Manganese Catalyzed Reductive Amination of Aldehydes using Hydrogen as Reductant

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General information.

All reactions were carried out with oven-dried glassware using standard Schlenk techniques under an inert atmosphere of dry argon or in an argon-filled glove-box. Toluene, THF, diethyl ether, and dichloromethane were dried over a Braun MB-SPS-800 solvent purification system and degassed by thaw-freeze cycles. Ethanol (EtOH absolute anhydrous, Pure, Carlo Erba) was degassed and stored on molecular sieves 4 Å. Technical grade petroleum ether and ethyl acetate were used for chromatography column. Analytical TLC was performed on Merck 60F254 silica gel plates (0.25 mm thickness). Column chromatography was performed on Acros Organics Ultrapure silica gel (mesh size 40-60 μm, 60 Å). All reagents were obtained from commercial sources and liquid reagents were dried on 4 Å molecular sieves and degassed prior to use. Manganese pentacarbonyl bromide, min. 98%, was purchased from Strem Chemicals.

$^1$H, $^{13}$C, $^{19}$F and $^{31}$P NMR spectra were recorded in CDCl$_3$, acetone-$d_6$, or CD$_3$OD, at 298 K, on Bruker, AVANCE 400 spectrometer at 400.1, 100.6, 376.5 and 162.2 MHz, respectively. $^1$H and $^{13}$C NMR spectra were calibrated against the residual solvent signal at the corresponding central peak ($^1$H: CDCl$_3$ 7.26 ppm, acetone-$d_6$ 2.05 ppm, CD$_3$OD 3.31 ppm; $^{13}$C: CDCl$_3$ 77.16 ppm, acetone-$d_6$ 29.84 ppm, CD$_3$OD 49.00 ppm). $^{19}$F and $^{31}$P NMR spectra calibrated against CFCl$_3$ and 85% H$_3$PO$_4$ internal standard, respectively. Chemical shift (δ) and coupling constants (J) are given in ppm and in Hz, respectively. The peak patterns are indicated as follows: (s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; m, multiplet, and br. for broad).

Non-stirred Parr autoclaves (22 mL) were used for the hydrogenation.

GC analyses were performed with GC-2014 (Shimadzu) 2010 equipped with a 30 m capillary column (Supelco, SPBTM-20, fused silica capillary column, 30 m × 0.25 mm × 0.25 mm film thickness).

Low Resolution mass spectra were obtained on a QP2010 GC/MS apparatus from Shimadzu equipped with a 30 m capillary column (Supelco, SLBTM-5ms, fused silica capillary column, 30 M × 0.25 mm × 0.25 mm film thickness).

Specific rotations (in deg cm$^2$ g$^{-1}$) were measured in a 1 dm thermostated quartz cell on a Jasco-P1010 polarimeter.

Manganese complexes 1-4 were synthesized according to the literature procedure.$^1$

General procedure for reductive amination reaction.

In an argon filled glove box, a 20 mL Schlenk tube was charged with aldehyde (0.5 mmol), amine (0.6 mmol) and anhydrous ethanol (2.0 mL). The reaction mixture was stirred at 100 °C (or at room temperature for aldehyde containing α-protons) for 24 h. After cooling to room temperature, the mixture was transferred to a 20 mL autoclave followed by manganese complex 2 (5.0 mg, 2 mol%) and tBuOK (2.8 mg, 5 mol%). The autoclave was charged with H$_2$ (50 bar) and the mixture was stirred at indicated temperature in an oil bath (see Table 2, main article). After cooling to room temperature, the solution was diluted with ethyl acetate (2.0 mL) and filtered through a small pad of celite (2 cm in a Pasteur pipette). The celite was washed with ethyl acetate (2×2.0 mL). The filtrate was evaporated and the crude residue was purified by column chromatography (SiO$_2$, mixture of petroleum ether/ethyl acetate as eluent).
Specific procedure for reductive amination reaction on large scale (Table 2, entry 4).

A 50 mL Maximator autoclave (“Réacteur à ouverture rapide”) was purged with N₂ and then charged with a solution of benzaldehyde (475 µL, 4.3 mmol) and p-toluidine (500.0 mg, 4.6 mmol, 1.08 equiv.) in EtOH (10 mL). After stirring for 2 h at r.t., a solution of complex 2 (43 mg, 2 mol%) in EtOH (4 mL) and a solution of tBuOK (28 mg, 5 mol%) in EtOH (4 mL) were added under N₂ flow. The autoclave was charged with H₂ (50 bar) and the mixture was stirred at 100 °C for 24 h. The solution was concentrated under reduced pressure, and the crude residue was purified by column chromatography (SiO₂, mixture of petroleum ether/ethyl acetate as eluent). N-benzyl-4-methylaniline d4 was obtained as pale yellow oil (663 mg, 78%)
Characterization of the products of the catalysis

\(N\)-benzylaniline\(^2\) \(d_1\)

Following the general procedure, benzaldehyde (51.0 µL, 0.5 mmol) and aniline (54.8 µL, 0.6 mmol) gave the title compound \(d_1\) as a brown liquid (85.2 mg, 93% yield).

\(^1\)H NMR (400.1 MHz, CDCl\(_3\)) \(\delta\) 7.43 – 7.36 (m, 4H), 7.34 – 7.28 (m, 1H), 7.23 – 7.19 (m, 2H), 6.76 (td, \(J = 7.3, 1.1\) Hz, 1H), 6.68 (d, \(J = 7.7\) Hz, 2H), 4.36 (s, 2H), 4.08 (br, 1H).

\(^{13}\)C\[^1\]H NMR (100.6 MHz, CDCl\(_3\)) \(\delta\) 148.2, 139.5, 129.4, 128.7, 127.6, 127.3, 117.7, 113.0, 48.5.

\(N\)-(2-methylbenzyl)aniline\(^3\) \(d_2\)

Following the general procedure, 2-methylbenzaldehyde (57.8 µL, 0.5 mmol) and aniline (54.8 µL, 0.6 mmol) gave the title compound \(d_2\) as a dark brown liquid (52.7 mg, 94% yield).

\(^1\)H NMR (400.1 MHz, CDCl\(_3\)) \(\delta\) 7.35 (d, \(J = 6.7\) Hz, 1H), 7.26 – 7.17 (m, 5H), 6.74 (tt, \(J = 7.3, 1.1\) Hz, 1H), 6.67 – 6.64 (m, 2H), 4.29 (s, 2H), 3.84 (s, 1H), 2.39 (s, 3H).

\(^{13}\)C\[^1\]H NMR (100.6 MHz, CDCl\(_3\)) \(\delta\) 148.4, 137.1, 136.5, 130.5, 129.4, 128.4, 127.6, 126.3, 117.6, 112.8, 46.5, 19.1.

\(N\)-benzyl-4-methoxyaniline\(^2\) \(d_3\)

Following the general procedure, benzaldehyde (51.0 µL, 0.5 mmol) and 4-methoxyaniline (73.9 mg, 0.6 mmol) gave the title compound \(d_3\) as a brown solid (76.8 mg, 72% yield).

\(^1\)H NMR (400.1 MHz, CDCl\(_3\)) \(\delta\) 7.40 – 7.33 (m, 4H), 7.29 (d, \(J = 7.1\) Hz, 1H), 6.81 – 6.77 (m, 2H), 6.64 – 6.60 (m, 2H), 4.30 (s, 2H), 3.75 (s, 3H).

\(^{13}\)C\[^1\]H NMR (100.6 MHz, CDCl\(_3\)) \(\delta\) 152.4, 142.5, 139.8, 128.7, 127.7, 127.3, 115.0, 114.3, 55.9, 49.4.

\(N\)-benzyl-4-methylaniline\(^2\) \(d_4\)

Following the specific procedure, benzaldehyde (475.0 µL, 4.3 mmol) and 4-methylaniline (500.0 mg, 4.6 mmol) gave the title compound \(d_4\) as a pale yellow oil (663 mg, 78% yield).
$^1$H NMR (400.1 MHz, CDCl$_3$) $\delta$ 7.50 – 7.21 (m, 5H), 7.14 – 6.96 (m, 2H), 6.68 – 6.57 (m, 2H), 4.36 (s, 2H), 3.94 (s, 1H), 2.31 (s, 3H).

