

# Supporting Information

## Anchoring Triazole-Gold(I) Complex into Porous Organic Polymer to Boost the Stability and Reactivity of Gold(I) Catalyst

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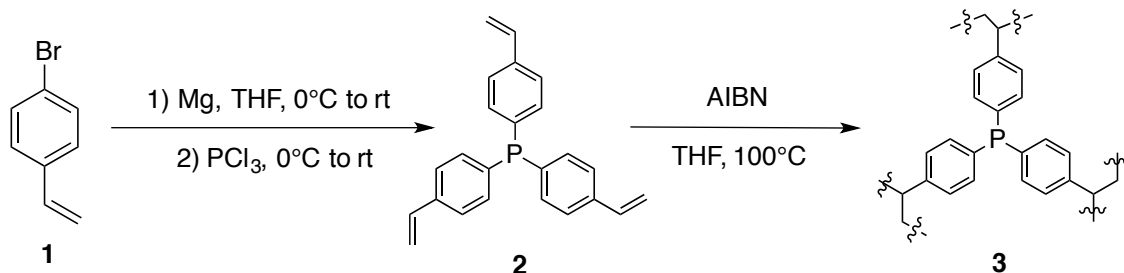
## I. General Methods and materials:

All of the reactions dealing with air and/or moisture-sensitive reactions were carried out under an atmosphere of nitrogen using oven/flame-dried glassware and standard syringe/septa techniques. Unless otherwise noted, all commercial reagents and solvents were obtained from the commercial provider and used without further purification.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on Agilent 400 MHz spectrometers/ Varian 500 MHz spectrometers. Chemical shifts were reported relative to internal tetramethylsilane ( $\delta$  0.00 ppm) for  $^1\text{H}$  NMR and  $\text{CDCl}_3$  ( $\delta$  77.0 ppm) for  $^{13}\text{C}$  NMR. Flash column chromatography was performed on 230-430 mesh silica gel. Analytical thin layer chromatography was performed with pre-coated glass baked plates (250 $\mu$ ) and visualized by UV lamp.

Nitrogen sorption isotherms at the temperature of liquid nitrogen were measured using Micromeritics ASAP 2020M and Tristar system. The samples were outgassed for 10 h at 80 $^\circ\text{C}$  before the measurements. XPS spectra were performed on a Thermo ESCALAB 250 with Al K $\alpha$  irradiation at  $\theta=90^\circ$  for X-ray sources, and the binding energies were calibrated using the C1s peak at 284.9 eV.  $^{31}\text{P}$  (161.8 MHz) MAS solid-state NMR experiments were recorded on a Varian infinity plus 400 spectrometer equipped with a magic-angle spin probe in a 4-mm  $\text{ZrO}_2$  rotor. IR spectra were recorded on a Nicolet Impact 410 FTIR spectrometer. The  $^{31}\text{P}$  NMR chemical shifts were referenced to the  $(\text{NH}_4)_2\text{HPO}_4$ . Transmission electron microscope (TEM) images were performed using a Hitachi HT-7700.

## II. General procedures:

### A. Preparation of the porous organic ligand (POP-PPh<sub>3</sub>):

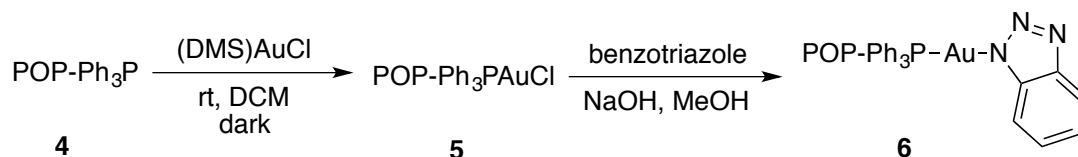


The preparation of porous organic ligand is adapted from literature report with slight modifications. (Sun, Q.; Jiang, M.; Shen, Z.; Jin, Y.; Pan, S.; Wang, L.; Meng, X.; Chen, W.; Ding, Y.; Li, J.; Xiao, F.-S. *Chem. Commun.* **2014**, *50*, 11844-11847.) The 4-bromostyrene **1** was purified freshly via vacuum distillation prior to usage. Magnesium strips (3.56 g, 146 mmol, 1.2 equiv) were cut into small pieces, placed in a flame-dried round-bottom flask, and protected with Ar. Freshly distilled THF (200 mL) was added to the flask, followed by the addition of 0.5 mL 1,2-dibromoethane. After the mixture is cooled to 0  $^\circ\text{C}$ , a solution of 4-bromostyrene **1** (22.34 g, 122 mmol, 1.0 equiv) in 10 mL THF was added slowly in an ice bath and stirred for 4 h. A solution of  $\text{PCl}_3$  (2.6 mL, 30 mmol, <0.3 equiv) in 10 mL THF was added to the mixture at 0  $^\circ\text{C}$  over 1 h using a

syringe pump. After stirred overnight, the reaction was quenched using saturated  $\text{NH}_4\text{Cl}$  solution and extracted with hexanes. The organic layers were combined, dried with  $\text{MgSO}_4$  and evaporated under reduced pressure. The residue was dissolved in hexanes, passed through a short silica column, and eluted with hexanes. After evaporating the solvent, methanol was added to yield a white solid, which was collected using a Hirsch funnel and washed with methanol (74% yield for **2**).

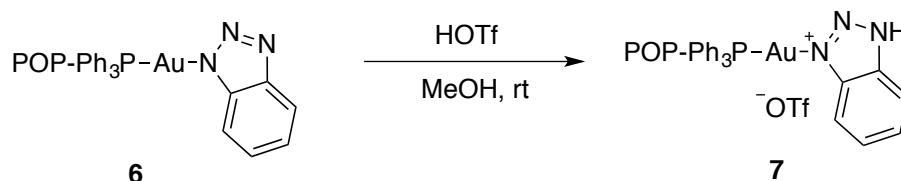
The tris(4-vinylphenyl)phosphane **2** (1 g) was dissolved in 10 mL THF, followed by the addition of 25 mg AIBN. The solution was transferred into an autoclave at  $100^\circ\text{C}$  for 16 h. The resulting solid was dried under vacuum and washed with methanol and acetone.

### B. Preparation of the heterogeneous triazole-gold complex:



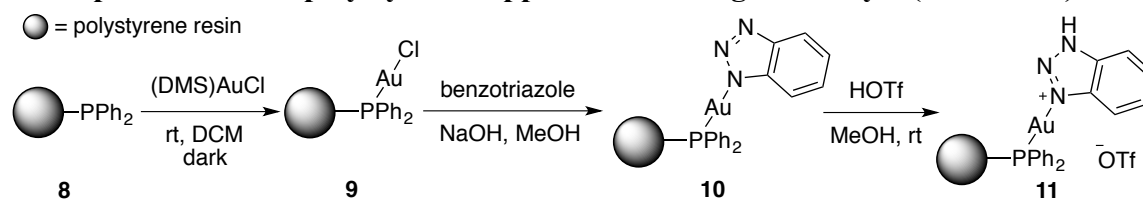
The polymer ligand POP- $\text{PPh}_3$  **4** (1 g, 5.0 equiv) was suspended in 100 mL DCM. A solution of  $(\text{DMS})\text{AuCl}$  (173 mg, 0.588 mmol, 1.0 equiv) in DCM was added. The mixture was stirred in dark at room temperature for 12 h. The product **5** was collected on a Hirsch funnel, washed with DCM and methanol, and suspended in 100 mL MeOH. Benzotriazole (142 mg, 1.2 mmol, 2.0 equiv) was dissolved in 10 mL methanol and mixed with 2.4 mL 0.5 M NaOH / MeOH solution. The mixed solution was added to the slurry of **5** and stirred for 12 h. The product POP-TAA-Au **6** was collected on a Hirsch funnel, washed with methanol and dried under vacuum to yield a white solid.

