Electronic Supplementary Information

Metal vapor synthesis of ultrasmall Pd nanoparticles functionalized with N-heterocyclic carbenes

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1. Experimental

1.1. *Materials and methods*

Mesitylene and *n*-hexene were purified by conventional methods, distilled and stored under nitrogen. Toluene, *n*-pentane and R-(+)-limonene were purchased from Aldrich and used without further purification. The co-condensation of palladium and the appropriate solvent was carried out in a previously described static reactor.[1,2] Vulcan XC72R (graphitized carbon) from Cabot (surface area of 218 m^2 g^{-1}, pore volume of 0.41 mL g−1).

High resolution transmission electron microscopy (HRTEM) analyses of the PdNPs were carried out with a ZEISS LIBRA 200FE HRTEM instrument, equipped with a FEG source operating at 200 kV, in column second-generation omega filter, HAADF STEM facility, EDS probe for chemical analysis. The LC-NHC@Pd NPs were ultrasonically dissolved in toluene and a drop of the obtained solution was deposited on a ultrathin carbon film supported onto a copper TEM grid (300 mesh). The carbon-supported samples were ultrasonically dissolved in a 2-propanol and a drop of the obtained solution was deposited on a holey-carbon film supported on a copper TEM grid (300 mesh). Histograms of the particle size distribution were obtained by counting at least 500 particles. The mean particle diameter (d_m) was calculated by using the formula $d_m = \sum d_i n_i / \sum n_i$, where n_i is the number of particles with diameter d_i. Inductively coupled plasma-optical emission spectrometry (ICP-OES) was carried out with an iCAP 6200 Duo upgrade, Thermofisher instrument. A sample (0.5 mL) of Pd-solvated metal atoms (SMA) solution was heated over a heating plate in a porcelain crucible in the presence of *aqua regia* (2.0 mL) for three times followed by dissolving the solid residue in 0.5 M aqueous HCl to a final weight of 50 g. Pd leaching was measured by ICP-OES apparatus and an external calibration methodology after evaporation and digestion (5 mL HNO_3 65% + 1 mL H_2O_2 30% and further 2 mL of *aqua regia*) of 5 g of the reaction mixture after catalyst filtration at the end of the reaction. The samples were then diluted with

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[1] G. Vitulli, C. Evangelisti, A. M. Caporusso, P. Pertici, N. Panziera, S. Bertozzi und P. Salvadori, in “Metal Nanoclusters in Catalysis and Materials Science - The Issue of Size Control”, Elsevier, Amsterdam, 2008, S. 437–451.

[2] K. Klabunde, G. Sergeev, “Nanochemistry”, Elsevier, Amsterdam, 2013.

highly deionized water (Milli-Q Academic, Millipore) to a final weight of 8 g. The detection limit of the analysis is ≤ 10 ppb.

^{1}H and ^{13}C NMR spectra were recorded in the solvent indicated using a Bruker Advance II 300 spectrometer. Data are expressed as chemical shifts in parts per million (ppm) relative to residual solvent (benzene, δ_H = 7.15 ppm, δ_C = 128.0 ppm). TGA was measured on TGA Q5000 V3.15 from TA INSTRUMENTS under nitrogen atmosphere at the MEET (Münster).

XPS measurements were performed with an Axis Ultra DLD (Kratos Analytical Ltd, UK). A monochromatic Al Kαsource (hν = 1486.6 eV) at 10 mA filament current and 12 kV filament voltage source energies was used. The pass energy was set to 20 eV for high resolution scans. The charge neutralizer was used to compensate for sample charging. All measurements were carried out in the “electrostatic mode”. The data were evaluated with CasaXPS (version 2.3.15, Casa Software Ltd, UK) and the spectra were calibrated to aliphatic carbon (C1s = 285 eV).

