CHEMISTRY & SUSTAINABILITY
CHEMSUSCHEM
ENERGY & MATERIALS

Supporting Information

C–C Cross-Coupling of Primary and Secondary Benzylic Alcohols Using Supported Gold-Based Bimetallic Catalysts

Xiang Liu, Ran-Sheng Ding, Lin He, Yong-Mei Liu, Yong Cao,* He-Yong He, and Kang-Nian Fan[a]

cssc_201200804_sm_miscellaneous_information.pdf

1. Materials and Methods

1.1 Catalytic materials

Metal oxides including CeO_2 (Evonik, Adnano 90, specific surface area: 90 $m^2·g^{-1}$), TiO_2 (Evonik P25, specific surface area: 45 $m^2·g^{-1}$ nonporous, 70% anatase and 30% rutile), SiO_2 (Evonik, Aerosil 380, specific surface area: 380 $m^2·g^{-1}$), Al_2O_3 (Aluminum oxide C, Evonik, 100 $m^2·g^{-1}$), were supplied from the Degussa. Palladium chloride ($PdCl_2$), rhodium chloride hydrate ($RhCl_3·xH_2O$), Ruthenium chloride hydrate ($RuCl_3·xH_2O$), silver nitrate ($AgNO_3$), chloroplatonic acid hexahydrate ($H_2PtCl_6·6H_2O$) and chloroauric acid tetrahydrate ($HAuCl_4·4H_2O$), were supplied by Aldrich and used without further purification.

1.2 Catalyst preparation

Preparation of Hydrotalcite (HT)

Mg-Al hydrotalcite (Mg/Al = 3) was synthesized by co-precipitation method following the procedure as described in Ref. S1. An aqueous solution (A) of $Mg(NO_3)_2·6H_2O$ (60 mmol) and $Al(NO_3)_3·9H_2O$ (20 mmol) in 80 mL double distilled deionized water was prepared. The solution A was added dropwise into a second solution (B) containing Na_2CO_3 (40 mmol) and NaOH (160 mmol) in 100 mL double distilled deionized water, in around 1 h under vigorous stirring at room temperature. The formed suspension was stirred and aged for 18 h at 65 ^oC, filtered and washed extensively with water. The obtained solid was dried in oven overnight at 100 ^oC. XRD measurements confirmed the formation of the HT structure (See Figure S5a). The BET surface area of the resultant Mg-Al HT was 141 $m^2·g^{-1}$.

Preparation of ZrO_2

ZrO_2 powders were prepared by a conventional precipitation method following the reported procedure.[S3] Briefly, 8.0 g $ZrOCl_2·8H_2O$ was dissolved in 200 mL deionized water at room temperature, the pH was adjusted to 9.5 by dropwise addition of NH_4OH (2.5 M). The resultant hydrogel was washed with deionized water until free of chloride ions after stirring for 8 h. The precipitate was then dried at 100 ^oC overnight and calcined at 400 ^oC for 2 h in air. The BET surface area of the resultant material was 115 $m^2·g^{-1}$. The crystal phase of ZrO_2 was composed of 56 % monoclinic phase and 44 % tetragonal phase.

Preparation of La_2O_3

La_2O_3 powders were prepared through a liquid-precipitation method.[S4] An aqueous solution of $La(NO_3)_3$ was prepared, then an aqueous solution of $(NH4)_2CO_3$ (1 mol/L) was added dropwise to the solution under stirring until the pH was brought to about 8.0. The resulting mixture was aged for 1 h, filtered, repeatedly washed with distilled water, dried at 120 ^oC, and calcined at 750 ^oC for 2 h.

Preparation of MgO

MgO powders were prepared following the reported procedure.[S5] Initially, the pH of 200 mL of distilled water was adjusted to 10.5 by addition of liquid ammonia. To this solution, 0.1 M magnesium nitrate solution was added dropwise with continuous stirring. The rate of addition of the salt solution was kept at 20 mL/h. During the addition, the pH of the mixture decreased due to hydrolysis of the salt. The pH was maintained at 10.5 by controlled addition of liquid ammonia solution. After completion of the precipitation procedure, the mixture was stirred at room temperature for 12 h, filtered, repeatedly washed with distilled water, dried at 120 ^oC, and calcined at 500 ^oC for 2 h.

Preparation of Au/HT catalysts:

A modified deposition-precipitation (DP) procedure has been employed to prepare the Au/HT. The obtained HT (1.0 g) was dispersed in an aqueous solution of $HAuCl_4·4H_2O$ (50 mL, $1.02×10^{-3}$ M) with vigorously stirring. After agitation for 2 h at 25 ^oC, the mixtures were filtrated and washed thoroughly with deionized water until no Cl^- was detected in the filtrate by using $AgNO_3$. The resulting compound was dried for 12 h in *vacuo* at room temperature, and finally reduced by 5% H_2/Ar at 300 ^oC for 2 h. The BET surface area of the resultant Au/HT catalyst was 113 m^2 g^{-1}. The concentration of gold was 0.5 % Au by weight (ICP-AES). A large fraction of the Au particles in this catalyst was within 1-5 nm in diameter (TEM in Figure S3a). 0.24 wt% Au/HT and 1.09 wt% Au/HT were prepared by the same procedures.

Preparation of Au/CeO_2 catalysts

0.5 wt% Au/CeO_2 catalysts were prepared by a routine DP method.[S6] An appropriate amount of aqueous solutions of $HAuCl_4$ was heated to 80 ^oC under vigorous stirring. The pH was adjusted to 10 by dropwise addition of NaOH (0.2 M), and then suitable amount of CeO_2 was dispersed in the solution. The mixture was aged for 2 h at 80 ^oC, after which the suspension was cooled to room temperature. Extensive washing with deionized water was then followed until it was free of chloride ions. The samples were dried under vacuum at room temperature for 12 h, and reduced in 5% H_2/Ar at 300 ^oC for 2 h.

Preparation of Au/TiO_2 catalysts

A slightly modified deposition-precipitation (DP) procedure has been employed to prepare the 0.5 wt% Au/TiO_2 sample.[S7] TiO_2 was added to 100 mL of an appropriate amounts of aqueous solution of $HAuCl_4$ at a fixed pH = 8 adjusting with 0.2 M NaOH. The mixture was aged for 2 h at 80 ^oC under vigorous stirring, after which the suspension was cooled to room temperature. Extensive washing with 0.2 M NH_4NO_3 and then deionized water was followed to remove Na^+ and Cl^-. The samples were dried under vacuum at room temperature for 12 h before reduced in 5% H_2/Ar at 300 ^oC for 2 h. All of the preparations were performed in the absence of light.

Preparation of Au/MgO catalysts

The 0.5 wt% Au/MgO sample was prepared by the modified DP procedure as described above. MgO (1.0 g) was added to 100 mL of an appropriate amounts of aqueous solution of $HAuCl_4$ at a fixed pH = 9 adjusting with 0.2 M NaOH. The mixture was aged for 2 h at 80 ^oC, after which the suspension was cooled to room temperature. Extensive washing with 0.2 M NH_4NO_3 and then deionized water was followed to remove Na^+ and Cl^-. The samples were dried under vacuum at room temperature for 12 h before reduced in 5% H_2/Ar at 300 ^oC for 2 h.

Preparation of Au-Pd/HT catalysts:

Au-Pd/HT catalysts were prepared by following the same procedure as Au/HT. The obtained HT (1.0 g) was dispersed into 50 mL of an appropriate amount of aqueous solution of $HAuCl_4$ and $PdCl_2$ with varying Au/Pd atomic ratios, with vigorously stirring. The total metal loading was kept around 0.5 wt%. After agitation for 2 h at 25 ^oC, the mixtures were filtrated and washed thoroughly with deionized water until no Cl^- was detected in the filtrate by using $AgNO_3$. The resulting compound was dried for 12 h in *vacuo* at room temperature, and finally reduced by 5% H_2/Ar at 300 ^oC for 2 h.

