SUPPORTING INFORMATION

A silica-based magnetic platform decorated with mixed ligand gold nanoparticles: A recyclable catalyst for esterification reactions

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Part I. Experimental Details

All chemicals and solvents are used without further purification unless otherwise is stated.

Materials characterization: The morphology of the synthesized materials is characterized by transmission electron microscopy (TEM) using a JEOL 1210 microscope operating at 120 kV, a FEI Technai CM12 microscope operating at 120 kV, and a Technai Spirit BioTWIN microscope operating at 80 kV. Particles mean diameter and polydispersity are determined by adjusting to a Gaussian distribution the particle size histogram of at least 200 counts measured from TEM images using ImageJ. The magnetic properties of the core@shell particles are studied with a superconducting quantum interference device (SQUID) magnetometer from Quantum Design MPMS5XL. Approximately 10 mg of nanospheres as dried powder is introduced into a resin capsule. The as-prepared sample is inserted in the SQUID magnetometer sample holder and M(H) is measured at 300 K and 5 K up to 6 T. The zero field cooled-field cooled magnetization vs. temperature with a 50 Oe applied field is also measured. The presence of organic ligands onto the MPSA:OT protected AuNPs is quantified by thermogravimetric analysis (TGA) using the TGA 4000, Perkin Elmer instrument working under N_2 flow with a 5 ºC/min heating rate. The measurement is performed from 30 ^{o}C to 800 ^{o}C. ^{1}H Nuclear magnetic resonance (^{1}H NMR) in solution state is performed to both obtain the mixed ligands molar ratio on the MPSA:OT covered AuNPs in deuterated methanol (Sigma Aldrich) and to evaluate the efficiency of the catalytic reaction by analysing the reaction products in deuterated acetonitrile (Sigma Aldrich). The measurements are acquired on a Bruker AVANCE-400 MHz NMR spectrometer. All spectra are recorded at 25 ^{o}C. Chemical shifts are given in parts per million (ppm). Multiplet analyses of all spectra are processed by MestRenova.

Acidification process prior to catalytic reaction: 50 mg of hierarchical nanospheres, Fe_2O_3@SiO_2 nanospheres or MPSA:OT covered AuNPs are dispersed in 10 mL of 1.5 M sulphuric acid under 5 min ultrasonication. The reaction is left to stir 6 h at 30 ^{o}C and finally 10 mL of ethanol is added to the reaction mixture. Magnetic decantation technique is used to collect the particles. After removal of supernatant, particles are cleaned two times with 10 mL of ethanol spiked with a drop of acetic acid.

Part II. Supplementary figures

Determination of MPSA:OT Ligand Ratio on the surface of AuNPs by ^{1}H NMR

^{1}H NMR (400 MHz, Methanol-d4) δ 3.01-2.80 (m, 11H), 2.74 (td, J = 7.2, 1.1 Hz, 1H), 2.27- 2.13 (m, 5H), 1.70 (dd, J = 7.9, 6.6 Hz, 1H), 1.43 (d, J = 7.8 Hz, 1H), 1.38 -1.29 (m, 3H), 0.92 (ddd, J = 7.0, 5.2, 1.8 Hz, 1H).