### C. Activation of the heterogeneous triazole-gold complex:



The POP-TAA-Au **6** (655 mg) was suspended in 10 mL MeOH. To this mixture was added 20 mL 0.1 M HOTf / MeOH solution. After stirred for 12 h, the activated gold catalyst POP-TA-Au **7** was isolated as a white solid by vacuum filtration, washed with methanol and acetone, and dried under vacuum.

### D. Preparation of the polystyrene-supported triazole gold catalyst (PS-TA-Au):



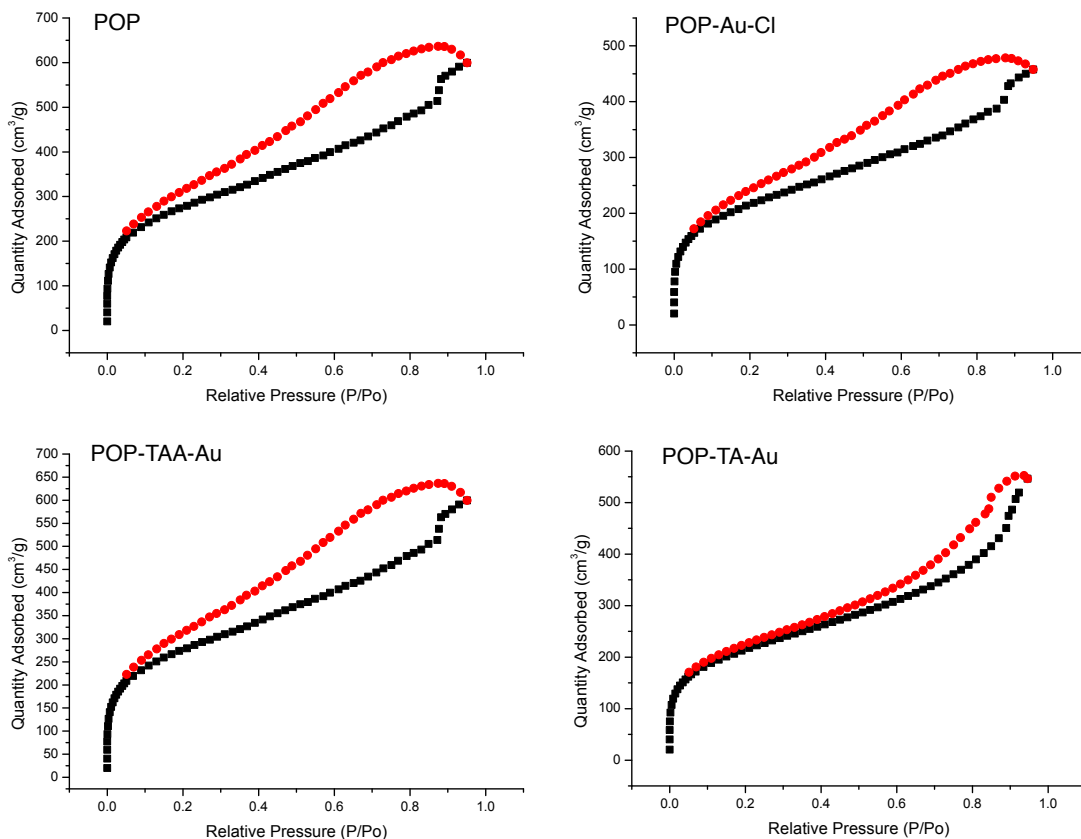
The triphenylphosphine resin (polystyrene-supported, 100-200 mesh,  $\sim 3.0$  mmol/g loading, 2% cross-linked with divinylbenzene) was purchased from Oakwood. The preparation of PS-TA-Au is similar to the previously described POP-TA-Au (procedures

B and C). When the phosphine to gold molar ratio is 1:1, a purple solid was obtained. When the phosphine to gold molar ratio is 5:1, a white solid was obtained.