Preparation of Pd/HT, Pt/HT, Ag/HT, Ru/HT, Rh/HT catalysts

1 wt% Pd/HT, 1 wt% Pt/HT, 1 wt% Ag/HT, 1 wt% Ru/HT and 1 wt% Rh/HT catalysts were prepared by incipient-wetness impregnation of the support, with aqueous solution of $PdCl_2$, $H_2PtCl_6 \cdot 6H_2O$, $AgNO_3$, $RuCl_3$, $RhCl_3$ precursors of appropriate concentrations (typically 1.0 mL/g support). After a perfect mixing of the corresponding slurries, samples were dried under vacuum at room temperature for 12 h and then reduced in 5% H_2/Ar at 400 ^oC for 2 h.

1.3 Catalyst characterization

Elemental analysis: The Au and Pd loading of the catalysts was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Thermo Electron IRIS Intrepid II XSP spectrometer. The detection limit for Au or Pd was 0.10 ppm.

BET analysis: The BET specific surface areas of the prepared catalysts were determined by adsorption–desorption of nitrogen at liquid nitrogen temperature, using a Micromeritics TriStar 3000 equipment. Sample degassing was carried out at 300 ^oC prior to acquiring the adsorption isotherm.

X-ray diffraction (XRD) analysis: The crystal structures of HT were characterized with powder X-ray diffraction (XRD) on a Bruker D8 Advance X-ray diffractometer using the Ni-filtered Cu Kα radiation source at 40 kV and 40 mA.

X-ray photoelectron spectroscopy (XPS): XPS data were recorded with a Perkin Elmer PHI 5000C system equipped with a hemispherical electron energy analyzer. The spectrometer was operated at 15 kV and 20 mA, and a magnesium anode (Mg Kα, hv = 1253.6 eV) was used. The C 1s line (284.6 eV) was used as the reference to calibrate the binding energies (BE).

Transmission electron microscopy (TEM) and energy-dispersive X-ray (EDX) spectrum: A JEOL 2011 microscope operating at 200 kV equipped with an EDX unit (Si(Li) detector) was used for the TEM and EDX investigations. The samples for electron microscopy were prepared by grinding and subsequent dispersing the powder in ethanol and applying a drop of very dilute suspension on carbon-coated grids.

CO_2/NH_3-Temperature-programmed desorption (CO_2/NH_3-TPD): Typically, the sample (100 mg) loaded in a quartz reactor was pretreated with high-purity Ar at 300 ^{o}C for 1 h. After cooling the sample to 100 ^{o}C, CO_2 adsorption was performed by switching the Ar flow to a CO_2 gas until adsorption saturation. The gas-phase (and/or weakly adsorbed) NH_3, was purged by Ar at the same temperature for about 1h. CO_2-TPD was then performed in the Ar flow by raising the temperature to 700 ^{o}C at a rate of 10 $^{o}C\cdot min^{-1}$. The desorbed CO_2 molecules were monitored by a OmniStar mass spectrometer (QMS-200) with the signal of m/e = 44. NH_3-TPD was performed by using a similar procedure.

2. Catalytic activity measurements

2.1 General procedure for the Aldol condensation of benzaldehyde and acetophenone

A mixture of benzaldehyde (1 mmol), acetophenone (1 mmol), inorganic material catalysts (400 mg), *p*-xylene (3 mL), and *n*-dodecane (10 µL) as internal standard were placed into a flask (25 mL). The resulting mixture was vigorously stirred at 120 °C under N_2 atmosphere (1 atm) for given reaction time. The conversion and product selectivity were determined by GC-17A gas chromatograph equipped with a HP-FFAP column (30 m × 0.25 mm) and a flame ionization detector (FID).

2.2 General procedure for transfer reduction of *trans*-chalcone by benzyl alcohol

A mixture of benzyl alcohol (2 mmol), *trans*-chalcone (1 mmol), metal catalysts (1 mol% metal， based on *trans*-chalcone), *p*-xylene (3 mL), and *n*-dodecane (10 µL) as internal standard were placed into a flask (25 mL). The resulting mixture was vigorously stirred at 120 °C under N_2 atmosphere (1 atm) for 4h. The product was identified by GC–MS and the spectra obtained were compared with the standard spectra. The conversion and product selectivity were determined by GC-17A gas chromatograph equipped with a HP-FFAP column (30 m × 0.25 mm) and a flame ionization detector (FID).

2.3 General procedure for direct cross-coupling of secondary and primary alcohols

A mixture of primary alcohol (1 mmol), secondary alcohol (1 mmol), metal catalysts (1 mol% metal), *p*-xylene (3 mL), and *n*-dodecane (10 µL) as internal standard were placed into a flask (25 mL). The resulting mixture was vigorously stirred at 120 °C under N_2 atmosphere (1 atm) for given reaction time. The product was identified by GC–MS and the spectra obtained were compared with the standard spectra. The conversion and product selectivity were determined by GC-17A gas chromatograph equipped with a HP-FFAP column (30 m × 0.25 mm) and a flame ionization detector (FID). For isolation, the catalyst was removed by centrifugation and washed with Et_2O (2×5 mL). The combined supernatant was concentrated under reduced pressure and then subject to purification by silica gel column chromatography (petroleum ether (60–90 ^{o}C)-EtOAc mixture).

2.4 Procedure for kinetic experiments of sequential transformation between 1-phenethyl alcohol and benzyl alcohol

A mixture of reactants, 0.5% Au/HT (400 mg), *p*-xylene (3 mL), and *n*-dodecane (10 µL) as internal standard were placed into a flask (25 mL). The resulting mixture was vigorously stirred at 120 °C under N_2 atmosphere (1 atm) for 15 min. The conversion and product selectivity were determined by GC-17A gas chromatograph equipped with a HP-FFAP column (30 m × 0.25 mm) and a flame ionization detector (FID). The results are shown in Scheme S1.

2.5 Recovery and reuse of Au-Pd(13:1)/HT

The reused catalyst was recovered by centrifuging the solid Au-Pd(13:1)/HT from liquid phase after reaction. The recovered catalyst was washed with acetone for several times. The catalyst was then dried under vacuum at room temperature for 12 h. In the three successive cycles, the yields of 1,3-diphenylpropan-1-one (**4a**) were 97%, 96%, and 96% (GC analysis), respectively.

2.6 Procedure for 10-mmol scale cross-coupling of phenethyl alcohol and benzyl alcohol

A mixture of 1-phenylethanol (10 mmol), benzyl alcohol (10 mmol), Au-Pd(13:1)/HT (1.00 g), and *n*-dodecane (10 µL) as internal standard were placed into a flask (25 mL). The resulting mixture was vigorously stirred at 130 °C under N_2 atmosphere (1 atm) for 72h. The mixture was extracted with Et_2O for 3 times and passed through a short silica gel column before GC analysis. For isolation, the combined organic layer was dried over anhydrous Na_2SO_4, concentrated, and purified by silica gel column chromatography. 1,3-diphenylpropan-1-one (**4a**) was obtained as a white flake solid. The yields of **4a** was 89% (GC analysis).

2.7 Procedure for direct cross-coupling of phenethyl alcohol and benzyl alcohol under O_2 atmosphere.

A mixture of 1-phenylethanol (1 mmol), benzyl alcohol (1 mmol), Au-Pd(13:1)/HT (1 mol%), *p*-xylene (3 mL), and *n*-dodecane (10 µL) as internal standard were placed into a flask (25 mL). The resulting mixture was vigorously stirred at 120 °C under O_2 atmosphere (1 atm) for 7 h and gave *trans*-chalcone in 90% yield.

