

Supporting Information

Wet synthesis and quantification of ligand-free sub-nanometric Au clusters in solid matrices.

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General.

Glassware was dried in an oven at 175 °C before use. Reactions were performed in 2.0 ml vials equipped with a magnetic stirrer and closed with a steel cap having a rubber septum part to take samples out. Reagents and solvents were obtained from commercial sources and were used without further purification otherwise indicated. The solid Au-catalysts were purchased from Strem Chemicals Co. (Au-Al₂O₃, Au-ZnO, Au-TiO₂) or Johnson-Matthey Co (Au-Ce₂O₃, Au-C). The products of the reaction test were characterised by GC-MS, ¹H- and ¹³C-NMR, and DEPT, and compared with the given literature. Gas chromatographic analyses were performed in an instrument equipped with a 25 m capillary column of 5% phenylmethylsilicone. Dodecane was used as an external standard. GC/MS analyses were performed on a spectrometer equipped with the same column as the GC and operated under the same conditions. ¹H, ¹³C and DEPT measurements were recorded in a 300 MHz instrument using CDCl₃ as a solvent, containing TMS as an internal standard. The metal content of the solids and filtrates was determined by X-Ray fluorescence or by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) by disaggregation of the solid in aqueous acid mixture or after dilution of the filtrates in 1 ml of ether and extraction with 3 mL (x3 times) of aqua regia.

X-ray photoelectron spectroscopy (XPS) measurements were performed on a SPECS spectrometer equipped with a Phoibos 150 MCD-9 analyzer using non-monochromatic Mg KR (1253.6 eV) X-ray source working at 50 W. As an internal reference for the peak positions in the XPS spectra, the C1s peak has been set at 284.5 eV. The samples were prepared by dropping a solid water suspension onto a molybdenum plate followed by air drying. High Resolution Transmission Electron Microscopy measurements were performed in a 200 KeV Jeol microscope by impregnating a copper-carbon filmed grid with a drop of the corresponding solid after dispersing in dichloromethane and leaving evaporation for at least 5 hours. Absorption spectra were recorded on a Cary 300 UV-Vis spectrophotometer (UV0811M209, Varian). Fluorescence spectra were obtained with a LP S-220B (Photon Technology International) equipped with 75 W Xe lamp. The photophysical measurements were performed under air at room temperature in a quartz cell of 1.0 cm optical path length.

Preparation of the Au catalysts.

Au–TiO₂ (1.5 wt%, 4.3 nm average size) was prepared following a reported procedure (see main text).

Au–*n*CeO₂ was prepared by impregnating on 1 g of the support the corresponding amount of Au chloride (1 wt%) and hydrogenating at 200–300 °C under a flow of 100 ml per min. of N₂:H₂ (10:1) gas for 2–3 h. For comparison, another sample of Au–*n*CeO₂ was obtained after a stronger reduction treatment: 1 g of nanoceria impregnated with Au chloride (1 wt%) treated with 5 ml of phenylethanol at 160 °C for 1 h. This solid was nearly avoided of Au clusters. A solution of Au clusters in DMF or NMP was prepared by placing 10 mg of Au–*n*CeO₂ (1 wt%) in a round-bottomed flask equipped with a magnetic bar and heating in a magnetically stirred oil-bath at 135 °C in the corresponding solvent for a few minutes. Then, the supernatant was passed through a syringe filter in hot and an aliquot was taken for analysis by ICP–AES, as indicated above.

Au@EVOH. Pellets (2 mm diameter, 3 mm long) of EVOH with ethylene molar contents of 26 (EVOH26), 29 (EVOH29), 32 (EVOH32) and 44 (EVOH44) were gently supplied by The Nippon Chemical Company (Osaka, Japan). 13 g of EVOH29 were initially dissolved in 100 mL of a 1:1 (v:v) 1-propanol: distilled water mixture heated at 75 °C under reflux. Once the copolymer was completely dissolved the mixture was left to cool to room temperature, then HAuCl₄·3H₂O were added in order to obtain a metal loading of 0.031 mmolAu/ g dry polymer. The resultant suspension was spread on a Teflon coated glass plate by using a 200 μm spiral bar coater. By using a digital Mitutoyo micrometer (Metrotec, San Sebastian, Spain) film thickness was determined, obtaining an average value of 0.012 ± 0.003 mm.

To evaluate the influence of film thickness, ethylene molar percentage of EVOH as well as the influence of UV radiation of the film in formation of Au clusters different materials were obtained. To obtain thicker films, a 100 μm spiral bar coater was also used providing films with 0.022 ± 0.004 mm of thickness. To check the effect of copolymer composition, films based on three EVOH precursors (EVOH26, EVOH32 and EVOH44) were also prepared by the same procedure. To check for the effect of

radiation on cluster formation in the films, Au@EVOH films were exposed to the radiation of a Heraeus NIQ 80/36U lamp at 5 cm distance during 15 min.

