On the quantitative recycling of Raney-Nickel catalysts on a lab-scale

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Supporting information

General
Toluene was freshly dried and distilled over sodium/benzophenone under an atmosphere of argon. [1,10]phenanthrolines and 2,9-dimethyl[1,10]phenanthrolines are commercially available from Lancaster and Acros. Synthesis of the 2,9-bisfunctionalized phenanthrolines was effected via sequential organolithium addition and MnO2-mediated oxidation (R = s-Bu, t-Bu, Ph, n-Bu; publication in preparation). All reactions were performed under argon in flame dried glassware using syringe-septum techniques. NMR spectra were obtained on a Bruker DPX 300. High pressure hydrogenations were performed in a 300 mL Parr autoclave (Parr 4842) fitted with a temperature control, gas inlet, and stirrer. Nickel atom absorption spectroscopy was performed with a Varian Techtron AA6 at 232 nm and referenced vs. nickel(II) standard solutions. High resolution mass spectra (HRMS) were obtained on a Varian MAT 711 and Finnigan Incos 500. Silica gel chromatography was performed with 60 (0.040-0.063 mm; pH = 6.5-7.5) silica gel from KMF. Uncorrected melting points were measured on a Büchi Dr. Tottoli 510 apparatus. CHN analysis was performed with an Elementar Vario EL.

Representative procedure:
A 50 mL Parr® high pressure reactor was charged with 0.83 mmol of 2,9-bisfunctionalized phenanthroline and 6 ml abs. ethanol. A teflon-coated magnetic stir bar covered with Raney-Nickel (5 mg, 0.083 mmol, 10 mol%) was added, and the reactor was pressurized with hydrogen (20 bar). The reaction was stirred at 100 °C (25 bar). After 16 h, the reactor was cooled to rt and slowly depressurized. The catalyst-covered stir bar was retrieved with a pair of tweezers, washed with ethanol (2 × 1 mL), and the solution passed through a Celite pad (3 cm). The filtrate was concentrated in an oil pump vacuum to give the analytically pure octahydrophenanthroline derivative. The stir bar was stored in ethanol or used for a new reaction without further manipulation within 7 days.
1,2,3,4,7,8,9,10-Octahydro[1,10]phenanthroline (1)

\[
\begin{align*}
1 & \quad 2 \quad 3 \quad NH \\
\text{NH} & \\
4 & \quad 5 & \quad 6
\end{align*}
\]

\( ^{1}H\text{-NMR (300 MHz, CDCl}_3 \text{): } \delta = 1.91 \text{ (m, 4H, H-5), 2.76 (t, 4H, 6.33 Hz, H-4), 3.32 (m, 4H, H-6), 6.47 (s, 2H, H-1) } \)

\( ^{13}C\text{-NMR (75 MHz, CDCl}_3 \text{): } \delta = 22.53 \text{ (C-4), 26.93 (C-5), 42.63 (C-6), 119.14 (C-1), 120.47 (C-2), 132.84 (C-3) } \)

\( \text{Mp. 70°C IR ATR [cm}^{-1}\text{]: 3334 (br,m), 3039 (w), 2920 (s), 2838 (s), 1614 (m), 1578 (s), 1491 (s), 1328 (s), 1264 (m), 1177 (m), 1117 (m) LR MS (EI, 70 eV, m/z): 188 M^+, 170, 159, 154, 145, 130, 117, 104, 91, 86, 80, 72, 65, 58, 51 } \)

2.9-Dimethyl-1,2,3,4,7,8,9,10-octahydro[1,10]phenanthroline (2)

\[
\begin{align*}
1 & \quad 2 \quad 3 \quad NH \\
\text{NH} & \\
4 & \quad 5(a,b) \quad 6 \quad 7
\end{align*}
\]

\( \text{dr: 2.2 / 1 (meso/rac) } ^{1}H\text{-NMR (300 MHz, CDCl}_3 \text{): } \delta = 1.31 \text{ (d, 6H, 5.9 Hz, H-7), 1.54 (m, 2H, H-5a), 1.94 (m, 2H, H-5b), 2.76 (m, 4H, H-4), 3.35 (br, 2H, H-6), 6.50 (s, 2H, H-7) } ^{13}C\text{-NMR (75 MHz, CDCl}_3 \text{): } \delta = 22.62 \text{ (C-7), 26.81 (C-4), 30.42 (C-5), 47.92 (C-6), 118.78 (C-1), 120.16 (C-2), 132.69 (C-3) } \)

