

**Supplementary Information for**

**Selective Hydrogenation of  $\alpha,\beta$ -unsaturated Carbonyl Compounds on Silica-supported Copper Nanoparticles**

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## Experimental

### General Methods

All experiments were performed using dry, oxygen-free solvents using standard schlenk techniques or in N<sub>2</sub> or Ar-filled gloveboxes. The solvents were degassed and purified by double solvent purification alumina columns (MBraun). Benzene-d<sub>6</sub> was vacuum distilled from purple Na/benzophenone and stored over 3 Å sieves. Liquid substrates were obtained from commercial suppliers and purified by distillation. The other reagents unless otherwise noted, were used as received.

### Synthetic procedures

**SiO<sub>2-700</sub>** - Silica support was prepared by compacting Aerosil-200: silica was mixed with water, forming a gel that was dried for 72 h at 120 °C. The compacted silica was sieved with a 450-250 mesh grid and calcined at 700 °C (5 °C.min<sup>-1</sup>) for 12 h under synthetic Air. After cooling down, the silica was evacuated under high vacuum (10<sup>-5</sup> mbar) at room temperature for 3 h. The concentration of silanol groups was determined by titration with [Mg(CH<sub>2</sub>Ph)<sub>2</sub>(THF)<sub>2</sub>] with values in agreement with the reported number<sup>1</sup> for 0.29 mmol SiOH.g<sup>-1</sup>; 0.87 OH nm<sup>-1</sup>.

**[Cu(OtBu)]<sub>4</sub> - Copper(I) tert-butoxide** - was prepared according to the literature procedure.<sup>2</sup>

**Copper particles synthesis**<sup>2</sup> - In a double Schlenk under argon atmosphere, a solution of [Cu(OtBu)]<sub>4</sub> (140 mg, 57 μmol) dissolved in pentane (20 mL) was added to 1.0 g of the SiO<sub>2-700</sub>.<sup>3, 4</sup> After 3 h of stirring at room temperature, the solid was washed three times with 20 mL of pentane and dried under high vacuum conditions (~10<sup>-5</sup> mbar). The sample was reduced at 500 °C (1 °C.min<sup>-1</sup>) under H<sub>2</sub> atmosphere for 5 h. After reduction, the sample turned red; it was cooled down to room temperature and evacuated under (~10<sup>-5</sup> mbar).

**Substrates** - Substrates used are presented in Figure SI 1. After distillation, all liquids were degassed by 3 freeze-pump-thaw cycles and filtered through alumina (activated under high vacuum at 500 °C). Filtration was done in a glovebox and repeated until the pad of alumina was colorless. Solid substrates were evacuated for 3 h under vacuum (Schlenk line).

Substrates **(2)** and **(5)** were synthesized by esterification of the corresponding carboxylic acid using ethanol in acid media.<sup>5</sup> The substrate **(13)** was synthesized from cinnamic acid and trimethylamine.<sup>6</sup>

### Characterization

**N<sub>2</sub> physisorption** – The specific surface area of the support and catalyst were measured from a nitrogen physisorption isotherm recorded at -196 °C on a BEL JAPAN BELSORP-min apparatus. The data were analyzed by the BET method.

**H<sub>2</sub> chemisorption** – Hydrogen chemisorption was investigated using BEL JAPAN BELSORP-MAX. Approximately 100 mg of the samples were loaded into cells in an Ar-filled solvent-free glovebox. For the pre-treatment, the samples were heated at 350 °C for 5 h under vacuum. Adsorption experiments were performed at 25 and 40 °C.<sup>1</sup>

**N<sub>2</sub>O titration** – N<sub>2</sub>O titration was carried out according to the methods developed by Evans et al.<sup>6</sup> About 50- 100 mg of the prepared Cu/SiO<sub>2</sub> catalysts were placed in the quartz tube, connected to a flow system (BEL Japan, INC., BELCAT-B) and treated at 300 °C for 2 h in 50%H<sub>2</sub>/He. He gas was used as a carrier gas at 30 mL min<sup>-1</sup>, and the successive doses of 10%N<sub>2</sub>O/He gas were subsequently introduced into the He stream by means of a calibrated injection valve (0.0277 mL<sub>N<sub>2</sub>O</sub> (stp) per pulse<sup>-1</sup> or 1.23 μmolN<sub>2</sub>O.pulse<sup>-1</sup>) at 90 °C. The amount of outlet N<sub>2</sub>O and N<sub>2</sub> was analyzed by a thermal conductivity detector, and the calculated N<sub>2</sub>O uptake.<sup>1</sup>



**EA** - Elemental analysis of copper loading was performed by the Mikroanalytisches Labor Pascher, Remagen, Germany.

**TEM** – The morphology of the samples was obtained – by transmission electron microscopy (TEM, Philips CM12) and by high-resolution TEM (FEI Tecnai F30).

