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Supporting Information

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Mara Klarner, Sandra Bieger, Markus Drechsler, and Rhett Kempe*

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Experimental Procedures

General Methods

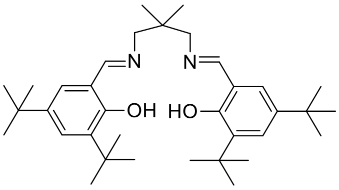
All chemicals and solvents were purchased commercially from chemical suppliers with purity over 95 % and used without further purification. The activated char coal CA1 was purchased from Norit.

Elemental analyses (CHN) were performed in tin capsules using an UNICUBE element analyst. Sulfanilamide was used as a standard. NMR spectra were measured using a Varian INOVA 400 MHz and a Bruker Avance III HD 500 MHz spectrometer. Chemical shifts are reported in ppm relative to the deuterated solvent. X-ray crystal structure analysis was performed with a STOE STADIVARI ($Mo_{K\alpha}$ radiation, 0.71073 Å) equipped with an Oxford Cryostream low temperature unit. Structure solution and refinement were achieved with OLEXS.[S1] The structure was visualized using Mercury 4.1.3.[S2] Fourier transform infrared (FT-IR) spectroscopy measurements were performed with a JASCO FT-IR 6100 spectrometer in the range 4000 cm^{-1} to 700 cm^{-1} with a resolution of 4 cm^{-1} an a N_2 flow. UV-vis spectra were measured on a CARY 60 (Agilent Technologies). Thermogravimetric analysis was performed from 30 °C to 1000 °C (10 °C min^{-1}) using a TGA/SDTA 851^e (Mettler) under nitrogen atmosphere. Samples were placed in Al_2O_3 crucibles with lid. Catalyst materials were generated by pyrolysis (N_2) und reduction (N_2/H_2, 10/90) on a Chem-BET Pulsar (Quantachrome) using tubes of quartz glass. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was carried out according to standard protocol digestion with a Vista-Pro radial (Varian). Argon physisorption isotherms were determined at 87 K using a 3P Micro100C (3P instruments) apparatus equipped with a cryoTune87. Specific surface areas were calculated by using p/p_0-values from 0.005-0.1 by the BET model. Specific total pore volumes were determined by DFT calculations (Ar at 87 K on cylindrical pore (MDFT)). X-ray photoelectron spectroscopy (XPS) was performed using a PHI Versa Probe III instrument of Physical Electronics. As X-ray source a monochromatic $Al_{K\alpha}$ with a spot size of 100 µm (24.5 W) was used. The kinetic pass energy of the photoelectrons was determined with a hemispheric analyzer (45°) set to pass energy of 26 eV for high-resolution spectra. Transmission electron microscopy (TEM) measurements were carried out using a LEO 922O microscope (Zeiss, 200 kV) and a JEOL JEM-2200FS (200 kV). The samples were suspended in chloroform and sonicated for 5 min. 2 µL of the suspension were placed on a CF200-Cu-grid or a LC200-Cu-grid (Electron Microscopy Sciences) and allowed to dry. X-ray powder diffraction (PXRD) analysis in the range of 2-80 °2θ was performed using a XPERT-PRO diffractometer (Panalytical) ($Cu_{K\alpha}$ radiation, 1.54178 Å) in θ-2θ geometry with a position sensitive detector. The reference card number for comparison is 00-001-1260 for cubic Ni. Gas chromatography (GC) analyses were performed using an Agilent Technologies 6850 gas chromatograph equipped with a flame ionization detector (FID) and a MN Optima 17 capillary column (30.0 m x 0.32 mm x 0.25 µm) using *n*-dodecane as internal standard. GC-MS analyses were performed using an Agilent Technologies 7890A gas chromatograph with a MN-MS HP-5 capillary column (30.0 m x 0.32 mm x 0.25 µm) and a coupled mass spectrometer (5975C MSD) as detector. Hydrogenation experiments were carried out with Parr Instrument stainless steel autoclaves N-MT5 300 mL equipped with heating mantles and temperature controller.

