Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

Tandem process for in situ H_2O_2 formation coupled with alcohol oxidation by Pd-Au bimetallic catalysts.

Jordan Santiago Martinez,[a] Jaime Mazarío,[a] Silvia Gutiérrez-Tarriño,[a] Carmen Galdeano-Ruano,[a] José Gaona-Miguélez,[a] Marcelo E. Domine, [a] and Pascual Oña-Burgos [*,a,b]

[a] *Instituto de Tecnología Química (ITQ) Universitat Politécnica de Valencia-CSIC, Av. de los Naranjos - s/n 46022 Valencia, Spain.*

[b] *Department of Chemistry and Physics, Research Centre CIAIMBITAL, University of Almería, Ctra. Sacramento, s/n, 04120 Almería Spain.*

Table of content

1- Detailed Syntheses

Synthesis of Pd-Au-NBH catalyst supported on carbon.

The catalysts named **xPd-yAu-NBH** (x the % of Pd and y the % of Au) were synthesized following a reported method.[1] As an example, **0.2Pd-0.8Au-NBH**, 0.024 mmol (9.53 mg) of $NaAuCl_4 \cdot 2H_2O$, 235 µL of 2% wt PVA (89000-99000 M_w) solution and 47 mL of H_2O mili-Q were stirred in a 100 mL round bottom flask. After a few minutes under vigorous stirring, 940 µL of 0.1M $NaBH_4$ solution were added to the previous mixture. UV-visible spectra of the resulting ruby-red Au(0) solution was recorded to check the complete metal reduction. The total extinction of $AuCl_4^-$ absorption band at 204 nm and the gold plasmon band's appearance must be observed to prove the reduction treatment's success (Figure S1a). The colloidal solution is then acidified until pH ≈ 2 with a few drops of sulfuric acid. 297mg of activated carbon Vulcan XC72R (depending on the desired metal loading catalyst, in this case 1wt% of metals) was introduced and vigorously stirred for 2 hours. The resulting slurry is then filtered under vacuum on a nylon membrane. The solid was washed with distilled water until obtaining neutral mother liquors and then dried at 100°C overnight. ICP analysis of the filtrate was carried out in order to check the metal loading of the material (loss of gold was found to be 1.7% with respect to the introduced mass). After that, 0.012 mmol (3.6 mg) of Na_2PdCl_4 and 235µL of 2%wt PVA (89000-99000 Mw) in 47 mL of H_2O milli-Q were added to the previously prepared material and stirred. After a few minutes under vigorous stirring, 236 µL of 0.1M $NaBH_4$ solution were added to the orange Pd(II) solution. UV-visible spectra of the resulting brown Pd (0) solution were recorded in order to check the complete reduction of the metal. The total extinction of the absorption band at 210 nm must be observed (Figure S1b). The colloidal solution was then acidified until pH 2 with a few drops of sulfuric acid and vigorously stirred for 2 hours. The resulting slurry was then filtered under vacuum on a nylon membrane. The solid was washed with distilled water until neutral mother liquors and then dried at 100°C overnight. ICP analysis was carried out of the filtrate to check the metal loading of the material (loss of palladium was evaluated at 2.3% with respect to the total mass introduced), obtaining a material with a total metal loading of 1%wt (0.2% Pd and 0.8% Au).

2- UV-Visible spectra

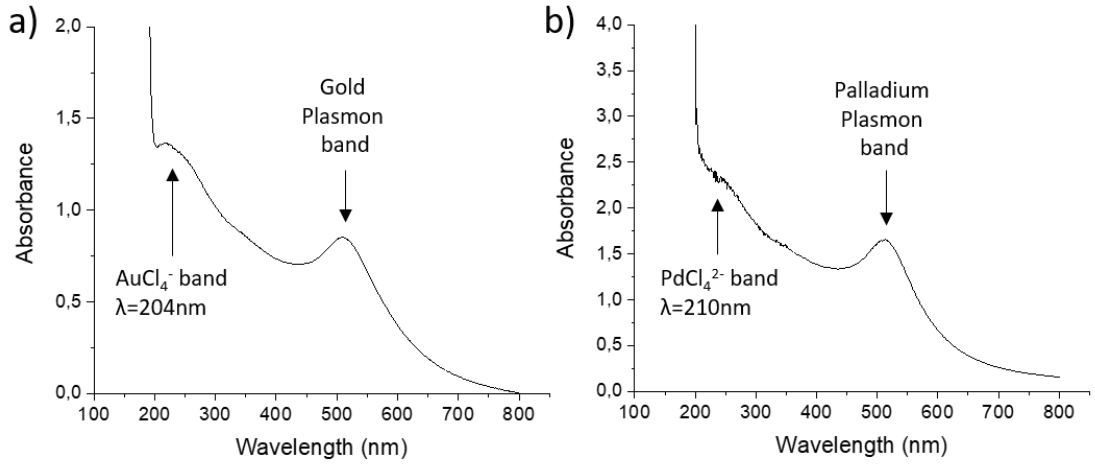

Figure S1. a) UV-visible spectra of the resulting ruby-red Au(0) solution during the synthesis of **0.2Pd-0.8Au-NBH**, b) UV-visible spectra of the resulting brown Pd (0) solution during the synthesis of **0.2Pd-0.8Au-NBH**.