**GC** - Gas chromatography analyses were performed on Shimadzu-QP 2010 Ultra equipped with FID (40:400 H<sub>2</sub>:He) and MS detectors using an HP-5MS column -60 to 350 °C, He as a carrier gas (make up of 25 mL.min<sup>-1</sup>) injector temperature 260 °C, detector temperature 270 °C and the following temperature program: plateau at 40 °C for 8 min, ramp of 20 °C.min<sup>-1</sup> from 40 °C

to 200 °C, ramp of 40 °C.min<sup>-1</sup> from 200 °C to 260 °C, plateau at 260 °C for 4.5 min. The reaction mixture was quantified by the calibration curve of the substrates; these response factors were extrapolated to the respective products.<sup>7</sup>

**NMR** - spectra were recorded on a Bruker DPX-300 instrument operating at the denoted spectrometer frequency given in MHz for the specified nucleus. The <sup>1</sup>H chemical shifts are calibrated with the residual solvent peak.

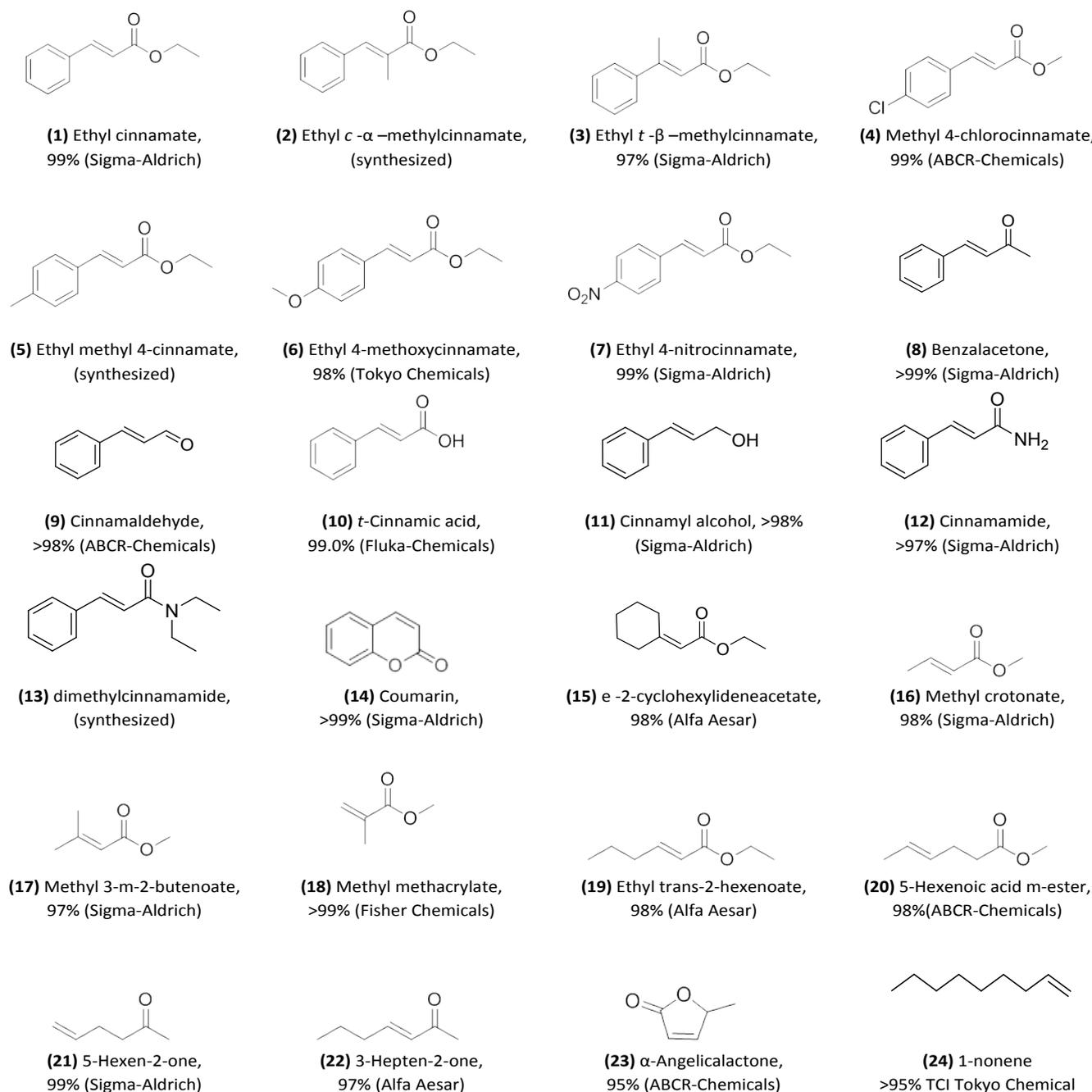


Figure SI 1. Substrates investigated in this work.