Salen-Complex Synthesis (adapted from ref. [S3])

Salen(prop)(di-*tert*-butyl)

3,5-Di-*tert*-butylsalicylaldehyde (2.344 g, 10 mmol, 2 eq.) was dissolved in ethanol (50 mL), 2,2-dimethylpropan-1,3-diamine (0.600 mL, 5 mmol, 1 eq.) was added at room temperature. A yellow solid crystallized, immediately. This solid was filtered off, washed with ethanol, and dried in vacuum to yield the ligand salen(prop)(di-*tert*-butyl).



FW ($C_{35}H_{54}N_2O_2$) = 534.82 g mol^{-1}

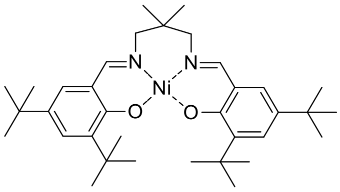
Yield 5.241 g, 9.8 mmol, 98 %)

^{1}H-NMR (CDCl$_3$, 500 MHz) δ = 13.88 (s, 2H, O*H*), 8.38 (s, 2H, C*H*=N), 7.41-7.40 (d, 2H, Ar-*H*), 7.13-7.12 (d, 2H, Ar-*H*), 3.49 (s, 4H, C*H*$_2$), 1.48 (s, 18H, C(C*H*$_3$)$_3$), 1.33 (s, 18H, C(C*H*$_3$)$_3$), 1.12 (s, 6H, C*H*$_3$) ppm.

CHN C 78.73 (78.60), H 10.13 (10.18), N 5.33 (5.24) %.

Ni-Salen(prop)(di-*tert*-butyl)

Salen(prop)(di-*tert*-butyl) L4 (1.604 g, 3 mmol, 1 eq.) was suspended in methanol (30 mL) and nickel acetate tetrahydrate (0.747 g, 3 mmol, 1 eq.) dissolved in methanol (15 mL) was added. The reaction was stirred at room temperature for 16 h, then the green solid was filtered off, washed with methanol, and dried in vacuum to yield the complex Ni-Salen(prop)(di-*tert*-butyl) as a green, fluffy solid. Crystals suitable for X-ray analysis were grown from a saturated solution of the compound in dichloromethane.



FW ($NiC_{35}H_{52}N_2O_2$) = 591.49 g mol^{-1}

Yield 1.721 g (2.91 mmol, 97 %)

^{1}H-NMR (CDCl$_3$, 500 MHz) δ = 7.30-7.29 (d, 2H, C*H*=N), 7.08 (s, 2H, Ar-*H*), 6.86-6.86 (d, 2H, Ar-*H*), 3.24 (s, 4H, C*H*$_2$), 1.41 (s, 18H, C(C*H*$_3$)$_3$), 1.27 (s, 18H, C(C*H*$_3$)$_3$), 0.89 (s, 6H, C*H*$_3$) ppm.

^{13}C-NMR (CDCl$_3$, 500 MHz) δ =164.10, 162.30, 140.39, 135.88, 129.07, 125.48, 119.81, 67.86, 35.78, 34.29, 33.76, 31.30, 29.54, 25.29 ppm.

CHN C 70.90 (71.07), H 9.03 (8.86), N 4.95 (4.74) %.