\( \text{Mp. 76°C (from EtOH) IR ATR [cm}^{-1}\text{]: 3348 (w,br), 3059 (w), 2843 (s), 1615 (w), 1581 (s), 1447 (s), 1332 (s), 1256 (s), 1160 (m), 778 (m) LR MS (EI, 70 eV, m/z): 216 M^+, 201 (M-CH}_3, 185 (M-C}_2H}_5, 173, 159, 144, 130, 117, 103, 93, 86, 77, 65, 51 HR MS (m/z): } \text{calc. 216.163 M}^+ \text{ found 216.163 M}^+ \)

Crystal structure: The unit cell contains meso and rac isomers and exhibits some disorder with respect to C29 and C30 of the \( R,R-2 \) and meso-2 isomers (highlighted in yellow and blue atoms). \( S,S-2 \) exhibited no disordering. Structure refinement resulted in a statistical 3/1 (rac/meso) mixture in the crystal.

Crystal structures of the \( S,S\text{- meso-}, \text{ and } R,R\text{-isomers:} \)
Crystal data: (CCDC# 647735)

Temperature 100(2) K
Wavelength 0.71073 Å
Space-group P -1 - triclinic
Cell a=8.952(2), Å b=10.126(3), Å c=14.757(4) Å
      α=70.511(10)°, β=79.526(10)°, γ=76.960(10)°
Volume 1220.2(5) Å³
Z 4
Calculated density 1.178 g/m³
Absorption coefficient 0.070 mm⁻¹
F(000) 472
Crystal size 0.2 x 0.1 x 0.05 mm
Theta range for data collection 1.47 to 25.00 deg.
Limiting indices -10≤h≤10, -11≤k≤12, -13≤l≤17
Reflections collected / unique 4976 / 4031 [R(int) = 0.0556]
Reflection observed [I>2 σ (I)] 1380
Completeness to theta = 25.00 93.9 %
Absorption correction None
Refinement method Full-matrix least-squares on F²
Data / restraints / parameters 4031 / 0 / 326
Goodness-of-fit on F² 0.965
Final R indices [I>2 σ (I)] R1 = 0.0821, wR2 = 0.1982
R indices (all data) R1 = 0.2403, wR2 = 0.2672
Largest diff. peak and hole 0.293 and -0.230 e. Å⁻³

2,9-Di-sec-butyl-1,2,3,4,7,8,9,10-octahydro[1,10]phenanthroline (3)
**2,9-Di-tert-butyl-1,2,3,4,7,8,9,10-octahydro[1,10]phenanthroline (4)***

\[
\begin{align*}
\text{dr:} \quad 1.3 / 1 \quad (\text{meso/rac}) \\
^1\text{H-NMR (300 MHz, CDCl}_3\text{):} \quad \delta = 0.96 \text{ (br, H-5, 4H)}, 1.29 \text{ (s, br, H-5, 4H)}, 1.57 \text{ (m, H-7, H-9, 8H)}, 2.73 \text{ (m, H-4, 4H)}, 3.07 \text{ (m, H-6, 2H)} \\
^13\text{C-NMR (75 MHz, CDCl}_3\text{):} \quad \delta = 12.17 \text{ (C-10), 14.81 \text{ (C-8), 25.73 \text{ (C-9), 27.22 \text{ (C-4), 29.71 \text{ (C-5), 39.32 \text{ (C-7), 56.39 \text{ (C-6), 118.69 \text{ (C-1), 120.48 \text{ (C-2), 133.10 \text{ (C-3) IR ATR [cm}^{-1}]}}: 3048 \text{ (w), 2920 \text{ (s), 2853 \text{ (s), 1583 \text{ (m), 1480 \text{ (s), 1462 \text{ (s), 1347 \text{ (m), 1260 \text{ (m), 804 \text{ (m), 728 \text{ (m) LR MS (EI, 70 eV, m/z): 300 M}^+, 293, 243 \text{ (M-C}_4\text{H}_3\text{), 185, 171, 159, 144, 130, 117, 106, 93, 77, 67, 55 HR MS (m/z): calc. 300.257 M}^+ \text{ found 300.257 M}^+}}}}}}}}}}}}}
\end{align*}
\]