## Catalytic tests

**Reactors** - The catalytic hydrogenation experiments were performed at the High Throughput Experimentation facility of the ETH Zürich (HTE@ETH) on a custom-made 96-parallel autoclave (ILS GmbH) Figure SI 2. (a-b) or in an 8-parallel reactor auto-clave (Endeavour, Biotage), Figure SI 2 (c).

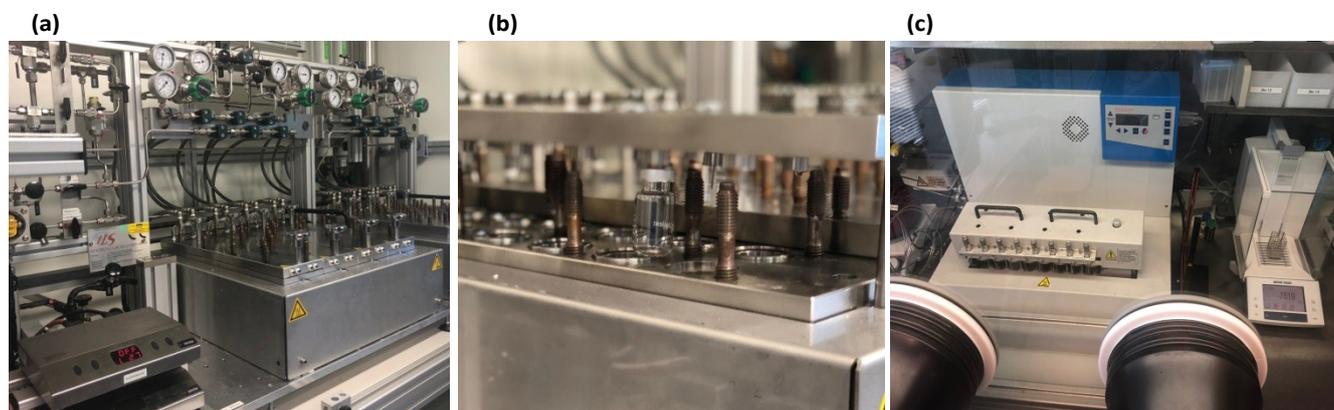


Figure SI 2. High throughput setups used in this work.

**Reaction protocol** - Cu/SiO<sub>2-700</sub> (10 mg) was loaded inside a glovebox into a 10 mL reactor vial, to which 3 mL of toluene plus 0.5 mL of a 1 M stock toluene solution of a substrate containing 0.25 M of internal standard (tridecane) was added. Vials were then sealed using septa crimp-caps inside the glovebox, and loaded into the high-pressure reactor outside the glovebox under an inert atmosphere. All reactions were heated to 100 or 150 °C and magnetically stirred (250 rpm) under H<sub>2</sub> (25 bar) for 15 h. For substrates (**7**, **12**, **13**) that were not completely soluble, a saturated solution of the substrate in toluene was used instead.

**Recycling tests** – Following the reaction protocol presented above, after each reaction, the catalyst was washed twice with 2 mL of fresh toluene inside the glovebox. A new reaction mixture was added, and a new reaction was performed. This procedure was repeated 5 times, using ethyl cinnamate as a model substrate.

**Leaching tests** – After catalytic tests – cycle 1, 3 and 5 – 1 mL of the reacted solution was collected. The solution was filtered hot, loaded with a new batch of substrate. Hydrogenation under the same reaction conditions showed no conversion, indicating the active catalysts correspond to supported Cu nanoparticles. In addition, the solution analysed by EA shows values <0.01 wt% of copper, indicating the absence of significant leaching.

**Products identification and Mass balance** - The products were identified and quantified by GC-MS, by diluting an aliquot of a reaction mixture (0.2 mL) with 0.8 mL of toluene. NMR spectroscopy was used to double check our quantification, analyzing ethyl cinnamate was before and after the reaction.

## Characterization

**Physical-chemical characterization** – the results of catalyst characterization are present in Table SI 1, comparing the support and the catalyst. A small decrease in surface area is observed by BET, as expected after particles formation.

Table SI 1. Physical and chemical characterization data of the support and the catalyst.