Ni/C Catalyst Preparation

A solution of Ni-Salen(prop)(di-*tert*-butyl) (0.178 mmol, 10.4 mg of Ni, 4 wt.% Ni ideally) in 30 mL tetrahydrofuran was added to 250 mg activated char coal and the suspension was stirred vigorously. For comparison, nickel acetate tetrahydrate (0.178 mmol, 10.4 mg of Ni, 4 wt.% Ni) in 15 mL tetrahydrofuran was impregnated on 250 mg activated coal. After evaporation of the solvent at 90 °C, the impregnated sample was pyrolyzed under N_2 and finally reduced by a N_2/H_2 (90/10) mixture in a ChemBET Pulsar with the following program:

$$\text{rt} \xrightarrow[N_2]{\text{2 K/min}} 300\ ^\circ\text{C (0.5 h)} \xrightarrow[N_2]{\text{10 K/min}} 700\ ^\circ\text{C (0.5 h)} \xrightarrow[N_2]{\text{20 K/min}} 100\ ^\circ\text{C} \xrightarrow[N_2/H_2]{\text{5 K/min}} 550\ ^\circ\text{C (3 h)} \xrightarrow[N_2/H_2]{\text{5 K/min}} \text{rt}$$

Catalysts were stored in inert atmosphere.

General Procedure for the Hydrogenation of Styrene Derivatives

In a typical experiment, a 5 mL reaction vial was charged with 1.35 mol.% Ni (0.0068 mmol Ni, 0.4 mg Ni) in form of the Ni/C catalyst and a magnetic stirring bar. 0.5 mmol styrene derivative and 2.5 mL methanol were added. The vial was placed in a 250 mL stainless steel autoclave (Parr Instruments) which was flushed five times with 1 MPa hydrogen. The autoclave was pressurized by 0.2 MPa (or 1 MPa) hydrogen and stirred for 20 h at 40 °C (or 80 °C). After the autoclave was cooled to room temperature and the hydrogen pressure was released, the reaction solution was filtered over Na_2SO_4 to remove residual catalyst. Yields were determined by gas chromatography using *n*-dodecane as an internal standard. Products were analyzed by GC-MS by comparing the mass spectra with those in the literature. Selected examples were isolated. After stopping the reaction, the catalyst was removed by centrifugation. The reaction mixture was filtered, and the solvent was removed in vacuo. The isolated products were identified by ^{1}H-NMR analysis.

General Procedure for the Hydrogenation of Olefins

In a typical experiment, a 5 mL reaction vial was charged with 1.2 mol.% Ni (0.0068 mmol Ni, 0.4 mg Ni) in form of the Ni/C catalyst and a magnetic stirring bar. 0.5 mmol olefin and 2.5 mL methanol (or 2.5 mL H_2O) were added. The vial was placed in a 250 mL stainless steel autoclave (Parr Instruments) which was flushed five times with 1 MPa hydrogen. The autoclave was pressurized by 1 MPa hydrogen and stirred for 20 h at 80 °C. After the autoclave was cooled to room temperature and the hydrogen pressure was released, the reaction solution was filtered over Na_2SO_4 to remove residual catalyst. Yields were determined by gas chromatography using *n*-dodecane as an internal standard. Products were analyzed by GC-MS by comparing the mass spectra with those in the literature. Selected examples were isolated. After stopping the reaction, the catalyst was removed by centrifugation. The reaction mixture was filtered, and the aqueous layer was extracted three times with methyl *tert*-

butyl ether, dried over Na_2SO_4, and the solvent was then removed in vacuo. The isolated products were identified by ^{1}H-NMR analysis.

Recyclability Study for Ni/C

The hydrogenation of styrene was chosen as the test reaction for the recyclability study on the Ni/C catalyst. For comparability, runs were performed with about 60 % yield of ethylbenzene. The optimized reaction conditions were used, but the reaction time was shortened to 4 h. The reaction was carried out in the same way as for the Ni/C catalyst. The yield of ethylbenzene was determined by GC using *n*-dodecane as an internal standard. After each run, the reaction mixture was centrifuged, the catalyst was washed three times with methanol and used directly in the next run. Five consecutive runs were performed.

See Supplementary Figure S8.

Large Scale Reactions using Ni/C

For large-scale reactions, 20 times the amount of substrate (10 mmol) was used, the amount of solvent and catalyst was increased accordingly. The reaction time was increased to 24 h. The upscaling was performed in a 60mL Schott bottle, which was placed stainless steel autoclave (Parr Instruments). In all other steps, the reaction was carried out analogously to the general procedure. Reaction conditions: 10 mmol styrene (1146 µL), 50 mL MeOH, 1.35 mol% Ni (294 mg Ni/C, 2.7 wt.% Ni), 40 °C, 0.2 MPa H_2, 24 h.

Crystallographic data of Ni-salen(prop)(di-*tert*-butyl)

Crystals suitable for X-ray analysis were grown from a saturated solution of the compound in dichloromethane.

Deposition Number: 2076115

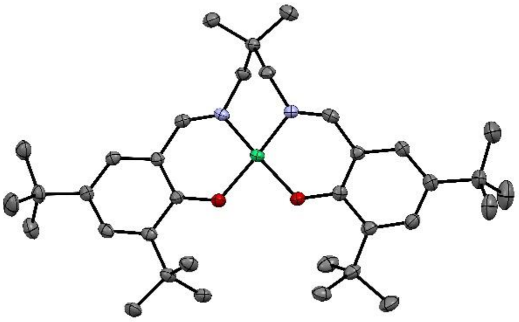


Table S1. Crystallographic details of Ni-salen(prop)(di-*tert*-butyl) used in this study.

Compound	Ni-salen(prop)(di-*tert*-butyl) SV582
Formula	$C_{35}H_{52}N_2NiO_2$
Formula weight	591.49
Crystal system	triclinic
Space group	P-1
a / Å	10.940(2)
b / Å	12.260(3)
c / Å	14.430(3)
α / °	113.30(3)
β / °	100.60(3)
γ / °	97.60(3)
Cell volume / $Å^3$	1701.6(7)
Z	2
Crystal size / mm^3	0.47*0.042*0.005
Habit	needle
Color	green
Density / gcm^{-1}	1.154
T / K	293
Theta range	2.921-28.446
Unique reflections	8021
Observed reflections [I>2s(I)]	5757
Parameters	376
wR2 all data	0.2148
R [I>2s(I)]	0.0739

Material Characterization

Salen ligand and Ni-salen complex

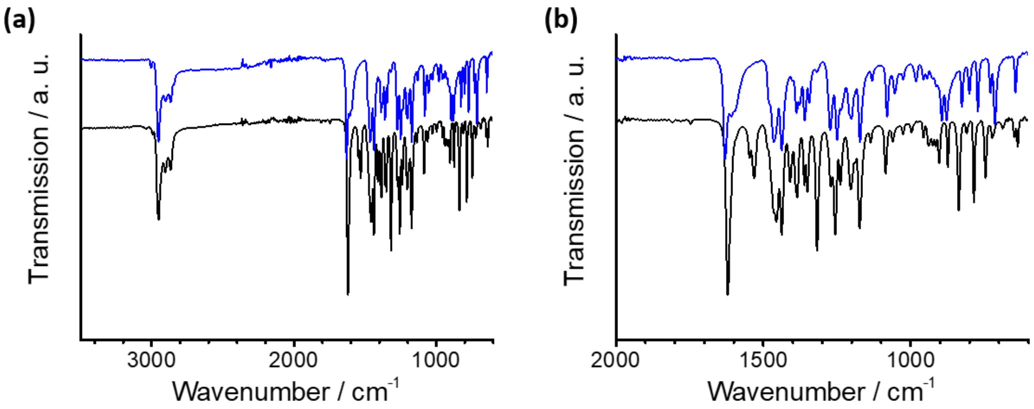


Figure S1 FT-IR analysis of the salen ligand (blue) and the Ni-salen(prop)(di-*tert*-butyl) complex (black).

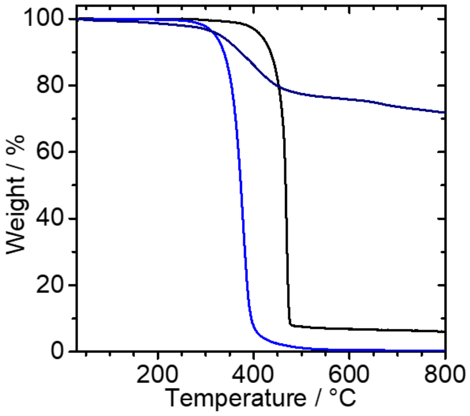


Figure S2 TGA analysis of salen ligand (blue), Ni-salen(prop)(di-*tert*-butyl) complex (black) and impregnated complex on charcoal (dark blue). Measurements were performed in the range of 30 800 °C (heating ramp 10 K/min) in constant N_2 flow. The sublimation temperature (T_{subl} = 469 °C) of Ni-salen(prop)(di-*tert*-butyl) was determined from the zero of the first derivative of the TGA curve.

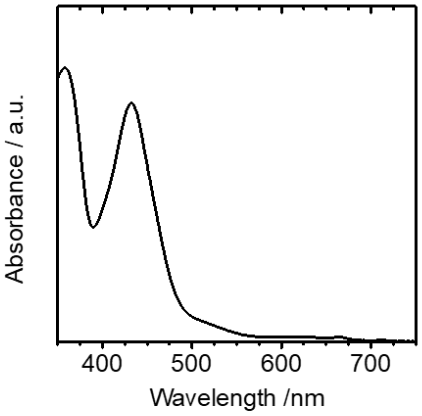


Figure S3 UV-vis spectrum of Ni-salen(prop)(di-*tert*-butyl) measured in tetrahydrofuran in the range of 350-750 nm.

