# Electronic Supplementary Information for 

# Catalytic domino amination and oxidative coupling of gold acetylides and isolation of key vinylene digold intermediates as a new class of ditopic $\mathbf{N}$-heterocyclic carbene complexes 

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## General Information:

Unless otherwise stated, all reactions and manipulations were performed using standard Schlenk techniques. All solvents were purified by distillation using standard methods. Commercially available reagents were used without further purification. NMR spectra were recorded by using a Bruker 400 MHz spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ( ${ }^{1} \mathrm{H}$ NMR $\mathrm{CDCl}_{3}: 7.26$ ppm; ${ }^{13} \mathrm{C}$ NMR $\mathrm{CDCl}_{3}: 77.0 \mathrm{ppm} ;{ }^{13} \mathrm{C}$ NMR DMSO: 39.43 ppm ). Mass spectra were recorded on the HP-5989 instrument by EI/ESI methods. X-ray diffraction analysis was performed by using a Bruker Smart-1000X-ray diffractometer.

Propiolic acid is commercially available and was used as received without further purification. Compounds 1a, $\mathbf{1 b}$ were synthesized by the procedures we previously reported. ${ }^{1}$ $\mathrm{IPrAuOH}^{2}$ was prepared according to literature methods.

## Preparation and characterization

## Synthesis of complex 4a

The mixture of $\mathbf{1 a}(100 \mathrm{mg}, 0.24 \mathrm{mmol})$ and ethyldiisopropylamine ( $31 \mathrm{mg}, 0.24 \mathrm{mmol}$ ) was stirred in the DCE ( 3 mL ) at $25^{\circ} \mathrm{C}$, and then $\mathrm{AuCl} \cdot \mathrm{Me}_{2} \mathrm{~S}(141 \mathrm{mg}, 0.48 \mathrm{mmol})$ was added. After stirring for 20 min , all volatiles were removed under vacuum, the resultant solid was solvents in DCM, and filtered through a pad of Celite. The rude product was washed twice with diethyl ether to afford pure $\mathbf{4 a}$ as a yellow-green solid ( $218 \mathrm{mg}, 90 \%$ ). ${ }^{1} \mathrm{H}$ NMR ( 400 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta=8.47(\mathrm{~s}, 1 \mathrm{H}), 8.27(\mathrm{~s}, 1 \mathrm{H}), 7.47-7.40(\mathrm{~m}, 2 \mathrm{H}), 7.26-7.20(\mathrm{~m}, 4 \mathrm{H}), 3.95-3.86$ (m, 2H), 3.31-3.23 (m, 2H), 2.91-2.82 (m, 2H), 2.73-2.65 (m, 2H), $1.54(\mathrm{~d}, J=6.4 \mathrm{~Hz}, 12 \mathrm{H})$, 1.49-1.43 (m, 12H), $1.22(\mathrm{~d}, J=6.4 \mathrm{~Hz}, 6 \mathrm{H}), 1.18-1.15(\mathrm{~m}, 9 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta=184.28,156.96,151.09,146.79,145.15,144.43,139.07,132.23,130.84,124.46,54.75$, 42.95, 28.91, 28.70, 24.57, 24.30, 24.00, 19.05, 17.71, 12.48; HRMS (ESI): m/z [2M-AuCl$\left.2\left[\mathrm{~N}\left({ }^{( } \mathrm{Pr}\right)_{2} \mathrm{Et} \cdot \mathrm{HCl}\right]+\mathrm{H}\right]^{+}$calcd. for $\mathrm{C}_{56} \mathrm{H}_{71} \mathrm{Au}_{3} \mathrm{ClN}_{4} \mathrm{O}_{2}^{+}: 1457.4262$; found: 1457.4268. Anal. Calcd. For $\mathrm{C}_{36} \mathrm{H}_{55} \mathrm{Au}_{2} \mathrm{Cl}_{2} \mathrm{~N}_{3} \mathrm{O} \cdot 0.5\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right)$ : C, 41.63; H, 5.36; N, 3.99; Found: C, 41.83; H, 5.46; N, 3.97 \%.

