Electronic Supplementary Information for

Recyclable Cobalt(0) Nanoparticle Catalysts for Hydrogenations

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1 General information

Analytical Thin-Layer Chromatography: TLC was performed using aluminium plates with silica gel and fluorescent indicator (Merck, 60, F254). Thin layer chromatography plates were visualized by exposure to ultraviolet light (366 or 254 nm) or by immersion in a staining solution of molybdatophosphoric acid in ethanol or potassium permanganate in water.

Chemicals and Solvents: Commercially available olefins were distilled under reduced pressure prior to use. Solvents (THF, Et₂O, n-hexane, toluene) were distilled over sodium and benzophenone and stored over molecular sieves (4 Å). Oleylamine was stored over molecular sieve (4 Å) for 30 days and degassed in vacuum. Cobalt(II)chloride (99.999%, ABCR), lithium (99%, Alfa Aesar) and naphthalene (99%, Alfa Aesar) were used as received.

Column Chromatography: Flash column chromatography with silica gel 60 from KMF (0.040-0.063 mm). Mixtures of solvents used are noted in brackets.

High Pressure Reactor: Hydrogenation reactions were carried out in 160 and 300 mL high pressure reactors (Parr™) in 4 mL glass vials. The reactors were loaded under argon, purged with H₂ (1 min), then three times with 2 bar H₂, sealed and the internal pressure was adjusted. Hydrogen (99.9992%) was purchased from Linde.

¹H- und ¹³C-NMR-Spectroscopy: Nuclear magnetic resonance spectra were recorded on a Bruker Avance 300 (300 MHz) and Bruker Avance 400 (400 MHz). ¹H-NMR: The following abbreviations are used to indicate multiplicities: s = singlet; d = doublet; t = triplet, q = quartet; m = multiplet, dd = doublet of doublet, dt = doublet of triplet, dq = doublet of quartet, ddt = doublet of doublet of quartet. Chemical shift δ is given in ppm to tetramethylsilane.

Fourier-Transformations-Infrared-Spectroscopy (FT-IR): Spectra were recorded on a Agilent Cary 630 FTIR with ATR-device. All spectra were recorded at room temperature. Wave number is given in cm⁻¹. Bands are marked as s = strong, m = medium, w = weak and b = broad.

Gas chromatography with FID (GC-FID): HP6890 GC-System with injector 7683B and Agilent 7820A System. Column: HP-5, 19091J-413 (30 m × 0.32 mm × 0.25 µm),
carrier gas: N\textsubscript{2}. GC-FID was used for reaction control and catalyst screening (Calibration with internal standard n-pentadecane and analytically pure samples).

Gas chromatography with mass-selective detector (GC-MS): Agilent 6890N Network GC-System, mass detector 5975 MS. Column: HP-5MS (30 m × 0.25 mm × 0.25 µm, 5% phenylmethylsiloxane, carrier gas: H\textsubscript{2}. Standard heating procedure: 50 °C (2 min), 25 °C/min -> 300 °C (5 min)

High resolution mass spectrometry (HRMS): The spectra were recorded by the Central Analytics Lab at the Department of Chemistry, University of Regensburg, on a MAT SSQ 710 A from Finnigan.

Inductively coupled plasma optical emission spectrometry (ICP-OES): ICP-OES measurements were carried out on a Spectro Analytical Instruments Spectroflame (Type: FSMEA85C).

Inductively coupled plasma mass spectrometry (ICP-MS): ICP-MS measurements were carried out on a Perkin Elmer Elan 9000.

Gas-uptake reaction monitoring: Gas-uptake was monitored with a Man On the Moon X201 kinetic system to maintain a constant reaction pressure. The system was purged with hydrogen prior to use. Reservoir pressure was set to about 9 bar H\textsubscript{2}. Calibration of the reservoir pressure drop in relation to H\textsubscript{2} consumption was performed by quantitative hydrogenation of various amounts of α-methylstyrene with a Pd/C catalyst in 1 mL of THF.

Transmission electron microscopy (TEM): TEM, high-resolution (HR)TEM, and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) were conducted with an aberration-corrected FEI Titan\textsuperscript{3} 80-300 microscope operating at 300 and 80 kV, a FEI Osiris microscope at 200 kV, and a Philips CM 200 FEG/ST microscope at 200 kV. TEM samples were prepared by evaporating DME, THF or n-heptane suspensions on amorphous carbon (lacey-)film suspended on copper grids. The deposition of the samples on the carbon (lacey-)film copper grids was performed under argon atmosphere in a glovebox. The grids were thereafter transferred with a suitable vacuum/inert gas transfer module into the transmission electron microscope without any contact to air. Average particle diameters were calculated by statistical evaluation of at least 150 particles (ImageJ 1.47v software).
**X-ray powder diffraction (XRD):** X-ray powder diffraction was carried out with a Stoe STADI-P diffractometer operating with Ge-monochromatized Cu-Kα radiation. Co⁰ powder samples sintered at 800 °C for 7 h in vacuum for crystallization of the metal and eventual oxide impurities. The powder samples were measured on a Stoe IPDS II image plate diffractometer using Mo-Kα radiation (graphite monochromator). Samples were diluted with glass spheres (9-13 µm, Sigma-Aldrich) to reduce the X-ray absorption of the metal nanoparticles and prepared in glass capillaries under argon. Since the scattering power of the small-sized metal nanoparticles (diameter ≤10 nm) is low, certain non-specific background is observed for all nanoparticles. This non-specific scattering was fitted by background correction.
2 General procedures

Synthesis of Co nanoparticles

Cobalt(II)chloride (519 mg, 4.0 mmol), lithium (56 mg, 8.0 mmol) and naphthalene (1.20 g, 9.4 mmol) were stirred in 20 mL THF for 24 h. The resultant nanoparticles were separated by centrifugation (20,000 rpm) and purified by redispersion and centrifugation (3×20 mL THF). Subsequently, the solids were dried in vacuum (for storage as powder) or redispersed in 40 mL THF (Co-NPs, for catalytic applications). The preparation of amine-stabilized nanoparticles (aCo-NPs) was effected by treatment of the dried solids with 38 mL THF and 2 mL oleylamine (aCo-NP). As an alternative to the separation by centrifugation, the particles can be separated by an external commercial neodymium magnet (mCo-NPs). The preparation of related nanoparticles followed the same reduction protocol but without the washing procedures (in situ Co-NPs). The primary THF solutions (containing the by-products LiCl, naphthalene) were directly employed in catalytic reactions. The removal of the magnetic stir bar appeared to important to ensure long-term catalyst stability. After extended periods of storage of the catalysts suspensions, ultrasonification for 15-60 min effected complete redispersion and secured highest reproducibility.

General procedure for hydrogenation

Under an atmosphere of argon, a 5 mL screw cap vial with a PTFE septum and magnetic stir bar was charged with the substrate (0.25 mmol) and THF (875 µL). The catalyst suspension (125 µL; 0.0125 mmol Co) was added and the septum punctured with a short needle (Braun). The vial was placed into a high-pressure reactor (Parr Instr.), which was sealed, removed from the glove box, placed on a magnetic stirrer plate, and purged with H₂. After 3 h at r.t. under an atmosphere of H₂ (2 bar), the pressure was released, the vial retrieved, and the reaction quenched with saturated aqueous NH₄Cl (1 mL). For quantitative GC-FID analyses, n-pentadecane was added as internal standard. The mixture was extracted with ethyl acetate and the combined organic layers were dried (Na₂SO₄). For isolation of the products, the reaction mixture was filtered through a Pasteur pipette filled with SiO₂. The pipette was washed with n-pentane (3 x 1 mL) and the solvents evaporated. Amines were isolated as the corresponding ammonium salts after addition of HCl·Et₂O.
General method for kinetic examination in catalytic hydrogenation

A flame-dried 10 mL two-neck flask was connected to a Man on the Moon X201 gas-uptake system. After purging with H₂, the system was set to a reaction pressure of 1.9 bar. The catalyst mixture in THF (2 ml) was added using a Teflon septum. Monitoring of the hydrogen uptake started with the addition of the substrate (0.5 mmol). The pressure was recorded every two seconds until the pressure in the reaction vessel remained stationary.
3 Synthesis of starting materials

General procedure for the synthesis of imines

Silica (6 g) was weighed into a 100 ml round-bottom flask and suspended in ethanol (35 ml). After addition of the aldehyde (20 mmol) and amine (20 mmol, 1 equiv.), the flask was put into an ultrasonic bath for 20 min at room temperature.

The mixture was stirred overnight, filtered and the solvent removed. The crude product mixture was vacuum distilled (80 °C, 0.02 mbar) and the imines collected.