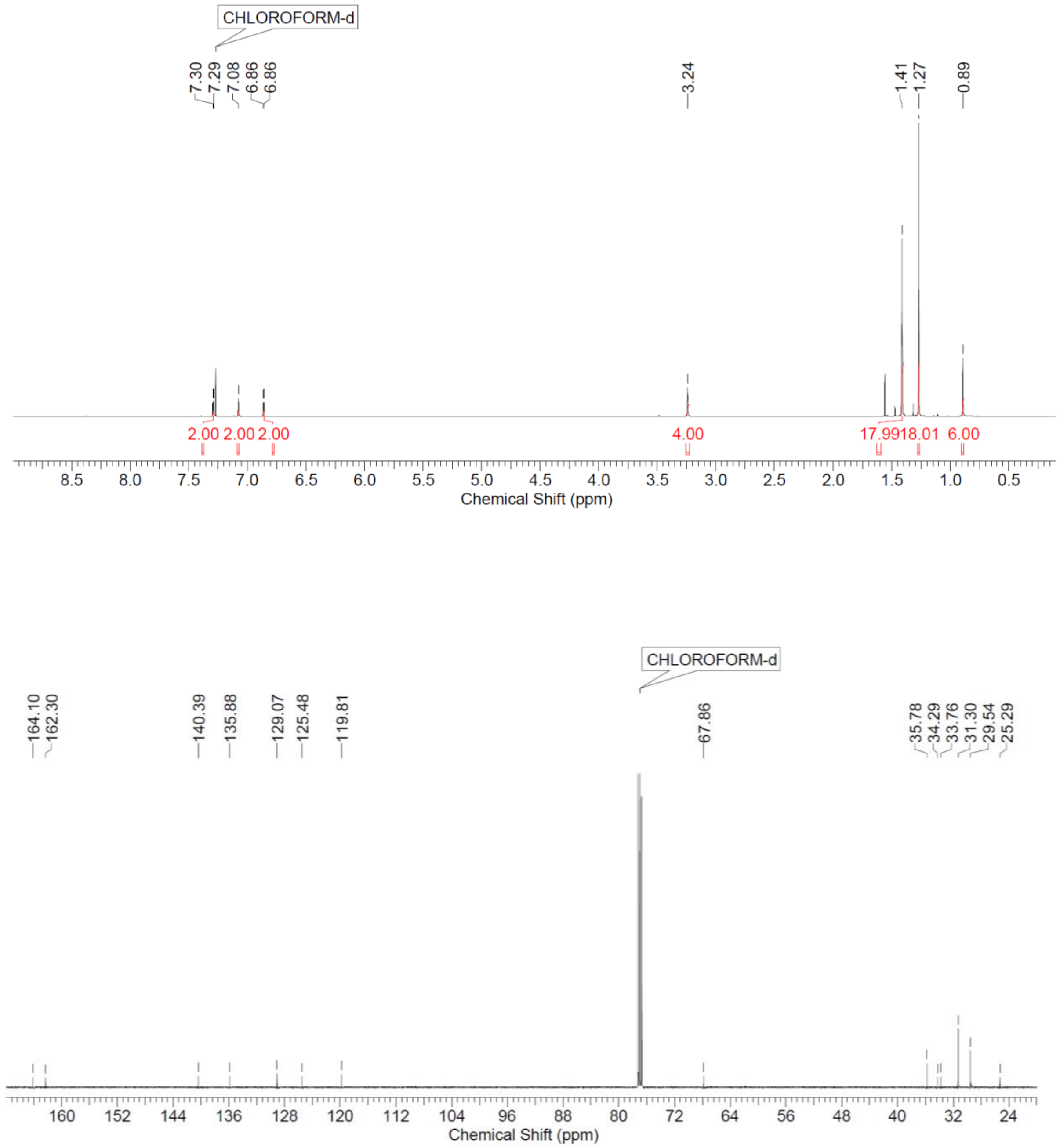


Figure S4 ^{1}H and ^{13}C NMR of Ni-salen(prop)(di-*tert*-butyl) complex in $CDCl_3$ (500 MHz)

Ni/C Catalyst

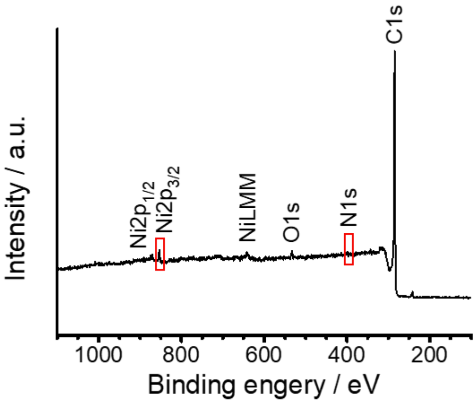


Figure S5. XPS survey of Ni/C. Regions for which a detailed analysis was performed are marked with a red box.

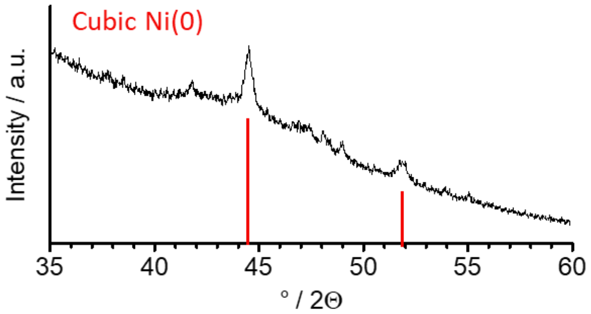


Figure S6. Powder XRD pattern of Ni/C. Reflex position for cubic Ni(0) are marked in red.