	BET (m <sup>2</sup> /g)	TEM (nm)	EA (%)	H <sub>2</sub> chem. (μmol/g)	H <sub>2</sub> chem. (μmol Cu <sub>surface</sub> ·g <sup>-1</sup> )	N <sub>2</sub> O titr. (μmol/g)	N <sub>2</sub> O titr. (μmol Cu <sub>surface</sub> ·g <sup>-1</sup> )
SiO <sub>2</sub>	190	-	-	-	-	-	-
Cu/SiO <sub>2</sub>	175	3.2 ± 0.8	Cu: 5.9	66	132	57	114

**TEM** – images before and after the particle formation by SOMC. Well-defined particles with narrow size distribution are observed in Figure SI 3 (b).

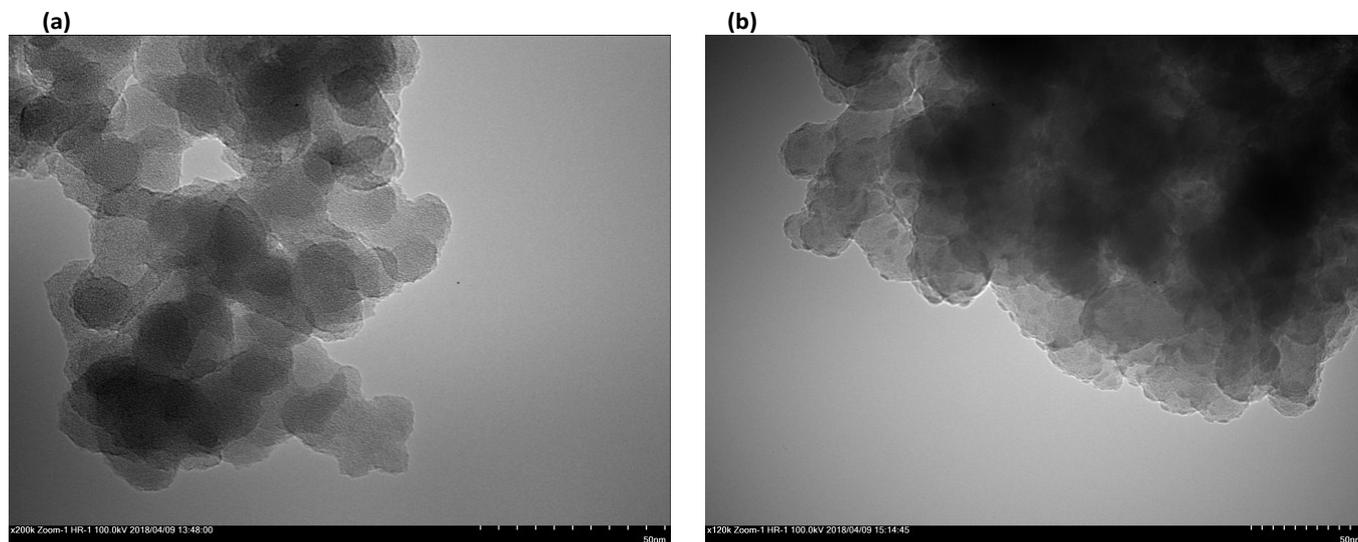


Figure SI 3. TEM images of SiO<sub>2</sub> and Cu/SiO<sub>2</sub>.

**NMR** – To confirm the GC-MS quantification, <sup>1</sup>H-NMR were taken before and after the reaction with ethyl cinnamate; Figure SI 4 shows 2 signals at 6.7 and 6.8 ppm corresponding to the hydrogen of the alkene bond that is not present after the reaction (Figure SI 5), confirming the selective hydrogenation of the olefin moiety.<sup>8</sup>