## Synthesis of complex 4b

Following a similar procedure to that described for $\mathbf{4 a}$, the mixture of $\mathbf{1 b}(100 \mathrm{mg}, 0.30$ $\mathrm{mmol})$, ethyldiisopropylamine ( $39 \mathrm{mg}, 0.30 \mathrm{mmol}$ ) and $\mathrm{AuCl} \cdot \mathrm{Me}_{2} \mathrm{~S}(176 \mathrm{mg}, 0.60 \mathrm{mmol})$ was stirred in the DCE $(3 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ to afford pure $\mathbf{4 b}$ as a green solid $(255 \mathrm{mg}, 92 \%) .{ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta=8.46(\mathrm{~s}, 1 \mathrm{H}), 8.12(\mathrm{~s}, 1 \mathrm{H}), 6.95(\mathrm{~d}, J=6.4 \mathrm{~Hz}, 4 \mathrm{H}), 3.99-3.86(\mathrm{~m}, 2 \mathrm{H})$, 3.34-3.23 (m, 2H), $2.29(\mathrm{~d}, J=4.4 \mathrm{~Hz}, 6 \mathrm{H}), 2.24(\mathrm{~s}, 6 \mathrm{H}), 2.12(\mathrm{~s}, 6 \mathrm{H}), 1.59-1.56(\mathrm{~m}, 9 \mathrm{H})$, $1.46(\mathrm{~d}, J=6.8 \mathrm{~Hz}, 6 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta=183.43,156.46,151.99,147.26$, $140.19,139.89,139.58,134.16,133.44,132.82,129.57,54.76,43.49,42.99,21.07,19.08$, 17.98, 17.67, 12.56; HRMS (ESI): m/z [2M-2[N( $\left.\left.\left.{ }^{( } \mathrm{Pr}\right)_{2} \mathrm{Et} \cdot \mathrm{HCl}\right]-\mathrm{Cl}+\mathrm{CH}_{3} \mathrm{OH}\right]^{+}$calcd. for $\mathrm{C}_{45} \mathrm{H}_{50} \mathrm{Au}_{4} \mathrm{ClN}_{4} \mathrm{O}_{3}{ }^{+}$: 1517.2234 ; found: 1517.2990. Anal. Calcd. For $\mathrm{C}_{30} \mathrm{H}_{43} \mathrm{Au}_{2} \mathrm{Cl}_{2} \mathrm{~N}_{3} \mathrm{O} \cdot 0.5$ $\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right): \mathrm{C}, 37.81 ; \mathrm{H}, 4.58 ; \mathrm{N}, 4.34$; Found: C, $38.05 ; \mathrm{H}, 4.97 ; \mathrm{N}, 4.27 \%$.

## Synthesis of complex 4c

The mixture of $\mathbf{4 a}(100 \mathrm{mg}, 0.1 \mathrm{mmol})$ and $\mathrm{PPh}_{3} \operatorname{AgOTf}(103 \mathrm{mg}, 0.2 \mathrm{mmol})$ was stirred in the DCE ( 2.5 mL ) at $25^{\circ} \mathrm{C}$ for 3 h . All volatiles were removed under vacuum, the resultant solid was solvents in DCM, and filtered through a pad of Celite. Water ( 2 mL ) was added to the filtrate and vigorously stirred for a few minutes, the organic phase was transferred to a test tube and then the solvents were evaporated. The rude product was washed twice with diethyl ether to afford pure $\mathbf{4 c}$ as a yellow solid ( $108 \mathrm{mg}, 73 \%$ ). ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta=8.60$ $(\mathrm{d}, J=1.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.68-7.64(\mathrm{~m}, 1 \mathrm{H}), 7.63-7.57(\mathrm{~m}, 4 \mathrm{H}), 7.52(\mathrm{q}, J=6.4,4 \mathrm{H}), 7.45-7.35(\mathrm{~m}$, 9H), 7.34-7.31 (m, 4H), 7.30-7.27 (m, 4H), $7.21(\mathrm{td}, J=7.8,2.3 \mathrm{~Hz}, 5 \mathrm{H}), 7.04(\mathrm{dd}, J=12.8$, $7.2 \mathrm{~Hz}, 5 \mathrm{H}), 2.96-2.85(\mathrm{~m}, 2 \mathrm{H}), 2.77-2.65(\mathrm{~m}, 2 \mathrm{H}), 1.29(\mathrm{~d}, J=6.8 \mathrm{~Hz}, 6 \mathrm{H}), 1.27-1.18(\mathrm{~m}$, $18 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta=201.15\left(\mathrm{~d},{ }^{2} J_{\mathrm{P}-\mathrm{C}}=133.2 \mathrm{HZ}\right), 167.89\left(\mathrm{~d},{ }^{2} J_{\mathrm{P}-\mathrm{C}}=116.7\right.$ HZ), 157.67, 157.37, 149.77, 144.81, 138.28, 134.20, 133.44, 132.92, 131.86, 131.44, 130.02, $129.54,129.10,128.37,127.08,126.78,125.12,124.73,29.14,28.83,24.30 ;{ }^{31} \mathrm{P}$ NMR (162 $\mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta=41.70$ (s), 40.65 (s). HRMS (MALDI): m/z [M-OTf] ${ }^{+}$calcd. for $\mathrm{C}_{64} \mathrm{H}_{65} \mathrm{Au}_{2} \mathrm{~N}_{2} \mathrm{OP}_{2}{ }^{+}$: 1333.3903; found: 1333.3723. Anal. Calcd. For $\mathrm{C}_{65} \mathrm{H}_{65} \mathrm{Au}_{2} \mathrm{~F}_{3} \mathrm{~N}_{2} \mathrm{O}_{4} \mathrm{P}_{2} \mathrm{~S}^{2} \mathrm{CH}_{2} \mathrm{Cl}_{2}$ : C, 50.55; H, 4.31; N, 1.79; Found: C, 50.29; H, 4.45; N, 1.72 \%.