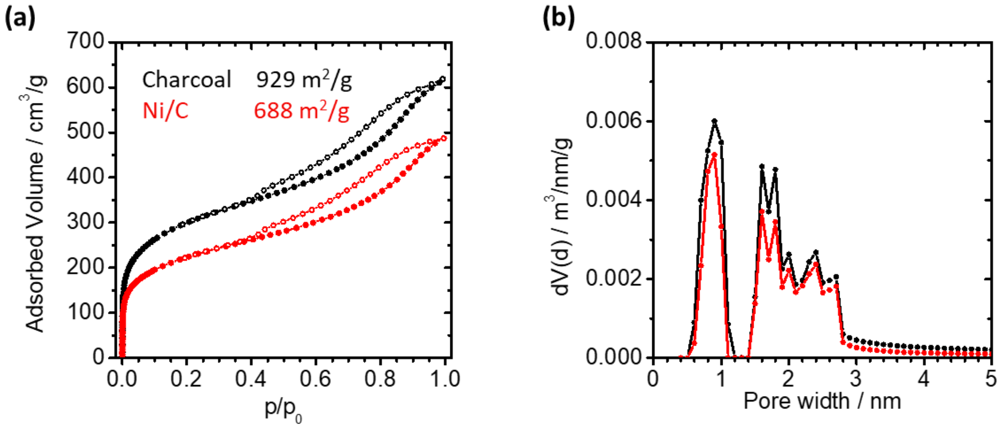
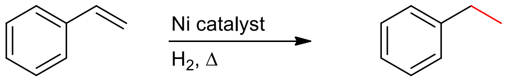


Figure S7. (a) Ar physisorption isotherms of charcoal (929 m^2/g) and Ni/C (688 m^2/g) with respective surface areas determined by BET-model (0.005-0.1 p/p0). Adsorption is depicted in filled dots, desorption in rings. (b) Pore size distribution of charcoal compared to Ni/C.

Catalytic Reactions

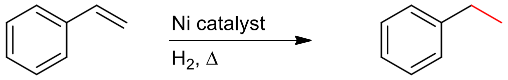
Table S2. Screening of hydrogen pressure and reaction temperature.



Catalyst	Temperature / °C	H_2 pressure / MPa	Yield / %
Ni/C	50	2	99
Ni/C	40	0.5	99
Ni/C	40	0.2	99
Ni/C[a]	40	0.2	99
Ni/C	rt	0.1	50
Ni/C[b]	40	0.2	22
Ni/C[c]	40	0.2	0
Ra-Nickel[d]	40	0.2	99
Ni/Al_2O_3	40	0.2	0
Ni/CeO_2	40	0.2	0
Ni/SiO_2	40	0.2	64
Ni/TiO_2	40	0.2	0

Reaction conditions: 0.5 mmol styrene, 2.5 ml MeOH, 1.35 mol% Ni (14.7 mg Ni/C, 2.7 wt.% Ni), 20 h. Yields determined by GC using *n*-dodecane as an internal standard. [a] Stored in Ar atmosphere for 4 months. [b] 0.68mol% Ni (7.4 mg Ni/C, 2.7 wt.% Ni)). [c] Nickel acetate tetra hydrate (4 wt.%) was used as Ni precursor for the catalyst synthesis on the carbon support. [d] 1.35 mol% Raney-Ni.

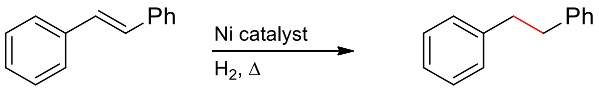
Table S3. Screening of solvent and amount of solvent in the styrene hydrogenation.



Solvent	Amount of solvent / ml	Yield / %
Methanol	2.5	99
Ethanol	2.5	87
H_2O[a]	2.5	79
Toluene	2.5	43
Methylcyclohexane	2.5	0
Acetonitrile	2.5	24
Methanol	1.0	31
Methanol	1.5	73
Methanol	2.0	81
Methanol	3.0	56

Reaction conditions: 0.5 mmol styrene, solvent, 1.35 mol% Ni (14.7 mg Ni/C, 2.7 wt.% Ni), 40 °C, 0.2 MPa H_2, 20 h. Yields determined by GC using *n*-dodecane as an internal standard. [a] Aqueous phase was extracted with ethyl acetate und dried over Na_2SO_4 before analysis.