3. Results

A. CO_2- and NH_3-TPD measurements

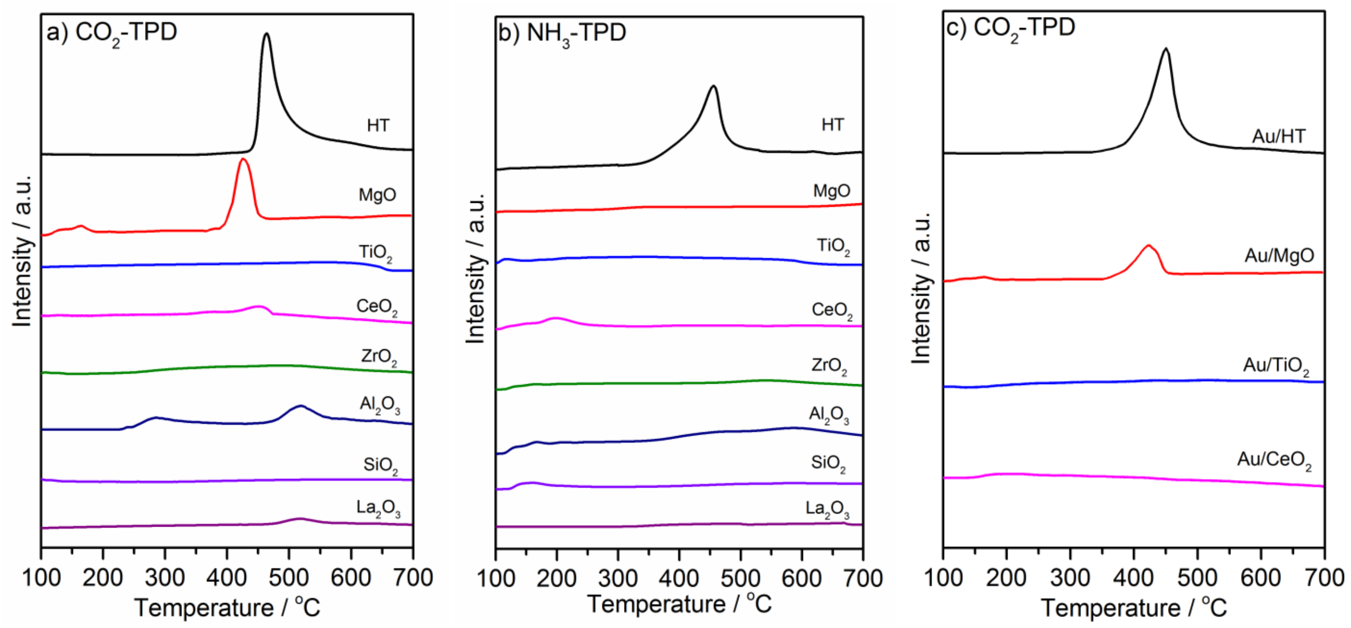
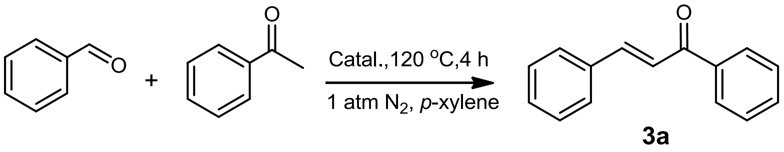


Figure S1. CO_2- and NH_3-TPD profiles of various catalysts.

B. ***Table S1.*** Surface basicity and acidity properties of various catalysts.

Catalysts	CO_2 desorbed ($mmol/g_{cat}$)	NH_3 desorbed ($mmol/g_{cat}$)
HT	0.54	0.28
Au/HT	0.58	-
MgO	0.45	0.02
Au/MgO	0.21	-
TiO_2	0.07	0.11
Au/TiO_2	0.03	-
CeO_2	0.12	0.08
Au/CeO_2	0.04	-
ZrO_2	0.09	0.07
Al_2O_3	0.18	0.20
SiO_2	0.02	0.08
La_2O_3	0.04	0.02

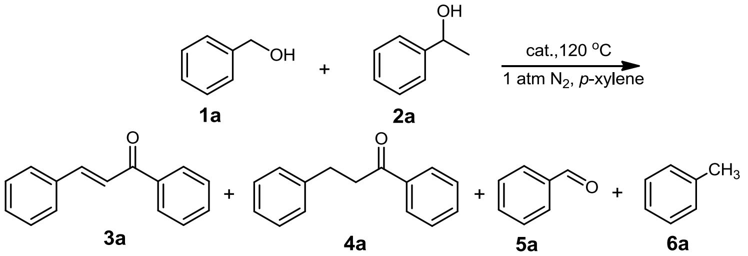
C. ***Table S2*****.** Aldol condensation of benzaldehyde and acetophenone catalyzed by various supported metal catalysts.[a]



Entry	Catalyst	Conv.[%][b]	Yield [%][b]
1	Au/HT	98	98
2	Au/TiO_2	18	18
3	Au/MgO	57	57
4	Au/CeO_2	6	6
5	Pd/HT	96	96
6	Pd/TiO_2	22	22
7	Pd /MgO	65	65
8	Pd /CeO_2	8	8
9	Pt/HT	97	97
10	Pt/TiO_2	40	40
11	Pt/MgO	53	53
12	Pt/CeO_2	11	11

[a] Reaction conditions: benzaldehyde (1 mmol), acetophenone (1 mmol), *p*-xylene (3 mL), catalyst (400 mg), 120 °C, 1 atm N_2, 4 h. [b] Conversion and yield based on benzaldehyde consumption. Determined by GC using *n*-dodecane as the internal standard.

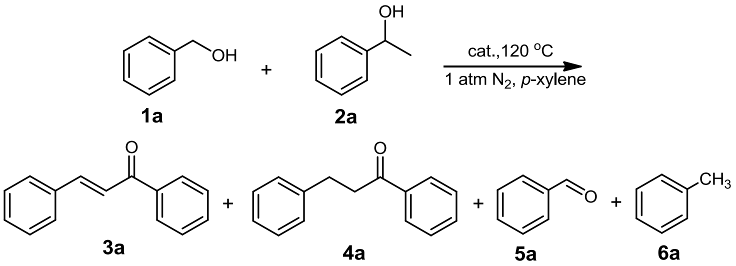
D. ***Table S3*****.** The examination of a series of Au/HT samples for the direct cross-coupling of benzyl alcohol **1a** with 1-phenylenthanol **2a.**[a]



Entry	Catalyst	Au particle size (nm) [b]	Conv.%[c]	Yield %[c]			
				3a	**4a**	**5a**	**6a**
1	0.24 wt% Au/HT	2.2	100	13	83	3	<1
2	0.50 wt% Au/HT	2.4	100	12	85	2	<1
3	1.10 wt% Au/HT	2.9	85	16	63	5	<1

[a] Reaction conditions: benzyl alcohol (1 mmol), 1-phenylethanol (1 mmol), *p*-xylene (3 mL), Au/HT (Au: 1 mol%), 5h, 1 atm N_2, n.d. = not detected. [b] Au particle size was dertermined by transmission electron microscope (TEM) micrographs (see Figure S3a-c). [c]Conversion and yield based on benzyl alcohol consumption were determined by GC using *n*-dodecane as the internal standard.

E. ***Table S4.*** Reaction of benzyl alcohol **1a** with 1-phenylenthanol **2a** catalyzed by 0.5 wt% Au/HT under various conditions.[a]



Entry	Solvent	T/°C	t/h	Conv.%[b]	Yield %[b]			
					3a	**4a**	**5a**	**6a**
1	mesitylene	110	6	100	30	13	57	1
2	o-xylene	110	6	100	47	8	45	5
3	dioxane	100	6	14	2	2	10	n.d.
4	p-xylene	80	6	53	20	21	11	<1
5	p-xylene	100	6	84	18	56	9	<1
6	p-xylene	110	6	100	15	75	9	<1
7	p-xylene	120	5	100	12	85	2	<1
8	p-xylene	135	5	100	13	84	2	<1

[a] Reaction conditions: benzyl alcohol (1 mmol), 1-phenylethanol (1 mmol), *p*-xylene (3 mL), 0.5% Au/HT (Au: 1 mol%), 1 atm N_2, n.d. = not detected. [b] Conversion and yield based on benzyl alcohol consumption were determined by GC using *n*-dodecane as the internal standard.

F. ***Table S5.*** Characterization results of Au-Pd/HT catalysts.

Catalyst	Au/Pd theoretical molar ratio	Au/Pd actual molar ratio	Metal content (wt%)[a]	
			Au	Pd
Au-Pd(13:1)/HT	10:1	13:1	0.47	0.02
Au-Pd(8:1)/HT	8:1	8:1	0.45	0.03
Au-Pd(4:1)/HT	5:1	4:1	0.42	0.05
Au-Pd(5:2)/HT	5:2	5:2	0.41	0.09

[a] The weight concentration of Au or Pd was determined by ICP-AES.