GC analyses were performed with a Agilent 6890 Series gaschromatograph equipped with a flame ionization detector and a 30 m (0.25 mm i.d., 0.25 µm film thickness) HP-5 ((5% phenyl)-methyl-polysiloxane) capillary column column. GC–MS were performed with HP-5890 series, equipped with HP5 capillary column (30 mm, 0.25 mm i.d., 0.25 µm film thickness).

1.2. Synthesis of long-chain imidazolium salt (LC-NHC·HI)

LC-NHC·HI was synthesized according to the procedure described in the literature.[3]

1.3. Synthesis of LC-NHC@PdNPs

In a typical synthesis procedure, Pd vapor generated at 1.5×10^{-6} psi by resistive heating of the metal (500.0 mg) in an alumina-coated tungsten crucible was co-condensed with a 1:1 mixture of mesitylene (40.0 mL) and 1-hexene (40.0 mL) in a glass reactor at liquid nitrogen temperature. The reactor chamber was heated to the melting point of the solid matrix (ca. -40 °C), and the resulting brown solution was siphoned and

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[3] C. Richter, K. Schaepe, F. Glorius und B. J. Ravoo, Chem. Commun., 2014, 50, 3204–3207.

handled at low temperature (-20 °C) with the Schlenk tube technique. The Pd-content of the obtained Pd solvated metal atoms (SMA) determined by ICP-OES analysis was 0.19 mg of Pd/mL. The imidazolium salt of LC-NHC (LC-NHC·HI) (73 mg, 0.136 mmol, 1.0 eq.) and KO^{t}Bu (15.3 mg, 0.136 mmol, 1.0 eq.) were charged into a Schlenk tube and dissolved in de-aerated mesitylene (10.0 mL). After stirring for 30 min at 25 °C, a portion of the Pd SMA (13.3 mg, 0.068 mmol of Pd, 70 mL) was added to the solution of *in situ* generated carbene under nitrogen atmosphere and the resulting mixture was allowed to stir at 25 °C overnight. The stable Pd particles were purified by precipitation with acetonitrile (10 mL) and centrifugation at 1000 rpm for 20 min. The brown solid obtained was dissolved in toluene (10 mL) and further re-precipitated by addition of acetonitrile (3 x 5 mL). After drying, the LC-NHC protected PdNPs were obtained as brown solid (35.6 mg). Elemental analysis experimental (wt. %): C 49.43, H 6.17, N 3.28.

1.4. Synthesis of LC-NHC@PdNPs/C

A portion (10 mL) of a solution of LC-NHC@PdNPs (1 mg/mL) in toluene was added to a suspension of carbon (1.00 g) in toluene (10 mL). The mixture was stirred for 12 h at 25°C. The colorless supernatant was removed and the solid was washed with *n*-pentane (3 x 20 mL) and dried under reduced pressure. The sample contained 1.0 wt.% of Pd as determined by ICP-OES analysis.

1.5. Synthesis of Pd/C

The Pd/mesitylene-1-hexene solution (52 mL, 10 mg Pd) was added to a suspension of carbon (1.00 g) in mesitylene (10 mL). The mixture was stirred for 12 h at room temperature. The colorless supernatant was removed and the solid was washed with *n*-pentane (3 x 20 mL) and dried under reduced pressure. The sample contained 1.0 wt. % of Pd as determined by ICP-OES analysis.

2.5. Catalytic Limonene hydrogenation reactions

The catalytic activity tests were performed in a 300 mL autoclave advanced with an internal aluminum plate to include seven uniform reaction glass vials (4 mL) with cap, septum, needle and stirring bar. The autoclave is placed into an aluminum block as heating system to perform the reactions (30°C). R-(+)-limonene (0.16 mmol, 1.1 mL), carbon-supported Pd catalyst (35 mg, 1 wt. Pd %, 0.033 mmol Pd) were mixed with 2 mL toluene (when used) in a reaction vial (4 mL). The autoclave was flushed with hydrogen gas twice and pressurized with hydrogen stirred at 1200 rpm. After completion of the reaction time, the stirring was stopped and hydrogen was released from the autoclave. Dodecane (50 µL) was added to the crude reaction mixture as internal standard and analyzed by GC-FID and GC-MS.

