Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

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

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Experimental

Synthesis of $Au_{38}(SC_2H_4Ph)_{24}$ and $Au_{25}(SC_2H_4Ph)_{18}$ Nanoclusters. The syntheses of $Au_{38}(SC_2H_4Ph)_{24}$ and $Au_{25}(SC_2H_4Ph)_{18}$ nanoclusters followed the previously reported methods.[1,2]

Preparation of the Au(I)-S-C_2H_4Ph catalyst. 1 mL solution of 200 mg $HAuCl_4$ was mixed with another methanol solution (7 mL) containing PhC_2H_4SH (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_2H_4SH. The Au(I)-S-C_2H_4Ph was obtained.

Preparation of the supported $Au_{38}(SR)_{24}$/oxide catalyst. To prepare the oxide-supported catalyst, 1 mg of $Au_{38}(SR)_{24}$ was dissolved in 5 ml CH_2Cl_2, and 100 mg $CeO_2/TiO_2/SiO_2$ was added. After stirring for 12 h at r.t., the clusters were adsorbed onto the oxide surfaces. The $Au_{38}(SR)_{24}$/oxide-support catalysts were collected by centrifugation and dried in vacuum.

Catalytic reaction. Typically, 1 equiv of benzaldehyde (1mmol), 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 $Au_{38}(SC_2H_4Ph)_{24}$ 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 ^{o}C for 6 h. The products of this catalytic reaction were analyzed by NMR spectroscopy.

[1] H. Qian, Y. Zhu and R. Jin, *ACS Nano*, 2009, **3**, 3795

[2] Z. Wu, J. Suhan and R. Jin, *J. Mater. Chem.*, 2009, **19**, 622.

Supporting Figures

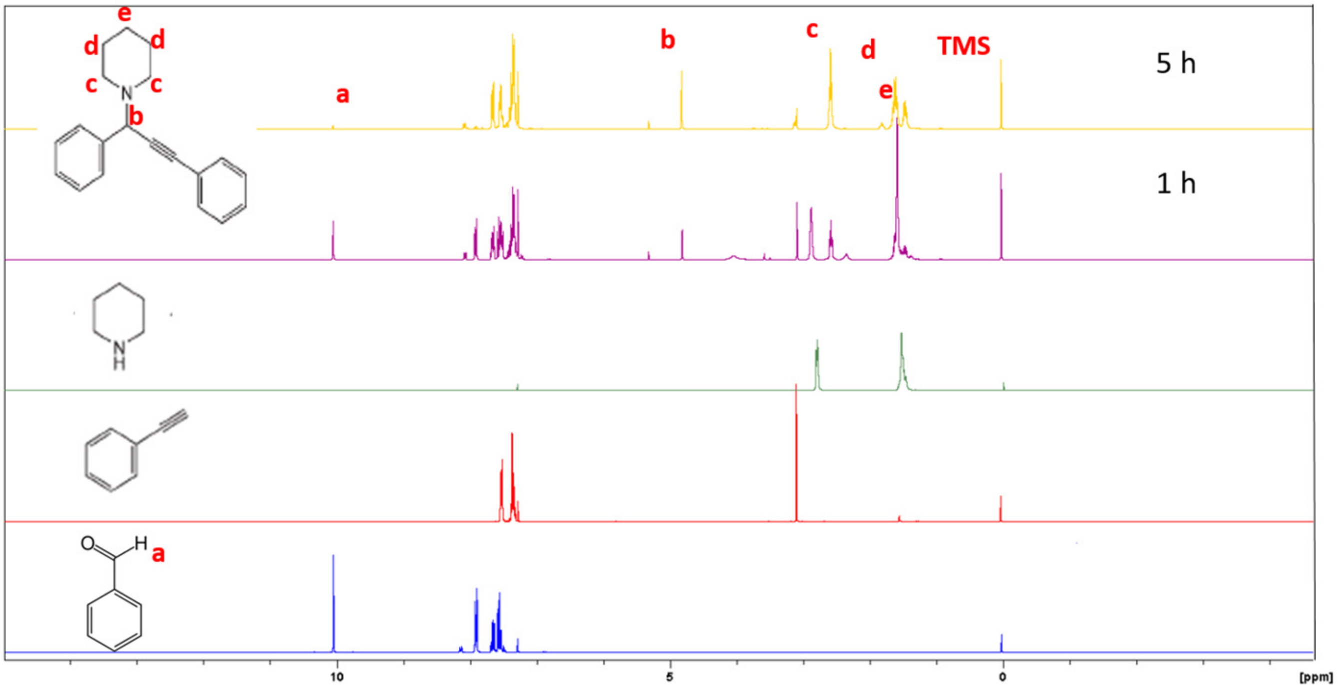

Figure S1. NMR spectra of benzaldehyde, phenylacetylene, piperidine, and the reaction mixture (after 1 h and 5 h, respectively). The NMR peaks of various H's are as indicated in the figure.