G. Kinetic experiments of sequential transformation between 1-phenylethanol and benzyl alcohol

Dehydrogenation of benzyl alcohol (1a)

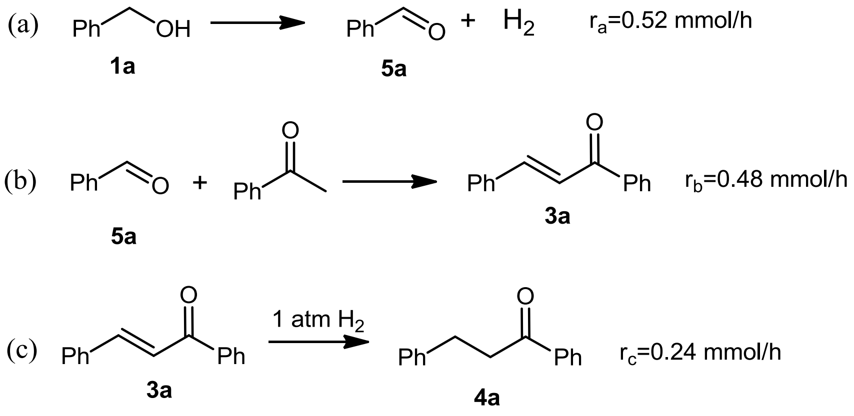
A mixture of **1a** (1 mmol), 0.5% Au/HT (400 mg), *p*-xylene (3 mL), and *n*-dodecane (10 µL) as internal standard were placed into a flask (25 mL). The resulting mixture was vigorously stirred at 120 °C under N_2 atmosphere (1 atm) for 15 min to give **5a** in 13% yield (Scheme S1a).

Aldol condensation of benzaldehyde (5a) and acetophenone

A mixture of **5a** (1 mmol), acetophenone (1 mmol), 0.5% Au/HT (400 mg) (400 mg), *p*-xylene (3 mL), and *n*-dodecane (10 µL) as internal standard were placed into a flask (25 mL). The resulting mixture was vigorously stirred at 120 °C under N_2 atmosphere (1 atm) for 15 min to give **3a** in 12% yield (Scheme S1b).

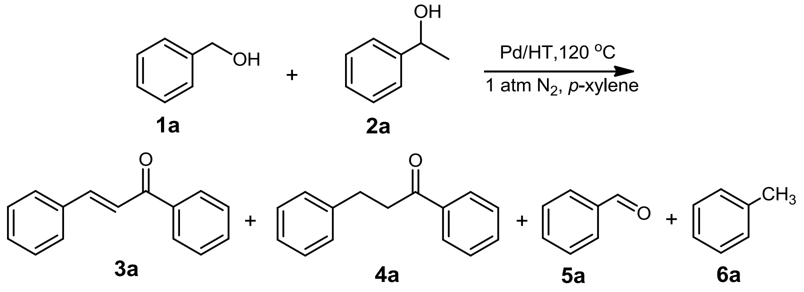
Hydrogenation of *trans*-chalcone (3a)

A mixture of **3a** (1 mmol), 0.5% Au/HT (400 mg), *p*-xylene (3 mL), and *n*-dodecane (10 µL) as internal standard were placed into a flask (25 mL). The resulting mixture was vigorously stirred at 120 °C under H_2 atmosphere (1 atm) for 15 min to give **4a** in 6% yield (Scheme S1c).



Scheme S1. Initial reaction rates (r) calculated for the sequential transformation between 1-phenyethanol and benzyl alcohol catalyzed by 0.5% Au/HT at 120 °C

H. Reaction profiles for cross-coupling of 1a and 2a using Pd/HT



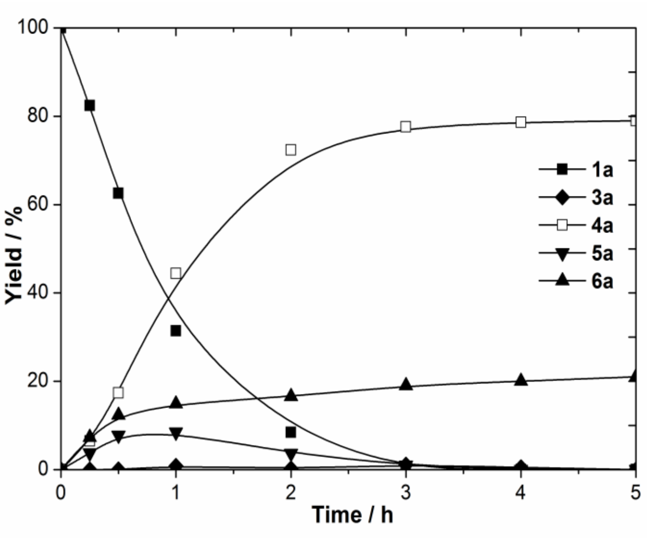


Figure S2. Reaction profiles for cross-coupling of phenethyl and benzyl alcohols 1% Pd/HT. Reaction conditions: 1-phenylethanol (1 mmol), benzyl alcohol (1 mmol), *p*-xylene (3 mL), catalyst (metal: 1 mol%), 120 °C, under N_2.

K. XRD patterns of HT-based catalysts

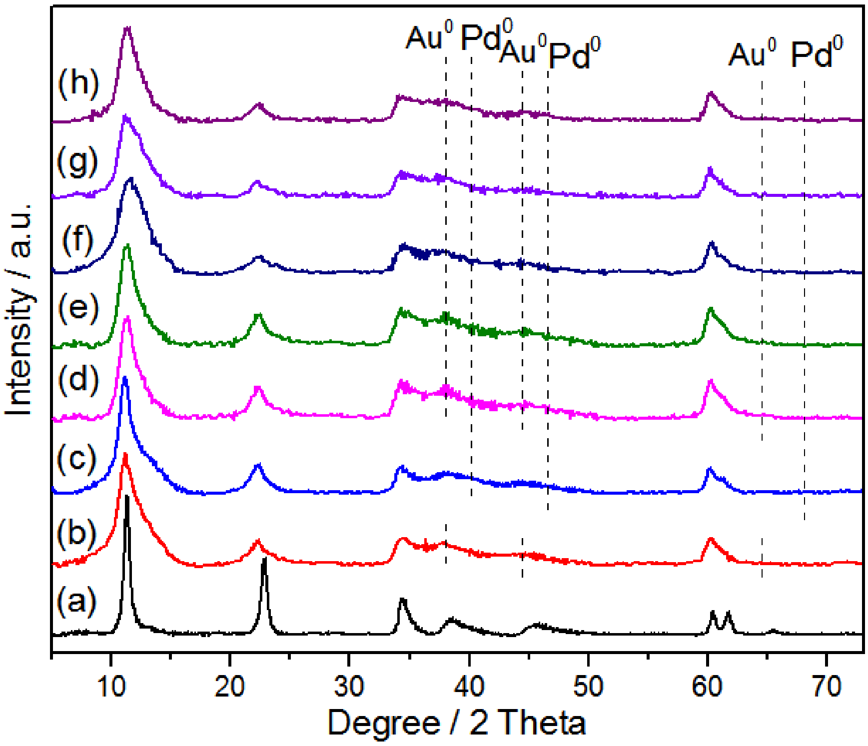
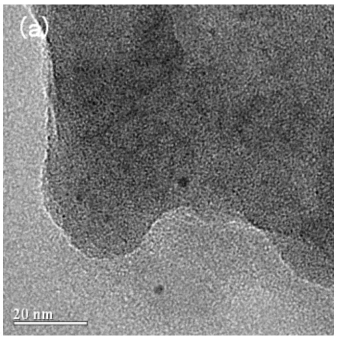
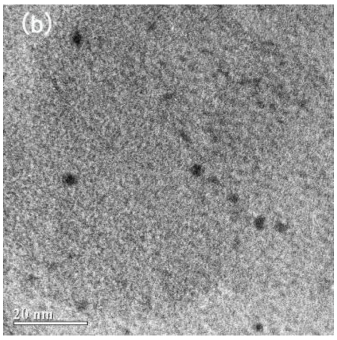
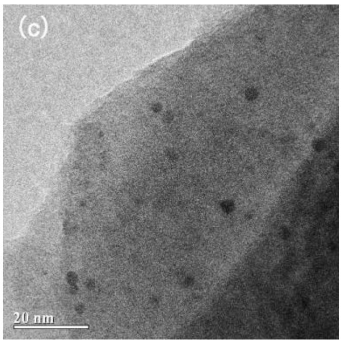


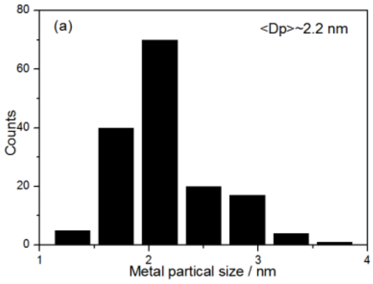
Figure S3. Powder XRD patterns of HT (a); Au/HT (b); Pd/HT (c); Au-Pd(13:1)/HT before (d) and after (e) three reaction cycles; Au-Pd(8:1)/HT (f); Au-Pd(4:1)/HT (g); Au-Pd(5:2)/HT (h). Note that the crystalline structure of HT were largely maintained in the Au- or/and Pd-containing samples. No diffraction lines of metallic gold or palladium were observed in all of the metal-loaded samples, which indicated that the gold or/ and Pd particles were highly dispersed and the sizes were very small (< 5 nm).

