1. General information

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. THF was distilled over sodium/benzophenone. Carbon monoxide of >98% purity was obtained from NII KM (Moscow, Russia). $^1$H and $^{13}$C spectra were recorded in CDCl$_3$ and DMSO-$d_6$ on Bruker Avance 300, Bruker Avance 400, Varian Inova 400 spectrometers. Chemical shifts $\delta$ are reported in ppm relative to the solvent resonance signal as an internal standard. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet, br = broad; coupling constants are given in Hertz (Hz).

2. Experimental section

\textbf{$N$-(4-chlorobenzyl)-4-methoxyaniline}

\[\text{Cl} \quad \text{N} \quad \text{H} \quad \text{O} \quad \text{Cl}\]

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.34 (s, 4H), 6.82 (d, $J = 8.8$ Hz, 2H), 6.61 (d, $J = 8.8$ Hz, 2H) 4.28 (s, 2H), 3.77 (s, 3H).

NMR spectra are in agreement with the literature data.$^1$

\textbf{Rh/CO}

Rh$_2$(OAc)$_4$ (5.1 mg, 12 $\mu$mol, 0.7 mol %), $p$-anisidine (243.9 mg, 1.98 mmol) and 4-chlorobenzaldehyde (231.9 mg, 1.65 mmol) were charged into a glass vial in a 10 mL stainless autoclave. 0.7 mL of THF was added and autoclave was sealed, flushed three times with 3 atm of CO, and then charged with 50 atm CO. The reactor was placed into an oil bath preheated to 120 $^\circ$C. After 22 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH$_2$Cl$_2$; in order to get rid of catalyst reaction mixture was passed through small pad of silica gel; combined solvents were removed on a rotary evaporator. The yield of $N$-(4-chlorobenzyl)-4-methoxyaniline (94%) was determined by $^1$H NMR with mesitylene as internal standard.

\textbf{NaBH$_4$}

A 10 mL round bottom flask was charged with 4-chlorobenzaldehyde (33.7 mg, 0.24 mmol), $p$-anisidine (24.6 mg, 0.2 mmol) and MeOH (2 mL). The mixture was refluxed for 2 h. Sodium borohydride (15.1 mg, 0.4 mmol) was added to reaction mixture. The suspension was stirred at room temperature overnight. Then reaction mixture was refluxed for additional 2 h. After reaction completion, it was diluted with water, and the product extracted with EtOAc. Organic layer was washed with brine 2 times, dried (Na$_2$SO$_4$), and solvent was evaporated to give the product. The
yield of \(N\)-(4-chlorobenzyl)-4-methoxyaniline (94\%) was determined by \(^1\)H NMR with DMF as internal standard.

**NaBH\((\text{OAc})_3\)**

A 10 mL round bottom flask with input for Ar was charged with 4-chlorobenzaldehyde (28.1 mg, 0.2 mmol), \(p\)-anisidine (24.6 mg, 0.2 mmol) and 1,2-dichloroethane (0.7 mL). The mixture was stirred at room temperature under Ar atmosphere for 15 min. Sodium triacetoxyborohydride (59.4 mg, 0.28 mmol) was added to reaction mixture. The suspension was stirred at room temperature under Ar atmosphere for 18 h. Then the reaction mixture was quenched with aqueous saturated \(\text{NaHCO}_3\) and extracted three times with 10 mL of EtOAc. The organic layer was dried over anhydrous \(\text{Na}_2\text{SO}_4\), filtered and evaporated. The yield of \(N\)-(4-chlorobenzyl)-4-methoxyaniline (99\%) was determined by \(^1\)H NMR with DMF as internal standard.

**NaBH\(_3\)CN**

A penicillin vial was charged with \(p\)-anisidine (24 mg, 0.20 mmol), glacial acetic acid (11 µL, 0.20 mmol) and methanol (2 mL). After that, 4-chlorobenzaldehyde (28 mg, 0.20 mmol) and solution of NaBH\(_3\)CN (25 mg, 0.40 mmol) in 1 mL of MeOH were added. The reaction mixture was stirred at room temperature overnight. Then the solution was evaporated and the residue was taken up with 10 mL of water and extracted two times with 15 mL of CH\(_2\)Cl\(_2\). The organic layers were combined, dried over anhydrous \(\text{Na}_2\text{SO}_4\), filtered and evaporated. The yield of \(N\)-(4-chlorobenzyl)-4-methoxyaniline (93\%) was determined by \(^1\)H NMR with mesitylene as internal standard.

**\(H_2/Pd/C\), general conditions**

10\% Pd/C (wet support, water content is 56\%) (24 mg, 10 µmol, 5 mol\%), \(p\)-anisidine (24.6 mg, 0.2 mmol), 4-chlorobenzaldehyde (28.1 mg, 0.2 mmol) and stirring bar were charged into a glass vial in a 10 mL stainless autoclave. 0.5 mL of EtOH was added and autoclave was sealed and charged with 5 atm H\(_2\) at 40 °C. After 24 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH\(_2\)Cl\(_2\); combined solvents were removed on a rotary evaporator. No product was detected. Main component of the resulting reaction mixture is \(p\)-anisidine hydrochloride.

**\(H_2/Pd/C\), 1\% of Pd**

10\% Pd/C (wet support, water content is 56\%) (4.8 mg, 2 µmol, 1 mol\%), \(p\)-anisidine (24.6 mg, 0.20 mmol), 4-chlorobenzaldehyde (28.1 mg, 0.20 mmol), 0.2 mL of MeOH and stirring bar were charged into a glass vial in a 10 mL stainless autoclave. Reaction mixture was stirred overnight at room temperature. Then autoclave was charged with 3 atm H\(_2\) at room temperature. After 15 h of stirring, the reactor was depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH\(_2\)Cl\(_2\); combined solvents were removed on a rotary evaporator. No product was detected. Main component of the resulting reaction mixture is \(p\)-anisidine hydrochloride.

**4-(((4-methoxyphenyl)amino)methyl)phenol**

S2
\( ^1H \text{ NMR} (400 \text{ MHz, DMSO-}d_6) \delta 9.24 (s, 1H), 7.13 (d, J = 8.4 \text{ Hz, } 2H), 6.71 \text{ – } 6.63 (m, 4H), 6.51 (d, J = 8.9 \text{ Hz, } 2H), 4.05 (s, 2H), 3.60 (s, 3H). \)

NMR spectra are in agreement with the literature data.\(^2\)

**Rh/CO**

Rh\(_2\)(OAc)\(_4\) (5.1 mg, 12 \( \mu \text{mol, 0.7 mol }% \)), \( p \)-anisidine (243.9 mg, 1.98 \( \text{ mmol} \)) and 4-hydroxybenzaldehyde (201.5 mg, 1.65 \( \text{ mmol} \)) were charged into a glass vial in a 10 mL stainless autoclave. 0.7 mL of THF was added and autoclave was sealed, flushed three times with 3 atm of CO, and then charged with 50 atm CO. The reactor was placed into an oil bath preheated to 120 \( ^\circ \text{C} \). After 22 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH\(_2\)Cl\(_2\); in order to get rid of catalyst reaction mixture was passed through small pad of silica gel; combined solvents were removed on a rotary evaporator. The yield of 4-(((4-methoxyphenyl)amino)methyl)phenol (85\%) was determined by \( ^1H \text{ NMR} \) with mesitylene as internal standard.

**NaBH\(_4\)**

A 10 mL round bottom flask was charged with 4-hydroxybenzaldehyde (29.3 mg, 0.24 \( \text{ mmol} \)), \( p \)-anisidine (24.6 mg, 0.2 \( \text{ mmol} \)) and MeOH (2 mL). The mixture was refluxed for 2 h. Sodium borohydride (15.1 mg, 0.4 \( \text{ mmol} \)) was added to reaction mixture. The suspension was stirred at room temperature overnight. Then reaction mixture was refluxed for additional 2 h. After reaction completion, it was diluted with water, and the product extracted with EtOAc. Organic layer was washed with brine 2 times, dried (Na\(_2\)SO\(_4\)), and solvent was evaporated to give the product. The yield of 4-(((4-methoxyphenyl)amino)methyl)phenol (96\%) was determined by \( ^1H \text{ NMR} \) with DMF as internal standard.

**NaBH\(_3\)(OAc)\(_3\)**

A 10 mL round bottom flask with input for Ar was charged with 4-hydroxybenzaldehyde (24.4 mg, 0.2 \( \text{ mmol} \)), \( p \)-anisidine (24.6 mg, 0.2 \( \text{ mmol} \)) and 1,2-dichloroethane (0.7 mL). The mixture was stirred at room temperature under Ar atmosphere for 15 min. Sodium triacetoxymethoxyborohydride (59.4 mg, 0.28 \( \text{ mmol} \)) was added to reaction mixture. The suspension was stirred at room temperature under Ar atmosphere for 18 h. Then the reaction mixture was quenched with aqueous saturated NaHCO\(_3\) and extracted three times with 10 mL of EtOAc. The organic layer was dried over anhydrous Na\(_2\)SO\(_4\), filtered and evaporated. The yield of 4-(((4-methoxyphenyl)amino)methyl)phenol (93\%) was determined by \( ^1H \text{ NMR} \) with DMF as internal standard.

**NaBH\(_3\)CN**

S3
A penicillin vial was charged with \( p \)-anisidine (23 mg, 0.19 mmol), glacial acetic acid (11 \( \mu \)L, 0.19 mmol) and methanol (2 mL). After that, 4-hydroxybenzaldehyde (23 mg, 0.19 mmol) and solution of NaBH\(_4\)CN (24 mg, 0.38 mmol) in 1 mL of MeOH were added. The reaction mixture was stirred at room temperature overnight. Then the solution was evaporated and the residue was taken up with 10 mL of water and extracted two times with 15 mL of CH\(_2\)Cl\(_2\). The organic layers were combined, dried over anhydrous Na\(_2\)SO\(_4\), filtered and evaporated. The yield of 4-(((4-methoxyphenyl)amino)methyl)phenol (82\%) was determined by \(^1\)H NMR with mesitylene as internal standard.

\( \text{H}_2/\text{Pd/C, general conditions} \)

10\% Pd/C (wet support, water content is 56\%) (24 mg, 10 \( \mu \)mol, 5 mol\%), \( p \)-anisidine (24.6 mg, 0.2 mmol), 4-hydroxybenzaldehyde (24.5 mg, 0.2 mmol) and stirring bar were charged into a glass vial in a 10 mL stainless autoclave. 0.5 mL of EtOH was added and autoclave was sealed and charged with 5 atm H\(_2\) at 40 \(^\circ\)C. After 24 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH\(_2\)Cl\(_2\); combined solvents were removed on a rotary evaporator. No product was detected. Resulting reaction mixture consists of \( p \)-anisidine and \( p \)-cresol.