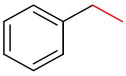
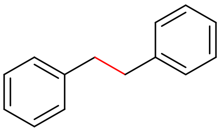
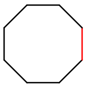
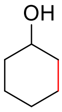
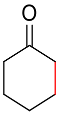
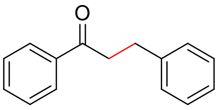
Table S4. Screening of temperature and H_2 pressure in the olefin hydrogenation.



Catalyst	Temperature / °C	H_2 pressure / MPa	Yield / %
Ni/C	40	0.2	21
Ni/C	60	0.5	66
Ni/C	60	0.1	73
Ni/C	80	0.5	72
Ni/C	80	0.1	99

Reaction conditions: 0.5 mmol *trans*-stilbene, 2.5 ml MeOH, 1.35 mol% Ni (14.7 mg Ni/C, 2.7 wt.% Ni), 20 h. Yields determined by GC using *n*-dodecane as an internal standard.

Table S5. List of isolated products and ^{1}H NMR data.

Saturated product	
	**Yield** 98 % **^{1}H-NMR** δ = 7.39-7.28 (m, 5H), 2.77-2.72 (q, 2H), 1.36-1.32 (t, 3H) ppm
	**Yield** 90 % **^{1}H-NMR** δ = 7.46-7.42 (m, 4H), 7.37-7.33 (m, 6H), 3.08 (s, 4H) ppm
	**Yield** 99 % **^{1}H-NMR** δ = 1.54 (s, 16H) ppm
	**Yield** 97 % **^{1}H-NMR** δ =3.59-3.55 (sept, 1H), 2.22 (s, 1H), 1.88-1.87 (m, 2H), 1.72-1.70 (m, 2H), 1.53-1.50 (m, 1H), 1-27-1.20 (m, 4H) 1.15 (m, 1H) ppm
	**Yield** 99 % **^{1}H-NMR** δ = 2.26-2.22 (t, 4H), 1.80-1.74 (m, 4H), 1.66-1.60 (m, 2H) ppm
	**Yield** 80 % **^{1}H-NMR** δ = 8.03-8.01 (d, 2H), 7.64-7.60 (t, 1H), 7.53-7.49 (t, 2H), 7.39-7.25 (m, 5H), 3.39-3.35 (t, H2), 3.10-3.21 (t, 2H) ppm

^{1}H NMR measured in $CDCl_3$ at 400 MHz. For reaction conditions refer to General Procedure.

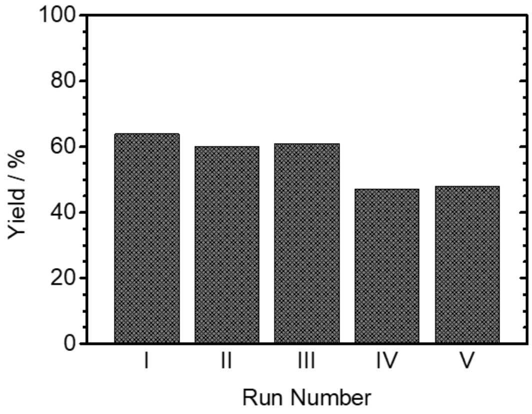


Figure S8. Recyclability study using the hydrogenation of styrene at about 60 % yield. Reaction conditions: 0.5 mmol styrene, 2.5 mL MeOH, 1.35 mol% Ni (14.7 mg Ni/C, 2.7 wt.% Ni), 40 °C, 0.2 MPa H_2, 4 h. Yields were determined by GC using *n*-dodecane as an internal standard.

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[S2] C. F. Macrae, I. Sovago, S. J. Cottrell, P. T. A. Galek, P. McCabe, E. Pidcock, M. Platings, G. P. Shields, J. S. Stevens, M. Towler and P. A. Wood, *J. Appl. Cryst*. **2020**, *53*, 226-235.

[S3] H.-R. Wen, S.-J. Liu, X.-R. Xie, J. Bao, C.-M. Liu, J.-L. Chen, *Inorg. Chim. Acta* **2015**, *435*, 274–282.