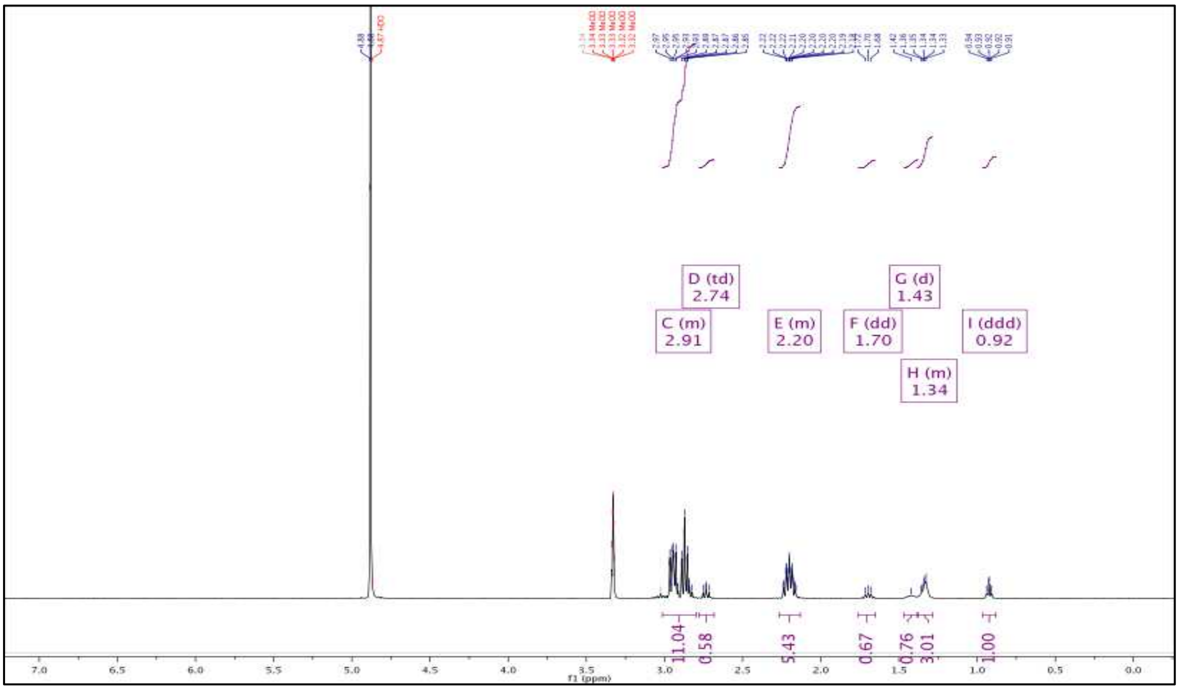

Fig. S1 ^{1}H NMR spectrum of MPSA:OT covered AuNPs in deuterated methanol after etching the gold core with iodine.

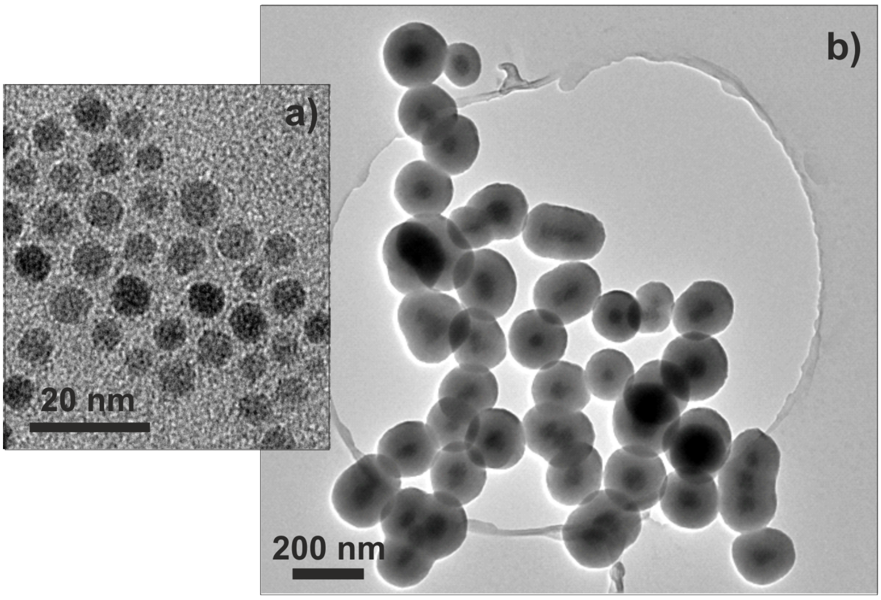

Fig. S2 TEM images of a) γ-Fe_2O_3 nanoparticles and b) Fe_2O_3@SiO_2 nanospheres.