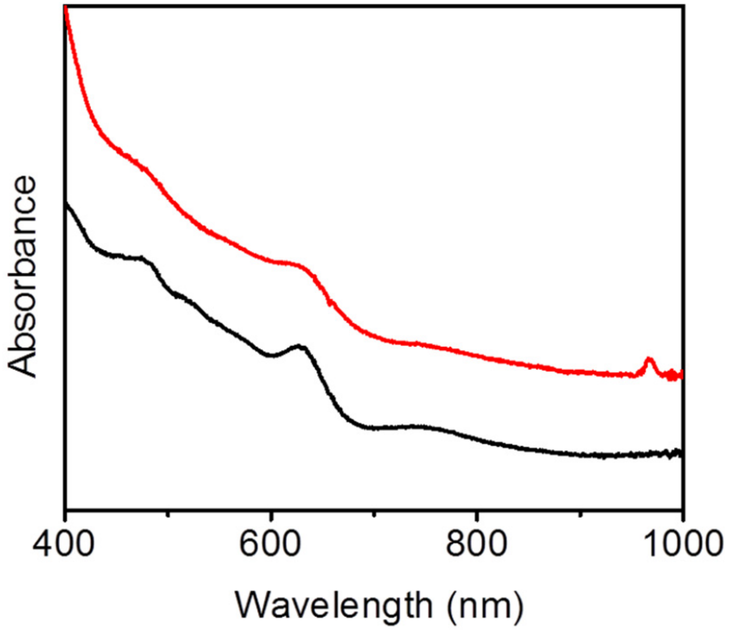

Figure S2. UV-Vis spectra of the $Au_{38}(SC_2H_4Ph)_{24}$ catalyst before (black curve) and after the A3-coupling reaction (red curve).

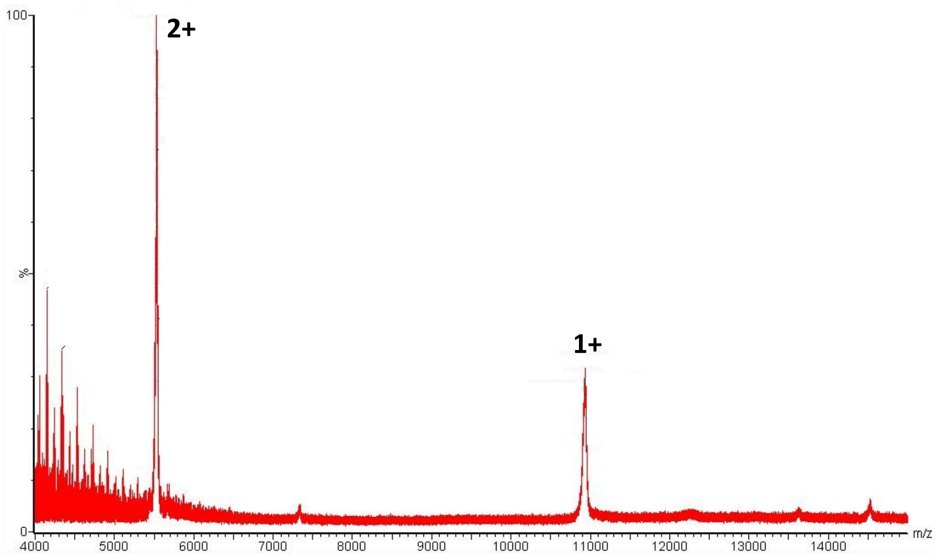

Figure S3. ESI-Mass spectrum of $Au_{38}(SC_2H_4Ph)_{24}$ after the A3-coupling reaction. Cesium acetate (CsOAc) was added to form adducts with the charge neutral clusters. The low-mass, comb-like peaks (m/z <5300) are from $[(CsOAc)_nCs]^+$ with spacing of one CsOAc.

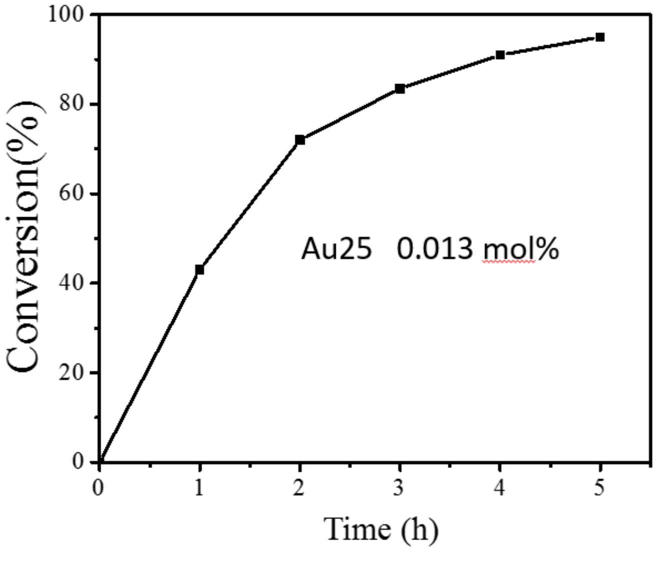

Figure S4. Conversion of benzaldehyde, phenylacetylene and piperidine as a function of reaction time over the $Au_{25}(SC_2H_4Ph)_{18}^-$ catalyst.