Supporting Information

Highly Efficient Three-Component Coupling Reaction Catalyzed by Atomically Precise Ligand-Protected Au_{38} Nanoclusters

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Experimental

Synthesis of Au_{38}(SC\textsubscript{2}H\textsubscript{4}Ph)\textsubscript{24} and Au\textsubscript{25}(SC\textsubscript{2}H\textsubscript{4}Ph)\textsubscript{18} Nanoclusters. The syntheses of Au_{38}(SC\textsubscript{2}H\textsubscript{4}Ph)\textsubscript{24} and Au_{25}(SC\textsubscript{2}H\textsubscript{4}Ph)\textsubscript{18} nanoclusters followed the previously reported methods.\textsuperscript{1,2}

Preparation of the Au(I)-S-C\textsubscript{2}H\textsubscript{4}Ph catalyst. 1 mL solution of 200 mg HAuCl\textsubscript{4} was mixed with another methanol solution (7 mL) containing PhC\textsubscript{2}H\textsubscript{4}SH (0.3 mL) under vigorous stirring for 30 min. After centrifugation at \~6500 rpm, the solution was then removed and the precipitate was washed several times with ethanol/water to remove the redundant PhC\textsubscript{2}H\textsubscript{4}SH. The Au(I)-S-C\textsubscript{2}H\textsubscript{4}Ph was obtained.

Preparation of the supported Au_{38}(SR)\textsubscript{24}/oxide catalyst. To prepare the oxide-supported catalyst, 1 mg of Au_{38}(SR)\textsubscript{24} was dissolved in 5 ml CH\textsubscript{2}Cl\textsubscript{2}, and 100 mg CeO\textsubscript{2}/TiO\textsubscript{2}/SiO\textsubscript{2} was added. After stirring for 12 h at r.t., the clusters were adsorbed onto the oxide surfaces. The Au_{38}(SR)\textsubscript{24}/oxide-support catalysts were collected by centrifugation and dried in vacuum.

Catalytic reaction. Typically, 1 equiv of benzaldehyde (1 mmol), 1.2 equiv of piperidine and 1.3 equiv of phenylacetylene were added to a 10 mL round-bottom flask containing \~1 mg of the Au_{38}(SC\textsubscript{2}H\textsubscript{4}Ph)\textsubscript{24} cluster (0.1 µmol). 1 ml solvent (e.g., water, toluene) was added into the flask if needed. This reaction mixture was then stirred at 80 °C for 6 h. The products of this catalytic reaction were analyzed by NMR spectroscopy.


Supporting Figures
Figure S1. NMR spectra of benzaldehyde, phenylacetylene, piperidine, and the reaction mixture (after 1 h and 5 h, respectively). The NMR peaks of various H’s are as indicated in the figure.

Figure S2. UV-Vis spectra of the Au$_{38}$(SC$_2$H$_4$Ph)$_{24}$ catalyst before (black curve) and after the A3-coupling reaction (red curve).
**Figure S3.** ESI-Mass spectrum of Au$_{36}$(SC$_2$H$_4$Ph)$_{24}$ after the A3-coupling reaction. Cesium acetate (CsOAc) was added to form adducts with the charge neutral clusters. The low-mass, comb-like peaks (m/z <5300) are from [(CsOAc)$_n$Cs]$^+$ with spacing of one CsOAc.

**Figure S4.** Conversion of benzaldehyde, phenylacetylene and piperidine as a function of reaction time over the Au$_{25}$(SC$_2$H$_4$Ph)$_{18}^-$ catalyst.