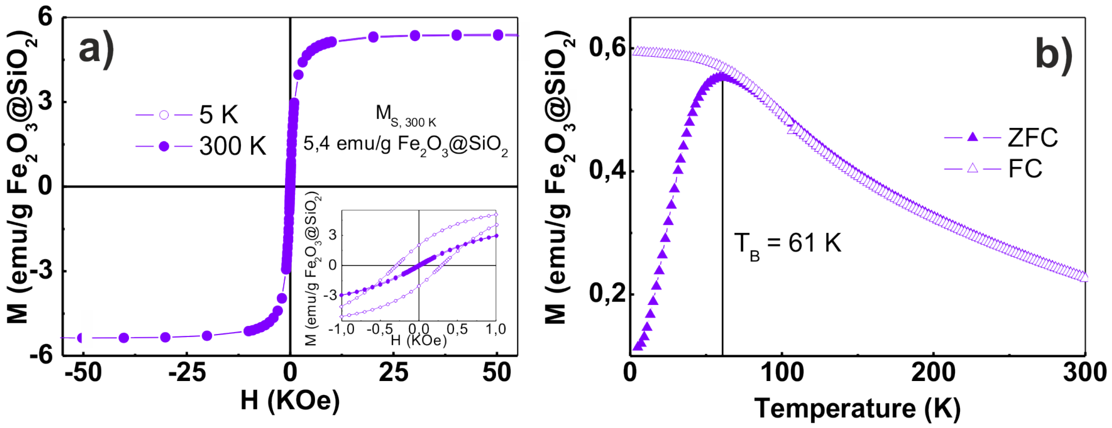

Fig. S3 a) M(H) at 300K, inset: M(H) at small fields at 300 K and 5 K and b) ZFC-FC magnetization curves for the Fe_2O_3@SiO_2 nanospheres at 50 Oe applied field.

Control Coupling Reaction Between Fe_2O_3@SiO_2-NH_2 Nanospheres and MPSA:OT covered AuNPs

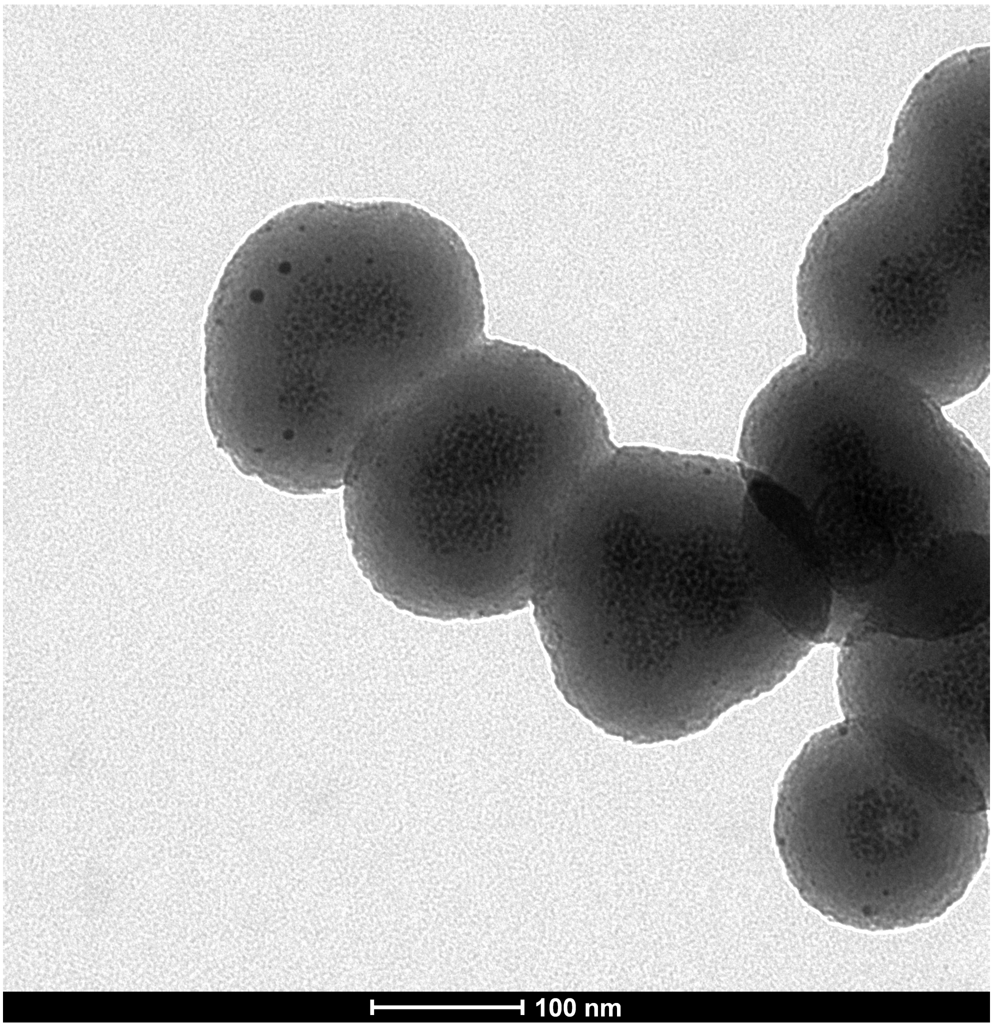

Fig. S4 TEM image of Fe_2O_3@SiO_2@NH_2 nanospheres after reaction between MPSA:OT covered AuNPs.