\( \text{H}_2/\text{Pd/C, 1\% of Pd} \)

10\% Pd/C (wet support, water content is 56\%) (4.8 mg, 2 \( \mu \)mol, 1 mol\%), \( p \)-anisidine (24.6 mg, 0.2 mmol), 4-hydroxybenzaldehyde (24.5 mg, 0.20 mmol), 0.2 mL of MeOH and stirring bar were charged into a glass vial in a 10 mL stainless autoclave. Reaction mixture was stirred overnight at room temperature. Then autoclave was charged with 3 atm H\(_2\) at room temperature. After 15 h of stirring, the reactor was depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH\(_2\)Cl\(_2\); combined solvents were removed on a rotary evaporator. The yield of 4-(((4-methoxyphenyl)amino)methyl)phenol (48\%) was determined by \(^1\)H NMR with mesitylene as internal standard. The rest is \( p \)-anisidine and \( p \)-cresol.

4-methoxy-\( N \)-(pyridin-4-yl)methyl)aniline

\( ^1 \)H NMR (300 MHz, CDCl\(_3\)) \( \delta \) 8.55 (d, \( J = 4.5 \) Hz, 2H), 7.32 – 7.28 (d, \( J = 4.5 \) Hz, 2H), 6.81 – 6.75 (d, \( J = 9.0 \) Hz, 2H), 6.54 (d, \( J = 9.0 \) Hz, 2H), 4.32 (s, 2H), 3.74 (s, 3H).

NMR spectra are in agreement with the literature data.\(^3\)

\( \text{Rh/CO} \)

Rh\(_2\)(OAc)\(_4\) (5.1 mg, 12 \( \mu \)mol, 0.7 mol \%), \( p \)-anisidine (243.9 mg, 1.98 mmol) and 4-pyridinecarboxaldehyde (155 \( \mu \)L, 1.65 mmol) were charged into a glass vial in a 10 mL stainless autoclave. 0.7 mL of THF was added and autoclave was sealed, flushed three times with 3 atm of CO, and then charged with 50 atm CO. The reactor was placed into an oil bath preheated to 120
°C. After 22 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH₂Cl₂; in order to get rid of catalyst reaction mixture was passed through small pad of silica gel; combined solvents were removed on a rotary evaporator. The yield of 4-methoxy-N-(pyridin-4-ylmethyl)aniline (89%) was determined by ¹H NMR with mesitylene as internal standard.

\textbf{NaBH₄}

A 10 mL round bottom flask was charged with 4-pyridinecarboxaldehyde (23 µL, 0.24 mmol), \( p \)-anisidine (24.6 mg, 0.2 mmol) and MeOH (2 mL). The mixture was refluxed for 2 h. Sodium borohydride (15.1 mg, 0.4 mmol) was added to reaction mixture. The suspension was stirred at room temperature overnight. Then reaction mixture was refluxed for additional 2 h. After reaction completion, it was diluted with water, and the product extracted with EtOAc. Organic layer was washed with brine 2 times, dried (Na₂SO₄), and solvent was evaporated to give the product. The yield of 4-methoxy-N-(pyridin-4-ylmethyl)aniline (92%) was determined by ¹H NMR with DMF as internal standard.

\textbf{NaBH(OAc)₃}

A 10 mL round bottom flask with input for Ar was charged with 4-pyridinecarboxaldehyde (18.8 µL, 0.2 mmol), \( p \)-anisidine (24.6 mg, 0.2 mmol) and 1,2-dichloroethane (0.7 mL). The mixture was stirred at room temperature under Ar atmosphere for 15 min. Sodium triacetoxyborohydride (59.4 mg, 0.28 mmol) was added to reaction mixture. The suspension was stirred at room temperature under Ar atmosphere for 18 h. Then the reaction mixture was quenched with aqueous saturated NaHCO₃ and extracted three times with 10 mL of EtOAc. The organic layer was dried over anhydrous Na₂SO₄, filtered and evaporated. The yield of 4-methoxy-N-(pyridin-4-ylmethyl)aniline (83%) was determined by ¹H NMR with mesitylene as internal standard.

\textbf{NaBH₃CN}

A penicillin vial was charged with \( p \)-anisidine (25 mg, 0.21 mmol), glacial acetic acid (12 µL, 0.21 mmol) and methanol (2 mL). After that, 4-pyridinecarboxaldehyde (19 µL, 0.21 mmol) and solution of NaBH₃CN (26 mg, 0.42 mmol) in 1 mL of MeOH were added. The reaction mixture was stirred at room temperature overnight. Then the solution was evaporated and the residue was taken up with 10 mL of water and extracted two times with 15 mL of CH₂Cl₂. The organic layers were combined, dried over anhydrous Na₂SO₄, filtered and evaporated. The yield of 4-methoxy-N-(pyridin-4-ylmethyl)aniline (92%) was determined by ¹H NMR with mesitylene as internal standard.

\textbf{H₂/Pd/C, general conditions}

10% Pd/C (wet support, water content is 56%) (24 mg, 10 µmol, 5 mol%), \( p \)-anisidine (24.6 mg, 0.2 mmol), 4-pyridinecarboxaldehyde (19 µL, 0.2 mmol) and stirring bar were charged into a glass vial in a 10 mL stainless autoclave. 0.5 mL of EtOH was added and autoclave was sealed and charged with 5 atm H₂ at 40 °C. After 24 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH₂Cl₂; combined solvents were removed on a rotary evaporator. 11% of the product was detected by NMR with DMF as internal standard. The rest is complex mixture of byproducts.
$H_2/Pd/C$, 1% of Pd

10% Pd/C (wet support, water content is 56%) (4.8 mg, 2 µmol, 1 mol%), $p$-anisidine (24.6 mg, 0.2 mmol), 4-pyridinecarboxaldehyde (19 µL, 0.2 mmol), 0.2 mL of MeOH and stirring bar were charged into a glass vial in a 10 mL stainless autoclave. Reaction mixture was stirred overnight at room temperature. Then autoclave was charged with 3 atm H$_2$ at room temperature. After 15 h of stirring, the reactor was depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH$_2$Cl$_2$; combined solvents were removed on a rotary evaporator. The yield of 4-methoxy-$N$-(pyridin-4-ylmethyl)aniline (41%) was determined by $^1$H NMR with mesitylene as internal standard. The rest is complex mixture of byproducts.

$N$-(3-nitrobenzyl)aniline

\[
\begin{align*}
\text{O}_2\text{N} & \quad \text{Ph} \\
\text{N} & \quad \text{Ph}
\end{align*}
\]

$^1$H NMR (300 MHz, CDCl$_3$) δ 8.26 (s, 1H), 8.13 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 7.5 Hz, 1H), 7.51 (t, J = 7.9 Hz, 1H), 7.19 (d, J = 7.4 Hz, 2H), 6.77 (t, J = 7.3 Hz, 1H), 6.62 (d, J = 7.7 Hz, 2H), 4.47 (s, 2H).

NMR spectra are in agreement with the literature data.$^4$

Rh/CO

Rh$_2$(OAc)$_4$ (5.1 mg, 12 µmol, 0.7 mol %), aniline (181 µL, 1.98 mmol) and 3-nitrobenzaldehyde (250 mg, 1.65 mmol) were charged into a glass vial in a 10 mL stainless autoclave. 0.7 mL of THF was added and autoclave was sealed, flushed three times with 3 atm of CO, and then charged with 50 atm CO. The reactor was placed into an oil bath preheated to 120 °C. After 22 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH$_2$Cl$_2$; in order to get rid of catalyst reaction mixture was passed through small pad of silica gel; combined solvents were removed on a rotary evaporator. The yield of $N$-(3-nitrobenzyl)aniline (86%) was determined by $^1$H NMR with mesitylene as internal standard.

NaBH$_4$

A 10 mL round bottom flask was charged with 3-nitrobenzaldehyde (36.3 mg, 0.24 mmol), aniline (18 µL, 0.20 mmol) and MeOH (2 mL). The mixture was refluxed for 2 h. Sodium borohydride (15.1 mg, 0.4 mmol) was added to reaction mixture. The suspension was stirred at room temperature overnight. Then reaction mixture was refluxed for additional 2 h. After reaction completion, it was diluted with water, and the product extracted with EtOAc. Organic layer was washed with brine 2 times, dried (Na$_2$SO$_4$), and solvent was evaporated to give the product. The yield of $N$-(3-nitrobenzyl)aniline (10%) was determined by $^1$H NMR with DMF as internal standard. The rest is a mixture of 3-nitrobenzyl alcohol and aniline.

NaBH$_4$ + Ti(OiPr)$_4$
After removing traces of moisture and oxygen of air from Schlenk glassware, it was charged with 3-nitrobenzaldehyde (36.3 mg, 0.24 mmol), aniline (18 µL, 0.20 mmol), Ti(Oi-Pr)$_4$ (119 µL, 0.4 mmol) and dry THF (1.5 mL). Reaction mixture was stirred at room temperature for 3 h under Ar. Then, THF was evaporated under reduced pressure. Sodium borohydride (15.1 mg, 0.4 mmol) and MeOH (2 mL) were added and refluxed for 4 h. After reaction completion, reaction mixture was diluted with distilled water and extracted two times with 15 mL of CH$_2$Cl$_2$. The CH$_2$Cl$_2$ extract was dried (Na$_2$SO$_4$), and solvent was evaporated to give the product. The yield of N-(3-nitrobenzyl)aniline (77%) was determined by $^1$H NMR with mesitilene as internal standard.

$\text{NaBH}_4(OAc)_3$

A 10 mL round bottom flask with input for Ar was charged with 3-nitrobenzaldehyde (30.2 mg, 0.2 mmol), aniline (18.3 µL, 0.2 mmol) and 1,2-dichloroethane (0.7 mL). The mixture was stirred at room temperature under Ar atmosphere for 15 min. Sodium triacetoxyborohydride (59.4 mg, 0.28 mmol) was added to reaction mixture. The suspension was stirred at room temperature under Ar atmosphere for 18 h. Then the reaction mixture was quenched with aqueous saturated NaHCO$_3$ and extracted three times with 10 mL of EtOAc. The organic layer was dried over anhydrous Na$_2$SO$_4$, filtered and evaporated. The yield of N-(3-nitrobenzyl)aniline (75%) was determined by $^1$H NMR with DMF as internal standard.

