Electronic Supplementary Material (ESI) for Catalysis Science & Technology

NHC-stabilized Ruthenium Nanoparticles as New Catalysts for Hydrogenation Reactions

David Gonzalez-Galvez,[a ‡] Patricia Lara,[b,c ‡] Orestes Rivada-Wheelaghan,[d] Salvador Conejero,[d]
Bruno Chaudret,[e] Karine Philippot,[b,c] Piet W. N. M. Van Leeuwen*[a]

[a] *Institute of Chemical Research of Catalonia (ICIQ), Av. Països Catalans 16, 43007-Tarragona, Spain*

[b,c] *Laboratoire de Chimie de Coordination; CNRS; LCC; 205 Route de Narbonne, F-31077 Toulouse, France; Université de Toulouse; UPS, INPT; LCC; F-31077 Toulouse, France*

[d] *Instituto de Investigaciones Químicas, Avenida Américo Vespucio 49, 41092 Isla de la Cartuja, Sevilla, Spain*

[e] *LPCNO; Laboratoire de Physique et Chimie de Nano-Objets, 135 Avenue de Rangueil, F-31077 Toulouse, France*

‡*These authors contributed equally to this work.*

Electronic Supplementary Material

Content

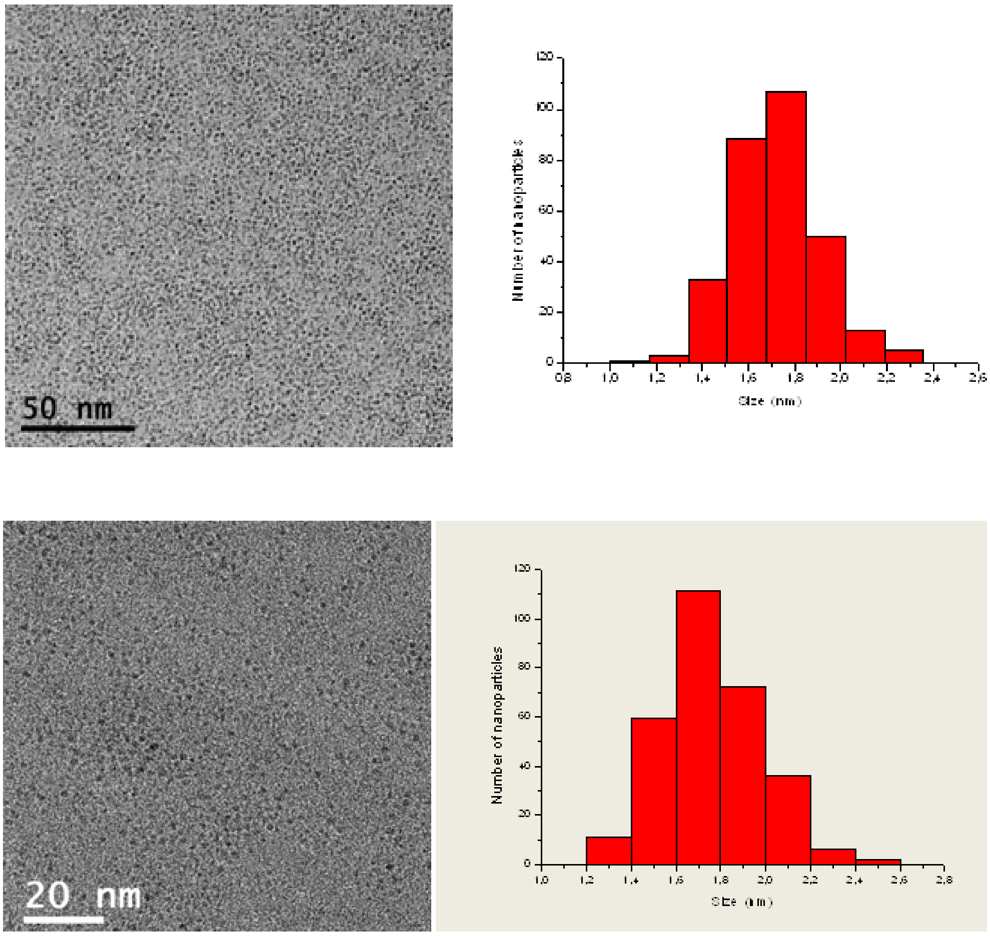
Experimental Section

General Procedures. Solvents and reactants were purchased from Sigma-Aldrich as HPLC grade and dried with a MB SPS800 of MBraun. $\mathrm{RuI}^{t}\mathrm{Bu}^{0.2}$, $\mathrm{RuIPr}^{0.2}$ and $\mathrm{RuIPr}^{0.5}$ were prepared following a reported procedure.