N-(2-Furanyl methylene)-benzenamine

![Chemical structure]

C_{11}H_{9}NO

171.20 g/mol

Pale yellow liquid

Yield 1.72 g, 10.0 mmol (50%)

^1H-NMR (300 MHz, MeOD) δ 8.37 (s, 1H), 7.77 (d, J = 1.8 Hz, 1H), 7.44 – 7.33 (m, 2H), 7.29 – 7.19 (m, 3H), 7.12 (dd, J = 3.5, 0.7 Hz, 1H), 6.64 (dd, J = 3.5, 1.8 Hz, 1H).

^13C-NMR (75 MHz, MeOD) δ 153.08, 151.98, 150.21, 147.68, 130.38, 127.63, 122.05, 118.77, 113.52.

GC-MS t_R = 8.044 min, (EI, 70 eV): m/z = 171 [M^+], 142, 115, 104, 93, 77, 66, 51.

**$N$-(2-Furanylmethylene)-cyclohexylamine**

![Chemical structure](image)

$C_{11}H_{15}NO$

177.25 g/mol

Yellow liquid

**Yield**

2.68 g, 15.1 mmol (76%)

**$^1$H-NMR**

$(300 \text{ MHz, MeOD}) \delta 8.16 (s, 1H), 7.67 (d, J = 1.8 \text{ Hz}, 1H), 6.91 (dd, J = 3.6, 0.8 \text{ Hz}, 1H), 6.56 (dd, J = 3.5, 1.8 \text{ Hz}, 1H), 3.18 (tt, J = 10.8, 4.1 \text{ Hz}, 1H), 1.88 – 1.78 (m, 1H), 1.78 – 1.66 (m, 2H), 1.62 – 1.46 (m, 2H), 1.46 – 1.15 (m, 3H).

**$^{13}$C-NMR**

$(75 \text{ MHz, MeOD}) \delta 152.56, 150.41, 146.59, 116.23, 112.95, 70.97, 35.25, 26.56, 25.89.$

**GC-MS**

$t_R = 7.46 \text{ min, (EI, 70 eV): } m/z = 177 [M^+], 162, 148, 134, 122, 107, 94, 81, 67, 53.$

**HRMS**

found 177.11437 (calculated: 177.11482)

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**$(rac)$-$N$-(2-Butenylidene)-cyclohexylamine**

![Chemical structure](image)

$C_{10}H_{17}N$

151.25 g/mol

**Yield**

2.04 g, 13.5 mmol (68%)

**$^1$H-NMR**

$(300 \text{ MHz, MeOD}) \delta 7.93 – 7.87 (m, 1H), 7.76 (t, J = 2.8 \text{ Hz}, 1H), 6.43 – 6.29 (m, 1H), 6.19 (ddq, J = 15.4, 8.8, 1.4 \text{ Hz}, 1H), 3.67 – 3.56 (m, 1H), 3.08 – 2.95 (m, 2H), 1.89 (d, J = 6.7 \text{ Hz}, 3H), 1.84 – 1.61 (m, 11H), 1.50 – 1.31 (m, 7H), 1.17 (d, J = 6.2 \text{ Hz}, 3H).$

**$^{13}$C-NMR**

$(75 \text{ MHz, MeOD}) \delta 164.2, 163.6, 163.6, 143.6, 143.5, 132.0, 75.8, 70.5, 70.0, 36.9, 35.4, 35.3, 35.3, 26.6, 26.3, 25.8, 25.8, 19.5, 18.6, 18.5.$

**GC-MS**

$t_R = 6.26 \text{ min, (EI, 70 eV): } m/z = 150 [M^+ - H], 136, 122, 110, 94, 82, 68, 55.$

## 4 Hydrogenation reactions

### 4.1 Catalyst & substrate screening

*Table S1.* Hydrogenation of alkenes, alkynes, imines, and quinolines catalyzed by cobalt(0) nanoparticles isolated by centrifugation (Co-NP), isolated by magnetic separation (mCo-NP), prepared and used in situ (in situ Co-NP), and isolated by centrifugation and stabilized by oleyl amine (aCo-NP). Standard conditions: 0.25 mmol substrate, 1 mL in THF or 0.5 mmol substrate, 2 mL THF. If not otherwise noted, yields were determined by GC-FID vs. internal n-pentadecane.

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<th>[Co]</th>
<th>[mol%]</th>
<th>[bar]</th>
<th>[°C]</th>
<th>[h]</th>
<th>Yield [%]</th>
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<td>2 20</td>
<td>3</td>
<td>96 (isol.)</td>
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<td>2 20</td>
<td>3</td>
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<td>2 20</td>
<td>3</td>
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<td>-</td>
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<tr>
<td>1ao</td>
<td>mCo-NP</td>
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<td>10</td>
<td>60</td>
<td>24</td>
<td>94</td>
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<tr>
<td>2a</td>
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<td>60</td>
<td>6</td>
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<td>60</td>
<td>24</td>
<td>98 (isol.)</td>
<td>mixture (vide infra)</td>
</tr>
<tr>
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</tr>
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<td>5</td>
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<td>60</td>
<td>24</td>
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<td>mixture (vide infra)</td>
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<td>-</td>
</tr>
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<td>100</td>
<td>24</td>
<td>99 (isol.)</td>
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<td>80</td>
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<td>80</td>
<td>24</td>
<td>39 (isol.)</td>
<td>-</td>
</tr>
<tr>
<td>2o</td>
<td>mCo-NP</td>
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<td>80</td>
<td>24</td>
<td>77 (isol.)</td>
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<td>[mol%]</td>
<td>[bar]</td>
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<td>Yield [%]</td>
<td>Comment</td>
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<td>80</td>
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<td>24</td>
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<td>80</td>
<td>24</td>
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<td>-</td>
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<tr>
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<td>10</td>
<td>60</td>
<td>24</td>
<td>97 (isol)</td>
<td>-</td>
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4.2 Isolated hydrogenation reaction products

**Trimethyl(phenethyl)silane (1f)**

\[
\text{C}_{11}\text{H}_{18}\text{Si} \quad 178.35 \text{ g/mol}
\]

**Yield**

85.2 mg, 0.48 mmol (96%)

**\(^1\)H-NMR**

(300 MHz, CDCl\(_3\)) \(\delta\) 7.30 – 7.10 (m, 5H), 2.66 – 2.56 (m, 2H), 0.91 – 0.80 (m, 2H), 0.00 (s, 9H).

**\(^13\)C-NMR**

(75 MHz, CDCl\(_3\)) \(\delta\) 145.5, 128.4, 127.9, 125.6, 30.2, 18.8, -1.6.

**GC-MS**

\(t_R = 6.16\) min, (EI, 70 eV): \(m/z = 178 [M^+], 163, 135, 104, 91, 73, 59, 51.\)

Analytical data were in full agreement with E. Negishi, D. R. Swanson, C. J. Rousset, *J. Org. Chem.* 1990, 55, 5406.

**1-Ethyl-2-methoxybenzene (1i)**

\[
\text{C}_{9}\text{H}_{12}\text{O} \quad 136.19 \text{ g/mol}
\]

**Yield**

52.2 mg, 0.38 mmol (72%)

**\(^1\)H-NMR**

(400 MHz, CDCl\(_3\)) \(\delta\) 7.22 – 7.13 (m, 2H), 6.91 (td, \(J = 7.4, 1.1 \text{ Hz}, 1\)H), 6.86 (dd, \(J = 8.0, 1.1 \text{ Hz}, 1\)H), 3.84 (s, 3H), 2.66 (q, \(J = 7.5 \text{ Hz}, 2\)H), 1.21 (t, \(J = 7.5 \text{ Hz}, 3\)H).

**\(^13\)C-NMR**

(75 MHz, CDCl\(_3\)) \(\delta\) 157.5, 132.7, 129.0, 126.9, 120.6, 110.3, 55.4, 23.4, 14.3.

**GC-MS**

\(t_R = 5.30\) min, (EI, 70 eV): \(m/z = 136 [M^+], 121, 103, 91, 77, 65, 51.\)

2-Phenylpentane (1l)

\[
\text{C}_11\text{H}_{16}
\]

148.25 g/mol

Yield

53.4 mg, 0.36 mmol (69%)

\(^1\text{H-NMR}\)

(300 MHz, CDCl\(_3\)) \(\delta\) 7.33 – 7.26 (m, 2H), 7.22 – 7.14 (m, 3H), 2.70 (t, \(J = 7.0\) Hz, 1H), 1.65 – 1.43 (m, 2H), 1.36 – 1.09 (m, 5H), 0.87 (t, \(J = 7.3\) Hz, 3H)

\(^{13}\text{C-NMR}\)

(75 MHz, CDCl\(_3\)) \(\delta\) 148.1, 128.4, 127.1, 125.9, 40.9, 39.8, 22.4, 21.0, 14.3.