Re-dispersion of Au-supported catalyst. 500 mg of Au-Al₂O₃, Au-TiO₂, Au-ZnO and Au-C were dispersed in a solution of 50 mg of I₂ in water, 1,2-dichloromethane or 1,2-dichloroethane. The reaction mixture was heated at 60 °C during 24 hours. After cooling to rt, the solids were filtered and washed with water and acetone. The solids were analysed by X-Ray Fluorescence and UV-vis to confirm the formation of clusters and the quantity of gold supported.

Reaction procedures and characterisation.

Reaction test. The Au supported catalyst (0.01 mol%), heptanoyl chloride **1** (1 mmol) and propargylic alcohol **2** (10 mmol) were placed in a 2 ml vial equipped with a magnetic stir bar. The vial was sealed and the resulting mixture was magnetically stirred for 30 min at 25 °C. Then, water (1 mmol) was added and the mixture was stirred and aliquots of 25 µl were periodically taken, diluted in *n*-hexane, and analyzed by GC in order to follow the reaction, using dodecane as an external standard. Product 2-methyl-3-oxobutan-2-yl heptanoate **4** was isolated and characterization agrees that previously reported (see references in main text). GC-MS (*m/z*, relative intensity): 215 (M+H, 1), 171 (17), 130, (1), 113 (100), 85 (29), 57 (9), 43 (23). IR (ν, cm⁻¹): 2939 (m), 2863 (l), 1733 (vi), 1724 (vi), 1150 (i), 1120 (i). ¹H NMR (δ, ppm; *J*, Hz): 2.26 (COCH, 2H, dd, *J*= 9.6, 9.6), 2.04 (COCH₃, 3H, s), 1.61-1.51 (aliphatic CH₂, 2H, mult), 1.39 (CH₃, 6H, s), 1.24 (aliphatic CH, 6H, mult), 0.84-0.80 (aliphatic CH₃, 3H, m). ¹³C NMR (δ, ppm): 206.7 (ketone, C), 173.0 (ester, C), 83.3 (aliphatic, C), 34.2 (aliphatic, CH₂), 31.2 (aliphatic, CH₂), 28.6 (aliphatic, CH₂), 24.6 (aliphatic, CH₂), 23.4 (methyl, 2CH₃), 23.2 (methyl, COCH₃), 22.3 (aliphatic, CH₂), 13.8 (methyl, CH₃). HRMS (ESI) [M+H⁺; calculated for C₁₂H₂₃O₃: 215.0899] found *m/z* 215.0895.

Synthesis of ester intermediate 3. The heptanoyl chloride **1** (13 mmol) was added to the propargylic alcohol (130 mmol) and the mixture was stirred in a 25 ml round-bottom flask equipped with a magnetic stir bar during 1 hour. The crude was purified by column chromatography on basic alumina (20 % AcOEt in *n*-hexane) to achieve 2-methylbut-3-yn-2-yl heptanoate **3** as a colourless oil (2.51 g, 13 mmol, 99 %). Characterization agrees that previously reported (see references in main text). GC-MS (*m/z*, relative intensity): 196 (M⁺, 4), 113 (100), 98 (10), 85 (37), 83 (43), 67 (100), 55

(29), 43 (43). IR (ν , cm^{-1}): 3270 (l), 2927 (i), (1742 (vi), 1234 (m), 1131 (vi). ^1H NMR (δ , ppm; J , Hz): 2.43 (CH, 1H, s), 2.17 (COCH, 2H, dd, $J=7.5, 7.5$), 1.57 (CH_3 , 6H, s), 1.52 (aliphatic CH, 2H, mult), 1.21 (aliphatic CH, 6H, mult), 0.79 (aliphatic CH_3 , 3H, m). ^{13}C NMR (δ , ppm): 171.8 (ester, C), 84.6 (alkyne, C), 72.0 (alkyne, CH), 71.1 (aliphatic, C), 34.7 (aliphatic, CH_2), 31.3 (aliphatic, CH_2), 28.7 (methyl, 2CH_3), 28.5 (aliphatic, CH_2), 24.6 (aliphatic, CH_2), 22.3 (aliphatic, CH_2), 13.8 (methyl, CH_3).

Leaching studies. Two parallel reaction mixtures were followed by GC, taking aliquots periodically, under typical reaction conditions and one of them was filtered at a determined conversion through a 0.2 μm PTFE filter. The resulting filtrates were placed under the same conditions (stirring and temperature) that the original reaction and also followed by GC.