$^{13}$C($^1$H) NMR (100.6 MHz, CDCl$_3$) $\delta$ 146.0, 139.8, 129.9, 128.7, 127.6, 127.2, 126.8, 113.1, 48.7, 20.5.

$N$-(4-methoxybenzyl)aniline$^2$ d5

![Structure](image)

Following the general procedure, 4-methoxybenzaldehyde (60.8 µL, 0.5 mmol) and aniline (54.8 µL, 0.6 mmol) gave the title compound d5 as a yellow liquid (92.8 mg, 87% yield).

$^1$H NMR (400.1 MHz, CDCl$_3$) $\delta$ 7.30 (d, $J = 8.6$, 2H), 7.21 – 7.16 (m, 2H), 6.89 (d, $J = 8.6$ Hz, 2H), 6.73 (t, $J = 7.3$ Hz, 1H), 6.66 (dd, $J = 7.7, 1.1$ Hz, 2H), 4.27 (s, 2H), 3.81 (s, 3H).

$^{13}$C($^1$H) NMR (100.6 MHz, CDCl$_3$) $\delta$ = 159.0, 148.2, 131.4, 129.4, 129.0, 117.8, 114.2, 113.1, 55.4, 48.0.

$N$-benzyl-4-fluoroaniline$^2$ d6

![Structure](image)

Following the general procedure, benzaldehyde (51.0 µL, 0.5 mmol) and 4-fluoroaniline (57.6 µL, 0.6 mmol) gave the title compound d6 as a brown solid (28.2 mg, 28% yield).

$^1$H NMR (400.1 MHz, CDCl$_3$) $\delta$ 7.39 – 7.26 (m, 5H), 6.89 (t, $J = 8.7$, 2H), 6.60 – 6.55 (m, 2H), 4.30 (s, 2H), 3.94 (br, 1H).

$^{19}$F NMR (376.5 MHz, CDCl$_3$) $\delta$ -127.91.

$^{13}$C($^1$H) NMR (100.6 MHz, CDCl$_3$) $\delta$ 156.0 (d, $^{1}$J$_{CF}$ = 235.0), 144.6 (d, $^{1}$J$_{CF}$ = 1.5 Hz), 139.4, 128.8, 127.6, 127.4, 115.8 (d, $^{1}$J$_{CF}$ = 22.3 Hz), 113.8 (d, $^{1}$J$_{CF}$ = 7.4 Hz), 49.1.

$N$-(3-fluorobenzyl)aniline$^4$ d7

![Structure](image)

Following the general procedure, 3-fluorobenzaldehyde (53.0 µL, 0.5 mmol) and aniline (54.8 µL, 0.6 mmol) gave the title compound d7 as a pale yellow solid (90.6 mg, 90% yield).

$^1$H NMR (400.1 MHz, CDCl$_3$) $\delta$ 7.30 (td, $J = 7.9, 7.3$ Hz, 1H), 7.20-7.14 (m, 3H), 7.09 (dt, $J = 9.8, 2.0$ Hz, 1H), 6.96 (td, $J = 8.4, 2.6$ Hz, 1H), 6.74 (t, $J = 7.3$ Hz, 1H), 6.62 (d, $J = 7.9$ Hz, 2H), 4.35 (s, 2H), 4.09 (br, 1H).

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -113.00.
$^{13}$C$^\text{[H]}$ NMR (75 MHz, CDCl$_3$) δ 163.2 (d, $J_{CF} = 246.2$ Hz), 147.9, 142.4 (d, $J_{CS} = 6.8$ Hz), 130.2 (d, $J_{CS} = 8.2$ Hz), 129.4, 122.9 (d, $J_{CF} = 2.8$ Hz), 117.9, 114.4 (d, $J_{CS} = 8.3$ Hz), 114.1 (d, $J_{CF} = 7.9$ Hz), 113.0, 47.9.

GC-MS, m/z (%) = 201 ([M]+, 100), 109 (100), 77 (57), 65 (18), 51 (20).

$^N$-(4-chlorobenzyl)aniline$^5$ d8

Following the general procedure, 4-chlorobenzaldehyde (70.3 mg, 0.5 mmol) and aniline (54.8 µL, 0.6 mmol) gave the title compound d8 as a pale yellow liquid (87.1 mg, 80% yield).

$^1$H NMR (400.1 MHz, CDCl$_3$) δ 7.31 (s, 4H), 7.18 (t, $J = 7.9$ Hz, 2H), 6.74 (t, $J = 7.3$ Hz, 1H), 6.62 (d, $J = 7.8$ Hz, 2H), 4.32 (s, 2H), 4.06 (br, 1H).

$^{13}$C$^\text{[H]}$ NMR (100.6 MHz, CDCl$_3$) δ 147.9, 138.1, 133.0, 129.4, 128.9, 128.8, 117.9, 113.0, 47.8.

$N$-(4-bromobenzyl)-4-iodoaniline d9

Following the general procedure, 4-bromobenzaldehyde (92.5 mg, 0.5 mmol) and 4-iodoaniline (131.4 mg, 0.6 mmol) gave the title compound d9 as a white solid (190.1 mg, 98% yield). The isolated product contains about 13% of 4-bromobenzylaniline$^4$ resulting from deiodination.

$^1$H NMR (400.1 MHz, CDCl$_3$) δ = 7.46 (d, $J = 7.9$, 2H), 7.41 (d, $J = 8.1$, 2H), 7.21 (d, $J = 8.1$, 2H), 6.38 (d, $J = 8.2$, 2H), 4.26 (s, 2H), 4.12 (br, 1H).

$^{13}$C$^\text{[H]}$ NMR (100.6 MHz, CDCl$_3$) δ = 147.4, 138.03, 137.99, 131.9, 129.1, 121.3, 115.2, 78.6, 47.6.

GC-MS, m/z (%) = 389 ([M]+, 67), 308 (8), 169 (100), 90 (53), 76 (18), 63 (11), 50 (10).

$N$-benzyl-4-iodoaniline$^6$ d10

Following the general procedure, benzaldehyde (51.0 µL, 0.5 mmol) and 4-iodoaniline (131.4 mg, 0.6 mmol) gave the title compound d10 as a brown liquid (149.9 mg, 97% yield). The isolated product contains about 10% of benzylaniline resulting from deiodination.

$^1$H NMR (400.1 MHz, CDCl$_3$) δ 7.41 (d, $J = 8.6$ Hz, 2H), 7.37 – 7.34 (m, 5H), 6.42 (d, $J = 8.6$ Hz, 2H), 4.30 (d, $J = 3.9$ Hz, 2H), 4.10 (br, 1H).

$^{13}$C$^\text{[H]}$ NMR (100.6 MHz, CDCl$_3$) δ 147.8, 139.0, 137.9, 128.8, 127.6, 127.5, 115.2, 78.3, 48.2.
**N,N-dimethyl-4-((p-tolyl amino)methyl)aniline** \( \text{d}11 \)

Following the general procedure, 4-(dimethylamino)benzaldehyde (74.6 mg, 0.5 mmol) and \( p \)-toluidine (64.3 mg, 0.6 mmol) gave the title compound \( \text{d}11 \) as a colorless solid (117.8 mg, 97% yield).

\(^1\)H NMR (400.1 MHz, CDCl\(_3\)) \( \delta \) 7.25 (d, \( J = 8.8 \) Hz, 2H), 6.99 (d, \( J = 7.9 \) Hz, 2H), 6.73 (d, \( J = 8.2 \) Hz, 2H), 6.58 (d, \( J = 8.0 \) Hz, 2H), 4.19 (s, 2H), 3.76 (br, 1H), 2.94 (s, 6H), 2.25 (s, 3H).

\(^{13}\)C\({}^{1}\)H NMR (100.6 MHz, CDCl\(_3\)) \( \delta \) 150.1, 146.4, 129.8, 128.8, 127.5, 126.6, 113.1, 112.9, 48.4, 40.9, 20.5.