\text{GC-MS}

\(t_R = 5.42\) min, (EI, 70 eV): \(m/z = 148\ [M^+], 105, 91, 77, 65, 51.\)


2-Methoxy-4-propylphenol (1n/1aj)

\[
\text{C}_{10}\text{H}_{14}\text{O}_2
\]

166.22 g/mol

Yield

From eugenol: 75.6 mg, 0.45 mmol (89%)

from isoeugenol: 75.7 mg, 0.46 mmol (91%)

\(^1\text{H-NMR}\)

(300 MHz, CDCl\(_3\)) \(\delta\) 6.86 – 6.81 (m, 1H), 6.71 – 6.65 (m, 2H), 5.48 (brs, 1H), 3.88 (s, 3H), 2.52 (t, \(J = 7.8\) Hz, 2H), 1.69 – 1.55 (m, 2H), 0.94 (t, \(J = 7.3\) Hz, 3H).

\(^{13}\text{C-NMR}\)

(75 MHz, CDCl\(_3\)) \(\delta\) 146.4, 143.6, 134.8, 121.1, 114.2, 111.1, 56.0, 37.9, 25.0, 14.0.

\text{GC-MS}

\(t_R = 7.038\) min, (EI, 70 eV): \(m/z = 166\ [M^+], 137, 122, 107, 94, 77, 65, 51.\)

4-Isopropyl-1-methylcyclohexene (1q)

\[
\text{C}_{10}\text{H}_{18}
\]

138.25 g/mol

**Yield**

33.7 mg, 0.24 mmol (95%; 78% purity)

Due to the volatile nature of the product, the solvents could not be removed completely. NMR-analysis showed 74% hydrogenation product, 14% THF, 7% n-pentane

**\(^1\)H-NMR**

(400 MHz, CDCl\(_3\)) δ 5.46 – 5.28 (m, 1H), 2.08 – 1.91 (m, 3H), 1.80 – 1.67 (m, 2H), 1.64 (s, 3H), 1.46 (dq, J = 13.1, 7.1, 6.5 Hz, 1H), 1.35 – 1.16 (m, 2H), 0.92 – 0.84 (m, 6H).

**\(^{13}\)C-NMR**

(101 MHz, CDCl\(_3\)) δ 134.1, 121.2, 40.2, 32.4, 31.0, 29.1, 26.6, 23.6, 20.2, 19.9.

**GC-MS**

\(t_n = 4.84\) min, (EI, 70 eV): \(m/z = 138\) [M\(^+\)], 123, 109, 95, 81, 67, 55.


**n-Hexadecane (1t)**

\[
\text{C}_{16}\text{H}_{34}
\]

226.45 g/mol

**Yield**

59.3 mg, 0.26 mmol (99%)

**\(^1\)H-NMR**

(300 MHz, CDCl\(_3\)) δ 1.26 (s, 28H), 0.94 – 0.82 (m, 6H).

**\(^{13}\)C-NMR**

(75 MHz, CDCl\(_3\)) δ 32.1, 29.9, 29.8, 29.6, 22.9, 14.3.

**GC-MS**

\(t_n = 8.185\) min, (EI, 70 eV): \(m/z = 226\) [M\(^+\)], 197, 183, 169, 155, 141, 127, 113, 99, 85, 71, 57.

**n-Dodecane (1u)**

\[
\text{C}_{12}\text{H}_{26}
\]

170.34 g/mol

**Yield**

78.6 mg, 0.46 mmol (93%)

**\(^1\text{H}-\text{NMR}\)**

(400 MHz, CDCl\textsubscript{3}) \(\delta\) 1.26 (s, 20H), 0.94 – 0.84 (m, 6H).

**\(^{13}\text{C}-\text{NMR}\)**

(101 MHz, CDCl\textsubscript{3}) \(\delta\) 32.1, 29.9, 29.8, 29.5, 22.9, 14.3.

**GC-MS**

\(t_\text{R} = 6.01\) min, (EI, 70 eV): \(m/z = 170\) [M\(^+\)], 141, 127, 112, 98, 85, 71, 57.

Analytical data were in full agreement with X. Xu, D. Cheng, W. Pei, *J. Org. Chem.* 2006, 71, 6637.

---

**4-Phenylbutan-2-ol (1v)**

\[
\text{C}_{10}\text{H}_{14}\text{O}
\]

150.22 g/mol

**Yield**

73.9 mg, 0.49 mmol (96%)

Purity: 93%; 7% semihydrogenation product

**\(^1\text{H}-\text{NMR}\)**

(300 MHz, CDCl\textsubscript{3}) \(\delta\) 7.26 – 7.31 (m, 2H), 7.17 – 7.24 (m, 3H), 3.84 (dq, 1H, \(J = 6.22, 12.10\) Hz), 2.61 – 2.83 (m, 2H), 1.73 – 1.83 (m, 2H), 1.53 (br s, 1H), 1.24 (d, 3H, \(J = 6.17\) Hz).

**\(^{13}\text{C}-\text{NMR}\)**

(75 MHz, CDCl\textsubscript{3}) \(\delta\) 142.2, 128.5, 125.9, 67.6, 41.0, 32.3, 23.8.

**GC-MS**

\(t_\text{R} = 6.51\) min, (EI, 70 eV): \(m/z = 150\) [M\(^+\)], 132, 117, 91, 77, 65, 51.

4-Cyclohexyl-N,N-dimethylaniline (1ac)

![Chemical structure of 4-Cyclohexyl-N,N-dimethylaniline (1ac)]

\[
\text{C}_{14}\text{H}_{21}\text{N} \\
203.33 \text{ g/mol}
\]

**Yield**
100.7 mg, 0.50 mmol (99%)

**\(^1\)H-NMR**
(400 MHz, CDCl\(_3\)) \(\delta 7.15 - 7.08\) (m, 2H), 6.77 – 6.70 (m, 2H), 2.93 (s, 6H), 2.43 (tq, \(J = 9.0, 3.3\) Hz, 1H), 1.92 – 1.81 (m, 4H), 1.75 (dtt, \(J = 12.6, 3.1, 1.4\) Hz, 1H), 1.47 – 1.33 (m, 4H), 1.27 (ddt, \(J = 14.5, 9.0, 3.3\) Hz, 1H).

**\(^{13}\)C-NMR**
(101 MHz, CDCl\(_3\)) \(\delta 149.1, 136.8, 127.4, 113.1, 43.6, 41.1, 34.9, 27.2, 26.4\).

**GC-MS**
\(t_\text{R} = 9.15\) min, (EI, 70 eV): \(m/z = 203 [M^+]\), 160, 146, 134, 115, 103, 93, 77, 51.


---

2-Ethylpyridine hydrochloride (1ad)

![Chemical structure of 2-Ethylpyridine hydrochloride (1ad)]

\[
\text{C}_7\text{H}_{10}\text{ClN} \\
143.61 \text{ g/mol}
\]

**Yield**
36.1 mg, 0.25 mmol (99%)

**\(^1\)H-NMR**
(300 MHz, MeOD) \(\delta 8.75\) (dt, \(J = 4.8, 2.3\) Hz, 1H), 8.65 – 8.53 (m, 1H), 8.04 (d, \(J = 8.1\) Hz, 1H), 8.00 – 7.90 (m, 1H), 3.21 – 3.06 (m, 2H), 2.02 (s, 1H), 1.50 – 1.41 (m, 3H).

**\(^{13}\)C-NMR**
(75 MHz, MeOD) \(\delta 160.0, 148.3, 142.1, 128.0, 126.0, 27.8, 13.3\).

**GC-MS (freebase)**
\(t_\text{R} = 3.792\) min, (EI, 70 eV): \(m/z = 106 [M^+]\), 92, 79, 65, 51.
3,7-Dimethyl-1-octanol (1ae: from citronellol; 1af: from geraniol)

\[
\begin{align*}
\text{C}_{10}\text{H}_{22}\text{O} & \\
\text{158.29 g/mol} & \\
\text{Yield} & \\
\text{From citronellol: 68.3 mg, 0.43 mmol (88%),} & \\
\text{from geraniol: 40.4 mg, 0.26 mmol (99%)} & \\
\text{'H-NMR} & \\
(300 MHz, CDCl}_3) \delta 3.76 – 3.57 (m, 2H), 1.67 – 1.46 (m, 3H), 1.43 – 1.32 (m, 2H), 1.32 – 1.21 (m, 3H), 1.19 – 1.06 (m, 3H), 0.87 (dd, \text{J} = 8.0, 6.5 \text{ Hz, 9H}). & \\
\text{'C-NMR} & \\
(75 MHz, CDCl}_3) \delta 61.4, 40.1, 39.4, 37.5, 29.6, 28.1, 24.8, 22.8, 22.7, 19.7. & \\
\text{GC-MS} & \\
t_r = 6.016 \text{ min, (EI, 70 eV): } m/2 = 140 [\text{M}^{+}-\text{OH}_2], 125, 112, 97, 83, 70, 55. & \\
\text{HRMS} & \\
\text{Calcd. for C}_{10}\text{H}_{21}\text{O 157.15869; found: 157.15836.} & \\
\text{IR} & \\
3324 (b), 2955 (s), 2926 (s), 2870 (s), 1461 (m), 1379 (m), 1260 (m), 1051 (s), 805 (s) \text{ cm}^{-1}. & \\
\end{align*}
\]