$\text{NaBH}_3\text{CN}$

A penicillin vial was charged with aniline (18 µL, 0.20 mmol), glacial acetic acid (11 µL, 0.20 mmol) and methanol (2 mL). After that, 3-nitrobenzaldehyde (30 mg, 0.20 mmol) and solution of NaBH$_3$CN (25 mg, 0.40 mmol) in 1 mL of MeOH were added. The reaction mixture was stirred at room temperature overnight. Then the solution was evaporated and the residue was taken up with 10 mL of water and extracted two times with 15 mL of CH$_2$Cl$_2$. The organic layers were combined, dried over anhydrous Na$_2$SO$_4$, filtered and evaporated. The yield of N-(3-nitrobenzyl)aniline (99%) was determined by $^1$H NMR with DMF as internal standard.

$\text{H}_2$/Pd/C, general conditions

10% Pd/C (wet support, water content is 56%) (24 mg, 10 µmol, 5 mol%), aniline (18 µL, 0.20 mmol), 3-nitrobenzaldehyde (30.2 mg, 0.2 mmol) and stirring bar were charged into a glass vial in a 10 mL stainless autoclave. 0.5 mL of EtOH was added and autoclave was sealed and charged with 5 atm H$_2$ at 40 °C. After 24 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH$_2$Cl$_2$; combined solvents were removed on a rotary evaporator. Product was not detected by NMR. NMR analysis have shown complete reduction of nitro group.

$\text{H}_2$/Pd/C, 1% of Pd

10% Pd/C (wet support, water content is 56%) (4.8 mg, 2 µmol, 1 mol%), aniline (18 µL, 0.20 mmol), 3-nitrobenzaldehyde (30.2 mg, 0.20 mmol), 0.2 mL of MeOH and stirring bar were charged into a glass vial in a 10 mL stainless autoclave. Reaction mixture was stirred overnight at room temperature. Then autoclave was charged with 3 atm H$_2$ at room temperature. After 15 h of stirring, the reactor was depressurized. The reaction mixture was transferred into a flask and the
autoclave was washed with CH₂Cl₂; combined solvents were removed on a rotary evaporator. Product was not detected by NMR. NMR analysis have shown complete reduction of nitro group.

**N-benzyl-1-phenylethan-1-amine**

\[
\begin{align*}
\text{N} & \text{-benzyl-1-phenylethan-1-amine} \\
\end{align*}
\]

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.33-7.18 (m, 10H), 3.78 (q, \(J = 6.6\) Hz, 1H), 3.63 (d, \(J = 13.3\) Hz, 1H) 3.57 (d, \(J = 13.3\) Hz, 1H), 1.33 (d, \(J = 6.6\) Hz, 3H).

NMR spectra are in agreement with the literature data.\(^5\)

**Rh/CO**

Rh\(_2\)(OAc)\(_4\) (5.1 mg, 12 µmol, 0.7 mol %), benzylamine (216 µL, 1.98 mmol) and acetophenone (193 µL, 1.65 mmol) were charged into a glass vial in a 10 mL stainless autoclave. 0.7 mL of THF was added and autoclave was sealed, flushed three times with 3 atm of CO, and then charged with 50 atm CO. The reactor was placed into an oil bath preheated to 120 °C. After 22 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH₂Cl₂; in order to get rid of catalyst reaction mixture was passed through small pad of silica gel; combined solvents were removed on a rotary evaporator. The yield of N-benzyl-1-phenylethan-1-amine (85%) was determined by \(^1\)H NMR with mesitylene as internal standard.

**NaBH\(_4\)**

A 10 mL round bottom flask was charged with acetophenone (28 µL, 0.24 mmol), benzyamine (22 µL, 0.20 mmol) and MeOH (2 mL). The mixture was refluxed for 2 h. Sodium borohydride (15.1 mg, 0.4 mmol) was added to reaction mixture. The suspension was stirred at room temperature overnight. Then reaction mixture was refluxed for additional 2 h. After reaction completion, it was diluted with water, and the product extracted with EtOAc. Organic layer was washed with brine two times, dried (Na\(_2\)SO\(_4\)), and solvent was evaporated to give the product. The yield of N-benzyl-1-phenylethan-1-amine (32%) was determined by \(^1\)H NMR with DMF as internal standard. The rest is a mixture of 1-phenylethan-1-ol and benzylamine.

**NaBH\(_4\) + Ti(OiPr)\(_4\)**

After removing traces of moisture and oxygen of air from Schlenk glassware, it was charged with acetophenone (28 µL, 0.24 mmol), benzylamine (22 µL, 0.20 mmol), Ti(Oi-Pr)\(_4\) (119 µL, 0.4 mmol) and dry THF (1.5 mL). Reaction mixture was stirred at room temperature for 3 h under Ar. Then, THF was evaporated under reduced pressure. Sodium borohydride (15.1 mg, 0.4 mmol) and MeOH (2 mL) were added and refluxed for 4 h. After reaction completion, reaction mixture was diluted with distilled water and extracted two times with 15 mL of CH\(_2\)Cl\(_2\). The CH\(_2\)Cl\(_2\) extract was dried (Na\(_2\)SO\(_4\)), and solvent was evaporated to give the product. The yield of N-benzyl-1-phenylethan-1-amine (>99%) was determined by \(^1\)H NMR with mesitylene as internal standard.
**NaBH(OAc)$_3$**

A 10 mL round bottom flask with input for Ar was charged with acetophenone (23 µL, 0.2 mmol), benzylamine (22 µL, 0.2 mmol) and 1,2-dichloroethane (0.7 mL). The mixture was stirred at room temperature under Ar atmosphere for 15 min. Sodium triacetoxyborohydride (59.4 mg, 0.28 mmol) was added to reaction mixture. The suspension was stirred at room temperature under Ar atmosphere for 18 h. Then the reaction mixture was quenched with aqueous saturated NaHCO$_3$ and extracted three times with 10 mL of EtOAc. The organic layer was dried over anhydrous Na$_2$SO$_4$, filtered and evaporated. The yield of N-benzyl-1-phenylethan-1-amine (range of yields for four experiments 58-74%) was determined by $^1$H NMR with mesitylene as internal standard. The rest is acetophenone and mixture of byproducts.

**NaBH(OAc)$_3$ + AcOH optimized conditions**

A 10 mL round bottom flask with input for Ar was charged with acetophenone (23 µL, 0.2 mmol), benzylamine (22 µL, 0.2 mmol), glacial acetic acid (12 µL, 0.2 mmol) and 1,2-dichloroethane (0.7 mL). The mixture was stirred at room temperature under Ar atmosphere for 15 min. Sodium triacetoxyborohydride (59.4 mg, 0.28 mmol) was added to reaction mixture. The suspension was stirred at room temperature under Ar atmosphere for 18 h. Then the reaction mixture was quenched with aqueous saturated NaHCO$_3$ and extracted three times with 10 mL of EtOAc. The organic layer was dried over anhydrous Na$_2$SO$_4$, filtered and evaporated. The yield of N-benzyl-1-phenylethan-1-amine (69%) was determined by $^1$H NMR with mesitylene as internal standard. The rest is acetophenone (11%).

**NaBH$_3$CN**

A penicillin vial was charged with benzylamine (18 µL, 0.17 mmol), glacial acetic acid (10 µL, 0.17 mmol) and methanol (2 mL). After that, acetophenone (19 µL, 0.17 mmol) and solution of NaBH$_3$CN (21 mg, 0.34 mmol) in 1 mL of MeOH were added. The reaction mixture was stirred at room temperature overnight. Then the solution was evaporated and the residue was taken up with 10 mL of water and extracted two times with 15 mL of CH$_2$Cl$_2$. The organic layers were combined, dried over anhydrous Na$_2$SO$_4$, filtered and evaporated. The yield of N-benzyl-1-phenylethan-1-amine (23%) was determined by $^1$H NMR with mesitylene as internal standard. The rest is starting materials.

**NaBH$_3$CN + Ti(OiPr)$_4$**

After removing traces of moisture and oxygen of air from Schlenk glassware, it was charged with acetophenone (22 µL, 0.19 mmol), benzylamine (21 mg, 0.19 mmol), Ti(Oi-Pr)$_4$ (113 µL, 0.38 mmol) and dry THF (1.5 mL). Reaction mixture was stirred at room temperature for 4 h under Ar. Then, THF was evaporated under reduced pressure. Solution of sodium cyanoborohydride (24 mg, 0.38 mmol) in MeOH (2 mL) was added and refluxed for 4 h. After reaction completion, reaction mixture was diluted with distilled water and extracted two times with 15 mL of CH$_2$Cl$_2$. The CH$_2$Cl$_2$ extract was dried (Na$_2$SO$_4$), and solvent was evaporated. The yield of N-benzyl-1-phenylethan-1-amine (65%) was determined by $^1$H NMR with mesitylene as internal standard.

**H$_2$/Pd/C, general conditions**

S9
10% Pd/C (wet support, water content is 56%) (24 mg, 10 µmol, 5 mol%), benzylationine (22 µL, 0.20 mmol), acetophenone (23 µL, 0.2 mmol) and stirring bar were charged into a glass vial in a 10 mL stainless autoclave. 0.5 mL of EtOH was added and autoclave was sealed and charged with 5 atm H₂ at 40 °C. After 24 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH₂Cl₂; combined solvents were removed on a rotary evaporator. Product was not detected by NMR. The main component of reaction mixture is 1-phenylethan-1-ol.

**H₂/Pd/C, 1% of Pd**

10% Pd/C (wet support, water content is 56%) (4.8 mg, 2 µmol, 1 mol%), benzylationine (22 µL, 0.20 mmol), acetophenone (23 µL, 0.20 mmol), 0.2 mL of MeOH and stirring bar were charged into a glass vial in a 10 mL stainless autoclave. Reaction mixture was stirred overnight at room temperature. Then autoclave was charged with 3 atm H₂ at room temperature. After 15 h of stirring, the reactor was depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH₂Cl₂; combined solvents were removed on a rotary evaporator. Product was not detected by NMR.

**4-methoxy-N-(3-phenylpropyl)aniline**

![Structure](image)

1H NMR (400 MHz, CDCl₃) δ 7.26 – 7.22 (m, 2H), 7.17-7.14 (m, 3H), 6.76 – 6.71 (m, 2H), 6.51-6.49 (m, 2H), 3.69 (s, 3H), 3.05 (t, J = 7.0 Hz, 2H), 2.67 (t, J = 7.7 Hz, 2H), 1.88 (dt appears as p, J = 7.2 Hz, 2H).