3- Gas-Chromatography

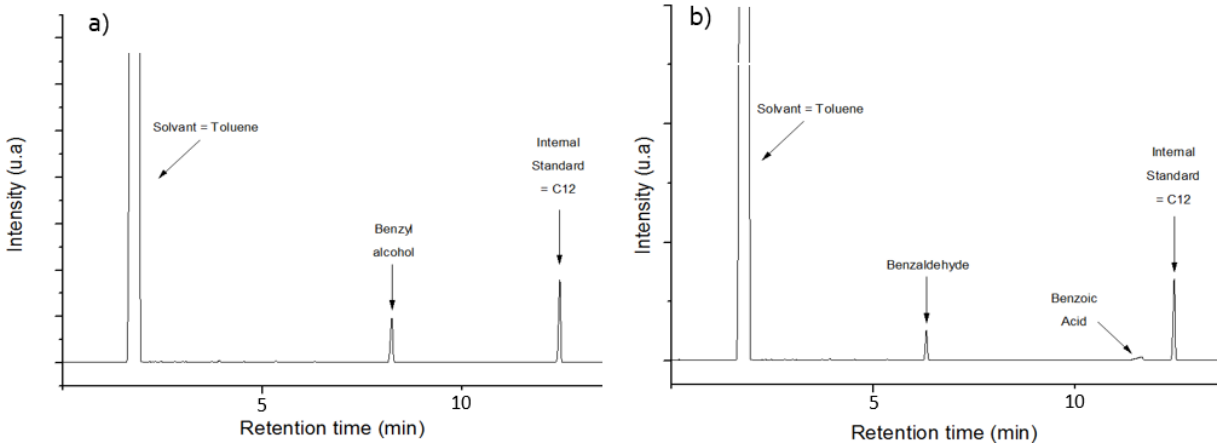

Figure S2. Chromatograms of reaction crude before and after oxidation reaction a) benzyl alcohol before reaction, b) crude after benzyl alcohol oxidation.

4- EDX

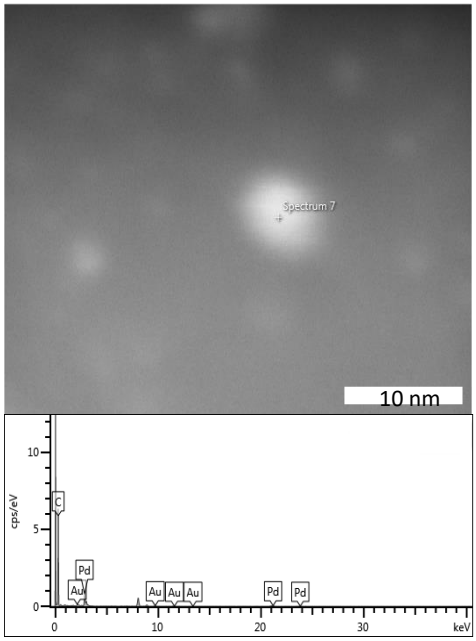

Figure S3. EDX spectra of **0.8Pd-0.2Au-H**.

5- CO-Chemisorption

Table S1. CO-Chemisorption data for **0.2Pd-0.8Au-NBH**, **0.2Pd-0.8Au-H** and **0.8Pd-0.2Au-H**.

Catalyst	Reduction method	Active Metal Surface Area (m^2/g)	CO-uptake (µmol CO/g)
0.2Pd-0.8Au-NBH	$NaBH_4$	0.136	2.9
0.2Pd-0.8Au-H	H_2	0.351	7.4
0.8Pd-0.2Au-H	H_2	0.733	15.4

6- XRD-Lattice constant

Table S2. Average lattice constant (Å) of monometallic and bimetallic PdAu NPs (Theoretical vs experimental).