2,6-Dimethyloctane (1ag)

\[
\begin{align*}
\text{C}_{10}\text{H}_{22} & \\
\text{142.29 g/mol} & \\
\text{Yield} & \\
57.6 \text{ mg, 0.40 mmol (79%)} & \\
\text{'H-NMR} & \\
(300 MHz, CDCl}_3) \delta 1.52 (dp, \text{J} = 13.1, 6.6 \text{ Hz, 1H}), 1.38 – 1.22 (m, 5H), 1.18 – 1.01 (m, 4H), 0.85 (t, \text{J} = 6.8 \text{ Hz, 12H}). & \\
\text{'C-NMR} & \\
(75 MHz, CDCl}_3) \delta 39.5, 37.0, 34.6, 29.7, 28.2, 25.0, 22.9, 22.8, 19.4, 11.6. & \\
\text{GC-MS} & \\
t_r = 4.03 \text{ min, (EI, 70 eV): } m/2 = 142 [\text{M}^{+}], 127, 113, 97, 85, 71, 57. & \\
\end{align*}
\]

**Ethylsulfonyl)benzene (1ai)**

![Chemical Structure]

\[ \text{C}_8\text{H}_{10}\text{O}_2\text{S} \]

170.23 g/mol

**Yield**

77.1 mg, 0.45 mmol (91%)

Purity: 89%; 12% starting material

\(^1\text{H-NMR}\) (300 MHz, CDCl\(_3\)) \(\delta 7.93 - 7.86 \text{ (m, 2H)}, 7.72 - 7.59 \text{ (m, 1H)}, 7.60 - 7.53 \text{ (m, 2H)}, 3.11 \text{ (q, } J = 7.4 \text{ Hz, 2H)}, 1.26 \text{ (t, } J = 7.4 \text{ Hz, 3H}).

\(^{13}\text{C-NMR}\) (75 MHz, CDCl\(_3\)) \(\delta 138.6, 133.8, 129.4, 128.3, 50.7, 7.6.

**GC-MS**

\(t_R = 9.00 \text{ min}, \text{ (EI, 70 eV)}: m/z = 170 [M^+], 154, 141, 125, 105, 94, 77, 65, 51.


**Diethyl cis-1,2-cyclohexanedicarboxylate (1ak)**

![Chemical Structure]

\[ \text{C}_{12}\text{H}_{20}\text{O}_4 \]

228.29 g/mol

**Yield**

107.8 mg, 0.47 mmol (95%)

\(^1\text{H-NMR}\) (300 MHz, CDCl\(_3\)) \(\delta 4.12 \text{ (q, } J = 7.1 \text{ Hz, 4H)}, 2.85 - 2.74 \text{ (m, 2H)}, 2.10 - 1.89 \text{ (m, 2H)}, 1.83 - 1.66 \text{ (m, 2H)}, 1.58 - 1.30 \text{ (m, 4H)}, 1.23 \text{ (t, } J = 7.2 \text{ Hz, 6H}).

\(^{13}\text{C-NMR}\) (75 MHz, CDCl\(_3\)) \(\delta 173.8, 60.4, 42.8, 26.4, 23.9, 14.3.

**GC-MS**

\(t_R = 9.33 \text{ min}, \text{ (EI, 70 eV)}: m/z = 228 [M^+], 183, 154, 140, 125, 108, 99, 81, 67, 55.

2,3-Dimethyloctahydrophthalazine-1,4-dione (1al)

\[
\text{C}_{10}\text{H}_{16}\text{N}_{2}\text{O}_{2}
\]

196.25 g/mol

Yield

79.5 mg, 0.41 mmol (81%)

\(^1\)H-NMR

(300 MHz, CDCl\textsubscript{3}) \(\delta\) 3.24 (s, 6H), 2.79 – 2.62 (m, 2H), 1.97 – 1.49 (m, 6H), 1.49 – 1.29 (m, 2H).

\(^{13}\)C-NMR

(75 MHz, CDCl\textsubscript{3}) \(\delta\) 170.4, 32.7, 24.3.

GC-MS

\(t_{R} = 8.78\) min, (EI, 70 eV): \(m/z = 196\ [M^+], 180, 166, 153, 141, 125, 109, 96, 81, 67, 59.\)

(3aR,7aS)-2-Methylhexahydro-1H-isoindole-1,3(2H)-dione (1am)

\[
\text{C}_{9}\text{H}_{13}\text{NO}_{2}
\]

167.21 g/mol

Yield

78.3 mg, 0.47 mmol (93%)

\(^1\)H-NMR

(300 MHz, CDCl\textsubscript{3}) \(\delta\) 2.96 (s, 3H), 2.90 – 2.79 (m, 2H), 1.93 – 1.66 (m, 4H), 1.51 – 1.34 (m, 4H).

\(^{13}\)C-NMR

(75 MHz, CDCl\textsubscript{3}) \(\delta\) 180.1, 39.9, 24.8, 23.8, 21.7.

GC-MS

\(t_{R} = 7.46\) min, (EI, 70 eV): \(m/z = 167\ [M^+], 152, 138, 125, 113, 82, 67, 54.\)

(3aR,7aS)-2-Cyclohexylhexahydro-1H-isooindole-1,3(2H)-dione (1an)

\[
\text{C}_{14}\text{H}_{21}\text{NO}_2
\]

235.33 g/mol

**Yield**

111.0 mg, 0.47 mmol (96%)

**\(^1\)H-NMR**

(300 MHz, CDCl\(_3\)) \(\delta\) 3.92 (tt, \(J = 12.3, 3.9\) Hz, 1H), 2.77 (ddd, \(J = 6.4, 4.4, 2.1\) Hz, 2H), 2.11 (qd, \(J = 12.3, 3.4\) Hz, 2H), 1.89 – 1.76 (m, 4H), 1.75 – 1.51 (m, 5H), 1.49 – 1.34 (m, 4H), 1.34 – 1.15 (m, 3H).

**\(^{13}\)C-NMR**

(75 MHz, CDCl\(_3\)) \(\delta\) 180.0, 51.3, 39.7, 28.9, 26.0, 25.2, 24.0, 21.8.

**GC-MS**

\(t_R = 9.83\) min, (EI, 70 eV): \(m/z = 235\) [M\(^+\)], 207, 192, 178, 164, 154, 136, 124, 108, 98, 81, 67, 55.


**exo-3,6-Epoxy-N-methyl-hexahydrophthalimide (1ao)**

\[
\text{C}_{9}\text{H}_{11}\text{NO}_3
\]

181.19 g/mol

**Yield**

85.2 mg, 0.47 mmol (94%)

**\(^1\)H-NMR**

(300 MHz, CDCl\(_3\)) \(\delta\) 4.86 (dd, \(J = 3.3, 2.1\) Hz, 2H), 2.95 (s, 3H), 2.87 (s, 2H), 1.92 – 1.80 (m, 2H), 1.64 – 1.53 (m, 2H).

**\(^{13}\)C-NMR**

(75 MHz, CDCl\(_3\)) \(\delta\) 177.4, 79.1, 50.1, 28.7, 25.2.

**GC-MS**

\(t_R = 9.65\) min, (EI, 70 eV): \(m/z = 181\) [M\(^+\)], 152, 140, 125, 108, 99, 81, 67, 55.
**N-Benzylaniline hydrochloride (2a)**

![Chemical structure of N-Benzylaniline hydrochloride](image)

\[ \text{C}_{13}\text{H}_{14}\text{ClN} \]

Yield 99.4 mg, 0.45 mmol (91%)

\({}^1\text{H-NMR}\) (300 MHz, MeOD) \(\delta 7.59 - 7.50 (m, 3H), 7.48 - 7.38 (m, 7H), 4.61 \) (s, 2H).

\({}^{13}\text{C-NMR}\) (75 MHz, MeOD) \(\delta 136.2, 131.9, 131.5, 131.4, 131.0, 130.9, 130.2, 124.3, 57.0\).

**GC-MS (freebase)** \(t_R = 8.97 \) min, (EI, 70 eV): \(m/z = 183 \) [M\(^+\)], 154, 107, 91, 77, 65, 51.

**Elemental Analysis**

Calcd: 71.07% C, 6.42% H, 6.38% N; found: 70.57% C, 6.80% H, 6.27% N

Analytical data were in full agreement with T. Li, X. Cui, L. Sun, C. Li, *RSC Adv.* 2014, 4, 33599.