### III. Catalyst Characterization

#### A. BET measurement

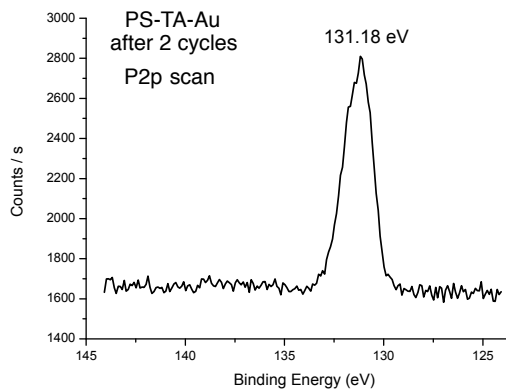
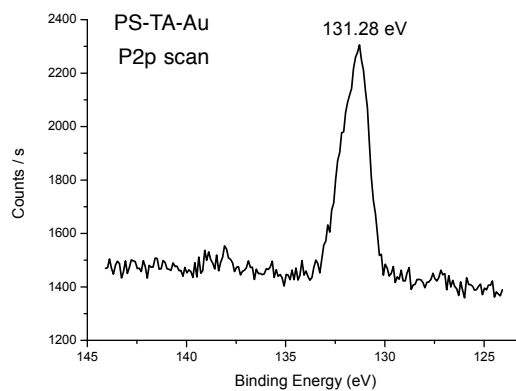
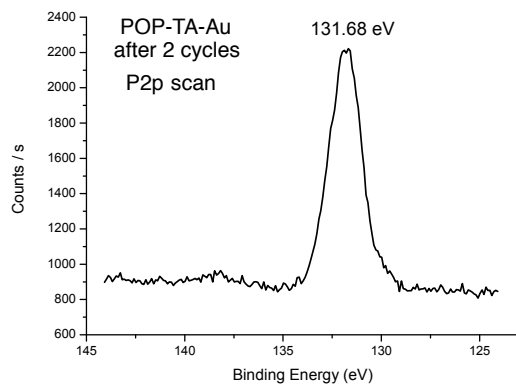
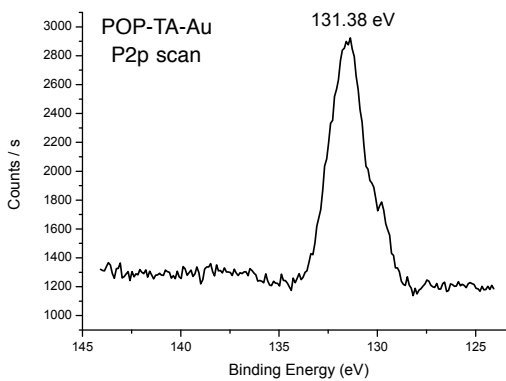
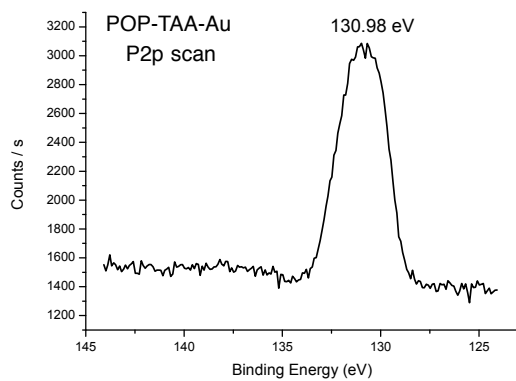
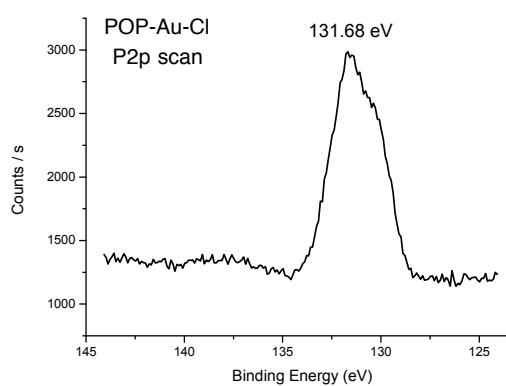
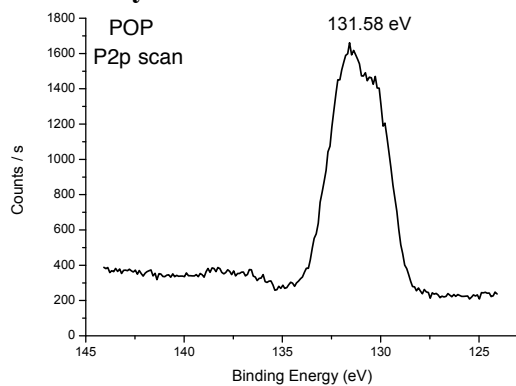
Nitrogen sorption isotherms for the polymer complexes:

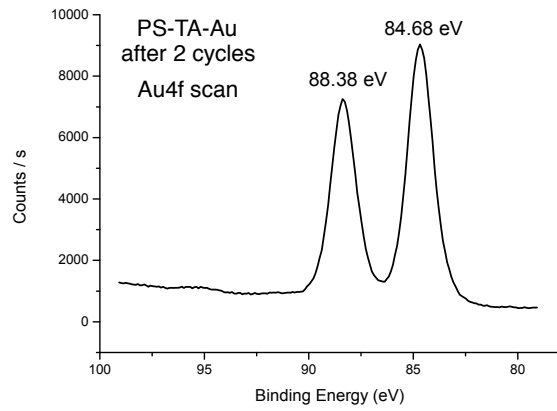
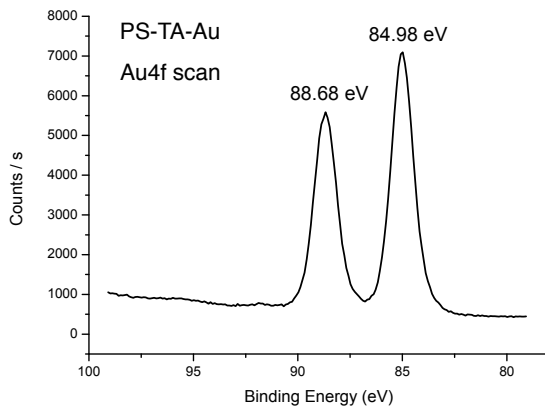
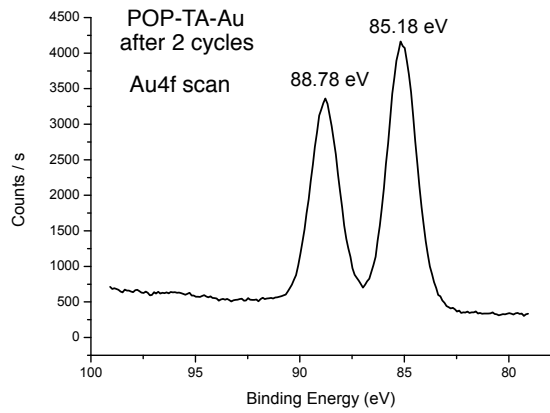
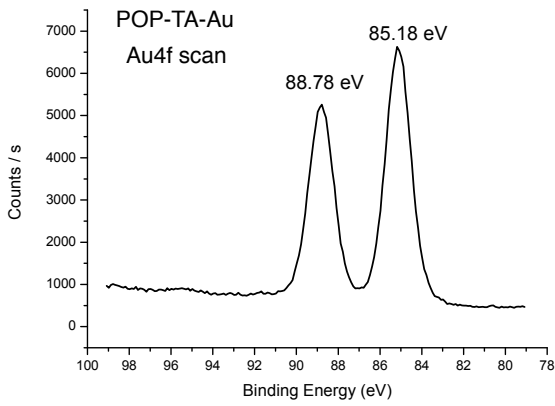
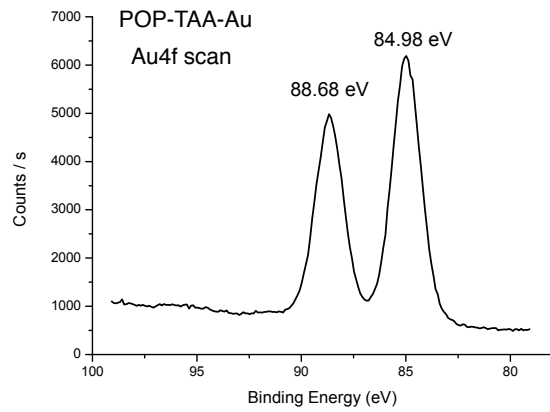
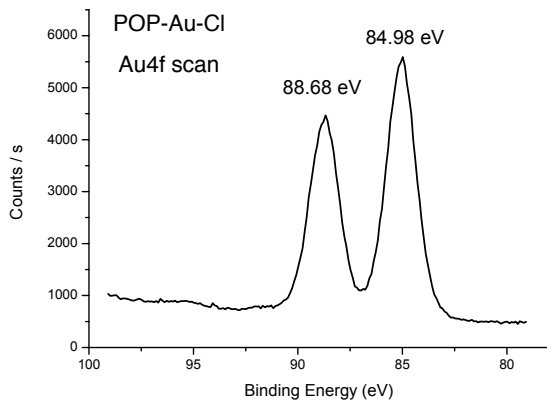


The measured BET surface areas are:

