Experimental Details

1. Catalytic materials

Au/TiO_2-WGC (1.5 wt% Au, type A, lot no. Au/TiO_2 no. 02-1) and 4.5 wt% Au/Fe_2O_3 were supplied by the World Gold Council (WGC). 0.9 wt% Au/Al_2O_3 and 1 wt% Au/ZnO were provided by Mintek.

Preparation of Au/TiO_2-VS catalyst: A slightly modified deposition-precipitation (DP) procedure has been employed to prepare the Au/TiO_2-VS sample. TiO_2 (1.0 g, Degussa P25, S_{BET}: 45 m^2/g, nonporous, 70% anatase and 30% rutile) was added to 100 mL of an appropriate amounts of aqueous solution of $HAuCl_4$ at a fixed pH = 8 adjusted 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 calcination at 300 ^oC for 4 h in static air. All procedures were performed in the absence of light. The as-prepared sample featuring very small Au nanoparticles (*ca.* 1.8 nm, see TEM data in Fig. S1) deposited on titania is denoted as Au/TiO_2-VS. Elemental analysis results revealed that the real gold loading was 0.49 wt% in Au/TiO_2-VS.

Preparation of Au/ZrO_2 catalyst: The 0.1**%** Au/ZrO_2 catalysts was prepared by modified deposition- precipitation method by mixing ZrO_2 powders (2 g) with appropriate amounts of aqueous solutions of $HAuCl_4$ at a fixed pH=9.0 ± 0.1 adjusted with 0.25 M ammonia. The aqueous dispersion was stirred for 6 h at room temperature, and then filtered. 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 then reduced in 5% H_2/Ar at 300 ^oC for 2 h. Elemental analysis results revealed that the real gold loading was 0.08 wt% in Au/ZrO_2.

Preparation of Au/CeO_2 catalyst: The 0.5 wt% Au/CeO_2 sample was prepared by the modified DP procedure as described above. CeO_2 (1.0 g, Degussa, Adnano 90, specific surface area: 90 m^2/g) was added to 100 mL of an appropriate amounts of aqueous solution of $HAuCl_4$ at a fixed pH=9 adjusted 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. Elemental analysis results revealed that the real gold loading was 0.5 wt% in Au/CeO_2.

Preparation of Pd/TiO_2 and Ru/TiO_2 catalysts: 0.5 wt% Pd/TiO_2 and 0.5 wt% Ru/TiO_2 catalysts were prepared by incipient wetness impregnation of the support (Degussa P25, specific surface area: 45 m^2/g nonporous, 70% anatase and 30% rutile, purity > 99.5%), with aqueous solution of Pd $(NO_3)_2 \cdot 6H_2O$ or $RuCl_3$ (Aldrich) of appropriate concentrations (typically 1.0 mL/g support). After a perfect mixing of the corresponding slurries, samples were dried at 100 ^oC for 5 h and then reduced under 5% H_2/Ar (flow rate 30 mL/min) at 450 ^oC for 3 h. TEM showed that the mean diameters of the Pd and Ru NPs formed on the TiO_2 support were ca. 2.0 and 2.8 nm, respectively.

2. Catalytic activity measurements

General procedure for the direct secondary or tertiary amines formation from nitroarenes and alcohols: A certain amount of nitroarenes, alcohols, metal catalysts (0.5 mol% metal), toluene (1 mL) and *n*-dodecane (10 μL) as internal standard were placed into a Teflon-lined autoclave (4 mL capacity). The resulting mixture was vigorously stirred at the given temperature under Argon atmosphere (1 atm) for the 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 combined organic layer was dried over anhydrous Na_2SO_4, concentrated, and purified by silica gel column chromatography.