## Synthesis of complex 5a

## From the reaction of 4 a with AgOTf:

The mixture of $\mathbf{4 a}(100 \mathrm{mg}, 0.10 \mathrm{mmol})$ and silver triflate $(26 \mathrm{mg}, 0.10 \mathrm{mmol})$ was stirred in the DCE ( 1.5 mL ) at $25^{\circ} \mathrm{C}$. After stirring for 8 h , all volatiles were removed under vacuum, the resultant solid was solvents in DCM, and filtered through a pad of Celite. Water ( 2 mL ) was added to the filtrate and vigorously stirred for a few minutes, the organic phase was transferred to a test tube and then the solvents were evaporated. The rude product was washed twice with diethyl ether to afford pure 5a as a yellow solid ( $49 \mathrm{mg}, 76 \%$ ). ${ }^{1} \mathrm{H}$ NMR ( 400 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta=8.60(\mathrm{~s}, 1 \mathrm{H}), 7.52-7.45(\mathrm{~m}, 2 \mathrm{H}), 7.36-7.28(\mathrm{~m}, 3 \mathrm{H}), 7.25-7.21(\mathrm{~m}, 1 \mathrm{H}), 3.18-3.08$ $(\mathrm{m}, 1 \mathrm{H}), 2.94-2.84(\mathrm{~m}, 1 \mathrm{H}), 2.84-2.70(\mathrm{~m}, 2 \mathrm{H}), 1.55(\mathrm{~d}, J=6.7 \mathrm{~Hz}, 3 \mathrm{H}), 1.40(\mathrm{~d}, J=6.7 \mathrm{~Hz}$, $3 \mathrm{H}), 1.28-1.20(\mathrm{~m}, 18 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $\left.100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta=187.83,154.33,150.39,146.26$, $145.74,144.81,143.46,138.98,132.45,131.62,130.11,125.54,125.19,124.36,43.45,29.45$, 29.37, 29.14, 24.51, 23.97; HRMS (ESI): m/z $[\mathrm{M}-\mathrm{Cl}]^{+}$calcd. for $\mathrm{C}_{56} \mathrm{H}_{70} \mathrm{Au}_{2} \mathrm{ClN}_{4} \mathrm{O}_{2}{ }^{+}$: 1259.4518; found: 1259.4514. Anal. Calcd. For $\mathrm{C}_{56} \mathrm{H}_{70} \mathrm{Au}_{2} \mathrm{Cl}_{2} \mathrm{~N}_{4} \mathrm{O}_{2}$ : C, 51.90; H, 5.44; N , 4.32; Found: C, 51.96; H, 5.64; N, 4.33 \%.

## From the reaction of 4 c in the presence of $\mathrm{AuCl} \cdot \mathrm{Me}_{2} \mathrm{~S}$ :

The mixture of $\mathbf{4 c}(50 \mathrm{mg}, 0.034 \mathrm{mmol})$ and $\mathrm{AuCl} \cdot \mathrm{Me}_{2} \mathrm{~S}(20 \mathrm{mg}, 0.068 \mathrm{mmol})$ was stirred in the DCE ( 1 mL ) at $25^{\circ} \mathrm{C}$ for 24 h . All volatiles were then removed under vacuum, and afford 5a in a $68 \%$ NMR yield.