**Ethyl 4-((phenylamino)methyl)benzoate** \( \text{d}12 \)

Following the general procedure, methyl 4-formylbenzoate (82.1 mg, 0.5 mmol) and aniline (54.8 µL, 0.6 mmol) gave the title compound \( \text{d}12 \) as a pale yellow liquid (117.4 mg, 92% yield).

\(^1\)H NMR (400.1 MHz, CDCl\(_3\)) \( \delta \) 8.02 (d, \( J = 8.2 \) Hz, 1H), 7.44 (d, \( J = 8.1 \) Hz, 2H), 7.17 (t, \( J = 7.9 \) Hz, 2H), 6.73 (t, \( J = 7.3 \) Hz, 1H), 6.61 (d, \( J = 8.1 \) Hz, 2H), 4.41 – 4.34 (m, 5H, \( N\text{-CH}_2\text{+CH}_2\text{+NH} \)), 1.39 (t, \( J = 7.1 \) Hz, 3H).

\(^{13}\)C\({}^{1}\)H NMR (100.6 MHz, CDCl\(_3\)) \( \delta \) 166.6, 147.9, 145.0, 130.0, 129.4, 127.2, 118.0, 113.0, 61.1, 48.1, 14.5.

GC-MS, \( m/z(%) = 255 \) ([M]+, 100), 226(24), 210(28), 182(49), 163(100), 135(60), 106(51), 89(34), 77(40), 65(10), 51(8).

**N-((4-methoxyphenyl)amino)methyl)(phenyl)acetamide** \( \text{d}13 \)

Following the general procedure, \( N \)-((4-formylphenyl)acetamide (81.6 mg, 0.5 mmol) and 4-methoxyaniline (73.9, 0.6 mmol) gave the title compound \( \text{d}13 \) as a pale yellow solid (128.4 mg, 95% yield).

\(^1\)H NMR (400.1 MHz, CDCl\(_3\)) \( \delta \) 7.45 (d, \( J = 8.3 \) Hz, 2H), 7.31 (d, \( J = 8.2 \) Hz, 2H), 6.77 (d, \( J = 8.9 \) Hz, 2H), 6.59 (d, \( J = 8.9 \) Hz, 2H), 4.24 (s, 2H), 3.74 (s, 3H), 2.16 (s, 3H), 1.67 (br, 1H).

\(^{13}\)C\({}^{1}\)H NMR (100.6 MHz, CDCl\(_3\)) \( \delta \) 168.4, 152.3, 142.5, 137.0, 135.8, 128.3, 120.3, 115.0, 114.3, 56.0, 48.9, 24.7.
**N-(4-(phenylimino)ethyl)benzyl)aniline d14**

Following the general procedure, 4-acetylbenzaldehyde (74.1 mg, 0.5 mmol) and aniline (100.4 µL, 1.1 mmol) gave the title compound **d14** as a dark brown liquid (132.2 mg, 88% yield, 95% purity).

$^1$H NMR (400.1 MHz, CDCl$_3$) δ 7.96 (d, $J = 8.3$ Hz, 2H), 7.45 (d, $J = 8.1$ Hz, 2H), 7.36 (t, $J = 7.8$ Hz, 2H), 7.18 (t, $J = 7.3$ Hz, 2H), 7.09 (t, $J = 7.3$ Hz, 1H), 6.80 (d, $J = 7.3$ Hz, 2H), 6.74 (t, $J = 7.3$ Hz, 1H), 6.64 (d, $J = 7.8$ Hz, 2H), 4.41 (s, 2H), 4.12 (br, 1H), 2.23 (s, 3H).

$^{13}$C($^1$H) NMR (100.6 MHz, CDCl$_3$) δ 165.3, 151.8, 148.1, 142.3, 138.7, 129.4, 129.1, 127.7, 127.4, 123.3, 119.5, 117.9, 113.1, 48.1, 17.5.

GC-MS, m/z(%) = 300 ([M]+, 100), 285(23), 208(68), 193(33), 143(17), 116(15), 105(88), 90(30), 77(55), 51(14)

1-(4-((Phenylamino)methyl)phenyl)ethan-1-one d15

Following the general procedure, 4-acetylbenzaldehyde (74.1 mg, 0.5 mmol) and aniline (54.8 µL, 0.6 mmol) gave the title compound **d15** as a pale yellow solid (82.2 mg, 73% yield).

$^1$H NMR (400.1 MHz, CDCl$_3$) δ 7.93 (d, $J = 8.2$ Hz, 2H), 7.47 (d, $J = 8.2$ Hz, 2H), 7.17 (dd, $J = 8.6$, 7.2 Hz, 2H), 6.73 (t, $J = 7.3$ Hz, 1H), 6.61 (d, $J = 7.7$ Hz, 2H), 4.42 (s, 2H), 4.19 (s, br, 1H), 2.23 (s, 3H).

$^{13}$C($^1$H) NMR (100.6 MHz, CDCl$_3$) δ 197.9, 147.8, 145.3, 136.3, 129.4, 128.9, 127.4, 118.0, 113.1, 48.1, 26.7.

1-(4-(Benzylamino)phenyl)ethan-1-one d16

Following the general procedure, benzaldehyde (51.0 µL, 0.5 mmol) and 4-amino acetophenone (67.6 mg, 0.5 mmol) gave the title compound **d16** as a pale yellow solid (108.1 mg, 96% yield).

$^1$H NMR (400.1 MHz, CDCl$_3$) δ 7.82 (d, $J = 8.6$ Hz, 2H), 7.38 – 7.30 (m, 5H), 6.60 (d, $J = 8.6$ Hz, 2H), 4.58 (br, 1H), 4.41 (d, $J = 5.5$ Hz, 2H), 2.49 (s, 3H).

$^{13}$C($^1$H) NMR (100.6 MHz, CDCl$_3$) δ 196.5, 152.1, 138.4, 130.9, 128.9, 127.6, 127.4, 127.0, 111.7, 47.6, 26.1.
Following the general procedure, ferrocenecarboxaldehyde (107.0 mg, 0.5 mmol) and \( p \)-toluidine (64.3 mg, 0.6 mmol) gave the title compound \( \text{d17} \) as a dark brown liquid (149.5 mg, 98% yield).

\(^1\)H NMR (400.1 MHz, CDCl\(_3\)) \( \delta \) 7.02 (d, \( J = 8.1 \text{ Hz}, 2\)H), 6.60 (d, \( J = 8.3 \text{ Hz}, 2\)H), 4.24 (t, \( J = 1.9 \text{ Hz}, 2\)H), 4.18 (s, 5H), 4.14 (t, \( J = 1.8 \text{ Hz}, 2\)H), 3.94 (s, 2H), 3.75 (br, 1H), 2.26 (s, 3H).

\(^{13}\)C\(^{1}\)H) NMR (100.6 MHz, CDCl\(_3\)) \( \delta \) 146.3, 129.9, 126.9, 113.2, 86.9, 68.6, 68.2, 68.0, 43.9, 20.6.

Following the general procedure, \( 1 \)-methyl-1\( H \)-pyrrole-2-carbaldehyde (53.7 µL, 0.5 mmol) and 4-methoxyaniline (73.9 mg, 0.6 mmol) gave the title compound \( \text{d18} \) as a dark brown liquid (104.9 mg, 97% yield).

\(^1\)H NMR (400.1 MHz, CDCl\(_3\)) \( \delta \) 6.84 – 6.79 (m, 2H), 6.67 – 6.66 (m, 2H), 6.63 – 6.62 (m, 1H), 6.12 – 6.11 (m, 1H), 6.08 (t, \( J = 3.1 \text{ Hz}, 1\)H), 4.17 (s, 2H), 3.76 (s, 3H), 3.64 (s, 3H), 3.41 (br, 1H).

\(^{13}\)C\(^{1}\)H) NMR (100.6 MHz, CDCl\(_3\)) \( \delta \) 152.5, 142.6, 130.1, 122.9, 115.1, 114.4, 108.5, 106.9, 56.0, 41.5, 33.9.