Direct N-alkylation of N-phenylbenzylamine (3a) with benzyl alcohol by using Au/TiO_2-VS at 150 °C or 120 °C: A mixture of phenylbenzylamine (1 mmol), benzyl alcohol (8 mmol), Au/TiO_2-VS (0.5 mol% Au), toluene (1 mL) and *n*-dodecane (10 µL) as internal standard were placed into a Teflon-lined autoclave (4 mL capacity). The resulting mixture was vigorously stirred at 150 or 120 °C under Argon atmosphere (1 atm) for 48 h. The yield (based on the starting amine) of tertiary amine (**3a’’**) was up to 99% for the case at 150 °C. In contrast, the same reaction was found to proceed sluggishly at 120 °C, with less than 5% of phenylbenzylamine was converted to tertiary amine. These results indicate that the second N-alkylation depends critically on the reaction temperature.

3. Characterization

Elemental analysis: The precise Au loading of the catalysts was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Thermo Electron IRIS Intrepid II XSP spectrometer.

Transmission electron microscopy (TEM): TEM images for supported gold catalysts were taken with a JEOL 2011 electron microscope operating at 200 kv. Before being transferred into the TEM chamber, the samples dispersed with ethanol were deposited onto a carbon-coated copper grid and then quickly moved into the vacuum evaporator. The size distribution of Au was determined by randomly measuring for each sample ca. at least 200 particles by TEM, and the average size of Au was calculated according to the equation $d=\Sigma n_i d_i/n_{i.}$

$$R_2CH_2OH \longrightarrow R_2CHO + H_2 \cdots\cdots \quad (1)$$

$$R_2CH_2OH + R_2CHO \longrightarrow R_2COOCH_2R_2 + H_2 \cdots\cdots \quad (2)$$

$$R_1NO_2 + 3R_2CH_2OH \longrightarrow R_1NH_2 + 3R_2CHO + 3H_2O \cdots\cdots \quad (3)$$

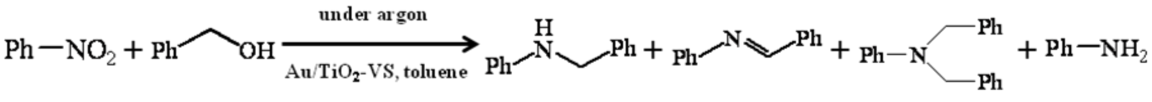
$$R_1NO_2 + 3R_2CH_2OH \longrightarrow R_2CH{=}NR_1 + 2R_2CHO + 3H_2O \cdots\cdots \quad (4)$$

$$R_1NO_2 + 4R_2CH_2OH \longrightarrow R_2CH_2NHR_1 + 3R_2CHO + 3H_2O \cdots\cdots \quad (5)$$

$$R_1NO_2 + 5R_2CH_2OH \longrightarrow (R_2CH_2)_2NR_1 + 3R_2CHO + 4H_2O \cdots\cdots \quad (6)$$

Scheme S1. Possible reaction stoichiometries during the direct amination of nitroarenes with alcohols: (1) Dehydrogenation of alcohol to the corresponding aldehyde; (2) Dehydrogenative condensation of alcohol with the intermediate aldehyde to the corresponding ester; (3) Aniline generation via the catalytic transfer reduction of nitroarene; (4) Imine formation via direct condensation of the nitroarene and alcohol; (5) Synthesis of secondary amine via direct condensation of the nitroarene and alcohol; (6) Generation of tertiary amine via the direct condensation of nitroarene and alcohol.

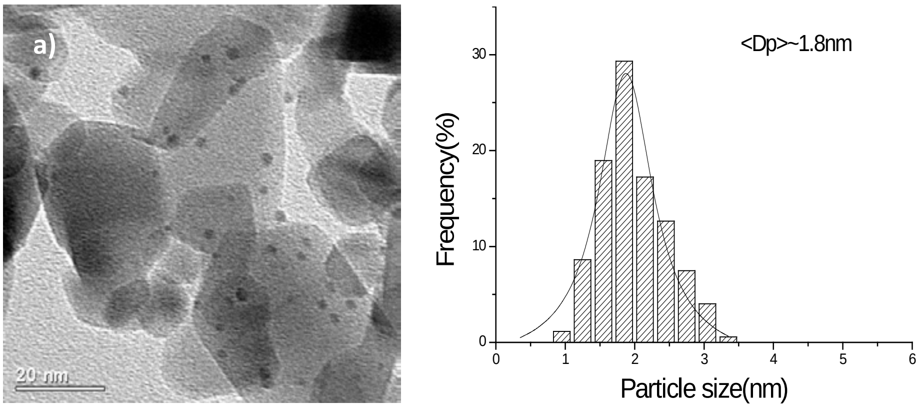
Table S1. Catalytic reaction of nitrobenzene with benzyl alcohol under various conditions.[a]