Figures.

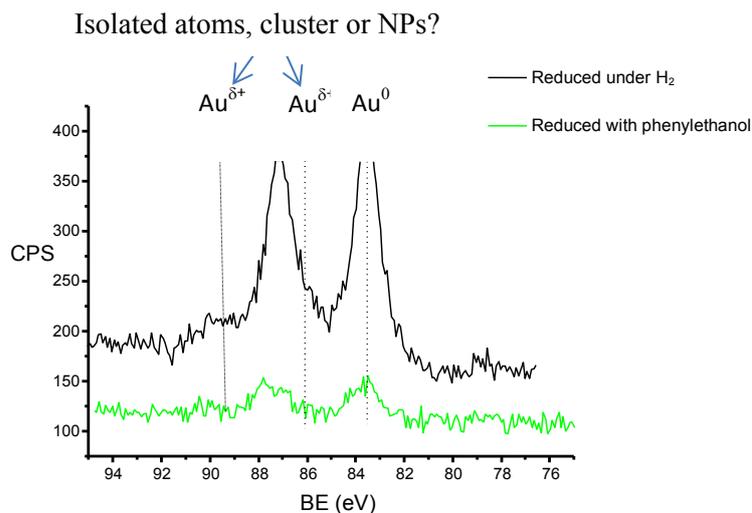


Figure S1. XPS spectrum of a sample of Au-*n*CeO₂ after hydrogenation of 1 g of Au chloride on *n*ceria at 200-300 °C under a flow of 100 ml per min of N₂:H₂ (10:1) (black line). The percentage of cationic Au in the reduced sample is 15% after deconvolution. For comparison, a sample of Au-*n*CeO₂ with a stronger reduction treatment –1 g of Au chloride on ceria with 5 ml of phenylethanol at 160 °C for 1 h (green line)– is also presented. The percentage of cationic Au decreases significantly to 2%.

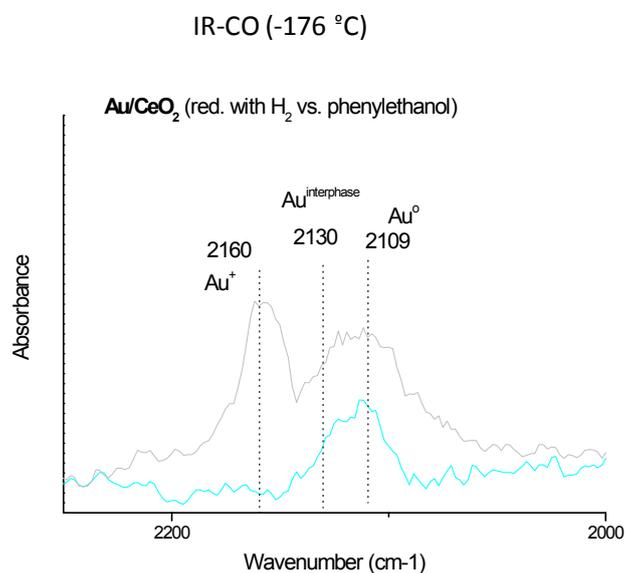


Figure S2. CO-IR of the Au-CeO₂ sample prepared by hydrogenation at 200 °C. The presence of cationic Au not present in the interphase is clearly seen. For comparison, the sample of Au-CeO₂ reduced with phenylethanol shows only cationic Au in the interphase.

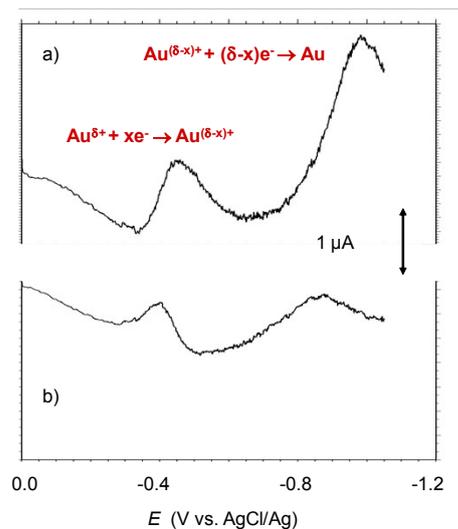


Figure S3. Linear potential scan voltammograms at glassy carbon electrodes modified with films of: a) pristine Au-*n*CeO₂; and b) Au-*n*CeO₂ reduced at 200 °C in H₂/N₂ atmosphere, immersed into air-saturated 0.1 M aqueous NaOH. The plotted curves were obtained after subtracting the corresponding voltammogram for nanoparticulated ceria. Potential scan rate 20 mV/s.