Following the general procedure, 5-methylfuran-2-carbaldehyde (50.1 µL, 0.5 mmol) and 4-methoxyaniline (73.9 mg, 0.6 mmol) gave the title compound \( \text{d19} \) as a brown solid (97.8 mg, 90% yield).

\(^1\)H NMR (400.1 MHz, CDCl\(_3\)) \( \delta \) 6.79 (d, \( J = 8.9 \text{ Hz}, 2\)H), 6.65 (d, \( J = 8.8 \text{ Hz}, 2\)H), 6.09 (d, \( J = 3.0 \text{ Hz}, 1\)H), 5.98 (d, \( J = 2.5 \text{ Hz}, 1\)H), 4.21 (s, 2H), 3.75 (s, 4H, OCH\(_3\)+NH), 2.28 (s, 3H).

\(^{13}\)C\(^{1}\)H) NMR (100.6 MHz, CDCl\(_3\)) \( \delta \) 152.7, 151.7, 151.2, 142.1, 115.0, 114.8, 107.9, 106.2, 55.9, 42.7, 13.7.

Following the general procedure, \( 1 \)-pyridin-2-ylmethyl)aniline \( \text{d20} \)
Following the general procedure, pyridine-2-carboxaldehyde (47.6 µL, 0.5 mmol) and aniline (54.8 µL, 0.6 mmol) gave the title compound **d20** as a brown liquid (62.6 mg, 68% yield, 90% purity by \(^1\)H NMR).

\(^1\)H NMR (400.1 MHz, CDCl\(_3\)) \(\delta\) 8.59 (d, \(J = 4.8\) Hz, 1H), 7.63 (td, \(J = 7.7, 1.8\) Hz, 1H), 7.34 (d, \(J = 7.8\) Hz, 1H), 7.21 – 7.16 (m, 3H), 6.73 (tt, \(J = 7.4, 1.1\) Hz, 1H), 6.69 – 6.66 (m, 2H), 4.84 (br, 1H), 4.47 (s, 2H).

\(^13\)C\{\(^1\)H\} NMR (100.6 MHz, CDCl\(_3\)) \(\delta\) 158.6, 149.2, 147.9, 136.7, 129.3, 122.2, 121.7, 117.6, 113.1, 49.3.

N-benzylpyridin-2-amine\(^5\) **d21**

Following the general procedure, benzaldehyde (51.0 µL, 0.5 mmol) and 2-aninopyridine (56.5 mg, 0.6 mmol) gave the title compound **d21** as a colorless solid (50.7 mg, 55% yield).

\(^1\)H NMR (400.1 MHz, CDCl\(_3\)) \(\delta\) 8.12 (ddd, \(J = 5.0, 2.0, 0.9\) Hz, 1H), 7.44 – 7.34 (m, 5H), 7.32 – 7.28 (m, 1H), 6.61 (ddd, \(J = 7.1, 5.0, 0.9\) Hz, 1H), 6.39 (dt, \(J = 8.3, 1.0\) Hz, 1H), 5.05 (s, 1H), 4.53 (d, \(J = 5.8\) Hz, 2H).

\(^13\)C\{\(^1\)H\} NMR (100.6 MHz, CDCl\(_3\)) \(\delta\) 158.8, 148.3, 139.3, 137.6, 128.7, 127.5, 127.3, 113.2, 106.9, 46.4.

2-((Benzylamino)thiophene-3-carbonitrile **d22**

Following the general procedure, benzaldehyde (51.0 µL, 0.5 mmol) and 2-aminothiophene-3-carbonitrile (74.5 mg, 0.6 mmol) gave the title compound **d22** as a dark green solid (96.4 mg, 90% yield).

\(^1\)H NMR (400.1 MHz, CDCl\(_3\)) \(\delta\) 7.41 – 7.30 (m, 5H), 6.78 (d, \(J = 5.7\) Hz, 1H), 6.29 (d, \(J = 5.7\) Hz, 1H), 5.57 (br, 1H), 4.41 (s, 2H).

\(^13\)C\{\(^1\)H\} NMR (100.6 MHz, CDCl\(_3\)) \(\delta\) 165.3, 136.6, 128.9, 128.2, 127.8, 126.1, 116.4, 108.7, 84.5, 51.8.

GC-MS, m/z(%) = 214 ([M]+, 19), 91(100), 65(15).

N-benzyl-5-methylthiazol-2-amine\(^10\) **d23**

Following the general procedure, benzaldehyde (51.0 µL, 0.5 mmol) and 5-methylthiazol-2-amine (68.5 mg, 0.6 mmol) gave the title compound **d23** as a colorless solid (94.0 mg, 92% yield, 95% purity).

\(^1\)H NMR (400.1 MHz, CDCl\(_3\)) \(\delta\) 7.38 – 7.26 (m, 5H), 6.65 (s, 1H), 6.28 (br, 1H), 4.42 (s, 2H), 2.26 (s, 3H).

\(^13\)C\{\(^1\)H\} NMR (100.6 MHz, CDCl\(_3\)) \(\delta\) 169.2, 138.0, 135.3, 128.7, 127.74, 127.66, 121.0, 49.9, 12.1.
**N-(4-bromobenzyl)benzenesulfonamide d24**

![Chemical Structure](image)

Following the general procedure, 4-bromobenzaldehyde (92.5 mg, 0.5 mmol) and benzenesulfonamide (94.3 mg, 0.6 mmol) gave the title compound **d24** as a white solid (151.7 mg, 93% yield, 90% purity).

$^1$H NMR (400.1 MHz, CDCl$_3$) δ 7.81 (d, $J = 7.6$ Hz, 2H), 7.57 (t, $J = 7.4$ Hz, 1H), 7.47 (t, $J = 7.7$ Hz, 2H), 7.34 (d, $J = 8.3$ Hz, 2H), 7.04 (d, $J = 8.2$ Hz, 2H), 5.43 (t, $J = 6.4$ Hz, 1H), 4.06 (d, $J = 5.8$ Hz, 2H).

$^{13}$C{$_1^H$} NMR (100.6 MHz, CDCl$_3$) δ 139.9, 135.5, 132.9, 131.9, 129.6, 129.3, 127.2, 121.9, 46.7.

GC-MS, m/z(%) = 325 ([M]+, 0.5), 246(0.5), 184(100), 157(10), 143(20), 125(11), 104(10), 90(13), 77(91), 51(31).

**Dibenzyamine² d25**

![Chemical Structure](image)

Following the general procedure, benzaldehyde (51.0 µL, 0.5 mmol) and benzylamine (65.5 µL, 0.6 mmol) gave the title compound **d25** as a pale yellow liquid (88.8 mg, 90% yield).

$^1$H NMR (400.1 MHz, CDCl$_3$) δ 7.38 – 7.26 (m, 10H), 3.84 (s, 4H), 1.91 (br, 1H).

$^{13}$C{$_1^H$} NMR (100.6 MHz, CDCl$_3$) δ 140.4, 128.5, 128.3, 127.1, 53.3.

**N-benzyldodecan-1-amine¹¹ d26**

![Chemical Structure](image)

Following the general procedure, benzaldehyde (51.0 µL, 0.5 mmol) and dodecylamine (111.2 mg, 0.6 mmol) gave the title compound **d26** as a pale yellow liquid (130.9 mg, 95% yield).

$^1$H NMR (400.1 MHz, CDCl$_3$) δ 7.37 – 7.22 (m, 5H), 3.79 (s, 2H), 2.63 (t, $J = 7.0$ Hz, 2H), 1.58 -1.47 (m, 2H), 1.35 –1.26 (m, 20H), 0.88 (t, $J = 6.8$ Hz, 3H).

$^{13}$C{$_1^H$} NMR (100.6 MHz, CDCl$_3$) δ 140.7, 128.5, 128.3, 127.0, 54.2, 49.7, 32.1, 30.3, 29.81, 29.79, 29.76, 29.72, 29.5, 27.5, 22.8, 14.3.

**N-benzylcyclohexanamine¹² d27**

![Chemical Structure](image)
Following the general procedure, benzaldehyde (51.0 µL, 0.5 mmol) and cyclohexanamine (68.8 µL, 0.6 mmol) gave the title compound d27 as a pale yellow liquid (89.0 mg, 94% yield).