## From the $\mathrm{AuCl} \cdot \mathrm{Me}_{2} \mathrm{~S}$-catalyzed reaction of 1 a in the presence of ethyldiisopropylamine and $\mathrm{PhI}(\mathrm{OAc})_{2}$ :

The mixture of $1 \mathbf{a}(100 \mathrm{mg}, 0.24 \mathrm{mmol})$, ethyldiisopropylamine ( $31 \mathrm{mg}, 0.24 \mathrm{mmol}$ ), $\mathrm{AuCl} \cdot \mathrm{Me}_{2} \mathrm{~S}(78 \mathrm{mg}, 0.26 \mathrm{mmol})$ and $\mathrm{PhI}(\mathrm{OAc})_{2}(77 \mathrm{mg}, 0.24 \mathrm{mmol})$ was stirred in the DCE (3 mL ) at $80^{\circ} \mathrm{C}$. After stirring for 3 h , all volatiles were removed under vacuum, the resultant solid was solvents in DCM, and filtered through a pad of Celite. Water ( 2 mL ) was added to the filtrate and vigorously stirred for a few minutes, the organic phase was transferred to a test tube and then the solvents were evaporated. The rude product was washed twice with diethyl ether to afford pure $\mathbf{5 a}$ as a yellow solid ( $106 \mathrm{mg}, 68 \%$ ).

## From the reaction of 1 a with $\mathrm{AuCl} \cdot \mathrm{Me}_{2} \mathrm{~S}$ in the presence of ethyldiisopropylamine:

The mixture of $\mathbf{1 a}(100 \mathrm{mg}, 0.24 \mathrm{mmol})$, ethyldiisopropylamine ( $31 \mathrm{mg}, 0.24 \mathrm{mmol}$ ) and $\mathrm{AuCl} \cdot \mathrm{Me}_{2} \mathrm{~S}(141 \mathrm{mg}, 0.48 \mathrm{mmol})$ was stirred in the $\mathrm{DCE}(3 \mathrm{~mL})$ at $80^{\circ} \mathrm{C}$. After stirring for 8 $h$, all volatiles were removed under vacuum, the resultant solid was solvents in DCM, and filtered through a pad of Celite. Water ( 2 mL ) was added to the filtrate and vigorously stirred for a few minutes, the organic phase was transferred to a test tube and then the solvents were evaporated. The rude product was washed twice with diethyl ether to afford a mixture of $\mathbf{5 a}$ and $\mathbf{6 a}$ in the ratio of $5: 1$ with a conversion of one hundred percent.

## From heating 4a in the DCE at $80{ }^{\circ} \mathrm{C}$ :

4a (100 mg, 0.10 mmol ) was stirred in the DCE $(1.5 \mathrm{~mL})$ at $80^{\circ} \mathrm{C}$. After stirring for 8 h , all volatiles were removed under vacuum, the resultant solid was solvents in DCM, and filtered through a pad of Celite. Water ( 2 mL ) was added to the filtrate and vigorously stirred for a few minutes, the organic phase was transferred to a test tube and then the solvents were evaporated. The rude product was washed twice with diethyl ether to afford mixture of 5a and 6a in the ratio of $5: 1$ with a conversion of one hundred percent.

## From heating 7 in the presence of $\mathrm{AuCl} \cdot \mathrm{Me}_{2} \mathrm{~S}$ at $60{ }^{\circ} \mathrm{C}$ :

The mixture of $7(50 \mathrm{mg}, 0.05 \mathrm{mmol})$ and $\mathrm{AuCl} \cdot \mathrm{Me}_{2} \mathrm{~S}(18 \mathrm{mg}, 0.06 \mathrm{mmol})$ was stirred in the DCE ( 1 mL ) at $60^{\circ} \mathrm{C}$. After stirring for 8 h , all volatiles were then removed under vacuum, and afford $\mathbf{5 a}$ in a $67 \%$ NMR yield.

## Synthesis of complex 5b

## From the reaction of $\mathbf{4 b}$ with $A g O T f:$

Following a similar procedure to that described for $\mathbf{5 a}$, the mixture of $\mathbf{4 b}(100 \mathrm{mg}, 0.11$ $\mathrm{mmol})$ and silver triflate ( $28 \mathrm{mg}, 0.11 \mathrm{mmol}$ ) was stirred in the DCE $(3 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ to afford pure $\mathbf{5 b}$ as a yellow solid ( $58 \mathrm{mg}, 94 \%$ ). ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta=8.36(\mathrm{~s}, 1 \mathrm{H}), 7.03-$ $6.93(\mathrm{~m}, 4 \mathrm{H}), 2.43(\mathrm{~s}, 3 \mathrm{H}), 2.32-2.21(\mathrm{~m}, 12 \mathrm{H}), 2.14(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C} \mathrm{NMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta=$ 187.34, 153.49, 151.18, 141.30, 140.96, 139.62, 134.56, 134.27, 133.37, 132.70, 130.81,
130.20, 129.83, 43.46, 21.15, 18.93, 18.21, 17.85, 17.55; HRMS (ESI): m/z [M-Cl] ${ }^{+}$calcd. for $\mathrm{C}_{44} \mathrm{H}_{46} \mathrm{Au}_{2} \mathrm{ClN}_{4} \mathrm{O}_{2}^{+}$: 1091.2640; found: 1091.2635. Anal. Calcd. For $\mathrm{C}_{44} \mathrm{H}_{46} \mathrm{Au}_{2} \mathrm{Cl}_{2} \mathrm{~N}_{4} \mathrm{O}_{2} \cdot \mathrm{CH}_{2} \mathrm{Cl}_{2}$ : C, 44.57; H, 3.99; N, 4.62; Found: C, 44.89; H, 4.09; N, $4.51 \%$.

