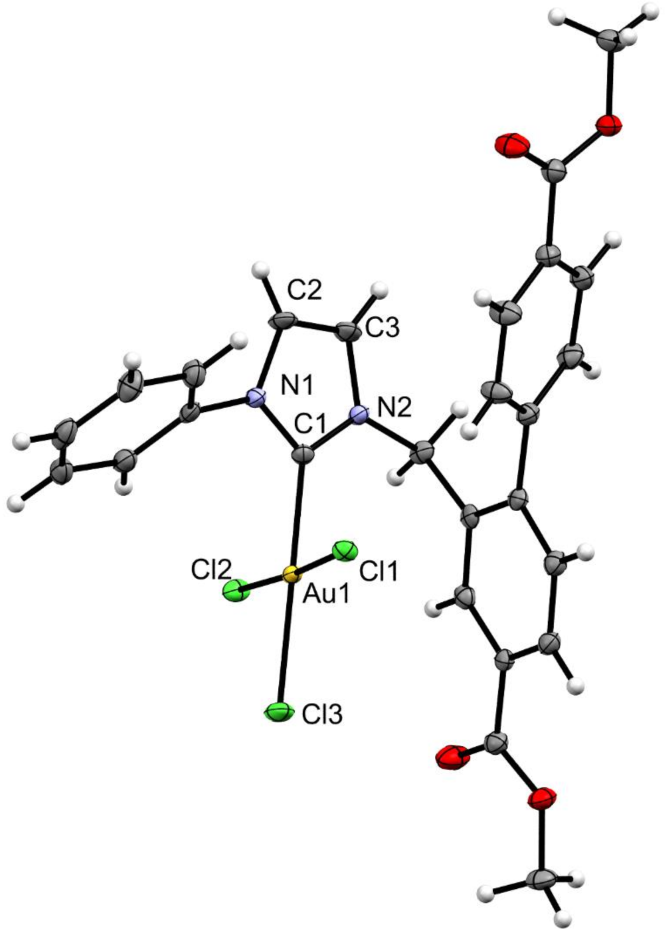


Figure S44. ORTEP plot of **2j** with 50% ellipsoids. Selected bond distances (Å) and angles (°): C1-Au1 2.003(3), Au1-Cl3 2.3144(7), Cl2-Au1 2.2952(7), Cl1-Au1 2.3004(7), N1-C1 1.347(3), C1-N2 1.337(3); C1-Au1-Cl1 87.12(8), Cl2-Au1-Cl3 91.38(3), Cl3-Au1-Cl1 91.47(3), C1-Au1-Cl2 90.00(8)

Crystallographic structure determination of 2k

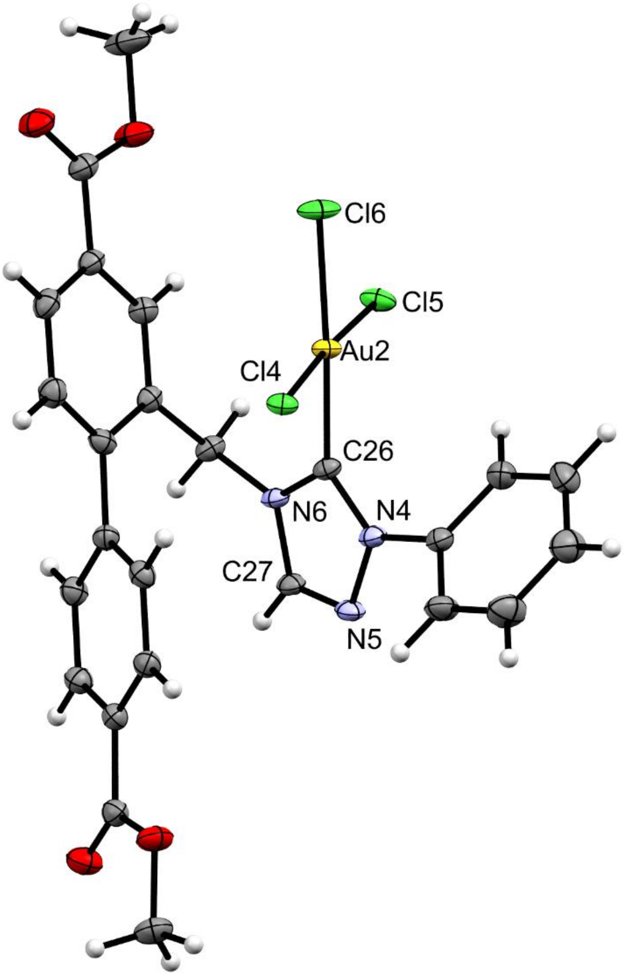


Figure S45. ORTEP plot of **2k** with 50% ellipsoids. Selected bond distances (Å) and angles (°): C26-Au2 2.009(4), Cl6-Au2 2.314(1), Au2-Cl4 2.303(1), Au2-Cl5 2.294(1), N4-C26 1.332(4), C26-N6 1.346(4), N6-C27 1.366(5), C27-N5 1.299(4), N5-N4 1.379(5); Cl6-Au2-Cl5 91.43(4), Cl6-Au2-Cl4 90.99(3), Cl4-Au2-C26 89.3(1), C26-Au2-Cl5 88.5(1), N6-C26-Au2 125.8(2), Au2-C26-N4 128.3(3), N6-C26-N4 105.8(3).