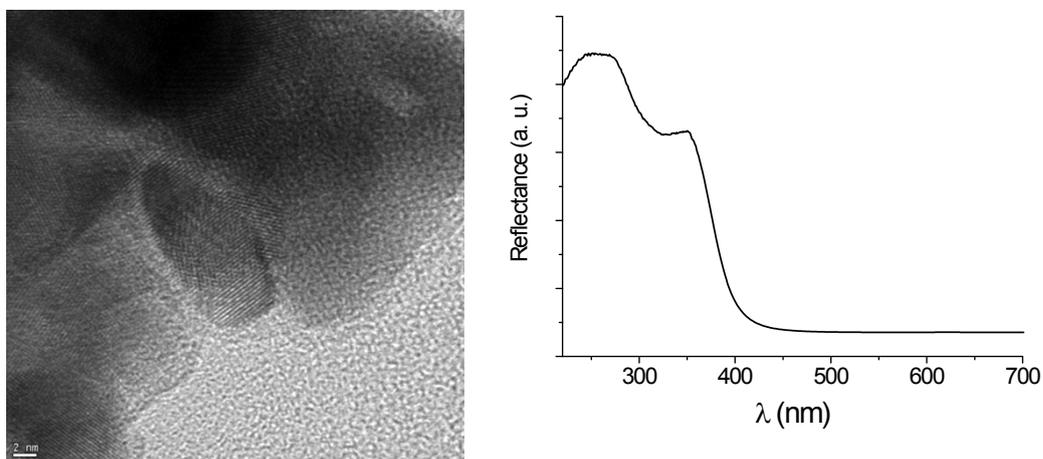


Figure S4. Left: A typical HR-TEM image of Au-*n*CeO₂ solids. Only nanometric Au particles can be distinguish and not sub-nanometric particles or isolated Au cations. Right: Reflectance-diffuse UV-vis spectrum of *n*CeO₂, which avoids the detection of any absorption band of Au clusters.

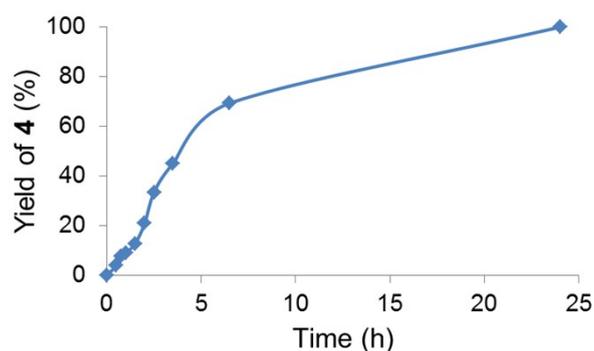


Figure S5. Reaction test for the Au-*n*CeO₂ sample reduced at 200 °C under hydrogen, see main text for reaction conditions.

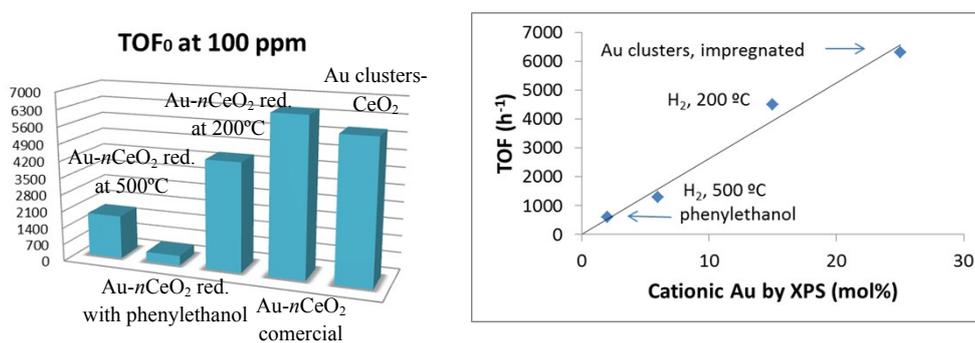


Figure S6. Left: TOF₀ (h⁻¹) values in the reaction test for different Au-*n*CeO₂ samples after different reductive treatments, including a commercial sample reduced at 200 °C under hydrogen and *n*CeO₂ impregnated with 15% neat Au_{3.7} clusters in aqueous solution. See main text for reaction conditions. Right: Linear correlation for the different Au-*n*CeO₂ solids between TOF values in the reaction test and amount of cationic Au found by quantitative XPS measurements.