## From the $\mathrm{AuCl} \cdot \mathrm{Me}_{2} \mathrm{~S}$-catalyzed reaction of 1 b in the presence of ethyldiisopropylamine and $\mathrm{PhI}(\mathrm{OAc})_{2}$ :

The mixture of $\mathbf{1 b}(100 \mathrm{mg}, 0.30 \mathrm{mmol})$, ethyldiisopropylamine ( $39 \mathrm{mg}, 0.30 \mathrm{mmol}$ ), $\mathrm{AuCl} \cdot \mathrm{Me}_{2} \mathrm{~S}(97 \mathrm{mg}, 0.33 \mathrm{mmol})$ and $\mathrm{PhI}(\mathrm{OAc})_{2}(97 \mathrm{mg}, 0.30 \mathrm{mmol})$ was stirred in the DCE $(3.5 \mathrm{~mL})$ at $80{ }^{\circ} \mathrm{C}$. After stirring for 3 h , all volatiles were removed under vacuum, the resultant solid was solvents in DCM, and filtered through a pad of Celite. Water ( 2 mL ) was added to the filtrate and vigorously stirred for a few minutes, the organic phase was transferred to a test tube and then the solvents were evaporated. The rude product was washed twice with diethyl ether to afford pure $\mathbf{5 b}$ as a yellow solid ( $128 \mathrm{mg}, 76 \%$ ).

## From the oxidation reaction of $4 b$ in the presence of $\mathrm{PhI}(\mathrm{OAc})_{2}$ :

The mixture of $\mathbf{4 b}(100 \mathrm{mg}, 0.11 \mathrm{mmol})$ and $\mathrm{PhI}(\mathrm{OAc})_{2}(35 \mathrm{mg}, 0.11 \mathrm{mmol})$ was stirred in the $\mathrm{DCE}(1.5 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$. After stirring for 12 h , all volatiles were removed under vacuum, the resultant solid was solvents in DCM, and filtered through a pad of Celite. Water ( 2 mL ) was added to the filtrate and vigorously stirred for a few minutes, the organic phase was transferred to a test tube and then the solvents were evaporated. The rude product was washed twice with diethyl ether to afford pure $\mathbf{5 b}$ as a yellow solid ( $102 \mathrm{mg}, 82 \%$ ).

## From the reaction of $\mathbf{1 b}$ with $\mathrm{AuCl} \cdot \mathrm{Me}_{2} \mathrm{~S}$ in the presence of ethyldiisopropylamine:

The mixture of $\mathbf{1 b}(100 \mathrm{mg}, 0.30 \mathrm{mmol})$, ethyldiisopropylamine ( $39 \mathrm{mg}, 0.30 \mathrm{mmol}$ ) and $\mathrm{AuCl} \cdot \mathrm{Me}_{2} \mathrm{~S}(176 \mathrm{mg}, 0.60 \mathrm{mmol})$ was stirred in the DCE $(3 \mathrm{~mL})$ at $80^{\circ} \mathrm{C}$. After stirring for 8 $h$, all volatiles were removed under vacuum, the resultant solid was solvents in DCM, and filtered through a pad of Celite. Water $(2 \mathrm{~mL})$ was added to the filtrate and vigorously stirred for a few minutes, the organic phase was transferred to a test tube and then the solvents were evaporated. The rude product was washed twice with diethyl ether to afford a mixture of $\mathbf{5 b}$ and $\mathbf{6 b}$ in the ratio of $3: 1$ with a conversion of one hundred percent.

## From heating 4 b in the DCE at $80^{\circ} \mathrm{C}$ :

4b ( $100 \mathrm{mg}, 0.11 \mathrm{mmol}$ ) was dissolved in the $\mathrm{DCE}(1.5 \mathrm{~mL})$ and stirred at $80^{\circ} \mathrm{C}$. After stirring for 8 h , all volatiles were removed under vacuum, the resultant solid was solvents in DCM, and filtered through a pad of Celite. Water ( 2 mL ) was added to the filtrate and vigorously stirred for a few minutes, the organic phase was transferred to a test tube and then the solvents were evaporated. The rude product was washed twice with diethyl ether to afford a mixture of $\mathbf{5 b}$ and $\mathbf{6 b}$ in the ratio of 3:1 with a conversion of one hundred percent.

