† Electronic Supporting Information

Novel Nickel Nanoparticles Stabilized by Imidazolium-Amidinate Ligands for Selective Hydrogenation of Alkynes

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S1. TEM of Ni@L3

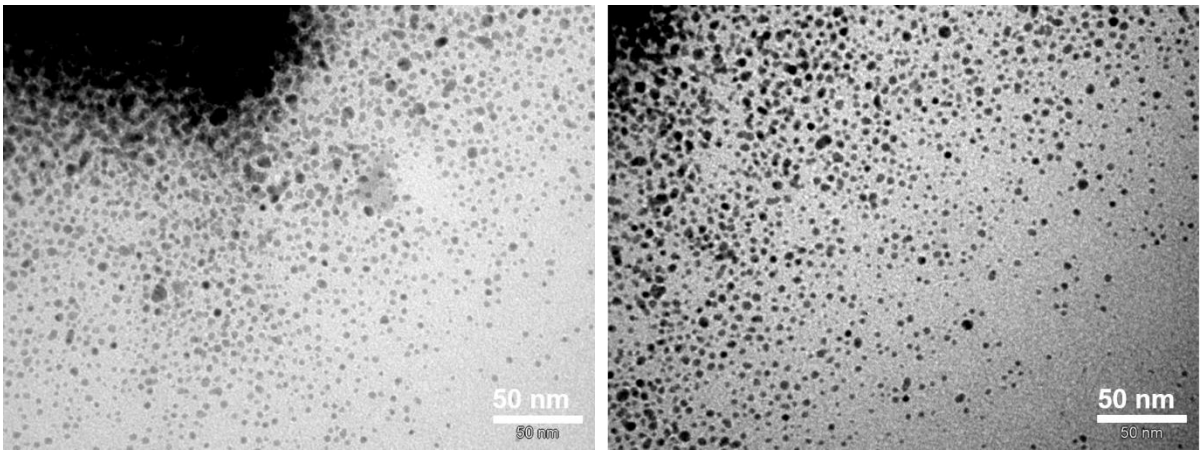

Figure S1. TEM images of **Ni@L3** showing the polydispersity of the nanoparticles.

S2. HRTEM of Ni@L1

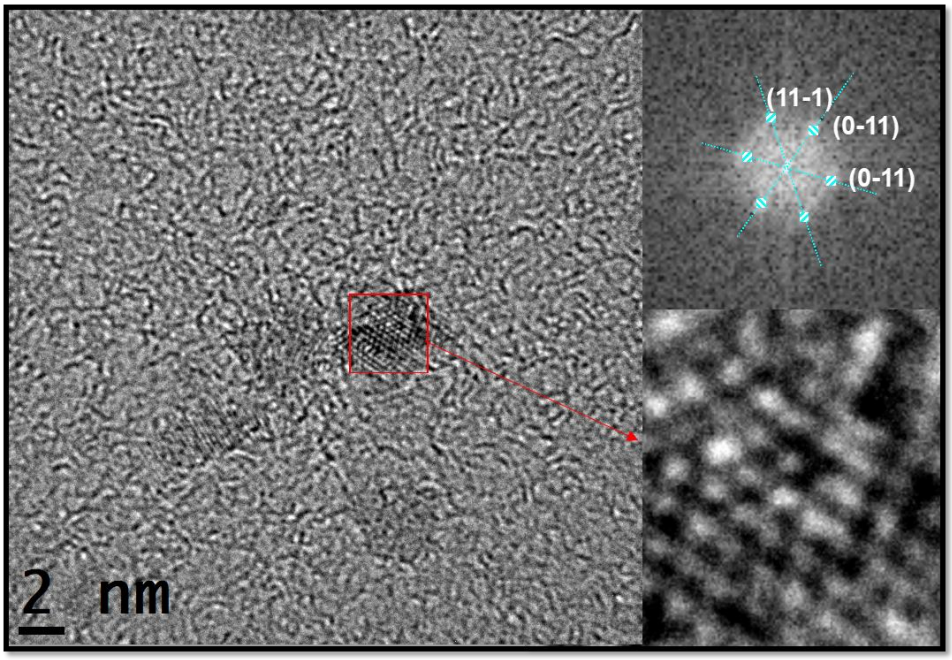

Figure S2. HRTEM image of **Ni@L1** (left, right bottom) and the Fourier Transform Analysis (right, top) with planar reflections.

S3. WAXS analysis of Ni@L1, Ni@L2 and Ni@L3.