Determination of Conversion Ratio of BzOH to BzAc by ^{1}H NMR

The reaction products were analysed by ^{1}H nuclear magnetic resonance spectroscopy (^{1}H NMR). The conversion efficiencies of the hierarchical nanospheres and MPSA:OT covered AuNPs are averages of three independent measurements. Here, we present the NMR spectrum of only one of the replicates for practical reasons, however; the spectra corresponding to other replicates can be found at EPFL Infoscience page dedicated to this paper. All conversion efficacies were attained by using the same quantity of MPSA:OT covered AuNPs in the reaction medium, as determined by optical absorption. The amount of MPSA:OT AuNPs on the surface of Fe_2O_3@SiO_2 nanospheres is calculated from UV-vis absorption spectra of the unreacted AuNPs after the coupling reaction between Fe_2O_3@SiO_2@NH_2 spheres and AuNPs. After the coupling reaction, all the supernatants collected during cleaning step were combined and its optical density were measured. The amount of unreacted AuNPs to the surface of Fe_2O_3@SiO_2 nanospheres is then determined from optical density vs. concentration calibration curve of MPSA:OT covered AuNPs.

After 3 hours of the reaction, the hierarchical nanoparticles and Fe_2O_3@SiO_2 nanospheres are separated from the reaction medium by magnetic separation whereas MPSA:OT covered AuNPs are separated *via* centrifugation at 5000 rpm for 15 min. Then, 50 µL of supernatant is dissolved in acetonitrile-d3. Conversion of benzyl alcohol to benzyl acetate is calculated as a percentage by taking the ratio between the integrated peaks corresponds to benzyl alcohol and benzyl acetate that are located 4.6 ppm and 5.1 ppm, respectively. Calculations are based on the assumption that formation of benzyl acetate results in the equivalent mole decrease in the initial mole of benzyl alcohol.

^{1}H NMR (400 MHz, Acetonitrile-d3) δ 7.46 - 7.23 (m, 19H), 5.11 (d, *J* = 1.0 Hz, 4H), 4.61 -4.55 (m, 5H), 2.08 (s, 2H), 2.02 -1.93 (m, 1H).

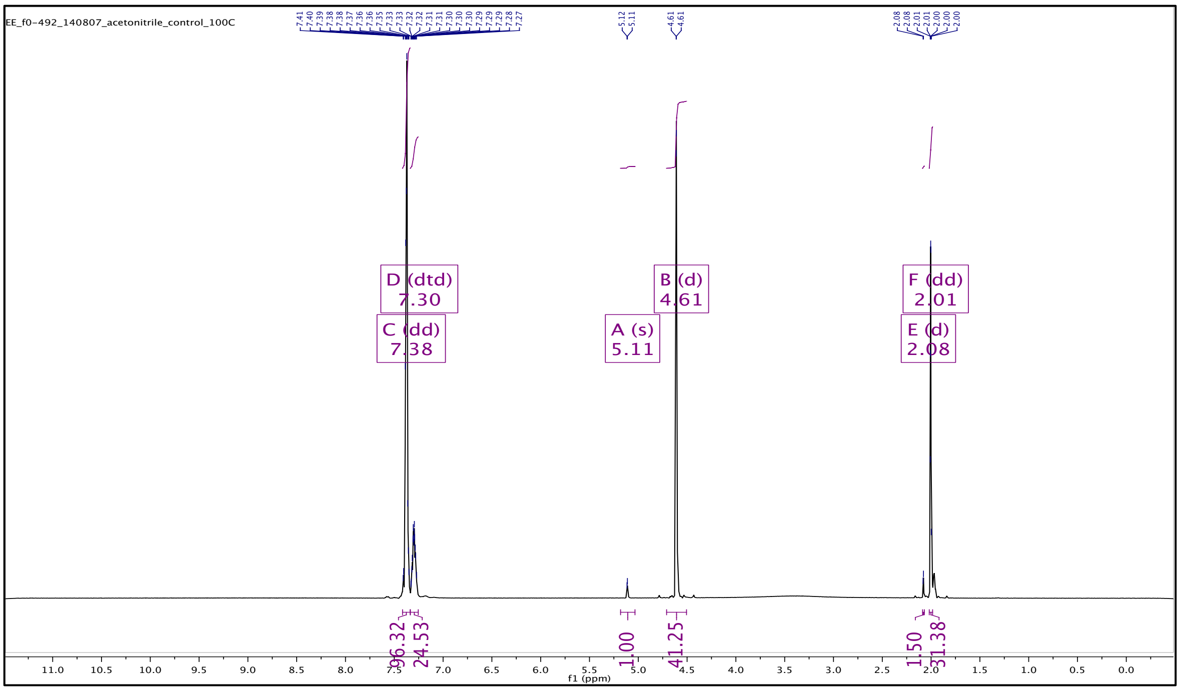

Fig. S5 ^{1}H NMR spectrum of reaction medium after 3 hours at 100 ^{0}C without particles (Control).