**Methyl 4-(benzylamino)benzoate (2b)**

![Chemical structure of Methyl 4-(benzylamino)benzoate](image)

\[ \text{C}_{15}\text{H}_{15}\text{NO}_2 \]

Yield 49.0 mg, 0.20 mmol (83%)

\({}^1\text{H-NMR}\) (300 MHz, CDCl\(_3\)) \(\delta 7.87 \) (d, \(J = 8.8 \) Hz, 2H), 7.41 - 7.27 (m, 5H), 6.61 (d, \(J = 8.8 \) Hz, 2H), 4.81 (br s, 1H), 4.39 (s, 2H), 3.85 (s, 3H).

\({}^{13}\text{C-NMR}\) (75 MHz, CDCl\(_3\)) \(\delta 167.4, 151.6, 138.3, 131.7, 128.9, 127.7, 127.6, 119.0, 112.0, 51.7, 48.0\).

**GC-MS** \(t_R = 11.24 \) min, (EI, 70 eV): \(m/z = 241 \) [M\(^+\)], 210, 180, 164, 151, 135, 119, 104, 91, 78, 65, 51.

**Elemental Analysis**

Calculated: 74.67% C, 6.27% H, 5.81% N; found: 73.82% C, 6.37% H, 5.63% N.

**N-(4-Methoxybenzyl)aniline hydrochloride (2c)**

![Chemical structure of N-(4-Methoxybenzyl)aniline hydrochloride (2c)](image)

\[ \text{C}_{14}\text{H}_{16}\text{ClNO} \]

249.74 g/mol

**Yield**

110.1 mg, 0.44 mmol (88%)

**\(^1\text{H-NMR}\)**

(400 MHz, MeOD) \(\delta\) 7.59 – 7.48 (m, 3H), 7.45 – 7.36 (m, 2H), 7.35 – 7.30 (m, 2H), 6.97 – 6.92 (m, 2H), 4.54 (s, 2H), 3.80 (s, 3H).

**\(^{13}\text{C-NMR}\)**

(101 MHz, MeOD) \(\delta\) 162.29, 136.10, 133.05, 131.34, 130.97, 124.34, 123.53, 115.41, 56.77, 55.82.

**GC-MS (freebase)**

\(t_R = 10.12\) min, (El, 70 eV): \(m/z = 213 [M^+]\), 196, 180, 168, 152, 142, 121, 106, 91, 77, 65, 51.

**HRMS**

Calcd. for \(\text{C}_{14}\text{H}_{16}\text{NO}\): 214.1226; found: 214.1226.

**IR**

3060 (w), 2896 (m), 2840 (m), 2669 (s), 2550 (s), 2423 (s), 1595 (s), 1513 (s), 1305 (m), 1249 (s), 1033 (s), 815 (s), 795 (s) cm\(^{-1}\).
N-(2,4,6-Trimethylphenyl)-2-pyridinemethanamine hydrochloride (2d)

\[
\text{C}_{15}\text{H}_{19}\text{ClN}_2
\]

Yield

128.2 mg, 0.49 mmol (98%)

23% pyridine hydrogenation

\(^1\text{H}-\text{NMR}\)

(300 MHz, MeOD) \(\delta 8.85\) (ddd, \(J = 5.5, 1.6, 0.8\) Hz, 1H), 8.37 (td, \(J = 7.9, 1.7\) Hz, 1H), 7.93 (dd, \(J = 7.9, 1.1\) Hz, 1H), 7.93 – 6.99 (m, 1H), 7.03 (s, 2H), 4.77 (s, 2H), 2.41 (s, 6H), 2.29 (s, 3H).

\(^{13}\text{C}-\text{NMR}\)

(75 MHz, MeOD) \(\delta 151.3, 146.4, 144.4, 139.8, 132.8, 131.8, 127.5, 127.3, 52.7, 20.8, 18.0\).

\text{GC-MS (freebase)}

\(t_R = 9.839\) min, (EI, 70 eV): \(m/z = 226\) [M\(^+\)], 211, 196, 181, 148, 134, 120, 107, 93, 79, 65, 51.

\text{HRMS}

Calcd. for C\(_{15}\)H\(_{19}\)N\(_2\) 227.1543; found: 227.1543;

N-(2-Furanylmethyl)aniline (2e)

\[
\begin{align*}
\text{C}_{11}\text{H}_{11}\text{NO} & \quad 173.22 \text{ g/mol} \\
\end{align*}
\]

Yield 88.8 mg, 0.51 mmol (99%); Selectivity: 81%

Only detectable side product:

\[\text{1H-NMR} \quad (400 \text{ MHz, CDCl}_3) \delta 7.38 \text{ (dd, } J = 1.9, 0.8 \text{ Hz, 1H, 1}), 7.20 \text{ (qd, } J = 6.6, 6.1, 1.7 \text{ Hz, 3H, 8}), 6.76 \text{ (t, } J = 7.3 \text{ Hz, 1H, 9}), 6.73 - 6.62 \text{ (m, 2H, 7)}, 6.34 \text{ (dd, } J = 3.2, 1.9 \text{ Hz, 1H, 2}), 6.25 \text{ (dd, } J = 3.2, 0.9 \text{ Hz, 1H, 3}), 4.33 \text{ (s, 2H, 5}).\]

Side product (400 MHz, CDCl₃) \( \delta 7.18 - 7.15 \text{ (m, 2H, 8')}, 6.67 - 6.63 \text{ (m, 3H, 7'/9')}, 4.15 \text{ (qd, } J = 7.2, 3.8 \text{ Hz, 1H, 4'}), 3.91 \text{ (dt, } J = 8.3, 6.7 \text{ Hz, 1H, 1'}), 3.80 \text{ (dt, } J = 8.2, 6.8 \text{ Hz, 1H, 1'}), 3.28 \text{ (dd, } J = 12.3, 3.8 \text{ Hz, 1H, 5'}), 3.10 \text{ (dd, } J = 12.3, 7.5 \text{ Hz, 1H, 5'}), 2.10 - 2.00 \text{ (m, 1H, 3'}), 1.99 - 1.89 \text{ (m, 2H, 2')}, 1.67 \text{ (ddt, } J = 11.6, 8.3, 7.0 \text{ Hz, 1H, 3'}).\]

\[\text{13C-NMR} \quad (101 \text{ MHz, CDCl}_3) \delta 152.9 (\text{6}), 147.8 (\text{4}), 142.0 (\text{1}), 129.4 (\text{8}), 118.1 (\text{9}), 113.3 (\text{7}), 110.5 (\text{2}), 107.1 (\text{3}), 41.6 (\text{5}).\]

Side product (101 MHz, CDCl₃) \( \delta 148.5 (\text{6'}), 129.3 (\text{8'}), 117.6 (\text{9'}), 113.2 (\text{7'}), 77.7 (\text{4'}), 68.2 (\text{1'}), 48.3 (\text{5'}), 29.2 (\text{3'}), 25.9 (\text{2'}).\)

\[\text{GC-MS} \quad t_i = 7.97 \text{ min, (EI, 70 eV): } m/z = 173 [M^+], 144, 130, 115, 104, 91, 81, 65, 53.\]

**N-(2-Furanylmethyl)cyclohexylamine (2f)**

\[
\text{C}_{11}\text{H}_{17}\text{NO}
\]

179.26 g/mol

**Yield**

58.8 mg, 0.33 mmol (67%); Selectivity 53%

Only detectable side product:

**\(^1\text{H-NMR}\)**

(400 MHz, CDCl\(_3\)) \(\delta\) 7.34 (dd, \(J = 1.9, 0.8\) Hz, 1H, 1), 6.29 (dd, \(J = 3.2, 1.9\) Hz, 1H, 2), 6.15 (d, \(J = 3.1\) Hz, 1H, 3), 3.80 (s, 2H, 5), 2.44 (tt, \(J = 10.4, 3.8\) Hz, 1H, 6), 1.63 – 1.57 (m, 2H, 7/7'), 1.91 – 1.83 (m, 5H, 7/7'), 1.72 (dt, \(J = 12.5, 3.6\) Hz, 4H, 7/7'), 1.57 – 1.47 (m, 1H, 3'), 1.30 – 1.02 (m, 8H, 7/7').

Side product (400 MHz, CDCl\(_3\)) \(\delta\) 3.99 (ddt, \(J = 11.1, 7.4, 3.7\) Hz, 1H, 4'), 3.84 (dt, \(J = 8.4, 6.7\) Hz, 1H, 1'), 3.73 (dt, \(J = 8.2, 6.8\) Hz, 1H, 1'), 2.74 (dd, \(J = 11.8, 3.7\) Hz, 1H, 5'), 2.63 (dd, \(J = 11.8, 8.1\) Hz, 1H, 5'), 2.44 (tt, \(J = 10.4, 3.8\) Hz, 1H, 6'), 2.03 – 1.92 (m, 1H, 3'), 1.91 – 1.83 (m, 2H, 2'), 1.91 – 1.83 (m, 5H, 7/7'), 1.72 (dt, \(J = 12.5, 3.6\) Hz, 4H, 7/7'), 1.63 – 1.57 (m, 2H, 7/7'), 1.57 – 1.47 (m, 1H, 3'), 1.30 – 1.02 (m, 8H, 7/7').