[1] Analyses of the catalytic reactions were performed on a GC-FID equipped with a β-DEX 225 (25% 2,3-di-*O*-acetyl-6-*O*-TBDMS-β-cyclodextrin in SPB-20 polyphase capillary column; 30 m x 0.25 mm). NMR spectra were recorded on a Bruker 500 MHz Ultrashield™.

Hydrogenation of aromatic compounds. In a typical experiment the chosen amount of RuNP was placed in a 25 ml Berghoff autoclave. A 0.125 M solution of the reactant in the chosen solvent or pure reactant was added through a liquid injection port and the autoclave was pressurized with 40 bar of dihydrogen. After the chosen time, the autoclave was depressurized. The solution was analyzed by GC (*o*-methylanisole, *m*-methylanisole, *o*-cresol, acetophenone, toluene, benzonitrile, bromobenzene) or NMR spectroscopy (benzene, *N*,*N*-dimethylaniline, benzoic acid, 3-acetylpyridine) to determine conversion and selectivity. All the experiments were done in triplicate.

For the catalytic studies, the same procedure was used but doing the reaction in an SPR16 Slurry Phase Reactor (Amtec GmbH) and continuously monitoring dihydrogen consumption. In the case of acetophenone hydrogenation, 100 µl samples were collected from the reactor after 30 min, 1 h, and each hour till the experiment was finished, and analyzed by GC.

Figure S1. TEM images corresponding to RuI^{t}Bu NPs (top) and RuIPr$^{0.2}$ NPs (bottom).



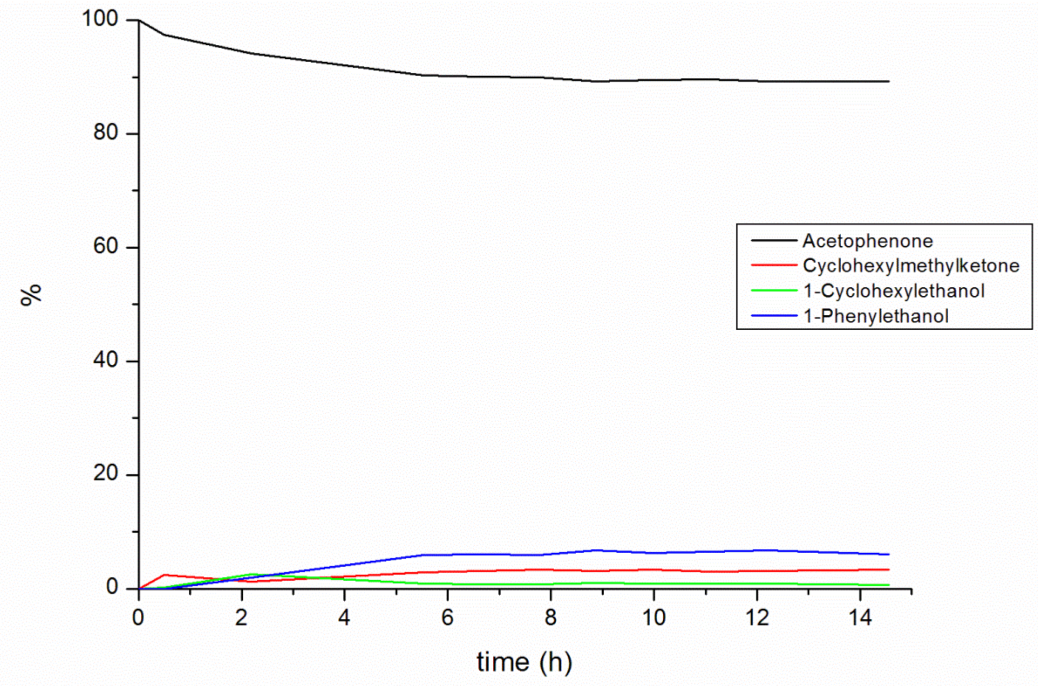


Figure S2. Hydrogenation of acetophenone (0.5 M in MeOH) at 298 K under 40 bar of H_2 in presence of 0.1 %RuIPr$^{0.2}$.

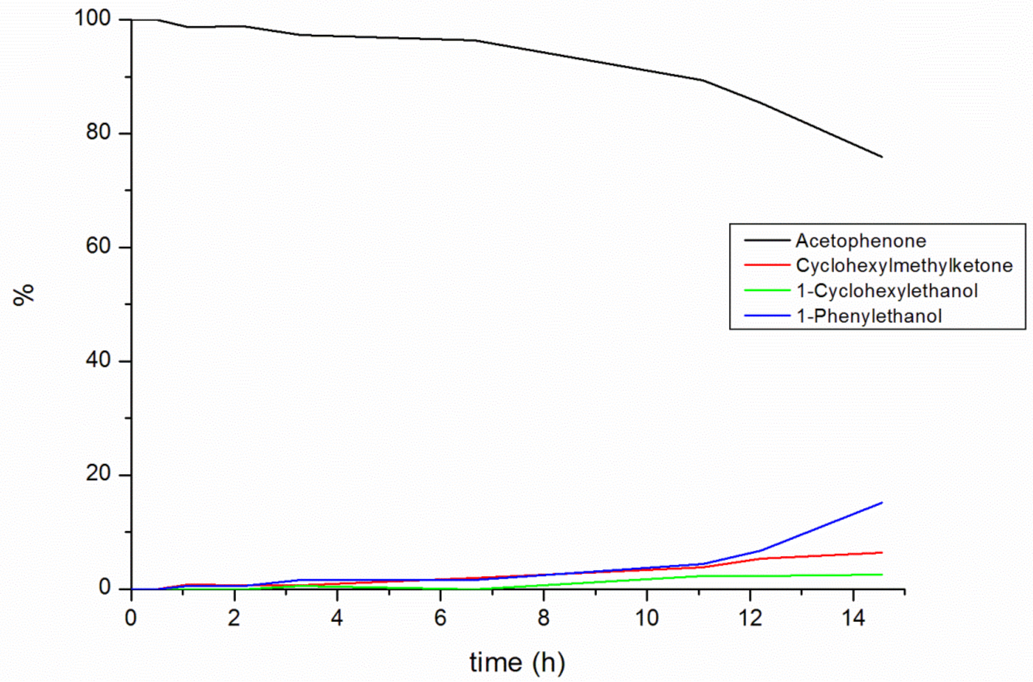


Figure S3. Hydrogenation of acetophenone (0.5 M in pentane) at 298 K under 40 bar of H_2 in presence of 0.1 %RuIPr$^{0.2}$.

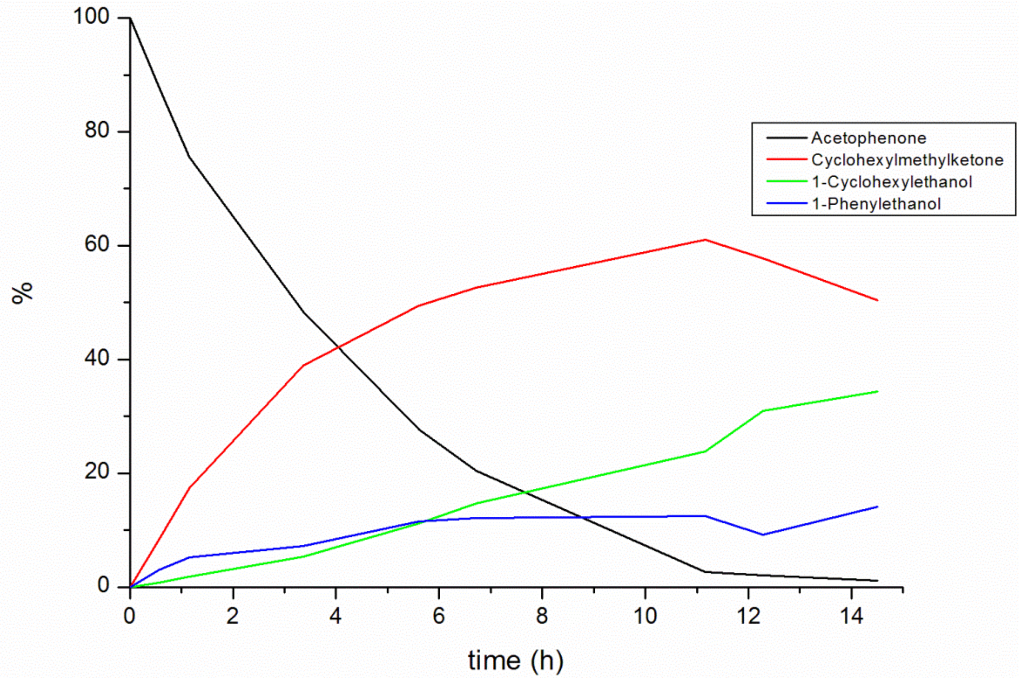


Figure S4. Hydrogenation of acetophenone (0.5 M in THF) at 298 K under 40 bar of H_2 in presence of 0.1 %RuIPr$^{0.2}$.

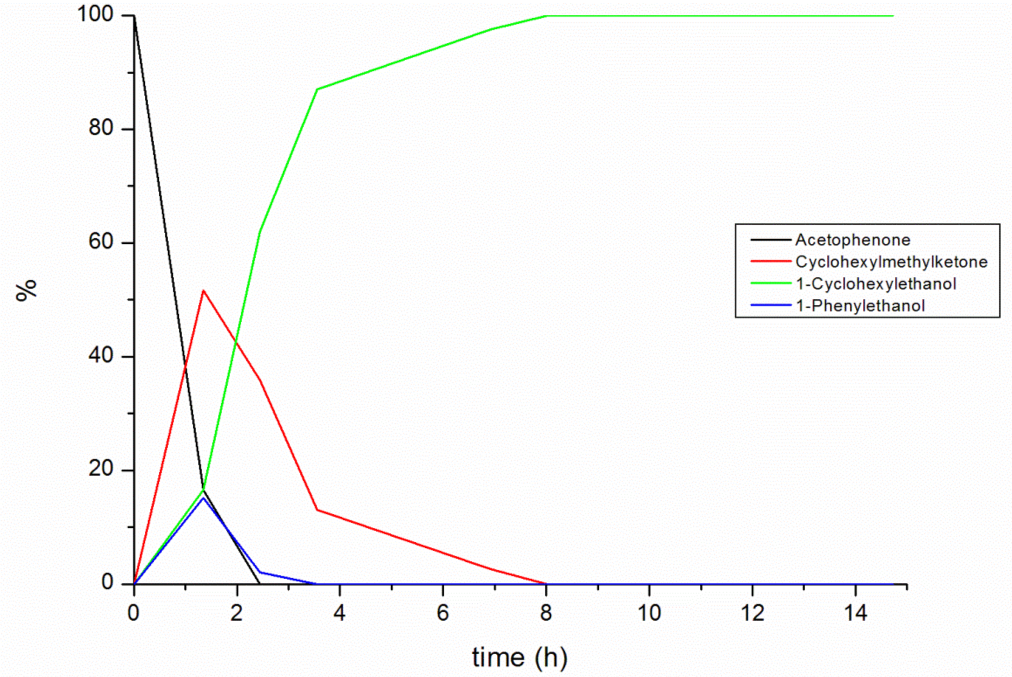


Figure S5. Hydrogenation of acetophenone (0.5 M in THF) at 298 K under 40 bar of H_2 in presence of 1 % RuIPr$^{0.2}$.

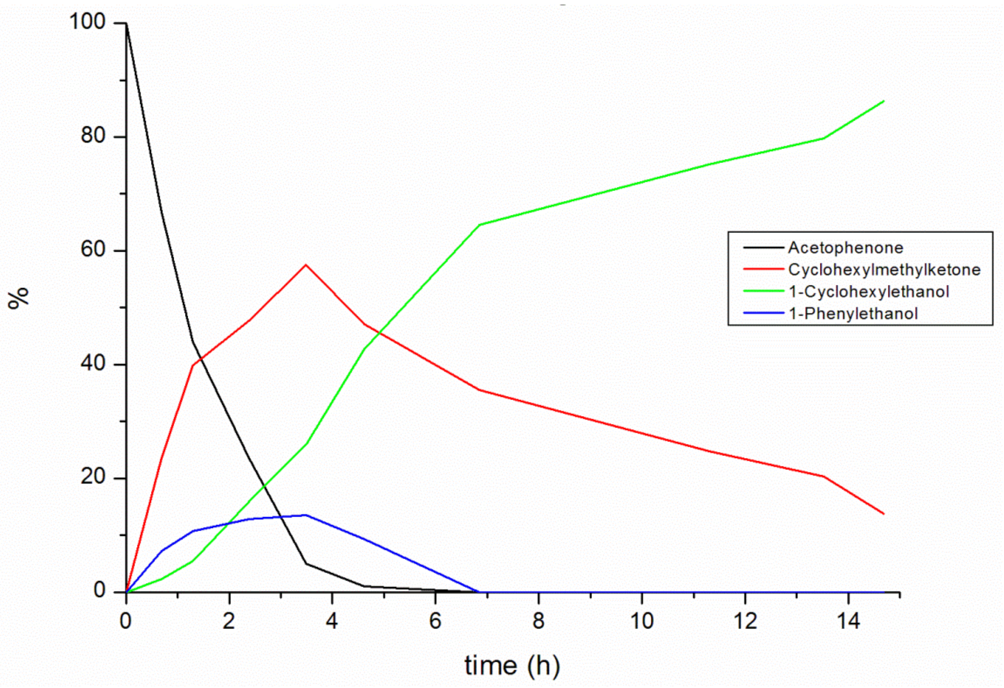


Figure S6. Hydrogenation of acetophenone (0.5 M in THF) at 298 K under 40 bar of H_2 in presence of 0.3 % $RuIPr^{0.2}$.

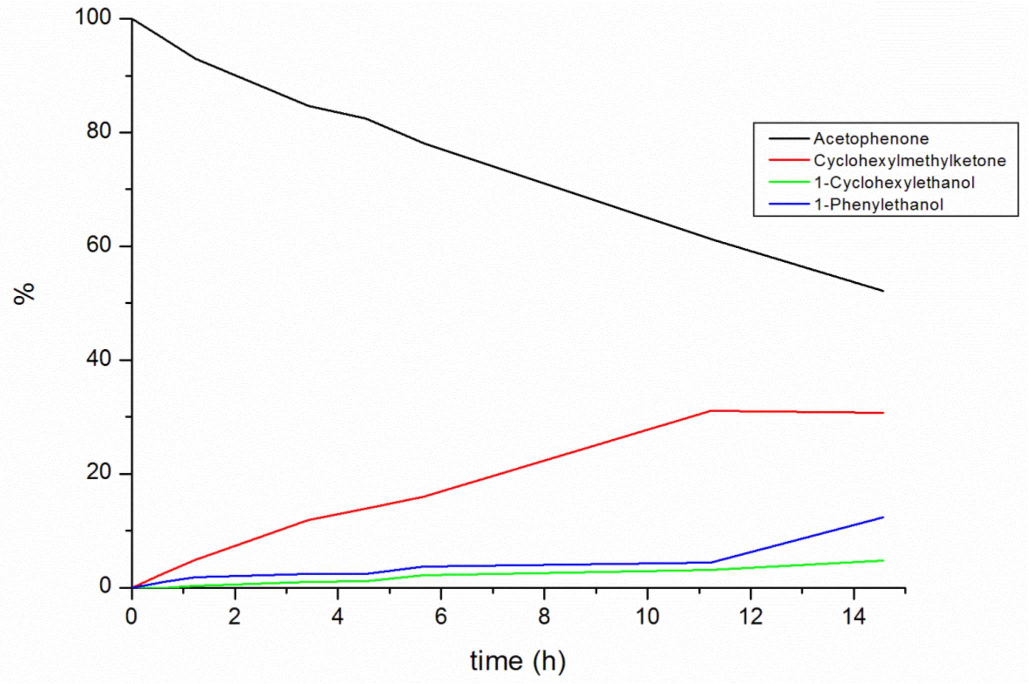


Figure S7. Hydrogenation of acetophenone (0.5 M in THF) at 298 K under 40 bar of H_2 in presence of 0.03 % $RuIPr^{0.2}$.

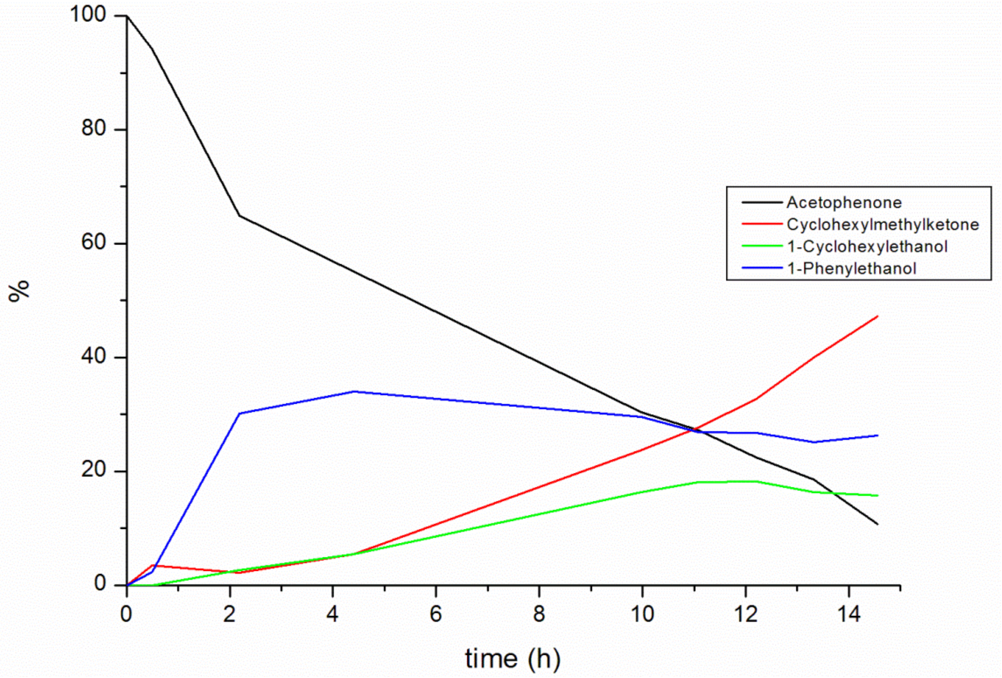


Figure S8. Hydrogenation of acetophenone (0.5 M in THF) at 298 K under 10 bar of H_2 in presence of 0.3 % RuIPr$^{0.2}$.

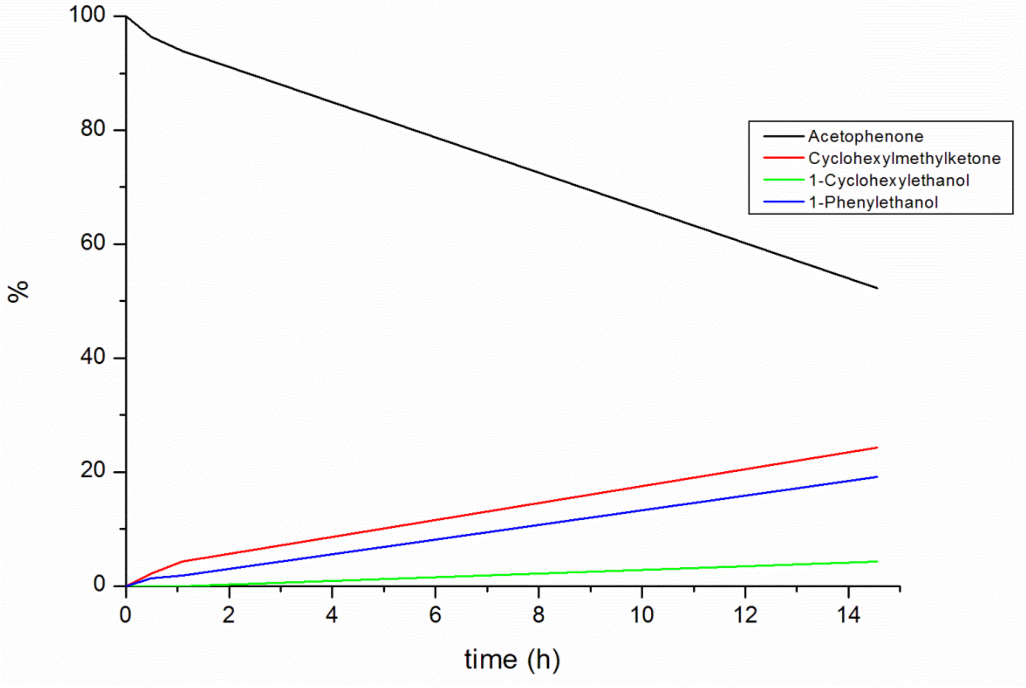


Figure S9. Hydrogenation of acetophenone (0.5 M in THF) at 298 K under 10 bar of H_2 in presence of 0.1 % RuIPr$^{0.2}$.

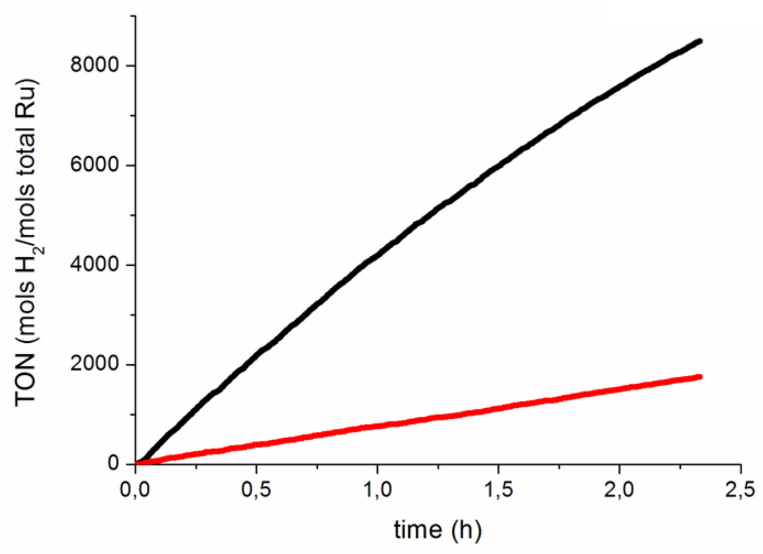


Figure S10. Hydrogenation of acetophenone (black) and 3-acetylpyridine (red) at 353 K and 40 bar of H_2 in presence of 0.3% of $RuIPr^{0.2}$.

1. P. Lara, O. Rivada-Wheelaghan, S. Conejero, R. Poteau, K. Philippot and B. Chaudret, *Angew. Chem., Int. Ed. Engl.*, 2011, **50**, 12080-12084.