Recycling experiments of the LC-NHC@Pd/C catalyst were carried out by removing the liquid part of the mixture by centrifugation and loading with fresh limonene (1.1 mL).

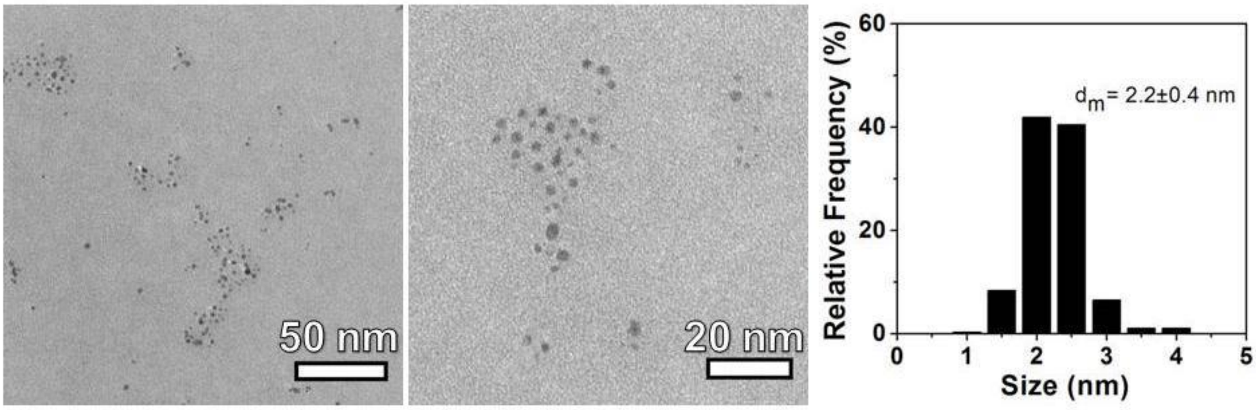


Figure S1. Representative TEM micrograph and corresponding histogram of particle size distribution of LC-NHC@Pd.

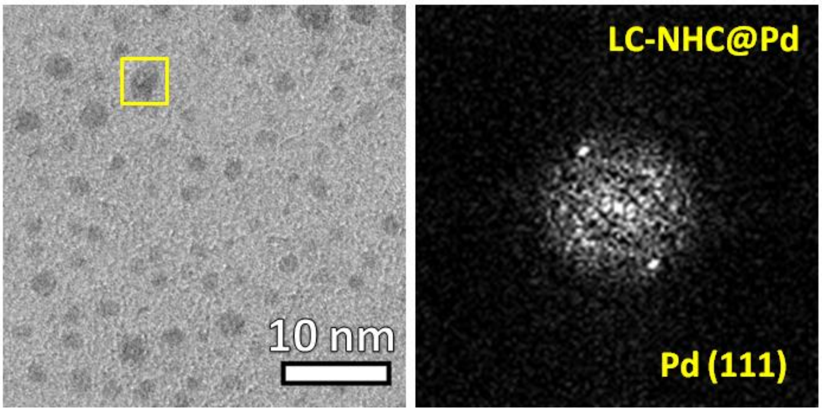


Figure S2. High resolution TEM micrograph of LC-NHC@Pd (left side) and FFT pattern of the selected Pd nanoparticle (right side) exhibiting spots at 2.3 Å, ascribed to the spacing of {111} planes of face centered cubic (fcc) structure of metallic Pd.