NMR spectra are in agreement with the literature data.⁶

**Rh/CO**

Rh₂(OAc)₄ (5.1 mg, 12 µmol, 0.7 mol %), p-anisidine (243.9 mg, 1.98 mmol) and hydrocinnamaldehyde (219 µL, 1.65 mmol) were charged into a glass vial in a 10 mL stainless autoclave. 0.7 mL of THF was added and autoclave was sealed, flushed three times with 3 atm of CO, and then charged with 50 atm CO. The reactor was placed into an oil bath preheated to 120 °C. After 22 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH₂Cl₂; in order to get rid of catalyst reaction mixture was passed through small pad of silica gel; combined solvents were removed on a rotary evaporator. The yield of 4-methoxy-N-(3-phenylpropyl)aniline (21-26%, range of yields for two experiments) was determined by ¹H NMR with mesitylene as internal standard. The rest is a complex mixture of self-condensation of aldehyde.

**Rh/CO optimized conditions**

Rh₂(OAc)₄ (1.77 mg, 4 µmol, 2 mol %), p-anisidine (49.3 mg, 0.4 mmol) and hydrocinnamaldehyde (27 µL, 0.2 mmol) were charged into a glass vial in a 10 mL stainless autoclave. 2 mL of toluene was added and autoclave was sealed, flushed three times with 3 atm of
CO, and then charged with 50 atm CO. The reactor was placed into an oil bath preheated to 160 °C. After 22 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH₂Cl₂; in order to get rid of catalyst reaction mixture was passed through small pad of silica gel; combined solvents were removed on a rotary evaporator. The yield of 4-methoxy-N-(3-phenylpropyl)aniline (41%) was determined by ¹H NMR with mesitylene as internal standard. The rest is a complex mixture of self-condensation products of aldehyde.

**NaBH₄**

A 10 mL round bottom flask was charged with hydrocinnamaldehyde (32 µL, 0.24 mmol), p-anisidine (24.6 mg, 0.20 mmol) and MeOH (2 mL). The mixture was refluxed for 2 h. Sodium borohydride (15.1 mg, 0.4 mmol) was added to reaction mixture. The suspension was stirred at room temperature overnight. Then reaction mixture was refluxed for additional 2 h. After reaction completion, it was diluted with water, and the product extracted with EtOAc. Organic layer was washed with brine 2 times, dried (Na₂SO₄), and solvent was evaporated to give the product. The yield of 4-methoxy-N-(3-phenylpropyl)aniline (27%) was determined by ¹H NMR with DMF as internal standard. The rest is a complex mixture of byproducts.

**NaBH₄ + Ti(OiPr)₄**

After removing traces of moisture and oxygen of air from Schlenk glassware, it was charged with hydrocinnamaldehyde (32 µL, 0.24 mmol), p-anisidine (24.6 mg, 0.20 mmol), Ti(Oi-Pr)₄ (119 µL, 0.4 mmol) and dry THF (1.5 mL). Reaction mixture was stirred at room temperature for 3 h under Ar. Then, THF was evaporated under reduced pressure. Sodium borohydride (15.1 mg, 0.4 mmol) and MeOH (2 mL) were added and refluxed for 4 h. After reaction completion, reaction mixture was diluted with distilled water and extracted two times with 15 mL of CH₂Cl₂. The CH₂Cl₂ extract was dried (Na₂SO₄), and solvent was evaporated to give the product. The yield of 4-methoxy-N-(3-phenylpropyl)aniline (>99%) was determined by ¹H NMR with DMF as internal standard. The rest consists of 3-phenylpropan-1-ol (15%) mixture of byproducts.

**NaBH(OAc)₃**

A 10 mL round bottom flask with input for Ar was charged with hydrocinnamaldehyde (26.6 µL, 0.2 mmol), p-anisidine (24.6 mg, 0.2 mmol) and 1,2-dichloroethane (0.7 mL). The mixture was stirred at room temperature under Ar atmosphere for 15 min. Sodium triacetoxyborohydride (59.4 mg, 0.28 mmol) was added to reaction mixture. The suspension was stirred at room temperature under Ar atmosphere for 18 h. Then the reaction mixture was quenched with aqueous saturated NaHCO₃ and extracted three times with 10 mL of EtOAc. The organic layer was dried over anhydrous Na₂SO₄, filtered and evaporated. The yield of 4-methoxy-N-(3-phenylpropyl)aniline (52-66%, range of yields for three experiments) was determined by ¹H NMR with mesitylene as internal standard. The rest consists of 3-phenylpropan-1-ol (15%) mixture of byproducts.

**NaBH(OAc)₃ + Ti(OiPr)₄**

After removing traces of moisture and oxygen of air from Schlenk glassware, it was charged with hydrocinnamaldehyde (26.6 µL, 0.2 mmol), p-anisidine (24.6 mg, 0.2 mmol), Ti(Oi-Pr)₄ (119 µL, 0.4 mmol) and dry THF (1.5 mL). Reaction mixture was stirred at room temperature for 3 h under Ar. Then, THF was evaporated under reduced pressure. Sodium triacetoxyborohydride (59.4 mg,
0.28 mmol) and 1,2-dichloroethane (0.7 mL) were added and stirred for 18 h. After reaction completion, reaction mixture was diluted with distilled water and extracted two times with 15 mL of CH₂Cl₂. The organic layer was dried over anhydrous Na₂SO₄, filtered and evaporated. The yield of 4-methoxy-N-(3-phenylpropyl)aniline (55%) was determined by ¹H NMR with mesitylene as internal standard. The rest is 3-phenylpropan-1-ol (12%) and mixture of byproducts.

**NaBH₃CN**

A penicillin vial was charged with p-anisidine (27 mg, 0.22 mmol), glacial acetic acid (12 µL, 0.22 mmol) and methanol (2 mL). After that, hydrocinnamaldehyde (29 µL, 0.22 mmol) and solution of NaBH₃CN (27 mg, 0.44 mmol) in 1 mL of MeOH were added. The reaction mixture was stirred at room temperature overnight. Then the solution was evaporated and the residue was taken up with 10 mL of water and extracted two times with 15 mL of CH₂Cl₂. The organic layers were combined, dried over anhydrous Na₂SO₄, filtered and evaporated. The yield of 4-methoxy-N-(3-phenylpropyl)aniline (33%) was determined by ¹H NMR with mesitylene as internal standard. The rest is a complex mixture of self-condensation products of aldehyde.

**NaBH₃CN + Ti(OiPr)₄**

After removing traces of moisture and oxygen of air from Schlenk glassware, it was charged with hydrocinnamaldehyde (24 µL, 0.18 mmol), p-anisidine (22 mg, 0.18 mmol), Ti(Oi-Pr)₄ (107 µL, 0.36 mmol) and dry THF (1.5 mL). Reaction mixture was stirred at room temperature for 4 h under Ar. Then, THF was evaporated under reduced pressure. Solution of sodium cyanoborohydride (23 mg, 0.36 mmol) in MeOH (2 mL) was added and refluxed for 4 h. After reaction completion, reaction mixture was diluted with distilled water and extracted two times with 15 mL of CH₂Cl₂. The CH₂Cl₂ extract was dried (Na₂SO₄), and solvent was evaporated. The yield of 4-methoxy-N-(3-phenylpropyl)aniline (>99%) was determined by ¹H NMR with mesitylene as internal standard.

**H₂/Pd/C, general conditions**

10% Pd/C (wet support, water content is 56%) (24 mg, 10 µmol, 5 mol%) p-anisidine (24.6 mg, 0.20 mmol), hydrocinnamaldehyde (26 µL, 0.2 mmol) and stirring bar were charged into a glass vial in a 10 mL stainless autoclave. 0.5 mL of EtOH was added and autoclave was sealed and charged with 5 atm H₂ at 40 °C. After 24 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH₂Cl₂; combined solvents were removed on a rotary evaporator. The yield of 4-methoxy-N-(3-phenylpropyl)aniline (61%) was determined by ¹H NMR with mesitylene as internal standard. The rest is complex mixture of byproducts.

**H₂/Pd/C, 1% of Pd**

10% Pd/C (wet support, water content is 56%) (4.8 mg, 2 µmol, 1 mol%) p-anisidine (24.6 mg, 0.20 mmol), hydrocinnamaldehyde (26 µL, 0.2 mmol), 0.2 mL of MeOH and stirring bar were charged into a glass vial in a 10 mL stainless autoclave. Reaction mixture was stirred overnight at room temperature. Then autoclave was charged with 3 atm H₂ at room temperature. After 15 h of stirring, the reactor was depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH₂Cl₂; combined solvents were removed on a rotary evaporator. The
yield of 4-methoxy-N-(3-phenylpropyl)aniline (18%) was determined by $^1$H NMR with mesitylene as internal standard. The rest is complex mixture of byproducts.

**N-(4-methoxyphenyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-amine**

![Chemical structure](attachment:structure.png)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.78 (d, $J = 8.8$ Hz, 2H), 6.55 (d, $J = 8.8$ Hz, 2H), 3.75 (s, 3H), 3.51 (br s, 1H), 3.22 (dd, $J = 8.3$, 4.7 Hz, 2H), 1.87 (dd, $J = 12.7$, 8.3 Hz, 1H), 1.82 – 1.53 (m, 4H), 1.32 – 1.12 (m, 2H), 1.04 (s, 3H), 0.94 (s, 3H), 0.87 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 151.5, 142.6, 114.9, 113.8, 62.4, 55.9, 48.8, 47.2, 45.2, 40.8, 36.8, 27.4, 20.5, 12.3.

**Rh/CO**

Rh$_2$(OAc)$_4$ (2.0 mg, 4.6 µmol, 0.7 mol %), p-anisidine (97.5 mg, 0.792 mmol) and D-camphor (100.5 mg, 0.66 mmol) were charged into a glass vial in a 10 mL stainless autoclave. 0.3 mL of THF was added and autoclave was sealed, flushed three times with 3 atm of CO, and then charged with 50 atm CO. The reactor was placed into an oil bath preheated to 120 °C. After 22 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH$_2$Cl$_2$; in order to get rid of catalyst reaction mixture was passed through small pad of silica gel; combined solvents were removed on a rotary evaporator. The yield of (1S,2R,4R)-N-(4-methoxyphenyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-amine (8%) was determined by $^1$H NMR with DMF as internal standard. The rest is corresponding Schiff Base (26%) and starting compounds.