## Synthesis of complex 6a and 6b

4a,4b $\xrightarrow[\substack{8 \mathrm{~h} \\ \mathbf{6} \mathbf{a}, 89 \% \\ \mathbf{6 b}, 91 \%}]{150^{\circ} \mathrm{C}} \mathbf{6 a , 6 b}$

Scheme S1 Formation of $\mathbf{6 a}$ or $\mathbf{6 b}$ by heating 4a or $\mathbf{4 b}$ under neat condition

## From the reaction of heated 4a under neat condition to synthesis 6a:

$4 \mathbf{a}(100 \mathrm{mg}, 0.10 \mathrm{mmol})$ was heated at $150^{\circ} \mathrm{C}$ under neat condition. After stirring for 8 h , the resultant solid was solvents in DCM, and filtered through a pad of Celite. After washing the solid several times with DCM, and the solvents in the filtrate were evaporated. The rude product was washed twice with diethyl ether to afford pure $\mathbf{6 a}$ as a gray solid ( $58 \mathrm{mg}, 89 \%$ ). ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta=8.48(\mathrm{~s}, 1 \mathrm{H}), 7.56-7.49(\mathrm{~m}, 2 \mathrm{H}), 7.36-7.27(\mathrm{~m}, 4 \mathrm{H}), 6.88(\mathrm{~s}$, $1 \mathrm{H}), 2.81-2.69(\mathrm{~m}, 2 \mathrm{H}), 2.67-2.56(\mathrm{~m}, 2 \mathrm{H}), 1.50(\mathrm{~d}, J=6.8 \mathrm{~Hz}, 6 \mathrm{H}), 1.28-1.18(\mathrm{~m}, 18 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{DMSO}) ~ \delta=185.06,154.96,144.50,143.65,139.19,131.11,124.53,54.84$, 28.61, 23.52; HRMS (ESI): $\mathrm{m} / \mathrm{z}[2 \mathrm{M}-\mathrm{Cl}]^{+}$calcd. for $\mathrm{C}_{56} \mathrm{H}_{72} \mathrm{Au}_{2} \mathrm{ClN}_{4} \mathrm{O}_{2}{ }^{+}$: 1261.4675 ; found: 1261.4677. Anal. Calcd. For $\mathrm{C}_{28} \mathrm{H}_{36} \mathrm{AuClN}_{2} \mathrm{O} \cdot 0.5\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right): \mathrm{C}, 49.50 ; \mathrm{H}, 5.39$; N, 4.05; Found: C, 49.49; H, 5.48; N, 4.11 \%.

## From the reaction of heated $\mathbf{5 b}$ under neat condition to synthesis $\mathbf{6 b}$ :

Following a similar procedure to that described for $\mathbf{6 a}, \mathbf{4 b}(130 \mathrm{mg}, 0.14 \mathrm{mmol})$ afford $\mathbf{6 b}$ as a gray solid ( $71 \mathrm{mg}, 90 \%$ ). ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta=8.33(\mathrm{~s}, 1 \mathrm{H}), 7.04(\mathrm{~s}, 2 \mathrm{H}), 7.00$ (s, 2H), 6.91 (s, 1H), 2.33 (d, $J=8.4 \mathrm{~Hz}, 6 \mathrm{H}$ ), 2.24 (s, 6H), 2.16 ( $\mathrm{s}, 6 \mathrm{H}$ ); ${ }^{13} \mathrm{C}$ NMR ( 100 MHz , DMSO) $\delta=183.65,155.32,153.49,139.96,139.62,134.18,133.29,131.02,129.23,123.88$, 20.56, 17.39, 17.08; HRMS (ESI): m/z [2M-Cl] calcd. for $\mathrm{C}_{44} \mathrm{H}_{48} \mathrm{Au}_{2} \mathrm{ClN}_{4} \mathrm{O}_{2}{ }^{+}$: 1093.2797;
found: 1093.2794. Anal. Calcd. For $\mathrm{C}_{22} \mathrm{H}_{24} \mathrm{AuClN}_{2} \mathrm{O}^{2} \mathrm{CH}_{2} \mathrm{Cl}_{2}: \mathrm{C}, 42.51 ; \mathrm{H}, 4.03 ; \mathrm{N}, 4.31$; Found: C, 42.79; H, 4.14; N, 4.52 \%.