**\(^{13}\text{C-NMR}\)**

(101 MHz, CDCl\(_3\)) \(\delta\) 154.4 (4), 141.8 (1), 110.2 (3), 106.7 (2), 55.9 (6), 43.5 (5), 33.5 (7/7'), 33.5 (7/7'), 33.4 (7/7'), 26.3 (7/7'), 25.2 (7/7'), 25.1 (7/7').

Side product (101 MHz, CDCl\(_3\)) \(\delta\) 78.6 (4'), 68.0 (1'), 57.1 (6'), 51.6 (5'), 33.5 (7/7'), 33.5 (7/7'), 33.4 (7/7'), 29.6 (3'), 26.3 (7/7'), 25.9 (2'), 25.2 (7/7'), 25.2 (7/7'), 25.1 (7/7').

**GC-MS**

\(t_R = 7.24\) min, (EI, 70 eV): \(m/z = 179\) [M⁺], 150, 136, 122, 96, 81, 67, 53.

Side product: \(t_R = 7.65\) min, (EI, 70 eV): \(m/z = 183\) [M⁺], 140, 122, 112, 105, 96, 83, 68, 55.
HRMS

Calcd. for C_{11}H_{18}NO 180.1383; found: 180.1386;
Calcd. for C_{11}H_{22}NO (side product) 184.1696; found: 184.1700.

**N,N-Dibenzylamine hydrochloride (2g)**

\[
\text{C}_{14}\text{H}_{16}\text{ClN} \\
\text{233.10 g/mol}
\]

Yield 49.0 mg, 0.21 mmol (84%)

\(^1\text{H}-\text{NMR}\)

(400 MHz, MeOD) \(\delta\) 7.55 – 7.49 (m, 4H), 7.49 – 7.44 (m, 6H), 4.25 (s, 4H).

\(^{13}\text{C}-\text{NMR}\)

(101 MHz, MeOD) \(\delta\) 132.4, 131.1, 130.7, 130.3, 52.0.

**GC-MS** (freebase) \(t_R = 10.9\) min, (EI, 70 eV): \(m/z = 196\ [\text{M-H}^+], 179, 165, 152, 139, 120, 106, 91, 77, 65, 51.\)

Analytical data were in full agreement with L. Xing, C. Cheng, R. Zhu, B. Zhang, X. Wang, Y. Hu, *Tetrahedron* 2008, 64, 11783.

**N-Benzylmethylamine hydrochloride (2h)**

\[
\text{C}_{8}\text{H}_{12}\text{ClN} \\
\text{157.64 g/mol}
\]

Yield 52.7 mg, 0.33 mmol (63%)

\(^1\text{H}-\text{NMR}\)

(400 MHz, MeOD) \(\delta\) 7.53 – 7.43 (m, 5H), 4.19 (s, 2H), 2.72 (s, 3H).

\(^{13}\text{C}-\text{NMR}\)

(101 MHz, MeOD) \(\delta\) 132.56, 130.90, 130.72, 130.31, 53.61, 33.12.

**GC-MS** \(t_R = 5.22\) min, (EI, 70 eV): \(m/z = 120\ [\text{M}^+], 104, 91, 78, 65, 51.\)

Analytical data were in full agreement with N. L. Lampland, M. Hovey, D. Mukherjee, A. D. Sadow, *ACS Catal.* 2015, 5, 4219.
N-Butyl-cyclohexylamine (2i)

\[
\begin{align*}
\text{C}_{10}\text{H}_{21}\text{N} \\
155.29 \text{ g/mol}
\end{align*}
\]

**Yield** 72.0 mg, 0.46 mmol (92%)

**\(^1\)H-NMR** (400 MHz, MeOD) \(\delta 3.12 – 2.95 \text{ (m, 3H), 2.20 – 2.03 \text{ (m, 2H), 1.93 – 1.82 \text{ (m, 2H), 1.78 – 1.61 \text{ (m, 3H), 1.45 (dt, J = 15.1, 7.5 Hz, 2H), 1.42 – 1.31 \text{ (m, 4H), 1.31 – 1.15 \text{ (m, 1H), 0.99 (t, J = 7.4 Hz, 3H).}}}}
\]

**\(^{13}\)C-NMR** (101 MHz, MeOD) \(\delta 58.39, 45.58, 30.35, 29.52, 26.12, 25.48, 20.90, 13.92.

**GC-MS** \(t_R = 6.00 \text{ min, (EI, 70 eV): } m/z = 155 \text{ [M\(^+\)], 126, 112, 98, 84, 70, 56.}\)


\[\]

\[\]

N-(3-Phenylpropyl)aniline hydrochloride (2j)

\[
\begin{align*}
\text{C}_{15}\text{H}_{18}\text{ClN} \\
247.77 \text{ g/mol}
\end{align*}
\]

**Yield** 58.2 mg, 0.23 mmol (96%)

**\(^1\)H-NMR** (300 MHz, MeOD) \(\delta 7.69 – 7.46 \text{ (m, 5H), 7.34 – 7.17 \text{ (m, 5H), 3.53 – 3.36 \text{ (m, 2H), 2.75 (t, J = 7.6 Hz, 2H), 2.14 – 1.98 \text{ (m, 2H).}}}}
\]

**\(^{13}\)C-NMR** (75 MHz, MeOD) \(\delta 141.5, 136.7, 131.6, 131.1, 129.7, 129.4, 127.5, 123.8, 52.9, 33.4, 28.9.

**GC-MS (freebase)** \(t_R = 9.88 \text{ min, (EI, 70 eV): } m/z = 211 \text{ [M\(^+\)], 118, 106, 91, 77, 65, 51.}\)

**HRMS** Calcd. for \(\text{C}_{15}\text{H}_{18}\text{N}\) 212.1434; found: 212.1436.

**IR** 3370 (b), 3063 (w), 3026 (m), 2870 (m), 2646 (m), 2017 (m), 1603 (m), 1491 (m), 749 (s), 690 (s) cm\(^{-1}\).
**N-(1-Phenylethyl)aniline (2k)**

![ChemicalStructure]

\[ \text{C}_{14}\text{H}_{18}\text{N} \]

197.28 g/mol

**Yield**  
87.5 mg, 0.44 mmol (89%)  
Starting material could not be separated (5%)

**\(^1\text{H-NMR}\)**  
\(400 \text{ MHz, CDCl}_3 \) \( \delta \) 7.41 – 7.37 (m, 2H), 7.38 – 7.29 (m, 2H), 7.28 – 7.22 (m, 1H), 7.11 (dd, \( J = 8.6, 7.3 \text{ Hz}, \text{ 2H} \)), 6.68 (tt, \( J = 7.3, 1.1 \text{ Hz}, \text{ 1H} \)), 6.57 – 6.52 (m, 2H), 4.51 (q, \( J = 6.7 \text{ Hz}, \text{ 1H} \)), 4.20 (brs, 1H), 1.54 (d, \( J = 6.7 \text{ Hz}, \text{ 3H} \)).

**\(^{13}\text{C-NMR}\)**  
\(101 \text{ MHz, CDCl}_3 \) \( \delta \) 147.2, 145.2, 129.2, 128.8, 127.0, 126.0, 117.5, 113.6, 53.7, 25.1.

**GC-MS**  
\( t_R = 8.83 \text{ min, (EI, 70 eV):} m/z = 197 [\text{M}^+], 182, 167, 152, 120, 105, 93, 77, 65, 51. \)

Analytical data were in full agreement with A. H. Vetter, A. Berkessel, *Synthesis* 1995, 419.

**1,2,3,4-Tetrahydroquinoline hydrochloride (2l)**

![ChemicalStructure]

\[ \text{C}_9\text{H}_{12}\text{ClN} \]

169.65 g/mol

**Yield**  
43.8 mg, 0.26 mmol (99%)

**\(^1\text{H-NMR}\)**  
\(300 \text{ MHz, CDCl}_3 \) \( \delta \) 7.46 – 7.33 (m, 3H), 7.30 (dd, \( J = 8.2, 1.7 \text{ Hz}, \text{ 1H} \)), 3.56 – 3.50 (m, 2H), 2.97 (t, \( J = 6.5 \text{ Hz}, \text{ 2H} \)), 2.25 – 2.07 (m, 2H).