**Rh/CO, optimized conditions**

Rh$_2$(OAc)$_4$ (1.0 mg, 2.3 µmol, 0.7 mol %), p-anisidine (48.7 mg, 0.396 mmol) and D-camphor (50.2 mg, 0.33 mmol) were charged into a glass vial in a 10 mL stainless autoclave. 0.15 mL of THF was added and autoclave was sealed, flushed three times with 3 atm of CO, and then charged with 50 atm CO. The reactor was placed into an oil bath preheated to 160 °C. After 46 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH$_2$Cl$_2$; in order to get rid of catalyst reaction mixture was passed through small pad of silica gel; combined solvents were removed on a rotary evaporator. The yield of (1S,2R,4R)-N-(4-methoxyphenyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-amine (69%) was determined by $^1$H NMR with DMF as internal standard. The rest is corresponding Schiff Base (15%) and starting compounds.

**NaBH$_4$**

A 10 mL round bottom flask was charged with D-camphor (36.5 mg, 0.24 mmol), p-anisidine (24.6 mg, 0.20 mmol) and MeOH (2 mL). The mixture was refluxed for 2 h. Sodium borohydride (15.1 mg, 0.4 mmol) was added to reaction mixture. The suspension was stirred at room
temperature overnight. Then reaction mixture was refluxed for additional 2 h. After reaction completion, it was diluted with water, and the product extracted with EtOAc. Organic layer was washed with brine two times, dried (Na$_2$SO$_4$), and solvent was evaporated to give the product. Product was not detected by NMR. Reaction mixture consists of unreacted D-camphor and p-anisidine.

$\text{NaBH}_4 + \text{Ti(OiPr)}_4$

After removing traces of moisture and oxygen of air from Schlenk glassware, it was charged with D-camphor (36.5 mg, 0.24 mmol), p-anisidine (24.6 mg, 0.20 mmol), Ti(Oi-Pr)$_4$ (119 µL, 0.4 mmol) and dry THF (1.5 mL). Reaction mixture was stirred at room temperature for 3 h under Ar. Then, THF was evaporated under reduced pressure. Sodium borohydride (15.1 mg, 0.4 mmol) and MeOH (2 mL) was added and refluxed for 4 h. After reaction completion, reaction mixture was diluted with distilled water and extracted two times with 15 mL of CH$_2$Cl$_2$. The CH$_2$Cl$_2$ extract was dried (Na$_2$SO$_4$), and solvent was evaporated. Product was not detected by NMR. Reaction mixture consists of unreacted D-camphor and p-anisidine.

$\text{NaBH(OAc)}_3$

A 10 mL round bottom flask with input for Ar was charged with D-camphor (30.0 mg, 0.2 mmol), p-anisidine (24.6 mg, 0.2 mmol) and 1,2-dichloroethane (0.7 mL). The mixture was stirred at room temperature under Ar atmosphere for 15 min. Sodium triacetoxyborohydride (59.4 mg, 0.28 mmol) was added to reaction mixture. The suspension was stirred at room temperature under Ar atmosphere for 18 h. Then the reaction mixture was quenched with aqueous saturated NaHCO$_3$ and extracted three times with 10 mL of EtOAc. The organic layer was dried over anhydrous Na$_2$SO$_4$, filtered and evaporated. Product was not detected by NMR. Reaction mixture consists of unreacted D-camphor and p-anisidine.

$\text{NaBH(OAc)}_3 + \text{AcOH}$

A 10 mL round bottom flask with input for Ar was charged with D-camphor (30.0 mg, 0.2 mmol), p-anisidine (24.6 mg, 0.2 mmol), glacial acetic acid (12 µL, 0.2 mmol) and 1,2-dichloroethane (0.7 mL). The mixture was stirred at room temperature under Ar atmosphere for 15 min. Sodium triacetoxyborohydride (59.4 mg, 0.28 mmol) was added to reaction mixture. The suspension was stirred at room temperature under Ar atmosphere for 18 h. Then the reaction mixture was quenched with aqueous saturated NaHCO$_3$ and extracted three times with 10 mL of EtOAc. The organic layer was dried over anhydrous Na$_2$SO$_4$, filtered and evaporated. Product was not detected by NMR. Reaction mixture consists of unreacted camphor and p-anisidine.

$\text{NaBH(OAc)}_3 + \text{Ti(OiPr)}_4$

After removing traces of moisture and oxygen of air from Schlenk glassware, it was charged with D-camphor (30.0 mg, 0.2 mmol), p-anisidine (24.6 mg, 0.20 mmol), Ti(Oi-Pr)$_4$ (119 µL, 0.4 mmol) and dry THF (1.5 mL). Reaction mixture was stirred at room temperature for 3 h under Ar. Then, THF was evaporated under reduced pressure. Sodium triacetoxyborohydride (59.4 mg, 0.28 mmol) and dichloroethane (0.7 mL) were added and stirred at room temperature for 18 h. After reaction completion, reaction mixture was diluted with distilled water and extracted two times with 15 mL
of CH\(_2\)Cl\(_2\). The CH\(_2\)Cl\(_2\) extract was dried (Na\(_2\)SO\(_4\)), and solvent was evaporated. Product was not detected by NMR. Reaction mixture consists of unreacted D-camphor and p-anisidine.

**NaBH\(_3\)CN**

A penicillin vial was charged with p-anisidine (23 mg, 0.18 mmol), glacial acetic acid (10 \(\mu\)L, 0.18 mmol) and methanol (2 mL). After that, D-camphor (28 mg, 0.18 mmol) and solution of NaBH\(_3\)CN (23 mg, 0.36 mmol) in 1 mL of MeOH were added. The reaction mixture was stirred at room temperature overnight. Then the solution was evaporated and the residue was taken up with 10 mL of water and extracted two times with 15 mL of CH\(_2\)Cl\(_2\). The organic layers were combined, dried over anhydrous Na\(_2\)SO\(_4\), filtered and evaporated. Product was not detected by NMR. Reaction mixture consists of unreacted D-camphor and p-anisidine.

**NaBH\(_3\)CN + Ti(OiPr)\(_4\)**

After removing traces of moisture and oxygen of air from Schlenk glassware, it was charged with D-camphor (27 mg, 0.18 mmol), p-anisidine (22 mg, 0.18 mmol), Ti(Oi-Pr)\(_4\) (107 \(\mu\)L, 0.36 mmol) and dry THF (1.5 mL). Reaction mixture was stirred at room temperature for 4 h under Ar. Then, THF was evaporated under reduced pressure. Solution of sodium cyanoborohydride (23 mg, 0.36 mmol) in MeOH (2 mL) was added and refluxed for 4 h. After reaction completion, reaction mixture was diluted with distilled water and extracted two times with 15 mL of CH\(_2\)Cl\(_2\). The CH\(_2\)Cl\(_2\) extract was dried (Na\(_2\)SO\(_4\)), and solvent was evaporated. Product was not detected by NMR. Reaction mixture consists of unreacted D-camphor and p-anisidine.

**H\(_2\)/Pd/C, general conditions**

10% Pd/C (wet support, water content is 56%) (24 mg, 10 \(\mu\)mol, 5 mol%), p-anisidine (24.6 mg, 0.20 mmol), D-camphor (30.5 mg, 0.2 mmol) and stirring bar were charged into a glass vial in a 10 mL stainless autoclave. 0.5 mL of EtOH was added and autoclave was sealed and charged with 5 atm H\(_2\) at 40 °C. After 24 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH\(_2\)Cl\(_2\); combined solvents were removed on a rotary evaporator. Product was not detected by NMR. Reaction mixture consists of unreacted D-camphor and p-anisidine.

**H\(_2\)/Pd/C, 1% of Pd**

10% Pd/C (wet support, water content is 56%) (4.8 mg, 2 \(\mu\)mol, 1 mol%) p-anisidine (24.6 mg, 0.20 mmol), D-camphor (30.5 mg, 0.2 mmol), 0.2 mL of MeOH and stirring bar were charged into a glass vial in a 10 mL stainless autoclave. Reaction mixture was stirred overnight at room temperature. Then autoclave was charged with 3 atm H\(_2\) at room temperature. After 15 h of stirring, the reactor was depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH\(_2\)Cl\(_2\); combined solvents were removed on a rotary evaporator. Product was not detected by NMR. Reaction mixture consists of unreacted D-camphor and p-anisidine.

**1-(4-phenylbutan-2-yl)piperidine**

![1-(4-phenylbutan-2-yl)piperidine](image)
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.29 (t, $J = 7.5$ Hz, 2H), 7.25 – 7.13 (m, 3H), 2.77 – 2.48 (m, 5H), 2.45 – 2.36 (m, 2H), 1.89 (ddt, $J = 12.3$, 9.9, 5.9 Hz, 1H), 1.68 – 1.52 (m, 5H), 1.50 – 1.40 (m, 2H), 1.02 (d, $J = 6.6$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 142.9, 128.5, 128.2, 125.6, 58.9, 49.3, 35.6, 33.3, 26.6, 25.1, 13.8.

**Rh/CO**

Rh$_2$(OAc)$_4$ (5.1 mg, 11.6 µmol, 0.7 mol %), piperidine (196 µL, 1.98 mmol) and benzylacetone (247 µL, 1.65 mmol) were charged into a glass vial in a 10 mL stainless autoclave. 0.7 mL of THF was added and autoclave was sealed, flushed three times with 3 atm of CO, and then charged with 50 atm CO. The reactor was placed into an oil bath preheated to 120 °C. After 22 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH$_2$Cl$_2$; in order to get rid of catalyst reaction mixture was passed through small pad of silica gel; combined solvents were removed on a rotary evaporator. The yield of 1-(4-phenylbutan-2-yl)piperidine (>99%) was determined by $^1$H NMR with mesitylene as internal standard.

**NaBH$_4$**

A 10 mL round bottom flask was charged with benzylacetone (36 µL, 0.24 mmol), piperidine (20 µL, 0.20 mmol) and MeOH (2 mL). The mixture was refluxed for 2 h. Sodium borohydride (15.1 mg, 0.4 mmol) was added to reaction mixture. The suspension was stirred at room temperature overnight. Then reaction mixture was refluxed for additional 2 h. After reaction completion, it was diluted with water, and the product extracted with EtOAc. Organic layer was washed with brine 2 times, dried (Na$_2$SO$_4$), and solvent was evaporated. Product was not detected by NMR. Reaction mixture consists of pure 4-phenylbutan-2-ol.