Name	Pd content (wt%)	JCPDS database	Average lattice constant (Å)
Pd	1.00	98-002-1995	3.88
Pd-Au	0.5	98-007-0837	3.98
Pd-Au	0.45	98-007-0838	3.99
Au	0	98-006-2856	4.07
1.00Pd-H	1.00	Experimental	3.91
0.8Pd-0.2Au-H	0.8	Experimental	4.05
0.5Pd-0.5Au-H	0.5	Experimental	4.04
0.2Pd-0.8Au-H	0.2	Experimental	4.09
1.00Au-H	0.0	Experimental	4.10

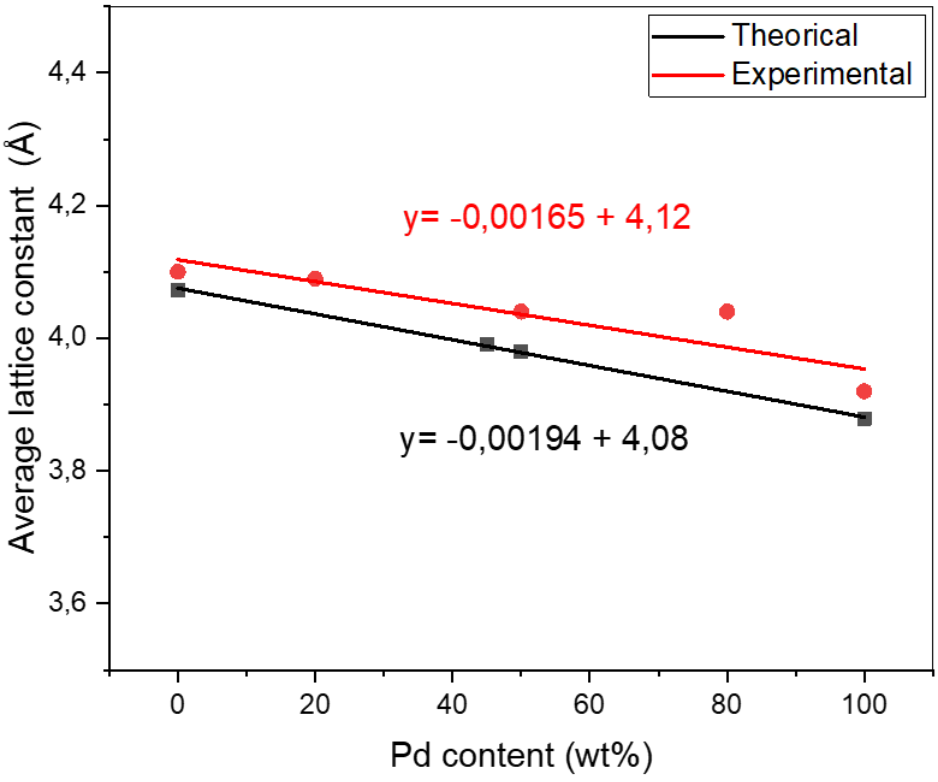

Figure S4. Theorical vs Experimental lattice constant of PdAu nanoparticles in function of the Pd content in wt% and its corresponding linear fitting tendencies.

7- XPS

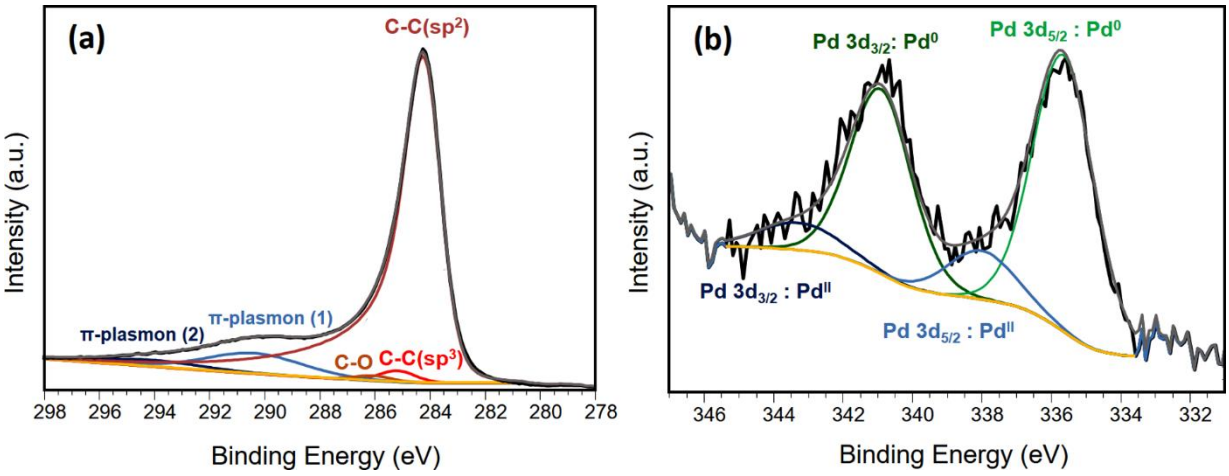

Figure S5. XPS spectra of **in situ reduced 1.00Pd-H** after peak fitting of (a) *C1s* and (b) *Pd3d*.