$^1$H NMR (400.1 MHz, CDCl$_3$) δ 7.35 – 7.22 (m, 5H), 3.82 (s, 2H), 2.52 – 2.47 (m, 1H), 1.93 – 1.91 (m, 2H), 1.76 – 1.71 (m, 2H), 1.64 – 1.59 (m, 1H), 1.42 (br, 1H), 1.31 – 1.08 (m, 5H).

$^{13}$C($^1$H) NMR (100.6 MHz, CDCl$_3$) δ 141.1, 128.5, 128.2, 126.9, 56.3, 51.2, 33.7, 26.3, 25.2.

Tribenzylamine d28

Following the general procedure, benzaldehyde (51.0 µL, 0.5 mmol) and dibenzylamine (116.1 µL, 0.6 mmol) gave the title compound d28 as a pale yellow solid (138.0 mg, 96% yield).

$^1$H NMR (400.1 MHz, CDCl$_3$) δ 7.47 (d, $J = 7.5$ Hz, 6H), 7.37 (t, $J = 7.4$ Hz, 6H), 7.29 (d, $J = 7.2$ Hz, 3H), 3.62 (s, 6H).

$^{13}$C($^1$H) NMR (100.6 MHz, CDCl$_3$) δ 139.8, 128.9, 128.3, 127.0, 58.1.

N-benzyl-N-ethylethanamine d29

Following the general procedure, benzaldehyde (51.0 µL, 0.5 mmol) and diethylamine (61.8 µL, 0.6 mmol) gave the title compound d29 as a pale yellow liquid (76.7 mg, 94% yield).

$^1$H NMR (400.1 MHz, CDCl$_3$) δ 7.38 – 7.21 (m, 5H), 3.57 (s, 2H), 2.52 (q, $J = 7.1$ Hz, 4H), 1.04 (t, $J = 7.1$ Hz, 6H).

$^{13}$C($^1$H) NMR (100.6 MHz, CDCl$_3$) δ 138.8, 129.3, 128.3, 127.1, 57.2, 46.5, 11.4.

1-Benzylpiperidine d30

Following the general procedure, benzaldehyde (51.0 µL, 0.5 mmol) and piperidine (59.3 µL, 0.6 mmol) gave the title compound d30 as a pale yellow liquid (81.5 mg, 93% yield).

$^1$H NMR (400.1 MHz, CDCl$_3$) δ 7.39 – 7.28 (m, 5H), 3.53 (s, 2H), 2.50 – 2.41 (m, 4H), 1.63 – 1.57 (m, 4H), 1.45 – 1.43 (m, 2H).

$^{13}$C($^1$H) NMR (100.6 MHz, CDCl$_3$) δ 138.0, 129.6, 128.3, 127.2, 63.7, 54.4, 25.9, 24.4.
$N,N'$-dibenzylethane-1,2-diamine$^{15}$ d31

Following the general procedure, benzaldehyde (122.4 µL, 1.2 mmol) and ethane-1,2-diamine (33.5 µL, 0.5 mmol) gave the title compound d31 as a pale yellow solid (114.2 mg, 95% yield).

$^1$H NMR (400.1 MHz, CDCl$_3$) δ 7.37-7.25 (m, 10H), 3.81 (s, 4H), 2.79 (s, 4H), 1.86 (s, 2H, NH).

$^{13}$C($^1$H) NMR (100.6 MHz, CDCl$_3$) δ 140.5, 128.5, 128.2, 127.0, 54.0, 48.8.

2-(Benzylamino)ethan-1-ol$^{16}$ d32

Following the general procedure, benzaldehyde (51.0 µL, 0.5 mmol) and 2-aminoethan-1-ol (30.0 µL, 0.5 mmol) gave the title compound d32 as a pale yellow liquid (65.0 mg, 86% yield).

$^1$H NMR (400.1 MHz, CDCl$_3$) δ 7.35 – 7.23 (m, 5H), 3.81 (s, 2H), 3.65 (t, $J = 5.2$ Hz, 2H), 2.80 (t, $J = 5.2$ Hz, 2H), 2.07 (br, 2H, NH + OH + H$_2$O).

$^{13}$C($^1$H) NMR (100.6 MHz, CDCl$_3$) δ 140.1, 128.6, 128.3, 127.2, 61.1, 53.6, 50.7.

3-(Benzylamino)propan-1-ol d33

Following the general procedure, benzaldehyde (51.0 µL, 0.5 mmol) and 3-aminopropan-1-ol (38.2 µL, 0.5 mmol) gave the title compound d33 as a colorless liquid (68.6 mg, 83% yield).

$^1$H NMR (400.1 MHz, CDCl$_3$) δ = 7.35 – 7.24 (m, 5H), 3.91 – 3.79 (m, 2H), 3.67 – 3.65 (m, 1H), 3.34 (br, 1H), 2.64 (br, 1H), 1.56 – 1.42 (m, 2H), 0.93 (t, $J = 6.8$, 3H).

$^{13}$C($^1$H) NMR (100.6 MHz, CDCl$_3$) δ = 139.7, 128.6, 128.3, 127.3, 64.4, 54.1, 49.5, 30.9.

GC-MS, m/z(%) = 165([M]+, 2), 120(50), 106(19), 91(100), 77(3), 65(9).

(R)-2-(Benzylamino)butan-1-ol$^{17}$ d34

Following the general procedure, benzaldehyde (51.0 µL, 0.5 mmol) and (R)-2-amino-1-butanol (CAS: 5856-63-3, 47.5 µL, 0.5 mmol) gave the title compound d34 as a white solid (86.9 mg, 97% yield).

$^1$H NMR (400.1 MHz, CDCl$_3$) δ 7.37 – 7.24 (m, 5H), 3.91 – 3.79 (m, 2H), 3.67 – 3.65 (m, 1H), 3.34 (br, 1H), 2.64 (br, 1H), 1.56 – 1.42 (m, 2H), 0.93 (t, $J = 6.8$, 3H).
$^{13}$C($^1$H) NMR (100.6 MHz, CDCl$_3$) δ 140.5, 128.6, 128.2, 127.2, 62.7, 59.8, 51.2, 24.5, 10.5.

$[\alpha]_D^{20} = -30.61$ (C 0.5, CH$_2$Cl$_2$).

Ethyl (R)-2-(benzylamino)-2-phenylacetate$^{18}$ d35

(R)-2-Phenylglycinemethyl ester hydrochloride (CAS: 19883-41-1, 121.0 mg, 0.6 mmol) was added into an Et$_3$N (111.5 µL, 0.8 mmol) solution in THF (5.0 mL) and stirred for 2 h. The solution was filtered through celite then washed with ethyl acetate (3×2.0 mL). The filtrate was evaporated to dryness to afford (R)-2-phenylglycinemethyl ester, which was used for the following step without further purification.

Following the general procedure, benzaldehyde (51.0 µL, 0.5 mmol) and (R)-2-phenylglycinemethyl ester hydrochloride (121.0 mg, 0.6 mmol) gave the title compound d35 as a pale yellow liquid (121.2 mg, 90% yield).

$^1$H NMR (400.1 MHz, CDCl$_3$) δ 7.41–7.24 (m, 10H), 4.39 (s, 1H), 4.24–4.09 (m, 2H), 3.75 (s, 2H), 1.21 (t, $J = 7.0$ Hz, 3H).

$^{13}$C($^1$H) NMR (100.6 MHz, CDCl$_3$) δ 173.1, 139.6, 138.3, 128.7, 128.5, 128.4, 128.1, 127.6, 127.2, 64.5, 61.2, 51.5, 14.2.

$[\alpha]_D^{20} = -4.98$ (C 1.2, CH$_2$Cl$_2$)

Ethyl benzyl-L-alaninate$^{19}$ d36

L-Alanine ethyl ester hydrochloride (CAS: 1115-59-9, 92.2 mg, 0.6 mmol) was added into an Et$_3$N (111.5 µL, 0.8 mmol) solution in THF (5.0 mL) and stirred for 2 h. The solution was filtered through celite then washed with ethyl acetate (3×2.0 mL). The filtrate was evaporated to dryness to afford L-alanine ethyl ester, which was used for the following step without further purification.