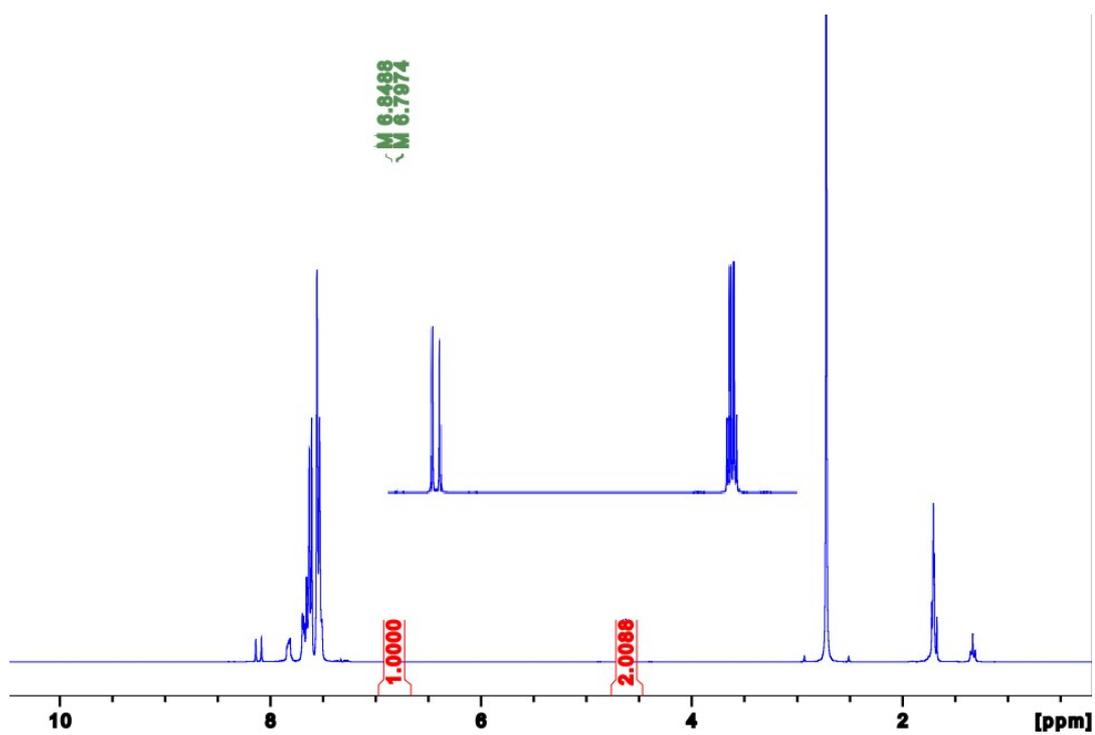


Figure 4. <sup>1</sup>H-NMR for ethyl cinnamate.

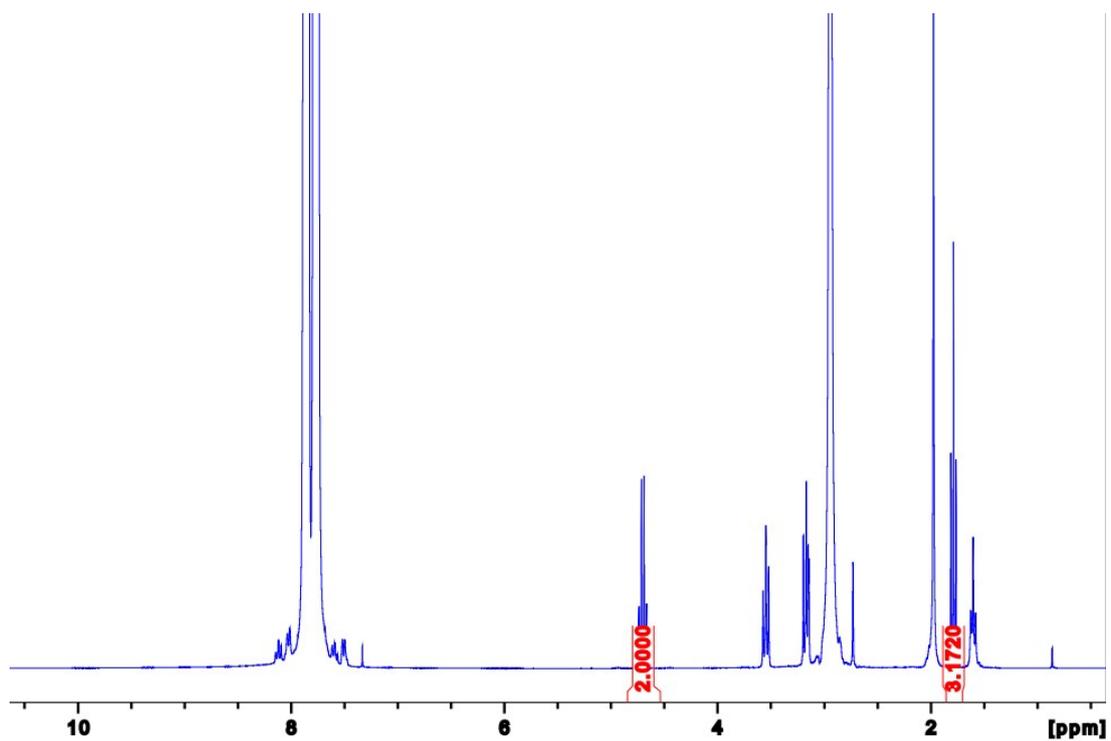


Figure 5. <sup>1</sup>H-NMR for ethyl hydrocinnamate.

## References

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