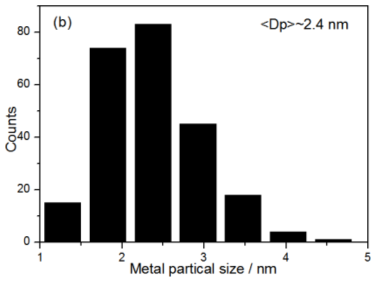
I. TEM images

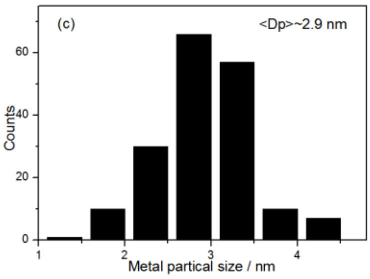

(a)
20 nm

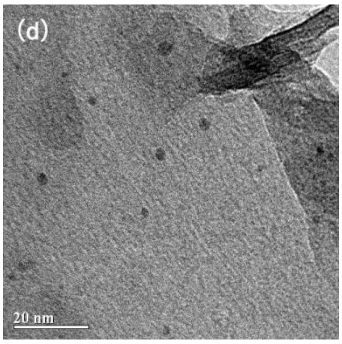

(b)
20 nm

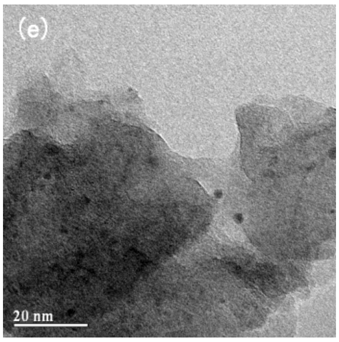

(c)
20 nm

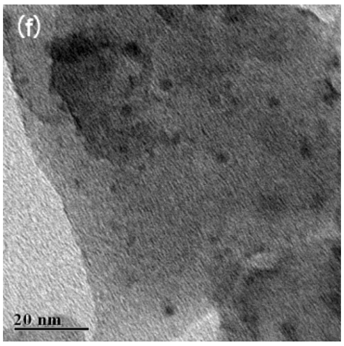

(a)
<Dp>~2.2 nm
Counts
0
20
40
60
80
1
2
3
4
Metal partical size / nm

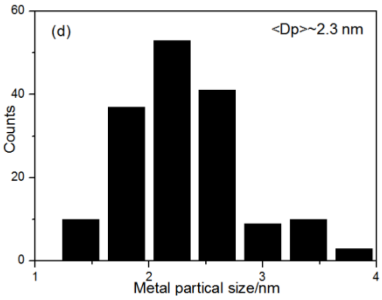

(b)
<Dp>~2.4 nm
Counts
0
20
40
60
80
1
2
3
4
5
Metal partical size / nm

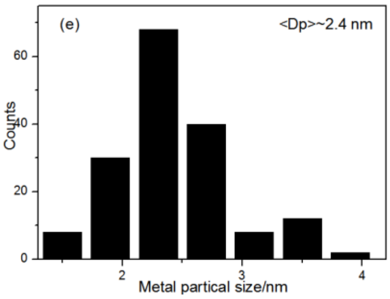

(c)
<Dp>~2.9 nm
Counts
0
20
40
60
1
2
3
4
Metal partical size / nm

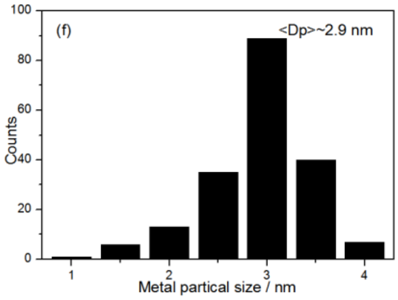

(d)
20 nm

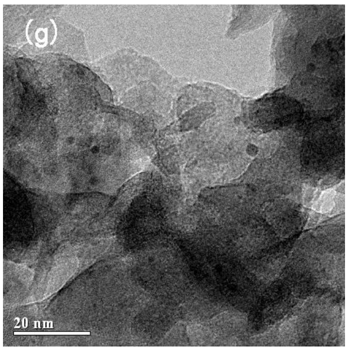

(e)
20 nm

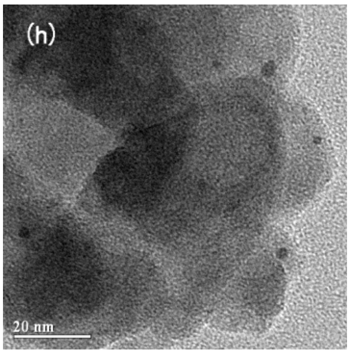

(f)
20 nm

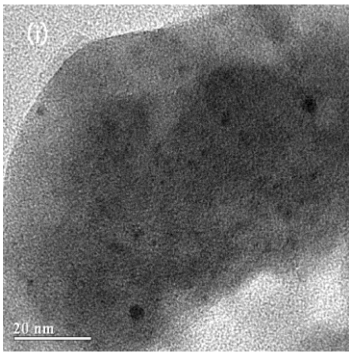

(d)
<Dp>~2.3 nm
Counts
0
20
40
60
1
2
3
4
Metal partical size/nm


(e)
<Dp>~2.4 nm
Counts
0
20
40
60
2
3
4
Metal partical size/nm


(f)
<Dp>~2.9 nm
Counts
0
20
40
60
80
100
1
2
3
4