**\(^{13}\text{C-NMR}\)**  
\(75 \text{ MHz, CDCl}_3 \) \( \delta \) 132.9, 132.2, 131.3, 130.4, 128.7, 124.1, 43.8, 25.8, 20.7.

**GC-MS**  
\( t_R = 7.01 \text{ min, (EI, 70 eV):} m/z = 132 [\text{M}^+-\text{H}], 118, 104, 91, 77, 65, 51. \)

6-Methyl-1,2,3,4-tetrahydroquinoline (2m)

\[
\text{C}_{10}\text{H}_{13}\text{N}
\]

147.22 g/mol

**Yield**

53.2 mg, 0.36 mmol (73%)

\(^1\text{H-NMR}\)

(400 MHz, CDCl\(_3\)) \(\delta\) 6.82 – 6.77 (m, 2H), 6.43 (d, \(J = 8.6\) Hz, 1H), 3.48 (brs, 1H), 3.31 – 3.25 (m, 2H), 2.75 (t, \(J = 6.4\) Hz, 2H), 2.22 (s, 3H), 2.00 – 1.89 (m, 2H).

\(^{13}\text{C-NMR}\)

(101 MHz, CDCl\(_3\)) \(\delta\) 142.4, 130.2, 127.4, 126.5, 121.8, 114.7, 42.3, 27.0, 22.5, 20.5.

**GC-MS**

\(t_R = 7.53\) min, (EI, 70 eV): \(m/z = 147\) [M\(^+\)], 132, 117, 103, 91, 77, 65, 51.


8-Methyl-1,2,3,4-tetrahydroquinoline (2n)

\[
\text{C}_{10}\text{H}_{13}\text{N}
\]

147.22 g/mol

**Yield**

28.4 mg, 0.19 mmol (39%)

\(^1\text{H-NMR}\)

(300 MHz, CDCl\(_3\)) \(\delta\) 6.92 – 6.82 (m, 2H), 6.57 (t, \(J = 7.4\) Hz, 1H), 3.59 (brs, 1H), 3.41 – 3.35 (m, 2H), 2.80 (t, \(J = 6.4\) Hz, 2H), 2.09 (s, 3H), 2.00 – 1.90 (m, 2H).

\(^{13}\text{C-NMR}\)

(75 MHz, CDCl\(_3\)) \(\delta\) 142.6, 128.0, 127.5, 121.5, 121.2, 116.7, 42.5, 27.4, 22.3, 17.3.

**GC-MS**

\(t_R = 7.48\) min, (EI, 70 eV): \(m/z = 147\) [M\(^+\)], 132, 117, 103, 91, 77, 65, 51.

6-Methoxy-1,2,3,4-tetrahydroquinoline (2o)

\[
\begin{align*}
\text{C}_{10}\text{H}_{13}\text{NO} & \quad 163.22 \text{ g/mol} \\
\text{Yield} & \quad 31.9 \text{ mg, 0.20 mmol (77\%)} \\
^{1}\text{H-NMR} & \quad (400 \text{ MHz, CDCl}_3 \delta 6.62 - 6.55 \text{ (m, 2H), 6.45 (d, } J = 8.5 \text{ Hz, 1H), 3.73 (s, 3H), 3.44 (brs, 1H), 3.26 (t, } J = 5.4 \text{ Hz, 2H), 2.76 (t, } J = 6.5 \text{ Hz, 2H), 1.98 - 1.89 \text{ (m, 2H)}.} \\
^{13}\text{C-NMR} & \quad (101 \text{ MHz, CDCl}_3 \delta 151.9, 139.0, 123.0, 115.7, 115.0, 113.0, 55.9, 42.5, 27.3, 22.6.} \\
\text{GC-MS} & \quad t_{R} = 8.31 \text{ min, (EI, 70 eV): } m/z = 163 [M^+], 148, 130, 118, 103, 91, 77, 65, 51.
\end{align*}
\]


6-Chloro-1,2,3,4-tetrahydroquinoline (2p)

\[
\begin{align*}
\text{C}_{9}\text{H}_{10}\text{ClN} & \quad 167.64 \text{ g/mol} \\
\text{Yield} & \quad 51.7 \text{ mg, 0.31 mmol (62\%)} \\
^{1}\text{H-NMR} & \quad (400 \text{ MHz, CDCl}_3 \delta 6.94 - 6.84 \text{ (m, 2H), 6.38 (dd, } J = 7.9, 0.9 \text{ Hz, 1H), 3.82 (brs, 1H), 3.28 (t, } J = 5.5 \text{ Hz, 2H), 2.72 (t, } J = 6.4 \text{ Hz, 2H), 1.97 - 1.84 \text{ (m, 2H)}.} \\
^{13}\text{C-NMR} & \quad (101 \text{ MHz, CDCl}_3 \delta 143.4, 129.2, 126.6, 123.0, 121.3, 115.2, 42.0, 27.0, 21.9.} \\
\text{GC-MS} & \quad t_{R} = 8.35 \text{ min, (EI, 70 eV): } m/z = 167 [M^+], 152, 130, 117, 103, 89, 77, 65, 51.
\end{align*}
\]

Methyl 1,2,3,4-tetrahydroquinoline-6-carboxylate (2q)

\[\text{C}_{11}\text{H}_{13}\text{NO}_2\]

Yield 93.4 mg, 0.49 mmol (98%)

\(^1H\)-NMR (300 MHz, CDCl\(\text{3}\)) \(\delta\) 7.66 – 7.61 (m, 2H), 6.41 – 6.37 (m, 1H), 4.35 (brs, 1H), 3.83 (s, 3H), 3.35 (t, \(J=5.7\) Hz, 2H), 2.76 (t, \(J=6.3\) Hz, 2H), 2.00 – 1.85 (m, 2H).

\(^{13}C\)-NMR (75 MHz, CDCl\(\text{3}\)) \(\delta\) 167.6, 148.8, 131.4, 129.2, 120.0, 117.6, 112.8, 51.6, 41.8, 27.0, 21.5.

GC-MS \(t_R = 9.68\) min, (EI, 70 eV): \(m/z = 191\) [M\(^+\)], 176, 160, 144, 132, 117, 104, 89, 77, 64, 51.

Analytical data were in full agreement with R. Adam, J. R. Cabrero-Antonino, A. Spannenberg, K. Junge, R. Jackstell, M. Beller, 

1,2,3,4-tetrahydroquinoxaline (2r)

\[\text{C}_{8}\text{H}_{10}\text{N}_2\]

Yield 64.2 mg, 0.48 mmol (95%)

\(^1H\)-NMR (400 MHz, XX) \(\delta\) 6.59 (dd, \(J=5.8, 3.4\) Hz, 2H), 6.50 (dd, \(J=5.8, 3.4\) Hz, 2H), 3.59 (brs, 2H), 3.42 (s, 4H).

\(^{13}C\)-NMR (101 MHz, XX) \(\delta\) 133.8, 118.9, 114.8, 41.5.

GC-MS \(t_R = 7.94\) min, (EI, 70 eV): \(m/z = 134\) [M\(^+\)], 119, 104, 92, 77, 66, 51.

Analytical data were in full agreement with R. Adam, J. R. Cabrero-Antonino, A. Spannenberg, K. Junge, R. Jackstell, M. Beller, 
Tetrahydroharmine (2s)

\[
\text{C}_{13}\text{H}_{18}\text{N}_{2}\text{O} \\
216.28 \text{ g/mol}
\]

**Yield**

104.6 mg, 0.48 mmol (97%)

**\(^1\)H-NMR**

(300 MHz, CDCl\(_3\)) \(\delta\) 8.06 (brs, 1H), 7.33 (d, \(J = 8.5\) Hz, 1H), 6.83 (d, \(J = 2.2\) Hz, 1H), 6.75 (dd, \(J = 8.6, 2.3\) Hz, 1H), 4.14 (q, \(J = 6.6\) Hz, 1H), 3.81 (s, 3H), 3.32 – 3.27 (m, 1H), 3.01 (ddd, \(J = 12.9, 8.6, 5.4\) Hz, 1H), 2.80 – 2.66 (m, 2H), 2.52 (brs, 1H), 1.43 (d, \(J = 6.7\) Hz, 3H).

**\(^{13}\)C-NMR**

(75 MHz, CDCl\(_3\)) \(\delta\) 156.2, 136.5, 135.8, 122.0, 118.7, 108.9, 108.2, 95.2, 55.9, 48.3, 42.7, 22.7, 20.8.

**GC-MS**

\(t_R = 10.76\) min, (EI, 70 eV): \(m/z = 216 [M^+], 201, 186, 172, 158, 144, 130, 115, 100, 89, 77, 63, 51.\)

5 ICP-OES measurement

The cobalt concentration in the organic layer after hydrogenation was determined by ICP-OES. Five stock solutions of CoCl\(_2\) in 35% HNO\(_3\) were prepared and a calibration curve was measured by integration of the emission signal of cobalt at 230.786 nm. Each data point corresponds to the mean value of three consecutive measurements correcting for the observed background signals.