## Synthesis of complex 7

The mixture of $\mathbf{1 a}(60 \mathrm{mg}, 0.14 \mathrm{mmol})$ and $\mathrm{IPrAuOH}(84 \mathrm{mg}, 0.14 \mathrm{mmol})$ was stirred in the toluene $(1.5 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ for 8 h . All volatiles were removed under vacuum, the resultant solid was solvents in DCM, and filtered through a pad of Celite. The rude product was washed twice with pentane and dried under vacuum to afford pure 7 as a white microcrystalline solid (125 mg, 89\%). ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta=8.98(\mathrm{~s}, 1 \mathrm{H}), 7.51-$ $7.44(\mathrm{~m}, 2 \mathrm{H}), 7.35-7.28(\mathrm{~m}, 1 \mathrm{H}), 7.25-7.16(\mathrm{~m}, 6 \mathrm{H}), 7.12(\mathrm{~s}, 2 \mathrm{H}), 7.04(\mathrm{~s}, 3 \mathrm{H}), 2.92-2.78(\mathrm{~m}$, $4 \mathrm{H}), 2.52-2.38(\mathrm{~m}, 4 \mathrm{H}), 1.22-1.17(\mathrm{~m}, 30 \mathrm{H}), 1.10-1.01(\mathrm{~m}, 18 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (100 MHz, $\left.\mathrm{CDCl}_{3}\right)$ $\delta=175.32,163.07,147.12,146.84,146.28,145.55,133.94,130.71,129.59,124.42,123.76$, 123.50, 123.04, 28.73, 28.27, 24.44, 23.97, 23.02; HRMS (ESI): m/z $[\mathrm{M}+\mathrm{H}]^{+}$calcd. for $\mathrm{C}_{55} \mathrm{H}_{72} \mathrm{AuN}_{4} \mathrm{O}^{+}: 1001.5372$; found: 1001.5368. Anal. Calcd. For $\mathrm{C}_{55} \mathrm{H}_{71} \mathrm{AuN}_{4} \mathrm{O} \cdot 0.5\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right): \mathrm{C}$, 63.87; H, 6.95; N, 5.37; Found: C, 63.75; H, 7.00; N, 5.33 \%.

## Reference:

1. Lv, S.; Wang, J.; Zhang, C.; Xu, S.; Shi, M.; Zhang, J. Angew. Chem., Int. Ed. 2015, 54, 14941.
2. Nahra, F.; Patrick, S. R.; Collado, A.; Nolan, S. P. Polyhedron 2014, 84, 59.

## NMR Spectra:

## Complex 4a


ju-wjw-7021
C13CPD CDC13 \{D: \data\research\nev\2015-10-30\} man 2



## Complex 4b


ju-wjw-7402


Mes -
$180 \quad 170$ $160 \quad 150 \quad 140$ 120 110 f 1 (ppa)

## Complex 4c



P31CPD CDC13 \{D: \data\research\nes $\backslash 2016-10-14\}$ nar 16
(ipp-


## Complex 5a

151030-JU-NJW-0707

$\begin{array}{l}\mathrm{ju}-w \mathrm{jw}-8122 \\ \text { C13CPD } \\ \text { CDC13 }\end{array}$ \{D: \data $\backslash$ research $\backslash$ new $\left.\backslash 2015-11-30\right\}$ nmr 49



## Complex 5b

PROTON CDC13 \{D:\datalresearch\nev\2015-11-30\} rarr 29
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## Complex 6a


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## Complex 6b




## Complex 7




X-Ray Crystallography. Each crystal was mounted on a glass fiber. Crystallographic measurements were made on a Bruker Smart Apex 100 CCD area detector using graphite monochromated Mo-Karadiation ( $\lambda_{\mathrm{Mo}-\mathrm{K} \alpha}=0.71073 \AA$ ). The structures were solved by directed methods (SHELXS-97) and refined on $F^{2}$ by full-matrix least squares (SHELX-97) using all unique data. All the calculations were carried out with the SHELXTL18 program.

Key details of the crystal and structure refinement data are summarized in Table S1-S3. Further crystallographic details may be found in the respective CIF files, which were deposited at the Cambridge Crystallographic Data Centre, Cambridge, UK [CCDC 1440090 (4a); 1514554 (4c); 1440089 (5a)].


Figure S1. Molecular structures of $\mathbf{4 c}$ with $20 \%$ probability. The counterion ( (Off $^{-}$) in $\mathbf{4 c}$, and H atoms in aryl rings have been omitted for clarity.