Metal partical size / nm


(g)
20 nm


(h)
20 nm


(i)
20 nm

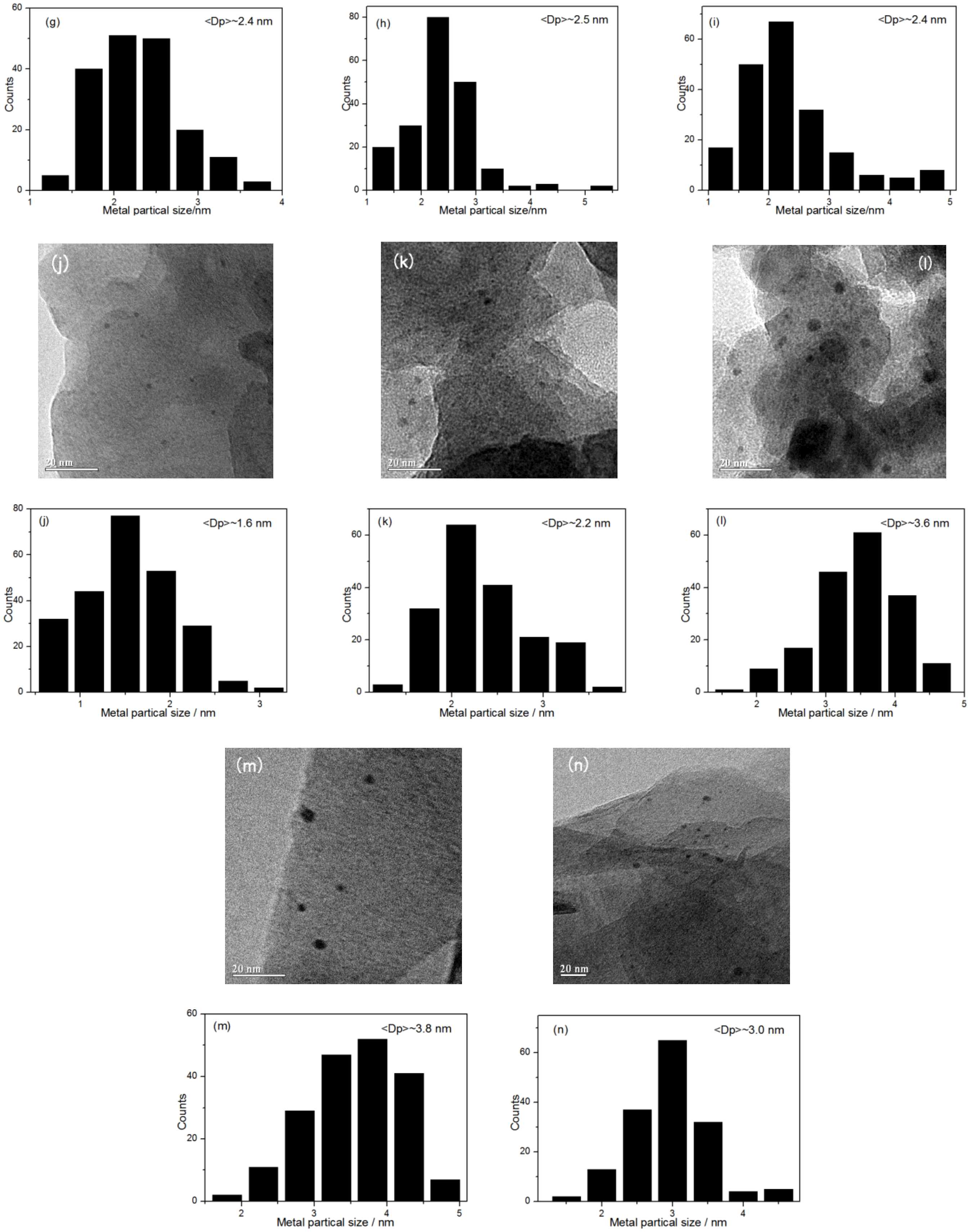


Figure S4. TEM image and gold particle size distribution of 0.24 wt% Au/HT (a); 0.50 wt% Au/HT (b); 1.10 wt% Au/HT (c); Au-Pd(13:1)/HT before (d) and after (e) three reaction cycles or (f) five reaction cycles; Au-Pd(8:1)/HT (g); Au-Pd(4:1)/HT (h); Au-Pd(5:2)/HT (i); Pd/HT (j); Ag/HT (k); Ru/HT (l); Rh/HT(m); Pt/HT (n). Note that no aggregated particles were observed on the same Au-Pd(13:1)/HT sample after three times reuse, while the particle size increased slightly after five times recycling.

J. EDX spectra

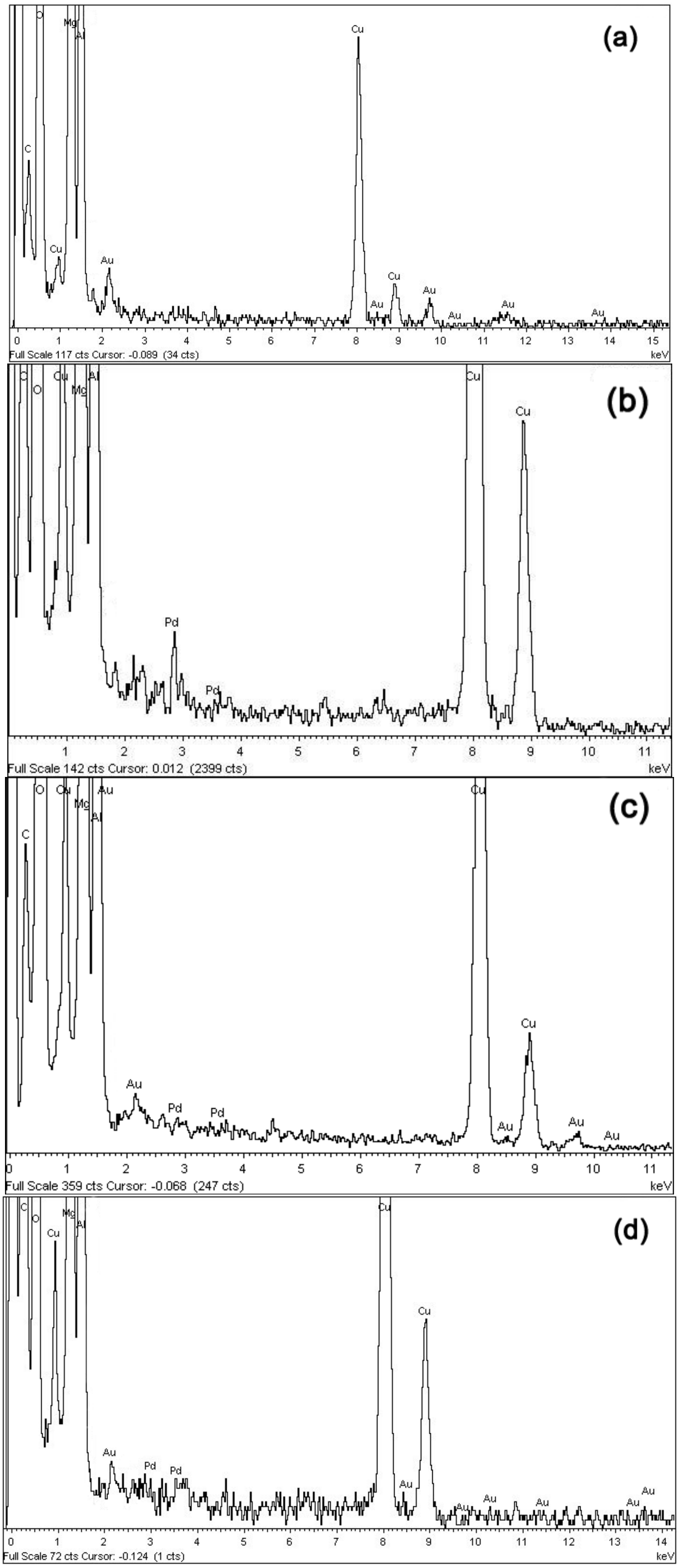


Figure S5. Representative EDX spectra of Au/HT (a); Pd/HT (b); Au-Pd(13:1)/HT before (c) and after (d) three reaction cycles; Cu in spectra originates from the TEM grid. Note that EDX also shows that some of the NPs are monometallic Au (not shown) in the Au-Pd(13:1)/HT sample .