Following the general procedure, benzaldehyde (51.0 µL, 0.5 mmol) and L-alanine ethyl ester hydrochloride (92.2 mg, 0.6 mmol) gave the title compound d36 as a pale yellow liquid (94.3 mg, 91% yield).

$^1$H NMR (400.1 MHz, CDCl$_3$) δ = 7.34–7.22 (m, 5H), 4.19 (q, $J = 7.1$, 2H), 3.83–3.66 (m, 2H), 3.40–3.38 (m, 1H), 2.10 (br, 1H), 1.32 (d, $J = 6.3$, 3H), 1.29 (t, $J = 7.0$, 4H).

$^{13}$C($^1$H) NMR (100.6 MHz, CDCl$_3$) δ = 175.9, 139.7, 128.5, 128.4, 127.2, 60.8, 56.0, 52.2, 19.2, 14.4.

$[\alpha]_D^{20} = + 3.17$ (C 0.9, CH$_2$Cl$_2$)
Following the general procedure, butyraldehyde (45.1 µL, 0.5 mmol) and dodecylamine (111.2 mg, 0.6 mmol) gave the title compound **d37** as a yellow-green liquid (115.9 mg, 96% yield). This compound was further purified by bulb to bulb distillation.

\[
^1H\text{NMR (400.1 MHz, CDCl}_3) \delta 2.59 (m, 4H), 1.70 - 1.12 (m, 25H), 0.93 - 0.86 (m, 6H).
\]

\[
^{13}C\{^1H\}\text{NMR (100.6 MHz, CDCl}_3) \delta 50.3, 49.9, 32.4, 32.1, 30.2, 29.82, 29.79, 29.77, 29.74, 29.5, 27.6, 22.8, 20.7, 14.27, 14.18.
\]

GC-MS, m/z(%) = 241 ([M]+, 25), 198(100), 184(9), 142(9), 87(100), 70(11), 57(27).

Following the general procedure, 5-norbornene-2-carboxaldehyde (52.6 µL, 0.5 mmol) and aniline (54.8 µL, 0.6 mmol) gave the title compound **d38** as mixture of endo/exo isomers as a brown liquid (94.7 mg, 95% yield).

\[
M = \text{Major isomer endo, } m = \text{minor isomer exo, ratio } M:m = 60:40
\]

\[
^1H\text{NMR (400.1 MHz, CDCl}_3) \delta 7.20 - 7.16 (m, 2H, M + m, CH=CH), 6.75 - 6.66 (m, 1H, M + m, CH=CH), 6.64 - 6.58 (m, 2H, CH=CH), 6.19 (dd, J = 5.7, 3.0 Hz, 1H, M, CH=CH), 6.15 - 6.02 (m, 2H, m, CH=CH), 5.97 (dd, J = 5.8, 2.9 Hz, 1H, M, CH=CH), 3.18 (dd, J = 11.9, 6.9 Hz, 1H, m, CH=N), 3.09 (dd, J = 11.9, 8.3 Hz, 1H, m, CH=N), 2.92 (br s, 1H, M, CH=CH), 2.90 - 2.76 (m, 4H, M, CH=N +CH, m, CH), 2.73 (br s, 1H, m, CH), 2.36 (m, 1H, CH), 1.92 (ddd, J = 11.5, 9.1, 3.9 Hz, 1H, M, CH=CH), 1.76 - 1.64 (m, 1H, m, CH), 1.47 (dd, J = 8.2, 2.2 Hz, 1H, M, CH=CH), 1.44 - 1.33 (m, 3H, m, CH=CH), 1.28 (dt, J = 8.3, 1.6 Hz, 1H, M, CH=CH), 1.23 (dt, J = 11.6, 3.8 Hz, 1H, m, CH=CH), 0.64 (ddd, J = 11.5, 4.4, 2.6 Hz, 1H, M, CH=CH).
\]

\[
^{13}C\{^1H\}\text{NMR (100.6 MHz, CDCl}_3) \delta 148.69 (C_qAr, M), 148.63 (C_qAr, m), 137.76 (M, CH=CH), 136.91 (m, CH=CH), 136.56 (m, CH=CH), 132.19 (M, CH=CH), 129.37 (m, CH=CH), 129.34 (M, CH=CH), 117.24 (m, CH=Ar), 117.20 (M, CH=CH), 112.83 (M, CH=CH), 112.78 (m, CH=CH), 49.72 (m, CH), 49.70 (M, CH), 48.33 (M, CH), 45.39 (m, CH), 44.63 (m, CH), 44.38 (M, CH), 42.53 (M, CH), 41.83 (m, CH), 39.14 (m, CH), 38.87 (M, CH), 31.41 (m, CH=CH), 30.59 (M, CH=CH).
\]

GC-MS, m/z(%) = 199([M]+, 47), 158(12), 132(88), 106(100), 91(13), 77(42), 65(13), 51(13)

Following the general procedure, N-(bicyclo[2.2.1]hept-5-en-2-yl)methyl)aniline **d38** gave the title compound as a mixture of endo/exo isomers as a brown liquid.
Following the general procedure, 2,6-dimethyl-5-heptenal (84.2 µL, 0.5 mmol) and aniline (54.8 µL, 0.6 mmol) gave the title compound **d39** as a brown liquid (104.3 mg, 96% yield).

$^1$H NMR (400.1 MHz, CDCl$_3$) δ 7.17 (td, $J = 7.4$, 1.8 Hz, 2H), 6.68 (tt, $J = 7.3$, 1.1 Hz, 1H), 6.60 (dd, $J = 8.6$, 1.1 Hz, 2H), 5.11 (m, 1H), 3.70 (br, 1H), 3.06 (dd, $J = 12.2$, 5.9 Hz, 1H), 2.89 (dd, $J = 12.2$, 7.3 Hz, 1H), 2.14 – 1.94 (m, 2H), 1.82 – 1.72 (m, 1H), 1.69 (s, 3H), 1.62 (s, 3H), 1.54 – 1.42 (m, 1H), 1.32 – 1.08 (m, 1H), 0.99 (d, $J = 6.7$, 3H).

$^{13}$C($^1$H) NMR (100.6 MHz, CDCl$_3$) δ 148.77, 131.71, 129.35, 124.64, 117.07, 112.77, 50.40, 35.02, 32.70, 25.87, 25.59, 18.17, 17.85.

GC-MS, m/z(%) = 217([M]+, 60), 146(100), 133(10), 106(95), 93(20), 77(35), 69(9), 51(9).

$N$-(3-phenylpropyl)aniline$^{20}$ **d40**

Following the general procedure cinnamaldehyde (62.9 µL, 0.5 mmol) and aniline (54.8 µL, 0.6 mmol) gave the title compound **d40** as pale yellow liquid (98.3 mg, 93% yield).

$^1$H NMR (400.1 MHz, CDCl$_3$) δ 7.36 – 7.11 (m, 7H), 6.70 (t, $J = 7.3$ Hz, 1H), 6.59 (d, $J = 7.9$ Hz, 2H), 3.62 (s, 1H), 3.16 (t, $J = 7.0$ Hz, 2H), 2.75 (t, $J = 7.5$ Hz, 2H), 1.97 (p, $J = 7.2$ Hz, 2H).