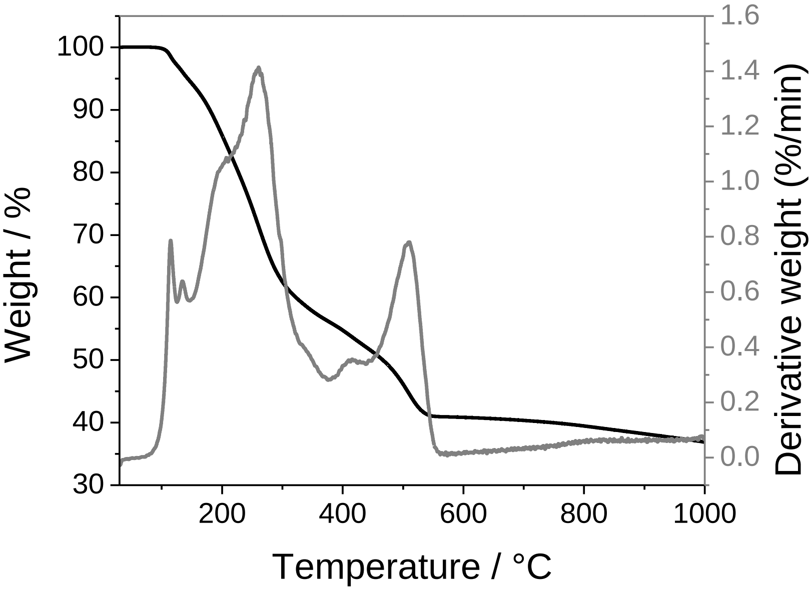


Figure S3. TGA analysis of LC-NHC@Pd.

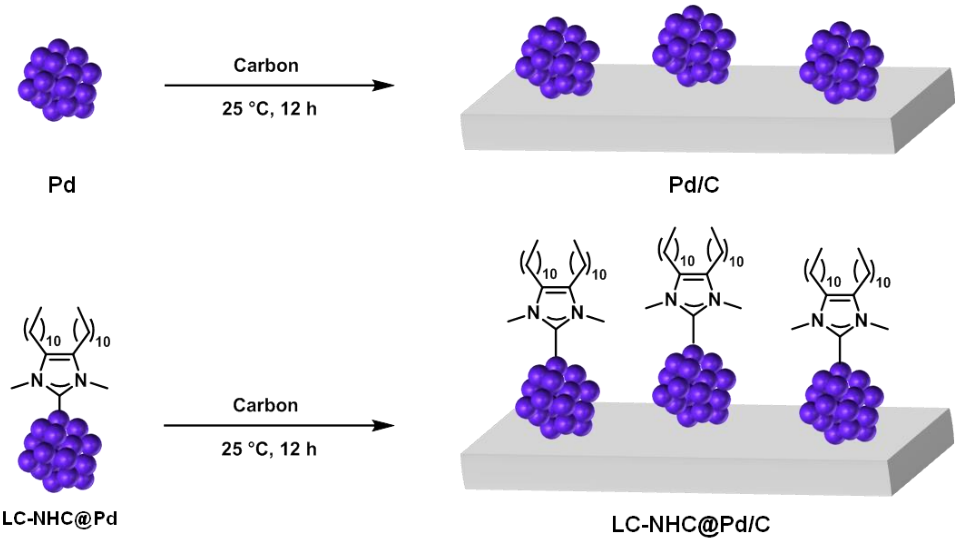


Figure S4. Schematic representation of the deposition of PdNPs (top) and LC-NHC@Pd (bottom) on Carbon support.