L. XP spectra

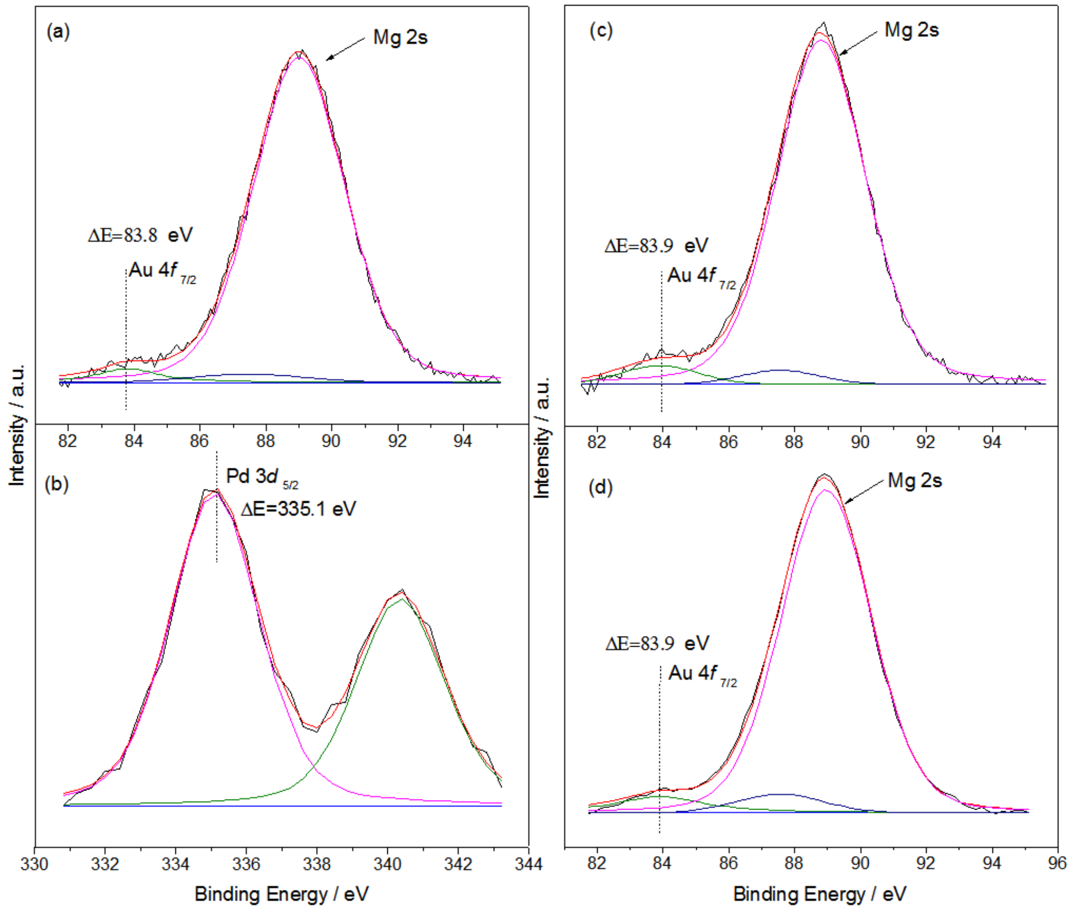
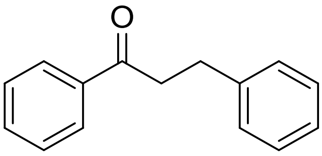
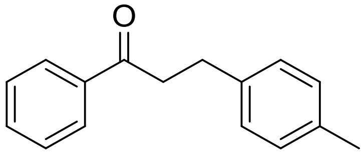


Figure S6. XPS of Au/HT (a); Pd/HT (b); Au-Pd(13:1)/HT before (c) and after (d) three reaction cycles. Note that the peaks of Pd 3d can not be observed for Au-Pd(13:1)/HT due to the low Pd-containing, and the binding energy of Au $4f_{7/2}$ for Au-Pd(13:1)/HT is shifted to higher by approximately 0.1 eV compared to the monometallic Au/HT sample. Such observed shifts for Au 4f may be attributed to the interaction between the two metals which lead to the electron transfer from Au to Pd. These results are consistent with the observation of the EDX spectra (Figure S5c-d). The metallic state of Au practically undergoes no change after the five successive runs.

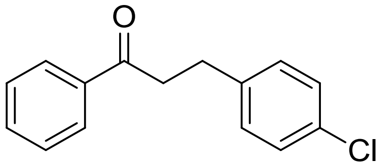
M. Characterization of Ketones



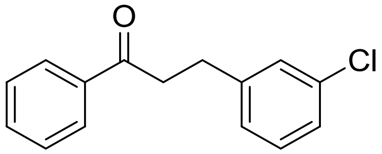
(Table 4, entry 1).[S8] White solid (petroleum ether-EtOAc); m.p.= 71-72 °C; ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.91-7.98 (2H, m), 7.50 -7.58 (1H, m), 7.40-7.48 (2H, m), 7.17-7.32 (5H, m), 3.30 (2H, t, J=8.0 Hz), 3.06 (2H, t, J=8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 199.3, 141.4, 136.9, 133.2, 128.7, 128.6, 128.5, 128.1, 126.2, 40.6, 30.2; MS: m/z (relative intensity) 210 (M^+, 59), 105 (100), 91(10), 77(36).



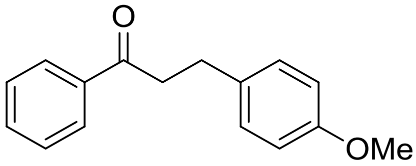
(Table 4, entry 2).[S9] Pale yellow oil; ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.89-8.02 (2H, m), 7.51-7.62 (1H, m), 7.38-7.50 (2H, m), 7.04-7.20 (4H, m), 3.26 (2H, t, J=7.2 Hz), 2.02 (2H, t, J=7.2 Hz), 2.33 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 199.5, 138.3, 137.0, 135.7, 133.2, 139.3, 128.7, 128.4, 128.2, 40.7, 29.8, 21.2.



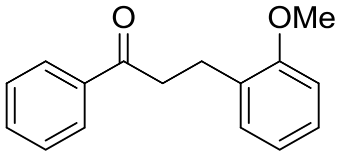
(Table 4, entry 3).[S10] White solid (petroleum ether-EtOAc); m.p. 57-58 °C; ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.89-8.02 (2H, m); 7.52–7.60 (1H, m), 7.42–7.48 (2H, m), 7.19–7.28 (4H, m), 3.27 (2H, t, J = 7.6 Hz), 3.03 (2H, t, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 189.9, 139.8, 136.8, 133.3, 132.0, 129.9, 128.7, 128.1, 40.2, 29.4.



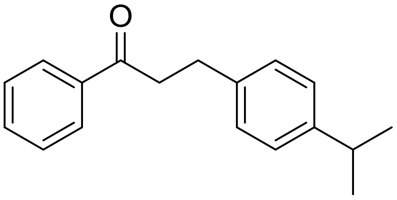
(Table 4, entry 4).[S11] White solid (petroleum ether-EtOAc); m.p. 74-75 °C;[S12] ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.88-8.01 (2H, m), 7.51-7.59 (1H, m), 7.42-7.48 (2H, m), 7.27-7.32 (4H, m), 3.30 (2H, t, J = 7.6 Hz), 3.05 (2H, t, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 198.5, 143.1, 136.6, 134.2, 133.0, 129.5, 128.5, 127.8, 126.5, 126.2, 39.8, 29.6.



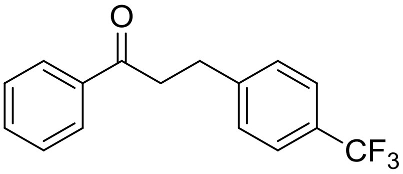
(Table 4, entry 5).[S10] White solid (petroleum ether-EtOAc); m.p. 66-67 °C; ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.90-8.03 (2H, m), 7.52-7.63 (1H, m), 7.39-7.51 (2H, m), 6.83-7.18 (4H, m), 3.79 (3H, s), 3.27 (2H, t, J = 7.6 Hz), 3.01 (2H, t, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 199.5, 158.1, 137.0, 133.4, 133.2, 139.5, 128.7, 128.1, 114.0, 55.4, 40.8, 29.4.



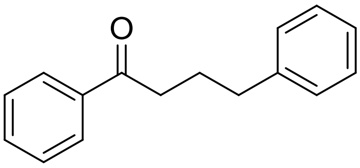
(Table 4, entry 6).[S9] Pale yellow oil; ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.94-8.06 (2H, m), 7.51-7.57 (1H, m), 7.41–7.50 (2H, m), 6.86-7.24 (4H, m), 3.85 (s, 3 H), 3.29 (2H, t, J = 7.6 Hz), 3.02 (2H, t, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 200.0, 137.0, 133.0, 130.2, 129.5, 128.7, 138.6, 128.4, 128.2, 127.6, 120.6, 110.3, 55.2, 39.0, 25.8.



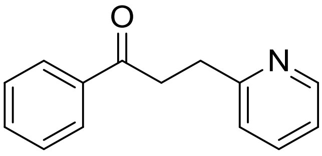
(Table 4, entry 7).[S13] Colorless oil; ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.93-8.01 (2H, m), 7.52-7.60 (1H, m), 7.41-7.50 (2H, m), 7.12-7.22 (4H, m), 3.30 (2H, t, J=7.6 Hz), 3.04 (2H, t, J=7.6 Hz), 2.84-2.94 (1H, m), 2.33 (6H, d).