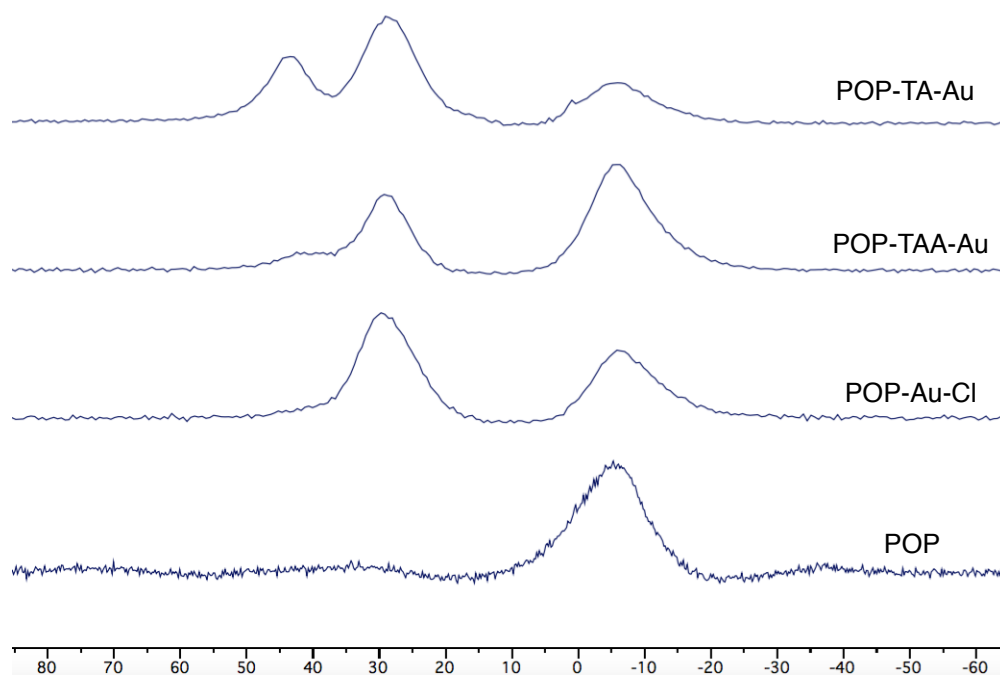
POP: 928 m<sup>2</sup>/g; POP-Au-Cl: 724 m<sup>2</sup>/g; POP-TAA-Au: 615 m<sup>2</sup>/g; POP-TA-Au: 722 m<sup>2</sup>/g.