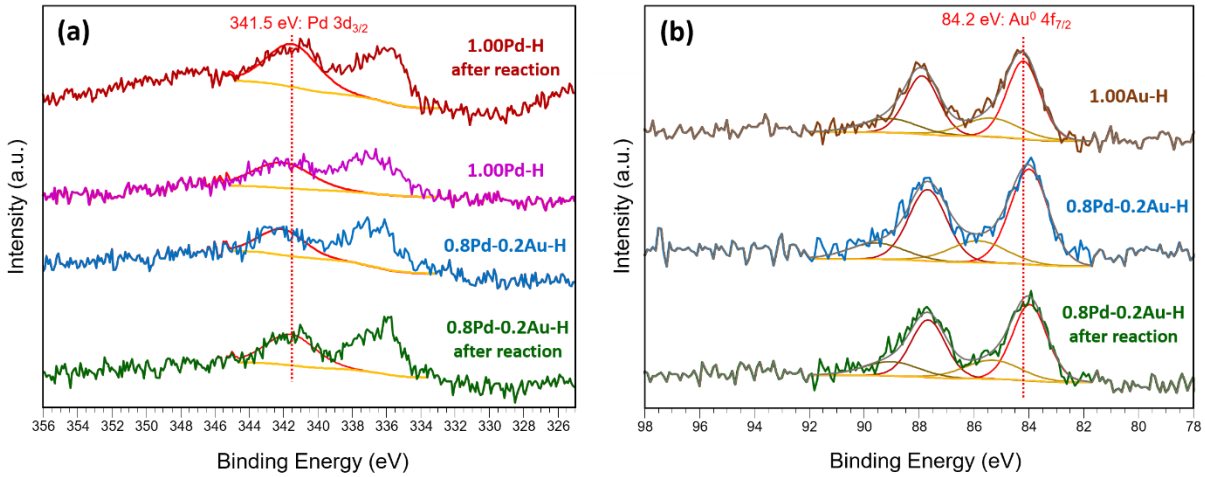

Figure S6. XPS spectra of **1.00Pd-H** and **0.8Pd-0.2Au-H** before and after reaction after peak fitting of (a) *Pd3d* and (b) *Au4f*.