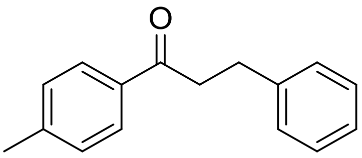
(Table 4, entry 8).[S11] Pale yellow oil; ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.92-8.02 (2H, m), 7.48-7.52 (1H, m), 7.54-7.56 (2H, m), 7.23-7.46 (4H, m), 3.32 (2H, t, J = 7.6 Hz), 3.14 (2H, t, J=7.6 Hz,); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 190.6, 145.2, 145.0, 136.5, 133.0, 128.6, 138.6, 127.8, 125.2, 125.0, 39.6, 29.6.



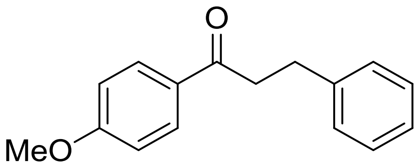
(Table 4, entry 9).[S14] White solid (petroleum ether-EtOAc); m.p. 55-56 °C; ^{1}H-NMR ($CDCl_3$, 400 MHz): 7.92-7.98 (2H, m), 7.55-7.59 (1H, m), 7.42-7.48 (2H, m), 7.29-7.37 (2H, m), 7.21-7.26 (3H, m), 3.00 (2H, t, J=7.2 Hz), 2.50 (2H, t, J=7.6 Hz), 2.07-2.15 (2H, m); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 200.3, 141.8, 137.2, 133.1, 128.7, 128.6, 128.5, 128.2, 126.1, 37.8, 35.3, 25.8.



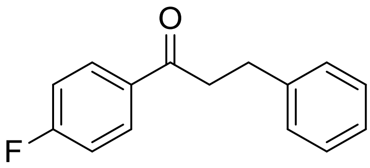
(Table 4, entry 10).[S15] Brown oil; ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.45-8.60 (d, 1H), 7.98-8.02 (d, 2H), 7.53-7.63 (m, 2H), 7.43-7.48 (m, 2H), 7.27 (d, 1H), 7.10-7.14 (m, 1H), 3.53 (t, 2H, J=8.0 Hz), 3.25 (t, 2H, J=8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 199.4, 160.8, 149.2, 136.5, 133.1, 128.6, 128.1, 123.4, 121.3, 37.9, 32.1.



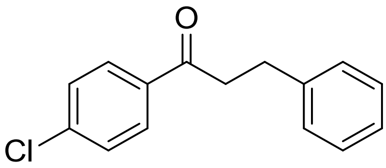
(Table 4, entry 13).[S15] White solid (petroleum ether-EtOAc); m.p. 67-68 ^{o}C; ^{1}H-NMR (CDCl$_3$, 400 MHz): δ 7.80-7.96 (2H, m), 7.14-7.40 (7H, m), 3.26 (2H, t, J=7.6 Hz), 3.06 (2H, t, J=7.6 Hz), 2.39 (3H, s); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 198.9, 143.9, 141.5, 134.5, 129.3, 129.2, 128.6, 128.5, 126.1, 40.4, 30.3, 21.6.



(Table 4, entry 14).[S16] Colorless solid (petroleum ether-EtOAc); m.p. 96-97 ^{o}C; ^{1}H-NMR (CDCl$_3$, 400 MHz): δ 7.95 (2H, d, J = 8.4 Hz), 7.18-7.32 (5H, m), 6.92 (2H, d, J = 8.4 Hz), 3.85 (3H, s), 3.25 (2H, t, J = 7.6 Hz), 3.05 (2H, t, J = 7.6 Hz); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 198.5, 163.2, 141.5, 130.2, 129.8, 128.3, 128.2, 125.7, 113.6, 55.3, 40.3, 30.5.



(Table 4, entry 15).[S17] ^{1}H-NMR (CDCl$_3$, 400 MHz): White solid; m.p. 37-38 °C;[S18] δ 7.88-7.92 (2H, m), 7.12-7.22 (5H, m), 7.02-7.06 (2H, m), 3.19 (2H, t, J = 7.6 Hz), 2.97 (2H, t, J = 7.6 Hz); ^{13}C NMR (CDCl$_3$, 100 MHz): 198.0, 166.1, 141.6, 133.7, 131.1, 129.0, 128.9, 126.6, 116.3, 40.8, 30.5.



(Table 4, entry 16).[S19] White solid (petroleum ether-EtOAc); m.p. 75-76 °C; ^{1}H-NMR (CDCl$_3$, 400 MHz): δ7.89 (d, 2H, J = 8.0 Hz), 7.43 (2H, d, J = 8.0 Hz), 7.20-7.32 (5H, m), 3.27 (2H, t, J = 7.6 Hz), 3.06 (2H, t, J = 7.6 Hz); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 197.9, 141.1, 139.6, 135.3, 129.5, 128.6, 128.5, 126.3, 40.1, 30.1.

References

[S1] F. Cavani, F. Trifirò, A. Vaccari, *Catal. Today* **1991**, *11*, 173-301.

[S2] H. Sun, F. Z. Su, J. Ni, Y. Cao, H. Y. He, K. N. Fan*, Angew. Chem.* **2009**, *121*, 4454-4457; *Angew. Chem. Int. Ed.* **2009**, *48*, 4390-4393.

[S3] Q. Y. Bi, X. L. Du, Y. M. Liu, Y. Cao, H. Y. He, K. N. Fan, *J. Am. Chem. Soc.* **2012**, *134,* 8926-8933.

[S4] Q. Y. Bi, L. Qian, L. Q. Xing, L. P. Tao, Q. Zhou, J. Q. Lu, M. F. Luo, *J. Fluor. Chem.* **2009**, *130*, 528-533.

[S5] D. Kumar, V. B. Reddy, B. G. Mishra, R. K. Rana, M. N. Nadagoudac, R. S. Varma, *Tetrahedron* **2007**, *63*, 3093-3097.

[S6] M. M. Wang, L. He, Y. M. Liu, Y. Cao, H. Y. He, K. N. Fan, *Green Chem.* **2011**, *13*, 602-607.
[S7] L. He, L. C. Wang, H. Sun, J. Ni, Y. Cao, H. Y. He, K. N. Fan, *Angew. Chem.* **2009**, *121*, 9702-9705; *Angew. Chem. Int. Ed.* **2009**, *48*, 9538-9541.
[S8] F.-X. Felpin, E. Fouquet, *Chem. Eur. J.* **2010**, *16*, 12440-12445.
[S9] T. Kuwahara, T. Fukuyama, I. Ryu, *Org. Lett.* **2012**,*14*, 4703-4705.
[S10] Y. Yu, L. S. Liebeskind, *J. Org. Chem.* **2004**, *69*, 3554-3557.
[S11] A. Stroba, F. Schaeffer, V. Hindie, L. Lopez-Garcia, I. Adrian, W. Frohner, R. W. Hartmann, R. M. Biondi, M. Engel, *J. Med. Chem.* **2009**, *52*, 4683-4693.
[S12] V. I. Yakovenko, E. E. Mikhlina, É. T. Oganesyan, L. N. Yakhontov, *Chem. Heterocycl. Comp.* **1975**, *11*, 1104-1106.
[S13] C. Matthias, D. Kuck, *Croat. Chem. Acta* **2009**, *82*, 7-19.
[S14] J. A. Murphy, A. G. J. Commeureuc, T. N. Snaldon, T. M. McGuire, T. A. Khan, K. Hisler, M. L. Dewis, R. Carling, *Org. Lett.* **2005**, *7*, 1427-1429.
[S15] X. Cui, Y. Zhang, F. Shi, Y. Deng, *Chem. Eur. J.* **2011**, *17*, 1021-1028
[S16] A. R. Hajipour, A. Zarei, L. Khazdooz, A. E. Ruoho, *Synth. Commun.* **2009**, *39*, 2702-2722.
[S17] J. Ruan, O. Saidi, J. A. Iggo, J. Xiao, *J. Am. Chem. Soc.* **2008**, *130*, 10510-10511.
[S18] F. Tian, S. Lu, S*ynlett* **2004**, *11*, 1953-1956.
[S19] T. Ikawa, H. Sajiki, K. Hirota, *Tetrahedron* **2005**, *61*, 2217-2231.