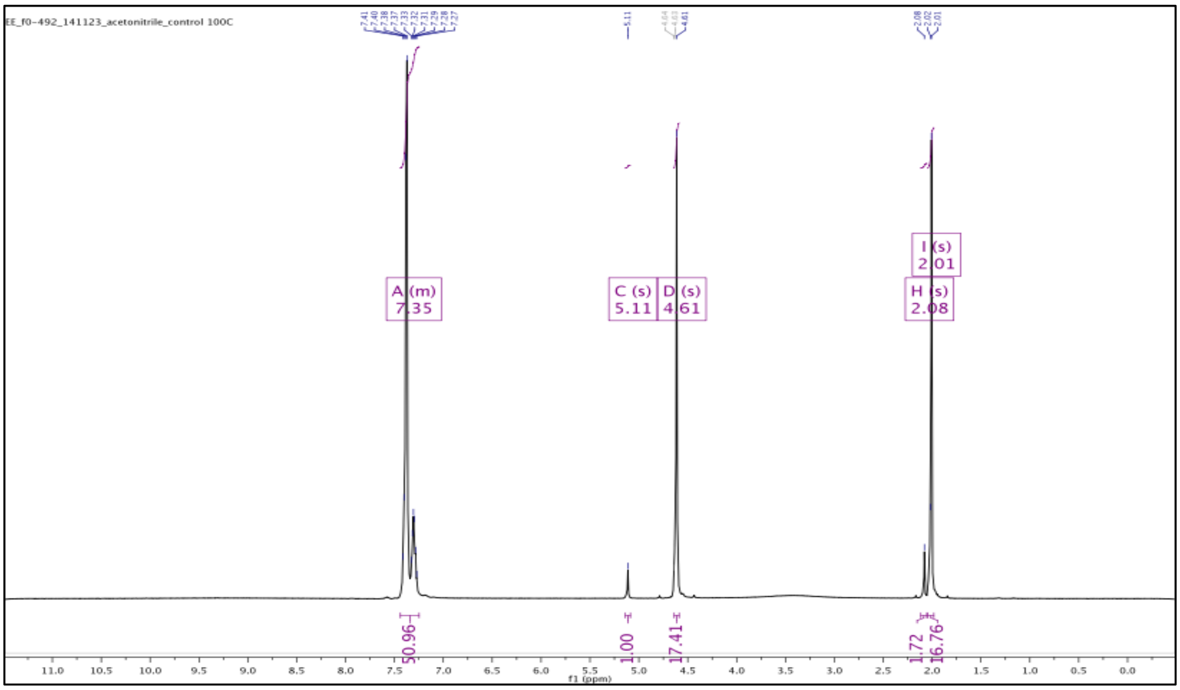

Fig. S6 ^{1}H NMR spectrum of reaction medium after 3 hours at 100 ^{0}C with Fe_2O_3@SiO_2 nanospheres.