## B. XPS analysis



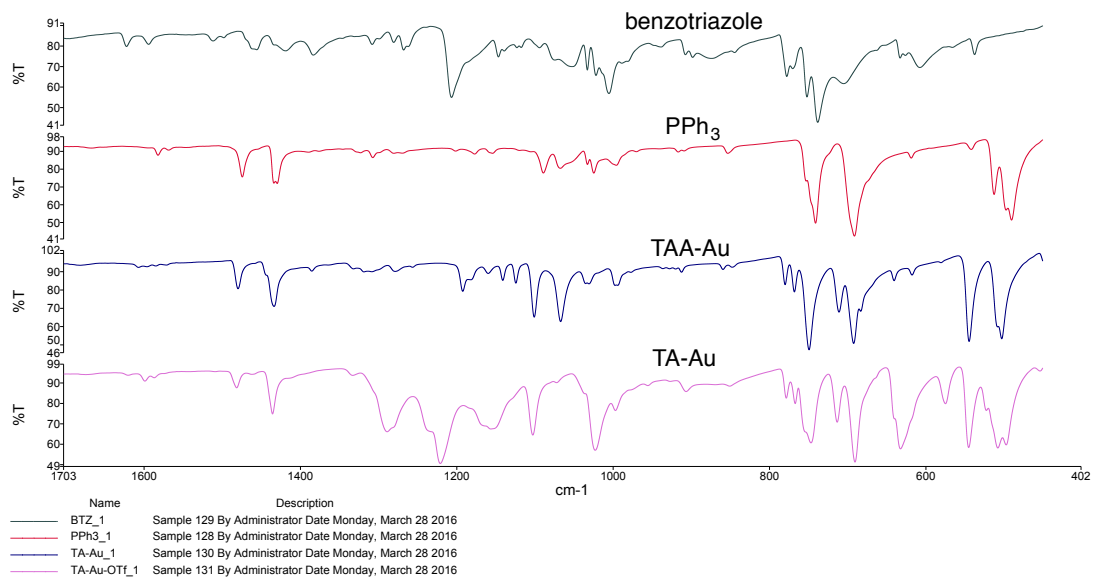


### C. solid state $^{31}\text{P}$ -NMR analysis

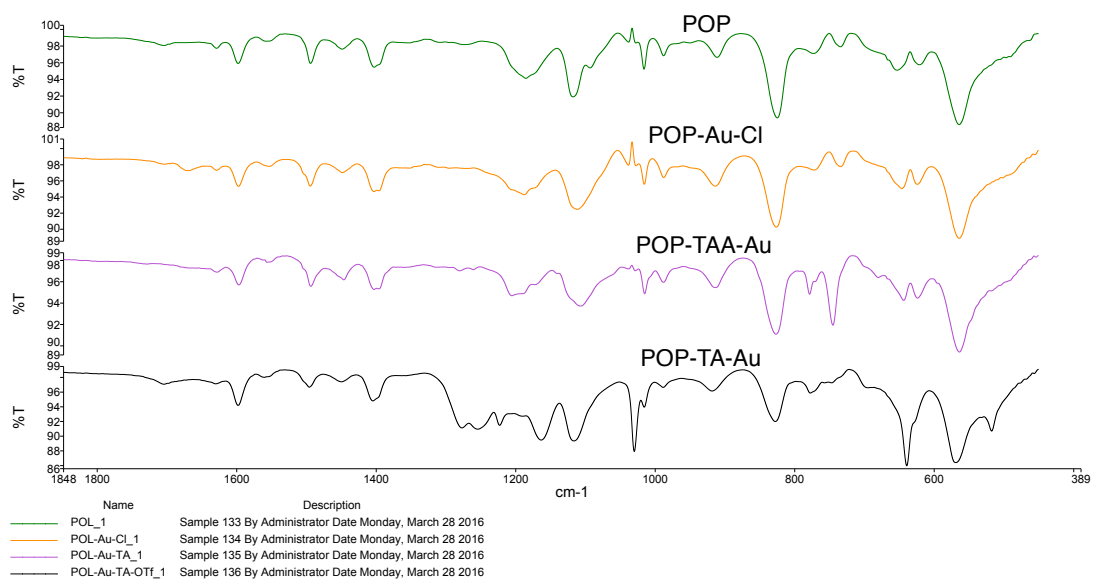


### D. IR analysis

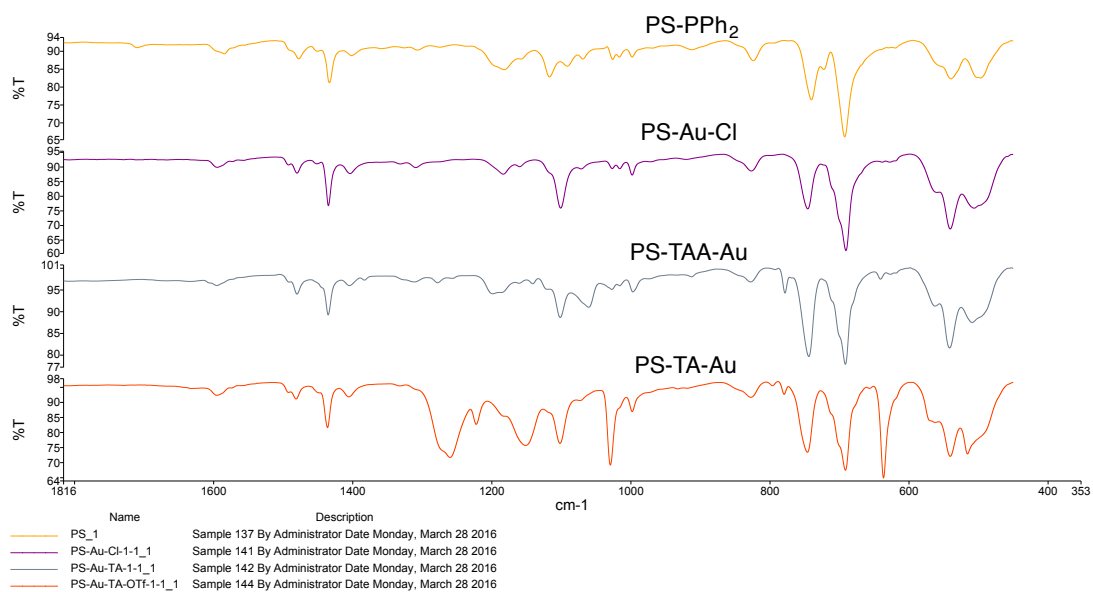
#### 1. IR comparison of the homogeneous triazole-gold catalyst



## 2. IR comparison of the porous polymer (POP) supported gold complexes

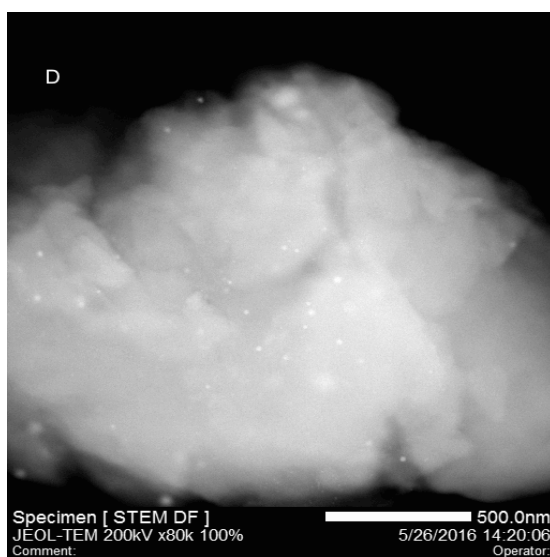
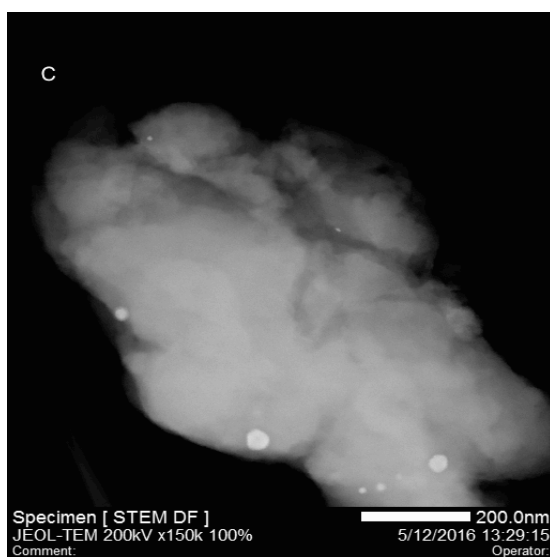
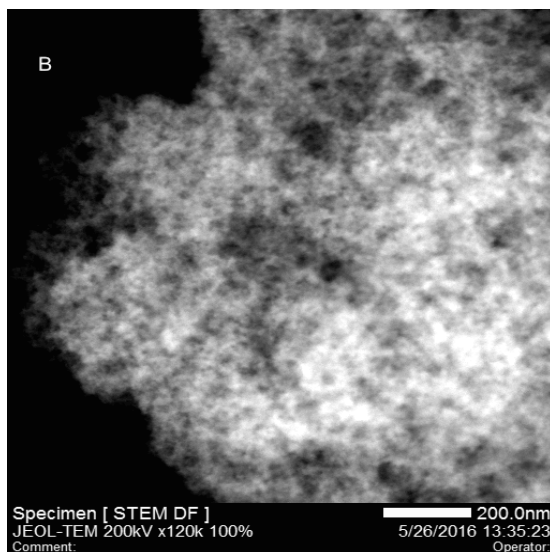
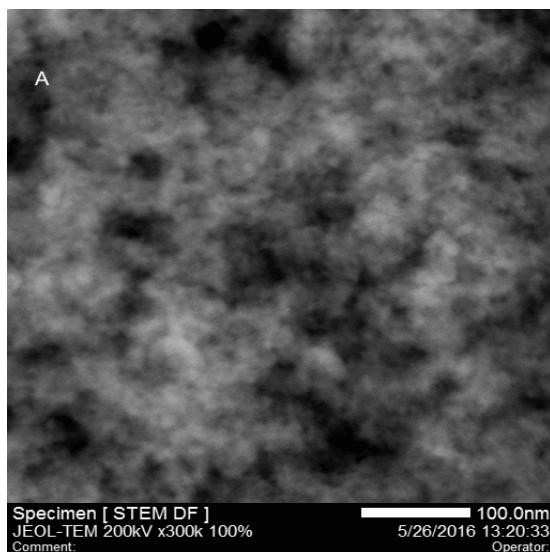


## 3. IR comparison of the polystyrene (PS) supported gold complexes





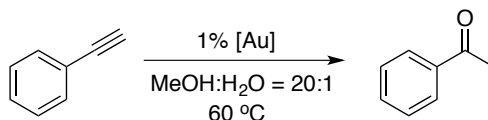
## E. STEM image



A) STEM of POP-TA-Au before reaction; B) STEM of POP-TA-Au after two cycles of hydration reaction of phenylacetylene; C) STEM of PS-TA-Au before reaction; D) STEM of PS-TA-Au after two cycles of hydration reaction.