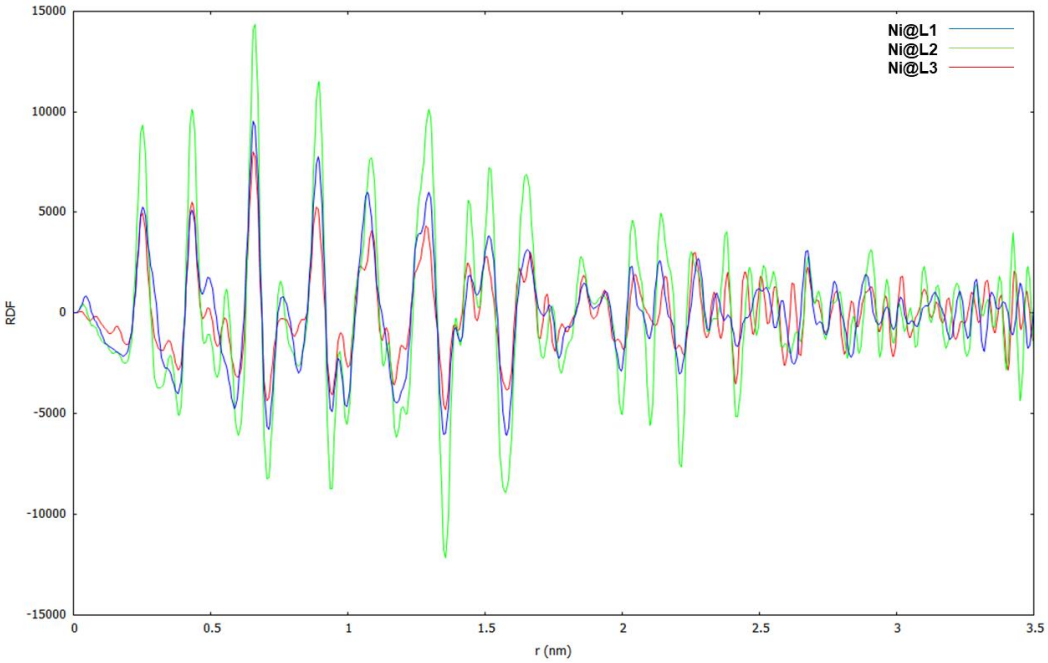

Figure S3. WAXS analysis of **Ni@L1** (blue), **Ni@L2** (green) and **Ni@L3** (red), which shows crystalline Ni NPs (*fcc*) with a coherence length close to 3 nm.

S4. AAS analysis for Ni@L1, Ni@L2 and Ni@L3

Table S1. Composition of **Ni@L**

Ni NP[a]	Size (nm)	% Ni [a]	Ni:L Ratio	$Ni_x:L_y$ [b]	Ni(s)[c]	$Ni(s)_x/L_y$
Ni@L1	2.8 (0.4)	75.9	25:1	1070:43	401	9.3
Ni@L2	2.8 (0.5)	71.1	21:1	1070:52	401	7.7
Ni@L3	3.4 (2.0)	45.5	7:1	1865:269	597	2.2

[a] % of Ni obtained by Atomic Absorption Spectroscopy (AAS) [b] The total number of atoms is determined, calculating the unit cell of Ni (fcc) per NP base on the diameter measured by TEM. [c] Number of surface atoms. Approximate values obtained from *ChemCatChem* **2011**, *3*, 1413-1418.