8- Kinetic studies

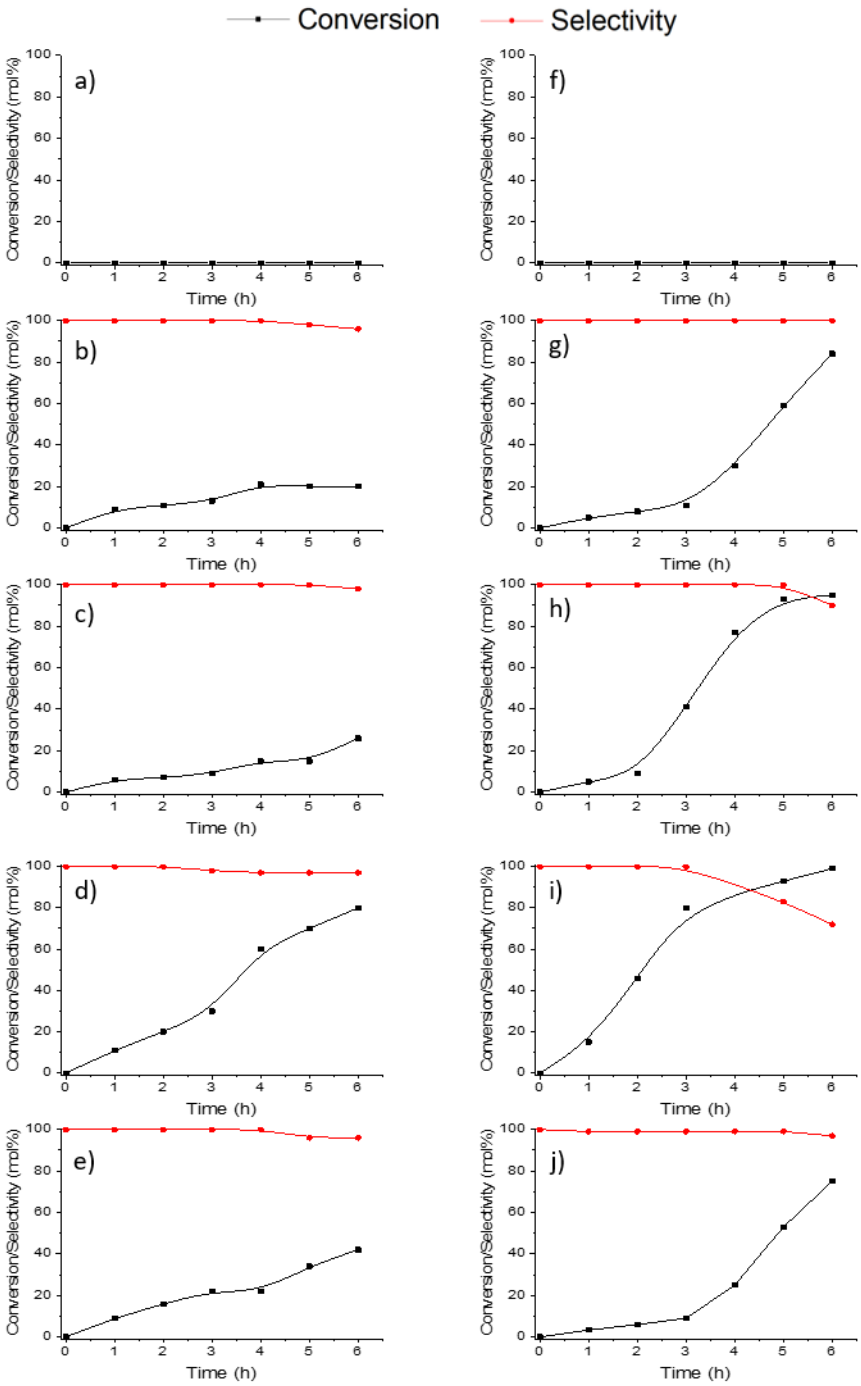

Figure S7. Benzyl alcohol conversion and benzaldehyde selectivity (mol %) in function of time for catalyst a) **1.00Au-NBH**, b) **1.00Pd-NBH**, c) **0.8Pd-0.2Au-NBH**, d) **0.5Pd-0.5Au-NBH**, e) **0.2Pd-0.8Au-NBH**, f) **1.00Au-H**, g) **1.00Pd-H**, h) **0.8Pd-0.2Au-H**, i) **0.5Pd-0.5Au-H**, j) **0.2Pd-0.8Au-H**. Reaction conditions: [benzyl alcohol] = 0.3 M, alcohol/metal ratio: 500/1 mol, 60 °C, 1.5 bar O_2. Note: Selectivity losses correspond to benzoic acid formation.

9- Oxidant Effect

Table S3. Study of the oxidant influence on benzyl alcohol oxidation for different catalysts.[a]

	Conversion (%)				
Oxidant	**1.00Pd-H**	**0.8Pd-0.2Au-H**	**0.5Pd-0.5Au-H**	**0.2Pd-0.8Au-H**	**1.00Au-H**
O_2	8	9	46	4	0
H_2O_2/N_2	8	8	15	0	0
H_2O_2/O_2	20	24	49	7	0

[a]Reaction conditions: [benzyl alcohol] = 0.3 M, alcohol/metal ratio: 500/1 mol, 60 °C, 1.5 bar O_2/N_2, 2 h.
[b]Selectivity 99%, at low conversion no by product has been detected.

10- H_2O_2 production and Tandem reaction results

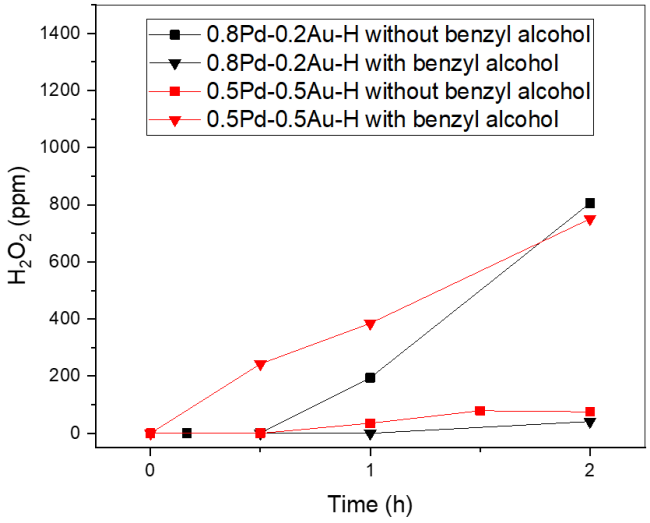

Figure S8. Hydrogen peroxide production with **0.8Pd-0.2Au-H** and **0.5Pd-0.5Au-H** as catalyst with and without benzyl alcohol in the reaction medium. Reaction conditions: H_20 as solvent, benzyl alcohol: 100 µL, alcohol/metal ratio: 750/1 mol, 0 °C, 10 bar O_2, 10 bar H_2, 20 bar CO_2.