Table S1. Crystal Data, Data Collection, and Structure Refinement for 4a, 4c and 5a。

|  | 4 a | 4c | 5a |
| :---: | :---: | :---: | :---: |
| Identification code | mo_51016b | mo_dm16665_0m | mo_51010b |
| Formula | $\begin{gathered} \mathrm{C}_{36} \mathrm{H}_{55} \mathrm{Au}_{2} \mathrm{Cl}_{2} \\ \mathrm{~N}_{3} \mathrm{O} \end{gathered}$ | $\begin{gathered} \mathrm{C}_{66} \mathrm{H}_{67} \mathrm{Au}_{2} \mathrm{Cl}_{2} \mathrm{~F}_{3} \\ \mathrm{~N}_{2} \mathrm{O}_{4} \mathrm{P}_{2} \mathrm{~S} \end{gathered}$ | $\begin{gathered} \mathrm{C}_{58} \mathrm{H}_{74} \mathrm{Au}_{2} \mathrm{Cl}_{4} \\ \mathrm{~N}_{4} \mathrm{O}_{2} \end{gathered}$ |
| Formula weight | 1010.66 | 1568.05 | 1394.94 |
| $T, \mathrm{~K}$ | 296(2) | 130 K | 296(2) |
| crystal system | Orthorhombic | Monoclinic | Trigonal |
| space group | P 212121 | P 1 21/n 1 | P 3221 |
| $a, \AA$ | 12.7762(14) | 18.1480(12) | 15.803(2) |
| $b, \AA$ | 17.0556(19) | 18.4838(12) | 15.803(2) |
| $c, \AA$ | 18.581(2) | 19.8362(14) | 21.901(3) |
| $\alpha$, deg | 90 | 90 | 90 |
| $\beta$, deg | 90 | 108.0470(10) | 90 |
| $\gamma, \operatorname{deg}$ | 90 | 90 | 120 |
| Volume, $\AA^{3}$ | 4048.9(8) | 6326.6(7) | 4736.5(15) |
| Z | 4 | 4 | 3 |
| $D_{\text {calc }}, \mathrm{Mg} / \mathrm{m}^{3}$ | 1.658 | 1.646 | 1.467 |
| absorption coefficient, $\mathrm{mm}^{-1}$ | 7.399 | 4.858 | 4.850 |
| $\mathrm{F}(000)$ | 1968 | 3096 | 2076 |
| crystal size, mm | $\begin{gathered} 0.180 \mathrm{x} 0.100 \mathrm{x} \\ 0.070 \end{gathered}$ | $0.3 \times 0.25 \times 0.2$ | $\begin{gathered} 0.500 \mathrm{x} 0.240 \mathrm{x} \\ 0.220 \end{gathered}$ |
| $2 \theta$ range, deg | 1.934 to 26.612 | 1.614 to 25.999 | 1.755 to 27.357 |
| reflections collected /unique | $\begin{gathered} 35920 / 8474 \\ {[\mathrm{R}(\mathrm{int})=0.0487]} \end{gathered}$ | $\begin{gathered} 45853 / 12444 \\ {[\mathrm{R}(\mathrm{int})=0.0241]} \end{gathered}$ | $\begin{gathered} 34011 / 7149 \\ {[\mathrm{R}(\text { int })=0.0393]} \end{gathered}$ |
| data / restraints/ parameters goodness of fit on $\mathrm{F}^{2}$ | $8474 / 26 / 416$ 0.998 | $12444 / 0 / 747$ 1.034 | $7149 / 1 / 328$ 1.052 |
| final R indices $[I>2 \sigma(I)]^{a}$ | $\begin{gathered} \mathrm{R} 1=0.0264, \\ \mathrm{wR} 2=0.0479 \end{gathered}$ | $\begin{gathered} \mathrm{R} 1=0.0251 \\ \mathrm{wR} 2=0.0547 \end{gathered}$ | $\begin{aligned} \mathrm{R} 1 & =0.0270, \mathrm{wR} 2 \\ & =0.0620 \end{aligned}$ |
| R indices (all data) | $\begin{gathered} \mathrm{R} 1=0.0395, \\ \mathrm{wR} 2=0.0514 \end{gathered}$ | $\begin{gathered} \mathrm{R} 1=0.0327 \\ \mathrm{wR} 2=0.0582 \end{gathered}$ | $\begin{aligned} \mathrm{R} 1= & 0.0380, \mathrm{wR} 2 \\ = & 0.0669 \end{aligned}$ |
| lgst diff peak and hole, e/ $/ \AA^{3}$ | 0.512 and -0.577 | 3.320 and -1.888 | 0.883 and -0.388 |


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