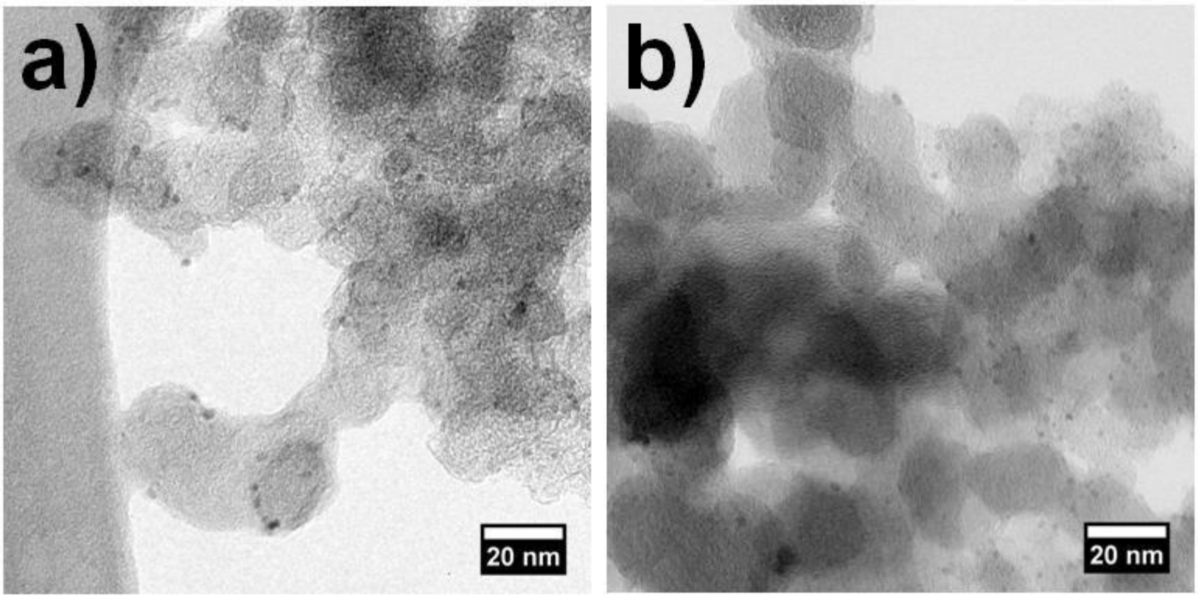


Fig. S5. Representative TEM micrograph of LC-NHC@Pd/C (a) and Pd/C (b).

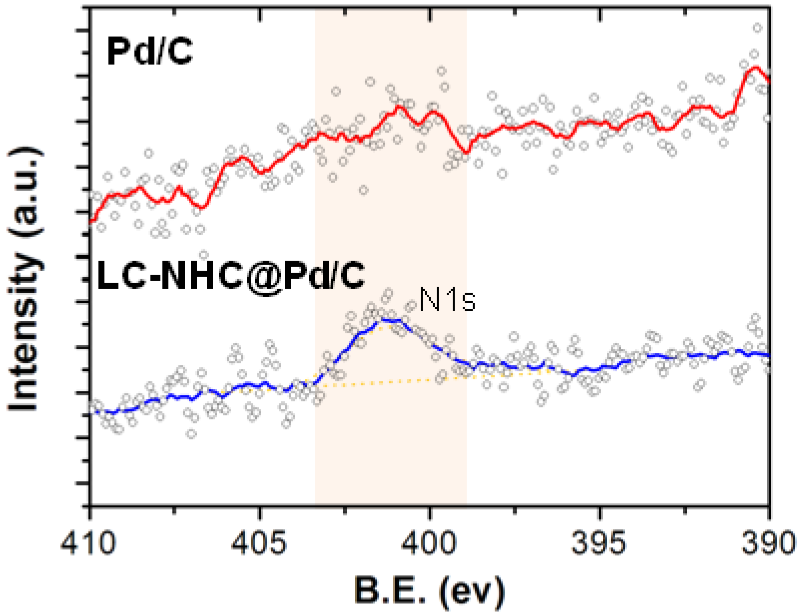


Fig. S6. N1s XPS spectra of Pd/C (above, red line) and LC-NHC@Pd/C (bottom, blue line).