**NaBH$_4$ + Ti(OiPr)$_4$**

After removing traces of moisture and oxygen of air from Schlenk glassware, it was charged with benzylacetone (36 µL, 0.24 mmol), piperidine (20 µL, 0.20 mmol), Ti(Oi-Pr)$_4$ (119 µL, 0.4 mmol) and dry THF (1.5 mL). Reaction mixture was stirred at room temperature for 3 h under Ar. Then, THF was evaporated under reduced pressure. Sodium borohydride (15.1 mg, 0.4 mmol) and MeOH (2 mL) was added and refluxed for 4 h. After reaction completion, reaction mixture was diluted with distilled water and extracted two times with 15 mL of CH$_2$Cl$_2$. The CH$_2$Cl$_2$ extract was dried (Na$_2$SO$_4$), and solvent was evaporated. Product was not detected by NMR. Product was not detected by NMR. Reaction mixture consists of pure 4-phenylbutan-2-ol.

**NaBH$_4$ + TiCl$_4$**

After removing traces of moisture and oxygen of air from Schlenk glassware, it was charged with benzylacetone (36 µL, 0.24 mmol), piperidine (20 µL, 0.20 mmol), TiCl$_4$ (10 µL, 0.1 mmol) and dry THF (1.5 mL). Reaction mixture was stirred at room temperature for 3 h under Ar. Then, THF was evaporated under reduced pressure. Sodium borohydride (15.1 mg, 0.4 mmol) and MeOH (2 mL) was added and refluxed for 4 h. After reaction completion, reaction mixture was diluted with distilled water and extracted two times with 15 mL of CH$_2$Cl$_2$. The CH$_2$Cl$_2$ extract was dried.
(Na₂SO₄), and solvent was evaporated. 8% of the product was detected by NMR (mesitylene as internal standard). The rest is 4-phenylbutan-2-ol.

**NaBH(OAc)₃**

A 10 mL round bottom flask with input for Ar was charged with benzylacetone (30.0 µL, 0.2 mmol), piperidine (19.8 µL, 0.2 mmol) and 1,2-dichloroethane (0.7 mL). The mixture was stirred at room temperature under Ar atmosphere for 15 min. Sodium triacetoxyborohydride (59.4 mg, 0.28 mmol) was added to reaction mixture. The suspension was stirred at room temperature under Ar atmosphere for 18 h. Then the reaction mixture was quenched with aqueous saturated NaHCO₃ and extracted three times with 10 mL of EtOAc. The organic layer was dried over anhydrous Na₂SO₄, filtered and evaporated. The yield of 1-(4-phenylbutan-2-yl)piperidine (13%) was determined by ¹H NMR with 1,4-dinitrobenzene as internal standard. Another major component of the reaction mixture is benzylacetone (22%) and mixture of byproducts.

**NaBH(OAc)₃ + AcOH**

A 10 mL round bottom flask with input for Ar was charged with benzylacetone (30.0 µL, 0.2 mmol), piperidine (19.8 µL, 0.2 mmol), glacial acetic acid (12 µL, 0.2 mmol) and 1,2-dichloroethane (0.7 mL). The mixture was stirred at room temperature under Ar atmosphere for 15 min. Sodium triacetoxyborohydride (59.4 mg, 0.28 mmol) was added to reaction mixture. The suspension was stirred at room temperature under Ar atmosphere for 22 h. Then the reaction mixture was quenched with aqueous saturated NaHCO₃ and extracted three times with 10 mL of EtOAc. The organic layer was dried over anhydrous Na₂SO₄, filtered and evaporated. The yield of 1-(4-phenylbutan-2-yl)piperidine (36%) was determined by ¹H NMR with 1,4-dinitrobenzene as internal standard. Another major component of the reaction mixture is benzylacetone (44%).

**NaBH(OAc)₃, optimized conditions**

A 10 mL round bottom flask with input for Ar was charged with benzylacetone (30.0 µL, 0.2 mmol), piperidine (19.8 µL, 0.2 mmol) and 1,2-dichloroethane (0.7 mL). The mixture was stirred at room temperature under Ar atmosphere for 15 min. Sodium triacetoxyborohydride (59.4 mg, 0.28 mmol) was added to reaction mixture. The suspension was stirred at room temperature under Ar atmosphere for 48 h. Then the reaction mixture was quenched with aqueous saturated NaHCO₃ and extracted three times with 10 mL of EtOAc. The organic layer was dried over anhydrous Na₂SO₄, filtered and evaporated. The yield of 1-(4-phenylbutan-2-yl)piperidine (54%) was determined by ¹H NMR with mesitylene as internal standard. Another major component of the reaction mixture is benzylacetone (42%).

**NaBH₃CN**

A penicillin vial was charged with piperidine (19 µL, 0.19 mmol), glacial acetic acid (11 µL, 0.19 mmol) and methanol (2 mL). After that, benzylacetone (28 µL, 0.19 mmol) and solution of NaBH₃CN (24 mg, 0.38 mmol) in 1 mL of MeOH were added. The reaction mixture was stirred at room temperature overnight. Then the solution was evaporated and the residue was taken up with 10 mL of water and extracted two times with 15 mL of CH₂Cl₂. The organic layers were combined, dried over anhydrous Na₂SO₄, filtered and evaporated. The yield of 1-(4-phenylbutan-
2-yl)piperidine (6%) was determined by $^1$H NMR with mesitylene as internal standard. The rest is unreacted benzylacetone.

$\text{NaBH}_3\text{CN} + \text{Ti(OiPr)}_4$

After removing traces of moisture and oxygen of air from Schlenk glassware, it was charged with piperidine (22 µL, 0.22 mmol), benzylacetone (33 µL, 0.22 mmol), Ti(Oi-Pr)$_4$ (130 µL, 0.44 mmol) and dry THF (1.5 mL). Reaction mixture was stirred at room temperature for 4 h under Ar. Then, THF was evaporated under reduced pressure. Solution of sodium cyanoborohydride (28 mg, 0.44 mmol) in MeOH (2 mL) was added and refluxed for 4 h. After reaction completion, reaction mixture was diluted with distilled water and extracted two times with 15 mL of CH$_2$Cl$_2$. The CH$_2$Cl$_2$ extract was dried (Na$_2$SO$_4$), and solvent was evaporated. The yield of 1-(4-phenylbutan-2-yl)piperidine (71%) was determined by $^1$H NMR with mesitylene as internal standard. The rest is unreacted benzylacetone.

$\text{H}_2/\text{Pd/C, general conditions}$

10% Pd/C (wet support, water content is 56%) (24 mg, 10 µmol, 5 mol%), piperidine (20 µL, 0.20 mmol), benzylacetone (30 µL, 0.2 mmol) and stirring bar were charged into a glass vial in a 10 mL stainless autoclave. 0.5 mL of EtOH was added and autoclave was sealed and charged with 5 atm H$_2$ at 40 °C. After 24 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH$_2$Cl$_2$; combined solvents were removed on a rotary evaporator. Product was not detected by NMR. The main component of reaction mixture is 4-phenylbutan-2-ol.

$\text{H}_2/\text{Pd/C, 1\% of Pd}$

10% Pd/C (wet support, water content is 56%) (4.8 mg, 2 µmol, 1 mol%) piperidine (20 µL, 0.20 mmol), benzylacetone (30 µL, 0.2 mmol), 0.2 mL of MeOH and stirring bar were charged into a glass vial in a 10 mL stainless autoclave. Reaction mixture was stirred overnight at room temperature. Then autoclave was charged with 3 atm H$_2$ at room temperature. After 15 h of stirring, the reactor was depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH$_2$Cl$_2$; combined solvents were removed on a rotary evaporator. The yield of 1-(4-phenylbutan-2-yl)piperidine (40%) was determined by $^1$H NMR with mesitylene as internal standard. Another major component of the reaction mixture is benzylacetone (38%).

$\text{N-(cyclohexylmethyl)-N-isopropylpropan-2-amine}$

\[ \text{NMR (400 MHz, CDCl}_3) \delta 2.96 \text{ (sept, } J = 6.6 \text{ Hz, 2H), 2.17 (d, } J = 7.0 \text{ Hz, 2H), 1.80 – 1.67 (m, 5H), 1.30 – 1.22 (m, 6H), 0.96 (d, } J = 6.6 \text{ Hz, 12H).} \]

NMR spectra are in agreement with the literature data.$^7$

$\text{Rh/CO}$
Rh$_2$(OAc)$_4$ (5.1 mg, 11.6 µmol, 0.7 mol %), diisopropylamine (280 µL, 1.98 mmol) and cyclohexanecarboxaldehyde (200 µL, 1.65 mmol) were charged into a glass vial in a 10 mL stainless autoclave. 0.7 mL of THF was added and autoclave was sealed, flushed three times with 3 atm of CO, and then charged with 50 atm CO. The reactor was placed into an oil bath preheated to 120 °C. After 22 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH$_2$Cl$_2$; in order to get rid of catalyst reaction mixture was passed through small pad of silica gel; combined solvents were removed on a rotary evaporator. The yield of N-(cyclohexylmethyl)-N-isopropylpropan-2-amine (18%) was determined by $^1$H NMR with mesitylene as internal standard.

**Rh/CO, optimized conditions**

Rh$_2$(OAc)$_4$ (2 mg, 4.6 µmol, 0.7 mol %), diisopropylamine (466 µL, 3.30 mmol) and cyclohexanecarboxaldehyde (80 µL, 0.66 mmol) were charged into a glass vial in a 10 mL stainless autoclave. 0.3 mL of THF was added and autoclave was sealed, flushed three times with 3 atm of CO, and then charged with 50 atm CO. The reactor was placed into an oil bath preheated to 140 °C. After 2 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH$_2$Cl$_2$; in order to get rid of catalyst reaction mixture was passed through small pad of silica gel; combined solvents were removed on a rotary evaporator. The yield of N-(cyclohexylmethyl)-N-isopropylpropan-2-amine (63%) was determined by $^1$H NMR with mesitylene as internal standard.

**NaBH$_4$**

A 10 mL round bottom flask was charged with cyclohexanecarboxaldehyde (29 µL, 0.24 mmol), diisopropylamine (28 µL, 0.20 mmol) and MeOH (2 mL). The mixture was refluxed for 2 h. Sodium borohydride (15.1 mg, 0.4 mmol) was added to reaction mixture. The suspension was stirred at room temperature overnight. Then reaction mixture was refluxed for additional 2 h. After reaction completion, it was diluted with water, and the product extracted with EtOAc. Organic layer was washed with brine 2 times, dried (Na$_2$SO$_4$), and solvent was evaporated. Product was not detected by NMR. Reaction mixture consists of pure cyclohexylmethanol.