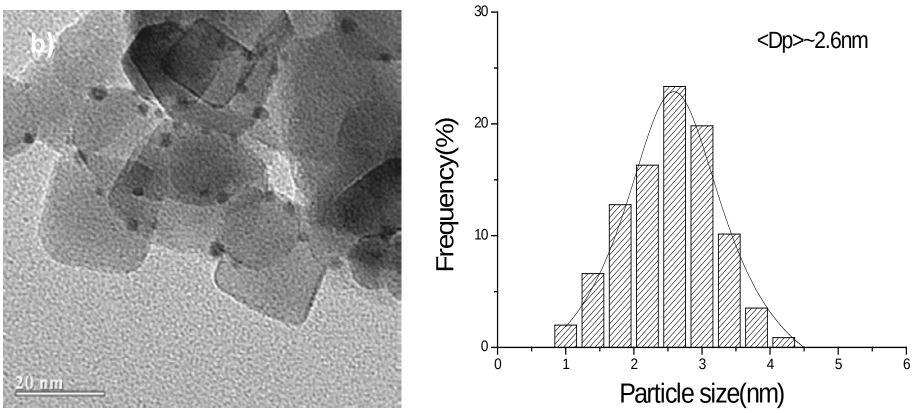


1a 2a 3a 3a' 3a'' 1a'

Entry	Solvent	T(°C)	n_{PhNO2}/ $n_{PhCH2OH}$	Con. (%)[c]	Sel. (%)[c]			
					3a	3a'	3a''	1a'
1	THF	120	1:8	100	7	47	-	46
2	cyclohexane	120	1:8	100	20	35	-	45
3	1,4-dioxane	120	1:8	100	28	29	-	43
4	toluene	120	1:8	100	>99	-	<1	-
5	toluene	100	1:8	100	8	56	-	36
6	toluene	80	1:8	100	2	42	-	56
7	toluene	120	1:3	81	-	60	-	40
8[b]	toluene	120	1:5	100	5	95	-	-
9	toluene	120	1:5	100	72	28	-	-
10	toluene	120	1:10	100	90	4	6	-
11	toluene	120	1:15	100	85	7	8	-

[a] Reaction conditions: nitrobenzene (1 mmol), solvent (1 mL), catalyst (Au/TiO_2-VS, metal: 0.5 mol%), 120 °C, 14 hr under argon atmosphere. [b] t=8 hr. [c] Selectivity based on nitrobenzene conversion, determined by GC using *n*-dodecane as the internal standard.





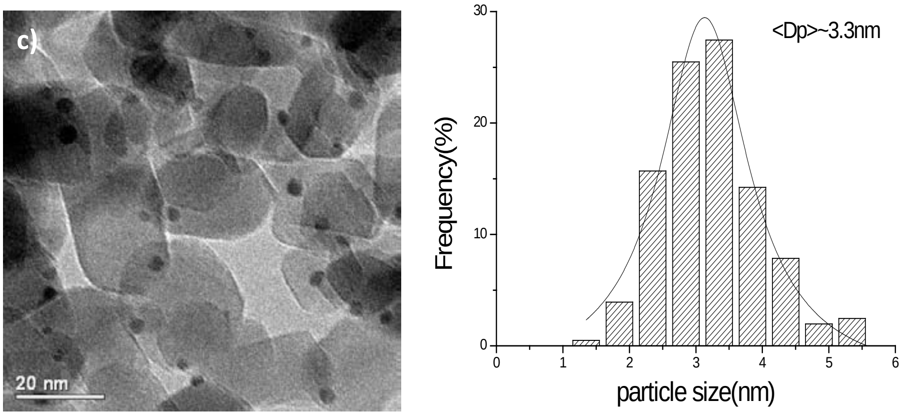
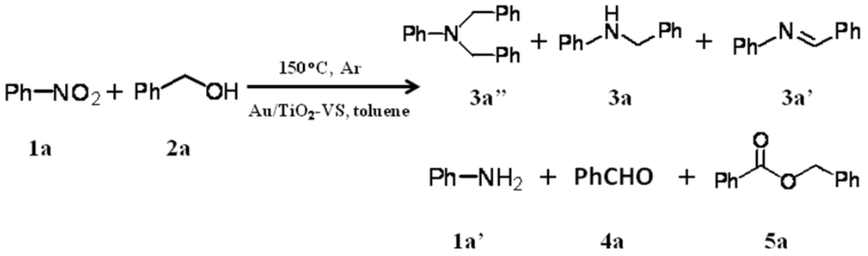


