Electronic Supplementary Information:

Au25 Nanocluster-Catalyzed Ullmann-Type Homocoupling Reaction of Aryl Iodides

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1. Experimental

Synthesis of Au25(SR)18 (R=CH2CH2Ph) nanoclusters. HAUCl4·3H2O (0.2 mmol, dissolved in 5 ml nanopure water) and tetraoctylammonium bromide (TOAB, 0.24 mmol, dissolved in 10 ml toluene) were combined in a 25 ml tri-neck round bottom flask. The solution was vigorously stirred for 15 min, and the aqueous was then removed. Thiol (HSCH2CH2Ph, 0.6 mmol) was added to the flask, and stirring was reduced to a very low speed (50 rpm). After the solution turned to clear (2 h), NaBH4 (2 mmol, in 5 ml cold aqueous solution) was rapidly added all at once. After aging overnight, methanol was added to separate the nanocluster product from TOAB and other side-products. The Au25(SR)18 nanoclusters were collected after removing the supernatant.

Preparation of Au25(SR)18/oxide catalyst. 1 mg Au25 clusters were dissolved in 5 ml dichloromethane (DCM), and 100 mg oxide were added. After stirring for 12h at r.t., the supernatant became faint yellow. The Au25/oxides catalysts were collected by centrifugation and dried in vacuum at r.t.

Procedure for homocoupling reaction. In a typical homocoupling reaction, iodobenzene (0.2 mmol), base (K3PO4 or K2CO3, 0.6 mmol), Au25/oxide (100 mg) and 1 mL solvent were added to a 6 mL round-bottom flask. The mixture was stirred under a N2 atmosphere at 130 °C for 48h as indicated in Table 1. After the reaction, 5 mL water was added to the flask, followed by extraction with ethyl acetate (EtOAc). The catalytic reaction product was obtained after removal of EtOAc in the extracted solution. The conversion of iodobenzene
was determined by $^1$H NMR (300 MHz) analysis. For the recyclability test, the Au$_{25}$/oxide catalyst was separated by centrifugation, washed with water to remove the base and then further washed with EtOAc, and dried in vacuum at r.t. prior to its re-use in the next round of reaction.

2. $^1$H NMR spectra:
3. Recyclability of the Au$_{25}$(SR)$_{18}$/CeO$_2$ catalysts. The conversion of iodobenzene is shown again the cycle number: