

Supplementary Materials

Immobilization of an Iridium(I)-NHC-phosphine catalyst for hydrogenation reactions under batch and flow conditions

Henrietta Kovács^{1,2}, Krisztina Orosz^{1,2}, Gábor Papp¹, Ferenc Joó^{1,3}, and Henrietta Horváth^{3,*}

¹ Department of Physical Chemistry, University of Debrecen, P.O.Box 400, Debrecen, H-4002 Hungary

² Doctoral School of Chemistry, University of Debrecen, P.O.Box 400, Debrecen, H-4002 Hungary

³ MTA-DE Redox and Homogeneous Catalytic Reaction Mechanisms Research Group, P.O.Box 400, Debrecen, H-4002 Hungary

Corresponding author: Henrietta Horváth, e-mail: henrietta.horvath@science.unideb.hu

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Equipment and methods used in this study

General

NMR measurements were carried out with the use of BRUKER DRX 360 (Company, City, State Abbr (if has), Country) or Bruker Avance I 400 MHz spectrometers. Chemical shifts were referenced to sodium 2,2-dimethyl-2-silapentane-5-sulfonate, DSS (^1H) and to 85% H_3PO_4 (^{31}P). Infrared spectra were recorded on a Perkin Elmer Spectrum Two FT-IR Spectrometer in ATR mode.

Optical microscopy photographs were taken using an Olympus BX41 confocal microscope with USB PC controlled 3 MegaPixel camera attached to the Horiba HR Labram Evo Microscope supplied with an XY manual mechanical stage, a white light illumination system by reflection with variable light intensity.

Anchoring of $\text{Na}_2[\text{Ir}(\text{cod})(\text{emim})(\text{mtppts})]$ on solid supports

Anion-exchange support materials were pretreated before heterogenization: they were washed alternately with 0.1 M NaOH and 0.1 M HCl three times, and finally with distilled water three times. They were dried in vacuo.

In a Schlenk tube, $\text{Na}_2[\text{Ir}(\text{cod})(\text{emim})(\text{mtppts})]$ (60 mg) was dissolved in deoxygenated 0.01 M HCl solution (12 mL) under argon atmosphere. With the use of a syringe, the solution was added onto 360 mg of pretreated Lewatit MonoPlus MP 500 ion-exchange beads under argon atmosphere. The reaction mixture was thermostated at 40 °C for 3 hours, during which the solution decolorized, and the beads turned red. The heterogenized complex was filtered under argon, washed with hexane and dried in vacuo. Yield: 390 mg supported catalyst (96%).

Spectrophotometric study of the immobilization process and leaching tests by acid-base treatment

The heterogenization process of $\text{Na}_2[\text{Ir}(\text{cod})(\text{emim})(\text{mtppts})]$ was investigated at room temperature in an argon-filled inert spectrophotometric cell, with the use of a Shimadzu UV-1700 spectrophotometer. 1.5 mg solid complex and 50 mg solid support were placed into the cuvette, placed under argon, then 1 mL of deoxygenated 0.01 M HCl solution was injected through the septum of the cell. The mixture in the cell was stirred well, then placed into the

spectrophotometer, and an absorption spectrum was obtained every 4 min, while shaking the cuvette between measurements, until absorbance reached zero value, indicating the end of the heterogenization process.

The acid-base leaching tests were carried out with the use of a Hettich Benelux MHR13 heating thermoshaker. 30 mg of the heterogenized catalyst was placed into the inert, septum-closed reaction vessels, flushed with argon, and then 2 ml of 0.1 M H_3PO_4 or Na_3PO_4 was injected through the septum. Each sample was shaken for an hour in the thermoshaker at room temperature, and then the UV-VIS absorption spectrum was recorded. The mass of the leached complex in the solution was calculated using a calibration curve (Figure S14).

Catalytic reactions

The reactions were performed in an H-Cube hydrogenation microreactor (ThalesNano Nanotechnology Inc, Budapest, Hungary), in continuous mode. 200 mg heterogenized catalyst was loaded into 30 × 4 mm CatCart stainless steel tubes. In continuous mode, the catalyst bed is consistently washed with the substrate solution (0.05 M phenylacetylene or 1-hexyne in methanol, 0.05 M diphenylacetylene or benzylideneacetone in toluene), without interruptions or pauses. Hydrogen was generated ‘in situ’ by the electrolysis of distilled water in the reactor. Reaction temperature ranged between 20–80 °C, pressure between 20–80 bar, and flow rate was either 0.5 or 1 mL/min in each case.

Organic-phase reaction mixtures were analyzed by gas chromatography (phenylacetylene, diphenylacetylene, 1-hexyne: Agilent 7890A equipment, OPTIMA 1 column, 30 m × 0.320 mm × 0.25 μm; benzylideneacetone: HP5890 Series II equipment, Supelcowax 10 column, 30 m × 0.320 mm × 0.25 μm). Column temperature programs were as follows. Phenylacetylene and its derivatives (OPTIMA 1 column): 80 °C for 3 min, then 100 °C/min to 250 °C, held at this temperature for 3 min. Diphenylacetylene and its derivatives (OPTIMA 1 column): 180 °C for 4 min, then 70 °C/min to 250 °C, held at this temperature for 3 min. 1-hexyne and its derivatives (OPTIMA-1 column): 40 °C for 3 min, then 100 °C/min to 250 °C, held at this temperature for 3 min. Benzylideneacetone and its derivatives (Supelcowax 10 column): 100 °C for 3 min, then 45 °C/min to 210 °C, held at this temperature for 2 min.

GC-MS measurements were carried out on a Skyray GC-MS 6800 instrument (Agilent DB-5 column).

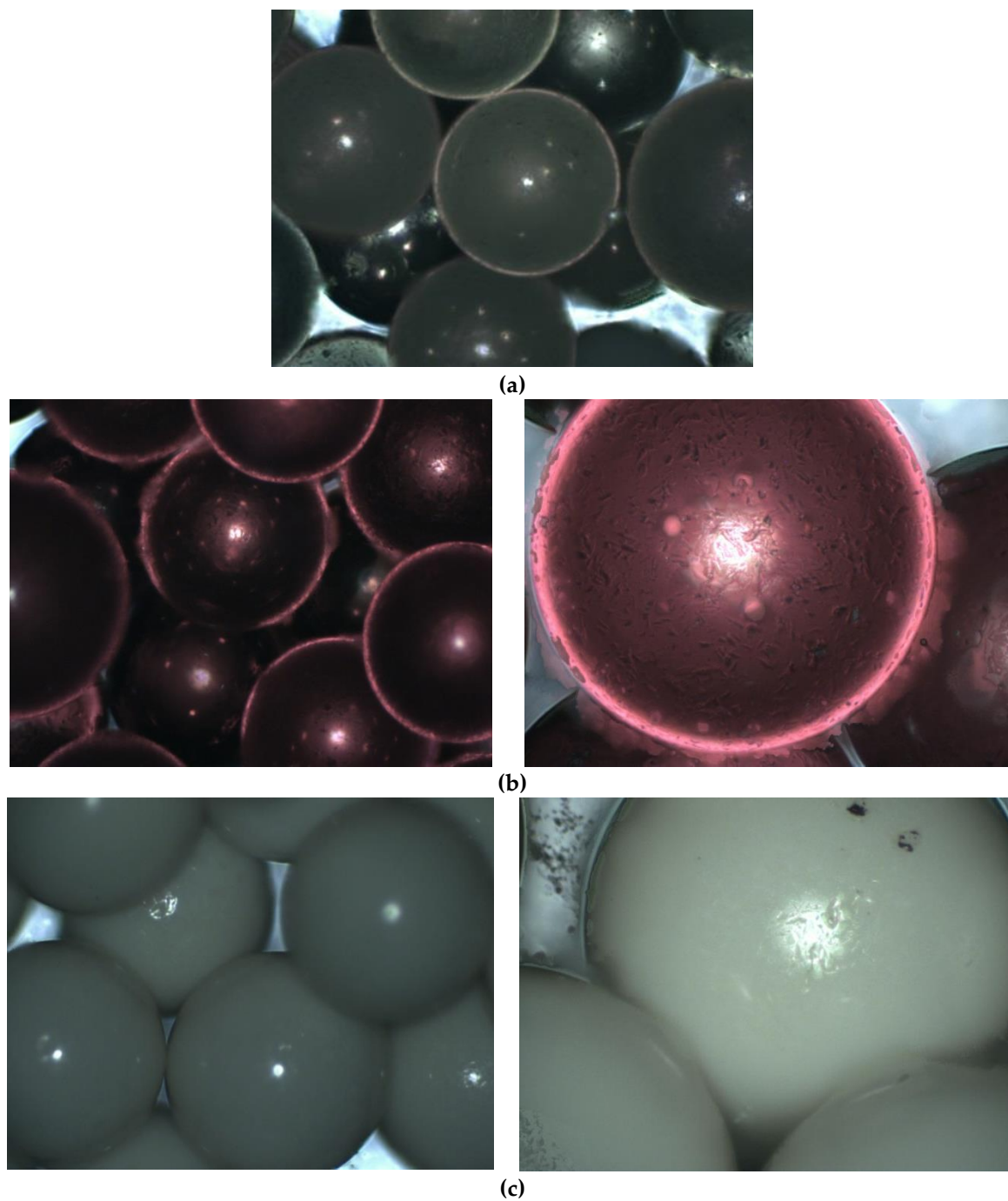


Figure S1. Optical microscopy photographs of (a) Lewatit MonoPlus MP 500 anion exchanger, in air
(b) $\text{Na}_2[\text{Ir}(\text{cod})(\text{emim})(\text{mtppts})]$ @Lewatit MonoPlus MP 500 before treatment with H_2 , in air
(c) $\text{Na}_2[\text{Ir}(\text{cod})(\text{emim})(\text{mtppts})]$ @Lewatit MonoPlus MP 500 after treatment with H_2

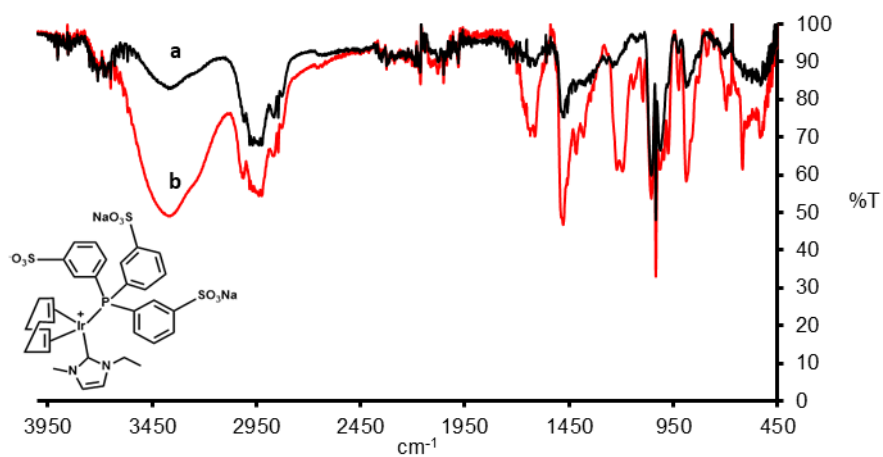


Figure S2. Infrared spectra of (a) Lewatit MonoPlus MP 500 anion exchanger and (b) Na₂[Ir(cod)(emim)(mtppts)]@Lewatit MonoPlus MP 500.

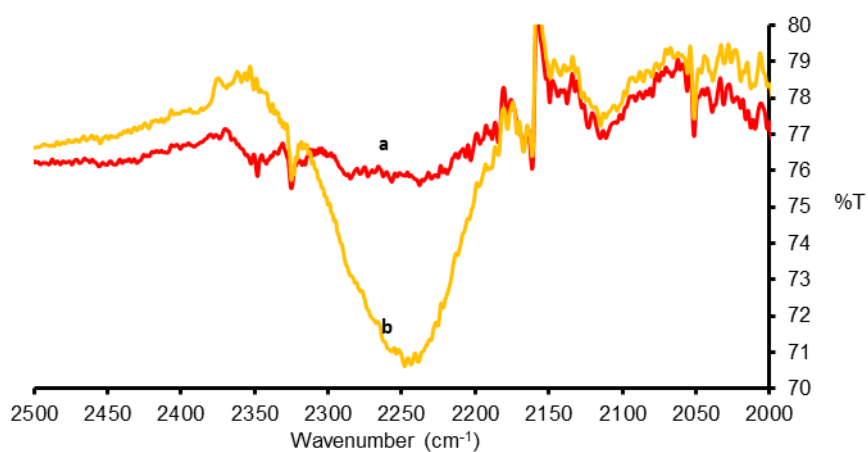


Figure S3. Infrared spectra of Na₂[Ir(cod)(emim)(mtppts)] complex catalyst, (a) before hydrogenation, (b) after 1 bar H₂.

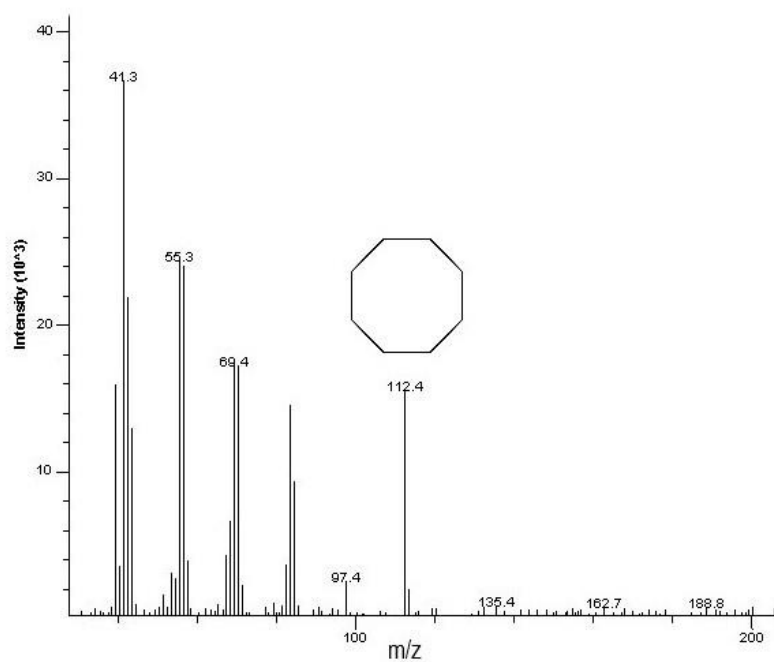


Figure S4. GC-MS detection of cyclooctane formed in the hydrogenation of $\text{Na}_2[\text{Ir}(\text{cod})(\text{emim})(\text{mtppts})]$ in methanol solvent.

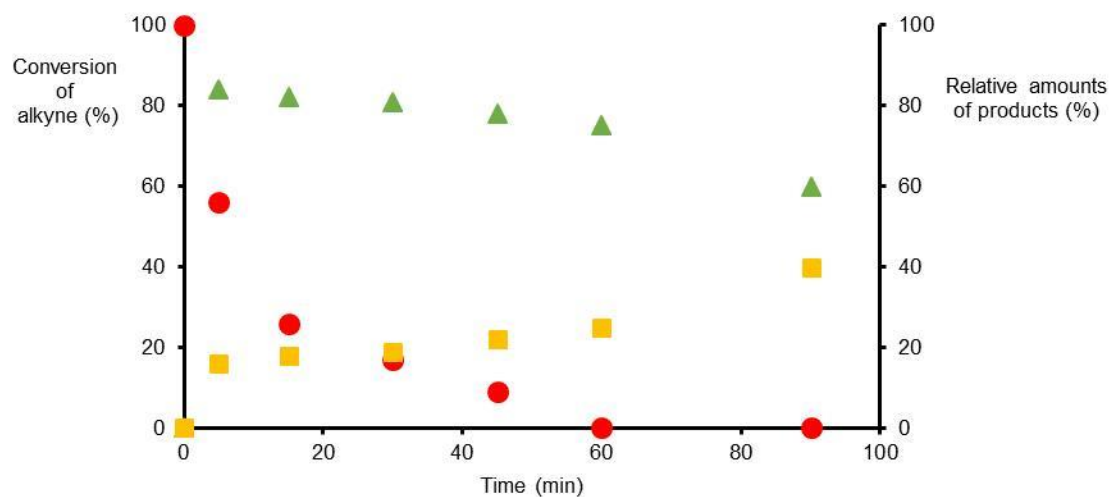


Figure S5. Time course of hydrogenation of phenylacetylene (●) and the ratio of styrene (▲) and ethylbenzene (■) catalyzed homogeneously by $\text{Na}_2[\text{Ir}(\text{cod})(\text{emim})(\text{mtppts})]$ in batch reactions. $[\text{substrate}] / [\text{cat}] = 100$, $P(\text{H}_2) = 10$ bar, $T = 20$ °C, solvent: methanol.

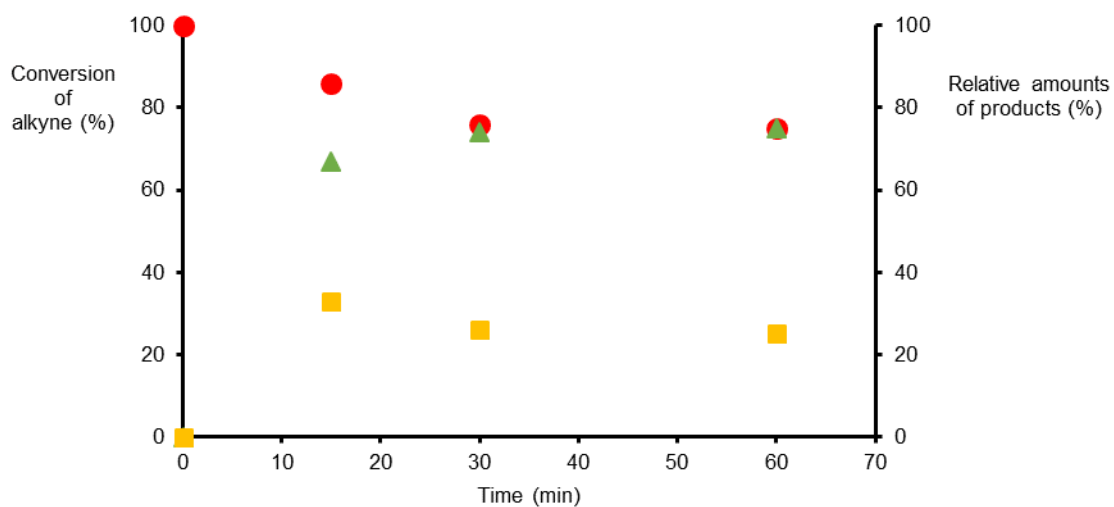


Figure S6. Time course of hydrogenation of phenylacetylene (●) and the ratio of styrene (▲) and ethylbenzene (■) catalyzed by the heterogeneous $\text{Na}_2[\text{Ir}(\text{cod})(\text{emim})(\text{mtppts})]@\text{Lewatit MonoPlus MP 500}$ catalyst in batch reactions. $[\text{substrate}] / [\text{cat}] = 100$, $P(\text{H}_2) = 10$ bar, $T = 20$ °C, solvent: methanol.

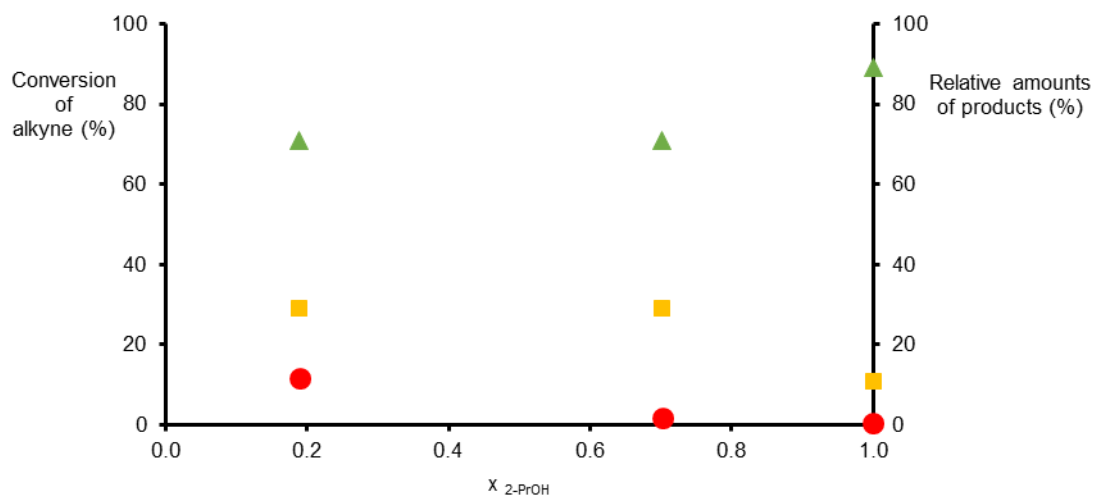


Figure S7. Effect of water on alkyne conversion (●) and the ratio of styrene (▲) and ethylbenzene (■) in hydrogenation of phenylacetylene catalyzed homogeneously by $\text{Na}_2[\text{Ir}(\text{cod})(\text{emim})(\text{mtppts})]$ in batch reactions. $[\text{substrate}] / [\text{cat}] = 100$, $P(\text{H}_2) = 10$ bar, $T = 20$ °C, $t = 30$ min, solvent: water/2-propanol.

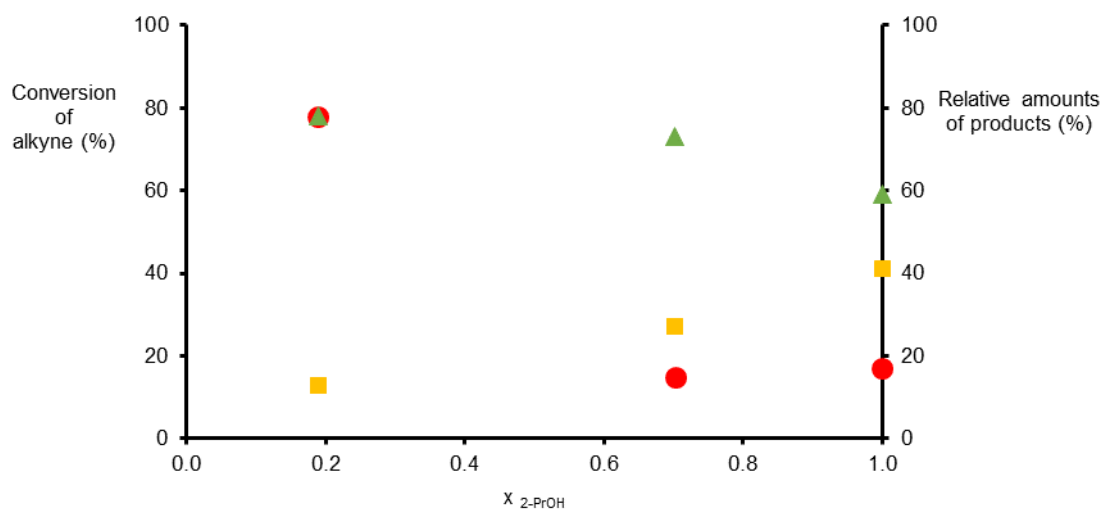


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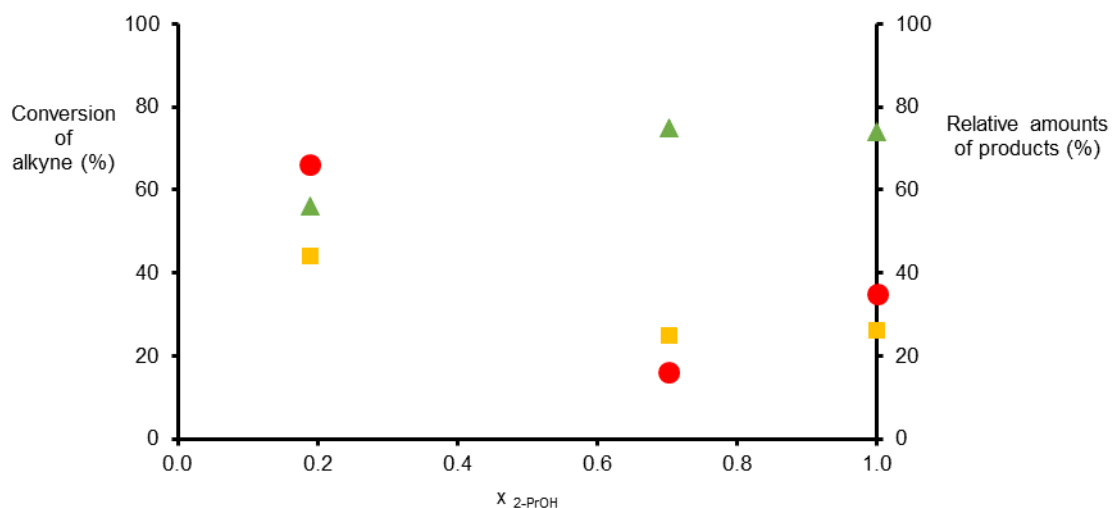


Figure S9. Effect of water on alkyne conversion (●) and the ratio of *cis*-stilbene (▲) and *trans*-stilbene (■) in hydrogenation of diphenylacetylene homogeneously catalyzed by $\text{Na}_2[\text{Ir}(\text{cod})(\text{emim})(\text{mtppts})]$ in batch reactions.

[substrate] / [cat] = 100, $P(\text{H}_2)$ = 10 bar, T = 70 °C, t = 30 min, solvent = water/2-propanol.

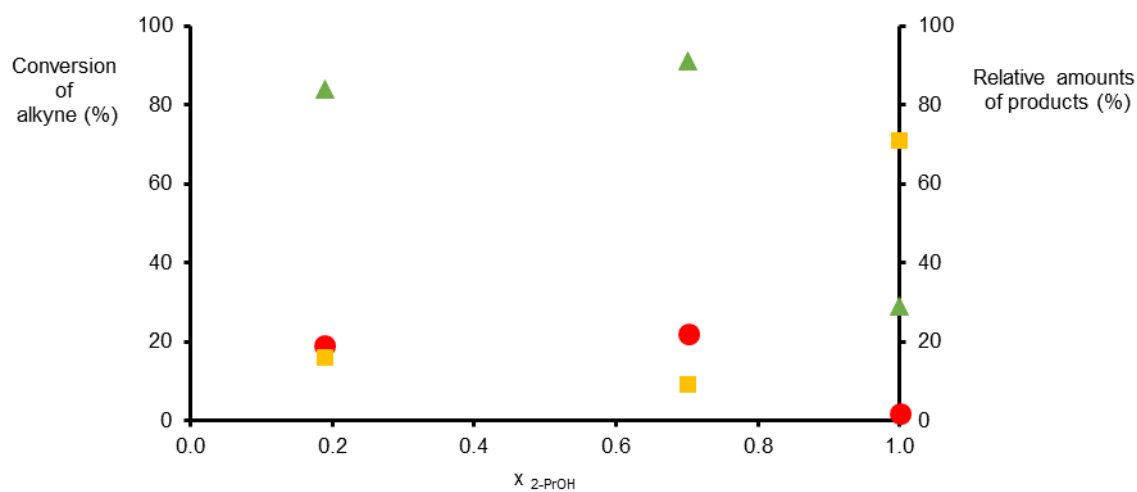


Figure S10. Effect of water on the conversion of diphenylacetylene (●) and the ratio of *cis*-stilbene (▲) and *trans*-stilbene (■) in hydrogenation catalyzed by the heterogeneous $\text{Na}_2[\text{Ir}(\text{cod})(\text{emim})(\text{mtppts})]@\text{Lewatit MonoPlus MP 500}$ catalyst in batch reactions.

[substrate] / [cat] = 100, $P(\text{H}_2)$ = 10 bar, T = 70 °C, t = 30 min, solvent: water/2-propanol.

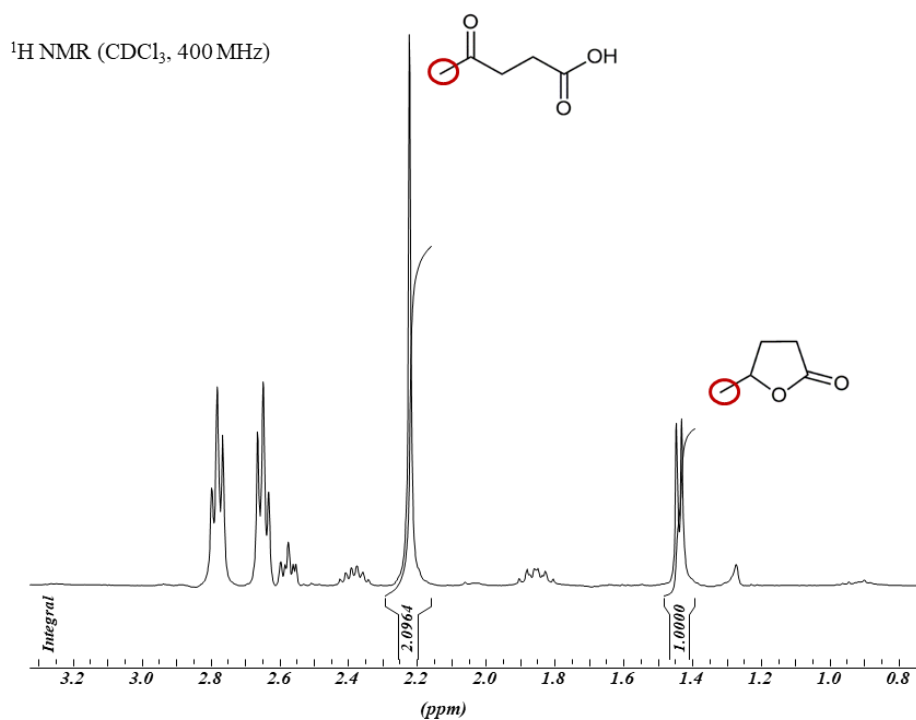


Figure S11. ^1H NMR spectrum of a reaction mixture (CHCl_3 extract) in hydrogenation of levulinic acid catalyzed by the heterogeneous $\text{Na}_2[\text{Ir}(\text{cod})(\text{emim})(\text{mtppts})]@\text{Lewatit MonoPlus MP 500}$ catalyst in batch reaction.

Conditions: $n(\text{catalyst}) = 0.01$ mmol, $[\text{substrate}] / [\text{cat}] = 50$, $P(\text{H}_2) = 10$ bar, $T = 70$ $^\circ\text{C}$, $t = 2$ h, solvent: water, 3 mL.

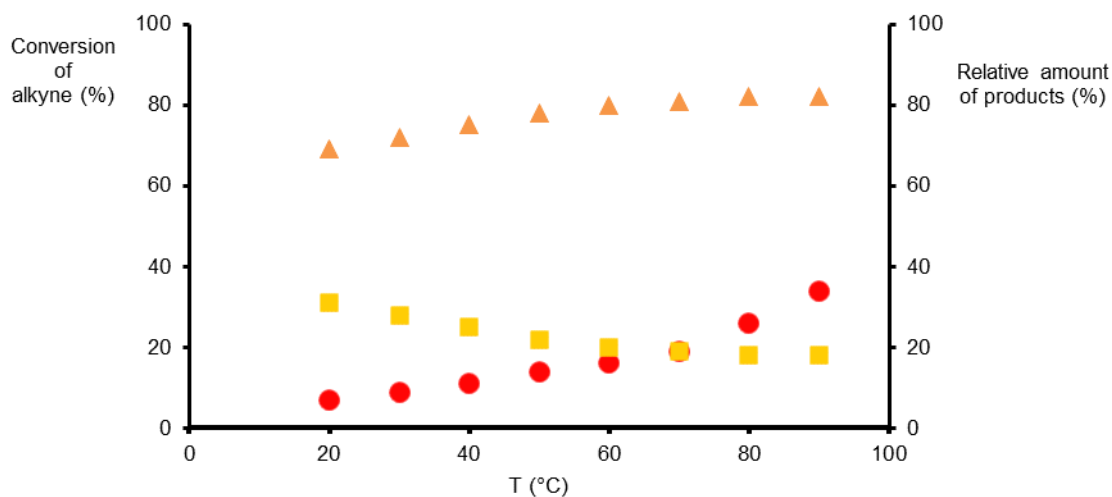


Figure S12. Temperature dependence of alkyne conversion (●) and the ratio of *cis*-stilbene (▲) and *trans*-stilbene (■) in hydrogenation of diphenylacetylene catalyzed by $\text{Na}_2[\text{Ir}(\text{cod})(\text{emim})(\text{mtppts})]$ @Lewatit MonoPlus MP 500 in an H-Cube flow reactor.

$c(\text{alkyne}) = 0.05 \text{ M}$, $m(\text{cat}) = 200 \text{ mg}$, $P(\text{H}_2) = 20 \text{ bar}$, $T = 20\text{--}90 \text{ }^{\circ}\text{C}$, $v = 1.0 \text{ mL/min}$, solvent: methanol.

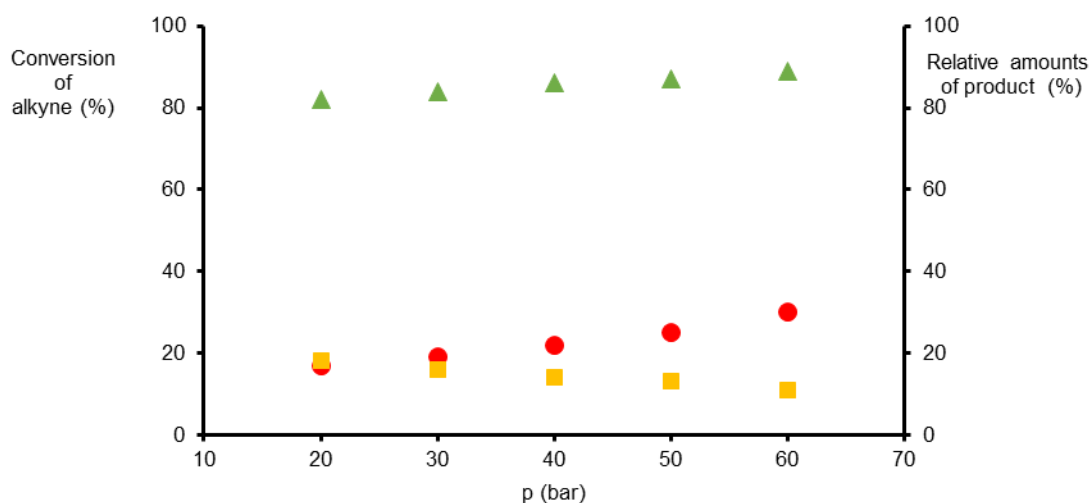


Figure S13. Pressure dependence of alkyne conversion (●) and the ratio of *cis*-stilbene (▲) and *trans*-stilbene (■) in hydrogenation of diphenylacetylene catalyzed by $\text{Na}_2[\text{Ir}(\text{cod})(\text{emim})(\text{mtppts})]$ @Lewatit MonoPlus MP 500 in an H-Cube flow reactor.

$c(\text{alkyne}) = 0.05 \text{ M}$, $m(\text{cat}) = 200 \text{ mg}$, $P(\text{H}_2) = 20\text{--}60 \text{ bar}$, $T = 60 \text{ }^{\circ}\text{C}$, $v = 1.0 \text{ mL/min}$, solvent: toluene.

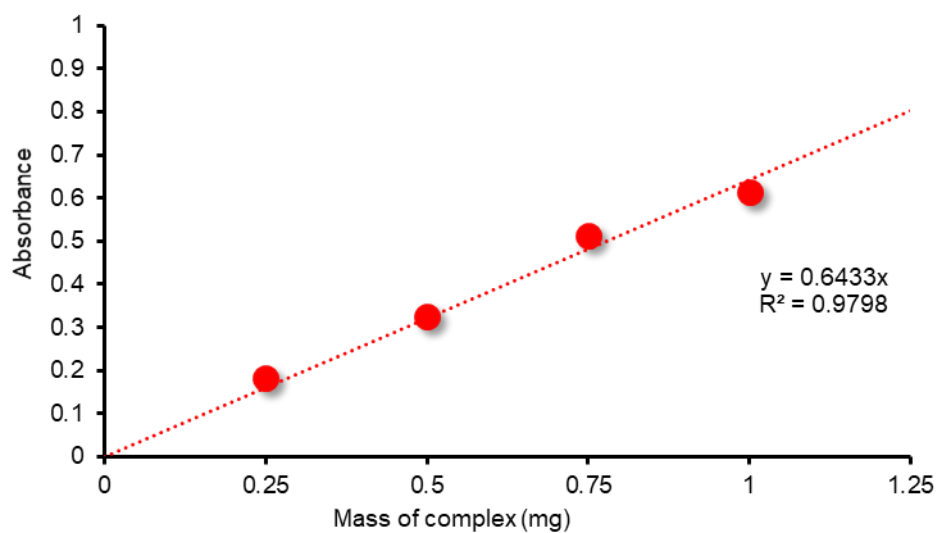


Figure S14. Calibration curve for spectrophotometric leaching tests.
 $m(\text{Na}_2[\text{Ir}(\text{cod})(\text{emim})(\text{mtppts})]) = 0.25, 0.5, 0.75, 1.0 \text{ mg}$, $V(\text{H}_2\text{O}) = 2.5 \text{ mL}$, $\lambda = 400 \text{ nm}$, $T = \text{r.t.}$