Figure S1. Representative TEM image and Au particle size distribution (Lines only to guide the eye: not curve fits) of a) 0.5 wt % Au/TiO_2-VS; b) 0.5 wt % Au/TiO_2-VS after fifth runs ; c) 1.5 wt % Au/TiO_2-WGC.



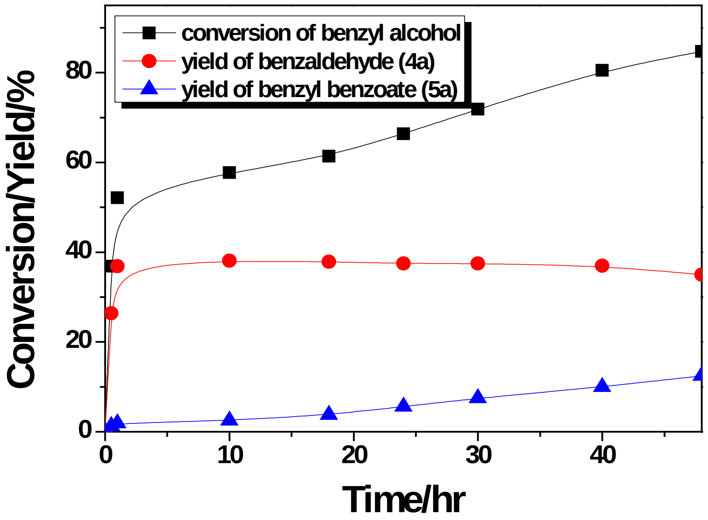


Figure S2. The evolution of alcohol dehydrogenative by-products including benzaldehyde (4a) and benzyl benzoate (5a) during the direct synthesis of tertiary amine. Reaction conditions: nitrobenzene (1 mmol), benzyl alcohol (8 mmol), toluene (1 mL), catalyst (Au/TiO_2-VS, metal: 0.5 mol%), 150 °C, 48 hr under argon atmosphere;Yields based on benzyl alcohol conversion.

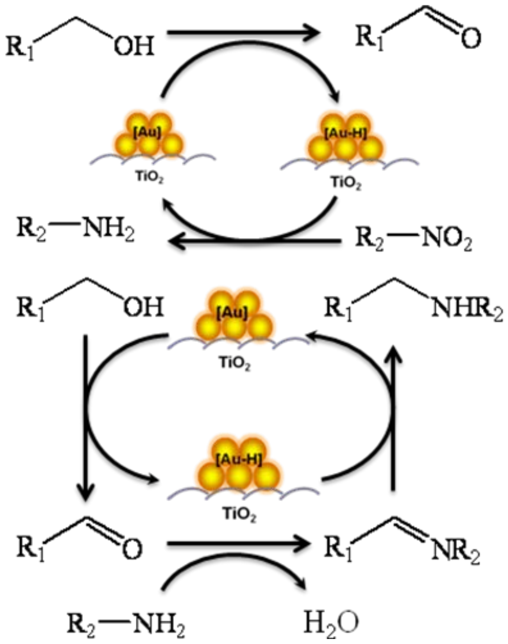


Figure S3. Tentative mechanism for the direct one-pot reductive amination of nitroarenes with alcohols.