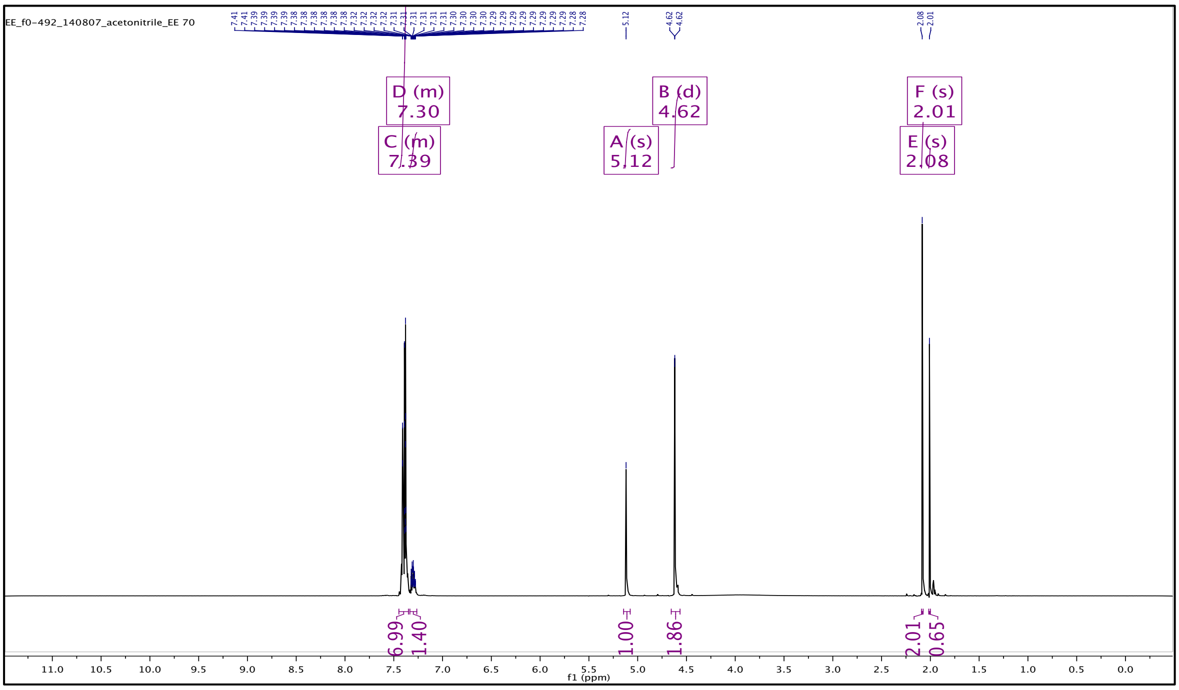

Fig. S7 ^{1}H NMR spectrum of reaction medium after 3 hours at 100 ºC with MPSA:OT AuNPs.

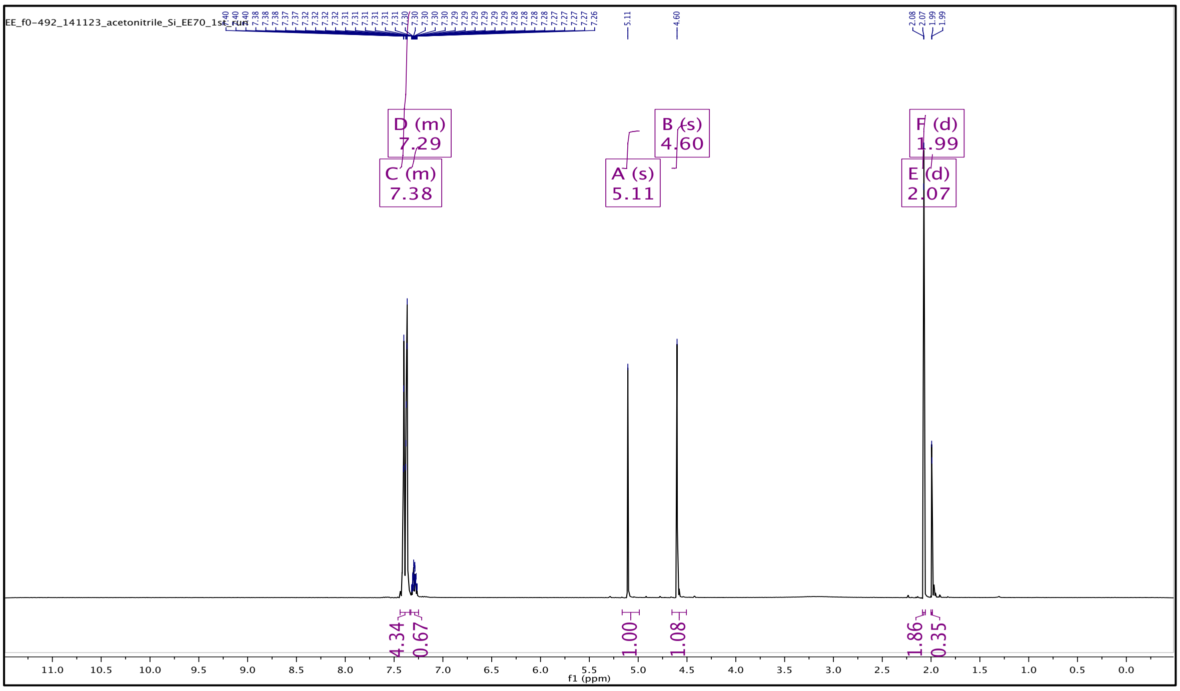

Fig. S8 ^{1}H NMR spectrum of reaction medium after 3 hours at 100 $^{\circ}$C with Fe_2O_3@SiO_2@Au nanospheres- 1st run.