$^{13}$C($^1$H) NMR (100.6 MHz, CDCl$_3$) δ 148.5, 141.8, 129.4, 128.6, 128.5, 126.1, 117.3, 112.9, 43.6, 33.5, 31.2.
### Supplementary tables

**Table S1. Hydrogenation of benzylideneaniline: influence of the solvent.**[^a]  

<table>
<thead>
<tr>
<th>Entry</th>
<th>Temp. (°C)</th>
<th>Solvent</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
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<td>130</td>
<td>Toluene</td>
<td>48</td>
</tr>
<tr>
<td>2</td>
<td>130</td>
<td>t-amyl alcohol</td>
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</tr>
<tr>
<td>3</td>
<td>130</td>
<td>Dimethyl carbonate</td>
<td>84</td>
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<td>4</td>
<td>130</td>
<td>THF</td>
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<td>5</td>
<td>130</td>
<td>1,4-dioxane</td>
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<tr>
<td>11</td>
<td>100</td>
<td>MeOH</td>
<td>84</td>
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</table>

[^a]: Conditions: An autoclave was charged in a glovebox with, in this order, c1 (45.3 mg, 0.25 mmol), solvent (2.0 mL), 2 (6.2 mg, 5.0 mol%), tBuOK (2.8 mg, 10 mol%), and then pressurized with H2 (50 bar) and heated at the indicated temperature. Yield determined by GC and ^1^H NMR spectroscopy.
**Table S2.** Hydrogenation of benzylideneaniline: influence of the base.[a]

![Chemical Structure]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Base (mol%)</th>
<th>Yield (%)</th>
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<tr>
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<td>tBuOK (2)</td>
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</tr>
<tr>
<td>2</td>
<td>tBuONa (2)</td>
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</tr>
<tr>
<td>3</td>
<td>Cs$_2$CO$_3$ (2)</td>
<td>57</td>
</tr>
<tr>
<td>4</td>
<td>KHMDMS (2)</td>
<td>41</td>
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</tbody>
</table>

[a] Conditions: An autoclave was charged in a glovebox with, in this order, c1 (90.6 mg, 0.5 mmol), anhydrous ethanol (2.0 mL), 2 (2.5 mg, 1.0 mol%), base (2 mol%), and then pressurized with H$_2$ (50 bar) and heated at 100 °C. Yield determined by GC and $^1$H NMR spectroscopy.
Table S3. Hydrogenation of benzylideneaniline: control experiments.\textsuperscript{[a]}

\[ \text{c1} \rightleftharpoons \text{d1} \]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst (mol%)</th>
<th>Base (mol%)</th>
<th>$\text{H}_2$ (bar)</th>
<th>Yield (%)</th>
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<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>$\text{tBuOK}$ (5)</td>
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<td>&lt; 1</td>
</tr>
<tr>
<td>2</td>
<td>2 (2)</td>
<td>-</td>
<td>50</td>
<td>3</td>
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<tr>
<td>3</td>
<td>2 (2)</td>
<td>$\text{tBuOK}$ (5)</td>
<td>25</td>
<td>87</td>
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</table>

\textsuperscript{[a]} Conditions: An autoclave was charged in a glovebox with, in this order, \textbf{c1} (90.6 mg, 0.5 mmol), anhydrous ethanol (2.0 mL), \textbf{2} (5.0 mg, 2.0 mol\%), \textbf{tBuOK} (2.8 mg, 5 mol\%), and then pressurized with $\text{H}_2$ (50 or 25 bar) and heated at 50 °C. Yield determined by GC and 1H NMR spectroscopy.
**Table S4.** Optimization of the procedure for reductive amination of benzaldehyde with aniline in the presence of manganese precatalyst complex 2

![Chemical structure](image)

<table>
<thead>
<tr>
<th>Condition</th>
<th>Yield (%)</th>
<th>Yield (%)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
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</tr>
<tr>
<td>B</td>
<td>29</td>
<td>7</td>
<td>61</td>
</tr>
<tr>
<td>C</td>
<td>2</td>
<td>87</td>
<td>11</td>
</tr>
</tbody>
</table>

Conditions A: an autoclave was charged with 2 (5.0 mg, 2 mol%), anhydrous ethanol (2.0 mL), aniline (46 µL, 0.5 mmol), benzaldehyde (51.0 µL, 0.5 mmol), tBuOK (2.8 mg, 5 mol%) and H₂ (50 bar) and heated at 80 °C for 20 h.

Conditions B: an autoclave was charged with 2 (5.0 mg, 2 mol%), anhydrous ethanol (2.0 mL), aniline (46 µL, 0.5 mmol), benzaldehyde (51.0 µL, 0.5 mmol) and tBuOK (2.8 mg, 5 mol%). After heating at 80 °C for 5 h, H₂ (50 bar) was charged and the mixture heated at 80 °C for 20 h.

Conditions C: in a 20 mL Schlenk tube aniline (46 µL, 0.5 mmol) and benzaldehyde (51.0 µL, 0.5 mmol) in anhydrous ethanol (2.0 mL) were heated at 100 °C for 24 h. The reaction mixture was transferred into an autoclave followed by 2 (5.0 mg, 2 mol%), tBuOK (2.8 mg, 5 mol%) and H₂ (50 bar), then heated at 80 °C for 20 h.
Table S5. Hydrogenation of ketimine.

![Chemical structure]

<table>
<thead>
<tr>
<th>Entry[^a]</th>
<th>2 (mol%)</th>
<th>tBuOK (mol%)</th>
<th>Temp. (°C)</th>
<th>Yield (%)</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>5</td>
<td>50</td>
<td>&lt;1</td>
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<tr>
<td>2</td>
<td>5</td>
<td>10</td>
<td>100</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

[^a] Conditions: an autoclave was charged in a glovebox with, in this order, ketimine (119.7 mg, 0.5 mmol), anhydrous ethanol (2.0 mL), 2 (2.0 or 5.0 mol%), tBuOK (5 or 10 mol%), pressurized with H₂ (50 bar), then heated at the indicated temperature.
NMR Spectra of the products of reductive amination

**Figure S1:** $^1$H NMR spectrum of the compound d1 in CDCl$_3$ recorded at 400.1 MHz.

**Figure S2:** $^{13}$C($^1$H) NMR spectrum of the compound d1 in CDCl$_3$ recorded at 100.6 MHz.
Figure S3: $^1$H NMR spectrum of the compound d2 in CDCl$_3$ recorded at 400.1 MHz.

Figure S4: $^{13}$C($^1$H) NMR spectrum of the compound d2 in CDCl$_3$ recorded at 100.6 MHz.
Figure S5: $^1$H NMR spectrum of the compound d3 in CDCl$_3$ recorded at 400.1 MHz.

Figure S6: $^{13}$C($^1$H) NMR spectrum of the compound d3 in CDCl$_3$ recorded at 100.6 MHz.
Figure S7: $^1$H NMR spectrum of the compound d4 in CDCl$_3$ recorded at 400.1 MHz.

Figure S8: $^{13}$C($^1$H) NMR spectrum of the compound d4 in CDCl$_3$ recorded at 100.6 MHz.
Figure S9: $^1$H NMR spectrum of the compound d5 in CDCl$_3$ recorded at 400.1 MHz.

Figure S10: $^{13}$C($^1$H) NMR spectrum of the compound d5 in CDCl$_3$ recorded at 100.6 MHz.
Figure S11: $^1$H NMR spectrum of the compound d6 in CDCl$_3$ recorded at 400.1 MHz.

Figure S12: $^{19}$F NMR spectrum of the compound d6 in CDCl$_3$ recorded at 376.5 MHz.
Figure S13: $^{13}$C($^1$H) NMR spectrum of the compound d6 in CDCl$_3$ recorded at 100.6 MHz.

Figure S14: $^1$H NMR spectrum of the compound d7 in CDCl$_3$ recorded at 400.1 MHz.
Figure S15: $^{19}$F NMR spectrum of the compound d7 in CDCl$_3$ recorded at 376.5 MHz.

Figure S16: $^{13}$C($^1$H) NMR spectrum of the compound d7 in CDCl$_3$ recorded at 100.6 MHz.
Figure S17: $^1$H NMR spectrum of the compound d8 in CDCl$_3$ recorded at 400.1 MHz.

Figure S18: $^{13}$C($^1$H) NMR spectrum of the compound d8 in CDCl$_3$ recorded at 100.6 MHz.
Figure S19: $^1$H NMR spectrum of the compound d9 in CDCl$_3$ recorded at 400.1 MHz.

Figure S20: $^{13}$C{$^1$H} NMR spectrum of the compound d9 in CDCl$_3$ recorded at 100.6 MHz.
Figure S21: $^1$H NMR spectrum of the compound d10 in CDCl$_3$ recorded at 400.1 MHz.