**NaBH$_4$ + Ti(OiPr)$_4$**

After removing traces of moisture and oxygen of air from Schlenk glassware, it was charged with cyclohexanecarboxaldehyde (29 µL, 0.24 mmol), diisopropylamine (28 µL, 0.20 mmol), Ti(OiPr)$_4$ (119 µL, 0.4 mmol) and dry THF (1.5 mL). Reaction mixture was stirred at room temperature for 3 h under Ar. Then, THF was evaporated under reduced pressure. Sodium borohydride (15.1 mg, 0.4 mmol) and MeOH (2 mL) were added and refluxed for 4 h. After reaction completion, reaction mixture was diluted with distilled water and extracted two times with 15 mL of CH$_2$Cl$_2$. The CH$_2$Cl$_2$ extract was dried (Na$_2$SO$_4$), and solvent was evaporated. Product was not detected by NMR. Reaction mixture consists of pure cyclohexylmethanol.

**NaBH$_4$ + TiCl$_4$**

After removing traces of moisture and oxygen of air from Schlenk glassware, it was charged with cyclohexanecarboxaldehyde (29 µL, 0.24 mmol), diisopropylamine (28 µL, 0.20 mmol), TiCl$_4$ (10 µL, 0.1 mmol) and dry THF (1.5 mL). Reaction mixture was stirred at room temperature for 3 h
under Ar. Then, THF was evaporated under reduced pressure. Sodium borohydride (15.1 mg, 0.4 mmol) and MeOH (2 mL) were added and refluxed for 4 h. After reaction completion, reaction mixture was diluted with distilled water and extracted two times with 15 mL of CH$_2$Cl$_2$. The CH$_2$Cl$_2$ extract was dried (Na$_2$SO$_4$), and solvent was evaporated. 16% of the product was detected by NMR (mesitylene as internal standard). The rest is cyclohexylmethanol.

$NaBH(OAc)_3$

A 10 mL round bottom flask with input for Ar was charged with cyclohexanecarboxaldehyde (24.2 µL, 0.2 mmol), diisopropylamine (28.0 µL, 0.2 mmol) and 1,2-dichloroethane (0.7 mL). The mixture was stirred at room temperature under Ar atmosphere for 15 min. Sodium triacetoxyborohydride (59.4 mg, 0.28 mmol) was added to reaction mixture. The suspension was stirred at room temperature under Ar atmosphere for 18 h. Then the reaction mixture was quenched with aqueous saturated NaHCO$_3$ and extracted three times with 10 mL of EtOAc. The organic layer was dried over anhydrous Na$_2$SO$_4$, filtered and evaporated. The yield of N-(cyclohexylmethyl)-N-isopropylpropan-2-amine (29%) was determined by $^1$H NMR with mesitylene as internal standard. The rest is a mixture of cyclohexylmethanol and other byproducts.

$NaBH(OAc)_3$, optimized conditions

A 10 mL round bottom flask with input for Ar was charged with cyclohexanecarboxaldehyde (1.2 mL, 10.0 mmol), diisopropylamine (1.4 mL, 10.0 mmol) and 1,2-dichloroethane (35 mL). Then sodium triacetoxyborohydride (3.0 g, 14.0 mmol) was added to reaction mixture. The suspension was stirred at room temperature under Ar atmosphere for 8 h. Then the reaction mixture was quenched with aqueous saturated NaHCO$_3$ and extracted three times with 35 mL of EtOAc. The organic layer was dried over anhydrous Na$_2$SO$_4$, filtered and evaporated. The yield of N-(cyclohexylmethyl)-N-isopropylpropan-2-amine (range of yields for two experiments 60-71%) was determined by $^1$H NMR with mesitylene as internal standard. The rest is a mixture of cyclohexylmethanol and other byproducts.

$NaBH_3CN$

A penicillin vial was charged with diisopropylamine (25 µL, 0.17 mmol), glacial acetic acid (10 µL, 0.17 mmol) and methanol (2 mL). After that, cyclohexanecarboxaldehyde (21 µL, 0.18 mmol) and solution of NaBH$_3$CN (22 mg, 0.34 mmol) in 1 mL of MeOH were added. The reaction mixture was stirred at room temperature overnight. Then the solution was evaporated and the residue was taken up with 10 mL of water and extracted two times with 15 mL of CH$_2$Cl$_2$. The organic layers were combined, dried over anhydrous Na$_2$SO$_4$, filtered and evaporated. Product was not detected by NMR. The main component of reaction mixture is cyclohexylmethanol. Another major component of the reaction mixture is cyclohexanecarboxaldehyde.

$NaBH_3CN + Ti(OiPr)_4$

After removing traces of moisture and oxygen of air from Schlenk glassware, it was charged with cyclohexanecarboxaldehyde (22 µL, 0.18 mmol), diisopropylamine (25 µL, 0.18 mmol), Ti(OiPr)$_4$ (107 µL, 0.36 mmol) and dry THF (1.5 mL). Reaction mixture was stirred at room temperature for 4 h under Ar. Then, THF was evaporated under reduced pressure. Solution of sodium cyanoborohydride (23 mg, 0.36 mmol) in MeOH (2 mL) was added and refluxed for 4 h. After
reaction completion, reaction mixture was diluted with distilled water and extracted two times with 15 mL of CH$_2$Cl$_2$. The CH$_2$Cl$_2$ extract was dried (Na$_2$SO$_4$), and solvent was evaporated. The yield of N-(cyclohexylmethyl)-N-isopropylpropan-2-amine (27%) was determined by $^1$H NMR with mesitylene as internal standard. Another major components of the reaction mixture are cyclohexylmethanol (23%) cyclohexanecarboxaldehyde (14%).

**H$_2$/Pd/C, general conditions**

10% Pd/C (wet support, water content is 56%) (24 mg, 10 µmol, 5 mol%), diisopropylamine (28 µL, 0.20 mmol), cyclohexanecarboxaldehyde (24 µL, 0.2 mmol) and stirring bar were charged into a glass vial in a 10 mL stainless autoclave. 0.5 mL of EtOH was added and autoclave was sealed and charged with 5 atm H$_2$ at 40 °C. After 24 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH$_2$Cl$_2$; combined solvents were removed on a rotary evaporator. Product was not detected by NMR. The main component of reaction mixture is cyclohexylmethanol.

**H$_2$/Pd/C, 1% of Pd**

10% Pd/C (wet support, water content is 56%) (4.8 mg, 2 µmol, 1 mol%), diisopropylamine (28 µL, 0.20 mmol), cyclohexanecarboxaldehyde (24 µL, 0.2 mmol), 0.2 mL of MeOH and stirring bar were charged into a glass vial in a 10 mL stainless autoclave. Reaction mixture was stirred overnight at room temperature. Then autoclave was charged with 3 atm H$_2$ at room temperature. After 15 h of stirring, the reactor was depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH$_2$Cl$_2$; combined solvents were removed on a rotary evaporator. The yield of N-(cyclohexylmethyl)-N-isopropylpropan-2-amine (17%) was determined by $^1$H NMR with mesitylene as internal standard. Another major component of the reaction mixture is cyclohexanecarboxaldehyde (31%).

**1-(4-methoxybenzyl)piperidine**

![1-(4-methoxybenzyl)piperidine](image)

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.21 (d, $J = 8.6$ Hz, 2H), 6.83 (d, $J = 8.6$ Hz, 2H), 3.78 (s, 3H), 3.40 (s, 2H), 2.48-2.23 (m, 4H), 1.58-1.52 (m, 4H), 1.49-1.35 (m, 2H).

NMR spectra are in agreement with the literature data.\(^8\)

**Rh/CO**

Rh$_2$(OAc)$_4$ (5.1 mg, 11.6 µmol, 0.7 mol %), piperidine (196 µL, 1.98 mmol) and p-anisaldehyde (201 µL, 1.65 mmol) were charged into a glass vial in a 10 mL stainless autoclave. 0.7 mL of THF was added and autoclave was sealed, flushed three times with 3 atm of CO, and then charged with 50 atm CO. The reactor was placed into an oil bath preheated to 120 °C. After 22 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH$_2$Cl$_2$; in order to get rid of catalyst reaction mixture was passed through small pad of silica gel; combined solvents were removed on a rotary
evaporator. The yield of 1-(4-methoxybenzyl)piperidine (98%) was determined by $^1$H NMR with DMF as internal standard.

**NaBH$_4$**

A 10 mL round bottom flask was charged with $p$-anisaldehyde (29 µL, 0.24 mmol), piperidine (20 µL, 0.20 mmol) and MeOH (2 mL). The mixture was refluxed for 2 h. Sodium borohydride (15.1 mg, 0.4 mmol) was added to reaction mixture. The suspension was stirred at room temperature overnight. Then reaction mixture was refluxed for additional 2 h. After reaction completion, it was diluted with water, and the product extracted with EtOAc. Organic layer was washed with brine 2 times, dried (Na$_2$SO$_4$), and solvent was evaporated. The yield of 1-(4-methoxybenzyl)piperidine (14%) was determined by $^1$H NMR with mesitylene as internal standard. The rest is (4-methoxyphenyl)methanol.

**NaBH$_4$ + Ti(OiPr)$_4$**

After removing traces of moisture and oxygen of air from Schlenk glassware, it was charged with $p$-anisaldehyde (29 µL, 0.24 mmol), piperidine (20 µL, 0.20 mmol), Ti(Oi-Pr)$_4$ (119 µL, 0.4 mmol) and dry THF (1.5 mL). Reaction mixture was stirred at room temperature for 3 h under Ar. Then, THF was evaporated under reduced pressure. Sodium borohydride (15.1 mg, 0.4 mmol) and MeOH (2 mL) were added and refluxed for 4 h. After reaction completion, reaction mixture was diluted with distilled water and extracted two times with 15 mL of CH$_2$Cl$_2$. The CH$_2$Cl$_2$ extract was dried (Na$_2$SO$_4$), and solvent was evaporated. The yield of 1-(4-methoxybenzyl)piperidine (30%) was determined by $^1$H NMR with mesitylene as internal standard. The rest is (4-methoxyphenyl)methanol.