Table S4. Study of the tandem process for different catalysts and different conditions.

Entry	Catalyst	time	Conversion (%)	Selectivity (%)
1	**0.8Pd-0.2Au-H**[a]	6h	62	79
2	**0.8Pd-0.2Au-H**[b]	8h	76	58
3	**0.5Pd-0.5Au-H**[a]	6h	27	79
4	**0.5Pd-0.5Au-H**[b]	8h	23	65

[a]Reaction conditions: H_20 as solvent, benzyl alcohol: 100 µL introduced at t = 2h, alcohol/metal ratio: 750/1 mol, 0 °C to 60 °C at t = 2h, 10 bar O_2, 10 bar H_2, 20 bar CO_2. [b]Reaction conditions: H_20 as solvent, benzyl alcohol: 100 µL introduced at t = 0h, alcohol/metal ratio: 750/1 mol, 0 °C to 60 °C at t = 2h, 10 bar O_2, 10 bar H_2, 20 bar CO_2.

11- ^{1}H NMR

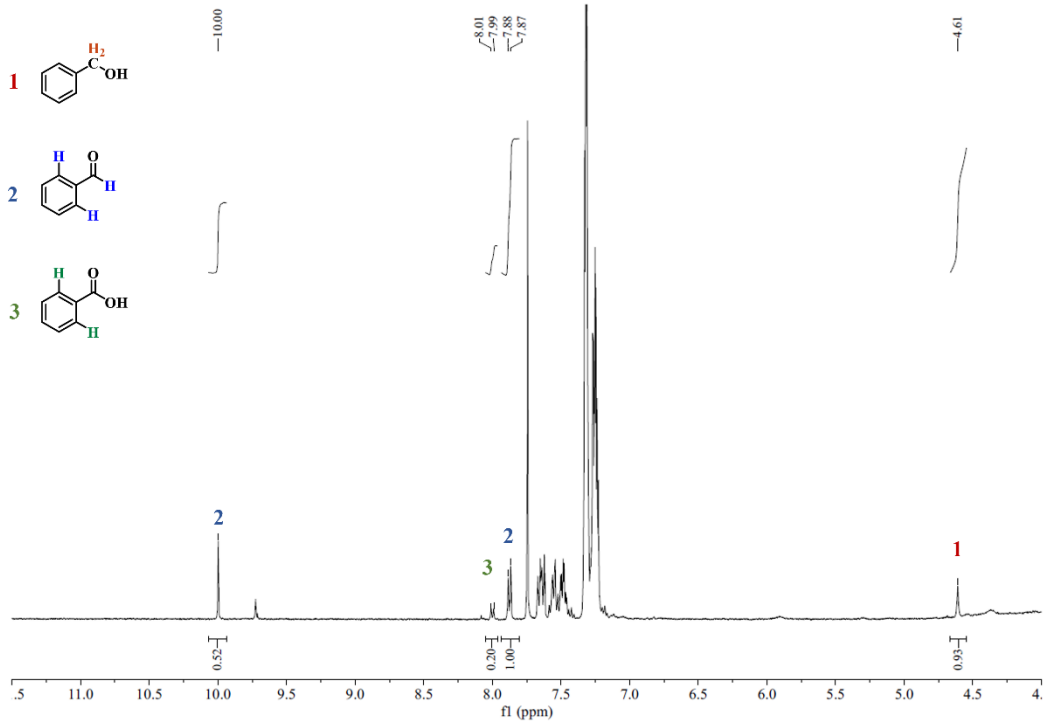

Figure S9. ^{1}H NMR of the crude reaction mixture after 6h of benzyl alcohol addition with **0.8Pd-0.2Au-H** in $CDCl_3$ (Results in Table S4 entry 1).