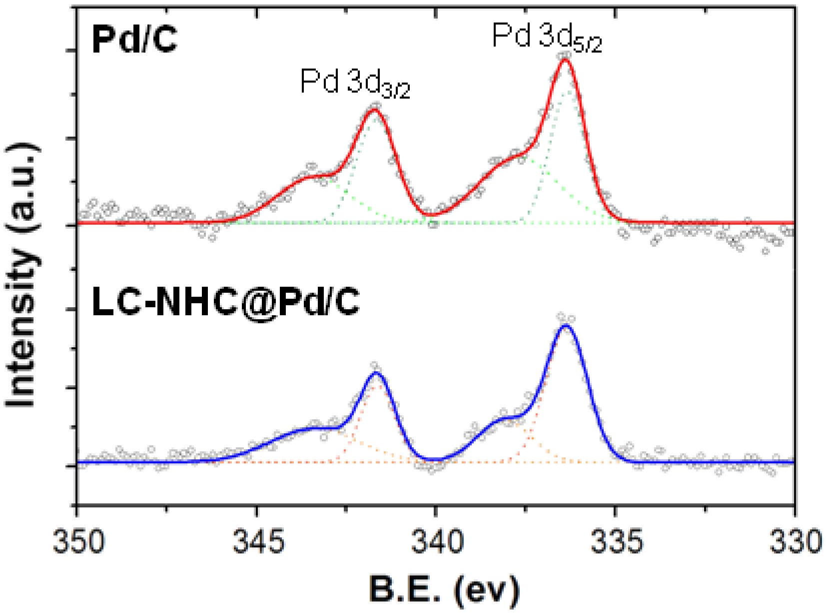


Fig. S7. Pd3d XPS spectra of Pd/C (above, red line) and LC-NHC@Pd/C (bottom, blue line).

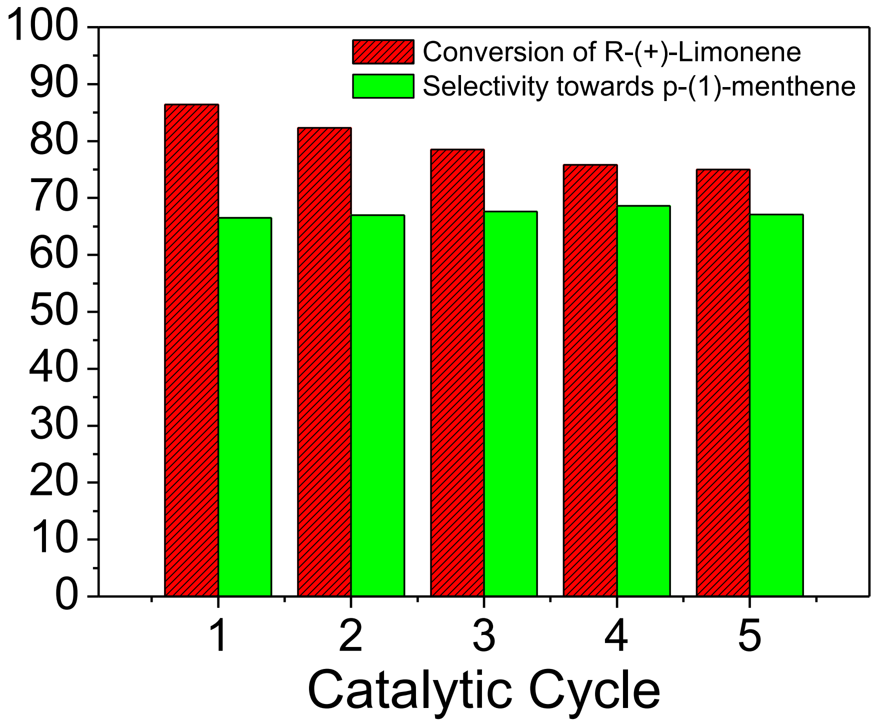
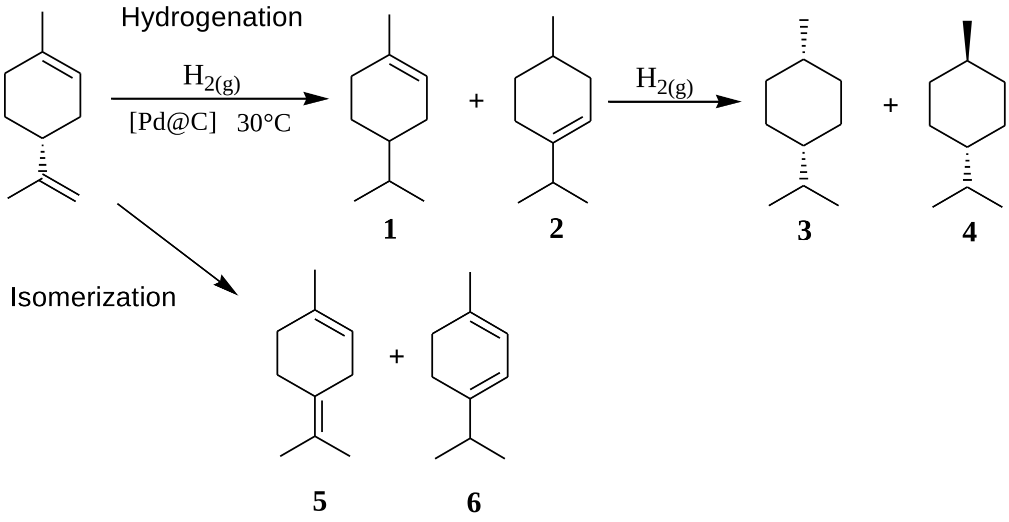