**NaBH(OAc)$_3$**

A 10 mL round bottom flask with input for Ar was charged with $p$-anisaldehyde (24.3 µL, 0.2 mmol), piperidine (19.8 µL, 0.2 mmol) and 1,2-dichloroethane (0.7 mL). The mixture was stirred at room temperature under Ar atmosphere for 15 min. Sodium triacetoxyborohydride (59.4 mg, 0.28 mmol) was added to reaction mixture. The suspension was stirred at room temperature under Ar atmosphere for 18 h. Then the reaction mixture was quenched with aqueous saturated NaHCO$_3$ and extracted three times with 10 mL of EtOAc. The organic layer was dried over anhydrous Na$_2$SO$_4$, filtered and evaporated. The yield of 1-(4-methoxybenzyl)piperidine (84%) was determined by $^1$H NMR with mesitylene as internal standard.

**NaBH$_3$CN**

A penicillin vial was charged with piperidine (18 µL, 0.18 mmol), glacial acetic acid (10 µL, 0.18 mmol) and methanol (2 mL). After that, $p$-anisaldehyde (22 µL, 0.18 mmol) and solution of NaBH$_3$CN (23 mg, 0.36 mmol) in 1 mL of MeOH were added. The reaction mixture was stirred at room temperature overnight. Then the solution was evaporated and the residue was taken up with 10 mL of water and extracted two times with 15 mL of CH$_2$Cl$_2$. The organic layers were combined, dried over anhydrous Na$_2$SO$_4$, filtered and evaporated. The yield of 1-(4-methoxybenzyl)piperidine (57%) was determined by $^1$H NMR with mesitylene as internal standard. Another component of the reaction mixture is $p$-anisaldehyde (10%).

S22
After removing traces of moisture and oxygen of air from Schlenk glassware, it was charged with p-anisaldehyde (22 µL, 0.18 mmol), piperidine (18 µL, 0.18 mmol), Ti(OiPr)_4 (108 µL, 0.36 mmol) and dry THF (1.5 mL). Reaction mixture was stirred at room temperature for 4 h under Ar. Then, THF was evaporated under reduced pressure. Solution of sodium cyanoborohydride (23 mg, 0.36 mmol) in MeOH (2 mL) was added and refluxed for 4 h. After reaction completion, reaction mixture was diluted with distilled water and extracted two times with 15 mL of CH₂Cl₂. The CH₂Cl₂ extract was dried (Na₂SO₄), and solvent was evaporated. The yield of 1-(4-methoxybenzyl)piperidine (79%) was determined by ¹H NMR with mesitylene as internal standard.

**H₂/Pd/C, general conditions**

10% Pd/C (wet support, water content is 56%) (24 mg, 10 µmol, 5 mol%) piperidine (20 µL, 0.20 mmol), p-anisaldehyde (29 µL, 0.2 mmol) and stirring bar were charged into a glass vial in a 10 mL stainless autoclave. 0.5 mL of EtOH was added and autoclave was sealed and charged with 5 atm H₂ at 40 °C. After 24 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH₂Cl₂; combined solvents were removed on a rotary evaporator. 66% of the product was detected by NMR with mesitylene as internal standard. The rest is (4-methoxyphenyl)methanol.

**H₂/Pd/C, 1% of Pd**

10% Pd/C (wet support, water content is 56%) (4.8 mg, 2 µmol, 1 mol%) piperidine (20 µL, 0.20 mmol), p-anisaldehyde (29 µL, 0.2 mmol), 0.2 mL of MeOH and stirring bar were charged into a glass vial in a 10 mL stainless autoclave. Reaction mixture was stirred overnight at room temperature. Then autoclave was charged with 3 atm H₂ at room temperature. After 15 h of stirring, the reactor was depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH₂Cl₂; combined solvents were removed on a rotary evaporator. The yield of 1-(4-methoxybenzyl)piperidine (6%) was determined by ¹H NMR with mesitylene as internal standard. The main component of reaction mixture is p-anisaldehyde (74%).

**Benzyl (4-((4-methylbenzyl)amino)phenyl)carbamate**

\[
\text{Benzyl (4-((4-methylbenzyl)amino)phenyl)carbamate}
\]

¹H NMR (400 MHz, CDCl₃) δ 7.44 – 7.36 (m, 5H), 7.28 (d, J = 8.0 Hz, 2H), 7.18-7.16 (m, 4H), 6.61 (d, J = 8.7 Hz, 2H), 6.54 (s, 1H), 5.21 (s, 2H), 4.29 (s, 2H), 2.38 (s, 3H).

NMR spectra are in agreement with the literature data.⁹

**Rh/CO**

Rh₂(OAc)₄ (0.3 mg, 0.3 µmol, 0.7 mol %), benzyl 4-aminophenylcarbamate (29 mg, 0.12 mmol), p-tolylaldehyde (12 µL, 0.1 mmol) were charged into a glass vial in a 10 mL stainless autoclave.

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⁹ NMR spectra are in agreement with the literature data.
0.7 mL of THF was added and autoclave was sealed, flushed three times with 3 atm of CO, and then charged with 50 atm CO. The reactor was placed into an oil bath preheated to 120 °C. After 22 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH$_2$Cl$_2$; in order to get rid of catalyst reaction mixture was passed through small pad of silica gel; combined solvents were removed on a rotary evaporator. The yield of benzyl (4-((4-methylbenzyl)amino)phenyl)carbamate (60%) was determined by $^1$H NMR with mesitylene as internal standard.

**NaBH$_4$**

A 10 mL round bottom flask was charged with $p$-tolylaldehyde (14 µL, 0.12 mmol), benzyl 4-aminophenylcarbamate (24 mg, 0.10 mmol) and MeOH (2 mL). The mixture was refluxed for 2 h. Sodium borohydride (7.5 mg, 0.2 mmol) was added to reaction mixture. The suspension was stirred at room temperature overnight. Then reaction mixture was refluxed for additional 2 h. After reaction completion, it was diluted with water, and the product extracted with EtOAc. Organic layer was washed with brine 2 times, dried (Na$_2$SO$_4$), and solvent was evaporated. The yield of benzyl (4-((4-methylbenzyl)amino)phenyl)carbamate (40%) was determined by $^1$H NMR with mesitylene as internal standard. The rest is a complex mixture of byproducts.

**NaBH(OAc)$_3$**

A 10 mL round bottom flask with input for Ar was charged with $p$-tolylaldehyde (12.0 µL, 0.1 mmol), benzyl 4-aminophenylcarbamate (33.6 mg, 0.1 mmol) and 1,2-dichloroethane (0.7 mL). The mixture was stirred at room temperature under Ar atmosphere for 15 min. Sodium triacetoxyborohydride (29.7 mg, 0.14 mmol) was added to reaction mixture. The suspension was stirred at room temperature under Ar atmosphere for 18 h. Then the reaction mixture was quenched with aqueous saturated NaHCO$_3$ and extracted three times with 10 mL of EtOAc. The organic layer was dried over anhydrous Na$_2$SO$_4$, filtered and evaporated. The yield of (4-((4-methylbenzyl)amino)phenyl)carbamate (59%) was determined by $^1$H NMR with mesitylene as internal standard.

**NaBH$_3$CN**

A penicillin vial was charged with benzyl 4-aminophenylcarbamate (36 mg, 0.15 mmol), glacial acetic acid (8 µL, 0.15 mmol) and methanol (2 mL). After that, $p$-tolylaldehyde (17 µL, 0.15 mmol) and solution of NaBH$_3$CN (19 mg, 0.30 mmol) in 1 mL of MeOH were added. The reaction mixture was stirred at room temperature overnight. Then the solution was evaporated and the residue was taken up with 10 mL of water and extracted two times with 15 mL of CH$_2$Cl$_2$. The organic layers were combined, dried over anhydrous Na$_2$SO$_4$, filtered and evaporated. The yield of Benzyl (4-((4-methylbenzyl)amino)phenyl)carbamate (87%) was determined by $^1$H NMR with mesitylene as internal standard.

**H$_2$/Pd/C, general conditions**

10% Pd/C (wet support, water content is 56%) (12 mg, 5 µmol, 5 mol%), benzyl 4-aminophenylcarbamate (20 mg, 0.08 mmol), $p$-tolylaldehyde (10 µL, 0.08 mmol) and stirring bar were charged into a glass vial in a 10 mL stainless autoclave. 0.5 mL of EtOH was added and
autoclave was sealed and charged with 5 atm H₂ at 40 °C. After 24 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH₂Cl₂; combined solvents were removed on a rotary evaporator. The yield of benzyl (4-((4-methylbenzyl)amino)phenyl)carbamate (4%) was determined by ¹H NMR with mesitylene as internal standard. The rest is complex mixture of byproducts.

H₂/Pd/C, 1% of Pd

10% Pd/C (wet support, water content is 56%) (2.4 mg, 2 µmol, 1 mol%) benzyl 4-aminophenylcarbamate (20 mg, 0.08 mmol), p-tolualdehyde (10 µL, 0.08 mmol), 0.2 mL of MeOH and stirring bar were charged into a glass vial in a 10 mL stainless autoclave. Reaction mixture was stirred overnight at room temperature. Then autoclave was charged with 3 atm H₂ at room temperature. After 15 h of stirring, the reactor was depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH₂Cl₂; combined solvents were removed on a rotary evaporator. No product detected by NMR with mesitylene as internal standard. The rest is p-phenylenediamine.

NOESY (400 MHz, CDCl₃) of N-(4-methoxyphenyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-amine
### 3. Cost evaluation\(^a\)

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<th>Reducing agent or reduction catalyst (catalog number)</th>
<th>Packing</th>
<th>Cost of 1 g, $</th>
<th>Amount in reaction, equiv.</th>
<th>Overall cost, $</th>
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\(a\) All pricing data are taken from Sigma-Aldrich catalog.

### 4. Reaction Mass Efficiency

For a general reductive amination reaction (Fig. S1) \(\text{RME} = \frac{D}{A*k_1+B*k_2+C*k_3} \)(%), where A-C indicate masses of the initial reagents including an amine, a carbonyl compound and a reducing agent, taken with coefficients \(k_1, k_2, k_3\) which indicate the molar ratio of the reagents, and \(D\) indicates mass of the product and is easily counted proceeding from molar weight of the product and its yield.
Another metric, Generalized RME (Table S1), takes into account the amounts of solvents used in the reactions, which are counted as if they are initial reagents.

**Table S1. Generalized RME**

<table>
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<tr>
<th>Product</th>
<th>Rh/CO</th>
<th>NaBH₄</th>
<th>NaBH(OAc)₃</th>
<th>NaBH₃CN</th>
<th>H₂/Pd</th>
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<tbody>
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<td>1</td>
<td>17.8%</td>
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<td>7.4%</td>
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<td>0.0%</td>
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<td>2</td>
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<td>1.4%</td>
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5. References