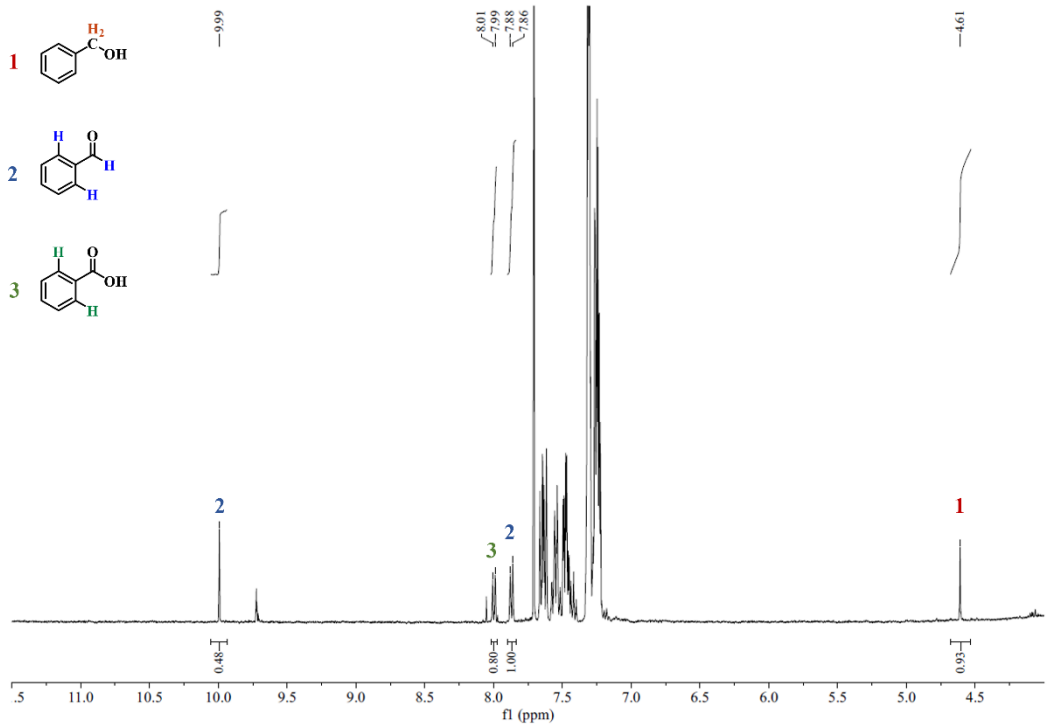

Figure S10. ^{1}H NMR of the crude reaction mixture after 8h of benzyl alcohol addition with **0.8Pd-0.2Au-H** in $CDCl_3$ (Results in Table S4 entry 2).

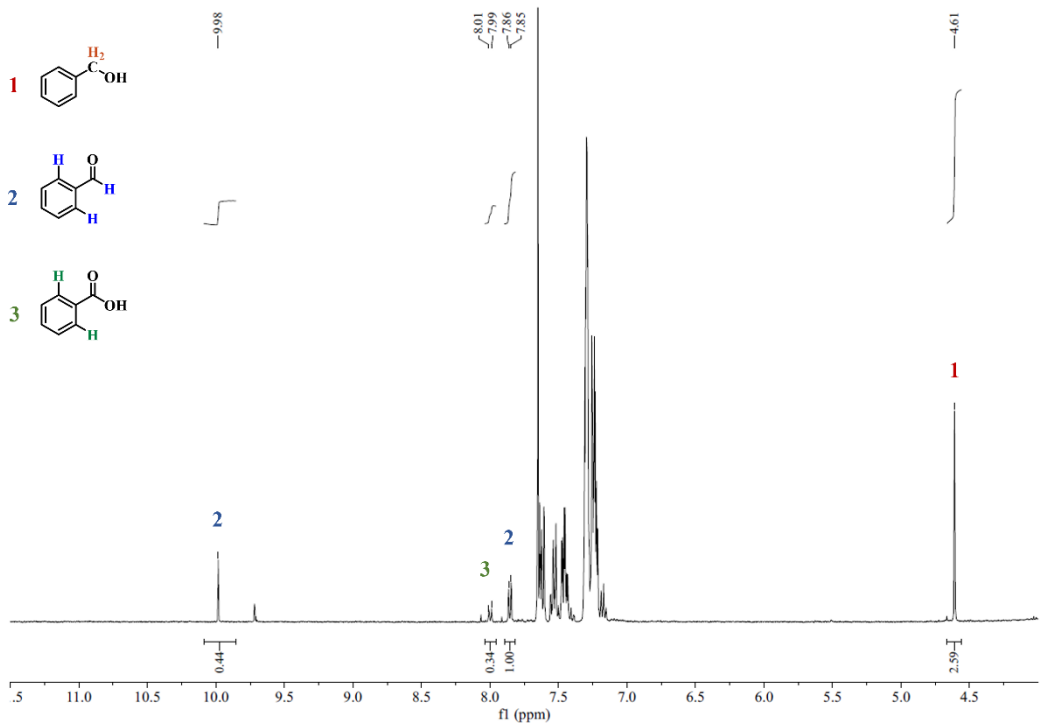

Figure S11. ^{1}H NMR of the crude reaction mixture after 6h of benzyl alcohol addition with **0.5Pd-0.5Au-H** in $CDCl_3$ (Results in Table S4 entry 3).