S5. Catalytic profile for semi-hydrogenation of 3-hexyne using Ni@L2 and Ni@L3

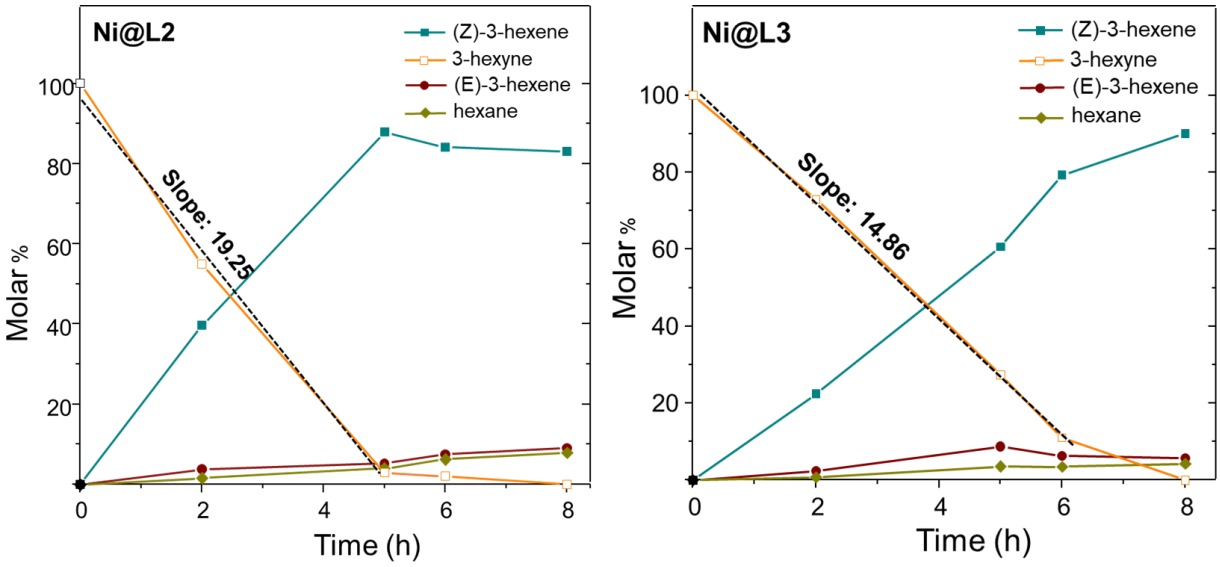

Figure S4. Time course of the product yield in the semi-hydrogenation of 3-hexyne using **Ni@L2** (left) and **Ni@L3** (right) as catalysts. Reaction conditions: 0.5 mmol of 3-hexyne, 3 mmol% catalyst, 0.75 mL toluene, 1 bar H_2.

S6. TEM after catalytic recycling experiments with Ni@L1

After the recycling experiments in the semi-hydrogenation of 3-hexyne, the isolate nanoparticles were analyzed by TEM according to the above mentioned procedure.

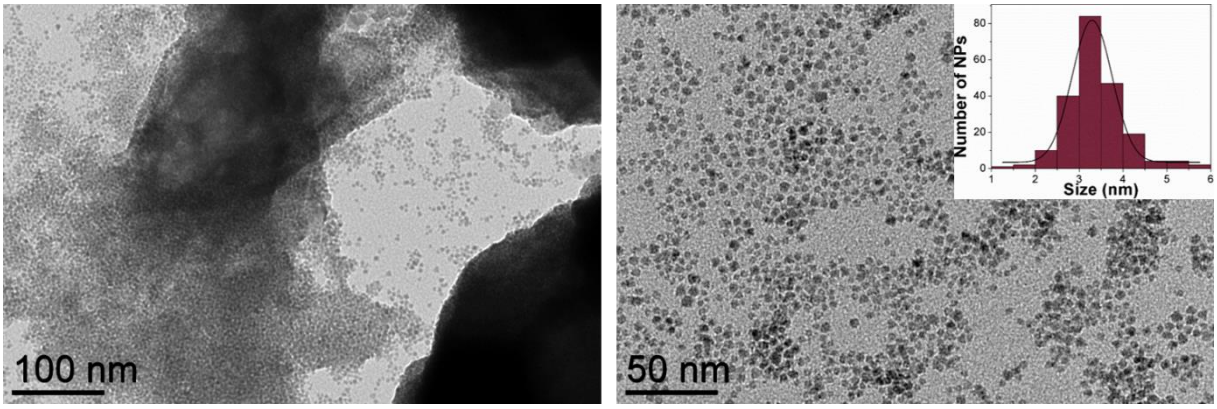

Figure S5. TEM images of **Ni@L1** after catalytic recycling (after 3 cycles) experiments.