**2,9-Diphenyl-1,2,3,4,7,8,9,10-octahydro[1,10]phenanthroline (5)**

\[
\begin{align*}
\text{dr:} \quad 1.3 / 1 \quad (\text{meso/rac}) \\
^1\text{H-NMR (300 MHz, CDCl}_3\text{):} \quad \delta = 1.04 \text{ (s, 18H, H-8), 2.01 \text{ (m, 4H, H-5), 2.79 \text{ (m, 4H, H-4), 2.89 \text{ (m, 2H, H-6), 6.47 \text{ (s, 2H, H-1) 13C-NMR (75 MHz, CDCl}_3\text{):} \quad \delta = 21.00 \text{ (C-4), 26.38 \text{ (C-8), 27.62 \text{ (C-7), 33.65 \text{ (C-5), 61.42 \text{ (C-6), 118.49 \text{ (C-1), 120.45 \text{ (C-2), 133.41 \text{ (C-3) IR ATR [cm}^{-1}]}}: 3038 \text{ (w), 2950 \text{ (s), 2866 \text{ (s), 1586 \text{ (m), 1495 \text{ (s), 1362 \text{ (s), 1335 \text{ (m), 1120 \text{ (m), 781 \text{ (m), 768 \text{ (m) LR MS (EI, 70 eV, m/z): 300 M}^+, 243, 185, 159, 144, 130, 91, 79, 57 HR MS (m/z): calc. 300.257 M}^+ \text{ found 300.257 M}^+}}}}}}}}}}}
\end{align*}
\]
2,9-Dibutyl-1,2,3,4,7,8,9,10-octahydro[1,10]phenanthroline (6)

\[
\begin{align*}
\text{dr: } & 1.3 / 1 (\text{meso}/\text{rac}) \\
\text{H-NMR (300 MHz, CDCl}_3\text{): } & \delta = 0.99 (t, 6H, H-10), 1.20-1.62 (12H, H-7, H8, H9), 2.77 (m, 4H, H-4), 3.21 (m, 4H, H-5), 3.34 (m, 2H, H-6), 6.49 (s, 2H, H-1) \\
\text{C-NMR (75 MHz, CDCl}_3\text{): } & \delta = 14.17 (C-10), 22.94 (C-9), 26.65 (C-4), 28.43 (C-8), 36.68 (C-7), 42.74 (C-6), 52.33 (C-5), 118.93 (C-1), 120.42 (C-2), 132.74 (C-3) 2.62 (C-7), 26.81 (C-4), 30.42 (C-5), 47.92 (C-6), 118.78 (C-1), 120.16 (C-2), 132.69 (C-3) \\
\text{IR ATR [cm}^{-1}\text{]: } & 3048 (w), 2995 (s), 2925 (s), 2872 (m), 2854 (m), 1560 (m), 1521 (m), 1461 (m), 1377 (m), 796 (m) \\
\text{LR MS (EI, 70 eV, m/z): } & 300 M^+, 293, 243, 185, 159, 144, 93, 55 \\
\text{HR MS (m/z): } & \text{calc. } 300.257 M^+ \text{ found } 300.257 M^+
\end{align*}
\]

1,2-Diphenylethane (7)

A round-bottomed flask was charged with 90 mg (0.5 mmol) \textit{trans}-stilbene and 2 mL abs. methanol. A teflon-coated magnetic stir bar covered with Raney-Nickel (2 mg, 7 mol\%) was added, and the reaction mixture was stirred at room temperature under an atmosphere of 1 bar hydrogen. After 12 h, the stir bar was retrieved with a pair of tweezers, washed with ethanol
(2 × 1 mL), and the solution passed through a Celite pad (3 cm). The filtrate was concentrated in an oil pump vacuum to give analytically pure 1,2-diphenylethane (7, 98 % yield).

1H-NMR (300 MHz, CDCl3): δ = 2.95 (s, 4H, H5), 7.21-7.40 (10H, m, H-1,2,3) 13C-NMR (75 MHz, CDCl3): δ = 38.1 (C-5) , 126.0 (C-1), 128.5, 128.6, 141.9 (C-4). LR MS (EI, 70 eV, m/z): 182 M⁺, 165, 152, 104, 91, 77, 65, 51, 39.

1,3-Diphenyl-1-propanol (8)
A round-bottomed flask was charged with 105 mg (0.5 mmol) trans-1,3-diphenylprop-2-en-1-ol and 2 mL abs. methanol. A teflon-coated magnetic stir bar covered with Raney-Nickel (2 mg, 7 mol%) was added, and the reaction mixture was stirred at room temperature under an atmosphere of hydrogen. After 12 h, the catalyst-covered stir bar was retrieved with a pair of tweezers, washed with ethanol (2 × 1 mL), and the solution passed through a Celite pad (3 cm). The filtrate was concentrated in an oil pump vacuum to give analytically pure 1,3-diphenylpropan-1-ol (8, 99 % yield).

1H-NMR (300 MHz, CDCl3): δ = 2.08 (m, 2H, H-6), 2.70 (m, 2H, H-5), 4.67 (m, 1H, H-7), 7.14-7.38 (10H, m, H-1,2,3,9,10,11). 13C-NMR (75 MHz, CDCl3): δ = 32.1, 40.5, 73.9, 125.9, 127.7, 128.5, 141.8, 144.6. LR MS (EI, 70 eV, m/z): 212 M⁺, 194, 179, 165, 152, 139, 128, 115, 107, 91, 79, 77, 65, 51, 39.