Crystallographic structure determination of 3b

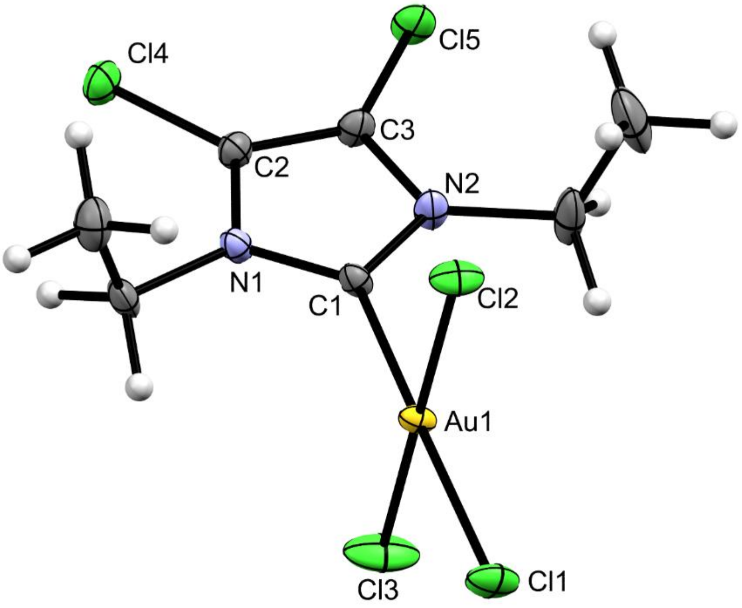


Figure S46. ORTEP plot of **3b** with 50% ellipsoids. Selected bond distances (Å) and angles (°): C1-Au1 2.004(3), Au1-Cl1 2.304(1), Au1-Cl2 2.273(1), Au-Cl3 2.271(1), C2-C3 1.349(6), C2-Cl4 1.692(4), C3-Cl5 1.691(4), C1-Au-Cl1 178.4(1), C1-Au-Cl2 86.9(1), C1-Au-Cl3 90.7(1), Cl4-C2-C3 128.4(3), Cl5-C3-C2 129.3(3).

Crystallographic structure determination of 4b

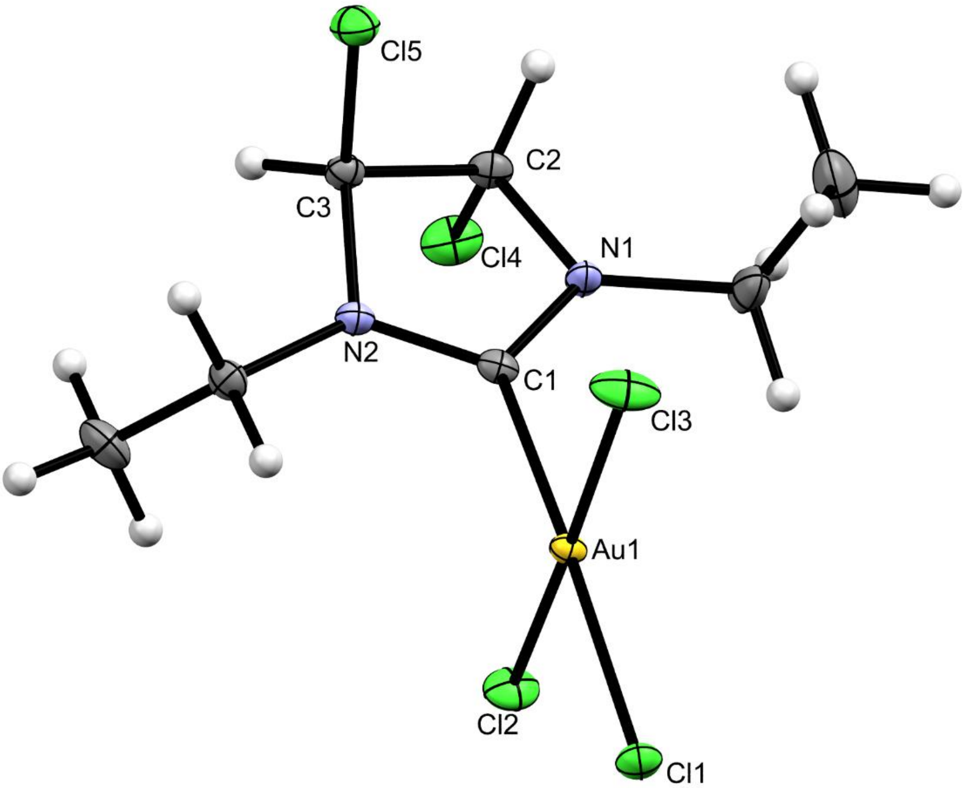


Figure S47. ORTEP plot of **4b** with 50% ellipsoids. Selected bond distances (Å) and angles (°): C1-Au1 1.993(3), Au1-Cl1 2.3192(8), Au1-Cl3 2.2744(9), Au1-Cl2 2.2782(9), C2-C3 1.517(4), C3-Cl5 1.805(3), C2-Cl4 1.809(3), C1-Au-Cl1 177.14(9), C1-Au-Cl3 87.57(9), C1-Au-Cl2 87.63(9), Cl5-C3-C2 109.0(2), Cl4-C2-C3 109.4(2).

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