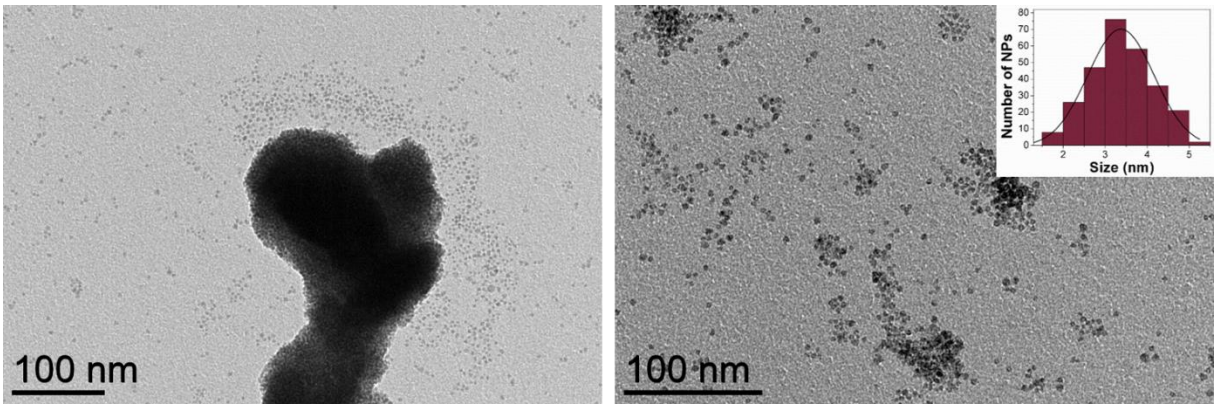

Figure S6. TEM images of **Ni@L1** after catalytic recycling (after 5 cycles) experiments.

S6. NMR

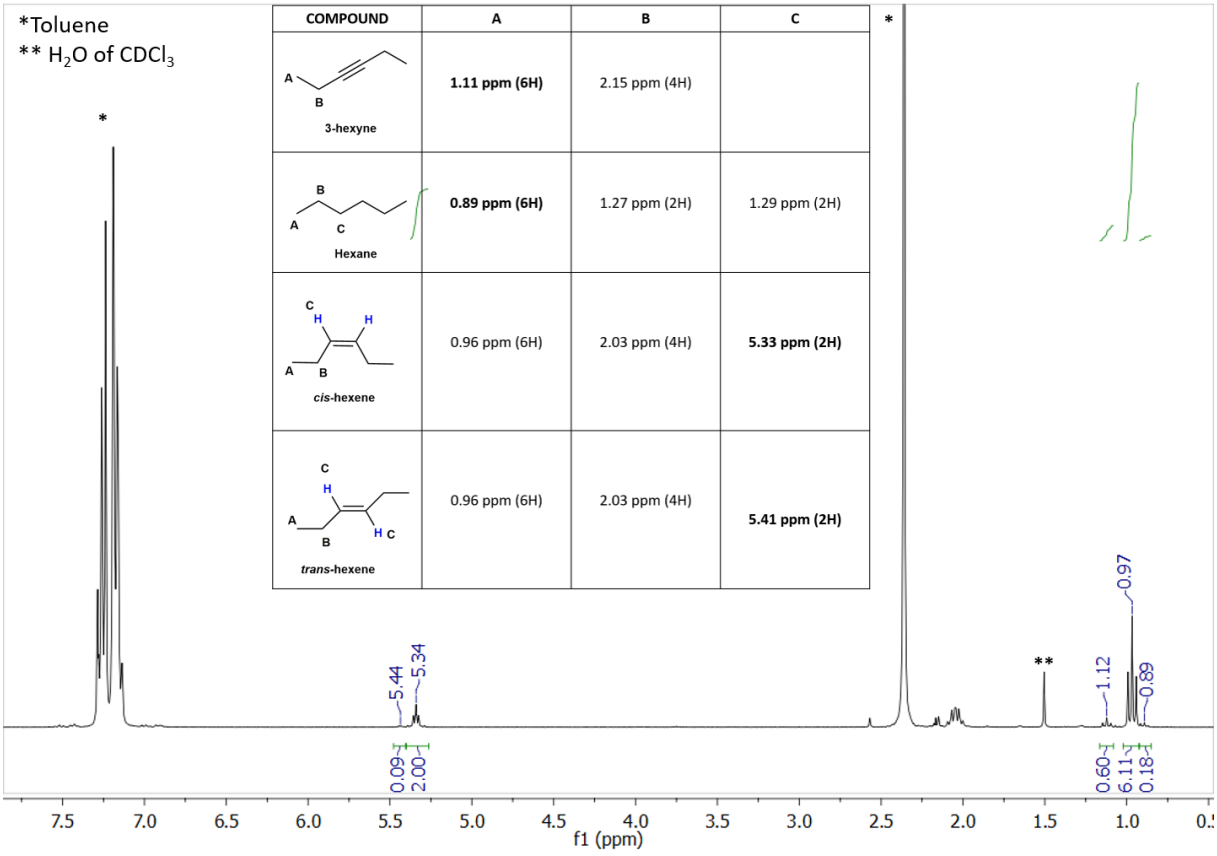

Figure S7. ^{1}H NMR spectrum after hydrogenation of 3-hexyne with **Ni@L1 (**5h, 1 bar H_2, r.t., toluene).