Figure S22: $^{13}$C[$^1$H] NMR spectrum of the compound d10 in CDCl$_3$ recorded at 100.6 MHz.
Figure S23: $^1$H NMR spectrum of the compound d11 in CDCl$_3$ recorded at 400.1 MHz.

Figure S24: $^{13}$C[$^1$H] NMR spectrum of the compound d11 in CDCl$_3$ recorded at 100.6 MHz.
Figure S25: $^1$H NMR spectrum of the compound d12 in CDCl$_3$ recorded at 400.1 MHz.

Figure S26: $^{13}$C[$^1$H] NMR spectrum of the compound d12 in CDCl$_3$ recorded at 100.6 MHz.
Figure S27: $^1$H NMR spectrum of the compound d13 in CDCl$_3$ recorded at 400.1 MHz.

Figure S28: $^{13}$C($^1$H) NMR spectrum of the compound d13 in CDCl$_3$ recorded at 100.6 MHz.
Figure S29: $^1$H NMR spectrum of the compound d14 in CDCl$_3$ recorded at 400.1 MHz.

Figure S30: $^{13}$C($^1$H) NMR spectrum of the compound d14 in CDCl$_3$ recorded at 100.6 MHz.
Figure S31: $^1$H NMR spectrum of the compound d15 in CDCl$_3$ recorded at 400.1 MHz.

Figure S32: $^{13}$C($^1$H) NMR spectrum of the compound d15 in CDCl$_3$ recorded at 100.6 MHz.
Figure S33: $^1$H NMR spectrum of the compound d16 in CDCl$_3$ recorded at 400.1 MHz.

Figure S34: $^{13}$C($^1$H) NMR spectrum of the compound d16 in CDCl$_3$ recorded at 100.6 MHz.
Figure S35: $^1$H NMR spectrum of the compound d17 in CDCl$_3$ recorded at 400.1 MHz.

Figure S36: $^{13}$C{${}^1$H} NMR spectrum of the compound d17 in CDCl$_3$ recorded at 100.6 MHz.
Figure S37: $^1$H NMR spectrum of the compound **d18** in CDCl$_3$ recorded at 400.1 MHz.

Figure S38: $^{13}$C($^1$H) NMR spectrum of the compound **d18** in CDCl$_3$ recorded at 100.6 MHz.
Figure S39: $^1$H NMR spectrum of the compound d19 in CDCl$_3$ recorded at 400.1 MHz.

Figure S40: $^{13}$C($^1$H) NMR spectrum of the compound d19 in CDCl$_3$ recorded at 100.6 MHz.
Figure S41: $^1$H NMR spectrum of the compound d20 in CDCl$_3$ recorded at 400.1 MHz.

Figure S42: $^{13}$C($^1$H) NMR spectrum of the compound d20 in CDCl$_3$ recorded at 100.6 MHz.
Figure S43: $^1$H NMR spectrum of the compound d21 in CDCl$_3$ recorded at 400.1 MHz.

Figure S44: $^{13}$C($^1$H) NMR spectrum of the compound d21 in CDCl$_3$ recorded at 100.6 MHz.
Figure S45: $^1$H NMR spectrum of the compound d22 in CDCl$_3$ recorded at 400.1 MHz.

Figure S46: $^{13}$C($^1$H) NMR spectrum of the compound d22 in CDCl$_3$ recorded at 100.6 MHz.
Figure S47: $^1$H NMR spectrum of the compound d23 in CDCl$_3$ recorded at 400.1 MHz.

Figure S48: $^{13}$C($^1$H) NMR spectrum of the compound d23 in CDCl$_3$ recorded at 100.6 MHz.
Figure S49: $^1$H NMR spectrum of the compound d24 in CDCl$_3$ recorded at 400.1 MHz.

Figure S50: $^{13}$C[$^1$H] NMR spectrum of the compound d24 in CDCl$_3$ recorded at 100.6 MHz.
Figure S51: $^1$H NMR spectrum of the compound $\text{d25}$ in CDCl$_3$ recorded at 400.1 MHz.

Figure S52: $^{13}$C($^1$H) NMR spectrum of the compound $\text{d25}$ in CDCl$_3$ recorded at 100.6 MHz.
Figure S53: $^1$H NMR spectrum of the compound d26 in CDCl$_3$ recorded at 400.1 MHz.

Figure S54: $^{13}$C($^1$H) NMR spectrum of the compound d26 in CDCl$_3$ recorded at 100.6 MHz.
Figure S55: $^1$H NMR spectrum of the compound d27 in CDCl$_3$ recorded at 400.1 MHz.

Figure S56: $^{13}$C($^1$H) NMR spectrum of the compound d27 in CDCl$_3$ recorded at 100.6 MHz.
Figure S57: $^1$H NMR spectrum of the compound d28 in CDCl$_3$ recorded at 400.1 MHz.

Figure S58: $^{13}$C($^1$H) NMR spectrum of the compound d28 in CDCl$_3$ recorded at 100.6 MHz.
Figure S59: $^1$H NMR spectrum of the compound d29 in CDCl$_3$ recorded at 400.1 MHz.

Figure S60: $^{13}$C($^1$H) NMR spectrum of the compound d29 in CDCl$_3$ recorded at 100.6 MHz.
**Figure S61.** $^1$H NMR spectrum of the compound d30 in CDCl$_3$ recorded at 400.1 MHz.

**Figure S62.** $^{13}$C($^1$H) NMR spectrum of the compound d30 in CDCl$_3$ recorded at 100.6 MHz.
Figure S63: $^1$H NMR spectrum of the compound d31 in CDCl$_3$ recorded at 400.1 MHz.

Figure S64: $^{13}$C($^1$H) NMR spectrum of the compound d31 in CDCl$_3$ recorded at 100.6 MHz.
Figure S65: $^1$H NMR spectrum of the compound d32 in CDCl$_3$ recorded at 400.1 MHz.

Figure S66: $^{13}$C($^1$H) NMR spectrum of the compound d32 in CDCl$_3$ recorded at 100.6 MHz.
Figure S67: $^1$H NMR spectrum of the compound d33 in CDCl$_3$ recorded at 400.1 MHz.

Figure S68: $^{13}$C($^1$H) NMR spectrum of the compound d33 in CDCl$_3$ recorded at 100.6 MHz.
Figure S69: $^1$H NMR spectrum of the compound d34 in CDCl$_3$ recorded at 400.1 MHz.

Figure S70: $^{13}$C($^1$H) NMR spectrum of the compound d34 in CDCl$_3$ recorded at 100.6 MHz.
Figure S71: $^1$H NMR spectrum of the compound d35 in CDCl$_3$ recorded at 400.1 MHz.

Figure S72: $^{13}$C($^1$H) NMR spectrum of the compound d35 in CDCl$_3$ recorded at 100.6 MHz.
Figure S73: $^1$H NMR spectrum of the compound d36 in CDCl$_3$ recorded at 400.1 MHz.

Figure S74: $^{13}$C($^1$H) NMR spectrum of the compound d36 in CDCl$_3$ recorded at 100.6 MHz.
Figure S7: $^1$H NMR spectrum of the compound d37 in CDCl$_3$ recorded at 400.1 MHz.

Figure S7: $^{13}$C($^1$H) NMR spectrum of the compound d37 in CDCl$_3$ recorded at 100.6 MHz.
Figure S77: $^1$H NMR spectrum of the compound d38 in CDCl$_3$ recorded at 400.1 MHz.

Figure S78: $^{13}$C($^1$H) NMR spectrum of the compound d38 in CDCl$_3$ recorded at 100.6 MHz.
Figure S79: $^1$H NMR spectrum of the compound d39 in CDCl$_3$ recorded at 400.1 MHz.

Figure S80: $^{13}$C($^1$H) NMR spectrum of the compound d39 in CDCl$_3$ recorded at 100.6 MHz.
Figure S81: $^1$H NMR spectrum of the compound d40 in CDCl$_3$ recorded at 400.1 MHz.

Figure S82: $^{13}$C($^1$H) NMR spectrum of the compound d40 in CDCl$_3$ recorded at 100.6 MHz.
References