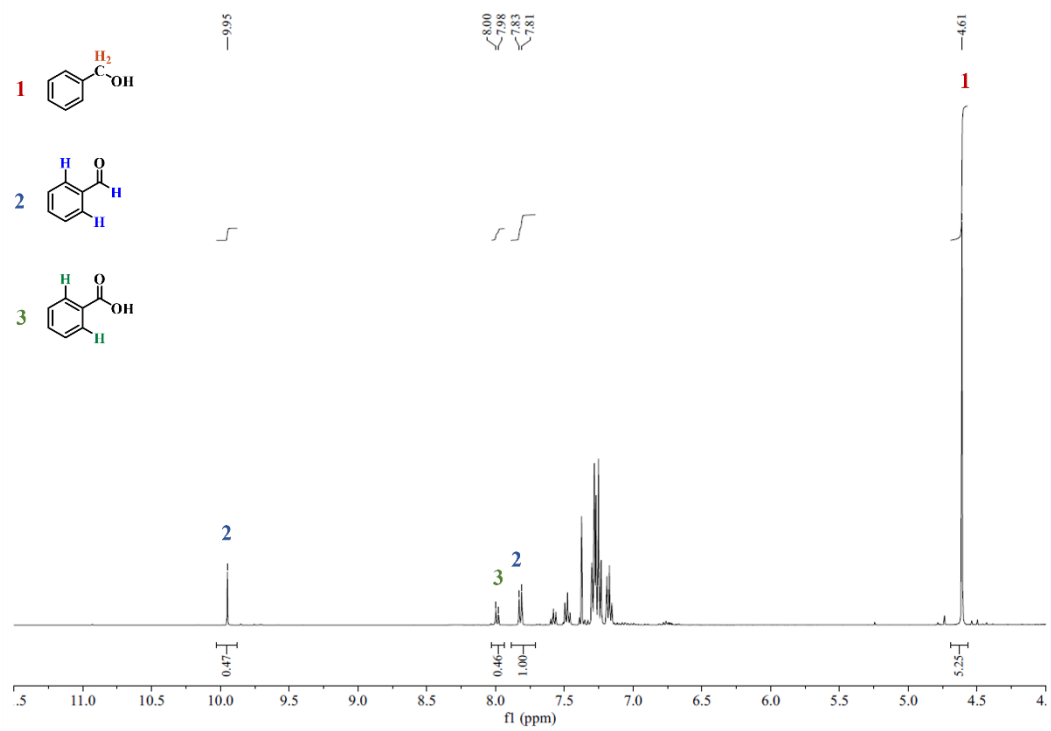

Figure S12. ^{1}H NMR of the crude reaction mixture after 8h of benzyl alcohol addition with **0.5Pd-0.5Au-H** in $CDCl_3$ (Results in Table S4 entry 4).

12- Microscopy

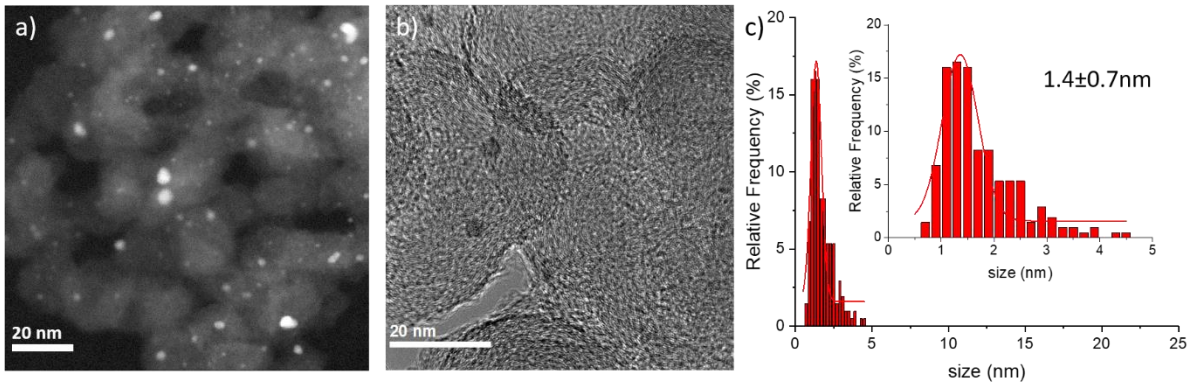

Figure S13. a) STEM image, b) TEM image and c) the corresponding NPs size distribution fitted by gaussian function of **0.8Pd-0.2Au-H after tandem reaction.**

13- References

1 N. Dimitratos, A. Villa, D. Wang, F. Porta, D. Su and L. Prati, *J. Catal.*, 2006, **244**, 113–121.