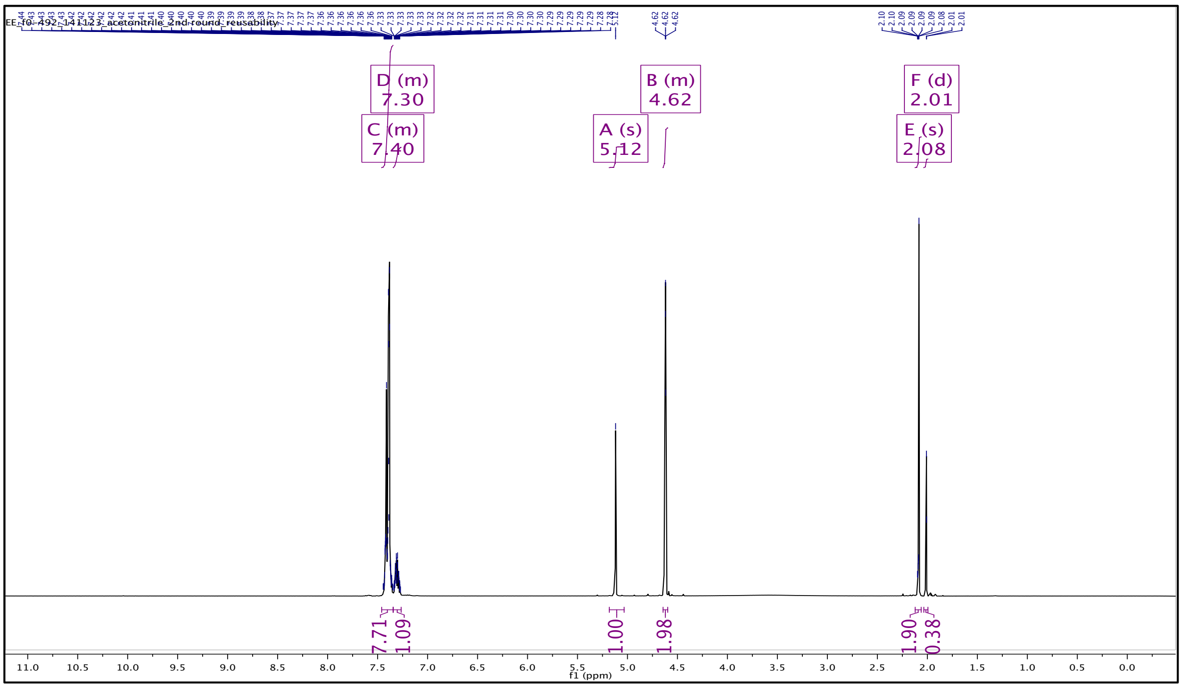

Fig. S9 ^{1}H NMR spectrum of reaction medium after 3 hours at 100 °C with Fe_2O_3@SiO_2@Au nanospheres- 2nd run.