## IV. Catalyst performance evaluation

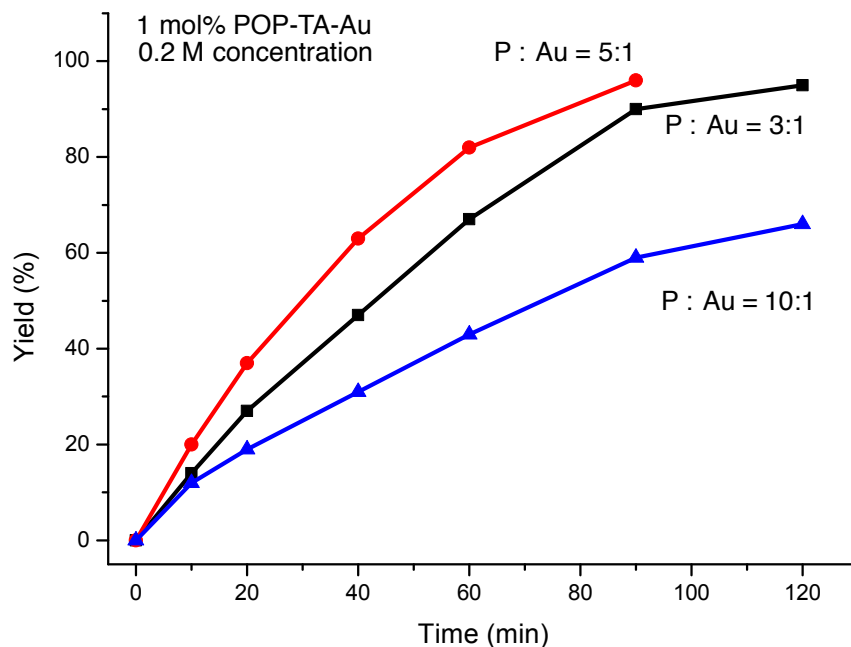
### A. Hydration reaction of phenylacetylene



Optimal condition: phenylacetylene (20.4 mg, 0.2 mmol) was dissolved in 0.4 mL MeOH with 20  $\mu$ L water. To this solution was added 8 mg POP-Au(TA-H)OTf (POP-TA-Au, P:Au = 5:1, 1 mol% Au). The mixture was stirred at 60 °C and checked by GC for completion. The yields were determined using GC with bromobenzene as the internal standard.

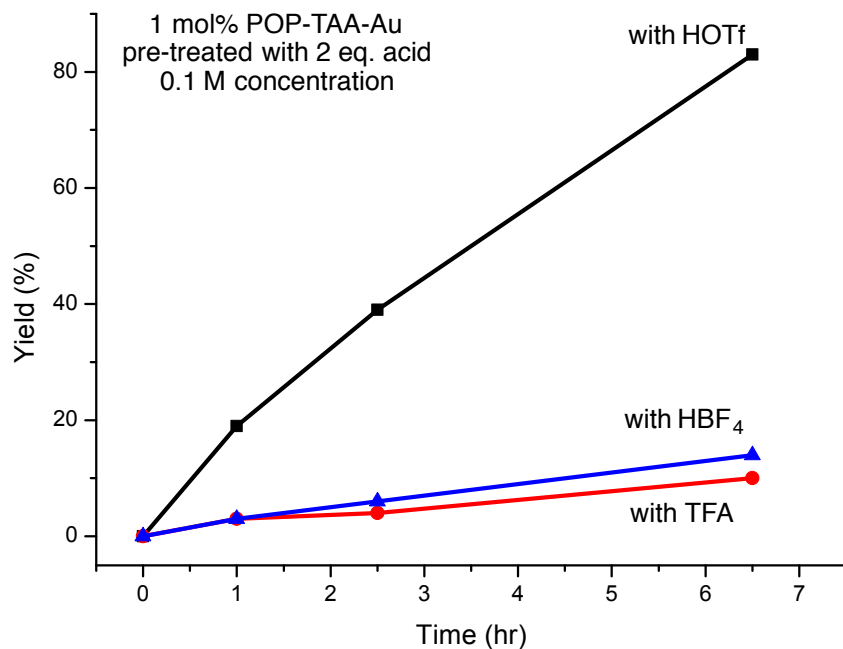
#### 1. Effects of P:Au ratio

Heterogeneous gold catalysts with different phosphine to gold ratios were tested under the same conditions (the amount of catalysts were calculated based on the amount of gold). The optimal P:Au ratio was determined to be 5:1.



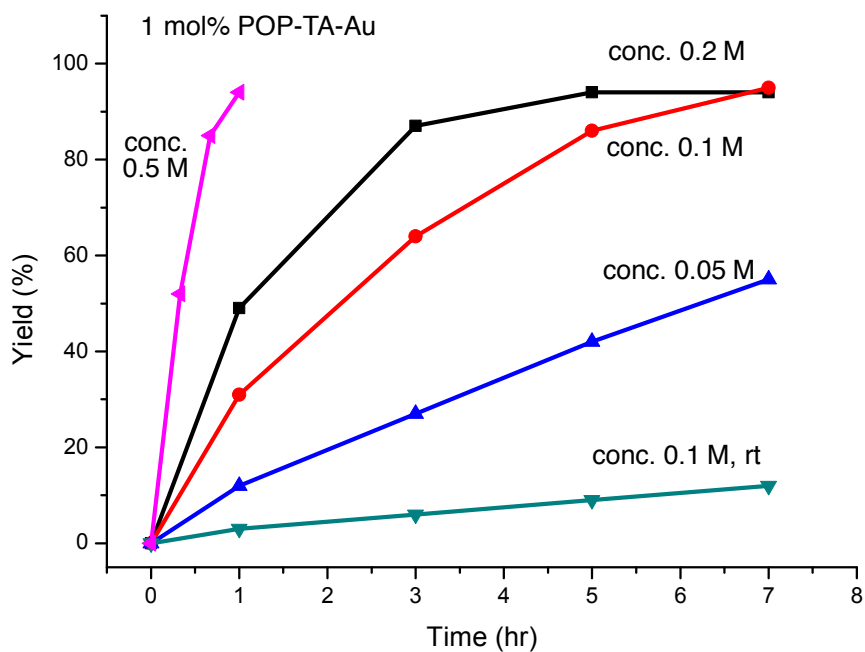
#### 2. Effects of acid

The polymer gold complex POP-Au(TA) (POP-TAA-Au, P:Au = 5:1, 1 mol% Au) was pre-treated with different acids (2 eq.) for 1h and washed with MeOH to remove the excess acids. Under the same conditions (0.1 M substrate concentration), the complex treated with HOTf showed the best reactivity.