Fig. S8. Recycling tests on LC-NHC@Pd/C system. Reaction conditions: (*R*)-(+)-Limonene (1.1 mL), catalyst 1 wt.% (35 mg), Sub/Pd molar ratio = 2000, p(H_2) = 4 bar; T = 30°C, t = 15 min. Selectivity calculated as mol of *p*-(1)-menthene / mol limonene conv.

Table S1. Hydrogenation of R-(+)-Limonene promoted by Pd catalysts in toluene as solvent.



Entry	Catalyst	time (min)	Limonene Conv. (%)	Isomerization (%)	Hydrogenation (%)	Hydrogenation Products Distribution (%)				2/1 molar ratio
						1	**2**	**3**	**4**	
1	Pd/C Commercial	30	15.0	0	15.0	46.5	51.4	0	2.1	1.1
2		120	55.4	31.0	24.4	44.2	53.7	0	2.1	1.2
3	Pd/C	30	49.2	21.6	27.6	46.3	54.5	0	0	1.2
4		60	89.4	39.3	50.1	40.1	55.9	2.1	1.9	1.4
5	LC-NHC@Pd/C	30	46.3	23.6	22.7	**77.5**	22.5	0	0	0.3
6		60	91.5	37.5	54.0	**64.8**	31.2	2.3	1.7	0.5

Reaction conditions: (*R*)-(+)-Limonene (1.1 mL), solvent = toluene (2 mL), catalyst 1 wt.% (35 mg), Sub/Pd molar ratio = 2000, p(H_2) = 4 bar; T = 30°C.

Table S2. Hydrogenation of R-(+)-Limonene promoted by Pd catalysts in neat conditions.

Entry	**Catalyst**	**time (min)**	**Limonene Conv. (%)**	**Isomerization (%)**	**Hydrogenation (%)**	**Hydrogenation Products Distribution (%)**				**2/1 molar ratio**
						1	**2**	**3**	**4**	
1	Pd/C	8	67.5	12.8	54.7	58.7	35.3	3.0	3.0	0.6
2		15	85.4	4.3	81.1	45.2	46.8	3.9	4.1	1.0
3		30	96.3	1.9	94.4	40.5	43.4	4.0	12.1	1.1
4	LC-NHC@Pd/C	8	68.3	9.6	58.7	**76.2**	17.8	3.2	2.8	0.2
5		15	86.4	3.5	82.9	**69.3**	22.6	5.1	5.0	0.3
6		30	98.2	2.0	96.2	**60.5**	20.3	7.3	11.9	0.3

Reaction conditions: (*R*)-(+)-Limonene (1.1 mL), catalyst 1 wt.% (35 mg), Sub/Pd molar ratio = 2000, p(H_2) = 4 bar; T = 30°C.