8-Hydroxy-1,2,3,4-tetrahydroquinoline (9)
A 50 mL Parr® high pressure reactor was charged with 73 mg (0.5 mmol) of 8 hydroxyquinoline and 2 mL abs. ethanol. A teflon-coated magnetic stir bar covered with Raney-Nickel (2 mg, 7 mol%) was added, and the reactor was pressurized with hydrogen (30 bar). The reaction was stirred at 60 °C. After 12 h, the reactor was cooled to rt and slowly depressurized. The catalyst-covered stir bar was retrieved with a pair of tweezers, washed with ethanol (2 × 1 mL), and the solution passed through a Celite pad (3 cm). The filtrate was purified with flash chromatography (ethyl acetate/cyclohexane 1/3) and concentrated by oil pump vacuum to give analytically pure 8-hydroxytetrahydroquinoline 9 (88 % yield). The stir
bar was stored in ethanol or used for a new reaction without further manipulation within 7 days.

$$\begin{align*}
\text{NH}_2 \\
\text{OH}
\end{align*}$$

$^1$H-NMR (300 MHz, CDCl$_3$): $\delta = 1.93$ (m, 2H, H-2), 2.76 (m, 2H, H-3), 3.29 (m, 2H, H-1), 4.37 (2H, br, OH, NH), 6.28 - 6.79 (m, 3H, H-5,6,7). $^{13}$C-NMR (75 MHz, CDCl$_3$): $\delta =$ 22.22, 26.57, 41.82, 112.51, 117.25, 121.88, 133.41, 143.23. LR MS (EI, 70 eV, m/z): 149 M$^+$, 132, 103, 77, 54, 39

4-Aminophenol (10)

A 50 mL Parr® high pressure reactor was charged with 70 mg (0.5 mmol) of 4-nitrophenol and 2 mL abs. ethanol. A teflon-coated magnetic stir bar covered with Raney-Nickel (2 mg, 7 mol%) was added, and the reactor was pressurized with hydrogen (30 bar). The reaction was stirred at 60 °C. After 12 h, the reactor was cooled to rt and slowly depressurized. The catalyst-covered stir bar was retrieved with a pair of tweezers, washed with ethanol (2 × 1 mL), and the solution passed through a Celite pad (3 cm). The filtrate was concentrated in an oil pump vacuum to give analytically pure 4-aminophenol (10, 91% yield). The stir bar was stored in ethanol or used for a new reaction without further manipulation within 7 days.

$$\begin{align*}
\text{NH}_2 \\
\text{OH}
\end{align*}$$

$^1$H-NMR (300 MHz, DMSO): $\delta = 4.35$ (br, NH$_2$), 6.23-6.60 (m, 2H), 8.34 (br, OH). $^{13}$C-NMR (75 MHz, DMSO): $\delta =$ 115.68, 115.94 (2C), 141.06, 148.61.

Benzimidazolium chloride (11)

$^1$H-NMR (300 MHz, D$^4$-MeOD): $\delta =$ 1.82 (d, 6H, H-7), 2.13 (br, 2H, H-5), 2.51 (br, 2H, H-5), 3.15 (br, 4H, H-4), 4.84 (br, 2H, H-6), 7.37 (s, 2H, H-1), 9.77 (s, 2H, H-8) $^{13}$C-NMR (75 MHz, D$^4$-MeOD): $\delta =$ 18.53 (C-7), 21.97 (C-4), 30.85 (C-5), 52.81 (C-6), 122.92 (C-3),
123.76 (C-1), 127.96 (C-2), 135.92 (C-8) **Mp.** 178-180°C (from EtOH) **IR ATR [cm⁻¹]**: 3457 (br,m), 2940 (m), 2845 (m), 2713 (w), 1539 (m), 1503 (s), 1314 (s), 1215 (s), 1103 (m), 1057 (m), 950 (m), 838 (m) **MS dip EI (70 eV +)**: 262M⁺, 254, 226, 211,185, 169, 144, 115, 91, 77 **HR MS ESI (m/z)**: calc. 227.1548 M⁺ found 227.155 M⁺
2,9-Dimethyloctahydro[1,10]phenanthroline (2)
2,9-Dibutyloctahydro[1,10]phenanthroline (6)
5,9-Dimethyl-3,4,5,9,10,11-hexahydroimidazo[1,5,4,3-lmn][1,10]phenanthroline-6-ium chloride (11)