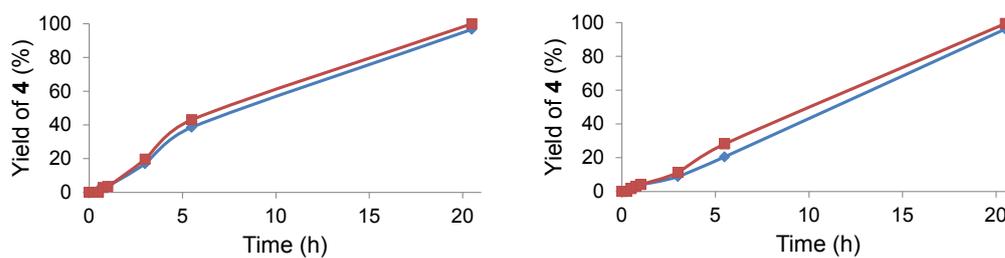


Figure S7. Leaching during the reaction test for Au-*n*CeO₂ reduced at 200 °C under hydrogen (left) and Au-Al₂O₃ (right).

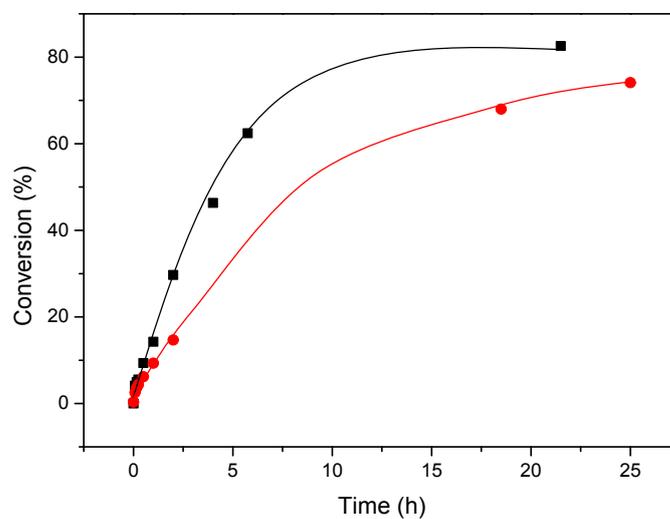
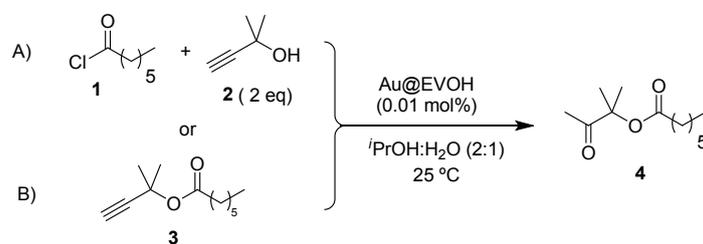


Figure S8. Kinetic plot for the reaction test catalyzed by Au@EVOH, either starting from acyl chloride **1** and propargylic alcohol **2** (squares) or from propargylic ester intermediate **3** (circles).

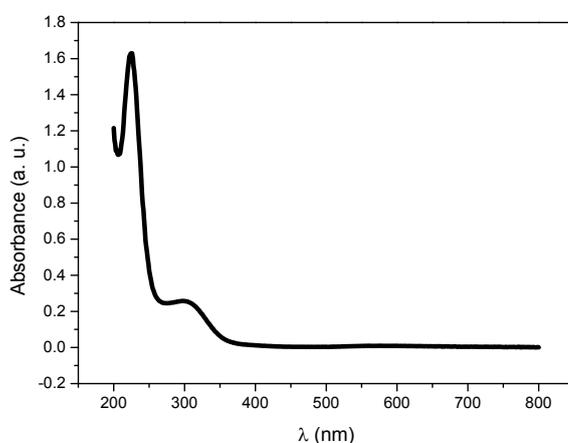
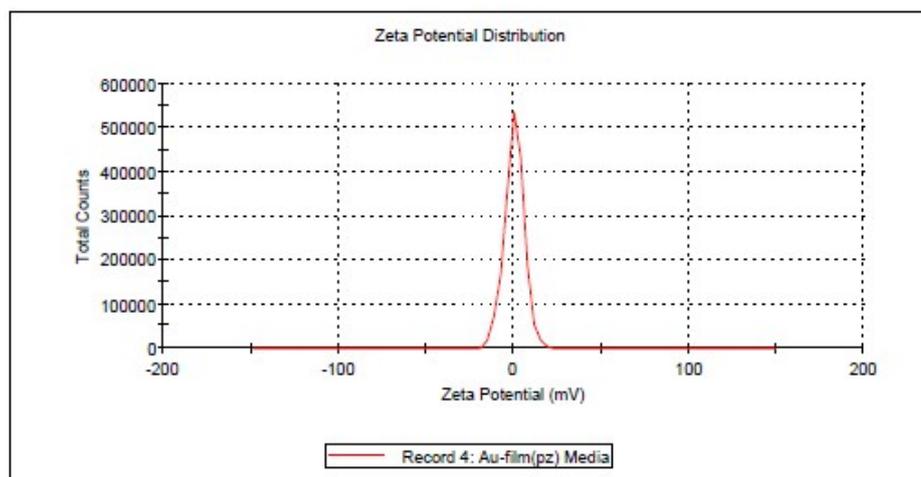