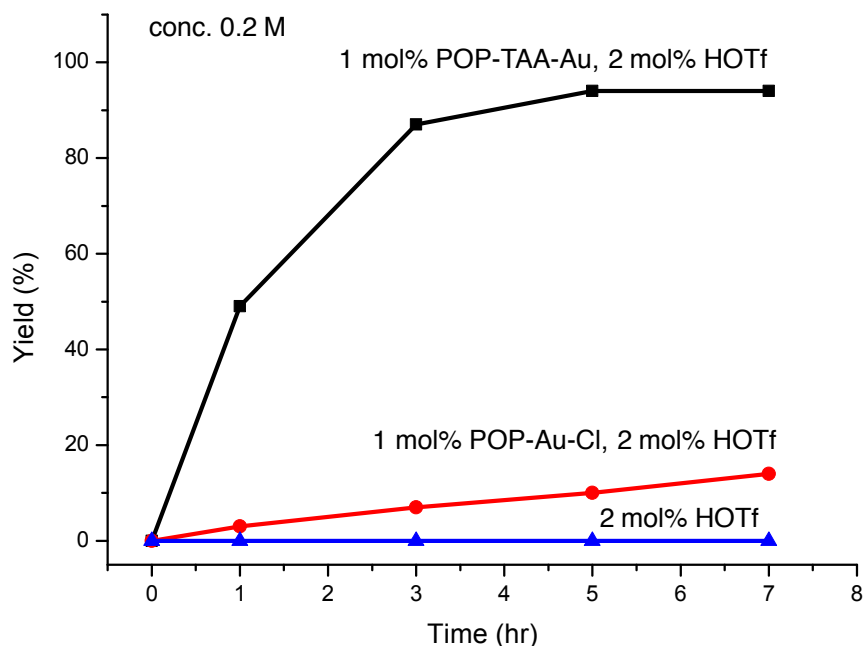
### 3. Effects of concentration

The reaction rate is proportional to the concentration of phenylacetylene. The optimal concentration was revealed to be 0.5 M. Further increase the concentration of phenylacetylene will lead to side reactions and the decomposition of the gold catalyst.



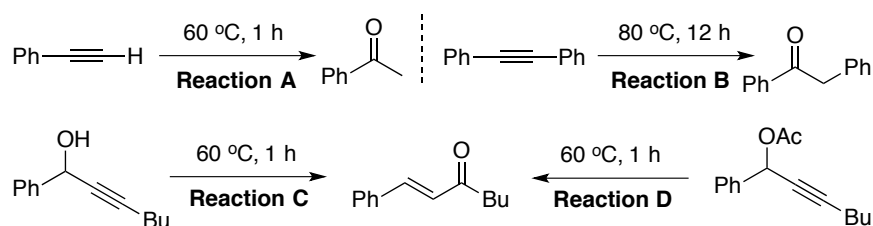
#### 4. Control experiment

To rule out the catalytic activity of HOTf in this hydration reaction, control reactions with 2 mol% HOTf or 2 mol% HOTf with 1 mol% POP-Au-Cl were performed. The results clearly suggest that HOTf cannot catalyze this Teles hydration reaction with or without the polymer solid support, unless the Cl attached to gold is substituted with the triazole ligand.



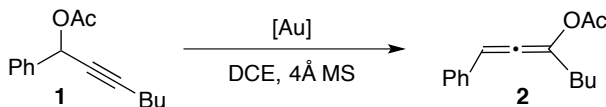
#### B. Recycle of the catalyst in other reactions

##### 1. Hydration reactions



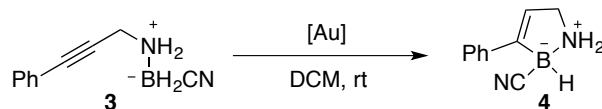
General procedure for all the tested hydration reactions (**Table 1**): the substrate (0.2 mmol) was dissolved in 0.4 mL MeOH with 20  $\mu\text{L}$  water. To this solution was added 8 mg POP-Au(TA-H)OTf (POP-TA-Au, P: Au = 5:1, 1 mol% Au). The mixture was stirred at corresponding temperature and monitored by GC for completion. After each cycle, the polymer gold catalyst POP-TA-Au was separated by centrifugation and treated with 2 eq. HOTf (relative to Au catalyst, using 0.1M HOTf solution in MeOH). After reacting for 10 minutes, the catalyst was washed with MeOH for three times before applied to the next cycle. The yields were determined using GC with bromobenzene as the internal standard.

## 2. Propargyl acetate rearrangement reaction



Procedure for the propargyl acetate rearrangement reaction (**Table 2**): the substrate (0.2 mmol) was dissolved in 0.4 mL anhydrous DCE. To this solution was added 8 mg POP-TA-Au (P: Au = 5:1, 1 mol% Au) and 100mg 4 Å molecular sieves. The mixture was stirred at 60 °C and monitored by GC for completion. After each cycle, the polymer gold catalyst POP-TA-Au was separated by centrifugation and treated with 2 eq. HOTf (relative to Au catalyst, using 0.1M HOTf solution in MeOH). After reacting for 10 minutes, the catalyst was washed with DCE for three times before applied to the next cycle. Another batch of 4 Å MS was added for the new cycle. The yields were determined using GC with bromobenzene as the internal standard.

## 3. Hydroboration reaction

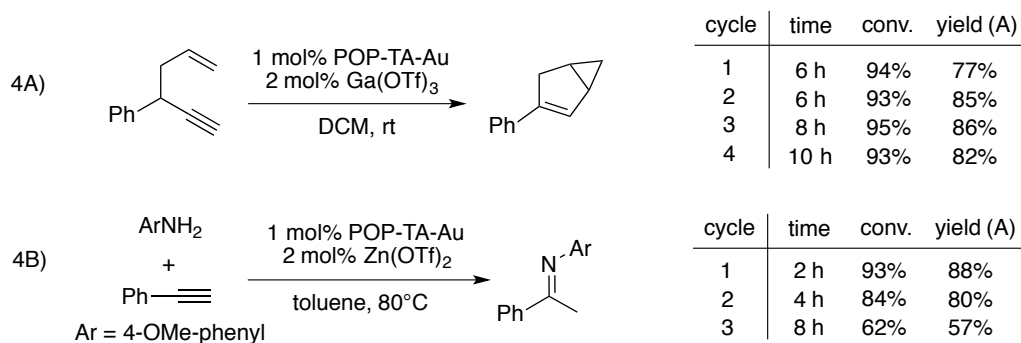


Procedure for the hydroboration reaction (**Table 3**): the amine-borane complex (0.05 mmol) was dissolved in 0.8 mL DCM. To this solution was added 20 mg POP-TA-Au (P: Au = 5:1, 10 mol% Au). The mixture was stirred at rt and monitored by NMR. After each cycle, the polymer gold catalyst POP-TA-Au was separated by centrifugation and treated with 2 eq. HOTf (relative to Au catalyst, using 0.1M HOTf solution in MeOH). After reacting for 15 minutes, the catalyst was washed with MeOH for three times followed by washing with DCM for three times before applied to the next cycle. The yields were determined using <sup>1</sup>H-NMR with *p*-xylene as the internal standard.