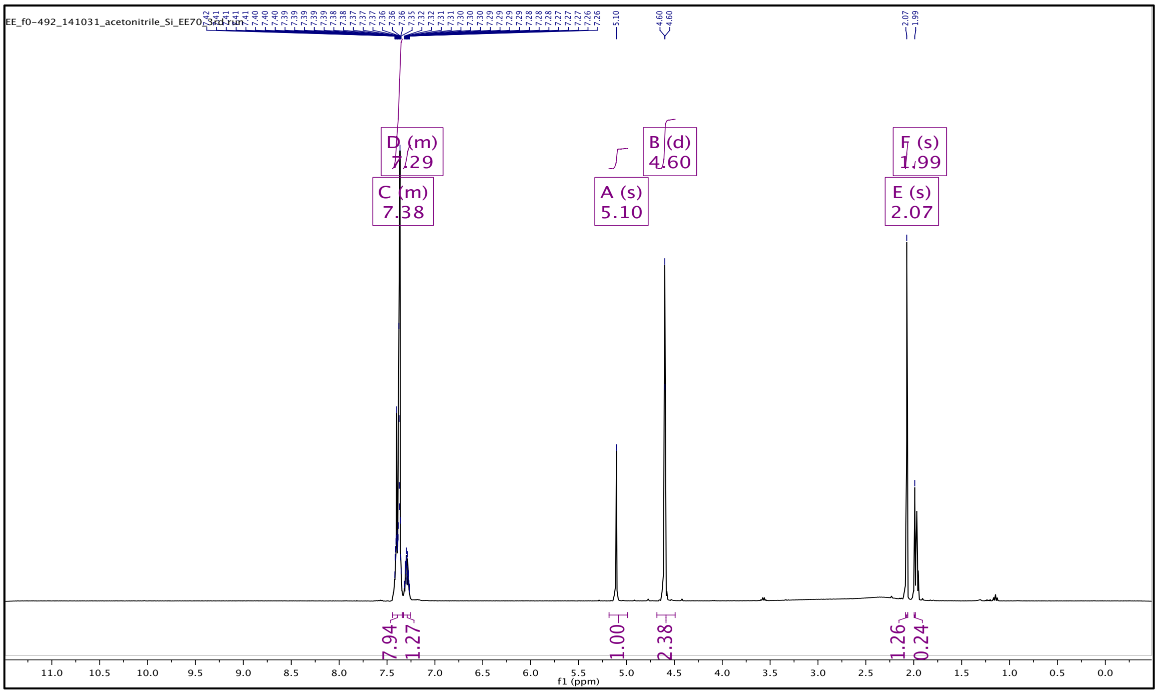

Fig. S10 ^{1}H NMR spectrum of reaction medium after 3 hours at 100 °C with Fe_2O_3@SiO_2@Au nanospheres- 3rd run.

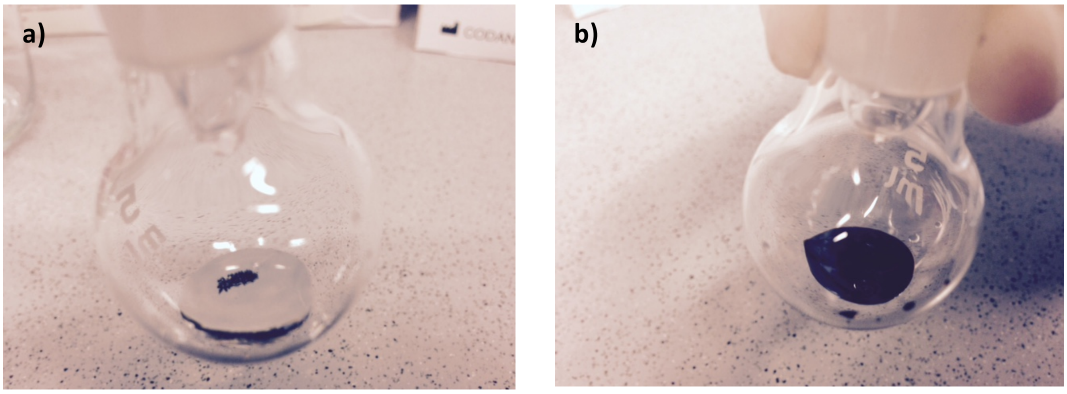

Fig. S11 Photographs shows the solubility of a) MPSA:OT covered AuNPs (poor dispersibility) and b) Fe_2O_3@SiO_2@Au nanospheres (enhanced dispersibility) at room temperature in the reaction medium prior to catalytic reaction.

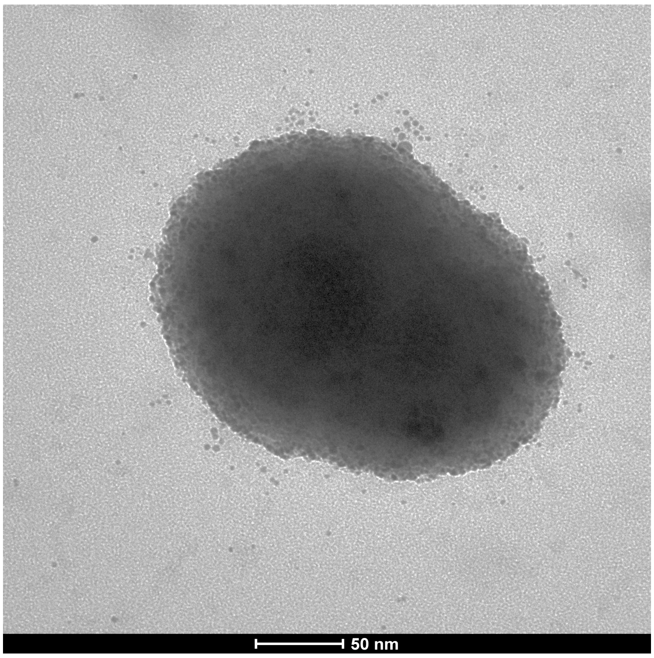

Fig. S12 TEM image of hierarchical nanospheres after the acidification step for third run prior to the cleaning step