Figure S9. Top: Zetasizer measurement for Au@EVOH. Bottom: UV-vis Au@EVOH after disaggregation

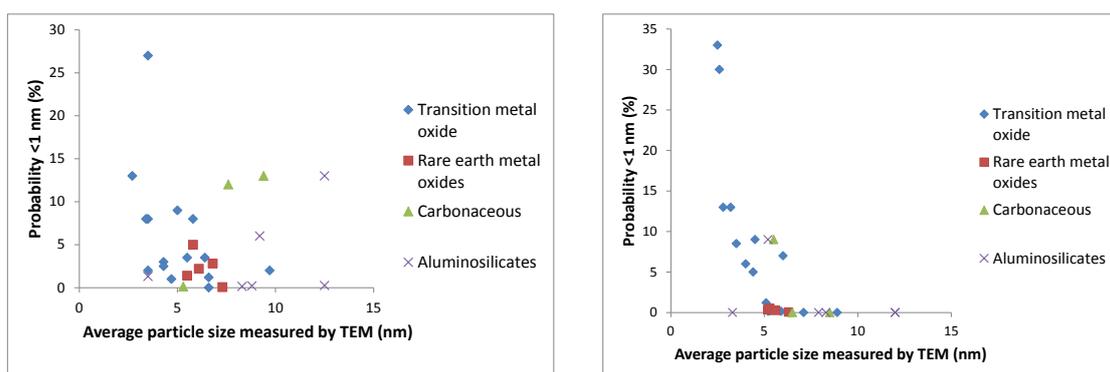
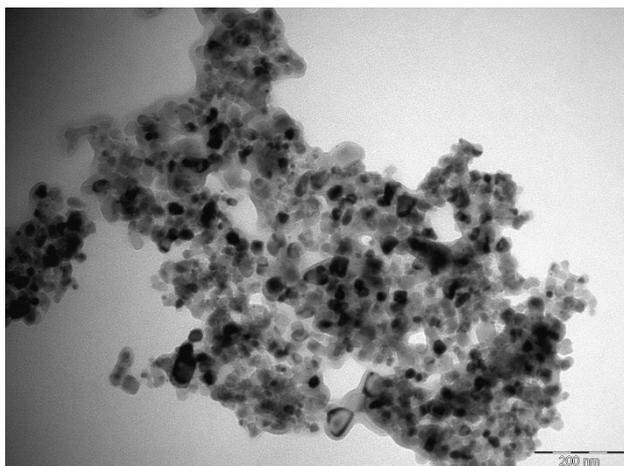


Figure S10. Normal (left) and lognormal (right) distributions for 30 different Au-supported catalysts described in the literature (see main text) as a function of the average particle size found by TEM.



Au loading: 1.5 wt%.

Average nanoparticle size: 4.3 nm.