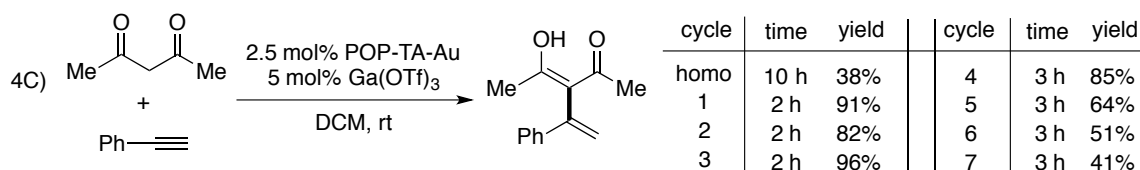
## 4. Lewis acid assisted reactions

General procedure for Lewis acid assisted reactions (**Figure 4**): the substrate (0.2 mmol) was dissolved in 0.4 mL solvent. To this solution was added 8 mg POP-TA-Au (P: Au = 5:1, 1 mol% Au) and 2 mol% Lewis acid. The mixture was stirred at rt and monitored by <sup>1</sup>H-NMR (**4A**, *p*-xylene as the internal standard) or GC (**4B**, dodecane as the internal standard). After each cycle, the POP-TA-Au catalyst was washed with the corresponding reaction solvent (DCM or toluene) for three times before applied to the next cycle. Another batch of Lewis acid was added in the new cycle. The recycle results are shown below. After certain cycles, the reactivity of the catalyst is decreased, possibly due to the decomposition of catalyst caused by the accumulation of Lewis acid in the reaction mixture. But compared with the corresponding homogeneous gold catalyst, the

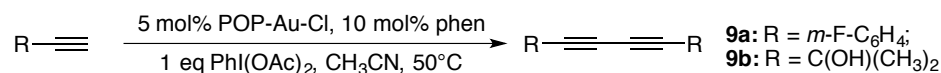
heterogeneous catalyst showed a much improved stability and reactivity.



Procedure for Lewis acid assisted Nakamura reaction (**Figure 4C**): the substrate (0.2 mmol) was dissolved in 0.4 mL DCM. To this solution was added 20 mg POP-TA-Au (P:Au = 5:1, 2.5 mol% Au) and 5 mol% Lewis acid. The mixture was stirred at rt and monitored by <sup>1</sup>H-NMR (p-xylene as the internal standard).



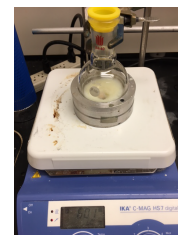
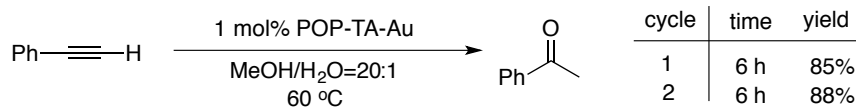
## 5. Oxidation reactions



General procedure for the oxidation reactions (**Figure 5**): the substrate (0.2 mmol) was dissolved in 0.4 mL CH<sub>3</sub>CN. To this solution was added 20 mg POP-TA-Au (P:Au = 5:1, 5 mol% Au), 1 equiv. PhI(OAc)<sub>2</sub> (64.4 mg, 0.2 mmol) and 10 mol% Phen (1.8 mg, 0.02 mmol). The mixture was stirred at 50 °C and monitored by NMR. The POP-TA-Au catalyst was washed with acetonitrile for three times before applied to the next cycle. Another batch of PhI(OAc)<sub>2</sub> and Phen were added each cycle. The yields were determined using <sup>1</sup>H-NMR with *p*-xylene as the internal standard or using <sup>19</sup>F-NMR with trifluorobenzene as the internal standard.

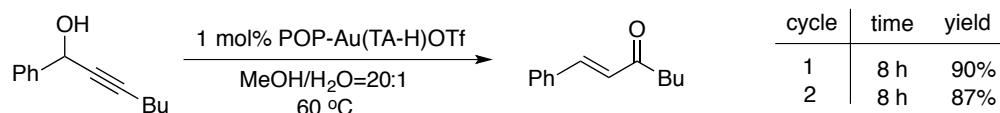
### C. Larger scale reactions

#### 1. Alkyne hydration reactions

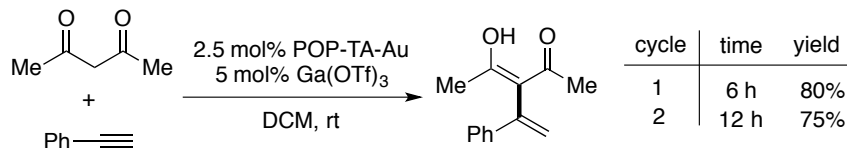


General procedure for alkyne hydration reactions: the substrate (10 mmol) was dissolved in 20 mL MeOH with 1 mL water. To this solution was added 400 mg POP-Au(TA-H)OTf (POP-TA-Au, P: Au = 5:1, 1 mol% Au). The mixture was stirred at 60 °C temperature and monitored by TLC for completion. Upon completion, the reaction mixture was filtrated and washed with MeOH. The filtrate was concentrated under reduced pressure and purified by flash chromatography on silica gel to give the desired product. After the first cycle, the polymer gold catalyst POP-TA-Au was treated with 2 eq. HOTf (relative to Au catalyst, using 0.1 M HOTf solution in MeOH). After reacting for 10 minutes, the catalyst was washed with MeOH for three times before applied to the next cycle.

After two cycles of hydration reaction of phenylacetylene, the recycled catalyst was further applied in the propargyl alcohol hydration reaction under same conditions. The POP-TA-Au catalyst was recycled for another two cycles without loss of reactivity.

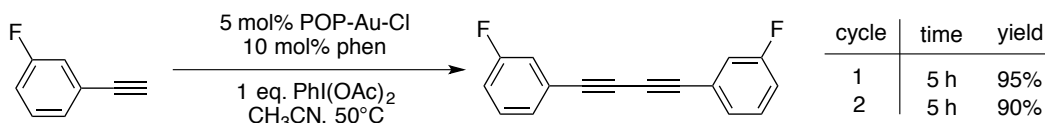


## 2. Lewis acid assisted Nakamura reaction



General procedure for Lewis acid assisted Nakamura reaction: acetone (1.0 g, 10 mmol) and phenylacetylene (2.0 g, 20 mmol) was dissolved in 20 mL DCM. To this solution was added 1.0 g POP-TA-Au (P: Au = 5:1, 2.5 mol% Au) and 257.5 mg Ga(OTf)<sub>3</sub> (5 mol%) Lewis acid. The mixture was stirred at room temperature and monitored by TLC for completion. After the reaction completed, the reaction mixture was filtrated and washed with DCM. The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel to give the desired product. The POP-TA-Au catalyst was washed with acetonitrile for three times before applied to the next cycle and another batch of Ga(OTf)<sub>3</sub> was added in the new cycle.

## 3. Oxidation reactions



General procedure for the oxidation reaction: the substrate (1.2 g, 10 mmol) was dissolved in 20 mL CH<sub>3</sub>CN. To this solution was added 1 g POP-TA-Au (P:Au = 5:1, 5 mol% Au) , 1 equiv. PhI(OAc)<sub>2</sub> (3.2 g, 1 mmol) and 10 mol% Phen (90 mg, 0.5 mmol). The mixture was stirred at 50 °C and monitored by TLC. The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel to give the desired product. The POP-TA-Au catalyst was washed with acetonitrile for three times before applied to the next cycle and another batch of PhI(OAc)<sub>2</sub> and Phen were added in the new cycle.