![Calibration Curve for Cobalt](image)

For the actual measurement, styrene (0.25 mmol) was hydrogenated using 5 mol% of the cobalt nanoparticles (12.5 mmol/L Co) under standard conditions (2 bar H\(_2\), 3 h in 1 ml THF). After reaction, two reaction vials were placed on separate neodymium magnets and allowed to settle down for 2 and 24 h respectively. The organic phase was removed with a Pasteur Pipette, the solvent removed under vacuum and the residue dissolved in 5 ml dilute HNO\(_3\).

<table>
<thead>
<tr>
<th>PBcat135_2h</th>
<th>Peak Area</th>
<th>c (µmol/L)</th>
<th>PBcat135_24h</th>
<th>Peak Area</th>
<th>c (µmol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run 1</td>
<td>41231</td>
<td>9,07</td>
<td>Run 1</td>
<td>31624,5</td>
<td>6,98</td>
</tr>
<tr>
<td>Run 2</td>
<td>42226</td>
<td>9,29</td>
<td>Run 2</td>
<td>31439,7</td>
<td>6,94</td>
</tr>
<tr>
<td>Run 3</td>
<td>41338,2</td>
<td>9,09</td>
<td>Run 3</td>
<td>31299,3</td>
<td>6,91</td>
</tr>
<tr>
<td>Average</td>
<td>41598,4</td>
<td>9,15</td>
<td>Average</td>
<td>31454,5</td>
<td>6,94</td>
</tr>
<tr>
<td>StdDev</td>
<td>546,15</td>
<td>0,12</td>
<td>StdDev</td>
<td>163,10</td>
<td>0,04</td>
</tr>
</tbody>
</table>

This results in a cobalt concentration of 45.75±0.6 and 34.7±0.2 µmol/L in the organic phase after 2 and 24 h settle time respectively, which corresponds to 0.37 and 0.28% of the cobalt concentration in the reaction vessel.
6 ICP-MS measurement

In preparation for the measurement, half of the vials were charged with styrene (1 mmol) and 5 mol% of the cobalt nanoparticles (12.5 mmol/L Co), the other vials omitting the cobalt catalyst (blank reaction solution). All were hydrogenated under standard conditions (2 bar H₂, 3 h in 4 ml THF). After the reaction, each vial was put on a neodymium magnet and the organic phase was transferred to a new vial, leaving behind most of the cobalt metal. The vials were washed twice with an additional 1 ml of ethyl acetate. To the first set of vials (Co-reaction and blank) was then added 1 ml saturated ammonium chloride solution which was extracted three times with ethyl acetate, the second set was eluted through a short silica plug inside a Pasteur pipette using ethyl acetate. The solvent was subsequently removed from all vials under vacuum and the residue dissolved in 50 ml dilute HNO₃.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Peak Area</th>
<th>c (ng/mL)</th>
<th>nCo (nmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extraction</td>
<td>838524.5</td>
<td>0.80</td>
<td>0.6780</td>
</tr>
<tr>
<td>Extraction (blank)</td>
<td>23595.3</td>
<td>0.02</td>
<td>0.01696</td>
</tr>
<tr>
<td>Silica</td>
<td>52582.7</td>
<td>0.05</td>
<td>0.0424</td>
</tr>
<tr>
<td>Silica (blank)</td>
<td>13541.0</td>
<td>0.01</td>
<td>0.00848</td>
</tr>
</tbody>
</table>

This results in a cobalt concentration of 165 nmol/L and 8.5 nmol/L in the organic phase after extraction and elution respectively, which corresponds to 13.2 and 0.68 ppm of the cobalt concentration in the reaction vessel.
7 Functional group tolerance tests

![Chemical reactions and yields](image)

**Additives and yield of cumene:**

<table>
<thead>
<tr>
<th>Additive</th>
<th>Cumene Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeOH</td>
<td>&gt;99 (&gt;99)</td>
</tr>
<tr>
<td>98 (&gt;99)</td>
<td></td>
</tr>
<tr>
<td>74 (&gt;99)</td>
<td>52 (53)</td>
</tr>
<tr>
<td>48 (50)</td>
<td>0 (0)</td>
</tr>
<tr>
<td>34 (43)</td>
<td>1 (1)</td>
</tr>
<tr>
<td>0 (20)</td>
<td>0 (0)</td>
</tr>
<tr>
<td>0 (1)</td>
<td>0 (1)</td>
</tr>
<tr>
<td>0 (6)</td>
<td>0 (1)</td>
</tr>
<tr>
<td>0 (1)</td>
<td>0 (0)</td>
</tr>
<tr>
<td>0 (1)</td>
<td>3 (1)</td>
</tr>
<tr>
<td>0 (0)</td>
<td>7 (7)</td>
</tr>
<tr>
<td>3 (4)</td>
<td>0 (0)</td>
</tr>
</tbody>
</table>

**Figure S1:** Functional group tolerance of Co-NP catalyzed hydrogenation of \( \alpha \)-Methylstyrene in presence of 1 equiv. additive. Standard conditions: 0.25 mmol substrate in 1 mL THF; yields of hydrogenation product (cumene) determined by quantitative GC vs. internal reference n-pentadecane. Conversion of \( \alpha \)-Methylstyrene shown in parentheses.
8 Comparison of different Co-Np preparations

Figure S2. Hydrogenation of styrene using the nanoparticles isolated by centrifugation, separation by a magnet and using the in situ protocol. The conditions were 1.9 bar H₂, 5 mol% [Co], r.t., THF. The reaction yield was determined by measuring the consumption of H₂.

Kinetic experiments were carried out to compare the catalytic activity of the different catalyst systems described previously. Figure S2 shows a similar catalytic activity of the various nanoparticles, yielding complete conversion after 17 to 24 minutes.
9 Recycling experiments

The reactions were set up according to the general hydrogenation procedure with styrene (0.5 mmol) as substrate in 2 ml THF. The hydrogenations were carried out for 30 min each (2 bar H\textsubscript{2}, r.t., 5 mol\% Co-NP). After reaction, the autoclave was introduced into the glovebox and the reaction vial put on top of a neodymium magnet (cylindrical, 10 x 20 mm (height x diameter), N45) for 5 min. The solvent was removed using a Pasteur pipette and the particles washed once with 2 ml THF. New substrate and solvent were added, the vial was put back into the autoclave and a new hydrogenation reaction started. The organic phase was analyzed using quantitative GC-FID. After nine consecutive reactions, the particles were dissolved in 1 mL THF and stirred inside the glovebox overnight. The next day, three more runs were carried out. After these three reactions the particles were stirred again inside the glovebox for another 72 hours before a last hydrogenation reaction was started.
10 Particle Analyses

Purity and crystallinity

The purity of the as-prepared Co(0) nanoparticles was proven by X-ray powder diffraction (XRD) after powder sintering (800 °C, Ar). This treatment ensured crystallization of all products including potentially amorphous residual components (e.g. oxides and hydroxides). Despite the resultant non-nanoparticulate state, the presence of pure cobalt (cubic modification as majority phase with traces of a hexagonal phase) and the absence of any cobalt oxide impurities was validated (Figure S2).

Figure S3. XRD Co(0) powder samples after annealing (800 °C, Ar).
Particle size distribution

Average particle diameters of the Co(0) nanoparticles before and after the hydrogenation reaction were calculated by statistical evaluation of >200 particles on TEM images using the ImageJ 1.47v software. Figure S2 shows the results for [NaNaph]-made Co(0) nanoparticles (Co-NPs) isolated by centrifugation. Figure S3 shows the results for in situ-generated cobalt nanoparticles (in situ Co-NPs). It should be noted that dynamic light scattering (DLS) as an alternative analytical tool gives less conclusive results due to the magnetic interaction of the nanoparticles.

Figure S4. Particle size distribution according to statistical evaluation of TEM images (>200 particles) of cobalt nanoparticles (Co-NPs) before (red) and after (blue) hydrogenation reaction.

Figure S5. Particle size distribution according to statistical evaluation of TEM images (>200 particles) of in situ generated cobalt nanoparticles (in situ Co-NPs) before (red) and after (blue) hydrogenation reaction.
TEM Measurements

TEM images of Co(0) nanoparticles before and after the catalytical reaction are shown in Figure S5 and Figure S6 for ex situ and in situ generated nanoparticles.

**Figure S6.** TEM measurement of cobalt nanoparticles (Co-NP) before (left) and after (right) hydrogenation reaction.

**Figure S7.** TEM measurement of in situ generated cobalt nanoparticles (in situ Co-NP) before (left) and after (right) hydrogenation reaction.
11 Selected NMR-Spectra