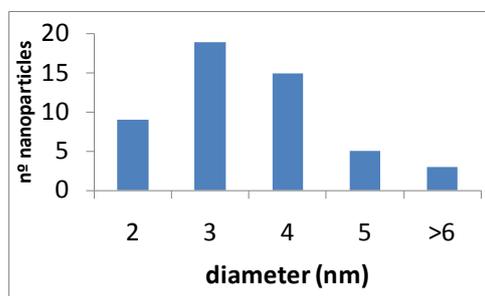
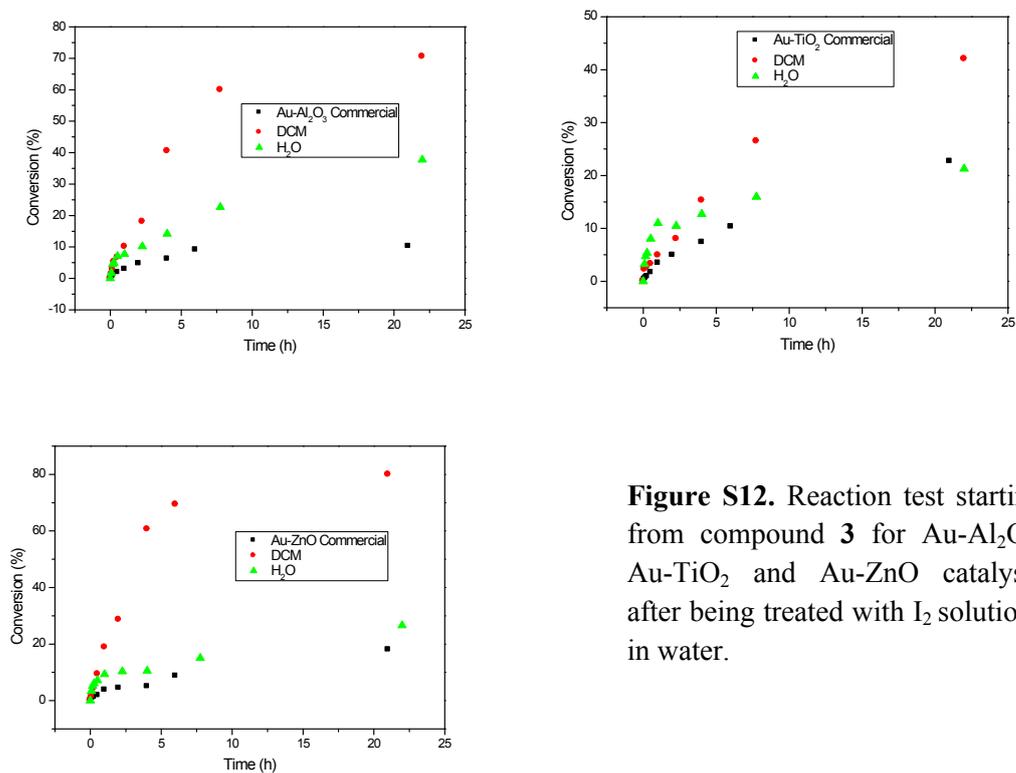
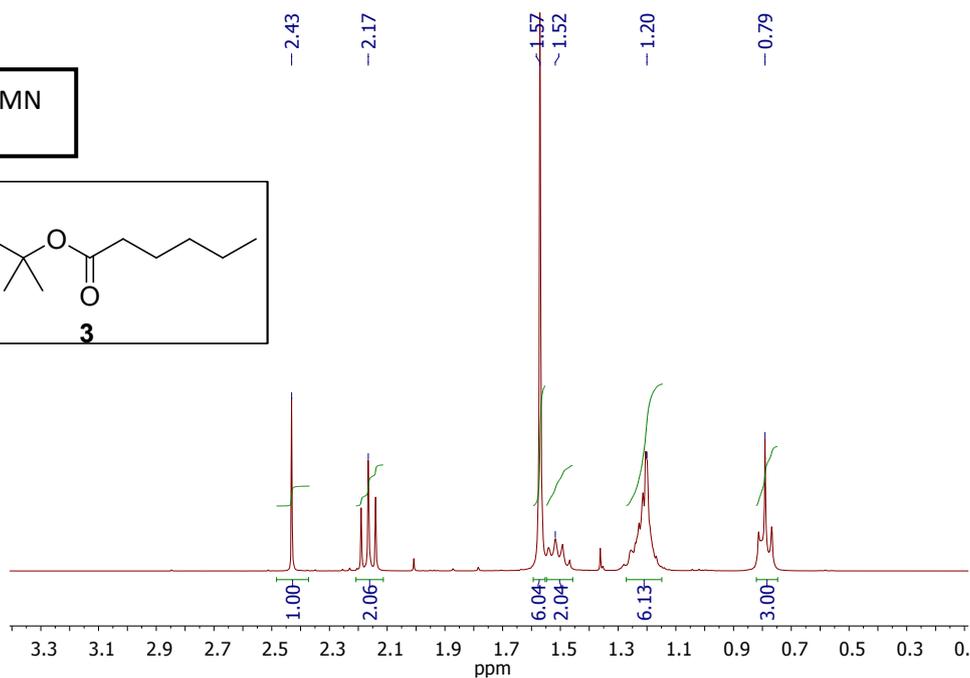
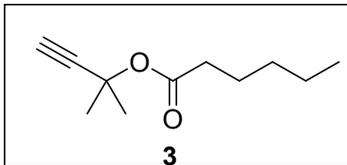


Figure S11. Transmission Electron Microscopy (TEM) image (left) and histogram of different samples (right) for Au-TiO₂.

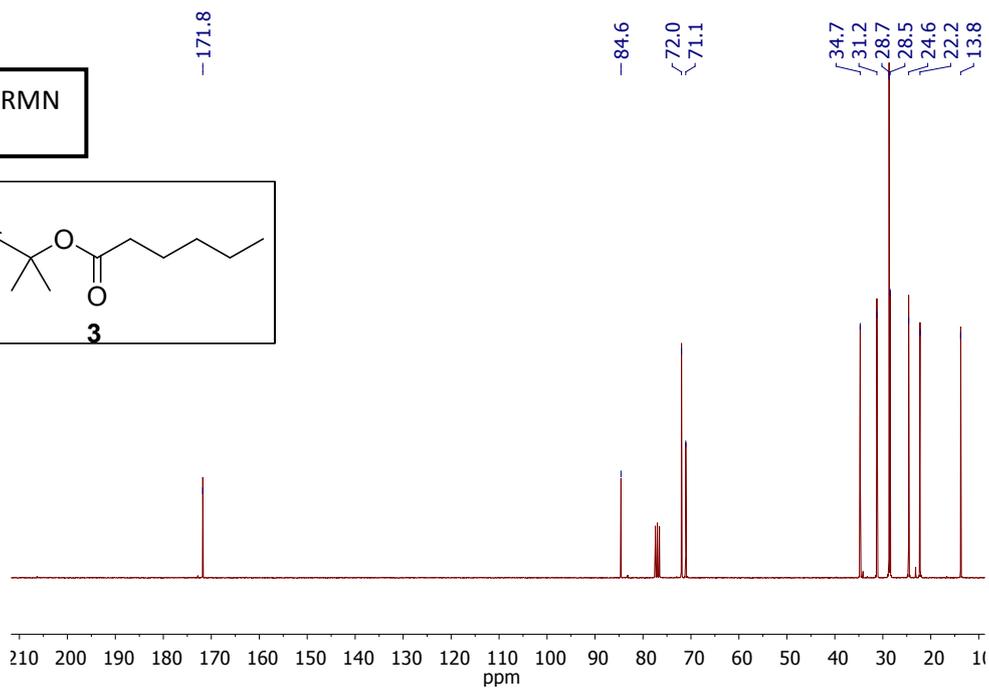
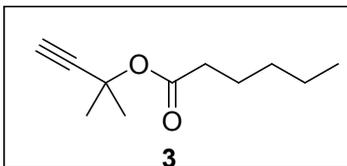


NMR copies.

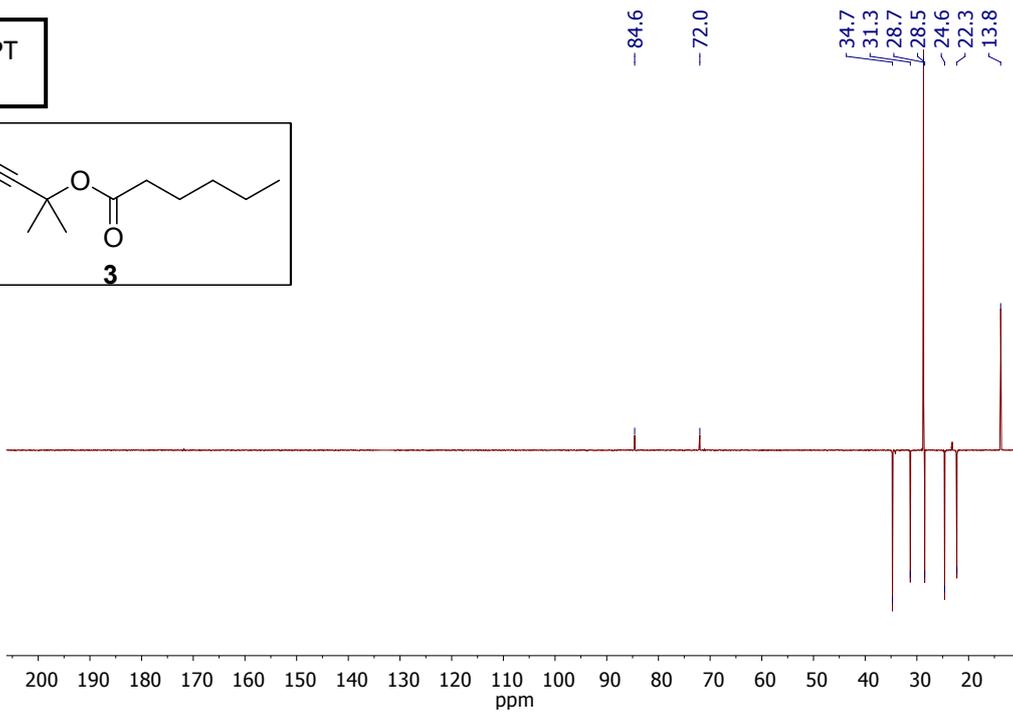
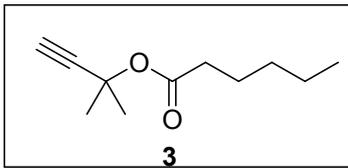
¹H-RMN



¹³C-RMN



DEPT



¹H-RMN

